Nickel-Catalyzed Asymmetric Cross-Couplings of Secondary Alkyl Electrophiles and Photoinduced, Copper-Catalyzed C–N Couplings

by

Junwon Choi

B.S., Chemistry, 2008
Seoul National University

Submitted to the Department of Chemistry
in Partial Fulfillment of the Requirements for the Degree of

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AT THE

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
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August 2014

Signature redacted

Signature of Author: _____
Department of Chemistry
August 4, 2014

Signature redacted

Certified by: _____
Gregory C. Fu
Thesis Supervisor

Signature redacted

Accepted by: _____
Robert W. Field
Robert T. Haslam and Bradley Dewey Professor of Chemistry
Chairman, Departmental Committee on Graduate Students

This doctoral thesis has been examined by a committee of the Department of Chemistry as follows:

Professor Mohammad Movassaghi: Signature redacted
Thesis Chairman

Professor Gregory C. Fu: Signature redacted
Thesis Supervisor

Professor Timothy M. Swager: Signature redacted
Committee Member

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ABSTRACT

Chapter 1 describes the development of three nickel-catalyzed asymmetric Negishi cross-couplings of secondary alkyl electrophiles via a stereoconvergent process. In Section 1.1, asymmetric Negishi arylations and alkenylations of α-bromonitriles with arylzinc and alkenylzinc reagents are achieved using a nickel/bis(oxazoline) catalyst. Section 1.2 describes stereoconvergent cross-couplings of secondary unactivated alkyl electrophiles, specifically, Negishi arylations and alkenylations of α-bromosulfonamides and α-bromosulfones with arylzinc reagents and alkenylzirconium reagents, respectively. Section 1.3 details progress toward asymmetric cross-couplings between α-haloboronate esters and alkylzinc reagents using a nickel/diamine catalyst.

Chapter 2 describes the development of photoinduced, copper-catalyzed C–N couplings between *N*-heterocycles and aryl halides. In particular, a variety of *N*-heterocycles, such as indoles, benzimidazoles, imidazoles, and carbazoles, undergo Ullmann couplings under mild conditions (room temperature) with an inexpensive catalyst (CuI, without an added ligand).

Thesis Supervisor: Gregory C. Fu
Title: Altair Professor of Chemistry, California Institute of Technology

PREFACE

Portions of this thesis have appeared in the previous publications:

"Catalytic Asymmetric Synthesis of Secondary Nitriles via Stereoconvergent Negishi Arylations and Alkenylations of Racemic α-Bromonitriles"
Choi, J.; Fu, G. C. *J. Am. Chem. Soc.* **2012**, *134*, 9102–9105.

"A Versatile Approach to Ullmann C–N Couplings at Room Temperature: New Families of Nucleophiles and Electrophiles for Photoinduced, Copper-Catalyzed Processes"
Ziegler, D. T.; Choi, J.; Muñoz-Molina, J. M.; Bissember, A. C.; Peters, J. C.; Fu, G. C. *J. Am. Chem. Soc.* **2013**, *135*, 13107–13112.

"Stereoconvergent Arylations and Alkenylations of Unactivated Alkyl Electrophiles: The Catalytic Enantioselective Synthesis of Secondary Sulfonamides and Sulfones"
Choi, J.; Martín-Gago, P.; Fu, G. C. *J. Am. Chem. Soc.* **2014**, DOI: 10.1021/ja506885s.

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I have been lucky to be surrounded by talented chemists in the Fu group over the years. I have learned from my colleagues in many ways, and it would have been difficult for me to successfully finish my graduate studies without their support. When I first joined the group, Sha, Carlos, and Wataru not only helped me to pursue my research, but they also shared their friendship. Alex, Ashraf, J.T., Yuji, and Nathan are brilliant chemists and were incredibly helpful resources. I always enjoyed having insightful discussions with them.

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Special thanks to YJ, CJ, and JM who I met at MIT. I cannot imagine my graduate life without them. Spending time with them outside of the lab was always refreshing, and I cannot forget the time that we shared together.

When I first heard about moving to Caltech from Greg, I could not believe it. I have missed Boston a lot since I moved to Pasadena, especially the Boston skyline seen from MIT and the snow in winter. But it has been an exceptional experience spending time at both MIT and Caltech. Designing and setting up a lab from scratch was a priceless experience, and it will be helpful in the future.

마지막으로 항상 응원해주시고 걱정하시는 부모님과 나 대신 한국에서 고생하는 형에게 감사한 마음을 전합니다.

TABLE OF CONTENTS

ABBREVIATIONS

Ar	aryl
Boc	*tert*-butoxycarbonyl
Box	bis(oxazoline)
Bn	benzyl
Bu	butyl
Cbz	carboxybenzyl
Cp	cyclopentadienyl
Cy	cyclohexyl
d	doublet
DABCO	1,4-diazabicyclo[2.2.2]octane
dba	dibenzylideneacetone
diglyme	diethylene glycol dimethyl ether
DMA	*N*,*N*-dimethylacetamide
DME	1,2-dimethoxyethane
DMI	1,3-dimethyl-2-imidazolidinone
ee	enantiomeric excess
Et	ethyl
Eq	equation
equiv	equivalents
GC	gas chromatography
glyme	1,2-dimethoxyethane
Hex	hexyl
HB(pin)	4,4,5,5-tetramethyl-1,3,2-dioxaborolane
HPLC	high-performance liquid chromatography
Hz	hertz
i	*iso*
IR	infrared
m	multiplet
Me	methyl
Ms	methanesulfonyl
MS	mass spectrometry
n	normal
nbd	norbornadiene
NHC	N-heterocyclic carbine

o	*ortho*
p	*para*
Ph	phenyl
Pr	propyl
pybox	pyridine bis(oxazoline)
r.t.	room temperature
s	singlet
t	triplet
t	*tert*
TBS	*tert*-butyldimethylsilyl
Tf	trifluoromethylsulfonyl
THF	tetrahydrofuran
TLC	thin-layer chromatography
TMEDA	*N*,*N*,*N*',*N*'-tetramethylethylenediamine
TMS	trimethylsilyl
Ts	4-toluenesulfonyl
9-BBN	9-borabicyclo[3.3.1]nonane

CHAPTER 1

Nickel-Catalyzed Asymmetric Cross-Couplings of Secondary Alkyl Electrophiles

Section 1.1

Catalytic Asymmetric Synthesis of Secondary Nitriles via Stereoconvergent Negishi Arylations and Alkenylations of Racemic α-Bromonitriles

A. Introduction

A nitrile attached to a stereogenic carbon can be found in many bioactive compounds.[1] Furthermore, nitrile groups are important synthetic intermediates because they can be readily transformed into diverse functional groups including heterocycles, aldehydes, ketones, amines, amides, and carboxylic acids.[2] Enantioenriched α-alkyl-α-arylnitriles are particularly noteworthy targets because they can be converted into α-arylcarboxylic acids, which are useful nonsteroidal anti-inflammatory drugs (e.g., naproxen).[3]

A variety of catalytic enantioselective methods have been developed to synthesize enantioenriched α-alkyl-α-arylnitriles. An array of α-alkyl-α-arylnitriles can prepared by nickel-catalyzed asymmetric hydrocyanation of vinylarenes with high ee, but this process is not efficient for substituted styrenes.[4] The asymmetric conjugate addition of H–CN to β-aryl-α,β-unsaturated carbonyl compounds provides an alternative route to access enantioenriched α-alkyl-α-arylnitriles with the limitation of primary alkyl substitution at the α-position.[5]

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[1] (a) Fleming, F. F. *Nat. Prod. Rep.* **1999**, *16*, 597–606. (b) Fleming, F. F.; Yao, L.; Ravikumar, P. C.; Funk, L.; Shook, B. C. *J. Med. Chem.* **2010**, *53*, 7902–7917.

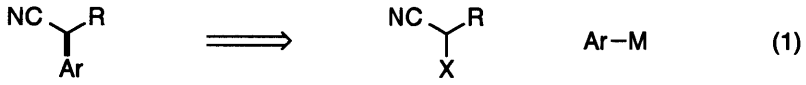
[2] For leading references, see: *Science of Synthesis*; Murahashi, S.-I., Ed.; Georg Thieme Verlag: Stuttgart, Germany, 2004; *Vol. 19*.

[3] For leading references, see: (a) Landoni, M. F.; Soraci, A. *Curr. Drug Metab.* **2001**, *2*, 37–51. (b) Kumaresan, C. *Int. J. Curr. Pharm. Res.* **2010**, *2*, 1–3. (c) Casalnuovo, A. L.; Rajanbabu, T. V. In *Chirality in Industry II*; Collins, A. N., Sheldrake, G. N., Crosby, J., Eds.; John Wiley & Sons: New York, 1997; Chapter 15.

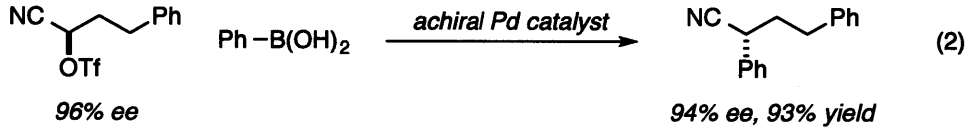
[4] For reviews of catalytic asymmetric hydrocyanations of olefins, see: (a) van Leeuwen, P. W. N. In *Science of Synthesis, Stereoselective Synthesis*; De Vries, J. G., Molander, G. A., Evans, P. A., Eds.; Georg Thieme Verlag: Stuttgart, Germany, 2011; *vol. 1*, pp 409–475. (b) RajanBabu, T. V.; Casalnuovo, A. L. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: New York, 1999; *Vol. 1*, pp 267–378.

[5] For examples of catalytic asymmetric conjugate additions of H–CN to generate α-alkyl-α-arylnitriles, see: (a) α substituent = primary alkyl group: Mita, T.; Sasaki, K.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2005**, *127*, 514–515. Mazet, C.; Jacobsen, E. N. *Angew. Chem., Int. Ed.* **2008**, *47*, 1762–1765. Kurono, N.; Nu, N.; Sakaguchi, Y.; Uemura, M.; Ohkuma, T. *Angew. Chem., Int. Ed.* **2011**, *50*, 5541–5544. (b) α substituent = secondary alkyl group: Wang, J.; Li, W.; Liu, Y.; Chu, Y.; Lin, L.; Liu, X.; Feng, X. *Org. Lett.* **2010**, *12*, 1280–1283.

Although transition-metal-catalyzed cross-couplings of secondary alkyl electrophiles with aryl nucleophiles can be an attractive strategy to prepare enantioenriched secondary arylnitriles (eq 1), only a few cross-couplings, with achiral catalysts, have been reported.[6] In addition, to the best of our knowledge, there is no precedent for asymmetric cross-couplings of secondary electrophiles furnishing enantioenriched α-alkyl-α-arylnitriles.



In 2010, Falck established Suzuki arylations of α-cyanohydrin triflates in the presence of an achiral palladium catalyst.[6c] In this report, enantiomerically enriched secondary arylnitriles could be prepared from nonracemic α-cyanohydrin triflates with inversion of the stereocenter with little erosion in ee (eq 2). However, he did not show the stereochemical outcome for the Suzuki arylation of electrophiles bearing a secondary alkyl substituent.

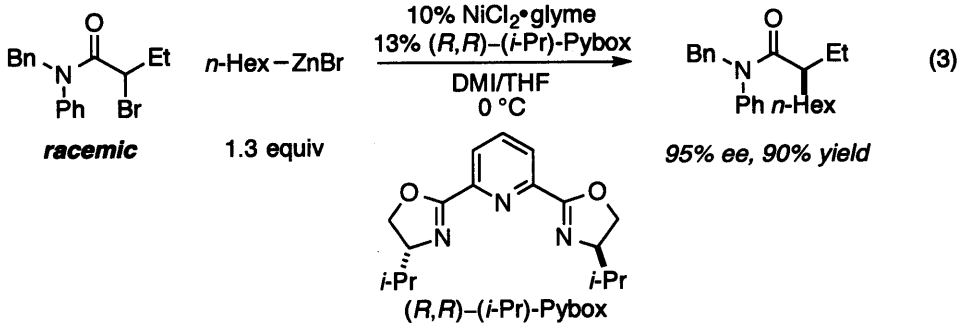


To overcome the limitation of existing methods, it was necessary to develop an asymmetric arylation of secondary α-bromonitriles with particular interest in hindered electrophiles and high functional-group compatibility. Among various cross-coupling processes, Negishi couplings are attractive due to the tolerance of organozinc reagents

[6] (a) Negishi reactions: Frejd, T.; Klingstedt, T. *Synthesis* **1987**, 40–42. (b) Hiyama reactions: Strotman, N. A.; Sommer, S.; Fu, G. C. *Angew. Chem., Int. Ed.* **2007**, *46*, 3556–3558. (c) Suzuki reactions: He, A.; Falck, J. R. *J. Am. Chem. Soc.* **2010**, *132*, 2524–2525. (d) Suzuki reactions: Yang, Y.; Tang, S.;Liu, C.; Zhang, H.; Sun, Z.; Lei, A. *Org. Biomol. Chem.* **2011**, *9*, 5343–5345.

with a variety of functional groups. Moreover, Negishi reactions proceed under mild conditions in the absence of a stoichiometric amount of additives.[7]

In previous studies, the Fu group has shown that several activated secondary electrophiles are suitable coupling partners in asymmetric Negishi alkylations or arylations. In 2005, Fischer disclosed the asymmetric Negishi alkylation of α-bromoamides with primary alkylzinc reagents, which was the first nickel-catalyzed stereoconvergent asymmetric cross-coupling of racemic electrophiles (eq 3).[8] Under the developed reaction conditions, he found that a nickel/pybox complex successfully catalyzes C–C bond formations in good ee and good yield. In regard to expanding the electrophile scope, Arp reported asymmetric Negishi alkylations of benzylic halides as the electrophilic partner.[9] Son subsequently showed that a nickel/pybox complex is also an effective catalyst for cross-couplings of allylic chlorides with alkylzinc reagents.[10]

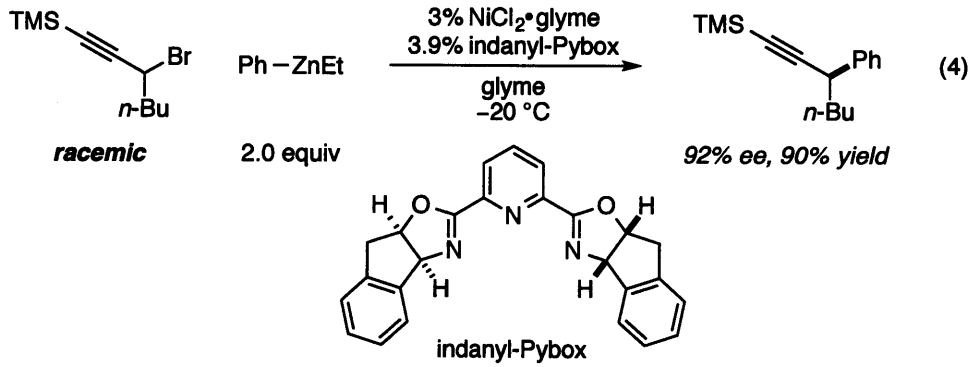


(3)

In 2008, Smith established the first nickel-catalyzed asymmetric Negishi *arylation* of propargylic halides with arylzinc reagents (eq 4).[11] In this report, an array of propargylic halides undergo cross-coupling reactions with arylzinc reagents in a

[7] For a review, see: Negishi, E.-i.; Hu, Q.; Huang, Z.; Wang, G.; Yin, N. In *The Chemistry of Organozinc Compounds*; Rappoport, Z., Marek, I., Eds.; Wiley: New York, 2006; Chapter 11.
[8] Fischer, C.; Fu, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 4594–4595.
[9] Arp, F. O.; Fu, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 10482–10483.
[10] Son, S.; Fu, G. C. *J. Am. Chem. Soc.* **2008**, *130*, 2756–2757.
[11] Smith, S. W.; Fu, G. C. *J. Am. Chem. Soc.* **2008**, *130*,12645–12647.

stereoconvergent process. Later, we also discovered that propargylic carbonates are suitable cross-coupling partners for stereoconvergent Negishi arylations with arylzinc reagents.[12] As part of our attempts to expand the class of electrophiles for this useful transformation, Lundin reported that a nickel/pybox catalyst can achieve enantioselective C–C bond formations of α-bromoketones with arylzinc reagents under mild reaction conditions with good ee and good yield.[13]



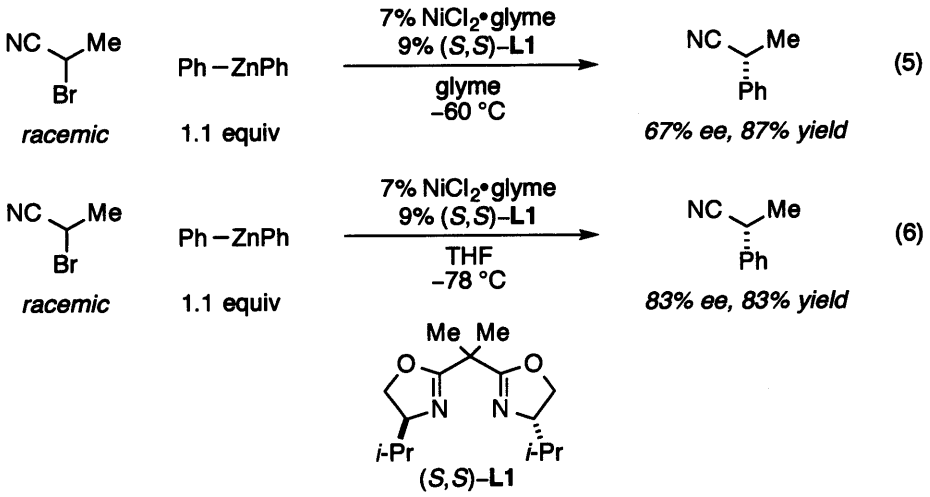
Given our progress toward nickel-catalyzed asymmetric Negishi couplings of secondary alkyl electrophiles, we were interested in the development of asymmetric Negishi arylations furnishing useful α-alkyl-α-arylnitriles in good ee and yield.

[12] Oelke, A. J.; Sun, J.; Fu, G. C. *J. Am. Chem. Soc.* **2012**, *134*, 2966–2969.
[13] Lundin, P. M.; Esquivias, J.; Fu, G. C. *Angew. Chem., Int. Ed.* **2009**, *48*, 154–156.

B. Results and Discussion

In our previous work, we determined that several classes of electrophiles are suitable coupling partners for asymmetric Negishi arylations or alkylations, and in each case, a pybox was the ligand of choice for this reaction.[8–13] However, when we applied these Negishi arylation conditions for the cross-coupling reaction of α-halonitriles with arylzinc reagents, we obtained disappointing results (<40% ee).

We therefore decided to evaluate other ligands beyond tridentate pybox compounds for the stereoconvergent Negishi cross-coupling of α-halonitriles, and we found that nickel and a bidentate bis(oxazoline) ligand facilitate the C–C bond formation of an α-bromonitrile with Ph_2Zn with 67% ee and 87% yield (eq 5).[14] Further investigation of the reaction parameters revealed that the asymmetric phenylation reaction proceeded in 83% ee and 83% yield in THF at −78 °C (eq 6).



Alterations to the ligand (**L1**), particularly the substitution on the linker between the oxazolines, resulted in further improvement of the ee (Figure 1). The substitutions on

[14] The reaction conditions were adapted from nickel-catalyzed asymmetric Kumada couplings of α-bromoketones. For the original reaction conditions, see: Lou, S.; Fu, G. C. *J. Am. Chem. Soc.* **2010**, *132*, 1264–1266.

the linker played an important role for achieving optimal enantioselectivity for the stereoconvergent arylation; indeed, bis(oxazoline) **L2** having a cyclopentyl ring on the linker provided the highest ee (86% ee and 96% yield).

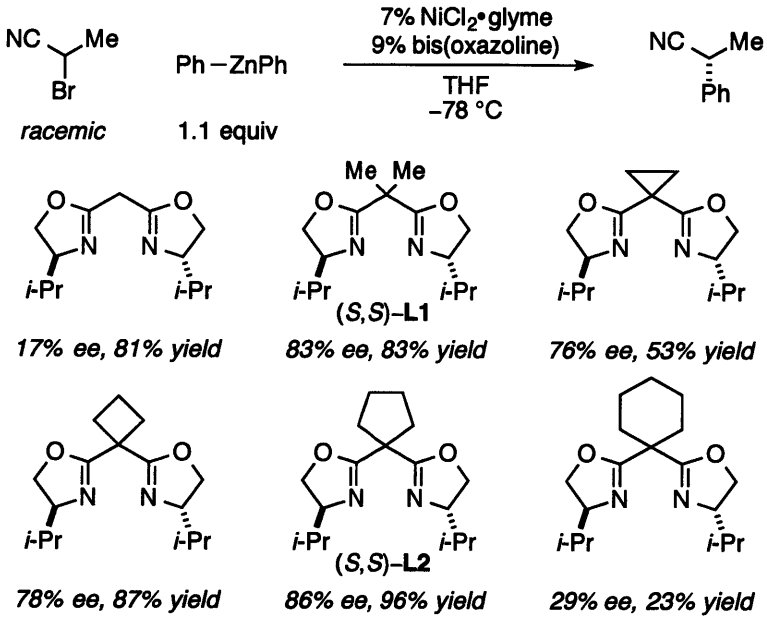


Figure 1. Ligand screen

Although discrete Ph_2Zn served as an excellent nucleophile for the asymmetric C–C bond-forming reactions, unfortunately, other functionalized diarylzinc reagents are not commercially available. To expand the nucleophile scope, we turned our efforts to generating functionalized diarylzinc species in situ from Grignard reagents and zinc salts. Since this C–C bond-forming process is sensitive to salts,[15] we tried to minimize the salt effects by investigating zinc sources. After intensive studies, we were pleased to obtain highly enantioenriched products by employing $Zn(OMe)_2$ as a zinc source.[16] When ZnX_2

[15] Similar results were also reported in our previous asymmetric cross-coupling reactions of propargylic halides (ref 11).

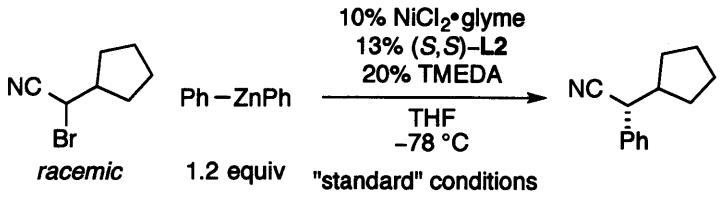
[16] For a report of the use of $Zn(OMe)_2$ to generate organozinc reagents, see: Côté, A.; Charette, A. B. *J. Am. Chem. Soc.* **2008**, *130*, 2771–2773.

(X = Cl, Br, or I) was employed instead of $Zn(OMe)_2$, somewhat lower ee and/or yield were observed.

After substantial effort, we determined final reaction conditions for the Negishi phenylation of α-bromonitriles, which furnishes α-alkyl-α-arylnitriles with good ee and yield. Under the optimized reaction conditions, an α-bromonitrile cross-couples with Ph_2Zn in 94% ee and 98% yield (Table 1, entry 1). As illustrated in Table 1, essentially no reaction occurs in the absence of nickel (entry 2) or of bis(oxazoline) **L2** (entry 3). Phenylzinc halides are not efficient nucleophilic partners for this asymmetric phenylation reaction (entry 4). The reaction proceeds in poor ee and yield when the reaction is carried out at room temperature instead of −78 °C (entry 5). A bis(oxazoline) ligand derived from phenyl glycine (**L3**) provides modest results (entry 6), and valine-derived bis(oxazoline) **L4** without gem-dimethyl substitution on the linker gives inferior results (entry 7). Pybox **L5** and diamine **L6**, which have been used for other nickel-catalyzed asymmetric cross-coupling reactions are not optimal (entries 8 and 9). A reduced amount of either Ph_2Zn or catalyst leads to decreased yield but no loss in enantioselectivity (entries 10 and 11). The cross-coupling reaction proceeds at –78 °C, which is, to the best of our knowledge, the lowest temperature that has been employed to date for cross-coupling reactions of alkyl electrophiles.[17] When PhMgBr is employed as the nucleophile under the reaction conditions, Kumada coupling occurs in 88% ee and 6% yield.

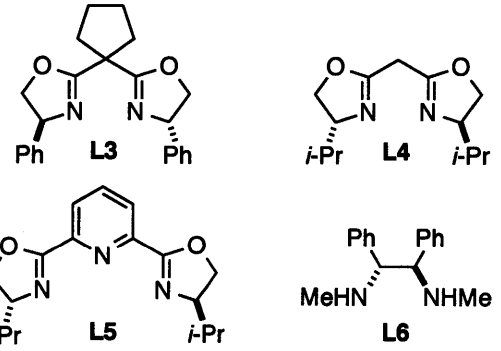
[17] For asymmetric Kumada cross-couplings of α-bromoketones that proceeds at –60 °C, see: ref 14.

Table 1. Stereoconvergent Negishi Phenylation of a Racemic α-Bromonitrile: Effect of Reaction Parameters[a]



entry	variation from the "standard conditions"	ee (%)	yield (%)[b]
1	none	94	98
2	no $NiCl_2$•glyme	–	<2
3	no **L2**	<2	3
4	PhZnX, instead of Ph_2Zn	90	6
5	r.t., instread of –78 °C	4	16
6	**L3**, instead of **L2**	84	89
7	**L4**, instead of **L2**	8	88
8	**L5**, instead of **L2**	8	32
9	**L6**, instead of **L2**	32	25
10	0.6 equiv Ph_2Zn	93	48
11	5% $NiCl_2$•glyme, 6.5% (*S,S*)-**L2**	93	68

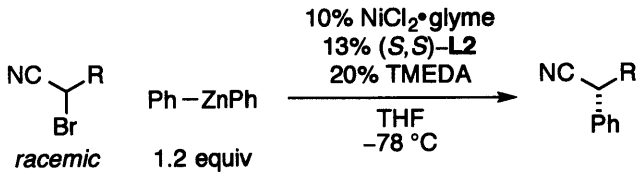
[a]All data are the average of two experiments. [b]Yield determined by GC analysis versus a calibrated internal standard.

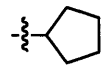
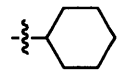
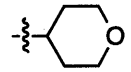
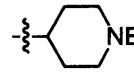
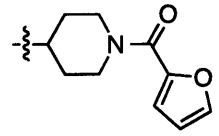
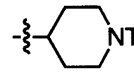
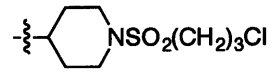
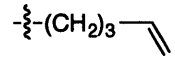
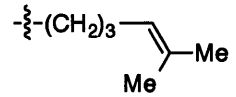


Under the developed reaction conditions, an array of racemic α-bromonitriles can be successfully transformed into α-phenylnitriles in good ee and yield (Table 2). A wide variety of functional groups are compatible, including an ether (entry 5), a carbamate (entry 6), an amide and a furan (entry 7), a sulfonamide (entries 8 and 9), an unactivated primary alkyl chloride (entry 9), and an alkene (entries 11 and 12). On a gram scale, the electrophile in entry 8 in Table 2 undergoes the phenylation reaction in 90% ee and 93% yield. In addition, no erosion in the enantiomeric excess of the product during the course

of the cross-coupling is observed. Under the standard reaction conditions, an α-chloronitrile and an α-iodonitrile are not suitable coupling partners.

Table 2. Stereoconvergent Negishi Phenylations of Racemic α-Bromonitriles[a]



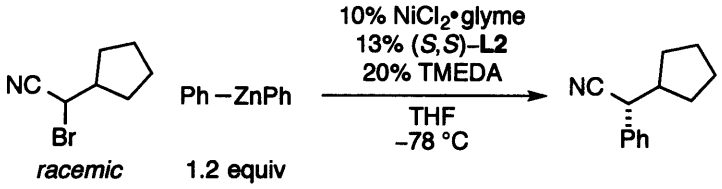
entry	R	ee (%)	yield (%)[b]
1	*i*-Pr	92	77
2		92	98
3		92	92
4[c]		92	92
5		92	94
6		90	96
7		85	95
8		91	94
9		90	94
10	Me	82	67 (83)[d]
11		78	88
12		76	94

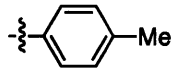
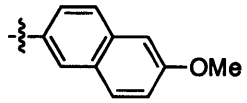
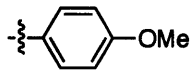
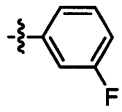
[a]All data are the average of two experiments. [b]Yield of purified product. [c]Reaction temperature: −60 °C. [d]Yield determined by GC analysis versus a calibrated internal standard.

This method for catalytic asymmetric Negishi reactions is not restricted to phenylation of α-bromonitrile compounds (Table 3). Both electron-rich (entries 1–3) and

electron-poor (entry 4) diarylzincs can be employed as the coupling partner with high ee and high yield. The asymmetric arylation reaction illustrated in entry 4 of Table 3 proceeds in 94% ee and 42% yield at –78 °C, but the yield can be improved by running the reaction at higher temperature, –60 °C, without loss in ee. Under our standard reaction conditions, $(o\text{-tol})_2Zn$ does not efficiently cross-couple.

Table 3. Stereoconvergent Negishi Arylations of Racemic α-Bromonitriles[a]



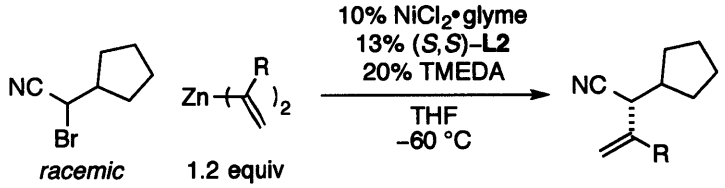
entry	Ar	ee (%)	yield (%)[b]
1		94	94
2		94	92
3		94	81
4[c]		93	99

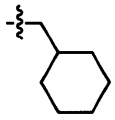
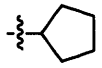
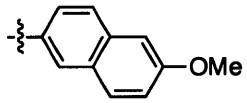
[a]All data are the average of two experiments. [b]Yield of purified product. [c]Reaction temperature: –60 °C.

Although we have demonstrated examples of Negishi reactions of activated electrophiles with alkyl- and arylzinc reagents, we have not been able to achieve corresponding cross-couplings with alkenylzinc reagents.[8–13] To expand the nucleophile scope, we re-evaluated the reaction parameters with an alkenylzinc reagent. We were pleased to find that the asymmetric Negishi arylation conditions (except reaction temperature) can be applied to the asymmetric alkenylation of α-bromonitriles with alkenylzinc reagents (Table 4). As depicted in Table 4, an array of alkenylzinc reagents

undergo cross-coupling with good ee. This reaction provides access to enantioenriched allylic nitriles.[18]

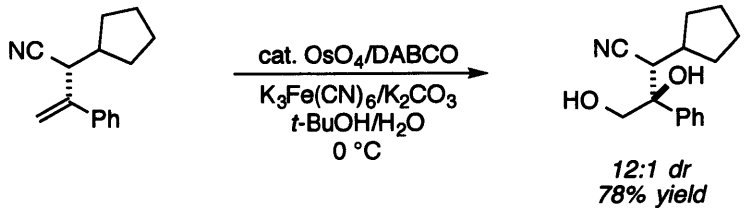
Table 4. Stereoconvergent Negishi Alkenylations of Racemic α-Bromonitriles[a]



entry	R	ee (%)	yield (%)[b]
1	-(CH$_2$)$_3$Ph	80	64
2		86	59
3		89	78
4	Ph	91	94
5		92	92

[a]All data are the average of two experiments. [b]Yield of purified product.

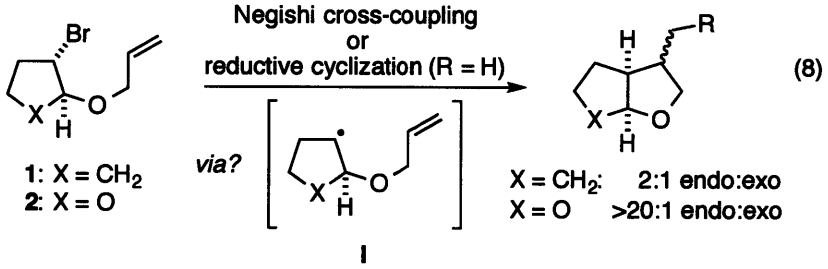
The enantioenriched allylic nitriles generated by these asymmetric Negishi alkenylations are suitable substrates for stereoselective transformations. For instance, osmium-catalyzed dihydroxylation can be achieved with good diastereoselectivity (eq 7).



(7)

[18] There have been a few reports of catalytic asymmetric hydrocyanations of 1,3-dienes to generate allylic nitriles (up to 86% ee): (a) Wilting, J.; Janssen, M.; Müller, C.; Vogt, D. *J. Am. Chem. Soc.* **2006**, *128*, 11374–11375. (b) Saha, B.; RajanBabu, T. V. *Org. Lett.* **2006**, *8*, 4657–4659.

We have previously proposed that a radical intermediate may be involved in the oxidative addition step of certain nickel-catalyzed cross-couplings of unactivated secondary alkyl halides.[19] Related to this hypothesis, we have shown that electrophiles having a pendant olefin (**1** and **2**) furnish cyclization/cross-coupling products under Stille and Suzuki reaction conditions with the same diastereoselectivity as for reductive radical cyclizations of corresponding electrophiles.[20] When this experiment was conducted under Negishi reaction conditions, the same stereochemistry of cyclization/cross-coupling products was observed, which is consistent with a common intermediate (**I**) for the cyclization step in all of these processes (eq 8).



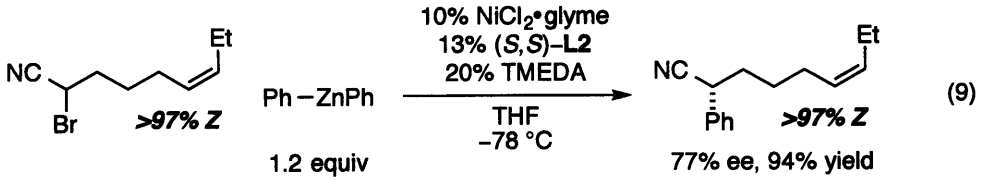
(8)

I

As part of our ongoing efforts to understand the mechanism of these nickel-catalyzed asymmetric cross-coupling reactions, we were interested whether cyclization of a radical intermediate might occur in the Negishi arylation of α-bromonitriles. As we described in entries 11 and 12 of Table 2, these α-bromonitriles having pendant olefins undergo the cross-coupling reaction without forming cyclization/cross-coupling products. To address whether a cyclized radical intermediate is formed transiently but reversibly in the course of the cross-coupling process, an electrophile having a (*Z*)-olefin was employed as a mechanistic probe (eq 9). If the radical cyclization occurs during the

[19] For a recent discussion, see: Zultanski, S. L.; Fu, G. C. *J. Am. Chem. Soc.* **2011**, *133*, 15362–15364.
[20] For examples of unactivated electrophiles, see: (a) Stille reactions: Powell, D. A.; Maki, T.; Fu, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 510–511. (b) Suzuki reactions: González-Bobes, F.; Fu, G. C. *J. Am. Chem. Soc.* **2006**, *128*, 5360–5361.

reaction, but the acyclic radical preferentially undergoes C–C bond formation, then the (*Z*)-olefin may isomerize to the (*E*)-olefin. When the (*Z*)-olefin was subjected to the cross-coupling reaction, we exclusively observed the (*Z*)-isomer, which suggests that radical cyclization is not occurring in this Negishi reaction. This result contrasts to our previous observations of cross-couplings of unactivated secondary alkyl electrophiles.



(9)

C. Conclusion

In conclusion, the nickel-catalyzed asymmetric cross-coupling of secondary activated alkyl electrophiles has been developed, specifically, Negishi arylations and alkenylations of α-bromonitriles with aryl- and alkenylzinc reagents, respectively. This process is particularly efficient for the synthesis of enantioenriched α-alkyl-α-arylnitriles where the alkyl group is branched. This is the first example demonstrating alkenylzinc reagents as the nucleophilic partner in stereoconvergent Negishi cross-couplings of secondary alkyl electrophiles. In addition, a new class of ligands, other than tridentate pybox ligands, was shown to be optimal in this cross-coupling reaction, which is significant for the future exploration of Negishi reactions. The C–C bond formation reaction occurs at low temperature (–78 °C), the lowest temperature to date employed for such asymmetric cross-coupling reactions of secondary alkyl electrophiles. Finally, in contrast to the observation of nickel-catalyzed cross-couplings of unactivated secondary alkyl electrophiles, a mechanistic study suggests that the putative stabilized alkyl radical intermediate does not detectably cyclize under the reaction conditions.

After our asymmetric cross-couplings of α-bromonitriles with organozinc reagents were reported, List disclosed an alternative synthetic method for enantioenriched α-alkyl-α-arylnitriles via the catalytic asymmetric protonation of silyl ketene imines.[21]

[21] Guin, J.; Varseev, G.; List, B. *J. Am. Chem. Soc.* **2013**, *135*, 2100–2103.

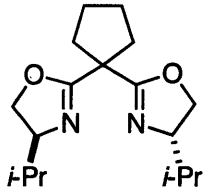
D. Experimental

I. General Information

The following reagents were purchased and used as received, unless otherwise noted: $NiCl_2$•glyme (Strem), THF (Aldrich; anhydrous), TMEDA (Aldrich; purified by distillation), and $Zn(OMe)_2$ (Aldrich; ground). The Grignard reagents were purchased (Aldrich) or prepared from aryl bromides and magnesium turnings (Strem). All reactions were carried out in oven-dried glassware under an inert atmosphere.

HPLC analyses were carried out on an Agilent 1100 series system with Daicel CHIRALPAK® columns or Daicel CHIRALCEL® columns (internal diameter 4.6 mm, column length 250 mm, particle size 5 μm or 3 μm). GC analyses were carried out on an Agilent 6890 series system with a DB-1 column (length 30 m, I.D. 0.25 mm) or an Agilent 6850 series system with a G-TA column (length 30 m, I.D. 0.25 mm) or a CP-Chirasil-Dex CB column (length 30 m, I.D. 0.25 mm). Supercritical fluid chromatography (SFC) analyses were carried out on a Berger SFC MiniGram system with Daicel CHIRALCEL® columns (internal diameter 4.6 mm, column length 250 mm, particle size 3 μm).

II. Preparation of Materials



(4*S*,4'*S*)-2,2'-(Cyclopentane-1,1-diyl)bis(4-isopropyl-4,5-dihydrooxazole). Cyclopentane-1,1-dicarbonitrile was prepared from malononitrile and 1,4-dibromobutane according to a literature procedure.[22] A 500-mL round-bottom flask charged with cyclopentane-1,1-dicarbonitrile (2.85 g, 23.7 mmol) and zinc triflate (8.63 g, 23.7 mmol) was purged with argon, and anhydrous toluene (158 mL) was added. The mixture was stirred for 10 min, and then a solution of L-valinol (5.14 g, 49.8 mmol) in toluene (79 mL) was added. The mixture was heated at reflux for 48 h. Then, the mixture was allowed to cool to r.t., and the solution was washed with brine (3 × 60 mL) and saturated aqueous $NaHCO_3$ (3 × 60 mL). The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography (2%→15% ethyl acetate and 1% NEt_3 in hexanes), which furnished a colorless oil (6.28 g, 91%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.20 (dd, 2H, J = 7.8, 9.1 Hz), 4.01–3.94 (m, 4H), 2.37–2.31 (m, 2H), 2.18–2.13 (m, 2H), 1.83–1.67 (m, 6H), 0.91 (d, 6H, J = 6.8 Hz), 0.85 (d, 6H, J = 6.8 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 71.6, 70.1, 49.2, 35.5, 32.4, 25.0, 18.6, 17.6.

FT-IR (neat): 2958, 2873, 1661, 1468, 1386, 1350, 1301, 1273, 1238, 1158, 1116, 998, 962, 907, 893 cm^{-1}.

MS (EI) *m/z* (M^+): calcd for $C_{17}H_{28}N_2O_2$: 292, found: 292.

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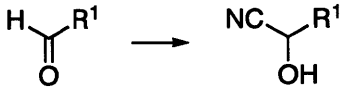
[22] Tsai, T.-Y.; Shia, K.-S.; Liu, H.-J. *Synlett* **2003**, 97–101.

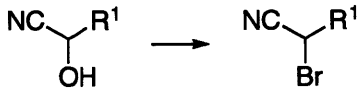
$[\alpha]^{25}_D = -68.0°$ (c = 1.00, $CHCl_3$).

Synthesis of starting materials. These procedures have not been optimized.



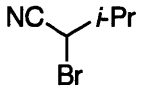
Representative experimental procedure for the synthesis of cyanohydrins from aldehydes: Trimethylsilyl cyanide (4.50 mL, 30.0 mmol) was added to a solution of the aldehyde (30.0 mmol) and K_2CO_3 (0.830 g, 6.00 mmol) in Et_2O (60 mL) in a 250-mL round-bottom flask. The reaction mixture was stirred for 6 h at r.t., and then the reaction was quenched by the addition of saturated aqueous $NaHCO_3$ (30 mL). The reaction mixture was extracted with Et_2O (2 × 20 mL), and the combined organic layer was concentrated.

Next, an aqueous solution of HCl (1 M; 100 mL) was added to the residue, and the mixture was stirred for 2 h. Then, the reaction mixture was extracted with Et_2O (3 × 50 mL), and the combined organic layer was rinsed with saturated aqueous $NaHCO_3$ (50 mL) and brine (50 mL), dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography (10%→80% Et_2O/hexanes).



Representative experimental procedure for the synthesis of secondary bromides from cyanohydrins: Triphenylphosphine dibromide (15.2 g, 36.0 mmol) and then imidazole (2.45 g, 36.0 mmol) was added to a solution of the cyanohydrin (30.0 mmol) in dichloromethane (150 mL) at 0 °C. The solution was allowed to warm to r.t.,

and it was stirred for 6 h. Next, the reaction was quenched by the addition of saturated aqueous NH_4Cl (100 mL). The aqueous layer was extracted with dichloromethane (2 × 50 mL), and the combined organic layer was rinsed with brine (50 mL), dried over $MgSO_4$, and concentrated.



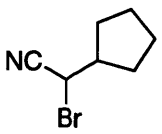
2-Bromo-3-methylbutanenitrile. The title compound was prepared from 2-hydroxy-3-methylbutanenitrile (2.39 g, 24.1 mmol). The product was purified by column chromatography (10% Et_2O/hexanes): 2.19 g (56%). Colorless oil.

^1H NMR (500 MHz, $CDCl_3$) δ 4.24 (d, 1H, J = 5.1 Hz), 2.19 (doublet of septets, 1H, J = 5.0, 6.7 Hz), 1.18 (d, 3H, J = 6.7 Hz), 1.18 (d, 3H, J = 6.7 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 116.6, 35.8, 34.0, 19.7, 19.2.

FT-IR (neat) 2972, 2936, 2878, 2242, 1466, 1392, 1373, 1319, 1271, 1187, 1120, 993, 966, 933, 911, 811, 695, 674 cm^{-1}.

MS (ESI) *m/z* (M^++H) calcd for C_5H_9BrN: 162.0, found: 162.0.



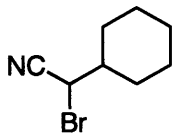
2-Bromo-2-cyclopentylacetonitrile. The title compound was prepared from 2-cyclopentyl-2-hydroxyacetonitrile (3.28 g, 26.2 mmol). The product was purified by column chromatography (2%→5% Et_2O/hexanes): 4.75 g (96%). Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.28 (d, 1H, J = 6.9 Hz), 2.53–2.45 (m, 1H), 2.04–1.93 (m, 2H), 1.82–1.72 (m, 2H), 1.71–1.61 (m, 2H), 1.57–1.43 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 117.1, 45.1, 32.7, 31.0, 30.5, 25.6.

FT-IR (neat) 2962, 2871, 2243, 1451, 1350, 1303, 1020, 1192, 771, 922, 690 cm^{-1}.

MS (EI) *m/z* (M^+–HCN) calcd for C_6H_9Br: 160, found: 160.



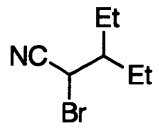
2-Bromo-2-cyclohexylacetonitrile. The title compound was prepared from 2-cyclohexyl-2-hydroxyacetonitrile (1.03 g, 7.43 mmol). The product was purified by column chromatography (1%→5% Et_2O/hexanes): 1.30 g (87%). Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.19 (d, 1H, J = 5.7 Hz), 2.04–1.99 (m, 1H), 1.96–1.91 (m, 1H), 1.87–1.77 (m, 3H), 1.72–1.66 (m, 1H), 1.34–1.22 (m, 3H), 1.22–1.13 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 116.7, 42.8, 34.5, 30.5, 29.6, 25.6 (2C), 25.5.

FT-IR (neat) 2931, 2856, 2241, 1450, 1370, 1351, 1302, 1273, 1241, 1196, 1164, 1137, 970, 940, 916, 892, 855 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_8H_{12}BrNNa$: 224.0, found: 224.0.



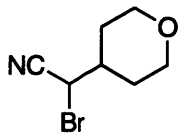
2-Bromo-3-ethylpentanenitrile. The title compound was prepared from 3-ethyl-2-hydroxypentanenitrile (1.93 g, 15.2 mmol). The product was purified by column chromatography (1%→5% Et_2O/hexanes): 2.39 g (83%). Colorless oil.

^1H NMR (500 MHz, $CDCl_3$) δ 4.43 (d, 1H, J = 4.1 Hz), 1.69–1.51 (m, 5H), 0.98 (t, 3H, J = 7.5 Hz), 0.96 (t, 3H, J = 7.2 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 117.2, 46.2, 33.1, 24.0, 23.4, 11.3, 11.2.

FT-IR (neat) 2968, 2937, 2879, 2242, 1462, 1385, 1358, 1316, 1264, 1176, 1118, 1092, 1014, 988, 945, 912, 827, 781, 755, 690, 666 cm^{-1}.

MS (ESI) *m/z* (M^++H) calcd for $C_7H_{13}BrN$: 190.0, found: 190.0.



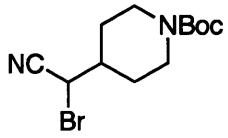
2-Bromo-2-(tetrahydro-2*H*-pyran-4-yl)acetonitrile. The title compound was prepared from 2-hydroxy-2-(tetrahydro-2*H*-pyran-4-yl)acetonitrile (0.85 g, 6.0 mmol). The product was purified by column chromatography (5%→100% Et_2O/hexanes): 0.71 g (58%). Light-yellow oil.

^1H NMR (500 MHz, $CDCl_3$) δ 4.18 (d, 1H, J = 6.4 Hz), 4.05 (ddd, 2H, J = 5.9, 5.9, 11.7 Hz), 3.39 (ddd, 1H, J = 2.2, 11.9, 11.9 Hz), 3.38 (ddd, 1H, J = 2.3, 12.0, 12.0 Hz), 2.06 (ddddd, 1H, J = 3.7, 3.7, 6.6, 11.8, 11.8 Hz), 1.92–1.87 (m, 1H), 1.87–1.82 (m, 1H), 1.61–1.47 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 116.0, 67.1 (2C), 40.4, 33.2, 30.3, 29.7.

FT-IR (neat) 2947, 2849, 2763, 2242, 1468, 1446, 1388, 1371, 1275, 1238, 1172, 1133, 1114, 1090, 1014, 987, 947, 909, 874, 859, 816, 796 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_7H_{10}BrNNaO$: 226.0, found: 226.0.



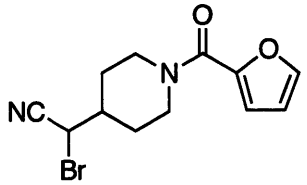
***tert*-Butyl 4-(bromo(cyano)methyl)piperidine-1-carboxylate.** The title compound was prepared from *tert*-butyl 4-(cyano(hydroxy)methyl)piperidine-1-carboxylate (3.77 g, 15.7 mmol). The product was purified by column chromatography (5%→100% Et_2O/hexanes): 3.53 g (74%). White solid.

^1H NMR (500 MHz, $CDCl_3$) δ 4.22 (br s, 2H), 4.21 (d, 1H, J = 5.8 Hz), 2.70 (br s, 2H), 2.00–1.89 (m, 3H), 1.45 (s, 9H), 1.43–1.32 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.6, 116.0, 80.0, 43.3, 41.6, 33.1, 29.7, 29.1, 28.5.

FT-IR (neat) 2976, 2947, 2859, 2242, 1687, 1469, 1450, 1425, 1367, 1322, 1301, 1280, 1236, 1164, 1127, 1063, 1004, 974, 866, 770, 705 cm^{-1}.

MS (ESI) *m/z* (M^+–Boc+2H) calcd for $C_7H_{12}BrN_2$: 203.0, found: 203.0.



2-Bromo-2-(1-(furan-2-carbonyl)piperidin-4-yl)acetonitrile. Furan-2-yl(4-(hydroxymethyl)piperidin-1-yl)methanone was prepared from 4-piperidinemethanol and

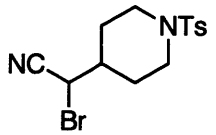
2-furoyl chloride following a literature procedure. The title compound was prepared from 2-(1-(furan-2-carbonyl)piperidin-4-yl)-2-hydroxyacetonitrile (1.35 g, 5.76 mmol). The product was purified by column chromatography (10%→100% Et_2O/hexanes): 0.77 g (50%). White solid.

^1H NMR (500 MHz, $CDCl_3$) δ 7.48 (dd, 1H, J = 0.8, 1.7 Hz), 7.01 (dd, 1H, J = 0.8, 3.4 Hz), 6.48 (dd, 1H, J = 1.8, 3.5 Hz), 4.70 (br s, 2H), 4.25 (d, 1H, J = 6.0 Hz), 2.93 (br s, 2H), 2.17–2.02 (m, 3H), 1.59–1.46 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 147.9, 143.8, 116.6, 116.0, 111.4, 44.1, 41.5, 32.7, 29.8, 29.3.

FT-IR (neat) 3119, 2946, 2859, 2242, 1623, 1569, 1487, 1437, 1372, 1303, 1284, 1249, 1180, 1102, 1012, 977, 935, 886, 855, 756 cm^{-1}.

MS (ESI) *m/z* (M^++H) calcd for $C_{12}H_{14}BrN_2O_2$: 297.0, found: 297.0.



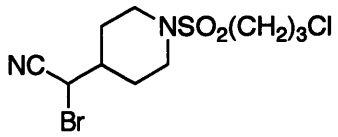
2-Bromo-2-(1-tosylpiperidin-4-yl)acetonitrile. (1-Tosylpiperidin-4-yl)methanol was prepared from 4-piperidinemethanol and *p*-toluenesulfonyl chloride following a literature procedure. The title compound was prepared from 2-hydroxy-2-(1-tosylpiperidin-4-yl)acetonitrile (4.63 g, 15.7 mmol). The product was purified by column chromatography (5%→100% ethyl acetate/hexanes): 3.37 g (60%). White solid.

^1H NMR (500 MHz, $CDCl_3$) δ 7.65–7.62 (m, 2H), 7.33 (d, 2H, J = 7.9 Hz), 4.18 (d, 1H, J = 6.4 Hz), 3.92–3.89 (m, 2H), 2.43 (s, 3H), 2.27 (dddd, 2H, J = 2.6, 3.2, 12.0, 12.0), 2.04–1.95 (m, 2H), 1.80–1.72 (m, 1H), 1.64–1.51 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.0, 133.0, 129.9, 127.8, 115.9, 45.6 (2C), 40.6, 32.4, 29.0, 28.6, 21.7.

FT-IR (neat) 3031, 2961, 2926, 2854, 2245, 1598, 1493, 1469, 1448, 1354, 1330, 1306, 1253, 1164, 1113, 1094, 1071, 1049, 1011, 994, 932, 844, 813, 726, 706, 696, 652, 599 cm^{-1}.

MS (ESI) *m/z* (M^++H) calcd for $C_{14}H_{18}BrN_2O_2S$: 357.0, found: 357.0.



2-Bromo-2-(1-((3-chloropropyl)sulfonyl)piperidin-4-yl)acetonitrile. (1-((3-Chloropropyl)sulfonyl)piperidin-4-yl)methanol was prepared from 4-piperidinemethanol and 3-chloropropanesulfonyl chloride following a literature procedure.[23] The title compound was prepared from 2-(1-((3-chloropropyl)sulfonyl)piperidin-4-yl)-2-hydroxyacetonitrile (4.77 g, 17.0 mmol). The product was purified by column chromatography (5%→100% ethyl acetate/hexanes): 3.20 g (55%). White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.25 (d, 1H, J = 6.0 Hz), 3.95–3.90 (m, 2H), 3.68 (dd, 2H, J = 6.1, 6.1 Hz), 3.09 (dd, 2H, J = 7.4, 7.4 Hz), 2.81 (dddd, 2H, J = 2.6, 3.5, 12.4, 12.4 Hz), 2.30–2.24 (m, 2H), 2.10–2.03 (m, 2H), 2.00–1.93 (m, 1H), 1.64–1.51 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 115.9, 47.1, 45.3, 45.2, 43.0, 40.8, 32.5, 29.5, 29.1, 26.4.

FT-IR (neat) 2956, 2927, 2858, 2243, 1469, 1448, 1407, 1330, 1251, 1145, 1070, 1048, 993, 935, 798, 742, 696 cm^{-1}.

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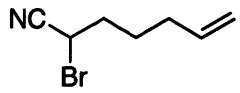
[23] Wilsily, A.; Tramutola, F.; Owston, N. A.; Fu, G. C. *J. Am. Chem. Soc.* **2012**, *134*, 5794–5797.

MS (ESI) *m/z* (M^++H) calcd for $C_{10}H_{17}BrClN_2O_2S$: 345.0, found: 345.0.



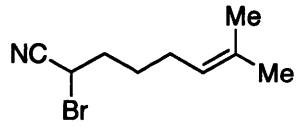
2-Bromohept-6-enenitrile. The title compound was prepared from 2-hydroxyhept-6-enenitrile (3.25 g, 26.0 mmol). The product was purified by column chromatography (5% Et_2O/hexanes): 4.10 g (84%). Colorless oil.

^1H NMR (500 MHz, $CDCl_3$) δ 5.78 (dddd, 1H, J = 6.7, 6.7, 10.3, 17.0 Hz), 5.08–5.02 (m, 2H), 4.31 (t, 1H, J = 7.0 Hz), 2.16–2.08 (m, 4H), 1.72–1.65 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.0, 117.4, 116.0, 35.7, 32.4, 27.1, 26.0.

FT-IR (neat) 3079, 2935, 2865, 2244, 1641, 1458, 1418, 1290, 1220, 994, 917, 767, 698, 616 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_7H_{10}BrNNa$: 210.0, found: 210.0.



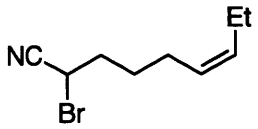
2-Bromo-7-methyloct-6-enenitrile. The title compound was prepared from 2-hydroxy-7-methyloct-6-enenitrile (1.81 g, 11.8 mmol). The product was purified by column chromatography (2%→15% Et_2O/hexanes): 2.53 g (88%). Colorless oil.

^1H NMR (500 MHz, $CDCl_3$) δ 5.08 (septet of triplets, 1H, J = 1.4, 7.2 Hz), 4.29 (t, 1H, J = 7.0 Hz), 2.11–2.04 (m, 4H), 1.70 (s, 3H), 1.65–1.58 (m, 5H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 133.1, 122.9, 117.4, 36.0, 27.2, 27.1, 26.8, 25.8, 17.8.

FT-IR (neat) 2931, 2861, 2243, 1673, 1451, 1378, 1293, 1226, 1109, 1063, 985, 834, 771, 736, 696, 616 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_9H_{14}BrN$: 215, found: 215.



(*Z*)-2-Bromonon-6-enenitrile. The title compound was prepared from (*Z*)-2-hydroxynon-6-enenitrile (4.29 g, 28.0 mmol). The product was purified by column chromatography (5% Et_2O/hexanes): 5.71 g (94%). Colorless oil.

^1H NMR (500 MHz, $CDCl_3$) δ 5.45 (ddddd, 1H, J = 1.5, 1.5, 7.2, 7.2, 10.8 Hz), 5.29 (ddddd, 1H, J = 1.6, 1.6, 7.3, 7.3, 10.8 Hz), 4.30 (t, 1H, J = 7.0 Hz), 2.14–2.00 (m, 6H), 1.68–1.61 (m, 2H), 0.97 (t, 3H, J = 7.5 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 133.3, 127.1, 117.4, 35.9, 27.2, 26.9, 25.8, 20.6, 14.3.

FT-IR (neat) 3007, 2963, 2871, 2244, 1653, 1457, 1305, 1218, 1070, 691 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_9H_{14}BrNNa$: 238.0, found: 238.0.

III. Negishi Cross-Coupling Reactions

General procedure for Grignard reagent preparation: A 25-mL two-neck round-bottom flask equipped with a reflux condenser and a stir bar was capped with a septum. Magnesium turnings (249 mg, 10.2 mmol) were added to the flask, and the flask was flame-dried under vacuum. The flask was filled with argon, and a solution of the aryl bromide (2.0 mmol) in THF (1.3 mL) was added dropwise over ~1 min. The

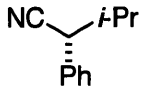
reaction was initiated by gently heating the flask with a heat gun. Once the reaction had initiated, a solution of the aryl bromide (8.0 mmol) in THF (8.7 mL) was added dropwise over 15 min. The resulting mixture was stirred at reflux for 3 h, and then it was allowed to cool to r.t., transferred to a syringe, and filtered through an acrodisc into an oven-dried 20-mL vial sealed with a PTFE-lined septum cap under a positive pressure of argon. The Grignard reagent was titrated with I_2.[24]

General procedure for asymmetric cross-coupling reactions with diarylzinc reagents prepared in situ (Tables 2, 3, and 4; no glovebox): An oven-dried 8-mL vial equipped with a magnetic stir bar was capped with a PTFE-lined septum cap, cooled under vacuum, and filled with argon. $Zn(OMe)_2$ (124 mg, 0.972 mmol) was added to the vial, which was placed under vacuum. The vial was filled with argon, and this evacuation-refill cycle was repeated three times. THF (2.1 mL) was added to the vial, and then a solution of ArMgBr (1.0 M in THF; 1.92 mL). The mixture was stirred for 60 min at r.t. $NiCl_2$•glyme (17.6 mg, 0.080 mmol) and (*S,S*)–**L2** (30.4 mg, 0.104 mmol) were added to an oven-dried 4-mL vial equipped with a magnetic stir bar. The vial was sealed with a PTFE-lined septum cap. The vial was placed under vacuum and then filled with argon; this cycle was repeated three times. Then, THF (0.80 mL) was added, and the mixture was stirred at r.t. for 10 min, at which time it had become homogenous. An oven-dried 20-mL vial equipped with a magnetic stir bar was charged with 2-bromo-2-cyclopentylacetonitrile (150 mg, 0.80 mmol) and TMEDA (24 μL, 0.16 mmol) and then capped with a PTFE-lined septum cap. Next, the vial was purged with argon for 10 min, and THF (3.2 mL) was added. An argon balloon was attached to the vial that contained the solution of the electrophile, which was cooled to –78 °C (any condensation around

[24] Krasovskiy, A.; Knochel, P. *Synthesis* **2006**, 890–891.

the septum cap on the 20-mL vial was removed), and then a 5-mL syringe containing the solution of diarylzinc and a 1-mL syringe containing the solution of $NiCl_2$•glyme and (*S,S*)–**L2** were attached to the 20-mL vial containing the solution of the electrophile. The solution of the diarylzinc was injected, and the mixture was stirred for 10 min. Next, the solution of $NiCl_2$•glyme and (*S,S*)–**L2** was added by syringe over 10 min. The argon-filled balloon was removed, and the septum cap was covered with grease. The reaction mixture was stirred at –78 °C for 48 h, and then the reaction was quenched by the addition of ethanol (0.8 mL). The mixture was allowed to warm to r.t., and then it was filtered through a pad of silica (eluted with Et_2O). The solution was concentrated, and the residue was purified by column chromatography.

A second run was conducted with (*R,R*)–**L2**.



(*R*)-3-Methyl-2-phenylbutanenitrile (Table 2, entry 1). 2-Bromo-3-methylbutanenitrile (97 mg, 0.60 mmol) was used. The product was purified by column chromatography (2% Et_2O/hexanes). Light-yellow oil. First run: 75 mg (79%, 92% ee). Second run: 72 mg (75%, 92% ee).

The ee was determined by GC analysis on a G-TA column (100 °C hold 5 min, then 100 °C→180 °C @ 5 °C/min, hold 10 min, 1.7 mL/min) with t_r = 12.8 min (major), 13.8 min (minor).

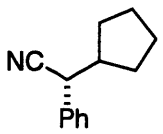
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.36 (m, 2H), 7.34–7.29 (m, 3H), 3.66 (d, 1H, J = 6.3 Hz), 2.13 (apparent octet, 1H, J = 6.7 Hz), 1.06 (d, 3H, J = 6.7 Hz), 1.04 (d, 3H, J = 6.7 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.1, 128.9, 128.1, 128.0, 120.0, 45.3, 33.9, 20.9, 18.9.

FT-IR (neat) 3032, 2966, 2930, 2875, 2238, 1493, 1454, 1390, 1372, 1173, 1074, 1031, 918 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_{11}H_{13}N$: 159, found: 159.

$[\alpha]^{24}_D$ = +26.5° (c = 1.01, $CHCl_3$).



(*R*)-2-Cyclopentyl-2-phenylacetonitrile (Table 2, entry 2). 2-Bromo-2-cyclopentylacetonitrile (113 mg, 0.80 mmol) was used. The product was purified by column chromatography (1.5%→3% Et_2O/hexanes). White solid. First run: 147 mg (99%, 92% ee). Second run: 142 mg (96%, 93% ee).

The ee was determined by GC analysis on a G-TA column (100 °C hold 5 min, then 100 °C→180 °C @ 5 °C/min, hold 10 min, 1.7 mL/min) with t_r = 20.0 min (major), 20.4 min (minor).

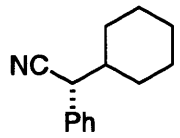
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.35 (m, 2H), 7.33–7.30 (m, 3H), 3.71 (d, 1H, *J* = 7.7 Hz), 2.35–2.27 (m, 1H), 1.89–1.83 (m, 1H), 1.77–1.65 (m, 3H), 1.62–1.47 (m, 3H), 1.39–1.29 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 136.0, 129.0, 128.0, 127.7, 120.7, 45.4, 42.6, 31.1, 30.3, 25.0, 24.9.

FT-IR (neat) 3033, 2955, 2868, 2233, 1647, 1495, 1456, 1361, 1302, 1146, 1078, 1030, 1003, 908, 755, 698 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_{13}H_{15}N$: 185, found: 185.

$[\alpha]^{25}_D = +35.7°$ (c = 1.00, $CHCl_3$).



(*R*)-2-Cyclohexyl-2-phenylacetonitrile (Table 2, entry 3). 2-Bromo-2-cyclohexylacetonitrile (121 mg, 0.60 mmol) was used. The product was purified by column chromatography (3% Et_2O/hexanes). White solid. First run: 106 mg (89%, 92% ee). Second run: 113 mg (95%, 93% ee).

The ee was determined by GC analysis on a G-TA column (130 °C hold 25 min, then 130 °C→180 °C @ 1 °C/min, hold 10 min, 1.5 mL/min) with t_r = 39.0 min (major), 40.3 min (minor).

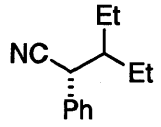
^1H NMR (500 MHz, $CDCl_3$) δ 7.39–7.35 (m, 2H), 7.33–7.27 (m, 3H), 3.63 (d, 1H, *J* = 6.7 Hz), 1.85–1.83 (m, 1H), 1.78–1.74 (m, 3H), 1.67–1.65 (m, 2H), 1.25–1.10 (m, 5H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 134.8, 128.9, 128.1, 128.0, 120.3, 44.5, 42.9, 31.3, 29.7, 26.1, 26.0, 25.9.

FT-IR (neat) 2934, 2855, 2233, 1599, 1494, 1455, 1368, 1308, 1279, 1188, 1125, 1078, 1064, 1028, 982, 887, 753, 697 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_{14}H_{17}N$: 199, found: 199.

$[\alpha]^{24}_D = +27.9°$ (c = 1.01, $CHCl_3$).



(*R*)-3-Ethyl-2-phenylpentanenitrile (Table 2, entry 4). 2-Bromo-3-ethylpentanenitrile (114 mg, 0.60 mmol) was used. The product was purified by column chromatography (3% Et_2O/hexanes). Colorless oil. First run: 102 mg (91%, 92% ee). Second run: 105 mg (93%, 93% ee).

The ee was determined by GC analysis on a G-TA column (110 °C hold 20 min, then 110 °C→150 °C @ 1 °C/min, hold 10 min, 1.7 mL/min) with t_r = 30.5 min (major), 31.9 min (minor).

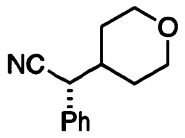
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.36 (m, 2H), 7.33–7.30 (m, 3H), 3.92 (d, 1H, J = 6.0 Hz), 1.72–1.66 (m, 1H), 1.56–1.37 (m, 4H), 0.96 (t, 3H, J = 7.4 Hz), 0.87 (t, 3H, J = 7.4 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.2, 129.0, 128.1, 128.0, 120.2, 46.4, 40.8, 23.3, 22.6, 11.2, 11.1.

FT-IR (neat) 3065, 3032, 2965, 2935, 2878, 2238, 1602, 1494, 1455, 1384, 1315, 1228, 1157, 1077, 1031, 909, 821, 764, 747, 725, 699 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_{13}H_{17}N$: 187, found: 187.

$[\alpha]^{23}_D$ = +37.2° (c = 1.00, $CHCl_3$).



(*R*)-2-Phenyl-2-(tetrahydro-2*H*-pyran-4-yl)acetonitrile (Table 2, entry 5). 2-Bromo-2-(tetrahydro-2*H*-pyran-4-yl)acetonitrile (122 mg, 0.60 mmol) was used. The

product was purified by column chromatography (40% Et_2O/hexanes). White solid. First run: 114 mg (94%, 92% ee). Second run: 114 mg (94%, 91% ee).

The ee was determined by HPLC analysis on a CHIRALCEL OD-H column (5% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 16.8 min (minor), 19.1 min (major).

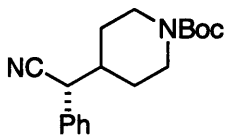
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.36 (m, 2H), 7.36–7.32 (m, 1H), 7.32–7.27 (m, 2H), 4.05–3.99 (m, 1H), 3.98–3.94 (m, 1H), 3.61 (d, 1H, J = 7.6 Hz), 3.36–3.26 (m, 2H), 2.04–1.94 (m, 1H), 1.81–1.78 (m, 1H), 1.59–1.50 (m, 1H), 1.49–1.45 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 133.8, 129.1, 128.4, 128.1, 119.6, 67.6, 67.5, 44.0, 40.4, 31.0, 30.2.

FT-IR (neat) 2969, 2932, 2854, 2233, 1494, 1455, 1393, 1366, 1303, 1278, 1263, 1244, 1215, 1139, 1116, 1092, 1068, 1018, 985, 912, 876, 823, 753, 697 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_{13}H_{15}NO$: 201, found: 201.

$[\alpha]^{24}_D$ = +27.9° (c = 1.01, $CHCl_3$).



(*R*)-*tert*-Butyl 4-(cyano(phenyl)methyl)piperidine-1-carboxylate (Table 2, entry 6). *tert*-Butyl 4-(bromo(cyano)methyl)piperidine-1-carboxylate (182 mg, 0.60 mmol) was used. The product was purified by column chromatography (30%→40% Et_2O/hexanes). White solid. First run: 172 mg (95%, 90% ee). Second run: 175 mg (97%, 90% ee).

The ee was determined by HPLC analysis on a CHIRALPAK AD-H column (3% *i*-PrOH/hexanes, 0.8 mL/min) with t_r = 24.7 min (major), 27.1 min (minor).

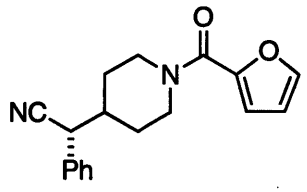
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.37 (m, 2H), 7.36–7.32 (m, 1H), 7.29–7.28 (m, 2H), 4.15 (br s, 2H), 3.64 (d, 1H, J = 7.0 Hz), 2.62 (br s, 2H), 1.93–1.86 (m, 1H), 1.85–1.81 (m, 1H), 1.58–1.54 (m, 1H), 1.44 (s, 9H), 1.39–1.25 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.7, 133.9, 129.2, 128.5, 128.1, 119.6, 79.8, 43.8, 43.6, 41.5, 30.2, 29.3, 28.6.

FT-IR (neat) 2976, 2937, 2856, 2239, 1690, 1494, 1454, 1424, 1366, 1318, 1279, 1248, 1169, 1125, 1081, 1058, 1031, 1004, 975, 952, 921, 868, 818, 758, 734, 702 cm^{-1}.

MS (ESI) *m/z* (M^+–Boc+2H) calcd for $C_{13}H_{17}N_2$: 201.1, found: 201.1.

$[\alpha]^{23}_D$ = +23.1° (c = 1.00, $CHCl_3$).



(*R*)-2-(1-(Furan-2-carbonyl)piperidin-4-yl)-2-phenylacetonitrile (Table 2, entry 7). 2-Bromo-2-(1-(furan-2-carbonyl)piperidin-4-yl)acetonitrile (178 mg, 0.60 mmol) was used. The product was purified by column chromatography (40%→50% ethyl acetate/hexanes). Light –yellow solid. First run: 166 mg (94%, 85% ee). Second run: 169 mg (96%, 85% ee).

The ee was determined by HPLC analysis on a CHIRALCEL OD-H column (50% *i*-PrOH/hexanes, 0.7 mL/min) with t_r = 11.8 min (minor), 14.5 min (major).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, 1H, J = 0.9 Hz), 7.41–7.33 (m, 3H), 7.30–7.23 (m, 2H), 6.96 (dd, 1H, J = 0.6, 3.4 Hz), 6.46 (dd, 1H, J = 1.8, 3.4 Hz), 4.61 (br s,

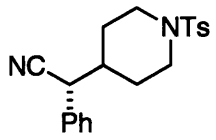
2H), 3.66 (d, 1H, J = 7.3 Hz), 2.84 (br s, 2H), 2.09–2.01 (m, 1H), 1.99–1.94 (m, 1H), 1.70–1.65 (m, 1H), 1.52–1.37 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 148.0, 143.7, 133.6, 129.2, 128.5, 128.0, 119.5, 116.4, 111.4, 46.1, 43.5, 43.2, 41.6, 30.4, 29.8.

FT-IR (neat) 3117, 3032, 2923, 2857, 2238, 1625, 1569, 1488, 1437, 1372, 1319, 1283, 1222, 1173, 1098, 1057, 1012, 976, 938, 886, 757, 703 cm^{-1}.

MS (ESI) *m/z* (M^++H) calcd for $C_{18}H_{19}N_2O_2$: 295.1, found: 295.1.

$[\alpha]^{25}_D$ = +19.7° (c = 1.00, $CHCl_3$).



(*R*)-2-Phenyl-2-(1-tosylpiperidin-4-yl)acetonitrile (Table 2, entry 8). 2-Bromo-2-(1-tosylpiperidin-4-yl)acetonitrile (244 mg, 0.60 mmol) was used. The product was purified by column chromatography (20%→25% ethyl acetate/hexanes). White solid. First run: 199 mg (94%, 91% ee). Second run: 202 mg (95%, 91% ee).

The ee was determined by HPLC analysis on a CHIRALPAK IB-3 column (20% *i*-PrOH/hexanes, 0.9 mL/min) with t_r = 28.0 min (minor), 42.3 min (major).

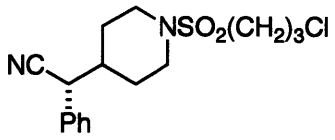
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62–7.60 (m, 2H), 7.38–7.32 (m, 3H), 7.32–7.29 (m, 2H), 7.23–7.21 (m, 2H), 3.88–3.84 (m, 1H), 3.82–3.78 (m, 1H), 3.57 (d, 1H, J = 7.6 Hz), 2.42 (s, 3H), 2.20 (ddd, 1H, J = 2.8, 12.0, 12.0 Hz), 2.15 (ddd, 1H, J = 2.8, 12.0, 12.0 Hz), 1.97–1.92 (m, 1H), 1.71–1.64 (m, 1H), 1.61–1.50 (m, 2H), 1.49–1.40 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.8, 133.5, 133.0, 129.8, 129.2, 128.6, 128.0, 127.8, 119.4, 46.1, 46.0, 43.3, 40.7, 29.4, 28.9, 21.7.

FT-IR (neat) 3032, 2924, 2852, 2240, 1598, 1494, 1467, 1454, 1339, 1306, 1251, 1164, 1094, 1047, 932, 817, 761, 729, 702, 650 cm^{-1}.

MS (ESI) *m/z* (M^++H) calcd for $C_{20}H_{23}N_2O_2S$: 355.1, found: 355.1.

$[\alpha]^{24}_D$ = +22.1° (c = 1.00, $CHCl_3$).



(*R*)-2-(1-((3-Chloropropyl)sulfonyl)piperidin-4-yl)-2-phenylacetonitrile (Table 2, entry 9). 2-Bromo-2-(1-((3-chloropropyl)sulfonyl)piperidin-4-yl)acetonitrile (206 mg, 0.60 mmol) was used. The product was purified by column chromatography (20%→35% ethyl acetate/hexanes). White solid. First run: 191 mg (93%, 89% ee). Second run: 192 mg (94%, 90% ee).

The ee was determined by SFC analysis on a CHIRALCEL OD-H column (15% MeOH/CO_2, 3.0 mL/min) with t_r = 7.5 min (minor), 8.5 min (major).

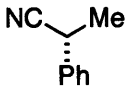
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.34 (m, 3H), 7.28 (d, 2H, *J* = 7.2 Hz), 3.87 (apparent d, 1H, *J* = 12.6 Hz), 3.82 (apparent d, 1H, *J* = 12.6 Hz), 3.67–3.65 (m, 3H), 3.05 (dd, 2H, *J* = 7.3, 7.3 Hz), 2.74 (ddd, 1H, *J* = 2.4, 12.3, 12.3 Hz), 2.69 (ddd, 1H, *J* = 2.4, 12.3, 12.3 Hz), 2.25 (ddd, 2H, *J* = 6.4, 6.4, 12.9 Hz), 1.99 (apparent d, 1H, *J* = 13.1 Hz), 1.92–1.85 (m, 1H), 1.66 (apparent d, 1H, *J* = 13.2 Hz), 1.53 (dddd, 1H, *J* = 4.3, 12.4, 12.4, 12.4 Hz), 1.44 (dddd, 1H, *J* = 4.3, 12.4, 12.4, 12.4 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 133.4, 129.3, 128.6, 128.0, 119.4, 46.9, 45.6 (2C), 43.3, 43.0, 40.8, 29.9, 29.3, 26.5.

FT-IR (neat) 3032, 2987, 2925, 2869, 2857, 2240, 1494, 1469, 1453, 1360, 1334, 1305, 1250, 1148, 1102, 1070, 1047, 1005, 993, 936, 914, 800, 761, 736, 703, 640, 623, 612 cm^{-1}.

MS (ESI) *m/z* (M^++H) calcd for $C_{16}H_{22}ClN_2O_2S$: 341.1, found: 341.1.

$[\alpha]^{24}_D = +17.8°$ (c = 1.02, $CHCl_3$).



(*R*)-2-Phenylpropanenitrile (Table 2, entry 10). 2-Bromopropanenitrile (80 mg, 0.60 mmol; Adrich) was used. The product was purified by column chromatography (5% Et_2O/hexanes). Colorless oil. First run: 54 mg (69%, 81% ee). Second run: 51 mg (65%, 82% ee).

The ee was determined by GC analysis on a G-TA column (100 °C hold 5 min, then 100 °C→180 °C @ 5 °C/min, hold 10 min, 1.7 mL/min) with t_r = 10.7 min (major), 11.9 min (minor).

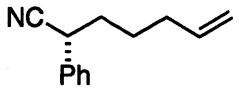
^1H NMR (500 MHz, $CDCl_3$) δ 7.41–7.31 (m, 5H), 3.91 (q, 1H, *J* = 7.3 Hz), 1.65 (d, 3H, *J* = 7.3 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.2, 129.3, 128.2, 126.8, 121.7, 31.4, 21.6.

FT-IR (neat) 3065, 3032, 2985, 2932, 2242, 1955, 1881, 1808, 1726, 1600, 1493, 1451, 1379, 1285, 1078, 1030, 988 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for C_9H_9N: 131, found: 131.

$[\alpha]^{23}_D = +15.9°$ (c = 1.00, $CHCl_3$).



(*R*)-2-Phenylhept-6-enenitrile (Table 2, entry 11). 2-Bromohept-6-enenitrile (113 mg, 0.60 mmol) was used. The product was purified by column chromatography (2% Et_2O/hexanes). Colorless oil. First run: 104 mg (94%, 77% ee). Second run: 92 mg (83%, 78% ee).

The ee was determined by GC analysis on a G-TA column (100 °C hold 5 min, then 100 °C→180 °C @ 3 °C/min, hold 10 min, 1.7 mL/min) with t_r = 23.0 min (major), 23.5 min (minor).

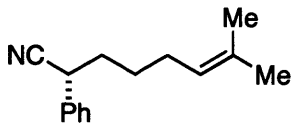
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.36 (m, 2H), 7.34–7.31 (m, 3H), 5.76 (dddd, 1H, J = 6.8, 6.8, 10.2, 17.0 Hz), 5.04–4.97 (m, 2H), 3.79 (dd, 1H, J = 6.3, 8.6 Hz), 2.13–2.08 (m, 2H), 1.98–1.84 (m, 2H), 1.67–1.51 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.7, 136.0, 129.2, 128.2, 127.4, 120.9, 115.6, 37.4, 35.3, 33.1, 26.2.

FT-IR (neat) 3066, 3032, 2978, 2929, 2863, 2240, 1954, 1811, 1641, 1601, 1494, 1455, 1416, 1344, 1079, 1031, 994, 914, 757, 699 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_{13}H_{15}N$: 185, found: 185.

$[\alpha]^{24}_D$ = +16.8° (c = 1.01, $CHCl_3$).



(*R*)-7-Methyl-2-phenyloct-6-enenitrile (Table 2, entry 12). 2-Bromo-7-methyloct-6-enenitrile (130 mg, 0.60 mmol) was used. The product was purified by

column chromatography (2%→5% Et_2O/hexanes). Colorless oil. First run: 119 mg (93%, 76% ee). Second run: 120 mg (94%, 77% ee).

The ee was determined by GC analysis on a G-TA column (110 °C hold 5 min, then 110 °C→180 °C @ 1 °C/min, hold 10 min, 1.7 mL/min) with t_r = 46.6 min (major), 47.7 min (minor).

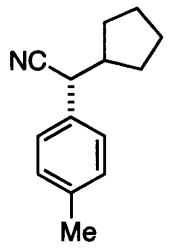
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.37 (m, 2H), 7.33–7.31 (m, 3H), 5.06 (t, 1H, J = 7.1 Hz), 3.77 (dd, 1H, J = 6.3, 8.5 Hz), 2.02, (q, 2H, J = 7.2 Hz), 1.97–1.82 (m, 2H), 1.68 (s, 3H), 1.59 (s, 3H), 1.57–1.45 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 136.2, 132.6, 129.2, 128.1, 127.4, 123.5, 121.0, 37.5, 35.5, 27.4, 27.3, 25.8, 17.9.

FT-IR (neat) 3032, 2928, 2861, 2240, 1602, 1495, 1454, 1377, 1110, 1080, 1031, 912, 833, 755, 699 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_{15}H_{19}N$: 213, found: 213.

$[\alpha]^{23}_D$ = +14.0° (c = 1.00, $CHCl_3$).



(*R*)-2-Cyclopentyl-2-(*p*-tolyl)acetonitrile (Table 3, entry 1). 2-Bromo-2-cyclopentylacetonitrile (150 mg, 0.80 mmol) and *p*-tolylmagnesium bromide (1.05 M in THF; Aldrich) were used. The product was purified by column chromatography (2%→3.5% Et_2O/hexanes). Colorless oil. First run: 149 mg (93%, 93% ee). Second run: 151 mg (95%, 94% ee).

The ee was determined by HPLC analysis on a CHIRALCEL OJ-H column (1% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 10.4 min (major), 11.7 min (minor).

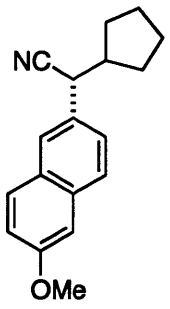
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21–7.16 (m, 4H), 3.67 (d, 1H, J = 7.8 Hz), 2.35 (s, 3H), 2.33–2.25 (m, 1H), 1.88–1.82 (m, 1H), 1.76–1.64 (m, 3H), 1.61–1.42 (m, 3H), 1.37–1.29 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.8, 133.0, 129.7, 127.6, 120.9, 45.4, 42.2, 31.1, 30.4, 25.0 (2C), 21.2.

FT-IR (neat) 3026, 2957, 2870, 2239, 1904, 1799, 1653, 1616, 1515, 1452, 1417, 1380, 1351, 1309, 1215, 1186, 1113, 1041, 1022, 813, 770, 719 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_{14}H_{17}N$: 199, found: 199.

$[\alpha]^{24}_D$ = +29.6° (c = 0.99, $CHCl_3$).



(*R*)-2-Cyclopentyl-2-(6-methoxynaphthalen-2-yl)acetonitrile (Table 3, entry 2). 2-Bromo-2-cyclopentylacetonitrile (150 mg, 0.80 mmol) and (6-methoxynaphthalen-2-yl)magnesium bromide (1.22 M in THF) were used. The product was purified by column chromatography (5%→10% Et_2O/hexanes). Light-yellow solid. First run: 203 mg (96%, 94% ee). Second run: 184 mg (87%, 95% ee).

The ee was determined by HPLC analysis on a CHIRALCEL OJ-H column (10% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 16.5 min (minor), 24.4 min (major).

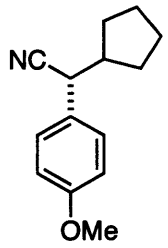
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75–7.71 (m, 3H), 7.37 (dd, 1H, J = 1.8, 8.5 Hz), 7.18 (dd, 1H, J = 2.5, 8.9 Hz), 7.13 (d, 1H, J = 2.5 Hz), 3.93 (s, 3H), 3.84 (d, 1H, J = 7.8 Hz), 2.44–2.36 (m, 1H), 1.90–1.84 (m, 1H), 1.78–1.67 (m, 3H), 1.63–1.51 (m, 3H), 1.43–1.35 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 134.1, 131.0, 129.4, 128.8, 127.7, 126.6, 125.8, 120.8, 119.6, 105.7, 55.5, 45.3, 42.6, 31.1, 30.4, 25.1, 25.0.

FT-IR (neat) 2957, 2869, 2237, 1635, 1607, 1507, 1485, 1457, 1419, 1393, 1348, 1266, 1230, 1213, 1174, 1121, 1031, 890, 852, 811, 673 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_{18}H_{19}NO$: 265, found: 265.

$[\alpha]^{25}_D$ = +26.4° (c = 1.00, $CHCl_3$).



(*R*)-2-Cyclopentyl-2-(4-methoxyphenyl)acetonitrile (Table 3, entry 3). 2-Bromo-2-cyclopentylacetonitrile (150 mg, 0.80 mmol) and 4-methoxyphenylmagnesium bromide (0.42 M in THF; Aldrich) were used. The product was purified by column chromatography (5%→10% Et_2O/hexanes). Light-yellow solid. First run: 135 mg (78%, 94% ee). Second run: 144 mg (84%, 95% ee).

The ee was determined by HPLC analysis on a CHIRALPAK AS-H column (10% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 12.4 min (major), 16.1 min (minor).

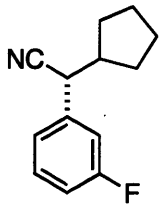
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, 2H, J = 8.8 Hz), 6.89 (d, 2H, J = 8.5 Hz), 3.81 (s, 3H), 3.65 (d, 1H, J = 7.9 Hz), 2.32–2.24 (m, 1H), 1.89–1.83 (m, 1H), 1.75–1.64 (m, 3H), 1.62–1.45 (m, 3H), 1.35–1.29 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.3, 128.8, 128.0, 121.0, 114.4, 55.5, 45.5, 41.8, 31.0, 30.4, 25.0 (2C).

FT-IR (neat) 2959, 2868, 2838, 2234, 1613, 1514, 1465, 1442, 1424, 1348, 1303, 1252, 1180, 1107, 1035, 824 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_{14}H_{17}NO$: 215, found: 215.

$[\alpha]^{25}_D$ = +25.0° (c = 1.00, $CHCl_3$).



(*R*)-2-Cyclopentyl-2-(3-fluorophenyl)acetonitrile (Table 3, entry 4). 2-Bromo-2-cyclopentylacetonitrile (150 mg, 0.80 mmol) and (3-fluorophenyl)magnesium bromide (0.86 M in THF; Aldrich) were used. The reaction was run at –60 °C. The product was purified by column chromatography (1.6%→3% Et_2O/hexanes). Colorless oil. First run: 164 mg (100%, 93% ee). Second run: 161 mg (99%, 93% ee).

The ee was determined by GC analysis on a G-TA column (100 °C hold 5 min, then 100 °C→180 °C @ 5 °C/min, hold 10 min, 1.7 mL/min) with t_r = 19.7 min (major), 20.4 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (apparent ddd, 1H, J = 5.9, 7.9, 7.9 Hz), 7.12–7.10 (m, 1H), 7.06–7.03 (m, 1H), 7.01 (ddd, 1H, J = 0.9, 2.5, 3.4 Hz), 3.72 (d, 1H, J = 7.6

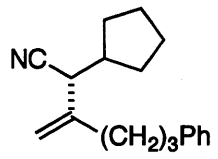
Hz), 2.34–2.26 (m, 1H), 1.88–1.82 (m, 1H), 1.77–1.67 (m, 3H), 1.63–1.45 (m, 3H), 1.39–1.31 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.0 (d, J = 248 Hz), 138.4, 130.7 (d, J = 8 Hz), 123.4 (d, J = 3 Hz), 120.1, 115.2 (d, J = 21 Hz), 114.9 (d, J = 22 Hz), 45.3, 42.3, 31.1, 30.3, 25.0, 24.9.

FT-IR (neat) 3064, 2958, 2918, 2871, 2241, 1616, 1593, 1489, 1449, 1355, 1318, 1265, 1248, 1140, 1078, 871, 786, 761, 694 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_{13}H_{14}FN$: 203, found: 203.

$[\alpha]^{25}_D$ = +29.5° (c = 1.01, $CHCl_3$).



(*R*)-2-Cyclopentyl-3-methylene-6-phenylhexanenitrile (Table 4, entry 1). 2-Bromo-2-cyclopentylacetonitrile (150 mg, 0.80 mmol) and (5-phenylpent-1-en-2-yl)magnesium bromide (0.75 M in THF) were used. (4-Bromopent-4-en-1-yl)benzene was prepared from pent-4-yn-1-ylbenzene following a literature procedure.[25] The reaction was run at –60 °C. The product was purified by column chromatography (3%→5% Et_2O/hexanes). Colorless oil. First run: 131 mg (65%, 80% ee). Second run: 128 mg (63%, 80% ee).

The ee was determined by HPLC analysis on a CHIRALCEL OJ-H column (1% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 18.6 min (minor), 20.7 min (major).

[25] Hara, S.; Dojo, H.; Takinami, S.; Suzuki, A. *Tetrahedron Lett.* **1983**, *24*, 731–734.

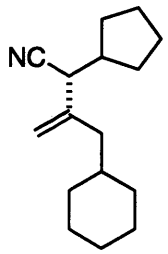
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.28 (m, 2H), 7.21–7.18 (m, 3H), 5.15 (s, 1H), 5.02 (s, 1H), 3.13 (d, 1H, J = 7.5 Hz), 2.71–2.60 (m, 2H), 2.24–2.16 (m, 2H), 2.13–2.05 (m, 1H), 1.89–1.78 (m, 3H), 1.79–1.65 (m, 3H), 1.63–1.51 (m, 2H), 1.45–1.36 (m, 1H), 1.36–1.24 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.9, 142.0, 128.5 (2C), 126.1, 120.3, 114.0, 43.7, 40.7, 35.5, 33.2, 31.2, 30.2, 29.4, 25.3, 25.1.

FT-IR (neat) 3085, 3062, 3027, 2948, 2868, 2237, 1647, 1603, 1496, 1453, 1353, 1080, 1030, 905, 750, 699 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{18}H_{23}NNa$: 276.2, found: 276.2.

$[\alpha]^{24}_D = -2.9°$ (c = 1.00, $CHCl_3$).



(*R*)-3-(Cyclohexylmethyl)-2-cyclopentylbut-3-enenitrile (Table 4, entry 2). 2-Bromo-2-cyclopentylacetonitrile (150 mg, 0.80 mmol) and (3-cyclohexylprop-1-en-2-yl)magnesium bromide (0.72 M in THF) were used. (2-Bromoallyl)cyclohexane was prepared from prop-2-yn-1-ylcyclohexane following a literature procedure.[25] The reaction was run at –60 °C. The product was purified by column chromatography (2%→3% Et_2O/hexanes). Light-yellow oil. First run: 112 mg (61%, 85% ee). Second run: 106 mg (57%, 86% ee).

The ee was determined by GC analysis on a G-TA column (75 °C hold 1 min, then 75 °C→180 °C @ 2 °C/min, hold 15 min, 1.0 mL/min) with t_r = 52.7 min (minor), 53.2 min (major).

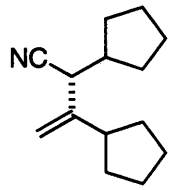
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.18 (s, 1H), 4.97 (d, 1H, J = 0.6 Hz), 3.13 (d, 1H, J = 7.1 Hz), 2.25–2.17 (m, 1H), 2.01–1.93 (m, 2H), 1.86–1.64 (m, 8H), 1.61–1.54 (m, 2H), 1.49–1.31 (m, 3H), 1.29–1.10 (m, 4H), 0.94–0.81 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 120.4, 114.9, 43.1, 42.2, 40.5, 35.7, 33.6, 33.0, 31.2, 30.0, 26.6, 26.4, 26.3, 25.4, 25.2.

FT-IR (neat) 3084, 2924, 2852, 2665, 2238, 1647, 1449, 1350, 1262, 1080, 905 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_{16}H_{25}N$: 231, found: 231.

$[\alpha]^{24}_D = -11.3°$ (c = 1.00, $CHCl_3$).



(*R*)-2,3-Dicyclopentylbut-3-enenitrile (Table 4, entry 3). 2-Bromo-2-cyclopentylacetonitrile (150.5 mg, 0.80 mmol) and (1-cyclopentylvinyl)magnesium bromide (0.73 M in THF) were used. (1-Bromovinyl)cyclopentane was prepared from ethynylcyclopentane following a literature procedure.[25] The reaction was run at –60 °C. The product was purified by column chromatography (3% Et_2O/hexanes). Colorless oil. First run: 125 mg (77%, 88% ee). Second run: 129 mg (79%, 90% ee).

The ee was determined by GC analysis on a CP-Chirasil-Dex CB column (120 °C hold 60 min, 1.0 mL/min) with t_r = 44.0 min (major), 46.0 min (minor).

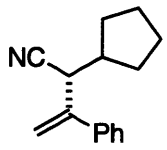
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.13 (s, 1H), 5.06 (d, 1H, J = 1.3 Hz), 3.18 (d, 1H, J = 7.2 Hz), 2.43–2.37 (m, 1H), 2.30–2.22 (m, 1H), 1.94–1.82 (m, 3H), 1.81–1.67 (m, 5H), 1.64–1.54 (m, 4H), 1.49–1.31 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.4, 120.6, 111.9, 44.3, 43.5, 41.0, 32.9, 32.6, 31.3, 30.1, 25.3, 25.2, 25.0, 24.9.

FT-IR (neat) 3091, 2956, 2869, 2237, 1645, 1473, 1452, 1351, 1306, 1162, 902 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{14}H_{21}NNa$: 226.2, found: 226.2.

$[\alpha]^{24}_D$ = +7.2° (c = 1.00, $CHCl_3$).



(*R*)-2-Cyclopentyl-3-phenylbut-3-enenitrile (Table 4, entry 4). 2-Bromo-2-cyclopentylacetonitrile (150 mg, 0.80 mmol) and (1-phenylvinyl)magnesium bromide (0.80 M in THF) were used. The reaction was run at –60 °C. The product was purified by column chromatography (2%→3% Et_2O/hexanes). Colorless oil. First run: 157 mg (93%, 91% ee). Second run: 162 mg (96%, 91% ee).

The ee was determined by HPLC analysis on a CHIRALCEL OJ-H column (1% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 9.1 min (major), 15.3 min (minor).

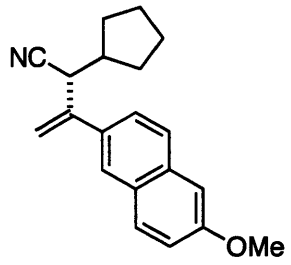
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.31 (m, 5H), 5.55 (d, 1H, J = 1.2 Hz), 5.42 (s, 1H), 3.83 (dd, 1H, J = 1.1, 6.1 Hz), 2.12–2.04 (m, 1H), 1.76–1.64 (m, 4H), 1.54–1.36 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.4, 139.1, 128.8, 128.4, 126.7, 120.0, 116.6, 42.5, 40.7, 31.2, 29.3, 25.5, 25.1.

FT-IR (neat) 3057, 2956, 2869, 2240, 1954, 1830, 1630, 1576, 1495, 1445, 1294, 1075, 1029, 910, 775, 700 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_{15}H_{17}N$: 211, found: 211.

$[\alpha]^{25}_D = -16.4°$ (c = 1.00, $CHCl_3$).



(*R*)-2-Cyclopentyl-3-(6-methoxynaphthalen-2-yl)but-3-enenitrile (Table 4, entry 5). 2-Bromo-2-cyclopentylacetonitrile (113 mg, 0.60 mmol) and (1-(6-methoxynaphthalen-2-yl)vinyl)magnesium bromide (0.51 M in THF) were used. The reaction was run at –60 °C. The product was purified by column chromatography (first purification: 5% Et_2O/hexanes, second purification: 50% toluene/hexanes). Yellow liquid. First run: 162 mg (93%, 92% ee). Second run (0.20 mmol): 53 mg (91%, 92% ee).

The ee was determined by HPLC on a CHIRALPAK IA column (1% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 15.4 min (major), 20.0 min (minor).

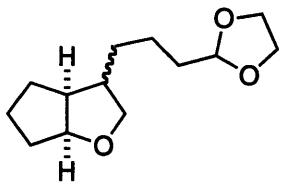
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75–7.72 (m, 3H), 7.45 (dd, 1H, J = 2.0, 8.5 Hz), 7.18 (dd, 1H, J = 2.5, 9.0 Hz), 7.13 (d, 1H, J = 2.5 Hz), 5.60 (d, 1H, J = 1.0 Hz), 5.53 (s, 1H), 3.95–3.93 (m, 4H), 2.17–2.09 (m, 1H), 1.78–1.65 (m, 4H), 1.52–1.40 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 143.4, 134.4, 134.2, 129.8, 128.8, 127.3, 125.4, 125.2, 120.2, 119.6, 116.4, 105.8, 55.5, 42.5, 41.0, 31.3, 29.4, 25.5, 25.1.

FT-IR (neat) 3058, 2956, 2869, 2239, 1630, 1603, 1502, 1484, 1463, 1453, 1411, 1392, 1336, 1270, 1208, 1165, 1127, 1032, 898, 854, 810, 758 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_{20}H_{21}NO$: 291, found: 291.

$[\alpha]^{26}_D$ = –23.9° (c = 1.00, $CHCl_3$).



3-(3-(1,3-Dioxolan-2-yl)propyl)hexahydro-2*H*-cyclopenta[*b*]furan (eq 8). The title compound was prepared from *trans*-1-(allyloxy)-2-bromocyclopentane (123 mg, 0.60 mmol) and (2-(1,3-dioxolan-2-yl)ethyl)zinc bromide (0.96 mmol; ~0.75 M in DMA) following a procedure for nickel-catalyzed Negishi cross-couplings.[26] The product was purified by column chromatography on silica gel (20% ethyl acetate/hexanes) and then on C-18 silica gel (10%→100% acetonitrile/water). Light-yellow oil. First run: 103 mg (76%, endo:exo = 2.3:1). Second run: 111 mg (82%, endo:exo = 2.3:1). The spectral data matched previously reported data.[27]

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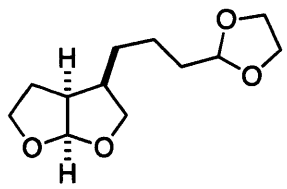
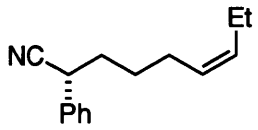
[26] Zhou, J.; Fu, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 14726–14727.
[27] Phapale, V. B.; Bunuel, E.; García-Iglesias, M.; Cárdenas, D. J. *Angew. Chem., Int. Ed.* **2007**, *46*, 8790–8795.



(3*R,3a*S**,6a*R**)-3-(3-(1,3-dioxolan-2-yl)propyl)hexahydrofuro[2,3-*b*]furan (eq 8).** The title compound was prepared from *trans*-2-(allyloxy)-3-bromotetrahydrofuran (124 mg, 0.60 mmol) and (2-(1,3-dioxolan-2-yl)ethyl)zinc bromide (0.96 mmol; ~0.75 M in DMA) following a procedure for nickel-catalyzed Negishi cross-couplings.[26] The product was purified by column chromatography (40% ethyl acetate/hexanes). Light-yellow oil. First run: 118 mg (86%, endo:exo = 44:1). Second run: 120 mg (88%, endo:exo = 44:1). The spectral data matched previously reported data.[27]



(*R*,*Z*)-2-Phenylnon-6-enenitrile (eq 9). (*Z*)-2-Bromonon-6-enenitrile (130 mg, 0.60 mmol) was used. The product was purified by column chromatography (2%→3% Et_2O/hexanes). Colorless oil. First run: 122 mg (95%, 77% ee). Second run: 120 mg (94%, 77% ee).

The ee was determined by HPLC analysis on a CHIRALCEL OJ-H column (1% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 9.1 min (major), 11.0 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.36 (m, 2H), 7.34–7.31 (m, 3H), 5.40 (ddddd, 1H, *J* = 1.6, 1.6, 7.2, 7.2, 10.8 Hz), 5.27 (ddddd, 1H, *J* = 1.5, 1.5, 7.2, 7.2, 10.8

Hz), 3.78 (dd, 1H, J = 6.3, 8.5 Hz), 2.08 (q, 2H, J = 7.3 Hz), 2.02 (quintet, 2H, J = 7.5 Hz), 1.98–1.84 (m, 2H), 1.62–1.47 (m, 2H), 0.95 (t, 3H, J = 7.5 Hz).

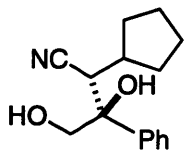
^{13}C NMR (126 MHz, $CDCl_3$) δ 136.1, 132.9, 129.2, 128.2, 127.8, 127.4, 121.0, 37.4, 35.5, 27.1, 26.4, 20.7, 14.4.

FT-IR (neat) 3066, 3007, 2931, 2863, 2240, 1653, 1602, 1495, 1455, 1405, 1373, 1304, 1070, 1030, 969, 912, 756, 698 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_{13}H_{19}N$: 213, found: 213.

$[\alpha]^{24}_D$ = +12.6° (c = 1.00, $CHCl_3$).

IV. Functionalization of the Cross-Coupling Product



(2*S*,3*S*)-2-Cyclopentyl-3,4-dihydroxy-3-phenylbutanenitrile (eq 7). The title compound was prepared via a modification of a literature procedure.[28] (*R*)-2-Cyclopentyl-3-phenylbut-3-enenitrile (80 mg, 0.38 mmol; Table 4, entry 4; from a reaction using (*S*,*S*)–**L2**), $K_3Fe(CN)_6$ (374 mg, 1.14 mmol), K_2CO_3 (157 mg, 1.14 mmol), 1,4-diazabicyclo[2.2.2]octane (21 mg, 0.19 mmol), water (1.89 mL), and *t*-BuOH (1.31 mL) were added to a 20-mL vial equipped with a magnetic stir bar. The vial was sealed with a PTFE-lined septum cap, and the mixture was stirred at r.t. for 10 min. Then, the solution was cooled to 0 °C, and OsO_4 (0.58 mL; 2.5 wt% solution in *t*-BuOH; Aldrich) was added to the vial. The reaction mixture was stirred at 0 °C for 72 h, and then the

[28] Petrova, K. V.; Mohr , J. T.; Stoltz, B. M. *Org. Lett.* **2009**, *11*, 293–295.

reaction was quenched by the addition of saturated aqueous Na_2SO_3 (5 mL). The solution was stirred for 1 h, and then the reaction mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated. The product was purified by column chromatography (20%→25% ethyl acetate/hexanes). Brown oil. First run: 75 mg (80% yield, 13:1 dr). Second run (0.43 mmol; from a reaction using (*R*,*R*)–**L2**): 79 mg (75% yield, 12:1 dr).

The dr was determined by HPLC analysis on a CHIRALCEL OD-H column (10% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 9.3, 12.6 min (major), 17.9, 23.7 min (minor). The stereochemistry of the major isomer was assigned on the basis of an X-ray crystal structure of the cyclic-carbonate derivative.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60–7.57 (m, 2H), 7.43–7.39 (m, 2H), 7.36–7.33 (m, 1H), 4.12 (dd, 1H, *J* = 11.1, 7.0 Hz), 4.04 (dd, 1H, *J* = 11.1, 4.0 Hz), 3.19 (d, 1H, *J* = 4.8 Hz), 3.12 (s, 1H), 2.10–2.02 (m, 1H), 1.86–1.80 (m, 2H), 1.65–1.51 (m, 2H), 1.45–1.31 (m, 3H), 1.30–1.23 (m, 1H), 1.13–1.05 (m, 1H).

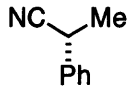
^{13}C NMR (126 MHz, $CDCl_3$) δ 140.0, 128.8, 128.4, 125.9, 119.6, 76.7, 68.4, 45.6, 37.0, 33.2, 30.1, 25.2, 24.8.

FT-IR (neat) 3439, 2955, 2870, 2242, 1496, 1449, 1395, 1289, 1184, 1135, 1069, 959, 909, 771, 703 cm^{-1}.

MS (EI) *m/z* (M^++H) calcd for $C_{15}H_{20}NO_2$: 246.1, found: 246.1.

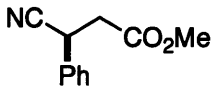
$[\alpha]^{24}_D$ = 37.4° (c = 0.96, $CHCl_3$).

V. Assignment of Absolute Stereochemistry



(*R*)-2-Phenylpropanenitrile (from a reaction using (*S,S*)–L2). 2-Phenylpropanenitrile was prepared from 2-bromopropanenitrile and Ph_2Zn according to the general procedure.

To determine the absolute stereochemistry, the specific rotation of the product was compared with the literature: $[\alpha]^{25}_D = +22.6°$ (c = 1.00, $CHCl_3$; 90% ee); lit.[29] $[\alpha]^{RT}_D = +18.5°$ (c = 1.2, $CHCl_3$; ≥95% ee; *R* enantiomer). Therefore, the absolute configuration of the cross-coupling product is assigned as *R*.



(*S*)-Methyl 3-cyano-3-phenylpropanoate (from a reaction using (*R,R*)–L2). Methyl 3-cyano-3-phenylpropanoate was prepared from methyl 3-bromo-3-cyanopropanoate and Ph_2Zn according to the general procedure.

To determine the absolute stereochemistry, the specific rotation of the product was compared with the literature: $[\alpha]^{25}_D = -16.0°$ (c = 1.02, MeOH; 88% ee); lit.[30] $[\alpha]^{29}_D = -15.3°$ (c = 1.15, MeOH; 94% ee). Therefore, the absolute configuration of the cross-coupling product is assigned as *S*.

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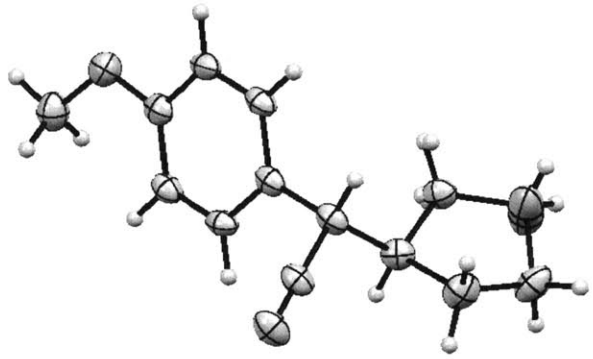
[29] Enders, D.; Plant, A.; Backhaus, D.; Reinhold, U. *Tetrahedron* **1995**, *51*, 10699–10714.
[30] Fryszkowska, A.; Fisher, K.; Gardiner, J. M.; Stephens, G. M. *Org. Biomol. Chem.* **2010**, *8*, 533–535.

Product from entry 4 of Table 3 (run with (*R*,*R*)–L2). (*S*)-2-Cyclopentyl-2-(4-methoxyphenyl)acetonitrile. A crystal suitable for X-ray crystallography was grown by vapor diffusion with dichloromethane and pentane.



Reference for the Hooft/Spek method: Hooft, R. W. W.; Straver, L. H.; Spek, A. L. *J. Appl. Cryst.* **2007**, *41*, 96–103. Absolute configuration: The Flack test is inconclusive because this is a light-atom structure. However the method by Spek and Hooft, which is based on Bayesian statistics, results in the following probabilities (see also file X11176_t4.lis): The probability P2(true) of the model to be correct assuming that the structure is either right or wrong is 1.000. The probability P3(true) of the model to be correct assuming that the structure is either right or wrong or a 50:50 racemic twin is 1.000. The probability P3(rac-twin) of the model to be a 50:50 racemic twin is 0.1E-14. The probability P3(false) of the model to be wrong is 0.4E-95. There are two independent molecules in the asymmetric unit, and two of the atoms in the cyclohexane group in both are disordered with appropriate restraints. For the second molecule the anisotropic displacement parameters of one of the carbons was constrained to be equivalent to the major component.

Table 1. Crystal data and structure refinement for X11176_t5.

Identification code	x11176_t5	
Empirical formula	C14 H17 N O	
Formula weight	215.29	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 5.6768(2) Å	a= 90°.
	b = 9.5536(3) Å	b= 92.523(2)°.
	c = 21.6728(7) Å	g = 90°.
Volume	1174.26(7) $Å^3$	
Z	4	
Density (calculated)	1.218 Mg/m^3	
Absorption coefficient	0.595 mm^{-1}	
F(000)	464	
Crystal size	0.25 x 0.20 x 0.15 mm^3	
Theta range for data collection	2.04 to 70.23°.	
Index ranges	-6<=h<=6, -11<=k<=11, -26<=l<=26	
Reflections collected	4343	
Independent reflections	4349 [R(int) = 0.0395]	
Completeness to theta = 70.23°	98.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9160 and 0.8655	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4349 / 276 / 324	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0326, wR2 = 0.0841	
R indices (all data)	R1 = 0.0326, wR2 = 0.0842	
Absolute structure parameter	0.1(3)	
Largest diff. peak and hole	0.188 and -0.131 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for X11176_t5. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	560(3)	7685(2)	7064(1)	39(1)
C(1)	335(4)	7459(2)	6444(1)	29(1)
C(2)	-1575(4)	7894(2)	6066(1)	30(1)
C(3)	-1634(3)	7582(2)	5445(1)	27(1)
C(4)	169(3)	6828(2)	5181(1)	26(1)
C(8)	16(3)	6448(2)	4500(1)	28(1)
C(9)	-2195(3)	5676(2)	4359(1)	30(1)
N(1)	-3973(3)	5142(2)	4254(1)	41(1)
C(11)	128(3)	7724(2)	4060(1)	29(1)
C(12)	-12(4)	7273(2)	3370(1)	38(1)
C(13)	2458(7)	7515(5)	3145(1)	39(1)
C(14)	3199(9)	8845(5)	3500(2)	38(1)
C(13A)	1792(15)	8262(11)	3060(3)	42(2)
C(14A)	3776(16)	8333(12)	3523(4)	42(2)
C(15)	2483(4)	8523(2)	4148(1)	32(1)
C(5)	2074(3)	6414(2)	5563(1)	28(1)
C(6)	2165(3)	6723(2)	6182(1)	30(1)
C(7)	-1410(4)	8310(2)	7347(1)	41(1)
O(2)	5483(3)	782(2)	-1866(1)	38(1)
C(21)	5262(4)	955(2)	-1248(1)	30(1)
C(22)	3345(3)	495(2)	-922(1)	29(1)
C(23)	3308(3)	751(2)	-293(1)	28(1)
C(24)	5113(3)	1475(2)	22(1)	27(1)
C(28)	5070(3)	1744(2)	709(1)	30(1)
C(29)	2855(3)	2478(2)	856(1)	30(1)
N(2)	1111(3)	2998(2)	971(1)	39(1)
C(31)	5303(4)	406(2)	1111(1)	31(1)
C(32)	5310(4)	713(2)	1808(1)	40(1)
C(33)	6727(6)	-446(3)	2101(1)	40(1)
C(34)	8690(16)	-650(8)	1662(2)	61(2)
C(33A)	7840(20)	314(15)	2046(4)	49(3)
C(34A)	8510(60)	-890(30)	1651(7)	61(2)
C(35)	7639(3)	-378(2)	1014(1)	32(1)
C(25)	7020(3)	1919(2)	-313(1)	30(1)
C(26)	7097(3)	1662(2)	-934(1)	32(1)
C(27)	3583(4)	110(2)	-2202(1)	40(1)

Table 3. Bond lengths [Å] and angles [°] for X11176_t5.

O(1)-C(1)	1.362(2)
O(1)-C(7)	1.429(3)
C(1)-C(2)	1.392(3)
C(1)-C(6)	1.395(3)
C(2)-C(3)	1.378(2)
C(2)-H(2)	0.9500
C(3)-C(4)	1.395(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.390(2)
C(4)-C(8)	1.519(2)
C(8)-C(9)	1.475(2)
C(8)-C(11)	1.551(2)
C(8)-H(8)	1.0000
C(9)-N(1)	1.145(3)
C(11)-C(15)	1.544(3)
C(11)-C(12)	1.554(2)
C(11)-H(11)	1.0000
C(12)-C(13)	1.522(4)
C(12)-C(13A)	1.567(7)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(12)-H(12C)	0.9900
C(12)-H(12D)	0.9900
C(13)-C(14)	1.535(5)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-C(15)	1.512(4)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(13A)-C(14A)	1.478(11)
C(13A)-H(13C)	0.9900
C(13A)-H(13D)	0.9900
C(14A)-C(15)	1.579(9)
C(14A)-H(14C)	0.9900
C(14A)-H(14D)	0.9900
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(15)-H(15C)	0.9900
C(15)-H(15D)	0.9900
C(5)-C(6)	1.374(2)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
O(2)-C(21)	1.361(2)
O(2)-C(27)	1.427(3)
C(21)-C(26)	1.394(3)
C(21)-C(22)	1.394(3)
C(22)-C(23)	1.384(2)
C(22)-H(22)	0.9500
C(23)-C(24)	1.390(2)

C(23)-H(23)	0.9500
C(24)-C(25)	1.396(3)
C(24)-C(28)	1.512(2)
C(28)-C(29)	1.486(2)
C(28)-C(31)	1.549(2)
C(28)-H(28)	1.0000
C(29)-N(2)	1.145(3)
C(31)-C(32)	1.538(2)
C(31)-C(35)	1.545(2)
C(31)-H(31)	1.0000
C(32)-C(33)	1.493(3)
C(32)-C(33A)	1.550(9)
C(32)-H(32A)	0.9900
C(32)-H(32B)	0.9900
C(32)-H(32C)	0.9900
C(32)-H(32D)	0.9900
C(33)-C(34)	1.509(8)
C(33)-H(33A)	0.9900
C(33)-H(33B)	0.9900
C(34)-C(35)	1.523(5)
C(34)-H(34A)	0.9900
C(34)-H(34B)	0.9900
C(33A)-C(34A)	1.497(16)
C(33A)-H(33C)	0.9900
C(33A)-H(33D)	0.9900
C(34A)-C(35)	1.526(14)
C(34A)-H(34C)	0.9900
C(34A)-H(34D)	0.9900
C(35)-H(35A)	0.9900
C(35)-H(35B)	0.9900
C(35)-H(35C)	0.9900
C(35)-H(35D)	0.9900
C(25)-C(26)	1.371(3)
C(25)-H(25)	0.9500
C(26)-H(26)	0.9500
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800

C(1)-O(1)-C(7)	116.65(16)
O(1)-C(1)-C(2)	124.69(17)
O(1)-C(1)-C(6)	116.22(17)
C(2)-C(1)-C(6)	119.09(16)
C(3)-C(2)-C(1)	119.63(17)
C(3)-C(2)-H(2)	120.2
C(1)-C(2)-H(2)	120.2
C(2)-C(3)-C(4)	121.72(17)
C(2)-C(3)-H(3)	119.1
C(4)-C(3)-H(3)	119.1
C(5)-C(4)-C(3)	117.90(16)
C(5)-C(4)-C(8)	121.38(16)
C(3)-C(4)-C(8)	120.71(16)
C(9)-C(8)-C(4)	109.38(15)
C(9)-C(8)-C(11)	108.86(14)

C(4)-C(8)-C(11)	114.07(14)
C(9)-C(8)-H(8)	108.1
C(4)-C(8)-H(8)	108.1
C(11)-C(8)-H(8)	108.1
N(1)-C(9)-C(8)	176.43(19)
C(15)-C(11)-C(8)	111.79(14)
C(15)-C(11)-C(12)	105.32(15)
C(8)-C(11)-C(12)	111.84(14)
C(15)-C(11)-H(11)	109.3
C(8)-C(11)-H(11)	109.3
C(12)-C(11)-H(11)	109.3
C(13)-C(12)-C(11)	104.93(18)
C(13)-C(12)-C(13A)	30.9(3)
C(11)-C(12)-C(13A)	103.8(3)
C(13)-C(12)-H(12A)	110.8
C(11)-C(12)-H(12A)	110.8
C(13A)-C(12)-H(12A)	135.5
C(13)-C(12)-H(12B)	110.8
C(11)-C(12)-H(12B)	110.8
C(13A)-C(12)-H(12B)	83.0
H(12A)-C(12)-H(12B)	108.8
C(13)-C(12)-H(12C)	134.3
C(11)-C(12)-H(12C)	111.0
C(13A)-C(12)-H(12C)	111.0
H(12A)-C(12)-H(12C)	82.0
H(12B)-C(12)-H(12C)	29.6
C(13)-C(12)-H(12D)	82.3
C(11)-C(12)-H(12D)	111.0
C(13A)-C(12)-H(12D)	111.0
H(12A)-C(12)-H(12D)	30.0
H(12B)-C(12)-H(12D)	130.6
H(12C)-C(12)-H(12D)	109.0
C(12)-C(13)-C(14)	101.6(3)
C(12)-C(13)-H(13A)	111.5
C(14)-C(13)-H(13A)	111.5
C(12)-C(13)-H(13B)	111.5
C(14)-C(13)-H(13B)	111.5
H(13A)-C(13)-H(13B)	109.3
C(15)-C(14)-C(13)	102.7(3)
C(15)-C(14)-H(14A)	111.2
C(13)-C(14)-H(14A)	111.2
C(15)-C(14)-H(14B)	111.2
C(13)-C(14)-H(14B)	111.2
H(14A)-C(14)-H(14B)	109.1
C(14A)-C(13A)-C(12)	103.2(6)
C(14A)-C(13A)-H(13C)	111.1
C(12)-C(13A)-H(13C)	111.1
C(14A)-C(13A)-H(13D)	111.1
C(12)-C(13A)-H(13D)	111.1
H(13C)-C(13A)-H(13D)	109.1
C(13A)-C(14A)-C(15)	102.7(6)
C(13A)-C(14A)-H(14C)	111.2
C(15)-C(14A)-H(14C)	111.2
C(13A)-C(14A)-H(14D)	111.2

C(15)-C(14A)-H(14D)	111.2
H(14C)-C(14A)-H(14D)	109.1
C(14)-C(15)-C(11)	104.6(2)
C(14)-C(15)-C(14A)	21.9(3)
C(11)-C(15)-C(14A)	105.6(4)
C(14)-C(15)-H(15A)	110.8
C(11)-C(15)-H(15A)	110.8
C(14A)-C(15)-H(15A)	127.9
C(14)-C(15)-H(15B)	110.8
C(11)-C(15)-H(15B)	110.8
C(14A)-C(15)-H(15B)	90.7
H(15A)-C(15)-H(15B)	108.9
C(14)-C(15)-H(15C)	128.9
C(11)-C(15)-H(15C)	110.6
C(14A)-C(15)-H(15C)	110.6
H(15A)-C(15)-H(15C)	90.0
H(15B)-C(15)-H(15C)	21.4
C(14)-C(15)-H(15D)	91.3
C(11)-C(15)-H(15D)	110.6
C(14A)-C(15)-H(15D)	110.6
H(15A)-C(15)-H(15D)	20.9
H(15B)-C(15)-H(15D)	125.3
H(15C)-C(15)-H(15D)	108.8
C(6)-C(5)-C(4)	121.05(17)
C(6)-C(5)-H(5)	119.5
C(4)-C(5)-H(5)	119.5
C(5)-C(6)-C(1)	120.59(17)
C(5)-C(6)-H(6)	119.7
C(1)-C(6)-H(6)	119.7
O(1)-C(7)-H(7A)	109.5
O(1)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
O(1)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(21)-O(2)-C(27)	117.16(15)
O(2)-C(21)-C(26)	116.10(17)
O(2)-C(21)-C(22)	124.65(17)
C(26)-C(21)-C(22)	119.24(17)
C(23)-C(22)-C(21)	119.25(17)
C(23)-C(22)-H(22)	120.4
C(21)-C(22)-H(22)	120.4
C(22)-C(23)-C(24)	121.93(16)
C(22)-C(23)-H(23)	119.0
C(24)-C(23)-H(23)	119.0
C(23)-C(24)-C(25)	117.87(17)
C(23)-C(24)-C(28)	121.68(17)
C(25)-C(24)-C(28)	120.43(17)
C(29)-C(28)-C(24)	109.97(15)
C(29)-C(28)-C(31)	108.73(15)
C(24)-C(28)-C(31)	114.12(14)
C(29)-C(28)-H(28)	107.9
C(24)-C(28)-H(28)	107.9
C(31)-C(28)-H(28)	107.9

N(2)-C(29)-C(28)	177.56(19)
C(32)-C(31)-C(35)	105.09(15)
C(32)-C(31)-C(28)	113.05(15)
C(35)-C(31)-C(28)	112.10(14)
C(32)-C(31)-H(31)	108.8
C(35)-C(31)-H(31)	108.8
C(28)-C(31)-H(31)	108.8
C(33)-C(32)-C(31)	104.72(16)
C(33)-C(32)-C(33A)	37.2(5)
C(31)-C(32)-C(33A)	104.0(4)
C(33)-C(32)-H(32A)	110.8
C(31)-C(32)-H(32A)	110.8
C(33A)-C(32)-H(32A)	76.9
C(33)-C(32)-H(32B)	110.8
C(31)-C(32)-H(32B)	110.8
C(33A)-C(32)-H(32B)	139.0
H(32A)-C(32)-H(32B)	108.9
C(33)-C(32)-H(32C)	76.5
C(31)-C(32)-H(32C)	111.0
C(33A)-C(32)-H(32C)	111.0
H(32A)-C(32)-H(32C)	133.7
H(32B)-C(32)-H(32C)	36.0
C(33)-C(32)-H(32D)	138.2
C(31)-C(32)-H(32D)	111.0
C(33A)-C(32)-H(32D)	111.0
H(32A)-C(32)-H(32D)	35.7
H(32B)-C(32)-H(32D)	76.2
H(32C)-C(32)-H(32D)	109.0
C(32)-C(33)-C(34)	103.1(3)
C(32)-C(33)-H(33A)	111.1
C(34)-C(33)-H(33A)	111.1
C(32)-C(33)-H(33B)	111.1
C(34)-C(33)-H(33B)	111.1
H(33A)-C(33)-H(33B)	109.1
C(33)-C(34)-C(35)	106.8(4)
C(33)-C(34)-H(34A)	110.4
C(35)-C(34)-H(34A)	110.4
C(33)-C(34)-H(34B)	110.4
C(35)-C(34)-H(34B)	110.4
H(34A)-C(34)-H(34B)	108.6
C(34A)-C(33A)-C(32)	104.8(12)
C(34A)-C(33A)-H(33C)	110.8
C(32)-C(33A)-H(33C)	110.8
C(34A)-C(33A)-H(33D)	110.8
C(32)-C(33A)-H(33D)	110.8
H(33C)-C(33A)-H(33D)	108.9
C(33A)-C(34A)-C(35)	100.8(10)
C(33A)-C(34A)-H(34C)	111.6
C(35)-C(34A)-H(34C)	111.6
C(33A)-C(34A)-H(34D)	111.6
C(35)-C(34A)-H(34D)	111.6
H(34C)-C(34A)-H(34D)	109.4
C(34)-C(35)-C(34A)	9.6(18)
C(34)-C(35)-C(31)	105.2(3)

C(34A)-C(35)-C(31)	106.3(9)
C(34)-C(35)-H(35A)	110.7
C(34A)-C(35)-H(35A)	101.8
C(31)-C(35)-H(35A)	110.7
C(34)-C(35)-H(35B)	110.7
C(34A)-C(35)-H(35B)	118.2
C(31)-C(35)-H(35B)	110.7
H(35A)-C(35)-H(35B)	108.8
C(34)-C(35)-H(35C)	119.1
C(34A)-C(35)-H(35C)	110.5
C(31)-C(35)-H(35C)	110.5
H(35A)-C(35)-H(35C)	9.5
H(35B)-C(35)-H(35C)	100.7
C(34)-C(35)-H(35D)	102.6
C(34A)-C(35)-H(35D)	110.5
C(31)-C(35)-H(35D)	110.5
H(35A)-C(35)-H(35D)	116.4
H(35B)-C(35)-H(35D)	9.0
H(35C)-C(35)-H(35D)	108.7
C(26)-C(25)-C(24)	120.97(17)
C(26)-C(25)-H(25)	119.5
C(24)-C(25)-H(25)	119.5
C(25)-C(26)-C(21)	120.73(17)
C(25)-C(26)-H(26)	119.6
C(21)-C(26)-H(26)	119.6
O(2)-C(27)-H(27A)	109.5
O(2)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
O(2)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5

Symmetry transformations used to generate equivalent atoms:

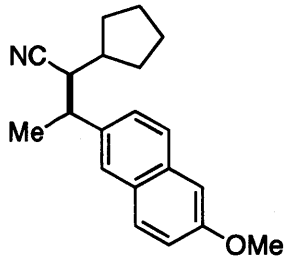
Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for X11176_t5. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	39(1)	45(1)	34(1)	0(1)	1(1)	1(1)
C(1)	29(1)	24(1)	34(1)	3(1)	4(1)	-3(1)
C(2)	26(1)	24(1)	39(1)	2(1)	7(1)	0(1)
C(3)	25(1)	21(1)	36(1)	4(1)	-1(1)	-1(1)
C(4)	25(1)	18(1)	36(1)	3(1)	4(1)	-2(1)
C(8)	24(1)	20(1)	39(1)	-2(1)	1(1)	0(1)
C(9)	31(1)	22(1)	36(1)	-3(1)	-1(1)	1(1)
N(1)	33(1)	30(1)	59(1)	-7(1)	-3(1)	-2(1)
C(11)	34(1)	24(1)	31(1)	-1(1)	0(1)	4(1)
C(12)	40(1)	42(1)	32(1)	-5(1)	-2(1)	-1(1)
C(13)	44(2)	37(2)	36(1)	-4(1)	5(1)	5(2)
C(14)	42(2)	34(2)	39(2)	0(2)	7(2)	0(2)
C(13A)	54(4)	41(4)	31(2)	1(3)	5(2)	-1(4)
C(14A)	46(4)	45(5)	35(3)	8(4)	9(3)	-6(4)
C(15)	37(1)	26(1)	34(1)	-4(1)	3(1)	-4(1)
C(5)	24(1)	19(1)	41(1)	2(1)	3(1)	0(1)
C(6)	25(1)	25(1)	40(1)	6(1)	-4(1)	-2(1)
C(7)	43(1)	45(1)	35(1)	-2(1)	8(1)	-6(1)
O(2)	38(1)	41(1)	34(1)	4(1)	1(1)	0(1)
C(21)	28(1)	22(1)	39(1)	4(1)	0(1)	3(1)
C(22)	24(1)	23(1)	40(1)	1(1)	-2(1)	-2(1)
C(23)	22(1)	22(1)	40(1)	4(1)	5(1)	-1(1)
C(24)	23(1)	18(1)	40(1)	1(1)	0(1)	2(1)
C(28)	25(1)	23(1)	40(1)	-3(1)	0(1)	2(1)
C(29)	28(1)	26(1)	38(1)	-7(1)	-2(1)	-2(1)
N(2)	32(1)	35(1)	49(1)	-10(1)	0(1)	7(1)
C(31)	32(1)	26(1)	34(1)	-3(1)	5(1)	0(1)
C(32)	49(1)	37(1)	36(1)	-3(1)	8(1)	7(1)
C(33)	58(2)	31(1)	31(1)	1(1)	12(1)	5(1)
C(34)	54(2)	89(3)	41(1)	8(1)	7(1)	31(2)
C(33A)	45(5)	62(6)	41(4)	5(4)	4(3)	7(5)
C(34A)	54(2)	89(3)	41(1)	8(1)	7(1)	31(2)
C(35)	31(1)	29(1)	36(1)	0(1)	6(1)	4(1)
C(25)	22(1)	24(1)	43(1)	2(1)	-2(1)	-3(1)
C(26)	22(1)	30(1)	44(1)	10(1)	3(1)	0(1)
C(27)	45(1)	42(1)	34(1)	-3(1)	-2(1)	4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for X11176_t5.

	x	y	z	U(eq)
H(2)	-2830	8402	6236	35
H(3)	-2936	7889	5190	33
H(8)	1365	5813	4415	33
H(11)	-1207	8373	4139	35
H(12A)	-459	6274	3329	46
H(12B)	-1183	7846	3131	46
H(12C)	-1623	7407	3186	46
H(12D)	443	6279	3325	46
H(13A)	2431	7668	2693	47
H(13B)	3517	6721	3253	47
H(14A)	4919	9004	3487	46
H(14B)	2356	9677	3331	46
H(13C)	2304	7863	2666	50
H(13D)	1103	9200	2980	50
H(14C)	4819	9139	3445	50
H(14D)	4720	7461	3527	50
H(15A)	2268	9396	4386	39
H(15B)	3687	7938	4369	39
H(15C)	3445	8129	4499	39
H(15D)	2194	9527	4230	39
H(5)	3333	5909	5393	34
H(6)	3486	6434	6435	37
H(7A)	-1648	9261	7187	61
H(7B)	-1105	8348	7795	61
H(7C)	-2827	7750	7253	61
H(22)	2078	12	-1128	35
H(23)	2012	423	-71	34
H(28)	6422	2375	827	35
H(31)	3956	-233	1000	37
H(32A)	6045	1632	1903	49
H(32B)	3684	713	1956	49
H(32C)	4116	138	2010	49
H(32D)	4985	1714	1885	49
H(33A)	5772	-1307	2134	47
H(33B)	7358	-176	2517	47
H(34A)	9313	-1617	1694	73
H(34B)	9995	11	1760	73
H(33C)	8933	1109	1999	59
H(33D)	7851	38	2486	59
H(34C)	7703	-1766	1768	73
H(34D)	10238	-1048	1670	73
H(35A)	7340	-1269	792	38
H(35B)	8716	203	774	38
H(35C)	7372	-1177	729	38
H(35D)	8810	259	838	38
H(25)	8284	2407	-107	35
H(26)	8415	1969	-1153	38
H(27A)	3419	-851	-2052	61
H(27B)	3907	96	-2642	61

H(27C)	2118	626	-2142	61



(2*S*,3*S*)-2-Cyclopentyl-3-(6-methoxynaphthalen-2-yl)butanenitrile. (*S*)-2-Cyclopentyl-3-(6-methoxynaphthalen-2-yl)but-3-enenitrile (32 mg, 0.11 mmol; Table 4, entry 5; from a reaction using (*R*,*R*)–**L2**) and Pd/C (3.2 mg; 10 wt%; Aldrich) were added to a 4-mL vial equipped with a magnetic stir bar. The vial was sealed with a PTFE-lined septum cap, and it was placed under vacuum. The vial was filled with hydrogen, and this evacuation-refill cycle was repeated three times. EtOH (1.1 mL) was added to the vial, and the mixture was stirred overnight under hydrogen. Next, the mixture was filtered through a pad of celite (eluted with Et_2O), and the solution was concentrated. The major diastereomer (3:1 dr) was isolated by preparative HPLC on a Daicel CHIRALPAK IC column (250 mm x 250 mm, 5 μm; 1% *i*-PrOH/hexanes, 20 mL/min) with t_r = 26.4 min (minor), 29.3 min (major). White solid. 22 mg (68%, 91% ee).

The ee was determined by HPLC analysis on a CHIRALPAK AD-H column (3% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 24.1 min (minor), 27.8 min (major).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73–7.68 (m, 3H), 7.46 (dd, 1H, J = 1.9, 8.4 Hz), 7.16 (dd, 1H, J = 2.6, 8.7 Hz), 7.13 (d, 1H, J = 2.5 Hz), 3.92 (s, 3H), 3.12 (pentet, 1H, J = 7.0 Hz), 2.76 (dd, 1H, J = 6.3 Hz, 7.9 Hz), 1.94–1.84 (m, 2H), 1.83–1.77 (m, 1H), 1.72–1.62 (m, 2H), 1.56–1.44 (m, 2H), 1.52 (d, 3H, J = 7.2 Hz), 1.40–1.29 (m, 2H).

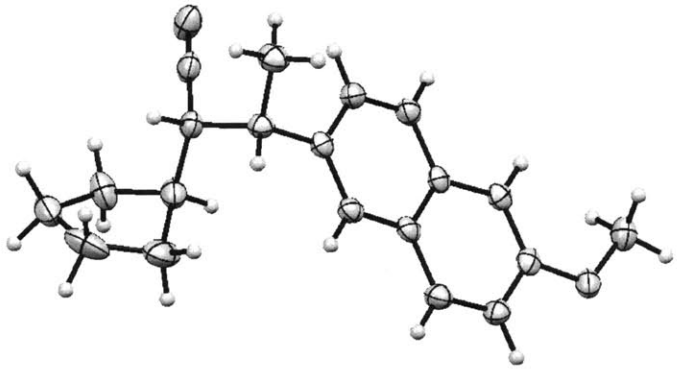
^{13}C NMR (126 MHz, $CDCl_3$) δ 157.7, 137.4, 133.9, 129.5, 129.0, 127.3, 126.5, 126.4, 120.9, 119.1, 105.7, 55.5, 45.2, 40.4, 39.8, 31.4, 30.8, 25.3, 25.1, 20.7.

FT-IR (neat) 2961, 2933, 2869, 2235, 1631, 1606, 1506, 1484, 1463, 1382, 1266, 1241, 1220, 1197, 1184, 1164, 1029, 891, 858, 818 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_{20}H_{23}NO$: 293, found: 293.

$[\alpha]^{24}_D = -16.0°$ (c = 0.98, $CHCl_3$).

A crystal suitable for X-ray crystallography was grown by vapor diffusion with Et_2O and pentane.



Stereochemistry at C1: S; stereochemistry at C2: S

Eight independent molecules, refined using residues. Two molecules (number seven and eight) show disorder in the five-membered ring. Pseudo-merohedral twin. Twin-law 0 0 1 0 -1 0 1 0 0. Twin ratio: 0.3500(7). Flack-x has high standard uncertainty; Hooft test gives more reliable results. See Platon output.

Table 1. Crystal data and structure refinement for X12022.

Identification code	x12022	
Empirical formula	C20 H23 N O	
Formula weight	293.39	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 14.4823(5) Å	a= 90°.
	b = 32.2596(10) Å	b= 104.760(2)°.
	c = 14.5199(5) Å	g = 90°.
Volume	6559.7(4) $Å^3$	
Z	16	
Density (calculated)	1.188 Mg/m^3	
Absorption coefficient	0.559 mm^{-1}	
F(000)	2528	
Crystal size	0.30 x 0.11 x 0.08 mm^3	
Theta range for data collection	1.37 to 68.22°.	
Index ranges	-17<=h<=15, -38<=k<=38, -17<=l<=17	
Reflections collected	196268	
Independent reflections	23690 [R(int) = 0.0369]	
Completeness to theta = 68.22°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9567 and 0.8503	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	23690 / 1932 / 1676	
Goodness-of-fit on F^2	1.065	
Final R indices [I>2sigma(I)]	R1 = 0.0405, wR2 = 0.1032	
R indices (all data)	R1 = 0.0421, wR2 = 0.1066	
Absolute structure parameter	0.06(13)	
Largest diff. peak and hole	0.300 and -0.159 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for X12022. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O11	4117(1)	-79(1)	3269(1)	33(1)
N11	4239(2)	2770(1)	3836(2)	39(1)
C21	3141(2)	2128(1)	5186(2)	24(1)
C31	3901(2)	2261(1)	6076(2)	29(1)
C41	3631(2)	2659(1)	4144(2)	29(1)
C11	2831(2)	2506(1)	4508(2)	25(1)
C111	1971(2)	2421(1)	3653(2)	28(1)
C121	1079(2)	2278(1)	3934(2)	36(1)
C131	238(2)	2402(1)	3107(2)	48(1)
C141	647(2)	2674(1)	2442(2)	42(1)
C151	1620(2)	2809(1)	3057(2)	35(1)
C211	3445(2)	1753(1)	4707(2)	23(1)
C221	2862(2)	1412(1)	4473(2)	24(1)
C231	3162(2)	1046(1)	4091(2)	25(1)
C241	2565(2)	691(1)	3866(2)	28(1)
C251	2896(2)	335(1)	3580(2)	31(1)
C261	3860(2)	308(1)	3499(2)	27(1)
C271	4432(2)	649(1)	3652(2)	27(1)
C281	4098(2)	1027(1)	3956(2)	24(1)
C291	4678(2)	1382(1)	4167(2)	26(1)
C301	4370(2)	1734(1)	4529(2)	26(1)
C311	5085(2)	-140(1)	3252(2)	39(1)
O12	8399(1)	4941(1)	4274(1)	38(1)
N12	8122(2)	7771(1)	3561(2)	31(1)
C22	9384(2)	7146(1)	2336(2)	28(1)
C32	8683(2)	7283(1)	1409(2)	32(1)
C42	8772(2)	7662(1)	3326(2)	27(1)
C12	9630(2)	7514(1)	3045(2)	28(1)
C112	10429(2)	7422(1)	3942(2)	29(1)
C122	11389(2)	7322(1)	3726(2)	38(1)
C132	12121(2)	7372(1)	4673(2)	44(1)
C142	11678(2)	7673(1)	5257(2)	40(1)
C152	10690(2)	7790(1)	4627(2)	36(1)
C212	9050(2)	6763(1)	2763(2)	26(1)
C222	9651(2)	6435(1)	3071(2)	27(1)
C232	9347(2)	6065(1)	3442(2)	26(1)
C242	9968(2)	5724(1)	3750(2)	30(1)
C252	9634(2)	5367(1)	4038(2)	34(1)
C262	8653(2)	5326(1)	4026(2)	30(1)
C272	8043(2)	5653(1)	3773(2)	30(1)
C282	8374(2)	6031(1)	3471(2)	26(1)
C292	7772(2)	6376(1)	3181(2)	27(1)
C302	8085(2)	6726(1)	2837(2)	28(1)
C312	7417(2)	4870(1)	4225(2)	40(1)
O13	648(1)	4934(1)	1887(1)	36(1)
N13	779(2)	7775(1)	1196(2)	40(1)
C23	2056(2)	7105(1)	101(2)	24(1)
C33	1412(2)	7275(1)	-829(2)	31(1)

C43	1460(2)	7639(1)	1039(2)	30(1)
C13	2333(2)	7456(1)	859(2)	24(1)
C113	3005(2)	7319(1)	1810(2)	29(1)
C123	3964(2)	7165(1)	1696(2)	41(1)
C133	4520(2)	7558(1)	1627(2)	46(1)
C143	4189(2)	7873(1)	2262(2)	39(1)
C153	3308(2)	7684(1)	2506(2)	37(1)
C213	1639(2)	6729(1)	464(2)	24(1)
C223	2174(2)	6383(1)	747(2)	27(1)
C233	1798(2)	6018(1)	1071(2)	25(1)
C243	2345(2)	5656(1)	1367(2)	29(1)
C253	1951(2)	5311(1)	1645(2)	32(1)
C263	964(2)	5306(1)	1626(2)	29(1)
C273	410(2)	5651(1)	1369(2)	29(1)
C283	812(2)	6016(1)	1086(2)	26(1)
C293	269(2)	6376(1)	799(2)	29(1)
C303	659(2)	6722(1)	498(2)	27(1)
C313	-347(2)	4900(1)	1820(2)	42(1)
O14	5487(1)	6351(1)	1998(1)	32(1)
N14	5042(2)	3488(1)	2051(2)	42(1)
C24	3910(2)	4129(1)	3349(2)	26(1)
C34	2984(2)	3954(1)	2711(2)	36(1)
C44	4892(2)	3617(1)	2728(2)	33(1)
C14	4702(2)	3789(1)	3602(2)	28(1)
C114	5650(2)	3936(1)	4276(2)	35(1)
C124	5543(2)	4042(1)	5266(2)	52(1)
C134	5598(2)	3626(1)	5763(2)	57(1)
C144	6240(2)	3353(1)	5341(2)	47(1)
C154	6413(2)	3596(1)	4515(2)	45(1)
C214	4239(2)	4518(1)	2931(2)	26(1)
C224	4505(2)	4867(1)	3475(2)	26(1)
C234	4792(2)	5234(1)	3106(2)	26(1)
C244	5053(2)	5598(1)	3670(2)	30(1)
C254	5284(2)	5954(1)	3275(2)	29(1)
C264	5274(2)	5971(1)	2302(2)	27(1)
C274	5068(2)	5625(1)	1742(2)	27(1)
C284	4821(2)	5249(1)	2142(2)	25(1)
C294	4563(2)	4884(1)	1586(2)	28(1)
C304	4279(2)	4536(1)	1969(2)	29(1)
C314	5449(2)	6392(1)	1016(2)	36(1)
O15	8020(1)	6326(1)	-607(1)	35(1)
N15	7392(2)	3495(1)	-562(1)	32(1)
C25	6164(2)	4143(1)	659(2)	26(1)
C35	5227(2)	3997(1)	-11(2)	32(1)
C45	7154(2)	3614(1)	80(2)	27(1)
C15	6872(2)	3774(1)	918(2)	26(1)
C115	7782(2)	3869(1)	1699(2)	29(1)
C125	7572(2)	4004(1)	2640(2)	41(1)
C135	8492(2)	3918(1)	3382(2)	54(1)
C145	8997(2)	3576(1)	2999(2)	62(1)
C155	8438(2)	3491(1)	1987(2)	39(1)
C215	6581(2)	4520(1)	283(2)	25(1)
C225	6840(2)	4870(1)	832(2)	27(1)
C235	7187(2)	5228(1)	482(2)	26(1)

C245	7435(2)	5594(1)	1033(2)	30(1)
C255	7714(2)	5945(1)	650(2)	31(1)
C265	7765(2)	5951(1)	-302(2)	29(1)
C275	7570(2)	5601(1)	-857(2)	26(1)
C285	7273(2)	5233(1)	-463(2)	25(1)
C295	7021(2)	4870(1)	-1024(2)	26(1)
C305	6688(2)	4527(1)	-656(2)	26(1)
C315	7967(2)	6364(1)	-1592(2)	38(1)
O16	-584(1)	11364(1)	2997(1)	39(1)
N16	-222(2)	8558(1)	2784(2)	41(1)
C26	1306(2)	9170(1)	1840(2)	26(1)
C36	2173(2)	8999(1)	2580(2)	36(1)
C46	140(2)	8671(1)	2219(2)	32(1)
C16	562(2)	8821(1)	1463(2)	27(1)
C116	-247(2)	8952(1)	601(2)	34(1)
C126	141(2)	9072(1)	-253(2)	43(1)
C136	-602(2)	8917(1)	-1114(2)	52(1)
C146	-898(3)	8509(1)	-758(2)	61(1)
C156	-981(2)	8604(1)	218(2)	40(1)
C216	876(2)	9548(1)	2200(2)	26(1)
C226	630(2)	9897(1)	1637(2)	26(1)
C236	264(2)	10257(1)	1963(2)	26(1)
C246	12(2)	10619(1)	1389(2)	30(1)
C256	-274(2)	10971(1)	1754(2)	33(1)
C266	-340(2)	10983(1)	2707(2)	32(1)
C276	-156(2)	10638(1)	3271(2)	29(1)
C286	147(2)	10266(1)	2899(2)	26(1)
C296	370(2)	9904(1)	3460(2)	28(1)
C306	720(2)	9558(1)	3115(2)	28(1)
C316	-547(2)	11405(1)	3976(2)	44(1)
O17	6944(1)	11381(1)	5395(1)	34(1)
N17	7070(2)	8562(1)	5122(2)	41(1)
C27	8557(2)	9156(1)	4110(2)	25(1)
C37	9406(2)	8957(1)	4819(2)	36(1)
C47	7375(2)	8677(1)	4528(2)	31(1)
C17	7754(2)	8833(1)	3742(2)	24(1)
C117	6927(2)	8996(1)	2932(2)	33(1)
C127	7264(4)	9005(2)	1977(4)	36(1)
C137	7091(4)	8566(2)	1579(3)	32(1)
C147	6326(4)	8380(2)	1989(4)	27(1)
C157	6049(3)	8719(2)	2613(3)	26(1)
C12A7	7109(11)	9135(4)	2057(8)	40(2)
C13A7	7151(9)	8739(5)	1540(9)	41(2)
C14A7	6565(12)	8420(4)	1855(11)	39(2)
C15A7	6251(9)	8605(4)	2698(9)	36(2)
C217	8206(2)	9544(1)	4511(2)	24(1)
C227	7966(2)	9895(1)	3959(2)	25(1)
C237	7658(2)	10262(1)	4316(2)	24(1)
C247	7419(2)	10623(1)	3752(2)	29(1)
C257	7173(2)	10980(1)	4134(2)	30(1)
C267	7150(2)	10999(1)	5095(2)	28(1)
C277	7330(2)	10652(1)	5659(2)	27(1)
C287	7592(2)	10274(1)	5272(2)	24(1)
C297	7815(2)	9910(1)	5821(2)	27(1)

C307	8110(2)	9560(1)	5454(2)	28(1)
C317	6952(2)	11421(1)	6372(2)	39(1)
O18	6802(1)	-82(1)	645(1)	31(1)
N18	6507(2)	2740(1)	1046(2)	44(1)
C28	5428(2)	2100(1)	2395(2)	28(1)
C38	6140(2)	2273(1)	3280(2)	39(1)
C48	5888(2)	2618(1)	1327(2)	31(1)
C18	5078(2)	2449(1)	1644(2)	26(1)
C118	4288(2)	2316(1)	762(2)	37(1)
C128	3421(5)	2123(2)	903(6)	40(2)
C138	2846(5)	2478(3)	1107(5)	43(2)
C148	3092(6)	2850(2)	556(7)	34(1)
C158	3904(8)	2708(3)	162(7)	37(2)
C12A8	3339(7)	2241(3)	1132(8)	46(2)
C13A8	2886(6)	2660(4)	1100(7)	41(2)
C14A8	3225(10)	2909(4)	361(10)	42(2)
C15A8	3917(9)	2639(4)	18(9)	39(2)
C218	5828(2)	1726(1)	1996(2)	25(1)
C228	5304(2)	1370(1)	1781(2)	26(1)
C238	5672(2)	1008(1)	1446(2)	25(1)
C248	5135(2)	638(1)	1228(2)	30(1)
C258	5528(2)	288(1)	956(2)	34(1)
C268	6494(2)	293(1)	891(2)	27(1)
C278	7020(2)	648(1)	1061(2)	27(1)
C288	6623(2)	1013(1)	1342(2)	25(1)
C298	7154(2)	1383(1)	1562(2)	27(1)
C308	6778(2)	1728(1)	1880(2)	27(1)
C318	7787(2)	-116(1)	655(2)	38(1)

Table 3. Bond lengths [Å] and angles [°] for X12022.

O11-C261	1.369(3)
O11-C311	1.422(3)
N11-C41	1.142(3)
C21-C211	1.516(3)
C21-C31	1.530(3)
C21-C11	1.559(3)
C21-H21	1.0000
C31-H3A1	0.9800
C31-H3B1	0.9800
C31-H3C1	0.9800
C41-C11	1.475(3)
C11-C111	1.543(3)
C11-H11	1.0000
C111-C121	1.522(3)
C111-C151	1.531(3)
C111-H111	1.0000
C121-C131	1.529(3)
C121-H12A1	0.9900
C121-H12B1	0.9900
C131-C141	1.531(4)
C131-H13A1	0.9900
C131-H13B1	0.9900
C141-C151	1.526(3)
C141-H14A1	0.9900
C141-H14B1	0.9900
C151-H15A1	0.9900
C151-H15B1	0.9900
C211-C221	1.376(3)
C211-C301	1.430(3)
C221-C231	1.420(3)
C221-H221	0.9500
C231-C281	1.418(3)
C231-C241	1.421(3)
C241-C251	1.351(3)
C241-H241	0.9500
C251-C261	1.434(3)
C251-H251	0.9500
C261-C271	1.360(3)
C271-C281	1.422(3)
C271-H271	0.9500
C281-C291	1.408(3)
C291-C301	1.371(3)
C291-H291	0.9500
C301-H301	0.9500
C311-H31A1	0.9800
C311-H31B1	0.9800
C311-H31C1	0.9800
O12-C262	1.368(3)
O12-C312	1.424(3)
N12-C42	1.135(3)
C22-C212	1.515(3)
C22-C32	1.531(3)
C22-C12	1.553(3)
C22-H22	1.0000
C32-H3A2	0.9800
C32-H3B2	0.9800

C32-H3C2	0.9800
C42-C12	1.482(3)
C12-C112	1.535(3)
C12-H12	1.0000
C112-C152	1.533(3)
C112-C122	1.536(3)
C112-H112	1.0000
C122-C132	1.517(3)
C122-H12A2	0.9900
C122-H12B2	0.9900
C132-C142	1.535(4)
C132-H13A2	0.9900
C132-H13B2	0.9900
C142-C152	1.536(3)
C142-H14A2	0.9900
C142-H14B2	0.9900
C152-H15A2	0.9900
C152-H15B2	0.9900
C212-C222	1.372(3)
C212-C302	1.433(3)
C222-C232	1.423(3)
C222-H222	0.9500
C232-C242	1.419(3)
C232-C282	1.424(3)
C242-C252	1.357(3)
C242-H242	0.9500
C252-C262	1.423(4)
C252-H252	0.9500
C262-C272	1.364(3)
C272-C282	1.420(3)
C272-H272	0.9500
C282-C292	1.410(3)
C292-C302	1.360(3)
C292-H292	0.9500
C302-H302	0.9500
C312-H31A2	0.9800
C312-H31B2	0.9800
C312-H31C2	0.9800
O13-C263	1.373(3)
O13-C313	1.424(3)
N13-C43	1.153(3)
C23-C213	1.509(3)
C23-C33	1.533(3)
C23-C13	1.559(3)
C23-H23	1.0000
C33-H3A3	0.9800
C33-H3B3	0.9800
C33-H3C3	0.9800
C43-C13	1.478(3)
C13-C113	1.539(3)
C13-H13	1.0000
C113-C123	1.523(3)
C113-C153	1.542(3)
C113-H113	1.0000
C123-C133	1.518(4)
C123-H12A3	0.9900
C123-H12B3	0.9900
C133-C143	1.531(4)

C133-H13A3	0.9900
C133-H13B3	0.9900
C143-C153	1.535(4)
C143-H14A3	0.9900
C143-H14B3	0.9900
C153-H15A3	0.9900
C153-H15B3	0.9900
C213-C223	1.361(3)
C213-C303	1.433(3)
C223-C233	1.426(3)
C223-H223	0.9500
C233-C243	1.416(3)
C233-C283	1.434(3)
C243-C253	1.359(3)
C243-H243	0.9500
C253-C263	1.422(4)
C253-H253	0.9500
C263-C273	1.368(4)
C273-C283	1.419(3)
C273-H273	0.9500
C283-C293	1.406(3)
C293-C303	1.370(3)
C293-H293	0.9500
C303-H303	0.9500
C313-H31A3	0.9800
C313-H31B3	0.9800
C313-H31C3	0.9800
O14-C264	1.364(3)
O14-C314	1.418(3)
N14-C44	1.139(3)
C24-C214	1.521(3)
C24-C34	1.530(3)
C24-C14	1.560(3)
C24-H24	1.0000
C34-H3A4	0.9800
C34-H3B4	0.9800
C34-H3C4	0.9800
C44-C14	1.473(3)
C14-C114	1.544(3)
C14-H14	1.0000
C114-C124	1.522(4)
C114-C154	1.534(3)
C114-H114	1.0000
C124-C134	1.514(5)
C124-H12A4	0.9900
C124-H12B4	0.9900
C134-C144	1.517(4)
C134-H13A4	0.9900
C134-H13B4	0.9900
C144-C154	1.506(4)
C144-H14A4	0.9900
C144-H14B4	0.9900
C154-H15A4	0.9900
C154-H15B4	0.9900
C214-C224	1.375(3)
C214-C304	1.415(3)
C224-C234	1.406(3)
C224-H224	0.9500

C234-C284	1.412(3)
C234-C244	1.425(3)
C244-C254	1.362(4)
C244-H244	0.9500
C254-C264	1.411(4)
C254-H254	0.9500
C264-C274	1.368(3)
C274-C284	1.430(3)
C274-H274	0.9500
C284-C294	1.422(3)
C294-C304	1.361(3)
C294-H294	0.9500
C304-H304	0.9500
C314-H31A4	0.9800
C314-H31B4	0.9800
C314-H31C4	0.9800
O15-C265	1.373(3)
O15-C315	1.417(3)
N15-C45	1.138(3)
C25-C215	1.521(3)
C25-C35	1.529(3)
C25-C15	1.551(3)
C25-H25	1.0000
C35-H3A5	0.9800
C35-H3B5	0.9800
C35-H3C5	0.9800
C45-C15	1.473(3)
C15-C115	1.534(3)
C15-H15	1.0000
C115-C155	1.536(3)
C115-C125	1.536(3)
C115-H115	1.0000
C125-C135	1.511(3)
C125-H12A5	0.9900
C125-H12B5	0.9900
C135-C145	1.505(4)
C135-H13A5	0.9900
C135-H13B5	0.9900
C145-C155	1.511(4)
C145-H14A5	0.9900
C145-H14B5	0.9900
C155-H15A5	0.9900
C155-H15B5	0.9900
C215-C225	1.377(3)
C215-C305	1.411(3)
C225-C235	1.408(3)
C225-H225	0.9500
C235-C285	1.408(3)
C235-C245	1.418(3)
C245-C255	1.367(4)
C245-H245	0.9500
C255-C265	1.404(4)
C255-H255	0.9500
C265-C275	1.372(3)
C275-C285	1.430(3)
C275-H275	0.9500
C285-C295	1.422(3)
C295-C305	1.368(3)

C295-H295	0.9500
C305-H305	0.9500
C315-H31A5	0.9800
C315-H31B5	0.9800
C315-H31C5	0.9800
O16-C266	1.374(3)
O16-C316	1.415(4)
N16-C46	1.138(3)
C26-C216	1.521(3)
C26-C36	1.532(3)
C26-C16	1.558(3)
C26-H26	1.0000
C36-H3A6	0.9800
C36-H3B6	0.9800
C36-H3C6	0.9800
C46-C16	1.469(3)
C16-C116	1.540(3)
C16-H16	1.0000
C116-C126	1.534(3)
C116-C156	1.549(3)
C116-H116	1.0000
C126-C136	1.512(3)
C126-H12A6	0.9900
C126-H12B6	0.9900
C136-C146	1.514(4)
C136-H13A6	0.9900
C136-H13B6	0.9900
C146-C156	1.486(4)
C146-H14A6	0.9900
C146-H14B6	0.9900
C156-H15A6	0.9900
C156-H15B6	0.9900
C216-C226	1.385(3)
C216-C306	1.403(3)
C226-C236	1.407(3)
C226-H226	0.9500
C236-C286	1.412(3)
C236-C246	1.426(3)
C246-C256	1.362(4)
C246-H246	0.9500
C256-C266	1.412(4)
C256-H256	0.9500
C266-C276	1.366(4)
C276-C286	1.431(3)
C276-H276	0.9500
C286-C296	1.414(3)
C296-C306	1.373(3)
C296-H296	0.9500
C306-H306	0.9500
C316-H31A6	0.9800
C316-H31B6	0.9800
C316-H31C6	0.9800
O17-C267	1.364(3)
O17-C317	1.422(3)
N17-C47	1.128(3)
C27-C217	1.522(3)
C27-C37	1.529(3)
C27-C17	1.551(3)

C27-H27	1.0000
C37-H3A7	0.9800
C37-H3B7	0.9800
C37-H3C7	0.9800
C47-C17	1.475(3)
C17-C117	1.542(3)
C17-H17	1.0000
C117-C12A7	1.432(10)
C117-C157	1.528(4)
C117-C15A7	1.579(10)
C117-C127	1.582(6)
C117-H11A7	1.0000
C117-H11B7	1.0000
C127-C137	1.524(5)
C127-H12A7	0.9900
C127-H12B7	0.9900
C137-C147	1.510(5)
C137-H13A7	0.9900
C137-H13B7	0.9900
C147-C157	1.538(5)
C147-H14A7	0.9900
C147-H14B7	0.9900
C157-H15A7	0.9900
C157-H15B7	0.9900
C12A7-C13A7	1.492(10)
C12A7-H12C7	0.9900
C12A7-H12D7	0.9900
C13A7-C14A7	1.478(11)
C13A7-H13C7	0.9900
C13A7-H13D7	0.9900
C14A7-C15A7	1.532(11)
C14A7-H14C7	0.9900
C14A7-H14D7	0.9900
C15A7-H15C7	0.9900
C15A7-H15D7	0.9900
C217-C227	1.379(3)
C217-C307	1.411(3)
C227-C237	1.412(3)
C227-H227	0.9500
C237-C247	1.415(3)
C237-C287	1.416(3)
C247-C257	1.363(3)
C247-H247	0.9500
C257-C267	1.406(4)
C257-H257	0.9500
C267-C277	1.372(3)
C277-C287	1.432(3)
C277-H277	0.9500
C287-C297	1.410(3)
C297-C307	1.364(3)
C297-H297	0.9500
C307-H307	0.9500
C317-H31A7	0.9800
C317-H31B7	0.9800
C317-H31C7	0.9800
O18-C268	1.366(3)
O18-C318	1.428(3)
N18-C48	1.144(3)

C28-C218	1.517(3)
C28-C38	1.533(3)
C28-C18	1.559(3)
C28-H28	1.0000
C38-H3A8	0.9800
C38-H3B8	0.9800
C38-H3C8	0.9800
C48-C18	1.472(3)
C18-C118	1.545(3)
C18-H18	1.0000
C118-C128	1.462(7)
C118-C15A8	1.500(9)
C118-C158	1.554(7)
C118-C12A8	1.615(9)
C118-H11A8	1.0000
C118-H11B8	1.0000
C128-C138	1.491(7)
C128-H12A8	0.9900
C128-H12B8	0.9900
C138-C148	1.532(6)
C138-H13A8	0.9900
C138-H13B8	0.9900
C148-C158	1.504(8)
C148-H14A8	0.9900
C148-H14B8	0.9900
C158-H15A8	0.9900
C158-H15B8	0.9900
C12A8-C13A8	1.499(9)
C12A8-H12C8	0.9900
C12A8-H12D8	0.9900
C13A8-C14A8	1.519(9)
C13A8-H13C8	0.9900
C13A8-H13D8	0.9900
C14A8-C15A8	1.504(10)
C14A8-H14C8	0.9900
C14A8-H14D8	0.9900
C15A8-H15C8	0.9900
C15A8-H15D8	0.9900
C218-C228	1.368(3)
C218-C308	1.427(3)
C228-C238	1.419(3)
C228-H228	0.9500
C238-C248	1.417(3)
C238-C288	1.423(3)
C248-C258	1.366(4)
C248-H248	0.9500
C258-C268	1.426(4)
C258-H258	0.9500
C268-C278	1.363(3)
C278-C288	1.417(3)
C278-H278	0.9500
C288-C298	1.411(3)
C298-C308	1.371(3)
C298-H298	0.9500
C308-H308	0.9500
C318-H31A8	0.9800
C318-H31B8	0.9800
C318-H31C8	0.9800

C261-O11-C311	117.48(19)
C211-C21-C31	112.36(18)
C211-C21-C11	113.87(17)
C31-C21-C11	110.12(17)
C211-C21-H21	106.7
C31-C21-H21	106.7
C11-C21-H21	106.7
C21-C31-H3A1	109.5
C21-C31-H3B1	109.5
H3A1-C31-H3B1	109.5
C21-C31-H3C1	109.5
H3A1-C31-H3C1	109.5
H3B1-C31-H3C1	109.5
N11-C41-C11	177.8(3)
C41-C11-C111	108.50(19)
C41-C11-C21	111.21(17)
C111-C11-C21	114.37(17)
C41-C11-H11	107.5
C111-C11-H11	107.5
C21-C11-H11	107.5
C121-C111-C151	102.53(19)
C121-C111-C11	113.87(19)
C151-C111-C11	113.17(18)
C121-C111-H111	109.0
C151-C111-H111	109.0
C11-C111-H111	109.0
C111-C121-C131	105.7(2)
C111-C121-H12A1	110.6
C131-C121-H12A1	110.6
C111-C121-H12B1	110.6
C131-C121-H12B1	110.6
H12A1-C121-H12B1	108.7
C121-C131-C141	106.7(2)
C121-C131-H13A1	110.4
C141-C131-H13A1	110.4
C121-C131-H13B1	110.4
C141-C131-H13B1	110.4
H13A1-C131-H13B1	108.6
C151-C141-C131	103.98(19)
C151-C141-H14A1	111.0
C131-C141-H14A1	111.0
C151-C141-H14B1	111.0
C131-C141-H14B1	111.0
H14A1-C141-H14B1	109.0
C141-C151-C111	102.87(18)
C141-C151-H15A1	111.2
C111-C151-H15A1	111.2
C141-C151-H15B1	111.2
C111-C151-H15B1	111.2
H15A1-C151-H15B1	109.1
C221-C211-C301	117.7(2)
C221-C211-C21	121.3(2)
C301-C211-C21	120.89(19)
C211-C221-C231	122.1(2)
C211-C221-H221	118.9
C231-C221-H221	118.9
C281-C231-C221	119.2(2)

C281-C231-C241	118.7(2)
C221-C231-C241	122.0(2)
C251-C241-C231	120.8(2)
C251-C241-H241	119.6
C231-C241-H241	119.6
C241-C251-C261	120.4(2)
C241-C251-H251	119.8
C261-C251-H251	119.8
C271-C261-O11	125.9(2)
C271-C261-C251	120.2(2)
O11-C261-C251	113.9(2)
C261-C271-C281	120.1(2)
C261-C271-H271	119.9
C281-C271-H271	119.9
C291-C281-C231	118.2(2)
C291-C281-C271	122.2(2)
C231-C281-C271	119.5(2)
C301-C291-C281	121.5(2)
C301-C291-H291	119.2
C281-C291-H291	119.2
C291-C301-C211	121.1(2)
C291-C301-H301	119.5
C211-C301-H301	119.5
O11-C311-H31A1	109.5
O11-C311-H31B1	109.5
H31A1-C311-H31B1	109.5
O11-C311-H31C1	109.5
H31A1-C311-H31C1	109.5
H31B1-C311-H31C1	109.5
C262-O12-C312	117.6(2)
C212-C22-C32	112.66(19)
C212-C22-C12	113.34(18)
C32-C22-C12	110.51(18)
C212-C22-H22	106.6
C32-C22-H22	106.6
C12-C22-H22	106.6
C22-C32-H3A2	109.5
C22-C32-H3B2	109.5
H3A2-C32-H3B2	109.5
C22-C32-H3C2	109.5
H3A2-C32-H3C2	109.5
H3B2-C32-H3C2	109.5
N12-C42-C12	178.4(2)
C42-C12-C112	109.42(19)
C42-C12-C22	111.21(18)
C112-C12-C22	114.26(18)
C42-C12-H12	107.2
C112-C12-H12	107.2
C22-C12-H12	107.2
C152-C112-C12	114.13(18)
C152-C112-C122	102.19(19)
C12-C112-C122	113.2(2)
C152-C112-H112	109.0
C12-C112-H112	109.0
C122-C112-H112	109.0
C132-C122-C112	104.6(2)
C132-C122-H12A2	110.8
C112-C122-H12A2	110.8

C132-C122-H12B2	110.8
C112-C122-H12B2	110.8
H12A2-C122-H12B2	108.9
C122-C132-C142	105.9(2)
C122-C132-H13A2	110.5
C142-C132-H13A2	110.5
C122-C132-H13B2	110.5
C142-C132-H13B2	110.5
H13A2-C132-H13B2	108.7
C132-C142-C152	106.53(19)
C132-C142-H14A2	110.4
C152-C142-H14A2	110.4
C132-C142-H14B2	110.4
C152-C142-H14B2	110.4
H14A2-C142-H14B2	108.6
C112-C152-C142	103.51(19)
C112-C152-H15A2	111.1
C142-C152-H15A2	111.1
C112-C152-H15B2	111.1
C142-C152-H15B2	111.1
H15A2-C152-H15B2	109.0
C222-C212-C302	117.5(2)
C222-C212-C22	121.3(2)
C302-C212-C22	121.2(2)
C212-C222-C232	122.5(2)
C212-C222-H222	118.8
C232-C222-H222	118.8
C242-C232-C222	122.4(2)
C242-C232-C282	118.8(2)
C222-C232-C282	118.8(2)
C252-C242-C232	120.6(2)
C252-C242-H242	119.7
C232-C242-H242	119.7
C242-C252-C262	120.6(2)
C242-C252-H252	119.7
C262-C252-H252	119.7
C272-C262-O12	125.0(2)
C272-C262-C252	120.4(2)
O12-C262-C252	114.6(2)
C262-C272-C282	120.1(2)
C262-C272-H272	120.0
C282-C272-H272	120.0
C292-C282-C272	122.6(2)
C292-C282-C232	118.1(2)
C272-C282-C232	119.4(2)
C302-C292-C282	121.8(2)
C302-C292-H292	119.1
C282-C292-H292	119.1
C292-C302-C212	121.2(2)
C292-C302-H302	119.4
C212-C302-H302	119.4
O12-C312-H31A2	109.5
O12-C312-H31B2	109.5
H31A2-C312-H31B2	109.5
O12-C312-H31C2	109.5
H31A2-C312-H31C2	109.5
H31B2-C312-H31C2	109.5
C263-O13-C313	116.8(2)

C213-C23-C33	112.84(18)
C213-C23-C13	113.02(18)
C33-C23-C13	110.54(18)
C213-C23-H23	106.7
C33-C23-H23	106.7
C13-C23-H23	106.7
C23-C33-H3A3	109.5
C23-C33-H3B3	109.5
H3A3-C33-H3B3	109.5
C23-C33-H3C3	109.5
H3A3-C33-H3C3	109.5
H3B3-C33-H3C3	109.5
N13-C43-C13	178.4(3)
C43-C13-C113	109.27(19)
C43-C13-C23	109.67(18)
C113-C13-C23	114.49(18)
C43-C13-H13	107.7
C113-C13-H13	107.7
C23-C13-H13	107.7
C123-C113-C13	112.47(19)
C123-C113-C153	101.79(19)
C13-C113-C153	112.13(19)
C123-C113-H113	110.1
C13-C113-H113	110.1
C153-C113-H113	110.1
C133-C123-C113	104.5(2)
C133-C123-H12A3	110.9
C113-C123-H12A3	110.9
C133-C123-H12B3	110.9
C113-C123-H12B3	110.9
H12A3-C123-H12B3	108.9
C123-C133-C143	105.2(2)
C123-C133-H13A3	110.7
C143-C133-H13A3	110.7
C123-C133-H13B3	110.7
C143-C133-H13B3	110.7
H13A3-C133-H13B3	108.8
C133-C143-C153	106.28(19)
C133-C143-H14A3	110.5
C153-C143-H14A3	110.5
C133-C143-H14B3	110.5
C153-C143-H14B3	110.5
H14A3-C143-H14B3	108.7
C143-C153-C113	105.6(2)
C143-C153-H15A3	110.6
C113-C153-H15A3	110.6
C143-C153-H15B3	110.6
C113-C153-H15B3	110.6
H15A3-C153-H15B3	108.8
C223-C213-C303	118.0(2)
C223-C213-C23	121.1(2)
C303-C213-C23	120.8(2)
C213-C223-C233	122.6(2)
C213-C223-H223	118.7
C233-C223-H223	118.7
C243-C233-C223	123.3(2)
C243-C233-C283	118.3(2)
C223-C233-C283	118.4(2)

C253-C243-C233	121.4(2)
C253-C243-H243	119.3
C233-C243-H243	119.3
C243-C253-C263	120.0(2)
C243-C253-H253	120.0
C263-C253-H253	120.0
C273-C263-O13	125.1(2)
C273-C263-C253	120.8(2)
O13-C263-C253	114.1(2)
C263-C273-C283	119.9(2)
C263-C273-H273	120.0
C283-C273-H273	120.0
C293-C283-C273	122.1(2)
C293-C283-C233	118.4(2)
C273-C283-C233	119.5(2)
C303-C293-C283	121.5(2)
C303-C293-H293	119.3
C283-C293-H293	119.3
C293-C303-C213	121.1(2)
C293-C303-H303	119.5
C213-C303-H303	119.5
O13-C313-H31A3	109.5
O13-C313-H31B3	109.5
H31A3-C313-H31B3	109.5
O13-C313-H31C3	109.5
H31A3-C313-H31C3	109.5
H31B3-C313-H31C3	109.5
C264-O14-C314	117.06(19)
C214-C24-C34	112.15(19)
C214-C24-C14	112.73(18)
C34-C24-C14	111.26(19)
C214-C24-H24	106.8
C34-C24-H24	106.8
C14-C24-H24	106.8
C24-C34-H3A4	109.5
C24-C34-H3B4	109.5
H3A4-C34-H3B4	109.5
C24-C34-H3C4	109.5
H3A4-C34-H3C4	109.5
H3B4-C34-H3C4	109.5
N14-C44-C14	179.2(3)
C44-C14-C114	109.3(2)
C44-C14-C24	110.46(19)
C114-C14-C24	114.55(19)
C44-C14-H14	107.4
C114-C14-H14	107.4
C24-C14-H14	107.4
C124-C114-C154	100.8(2)
C124-C114-C14	112.3(2)
C154-C114-C14	113.4(2)
C124-C114-H114	110.0
C154-C114-H114	110.0
C14-C114-H114	110.0
C134-C124-C114	104.3(2)
C134-C124-H12A4	110.9
C114-C124-H12A4	110.9
C134-C124-H12B4	110.9
C114-C124-H12B4	110.9

H12A4-C124-H12B4	108.9
C124-C134-C144	106.5(2)
C124-C134-H13A4	110.4
C144-C134-H13A4	110.4
C124-C134-H13B4	110.4
C144-C134-H13B4	110.4
H13A4-C134-H13B4	108.6
C154-C144-C134	105.3(2)
C154-C144-H14A4	110.7
C134-C144-H14A4	110.7
C154-C144-H14B4	110.7
C134-C144-H14B4	110.7
H14A4-C144-H14B4	108.8
C144-C154-C114	107.2(2)
C144-C154-H15A4	110.3
C114-C154-H15A4	110.3
C144-C154-H15B4	110.3
C114-C154-H15B4	110.3
H15A4-C154-H15B4	108.5
C224-C214-C304	117.2(2)
C224-C214-C24	121.2(2)
C304-C214-C24	121.6(2)
C214-C224-C234	122.6(2)
C214-C224-H224	118.7
C234-C224-H224	118.7
C224-C234-C284	119.4(2)
C224-C234-C244	122.4(2)
C284-C234-C244	118.1(2)
C254-C244-C234	120.7(2)
C254-C244-H244	119.7
C234-C244-H244	119.7
C244-C254-C264	120.9(2)
C244-C254-H254	119.6
C264-C254-H254	119.6
O14-C264-C274	125.0(2)
O14-C264-C254	114.5(2)
C274-C264-C254	120.5(2)
C264-C274-C284	119.4(2)
C264-C274-H274	120.3
C284-C274-H274	120.3
C234-C284-C294	117.8(2)
C234-C284-C274	120.3(2)
C294-C284-C274	121.9(2)
C304-C294-C284	120.9(2)
C304-C294-H294	119.6
C284-C294-H294	119.6
C294-C304-C214	122.0(2)
C294-C304-H304	119.0
C214-C304-H304	119.0
O14-C314-H31A4	109.5
O14-C314-H31B4	109.5
H31A4-C314-H31B4	109.5
O14-C314-H31C4	109.5
H31A4-C314-H31C4	109.5
H31B4-C314-H31C4	109.5
C265-O15-C315	116.8(2)
C215-C25-C35	112.72(19)
C215-C25-C15	113.70(18)

C35-C25-C15	110.12(18)
C215-C25-H25	106.6
C35-C25-H25	106.6
C15-C25-H25	106.6
C25-C35-H3A5	109.5
C25-C35-H3B5	109.5
H3A5-C35-H3B5	109.5
C25-C35-H3C5	109.5
H3A5-C35-H3C5	109.5
H3B5-C35-H3C5	109.5
N15-C45-C15	178.3(3)
C45-C15-C115	108.28(19)
C45-C15-C25	111.97(18)
C115-C15-C25	114.69(18)
C45-C15-H15	107.2
C115-C15-H15	107.2
C25-C15-H15	107.2
C15-C115-C155	113.55(19)
C15-C115-C125	112.70(19)
C155-C115-C125	103.35(19)
C15-C115-H115	109.0
C155-C115-H115	109.0
C125-C115-H115	109.0
C135-C125-C115	104.1(2)
C135-C125-H12A5	110.9
C115-C125-H12A5	110.9
C135-C125-H12B5	110.9
C115-C125-H12B5	110.9
H12A5-C125-H12B5	108.9
C145-C135-C125	107.1(2)
C145-C135-H13A5	110.3
C125-C135-H13A5	110.3
C145-C135-H13B5	110.3
C125-C135-H13B5	110.3
H13A5-C135-H13B5	108.6
C135-C145-C155	107.6(2)
C135-C145-H14A5	110.2
C155-C145-H14A5	110.2
C135-C145-H14B5	110.2
C155-C145-H14B5	110.2
H14A5-C145-H14B5	108.5
C145-C155-C115	105.2(2)
C145-C155-H15A5	110.7
C115-C155-H15A5	110.7
C145-C155-H15B5	110.7
C115-C155-H15B5	110.7
H15A5-C155-H15B5	108.8
C225-C215-C305	117.8(2)
C225-C215-C25	121.4(2)
C305-C215-C25	120.7(2)
C215-C225-C235	122.3(2)
C215-C225-H225	118.9
C235-C225-H225	118.9
C225-C235-C285	119.3(2)
C225-C235-C245	122.8(2)
C285-C235-C245	117.9(2)
C255-C245-C235	121.1(2)
C255-C245-H245	119.4

C235-C245-H245	119.4
C245-C255-C265	120.5(2)
C245-C255-H255	119.8
C265-C255-H255	119.8
C275-C265-O15	124.6(2)
C275-C265-C255	120.8(2)
O15-C265-C255	114.6(2)
C265-C275-C285	119.0(2)
C265-C275-H275	120.5
C285-C275-H275	120.5
C235-C285-C295	118.4(2)
C235-C285-C275	120.6(2)
C295-C285-C275	121.0(2)
C305-C295-C285	120.5(2)
C305-C295-H295	119.7
C285-C295-H295	119.7
C295-C305-C215	121.8(2)
C295-C305-H305	119.1
C215-C305-H305	119.1
O15-C315-H31A5	109.5
O15-C315-H31B5	109.5
H31A5-C315-H31B5	109.5
O15-C315-H31C5	109.5
H31A5-C315-H31C5	109.5
H31B5-C315-H31C5	109.5
C266-O16-C316	116.4(2)
C216-C26-C36	112.36(19)
C216-C26-C16	113.09(18)
C36-C26-C16	110.88(19)
C216-C26-H26	106.7
C36-C26-H26	106.7
C16-C26-H26	106.7
C26-C36-H3A6	109.5
C26-C36-H3B6	109.5
H3A6-C36-H3B6	109.5
C26-C36-H3C6	109.5
H3A6-C36-H3C6	109.5
H3B6-C36-H3C6	109.5
N16-C46-C16	177.3(3)
C46-C16-C116	108.8(2)
C46-C16-C26	111.01(19)
C116-C16-C26	113.73(18)
C46-C16-H16	107.7
C116-C16-H16	107.7
C26-C16-H16	107.7
C126-C116-C16	111.5(2)
C126-C116-C156	104.6(2)
C16-C116-C156	113.8(2)
C126-C116-H116	108.9
C16-C116-H116	108.9
C156-C116-H116	108.9
C136-C126-C116	104.8(2)
C136-C126-H12A6	110.8
C116-C126-H12A6	110.8
C136-C126-H12B6	110.8
C116-C126-H12B6	110.8
H12A6-C126-H12B6	108.9
C126-C136-C146	102.0(2)

C126-C136-H13A6	111.4
C146-C136-H13A6	111.4
C126-C136-H13B6	111.4
C146-C136-H13B6	111.4
H13A6-C136-H13B6	109.2
C156-C146-C136	104.2(2)
C156-C146-H14A6	110.9
C136-C146-H14A6	110.9
C156-C146-H14B6	110.9
C136-C146-H14B6	110.9
H14A6-C146-H14B6	108.9
C146-C156-C116	106.1(2)
C146-C156-H15A6	110.5
C116-C156-H15A6	110.5
C146-C156-H15B6	110.5
C116-C156-H15B6	110.5
H15A6-C156-H15B6	108.7
C226-C216-C306	117.5(2)
C226-C216-C26	121.0(2)
C306-C216-C26	121.5(2)
C216-C226-C236	122.3(2)
C216-C226-H226	118.8
C236-C226-H226	118.8
C226-C236-C286	119.2(2)
C226-C236-C246	122.7(2)
C286-C236-C246	118.0(2)
C256-C246-C236	120.9(2)
C256-C246-H246	119.5
C236-C246-H246	119.5
C246-C256-C266	120.4(2)
C246-C256-H256	119.8
C266-C256-H256	119.8
C276-C266-O16	124.8(2)
C276-C266-C256	120.9(2)
O16-C266-C256	114.3(2)
C266-C276-C286	119.2(2)
C266-C276-H276	120.4
C286-C276-H276	120.4
C236-C286-C296	118.2(2)
C236-C286-C276	120.3(2)
C296-C286-C276	121.5(2)
C306-C296-C286	120.9(2)
C306-C296-H296	119.6
C286-C296-H296	119.6
C296-C306-C216	121.8(2)
C296-C306-H306	119.1
C216-C306-H306	119.1
O16-C316-H31A6	109.5
O16-C316-H31B6	109.5
H31A6-C316-H31B6	109.5
O16-C316-H31C6	109.5
H31A6-C316-H31C6	109.5
H31B6-C316-H31C6	109.5
C267-O17-C317	117.1(2)
C217-C27-C37	112.13(18)
C217-C27-C17	112.93(17)
C37-C27-C17	110.77(18)
C217-C27-H27	106.9

C37-C27-H27	106.9
C17-C27-H27	106.9
C27-C37-H3A7	109.5
C27-C37-H3B7	109.5
H3A7-C37-H3B7	109.5
C27-C37-H3C7	109.5
H3A7-C37-H3C7	109.5
H3B7-C37-H3C7	109.5
N17-C47-C17	178.7(3)
C47-C17-C117	109.7(2)
C47-C17-C27	110.89(18)
C117-C17-C27	113.72(17)
C47-C17-H17	107.4
C117-C17-H17	107.4
C27-C17-H17	107.4
C12A7-C117-C157	104.0(6)
C12A7-C117-C17	120.0(6)
C157-C117-C17	117.1(3)
C12A7-C117-C15A7	107.6(7)
C157-C117-C15A7	17.1(4)
C17-C117-C15A7	102.1(5)
C12A7-C117-C127	18.4(5)
C157-C117-C127	99.5(3)
C17-C117-C127	108.7(3)
C15A7-C117-C127	97.9(5)
C12A7-C117-H11A7	92.2
C157-C117-H11A7	110.3
C17-C117-H11A7	110.3
C15A7-C117-H11A7	126.0
C127-C117-H11A7	110.3
C12A7-C117-H11B7	108.8
C157-C117-H11B7	95.0
C17-C117-H11B7	108.8
C15A7-C117-H11B7	108.8
C127-C117-H11B7	127.2
H11A7-C117-H11B7	19.9
C137-C127-C117	105.0(3)
C137-C127-H12A7	110.8
C117-C127-H12A7	110.8
C137-C127-H12B7	110.8
C117-C127-H12B7	110.8
H12A7-C127-H12B7	108.8
C147-C137-C127	106.7(3)
C147-C137-H13A7	110.4
C127-C137-H13A7	110.4
C147-C137-H13B7	110.4
C127-C137-H13B7	110.4
H13A7-C137-H13B7	108.6
C137-C147-C157	106.0(3)
C137-C147-H14A7	110.5
C157-C147-H14A7	110.5
C137-C147-H14B7	110.5
C157-C147-H14B7	110.5
H14A7-C147-H14B7	108.7
C117-C157-C147	105.9(3)
C117-C157-H15A7	110.6
C147-C157-H15A7	110.6
C117-C157-H15B7	110.6

C147-C157-H15B7	110.6
H15A7-C157-H15B7	108.7
C117-C12A7-C13A7	102.7(7)
C117-C12A7-H12C7	111.2
C13A7-C12A7-H12C7	111.2
C117-C12A7-H12D7	111.2
C13A7-C12A7-H12D7	111.2
H12C7-C12A7-H12D7	109.1
C14A7-C13A7-C12A7	109.8(9)
C14A7-C13A7-H13C7	109.7
C12A7-C13A7-H13C7	109.7
C14A7-C13A7-H13D7	109.7
C12A7-C13A7-H13D7	109.7
H13C7-C13A7-H13D7	108.2
C13A7-C14A7-C15A7	106.6(9)
C13A7-C14A7-H14C7	110.4
C15A7-C14A7-H14C7	110.4
C13A7-C14A7-H14D7	110.4
C15A7-C14A7-H14D7	110.4
H14C7-C14A7-H14D7	108.6
C14A7-C15A7-C117	101.0(7)
C14A7-C15A7-H15C7	111.6
C117-C15A7-H15C7	111.6
C14A7-C15A7-H15D7	111.6
C117-C15A7-H15D7	111.6
H15C7-C15A7-H15D7	109.4
C227-C217-C307	117.6(2)
C227-C217-C27	120.7(2)
C307-C217-C27	121.69(19)
C217-C227-C237	122.1(2)
C217-C227-H227	118.9
C237-C227-H227	118.9
C227-C237-C247	122.1(2)
C227-C237-C287	119.3(2)
C247-C237-C287	118.6(2)
C257-C247-C237	120.6(2)
C257-C247-H247	119.7
C237-C247-H247	119.7
C247-C257-C267	121.1(2)
C247-C257-H257	119.5
C267-C257-H257	119.5
O17-C267-C277	124.8(2)
O17-C267-C257	114.8(2)
C277-C267-C257	120.5(2)
C267-C277-C287	119.3(2)
C267-C277-H277	120.3
C287-C277-H277	120.3
C297-C287-C237	118.0(2)
C297-C287-C277	122.2(2)
C237-C287-C277	119.8(2)
C307-C297-C287	121.2(2)
C307-C297-H297	119.4
C287-C297-H297	119.4
C297-C307-C217	121.8(2)
C297-C307-H307	119.1
C217-C307-H307	119.1
O17-C317-H31A7	109.5
O17-C317-H31B7	109.5

H31A7-C317-H31B7	109.5
O17-C317-H31C7	109.5
H31A7-C317-H31C7	109.5
H31B7-C317-H31C7	109.5
C268-O18-C318	117.36(19)
C218-C28-C38	111.7(2)
C218-C28-C18	113.26(18)
C38-C28-C18	110.71(19)
C218-C28-H28	106.9
C38-C28-H28	106.9
C18-C28-H28	106.9
C28-C38-H3A8	109.5
C28-C38-H3B8	109.5
H3A8-C38-H3B8	109.5
C28-C38-H3C8	109.5
H3A8-C38-H3C8	109.5
H3B8-C38-H3C8	109.5
N18-C48-C18	177.1(3)
C48-C18-C118	109.0(2)
C48-C18-C28	110.10(18)
C118-C18-C28	114.90(18)
C48-C18-H18	107.5
C118-C18-H18	107.5
C28-C18-H18	107.5
C128-C118-C15A8	103.6(6)
C128-C118-C18	118.9(4)
C15A8-C118-C18	117.3(6)
C128-C118-C158	103.2(5)
C15A8-C118-C158	11.4(8)
C18-C118-C158	108.8(5)
C128-C118-C12A8	19.4(4)
C15A8-C118-C12A8	99.5(6)
C18-C118-C12A8	106.2(5)
C158-C118-C12A8	95.5(5)
C128-C118-H11A8	108.5
C15A8-C118-H11A8	97.9
C18-C118-H11A8	108.5
C158-C118-H11A8	108.5
C12A8-C118-H11A8	127.8
C128-C118-H11B8	92.1
C15A8-C118-H11B8	111.0
C18-C118-H11B8	111.0
C158-C118-H11B8	122.3
C12A8-C118-H11B8	111.0
H11A8-C118-H11B8	18.6
C118-C128-C138	104.0(4)
C118-C128-H12A8	111.0
C138-C128-H12A8	111.0
C118-C128-H12B8	111.0
C138-C128-H12B8	111.0
H12A8-C128-H12B8	109.0
C128-C138-C148	106.4(5)
C128-C138-H13A8	110.5
C148-C138-H13A8	110.5
C128-C138-H13B8	110.5
C148-C138-H13B8	110.5
H13A8-C138-H13B8	108.6
C158-C148-C138	105.6(5)

C158-C148-H14A8	110.6
C138-C148-H14A8	110.6
C158-C148-H14B8	110.6
C138-C148-H14B8	110.6
H14A8-C148-H14B8	108.8
C148-C158-C118	103.7(5)
C148-C158-H15A8	111.0
C118-C158-H15A8	111.0
C148-C158-H15B8	111.0
C118-C158-H15B8	111.0
H15A8-C158-H15B8	109.0
C13A8-C12A8-C118	104.9(6)
C13A8-C12A8-H12C8	110.8
C118-C12A8-H12C8	110.8
C13A8-C12A8-H12D8	110.8
C118-C12A8-H12D8	110.8
H12C8-C12A8-H12D8	108.8
C12A8-C13A8-C14A8	106.3(7)
C12A8-C13A8-H13C8	110.5
C14A8-C13A8-H13C8	110.5
C12A8-C13A8-H13D8	110.5
C14A8-C13A8-H13D8	110.5
H13C8-C13A8-H13D8	108.7
C15A8-C14A8-C13A8	106.9(8)
C15A8-C14A8-H14C8	110.3
C13A8-C14A8-H14C8	110.3
C15A8-C14A8-H14D8	110.3
C13A8-C14A8-H14D8	110.3
H14C8-C14A8-H14D8	108.6
C118-C15A8-C14A8	108.1(8)
C118-C15A8-H15C8	110.1
C14A8-C15A8-H15C8	110.1
C118-C15A8-H15D8	110.1
C14A8-C15A8-H15D8	110.1
H15C8-C15A8-H15D8	108.4
C228-C218-C308	118.2(2)
C228-C218-C28	120.8(2)
C308-C218-C28	120.9(2)
C218-C228-C238	122.3(2)
C218-C228-H228	118.9
C238-C228-H228	118.9
C248-C238-C228	122.5(2)
C248-C238-C288	118.5(2)
C228-C238-C288	119.0(2)
C258-C248-C238	121.0(2)
C258-C248-H248	119.5
C238-C248-H248	119.5
C248-C258-C268	119.9(2)
C248-C258-H258	120.0
C268-C258-H258	120.0
C278-C268-O18	125.8(2)
C278-C268-C258	120.7(2)
O18-C268-C258	113.6(2)
C268-C278-C288	120.1(2)
C268-C278-H278	120.0
C288-C278-H278	120.0
C298-C288-C278	122.1(2)
C298-C288-C238	118.2(2)

C278-C288-C238	119.7(2)
C308-C298-C288	121.5(2)
C308-C298-H298	119.2
C288-C298-H298	119.2
C298-C308-C218	120.9(2)
C298-C308-H308	119.6
C218-C308-H308	119.6
O18-C318-H31A8	109.5
O18-C318-H31B8	109.5
H31A8-C318-H31B8	109.5
O18-C318-H31C8	109.5
H31A8-C318-H31C8	109.5
H31B8-C318-H31C8	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for X12022. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O11	36(1)	26(1)	33(1)	-4(1)	5(1)	4(1)
N11	38(1)	26(1)	58(1)	6(1)	18(1)	1(1)
C21	22(1)	24(1)	22(1)	0(1)	-1(1)	-2(1)
C31	25(1)	32(1)	26(1)	-2(1)	-4(1)	1(1)
C41	31(1)	18(1)	34(1)	2(1)	3(1)	4(1)
C11	22(1)	21(1)	28(1)	1(1)	-1(1)	1(1)
C111	29(1)	23(1)	25(1)	-1(1)	-6(1)	-1(1)
C121	27(1)	40(1)	38(1)	6(1)	0(1)	-2(1)
C131	25(1)	52(2)	55(2)	9(1)	-11(1)	-5(1)
C141	30(1)	42(1)	42(1)	5(1)	-12(1)	6(1)
C151	36(1)	31(1)	32(1)	8(1)	0(1)	3(1)
C211	22(1)	22(1)	22(1)	4(1)	0(1)	0(1)
C221	19(1)	26(1)	24(1)	3(1)	0(1)	0(1)
C231	22(1)	28(1)	22(1)	5(1)	0(1)	-2(1)
C241	24(1)	28(1)	30(1)	0(1)	4(1)	-2(1)
C251	32(1)	31(1)	27(1)	-3(1)	3(1)	-5(1)
C261	35(1)	24(1)	20(1)	-1(1)	-1(1)	3(1)
C271	25(1)	32(1)	22(1)	2(1)	2(1)	3(1)
C281	24(1)	25(1)	20(1)	4(1)	-1(1)	1(1)
C291	18(1)	28(1)	29(1)	5(1)	2(1)	1(1)
C301	21(1)	24(1)	32(1)	4(1)	3(1)	-4(1)
C311	49(2)	28(1)	42(2)	2(1)	16(1)	8(1)
O12	46(1)	30(1)	35(1)	4(1)	4(1)	-7(1)
N12	30(1)	26(1)	38(1)	0(1)	9(1)	3(1)
C22	24(1)	27(1)	32(1)	-2(1)	7(1)	1(1)
C32	30(1)	34(1)	31(1)	3(1)	4(1)	2(1)
C42	32(1)	20(1)	27(1)	2(1)	2(1)	-2(1)
C12	24(1)	22(1)	36(1)	0(1)	4(1)	0(1)
C112	27(1)	26(1)	32(1)	-2(1)	1(1)	0(1)
C122	25(1)	44(1)	41(1)	-4(1)	1(1)	3(1)
C132	27(1)	56(2)	42(1)	1(1)	-5(1)	-1(1)
C142	31(1)	48(1)	35(1)	-4(1)	-2(1)	-5(1)
C152	35(1)	28(1)	40(1)	-6(1)	-3(1)	0(1)
C212	24(1)	24(1)	28(1)	-8(1)	6(1)	-3(1)
C222	20(1)	30(1)	28(1)	-4(1)	2(1)	-5(1)
C232	22(1)	31(1)	24(1)	-6(1)	2(1)	2(1)
C242	24(1)	32(1)	32(1)	-1(1)	1(1)	2(1)
C252	33(1)	33(1)	32(1)	1(1)	0(1)	4(1)
C262	38(1)	29(1)	22(1)	0(1)	2(1)	-3(1)
C272	29(1)	34(1)	25(1)	-4(1)	4(1)	-4(1)
C282	24(1)	29(1)	22(1)	-5(1)	1(1)	-2(1)
C292	18(1)	31(1)	30(1)	-7(1)	2(1)	-1(1)
C302	22(1)	27(1)	33(1)	-5(1)	2(1)	2(1)
C312	51(2)	32(1)	39(1)	-6(1)	15(1)	-11(1)
O13	46(1)	28(1)	32(1)	1(1)	5(1)	-8(1)
N13	35(1)	29(1)	60(1)	-6(1)	17(1)	-2(1)
C23	19(1)	25(1)	25(1)	-1(1)	0(1)	1(1)
C33	28(1)	34(1)	27(1)	4(1)	1(1)	2(1)
C43	28(1)	22(1)	38(1)	-1(1)	6(1)	-4(1)

C13	24(1)	21(1)	27(1)	-1(1)	3(1)	-2(1)
C113	34(1)	25(1)	24(1)	1(1)	1(1)	-7(1)
C123	32(1)	44(1)	36(1)	-7(1)	-11(1)	7(1)
C133	24(1)	76(2)	33(1)	10(1)	0(1)	1(1)
C143	31(1)	33(1)	42(1)	7(1)	-10(1)	-6(1)
C153	44(1)	38(1)	28(1)	-8(1)	4(1)	-12(1)
C213	20(1)	25(1)	23(1)	-6(1)	-1(1)	-2(1)
C223	21(1)	32(1)	23(1)	-4(1)	-1(1)	-2(1)
C233	26(1)	26(1)	22(1)	-2(1)	4(1)	1(1)
C243	25(1)	32(1)	26(1)	-2(1)	0(1)	3(1)
C253	40(1)	27(1)	26(1)	2(1)	2(1)	0(1)
C263	37(1)	27(1)	21(1)	-3(1)	4(1)	-8(1)
C273	29(1)	30(1)	29(1)	-5(1)	7(1)	-5(1)
C283	24(1)	28(1)	25(1)	-5(1)	4(1)	-1(1)
C293	20(1)	30(1)	35(1)	-5(1)	3(1)	1(1)
C303	21(1)	25(1)	31(1)	-4(1)	1(1)	3(1)
C313	50(2)	38(1)	41(2)	-5(1)	16(1)	-18(1)
O14	29(1)	27(1)	37(1)	6(1)	0(1)	-2(1)
N14	56(1)	30(1)	45(1)	1(1)	22(1)	6(1)
C24	24(1)	27(1)	27(1)	-2(1)	4(1)	-2(1)
C34	31(1)	41(1)	34(1)	-1(1)	3(1)	-6(1)
C44	40(1)	22(1)	36(1)	5(1)	9(1)	4(1)
C14	33(1)	23(1)	28(1)	2(1)	8(1)	0(1)
C114	31(1)	29(1)	40(1)	6(1)	0(1)	-2(1)
C124	41(2)	57(2)	47(2)	-16(1)	-12(1)	8(1)
C134	50(2)	90(2)	25(1)	-2(1)	-2(1)	-12(2)
C144	48(2)	40(1)	42(2)	11(1)	-7(1)	-6(1)
C154	40(1)	48(1)	43(1)	16(1)	4(1)	9(1)
C214	22(1)	27(1)	27(1)	1(1)	2(1)	4(1)
C224	24(1)	29(1)	24(1)	-1(1)	3(1)	4(1)
C234	20(1)	29(1)	25(1)	0(1)	0(1)	4(1)
C244	29(1)	32(1)	26(1)	-2(1)	3(1)	-2(1)
C254	25(1)	26(1)	34(1)	-2(1)	2(1)	-2(1)
C264	16(1)	26(1)	35(1)	3(1)	2(1)	2(1)
C274	21(1)	29(1)	28(1)	2(1)	4(1)	4(1)
C284	19(1)	26(1)	27(1)	2(1)	2(1)	5(1)
C294	30(1)	29(1)	25(1)	1(1)	5(1)	6(1)
C304	30(1)	26(1)	29(1)	-2(1)	2(1)	2(1)
C314	37(1)	30(1)	42(1)	8(1)	11(1)	2(1)
O15	30(1)	27(1)	43(1)	3(1)	3(1)	-3(1)
N15	38(1)	27(1)	31(1)	-4(1)	9(1)	1(1)
C25	22(1)	26(1)	26(1)	-3(1)	1(1)	1(1)
C35	25(1)	36(1)	32(1)	0(1)	2(1)	-2(1)
C45	26(1)	21(1)	30(1)	1(1)	-2(1)	-2(1)
C15	25(1)	23(1)	27(1)	-3(1)	4(1)	-4(1)
C115	26(1)	26(1)	30(1)	-1(1)	0(1)	1(1)
C125	41(1)	48(2)	28(1)	-6(1)	-2(1)	5(1)
C135	40(2)	80(2)	34(1)	-6(1)	-5(1)	10(1)
C145	66(2)	66(2)	41(2)	3(1)	-10(1)	24(2)
C155	36(1)	34(1)	38(1)	1(1)	-5(1)	8(1)
C215	18(1)	27(1)	26(1)	-1(1)	0(1)	4(1)
C225	22(1)	30(1)	25(1)	-2(1)	0(1)	2(1)
C235	19(1)	28(1)	26(1)	-2(1)	-3(1)	4(1)
C245	27(1)	34(1)	28(1)	-6(1)	3(1)	-4(1)

C255	24(1)	28(1)	39(1)	-10(1)	3(1)	-3(1)
C265	16(1)	25(1)	43(1)	1(1)	2(1)	3(1)
C275	22(1)	26(1)	31(1)	2(1)	4(1)	3(1)
C285	15(1)	26(1)	30(1)	1(1)	1(1)	4(1)
C295	28(1)	25(1)	24(1)	0(1)	2(1)	5(1)
C305	26(1)	22(1)	27(1)	-1(1)	-1(1)	4(1)
C315	37(1)	27(1)	52(2)	4(1)	17(1)	3(1)
O16	35(1)	27(1)	51(1)	-8(1)	5(1)	5(1)
N16	55(1)	29(1)	42(1)	-4(1)	20(1)	-10(1)
C26	25(1)	24(1)	29(1)	2(1)	6(1)	-1(1)
C36	29(1)	37(1)	37(1)	-2(1)	2(1)	4(1)
C46	39(1)	23(1)	33(1)	-5(1)	10(1)	-4(1)
C16	26(1)	24(1)	30(1)	-1(1)	8(1)	-2(1)
C116	32(1)	33(1)	33(1)	-5(1)	4(1)	-6(1)
C126	40(1)	54(2)	30(1)	5(1)	-2(1)	-9(1)
C136	53(2)	63(2)	30(1)	2(1)	-8(1)	-10(1)
C146	71(2)	58(2)	47(2)	-16(1)	2(2)	-18(2)
C156	36(1)	44(1)	40(1)	-8(1)	7(1)	-16(1)
C216	19(1)	26(1)	29(1)	-2(1)	0(1)	-6(1)
C226	22(1)	28(1)	26(1)	1(1)	3(1)	-4(1)
C236	20(1)	26(1)	29(1)	0(1)	-2(1)	-4(1)
C246	26(1)	30(1)	32(1)	3(1)	4(1)	0(1)
C256	25(1)	28(1)	41(1)	7(1)	2(1)	3(1)
C266	19(1)	25(1)	49(2)	-4(1)	3(1)	-2(1)
C276	22(1)	30(1)	32(1)	-4(1)	3(1)	-3(1)
C286	17(1)	26(1)	32(1)	-4(1)	1(1)	-6(1)
C296	28(1)	29(1)	26(1)	-2(1)	4(1)	-8(1)
C306	27(1)	22(1)	30(1)	0(1)	0(1)	-6(1)
C316	41(2)	31(1)	62(2)	-14(1)	17(1)	-4(1)
O17	33(1)	26(1)	40(1)	-5(1)	4(1)	2(1)
N17	61(2)	29(1)	36(1)	-3(1)	20(1)	-10(1)
C27	22(1)	28(1)	23(1)	-1(1)	2(1)	2(1)
C37	29(1)	45(1)	29(1)	-3(1)	-3(1)	10(1)
C47	37(1)	21(1)	35(1)	-6(1)	8(1)	-5(1)
C17	27(1)	20(1)	25(1)	-2(1)	4(1)	2(1)
C117	25(1)	26(1)	38(1)	-8(1)	-7(1)	5(1)
C127	33(2)	30(3)	34(2)	15(2)	-11(2)	-5(2)
C137	32(2)	39(3)	22(2)	-2(2)	1(1)	-3(2)
C147	26(2)	24(2)	27(2)	-3(1)	-1(2)	-2(1)
C157	17(2)	33(2)	24(2)	-3(2)	-2(1)	0(2)
C12A7	37(4)	26(4)	40(3)	14(3)	-20(3)	-6(4)
C13A7	35(4)	44(5)	39(3)	0(4)	3(3)	-6(4)
C14A7	35(5)	36(4)	40(4)	-9(3)	-3(3)	-5(3)
C15A7	28(4)	34(4)	41(4)	5(3)	0(3)	2(3)
C217	17(1)	25(1)	28(1)	-3(1)	0(1)	-6(1)
C227	22(1)	31(1)	20(1)	1(1)	1(1)	-4(1)
C237	17(1)	26(1)	24(1)	-2(1)	-3(1)	-2(1)
C247	28(1)	32(1)	25(1)	2(1)	2(1)	2(1)
C257	29(1)	27(1)	32(1)	5(1)	2(1)	4(1)
C267	18(1)	26(1)	38(1)	-4(1)	3(1)	-3(1)
C277	23(1)	28(1)	29(1)	-4(1)	5(1)	-4(1)
C287	18(1)	26(1)	26(1)	-1(1)	1(1)	-6(1)
C297	27(1)	31(1)	21(1)	-2(1)	2(1)	-6(1)
C307	30(1)	24(1)	27(1)	0(1)	1(1)	-5(1)

C317	40(1)	30(1)	49(2)	-12(1)	13(1)	-5(1)
O18	33(1)	26(1)	32(1)	1(1)	2(1)	3(1)
N18	40(1)	30(1)	67(2)	12(1)	22(1)	4(1)
C28	25(1)	27(1)	33(1)	5(1)	8(1)	0(1)
C38	38(1)	41(1)	36(1)	-3(1)	8(1)	3(1)
C48	31(1)	24(1)	39(1)	4(1)	10(1)	4(1)
C18	24(1)	21(1)	33(1)	-1(1)	9(1)	-1(1)
C118	35(1)	28(1)	40(1)	0(1)	-4(1)	5(1)
C128	33(2)	31(3)	45(3)	9(2)	-13(2)	-5(2)
C138	33(2)	47(4)	50(3)	14(3)	10(2)	-3(3)
C148	23(3)	33(3)	39(3)	3(2)	-3(2)	0(2)
C158	36(3)	38(3)	34(3)	8(2)	3(2)	1(2)
C12A8	36(3)	37(4)	57(4)	6(3)	-4(3)	-11(3)
C13A8	23(3)	53(4)	47(3)	-2(3)	8(2)	-1(3)
C14A8	33(4)	43(3)	47(4)	7(3)	3(3)	3(3)
C15A8	22(3)	57(4)	36(4)	12(3)	2(2)	12(3)
C218	24(1)	24(1)	25(1)	7(1)	1(1)	4(1)
C228	19(1)	32(1)	27(1)	7(1)	3(1)	3(1)
C238	24(1)	27(1)	21(1)	6(1)	1(1)	-2(1)
C248	24(1)	34(1)	31(1)	3(1)	3(1)	-4(1)
C258	33(1)	31(1)	33(1)	-2(1)	1(1)	-7(1)
C268	29(1)	25(1)	24(1)	1(1)	1(1)	4(1)
C278	23(1)	31(1)	26(1)	8(1)	3(1)	3(1)
C288	24(1)	26(1)	20(1)	7(1)	0(1)	1(1)
C298	20(1)	27(1)	33(1)	6(1)	6(1)	0(1)
C308	22(1)	24(1)	31(1)	7(1)	3(1)	-2(1)
C318	43(2)	32(1)	41(1)	5(1)	15(1)	9(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for X12022.

	x	y	z	U(eq)
H21	2567	2043	5404	29
H3A1	4094	2021	6496	44
H3B1	3639	2476	6414	44
H3C1	4458	2371	5890	44
H11	2645	2735	4890	30
H111	2154	2206	3237	34
H12A1	1032	2415	4531	44
H12B1	1091	1974	4030	44
H13A1	-242	2558	3346	57
H13B1	-71	2153	2766	57
H14A1	716	2515	1881	50
H14B1	233	2917	2222	50
H15A1	1559	3047	3467	41
H15B1	2058	2884	2660	41
H221	2238	1422	4571	29
H241	1925	705	3918	34
H251	2488	101	3432	37
H271	5056	635	3556	32
H291	5296	1378	4056	31
H301	4779	1969	4663	32
H31A1	5234	35	2758	58
H31B1	5184	-432	3113	58
H31C1	5505	-67	3873	58
H22	9990	7068	2169	33
H3A2	8515	7044	981	48
H3B2	8981	7497	1103	48
H3C2	8105	7394	1550	48
H12	9854	7747	2704	33
H112	10234	7183	4288	35
H12A2	11392	7035	3485	46
H12B2	11520	7515	3246	46
H13A2	12725	7485	4578	53
H13B2	12257	7101	5003	53
H14A2	12082	7923	5426	48
H14B2	11615	7539	5852	48
H15A2	10220	7824	5012	44
H15B2	10719	8051	4276	44
H222	10296	6455	3036	32
H242	10623	5746	3755	37
H252	10059	5142	4249	41
H272	7397	5628	3799	36
H292	7130	6362	3226	32
H302	7656	6951	2643	34
H31A2	7039	4906	3566	60
H31B2	7202	5069	4637	60
H31C2	7334	4588	4437	60
H23	2661	7013	-48	29
H3A3	1265	7053	-1305	46

H3B3	1741	7501	-1065	46
H3C3	817	7380	-711	46
H13	2665	7678	586	29
H113	2692	7098	2110	35
H12A3	4296	6997	2253	49
H12B3	3880	6995	1113	49
H13A3	4377	7657	960	55
H13B3	5216	7508	1856	55
H14A3	4023	8140	1922	47
H14B3	4699	7924	2850	47
H15A3	2788	7891	2419	45
H15B3	3467	7585	3173	45
H223	2825	6385	729	32
H243	3002	5655	1371	35
H253	2334	5073	1852	39
H273	-243	5647	1381	35
H293	-383	6380	814	35
H303	273	6961	310	32
H31A3	-533	5111	2224	64
H31B3	-487	4624	2032	64
H31C3	-708	4942	1157	64
H24	3766	4213	3960	32
H3A4	2496	4172	2578	54
H3B4	2763	3723	3035	54
H3C4	3101	3857	2111	54
H14	4451	3559	3929	34
H114	5902	4181	3996	42
H12A4	6065	4227	5605	63
H12B4	4923	4178	5228	63
H13A4	4954	3502	5653	68
H13B4	5869	3659	6457	68
H14A4	6849	3297	5818	56
H14B4	5923	3086	5122	56
H15A4	6365	3412	3959	54
H15B4	7059	3721	4689	54
H224	4495	4860	4127	32
H244	5067	5592	4327	36
H254	5453	6194	3660	35
H274	5088	5635	1093	32
H294	4589	4883	939	34
H304	4103	4298	1577	35
H31A4	5909	6201	851	54
H31B4	5608	6677	884	54
H31C4	4805	6325	635	54
H25	6010	4231	1263	31
H3A5	4780	4230	-158	48
H3B5	4950	3776	296	48
H3C5	5350	3892	-602	48
H15	6531	3546	1159	31
H115	8145	4094	1473	35
H12A5	7407	4302	2625	49
H12B5	7039	3841	2768	49
H13A5	8894	4170	3502	65
H13B5	8356	3831	3988	65

H14A5	9028	3323	3392	74
H14B5	9657	3662	3012	74
H15A5	8057	3234	1954	46
H15B5	8872	3462	1564	46
H225	6782	4868	1469	32
H245	7407	5594	1680	37
H255	7874	6186	1032	37
H275	7630	5604	-1493	32
H295	7085	4864	-1659	31
H305	6524	4287	-1043	32
H31A5	8392	6160	-1771	56
H31B5	8163	6644	-1725	56
H31C5	7310	6314	-1961	56
H26	1544	9265	1285	31
H3A6	2623	9225	2819	53
H3B6	2487	8787	2286	53
H3C6	1962	8877	3111	53
H16	908	8584	1259	32
H116	-588	9196	784	40
H12A6	218	9376	-283	52
H12B6	766	8938	-209	52
H13A6	-326	8875	-1664	62
H13B6	-1148	9111	-1297	62
H14A6	-1517	8414	-1168	73
H14B6	-411	8293	-744	73
H15A6	-836	8355	629	48
H15B6	-1636	8699	202	48
H226	711	9894	1008	32
H246	43	10614	743	36
H256	-430	11211	1364	39
H276	-229	10646	3902	35
H296	276	9900	4084	34
H306	861	9318	3507	33
H31A6	-1005	11214	4142	66
H31B6	-708	11690	4107	66
H31C6	98	11339	4357	66
H27	8789	9245	3548	30
H3A7	9908	9165	5036	54
H3B7	9655	8728	4509	54
H3C7	9199	8851	5367	54
H17	8045	8593	3484	29
H11A7	6735	9280	3087	39
H11B7	6588	9221	3188	39
H12A7	6889	9209	1524	43
H12B7	7949	9078	2108	43
H13A7	6877	8574	875	39
H13B7	7685	8401	1768	39
H14A7	6573	8132	2376	32
H14B7	5766	8297	1473	32
H15A7	5496	8880	2244	31
H15B7	5879	8594	3172	31
H12C7	7721	9288	2174	48
H12D7	6587	9315	1698	48
H13C7	6910	8784	845	49

H13D7	7821	8643	1668	49
H14C7	6944	8165	2052	47
H14D7	6001	8349	1331	47
H15C7	6364	8411	3242	43
H15D7	5569	8687	2515	43
H227	8009	9888	3317	30
H247	7431	10617	3101	35
H257	7014	11219	3745	37
H277	7281	10662	6299	32
H297	7759	9909	6459	32
H307	8256	9320	5843	34
H31A7	6471	11236	6518	59
H31B7	6805	11708	6503	59
H31C7	7584	11347	6770	59
H28	4858	2003	2604	34
H3A8	6362	2049	3738	58
H3B8	5827	2487	3573	58
H3C8	6687	2395	3095	58
H18	4814	2678	1965	31
H11A8	4575	2126	367	44
H11B8	4473	2058	471	44
H12A8	3574	1926	1444	49
H12B8	3074	1973	323	49
H13A8	3011	2538	1799	52
H13B8	2156	2415	895	52
H14A8	2535	2930	34	40
H14B8	3287	3090	984	40
H15A8	4404	2924	244	44
H15B8	3677	2638	-523	44
H12C8	2902	2044	711	55
H12D8	3506	2130	1789	55
H13C8	3084	2796	1731	49
H13D8	2181	2636	917	49
H14C8	2678	2984	-176	51
H14D8	3543	3167	647	51
H15C8	3591	2506	-593	47
H15D8	4451	2809	-86	47
H228	4673	1364	1858	32
H248	4491	632	1271	36
H258	5158	42	810	40
H278	7655	650	990	33
H298	7787	1393	1488	33
H308	7154	1972	2025	32
H31A8	7939	83	207	57
H31B8	7918	-398	467	57
H31C8	8182	-59	1298	57

VI. ^{1}H NMR Spectra of Selected Compounds

JC7061 1H CDCl3

exp1 s2pul

SAMPLE		DEC. & VT	
date	Jan 7 2012	dfrq	125.844
solvent	CDCl3	dn	C13
file	/data/export/~	dpwr	30
home/gfu/FUjcho/ca~		dof	0
sper/JC7061_1H_CDC~		dm	nnn
	13.fid	dmm	c
ACQUISITION		dmf	200
sfrq	500.431	dseq	
tn	H1	dres	1.0
at	4.999	homo	n
np	120102	PROCESSING	
sw	12012.0	wtfile	
fb	not used	proc	ft
bs	8	fn	262144
tpwr	60	math	f
pw	8.0		
d1	0.100	werr	
tof	3003.2	wexp	
nt	16	wbs	
ct	16	wnt	
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	45.1		
wp	4954.0		
vs	38		
sc	0		
wc	250		
hzmm	19.82		
is	33.57		
rfl	4148.0		
rfp	3633.1		
th	7		
ins	1.000		
ai cdc ph			

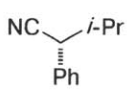


Table 2, entry 1

JC6205 1H CDCl3

exp1 s2pul

SAMPLE		DEC. & VT	
date	Sep 24 2011	dfrq	125.844
solvent	CDCl3	dn	C13
file	/data/export/~	dpwr	30
home/gfu/FUjcho/ca~		dof	0
sper/JC6205_1H_CDC~		dm	nnn
	13.fid	dmm	c
ACQUISITION		dmf	200
sfrq	500.431	dseq	
tn	H1	dres	1.0
at	4.999	homo	n
np	120102	PROCESSING	
sw	12012.0	wtfile	
fb	not used	proc	ft
bs	8	fn	262144
tpwr	60	math	f
pw	8.0		
d1	0.100	werr	
tof	3003.2	wexp	
nt	16	wbs	
ct	16	wnt	
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	42.0		
wp	4961.5		
vs	46		
sc	0		
wc	250		
hzmm	19.85		
is	33.57		
rfl	4149.1		
rfp	3633.1		
th	7		
ins	1.000		
ai cdc ph			

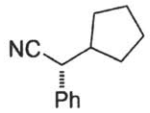
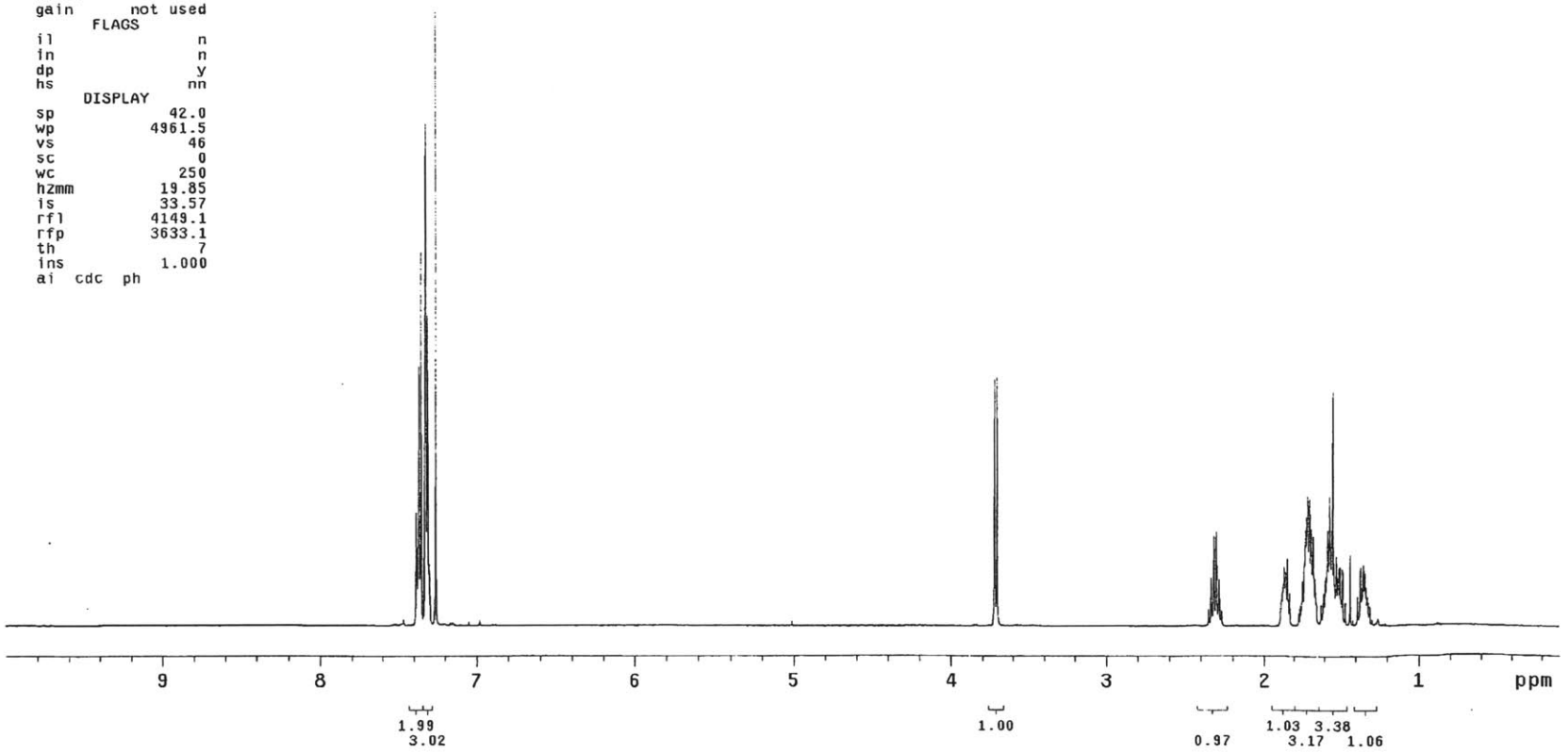


Table 2, entry 2



JC7189B 1H CDCl3

exp2 s2pul

SAMPLE		DEC. & VT	
date	Feb 22 2012	dfrq	125.672
solvent	CDCl3	dn	C13
file	/data/export/~	dpwr	30
	home/gfu/FUjcho/bu~	dof	0
	llwinkle/JC7189B_1~	dm	nnn
	H_CDCl3.fid	dmm	w
ACQUISITION		dmf	10000
sfrq	499.746	dseq	
tn	H1	dres	1.0
at	3.001	homo	n
np	63050	PROCESSING	
sw	10504.2	wtfile	
fb	not used	proc	ft
bs	8	fn	262144
tpwr	56	math	f
pw	8.6		
d1	2.000	werr	
tof	1519.5	wexp	
nt	16	wbs	
ct	16	wnt	wft
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	40.8		
wp	4958.9		
vs	93		
sc	0		
wc	250		
hzmm	19.84		
is	33.57		
rfl	4866.4		
rfp	3628.1		
th	7		
ins	1.000		
ai cdc ph			

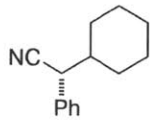
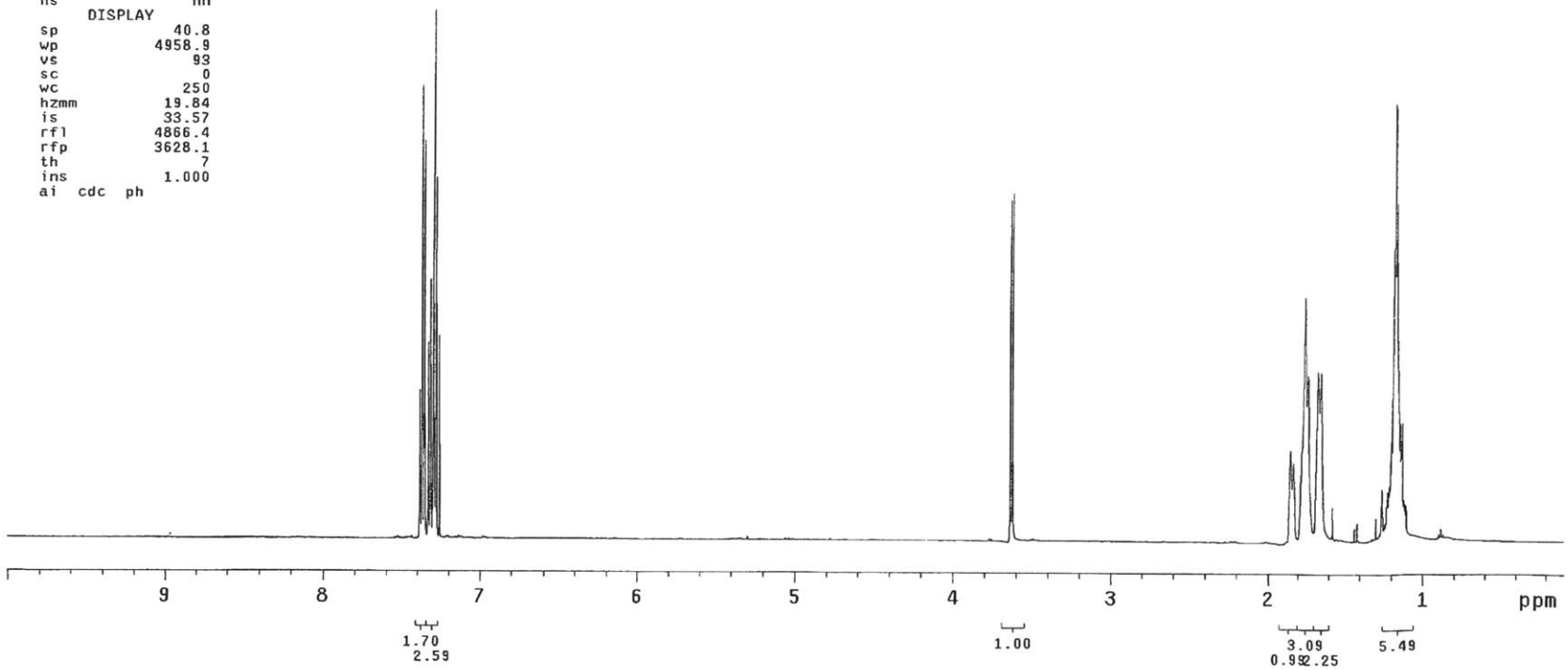


Table 2, entry 3



JC7243A 1H CDCl3

exp1 s2pul

SAMPLE		DEC. & VT	
date	Mar 15 2012	dfrq	125.672
solvent	CDCl3	dn	C13
file	/data/export/~	dpwr	30
home/gfu/FUjcho/bu~		dof	0
llwinkle/JC7243A_1~		dm	nnn
H_CDCl3.fid		dmm	w
ACQUISITION		dmf	10000
sfrq	499.746	dseq	
tn	H1	dres	1.0
at	3.001	homo	n
np	63050	temp	22.0
sw	10504.2	PROCESSING	
fb	not used	wtfile	
bs	8	proc	ft
tpwr	56	fn	262144
pw	8.6	math	f
d1	2.000		
tof	1519.5	werr	
nt	16	wexp	
ct	16	wbs	
alock	n	wnt	wft
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	39.9		
wp	4960.9		
vs	57		
sc	0		
wc	250		
hzmm	19.84		
is	33.57		
rfl	4865.4		
rfp	3628.1		
th	7		
ins	1.000		
ai cdc ph			

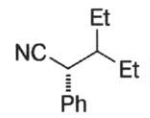


Table 2, entry 4

JC7211B 1H CDCl3

exp1 s2pul

SAMPLE		DEC. & VT	
date	Feb 28 2012	dfrq	125.844
solvent	CDCl3	dn	C13
file	/data/export/~	dpwr	30
	home/gfu/FUjcho/ca~	dof	0
	sper/JC7211B_1H_CD~	dm	nnn
	C13.fid	dmm	c
ACQUISITION		dmf	200
sfrq	500.431	dseq	
tn	H1	dres	1.0
at	4.999	homo	n
np	120102	PROCESSING	
sw	12012.0	wtfile	
fb	not used	proc	ft
bs	8	fn	262144
tpwr	60	math	f
pw	8.0		
d1	0.100	werr	
tof	3003.2	wexp	
nt	16	wbs	
ct	16	wnt	
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	51.4		
wp	4947.8		
vs	50		
sc	0		
wc	250		
hzmm	19.79		
is	176.67		
rfl	4148.0		
rfp	3633.1		
th	7		
ins	1.000		
ai cdc ph			

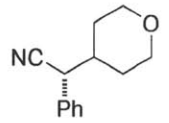
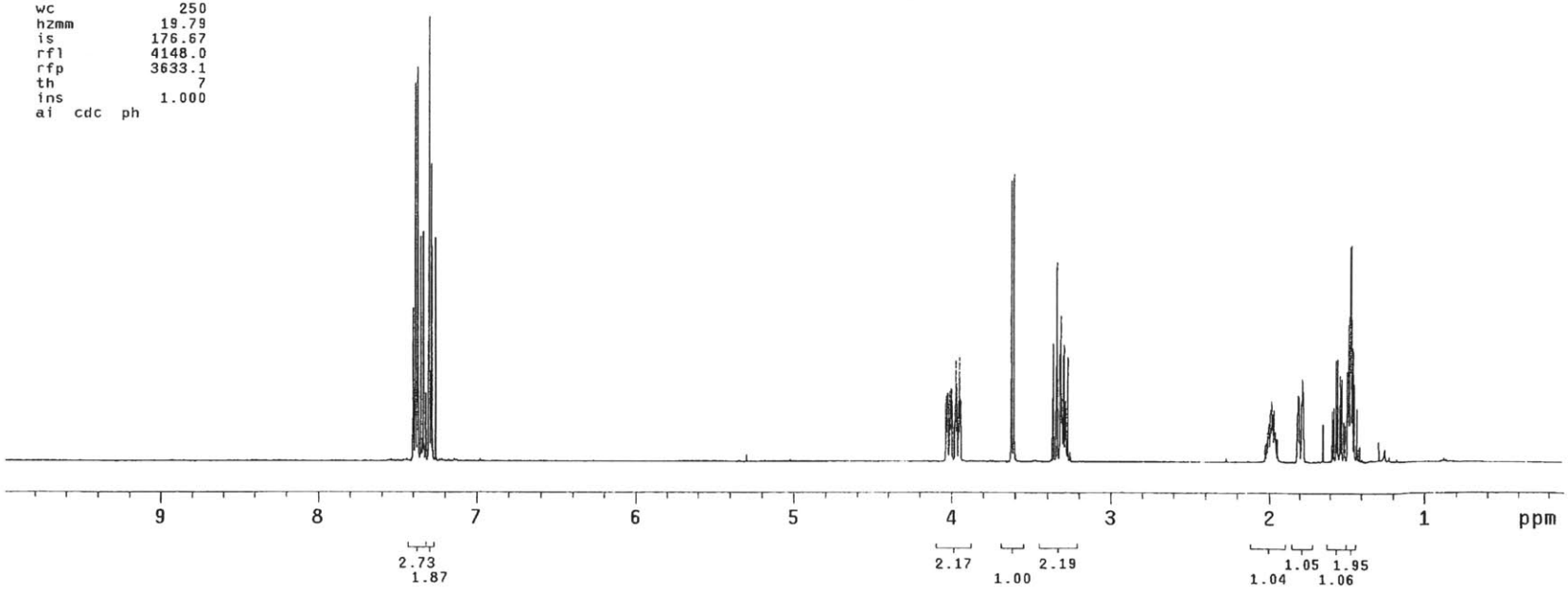


Table 2, entry 5



JC7229A 1H CDCl3

expl s2pul

SAMPLE		DEC. & VT	
date	Mar 11 2012	dfrq	125.844
solvent	CDCl3	dn	C13
file	/data/export/~	dpwr	30
home/gfu/FUjcho/ca~		dof	0
sper/JC7229A_1H_CD~		dm	nnn
	C13.fid	dmm	c
ACQUISITION		dmf	200
sfrq	500.431	dseq	
tn	H1	dres	1.0
at	4.999	homo	n
np	120102	PROCESSING	
sw	12012.0	wtfile	
fb	not used	proc	ft
bs	8	fn	262144
tpwr	60	math	f
pw	8.0		
d1	0.100	werr	
tof	3003.2	wexp	
nt	16	wbs	
ct	16	wnt	
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	47.5		
wp	4956.6		
vs	92		
sc	0		
wc	250		
hzmm	19.83		
is	33.57		
rfl	4148.6		
rfp	3633.1		
th	7		
ins	1.000		
ai cdc ph			

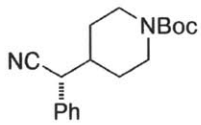


Table 2, entry 6

JC7257A 1H CDCl3

exp2 s2pul

SAMPLE		DEC. & VT	
date	Mar 27 2012	dfrq	125.672
solvent	CDCl3	dn	C13
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	499.746	dm	nnn
tn	H1	dmm	w
at	3.001	dmf	10000
np	63050	dseq	
sw	10504.2	dres	1.0
fb	not used	homo	n
bs	8	DEC2	
tpwr	56	dfrq2	0
pw	8.6	dn2	
d1	2.000	dpwr2	1
tof	1519.5	dof2	0
nt	16	dm2	n
ct	16	dmm2	c
alock	n	dmf2	200
gain	not used	dseq2	
FLAGS		dres2	1.0
il	n	homo2	n
in	n	DEC3	
dp	y	dfrq3	0
hs	nn	dn3	
DISPLAY		dpwr3	1
sp	48.4	dof3	0
wp	4952.3	dm3	n
vs	83	dmm3	c
sc	0	dmf3	200
wc	250	dseq3	
hzmm	19.81	dres3	1.0
is	33.57	homo3	n
rfl	4865.7	PROCESSING	
rfp	3628.1	wtfile	
th	7	proc	ft
ins	1.000	fn	262144
ai cdc ph		math	f
		werr	
		wexp	
		wbs	
		wnt	wft

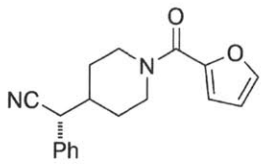
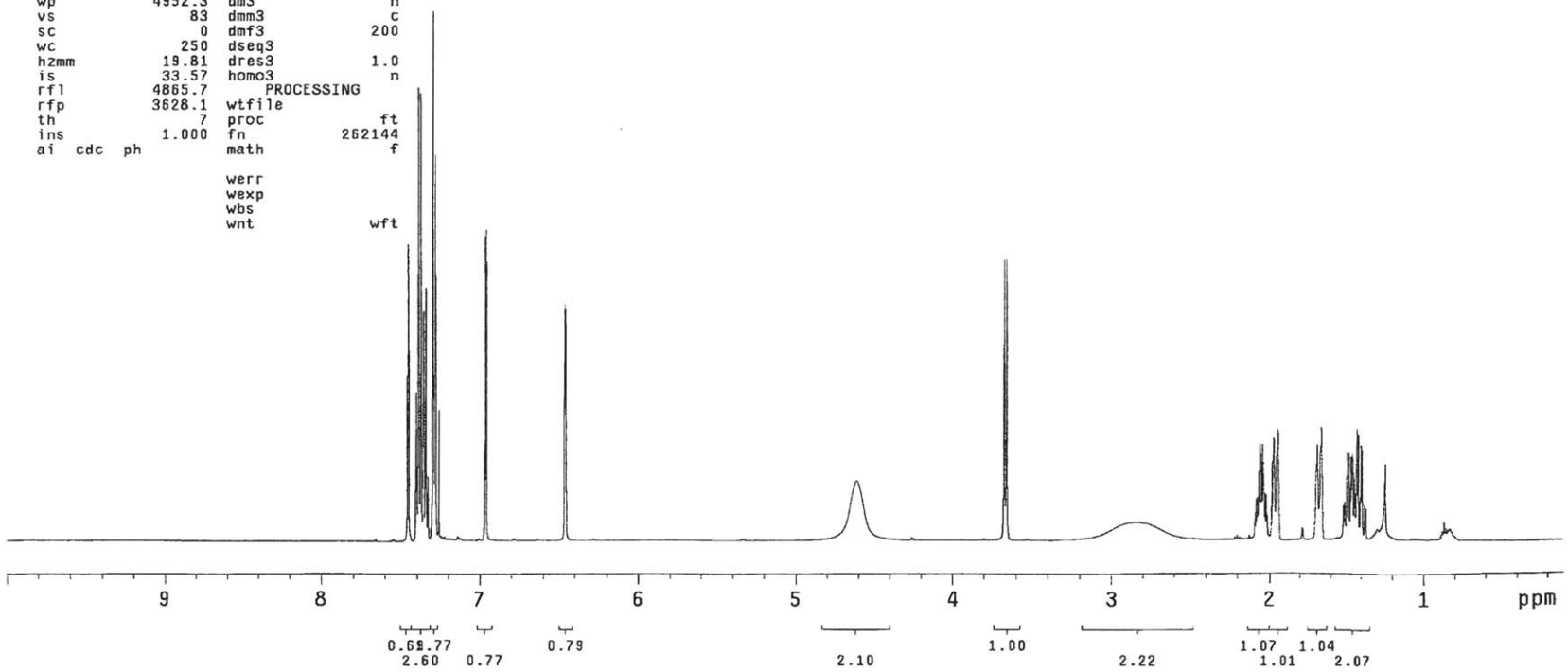


Table 2, entry 7



JC7255A 1H CDCl3

exp1 s2pul

SAMPLE		DEC. & VT	
date	Mar 23 2012	dfrq	125.844
solvent	CDCl3	dn	C13
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	500.431	dm	nnn
tn	H1	dmm	c
at	4.999	dmf	200
np	120102	dseq	
sw	12012.0	dres	1.0
fb	not used	homo	n
bs	8	PROCESSING	
tpwr	60	wtfile	
pw	8.0	proc	ft
d1	0.100	fn	262144
tof	3003.2	math	f
nt	16		
ct	16	werr	
alock	n	wexp	
gain	not used	wbs	
FLAGS		wnt	
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	61.2		
wp	4947.8		
vs	42		
sc	0		
wc	250		
hzmm	19.79		
is	33.57		
rfl	4148.2		
rfp	3633.1		
th	7		
ins	1.000		
ai cdc ph			

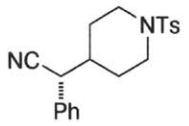


Table 2, entry 8

JC7231B 1H CDCl3

exp1 s2pul

SAMPLE		DEC. & VT	
date	Mar 15 2012	dfrq	125.844
solvent	CDCl3	dn	C13
file	/data/export/~	dpwr	30
	home/gfu/FUjcho/ca~	dof	0
	sper/JC7231B_1H_CD~	dm	nnn
	C13.fid	dmm	c
ACQUISITION		dmf	200
sfrq	500.431	dseq	
tn	H1	dres	1.0
at	4.999	homo	n
np	120102	PROCESSING	
sw	12012.0	wtfile	
fb	not used	proc	ft
bs	8	fn	262144
tpwr	60	math	f
pw	8.0		
d1	0.100	werr	
tof	3003.2	wexp	
nt	8	wbs	
ct	8	wnt	
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	35.2		
wp	4969.1		
vs	76		
sc	0		
wc	250		
hzmm	19.88		
is	33.57		
rfl	4148.4		
rfp	3633.1		
th	7		
ins	2.000		
ai cdc ph			

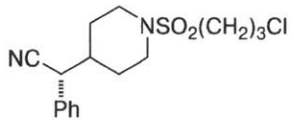
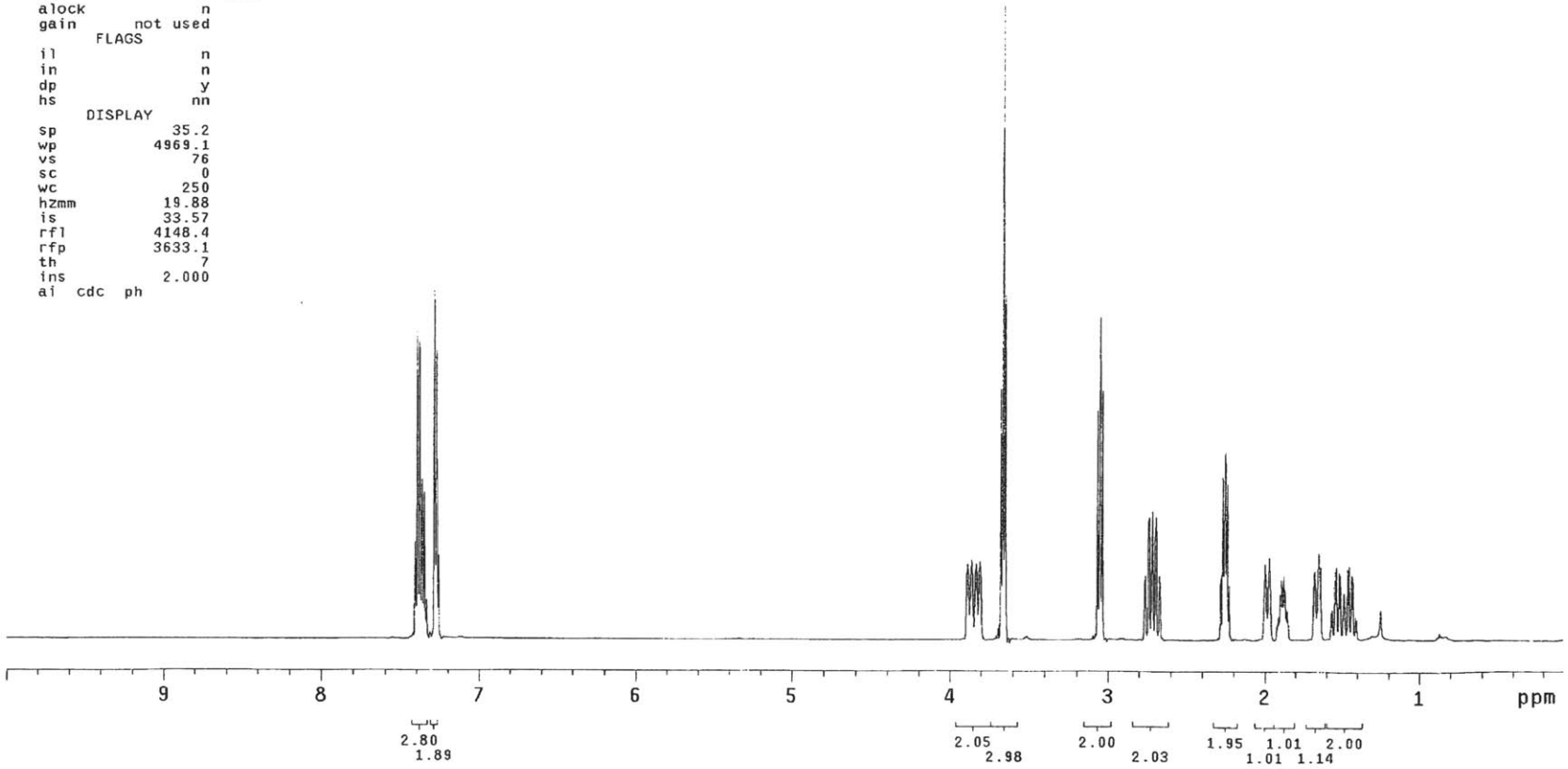


Table 2, entry 9



JC7183B 1H CDCl3

exp1 s2pul

SAMPLE		DEC. & VT	
date	Feb 20 2012	dfrq	125.844
solvent	CDCl3	dn	C13
file	/data/export/~	dpwr	30
home/gfu/FUjcho/ca~		dof	0
sper/JC7183B_1H_CD~		dm	nnn
	Cl3.fid	dmm	c
ACQUISITION		dmf	200
sfrq	500.431	dseq	
tn	H1	dres	1.0
at	4.999	homo	n
np	120102	PROCESSING	
sw	12012.0	wtfile	
fb	not used	proc	ft
bs	8	fn	262144
tpwr	60	math	f
pw	8.0		
d1	0.100	werr	
tof	3003.2	wexp	
nt	16	wbs	
ct	16	wnt	
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	37.1		
wp	4961.5		
vs	14		
sc	0		
wc	250		
hzmm	19.85		
is	33.57		
rfl	515.5		
rfp	0		
th	7		
ins	1.000		
ai cdc ph			

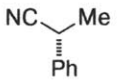


Table 2, entry 10

JC7197B 1H CDCl3

exp1 s2pul

SAMPLE		DEC. & VT	
date	Feb 23 2012	dfrq	125.844
solvent	CDCl3	dn	C13
file	/data/export/~	dpwr	30
home/gfu/FUjcho/ca~		dof	0
sper/JC7197B_1H_CD~		dm	nnn
	C13.fid	dmm	c
ACQUISITION		dmf	200
sfrq	500.431	dseq	
tn	H1	dres	1.0
at	4.999	homo	n
np	120102	PROCESSING	
sw	12012.0	wtfile	
fb	not used	proc	ft
bs	8	fn	262144
tpwr	60	math	f
pw	8.0		
d1	0.100	werr	
tof	3003.2	wexp	
nt	16	wbs	
ct	16	wnt	
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	40.7		
wp	4967.7		
vs	64		
sc	0		
wc	250		
hzmm	19.87		
is	33.57		
rfl	4148.8		
rfp	3633.1		
th	7		
ins	1.000		
ai cdc ph			

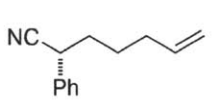
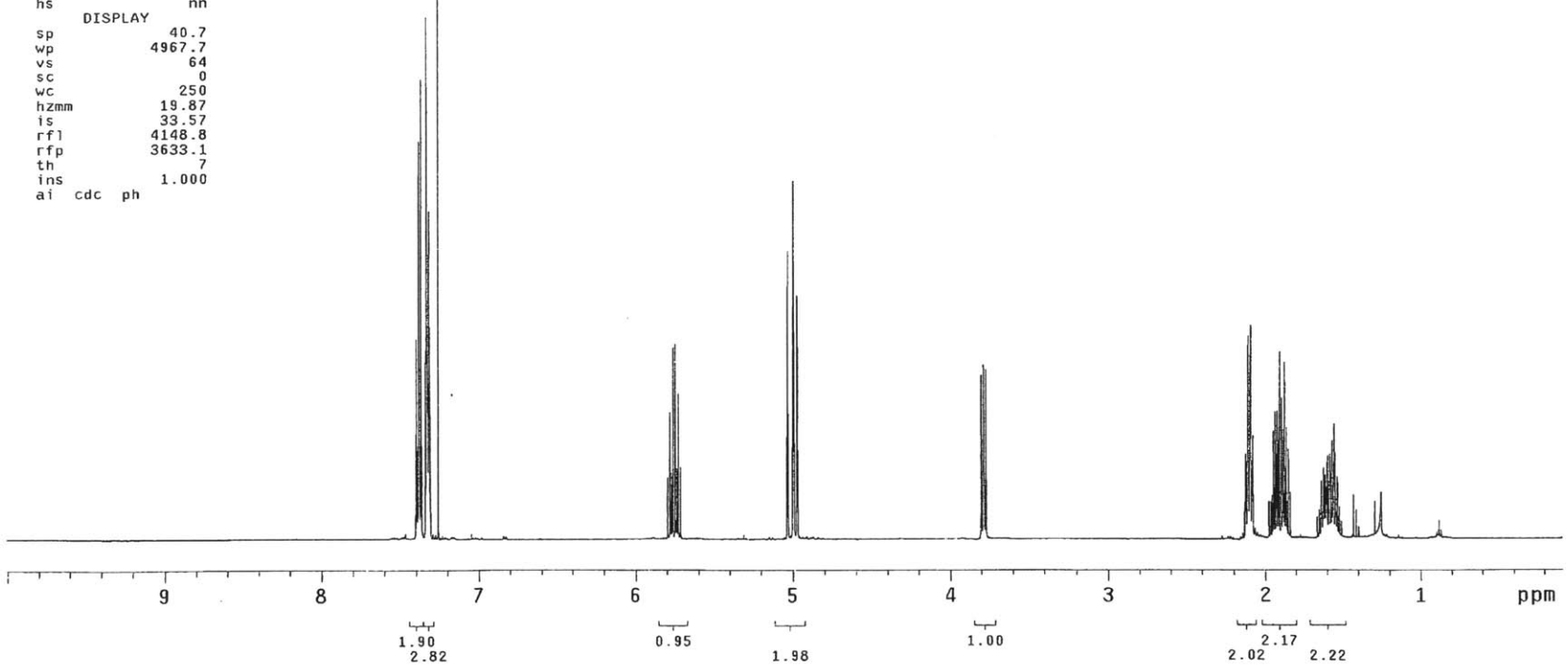


Table 2, entry 11



JC7203B_1H_CDCl3

expl s2pul

SAMPLE		DEC. & VT	
date	Feb 24 2012	dfrq	125.844
solvent	CDCl3	dn	C13
file	/data/export/~	dpwr	30
home/gfu/FUjcho/ca~		dof	0
sper/JC7203B_1H_CD~		dm	nnn
	C13.fid	dmm	c
ACQUISITION		dmf	200
sfrq	500.431	dseq	
tn	H1	dres	1.0
at	4.999	homo	n
np	120102	PROCESSING	
sw	12012.0	wtfile	
fb	not used	proc	ft
bs	8	fn	262144
tpwr	60	math	f
pw	8.0		
d1	0.100	werr	
tof	3003.2	wexp	
nt	16	wbs	
ct	16	wnt	
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	50.8		
wp	4957.7		
vs	54		
sc	0		
wc	250		
hzmm	19.83		
is	33.57		
rfl	4148.6		
rfp	3633.1		
th	7		
ins	1.000		
ai cdc ph			

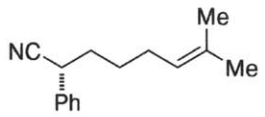


Table 2, entry 12

JC6221A 1H CDCl3

exp1 s2pul

SAMPLE		DEC. & VT	
date	Sep 30 2011	dfrq	125.844
solvent	CDCl3	dn	C13
file	/data/export/~	dpwr	30
	home/gfu/FUjcho/ca~	dof	0
	sper/JC6221A_1H_CD~	dm	nnn
	C13.fid	dmm	c
ACQUISITION		dmf	200
sfrq	500.431	dseq	
tn	H1	dres	1.0
at	4.999	homo	n
np	120102	PROCESSING	
sw	12012.0	wtfile	
fb	not used	proc	ft
bs	8	fn	262144
tpwr	60	math	f
pw	8.0		
d1	0.100	werr	
tof	3003.2	wexp	
nt	16	wbs	
ct	16	wnt	
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	53.5		
wp	4949.2		
vs	31		
sc	0		
wc	250		
hzmm	19.80		
is	33.57		
rfl	4149.7		
rfp	3633.1		
th	7		
ins	1.000		
ai cdc ph			

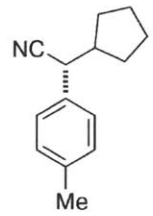


Table 3, entry 1

JC6223A_1H_CDCl3

exp2 s2pul

SAMPLE		DEC. & VT	
date	Oct 11 2011	dfrq	125.844
solvent	CDCl3	dn	C13
file	/data/export/~	dpwr	30
home/gfu/FUjcho/ca~		dof	0
sper/JC6223A_1H_CD~		dm	nnn
	Cl3.fid	dmm	c
ACQUISITION		dmf	200
sfrq	500.431	dseq	
tn	H1	dres	1.0
at	4.999	homo	n
np	120102	PROCESSING	
sw	12012.0	wtfile	
fb	not used	proc	ft
bs	8	fn	262144
tpwr	60	math	f
pw	8.0		
d1	0.100	werr	
tof	3003.2	wexp	
nt	16	wbs	
ct	16	wnt	
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	0.8		
wp	5004.9		
vs	31		
sc	0		
wc	250		
hzmm	20.02		
is	33.57		
rfl	4149.0		
rfp	3633.1		
th	7		
ins	1.000		
ai cdc ph			

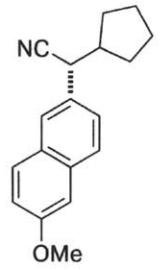


Table 3, entry 2

JC6217A 1H CDCl3

exp1 s2pul

SAMPLE		DEC. & VT	
date	Sep 30 2011	dfrq	125.844
solvent	CDCl3	dn	C13
file	/data/export/~	dpwr	30
	home/gfu/FUjcho/ca~	dof	0
	sper/JC6217A_1H_CD~	dm	nnn
	C13.fid	dmm	c
ACQUISITION		dmf	200
sfrq	500.431	dseq	
tn	H1	dres	1.0
at	4.999	homo	n
np	120102	PROCESSING	
sw	12012.0	wtfile	
fb	not used	proc	ft
bs	8	fn	262144
tpwr	60	math	f
pw	8.0		
d1	0.100	werr	
tof	3003.2	wexp	
nt	16	wbs	
ct	16	wnt	
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	42.9		
wp	4954.0		
vs	34		
sc	0		
wc	250		
hzmm	19.82		
is	33.57		
rfl	4148.2		
rfp	3633.1		
th	7		
ins	1.000		
ai cdc ph			

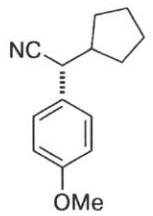


Table 3, entry 3

JC6239A 1H CDCl3

expl s2pul

SAMPLE		DEC. & VT	
date	Oct 26 2011	dfrq	125.844
solvent	CDCl3	dn	C13
file	/data/export/~	dpwr	30
home/gfu/FUjcho/ca~		dof	0
sper/JC6239A_1H_CD~		dm	nnn
	C13.fid	dmm	c
ACQUISITION		dmf	200
sfrq	500.431	dseq	
tn	H1	dres	1.0
at	4.999	homo	n
np	120102	PROCESSING	
sw	12012.0	wtfile	
fb	not used	proc	ft
bs	8	fn	262144
tpwr	60	math	f
pw	8.0		
d1	0.100	werr	
tof	3003.2	wexp	
nt	16	wbs	
ct	16	wnt	
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	44.7		
wp	4964.9		
vs	64		
sc	0		
wc	250		
hzmm	19.86		
is	33.57		
rfl	4148.6		
rfp	3633.1		
th	7		
ins	1.000		
ai cdc ph			

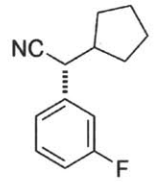
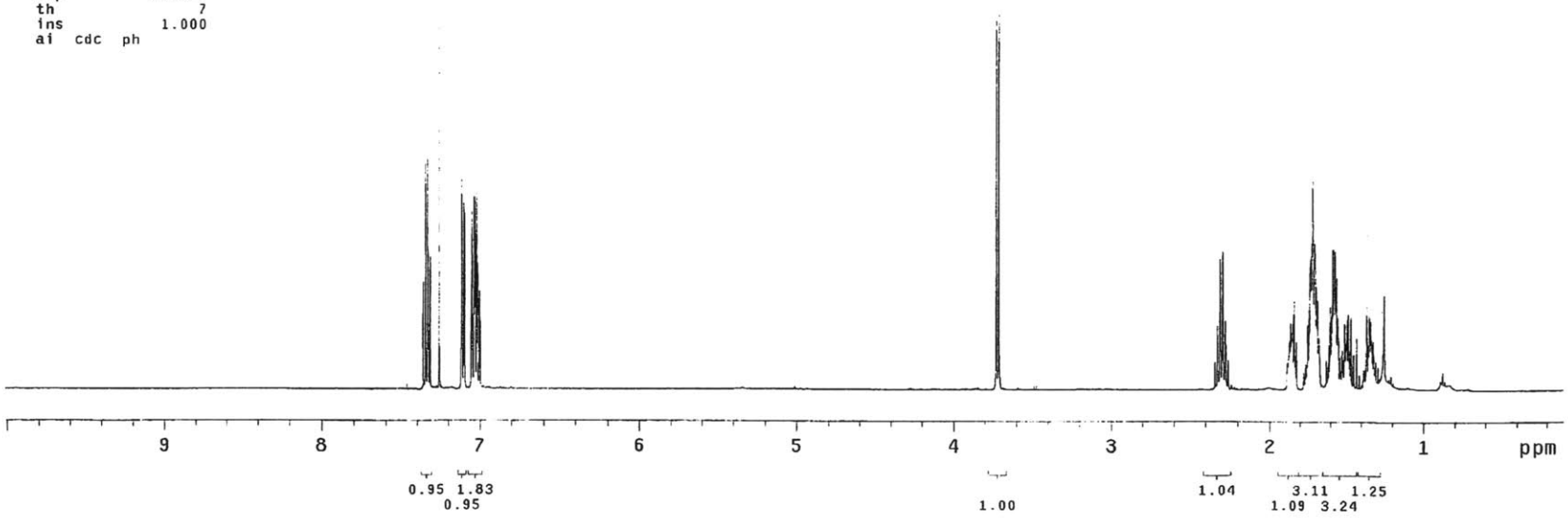


Table 3, entry 4



JC7005A 1H CDCl3

exp1 s2pul

SAMPLE		DEC. & VT	
date	Dec 2 2011	dfrq	125.844
solvent	CDCl3	dn	C13
file	/data/export/~	dpwr	30
	home/gfu/FUjcho/ca~	dof	0
	sper/JC7005A_1H_CD~	dm	nnn
	C13.fid	dmm	c
ACQUISITION		dmf	200
sfrq	500.431	dseq	
tn	H1	dres	1.0
at	4.999	homo	n
np	120102	PROCESSING	
sw	12012.0	wtfile	
fb	not used	proc	ft
bs	8	fn	262144
tpwr	60	math	f
pw	8.0		
d1	0.100	werr	
tof	3003.2	wexp	
nt	16	wbs	
ct	16	wnt	
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	40.8		
wp	4960.4		
vs	82		
sc	0		
wc	250		
hzmm	19.84		
is	33.57		
rfl	4148.9		
rfp	3633.1		
th	7		
ins	1.000		
ai cdc ph			

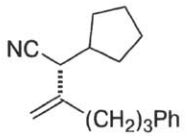
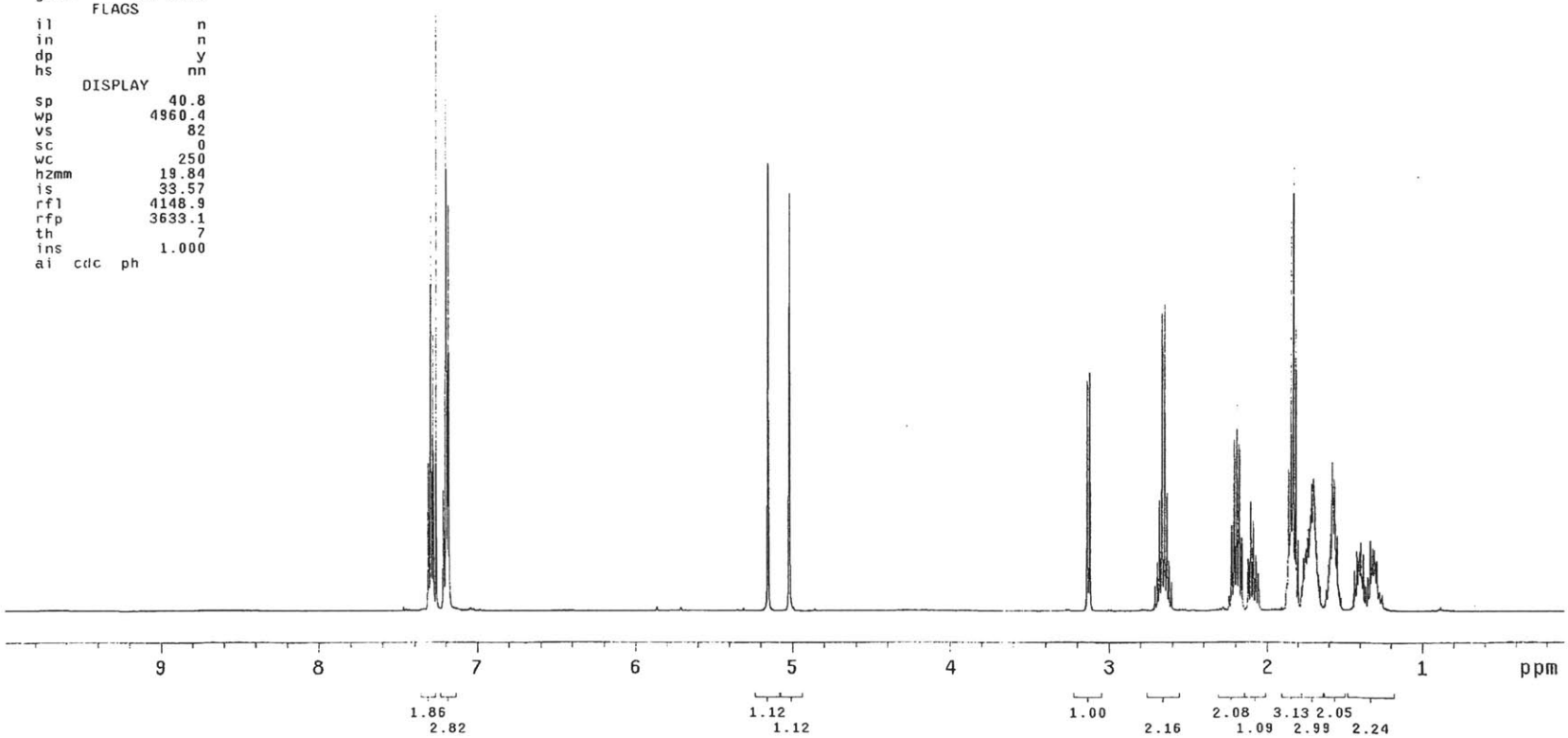


Table 4, entry 1



JC7011A 1H CDCl3

expl s2pul

SAMPLE		DEC. & VT	
date	Dec 6 2011	dfrq	125.844
solvent	CDCl3	dn	C13
file	/data/export/~	dpwr	30
home/gfu/FUjcho/ca~		dof	0
sper/JC7011A_1H_CD~		dm	nnn
	C13.fid	dmm	c
ACQUISITION		dmf	200
sfrq	500.431	dseq	
tn	H1	dres	1.0
at	4.999	homo	n
np	120102	PROCESSING	
sw	12012.0	wtfile	
fb	not used	proc	ft
bs	8	fn	262144
tpwr	60	math	f
pw	8.0		
d1	0.100	werr	
tof	3003.2	wexp	
nt	16	wbs	
ct	16	wnt	
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	50.8		
wp	4957.5		
vs	122		
sc	0		
wc	250		
hzmm	19.83		
is	33.57		
rfl	4148.6		
rfp	3633.1		
th	7		
ins	1.000		
ai cdc ph			

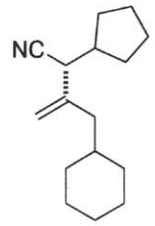
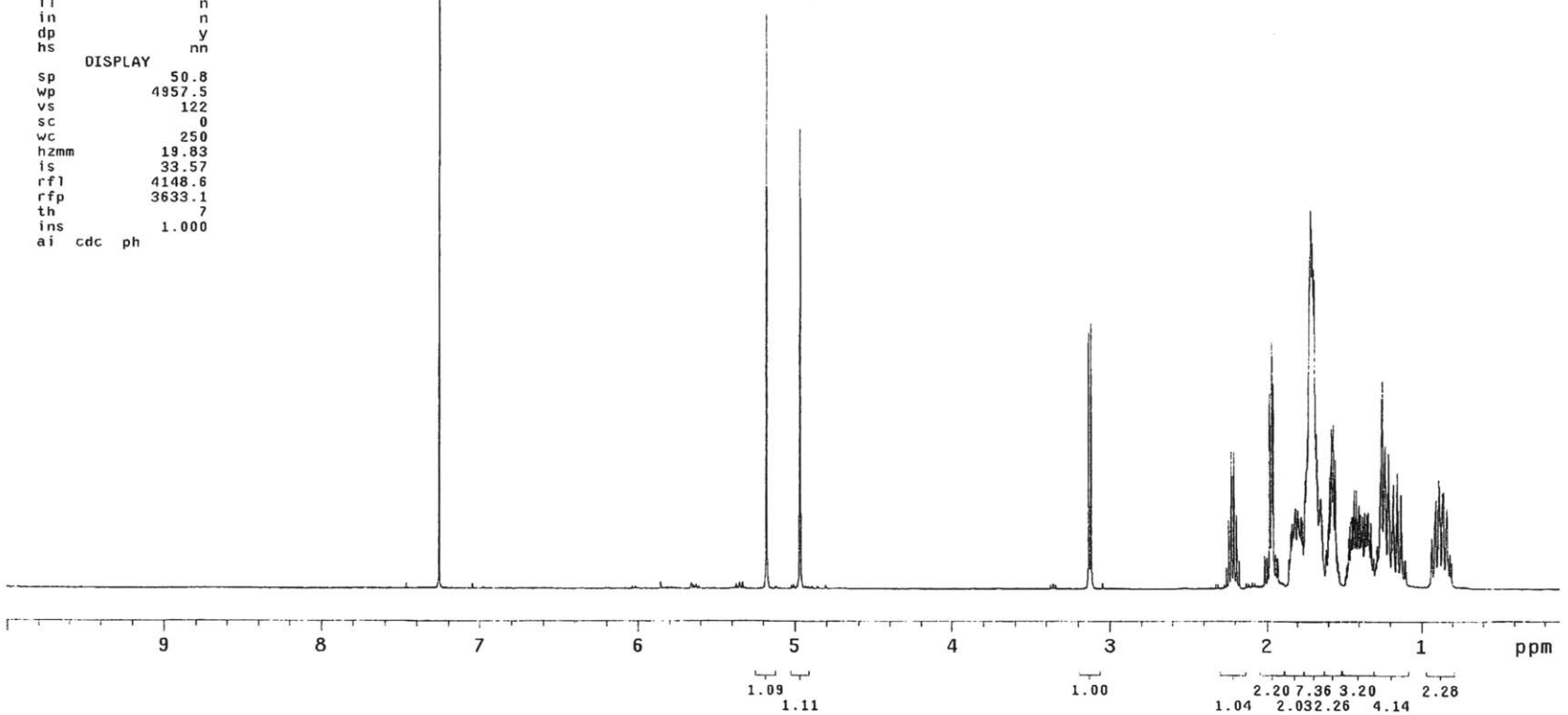


Table 4, entry 2



JC7009A 1H CDCl3

expl s2pul

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date	Dec 4 2011	dfrq	125.844
solvent	CDCl3	dn	C13
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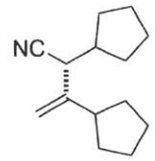
	sper/JC7009A_1H_CD~	dm	nnn
	C13.fid	dmm	c
ACQUISITION		dmf	200
sfrq	500.431	dseq	
tn	H1	dres	1.0
at	4.999	homo	n
np	120102	PROCESSING	
sw	12012.0	wtfile	
fb	not used	proc	ft
bs	8	fn	262144
tpwr	60	math	f
pw	8.0		
d1	0.100	werr	
tof	3003.2	wexp	
nt	16	wbs	
ct	16	wnt	
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	59.7		
wp	4939.5		
vs	120		
sc	0		
wc	250		
hzmm	19.76		
is	33.57		
rfl	4148.6		
rfp	3633.1		
th	7		
ins	1.000		
ai cdc ph			



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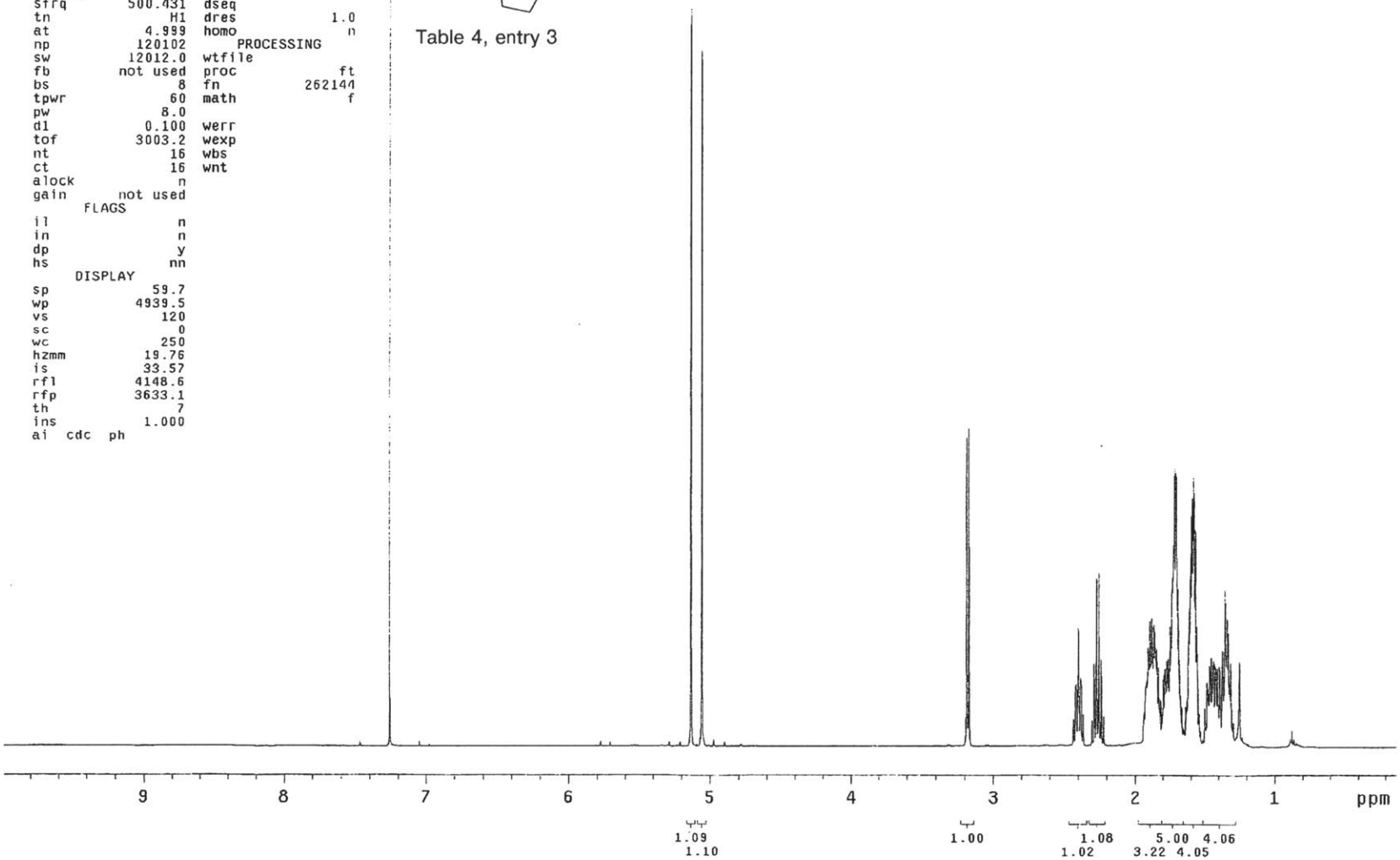

JC6275B 1H CDCl3

exp1 s2pul

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solvent	CDCl3	dn	C13
file	/data/export/~	dpwr	30
home/gfu/FUjcho/ca~		dof	0
sper/JC6275B_1H_CD~		dm	nnn
	C13.fid	dmm	c
ACQUISITION		dmf	200
sfrq	500.431	dseq	
tn	H1	dres	1.0
at	4.999	homo	n
np	120102	PROCESSING	
sw	12012.0	wtfile	
fb	not used	proc	ft
bs	8	fn	262144
tpwr	60	math	f
pw	8.0		
d1	0.100	werr	
tof	3003.2	wexp	
nt	16	wbs	
ct	16	wnt	
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-4.3		
wp	5010.2		
vs	33		
sc	0		
wc	250		
hzmm	20.04		
is	33.57		
rfl	4147.8		
rfp	3633.1		
th	79		
ins	1.000		

ai cdc ph

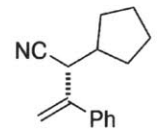
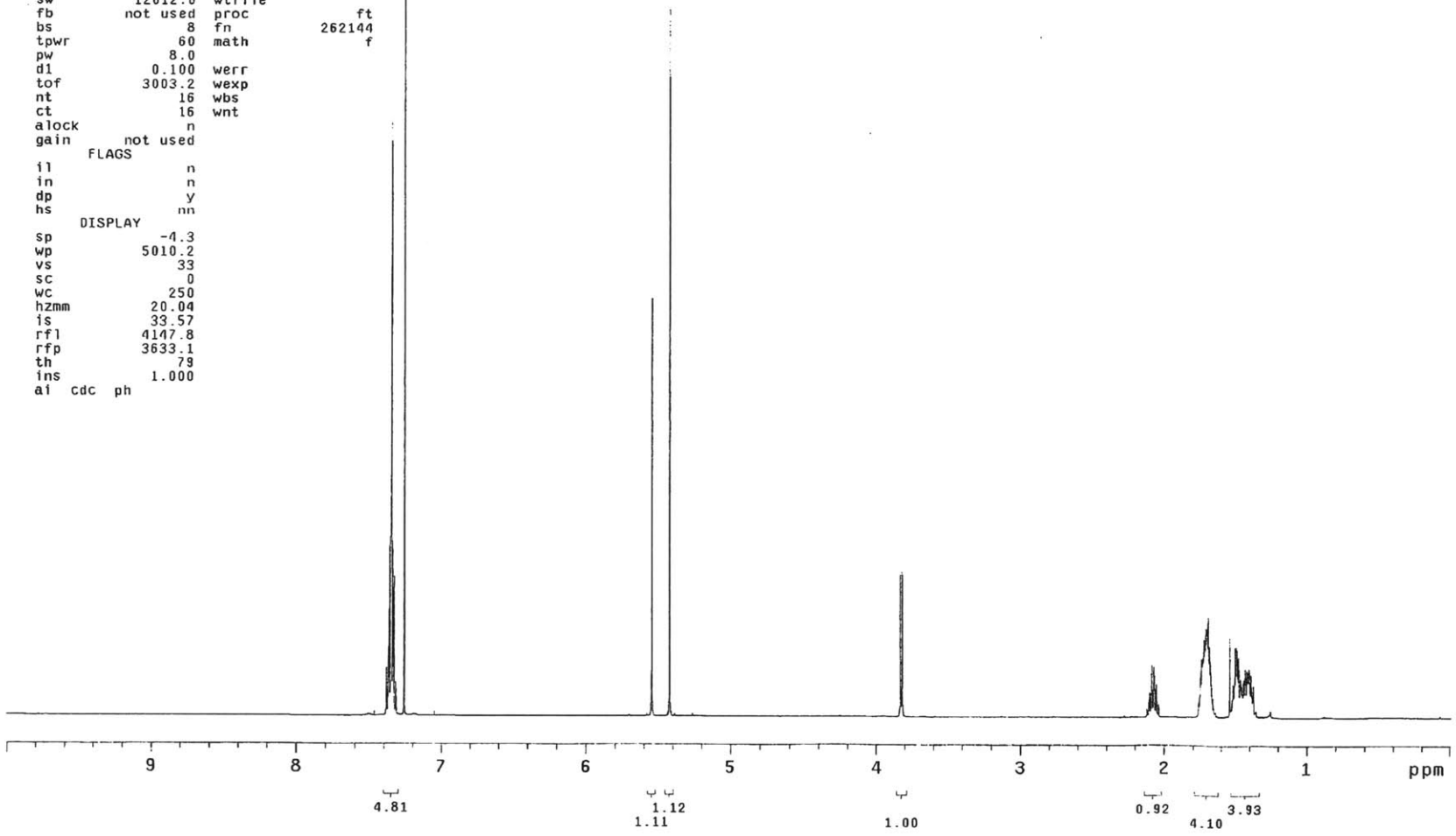


Table 4, entry 4



JC7099 1H CDCl3

exp2 s2pul

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date	Jan 27 2012	dfrq	125.844
solvent	CDCl3	dn	C13
file	/data/export/~	dpwr	30
home/gfu/FUjcho/ca~		dof	0
sper/JC7099_1H_CDC~		dm	nnn
	13.fid	dmm	c
ACQUISITION		dmf	200
sfrq	500.431	dseq	
tn	H1	dres	1.0
at	4.999	homo	n
np	120102	PROCESSING	
sw	12012.0	wtfile	
fb	not used	proc	ft
bs	8	fn	262144
tpwr	60	math	f
pw	8.0		
d1	0.100	werr	
tof	3003.2	wexp	
nt	64	wbs	
ct	24	wnt	
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	51.1		
wp	4957.7		
vs	21		
sc	0		
wc	250		
hzmm	19.83		
is	33.57		
rfl	4148.4		
rfp	3633.1		
th	7		
ins	1.000		
ai cdc ph			

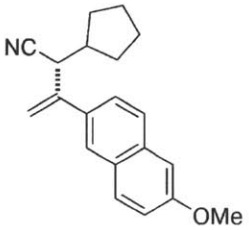

Table 4, entry 5

JC7279A 1H CDCl3

exp1 s2pul

SAMPLE		DEC. & VT	
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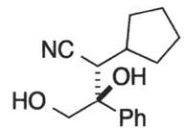
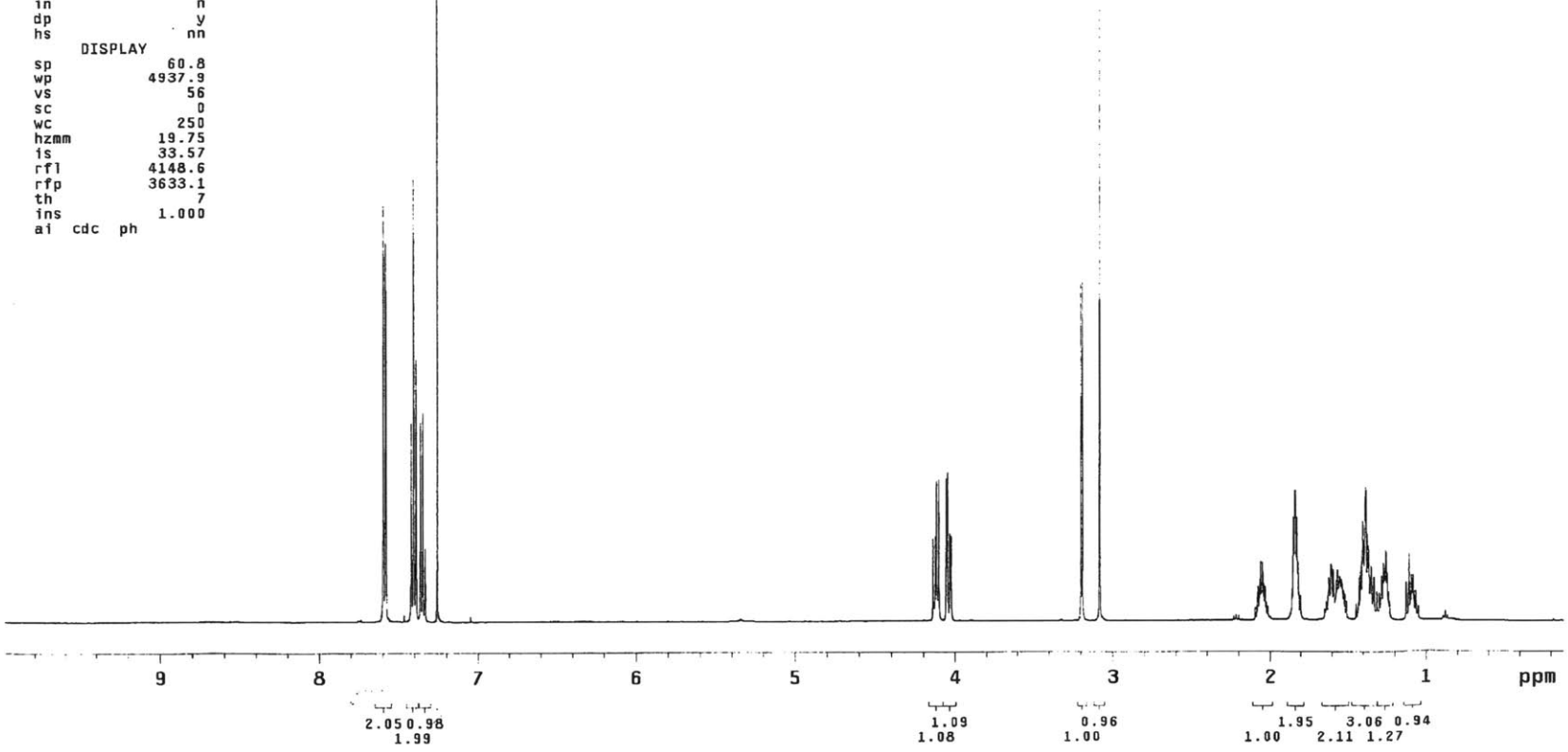
solvent	CDCl3	dn	C13
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	500.431	dm	nnn
tn	H1	dmm	c
at	4.999	dmf	200
np	120102	dseq	
sw	12012.0	dres	1.0
fb	not used	homo	n
bs	8	PROCESSING	
tpwr	60	wtfile	
pw	8.0	proc	ft
d1	0.100	fn	262144
tof	3003.2	math	f
nt	16		
ct	16	werr	
alock	n	wexp	
gain	not used	wbs	
FLAGS		wnt	
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	60.8		
wp	4937.9		
vs	56		
sc	0		
wc	250		
hzmm	19.75		
is	33.57		
rfl	4148.6		
rfp	3633.1		
th	7		
ins	1.000		
ai cdc ph			



eq 7



JC7151A Major Diastereomer 1H CDCl3

exp2 s2pul

SAMPLE		DEC. & VT	
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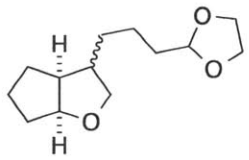
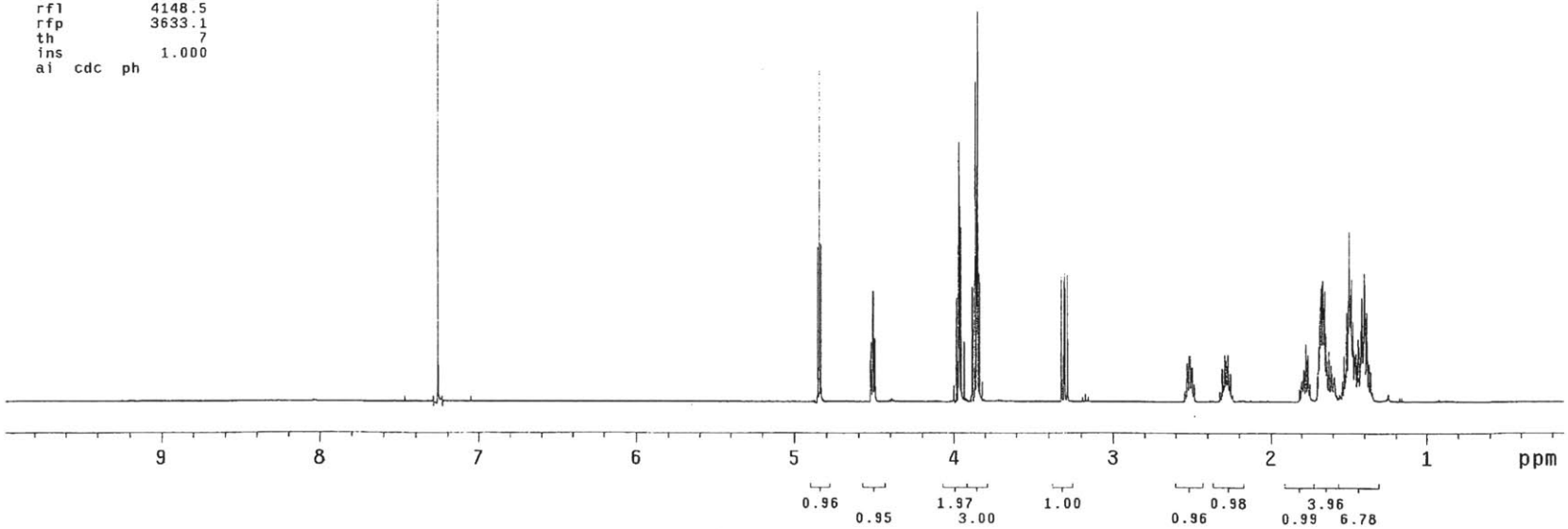
solvent	CDCl3	dn	C13
file	/data/export/~	dpwr	30
	home/gfu/FUjcho/ca~	dof	0
	sper/JC7151A_Major~	dm	nnn
	-Diastereomer_1H_C~	dmm	c
	DCl3.fid	dmf	200
ACQUISITION		dseq	
sfrq	500.431	dres	1.0
tn	H1	homo	n
at	4.999	PROCESSING	
np	120102	wtfile	
sw	12012.0	proc	ft
fb	not used	fn	262144
bs	8	math	f
tpwr	60		
pw	8.0	werr	
d1	0.100	wexp	
tof	3003.2	wbs	
nt	16	wnt	
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	60.9		
wp	4937.9		
vs	61		
sc	0		
wc	250		
hzmm	19.75		
is	33.57		
rfl	4148.5		
rfp	3633.1		
th	7		
ins	1.000		
ai cdc ph			



eq 8



JC7153B Major 1H CDCl3

exp1 s2pul

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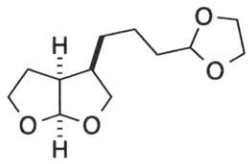
llwinkle/JC7153B_M~		dm	nnn
ajor_1H_CDCl3.fid		dmm	w
ACQUISITION		dmf	10000
sfrq	499.746	dseq	
tn	H1	dres	1.0
at	3.001	homo	n
np	63050	PROCESSING	
sw	10504.2	wtfile	
fb	not used	proc	ft
bs	8	fn	262144
tpwr	56	math	f
pw	8.6		
d1	2.000	werr	
tof	1519.5	wexp	
nt	16	wbs	
ct	16	wnt	wft
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	39.1		
wp	4960.9		
vs	102		
sc	0		
wc	250		
hzmm	19.84		
is	33.57		
rfl	4866.2		
rfp	3628.1		
th	7		
ins	1.000		
ai cdc ph			



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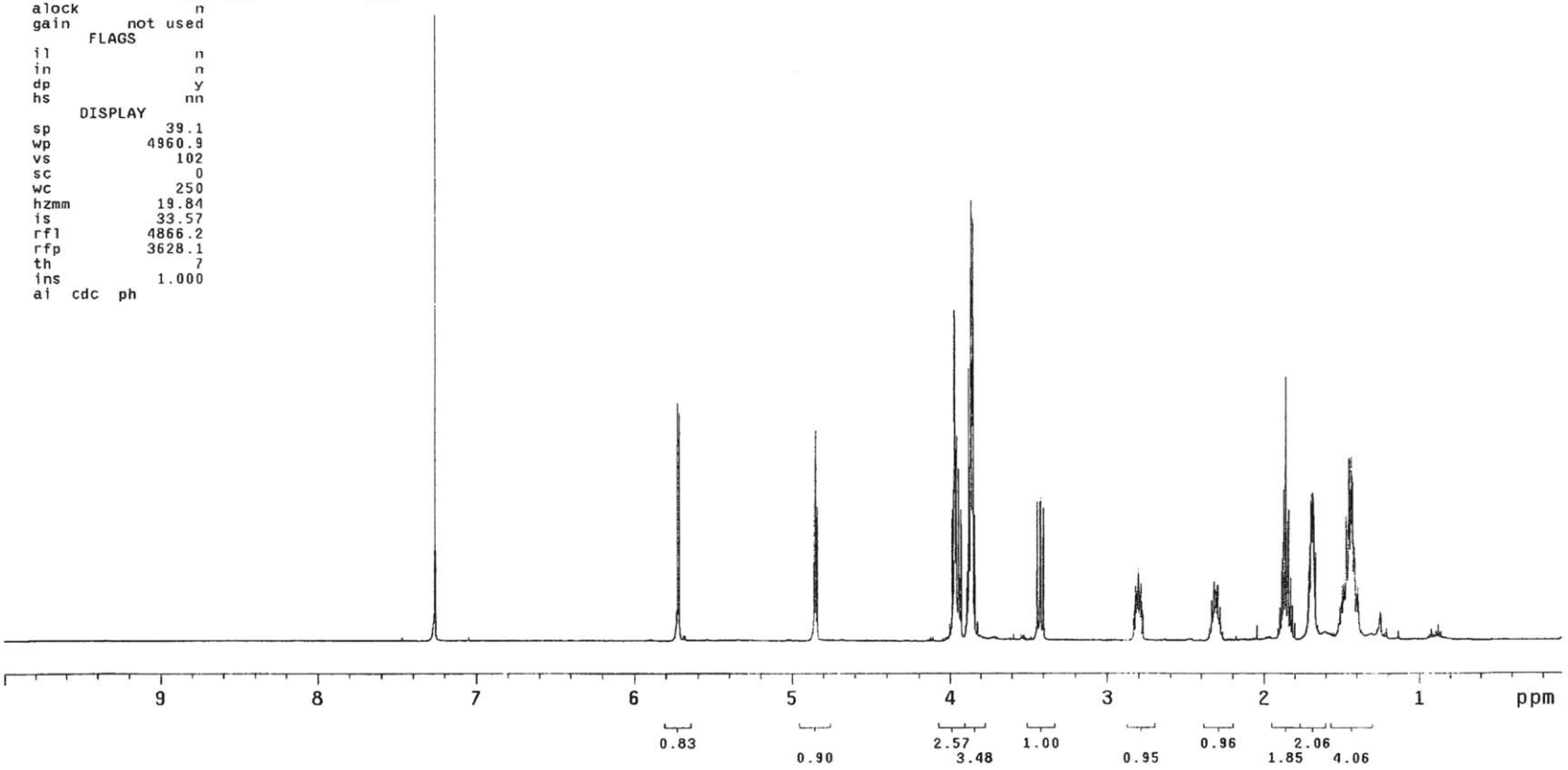

JC7205A 1H CDCl3

exp2 s2pul

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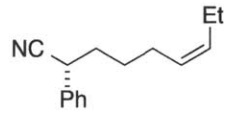
sper/JC7205A_1H_CD~		dm	nnn
C13.fid		dmm	c
ACQUISITION		dmf	200
sfrq	500.431	dseq	
tn	H1	dres	1.0
at	4.999	homo	n
np	120102	**PROCESSING**	
sw	12012.0	wtfile	
fb	not used	proc	ft
bs	8	fn	262144
tpwr	60	math	f
pw	8.0		
d1	0.100	werr	
tof	3003.2	wexp	
nt	16	wbs	
ct	16	wnt	
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	50.9		
wp	4947.8		
vs	42		
sc	0		
wc	250		
hzmm	19.79		
is	1701.11		
rfl	4148.6		
rfp	3633.1		
th	7		
ins	1.000		
ai cdc ph			



eq 9

Section 1.2

Stereoconvergent Arylations and Alkenylations of Unactivated Alkyl Electrophiles: The Catalytic Enantioselective Synthesis of Secondary Sulfonamides and Sulfones

A. Introduction

Sulfonamides and sulfones serve as useful building blocks in organic synthesis[31] and as important therapeutics (e.g., Celebrex™ (NSAID), Crestor™ (cardiovascular), and Viagra™ (erectile dysfunction)).[32] Enantioenriched secondary benzylic sulfonamides and sulfones are especially noteworthy targets because of their biological activity, for example, as protein tyrosine phosphatase inhibitors,[33] anti-sepsis agents,[34] and γ-secretase inhibitors. [35] Despite the potential applications of enantioenriched α-alkyl-α-arylsulfonamides, to the best of our knowledge, there is no catalytic asymmetric synthesis of such sulfonamides. Instead, limited examples of the catalytic synthesis of racemic benzylic sulfonamides via α-arylation (C–H to C–Ar) have been reported.[36]

For the preparation of enantioenriched α-alkyl-α-arylsulfones, few catalytic enantioselective preparations that install a stereocenter at the α-position to sulfones have been developed. Toru disclosed the enantioselective addition of α-sulfonyl carbanions to aromatic aldehydes with good enantio- and diastereoselectivity, but a

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[31] For leading references, see: (a) Ashfaq, M.; Shah, S. S. A.; Najjam, T.; Shaheen, S.; Rivera, G. *Mini-Rev. Org. Chem.* **2013**, *10*, 160–170. (b) Wilden, J. D. *J. Chem. Res.* **2010**, *34*, 541–548. (c) *Organosulfur Chemistry in Asymmetric Synthesis*; Toru, T., Bolm, C., Eds.; Wiley–VCH: Weinheim, 2008. (d) Simpkins, N. S. *Sulfones in Organic Synthesis*; Pergamon: Oxford, 1993.

[32] For leading references, see: (a) Shah, S. S. A.; Rivera, G.; Ashfaq, M. *Mini-Rev. Med. Chem.* **2013**, *13*, 70–86. (b) Scozzafava, A.; Carta, F.; Supuran, C. T. *Expert Opin. Ther. Patents* **2013**, *23*, 203–213. (c) Chen, X.; Hussain, S.; Parveen, S.; Zhang, S.; Yang, Y.; Zhu, C. *Curr. Med. Chem.* **2012**, *19*, 3578–3604. (d) Kalgutkar, A. S.; Jones, R.; Sawant, A. *RSC Drug Discovery Series* **2010**, *1*, 210–274.

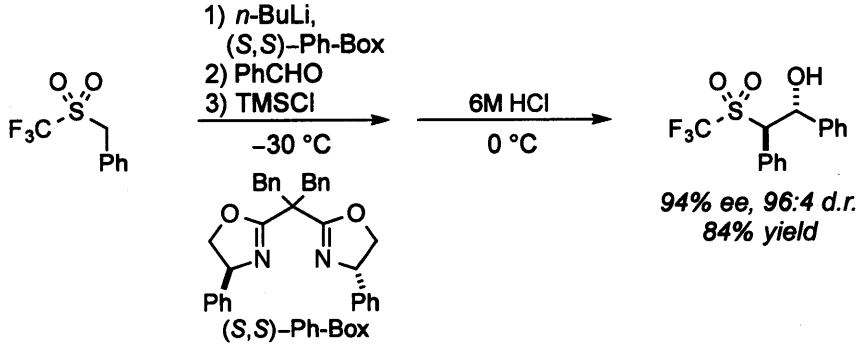
[33] (a) Rawls, K. A.; Grundner, C.; Ellman, J. A. *Org. Biomol. Chem.* **2010**, *8*, 4066–4070. (b) Yue, E. W.; Wayland, B.; Douty, B.; Crawley, M. L.; McLaughlin, E.; Takvorian, A.; Wasserman, Z.; Bower, M. J.; Wei, M.; Li, Y.; Ala, P. J.; Gonneville, L.; Wynn, R.; Burn, T. C.; Liu, P. C. C.; Combs, A. P. *Bioorg. Med. Chem.* **2006**, *14*, 5833–5849.

[34] Yamada, M.; Ichikawa, T.; Ii, M.; Itoh, K.; Tamura, N.; Kitazaki, T. *Bioorg. Med. Chem.* **2008**, *16*, 3941–3958.

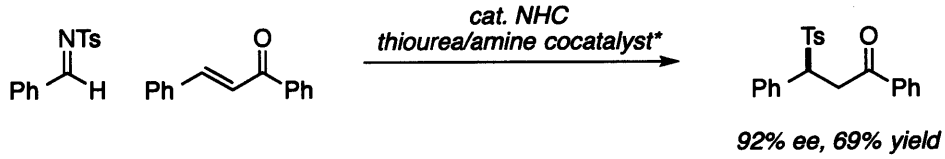
[35] Teall, M.; Oakley, P.; Harrison, T.; Shaw, D.; Kay, E.; Elliott, J.; Gerhard, U.; Castro, J. L.; Shearman, M.; Ball, R. G.; Tsou, N. N. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 2685–2688.

[36] (a) Grimm, J. B.; Katcher, M. H.; Witter, D. J.; Northrup, A. B. *J. Org. Chem.* **2007**, *72*, 8135–8138. (b) Zhou, G.; Ting, P.; Aslanian, R.; Piwinski, J. J. *Org. Lett.* **2008**, *10*, 2517–2520.

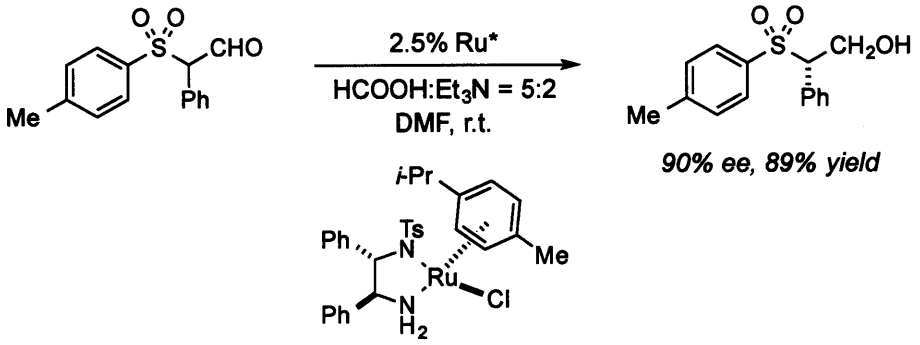
trifluoromethylsulfonyl group is necessary to achieve high enantioselectivity (eq 10).[37] Enantioselective sulfonation of enones with sulfonyl imines is another method to access enantioenriched benzylic sulfonamides, but the reaction with *N*-mesylimine proceeds in moderate enantioselectivity (eq 11).[38] In addition, enantioenriched secondary benzylic sulfones can be synthesized by the asymmetric transfer hydrogenation of α-sulfonyl aldehydes, but only aryl sulfones are reported (eq 12).[39]



(10)



(11)

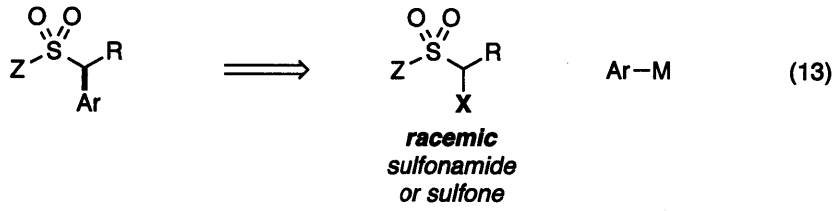


(12)

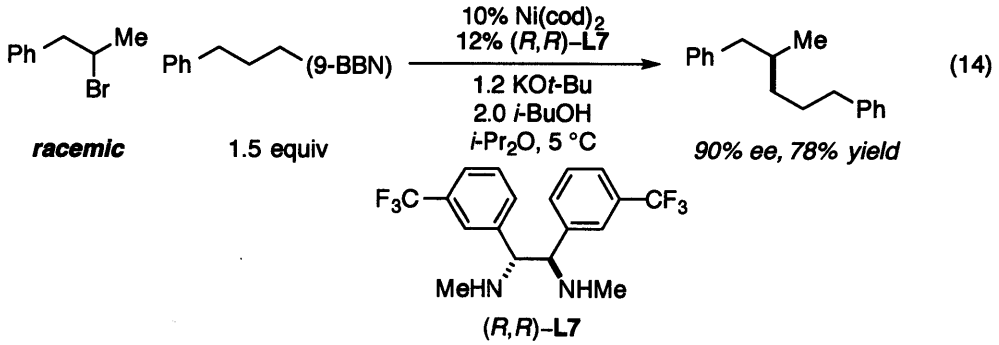
Due to the limitations of existing approaches, it was important to develop a complementary method with a broader scope of sulfonamides and sulfones and with

[37] Nakamura, S.; Hirata, N.; Yamada, R.; Kita, T.; Shibata, N.; Toru, T. *Chem.–Eur. J.* **2008**, *14*, 5519–5527.
[38] Jin, Z.; Xu, J.; Yang, S.; Song, B.-A.; Chi, Y. R. *Angew. Chem., Int. Ed.* **2013**, *52*, 12354–12358.
[39] Wu, G.; Zhu, J.; Ding, Z.; Shen, Z.; Zhang, Y. *Tetrahedron Lett.* **2009**, *50*, 427–429.

greater functional-group compatibility. Therefore, we sought to develop a method for the synthesis of these sulfonamides and sulfones via stereoconvergent cross-coupling of racemic α-halosulfonamides and -sulfones with an appropriate nucleophile (eq 13).

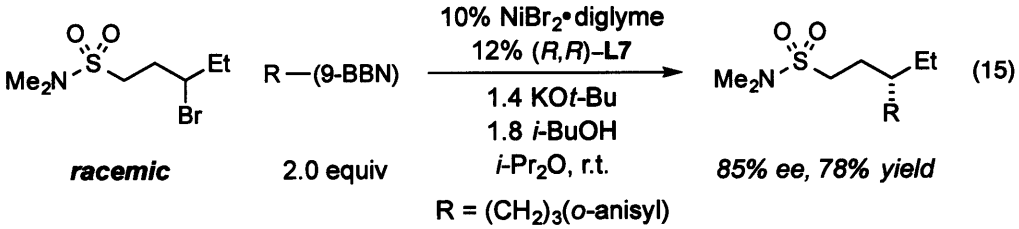


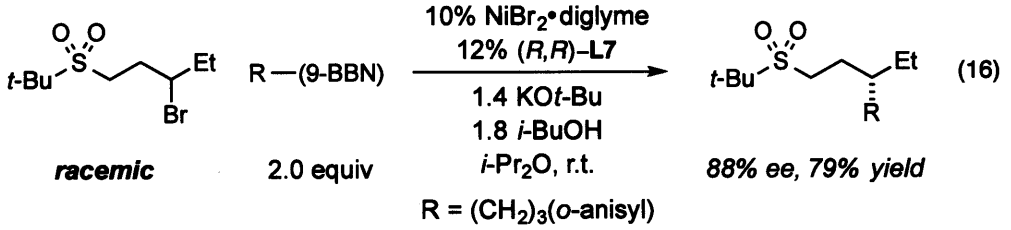
During the past several years, the Fu group has demonstrated nickel-catalyzed asymmetric Suzuki–Miyaura cross-couplings of unactivated secondary alkyl electrophiles. In 2008, Saito found that racemic homobenzylic bromides successfully cross-couple with alkyl–(9-BBN) reagents in good ee (eq 14).[40] In this study, we suggested that a secondary interaction between the aryl group on the electrophile and the catalyst is important to achieve good ee. We envisioned that other functional groups can act as a directing group for asymmetric Suzuki–Miyaura cross-couplings of unactivated alkyl electrophiles; indeed, a variety of functional-group directed stereoconvergent cross-couplings of secondary alkyl electrophiles with alkyl nucleophiles have been discovered.[19,23,41]



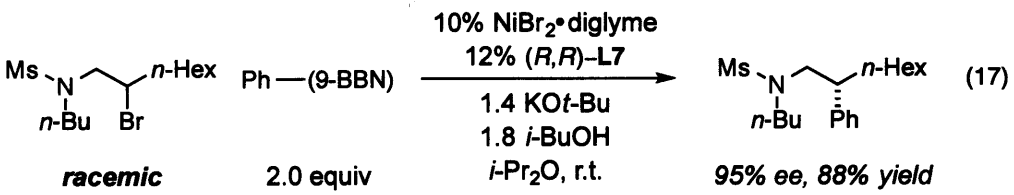
[40] Saito, B.; Fu, G. C. *J. Am. Chem. Soc.* **2008**, *130*, 6694–6695.
[41] (a) Owston, N. A.; Fu, G. C. *J. Am. Chem. Soc.* **2010**, *132*, 11908–11909. (b) Lu, Z.; Wilsily, A.; Fu, G. C. *J. Am. Chem. Soc.* **2011**, *133*, 8154–8157.

As part of our efforts to expand the scope of directing groups in asymmetric Suzuki cross-couplings of secondary alkyl electrophiles, sulfonamides and sulfones were exploited as directing groups by Wilsily et al.[23] Racemic alkyl bromides having these directing groups undergo C–C bond formation in a stereoconvergent process in good ee and yield (eqs 15 and 16).





Wilsily also showed that Ph–(9-BBN) serves as the nucleophilic partner for sulfonamide-directed Suzuki arylations of an unactivated alkyl electrophile, which was the first time that we had achieved asymmetric arylations of unactivated secondary electrophiles in good enantioselectivity and yield (eq 17).

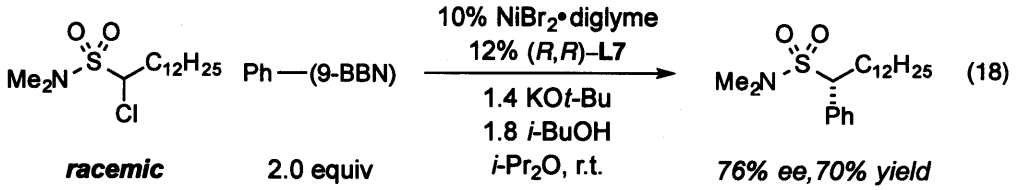


Because the sulfonyl group does not effectively stabilize an adjacent radical (homolytic bond dissociation energy for a C–H bond of dimethylsulfone: 99 kcal/mol), we view α-halosulfonamides and -sulfones as unactivated alkyl electrophiles.[42] Since we

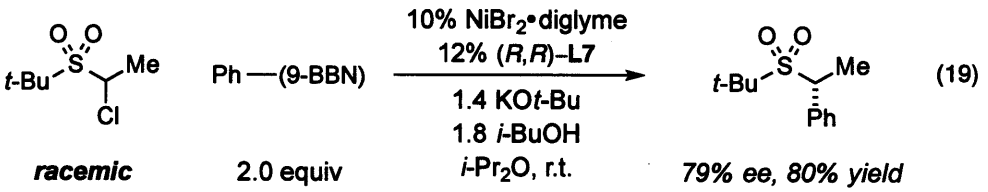
[42] Luo, Y.-R. *Chemical Bond Energies*; CRC Press: Boca Raton, 2007.

had success with sulfonamide-directed asymmetric Suzuki arylations of unactivated alkyl electrophiles, the initial reaction development of nickel-catalyzed asymmetric arylations of α-halosulfonamides and -sulfones focused on Suzuki arylation conditions.

Wilsily started exploring the stereoconvergent arylations under Suzuki reaction conditions and found that Ph–(9-BBN) coupled with an α-chlorosulfonamide catalyzed by a nickel/diamine **L7** complex in 76% ee and 70% yield (eq 18). The same catalyst also facilitated C–C bond formation between an α-chlorosulfone and Ph–(9-BBN) in 79% ee and 80% yield (eq 19).



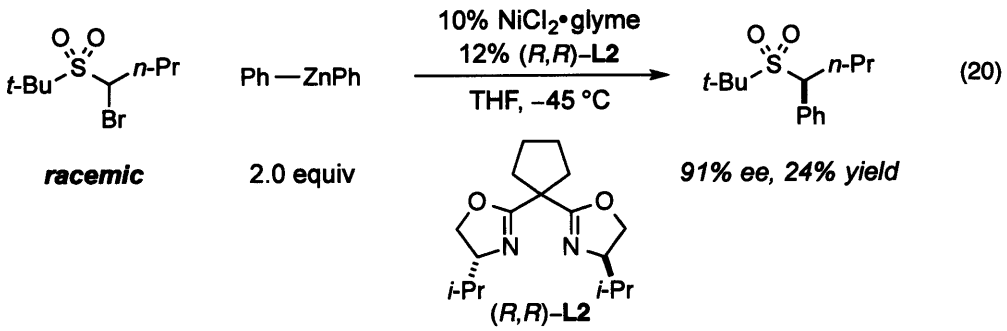
(18)



(19)

Unfortunately, further investigations of the reaction parameters failed to improve the enantioselectivity of the asymmetric arylation (<80% ee). As a result, we decided to evaluate other families of cross-coupling reactions for the synthesis of enantioenriched secondary benzylic sulfonamides and sulfones. In initial attempts to develop new asymmetric Negishi C–C bond formations between α-bromosulfonamides and arylzinc nucleophiles, Martín-Gago found that the catalyst used for Negishi arylations of α-bromonitriles, nickel/*bis*(*oxazoline*), cross-coupled an α-bromosulfone with Ph_2Zn in good ee but low yield (eq 20).[43]

[43] Choi, J.; Fu, G. C. *J. Am. Chem. Soc.* **2012**, *134*, 9102–9105.


10% NiCl2•glyme
12% (R,R)–L2
THF, –45 °C
t-Bu
n-Pr
Br
Ph—ZnPh
Ph
racemic
2.0 equiv
91% ee, 24% yield
i-Pr
i-Pr
(R,R)–L2

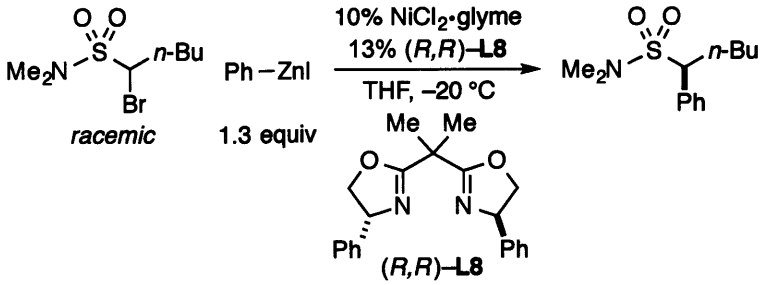
(20)

B. Results and Discussion

Starting from the result illustrated in eq 20, we surveyed various reaction parameters to optimize the stereoconvergent Negishi arylation. We determined that the nickel catalyst generated from commercially available $NiCl_2$•glyme and commercially available **L8** facilitates the asymmetric arylation reaction of an α-bromosulfonamide with PhZnI in good ee and good yield (Table 5, entry 1).

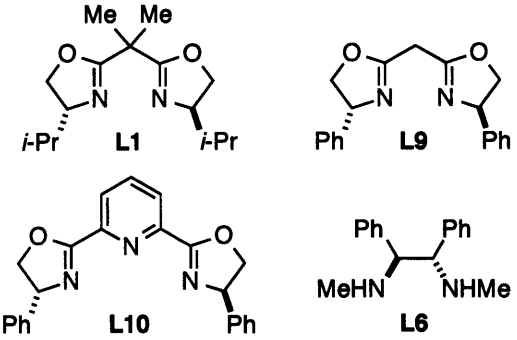
As depicted in Table 5, no C–C bond formation is observed in the absence of $NiCl_2$•glyme (entry 2), whereas a small amount of product is formed without ligand **L8** (entry 3). The reaction proceeds in similar ee but with lower yield at room temperature (entry 4). For the room-temperature reaction, hydrodebromination is predominant. The corresponding valine-derived ligand **L1** can also form a complex that catalyzes the phenylation reaction, but with slightly lower ee and yield (entry 5) than ligand **L8.** The Negishi reaction proceeds poorly with bis(oxazoline) ligand **L9** (entry 6). In addition, pybox and diamine ligands are not effective for this cross-coupling reaction (entries 7 and 8). The reaction of PhMgBr instead of PhZnI results in a small loss in ee and a substantial loss in yield (entry 9). Lower catalyst loading leads to diminished yield without impacting ee (entry 10). The stereoconvergent arylation is somewhat oxygen-sensitive (entry 11), but not moisture-sensitive (entry 12).

Table 5. Stereoconvergent Negishi Phenylation of a Racemic α-Bromosulfonamide: Effect of Reaction Parameters[a]



entry	change from the "standard conditions"	ee (%)	yield (%)[b]
1	none	96	88
2	no $NiCl_2$ • glyme	–	<2
3	no **L1**	–	16
4	r.t., instead of –20 °C	93	39
5	**L1**, instead of **L8**	93	84
6	**L9**, instead of **L8**	78	28
7	**L10**, instead of **L8**	56	6
8	**L6**, instead of **L8**	70	44
9	PhMgBr, instead of PhZnI	89	44
10	5% $NiCl_2$·glyme, 6.5% **L1**	96	72
11	under air, rather than under N_2 (capped vial)	96	52
12	0.1 equiv of water added	97	84

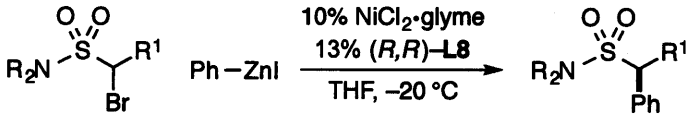
[a] All data are the average of two experiments. [b] The yield was determined through GC analysis with the aid of a calibrated internal standard.

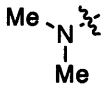
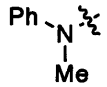
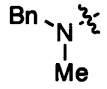
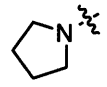
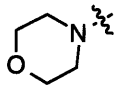
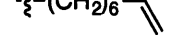
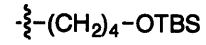
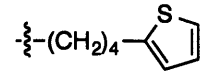
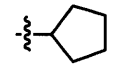


Under the optimized reaction conditions, a variety of sulfonamides bearing different substituents on the nitrogen group undergo Negishi phenylation reactions in good ee and good yield (Table 6, entries 1–5). The cross-coupling reaction of a hindered sulfonamide furnishes the product with high enantioselectivity (entry 9). An array of

functional groups are compatible under the Negishi phenylation reaction conditions including a terminal olefin (entry 6), a silyl ether (entry 7), and a thiophene (entry 8). A gram-scale reaction with the sulfonamide illustrated in entry 2 proceeds in 92% ee and 98% yield. Under our standard reaction condition, the ee of the product stays constant during the course of the cross-coupling reaction, and a modest kinetic resolution of an α-bromosulfonamide is observed (33% ee at 75% conversion). Neither an α-chlorosulfonamide nor an alkylzinc halide is an the effective cross-coupling partner.

Table 6. Nickel-Catalyzed Asymmetric Negishi Phenylations of Racemic α-Bromosulfonamides: Scope with Respect to the Sulfonamide[a]

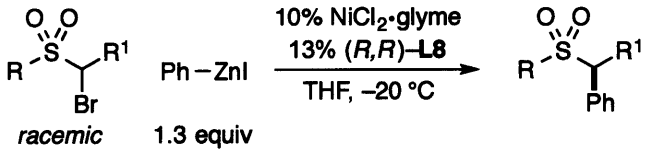


entry	R_2N	R^1	ee (%)	yield (%)[b]
1		*n*-Bu	96	90
2		*n*-Bu	94	95
3		*n*-Bu	94	94
4		*n*-Bu	96	85
5		*n*-Bu	96	92
6	Me_2N		95	88
7	Me_2N		98	92
8[c]	Me_2N		90	54
9[c]	Me_2N		99	44

[a] All data are the average of two experiments. [b] Yield of purified product. [c] Amount of PhZnI: 1.5 equiv.

The conditions developed for the Negishi reaction of α-bromosulfonamides (Table 6) can be applied without modification to the corresponding sulfones (Table 7). Various sulfones such as alkyl or aryl sulfones undergo Negishi phenylation reactions in good ee and yield (entries 1, 4, and 5). The cross-coupling of a hindered sulfone furnishes the product with good enantioselectivity (entry 2). However, an α-chlorosulfone is not a suitable coupling partner.

Table 7. Stereoconvergent Negishi Phenylations of Racemic α-Bromosulfones: Scope with Respect to the Sulfone[a]



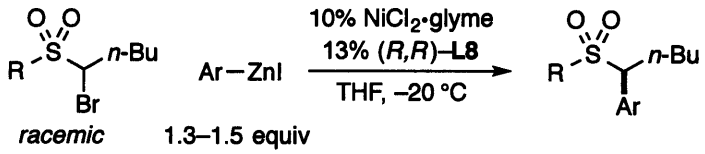
entry	R	R^1	ee (%)	yield (%)[b]
1	Me	*n*-Bu	94	96
2[c]	Me	Cy	99	83
3	Me	$(CH_2)_6NBnCbz$	90	74
4	*t*-Bu	*n*-Bu	98	96
5	Ph	*n*-Bu	84	96

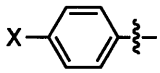
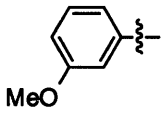
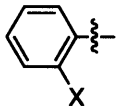
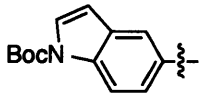
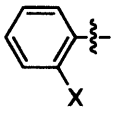
[a] All data are the average of two experiments. [b] Yield of purified product. [c] Amount of PhZnI: 1.5 equiv.

An array of nucleophiles were examined under the developed asymmetric Negishi cross-coupling conditions (Table 8). Both electron-rich (entries 1, 4–6, and 8–10) and electron-deficient (entries 2 and 3) arylzinc reagents are suitable nucleophilic partners for the arylation reaction. Furthermore, the asymmetric arylation reaction proceeds with an indolylzinc reagent in good ee (entry 7). It is noteworthy that *o*-substituted nucleophiles smoothly undergo cross-coupling reactions with both α-bromosulfonamides and -sulfones (entries 4–6 and 8–10); in previous studies, we showed limited scope with respect to *o*-

substituted nucleophiles in nickel-catalyzed asymmetric arylation reactions. [44] Unfortunately, doubly *o*-substituted arylzinc reagents are not suitable coupling partners.

Table 8. Stereoconvergent Negishi Arylations of Racemic α-Bromosulfonamides and -Sulfones: Scope with Respect to the Arylzinc Reagent[a]



entry	R	Ar		ee (%)	yield (%)[b]
1	Me_2N		X = Me	96	89
2	Me_2N		CF_3	98	94
3	Me_2N			96	88
4	Me_2N		X = OMe	96	64
5	Me_2N		Me	97	78
6[c]	Me_2N		Et	97	86
7	Me_2N			89	68
8	Me		X = OMe	96	84
9	Me		Me	97	80
10[c]	Me		Et	98	82

[a] All data are the average of two experiments. [b] Yield of purified product. [c] Amount of ArZnI: 2.0 equiv; amount of catalyst: 20% $NiCl_2$·glyme, 26% (*R,R*)-L8.

In our recent studies, we reported the cross-coupling between secondary alkyl electrophiles and alkenylzinc reagents.[43] Thus, we turned our attention to expanding the scope of the stereoconvergent cross-couplings of α-bromosulfonamides and -sulfones to include alkenylmetal reagents. However, alkenylation reactions of corresponding electrophiles with alkenylzinc nucleophiles under the standard conditions described

[44] For recent examples, see: (a) Do, H.-Q.; Chandrashekar, E. R. R.; Fu, G. C. *J. Am. Chem. Soc.* **2013**, *135*, 16288–16291. (b) Liang, Y.; Fu, G. C. *J. Am. Chem. Soc.* **2014**, *136*, 5520–5524.

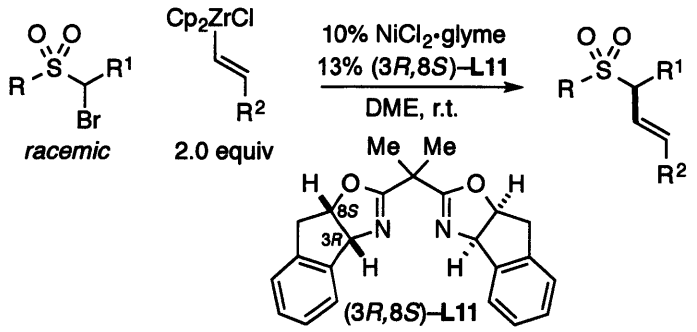
above proceed in low yield. After investigation of the effects of reaction parameters, we found that alkenylzirconium reagents can be employed as nucleophilic partners for the nickel-catalyzed process under modified conditions (Table 9).[45]

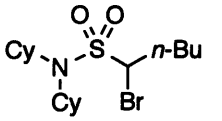
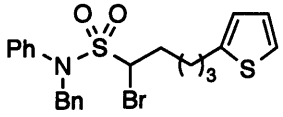
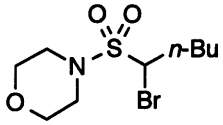
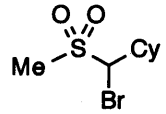
As described in Table 9, we can accomplish asymmetric alkenylations of α-bromosulfonamides and -sulfones with organozirconium reagents; thus allylic sulfonamides and sulfones can be synthesized in good ee and good yield. A silyl ether (entry 2), a primary alkyl chloride (entry 3), and a thiophene (entry 3) are compatible with the reaction conditions. Furthermore, an α-bromosulfone can serve as the electrophile, providing access to enantioenriched allylic sulfones that are useful synthetic intermediates (entry 5).[46] We observed that an alkenylzirconium reagent derived from the hydrozirconation of an internal alkyne is not a suitable coupling partner.

[45] For a report of the nickel-catalyzed asymmetric cross-coupling of secondary electrophiles with organozirconium reagents, see: Lou, S.; Fu, G. C. *J. Am. Chem. Soc.* **2010**, *132*, 5010–5011.

[46] For leading references to the synthesis and utility of these compounds, see: (a) Gais, H.-J. In *Asymmetric Synthesis with Chemical and Biological Methods*; Enders, D., Jäger, K.-E., Eds.; Wiley–VCH: Weinheim, 2007; pp 215–250. (b) Wu, X.-S.; Chen, Y.; Li, M.-B.; Zhou, M.-G.; Tian, S.-K. *J. Am. Chem. Soc.* **2012**, *134*, 14694–14697.

Table 9. Stereoconvergent Negishi Cross-Couplings of Racemic α-Bromosulfonamides and -Sulfones: Alkenylzirconium Reagents as Nucleophiles[a]



entry	electrophile	R^2	ee (%)	yield (%)[b]
1		CH_2Ph	94	83
2		$(CH_2)_2OTBDPS$	94	82
3		$(CH_2)_4Cl$	80	62
4		Ph	96	68
5[c]		CH_2Ph	93	50

[a] All data are the average of two experiments. [b] Yield of purified product. [c] Ligand used: (*R,R*)–**L8**.

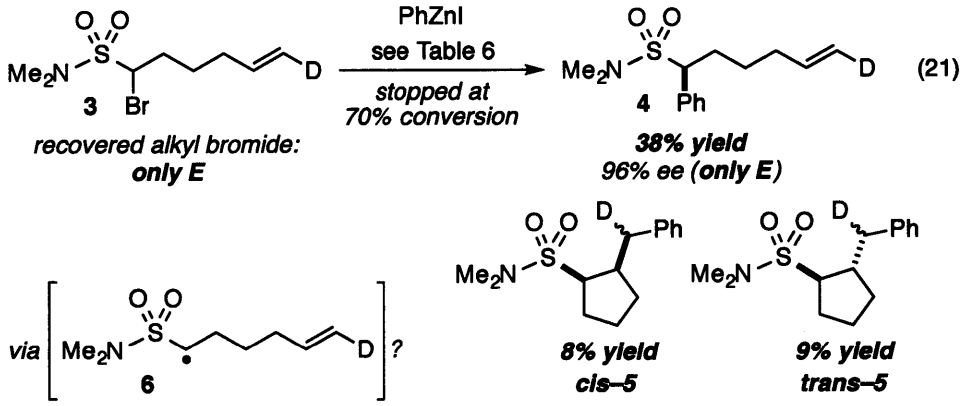
For the nickel-catalyzed asymmetric cross-coupling reaction of unactivated alkyl electrophiles, we have proposed that an alkyl radical intermediate might be involved in the oxidative addition step.[47,48] Related to this hypothesis, we have shown that unactivated secondary alkyl electrophiles bearing a pendant olefin undergo the cross-

[47] (a) For an early suggestion, see: Zhou, J.; Fu, G. C. *J. Am. Chem. Soc.* **2004**, *126*, 1340–1341. (b) For a recent discussion and leading references, see: Zultanski, S. L.; Fu, G. C. *J. Am. Chem. Soc.* **2013**, *135*, 624–627.

[48] For early mechanistic studies by others of nickel-catalyzed cross-couplings of unactivated alkyl electrophiles, see: (a) Jones, G. D.; Martin, J. L.; McFarland, C.; Allen, O. R.; Hall, R. E.; Haley, A. D.; Brandon, R. J.; Konovalova, T.; Desrochers, P. J.; Pulay, P.; Vicic, D. A. *J. Am. Chem. Soc.* **2006**, *128*, 13175–13183. (b) Lin, X.; Phillips, D. L. *J. Org. Chem.* **2008**, *73*, 3680–3688. (c) ref 27.

coupling via cyclization/C–C bond formation;[20,43] in contrast, an activated cyclizable electrophile cross-couples with a nucleophile without cyclization.[43] In this regard, it was interesting to understand the mechanism of stereoconvergent arylations of other alkyl electrophiles such as α-bromosulfonamides.

To investigate whether a radical intermediate cyclizes in this arylation, we examined the Negishi reaction of an α-bromosulfonamide having a deuterium-labeled pendant olefin (eq 21). At 70% conversion of the electrophile, we observe a 38% yield of the direct-coupling product (**4**) and a 17% combined yield of cyclization/cross-coupling products (**5**). A 1:1 mixture of diastereomers (differing in the relative stereochemistry at the deuterium-bearing carbon) of each cis and trans cyclization/cross-coupling products (**5**) is consistent with radical cyclization of the radical intermediate (**6**). This observation also suggests that cyclic products (**5**) are not produced by simple β-migratory insertion of an alkyl–nickel intermediate followed by reductive elimination. In addition, no cis/trans isomerization of the double bond is detected in the direct-coupling product, which suggests the cyclization step of the radical intermediate (**6**) is irreversible. We also observe side-reactions such as olefin isomerization during the later stages of the cross-coupling.



Simple 5-hexenyl radical cyclizes with a first-order rate of ~10^5 s^{-1}.[49] Although, to the best of our knowledge, the rate of cyclization of sulfonamide radical **6** has not been reported, it is probably significantly slower than the rate of diffusion (~10^9 s^{-1}).[50] Therefore, our observation of cyclization/cross-coupling products (**5**) is evidence that the nickel-catalyzed cross-coupling reaction may include a non-cage radical pathway. In addition, Weix showed that a non-cage radical pathway could be operative in some nickel-catalyzed reductive-coupling reactions by demonstrating the correlation between nickel concentration and product distribution for the nickel-catalyzed coupling of aryl halides with alkyl halides.[51]

To elucidate the mechanism of the nickel-catalyzed cross-coupling of α-bromosulfonamides, we decided to study the effect of catalyst concentration on the product distribution of the reaction with a cyclizable electrophile (Figure 2). If the enantioselective arylation proceeds following a non-cage radical mechanism, the ratio of direct-coupling product (**D**) to cyclization/cross-coupling products (**C**) should increase at higher nickel-concentration because an alkyl radical intermediate is more likely to be captured by the catalyst before it cyclizes. Under the asymmetric Negishi arylation conditions, we do observe that the ratio (**D/C**) depends on catalyst concentration, which is consistent with a non-cage process. Moreover, it is interesting to note that the ratio (**D/C**) decreases over the course of the reaction, which suggests that the effective nickel concentration may be diminishing due to catalyst decomposition.

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[49] Newcomb, M. In *Encyclopedia of Radicals in Chemistry, Biology and Materials*; Chatgilialoglu, C., Studer, A., Eds.; John Wiley & Sons: Chichester, 2012; Vol. 1, pp 107–124.
[50] Paquette, L. A. *Synlett* **2001**, 1–12.
[51] Biswas, S.; Weix, D. J. *J. Am. Chem. Soc.* **2013**, *135*, 16192–16197.

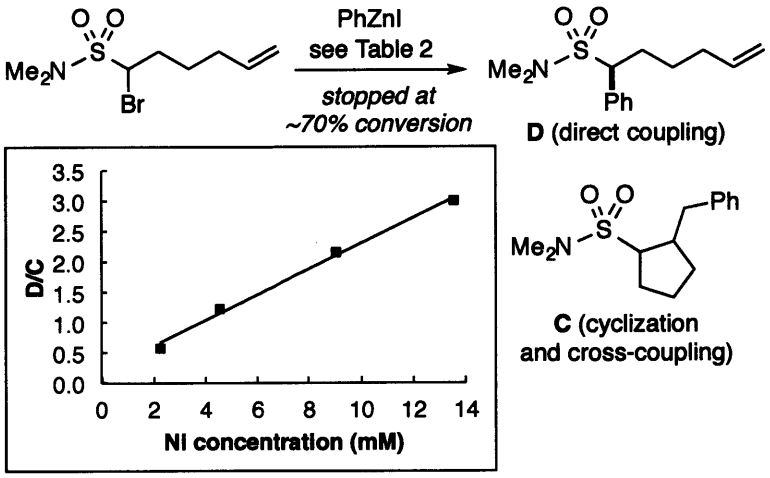


Figure 2. Dependence of the ratio of uncyclized (**D**)/cyclized (**C**) product on the concentration of nickel.

C. Conclusion

In summary, we have developed nickel-catalyzed cross-couplings of secondary alkyl electrophiles, specifically, stereoconvergent Negishi arylations and alkenylations of α-bromosulfonamides and α-bromosulfones with arylzinc reagents and alkenylzirconium reagents, respectively. Under the developed reaction conditions, both α-bromosulfonamides and α-bromosulfones undergo stereoconvergent Negishi arylations and alkenylations in high ee and yield with broad functional-group compatibility. The stereochemistry of the sulfur-bearing carbon can be controlled by this direct catalytic asymmetric approach. In mechanistic studies, we have shown that a radical intermediate has a sufficient lifetime to escape from a solvent cage and cyclizes irreversibly under the Negishi arylation conditions.

D. Experimental

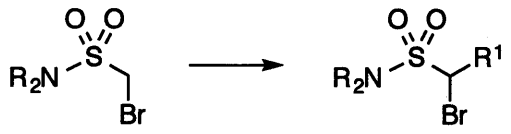
I. General Information

The following reagents were purchased and used as received: $NiCl_2$•glyme (Strem), ZnI_2 (Strem), and Cp_2ZrHCl (Strem). Ligands **L8** (available from Aldrich) and **L11** were prepared according to a literature procedure.[43] Grignard reagents were prepared from aryl bromides and magnesium turnings (Strem) or from aryl iodides and *i*-PrMgCl (Aldrich; 2.0 M in THF); on occasion, we have found purchased Grignard reagents to be less suitable. THF was deoxygenated and dried by sparging with argon followed by passage through an activated alumina column (S. G. Water) prior to use. All reactions were carried out in oven-dried glassware under an inert atmosphere.

^{1}H NMR data and ^{13}C NMR data were collected on a VARIAN 500 MHz spectrometer at ambient temperature. HPLC analyses were carried out on an Agilent 1100 series system with Daicel CHIRALPAK® columns or Daicel CHIRALCEL® columns (internal diameter 4.6 mm, column length 250 mm, particle size 5 μm or 3 μm). GC analyses were carried out on an Agilent 6890 series system with an HP-5 column (length 30 m, I.D. 0.25 mm).

II. Preparation of Electrophiles

These procedures have not been optimized.



Representative experimental procedure for the preparation of α-bromosulfonamides. LDA was prepared by the dropwise addition of *n*-BuLi (1.6 M in hexanes; 13.8 mL, 22 mmol) to a solution of *i*-Pr_2NH (3.36 mL, 24.0 mmol) in THF (71 mL) in a 500-mL round-bottom flask at −78 °C. The reaction mixture was stirred at 0 °C for 15 min, and then it was cooled to −78 °C. A solution of the 1-bromomethanesulfonamide (20.0 mmol; prepared according to a literature procedure from bromomethanesulfonyl chloride[52] and a secondary amine[53]) in THF (40.0 mL) was added over 15 min to the LDA solution at −78 °C. The mixture was stirred for 30 min, and then a solution of the alkyl bromide (26.0 mmol) in THF (43.3 mL) was added over 15 min. The solution was stirred at −78 °C for 2 h, and then it was allowed to slowly warm to r.t. The reaction mixture was stirred at r.t. for 12 h, and then the reaction was quenched by the addition of saturated aqueous NH_4Cl (100 mL). The mixture was extracted with Et_2O (3 × 50 mL), and the combined organic layers were rinsed with brine (50 mL), dried over $MgSO_4$, and concentrated.

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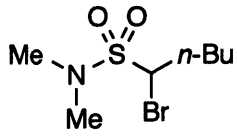
[52] Gao, F.; Yan, X.; Zahr, O.; Larsen, A.; Vong, K.; Auclair, K. *Bioorg. Med. Chem. Lett.* **2008**, *18*, 5518–5522.

[53] Brienne, M.-J.; Varech, D.; Leclercq, M.; Jacques, J.; Radembino, N.; Dessalles, M.-C.; Mahuzier, G.; Gueyouche, C.; Bories, C. Loiseau, P.; Gayral, P. *J. Med. Chem.* **1987**, *30*, 2232–2239.



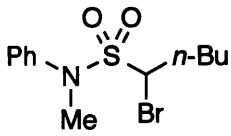
1-Bromo-*N*,*N*-dimethylpentane-1-sulfonamide. The title compound was prepared from 1-bromo-*N*,*N*-dimethylmethanesulfonamide (5.00 g, 24.7 mmol) and 1-bromobutane (3.45 mL, 32.2 mmol). The product was purified by column chromatography (3%→20% ethyl acetate/hexanes): 3.00 g (47%). Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.81 (dd, 1H, J = 10.7, 3.1 Hz), 3.03 (s, 6H), 2.34 (dddd, 1H, J = 14.4, 10.0, 5.5, 3.1 Hz), 2.10–2.02 (m, 1H), 1.70–1.61 (m, 1H), 1.47–1.30 (m, 3H), 0.94 (t, 3H, J = 7.2 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 63.3, 38.8, 32.9, 29.2, 21.9, 13.9.

FT-IR (neat) 2958, 2873, 2814, 1483, 1458, 1435, 1414, 1380, 1342, 1287, 1237, 1203, 1171, 1145, 1106, 1064, 973, 930, 782, 750, 734 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_7H_{16}BrNO_2S$: 257, found: 257.



1-Bromo-*N*-methyl-*N*-phenylpentane-1-sulfonamide. The title compound was prepared from 1-bromo-*N*-methyl-*N*-phenylmethanesulfonamide (3.82 g, 14.5 mmol) and 1-bromobutane (2.02 mL, 18.8 mmol). The product was purified by column chromatography on silica gel (2%→15% ethyl acetate/hexanes) and then on C-18 silica gel (10%→100% acetonitrile/water): 3.60 g (78%). Colorless oil.

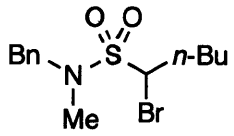
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50–7.48 (m, 2H), 7.43–7.39 (m, 2H), 7.35–7.31 (m, 1H), 4.74 (dd, 1H, J = 10.5, 3.1 Hz), 3.52 (s, 3H), 2.27 (dddd, 1H, J = 14.5, 10.2, 5.3,

3.1 Hz), 2.11–2.03 (m, 1H), 1.66–1.58 (m, 1H), 1.40–1.24 (m, 3H), 0.89 (t, 3H, J = 7.2 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.8, 129.7, 128.1, 127.3, 63.3, 42.0, 32.7, 29.1, 21.9, 13.9.

FT-IR (neat) 3062, 3039, 2957, 2931, 2872, 1595, 1493, 1466, 1453, 1436, 1351, 1270, 1237, 1183, 1143, 1106, 1068, 1026, 917, 886, 767, 725 cm^{-1}.

MS (ESI) *m/z* (M^++H) calcd for $C_{12}H_{19}BrNO_2S$: 320, found: 320.



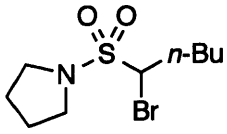
***N*-Benzyl-1-bromo-*N*-methylpentane-1-sulfonamide.** The title compound was prepared from *N*-benzyl-1-bromo-*N*-methylmethanesulfonamide (3.75 g, 13.5 mmol) and 1-bromobutane (1.88 mL, 17.5 mmol). The product was purified by column chromatography (2%→15% ethyl acetate/hexanes): 2.04 g (45%). Light-yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.35 (m, 4H), 7.34–7.30 (m, 1H), 4.84 (dd, 1H, J = 10.7, 3.1 Hz), 4.61 (d, 1H, J = 14.8 Hz), 4.36 (d, 1H, J = 14.8 Hz), 2.88 (s, 3H), 2.40 (dddd, 1H, J = 14.4, 10.0, 5.6, 3.1 Hz), 2.15–2.07 (m, 1H), 1.72–1.64 (m, 1H), 1.50–1.31 (m, 3H), 0.95 (t, 3H, J = 7.2 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.8, 128.9, 128.3, 128.2, 64.1, 55.5, 35.5, 32.9, 29.3, 21.9, 13.9.

FT-IR (neat) 3088, 3064, 3031, 2958, 2931, 2872, 1605, 1587, 1496, 1467, 1455, 1338, 1278, 1212, 1196, 1151, 1106, 1077, 1029, 994, 944, 910, 858, 787, 733 cm^{-1}.

MS (ESI) *m/z* (M^++H) calcd for $C_{13}H_{21}BrNO_2S$: 334, found: 334.



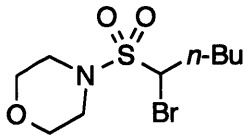
1-((1-Bromopentyl)sulfonyl)pyrrolidine. The title compound was prepared from 1-((bromomethyl)sulfonyl)pyrrolidine (3.02 g, 13.2 mmol) and 1-bromobutane (1.85 mL, 17.2 mmol). The product was purified by column chromatography (2%→15% ethyl acetate/hexanes): 1.96 g (52%). Light-yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.84 (dd, 1H, J = 10.7, 3.1 Hz), 3.62–3.56 (m, 2H), 3.49–3.43 (m, 2H), 2.36 (dddd, 1H, J = 14.4, 10.0, 5.6, 3.1 Hz), 2.11–2.03 (m, 1H), 1.99–1.94 (m, 4H), 1.70–1.61 (m, 1H), 1.48–1.30 (m, 3H), 0.94 (t, 3H, J = 7.2 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 63.7, 49.4, 32.7, 29.3, 26.1, 21.9, 13.9.

FT-IR (neat) 2957, 2872, 1461, 1334, 1238, 1200, 1148, 1076, 1014, 929, 781 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_9H_{18}BrNO_2S$: 283, found: 283.



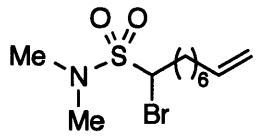
4-((1-Bromopentyl)sulfonyl)morpholine. The title compound was prepared from 4-((bromomethyl)sulfonyl)morpholine (3.01 g, 12.3 mmol) and 1-bromobutane (1.72 mL, 16.0 mmol). The product was purified by column chromatography (2%→20% ethyl acetate/hexanes): 1.28 g (35%). White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.72 (dd, 1H, J = 10.7, 3.1 Hz), 3.75–3.68 (m, 4H), 3.50–3.42 (m, 4H), 2.32 (dddd, 1H, J = 14.3, 9.9, 5.5, 3.0 Hz), 2.05–1.97 (m, 1H), 1.67–1.58 (m, 1H), 1.45–1.27 (m, 3H), 0.92 (t, 3H, J = 7.2 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 67.0, 63.8, 47.3, 32.8, 29.1, 21.8, 13.8.

FT-IR (neat) 2959, 2925, 2860, 1467, 1460, 1450, 1434, 1347, 1328, 1299, 1261, 1237, 1204, 1153, 1114, 1074, 1014, 958, 846, 778, 732 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_9H_{18}BrNO_3S$: 299, found: 299.



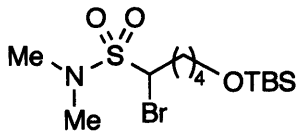
1-Bromo-*N*,*N*-dimethylnon-8-ene-1-sulfonamide. The title compound was prepared from 1-bromo-*N*,*N*-dimethylmethanesulfonamide (1.76 g, 8.71 mmol) and 8-bromo-1-octene (1.90 mL, 11.3 mmol). The product was purified by column chromatography (2%→20% ethyl acetate/hexanes): 1.30 g (48%). Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.80 (ddt, 1H, *J* = 16.9, 10.2, 6.7 Hz), 5.00 (ddt, 1H, *J* = 17.1, 2.2, 1.6 Hz), 4.94 (ddt, 1H, *J* = 10.2, 2.2, 1.2 Hz), 4.81 (dd, 1H, *J* = 10.6, 3.1 Hz), 3.03 (s, 6H), 2.33 (dddd, 1H, *J* = 14.3, 10.0, 5.8, 3.1 Hz), 2.10–2.02 (m, 3H), 1.71–1.63 (m, 1H), 1.48–1.25 (m, 7H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.0, 114.5, 63.3, 38.8, 33.8, 33.1, 28.8, 28.6, 27.1.

FT-IR (neat) 3075, 2923, 2852, 1640, 1479, 1454, 1414, 1340, 1285, 1204, 1143, 1063, 971, 907, 783 cm^{-1}.

MS (ESI) *m/z* (M^++H) calcd for $C_{11}H_{23}BrNO_2S$: 312, found: 312.



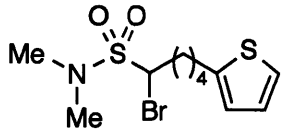
1-Bromo-5-((*tert*-butyldimethylsilyl)oxy)-*N*,*N*-dimethylpentane-1-sulfonamide. A 250-mL round-bottom flask was charged with 1-bromo-*N*,*N*-dimethylmethanesulfonamide (0.808 g, 4.00 mmol) and toluene (24 mL). *tert*-Butyl(4-iodobutoxy)dimethylsilane (5.03 g, 16.0 mmol), aqueous NaOH (50% w/v; 24 mL), and benzyltriethylammonium chloride (0.911 g, 4.00 mmol) were added to the solution at r.t. The resulting mixture was stirred at r.t. for 24 h, and then water (50 mL) was added. The organic phase was separated, and the aqueous solution was extracted with ethyl acetate (2 × 25 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. The product was purified by column chromatography (hexanes→30% ethyl acetate/hexanes): 1.21 g (78%). Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.82 (dd, 1H, J = 10.7, 3.1 Hz), 3.62 (t, 2H, J = 6.1 Hz), 3.02 (s, 6H), 2.38–2.32 (m, 1H), 2.13–2.04 (m, 1H), 1.79–1.70 (m, 1H), 1.67–1.45 (m, 3H), 0.89 (s, 9H), 0.05 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 63.2, 62.6, 38.8, 33.0, 31.8, 26.1, 23.7, 18.5, –5.2.

FT-IR (neat) 2952, 2929, 2885, 2856, 1471, 1462, 1389, 1343, 1287, 1256, 1205, 1146, 1127, 1106, 1006, 973, 939, 836, 812, 776, 740 cm^{-1}.

MS (ESI) *m/z* (M^++H) calcd for $C_{13}H_{31}BrNO_3SSi$: 388, found: 388.



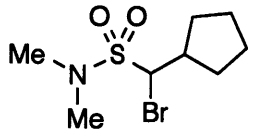
1-Bromo-*N*,*N*-dimethyl-5-(thiophen-2-yl)pentane-1-sulfonamide. The title compound was prepared from 1-bromo-*N*,*N*-dimethylmethanesulfonamide (3.00 g, 14.8 mmol) and 2-(4-bromobutyl)thiophene (4.23 g, 19.3 mmol). The product was purified by column chromatography (3%→20% ethyl acetate/hexanes): 1.44 g (29%). Light-yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (dd, 1H, J = 5.1, 1.2 Hz), 6.92 (dd, 1H, J = 5.1, 3.4 Hz), 6.79 (dddd, 1H, J = 3.3, 1.0, 1.0, 1.0 Hz), 4.80 (dd, 1H, J = 10.5, 3.2 Hz), 3.02 (s, 6H), 2.92–2.82 (m, 2H), 2.40–2.34 (m, 1H), 2.14–2.07 (m, 1H), 1.80–1.69 (m, 3H), 1.56–1.47 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8, 126.9, 124.4, 123.2, 63.0, 38.8, 33.0, 30.9, 29.7, 26.6.

FT-IR (neat) 2935, 2857, 1480, 1454, 1414, 1340, 1286, 1203, 1180, 1145, 1063, 972, 850, 784 cm^{-1}.

MS (ESI) *m/z* (M^++H) calcd for $C_{11}H_{19}BrNO_2S_2$: 340, found: 340.



1-Bromo-1-cyclopentyl-*N*,*N*-dimethylmethanesulfonamide. The title compound was prepared from 1-bromo-*N*,*N*-dimethylmethanesulfonamide (3.03 g, 15.0 mmol) and cyclopentyl 4-methylbenzenesulfonate (4.69 g, 19.5 mmol). The product was

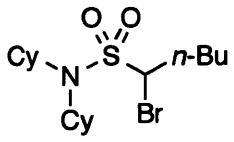
purified by column chromatography (10% ethyl acetate/hexanes): 668 mg (16%). Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.99 (d, 1H, J = 4.8 Hz), 3.00 (s, 6H), 2.66–2.59 (m, 1H), 1.99–1.88 (m, 2H), 1.75–1.55 (m, 5H), 1.54–1.45 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 68.5, 41.8, 38.7, 31.8, 30.0, 25.6, 25.5.

FT-IR (neat) 2947, 2869, 2812, 1481, 1452, 1413, 1333, 1284, 1205, 1180, 1142, 1063, 969, 898, 862, 786 cm^{-1}.

MS (EI) *m/z* (M^+–Br) calcd for $C_8H_{16}NO_2S$: 190, found: 190.



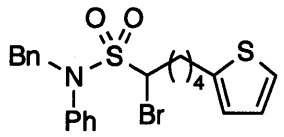
1-Bromo-*N*,*N*-dicyclohexylpentane-1-sulfonamide. The title compound was prepared from 1-bromo-*N*,*N*-dicyclohexylmethanesulfonamide (2.10 g, 6.21 mmol) and 1-bromobutane (0.867 mL, 8.07 mmol). The product was purified by column chromatography (1%→8% ethyl acetate/hexanes): 2.06 g (84%). Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.57 (dd, 1H, J = 10.6, 2.9 Hz), 3.38–3.33 (br m, 2H), 2.35 (dddd, 1H, J = 14.3, 10.1, 5.3, 2.9 Hz), 2.07–2.00 (m, 1H), 1.95–1.91 (m, 2H), 1.86–1.59 (m, 13H), 1.45–1.23 (m, 7H), 1.09 (qt, 2H, J = 13.1, 3.5 Hz), 0.92 (t, 3H, J = 7.2 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 66.6, 59.3, 33.9, 33.3, 32.4, 29.5, 26.6, 25.4, 22.0, 13.9.

FT-IR (neat) 2931, 2855, 1467, 1454, 1401, 1381, 1329, 1275, 1256, 1235, 1188, 1166, 1142, 1101, 1074, 1048, 1027, 997, 982, 929, 917, 895, 856, 847, 824, 801, 774, 760, 749, 733 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_{17}H_{32}BrNO_2S$: 393, found: 393.



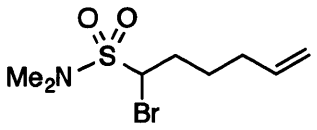
***N*-Benzyl-1-bromo-*N*-phenyl-5-(thiophen-2-yl)pentane-1-sulfonamide.** The title compound was prepared from *N*-benzyl-1-bromo-*N*-phenylmethanesulfonamide (2.70 g, 7.94 mmol) and 2-(4-bromobutyl)thiophene (2.26 g, 10.3 mmol). The product was purified by column chromatography on silica gel (2%→12% ethyl acetate/hexanes) and then preparative HPLC on C-18 silica gel (80%→100% acetonitrile/water; water was doped with 0.1% AcOH): 0.881 g (23%). White solid.

^1H NMR (500 MHz, $CDCl_3$) δ 7.34–7.27 (m, 5H), 7.26–7.20 (m, 5H), 7.11 (dd, 1H, J = 5.1, 1.2 Hz), 6.90 (dd, 1H, J = 5.1, 3.4 Hz), 6.76 (dddd, 1H, J = 3.2, 1.0, 1.0, 1.0 Hz), 5.34 (d, 1H, J = 14.8 Hz), 4.75 (dd, 1H, J = 10.5, 3.1 Hz), 4.69 (d, 1H, J = 14.9 Hz), 2.88–2.78 (m, 2H), 2.38–2.31 (m, 1H), 2.21–2.13 (m, 1H), 1.79–1.65 (m, 3H), 1.51–1.43 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8, 138.1, 136.3, 129.6, 129.4, 128.7, 128.6, 128.5, 127.9, 126.9, 124.4, 123.2, 63.3, 58.9, 32.7, 30.9, 29.6, 26.6.

FT-IR (neat) 3064, 3031, 2932, 2858, 1594, 1492, 1454, 1439, 1348, 1214, 1178, 1150, 1093, 1066, 1028, 917, 868, 822, 781 cm^{-1}.

MS (ESI) *m/z* (M^++H) calcd for $C_{22}H_{25}BrNO_2S_2$: 478, found: 478.



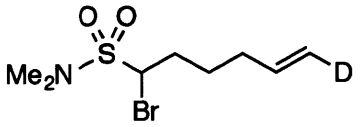
1-Bromo-*N*,*N*-dimethylhex-5-ene-1-sulfonamide. The title compound was prepared from 1-bromo-*N*,*N*-dimethylmethanesulfonamide (4.00 g, 19.8 mmol) and 5-bromo-1-pentene (3.05 mL, 25.7 mmol). The product was purified by column chromatography (3%→15% ethyl acetate/hexanes): 2.29 g (43%). Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.79 (ddt, 1H, J = 16.9, 10.2, 6.7 Hz), 5.05 (dq, 1H, J = 17.1, 1.7 Hz), 5.01 (ddt, 1H, J = 10.2, 1.9, 1.2 Hz), 4.82 (dd, 1H, J = 10.5, 3.2 Hz), 3.02 (s, 6H), 2.35 (dddd, 1H, J = 14.5, 10.2, 6.0, 3.2 Hz), 2.19–2.04 (m, 3H), 1.84–1.75 (m, 1H), 1.60–1.51 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.5, 115.8, 63.0, 38.8, 32.8, 32.7, 26.4.

FT-IR (neat) 3076, 2918, 1640, 1482, 1454, 1415, 1341, 1285, 1204, 1143, 1063, 970, 912, 856, 786, 738 cm^{-1}.

MS (ESI) *m/z* (M^++H) calcd for $C_8H_{17}BrNO_2S$: 270, found: 270.



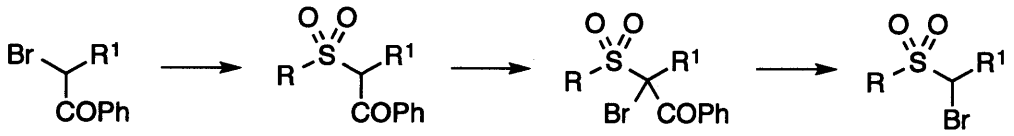
(*E*)-1-Bromo-*N*,*N*-dimethylhex-5-ene-1-sulfonamide-6-*d*. The title compound was prepared from 1-bromo-*N*,*N*-dimethylmethanesulfonamide (762 mg, 3.77 mmol) and (*E*)-pent-4-en-1-yl-5-*d* 4-methylbenzenesulfonate (1.18 g, 4.90 mmol). The product was purified by column chromatography (2%→20% ethyl acetate/hexanes): 408 mg (40%). Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.78 (dt, 1H, J = 16.9, 6.5 Hz), 5.05–5.00 (m, 1H), 4.82 (dd, 1H, J = 10.5, 3.2 Hz), 3.01 (s, 6H), 2.37–2.30 (m, 1H), 2.18–2.03 (m, 3H), 1.83–1.74 (m, 1H), 1.59–1.50 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.4, 115.5 (t, J = 24 Hz), 63.1, 38.8, 32.8, 32.7, 26.4.

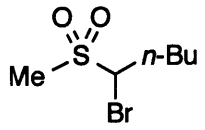
FT-IR (neat) 3028, 2949, 2862, 2264, 1621, 1483, 1455, 1435, 1414, 1342, 1287, 1204, 1183, 1144, 1064, 972, 868, 785, 744 cm^{-1}.

MS (ESI) *m/z* (M^++H) calcd for $C_8H_{16}DBrNO_2S$: 271, found: 271.



Representative experimental procedure for the preparation of α-bromosulfones. The target molecules were prepared according to literature procedures from α-bromoketones.[54,55] A 100-mL round-bottom flask was charged with the α-bromo-β-keto-sulfone (10.0 mmol) and aqueous KOH (30% w/v; 50 mL), and the mixture was stirred at r.t. for 48 h. When the reaction was complete (monitored by TLC), the reaction mixture was extracted with dichloromethane (3 × 30 mL). The combined organic layers were dried over $MgSO_4$ and concentrated.

[54] Suryakiran, N.; Reddy, T. S.; Ashalatha, K.; Lakshman, M.; Venkateswarlu, Y. *Tetrahedron Lett.* **2006**, *47*, 3853–3856.
[55] Suryakiran, N.; Prabhakar, P.; Reddy, T. S.; Mahesh, K. C.; Rajesh, K.; Venkateswarlu, Y. *Tetrahedron Lett.* **2007**, *48*, 877–881.



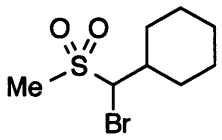
1-Bromo-1-(methylsulfonyl)pentane. The title compound was prepared from 2-bromo-2-(methylsulfonyl)-1-phenylhexan-1-one (12.0 g, 36.0 mmol). The product was purified by column chromatography (hexanes→20% ethyl acetate/hexanes): 8.08 g (98%). White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.61 (dd, 1H, J = 11.0, 3.0 Hz), 3.09 (s, 3H), 2.43 (dddd, 1H, J = 14.4, 9.9, 5.7, 3.0 Hz), 1.96 (dddd, 1H, J = 14.2, 11.1, 9.5, 4.4 Hz), 1.72–1.64 (m, 1H), 1.50–1.31 (m, 3H), 0.94 (t, 3H, J = 7.2 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 64.3, 37.6, 30.1, 29.2, 21.8, 13.8.

FT-IR (neat) 3010, 2958, 2932, 2873, 1467, 1454, 1434, 1413, 1381, 1311, 1237, 1208, 1140, 1121, 1106, 956, 928, 815, 771, 748, 735 cm^{-1}.

MS (ESI) *m/z* (M^++H) calcd for $C_6H_{14}BrO_2S$: 229, found: 229.



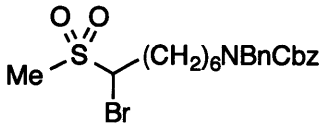
(Bromo(methylsulfonyl)methyl)cyclohexane. The bromination of 2-cyclohexyl-2-(methylsulfonyl)-1-phenylethan-1-one was conducted at 60 °C, and extra KBr and H_2O_2 were added until the reaction was complete. The title compound was prepared from 2-bromo-2-cyclohexyl-2-(methylsulfonyl)-1-phenylethan-1-one (8.13 g, 22.6 mmol). The reaction was run at 40 °C for 96 h. The product was purified by column chromatography on silica gel (5%→30% ethyl acetate/hexanes) and then on C-18 silica gel (10%→100% acetonitrile/water): 1.69 g (29%). White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.60 (d, 1H, J = 2.7 Hz), 3.10 (s, 3H), 2.41–2.35 (m, 1H), 2.08–2.04 (m, 1H), 1.84–1.76 (m, 2H), 1.72–1.67 (m, 1H), 1.64–1.61 (m, 1H), 1.48–1.30 (m, 4H), 1.21–1.12 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 71.0, 39.9, 37.4, 31.8, 28.5, 26.0, 25.6, 25.3.

FT-IR (neat) 3011, 2930, 2855, 1452, 1411, 1370, 1310, 1240, 1171, 1138, 1090, 1080, 1060, 1032, 968, 922, 896, 885, 848, 792, 774, 728 cm^{-1}.

MS (ESI) *m/z* (M^++H) calcd for $C_8H_{16}BrO_2S$: 255, found: 255.



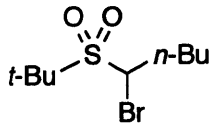
Benzyl benzyl(7-bromo-7-(methylsulfonyl)heptyl)carbamate. The title compound was prepared from benzyl benzyl(7-bromo-7-(methylsulfonyl)-8-oxo-8-phenyloctyl)carbamate (3.08 g, 5.13 mmol). The product was purified by column chromatography on silica gel (10%→50% ethyl acetate/hexanes) and then on C-18 silica gel (10%→100% acetonitrile/water): 1.57 g (62%). Viscous colorless oil.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.39–7.20 (br m, 10H), 5.18–5.14 (m, 2H), 4.68–4.60 (m, 1H), 4.50 (s, 2H), 3.28–3.20 (m, 2H), 3.06 (s, 3H), 2.40–2.30 (br m, 1H), 1.97–1.86 (br m, 1H), 1.70–1.25 (br m, 8H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 156.9, 156.4, 138.6, 137.6, 128.82, 128.78, 128.2, 128.05, 127.98, 127.5, 67.3, 64.7, 50.8, 50.5, 47.4, 46.7, 37.8, 30.7, 28.6, 28.3, 27.9, 27.2, 26.7.

FT-IR (neat) 3087, 3062, 3030, 2930, 2858, 1692, 1605, 1585, 1496, 1467, 1453, 1421, 1365, 1315, 1230, 1140, 1119, 1072, 1028, 955, 915, 819, 768, 733 cm^{-1}.

MS (ESI) *m/z* (M^++H) calcd for $C_{23}H_{31}BrNO_4S$: 496, found: 496.



1-Bromo-1-(*tert*-butylsulfonyl)pentane. A mixture of 2-bromo-1-phenylhexan-1-one (5.10 g, 20.0 mmol), 2-methyl-2-propanethiol (1.80 g, 20.0 mmol), benzyltriethylammonium bromide (0.272 g, 1.00 mmol), and NaOH (3.00 g, 75.0 mmol) in dichloromethane (40 mL) and water (40 mL) in a 250-mL round-bottom flask was stirred at r.t. for 8 h. Then, water (100 mL) was added, and the mixture was extracted with dichloromethane (3 × 50 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. The residue was dissolved in MeOH (50 mL) and water (50 mL), and then oxone® (30.7 g, 100 mmol) was added. The reaction mixture was stirred at r.t. overnight, and most of the MeOH was removed under reduced pressure. The resulting aqueous mixture was extracted with dichloromethane (3 × 30 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. 2-(*tert*-Butylsulfonyl)-1-phenylhexan-1-one was purified by column chromatography (5%→60% ethyl acetate/hexanes): 5.34 g (90%). White solid.

2-Bromo-2-(*tert*-butylsulfonyl)-1-phenylhexan-1-one was prepared from 2-(*tert*-butylsulfonyl)-1-phenylhexan-1-one following the described procedure.

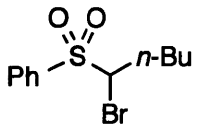
The title compound was prepared from 2-bromo-2-(*tert*-butylsulfonyl)-1-phenylhexan-1-one (2.30 g, 6.13 mmol). The reaction was conducted at 40 °C. The product was purified by column chromatography (hexanes→20% ethyl acetate/hexanes): 1.41 g (85%). White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.84 (dd, 1H, J = 10.5, 3.0 Hz), 2.43 (dddd, 1H, J = 14.5, 10.2, 5.3, 2.9 Hz), 2.11–2.03 (m, 1H), 1.75–1.66 (m, 1H), 1.55 (s, 9H), 1.48–1.30 (m, 3H), 0.94 (t, 3H, J = 7.2 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 63.3, 59.2, 30.8, 28.8, 25.2, 22.0, 13.9.

FT-IR (neat) 2959, 2933, 2873, 1479, 1467, 1399, 1366, 1305, 1192, 1167, 1118, 1104, 1020, 986, 964, 929, 801, 733 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_9H_{19}BrNaO_2S$: 293, found: 293.



((1-Bromopentyl)sulfonyl)benzene. The title compound was prepared from 2-bromo-1-phenyl-2-(phenylsulfonyl)hexan-1-one (12.0 g, 30.4 mmol). The reaction was conducted at 60 °C. The product was purified by column chromatography (hexanes→20% ethyl acetate/hexanes): 8.50 g (96%). White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98–7.95 (m, 2H), 7.72–7.68 (m, 1H), 7.61–7.57 (m, 2H), 4.70 (dd, 1H, J = 11.1, 2.9 Hz), 2.41 (dddd, 1H, J = 14.3, 9.9, 5.8, 2.9 Hz), 1.89 (dddd, 1H, J = 14.1, 11.1, 9.4, 4.4 Hz), 1.67–1.58 (m, 1H), 1.45–1.26 (m, 3H), 0.91 (t, 3H, J = 7.2 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.5, 134.6, 130.2, 129.2, 66.0, 31.0, 29.2, 21.8, 13.8.

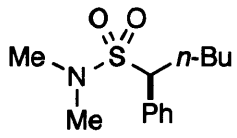
FT-IR (neat) 3065, 2958, 2932, 2872, 1584, 1478, 1466, 1447, 1381, 1324, 1309, 1236, 1203, 1149, 1133, 1083, 1024, 999, 929, 792, 778, 746 cm^{-1}.

MS (ESI) *m/z* (M^++H) calcd for $C_{11}H_{16}BrO_2S$: 291, found: 291.

III. Enantioselective Arylations

General Procedure. An oven-dried 8-mL vial equipped with a magnetic stir bar was capped with a PTFE-lined septum cap, cooled under vacuum, and then filled with nitrogen. ZnI_2 (290 mg, 0.910 mmol) was added to the vial, and the vial was then immediately placed under vacuum and re-filled with nitrogen (three cycles). Next, THF (2.73 mL) was added to the vial, followed by a solution of ArMgBr (prepared according to a literature procedure;[43] 1.00 M in THF; 0.910 mL, 0.910 mmol). The mixture was stirred at r.t. for 30 min. An oven-dried 20-mL vial equipped with a magnetic stir bar was charged with $NiCl_2$•glyme (15.4 mg, 0.070 mmol), (*R*,*R*)–**L8** (30.4 mg, 0.091 mmol), and the electrophile (0.70 mmol). The vial was sealed with a PTFE-lined septum cap, placed under vacuum, and then filled with nitrogen; this cycle was repeated three times. THF (4.14 mL) was added, and the mixture was stirred at r.t. for 20 min, at which time it had become homogenous. Both vials were wrapped with electrical tape, attached with nitrogen-filled balloons, and cooled to –20 °C for 15 min. The heterogeneous mixture of the nucleophile was then transferred by syringe over 2 min to the vial that contained the electrophile. The nitrogen-filled balloon was removed, and the septum cap was covered with grease. The reaction mixture was stirred at –20 °C for 24 h, and then the reaction was quenched by the addition of ethanol (0.70 mL). The solution was allowed to warm to r.t., and then it was filtered through a pad of silica (eluted with Et_2O). The filtrate was concentrated, and the residue was purified by column chromatography.

A second run was conducted with (*S*,*S*)–**L8**.



(*S*)-*N*,*N*-Dimethyl-1-phenylpentane-1-sulfonamide (Table 6, entry 1). 1-Bromo-*N*,*N*-dimethylpentane-1-sulfonamide (181 mg, 0.700 mmol) and phenylzinc iodide (0.910 mmol) were used. The product was purified by column chromatography (20%→25% Et_2O/hexanes). Light-yellow solid. First run: 159 mg (89%, 96% ee). Second run: 162 mg (91%, 96% ee).

The ee was determined by HPLC on a CHIRALCEL OD-H column (1% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 10.9 min (major), 13.4 min (minor).

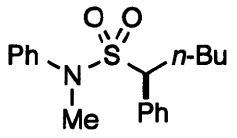
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.34 (m, 5H), 4.08 (dd, 1H, *J* = 11.3, 3.8 Hz), 2.53 (s, 6H), 2.34 (dddd, 1H, *J* = 13.7, 10.2, 6.5, 3.8 Hz), 2.15 (dddd, 1H, *J* = 13.6, 11.4, 10.0, 5.1 Hz), 1.38–1.23 (m, 2H), 1.22–1.09 (m, 2H), 0.84 (t, 3H, *J* = 7.3 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 133.9, 129.6, 129.0, 128.9, 67.7, 37.8, 29.6, 28.9, 22.4, 13.9.

FT-IR (neat) 3017, 2952, 2930, 2872, 1497, 1455, 1326, 1305, 1288, 1204, 1137, 1109, 1064, 973, 820, 808 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{13}H_{21}NNaO_2S$: 278, found: 278.

$[\alpha]^{25}_D = -30°$ (c = 1.02, $CHCl_3$).



(*S*)-*N*-Methyl-*N*,1-diphenylpentane-1-sulfonamide (Table 6, entry 2). 1-Bromo-*N*-methyl-*N*-phenylpentane-1-sulfonamide (224 mg, 0.700 mmol) and phenylzinc

iodide (0.910 mmol) were used. The product was purified by column chromatography (10% Et_2O/hexanes). Light-yellow solid. First run: 211 mg (95%, 93% ee). Second run: 211 mg (95%, 95% ee).

The ee was determined by HPLC on a CHIRALCEL OD-H column (2% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 10.5 min (major), 11.7 min (minor).

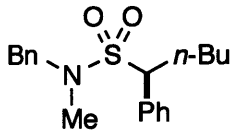
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.35 (m, 5H), 7.31–7.27 (m, 2H), 7.21–7.18 (m, 1H), 7.17–7.14 (m, 2H), 4.11 (dd, 1H, J = 11.4, 3.7 Hz), 2.88 (s, 3H), 2.32 (dddd, 1H, J = 13.6, 10.1, 6.5, 3.7 Hz), 2.14 (dddd, 1H, J = 13.4, 11.4, 9.9, 5.2 Hz), 1.34–1.18 (m, 2H), 1.17–1.03 (m, 2H), 0.80 (t, 3H, J = 7.3 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.7, 133.7, 129.9, 129.1, 129.0, 128.8, 126.5, 125.8, 68.2, 39.2, 30.0, 28.9, 22.4, 13.9.

FT-IR (neat) 3063, 3030, 2957, 2932, 2872, 1596, 1493, 1455, 1423, 1380, 1342, 1266, 1179, 1143, 1108, 1067, 1028, 1003, 969, 917, 880, 801, 765 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{18}H_{23}NNaO_2S$: 340, found: 340.

$[\alpha]^{25}_D = -105°$ (c = 1.01, $CHCl_3$).



(*S*)-*N*-Benzyl-*N*-methyl-1-phenylpentane-1-sulfonamide (Table 6, entry 3). *N*-Benzyl-1-bromo-*N*-methylpentane-1-sulfonamide (234 mg, 0.700 mmol) and phenylzinc iodide (0.910 mmol) were used. The product was purified by column chromatography (7% ethyl acetate/hexanes). Light-yellow solid. First run: 219 mg (94%, 94% ee). Second run: 221 mg (95%, 93% ee).

The ee was determined by HPLC on a CHIRALPAK AD-H column (2% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 25.8 min (major), 28.9 min (minor).

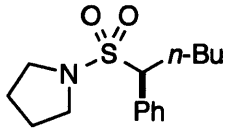
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.36 (m, 5H), 7.31–7.23 (m, 3H), 7.22–7.18 (m, 2H), 4.12 (dd, 1H, *J* = 11.3, 3.8 Hz), 4.01 (d, 1H, *J* = 14.7 Hz), 3.68 (br d, 1H, *J* = 11.0 Hz), 2.42 (s, 3H), 2.38 (dddd, 1H, *J* = 13.7, 10.1, 6.2, 3.8 Hz), 2.21 (dddd, 1H, *J* = 13.5, 11.3, 9.8, 5.2 Hz), 1.42–1.26 (m, 2H), 1.26–1.12 (m, 2H), 0.85 (t, 3H, *J* = 7.3 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 136.3, 133.9, 129.7, 129.0, 128.9, 128.6, 128.3, 127.9, 68.5, 54.2, 34.6, 29.6, 29.0, 22.4, 13.9.

FT-IR (neat) 3063, 3030, 2954, 2930, 2870, 1495, 1454, 1363, 1327, 1214, 1149, 1133, 1075, 1003, 944, 890, 807, 760 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{19}H_{25}NNaO_2S$: 354, found: 354.

$[\alpha]^{25}_D = -54°$ (c = 1.03, $CHCl_3$).



(*S*)-1-((1-Phenylpentyl)sulfonyl)pyrrolidine (Table 6, entry 4). 1-((1-Bromopentyl)sulfonyl)pyrrolidine (199 mg, 0.700 mmol) and phenylzinc iodide (0.910 mmol) were used. The product was purified by column chromatography (10% ethyl acetate/hexanes). White solid. First run: 166 mg (84%, 96% ee). Second run: 170 mg (86%, 96% ee).

The ee was determined by HPLC on a CHIRALPAK AD-H column (2% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 13.8 min (minor), 20.2 min (major).

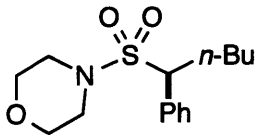
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43–7.39 (m, 2H), 7.39–7.33 (m, 3H), 4.11 (dd, 1H, J = 11.3, 3.8 Hz), 3.21–3.13 (m, 2H), 2.84–2.77 (m, 2H), 2.33 (dddd, 1H, J = 13.8, 10.1, 6.4, 3.8 Hz), 2.17 (dddd, 1H, J = 13.5, 11.3, 9.6, 5.2 Hz), 1.74–1.67 (m, 2H), 1.67–1.58 (m, 2H), 1.39–1.24 (m, 2H), 1.24–1.10 (m, 2H), 0.84 (t, 3H, J = 7.3 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 134.3, 129.7, 128.8, 128.7, 67.7, 48.2, 29.2, 29.0, 25.9, 22.4, 13.9.

FT-IR (neat) 3436, 2957, 2887, 2872, 2857, 1498, 1467, 1456, 1325, 1294, 1240, 1198, 1143, 1128, 1084, 1015, 829, 806, 728 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{15}H_{23}NNaO_2S$: 304, found: 304.

$[\alpha]^{25}_D = -51°$ (c = 0.97, $CHCl_3$).



(*S*)-4-((1-Phenylpentyl)sulfonyl)morpholine (Table 6, entry 5). 4-((1-Bromopentyl)sulfonyl)morpholine (210 mg, 0.700 mmol) and phenylzinc iodide (0.910 mmol) were used. The product was purified by column chromatography (20% ethyl acetate/hexanes). White solid. First run: 197 mg (95%, 98% ee). Second run: 186 mg (89%, 95% ee).

The ee was determined by HPLC on a CHIRALCEL OD-H column (3% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 13.9 min (major), 16.7 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44–7.35 (m, 5H), 4.02 (dd, 1H, J = 11.3, 3.8 Hz), 3.56–3.52 (m, 2H), 3.48–3.43 (m, 2H), 3.06–3.02 (m, 2H), 2.75 (br s, 2H), 2.34 (dddd,

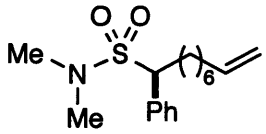
1H, J = 13.8, 10.1, 6.3, 3.8 Hz), 2.13 (dddd, 1H, J = 13.4, 11.3, 9.8, 5.1 Hz), 1.39–1.23 (m, 2H), 1.23–1.08 (m, 2H), 0.84 (t, 3H, J = 7.3 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 133.5, 129.7, 129.2, 129.0, 68.5, 67.0, 46.3, 29.7, 28.9, 22.4, 13.9.

FT-IR (neat) 2955, 2923, 2859, 1496, 1455, 1336, 1323, 1257, 1214, 1152, 1128, 1110, 1076, 955, 924, 848, 803 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{15}H_{23}NNaO_3S$: 320, found: 320.

$[\alpha]^{25}_D = -34°$ (c = 1.02, $CHCl_3$).



(*S*)-*N*,*N*-Dimethyl-1-phenylnon-8-ene-1-sulfonamide (Table 6, entry 6). 1-Bromo-*N*,*N*-dimethylnon-8-ene-1-sulfonamide (219 mg, 0.700 mmol) and phenylzinc iodide (0.910 mmol) were used. The product was purified by column chromatography (5%→10% ethyl acetate/hexanes). Light-yellow solid. First run: 192 mg (89%, 95% ee). Second run: 189 mg (87%, 95% ee).

The ee was determined by HPLC on a CHIRALCEL OD-H column (1% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 12.8 min (major), 20.6 min (minor).

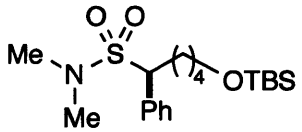
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.34 (m, 5H), 5.76 (dddd, 1H, J = 16.9, 10.2, 6.7, 6.7 Hz), 4.96 (dddd, 1H, J = 17.1, 2.2, 1.6, 1.6 Hz), 4.91 (dddd, 1H, J = 10.2, 2.3, 1.2, 1.2 Hz), 4.08 (dd, 1H, J = 11.3, 3.9 Hz), 2.53 (s, 6H), 2.30 (dddd, 1H, J = 13.7, 10.2, 6.5, 3.9 Hz), 2.19–2.11 (m, 1H), 2.01–1.96 (m, 2H), 1.35–1.11 (m, 8H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.1, 133.9, 129.6, 129.0, 128.9, 114.4, 67.7, 37.8, 33.8, 29.8, 29.1, 28.8, 26.7.

FT-IR (neat) 3062, 2924, 2853, 1640, 1497, 1468, 1456, 1414, 1327, 1208, 1137, 1066, 977, 912, 824 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{17}H_{27}NNaO_2S$: 332, found: 332.

$[\alpha]^{25}_D = -19.2°$ (c = 0.98, $CHCl_3$).



(*S*)-5-((*tert*-Butyldimethylsilyl)oxy)-*N*,*N*-dimethyl-1-phenylpentane-1-sulfonamide (Table 6, entry 7). 1-Bromo-5-((*tert*-butyldimethylsilyl)oxy)-*N*,*N*-dimethylpentane-1-sulfonamide (272 mg, 0.700 mmol) and phenylzinc iodide (0.910 mmol) were used. The product was purified by column chromatography (2%→20% ethyl acetate/hexanes). White solid. First run: 248 mg (92%, >99% ee). Second run: 250 mg (93%, 98% ee).

The ee was determined by HPLC on a CHIRALCEL OD-H column (2% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 8.2 min (major), 11.0 min (minor).

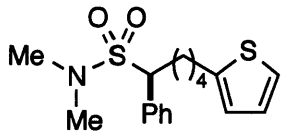
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.33 (m, 5H), 4.09 (dd, 1H, *J* = 11.3, 3.9 Hz), 3.56–3.49 (m, 2H), 2.53 (s, 6H), 2.35–2.28 (m, 1H), 2.21–2.13 (m, 1H), 1.57–1.42 (m, 2H), 1.27–1.18 (m, 2H), 0.82 (s, 9H), –0.02 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 133.7, 129.6, 129.0, 128.9, 67.6, 62.7, 37.8, 32.4, 29.7, 26.0, 23.1, 18.4, –5.2.

FT-IR (neat) 3065, 2931, 2897, 2860, 1458, 1385, 1359, 1329, 1280, 1257, 1200, 1143, 1132, 1110, 1092, 966, 900, 872, 833, 808, 779, 736 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{19}H_{35}NNaO_3SSi$: 408, found: 408.

$[\alpha]^{25}_D = -15.0°$ (c = 0.98, $CHCl_3$).



(*S*)-*N*,*N*-Dimethyl-1-phenyl-5-(thiophen-2-yl)pentane-1-sulfonamide (Table 6, entry 8). 1-Bromo-*N*,*N*-dimethyl-5-(thiophen-2-yl)pentane-1-sulfonamide (238 mg, 0.700 mmol) and phenylzinc iodide (1.05 mmol) were used. The product was purified by column chromatography (10%→15% ethyl acetate/hexanes). Yellow solid. First run: 128 mg (54%, 90% ee). Second run: 131 mg (55%, 91% ee).

The ee was determined by HPLC on a CHIRALCEL OD-H column (5% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 18.3 min (major), 22.8 min (minor).

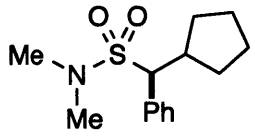
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.34 (m, 5H), 7.08 (dd, 1H, *J* = 5.1, 1.2 Hz), 6.88 (dd, 1H, *J* = 5.1, 3.4 Hz), 6.71 (dddd, 1H, *J* = 3.3, 1.0, 1.0, 1.0 Hz), 4.08 (dd, 1H, *J* = 11.2, 3.9 Hz), 2.82–2.70 (m, 2H), 2.52 (s, 6H), 2.39–2.32 (m, 1H), 2.23–2.15 (m, 1H), 1.74–1.61 (m, 2H), 1.35–1.21 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.1, 133.8, 129.6, 129.0, 128.9, 126.8, 124.2, 123.0, 67.6, 37.8, 31.4, 29.65, 29.59, 26.2.

FT-IR (neat) 3064, 2932, 2856, 1495, 1480, 1454, 1331, 1282, 1200, 1140, 1062, 1030, 967, 849, 820 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{17}H_{23}NNaO_2S_2$: 360, found: 360.

$[\alpha]^{25}_D = -9.4°$ (c = 0.99, $CHCl_3$).



(*S*)-1-Cyclopentyl-*N*,*N*-dimethyl-1-phenylmethanesulfonamide (Table 6, entry 9). 1-Bromo-1-cyclopentyl-*N*,*N*-dimethylmethanesulfonamide (189 mg, 0.700 mmol) and phenylzinc iodide (1.05 mmol) were used. The product was purified by column chromatography (first purification: 10% ethyl acetate/hexanes; second purification: 12%→100% dichloromethane/hexanes). White solid. First run: 86 mg (46%, >99% ee). Second run: 79 mg (42%, >99% ee).

The ee was determined by HPLC on a CHIRALCEL OD-H column (1% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 12.7 min (major), 14.6 min (minor).

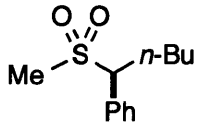
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.38 (m, 2H), 7.37–7.31 (m, 3H), 3.92 (d, 1H, *J* = 10.3 Hz), 2.78–2.69 (m, 1H), 2.43 (s, 6H), 2.29–2.22 (m, 1H), 1.75–1.67 (m, 1H), 1.66–1.60 (m, 1H), 1.59–1.41 (m, 4H), 1.03–0.95 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.2, 129.7, 128.69, 128.67, 73.2, 41.8, 37.6, 32.3, 32.1, 25.5, 24.1.

FT-IR (neat) 3090, 3064, 3025, 2960, 2871, 2812, 1496, 1479, 1452, 1323, 1293, 1206, 1188, 1131, 1081, 1063, 1030, 1003, 969, 911, 872, 848, 807, 732 cm^{-1}.

MS (EI) *m/z* (M^+–SO_2NMe_2) calcd for $C_{12}H_{15}$: 159, found: 159.

$[\alpha]^{25}_D = -43°$ (c = 1.04, $CHCl_3$).



(*S*)-(1-(Methylsulfonyl)pentyl)benzene (Table 7, entry 1). 1-Bromo-1-(methylsulfonyl)pentane (160 mg, 0.700 mmol) and phenylzinc iodide (0.910 mmol) were used. The product was purified by column chromatography (20%→30% ethyl acetate/hexanes). White solid. First run: 150 mg (95%, 94% ee). Second run: 153 mg (97%, 94% ee).

The ee was determined by HPLC on a CHIRALCEL OD-H column (5% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 17.6 min (major), 20.8 min (minor).

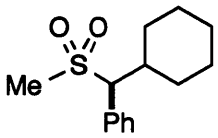
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.37 (m, 5H), 3.99 (dd, 1H, *J* = 11.5, 3.7 Hz), 2.59 (s, 3H), 2.45–2.37 (m, 1H), 2.12 (dddd, 1H, *J* = 13.6, 11.5, 9.6, 5.3 Hz), 1.41–1.26 (m, 2H), 1.25–1.14 (m, 2H), 0.85 (t, 3H, *J* = 7.1 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 133.4, 129.5, 129.28, 129.27, 70.4, 38.7, 28.9, 26.7, 22.4, 13.9.

FT-IR (neat) 3088, 3065, 3051, 3011, 2931, 2869, 1496, 1468, 1456, 1417, 1379, 1292, 1277, 1263, 1211, 1158, 1130, 1107, 1072, 1036, 966, 936, 904, 805, 722 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{12}H_{18}NaO_2S$: 249, found: 249.

$[\alpha]^{25}_D = -6.2°$ (c = 1.00, $CHCl_3$).



(*S*)-(Cyclohexyl(methylsulfonyl)methyl)benzene (Table 7, entry 2). (Bromo(methylsulfonyl)methyl)cyclohexane (179 mg, 0.700 mmol) and phenylzinc

iodide (1.05 mmol) were used. The product was purified by column chromatography (10%→15% ethyl acetate/hexanes). White solid. First run: 145 mg (82%, 99% ee). Second run: 148 mg (84%, 99% ee).

The ee was determined by HPLC on a CHIRALPAK AD-H column (4% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 16.7 min (minor), 25.8 min (major).

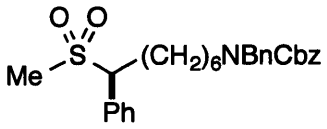
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43–7.36 (m, 5H), 3.87 (d, 1H, J = 7.9 Hz), 2.53–2.45 (m, 1H), 2.46 (s, 3H), 2.29–2.24 (m, 1H), 1.80–1.74 (m, 1H), 1.67–1.56 (m, 3H), 1.42–1.33 (m, 1H), 1.28–1.18 (m, 2H), 1.14–1.05 (m, 1H), 0.93–0.85 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 133.9, 129.8, 129.2, 129.1, 75.9, 41.4, 38.1, 32.4, 30.6, 26.11, 26.06, 26.0.

FT-IR (neat) 3004, 2930, 2853, 1496, 1454, 1413, 1378, 1348, 1319, 1302, 1292, 1244, 1221, 1170, 1127, 1076, 1036, 970, 896, 854, 804, 742 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{14}H_{20}NaO_2S$: 275, found: 275.

$[\alpha]^{25}_D = -40°$ (c = 1.06, $CHCl_3$).



Benzyl (*S*)-benzyl(7-(methylsulfonyl)-7-phenylheptyl)carbamate (Table 7, entry 3). Benzyl benzyl(7-bromo-7-(methylsulfonyl)heptyl)carbamate (199 mg, 0.400 mmol) and phenylzinc iodide (0.520 mmol) were used. The product was purified by column chromatography on silica gel (25% ethyl acetate/hexanes) and then preparative HPLC on C-18 silica gel (80%→100% acetonitrile/water; water was doped with 0.1%

AcOH). Viscous colorless oil. First run: 149 mg (75%, 89% ee). Second run: 145 mg (73%, 91% ee).

The ee was determined by HPLC on a CHIRALCEL OD-H column (20% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 31.5 min (major), 40.0 min (minor).

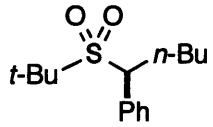
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.44–7.17 (m, 15H), 5.14–5.12 (m, 2H), 4.45 (s, 2H), 4.01–3.95 (m, 1H), 3.22–3.15 (m, 2H), 2.59 (s, 3H), 2.35–2.23 (br m, 1H), 2.12–1.99 (br m, 1H), 1.48–1.40 (br m, 2H), 1.35–1.09 (br m, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 156.9, 156.3, 138.7, 137.6, 133.6, 129.9, 129.40, 129.36, 128.8, 128.7, 128.2, 128.01, 127.95, 127.5, 70.3, 67.3, 50.8, 50.4, 47.4, 46.7, 38.9, 29.2, 28.4, 27.9, 27.4, 26.9, 26.8.

FT-IR (neat) 3088, 3063, 3031, 3007, 2931, 2858, 1697, 1605, 1586, 1496, 1468, 1454, 1422, 1366, 1305, 1232, 1137, 1086, 1071, 1029, 1002, 954, 916, 801 cm^{-1}.

MS (ESI) *m/z* (M^++H) calcd for $C_{29}H_{36}NO_4S$: 494, found: 494.

$[\alpha]^{25}_D = -0.037°$ (c = 4.1, $CHCl_3$).



(*S*)-(1-(*tert*-Butylsulfonyl)pentyl)benzene(Table 7, entry 4). 1-Bromo-1-(*tert*-butylsulfonyl)pentane (190 mg, 0.700 mmol) and phenylzinc iodide (0.910 mmol) were used. The product was purified by column chromatography (15% ethyl acetate/hexanes). White solid. First run: 179 mg (95%, 99% ee). Second run: 182 mg (97%, 98% ee).

The ee was determined by HPLC on a CHIRALPAK IB-3 column (1% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 8.4 min (major), 9.9 min (minor).

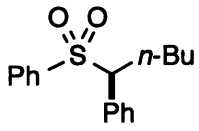
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.45 (m, 2H), 7.39–7.32 (m, 3H), 4.14 (dd, 1H, J = 11.6, 3.3 Hz), 2.47 (dddd, 1H, J = 13.6, 10.6, 6.2, 3.3 Hz), 2.06 (dddd, 1H, J = 13.4, 11.6, 10.2, 4.9 Hz), 1.40–1.30 (m, 1H), 1.29–1.21 (m, 1H), 1.16 (s, 9H), 1.15–1.01 (m, 2H), 0.82 (t, 3H, J = 7.3 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 134.9, 129.6, 129.0, 128.9, 65.3, 62.1, 28.9, 28.7, 24.4, 22.4, 13.9.

FT-IR (neat) 3032, 2986, 2954, 2872, 1497, 1466, 1455, 1366, 1279, 1190, 1115, 1100, 782 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{15}H_{24}NaO_2S$: 291, found: 291.

$[\alpha]^{25}_D = -20.3°$ (c = 1.01, $CHCl_3$).



(*S*)-((1-Phenylpentyl)sulfonyl)benzene (Table 7, entry 5). ((1-Bromopentyl)sulfonyl)benzene (204 mg, 0.700 mmol) and phenylzinc iodide (0.910 mmol) were used. The product was purified by column chromatography (10%→20% Et_2O/hexanes). White solid. First run: 195 mg (97%, 86% ee). Second run: 193 mg (96%, 83% ee).

The ee was determined by HPLC on a CHIRALCEL OD-H column (1% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 13.6 min (major), 18.7 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54–7.49 (m, 3H), 7.38–7.34 (m, 2H), 7.29–7.26 (m, 1H), 7.24–7.20 (m, 2H), 7.10–7.07 (m, 2H), 4.01 (dd, 1H, J = 11.6, 3.6 Hz), 2.46–

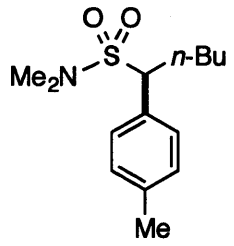
2.39 (m, 1H), 2.20–2.10 (m, 1H), 1.38–1.23 (m, 2H), 1.22–1.13 (m, 2H), 0.83 (t, 3H, J = 7.3 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.6, 133.5, 132.6, 130.0, 129.2, 128.8, 128.7, 128.6, 71.8, 29.0, 27.1, 22.4, 13.9.

FT-IR (neat) 2952, 2926, 2857, 1584, 1496, 1467, 1455, 1447, 1379, 1316, 1304, 1294, 1214, 1147, 1084, 1070, 1037, 1024, 998, 968, 800, 758, 713 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{17}H_{20}NaO_2S$: 311, found: 311.

$[\alpha]^{25}_D = -78°$ (c = 1.08, $CHCl_3$).



(*S*)-*N*,*N*-Dimethyl-1-(*p*-tolyl)pentane-1-sulfonamide (Table 8, entry 1). 1-Bromo-*N*,*N*-dimethylpentane-1-sulfonamide (181 mg, 0.700 mmol) and *p*-tolylzinc iodide (0.910 mmol) were used. The product was purified by column chromatography (20% Et_2O/hexanes). Light-yellow oil. First run: 172 mg (91%, 96% ee). Second run: 165 mg (87%, 95% ee).

The ee was determined by HPLC on a CHIRALCEL OD-H column (2% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 8.1 min (major), 10.1 min (minor).

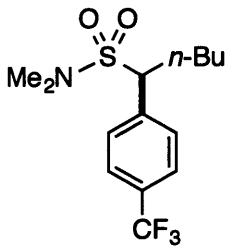
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.27 (m, 2H), 7.19–7.17 (m, 2H), 4.05 (dd, 1H, J = 11.3, 3.8 Hz), 2.54 (s, 6H), 2.36 (s, 3H), 2.29 (dddd, 1H, J = 13.7, 10.1, 6.4, 3.8 Hz), 2.12 (dddd, 1H, J = 13.5, 11.4, 9.7, 5.3 Hz), 1.38–1.22 (m, 2H), 1.22–1.09 (m, 2H), 0.83 (t, 3H, J = 7.3 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.8, 130.8, 129.6, 129.5, 67.4, 37.8, 29.6, 28.9, 22.4, 21.3, 13.9.

FT-IR (neat) 3025, 2956, 2932, 2872, 2811, 1515, 1479, 1457, 1413, 1380, 1331, 1283, 1204, 1141, 1107, 1062, 1022, 968, 843, 832, 716 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{14}H_{23}NNaO_2S$: 292, found: 292.

$[\alpha]^{25}_D = -30°$ (c = 0.99, $CHCl_3$).



(*S*)-*N*,*N*-Dimethyl-1-(4-(trifluoromethyl)phenyl)pentane-1-sulfonamide (Table 8, entry 2). An oven-dried 8-mL vial equipped with a magnetic stir bar was capped with a PTFE-lined septum cap, cooled under vacuum, and filled with nitrogen. 4-Iodobenzotrifluoride (248 mg, 0.910 mmol) and THF (1.35 mL) were added to the vial, followed by the dropwise addition over 1 min of *i*-PrMgCl (1.92 M in THF; 0.474 mL, 0.910 mmol), and the resulting mixture was stirred at r.t. for 1 h. An oven-dried 4-mL vial equipped with a magnetic stir bar was capped with a PTFE-lined septum cap, cooled under vacuum, and filled with nitrogen. ZnI_2 (290 mg, 0.910 mmol) was added into the vial. The vial was immediately evacuated and refilled with nitrogen (three cycles), and then THF (1.82 mL) was added to the vial. The solution of ZnI_2 was transferred by syringe to the Grignard reagent, and then the reaction mixture was stirred at r.t. for 30 min.

1-Bromo-*N*,*N*-dimethylpentane-1-sulfonamide (181 mg, 0.700 mmol) and (4-(trifluoromethyl)phenyl)zinc iodide (0.910 mmol) were used. The product was purified by column chromatography (20% Et_2O/hexanes). Light-yellow solid. First run: 209 mg (92%, 98% ee). Second run: 216 mg (95%, 98% ee).

The ee was determined by HPLC on a CHIRALCEL OD-H column (3% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 8.8 min (major), 12.0 min (minor).

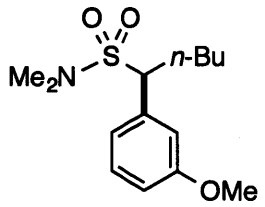
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, 2H, J = 8.2 Hz), 7.55 (d, 2H, J = 8.2 Hz), 4.14 (dd, 1H, J = 11.4, 3.8 Hz), 2.58 (s, 6H), 2.32 (dddd, 1H, J = 13.9, 10.3, 6.3, 3.9 Hz), 2.14 (dddd, 1H, J = 13.7, 11.4, 10.1, 4.9 Hz), 1.38–1.24 (m, 2H), 1.22–1.06 (m, 2H), 0.84 (t, 3H, J = 7.3 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.2 (d, J_{CF} = 1.3 Hz), 131.1 (q, J_{CF} = 32.7 Hz), 130.0, 125.8 (q, J_{CF} = 3.7 Hz), 123.6 (q, J_{CF} = 272.2 Hz), 67.3, 37.8, 29.6, 28.8, 22.3, 13.8.

FT-IR (neat) 2958, 2875, 1325, 1167, 1122, 1069, 1019, 968, 856, 727 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{14}H_{20}F_3NNaO_2S$: 346, found: 346.

$[\alpha]^{25}_D$ = −23.3° (c = 1.02, $CHCl_3$).



(*S*)-1-(3-Methoxyphenyl)-*N*,*N*-dimethylpentane-1-sulfonamide (Table 8, entry 3). 1-Bromo-*N*,*N*-dimethylpentane-1-sulfonamide (181 mg, 0.700 mmol) and (3-methoxyphenyl)zinc iodide (0.910 mmol) were used. The product was purified by

column chromatography (15% ethyl acetate/hexanes). White solid. First run: 175 mg (88%, 95% ee). Second run: 174 mg (87%, 96% ee).

The ee was determined by HPLC on a CHIRALCEL OD-H column (3% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 10.5 min (major), 12.9 min (minor).

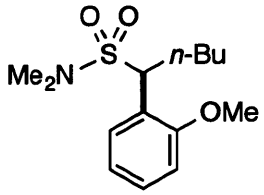
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.27 (m, 1H), 6.99–6.97 (m, 2H), 6.90–6.88 (m, 1H), 4.05 (dd, 1H, *J* = 11.3, 3.8 Hz), 3.82 (s, 3H), 2.56 (s, 6H), 2.29 (dddd, 1H, *J* = 13.6, 10.2, 6.6, 3.8 Hz), 2.12 (dddd, 1H, *J* = 13.5, 11.3, 9.8, 5.2 Hz), 1.38–1.23 (m, 2H), 1.23–1.10 (m, 2H), 0.84 (t, 3H, *J* = 7.3 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.9, 135.4, 129.8, 122.0, 115.2, 114.2, 67.6, 55.5, 37.8, 29.7, 28.9, 22.4, 13.9.

FT-IR (neat) 3002, 2956, 2873, 2839, 1601, 1585, 1489, 1456, 1438, 1380, 1330, 1262, 1204, 1142, 1111, 1049, 968, 888, 806 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{14}H_{23}NNaO_3S$: 308, found: 308.

$[\alpha]^{25}_D = -28°$ (c = 1.00, $CHCl_3$).



(*S*)-1-(2-Methoxyphenyl)-*N*,*N*-dimethylpentane-1-sulfonamide (Table 8, entry 4). 1-Bromo-*N*,*N*-dimethylpentane-1-sulfonamide (181 mg, 0.700 mmol) and (2-methoxyphenyl)zinc iodide (1.05 mmol) were used. The product was purified by column chromatography on silica gel (10%→15% ethyl acetate/hexanes) and then on C-18 silica

gel (10%→100% acetonitrile/water). Light-yellow oil. First run: 125 mg (63%, 96% ee). Second run: 128 mg (64%, 96% ee).

The ee was determined by HPLC on a CHIRALPAK AS-H column (5% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 16.6 min (major), 19.3 min (minor).

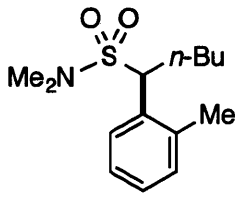
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, 1H, *J* = 7.8, 1.7 Hz), 7.30 (ddd, 1H, *J* = 8.2, 7.4, 1.7 Hz), 7.00 (ddd, 1H, *J* = 7.6, 7.6, 1.1 Hz), 6.91 (dd, 1H, *J* = 8.3, 1.1 Hz), 4.87 (dd, 1H, *J* = 11.4, 3.9 Hz), 3.87 (s, 3H), 2.51 (s, 6H), 2.32 (dddd, 1H, *J* = 13.7, 10.2, 6.4, 3.9 Hz), 2.13–2.05 (m, 1H), 1.36–1.22 (m, 2H), 1.22–1.07 (m, 2H), 0.83 (t, 3H, *J* = 7.3 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.7, 129.7, 129.6, 122.2, 121.1, 110.5, 57.3, 55.8, 37.6, 29.7, 28.6, 22.4, 13.9.

FT-IR (neat) 3070, 3005, 2957, 2873, 1601, 1587, 1494, 1463, 1442, 1380, 1330, 1290, 1247, 1202, 1142, 1124, 1090, 1052, 1026, 967, 796, 756, 726 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{14}H_{23}NNaO_3S$: 308, found: 308.

$[\alpha]^{25}_D$ = +40° (c = 1.03, $CHCl_3$).



(*S*)-*N*,*N*-Dimethyl-1-(*o*-tolyl)pentane-1-sulfonamide (Table 8, entry 5). 1-Bromo-*N*,*N*-dimethylpentane-1-sulfonamide (181 mg, 0.700 mmol) and *o*-tolylzinc iodide (1.05 mmol) were used. The product was purified by column chromatography

(5%→10% ethyl acetate/hexanes). Light-yellow oil. First run: 148 mg (78%, 97% ee). Second run: 149 mg (79%, 97% ee).

The ee was determined by HPLC on a CHIRALCEL OD-H column (2% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 9.8 min (major), 11.9 min (minor).

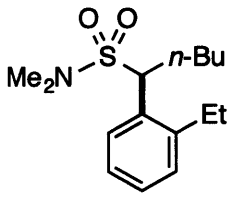
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62–7.58 (m, 1H), 7.25–7.19 (m, 3H), 4.43 (dd, 1H, J = 11.3, 3.8 Hz), 2.60 (s, 6H), 2.39 (s, 3H), 2.33 (dddd, 1H, J = 13.6, 10.1, 6.1, 3.8 Hz), 2.16–2.08 (m, 1H), 1.37–1.22 (m, 2H), 1.21–1.06 (m, 2H), 0.83 (t, 3H, J = 7.3 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.4, 132.3, 130.7, 128.4, 128.3, 126.6, 63.2, 38.0, 30.7, 28.7, 22.6, 20.1, 13.9.

FT-IR (neat) 3064, 3023, 2957, 2872, 2813, 1604, 1493, 1461, 1380, 1329, 1283, 1203, 1178, 1141, 1119, 1063, 967, 834, 802 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{14}H_{23}NNaO_2S$: 292, found: 292.

$[\alpha]^{25}_D$ = +7.9° (c = 1.05, $CHCl_3$).



(*S*)-1-(2-Ethylphenyl)-*N*,*N*-dimethylpentane-1-sulfonamide (Table 8, entry 6). 1-Bromo-*N*,*N*-dimethylpentane-1-sulfonamide (181 mg, 0.700 mmol), (2-ethylphenyl)zinc iodide (1.40 mmol), $NiCl_2$•glyme (30.8 mg, 0.140 mmol), and (*R*,*R*)-**L8** (60.9 mg, 0.182 mmol) were used. The product was purified by column chromatography (first purification: 10% ethyl acetate/hexanes; second purification: 15%→90%

dichloromethane/hexanes). Light-yellow oil. First run: 178 mg (90%, 97% ee). Second run: 165 mg (83%, 97% ee).

The ee was determined by HPLC on a CHIRALPAK IC column (15% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 16.9 min (minor), 22.7 min (major).

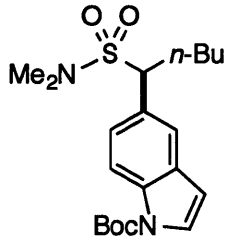
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.57–7.54 (m, 1H), 7.30–7.22 (m, 3H), 4.46 (dd, 1H, J = 11.1, 4.0 Hz), 2.79 (dq, 1H, J = 14.9, 7.5 Hz), 2.68 (dq, 1H, J = 15.2, 7.6 Hz), 2.62 (s, 6H), 2.29–2.22 (m, 1H), 2.15–2.07 (m, 1H), 1.39–1.24 (m, 2H), 1.22 (t, 3H, J = 7.6 Hz), 1.24–1.15 (m, 1H), 1.13–1.04 (m, 1H), 0.84 (t, 3H, J = 7.3 Hz).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 144.1, 131.9, 129.2, 128.7, 128.5, 126.5, 62.8, 38.0, 30.8, 29.3, 26.0, 23.0, 15.7, 13.9.

FT-IR (neat) 3063, 3021, 2959, 2933, 2873, 2813, 1490, 1455, 1378, 1330, 1282, 1201, 1177, 1141, 1120, 1062, 968, 803, 760 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{15}H_{25}NNaO_2S$: 306, found: 306.

$[\alpha]^{25}_D$ = +8.9° (c = 1.03, $CHCl_3$).



***tert*-Butyl (*S*)-5-(1-(*N*,*N*-dimethylsulfamoyl)pentyl)-1*H*-indole-1-carboxylate (Table 8, entry 7).** An oven-dried 8-mL vial equipped with a magnetic stir bar was capped with a PTFE-lined septum cap, cooled under vacuum, and filled with nitrogen. *tert*-Butyl 5-iodo-1*H*-indole-1-carboxylate (360 mg, 1.05 mmol) was added to the vial, and then the vial was evacuated and refilled with nitrogen (three cycles). THF (1.56 mL)

was added to the vial, and the vial was wrapped with electrical tape and fitted with a nitrogen-filled balloon. Then, the reaction mixture was cooled to –20 °C. *i*-PrMgCl (1.93 M in THF; 0.544 mL, 1.05 mmol) was added over 1 min, and the mixture was stirred at –20 °C for 2 h. An oven-dried 4-mL vial equipped with a magnetic stir bar was capped with a PTFE-lined septum cap, cooled under vacuum, and filled with nitrogen. ZnI_2 (338 mg, 1.06 mmol) was added to the vial. The vial was immediately placed under vacuum and then filled with nitrogen. This evacuation-refill cycle was repeated three times, and then THF (2.10 mL) was added to the vial. The solution of ZnI_2 was transferred by syringe to the Grignard reagent, and then the reaction mixture was stirred at –20 °C for 30 min. The reaction mixture was allowed to warm to r.t. and stirred for an additional 30 min.

1-Bromo-*N*,*N*-dimethylpentane-1-sulfonamide (181 mg, 0.700 mmol) and (1-(*tert*-butoxycarbonyl)-1*H*-indol-5-yl)zinc iodide (1.05 mmol) were used. The product was purified by column chromatography on silica gel (10%→15% ethyl acetate/hexanes) and then on C-18 silica gel (10%→100% acetonitrile/water). Yellow solid. First run: 180 mg (65%, 88% ee). Second run: 200 mg (72%, 90% ee).

The ee was determined by HPLC on a CHIRALCEL OD-H column (2% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 11.7 min (major), 15.4 min (minor).

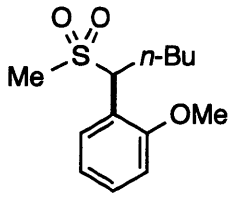
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, 1H, *J* = 8.5 Hz), 7.63–7.62 (m, 2H), 7.33 (dd, 1H, *J* = 8.6, 1.8 Hz), 6.58 (dd, 1H, *J* = 3.7, 0.8 Hz), 4.18 (dd, 1H, *J* = 11.4, 3.8 Hz), 2.51 (s, 6H), 2.36 (dddd, 1H, *J* = 13.7, 10.2, 6.4, 3.8 Hz), 2.20 (dddd, 1H, *J* = 13.6, 11.4, 10.0, 5.0 Hz), 1.68 (s, 9H), 1.38–1.23 (m, 2H), 1.22–1.08 (m, 2H), 0.82 (t, 3H, *J* = 7.3 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.7, 135.4, 130.9, 128.0, 126.9, 125.7, 121.9, 115.4, 107.4, 84.2, 67.6, 37.9, 29.9, 28.9, 28.3, 22.4, 13.9.

FT-IR (neat) 3152, 3120, 2956, 2934, 2873, 1736, 1536, 1470, 1445, 1374, 1351, 1329, 1256, 1218, 1193, 1164, 1138, 1107, 1084, 1042, 1024, 968, 841, 768, 729 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{20}H_{30}N_2NaO_4S$: 417, found: 417.

$[\alpha]^{25}_D = -23.7°$ (c = 1.04, $CHCl_3$).



(*S*)-1-Methoxy-2-(1-(methylsulfonyl)pentyl)benzene (Table 8, entry 8). 1-Bromo-1-(methylsulfonyl)pentane (160 mg, 0.700 mmol) and (2-methoxyphenyl)zinc iodide (0.910 mmol) were used. The product was purified by column chromatography (20%→25% ethyl acetate/hexanes). Colorless oil. First run: 148 mg (82%, 96% ee). Second run: 154 mg (86%, 96% ee).

The ee was determined by HPLC on a CHIRALCEL OD-H column (5% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 17.6 min (minor), 18.9 min (major).

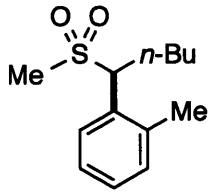
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (dd, 1H, *J* = 7.8, 1.7 Hz), 7.34 (ddd, 1H, *J* = 8.3, 7.4, 1.7 Hz), 7.04 (ddd, 1H, *J* = 7.6, 7.6, 1.1 Hz), 6.93 (dd, 1H, *J* = 8.3, 1.1 Hz), 4.81 (dd, 1H, *J* = 11.5, 3.9 Hz), 3.87 (s, 3H), 2.58 (s, 3H), 2.40 (dddd, 1H, *J* = 13.5, 9.6, 6.9, 3.9 Hz), 2.05 (dddd, 1H, *J* = 13.5, 11.5, 9.4, 5.3 Hz), 1.38–1.24 (m, 2H), 1.23–1.12 (m, 2H), 0.84 (t, 3H, *J* = 7.3 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.6, 130.1, 129.2, 121.7, 121.6, 110.9, 60.4, 55.9, 38.6, 28.7, 25.9, 22.4, 13.9.

FT-IR (neat) 3009, 2957, 2872, 1601, 1587, 1494, 1464, 1440, 1412, 1380, 1296, 1247, 1192, 1164, 1137, 1090, 1051, 1025, 956, 792, 755 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{13}H_{20}NaO_3S$: 279, found: 279.

$[\alpha]^{25}_D$ = +61° (c = 1.00, $CHCl_3$).



(*S*)-1-Methyl-2-(1-(methylsulfonyl)pentyl)benzene (Table 8, entry 9). 1-Bromo-1-(methylsulfonyl)pentane (160 mg, 0.700 mmol) and *o*-tolylzinc iodide (0.910 mmol) were used. The product was purified by column chromatography (15%→20% ethyl acetate/hexanes). Colorless oil. First run: 137 mg (81%, 97% ee). Second run: 134 mg (80%, 97% ee).

The ee was determined by HPLC on a CHIRALPAK AS-H column (10% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 18.4 min (minor), 28.0 min (major).

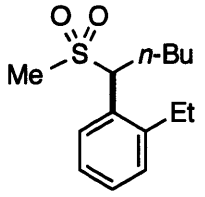
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.52–7.50 (m, 1H), 7.30–7.23 (m, 3H), 4.37 (dd, 1H, *J* = 11.4, 3.7 Hz), 2.61 (s, 3H), 2.40 (s, 3H), 2.37–2.31 (m, 1H), 2.12–2.04 (m, 1H), 1.40–1.24 (m, 2H), 1.24–1.10 (m, 2H), 0.84 (t, 3H, *J* = 7.3 Hz).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 138.4, 132.0, 131.2, 129.0, 127.9, 127.1, 65.0, 38.7, 29.1, 28.5, 22.8, 20.3, 13.9.

FT-IR (neat) 3025, 2957, 2931, 2872, 1493, 1464, 1411, 1380, 1294, 1224, 1208, 1177, 1138, 1113, 1051, 958, 825, 796, 771, 736 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{13}H_{20}NaO_2S$: 263, found: 263.

$[\alpha]^{25}_D$ = +24.2° (c = 0.99, $CHCl_3$).



(*S*)-1-Ethyl-2-(1-(methylsulfonyl)pentyl)benzene (Table 8, entry 10). 1-Bromo-1-(methylsulfonyl)pentane (160 mg, 0.700 mmol), (2-ethylphenyl)zinc iodide (1.40 mmol), $NiCl_2$•glyme (30.8 mg, 0.140 mmol), and (*R*,*R*)–**L8** (60.9 mg, 0.182 mmol) were used. The product was purified by column chromatography (15% ethyl acetate/hexanes). Light-yellow oil. First run: 145 mg (81%, 98% ee). Second run: 146 mg (82%, 98% ee).

The ee was determined by HPLC on a CHIRALPAK AS-H column (10% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 13.1 min (minor), 22.1 min (major).

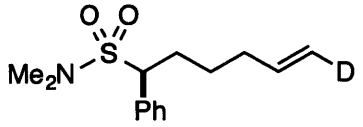
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.52–7.51 (m, 1H), 7.34–7.26 (m, 3H), 4.41 (dd, 1H, *J* = 11.2, 3.9 Hz), 2.82–2.75 (m, 1H), 2.73–2.66 (m, 1H), 2.62 (s, 3H), 2.35 (dddd, 1H, *J* = 13.5, 11.0, 5.7, 3.8 Hz), 2.12–2.04 (m, 1H), 1.41–1.20 (m, 3H), 1.23 (t, 3H, *J* = 7.6 Hz), 1.19–1.09 (m, 1H), 0.85 (t, 3H, *J* = 7.2 Hz).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 144.4, 131.2, 129.6, 129.1, 127.9, 126.9, 64.5, 38.8, 29.3, 28.7, 26.2, 23.0, 15.7, 13.9.

FT-IR (neat) 3063, 3026, 2960, 2932, 2873, 1491, 1453, 1411, 1379, 1294, 1218, 1176, 1138, 1113, 1061, 958, 831, 797, 757 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{14}H_{22}NaO_2S$: 277, found: 277.

$[\alpha]^{25}_D$ = +24.1° (c = 1.01, $CHCl_3$).



(*S*,*E*)-*N*,*N*-Dimethyl-1-phenylhex-5-ene-1-sulfonamide-6-*d* (eq 21). White solid.

The ee was determined by HPLC on a CHIRALCEL OD-H column (1% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 13.9 min (major), 17.4 min (minor).

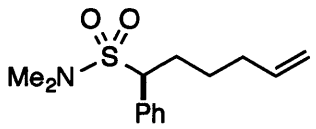
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.34 (m, 5H), 5.70 (dt, 1H, *J* = 17.0, 6.5 Hz), 4.95 (dt, 1H, *J* = 17.1, 1.6 Hz), 4.09 (dd, 1H, *J* = 11.2, 3.9 Hz), 2.53 (s, 6H), 2.32 (dddd, 1H, *J* = 13.9, 10.3, 6.4, 3.9 Hz), 2.20–2.12 (m, 1H), 2.10–1.98 (m, 2H), 1.36–1.22 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.8, 134.0, 129.6, 129.0, 128.9, 115.0 (t, *J* = 24 Hz), 67.8, 37.8, 33.3, 29.5, 26.2.

FT-IR (neat) 3088, 3065, 3024, 2926, 2860, 2822, 2261, 1623, 1496, 1480, 1456, 1436, 1326, 1292, 1256, 1200, 1140, 1064, 1043, 984, 970, 917, 906, 822, 799, 778, 745 cm^{-1}.

MS (EI) *m/z* (M^+–SO_2NMe_2) calcd for $C_{12}H_{14}D$: 160, found: 160.

$[\alpha]^{25}_D$ = –34° (c = 0.99, $CHCl_3$); 96% ee.



(*S*)-*N*,*N*-Dimethyl-1-phenylhex-5-ene-1-sulfonamide (Figure 2). White solid.

The ee was determined by HPLC on a CHIRALCEL OD-H column (1% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 14.1 min (major), 17.8 min (minor).

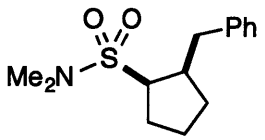
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.34 (m, 5H), 5.70 (ddt, 1H, *J* = 17.0, 10.3, 6.7 Hz), 4.98–4.92 (m, 2H), 4.09 (dd, 1H, *J* = 11.2, 3.9 Hz), 2.53 (s, 6H), 2.32 (dddd, 1H, *J* = 14.1, 10.3, 6.3, 3.9 Hz), 2.20–2.12 (m, 1H), 2.10–1.98 (m, 2H), 1.36–1.22 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.0, 134.0, 129.6, 129.0, 128.9, 115.3, 67.8, 37.8, 33.4, 29.5, 26.2.

FT-IR (neat) 3067, 3033, 2934, 2908, 2868, 2821, 1640, 1497, 1480, 1455, 1417, 1329, 1282, 1199, 1141, 1063, 1043, 993, 966, 916, 906, 870, 814, 781, 746, 735 cm^{-1}.

MS (EI) *m/z* (M^+–SO_2NMe_2) calcd for $C_{12}H_{15}$: 159, found: 159.

$[\alpha]^{25}_D$ = −33° (c = 0.82, $CHCl_3$); 97% ee.



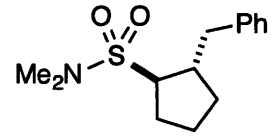
***syn*-2-Benzyl-*N*,*N*-dimethylcyclopentane-1-sulfonamide (Figure 2).** White solid.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.30–7.26 (m, 2H), 7.20–7.16 (m, 3H), 3.54 (ddd, 1H, *J* = 8.7, 8.7, 6.3 Hz), 3.31–3.25 (m, 1H), 2.89 (s, 6H), 2.60–2.52 (m, 2H), 2.15–2.07 (m, 1H), 2.04–1.97 (m, 1H), 1.95–1.87 (m, 1H), 1.66–1.44 (m, 3H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 141.8, 129.4, 128.6, 126.2, 62.8, 44.7, 37.8, 35.7, 29.7, 26.8, 22.7.

FT-IR (neat) 3084, 3060, 3024, 2922, 2874, 2850, 2806, 1602, 1583, 1495, 1473, 1452, 1332, 1273, 1195, 1136, 1073, 1058, 1029, 958, 845, 822, 727 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_{14}H_{21}NO_2S$: 267, found: 267.



***anti*-2-Benzyl-*N*,*N*-dimethylcyclopentane-1-sulfonamide (Figure 2).** Colorless oil.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.32–7.28 (m, 2H), 7.22–7.19 (m, 3H), 3.20 (ddd, 1H, J = 8.9, 6.1, 6.1 Hz), 2.97 (dd, 1H, J = 12.6, 4.9 Hz), 2.78 (s, 6H), 2.65–2.53 (m, 2H), 2.08–1.95 (m, 2H), 1.82–1.74 (m, 1H), 1.73–1.61 (m, 2H), 1.42–1.35 (m, 1H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 140.7, 129.6, 128.7, 126.5, 64.5, 43.6, 41.3, 37.8, 32.1, 28.5, 24.9.

FT-IR (neat) 3084, 3060, 3025, 2917, 2849, 1602, 1583, 1494, 1461, 1453, 1435, 1315, 1199, 1136, 1082, 1059, 1029, 960, 882, 849, 733 cm^{-1}.

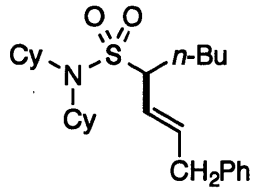
MS (EI) *m/z* (M^+) calcd for $C_{14}H_{21}NO_2S$: 267, found: 267.

IV. Enantioselective Alkenylations

General Procedure. Cp_2ZrHCl (Schwartz's reagent; 258 mg, 1.00 mmol) was added to an oven-dried 4-mL vial equipped with a magnetic stir bar, and then the vial was

capped with a PTFE-lined septum cap. The vial was evacuated and refilled with nitrogen (three cycles). 1,2-Dimethoxyethane (1.00 ml) was added to the vial, followed by the alkyne (1.00 mmol). The reaction mixture was stirred at r.t. for 1.5 h, at which time it had become homogenous. An oven-dried 20-mL vial equipped with a magnetic stir bar was charged with $NiCl_2$•glyme (11.0 mg, 0.050 mmol), (3*R*,8*S*)–**L11** (23.3 mg, 0.065 mmol), and the electrophile (0.500 mmol). The vial was sealed with a PTFE-lined septum cap, placed under vacuum, and then filled with nitrogen. This evacuation-refill cycle was repeated three times. 1,2-Dimethoxyethane (2.57 mL) was added, and the mixture was stirred at r.t. for 1 h. The solution of the nucleophile was transferred by syringe over 2 min to the vial that contained the electrophile. The reaction mixture was stirred at r.t. for 24 h, and then the reaction was quenched by the addition of ethanol (0.50 mL). The solution was filtered through a pad of silica (eluted with Et_2O). The filtrate was concentrated, and the resulting residue was purified by column chromatography.

A second run was conducted with (3*S*,8*R*)–**L11**.



(*S*,*E*)-*N*,*N*-Dicyclohexyl-1-phenyloct-2-ene-4-sulfonamide (Table 9, entry 1). 1-Bromo-*N*,*N*-dicyclohexylpentane-1-sulfonamide (197 mg, 0.500 mmol) and (*E*)-(3-phenylprop-1-en-1-yl)zirconium reagent (1.00 mmol) were used. The product was purified by column chromatography on silica gel (5% Et_2O/hexanes) and then on C-18

silica gel (10%→100% acetonitrile/water). Viscous light-yellow oil. First run: 179 mg (83%, 95% ee). Second run: 180 mg (83%, 94% ee).

The ee was determined by HPLC on a CHIRALPAK AD-H column (1% *i*-PrOH/hexanes, 0.6 mL/min) with t_r = 16.6 min (major), 17.7 min (minor).

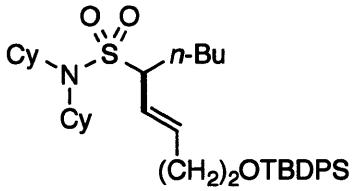
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.31–7.28 (m, 2H), 7.22–7.17 (m, 3H), 5.80 (dddd, 1H, *J* = 15.3, 7.4, 6.0, 0.4 Hz), 5.42 (dddd, 1H, *J* = 15.4, 9.8, 1.5, 1.5 Hz), 3.48–3.38 (m, 2H), 3.33 (ddd, 1H, *J* = 10.8, 10.0, 3.2 Hz), 3.17–3.10 (m, 2H), 2.04–1.97 (m, 1H), 1.79–1.56 (m, 15H), 1.41–1.16 (m, 8H), 1.08 (qt, 2H, *J* = 13.1, 3.4 Hz), 0.89 (t, 3H, *J* = 7.2 Hz).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 140.1, 136.6, 128.9, 128.8, 126.6, 126.0, 69.0, 58.4, 39.2, 34.0, 33.1, 29.5, 29.3, 26.99, 26.97, 25.8, 22.7, 14.1.

FT-IR (neat) 3084, 3062, 3027, 2931, 2855, 1603, 1495, 1466, 1453, 1401, 1381, 1322, 1274, 1256, 1188, 1164, 1139, 1108, 1074, 1047, 1028, 981, 895, 854, 823, 750 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{26}H_{41}NNaO_2S$: 454, found: 454.

$[\alpha]^{25}_D = -6.9°$ (c = 1.02, $CHCl_3$).



(*S*,*E*)-1-((*tert*-Butyldiphenylsilyl)oxy)-*N*,*N*-dicyclohexylnon-3-ene-5-sulfonamide (Table 9, entry 2). 1-Bromo-*N*,*N*-dicyclohexylpentane-1-sulfonamide (197 mg, 0.500 mmol) and (*E*)-(4-((*tert*-butyldiphenylsilyl)oxy)but-1-en-1-yl)zirconium

reagent (1.00 mmol) were used. The product was purified by column chromatography on silica gel (3% ethyl acetate/hexanes) and then on C-18 silica gel (10%→100% acetonitrile/water). Viscous light-yellow oil. First run: 254 mg (81%, 95% ee). Second run: 259 mg (83%, 94% ee).

The ee was determined by HPLC on a CHIRALPAK AD-H column (0.5% *i*-PrOH/hexanes, 0.8 mL/min) with t_r = 14.6 min (minor), 17.9 min (major).

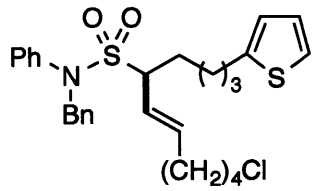
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67–7.64 (m, 4H), 7.45–7.41 (m, 2H), 7.40–7.36 (m, 4H), 5.69 (ddd, 1H, *J* = 15.5, 6.4, 6.4 Hz), 5.42 (dddd, 1H, *J* = 15.5, 9.7, 1.4, 1.4 Hz), 3.75–3.68 (m, 2H), 3.26 (ddd, 1H, *J* = 10.6, 9.5, 3.2 Hz), 3.15–3.09 (m, 2H), 2.39–2.29 (m, 2H), 2.08–2.01 (m, 1H), 1.76–1.57 (m, 14H), 1.39–1.14 (m, 9H), 1.12–1.02 (m, 2H), 1.05 (s, 9H), 0.86 (t, 3H, *J* = 7.2 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.7, 135.6, 134.3, 133.9, 133.8, 129.79, 129.78, 127.79, 127.78, 126.10, 69.5, 63.2, 58.2, 36.0, 33.9, 32.8, 29.3, 29.0, 26.9, 26.7, 25.5, 22.5, 19.3, 14.0.

FT-IR (neat) 3071, 3048, 2931, 2856, 1590, 1471, 1453, 1428, 1389, 1323, 1257, 1221, 1188, 1164, 1138, 1110, 1048, 1028, 998, 980, 939, 895, 854, 822, 764, 738 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{37}H_{57}NNaO_3SSi$: 646, found: 646.

$[\alpha]^{25}_D$ = +1.7° (c = 0.99, $CHCl_3$).



(*S*,*E*)-*N*-Benzyl-11-chloro-*N*-phenyl-1-(thiophen-2-yl)undec-6-ene-5-sulfonamide (Table 9, entry 3). *N*-Benzyl-1-bromo-*N*-phenyl-5-(thiophen-2-yl)pentane-1-sulfonamide (239 mg, 0.500 mmol) and (*E*)-(6-chlorohex-1-en-1-yl)zirconium reagent (1.00 mmol) were used. The product was purified by column chromatography (first purification: 5% ethyl acetate/hexanes; second purification: 15% cyclopentyl methyl ether/hexanes). Viscous light-yellow oil. First run: 165 mg (64%, 80% ee). Second run: 156 mg (60%, 81% ee).

The ee was determined by HPLC on a CHIRALPAK AD-H column (10% *i*-PrOH/hexanes, 0.8 mL/min) with t_r = 17.5 min (major), 23.8 min (minor).

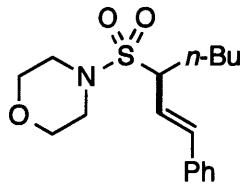
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.32–7.28 (m, 2H), 7.27–7.19 (m, 8H), 7.12 (dd, 1H, *J* = 5.1, 1.2 Hz), 6.91 (dd, 1H, *J* = 5.1, 3.4 Hz), 6.77 (dddd, 1H, *J* = 3.3, 1.0, 1.0, 1.0 Hz), 5.80 (ddd, 1H, *J* = 15.3, 6.8, 6.8 Hz), 5.46 (dddd, 1H, *J* = 15.4, 9.7, 1.5, 1.5 Hz), 4.99 (d, 1H, *J* = 15.1 Hz), 4.67 (d, 1H, *J* = 15.1 Hz), 3.60–3.55 (m, 1H), 3.58 (t, 2H, *J* = 6.6 Hz), 2.87–2.76 (m, 2H), 2.26–2.13 (m, 2H), 2.04 (dddd, 1H, *J* = 13.6, 9.9, 6.3, 3.4 Hz), 1.86–1.72 (m, 3H), 1.72–1.56 (m, 4H), 1.50–1.41 (m, 1H), 1.32–1.22 (m, 1H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 145.6, 139.7, 139.0, 137.3, 129.4, 129.3, 128.7, 128.6, 127.9, 127.8, 127.0, 124.5, 124.2, 123.2, 66.7, 56.7, 45.4, 32.5, 32.2, 31.6, 29.9, 29.2, 26.5, 26.2.

FT-IR (neat) 3064, 3032, 2933, 2860, 1595, 1493, 1454, 1337, 1216, 1145, 1093, 1065, 1028, 976, 916, 862, 775 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{28}H_{34}ClNNaO_2S_2$: 538, found: 538.

$[\alpha]^{25}_D = -23.0°$ (c = 1.03, $CHCl_3$).



(*S*,*E*)-4-((1-Phenylhept-1-en-3-yl)sulfonyl)morpholine (Table 9, entry 4). 4-((1-Bromopentyl)sulfonyl)morpholine (150 mg, 0.500 mmol), and (*E*)-styrylzirconium reagent (1.00 mmol) were used. The product was purified by column chromatography (15% ethyl acetate/hexanes). White solid. First run: 110 mg (68%, 97% ee). Second run: 110 mg (68%, 95% ee).

The ee was determined by HPLC on a CHIRALPAK AS-H column (10% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 18.7 min (minor), 30.1 min (major).

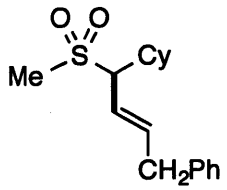
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.39 (m, 2H), 7.38–7.34 (m, 2H), 7.32–7.29 (m, 1H), 6.62 (d, 1H, *J* = 15.9 Hz), 6.06 (dd, 1H, *J* = 15.9, 9.8 Hz), 3.70–3.62 (m, 5H), 3.38–3.30 (m, 4H), 2.17–2.10 (m, 1H), 1.87–1.79 (m, 1H), 1.45–1.22 (m, 4H), 0.90 (t, 3H, *J* = 7.0 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.0, 135.7, 129.0, 128.7, 126.7, 122.7, 67.1, 67.0, 46.8, 29.0, 28.8, 22.4, 14.0.

FT-IR (neat) 2958, 2923, 2859, 1450, 1339, 1324, 1260, 1148, 1114, 1073, 955, 743 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{17}H_{25}NNaO_3S$: 346, found: 346.

$[\alpha]^{25}_D = -82°$ (c = 0.98, $CHCl_3$).



(*S*,*E*)-(4-Cyclohexyl-4-(methylsulfonyl)but-2-en-1-yl)benzene (Table 9, entry 5). (Bromo(methylsulfonyl)methyl)cyclohexane (179 mg, 0.700 mmol), (*E*)-(3-phenylprop-1-en-1-yl)zirconium reagent (1.40 mmol), and (*R*,*R*)–**L8** (30.4 mg, 0.091 mmol) were used. The product was purified by column chromatography (15% ethyl acetate/hexanes). Light-yellow oil. First run: 109 mg (53%, 93% ee). Second run: 98 mg (48%, 93% ee).

The ee was determined by HPLC on a CHIRALPAK IB-3 column (5% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 13.0 min (minor), 22.9 min (major).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.30 (m, 2H), 7.25–7.21 (m, 1H), 7.18–7.16 (m, 2H), 5.89 (ddd, 1H, *J* = 15.2, 6.9, 6.9 Hz), 5.71 (dddd, 1H, *J* = 15.3, 10.4, 1.4, 1.4 Hz), 3.48 (d, 2H, *J* = 6.9 Hz), 3.29 (dd, 1H, *J* = 10.4, 3.8 Hz), 2.76 (s, 3H), 2.32 (tq, 1H, *J* = 11.9, 3.5 Hz), 2.08–2.02 (m, 1H), 1.78–1.72 (m, 2H), 1.70–1.61 (m, 2H), 1.40–1.26 (m, 2H), 1.23–1.07 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.2, 139.0, 128.8, 128.6, 126.6, 122.6, 73.2, 39.8, 39.3, 36.0, 32.2, 28.9, 26.4, 26.1, 26.0.

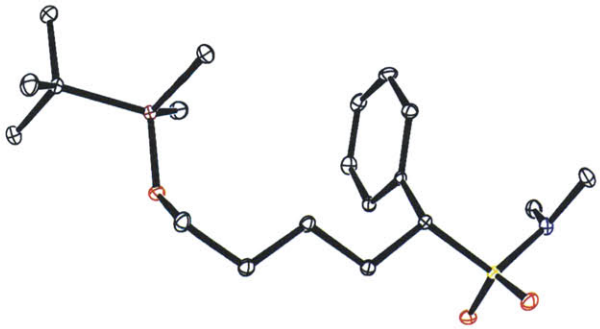
FT-IR (neat) 3083, 3060, 3026, 2927, 2852, 1660, 1602, 1494, 1452, 1411, 1351, 1295, 1240, 1173, 1133, 1077, 1029, 978, 894, 852, 784, 751, 700 cm^{-1}.

MS (ESI) *m/z* (M^++Na) calcd for $C_{17}H_{24}NaO_2S$: 315, found: 315.

$[\alpha]^{25}_D$ = +60.8° (c = 1.00, $CHCl_3$).

V. Determination of Absolute Stereochemistry

Product from entry 7 of Table 6 (run with (*S,S*)–L8). (*R*)-5-((*tert*-Butyldimethylsilyl)oxy)-*N,N*-dimethyl-1-phenylpentane-1-sulfonamide. A crystal suitable for X-ray crystallography was grown by vapor diffusion with dichloromethane and pentane.



A suitable crystal of $C_{19}H_{35}NO_3SSi$ was selected for analysis. All measurements were made on a Bruker SMART 1000 CCD with filtered Mo-Kα radiation at a temperature of 100 K. Using Olex2,[56] the structure was solved with the ShelXS[57] structure solution program using Direct Methods and refined with the ShelXL[57] refinement package using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

[56] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
[57] Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112–122.

Table 1. Crystal data and structure refinement for crystal01.

Identification code	crystal01	
Empirical formula	$C_{19}H_{35}NOSSi$	
Formula weight	385.63	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 5.9209(6) Å	α = 90°.
	b = 10.6607(12) Å	β = 99.2230(10) °.
	c = 17.0647(19) Å	γ = 90 °.
Volume	1063.2(2) $Å^3$	
Z	2	
Density (calculated)	1.205 Mg/m^3	
Absorption coefficient	0.226 mm^{-1}	
F(000)	420	
Crystal size	0.4 x 0.4 x 0.1 mm^3	
Theta range for data collection	1.209 to 29.107°.	
Index ranges	-7<=h<=8, -13<=k<=14, -22<=l<=23	
Reflections collected	16770	
Independent reflections	5160 [R(int) = 0.0236]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.9257	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5160 / 1 / 233	
Goodness-of-fit on F^2	1.098	
Final R indices [I>2sigma(I)]	R1 = 0.0279, wR2 = 0.0669	
R indices (all data)	R1 = 0.0308, wR2 = 0.0690	
Absolute structure parameter	0.02(2)	
Largest diff. peak and hole	0.325 and -0.163 $e/Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for crystal01. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	-4031(1)	5489(1)	517(1)	14(1)
Si(1)	2618(1)	1014(1)	3465(1)	14(1)
O(1)	-3746(3)	5244(1)	-291(1)	20(1)
O(2)	-6212(2)	5232(1)	755(1)	19(1)
O(3)	648(2)	432(2)	2769(1)	19(1)
N(1)	-3503(3)	6967(2)	689(1)	16(1)
C(1)	-4272(4)	7610(2)	1361(1)	20(1)
C(2)	-1459(4)	7506(2)	435(1)	22(1)
C(3)	-1857(3)	4582(2)	1132(1)	12(1)
C(4)	-2416(3)	3172(2)	1032(1)	15(1)
C(5)	-552(3)	2381(2)	1521(1)	16(1)
C(6)	-952(4)	967(2)	1416(1)	18(1)
C(7)	820(4)	204(2)	1957(1)	21(1)
C(8)	-1531(3)	5030(2)	1983(1)	12(1)
C(9)	508(3)	5621(2)	2311(1)	17(1)
C(10)	842(3)	6027(2)	3095(1)	21(1)
C(11)	-835(4)	5849(2)	3558(1)	21(1)
C(12)	-2858(4)	5251(2)	3243(1)	20(1)
C(13)	-3211(3)	4849(2)	2456(1)	16(1)
C(14)	1116(4)	2120(2)	4054(1)	24(1)
C(15)	4837(4)	1893(2)	3029(1)	27(1)
C(16)	3960(3)	-312(2)	4110(1)	15(1)
C(17)	5647(4)	216(2)	4811(1)	23(1)
C(18)	2103(4)	-1074(2)	4431(1)	22(1)
C(19)	5248(4)	-1178(2)	3614(1)	24(1)

Table 3. Bond lengths [Å] and angles [°] for crystal01.

S(1)-O(1)	1.4394(15)
S(1)-O(2)	1.4405(15)
S(1)-N(1)	1.6247(18)
S(1)-C(3)	1.8048(19)
Si(1)-O(3)	1.6471(14)
Si(1)-C(14)	1.865(2)
Si(1)-C(15)	1.863(2)
Si(1)-C(16)	1.886(2)
O(3)-C(7)	1.426(2)
N(1)-C(1)	1.469(3)
N(1)-C(2)	1.466(3)
C(3)-C(4)	1.543(3)
C(3)-C(8)	1.512(3)
C(4)-C(5)	1.526(3)
C(5)-C(6)	1.532(3)
C(6)-C(7)	1.517(3)
C(8)-C(9)	1.396(3)
C(8)-C(13)	1.391(3)
C(9)-C(10)	1.390(3)
C(10)-C(11)	1.378(3)
C(11)-C(12)	1.387(3)
C(12)-C(13)	1.393(3)
C(16)-C(17)	1.537(3)
C(16)-C(18)	1.537(3)
C(16)-C(19)	1.535(3)
O(1)-S(1)-O(2)	118.93(9)
O(1)-S(1)-N(1)	107.45(9)
O(1)-S(1)-C(3)	106.10(9)
O(2)-S(1)-N(1)	106.79(9)
O(2)-S(1)-C(3)	108.81(9)
N(1)-S(1)-C(3)	108.40(9)
O(3)-Si(1)-C(14)	106.44(9)
O(3)-Si(1)-C(15)	111.35(9)
O(3)-Si(1)-C(16)	108.79(9)
C(14)-Si(1)-C(16)	110.66(10)
C(15)-Si(1)-C(14)	108.96(11)
C(15)-Si(1)-C(16)	110.57(10)
C(7)-O(3)-Si(1)	127.79(13)
C(1)-N(1)-S(1)	121.23(14)
C(2)-N(1)-S(1)	118.06(14)
C(2)-N(1)-C(1)	114.98(17)
C(4)-C(3)-S(1)	109.70(13)
C(8)-C(3)-S(1)	111.03(13)
C(8)-C(3)-C(4)	113.95(16)
C(5)-C(4)-C(3)	110.75(15)
C(4)-C(5)-C(6)	113.27(16)
C(7)-C(6)-C(5)	112.19(16)
O(3)-C(7)-C(6)	110.46(17)
C(9)-C(8)-C(3)	119.76(17)
C(13)-C(8)-C(3)	121.38(17)
C(13)-C(8)-C(9)	118.86(18)

C(10)-C(9)-C(8)	120.46(18)
C(11)-C(10)-C(9)	120.29(19)
C(10)-C(11)-C(12)	119.91(19)
C(11)-C(12)-C(13)	120.06(19)
C(8)-C(13)-C(12)	120.41(19)
C(17)-C(16)-Si(1)	109.87(14)
C(17)-C(16)-C(18)	109.15(17)
C(18)-C(16)-Si(1)	110.21(14)
C(19)-C(16)-Si(1)	109.22(14)
C(19)-C(16)-C(17)	109.34(17)
C(19)-C(16)-C(18)	109.03(17)

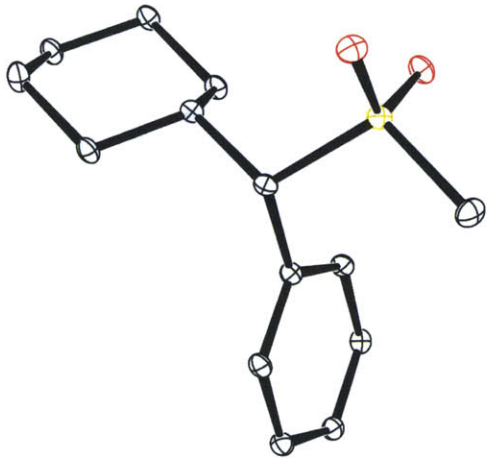
Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for crystal01. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	14(1)	14(1)	12(1)	1(1)	-1(1)	0(1)
Si(1)	14(1)	12(1)	15(1)	2(1)	1(1)	-1(1)
O(1)	26(1)	21(1)	13(1)	0(1)	-2(1)	0(1)
O(2)	14(1)	19(1)	23(1)	1(1)	-1(1)	-1(1)
O(3)	21(1)	20(1)	14(1)	2(1)	-2(1)	-6(1)
N(1)	20(1)	13(1)	16(1)	2(1)	4(1)	1(1)
C(1)	24(1)	14(1)	22(1)	0(1)	5(1)	3(1)
C(2)	27(1)	17(1)	24(1)	2(1)	8(1)	-6(1)
C(3)	12(1)	13(1)	11(1)	1(1)	1(1)	2(1)
C(4)	18(1)	13(1)	12(1)	-2(1)	1(1)	0(1)
C(5)	19(1)	14(1)	13(1)	-1(1)	-1(1)	2(1)
C(6)	24(1)	15(1)	14(1)	-1(1)	-2(1)	0(1)
C(7)	27(1)	15(1)	18(1)	-1(1)	-1(1)	4(1)
C(8)	15(1)	10(1)	12(1)	1(1)	1(1)	1(1)
C(9)	14(1)	20(1)	18(1)	1(1)	3(1)	0(1)
C(10)	18(1)	20(1)	22(1)	-5(1)	-5(1)	-1(1)
C(11)	30(1)	19(1)	14(1)	-3(1)	0(1)	5(1)
C(12)	24(1)	21(1)	16(1)	0(1)	8(1)	2(1)
C(13)	18(1)	14(1)	15(1)	1(1)	2(1)	0(1)
C(14)	23(1)	20(1)	29(1)	-5(1)	0(1)	4(1)
C(15)	23(1)	28(1)	29(1)	12(1)	2(1)	-8(1)
C(16)	16(1)	14(1)	15(1)	2(1)	1(1)	1(1)
C(17)	23(1)	25(1)	20(1)	5(1)	-4(1)	-2(1)
C(18)	24(1)	17(1)	24(1)	5(1)	4(1)	-2(1)
C(19)	24(1)	21(1)	29(1)	1(1)	5(1)	6(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for crystal01.

	x	y	z	U(eq)
H(1A)	-5587	7185	1497	30
H(1B)	-4669	8461	1216	30
H(1C)	-3064	7603	1809	30
H(2A)	-208	7483	869	33
H(2B)	-1761	8359	270	33
H(2C)	-1070	7027	-1	33
H(3)	-413	4726	934	15
H(4A)	-3873	3002	1201	18
H(4B)	-2546	2944	476	18
H(5A)	-473	2592	2077	19
H(5B)	911	2591	1368	19
H(6A)	-2463	763	1529	22
H(6B)	-902	741	869	22
H(7A)	586	-681	1840	25
H(7B)	2340	428	1861	25
H(9)	1649	5743	2003	20
H(10)	2205	6421	3308	25
H(11)	-611	6130	4081	26
H(12)	-3980	5118	3558	24
H(13)	-4578	4458	2246	19
H(14A)	483	2801	3721	36
H(14B)	2183	2444	4490	36
H(14C)	-93	1686	4254	36
H(15A)	5788	1311	2802	40
H(15B)	5761	2371	3437	40
H(15C)	4107	2449	2624	40
H(17A)	6824	681	4613	35
H(17B)	6325	-463	5136	35
H(17C)	4846	759	5121	35
H(18A)	1374	-556	4777	32
H(18B)	2791	-1786	4721	32
H(18C)	986	-1356	3996	32
H(19A)	4214	-1474	3160	37
H(19B)	5860	-1880	3931	37
H(19C)	6475	-722	3439	37

Product from entry 2 of Table 7: (*S*)-(Cyclohexyl(methylsulfonyl)methyl)benzene (from a reaction using (*R*,*R*)–L8). A crystal suitable for X-ray crystallography was grown by vapor diffusion with dichloromethane and pentane.



A suitable crystal of $C_{14}H_{20}O_2S$ was selected for analysis. All measurements were made on a Bruker APEX-II CCD with filtered Mo-Kα radiation at a temperature of 100 K. Using Olex2,[56] the structure was solved with the ShelXS[57] structure solution program using Direct Methods and refined with the ShelXL[57] refinement package using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table 1. Crystal data and structure refinement for crystal03.

Identification code	crystal03	
Empirical formula	$C_{14}H_{20}O_2S$	
Formula weight	252.36	
Temperature	100.15 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.2283(3) Å	α = 90°.
	b = 13.7866(7) Å	β = 90 °.
	c = 15.3937(8) Å	γ = 90 °.
Volume	1321.81(12) $Å^3$	
Z	4	
Density (calculated)	1.268 Mg/m^3	
Absorption coefficient	0.233 mm^{-1}	
F(000)	544	
Crystal size	0.62 x 0.16 x 0.09 mm^3	
Theta range for data collection	1.983 to 33.731°.	
Index ranges	-9<=h<=9, -21<=k<=20, -23<=l<=23	
Reflections collected	39471	
Independent reflections	4910 [R(int) = 0.0621]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.8575	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4910 / 0 / 155	
Goodness-of-fit on F^2	1.141	
Final R indices [I>2sigma(I)]	R1 = 0.0540, wR2 = 0.1115	
R indices (all data)	R1 = 0.0741, wR2 = 0.1179	
Absolute structure parameter	0.01(3)	
Largest diff. peak and hole	0.692 and -0.385 $e/Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for crystal03. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	7502(1)	3757(1)	4892(1)	17(1)
O(1)	6971(3)	3206(1)	5662(1)	21(1)
O(2)	9662(3)	4136(1)	4836(1)	21(1)
C(1)	5566(4)	4731(2)	4817(2)	14(1)
C(2)	5963(4)	5465(2)	5570(2)	14(1)
C(3)	7759(4)	6208(2)	5418(2)	17(1)
C(4)	8064(4)	6849(2)	6224(2)	20(1)
C(5)	5993(4)	7371(2)	6464(2)	21(1)
C(6)	4161(4)	6651(2)	6587(2)	23(1)
C(7)	3868(4)	5994(2)	5790(2)	19(1)
C(8)	5392(4)	5139(2)	3904(2)	15(1)
C(9)	7131(4)	5552(2)	3461(2)	17(1)
C(10)	6869(4)	5905(2)	2620(2)	18(1)
C(11)	4895(4)	5840(2)	2207(2)	18(1)
C(12)	3168(4)	5434(2)	2644(2)	19(1)
C(13)	3419(4)	5081(2)	3483(2)	17(1)
C(14)	7027(5)	3018(2)	3977(2)	23(1)

Table 3. Bond lengths [Å] and angles [°] for crystal03.

S(1)-O(1)	1.4458(19)
S(1)-O(2)	1.4461(19)
S(1)-C(1)	1.809(2)
S(1)-C(14)	1.763(3)
C(1)-H(1)	1.0000
C(1)-C(2)	1.557(3)
C(1)-C(8)	1.518(3)
C(2)-H(2)	1.0000
C(2)-C(3)	1.535(3)
C(2)-C(7)	1.533(3)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(3)-C(4)	1.536(3)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(4)-C(5)	1.523(4)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(5)-C(6)	1.524(4)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(6)-C(7)	1.536(4)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(9)	1.401(3)
C(8)-C(13)	1.391(4)
C(9)-H(9)	0.9500
C(9)-C(10)	1.393(3)
C(10)-H(10)	0.9500
C(10)-C(11)	1.387(4)
C(11)-H(11)	0.9500
C(11)-C(12)	1.386(4)
C(12)-H(12)	0.9500
C(12)-C(13)	1.390(4)
C(13)-H(13)	0.9500
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
O(1)-S(1)-O(2)	116.89(12)
O(1)-S(1)-C(1)	106.82(11)
O(1)-S(1)-C(14)	108.23(11)
O(2)-S(1)-C(1)	110.34(10)
O(2)-S(1)-C(14)	108.51(13)
C(14)-S(1)-C(1)	105.43(13)
S(1)-C(1)-H(1)	105.6
C(2)-C(1)-S(1)	109.22(16)
C(2)-C(1)-H(1)	105.6
C(8)-C(1)-S(1)	112.41(17)
C(8)-C(1)-H(1)	105.6
C(8)-C(1)-C(2)	117.36(18)
C(1)-C(2)-H(2)	107.1

C(3)-C(2)-C(1)	115.9(2)
C(3)-C(2)-H(2)	107.1
C(7)-C(2)-C(1)	109.8(2)
C(7)-C(2)-H(2)	107.1
C(7)-C(2)-C(3)	109.60(18)
C(2)-C(3)-H(3A)	109.5
C(2)-C(3)-H(3B)	109.5
C(2)-C(3)-C(4)	110.6(2)
H(3A)-C(3)-H(3B)	108.1
C(4)-C(3)-H(3A)	109.5
C(4)-C(3)-H(3B)	109.5
C(3)-C(4)-H(4A)	109.4
C(3)-C(4)-H(4B)	109.4
H(4A)-C(4)-H(4B)	108.0
C(5)-C(4)-C(3)	111.3(2)
C(5)-C(4)-H(4A)	109.4
C(5)-C(4)-H(4B)	109.4
C(4)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5
C(4)-C(5)-C(6)	110.9(2)
H(5A)-C(5)-H(5B)	108.1
C(6)-C(5)-H(5A)	109.5
C(6)-C(5)-H(5B)	109.5
C(5)-C(6)-H(6A)	109.2
C(5)-C(6)-H(6B)	109.2
C(5)-C(6)-C(7)	111.9(2)
H(6A)-C(6)-H(6B)	107.9
C(7)-C(6)-H(6A)	109.2
C(7)-C(6)-H(6B)	109.2
C(2)-C(7)-C(6)	110.9(2)
C(2)-C(7)-H(7A)	109.5
C(2)-C(7)-H(7B)	109.5
C(6)-C(7)-H(7A)	109.5
C(6)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	108.1
C(9)-C(8)-C(1)	123.1(2)
C(13)-C(8)-C(1)	118.2(2)
C(13)-C(8)-C(9)	118.7(2)
C(8)-C(9)-H(9)	119.9
C(10)-C(9)-C(8)	120.2(2)
C(10)-C(9)-H(9)	119.9
C(9)-C(10)-H(10)	119.7
C(11)-C(10)-C(9)	120.5(2)
C(11)-C(10)-H(10)	119.7
C(10)-C(11)-H(11)	120.3
C(12)-C(11)-C(10)	119.4(2)
C(12)-C(11)-H(11)	120.3
C(11)-C(12)-H(12)	119.8
C(11)-C(12)-C(13)	120.4(2)
C(13)-C(12)-H(12)	119.8
C(8)-C(13)-H(13)	119.6
C(12)-C(13)-C(8)	120.8(2)
C(12)-C(13)-H(13)	119.6
S(1)-C(14)-H(14A)	109.5

S(1)-C(14)-H(14B)	109.5
S(1)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5

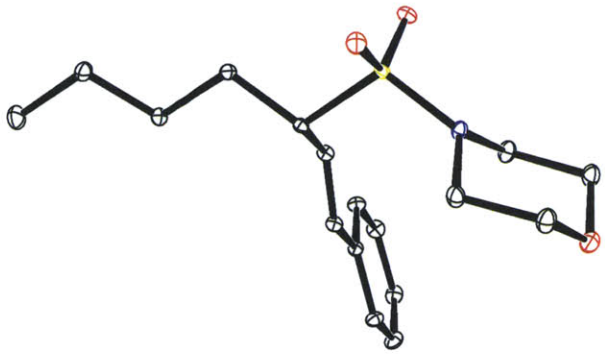
Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for crystal03. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	19(1)	13(1)	18(1)	1(1)	-1(1)	-1(1)
O(1)	26(1)	17(1)	20(1)	2(1)	-1(1)	-2(1)
O(2)	17(1)	16(1)	29(1)	2(1)	0(1)	0(1)
C(1)	11(1)	15(1)	17(1)	1(1)	-1(1)	-3(1)
C(2)	14(1)	11(1)	18(1)	2(1)	-1(1)	-2(1)
C(3)	11(1)	17(1)	24(1)	-2(1)	0(1)	-3(1)
C(4)	15(1)	16(1)	28(1)	-2(1)	-3(1)	-2(1)
C(5)	18(1)	15(1)	29(1)	-4(1)	-1(1)	2(1)
C(6)	17(1)	22(1)	31(2)	-6(1)	4(1)	0(1)
C(7)	12(1)	18(1)	26(1)	-2(1)	0(1)	0(1)
C(8)	15(1)	12(1)	18(1)	1(1)	0(1)	0(1)
C(9)	14(1)	17(1)	20(1)	0(1)	-1(1)	-3(1)
C(10)	19(1)	14(1)	20(1)	1(1)	4(1)	-1(1)
C(11)	22(1)	14(1)	18(1)	0(1)	-1(1)	3(1)
C(12)	18(1)	18(1)	21(1)	-2(1)	-3(1)	2(1)
C(13)	12(1)	17(1)	21(1)	0(1)	1(1)	-2(1)
C(14)	32(2)	14(1)	22(1)	-3(1)	-2(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for crystal03.

	x	y	z	U(eq)
H(1)	4140	4428	4942	17
H(2)	6373	5077	6093	17
H(3A)	7392	6620	4912	21
H(3B)	9117	5865	5286	21
H(4A)	8533	6442	6719	23
H(4B)	9203	7333	6109	23
H(5A)	5613	7837	6000	25
H(5B)	6210	7741	7009	25
H(6A)	2812	7011	6695	28
H(6B)	4457	6244	7103	28
H(7A)	2725	5513	5908	22
H(7B)	3415	6392	5286	22
H(9)	8494	5592	3736	20
H(10)	8051	6192	2327	21
H(11)	4728	6071	1629	22
H(12)	1806	5398	2368	23
H(13)	2229	4797	3773	20
H(14A)	7233	3400	3447	34
H(14B)	5551	2773	3996	34
H(14C)	8032	2471	3980	34

Product from entry 4 of Table 9 (run with (3*R*,8*S*)–L11). (*S*,*E*)-4-((1-Phenylhept-1-en-3-yl)sulfonyl)morpholine. A crystal suitable for X-ray crystallography was grown by vapor diffusion with Et_2O and pentane.



A suitable crystal of $C_{17}H_{25}NO_3S$ was selected for analysis. All measurements were made on a Bruker APEX-II CCD with filtered Mo-Kα radiation at a temperature of 100 K. Using Olex2,[56] the structure was solved with the ShelXS[57] structure solution program using Direct Methods and refined with the ShelXL[57] refinement package using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

Table 1. Crystal data and structure refinement for crystal02.

Identification code	crystal02	
Empirical formula	$C_{17}H_{25}NO_3S$	
Formula weight	323.44	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 12.8350(6) Å	α = 90°.
	b = 5.6272(3) Å	β = 113.133(2) °.
	c = 12.9187(6) Å	γ = 90 °.
Volume	858.03(7) $Å^3$	
Z	2	
Density (calculated)	1.252 Mg/m^3	
Absorption coefficient	0.201 mm^{-1}	
F(000)	348	
Crystal size	0.5 x 0.12 x 0.12 mm^3	
Theta range for data collection	1.714 to 31.552°.	
Index ranges	-18<=h<=18, -8<=k<=8, -19<=l<=19	
Reflections collected	57330	
Independent reflections	5731 [R(int) = 0.0344]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.8839	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5731 / 1 / 200	
Goodness-of-fit on F^2	1.073	
Final R indices [I>2sigma(I)]	R1 = 0.0258, wR2 = 0.0683	
R indices (all data)	R1 = 0.0273, wR2 = 0.0695	
Absolute structure parameter	0.019(11)	
Largest diff. peak and hole	0.444 and -0.190 $e/Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for crystal02. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	4726(1)	7787(1)	3347(1)	12(1)
O(1)	4294(1)	10123(2)	2942(1)	19(1)
O(2)	5535(1)	7480(2)	4482(1)	18(1)
O(3)	6358(1)	4985(2)	1135(1)	21(1)
N(1)	5344(1)	6838(2)	2534(1)	14(1)
C(1)	3537(1)	5903(2)	3176(1)	11(1)
C(2)	3067(1)	6643(2)	4055(1)	13(1)
C(3)	2154(1)	4910(2)	4061(1)	14(1)
C(4)	1833(1)	5268(3)	5067(1)	18(1)
C(5)	944(1)	3484(3)	5081(1)	25(1)
C(6)	2671(1)	6069(2)	1991(1)	13(1)
C(7)	2415(1)	4264(2)	1261(1)	13(1)
C(8)	1574(1)	4329(2)	93(1)	12(1)
C(9)	797(1)	6196(2)	-325(1)	16(1)
C(10)	21(1)	6194(3)	-1441(1)	19(1)
C(11)	9(1)	4336(3)	-2156(1)	20(1)
C(12)	764(1)	2453(3)	-1748(1)	20(1)
C(13)	1539(1)	2453(2)	-630(1)	16(1)
C(14)	4862(1)	7376(2)	1320(1)	18(1)
C(15)	5820(1)	7255(3)	909(1)	21(1)
C(16)	6847(1)	4566(3)	2317(1)	21(1)
C(17)	5947(1)	4555(3)	2806(1)	19(1)

Table 3. Bond lengths [Å] and angles [°] for crystal02.

S(1)-O(1)	1.4424(10)
S(1)-O(2)	1.4360(9)
S(1)-N(1)	1.6356(11)
S(1)-C(1)	1.7985(12)
O(3)-C(15)	1.4267(18)
O(3)-C(16)	1.4241(17)
N(1)-C(14)	1.4733(16)
N(1)-C(17)	1.4694(17)
C(1)-C(2)	1.5379(17)
C(1)-C(6)	1.5001(15)
C(2)-C(3)	1.5265(17)
C(3)-C(4)	1.5241(18)
C(4)-C(5)	1.525(2)
C(6)-C(7)	1.3364(17)
C(7)-C(8)	1.4711(16)
C(8)-C(9)	1.4021(17)
C(8)-C(13)	1.3993(17)
C(9)-C(10)	1.3937(16)
C(10)-C(11)	1.391(2)
C(11)-C(12)	1.393(2)
C(12)-C(13)	1.3954(17)
C(14)-C(15)	1.5194(19)
C(16)-C(17)	1.5189(19)

O(1)-S(1)-N(1)	106.16(6)
O(1)-S(1)-C(1)	107.85(6)
O(2)-S(1)-O(1)	120.05(6)
O(2)-S(1)-N(1)	106.10(6)
O(2)-S(1)-C(1)	107.05(6)
N(1)-S(1)-C(1)	109.34(6)
C(16)-O(3)-C(15)	109.98(11)
C(14)-N(1)-S(1)	120.64(9)
C(17)-N(1)-S(1)	118.32(9)
C(17)-N(1)-C(14)	113.32(11)
C(2)-C(1)-S(1)	108.03(8)
C(6)-C(1)-S(1)	109.94(8)
C(6)-C(1)-C(2)	112.83(10)
C(3)-C(2)-C(1)	110.77(10)
C(4)-C(3)-C(2)	112.63(10)
C(3)-C(4)-C(5)	112.19(12)
C(7)-C(6)-C(1)	123.45(11)
C(6)-C(7)-C(8)	125.69(11)
C(9)-C(8)-C(7)	122.55(11)
C(13)-C(8)-C(7)	118.95(11)
C(13)-C(8)-C(9)	118.50(11)
C(10)-C(9)-C(8)	120.60(12)
C(11)-C(10)-C(9)	120.30(13)
C(10)-C(11)-C(12)	119.73(12)
C(11)-C(12)-C(13)	119.96(12)
C(12)-C(13)-C(8)	120.90(12)
N(1)-C(14)-C(15)	107.67(11)
O(3)-C(15)-C(14)	111.21(11)

O(3)-C(16)-C(17)	111.08(11)
N(1)-C(17)-C(16)	108.16(11)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for crystal02. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	12(1)	11(1)	11(1)	-1(1)	4(1)	-3(1)
O(1)	24(1)	11(1)	23(1)	0(1)	11(1)	-2(1)
O(2)	15(1)	26(1)	12(1)	-3(1)	2(1)	-7(1)
O(3)	22(1)	22(1)	21(1)	0(1)	12(1)	1(1)
N(1)	16(1)	16(1)	13(1)	3(1)	7(1)	2(1)
C(1)	10(1)	10(1)	11(1)	0(1)	3(1)	-1(1)
C(2)	12(1)	12(1)	13(1)	-1(1)	5(1)	0(1)
C(3)	11(1)	16(1)	14(1)	1(1)	4(1)	0(1)
C(4)	18(1)	20(1)	19(1)	-2(1)	10(1)	-1(1)
C(5)	22(1)	29(1)	28(1)	2(1)	15(1)	-4(1)
C(6)	11(1)	13(1)	12(1)	1(1)	2(1)	0(1)
C(7)	11(1)	14(1)	12(1)	0(1)	2(1)	0(1)
C(8)	11(1)	14(1)	11(1)	-2(1)	3(1)	-2(1)
C(9)	15(1)	16(1)	14(1)	-1(1)	3(1)	1(1)
C(10)	15(1)	21(1)	16(1)	2(1)	2(1)	2(1)
C(11)	16(1)	29(1)	12(1)	-2(1)	2(1)	-4(1)
C(12)	18(1)	26(1)	15(1)	-7(1)	6(1)	-3(1)
C(13)	13(1)	18(1)	17(1)	-4(1)	5(1)	0(1)
C(14)	18(1)	23(1)	13(1)	4(1)	7(1)	3(1)
C(15)	24(1)	23(1)	19(1)	4(1)	12(1)	1(1)
C(16)	18(1)	24(1)	23(1)	4(1)	10(1)	4(1)
C(17)	21(1)	16(1)	22(1)	7(1)	12(1)	4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for crystal02.

	x	y	z	U(eq)
H(1)	3809	4223	3327	13
H(2A)	3691	6680	4811	15
H(2B)	2742	8262	3881	15
H(3A)	1471	5115	3359	16
H(3B)	2431	3264	4072	16
H(4A)	1536	6898	5045	22
H(4B)	2520	5104	5770	22
H(5A)	764	3776	5741	37
H(5B)	1241	1868	5118	37
H(5C)	257	3664	4395	37
H(6)	2285	7535	1747	16
H(7)	2810	2813	1519	15
H(9)	800	7474	156	19
H(10)	-503	7467	-1715	23
H(11)	-513	4352	-2920	24
H(12)	752	1170	-2231	24
H(13)	2051	1161	-356	19
H(14A)	4520	8982	1187	22
H(14B)	4266	6206	911	22
H(15A)	5514	7563	89	25
H(15B)	6385	8503	1288	25
H(16A)	7412	5819	2689	25
H(16B)	7245	3017	2467	25
H(17A)	5409	3231	2480	23
H(17B)	6304	4338	3632	23

VI. ^{1}H NMR Spectra of Selected Compounds

JC9121A CDCl3

exp20 PROTON

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1A_CDCl3/PROTON01		gain	not used
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at	2.500	pw90	9.700
np	40000	alfa	6.600
fb	not used	FLAGS	
bs	32	il	n
d1	1.000	in	n
nt	16	dp	y
ct	16	hs	nn
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tn	H1	lb	0.20
sfrq	499.708	fn	not used
tof	499.7	DISPLAY	
tpwr	61	sp	-0.1
pw	4.850	wp	4996.8
DECOUPLER		rfl	4630.1
dn	C13	rfp	3627.9
dof	0	rp	3.9
dm	nnn	lp	5.2
decwave	g	PLOT	
dpwr	35	wc	250
dmf	32258	sc	0
		vs	49
		th	54
		ai	cdc ph

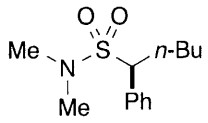

Table 6, entry 1

JC9153A CDCl3

exp23 PROTON

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fb	4000
bs	32
d1	1.000
nt	16
ct	16
TRANSMITTER	
tn	H1
sfrq	499.708
tof	499.7
tpwr	61
pw	4.850
DECOUPLER	
dn	C13
dof	0
dm	nnn
decwave	g
dpwr	35
dmf	32258

PRESATURATION	
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wet	n
SPECIAL	
temp	not used
gain	30
spin	20
hst	0.008
pw90	9.700
alfa	10.000
FLAGS	
il	n
in	n
dp	y
hs	nn
PROCESSING	
lb	0.20
fn	not used
DISPLAY	
sp	-0.1
wp	4997.0
rfl	4627.6
rfp	3627.9
rp	46.6
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PLOT	
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sc	0
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th	50
ai	cdc ph

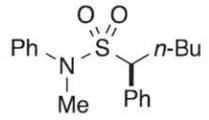
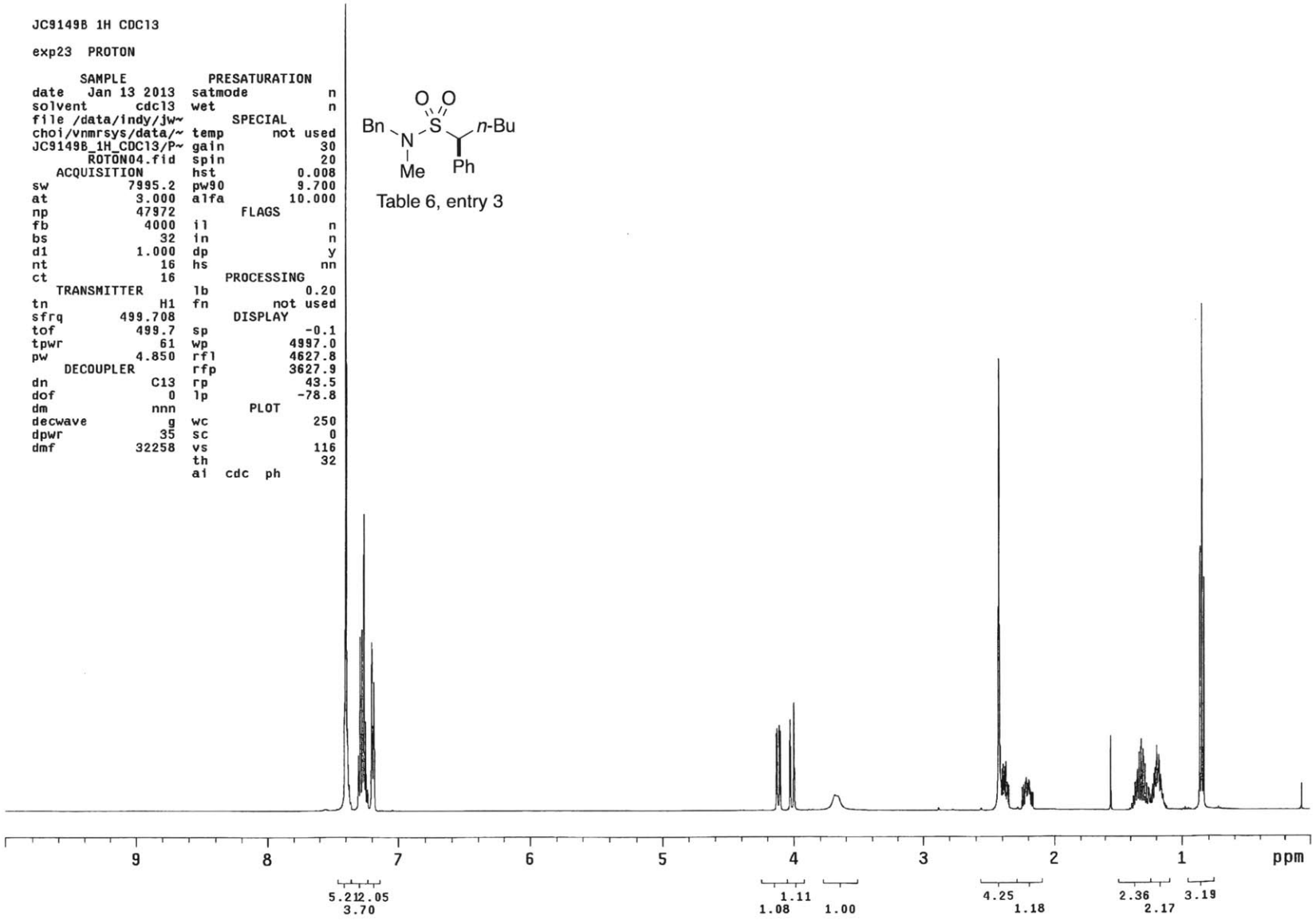


Table 6, entry 2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date Jan 13 2013
solvent cdcl3
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ct 16
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decwave g
dpwr 35
dmf 32258
PRESATURATION
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spin 20
hst 0.008
pw90 9.700
alfa 10.000
FLAGS
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in n
dp y
hs nn
PROCESSING
lb 0.20
fn not used
DISPLAY
sp -0.1
wp 4997.0
rfl 4627.8
rfp 3627.9
rp 43.5
lp -78.8
PLOT
wc 250
sc 0
vs 116
th 32
ai cdc ph
Bn
N
S
O O
n-Bu
Me
Ph
Table 6, entry 3
9
8
7
6
5
4
3
2
1
ppm
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1.11
1.08
1.00
4.25
1.18
2.36
2.17
3.19

JC9147A 1H CDCl3

exp23 PROTON

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	ROTON01.fid	spin	20
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at	3.000	alfa	10.000
np	47972	FLAGS	
fb	4000	il	n
bs	32	in	n
d1	1.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4997.0
pw	4.850	rfl	4627.6
DECOUPLER		rfp	3627.9
dn	C13	rp	47.0
dof	0	lp	-86.6
dm	nnn	PLOT	
decwave	g	wc	250
dpwr	35	sc	0
dmf	32258	vs	24
		th	35
		ai cdc ph	

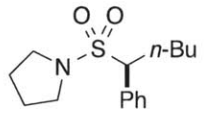
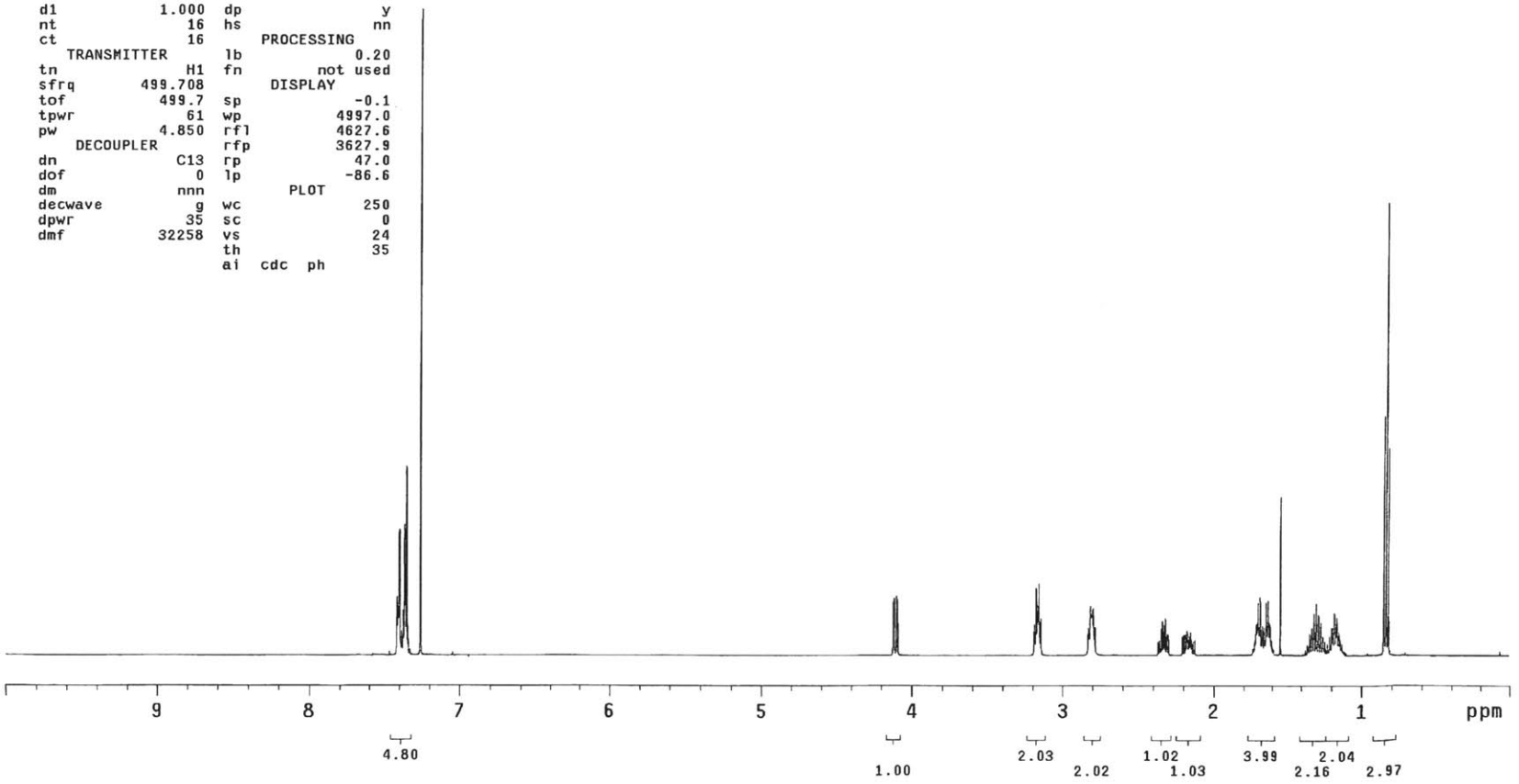


Table 6, entry 4



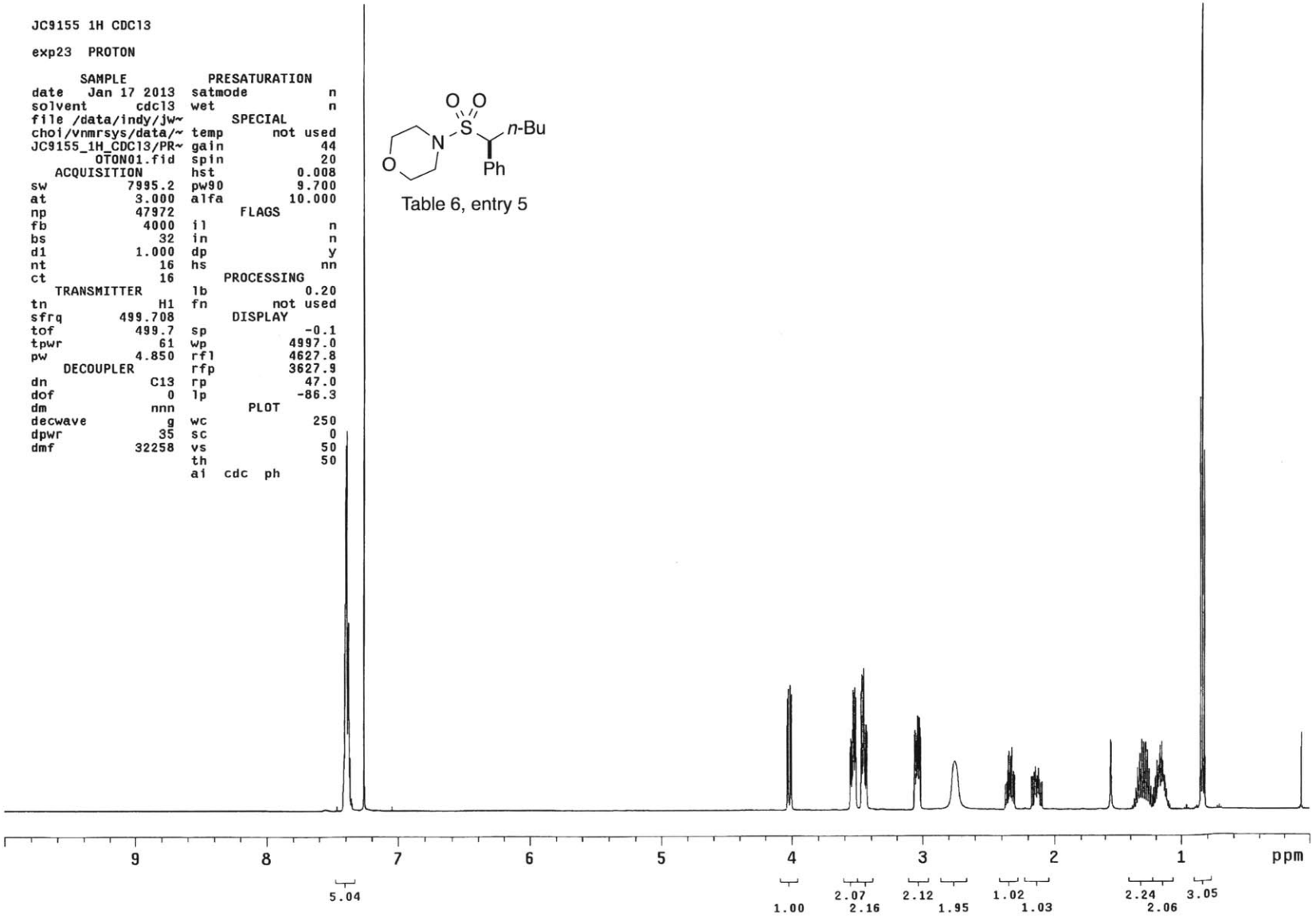


Table 6, entry 5

JC10093B 1H CDCl3

exp24 PROTON

SAMPLE		PRESATURATION	
date	May 14 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC100~		temp	not used
93B_1H_CDCl3/PROTO~		gain	32
	N01.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.950	rfl	4630.1
DECOUPLER		rfp	3627.9
dn	C13	rp	6.8
dof	0	lp	-79.6
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	65
dmf	32258	th	13
		ai cdc ph	

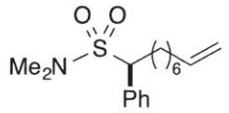


Table 6, entry 6

PM2-21A 1H CDCl3

exp30 PROTON

SAMPLE		PRESATURATION	
date	Oct 21 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/PM2-2~		temp	not used
1A_1H_CDCl3/PROTON~		gain	26
	01.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.698	DISPLAY	
tof	499.7	sp	-499.9
tpwr	61	wp	5496.6
pw	4.950	rfl	4632.1
DECOUPLER		rfp	3627.8
dn	C13	rp	-87.1
dof	0	lp	-73.6
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	16
dmf	32258	th	25
		ai cdc ph	

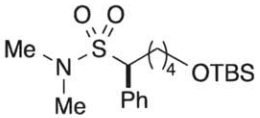


Table 6, entry 7

JC9221B 1H CDCl3

exp23 PROTON

SAMPLE		PRESATURATION	
date	Feb 22 2013	satmode	n
solvent	cdcl3	wet	n
file	/data/indy/jw~	SPECIAL	
choi/vnmrsys/data/~		temp	not used
JC9221B_1H_CDCl3/P~		gain	30
	ROTON01.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.700
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	1.000	dp	y
nt	32	hs	nn
ct	32	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.850	rfl	4630.1
DECOUPLER		rfp	3627.9
dn	C13	rp	46.0
dof	0	lp	-72.7
dm	nnn	PLOT	
decwave	g	wc	250
dpwr	35	sc	0
dmf	32258	vs	111
		th	13
		ai	cdc ph

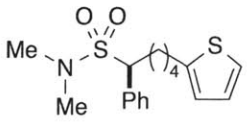


Table 6, entry 8

JC12043A CDCl3

exp57 PROTON

SAMPLE		PRESATURATION	
date	Jun 18 2014	satmode	n
solvent	cdcl3	wet	n
file	/indy/heinisc~	SPECIAL	
h/vnmrsys/data/JC1~		temp	not used
2043A_CDCl3/PROTON~		gain	26
	01.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.689	DISPLAY	
tof	499.7	sp	-0.2
tpwr	61	wp	4996.8
pw	4.950	rfl	4635.7
DECOUPLER		rfp	3627.7
dn	C13	rp	-166.7
dof	0	lp	-78.7
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	64
dmf	32258	th	25
		ai cdc ph	

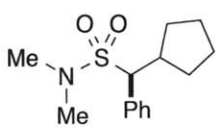


Table 6, entry 9

JC9111B 1H CDCl3

exp23 PROTON

SAMPLE		PRESATURATION	
date	Dec 9 2012	satmode	n
solvent	cdcl3	wet	n
file	/data/indy/jw~	SPECIAL	
choi/vnmrsys/data/~		temp	not used
JC9111B_1H_CDCl3/P~		gain	not used
	ROTON03.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.700
at	2.500	alfa	6.600
np	40000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	1.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.850	rfl	4630.1
DECOUPLER		rfp	3627.9
dn	C13	rp	5.2
dof	0	lp	5.6
dm	nnn	PLOT	
decwave	g	wc	250
dpwr	35	sc	0
dmf	32258	vs	37
		th	54
		ai	cdc ph

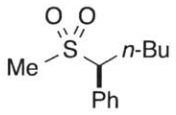


Table 7, entry 1

JC10185 CDCl3

exp23 PROTON

SAMPLE		PRESATURATION	
date	Jul 19 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC101~		temp	not used
85_CDCl3/PROTON01.~		gain	32
	fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.698	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.950	rfl	1001.8
DECOUPLER		rfp	0
dn	C13	rp	-76.4
dof	0	lp	-76.7
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	59
dmf	32258	th	13
		ai cdc ph	

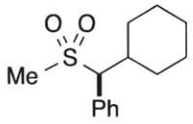


Table 7, entry 2

JC10181 CD2C12

exp2 PROTON

SAMPLE		PRESATURATION	
date	Aug 7 2013	satmode	n
solvent	cd2c12	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC101~		temp	not used
81_CD2C12/PROTON02~		gain	20
	.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	5.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.699	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.950	rfl	3669.9
DECOUPLER		rfp	2658.4
dn	C13	rp	-67.4
dof	0	lp	-76.2
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	284
dmf	32258	th	41
		ai cdc ph	

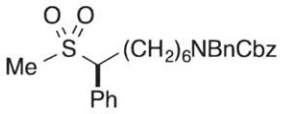
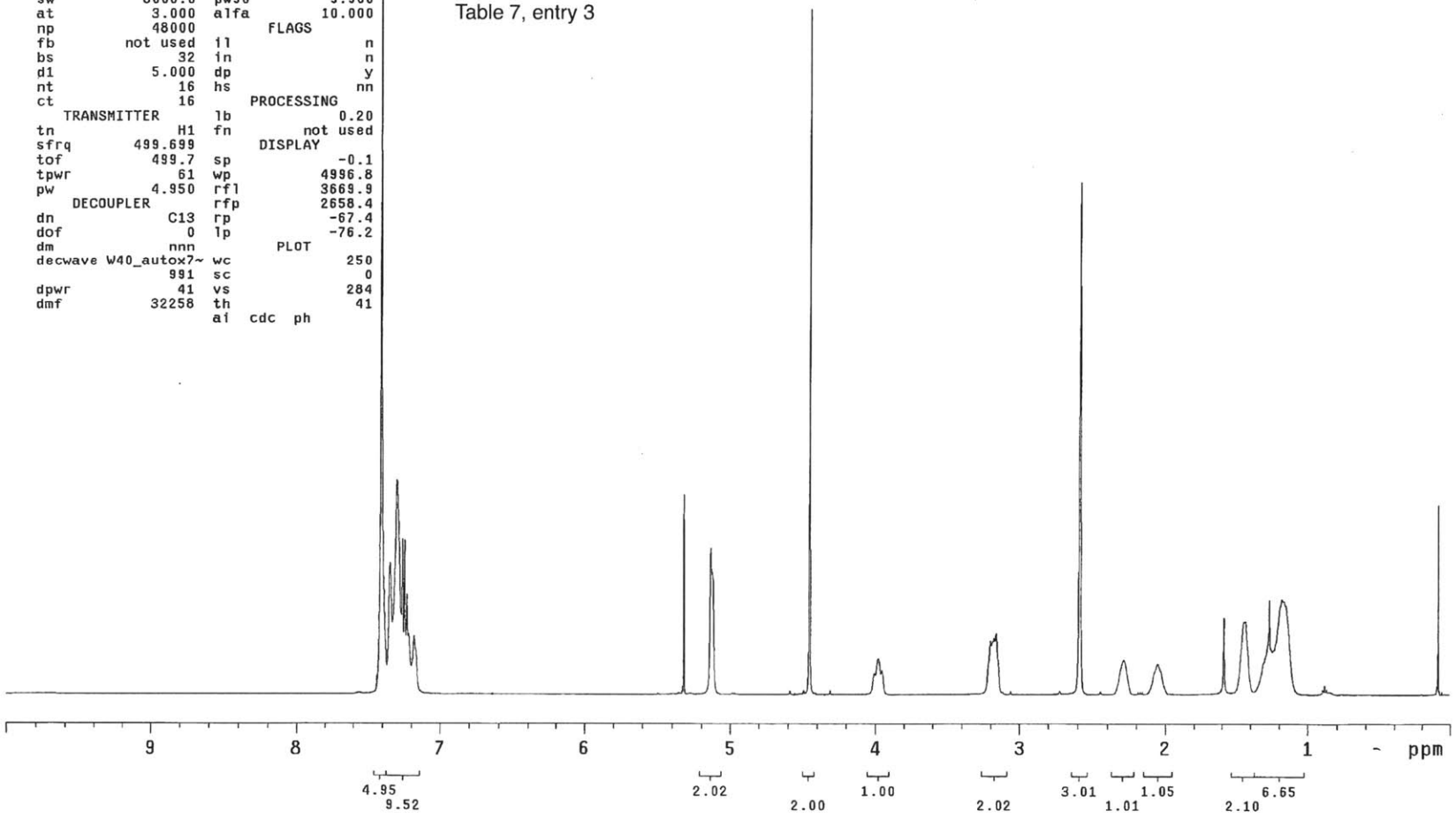


Table 7, entry 3



PM 2-20A CDCl3

exp27 PROTON

SAMPLE		PRESATURATION	
date	Aug 1 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/PM_2--~		temp	not used
20A_CDCl3/PROTON01~		gain	32
	.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.698	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.950	rfl	4632.1
DECOUPLER		rfp	3627.8
dn	C13	rp	-85.4
dof	0	lp	-74.5
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	63
dmf	32258	th	13
		ai cdc ph	

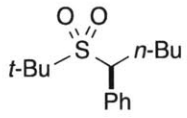


Table 7, entry 4

JC9119A CDCl3

exp30 PROTON

SAMPLE		PRESATURATION	
date	Dec 14 2012	satmode	n
solvent	cdcl3	wet	n
file	/data/indy/jw~choi/vnmrsys/data/~JC9119A_CDCl3/PROT~ON01.fid	SPECIAL	
		temp	not used
		gain	not used
ACQUISITION		spin	20
sw	8000.0	hst	0.008
at	2.500	pw90	9.700
np	40000	alfa	6.600
fb	not used	FLAGS	
bs	32	il	n
d1	1.000	in	n
nt	16	dp	y
ct	16	hs	nn
TRANSMITTER		PROCESSING	
tn	H1	lb	0.20
sfrq	499.708	fn	not used
tof	499.7	DISPLAY	
tpwr	61	sp	-0.1
pw	4.850	wp	4996.8
DECOUPLER		rfl	4630.1
dn	C13	rfp	3627.9
dof	0	rp	4.4
dm	nnn	lp	2.1
decwave	g	PLOT	
dpwr	35	wc	250
dmf	32258	sc	0
		vs	122
		th	2
		ai cdc ph	

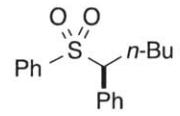


Table 7, entry 5

JC9229 CDCl3

exp23 PROTON

SAMPLE		PRESATURATION	
date	Feb 16 2013	satmode	n
solvent	cdcl3	wet	n
file	/data/indy/jw~	SPECIAL	
choi/vnmrsys/data/~		temp	not used
JC9229_1H_13C_CDCl~		gain	30
3/PROTON02.fid		spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.700
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	1.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.850	rfl	4630.1
DECOUPLER		rfp	3627.9
dn	C13	rp	43.7
dof	0	lp	-71.3
dm	nnn	PLOT	
decwave	g	wc	250
dpwr	35	sc	0
dmf	32258	vs	45
		th	50
		ai cdc ph	

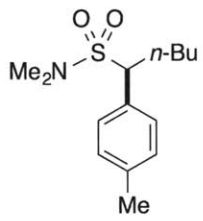


Table 8, entry 1

JC9219B CDCl3

exp23 PROTON

SAMPLE		PRESATURATION	
date	Feb 11 2013	satmode	n
solvent	cdcl3	wet	n
file	/data/indy/jw~	SPECIAL	
choi/vnmrsys/data/~		temp	not used
JC9219B_1H_13C_CDC~		gain	30
l3/PROTON01.fid		spin	20
ACQUISITION		hst	0.008
sw	7995.2	pw90	9.700
at	3.000	alfa	10.000
np	47972	FLAGS	
fb	4000	il	n
bs	32	in	n
d1	1.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4997.0
pw	4.850	rfl	4627.6
DECOUPLER		rfp	3627.9
dn	C13	rp	55.7
dof	0	lp	-87.5
dm	nnn	PLOT	
decwave	g	wc	250
dpwr	35	sc	0
dmf	32258	vs	11
		th	50
		ai cdc ph	

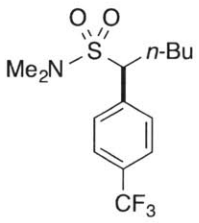


Table 8, entry 2

JC9159B CDCl3

exp23 PROTON

SAMPLE		PRESATURATION	
date	Jan 17 2013	satmode	n
solvent	cdcl3	wet	n
file	/data/indy/jw~	SPECIAL	
choi/vnmrsys/data/~		temp	not used
JC9159B_CDCl3/PROT~		gain	30
	ON01.fid	spin	20
ACQUISITION		hst	0.008
sw	7995.2	pw90	9.700
at	3.000	alfa	10.000
np	47972	FLAGS	
fb	4000	il	n
bs	32	in	n
d1	1.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4997.0
pw	4.850	rfl	4627.6
DECOUPLER		rfp	3627.9
dn	C13	rp	47.3
dof	0	lp	-86.6
dm	nnn	PLOT	
decwave	g	wc	250
dpwr	35	sc	0
dmf	32258	vs	36
		th	50
		ai cdc ph	

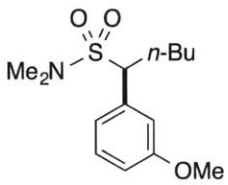


Table 8, entry 3

JC10223B CDCl3

exp28 PROTON

SAMPLE		PRESATURATION	
date	Aug 6 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC102~		temp	not used
23B_CDCl3/PROTON01~		gain	32
	.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.698	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.950	rfl	4632.1
DECOUPLER		rfp	3627.8
dn	C13	rp	-84.4
dof	0	lp	-75.3
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	24
dmf	32258	th	50
		ai cdc ph	

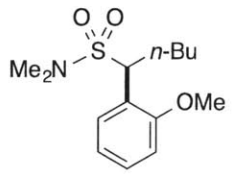


Table 8, entry 4

JC10209B CDCl3

exp28 PROTON

SAMPLE		PRESATURATION	
date	Aug 9 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC102~		temp	not used
09B_CDCl3/PROTON01~		gain	20
	.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.698	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.950	rfl	4632.1
DECOUPLER		rfp	3627.8
dn	C13	rp	-81.2
dof	0	lp	-72.5
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	72
dmf	32258	th	50
		ai cdc ph	

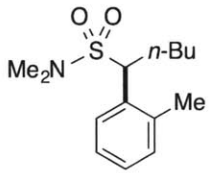


Table 8, entry 5

JC11021 CD2Cl2

exp30 PROTON

SAMPLE		PRESATURATION	
date	Oct 16 2013	satmode	n
solvent	cd2cl2	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC110~		temp	not used
21_CD2Cl2/PROTON01~		gain	28
	.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.699	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.950	rfl	3669.9
DECOUPLER		rfp	2658.4
dn	C13	rp	-85.2
dof	0	lp	-72.4
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	27
dmf	32258	th	50
		ai cdc ph	

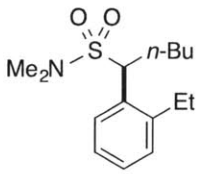
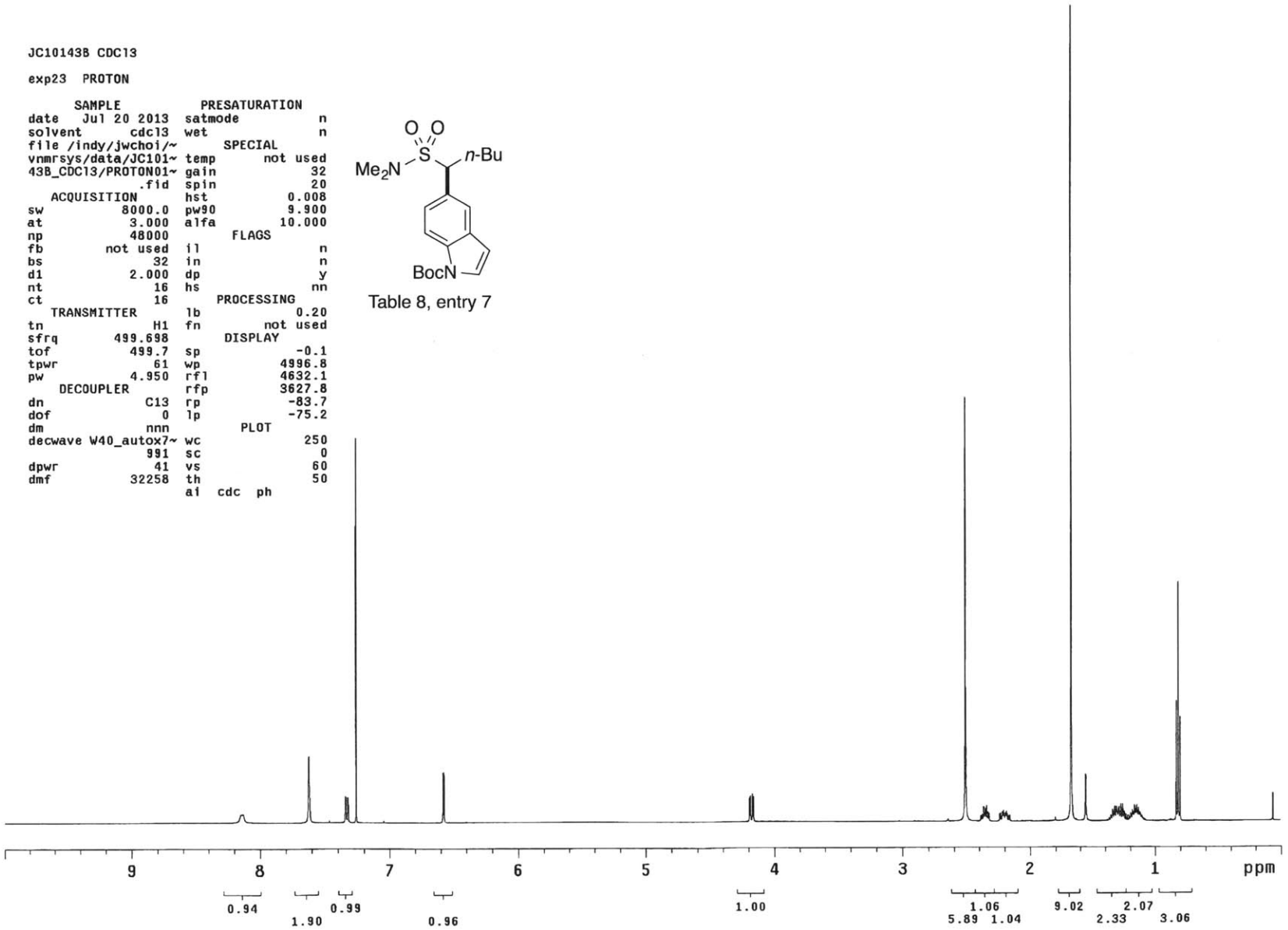


Table 8, entry 6


JC10143B CDCl3
exp23 PROTON
SAMPLE
date Jul 20 2013
solvent cdcl3
file /indy/jwchoi/~
vnmrsys/data/JC101~
43B_CDCl3/PROTON01~
.fid
ACQUISITION
sw 8000.0
at 3.000
np 48000
fb not used
bs 32
d1 2.000
nt 16
ct 16
TRANSMITTER
tn H1
sfrq 499.698
tof 499.7
tpwr 61
pw 4.950
DECOUPLER
dn C13
dof 0
dm nnn
decwave W40_autox7~
991
dpwr 41
dmf 32258
PRESATURATION
satmode n
wet n
SPECIAL
temp not used
gain 32
spin 20
hst 0.008
pw90 9.900
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 0.20
fn not used
DISPLAY
sp -0.1
wp 4996.8
rfl 4632.1
rfp 3627.8
rp -83.7
lp -75.2
PLOT
wc 250
sc 0
vs 60
th 50
ai cdc ph
Me2N
n-Bu
BocN
Table 8, entry 7
9
8
7
6
5
4
3
2
1
ppm
0.94
1.90
0.99
0.96
1.00
1.06
5.89
1.04
9.02
2.07
2.33
3.06

JC10219B CDCl3

exp26 PROTON

SAMPLE		PRESATURATION	
date	Aug 1 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC102~		temp	not used
19B_CDCl3/PROTON01~		gain	32
	.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.698	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.950	rfl	4632.1
DECOUPLER		rfp	3627.8
dn	C13	rp	-83.0
dof	0	lp	-73.0
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	28
dmf	32258	th	50
		ai cdc ph	

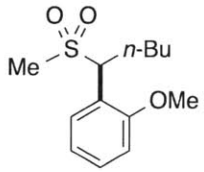


Table 8, entry 8

JC10215A CD2Cl2

exp34 PROTON

SAMPLE		PRESATURATION	
date	Jul 30 2013	satmode	n
solvent	cd2cl2	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC102~		temp	not used
15A_CD2Cl2/PROTON0~		gain	32
	1.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.699	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.950	rfl	3669.9
DECOUPLER		rfp	2658.4
dn	C13	rp	-74.6
dof	0	lp	-73.4
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	37
dmf	32258	th	50
		ai cdc ph	

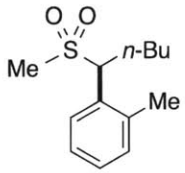


Table 8, entry 9

JC11023A 1H CD2Cl2

exp30 PROTON

SAMPLE		PRESATURATION	
date	Oct 17 2013	satmode	n
solvent	c6d6	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC110~		temp	not used
23A_1H_CD2Cl2/PROT~		gain	32
	ON01.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.698	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.950	rfl	4584.5
DECOUPLER		rfp	2658.4
dn	C13	rp	-86.5
dof	0	lp	-76.6
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	24
dmf	32258	th	50
		ai cdc ph	

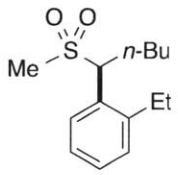
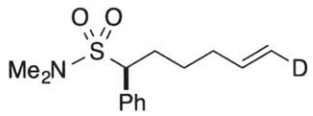


Table 8, entry 10

JC11079 CDCl3

exp51 PROTON

SAMPLE		PRESATURATION	
date	Jun 5 2014	satmode	n
solvent	cdcl3	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC110~		temp	not used
79_CDCl3/PROTON02.~		gain	28
	fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.689	DISPLAY	
tof	499.7	sp	-0.2
tpwr	61	wp	4996.8
pw	4.950	rfl	4635.7
DECOUPLER		rfp	3627.7
dn	C13	rp	-169.3
dof	0	lp	-79.4
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	42
dmf	32258	th	13
		ai cdc ph	



eq 21

JC10045B1 CDC13

exp51 PROTON

SAMPLE		PRESATURATION	
date	Jun 3 2014	satmode	n
solvent	cdcl3	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC100~		temp	not used
45B1_CDC13/PROTON0~		gain	28
	1.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.689	DISPLAY	
tof	499.7	sp	-0.2
tpwr	61	wp	4996.8
pw	4.950	rfl	4635.3
DECOUPLER		rfp	3627.7
dn	C13	rp	-167.5
dof	0	lp	-79.6
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	47
dmf	32258	th	25
		ai cdc ph	

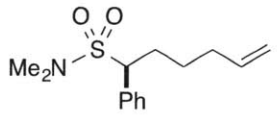


Figure 2

JC10187A IC-1 CD2Cl2

exp1 PROTON

SAMPLE		PRESATURATION	
date	Nov 9 2013	satmode	n
solvent	cd2cl2	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC101~		temp	not used
87A_IC-1_CD2Cl2/PR~		gain	24
	OTON01.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.699	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.950	rfl	3669.7
DECOUPLER		rfp	2658.4
dn	C13	rp	-70.6
dof	0	lp	-73.6
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	19
dmf	32258	th	6
		ai cdc ph	

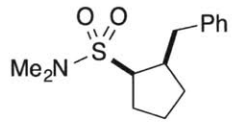


Figure 2

JC10187A IA-1 CD2Cl2

exp1 PROTON

SAMPLE		PRESATURATION	
date	Nov 10 2013	satmode	n
solvent	cd2cl2	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC101~		temp	not used
87A_IA-1_CD2Cl2/PR~		gain	24
OTON01.fid		spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.699	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.950	rfl	3670.2
DECOUPLER		rfp	2658.4
dn	C13	rp	-66.3
dof	0	lp	-80.4
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	26
dmf	32258	th	6
		ai cdc ph	

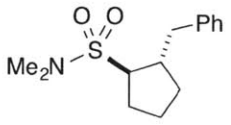


Figure 2

JC10275 CD2Cl2

exp30 PROTON

SAMPLE		PRESATURATION	
date	Sep 5 2013	satmode	n
solvent	cd2cl2	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC102~		temp	not used
75_CD2Cl2/PROTON01~		gain	28
	.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.699	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.950	rfl	3669.9
DECOUPLER		rfp	2658.4
dn	C13	rp	-71.9
dof	0	lp	-76.8
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	131
dmf	32258	th	50
		ai cdc ph	

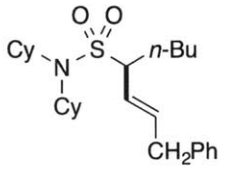
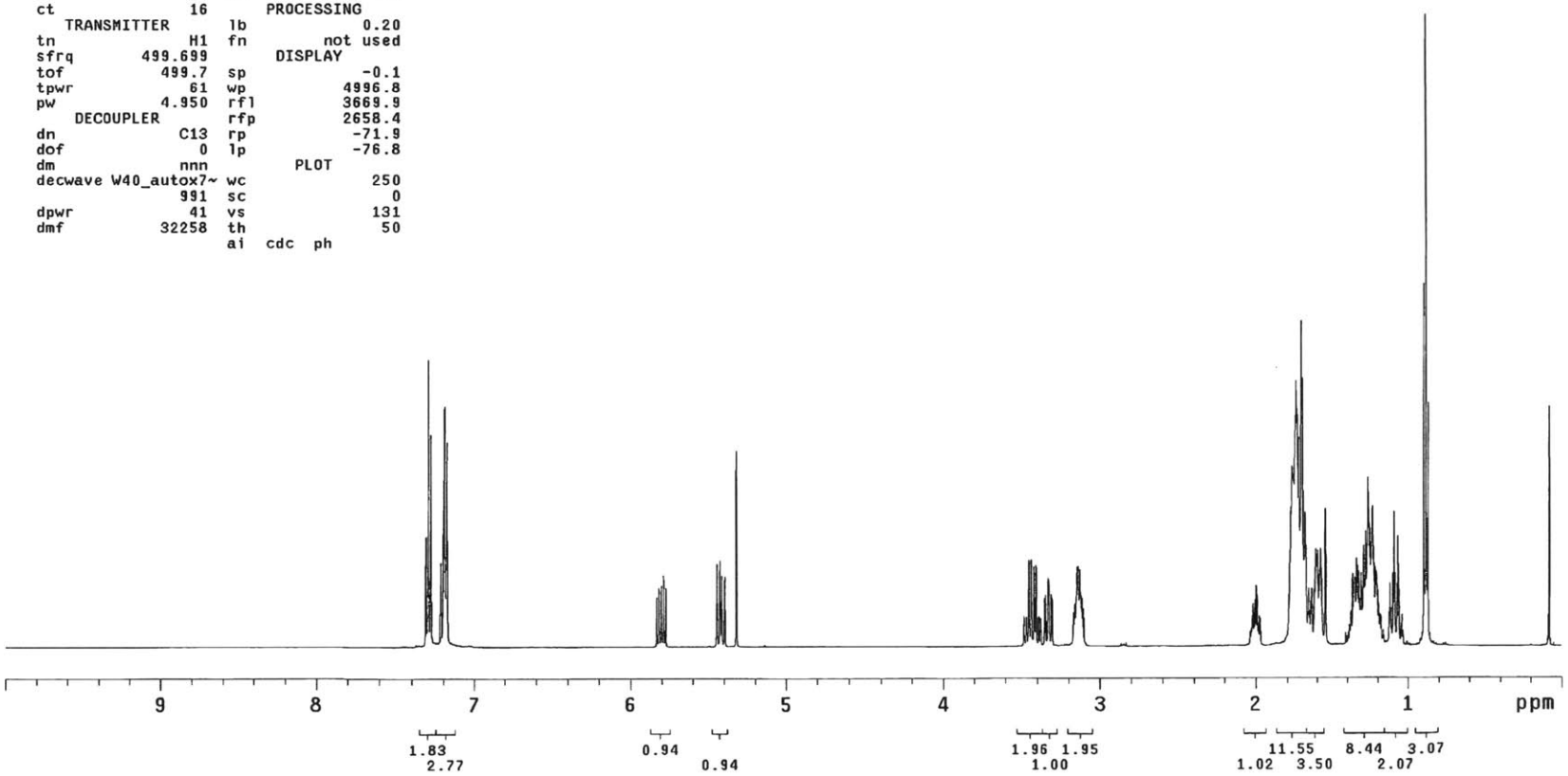


Table 9, entry 1



JC11025A 1H CDCl3

exp1 PROTON

SAMPLE		PRESATURATION	
date	Oct 23 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC110~		temp	not used
25A_1H_CDCl3/PROTO~		gain	26
	N04.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.698	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.950	rfl	4632.1
DECOUPLER		rfp	3627.8
dn	C13	rp	-87.5
dof	0	lp	-72.5
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	37
dmf	32258	th	13
		ai cdc ph	

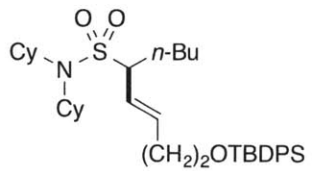


Table 9, entry 2

JC10279A CD2Cl2

exp30 PROTON

SAMPLE		PRESATURATION	
date	Sep 16 2013	satmode	n
solvent	cd2cl2	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC102~		temp	not used
79A_CD2Cl2/PROTON0~		gain	24
	1.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.699	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.950	rfl	3669.9
DECOUPLER		rfp	2658.4
dn	C13	rp	-68.2
dof	0	lp	-78.6
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	80
dmf	32258	th	38
		ai cdc ph	

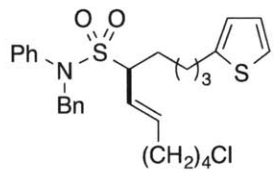
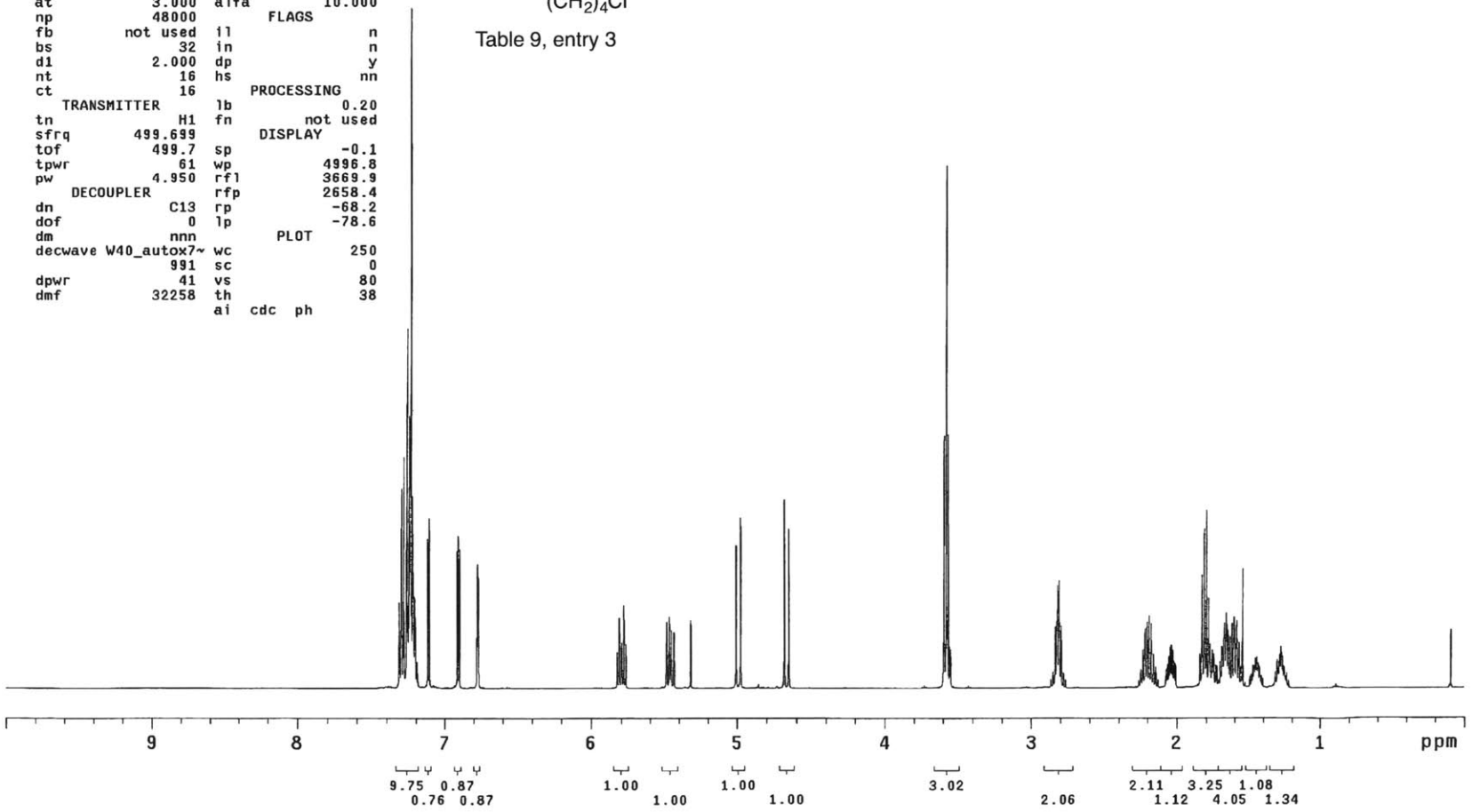


Table 9, entry 3



JC10281A 1H CDCl3

exp2 PROTON

SAMPLE		PRESATURATION	
date	Nov 2 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC102~		temp	not used
81A_1H_CDCl3/PROTO~		gain	24
	N01.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.698	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.950	rfl	4632.1
DECOUPLER		rfp	3627.8
dn	C13	rp	-79.0
dof	0	lp	-77.6
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	103
dmf	32258	th	50
		ai cdc ph	

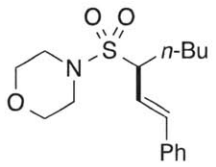


Table 9, entry 4

JC11123 CDCl3

exp37 PROTON

SAMPLE		PRESATURATION	
date	Feb 5 2014	satmode	n
solvent	cdcl3	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC111~		temp	not used
23_CDCl3/PROTON02.~		gain	26
	fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.698	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.950	rfl	4632.1
DECOUPLER		rfp	3627.8
dn	C13	rp	-77.7
dof	0	lp	-77.4
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	41
dmf	32258	th	13
		ai cdc ph	

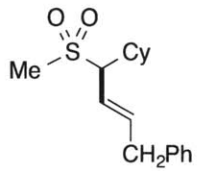


Table 9, entry 5

Section 1.3

Stereoconvergent Alkylations of α-Haloboronate Esters: The Catalytic Enantioselective Synthesis of Secondary Boronate Esters

A. Introduction

Chiral boronate esters are versatile synthetic intermediates in organic chemistry because C–B bonds can be readily converted into C–C, C–N, or C–O bonds by stereoselective transformations.[58] Due to the importance of such compounds, significant progress has been made in catalytic enantioselective strategies for the preparation of chiral boronate esters, such as hydroboration,[59,60] conjugate borylation,[61] allylic borylation,[62] conjugate addition and allylic substitution with borylated electrophiles,[63] hydrogenation of vinyl boronate esters,[64] and diborylation of alkenes[65] or alkynes.[66] However, the substrate scope of these enantioselective catalytic reactions is still limited; in many cases, these methods are particularly efficient for the synthesis of enantioenriched benzylic or allylic boronate esters.

In contrast, there are few examples of enantioselective catalytic syntheses of enantioenriched α,α-di*alkyl* boronate esters (e.g., via asymmetric hydroboration,

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[58] For reviews, see: (a) Brown, H. C.; Singaram, B. *Acc. Chem. Res.* **1988**, *21*, 287–293. (b) Brown, H. C.; Ramachandran, P. V. *Pure Appl. Chem.* **1991**, *63*, 307–316. (c) Brown, H. C; Ramachandran, V. P. *J. Organomet. Chem.* **1995**, *500*, 1–19. (d) Crudden, C. M.; Glasspoole, B. W.; Lata, C. J. *Chem. Commun.* **2009**, 6704–6716. (e) Hall, D. G. *Boronic Acids*, 2nd ed.; Wiley–VHC: Weinheim, 2011.

[59] For a review of Rh-catalyzed asymmetric hydroboration, see: Carroll, A.-M.; O'Sullivan, T. P.; Guiry, P. J. *Adv. Synth. Catal.* **2005**, *347*, 609–631.

[60] For leading references, see: (a) Smith, S. M.; Thacker, N. C., Takacs, J. M. *J. Am. Chem. Soc.* **2008**, *130*, 3734–3735. (b) Lee, Y.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 3160–3161. (c) Noh, D.; Chea, H.; Ju, J.; Yun, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 6062–6064. (d) Smith, S. M.; Takacs, J. M. *J. Am. Chem. Soc.* **2010**, *132*, 1740–1741.

[61] For a review, see: Calow, A. D. J.; Whiting, A. *Org. Biomol. Chem.* **2012**, *10*, 5485–5497.

[62] (a) Ito, H.; Ito, S.; Sasaki, Y.; Matsuura, K.; Sawamura, M. *J. Am. Chem. Soc.* **2007**, *129*, 14856–14857. (b) Guzman-Martinez, A.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2010**, *132*, 10634–10637. (c) Ito, H.; Kunii, S.; Sawamura, M. *Nat. Chem.* **2010**, *2*, 972–976. (d) Park, J. K.; Lackey, H. H.; Ondrusek, B. A.; McQuade, D. T. *J. Am. Chem. Soc.* **2011**, *133*, 2410–2413.

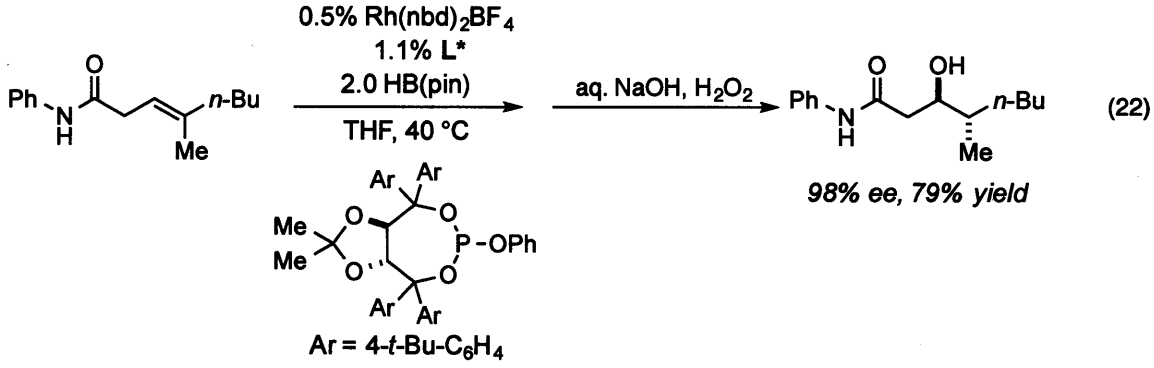
[63] (a) Carosi, L.; Hall, D. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 5913–5915. (b) Lee, J. C. H.; Hall, D. G. *J. Am. Chem. Soc.* **2010**, *132*, 5544–5545.

[64] (a) Morgan, J. B.; Morken, J. P. *J. Am. Chem. Soc.* **2004**, *126*, 15338–15339. (b) Moran, W. J.; Morken, J. P. *Org. Lett.* **2006**, *8*, 2413–2415. (c) Paptchikhine, A.; Cheruku, P.; Engman, M.; Andersson, P. G. *Chem. Commun.* **2009**, 5996–5998. (d) Ganić, A.; Pfaltz, A. *Chem. –Eur. J.* **2012**, *18*, 6724–6728.

[65] For leading references, see: (a) Burks, H. E.; Kliman, L. T.; Morken, J. P. *J. Am. Chem. Soc.* **2009**, *131*, 9134–9135. (b) Coombs, J. R.; Haeffner, F.; Kliman, L. T.; Morken, J. P. *J. Am. Chem. Soc.* **2013**, *135*, 11222–11231. (c) Toribatake, K.; Nishiyama, H. *Angew. Chem., Int. Ed.* **2013**, *52*, 11011–11015.

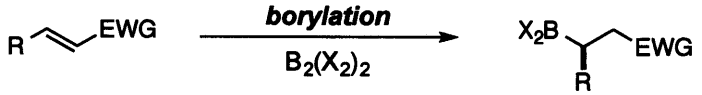
[66] Lee, Y.; Jang, H.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 18234–18235.

asymmetric conjugate addition, asymmetric hydrogenation, and asymmetric diborylation). Takacs disclosed amine-directed asymmetric hydroboration furnishing enantioenriched secondary alcohols after stereoselective oxidation of the C–B bond.[60a,60d] Under the developed reaction conditions, even trisubstituted alkenes undergo asymmetric hydroboration with high enantio- and diastereoselectivity; however, to achieve such high selectivity, an amide group is necessary (eq 22). Hoveyda also reported the enantioselective synthesis of secondary homobenzylic boronate esters via asymmetric hydroboration of β-substituted styrenes.[60b]



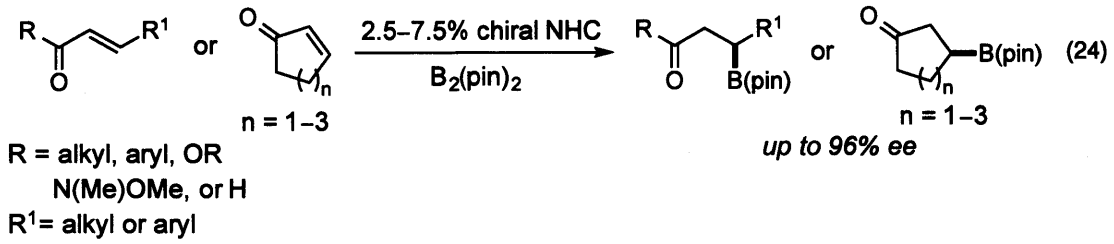
(22)

Asymmetric conjugate borylation of electron-deficient alkenes is another possible way to install a stereocenter at the α-position of boronate esters (eq 23).[61] For instance, in 2012, Hoveyda demonstrated NHC-catalyzed enantioselective conjugate addition of $B_2(pin)_2$ to both cyclic and acyclic α,β-unsaturated carbonyl compounds (eq 24).[67] In this study, the Hoveyda group not only showed a broad substrate scope (e.g., ketones, ester, aldehydes, and amides), but the reaction also proceeds in the absence of a metal catalyst.

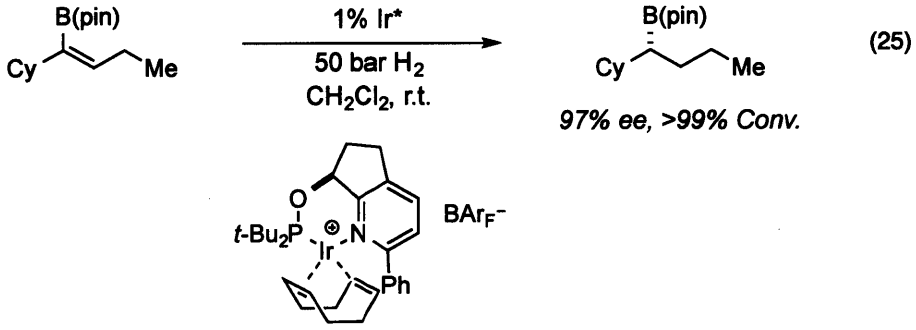


(23)

[67] Wu, H.; Radomkit, S.; O'Brien, J. M.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2012**, *134*, 8277–8285.

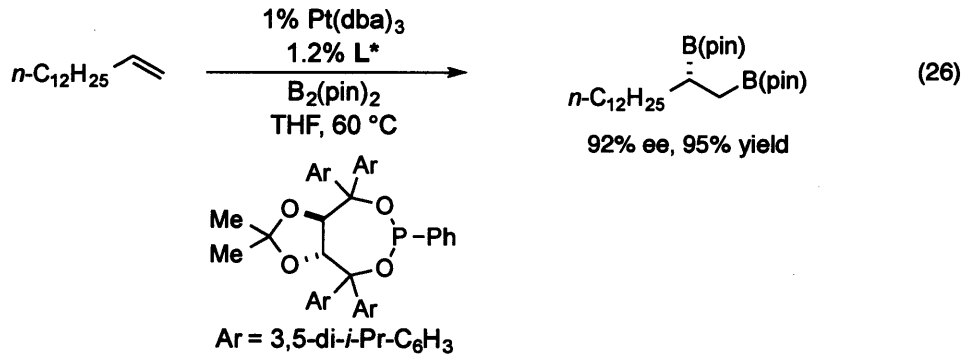


Although enantioenriched secondary boronate esters can be prepared by asymmetric hydrogenation of alkenyl boronate esters, this reaction is typically more efficient with terminal alkenes.[64] Recently, Pfaltz reported iridium-catalyzed asymmetric hydrogenation conditions which can be applied to various substituted alkenyl boronate esters.[64d] Under the optimized reaction conditions, even trisubstituted alkenes undergo asymmetric hydrogenation reaction in good ee and yield (eq 25). However, the asymmetric hydrogenation of a trisubstituted alkene bearing linear alkyl chains was not demonstrated. Moreover, a limited range of functional groups was shown to be compatible under the hydrogenation conditions.



Asymmetric diborylation of alkenes can also be used to access enantioenriched secondary alkyl boronate esters. The Morken group has explored transition-metal-catalyzed enantioselective diborylations of simple alkenes or monosubstituted alkenes for

the preparation of enantioenriched alkyl boronate esters.[68] Recently, he discovered Pt-catalyzed asymmetric diborylations of monosubstituted alkenes furnishing an array of secondary boronate esters in good ee and good yield (eq 26).[65b] The Nishiyama group also disclosed a similar reaction with a rhodium catalyst.[65c] In addition, the same family of compounds can be prepared via enantioselective diborylations of terminal alkynes using a NHC–Cu catalyst.[66] Whereas these reactions proceed in high enantioselectivity, the utility of diborylated compounds is limited due to the lack of selective functionalization methods among two boronate esters.[69]



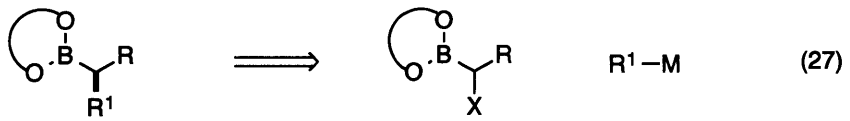
(26)

The catalytic asymmetric methods for the synthesis of these secondary alkyl boronate esters described above require either directing groups or differentiation between two alkyl groups to achieve both good enantioselectivity and regioselectivity. Transition-metal-catalyzed cross-coupling of secondary electrophiles with alkylmetal reagents is a possible solution to overcome these existing limitations (eq 27); however, to the best of our knowledge, no asymmetric cross-couplings of α-haloboronate esters furnishing enantioenriched secondary boronate esters have been reported.

---

[68] For examples of Rh-catalyzed asymmetric diborylations, see: (a) Morgan, J. B.; Miller, S. P.; Morken, J. P. *J. Am. Chem. Soc.* **2003**, *125*, 8702–8703. (b) Trudeau, S.; Morgan, J. B.; Shrestha, M.; Morken, J. P. *J. Org. Chem.* **2005**, *70*, 9538–9544.

[69] Mlynarski, S. N.; Schuster, C. H.; Morken, J. P. *Nature* **2014**, *505*, 386–390.

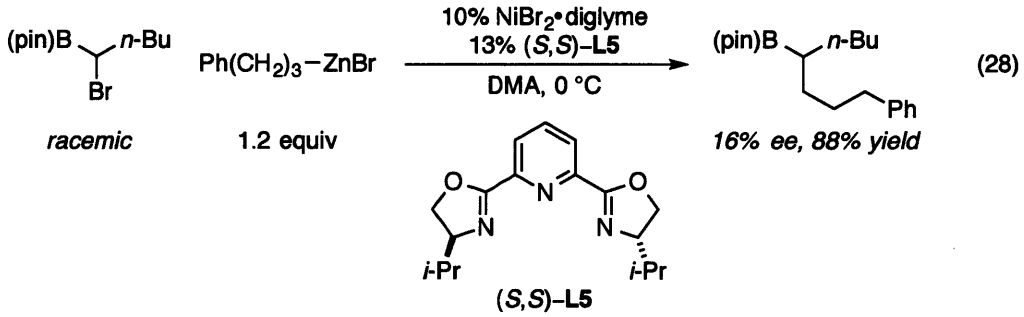


(27)

The Fu group has developed transition-metal-catalyzed C–C bond formations with particular interest in Ni-catalyzed asymmetric cross-couplings of secondary alkyl electrophiles. As described in section 1.1.A, we have shown that α-bromoamides,[8] benzylic halides,[9] and allylic chlorides[10] are effective coupling partners for Ni-catalyzed asymmetric Negishi alkylations. With this success in developing asymmetric Negishi alkylations of secondary alkyl electrophiles, we were interested in finding Negishi alkylation reaction conditions for α-haloboronate esters for synthesizing enantioenriched secondary alkyl boronate esters in good ee and yield. Although we also have developed Ni-catalyzed asymmetric Suzuki alkylations of secondary alkyl electrophiles,[19,23,40,41] Negishi alkylation is more attractive for the cross-coupling of α-haloboronate esters because it does not require a stoichiometric quantity of a Brønsted-base additive, which could cause a problem by interacting with the boronate ester.

B. Results and Discussion

In our previous studies, a nickel/pybox complex successfully catalyzed C–C bond formations between secondary alkyl electrophiles and alkylzinc reagents in good yield and ee.[8–10] Unfortunately, when an α-bromoboronate ester was subjected under one of the asymmetric Negishi alkylation conditions,[9] the reaction proceeded in 88% yield but 16% ee (eq 28).



(28)

Other pybox ligands were evaluated under the stereoconvergent Negishi alkylation conditions (Figure 3). However, no improvement in ee was observed. The C–C bond formation between an α-bromoboronate ester and an alkylzinc reagent was somewhat efficient, but the ee of these reactions was disappointing (<20% ee).

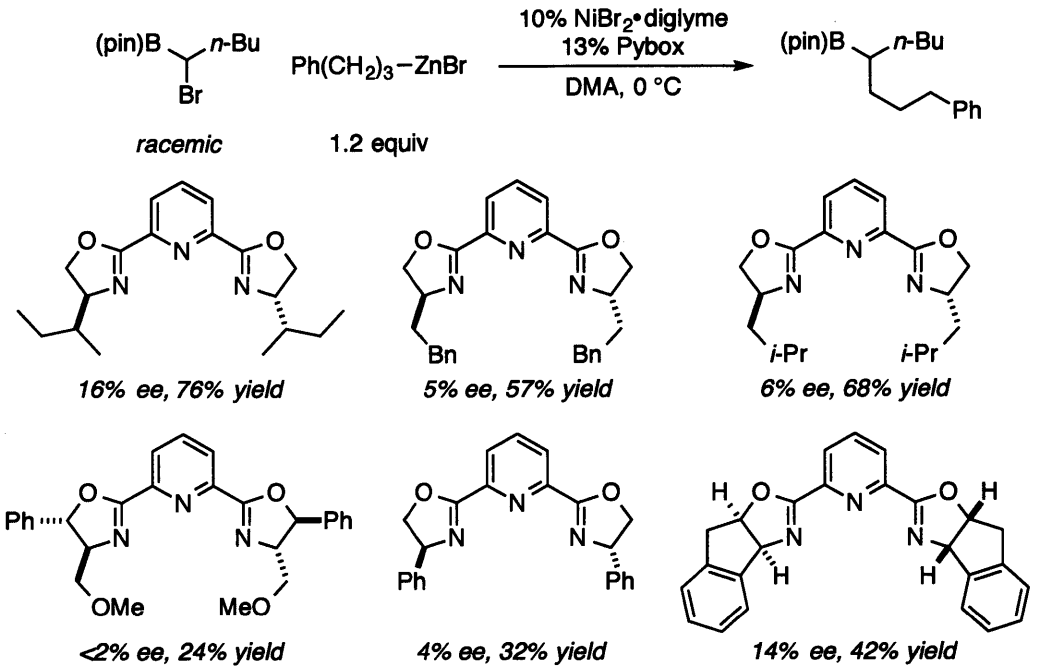


Figure 3. Pybox ligand screen

To improve enantioselectivity, we decided to explore other families of ligands such as bis(oxazoline), pyridine-oxazoline, and diamine ligands for the development of the stereoconvergent Negishi alkylation of α-bromoboronate esters. As illustrated in Figure 4, oxazoline-based ligands were not effective for achieving high enantioselectivity (<35% ee); instead, a diamine ligand (**L6**) gave promising results. In the presence of nickel and ligand **L6**, an α-bromopinacol boronate ester was found to couple with an alkyl zinc reagent in 57% ee and 90% yield.[70]

[70] For examples of diamine ligands in nickel-catalzyed asymmetric cross-couplings of secondary alkyl electrophiles, see: ref 19, ref 23, ref 40, and ref 41.

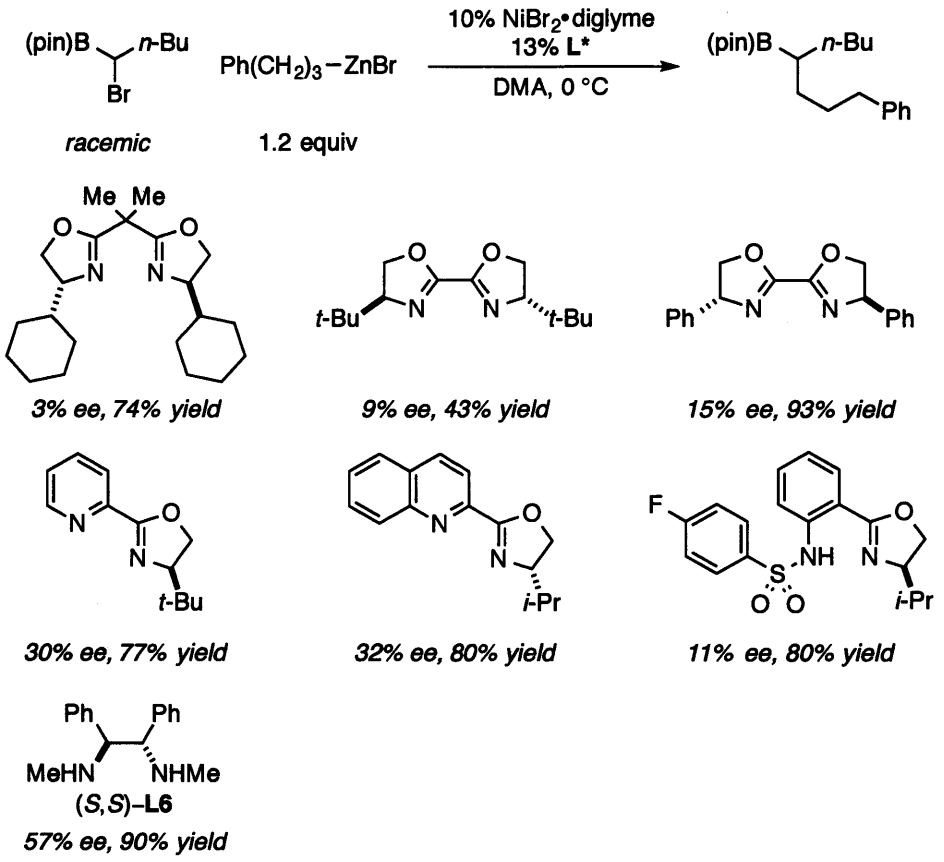
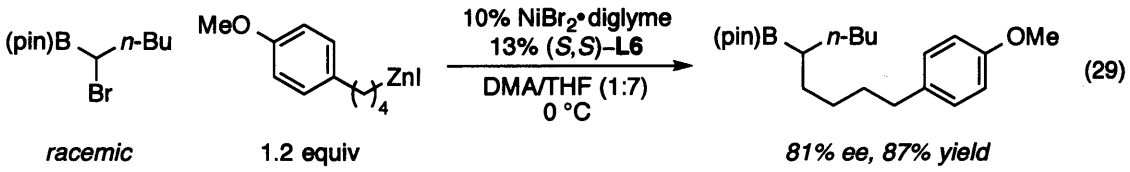


Figure 4. Ligand screen

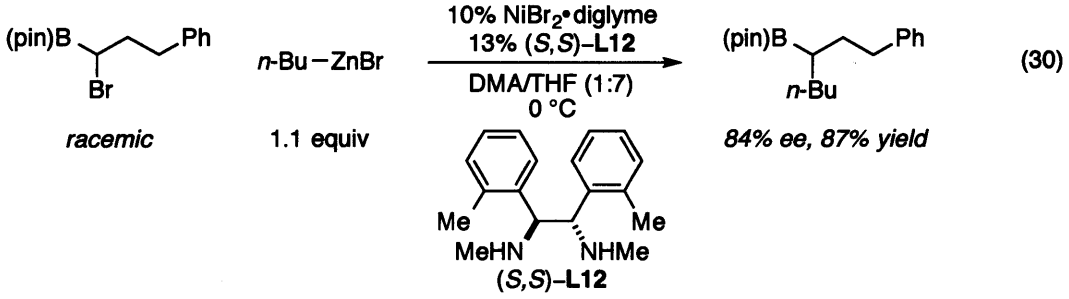
With a promising ligand (**L6**) in hand, extensive optimization of the reaction parameters was conducted. We found that a DMA/THF solvent mixture is crucial to obtain good enantioselectivity for the Negishi alkylation of α-bromopinacol boronate esters. In a DMA/THF solvent mixture, the cross-coupling proceeded in 81% ee and 87% yield (eq 29). When the asymmetric alkylation was conducted in pure THF rather than in a solvent mixture, the reaction was sluggish (<20% yield). We believe that a coordinating solvent such as DMA facilitates the C–C bond formation in this asymmetric Negishi alkylation. This is the first time that the cross-coupling between a racemic secondary alkyl electrophile and a primary alkylzinc reagent has been effectively catalyzed by a nickel/diamine complex in good ee and good yield. In previous cases for asymmetric

Negishi alkylations with racemic alkyl electrophiles, a pybox was the ligand of choice.[8–10,71]



(29)

After re-evaluation of a number of diamine ligands under these conditions, the optimized reaction conditions for the cross-couplings of α-bromopinacol boronate esters with alkylzinc reagents were obtained. A nickel/diamine ligand **L12** complex effectively facilitates the C–C bond formation between α-bromopinacol boronate esters and alkylzinc reagents. Under these conditions, an α-bromopinacol boronate cross-couplings with an alkylzinc reagent furnishing a secondary boronate ester in 84% ee and 87% yield (eq 30).

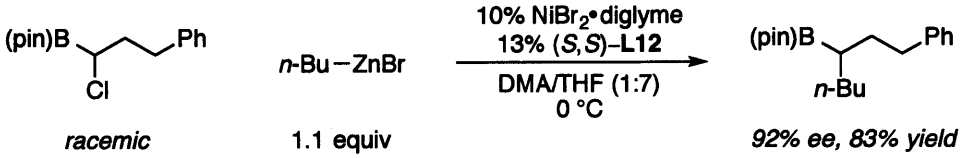


(30)

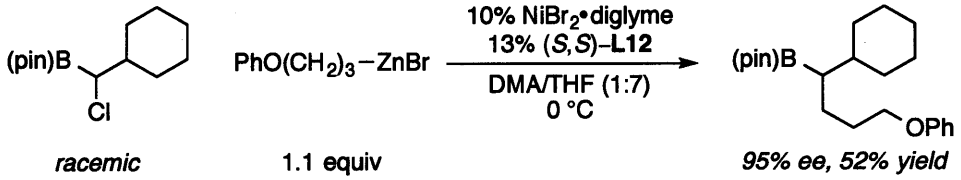
We were interested whether these reaction conditions could be applied to the coupling of α-chloropinacol boronate esters; therefore, the reactivity of an α-chloropinacol boronate was evaluated. It is noteworthy that the cross-coupling of the secondary alkyl chloride proceeded in higher enantioselectivity than the alkyl bromide and with similar yield (eq 31). Furthermore, a hindered α-chloropinacol boronate ester

[71] For an example of enantioselective alkyl–alkyl cross-couplings with a Ni/diamine catalyst, see: Cordier, C. J.; Lundgren, R. J.; Fu, G. C. *J. Am. Chem. Soc.* **2013**, *135*, 10946–10949.

was also an effective coupling partner for this asymmetric Negishi alkylation reaction (eq 32).



(31)



(32)

C. Conclusion and Future Outlook

Nickel-catalyzed asymmetric cross-couplings between secondary α-haloboronate esters and alkylzinc reagents have been established. The nickel/diamine **L12** catalyst furnishes enantioenriched secondary alkyl boronate esters from racemic α-haloboronate esters via a stereoconvergent process. Both α-chloropinacol boronate esters and α-bromopinacol boronate esters undergo cross-couplings in good ee and good yield, but α-chloropinacol boronate esters provide higher ee.

With respect to the boronate ester scope, an array of boronate esters will be prepared and evaluated under the stereoconvergent Negishi alkylation conditions. Chiral boronate esters such as pinanediol boronate esters will be studied to investigate whether the stereochemistry of the chiral boronate ester affects the stereochemical outcome of this asymmetric C–C bond-forming process. To develop general cross-coupling conditions, electrophiles and nucleophiles bearing a variety of functional groups will be prepared, and the final Negishi alkylation conditions will be determined that provide good enantioselectivity and yield with broad functional-group compatibility. Additional studies to elucidate the mechanism of this cross-coupling reaction will be conducted.

D. Experimental

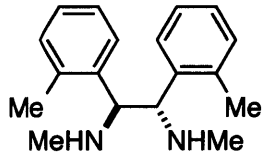
I. General Information

The following reagents were purchased and used as received: 1,2-bis(2-hydroxyphenyl)ethylenediamine ((*R*,*R*) and (*S*,*S*); Aldrich), $NiBr_2$•diglyme (Aldrich), and DMA (absolute, over molecular sieves; Aldrich). Alkylzinc halides were prepared according to a literature procedure.[10] THF was deoxygenated and dried by sparging with argon followed by passage through an activated alumina column (S. G. Water) prior to use. All reactions were carried out in oven-dried glassware under an inert atmosphere.

^{1}H NMR data and ^{13}C NMR data were collected on a VARIAN 500 MHz spectrometer at ambient temperature. HPLC analyses were carried out on an Agilent 1100 series system with Daicel CHIRALPAK® columns or Daicel CHIRALCEL® columns (internal diameter 4.6 mm, column length 250 mm, particle size 5 μm or 3 μm). SFC analyses were performed on a Thar SFC system equipped with an Agilent 1315B DAD detector using Daicel CHIRALCEL® columns or Daicel CHIRALPAK® columns (I.D. 4.6 mm, column length 250 mm, particle size 3 μm or 5 μm) at 40 °C. GC analyses were carried out on an Agilent 6890 series system with an HP-5 column (length 30 m, I.D. 0.25 mm).

II. Preparation of Materials

These procedures have not been optimized.



(1*S*,2*S*)-N^1,N^2-Dimethyl-1,2-di-*o*-tolylethane-1,2-diamine. The title compound was prepared from (1*S*,2*S*)-1,2-di-*o*-tolylethane-1,2-diamine dihydrochloride (988 mg, 3.15 mmol) according to a literature procedure:[71] 320 mg (38%). White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (dd, 2H, J = 7.8, 1.4 Hz), 7.14 (t, 2H, J = 7.3 Hz), 7.01 (td, 2H, J = 7.4, 1.4 Hz), 6.86 (d, 2H, J = 7.5 Hz), 3.90 (s, 2H), 2.23 (s, 6H), 2.13–1.97 (br s, 2H), 1.92 (s, 6H).

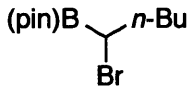
^{13}C NMR (126 MHz, $CDCl_3$) δ 139.9, 137.1, 129.9, 126.9, 126.6, 125.9, 65.5, 34.5, 19.6.

FT-IR (neat) 3297, 3233, 3073, 2981, 2923, 2861, 2840, 2783, 1490, 1463, 1448, 1437, 1424, 1411, 1378, 1338, 1286, 1252, 1175, 1139, 1106, 1050, 902, 876, 864, 823, 780, 768, 760, 751, 731, 628, 619 cm^{-1}.

MS (ESI) *m/z* (M^++H): calcd for $C_{18}H_{25}N_2$: 269, found: 269.

$[\alpha]^{25}_D$ = +0.92° (c = 1.01, $CHCl_3$).

Representative experimental procedure for the preparation of α-bromopinacol boronate ester. In accordance with a literature procedure,[72] a solution of an alkenyl pinacol boronate ester (4.5 mmol) in dichloromethane (9.0 mL) was added to a suspension of Cp_2ZrHCl (3.48 g, 13.5 mmol) in dichloromethane (27.0 mL) in a 100-mL round-bottom flask. The mixture was stirred at r.t. for 40 min, during which time it became a clear solution, and then *N*-bromosuccinimide (961 mg, 5.40 mmol) was added. The reaction mixture was stirred at r.t. for 1 h, and then the reaction was concentrated. The product was extracted from the resulting residue with hexanes, and the combined organic extracts were concentrated.



2-(1-Bromopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. The title compound was prepared from (*E*)-4,4,5,5-tetramethyl-2-(pent-1-en-1-yl)-1,3,2-dioxaborolane (881 mg, 4.50 mmol). The product was purified by column chromatography (hexanes): 615 mg (49%). Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.31 (t, 1H, J = 7.9 Hz), 1.94–1.85 (m, 2H), 1.49–1.39 (m, 1H), 1.38–1.28 (m, 3H), 1.279 (s, 6H), 1.276 (s, 6H), 0.90 (t, 3H, J = 7.2 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 84.3, 33.9, 31.1, 24.7, 24.5, 22.3, 14.1.

FT-IR (neat) 2978, 2959, 2932, 2872, 1638, 1467, 1415, 1386, 1342, 1290, 1266, 1238, 1215, 1167, 1146, 1136, 1113, 1030, 1005, 967, 897, 871, 846, 825, 672, 621 cm^{-1}.

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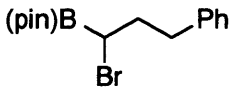
[72] Zheng, B.; Srebnik, M. *Tetrahedron Lett.* **1994**, *35*, 1145–1148.

MS (FAB) *m/z* (M^++H) calcd for $C_{11}H_{23}BBrO_2$: 277, found: 277.



2-(1-Bromo-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. The title compound was prepared from (*E*)-4,4,5,5-tetramethyl-2-(3-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane. The product was purified by column chromatography (5% Et_2O/hexanes). Light-yellow oil.

^1H NMR (500 MHz, $CDCl_3$) δ 7.30–7.27 (m, 2H), 7.22–7.18 (m, 3H), 3.32 (dd, 1H, *J* = 8.7, 6.7 Hz), 2.84 (ddd, 1H, *J* = 14.0, 8.3, 6.0 Hz), 2.75–2.69 (m, 1H), 2.24–2.13 (m, 2H), 1.29 (s, 12H).

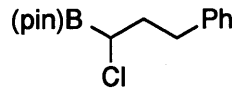
^{13}C NMR (126 MHz, $CDCl_3$) δ 141.1, 128.7, 128.6, 126.2, 84.4, 35.8, 34.8, 24.7, 24.6.

FT-IR (neat) 3085, 3062, 3026, 2978, 2933, 1603, 1584, 1497, 1479, 1469, 1454, 1414, 1383, 1342, 1292, 1269, 1236, 1214, 1167, 1142, 1107, 1077, 1030, 1006, 968, 914, 895, 873, 850, 821, 769, 750, 700, 672, 627 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_{15}H_{22}BBrO_2$: 324, found: 324.

Representative experimental procedure for the preparation of α-chloropinacol boronate ester. A solution of RMgX (1.00 M in THF; 10.0 mL, 10.0 mmol) was added to a solution of the 2-(dichloromethyl)-4,4,5,5-tetramethyl-1,3,2-

dioxaborolane (10.0 mmol; prepared according to a literature procedure[73]) in Et_2O (26.0 mL) in a 100-mL round-bottom flask at –78 °C. Then, $ZnCl_2$ (anhydrous; 984 mg, 7.22 mmol) was added quickly. The reaction mixture was stirred at −78 °C overnight. The solid was filtered, and the filtrate was washed with saturated aqueous NH_4Cl. The organic layer was dried over Na_2SO_4 and concentrated.



2-(1-Chloro-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. The title compound was prepared from 2-(dichloromethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.04 g, 14.4 mmol) and phenethylmagnesium chloride (1.00 M in THF; 14.4 mL, 14.4 mmol; Aldrich). The product was purified by column chromatography (10% ethyl acetate/hexanes): 2.19 g (54%). Colorless oil.

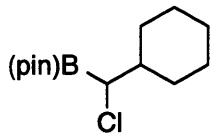
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.28 (m, 2H), 7.23–7.19 (m, 3H), 3.43 (t, 1H, J = 7.4 Hz), 2.86 (dt, 1H, J = 14.1, 7.3 Hz), 2.77 (dt, 1H, J = 13.6, 8.0 Hz), 2.17–2.10 (m, 2H), 1.29 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.2, 128.7, 128.5, 126.1, 84.6, 35.8, 33.4, 24.74, 24.72.

FT-IR (neat) 3085, 3062, 3026, 2979, 2933, 1603, 1497, 1469, 1454, 1415, 1383, 1373, 1346, 1269, 1214, 1168, 1142, 1110, 967, 897, 874, 849, 750, 700, 675, 653 cm^{-1}.

MS (FAB) *m/z* (M^++H) calcd for $C_{15}H_{23}BClO_2$: 281, found: 281.

[73] Raheem, I. T.; Goodman, S. N.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2004**, *126*, 706–707.



2-(Chloro(cyclohexyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. The title compound was prepared from 2-(dichloromethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.03 g, 4.88 mmol) and cyclohexylmagnesium chloride (2.00 M in Et_2O; 2.44 mL, 4.88 mmol; Aldrich). The product was purified by column chromatography (10% ethyl acetate/hexanes): 721 mg (57%). Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.23 (d, 1H, J = 7.3 Hz), 1.98–1.91 (m, 1H), 1.78–1.61 (m, 5H), 1.34–1.20 (m, 2H), 1.28 (s, 12H), 1.17–1.02 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 84.4, 41.4, 31.0, 30.6, 26.3, 26.2, 26.1, 24.8, 24.7.

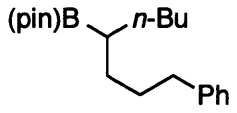
FT-IR (neat) 2979, 2927, 2853, 1480, 1469, 1450, 1412, 1382, 1372, 1362, 1342, 1312, 1273, 1214, 1188, 1167, 1142, 1108, 972, 883, 866, 849, 681, 655 cm^{-1}.

MS (FAB) *m/z* (M^++H) calcd for $C_{13}H_{25}BClO_2$: 259, found: 259.

III. Enantioselective Alkylations

General Procedure. In a nitrogen-atmosphere glovebox, $NiBr_2$•diglyme (3.5 mg, 0.010 mmol), (*S*,*S*)–**L12** (3.5 mg, 0.013 mmol), and the electrophile (0.10 mmol) were added to a 4-mL vial equipped with a magnetic stir bar. Next, THF (875 μL) and DMA (15 μL) were added to the vial, and the vial was sealed with a PTFE-lined septum cap. The reaction mixture was stirred for 30 min. The vial was removed from the glovebox, and it was cooled to 0 °C. Then, the pre-cooled alkylzinc reagent (1.0 M in DMA; 0.11 mL, 0.11 mmol) was added to the vial that contained the electrophile. The

reaction mixture was stirred at 0 °C for 12 h, and then the reaction was quenched by the addition of ethanol (0.10 mL). The solution was allowed to warm to r.t., and tetradecane (26 μL, 0.10 mmol) was added as an internal standard. The mixture was filtered through a plug of silica, eluting with Et_2O. The yield was determined by calibrated GC analysis. Then, the filtrate was concentrated, and the crude was purified by preparatory TLC for HPLC analysis.



4,4,5,5-Tetramethyl-2-(1-phenyloctan-4-yl)-1,3,2-dioxaborolane (eq 28 and Figures 3 and 4).

The ee was determined after oxidation to 1-phenyloctan-4-ol according to a literature procedure[74] by HPLC on a CHIRALCEL OJ-H column. (1% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 14.2 min (major), 17.1 min (minor).

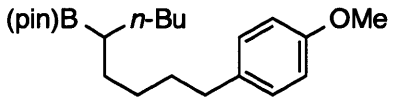
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.25 (m, 2H), 7.18–7.15 (m, 3H), 2.65–2.56 (m, 2H), 1.68–1.56 (m, 2H), 1.53–1.45 (m, 1H), 1.44–1.32 (m, 3H), 1.32–1.22 (m, 4H), 1.24 (s, 12H), 1.00 (tt, 1H, J = 8.9, 5.9 Hz), 0.88 (t, 3H, J = 7.0 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.1, 128.5, 128.3, 125.6, 83.0, 36.4, 31.7, 31.3, 31.2, 25.0, 24.9, 23.1, 14.2.

FT-IR (neat) 3085, 3062, 3026, 2977, 2955, 2926, 2856, 1604, 1496, 1480, 1461, 1453, 1410, 1387, 1379, 1370, 1354, 1314, 1268, 1233, 1214, 1165, 1144, 1112, 1074, 1303, 1004, 968, 855, 748, 698 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_{20}H_{33}BO_2$: 316, found: 316.

[74] Toribatake, K.; Zhou, L.; Tsuruta, A.; Nishiyama, H. *Tetrahedron* **2013**, *69*, 3551–3560.



2-(1-(4-Methoxyphenyl)nonan-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (eq 29).

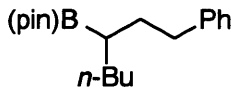
The ee was determined after oxidation to 1-(4-methoxyphenyl)nonan-5-ol according to a literature procedure[74] by SFC analysis on a CHIRALCEL OJ-H column (4% *i*-PrOH/CO_2, 3.0 mL/min) with t_r = 18.9 min (minor), 19.7 min (major).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09–7.07 (m, 2H), 6.82–6.79 (m, 2H), 3.78 (s, 3H), 2.53 (t, 2H, J = 7.6 Hz), 1.63–1.51 (m, 2H), 1.46–1.36 (m, 3H), 1.35–1.22 (m, 7H), 1.211 (s, 6H), 1.210 (s, 6H), 0.99–0.92 (m, 1H), 0.87 (t, 3H, J = 7.0 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.7, 135.2, 129.4, 113.7, 82.9, 55.4, 35.1, 32.1, 31.7, 31.5, 31.3, 29.0, 24.9, 23.1, 14.2.

FT-IR (neat) 2976, 2954, 2926, 2854, 1612, 1584, 1512, 1464, 1442, 1410, 1388, 1379, 1370, 1315, 1246, 1215, 1175, 1166, 1144, 1113, 1039, 967, 862, 819, 807, 688 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_{22}H_{37}BO_3$: 360, found: 360.



(4,4,5,5-Tetramethyl-2-(1-phenylheptan-3-yl)-1,3,2-dioxaborolane (eqs 30 and 31).

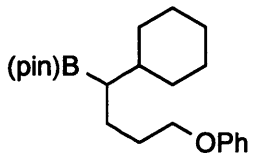
The ee was determined after oxidation to 1-phenylheptan-3-ol according to a literature procedure[74] by HPLC on a CHIRALCEL OD-H column. (5% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 9.0 min (major), 12.7 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.26 (m, 2H), 7.20–7.15 (m, 3H), 2.66–2.55 (m, 2H), 1.76 (dddd, 1H, J = 13.1, 10.1, 9.0, 5.9 Hz), 1.70–1.62 (m, 1H), 1.51–1.37 (m, 2H), 1.35–1.25 (m, 4H), 1.28 (s, 12H), 1.05 (tt, 1H, J = 8.9, 5.9 Hz), 0.89 (t, 3H, J = 7.0 Hz).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.3, 128.5, 128.3, 125.6, 83.0, 35.8, 33.7, 31.6, 31.1, 25.01, 24.95, 23.1, 14.2.

FT-IR (neat) 3085, 3062, 3026, 2977, 2956, 2925, 2857, 1604, 1496, 1454, 1410, 1388, 1379, 1371, 1316, 1272, 1261, 1233, 1214, 1165, 1144, 1111, 967, 866, 851, 748, 699 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_{19}H_{31}BO_2$: 302, found: 302.



2-(1-Cyclohexyl-4-phenoxybutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (eq 32).

The ee was determined by HPLC on a CHIRALPAK IB-3 column (0.5% *i*-PrOH/hexanes, 1.0 mL/min) with t_r = 4.5 min (minor), 5.2 min (major).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.24 (m, 2H), 6.93–6.88 (m, 3H), 3.94 (t, 2H, J = 6.6 Hz), 1.84–1.61 (m, 7H), 1.60–1.53 (m, 2H), 1.45–1.38 (m, 1H), 1.26 (s, 6H), 1.25 (s, 6H), 1.30–1.17 (m, 2H), 1.13 (tt, 1H, J = 12.3, 3.0 Hz), 1.08–0.96 (m, 2H), 0.94–0.89 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 129.5, 120.5, 114.6, 83.0, 68.2, 39.8, 33.0, 32.5, 29.3, 26.93, 26.90, 26.87, 25.18, 25.15, 24.9.

FT-IR (neat) 2977, 2923, 2850, 1600, 1586, 1497, 1469, 1448, 1379, 1371, 1359, 1314, 1245, 1170, 1144, 1111, 1079, 1036, 971, 863, 846, 814, 752, 691, 672 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_{22}H_{35}BO_3$: 358, found: 358.

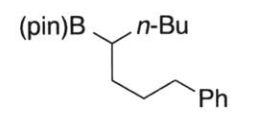
$[\alpha]^{25}_D$ = +3.6° (c = 0.99, $CHCl_3$); 94% ee.

IV. ^{1}H NMR Spectra of Selected Compounds

JC11241 CDCl3

exp61 PROTON

SAMPLE		PRESATURATION	
date	Jul 27 2014	satmode	n
solvent	cdcl3	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC112~		temp	25.0
41_CDCl3/PROTON01.~		gain	20
	fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.689	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.950	rfl	4635.6
DECOUPLER		rfp	3627.7
dn	C13	rp	-172.6
dof	0	lp	-75.2
dm	nnn	PLOT	
decwave	W40_autox7~	wc	234
	991	sc	8
dpwr	41	vs	14
dmf	32258	th	11
		ai cdc ph	

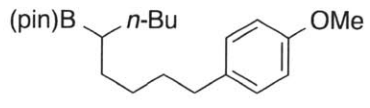


eq 28 and Figures 3 and 4

JC12073 CDCl3

exp61 PROTON

SAMPLE		PRESATURATION	
date	Jul 28 2014	satmode	n
solvent	cdcl3	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC120~		temp	25.0
73_CDCl3/PROTON01.~		gain	24
	fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.689	DISPLAY	
tof	499.7	sp	-0.2
tpwr	61	wp	4996.8
pw	4.950	rfl	4635.5
DECOUPLER		rfp	3627.7
dn	C13	rp	-172.1
dof	0	lp	-77.8
dm	nnn	PLOT	
decwave	W40_autox7~	wc	234
	991	sc	8
dpwr	41	vs	31
dmf	32258	th	44
		ai cdc ph	



eq 29

JC11271 1H CDCl3

exp61 PROTON

SAMPLE		PRESATURATION	
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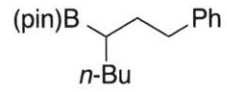
solvent	cdcl3	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC112~		temp	25.0
71_1H_CDCl3/PROTON~		gain	20
	01.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.689	DISPLAY	
tof	499.7	sp	-0.2
tpwr	61	wp	4996.8
pw	4.950	rfl	4632.8
DECOUPLER		rfp	3627.7
dn	C13	rp	-174.1
dof	0	lp	-76.3
dm	nnn	PLOT	
decwave	W40_autox7~	wc	234
	991	sc	8
dpwr	41	vs	15
dmf	32258	th	11
		ai cdc ph	

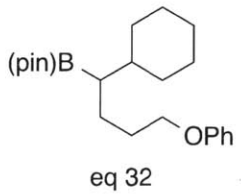


eqs 30 and 31

JC12027A CDCl3

exp61 PROTON

SAMPLE		PRESATURATION	
date	Jul 27 2014	satmode	n
solvent	cdcl3	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC120~		temp	25.0
27A_CDCl3/PROTON01~		gain	16
	.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.689	DISPLAY	
tof	499.7	sp	-0.2
tpwr	61	wp	4996.8
pw	4.950	rfl	4635.5
DECOUPLER		rfp	3627.7
dn	C13	rp	-174.6
dof	0	lp	-74.6
dm	nnn	PLOT	
decwave	W40_autox7~	wc	234
	991	sc	8
dpwr	41	vs	34
dmf	32258	th	44
		ai cdc ph	



eq 32

CHAPTER 2

A Versatile Approach to Ullmann C–N Couplings at Room Temperature: New Families of Nucleophiles for Photoinduced, Copper-Catalyzed Processes

A. Introduction

Nitrogen-containing heterocycles are one of the most common motifs in bioactive compounds.[75] For the preparation of these core scaffolds, versatile methods for C_{aryl}–N bond formation, such as Ullmann couplings[76] and Buchwald–Hartwig reactions,[77] have been developed. A variety of transition metals including copper and palladium are widely used for this transformation, but copper is a particularly attractive catalyst due to its low cost and low toxicity.

The first C–N bond formation between aniline and aryl halides in the presence of stoichiometric copper was reported by Ullmann in 1903.[76] To achieve this bond formation, an elevated temperature was required, which led to the limited application of this C–N bond-forming process. During the past twenty years, significant progress has been made in C–N coupling reactions, particularly copper-catalyzed Ullmann reactions under milder conditions (generally 50–120 °C) by the combination of copper and various ligands. Due to recent developments, an array of electrophiles, aryl or alkenyl halides, can be successfully cross-coupled with *N*-heterocycles, amines, or amides with broad functional-group compatibility using a catalytic amount of copper.[78]

Although many Ullmann C–N couplings have been discovered, the mechanism of these C–N bond formations is still unclear. It is believed that Ullmann coupling generally starts with the formation of a Cu–N bond followed by oxidative addition of the

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[75] For examples, see (a) Roughley, S. D.; Jordan, A. M. *J. Med. Chem.* **2011**, *54*, 3451–3479. (b) Welsch, M. E.; Snyder, S. A.; Stockwell, B. R. *Curr. Opin. Chem. Biol.* **2010**, *14*, 347–361. (c) *The Alkaloids: Chemistry and Biology*; Knölker, H.-J., Ed.; Elsevier: San Diego, CA, 2012; Vol. *71*.

[76] Ullmann, F. *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 2382–2384.

[77] For leading references, see: (a) Surry, D. S.; Buchwald, S. L. *Chem. Sci.* **2011**, *2*, 27–50. (b) Hartwig, J. F.; Shekhar, S.; Shen, Q.; Barrios–Landeros, F. In *Chemistry of Anilines*; Rapaport, Z., Ed.; John Wiley & Sons: New York, 2007; Vol. *1*, pp 455–536.

[78] For recent reviews, see: (a) Monnier, F.; Taillefer, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 6954–6971. (b) Evano, G.; Blanchard, N.; Toumi, M. *Chem. Rev.* **2008**, *108*, 3054–3131.

electrophilic partner to the copper complex. A variety of pathways for the oxidative addition step have been proposed, including a concerted oxidative addition and a single-electron transfer (SET) (Figure 5).[79] Although Buchwald and Houk suggested a radical pathway via SET may be operative in some cases,[80] there was no direct experimental evidence for the viability of an SET mechanism.

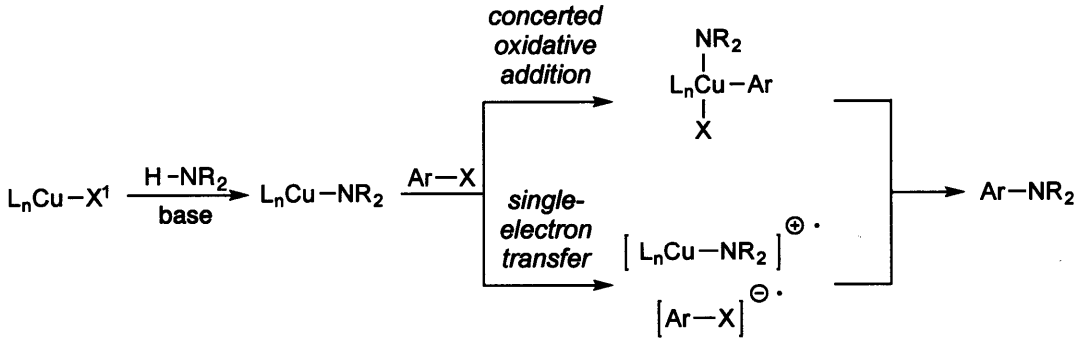


Figure 5. Outline of two possible mechanisms for Ullmann C–N bond formation.

In 2010, Peters reported the photoluminescent properties of copper(I)-carbazolide complexes, finding that the photophysical properties of these copper complexes are highly dependent on the nature of the amide groups.[81] We hypothesized that, if single-electron transfer from copper-carbazolide to an aryl halide is possible to afford an aryl radical, then it might undergo C–N bond formation (Figure 6). In 2012, Fu and Peters demonstrated the first *photoinduced*, Ullmann C–N bond formation between a copper-carbazolide complex (**8**) and iodobenzene under 13-watt compact fluorescent light at room temperature (eq 33).[82] Furthermore, the catalytic C–N bond formation between

[79] For examples of Ullmann C–N coupling via a concerted oxidative addition pathway, see: (a) Tye, J. W.; Weng, Z.; Johns, A. M.; Incarvito, C. D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2008**, *130*, 9971–9983. (b) Giri. R.; Hartwig, J. F. *J. Am. Chem. Soc.* **2010**, *132*, 15860–15863.
[80] Jones, G. O.; Liu, P.; Houk, K. N.; Buchwald, S. L. *J. Am. Chem. Soc.* **2010**, *132*, 6205–6213.
[81] Lotito, K. J.; Peters, J. C. *Chem. Commun.* **2010**, *46*, 3690–3692.
[82] Creutz, S. E.; Lotito, K. J.; Fu, G. C.; Peters, J. C. *Science*, **2012**, *338*, 647–651.

lithium carbazolide and iodobenzene could be achieved in 65% yield with a 100-watt mercury lamp (eq 34).

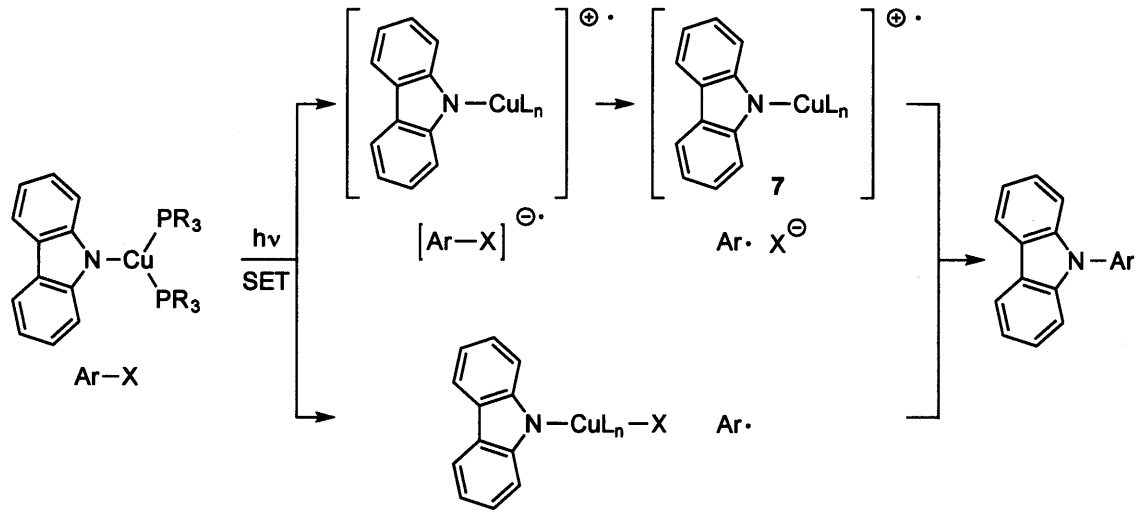
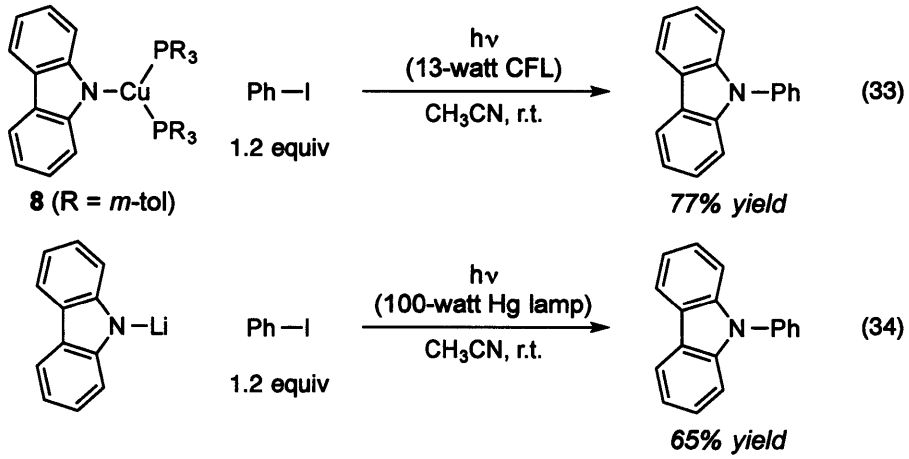
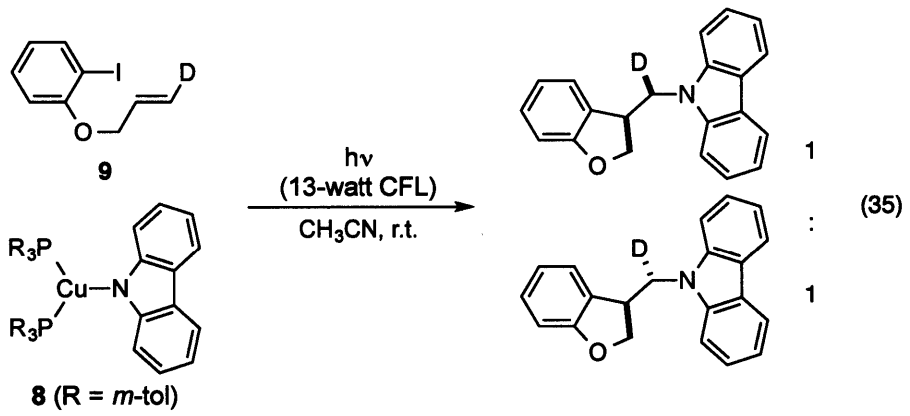


Figure 6. Outline of a possible pathway for photoinduced Ullmann C–N bond formation



In this study, we provided experimental evidence that supports a radical pathway. For instance, the photoinduced Ullmann reaction proceeds with higher yield in CD_3CN than in CH_3CN, which suggests a kinetic isotope effect for undesired hydrogen/deuterium abstraction from the solvent by radical cation **7** or phenyl radical. The detection of benzene and unsubstituted N*H*/N*D* carbazole as side products is consistent with our hypothesis. Electron-paramagnetic resonance (EPR) data are also consistent with

photoinduced generation of a copper-containing radical. Furthermore, the coupling between the copper-carbazolide complex (**8**) and an iodobenzene bearing a deuterium-labeled pendant olefin (**9**) furnishes a 1:1 mixture of diastereomers of cyclized products without the formation of the direct-coupling product, which strongly supports a radical pathway (eq 35).



(35)

In an effort to expand the scope of photoinduced Ullmann C–N couplings, we were able to demonstrate photoinduced alkylations of carbazoles with alkyl halides at 0 °C.[83] With respect to the mechanism of the photoinduced Ullmann couplings of carbazoles, we proposed that these photoinduced C–N coupling reactions may proceed through initial photoexcitation of a copper–carbazolide complex followed by single-electron transfer (SET) to the aryl halide (Figure 7). However, due to the effect of the amide ligand on the photoluminescent properties of the copper complex, it was unclear whether other nitrogen-containing heterocycles would form copper–nucleophile complexes that could undergo this photoexcitation/electron transfer process. Therefore, we decided to determine if we could develop a set of photoinduced, Ullmann reaction

[83] Bissember, A. C.; Lundgren, R. J.; Creutz, S. E.; Peters, J. C.; Fu, G. C. *Angew. Chem., Int. Ed.* **2013**, *52*, 5129–5133.

conditions that can be applied to a variety of other nitrogen nucleophiles, such as indoles, benzimidazoles, and imidazoles.

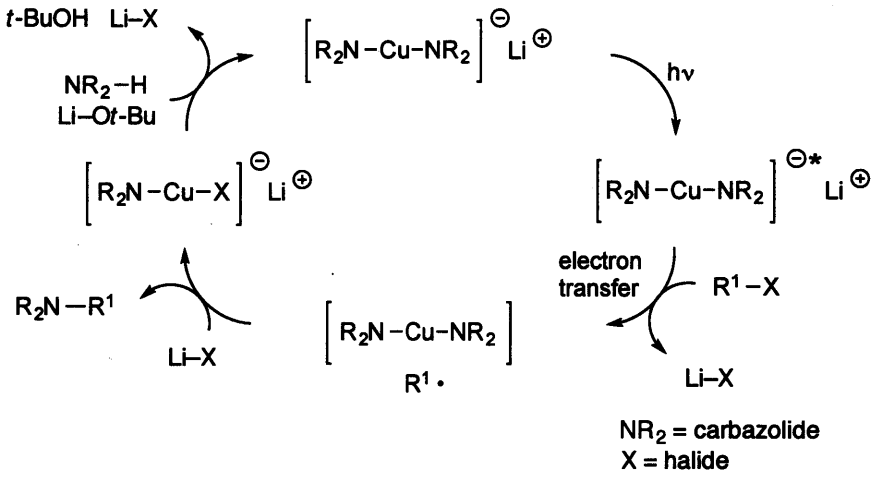
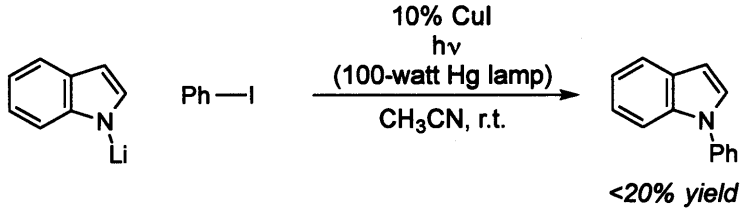


Figure 7. Outline of a possible pathway for photoinduced Ullmann C–N bond formation

B. Results and Discussion

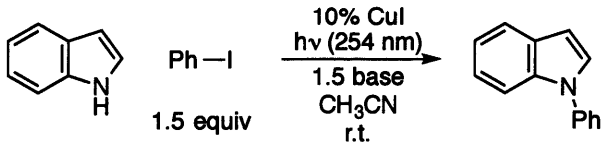
In initial studies, we found that the conditions developed for the N-arylation of carbazole were not efficient for the arylation of indole. The photoinduced Ullmann coupling of lithium indolide furnished *N*-phenylindole in less than 20% yield under a 100-watt mercury lamp (eq 36).



(36)

After investigating various reaction parameters, Ziegler found that irradiating at 254 nm rather than 350 nm is necessary to achieve optimal C–N bond formation; moreover, a reactive copper–nucleophile could be generated in situ from indole and LiO-*t*Bu instead of using preformed lithium indolide (Table 10, entry 1). From a practical standpoint, the generation of an active nucleophile in situ is more user-friendly than the use of a preformed nucleophile complex. We examined the efficiency of this N-phenylation reaction with indole and other bases under photoinduced Ullmann conditions, but LiO*t*-Bu turned out to be the most efficient base (Table 10). Whereas the coupling between indole and iodobenzene proceeded in good yield in the presence of LiO-*t*Bu, KO-*t*Bu led to poor product formation (entries 1 and 2). Other alkoxide or inorganic bases were not as effective as LiO*t*-Bu (entries 3–9).

Table 10. N-Phenylation of Indoles: Effect of Base

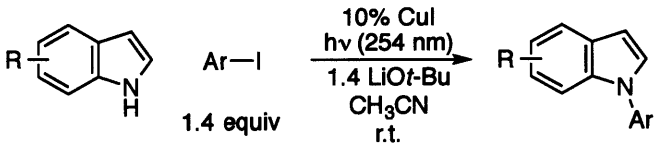


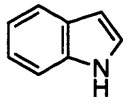
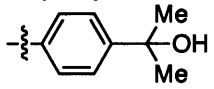
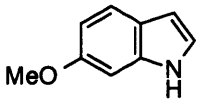
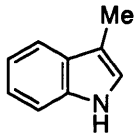
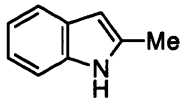
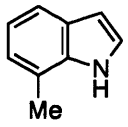
entry	base	yield (%)[a]
1	LiO*t*-Bu	76
2	KO*t*-Bu	26
3	LiO*i*-Pr	<2
4	LiOMe	<2
5	Li_3PO_4	<2
6	K_3PO_4	13
7	Li_2CO_3	<2
8	K_2CO_3	<2
9	Cs_2CO_3	18

[a] The yield was determined by GC analysis versus a calibrated internal standard.

After an evaluation of reaction parameters, we determined optimal conditions for the photoinduced Ullmann C–N coupling of indoles with aryl iodides. At room temperature, an array of indoles smoothly undergo C–N bond formation with iodobenzene (Table 11, entries 1, 4, 6, 8, and 9). An *o*-substituted (entry 5) and a deactivated (entry 7) aryl iodide are suitable coupling partners for this N-arylation; however, an iodothiophene, an iodoaniline, and an iodo-substituted α-aryl ester are poor electrophiles. Very electron-poor indoles cross-couple with electrophiles in poor yield. Under photoinduced Ullmann coupling conditions, N-phenylindole can be prepared on a gram scale from indole and iodobenzene (65% yield). The reaction is not highly sensitive to water; 10% water doping leads to only a few percent yield loss for the coupling between indole and iodobenzene. In contrast, the reaction proceeds in poor yield under air.

Table 11. N-Arylation of Indoles at Room Temperature



entry	indole	Ar	yield (%)[a]
1		Ph	75
2		*p*-tolyl	68
3			57
4		Ph	66
5		*o*-tolyl	68
6		Ph	72
7		*p*-anisyl	58
8		Ph	60
9		Ph	66

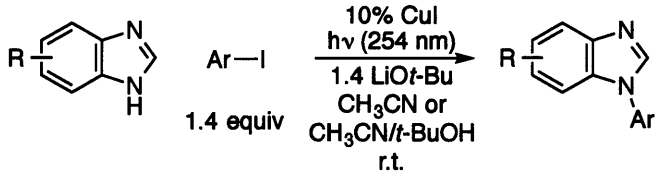
[a] Yield of purified product (average of two experiments)

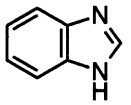
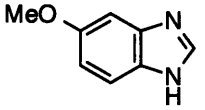
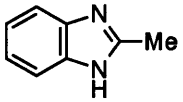
The same photoinduced, copper-catalyzed Ullmann reaction conditions can also be applied to the coupling of benzimidazoles with aryl iodides (Table 12). Benzimidazole undergoes N-arylation with iodobenzene, an activated aryl iodide, and a deactivated aryl iodide in good yield (entries 1–3). The arylation of a 5-substituted benzimidazole gives approximately a 1:1 mixture of regioisomers.[84] A hindered benzimidazole cross-couplings with a heteroaryl iodide and even with an *o*-substituted aryl iodide (entries 6–7). We found that the solubility of the benzimidazole effects the efficiency of the C–N

[84] For examples of Ullmann couplings of 5-substituted bezimidazoles, see: Combs, A. P.; Saubern, S.; Rafalski, M.; Lam, P. Y. S. *Tetrahedron Lett.* **1999**, *40*, 1623–1626.

bond formation. The cross-coupling of benzimidazole proceeds in better yield in a CH_3CN/*t*-BuOH mixture that provides a relatively homogenous reaction.

Table 12. N-Arylation of Benzimidazoles at Room Temperature

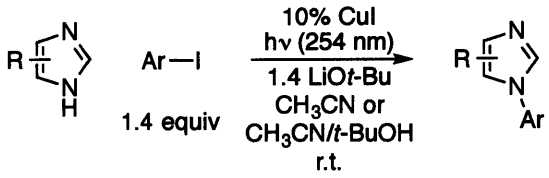


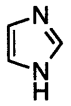
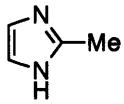
entry	benzimidazole	Ar	yield (%)[a]
1		Ph	83
2		4-CN-C_6H_4	83
3		*p*-anisyl	76
4		Ph	83[b]
5		Ph	82
6		*o*-tolyl	76
7		3-pyridyl	66

[a] Yield of purified product (average of two experiments).
[b] 1.1:1 mixture of isomers.

Under the photoinduced copper-catalyzed conditions, imidazoles can react with iodobenzene and hindered *o*-tolyliodide in acceptable yield (Table 13, entries 1 and 2). Unfortunately, hindered 2-methylimidazole undergoes C–N bond formation with iodobenzene in somewhat lower yield (entry 3).

Table 13. N-Arylation of Imidazoles at Room Temperature

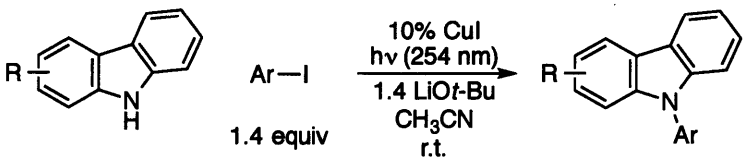


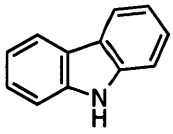
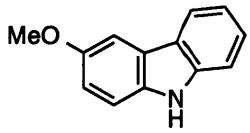
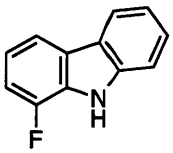
entry	imidazole	Ar	yield (%)[a]
1		Ph	68
2		*o*-tolyl	66
3		Ph	46

[a] Yield of purified product (average of two experiments).

Furthermore, the reaction conditions that we have developed for the photoinduced copper-catalyzed C–N bond-forming reaction of indoles, benzimidazoles, and imidazoles can be successfully applied to reactions with carbazoles (Table 14). In our original paper on the photoinduced Ullmann coupling between copper–carbazolide and iodobenzene, we showed that the C–N bond formation between lithium carbazolide and iodobenzene can be achieved under catalytic conditions in 64% yield.[82] Gratifyingly, under the conditions that we have developed for the arylation of *N*-heterocycles, carbazole efficiently undergoes Ullmann coupling with iodobenzene in substantially higher yield (entry 1). An array of electrophiles including activated, deactivated, hindered, and heteroaryl iodides react in good yield at room temperature (entries 2–5) and substituted indoles are also suitable coupling partners with an *o*-substituted aryl iodide (entries 6 and 7).

Table 14. N-Arylation of Carbazoles at Room Temperature

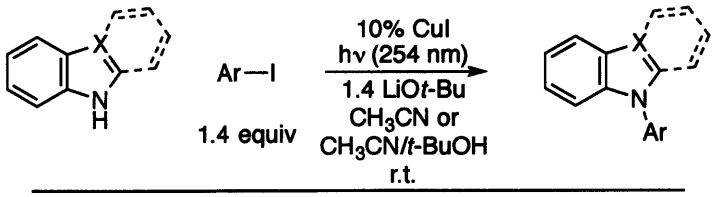


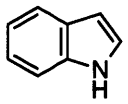
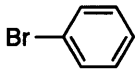
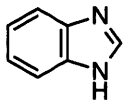
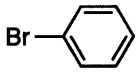
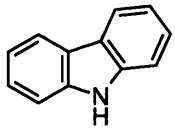
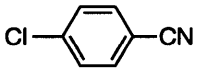
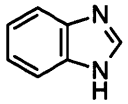
entry	carbazole	Ar	yield (%)[a]
1		Ph	86
2		4-CN-C_6H_4	77
3		*p*-anisyl	76
4		*o*-tolyl	81
5		3-pyridyl	66
6		*o*-tolyl	76
7		*o*-tolyl	74

[a] Yield of purified product (average of two experiments).

Although we described the coupling between copper–carbazolide and aryl halides (X = Cl, Br, and I) in our previous studies, we only showed the coupling between carbazole and iodobenzene under copper-catalyzed conditions.[82] The arylation of *N*-heterocycles was examined under these photoinduced copper-catalyzed reaction conditions with aryl bromides and chlorides (Table 15). We determined that a variety of *N*-heterocycles react with an unactivated aryl bromide and even with an activated aryl chloride at room temperature. Indole and benzimidazole are suitable nucleophilic partners for the reaction with bromobenzene (entries 1 and 2). Furthermore, carbazole and benzimidazole undergo the C–N bond formation with 4-chlorobenzonitrile in acceptable yield (entries 3 and 4).

Table 15. An Unactivated Aryl Bromide and an Activated Aryl Chloride as Electrophile

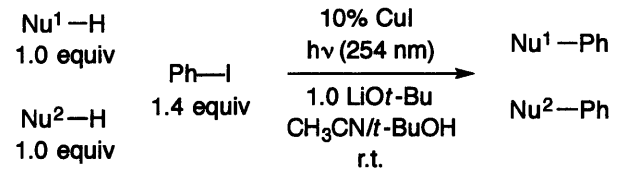


entry	nucleophile	electrophile	yield (%)[a]
1			62
2			62
3			72
4			61

[a] Yield of purified product (average of two experiments).

We were interested in investigating the selectivity of photoinduced Ullmann reactions with respect to the nucleophile. In a 1:1 mixture of two nucleophiles in the presence of 1.0 equivalent of base, we observed good-to-excellent selectivity between nucleophilic partners; the more acidic nucleophile can selectively undergo the C–N bond formation (Table 16). This result suggests that our photoinduced Ullmann reaction could be applied to the arylation of the more acidic nitrogen in a molecule containing multiple *N*-heterocycles with good selectivity.

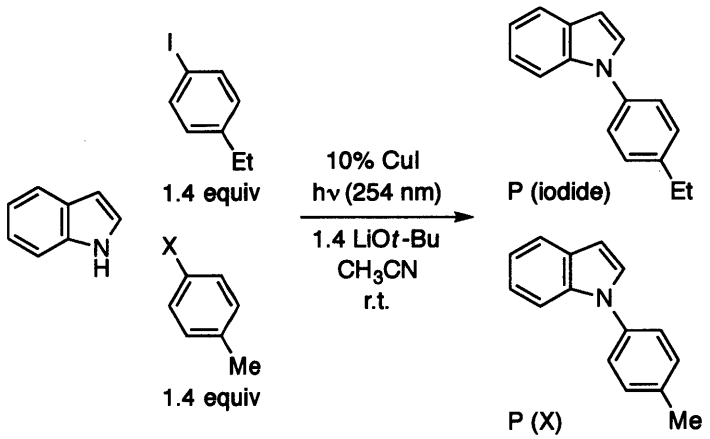
Table 16. Relative Reactivity of Nucleophilic Coupling Partners



Nu^1—H	Nu^2—H	$\left(\frac{Nu^1\text{—Ph}}{Nu^2\text{—Ph}}\right)$
imidazole (14.4)	carbazole (19.9)	13:1
imidazole (14.4)	indole (21.0)	>50:1
benzimidazole (16.4)	carbazole (19.9)	>50:1
benzimidazole (16.4)	indole (21.0)	>50:1
carbazole (19.9)	indole (21.0)	6:1

All ratios are the average of two experiments. pK_a values are provided in parentheses.

With regard to the competition experiment between electrophiles, we observed that aryl iodides are more reactive toward indole than aryl chlorides and aryl bromides (eq 37). This result is consistent with our hypothesis that the oxidative addition occurs via a single-electron transfer pathway under our photoinduced Ullmann coupling conditions (Figure 5). The electrophile with a higher reduction potential should be more reactive toward the oxidative addition by a single-electron transfer, which leads to more product formation (the weaker C–X bond is also more reactive toward concerted oxidative addition).

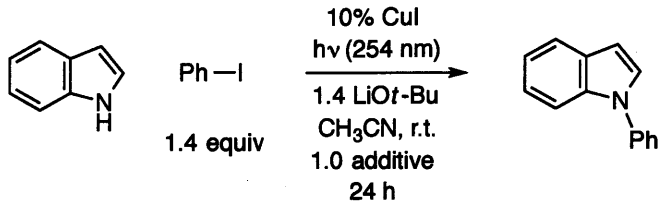


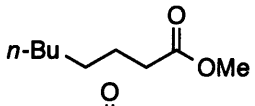
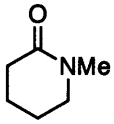
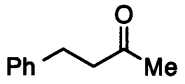
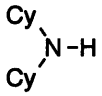
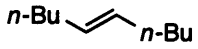
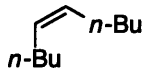
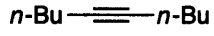
(37)

X	$\left(\frac{\text{P (iodide)}}{\text{P (X)}}\right)$
Br	7
Cl	18

We were interested in the functional-group compatibility under the photoinduced Ullmann coupling conditions. As illustrated in Tables 11–15, an ether, a nitrile, a pyridine, an aryl fluoride, and a tertiary alcohol are tolerated under the photoinduced reaction conditions. For further examination of the functional-group tolerance, the coupling reaction between indole and iodobenzene was conducted in the presence of 1.0 equivalent of an additive containing a functional group. The C–N bond formation proceeds with only modest impact on the yield in the presence of an ester, amide, ketone, secondary amine, primary amine, aryl chloride, *cis*-alkene, *trans*-alkene, and internal alkyne. In every case, ≥82% of the additive is recovered at the end of the reaction. For the *cis*-alkene and *trans*-alkene, olefin isomerization is negligible. The inhibitory effect caused by the stoichiometric amount of additive can be partially overcome by running the reaction for a longer period of time (48 h). For instance, in the case of benzylacetone, *N*-phenylindole formation can be improved from 62% to 66% by a longer reaction time. Similarly, the yield in the presence of Cy_2NH can also be increased from 58% to 66%.

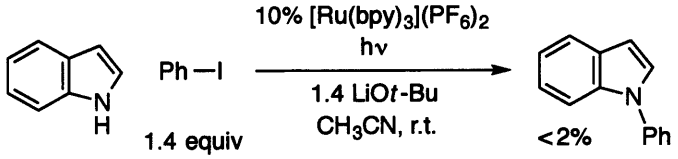
Table 17. Functional-Group Tolerance



additive	yield (%)	recovery of additive (%)
no additive	79	–
	69	>95
	72	>95
	62	85
	73	>95
$Cy-NH_2$	58	82
	72	90
	66	>95
	73	>95
	74	>95

All data are the average of two experiments.

We were interested whether a photoredox catalyst such as $[Ru(bpy)_3]X_2$, which shuttles electrons without being involved with direct inner-sphere bond formation, could replace copper under our photoinduced reaction conditions. In control experiments, we determined that $[Ru(bpy)_3](PF_6)_2$ cannot replace CuI for the C–N bond-forming process under our standard or related conditions (eq 38). In addition, we observed essentially no bond formation in the absence of light, copper, or light and copper for a representative example of each family of nucleophile.



(38)

Conditions
254 nm
compact fluorescent light bulb
compact fluorescent light bulb; 10% CuI

C. Conclusion

In summary, we have developed a unified set of photoinduced, copper-catalyzed reaction conditions for the N-arylation of various nitrogen nucleophiles, including indoles, benzimidazoles, imidazoles, and carbazoles. With this method, C–N bond formation can be accomplished under unusually mild conditions (room temperature) with an inexpensive catalyst (CuI, without added ligand) with tolerance of moisture and a variety of functional groups. Current investigations are focused on expanding the families of nucleophiles and electrophiles. Recently, we have achieved arylations of aryl thiols[85] and phenols [86] by photoinduced, copper-catalyzed cross-couplings. We also reported photoinduced, copper-catalyzed alkylations of amides with unactivated secondary alkyl halides.[87]

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[85] Uyeda, C.; Tan, Y.; Fu, G. C.; Peters, J. C. *J. Am. Chem. Soc.*, **2013**, *135*, 9548–9552.
[86] Tan, Y.; Muñoz-Molina, J. M.; Fu, G. C.; Peters, J. C. *Chem. Sci.* **2014**, *5*, 2831–3835.
[87] Do, H.-Q.; Bachman, S.; Bissember, A. C.; Peters, J. C.; Fu, G. C. *J. Am. Chem. Soc.* **2014**, *136*, 2162–2167.

D. Experimental

I. General Information

The following reagents were purchased and used as received unless otherwise specified: indole (Aldrich), 6-methoxyindole (AstaTech), 3-methylindole (Aldrich), 2-methylindole (Alfa Aesar), 7-methylindole (Aldrich), benzimidazole (Alfa Aesar), 5-methoxybenzimidazole (Aldrich), 2-methylbenzimidazole (Aldrich), imidazole (Alfa Aesar), 2-methylimidazole (Aldrich), carbazole (Aldrich; recrystallized), 3-methoxycarbazole (Matrix Scientific), iodobenzene (Aldrich), 4-iodotoluene (Aldrich), 2-iodotoluene (Aldrich), 4-iodoanisole (Aldrich), 4-iodobenzonitrile (Aldrich), 3-iodopyridine (Aldrich), bromobenzene (Avocado), 4-chlorobenzonitrile (Avocado), 1-ethyl-4-iodobenzene (Avocado), 4-bromotoluene (Aldrich), 4-chlorotoluene (Aldrich), methyl octanoate (Acros), 1-methyl-2-piperidone (Aldrich), benzylacetone (Aldrich), dicyclohexylamine (Aldrich), cyclohexylamine (Aldrich), chlorobenzene (Aldrich), *trans*-5-decene (Aldrich), *cis*-5-decene (TCI), 5-decyne (Lancaster), dibenzyl ether (Alfa Aesar), bromomethylenecyclohexane (Aldrich), CuI (Aldrich), LiO*t*-Bu (Alfa Aesar), and *t*-BuOH (Aldrich; anhydrous). CH_3CN was deoxygenated and dried by sparging with nitrogen followed by passage through an activated alumina column (S. G. Water) prior to use.

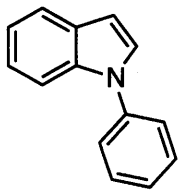
All coupling reactions were carried out using a Luzchem LZC–4V photoreactor at 254 nm (UVC). ^{1}H NMR data and ^{13}C NMR data were collected on a VARIAN 500 MHz spectrometer at ambient temperature. GC analyses were carried out on an Agilent 6890 series system with a DB-1 column (length 30 m, I.D. 0.25 mm) or an HP-5 column (length 30 m, I.D. 0.25 mm) or on an Agilent 6850 series system with a BETA DEX 120 column (length 30 m, I.D. 0.25 mm).

II. Photoinduced, Copper-Catalyzed N-Arylations

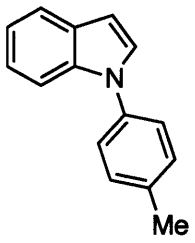
General Procedure. The nitrogen heterocycle (1.00 mmol), LiO*t*-Bu (112 mg, 1.40 mmol), and CuI (19.0 mg, 0.10 mmol) were added to an oven-dried 10-mL quartz test tube that contained a stir bar. The test tube was fitted with a rubber septum, the joint was wrapped with electrical tape, and the test tube was evacuated and backfilled with nitrogen (three cycles). Then, CH_3CN (4.0 mL) and the aryl iodide (1.40 mmol; if the aryl iodide is a solid, then it was added immediately after the addition of CuI) were added in turn via syringe. The test tube was detached from the nitrogen manifold, and the puncture holes in the septum were covered with vacuum grease. The resulting mixture was stirred for 5 min, and then the test tube was transferred to a Luzchem LZC–4V photoreactor, where it was irradiated at 254 nm for 24 h (adequate stirring is important). Next, the mixture was passed through a long plug of silica gel (monitored by TLC), the solvent was removed, and the residue was purified by column chromatography.

Notes: (a) A Honeywell ultraviolet air treatment system (model #RUVLAMP1), available for ~$110 from retail outlets such as Amazon or The Home Depot, furnishes a comparable result: indole and iodobenzene couple in 63% yield (calibrated GC analysis)

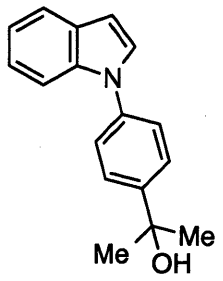
after 48 h. (b) Use of a borosilicate, rather than a quartz, test tube leads to a low yield of the C–N coupling product.



1-Phenyl-1*H*-indole (Table 11, entry 1) [16096-33-6]. The title compound was synthesized according to the General Procedure from indole (117 mg, 1.00 mmol), LiO*t*-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (286 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% ethyl acetate/hexanes) and purified by column chromatography (hexanes). Pale-yellow oil. First run: 142 mg (73% yield). Second run: 148 mg (77% yield).



1-(*p*-Tolyl)-1*H*-indole (Table 11, entry 2) [167283-32-1]. The title compound was synthesized according to the General Procedure from indole (117 mg, 1.00 mmol), LiO*t*-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 4-iodotoluene (305 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% ethyl acetate/hexanes) and purified by column chromatography on silica gel (hexanes→1% Et_2O/hexanes). Colorless oil. First run: 140 mg (68%). Second run: 143 mg (69%).



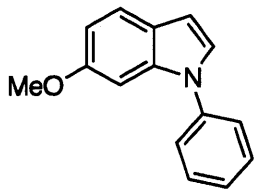
2-(4-(1*H*-Indol-1-yl)phenyl)propan-2-ol (Table 11, entry 3). The title compound was synthesized according to the General Procedure from indole (117 mg, 1.00 mmol), LiO*t*-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 2-(4-iodophenyl)propan-2-ol (367 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (20% ethyl acetate/hexanes) and purified by column chromatography on silica gel (7.5% ethyl acetate/hexanes→15% ethyl acetate/hexanes). Pale-orange solid. First run: 144 mg (57%). Second run: 143 mg (57%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71–7.69 (m, 1H), 7.67–7.62 (m, 2H), 7.60–7.56 (m, 1H), 7.51–7.46 (m, 2H), 7.34 (d, 1H, J = 3.0 Hz), 7.23 (ddd, 1H, J = 8.0, 7.0, 1.0 Hz), 7.18 (ddd, 1H, J = 8.0, 7.0, 1.0 Hz), 6.69 (dd, 1H, J = 3.0, 1.0 Hz), 1.81 (br s, 1H), 1.66 (s, 6H).

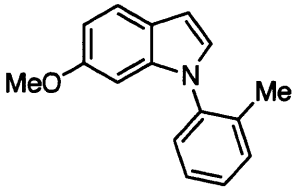
^{13}C NMR (126 MHz, $CDCl_3$) δ 147.5, 138.5, 136.0, 129.4, 128.1, 125.9, 124.2, 122.4, 121.2, 120.5, 110.7, 103.6, 72.6, 32.0.

FT-IR (neat) 3541, 3399, 3103, 3049, 2974, 2927, 2868, 1606, 1582, 1570, 1519, 1475, 1457, 1412, 1363, 1347, 1334, 1317, 1298, 1281, 1256, 1234, 1213, 1170, 1137, 1114, 1094, 1066, 1015, 955, 909, 883, 862, 840, 770, 762, 742, 720 cm^{-1}.

MS (ESI) *m/z* (M^++H) calcd for $C_{17}H_{18}NO$: 252, found: 252.



6-Methoxy-1-phenyl-1*H*-indole (Table 11, entry 4) [487058-34-4]. The title compound was synthesized according to the General Procedure from 6-methoxyindole (147 mg, 1.00 mmol), LiO*t*-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (286 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% ethyl acetate/hexanes) and purified by normal-phase column chromatography on silica gel (hexanes→1% Et_2O/hexanes) followed by reverse-phase column chromatography on C-18 silica gel (10%→100% CH_3CN/water). White solid. First run: 147 mg (66%). Second run: 150 mg (67%).



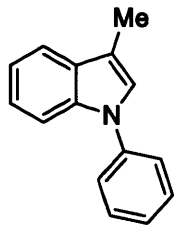
6-Methoxy-1-(*o*-tolyl)-1*H*-indole (Table 1, entry 5). The title compound was synthesized according to the General Procedure from 6-methoxyindole (147 mg, 1.00 mmol), LiO*t*-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 2-iodotoluene (305 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% ethyl acetate/hexanes) and purified by normal-phase column chromatography on silica gel (hexanes→1% Et_2O/hexanes) followed by reverse-phase column chromatography on C-18 silica gel (10%→100% CH_3CN/water). Yellow oil. First run: 154 mg (65% yield). Second run: 165 mg (70% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, 1H, J = 8.5 Hz), 7.40–7.36 (m, 2H), 7.35–7.31 (m, 2H), 7.06 (d, 1H, J = 3.2 Hz), 6.82 (dd, 1H, J = 8.5, 2.2 Hz), 6.59 (d, 1H, J = 3.2 Hz), 6.50 (s, 1H), 3.76 (s, 3H), 2.09 (s, 3H).

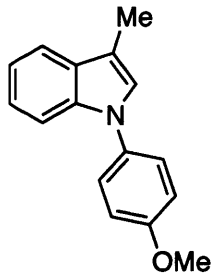
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.8, 138.5, 137.8, 136.0, 131.4, 128.3, 128.2, 127.8, 127.0, 122.6, 121.5, 110.1, 102.5, 94.0, 55.8, 17.8.

FT-IR (neat) 3102, 3026, 2994, 2952, 2831, 1621, 1603, 1573, 1513, 1487, 1459, 1380, 1340, 1324, 1292, 1279, 1225, 1205, 1177, 1121, 1095, 1031, 927, 806, 769, 746, 720 cm^{-1}.

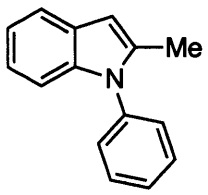
MS (ESI) *m/z* (M^++H) calcd for $C_{16}H_{16}NO$: 238, found: 238.



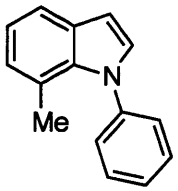
3-Methyl-1-phenyl-1*H*-indole (Table 11, entry 6) [112817-88-6]. The title compound was synthesized according to the General Procedure from 3-methylindole (131 mg, 1.00 mmol), LiO*t*-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (286 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% ethyl acetate hexanes) and purified by column chromatography on silica gel (hexanes→1% Et_2O/hexanes). Colorless oil. First run: 152 mg (73%). Second run: 145 mg (70%).



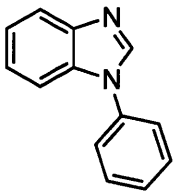
1-(4-Methoxyphenyl)-3-methyl-1*H*-indole (Table 11, entry 7) [876337-56-3]. The title compound was synthesized according to the General Procedure from 3-methylindole (131 mg, 1.00 mmol), LiO*t*-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 4-iodoanisole (328 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% ethyl acetate/hexanes) and purified by column chromatography on silica gel (hexanes→2% Et_2O/hexanes). Colorless oil. First run: 138 mg (58%). Second run: 138 mg (58%).



2-Methyl-1-phenyl-1*H*-indole (Table 11, entry 8) [16176-77-5]. The title compound was synthesized according to the General Procedure from 2-methylindole (131 mg, 1.00 mmol), LiO*t*-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (286 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% ethyl acetate/hexanes) and purified by column chromatography on silica gel (hexanes→1% Et_2O/hexanes). Colorless oil. First run: 122 mg (59%). Second run: 124 mg (60%).

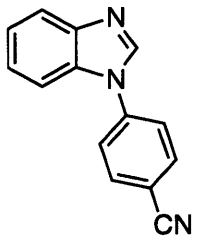


7-Methyl-1-phenyl-1*H*-indole (Table 11, entry 9) [473918-43-3]. The title compound was synthesized according to the General Procedure from 7-methylindole (131 mg, 1.00 mmol), LiO*t*-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (286 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% ethyl acetate/hexanes) and purified by column chromatography on silica gel (hexanes→1% Et_2O/hexanes). White solid. First run: 139 mg (67%). Second run: 133 mg (64%).



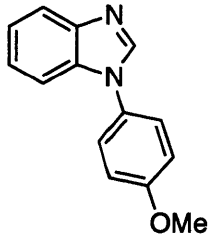
1-Phenyl-1*H*-benzo[*d*]imidazole (Table 12, entry 1) [2622-60-8]. The title compound was synthesized according to the General Procedure from benzimidazole (118 mg, 1.00 mmol), LiO*t*-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (286 mg, 1.40 mmol), except that a mixture of *t*-BuOH (1.0 mL) and CH_3CN (3.0 mL) was used as the solvent (*t*-BuOH and CH_3CN were added in turn via syringe), due to the poor solubility of the heterocycle in neat CH_3CN. The reaction mixture was filtered through a plug of silica gel (5% MeOH/CH_2Cl_2) and purified by column chromatography on silica gel (0.75% MeOH/CH_2Cl_2, then 15%→25% ethyl acetate/hexanes). Yellow oil. First run: 158 mg (81%). Second run: 165 mg (85%).

Note: The reaction mixture was stirred until it became homogeneous, and then it was immediately transferred to the photoreactor before it turned to a white heterogeneous mixture. The reaction proceeded in poor yield when the white precipitate formed.



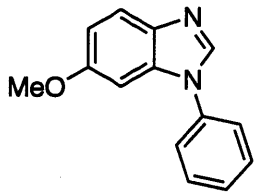
4-(1*H*-Benzo[*d*]imidazol-1-yl)benzonitrile (Table 12, entry 2) [25699-95-0]. The title compound was synthesized according to the General Procedure from benzimidazole (118 mg, 1.00 mmol), LiO*t*-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 4-iodobenzonitrile (321 mg, 1.40 mmol), except that a mixture of *t*-BuOH (1.0 mL) and CH_3CN (3.0 mL) was used as the solvent (*t*-BuOH and CH_3CN were added in turn via syringe), due to the poor solubility of the heterocycle in neat CH_3CN. The product was filtered through a plug of silica gel (5% MeOH/CH_2Cl_2) and purified by column chromatography on silica gel (1% MeOH/CH_2Cl_2, then 40%→55% ethyl acetate/hexanes). Yellow solid. First run: 185 mg (84%). Second run: 180 mg (82%).

Note: The reaction mixture was stirred until it became homogeneous, and then it was immediately transferred to the photoreactor before it turned to a white heterogeneous mixture. The reaction proceeded in poor yield when the white precipitate formed.



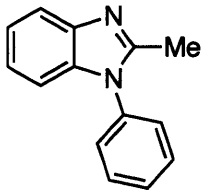
1-(4-Methoxyphenyl)-1*H*-benzo[*d*]imidazole (Table 12, entry 3) [2622-61-9]. The title compound was synthesized according to the General Procedure from benzimidazole (118 mg, 1.00 mmol), LiO*t*-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 4-iodoanisole (328 mg, 1.40 mmol), except that a mixture of *t*-BuOH (1.0 mL) and CH_3CN (3.0 mL) was used as the solvent (*t*-BuOH and CH_3CN were added in turn via syringe), due to the poor solubility of the heterocycle in neat CH_3CN. The reaction mixture was filtered through a plug of silica gel (5% MeOH/CH_2Cl_2) and purified by column chromatography on silica gel (1% MeOH/CH_2Cl_2, then 30%→50% ethyl acetate/hexanes). Yellow solid. First run: 177 mg (79%). Second run: 164 mg (73%).

Note: The reaction mixture was stirred until it became homogeneous, and then it was immediately transferred to the photoreactor before it turned to a white heterogeneous mixture. The reaction proceeded in poor yield when the white precipitate formed.



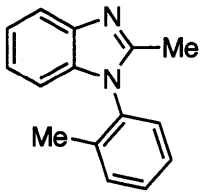
6-Methoxy-1-phenyl-1*H*-benzo[*d*]imidazole (Table 12, entry 4) [69445-55-2]. The title compound was synthesized according to the General Procedure from 5-

methoxybenzimidazole (148 mg, 1.00 mmol), LiO*t*-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (286 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% MeOH/CH_2Cl_2) and purified by column chromatography (1%→5% MeOH/CH_2Cl_2, then 20%→35% ethyl acetate/hexanes). Yellow solid. First run: 182 mg (81%, 6-methoxy-1-phenyl-1*H*-benzo[*d*]imidazole/5-methoxy-1-phenyl-1*H*-benzo[*d*]imidazole = 1.0:1). Second run: 190 mg (85%, 6-methoxy-1-phenyl-1*H*-benzo[*d*]imidazole/5-methoxy-1-phenyl-1*H*-benzo[*d*]imidazole = 1.1:1).



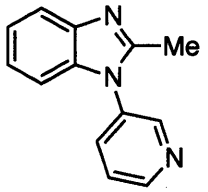
2-Methyl-1-phenyl-1*H*-benzo[*d*]imidazole (Table 12, entry 5) [1484-39-5]. The title compound was synthesized according to the General Procedure from 2-methylbenzimidazole (132 mg, 1.00 mmol), LiO*t*-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (286 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (5% MeOH/CH_2Cl_2) and purified by column chromatography on silica gel (1%→5% MeOH/CH_2Cl_2, then 20%→35% ethyl acetate/hexanes). Yellow solid. First run: 169 mg (81%). Second run: 175 mg (84%).

Note: The reaction mixture was stirred until it became homogeneous, and then it was immediately transferred to the photoreactor before it turned to a white heterogeneous mixture. The reaction proceeded in poor yield when the white precipitate formed.



2-Methyl-1-(*o*-tolyl)-1*H*-benzo[*d*]imidazole (Table 12, entry 6) [68874-09-9]. The title compound was synthesized according to the General Procedure from 2-methylbenzimidazole (132 mg, 1.00 mmol), LiO*t*-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 2-iodotoluene (305 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica (10% MeOH/CH_2Cl_2) and purified by column chromatography (1% MeOH/CH_2Cl_2, then 20% ethyl acetate/hexanes). Yellow solid. First run: 170 mg (76%). Second run: 166 mg (75%).

Note: The reaction mixture was stirred until it became homogeneous, and then it was immediately transferred to the photoreactor before it turned to a white heterogeneous mixture. The reaction proceeded in poor yield when the white precipitate formed.



2-Methyl-1-(pyridin-3-yl)-1*H*-benzo[*d*]imidazole (Table 12, entry 7). The title compound was synthesized according to the General Procedure from 2-methylbenzimidazole (132 mg, 1.00 mmol), LiO*t*-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 3-iodopyridine (287 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica (10% MeOH/CH_2Cl_2) and purified by column chromatography on

silica gel (2% MeOH/CH_2Cl_2). Yellow solid. First run: 139 mg (66%). Second run: 140 mg (67%).

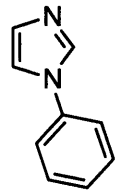
Note: The reaction mixture was stirred until it became homogeneous, and then it was immediately transferred to the photoreactor before it turned to a white heterogeneous mixture. The reaction proceeded in poor yield when the white precipitate formed.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 (d, 1H, J = 3.2 Hz), 8.70 (s, 1H), 7.45 (apparent t, 2H, J = 3.2 Hz), 7.55 (dd, 1H, J = 7.9, 5.1 Hz), 7.28 (t, 1H, J = 7.8 Hz), 7.21 (t, 1H, J = 7.8 Hz), 7.10 (d, 1H, J = 8.0 Hz), 2.52 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.4, 150.1, 148.3, 142.8, 136.3, 134.6, 133.0, 124.5, 123.2, 123.0, 119.4, 109.6, 14.6.

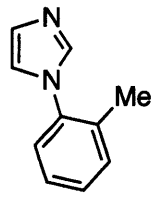
FT-IR (neat) 3391, 3053, 2927, 2851, 1615, 1587, 1575, 1524, 1486, 1456, 1427, 1393, 1372, 1314, 1287, 1249, 1187, 1149, 1105, 1050, 1029, 1015, 999, 929, 878, 810, 765, 745, 712 cm^{-1}.

MS (ESI) *m/z* (M^++H) calcd for $C_{13}H_{12}N_3$: 210, found: 210.

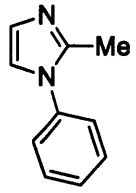


1-Phenyl-1*H*-imidazole (Table 13, entry 1) [7164-98-9]. The title compound was synthesized according to the General Procedure from imidazole (102 mg, 1.50 mmol), LiO*t*-Bu (168 mg, 2.10 mmol), CuI (28.6 mg, 0.15 mmol), and iodobenzene (428 mg, 2.10 mmol), except that a mixture of *t*-BuOH (1.5 mL) and CH_3CN (4.5 mL) was used as the solvent (*t*-BuOH and CH_3CN were added in turn via syringe), due to the poor

solubility of the heterocycle in neat CH_3CN. The reaction mixture was filtered through a plug of silica gel (1% MeOH/CH_2Cl_2) and purified by column chromatography (1% MeOH/CH_2Cl_2, then 40%→50% ethyl acetate/hexanes). Pale-yellow oil. First run: 150 mg (69%). Second run: 148 mg (68%).

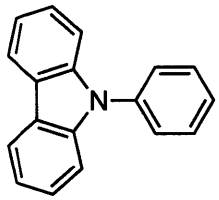


1-(*o*-Tolyl)-1*H*-imidazole (Table 13, entry 2) [25371-93-1]. The title compound was synthesized according to the General Procedure from imidazole (102 mg, 1.50 mmol), LiO*t*-Bu (168 mg, 2.10 mmol), CuI (28.6 mg, 0.15 mmol), and 2-iodotoluene (458 mg, 2.10 mmol), except that a mixture of *t*-BuOH (1.5 mL) and CH_3CN (4.5 mL) was used as the solvent (*t*-BuOH and CH_3CN were added in turn via syringe), due to the poor solubility of the heterocycle in neat CH_3CN. The reaction mixture was filtered through a plug of silica gel (5% MeOH/CH_2Cl_2) and purified by column chromatography (1%→3% MeOH/CH_2Cl_2, then 30%→50% ethyl acetate/hexanes). Yellow oil. First run: 154 mg (65%). Second run: 161 mg (68%).

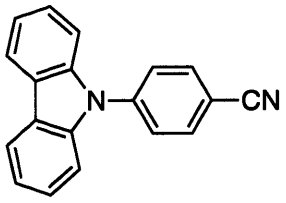


2-Methyl-1-phenyl-1*H*-imidazole (Table 13, entry 3) [60053-07-8]. The title compound was synthesized according to the General Procedure from 2-methylimidazole

(123 mg, 1.50 mmol), LiO*t*-Bu (168 mg, 2.10 mmol), CuI (28.6 mg, 0.15 mmol), and iodobenzene (428 mg, 2.10 mmol). The reaction mixture was filtered through a plug of silica gel (10% MeOH/CH_2Cl_2) and purified by column chromatography (2% MeOH/CH_2Cl_2, then 40%→50% ethyl acetate/hexanes). Yellow oil. First run: 106 mg (45%). Second run: 109 mg (46%).

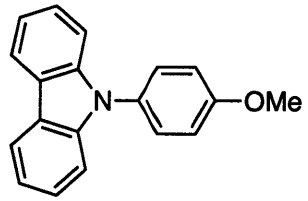


9-Phenyl-9*H*-carbazole (Table 14, entry 1) [1150-62-5]. The title compound was synthesized according to the General Procedure from carbazole (167 mg, 1.00 mmol), LiO*t*-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and iodobenzene (286 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% ethyl acetate/hexanes) and purified by column chromatography on silica gel (hexanes→1% Et_2O/hexanes). White solid. First run: 212 mg (87%). Second run: 206 mg (85%).

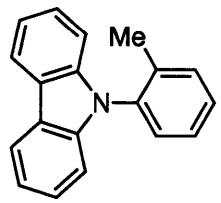


4-(9*H*-Carbazol-9-yl)benzonitrile (Table 14, entry 2) [57103-17-0]. The title compound was synthesized according to the General Procedure from carbazole (167 mg, 1.00 mmol), LiO*t*-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 4-iodobenzonitrile (321 mg, 1.40 mmol). The reaction mixture was filtered through a plug

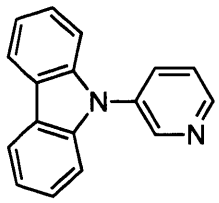
of silica gel (10% ethyl acetate/hexanes) and purified by column chromatography on silica gel (hexanes→2% Et_2O/hexanes). Yellow solid. First run: 203 mg (76%). Second run: 209 mg (78%).



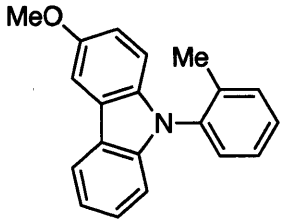
9-(4-Methoxyphenyl)-9*H*-carbazole (Table 14, entry 3) [19264-74-5]. The title compound was synthesized according to the General Procedure from carbazole (167 mg, 1.00 mmol), LiO*t*-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 4-iodoanisole (328 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% ethyl acetate/hexanes) and purified by column chromatography on silica gel (hexanes→1% Et_2O/hexanes). White solid. First run: 215 mg (79%). Second run: 196 mg (72%).



9-(*o*-Tolyl)-9*H*-carbazole (Table 14, entry 4) [19155-50-1]. The title compound was synthesized according to the General Procedure from carbazole (167 mg, 1.00 mmol), LiO*t*-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 2-iodotoluene (305 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% ethyl acetate/hexanes) and purified by column chromatography on silica gel (hexanes→1% Et_2O/hexanes). White solid. First run: 213 mg (83%). Second run: 204 mg (79%).



9-(Pyridin-3-yl)-9*H*-carbazole (Table 14, entry 5) [168127-56-8]. The title compound was synthesized according to the General Procedure from carbazole (167 mg, 1.00 mmol), LiO*t*-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 3-iodopyridine (287 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (50% ethyl acetate/hexanes) and purified by column chromatography on silica gel (10% ethyl acetate/hexanes). White solid. First run: 154 mg (63%). Second run: 166 mg (68%).



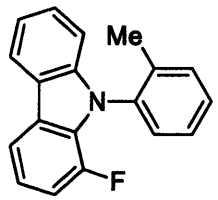
3-Methoxy-9-(*o*-tolyl)-9*H*-carbazole (Table 14, entry 6). The title compound was synthesized according to the General Procedure from 3-methoxycarbazole (100 mg, 0.51 mmol), LiO*t*-Bu (56.8 mg, 0.71 mmol), CuI (9.7 mg, 0.051 mmol), and 2-iodotoluene (155 mg, 0.71 mmol). The reaction mixture was filtered through a plug of silica gel (10% ethyl acetate/hexanes) and purified by column chromatography on silica gel (hexanes→1% Et_2O/hexanes). Colorless oil. First run: 110 mg (76%). Second run: 110 mg (76%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, 1H, J = 7.5 Hz), 7.65 (d, 1H, J = 2.0 Hz), 7.50–7.33 (m, 5H), 7.27–7.23 (m, 1H), 7.06–7.01 (m, 2H), 6.96 (d, 1H, J = 9.0 Hz), 3.96 (s, 3H), 1.97 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 154.2, 141.8, 137.5, 136.4, 136.3, 131.6, 129.4, 128.8, 127.4, 126.0, 123.5, 123.0, 120.4, 119.2, 115.1, 110.7, 110.0, 103.4, 56.3, 17.7.

FT-IR (neat) 3050, 2993, 2932, 2830, 1627, 1600, 1580, 1498, 1485, 1462, 1438, 1381, 1359, 1329, 1285, 1254, 1236, 1206, 1179, 1167, 1149, 1119, 1098, 1035, 943, 912, 860, 847, 806, 764, 746, 720 cm^{-1}.

MS (ESI) *m/z* (M^+) calcd for $C_{20}H_{17}NO$: 287, found: 287.



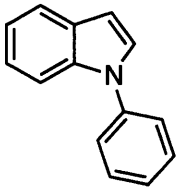
1-Fluoro-9-(*o*-tolyl)-9*H*-carbazole (Table 14, entry 7). The title compound was synthesized according to the General Procedure from 1-fluorocarbazole (100 mg, 0.54 mmol), LiO*t*-Bu (60.5 mg, 0.76 mmol), CuI (10.3 mg, 0.054 mmol), and 2-iodotoluene (165 mg, 0.76 mmol). The reaction mixture was filtered through a plug of silica gel (10% ethyl acetate/hexanes) and purified by column chromatography on silica gel (hexanes→1% Et_2O/hexanes). Pale-yellow oil. First run: 111 mg (75%). Second run: 110 mg (74%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, 1H, J = 8.0 Hz), 7.93 (d, 1H, J = 7.5 Hz), 7.47–7.34 (m, 5H), 7.30 (t, 1H, J = 7.5 Hz), 7.18 (td, 1H, J = 8.0, 4.0 Hz), 7.10 (dd, 1H, J = 12.0, 7.5 Hz), 7.01 (d, 1H, J = 8.5 Hz), 2.01 (s, 3H).

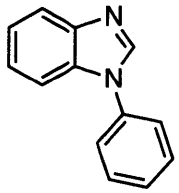
^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6 (d, J_{CF} = 245.8 Hz), 141.9, 137.4, 137.3, 131.1, 129.0, 128.9, 128.7 (d, J_{CF} = 8.7 Hz), 127.0 (d, J_{CF} = 4.8 Hz), 126.9, 126.7, 123.0 (d, J_{CF} = 2.9 Hz), 120.5, 120.2, 119.8 (d, J_{CF} = 6.8 Hz), 116.2 (d, J_{CF} = 3.9 Hz), 112.1 (d, J_{CF} = 17.3 Hz), 110.3, 17.5.

FT-IR (neat) 3058, 2955, 2924, 1635, 1602, 1577, 1498, 1455, 1435, 1381, 1354, 1339, 1316, 1290, 1248, 1226, 1184, 1154, 1116, 1081, 1053, 1014, 951, 925, 884, 787, 745, 733, 722 cm^{-1}.

MS (EI) *m/z* (M^+) calcd for $C_{19}H_{14}FN$: 275, found: 275.

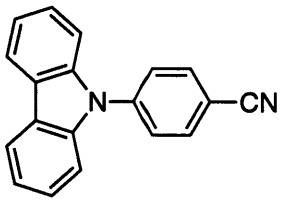


1-Phenyl-1*H*-indole (Table 15, entry 1) [16096-33-6]. The title compound was synthesized according to the General Procedure from indole (117 mg, 1.00 mmol), LiO*t*-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and bromobenzene (220 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (10% ethyl acetate/hexanes) and purified by column chromatography (hexanes). Pale-yellow oil. First run: 115 mg (60% yield). Second run: 122 mg (63% yield).



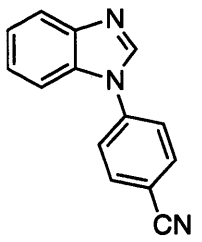
1-Phenyl-1*H*-benzo[*d*]imidazole (Table 15, entry 2) [2622-60-8]. The title compound was synthesized according to the General Procedure from benzimidazole (118 mg, 1.00 mmol), LiO*t*-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and bromobenzene (220 mg, 1.40 mmol), except that a mixture of *t*-BuOH (1.0 mL) and CH_3CN (3.0 mL) was used as the solvent (*t*-BuOH and CH_3CN were added in turn via syringe), due to the poor solubility of the heterocycle in neat CH_3CN. Reaction time: 48 h. The reaction mixture was filtered through a plug of silica gel (5% MeOH/CH_2Cl_2) and purified by normal-phase column chromatography on silica gel (0.75% MeOH/CH_2Cl_2) followed by reverse-phase column chromatography on C-18 silica gel (10%→100% CH_3CN/water). Yellow oil. First run: 118 mg (61%). Second run: 125 mg (64%).

Note: The reaction mixture was stirred until it became homogeneous, and then it was immediately transferred to the photoreactor before it turned to a white heterogeneous mixture. The reaction proceeded in poor yield when the white precipitate formed.



4-(9*H*-Carbazol-9-yl)benzonitrile (Table 15, entry 3) [57103-17-0]. The title compound was synthesized according to the General Procedure from carbazole (167 mg, 1.00 mmol), LiO*t*-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 4-

chlorobenzonitrile (193 mg, 1.40 mmol). The reaction mixture was filtered through a plug of silica gel (20% ethyl acetate/hexanes) and purified by normal-phase column chromatography on silica gel (hexanes→2% Et_2O/hexanes) followed by reverse-phase column chromatography on C-18 silica gel (10%→100% CH_3CN/water). Yellow solid. First run: 192 mg (72%). Second run: 194 mg (72%).



4-(1*H*-Benzo[*d*]imidazol-1-yl)benzonitrile (Table 15, entry 4) [25699-95-0]. The title compound was synthesized according to the General Procedure from benzimidazole (118 mg, 1.00 mmol), LiO*t*-Bu (112 mg, 1.40 mmol), CuI (19.0 mg, 0.10 mmol), and 4-chlorobenzonitrile (193 mg, 1.40 mmol), except that a mixture of *t*-BuOH (1.0 mL) and CH_3CN (3.0 mL) was used as the solvent (*t*-BuOH and CH_3CN were added in turn via syringe), due to the poor solubility of the heterocycle in neat CH_3CN. Reaction time: 48 h. The product was filtered through a plug of silica gel (5% MeOH/CH_2Cl_2) and purified by column chromatography on silica gel (1% MeOH/CH_2Cl_2, then 40%→55% ethyl acetate/hexanes). Yellow solid. First run: 131 mg (60%). Second run: 135 mg (62%).

Note: The reaction mixture was stirred until it became homogeneous, and then it was immediately transferred to the photoreactor before it turned to a white heterogeneous mixture. The reaction proceeded in poor yield when the white precipitate formed.

III. Nucleophile Competition Experiments (Table 16)

Procedure. Both of the nitrogen heterocycles (0.40 mmol each) and LiO*t*-Bu (32.0 mg, 0.40 mmol) were added to an oven-dried 10-mL quartz test tube that contained a stir bar. Next, the quartz tube was transferred to a glovebox, where *t*-BuOH (0.40 mL) and CH_3CN (0.40 mL) were added. The reaction mixture was stirred for 3 min, and then a solution of CuI in CH_3CN (0.80 mL, 0.050 M) was added, followed by iodobenzene (114 mg, 0.56 mmol) and dibenzyl ether (79.3 mg, 0.40 mmol; internal standard). The quartz test tube was capped with a rubber septum and transferred to a Luzchem LZC–4V photoreactor, where it was irradiated at 254 nm (adequate stirring is important). The ratio of products was determined by GC analysis after 2 h.

Note: Reactions with benzimidazole were quickly transferred to the photoreactor before they became heterogeneous.

IV. Electrophile Competition Experiments (eq 37)

Procedure. Indole (46.9 mg, 0.40 mmol) and LiO*t*-Bu (44.8 mg, 0.56 mmol) were added to an oven-dried 10-mL quartz test tube that contained a stir bar. Next, the quartz tube was transferred to a glovebox, where CH_3CN (0.80 mL), 1-ethyl-4-iodobenzene (130 mg, 0.56 mmol), and the aryl bromide or chloride (0.56 mmol) were added in turn. The reaction mixture was stirred for 3 min, and then a solution of CuI in CH_3CN (0.80 mL, 0.050 M) was added, followed by dibenzyl ether (79.3 mg, 0.40 mmol; internal standard). The quartz test tube was capped with a rubber septum and transferred

to a Luzchem LZC–4V photoreactor, where it was irradiated at 254 nm (adequate stirring is important). The ratio of products was determined by GC analysis after 1 h.

V. Functional-Group Tolerance Experiments (Table 17)

Procedure. Indole (46.9 mg, 0.40 mmol) and LiO*t*-Bu (44.8 mg, 0.56 mmol) were added to an oven-dried 10-mL quartz test tube that contained a stir bar. Next, the quartz test tube was transferred to a glovebox, where CH_3CN (0.80 mL) and the additive (0.40 mmol) were added in turn. The reaction mixture was stirred for 3 min, and then a solution of CuI in CH_3CN (0.80 mL, 0.050 M) was added, followed by iodobenzene (114 mg, 0.56 mmol) and dibenzyl ether (79.3 mg, 0.40 mmol; internal standard). The reaction mixture was stirred for 3 min, and then an aliquot was taken for a t = 0 time point. Next, the quartz test tube was capped with a rubber septum, the joint was wrapped with electrical tape, and the quartz tube was transferred to a Luzchem LZC–4V photoreactor, where it was irradiated at 254 nm for 24 h (adequate stirring is important). The yield of product and the percent recovery of the additive were determined by GC analysis.

VI. ^{1}H NMR Spectra of Selected Compounds

JC9265B CDCl3

exp20 PROTON

SAMPLE	
date	Mar 6 2013
solvent	cdcl3
file	/indy/jwchoi/~
vnmrsys/data/JC926~	
5B_1H_13C_CDCl3/PR~	
	OTON01.fid
ACQUISITION	
sw	8000.0
at	3.000
np	48000
fb	not used
bs	32
d1	2.000
nt	16
ct	16
TRANSMITTER	
tn	H1
sfrq	499.708
tof	499.7
tpwr	61
pw	4.850
DECOUPLER	
dn	C13
dof	0
dm	nnn
decwave	g
dpwr	35
dmf	32258

PRESATURATION	
satmode	n
wet	n
SPECIAL	
temp	not used
gain	30
spin	20
hst	0.008
pw90	9.700
alfa	10.000
FLAGS	
il	n
in	n
dp	y
hs	nn
PROCESSING	
lb	0.20
fn	not used
DISPLAY	
sp	-0.1
wp	4996.8
rfl	4630.1
rfp	3627.9
rp	25.2
lp	-59.8
PLOT	
wc	250
sc	0
vs	80
th	6
ai cdc ph	

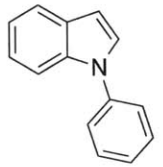
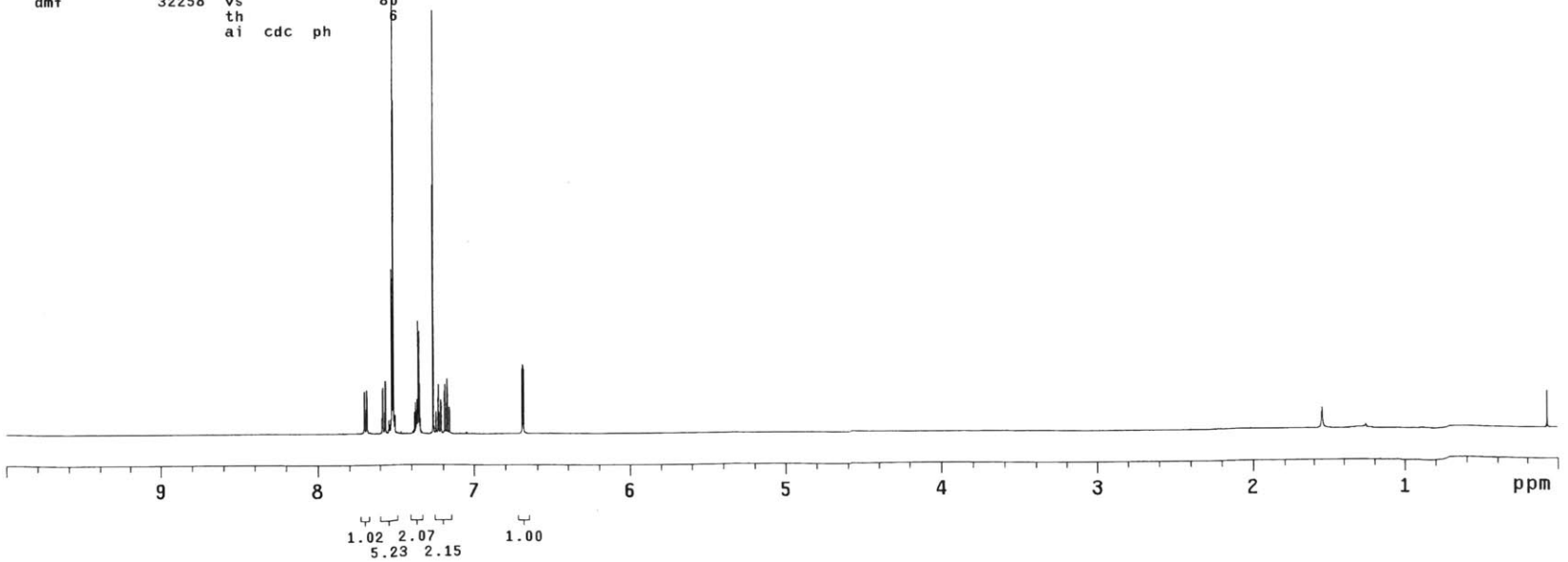


Table 11, entry 1



DZ-04-292-1-Purified

exp20 PROTON

SAMPLE		PRESATURATION	
date	Apr 2 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/dziegle~	SPECIAL	
r/vnmrsys/data/DZ-~		temp	not used
04-292-1-Purified/~		gain	32
PROTON01.fid		spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	1.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.950	rfl	4630.1
DECOUPLER		rfp	3627.9
dn	C13	rp	20.6
dof	0	lp	-73.7
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	40
dmf	32258	th	25
		ai cdc ph	

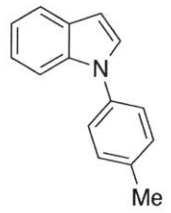


Table 11, entry 2

DZ-05-082-1-Purified

exp25 PROTON

SAMPLE		PRESATURATION	
date	Jul 26 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/dziegle~	SPECIAL	
r/vnmrsys/data/DZ-~		temp	not used
05-082-1-Purified/~		gain	32
PROTON01.fid		spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	1.000	dp	y
nt	32	hs	nn
ct	32	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.698	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.950	rfl	4632.1
DECOUPLER		rfp	3627.8
dn	C13	rp	-81.8
dof	0	lp	-72.7
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	11
dmf	32258	th	16
		ai cdc ph	

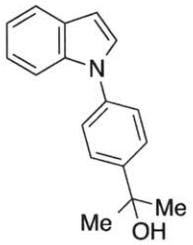


Table 11, entry 3

DZ-04-200-2-Purified

exp20 PROTON

SAMPLE		PRESATURATION	
date	Mar 21 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/dziegle~	SPECIAL	
r/vnmrsys/data/DZ-~		temp	not used
04-200-2-Purified/~		gain	30
	PROTON02.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.700
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	1.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.850	rfl	4630.1
DECOUPLER		rfp	3627.9
dn	C13	rp	42.6
dof	0	lp	-72.6
dm	nnn	PLOT	
decwave	g	wc	250
dpwr	35	sc	0
dmf	32258	vs	48
		th	13
		ai cdc ph	

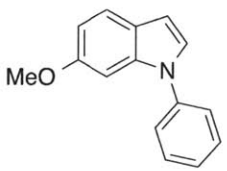


Table 11, entry 4

JC9267 1H CDCl3

exp20 PROTON

SAMPLE		PRESATURATION	
date	Mar 10 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC926~		temp	not used
7_1H_CDCl3/PROTON0~		gain	30
	1.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.700
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.850	rfl	4630.1
DECOUPLER		rfp	3627.9
dn	C13	rp	42.0
dof	0	lp	-73.7
dm	nnn	PLOT	
decwave	g	wc	250
dpwr	35	sc	0
dmf	32258	vs	63
		th	50
		ai	cdc ph

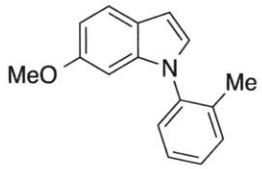
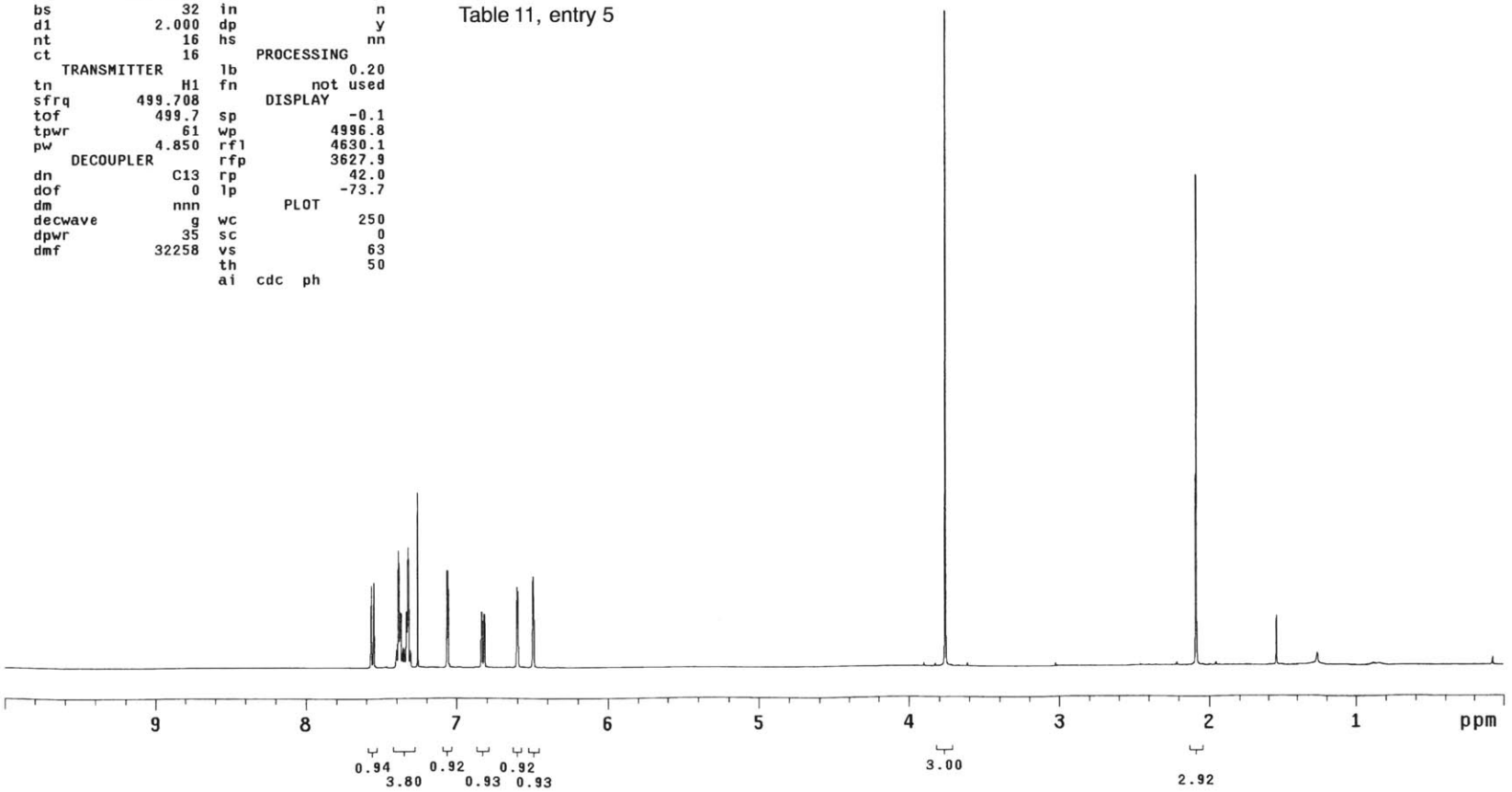


Table 11, entry 5



DZ-04-244-1-Purified

exp21 PROTON

SAMPLE		PRESATURATION	
date	Mar 16 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/dziegle~	SPECIAL	
r/vnmrsys/data/DZ-~		temp	not used
04-244-1-Purified/~		gain	30
PROTON01.fid		spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.700
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	1.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.850	rfl	4630.1
DECOUPLER		rfp	3627.9
dn	C13	rp	42.9
dof	0	lp	-72.2
dm	nnn	PLOT	
decwave	g	wc	250
dpwr	35	sc	0
dmf	32258	vs	61
		th	41
		ai cdc ph	

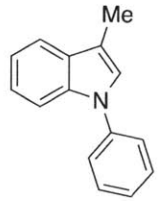
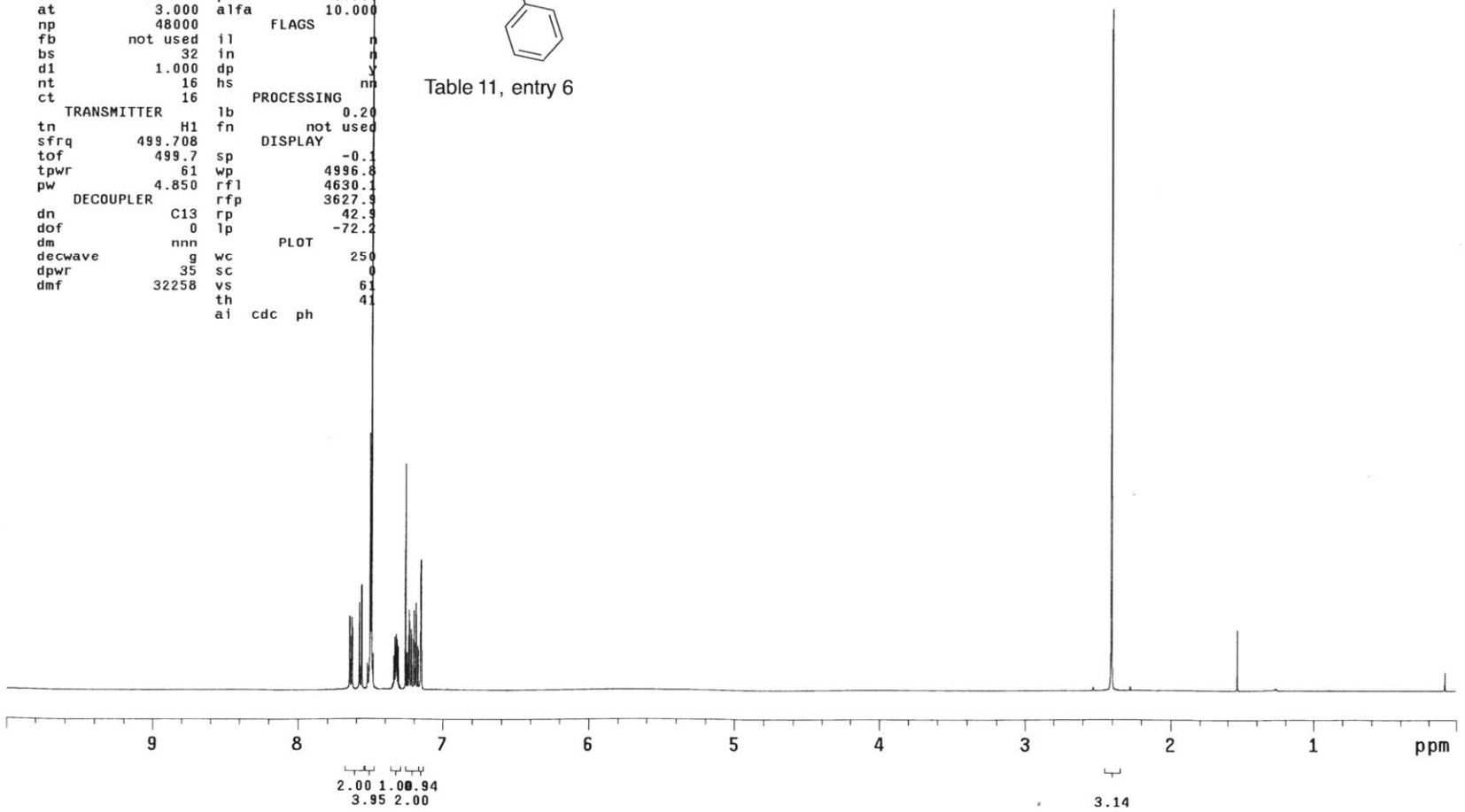


Table 11, entry 6



JC9299 CDCl3

exp20 PROTON

SAMPLE		PRESATURATION	
date	Mar 21 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC929~		temp	not used
9_1H_13C_CDCl3/PRO~		gain	30
TON01.fid		spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.700
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.850	rf1	4630.1
DECOUPLER		rfp	3627.9
dn	C13	rp	42.3
dof	0	lp	-72.5
dm	nnn	PLOT	
decwave	g	wc	250
dpwr	35	sc	0
dmf	32258	vs	22
		th	50
		ai cdc ph	

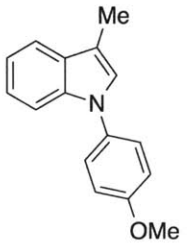


Table 11, entry 7

DZ-04-266-2-Purified

exp20 PROTON

SAMPLE		PRESATURATION	
date	Mar 20 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/dziegle~	SPECIAL	
r/vnmrsys/data/DZ-~		temp	not used
04-266-2-Purified/~		gain	30
	PROTON01.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.700
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	1.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.850	rfl	4630.1
DECOUPLER		rfp	3627.9
dn	C13	rp	42.7
dof	0	lp	-73.7
dm	nnn	PLOT	
decwave	g	wc	250
dpwr	35	sc	0
dmf	32258	vs	79
		th	25
		ai cdc ph	

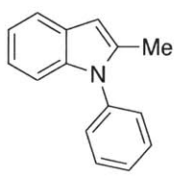


Table 11, entry 8

DZ-04-246-1-Purified

exp20 PROTON

SAMPLE		PRESATURATION	
date	Mar 16 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/dziegle~	SPECIAL	
r/vnmrsys/data/DZ-~		temp	not used
04-246-1-Purified/~		gain	30
PROTON01.fid		spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.700
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	1.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.850	rfl	4630.1
DECOUPLER		rfp	3627.9
dn	C13	rp	41.9
dof	0	lp	-70.9
dm	nnn	PLOT	
decwave	g	wc	250
dpwr	35	sc	0
dmf	32258	vs	85
		th	25
		ai cdc ph	

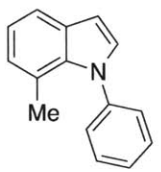


Table 11, entry 9

DZ-04-196-1-Purified

exp20 PROTON

SAMPLE		PRESATURATION	
date	Mar 23 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/dziegle~	SPECIAL	
r/vnmrsys/data/DZ-~		temp	not used
04-196-1-Purified/~		gain	30
PROTON02.fid		spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.700
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	1.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.850	rfl	4630.1
DECOUPLER		rfp	3627.9
dn	C13	rp	44.9
dof	0	lp	-72.3
dm	nnn	PLOT	
decwave	g	wc	250
dpwr	35	sc	0
dmf	32258	vs	65
		th	33
		ai cdc ph	

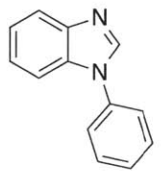
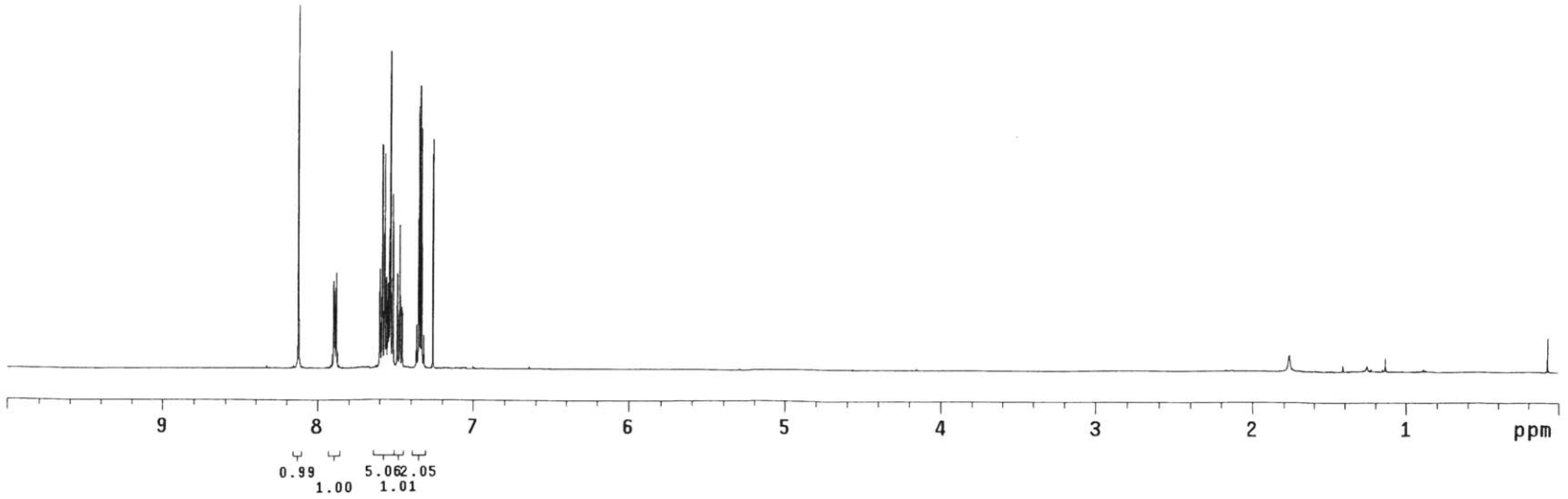


Table 12, entry 1



DZ-04-270-1-Purified

exp20 PROTON

SAMPLE		PRESATURATION	
date	Mar 26 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/dziegle~	SPECIAL	
r/vnmrsys/data/DZ-~		temp	not used
04-270-1-Purified/~		gain	32
	PROTON01.fid	spin	0
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	1.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.950	rfl	4629.9
DECOUPLER		rfp	3627.9
dn	C13	rp	24.7
dof	0	lp	-72.1
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	135
dmf	32258	th	4
		ai cdc ph	

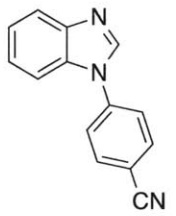
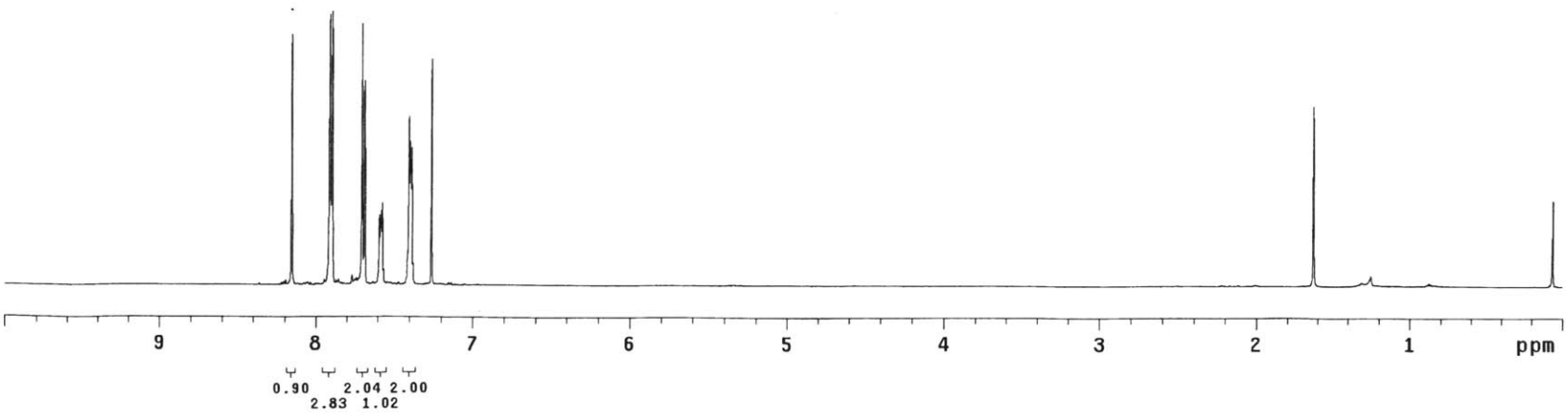


Table 12, entry 2



DZ-04-268-3-Purified

exp20 PROTON

SAMPLE		PRESATURATION	
date	Apr 2 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/dziegle~	SPECIAL	
r/vnmrsys/data/DZ-~		temp	not used
04-268-3-Purified/~		gain	32
	PROTON02.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	1.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.950	rfl	4630.1
DECOUPLER		rfp	3627.9
dn	C13	rp	21.6
dof	0	lp	-79.4
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	25
dmf	32258	th	13
		ai cdc ph	

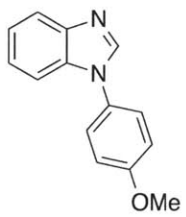


Table 12, entry 3

JC9273A 1H 13C CDCl3

exp20 PROTON

SAMPLE		PRESATURATION	
date	Mar 14 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC927~		temp	not used
3A_1H_13C_CDCl3/PR~		gain	18
	OTON02.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.700
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.850	rfl	4630.1
DECOUPLER		rfp	3627.9
dn	C13	rp	47.4
dof	0	lp	-81.6
dm	nnn	PLOT	
decwave	g	wc	250
dpwr	35	sc	0
dmf	32258	vs	17
		th	25
		ai cdc ph	

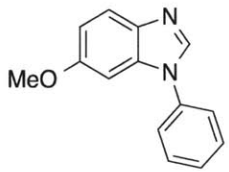
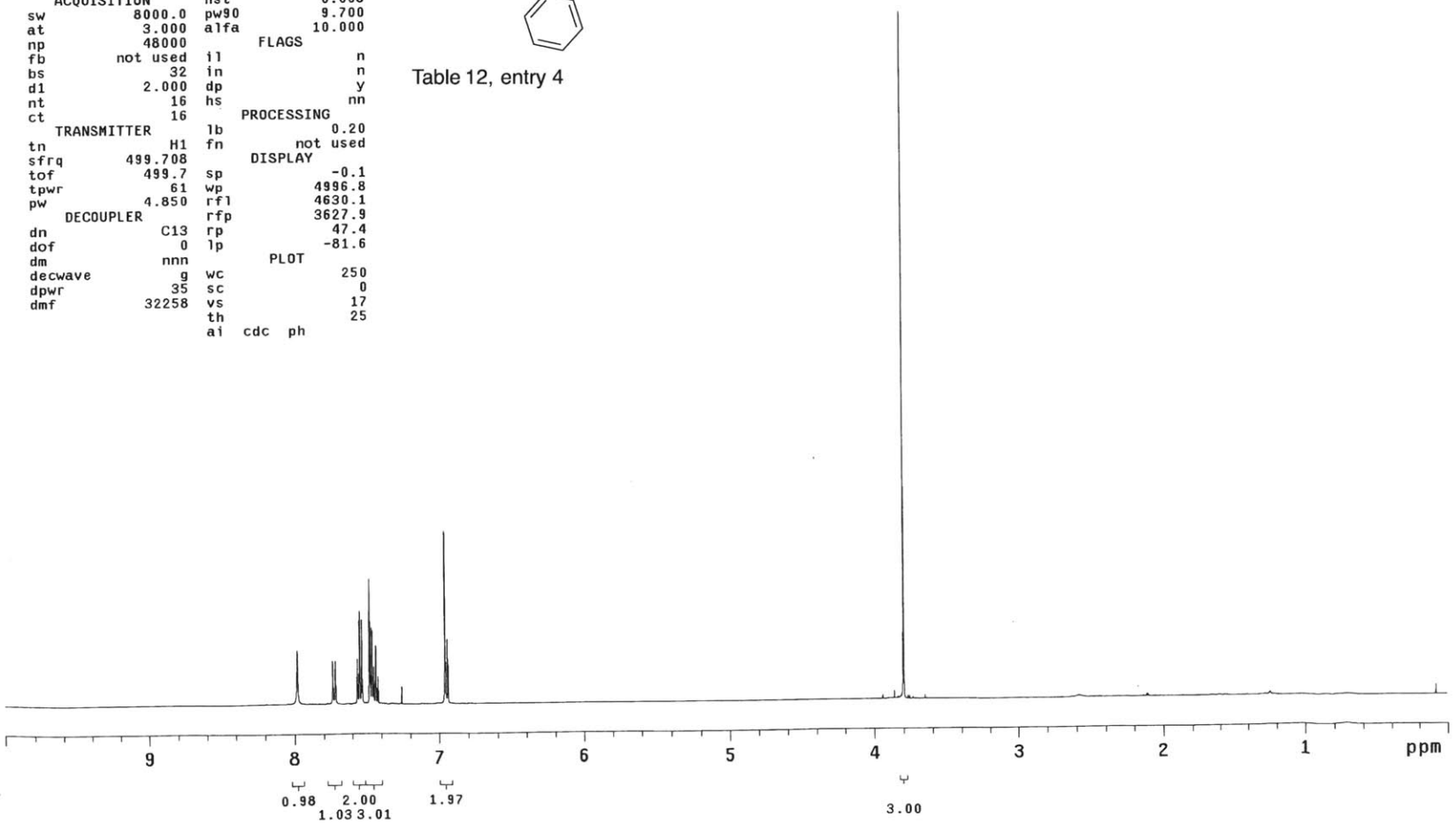


Table 12, entry 4



JC9273 Lower-spot 1H CDCl3

exp20 PROTON

SAMPLE		PRESATURATION	
date	Mar 10 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC927~		temp	not used
3_Lower-spot_1H_CD~		gain	30
C13/PROTON02.fid		spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.700
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.850	rfl	4630.1
DECOUPLER		rfp	3627.9
dn	C13	rp	38.0
dof	0	lp	-68.1
dm	nnn	PLOT	
decwave	g	wc	250
dpwr	35	sc	0
dmf	32258	vs	51
		th	13
		ai cdc ph	

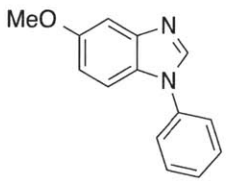
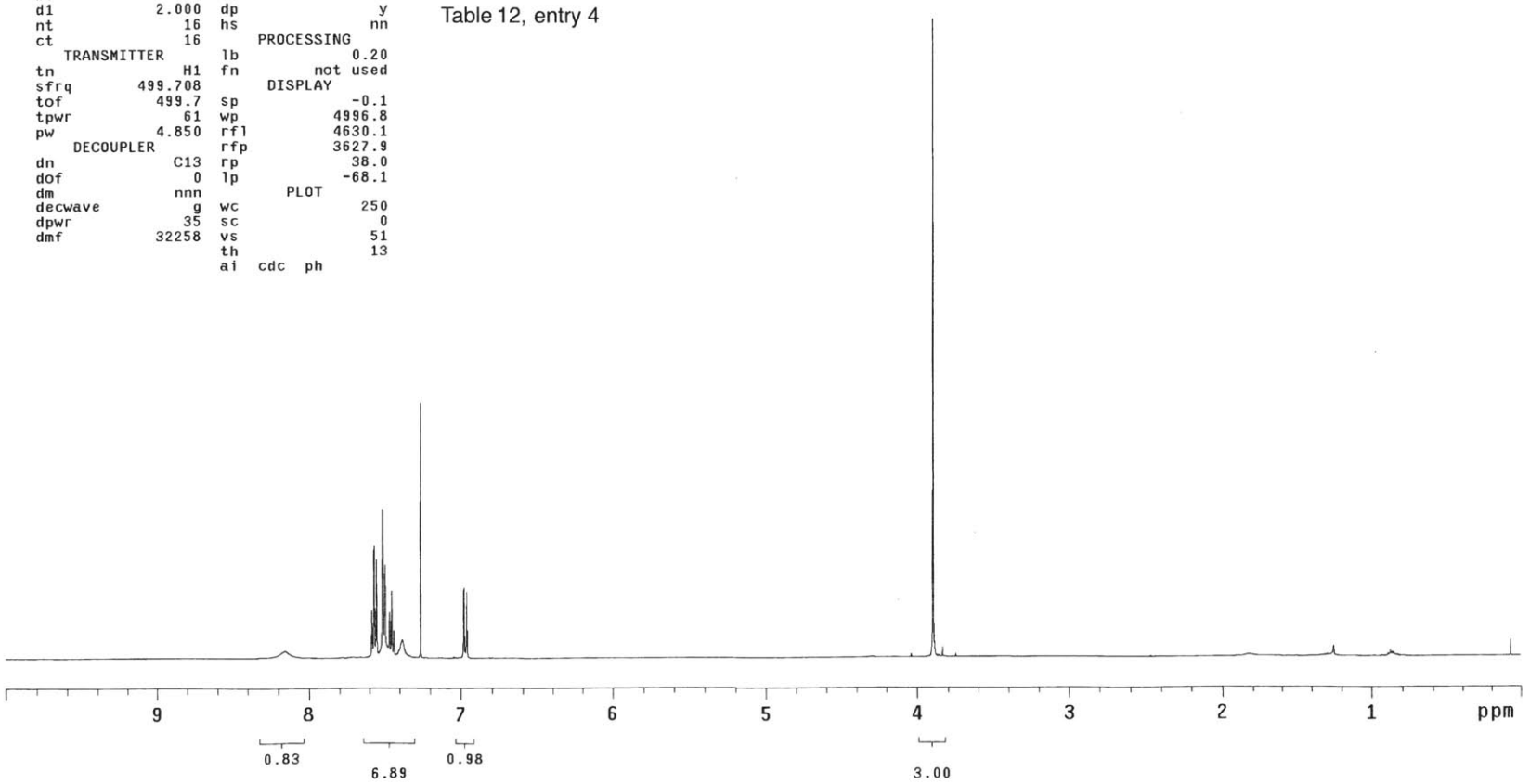


Table 12, entry 4



JC9291 1H CDCl3

exp20 PROTON

SAMPLE		PRESATURATION	
date	Mar 21 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC929~		temp	not used
1_1H_CDCl3/PROTON0~		gain	30
	2.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.700
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.850	rfl	4630.1
DECOUPLER		rfp	3627.9
dn	C13	rp	41.9
dof	0	lp	-68.8
dm	nnn	PLOT	
decwave	g	wc	250
dpwr	35	sc	0
dmf	32258	vs	43
		th	6
		ai cdc ph	

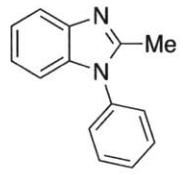


Table 12, entry 5

JC9303B CDCl3

exp20 PROTON

SAMPLE		PRESATURATION	
date	Mar 25 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC930~		temp	not used
3B_1H_13C_CDCl3/PR~		gain	32
	OTON01.fid	spin	0
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.950	rfl	4629.9
DECOUPLER		rfp	3627.9
dn	C13	rp	28.6
dof	0	lp	-75.3
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	39
dmf	32258	th	50
		ai cdc ph	

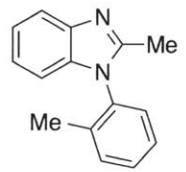
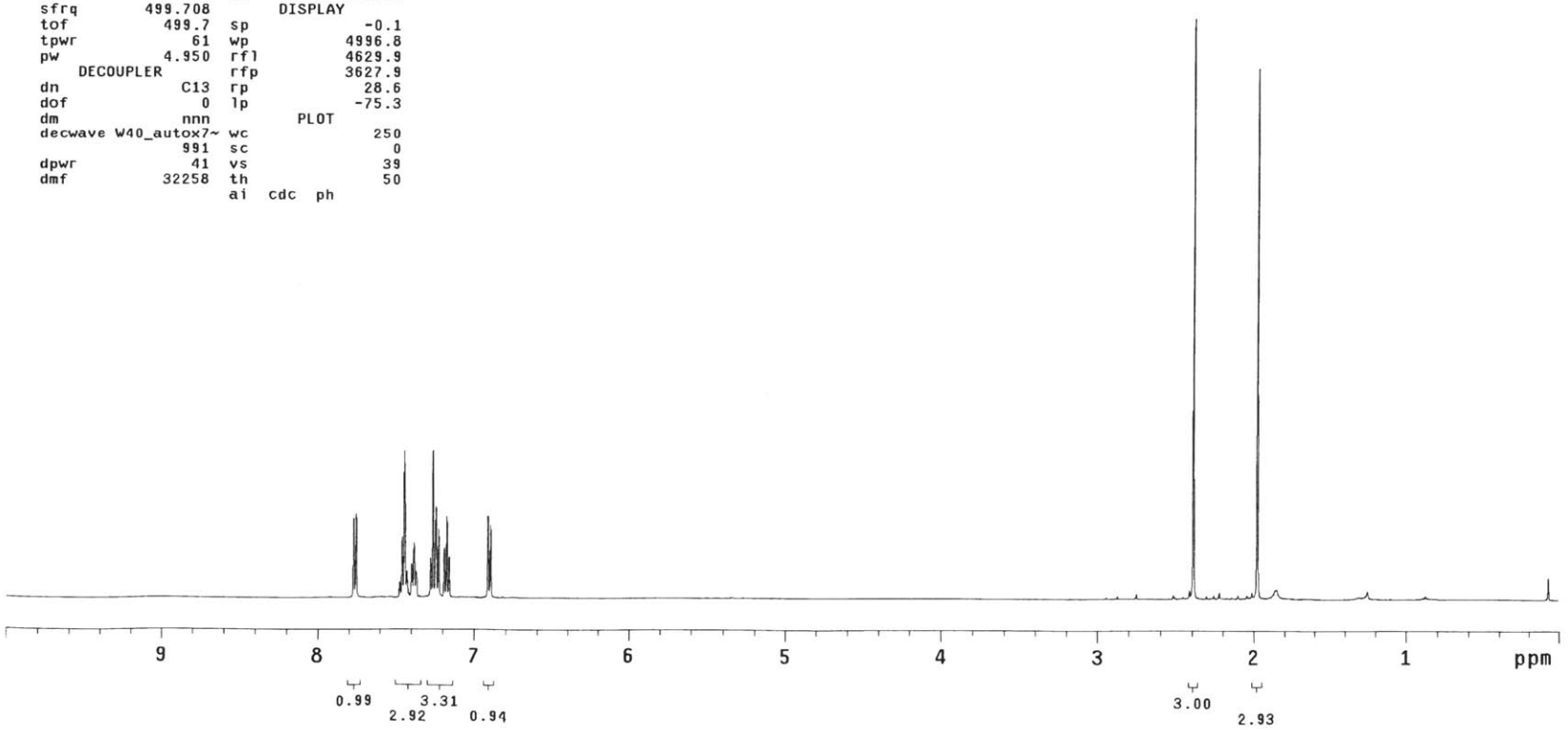


Table 12, entry 6



JC10009 CDCl3

exp20 PROTON

SAMPLE		PRESATURATION	
date	Mar 29 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC100~		temp	not used
09_1H_13C_CDCl3/PR~		gain	20
OTON01.fid		spin	0
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.0
tpwr	61	wp	4996.8
pw	4.950	rfl	1001.7
DECOUPLER		rfp	0
dn	C13	rp	28.6
dof	0	lp	-73.4
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	77
dmf	32258	th	13
		ai cdc ph	

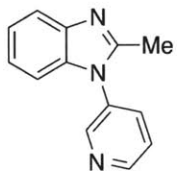
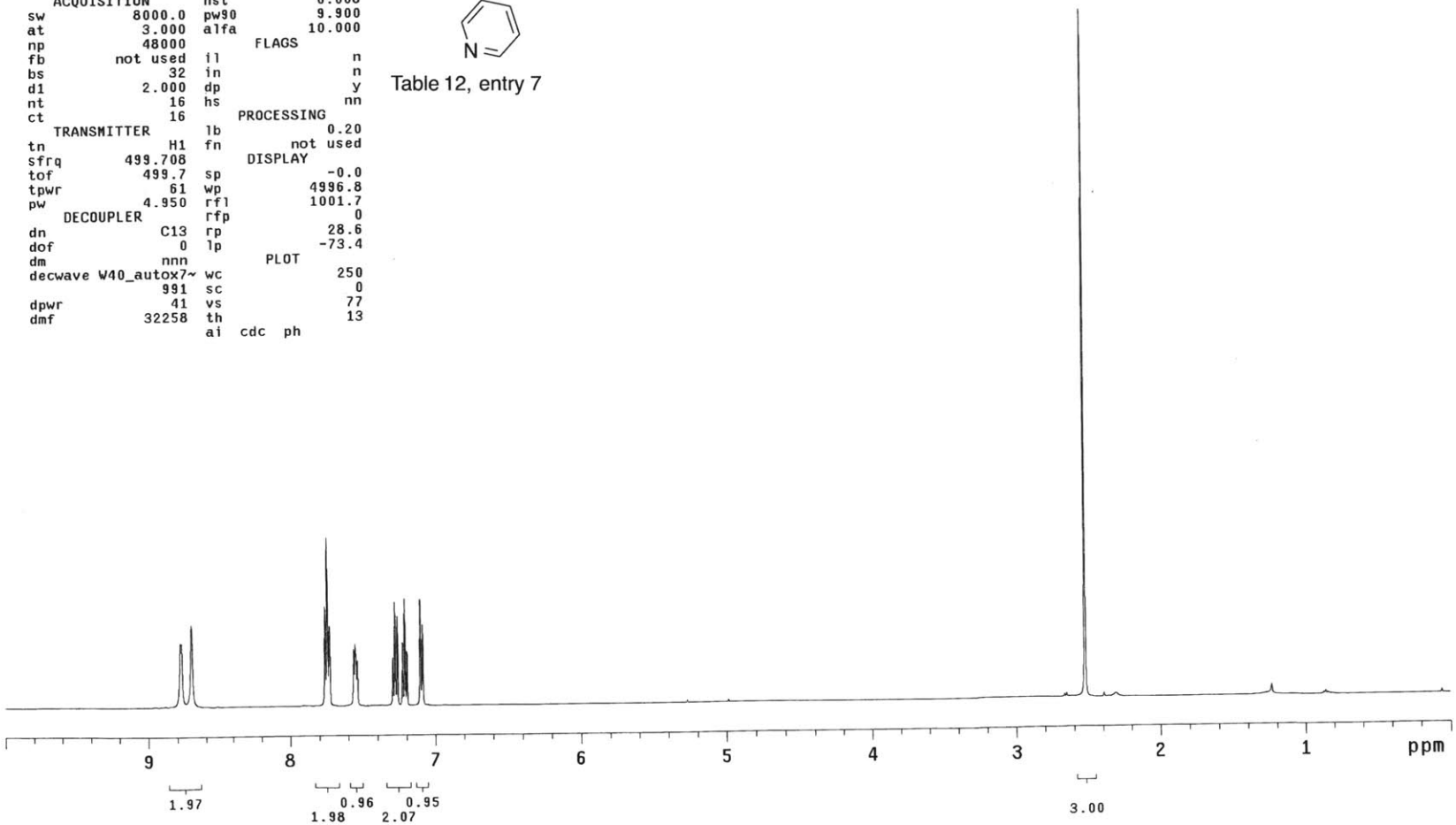


Table 12, entry 7



DZ-Ph-imidazole 1H CDCl3

exp10 PROTON

SAMPLE		PRESATURATION	
date	Mar 29 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/DZ-Ph~		temp	not used
-imidazole_1H_CDCl~		gain	32
3/PROTON01.fid		spin	0
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.950	rfl	4629.9
DECOUPLER		rfp	3627.9
dn	C13	rp	27.6
dof	0	lp	-76.2
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	100
dmf	32258	th	49
		ai cdc ph	

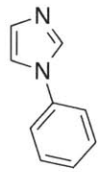
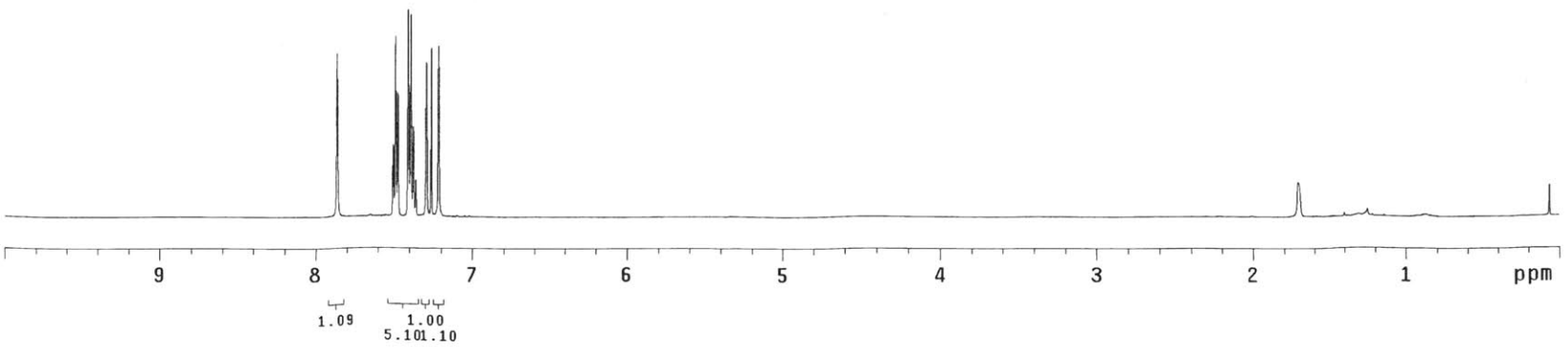


Table 13, entry 1



JC10013 CDCl3

exp20 PROTON

SAMPLE		PRESATURATION	
date	Mar 31 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC100~		temp	not used
13_1H_13C_CDCl3/PR~		gain	32
	OTON01.fid	spin	0
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.950	rfl	4629.9
DECOUPLER		rfp	3627.9
dn	C13	rp	22.8
dof	0	lp	-73.0
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	39
dmf	32258	th	25
		ai cdc ph	

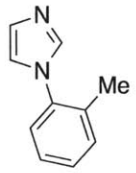
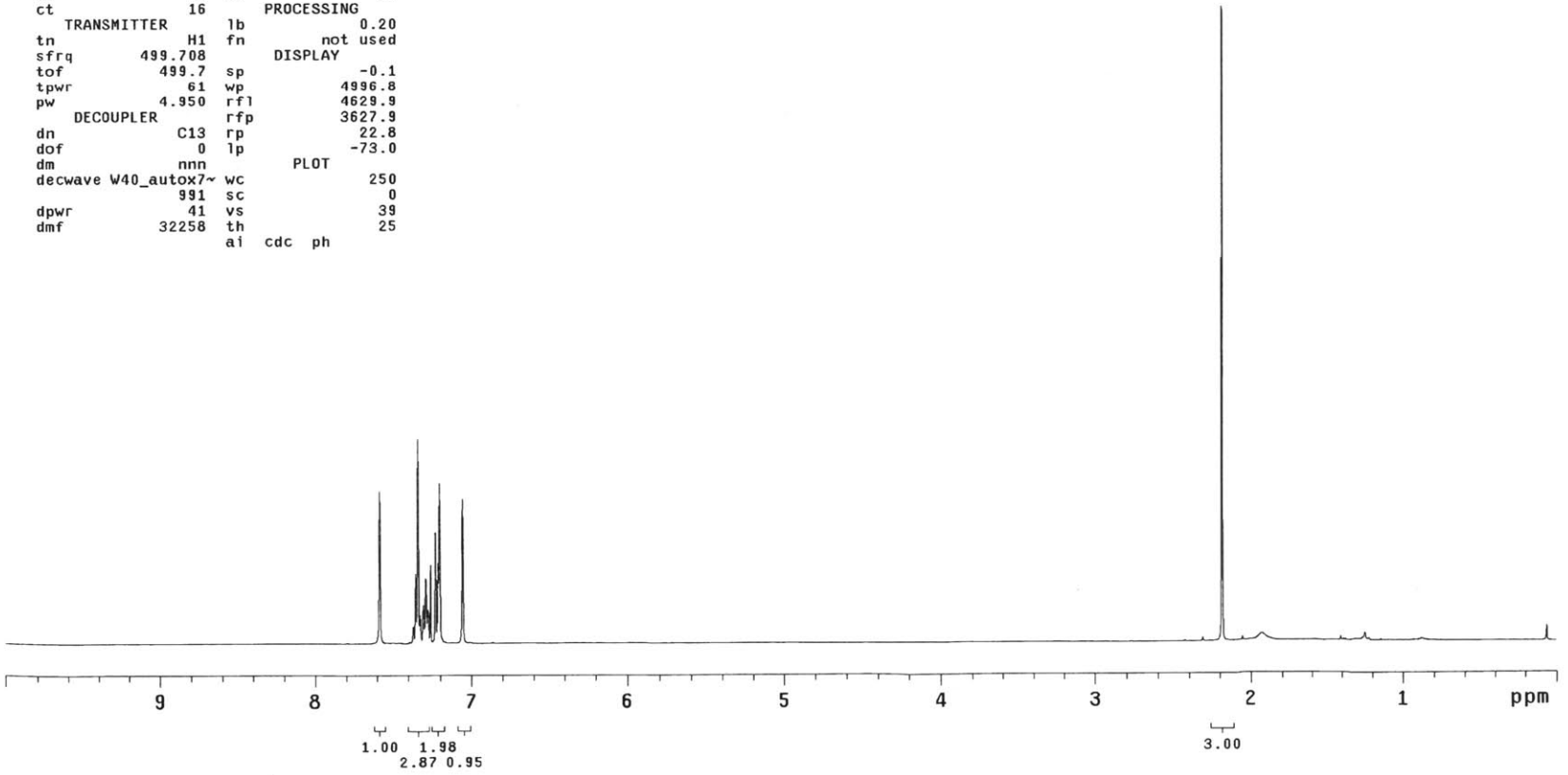


Table 13, entry 2



DZ-04-254-1-Purified

exp10 PROTON

SAMPLE	
date	Mar 16 2013
solvent	cdcl3
file	/indy/dziegle~
r/vnmrsys/data/DZ-~	
04-254-1-Purified/~	
	PROTON01.fid

ACQUISITION	
sw	8000.0
at	3.000
np	48000
fb	not used
bs	32
d1	1.000
nt	16
ct	16

TRANSMITTER	
tn	H1
sfrq	499.708
tof	499.7
tpwr	61
pw	4.850

DECOUPLER	
dn	C13
dof	0
dm	nnn
decwave	g
dpwr	35
dmf	32258

PRESATURATION	
satmode	n
wet	n

SPECIAL	
temp	not used
gain	30
spin	20
hst	0.008
pw90	9.700
alfa	10.000

FLAGS	
il	n
in	n
dp	y
hs	nn

PROCESSING	
lb	0.20
fn	not used

DISPLAY	
sp	-0.1
wp	4996.8
rfl	4630.1
rfp	3627.9
rp	42.5
lp	-73.7

PLOT	
wc	250
sc	0
vs	23
th	13
ai	cdc ph

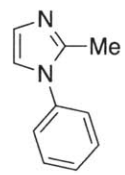


Table 13, entry 3

DZ-04-230-3-Purified

exp20 PROTON

SAMPLE		PRESATURATION	
date	Mar 18 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/dziegle~	SPECIAL	
r/vnmrsys/data/DZ-~		temp	not used
04-230-3-Purified/~		gain	30
	PROTON01.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.700
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	1.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.850	rfl	4630.1
DECOUPLER		rfp	3627.9
dn	C13	rp	40.0
dof	0	lp	-71.1
dm	nnn	PLOT	
decwave	g	wc	250
dpwr	35	sc	0
dmf	32258	vs	50
		th	38
		ai cdc ph	

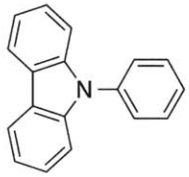
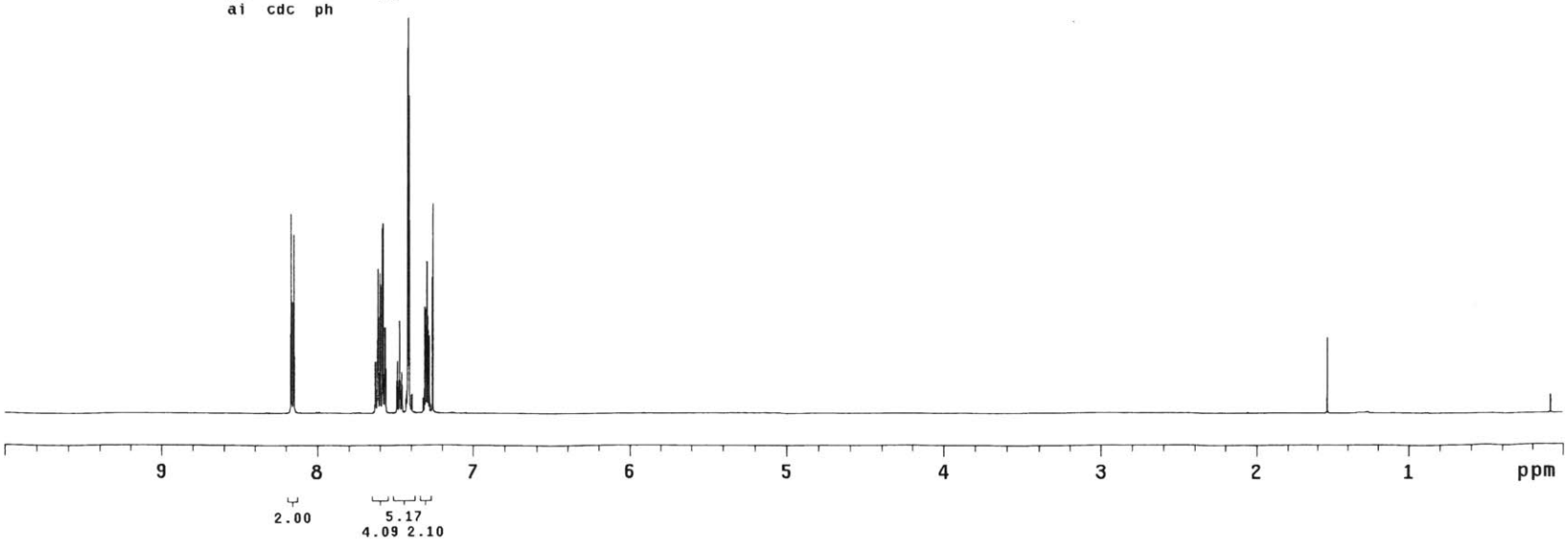


Table 14, entry 1



JC9283 1H CDCl3

exp20 PROTON

SAMPLE		PRESATURATION	
date	Mar 17 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC928~		temp	not used
3_1H_CDCl3/PROTON0~		gain	30
	1.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.700
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.850	rfl	4630.1
DECOUPLER		rfp	3627.9
dn	C13	rp	43.3
dof	0	lp	-75.9
dm	nnn	PLOT	
decwave	g	wc	250
dpwr	35	sc	0
dmf	32258	vs	49
		th	37
		ai cdc ph	

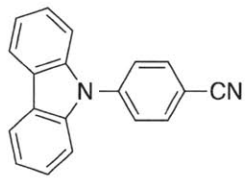
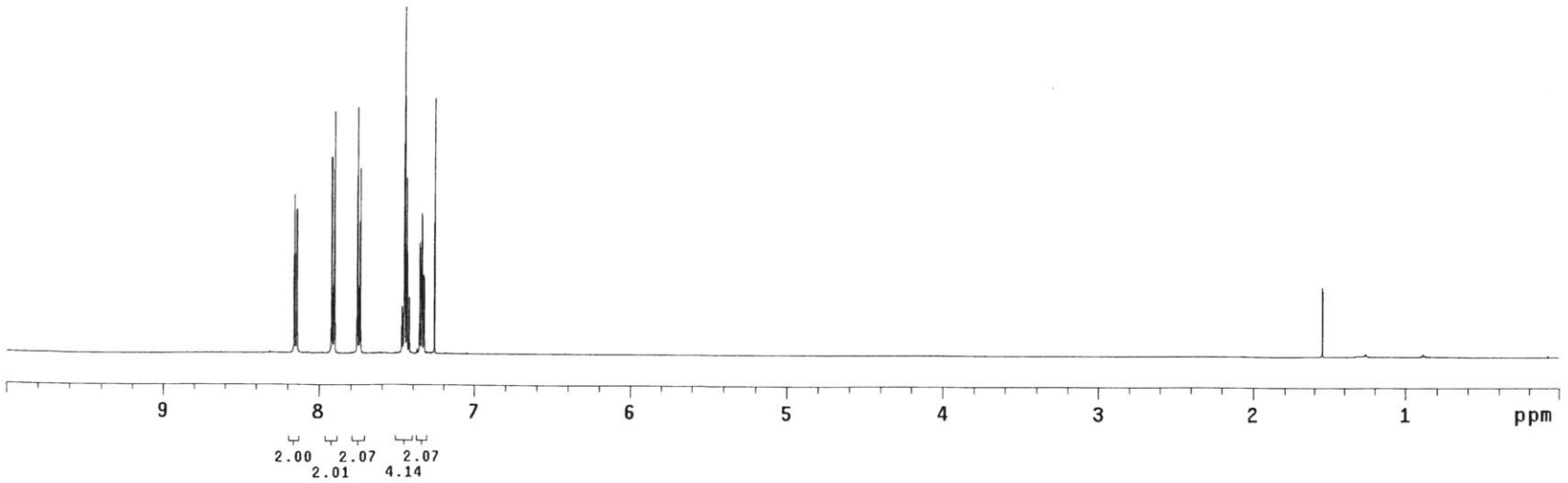


Table 14, entry 2



JC9281 CDCl3

exp20 PROTON

SAMPLE		PRESATURATION	
date	Mar 16 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC928~		temp	not used
1_1H_13C_CDCl3/PRO~		gain	30
TON01.fid		spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.700
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.850	rfl	4630.1
DECOUPLER		rfp	3627.9
dn	C13	rp	41.5
dof	0	lp	-74.5
dm	nnn	PLOT	
decwave	g	wc	250
dpwr	35	sc	0
dmf	32258	vs	42
		th	25
		ai cdc ph	

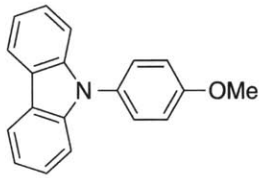


Table 14, entry 3

JC9275B CDCl3

exp20 PROTON

SAMPLE	
date	Mar 13 2013
solvent	cdcl3
file	/indy/jwchoi/~
vnmrsys/data/JC927~	
5B_CDCl3/PROTON01.~	
	fid
ACQUISITION	
sw	8000.0
at	3.000
np	48000
fb	not used
bs	32
d1	2.000
nt	16
ct	16
TRANSMITTER	
tn	H1
sfrq	499.708
tof	499.7
tpwr	61
pw	4.850
DECOUPLER	
dn	C13
dof	0
dm	nnn
decwave	g
dpwr	35
dmf	32258

PRESATURATION	
satmode	n
wet	n
SPECIAL	
temp	not used
gain	30
spin	20
hst	0.008
pw90	9.700
alfa	10.000
FLAGS	
il	n
in	n
dp	y
hs	nn
PROCESSING	
lb	0.20
fn	not used
DISPLAY	
sp	-0.1
wp	4996.8
rfl	4630.1
rfp	3627.9
rp	54.2
lp	-75.4
PLOT	
wc	250
sc	0
vs	141
th	25
ai cdc ph	

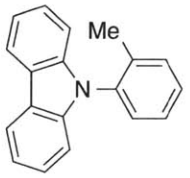
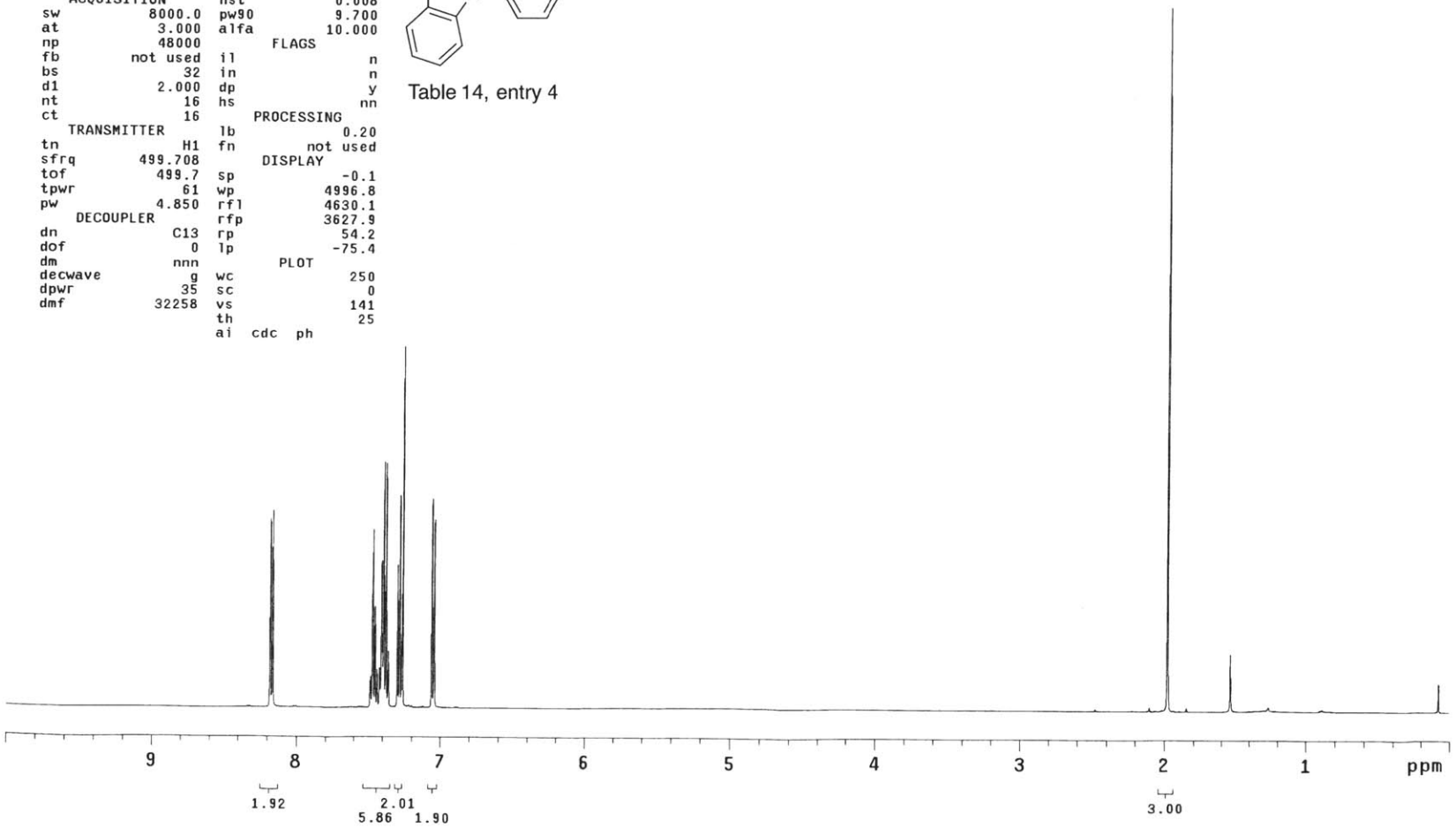


Table 14, entry 4



DZ-04-252-1-Purified

exp20 PROTON

SAMPLE		PRESATURATION	
date	Mar 18 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/dziegle~	SPECIAL	
r/vnmrsys/data/DZ-~		temp	not used
04-252-1-Purified/~		gain	30
	PROTON01.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.700
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	1.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.850	rfl	4630.1
DECOUPLER		rfp	3627.9
dn	C13	rp	41.0
dof	0	lp	-73.0
dm	nnn	PLOT	
decwave	g	wc	250
dpwr	35	sc	0
dmf	32258	vs	75
		th	40
		ai cdc ph	

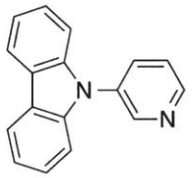
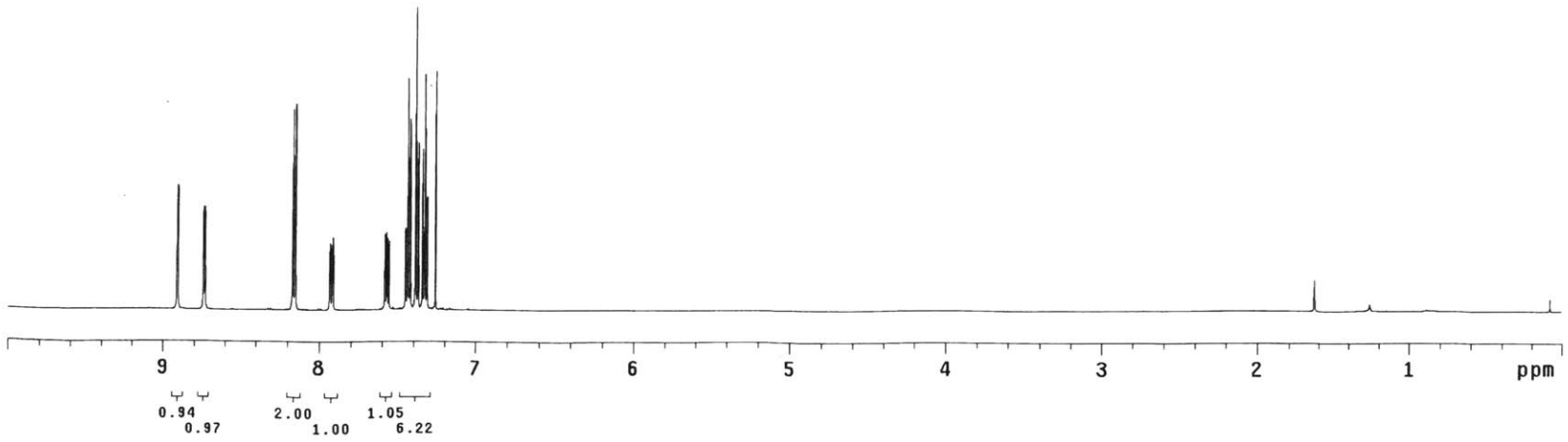


Table 14, entry 5



DZ-04-262-1-Purified

exp20 PROTON

SAMPLE		PRESATURATION	
date	Mar 18 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/dziegle~	SPECIAL	
r/vnmrsys/data/DZ-~		temp	not used
04-262-1-Purified/~		gain	30
PROTON02.fid		spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.700
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	1.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.850	rfl	4630.1
DECOUPLER		rfp	3627.9
dn	C13	rp	40.0
dof	0	lp	-70.0
dm	nnn	PLOT	
decwave	g	wc	250
dpwr	35	sc	0
dmf	32258	vs	44
		th	50
		ai cdc ph	

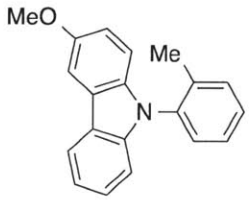


Table 14, entry 6

DZ-04-264-1-Purified

exp20 PROTON

SAMPLE		PRESATURATION	
date	Mar 18 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/dziegle~	SPECIAL	
r/vnmrsys/data/DZ-~		temp	not used
04-264-1-Purified/~		gain	30
PROTON02.fid		spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.700
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	1.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.850	rfl	4630.1
DECOUPLER		rfp	3627.9
dn	C13	rp	42.2
dof	0	lp	-74.1
dm	nnn	PLOT	
decwave	g	wc	250
dpwr	35	sc	0
dmf	32258	vs	97
		th	25
		ai cdc ph	

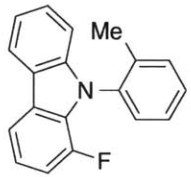


Table 14, entry 7

DZ-05-030-1-Purified

exp10 PROTON

SAMPLE		PRESATURATION	
date	Apr 19 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/dziegle~	SPECIAL	
r/vnmrsys/data/DZ-~		temp	not used
05-030-1-Purified/~		gain	32
	PROTON01.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	1.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.950	rf1	4630.1
DECOUPLER		rfp	3627.9
dn	C13	rp	13.3
dof	0	lp	-67.9
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	27
dmf	32258	th	7
		ai cdc ph	

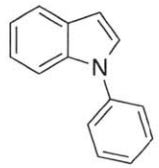
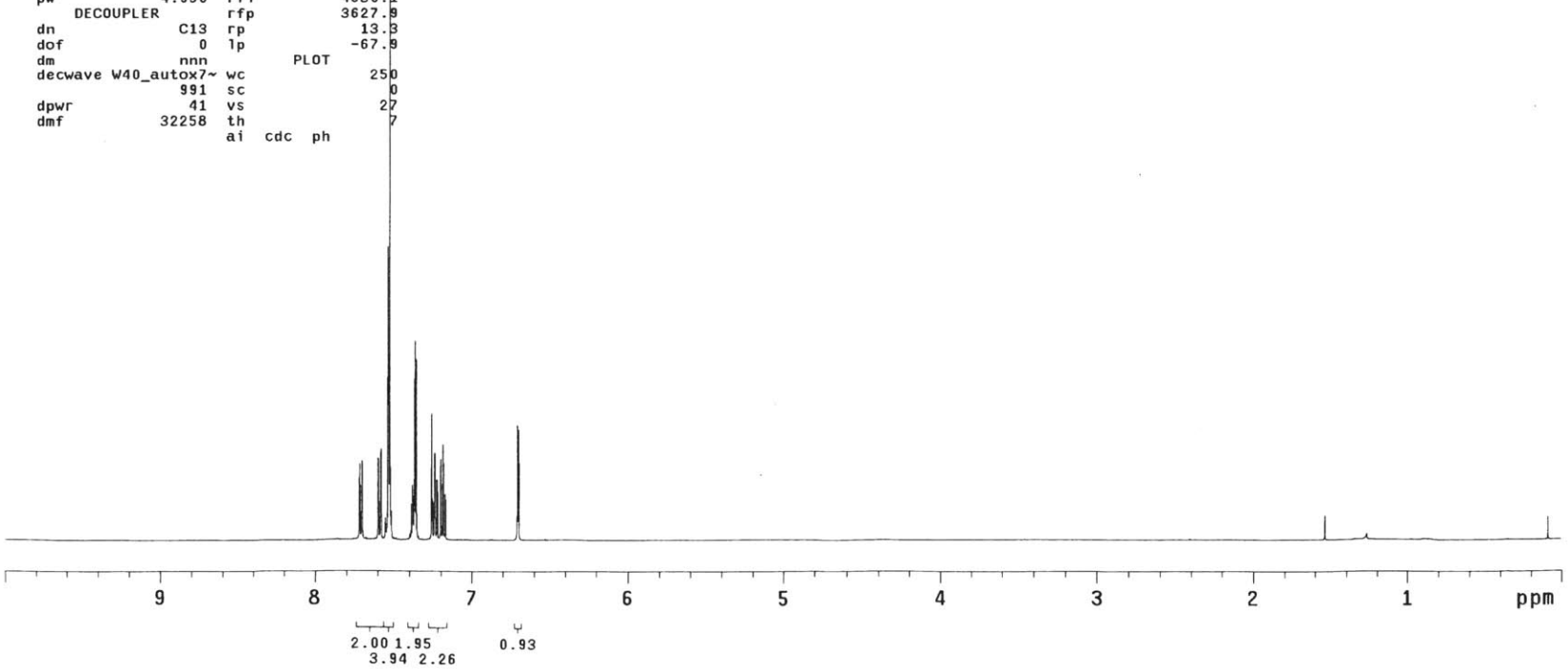


Table 15, entry 1



JMM1250

exp10 PROTON

SAMPLE		PRESATURATION	
date	Apr 27 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/jmmolin~	SPECIAL	
a/vnmrsys/data/JMM~		temp	not used
1250/PROTON01.fid		gain	20
ACQUISITION		spin	20
sw	8000.0	hst	0.008
at	3.000	pw90	9.900
np	48000	alfa	10.000
fb	not used	FLAGS	
bs	32	il	n
d1	2.000	in	n
nt	16	dp	y
ct	16	hs	nn
TRANSMITTER		PROCESSING	
tn	H1	lb	0.20
sfrq	499.708	fn	not used
tof	499.7	DISPLAY	
tpwr	61	sp	-0.0
pw	4.950	wp	4996.8
DECOUPLER		rfl	1001.7
dn	C13	rfp	0
dof	0	rp	24.3
dm	nnn	lp	-68.3
decwave	W40_autox7~	PLOT	
	991	wc	250
dpwr	41	sc	0
dmf	32258	vs	101
		th	31
		ai cdc ph	

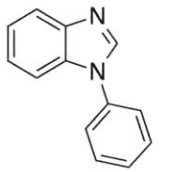
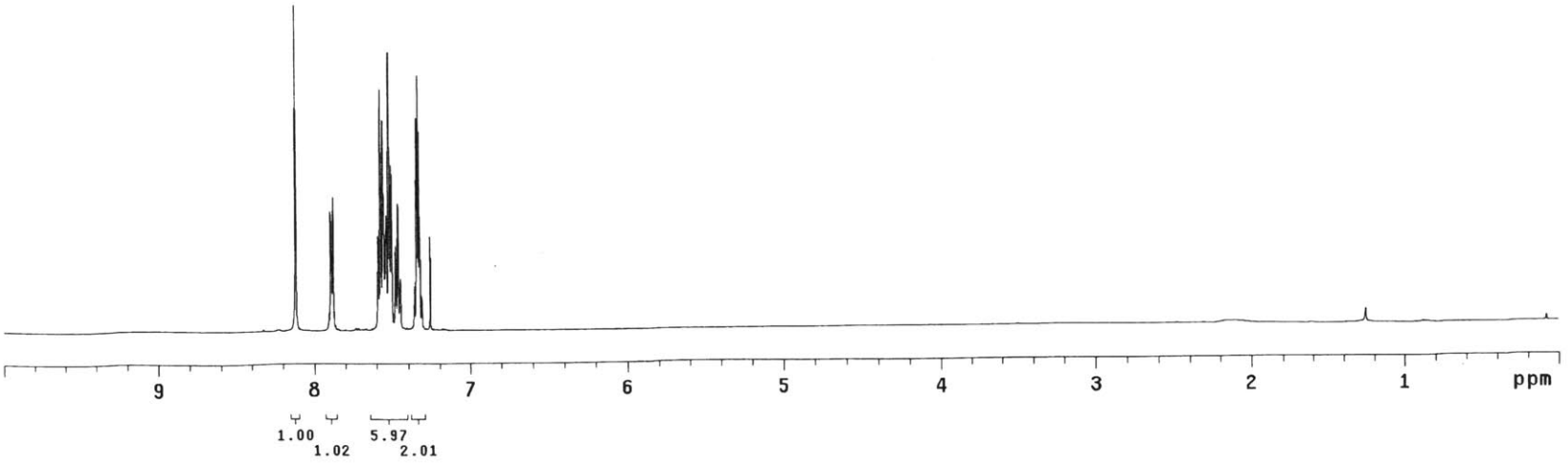


Table 15, entry 2



JC10065 1H CDCl3

exp10 PROTON

SAMPLE		PRESATURATION	
date	Apr 27 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/jwchoi/~	SPECIAL	
vnmrsys/data/JC100~		temp	not used
65_1H_CDCl3/PROTON~		gain	32
	02.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	2.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.950	rfl	4630.1
DECOUPLER		rfp	3627.9
dn	C13	rp	17.3
dof	0	lp	-64.2
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	97
dmf	32258	th	33
		ai cdc ph	

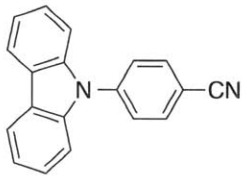
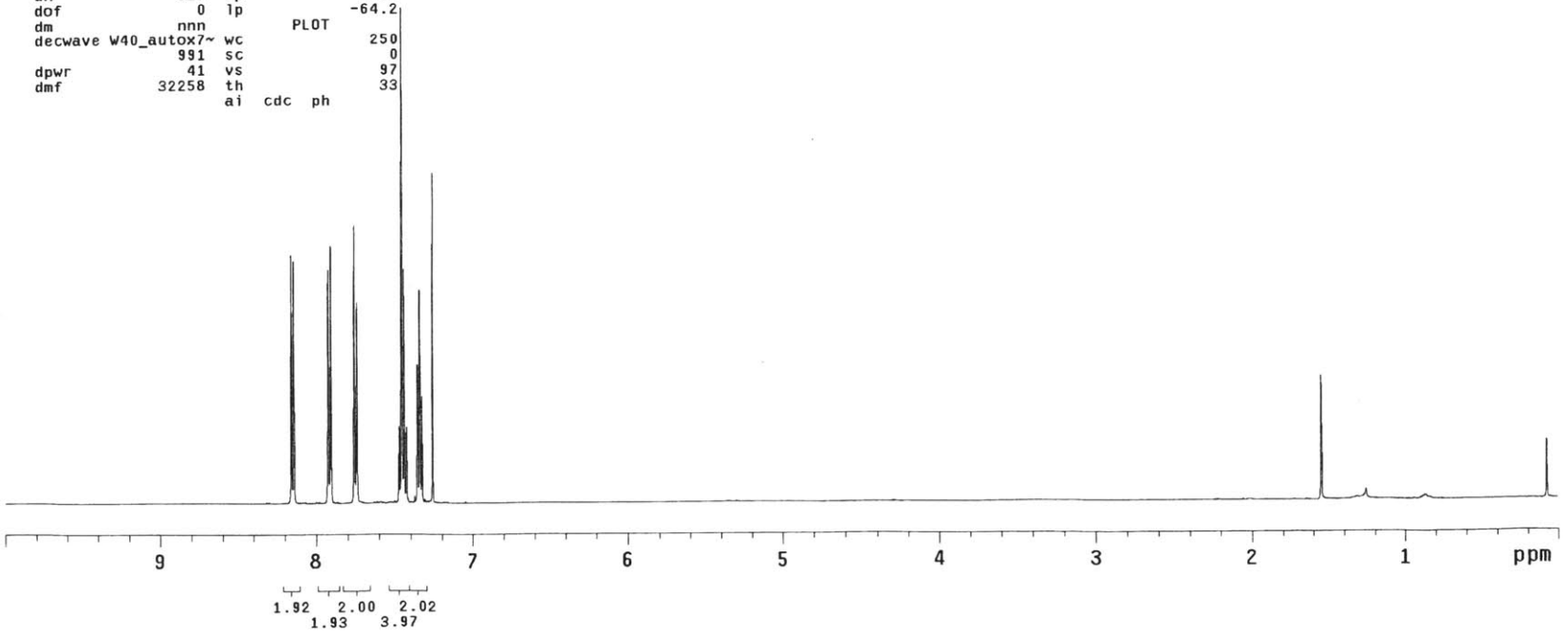


Table 15, entry 3



DZ-05-034-1-Purified

exp10 PROTON

SAMPLE		PRESATURATION	
date	Apr 19 2013	satmode	n
solvent	cdcl3	wet	n
file	/indy/dziegle~	SPECIAL	
r/vnmrsys/data/DZ-~		temp	not used
05-034-1-Purified/~		gain	32
	PROTON01.fid	spin	20
ACQUISITION		hst	0.008
sw	8000.0	pw90	9.900
at	3.000	alfa	10.000
np	48000	FLAGS	
fb	not used	il	n
bs	32	in	n
d1	1.000	dp	y
nt	16	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	0.20
tn	H1	fn	not used
sfrq	499.708	DISPLAY	
tof	499.7	sp	-0.1
tpwr	61	wp	4996.8
pw	4.950	rfl	4630.1
DECOUPLER		rfp	3627.9
dn	C13	rp	15.6
dof	0	lp	-72.5
dm	nnn	PLOT	
decwave	W40_autox7~	wc	250
	991	sc	0
dpwr	41	vs	100
dmf	32258	th	4
		ai cdc ph	

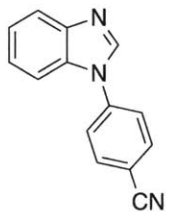
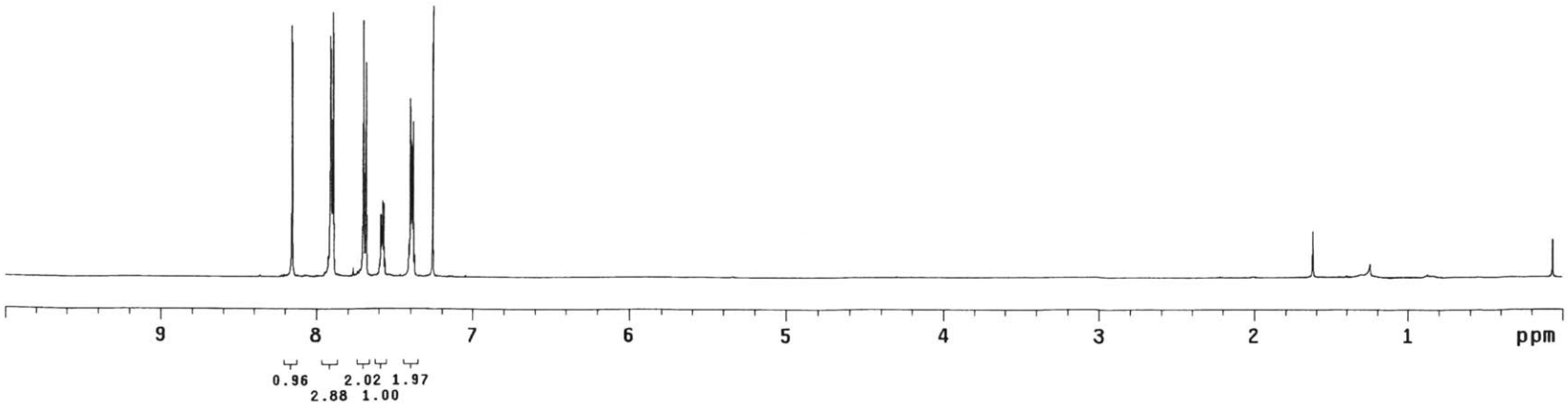


Table 15, entry 4



JUNWON CHOI

Department of Chemistry and Chemical Engineering, California Institute of Technology
1200 E. California Blvd, Chemistry, MC 101-20
Pasadena, CA 91125, USA

EDUCATION

2008 – 2014 **Massachusetts Institute of Technology**
Ph.D. in Organic Chemistry

2002 – 2008 **Seoul National University, Republic of Korea**
B.S. in Chemistry (*summa cum laude)*

RESEARCH EXPERIENCE

2012 – 2014 **Graduate Research Assistant**
California Institute of Technology
Advisor: Prof. Gregory C. Fu
Developed transition-metal-catalyzed C–C and C–N bond formations

2008 – 2012 **Graduate Research Assistant**
Massachusetts Institute of Technology
Advisor: Prof. Gregory C. Fu
Developed nickel-catalyzed asymmetric cross-coupling reactions of secondary alkyl electrophiles

2006 – 2008 **Undergraduate Research Assistant**
Seoul National University
Advisor: Prof. Jin-Soo Kim
Synthesized zinc-finger nucleases to generate a *FX* knockout cell line producing non-fucosylated antibodies

TEACHING EXPERIENCE

2013 – 2014 **Research Mentor:** Summer Undergraduate Research Fellowship (SURF) Program, Senior Thesis

2011 **Completion of the Graduate Student Teaching Certificate Program**

2009 **Teaching Assistant:** Laboratory Chemistry
Introduced experimental chemistry for non-major students

2008 **Teaching Assistant:** Introduction to Experimental Chemistry & Organic Structure Determination
Demonstrated basic experimental techniques and guided students' experimental procedures

AWARDS

2010 Outstanding Teaching Award from Department of Chemistry, MIT

2008 – 2013 The Kwanjeong Educational Foundation Award

2008 Valedictorian of College of Natural Sciences, Seoul National University

2007 Seoul National University–Chemistry Alumni Association Award for Academic Excellence

2005 The Lotte Foundation Scholarship

2004 Seoul National University–Chemistry Alumni Association Award for Academic Excellence

2004 Seoul National University–College of Natural Sciences Award for Academic Excellence

2004 – 2008 The Korea Foundation for Advanced Studies Scholarship

2002 – 2008 Honor Scholarship from Seoul National University for Academic Excellence

PUBLICATIONS

3. **Choi, J.**; Martín-Gago, P.; Fu, G. C. "Stereoconvergent Arylations and Alkenylations of Unactivated Alkyl Electrophiles: The Catalytic Enantioselective Synthesis of Secondary Sulfonamides and Sulfones" *J. Am. Chem. Soc.* **2014**, DOI: 10.1021/ja506885s.
2. Ziegler, D. T.; **Choi, J.**; Muñoz-Molina, J. M.; Bissember, A. C.; Peters, J. C.; Fu, G. C. "A Versatile Approach to Ullmann C–N Couplings at Room Temperature: New Families of Nucleophiles for Photoinduced, Copper-Catalyzed Processes" *J. Am. Chem. Soc.* **2013**, *135*, 13107–13112.
1. **Choi, J.**; Fu, G. C. "Catalytic Asymmetric Synthesis of Secondary Nitriles via Stereoconvergent Negishi Arylations and Alkenylations of Racemic α-Bromonitriles" *J. Am. Chem. Soc.* **2012**, *134*, 9102–9105.

PRESENTATIONS

3. **Choi, J.**; Martín-Gago, P.; Fu, G. C. "Catalytic Asymmetric Synthesis of Secondary Sulfonamides and Sulfones via Stereoconvergent Arylations and Alkenylations of Racemic α-Bromosulfonamides and α-Bromosulfones" 4th annual CCE Student Seminar Day, Pasadena, CA, **2013** (Poster presentation).
2. **Choi, J.**; Martín-Gago, P.; Fu, G. C. "Catalytic Enantioselective Carbon–Carbon Bond Formations of α-Bromosulfonamides and α-Bromosulfones via Negishi Arylations" 43rd National Organic Chemistry Symposium, Seattle, WA, **2013** (Poster presentation).
3. **Choi, J.**; Fu, G. C. "Nickel-Catalyzed Asymmetric Negishi Cross-Couplings of α-Bromonitriles with Diarylzinc Reagents" 242nd ACS National Meeting, Denver, CO, **2011** (Oral presentation).