Supporting Information

Regioselective and Stereospecific Copper-Catalyzed Aminoboration of Styrenes with Bis(pinacolato)diboron and *O*-Benzoyl-*N*,*N*-dialkylhydroxylamines

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Contents

Instrumentation and Chemicals

^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded at 400 MHz, 100 MHz, and 373 MHz respectively, for $CDCl_3$ solutions. MS data were obtained by EI, CI, or FAB. GC analysis was carried out using a silicon OV-17 column (i. d. 2.6 mm x 1.5 m) or a CBP-1 capillary column (i. d. 0.5 mm x 25 m). TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (60 N, spherical neutral, Kanto Chemical) was used for column chromatography. Gel permeation chromatography (GPC) was performed by LC-6AD (SHIMADZU, two in-line Shodex, $CHCl_3$, 3.5 mL/min, UV detector).

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. CuCl available from Wako Pure Chemical Co. was washed sequentially with 1M aq. HCl, EtOH, and Et_2O three times at each steps and dried under high vacuum for 6 h before use. Dppbz was also obtained from Wako Pure Chemical Co. (*S*,*S*)-Me-Duphos and LiO-*t*-Bu were purchased from Aldrich. *O*-Benzoyl-*N*,*N*-diethylhydroxylamine (**2a**) was obtained by the reaction of *N*,*N*-diethylhydroxylamine with benzoyl chloride, while other *O*-benzoyl-*N*,*N*-dialkylhydroxylamines **2b–i** were synthesized through the nucleophilic substitution of the corresponding amines with benzoyl

peroxide.[1] Styrenes **1c** and **1k** were prepared according to the literature.[2] All reactions were carried out under nitrogen atmosphere.

[1] (a) Berman, A. M.; Johnson, J. S. *J. Am. Chem. Soc.* **2004**, *126*, 5680. (b) Berman, A. M.; Johnson, *J. Org. Chem.* **2006**, *71*, 219.
[2] Kabalka, G. W.; Tejedor, D.; Li, N.-S.; Malladi, R. R.; Trotman, S. *Tetrahedron* **1998**, *54*, 15525.

Experimental Procedures

1. General procedure

A typical experiment procedure for copper-catalyzed aminoboration of *trans*-*β*-methylstyrene ((*E*)-**1a**) with bis(pinacolato)diboron and *O*-benzoyl-*N*,*N*-diethylhydroxylamine (**2a**) (Table 1, entry 1): CuCl (2.5 mg, 0.025 mmol), 1,2-bis(diphenylphosphino)benzene (dppbz, 11 mg, 0.025 mmol), and LiO-*t*-Bu (60 mg, 0.75 mmol) were placed in a 20 mL two-necked reaction flask, which was filled with nitrogen by using the standard Schlenk technique. THF (0.50 mL) was then added to the flask, and the suspension was stirred for 15 min at ambient temperature. Finally, a solution of *trans*-*β*-methylstyrene ((*E*)-**1a**, 30 mg, 0.25 mmol), bis(pinacolato)diboron (95 mg, 0.375 mmol), and *O*-benzoyl-*N*,*N*-diethylhydroxylamine (**2a**, 73 mg, 0.375 mmol) in THF (1.0 mL) was added dropwise. The solution was stirred at ambient temperature for additional 4 h. The resulting mixture was quenched with water. The mixture was extracted with ethyl acetate, and the combined organic layer was dried over sodium sulfate. Concentration under reduced pressure afforded the crude product. 1-Methylnaphthalene (ca. 25 mg) was then added as an internal standard, and the resulting mixture was analyzed by ^{1}H NMR in $CDCl_3$ solution. The yield of (1*S**,2*R**)-*N*,*N*-diethyl-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-amine (**3aa**) was estimated to be 81% by comparison with integrated intensity of 1-methylnaphthalene. After the above ^{1}H NMR analysis, the volatiles were evaporated, and the residue was purified by gel permeation chromatography (GPC) to give (1*S**,2*R**)-*N*,*N*-diethyl-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-amine (**3aa**, 52 mg, 0.17 mmol) in 66% yield.

2. Sequential aminoboration/conversion into borate salt (Scheme 3)

Synthesis of **3aa-BF$_3$**: CuCl (2.5 mg, 0.025 mmol), 1,2-bis(diphenylphosphino)benzene (dppbz, 11 mg, 0.025 mmol), and LiO-*t*-Bu (60 mg, 0.75 mmol) were placed in a 20 mL two-necked reaction flask, which was filled with nitrogen by using the standard Schlenk technique. THF (0.50 mL) was then added to the flask, and the suspension was stirred for 15 min at ambient temperature. Finally, a solution of *trans*-*β*-methylstyrene ((*E*)-**1a**, 30 mg, 0.25 mmol), bis(pinacolato)diboron (95 mg, 0.375 mmol), and *O*-benzoyl-*N*,*N*-diethylhydroxylamine (**2a**, 73 mg, 0.375 mmol) in THF (1.0 mL) was added dropwise. The solution was stirred at ambient temperature for additional 4 h. The resulting mixture was quenched with water. The mixture was extracted with ethyl acetate, and the combined organic layer was dried over sodium sulfate and concentrated in vacuo to give the crude

aminoborated product. The crude aminoborated product was dissolved in THF/H_2O (1.0/0.2 mL) and KHF_2 (156 mg, 2.0 mmol) was added. After the resulting mixture was stirred at ambient temperature for 2 h, the mixture was concentrated in vacuo. The dried solids were triturated with acetone and filtered to remove inorganic salts. The resulting filtrate was concentrated, and the residual solids was collected and rinsed with Et_2O to give (1*S**,2*R**)-1-*N*,*N*-diethylammonio-1-phenyl-2-(trifluoroboryl)propane (**3aa-BF$_3$**, 54 mg, 0.21 mmol) in 83% yield.

3. Sequential aminoboration/oxidation to 1,2-aminoalcohol (Scheme 4)

Synthesis of **4aa**: CuCl (2.5 mg, 0.025 mmol), 1,2-bis(diphenylphosphino)benzene (dppbz, 11 mg, 0.025 mmol), and LiO-*t*-Bu (60 mg, 0.75 mmol) were placed in a 20 mL two-necked reaction flask, which was filled with nitrogen by using the standard Schlenk technique. THF (0.50 mL) was then added to the flask, and the suspension was stirred for 15 min at ambient temperature. Finally, a solution of *trans*-*β*-methylstyrene ((*E*)-**1a**, 30 mg, 0.25 mmol), bis(pinacolato)diboron (95 mg, 0.375 mmol), and *O*-benzoyl-*N*,*N*-diethylhydroxylamine (**2a**, 73 mg, 0.375 mmol) in THF (1.0 mL) was added dropwise. The solution was stirred at ambient temperature for additional 4 h. The resulting mixture was quenched with water. The mixture was extracted with ethyl acetate, and the combined organic layer was dried over sodium sulfate and concentrated in vacuo to give the crude aminoborated product. To the crude aminoborated product in THF (1.5 mL) and H_2O (1.5 mL) was added $NaBO_3 \cdot OH_2$ (349 mg, 3.5 mmol). The resulting mixture was stirred at ambient temperature for 5 h. The resulting mixture was quenched with sat. $Na_2S_2O_3$ aq. The mixture was extracted with Et_2O, and the combined organic layer was dried over sodium sulfate. An aqueous solution of 4 M HCl (60 mL) was added to the organic layer. The aqueous layer was washed four times with Et_2O, neutralized with 6 M NaOH aq. (40 mL), and then extracted four times with Et_2O. The combined organic layer was dried over sodium sulfate and concentrated in vacuo to give (1*R**,2*R**)-1-(*N*,*N*-diethylamino)-1-phenylpropan-2-ol (**4aa**, 28 mg, 0.13 mmol) in 54% yield.

4. Sequential aminoboration/amination to 1,2-diamine (Scheme 4)

Synthesis of **5aa**: CuCl (2.5 mg, 0.025 mmol), 1,2-bis(diphenylphosphino)benzene (dppbz, 11 mg, 0.025 mmol), and LiO-*t*-Bu (60 mg, 0.75 mmol) were placed in a 20 mL two-necked reaction flask, which was filled with nitrogen by using the standard Schlenk technique. THF (0.50 mL) was then added to the flask, and the suspension was stirred for 15 min at ambient temperature. Finally, a

solution of *trans*-*β*-methylstyrene ((*E*)-**1a**, 30 mg, 0.25 mmol), bis(pinacolato)diboron (95 mg, 0.375 mmol), and *O*-benzoyl-*N*,*N*-diethylhydroxylamine (**2a**, 73 mg, 0.375 mmol) in THF (1.0 mL) was added dropwise. The solution was stirred at ambient temperature for additional 4 h. The resulting mixture was quenched with water. The mixture was extracted with ethyl acetate, the combined organic layer was dried over sodium sulfate, and concentrated in vacuo to give the crude aminoborated product. *O*-Methylhydroxylamine (2.70 M THF solution, 0.56 mL, 1.50 mmol) in THF (2.0 mL) were placed in an another 20 mL two-necked reaction flask, which was filled with nitrogen by using the standard Schlenk technique. *n*-BuLi (1.6 M hexane solution, 0.91 mL, 1.50 mmol) was added to the flask at -78 ^{o}C, and the suspension was stirred for 30 min at -78 ^{o}C. A THF (1.0 mL) solution of the crude aminoborated product prepared in advance was then added dropwise to the solution, and the solution was stirred at 60 ^{o}C for additional 24 h. The resulting mixture was allowed to cool to room temperature, and Boc_2O (0.34 mL, 1.50 mmol) was then added via a syringe. After being stirred at room temperature for 2 h, the resulting mixture was quenched with water. The mixture was extracted with ethyl acetate, and the combined organic layer was dried over sodium sulfate. Concentration in vacuo and purification by silica gel column chromatography with *n*-hexane/ethyl acetate (10:1, v/v) as an eluent gave *tert*-butyl [(1*R**,2*R**)-1-(*N*,*N*-diethylamino)-1-phenylpropan-2-yl]carbamate (**5aa**, 41 mg, 0.13 mmol) in 52% yield.

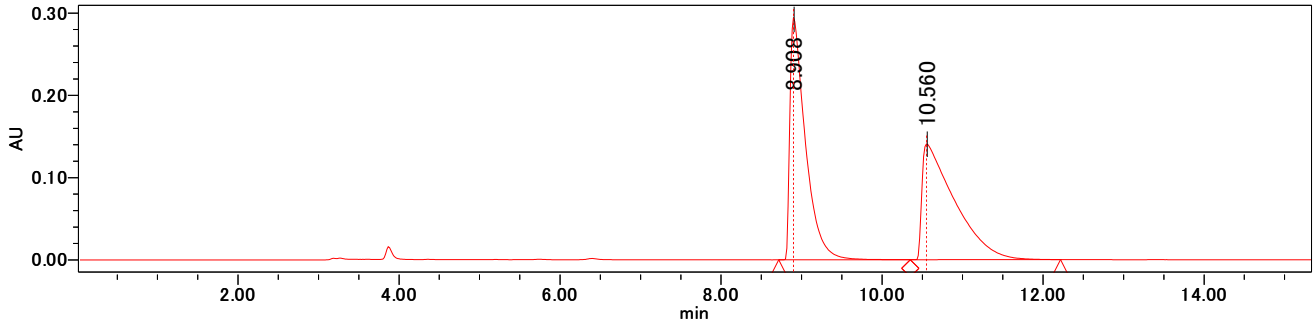
5. Enantioselective aminoboration (Scheme 5)

Synthesis of (1*S*,2*S*)-**4aa**: CuCl (2.5 mg, 0.025 mmol), (-)-1,2-bis[(2*S*,5*S*)-2,5-dimethylphospholano]benzene ((*S*,*S*)-Me-Duphos, 7.7 mg, 0.025 mmol), and LiO-*t*-Bu (60 mg, 0.75 mmol) were placed in a 20 mL two-necked reaction flask, which was filled with nitrogen by using the standard Schlenk technique. THF (0.50 mL) was then added to the flask, and the suspension was stirred for 15 min at ambient temperature. Finally, a solution of *trans*-*β*-methylstyrene ((*E*)-**1a**, 30 mg, 0.25 mmol), bis(pinacolato)diboron (95 mg, 0.375 mmol), and *O*-benzoyl-*N*,*N*-diethylhydroxylamine (**2a**, 73 mg, 0.375 mmol) in THF (1.0 mL) was added dropwise. The solution was stirred at ambient temperature for additional 4 h. The resulting mixture was quenched with water. The mixture was extracted with ethyl acetate, and the combined organic layer was dried over sodium sulfate. Concentration under reduced pressure afforded the crude product. 1-Methylnaphthalene (ca. 25 mg) was then added as an internal standard, and the resulting mixture was analyzed by ^{1}H NMR in $CDCl_3$ solution. The yield of (1*S*,2*R*)-*N*,*N*-diethyl-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-amine (1*S*,

2*R*)-**3aa**) was estimated to be 83% by comparison with integrated intensity of 1-methylnaphthalene. After the above ^{1}H NMR analysis, the volatiles were evaporated. The enantiomer ratio was determined after the conversion of the residue into the corresponding aminoalcohol under identical conditions in page S4.

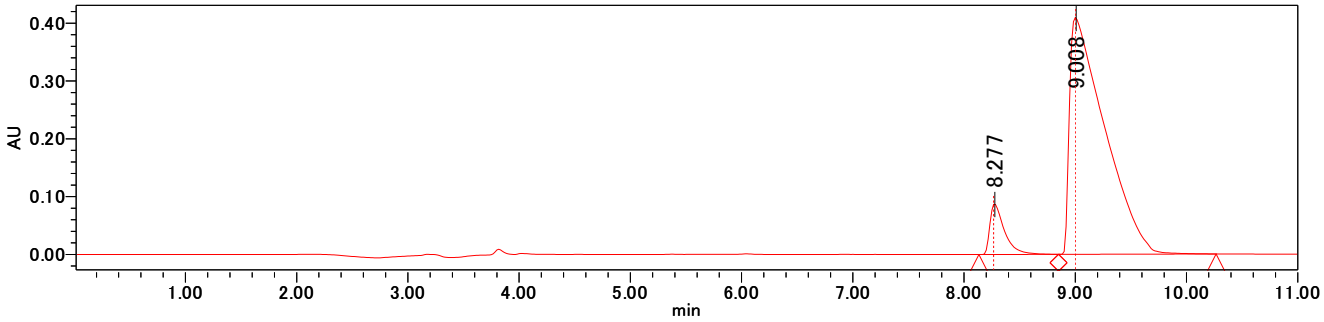
4aa (74% two-step yield): The enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic material (CHIRALCEL OD-3 column, 99.8/0.2 *n*-hexane/2-propanol, 1.0 mL/min, major isomer: t_R = 9.0 min, minor isomer: t_R = 8.3 min, UV detection at 231.9 nm, 30 °C.)

rac-**4aa**



Peak #	Ret. Time	Area	Area %
1	8.908	3947945	49.98
2	10.56	3951598	50.02

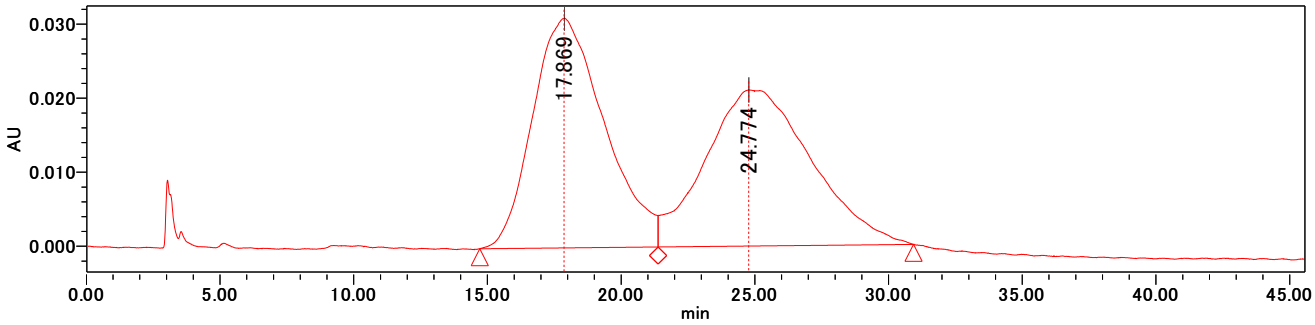
(1*S*,2*S*)-**4aa**



Peak #	Ret. Time	Area	Area %
1	8.277	795692	8.14
2	9.008	8976570	91.86

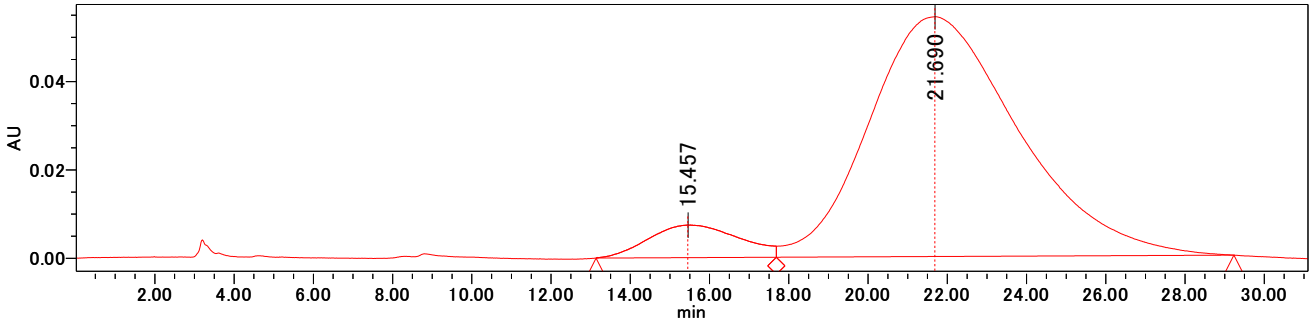
4ab (27% yield in the oxidation step, not optimized): The enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic material (CHIRALCEL OJ column, 99.9/0.1 *n*-hexane/2-propanol, 1.0 mL/min, major isomer: t_R = 21.7 min, minor isomer: t_R = 15.5 min, UV detection at 214.6 nm, 30 °C.)

rac-**4ab**



Peak #	Ret. Time	Area	Area %
1	17.869	5803167	49.93
2	24.774	5818437	50.07

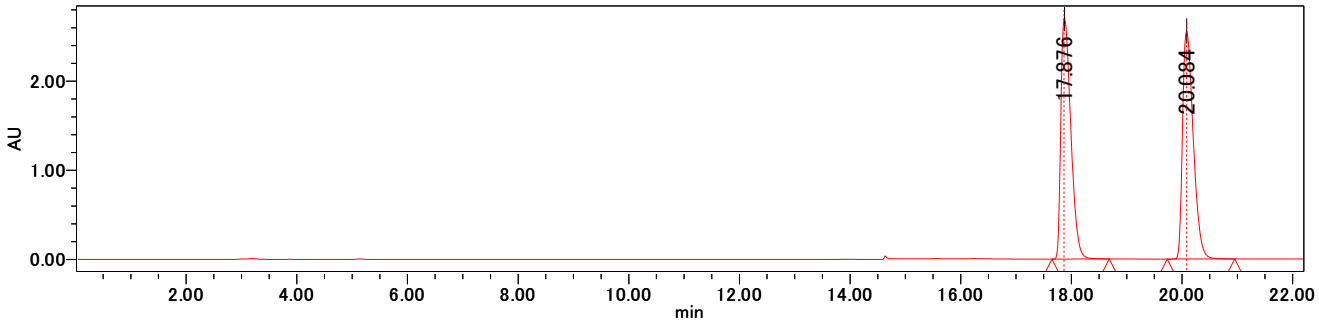
(1*S*,2*S*)-**4ab**



Peak #	Ret. Time	Area	Area %
1	15.457	1171454	7.61
2	21.69	14214121	92.39

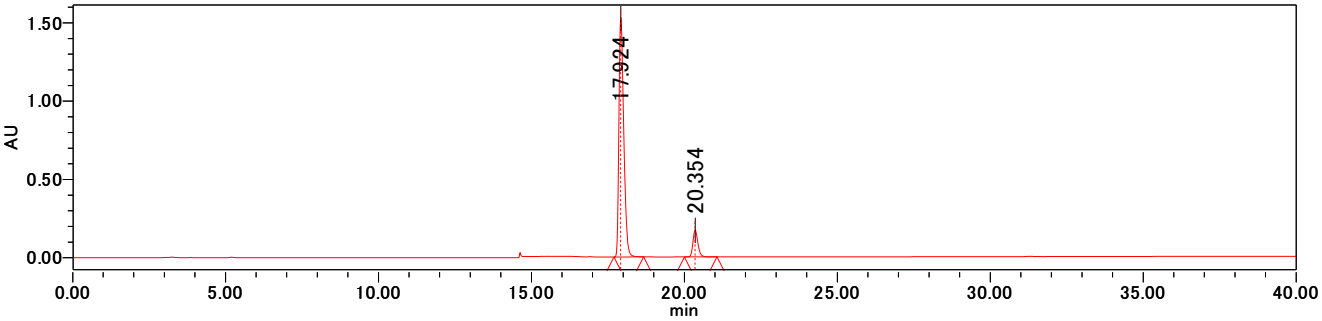
4bb (29% yield in the oxidation step, not optimized): The enantiomeric ratio was determined by HPLC analysis in comparison with authentic racemic material (CHIRALCEL OD-3 column, 99.9/0.1 *n*-hexane/2-propanol, 1.0 mL/min, major isomer: t_R = 17.9 min, minor isomer: t_R = 20.4 min, UV detection at 220.0 nm, 30 °C.)

rac-**4bb**



Peak #	Ret. Time	Area	Area %
1	17.876	33804181	49.69
2	20.084	34220689	50.31

(1*S*,2*S*)-**4bb**



Peak #	Ret. Time	Area	Area %
1	17.924	16708513	89.76
2	20.354	1906053	10.24

Stereochemical Assignment

1. Assignment of relative stereochemistry

Assignment of *syn*-**3aa** (Table 1, entry 1): The aminoboration of *trans*-*b*-methylstyrene ((*E*)-**1a**) with bis(pinacolato)diboron and *O*-benzoyl-*N*,*N*-diethylhydroxylamine (**2a**) was carried out according to the general procedure, and the crude material obtained was oxidized as follows. To the crude aminoborated product in THF (1.5 mL) and H_2O (1.5 mL) was added $NaBO_3 \cdot OH_2$ (349 mg, 3.5 mmol). The resulting mixture was stirred at ambient temperature for 5 h. The resulting mixture was quenched with sat. $Na_2S_2O_3$ aq. The mixture was extracted with Et_2O, the combined organic layer was dried over sodium sulfate. An aqueous solution of 4 M HCl (60 mL) was added to the organic layer. The aqueous layer was washed four times with Et_2O, neutralized with 6 M NaOH aq. (40 mL), and then extracted four times with Et_2O. The combined organic layer was dried over sodium sulfate, and concentrated in vacuo to give (1*R**,2*R**)-1-(*N*,*N*-diethylamino)-1-phenylpropan-2-ol (**4aa**, 28 mg, 0.13 mmol, *syn*/*anti* = >99:1) in 54% yield as an analytically pure form. The relative stereochemistry of **4aa** was confirmed by the literature.[3]

The stereochemistry of other aminoborated products from *E*-alkenes is tentatively assigned by the result of **3aa**.

Assignment of *anti*-**3ab** (Scheme 2): The aminoboration of *cis*-*b*-methylstyrene ((*Z*)-**1a**) with bis(pinacolato)diboron and *O*-benzoyl-*N*,*N*-benzylhydroxylamine (**2b**) was carried out according to the general procedure to form *anti*-**3ab** in 52% yield. The isolated *anti*-**3ab** was oxidized under the same conditions as those for *syn*-**3aa**. The crude material was purified by silica gel column chromatography with *n*-hexane/ethyl acetate (3:1, v/v) as an eluent to give (1*R**,2*R**)-1-(*N*,*N*-dibenzylamino)-1-phenylpropan-2-ol (*anti*-**4ab**, 52 mg, 0.16 mmol, *syn*/*anti* = <1:99) in 63% yield. The relative stereochemistry of *anti*-**4ab** was confirmed by the literature.[4]

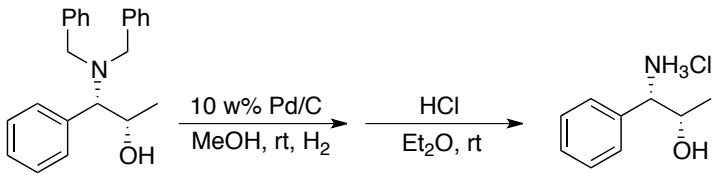
Assignment of *cis*-**3me** (Scheme 2): CuCl (2.5 mg, 0.025 mmol), 1,2-bis(diphenylphosphino)benzene (dppbz, 11 mg, 0.025 mmol), and NaO-*t*-Bu (48 mg, 0.50 mmol) were placed in a 20 mL two-necked reaction flask, which was filled with nitrogen by using the standard Schlenk technique. THF (0.50 mL) was then added to the flask, and the suspension was stirred for 15

[3] Xie, J.-H.; Liu, S.; Kong, W.-L.; Bai, W.-J.; Wang, X.-C.; Wang, L.-X.; Zhou, Q.-L. *J. Am. Chem. Soc.* **2009**, *131*, 4222.

[4] Schwerdtfeger, J.; Kolczewski, S.; Weber, B.; Fröhlich, R.; Hoppe, D. *Snthesis* **1999**, *9*, 1573.

min at ambient temperature. Finally, a solution of indene (**1m**, 29 mg, 0.25 mmol), bis(pinacolato)diboron (76 mg, 0.30 mmol), 1-piperidinyl benzoate (**2e**, 62 mg, 0.30 mmol), and 1-methylnaphthalene (ca. 25 mg, internal standard) in THF (1.0 mL) was added dropwise. The solution was stirred at ambient temperature for additional 4 h. The resulting mixture was quenched with water. The mixture was extracted with ethyl acetate, the combined organic layer was dried over sodium sulfate, and concentrated in vacuo to give the crude aminoborated product. The crude material was oxidized under the same conditions as those for *syn*-**3aa** to give (1*R**,2*S**)-1-(piperidin-1-yl)-2,3-dihydroinden-2-ol (**4me**, 24 mg, 0.11 mmol, *cis*/*trans* = >99:1) in 45% overall yield. The relative stereochemistry of **4me** was confirmed by the literature.[5]

2. Determination of the absolute configuration



(1*S*,2*S*)-**4ab** (1*S*,2*S*)-**6**

10 wt% Pd/C (16 mg, 0.015 mmol), (1*S*,2*S*)-**4ab** (50 mg, 0.15 mmol), and MeOH (1.0 mL) were placed in a 20 mL two-necked reaction flask, and the flask was flushed with hydrogen. The suspension was stirred at ambient temperature for 23 h. The resulting mixture was filtered through a syringe filter (Whatman, Puradisc™ 13mm), and the filtrate was concentrated. To the residue 1 M HCl (5 mL, Et_2O solution) was added, and the solution was stirred at ambient temperature for 2 h. The mixture was concentrated in vacuo to give (1*S*,2*S*)-1-amino-1-phenylpropan-2-ol hydrochloride ((1*S*,2*S*)-**6**, 27 mg, 0.14 mmol) in 96% yield. The absolute configuration of (1*S*,2*S*)-**6** was determined by comparison of the optical rotation with the reported value.[6]

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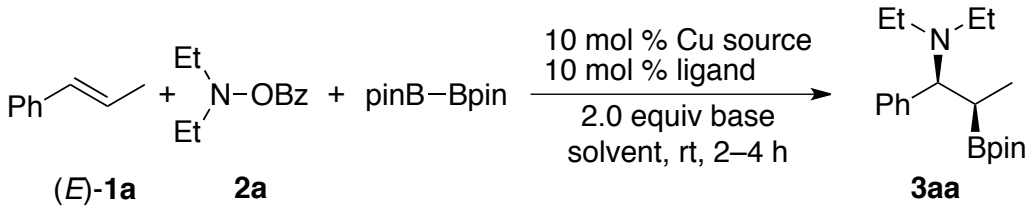
[5] Soh, J. Y.-T.; Tan, C.-H. *J. Am. Chem. Soc.* **2009**, *131*, 6904.

[6] Yuste, F.; Ortiz, B.; Carrasco, A.; Peralta, M.; Quintero, L.; Sánchez-Obregón, R.; Walls, F.; Ruano, J. L. G. *Tetrahedron: Asymmetry* **2000**, *11*, 3079.

Detailed Optimization Studies

Table S1. Optimization Studies for Copper-Catalyzed Aminoboration of *trans*-*β*-Methylstyrene ((*E*)-**1a**) with Bis(pinacolato)diboron and *O*-Benzoyl-*N*,*N*-diethylhydroxylamine (**2a**).[a]

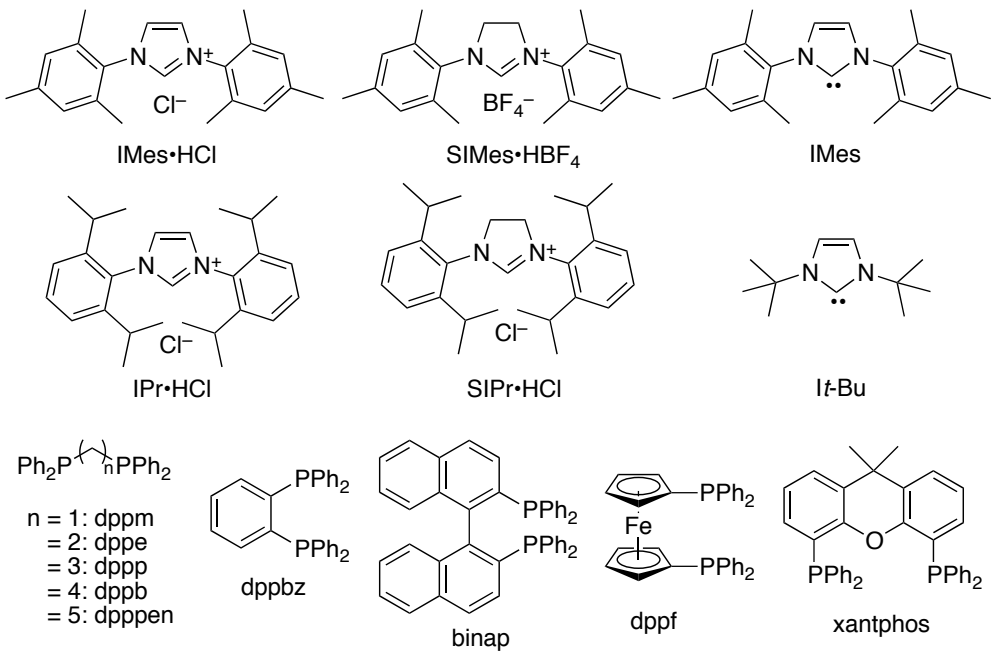


(*E*)-**1a** **2a** **3aa**

entry	Cu source/ligand	base	solvent	yield [%][b]
1	CuCl/IMes•HCl	LiO-*t*-Bu	THF	27
2	CuCl/IPr•HCl	LiO-*t*-Bu	THF	0
3	CuCl/SIMes•HBF_4	LiO-*t*-Bu	THF	25
4	CuCl/SIPr•HCl	LiO-*t*-Bu	THF	0
5	CuCl/IMes	LiO-*t*-Bu	THF	43
6	CuCl/I*t*-Bu	LiO-*t*-Bu	THF	0
7	***CuCl/dppbz***	***LiO-t-Bu***	***THF***	***78***
8	CuCl/dppm	LiO-*t*-Bu	THF	0
9	CuCl/dppe	LiO-*t*-Bu	THF	44
10	CuCl/dppp	LiO-*t*-Bu	THF	28
11	CuCl/dppb	LiO-*t*-Bu	THF	trace
12	CuCl/dpppen	LiO-*t*-Bu	THF	trace
13	CuCl/binap	LiO-*t*-Bu	THF	trace
14	CuCl/dppf	LiO-*t*-Bu	THF	49
15	CuCl/xantphos	LiO-*t*-Bu	THF	19
16	CuCl/$2PPh_3$	LiO-*t*-Bu	THF	0
17	CuCl/dppbz	LiO-*t*-Bu	1,4-dioxane	0
18	CuCl/dppbz	LiO-*t*-Bu	DME	53

19	CuCl/dppbz	LiO-*t*-Bu	CPME	35
20	***CuCl/dppbz***	***NaO-t-Bu***	***THF***	***82***
21	CuCl/dppbz	NaO-*t*-Bu	toluene	34
22	CuCl/dppbz	KO-*t*-Bu	THF	36
23	CuCl/dppbz	NaOMe	THF	49
24	$CuCl_2$/dppbz	LiO-*t*-Bu	THF	67
25	CuI/dppbz	LiO-*t*-Bu	THF	33
26	CuBr•SMe_2/dppbz	LiO-*t*-Bu	THF	75
27	CuOAc/dppbz	LiO-*t*-Bu	THF	trace
28	$Cu(OAc)_2$/dppbz	LiO-*t*-Bu	THF	61
29	$Cu(OTf)_2$/dppbz	LiO-*t*-Bu	THF	41
30[c]	***CuCl/dppbz***	***LiO-t-Bu***	***THF***	***81 (66)***
31[c]	CuCl/dppbz	NaO-*t*-Bu	THF	57
32[c]	none/dppbz	LiO-*t*-Bu	THF	0
33[c]	CuCl/none	LiO-*t*-Bu	THF	0
34[c]	none/none	LiO-*t*-Bu	THF	0

[a] Reaction conditions: Cu source (0.025 mmol), ligand (0.025 mmol), (*E*)-**1a** (0.25 mmol), **2a** (0.30 mmol), bis(pinacolato)diboron (0.30 mmol), base (0.50 mmol), solvent (1.5 mL), N_2, rt, 2–4 h. [b] Yield estimated by ^{1}H NMR. Yield of isolated product given in parenthesis. [c] With 0.375 mmol of **2a** and bis(pinacolato)diboron and 0.75 mmol of base.



We chose *trans*-β-methylstyrene ((*E*)-**1a**) and *O*-benzoyl-*N*,*N*-diethylhydroxylamine (**2a**) as model substrates and first investigated ligand effects in the presence of a CuCl salt and a LiO-*t*-Bu base in THF (Table S1, entries 1–16). Some mesityl-substituted NHCs formed a detectable amount of the desired aminoborated product **3aa** (entries 1, 3, and 5), while more bulky NHCs, IPr and I*t*-Bu showed no activity (entries 2, 4, and 6). Subsequent survey of phosphorous ligands (entries 7–14) revealed that bidentate biphosphines bearing a relatively small bite angle were more effective. In particular, 1,2-bis(diphenylphosphino)benzene (dppbz) was promising (entry 7). On the other hand, a monodentate ligand, PPh_3, resulted in no formation of **3aa** (entry 15). Solvent screening showed that other ethereal solvents were also tolerated, but THF was still superior (entries 17–19). As an alternative base, NaO-*t*-Bu gave a comparable result (entry 20), whereas other alkoxide bases were inferior (entries 22 and 23). Evaluation of copper salts identified CuCl to be the best catalyst precursor (entries 24–29). Finally, an increase in the amount of **2a**, bis(pinacolato)diboron, and LiO-*t*-Bu improved the yield to 86% (entry 30), while no positive effect was observed in the case of NaO-*t*-Bu (entry 31). On the basis of above studies, we determined conditions indicated of entries 20 and 30 to be optimal. Additionally notable is that in all cases *syn*-isomer was obtained exclusively. On the other hand, in the absence of CuCl, dppbz, or CuCl/dppbz, the aminoborated product was not detected at all (entries 32–34).

Complete Citations in References 2 and 10

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Characterization Data for Products

^{1}H and ^{13}C NMR spectra for all compounds are attached in the last part.

(1*S,2*R**)-*N*,*N*-Diethyl-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-amine (3aa)** oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.73 (d, *J* = 7.3 Hz, 3H), 1.06 (t, *J* = 7.3 Hz, 6H), 1.29 (s, 12H), 1.87-1.97 (m, 3H), 2.67 (qd, *J* = 12.8, 7.3 Hz, 2H), 3.78 (d, *J* = 12.4 Hz, 1H), 7.15 (d, *J* = 7.3 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.30 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.04, 13.85, 25.04, 25.25, 43.61, 66.66, 82.93, 126.86, 127.84, 129.42, 137.30; HRMS (CI) m/z ($[M+H]^+$) calcd for $C_{19}H_{33}BNO_2$: 318.2604, found: 318.2600.

(1*S,2*R**)-*N*,*N*-Dibenzyl-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-amine (*syn*-3ab)** m.p. 144.0-145.0 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.66 (d, *J* = 7.3 Hz, 3H), 1.36 (s, 6H), 1.37 (s, 6H), 2.10 (qd, *J* = 12.4, 7.3 Hz, 1H), 2.94 (d, *J* = 13.7 Hz, 2H), 3.85 (d, *J* = 12.4 Hz, 1H), 3.95 (d, *J* = 13.7 Hz, 2H), 7.14 (d, *J* = 7.3 Hz, 2H), 7.18-7.23 (m, 2H), 7.25-7.31 (m, 5H), 7.38 (t, *J* = 7.3 Hz, 2H), 7.42 (d, *J* = 7.3 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.09, 25.36, 25.51, 54.37, 65.80, 83.24, 126.79, 127.10, 127.96, 128.08, 129.38, 129.79, 136.46, 140.14; HRMS (CI) m/z ($[M+H]^+$) calcd for $C_{29}H_{37}BNO_2$: 442.2917, found: 442.2913.

(1*S,2*S**)-*N*,*N*-Dibenzyl-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-amine (*anti*-3ab)** m.p. 113.0-114.0 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.77 (s, 6H), 0.86 (s, 6H), 1.28 (d, *J* = 7.3 Hz, 3H), 2.03 (qd, *J* = 12.4, 7.3 Hz, 1H), 2.97 (d, *J* = 13.7 Hz, 2H), 3.66 (d, *J* = 12.4 Hz, 1H), 3.92 (d, *J* = 13.7 Hz, 2H), 7.13-7.35 (m, 11H), 7.42 (d, *J* = 7.3 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.62, 24.14, 24.39, 53.23, 64.56, 82.83, 126.81, 127.12, 127.77, 128.41, 129.03, 129.84, 138.15, 140.75; HRMS (CI) m/z ($[M+H]^+$) calcd for $C_{29}H_{37}BNO_2$: 442.2917, found: 442.2919.

(1*S,2*R**)-*N*-Benzyl-*N*-methyl-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-amine (3ac)** m.p. 65.0-66.5 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.77 (d, *J* = 7.3 Hz, 3H), 1.30 (s, 6H), 1.31 (s, 6H), 2.01 (qd, *J* = 12.4, 7.3 Hz, 1H), 2.05 (s, 3H), 3.07 (d, *J* = 12.4 Hz, 1H), 3.43 (d, *J* = 12.4 Hz, 1H), 3.77 (d, *J* = 12.4 Hz, 1H), 7.19-7.30 (m, 6H), 7.34-7.37 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.91, 24.99 (two signals are overlapped.), 37.83, 58.81, 71.76, 83.14, 126.81, 127.13, 127.94 (two signals are overlapped.), 129.54, 129.63, 136.54, 140.11; HRMS (CI) m/z ($[M+H]^+$) calcd for $C_{23}H_{33}BNO_2$: 366.2604, found: 366.2596.

***N*-Butyl-*N*-[(1*S**,2*R**)-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl]-4-pente n-1-amine (3ad)** oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.71 (d, *J* = 7.3 Hz, 3H), 0.90 (t, *J* = 7.3 Hz, 3H), 1.21-1.62 (m, 6H), 1.29 (s, 12H), 1.88-2.10 (m, 5H), 2.48-2.58 (m, 2H), 3.74 (d, *J* = 12.4 Hz, 1H), 4.93 (dd, *J* = 10.1, 1.8 Hz, 1H), 5.00 (dd, 16.9, 1.8 Hz, 1H), 5.83 (tdd, *J* = 16.9, 10.1, 6.4 Hz, 1H), 7.14 (d, *J* = 7.3 Hz, 2H), 7.21-7.33 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.28, 14.44, 21.07, 25.18, 25.20, 28.11, 31.13, 32.10, 50.28, 50.52, 67.48, 82.97, 114.33, 126.85, 127.83, 129.49, 137.40, 139.31; HRMS (EI) m/z (M^+) calcd for $C_{24}H_{40}BNO_2$: 385.3152, found: 385.3152.

4-[(1*S,2*R**)-1-Phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl]morpholine (3ag)** m.p. 59.0-60.0 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.75 (d, *J* = 7.3 Hz, 3H), 1.31 (s, 6H), 1.32 (s, 6H), 1.92 (qd, *J* = 11.9, 7.3 Hz, 1H), 2.27 (m, 2H), 2.51 (m, 2H), 3.55 (d, *J* = 11.9 Hz, 1H), 3.58-3.68 (m 4H), 7.13 (d, *J* = 7.3 Hz, 2H), 7.25 (t, *J* = 7.3 Hz, 1H), 7.33 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.56, 24.93, 25.36 (two signals are overlapped.), 67.37, 73.02, 83.07, 127.32, 127.98, 129.41, 135.95; HRMS (CI) m/z ($[M+H]^+$) calcd for $C_{19}H_{31}BNO_3$: 332.2397, found: 332.2398.

***tert*-Butyl 4-[(1*S**,2*R**)-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl] piperazine-1-carboxylate (3ah)** m.p. 142.0-143.0 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.74 (d, *J* = 7.3 Hz, 3H), 1.30 (s, 6H), 1.31 (s, 6H), 1.38 (s, 9H), 1.92 (qd, *J* = 12.2, 7.3 Hz, 1H), 2.19 (m, 2H), 2.46 (m, 2H), 3.34 (m, 4H), 3.60 (d, *J* = 12.2 Hz, 1H), 7.11 (d, *J* = 7.3 Hz, 2H), 7.25 (t, *J* = 7.3 Hz, 1H), 7.32 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.73, 24.92, 25.41, 28.56, 49.22, 73.00 (two signals are overlapped.), 79.54, 83.05, 127.33, 128.00, 129.33, 135.82, 154.82; HRMS (EI) m/z (M^+) calcd for $C_{24}H_{39}BN_2O_4$: 430.3003, found: 430.3007.

2-[(1*S,2*R**)-1-Phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl]-1,2,3,4-tetrahydr oisoquinoline (3ai)** m.p. 55.0-56.0 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 (d, *J* = 7.3 Hz, 3H), 1.13 (s, 12H), 2.06 (qd, *J* = 11.9, 7.3 Hz, 1H), 2.26-2.34 (m, 1H), 2.72-2.79 (m, 1H), 2.85-2.92 (m, 2H), 3.57 (d, *J* = 14.7 Hz, 1H), 3.68 (d, *J* = 14.7 Hz, 1H), 3.76 (d, *J* = 11.9 Hz, 1H), 6.95-7.04 (m, 4H), 7.23-7.26 (m, 3H), 7.33 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.61, 24.62, 25.05, 29.77, 46.40, 52.70, 72.50, 82.98, 125.32, 125.68, 126.61, 127.27, 127.99, 128.51, 129.39, 134.82, 136.03, 136.18; HRMS (CI) m/z ($[M+H]^+$) calcd for $C_{24}H_{33}BNO_2$: 378.2604, found: 378.2603.

(1*S,2*R**)-*N*,*N*-Dibenzyl-1-(4-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-amine (3bb)** m.p. 159.5-161.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.65 (d, *J* = 7.3 Hz, 3H), 1.36 (s, 6H), 1.37 (s, 6H), 2.05 (qd, *J* = 12.2, 7.3 Hz, 1H), 2.93 (d, *J* = 13.6 Hz, 2H), 3.81 (d, *J* = 12.2 Hz, 1H), 3.83 (s, 3H), 3.92 (d, *J* = 13.6 Hz, 2H), 6.92 (d, *J* = 7.3 Hz, 2H), 7.06 (d, *J* = 7.3 Hz, 2H), 7.17-7.28 (m, 6H), 7.42 (d, *J* = 7.3 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.13, 25.35, 25.50, 54.38, 55.35, 65.15, 83.20, 113.26, 126.76, 128.06, 128.57, 129.38, 130.75, 140.21, 158.61; HRMS (CI) m/z ($[M+H]^+$) calcd for $C_{30}H_{39}BNO_3$: 472.3023, found: 472.3018.

A 96:4 mixture of (1*S,2*R**) and (1*S**,2*S**)-*N*,*N*-dibenzyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) -1-[4-(trifluoromethyl)phenyl]propan-1-amine (*syn*- and *anti*-3cb)** m.p. 165.0-166.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.65 (d, *J* = 7.3 Hz, 0.96×3H for ***syn*-3cb**), 0.77 (s, 0.04×6H for ***anti*-3cb**), 0.85 (s, 0.04×6H for ***anti*-3cb**), 1.30 (d, *J* = 7.3 Hz, 0.04×3H for ***anti*-3cb**), 1.36 (s, 0.96×6H for ***syn*-3cb**), 1.38 (s, 0.96×6H for ***syn*-3cb**), 2.03 (qd, *J* = 12.4, 7.3 Hz, 0.04×1H for ***anti*-3cb**), 2.10 (qd, *J* = 12.4, 7.3 Hz, 0.96×1H for ***syn*-3cb**), 2.90 (d, *J* = 13.7 Hz, 0.96×2H for ***syn*-3cb**), 2.93 (d, *J* = 13.7 Hz, 0.04×2H for ***anti*-3cb**), 3.74 (d, *J* = 12.4 Hz, 0.04×1H for ***anti*-3cb**), 3.93 (d, *J* = 12.4 Hz, 0.96×1H for ***syn*-3cb**), 3.95 (d, *J* = 13.7 Hz, 0.04×2H for ***anti*-3cb**), 3.96 (d, *J* = 13.7 Hz, 0.96×2H for ***syn*-3cb**), 7.19-7.31 (m, 8H), 7.41 (d, *J* = 7.3 Hz, 4H), 7.64 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) for ***syn*-3cb**: δ 13.94, 25.37, 25.49, 54.37, 65.43, 83.41, 124.56 (q, *J* = 272.2 Hz), 124.97 (q, *J* = 3.8 Hz), 127.01, 128.22, 129.31 (q, *J* = 32.6 Hz), 129.32, 129.88, 139.64, 140.92; ^{19}F NMR (373 MHz, $CDCl_3$) δ -62.14 (s); HRMS (CI) m/z ($[M+H]^+$) calcd for $C_{30}H_{36}BF_3NO_2$: 510.2791, found: 510.2799.

***N*,*N*-Dibenzyl-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethanamine (3db)** m.p. 99.0-100.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (s, 6H), 1.10 (s, 6H), 1.41 (dd, *J* = 14.9, 10.4 Hz, 1H), 1.57 (dd, *J* = 14.9, 6.3 Hz, 1H), 3.27 (d, *J* = 14.0 Hz, 2H), 3.70 (d, *J* = 14.0 Hz, 2H), 4.08 (dd, *J* = 10.4, 6.3 Hz, 1H), 7.17-7.31 (m, 11H), 7.37 (d, *J* = 7.3 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.73, 24.97, 53.84, 59.05, 83.19, 126.78, 126.93, 127.89, 128.25, 128.90, 128.99, 140.73, 141.42; HRMS (EI) m/z (M^+) calcd for $C_{28}H_{34}BNO_2$: 427.2683, found: 427.2685.

***N*,*N*-Dibenzyl-1-(4-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethanamine (3eb)** m.p. 97.5-99.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (s, 6H), 1.11 (s, 6H), 1.37 (dd, *J* = 15.1, 10.1 Hz, 1H), 1.55 (dd, *J* = 15.1, 6.4 Hz, 1H), 3.26 (d, *J* = 13.7 Hz, 2H), 3.68 (d, *J* = 13.7 Hz, 2H), 3.79

(s, 3H), 4.04 (dd, *J* = 10.1, 6.4 Hz, 1H), 6.86 (d, *J* = 8.7 Hz, 2H), 7.16-7.28 (m, 8H), 7.37 (d, *J* = 7.3 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.75, 25.00, 53.74, 55.39, 58.32, 83.16, 113.15, 126.75, 128.23, 128.97, 129.89, 133.60, 140.79, 158.53; HRMS (CI) m/z ($[M+H]^+$) calcd for $C_{29}H_{37}BNO_3$: 458.2866, found: 458.2864.

***N*,*N*-Dibenzyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-[4-(trifluoromethyl)phenyl]eth anamine (3fb)** m.p. 118.0-119.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (s, 6H), 1.11 (s, 6H), 1.40 (dd, *J* = 15.1, 10.1 Hz, 1H), 1.59 (dd, *J* = 15.1, 6.0 Hz, 1H), 3.29 (d, *J* = 13.7 Hz, 2H), 3.68 (d, *J* = 13.7 Hz, 2H), 4.12 (dd, *J* = 10.1, 6.0 Hz, 1H), 7.20 (t, *J* = 7.3 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 4H), 7.35 (d, *J* = 7.3 Hz, 4H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.72, 24.91, 53.85, 58.66, 83.38, 124.55 (q, *J* = 272.2 Hz), 124.85 (q, *J* = 3.8 Hz), 127.02, 128.38, 128.96, 129.06, 129.14 (q, *J* = 31.6 Hz), 140.21, 146.10; ^{19}F NMR (373 MHz, $CDCl_3$) δ -62.15 (s); HRMS (EI) m/z (M^+) calcd for $C_{29}H_{33}BF_3NO_2$: 495.2556, found: 495.2554.

***N*,*N*-Dibenzyl-1-(2-bromophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethanamine (3gb)** m.p. 66.0-67.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (s, 6H), 1.02 (s, 6H), 1.40 (dd, *J* = 15.1, 11.0 Hz, 1H), 1.49 (dd, *J* = 15.1, 6.0 Hz, 1H), 3.57 (d, *J* = 14.2 Hz, 2H), 3.73 (d, *J* = 14.2 Hz, 2H), 4.60 (dd, *J* = 11.0, 6.0 Hz, 1H), 7.02 (td, *J* = 7.8, 1.8 Hz, 1H), 7.10-7.28 (m, 11H), 7.47 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.51 (dd, *J* = 7.8, 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.60, 24.77, 55.02, 61.10, 83.22, 126.23, 126.61, 127.02, 128.04, 128.38, 128.92, 129.85, 133.05, 140.77, 142.43; HRMS (EI) m/z (M^+) calcd for $C_{28}H_{33}BBrNO_2$: 505.1788, found: 505.1790.

***N*,*N*-Dibenzyl-1-(naphthalen-2-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethanamine (3hb)** oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (s, 6H), 1.07 (s, 6H), 1.51 (dd, *J* = 15.1, 10.5 Hz, 1H), 1.66 (dd, *J* = 15.1, 6.0 Hz, 1H), 3.39 (d, *J* = 13.7 Hz, 2H), 3.68 (d, *J* = 13.7 Hz, 2H), 4.25 (dd, *J* = 10.5, 6.0 Hz, 1H), 7.19 (t, *J* = 7.3 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 4H), 7.37 (d, *J* = 7.3 Hz, 4H), 7.41-7.46 (m, 2H), 7.54 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.69 (s, 1H), 7.80-7.82 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.78, 24.91, 53.86, 59.00, 83.22, 125.60, 125.89, 126.84 (two signals are overlapped.), 127.50, 127.70, 127.90, 128.07, 128.27, 129.06, 132.77, 133.16, 139.85, 140.67; HRMS (EI) m/z (M^+) calcd for $C_{32}H_{36}BNO_2$: 477.2839, found: 477.2836.

(1*S,2*S**)-*N*,*N*-Diethyl-3-methoxy-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pro**

pan-1-amine (3ia) m.p. 50.0-51.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (t, *J* = 7.3 Hz, 6H), 1.30 (s, 6H), 1.31 (s, 6H), 1.91 (qd, *J* = 12.8, 7.3 Hz, 2H), 2.38 (ddd, *J* = 12.4, 10.5, 5.5 Hz, 1H), 2.67 (qd, *J* = 12.8, 7.3 Hz, 2H), 3.07 (dd, *J* = 8.3, 5.5 Hz, 1H), 3.17 (s, 3H), 3.27 (dd, *J* = 10.5, 8.3 Hz, 1H), 3.90 (d, *J* = 12.4 Hz, 1H), 7.16 (d, *J* = 7.3 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.30 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.86, 25.11 (two signals are overlapped.), 43.47, 58.82, 62.16, 73.46, 83.21, 127.09, 127.95, 129.00, 137.26; HRMS (CI) m/z ($[M+H]^+$) calcd for $C_{20}H_{35}BNO_3$: 348.2710, found: 348.2707.

(1*S,2*S**)-*N*,*N*-Dibenzyl-3-methoxy-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-amine (3ib)** m.p. 135.0-136.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38 (s, 6H), 1.39 (s, 6H), 2.57 (ddd, *J* = 12.3, 10.9, 5.9 Hz, 1H), 2.91 (d, *J* = 13.6 Hz, 2H), 2.97 (dd, *J* = 8.2, 5.9 Hz, 1H), 3.108 (s, 3H), 3.111 (dd, *J* = 10.9, 8.2 Hz, 1H), 3.95 (d, *J* = 12.3 Hz, 1H), 3.96 (d, *J* = 13.6 Hz, 2H), 7.15 (d, *J* = 7.3 Hz, 2H), 7.18-7.38 (m, 9H), 7.41 (d, *J* = 7.3 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.40, 25.68, 54.15, 58.72, 61.58, 73.96, 83.58, 126.88, 127.37, 128.09, 128.12, 129.41, 129.48, 136.31, 139.88; HRMS (EI) m/z (M^+) calcd for $C_{30}H_{38}BNO_3$: 471.2945, found: 471.2938.

An 88:12 mixture of *N*,*N*-dibenzyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) octan-2-amine (3jb) and *N*,*N*-dibenzyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octan-1-amine (3jb') oil; ^{1}H NMR (400 MHz, $CDCl_3$) for mixture: δ 0.85 (t, *J* = 7.3 Hz, 3H), 1.17-1.29 (m, 10H), 1.22 (s, 12H), 1.36-1.48 (m, 1H), 1.54-1.63 (m, 0.88×1H for **3jb**), 2.39 (dd, *J* = 11.9, 7.3 Hz, 0.12×1H for **3jb'**), 2.58 (dd, *J* = 11.9, 8.2 Hz, 0.12×1H for **3jb'**), 2.83-2.90 (m, 0.88×1H for **3jb**), 3.38 (d, *J* = 13.7 Hz, 0.88×2H for **3jb**), 3.45 (d, *J* = 13.7 Hz, 0.12×2H for **3jb'**), 3.57 (d, *J* = 13.7 Hz, 0.12×2H for **3jb'**), 3.64 (d, *J* = 13.7 Hz, 0.88×2H for **3jb**), 7.18 (t, *J* = 7.3 Hz, 2H), 7.26 (t, *J* = 7.3 Hz, 4H), 7.36 (d, *J* = 7.3 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3jb**: δ 14.35, 22.89, 24.96, 25.14, 26.94, 29.42, 32.07, 33.81, 53.52, 54.69, 83.08, 126.68, 128.68, 129.21, 140.98; HRMS (EI) m/z (M^+) calcd for $C_{28}H_{42}BNO_2$: 435.3309, found: 435.3305.

(1*S,2*R**)-*N*,*N*-Dibenzyl-1-(3-chlorophenyl)-3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-amine (3kb)** m.p. 139.0-140.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.66 (d, *J* = 6.9 Hz, 3H), 0.90 (d, *J* = 6.9 Hz, 3H), 1.28-1.34 (m, 1H), 1.37 (s, 6H), 1.40 (s, 6H), 2.11 (dd, *J* = 12.8, 4.1 Hz, 1H), 2.89 (d, *J* = 13.7 Hz, 2H), 3.98 (d, *J* = 13.7 Hz, 2H), 4.08 (d, *J* = 12.8 Hz, 1H), 6.99 (dm, *J* = 6.4 Hz, 1H), 7.18-7.31 (m, 9H), 7.41 (d, *J* = 7.3 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.21, 23.77,

25.98, 26.08, 27.19, 54.54, 62.63, 83.43, 126.81, 127.24, 127.78, 128.09, 129.12, 129.37, 129.70, 134.00, 138.52, 139.60; HRMS (CI) m/z ($[M+H]^+$) calcd for $C_{31}H_{40}BClNO_2$: 504.2841, found: 504.2834.

A 90:10 mixture of *N*,*N*-dibenzyl-1-cyclohexyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethanamine (3lb) and *N*,*N*-dibenzyl-2-cyclohexyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethanamine (3lb') oil; ^{1}H NMR (400 MHz, $CDCl_3$) for **3lb**: δ 0.67-0.83 (m, 3H), 1.02-1.17 (m, 3H), 1.22 (s, 6H), 1.25 (s, 6H), 1.35-1.43 (m, 1H), 1.56-1.67 (m, 5H), 2.28-2.31 (m, 1H), 2.58-2.63 (m, 1H), 3.29 (d, *J* = 13.7 Hz, 2H), 3.71 (d, *J* = 13.7 Hz, 2H), 7.19 (t, *J* = 7.3 Hz, 2H), 7.27 (t, *J* = 7.3 Hz, 4H), 7.37 (d, *J* = 7.3 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3lb**: δ 24.99, 25.02, 26.85, 31.11, 31.14, 42.02, 54.17, 59.99, 83.06, 126.66, 128.10, 129.36, 140.94; HRMS (CI) m/z ($[M+H]^+$) calcd for $C_{28}H_{41}BNO_2$: 434.3231, found: 434.3232.

(1*S,2*R**)-{2-[1-(*N*,*N*-Diethylammonio)-1-phenyl]propyl}trifluoroborate (3aa-BF_3)** m.p. 132.0-133.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.73 (d, *J* = 7.3 Hz, 3H), 1.36 (t, *J* =7.3 Hz, 3H), 1.48 (m, 1H), 1.59 (t, *J* = 7.3 Hz, 3H), 2.15-2.26 (m, 1H), 2.83-2.94 (m, 1H), 3.11 (qd, *J* = 12.8, 7.3 Hz, 1H), 3.58 (qd, *J* = 12.8, 7.3 Hz, 1H), 4.41 (d, *J* = 12.3 Hz, 1H), 7.27-7.45 (m, 5H), 7.58 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.94, 11.43, 13.13, 13.15, 45.69, 45.72, 72.22, 129.28, 130.16, 130.90, 130.92; ^{19}F NMR (373 MHz, $CDCl_3$) δ -143.14 (s); HRMS (FAB) m/z ($[M-F]^+$) calcd for $C_{13}H_{21}BF_2N$: 240.1735, found: 240.1730.

(1*S,2*R**)-{2-[1-(*N*-Benzyl-*N*-methylammonio)-1-phenyl]propyl}trifluoroborate (3ac-BF_3)** (diastereomixture associated with the chirality on nitrogen) m.p. 141.0-142.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.74 (d, *J* = 7.3 Hz, 0.5×3H), 0.77 (d, *J* = 7.3 Hz, 0.5×3H), 1.48 (m, 0.5×1H), 1.68 (m, 0.5×1H), 2.43 (s, 0.5×3H), 2.56 (s, 0.5×3H), 3.09 (d, *J* = 12.8 Hz, 0.5×1H), 3.66 (d, *J* = 12.8 Hz, 0.5×1H), 4.40 (d, *J* = 12.8 Hz, 0.5×1H), 4.46 (d, *J* = 12.8 Hz, 0.5×1H), 4.50 (d, *J* = 12.8 Hz, 0.5×1H), 4.80 (d, *J* = 12.8 Hz, 0.5×1H), 7.26-7.52 (m, 10H), 8.52 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.11, 13.13, 13.35, 13.37, 31.16, 34.22, 39.46, 54.50, 61.00, 78.96, 129.03, 129.13, 129.19, 129.27, 129.42, 129.62, 129.84, 130.10, 130.42, 130.45 (three signals are overlapped.), 130.57, 130.63 (three signals are overlapped.); ^{19}F NMR (373 MHz, $CDCl_3$) δ -143.53 (s), -142.66 (s); HRMS (FAB) m/z ($[M-F]^+$) calcd for $C_{17}H_{21}BF_2N$: 288.1735, found: 288.1737.

(1*S,2*R**)-[2-(1-Phenyl-1-piperidiniumyl)propyl]trifluoroborate (3ae-BF_3)** m.p. 148.0-149.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.71 (d, *J* = 7.3 Hz, 3H), 1.12-1.23 (m, 1H), 1.45-1.53 (m, 1H), 1.76-1.94 (m, 5H), 2.18-2.29 (m, 1H), 2.58-2.67 (m, 1H), 3.47 (d, *J* = 12.8 Hz, 1H), 3.71 (d, *J* = 12.8 Hz, 1H), 4.17 (d, *J* = 12.8 Hz, 1H), 7.27-7.46 (m, 5H), 7.67 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.14, 13.16, 22.18, 24.13, 24.76, 48.35, 54.02, 78.03, 129.21, 130.11, 131.21, 131.23; ^{19}F NMR (373 MHz, $CDCl_3$) δ -144.30 (s); HRMS (FAB) m/z ($[M-F]^+$) calcd for $C_{14}H_{21}BF_2N$: 252.1735, found: 252.1739.

(1*S,2*R**)-[2-(1-Azepaniumyl-1-phenyl)propyl]trifluoroborate (3af-BF_3)** m.p. 136.0-137.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.70 (d, *J* = 7.3 Hz, 3H), 1.45-1.55 (m, 3H), 1.73-1.94 (m, 6H), 2.46 (m, 1H), 2.92 (m, 1H), 3.59-3.72 (m, 2H), 4.28 (d, *J* = 12.4 Hz, 1H), 7.37-7.45 (m, 5H), 7.89 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.02, 13.04, 24.91, 25.19, 25.51, 25.60, 49.41, 56.89, 79.10, 129.16, 130.06, 131.29, 131.31; ^{19}F NMR (373 MHz, $CDCl_3$) δ -143.69 (s); HRMS (FAB) m/z ($[M-F]^+$) calcd for $C_{15}H_{23}BF_2N$: 266.1892, found: 266.1890.

(1*S,2*S**)-{2-[1-(*N*,*N*-Diethylammonio)-1-phenyl-3-methoxy]propyl]trifluoroborate (3ia-BF_3)** m.p. 109.0-110.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (t, *J* = 7.3 Hz, 3H), 1.55 (t, *J* = 7.3 Hz, 3H), 1.70 (m, 1H), 2.34-2.44 (m, 1H), 2.97-3.04 (m, 1H), 3.05 (s, 3H), 3.13-3.19 (m, 1H), 3.23-3.27 (m, 1H), 3.55 (dd, *J* = 10.6, 6.0 Hz, 2H), 4.77 (d, *J* = 11.0 Hz, 1H), 7.18 (bs, 1H), 7.37-7.40 (m, 2H), 7.42-7.44 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.65, 11.18, 45.71, 45.92, 58.83, 70.43, 72.63, 72.65, 128.99, 129.90, 130.92 (two signals are overlapped.); ^{19}F NMR (373 MHz, $CDCl_3$) δ -140.24 (s); HRMS (FAB) m/z ($[M-F]^+$) calcd for $C_{14}H_{23}BF_2NO$: 270.1841, found: 270.1847.

(1*R,2*R**)-1-(*N*,*N*-Diethylamino)-1-phenylpropan-2-ol (4aa)** oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03 (d, *J* = 6.0 Hz, 3H), 1.10 (t, *J* = 7.3 Hz, 6H), 2.10 (qd, *J* = 12.8, 7.3 Hz, 2H), 2.71 (qd, *J* = 12.8, 7.3 Hz, 2H), 3.40 (d, *J* = 10.1 Hz, 1H), 4.15 (qd, *J* = 10.1, 6.0 Hz, 1H), 4.59 (bs, 1H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.26-7.35 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.30, 19.81, 43.50, 64.03, 70.90, 127.76, 128.28, 129.75, 135.61; HRMS (CI) m/z ($[M+H]^+$) calcd for $C_{13}H_{22}NO$: 208.1701, found: 208.1701.

(1*R,2*R**)-1-(*N*,*N*-Dibenzylamino)-1-phenylpropan-2-ol (*syn*-4ab)** oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (d, *J* = 6.0 Hz, 3H), 3.03 (d, *J* = 13.3 Hz, 2H), 3.40 (d, *J* = 10.1 Hz, 1H), 3.95 (d, *J* =

13.3 Hz, 2H), 4.37 (qd, *J* = 10.1, 6.0 Hz, 1H), 4.39 (bs, 1H), 7.20 (d, *J* = 7.3 Hz, 2H), 7.24-7.28 (m, 2H), 7.30-7.45 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.84, 53.84, 64.40, 69.46, 127.51, 128.11, 128.52, 128.82, 129.24, 130.11, 134.33, 138.95; HRMS (CI) m/z ($[M+H]^+$) calcd for $C_{23}H_{26}NO$: 332.2014, found: 332.2012.

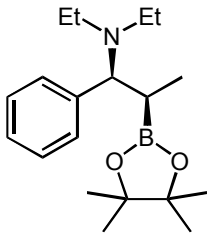
(1*R,2*S**)-1-(*N*,*N*-Dibenzylamino)-1-phenylpropan-2-ol (*anti*-4ab)** m.p. 115.0-116.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (d, *J* = 6.4 Hz, 3H), 3.07 (d, *J* = 13.7 Hz, 2H), 3.50 (d, *J* = 8.7 Hz, 1H), 3.85 (d, *J* = 13.7 Hz, 2H), 4.49 (qd, *J* = 8.7, 6.4 Hz, 1H), 7.22-7.46 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.91, 54.76, 67.10, 69.53, 127.22, 128.02, 128.58, 128.64, 128.98, 130.17, 135.33, 139.77; HRMS (CI) m/z ($[M+H]^+$) calcd for $C_{23}H_{26}NO$: 332.2014, found: 332.2015.

(1*R,2*R**)-1-(*N*,*N*-Dibenzylamino)-1-(4-methoxyphenyl)propan-2-ol (4bb)** oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (d, *J* = 6.0 Hz, 3H), 3.02 (d, *J* = 13.3 Hz, 2H), 3.36 (d, *J* = 10.1 Hz, 1H), 3.85 (s, 3H), 3.93 (d, *J* = 13.3 Hz, 2H), 4.31 (qd, *J* = 10.1, 6.0 Hz, 1H), 4.43 (bs, 1H), 6.96 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 7.24-7.28 (m, 2H), 7.29-7.36 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.87, 53.83, 55.44, 64.56, 68.81, 113.87, 126.31, 127.48, 128.80, 129.24, 131.14, 139.03, 159.38; HRMS (CI) m/z ($[M+H]^+$) calcd for $C_{24}H_{28}NO_2$: 362.2120, found: 362.2116.

(1*R,2*S**)-1-(Piperidin-1-yl)-2,3-dihydroinden-2-ol (4me)** m.p. 102.0-103.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40-1.43 (m, 2H), 1.51-1.67 (m, 4H), 2.37 (m, 2H), 2.55 (m, 2H), 2.76 (dd, *J* = 16.5, 7.8 Hz, 1H), 3.29 (dd, *J* = 16.5, 8.2 Hz, 1H), 4.04 (d, *J* = 7.8 Hz, 1H), 4.44 (ddd, *J* = 8.2, 7.8, 7.8 Hz, 1H), 5.01 (bs, 1H), 7.19-7.27 (m, 3H), 7.31-7.33 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.29, 26.82, 41.99, 52.81, 69.16, 70.97, 125.68, 126.57, 126.59, 128.60, 139.16, 141.90; HRMS (EI) m/z (M^+) calcd for $C_{14}H_{19}NO$: 217.1467, found: 217.1470.

***tert*-Butyl [(1*R**,2*R**)-1-(*N*,*N*-diethylamino)-1-phenylpropan-2-yl]carbamate (5aa)** oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01 (d, *J* = 6.0 Hz, 3H), 1.04 (t, *J* = 6.9 Hz, 6H), 1.48 (s, 9H), 2.11 (qd, *J* = 13.3, 6.9 Hz, 2H), 2.61 (qd, *J* = 13.3, 6.9 Hz, 2H), 3.48 (d, *J* = 10.1 Hz, 1H), 3.95-4.03 (m, 1H), 5.45 (bs, 1H), 7.18 (d, *J* = 7.3 Hz, 2H), 7.26-7.34 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.60, 18.97, 28.72, 43.04, 46.61, 68.31, 79.04, 127.62, 128.23, 129.51, 136.52, 156.64; HRMS (CI) m/z ($[M+H]^+$) calcd for $C_{18}H_{31}N_2O_2$: 307.2386, found: 307.2384.

[^{1}H and ^{13}C NMR Spectra of **3aa**]



3aa

No.	ppm	Hz	Height
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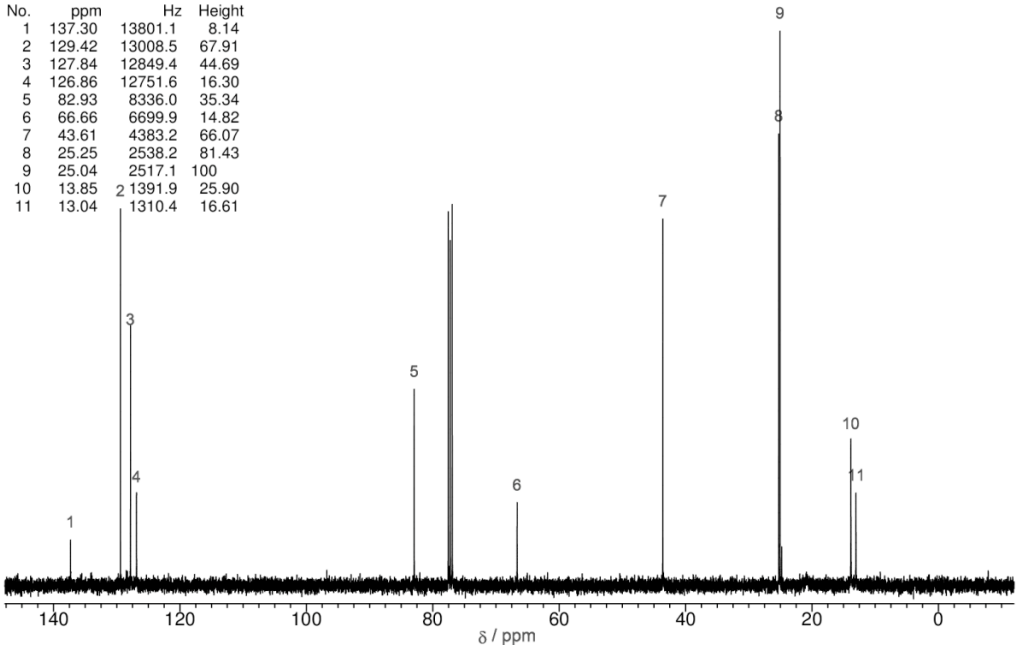
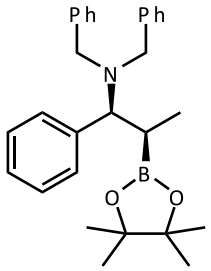
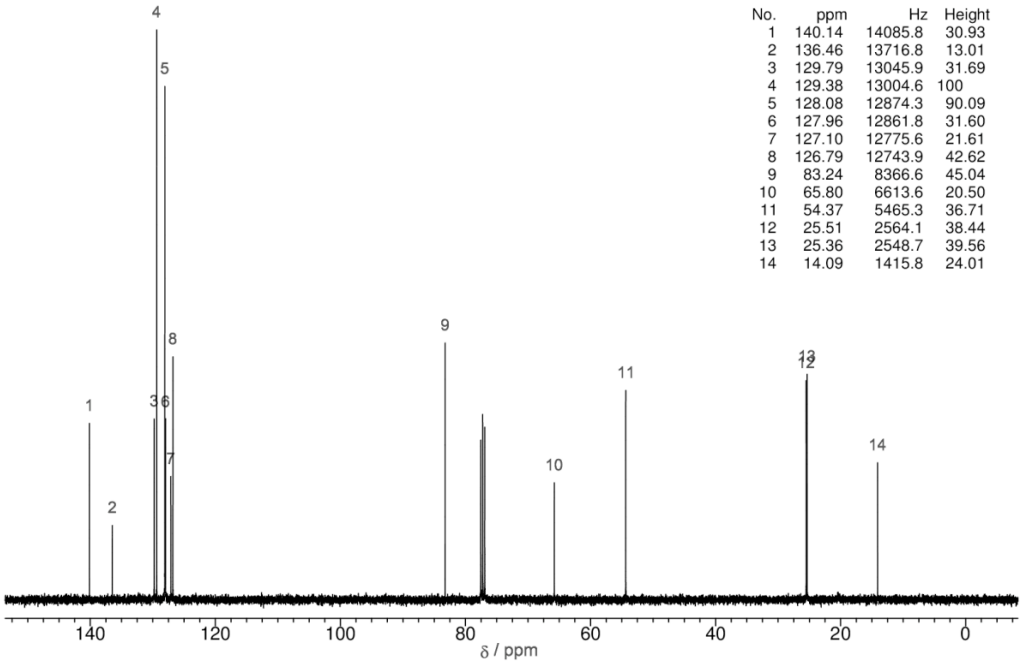
3	127.84	12849.4	44.69
4	126.86	12751.6	16.30
5	82.93	8336.0	35.34
6	66.66	6699.9	14.82
7	43.61	4383.2	66.07
8	25.25	2538.2	81.43
9	25.04	2517.1	100
10	13.85	1391.9	25.90
11	13.04	1310.4	16.61



[^{1}H and ^{13}C NMR Spectra of ***syn*-3ab**]



***syn*-3ab**



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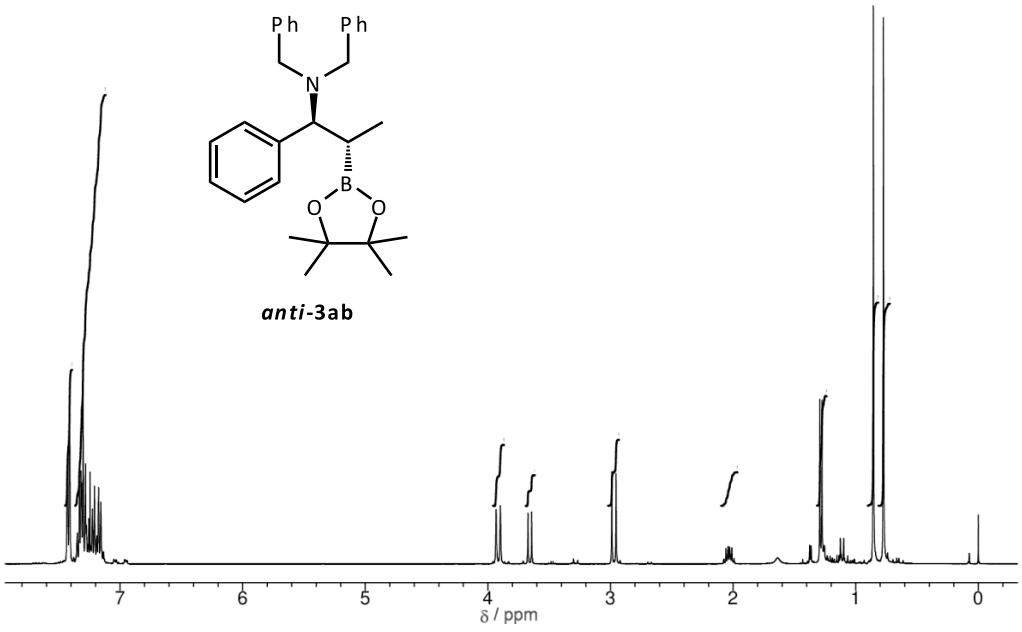
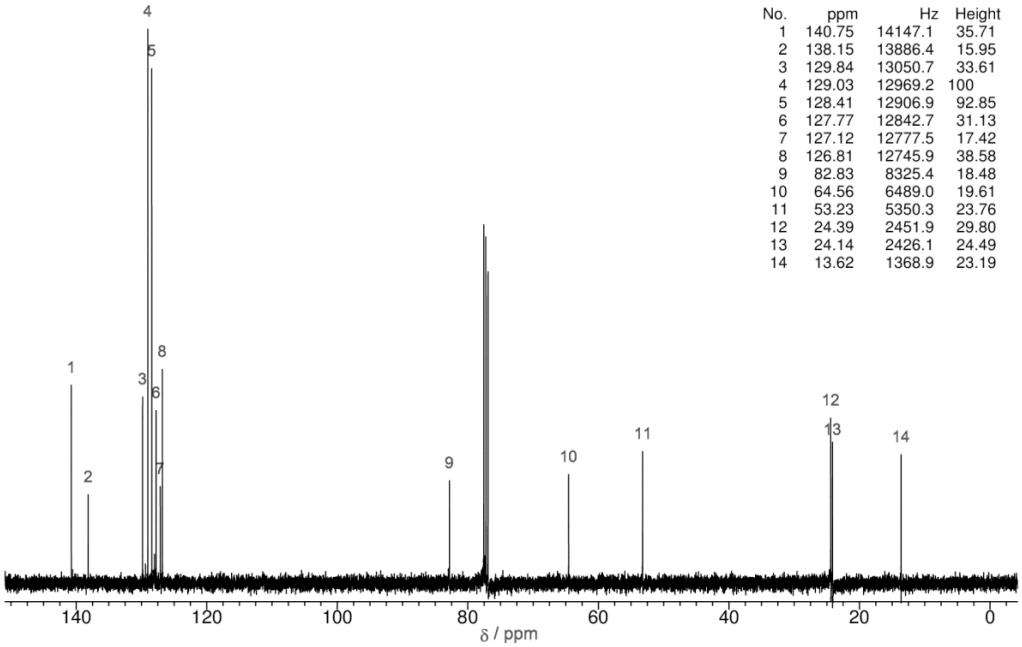
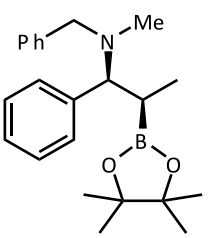
1	140.14	14085.8	30.93
2	136.46	13716.8	13.01
3	129.79	13045.9	31.69
4	129.38	13004.6	100
5	128.08	12874.3	90.09
6	127.96	12861.8	31.60
7	127.10	12775.6	21.61
8	126.79	12743.9	42.62
9	83.24	8366.6	45.04
10	65.80	6613.6	20.50
11	54.37	5465.3	36.71
12	25.51	2564.1	38.44
13	25.36	2548.7	39.56
14	14.09	1415.8	24.01

[^{1}H and ^{13}C NMR Spectra of ***anti*-3ab**]



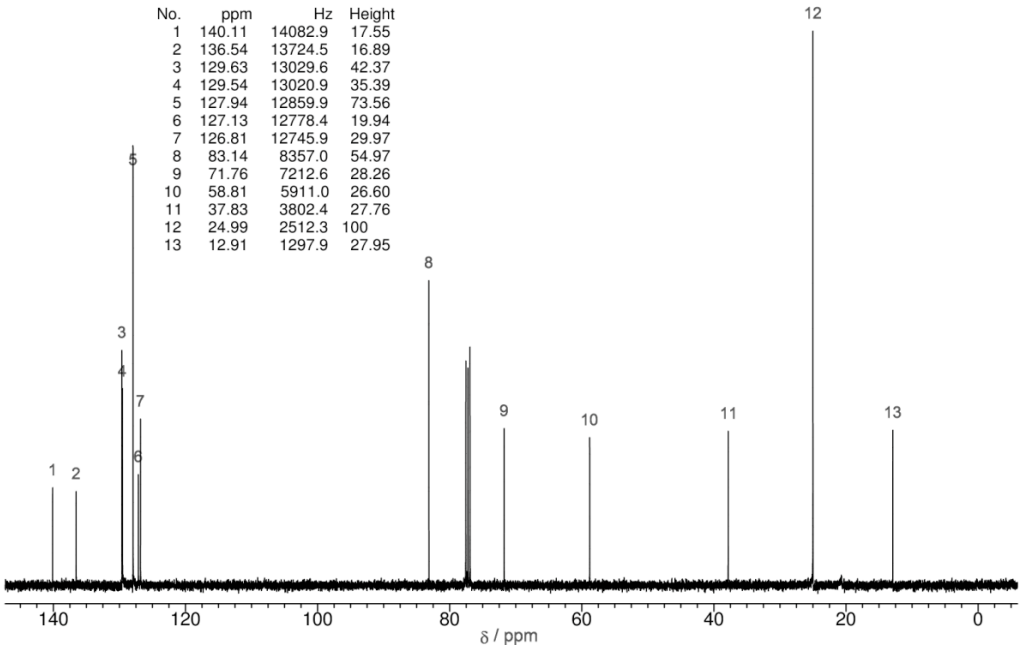


[^{1}H and ^{13}C NMR Spectra of **3ac**]

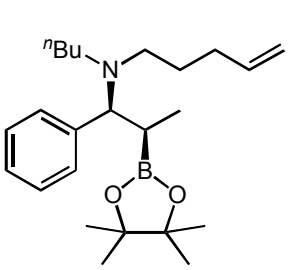


3ac

No.	ppm	Hz	Height
1	140.11	14082.9	17.55
2	136.54	13724.5	16.89
3	129.63	13029.6	42.37
4	129.54	13020.9	35.39
5	127.94	12859.9	73.56
6	127.13	12778.4	19.94
7	126.81	12745.9	29.97
8	83.14	8357.0	54.97
9	71.76	7212.6	28.26
10	58.81	5911.0	26.60
11	37.83	3802.4	27.76
12	24.99	2512.3	100
13	12.91	1297.9	27.95

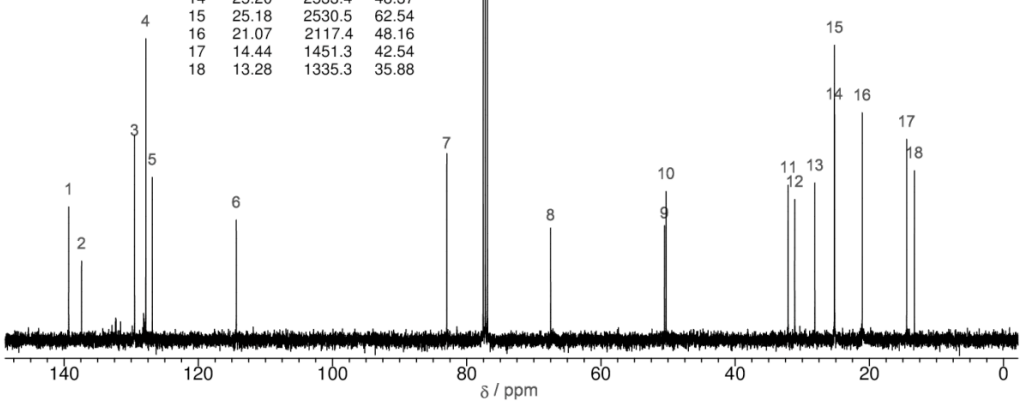


[^{1}H and ^{13}C NMR Spectra of **3ad**]

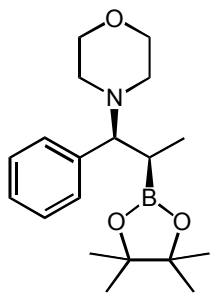


3ad

No.	ppm	Hz	Height
1	139.31	14002.4	28.17
2	137.40	13810.7	16.65
3	129.49	13016.1	40.67
4	127.83	12848.4	63.89
5	126.85	12750.7	34.45
6	114.33	11492.2	25.37
7	82.97	8339.8	37.96
8	67.48	6783.2	22.66
9	50.52	5078.1	23.11
10	50.28	5054.2	31.46
11	32.10	3226.4	32.80
12	31.13	3128.6	29.77
13	28.11	2825.7	33.26
14	25.20	2533.4	48.37
15	25.18	2530.5	62.54
16	21.07	2117.4	48.16
17	14.44	1451.3	42.54
18	13.28	1335.3	35.88

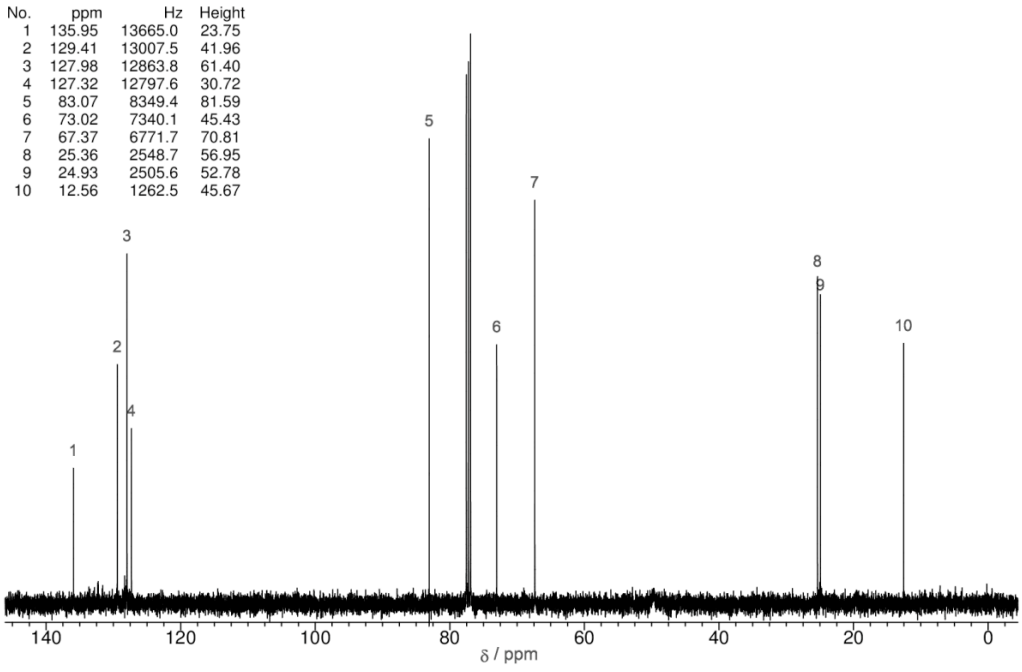


[^{1}H and ^{13}C NMR Spectra of **3ag**]

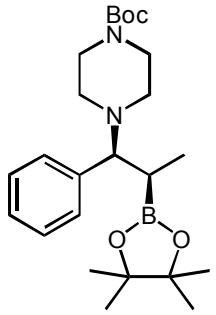


3ag

No.	ppm	Hz	Height
1	135.95	13665.0	23.75
2	129.41	13007.5	41.96
3	127.98	12863.8	61.40
4	127.32	12797.6	30.72
5	83.07	8349.4	81.59
6	73.02	7340.1	45.43
7	67.37	6771.7	70.81
8	25.36	2548.7	56.95
9	24.93	2505.6	52.78
10	12.56	1262.5	45.67

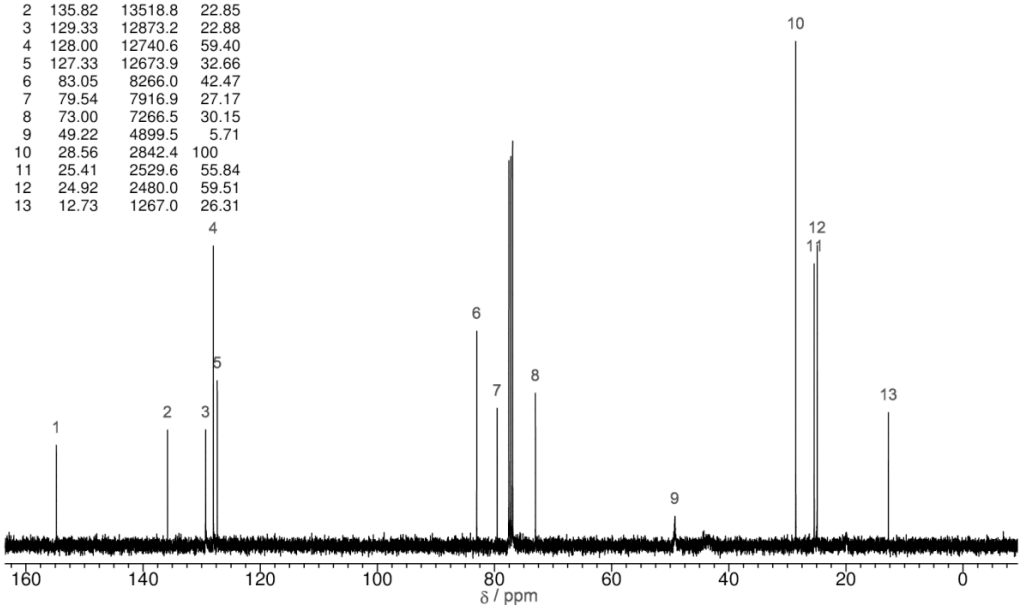


[^{1}H and ^{13}C NMR Spectra of **3ah**]

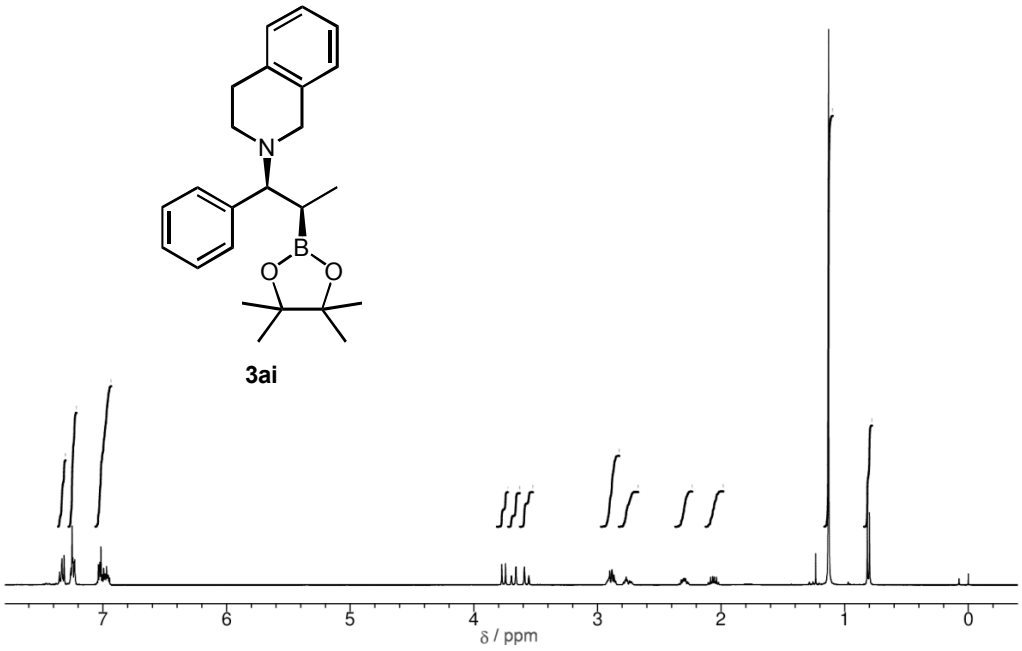


3ah

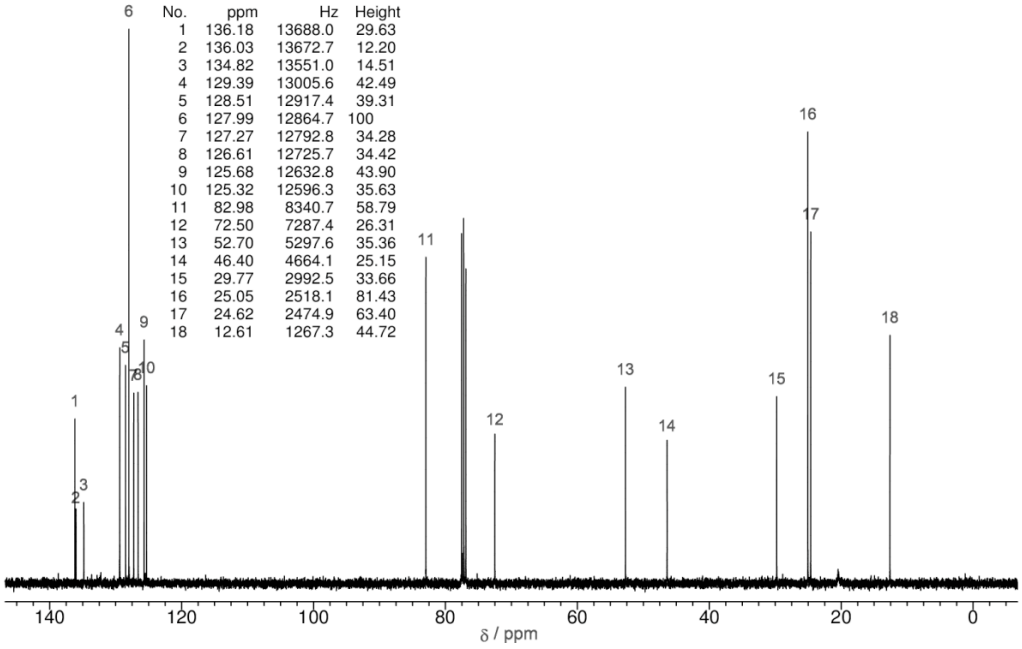
No.	ppm	Hz	Height
1	154.82	15410.0	19.83
2	135.82	13518.8	22.85
3	129.33	12873.2	22.88
4	128.00	12740.6	59.40
5	127.33	12673.9	32.66
6	83.05	8266.0	42.47
7	79.54	7916.9	27.17
8	73.00	7266.5	30.15
9	49.22	4899.5	5.71
10	28.56	2842.4	100
11	25.41	2529.6	55.84
12	24.92	2480.0	59.51
13	12.73	1267.0	26.31



[^{1}H and ^{13}C NMR Spectra of **3ai**]

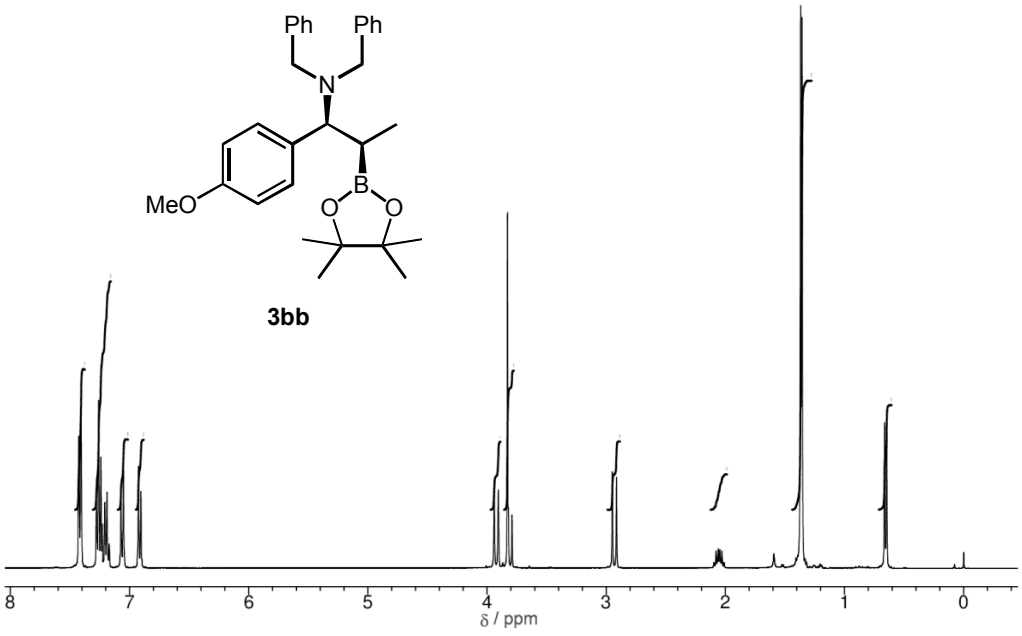


3ai

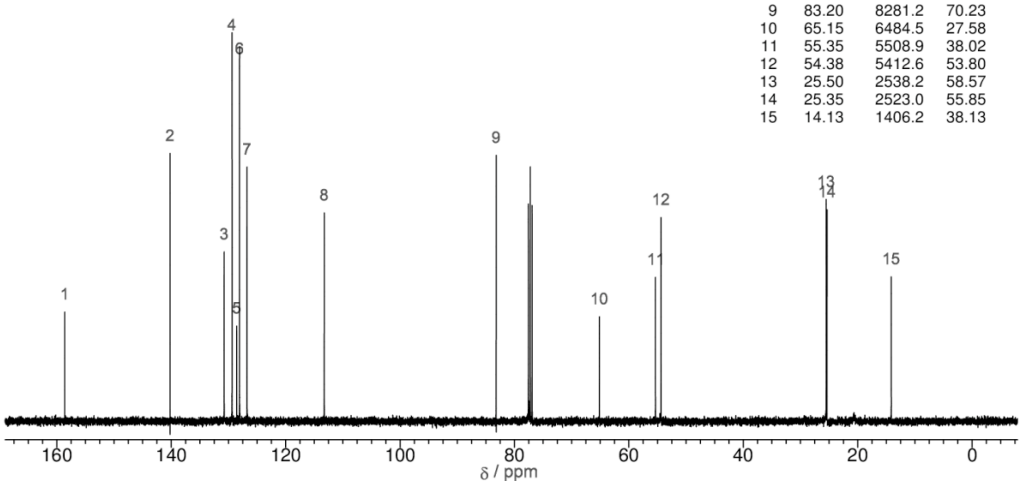


No.	ppm	Hz	Height
1	136.18	13688.0	29.63
2	136.03	13672.7	12.20
3	134.82	13551.0	14.51
4	129.39	13005.6	42.49
5	128.51	12917.4	39.31
6	127.99	12864.7	100
7	127.27	12792.8	34.28
8	126.61	12725.7	34.42
9	125.68	12632.8	43.90
10	125.32	12596.3	35.63
11	82.98	8340.7	58.79
12	72.50	7287.4	26.31
13	52.70	5297.6	35.36
14	46.40	4664.1	25.15
15	29.77	2992.5	33.66
16	25.05	2518.1	81.43
17	24.62	2474.9	63.40
18	12.61	1267.3	44.72

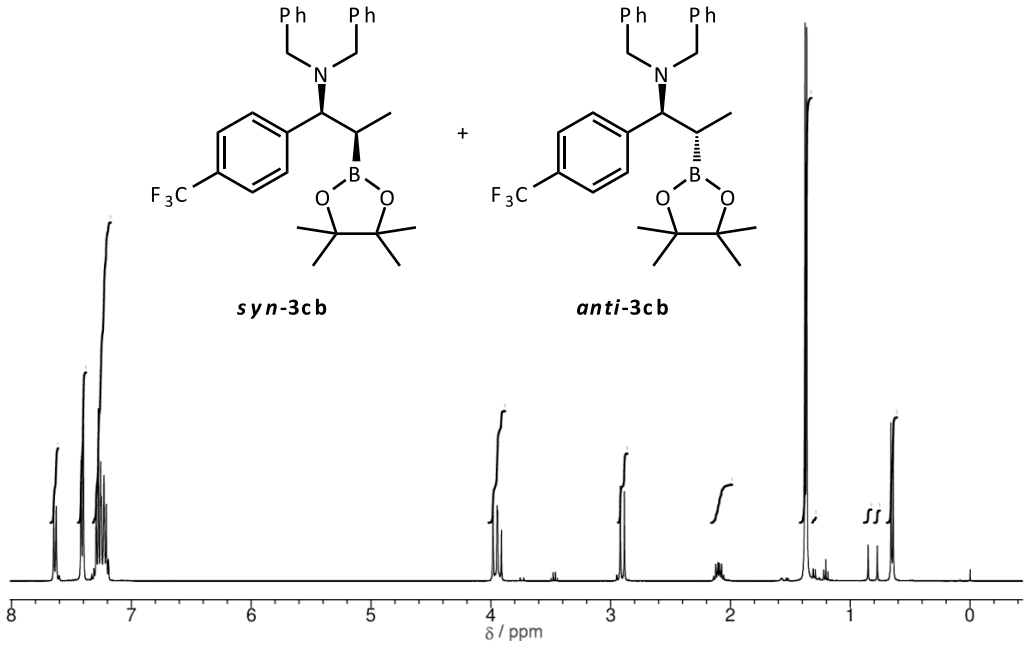
[^{1}H and ^{13}C NMR Spectra of **3bb**]

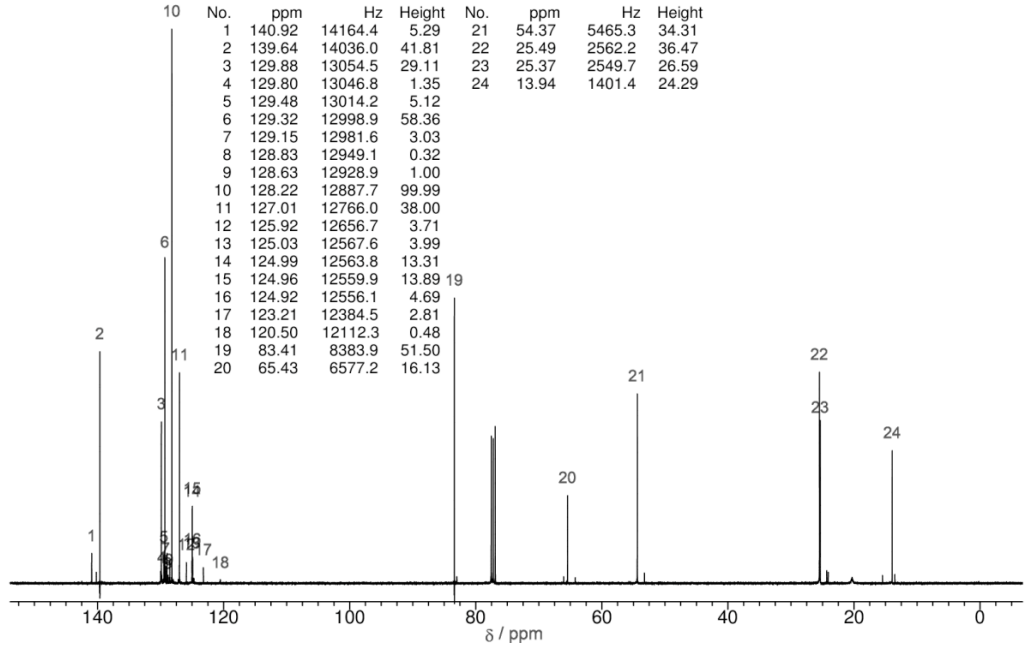


No.	ppm	Hz	Height
1	158.61	15787.6	28.81
2	140.21	13955.6	70.74
3	130.75	13014.3	44.70
4	129.38	12878.0	100
5	128.57	12796.9	25.13
6	128.06	12746.3	93.72
7	126.76	12616.6	67.13
8	113.26	11272.9	55.02
9	83.20	8281.2	70.23
10	65.15	6484.5	27.58
11	55.35	5508.9	38.02
12	54.38	5412.6	53.80
13	25.50	2538.2	58.57
14	25.35	2523.0	55.85
15	14.13	1406.2	38.13

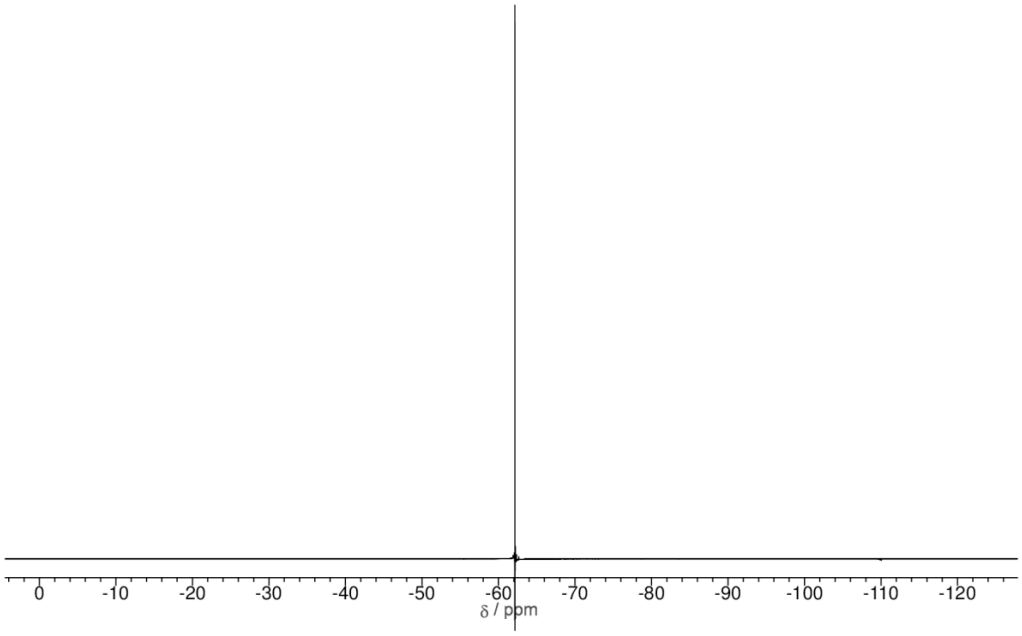


[^{1}H, ^{13}C, and ^{19}F NMR Spectra of a 96:4 mixture of ***syn-*** and ***anti-*****3cb**]

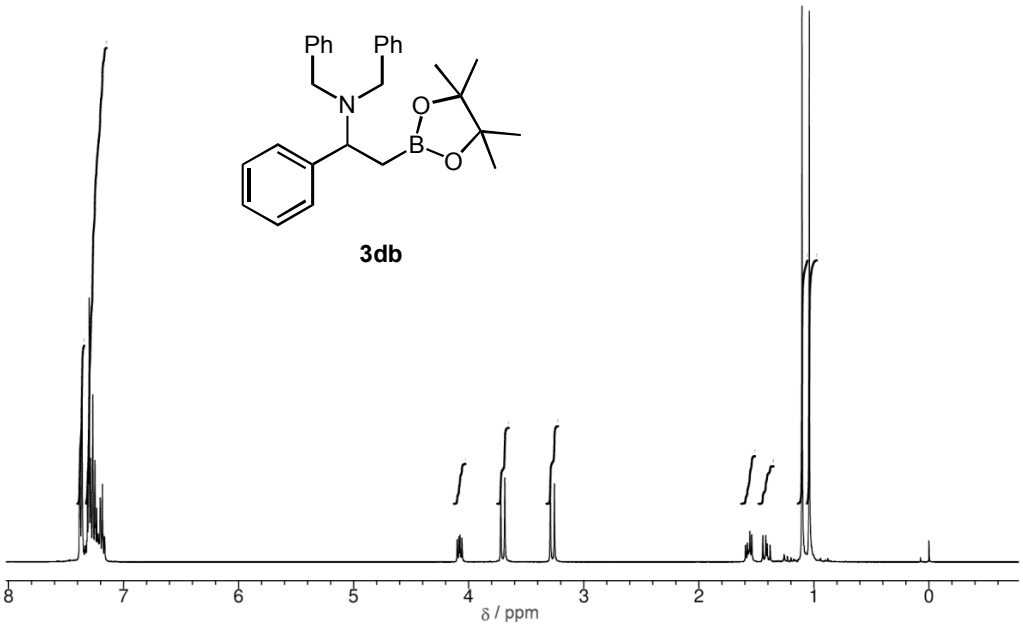


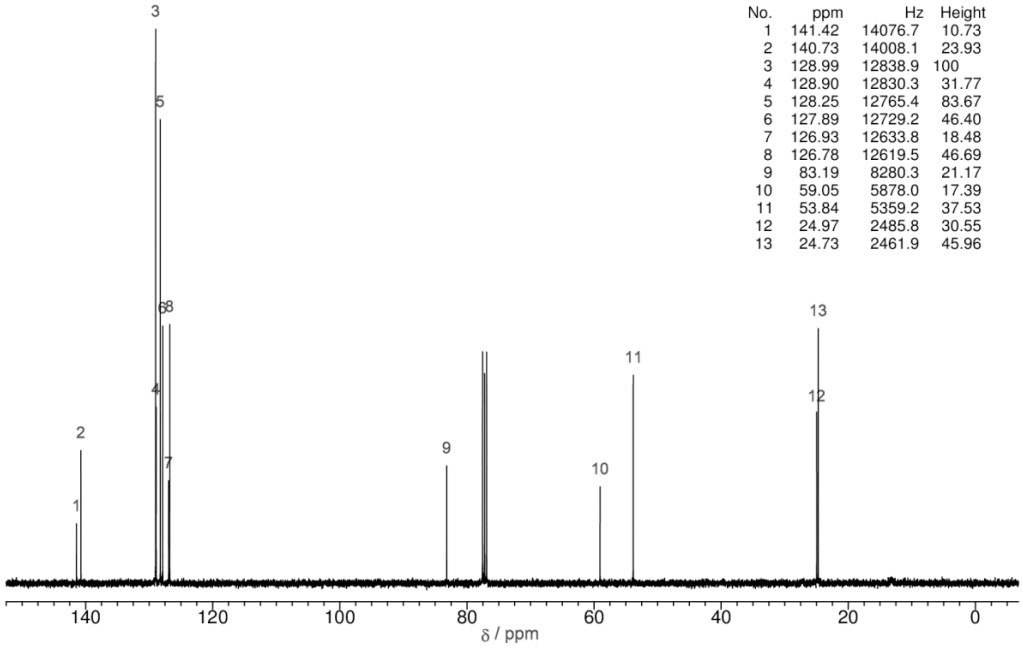


No.	ppm	Hz	Height	No.	ppm	Hz	Height
1	140.92	14164.4	5.29	21	54.37	5465.3	34.31
2	139.64	14036.0	41.81	22	25.49	2562.2	36.47
3	129.88	13054.5	29.11	23	25.37	2549.7	26.59
4	129.80	13046.8	1.35	24	13.94	1401.4	24.29
5	129.48	13014.2	5.12				
6	129.32	12998.9	58.36				
7	129.15	12981.6	3.03				
8	128.83	12949.1	0.32				
9	128.63	12928.9	1.00				
10	128.22	12887.7	99.99				
11	127.01	12766.0	38.00				
12	125.92	12656.7	3.71				
13	125.03	12567.6	3.99				
14	124.99	12563.8	13.31				
15	124.96	12559.9	13.89				
16	124.92	12556.1	4.69				
17	123.21	12384.5	2.81				
18	120.50	12112.3	0.48				
19	83.41	8383.9	51.50				
20	65.43	6577.2	16.13				


0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
δ / ppm

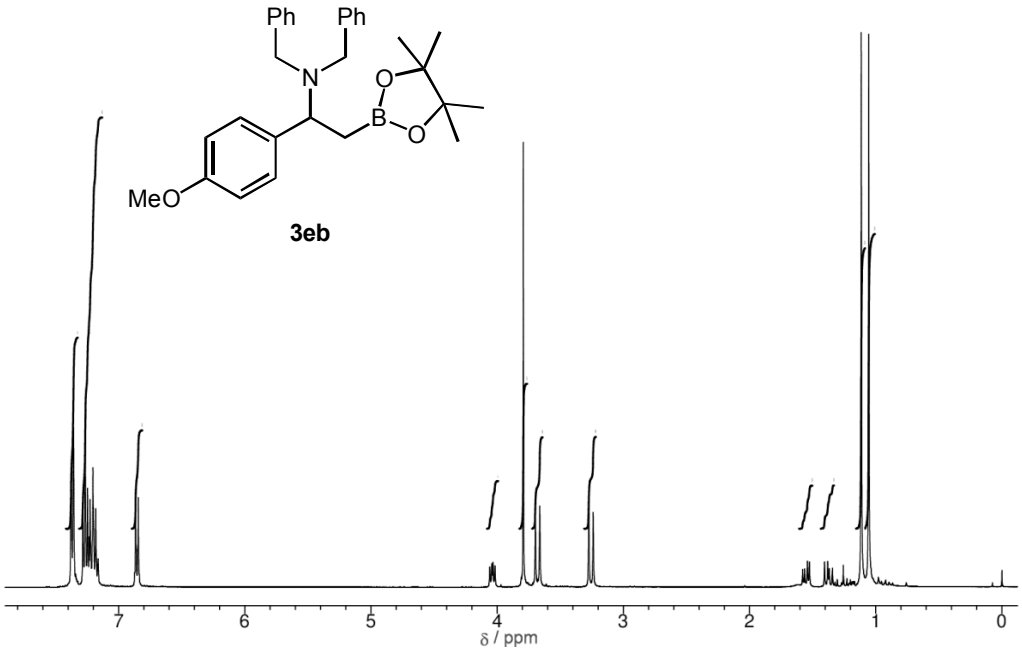
[^{1}H and ^{13}C NMR Spectra of **3db**]



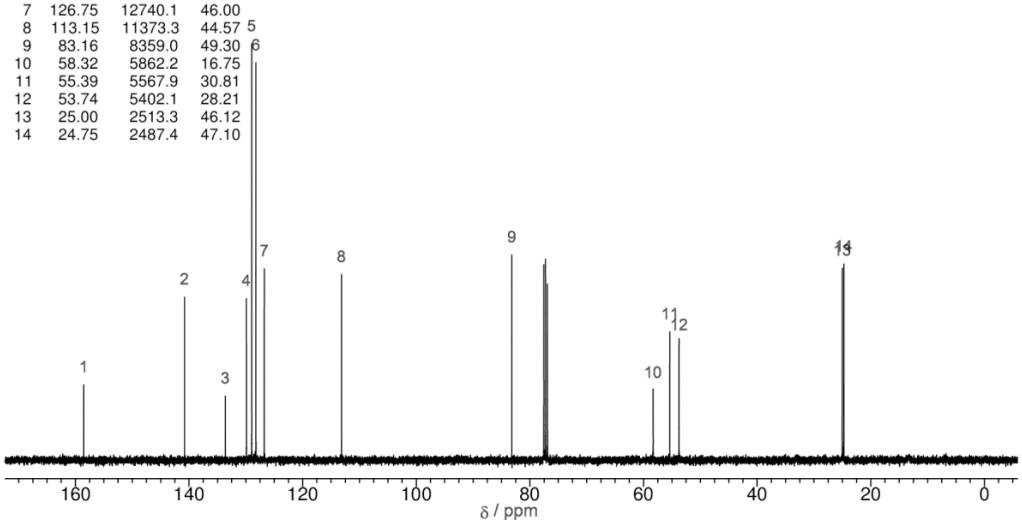


No.	ppm	Hz	Height
1	141.42	14076.7	10.73
2	140.73	14008.1	23.93
3	128.99	12838.9	100
4	128.90	12830.3	31.77
5	128.25	12765.4	83.67
6	127.89	12729.2	46.40
7	126.93	12633.8	18.48
8	126.78	12619.5	46.69
9	83.19	8280.3	21.17
10	59.05	5878.0	17.39
11	53.84	5359.2	37.53
12	24.97	2485.8	30.55
13	24.73	2461.9	45.96

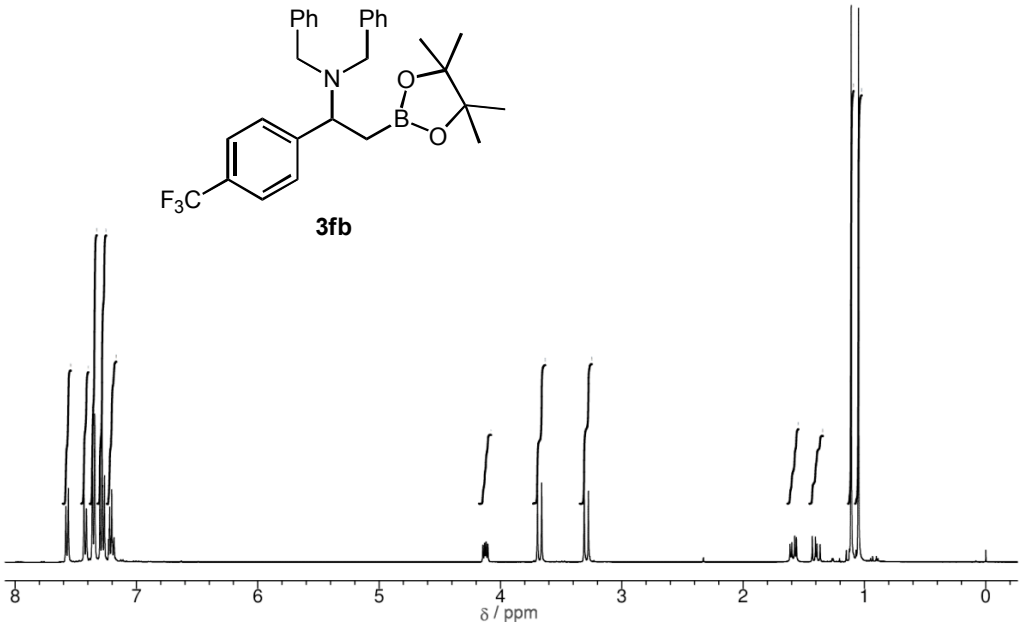
[^{1}H and ^{13}C NMR Spectra of **3eb**]

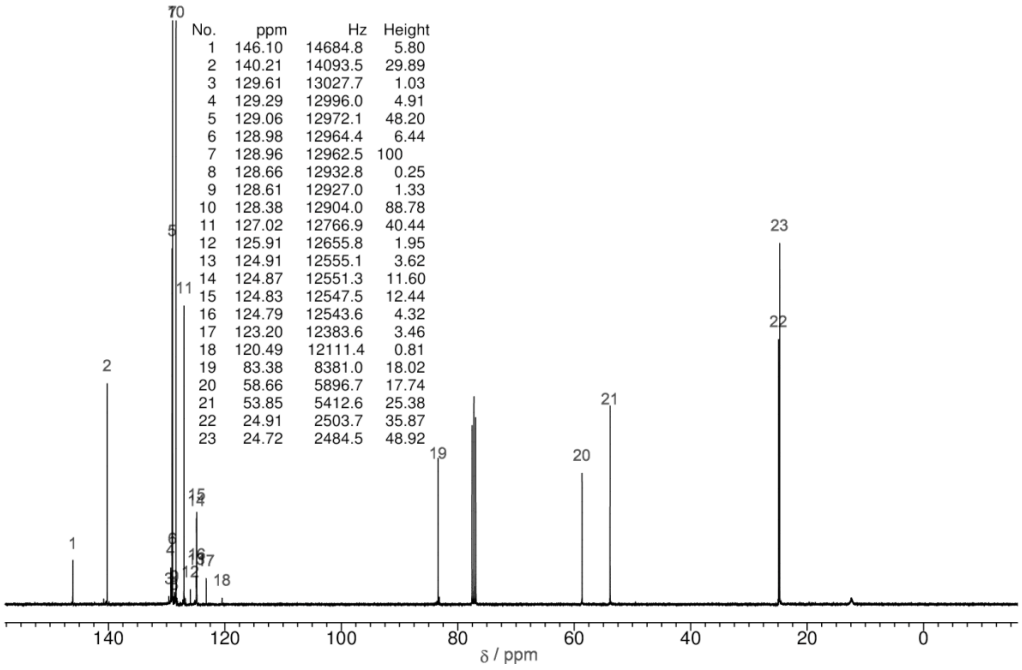


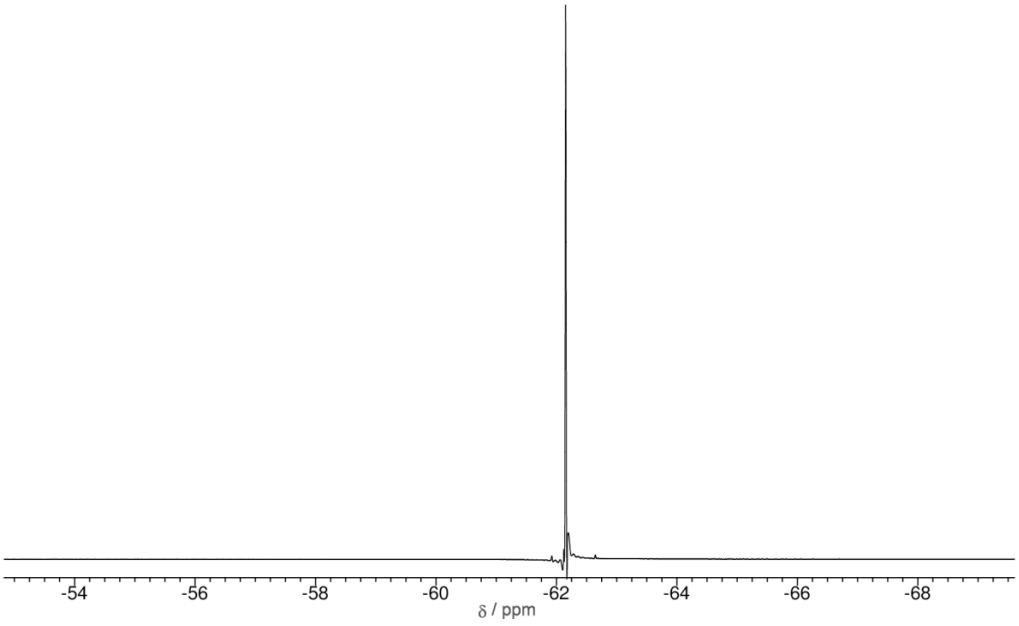
No.	ppm	Hz	Height
1	158.53	15934.7	18.08
2	140.79	14151.9	39.18
3	133.60	13429.2	15.37
4	129.89	13055.4	38.82
5	128.97	12963.4	100
6	128.23	12888.7	95.42
7	126.75	12740.1	46.00
8	113.15	11373.3	44.57
9	83.16	8359.0	49.30
10	58.32	5862.2	16.75
11	55.39	5567.9	30.81
12	53.74	5402.1	28.21
13	25.00	2513.3	46.12
14	24.75	2487.4	47.10



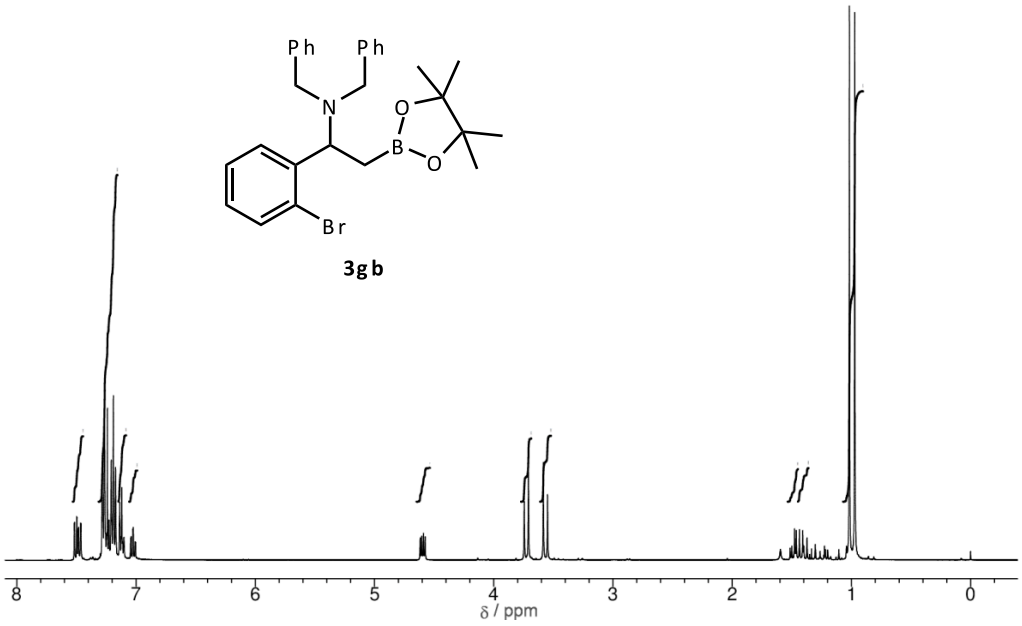
[^{1}H, ^{13}C, and ^{19}F NMR Spectra of **3fb**]

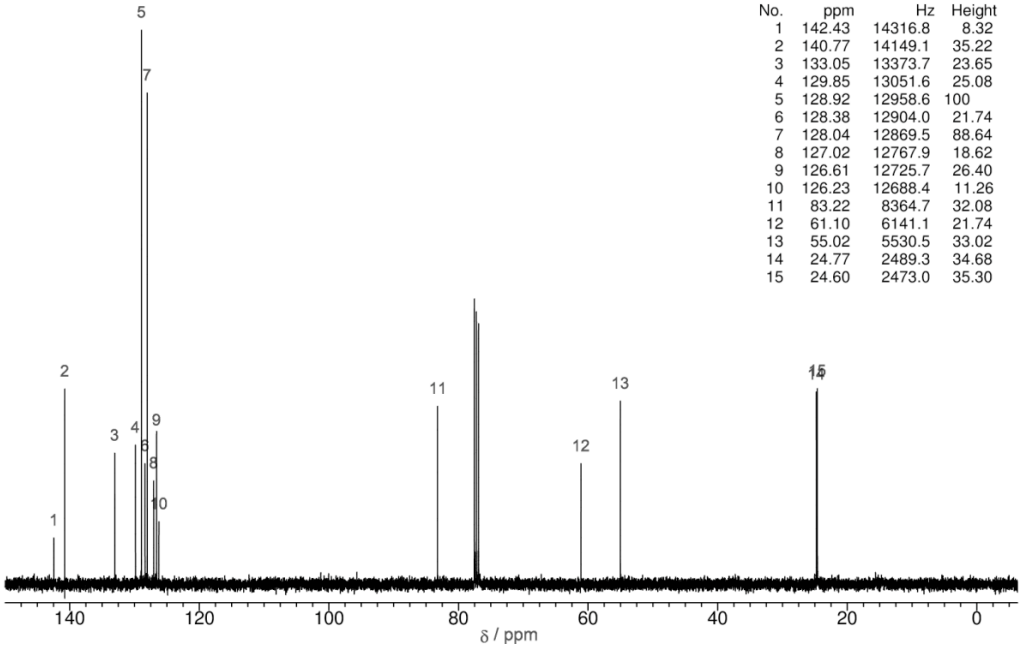




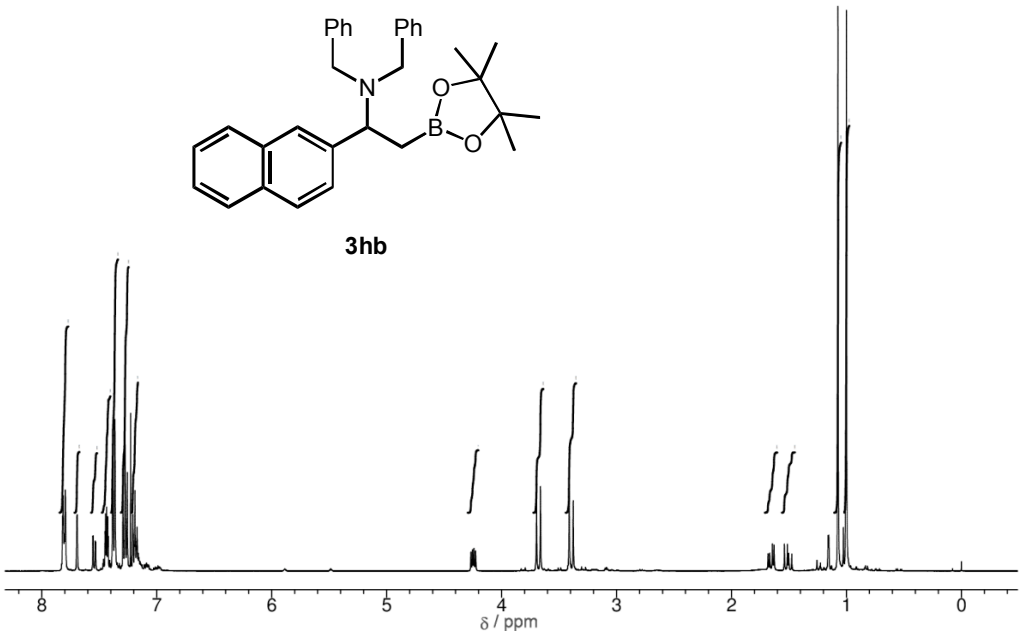

-54
-56
-58
-60
-62
-64
-66
-68
δ / ppm

[^{1}H and ^{13}C NMR Spectra of **3gb**]

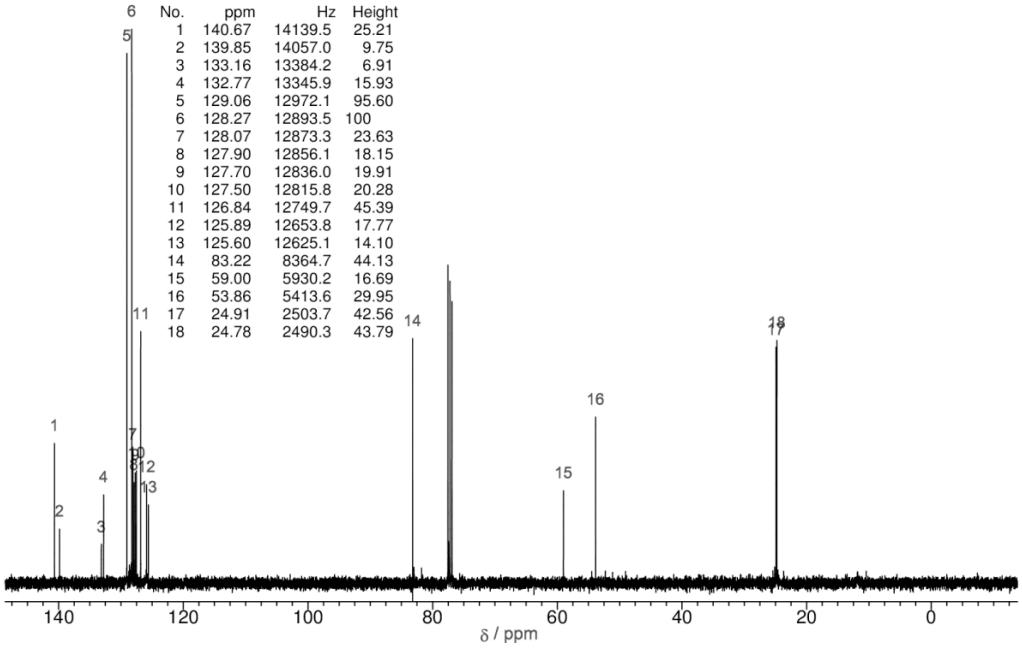




[^{1}H and ^{13}C NMR Spectra of **3hb**]

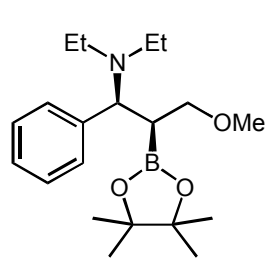


3hb



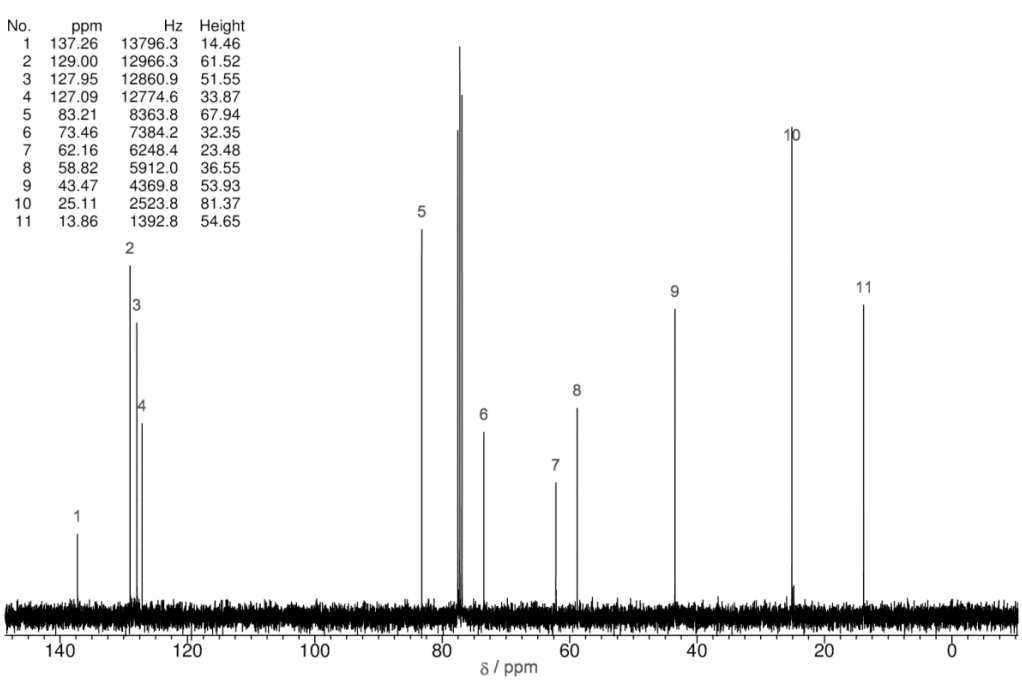
No.	ppm	Hz	Height
1	140.67	14139.5	25.21
2	139.85	14057.0	9.75
3	133.16	13384.2	6.91
4	132.77	13345.9	15.93
5	129.06	12972.1	95.60
6	128.27	12893.5	100
7	128.07	12873.3	23.63
8	127.90	12856.1	18.15
9	127.70	12836.0	19.91
10	127.50	12815.8	20.28
11	126.84	12749.7	45.39
12	125.89	12653.8	17.77
13	125.60	12625.1	14.10
14	83.22	8364.7	44.13
15	59.00	5930.2	16.69
16	53.86	5413.6	29.95
17	24.91	2503.7	42.56
18	24.78	2490.3	43.79

[^{1}H and ^{13}C NMR Spectra of **3ia**]

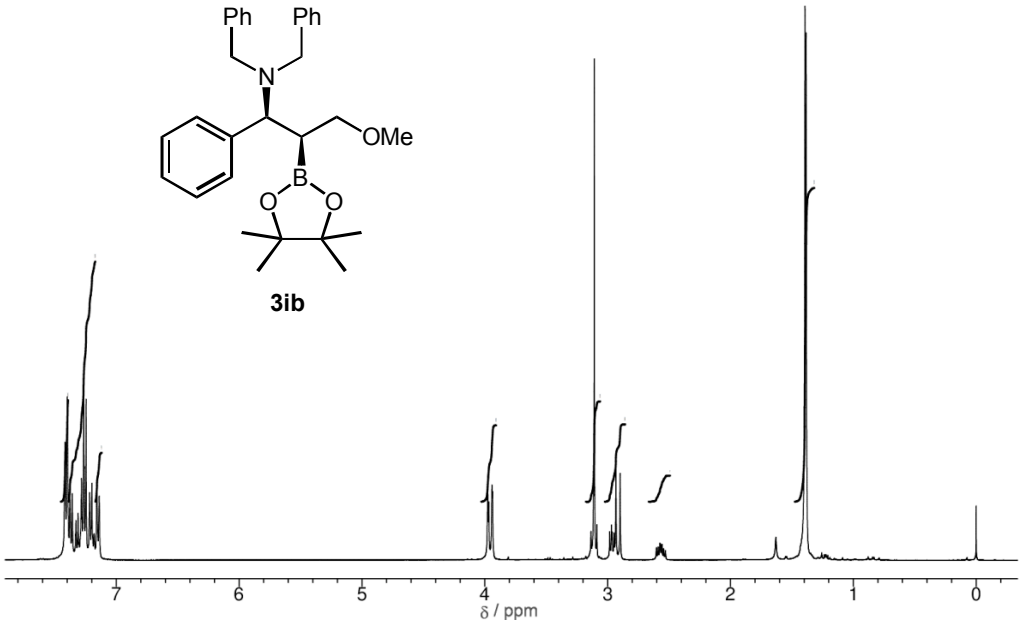


3ia

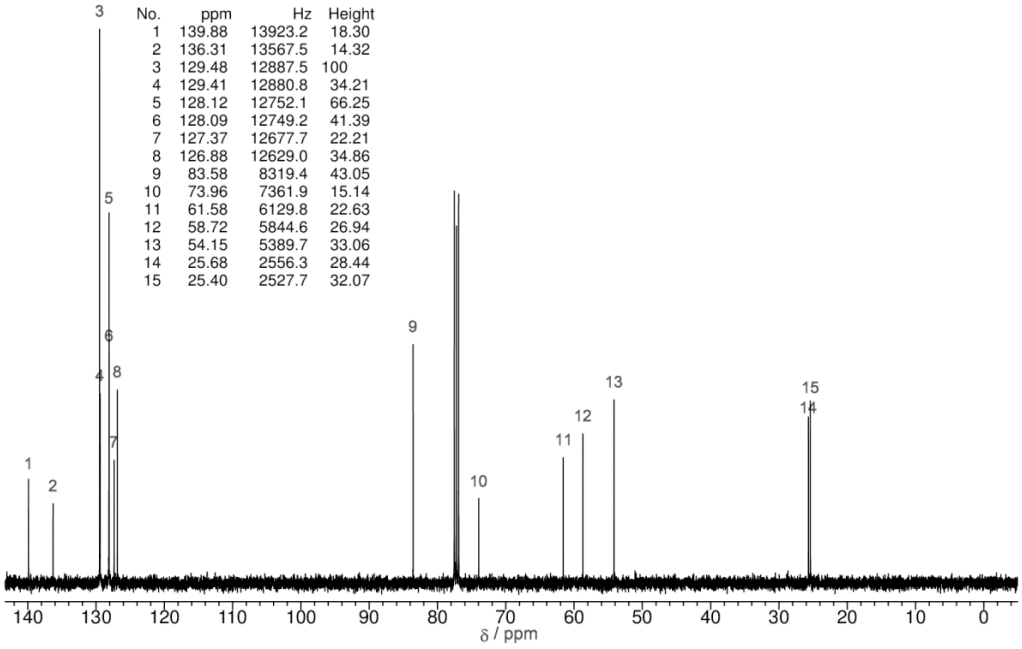
No.	ppm	Hz	Height
1	137.26	13796.3	14.46
2	129.00	12966.3	61.52
3	127.95	12860.9	51.55
4	127.09	12774.6	33.87
5	83.21	8363.8	67.94
6	73.46	7384.2	32.35
7	62.16	6248.4	23.48
8	58.82	5912.0	36.55
9	43.47	4369.8	53.93
10	25.11	2523.8	81.37
11	13.86	1392.8	54.65



[^{1}H and ^{13}C NMR Spectra of **3ib**]

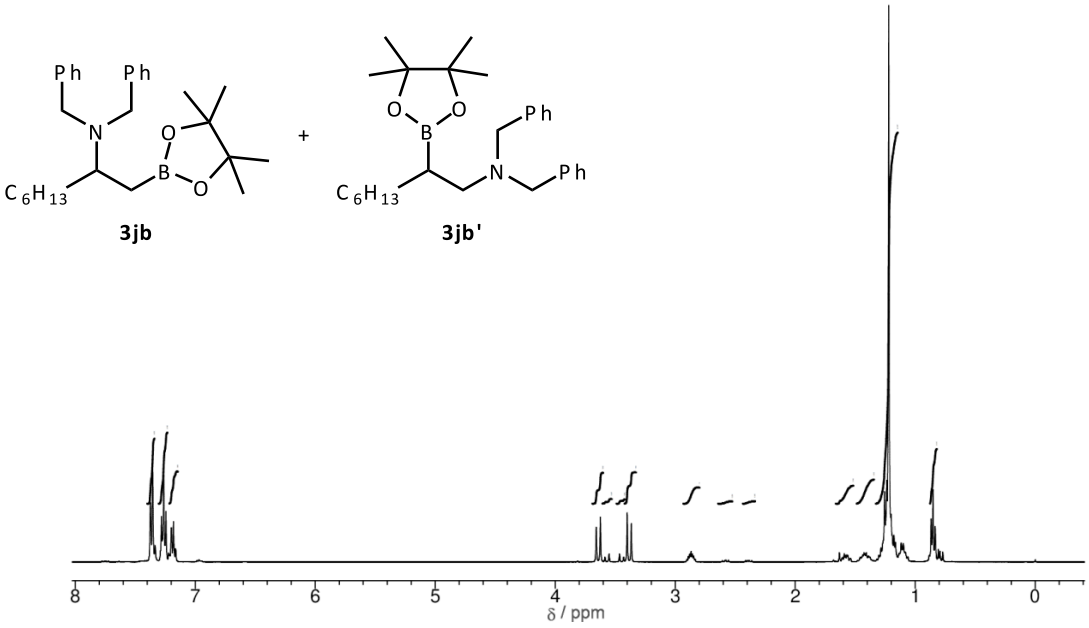


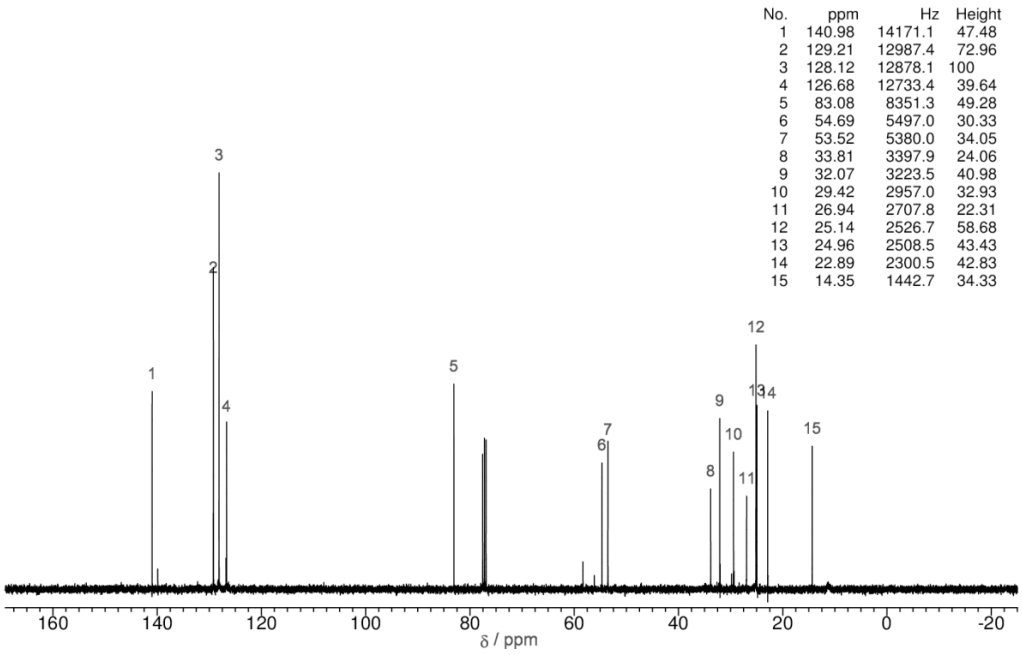
3ib



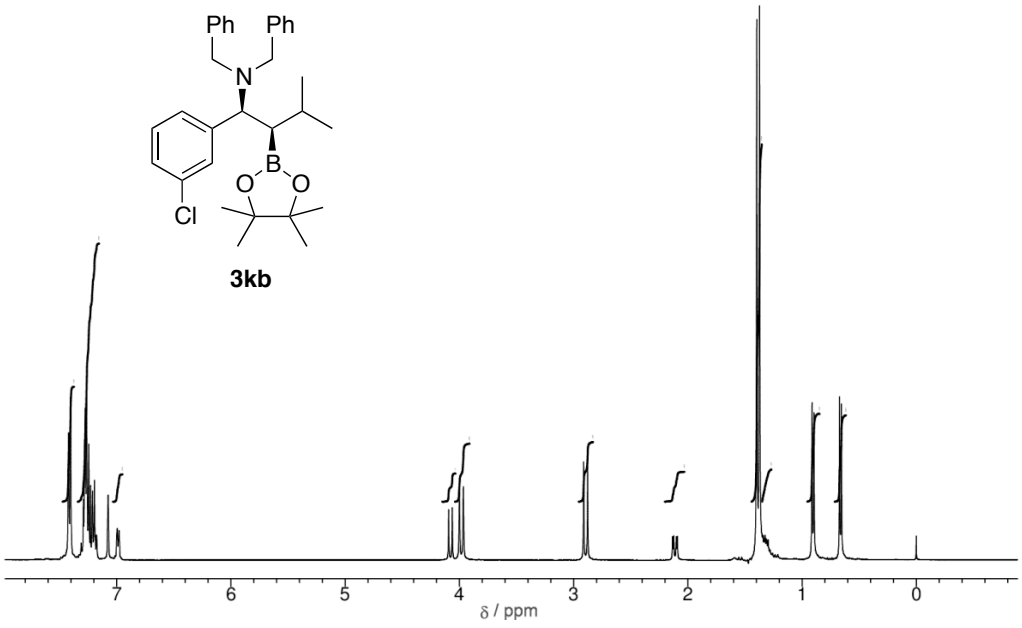
No.	ppm	Hz	Height
1	139.88	13923.2	18.30
2	136.31	13567.5	14.32
3	129.48	12887.5	100
4	129.41	12880.8	34.21
5	128.12	12752.1	66.25
6	128.09	12749.2	41.39
7	127.37	12677.7	22.21
8	126.88	12629.0	34.86
9	83.58	8319.4	43.05
10	73.96	7361.9	15.14
11	61.58	6129.8	22.63
12	58.72	5844.6	26.94
13	54.15	5389.7	33.06
14	25.68	2556.3	28.44
15	25.40	2527.7	32.07

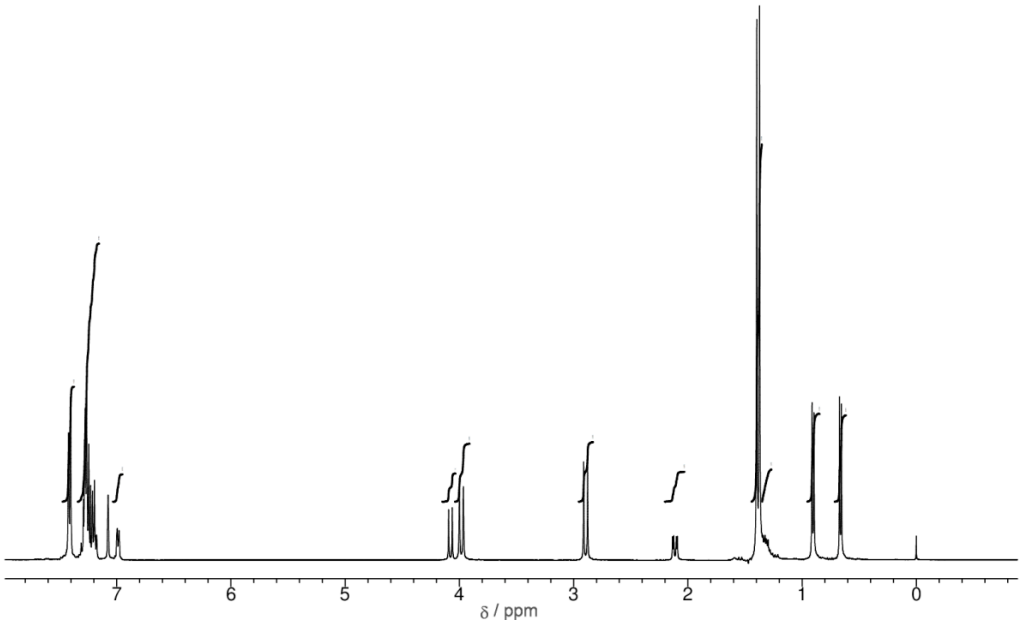
[^{1}H and ^{13}C NMR Spectra of an 88:12 mixture of **3jb** and **3jb'**]



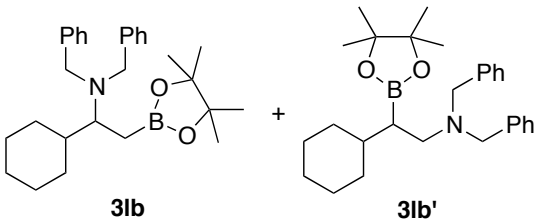


[^{1}H and ^{13}C NMR Spectra of **3kb**]

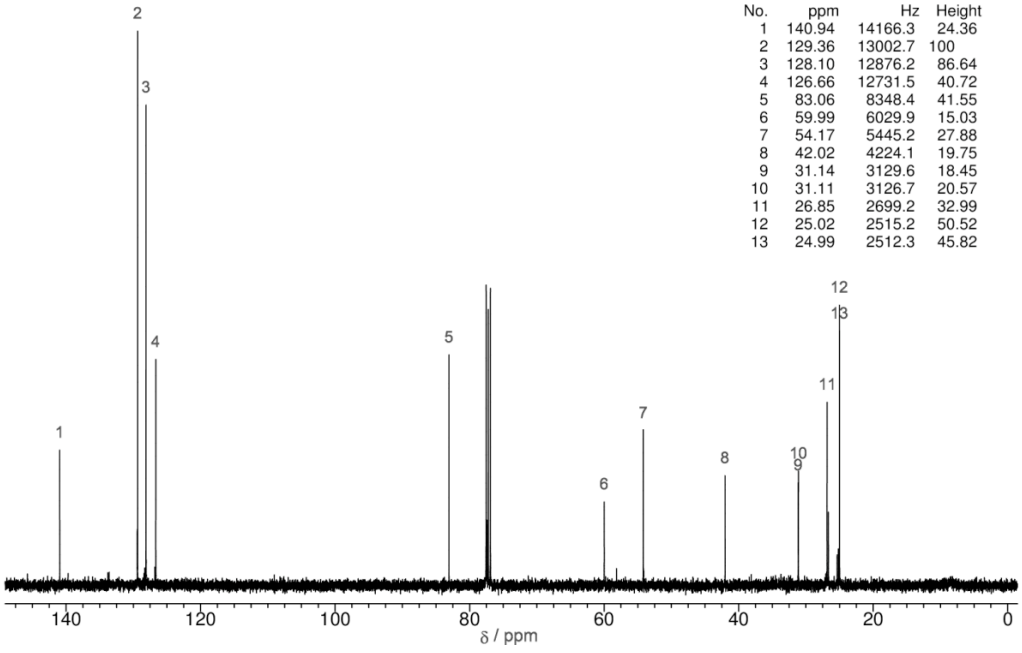




[^{1}H and ^{13}C NMR Spectra of a 90:10 mixture of **3lb** and **3lb'**]

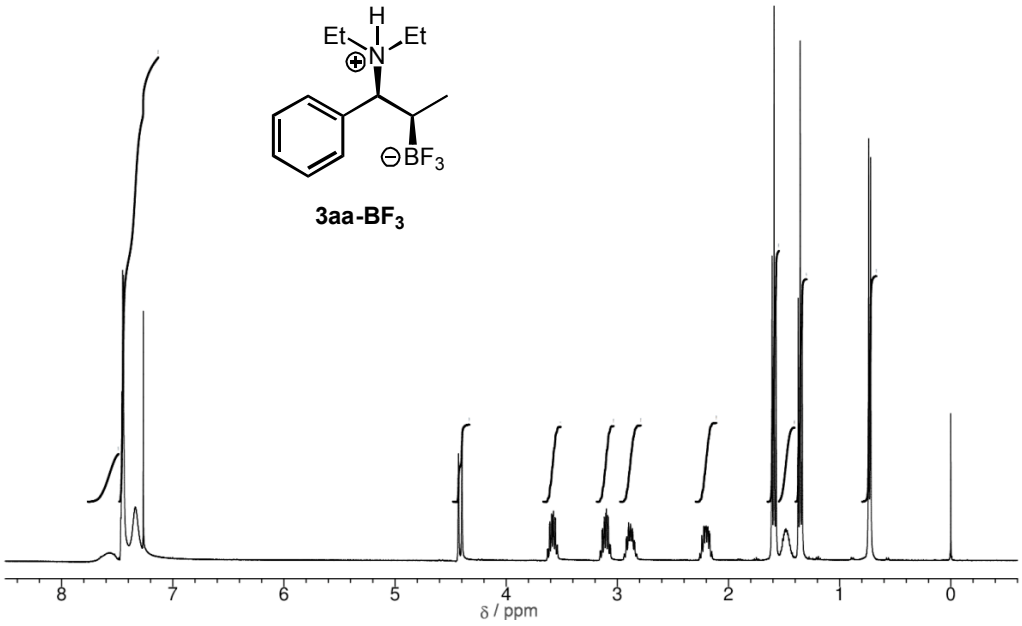


3lb **3lb'**

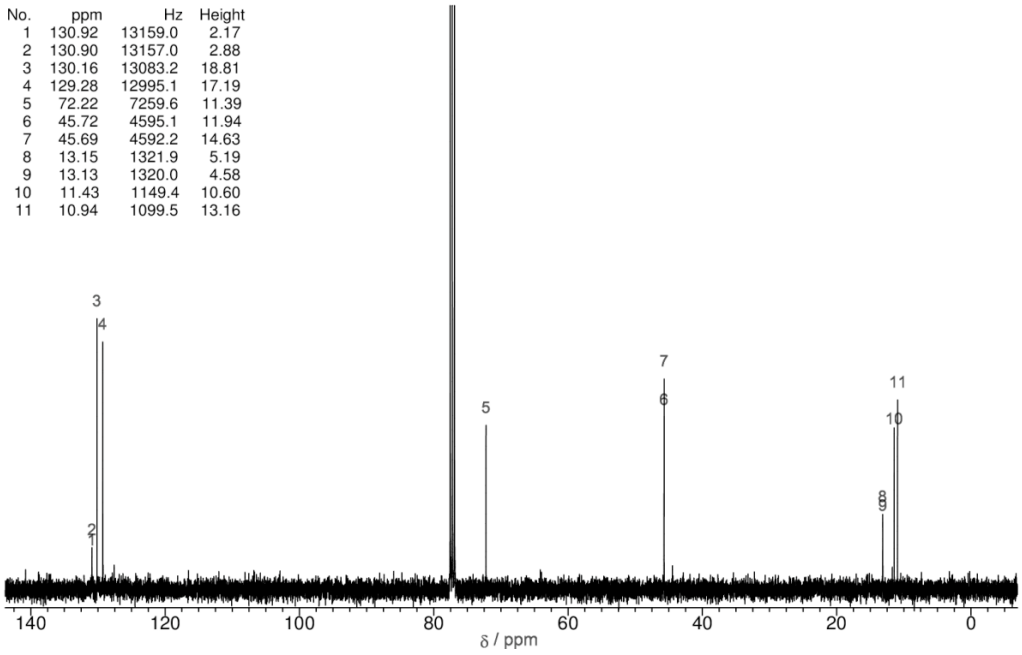


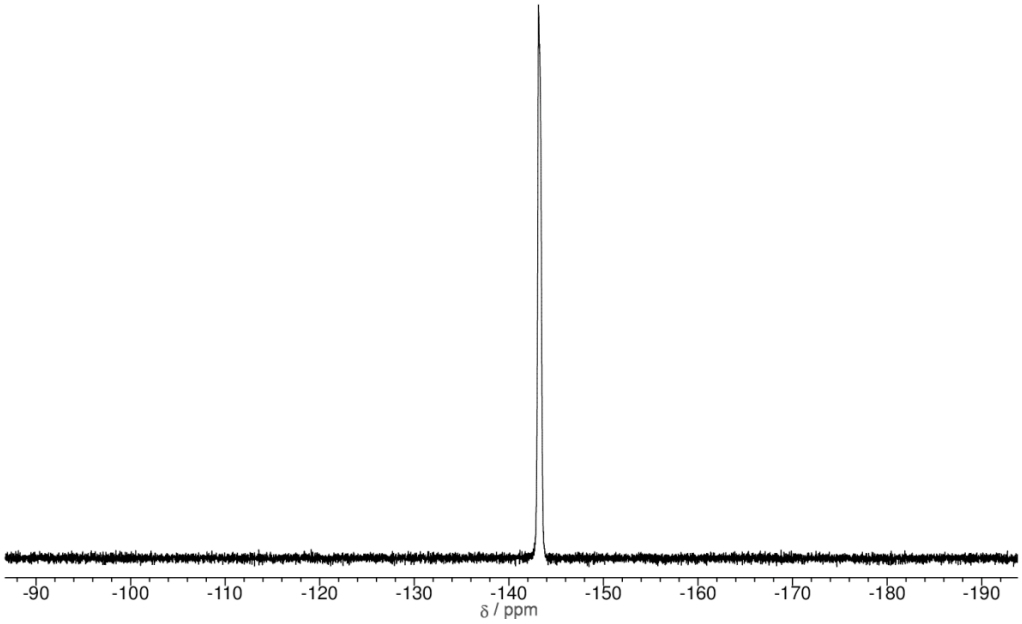
No.	ppm	Hz	Height
1	140.94	14166.3	24.36
2	129.36	13002.7	100
3	128.10	12876.2	86.64
4	126.66	12731.5	40.72
5	83.06	8348.4	41.55
6	59.99	6029.9	15.03
7	54.17	5445.2	27.88
8	42.02	4224.1	19.75
9	31.14	3129.6	18.45
10	31.11	3126.7	20.57
11	26.85	2699.2	32.99
12	25.02	2515.2	50.52
13	24.99	2512.3	45.82

[^{1}H, ^{13}C, and ^{19}F NMR Spectra of **3aa-BF$_3$**]

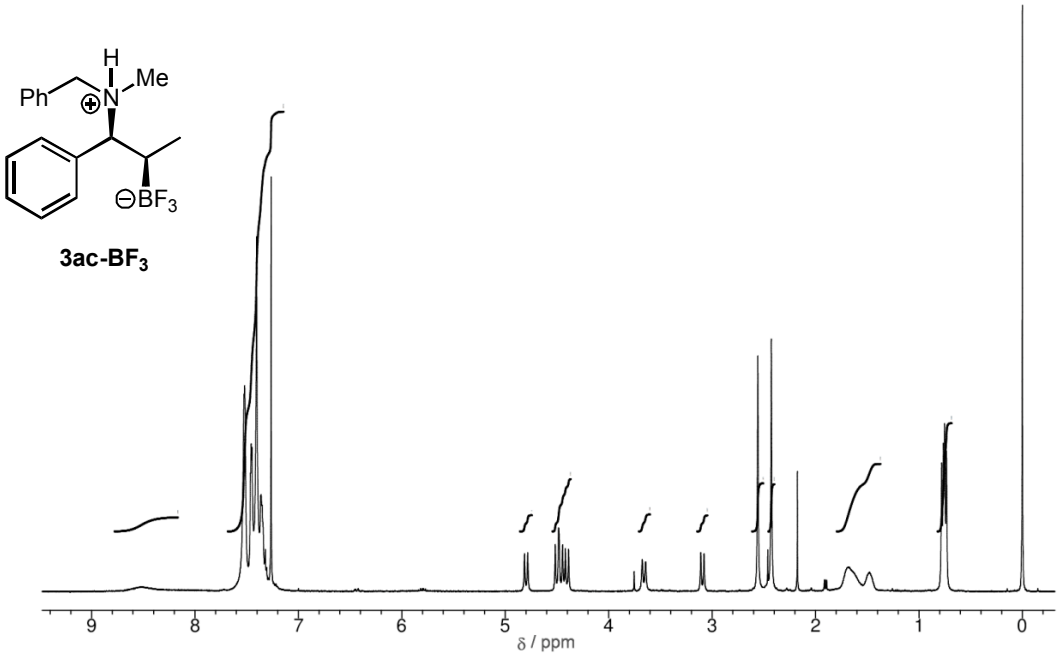


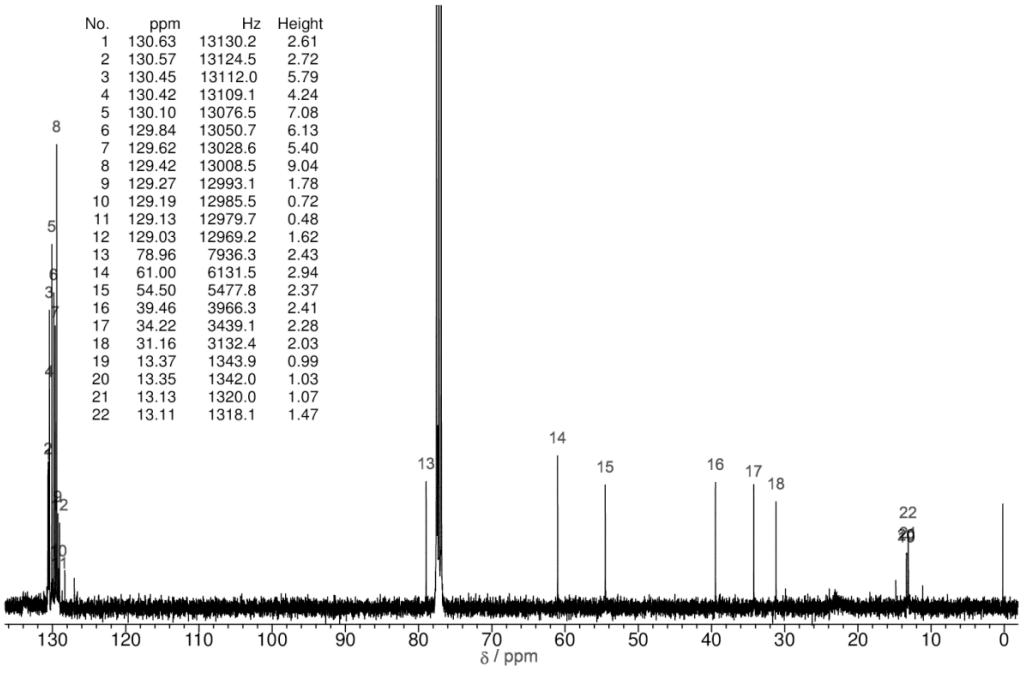
No.	ppm	Hz	Height
1	130.92	13159.0	2.17
2	130.90	13157.0	2.88
3	130.16	13083.2	18.81
4	129.28	12995.1	17.19
5	72.22	7259.6	11.39
6	45.72	4595.1	11.94
7	45.69	4592.2	14.63
8	13.15	1321.9	5.19
9	13.13	1320.0	4.58
10	11.43	1149.4	10.60
11	10.94	1099.5	13.16

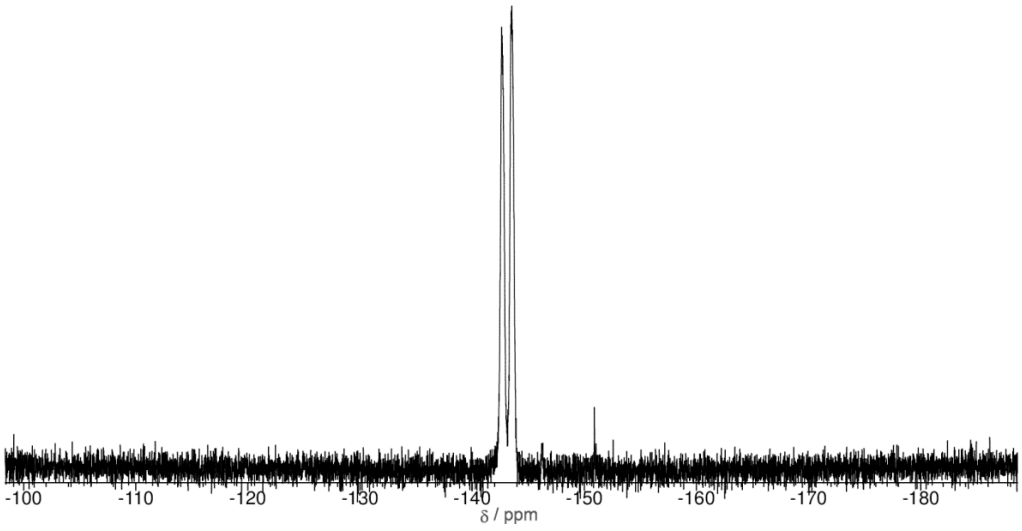



-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
δ / ppm

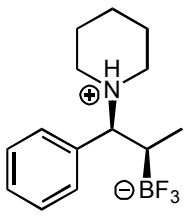
[^{1}H, ^{13}C, and ^{19}F NMR Spectra of **3ac-BF$_3$**]



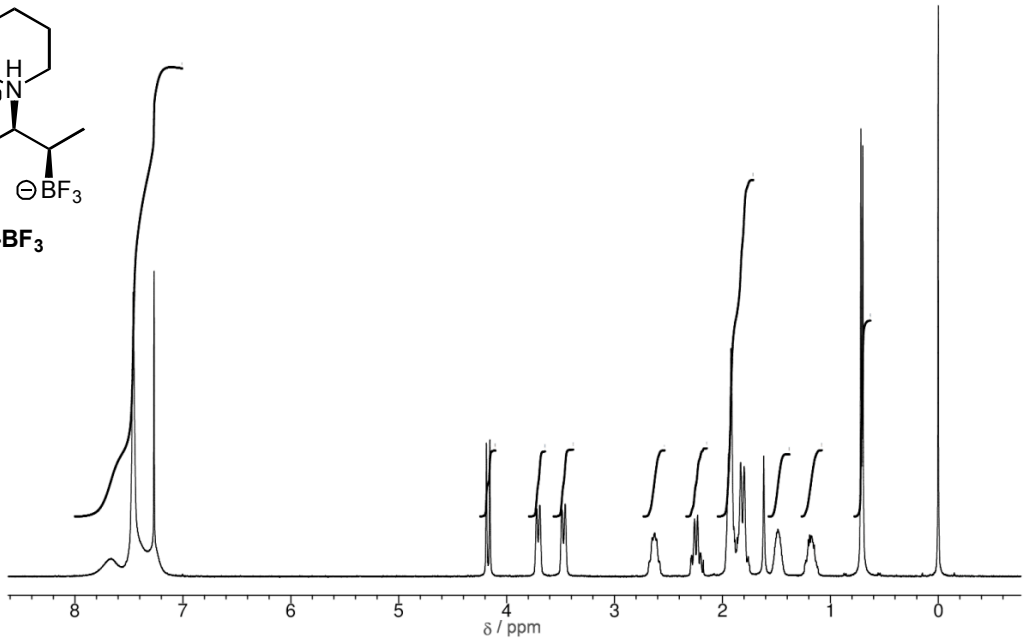



-100
-110
-120
-130
-140
-150
-160
-170
-180
δ / ppm

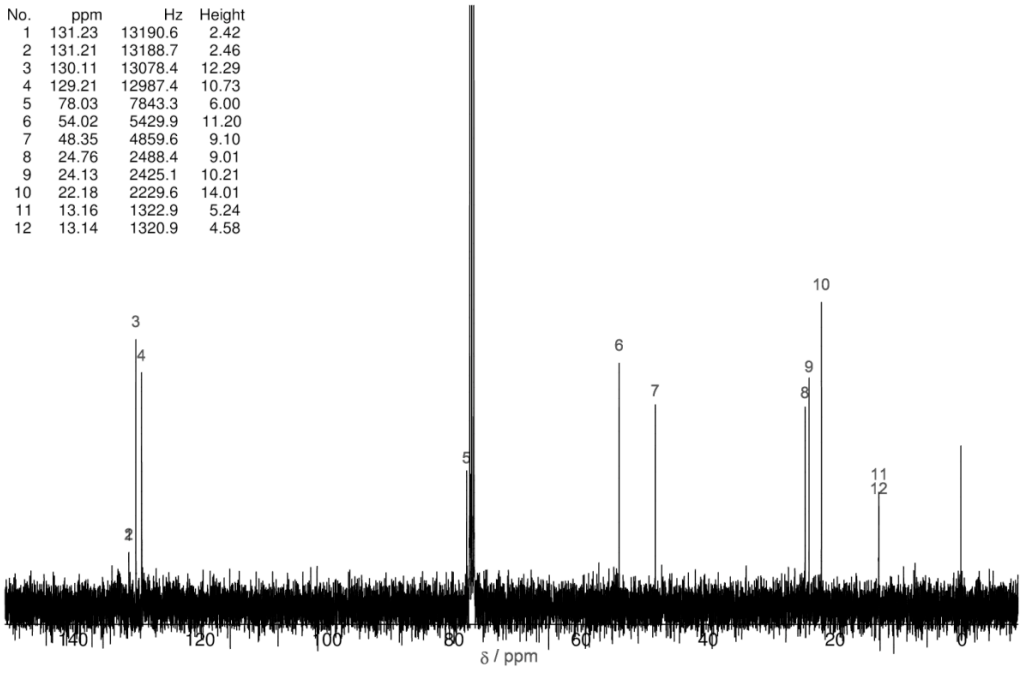
[^{1}H, ^{13}C, and ^{19}F NMR Spectra of **3ae-BF$_3$**]

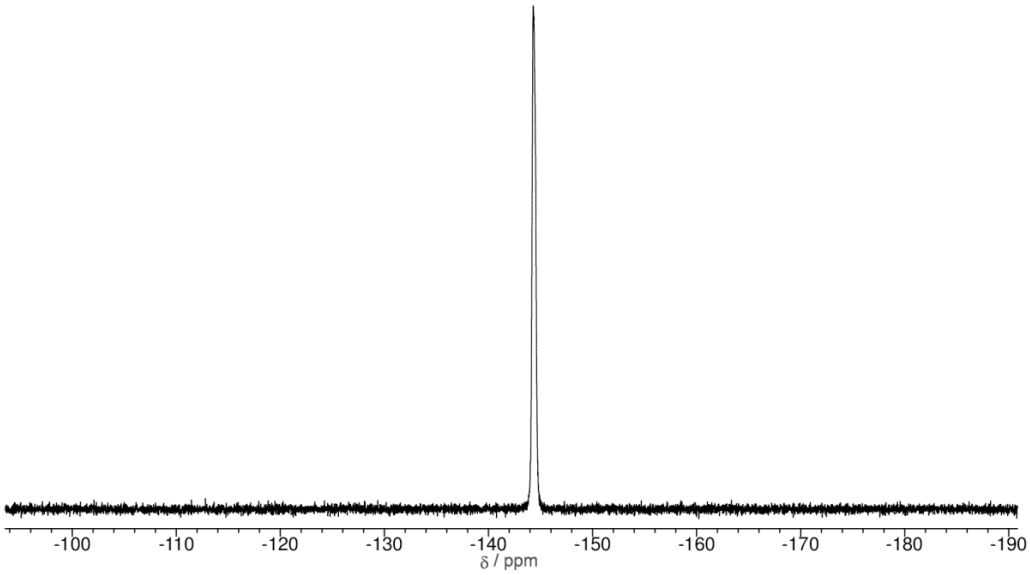


3ae-BF$_3$

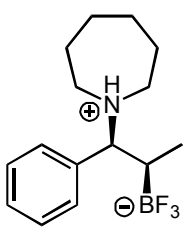


No.	ppm	Hz	Height
1	131.23	13190.6	2.42
2	131.21	13188.7	2.46
3	130.11	13078.4	12.29
4	129.21	12987.4	10.73
5	78.03	7843.3	6.00
6	54.02	5429.9	11.20
7	48.35	4859.6	9.10
8	24.76	2488.4	9.01
9	24.13	2425.1	10.21
10	22.18	2229.6	14.01
11	13.16	1322.9	5.24
12	13.14	1320.9	4.58

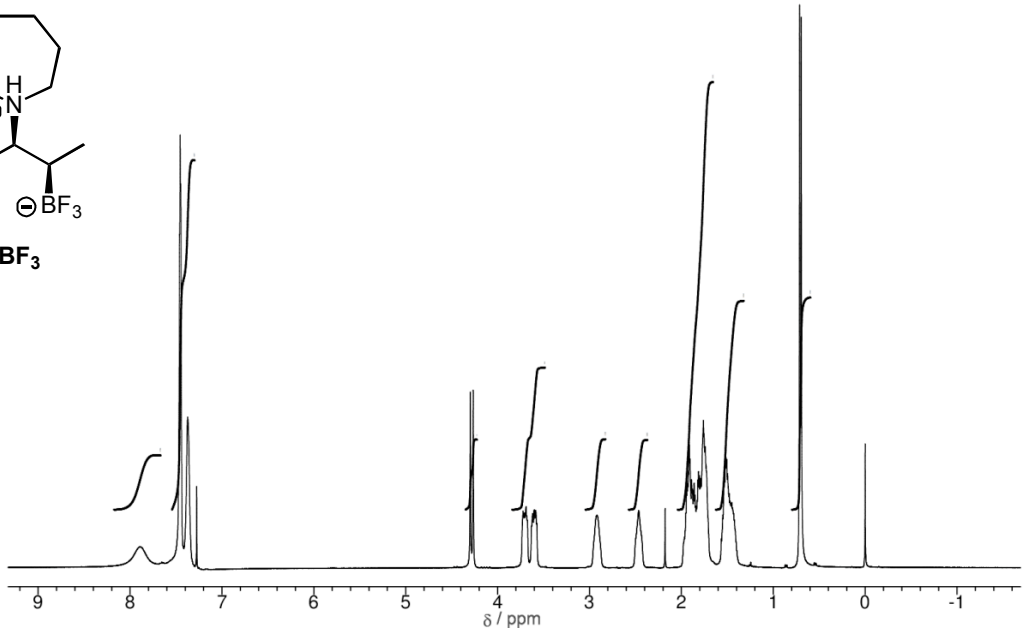



-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
δ / ppm

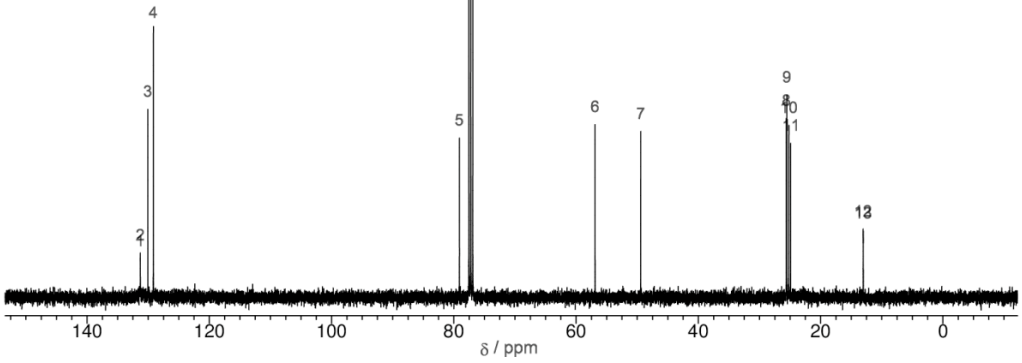
[^{1}H, ^{13}C, and ^{19}F NMR Spectra of **3af-BF$_3$**]

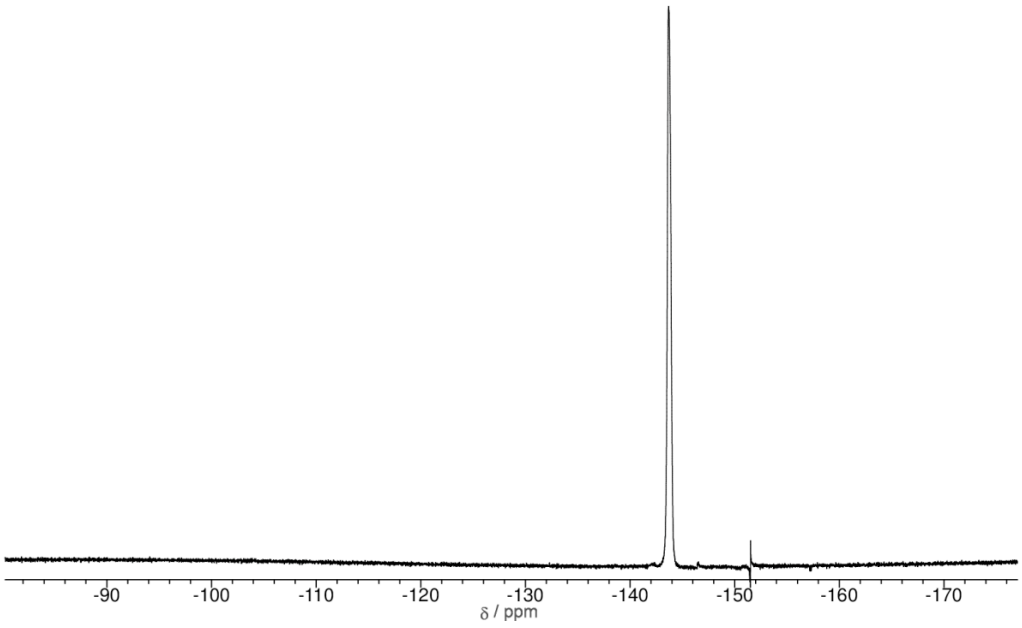


3af-BF$_3$

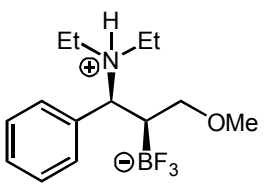


No.	ppm	Hz	Height
1	131.31	13198.3	6.94
2	131.29	13196.3	7.98
3	130.06	13072.7	33.89
4	129.16	12982.6	48.13
5	79.10	7950.7	28.71
6	56.89	5718.4	31.13
7	49.41	4966.9	29.90
8	25.60	2573.7	32.25
9	25.51	2564.1	36.48
10	25.19	2531.5	30.99
11	24.91	2503.7	27.77
12	13.04	1310.4	12.28
13	13.02	1308.5	11.94



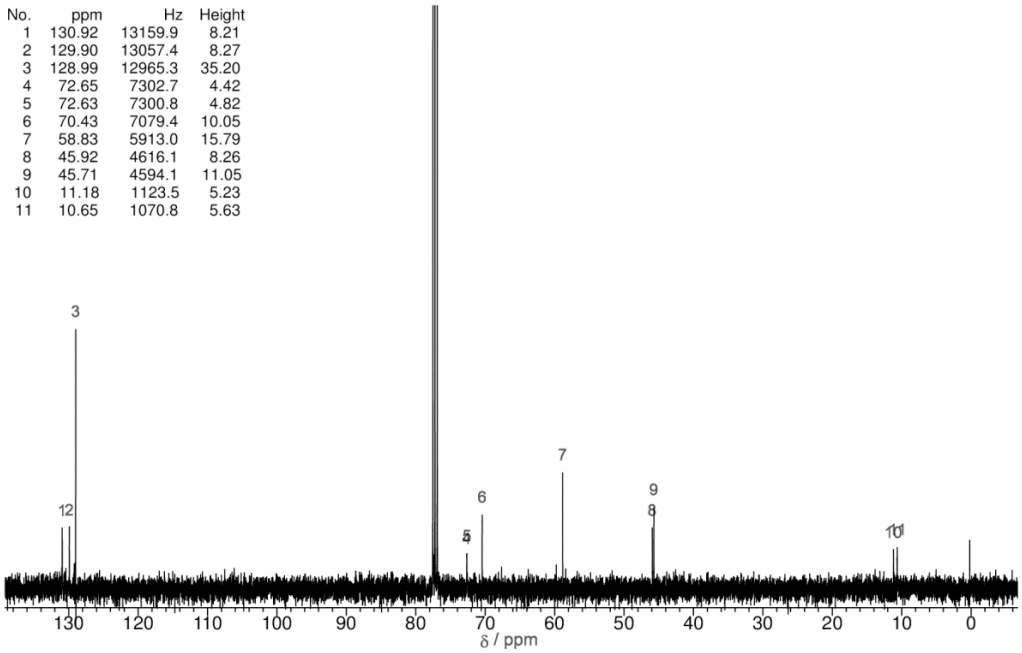

-90
-100
-110
-120
-130
-140
-150
-160
-170
δ / ppm

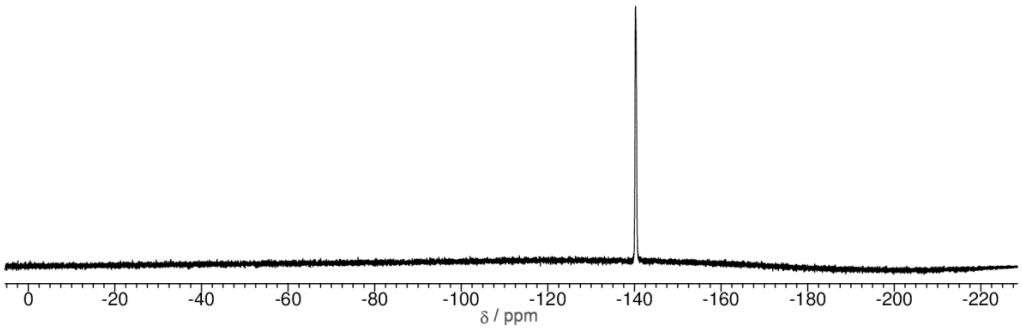
[^{1}H, ^{13}C, and ^{19}F NMR Spectra of **3ia-BF$_3$**]



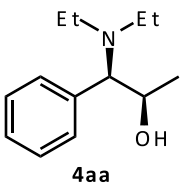
3ia-BF$_3$

No.	ppm	Hz	Height
1	130.92	13159.9	8.21
2	129.90	13057.4	8.27
3	128.99	12965.3	35.20
4	72.65	7302.7	4.42
5	72.63	7300.8	4.82
6	70.43	7079.4	10.05
7	58.83	5913.0	15.79
8	45.92	4616.1	8.26
9	45.71	4594.1	11.05
10	11.18	1123.5	5.23
11	10.65	1070.8	5.63

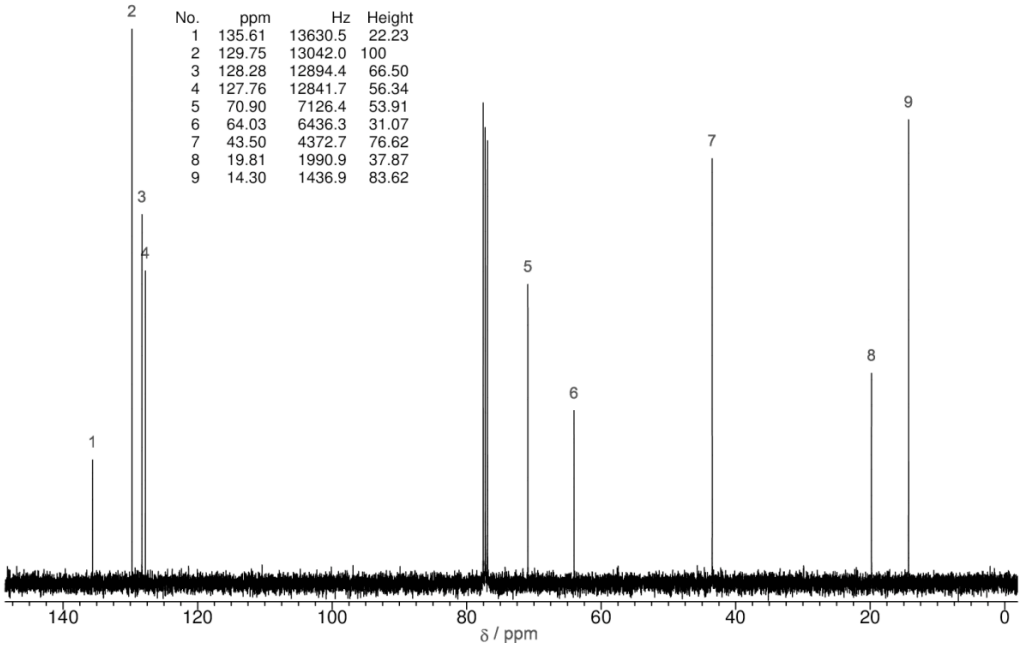



0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
δ / ppm

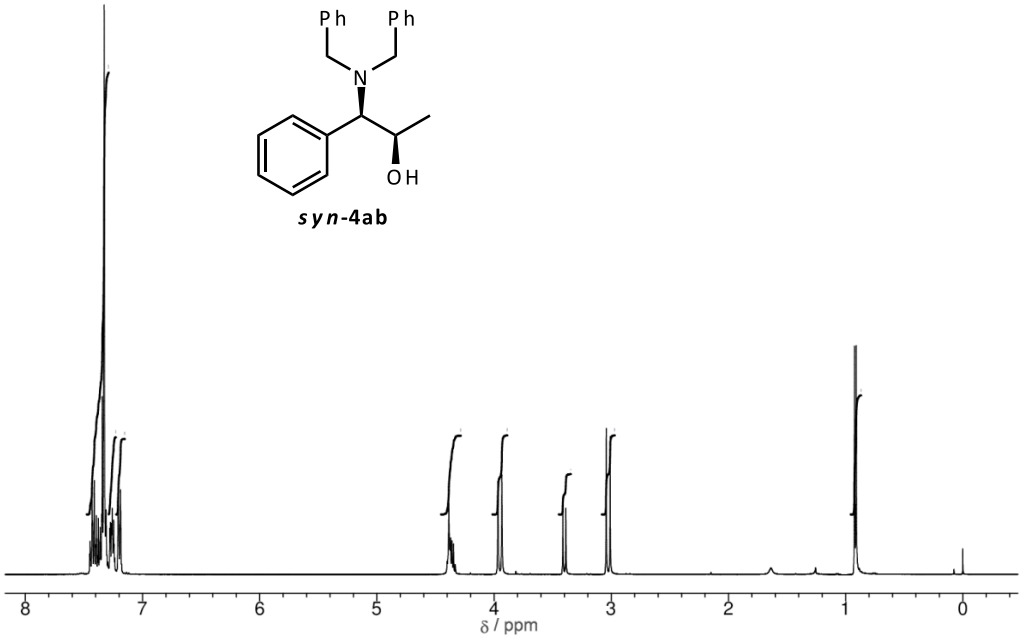
[^{1}H and ^{13}C NMR Spectra of **4aa**]

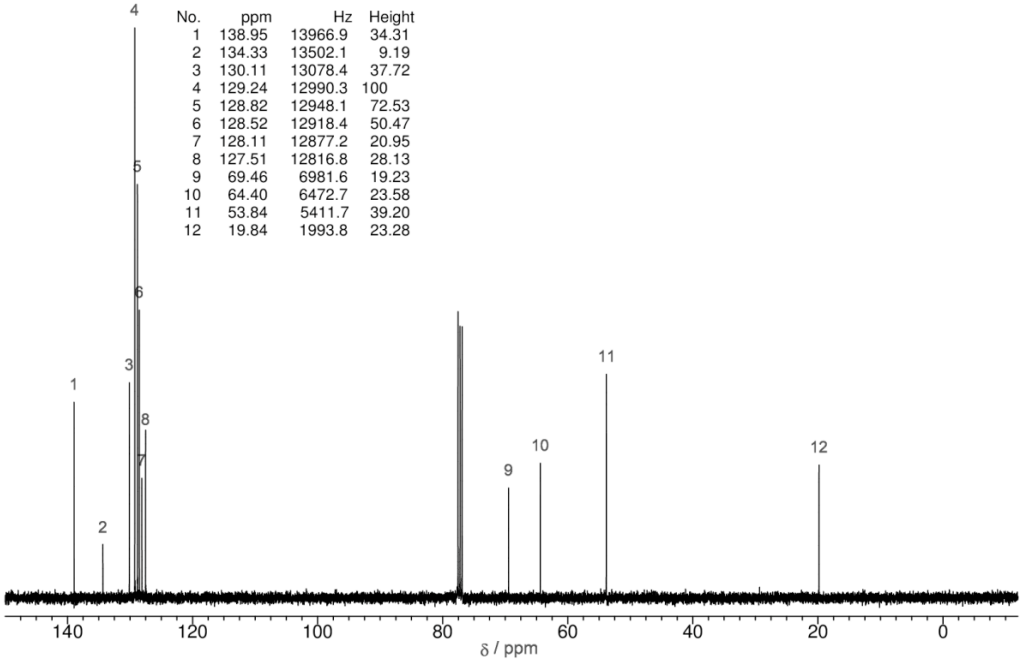


4aa

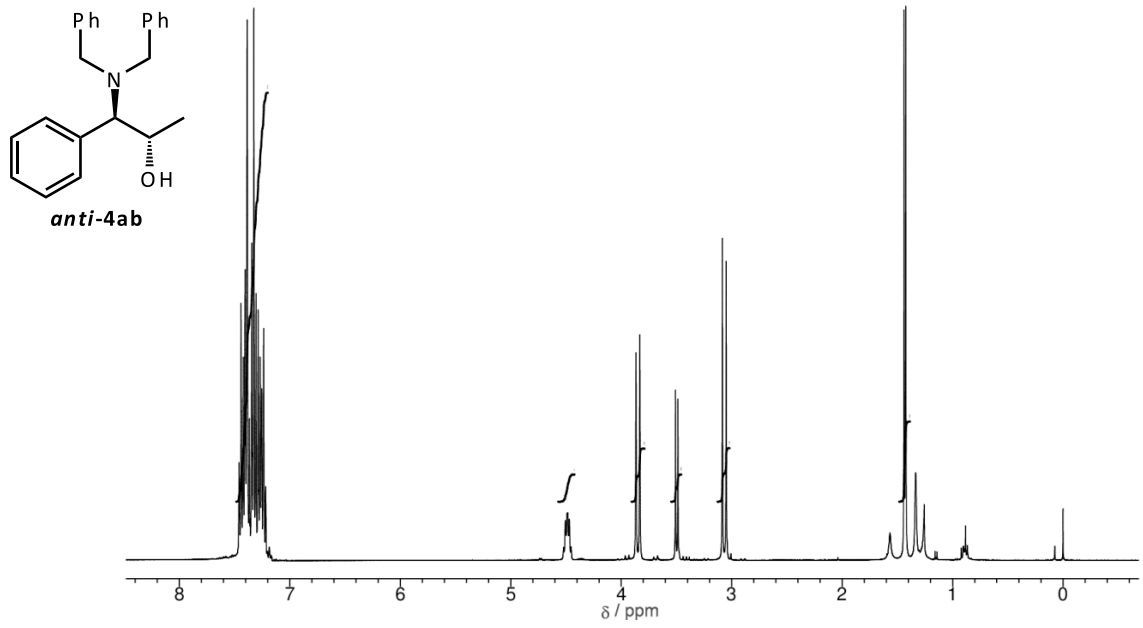


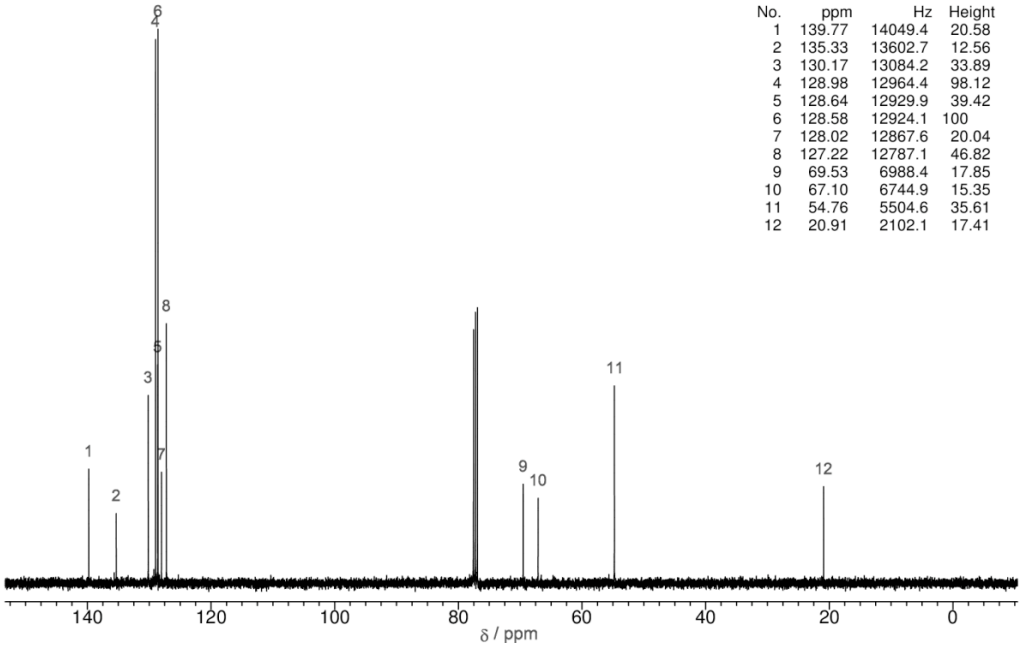
[^{1}H and ^{13}C NMR Spectra of ***syn*-4ab**]





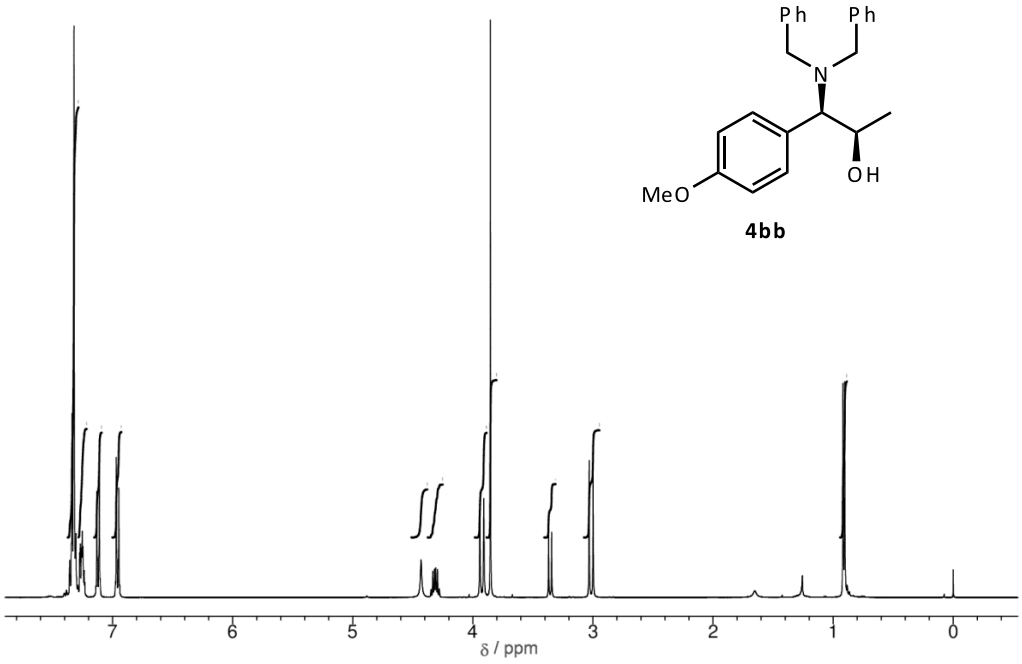
[^{1}H and ^{13}C NMR Spectra of ***anti*-4ab**]

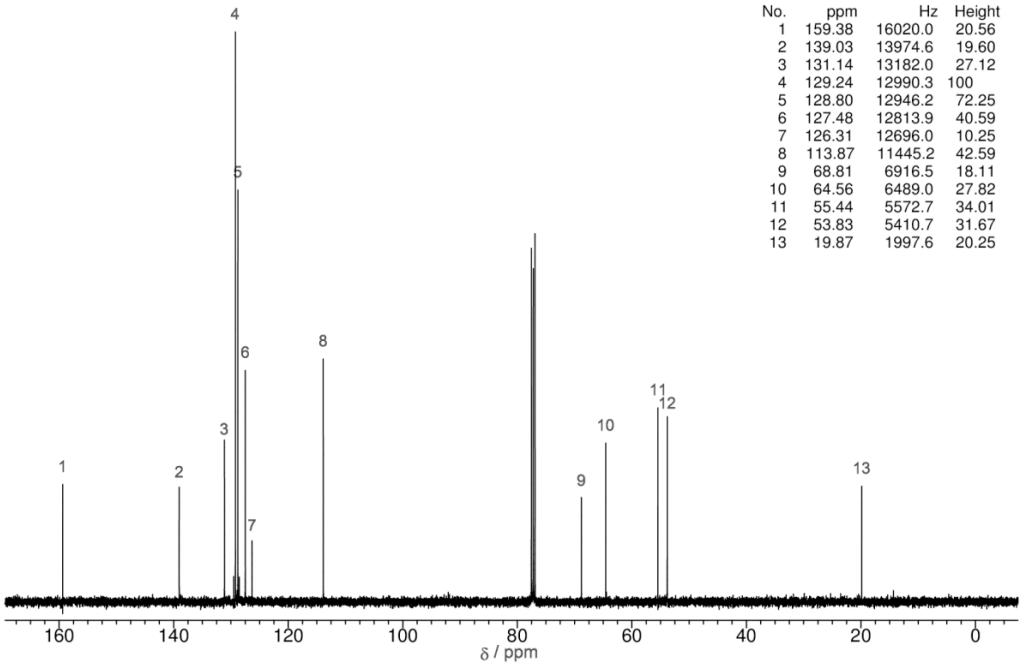




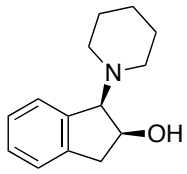
No.	ppm	Hz	Height
1	139.77	14049.4	20.58
2	135.33	13602.7	12.56
3	130.17	13084.2	33.89
4	128.98	12964.4	98.12
5	128.64	12929.9	39.42
6	128.58	12924.1	100
7	128.02	12867.6	20.04
8	127.22	12787.1	46.82
9	69.53	6988.4	17.85
10	67.10	6744.9	15.35
11	54.76	5504.6	35.61
12	20.91	2102.1	17.41

[^{1}H and ^{13}C NMR Spectra of **4bb**]

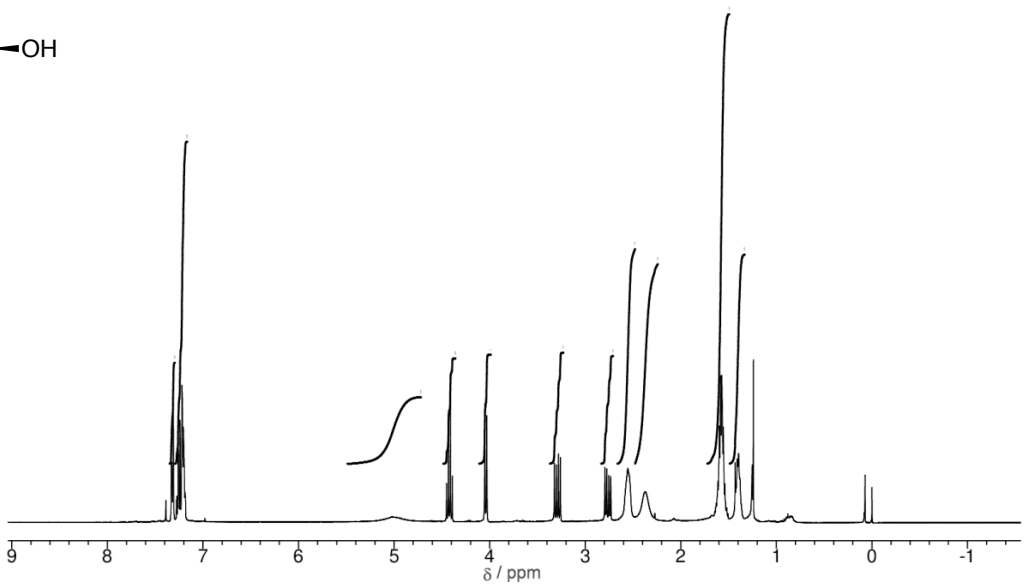




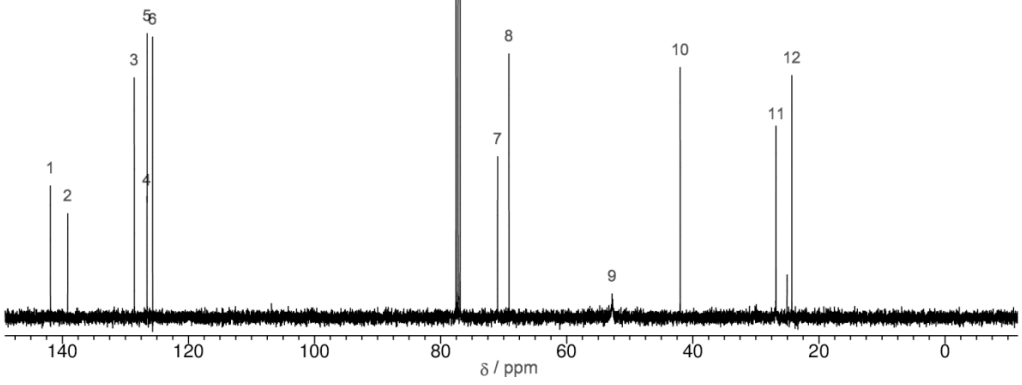
[^{1}H and ^{13}C NMR Spectra of **4me**]



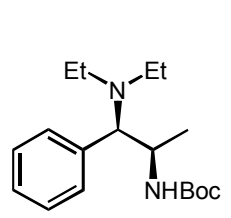
4me



No.	ppm	Hz	Height
1	141.90	14263.1	31.54
2	139.16	13988.0	24.87
3	128.60	12926.1	57.51
4	126.59	12723.8	28.63
5	126.57	12721.9	68.15
6	125.68	12632.8	67.30
7	70.97	7133.1	38.56
8	69.16	6951.9	63.26
9	52.81	5308.2	5.57
10	41.99	4220.3	59.96
11	26.82	2695.4	44.54
12	24.29	2441.4	58.04



[^{1}H and ^{13}C NMR Spectra of **5aa**]



5aa

No.	ppm	Hz	Height
1	156.64	15744.9	10.88
2	136.52	13722.5	21.47
3	129.51	13018.1	71.61
4	128.23	12888.7	37.21
5	127.62	12827.3	18.22
6	79.04	7944.9	6.27
7	68.31	6866.6	26.65
8	46.61	4685.2	12.68
9	43.04	4325.7	61.93
10	28.72	2887.1	100
11	18.97	1906.6	21.91
12	13.60	1366.9	51.02