Diastereo- and Enantioselective CuH-Catalyzed Hydroamination of Strained Trisubstituted Alkenes

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1. General Information

1.1 General Analytical Information

All new compounds were characterized by NMR spectroscopy, IR spectroscopy, elemental analysis or high resolution mass spectrometry, optical rotation (if chiral and non-racemic) and melting point analysis (if solids). ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ on a Bruker 400 or 500 MHz spectrometer. Chemical shifts for ^{1}H NMR are reported as follows: chemical shift in reference to residual $CHCl_3$ at 7.26 ppm (δ ppm), multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, sex = sextet, sep = septet, dd = double of doublets, td = triplet of doublets, m = multiplet), coupling constant (Hz), and integration. Chemical shifts for ^{13}C NMR are reported in terms of chemical shift in reference to the $CDCl_3$ solvent signal (77.16 ppm). Chemical shifts for ^{19}F NMR are reported in ppm relative to $CFCl_3$ (0.00 ppm). IR spectra were recorded on a Thermo Scientific Nicolet iS5 spectrometer (iD5 ATR, diamond) and are reported in terms of frequency of absorption (cm^{-1}). Melting points were measured on a Mel-Temp capillary melting point apparatus. Optical rotations were measured using a Jasco P-1010 digital polarimeter. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA. High-resolution mass spectra were recorded on a JEOL AccuTOF LC-Plus 46 DART system. Enantiomeric excesses (ee's) were determined by chiral SFC analysis using a Waters Acquity UPC2 instrument; specific columns and analytical methods are provided in the experimental details for individual compounds; the wavelengths of light used for chiral analyses are provided with the associated chromatograms. Thin-layer chromatography (TLC) was performed on silica gel 60Å F_{254} plates (SiliaPlate from Silicycle) and visualized with UV light, iodine or potassium permanganate stain. Preparatory thin-layer chromatography (Prep-TLC) was performed on silica gel GF with UV 254 (20 x 20 cm, 1000 microns, catalog # TLG-R10011B-341 from Silicycle) and visualized with UV light. Isolated yields reported reflect the average values from two independent runs.

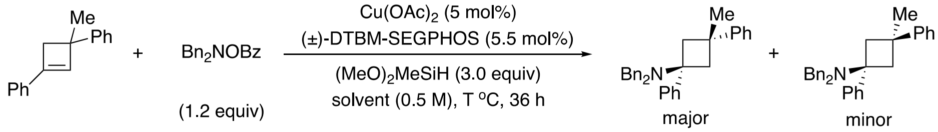
1.2 General Reagent Information

All reactions were performed under a nitrogen atmosphere using the indicated method in the general procedures. Tetrahydrofuran (THF) was purchased from J.T. Baker in CYCLE-TAINER® solvent delivery kegs and purified by passage under argon pressure through two packed columns of neutral alumina and copper(II) oxide. Anhydrous 1,4-dioxane was purchased from Aldrich Chemical Company in a Sure-Seal™ bottle and used as received. Copper(II) acetate was purchased from Strem and was used as received. 1,2-Bis((2*S*,5*S*)2,5-diphenylphospholano)ethane, 1,2-Bis((2*R*,5*R*)2,5-diphenylphospholano)ethane (Ph-BPE) ligands were purchased from Namena Corp. and stored in a nitrogen-filled glove box. DTBM-SEGPHOS was purchased from Takasago International Co. and used as received. Diethoxymethylsilane was purchased from TCI America. Dimethoxy(methyl)silane (DMMS) was purchased from Tokyo Chemical Industry Co. (TCI). Both silanes were stored in a nitrogen-filled glove box at −20 °C for long-term storage. (***Caution****: Dimethoxy(methyl)silane (DMMS, CAS#16881-77-9) is listed by several vendors (TCI, Alfa Aesar) SDS or MSDS as a H318, a category 1 Causes Serious Eye Damage Other vendors (Sigma-Aldrich, Gelest) list DMMS as a H319, a category II Eye Irritant. DMMS should be handled in a well-ventilated fumehood using proper precaution as outlined for the handling of hazardous materials in prudent practices in the laboratory*[1]*. At the end of the reaction either ammonium fluoride in methanol, aqueous sodium hydroxide (1 M) or aqueous hydrochloric acid (1 M) should be carefully added to the reaction mixture. This should be allowed to stir for at least 30 min or the time indicated in the detailed* *reaction procedure*). 1,2-Benzisoxazole was purchased from Tokyo Chemical Industry Co. (TCI) and stored in a refrigerator at 4 °C. All other solvents and commercial reagents were used as received from Sigma Aldrich, Alfa Aesar, Acros Organics, TCI and Combi-Blocks, unless otherwise noted. Flash column chromatography was performed using 40-63 µm silica gel (SiliaFlash® F60 from Silicycle), or with the aid of a Biotage Isolera Automated Flash Chromatography System using prepacked SNAP silica cartridges (10-100 g). Organic solutions were concentrated *in vacuo* using a Buchi rotary evaporator.

2. Optimization and General Procedures for Hydroamination Reactions

2.1 Optimization of CuH-Catalyzed Hydroamination of 1-Arylcyclobutenes

Table S1. Effect of Solvent and Temperature on Hydroamination of 1-Arylcyclobutenes [a]

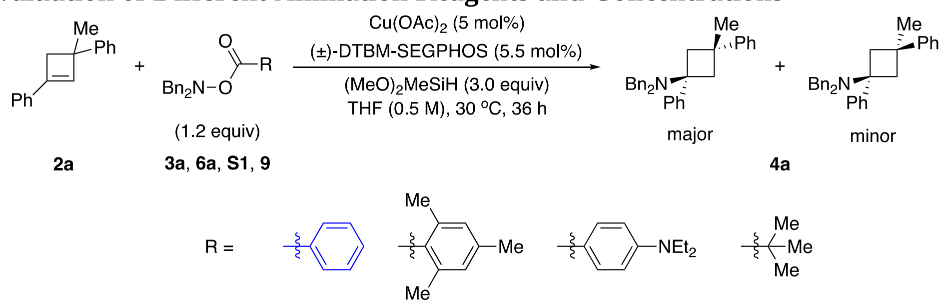


2a **3a** **4a**

solvent	T (°C)	yield (major + minor)
MTBE	40	70% + 10%
dioxane	40	70% + 8%
CyH	40	63% + 10%
toluene	40	68% + 9%
THF	40	80% + 8%
THF	50	80% + 8%
THF	30	80% +6%
THF	rt	61% + 5%
THF	0	<10%

[a]Reactions were conducted on 0.1 mmol scale. Yields were determined by ^{1}H NMR analysis of the crude reaction mixture using 1,1,2,2-tetrachloroethane as the internal standard.

Table S2. Evaluation of Different Amination Reagents and Concentrations[a]



2a **3a**, **6a**, **S1**, **9** **4a**

3a **6a** **S1** **9**

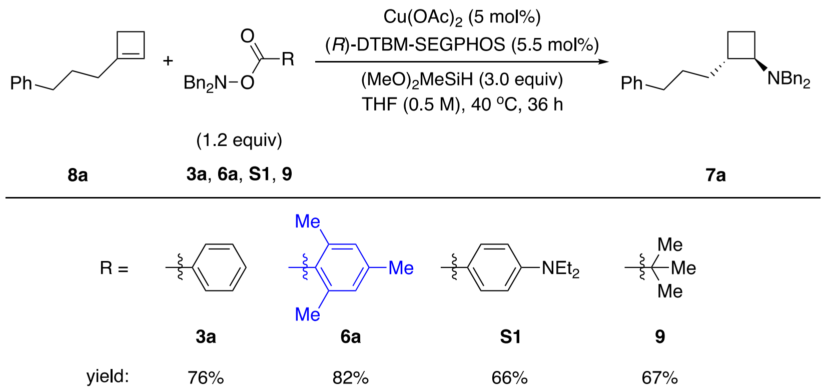
yield (major + minor): 80% + 6% 65% + 5% 74% + 6% 76% + 6%

R = Ph Concentration: 0.25 M (yield: 65% + 4%), 1.0 M (yield: 82% +7%)

[a]Reactions were conducted on 0.1 mmol scale. Yields were determined by ^{1}H NMR analysis of the crude reaction mixture using 1,1,2,2-tetrachloroethane as the internal standard.

2.2 Optimization of CuH-Catalyzed Hydroamination of 1-Arylcyclobutenes

Table S3. Evaluation of Different Amination Reagents[a]



[a]Reactions were conducted on 0.1 mmol scale. Yields were determined by ^{1}H NMR analysis of the crude reaction mixture using 1,1,2,2-tetrachloroethane as the internal standard.

2.3 General Procedures for CuH-Catalyzed Hydroamination Reactions[2]

General Procedure **A**

An oven-dried screw-cap reaction tube (Fisherbrand, 13*100 mm, part no. 1495935C) containing a magnetic stir bar was charged with $Cu(OAc)_2$ (5.9 mg, 0.033 mmol), (*R*)-DTBM-SEGPHOS (21.1 mg, 0.018 mmol), and (*S*)-DTBM-SEGPHOS (21.1 mg, 0.018 mmol). The reaction tube was loosely capped (cap: Thermo Scientific C4015-66; Septum: Thermo Scientific C4015-60), and then transferred into a nitrogen-filled glovebox. Anhydrous THF (0.65 mL) was added to the tube via a 1 mL syringe. The tube was capped and the mixture was stirred for 15 min at rt. Then dimethoxymethylsilane (DMMS) (0.24 mL, 1.95 mmol) was added in one portion via a 1 mL syringe and the stirring was continued for another 10 min at rt to prepare an orange CuH stock solution.

A separate oven-dried screw-cap reaction tube (Fisherbrand, 16*125 mm, part no. 1495935A) containing a magnetic stir bar was loosely capped (cap: Kimble Chase Open Top S/T Closure catalog no. 73804-15425; Septum: Thermo Scientific B7995-15), and then transferred into the glovebox. The alkene (0.5 mmol, 1.0 equiv) and the amine electrophile (0.6 mmol, 1.2 equiv) were added to the reaction tube. Then the CuH stock solution (0.68 mL) was added via a 1 mL syringe to the reaction tube in one portion. The reaction tube was capped and then removed from the glove box. The reaction mixture was allowed to stir at 30 °C for 36 h.

General Procedure **B**

An oven-dried screw-cap reaction tube (Fisherbrand, 13*100 mm, part no. 1495935C) containing a magnetic stir bar was charged with $Cu(OAc)_2$ (5.4 mg, 0.030 mmol) and (*R*)-DTBM-SEGPHOS (38.9 mg, 0.033 mmol). The reaction tube was loosely capped (cap: Thermo Scientific C4015-66; Septum: Thermo Scientific C4015-60), and then transferred into a nitrogen-filled glovebox. Anhydrous THF (1.20 mL) was added to the tube via syringe. The tube was capped and the mixture was stirred for 15 min at rt. Then DMMS (0.22 mL, 1.80 mmol) was added in one portion via a 1 mL syringe and the stirring was continued for another 10 min at rt to prepare an orange CuH stock solution.

A separate oven-dried screw-cap reaction tube (Fisherbrand, 16*125 mm, part no. 1495935A) containing a magnetic stir bar was loosely capped (cap: Kimble Chase Open Top S/T Closure catalog no. 73804-15425; Septum: Thermo Scientific B7995-15), and then transferred into the glovebox. The alkene (0.5 mmol, 1.0 equiv) and the amine electrophile (0.6 mmol or 0.75 mmol, as indicated for each substrate) were added to the reaction tube. Then the CuH stock solution (1.18 mL) was added via syringe to the reaction tube in one portion. The reaction tube was capped and then removed from the glove box. The reaction mixture was allowed to stir at 40 °C for 36 or 46 h as indicated for each substrate.

General Procedure **C**

An oven-dried screw-cap reaction tube (Fisherbrand, 13*100 mm, part no. 1495935C) containing a magnetic stir bar was charged with $Cu(OAc)_2$ (5.4 mg, 0.030 mmol) and (*R*)-DTBM-SEGPHOS (38.9 mg, 0.033 mmol). The reaction tube was loosely capped (cap: Thermo Scientific C4015-66; Septum: Thermo Scientific C4015-60), and then transferred into a nitrogen-filled glovebox. Anhydrous 1,4-dioxane (0.60 mL) was added to the tube with a 1 mL syringe. The tube was capped and the mixture was stirred for 10 min at rt. Then DMMS (0.22 mL, 1.80 mmol) was added in one portion via a 1 mL syringe and the stirring was continued for another 15 min at rt to prepare a dark red CuH stock solution.

A separate oven-dried screw-cap reaction tube (Fisherbrand, 16*125 mm, part no. 1495935A) containing a magnetic stir bar was loosely capped (cap: Kimble Chase Open Top S/T Closure catalog no. 73804-15425; Septum: Thermo Scientific B7995-15), and then transferred into the glovebox. The alkene (0.5 mmol, 1.0 equiv), the amine electrophile (0.6 mmol, 1.2 equiv), and anhydrous 1,4-dioxane (0.50 mL) were added to the reaction tube. Then the CuH stock solution (0.68 mL) was added via a 1 mL syringe to the reaction tube in one portion. The reaction tube was capped and then taken out of the glove box. The reaction mixture was allowed to stir at rt for 18 h.

General Procedure **D**

An oven-dried screw-cap reaction tube (Fisherbrand, 13*100 mm, part no. 1495935C) containing a magnetic stir bar was charged with $Cu(OAc)_2$ (5.4 mg, 0.030 mmol) and (*R*)-DTBM-SEGPHOS (38.9 mg, 0.033 mmol). The reaction tube was loosely capped (cap: Thermo Scientific C4015-66; Septum: Thermo Scientific C4015-60), and then transferred into a nitrogen-filled glovebox. Anhydrous 1,4-dioxane (0.60 mL) was added to the tube with a 1 mL syringe. The tube was capped and the mixture was stirred for 10 min at rt. Then DMMS (0.22 mL, 1.80 mmol) was added in one portion via a 1 mL syringe and the stirring was continued for another 15 min at rt to prepare a dark red CuH stock solution.

A second oven-dried screw-cap reaction tube (Fisherbrand, 13*100 mm, part no. 1495935C) was loosely capped (cap: Thermo Scientific C4015-66; Septum: Thermo Scientific C4015-60), and then transferred into the glovebox. 1,2-Benzisoxazole (92 μL) and anhydrous 1,4-dioxane (0.35 mL) were added to the tube to prepare the 1,2-benzisoxazole stock solution. The tube was capped and then gently swirled to mix the solution.

A third oven-dried screw-cap reaction tube (Fisherbrand, 16*125 mm, part no. 1495935A) containing a magnetic stir bar was loosely capped (cap: Kimble Chase Open Top S/T Closure catalog no. 73804-15425; Septum: Thermo Scientific B7995-15), and then transferred into the glovebox. The alkene (0.5 mmol, 1.0 equiv) and anhydrous 1,4-dioxane (0.50 mL) were added to the reaction tube. Then the CuH stock solution (0.68 mL) was added via a 1 mL syringe to the reaction tube in one portion. (Note: The CuH solution should be added directly into the alkene solution instead of along the wall of the reaction tube, otherwise the remaining CuH solution on the wall of the reaction tube may cause decomposition of the 1,2-benzisoxazole that was subsequently added slowly along the wall of the reaction tube.) The reaction mixture was stirred at rt for 30 s. Then while the reaction mixture was stirred at rt, 1,2-benzisoxazole (10 μL) was added over 1 min via microsyringe. The reaction tube was capped and the septum was punctured with a long needle attached to a 1 mL syringe containing the 1,2-benzisoxazole stock solution (0.32 mL). The reaction tube was then taken out of the glove box. While the reaction mixture was stirred at rt, the 1,2-benzisoxazole solution was added slowly via syringe pump at a rate of 0.13 or 0.16 mL/h (as indicated for each substrate). (Note: The tip of the needle should touch the wall of the reaction tube during the slow addition of 1,2-benzisoxazole.) The reaction mixture was allowed to stir at rt for 18 h.

Workup **A**

After the reaction was completed, the cap of the reaction tube was removed. While the reaction mixture was stirred at rt, sat. NH_4F in MeOH (1 mL) was added slowly to quench the reaction mixture (*Caution: gas evolution observed*). The mixture was stirred uncapped at rt for 30 min and transferred to a 100 mL round bottom flask with the aid of EtOAc. A small aliquot of the solution was transferred to a 20 mL scintillation vial, concentrated *in vacuo*, analyzed by ^1H NMR in $CDCl_3$ to determine the diastereomeric ratio (dr), and then the NMR sample was transferred backed to the 100 mL round bottom flask. The combined solution was concentrated *in vacuo*. The resulting mixture was dissolved in EtOAc, filtered through a short plug of Celite, and washed with additional EtOAc. The collected EtOAc solution was concentrated *in vacuo*, and the crude material was immediately purified by silica gel column chromatography (~ 30 g silica gel, diameter of the column ~ 2 cm, length of the packed column ~ 18 cm).

Workup **B**

After the reaction was completed, the cap of the reaction tube was removed. While the reaction mixture was stirred at rt, sat. NH_4F in MeOH (1 mL) was added slowly to quench the reaction mixture (*Caution: gas evolution observed*). The mixture was stirred uncapped at rt for 30 min, and then transferred to a 20 mL scintillation vial. The reaction tube was rinsed four times with additional EtOAc (5-10 mL in total). The combined EtOAc solution was concentrated *in vacuo*, and the crude material was immediately purified by silica gel column chromatography (~ 30 g silica gel, diameter of the column ~ 2 cm, length of the packed column ~ 18 cm).

Workup **C**

After the reaction was completed, the cap of the reaction tube was removed. While the reaction mixture was stirred vigorously at rt, sat. LiOH in MeOH (2.5 mL) was added slowly to quench the reaction mixture (*Caution: gas evolution observed*). The mixture was stirred uncapped at rt for 1 h, transferred to a 100 mL round bottom flask with the aid of EtOAc, and concentrated *in vacuo*. The resulting mixture was dissolved in EtOAc, sonicated for 5 min, filtered through a pad of Celite, and washed with additional EtOAc. The collected EtOAc solution was concentrated *in vacuo*, and the crude material was immediately purified by silica gel column chromatography (~ 30 g silica gel, diameter of the column ~ 2 cm, length of the packed column ~ 18 cm).

Workup **D**

After the reaction was completed, the cap of the reaction tube was removed, and the reaction mixture was diluted with EtOAc (1.5 mL). While the reaction mixture was stirred at 0 °C, sat. aq. $NaHCO_3$ (2 mL) was added slowly to quench the reaction mixture (*Caution: gas evolution observed*). The mixture was stirred uncapped at 0 °C for 5 min, and then at rt for 30 min. The mixture was transferred with the aid of EtOAc to a 125 mL separatory funnel containing brine

(30 mL) and EtOAc (30 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 x 10-15 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting residue was transferred to a 20 mL scintillation vial with the aid of EtOAc, and then concentrated *in vacuo*. The crude material was immediately purified by silica gel column chromatography (~ 30 g silica gel, diameter of the column was ~ 2 cm, length of the packed column was ~ 18 cm).

2.4 Structural Determination of the Hydroamination Products

Single Crystal X-ray Diffraction Data for Compound 7b (P19056)

A crystal of **7b** was obtained by slowly evaporating the EtOH solution of **7b** at 0 °C (in air). The absolute configuration of **7b** was determined by X-ray crystallographic analysis. The absolute configuration of **10a**, **7a-e**, **12**, and **15a-d** was assigned by analogy to **7b**.

CCDC 1945177 contains the supplementary crystallographic data for **7b**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

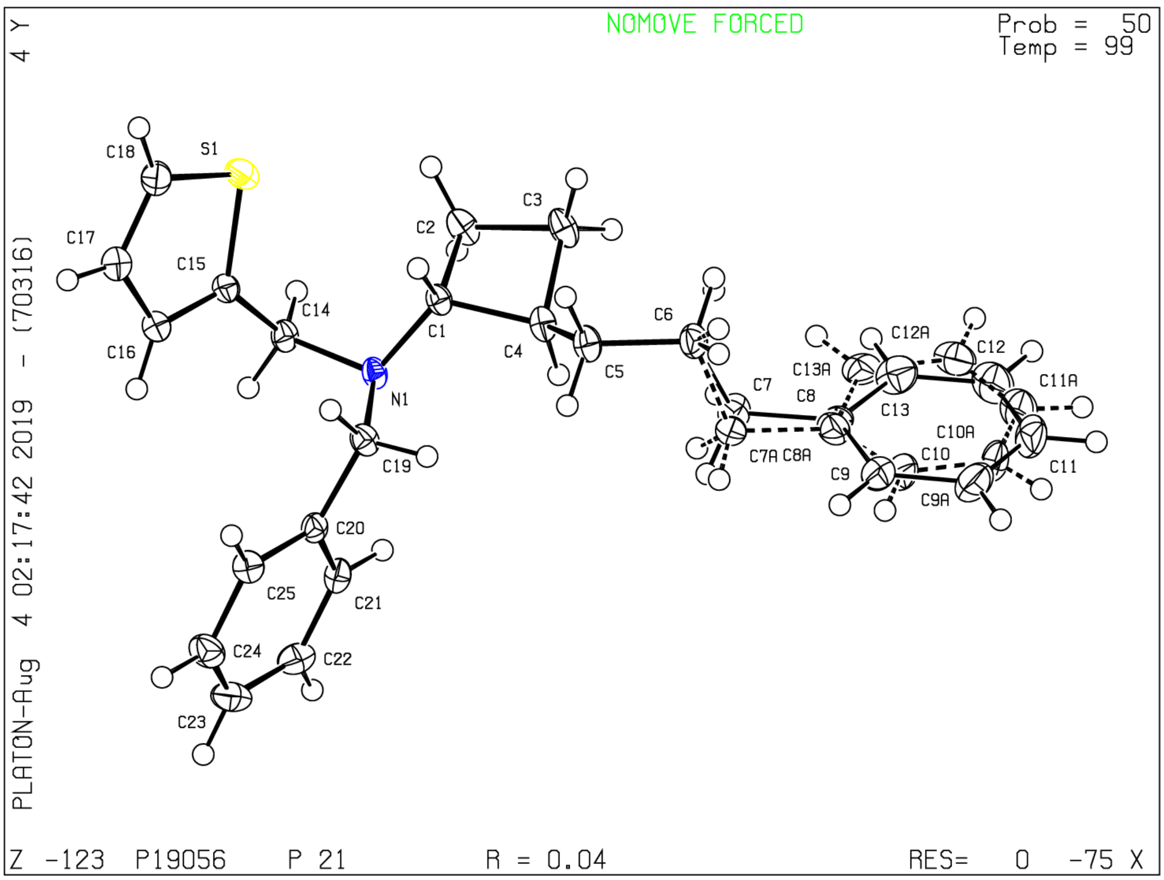


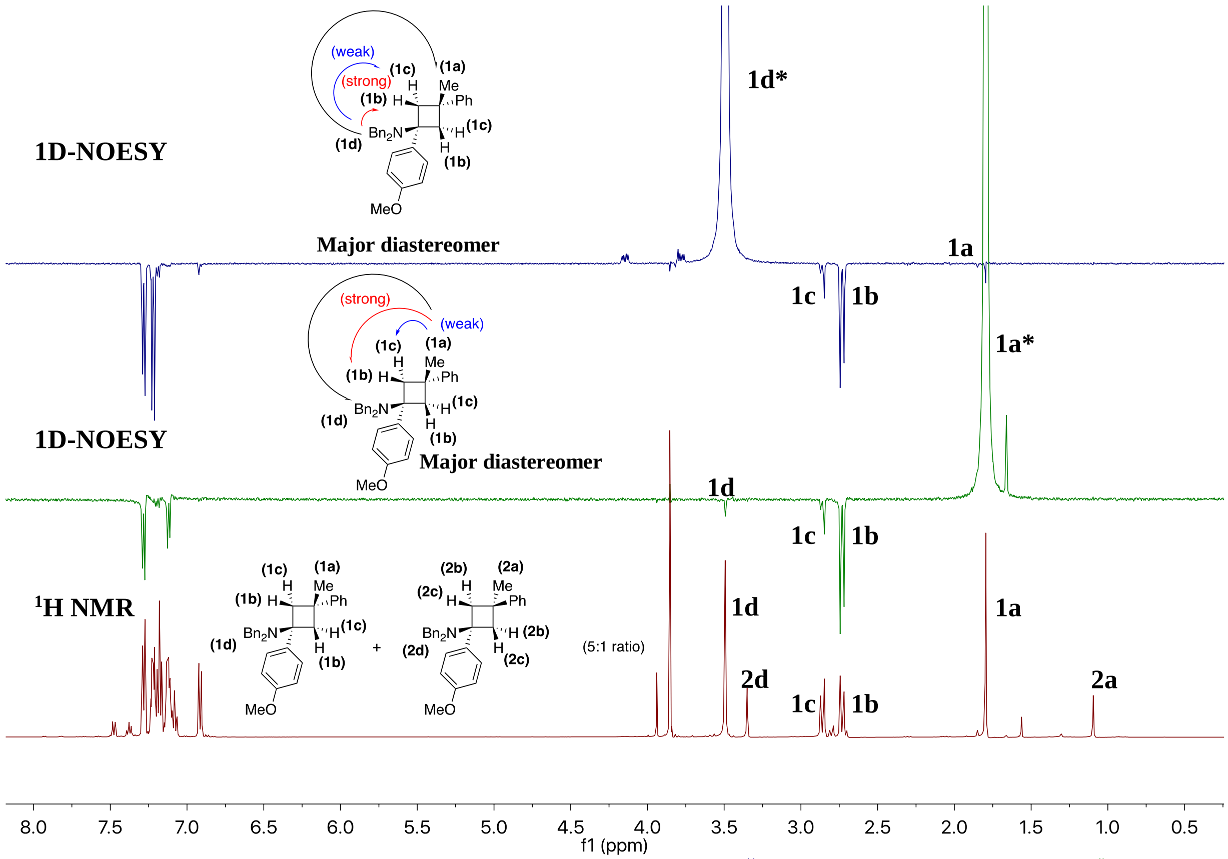
Table S4. Crystal data and structure refinement for 7b (P19056)

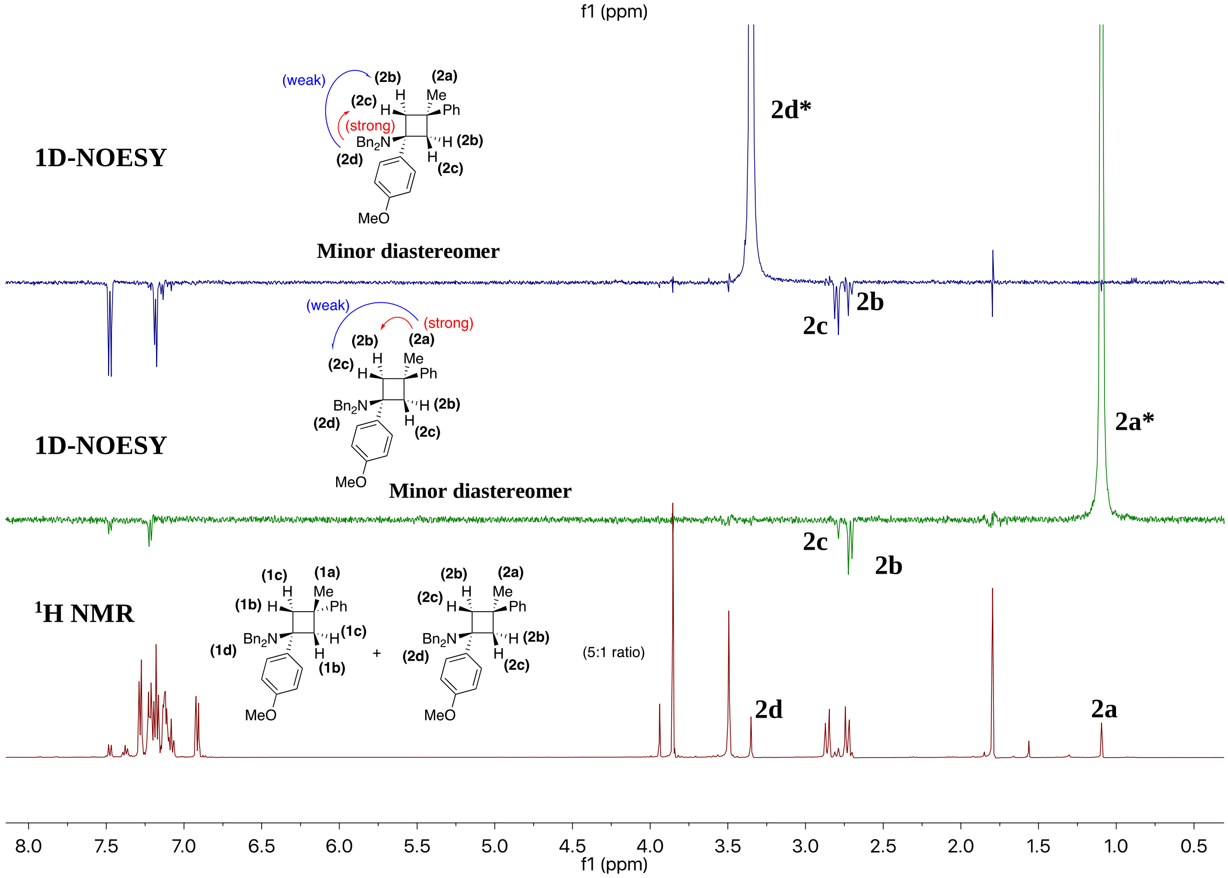
Identification code	P19056
Empirical formula	C25 H29 N S
Formula weight	375.55

Temperature	99(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 13.0414(11) Å	a= 90°.
	b = 5.7208(4) Å	b= 93.997(4)°.
	c = 14.1145(12) Å	g = 90°.
Volume	1050.48(15) $Å^3$	
Z	2	
Density (calculated)	1.187 Mg/m^3	
Absorption coefficient	0.163 mm^{-1}	
F(000)	404	
Crystal size	0.570 x 0.165 x 0.160 mm^3	
Theta range for data collection	1.446 to 30.541°.	
Index ranges	-18<=h<=18, -8<=k<=8, -20<=l<=20	
Reflections collected	89778	
Independent reflections	6421 [R(int) = 0.0653]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6421 / 366 / 309	
Goodness-of-fit on F^2	1.125	
Final R indices [I>2sigma(I)]	R1 = 0.0440, wR2 = 0.1092	
R indices (all data)	R1 = 0.0454, wR2 = 0.1098	
Absolute structure parameter	0.04(2)	
Extinction coefficient	0.192(12)	
Largest diff. peak and hole	0.365 and -0.438 e.$Å^{-3}$	

1D-NOESY Analysis of 4b (a 5:1 mixture of major and minor diastereomers)

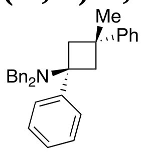
The configuration of the major and minor diastereomers in **4b** was determined by 1D-NOESY analysis of **4b** (a 5:1 mixture of major and minor diastereomers). The configuration of the major diastereomers in **4a**, **4c**, **4g-i** was assigned by analogy to **4b**.


1D-NOESY
(weak)
(strong)
(1c)
(1a)
(1b)
(1d)
Major diastereomer
1d*
1a
1c
1b
1D-NOESY
Major diastereomer
1a*
1d
1c
1b
¹H NMR
(5:1 ratio)
1d
1a
2d
1c
1b
2a
f1 (ppm)


1D-NOESY
(weak)
(strong)
(2b)
(2a)
(2c)
(2d)
Minor diastereomer
2d*
2c
2b
1D-NOESY
Minor diastereomer
2a*
2c
2b
¹H NMR
(5:1 ratio)
2d
2a
f1 (ppm)

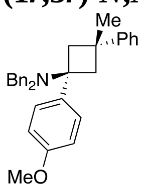
3. Characterization Data for the Hydroamination Products

(1*r*,3*r*)-*N*,*N*-dibenzyl-3-methyl-1,3-diphenylcyclobutan-1-amine (4a)



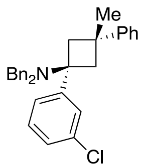
Following general procedure **A**, (3-methylcyclobut-1-ene-1,3-diyl)dibenzene (110 mg, 0.50 mmol, 1.0 equiv) and Bn_2NOBz (190 mg, 0.60 mmol, 1.2 equiv) were used. After Workup **A** and purification by column chromatography [hexanes (80 mL) followed by hexanes/EtOAc = 100:1], the title compound was obtained as a white solid (1st run: 181 mg, 87% yield, 13:1 dr; 2nd run: 174 mg, 83% yield, 13:1 dr). ^{1}H NMR analysis of the crude reaction mixture indicated 13:1 dr. **^{1}H NMR** (major diastereomer, 400 MHz, $CDCl_3$) δ 7.29-7.25 (m, 2H), 7.19-6.94 (m, 18H), 3.39 (s, 4H), 2.77 (d, *J* = 12.6 Hz, 2H), 2.64 (d, *J* = 12.7 Hz, 2H), 1.70 (s, 3H). **^{13}C NMR** (major diastereomer, 101 MHz, $CDCl_3$) δ 152.22, 141.73, 141.14, 128.93, 128.01, 127.79, 127.48, 127.36, 126.37, 126.28, 125.12, 125.02, 62.72, 55.02, 44.97, 36.07, 33.25. **m.p.** 128.0-129.7 °C. **IR** (thin film): 3063, 3024, 2842, 1600, 1491, 1454, 1272, 1029, 908, 692 cm^{-1}. **EA** Calcd. for $C_{31}H_{31}N$: C, 89.16; H, 7.48. Found: C, 88.96; H, 7.45.

(1*r*,3*r*)-*N*,*N*-dibenzyl-1-(4-methoxyphenyl)-3-methyl-3-phenylcyclobutan-1-amine (4b)



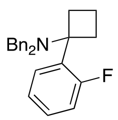
Following general procedure **A**, 1-methoxy-4-(3-methyl-3-phenylcyclobut-1-en-1-yl)benzene (125 mg, 0.50 mmol, 1.0 equiv) and Bn_2NOBz (190 mg, 0.60 mmol, 1.2 equiv) were used. After the reaction was completed, the reaction mixture was transferred to a 100 mL round bottom flask, and the reaction tube was rinsed with additional EtOAc. Then HCl in MeOH (1.25 M, 15 mL) was added to the flask to quench the reaction mixture and acidify the mixture. The flask was swirled gently to mix the components, allowed to sit for 30 min, and then the resulting mixture was concentrated *in* vacuo. Hexanes (~ 20 mL) was added. The precipitate was broken into small pieces using a spatula, and the resulting suspension was sonicated for 5-10 min. The suspension was filtered through a Buchner funnel (porosity: fine) under reduced pressure. The 100 mL flask was rinsed with hexane (~20 mL) and the suspension was poured into the funnel. The solid in the funnel was washed with additional hexanes (~10 mL). Then the solid in the above 100 mL round bottom flask and Buchner funnel was dissolved with 1 M NaOH (~ 50 mL in total) and CH_2Cl_2 (~50 mL in total). The resulting mixture was transferred to a separatory funnel, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were dried over Na_2SO_4, filtered, and the solution was collected in a 500 mL round bottom flask. A small aliquot of the solution was transferred to a 20 mL scintillation vial, concentrated *in vacuo*, analyzed by ^{1}H NMR in $CDCl_3$ to determine the diastereomeric ratio (dr), and then the NMR sample was transferred backed to the 500 mL round bottom flask. The combined solution was concentrated *in vacuo*, and immediately purified by column chromatography (~ 30 g silica gel) with a gradient of hexanes (100 mL) → hexanes/Et_2O = [30:1 (90 mL) → 20:1 (160 mL)]. The title compound was obtained as a white solid (1st run: 140 mg, 62% yield, 5:1 dr; 2nd run: 150 mg, 67% yield, 5:1 dr). ^{1}H NMR analysis of the crude reaction mixture indicated 5:1 dr. **^{1}H NMR** (major diastereomer, 400 MHz, $CDCl_3$) δ 7.30-7.28 (m, 4H), 7.25-7.07 (m, 13H), 6.94-6.90 (m, 2H), 3.86 (s, 3H), 3.50 (s, 4H), 2.87 (d, *J* = 12.6 Hz, 2H), 2.74 (d, *J* = 12.7 Hz, 2H), 1.80 (s, 3H). **^{13}C NMR** (major diastereomer, 101 MHz, $CDCl_3$) δ 157.91, 152.16, 141.23, 134.16, 128.92, 128.62, 127.98, 127.78, 126.34, 125.13, 124.99, 112.66, 62.21, 55.25, 55.02, 45.26, 35.87, 33.27. **m.p.** 134.5-136.8 °C. **IR** (thin film): 3059, 3025, 2931, 2834, 1605, 1511, 1247, 1179, 1028, 698 cm^{-1}. **HRMS** Calcd. m/z for $C_{32}H_{34}NO^+$ $[M+H]^+$: 448.2635; found 448.2655.

(1*r*,3*r*)-*N*,*N*-dibenzyl-1-(3-chlorophenyl)-3-methyl-3-phenylcyclobutan-1-amine (4c)



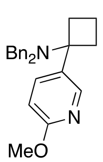
Following general procedure **A**, 1-chloro-3-(3-methyl-3-phenylcyclobut-1-en-1-yl)benzene (127 mg, 0.50 mmol, 1.0 equiv) and Bn_2NOBz (190 mg, 0.60 mmol, 1.2 equiv) were used. After Workup **A** and purification by column chromatography [hexanes (200 mL) followed by hexanes/EtOAc = 100:1], the title compound was obtained as a white solid (1st run: 180 mg, 80% yield, 29:1 dr; 2nd run: 178 mg, 78% yield, 29:1 dr). ^{1}H NMR analysis of the crude reaction mixture indicated 29:1 dr. **^{1}H NMR** (major diastereomer, 400 MHz, $CDCl_3$) δ 7.34-7.09 (m, 19H), 3.50 (s, 4H), 2.88-2.85 (m, 2H), 2.78-2.74 (m, 2H), 1.80 (s, 3H). **^{13}C NMR** (major diastereomer, 101 MHz, $CDCl_3$) δ 151.75, 143.88, 140.75, 133.60, 128.92, 128.70, 128.09, 127.90, 127.63, 126.54, 126.52, 125.64, 125.19, 125.10, 62.61, 54.91, 44.95, 36.12, 33.27. **m.p.** 142.6-144.0 °C. **IR** (thin film): 3061, 3025, 2933, 2838, 1592, 1494, 1262, 1172, 1027, 695 cm^{-1}. **HRMS** Calcd. m/z for $C_{31}H_{31}NCl^{+}$ $[M+H]^{+}$: 452.2140; found 452.2143.

***N*,*N*-dibenzyl-1-(2-fluorophenyl)cyclobutan-1-amine (4d)**



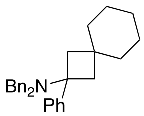
Following general procedure **B**, 1-(cyclobut-1-en-1-yl)-2-fluorobenzene (74 mg, 0.50 mmol, 1.0 equiv) and Bn_2NOPiv (178 mg, 0.60 mmol, 1.2 equiv) were used. The reaction was run at 40 °C for 36 h. After Workup **B** and purification by column chromatography with a gradient of hexanes (150 mL) → hexanes/Et_2O = [100:1 (100 mL) → 80:1 (240 mL) → 60:1 (60 mL)], the title compound was obtained as a colorless oil (1st run: 124 mg, 72% yield; 2nd run: 123 mg, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36-7.21 (m, 8H), 7.19-7.15 (m, 4H), 7.13-7.08 (m, 2H), 3.57 (s, 4H), 2.47-2.44 (m, 4H), 2.28-2.18 (m, 1H), 1.80-1.71 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.36 (d, J = 246.4 Hz), 141.51, 130.24 (d, J = 5.8 Hz), 129.04 (d, J = 14.6 Hz), 128.61, 128.53, 127.69, 126.22, 123.26 (d, J = 3.5 Hz), 116.28 (d, J = 24.6 Hz), 67.34 (d, J = 2.4 Hz), 54.76 (d, J = 2.9 Hz), 33.23 (d, J = 1.5 Hz), 16.30. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.85. **IR** (thin film): 3062, 3027, 2943, 2839, 1483, 1446, 1212, 1141, 1028, 695 cm^{-1}. **EA** Calcd. for $C_{24}H_{24}NF$: C, 83.44; H, 7.00. Found: C, 83.31; H, 7.14.

***N*,*N*-dibenzyl-1-(6-methoxypyridin-3-yl)cyclobutan-1-amine (4e)**



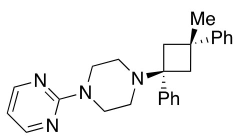
Following general procedure **B**, 5-(cyclobut-1-en-1-yl)-2-methoxypyridine (81 mg, 0.50 mmol, 1.0 equiv) and Bn_2NOPiv (178 mg, 0.60 mmol, 1.2 equiv) were used. The reaction was run at 40 °C for 36 h. After Workup **B** and purification by column chromatography with a gradient of hexanes (100 mL) → hexanes/Et_2O = [50:1 (100 mL) → 40:1 (40 mL) → 30:1 (90 mL) → 20:1 (100 mL) → 15:1 (90 mL) → 10:1 (100 mL)], the title compound was obtained as a colorless oil (1st run: 134 mg, 75% yield; 2nd run: 136 mg, 76% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (dd, J = 2.6, 0.8 Hz, 1H), 7.76 (dd, J = 8.6, 2.6 Hz, 1H), 7.34-7.28 (m, 4H), 7.25-7.22 (m, 4H), 7.18-7.14 (m, 2H), 6.88 (dd, J = 8.6, 0.7 Hz, 1H), 4.04 (s, 3H), 3.42 (s, 4H), 2.35 (qd, J = 9.3, 2.4 Hz, 2H), 2.22 (tt, J = 8.4, 2.9 Hz, 2H), 1.86-1.78 (m, 1H), 1.60-1.49 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.13, 146.23, 141.02, 138.71, 129.58, 128.82, 128.03, 126.67, 110.07, 66.31, 53.91, 53.56, 33.25, 14.80. **IR** (thin film): 3024, 2943, 2840, 1599, 1488, 1368, 1285, 1132, 1023, 696 cm^{-1}. **EA** Calcd. for $C_{24}H_{26}N_2O$: C, 80.41; H, 7.31. Found: C, 80.71; H, 7.08.

***N*,*N*-dibenzyl-2-phenylspiro[3.5]nonan-2-amine (4f)**



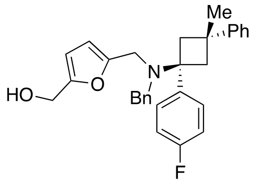
Following general procedure **A**, instead of using (*R*)-DTBM-SEGPHOS (21.1 mg) and (*S*)-DTBM-SEGPHOS (21.1 mg) to prepare the CuH stock solution, (*R*)-DTBM-SEGPHOS (42.2 mg) was used. 2-Phenylspiro[3.5]non-1-ene (99 mg, 0.50 mmol, 1.0 equiv) and Bn_2NOBz (190 mg, 0.60 mmol, 1.2 equiv) were also used. After Workup **A** and purification by column chromatography with a gradient of hexanes (150 mL) → hexanes/Et_2O = [100:1 (100 mL) → 80:1 (240 mL) → 60:1 (60 mL)], the title compound was obtained as a white solid (1st run: 177 mg, 89% yield; 2nd run: 179 mg, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49-7.45 (m, 2H), 7.42-7.40 (m, 2H), 7.35 (tt, *J* = 6.5, 1.4 Hz, 1H), 7.24-7.22 (m, 4H), 7.17-7.13 (m, 4H), 7.11-7.07 (m, 2H), 3.39 (s, 4H), 2.30 (d, *J* = 12.4 Hz, 2H), 2.22 (d, *J* = 12.4 Hz, 2H), 1.72-1.70 (m, 2H), 1.43 (p, *J* = 5.7 Hz, 2H), 1.33-1.28 (m, 4H), 1.18-1.15 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.49, 141.36, 128.96, 127.92, 127.78, 127.59, 126.33, 62.86, 54.65, 44.26, 40.60, 38.66, 31.81, 26.10, 22.95, 22.85. **m.p.** 81.8-82.5 °C. **IR** (thin film): 3060, 3025, 2920, 2847, 1493, 1444, 1296, 1171, 1028, 693 cm^{-1}. **HRMS** Calcd. m/z for $C_{29}H_{34}N^+$ $[M+H]^+$: 396.2686; found 396.2690.

2-(4-((1*r*,3*r*)-3-methyl-1,3-diphenylcyclobutyl)piperazin-1-yl)pyrimidine (4g)



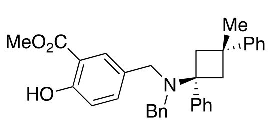
Following general procedure **A**, (3-methylcyclobut-1-ene-1,3-diyl)dibenzene (110 mg, 0.50 mmol, 1.0 equiv) and 4-(pyrimidin-2-yl)piperazin-1-yl benzoate (171 mg, 0.60 mmol, 1.2 equiv) were used. After the reaction was completed, the cap of the reaction tube was removed. While the reaction mixture was stirred at rt, sat. NH_4F in MeOH (1 mL) was added slowly to quench the reaction mixture (*Caution: gas evolution observed*). The mixture was stirred uncapped at rt for 30 min and transferred to a 100 mL round bottom flask with the aid of CH_2Cl_2. A small aliquot of the solution was transferred to a 20 mL scintillation vial, concentrated *in vacuo*, analyzed by ^{1}H NMR in $CDCl_3$ to determine the diastereomeric ratio (dr), and then the NMR sample was transferred backed to the 100 mL round bottom flask. The combined solution was concentrated *in vacuo*. The resulting mixture was dissolved in CH_2Cl_2, filtered through a cotton ball that was stuck in a pipette, and washed with additional CH_2Cl_2. The CH_2Cl_2 solution was collected in a 20 mL scintillation vial, concentrated *in vacuo*, and the crude material and immediately purified by column chromatography (~ 30 g silica gel, diameter of the column ~ 2 cm, length of the packed column ~ 18 cm) with a gradient of hexanes/EtOAc = [20:1 (60 mL) → 15:1 (150 mL) → 12:1 (60 mL) → 10:1 (200 mL) → 8:1 (80 mL) → 5:1 (100 mL) → 4:1 (100 mL) (the above volumes refer to the volume of hexanes used)]. The resulting material was redissolved in CH_2Cl_2 (3 mL), filtered through a short plug of basic activated alumina, and washed with additional EtOAc. The collected EtOAc solution was concentrated *in vacuo* to afford the pure product as a white solid (1st run: 128 mg, 66% yield, 13:1 dr; 2nd run: 128 mg, 66% yield, 13:1 dr). ^{1}H NMR analysis of the crude reaction mixture indicated 13:1 dr. **^{1}H NMR** (major diastereomer, 400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 4.7 Hz, 2H), 7.28-7.24 (m, 4H), 7.19-7.10 (m, 4H), 7.06-7.04 (m, 2H), 6.43 (t, *J* = 4.8 Hz, 1H), 3.88 (br, 4H), 2.81 (d, *J* = 11.4 Hz, 2H), 2.77 (d, *J* = 11.5 Hz, 2H), 2.42 (br, 4H), 1.77 (s, 3H). **^{13}C NMR** (major diastereomer, 101 MHz, $CDCl_3$) δ 151.75, 143.88, 140.75, 133.60, 128.92, 128.70, 128.09, 127.90, 127.63, 126.54, 126.52, 125.64, 125.19, 125.10, 62.61, 54.91, 44.95, 36.12, 33.27. **m.p.** 197.0-198.9 °C. **IR** (thin film): 3021, 2932, 2853, 1584, 1493, 1357, 1261, 1181, 1012, 700 cm^{-1}. **HRMS** Calcd. m/z for $C_{25}H_{29}N_4^+$ $[M+H]^+$: 385.2387; found 385.2396.

(5-((benzyl((1*r*,3*r*)-1-(4-fluorophenyl)-3-methyl-3-phenylcyclobutyl)amino)methyl)furan-2-yl)methanol (4h)



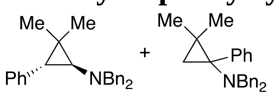
General procedure **A** was followed, except DMMS (0.32 mL, 2.60 mmol) (Note: An extra equivalence of DMMS was used in order to silylate the alcohol in the amination reagent.) was used to prepare the CuH stock solution. The stock CuH solution (0.74 mL) was added to the reaction tube containing 1-fluoro-4-(3-methyl-3-phenylcyclobut-1-en-1-yl)benzene (119 mg, 0.50 mmol, 1.0 equiv) and (5-(((benzoyloxy)(benzyl)amino)methyl)furan-2-yl)methanol (202 mg, 0.60 mmol, 1.2 equiv). After the reaction was completed, the cap of the reaction tube was removed. While the reaction mixture was stirred at rt, sat. NH_4F in MeOH (5 mL) was added slowly to quench the reaction mixture (*Caution: gas evolution observed*). The mixture was stirred uncapped at rt for 1 h and transferred to a 100 mL round bottom flask with the aid of CH_2Cl_2. A small aliquot of the solution was transferred to a 20 mL scintillation vial, concentrated *in vacuo*, analyzed by ^{1}H NMR in $CDCl_3$ to determine the diastereomeric ratio (dr), and then transferred backed to the 100 mL round bottom flask. The combined solution was concentrated *in vacuo*. The resulting mixture was dissolved in CH_2Cl_2, filtered through a cotton ball that was stuck in a pipette, and washed with additional CH_2Cl_2. The CH_2Cl_2 solution was collected in a 20 mL scintillation vial, concentrated *in vacuo*, and the crude material was immediately purified by column chromatography (~ 30 g silica gel, diameter of the column ~ 2 cm, length of the packed column ~ 18 cm) with a gradient of hexanes/EtOAc = [20:1 (60 mL) $\rightarrow$ 15:1 (150 mL) $\rightarrow$ 12:1 (60 mL) $\rightarrow$ 10:1 (200 mL) $\rightarrow$ 8:1 (80 mL) $\rightarrow$ 5:1 (100 mL) $\rightarrow$ 4:1 (100 mL) (the above volumes refer to the volume of hexanes used)]. The resulting material was redissolved in CH_2Cl_2 (3 mL), filtered through a short plug of basic activated alumina, and washed with additional EtOAc. The collected EtOAc solution was concentrated *in vacuo* to afford the pure product as a white solid (1st run: 173 mg, 76% yield, 11:1 dr; 2nd run: 182 mg, 80% yield, 11:1 dr). ^{1}H NMR analysis of the crude reaction mixture indicated 11:1 dr. **^{1}H NMR** (major diastereomer, 400 MHz, $CDCl_3$) δ 7.33-7.30 (m, 2H), 7.28-7.10 (m, 10H), 7.06-7.00 (m, 2H), 5.96 (d, *J* = 3.1 Hz, 1H), 5.78 (d, *J* = 3.1 Hz, 1H), 4.43 (d, *J* = 6.0 Hz, 2H), 3.54 (s, 2H), 3.49 (s, 2H), 2.92-2.88 (m, 2H), 2.82-2.78 (m, 2H), 1.84 (s, 3H), 1.43 (t, *J* = 6.0 Hz, 1H). **^{13}C NMR** (major diastereomer, 101 MHz, $CDCl_3$) δ 161.33 (d, *J* = 245.2 Hz), 153.72, 152.58, 151.96, 140.79, 137.56 (d, *J* = 3.1 Hz), 128.68, 128.60, 128.27, 128.11, 127.77, 126.28, 125.17, 125.07, 114.28 (d, *J* = 21.0 Hz), 108.49 (d, *J* = 19.7 Hz), 61.82, 57.55, 54.73, 46.93, 44.80, 35.81, 32.99. **^{19}F NMR** (major diastereomer, 376 MHz, $CDCl_3$) δ -116.55. **m.p.** 124.3-125.9 °C. **IR** (thin film): 3359, 3025, 2932, 2866, 1601, 1508, 1224, 1157, 1010, 699 cm^{-1}. **EA** Calcd. for $C_{30}H_{30}FNO_2$: C, 79.09; H, 6.64. Found: C, 79.01; H, 6.62.

methyl 5-((benzyl((1*r*,3*r*)-3-methyl-1,3-diphenylcyclobutyl)amino)methyl)-2-hydroxybenzoate (4i)



General procedure **A** was followed, except DMMS (0.32 mL, 2.60 mmol) was used to prepare the CuH stock solution. The stock CuH solution (0.74 mL) was added to the reaction tube containing (3-methylcyclobut-1-ene-1,3-diyl)dibenzene (110 mg, 0.50 mmol, 1.0 equiv) and methyl 5-(((benzoyloxy)(benzyl)amino)methyl)-2-hydroxybenzoate (235 mg, 0.60 mmol, 1.2 equiv). After Workup **A** (5 mL sat. NH_4F in MeOH was used to quench the reaction mixture) and purification by column chromatography with a gradient of hexanes (200 mL) $\rightarrow$ hexanes/Et_2O = [50:1 (100 mL) → 30:1 (180 mL) → 20:1 (100 mL)], the title compound was obtained as a white solid (1st run: 190 mg, 77% yield, 13:1 dr; 2nd run: 190 mg, 77% yield, 13:1 dr). ^{1}H NMR analysis of the crude reaction mixture indicated 13:1 dr. **^{1}H NMR** (major diastereomer, 400 MHz, $CDCl_3$) δ 10.55 (s, 1H), 7.57 (d, *J* = 2.2 Hz, 1H), 7.40-7.34 (m, 2H), 7.28-7.06 (m, 14H), 6.76 (d, *J* = 8.5 Hz, 1H), 3.94 (s, 3H), 3.50 (s, 2H), 3.45 (s, 2H), 2.96-2.92 (m, 2H), 2.82-2.78 (m, 2H), 1.85 (s, 3H). **^{13}C NMR** (major diastereomer, 101 MHz, $CDCl_3$) δ 170.64, 160.21, 152.26, 141.79, 141.05, 136.61, 131.76, 130.15, 128.94, 128.18, 127.85, 127.53, 127.40, 126.47, 126.38, 125.22, 117.04, 111.32, 62.77, 55.25, 54.47, 52.26, 45.13, 36.12, 33.35. **m.p.** 111.7-112.4 °C. **IR** (thin film): 3023, 2951, 2836, 1674, 1441, 1207, 1087, 908, 731, 696 cm^{-1}. **EA** Calcd. for $C_{33}H_{33}NO_3$: C, 80.62; H, 6.77. Found: C, 80.47; H, 6.84.

(1*S*,3*R*)-*N*,*N*-dibenzyl-2,2-dimethyl-3-phenylcyclopropan-1-amine (10a) + *N*,*N*-dibenzyl-2,2-dimethyl-1-phenylcyclopropan-1-amine (10b)



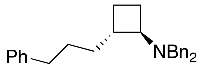
10a **10b**

Following general procedure **C**, 1,4-dioxane was replaced with an equal volume of THF, and (3,3-dimethylcycloprop-1-en-1-yl)benzene (72 mg, 0.50 mmol, 1.0 equiv, freshly prepared) and Bn_2NOPiv (178 mg, 0.60 mmol, 1.2 equiv) were used. After Workup **A** and purification by column chromatography with a gradient of hexanes (150 mL) → hexanes/Et_2O = [120:1 (180 mL) → 100:1 (150 mL) → 80:1 (80 mL)] (the product on TLC was visualized with I_2), a 8:1 mixture of the title compound (a mixture of **10a** and **10b**, 8:1 ratio**)** was obtained as a colorless oil (1st run: 101 mg, 59% yield, 69:31 er for **10a**; 2nd run: 98 mg, 57% yield, 69:31 er for **10a**). **EA** Calcd. for $C_{25}H_{27}N$: C, 87.93; H, 7.97. Found: C, 88.34; H, 7.96. ^{1}H NMR analysis of the crude reaction mixture indicated an 8:1 ratio of **10a** and **10b**. To separately obtain characterization data and confirm the structure of **10a** and **10b**, a small aliquot of the title compound was purified with preparative thin-layer chromatography (20 x 20 cm, 250 microns, catalog # TLG-R10014B-323 from Silicycle) eluting with hexane/EtOAc = 80:1 to give pure **10a** and **10b**.

Major regioisomer **10a**: White solid. **m.p.** 48.0-49.4 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.30 (m, 8H), 7.29-7.25 (m, 4H), 7.19-7.16 (m, 1H), 7.13-7.11 (m, 2H), 3.77 (d, *J* = 13.6 Hz, 2H), 3.68 (d, *J* = 13.6 Hz, 2H), 2.20 (d, *J* = 4.6 Hz, 1H), 1.76 (d, *J* = 4.6 Hz, 1H), 1.19 (s, 3H), 0.79 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.52, 138.72, 129.68, 128.66, 128.14, 127.93, 126.97, 125.58, 58.41, 53.80, 36.76, 27.80, 21.41, 20.58. **DEPT-135 NMR** (101 MHz, $CDCl_3$) δ 129.66, 128.64, 128.12, 127.92, 126.96, 125.57, 58.41 (CH_2), 53.80, 36.76, 21.40, 20.57. **SFC** analysis: OJ-H (5:95 IPA: $scCO_2$ to 30:70 IPA: $scCO_2$ linear gradient over 6 min with 1 min hold time, 2.50 mL/min), 3.96 min (minor), 4.84 min (major), 69:31 er. **Specific rotation** $[\alpha]_D^{23}$: +13.8 (c = 1.0, $CHCl_3$). **IR** (thin film): 3061, 3026, 2919, 1602, 1494, 1454, 1373, 1029, 745, 697 cm^{-1}. **EA** Calcd. for $C_{25}H_{27}N$: C, 87.93; H, 7.97. Found: C, 87.64; H, 8.04.

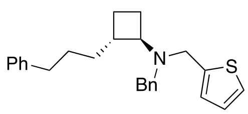
Minor regioisomer **10b**: White solid. **m.p.** 88.4-90.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47-7.17 (m, 15H), 4.13 (br, 1H), 3.43-3.40 (m, 3H), 1.61 (s, 3H), 0.85 (s, 3H), 0.53-0.50 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.31, 132.14, 129.22, 128.00, 127.63, 126.87, 126.63, 70.74, 56.33, 27.84, 25.25, 22.80, 21.43. **DEPT-135 NMR** (101 MHz, $CDCl_3$) δ 132.15, 129.22, 128.04, 127.63, 126.87, 126.57, 70.74 (CH_2), 27.85(CH_2), 25.25, 21.43. **IR** (thin film): 3026, 2925, 2865, 1494, 1454, 1377, 1122, 1027, 740, 697 cm^{-1}. **HRMS** Calcd. m/z for $C_{25}H_{28}N^+$ $[M+H]^+$: 342.2216; found 342.2228.

(1*R*,2*R*)-*N*,*N*-dibenzyl-2-(3-phenylpropyl)cyclobutan-1-amine (7a)



Following general procedure **B**, (3-(cyclobut-1-en-1-yl)propyl)benzene (86 mg, 0.50 mmol, 1.0 equiv) and $Bn_2NOC(O)Mes$ (270 mg, 0.75 mmol, 1.5 equiv) were used. The reaction was run at 40 °C for 46 h. After Workup **C** and purification by column chromatography with a gradient of hexanes (80 mL) → hexanes/Et_2O = [100:1 (100 mL) → 80:1 (until the majority of the product is eluted) → 40:1 (40 mL)] (the product on TLC was visualized with I_2), the title compound was obtained as a colorless oil (1st run: 145 mg, 78% yield, > 99.5:0.5 er, > 20:1 dr; 2nd run: 147 mg, 80% yield, > 99.5:0.5 er, > 20:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38-7.16 (m, 15H), 3.64 (d, *J* = 13.9 Hz, 2H), 3.54 (d, *J* = 14.0 Hz, 2H), 2.93 (q, *J* = 7.9 Hz, 1H), 2.61-2.48 (m, 2H), 2.35-2.26 (m, 1H), 1.92-1.75 (m, 3H), 1.60-1.46 (m, 3H), 1.36-1.26 (m, 1H), 1.19-1.09 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.91, 140.13, 128.91, 128.49, 128.35, 128.18, 126.76, 125.70, 63.46, 54.88, 41.10, 36.10, 35.66, 29.22, 23.04, 21.16. **SFC** analysis: OJ-H (5:95 IPA: $scCO_2$ to 40:60 IPA: $scCO_2$ linear gradient over 6 min with 2 min hold time, 2.50 mL/min), 5.27 min (major), 7.14 min (minor), > 99.5:0.5 er. **Specific rotation** $[\alpha]_D^{23}$: -37.1 (c = 1.0, $CHCl_3$). **IR** (thin film): 3060, 3025, 2929, 2854, 1602, 1493, 1452, 1143, 1028, 744 cm^{-1}. **EA** Calcd. for $C_{27}H_{31}N$: C, 87.75; H, 8.46. Found: C, 87.49; H, 8.48.

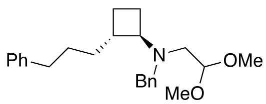
(1*R*,2*R*)-*N*-benzyl-2-(3-phenylpropyl)-*N*-(thiophen-2-ylmethyl)cyclobutan-1-amine (7b)



Following general procedure **B**, (3-(cyclobut-1-en-1-yl)propyl)benzene (86 mg, 0.50 mmol, 1.0 equiv) and *N*-benzyl-*N*-(thiophen-2-ylmethyl)-*O*-(2,4,6-trimethylbenzoyl)hydroxylamine (274 mg, 0.75 mmol, 1.5 equiv) were used. The reaction was run at 40 °C for 46 h. After the reaction was completed, the reaction mixture was filtered through a short plug of silica gel, and washed with additional EtOAc. The EtOAc solution was collected in a 20 mL scintillation vial, and then solvent was carefully removed under high vacuum by fitting a red septum onto the vial, inserting a needle into the septum, connecting the needle to a liquid N_2 trap, connecting the first liquid N_2 trap to a second liquid N_2 trap, and then connecting the second trap to the vacuum line on a Schlenk dual-manifold (Note: The liquid N_2 traps are necessary to insure that DMMS is completely trapped. After the evaporation process, the traps were maintained inside a fumehood. After their contents were thawed, the traps were washed thoroughly with acetone and the waste was poured into a container designated for organic liquid waste). The crude material was immediately purified by column chromatography (~ 30 g silica gel, diameter of the column ~ 2 cm, length of the packed column ~ 18 cm) with a gradient of hexanes (100 mL) → hexanes/Et_2O = [50:1 (100 mL) → 40:1 (40 mL) → 30:1 (150 mL) → 20:1 (80 mL) → 15:1 (60 mL) → 10:1 (200 mL) (the above volumes refer to the volume of hexanes used)] (the product on TLC was visualized with I_2). The title compound was obtained as a white solid (1st run: 146 mg, 78% yield, > 99.5:0.5 er, > 20:1 dr; 2nd run: 151 mg, 80% yield, > 99.5:0.5 er, > 20:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44-7.42 (m, 2H), 7.37-7.19 (m, 9H), 6.98 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.88 (dd, *J* = 3.4, 1.0 Hz, 1H), 3.85 (d, *J* = 14.8 Hz, 1H), 3.79 (d, *J* = 14.8 Hz, 1H), 3.68 (d, *J* = 14.0 Hz, 1H), 3.58 (d, *J* = 14.0 Hz, 1H), 2.99 (q, *J* = 7.8 Hz, 1H), 2.65-2.52 (m, 2H), 2.37-2.28 (m, 1H), 2.00-1.77 (m, 3H), 1.67-1.52 (m, 3H), 1.41-1.33 (m, 1H), 1.26-1.16 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.03, 142.86, 139.73, 128.95, 128.50, 128.35, 128.25, 126.88, 126.41, 125.74, 125.70, 124.65, 62.95, 54.20, 48.71, 41.33, 36.09, 35.73, 29.16, 23.32, 21.08. **m.p.** 50.6-51.3 °C. **SFC** analysis: CEL-1 (1:99 MeOH: $scCO_2$ to 3:97 MeOH: $scCO_2$ linear gradient over 6 min with 1 min hold time, 2.50 mL/min), 5.18 min (minor), 5.46 min (major), > 99.5:0.5 er.

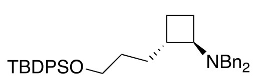
Specific rotation $[\alpha]_D^{23}$: -39.9 (c = 1.0, $CHCl_3$). **IR** (thin film): 3025, 2927, 2852, 1602, 1494, 1452, 1335, 1142, 1028, 694 cm^{-1}. **EA** Calcd. for $C_{25}H_{29}NS$: C, 79.95; H, 7.78. Found: C, 79.67; H, 7.79.

(1*R*,2*R*)-*N*-benzyl-*N*-(2,2-dimethoxyethyl)-2-(3-phenylpropyl)cyclobutan-1-amine (7c)



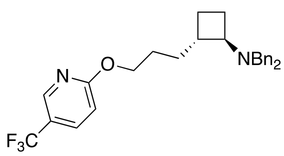
Following general procedure **B**, (3-(cyclobut-1-en-1-yl)propyl)benzene (86 mg, 0.50 mmol, 1.0 equiv) and *N*-benzyl-*N*-(2,2-dimethoxyethyl)-*O*-(2,4,6-trimethylbenzoyl)hydroxylamine (268 mg, 0.75 mmol, 1.5 equiv) were used. The reaction was run at 40 °C for 46 h. After Workup **C** and purification by column chromatography with a gradient of hexanes (100 mL) → hexanes/Et_2O = [50:1 (100 mL) → 40:1 (40 mL) → 30:1 (90 mL) → 20:1 (100 mL) → 15:1 (150 mL) → 10:1 (until the product is completely eluted)] (the product on TLC was visualized with I_2), the title compound was obtained as a colorless oil (1st run: 140 mg, 76% yield, > 99.5:0.5 er, > 20:1 dr; 2nd run: 135 mg, 74% yield, > 99.5:0.5 er, > 20:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39-7.24 (m, 7H), 7.22-7.18 (m, 3H), 4.30 (t, *J* = 5.2 Hz, 1H), 3.73 (d, *J* = 14.0 Hz, 1H), 3.65 (d, *J* = 14.0 Hz, 1H), 3.29 (s, 3H), 3.28 (s, 3H), 2.94 (q, *J* = 7.8 Hz, 1H), 2.70-2.53 (m, 4H), 2.27 (pd, *J* = 8.7, 3.8 Hz, 1H), 1.95 (q, *J* = 9.4, 8.7 Hz, 1H), 1.90-1.74 (m, 2H), 1.69-1.53 (m, 3H), 1.40-1.32 (m, 1H), 1.18 (p, *J* = 8.9, 8.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.87, 140.24, 128.99, 128.47, 128.34, 128.18, 126.82, 125.70, 104.06, 64.56, 56.35, 53.84, 53.78, 53.17, 41.42, 36.08, 35.61, 29.18, 23.68, 20.89. **SFC** analysis: OJ-H (5:95 IPA (0.15% DEA): $scCO_2$ to 15:85 IPA (0.15% DEA): $scCO_2$ linear gradient over 6 min with 1 min hold time, 2.50 mL/min), 4.36 min (major), 4.81 min (minor), > 99.5:0.5 er. **Specific rotation** $[\alpha]_D^{23}$: -50.5 (c = 1.0, $CHCl_3$). **IR** (thin film): 3025, 2930, 2828, 1495, 1452, 1368, 1191, 1123, 1073, 735 cm^{-1}. **EA** Calcd. for $C_{24}H_{33}NO_2$: C, 78.43; H, 9.05. Found: C, 78.23; H, 9.16.

(1*R*,2*S*)-*N*,*N*-dibenzyl-2-(3-((*tert*-butyldiphenylsilyl)oxy)propyl)cyclobutan-1-amine (7d)



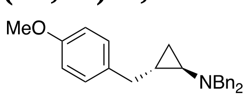
Following general procedure **B**, *tert*-butyl(3-(cyclobut-1-en-1-yl)propoxy)diphenylsilane (175 mg, 0.50 mmol, 1.0 equiv) and $Bn_2NOC(O)Mes$ (270 mg, 0.75 mmol, 1.5 equiv) were used. The reaction was run at 40 °C for 46 h. After the reaction was completed, the cap of the reaction tube was removed. While the reaction mixture was stirred at rt, sat. aq. $NaHCO_3$ (1 mL) was added slowly to quench the reaction mixture (*Caution: gas evolution observed*). The mixture was stirred uncapped at rt for 30 min. The mixture was transferred with the aid of EtOAc to a 125 mL separatory funnel containing brine (30 mL) and EtOAc (30 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 x 10-15 mL). The combined organic layers were concentrated *in vacuo*. The residue was redissolved in EtOAc, filtered through a short plug of Na_2SO_4, washed with additional EtOAc, and concentrated *in vacuo*. The crude material was immediately purified by column chromatography (~ 30 g silica gel, diameter of the column ~ 2 cm, length of the packed column ~ 18 cm) with a gradient of hexanes (100 mL) → hexanes/Et_2O = [60:1 (120 mL) → 50:1 (150 mL) → 40:1 (80 mL)] (the product on TLC was visualized with I_2), the title compound was obtained as a colorless oil (1st run: 205 mg, 75% yield, > 99.5:0.5 er, > 20:1 dr; 2nd run: 199 mg, 73% yield, > 99.5:0.5 er, > 20:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71-7.69 (m, 4H), 7.46-7.37 (m, 10H), 7.33-7.29 (m, 4H), 7.26-7.22 (m, 2H), 3.65-3.60 (m, 4H), 3.56 (d, *J* = 14.0 Hz, 2H), 2.94 (q, *J* = 8.1 Hz, 1H), 2.32-2.22 (m, 1H), 1.92-1.84 (m, 1H), 1.82-1.75 (m, 2H), 1.65-1.57 (m, 1H), 1.56-1.46 (m, 2H), 1.35-1.29 (m, 1H), 1.17-1.13 (m, 1H), 1.09 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.18, 135.72, 134.31, 129.62, 128.89, 128.17, 127.71, 126.75, 64.18, 63.52, 54.93, 41.04, 32.16, 30.49, 27.04, 23.06, 21.18, 19.38. **SFC** analysis: CEL-1 (1:99 MeOH (0.1% DEA): $scCO_2$, 2.50 mL/min), 12.57 min (major), 13.68 min (minor), > 99.5:0.5 er. **Specific rotation** $[\alpha]_D^{27}$: -61.7 (c = 1.0, $CHCl_3$). **IR** (thin film): 3027, 2929, 2856, 1493, 1427, 1360, 1110, 1028, 823, 698 cm^{-1}. **HRMS** Calcd. m/z for $C_{37}H_{46}NOSi^+$ $[M+H]^+$: 548.3343; found 548.3369.

(1*R*,2*S*)-*N*,*N*-dibenzyl-2-(3-((5-(trifluoromethyl)pyridin-2-yl)oxy)propyl)cyclobutan-1-amine (7e)



Following general procedure **B**, 2-(3-(cyclobut-1-en-1-yl)propoxy)-5-(trifluoromethyl)pyridine (129 mg, 0.50 mmol, 1.0 equiv) and $Bn_2NOC(O)Mes$ (216 mg, 0.60 mmol, 1.2 equiv) were used. The reaction was run at 40 °C for 46 h. After Workup **B** and purification by column chromatography with a gradient of hexanes (100 mL) → hexanes/Et_2O = [50:1 (100 mL) → 30:1 (90 mL) → 20:1 (160 mL) → 15:1 (120 mL) → 10:1 (80 mL) → 8:1 (80 mL) (the above volumes refer to the volume of hexanes used)] (the product on TLC was visualized with I_2), the title compound was obtained as a colorless oil (1st run: 157 mg, 69% yield, > 99.5:0.5 er, > 20:1 dr; 2nd run: 161 mg, 71% yield, > 99.5:0.5 er, > 20:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (br, 1H), 7.77 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.38-7.36 (m, 4H), 7.25-7.21 (m, 2H), 7.31 (t, *J* = 7.4 Hz, 4H), 6.80 (d, *J* = 8.7 Hz, 1H), 4.29 (t, *J* = 6.5 Hz, 2H), 3.66 (d, *J* = 14.0 Hz, 2H), 3.55 (d, *J* = 14.0 Hz, 2H), 2.97 (q, *J* = 8.1 Hz, 1H), 2.38-2.29 (m, 1H), 1.96-1.80 (m, 3H), 1.79-1.62 (m, 3H), 1.46-1.36 (m, 1H), 1.23-1.12 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.15, 145.06 (q, *J* = 4.5 Hz), 140.08, 135.62 (q, *J* = 3.1 Hz), 128.88, 128.20, 126.81, 124.23 (q, *J* = 271.2 Hz), 119.81 (q, *J* = 32.9 Hz), 111.34, 66.90, 63.52, 54.94, 40.92, 32.21, 26.80, 22.92, 21.16. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -61.47. **SFC** analysis: AD-H (8:92 IPA (0.15% DEA): $scCO_2$, 2.50 mL/min), 5.19 min (major), 5.81 min (minor), > 99.5:0.5 er. **Specific rotation** $[\alpha]_D^{27}$: -31.5 (c = 1.0, $CHCl_3$). **IR** (thin film): 3028, 2938, 2798, 1613, 1500, 1315, 1291, 1122, 1077, 698 cm^{-1}. **EA** Calcd. for $C_{27}H_{29}F_3N_2O$: C, 71.35; H, 6.43. Found: C, 71.35; H, 6.37.

(1*R*,2*R*)-*N*,*N*-dibenzyl-2-(4-methoxybenzyl)cyclopropan-1-amine (12)

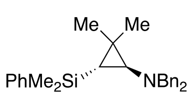


An oven-dried screw-cap reaction tube (Fisherbrand, 13*100 mm, part no. 1495935C) containing a magnetic stir bar was charged with $Cu(OAc)_2$ (5.4 mg, 0.030 mmol) and (*R*)-DTBM-SEGPHOS (38.9 mg, 0.033 mmol). The reaction tube was loosely capped (cap: Thermo Scientific C4015-66; Septum: Thermo Scientific C4015-60), and then transferred into a nitrogen-filled glovebox. Anhydrous THF (0.60 mL) was added to the tube via a 1 mL syringe. The tube was capped and the mixture was stirred for 15 min at rt. Then DMMS (0.22 mL, 1.80 mmol) was added in one portion via a 1 mL syringe and the stirring was continued for another 10 min at rt to prepare a dark red CuH stock solution.

A separate oven-dried screw-cap reaction tube (Fisherbrand, 13*100 mm, part no. 1495935C) containing a magnetic stir bar was loosely capped (cap: Thermo Scientific C4015-66; Septum: Thermo Scientific C4015-60), and then transferred into the glovebox. 1-(Cycloprop-1-en-1-ylmethyl)-4-methoxybenzene (53 mg, 73% purity[3], 0.24 mmol, 1.2 equiv, freshly prepared), Bn_2NOPiv (60 mg, 0.2 mmol, 1.0 equiv), and anhydrous THF (0.20 mL) were added to the reaction tube. Then the CuH stock solution (0.27 mL) was added via a 1 mL syringe to the reaction tube in one portion. The reaction tube was capped and then removed from the glove box. The reaction mixture was allowed to stir at rt for 18 h.

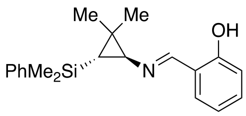
After the reaction was completed, the cap of the reaction tube was removed. While the reaction mixture was stirred at rt, sat. NH_4F in MeOH (0.4 mL) was added slowly to quench the reaction mixture (*Caution: gas evolution observed*). The mixture was stirred at rt for 30 min, and then transferred to a 20 mL scintillation vial with EtOAc. The solution was concentrated *in vacuo*, redissolved in hexane/EtOAc=2:1, and then passed through a short plug of silica gel eluting with hexane/EA=2:1. The resulting solution was collected in another 20 mL scintillation vial, concentrated *in vacuo*, and then $CDCl_3$ and 1,1,2,2-tetrachloroethane (16.8 mg, 0.1 mmol) were added. ^{1}H NMR analysis of the crude reaction mixture was carried out to determine the NMR yield. Then the solution in the NMR tube was transferred backed to the 20 mL vial with CH_2Cl_2. The solution was concentrated *in vacuo*. The residue was purified by preparative thin layer chromatography (20 x 20 cm, 1000 microns, catalog # TLG-R10011B-341 from Silicycle) eluting with hexane/EtOAc = 20:1, followed by another purification with preparative thin layer chromatography (20 x 20 cm, 250 microns, catalog # TLG-R10014B-323 from Silicycle) eluting with hexane/EtOAc = 15:1 to give the product. The title compound was obtained as a light yellow oil (1st run: 15.7 mg, 22% yield, 55.5:44.5 er, > 20:1 dr; 2nd run: 15.6 mg, 22% yield, 55.5:44.5 er, > 20:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36-7.26 (m, 10H), 7.06-7.04 (m, 2H), 6.84-6.81 (m, 2H), 3.81 (s, 3H), 3.71 (d, *J* = 13.5 Hz, 2H), 3.60 (d, *J* = 13.5 Hz, 2H), 2.50 (dd, *J* = 14.5, 5.9 Hz, 1H), 2.22 (dd, *J* = 14.5, 8.1 Hz, 1H), 1.73 (dt, *J* = 6.7, 3.4 Hz, 1H), 0.97-0.92 (m, 1H), 0.60 (dt, *J* = 8.6, 4.2 Hz, 1H), 0.41 (q, *J* = 5.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.88, 139.07, 133.84, 129.51, 129.37, 128.10, 126.89, 113.77, 58.51, 55.36, 43.56, 37.59, 23.51, 14.67. **SFC** analysis: CEL-1 (1:99 MeOH: $scCO_2$ to 2:98 MeOH: $scCO_2$ linear gradient over 16 min with 1 min hold time, 2.50 mL/min), 7.67 min (major), 10.17 min (minor), > 99.5:0.5 er. **Specific rotation** $[\alpha]_D^{23}$: -6.8 (c = 1.0, $CHCl_3$). **IR** (thin film): 3027, 2914, 2832, 1611, 1510, 1452, 1244, 1175, 1036, 747 cm^{-1}. **HRMS** Calcd. m/z for $C_{25}H_{28}NO^+$ $[M+H]^+$: 358.2165; found 358.2177.

(1*R*,3*R*)-*N*,*N*-dibenzyl-3-(dimethyl(phenyl)silyl)-2,2-dimethylcyclopropan-1-amine (15a)



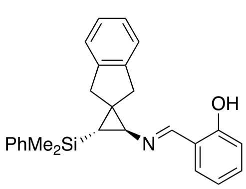
Following general procedure **C**, (3,3-dimethylcycloprop-1-en-1-yl)dimethyl(phenyl)silane (101 mg, 0.50 mmol, 1.0 equiv) and Bn_2NOPiv (178 mg, 0.60 mmol, 1.2 equiv) were used. After Workup **D** and purification by column chromatography with a gradient of hexanes (100 mL) → hexanes/Et_2O = [100:1 (100 mL) → 80:1 (240 mL) → 60:1 (60 mL)] (the product on TLC was visualized with I_2), the title compound was obtained as a white solid (1st run: 139 mg, 70% yield, 98.5:1.5 er, > 20:1 dr; 2nd run: 139 mg, 70% yield, 98.5:1.5 er, > 20:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56-7.54 (m, 2H), 7.38-7.24 (m, 13H), 3.71 (d, *J* = 13.6 Hz, 2H), 3.54 (d, *J* = 13.6 Hz, 2H), 1.82 (d, *J* = 6.0 Hz, 1H), 1.04 (s, 3H), 0.91 (s, 3H), 0.28 (s, 3H), 0.26 (s, 3H), -0.22 (d, *J* = 6.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.21, 139.16, 133.89, 129.52, 128.82, 128.10, 127.81, 126.90, 58.88, 54.76, 25.87, 23.77, 22.87, 19.43, -0.92, -1.20. **m.p.** 57.5-58.3 °C. **SFC** analysis: AD-H (5:95 IPA: $scCO_2$ to 20:80 IPA: $scCO_2$ linear gradient over 6 min with 1 min hold time, 2.50 mL/min), 2.68 min (major), 2.88 min (minor), 98.5:1.5 er. **Specific rotation** $[\alpha]_D^{23}$: +6.6 (c = 1.0, $CHCl_3$). **IR** (thin film): 3063, 3027, 2947, 1453, 1369, 1247, 1113, 1072, 812, 728 cm^{-1}. **EA** Calcd. for $C_{27}H_{33}NSi$: C, 81.14; H, 8.32. Found: C, 81.18; H, 8.31.

2-((*E*)-(((1*R*,3*R*)-3-(dimethyl(phenyl)silyl)-2,2-dimethylcyclopropyl)imino)methyl)phenol (15b)



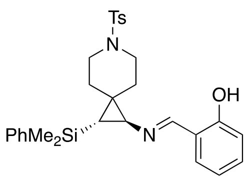
An oven-dried screw-cap reaction tube (Fisherbrand, 13*100 mm, part no. 1495935C) containing a magnetic stir bar was charged with $Cu(OAc)_2$ (2.2 mg, 0.012 mmol) and (*R*)-DTBM-SEGPHOS (15.6 mg, 0.013 mmol). The reaction tube was loosely capped (cap: Thermo Scientific C4015-66; Septum: Thermo Scientific C4015-60), and then transferred into a nitrogen-filled glovebox. Anhydrous THF (0.60 mL) was added to the tube via a 1 mL syringe. The tube was capped and the mixture was stirred for 15 min at rt. Then DMMS (0.22 mL, 1.80 mmol) was added in one portion via a 1 mL syringe and the stirring was continued for another 10 min at rt to prepare an orange CuH stock solution. A second oven-dried screw-cap reaction tube (Fisherbrand, 16*125 mm, part no. 1495935A) containing a magnetic stir bar was loosely capped (cap: Kimble Chase Open Top S/T Closure catalog no. 73804-15425; Septum: Thermo Scientific B7995-15), and then transferred into the glovebox. To the second reaction tube, (3,3-Dimethylcycloprop-1-en-1-yl)dimethyl(phenyl)silane (101 mg, 0.5 mmol, 1.0 equiv) was added, and then the CuH stock solution (0.68 mL) was added via a 1 mL syringe in one portion. The reaction mixture was stirred at rt for 0.5 min, and then 1,2-benzisoxazole (76 μL) was added slowly over 2 min via microsyringe while the reaction mixture was stirred at rt. The reaction tube was capped and then removed from the glove box. The reaction mixture was allowed to stir at rt for 18 h. After Workup **D** and purification by column chromatography (silica gel was pretreated with hexanes containing 1% NEt_3) with a gradient of hexanes (contain 0.1% NEt_3) (100 mL) → hexanes (contain 0.1% NEt_3)/Et_2O = [150:1 (75 mL) → 100:1 (100 mL) → 70:1 (70 mL) → 60:1 (60 mL) → 50:1 (100 mL)], the title compound was obtained as a yellow oil (1st run: 103 mg, 63% yield, 99.5:0.5 er, > 20:1 dr; 2nd run: 100 mg, 62% yield, 99.5:0.5 er, > 20:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 13.09 (s, 1H), 8.49 (s, 1H), 7.58-7.55 (m, 2H), 7.42-7.39 (m, 3H), 7.33-7.26 (m, 2H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.92 (td, *J* = 7.5, 1.1 Hz, 1H), 2.84 (d, *J* = 5.3 Hz, 1H), 1.39 (s, 3H), 1.14 (s, 3H), 0.46 (d, *J* = 5.3 Hz, 1H), 0.40 (s, 3H), 0.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.97, 160.57, 139.34, 133.86, 131.62, 130.62, 129.13, 127.99, 119.48, 118.80, 116.88, 57.25, 26.74, 24.36, 23.74, 23.62, -1.10, -1.18. **SFC** analysis: OJ-H (2:98 MeOH (0.1% DEA): $scCO_2$ to 7:93 MeOH (0.1% DEA): $scCO_2$ linear gradient over 10 min with 1 min hold time, 2.50 mL/min), 4.89 min (major), 7.50 min (minor), 99.5:0.5 er. **Specific rotation** $[\alpha]_D^{23}$: -107.2 (c = 1.0, $CHCl_3$). **IR** (thin film): 2948, 1620, 1495, 1414, 1277, 1200, 1113, 955, 905, 698 cm^{-1}. **EA** Calcd. for $C_{20}H_{25}NOSi$: C, 74.25; H, 7.79. Found: C, 74.42; H, 7.98.

2-((*E*)-(((2*R*,3*R*)-2-(dimethyl(phenyl)silyl)-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)imino)methyl)phenol (15c)



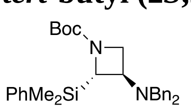
Following general procedure **D**, (1',3'-dihydrospiro[cyclopropane-1,2'-inden]-2-en-2-yl)dimethyl(phenyl)silane (138 mg, 0.50 mmol, 1.0 equiv) was used, and the 1,2-benzisoxazole solution was added slowly via syringe pump at a rate of 0.16 mL/h. After Workup **D** and purification by column chromatography (silica gel was pretreated with hexanes containing 1% NEt_3) with a gradient of hexanes (contain 0.1% NEt_3) (100 mL) → hexanes (contain 0.1% NEt_3)/Et_2O = [80:1 (80 mL) → 60:1 (60 mL) → 40:1 (80 mL) → 30:1 (60 mL) → 20:1 (40 mL) → 15:1 (60 mL) → 10:1 (40 mL)], the title compound was obtained as a yellow solid (1st run: 145 mg, 73% yield, 99.5:0.5 er, > 20:1 dr; 2nd run: 149 mg, 75% yield, 99.5:0.5 er, > 20:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 12.96 (s, 1H), 8.48 (s, 1H), 7.60-7.58 (m, 2H), 7.40-7.36 (m, 3H), 7.34-7.30 (m, 1H), 7.26-7.24 (m, 2H), 7.20-7.16 (m, 3H), 7.00 (d, *J* = 8.2 Hz, 1H), 6.91 (td, *J* = 7.5, 1.0 Hz, 1H), 3.40 (d, *J* = 16.7 Hz, 1H), 3.29-3.21 (m, 2H), 3.05 (d, *J* = 5.5 Hz, 1H), 2.77 (d, J = 16.2 Hz, 1H), 0.84 (d, J = 5.5 Hz, 1H), 0.43 (s, 3H), 0.42 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.24, 160.55, 142.44, 142.31, 138.66, 133.86, 131.88, 130.81, 129.32, 128.10, 126.50, 126.33, 124.55, 124.24, 119.32, 118.94, 116.90, 56.75, 40.72, 38.66, 35.31, 22.02, -1.46, -1.75. **m.p.** 123.4-124.1 °C. **SFC** analysis: AD-H (5:95 MeOH (0.1% DEA): $scCO_2$ to 20:80 MeOH (0.1% DEA): $scCO_2$ linear gradient over 6 min with 1 min hold time, 2.50 mL/min), 4.34 min (major), 4.65 min (minor), 99.5:0.5 er. **Specific rotation** $[\alpha]_D^{23}$: +67.8 (c = 1.0, $CHCl_3$). **IR** (thin film): 3066, 3019, 2951, 2891, 2836, 1619, 1426, 1277, 1113, 733 cm^{-1}. **EA** Calcd. for $C_{26}H_{27}NOSi$: C, 78.54; H, 6.85. Found: C, 78.28; H, 6.70.

2-((*E*)-(((1*R*,2*R*)-2-(dimethyl(phenyl)silyl)-6-tosyl-6-azaspiro[2.5]octan-1-yl)imino)methyl)phenol (15d)



Following general procedure **D**, 1-(dimethyl(phenyl)silyl)-6-tosyl-6-azaspiro[2.5]oct-1-ene (199 mg, 0.50 mmol, 1.0 equiv) was used, and the 1,2-benzisoxazole solution was added slowly via syringe pump at a rate of 0.13 mL/h. After Workup **D** and purification by column chromatography (silica gel was pretreated with hexanes containing 1% NEt_3) with a gradient of hexanes (contain 0.1% NEt_3)/CH_2Cl_2 = 50:1 (100 mL) → hexanes (contain 0.1% NEt_3)/EtOAc = [30:1 (60 mL) → 25:1 (50 mL) → 20:1 (40 mL) → 15:1 (60 mL) → 12:1 (60 mL) → 10:1 (80 mL) → 8:1 (80 mL) → 7:1 (140 mL) → 6:1 (60 mL) → 5:1 (100 mL) → 4:1 (40 mL) (the above volumes refer to the volume of hexanes used)], the title compound was obtained as a yellow solid (1st run: 163 mg, 63% yield, 98:2 er, > 20:1 dr; 2nd run: 147 mg, 57% yield, 98:2 er, > 20:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 12.62 (s, 1H), 8.42 (s, 1H), 7.60 (d, J = 8.2 Hz, 2H), 7.48-7.46 (m, 2H), 7.40-7.28 (m, 6H), 7.23 (dd, J = 7.6, 1.6 Hz, 1H), 6.96 (d, J = 8.1 Hz, 1H), 6.91 (td, J = 7.5, 1.0 Hz, 1H), 3.35 (dt, J = 9.8, 4.1 Hz, 1H), 3.23 (dt, J = 9.7, 4.0 Hz, 1H), 2.82 (d, J = 5.4 Hz, 1H), 2.71-2.63 (m, 2H), 2.43 (s, 3H), 2.04 (ddd, J = 13.5, 9.5, 3.9 Hz, 1H), 1.83 (dt, J = 13.8, 3.7 Hz, 1H), 1.76 (ddd, J = 13.4, 9.5, 3.9 Hz, 1H), 1.33 (dt, J = 13.4, 3.7 Hz, 1H), 0.43 (d, J = 5.4 Hz, 1H), 0.33 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.95, 160.38, 143.42, 138.28, 133.70, 133.61, 132.05, 130.82, 129.77, 129.42, 128.12, 127.68, 119.16, 119.00, 116.92, 55.55, 46.15, 45.80, 32.66, 32.62, 31.02, 23.21, 21.65, -1.24, -1.36. **m.p.** 60.1-62.8 °C. **SFC** analysis: AD-H (20:80 MeOH (0.1% DEA): $scCO_2$, 2.50 mL/min), 4.60 min (major), 5.80 min (minor), 98:2 er. **Specific rotation** $[\alpha]_D^{23}$: +13.8 (c = 1.0, $CHCl_3$). **IR** (thin film): 2953, 2844, 1619, 1427, 1334, 1276, 1163, 1090, 908, 722 cm^{-1}. **EA** Calcd. for $C_{29}H_{34}N_2O_3SSi$: C, 67.15; H, 6.61. Found: C, 67.54; H, 6.65.

***tert*-butyl (2*S*,3*R*)-3-(dibenzylamino)-2-(dimethyl(phenyl)silyl)azetidine-1-carboxylate (7f)**



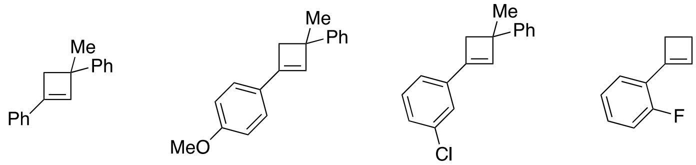
Following general procedure **B**, *tert*-butyl 4-(dimethyl(phenyl)silyl)azete-1(2*H*)-carboxylate (145 mg, 0.50 mmol, 1.0 equiv) and $Bn_2NOC(O)Mes$ (270 mg, 0.75 mmol, 1.5 equiv) were used. The reaction was run at 40 °C for 46 h. After Workup **D** and purification by column chromatography with a gradient of hexanes (100 mL) → hexanes/acetone = [80:1 (80 mL) → 70:1 (70 mL) → 50:1 (100 mL) → 30:1 (180 mL)] (the product on TLC was visualized with I_2), the title compound was obtained as a colorless oil (1st run: 223 mg, 92% yield, > 99.5:0.5 er, > 20:1 dr; 2nd run: 223 mg, 92% yield, > 99.5:0.5 er, > 20:1 dr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43-7.39 (m, 3H), 7.36-7.20 (m, 12H), 4.16 (d, J = 5.7 Hz, 1H), 3.94-3.92 (m, 1H), 3.63-3.45 (m, 6H), 1.43 (s, 9H), 0.40 (s, 3H), 0.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.64, 138.99, 136.27, 134.30, 129.42, 128.76, 128.33, 127.90, 127.09, 79.38, 57.41, 53.94, 52.87, 52.61, 28.56, -4.15, -4.68. **SFC** analysis: OJ-H (5:95 IPA:

$scCO_2$ to 20:80 IPA: $scCO_2$ linear gradient over 6 min with 1 min hold time, 2.50 mL/min), 2.87 min (major), 3.17 min (minor), > 99.5:0.5 er. **Specific rotation** $[\alpha]_D^{23}$: +11.1 (c = 1.0, $CHCl_3$). **IR** (thin film): 2973, 1691, 1408, 1364, 1248, 1154, 1111, 1028, 832, 696 cm^{-1}. **EA** Calcd. for $C_{30}H_{38}N_2O_2Si$: C, 74.03; H, 7.87. Found: C, 73.75; H, 8.04.

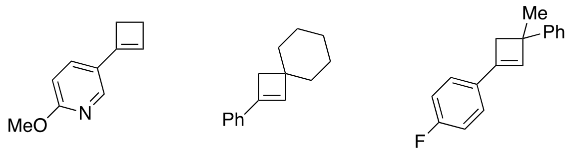
4. Preparation of Alkene Substrates and Amination Reagents

4.1 Synthesis of 1-Arylcyclobutenes

All the 1-arylcyclobutenes used in this paper are listed below. **2a-c**[5], **2f-g**[5] are known compounds and were prepared by following previously reported procedures.

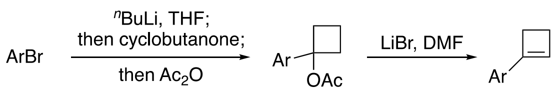


2a **2b** **2c** **2d**



2e **2f** **2g**

Synthesis of **2d**, **2e**.

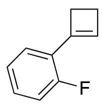


General Procedure **E**[6]

A 250 mL round bottom flask containing a magnetic stir bar was charged with the corresponding aryl bromide (21.0 mmol, 1.05 equiv) and then capped with a septum. The flask was evacuated and backfilled with argon (this process was repeated for a total of three times), and then attached to a balloon filled with argon. Anhydrous THF (63 mL) was added, and then the mixture was cooled to -78 °C. ^{n}BuLi (2.5 M in hexane, 1.1 equiv, 8.8 mL) was added dropwise at -78 °C. The reaction mixture was stirred at -78 °C for 15 min, and then cyclobutanone (20.0 mmol, 1.0 equiv, 1.40 g) in anhydrous THF (20 mL) was added dropwise at -78 °C. The mixture was stirred at -78 °C for 30 min, and was allowed to warm to rt and stirred for an additional 30 min. Then the reaction mixture was cooled to -78 °C, and Ac_2O (40.0 mmol, 2.0 equiv, 4.08 g) was added dropwise. The reaction mixture was allowed to warm to rt and stirred for 2 h. The septum was removed, and the reaction mixture was concentrated *in vacuo*. Et_2O and aq. $NaHCO_3$ were added. The layers were separated, and the organic layer was extracted with Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, concentrated *in vacuo*, and then purified by column chromatography on silica gel to afford the corresponding 1-arylcyclobutyl acetate.

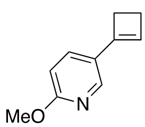
A 50 mL round bottom flask containing a magnetic stir bar was charged with the corresponding 1-arylcyclobutyl acetate (1.0 equiv) and LiBr (10.0 equiv), and then capped with a septum. The flask was evacuated and backfilled with argon (this process was repeated for a total of three times), and then attached to a balloon filled with argon. Anhydrous DMF (13 mL) was added, and then the reaction mixture was stirred at 100 °C for 1 h or overnight (as indicated for each substrate). The mixture was allowed to cool to rt, and was immediately quenched with water. Et_2O and aq. $NaHCO_3$ were added. The layers were separated, and the organic layer was extract with Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, concentrated *in vacuo*, and then purified by column chromatography on silica gel to afford the corresponding 1-arylcyclobutene (Note: **2d** and **2e** are very air-sensitive, and therefore need to be immediately stored under nitrogen in the glovebox freezer at -30 °C once prepared).

1-(cyclobut-1-en-1-yl)-2-fluorobenzene (2d)



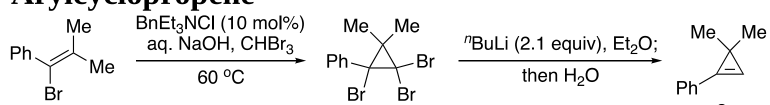
Following general procedure **E**, 1-(2-fluorophenyl)cyclobutyl acetate (6.29 mmmol, 1.31 g) was used. The title compound was obtained as a colorless oil (0.47 g, 36% yield over two steps) after purification by column chromatography on silica gel (eluting with pentane). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28-7.19 (m, 2H), 7.14-7.03 (m, 2H), 6.42-6.40 (m, 1H), 2.91-2.89 (m, 2H), 2.64-2.63 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.25 (d, J = 251.3 Hz), 140.96, 133.13 (d, J = 7.3 Hz), 128.66 (d, J = 8.4 Hz), 127.01 (d, J = 4.4 Hz), 123.97 (d, J = 3.5 Hz), 123.04 (d, J = 14.3 Hz), 115.61 (d, J = 21.0 Hz), 30.00, 27.96. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.94. **IR** (thin film): 3070, 2918, 2834, 1490, 1446, 1237, 1214, 1176, 1031, 747 cm^{-1}. **HRMS** Calcd. m/z for $C_{10}H_{10}F^+$ $[M+H]^+$: 149.0761; found 149.0757.

5-(cyclobut-1-en-1-yl)-2-methoxypyridine (2e)



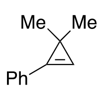
Following general procedure **E**, 1-(6-methoxypyridin-3-yl)cyclobutyl acetate (6.60 mmmol, 1.46 g) was used. The title compound was obtained as a white solid (0.26 g, 18% yield over two steps) after purification by column chromatography on silica gel (eluting with pentane ~ pentane/Et_2O = 30:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, J = 2.3 Hz, 1H), 7.57 (dd, J = 8.6, 2.4 Hz, 1H), 6.68 (dd, J = 8.6, 0.7 Hz, 1H), 6.20 (t, J = 1.2 Hz, 1H), 3.93 (s, 3H), 2.80-2.78 (m, 2H), 2.56-2.54 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.50, 143.39, 143.12, 134.78, 126.64, 124.65, 110.69, 77.48, 77.16, 76.84, 53.60, 28.90, 26.91. **m.p.** 46.7-48.0 °C. **IR** (thin film): 2948, 2840, 1723, 1681, 1601, 1492, 1372, 1288, 1020, 832 cm^{-1}. **HRMS** Calcd. m/z for $C_{10}H_{12}NO^+$ $[M+H]^+$: 162.0913; found 162.0905.

4.2 Synthesis of 1-Arylcyclopropene



8

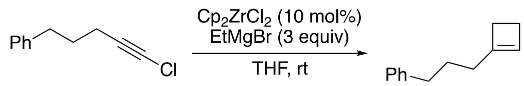
(3,3-dimethylcycloprop-1-en-1-yl)benzene (8)



A 25 mL round bottom flask containing a magnetic stir bar was charged with (1-bromo-2-methylprop-1-en-1-yl)benzene[7] (5.05 mmol, 1.0 equiv, 1.07 g), $BnEt_3NCl$ (0.505 mmol, 0.1 equiv, 115 mg), and bromoform (40.4 mmol, 8.0 equiv, 3.5 mL). While the reaction mixture was stirred vigorously at rt, NaOH (40.4 mmol, 8.0 equiv, 1.62 g) in water (1.6 mL) was added dropwise. Then the flask was capped with a septum and attached to a balloon filled with air. The reaction mixture was stirred vigorously at 60 °C for 36 h. The reaction mixture was allowed to cool to rt, and diluted with CH_2Cl_2 (100 mL) and water (50 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 70 mL). The combined organic layers were filtered through a short plug of silica gel and washed with Et_2O. The resulting solution was concentrated *in vacuo*, and then purified by column chromatography on silica gel eluting with hexanes to give (1,2,2-tribromo-3,3-dimethylcyclopropyl)benzene.

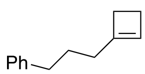
A 25 mL round bottom flask containing a magnetic stir bar was charged with (1,2,2-tribromo-3,3-dimethylcyclopropyl)benzene (2.0 mmol, 1.0 equiv, 766 mg) and then capped with a septum. The flask was evacuated and backfilled with argon (this process was repeated for a total of three times), and then attached to a balloon filled with argon. Anhydrous Et_2O (4 mL) was added, and then the mixture was cooled to -78 °C. *ⁿ*BuLi (2.5 M in hexane, 2.1 equiv, 1.68 mL) was added dropwise at -78 °C. The reaction mixture was allowed to slowly warmed to rt over 2 h while being stirred. Then the reaction mixture was cooled to 0 °C, and water (0.2 mL) was added dropwise. The reaction mixture was allowed to warm to rt and was stirred at rt for 10 min. Then saturated aqueous NH_4Cl (2 mL) was added dropwise, and the reaction mixture was stirred at rt for 5 min. The septum on the flask was removed. The reaction mixture was diluted with pentane (50 mL) and water (20 mL). The layers were separated, and the aqueous layer was extracted with pentane (50 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated *in vacuo* and purified by column chromatography on silica gel (eluting with pentane) to give the title compound as a colorless oil (0.25 g, 53% yield over two steps) (Note: **8** was stored under nitrogen in the glovebox freezer at -30 °C once prepared). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52-7.49 (m, 2H), 7.42-7.39 (m, 2H), 7.34-7.30 (m, 2H), 1.35 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 132.23, 129.58, 128.87, 128.73, 128.52, 115.19, 27.02, 19.41. **IR** (thin film): 2924, 2861, 1675, 1598, 1493, 1444, 1371, 1308, 1024, 700 cm^{-1}. **HRMS** Calcd. m/z for $C_{11}H_{13}^+$ $[M+H]^+$: 145.1012; found 145.1022.

4.3 Synthesis of 1-Alkylcyclobutenes[8,9]

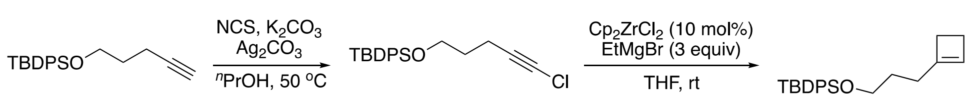


5a

(3-(cyclobut-1-en-1-yl)propyl)benzene (5a)

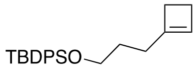


A 100 mL round bottom flask containing a magnetic stir bar was transferred into a nitrogen-filled glovebox. Cp_2ZrCl_2 (1.2 mmol, 0.1 equiv, 351 mg) was added to the flask. The flask was capped with a septum, removed from the glovebox, and then attached to a balloon filled with argon. Anhydrous THF (24 mL) was added. While the reaction mixture was stirred at rt, EtMgBr (1 M in THF, 36 mmol, 3.0 equiv, 36 mL) was added dropwise. Then (5-chloropent-4-yn-1-yl)benzene[10] (12 mmol, 1.0 equiv, 2.14 g) was added dropwise at rt. The reaction mixture was stirred at rt for 48 h. The reaction mixture was cooled to 0 °C in an ice bath, and water was added slowly to quench the reaction mixture. The mixture was diluted with water (50 mL) and pentane (50 mL). The layers were separated and the aqueous layer was extracted with pentane (50 mL). The combined organic layers were washed with water (50 mL), dried over Na_2SO_4, filtered, concentrated *in vacuo*, and purified by column chromatography on silica gel eluting with pentane (Note: (5-chloropent-4-yn-1-yl)benzene was not fully consumed in the reaction, and it could poison the CuH catalyst in the subsequent hydroamination reactions. Therefore, the last few product-containing fractions from the column chromatography were analyzed by GC to determine whether they contained (5-chloropent-4-yn-1-yl)benzene, and only the clean fractions were collected.) to afford the title compound as a colorless oil (0.58 g, 28% yield) (Note: **5a** was stored under nitrogen in the glovebox freezer at -30 °C once prepared). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32-7.28 (m, 2H), 7.21-7.18 (m, 3H), 5.71 (br, 1H), 2.67-2.63 (m, 2H), 2.44-2.42 (m, 2H), 2.37-2.35 (m, 2H), 2.06-2.03 (m, 2H), 1.81-1.74 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.47, 142.65, 128.61, 128.41, 127.15, 125.82, 35.76, 31.31, 30.80, 28.72, 26.71. **IR** (thin film): 3028, 2922, 2842, 1630, 1604, 1496, 1453, 1171, 1030, 698 cm^{-1}. **HRMS** Calcd. m/z for $C_{13}H_{17}^+$ $[M+H]^+$: 173.1325; found 173.1315.



5b

***tert*-butyl(3-(cyclobut-1-en-1-yl)propoxy)diphenylsilane (5b)**

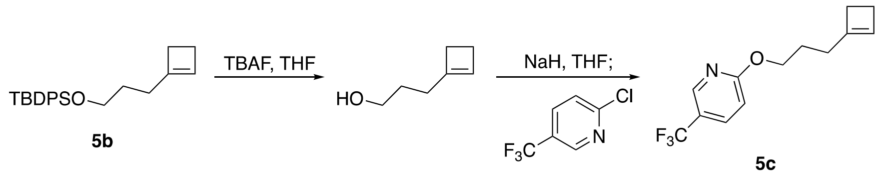


A 100 mL round bottom flask containing a magnetic stir bar was charged with NCS (22.0 mmol, 2.0 equiv, 2.95 g), K_2CO_3 (5.5 mmol, 0.5 equiv, 0.76 g), and

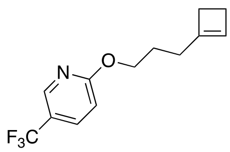
Ag_2CO_3 (0.11 mmol, 0.1 equiv, 0.30 g) and then capped with a septum. The flask was evacuated and backfilled with argon (this process was repeated for a total of three times), and then attached to a balloon filled with argon. Anhydrous ^{n}PrOH (22 mL) was added. Then *tert*-butyl(pent-4-yn-1-yloxy)diphenylsilane[11] (11.0 mmol, 1.0 equiv, 3.55 g) was added dropwise at rt. The reaction mixture was stirred at 50 °C for 48 h. Then the reaction mixture was cooled to 0 °C, and brine was added. The resulting mixture was extracted with Et_2O, and the combined organic layers were washed with water (100 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to give *tert*-butyl((5-chloropent-4-yn-1-yl)oxy)diphenylsilane.

A 100 mL round bottom flask containing a magnetic stir bar was transferred into a nitrogen-filled glovebox. Cp_2ZrCl_2 (1.2 mmol, 0.1 equiv, 351 mg) was added to the flask. The flask was capped with a septum, removed from the glovebox, and then attached to a balloon filled with argon. Anhydrous THF (24 mL) was added. While the reaction mixture was stirred at rt, EtMgBr (1 M in THF, 36 mmol, 3.0 equiv, 36 mL) was added dropwise. Then *tert*-butyl((5-chloropent-4-yn-1-yl)oxy)diphenylsilane (12 mmol, 1.0 equiv, 4.28 g) was added dropwise at rt. The reaction mixture was stirred at rt for 72 h. The reaction mixture was cooled to 0 °C in an ice bath, and water was added slowly to quench the reaction mixture. The mixture was diluted with water (50 mL) and Et_2O (50 mL). The layers were separated and the aqueous layer was extracted with Et_2O (50 mL). The combined organic layers were washed with water (50 mL), dried over Na_2SO_4, filtered, concentrated *in vacuo*, and purified by column chromatography on silica gel eluting with 0-2% EtOAc in hexanes to give a mixture of the title compound and the 1-chloroalkyne starting material. The isolated material contains 24% (w/w) *tert*-butyl((5-chloropent-4-yn-1-yl)oxy)diphenylsilane impurity, which was removed by carrying out a further transformation.

A 25 mL round bottom flask containing a magnetic stir bar was charged with the material isolated from the previous step (1.69 g material, contains 1.14 mmol of *tert*-butyl((5-chloropent-4-yn-1-yl)oxy)diphenylsilane, 1.0 equiv) and then capped with a septum. The flask was evacuated and backfilled with argon (this process was repeated for a total of three times), and then attached to a balloon filled with argon. Anhydrous THF (5.7 mL) was added, and then the mixture was cooled to -78 °C. ^{n}BuLi (2.5 M in hexane, 2.28 mmol, 2.0 equiv, 0.91 mL) was added dropwise at -78 °C. The reaction mixture was stirred at -78 °C for 1 h, and then anhydrous PhCHO (4.56 mmol, 4.0 equiv, 484 mg) was added dropwise at -78 °C. The mixture was stirred at -78 °C for 30 min, and was allowed to warm to rt and stirred for 30 min. Water was slowly added to quench the reaction mixture. The resulting mixture was extracted with hexane (2x). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel eluting with 0-2% EtOAc in hexanes to give the title compound as a colorless oil (1.21 g, 13% overall yield) (Note: **8b** was stored under nitrogen in the glovebox freezer at -30 °C once prepared). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69-7.66 (m, 4H), 7.45-7.36 (m, 6H), 5.63 (tt, J = 1.7, 0.9 Hz, 1H), 3.68 (t, J = 6.4 Hz, 2H), 2.39-2.37 (m, 2H), 2.32-2.29 (m, 2H), 2.11-2.07 (m, 2H), 1.74-1.67 (m, 2H), 1.05 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.39, 135.74, 134.25, 129.65, 127.73, 126.99, 63.70, 31.31, 29.90, 27.55, 27.03, 26.61, 19.40. **IR** (thin film): 3071, 2929, 2856, 1472, 1427, 1105, 953, 822, 737, 699 cm^{-1}. **EA** Calcd. for $C_{23}H_{30}OSi$: C, 78.80; H, 8.63. Found: C, 78.91; H, 8.63.

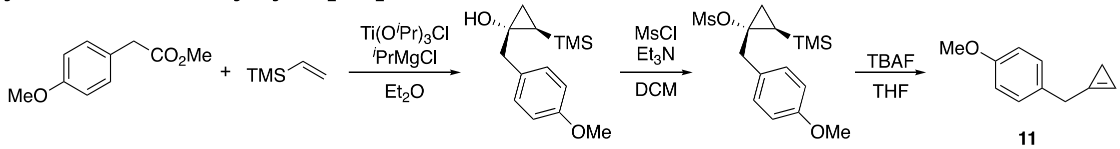


2-(3-(cyclobut-1-en-1-yl)propoxy)-5-(trifluoromethyl)pyridine (5c)

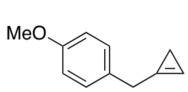


A 25 mL round bottom flask containing a magnetic stir bar was charged with **5b** (2.4 mmol, 1.0 equiv, 843 mg) and then capped with a septum. The flask was evacuated and backfilled with argon (this process was repeated for a total of three times), and then attached to a balloon filled with argon. Anhydrous THF (4.8 mL) was added, and then the mixture was cooled to 0 °C. TBAF (1 M in THF, 2.0 equiv, 4.8 mL) was added dropwise at 0 °C. The reaction mixture was allowed to warm to rt and was stirred at rt for 3 h. Then the reaction mixture was diluted with saturated aqueous NH_4Cl and Et_2O. The layers were separated and the aqueous layer was extracted with Et_2O. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (eluting with 0-40% Et_2O in pentane) to afford 3-(cyclobut-1-en-1-yl)propan-1-ol. A 25 mL round bottom flask containing a magnetic stir bar was charged with 3-(cyclobut-1-en-1-yl)propan-1-ol (2.24 mmol, 1.12 equiv, 251 mg) and then capped with a septum. The flask was evacuated and backfilled with argon (this process was repeated for a total of three times), and then attached to a balloon filled with argon. Anhydrous THF (4.5 mL) was added, and then the mixture was cooled to 0 °C. NaH (2.7 mmol, 1.35 equiv, 65 mg) was added in several portions at 0 °C. The mixture was allowed to warm to rt and was stirred at rt for 15 min. Then 2-chloro-5-(trifluoromethyl)pyridine (2.0 mmol, 1.0 equiv, 364 mg) was added and the reaction mixture was stirred at rt overnight. The reaction mixture was diluted with water and EtOAc. The layers were separated and the aqueous layer was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (eluting with 0-3% EtOAc in hexanes) to give the title compound as a colorless oil (0.50 g, 93% yield over two steps) (Note: **5c** was stored under nitrogen in the glovebox freezer at -30 °C once prepared). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44-8.41 (m, 1H), 7.75 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.80 (d, *J* = 8.7 Hz, 1H), 5.72 (br, 1H), 4.37 (t, *J* = 6.6 Hz, 2H), 2.44 (ddd, *J* = 4.2, 2.7, 1.1 Hz, 2H), 2.36-2.33 (m, 2H), 2.16 (dt, *J* = 7.7, 3.7 Hz, 2H), 1.93 (tt, *J* = 7.2, 6.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.13, 149.53, 145.07 (q, *J* = 4.4 Hz), 135.69 (q, *J* = 3.2 Hz), 127.60, 124.21 (q, *J* = 271.0 Hz), 119.91 (q, *J* = 33.0 Hz), 111.37, 66.50, 31.29, 27.65, 26.68, 26.25. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -61.52. **IR** (thin film): 2924, 2844, 1614, 1501, 1315, 1160, 1123, 1078, 1011, 834 cm^{-1}. **EA** Calcd. for $C_{13}H_{14}F_3NO$: C, 60.70; H, 5.49. Found: C, 60.72; H, 5.66.

4.4 Synthesis of 1-Alkylcyclopropene[12]



1-(cycloprop-1-en-1-ylmethyl)-4-methoxybenzene (11)

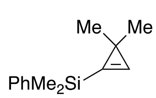


A 250 mL round bottom flask containing a magnetic stir bar was capped with a septum. The flask was evacuated and backfilled with argon (this process was repeated for a total of three times), and then attached to a balloon filled with argon. Anhydrous Et_2O (53 mL) and $Ti(O^iPr)_3Cl$ (7.50 mmol, 1.5 equiv, 1.95 g) were added, and then the mixture was cooled to -60 $^{\circ}$C. ^iPrMgCl (2.0 M in Et_2O, 2.9 equiv, 7.25 mL) was added dropwise at -60 $^{\circ}$C. The reaction mixture was stirred at -60 $^{\circ}$C for 10 min, and then a mixture of methyl 2-(4-methoxyphenyl)acetate (5.0 mmol, 1.0 equiv, 0.90 g) and trimethyl(vinyl)silane (7.5 mmol, 1.5 equiv, 0.75 g) in anhydrous Et_2O (0.27 mL) was added dropwise. The reaction mixture was allowed to warm to -25 $^{\circ}$C over 30 min, stirred at -25 ~ -20 $^{\circ}$C for 1 h, and then was warmed to 0 $^{\circ}$C and stirred for 2 h. Water (2.5 mL) in THF (10 mL) was added slowly, and then the reaction mixture was allowed to warm to rt and stirred for 30 min. The reaction mixture was passed through a short plug of Celite, washed with Et_2O, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (pretreated with 1% Et_3N in hexanes) and eluted with a gradient of hexanes/Et_2O = 8:1~3:1 to afford 1-(4-methoxybenzyl)-2-(trimethylsilyl)cyclopropan-1-ol.

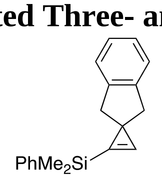
A 25 mL round bottom flask containing a magnetic stir bar was charged with 1-(4-methoxybenzyl)-2-(trimethylsilyl)cyclopropan-1-ol (1.8 mmol, 1.0 equiv, 0.45 g), and then CH_2Cl_2 (10 mL) and Et_3N (7.2 mmol, 4.0 equiv, 0.73 g) were added. The mixture was cooled to 0 $^{\circ}$C, and MsCl (3.6 mmol, 2.0 equiv, 0.41 g) was added dropwise. The reaction mixture was stirred at 0 $^{\circ}$C for 1 h. Then the reaction mixture was allowed to warm to rt, and saturated aqueous $NaHCO_3$ (10 mL) and Et_2O (10 mL) were added. The layers were separated, and the aqueous layer was extracted with Et_2O (2 x 30 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated *in vacuo*, and used in the next step without further purification.

A 100 mL round bottom flask containing a magnetic stir bar was charged with the crude material from the last step. The flask was evacuated and backfilled with argon (this process was repeated for a total of three times), and then attached to a balloon filled with argon. Anhydrous THF (10 mL) was added, and then TBAF (1 M in THF, 9.9 mL) was added dropwise at rt. The reaction mixture was stirred at rt for 2 h, and then saturated aqueous NH_4Cl (10 mL) and Et_2O (30 mL) were added. The layers were separated, and the aqueous layer was extracted with Et_2O (2 x 20 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated *in vacuo*, and immediately purified by column chromatography on silica gel (eluting with pentane and then pentane/Et_2O = 60:1) to give the title compound as a colorless oil (0.23 g, 73% purity[3], 21% yield over 3 steps) (Note: **11** was stored under nitrogen in the glovebox freezer at -30 $^{\circ}$C once prepared). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.20-7.17 (m, 2H), 6.88-6.86 (m, 2H), 6.57 (m, 1H), 3.81 (s, 3H), 3.79 (s, 2H), 1.01 (d, *J* = 1.8 Hz, 2H). **IR** (thin film): 2955, 2876, 2834, 1610, 1511, 1301, 1244, 1174, 1035, 840 cm^{-1}. **HRMS** Calcd. m/z for $C_{11}H_{13}O^+$ $[M+H]^+$: 161.0961; found 161.0972.

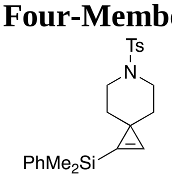
4.5 Synthesis of 1-Silyl Substituted Three- and Four-Membered Cycloalkenes



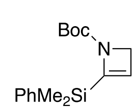
13a



13b

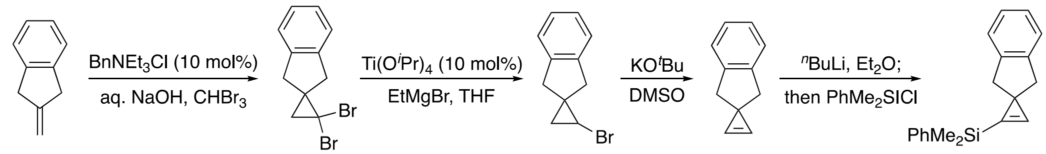


13c



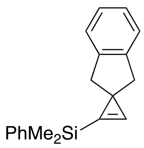
5d

All the 1-silyl substituted three- and four-membered cycloalkenes used in this paper are listed above. **13a**[13] is a known compound and was prepared by following previously reported procedures.



13b

(1',3'-dihydrospiro[cyclopropane-1,2'-inden]-2-en-2-yl)dimethyl(phenyl)silane (13b)

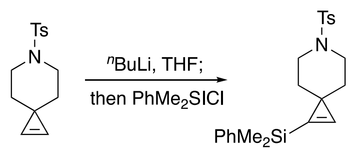


A 50 mL round bottom flask containing a magnetic stir bar was charged with 2-methylene-2,3-dihydro-1*H*-indene (19.0 mmol, 1.0 equiv, 2.51 g), $BnEt_3NCl$ (1.9 mmol, 0.1 equiv, 439 mg), and bromoform (76.0 mmol, 4.0 equiv, 6.7 mL). While the reaction mixture was stirred vigorously at rt, NaOH (76.0 mmol, 4.0 equiv, 3.1 g) in water (3.1 mL) was added dropwise. Then the flask was capped with a septum and attached to a balloon filled with air. The reaction mixture was stirred vigorously at 60 $^{\circ}$C for 24 h. The reaction mixture was allowed to cool to rt, and diluted with CH_2Cl_2 (100 mL) and water (50 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 70 mL). The combined organic layers were dried over Na_2SO_4, filtered, concentrated *in vacuo*, and then purified by column chromatography on silica gel eluting with hexanes/ CH_2Cl_2 = 100:1 to give 2,2-dibromo-1',3'-dihydrospiro[cyclopropane-1,2'-indene].

A 100 mL round bottom flask containing a magnetic stir bar was charged with 2,2-dibromo-1',3'-dihydrospiro[cyclopropane-1,2'-indene] (13.5 mmol, 1.0 equiv) and then capped with a septum. The flask was evacuated and backfilled with argon (this process was repeated for a total of three times), and then attached to a balloon filled with argon. Anhydrous THF (27 mL) and $Ti(O^iPr)_4$ (0.13 mmol, 0.1 equiv, 0.40 mL) were added. While the reaction mixture was stirred at rt, EtMgBr (3 M in Et_2O, 1.3 equiv, 5.8 mL) was added over 1 h via syringe pump. The reaction mixture was stirred at rt for 4 h. Then the reaction mixture was cooled to 0 $^{\circ}$C, and 10% aq. H_2SO_4 (10 mL) was added dropwise to quench the reaction mixture. The mixture was diluted with H_2O (100 mL) and Et_2O (100 mL). The layers were separated and the aqueous layer was extracted with E_2O (100 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and then concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (eluting with 0-2% Et_2O in pentane) to give 2-bromo-1',3'-dihydrospiro[cyclopropane-1,2'-indene].

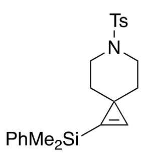
A 100 mL round bottom flask containing a magnetic stir bar was charged with 2-bromo-1',3'-dihydrospiro[cyclopropane-1,2'-indene] (6.0 mmol, 1.0 equiv, 1.34 g) and then capped with a septum. The flask was evacuated and backfilled with argon (this process was repeated for a total of three times), and then attached to a balloon filled with argon. Anhydrous DMSO (13 mL) was added. While the reaction mixture was stirred at rt, KO^tBu (9.0 mmol, 1.5 equiv, 1.01 g) in anhydrous DMSO (3.3 mL) was added dropwise. The reaction mixture was stirred at rt overnight. Then the reaction mixture was cooled to 0 $^{\circ}$C, and water (100 mL) was slowly added to quench the reaction mixture. Et_2O (75 mL) was added. The layers were separated and the aqueous layer was extract with Et_2O (100 mL). The combine organic layers were washed with water (3 x 75 mL), then washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (eluting with pentane) to give 1',3'-dihydrospiro[cyclopropane-1,2'-inden]-2-ene.

A 10 mL round bottom flask with a magnetic stir bar was charged with 1',3'-dihydrospiro[cyclopropane-1,2'-inden]-2-ene (1.35 mmol, 1.0 equiv, 192 mg) and anhydrous Et_2O (1.4 mL) under nitrogen. The mixture was cooled to -78 $^{\circ}$C, and ^nBuLi (2.5 M in hexane, 1.05 equiv, 0.57 mL) was added dropwise. The reaction mixture was stirred at -78 $^{\circ}$C for 1 h, and then at -10 $^{\circ}$C for 1 h. The resulting solution was added over 20 min to another 25 mL round bottom flask containing $PhMe_2SiCl$ (1.48 mmol, 1.1 equiv, 263 mg) and anhydrous Et_2O (2.8 mL) at -40 $^{\circ}$C under nitrogen. The reaction mixture was stirred at -40 $^{\circ}$C for 1 h and at rt for 2 h. The reaction mixture was quenched with saturated aqueous NH_4Cl (5 mL). Then water (20 mL) and Et_2O (60 mL) were added. The layers were separated and the aqueous layer was extracted with Et_2O (60 mL). The combined organic layers were dried over Na_2SO_4, and then concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (eluted with 0-2% CH_2Cl_2 in hexanes) to afford the title compound as a colorless oil (0.29 g, 20% yield over 4 steps) (Note: **13b** was stored under nitrogen in the glovebox freezer at -30 $^{\circ}$C once prepared). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96-7.95 (m, 1H), 7.56-7.53 (m, 2H), 7.41-7.32 (m, 3H), 7.16 (s, 4H), 2.87 (d, *J* = 17.0 Hz, 2H), 2.71 (d, *J* = 17.2 Hz, 2H), 0.43 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.63, 137.40, 133.81, 131.79, 129.44, 127.99, 126.85, 125.97, 124.27, 44.30, 26.60, -1.94. **IR** (thin film): 3068, 2957, 2880, 2825, 1676, 1482, 1427, 1248, 1113, 733 cm^{-1}. **EA** Calcd. for $C_{19}H_{20}Si$: C, 82.55; H, 7.29. Found: C, 82.74; H, 7.45.

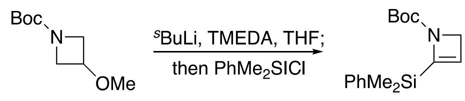


13c

1-(dimethyl(phenyl)silyl)-6-tosyl-6-azaspiro[2.5]oct-1-ene (13c)

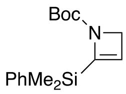


A 25 mL round bottom flask with a magnetic stir bar was charged with 6-tosyl-6-azaspiro[2.5]oct-1-ene[14] (3.0 mmol, 1.0 equiv, 790 mg) and anhydrous THF (8.7 mL) under nitrogen. The mixture was cooled to -78 $^{\circ}$C, and ^{n}BuLi (2.5 M in hexane, 1.02 equiv, 1.23 mL) was added dropwise (Note: The addition process of ^{n}BuLi needs to be terminated once the reaction mixture turns from colorless to slightly pinkish. Otherwise, disilylated byproduct, which is difficult to seperate from the product, is formed). Then the reaction mixture was stirred at -10 $^{\circ}$C for 1 h. The resulting suspension was added over 30 min to another 50 mL round bottom flask containing $PhMe_2SiCl$ (3.3 mmol, 1.1 equiv, 563 mg) and anhydrous THF (6.0 mL) at -40 $^{\circ}$C under nitrogen. The reaction mixture was stirred at -40 $^{\circ}$C for 1 h and at rt for 2 h. The reaction mixture was quenched with saturated aqueous NH_4Cl (20 mL). Then water (30 mL) and CH_2Cl_2 (60 mL) were added. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (60 mL). The combined organic layers were dried over Na_2SO_4, and then concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (eluted with hexanes/EtOAc/ CH_2Cl_2 = 30:1:2) to afford the title compound as a white solid (0.90 g, 76% yield) (Note: **13c** was stored under nitrogen in the glovebox freezer at -30 ^{o}C once prepared). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.64-7.62 (m, 2H), 7.41-7.39 (m, 2H), 7.37-7.27 (m, 5H), 3.11 (ddd, *J* = 10.8, 6.6, 3.9 Hz, 2H), 2.81 (ddd, *J* = 11.5, 8.5, 3.6 Hz, 2H), 2.47 (s, 3H), 1.61 (td, *J* = 8.6, 4.2 Hz, 2H), 1.41-1.35 (m, 2H), 0.32 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.29, 136.99, 136.86, 133.65, 133.51, 131.87, 129.62, 129.55, 127.99, 127.87, 47.20, 38.17, 22.52, 21.69, -2.25. **m.p.** 65.6-66.2 $^{\circ}$C. **IR** (thin film): 2937, 2903, 2837, 1667, 1428, 1351, 1247, 1162, 1112, 722 cm^{-1}. **EA** Calcd. for $C_{22}H_{27}NO_2SSi$: C, 66.46; H, 6.84. Found: C, 66.33; H, 6.61.



5d

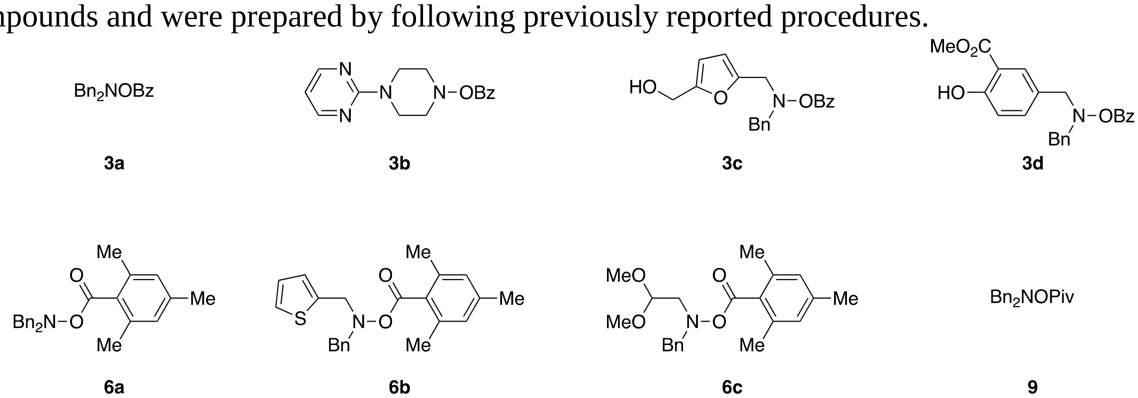
tert-butyl 4-(dimethyl(phenyl)silyl)azete-1(2*H*)-carboxylate[15] (5d)



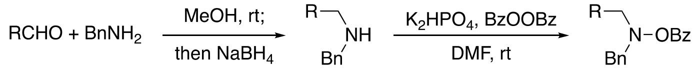
A 100 mL round bottom flask containing a magnetic stir bar was capped with a septum. The flask was evacuated and backfilled with argon (this process was repeated for a total of three times), and then attached to a balloon filled with argon. Then *tert*-butyl 3-methoxyazetidine-1-carboxylate (4.0 mmol, 1.0 equiv, 749 mg) and anhydrous THF (25 mL) were added, and the mixture was cooled to -78 °C. TMEDA (10.0 mmol, 2.5 equiv, 1.16 g) was added. Then ^{s}BuLi (1.3 M in cyclohexane, 2.5 equiv, 7.7 mL) was added dropwise over 10 min while the reaction mixture was stirred at -78 °C. The reaction mixture was stirred at -78 °C for 1 h, and then $PhMe_2SiCl$ (10.0 mmol, 2.5 equiv, 1.71 g) was added. The reaction mixture was stirred at -78 °C for 1 h, and then at rt for 1 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (30 mL). Then Et_2O (100 mL) was added. The layers were separated and the aqueous layer was extracted with Et_2O (50 mL). The combined organic layers were dried over Na_2SO_4, and then concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (eluted with 0-9% Et_2O in hexanes). The resulting material was redissolved in Et_2O (3 mL), filtered through a short plug of basic activated alumina, and washed with additional Et_2O. The collected Et_2O solution was concentrated *in vacuo* to afford the pure product as a colorless oil (0.47 g, 40% yield) (Note: **5d** was stored under nitrogen in the glovebox freezer at -30 °C once prepared). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.2 Hz, 2H), 7.40-7.33 (m, 3H), 5.89 (s, 1H), 4.55 (s, 2H), 1.33 (s, 9H), 0.47 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.48, 152.00, 136.47, 134.23, 129.46, 127.85, 126.31, 80.34, 59.78, 28.48, -3.07. **IR** (thin film): 2977, 1695, 1390, 1366, 1247, 1164, 1139, 1113, 1020, 814 cm^{-1}. **HRMS** Calcd. m/z for $C_{16}H_{24}NO_2Si^+$ $[M+H]^+$: 290.1571; found 290.1575.

4.6 Synthesis of Amination Reagents

All the amination reagents used in this paper are listed below. **3a**[16], **3b**[17], **6a**[18], **9**[19] are known compounds and were prepared by following previously reported procedures.



Synthesis of **3c**, **3d**.

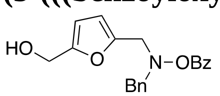


General Procedure **F**

A 100 mL round bottom flask containing a magnetic stir bar was charged with the corresponding aldehyde (1.0 equiv), $BnNH_2$ (1.0 equiv), and MeOH (2.0 M). The reaction mixture was stirred at rt for 6 h. Then $NaBH_4$ (2.0 equiv) was added in several portions at rt. The reaction mixture was stirred at rt overnight, and then quenched with 5 M aq. NaOH. The resulting mixture was concentrated *in vacuo*, and then diluted with CH_2Cl_2 and water. The layers were separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, concentrated *in vacuo*, and used in the next step without further purification.

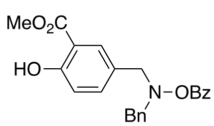
A 100 mL round bottom flask containing a magnetic stir bar was charged with the crude material from the first step, and then DMF and K_2HPO_4 were added. BzOOBz was then added in one portion at rt. The reaction mixture was stirred at rt until BzOOBz was completely consumed (as indicated by TLC analysis), and then diluted with EtOAc and water. The layers were separated and the aqueous layer was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, concentrated *in vacuo*, and then purified by column chromatography on silica gel to give the corresponding amination reagent.

(5-(((benzoyloxy)(benzyl)amino)methyl)furan-2-yl)methanol (3c)



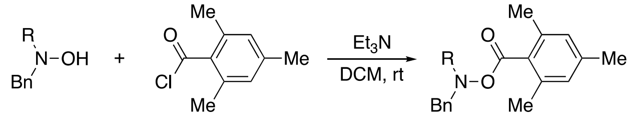
Following general procedure **F**, 5-(hydroxymethyl)furan-2-carbaldehyde (40 mmol, 5.0 g) and $BnNH_2$ (40 mmol, 4.4 mL) were used in the first step, and BzOOBz (contains 25% water, 40 mmol, 12.9 g), K_2HPO_4 (80 mmol, 13.9 g), and DMF (50 mL) were used in the second step. The title compound was obtained as a white solid (2.83 g, 21% yield over two steps). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92-7.90 (m, 2H), 7.54 (tt, *J* = 7.0, 1.3 Hz, 1H), 7.47-7.39 (m, 4H), 7.35-7.26 (m, 3H), 6.28 (d, *J* = 3.1 Hz, 1H), 6.23 (d, *J* = 3.1 Hz, 1H), 4.56 (s, 2H), 4.24 (s, 2H), 4.23 (s, 2H), 2.06 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.87, 154.34, 149.61, 135.46, 133.10, 129.68, 129.48, 129.25, 128.51, 128.47, 127.91, 111.05, 108.70, 62.08, 57.62, 54.12. **m.p.** 80.5-82.3 °C. **IR** (thin film): 3419, 3031, 2864, 1733, 1450, 1242, 1083, 1062, 1015, 698 cm^{-1}. **EA** Calcd. for $C_{20}H_{19}NO_4$: C, 71.20; H, 5.68. Found: C, 71.48; H, 5.74.

methyl 5-(((benzoyloxy)(benzyl)amino)methyl)-2-hydroxybenzoate (3d)

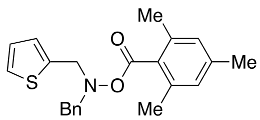


Following general procedure **F**, methyl 5-formyl-2-hydroxybenzoate (20 mmol, 3.6 g) and $BnNH_2$ (20 mmol, 2.2 mL) were used in the first step, and BzOOBz (contains 25% water, 22 mmol, 7.1 g), K_2HPO_4 (40 mmol, 7.0 g), and DMF (25 mL) were used in the second step. The title compound was obtained as a white solid (3.31 g, 42% yield over two steps). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.70 (s, 1H), 7.87-7.83 (m, 3H), 7.56 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.51 (tt, *J* = 7.0, 1.3 Hz, 1H), 7.44-7.42 (m, 2H), 7.39-7.24 (m, 5H), 6.93 (d, *J* = 8.5 Hz, 1H), 4.20 (s, 2H), 4.12 (s, 2H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.52, 164.88, 161.27, 137.26, 135.81, 133.02, 131.01, 129.57, 129.41, 129.31, 128.50, 128.44, 127.85, 126.77, 117.78, 112.16, 62.17, 61.36, 52.39. **m.p.** 111.7-112.4 °C. **IR** (thin film): 3032, 2953, 1739, 1674, 1595, 1489, 1441, 1241, 1086, 707 cm^{-1}. **EA** Calcd. for $C_{23}H_{21}NO_5$: C, 70.58; H, 5.41. Found: C, 70.33; H, 5.53.

Synthesis of **6b**, **6c**.

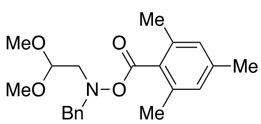


***N*-benzyl-*N*-(thiophen-2-ylmethyl)-*O*-(2,4,6-trimethylbenzoyl)hydroxylamine (6b)**



A 100 mL round bottom flask containing a magnetic stir bar was charged with *N*-benzyl-*N*-(thiophen-2-ylmethyl)hydroxylamine[18] (10.0 mmol, 1.0 equiv, 2.19 g), CH_2Cl_2 (25 mL), and Et_3N (14.4 mmol, 1.44 equiv, 2.0 mL). The mixture was cooled to 0 °C, and 2,4,6-trimethylbenzoyl chloride (12.0 mmol, 1.2 equiv, 2.19 g) in CH_2Cl_2 (5 mL) was added dropwise. Then the reaction mixture was stirred at rt overnight. The reaction mixture was passed through a short plug of basic alumina, and washed with additional EtOAc. The resulting solution was concentrated *in vacuo*, and then purified by column chromatography on silica gel to give the title compound as a white solid (1.51 g, 41% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51-7.49 (m, 2H), 7.36-7.27 (m, 4H), 7.06-7.05 (m, 1H), 6.97 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.76 (s, 2H), 4.43 (s, 2H), 4.16 (s, 2H), 2.25 (s, 3H), 1.95 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.30, 139.43, 138.16, 136.23, 135.28, 129.73, 129.41, 128.53, 128.26, 127.87, 127.51, 126.67, 126.05, 61.64, 56.74, 21.24, 19.11, 19.10. **m.p.** 84.3-85.4 °C. **IR** (thin film): 3029, 2921, 1747, 1611, 1431, 1235, 1160, 1053, 851, 696 cm^{-1}. **EA** Calcd. for $C_{22}H_{23}NO_2S$: C, 72.30; H, 6.34. Found: C, 72.21; H, 6.34.

***N*-benzyl-*N*-(2,2-dimethoxyethyl)-*O*-(2,4,6-trimethylbenzoyl)hydroxylamine (6c)**



A 100 mL round bottom flask containing a magnetic stir bar was charged with *N*-benzyl-*N*-(2,2-dimethoxyethyl)hydroxylamine[18] (8.0 mmol, 1.0 equiv, 1.69 g), CH_2Cl_2 (20 mL), and Et_3N (11.5 mmol, 1.15 equiv, 1.6 mL). The mixture was cooled to 0 °C, and 2,4,6-trimethylbenzoyl chloride (8.0 mmol, 1.0 equiv, 1.82 g) in CH_2Cl_2 (4 mL) was added dropwise. Then the reaction mixture was stirred at rt overnight. The reaction mixture was passed through a short plug of basic alumina, and washed with additional EtOAc. The resulting solution was concentrated *in vacuo*, and then purified by column chromatography on silica gel to give the title compound as a colorless oil (1.43 g, 50% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47-7.45 (m, 2H), 7.34-7.24 (m, 3H), 6.78 (s, 2H), 4.77 (t, *J* = 5.1 Hz, 1H), 4.21 (s, 2H), 3.40 (s, 6H), 3.24 (d, *J* = 5.1 Hz, 2H), 2.25 (s, 3H), 2.06 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.43, 139.54, 136.30, 135.31, 129.66, 129.49, 128.50, 128.38, 127.85, 102.05, 63.58, 60.33, 53.96, 21.24, 19.41. **IR** (thin film): 2921, 2833, 1748, 1612, 1454, 1238, 1127, 1054, 851, 698 cm^{-1}. **EA** Calcd. for $C_{21}H_{27}NO_4$: C, 70.56; H, 7.61. Found: C, 70.43; H, 7.49.

5. Computational Details

5.1 HOMO and LUMO Energies of Ground-State (Reactant) and Transition State Geometries of Cyclic Alkene Substrates and the CuH Catalyst

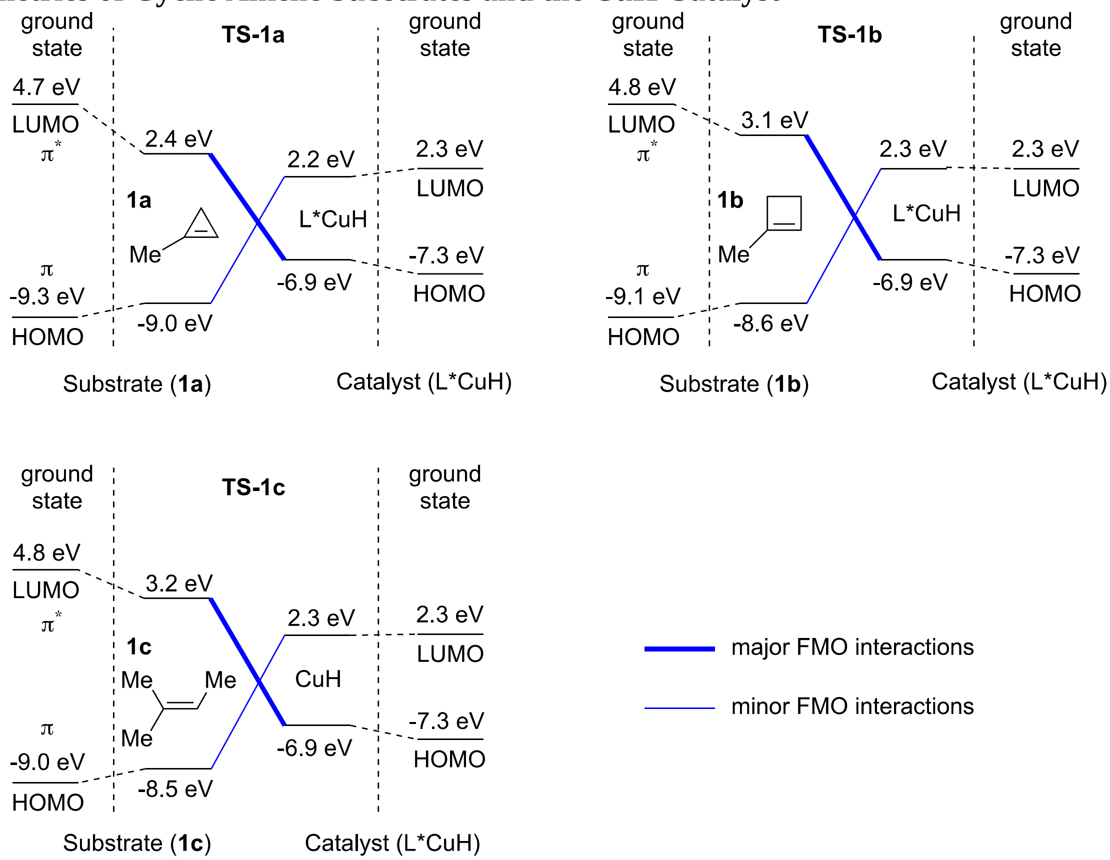


Figure S1. Frontier molecular orbital (FMO) interactions between the alkene and the L*CuH fragments. HOMO and LUMO energies were calculated at the HF/6-311G(d,p) level of theory. Although the LUMO of the alkenes have comparable energies in their ground state geometries, the greater pyramidalization of **1a** in **TS-1a** significantly lowers the LUMO energy of **1a** in its transition state geometry.

5.2 Substrate Distortion Energy versus the Out-of-Plane Dihedral Angle

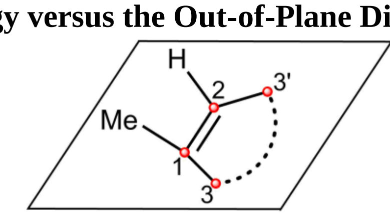


Figure S2. The definition of the out-of-plane dihedral angles (α_{Me} = D(C_{Me}-C1-C2-C3'); α_H = D(H-C2-C1-C3)).

The distortion energies of 1-methylcyclopropene, 1-methylcyclobutene, and 2-methylbut-2-butene at different out-of-plane dihedral angles (α_{Me} and α_H) (Figure 3c) were calculated at the M06/6-311+G(d,p) level of theory. The distortion energy is the single point energy difference between the distorted structures and the undistorted ground state (reactant) geometries of the alkenes. The out-of-plane angle (α) is defined as the dihedral angle between the H(Me)-C1-C2 plane and the C1-C2-C3(C3') plane (Figure S2). The out-of-plane dihedral angle is gradually changed from 180° to 120° by a step of 5° and the out-of-plane angle for Me is set to be the same as that for H in this process (*i.e.* Me and H are always placed in the same plane).

5.3 Dissecting the Activation Energy ($\Delta E^{\ddagger}$) using the Ligand-Substrate Interaction Model

$$\Delta E^{\ddagger} = \Delta E_{sub\text{-}dist} + \Delta E_{cat\text{-}dist} + \Delta E_{int\text{-}bond} + \Delta E_{int\text{-}space} \qquad (1)$$

Table S5. Computed energy terms to investigate the origin of regioselectivity. All energies are in kcal/mol.

	TS2a-a	**TS2a-b**	**ΔΔE‡ (TS2a-b – TS2a-a)**	**TS8-a**	**TS8-b**	**ΔΔE‡ (TS8-b – TS8-a)**
$\Delta E^{\ddagger}$	-10.5	-7.9	2.6	-13.9	-15.5	-1.6
$\Delta E_{sub\text{-}dist}$	20.2	25.0	4.8	20.0	23.6	3.6
$\Delta E_{cat\text{-}dist}$	9.4	9.8	0.4	10.8	9.0	-1.8
$\Delta E_{int\text{-}bond}$	-22.6	-25.8	-3.2	-31.9	-34.5	-2.6
$\Delta E_{int\text{-}space}$	-17.5	-16.9	0.6	-12.8	-13.6	-0.8

Table S6. Computed energy terms to investigate the origin of enantioselectivity. All energies are in kcal/mol.

	TS-1a	**TS-1a'**	**ΔΔE‡ (TS-1a' – TS-1a)**	**TS-1b**	**TS-1b'**	**ΔΔE‡ (TS-1b' – TS-1b)**
$\Delta E^{\ddagger}$	-11.1	-11.3	-0.2	-3.7	-1.0	2.7
$\Delta E_{sub\text{-}dist}$	22.4	22.6	0.2	22.2	23.2	1.0
$\Delta E_{cat\text{-}dist}$	7.7	8.3	0.6	7.9	9.5	1.6
$\Delta E_{int\text{-}bond}$	-33.9	-35.0	-1.1	-25.4	-26.2	-0.8
$\Delta E_{int\text{-}space}$	-7.3	-7.2	0.1	-8.4	-7.5	0.9

5.4 Free energy profiles of the alkene hydrocupration step

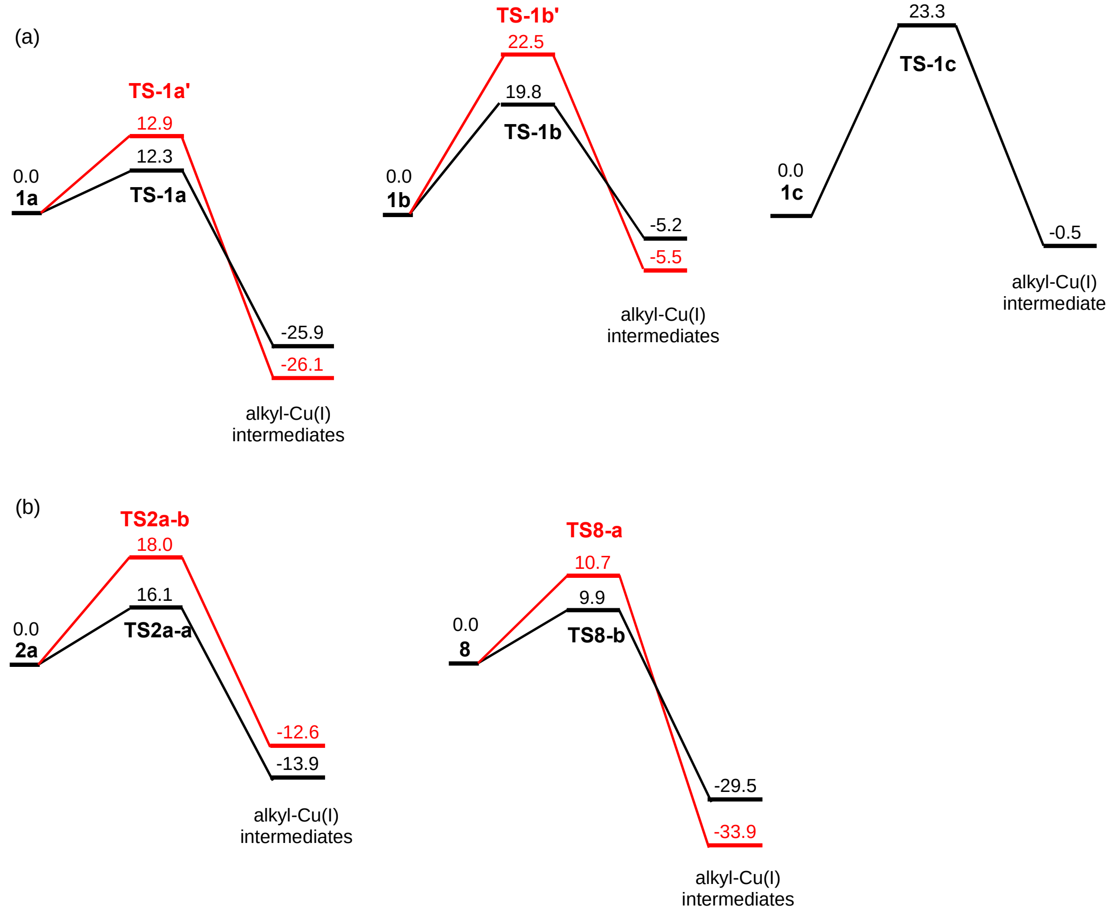


Figure S3. Computed activation Gibbs free energies and reaction free energies of hydrocupration with varies alkenes. All energies are in kcal/mol and are with respect to separated alkene substrate and the CuH catalyst. The hydrocupration reactions with cyclopropene and cyclobutene derivatives (**1a**, **1b**, **2a**, and **8**) are all exergonic.

5.5 Cartesian Coordinates

1-methylcyclopropene (1a)

B3LYP/6-31G(d) SCF energy: -155.941626 a.u.
B3LYP/6-31G(d) Enthalpy: -155.850995 a.u.
B3LYP/6-31G(d) Gibbs free energy: -155.883360 a.u.
M06/6-311+G(d,p) SCF energy in solution: -155.864889 a.u.
M06/6-311+G(d,p) enthalpy in solution: -155.774258 a.u.
M06/6-311+G(d,p) free energy in solution: -155.806622 a.u.
Three lowest frequencies (cm^{-1}): 156.9522 299.9446 321.1413

Cartesian coordinates:

ATOM	X	Y	Z
C	-0.15681600	0.08709000	-0.00023700
C	0.91649800	0.81545800	0.00020700
C	1.14941500	-0.67391600	-0.00001300
H	1.38594900	1.78825800	-0.00022200

H	1.48856900	-1.17714200	0.91294200
H	1.48942000	-1.17678300	-0.91284100
C	-1.62783900	-0.07120200	0.00003800
H	-1.95577900	-0.63833200	0.88094500
H	-2.13948600	0.89733700	0.00025000
H	-1.95621600	-0.63792200	-0.88103900

1-methylcyclobutene (1b)

B3LYP/6-31G(d) SCF energy: -195.292981 a.u.

B3LYP/6-31G(d) Enthalpy: -195.292981 a.u.

B3LYP/6-31G(d) Gibbs free energy: -195.205873 a.u.

M06/6-311+G(d,p) SCF energy in solution: -195.186430 a.u.

M06/6-311+G(d,p) enthalpy in solution: -195.065079 a.u.

M06/6-311+G(d,p) free energy in solution: -195.099321 a.u.

Three lowest frequencies (cm^{-1}): 164.7382 221.6528 317.6539

Cartesian coordinates:

ATOM	X	Y	Z
C	-0.57488800	-1.04137600	-0.00011400
C	-1.62727100	0.12365500	0.00016500
C	-0.42480100	1.04903100	-0.00013500
C	0.48155000	0.05702700	-0.00002300
H	-2.26759600	0.16426000	0.89045800
H	-2.26882700	0.16427900	-0.88921300
C	1.97175600	-0.01567400	0.00009600
H	2.42173300	0.98324700	0.00031700
H	2.34369500	-0.55689400	0.88106100
H	2.34383200	-0.55655300	-0.88103600
H	-0.59588200	-1.68451200	0.88934200
H	-0.59591800	-1.68337500	-0.89041500
H	-0.33911200	2.13356900	-0.00044500

2-methylbut-2-ene (1c)

B3LYP/6-31G(d) SCF energy: -196.539826 a.u.

B3LYP/6-31G(d) Enthalpy: -196.395113 a.u.

B3LYP/6-31G(d) Gibbs free energy: -196.432626 a.u.

M06/6-311+G(d,p) SCF energy in solution: -196.428300 a.u.

M06/6-311+G(d,p) enthalpy in solution: -196.283586 a.u.

M06/6-311+G(d,p) free energy in solution: -196.321100 a.u.

Three lowest frequencies (cm^{-1}): 126.9722 154.1021 188.5166

Cartesian coordinates:

ATOM	X	Y	Z
C	-0.73459300	-0.67178700	-0.00013700
H	-0.71444600	-1.76306000	-0.00104500
C	0.44964300	-0.04035700	0.00012600
C	1.74146800	-0.82442300	0.00006300
H	1.56392800	-1.90466200	-0.00019000

H	2.35423300	-0.58047600	-0.87966100
H	2.35374600	-0.58092600	0.88034400
C	0.63031000	1.45836200	-0.00008400
H	1.20518300	1.78009900	0.87982900
H	1.20628000	1.77957600	-0.87946600
H	-0.31347300	2.00866300	-0.00091500
C	-2.11557900	-0.07768100	0.00014700
H	-2.11503100	1.01571400	0.00029400
H	-2.68403500	-0.40961600	-0.87985600
H	-2.68387600	-0.40999600	0.87997600

1,3-diphenyl-3-methylcyclobut-1-ene (2a)

B3LYP/6-31G(d) SCF energy: -657.390971 a.u.

B3LYP/6-31G(d) Enthalpy: -657.098276 a.u.

B3LYP/6-31G(d) Gibbs free energy: -657.156364 a.u.

M06/6-311+G(d,p) SCF energy in solution: -657.051858 a.u.

M06/6-311+G(d,p) enthalpy in solution: -656.759163 a.u.

M06/6-311+G(d,p) free energy in solution: -656.817251 a.u.

Three lowest frequencies (cm^{-1}): 22.1352 35.7525 39.0999

Cartesian coordinates:

ATOM	X	Y	Z
C	1.03547700	-0.72847000	0.76961500
C	-0.02497000	-1.28479300	-0.26898900
C	-0.98987500	-0.27046300	0.32698000
C	-0.08260700	0.21804200	1.19635900
H	-0.29234600	-2.33957600	-0.12661400
H	0.24125900	-1.12372300	-1.31993300
H	-0.12387900	0.98569800	1.96563000
C	-2.39095200	0.00624900	0.02120500
C	-3.11102500	0.99819400	0.71378900
C	-3.05288200	-0.72223200	-0.98170400
C	-4.44583500	1.24998800	0.41189400
H	-2.61509800	1.57203400	1.49231900
C	-4.39093700	-0.46959700	-1.28402300
H	-2.51087600	-1.49075200	-1.52656900
C	-5.09254400	0.51671700	-0.58886400
H	-4.98611800	2.01971700	0.95693600
H	-4.88553200	-1.04358200	-2.06328700
H	-6.13495400	0.71467100	-0.82340100
C	2.27247500	-0.09370900	0.14788100
C	3.06934900	-0.82787900	-0.74447000
C	2.66989400	1.21005800	0.46922100
C	4.22441500	-0.27698000	-1.29885300
H	2.77922100	-1.84205000	-1.01073900
C	3.82769300	1.76559900	-0.08130400
H	2.06660500	1.80236900	1.15173200

C	4.60928300	1.02469500	-0.96795900
H	4.82310300	-0.86305500	-1.99168700
H	4.11501100	2.78062700	0.18149500
H	5.50810800	1.45676900	-1.39980300
C	1.43809700	-1.75048800	1.84933100
H	2.08976500	-2.52870200	1.43470300
H	1.98504500	-1.25851300	2.66231400
H	0.55035700	-2.23151900	2.27625100

1-phenylcyclopropene (8)
B3LYP/6-31G(d) SCF energy: -426.320456 a.u.
B3LYP/6-31G(d) Enthalpy: -426.114875 a.u.
B3LYP/6-31G(d) Gibbs free energy: -426.162512 a.u.
M06/6-311+G(d,p) SCF energy in solution: -426.093100 a.u.
M06/6-311+G(d,p) enthalpy in solution: -425.887519 a.u.
M06/6-311+G(d,p) free energy in solution: -425.935156 a.u.
Three lowest frequencies (cm^{-1}): 46.7760 85.3581 98.9093
Cartesian coordinates:

ATOM	X	Y	Z
C	1.77324100	1.48287300	-0.00123400
C	0.81779600	0.59200100	-0.00045100
C	2.23138000	0.04570300	-0.00011000
H	2.07749900	2.52057000	-0.00313600
C	-0.58837400	0.25099600	-0.00020300
C	-0.99243700	-1.09521200	0.00011900
C	-1.57445800	1.25573000	-0.00013800
C	-2.34568100	-1.42824700	0.00027900
H	-0.23497200	-1.87384500	0.00021200
C	-2.92484400	0.91987900	0.00003100
H	-1.26764200	2.29816900	-0.00025400
C	-3.31516100	-0.42317300	0.00018200
H	-2.64482300	-2.47306000	0.00046800
H	-3.67678000	1.70464400	0.00004900
H	-4.37023700	-0.68345100	0.00034600
C	2.81595200	-0.56449700	-1.27437200
H	3.90107900	-0.40012300	-1.32624500
H	2.65319400	-1.65041300	-1.31055000
H	2.36406100	-0.12366200	-2.16898800
C	2.81598500	-0.56184000	1.27553800
H	2.65324800	-1.64768500	1.31389100
H	3.90108800	-0.39729200	1.32725400
H	2.36388400	-0.11913400	2.16911100

DTBM-SEGPHOS-based CuH catalyst
B3LYP/6-31G(d) SCF energy: -4362.402757 a.u.
B3LYP/6-31G(d) Enthalpy: -4360.703810 a.u.

B3LYP/6-31G(d) Gibbs free energy: -4360.930343 a.u.
M06/6-311+G(d,p) SCF energy in solution: -4360.93433998 a.u.
M06/6-311+G(d,p) enthalpy in solution: -4359.23539398 a.u.
M06/6-311+G(d,p) free energy in solution: -4359.46192698 a.u.
Three lowest frequencies (cm^{-1}): 5.8740 11.1992 12.4341

Cartesian coordinates:

ATOM	X	Y	Z
Cu	0.00106100	-0.34194800	1.78481000
H	-0.09375000	-0.78380100	3.27835300
P	-1.71356400	0.17059400	0.30059300
C	-1.20521500	0.96270400	-1.29750500
C	-2.95075600	1.32981200	1.03106700
C	-2.74001000	-1.27806500	-0.18707600
C	-0.28069100	0.30183900	-2.17056600
C	-1.66490600	2.24905000	-1.61696600
C	-4.22899700	1.52581700	0.50940300
C	-2.57984200	2.04103900	2.17791000
C	-2.77629800	-2.35669000	0.69548500
C	-3.49301100	-1.34477300	-1.36563400
C	0.03224600	0.98705800	-3.33604400
C	0.30872100	-1.06684600	-2.00590200
C	-1.29017800	2.93130300	-2.78758100
H	-2.35302200	2.74271700	-0.94154200
C	-5.17331200	2.36641000	1.11978700
H	-4.50249400	1.00537900	-0.40118500
C	-3.47484800	2.87156100	2.86149900
H	-1.57613800	1.90123200	2.56014100
C	-3.60077800	-3.47506800	0.48633100
H	-2.13574100	-2.31993100	1.57094200
C	-4.37250800	-2.40285400	-1.61720000
H	-3.38424800	-0.55122000	-2.09359400
C	-0.44539100	2.25911300	-3.64188300
O	0.86560100	0.56608000	-4.35216700
C	-0.05851100	-2.03050900	-2.93472200
C	1.31403300	-1.46939500	-1.06370300
H	-1.66238300	3.92466100	-3.01324900
C	-4.80267100	2.93727500	2.36165300
C	-4.48088100	-3.40962500	-0.61779000
O	0.07495600	2.67332500	-4.84585100
C	0.64028700	1.49104700	-5.41809500
C	0.45938700	-3.32341700	-2.95920300
O	-0.98034300	-1.89839300	-3.95244300
C	1.81237400	-2.78043600	-1.09827700
P	1.83345900	-0.36481600	0.33364100
H	1.59052100	1.73609200	-5.89396600
H	-0.07166700	1.05552400	-6.13519400

C	1.39691400	-3.73715300	-2.04009800
O	-0.11578600	-4.03685800	-3.98242400
C	-0.80798300	-3.06163900	-4.76526400
H	2.56224400	-3.07379600	-0.37345900
C	3.31386500	-1.18917500	1.06953000
C	2.54423600	1.15071300	-0.43687700
H	1.80280600	-4.74279400	-2.04852400
H	-0.20349600	-2.80410300	-5.64791200
H	-1.78539800	-3.45210000	-5.05341900
C	4.54950400	-1.31772000	0.41972500
C	3.17233400	-1.72243300	2.34849900
C	2.36930600	2.35198700	0.24730700
C	3.26503600	1.16296800	-1.63813700
C	5.66143600	-1.87786500	1.05219400
H	4.64123400	-0.96002100	-0.59645200
C	4.23631200	-2.33639500	3.03445300
H	2.19885200	-1.64320900	2.82361500
C	2.94938800	3.55934900	-0.17777900
H	1.75201000	2.34615600	1.13968700
C	3.91442100	2.31365600	-2.09704000
H	3.31231500	0.25247300	-2.22141100
C	5.49931500	-2.29286800	2.40554400
C	3.81993600	3.47990000	-1.28765200
C	-5.12270500	-2.49472300	-2.97148000
C	-4.76695300	-3.83688900	-3.65839100
H	-5.08314600	-4.69020700	-3.05552600
H	-5.26002100	-3.90181400	-4.63663100
H	-3.68481600	-3.91361100	-3.81685400
C	-6.65828300	-2.39536200	-2.81048400
H	-7.12871400	-2.31020800	-3.79809200
H	-7.07549000	-3.27697100	-2.32364300
H	-6.93978800	-1.50726400	-2.23170800
C	-4.69793200	-1.36023200	-3.93016600
H	-4.99413600	-0.37201900	-3.55827900
H	-3.61729700	-1.35036900	-4.10532000
H	-5.19528000	-1.50484400	-4.89605900
C	-3.41307700	-4.67472200	1.45792800
C	-3.94495600	-4.30739100	2.86415200
H	-5.02441800	-4.11737700	2.85298300
H	-3.75822400	-5.12970100	3.56598100
H	-3.45241100	-3.41178400	3.25792600
C	-1.89060000	-4.96819700	1.57268900
H	-1.46261400	-5.19752300	0.59018100
H	-1.32558400	-4.13628500	2.00072200
H	-1.73431400	-5.83671400	2.22322100
C	-4.05687400	-6.00484400	1.00253200

H	-5.14596000	-6.00662200	1.05970200
H	-3.77312300	-6.26291500	-0.02186400
H	-3.69860100	-6.80365500	1.66305500
C	3.88605400	-3.02100000	4.38554200
C	3.53515400	-1.94789600	5.44448500
H	4.38792100	-1.29194600	5.65549200
H	2.70112500	-1.31853200	5.11635900
H	3.24318800	-2.42860300	6.38656300
C	2.63199800	-3.91274200	4.16278700
H	1.75286000	-3.34286600	3.85180000
H	2.82915000	-4.67987700	3.40465300
H	2.37636200	-4.42224100	5.09940600
C	4.96978700	-3.96471700	4.95558200
H	4.53295900	-4.52339300	5.79219700
H	5.31202100	-4.68822400	4.20996300
H	5.84473600	-3.44137100	5.34292900
C	6.97787200	-2.10508900	0.26430000
C	7.33528900	-3.61224700	0.29367900
H	8.25784900	-3.79061500	-0.27327700
H	7.48611000	-3.96585200	1.31558500
H	6.53856500	-4.20903000	-0.16610700
C	8.16285800	-1.28659800	0.83028900
H	7.90066300	-0.22660700	0.93158000
H	8.48875600	-1.66136900	1.80064700
H	9.01863400	-1.35392500	0.14702000
C	6.82625100	-1.70167900	-1.21942500
H	6.01812500	-2.24972600	-1.71658900
H	6.64050800	-0.62776500	-1.34070700
H	7.75634700	-1.93463000	-1.74958800
C	2.52486200	4.84929500	0.58009900
C	0.97414600	4.85529800	0.68676600
H	0.51312900	4.81768800	-0.30656500
H	0.58268500	4.01526500	1.26679000
H	0.64400800	5.77555900	1.18285100
C	2.89261700	6.18162500	-0.11343400
H	3.95961100	6.40490000	-0.09284200
H	2.56459200	6.19982200	-1.15656800
H	2.38265400	6.99607900	0.41533800
C	3.11439900	4.84495700	2.01088400
H	4.20988200	4.87472100	1.99739000
H	2.76338300	5.72209500	2.56854500
H	2.81388900	3.95082000	2.56803700
C	4.62351700	2.32043700	-3.47687400
C	3.96875400	3.40490800	-4.36922400
H	4.10409200	4.40163200	-3.94409200
H	4.42087800	3.39325100	-5.36944800

H	2.89270900	3.22598800	-4.47737900
C	4.46911200	0.96370600	-4.19889100
H	4.97973000	0.15259200	-3.66608500
H	3.42064500	0.67907000	-4.32983700
H	4.92625600	1.03530000	-5.19257500
C	6.14253500	2.59584200	-3.37104800
H	6.61471900	2.43212100	-4.34767400
H	6.35230100	3.62346900	-3.07468800
H	6.62099200	1.91648700	-2.65505100
C	-6.49900800	2.61152800	0.34249200
C	-6.14131500	2.98219500	-1.12394000
H	-5.53311900	3.89345200	-1.15749000
H	-5.59276900	2.19345900	-1.64567300
H	-7.06065900	3.16962500	-1.69108900
C	-7.35084000	1.31936900	0.32703300
H	-6.79937000	0.47900400	-0.10927200
H	-7.65638800	1.02507400	1.33744200
H	-8.26073500	1.47149100	-0.26684500
C	-7.37055500	3.78192700	0.85535700
H	-8.16148900	3.96931800	0.11891300
H	-7.86128000	3.57552100	1.80675600
H	-6.79017600	4.70183100	0.96809800
C	-2.98869900	3.72002200	4.06523700
C	-1.46813300	3.56252400	4.28903400
H	-1.18856000	2.54038600	4.56768600
H	-0.89043300	3.84829500	3.40283400
H	-1.16037200	4.22325400	5.10722600
C	-3.68005000	3.32426000	5.39188600
H	-4.73079200	3.61540100	5.40616200
H	-3.60752500	2.24507400	5.57082500
H	-3.18731400	3.83310100	6.22947500
C	-3.25866900	5.21697900	3.77151700
H	-2.72098200	5.53925200	2.87177400
H	-4.32355600	5.41012900	3.62614300
H	-2.90733800	5.83182200	4.60976600
O	-5.47220700	-4.36701700	-0.77918000
O	-5.74657600	3.60481200	3.12743500
O	6.63857300	-2.68467400	3.09388600
O	4.59329500	4.57430900	-1.64592800
C	-6.60538700	2.73635000	3.86837100
H	-7.25833500	3.38190500	4.46148400
H	-7.21771600	2.11140100	3.20927000
H	-6.03235000	2.08316300	4.53604800
C	-6.61185600	-4.16418300	0.05651000
H	-7.32374500	-4.95428000	-0.19647400
H	-6.35588500	-4.23562100	1.11887200

H	-7.07182200	-3.18587300	-0.12718700
C	5.75665400	4.74766200	-0.83614200
H	6.28539500	5.61573000	-1.23843500
H	5.49894200	4.93551800	0.21165000
H	6.40985100	3.86842800	-0.88313800
C	7.13329300	-1.69670700	3.99882500
H	6.40874400	-1.46867000	4.78747900
H	8.03654800	-2.11671000	4.44915800
H	7.38503200	-0.76700200	3.47496800

TS-1a

B3LYP/SDD-6-31G(d) SCF energy: -4518.336577 a.u.
B3LYP/SDD-6-31G(d) Enthalpy: -4516.546301 a.u.
B3LYP/SDD-6-31G(d) Gibbs free energy: -4516.781822 a.u.
M06/SDD-6-311+G(d,p) SCF energy in solution: -4516.803780 a.u.
M06/SDD-6-311+G(d,p) enthalpy in solution: -4515.013505 a.u.
M06/SDD-6-311+G(d,p) free energy in solution: -4515.249026 a.u.
Three lowest frequencies (cm^{-1}): -607.2594 8.4633 10.5981
Imaginary frequency: -607.2594 cm^{-1}

Cartesian coordinates:

ATOM	X	Y	Z
Cu	0.04614100	0.10743000	-1.63678500
H	0.28762400	-1.12019600	-2.63592800
P	1.77496700	0.36613800	-0.10195400
C	1.22884600	1.21382800	1.45893100
C	3.18210300	1.39339000	-0.73539300
C	2.61557500	-1.17126400	0.47479100
C	0.23052600	0.62092000	2.29972500
C	1.73368300	2.48453400	1.76980700
C	4.51367100	0.99742600	-0.63348900
C	2.89789300	2.60120500	-1.39330800
C	2.51790200	-2.30471200	-0.32829400
C	3.36081100	-1.24639400	1.65970400
C	-0.14020100	1.37437900	3.40548500
C	-0.32858700	-0.76708400	2.20634500
C	1.31365600	3.22875100	2.88507200
H	2.49738100	2.91620200	1.13463300
C	5.56916100	1.71637100	-1.22281100
H	4.74358000	0.09501600	-0.08272700
C	3.89346300	3.36836500	-2.00543900
H	1.86781300	2.93299000	-1.42801500
C	3.20856500	-3.49559800	-0.04153500
H	1.86989500	-2.24988700	-1.19715400
C	4.10141300	-2.38510300	1.99234000
H	3.36146900	-0.39157000	2.32379900
C	0.36882600	2.63782000	3.69324700

O	-1.05236000	1.02784800	4.38103800
C	0.00163100	-1.63485800	3.23991600
C	-1.23979000	-1.29054800	1.23255100
H	1.72563700	4.20743000	3.10577900
C	5.21381000	2.83871300	-2.00105100
C	4.09020300	-3.46149300	1.06110900
O	-0.21220100	3.12422100	4.84059000
C	-0.87031800	1.99444100	5.41794200
C	-0.45838000	-2.94523000	3.33438000
O	0.83487200	-1.37680800	4.31030700
C	-1.68586900	-2.61641400	1.34199900
P	-1.75531400	-0.29600900	-0.24849600
H	-1.84336500	2.29838900	5.80629400
H	-0.23618900	1.56577700	6.20862300
C	-1.30261800	-3.47606000	2.38496500
O	0.07078300	-3.54511700	4.45325000
C	0.61980100	-2.46464600	5.21107400
H	-2.36882200	-3.00150900	0.59466800
C	-3.09829800	-1.30630900	-1.02999500
C	-2.68490000	1.14470400	0.43472900
H	-1.66668000	-4.49582600	2.44645300
H	-0.09907900	-2.15954500	5.98670600
H	1.57216600	-2.77096200	5.64542600
C	-4.40128100	-1.38145400	-0.52017300
C	-2.78974000	-2.04034900	-2.17405900
C	-2.65432200	2.32348900	-0.30692900
C	-3.43218700	1.11264900	1.62020200
C	-5.41321600	-2.09065700	-1.17271000
H	-4.62761300	-0.85777800	0.39790000
C	-3.74629300	-2.80173000	-2.86971900
H	-1.76678700	-2.00668100	-2.53271800
C	-3.41348000	3.45381200	0.04169500
H	-2.00593100	2.35418800	-1.17721200
C	-4.24675300	2.18327800	2.00522200
H	-3.37209300	0.23130100	2.24586800
C	-5.07843800	-2.71508600	-2.40703700
C	-4.29515800	3.30805800	1.13528400
C	4.81871200	-2.48631100	3.36387600
C	4.28540400	-3.73120400	4.11714700
H	4.52758200	-4.65264900	3.58402700
H	4.73027200	-3.78469900	5.11913800
H	3.19610700	-3.68112000	4.22794000
C	6.35651800	-2.59163300	3.23182600
H	6.81880700	-2.50956100	4.22346000
H	6.66515700	-3.54622500	2.80513200
H	6.75916200	-1.78163700	2.61185100

C	4.52605600	-1.25099200	4.24422400
H	4.94713000	-0.33148100	3.82073400
H	3.45279000	-1.09725800	4.39555200
H	4.98932300	-1.39620800	5.22690200
C	2.88400300	-4.72661700	-0.93416000
C	3.44400500	-4.50831400	-2.35999700
H	4.53726800	-4.42788100	-2.35826600
H	3.17198500	-5.35148100	-3.00717200
H	3.04377800	-3.59447100	-2.81205400
C	1.33788700	-4.85648400	-1.02770400
H	0.89734300	-4.98678300	-0.03276100
H	0.86331600	-3.98864500	-1.49222800
H	1.08018000	-5.73436800	-1.63214600
C	3.38163400	-6.08890900	-0.39831600
H	4.46348300	-6.21325700	-0.45837400
H	3.08022800	-6.25070300	0.64045000
H	2.93205800	-6.88265900	-1.00734300
C	-3.23023200	-3.67083400	-4.05174200
C	-2.88578600	-2.77025100	-5.26272300
H	-3.76946100	-2.25226800	-5.65154100
H	-2.14552700	-2.00913800	-4.99419600
H	-2.46918400	-3.37601700	-6.07748200
C	-1.92734400	-4.39120600	-3.60630200
H	-1.11273500	-3.69886400	-3.37918000
H	-2.10363500	-5.01176400	-2.72020400
H	-1.58023800	-5.04626500	-4.41397400
C	-4.18976000	-4.79687300	-4.50372800
H	-3.65139500	-5.45059000	-5.20069200
H	-4.52132700	-5.40776500	-3.65829900
H	-5.07766400	-4.43492500	-5.02196100
C	-6.81022700	-2.24183100	-0.51572200
C	-7.13450100	-3.74695800	-0.34236800
H	-8.11714500	-3.86679100	0.13142900
H	-7.14982800	-4.26465000	-1.30324600
H	-6.39110300	-4.23203500	0.30142400
C	-7.93301000	-1.56479700	-1.33785900
H	-7.67980500	-0.52393000	-1.57251100
H	-8.13494300	-2.09415900	-2.26925600
H	-8.86334100	-1.55775100	-0.75633700
C	-6.84454700	-1.60471400	0.89137800
H	-6.09001500	-2.03624100	1.55850800
H	-6.69490600	-0.51932900	0.85877000
H	-7.82638400	-1.78787300	1.34194000
C	-3.15669400	4.74819000	-0.78007200
C	-1.62127500	4.98374300	-0.83139600
H	-1.21507300	5.11682200	0.17796200

H	-1.08134100	4.16040400	-1.30471500
H	-1.40811800	5.89344000	-1.40555600
C	-3.75242000	6.04752300	-0.19108600
H	-4.83887400	6.10317000	-0.26747300
H	-3.48051200	6.17952000	0.85987200
H	-3.34646900	6.89695100	-0.75416100
C	-3.67408600	4.56561400	-2.22703300
H	-4.75779700	4.40151600	-2.25031200
H	-3.45890600	5.46222000	-2.82181200
H	-3.19673400	3.71193300	-2.71969600
C	-4.98027700	2.16500100	3.37231500
C	-4.49695600	3.37447800	4.21159300
H	-4.75171100	4.31987600	3.72798200
H	-4.96613000	3.35755000	5.20385400
H	-3.40948100	3.34413600	4.34660300
C	-4.65633000	0.88333700	4.17092200
H	-5.03624800	-0.01769200	3.67483700
H	-3.58174900	0.75699300	4.33390400
H	-5.14279600	0.94265000	5.15150700
C	-6.52028000	2.22605000	3.23434600
H	-6.98366400	2.06010500	4.21492800
H	-6.85997700	3.19566000	2.87066100
H	-6.88991200	1.44508500	2.55894500
C	7.01059600	1.22315100	-0.90725800
C	7.13453900	1.04528500	0.63174200
H	6.96363900	1.99666600	1.14827300
H	6.43018200	0.31324000	1.03560100
H	8.14529400	0.70160300	0.88214000
C	7.25864500	-0.14684600	-1.58301800
H	6.52105500	-0.89252700	-1.26640300
H	7.20596500	-0.07256400	-2.67526500
H	8.25515000	-0.52419200	-1.32105900
C	8.15317300	2.18809200	-1.29999000
H	9.08604600	1.81141100	-0.86284200
H	8.31098900	2.25987200	-2.37658300
H	7.98426000	3.19750200	-0.91535100
C	3.56628800	4.76975500	-2.58511400
C	2.10830000	5.18020700	-2.28545300
H	1.38165900	4.54306900	-2.80138800
H	1.88290700	5.15989500	-1.21369200
H	1.94776800	6.20564800	-2.63670600
C	3.74550200	4.83883100	-4.12029200
H	4.79474100	4.78429700	-4.41197400
H	3.19710500	4.03145200	-4.62006900
H	3.34972800	5.79081800	-4.49516000
C	4.48189800	5.82291800	-1.91149300

H	4.32017200	5.84076900	-0.82706500
H	5.53686500	5.61620200	-2.10073200
H	4.25059200	6.82239100	-2.30080800
O	4.96264600	-4.51552600	1.29212200
O	6.16731800	3.47879500	-2.77966000
O	-6.11664900	-3.27249800	-3.13965700
O	-5.22809800	4.29720900	1.41574400
C	6.43220700	2.81918200	-4.01836100
H	7.16675100	3.43463400	-4.54433300
H	6.84513100	1.81597600	-3.86465900
H	5.52471600	2.73332000	-4.62708700
C	6.12369100	-4.49343500	0.46203400
H	6.74393700	-5.33690200	0.77661100
H	5.86955000	-4.60872100	-0.59733100
H	6.68592900	-3.56034100	0.58813500
C	-6.38128600	4.24953700	0.57550600
H	-7.05019600	5.04101800	0.92390200
H	-6.12733800	4.42871100	-0.47505600
H	-6.89011500	3.28132800	0.65247400
C	-6.54727200	-2.47673700	-4.24425900
H	-5.78428700	-2.41916400	-5.02758600
H	-7.43762400	-2.96667100	-4.64746300
H	-6.80290300	-1.45895000	-3.92768700
C	-0.22091300	1.61458100	-3.07353800
C	0.25386700	0.44257200	-3.67275600
C	-1.12192500	0.90290500	-4.06125500
H	-2.01388100	0.37823500	-3.71548500
H	-1.22139000	1.29006800	-5.08283600
C	1.42962200	0.09820600	-4.53562900
H	2.37128200	0.23148500	-3.99207300
H	1.44306200	0.77051500	-5.40716200
H	1.38596500	-0.93385800	-4.90124200
H	0.19823700	2.61300700	-3.12330900

TS-1b

B3LYP/SDD-6-31G(d) SCF energy: -4557.668218 a.u.
B3LYP/SDD-6-31G(d) Enthalpy: -4555.847183 a.u.
B3LYP/SDD-6-31G(d) Gibbs free energy: -4556.083737 a.u.
M06/SDD-6-311+G(d,p) SCF energy in solution: -4556.114176 a.u.
M06/SDD-6-311+G(d,p) enthalpy in solution: -4554.293141 a.u.
M06/SDD-6-311+G(d,p) free energy in solution: -4554.529695 a.u.
Three lowest frequencies (cm^{-1}): -779.5168 8.7874 11.4216
Imaginary frequency: -779.5168 cm^{-1}

Cartesian coordinates:

ATOM	X	Y	Z
Cu	0.00273400	0.03339700	-1.53417100

H	-0.26377500	1.30727400	-2.53037400
P	-1.75160700	-0.39004700	-0.11237200
C	-1.20521900	-1.30958100	1.40839700
C	-3.10193900	-1.43684900	-0.83674500
C	-2.68974100	1.05994500	0.54241200
C	-0.23795100	-0.74177900	2.30090700
C	-1.68326100	-2.60776700	1.63839000
C	-4.44895100	-1.08930600	-0.76422000
C	-2.75720700	-2.60270100	-1.54017000
C	-2.67757200	2.23146200	-0.20976300
C	-3.43739600	1.02739500	1.72741200
C	0.13659200	-1.55158600	3.36571800
C	0.29880600	0.65926500	2.31062800
C	-1.26357200	-3.40567000	2.71588200
H	-2.42466000	-3.02048300	0.96557200
C	-5.45947400	-1.81210900	-1.42375500
H	-4.72879200	-0.22324700	-0.17957600
C	-3.70396100	-3.36653700	-2.22876300
H	-1.71742000	-2.90357200	-1.54932800
C	-3.45449900	3.35416700	0.12573700
H	-2.02843400	2.26215100	-1.07918000
C	-4.25676400	2.09465800	2.11039700
H	-3.37758100	0.14431300	2.35064600
C	-0.34583500	-2.84097900	3.57256100
O	1.02773900	-1.24233100	4.37350500
C	-0.06357500	1.44743600	3.39576100
C	1.24460200	1.25095300	1.41114600
H	-1.65598300	-4.40449200	2.87286800
C	-5.04076800	-2.88052600	-2.24512700
C	-4.32552600	3.21016100	1.22881400
O	0.22914900	-3.37957600	4.69916800
C	0.85264600	-2.27029800	5.35026300
C	0.40829100	2.73877800	3.61415600
O	-0.93477900	1.11327800	4.41333400
C	1.71105800	2.55148300	1.65172800
P	1.77738400	0.36699200	-0.13628200
H	1.82645500	-2.57454300	5.73648800
H	0.19716300	-1.90208400	6.15402800
C	1.30273200	3.32761100	2.74923100
O	-0.15452900	3.25427500	4.75798800
C	-0.75481500	2.12874700	5.40232200
H	2.43025700	2.98476800	0.96789900
C	3.09507800	1.45456100	-0.85580600
C	2.72613000	-1.09252600	0.47532600
H	1.68428900	4.32957400	2.91271100
H	-0.08228100	1.75594100	6.18973600

H	-1.72547300	2.41621200	5.80895100
C	4.46587800	1.22035200	-0.69378100
C	2.69633900	2.55976500	-1.61118400
C	2.67990700	-2.25999300	-0.28336300
C	3.49454900	-1.07985400	1.64700200
C	5.43411300	1.98754900	-1.35265200
H	4.77832900	0.40516300	-0.05703100
C	3.61312600	3.41873800	-2.23999200
H	1.63213500	2.74919700	-1.71420200
C	3.44248400	-3.39784600	0.03418300
H	2.01354000	-2.27649300	-1.13950100
C	4.30364800	-2.16168500	2.00897200
H	3.45743000	-0.20110900	2.27797600
C	4.97203400	3.02868600	-2.20020900
C	4.33721300	-3.27268100	1.12079300
C	-4.97438500	2.08119600	3.48585700
C	-4.50964700	3.31384800	4.30161400
H	-4.79408300	4.24659100	3.81043100
H	-4.96320900	3.29755400	5.30099700
H	-3.41986300	3.31088500	4.42041500
C	-6.51660900	2.10224500	3.36414800
H	-6.96551900	1.94709500	4.35314600
H	-6.88373700	3.05529200	2.98332400
H	-6.87503400	1.29846400	2.70963600
C	-4.60739700	0.82097800	4.30025400
H	-4.97255000	-0.09778200	3.82637600
H	-3.52712000	0.72444000	4.44728900
H	-5.07900600	0.88573100	5.28761500
C	-3.23763900	4.63823000	-0.72352400
C	-3.83217000	4.44240900	-2.13893300
H	-4.91685100	4.28870400	-2.10679400
H	-3.63828000	5.32772000	-2.75740100
H	-3.38839000	3.57632700	-2.64185900
C	-1.70835000	4.87374900	-0.86671800
H	-1.23742200	4.98836800	0.11621200
H	-1.19948100	4.06089500	-1.39122000
H	-1.53213100	5.79302200	-1.43764900
C	-3.80036400	5.94162500	-0.11087400
H	-4.88900000	5.99693200	-0.12663100
H	-3.47104800	6.07731000	0.92339400
H	-3.42524000	6.78869800	-0.69807700
C	3.04304600	4.72788900	-2.85772400
C	2.15862000	4.40286400	-4.08452300
H	2.73938000	3.93466900	-4.88760400
H	1.34190400	3.72079000	-3.82538000
H	1.71574300	5.32298800	-4.48588800

C	2.15905000	5.41382300	-1.77953400
H	1.31995500	4.79277000	-1.45665400
H	2.75335000	5.66652600	-0.89352100
H	1.74248800	6.34481800	-2.18215000
C	4.09225200	5.79005700	-3.26002200
H	3.56414000	6.72372100	-3.48951300
H	4.79763800	5.99351400	-2.44951200
H	4.66714600	5.52208900	-4.14716400
C	6.94225400	1.74290200	-1.08623600
C	7.58696900	3.04775500	-0.55540700
H	8.65286400	2.88368400	-0.35203300
H	7.49658900	3.86068000	-1.27859800
H	7.11145200	3.36136900	0.38147400
C	7.69855500	1.27388900	-2.35219400
H	7.20286300	0.41149100	-2.81379900
H	7.78036700	2.06890400	-3.09352500
H	8.71727300	0.96807400	-2.08284800
C	7.15802500	0.65789300	-0.00831700
H	6.67216500	0.91621700	0.93909500
H	6.78896100	-0.32403200	-0.32634000
H	8.23149400	0.55904800	0.18778700
C	3.18583500	-4.67859100	-0.80931900
C	1.65005900	-4.88911400	-0.91632900
H	1.20025000	-4.99551300	0.07748400
H	1.14203000	-4.06887900	-1.42901700
H	1.44482400	-5.80530800	-1.48245300
C	3.73970200	-5.99126000	-0.20795800
H	4.82661200	-6.06530100	-0.24743900
H	3.43065000	-6.12166500	0.83323300
H	3.33746800	-6.83166600	-0.78679200
C	3.75255900	-4.49508000	-2.23743700
H	4.84045900	-4.36244600	-2.22831200
H	3.52892300	-5.37751600	-2.84996400
H	3.31570400	-3.62148000	-2.73285200
C	5.04773200	-2.16707400	3.37025100
C	4.58867200	-3.40208200	4.18547500
H	4.85867900	-4.33322700	3.68348600
H	5.05855400	-3.39509900	5.17737700
H	3.50107500	-3.39259000	4.32186000
C	4.70753600	-0.91083100	4.20221700
H	5.07144900	0.00897600	3.72925000
H	3.63104100	-0.80666900	4.37094800
H	5.19739500	-0.98768800	5.17977300
C	6.58672500	-2.20039100	3.21664900
H	7.05764900	-2.05721400	4.19725400
H	6.93740000	-3.15378600	2.82123900

H	6.93764100	-1.39526900	2.56015400
C	-6.92637300	-1.38323100	-1.13313300
C	-7.10347900	-1.27517200	0.40733400
H	-6.90979700	-2.23995700	0.88980600
H	-6.44265900	-0.53330200	0.86385200
H	-8.13470600	-0.98251200	0.63832600
C	-7.20440000	0.00471600	-1.75838200
H	-6.50297900	0.76098100	-1.38899400
H	-7.11823600	-0.02095700	-2.85064300
H	-8.22082400	0.33634400	-1.51093500
C	-8.01934900	-2.37209000	-1.60067800
H	-8.97836700	-2.05085000	-1.17583900
H	-8.14319800	-2.40341900	-2.68356300
H	-7.82145600	-3.39013500	-1.25422300
C	-3.30903300	-4.72282200	-2.86962800
C	-1.84362500	-5.09326600	-2.55505200
H	-1.13018700	-4.39899600	-3.01267900
H	-1.64625100	-5.12883400	-1.47817900
H	-1.63427300	-6.08935200	-2.96086400
C	-3.44994700	-4.72002500	-4.41043400
H	-4.49367800	-4.68871200	-4.72376400
H	-2.92040600	-3.86928200	-4.85546900
H	-3.01059100	-5.63703100	-4.82223600
C	-4.20095700	-5.84120500	-2.27374400
H	-4.06786500	-5.90654300	-1.18725900
H	-5.25778900	-5.66399100	-2.48281600
H	-3.92175400	-6.81129300	-2.70392100
O	-5.26596400	4.19091400	1.51200400
O	-5.94553900	-3.51126200	-3.08696300
O	5.90782300	3.68300100	-2.98818800
O	5.26641700	-4.26998900	1.38141900
C	-6.19686200	-2.79628700	-4.29750600
H	-6.88575800	-3.41209000	-4.88166200
H	-6.65843800	-1.82138400	-4.10529500
H	-5.27382500	-2.63955800	-4.86748000
C	-6.43373600	4.12562800	0.69391800
H	-7.12071100	4.88571300	1.07550000
H	-6.20835100	4.34035300	-0.35640300
H	-6.90979500	3.13983300	0.75651700
C	6.41932900	-4.22070900	0.54120000
H	7.09904300	-4.99598800	0.90478600
H	6.16996300	-4.42409800	-0.50595100
H	6.91468300	-3.24433600	0.60132800
C	5.88647300	3.28178700	-4.35883400
H	4.92867900	3.51487400	-4.83624200
H	6.68291000	3.84182800	-4.85592300

H	6.07598200	2.20688900	-4.46192200
C	0.24233100	-1.22269200	-3.23832500
C	-0.17393400	0.08029900	-3.69157800
C	1.18761300	0.31968500	-4.37237500
C	1.62324200	-1.10437700	-3.90015400
H	2.50947300	-1.13700400	-3.25243000
H	1.79475700	-1.79601000	-4.73763200
H	1.78069500	1.16421400	-4.01213700
H	1.08630500	0.39698200	-5.46294200
C	-1.49708700	0.42763500	-4.33519200
H	-2.33608300	0.07063600	-3.72869500
H	-1.56120100	-0.06134800	-5.31941500
H	-1.61339000	1.50836300	-4.47868500
H	-0.38980600	-2.10642000	-3.20799200

TS-1c

B3LYP/SDD-6-31G(d) SCF energy: -4558.907393 a.u.
B3LYP/SDD-6-31G(d) Enthalpy: -4557.063276 a.u.
B3LYP/SDD-6-31G(d) Gibbs free energy: -4557.301806 a.u.
M06/SDD-6-311+G(d,p) SCF energy in solution: -4557.351417 a.u.
M06/SDD-6-311+G(d,p) enthalpy in solution: -4555.507301 a.u.
M06/SDD-6-311+G(d,p) free energy in solution: -4555.745830 a.u.
Three lowest frequencies (cm^{-1}): -799.1215 10.7229 12.6260
Imaginary frequency: -799.1215 cm^{-1}

Cartesian coordinates:

ATOM	X	Y	Z
Cu	0.00424700	0.05103400	-1.56951500
H	-0.30199500	1.40997000	-2.44887200
P	-1.76043300	-0.37489600	-0.14904500
C	-1.21615600	-1.31290300	1.36041800
C	-3.10816800	-1.41943600	-0.87905400
C	-2.69798500	1.06549500	0.53201000
C	-0.25509700	-0.75091200	2.26216400
C	-1.69916600	-2.61103500	1.58043600
C	-4.46225500	-1.11267900	-0.76568300
C	-2.74675000	-2.55308200	-1.62430800
C	-2.66421200	2.25794900	-0.18547700
C	-3.45408500	1.01080000	1.71107000
C	0.10463500	-1.56328700	3.33048900
C	0.29116400	0.64609500	2.27477000
C	-1.29393300	-3.41216600	2.66103200
H	-2.43403300	-3.01982900	0.89808000
C	-5.46692000	-1.84860300	-1.42010200
H	-4.75172900	-0.27009300	-0.15175200
C	-3.68613100	-3.32550600	-2.31302600
H	-1.69807400	-2.81668300	-1.67075400

C	-3.42709400	3.38176800	0.17665100
H	-2.00656000	2.30500200	-1.04770900
C	-4.26208700	2.07796600	2.11797500
H	-3.40860000	0.11149700	2.31202700
C	-0.38650600	-2.85050200	3.53082100
O	0.98539600	-1.25954600	4.34945800
C	-0.06439500	1.43243700	3.36359400
C	1.24422800	1.23190100	1.37829900
H	-1.69102900	-4.41010800	2.81185900
C	-5.03709100	-2.88199900	-2.28077800
C	-4.30957600	3.21838900	1.26767000
O	0.16980600	-3.39100100	4.66598300
C	0.78311600	-2.28190000	5.32660700
C	0.42526900	2.71509700	3.59321900
O	-0.94184600	1.10283500	4.37737500
C	1.73002900	2.52241600	1.63243900
P	1.77594900	0.33708600	-0.16810500
H	1.74602700	-2.58860000	5.73707500
H	0.11034200	-1.90689800	6.11290800
C	1.33126800	3.29611700	2.73546000
O	-0.13068600	3.22900200	4.74095200
C	-0.74651500	2.10627600	5.37545800
H	2.46103300	2.95005700	0.95830100
C	3.11423400	1.40582900	-0.88394300
C	2.71652300	-1.11165600	0.48955300
H	1.72993100	4.28977500	2.90855200
H	-0.07848800	1.71668700	6.15862900
H	-1.71249000	2.40371300	5.78596600
C	4.47134600	1.06703400	-0.82973900
C	2.75520700	2.59591800	-1.52354200
C	2.66484200	-2.31281800	-0.21355000
C	3.48639800	-1.04980300	1.65906900
C	5.45470100	1.82000000	-1.48271400
H	4.76029200	0.18440600	-0.27878900
C	3.69796900	3.44923000	-2.12136600
H	1.70457800	2.86832100	-1.54470100
C	3.42226800	-3.43926400	0.15648300
H	2.00202000	-2.36523400	-1.06988900
C	4.28849800	-2.11759200	2.07259100
H	3.45532500	-0.14245000	2.24826700
C	5.02566000	2.96628200	-2.20077700
C	4.31736900	-3.26849700	1.23703100
C	-4.99134000	2.03490900	3.48672500
C	-4.53515600	3.24835900	4.33534100
H	-4.81507700	4.19240300	3.86392800
H	-4.99742900	3.20806900	5.32997500

H	-3.44654800	3.24222400	4.46373400
C	-6.53225100	2.05848900	3.35029500
H	-6.99119700	1.88635900	4.33189700
H	-6.89562000	3.01815600	2.98230400
H	-6.88421700	1.26652000	2.67812500
C	-4.63046300	0.75737200	4.27672400
H	-4.99369200	-0.15136200	3.78258400
H	-3.55087200	0.65752200	4.42719500
H	-5.10716700	0.80240000	5.26273300
C	-3.18254800	4.68698800	-0.63195200
C	-3.76560000	4.54242000	-2.05810600
H	-4.85301000	4.40675700	-2.04099900
H	-3.55029300	5.44143600	-2.64914500
H	-3.33201400	3.68304400	-2.58123200
C	-1.64803300	4.90378200	-0.75300400
H	-1.18492400	4.97912700	0.23750500
H	-1.14614000	4.10041300	-1.29882200
H	-1.45244500	5.83872500	-1.29147000
C	-3.73282500	5.97969300	0.01366200
H	-4.82055800	6.04950300	-0.00792800
H	-3.40941300	6.08161100	1.05371100
H	-3.34244600	6.83809300	-0.54654400
C	3.20149400	4.85653100	-2.56505600
C	2.24380300	4.73971800	-3.77297000
H	2.74823400	4.32030700	-4.65093800
H	1.38632900	4.09868700	-3.54628800
H	1.86131800	5.73041200	-4.04903400
C	2.41754300	5.48023100	-1.37680600
H	1.55026800	4.88650700	-1.07681500
H	3.06704500	5.59711700	-0.50115600
H	2.05200500	6.47481000	-1.65864800
C	4.31095800	5.87979600	-2.90161100
H	3.84582400	6.86836300	-2.99949000
H	5.06415900	5.93843400	-2.11103800
H	4.82429700	5.67369400	-3.84130200
C	6.95250900	1.44624800	-1.33501200
C	7.71957100	2.64370400	-0.72057800
H	8.78000200	2.38831600	-0.59967900
H	7.64920000	3.52877300	-1.35574400
H	7.31988400	2.89379600	0.26934700
C	7.60205000	1.05950400	-2.68560700
H	7.01769500	0.28751900	-3.20048600
H	7.70659300	1.91981800	-3.34686000
H	8.60674900	0.65508500	-2.51012000
C	7.14796000	0.24343500	-0.38587100
H	6.73666500	0.43256900	0.61170000

H	6.69091700	-0.67328000	-0.77626100
H	8.22093400	0.05334700	-0.26945600
C	3.16734500	-4.75913100	-0.62557200
C	1.63265600	-4.95485500	-0.76897300
H	1.14764000	-4.98321200	0.21335400
H	1.15414200	-4.16722800	-1.35597000
H	1.43075500	-5.90550600	-1.27616200
C	3.68199100	-6.04358800	0.06563300
H	4.76803500	-6.13549300	0.06383300
H	3.34081400	-6.10870400	1.10316400
H	3.28248400	-6.90986100	-0.47552400
C	3.77925600	-4.66473700	-2.04369900
H	4.86962700	-4.56219300	-2.01062000
H	3.54713800	-5.57008100	-2.61852800
H	3.38222100	-3.80509800	-2.59363900
C	5.03295700	-2.06036900	3.43256500
C	4.59329500	-3.26718800	4.29898800
H	4.87484100	-4.21485400	3.83638000
H	5.06399200	-3.21143900	5.28883000
H	3.50604300	-3.26593400	4.43673300
C	4.67392900	-0.77765200	4.21514200
H	5.02759800	0.12875100	3.70993700
H	3.59520000	-0.68311700	4.37547900
H	5.16054300	-0.81193700	5.19668600
C	6.57196300	-2.07763500	3.27711500
H	7.04228000	-1.89698900	4.25179900
H	6.93570900	-3.03802900	2.91107800
H	6.91131100	-1.28937900	2.59455900
C	-6.93890000	-1.47301900	-1.08545200
C	-7.08073100	-1.38816400	0.46004800
H	-6.83447300	-2.34846100	0.92727400
H	-6.44053400	-0.62327000	0.90778800
H	-8.11687900	-1.14141600	0.72039900
C	-7.28008800	-0.08814200	-1.68567900
H	-6.59754300	0.68735100	-1.32081300
H	-7.21689600	-0.09624400	-2.77968400
H	-8.30182800	0.20408700	-1.41172900
C	-8.00831100	-2.49452000	-1.53717100
H	-8.96686100	-2.21252500	-1.08431500
H	-8.15843800	-2.51899400	-2.61669300
H	-7.76544900	-3.50860700	-1.20776100
C	-3.26124000	-4.64571800	-3.00765800
C	-1.77536500	-4.97157000	-2.74158800
H	-1.10005500	-4.23508600	-3.19134300
H	-1.55112800	-5.03599900	-1.67135500
H	-1.53989600	-5.94494500	-3.18632800

C	-3.44095800	-4.59835700	-4.54370700
H	-4.49250300	-4.59338900	-4.83189600
H	-2.95156500	-3.71607700	-4.97319200
H	-2.98114000	-5.48604200	-4.99553400
C	-4.09643200	-5.81476500	-2.42748300
H	-3.92853300	-5.91401800	-1.34837100
H	-5.16454900	-5.66776600	-2.59924900
H	-3.79721600	-6.75852200	-2.90068900
O	-5.24147200	4.20207700	1.56927200
O	-5.94307300	-3.52044900	-3.11547200
O	5.96454800	3.63216300	-2.97507200
O	5.24159300	-4.25624200	1.54642000
C	-6.25068900	-2.78589700	-4.30103500
H	-6.91567200	-3.42071600	-4.89254400
H	-6.76037600	-1.84261600	-4.07504100
H	-5.34635600	-2.56488300	-4.87941100
C	-6.40109300	4.17283200	0.73771800
H	-7.08412100	4.92900500	1.13390600
H	-6.16228200	4.41488300	-0.30367600
H	-6.88798900	3.19070100	0.76701800
C	6.39831600	-4.25497000	0.71014100
H	7.08194500	-4.99817300	1.12915600
H	6.15579200	-4.53209800	-0.32133800
H	6.88603900	-3.27301600	0.70504500
C	5.83866800	3.38299800	-4.37565400
H	4.87668600	3.73129400	-4.76663000
H	6.64679600	3.93680600	-4.86068500
H	5.94121300	2.31492600	-4.60103400
C	0.11182500	-0.98460600	-3.42762500
C	-0.27568600	0.36714400	-3.73154500
C	0.68095900	1.22732400	-4.54611800
H	0.33777200	2.26594700	-4.59104400
H	0.72752300	0.83891900	-5.57533000
C	-1.73321400	0.57917700	-4.12501300
H	-2.40717000	-0.01064000	-3.49739900
H	-1.87371800	0.25616500	-5.16803400
H	-2.02586100	1.63328700	-4.05070600
H	-0.71233800	-1.69761700	-3.44137200
H	1.69483800	1.22237700	-4.13928500
C	1.43897400	-1.56425300	-3.88862300
H	2.30140100	-0.95744300	-3.58739500
H	1.59066600	-2.56328900	-3.46256900
H	1.50247000	-1.68120600	-4.98524600

TS2a-a

B3LYP/SDD-6-31G(d) SCF energy: -5019.762672 a.u.

B3LYP/SDD-6-31G(d) Enthalpy: -5017.770106 a.u.
B3LYP/SDD-6-31G(d) Gibbs free energy: -5018.028114 a.u.
M06/SDD-6-311+G(d,p) SCF energy in solution: -5017.988094 a.u.
M06/SDD-6-311+G(d,p) enthalpy in solution: -5015.995528 a.u.
M06/SDD-6-311+G(d,p) free energy in solution: -5016.253536 a.u.
Three lowest frequencies (cm^{-1}): -733.6981 7.1722 8.8518
Imaginary frequency: -733.6981 cm^{-1}

Cartesian coordinates:

ATOM	X	Y	Z
Cu	0.10724900	1.11312800	-0.01884300
H	0.36950500	2.00652600	-1.33949600
C	-0.16095200	2.94190900	1.23977800
C	-0.01563200	3.25229800	-0.15200500
H	-0.81074300	3.59907700	-0.80699000
P	1.77857000	-0.43992000	0.32609800
C	1.15013700	-2.08833400	0.91288100
C	3.03440600	0.05809600	1.59506300
C	2.81052800	-0.90161100	-1.13771100
C	0.24738400	-2.84839500	0.10040900
C	1.55755000	-2.58909100	2.15716600
C	4.40131800	0.09742400	1.33034200
C	2.59170500	0.46283500	2.86508900
C	2.78793700	-0.08745200	-2.26681500
C	3.60812600	-2.05455700	-1.15411300
C	-0.13503700	-4.07654200	0.62614800
C	-0.21851400	-2.54442700	-1.29269500
C	1.13227300	-3.82791100	2.66561800
H	2.25600500	-2.01479100	2.75213500
C	5.34167600	0.58796000	2.25543000
H	4.75281300	-0.26077800	0.37170600
C	3.46751300	0.95398200	3.83749000
H	1.53247100	0.39949100	3.08454100
C	3.59780100	-0.33216300	-3.39103200
H	2.09593800	0.74788800	-2.26751100
C	4.46763100	-2.34203000	-2.21838200
H	3.55037100	-2.73186500	-0.31189500
C	0.28664000	-4.55924800	1.86270700
O	-0.96916900	-5.00985100	0.04592100
C	0.18055100	-3.42990600	-2.28601300
C	-1.14798600	-1.53401400	-1.70628600
H	1.47307600	-4.19745200	3.62660000
C	4.83016400	1.11397800	3.46057500
C	4.51808700	-1.39937600	-3.28395500
O	-0.26210700	-5.79696000	2.09236200
C	-0.79005500	-6.19427800	0.82480600
C	-0.25941700	-3.36867800	-3.60586800

O	1.05118900	-4.49286200	-2.15573200
C	-1.57553200	-1.48899200	-3.04002500
P	-1.74984300	-0.25476800	-0.49533100
H	-1.75277500	-6.68567200	0.96828000
H	-0.07009700	-6.85675500	0.32057600
C	-1.14196100	-2.39749200	-4.02072700
O	0.31214400	-4.38184100	-4.33650300
C	0.89235500	-5.24778900	-3.35866600
H	-2.29190700	-0.73364900	-3.33649400
C	-3.04706600	0.69948400	-1.41661900
C	-2.73943900	-1.27163200	0.68903300
H	-1.50085100	-2.34713400	-5.04294400
H	0.21461300	-6.09460000	-3.17177700
H	1.86817700	-5.58838000	-3.70717100
C	-4.40833000	0.62528100	-1.09859300
C	-2.65224800	1.57952400	-2.42786100
C	-2.72718800	-0.96127600	2.04790700
C	-3.49838100	-2.36509300	0.25406800
C	-5.35787100	1.47301600	-1.68187700
H	-4.72471100	-0.09779300	-0.36142900
C	-3.55973700	2.40536000	-3.11131900
H	-1.60027800	1.61668800	-2.69149100
C	-3.49032700	-1.67550500	2.99050600
H	-2.09436000	-0.14658200	2.37795100
C	-4.31403600	-3.09520700	1.12257400
H	-3.44774100	-2.64149300	-0.79043800
C	-4.88809400	2.42392200	-2.62492200
C	-4.35745200	-2.67411600	2.48032300
C	5.25270200	-3.67995100	-2.25645300
C	4.90425000	-4.43892400	-3.56072900
H	5.20216400	-3.87476400	-4.44601300
H	5.41521800	-5.40979900	-3.57803200
H	3.82563200	-4.62139600	-3.61694800
C	6.78431200	-3.47720700	-2.18041200
H	7.28008400	-4.45035400	-2.07549700
H	7.17890500	-3.00466800	-3.08029500
H	7.06309300	-2.86838800	-1.31243000
C	4.85706500	-4.59614500	-1.07722600
H	5.14572000	-4.17395200	-0.10769600
H	3.78084000	-4.79835500	-1.05952200
H	5.37712200	-5.55523800	-1.18063400
C	3.36410200	0.56096400	-4.64258900
C	3.94346400	1.97576100	-4.40499200
H	5.03041600	1.95613600	-4.26903600
H	3.72671700	2.62337700	-5.26377000
H	3.50673200	2.43907400	-3.51412200

C	1.83247400	0.69882400	-4.86876900
H	1.36315600	-0.28394500	-4.98846500
H	1.32476000	1.21531100	-4.04976600
H	1.65099600	1.27775600	-5.78197600
C	3.92809100	-0.00846500	-5.96529300
H	5.01622800	0.01529900	-6.02282700
H	3.60550700	-1.04125500	-6.12875300
H	3.54560900	0.59867900	-6.79469000
C	-3.02084200	3.15710700	-4.36264000
C	-1.98470500	4.22515400	-3.94069800
H	-2.43204600	4.98872300	-3.29383200
H	-1.14515800	3.77653300	-3.39855000
H	-1.57915300	4.73158000	-4.82552700
C	-2.31096500	2.11664400	-5.27289700
H	-1.47361500	1.61712300	-4.77832000
H	-3.01682200	1.34619600	-5.60468300
H	-1.91483100	2.61647200	-6.16474600
C	-4.08944400	3.82362100	-5.25932100
H	-3.60369400	4.14538500	-6.18868800
H	-4.89214000	3.12904900	-5.52092700
H	-4.54280700	4.70893600	-4.81205400
C	-6.86484100	1.29779100	-1.35950800
C	-7.63554200	1.01000000	-2.67236600
H	-8.70245500	0.86959700	-2.45748100
H	-7.53413800	1.83260300	-3.38313600
H	-7.26548300	0.09313700	-3.14627900
C	-7.47639600	2.54025200	-0.66892500
H	-6.88942700	2.83660600	0.20888100
H	-7.54661800	3.39059600	-1.34733100
H	-8.49220400	2.30849600	-0.32530200
C	-7.10680000	0.09949600	-0.41562400
H	-6.72409600	-0.83822500	-0.83288600
H	-6.64996500	0.24762500	0.56980100
H	-8.18521500	-0.02224200	-0.26408100
C	-3.29279000	-1.34941100	4.49796700
C	-1.84513000	-0.84814100	4.74494400
H	-1.10474700	-1.54790100	4.34056000
H	-1.65878500	0.14114200	4.31797900
H	-1.67646800	-0.76310900	5.82450500
C	-3.46285700	-2.58976300	5.40865000
H	-4.47730100	-2.98417100	5.42775700
H	-2.80050300	-3.40217500	5.08788100
H	-3.18619600	-2.31746900	6.43413700
C	-4.24590000	-0.21524400	4.94648700
H	-5.30003300	-0.48303200	4.83859000
H	-4.07068800	0.02336600	6.00341000

H	-4.07015600	0.69480800	4.36467700
C	-5.08350100	-4.33872600	0.60256300
C	-4.74427300	-5.57601000	1.46969100
H	-5.05357700	-5.44254100	2.50653600
H	-5.24499200	-6.46486200	1.06559700
H	-3.66442700	-5.76055600	1.45956300
C	-4.67996300	-4.68564100	-0.84881900
H	-4.97152300	-3.90525900	-1.56110300
H	-3.60213500	-4.85454800	-0.94431600
H	-5.19362600	-5.60569700	-1.15009800
C	-6.61282300	-4.10786700	0.60095700
H	-7.11765700	-4.96572200	0.13903900
H	-7.01493800	-3.99448900	1.60785100
H	-6.87627700	-3.21507000	0.02167900
C	6.84177600	0.44808100	1.86851100
C	7.08787200	-1.01418200	1.40415400
H	6.85486000	-1.72194100	2.20789100
H	6.49270600	-1.29105700	0.53016300
H	8.14344500	-1.14278300	1.13673800
C	7.17379900	1.40076200	0.69505300
H	6.53630100	1.20694300	-0.17455500
H	7.03680000	2.45080200	0.97723200
H	8.21810500	1.27131000	0.38412400
C	7.85511500	0.68870100	3.01135800
H	8.84885200	0.38722000	2.65802300
H	7.92707300	1.73283000	3.31646600
H	7.61804200	0.09359200	3.89752000
C	2.96985300	1.22832600	5.28086500
C	1.50525600	0.77673300	5.46730600
H	0.80341900	1.36228700	4.86433100
H	1.36556900	-0.28200900	5.22313500
H	1.22267700	0.91162500	6.51746200
C	3.03417900	2.72619900	5.66248500
H	4.06103800	3.07368300	5.78181400
H	2.53567600	3.34991400	4.91099600
H	2.52115900	2.88461800	6.61895800
C	3.82671100	0.40598500	6.27652400
H	3.74039500	-0.66721500	6.06814300
H	4.88077100	0.68501900	6.22607400
H	3.47267500	0.57665400	7.30092300
O	5.48704200	-1.59495600	-4.25711400
O	5.66261400	1.79500900	4.33612300
O	-5.78413100	3.37640900	-3.08615200
O	-5.24455200	-3.34529700	3.30816400
C	5.90203000	3.15258300	3.96146600
H	6.51654700	3.58692600	4.75429800

H	6.43935400	3.22295900	3.00903100
H	4.96455400	3.71380700	3.87630600
C	6.61729900	-0.73063500	-4.14437200
H	7.34808900	-1.08286200	-4.87722900
H	6.35950400	0.31009500	-4.36801500
H	7.05663400	-0.77733300	-3.14084400
C	-6.44180800	-2.66439600	3.68044200
H	-7.23509400	-3.41578500	3.74265600
H	-6.33767600	-2.18948900	4.66158600
H	-6.71993700	-1.90648500	2.93985800
C	-5.60957500	4.66404700	-2.49083300
H	-4.62265000	5.08399600	-2.71317300
H	-6.38132900	5.30847800	-2.91965900
H	-5.73278500	4.61963100	-1.40263400
C	1.31775200	4.01385600	0.08799200
C	-1.36251400	3.00843700	2.06499000
C	-2.66601000	2.98220800	1.51444500
C	-1.26189700	3.21079000	3.46060200
C	-3.79219100	3.15828700	2.31139300
H	-2.78941200	2.83603900	0.44556400
C	-2.39403200	3.38971300	4.25558500
H	-0.27725600	3.25575700	3.91864500
C	-3.67145200	3.36830300	3.69082000
H	-4.77729800	3.14143500	1.84931000
H	-2.27453700	3.55469500	5.32427700
H	-4.55315800	3.51653600	4.30837900
C	1.19395600	3.57021700	1.59338300
H	1.99210800	2.90703800	1.94327400
H	1.11069200	4.41083400	2.29359200
C	2.58359000	3.54317500	-0.64142900
H	2.51160800	3.73616000	-1.71821700
H	3.45892100	4.08463200	-0.26107700
H	2.74772400	2.47263500	-0.49516700
C	1.16639800	5.52089200	-0.13123500
C	0.48625400	6.02446000	-1.24994300
C	1.78817700	6.44337400	0.72401000
C	0.41013500	7.39694300	-1.49441800
H	0.01157600	5.33740100	-1.94436600
C	1.71774200	7.81624600	0.48325400
H	2.33875700	6.08494000	1.58951200
C	1.02299500	8.30107900	-0.62603300
H	-0.12971300	7.75837200	-2.36635100
H	2.20560000	8.50766400	1.16603900
H	0.96199500	9.37013300	-0.81223700

TS2a-b

B3LYP/SDD-6-31G(d) SCF energy: -5019.757025 a.u.
B3LYP/SDD-6-31G(d) Enthalpy: -5017.765334 a.u.
B3LYP/SDD-6-31G(d) Gibbs free energy: -5018.023443 a.u.
M06/SDD-6-311+G(d,p) SCF energy in solution: -5017.984064 a.u.
M06/SDD-6-311+G(d,p) enthalpy in solution: -5015.992373 a.u.
M06/SDD-6-311+G(d,p) free energy in solution: -5016.250482 a.u.
Three lowest frequencies (cm^{-1}): -759.2091 10.8933 11.4513
Imaginary frequency: -759.2091 cm^{-1}
Cartesian coordinates:

ATOM	X	Y	Z
Cu	0.02373400	0.96072000	0.44622600
H	-0.22652700	1.21946600	2.04226500
C	-0.07755600	3.06152500	0.06207300
C	-0.37868900	2.84606000	1.45621100
P	-1.68199600	-0.31652400	-0.49431900
C	-1.04343200	-1.47904200	-1.79915200
C	-2.98720200	0.66835100	-1.36888000
C	-2.66499200	-1.41650300	0.61695400
C	-0.08054400	-2.48872000	-1.47036200
C	-1.47526500	-1.33878200	-3.12579400
C	-4.35039700	0.48277400	-1.15349700
C	-2.58763500	1.68188000	-2.25470600
C	-2.69044600	-1.12881300	1.97932800
C	-3.38180700	-2.52605400	0.14776900
C	0.34068600	-3.27949000	-2.53202800
C	0.40371300	-2.88713600	-0.10803000
C	-1.01600400	-2.15012300	-4.17722700
H	-2.21610200	-0.58495000	-3.36033700
C	-5.33145500	1.31097200	-1.72958000
H	-4.66524100	-0.32953900	-0.51189300
C	-3.50272700	2.55146700	-2.85542600
H	-1.52993600	1.78934100	-2.46040300
C	-3.46840200	-1.86467200	2.89134400
H	-2.06736600	-0.31500300	2.33473300
C	-4.20913800	-3.27777100	0.98759000
H	-3.28894300	-2.79635600	-0.89603900
C	-0.10385000	-3.12528600	-3.84260200
O	1.24216300	-4.32373400	-2.48794500
C	0.05130000	-4.16056500	0.32120600
C	1.29586100	-2.17199000	0.75556300
H	-1.37882800	-2.02799700	-5.19201600
C	-4.86899200	2.41190800	-2.48263200
C	-4.31288000	-2.85612800	2.34264200
O	0.49529400	-4.05942300	-4.65215300
C	1.09810100	-4.98611600	-3.74559800
C	0.48935300	-4.72985400	1.51389500

O	-0.77020900	-5.06119400	-0.32647900
C	1.72610600	-2.76380100	1.95123300
P	1.84053900	-0.44308100	0.32932500
H	2.08068100	-5.27551200	-4.12011200
H	0.43990400	-5.85994200	-3.62511500
C	1.33094000	-4.04793800	2.36307300
O	-0.04242400	-5.98978800	1.65223600
C	-0.57160400	-6.29793100	0.36092600
H	2.41139400	-2.22132400	2.58988600
C	3.11558800	-0.02462200	1.61046400
C	2.84586600	-0.71220900	-1.19964800
H	1.68668900	-4.48352000	3.29041000
H	0.15392700	-6.91137400	-0.19482200
H	-1.52780700	-6.81071900	0.47103600
C	4.48394800	0.06380700	1.32923500
C	2.68964400	0.25211500	2.91250800
C	2.76059900	0.20582800	-2.24351500
C	3.68290800	-1.82653500	-1.35150600
C	5.41131500	0.51654200	2.27612800
H	4.82611800	-0.20958400	0.34221000
C	3.57248800	0.63670400	3.93488200
H	1.63080500	0.16378800	3.13125100
C	3.54539700	0.10075300	-3.40726300
H	2.04914400	1.01831300	-2.14531700
C	4.52146100	-1.97691800	-2.45918300
H	3.67512900	-2.58499000	-0.57995000
C	4.91202800	0.88414700	3.55278600
C	4.50823600	-0.93419500	-3.42637100
C	-4.89975000	-4.56462800	0.46442300
C	-4.47508200	-5.76241300	1.35032000
H	-4.80446000	-5.63258800	2.38268000
H	-4.91045200	-6.69176100	0.96121000
H	-3.38451900	-5.87007400	1.35265900
C	-6.44298700	-4.45636500	0.45919100
H	-6.87220500	-5.33063400	-0.04594800
H	-6.85374100	-4.42651600	1.46858000
H	-6.77721300	-3.56377100	-0.08319500
C	-4.46550400	-4.88717900	-0.98304700
H	-4.80055100	-4.12480000	-1.69615800
H	-3.37906800	-4.98840700	-1.07333000
H	-4.91963100	-5.83710100	-1.28745500
C	-3.27750800	-1.55095900	4.40227200
C	-3.92587800	-0.19124000	4.75328000
H	-5.01041200	-0.20427600	4.59598800
H	-3.74671500	0.04989700	5.80886300
H	-3.51247300	0.62201400	4.14918100

C	-1.75314300	-1.44920400	4.68931400
H	-1.24104900	-2.38029000	4.42098900
H	-1.27122400	-0.63119800	4.14756000
H	-1.59649100	-1.26978500	5.75959800
C	-3.80770100	-2.63514700	5.36947500
H	-4.89582100	-2.68240800	5.41866000
H	-3.43958300	-3.63056100	5.10334100
H	-3.44803300	-2.40152700	6.37896700
C	2.99655000	0.69452700	5.37947200
C	2.00670800	1.87544500	5.51525000
H	2.50285900	2.84016200	5.35984200
H	1.19208900	1.79863400	4.78746000
H	1.56383600	1.88491300	6.51908300
C	2.21921400	-0.62616300	5.63916300
H	1.37706700	-0.76843500	4.95729300
H	2.88340600	-1.49335800	5.54482000
H	1.81593500	-0.62103200	6.65866600
C	4.04575600	0.77980000	6.51224800
H	3.53268100	0.61616700	7.46782200
H	4.81844600	0.01259900	6.40983600
H	4.54118800	1.74881100	6.57701500
C	6.92684200	0.51917900	1.94640900
C	7.67087700	-0.38286100	2.96276400
H	8.74359400	-0.40267300	2.73196700
H	7.54623900	-0.01830100	3.98432100
H	7.29810600	-1.41289600	2.91345200
C	7.54106100	1.93949700	1.97486700
H	6.96308000	2.63482000	1.35456700
H	7.59868500	2.33773600	2.98794800
H	8.56244500	1.90776000	1.57554300
C	7.20174600	-0.05573200	0.53963400
H	6.82174600	-1.07721300	0.42947200
H	6.76382400	0.56020500	-0.25441900
H	8.28434900	-0.08704600	0.37352900
C	3.24474000	1.09131400	-4.56809200
C	1.70467700	1.17503200	-4.75237600
H	1.27796300	0.18544700	-4.94991600
H	1.19343900	1.59268500	-3.88155300
H	1.47434700	1.82433700	-5.60511100
C	3.80169900	0.66879700	-5.94795300
H	4.88583700	0.74885900	-6.02461800
H	3.52272400	-0.35939700	-6.19766900
H	3.37192600	1.32938900	-6.71061800
C	3.76662600	2.50534000	-4.21965700
H	4.85601200	2.52288800	-4.10590200
H	3.50326500	3.21344500	-5.01525600

H	3.33080800	2.87269000	-3.28469100
C	5.35609800	-3.27222000	-2.64060800
C	5.02658500	-3.90807500	-4.01402400
H	5.29687000	-3.24642800	-4.83838500
H	5.57371800	-4.85196600	-4.13133500
H	3.95512600	-4.12463100	-4.08680600
C	5.00604800	-4.31961200	-1.55952400
H	5.29482300	-3.99300500	-0.55366300
H	3.93693400	-4.55679400	-1.55153500
H	5.55483100	-5.24483200	-1.76919900
C	6.87925600	-3.01720300	-2.55025400
H	7.41373500	-3.97542400	-2.55009300
H	7.24861700	-2.43737900	-3.39699300
H	7.14035700	-2.49128200	-1.62438700
C	-6.81489300	0.89489700	-1.51418400
C	-6.94755800	-0.61977500	-1.83598100
H	-6.65938400	-0.82438100	-2.87337600
H	-6.33565900	-1.25134200	-1.18651000
H	-7.99077100	-0.93181900	-1.70718300
C	-7.21903400	1.11852500	-0.03737900
H	-6.56252100	0.57090600	0.64740200
H	-7.17301600	2.17844600	0.23735000
H	-8.24738500	0.77463500	0.13109500
C	-7.84346600	1.59844900	-2.42967700
H	-8.81017300	1.09339000	-2.31320400
H	-7.99836500	2.64907100	-2.18348100
H	-7.55696900	1.53860700	-3.48344900
C	-3.03732700	3.56356700	-3.93442200
C	-1.54833100	3.36206600	-4.29059100
H	-0.88224000	3.58265700	-3.44889400
H	-1.33974500	2.34272200	-4.63308900
H	-1.28079800	4.04486700	-5.10466000
C	-3.19848600	5.03434100	-3.48097900
H	-4.24639400	5.32831200	-3.41487500
H	-2.72196800	5.20725700	-2.50878600
H	-2.71773500	5.69832300	-4.21021000
C	-3.84818800	3.33264700	-5.23443700
H	-3.69311000	2.31536500	-5.61349700
H	-4.91707900	3.48198600	-5.07213100
H	-3.51533300	4.03322700	-6.01052000
O	-5.25933300	-3.49026900	3.13465700
O	-5.75310700	3.39153000	-2.90907700
O	5.79372300	1.47654400	4.44477300
O	5.46242300	-0.99047600	-4.43150800
C	-6.08890200	4.34557600	-1.90027400
H	-6.69881900	5.10934600	-2.38975500

H	-6.66719500	3.89149600	-1.08751800
H	-5.19194000	4.81039400	-1.47536400
C	-6.44008600	-2.72066800	3.35921000
H	-7.13101400	-3.36898700	3.90472600
H	-6.23685500	-1.82693100	3.95864700
H	-6.90065700	-2.41204300	2.41302900
C	6.55861400	-0.09444100	-4.24969600
H	7.28829800	-0.33993000	-5.02586700
H	6.25348800	0.95142300	-4.36273800
H	7.01888500	-0.22227000	-3.26276400
C	5.63484200	2.89114000	4.56252000
H	4.65554000	3.15859000	4.97390900
H	6.41701100	3.23266500	5.24558400
H	5.75441300	3.38750200	3.59256100
C	1.16398900	3.93201000	0.38605200
H	-0.81951300	3.29246700	-0.69742200
C	0.92693100	3.54042800	1.88984200
C	-1.67713600	3.07997100	2.15446000
C	-2.88850500	3.13332300	1.44810100
C	-1.70542900	3.31944700	3.53830200
C	-4.08765600	3.41129300	2.10572200
H	-2.89082700	2.96039200	0.37684400
C	-2.90083500	3.61029900	4.19458500
H	-0.77804900	3.27875800	4.10372000
C	-4.10123300	3.65594600	3.48051300
H	-5.01403700	3.44440700	1.53747200
H	-2.89544500	3.80184200	5.26493500
H	-5.03448100	3.88203700	3.98978000
H	0.75210600	4.38981700	2.55755500
H	1.69364400	2.89490900	2.32500800
C	2.52545800	3.51563600	-0.19308300
H	2.54315100	3.66283700	-1.27982400
H	3.33762800	4.11941400	0.23396800
H	2.73041200	2.46198800	0.01523400
C	0.96653100	5.42372100	0.09871800
C	0.34635500	5.84947800	-1.08553300
C	1.47035000	6.41134400	0.95887400
C	0.21482800	7.20505300	-1.39095300
H	-0.03937700	5.10953100	-1.78107300
C	1.33967700	7.76936200	0.66162400
H	1.97643200	6.11719100	1.87512700
C	0.70702200	8.17396400	-0.51474500
H	-0.27570700	7.50349400	-2.31449500
H	1.73376300	8.51176400	1.35172700
H	0.60091000	9.23053200	-0.74679200

TS8-a
B3LYP/SDD-6-31G(d) SCF energy: -4788.700325 a.u.
B3LYP/SDD-6-31G(d) Enthalpy: -4786.794888 a.u.
B3LYP/SDD-6-31G(d) Gibbs free energy: -4787.043461 a.u.
M06/SDD-6-311+G(d,p) SCF energy in solution: -4787.036857 a.u.
M06/SDD-6-311+G(d,p) enthalpy in solution: -4785.131419 a.u.
M06/SDD-6-311+G(d,p) free energy in solution: -4785.379992 a.u.
Three lowest frequencies (cm^{-1}): -510.7480 8.9409 12.1263
Imaginary frequency: -510.7480 cm^{-1}
Cartesian coordinates:

ATOM	X	Y	Z
Cu	0.10214500	0.23573800	-1.47751600
H	0.28580300	-0.98164000	-2.47256700
C	-0.36755500	1.86254800	-2.88105700
C	-0.38974200	0.56708800	-3.41439700
P	1.82695400	0.25017600	0.06763900
C	1.29386700	0.34710200	1.84469100
C	3.01195400	1.66057100	-0.13025600
C	2.93153400	-1.23050100	0.03380200
C	0.44966500	-0.66109700	2.41337800
C	1.71976000	1.42517600	2.63340000
C	4.39444200	1.49178500	-0.13541600
C	2.49721100	2.95598300	-0.29685300
C	2.96717700	-2.01067700	-1.11872000
C	3.75269900	-1.58583500	1.11310100
C	0.14230200	-0.49060400	3.75736900
C	-0.03199600	-1.92871100	1.77334200
C	1.37190600	1.57418500	3.98660500
H	2.36806700	2.17326400	2.19479200
C	5.28804500	2.55085400	-0.37630300
H	4.79565000	0.50334900	0.04522000
C	3.32417200	4.05788700	-0.53356200
H	1.42340900	3.09173800	-0.25533500
C	3.85635900	-3.08854900	-1.27407200
H	2.25876400	-1.77676700	-1.90624600
C	4.69039400	-2.61905400	1.01699400
H	3.65544600	-1.03376000	2.03882700
C	0.58307000	0.58345600	4.52674100
O	-0.62775900	-1.31826200	4.54840700
C	0.43461700	-3.11904600	2.31618700
C	-1.03738300	-2.06523600	0.76182500
H	1.72626100	2.41164200	4.57758700
C	4.71552800	3.80280400	-0.68636400
C	4.79312900	-3.28710800	-0.23523800
O	0.11156800	0.46225700	5.81056900
C	-0.38548000	-0.87634500	5.88547100

C	-0.00387300	-4.37908900	1.91791100
O	1.38019200	-3.26868600	3.30980600
C	-1.46669700	-3.34243100	0.37756100
P	-1.71806100	-0.55562700	-0.08569300
H	-1.31944000	-0.88760400	6.44816500
H	0.37366600	-1.52216900	6.35224100
C	-0.95973200	-4.52682400	0.93857800
O	0.64831000	-5.35009800	2.63900900
C	1.29516600	-4.64177700	3.69821100
H	-2.23935400	-3.43238000	-0.37534500
C	-3.07016800	-1.19003500	-1.18530400
C	-2.64882100	0.28181200	1.27544800
H	-1.31737200	-5.50284400	0.62919500
H	0.69283300	-4.72475900	4.61557500
H	2.29956400	-5.04171600	3.84443400
C	-4.42290400	-0.90385200	-0.96296800
C	-2.73102300	-1.92523400	-2.32543800
C	-2.65376400	1.67378100	1.34889900
C	-3.34345600	-0.44578800	2.25146300
C	-5.41836500	-1.23847500	-1.88935800
H	-4.69869400	-0.39373000	-0.05178200
C	-3.68378900	-2.35811600	-3.26179500
H	-1.68561200	-2.16781100	-2.48500900
C	-3.38463700	2.37545600	2.32689100
H	-2.06415500	2.22611500	0.62601300
C	-4.12848000	0.18008800	3.22297100
H	-3.26591600	-1.52491000	2.23898800
C	-5.00600600	-1.88811900	-3.08207800
C	-4.21071300	1.59912000	3.17293700
C	5.50450700	-3.06083200	2.26148000
C	5.24744400	-4.56535700	2.52494700
H	5.58737200	-5.18155500	1.69059300
H	5.77729900	-4.88527900	3.43115200
H	4.17753400	-4.75025700	2.67276400
C	7.02493700	-2.82631200	2.09748800
H	7.53308000	-3.02124000	3.05010200
H	7.46245600	-3.49015500	1.35130600
H	7.23942200	-1.78886700	1.81481700
C	5.06174800	-2.29053000	3.52526000
H	5.28848500	-1.21997600	3.45879900
H	3.99062700	-2.40450200	3.72148100
H	5.60640500	-2.68339400	4.39136100
C	3.67408800	-3.97142600	-2.54092200
C	4.11302300	-3.18826300	-3.80131700
H	5.17932500	-2.93590400	-3.77189300
H	3.93727500	-3.79046100	-4.70145000

H	3.55229700	-2.25324400	-3.90698400
C	2.16355200	-4.31240500	-2.67680200
H	1.80311700	-4.84475300	-1.78915200
H	1.53604800	-3.42773400	-2.81461200
H	2.01281400	-4.96165600	-3.54749300
C	4.40473800	-5.33374600	-2.51041900
H	5.48805200	-5.25096000	-2.60325000
H	4.18698400	-5.89036500	-1.59427700
H	4.05308000	-5.93205000	-3.35981100
C	-3.19581100	-3.34787200	-4.35905200
C	-2.26080100	-2.62659900	-5.35886600
H	-2.77955000	-1.82135900	-5.89143900
H	-1.39247700	-2.18927200	-4.85447100
H	-1.88879900	-3.33594300	-6.10876300
C	-2.38712500	-4.47822400	-3.66387900
H	-1.50209800	-4.11016000	-3.13824200
H	-3.01247100	-5.01632100	-2.94180400
H	-2.04479100	-5.19931300	-4.41535800
C	-4.31430100	-4.07066100	-5.14616300
H	-3.85485500	-4.87105900	-5.73884300
H	-5.05106200	-4.52718200	-4.47893300
H	-4.84763400	-3.42184400	-5.84122600
C	-6.91163000	-0.97867600	-1.55924200
C	-7.68316800	-2.32176400	-1.60251300
H	-8.74021900	-2.15604000	-1.35810600
H	-7.62745700	-2.78134500	-2.59127700
H	-7.27593500	-3.02679600	-0.86809700
C	-7.57194500	0.02414700	-2.53552300
H	-6.98634300	0.94827700	-2.61193400
H	-7.69257100	-0.39769200	-3.53343100
H	-8.57066000	0.29271400	-2.16920400
C	-7.08650600	-0.39775000	-0.13879400
H	-6.66349400	-1.05265100	0.63073900
H	-6.62839900	0.59281900	-0.03557100
H	-8.15647500	-0.28948400	0.07102800
C	-3.17988300	3.91478400	2.41745100
C	-1.66830300	4.22699000	2.24166900
H	-1.06301500	3.68434400	2.97649100
H	-1.29602900	3.97883800	1.24452900
H	-1.50136400	5.30048800	2.38662700
C	-3.57353300	4.53529800	3.77918100
H	-4.64840800	4.55628600	3.95633100
H	-3.10768200	4.00179900	4.61400000
H	-3.21833600	5.57257000	3.80250700
C	-3.94528500	4.63230500	1.28102600
H	-5.02788400	4.48166700	1.35496500

H	-3.75704600	5.71246900	1.32443100
H	-3.62543900	4.27648400	0.29686400
C	-4.80438700	-0.65640000	4.34150100
C	-4.37076000	-0.11506600	5.72636600
H	-4.69734500	0.91482700	5.87695400
H	-4.79871200	-0.73637400	6.52323300
H	-3.27970600	-0.14389700	5.82160800
C	-4.36579400	-2.13661900	4.27604900
H	-4.71485300	-2.63417900	3.36386300
H	-3.27725100	-2.24267100	4.33156400
H	-4.80146600	-2.67520900	5.12534000
C	-6.34817700	-0.63527600	4.24475300
H	-6.77309500	-1.34792600	4.96274100
H	-6.76007400	0.34755100	4.47702300
H	-6.68775700	-0.92940100	3.24454700
C	6.80399700	2.23781100	-0.22576700
C	7.01389300	1.48695100	1.11888900
H	6.68437300	2.10177600	1.96427600
H	6.47698600	0.53612000	1.16559900
H	8.07956200	1.26821800	1.25562200
C	7.27109400	1.31730900	-1.37873800
H	6.69559700	0.38544700	-1.40743300
H	7.16015600	1.80390500	-2.35419700
H	8.32975000	1.05759200	-1.25245000
C	7.73664900	3.46875800	-0.15408800
H	8.73621500	3.12626000	0.14081000
H	7.84434000	3.99037000	-1.10543400
H	7.39589500	4.19345500	0.59052300
C	2.74116800	5.49518200	-0.54308500
C	1.25295800	5.50129100	-0.13222200
H	0.61107900	4.98879500	-0.85604100
H	1.09893400	5.04403700	0.85138900
H	0.90667200	6.53911600	-0.06967400
C	2.83435600	6.16600800	-1.93398100
H	3.86408400	6.40271300	-2.20466700
H	2.40382300	5.52542100	-2.71288300
H	2.27103600	7.10740800	-1.92849500
C	3.50009700	6.35797600	0.49701200
H	3.38561900	5.93956400	1.50424800
H	4.56526200	6.42262500	0.26768900
H	3.08703900	7.37442800	0.50888800
O	5.83725100	-4.18659100	-0.39433600
O	5.51383700	4.84461600	-1.13477200
O	-5.95572500	-2.07876600	-4.07431900
O	-5.11180700	2.20666900	4.03441300
C	5.83949900	4.76291400	-2.52300200

H	6.39122100	5.67533700	-2.76395100
H	6.46840200	3.89286900	-2.74309200
H	4.93643200	4.70723000	-3.14160800
C	6.92241400	-3.68149800	-1.17209300
H	7.69317100	-4.45668300	-1.16528400
H	6.62378000	-3.48002500	-2.20663000
H	7.32885800	-2.75974700	-0.73843700
C	-6.32050400	2.64976700	3.41857000
H	-7.00558400	2.90347500	4.23210400
H	-6.16055400	3.53769400	2.79801800
H	-6.76542800	1.86130700	2.80042000
C	-5.84705000	-1.16032900	-5.16340800
H	-4.90961000	-1.29120100	-5.71462900
H	-6.68788400	-1.37220800	-5.82904500
H	-5.90726500	-0.12221000	-4.81682000
C	0.59440400	1.53602400	-4.01313700
H	-1.16248000	-0.01495600	-3.90327600
C	-1.39096200	2.89807100	-2.76673800
C	-1.06681000	4.24666600	-3.02471800
C	-2.73729800	2.60007700	-2.46258200
C	-2.03940400	5.24627800	-2.99232700
H	-0.03835800	4.49834800	-3.27024800
C	-3.70561500	3.60070900	-2.42775400
H	-3.02194400	1.56856600	-2.27295400
C	-3.36684700	4.93300200	-2.69273300
H	-1.75790500	6.27502400	-3.20583900
H	-4.73711500	3.33806500	-2.20189500
H	-4.12577000	5.71039000	-2.66786500
C	2.09740000	1.41290400	-3.81391000
H	2.53615500	0.73571200	-4.56108600
H	2.58543300	2.39084200	-3.92703200
H	2.34367400	1.03088600	-2.82190300
C	0.23863500	2.03060500	-5.41692200
H	0.64986300	3.03182100	-5.60084100
H	0.65634000	1.36162900	-6.18181900
H	-0.84491500	2.08766100	-5.56562500

TS8-b

B3LYP/SDD-6-31G(d) SCF energy: -4788.696962 a.u.
B3LYP/SDD-6-31G(d) Enthalpy: -4786.791425 a.u.
B3LYP/SDD-6-31G(d) Gibbs free energy: -4787.039335 a.u.
M06/SDD-6-311+G(d,p) SCF energy in solution: -4787.038901 a.u.
M06/SDD-6-311+G(d,p) enthalpy in solution: -4785.133365 a.u.
M06/SDD-6-311+G(d,p) free energy in solution: -4785.381274 a.u.
Three lowest frequencies (cm^{-1}): -651.7995 9.6475 12.1776
Imaginary frequency: -651.7995 cm^{-1}

Cartesian coordinates:

ATOM	X	Y	Z
Cu	0.03136900	0.35949000	-1.35086800
H	-0.16864000	1.88587800	-1.78686300
P	-1.61491200	-0.48434400	0.14885200
C	-0.93744300	-1.72118000	1.36562600
C	-3.01036100	-1.39508100	-0.66944400
C	-2.50289800	0.75154900	1.19212600
C	0.08065500	-1.34843500	2.30182200
C	-1.38165500	-3.05124300	1.32305500
C	-4.34861800	-1.11557500	-0.40399100
C	-2.71882800	-2.38429900	-1.62349200
C	-2.55901200	2.06400800	0.72896700
C	-3.14304700	0.43321500	2.39767700
C	0.53241300	-2.36644300	3.13157200
C	0.59903500	0.02764600	2.58703400
C	-0.88052300	-4.06171800	2.16062700
H	-2.16503900	-3.32156000	0.62692900
C	-5.40838300	-1.73020100	-1.09544000
H	-4.58286700	-0.39422600	0.36735800
C	-3.71733400	-3.02728300	-2.36206900
H	-1.68156700	-2.64496300	-1.78982000
C	-3.29726100	3.06579800	1.38380600
H	-1.99748100	2.30786400	-0.16659100
C	-3.92556700	1.36719000	3.08460400
H	-3.02807700	-0.56720500	2.79431000
C	0.08328800	-3.68199000	3.06679100
O	1.47870000	-2.26744900	4.13133000
C	0.31375700	0.54416500	3.84485300
C	1.45126600	0.83532400	1.76732800
H	-1.24926900	-5.08029400	2.10783900
C	-5.05763400	-2.59732600	-2.15242800
C	-4.06597800	2.65564100	2.49599400
O	0.73747800	-4.44491000	4.00532300
C	1.37284400	-3.49195300	4.86047000
C	0.77083400	1.77592100	4.30339600
O	-0.45960300	-0.03839200	4.82880500
C	1.89925800	2.07508200	2.24868300
P	1.89903900	0.33490100	0.03136600
H	2.37044100	-3.84617500	5.12294000
H	0.75196300	-3.33149500	5.75479800
C	1.56644300	2.57826900	3.51701300
O	0.29903300	2.00489100	5.57424900
C	-0.20623400	0.73775900	6.00134900
H	2.54489500	2.67816500	1.62338200
C	3.19778000	1.57087100	-0.44781500

C	2.86587400	-1.22619900	0.20700100
H	1.93257500	3.53888100	3.86246400
H	0.55144900	0.23089400	6.61811700
H	-1.13772300	0.88258900	6.54972100
C	4.56911100	1.34771800	-0.27359400
C	2.78872500	2.79027100	-0.99047200
C	2.79663100	-2.13726700	-0.84461600
C	3.67474900	-1.52873500	1.31064500
C	5.53256000	2.25971700	-0.71768500
H	4.88775100	0.43240300	0.20355400
C	3.69662800	3.77535100	-1.41426400
H	1.72316000	2.96407900	-1.09715600
C	3.56990300	-3.31075400	-0.87878500
H	2.10798700	-1.92046300	-1.65483400
C	4.50148000	-2.65736300	1.33005400
H	3.65457700	-0.86052600	2.16222300
C	5.06686500	3.42871600	-1.37683400
C	4.50003200	-3.48315100	0.17109600
C	-4.52223800	1.02288200	4.47489300
C	-3.97550400	2.03435600	5.51353800
H	-4.29895000	3.05192000	5.28521100
H	-4.33412500	1.77547900	6.51809300
H	-2.87957900	2.02193500	5.52648700
C	-6.06901400	1.05779800	4.49668900
H	-6.43189900	0.66826600	5.45600300
H	-6.45688100	2.07035000	4.38661200
H	-6.49257800	0.42909600	3.70424100
C	-4.10239200	-0.39086200	4.93478900
H	-4.51420900	-1.17436800	4.28769300
H	-3.01501700	-0.51025300	4.96749600
H	-4.49168700	-0.56674400	5.94424100
C	-3.15056600	4.51583700	0.84239800
C	-3.87993500	4.65234100	-0.51583800
H	-4.95714700	4.47464300	-0.41876400
H	-3.74480800	5.66522400	-0.91588400
H	-3.49200400	3.94539700	-1.25647400
C	-1.63963700	4.79859300	0.61357600
H	-1.07369300	4.67838200	1.54442500
H	-1.19223000	4.14426400	-0.13902600
H	-1.51024300	5.83103700	0.26804000
C	-3.63808100	5.63011700	1.79776000
H	-4.72273800	5.67657400	1.89814900
H	-3.21152700	5.52079400	2.79921700
H	-3.30957200	6.59602500	1.39507700
C	3.09956600	5.14619200	-1.84304100
C	2.34356700	4.99956800	-3.18517000

H	3.01742500	4.71387500	-4.00074200
H	1.55998900	4.23716000	-3.12037800
H	1.87089800	5.95099500	-3.46003100
C	2.08309000	5.59295800	-0.75598600
H	1.24736200	4.89898400	-0.63916100
H	2.57503500	5.69788200	0.21808600
H	1.66162500	6.56820100	-1.02680500
C	4.11422800	6.30766500	-1.95438400
H	3.55398400	7.24331600	-2.07196600
H	4.72991100	6.39538900	-1.05446300
H	4.78281400	6.22449500	-2.81142200
C	7.03451500	2.02149900	-0.41188100
C	7.59101700	3.22726500	0.38611200
H	8.64957800	3.06286100	0.62430700
H	7.50658100	4.15493600	-0.18296900
H	7.04982000	3.34933100	1.33188800
C	7.87910900	1.81827900	-1.69248900
H	7.44543800	1.04238000	-2.33472700
H	7.97413200	2.73804000	-2.27016700
H	8.89196900	1.49673600	-1.41948700
C	7.24184700	0.76473800	0.46245800
H	6.69342100	0.82563300	1.40908500
H	6.93867400	-0.15525600	-0.05052700
H	8.30660900	0.67118400	0.70409400
C	3.28624200	-4.30746000	-2.03802400
C	1.74704100	-4.47509300	-2.16824700
H	1.31347700	-4.83865000	-1.22958900
H	1.23853400	-3.54626900	-2.43741300
H	1.52412100	-5.20830100	-2.95217700
C	3.84038700	-5.73647400	-1.83384700
H	4.92542300	-5.80244400	-1.91677200
H	3.55201400	-6.14595500	-0.86125300
H	3.41697800	-6.38394000	-2.61132200
C	3.82377200	-3.73502600	-3.37190600
H	4.91307800	-3.61620500	-3.35504200
H	3.57429900	-4.40827600	-4.20159400
H	3.38535300	-2.75512900	-3.58964900
C	5.29887100	-3.02740000	2.60821700
C	4.82926900	-4.42076000	3.09737000
H	5.04773300	-5.19413800	2.35775200
H	5.34048800	-4.68470800	4.03224200
H	3.74914500	-4.42546200	3.28357700
C	5.04109800	-2.01690800	3.74769100
H	5.41441100	-1.01585500	3.50012400
H	3.97945700	-1.93389200	3.99818100
H	5.57523700	-2.34913500	4.64529200

C	6.82994500	-3.05799600	2.38381700
H	7.33936500	-3.16386500	3.34959600
H	7.13576900	-3.89690000	1.75904700
H	7.18300000	-2.12676700	1.92498700
C	-6.84590800	-1.42592400	-0.58451600
C	-6.86378700	-1.61285300	0.95835600
H	-6.59652400	-2.64056400	1.22942300
H	-6.17904900	-0.93895100	1.47963900
H	-7.87267300	-1.41423600	1.33905600
C	-7.22127500	0.04080600	-0.90459900
H	-6.50422300	0.74438100	-0.46766200
H	-7.24692700	0.22479900	-1.98467600
H	-8.21473900	0.27470100	-0.50168400
C	-7.95637800	-2.35985700	-1.11913800
H	-8.87273500	-2.16754800	-0.54766800
H	-8.19469900	-2.19723500	-2.17038800
H	-7.69527100	-3.41411100	-0.99189500
C	-3.36560500	-4.20909800	-3.30326000
C	-1.86973600	-4.58077600	-3.21137700
H	-1.21654600	-3.78129000	-3.57793100
H	-1.56551700	-4.83068300	-2.18916000
H	-1.68423800	-5.46298700	-3.83418400
C	-3.65888000	-3.89523500	-4.78989000
H	-4.72881000	-3.84276000	-4.99233000
H	-3.19395900	-2.95018500	-5.09486500
H	-3.24331700	-4.68890800	-5.42286900
C	-4.17248000	-5.45950000	-2.87113700
H	-3.92695600	-5.74299100	-1.84068100
H	-5.24810100	-5.28444100	-2.93541400
H	-3.92153500	-6.30785800	-3.52020100
O	-4.97023600	3.52900600	3.08307800
O	-6.03123900	-3.08738300	-3.01027400
O	6.01410600	4.24946200	-1.97144700
O	5.43019000	-4.51142200	0.11959800
C	-6.42719100	-2.16479600	-4.02557200
H	-7.12261700	-2.70181600	-4.67600800
H	-6.93425100	-1.28937700	-3.60410700
H	-5.56715500	-1.82379500	-4.61343000
C	-6.20564100	3.64404800	2.37728500
H	-6.84650300	4.29213200	2.98101800
H	-6.06935600	4.09356800	1.38801200
H	-6.68719500	2.66641100	2.25568300
C	6.55408300	-4.23584900	-0.71628400
H	7.23164600	-5.08748800	-0.61237900
H	6.26470400	-4.13262300	-1.76741200
H	7.06948800	-3.32033200	-0.40270500

C	6.09662700	4.10550700	-3.39012100
H	5.17598400	4.42957700	-3.88699800
H	6.92373100	4.74171200	-3.71614000
H	6.30025400	3.06668500	-3.67426000
C	-0.15048000	-0.53211200	-3.24692200
C	-0.56154300	0.81841100	-3.29459300
C	0.57656500	0.39339600	-4.20155000
H	-0.75227900	-1.39828800	-3.50595200
C	-1.81015100	1.53281800	-3.65241000
C	-1.76382300	2.87686300	-4.06116300
C	-3.05245300	0.88091400	-3.64544900
C	-2.92039000	3.54810700	-4.45133000
H	-0.80632200	3.39127700	-4.06210400
C	-4.21476900	1.55539700	-4.02761400
H	-3.10194100	-0.15990300	-3.34206500
C	-4.15468900	2.88947700	-4.43252900
H	-2.86238300	4.58614500	-4.76974900
H	-5.16878500	1.03392600	-4.01000900
H	-5.05867800	3.41325500	-4.73282200
C	2.02737700	0.78880500	-3.98414700
H	2.69597800	0.03772200	-4.42930000
H	2.25465400	1.75344300	-4.45988200
H	2.26761600	0.87060300	-2.92435900
C	0.22717600	0.30856900	-5.68861900
H	0.41092600	1.26129300	-6.20399000
H	0.84965800	-0.45223000	-6.17895600
H	-0.82198000	0.03941000	-5.84726300

TS-1a'

B3LYP/SDD-6-31G(d) SCF energy: -4518.335229 a.u.
B3LYP/SDD-6-31G(d) Enthalpy: -4516.544833 a.u.
B3LYP/SDD-6-31G(d) Gibbs free energy: -4516.778987 a.u.
M06/SDD-6-311+G(d,p) SCF energy in solution: -4516.804310 a.u.
M06/SDD-6-311+G(d,p) enthalpy in solution: -4515.013914 a.u.
M06/SDD-6-311+G(d,p) free energy in solution: -4515.248068 a.u.
Three lowest frequencies (cm^{-1}): -572.7360 8.4966 12.3222
Imaginary frequency: -572.7360 cm^{-1}

Cartesian coordinates:

ATOM	X	Y	Z
Cu	0.03061700	0.08233500	-1.67586300
H	-0.18403100	1.41707100	-2.52906600
C	0.30846700	-1.27247800	-3.26082600
C	0.35995200	0.04782100	-3.72320500
P	-1.75155400	-0.32789700	-0.25235000
C	-1.23120300	-1.28573500	1.25564300
C	-3.12757400	-1.34340500	-0.96830700

C	-2.64507200	1.14946500	0.40094200
C	-0.29173800	-0.75140300	2.19618400
C	-1.70536500	-2.59597000	1.42012700
C	-4.46953600	-1.14083100	-0.65129100
C	-2.80135200	-2.37185800	-1.86415100
C	-2.61592400	2.30770900	-0.37183800
C	-3.37989600	1.15485500	1.59467900
C	0.04914400	-1.59612100	3.24534200
C	0.26967600	0.63713900	2.25425100
C	-1.31724700	-3.43100500	2.48105900
H	-2.41566000	-2.98985600	0.70393800
C	-5.50865700	-1.87573200	-1.24724600
H	-4.72210400	-0.38223400	0.07837800
C	-3.78212700	-3.13390100	-2.50812800
H	-1.75364500	-2.54522000	-2.07664600
C	-3.35947400	3.45461900	-0.04486400
H	-1.97835200	2.30888600	-1.24986200
C	-4.17728500	2.24418500	1.96341300
H	-3.32940000	0.28386600	2.23559400
C	-0.43589000	-2.89257100	3.39137600
O	0.91033700	-1.32228300	4.28927200
C	-0.08946700	1.40900500	3.35139900
C	1.25068700	1.21883100	1.38760700
H	-1.70618900	-4.43804300	2.58521000
C	-5.13814300	-2.78822900	-2.26038700
C	-4.22517300	3.34820200	1.06649900
O	0.10367800	-3.46865100	4.51701300
C	0.69892300	-2.37970400	5.22639200
C	0.41503200	2.68073500	3.60779500
O	-0.98573300	1.07564300	4.34674200
C	1.75194300	2.49818100	1.66762000
P	1.79395400	0.33112400	-0.15414000
H	1.65715700	-2.69504200	5.64126600
H	0.01109800	-2.03701100	6.01434700
C	1.34389400	3.26150100	2.77438400
O	-0.15363200	3.18579900	4.75346600
C	-0.79288100	2.06201500	5.36270200
H	2.50227900	2.92314000	1.01305900
C	3.15496100	1.38884500	-0.83629500
C	2.69081400	-1.15558100	0.46940500
H	1.75253900	4.24705900	2.96902000
H	-0.14154200	1.65239900	6.14951200
H	-1.76120000	2.36595600	5.76262100
C	4.51049100	1.05122400	-0.74506700
C	2.81147700	2.57177700	-1.49614900
C	2.60394900	-2.32423500	-0.28352700

C	3.45407900	-1.16747300	1.64449700
C	5.50874700	1.79863600	-1.38169000
H	4.78577600	0.17346800	-0.17896400
C	3.76571000	3.41343200	-2.09137000
H	1.76251000	2.84511700	-1.54449500
C	3.32301600	-3.48828600	0.03961100
H	1.93987000	-2.32169900	-1.14099400
C	4.21867200	-2.27821000	2.01480000
H	3.44805100	-0.28536200	2.27175700
C	5.09529900	2.93182800	-2.13033200
C	4.21727600	-3.39201500	1.12912400
C	-4.89608100	2.26491100	3.33826600
C	-4.38843900	3.48558100	4.14652700
H	-4.63683900	4.42378500	3.64599100
H	-4.84707300	3.49502400	5.14380400
H	-3.30002300	3.44486900	4.27084400
C	-6.43672100	2.34198400	3.21437300
H	-6.89222900	2.19676000	4.20184000
H	-6.76924200	3.30970300	2.83924900
H	-6.82245600	1.55541200	2.55465200
C	-4.58016700	0.99639100	4.16090200
H	-4.97737300	0.08944900	3.68947900
H	-3.50573300	0.85840600	4.31469900
H	-5.05486100	1.08352200	5.14514300
C	-3.11279600	4.72152500	-0.91198700
C	-3.71811100	4.52367500	-2.32242100
H	-4.80657200	4.40165900	-2.28407400
H	-3.50146000	5.39470100	-2.95350600
H	-3.30142300	3.63856000	-2.81515300
C	-1.57800800	4.91450800	-1.06362700
H	-1.10217100	5.03171800	-0.08323800
H	-1.09175900	4.08119600	-1.57748400
H	-1.38002000	5.82088200	-1.64801800
C	-3.63732500	6.04737800	-0.31350000
H	-4.72410100	6.13274800	-0.32604800
H	-3.30036900	6.18672300	0.71784400
H	-3.24146900	6.87662900	-0.91246500
C	3.26913200	4.80354300	-2.58479800
C	2.33031900	4.64017600	-3.80307800
H	2.85576300	4.20654900	-4.66167700
H	1.47811300	3.99196000	-3.57421200
H	1.93789100	5.61750500	-4.11092800
C	2.46436400	5.45883500	-1.42781500
H	1.59708900	4.86876700	-1.12105900
H	3.10083400	5.60805500	-0.54753600
H	2.09595100	6.44110500	-1.74647700

C	4.37657700	5.82306300	-2.93805600
H	3.90656000	6.80442300	-3.07644400
H	5.11678700	5.91390800	-2.13830600
H	4.90605500	5.58941800	-3.86232400
C	7.00342200	1.43355300	-1.18633000
C	7.74875600	2.64597000	-0.57453100
H	8.80629200	2.39731600	-0.41919000
H	7.69311700	3.51801800	-1.22889800
H	7.32072000	2.91385300	0.39870000
C	7.69165600	1.02446500	-2.51076900
H	7.12465600	0.24088000	-3.02759400
H	7.81077200	1.87363600	-3.18379700
H	8.69270000	0.62760600	-2.30058100
C	7.17639500	0.25056200	-0.20824200
H	6.73681600	0.45859300	0.77344700
H	6.73341400	-0.67565000	-0.59237700
H	8.24619200	0.06693100	-0.05793600
C	3.01903300	-4.76109400	-0.80010800
C	1.47594500	-4.91766400	-0.90206500
H	1.02550600	-5.00019200	0.09349100
H	0.99363300	-4.08454900	-1.41921000
H	1.23719500	-5.83047900	-1.46052900
C	3.52935600	-6.09091300	-0.19798600
H	4.61330000	-6.20139000	-0.23823000
H	3.21693200	-6.20977600	0.84350900
H	3.09865500	-6.91795500	-0.77549500
C	3.58872100	-4.60110400	-2.22981400
H	4.68107500	-4.51194200	-2.22441500
H	3.32723700	-5.47287300	-2.84236000
H	3.18625400	-3.70984400	-2.72385400
C	4.95368400	-2.30794400	3.38061700
C	4.46254100	-3.53540700	4.18858100
H	4.71832600	-4.47080100	3.68743700
H	4.92289600	-3.53926800	5.18488000
H	3.37416100	-3.50492700	4.31473600
C	4.63592000	-1.04825900	4.21647000
H	5.02719800	-0.13454600	3.75380100
H	3.56017300	-0.91898700	4.37357300
H	5.11261800	-1.14292700	5.19891200
C	6.49213500	-2.37575500	3.23392000
H	6.96231900	-2.24904700	4.21713400
H	6.82267300	-3.33485900	2.83444400
H	6.86454300	-1.57572100	2.58307200
C	-6.94253100	-1.63561900	-0.69335800
C	-6.88658300	-1.72171300	0.85748500
H	-6.53686900	-2.70885000	1.18047400

H	-6.23001800	-0.97046700	1.30468300
H	-7.89025000	-1.56648000	1.27078700
C	-7.43182000	-0.22153700	-1.08799200
H	-6.74929300	0.55526200	-0.72582700
H	-7.51094100	-0.11099900	-2.17540900
H	-8.42314900	-0.02849000	-0.65870100
C	-8.00686000	-2.67298800	-1.12042600
H	-8.91103000	-2.50493900	-0.52238600
H	-8.29638900	-2.59325200	-2.16853600
H	-7.66960900	-3.69763800	-0.94117800
C	-3.38040300	-4.34219600	-3.39327800
C	-1.85722500	-4.59249200	-3.34404600
H	-1.28472700	-3.76077900	-3.76765500
H	-1.50272000	-4.76656100	-2.32197100
H	-1.62606700	-5.48947600	-3.93010500
C	-3.75561900	-4.14320100	-4.88153200
H	-4.83393000	-4.18296300	-5.03952700
H	-3.37620500	-3.18747900	-5.26186400
H	-3.30612300	-4.94228900	-5.48398100
C	-4.07277500	-5.61973000	-2.85591500
H	-3.76466400	-5.82292400	-1.82323200
H	-5.16051300	-5.52827700	-2.88076700
H	-3.78524300	-6.48496600	-3.46666000
O	-5.13787400	4.35674400	1.34205500
O	-6.11141400	-3.39595700	-3.04108100
O	6.05008400	3.58440600	-2.89675200
O	5.11113200	-4.41961400	1.39395400
C	-6.60800400	-2.56380400	-4.08980500
H	-7.31576800	-3.17332100	-4.65787400
H	-7.12593900	-1.68120400	-3.69810800
H	-5.80019600	-2.23017100	-4.75109200
C	-6.30947500	4.31548000	0.52755200
H	-6.97071300	5.10319500	0.89843100
H	-6.08058300	4.50556900	-0.52656800
H	-6.81657400	3.34656500	0.60732300
C	6.26729500	-4.41007700	0.55672600
H	6.91663200	-5.21151300	0.91895500
H	6.01302300	-4.60009100	-0.49183200
H	6.79828600	-3.45289700	0.62148800
C	5.96052100	3.29856900	-4.29318800
H	5.00421600	3.62567900	-4.71517300
H	6.77383500	3.84917600	-4.77310600
H	6.07977800	2.22643800	-4.48879700
C	-0.77479100	-0.79901500	-4.21024300
C	1.34235400	0.85639300	-4.51199300
H	2.26471900	1.03260500	-3.94963400

H	1.60080600	0.30194500	-5.42727500
H	0.93041300	1.82737800	-4.80775700
H	1.04274900	-2.06098000	-3.39106200
H	-0.73381600	-1.08454800	-5.26865800
H	-1.79164000	-0.64195200	-3.84749900

TS-1b'

B3LYP/SDD-6-31G(d) SCF energy: -4557.663502 a.u.
B3LYP/SDD-6-31G(d) Enthalpy: -4555.842368 a.u.
B3LYP/SDD-6-31G(d) Gibbs free energy: -4556.078787 a.u.
M06/SDD-6-311+G(d,p) SCF energy in solution: -4556.110096 a.u.
M06/SDD-6-311+G(d,p) enthalpy in solution: -4554.288962 a.u.
M06/SDD-6-311+G(d,p) free energy in solution: -4554.525382 a.u.
Three lowest frequencies (cm^{-1}): -753.1673 8.9276 11.8897
Imaginary frequency: -753.1673 cm^{-1}

Cartesian coordinates:

ATOM	X	Y	Z
Cu	-0.00356400	0.03119000	-1.59636300
H	-0.14829700	1.38179300	-2.51004400
C	0.37542100	-1.12778200	-3.36309400
C	0.29283000	0.25992600	-3.73553300
P	-1.76181500	-0.36315900	-0.17838600
C	-1.24217200	-1.28629000	1.35627100
C	-3.14764400	-1.39138000	-0.86155200
C	-2.65183000	1.12591300	0.45779000
C	-0.27058900	-0.74025200	2.25649000
C	-1.74966100	-2.57316300	1.58981200
C	-4.48369300	-1.00535100	-0.78922100
C	-2.84276900	-2.60467900	-1.49806100
C	-2.59189600	2.29072500	-0.30238100
C	-3.40813200	1.12918700	1.63802700
C	0.08815600	-1.56010500	3.31968500
C	0.28983100	0.64996500	2.28543700
C	-1.35213100	-3.37978900	2.66891300
H	-2.49895800	-2.97238400	0.91903800
C	-5.52314000	-1.74445800	-1.38267200
H	-4.73205000	-0.09889300	-0.25378800
C	-3.81993500	-3.38997400	-2.11665900
H	-1.80845900	-2.92551600	-1.51334400
C	-3.32661300	3.44473600	0.02221500
H	-1.93710000	2.29078400	-1.16836100
C	-4.18868400	2.22920500	2.00919500
H	-3.38742300	0.24833700	2.26678600
C	-0.42148300	-2.83832200	3.52616000
O	0.98421600	-1.26926200	4.32886800
C	-0.06740400	1.42953900	3.37835700

C	1.26739000	1.22443000	1.41094800
H	-1.77028100	-4.36819300	2.82533400
C	-5.14607900	-2.87629200	-2.13695400
C	-4.20831500	3.34148000	1.12089700
O	0.13859700	-3.38967800	4.65328100
C	0.79481600	-2.29785500	5.30223000
C	0.44403300	2.69870200	3.63150700
O	-0.96440800	1.10334200	4.37600000
C	1.78011400	2.49914300	1.69251400
P	1.78723200	0.33084600	-0.13911100
H	1.76516500	-2.62663300	5.67743700
H	0.15696800	-1.91883100	6.11504800
C	1.37995500	3.26786400	2.79836900
O	-0.12104700	3.21063100	4.77581400
C	-0.76771700	2.09273100	5.38807200
H	2.53478000	2.91826200	1.04020600
C	3.13357000	1.39630700	-0.84405500
C	2.71789100	-1.13567300	0.48877800
H	1.79957900	4.24911200	2.99152400
H	-0.12014700	1.68297800	6.17802600
H	-1.73497700	2.40362400	5.78533000
C	4.47347400	0.99301500	-0.88139500
C	2.80349300	2.63846200	-1.39443500
C	2.64459800	-2.31555600	-0.24754000
C	3.50121300	-1.11488700	1.65041900
C	5.46001100	1.73981800	-1.53680900
H	4.74595300	0.06551900	-0.40045200
C	3.75556600	3.48271200	-1.98944700
H	1.76771400	2.95875200	-1.35447200
C	3.39443700	-3.45955800	0.07916100
H	1.96984400	-2.33688000	-1.09675700
C	4.29484400	-2.20378300	2.02354800
H	3.48914800	-0.22313800	2.26367000
C	5.05408900	2.94730500	-2.16160500
C	4.30306900	-3.32983700	1.15336200
C	-4.91447900	2.25372200	3.38045400
C	-4.39813800	3.46752800	4.19361400
H	-4.63777800	4.40969900	3.69644000
H	-4.85794000	3.47676100	5.19029900
H	-3.31032800	3.41682800	4.31911200
C	-6.45362400	2.34654100	3.25118000
H	-6.91394700	2.20920600	4.23757400
H	-6.77452100	3.31698100	2.87250700
H	-6.84629100	1.56254000	2.59253700
C	-4.61129600	0.98096400	4.20156300
H	-5.01507200	0.07813900	3.72829100

H	-3.53782600	0.83482900	4.35674700
H	-5.08630700	1.07083700	5.18540200
C	-3.05350800	4.71421300	-0.83300300
C	-3.63967100	4.53035800	-2.25332400
H	-4.72983800	4.41939500	-2.23144600
H	-3.40499500	5.40248300	-2.87635900
H	-3.22465300	3.64376300	-2.74478800
C	-1.51459000	4.89176600	-0.96018200
H	-1.05260200	4.99960800	0.02794400
H	-1.02958800	4.05522500	-1.47029300
H	-1.29808900	5.79873700	-1.53709200
C	-3.57413000	6.04215300	-0.23583600
H	-4.65983600	6.13790400	-0.26392500
H	-3.25099000	6.17378700	0.80088900
H	-3.16172600	6.87020700	-0.82523100
C	3.30154900	4.93142500	-2.33509500
C	2.30035100	4.92217300	-3.51360900
H	2.75866800	4.53954500	-4.43258000
H	1.42669300	4.29975900	-3.29488800
H	1.94653300	5.94081200	-3.71648800
C	2.58272700	5.51669200	-1.08754800
H	1.69183400	4.95171800	-0.80145800
H	3.25996200	5.54170100	-0.22565100
H	2.26422800	6.54515400	-1.29473500
C	4.44175100	5.92744100	-2.65060300
H	4.01570400	6.93779000	-2.67988200
H	5.21899600	5.91191500	-1.88134600
H	4.91958000	5.75373200	-3.61494500
C	6.94269200	1.28723200	-1.48853400
C	7.79812600	2.40502300	-0.84126100
H	8.84856900	2.09147700	-0.78940900
H	7.74395000	3.33152000	-1.41619600
H	7.45874700	2.61046400	0.18093700
C	7.50687400	0.95519700	-2.89083700
H	6.85982600	0.24614200	-3.42109000
H	7.62557400	1.84819200	-3.50473600
H	8.49630800	0.49180200	-2.79041700
C	7.12238000	0.01805200	-0.62622100
H	6.76881100	0.16126800	0.40067700
H	6.60230600	-0.84922900	-1.04937600
H	8.18892400	-0.22922400	-0.57674700
C	3.10915500	-4.74861200	-0.74192700
C	1.56938100	-4.94245100	-0.82116500
H	1.13395500	-5.02663500	0.18104100
H	1.06239600	-4.12508700	-1.33969600
H	1.34399000	-5.86540500	-1.36828000

C	3.65830700	-6.05955500	-0.13258400
H	4.74373000	-6.14566100	-0.18712500
H	3.36333200	-6.17382800	0.91449400
H	3.23876000	-6.90260800	-0.69498500
C	3.65466400	-4.59113800	-2.18142300
H	4.74396100	-4.47055600	-2.19234800
H	3.41046100	-5.47820800	-2.77901200
H	3.21944100	-3.71889300	-2.68147800
C	5.05253800	-2.19710400	3.37725800
C	4.60130700	-3.42200400	4.21169700
H	4.86216800	-4.35962800	3.71734100
H	5.08328900	-3.40445000	5.19752000
H	3.51558100	-3.40734100	4.36207100
C	4.72095100	-0.93220300	4.19970700
H	5.08541500	-0.01747000	3.71777200
H	3.64520300	-0.82355600	4.37168600
H	5.21441200	-1.00246800	5.17592400
C	6.58954200	-2.23398800	3.20679700
H	7.07217500	-2.08491200	4.18080100
H	6.93436500	-3.19061300	2.81360900
H	6.93444500	-1.43431800	2.54040600
C	-6.97387600	-1.26186000	-1.09370900
C	-7.11876700	-1.05435000	0.43977500
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H	-6.42928800	-0.30478300	0.83704500
H	-8.13717200	-0.71973600	0.67102100
C	-7.22983900	0.09141300	-1.79967200
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H	-8.23346500	0.46243900	-1.55639600
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H	-8.24420200	-2.34489000	-2.55600900
H	-7.92387900	-3.24733800	-1.07160700
C	-3.46358700	-4.79176800	-2.67769100
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H	-4.10460200	-6.85355700	-2.35809500
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O	-6.08301000	-3.54168500	-2.91424000
O	5.98811500	3.61694500	-2.93848400
O	5.22284400	-4.33462000	1.41776700
C	-6.34299400	-2.90534300	-4.16641300
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H	6.10120500	-4.52192100	-0.47844600
H	6.87690400	-3.34207800	0.60676700
C	5.79127100	3.45772100	-4.34405600
H	4.84043500	3.88963100	-4.67403900
H	6.61502800	3.98554300	-4.83185700
H	5.81344400	2.40010200	-4.63171500
C	-1.01735400	0.01925600	-4.50847500
C	-0.87304600	-1.49919800	-4.17890800
H	-1.72219100	-1.95592200	-3.66232300
H	-0.65831600	-2.10152200	-5.07420700
H	-1.90890300	0.52276700	-4.12281200
H	-0.91665100	0.25058800	-5.57689600
C	1.41372600	1.10347000	-4.29131700
H	2.29883600	1.07072300	-3.65015800
H	1.69538600	0.70835300	-5.27980800
H	1.11867000	2.15132900	-4.41242000
H	1.29883200	-1.70264800	-3.30513800

6. References and Notes

(1) "Prudent Practices in the Laboratory [electronic resource]: Handling and Management of Chemical Hazards / Committee on Prudent Practices in the Laboratory: An Update."; Board on Chemical Sciences and Technology, Division of Earth and Life Studies, National Research Council of the National Academies. Washington, D.C.: National Academies Press, 2011.

(2) The cyclobutene and cyclopropene substrates are air-sensitive, and therefore have to be stored in the glovebox. For this reason, the hydroamination reactions are set up in the glovebox.

(3) Cyclopropenes bearing 3-hydrogen polymerize through ene-reaction when in their liquid phase.[4] For this reason, characterization data of compound **12** by ^{13}C NMR was not provided. The purity of **12** was determined by ^{1}H NMR analysis with 1,1,2,2-tetrachloroethane as the internal standard.

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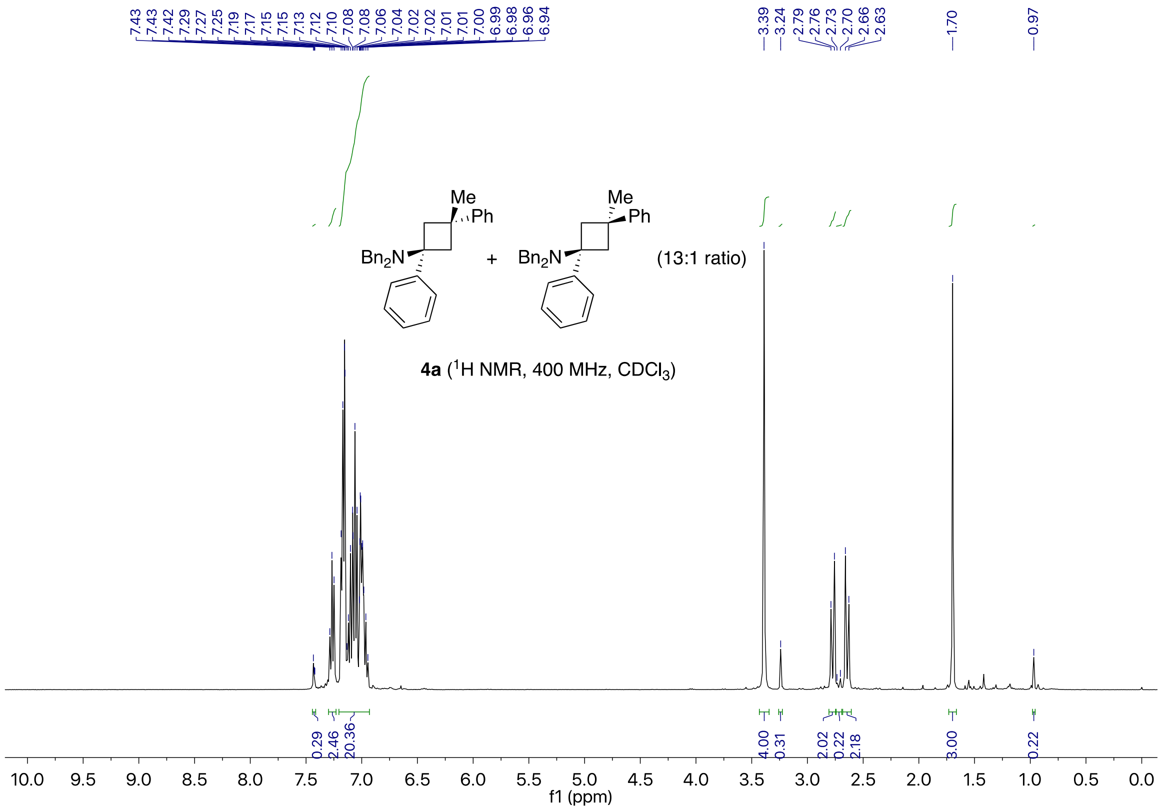
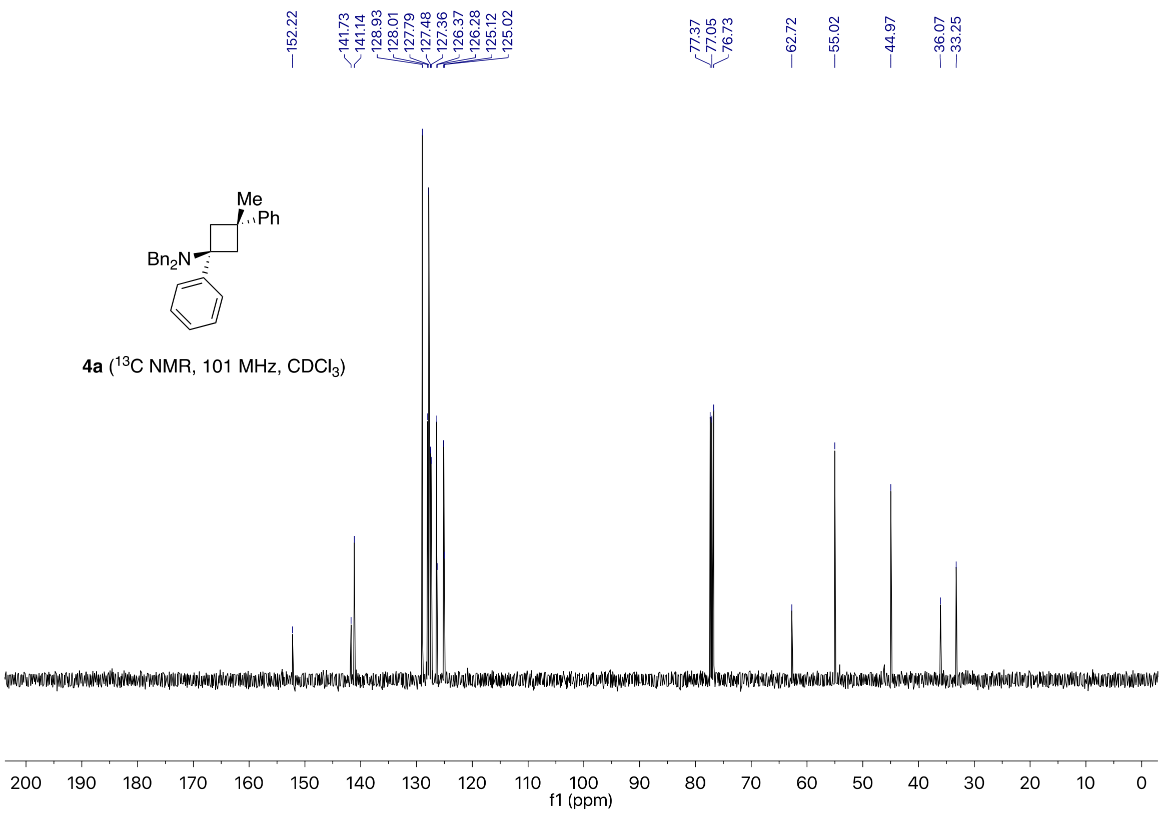
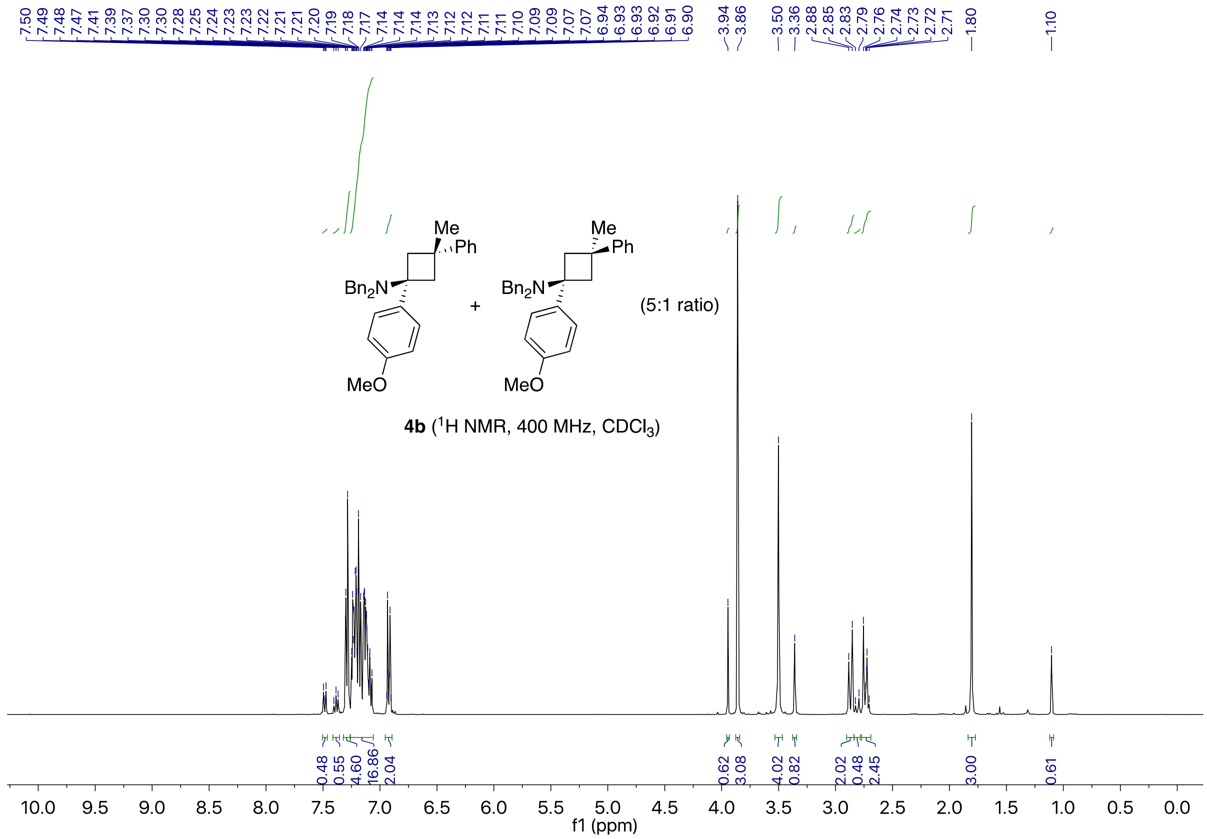
7. Spectroscopic Data



4a (^{1}H NMR, 400 MHz, $CDCl_3$)



4a (^{13}C NMR, 101 MHz, $CDCl_3$)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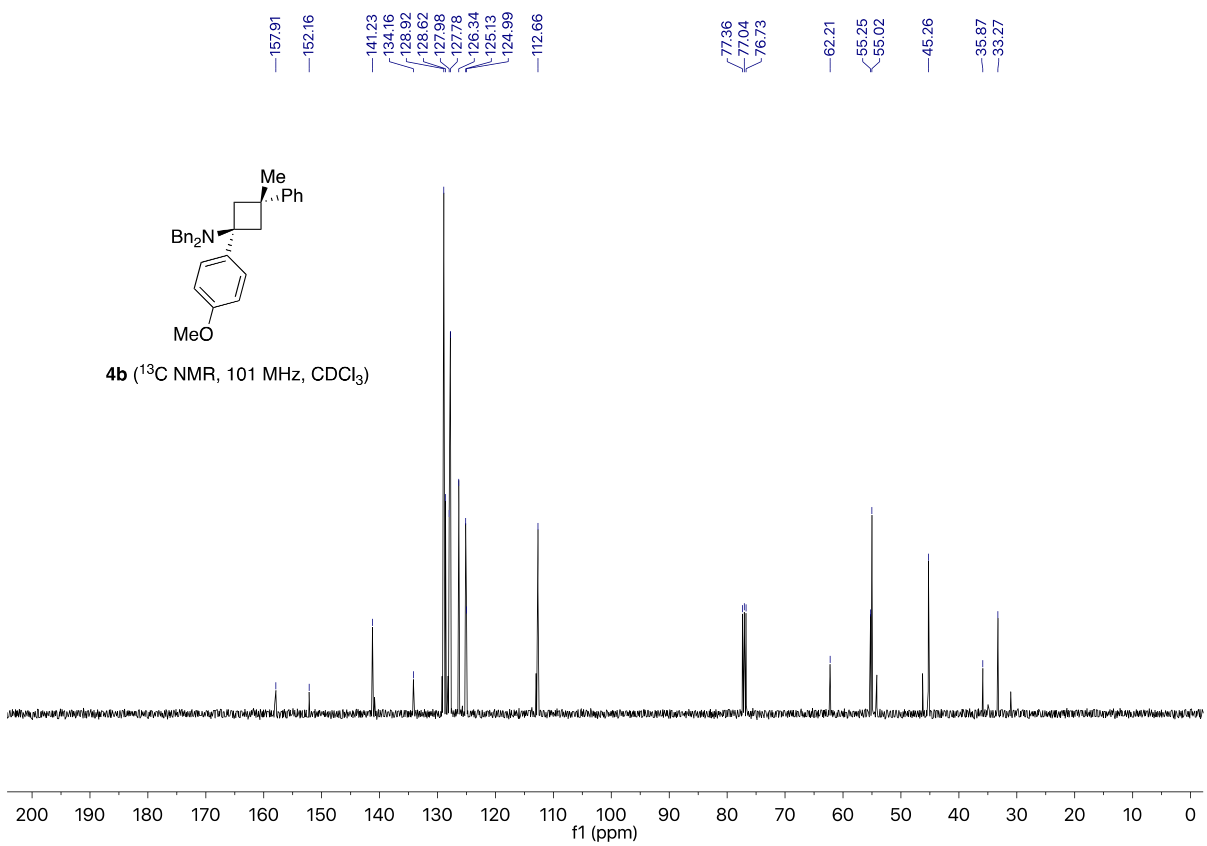
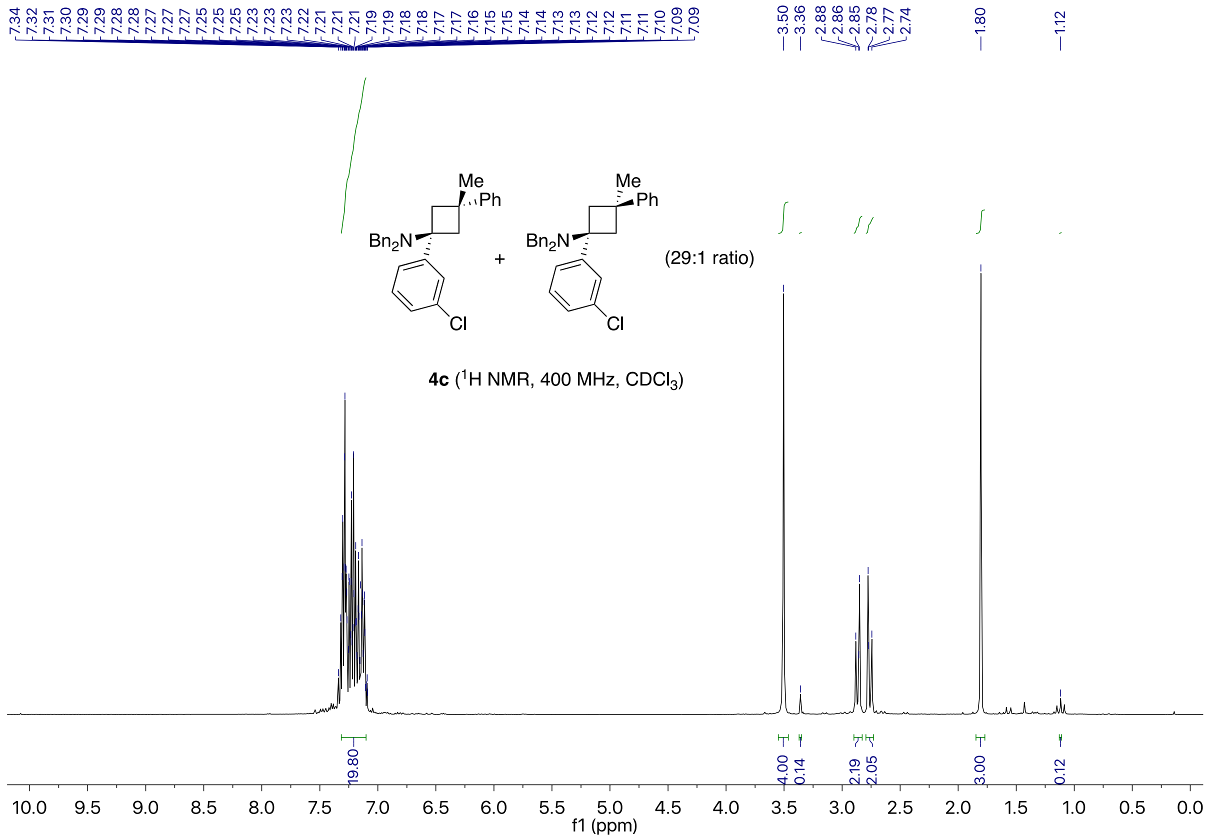
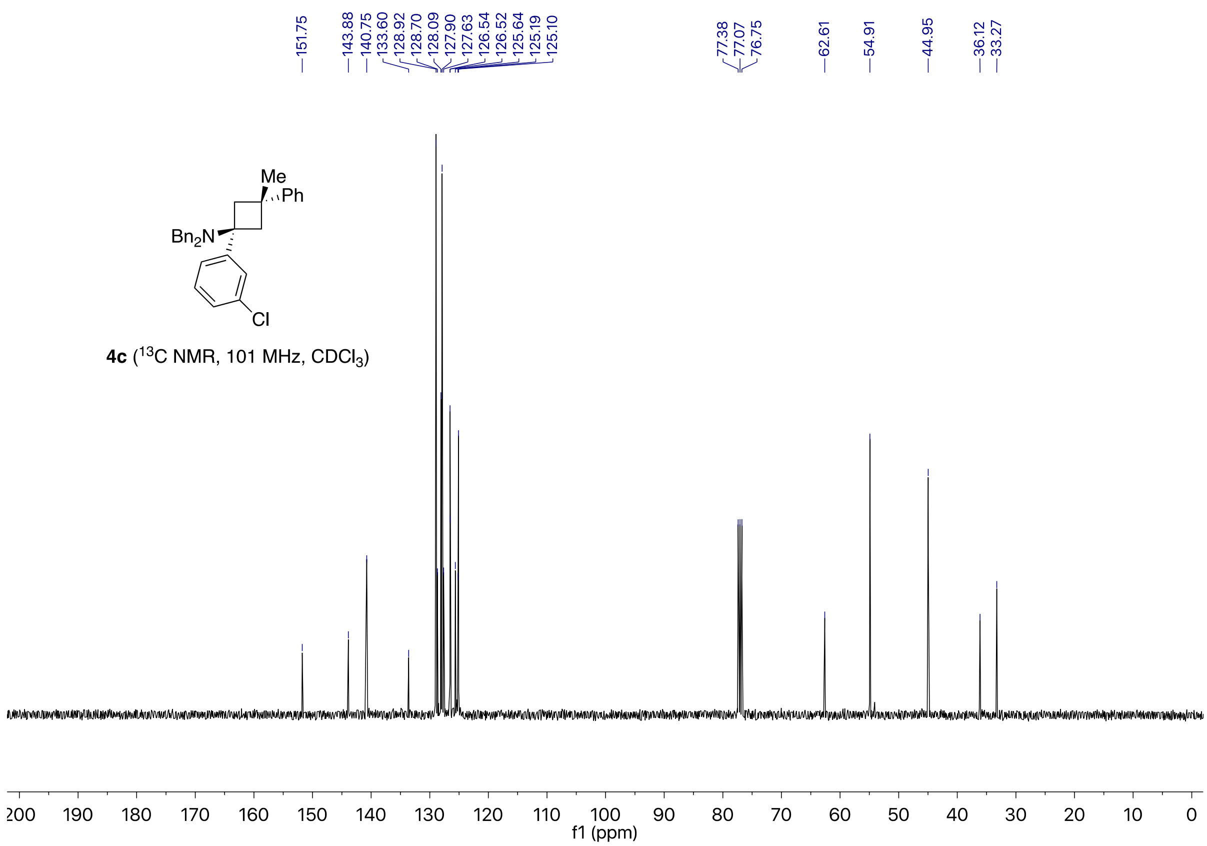
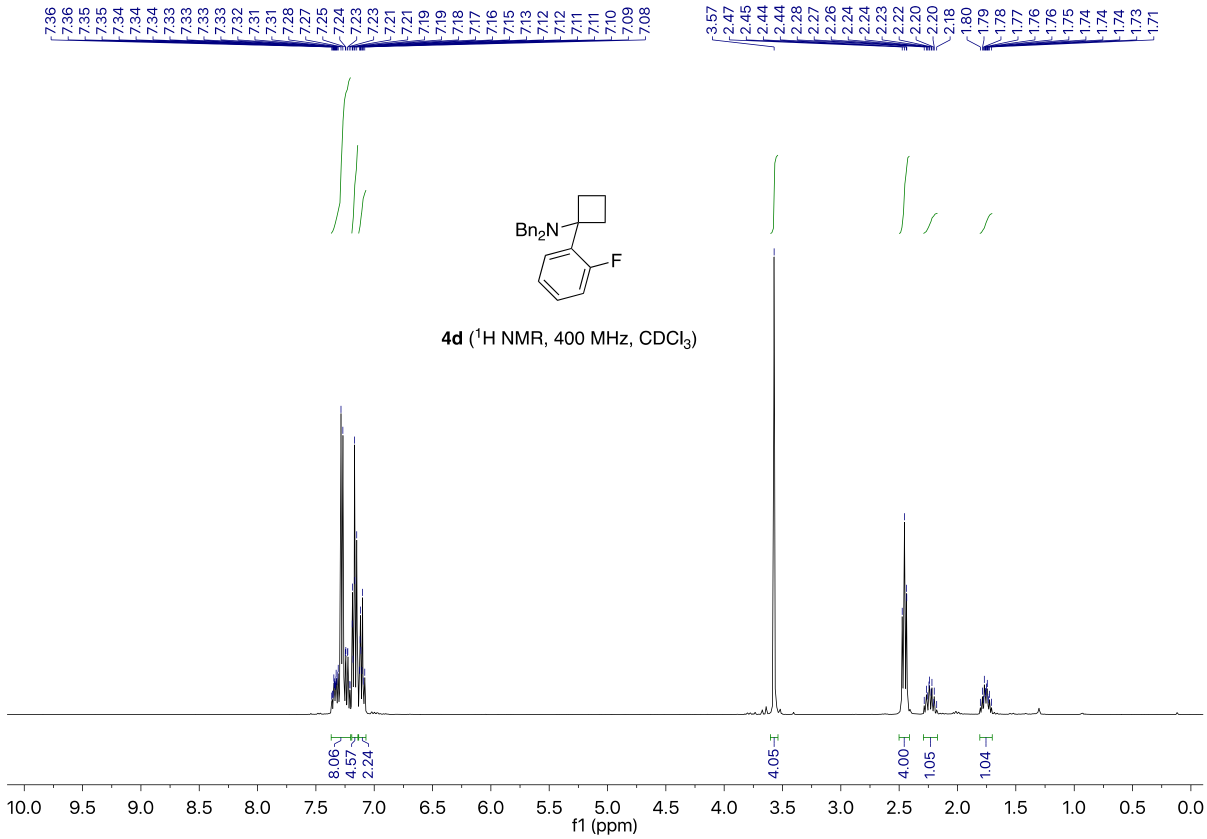
Me
Ph
Bn2N
MeO
+
(5:1 ratio)
4b (^{1}H NMR, 400 MHz, CDCl$_3$)
0.48 0.55 4.60 16.86 2.04 0.62 3.08 4.02 0.82 2.02 0.48 2.45 3.00 0.61
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


157.91 152.16 141.23 134.16 128.92 128.62 127.98 127.78 126.34 125.13 124.99 112.66 77.36 77.04 76.73 62.21 55.25 55.02 45.26 35.87 33.27
Me
Ph
Bn2N
MeO
4b (^{13}C NMR, 101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.34 7.32 7.31 7.30 7.29 7.29 7.28 7.28 7.27 7.27 7.27 7.25 7.25 7.25 7.23 7.23 7.23 7.22 7.21 7.21 7.21 7.19 7.19 7.18 7.18 7.17 7.17 7.16 7.15 7.15 7.14 7.14 7.13 7.13 7.12 7.12 7.11 7.11 7.10 7.09 7.09
3.50 3.36 2.88 2.86 2.85 2.78 2.77 2.74
1.80
1.12
Me
Ph
Bn2N
Cl
+
(29:1 ratio)
4c (1H NMR, 400 MHz, CDCl3)
19.80
4.00 0.14
2.19 2.05
3.00
0.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


151.75
143.88 140.75 133.60 128.92 128.70 128.09 127.90 127.63 126.54 126.52 125.64 125.19 125.10
77.38 77.07 76.75
62.61
54.91
44.95
36.12 33.27
Me
Ph
Bn2N
Cl
4c (13C NMR, 101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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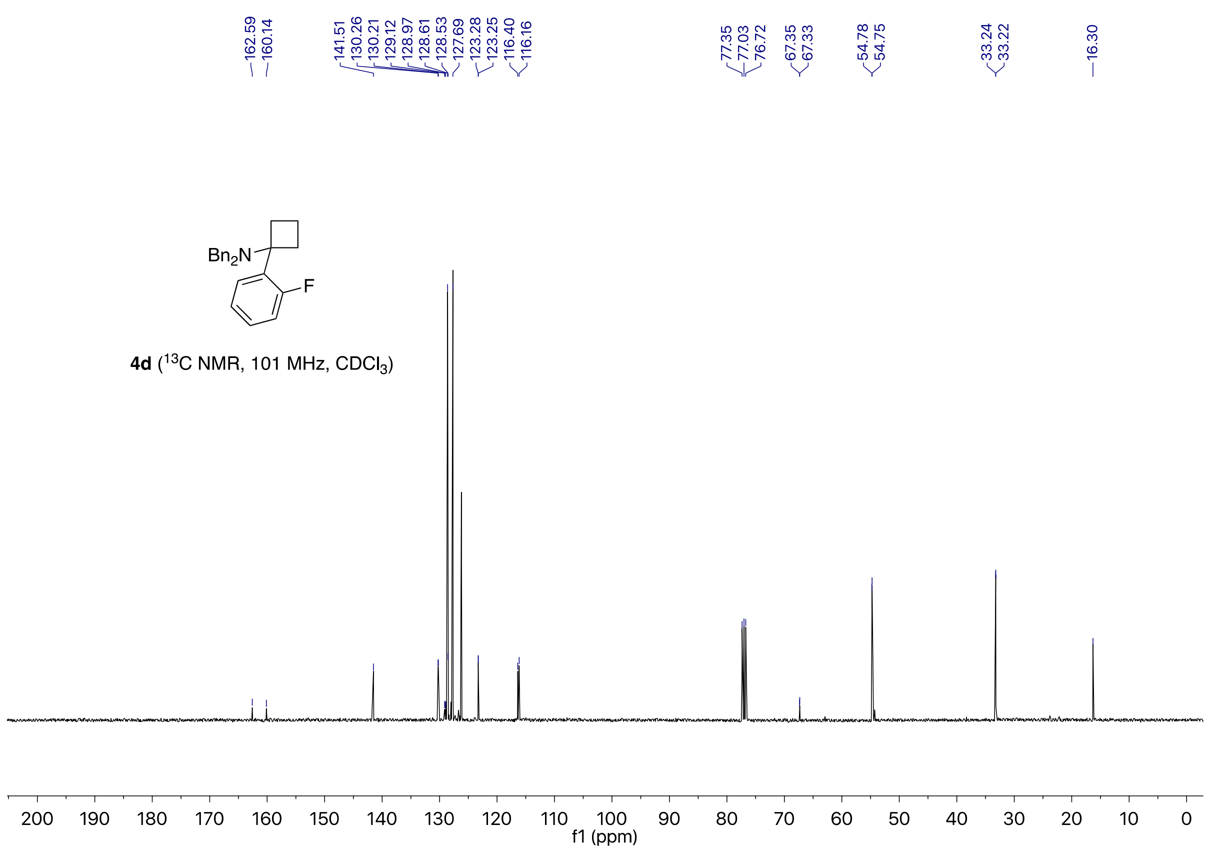
3.57 2.47 2.45 2.44 2.44 2.28 2.27 2.26 2.24 2.24 2.23 2.22 2.22 2.20 2.20 2.18 1.80 1.79 1.78 1.77 1.76 1.76 1.75 1.74 1.74 1.74 1.73 1.71
Bn2N
F
4d (1H NMR, 400 MHz, CDCl3)
8.06 4.57 2.24 4.05 4.00 1.05 1.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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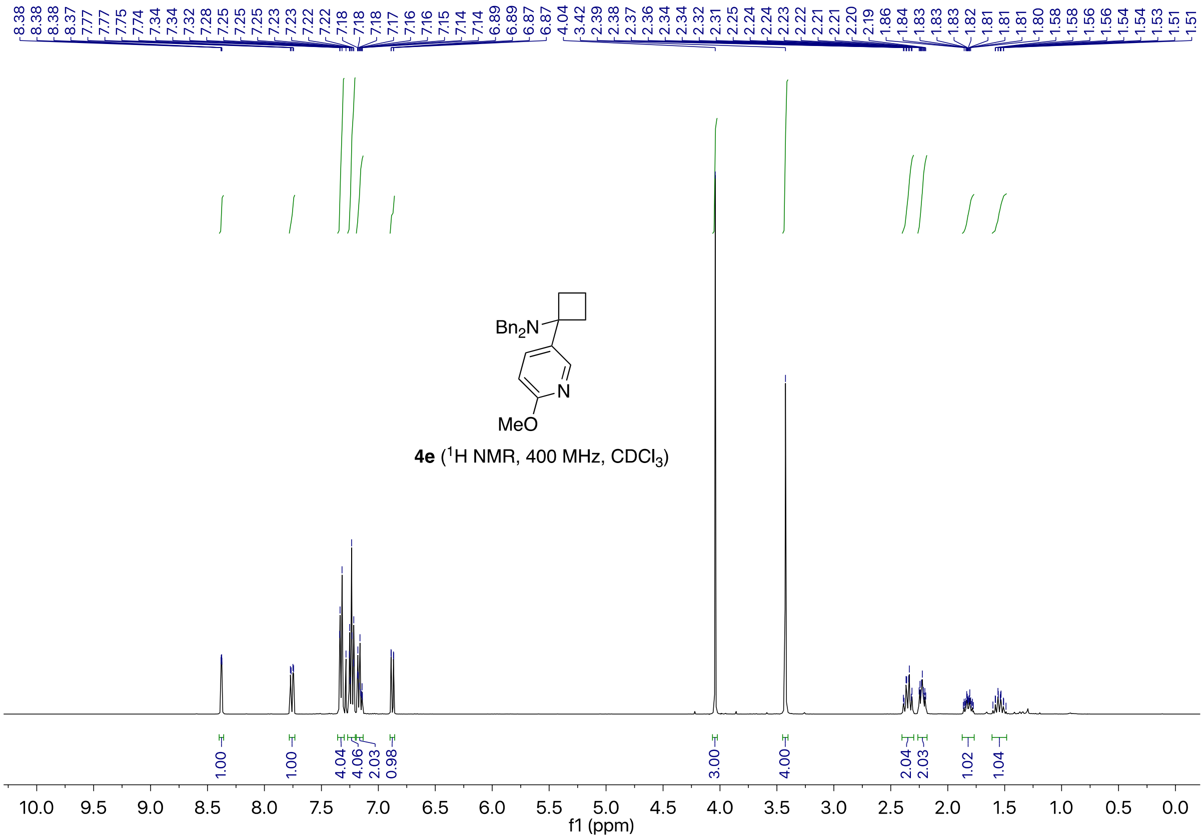
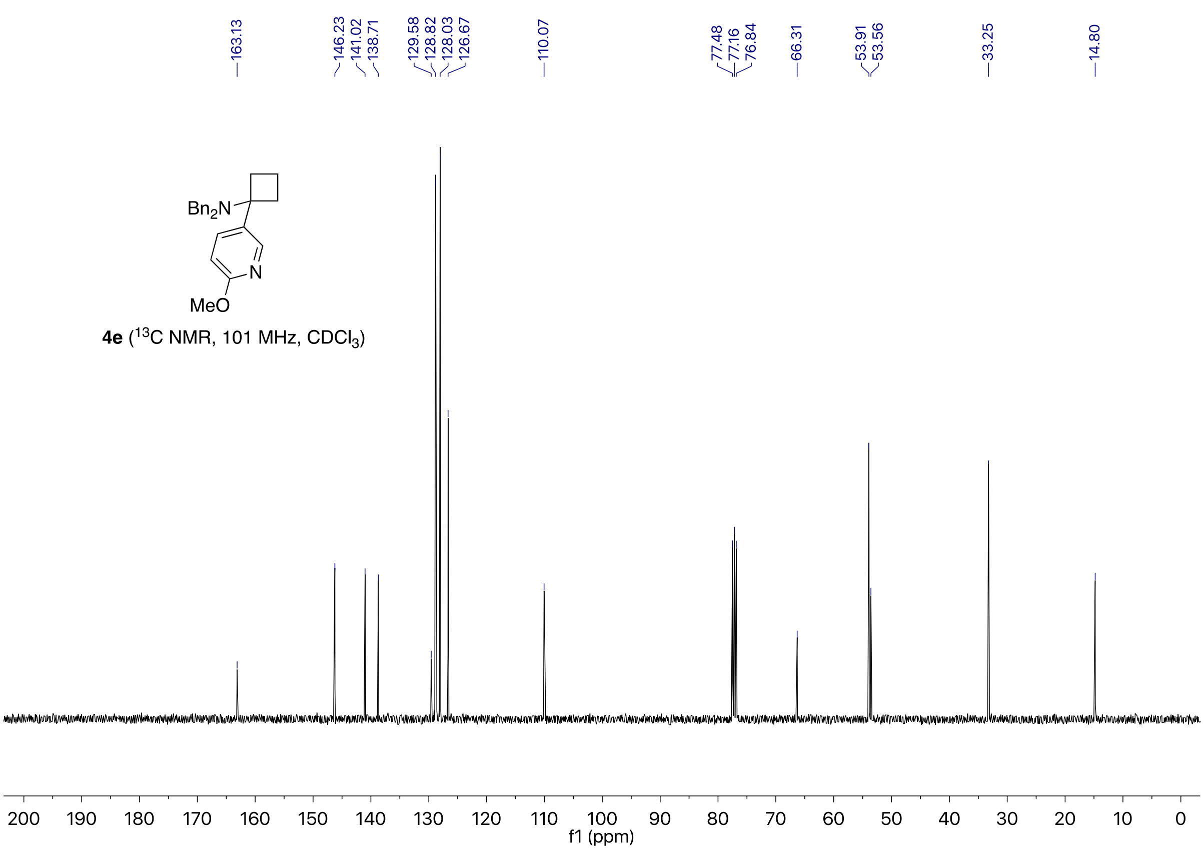
141.51 130.26 130.21 129.12 128.97 128.61 128.53 127.69 123.28 123.25 116.40 116.16
77.35 77.03 76.72 67.35 67.33
54.78 54.75
33.24 33.22
16.30
Bn2N
F
4d (13C NMR, 101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


4e (^{1}H NMR, 400 MHz, CDCl$_3$)
Bn$_2$N
N
MeO
f1 (ppm)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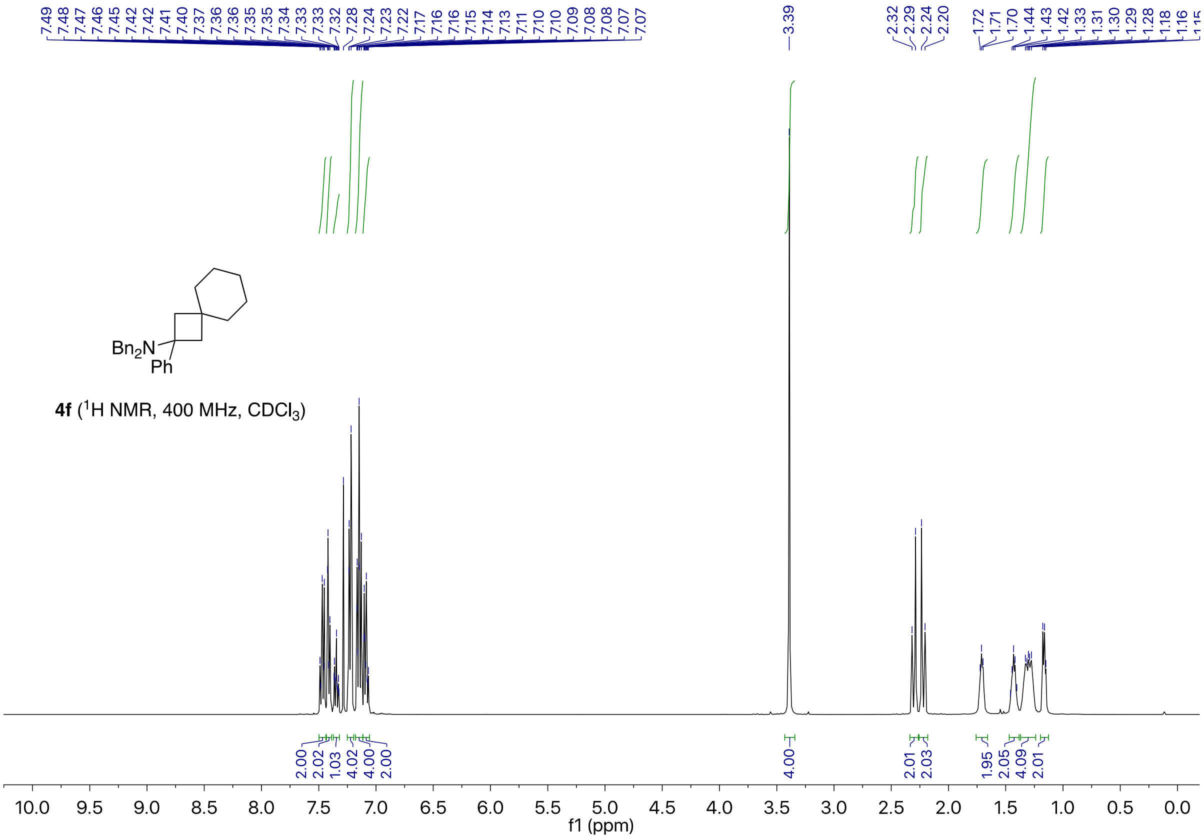
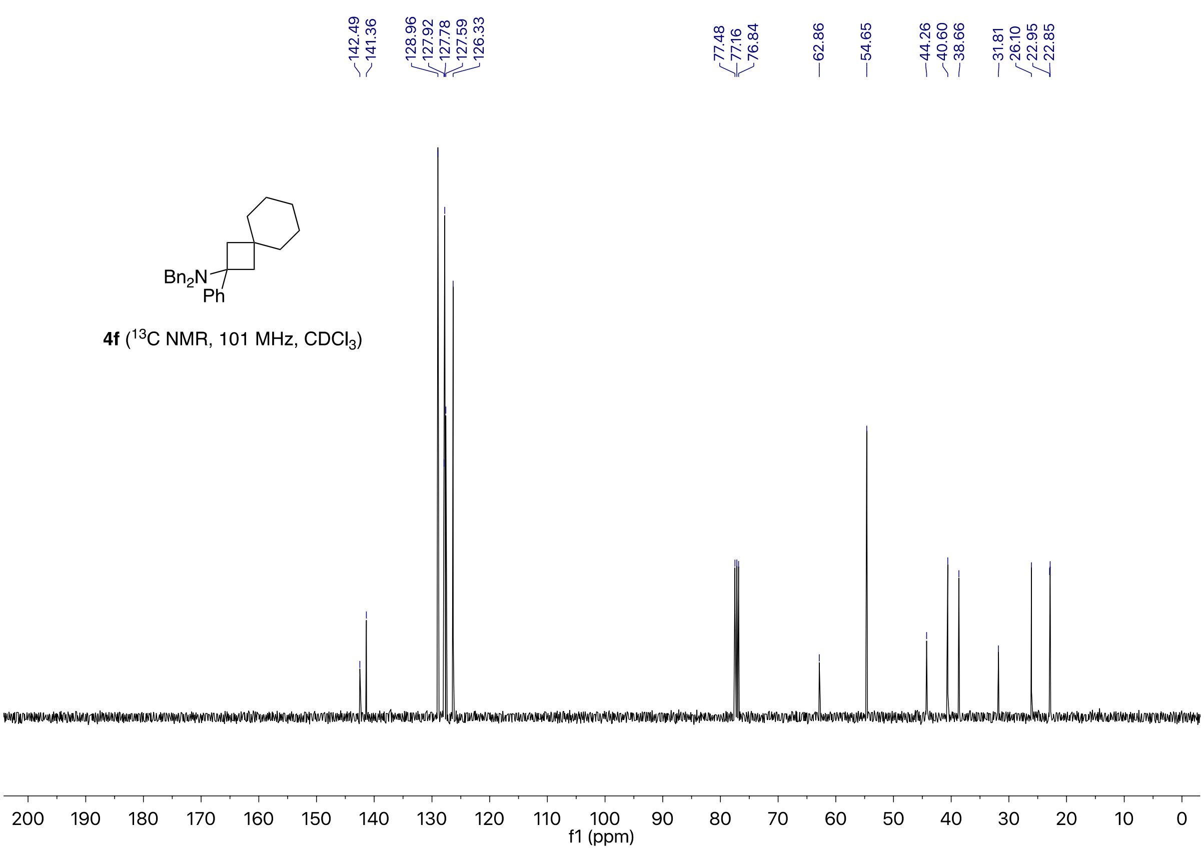
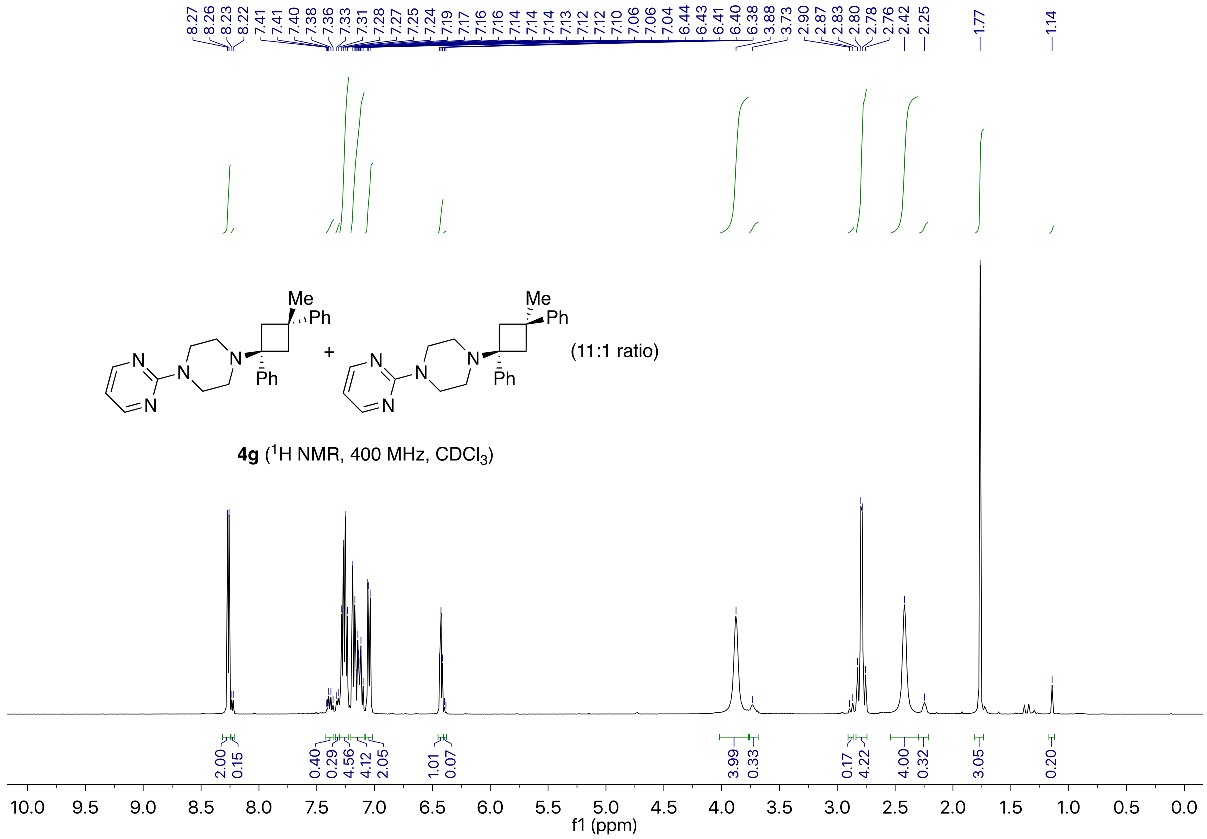
N
MeO
f1 (ppm)



4f (^{1}H NMR, 400 MHz, $CDCl_3$)



4f (^{13}C NMR, 101 MHz, $CDCl_3$)


(11:1 ratio)
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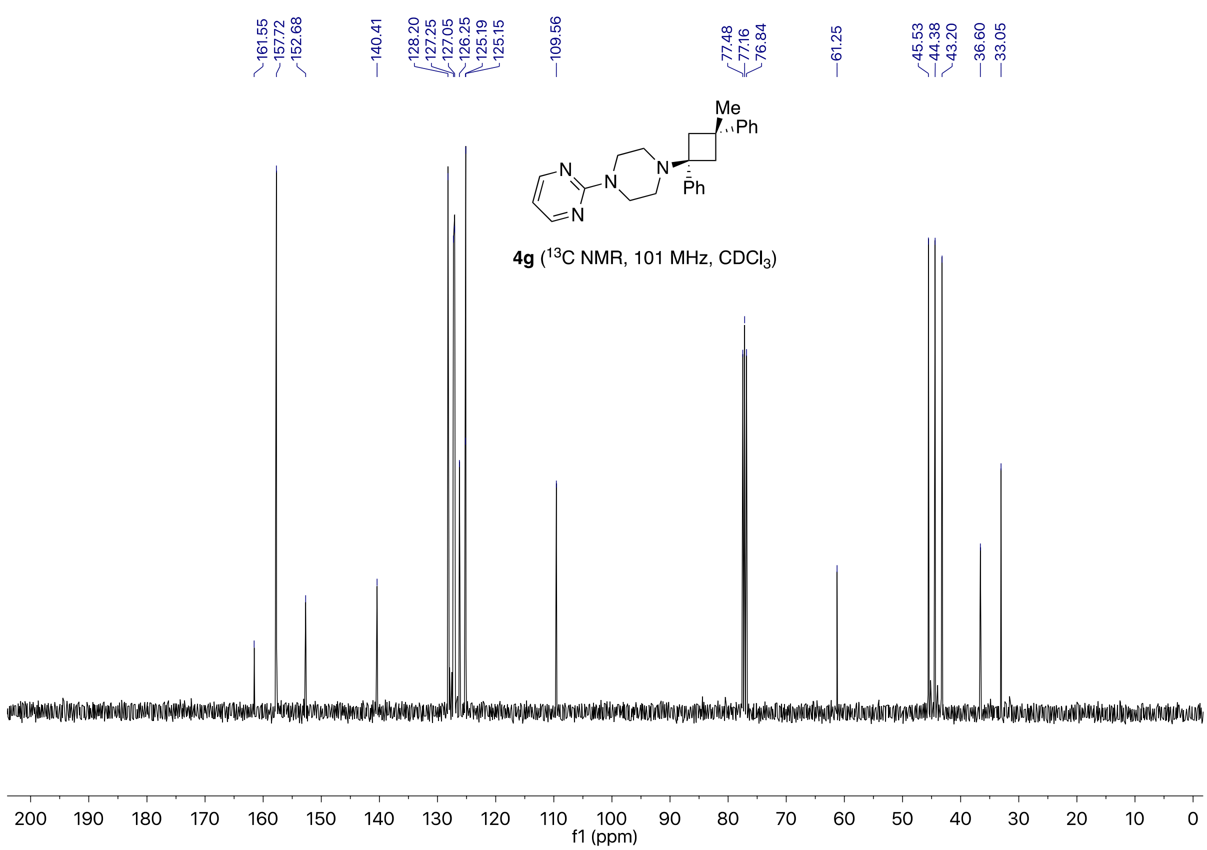
f1 (ppm)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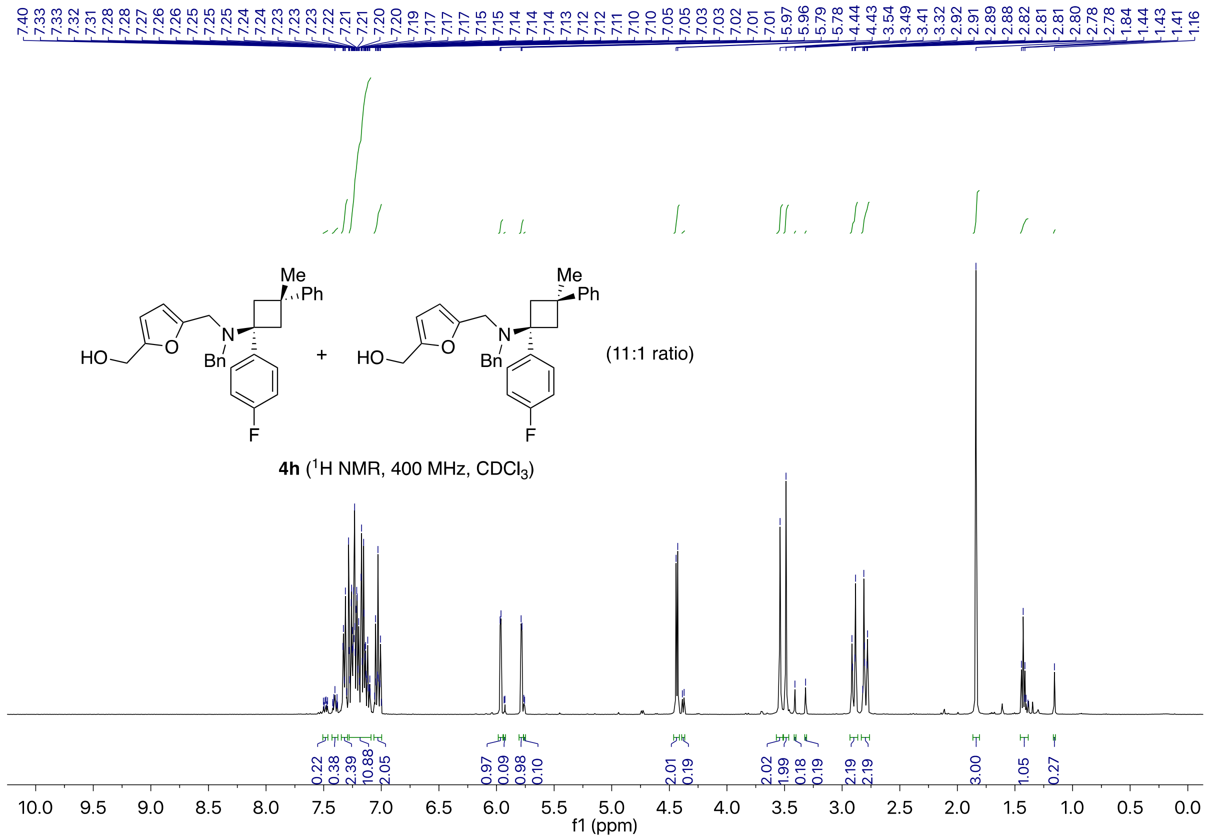
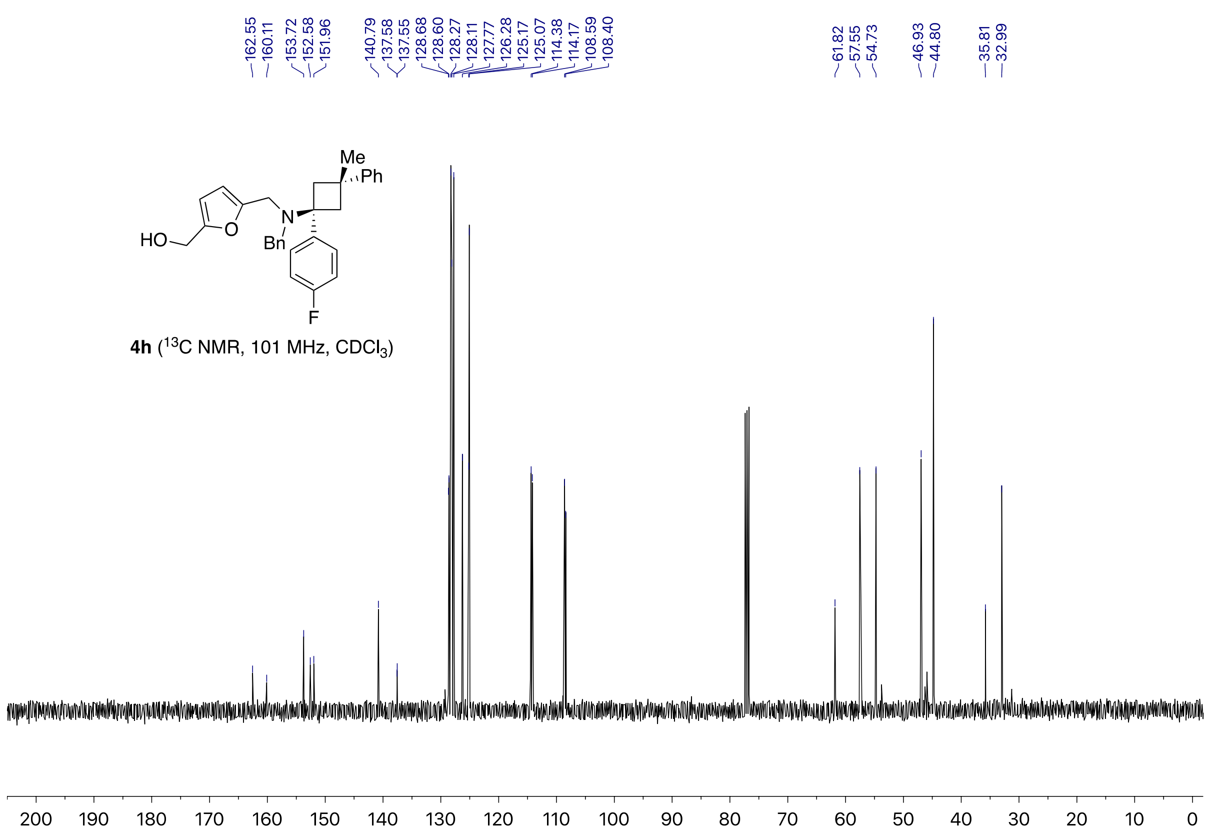
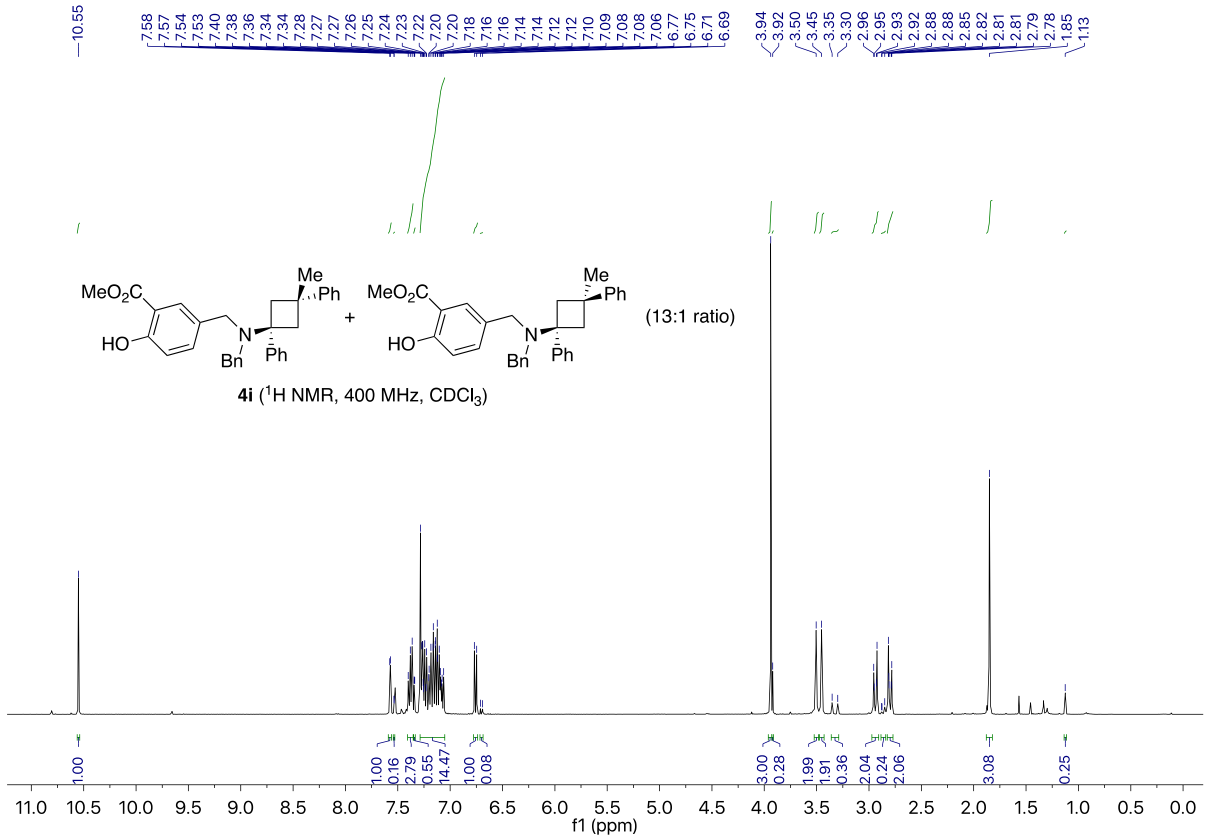
f1 (ppm)



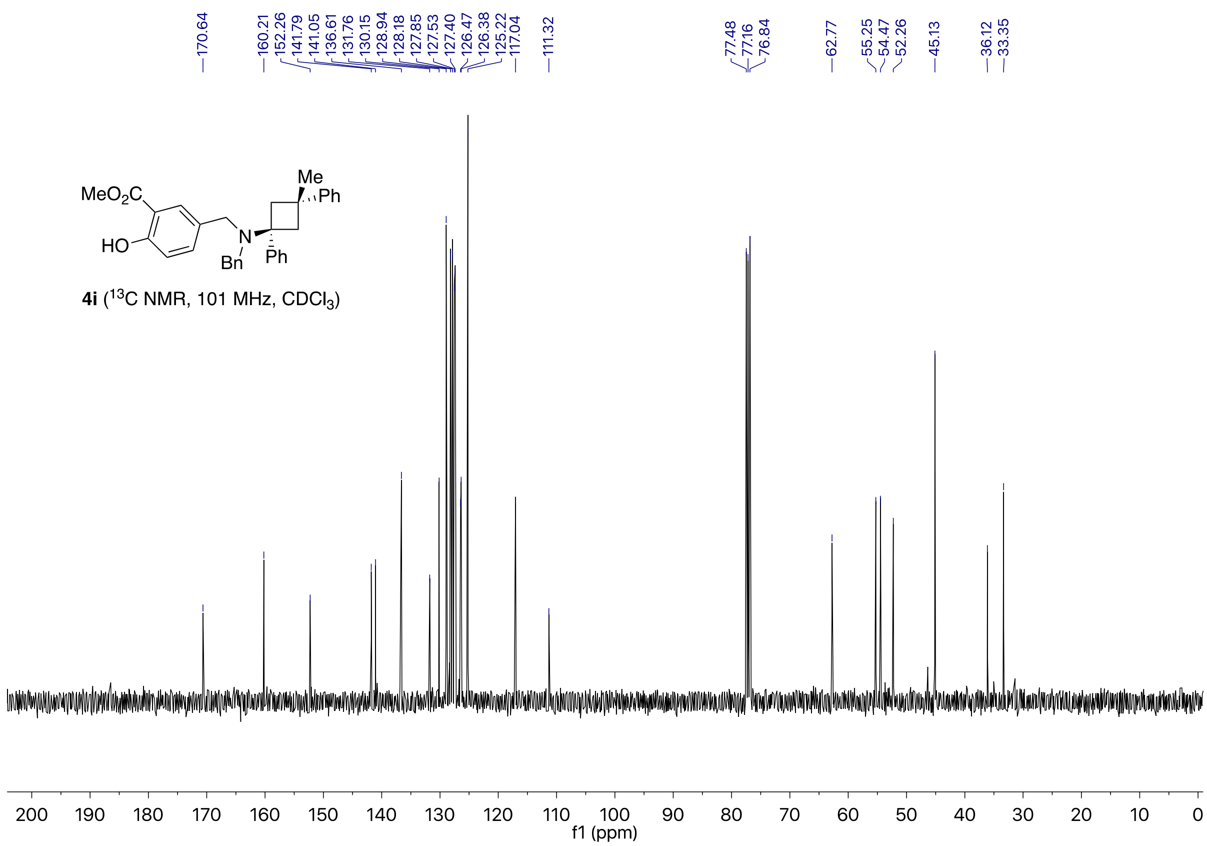
4h (^1H NMR, 400 MHz, $CDCl_3$)



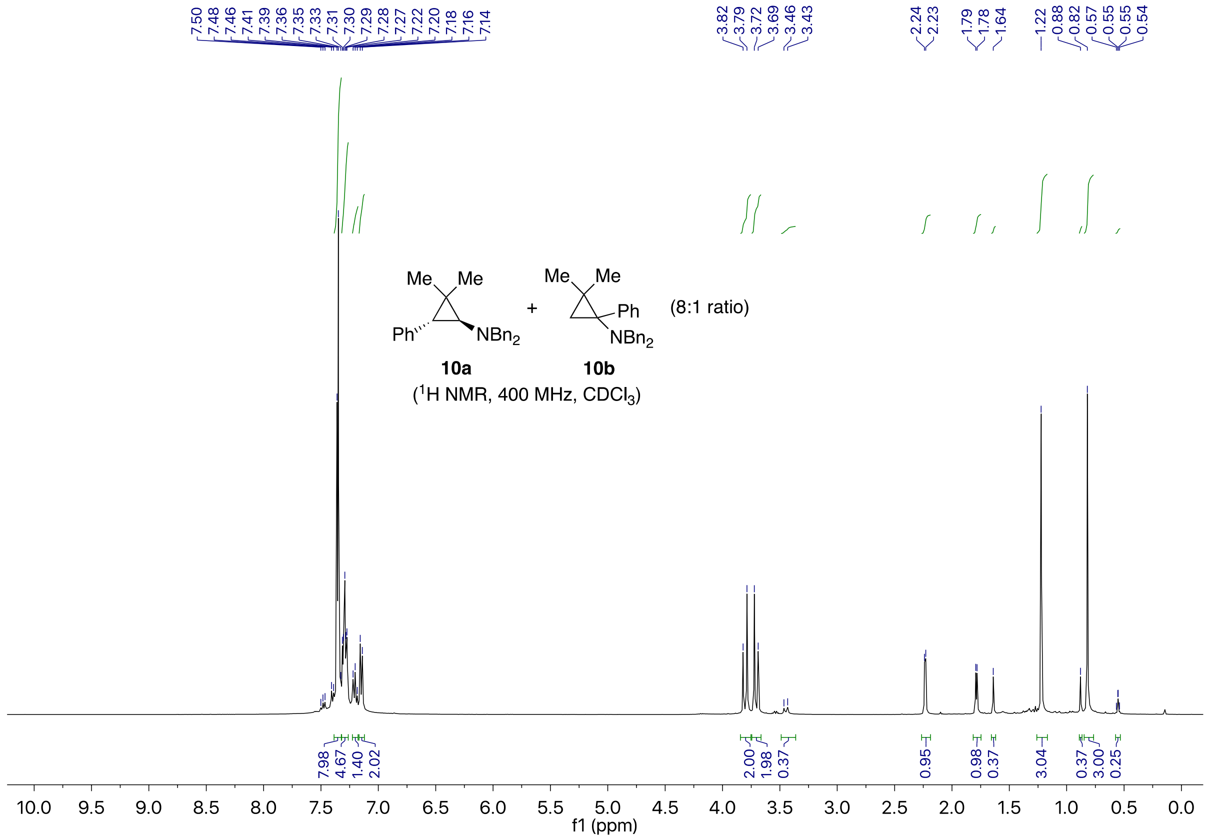
4h (^{13}C NMR, 101 MHz, $CDCl_3$)



4i (^{1}H NMR, 400 MHz, $CDCl_3$)



4i (^{13}C NMR, 101 MHz, $CDCl_3$)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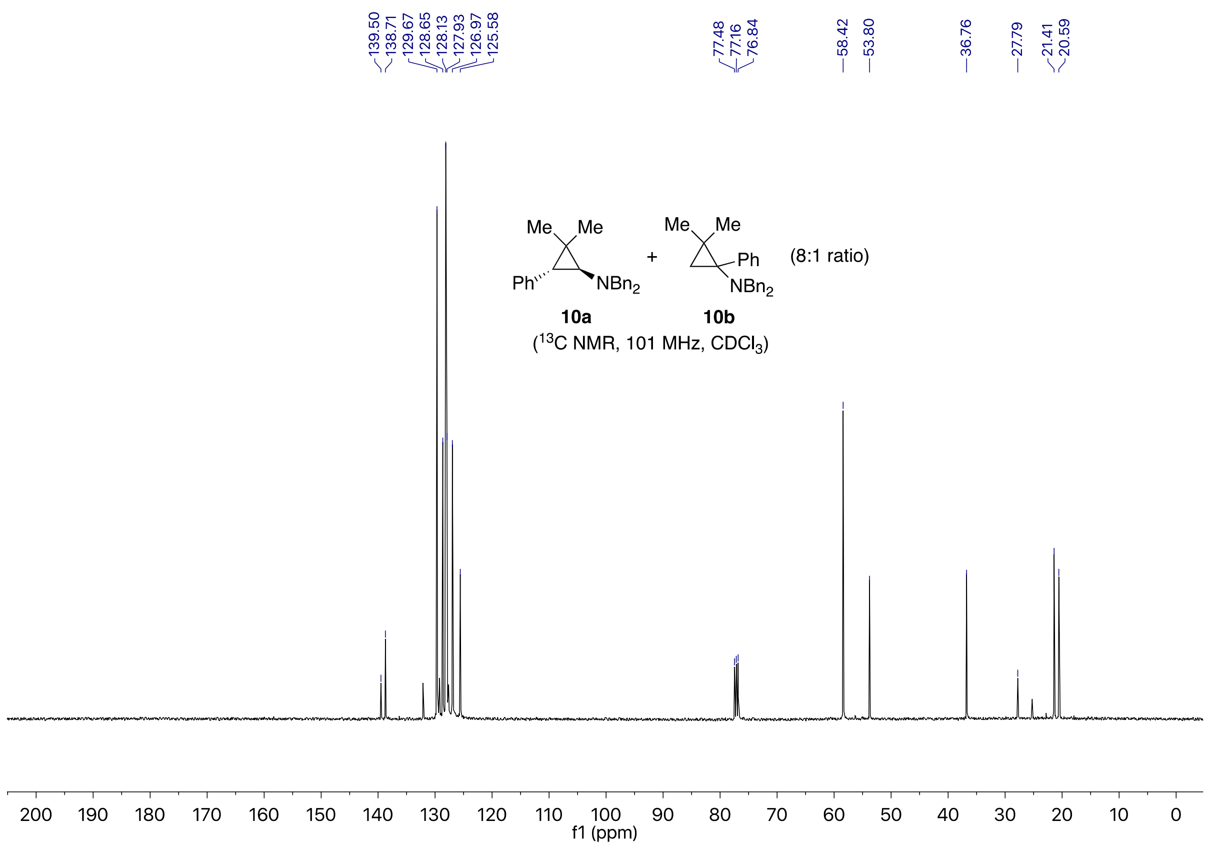
7.36
7.35
7.33
7.31
7.30
7.29
7.28
7.27
7.22
7.20
7.18
7.16
7.14
3.82
3.79
3.72
3.69
3.46
3.43
2.24
2.23
1.79
1.78
1.64
1.22
0.88
0.82
0.57
0.55
0.55
0.54
Me
Me
Ph
NBn2
10a
+
Me
Me
Ph
NBn2
10b
(8:1 ratio)
(1H NMR, 400 MHz, CDCl3)
7.98
4.67
1.40
2.02
2.00
1.98
0.37
0.95
0.98
0.37
3.04
0.37
3.00
0.25
f1 (ppm)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128.13
127.93
126.97
125.58
77.48
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76.84
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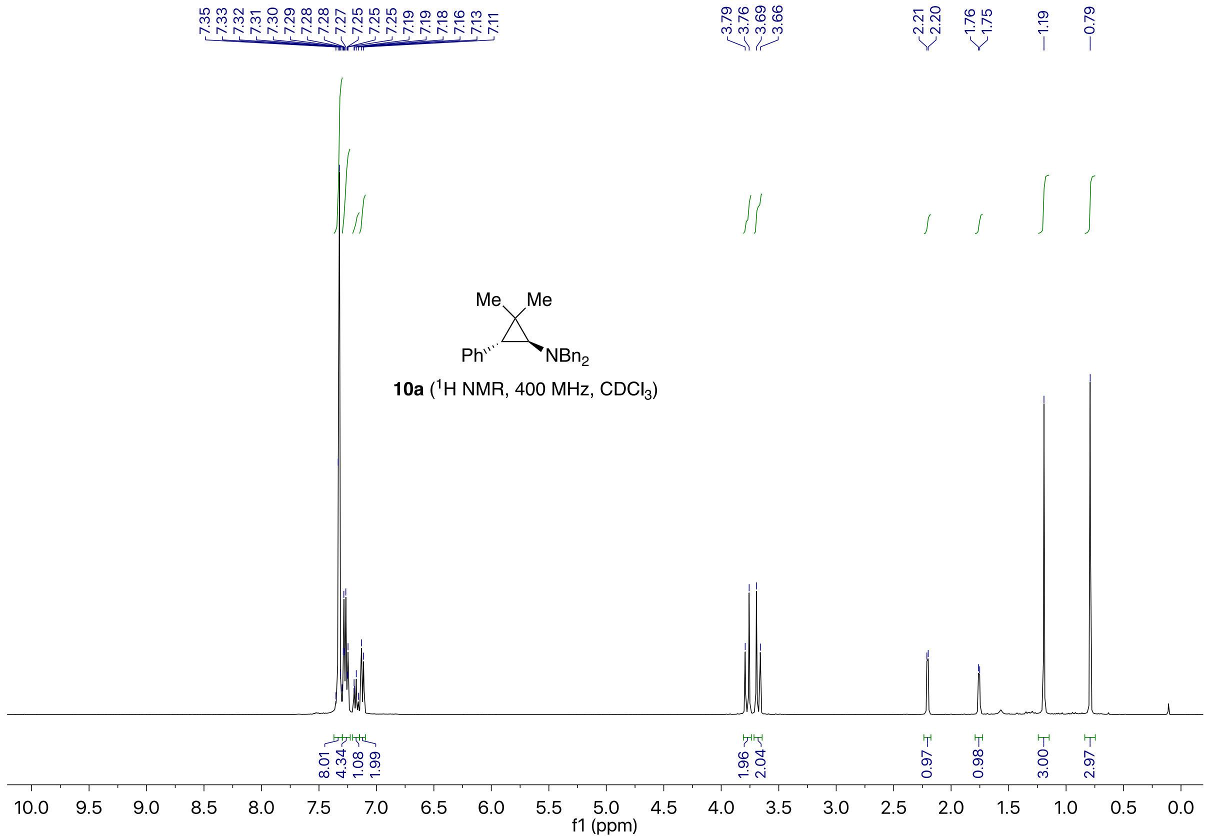
53.80
36.76
27.79
21.41
20.59
Me
Me
Ph
NBn2
10a
+
Me
Me
Ph
NBn2
10b
(8:1 ratio)
(13C NMR, 101 MHz, CDCl3)
f1 (ppm)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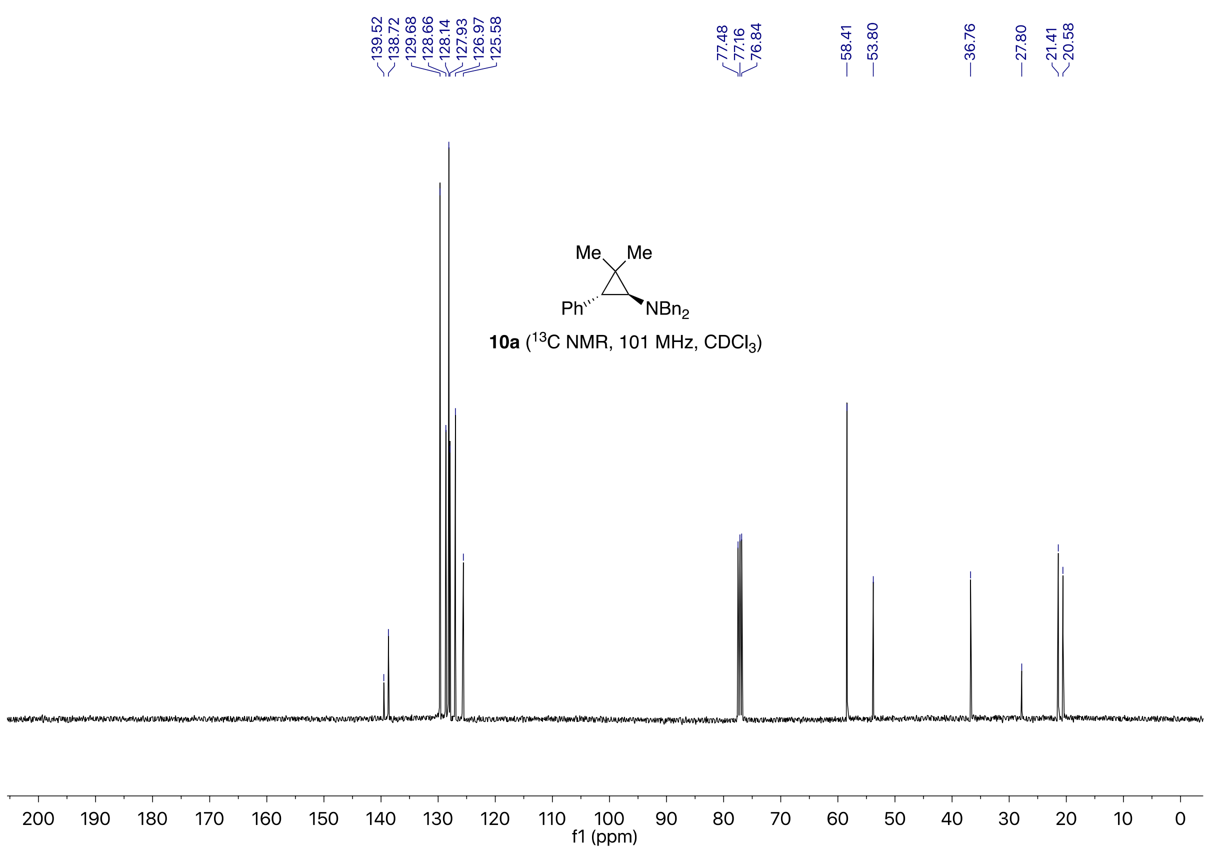
3.79 3.76 3.69 3.66
2.21 2.20
1.76 1.75
1.19
0.79
Me Me
Ph
NBn2
10a (1H NMR, 400 MHz, CDCl3)
8.01 4.34 1.08 1.99
1.96 2.04
0.97
0.98
3.00
2.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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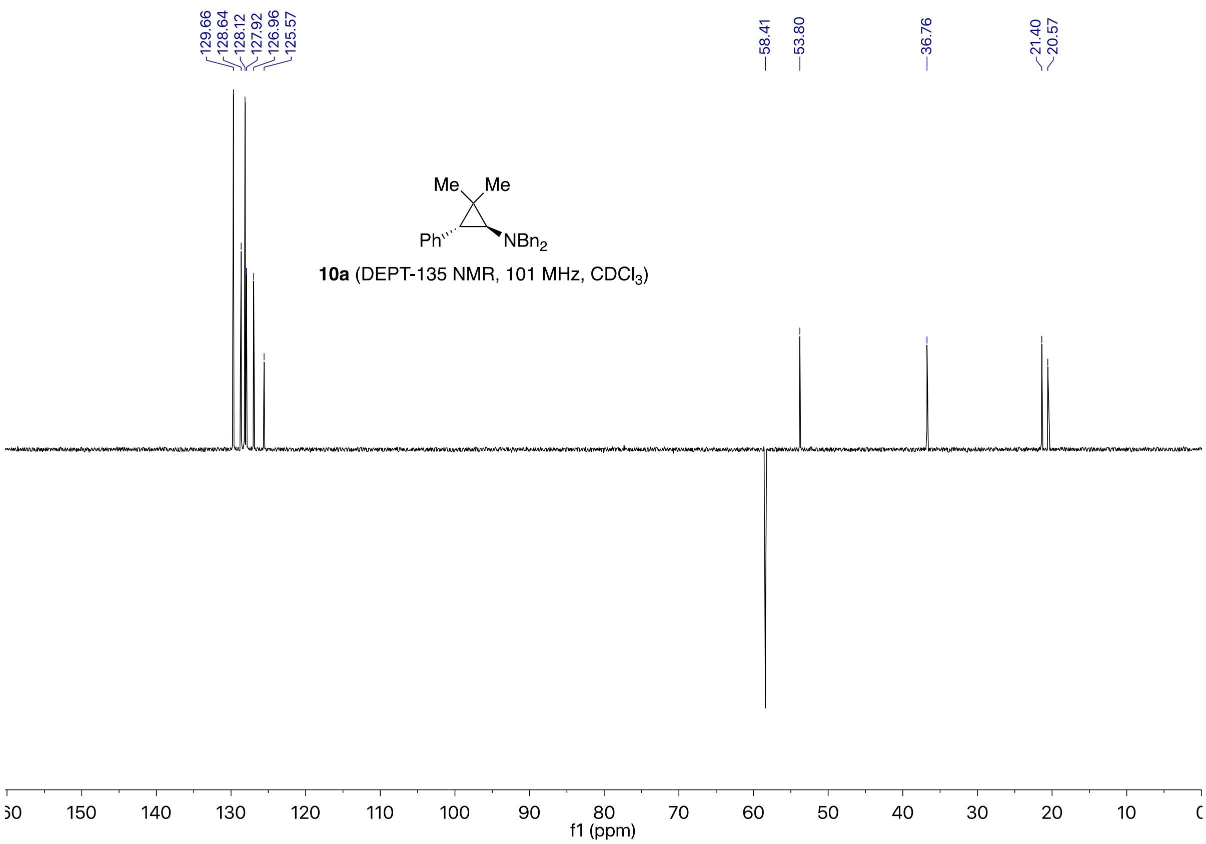
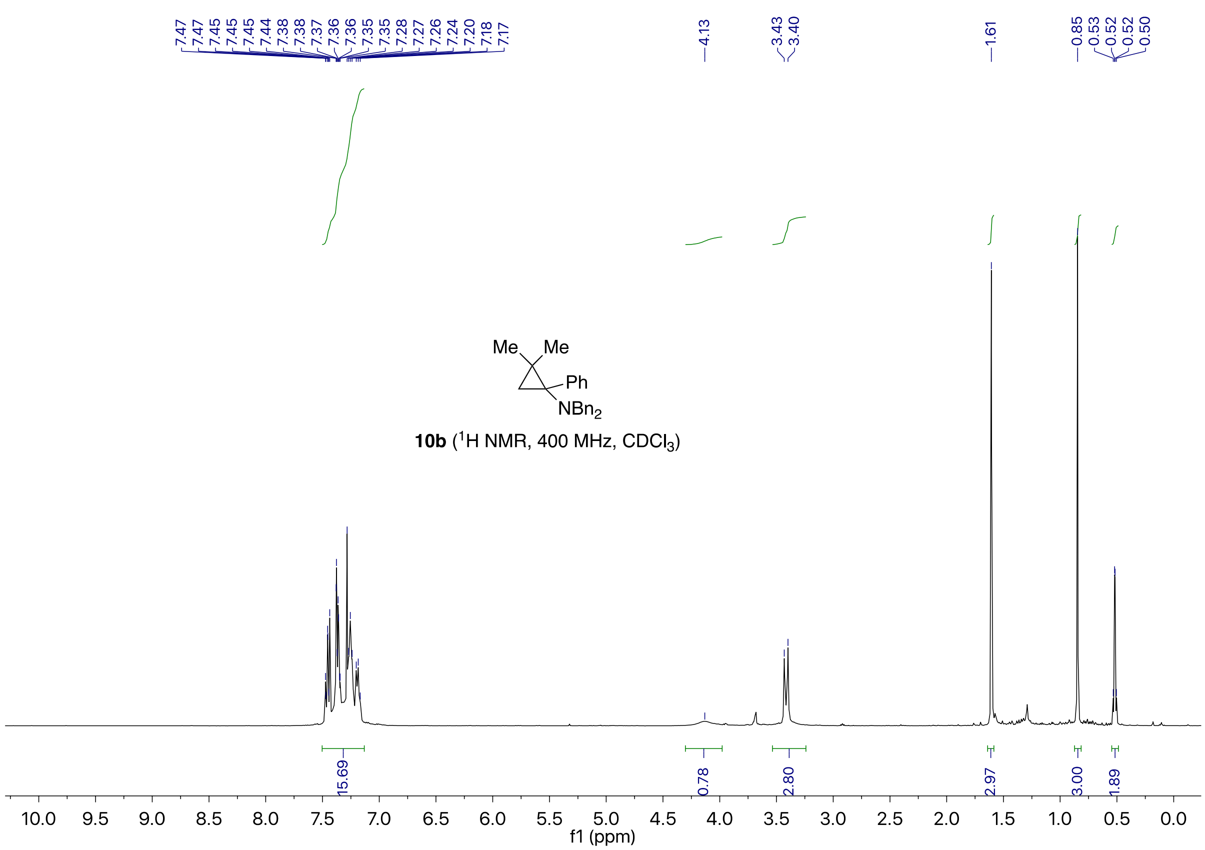
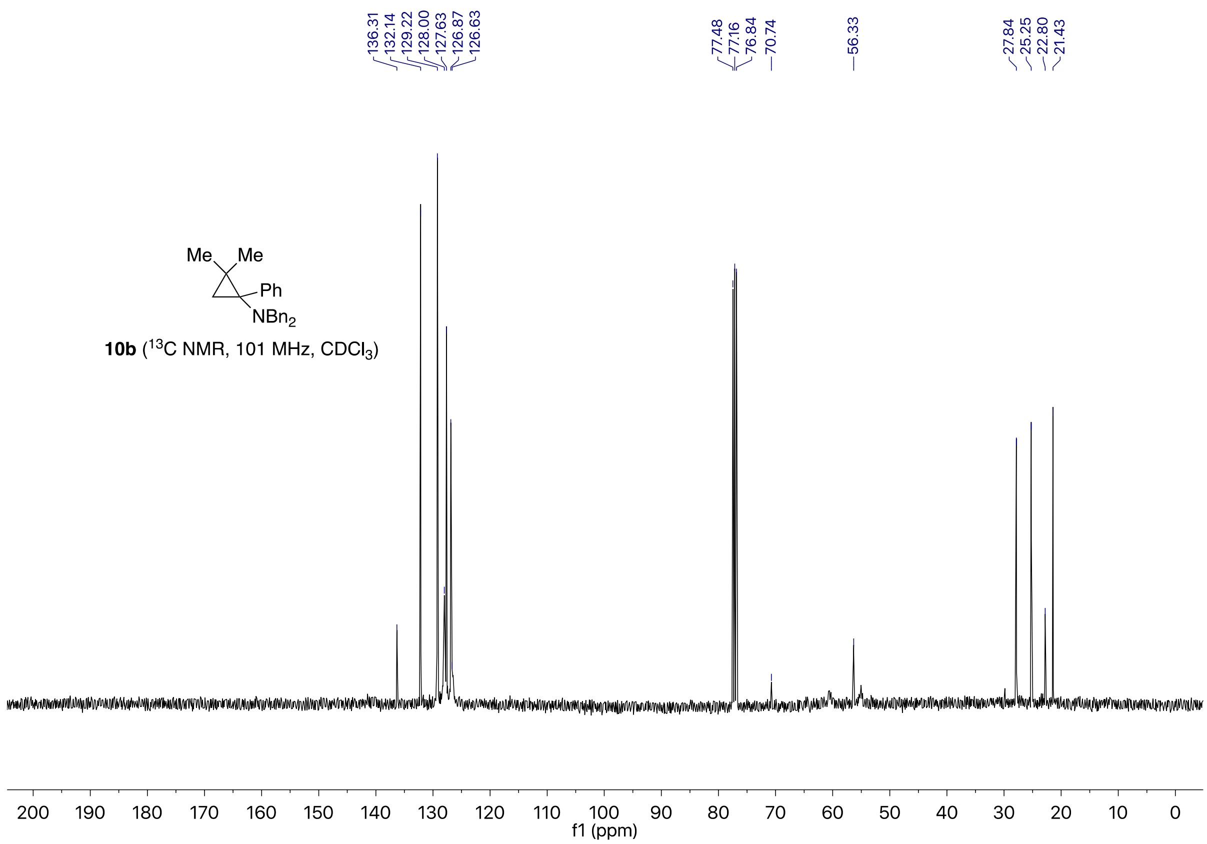
77.48 77.16 76.84
58.41
53.80
36.76
27.80
21.41 20.58
Me Me
Ph
NBn2
10a (13C NMR, 101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

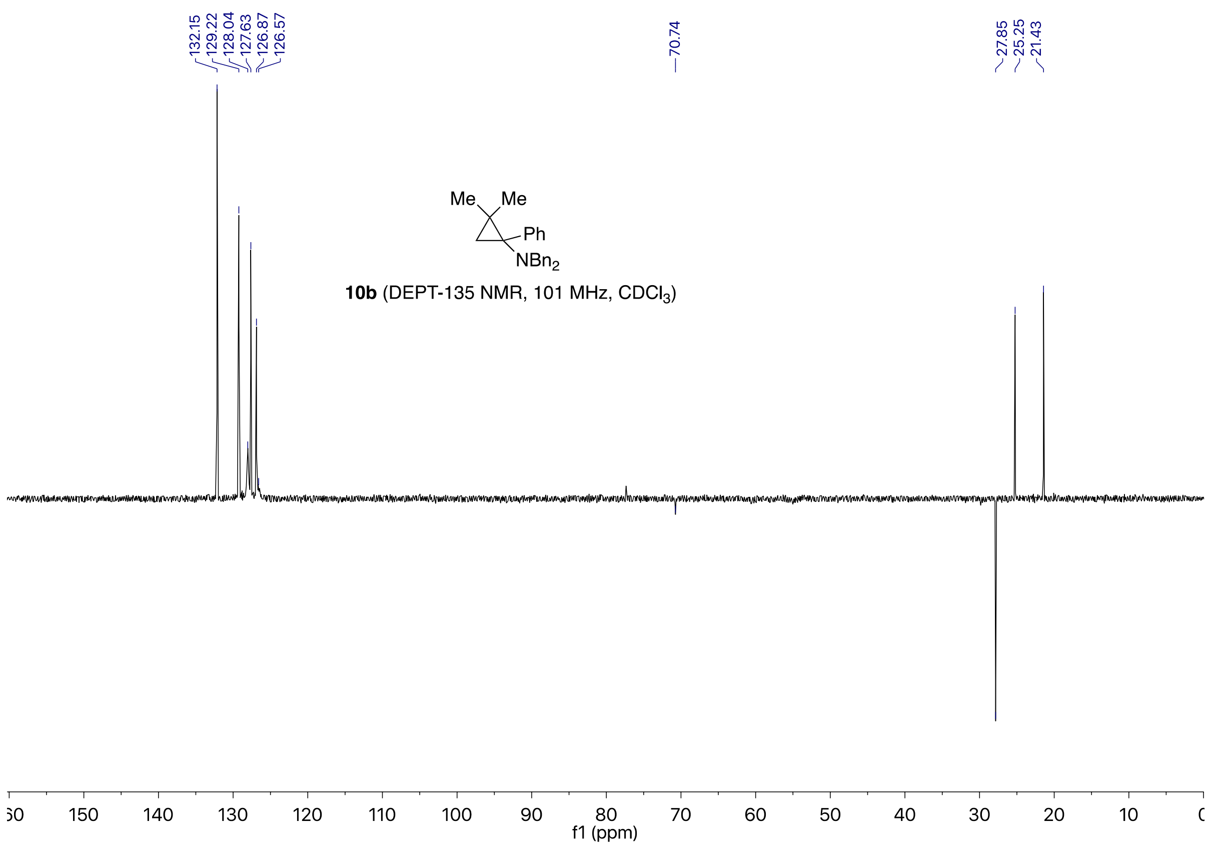


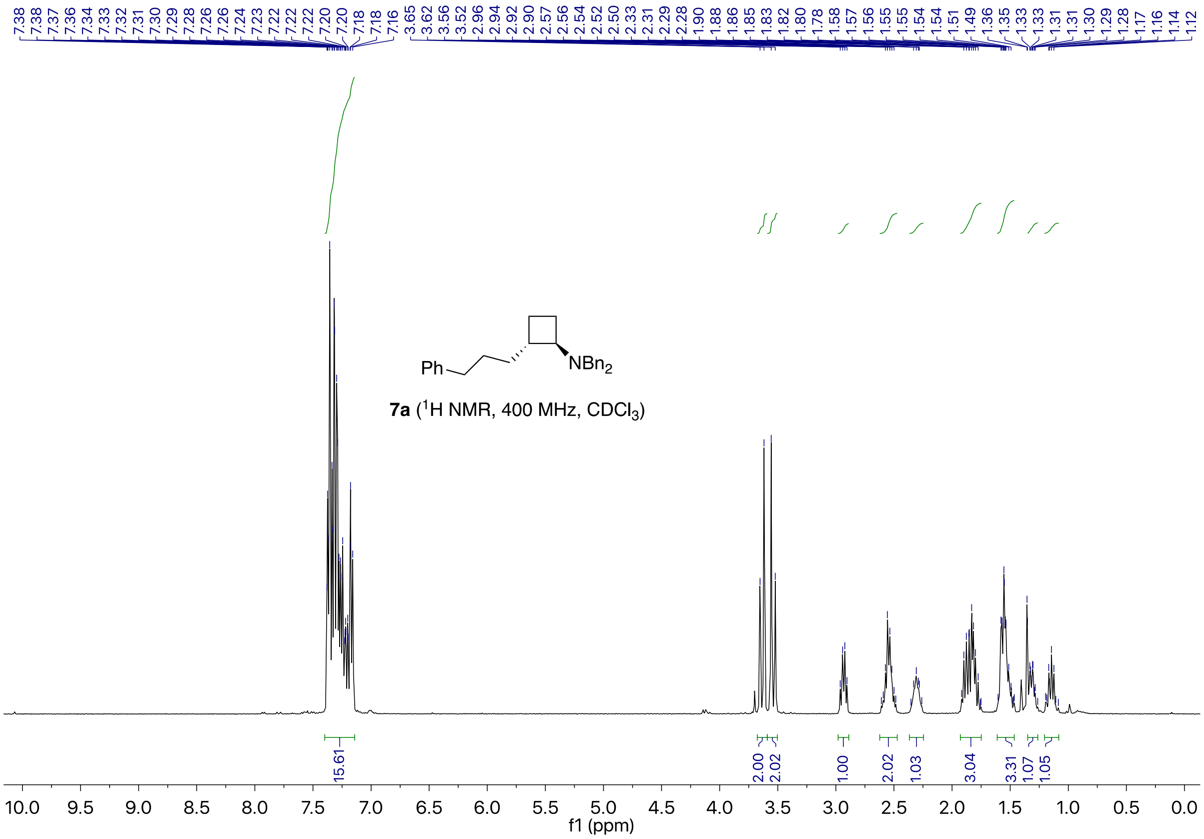
10a (DEPT-135 NMR, 101 MHz, $CDCl_3$)

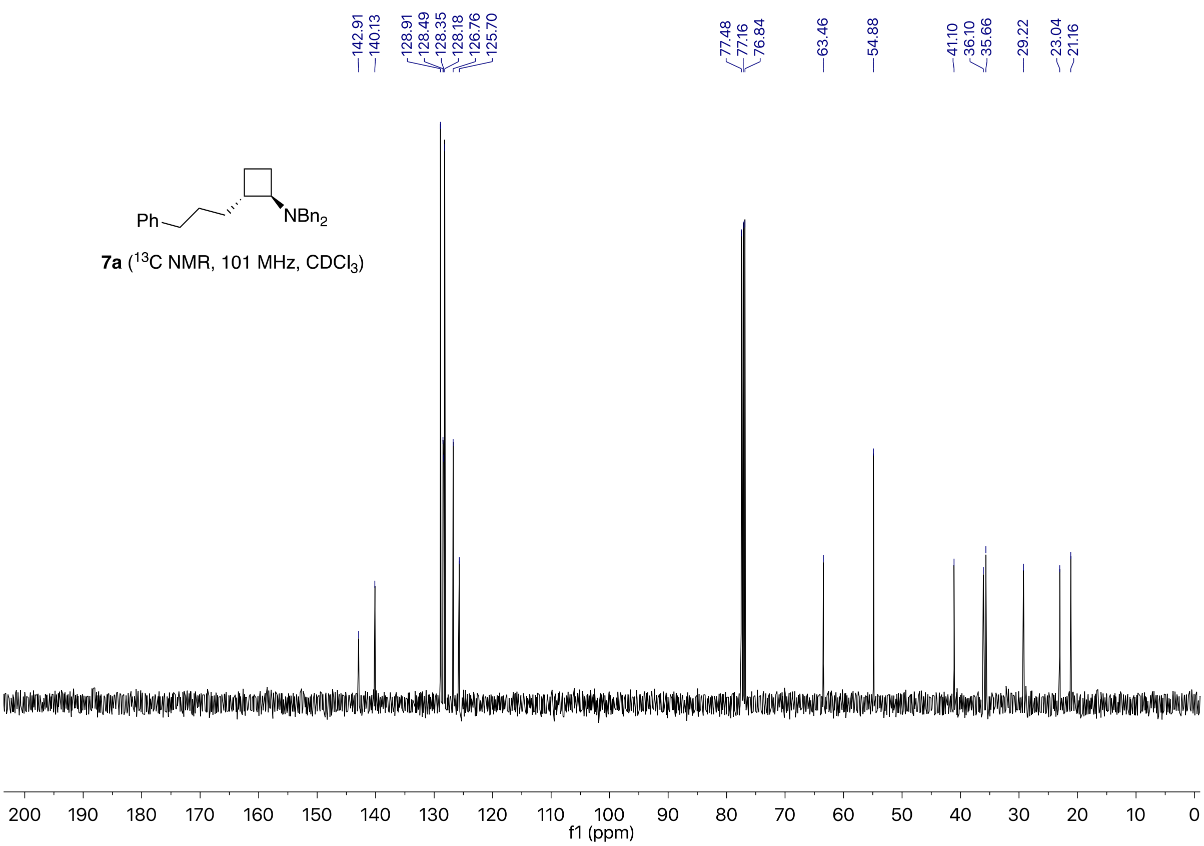


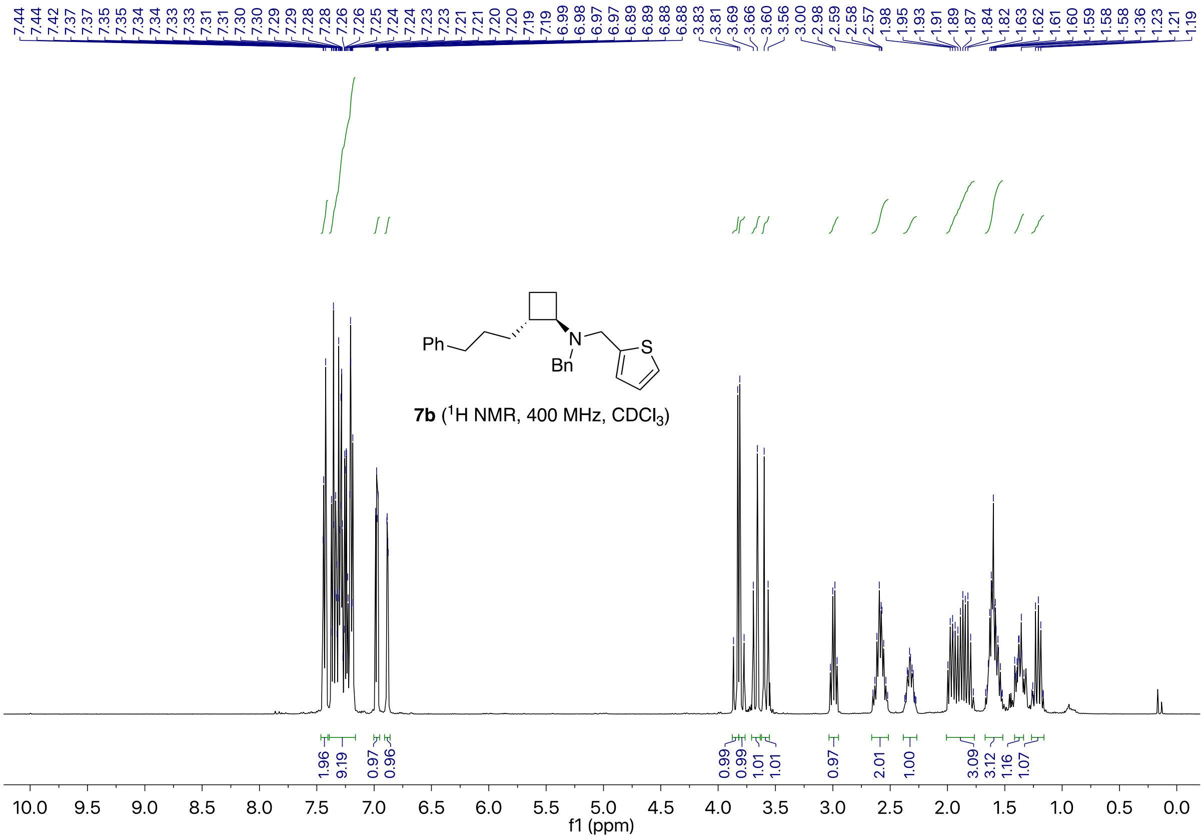
10b (^1H NMR, 400 MHz, $CDCl_3$)


136.31
132.14
129.22
128.00
127.63
126.87
126.63
77.48
77.16
76.84
70.74
56.33
27.84
25.25
22.80
21.43
Me
Me
Ph
NBn2
10b (13C NMR, 101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

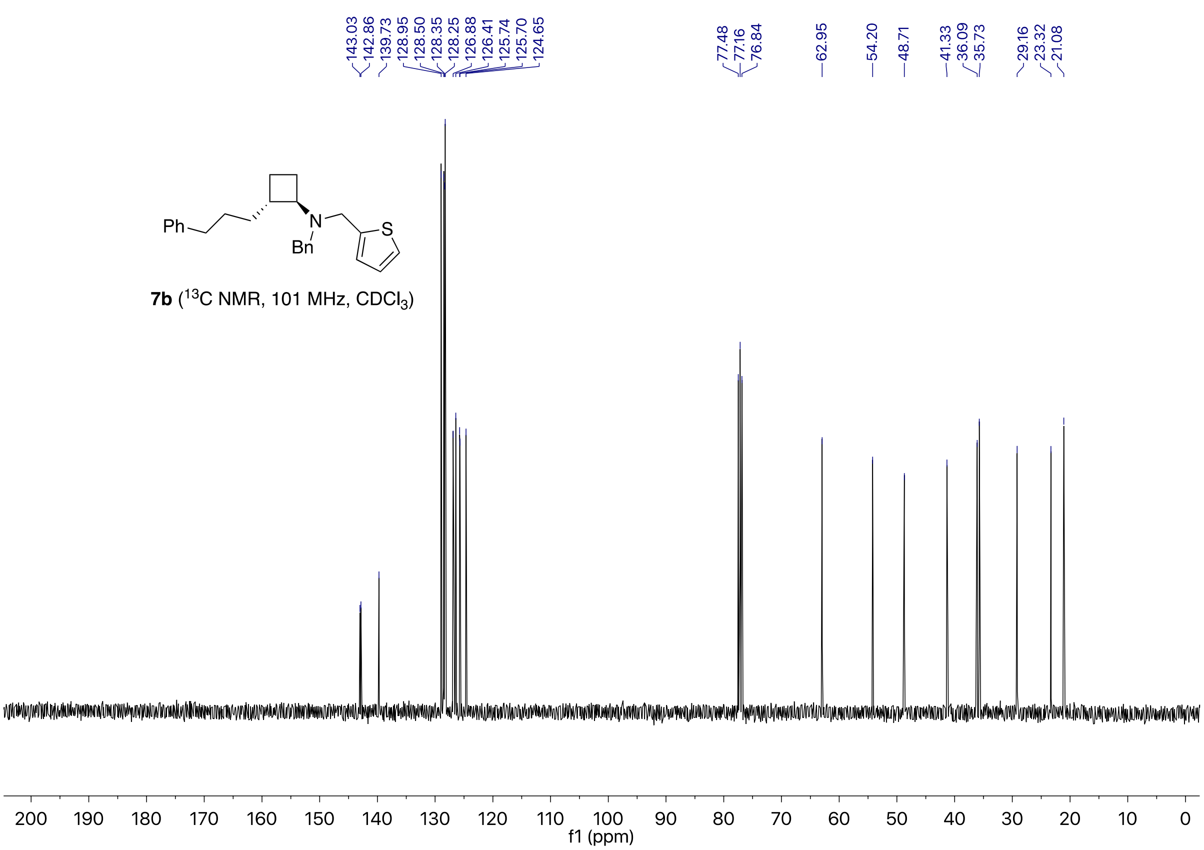

132.15
129.22
128.04
127.63
126.87
126.57
70.74
27.85
25.25
21.43
Me
Me
Ph
NBn2
10b (DEPT-135 NMR, 101 MHz, CDCl3)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7a (¹H NMR, 400 MHz, CDCl3)
f1 (ppm)

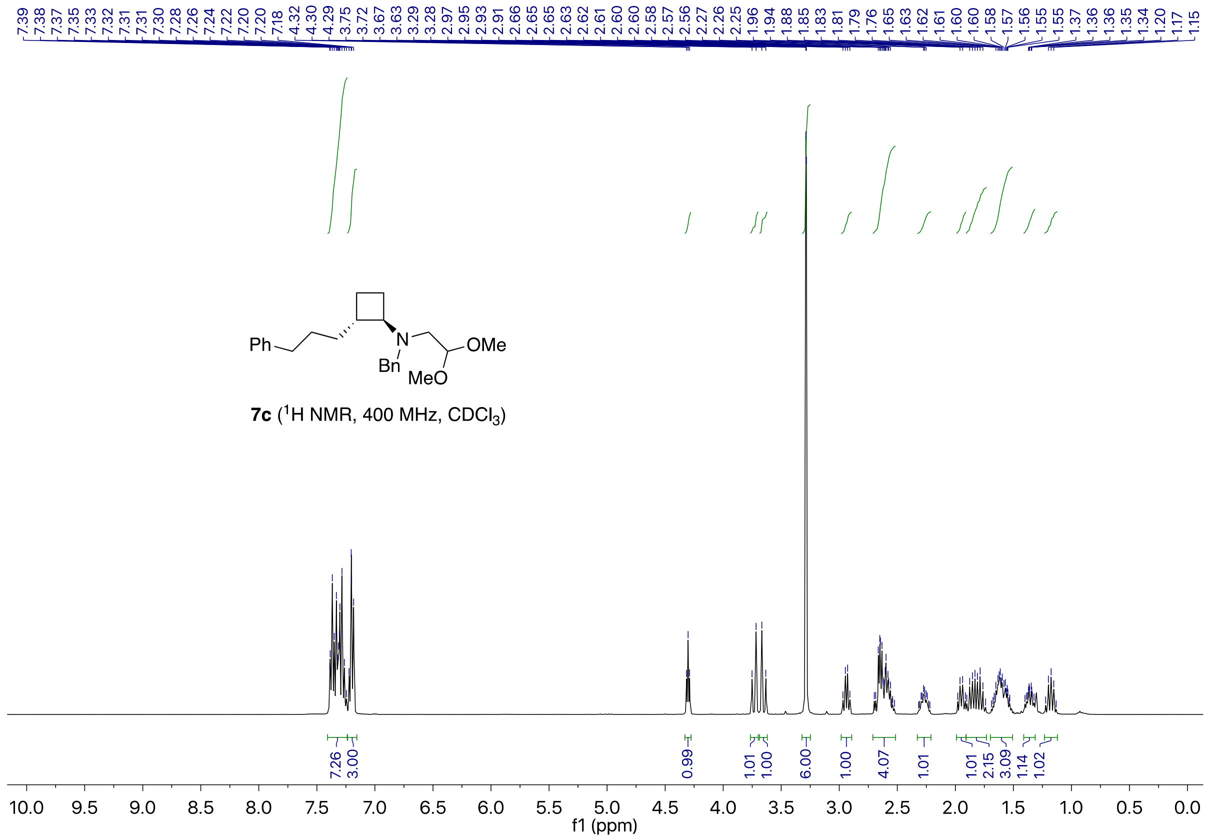

7a (¹³C NMR, 101 MHz, CDCl3)
f1 (ppm)



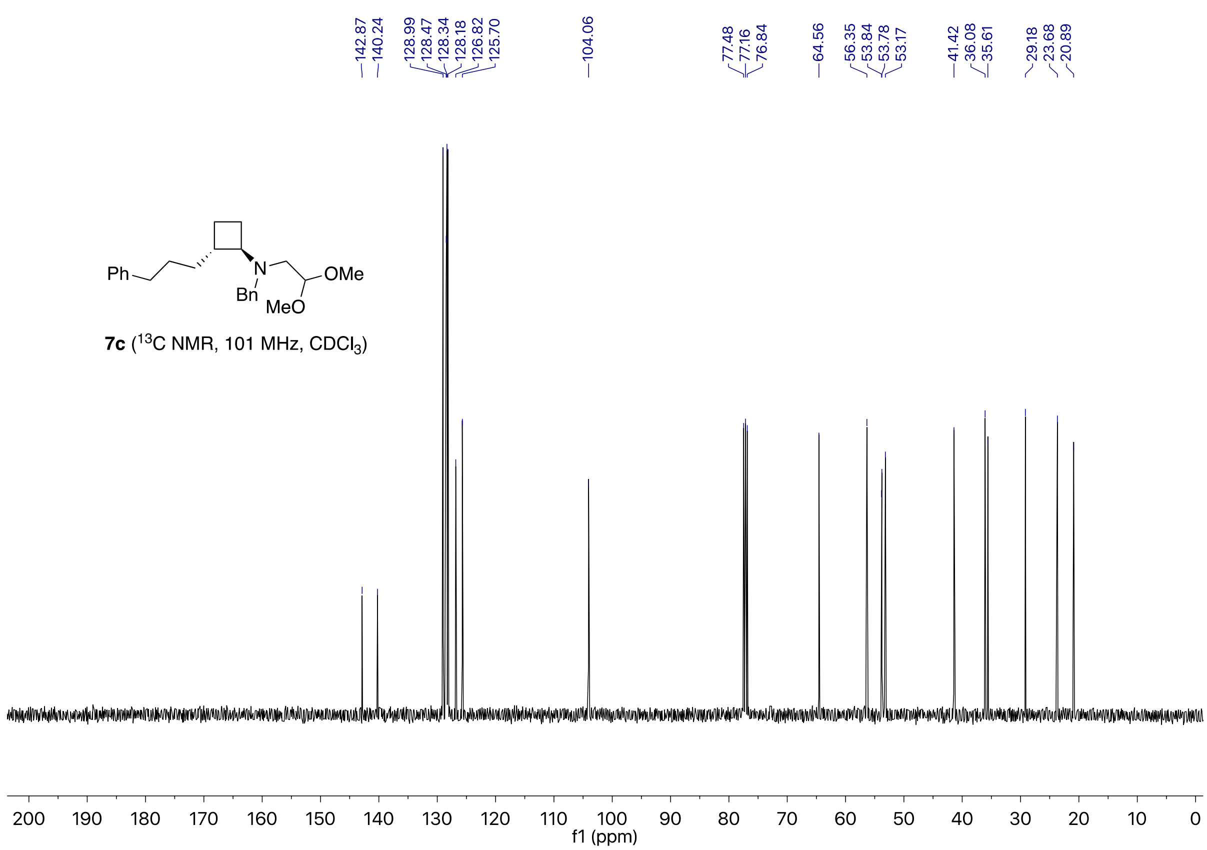
Ph
N
Bn
S
7b (1H NMR, 400 MHz, CDCl3)
f1 (ppm)



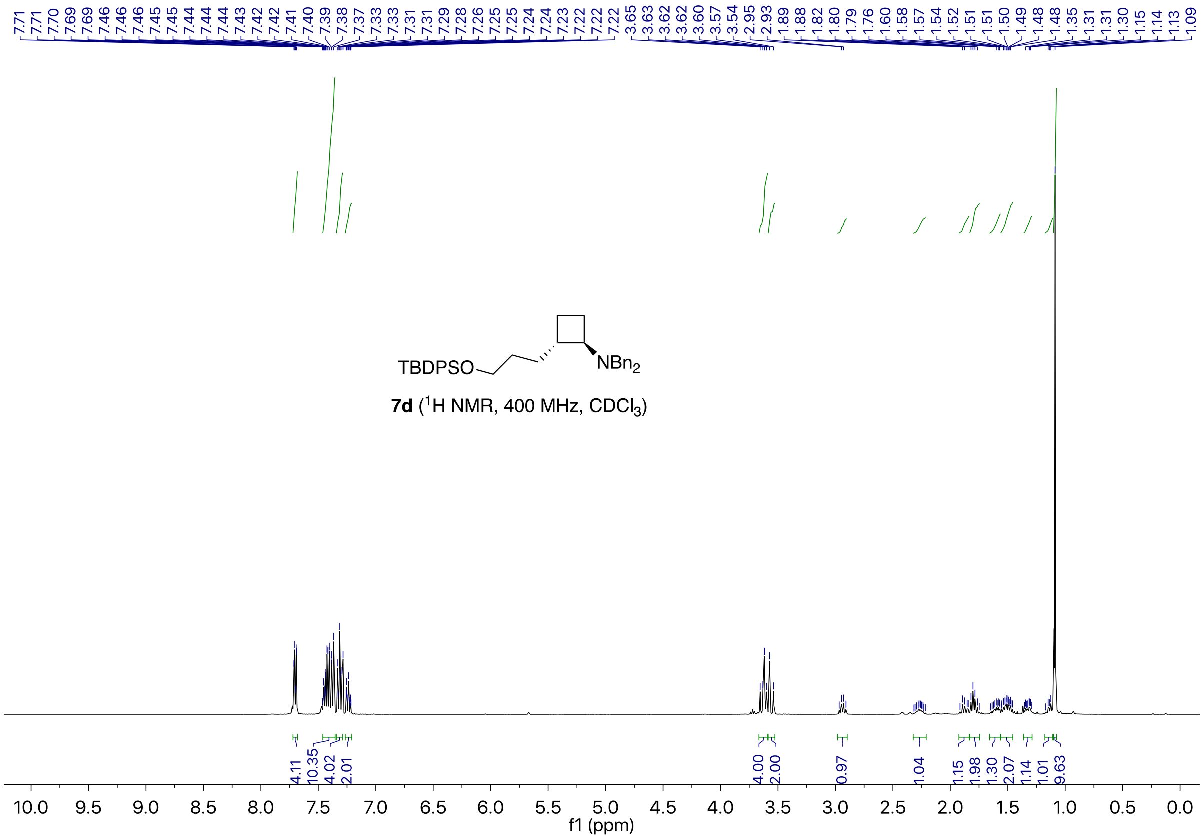
Ph
N
Bn
S
7b (13C NMR, 101 MHz, CDCl3)
f1 (ppm)

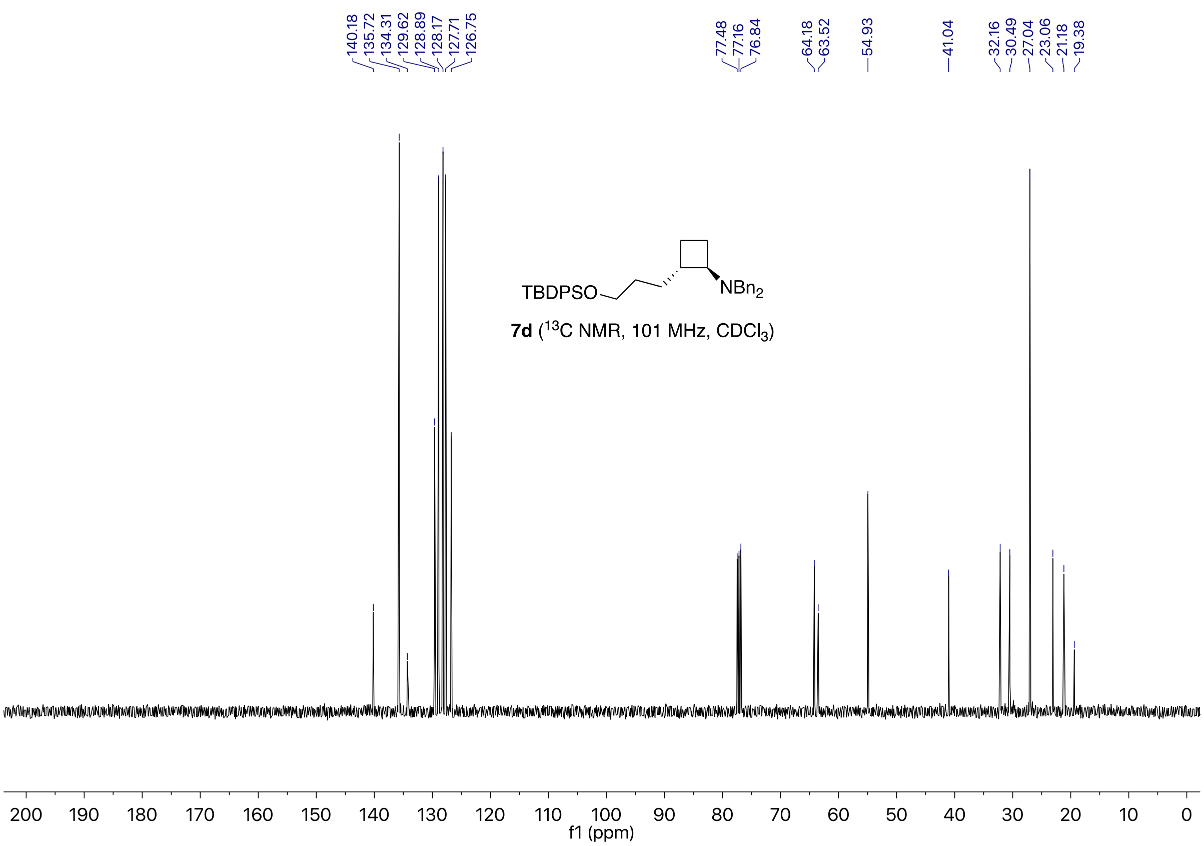


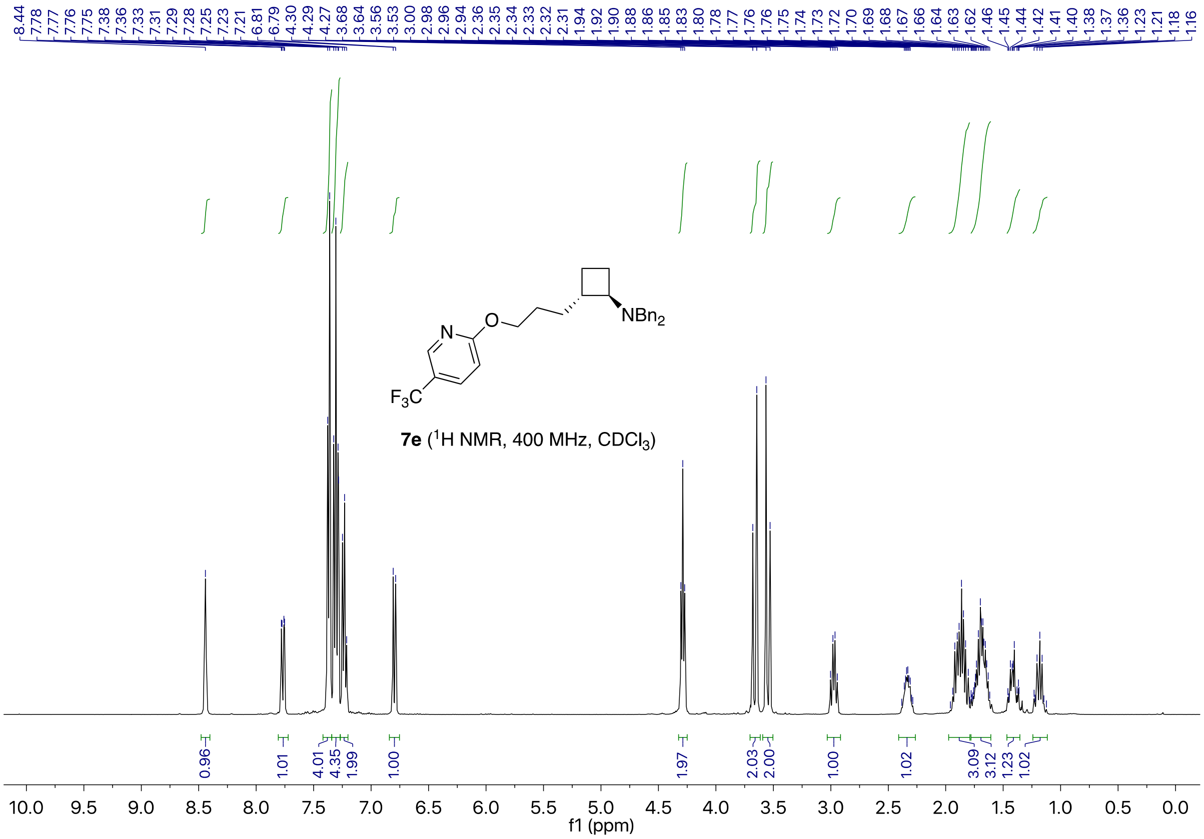
Ph
N
OMe
Bn
MeO
7c (1H NMR, 400 MHz, CDCl3)
7.26
3.00
0.99
1.01
1.00
6.00
1.00
4.07
1.01
1.01
2.15
3.09
1.14
1.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



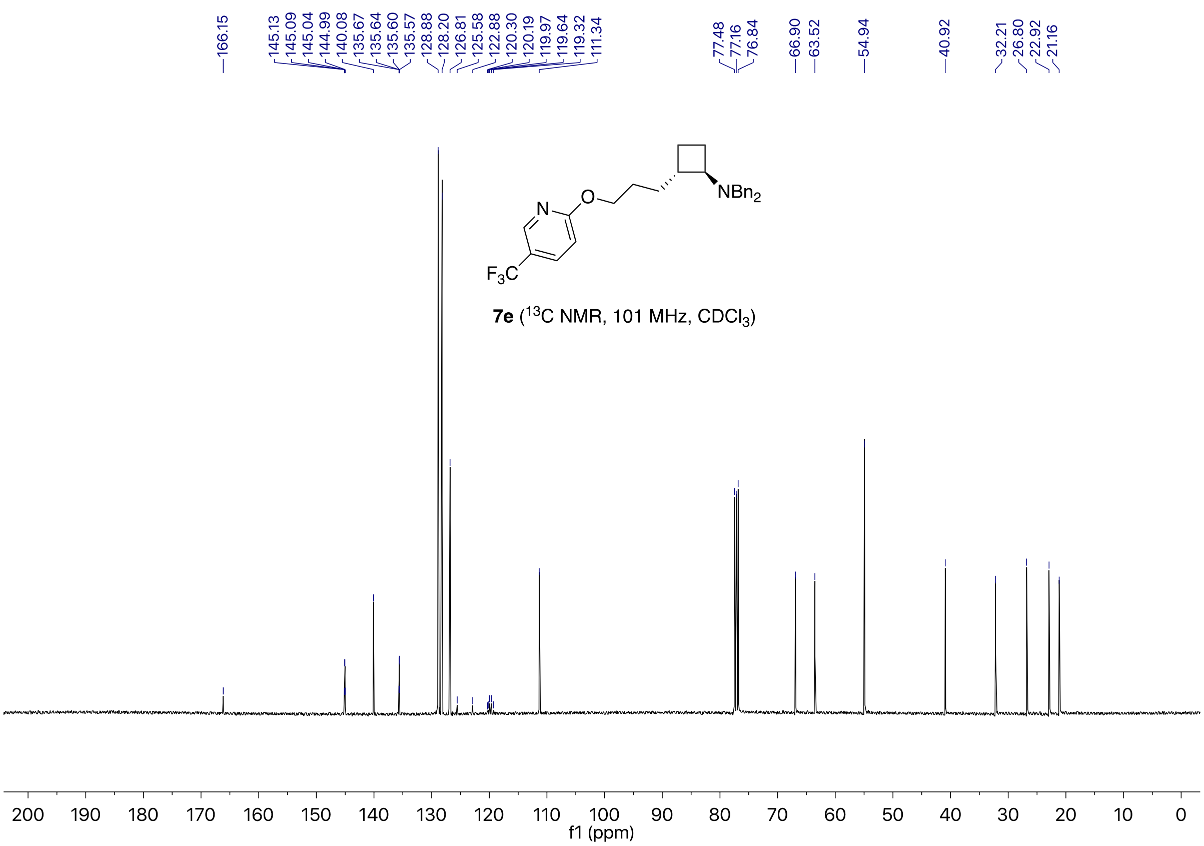
142.87
140.24
128.99
128.47
128.34
128.18
126.82
125.70
104.06
77.48
77.16
76.84
64.56
56.35
53.84
53.78
53.17
41.42
36.08
35.61
29.18
23.68
20.89
Ph
N
OMe
Bn
MeO
7c (13C NMR, 101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


TBDPSO
NBn₂
7d (¹H NMR, 400 MHz, CDCl₃)
f1 (ppm)

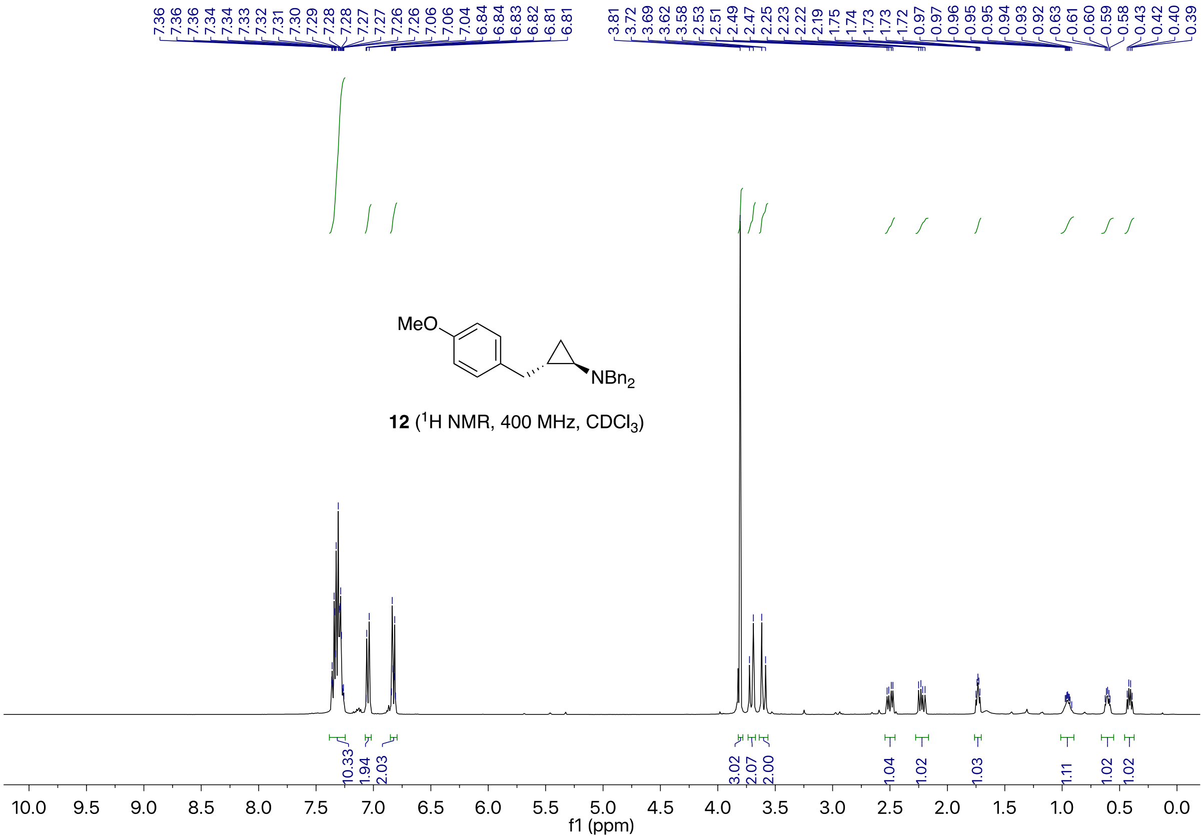

TBDPSO
NBn₂
7d (¹³C NMR, 101 MHz, CDCl₃)
f1 (ppm)



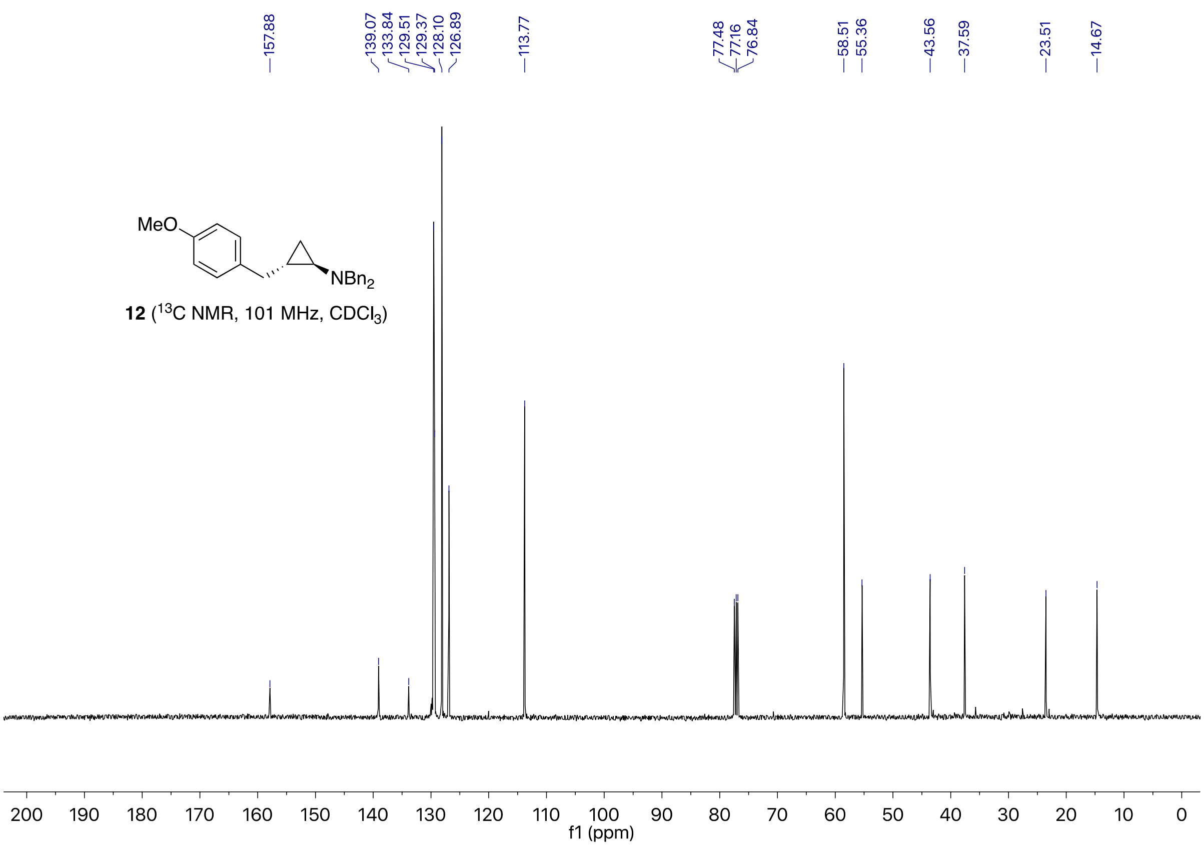
7e (^{1}H NMR, 400 MHz, $CDCl_3$)



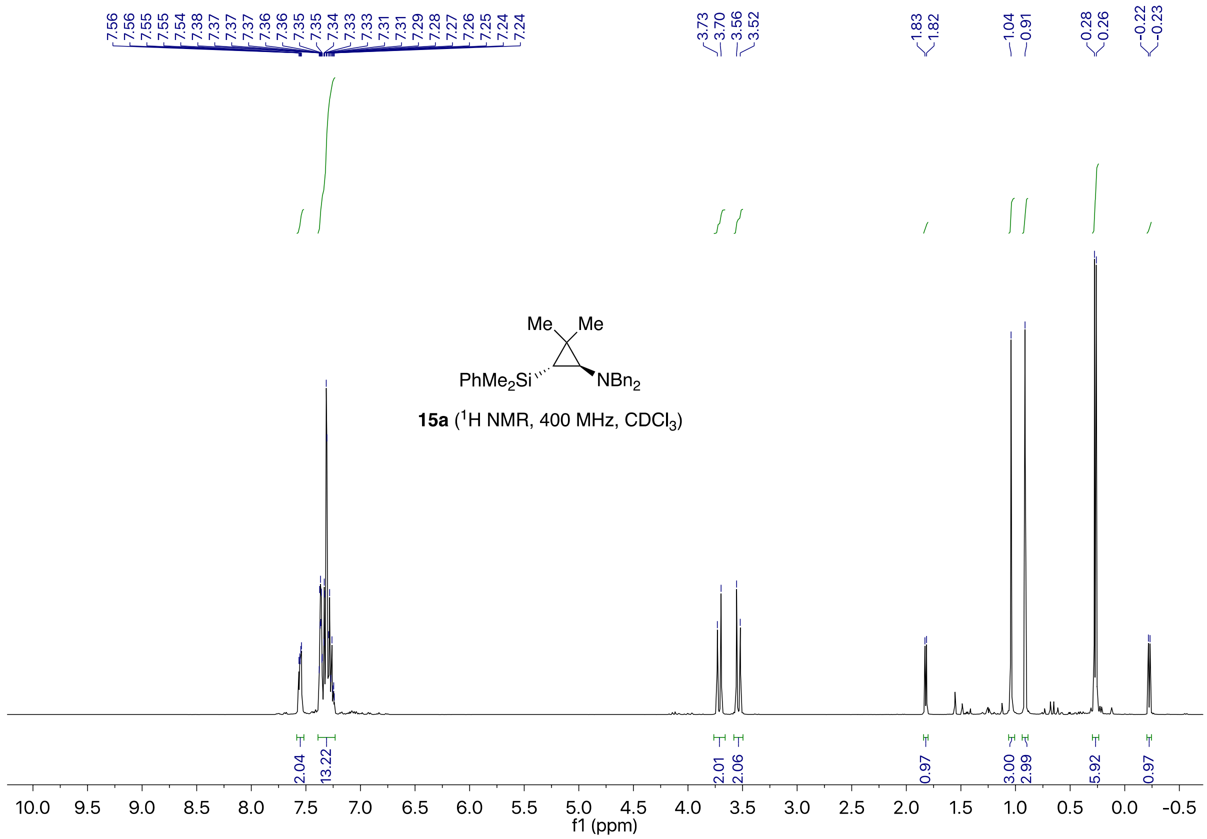
7e (^{13}C NMR, 101 MHz, $CDCl_3$)



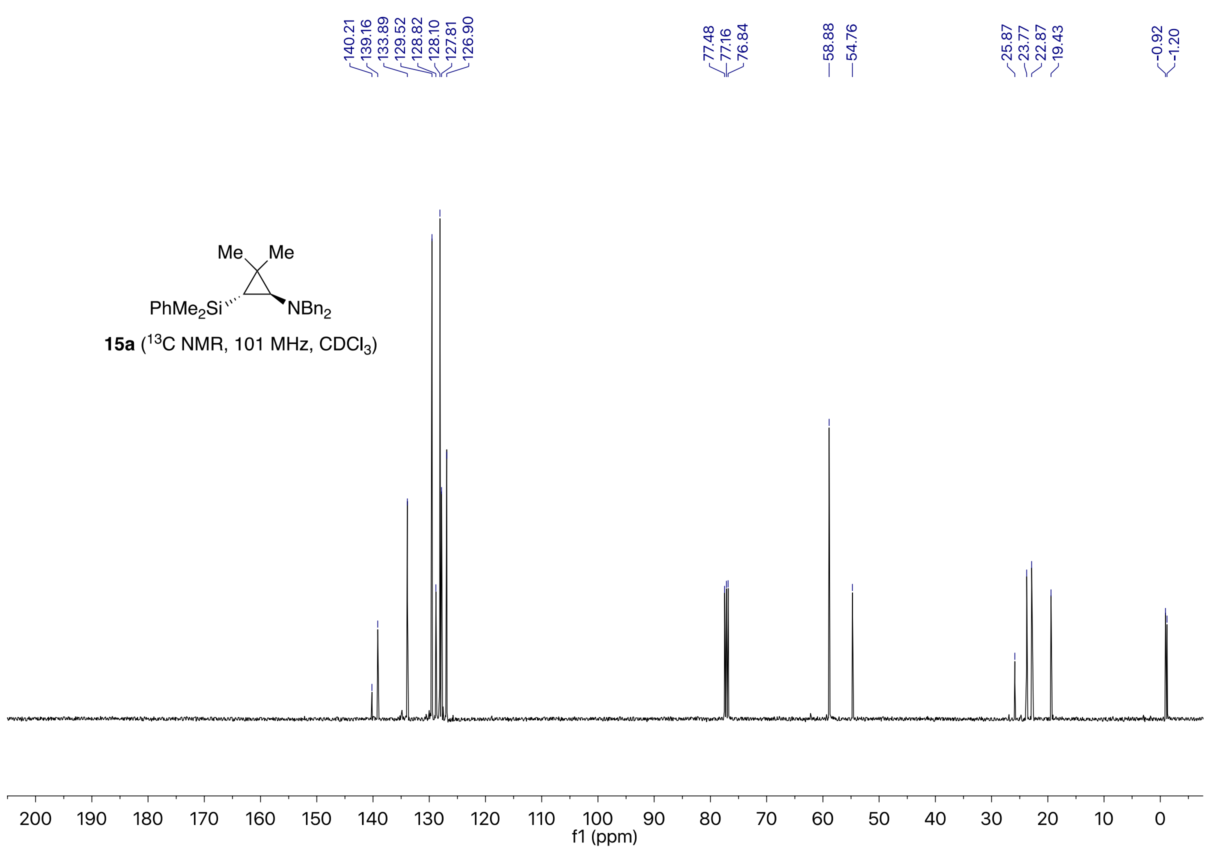
12 (^{1}H NMR, 400 MHz, $CDCl_3$)



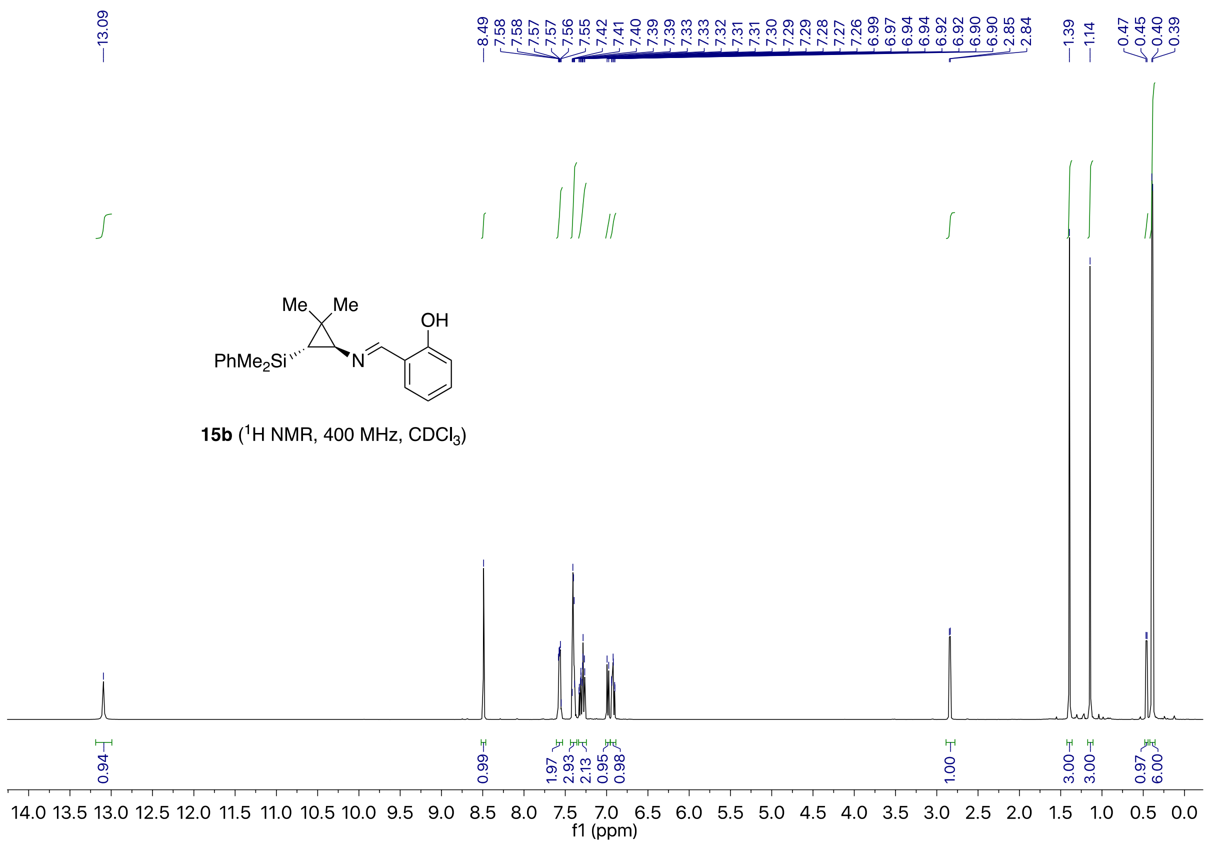
12 (^{13}C NMR, 101 MHz, $CDCl_3$)



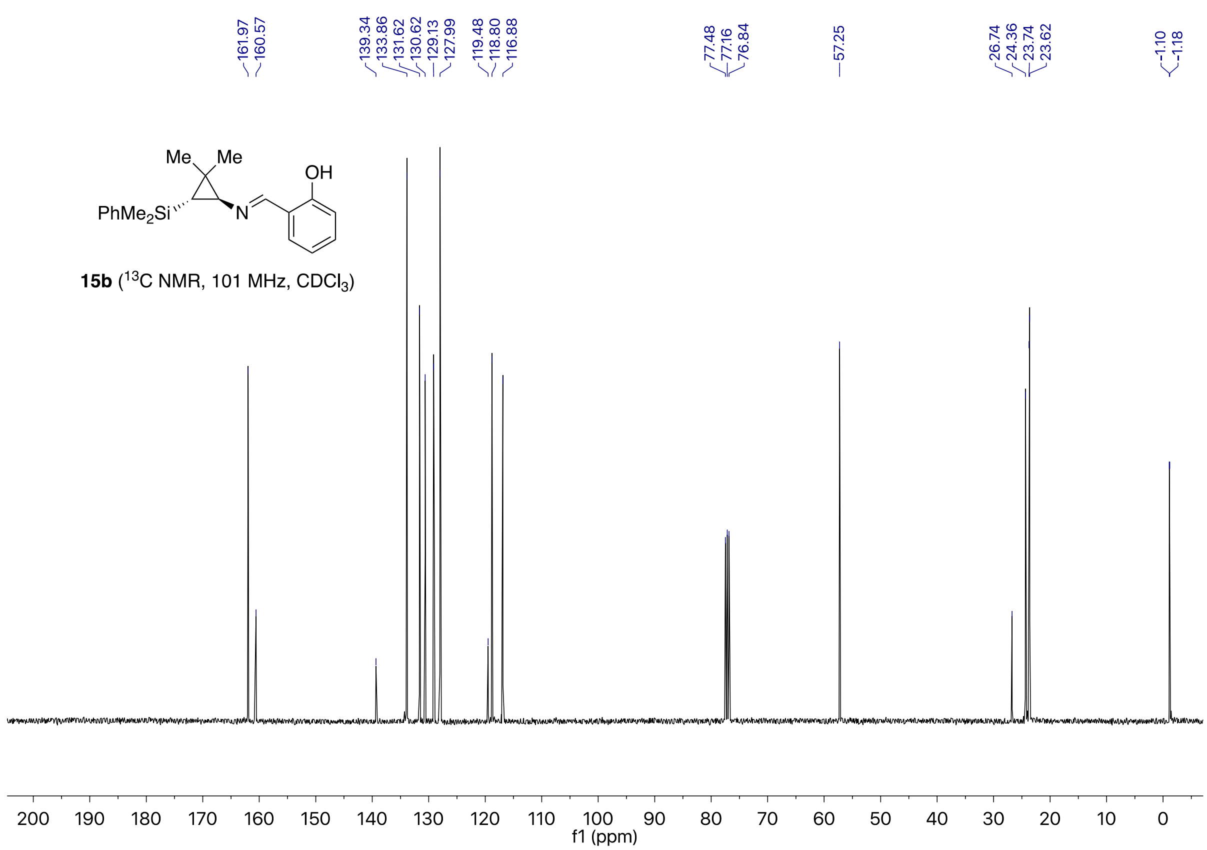
7.56 7.56 7.55 7.55 7.54 7.38 7.37 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.33 7.33 7.31 7.31 7.29 7.28 7.27 7.26 7.25 7.24 7.24
3.73 3.70 3.56 3.52
1.83 1.82
1.04 0.91
0.28 0.26
-0.22 -0.23
Me Me
PhMe2Si
NBn2
15a (1H NMR, 400 MHz, CDCl3)
2.04 13.22 2.01 2.06 0.97 3.00 2.99 5.92 0.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



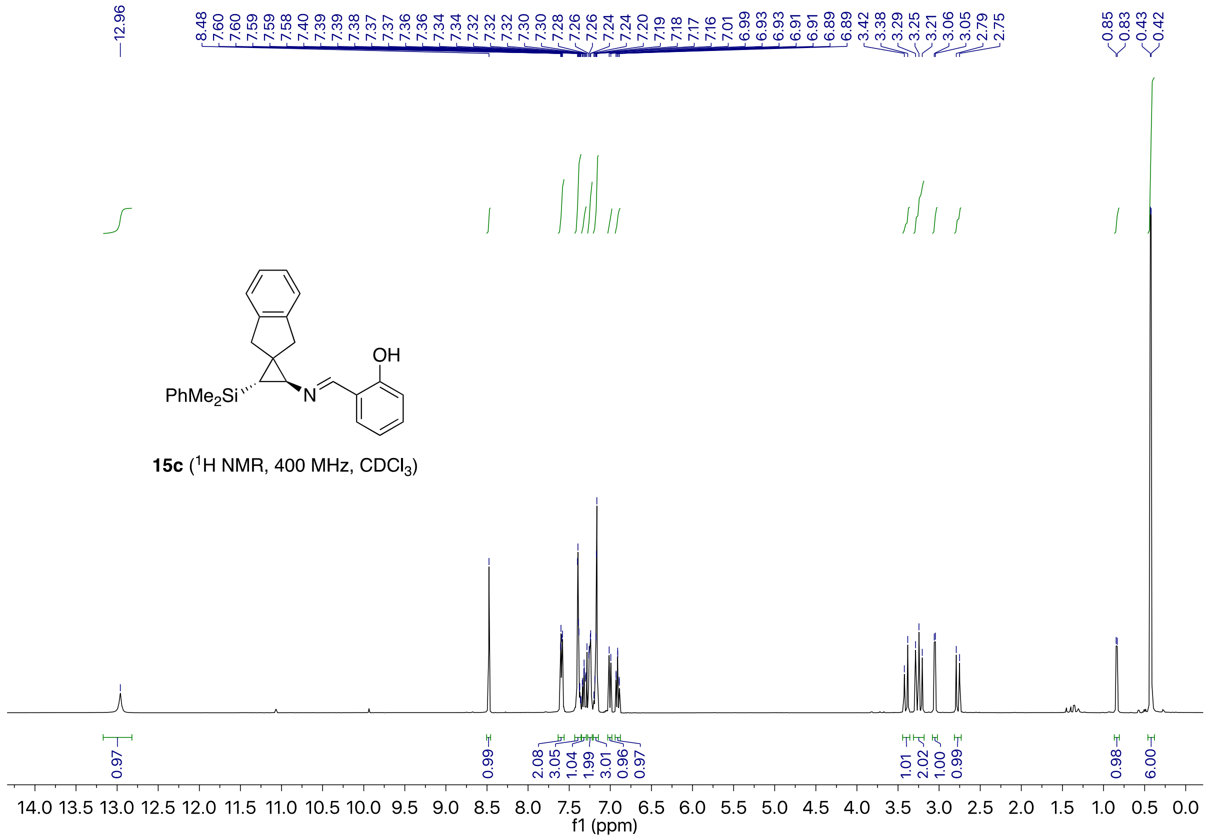
140.21 139.16 133.89 129.52 128.82 128.10 127.81 126.90
77.48 77.16 76.84
58.88 54.76
25.87 23.77 22.87 19.43
-0.92 -1.20
Me Me
PhMe2Si
NBn2
15a (13C NMR, 101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



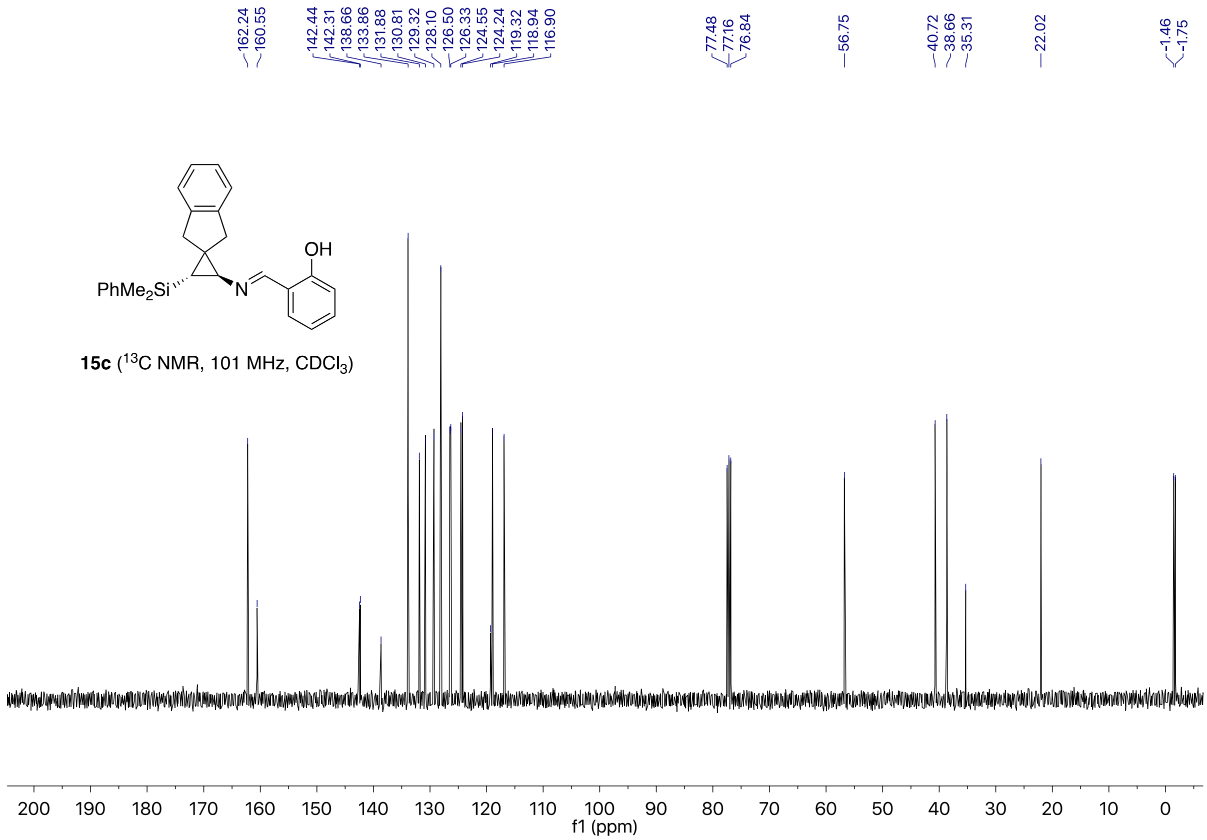
15b (^{1}H NMR, 400 MHz, $CDCl_3$)



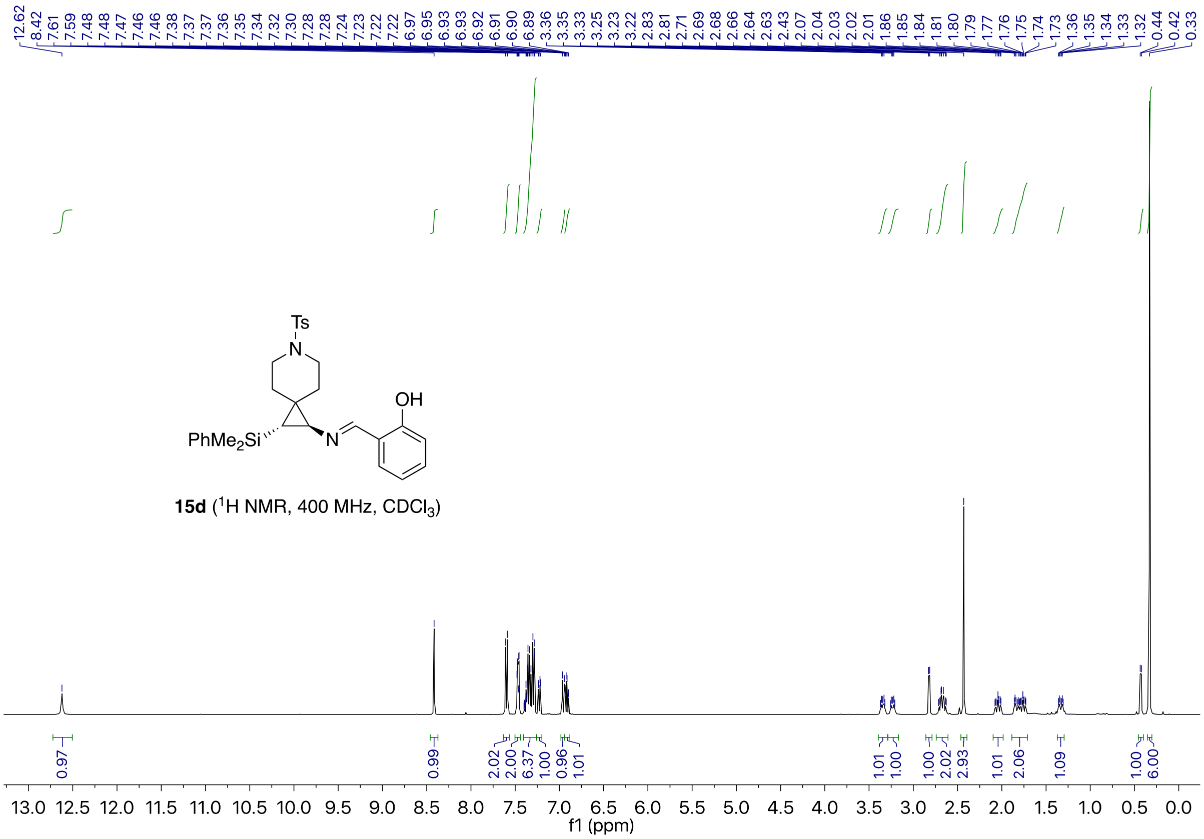
15b (^{13}C NMR, 101 MHz, $CDCl_3$)



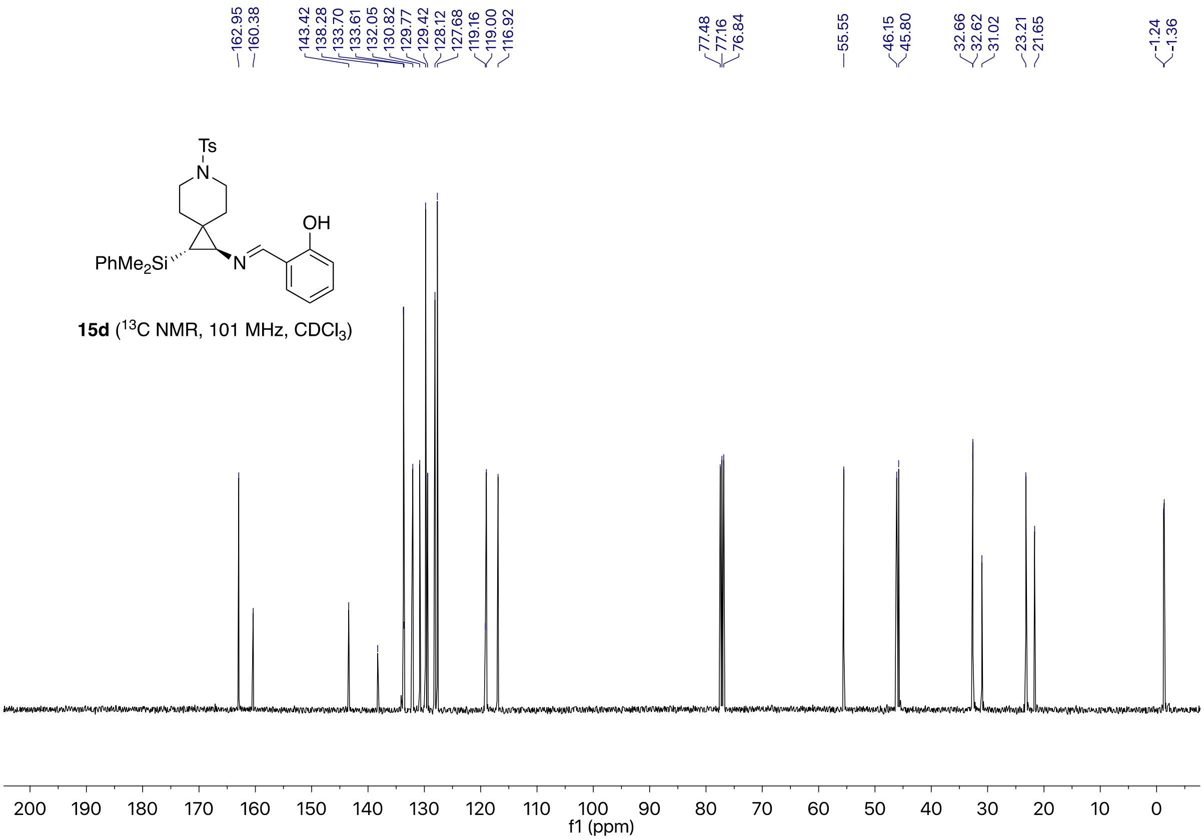
15c (^{1}H NMR, 400 MHz, $CDCl_3$)



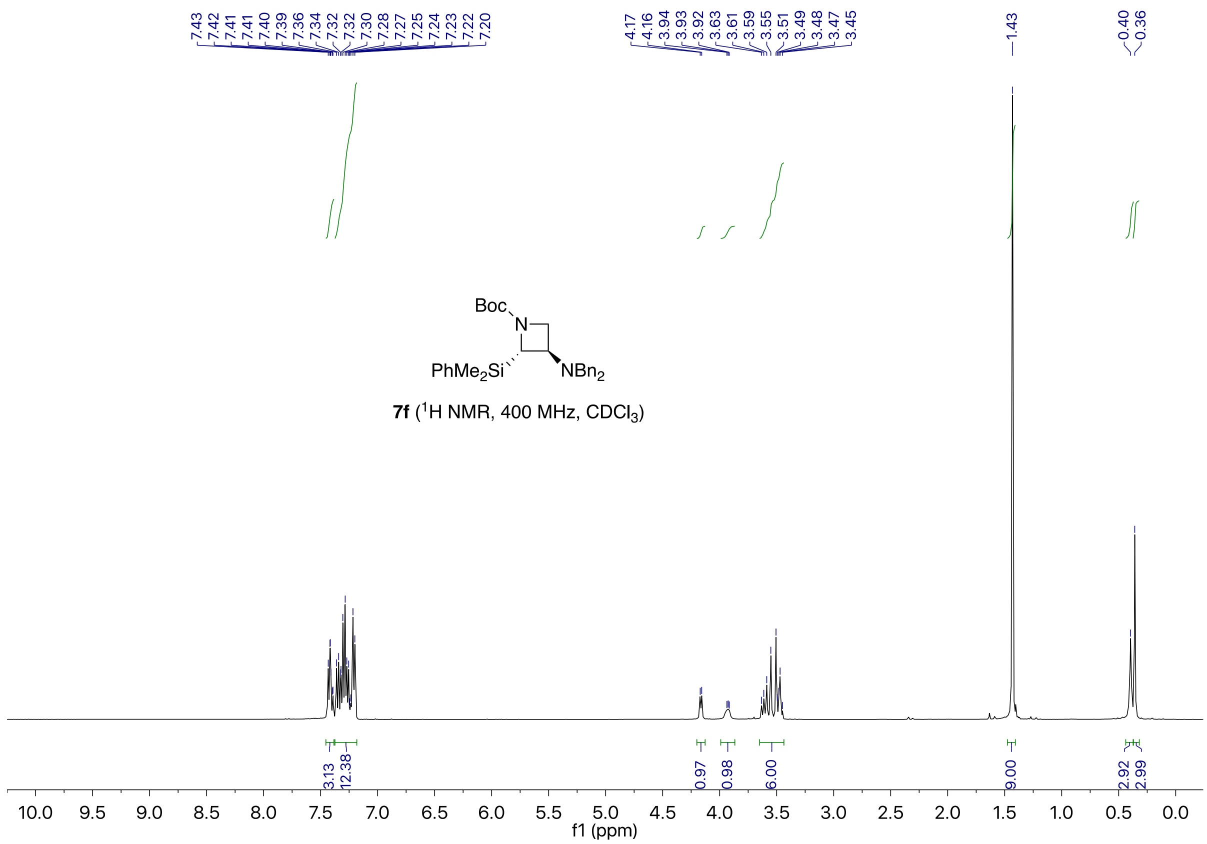
15c (^{13}C NMR, 101 MHz, $CDCl_3$)



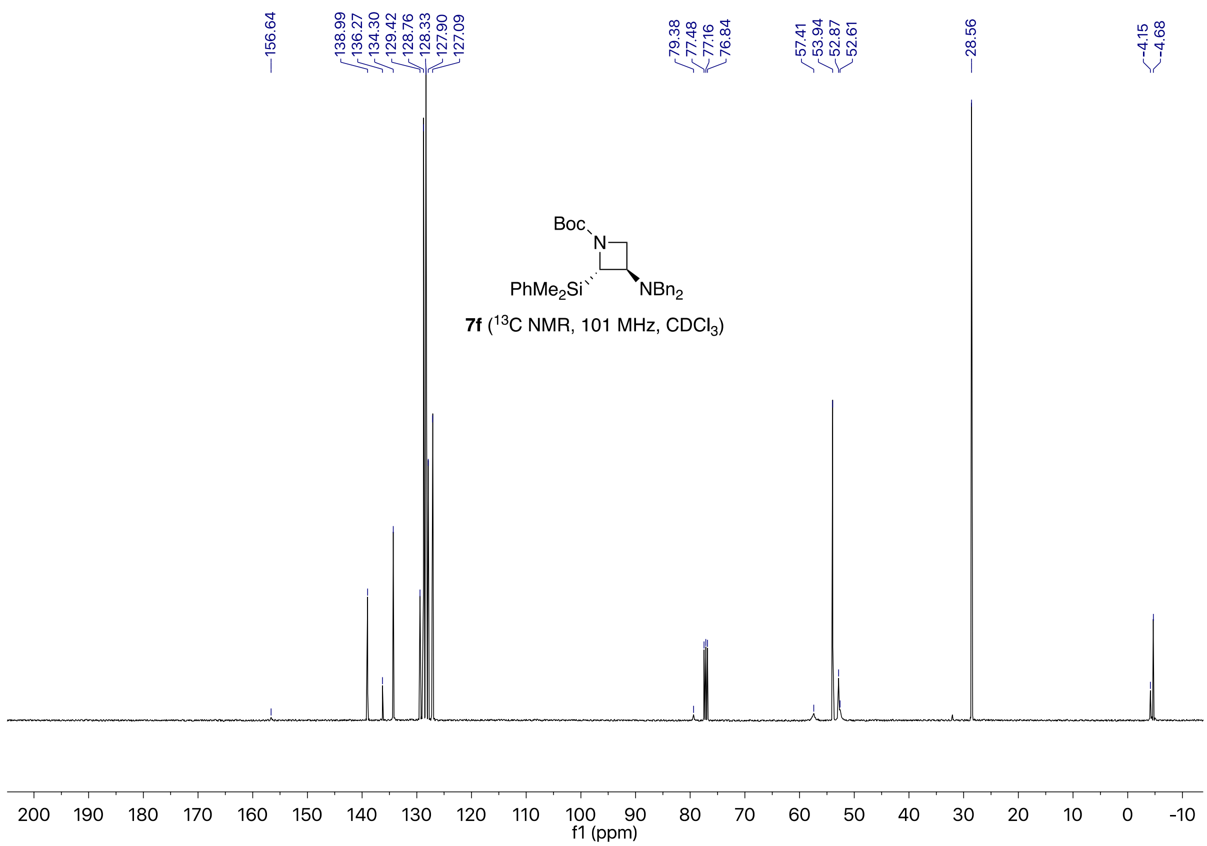
15d (^{1}H NMR, 400 MHz, $CDCl_3$)



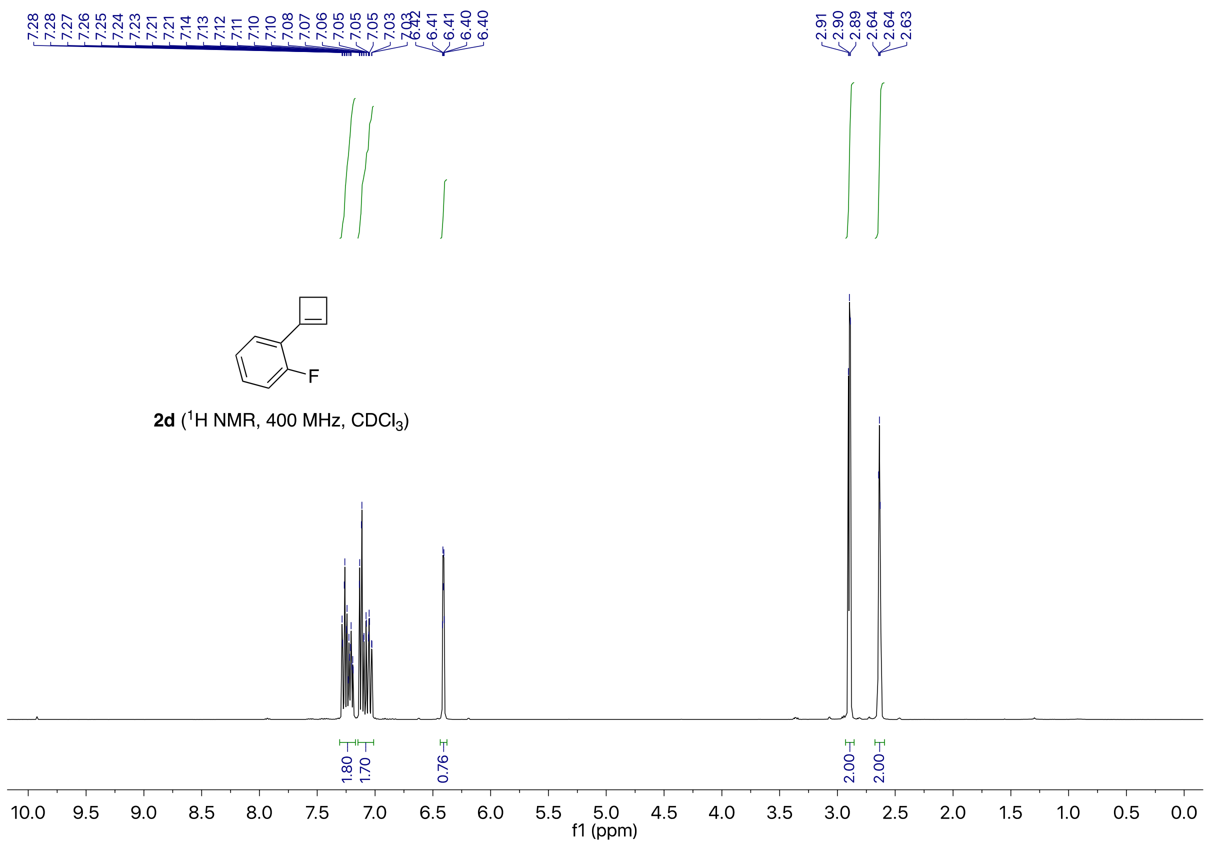
15d (^{13}C NMR, 101 MHz, $CDCl_3$)



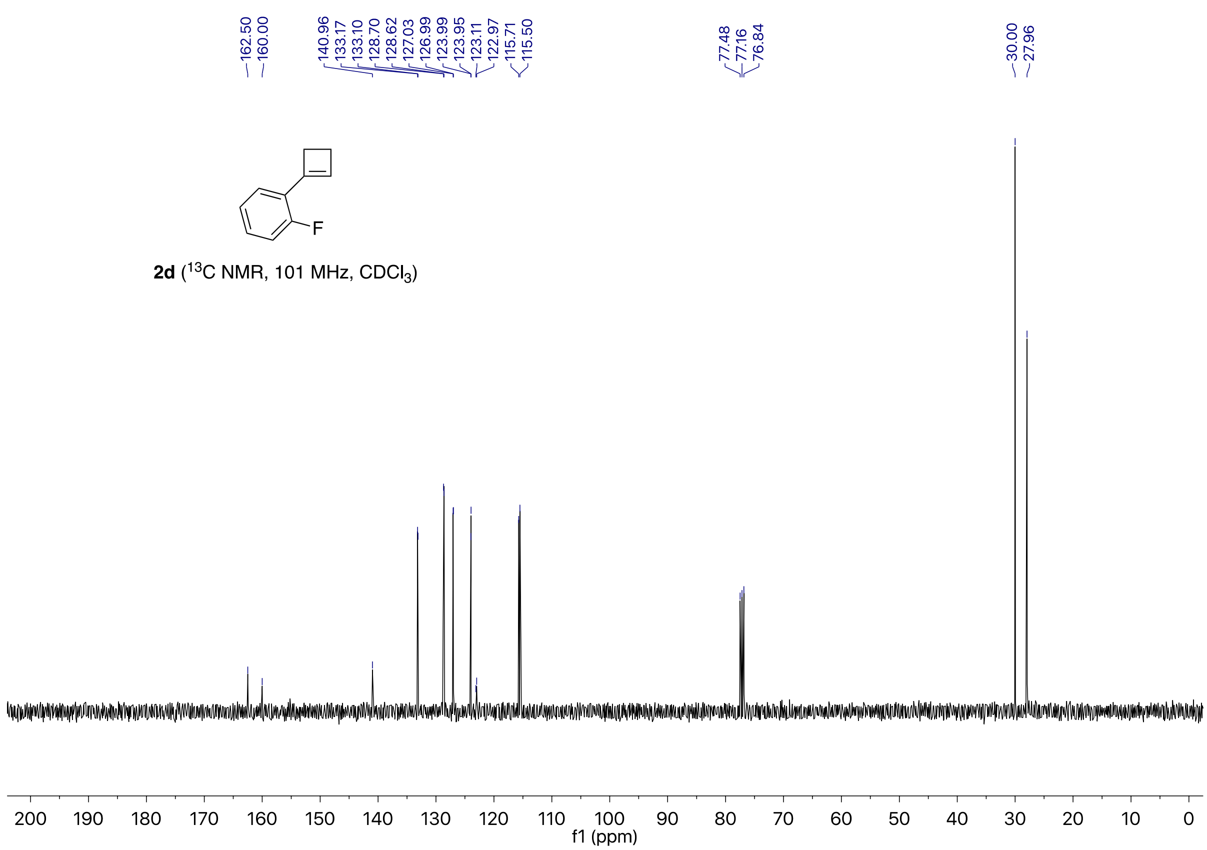
7.43 7.42 7.41 7.41 7.40 7.39 7.36 7.34 7.32 7.32 7.30 7.28 7.27 7.25 7.24 7.23 7.22 7.20
4.17 4.16 3.94 3.93 3.92 3.63 3.61 3.59 3.55 3.51 3.49 3.48 3.47 3.45
1.43
0.40 0.36
Boc
N
PhMe2Si
NBn2
7f (1H NMR, 400 MHz, CDCl3)
3.13 12.38 0.97 0.98 6.00 9.00 2.92 2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



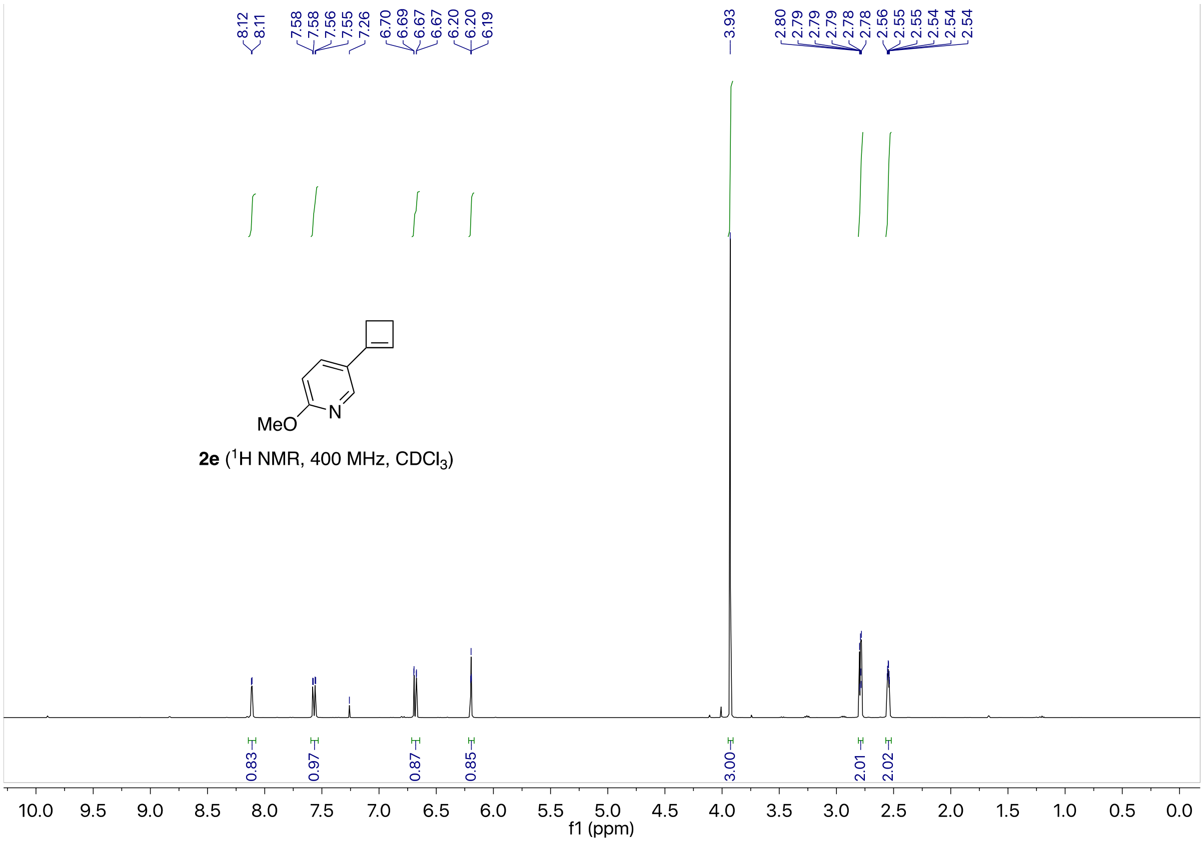
156.64
138.99 136.27 134.30 129.42 128.76 128.33 127.90 127.09
79.38 77.48 77.16 76.84
57.41 53.94 52.87 52.61
28.56
-4.15 -4.68
Boc
N
PhMe2Si
NBn2
7f (13C NMR, 101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



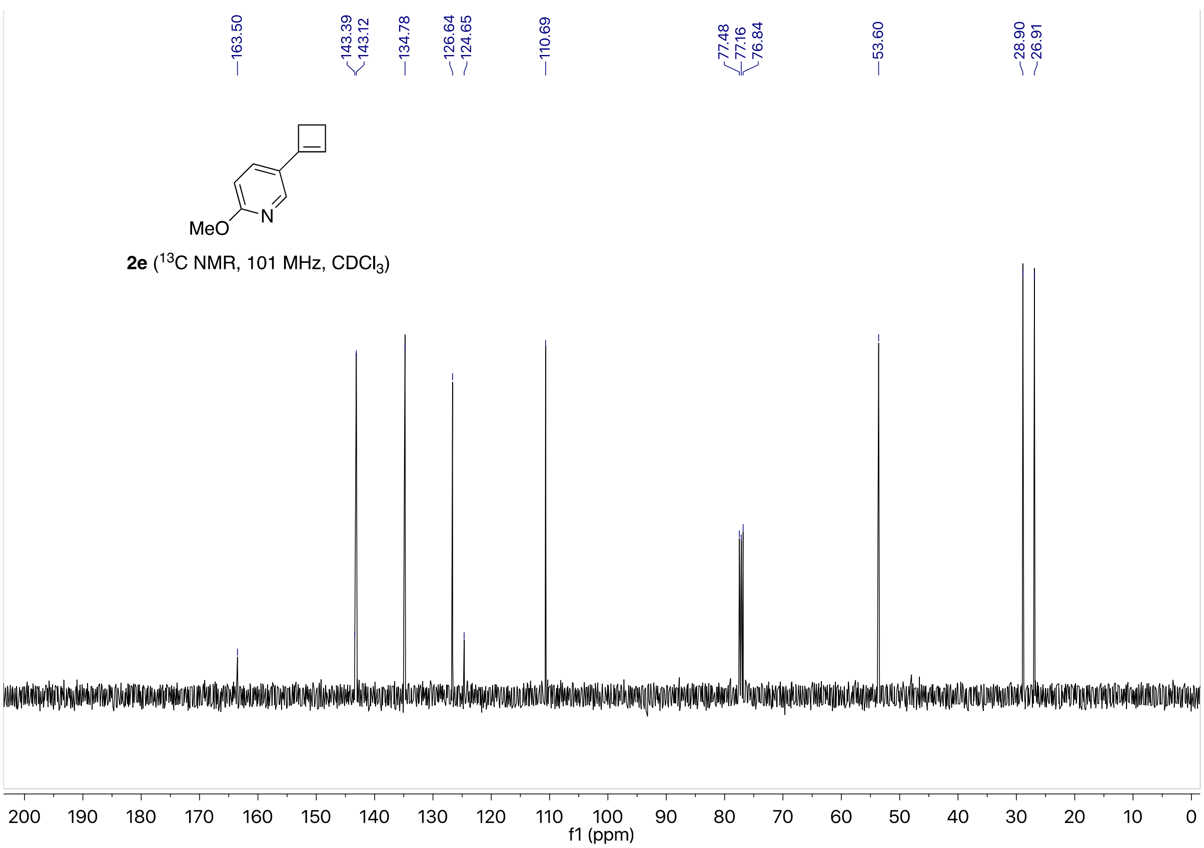
2d (^{1}H NMR, 400 MHz, $CDCl_3$)



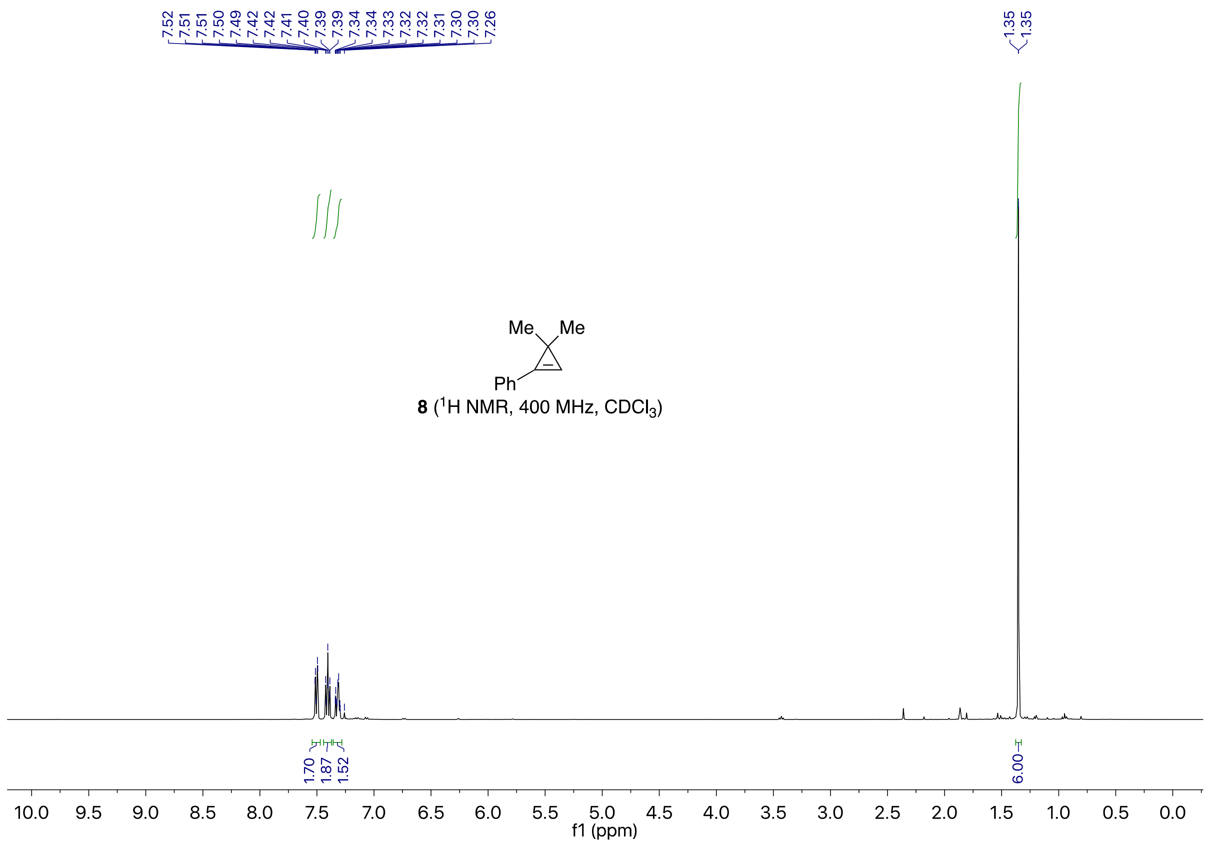
2d (^{13}C NMR, 101 MHz, $CDCl_3$)



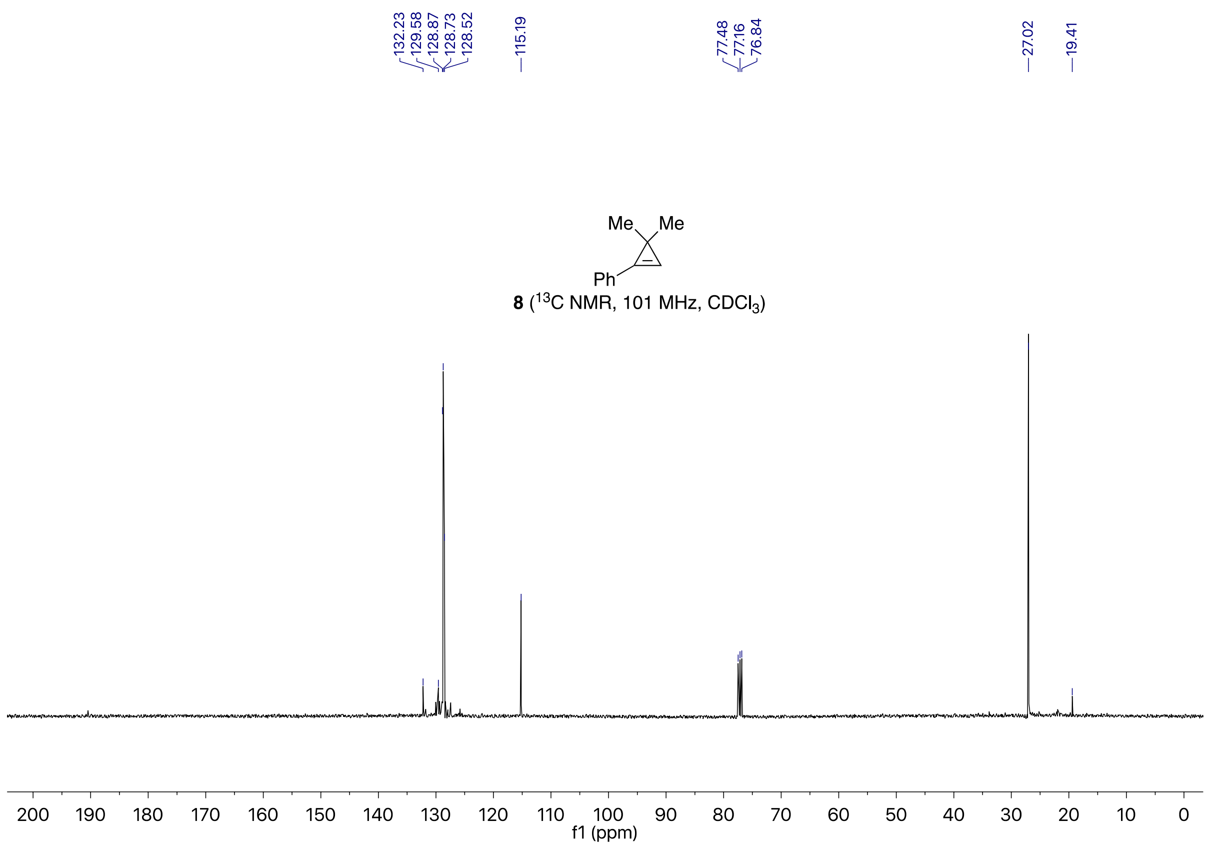
2e (^{1}H NMR, 400 MHz, $CDCl_3$)



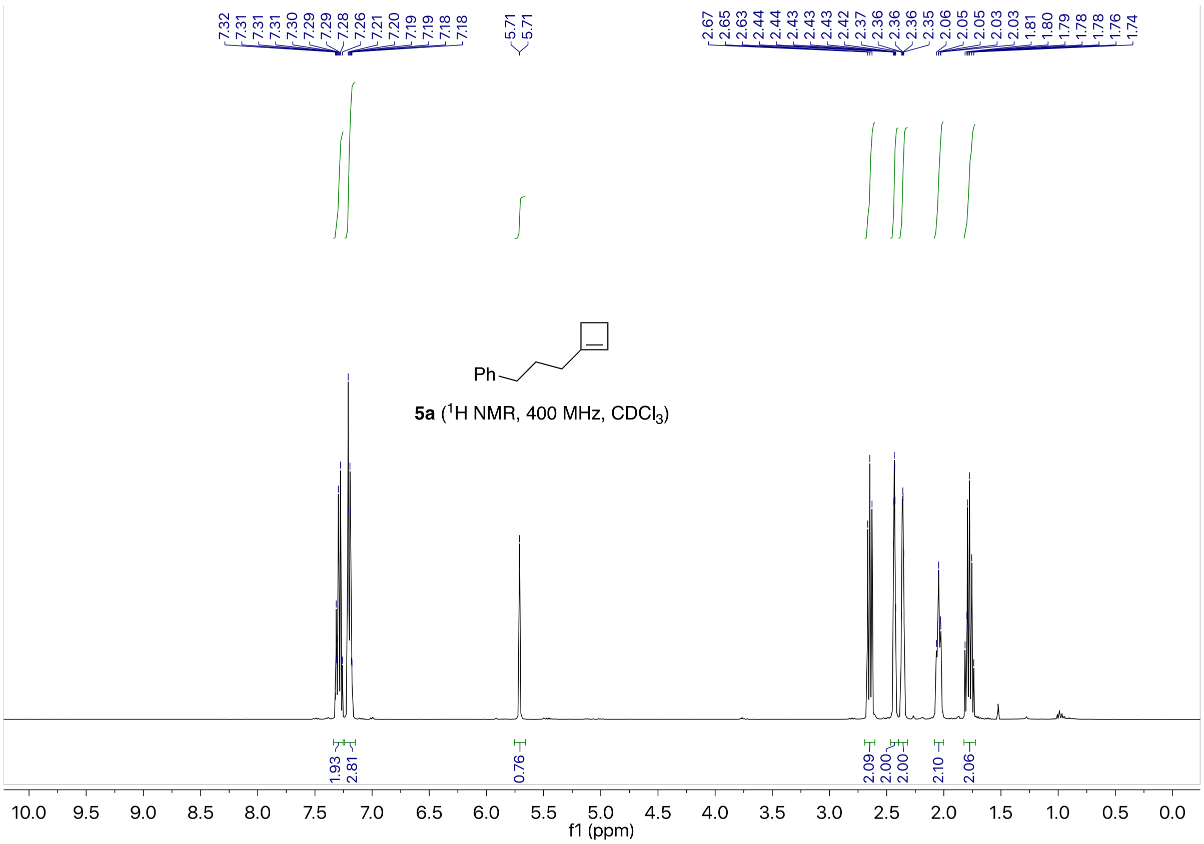
2e (^{13}C NMR, 101 MHz, $CDCl_3$)

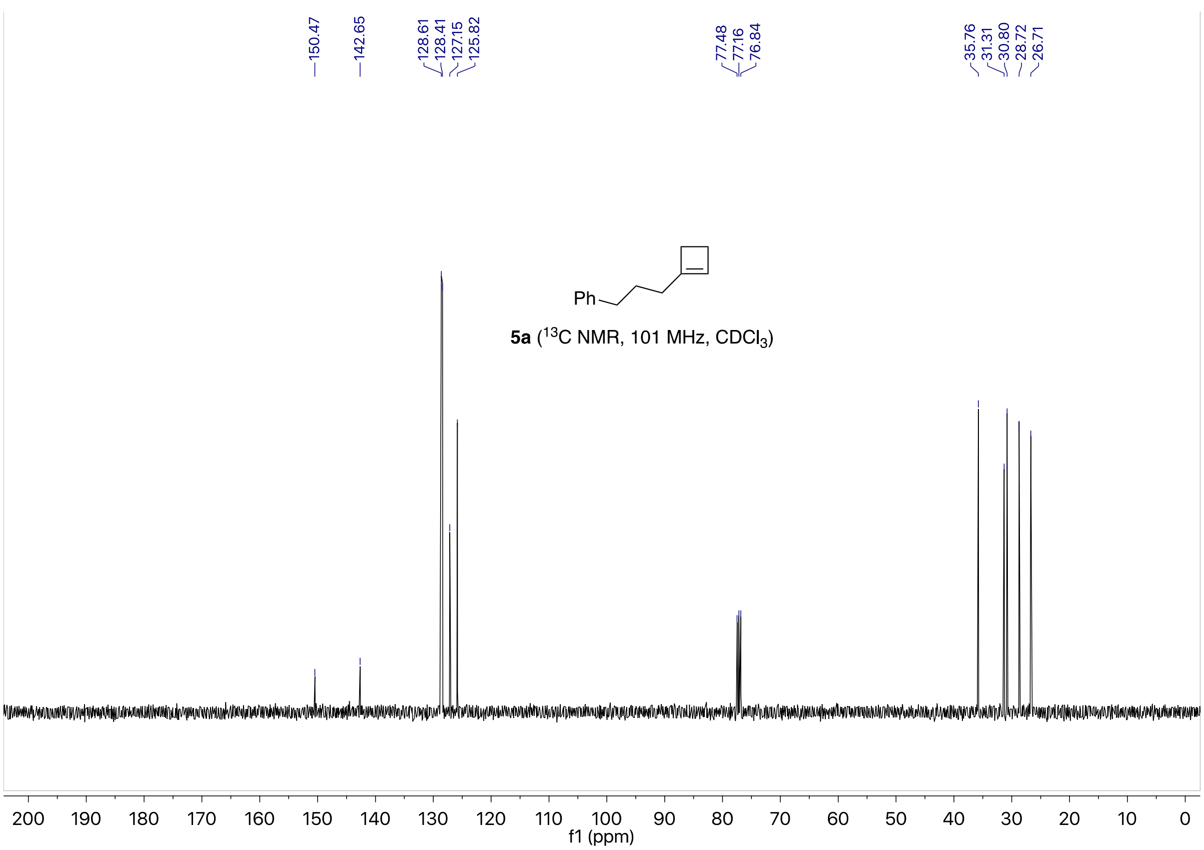


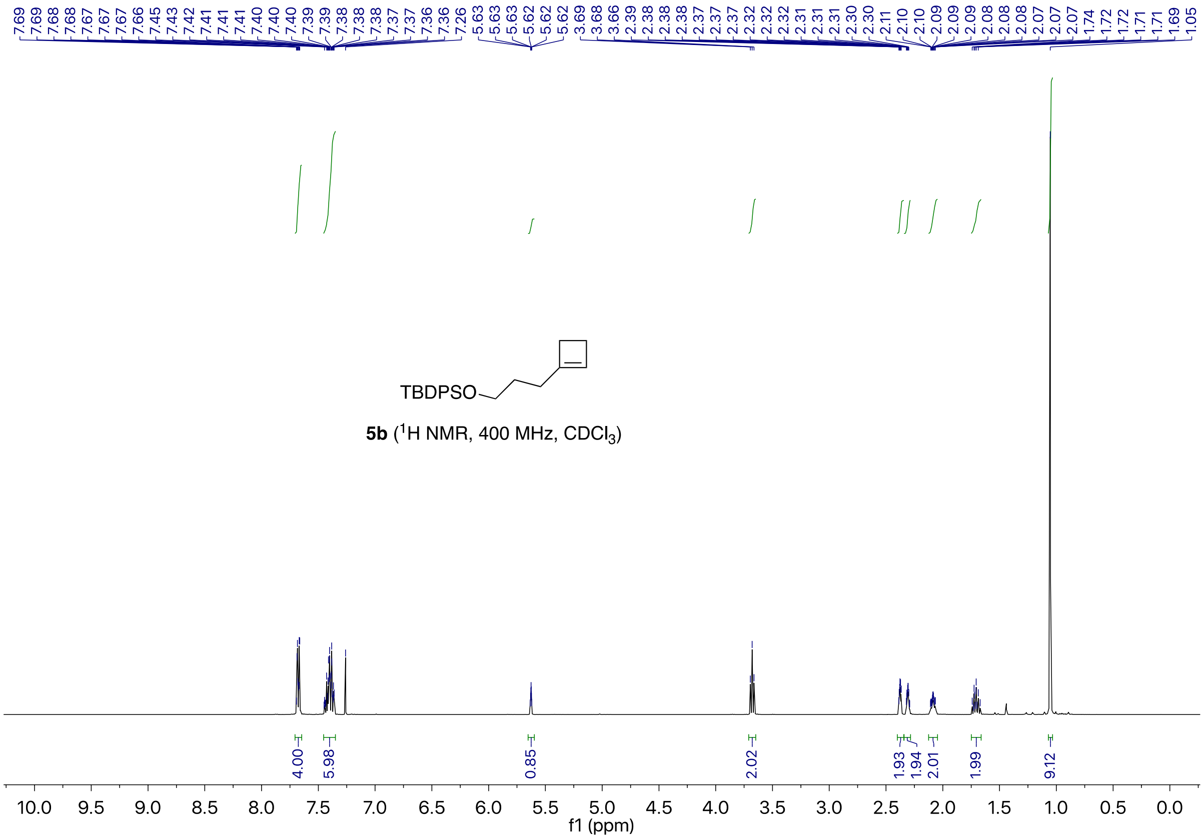
8 (^{1}H NMR, 400 MHz, $CDCl_3$)



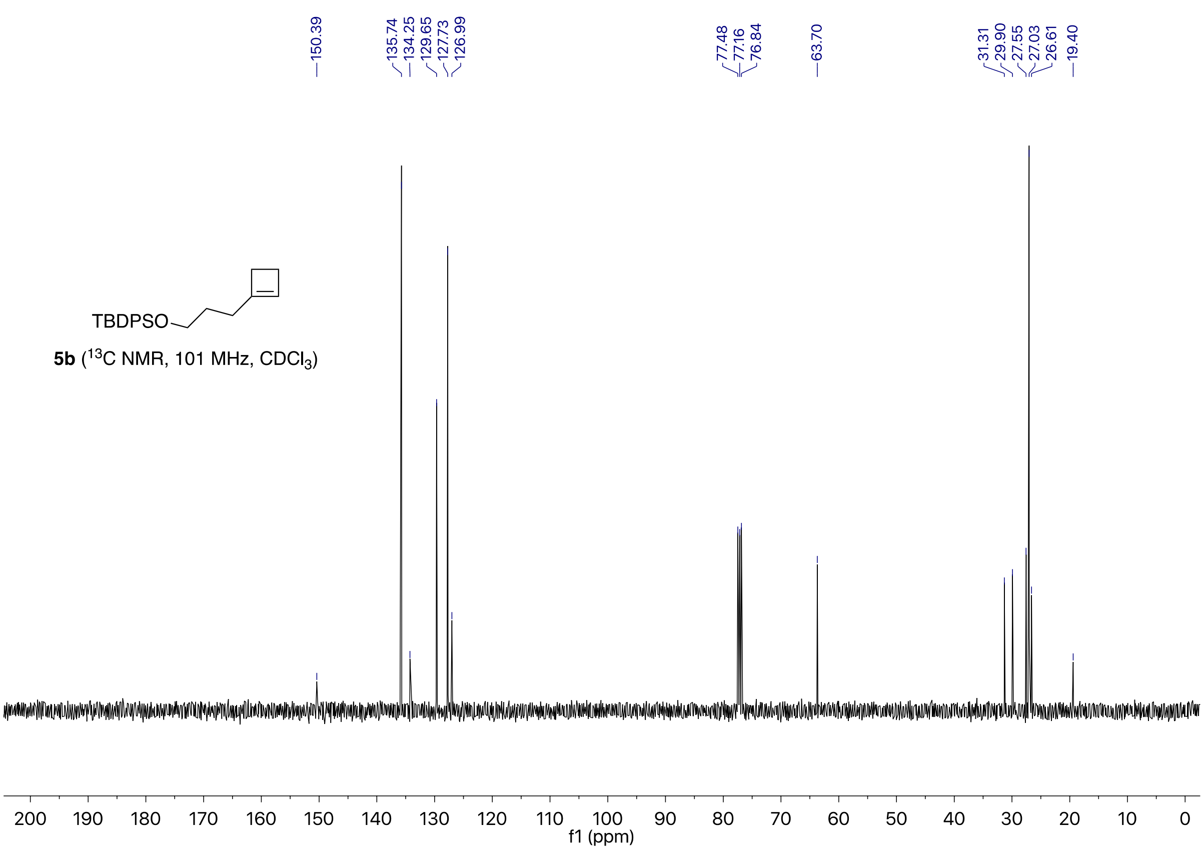
8 (^{13}C NMR, 101 MHz, $CDCl_3$)


7.32
7.31
7.31
7.30
7.29
7.29
7.28
7.26
7.21
7.20
7.19
7.19
7.18
7.18
5.71
5.71
2.67
2.65
2.63
2.44
2.44
2.43
2.43
2.43
2.42
2.37
2.36
2.36
2.36
2.35
2.06
2.05
2.05
2.03
2.03
1.81
1.80
1.79
1.78
1.78
1.76
1.74
Ph
5a (¹H NMR, 400 MHz, CDCl₃)
1.93
2.81
0.76
2.09
2.00
2.00
2.10
2.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

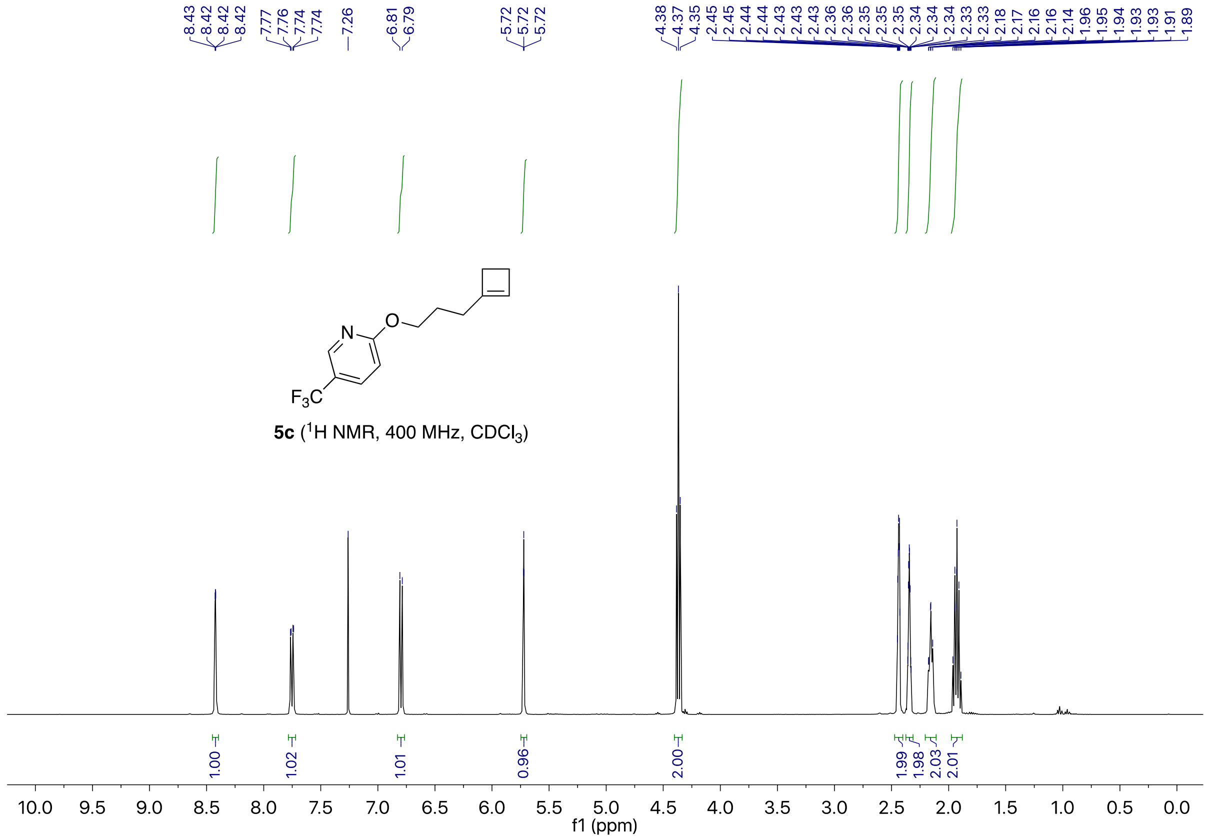

150.47
142.65
128.61
128.41
127.15
125.82
77.48
77.16
76.84
35.76
31.31
30.80
28.72
26.71
Ph
5a (¹³C NMR, 101 MHz, CDCl₃)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



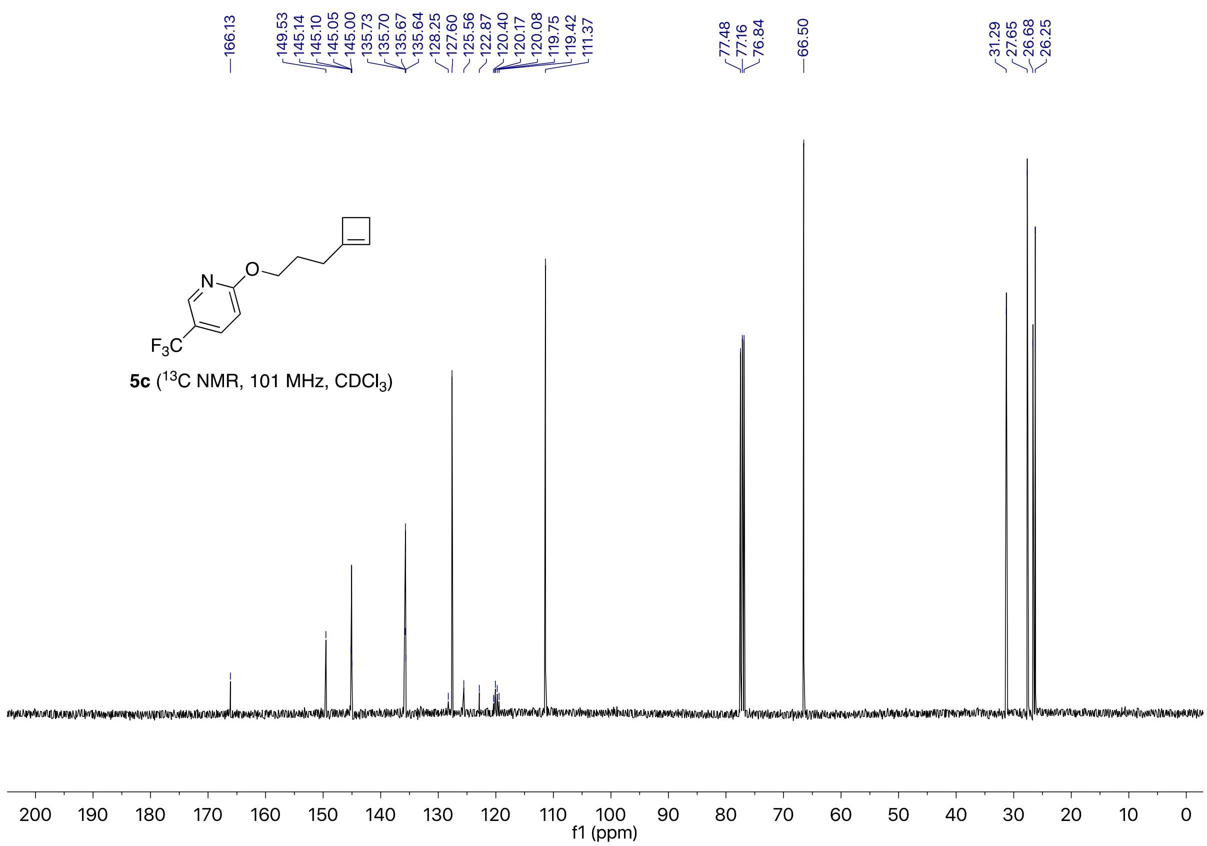
5b (^{1}H NMR, 400 MHz, $CDCl_3$)



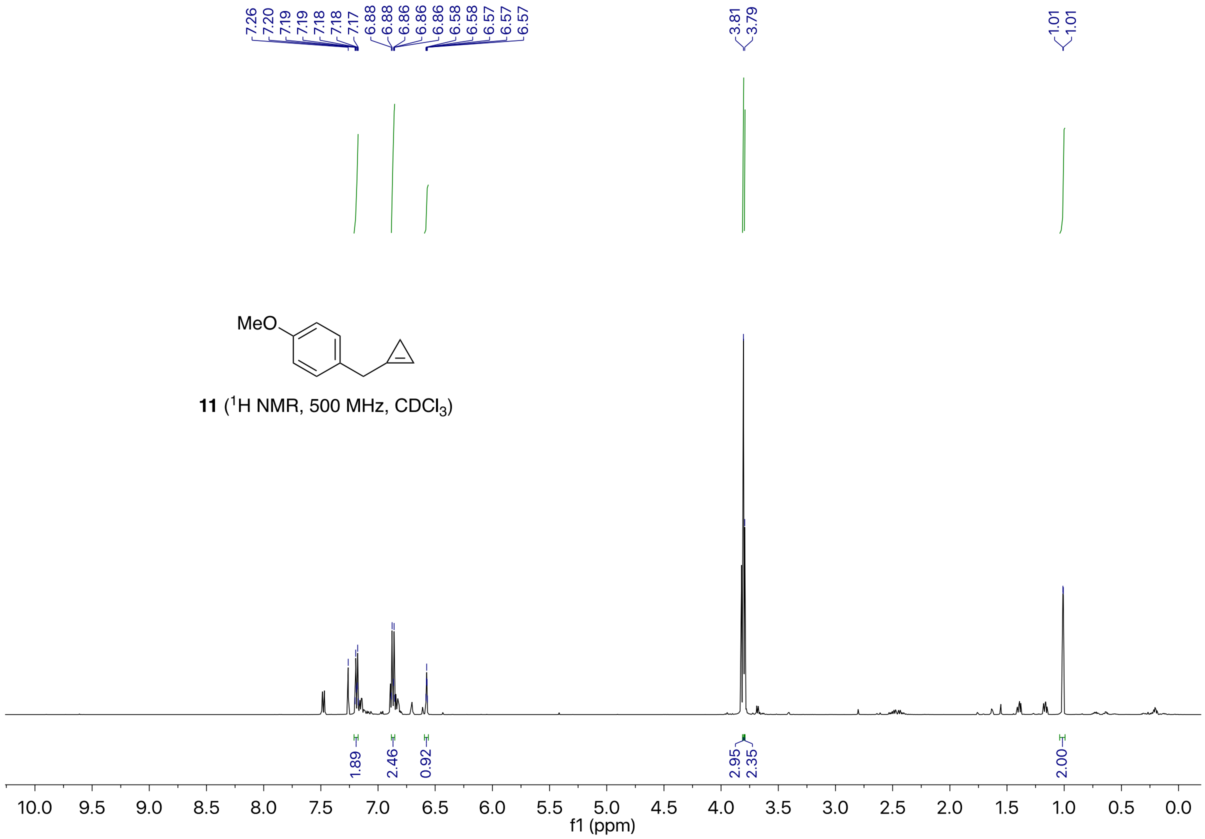
5b (^{13}C NMR, 101 MHz, $CDCl_3$)



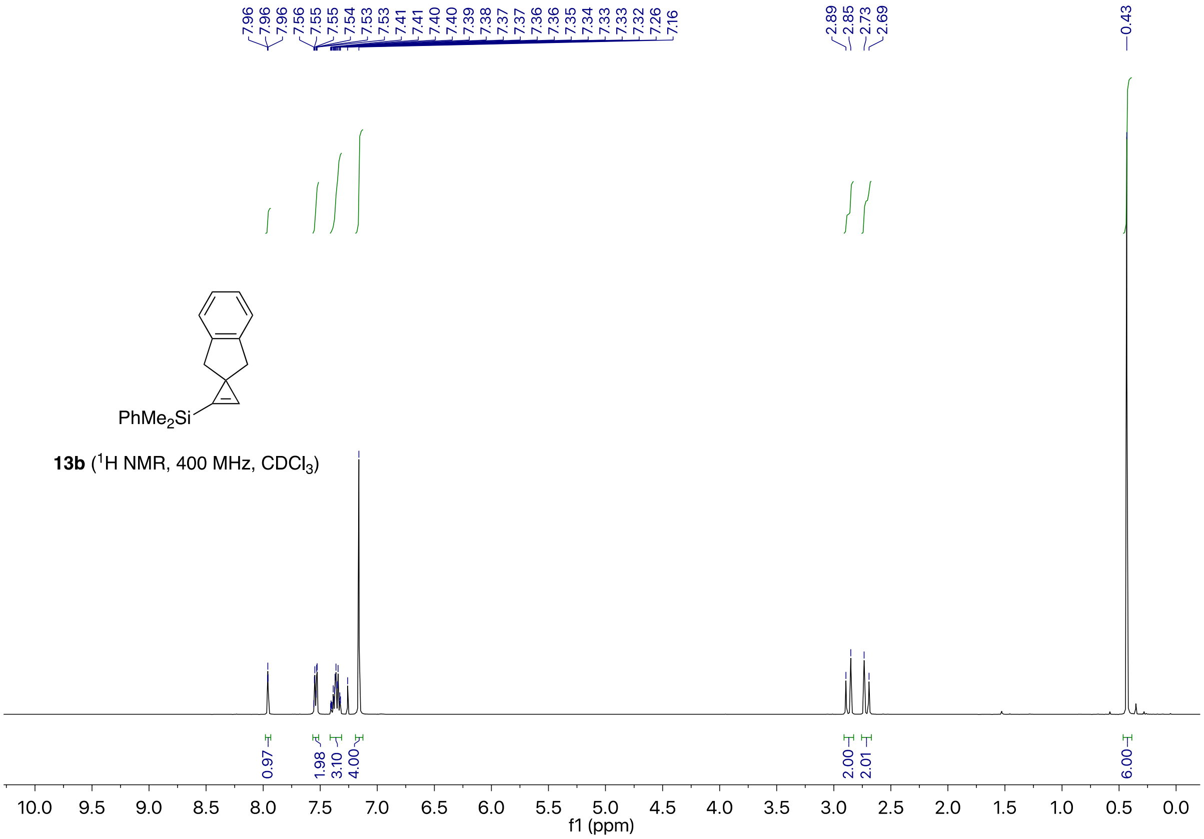
5c (^{1}H NMR, 400 MHz, $CDCl_3$)

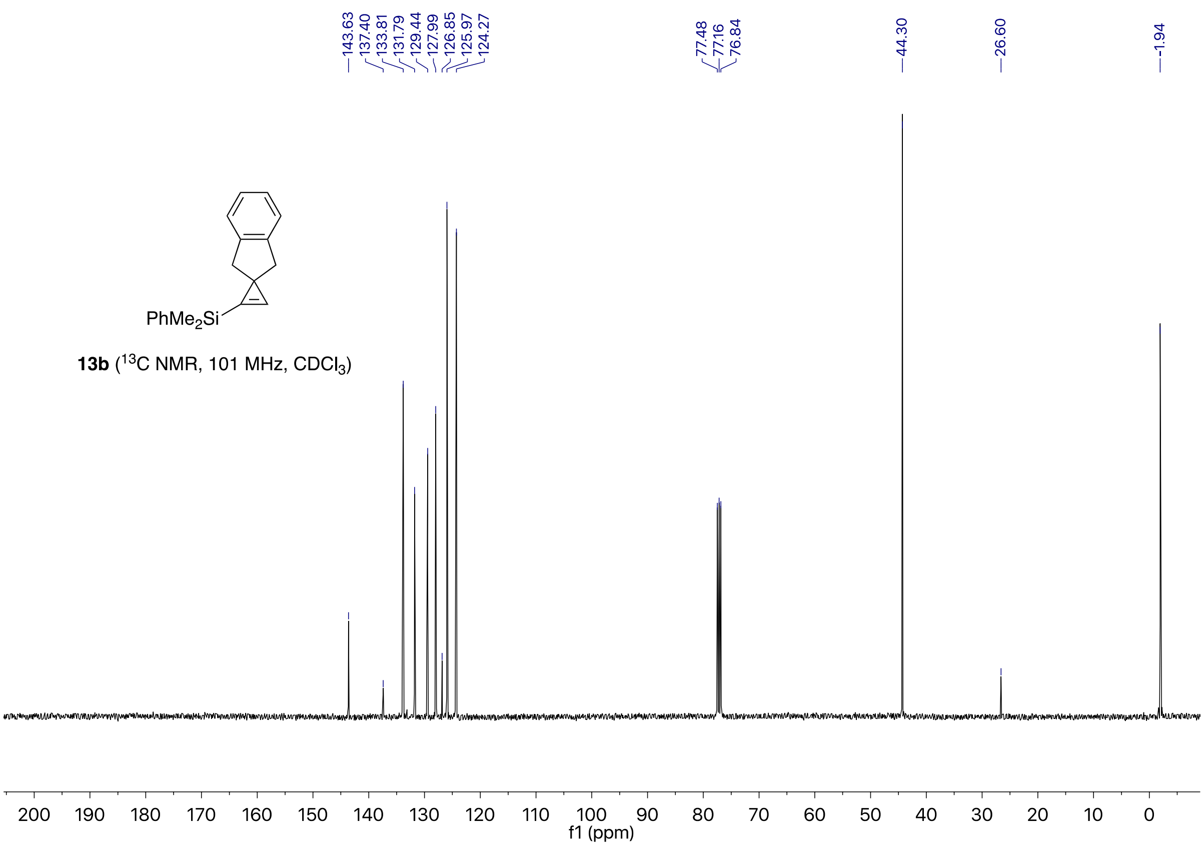


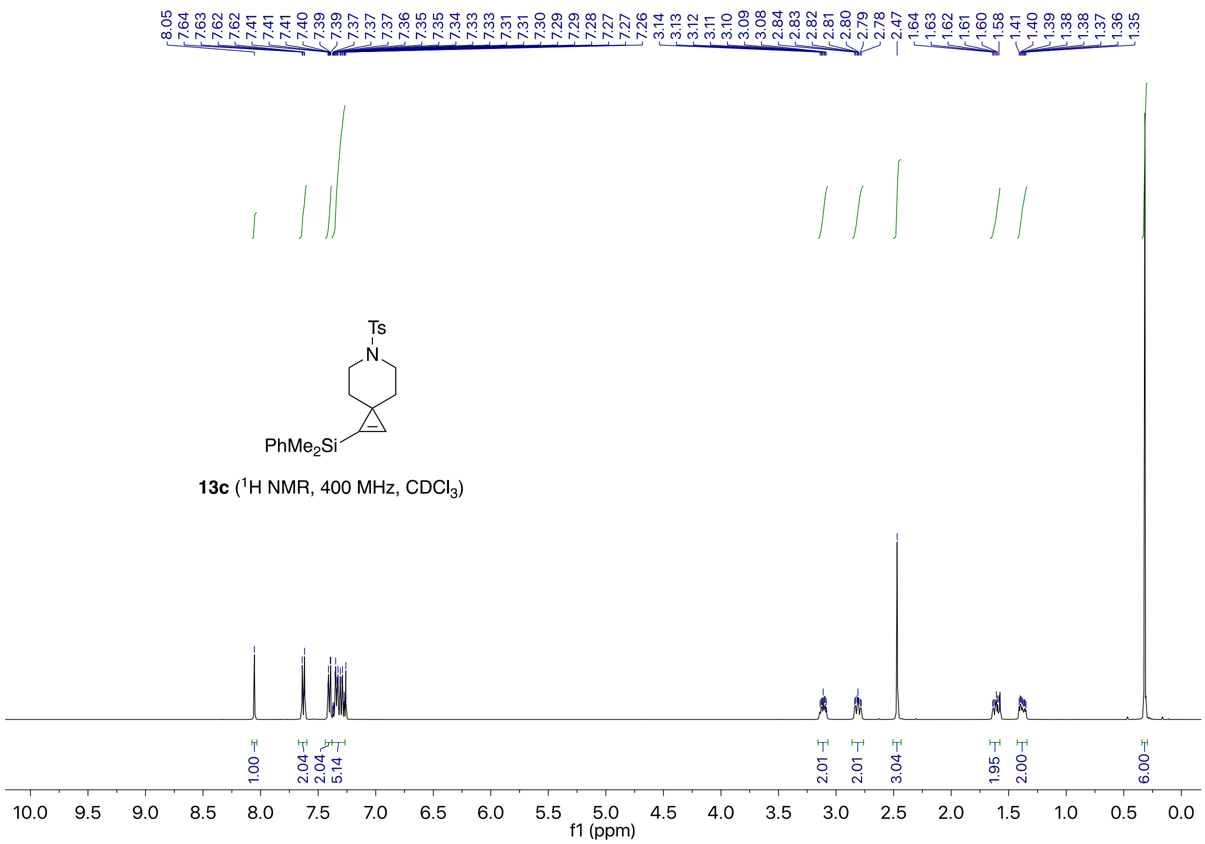
5c (^{13}C NMR, 101 MHz, $CDCl_3$)



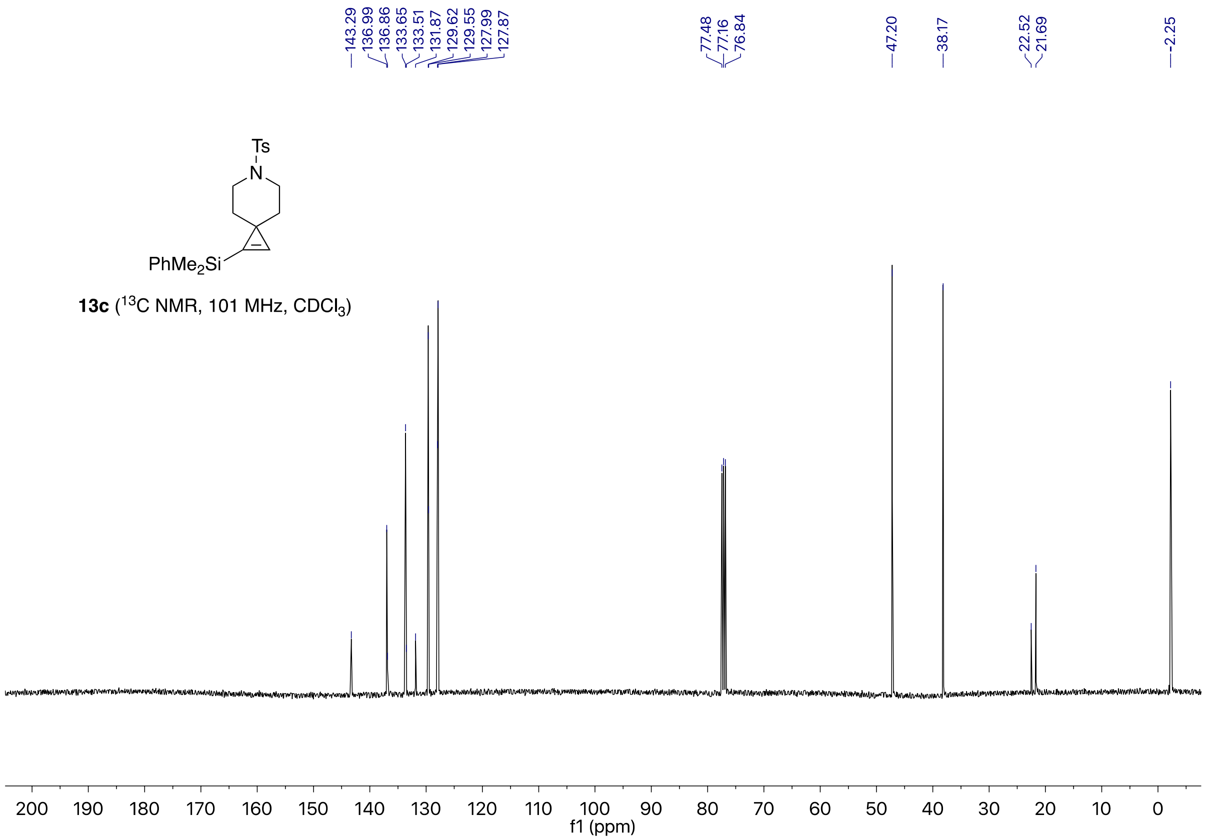
11 (^{1}H NMR, 500 MHz, $CDCl_3$)


7.96
7.96
7.96
7.56
7.55
7.55
7.54
7.53
7.53
7.41
7.41
7.40
7.40
7.39
7.38
7.37
7.37
7.36
7.36
7.35
7.34
7.33
7.33
7.32
7.26
7.16
2.89
2.85
2.73
2.69
0.43
PhMe2Si
13b (1H NMR, 400 MHz, CDCl3)
0.97
1.98
3.10
4.00
2.00
2.01
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

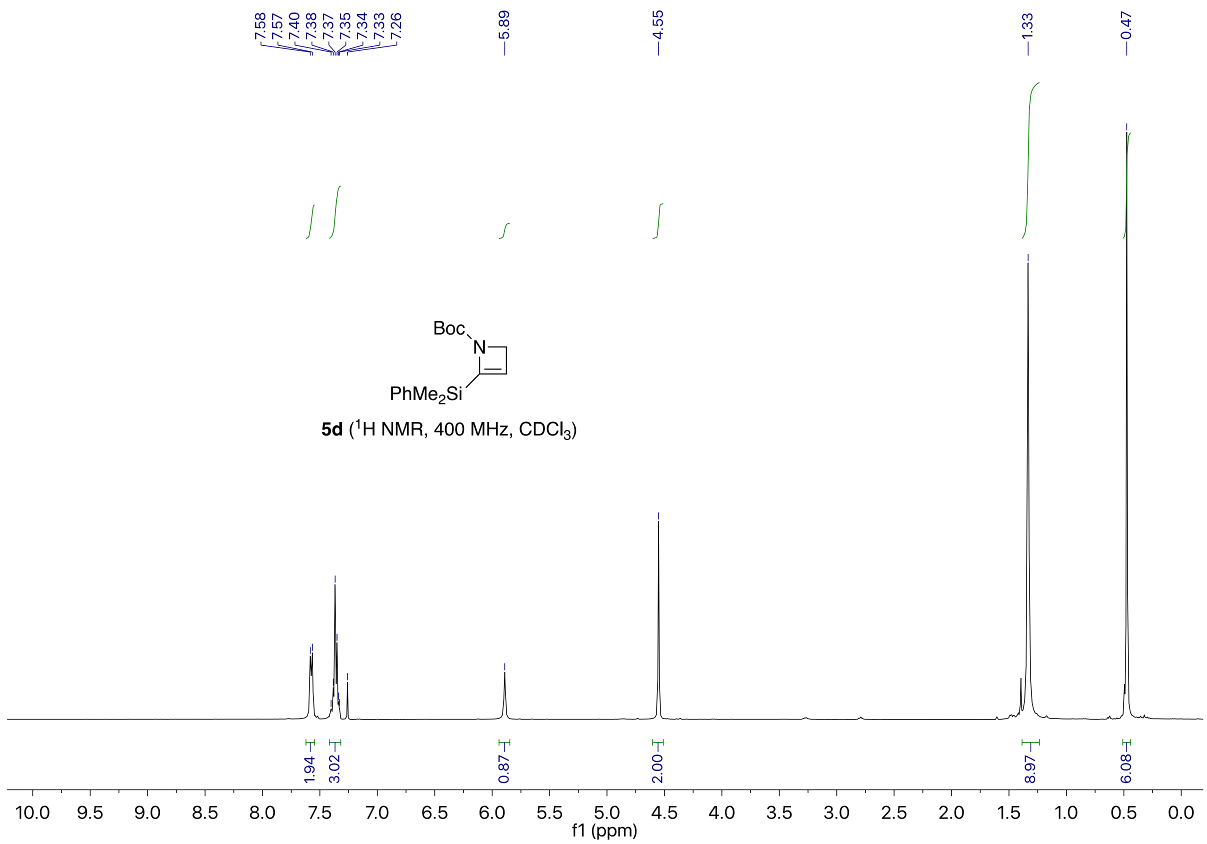

143.63
137.40
133.81
131.79
129.44
127.99
126.85
125.97
124.27
77.48
77.16
76.84
44.30
26.60
-1.94
PhMe2Si
13b (13C NMR, 101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



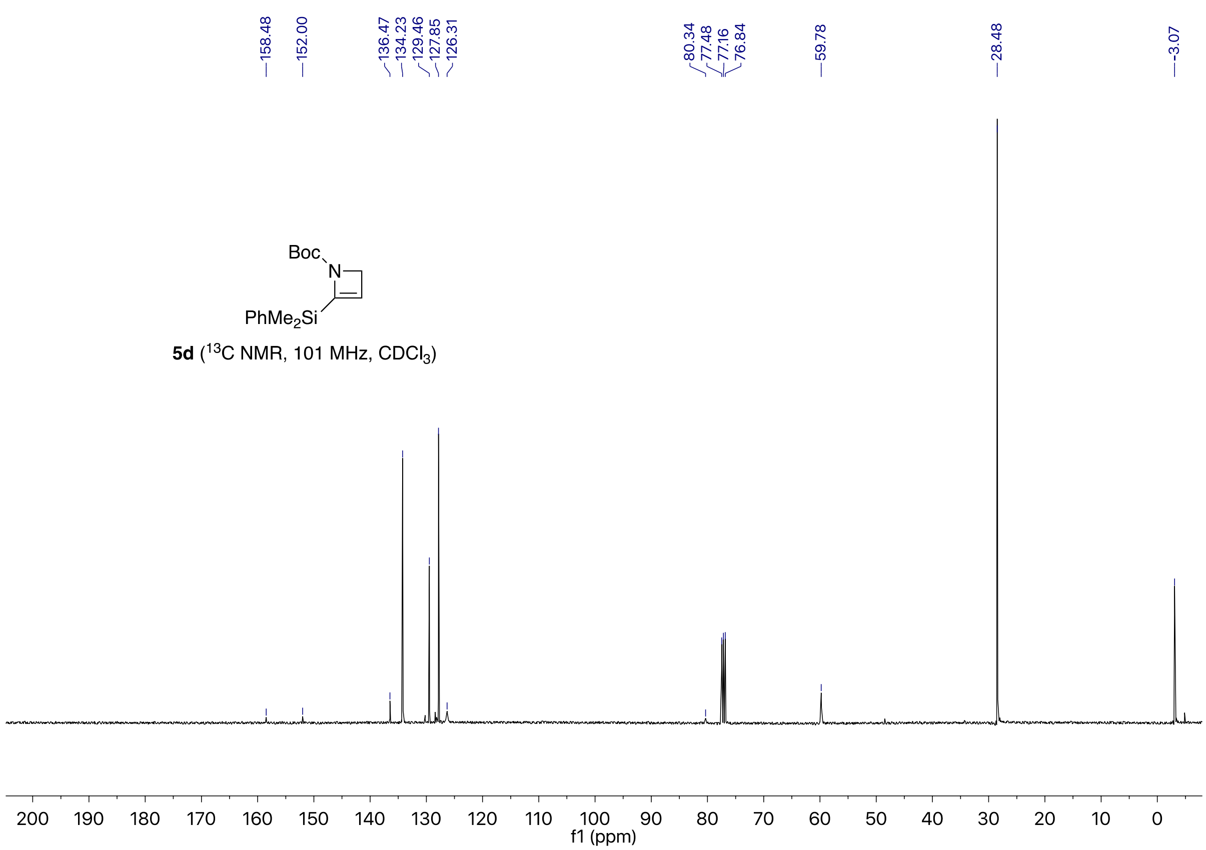
13c (^{1}H NMR, 400 MHz, $CDCl_3$)



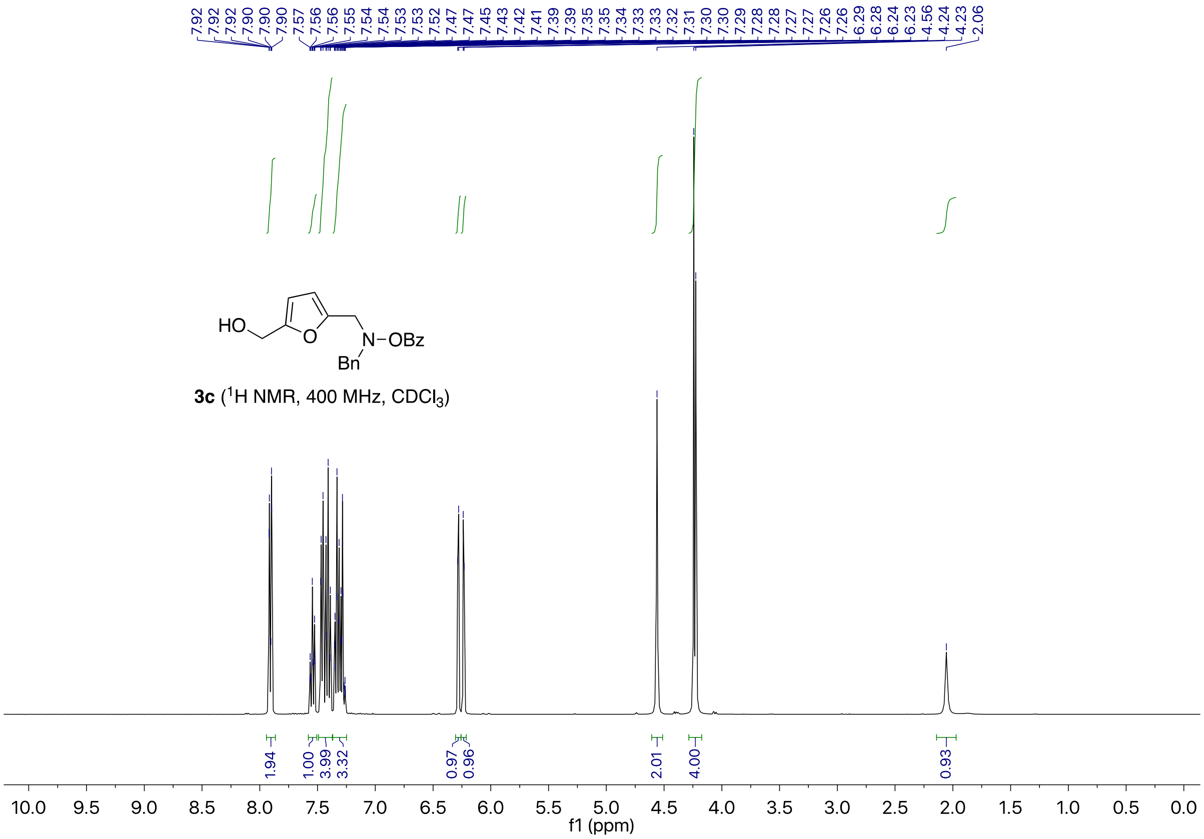
13c (^{13}C NMR, 101 MHz, $CDCl_3$)



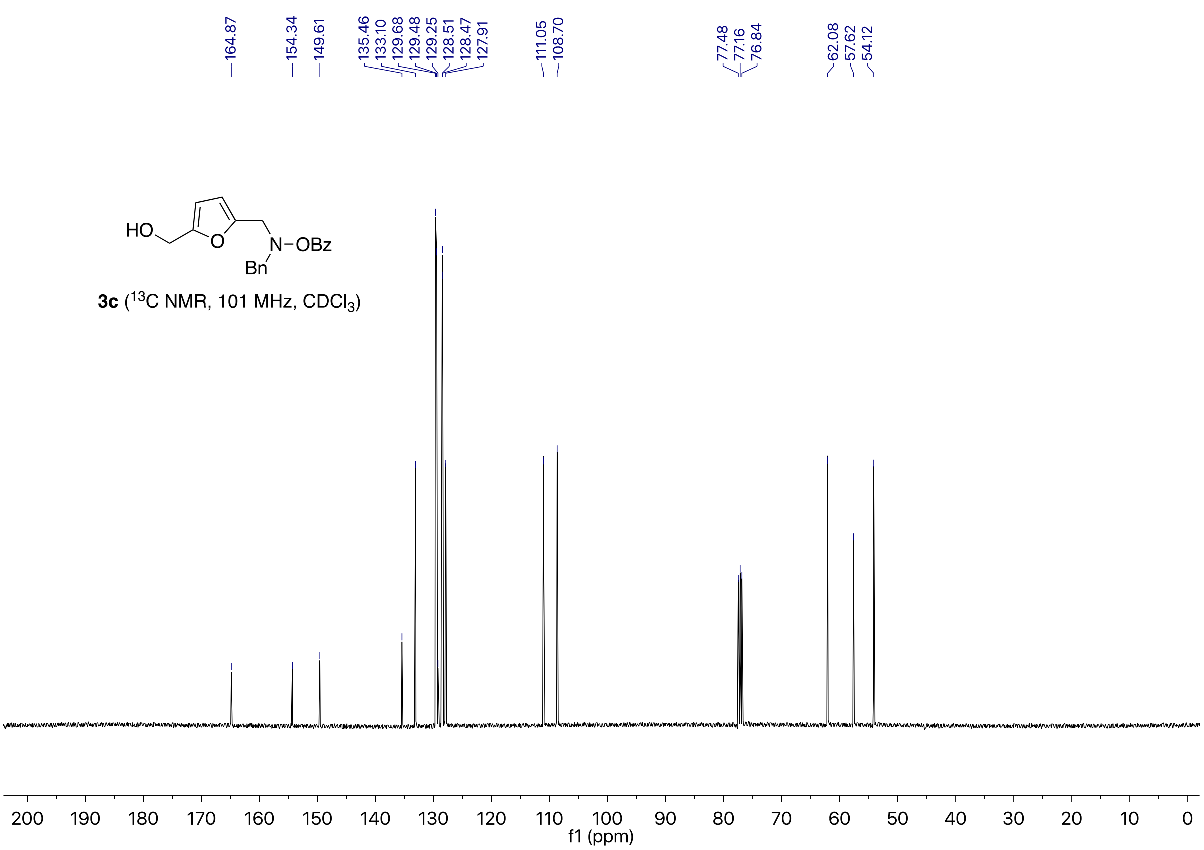
5d (^{1}H NMR, 400 MHz, $CDCl_3$)



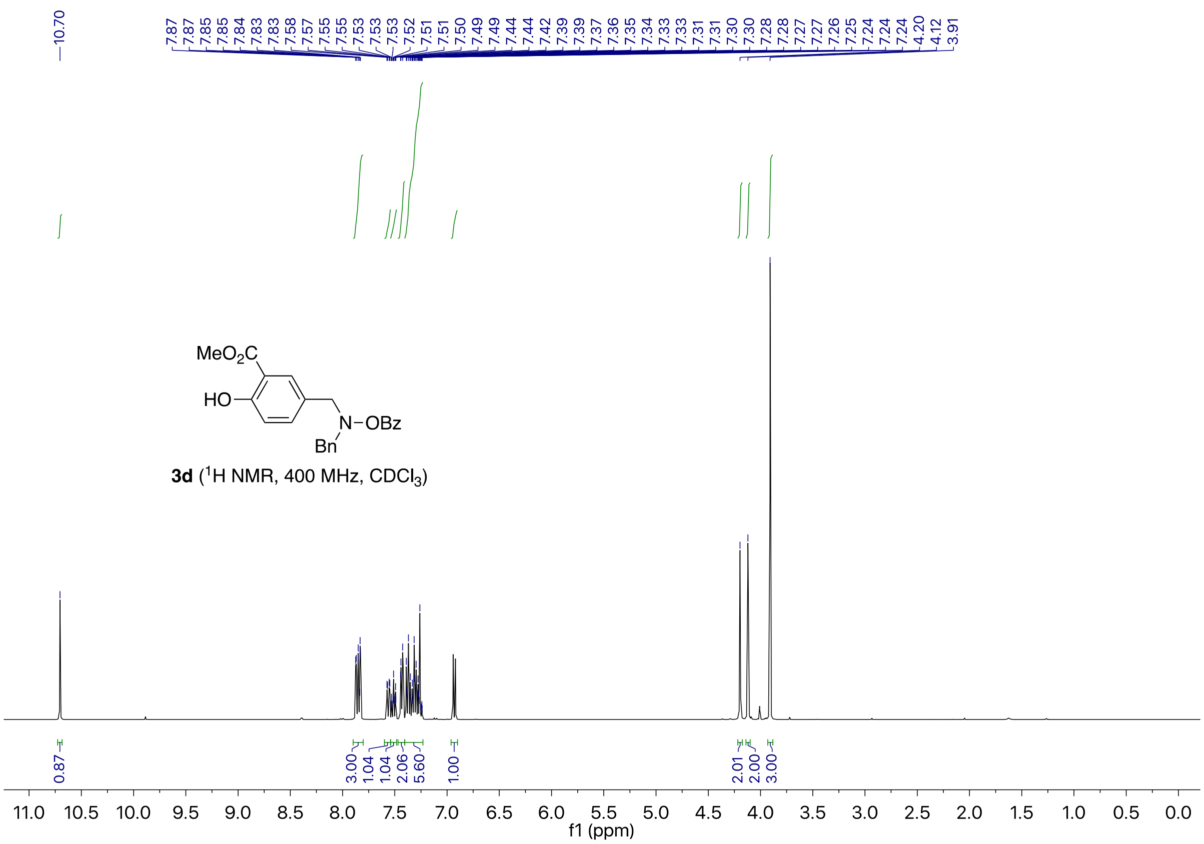
5d (^{13}C NMR, 101 MHz, $CDCl_3$)

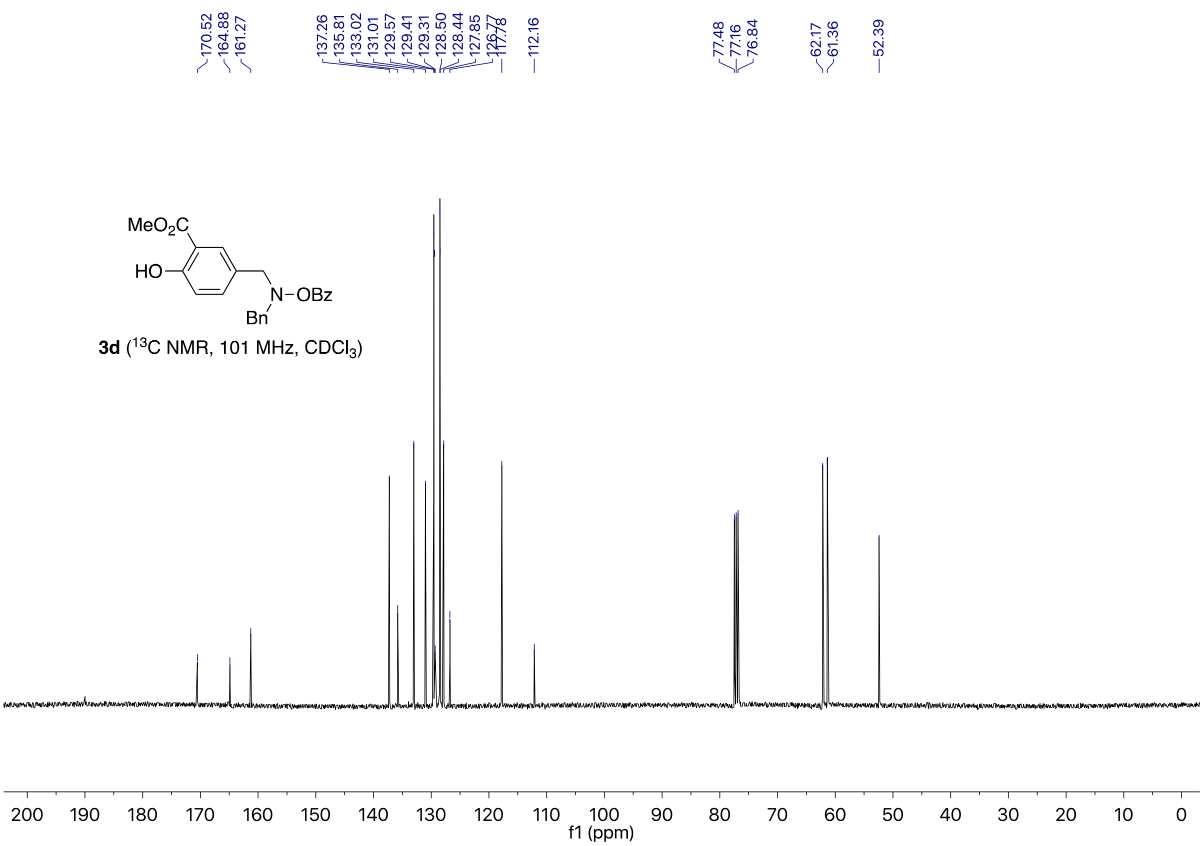


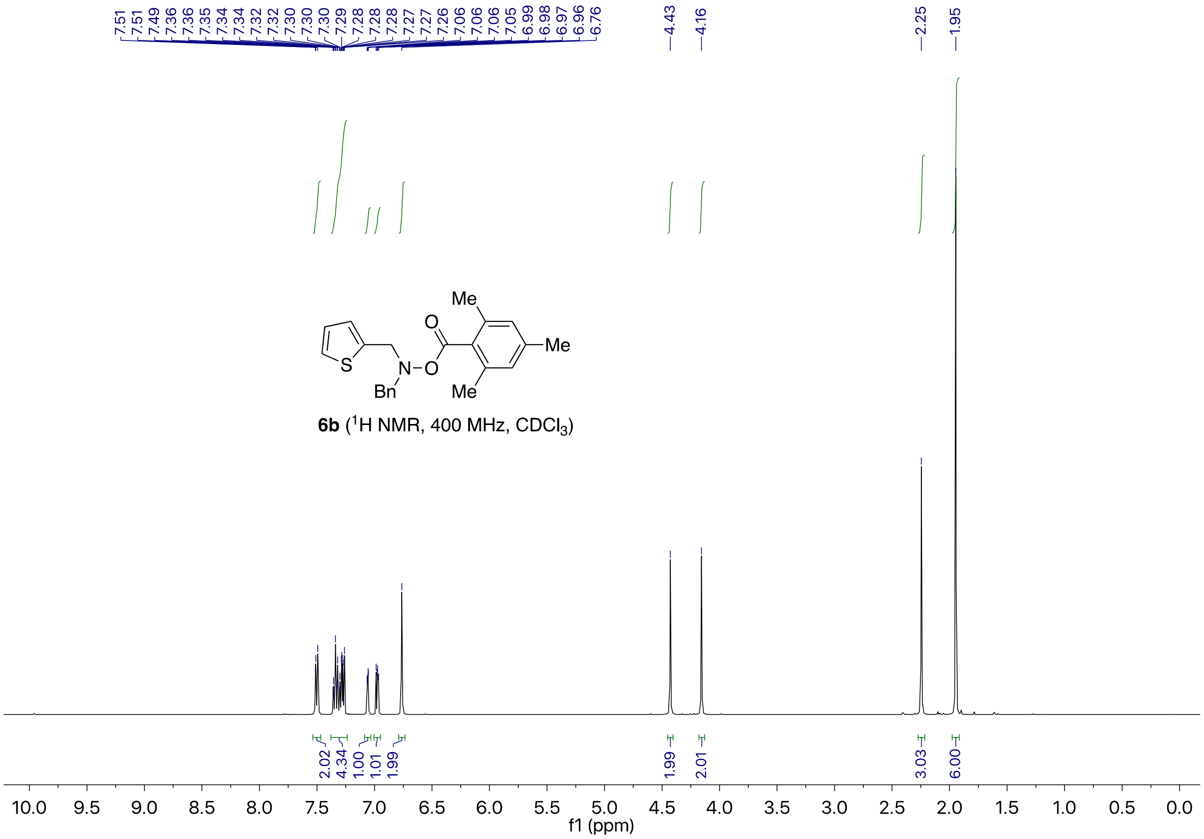
3c (^{1}H NMR, 400 MHz, $CDCl_3$)



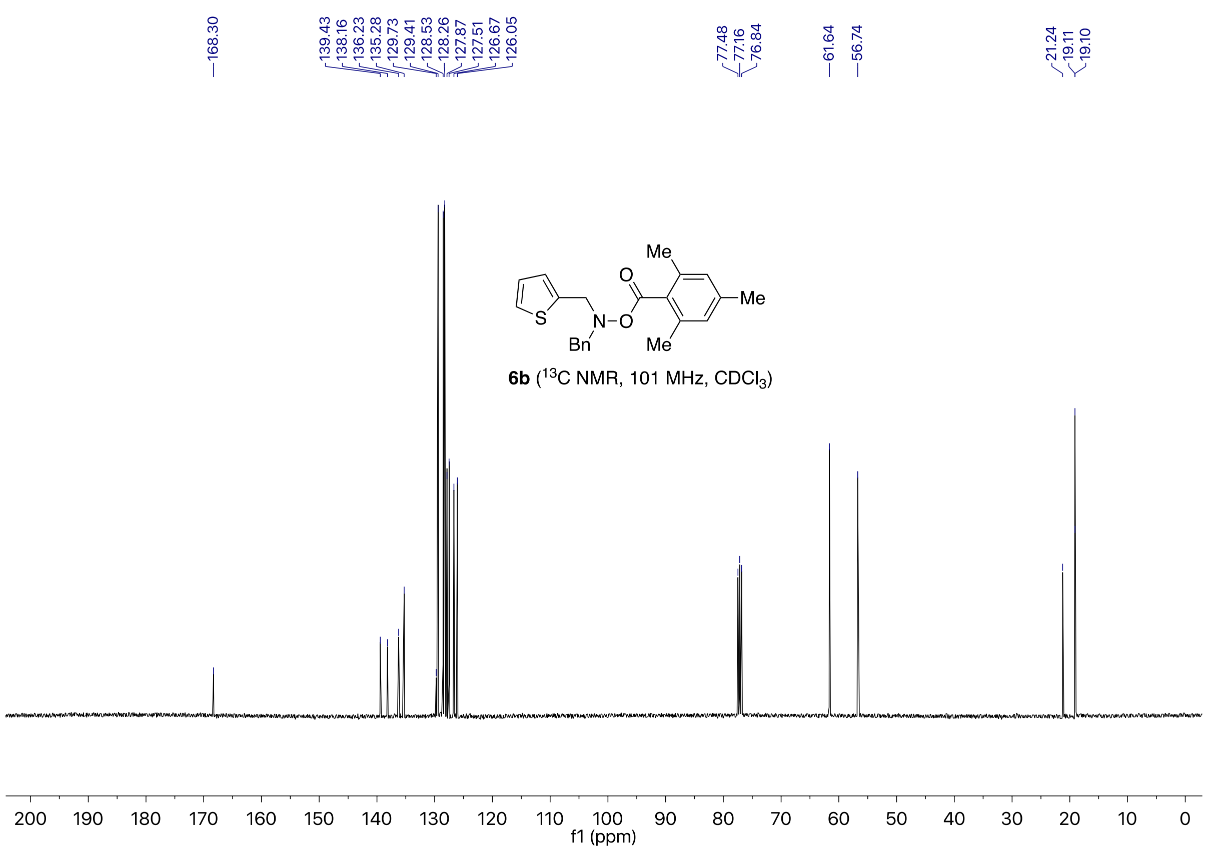
3c (^{13}C NMR, 101 MHz, $CDCl_3$)


MeO2C
HO
N−OBz
Bn
3d (1H NMR, 400 MHz, CDCl3)
f1 (ppm)

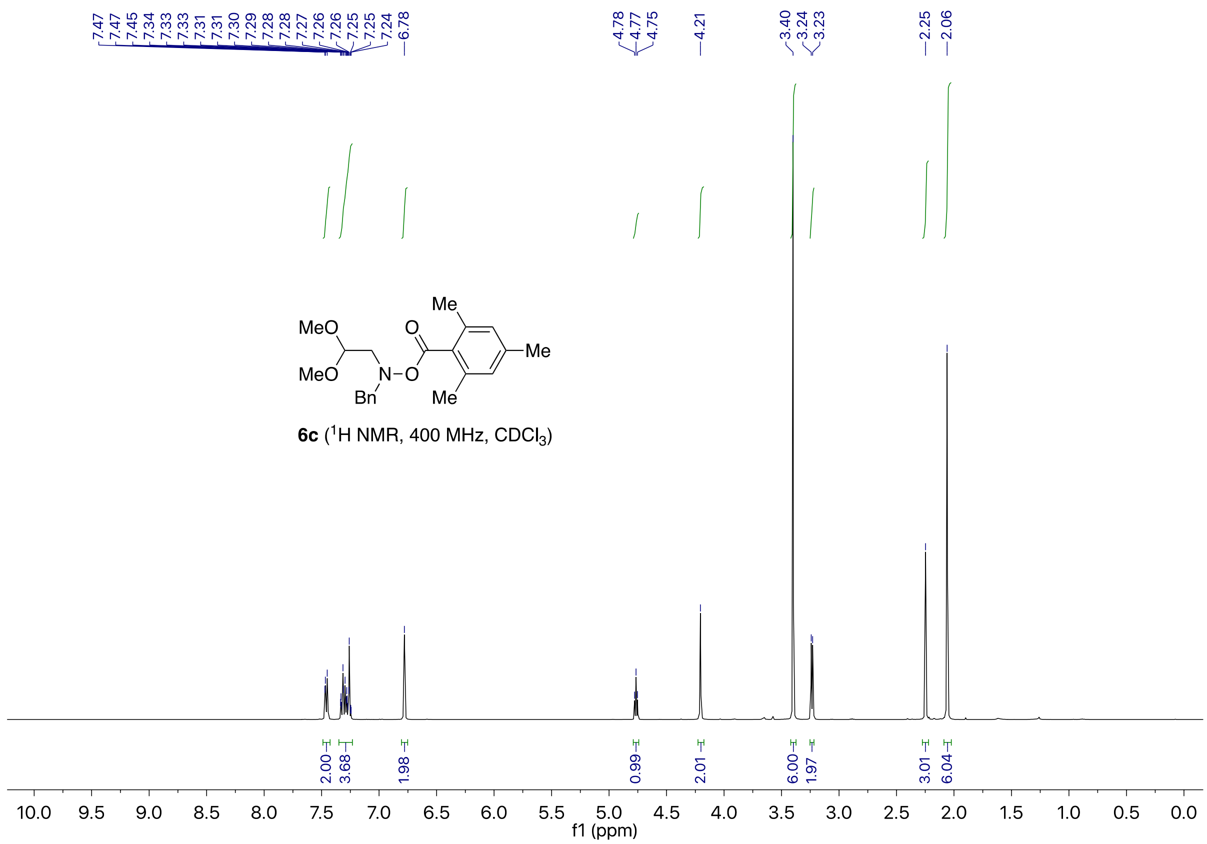

MeO2C
HO
N−OBz
Bn
3d (13C NMR, 101 MHz, CDCl3)
f1 (ppm)



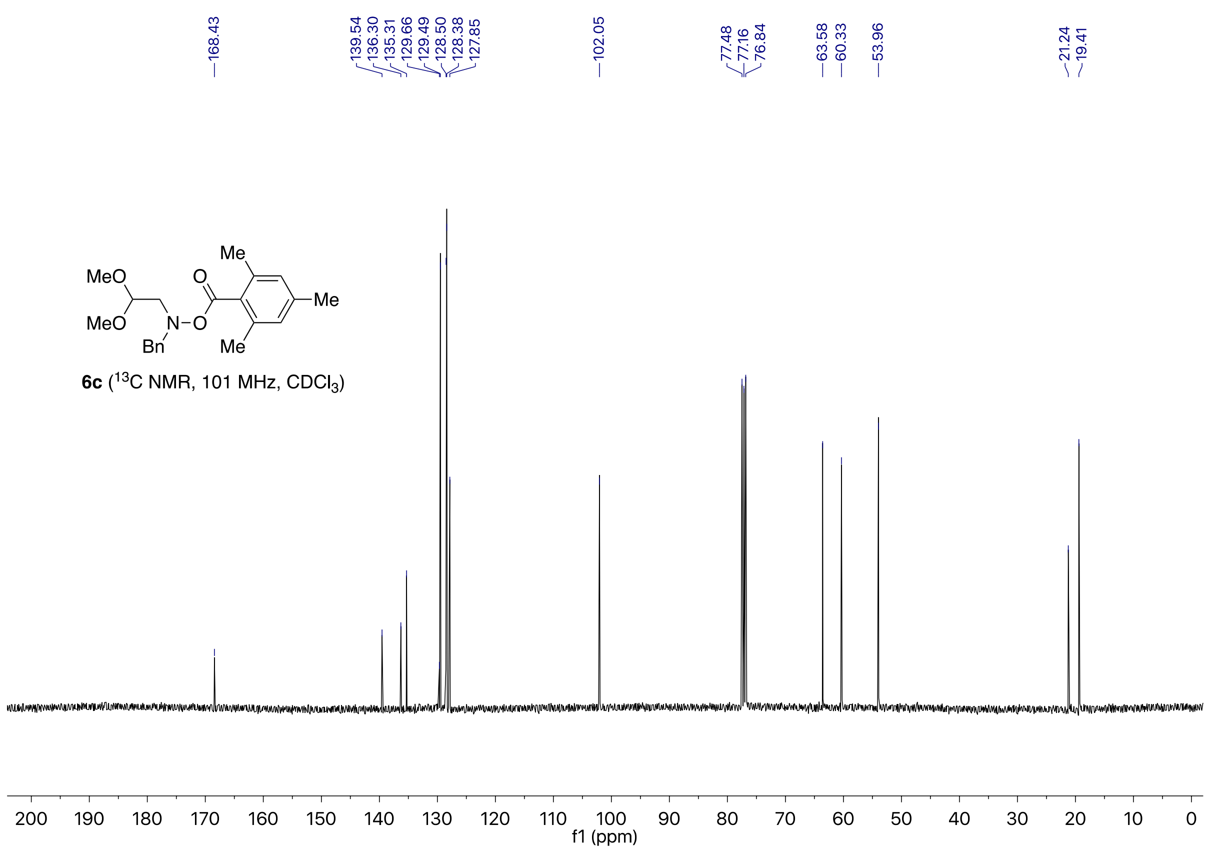
6b (^{1}H NMR, 400 MHz, $CDCl_3$)



6b (^{13}C NMR, 101 MHz, $CDCl_3$)



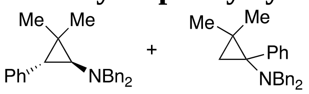
7.47
7.47
7.45
7.34
7.33
7.33
7.31
7.31
7.30
7.29
7.28
7.28
7.27
7.26
7.26
7.25
7.25
7.24
6.78
4.78
4.77
4.75
4.21
3.40
3.24
3.23
2.25
2.06
MeO
MeO
O
N–O
Bn
Me
Me
Me
6c (1H NMR, 400 MHz, CDCl3)
2.00
3.68
1.98
0.99
2.01
6.00
1.97
3.01
6.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



168.43
139.54
136.30
135.31
129.66
129.49
128.50
128.38
127.85
102.05
77.48
77.16
76.84
63.58
60.33
53.96
21.24
19.41
MeO
MeO
O
N–O
Bn
Me
Me
Me
6c (13C NMR, 101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

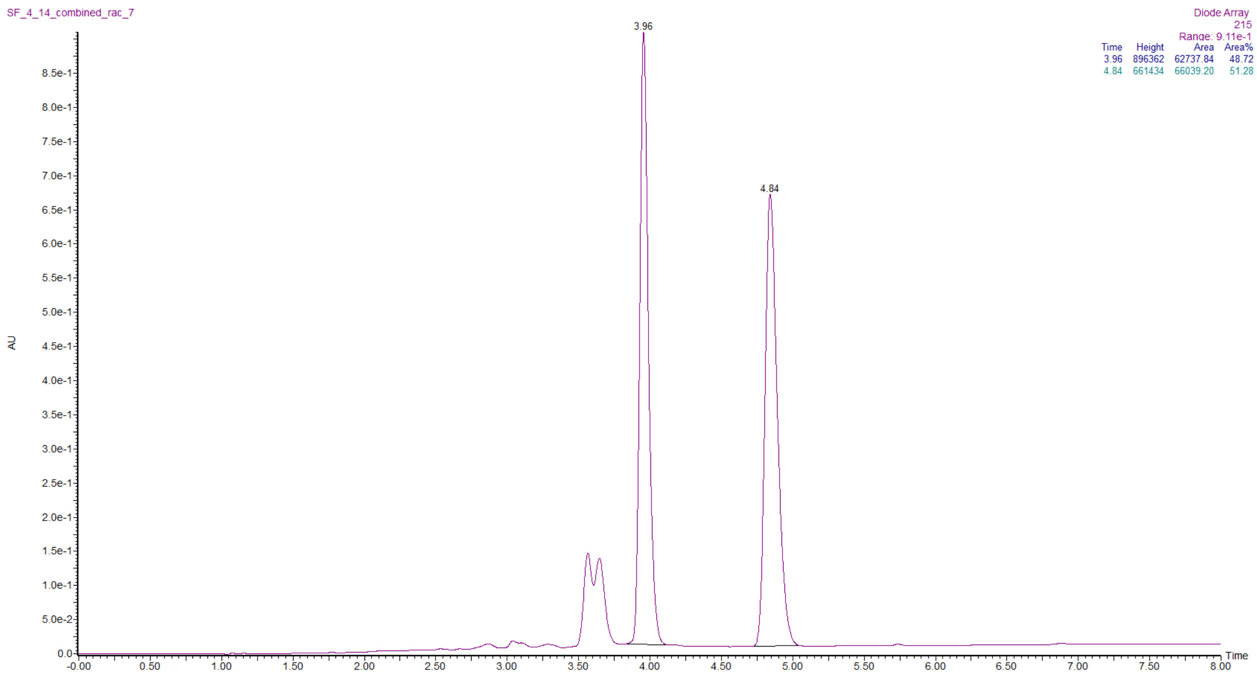
8. SFC Traces

(1*S*,3*R*)-*N*,*N*-dibenzyl-2,2-dimethyl-3-phenylcyclopropan-1-amine (10a) + *N*,*N*-dibenzyl-2,2-dimethyl-1-phenylcyclopropan-1-amine (10b)

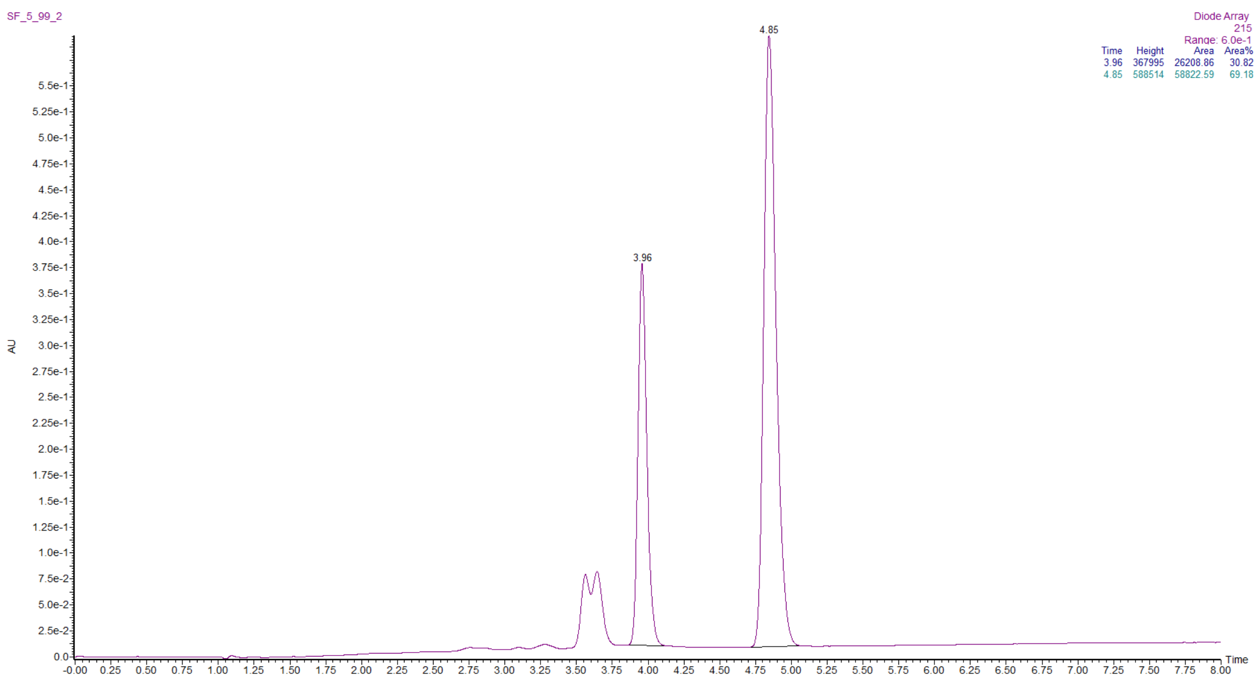


10a **10b** (8:1 ratio)

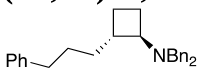
Racemic:



Enantioenriched:



(1*R*,2*R*)-*N*,*N*-dibenzyl-2-(3-phenylpropyl)cyclobutan-1-amine (7a)



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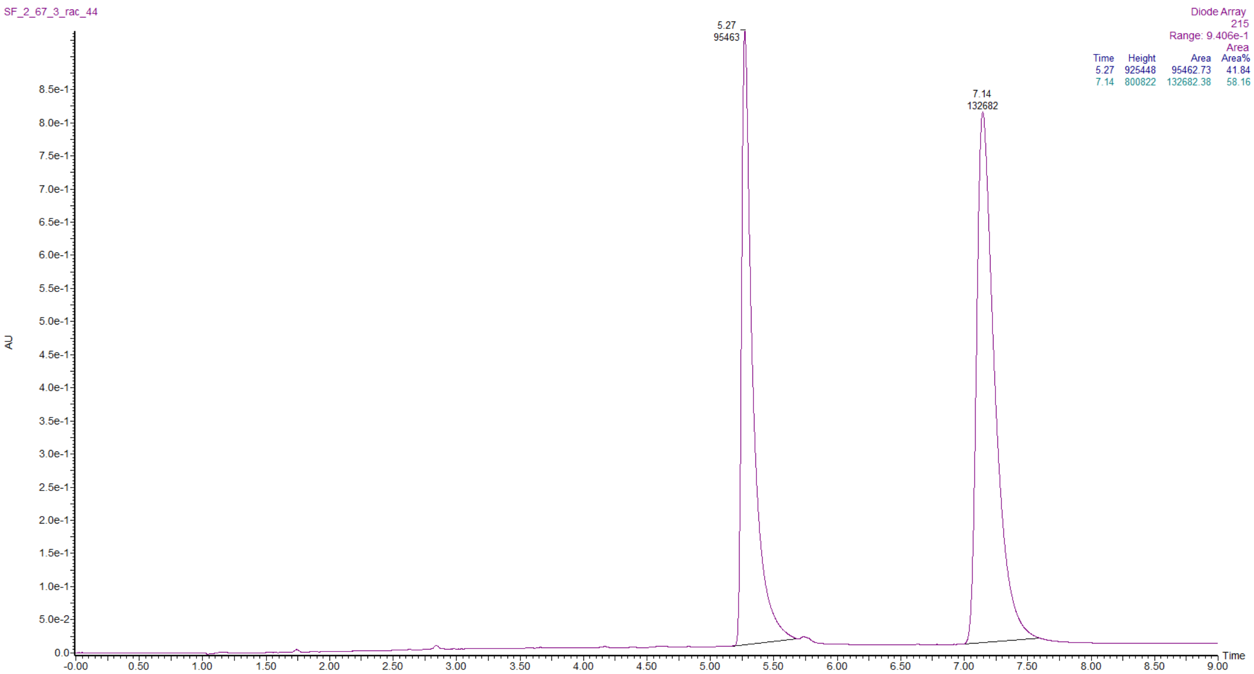
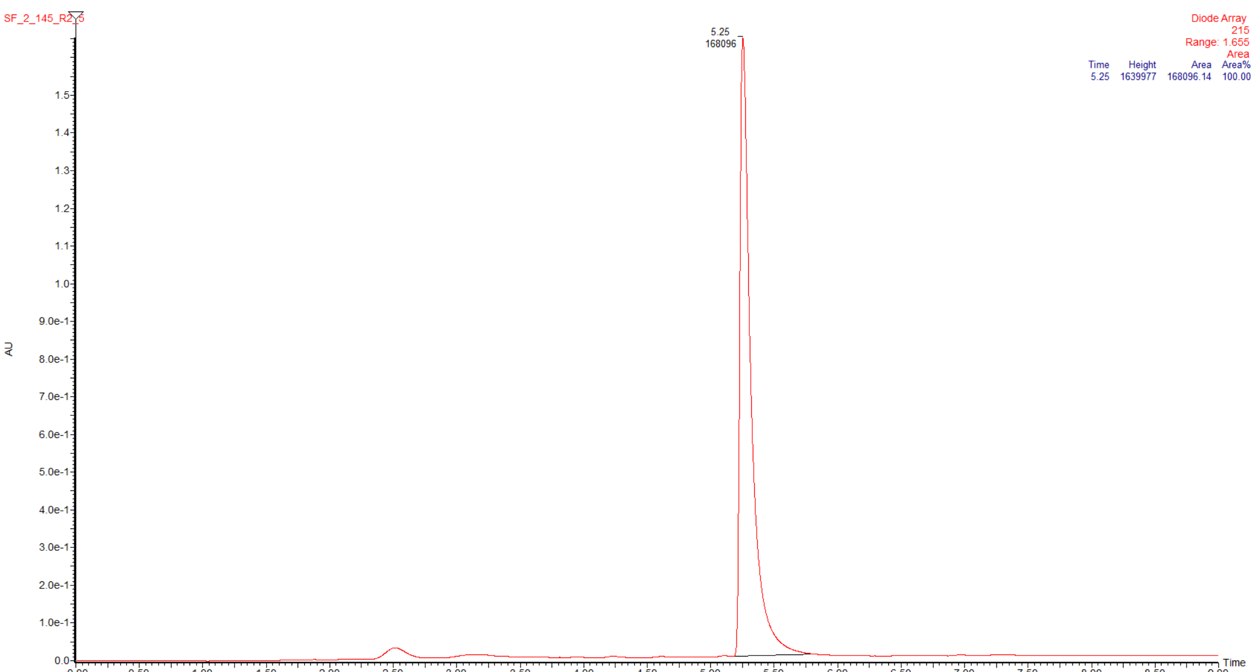
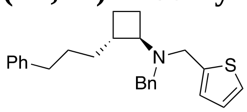


Enantioenriched:



(1*R*,2*R*)-*N*-benzyl-2-(3-phenylpropyl)-*N*-(thiophen-2-ylmethyl)cyclobutan-1-amine (7b)



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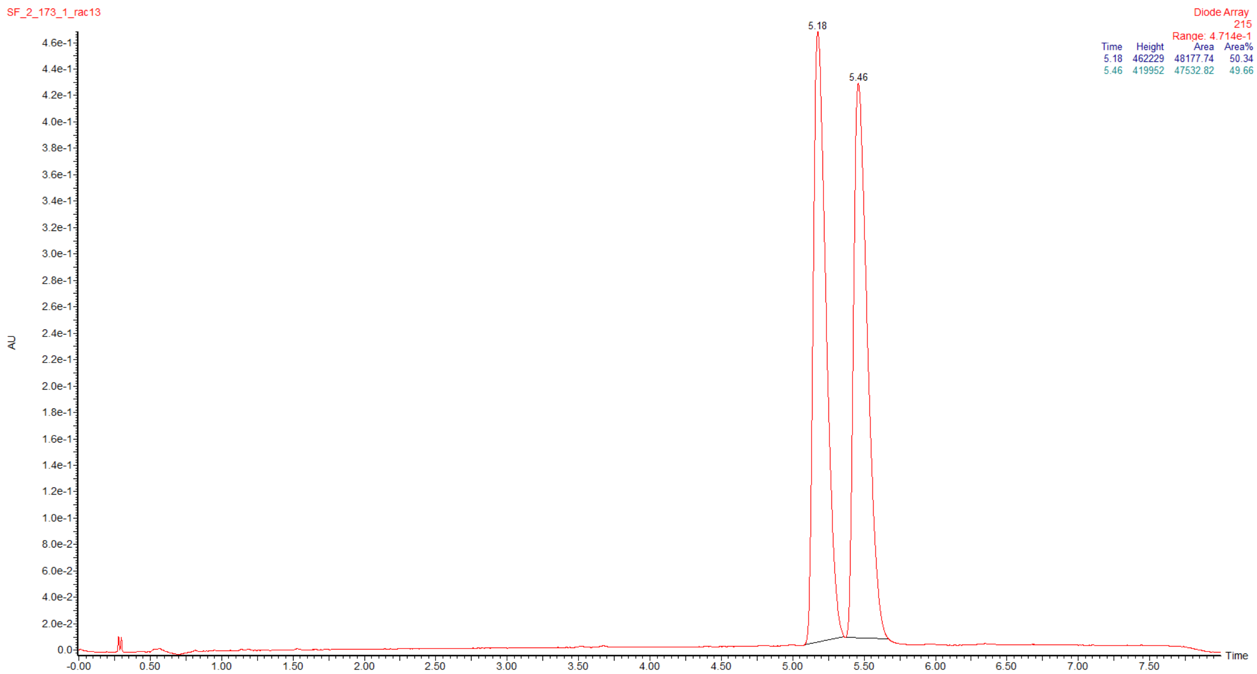
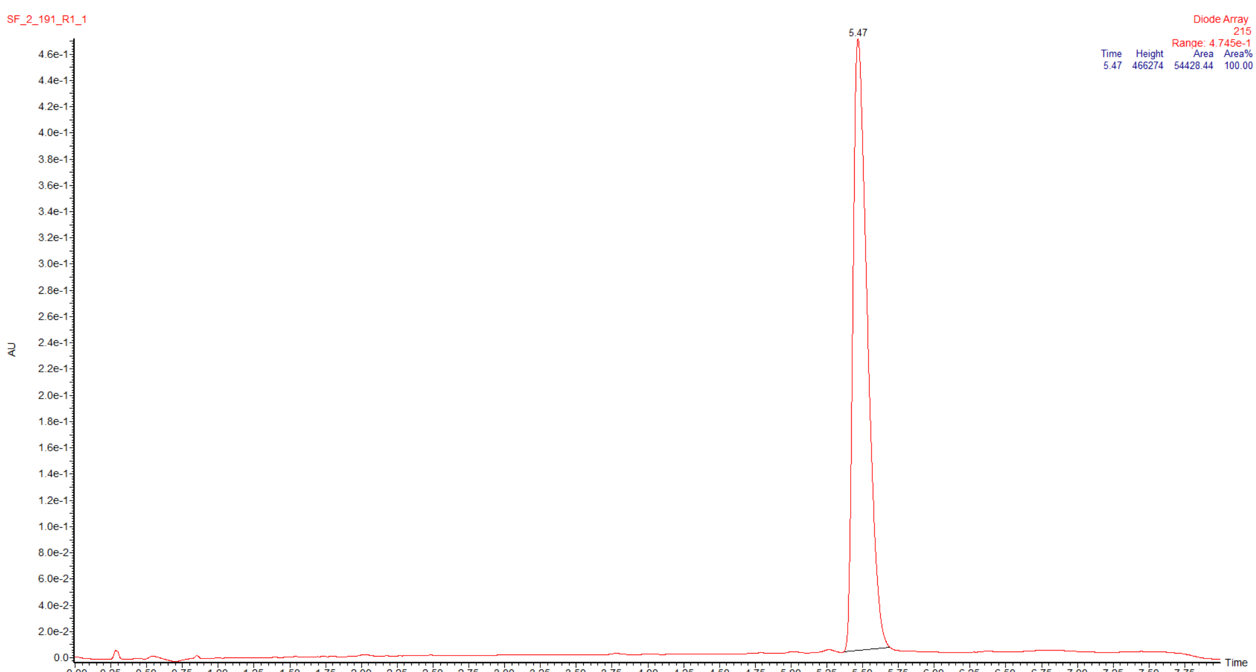
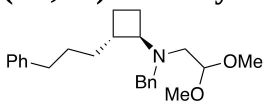


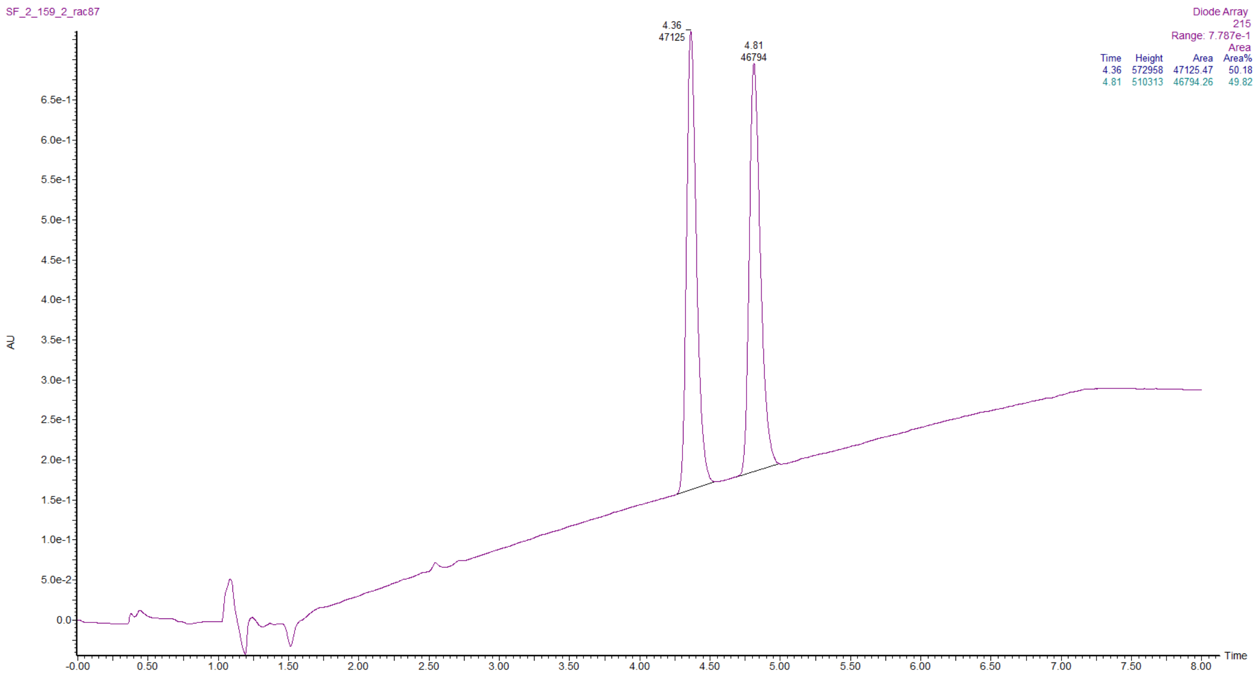
Enantioenriched:



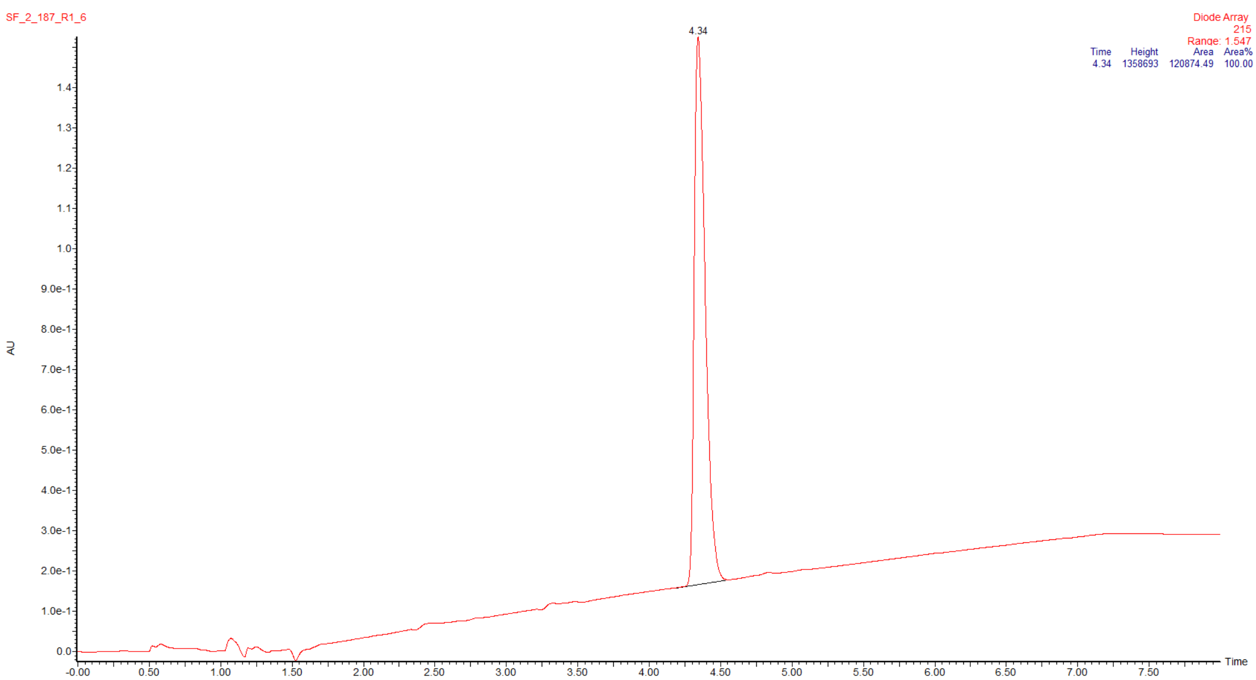
(1*R*,2*R*)-*N*-benzyl-*N*-(2,2-dimethoxyethyl)-2-(3-phenylpropyl)cyclobutan-1-amine (7c)



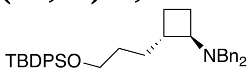
Racemic:



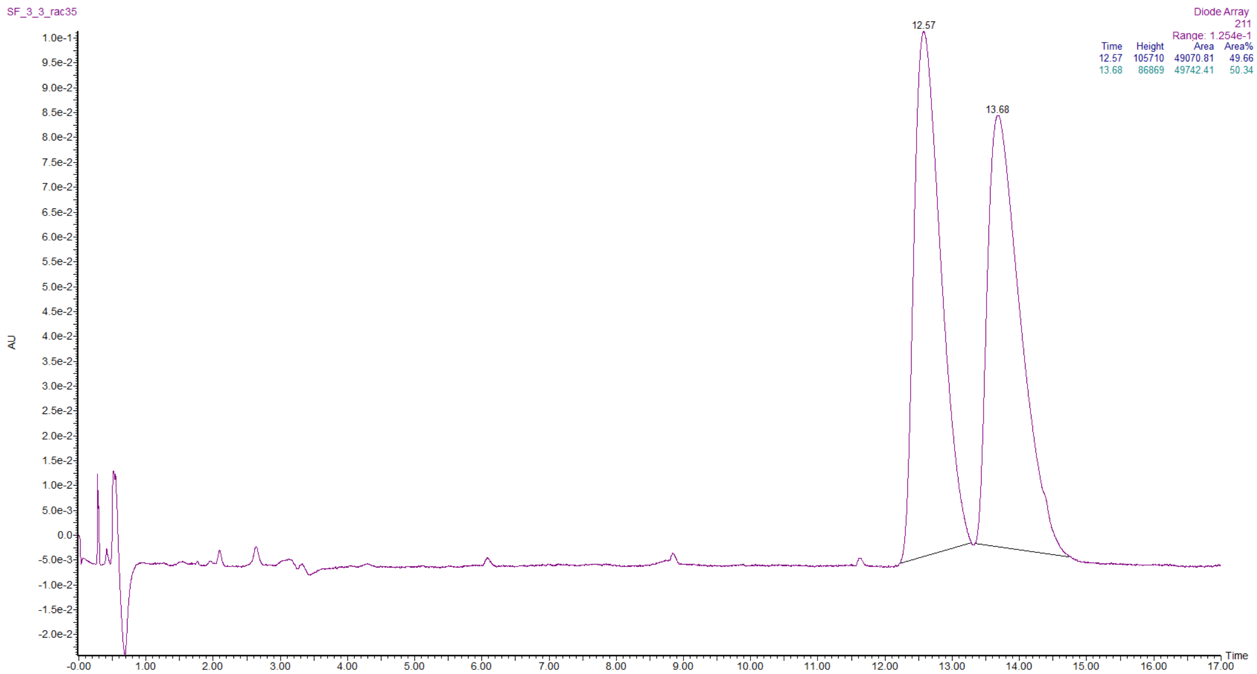
Enantioenriched:



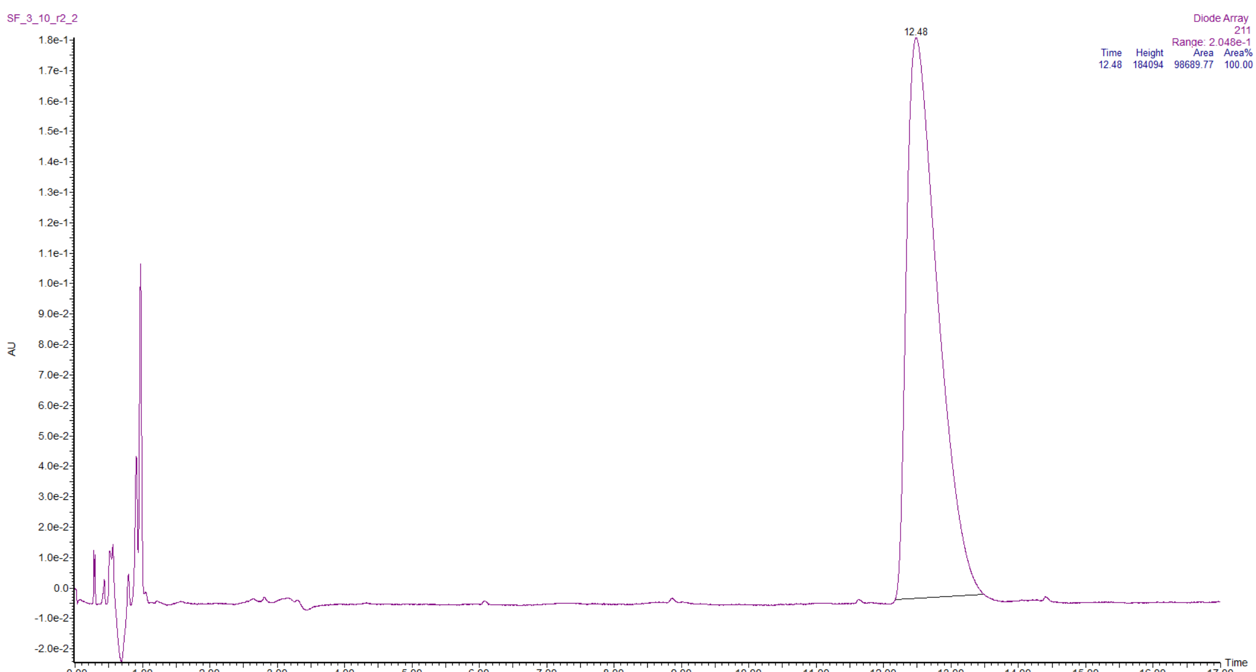
(1*R*,2*S*)-*N*,*N*-dibenzyl-2-(3-((*tert*-butyldiphenylsilyl)oxy)propyl)cyclobutan-1-amine (7d)



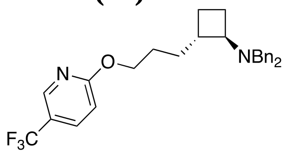
Racemic:



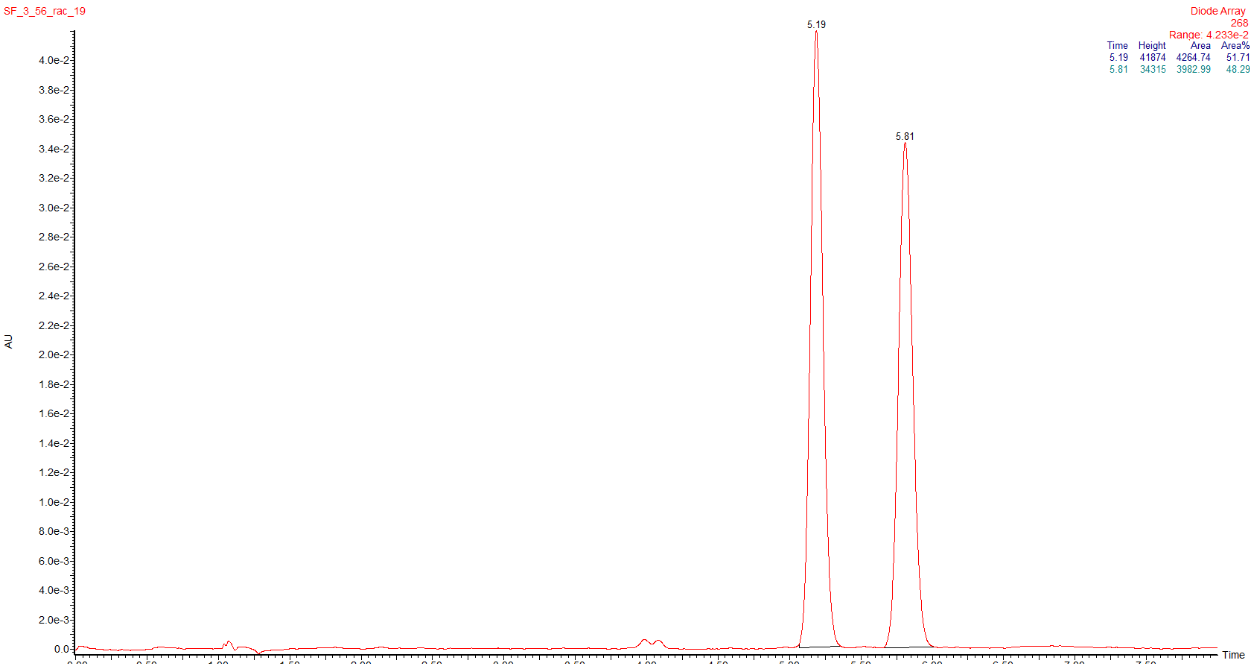
Enantioenriched:



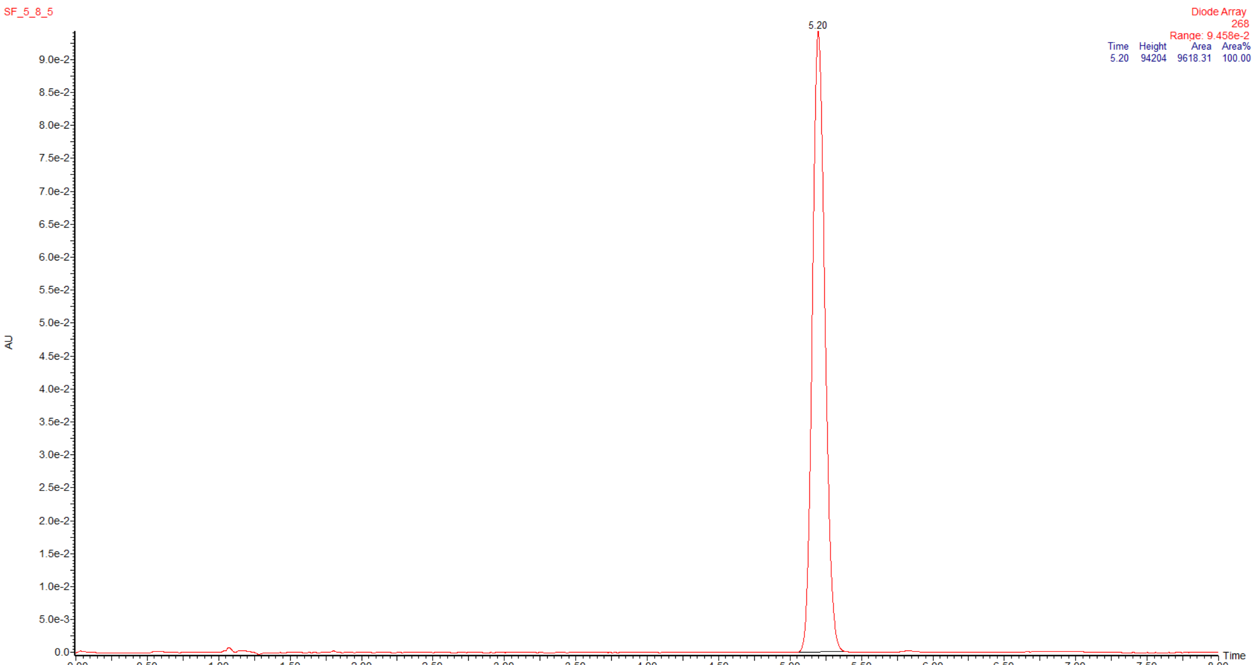
(1*R*,2*S*)-*N*,*N*-dibenzyl-2-(3-((5-(trifluoromethyl)pyridin-2-yl)oxy)propyl)cyclobutan-1-amine (7e)



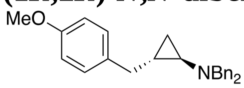
Racemic:



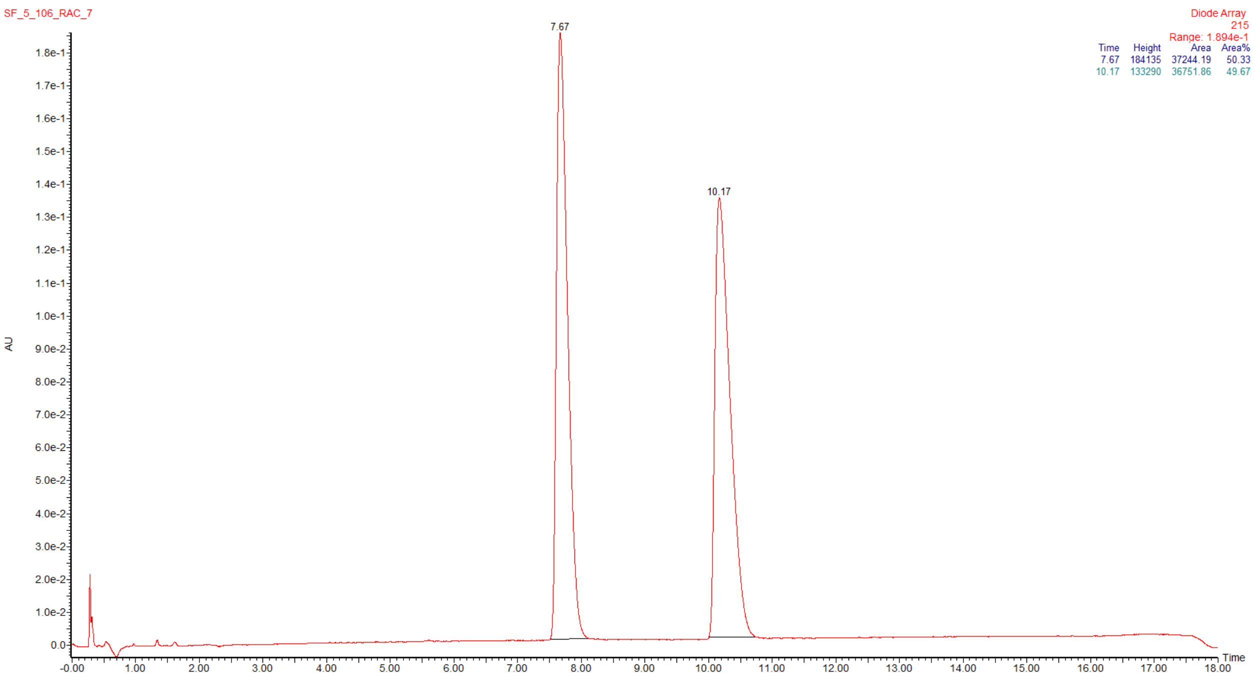
Enantioenriched:



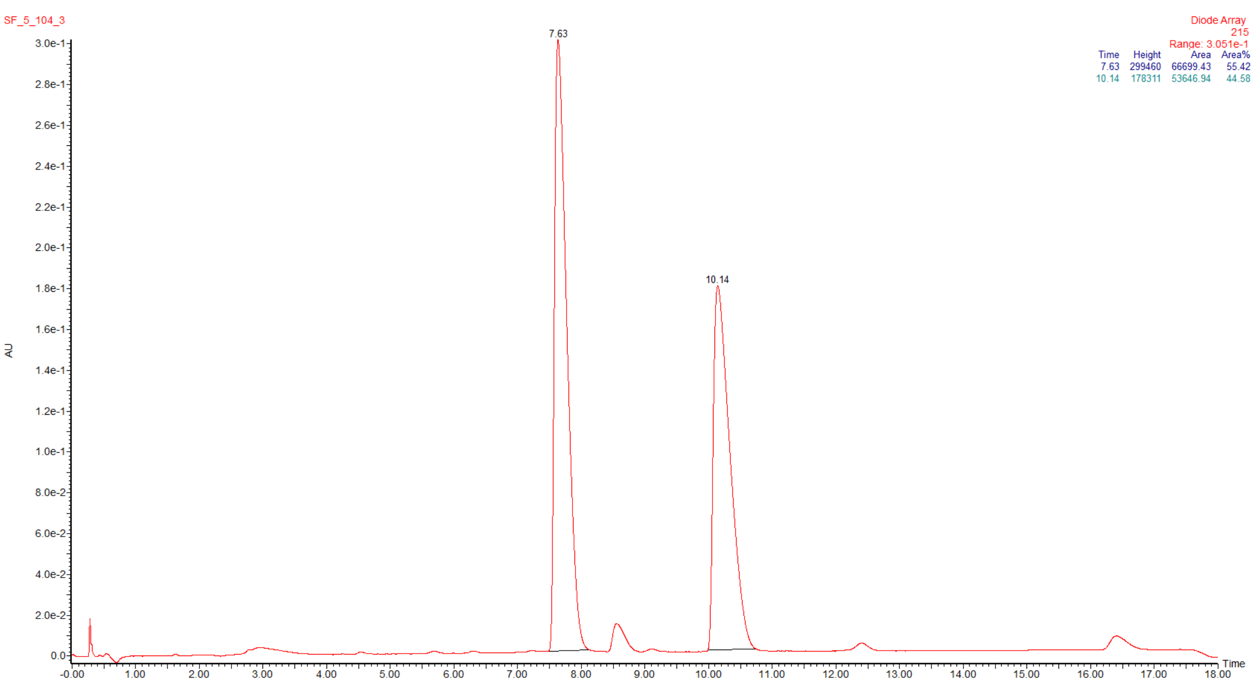
(1*R*,2*R*)-*N*,*N*-dibenzyl-2-(4-methoxybenzyl)cyclopropan-1-amine (12)



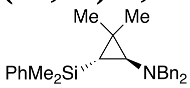
Racemic:



Enantioenriched:



(1*R*,3*R*)-*N*,*N*-dibenzyl-3-(dimethyl(phenyl)silyl)-2,2-dimethylcyclopropan-1-amine (15a)



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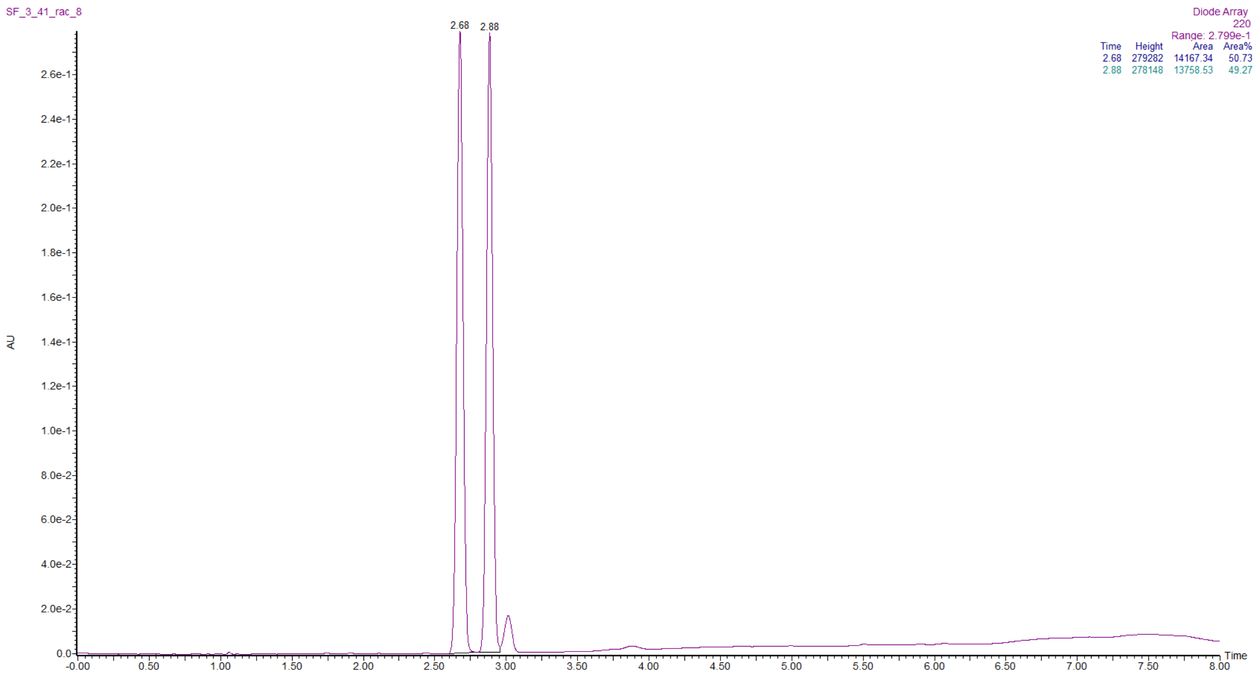

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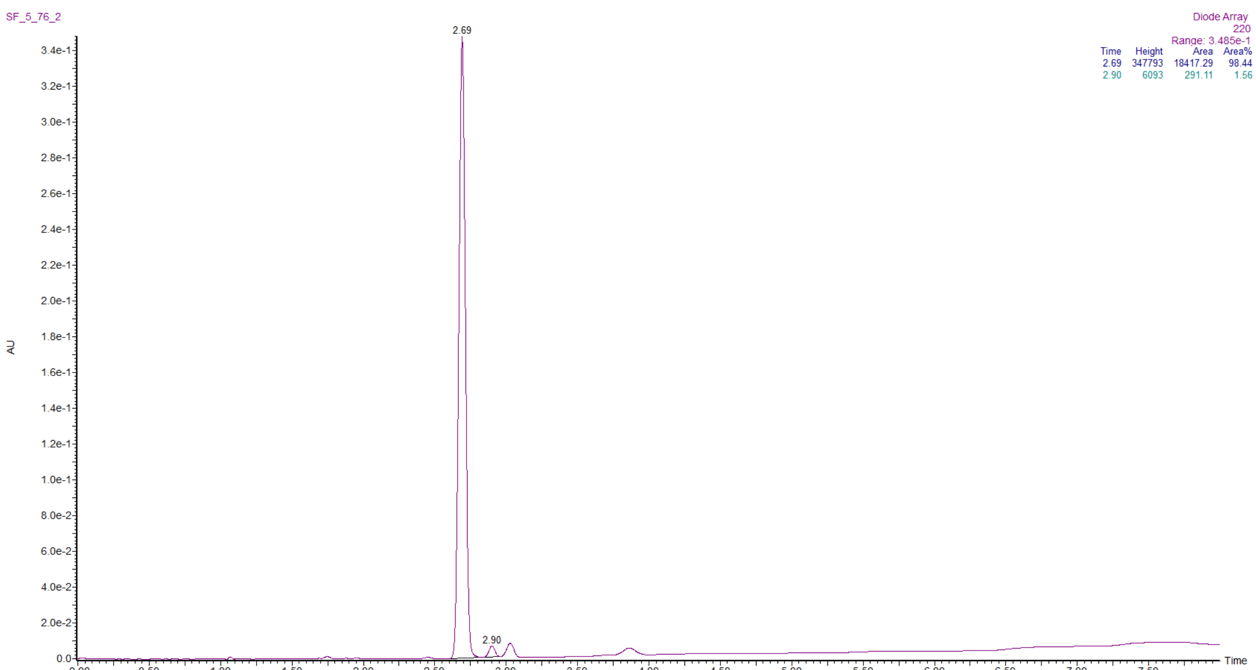
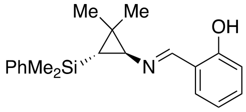


2-((*E*)-(((1*R*,3*R*)-3-(dimethyl(phenyl)silyl)-2,2-dimethylcyclopropyl)imino)methyl)phenol (15b)



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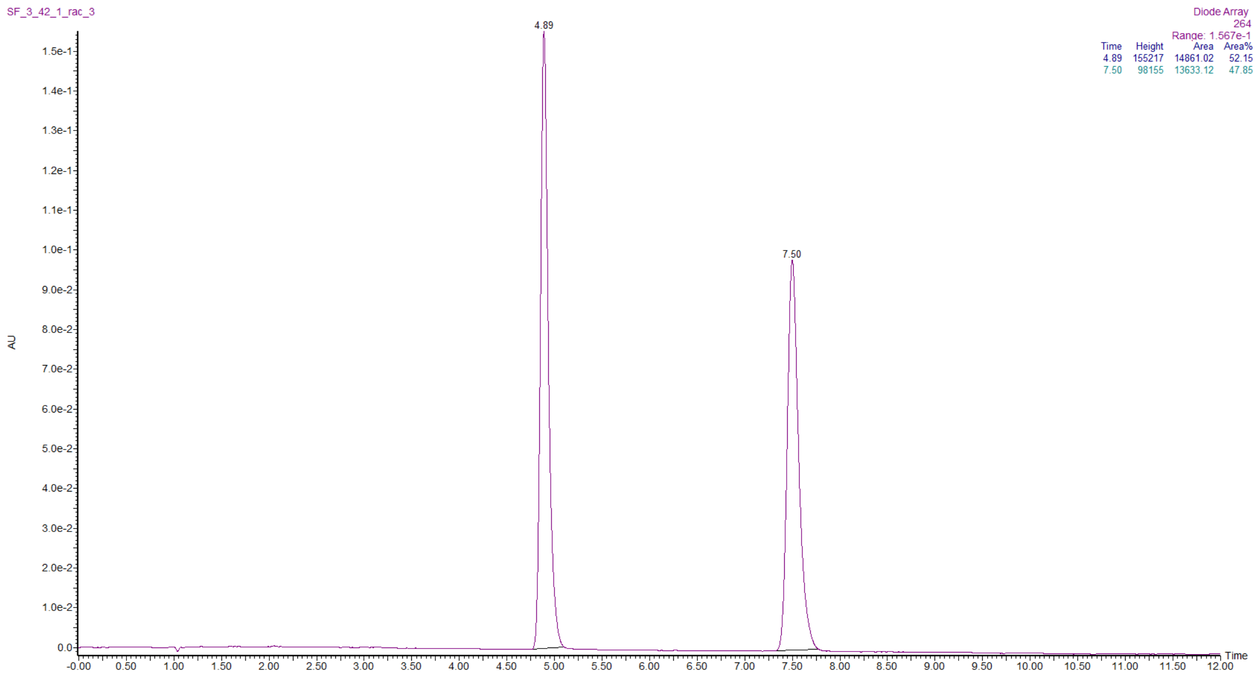

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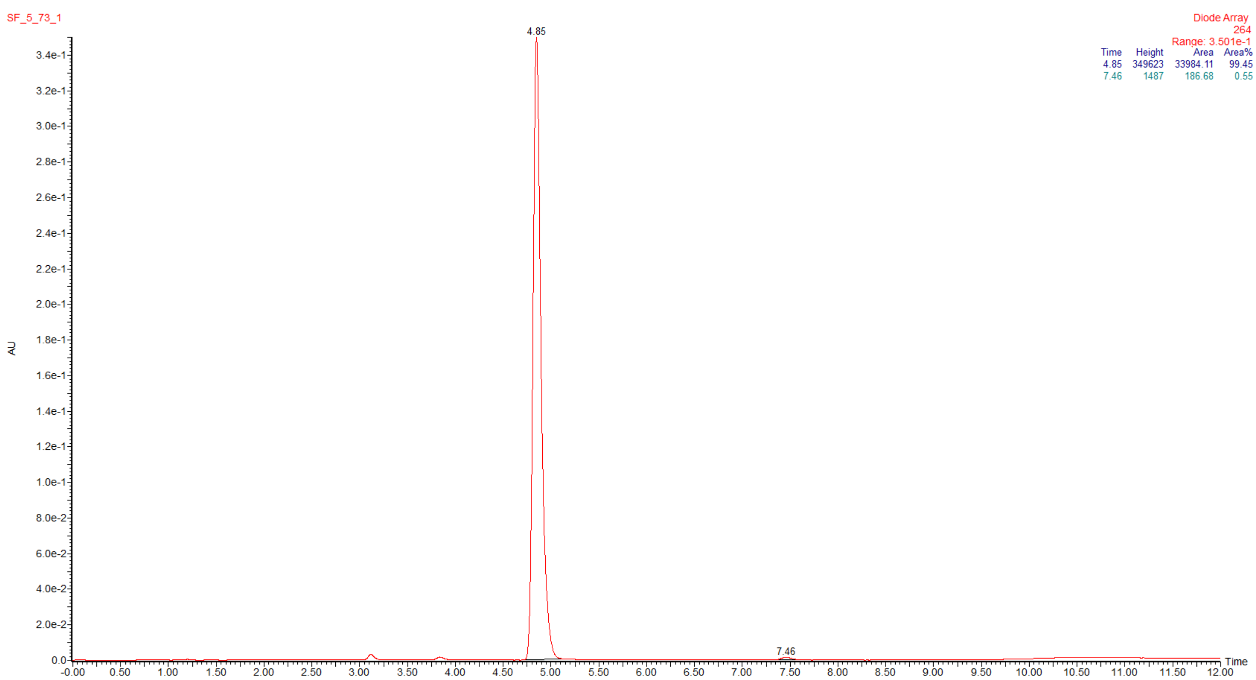
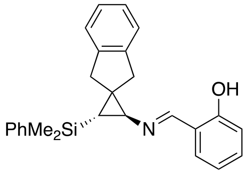


2-((*E*)-(((2*R*,3*R*)-2-(dimethyl(phenyl)silyl)-1',3'-dihydrospiro[cyclopropane-1,2'-inden]-3-yl)imino)methyl)phenol (15c)



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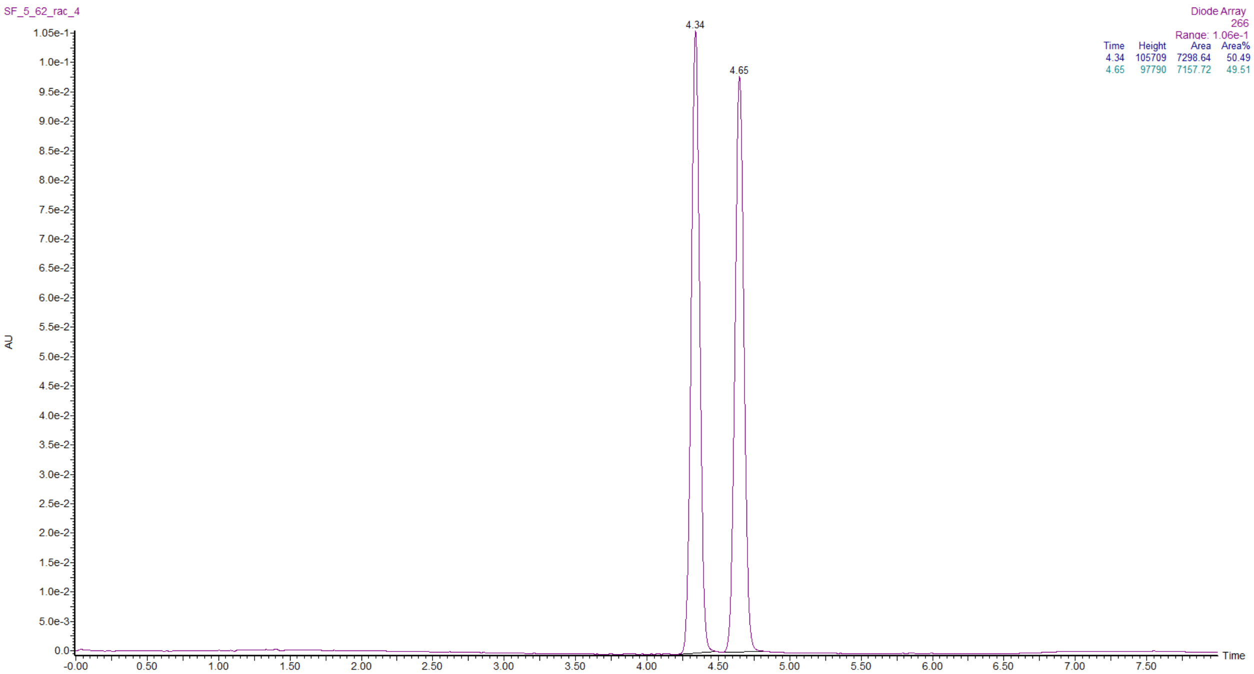

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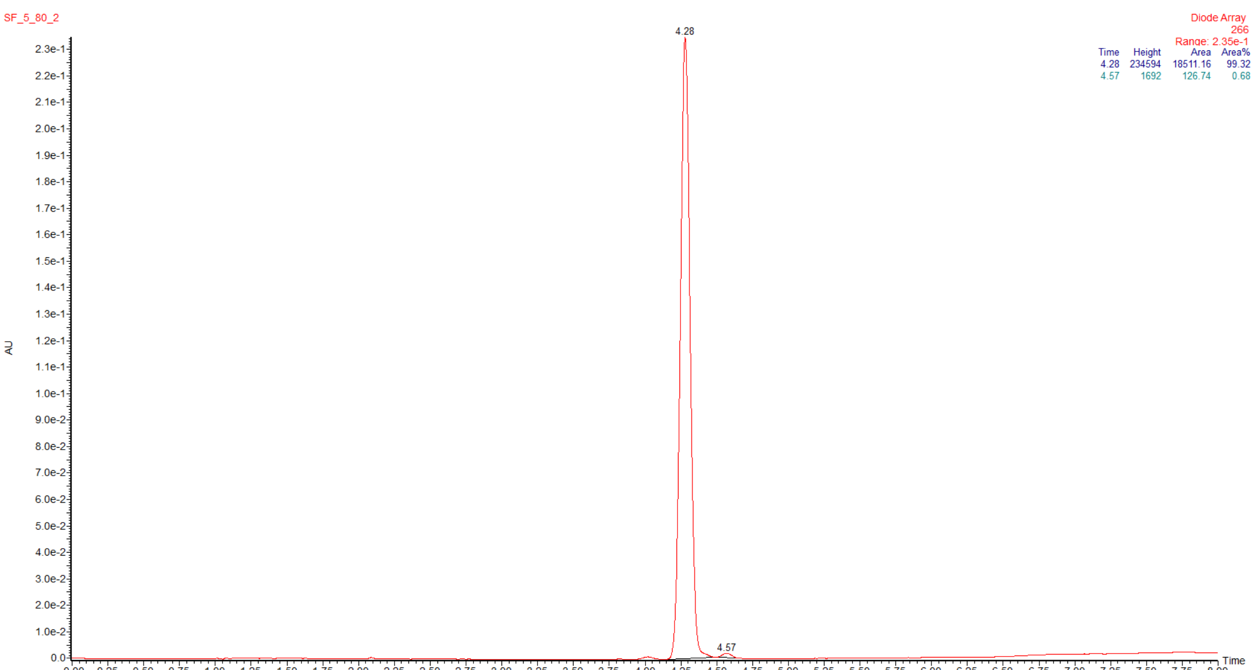
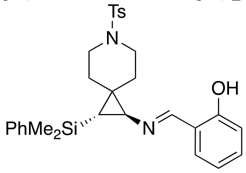


2-((*E*)-(((1*R*,2*R*)-2-(dimethyl(phenyl)silyl)-6-tosyl-6-azaspiro[2.5]octan-1-yl)imino)methyl)phenol (15d)



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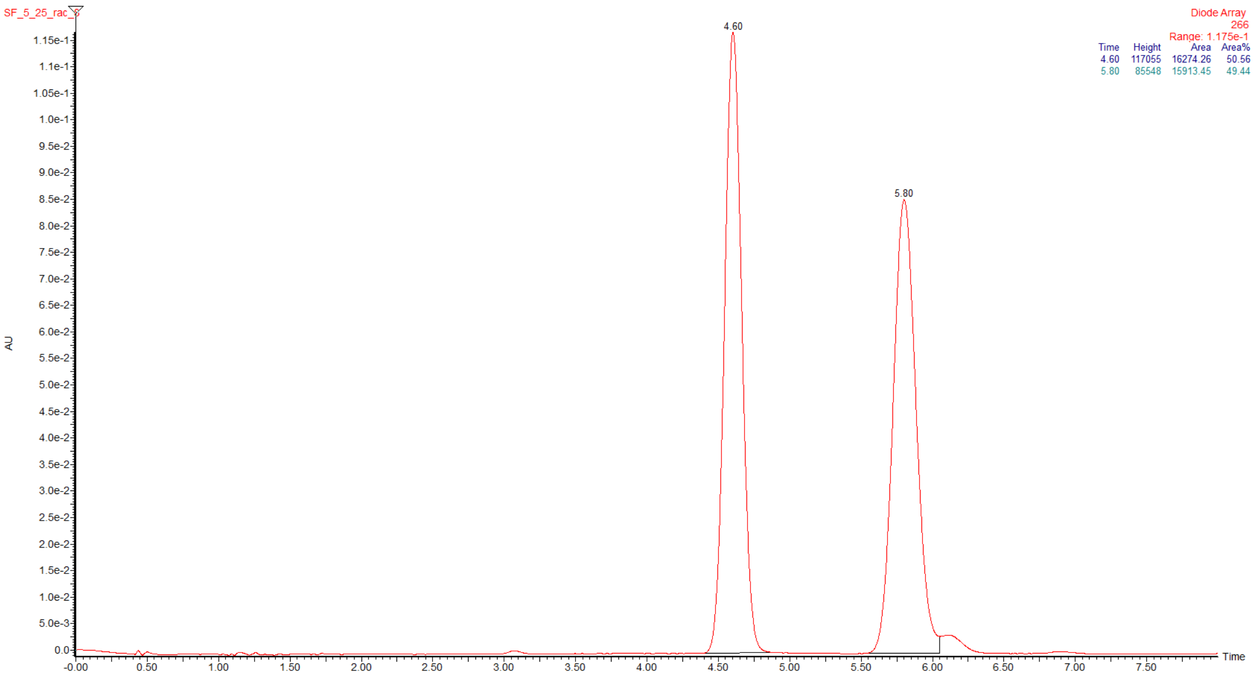

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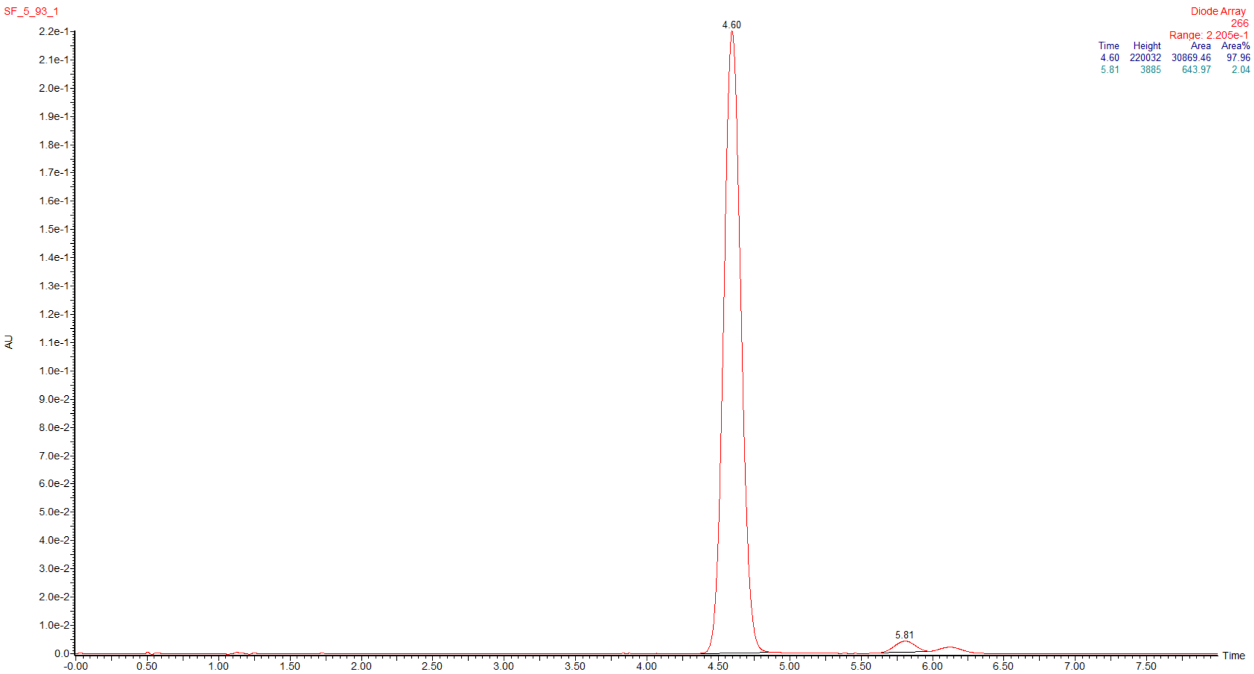
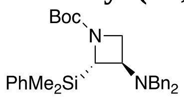
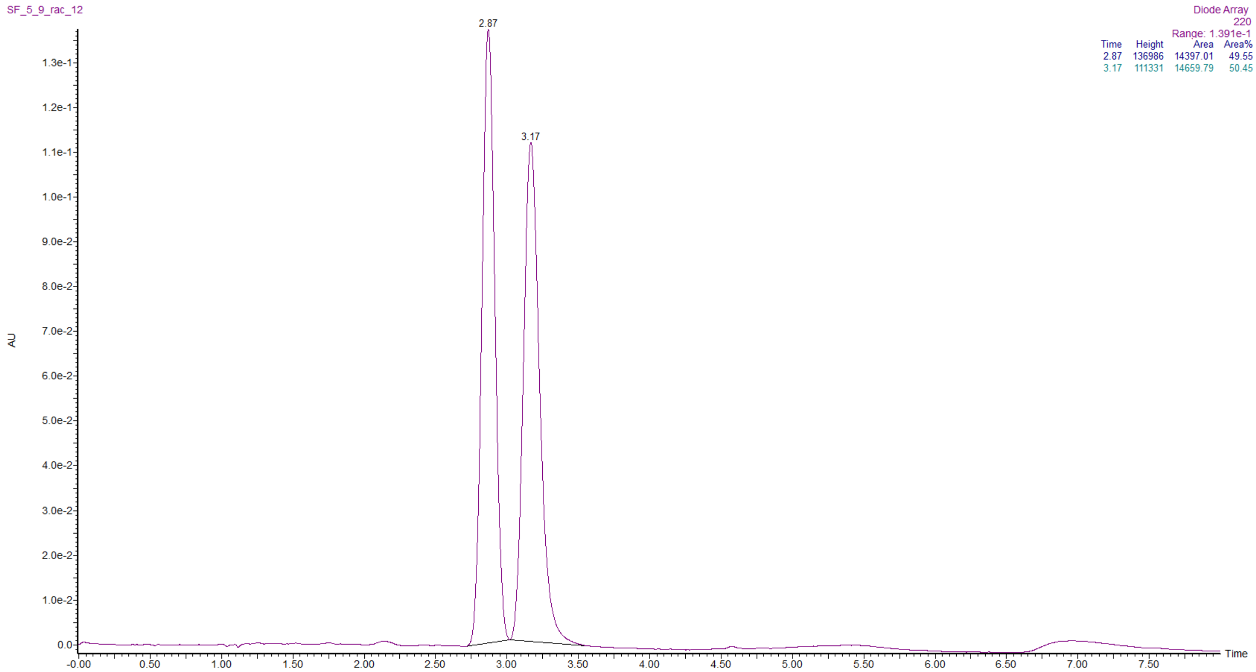


***tert*-butyl (2*S*,3*R*)-3-(dibenzylamino)-2-(dimethyl(phenyl)silyl)azetidine-1-carboxylate (7f)**



Racemic:



Enantioenriched: