Supporting Information

Copper-catalyzed non-directed hydrosilylation of cyclopropenes: highly diastereoselective synthesis of fully substituted cyclopropylsilanes

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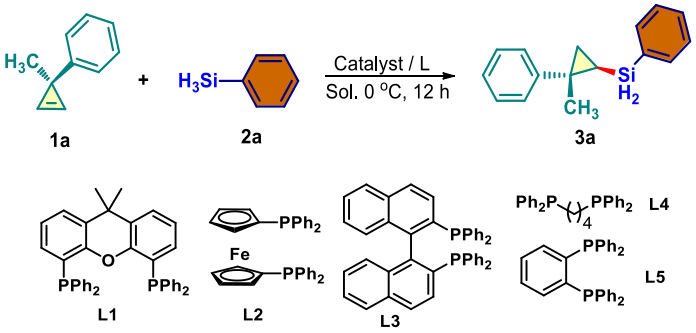
Table of Contents

I. General considerations

General. All reactions were performed under nitrogen atmosphere in flame dried flasks. All reactions were monitored by thin layer chromatography (TLC) using Macherey-Nagel 0.20 mm silica gel 60 plates. Flash column chromatography was performed on silica gel 60 (particle size 300-400 mesh ASTM, purchased from Taizhou, China). ^{1}H and ^{13}C and ^{29}Si nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV- 500 NMR spectrometersan and Bruker AV- 600 NMR spectrometers. ^{1}H and ^{13}C NMR spectra are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm for ^{1}H) and $CHCl_3$ (77.0 ppm for ^{13}C), respectively. High-resolution mass spectra (HRMS) were recorded on Bruck microtof.

Materials. Unless otherwise noted, commercial reagents were purchased from Energy-Chemical Limited, Alfa Aesar, and other commercial suppliers and were used as received. THF, Dioxane, MTBE, Toulene and Et_2O were distilled over sodium and stored under nitrogen atmosphere. CH_3CN was distilled over Calcium hydride and stored under nitrogen atmosphere. DMA was an ultra dry solvent purchased from Energy-Chemical. Cyclopropenes were prepared according to the previously reported methods.[1,2] Hydrosilane prepared according to the previous reported method.[3]

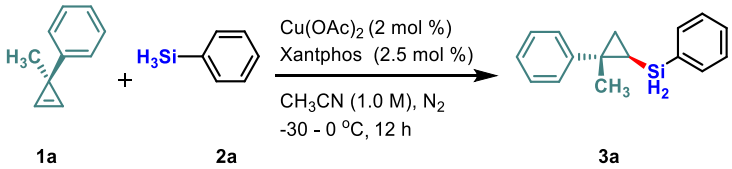
II. The optimization of the reaction



Entry	Catalyst	Ligand	Solvent	Yield (%)
1	$Cu(OAc)_2$	**L1**	THF	0
2	$Cu(OAc)_2$	**L1**	dioxane	21
3	$Cu(OAc)_2$	**L1**	MTBE	30
4	$Cu(OAc)_2$	**L1**	Tol	26
5	$Cu(OAc)_2$	**L1**	CH_3CN	52
6[c]	$Cu(OAc)_2$	**L1**	DMA	40
7[c]	$Cu(OAc)_2$	**L1**	CH_3CN	68
8[c,d]	$Cu(OAc)_2$	**L1**	CH_3CN	95
9[c,d,f]	$Cu(OAc)_2$	**L1**	CH_3CN	48
10[c,d,g]	$Cu(OAc)_2$	**L1**	CH_3CN	63
11[c,d,e]	CuCl	**L1**	CH_3CN	49
12[c,d,e]	CuCN	**L1**	CH_3CN	0
13[c,d]	$Cu(OAc)_2$	**L2**	CH_3CN	19
14[c,d]	$Cu(OAc)_2$	**L3**	CH_3CN	5
15[c,d]	$Cu(OAc)_2$	**L4**	CH_3CN	22
16[c,d]	$Cu(OAc)_2$	**L5**	CH_3CN	7

[a]Reaction conditions: cyclopropene **1a** (0.3 mmol), phenylsilane **2a** (0.9 mmol, 3.0 equiv), catalyst (2.0 mol %), ligand (2.5 mol %) in 0.6 mL dry solvent for 12 h at 0 °C. MTBE: methyl tertiary butyl ether. [b]Yield and diastereomeric ratio (dr) were determined by ^1H NMR spectroscopy of the crude mixture with methylene bromide as an internal standard. [c]0.3 mL dry solvent was used. [d]Phenylsilane **2a** (2.7 mmol) was used. [e]LiO^{t}Bu (0.6 mmol) was used. [f]Phenylsilane **2a** (3.0equiv) was used. [g]Phenylsilane **2a** (6.0equiv) was used.

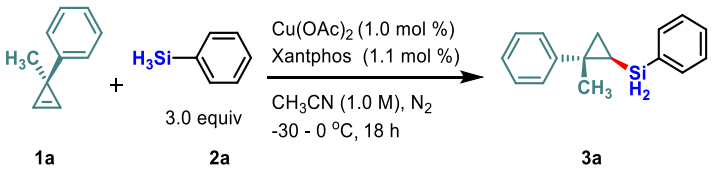
III. Experimental Details and Characterization



1a **2a** **3a**

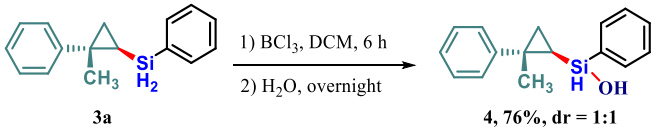
Taking 3a as an example: In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (1.1 mg, 6.0 μmol), Xantphos (4.3 mg, 7.5 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then phenylsilane (110 μL, 3.0 equiv) was added and the colour of this mixture changed from blue to brown. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then (1-methylcycloprop-2-en-1-yl)benzene **1a** (39.1 mg, 0.3 mmol) dissolved in phenylsilane (220 μL, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr) was assessed by ^1H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel (pure petroleum ether) to obtain product **3a**. The details and characterization data of the products are stated below. (Noting: there is no difference on either adding phenylsilane with one-time or twice.)

IV. Gram-Scale Synthesis and Applications of (3a)



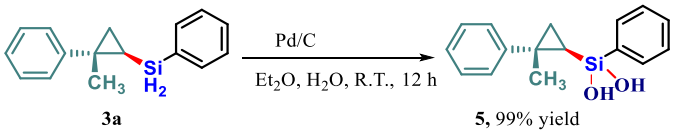
1a **2a** **3a**

In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (27.2 mg, 150 umol), Xantphos (95.5 mg, 165 umol), and anhydrous CH_3CN (4.5 mL). The resulting mixture was stirred for 10 min, then phenylsilane (1.85 mL, 1.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then (1-methylcycloprop-2-en-1-yl)benzene (1.95 g, 15 mmol) dissolved in phenylsilane (3.7 mL, 2.0 equiv) was added by using a 5.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 18 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr) was assessed by ^1H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel (pure petroleum ether) to obtain product **3a** (2.78 g, 78%).



3a **4, 76%, dr = 1:1**

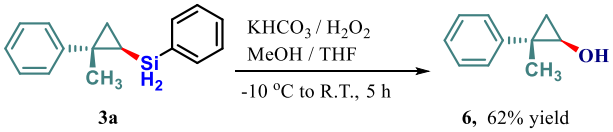
(2-methyl-2-phenylcyclopropyl)(phenyl)silanol (4) Prepared according to a previously reported method.[4] **3a** (119.2 mg, 0.5 mmol) and BCl_3 (0.5 mmol, 0.5 mL, 1.0 M in DCM) were added into a mixture of H_2O (1.2 mL) and DCM (2.0 mL). After stirred overnight, the mixture was then diluted with H_2O and extracted with DCM for three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The crude mixture was purified by flash column chromatography using PE/EA (10/1) as the eluent to give 96.7 mg (76% yield) of the title compound as a colorless oil with 1:1 dr. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.71 – 7.69 (m, 4H), 7.45 – 7.39 (m, 6H), 7.30 – 7.26 (m, 8H), 7.17 – 7.14 (m, 2H), 5.11 (d, *J* = 3.0 Hz, 1H), 5.08 (d, *J* = 3.6 Hz, 1H), 2.15 (s, 2H), 1.56 (s, 3H), 1.50 (s, 3H), 1.37 (dd, *J* = 10.2, 3.6 Hz, 1H), 1.33 (dd, *J* = 10.2, 3.6 Hz, 1H), 1.07 (dd, *J* = 7.8, 4.2 Hz, 1H), 0.99 (dd, *J* = 7.2, 3.6 Hz, 1H), 0.47 – 0.44 (m, 1H), 0.43 - 0.39 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.77, 147.76, 136.56, 136.19, 133.87, 133.81, 130.19, 128.23, 128.08, 128.04, 126.80, 126.75, 125.77, 125.75, 25.82, 25.57, 23.76, 23.67, 19.07, 18.86, 13.20, 12.64. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -12.56, -13.08. **HRMS** (ESI) calculated for $[C_{16}H_{18}NaOSi]^+$ requires m/z 277.1019, found m/z 277.1024.



3a **5,** 99% yield

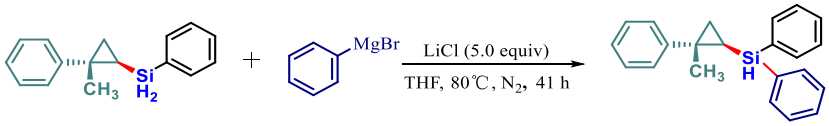
(2-methyl-2-phenylcyclopropyl)(phenyl)silanediol (5). Prepared according to a previous reported method.[4] **3a** (71.5 mg, 0.3 mmol) and Pd/C (30.0 mg, 0.03 mmol, 10% Wt) were added into a mixture of H_2O (0.2 mL) and Et_2O (2.0 mL). After stirred overnight, the mixture was then filtered through Celite, dried over Na_2SO_4 and concentrated in vacuo. The crude mixture was purified by

flash column chromatography using PE/EA = 4/1 as the eluent to give 80.3 mg (99% yield) of the title compound as a white solid. M.p. 98-100 °C **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 6.4 Hz, 2H), 7.47 – 7.39 (m, 3H), 7.27 – 7.26 (m, 4H), 7.18 – 7.15 (m, , 1H), 2.76 (s, 2H), 1.50 (s, 3H), 1.32 (dd, *J* = 10.4, 3.6 Hz, 1H), 1.04 (dd, *J* = 7.6, 3.6 Hz, 1H), 0.36 (dd, *J* = 10.0, 7.6 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.83, 135.86, 133.82, 130.31, 128.21, 128.00, 126.76, 125.72, 25.31, 23.60, 18.92, 12.34. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -19.20. **HRMS** (ESI) calculated for $[C_{16}H_{18}NaO_2Si]^+$ requires m/z293.0968, found m/z 293.0967.



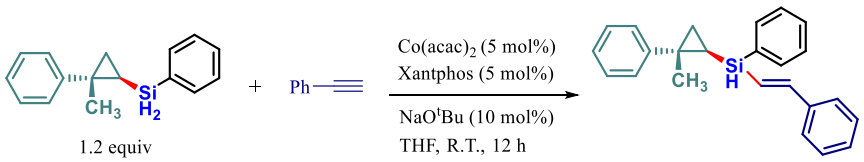
3a **6,** 62% yield

2-methyl-2-phenylcyclopropan-1-ol (6) Prepared according to a previous reported method.[6] $KHCO_3$ (500.0 mg, 5.0 mmol) and 30% aqueous H_2O_2 (2.0 mL) were added into a mixture of THF (2.0 mL) and methanol (2.0 mL) in a 10 mL screw-capped vial containing a magnetic stirring bar. The resulting mixture was stirred for 2 min. Subsequently, **3a** (119.2 mg, 0.5 mmol) was added dropwise slowly into the reaction mixture at -10 °C and then stirred at room temperature for 5 hours. Anhydrous sodium thiosulfate was then added to quench the excess H_2O_2. The mixture was extracted with CH_2Cl_2, the organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography with PE/EtOAc (v/v 10/1) to afford 8 as white solid (45.9 mg, 62%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 2H), 7.20 – 7.17 (m, 3H), 3.64 (dd, *J* = 7.0, 3.5 Hz, 1H), 2.02 (s, 1H), 1.52 (s, 3H), 1.20 (t, *J* = 6.5 Hz, 1H), 0.81 (dd, *J* = 6.0, 3.5 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 145.85, 128.34, 126.62, 125.75, 57.99, 25.93, 22.26, 18.44. **HRMS** (ESI) calculated for $[C_{10}H_{13}OSi]^+$ requires m/z 149.0961, found m/z 149.0951.



3a 5.0 equiv **7**, 86% yield

(2-methyl-2-phenylcyclopropyl)diphenylsilane (7) Prepared according to a previous reported method.[5] Phenyl magnesium bromide (1.0 M in THF, 1.0 mL, 1.0 mmol) was added to a suspension of LiCl (42.4 mg, 1.0 mmol) in 0.5 mL of THF, followed by (2-methyl-2-phenylcyclopropyl)(phenyl)silane (71.5 mg, 0.2 mmol) in 1.5 mL of THF, at room temperature under argon. After the reaction mixture was stirred at reflux for 41 h, the reaction was terminated by the addition of an aqueous solution of NH_4Cl (0.5 mL) at room temperature. The resulting heterogeneous mixture was filtered through Celite with the aid of ether. The organic phase was dried over Na_2SO_4 and concentrated in vacuo to give a crude oil, which was chromatographed on silica gel (hexane) to afford the title compound (54.1 mg, 86% yield) as a white solid. M.p. 41– 44 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.62 (m, 4H), 7.40 – 7.34 (m, 6H), 7.32 – 7.25 (m, 4H), 7.18 – 7.14 (m, 1H), 4.92 (d, *J* = 5.6 Hz, 1H), 1.47 (s, 3H), 1.45 (dd, *J* = 7.2, 3.6 Hz,1H), 0.98 (dd, *J* = 7.2, 3.6 Hz, 1H), 0.63 – 0.58 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.04, 135.32, 135.16, 135.03, 134.68, 129.57, 129.55, 128.25, 128.02, 127.98, 126.78, 125.72, 25.54, 23.80, 20.05, 10.85. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -14.56. **HRMS** (ESI) calculated for $[C_{22}H_{23}Si]^+$ requires m/z 315.1564, found m/z 315.1558.



1.2 equiv

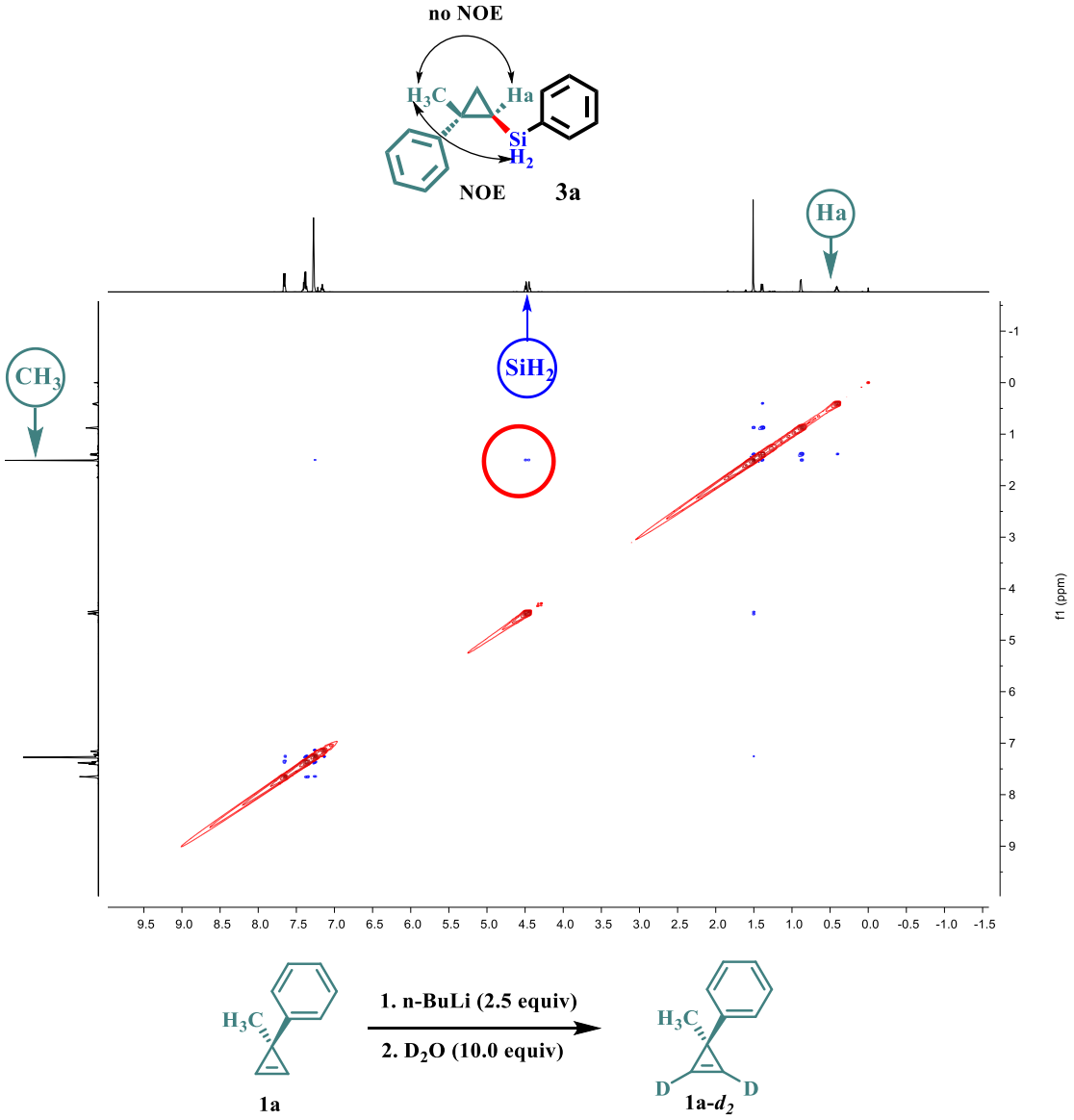
3a

8, 74% yield, 1.4:1 dr

(E)-(2-methyl-2-phenylcyclopropyl)(phenyl)(styryl)silane (8) Prepared according to a previous reported method.[6] In an Ar-filled glovebox, to a solution of $Co(acac)_2$ (6.4 mg, 25.0 μmol) in 2.0 mL THF, XantPhos (17.3 mg, 30.0 μmol) was added, and the mixture was stirred for 5 min at RT. Then **3a** (0.6 mmol, 1.2 equiv) and phenylacetylene (0.5 mmol, 1.0 equiv) were added to the mixture. After the solution was cooled to -30 ℃, NaO^{t}Bu (4.8 mg, 50.0 μmol) was slowly added. The reaction mixture was stirred for 12 h at RT and then was quenched by exposing the solution to air. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel eluting with PE/EA (v/v 50/1) to give the product **8** as colorless oil (125.8 mg, 74% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 4H), 7.46 (d, *J* = 7.8 Hz, 4H), 7.40 – 7.38 (m, 6H), 7.35 – 7.32 (m, 6H), 7.30 – 7.25 (m, 8H), 7.18 – 7.12 (m, 4H), 6.62 (td, *J* = 19.8, 3.0 Hz, 2H), 4.73 (dd, *J* = 8.4, 4.8 Hz, 2H), 1.55 (s, 3H), 1.49 (s, 3H), 1.42 (dd, *J* = 10.2, 3.6 Hz, 2H), 0.95 (td, *J* = 7.2, 3.6 Hz, 2H), 0.51 – 0.46 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.13, 147.92, 147.88, 138.00, 135.22, 135.10, 134.98, 134.82, 129.55, 129.50, 128.58, 128.56, 128.47, 128.44, 128.27, 128.24, 128.03, 128.01, 126.80, 126.69, 126.64, 125.69, 123.16, 122.78, 25.44, 25.33, 23.82, 23.73, 19.99, 19.77, 11.02, 10.59. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -29.85, -29.99. **HRMS** (ESI) calculated for $[C_{24}H_{24}Si]^+$ requires m/z 341.1720, found m/z 341.1735.

V. NOESY for representative compounds

According to the NOE experiment, we observed a signal between –CH_3 and –SiH_2–, which means the cis configuration of –CH_3 and –SiH_2–. In addition, no signal was observed between –CH_3 and H_a, hence the trans configuration between –CH_3 and H_a should be confirmed. As a result, the absolute configuration of the compound **3a** should be determined.

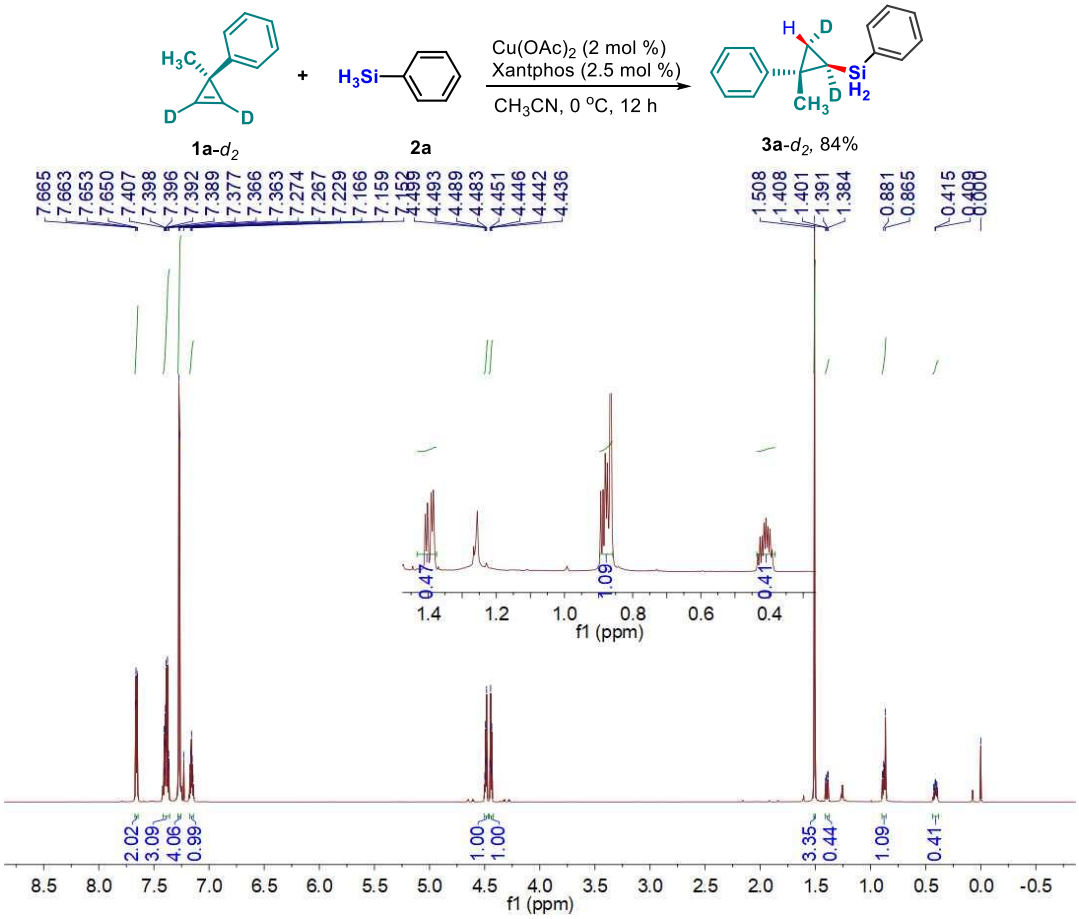


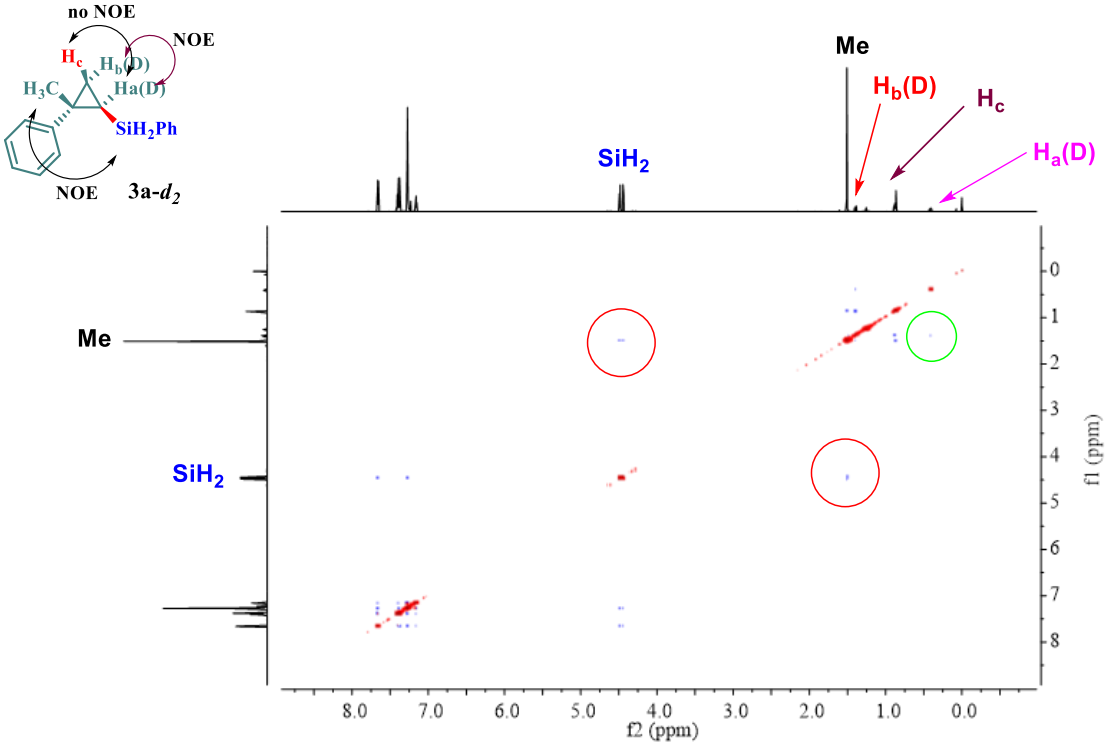
(1-methylcycloprop-2-en-1-yl-2,3-d_2)benzene (1a-*d_2*)

Prepared according to a previous reported method.[7] To a stirred solution of cyclopropene **1a** (1.00 g, 7.7 mmol) in anhydrous hexanes (10 mL) at -30 °C was added a solution of n-butyllithium (2.5 M in hexane, 7.7 mL, 19.0 mmol, 2.5 equiv). The mixture was stirred for 30 min at 0 °C and quenched with deuterium oxide (1.5 mL, 75 mmol, 10.0 equiv). The organic phase was separated, dried over $MgSO_4$, filtered, and concentrated. The residue was distilled in vacuum (bp 60-62 °C at 10 torr) to afford **1a-*d_2*** as a colorless oil.

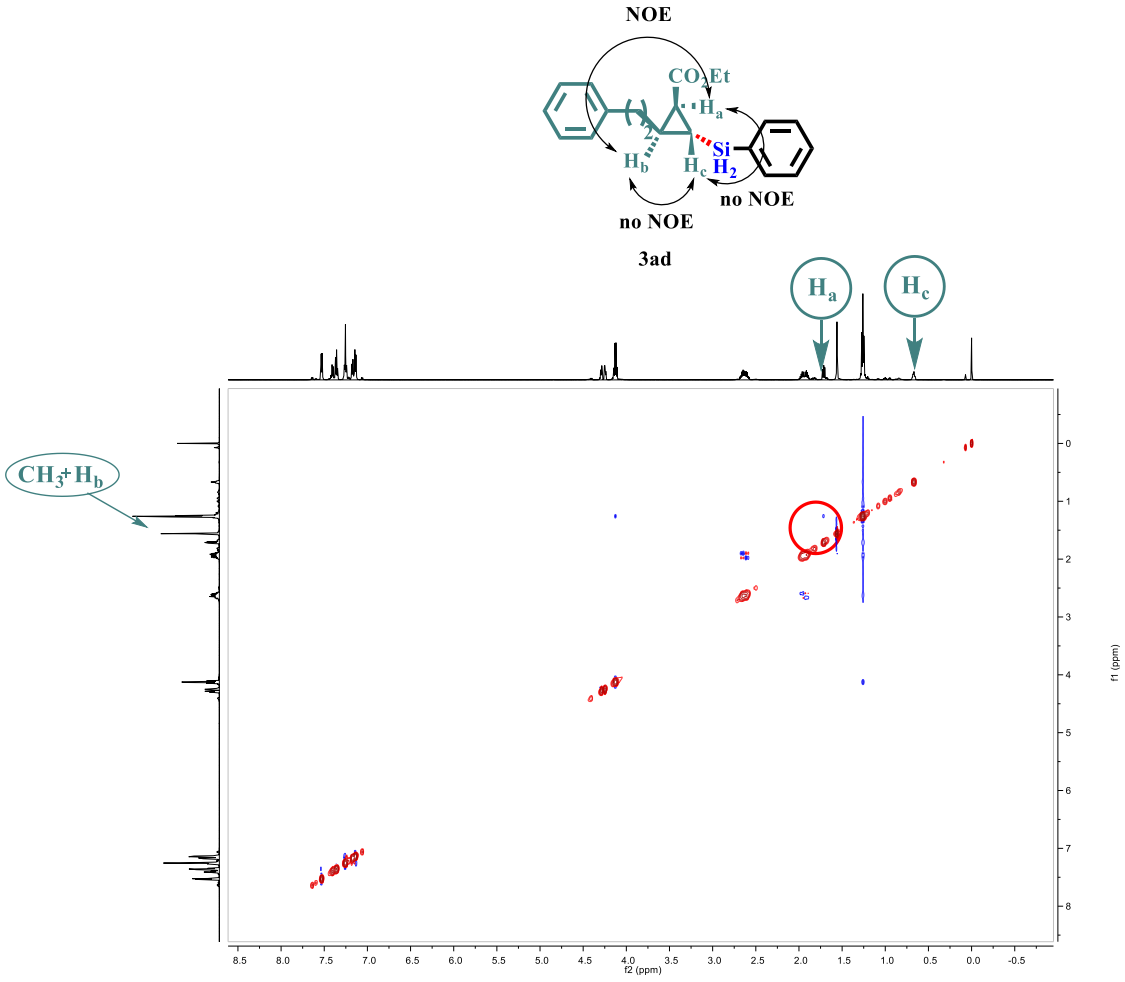
According to the NOE experiment, we observed a signal between H_a(D) and H_b(D), which means the cis configuration of H_a(D) and H_b(D). In addition, no signal was observed between H_a(D) and

H_c, hence the trans configuration between H_a(D) and H_c should be confirmed. As a result, the absolute configuration of the compound **3a**–d_2 should be determined.

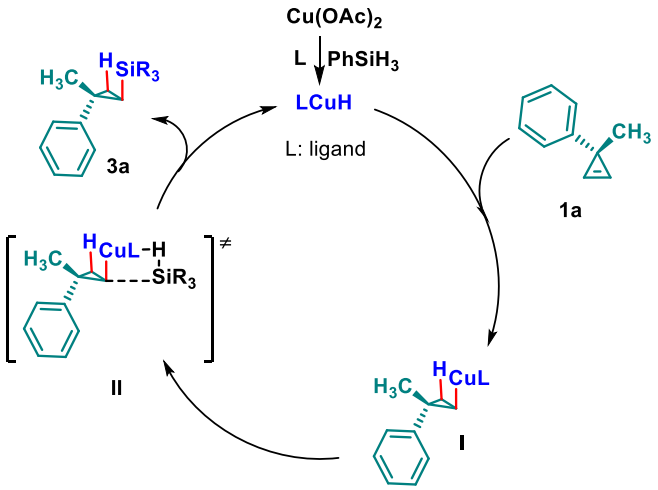




According to the NOE experiment, we observed a signal between H_a and H_b, which means the cis configuration of H_a and H_b. In addition, no signal was observed between H_b and H_c, hence the trans configuration between H_b and H_c should be confirmed. Meanwhile, no signal was observed between H_a and H_c, so the trans configuration between H_a and H_c should be confirmed. As a result, the absolute configuration of the compound **3ad** should be determined.

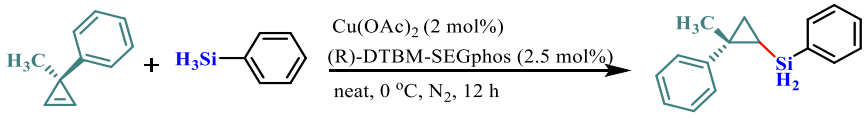


VI. The proposed mechanism

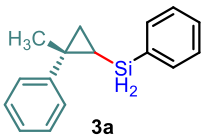


Based on the deuterium labeling experiment and previous report,[8] we proposed a possible mechanism. Firstly, the active copper hydride species could be efficitenly generated through combination $Cu(OAc)_2$ and silane in the presence of ligand. Then, a *syn*-addition of this copper hydride species to the C–C double bond in cyclopropene **1a** occurred and could provided cyclopropyl copper intermediate **I**, in which the copper and methyl group were on the same face of the cyclopropane ring, owing to steric hindrance. Finally, intermediate **I** underwent a stereoretentive transmetalation with arylsilane via a four-membered transition state **II,** furnishing the expected product **3a** and regeneration of LCuH catalyst.

VII. Experiment and HPLC spectrum of chiral compound 3a

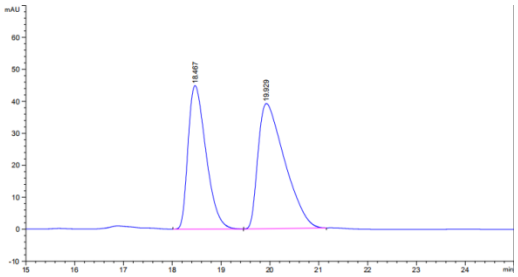


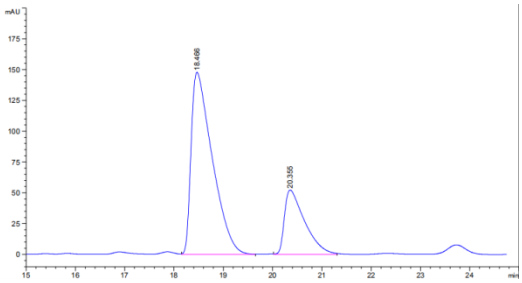
0.3 mmol 9.0 equiv **3a**, 39%, 12:1dr, 50% ee



3a

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (1.1 mg, 6.0 μmol), (R)-DTBM-SEGphos (8.84 mg, 7.5 μmol), and phenylsilane (110 μL, 3.0 equiv) was added. The vial was removed from the glovebox, and the mixture was stirred at 0 °C for 5 min. Then (1-methylcycloprop-2-en-1-yl)benzene (39.1 mg, 0.3 mmol) dissolved in phenylsilane (220 μL, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel (pure petroleum ether) to obtain product in 39% (27.8 mg) yield as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.67 – 7.65 (m, 2H), 7.42 – 7.36 (m, 3H), 7.28 – 7.27 (m, 4H), 7.17 – 7.15 (m, 1H), 4.50 – 4.48 (m, 1H), 4.45 – 4.44 (m, 1H), 1.51 (s, 3H), 1.40 (dd, *J* = 10.2, 3.6 Hz, 1H), 0.88 (dd, *J* = 7.2, 3.6 Hz, 1H), 0.43 – 0.39 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.7, 136.1, 133.5, 130.4, 129.0, 128.7, 127.6, 126.6, 26.1, 24.3, 21.2, 9.4. **HRMS** (ESI) calculated for $[C_{17}H_{21}OSi]^+$ requires m/z 269.1356, found m/z 269.1363. **Specific rotation** $[\alpha]^{14}_D$ = +18, (c =1.00, $CHCl_3$), $[\alpha]^{14}_D$ = +18, (c =1.00, $CHCl_3$)**, HPLC** analysis (OD-H, 100% Hexane, 0.4 mL/min, 250 nm) indicated 49.6% ee: tR (major) = 18.47 min, tR (minor) = 20.36 min.



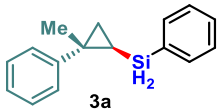


Peak #	PetTime [min]	Width [min]	Area [mAU*S]	Area %
1	18.467	0.4964	1146.74500	43.6295
2	19.929	0.4732	1181.62732	56.3705

Peak #	PetTime [min]	Width [min]	Area [mAU*S]	Area %
1	18.466	0.4964	4396.59277	74.8244
2	20.355	0.4732	1480.85681	25.1956

VIII. Analytical data of new compounds

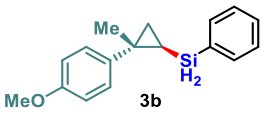
(2-methyl-2-phenylcyclopropyl)(phenyl)silane



3a

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (1.1 mg, 6.0 μmol), Xantphos (4.3 mg, 7.5 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then phenylsilane (110 μL, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then (1-methylcycloprop-2-en-1-yl)benzene (39.1 mg, 0.3 mmol) dissolved in phenylsilane (220 μL, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel (pure petroleum ether) to obtain product in 93% (66.5 mg) yield as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.67 – 7.65 (m, 2H), 7.42 – 7.36 (m, 3H), 7.28 – 7.27 (m, 4H), 7.17 – 7.15 (m, 1H), 4.50 – 4.48 (m, 1H), 4.45 – 4.44 (m, 1H), 1.51 (s, 3H), 1.40 (dd, *J* = 10.2, 3.6 Hz, 1H), 0.88 (dd, *J* = 7.2, 3.6 Hz, 1H), 0.43 – 0.39 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.7, 136.1, 133.5, 130.4, 129.0, 128.9, 127.6, 126. 6, 26.1, 24.3, 21.2, 9.4. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -31.59. **HRMS** (ESI) calculated for $[C_{17}H_{21}OSi]^+$ requires m/z 269.1356, found m/z 269.1363.

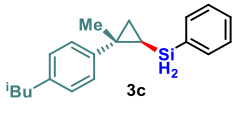
(2-(4-methoxyphenyl)-2-methylcyclopropyl)(phenyl)silane



3b

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (1.1 mg, 6.0 μmol), Xantphos (4.3 mg, 7.5 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then phenylsilane (110 μL, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then 1-methoxy-4-(1-methylcycloprop-2-en-1-yl)benzene (48.1 mg, 0.3 mmol) dissolved in phenylsilane (220 μL, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel using PE/EtOAc (50/1) as the eluent to obtain product in 62% (49.9 mg) yield as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.68 – 7.67 (m, 2H), 7.43 – 7.38 (m, 3H), 7.21 (d, *J* = 9.0 Hz, 2H), 6.83 (d, *J* = 9 Hz, 2H), 4.50 – 4.49 (m, 1H), 4.46 – 4.45 (m, 1H), 3.78 (s, 3H), 1.49 (s, 3H), 1.35 (dd, *J* = 10.2, 4.2 Hz, 1H), 0.86 (dd, *J* = 7.8, 4.2 Hz, 1H), 0.39 – 0.35 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.9, 140.4, 135.5, 133.0, 129.5, 128.2, 128.2, 113.8, 55.5, 25.1, 24.2, 20.4, 8.3. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -31.58. **HRMS** (ESI) calculated for $[C_{16}H_{19}Si]^+$ requires m/z 239.1251, found m/z 239.1247.

2-(4-isobutylphenyl)-2-methylcyclopropyl)(phenyl)silane

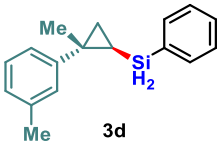


3c

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (1.1 mg, 6.0 μmol), Xantphos (4.3 mg, 7.5 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then phenylsilane (110 μL, 3.0 equiv) was added. The vial was removed from the glove box, and the

mixture was stirred at - 30 °C for 5 min. Then 1-isobutyl-4-(1-methylcycloprop-2-en-1-yl)ben -zene (55.9 mg, 0.3 mmol) dissolved in phenylsilane (220 μL, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel (pure petroleum ether) to obtain product in 62% (54.8 mg) yield as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 6.6 Hz, 2H), 7.42 – 7.37 (m, 3H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 7.8 Hz, 2H), 4.50 – 4.47 (m, 1H), 4.44 – 4.43 (m, 1H), 2.43 (d, *J* = 7.2 Hz, 2H), 1.86 – 1.80 (m,1 H), 1.50 (s, 3H), 1.38 (dd, *J* = 10.2, 3.6 Hz, 1H), 0.89 (d, *J* = 6.6 Hz, 6H), 0.86 (dd, *J* = 7.2, 4.2 Hz, 1H), 0.42 – 0.38 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 145.2, 139.2, 135.4, 133.0, 129.7, 129.1, 128.2, 126.5, 45.1, 30.3, 25.0, 23.7, 22.5, 20.7, 8.7. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -31.89. **HRMS** (ESI) calculated for $[C_{20}H_{26}NaSi]^+$ requires m/z 317.1696, found m/z 317.1701.

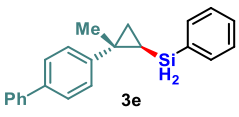
(2-methyl-2-(m-tolyl)cyclopropyl)(phenyl)silane



3d

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (2.8 mg, 15.0 μmol), Xantphos (10.3 mg, 18.0 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then phenylsilane (110 μL, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then 1-methyl-3-(1-methylcycloprop-2-en-1-yl)benzene (43.3mg, 0.3 mmol) dissolved in phenylsilane (220 μL, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel (pure petroleum ether) to obtain product in 93% (70.4 mg) yield as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.67 – 7.65 (m, 2H), 7.42 – 7.36 (m, 3H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.09 – 7.07 (m, 2H), 6.98 (d, *J* = 7.8 Hz, 1H), 4.50 – 4.49 (m, 1H), 4.45 – 4.43 (m, 1H), 2.32 (s, 3H), 1.50 (s, 3H), 1.38 (dd, *J* = 10.2, 3.6 Hz, 1H), 0.88 – 0.86 (m, 1H), 0.42 – 0.39 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.0, 139.0, 136.5, 134.0, 130.8, 129.4, 129.2, 128.8, 127.7, 125.0, 26.4, 24.8, 22.7, 21.6, 9.7. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -31.58. **HRMS** (ESI) calculated for $[C_{17}H_{20}NaSi]^+$ requires m/z 275.1226, found m/z 275.1234.

(2-([1,1'-biphenyl]-4-yl)-2-methylcyclopropyl)(phenyl)silane

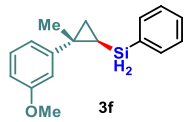


3e

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (2.8 mg, 15.0 μmol), Xantphos (10.3 mg, 18.0 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then phenylsilane (110 μL, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then 4-(1-methylcycloprop-2-en-1-yl)-1,1'-biphenyl (61.9 mg, 0.3 mmol) dissolved in phenylsilane (220 μL, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel using PE/EtOAc (30/1) as the

eluent to obtain product in 97% (91.5 mg) yield as a colorless oil.. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.68 – 7.67 (m, 2H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.38 (m, 5H), 7.35 – 7.31 (m, 3H), 4.51 (dd, *J* = 6.0, 3.6 Hz, 1H), 4.46 (dd, *J* = 6.0, 3.6 Hz, 1H), 1.55 (s, 3H), 1.45 (dd, *J* = 10.2, 4.2 Hz, 1H), 0.93 (dd, *J* = 7.2, 3.6 Hz, 1H), 0.48 – 0.44 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.0, 140.9, 138.7, 135.3, 132.7, 129.6, 128.7, 128.1, 127.0, 127.0, 24.9, 23.4, 20.7, 8.9. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -31.65. **HRMS** (ESI) calculated for $[C_{22}H_{23}Si]^+$ requires m/z 315.1564, found m/z 315.1568.

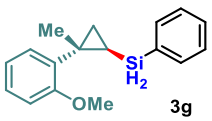
(2-(3-methoxyphenyl)-2-methylcyclopropyl)(phenyl)silane



3f

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (1.1 mg, 6.0 μmol), Xantphos (4.3 mg, 7.5 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then phenylsilane (110 μL, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then 1-methoxy-3-(1-methylcycloprop-2-en-1-yl)benzene (48.1 mg, 0.3 mmol) dissolved in phenylsilane (220 μL, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel using PE/EtOAc (50/1) as the eluent to obtain product in 90% (72.5 mg) yield as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.41 – 7.36 (m, 3H), 7.19 (t, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.83 – 6.82 (m, 1H), 6.71 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.48 – 4.47 (m, 1H), 4.45 – 4.43 (m, 1H), 3.77 (s, 3H), 1.50 (s, 3H), 1.39 (dd, *J* = 10.2, 3.6 Hz, 1H), 0.87 (dd, *J* = 7.2, 3.6 Hz, 1H), 0.43 - 0.39 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.9, 149.9, 135.6, 133.0, 129.9, 129.5, 128.4, 119. 5, 113.3, 111.10, 55.5, 25.6, 23.8, 20.8, 9.1. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -31.72. **HRMS** (ESI) calculated for $[C_{17}H_{21}OSi]^+$ requires m/z 269.1356, found m/z 269.1357.

(2-(2-methoxyphenyl)-2-methylcyclopropyl)(phenyl)silane

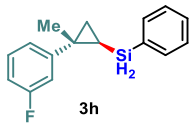


3g

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (2.8 mg, 15.0 μmol), Xantphos (10.3 mg, 18.0 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then phenylsilane (110 μL, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then 1-methoxy-2-(1-methylcycloprop-2-en-1-yl)benzene (48.1 mg, 0.3 mmol) dissolved in phenylsilane (220 μL, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr = 2:1) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel using PE/EtOAc (50/1) as the eluent to obtain product in 83% (66.8 mg) yield as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.72 – 7.7 (m, 2H), 7.41 – 7.37 (m, 3H), 7.23 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.18 – 7.15 (m, 1H), 6.85 (td, *J* = 7.8, 1.2 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 4.49 (dd, *J* = 5.4, 4.2 Hz, 1H), 4.45 (dd, *J* = 6.0, 3.6 Hz, 1H), 3.74 (s, 3H), 1.43 (s, 3H), 1.25 (dd, *J* = 10.2, 4.2 Hz, 1H), 0.80 (dd, *J* = 7.8, 4.2 Hz, 1H), 0.27 (ddd, *J* = 11.0, 7.6, 3.9 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.4, 136.1, 135.4, 133.3, 129.5, 129.4, 127. 9, 127.4, 120.1, 110.4, 55.0, 23.4, 22.8, 18.8, 6.3. **^{29}Si NMR** (99

MHz, $CDCl_3$) δ -31.20. **HRMS** (ESI) calculated for $[C_{17}H_{21}OSi]^+$ requires m/z 269.1356, found m/z 269.1363.

(2-(3-fluorophenyl)-2-methylcyclopropyl)(phenyl)silane



3h

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (1.1 mg, 6.0 μmol), Xantphos (4.3 mg, 7.5 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then phenylsilane (110 μL, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then 1-fluoro-3-(1-methylcycloprop-2-en-1-yl)benzene (44.5 mg, 0.3 mmol) dissolved in phenylsilane (220 μL, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel (pure petroleum ether) to obtain product in 63% (48.5 mg) yield as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.65 – 7.64 (m, 2H), 7.43 – 7.37 (m, 3H), 7.24 – 7.20 (m, 1H), 7.02 (dd, *J* = 7.8, 0.6 Hz, 1H), 6.95 (dd, *J* = 10.8, 1.2 Hz, 1H), 6.87 – 6.83 (m, 1H), 4.49 – 4.48 (m, 1H), 4.44 – 4.43 (m, 1H), 1.50 (s, 3H), 1.39 (dd, *J* = 10.2, 4.2 Hz, 1H), 0.95 (dd, *J* = 7.8, 4.2 Hz, 1H), 0.42 – 0.38 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 163.2 (d, *J* = 243.45 Hz), 150.9 (d, *J* = 7.05 Hz), 135.5, 132.7, 130.0, 129.9 (d, *J* = 8.55 Hz), 128.4, 122.4 (d, *J* = 2.7 Hz), 113.9 (d, *J* = 21 Hz), 112.8 (d, *J* = 21 Hz), 25.2, 23.4, 21.1, 9.6. **^{19}F NMR** (470 MHz, CDCl3) δ - 113.63 – -113.68 (m, 1F). **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -31.92. **HRMS** (ESI) calculated for $[C_{16}H_{17}FNaSi]^+$ requires m/z 279.0976, found m/z 279.0970.

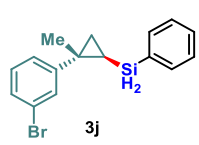
(2-(4-chlorophenyl)-2-methylcyclopropyl)(phenyl)silane

3i

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (1.1 mg, 6.0 μmol), Xantphos (4.3 mg, 7.5 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then phenylsilane (110 μL, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then 1-chloro-4-(1-methylcycloprop-2-en-1-yl)benzene (49.4 mg, 0.3 mmol) dissolved in phenylsilane (220 μL, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel (pure petroleum ether) to obtain product in 72% (58.9 mg) yield as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 7.8, 1.2 Hz, 2H), 7.41 – 7.35 (m, 3H), 7.22 – 7.20 (m, 2H), 7.18 – 7.16 (m, 2H), 4.47 – 4.45 (m, 1H), 4.42 – 4.40 (m, 1H), 1.50 (s, 3H), 1.34 (dd, *J* = 10.2, 4.2 Hz, 1H), 0.87 (dd, *J* = 7.2, 3.6 Hz, 1H), 0.36 – 0.33 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 146.2, 135.0, 132.3, 131.2, 129.5, 128.1, 128.0, 127.9, 24.6, 23.2, 20.2, 8.5. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -31.74.

HRMS (ESI) calculated for $[C_{16}H_{17}ClNaSi]^+$ requires m/z 295.0680, found m/z 295.0670.

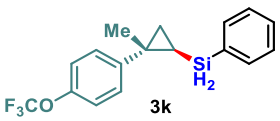
(2-(3-bromophenyl)-2-methylcyclopropyl)(phenyl)silane



3j

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (1.1 mg, 6.0 μmol), Xantphos (4.3 mg, 7.5 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then phenylsilane (110 μL, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then 1-bromo-3-(1-methylcycloprop-2-en-1-yl)benzene (62.7 mg, 0.3 mmol) dissolved in phenylsilane (220 μL, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel (pure petroleum ether) to obtain product in 84% (80.0 mg) yield as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.2 Hz, 2H), 7.43 – 7.38 (m, 4H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 4.50 – 4.48 (m, 1H), 4.44 – 4.42 (m, 1H), 1.49 (s, 3H), 1.38 (dd, *J* = 10.2, 3.6 Hz, 1H), 0.90 (dd, *J* = 7.2, 3.6 Hz, 1H), 0.42 – 0.37 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.6, 134.5, 131.6, 129.3, 129.1, 129.0, 128.1, 127.4, 124.7, 121.6, 24.3, 22.5, 19.8, 8.3. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -30.72. **HRMS** (ESI) calculated for $[C_{16}H_{17}BrSi]^+$ requires m/z 317.0356, found m/z 317.0349.

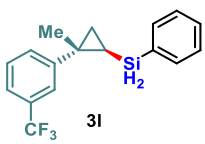
(2-methyl-2-(4-(trifluoromethoxy)phenyl)cyclopropyl)(phenyl)silane



3k

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (2.8 mg, 15.0 μmol), Xantphos (10.3 mg, 18.0 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then phenylsilane (110 μL, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then 1-(1-methylcycloprop-2-en-1-yl)-4-(trifluoromet-hoxy)benzene (64.3mg, 0.3 mmol) dissolved in phenylsilane (220 μL, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel (pure petroleum ether) to obtain product in 53% (51.3 mg) yield as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.66 – 7.64 (m, 2H), 7.44 – 7.38 (m, 3H), 7.28 – 7.27 (m, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 4.50 - 4.48 (m, 1H), 4.45 – 4.43 (m, 1H), 1.50 (s, 3H), 1.38 (dd, *J* = 10.2, 4.2 Hz, 1H), 0.91 (dd, *J* = 7.8, 4.2 Hz, 1H), 0.41 – 0.37 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.2, 146.6, 135.2, 132.4, 129.7, 128.2, 128.1, 120.5 (q, *J* = 255 Hz), 120.8, 24.9, 23.5, 20.45, 8.8. **^{19}F NMR** (470 MHz, CDCl3) δ - 57.93 (s, 3F). **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -28.56. **HRMS** (ESI) calculated for $[C_{17}H_{17}F_3NaSi]^+$ requires m/z 345.0893, found m/z 345.0889.

(2-methyl-2-(3-(trifluoromethyl)phenyl)cyclopropyl)(phenyl)silane

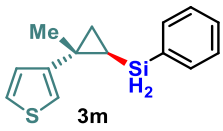


3l

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (1.1 mg, 6.0 μmol), Xantphos (4.3 mg, 7.5 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then phenylsilane (110 μL, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then 1-(1-methylcycloprop-2-en-1-yl)-3-

(trifluoromethyl)benzene(59.5 mg, 0.3 mmol) dissolved in phenylsilane (220 µL, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel (pure petroleum ether) to obtain product in 53% (48.7 mg) yield as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 6.6 Hz, 2H), 7.50 (s, 1H), 7.44 – 7.36 (m, 6H), 4.52 – 4.50 (m, 1H), 4.46 – 4.44 (m, 1H), 1.52 (s, 3H), 1.42 (dd, *J* = 10.2, 4.2 Hz, 1H), 0.95 (dd, *J* = 7.8, 4.2 Hz, 1H), 0.44 – 0.40 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 148.8, 135.3, 132.3, 130.6 (q, *J* = 31.65 Hz), 130.2, 129.8, 128.7, 128.1, 124.3 (q, *J* = 270.6 Hz), 123.5 (q, *J* = 3.75 Hz), 122.6 (q, *J* = 3.75 Hz), 25.1, 23.2, 20.5, 9.1. **^{19}F NMR** (470 MHz, CDCl3) δ - 62.51 (s, 3F). **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -31.75. **HRMS** (ESI) calculated for $[C_{17}H_{17}F_3NaSi]^+$ requires m/z 329.0944, found m/z 329.0953.

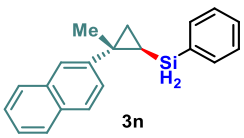
(2-methyl-2-(thiophen-3-yl)cyclopropyl)(phenyl)silane



3m

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (1.1 mg, 6.0 µmol), Xantphos (4.3 mg, 7.5 µmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then phenylsilane (110 µL, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then 3-(1-methylcycloprop-2-en-1-yl)thiophene (40.8 mg, 0.3 mmol) dissolved in phenylsilane (220 µL, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel (pure petroleum ether) to obtain product in 96% (70.3 mg) yield as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.63 – 7.62 (m, 2H), 7.41 – 7.35 (m, 3H), 7.21 (dd, *J* = 4.8, 3.0 Hz, 1H), 6.95 – 6.94 (m, 1H), 6.83 (dd,J = 5.4, 1.2 Hz, 1H), 4.46 (dd, *J* = 6.0, 4.2 Hz, 1H), 4.41 (dd, *J* = 6.0, 3.6 Hz, 1H), 1.54 (s, 3H), 1.38 (dd, *J* = 10.2, 3.6 Hz, 1H), 0.92 (dd, *J* = 7.8, 4.2 Hz, 1H), 0.44 – 0.40 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.5, 135.3, 132.5, 129.7, 128.1, 125.5, 125.4, 118.3, 22.1, 21.8, 21.4, 10.0. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -32.00. **HRMS** (ESI) calculated for $[C_{14}H_{17}SSi]^+$ requires m/z 245.0815, found m/z 245.0818.

(2-methyl-2-(naphthalen-2-yl)cyclopropyl)(phenyl)silane

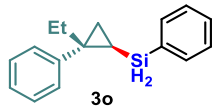


3n

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (2.8 mg, 15.0 µmol), Xantphos (10.3 mg, 18.0 µmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then phenylsilane (110 µL, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at -30 °C for 5 min. Then 2-(1-methylcycloprop-2-en-1-yl)naphthalene (54.1 mg, 0.3 mmol) dissolved in phenylsilane (220 µL, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel

using PE/EtOAc (40/1) as the eluent to obtain product in 76% (65.8 mg) yield as a white solid. M. P. 31-33 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.79 – 7.76 (m, 2H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.71 (s, 1H), 7.68 (d, *J* = 6.6 Hz, 2H), 7.45 – 7.36 (m, 6H), 4.55 – 4.53 (m, 1H), 4.49 – 4.48 (m, 1H), 1.60 (s, 3H), 1.51 (dd, *J* = 10.2, 3.6 Hz, 1H), 0.96 (dd, *J* = 7.2, 3.6 Hz, 1H), 0.54 – 0.50 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 145.7, 135.8, 133.9, 133.1, 132.3, 130.1, 128.5, 128.4, 128.0, 127.9, 126.4, 126.0, 125.8, 125.4, 25.9, 23.9, 20.9, 9.0. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -31.59. **HRMS** (ESI) calculated for $[C_{20}H_{20}Si]^+$ requires m/z 311.1226, found m/z 311.1236.

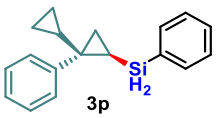
(2-ethyl-2-phenylcyclopropyl)(phenyl)silane



3o

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (1.1 mg, 6.0 μmol), Xantphos (4.3 mg, 7.5 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then phenylsilane (110 μL, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then (1-ethylcycloprop-2-en-1-yl)benzene (43.3 mg, 0.3 mmol) dissolved in phenylsilane (220 μL, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel (pure petroleum ether) to obtain product in 72% (54.5 mg) yield as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 6.2 Hz, 2H), 7.43 – 7.38 (m, 3H), 7.28 – 7.25 (m, 4H), 7.17 (t, *J* = 6.6 Hz, 1H), 4.55 – 4.54 (m, 1H), 4.43 – 4.41 (m, 1H), 1.83 – 1.77 (m, 1H), 1.68 – 1.62 (m, 1H), 1.33 (dd, *J* = 10.2, 3.6 Hz, 1H), 0.83 (t, *J* = 7.8 Hz, 3H), 0.80 (dd, *J* = 7.8, 3.7 Hz, 1H), 0.39 – 0.34 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 145.7, 135.2, 132.9, 129.5, 128.9, 127.9, 127.9, 125.9, 32.5, 30.9, 18.1, 11.8, 6.9. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -31.89. **HRMS** (ESI) calculated for $[C_{17}H_{20}NaSi]^+$ requires m/z 275.1226, found m/z 275.1233.

phenyl(1-phenyl-[1,1'-bi(cyclopropan)]-2-yl)silane

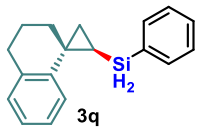


3p

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (1.1 mg, 6.0 μmol), Xantphos (4.3 mg, 7.5 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then phenylsilane (110 μL, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then [1,1'-bi(cyclopropan)]-2-en-1-ylbenzene (46.9 mg, 0.3 mmol) dissolved in phenylsilane (220 μL, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr = 3.4:1) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel (pure petroleum ether) to obtain product in 88% (69.8 mg) yield as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.70 – 7.68 (m, 2H), 7.40 – 7.36 (m, 3H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.26 (t, *J* = 7.2 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 4.58 – 4.56 (m, 1H), 4.50 – 4.48 (m, 1H), 1.24 – 1.22 (m, 1H), 1.18 (dd, *J* = 10.2, 4.2 Hz, 1H), 0.85 (dd, *J* = 7.2, 4.2 Hz, 1H), 0.55 – 0.47 (m, 2H), 0.43 – 0.39 (m, 1H), 0.21– 0.18 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 146.8, 135.4, 130.0, 129.7, 128.4, 128.2, 128.0, 126.2, 31.2, 16.7, 16.1, 9.1, 5.1, 4.7. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -30.44 (s), -32.28. **HRMS** (ESI)

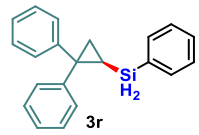
calculated for $[C_{18}H_{20}NaSi]^+$ requires m/z 287.1226, found m/z 287.1221.

(3',4'-dihydro-2'H-spiro[cyclopropane-1,1'-naphthalen]-2-yl)(phenyl)silane



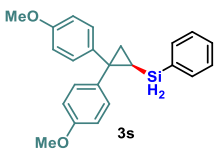
Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (2.8 mg, 15.0 μmol), Xantphos (10.3 mg, 18.0 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then phenylsilane (110 μL, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then 3',4'-dihydro-2'H-spiro[cyclopropane-1,1'-naphthalen]-2-ene (46.9 mg, 0.3 mmol) dissolved in phenylsilane (220 μL, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel (pure petroleum ether) to obtain product in 74% (58.7 mg) yield as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.62 – 7.61 (m, 2H), 7.39 – 7.34 (m, 3H), 7.09 – 7.02 (m, 3H), 6.75 (d, *J* = 7.2 Hz, 1H), 4.50 – 4.49 (m, 1H), 4.40 – 4.38 (m, 1H), 2.86 (t, *J* = 6.0 Hz, 2H), 1.89 – 1.82 (m, 4H), 1.46 (dd, *J* = 10.2, 4.2 Hz, 1H), 0.96 (dd, *J* = 7.8, 4.2 Hz, 1H), 0.53 – 0.49 (m, 1H).**^{13}C NMR** (150 MHz, $CDCl_3$) δ 141.1, 136.8, 134.6, 131.8, 128.9, 128.2, 127.3, 125.5, 124.3, 120.9, 31.9, 29.9, 23.4, 23.1, 21.8, 12.6. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -32.30. **HRMS** (ESI) calculated for $[C_{18}H_{21}Si]^+$ requires m/z 265.1407, found m/z 265.1411.

(2,2-diphenylcyclopropyl)(phenyl)silane



Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (1.1 mg, 6.0 μmol), Xantphos (4.3 mg, 7.5 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then phenylsilane (110 μL, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then cycloprop-2-ene-1,1-diyldibenzene (57.6 mg, 0.3 mmol) dissolved in phenylsilane (220 μL, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel (pure petroleum ether) to obtain product in 67% (60.4 mg) yield as a white solid. M.P. 39- 41 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.44 – 7.43 (m, 2H), 7.37 – 7.30 (m, 3H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.27 – 7.25 (m, 2H), 7.23 – 7.20 (m, 5H), 7.13 – 7.11 (m, 1H), 4.22 – 4.21 (m, 1H), 3.84 – 3.82 (m, 1H), 1.61 – 1.59 (m, 1H), 1.53 (dd, *J* = 10.8, 4.2 Hz, 1H), 1.06 –1.03 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.9, 143.4, 136.2, 133.2, 131.3, 130. 5, 129.2, 129.1, 128.8, 128.3, 127.6, 126.8, 36.3, 20.8, 10.4. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -30.60. **HRMS** (ESI) calculated for $[C_{21}H_{21}Si]^+$ requires m/z 301.1407, found m/z 301.1398.

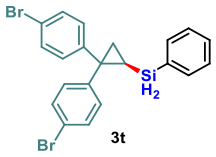
(2,2-bis(4-methoxyphenyl)cyclopropyl)(phenyl)silane



Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (2.8 mg, 15.0 μmol), Xantphos (10.3 mg, 18.0 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for

10 min, then phenylsilane (110 µL, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then 4,4'-(cycloprop-2-ene-1,1-diyl)bis(methoxybenzene) (75.7 mg, 0.3 mmol) dissolved in phenylsilane (220 µL, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel using PE/EtOAc (40/1) as the eluent to obtain product in 88% (95.2 mg) yield as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.51 – 7.50 (m, 2H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 9.0 Hz, 2H), 7.17 (d, *J* = 8.4 Hz 2H), 6.85 – 6.80 (m, 4H), 4.26 (dd, *J* = 6.0, 2.4 Hz, 1H), 3.90 – 3.89 (m, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 1.57 (dd, *J* = 7.2, 3.6 Hz, 1H), 1.50 (dd, *J* = 10.2, 3.6 Hz, 1H), 1.03 – 0.99 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.2, 157.7, 139.6, 135.2, 135.1, 132.5, 131.1, 129.4, 128.3, 127.8, 113.5, 113.5, 55.2, 55.2, 34.0, 19.7, 9.2. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -30.57. **HRMS** (ESI) calculated for $[C_{23}H_{24}NaO_2Si]^+$ requires m/z 383.1438, found m/z 383.1432.

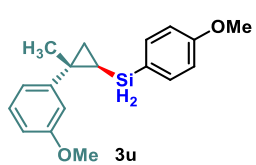
(2,2-bis(4-bromophenyl)cyclopropyl)(phenyl)silane



3t

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (2.8 mg, 15.0 µmol), Xantphos (10.3 mg, 18.0 µmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then phenylsilane (110 µL, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then 4,4'-(cycloprop-2-ene-1,1-diyl)bis(bromobenzene) (105.0 mg, 0.3 mmol) dissolved in phenylsilane (220 µL, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel (pure petroleum ether) to obtain product in 83% (114.1 mg) yield as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.42 – 7.40 (m, 2H), 7.38 – 7.36 (m, 3H), 7.34 – 7.30 (m, 4H), 7.15 – 7.13 (m, 2H), 7.04 – 7.02 (m, 2H), 4.20 (dd, *J* = 6.6, 2.4 Hz, 1H), 3.88 (dd, *J* = 6.6, 4.2 Hz, 1H), 1.56 (dd, *J* = 7.2, 4.2 Hz, 1H), 1.47 (dd, *J* = 10.2, 4.2 Hz, 1H), 1.04 – 0.99 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 145.4, 140.9, 135.2, 131.9, 131.5, 131.5, 131.3, 129.7, 129.1, 128.0, 120.9, 119.9, 34.4, 19.8, 9.5. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -30.79. **HRMS** (ESI) calculated for $[C_{21}H_{18}Br_2NaSi]^+$ requires m/z 478.9437, found m/z 478.9431.

(4-methoxyphenyl)(2-(3-methoxyphenyl)-2-methylcyclopropyl)silane

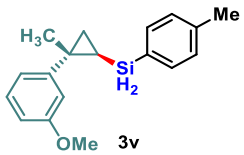


3u

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (2.8 mg, 15.0 µmol), Xantphos (10.3 mg, 18.0 µmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then (4-methoxyphenyl)silane (124.4 mg, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then1-methoxy-3-(1-methylcycloprop-2-en-1-yl)benzene (48.1 mg, 0.3 mmol) dissolved in (4-methoxyphenyl)silane (248.8 mg, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the

cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel using PE/EtOAc (30/1) as the eluent to obtain product in 71% (63.6 mg) yield as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.4 Hz, 2H), 7.17 (t, *J* = 8.4 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.81 – 6.80 (m, 1H), 6.69 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.45 – 4.43 (m, 1H), 4.41 – 4.39 (m, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 1.48 (s, 3H), 1.36 (dd, *J* = 10.2, 3.6 Hz, 1H), 0.89 (dd, *J* = 7.2, 3.6 Hz, 1H), 0.39 – 0.35 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.7, 159.3, 149.5, 136.5, 129.0, 123.0, 118.9, 113.7, 112.7, 110.5, 54.9, 54.8, 25.0, 23.1, 20.3, 8.9. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -32.21. **HRMS** (ESI) calculated for $[C_{18}H_{22}NaO_2Si]^+$ requires m/z 321.1281, found m/z 321.1265.

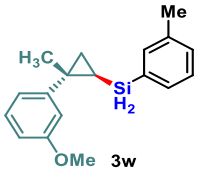
(2-(3-methoxyphenyl)-2-methylcyclopropyl)(p-tolyl)silane



3v

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (2.8 mg, 15.0 μmol), Xantphos (10.3 mg, 18.0 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then p-tolylsilane (110.0 mg, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then 1-methoxy-3-(1-methylcycloprop-2-en-1-yl)benzene (48.1 mg, 0.3 mmol) dissolved in p-tolylsilane (220.0 mg, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel using PE/EtOAc (50/1) as the eluent to obtain product in 60% (50.8 mg) yield as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.2 Hz, 2H), 7.21 – 7.17 (m, 3H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.82 (s, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 4.47 – 4.45 (m, 1H), 4.42 – 4.41 (m, 1H), 3.78 (s, 3H), 2.36 (s, 3H), 1.49 (s, 3H), 1.38 (dd, *J* = 10.2, 3.6 Hz, 1H), 0.86 (dd, *J* = 7.2, 3.6 Hz, 1H), 0.41 – 0.38 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.5, 149.6, 139.5, 135.2, 129.1, 128.8, 128.8, 119.1, 112.9, 110. 7, 55.1, 25.2, 23.3, 21.4, 20.4, 8.8. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -32.05. **HRMS** (ESI) calculated for $[C_{18}H_{23}OSi]^+$ requires m/z 283.1513, found m/z 283.1522.

(2-(3-methoxyphenyl)-2-methylcyclopropyl)(m-tolyl)silane

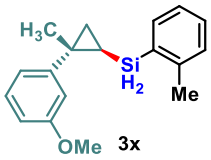


3w

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (2.8 mg, 15.0 μmol), Xantphos (10.3 mg, 18.0 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then m-tolylsilane (110.0 mg, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then 1-methoxy-3-(1-methylcycloprop-2-en-1-yl)benzene (48.1 mg, 0.3 mmol) dissolved in m-tolylsilane (220.0 mg, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel using PE/EtOAc (50/1) as the eluent to obtain product in 68% (57.6 mg) yield as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.2 Hz, 1H), 7.31 (t, *J* = 7.2

Hz, 1H), 7.21 – 7.17 (m, 3H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.83 (t, *J* = 2.4 Hz, 1H), 6.71 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.52 (dd, *J* = 5.4, 3.6 Hz, 1H), 4.45 (dd, *J* = 5.4, 3.6 Hz, 1H), 3.79 (s, 3H), 2.49 (s, 3H), 1.50 (s, 3H), 1.41 (dd, *J* = 10.2, 3.6 Hz, 1H), 0.85 (dd, *J* = 7.8, 4.2 Hz, 1H), 0.42 – 0.38 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.6, 149.6, 144.1, 136.4, 132.0, 130.1, 129.3, 129.2, 125.2, 119.0, 112.9, 110.7, 55.2, 25.3, 23.1, 22.6, 20.9, 8.6. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -30.48. **HRMS** (ESI) calculated for $[C_{18}H_{22}NaOSi]^+$ requires m/z 305.1332, found m/z 305.1338.

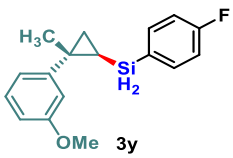
(2-(3-methoxyphenyl)-2-methylcyclopropyl)(o-tolyl)silane



3x

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (2.8 mg, 15.0 μmol), Xantphos (10.3 mg, 18.0 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then o-tolylsilane (110.0 mg, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then 1-methoxy-3-(1-methylcycloprop-2-en-1-yl)benzene (48.1 mg, 0.3 mmol) dissolved in o-tolylsilane (220.0 mg, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel using PE/EtOAc (50/1) as the eluent to obtain product in 62% (52.5 mg) yield as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.83 (s, 1H), 6.71 (dd, *J* = 7.8, 1.8 Hz, 1H), 4.46 (dd, *J* = 5.4, 3.6 Hz, 1H), 4.41 (dd, *J* = 5.4, 3.6 Hz, 1H), 3.79 (s, 3H), 2.36 (s, 3H), 1.50 (s, 3H), 1.39 (dd, *J* = 10.2, 3.6 Hz, 1H), 0.87 (dd, *J* = 7.8, 4.2 Hz, 1H), 0.42 – 0.38 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159. 6, 149.7, 137.4, 135.9, 132.5, 132.3, 130.4, 129.2, 128.0, 119.2, 113.0, 110.8, 55.2, 25.3, 23.4, 21.4, 20.5, 8.8. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -31.79. **HRMS** (ESI) calculated for $[C_{18}H_{22}NaOSi]^+$ requires m/z 305.1332, found m/z 305.1341.

(4-fluorophenyl)(2-(3-methoxyphenyl)-2-methylcyclopropyl)silane

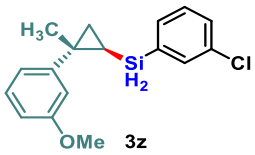


3y

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (2.8 mg, 15.0 μmol), Xantphos (10.3 mg, 18.0 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then (4-fluorophenyl)silane (113.6 mg, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then1-methoxy-3-(1-methylcycloprop-2-en-1-yl)benzene (48.1 mg, 0.3 mmol) dissolved in (4-fluorophenyl)silane (227.2 mg, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel using PE/EtOAc (50/1) as the eluent to obtain product in 65% (55.9 mg) yield as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.66 – 7.64 (m, 2H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.11 (t, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.85 (d, *J* = 1.2 Hz, 1H), 6.75 – 6.74 (m, 1H), 4.51 – 4.49 (m, 1H), 4.46 – 4.45 (m, 1H), 3.82 (s, 3H), 1.52 (s, 3H), 1.43 (dd, *J* = 10.2, 3.6 Hz, 1H), 0.90 (dd, *J* = 7.2, 3.6 Hz, 1H), 0.43 – 0.39 (m, 1H). **^{13}C NMR** (150 MHz,

$CDCl_3$) δ 164.0 (d, J = 247.4 Hz), 159.5, 149.4, 137.1 (d, *J* = 7.5 Hz), 129.2, 128.0 (d, *J* = 3.9 Hz), 119.0, 115.2 (d, *J* = 19.8 Hz), 112.9, 110.7, 55.1, 25.2, 23.3, 20.4, 8.7. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -110.81– -110.87 (m, 1F). **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -30.48. **HRMS** (ESI) calculated for $[C_{17}H_{20}FOSi]^+$ requires m/z 287.1262, found m/z 287.1256.

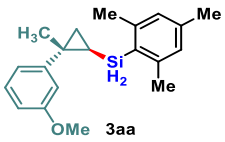
(3-chlorophenyl)(2-(3-methoxyphenyl)-2-methylcyclopropyl)silane



3z

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (2.8 mg, 15.0 μmol), Xantphos (10.3 mg, 18.0 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then (3-chlorophenyl)silane (128.4 mg, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then1-methoxy-3-(1-methylcycloprop-2-en-1-yl)benzene (48.1 mg, 0.3 mmol) dissolved in (3-chlorophenyl)silane (256.8 mg, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel using PE/EtOAc (50/1) as the eluent to obtain product in 67% (60.9 mg) yield as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 1.8 Hz, 1H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.80 (t, *J* = 2.4, 1H), 6.70 (dd, *J* = 7.8, 2.4 Hz, 1H), 4.45 – 4.44 (m, 1H), 4.40 – 4.39 (dd, *J* = 6.2, 3.9 Hz, 1H), 3.77 (s, 3H), 1.47 (s, 3H), 1.40 (dd, *J* = 10.2, 3.6 Hz, 1H), 0.88 (dd, *J* = 7.8, 4.2 Hz, 1H), 0.40 - 0.36 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 158.8, 148.6, 134.7, 134.2, 133.7, 132.4, 129.0, 128.8, 128.6, 118.4, 112.2, 110.2, 54.4, 24.7, 22.8, 19.7, 7.7. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -31.45. **HRMS** (ESI) calculated for $[C_{17}H_{20}ClOSi]^+$ requires m/z 303.0966, found m/z 303.0962.

mesityl(2-(3-methoxyphenyl)-2-methylcyclopropyl)silane

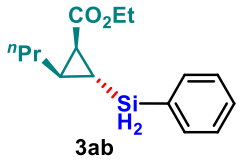


3aa

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (2.8 mg, 15.0 μmol), Xantphos (10.3 mg, 18.0 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then mesitylsilane (135.3 mg, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then 1-methoxy-3-(1-methylcycloprop-2-en-1-yl)benzene (48.1 mg, 0.3 mmol) dissolved in mesitylsilane (270.5 mg, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel using PE/EtOAc (30/1) as the eluent to obtain product in 31% (28.9 mg) yield as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.8 Hz, 1H), 6.87 (s, 2H), 6.82 (d, *J* = 8.0 Hz, 1H), 6. 78 (t, *J* = 1.8 Hz, 1H), 6.69 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.62 (dd, *J* = 5.4, 2.4 Hz, 1H), 4.46 (dd, *J* = 5.4, 4.2 Hz, 1H), 3.78 (s, 3H), 2.49 (s, 6H), 2.27 (s, 3H), 1.50 (s, 3H), 1.36 (dd, *J* = 10.2, 3.6 Hz, 1H), 0.80 (dd, *J* = 7.2, 3.8 Hz, 1H), 0.30 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.5, 149.7, 144.6, 139.6, 129.1, 128.2, 127.4, 118.9, 112.7, 110.6, 55.1, 25.3, 23.7, 23.1, 21.7, 21.2, 9.4. **^{29}Si NMR** (99 MHz,

$CDCl_3$) δ -30.36. **HRMS** (ESI) calculated for $[C_{20}H_{26}NaOSi]^+$ requires m/z 333.1645, found m/z 333.1653.

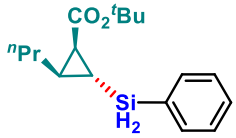
ethyl 2-(phenylsilyl)-3-propylcyclopropane-1-carboxylate



3ab

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (2.8 mg, 15.0 μmol), Xantphos (10.3 mg, 18.0 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then phenylsilane (110 μL, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then ethyl 2-propylcycloprop-2-ene-1-carboxylate (46.2 mg, 0.3 mmol) dissolved in phenylsilane (220 μL, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr = 16:1) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel using PE/EA (30/1) as the eluent to obtain product in 95% (74.8 mg) yield as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 – 7.55 (m, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.38 - 7.35 (m, 2H), 4.31 (dd, *J* = 6.6, 3.0 Hz, 1H), 4.26 (dd, *J* = 6.6, 3.0 Hz, 1H), 4.14 (qd, *J* = 7.2, 1.8 Hz, 2H), 1.71 (dd, *J* = 7.8, 6.6 Hz, 1H), 1.63 – 1.52 (m, 2H), 1.41 – 1.35 (m, 2H), 1.27 – 1.25 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H), 0.66 – 0.62 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.5, 135.3, 129.9, 128.1, 128.1, 60.5, 29.9, 26.5, 23.2, 22.8, 14.3, 13.8, 8.2. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -30.36. **HRMS** (ESI) calculated for $[C_{12}H_{22}NaO_2Si]^+$ requires m/z 285.1281, found m/z 285.1280.

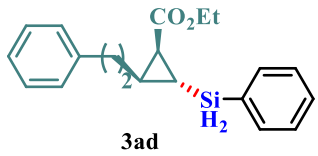
tert-butyl 2-(phenylsilyl)-3-propylcyclopropane-1-carboxylate



3ac

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (2.8 mg, 15.0 μmol), Xantphos (10.3 mg, 18.0 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then phenylsilane (110 μL, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then tert-butyl 2-propylcycloprop-2-ene-1-carboxylate (54.6 mg, 0.3 mmol) dissolved in phenylsilane (220 μL, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr > 20:1) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel using PE/EA (30/1) as the eluent to obtain product in 92% (80.1 mg) yield as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.57 – 7.55 (m, 2H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 2H), 4.32 (dd, *J* = 6.6, 2.4 Hz, 1H), 4.24 (dd, *J* = 6.6, 3.0 Hz, 1H), 1.66 – 1.63 (m, 1H), 1.61 – 1.50 (m, 2H), 1.45 (s, 9H), 1.40 – 1.32 (m, 2H), 1.22 – 1.17 (m, 1H), 0.89 (t, *J* = 7.2 Hz, 3H), 0.59 – 0.55 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.6, 135.3, 131.2, 129.8, 128.0, 80.3, 29.9, 28.2, 26.2, 24.3, 22.9, 13.8, 7.5. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -27.19. **HRMS** (ESI) calculated for $[C_{17}H_{26}NaO_2Si]^+$ requires m/z 313.1594, found m/z 313.1601.

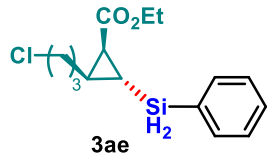
ethyl 2-phenethyl-3-(phenylsilyl)cyclopropane-1-carboxylate



3ad

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (2.8 mg, 15.0 μmol), Xantphos (10.3 mg, 18.0 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then phenylsilane (110 μL, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then ethyl 2-phenethylcycloprop-2-ene-1-carboxylate (64.9 mg, 0.3 mmol) dissolved in phenylsilane (220 μL, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr = 17:1) was assessed by ^1H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel using PE/EA (30/1) as the eluent to obtain product in 83% (80.7 mg) yield as a colorless oil. **^1H NMR** (600 MHz, $CDCl_3$) δ 7.54 – 7.52 (m, 2H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.37 – 7.34 (m, 2H), 7.26 – 7.24 (m, 2H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.2 Hz, 2H), 4.29 (dd, *J* = 6.6, 2.4 Hz, 1H), 4.25 (dd, *J* = 6.6, 3.0 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.68 – 2.58 (m, 2H), 2.00 – 1.88 (m, 2H), 1.71 (dd, *J* = 8.4, 6.6 Hz, 1H), 1.27 – 1.25 (m, 4H), 0.69 – 0.65 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.4, 141.7, 135.4, 130.8, 130.0, 128.5, 128.3, 128.1, 125.8, 60.6, 35.9, 29.8, 26.2, 23.2, 14.4, 8.5. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -30.36. **HRMS** (ESI) calculated for $[C_{20}H_{24}NaO_2Si]^+$ requires m/z 347.1438, found m/z 347.1438.

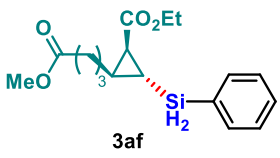
ethyl 2-(3-chloropropyl)-3-(phenylsilyl)cyclopropane-1-carboxylate



3ae

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (2.8 mg, 15.0 μmol), Xantphos (10.3 mg, 18.0 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then phenylsilane (110 μL, 3.0 equiv) was added. The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then ethyl 2-(3-chloropropyl)cycloprop-2-ene-1-carboxylate (56.4 mg, 0.3 mmol) dissolved in phenylsilane (220 μL, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr = 15:1) was assessed by ^1H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel using PE/EA (30/1) as the eluent to obtain product in 66% (58.6 mg) yield as a colorless oil. **^1H NMR** (600 MHz, $CDCl_3$) δ 7.56 – 7.55 (m, 2H), 7.43 – 7.41 (m, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 4.33 (dd, *J* = 6.6, 3.0 Hz, 1H), 4.27 (dd, *J* = 6.6, 3.0 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.49 (t, *J* = 6.0 Hz, 2H), 1.85 – 1.71 (m, 5H), 1.27 (m, 7.2 Hz, 3H), 1.25 – 1.22 (m, 1H), 0.69 – 0.65 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.2, 135.3, 130.6, 130.1, 128.2, 60.7, 44.4, 32.6, 25.6, 25.2, 23.2, 14.3, 8.4. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -26.34. **HRMS** (ESI) calculated for $[C_{15}H_{21}ClNaO_2Si]^+$ requires m/z 319.0892, found m/z 319.0902.

ethyl 2-(4-methoxy-4-oxobutyl)-3-(phenylsilyl)cyclopropane-1-carboxylate



3af

Prepared according to general procedure. In a nitrogen-filled glovebox, a flame-dried reaction tube equipped with a Teflon-coated magnetic stir bar were charged with $Cu(OAc)_2$ (2.8 mg, 15.0 μmol), Xantphos (10.3 mg, 18.0 μmol), and anhydrous CH_3CN (0.3 mL). The resulting mixture was stirred for 10 min, then phenylsilane (110 μL, 3.0 equiv) was added.

The vial was removed from the glove box, and the mixture was stirred at - 30 °C for 5 min. Then ethyl 2-(4-methoxy-4-oxobutyl)cycloprop-2-ene-1-carboxylate (63.6 mg, 0.3 mmol) dissolved in phenylsilane (220 μL, 6.0 equiv) was added by using a 1.0 mL syringe. Immediately after, the temperature was warmed to 0 °C and the mixture was stirred at 0 °C for 12 h. And then the cap was removed. After removal of solvent under reduced pressure with aid of a rotary evaporator, the diastereomeric ratio (dr = 20:1) was assessed by ^{1}H NMR in $CDCl_3$. The resulting crude product was purified by flash column chromatography on silica gel using PE/EA (10/1) as the eluent to obtain product in 83% (80.7 mg) yield as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 6.6 Hz, 2H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.2 Hz, 2H), 4.32 (dd, *J* = 6.6, 3.0 Hz, 1H), 4.27 (dd, *J* = 6.6, 3.0 Hz, 1H), 4.14 (qd, *J* = 7.2, 1.8 Hz, 2H), 3.65 (s, 3H), 2.29 (t, *J* = 7.0 Hz, 2H), 1.73 – 1.71 (m, 1H), 1.70 – 1.61 (m, 4H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.22 (dd, *J* = 13.8, 6.6 Hz, 1H), 0.64 (qd, *J* = 6.3, 2.9 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 173.8, 172.2, 135.3, 130.7, 130.0, 128.1, 60.6, 51.4, 33.6, 27.3, 26.1, 24.9, 23.1, 14.3, 8.3. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ -26.96. **HRMS** (ESI) calculated for $[C_{17}H_{24}NaO_4Si]^+$ requires m/z 343.1336, found m/z 343.134

IX. References

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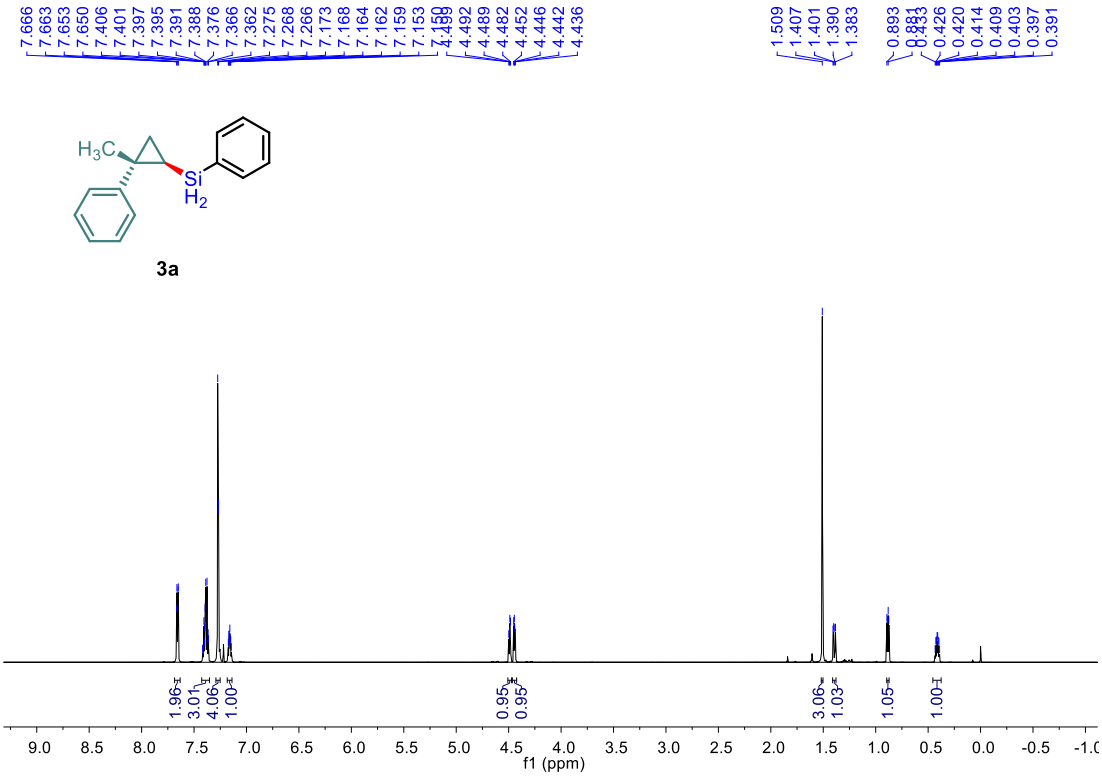
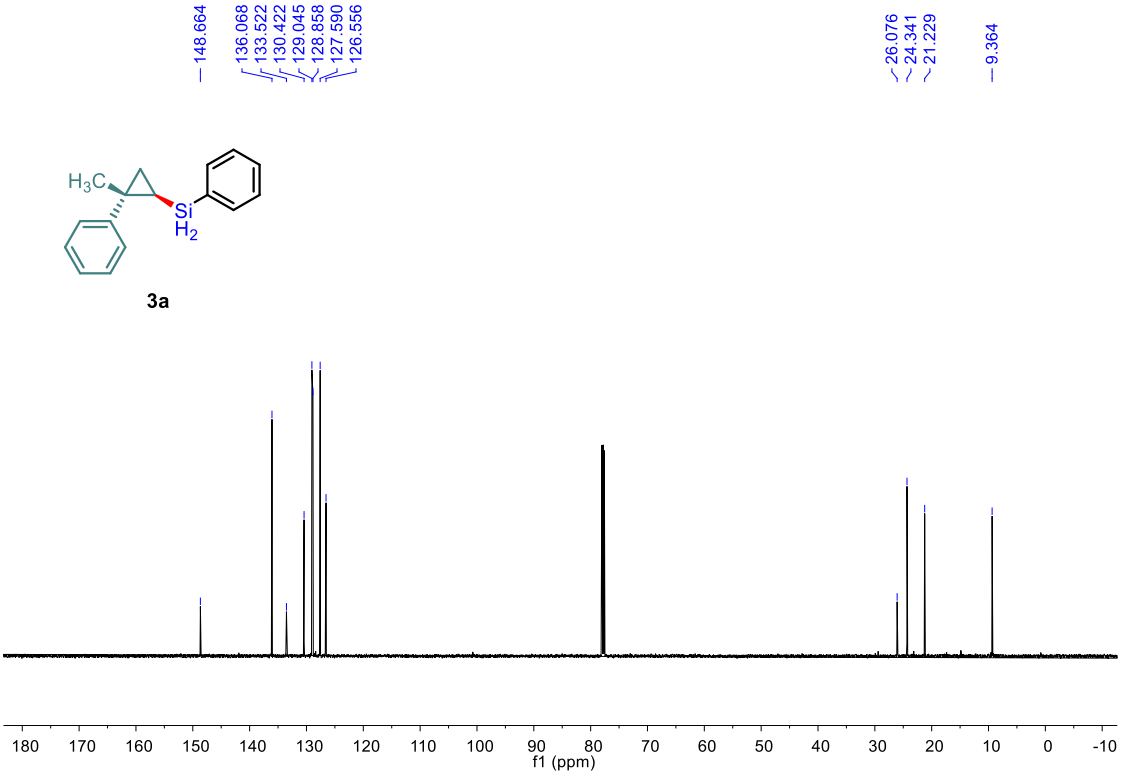
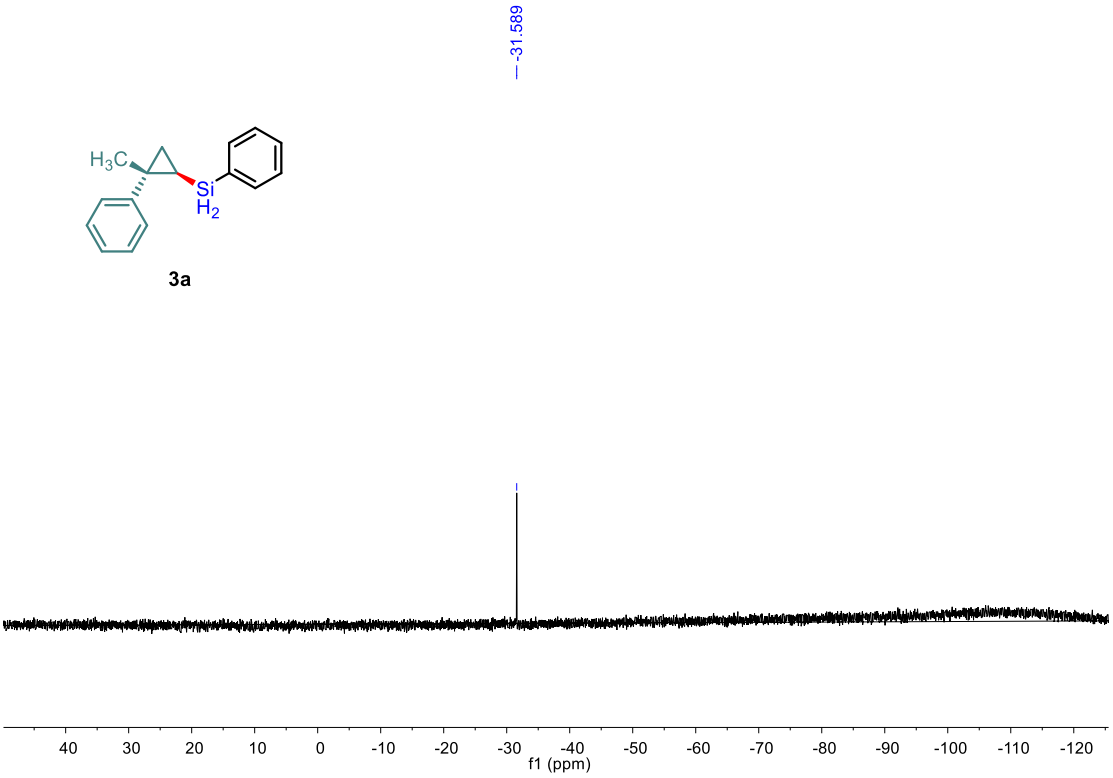
X. ^{1}H, ^{13}C and ^{19}F NMR Spectra of new compounds



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H2
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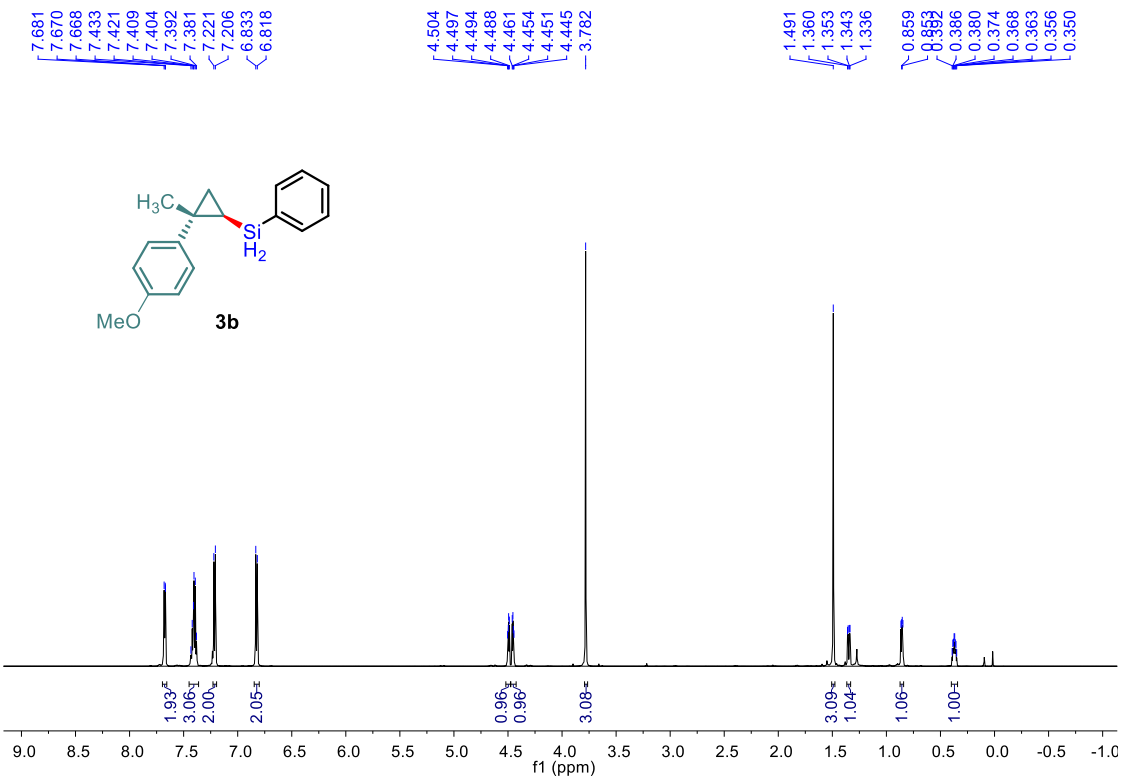
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
f1 (ppm)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4.461
4.454
4.451
4.445
3.782
1.491
1.360
1.353
1.343
1.336
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0.363
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Si
H2
MeO
3b
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3.08
3.09
1.04
1.06
1.00
9.0
8.5
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7.0
6.5
6.0
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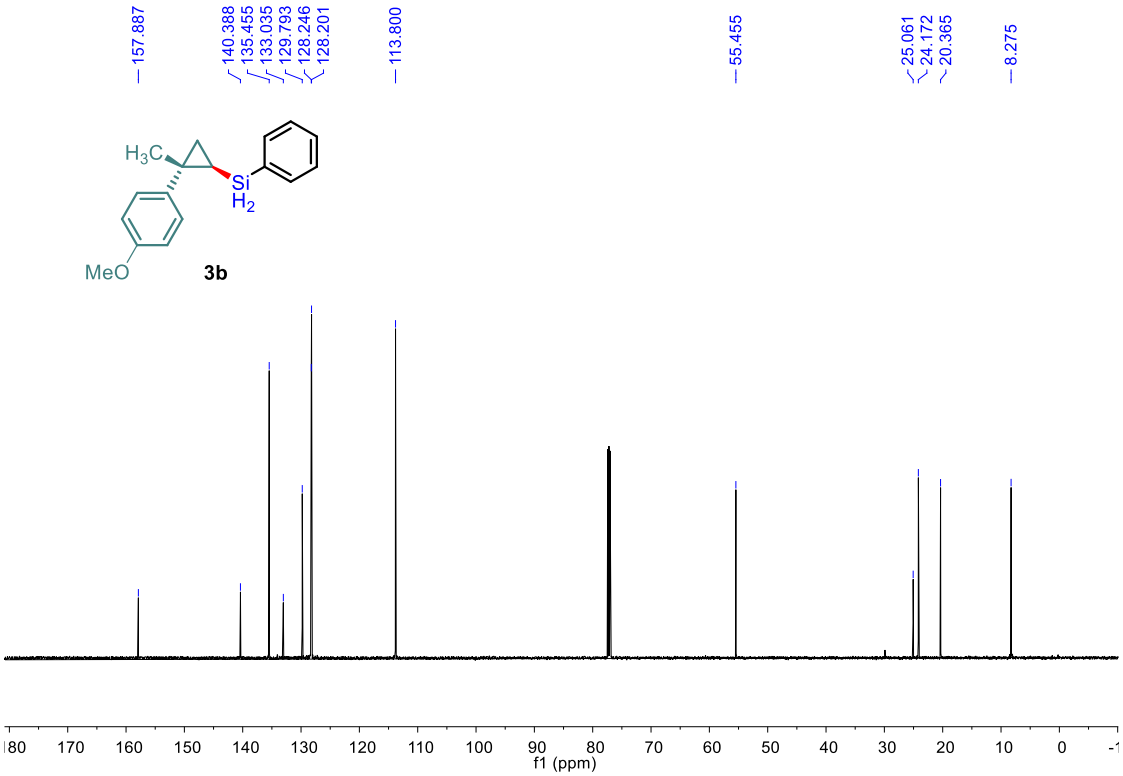
f1 (ppm)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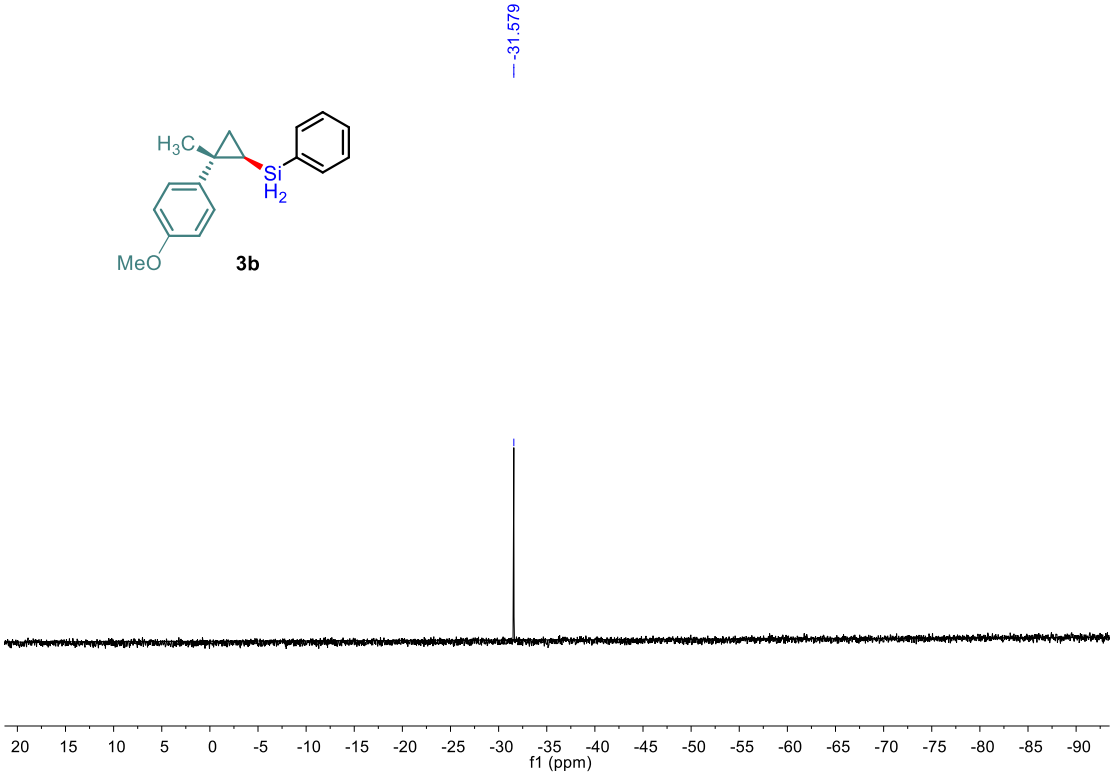
Si
H2
MeO
3b
f1 (ppm)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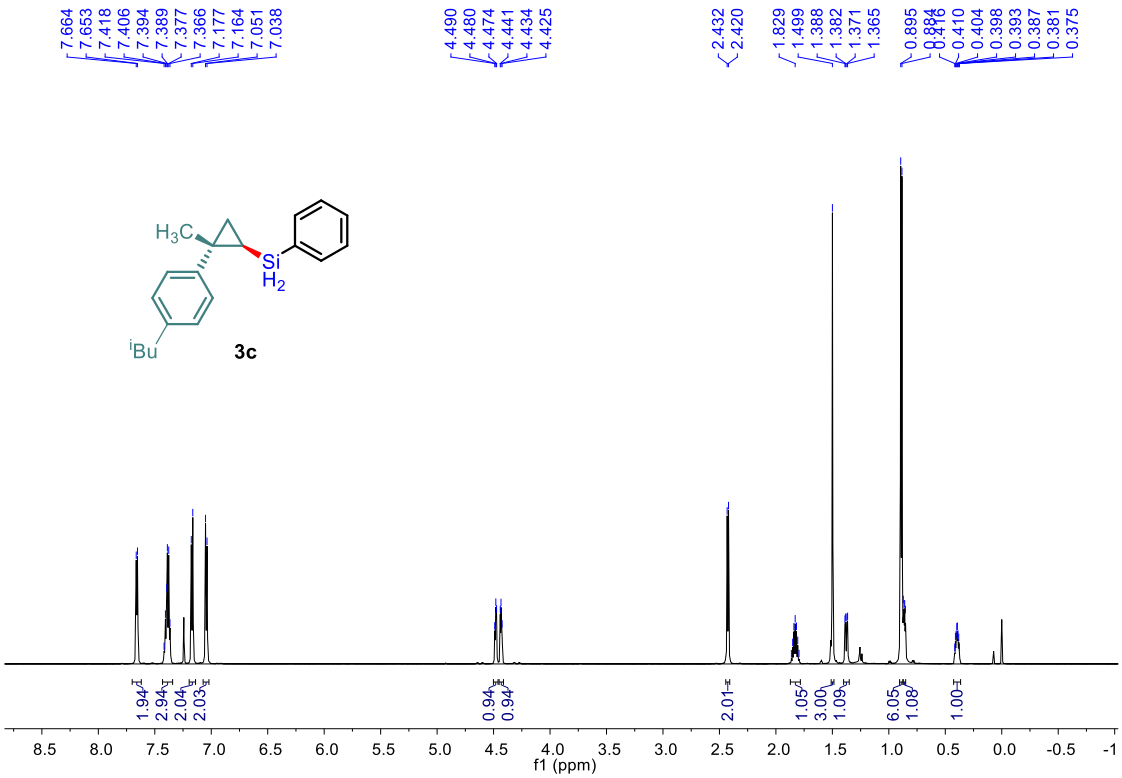
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Si
H2
iBu
3c
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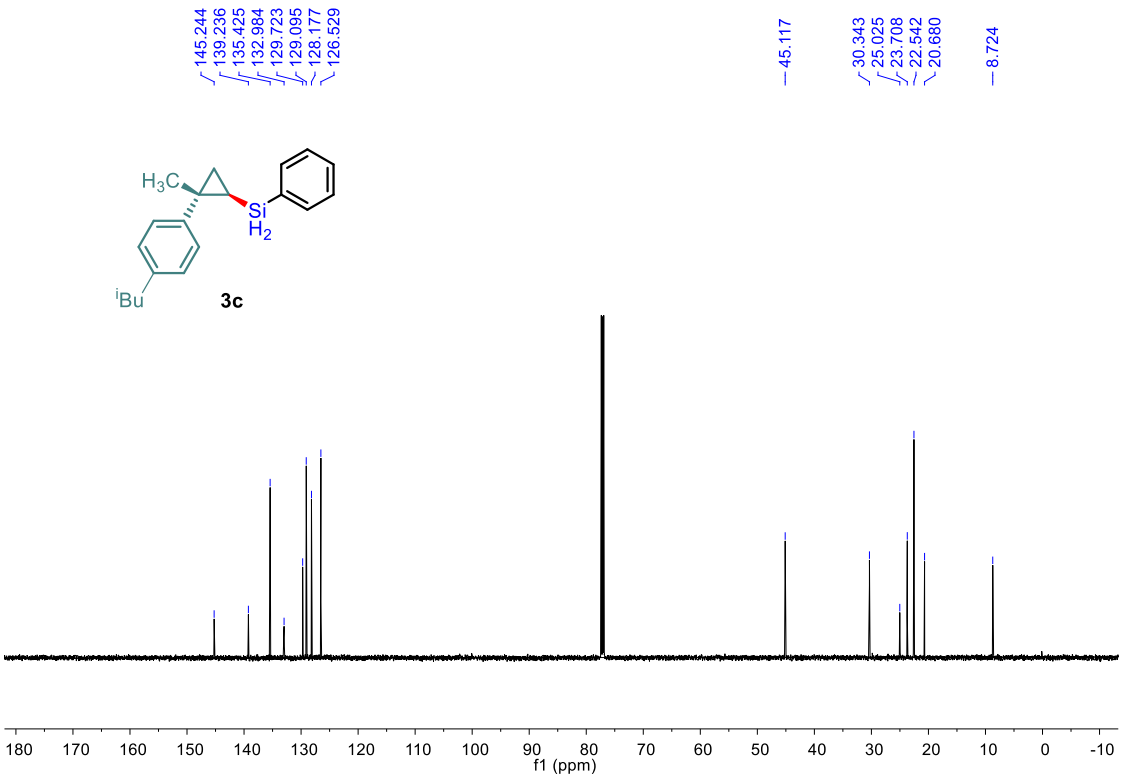
f1 (ppm)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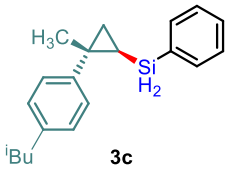
3c
f1 (ppm)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3c

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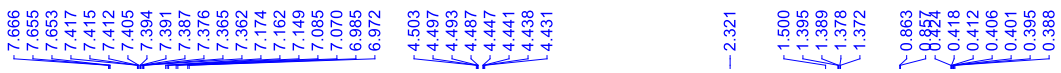
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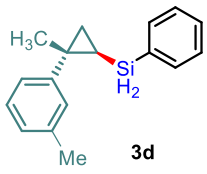
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Si
H2
Me

3d

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3.01
1.05
1.04
1.00
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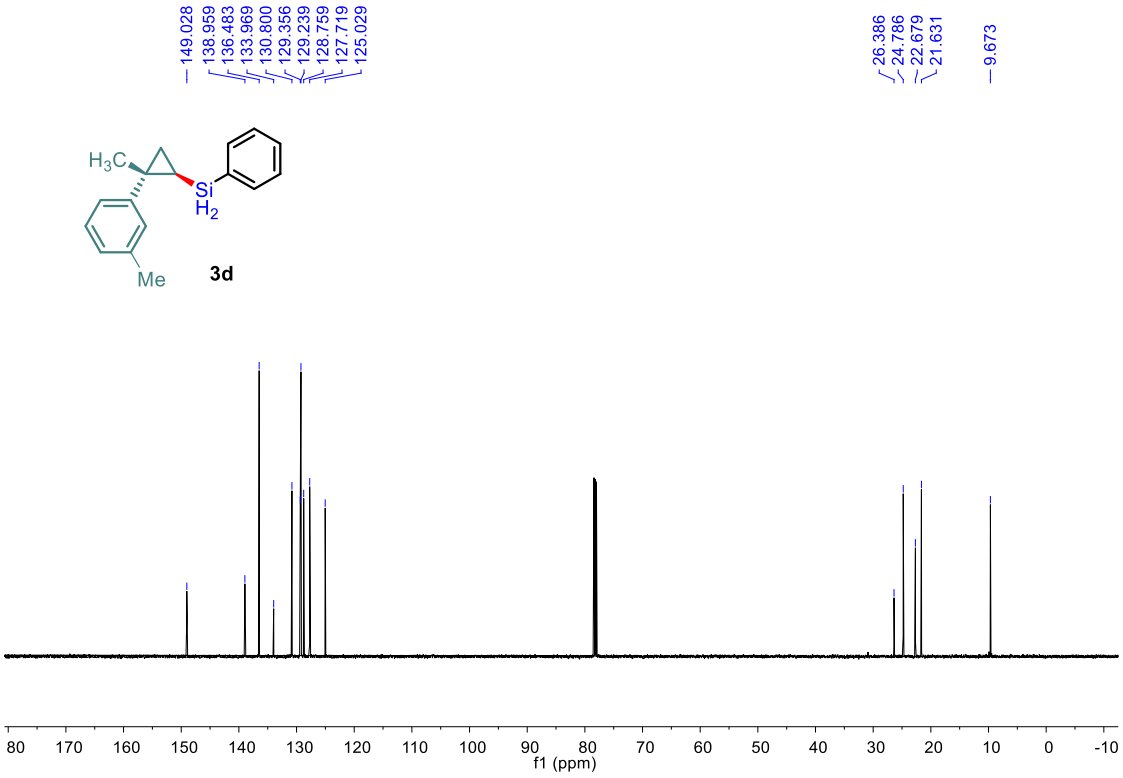
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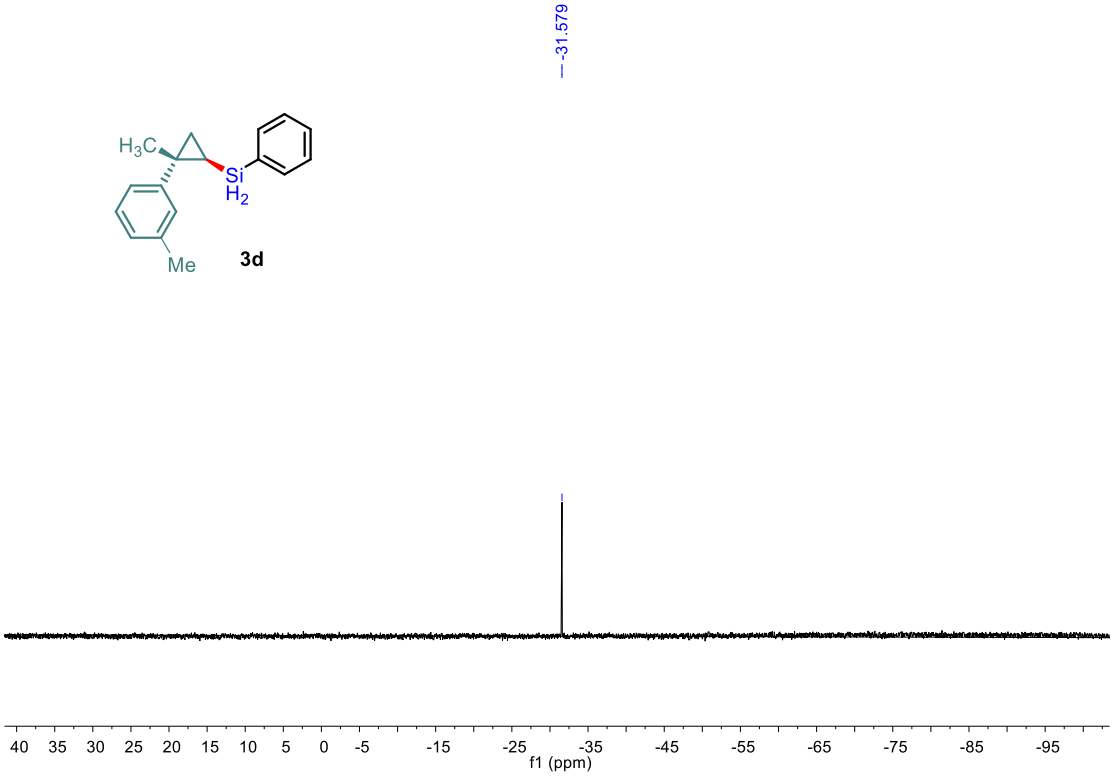
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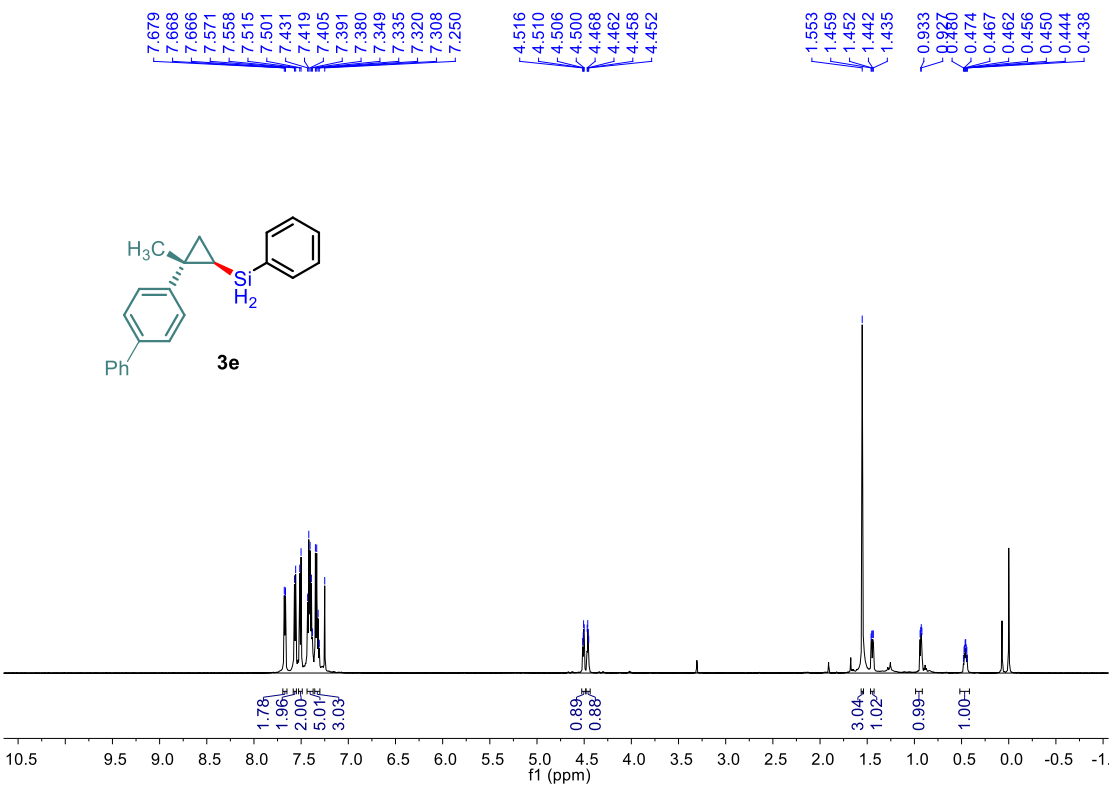
f1 (ppm)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4.500
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Si
H2
Ph
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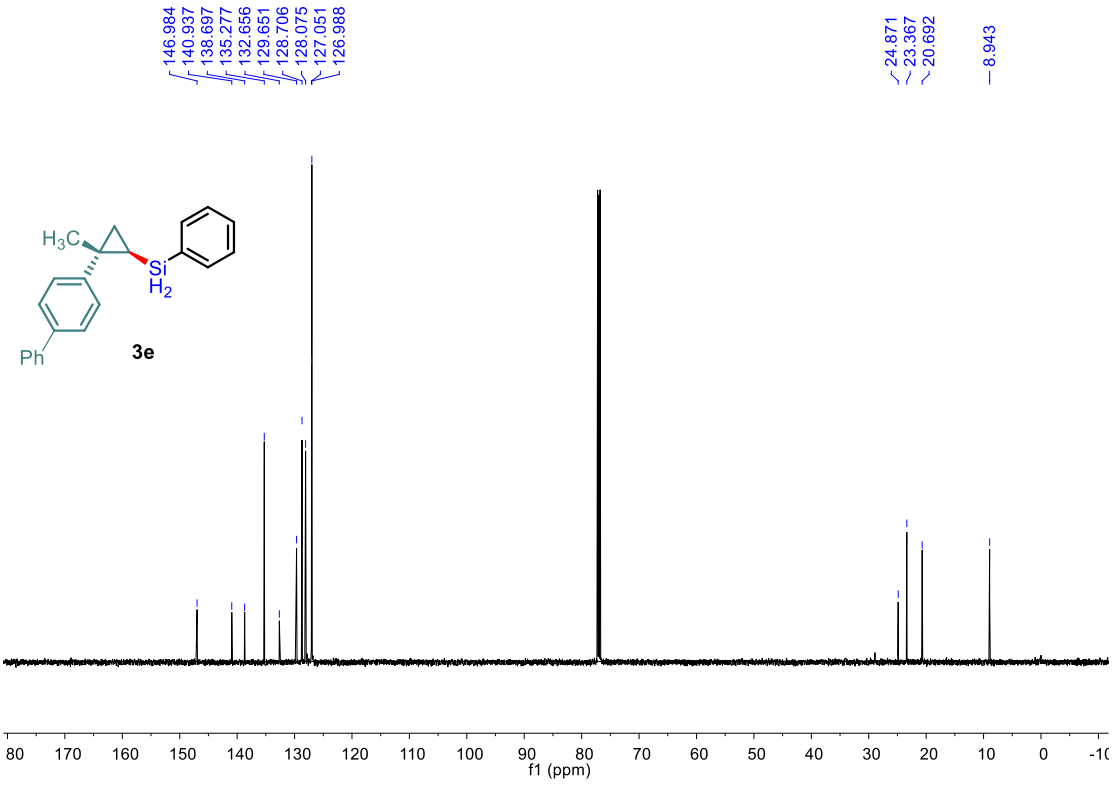
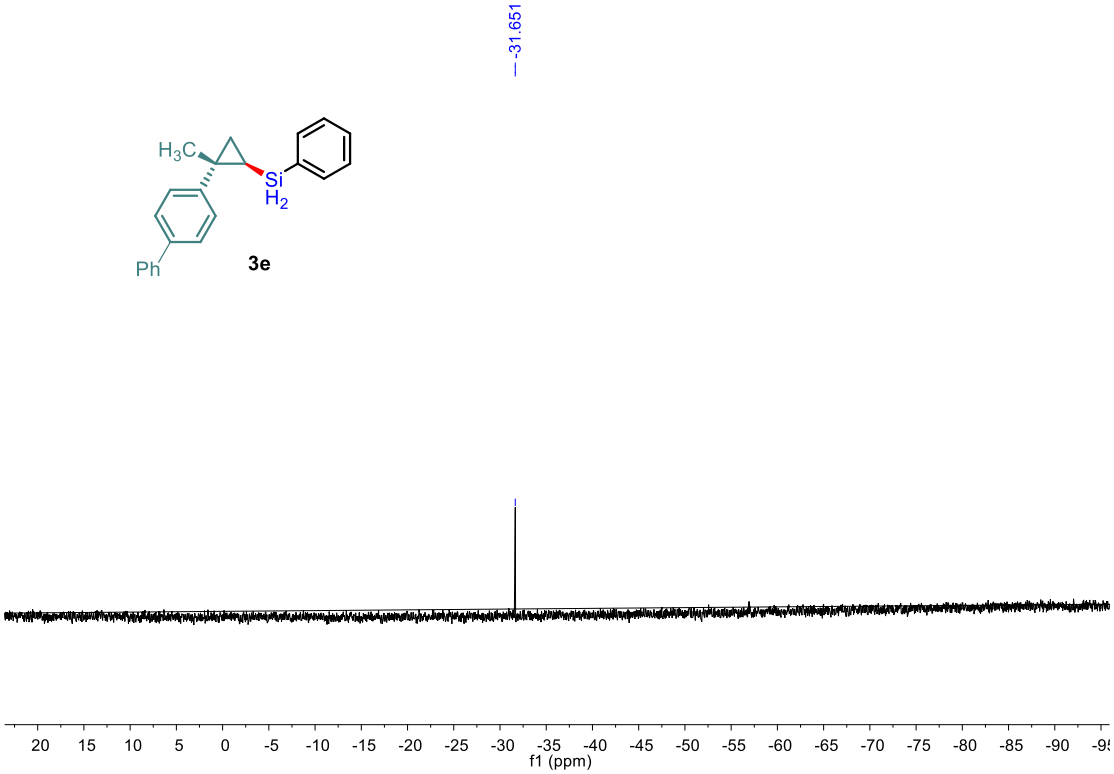
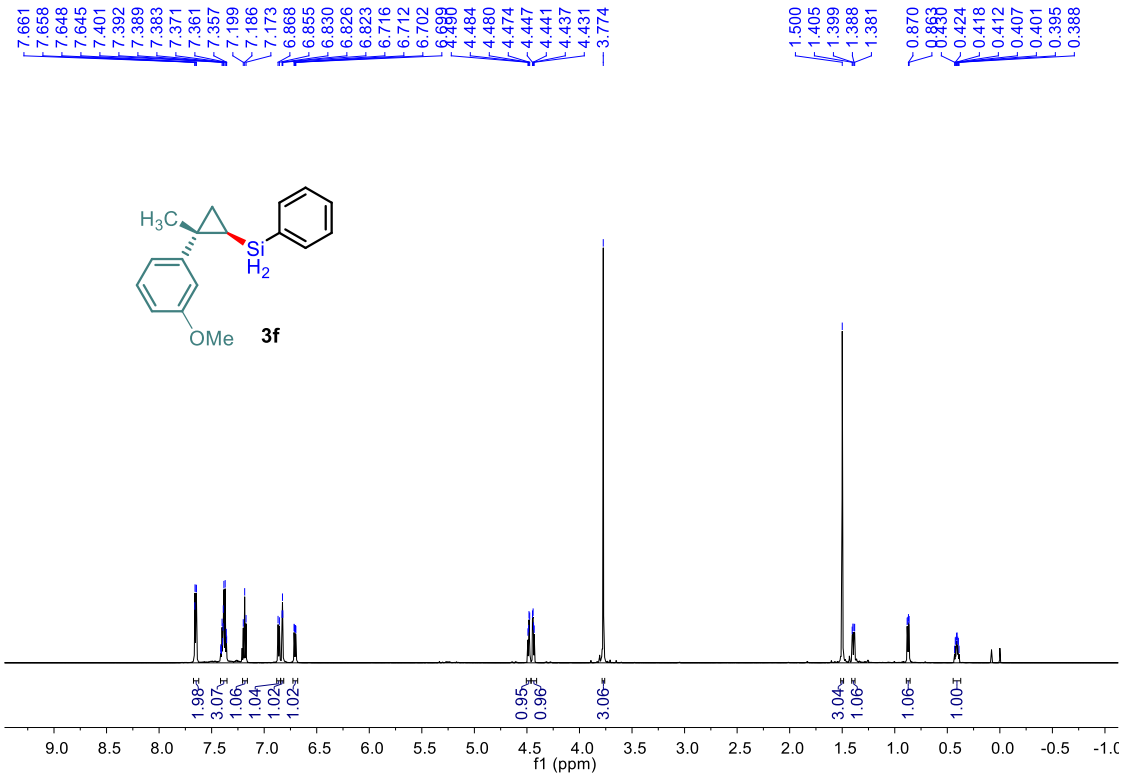
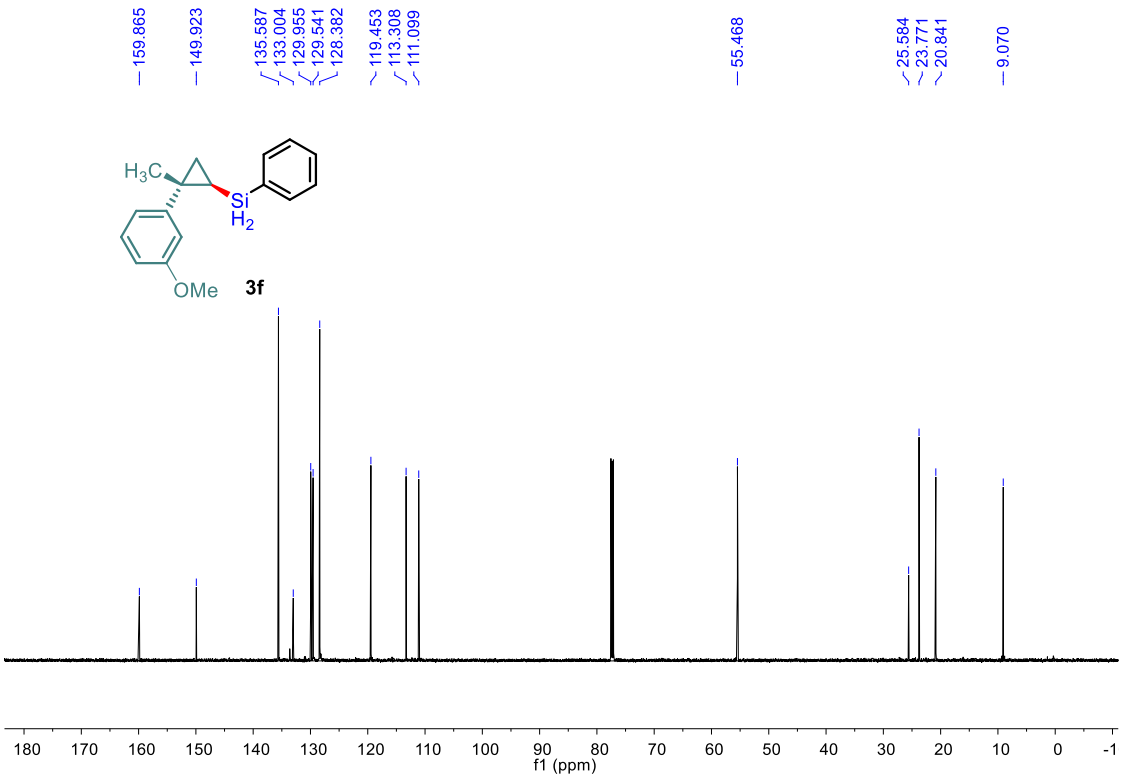
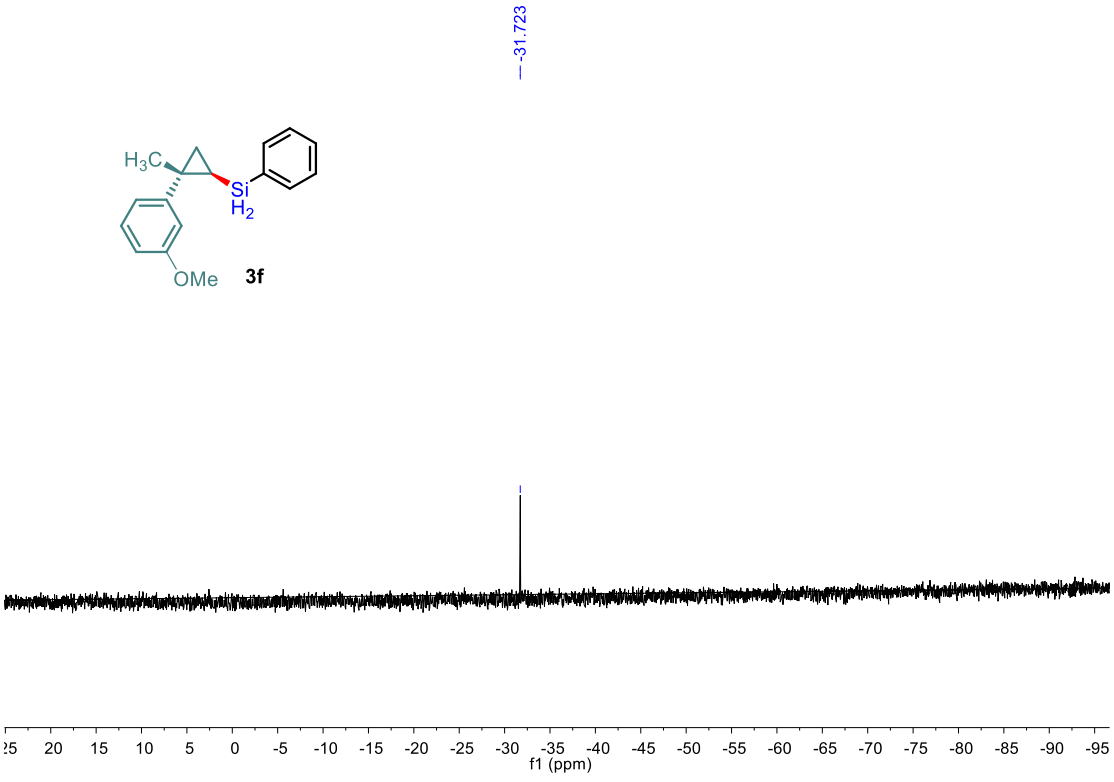
1.96
2.00
5.01
3.03
0.89
0.88
3.04
1.02
0.99
1.00
f1 (ppm)

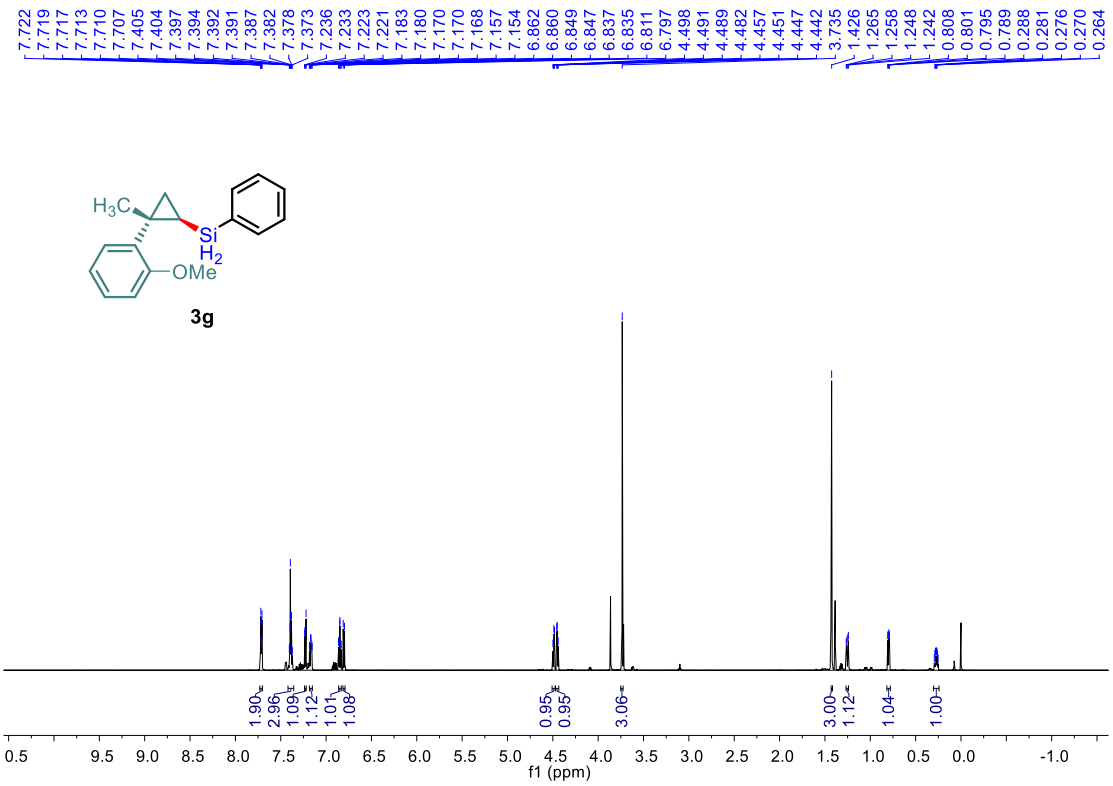

146.984
140.937
138.697
135.277
132.656
129.651
128.706
128.075
127.051
126.988
24.871
23.367
20.692
8.943
H3C
Si
H2
Ph
3e
f1 (ppm)

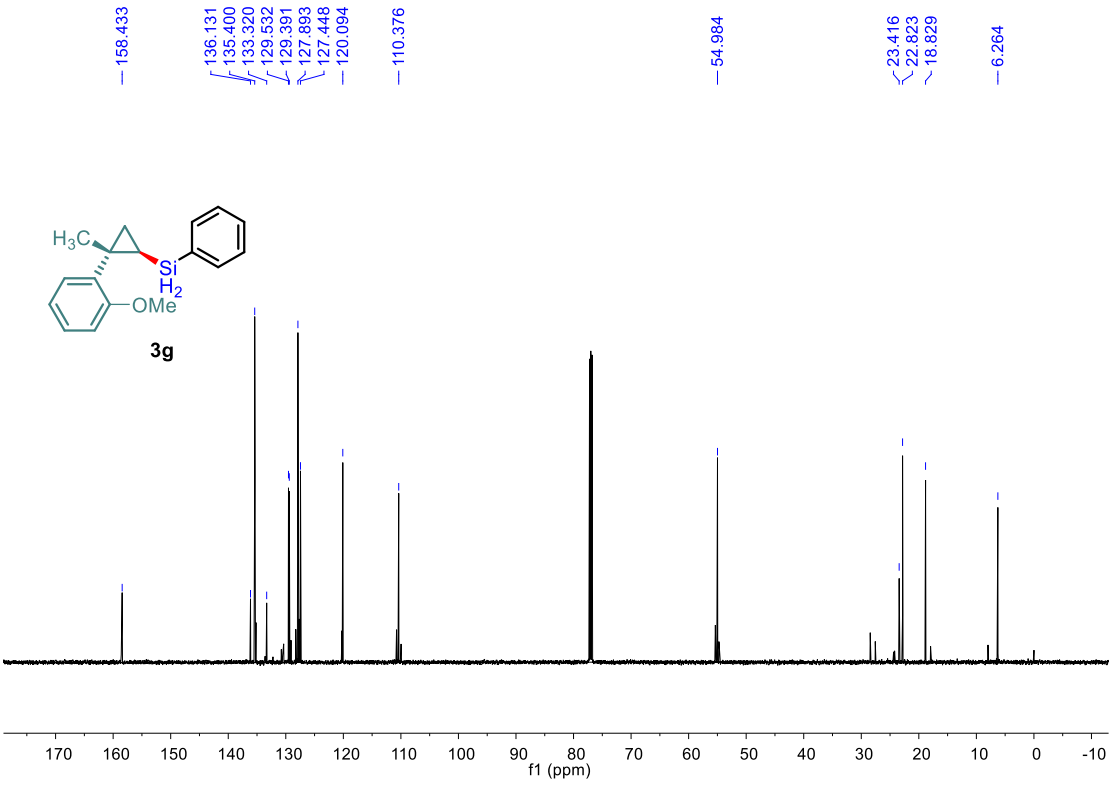

-31.651
H3C
Si
H2
Ph
3e
20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90
f1 (ppm)

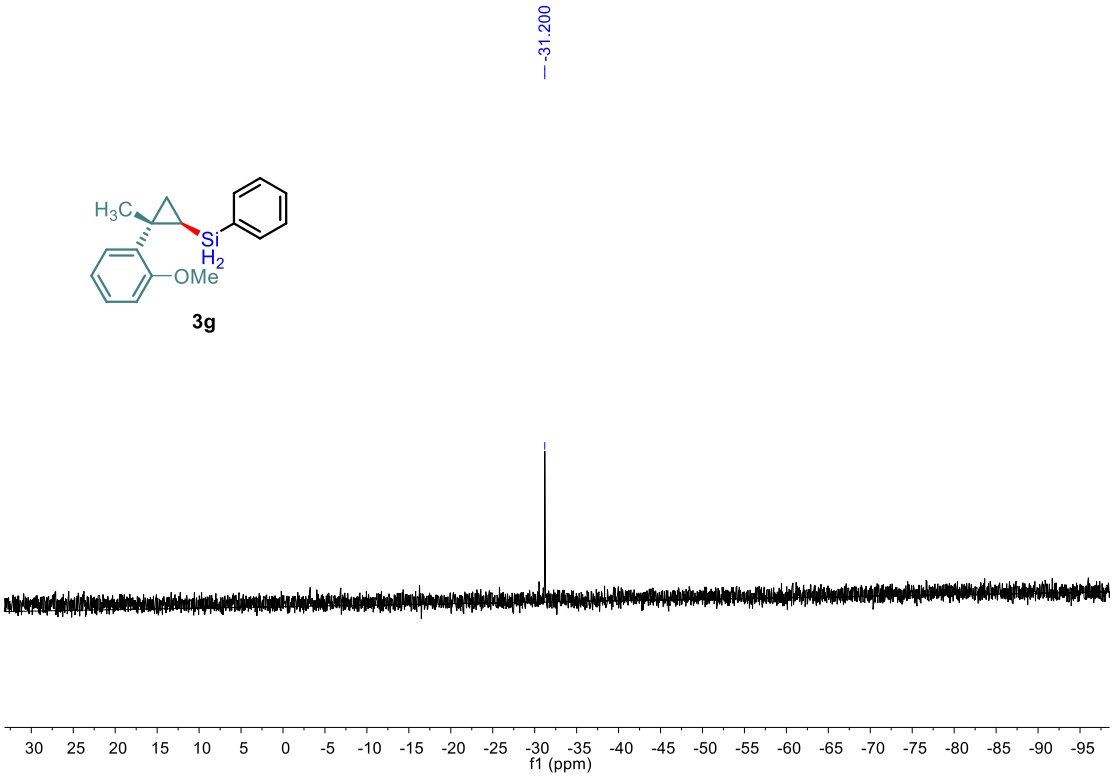

7.661
7.658
7.648
7.645
7.401
7.392
7.389
7.383
7.371
7.361
7.357
7.199
7.186
7.173
6.868
6.855
6.830
6.826
6.823
6.716
6.712
6.702
4.484
4.480
4.474
4.447
4.441
4.437
4.431
3.774
1.500
1.405
1.399
1.388
1.381
0.870
0.424
0.418
0.412
0.407
0.401
0.395
0.388
H3C
Si
H2
OMe
3f
1.98
3.07
1.06
1.04
1.02
1.02
0.95
0.96
3.06
3.04
1.06
1.06
1.00
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)

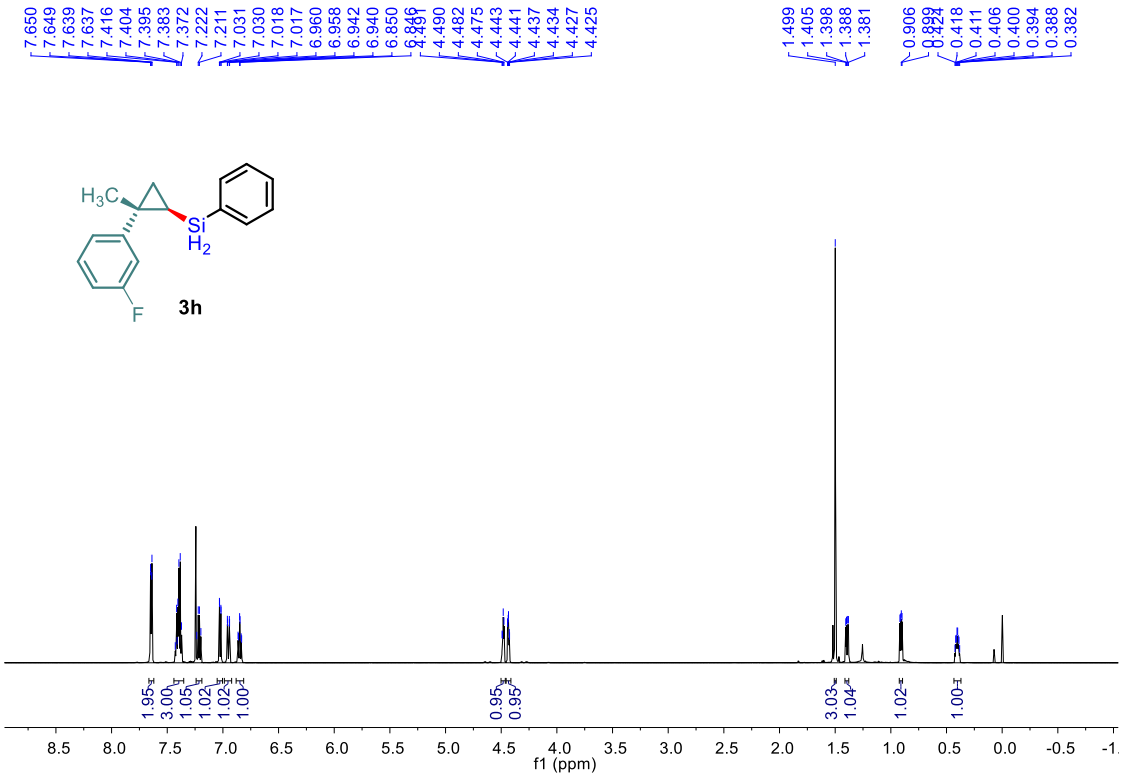

159.865
149.923
135.587
133.004
129.955
129.541
128.382
119.453
113.308
111.099
55.468
25.584
23.771
20.841
9.070
H3C
Si
H2
OMe
3f
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

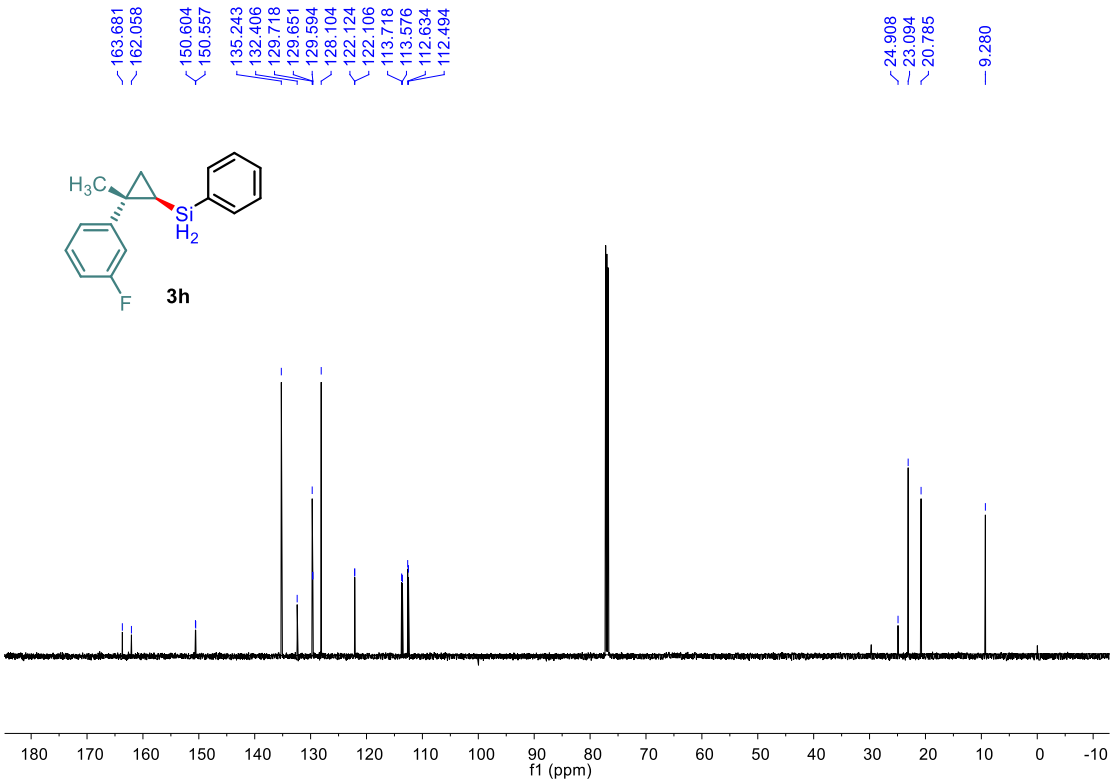

-31.723
H3C
Si
H2
OMe
3f
25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95
f1 (ppm)

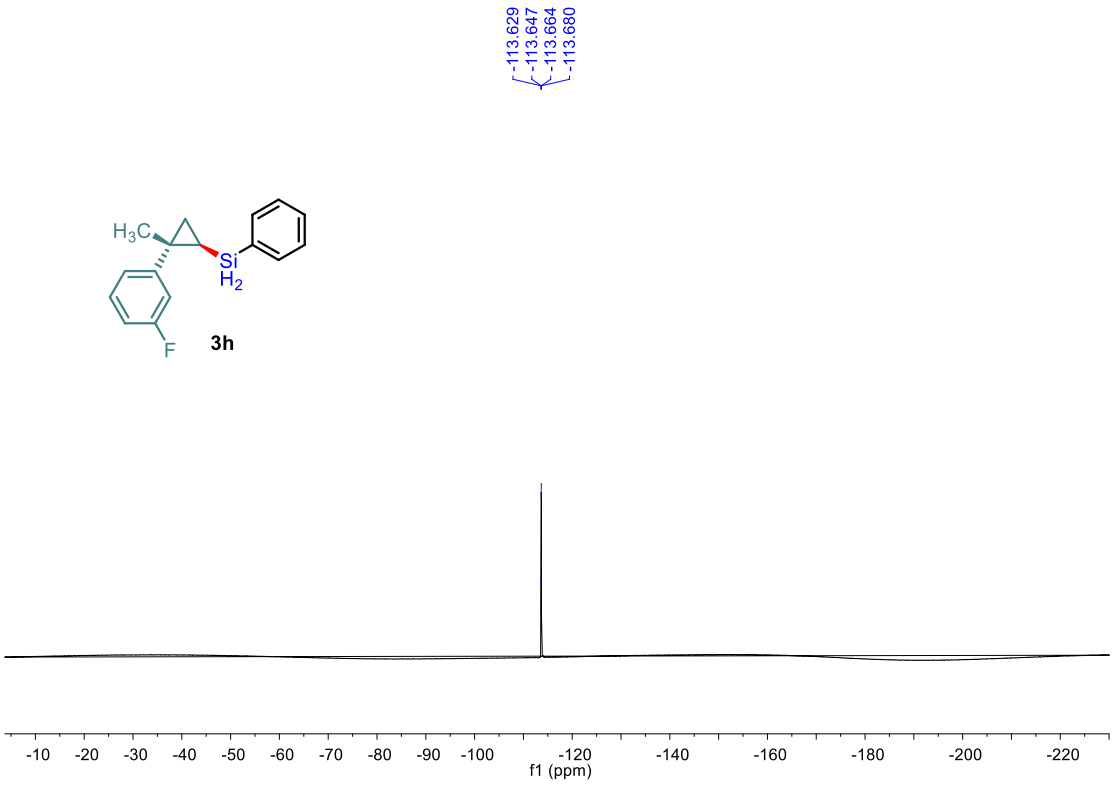

7.722
7.719
7.717
7.713
7.710
7.707
7.405
7.404
7.397
7.394
7.392
7.391
7.387
7.382
7.378
7.373
7.236
7.233
7.223
7.221
7.183
7.180
7.170
7.170
7.168
7.157
7.154
6.862
6.860
6.849
6.847
6.837
6.835
6.811
6.797
4.498
4.491
4.489
4.482
4.457
4.451
4.447
4.442
3.735
1.426
1.265
1.258
1.248
1.242
0.808
0.801
0.795
0.789
0.288
0.281
0.276
0.270
0.264
H3C
Si
H2
OMe
3g
1.90
2.96
1.09
1.12
1.01
1.08
0.95
0.95
3.06
3.00
1.12
1.04
1.00
f1 (ppm)

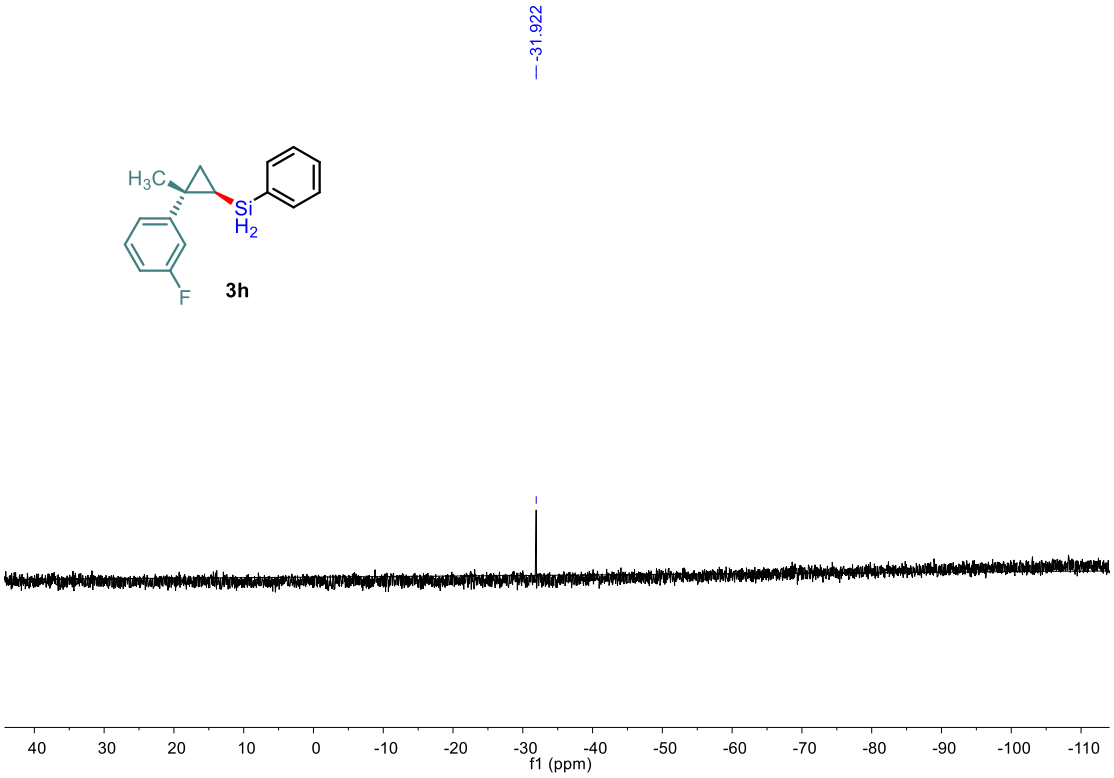

158.433
136.131
135.400
133.320
129.532
129.391
127.893
127.448
120.094
110.376
54.984
23.416
22.823
18.829
6.264
H3C
Si
H2
OMe
3g
f1 (ppm)

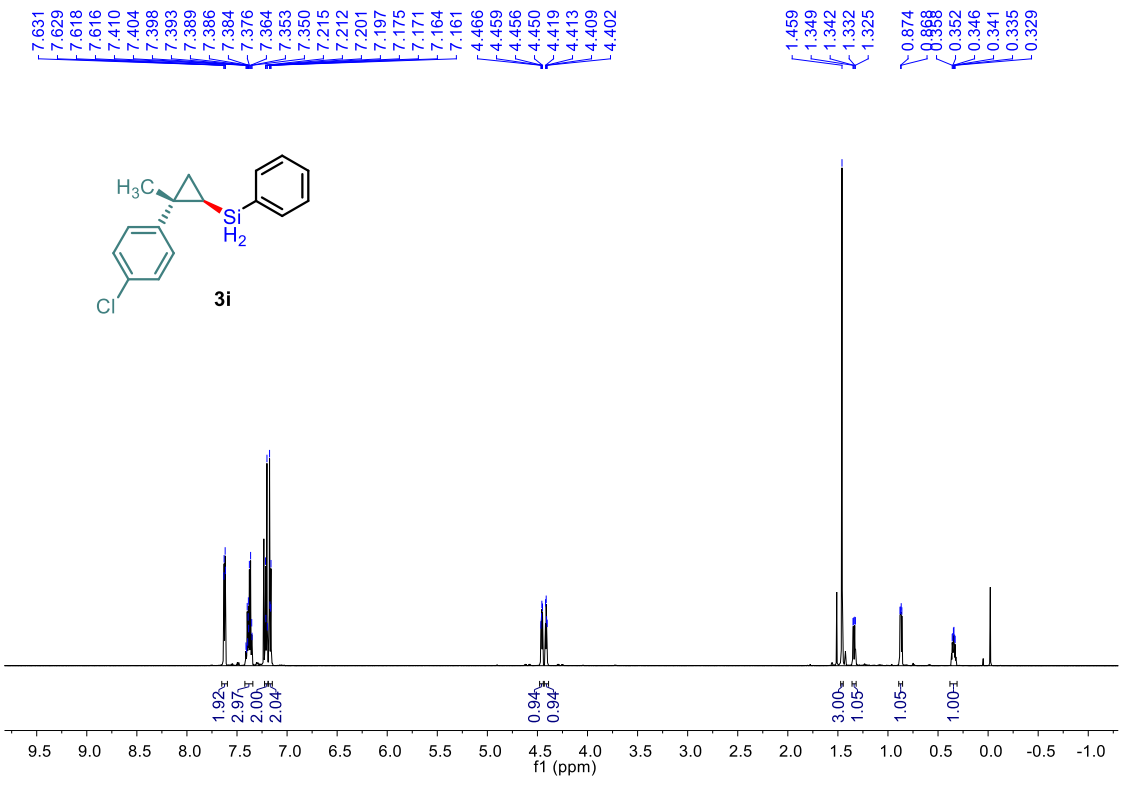

-31.200
H3C
Si
H2
OMe
3g
30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95
f1 (ppm)

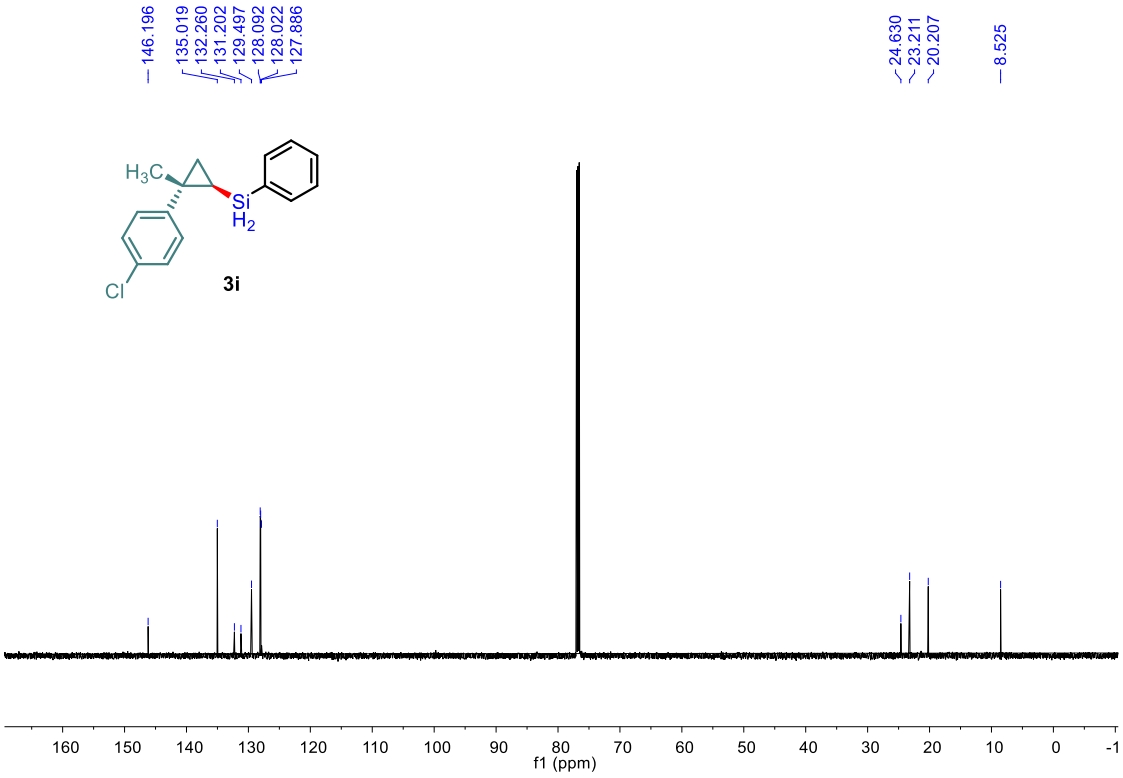

7.650 7.649 7.639 7.637 7.416 7.404 7.395 7.383 7.372 7.222 7.211 7.031 7.030 7.018 7.017 6.960 6.958 6.942 6.940 6.850 4.490 4.482 4.475 4.443 4.441 4.437 4.434 4.427 4.425
1.499 1.405 1.398 1.388 1.381
0.418 0.411 0.406 0.400 0.394 0.388 0.382
H3C
Si
H2
F
3h
1.95 3.00 1.05 1.02 1.02 1.00 0.95 0.95 3.03 1.04 1.02 1.00
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)

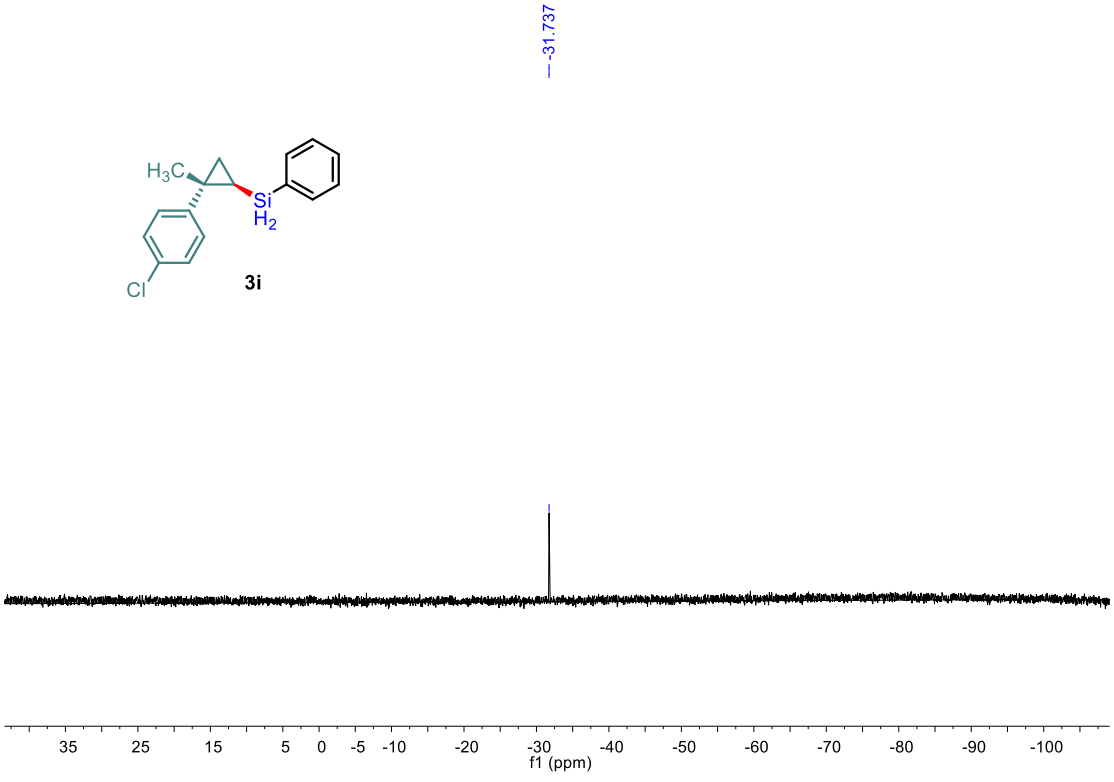

163.681
162.058
150.604
150.557
135.243
132.406
129.718
129.651
129.594
128.104
122.124
122.106
113.718
113.576
112.634
112.494
24.908
23.094
20.785
9.280
H3C
Si
H2
F
3h
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

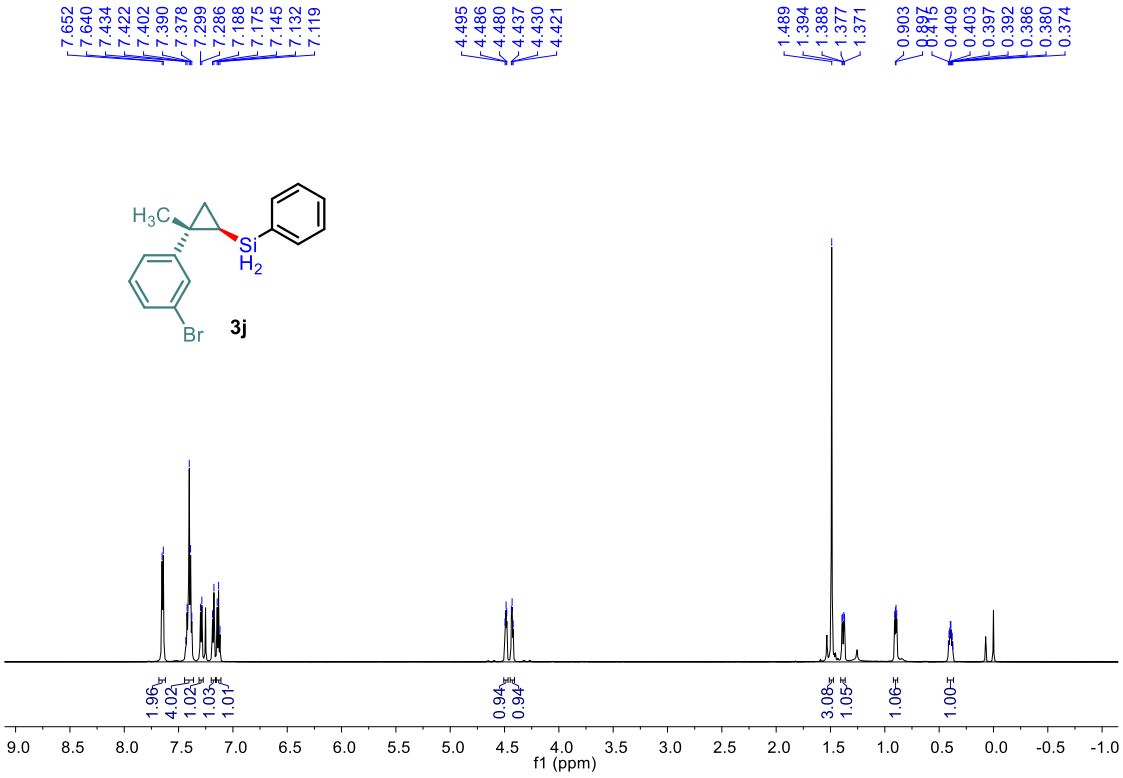

-113.629
-113.647
-113.664
-113.680
H3C
Si
H2
F
3h
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200 -220
f1 (ppm)

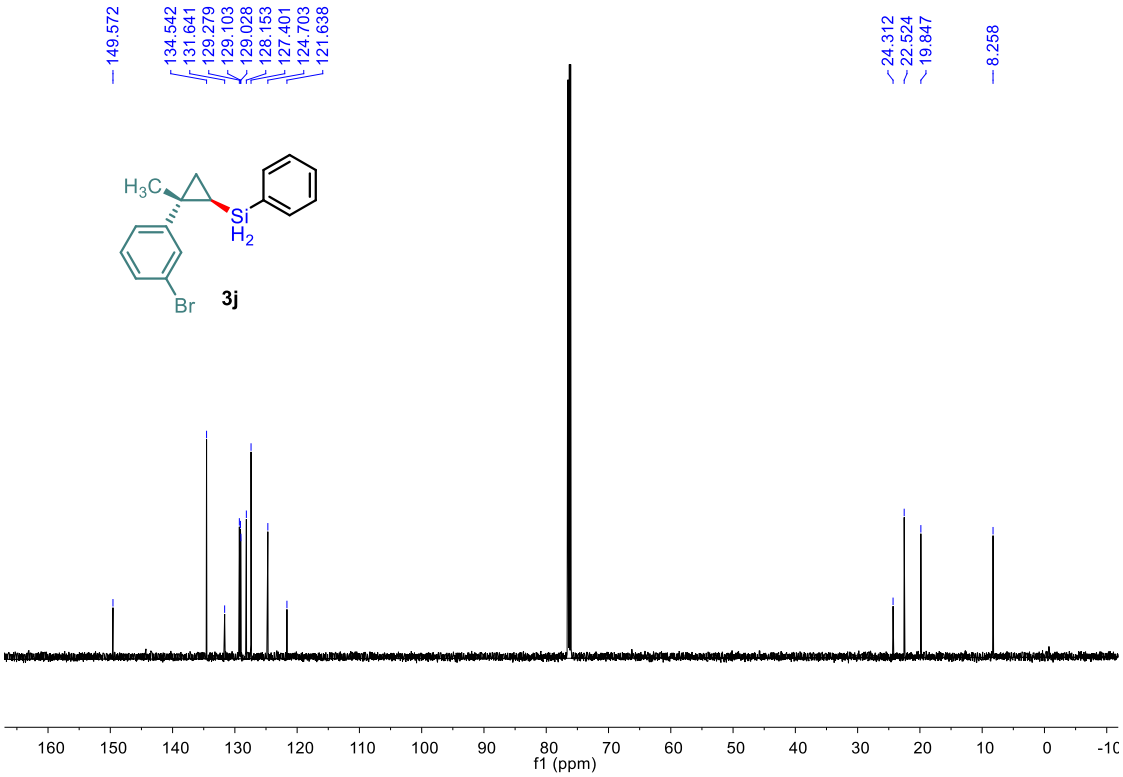

-31.922
H3C
Si
H2
F
3h
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)

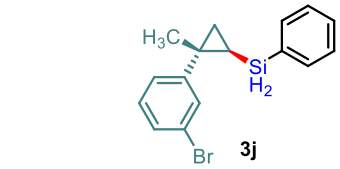

7.631 7.629 7.618 7.616 7.410 7.404 7.398 7.393 7.389 7.386 7.384 7.376 7.364 7.353 7.350 7.215 7.212 7.201 7.197 7.175 7.171 7.164 7.161
4.466 4.459 4.456 4.450 4.419 4.413 4.409 4.402
1.459 1.349 1.342 1.332 1.325
0.874 0.868 0.352 0.346 0.341 0.335 0.329
H3C
Si
H2
Cl
3i
1.92 2.97 2.00 2.04
0.94 0.94
3.00 1.05 1.05 1.00
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 -1.0
f1 (ppm)


146.196
135.019
132.260
131.202
129.497
128.092
128.022
127.886
24.630
23.211
20.207
8.525
H3C
Si
H2
Cl
3i
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


-31.737
H3C
Si
H2
Cl
3i
35 25 15 5 0 -5 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

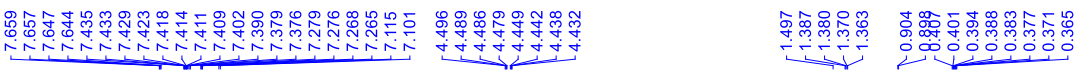

7.652
7.640
7.434
7.422
7.402
7.390
7.378
7.299
7.286
7.188
7.175
7.145
7.132
7.119
4.495
4.486
4.480
4.437
4.430
4.421
1.489
1.394
1.388
1.377
1.371
0.903
0.897
0.415
0.409
0.403
0.397
0.392
0.386
0.380
0.374
H3C
Si
H2
Br
3j
1.96
4.02
1.02
1.03
1.01
0.94
0.94
3.08
1.05
1.06
1.00
f1 (ppm)

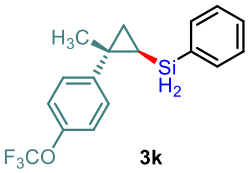

149.572
134.542
131.641
129.279
129.103
129.028
128.153
127.401
124.703
121.638
24.312
22.524
19.847
8.258
H3C
Si
H2
Br
3j
f1 (ppm)


H3C
Si
H2
Br

3j

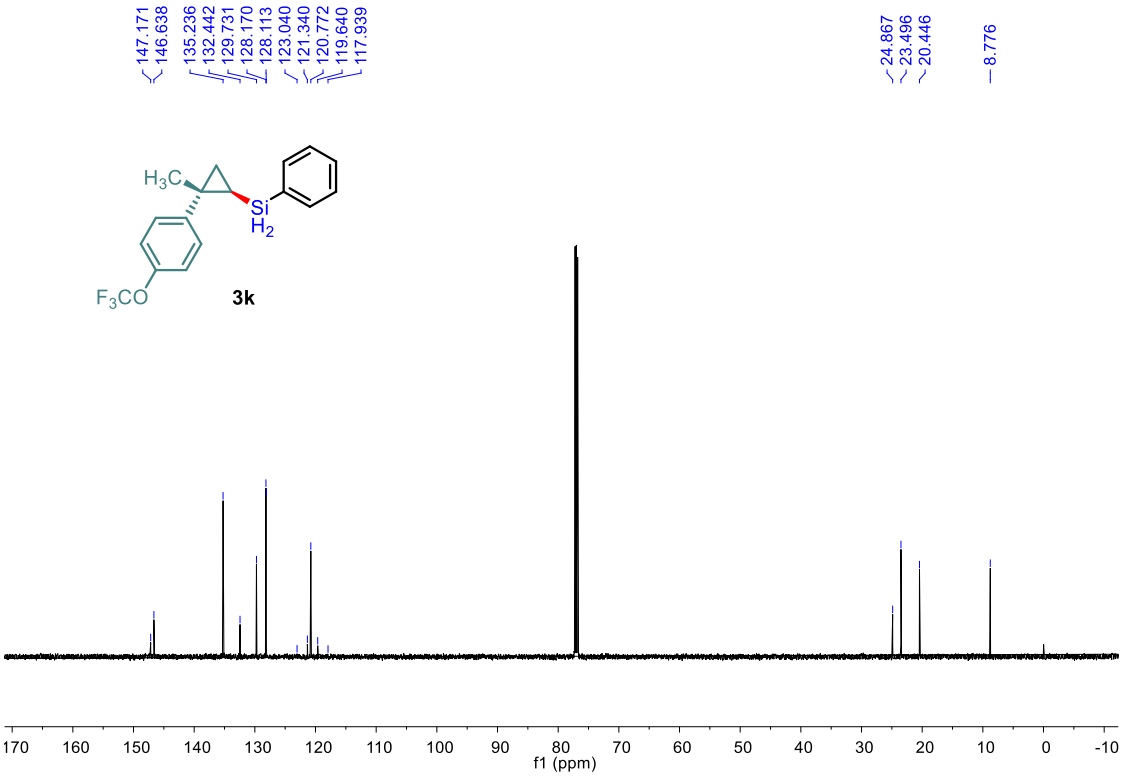
-30.723
35 30 25 20 15 10 5 0 -5 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

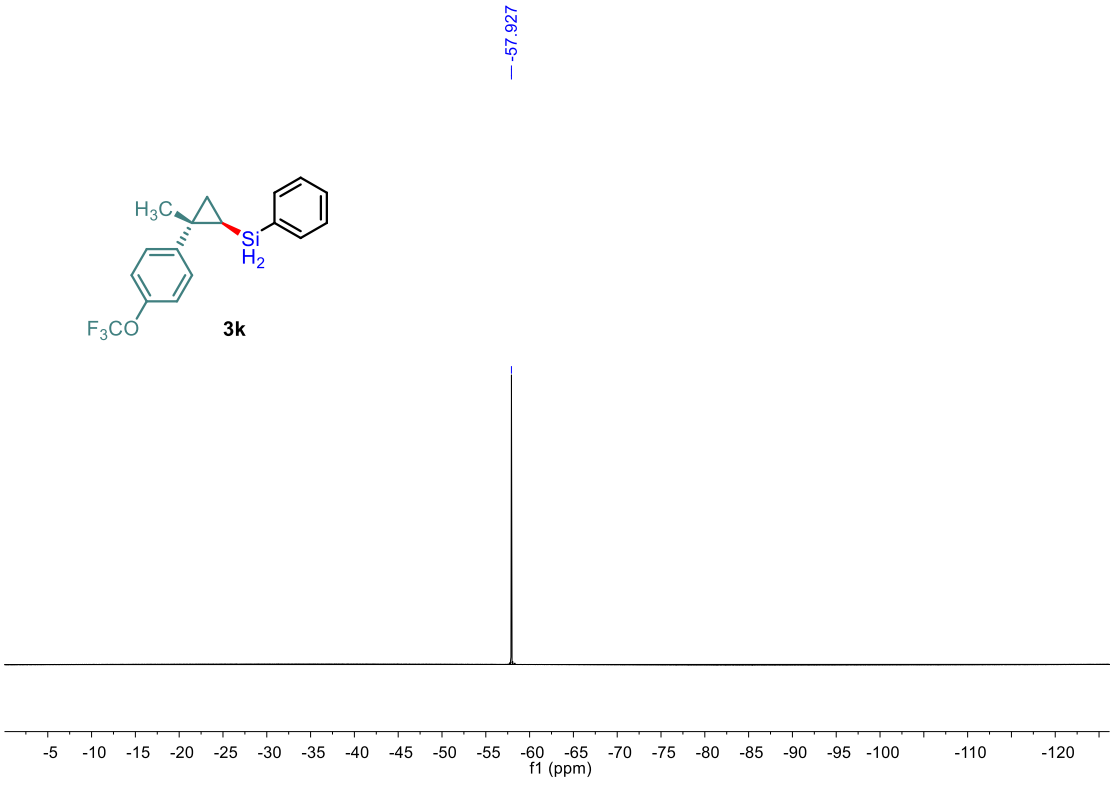

7.659
7.657
7.647
7.644
7.435
7.433
7.429
7.423
7.418
7.414
7.411
7.409
7.402
7.390
7.379
7.376
7.279
7.276
7.268
7.265
7.115
7.101
4.496
4.489
4.486
4.479
4.449
4.442
4.438
4.432
1.497
1.387
1.380
1.370
1.363
0.904
0.401
0.394
0.388
0.383
0.377
0.371
0.365

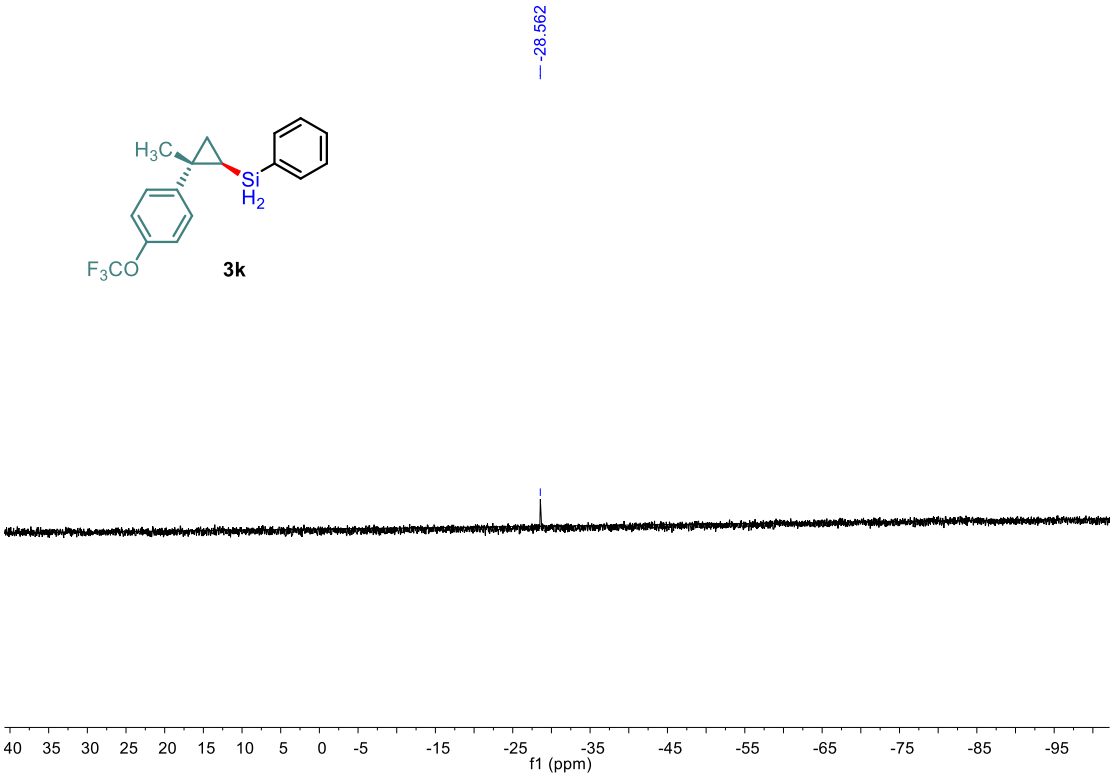

H3C
Si
H2
F3CO

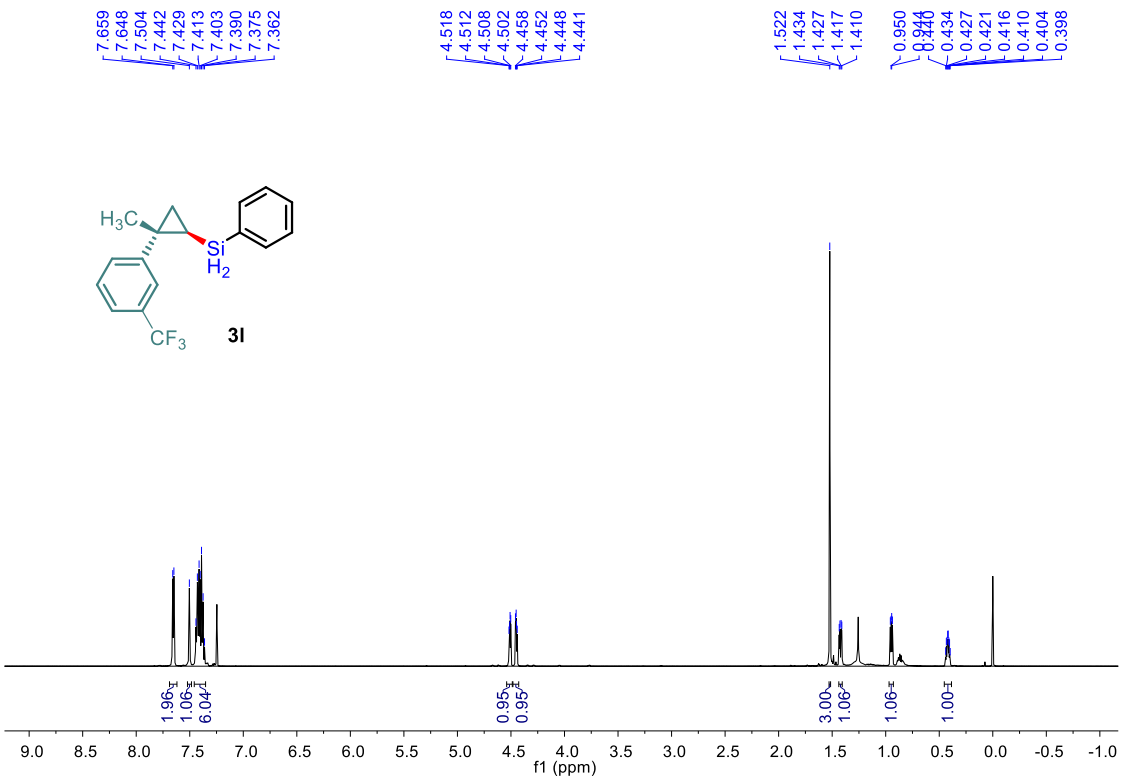
3k

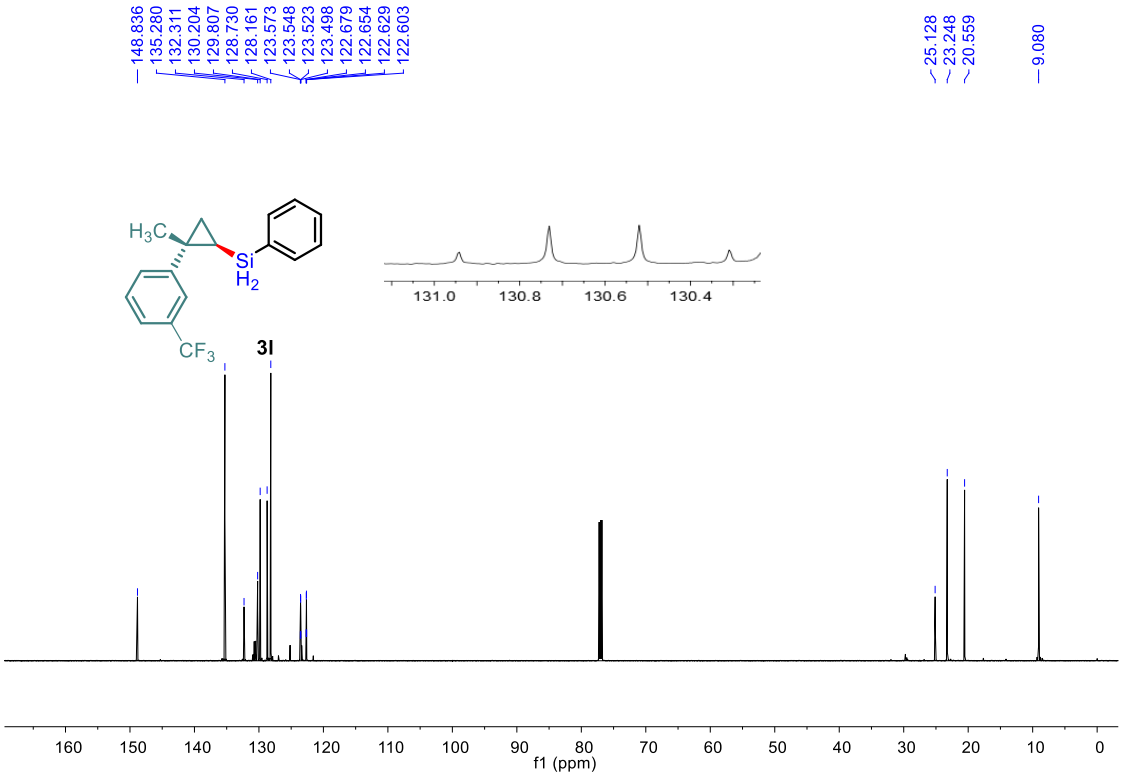
1.94
2.98
2.01
2.03
0.94
0.94
3.03
1.01
1.02
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

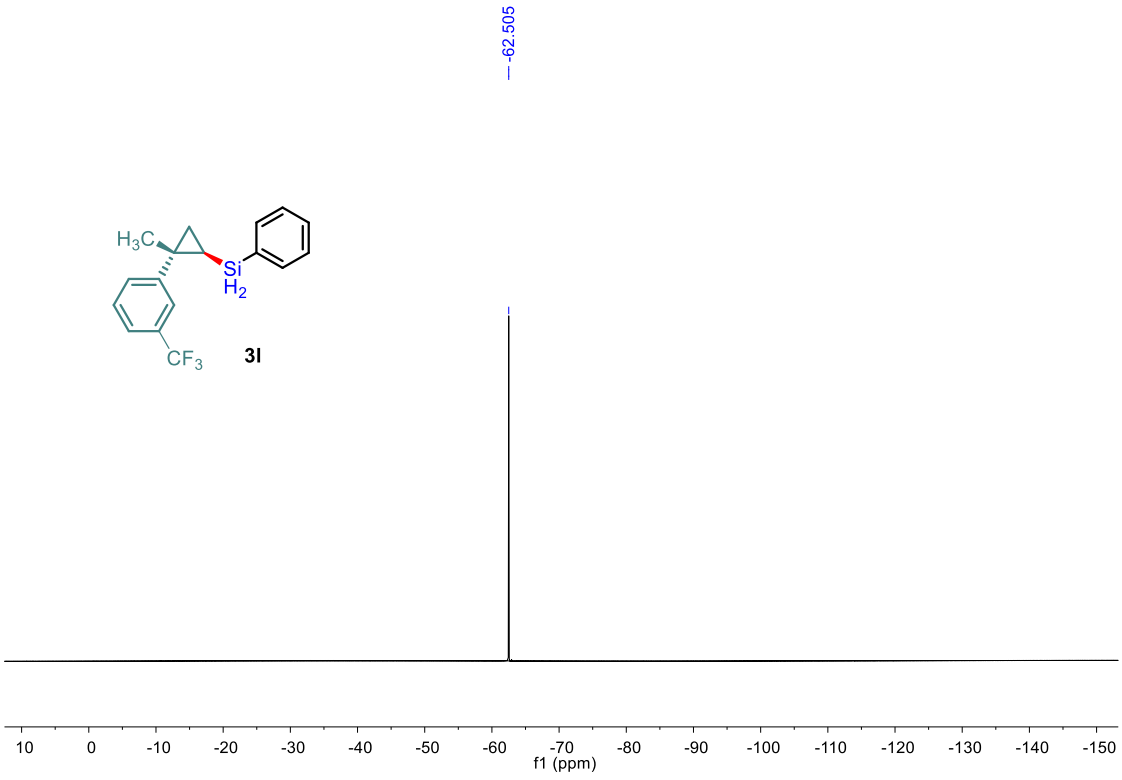

147.171
146.638
135.236
132.442
129.731
128.170
128.113
123.040
121.340
120.772
119.640
117.939
24.867
23.496
20.446
8.776
H3C
Si
H2
F3CO
3k
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-57.927
H3C
Si
H2
F3CO
3k
-5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -110 -120
f1 (ppm)


-28.562
H3C
Si
H2
F3CO
3k
40 35 30 25 20 15 10 5 0 -5 -15 -25 -35 -45 -55 -65 -75 -85 -95
f1 (ppm)


7.659
7.648
7.504
7.442
7.429
7.413
7.403
7.390
7.375
7.362
4.518
4.512
4.508
4.502
4.458
4.452
4.448
4.441
1.522
1.434
1.427
1.417
1.410
0.950
0.944
0.440
0.434
0.427
0.421
0.416
0.410
0.404
0.398
H3C
Si
H2
CF3
3l
1.96
1.06
6.04
0.95
0.99
3.00
1.08
1.06
1.00
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 -1.0
f1 (ppm)


148.836
135.280
132.311
130.204
129.807
128.730
128.161
123.573
123.548
123.523
123.498
122.679
122.654
122.629
122.603
25.128
23.248
20.559
9.080
H3C
Si
H2
CF3
3l
131.0
130.8
130.6
130.4
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-62.505
H3C
Si
H2
CF3
3l
10
0
-10
-20
-30
-40
-50
-60
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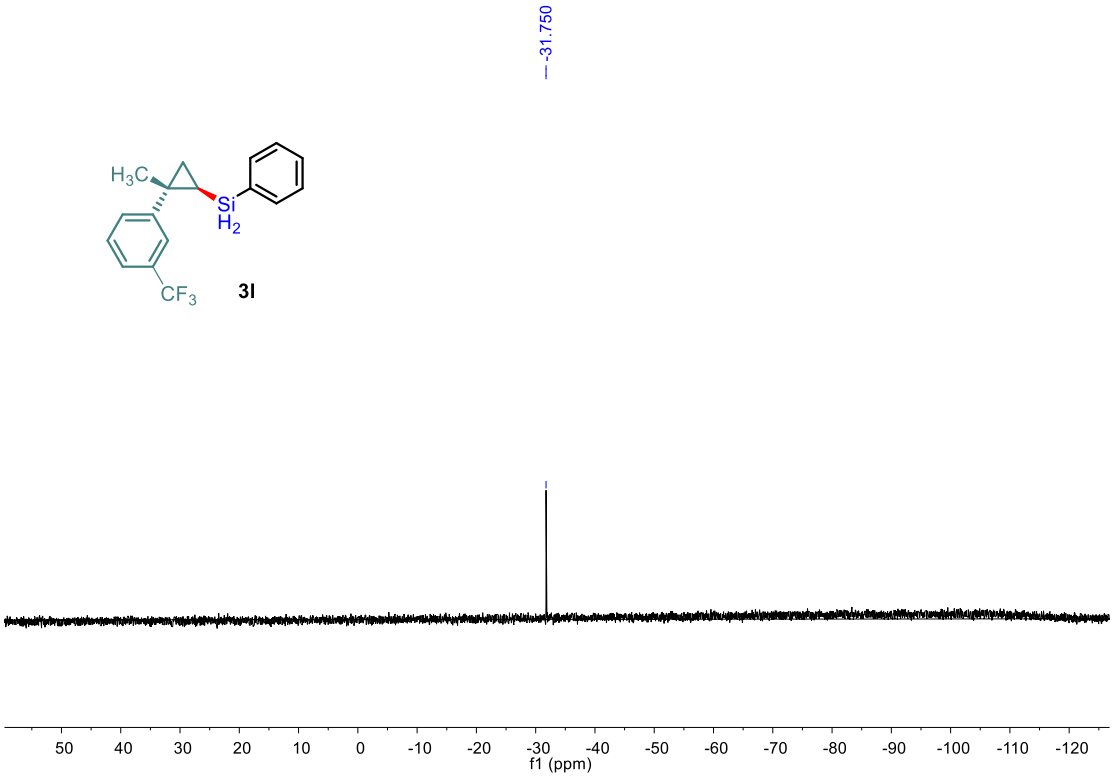
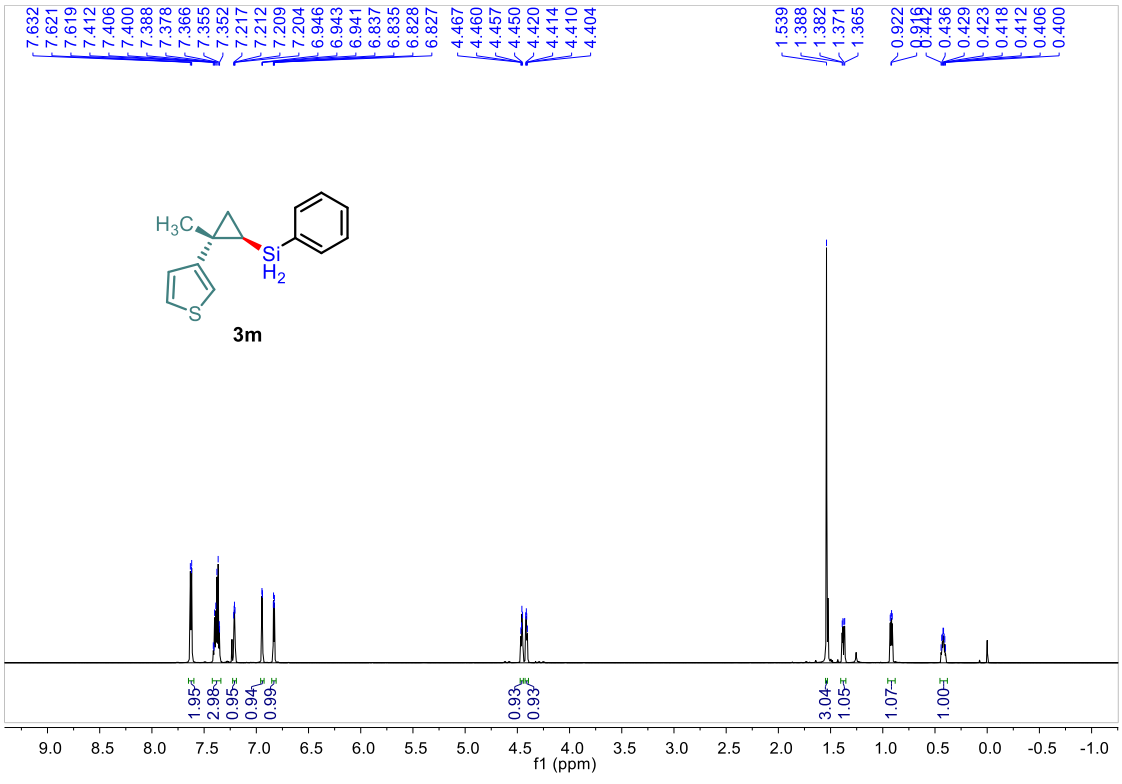
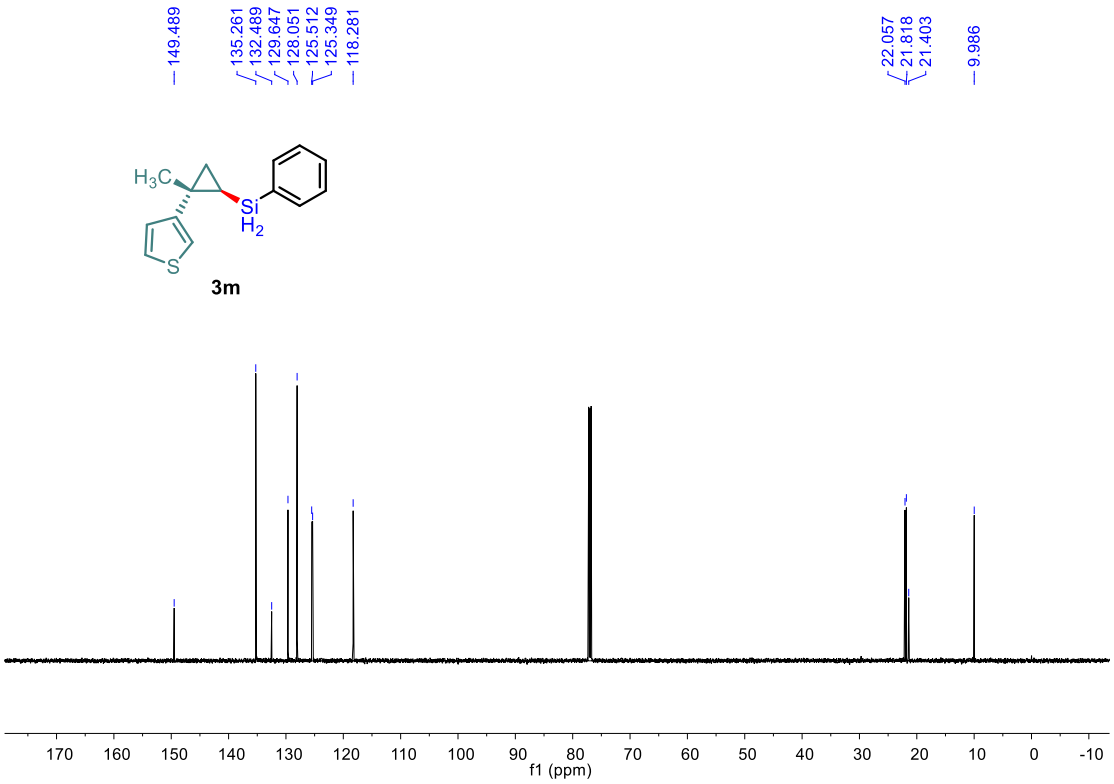
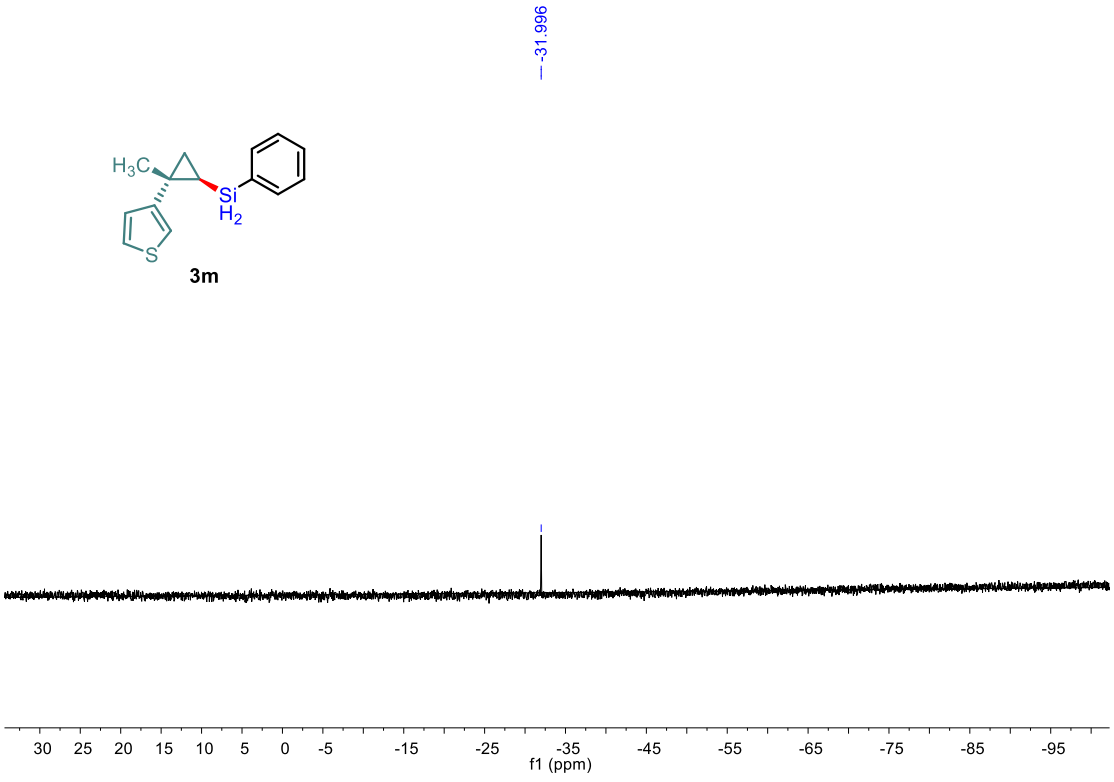
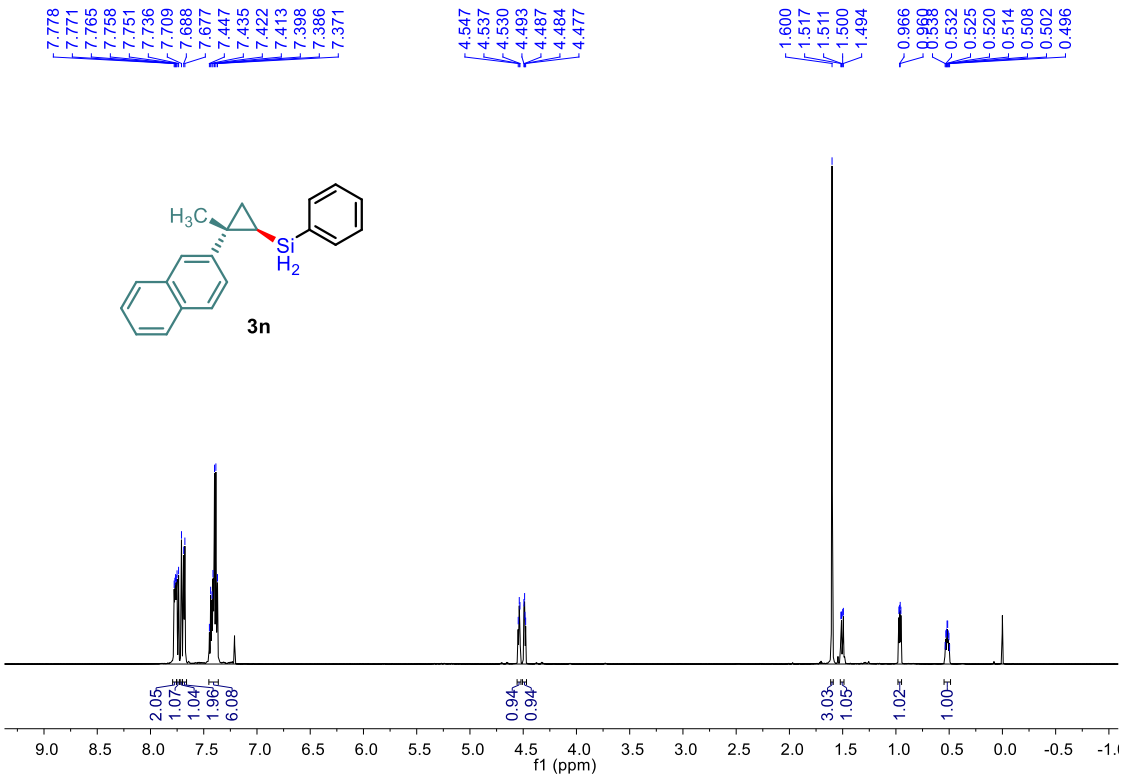
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)


-31.750
H3C
Si
H2
CF3
3l
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120
f1 (ppm)


7.632 7.621 7.619 7.412 7.406 7.400 7.388 7.378 7.366 7.355 7.352 7.217 7.212 7.209 7.204 6.946 6.943 6.941 6.837 6.835 6.828 6.827
4.467 4.460 4.457 4.450 4.420 4.414 4.410 4.404
1.539 1.388 1.382 1.371 1.365
0.922 0.916 0.442 0.436 0.429 0.423 0.418 0.412 0.406 0.400
H3C
Si
H2
S
3m
1.95 2.98 0.95 0.94 0.99
0.93 0.93
3.04 1.05 1.07 1.00
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 -1.0
f1 (ppm)


149.489
135.261
132.489
129.647
128.051
125.512
125.349
118.281
22.057
21.818
21.403
9.986
H3C
Si
H2
S
3m
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-31.996
H3C
Si
H2
S
3m
30 25 20 15 10 5 0 -5 -15 -25 -35 -45 -55 -65 -75 -85 -95
f1 (ppm)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7.771
7.765
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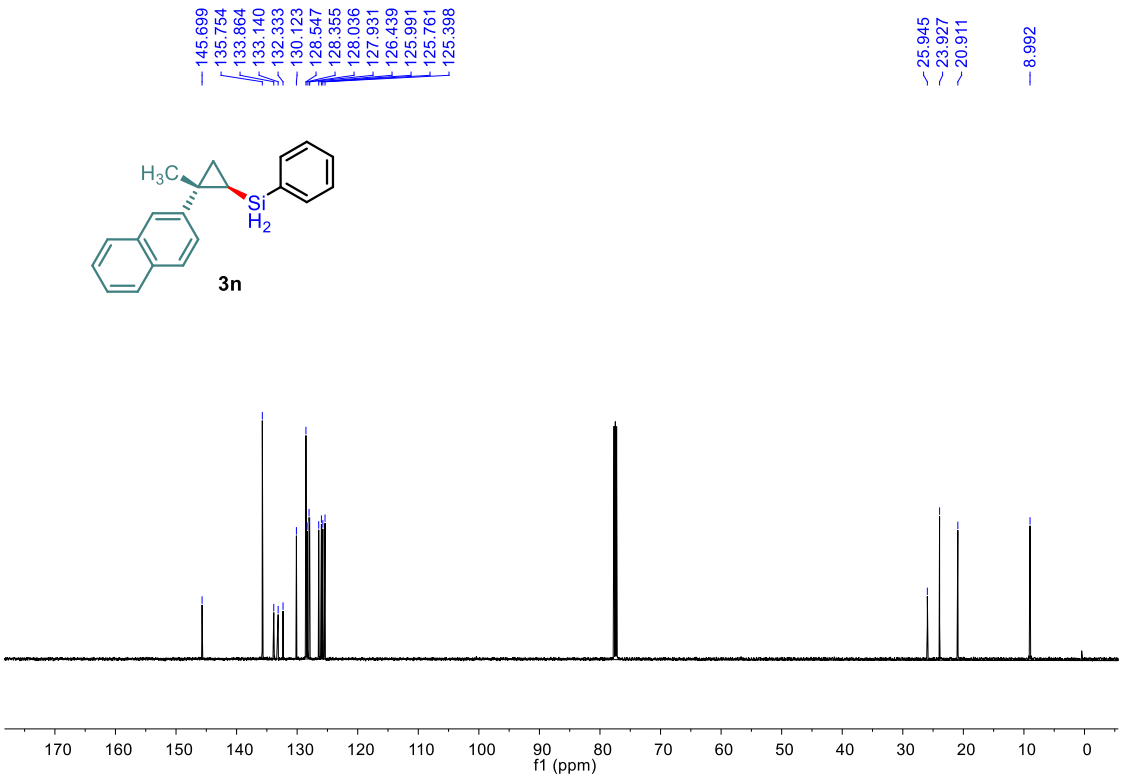
7.751
7.736
7.709
7.688
7.677
7.447
7.435
7.422
7.413
7.398
7.386
7.371
4.547
4.537
4.530
4.493
4.487
4.484
4.477
1.600
1.517
1.511
1.500
1.494
0.966
0.960
0.538
0.532
0.525
0.520
0.514
0.508
0.502
0.496
H3C
Si
H2
3n
2.05
1.07
1.04
1.96
6.08
0.94
0.94
3.03
1.05
1.02
1.00
f1 (ppm)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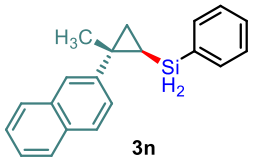
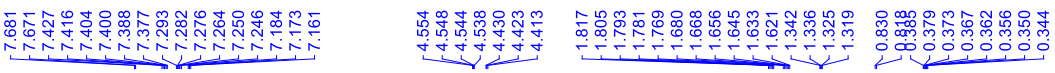
133.864
133.140
132.333
130.123
128.547
128.355
128.036
127.931
126.439
125.991
125.761
125.398
25.945
23.927
20.911
8.992
H3C
Si
H2
3n
f1 (ppm)


H3C
Si
H2

3n

-31.591
40 35 30 25 20 15 10 5 0 -5 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)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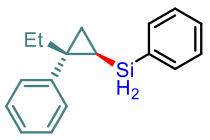
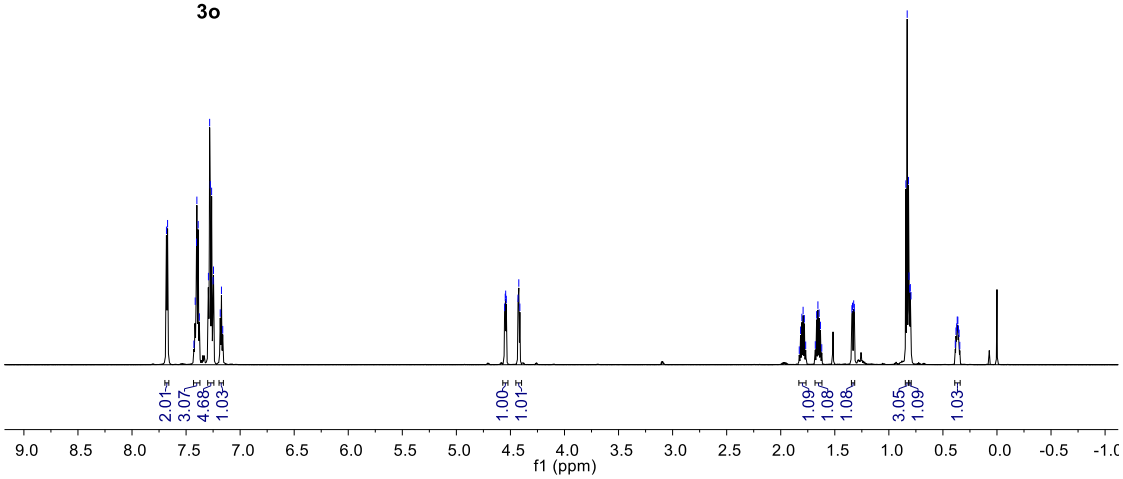
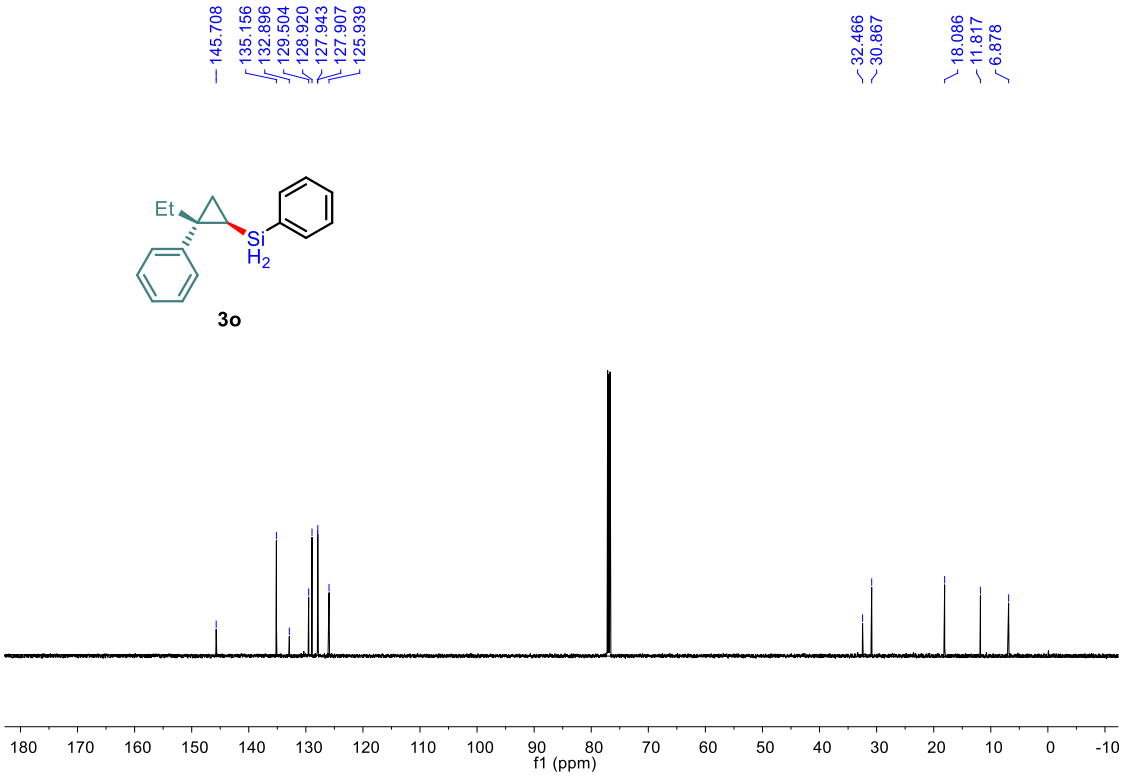
7.671
7.427
7.416
7.404
7.400
7.388
7.377
7.293
7.282
7.276
7.264
7.250
7.246
7.184
7.173
7.161
4.554
4.548
4.544
4.538
4.430
4.423
4.413
1.817
1.805
1.793
1.781
1.769
1.680
1.668
1.656
1.645
1.633
1.621
1.342
1.336
1.325
1.319
0.830
0.818
0.385
0.379
0.373
0.367
0.362
0.356
0.350
0.344


Et
Si
H2

3o


2.01
3.07
4.68
1.03
1.00
1.01
1.09
1.08
1.08
3.05
1.09
1.03
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)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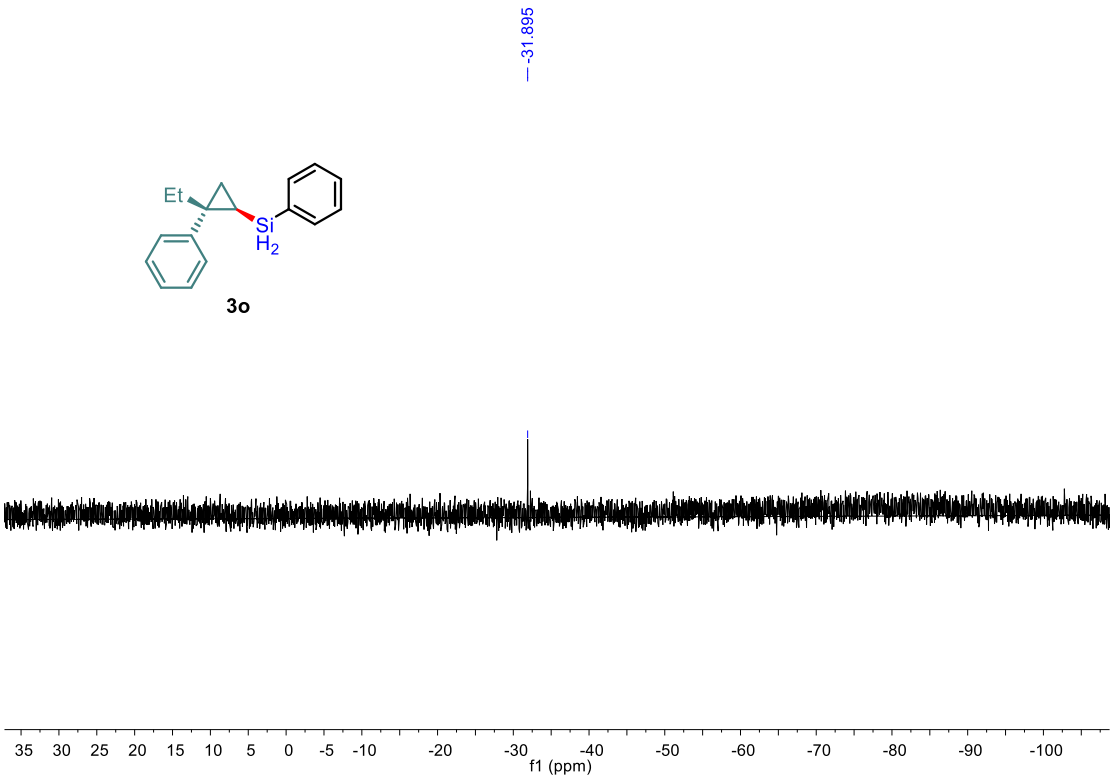
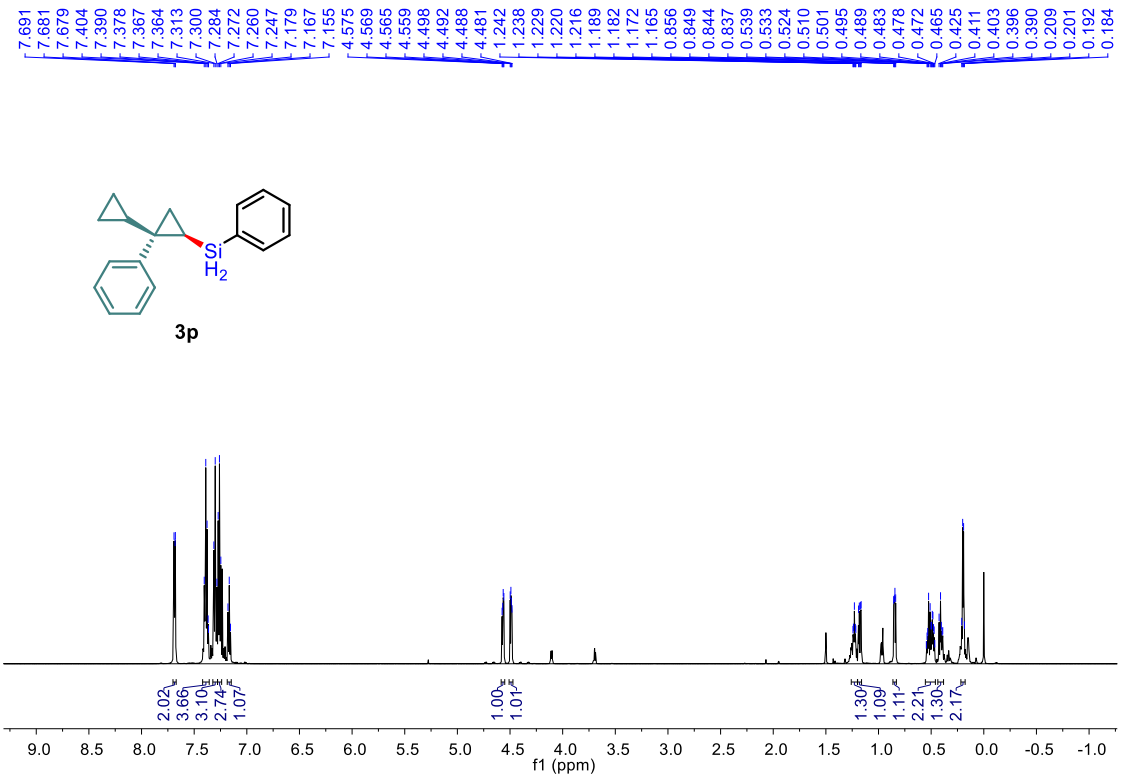
135.156
132.896
129.504
128.920
127.943
127.907
125.939
32.466
30.867
18.086
11.817
6.878
Et
Si
H2
3o
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-31.895
Et
Si
H2
3o
35 30 25 20 15 10 5 0 -5 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)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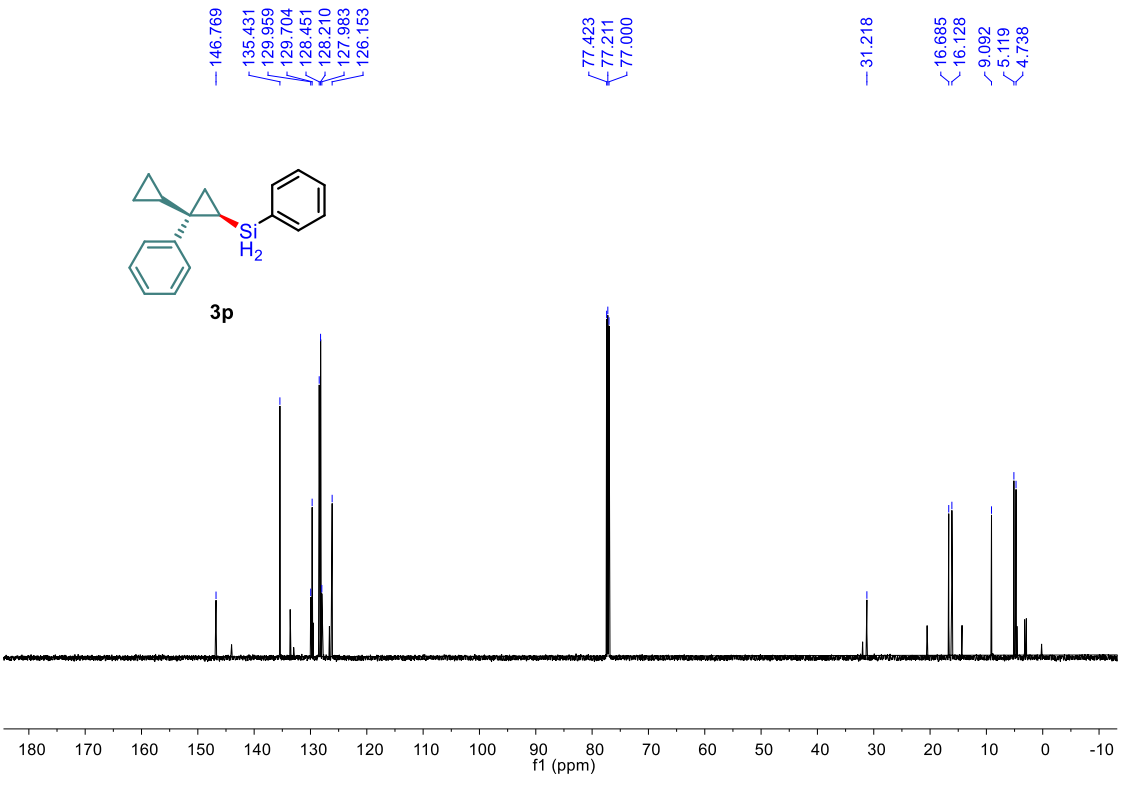
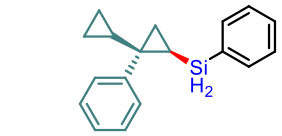
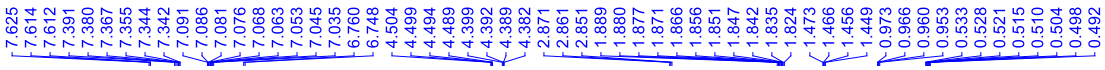
7.679
7.404
7.390
7.378
7.367
7.364
7.313
7.300
7.284
7.272
7.260
7.247
7.179
7.167
7.155
4.575
4.569
4.565
4.559
4.498
4.492
4.488
4.481
1.242
1.238
1.229
1.220
1.216
1.189
1.182
1.172
1.165
0.856
0.849
0.844
0.837
0.539
0.533
0.524
0.510
0.501
0.495
0.489
0.483
0.478
0.472
0.465
0.425
0.411
0.403
0.396
0.390
0.209
0.201
0.192
0.184
Si
H2
3p
2.02
3.66
3.10
2.74
1.07
1.00
1.01
1.30
1.09
1.11
2.21
1.30
2.17
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 -1.0
f1 (ppm)


146.769
135.431
129.959
129.704
128.451
128.210
127.983
126.153
77.423
77.211
77.000
31.218
16.685
16.128
9.092
5.119
4.738
Si
H2
3p
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3p

-30.439
-32.276
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
f1 (ppm)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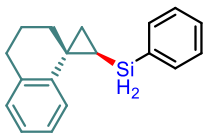
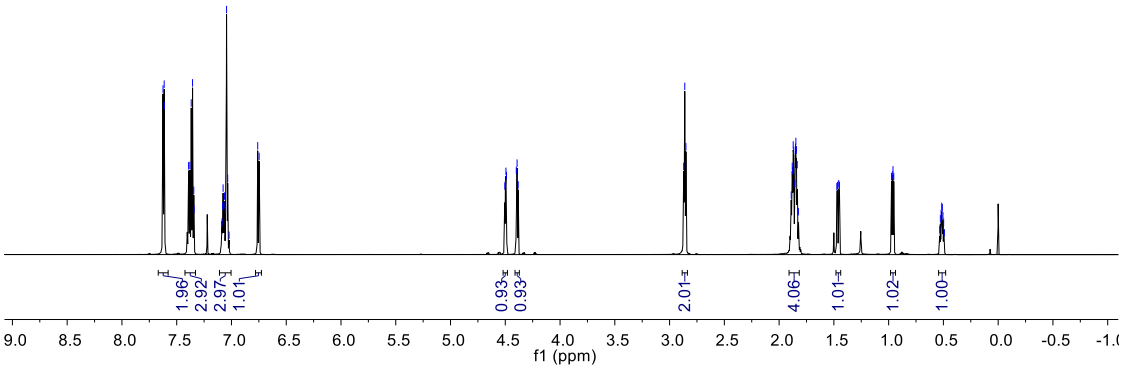
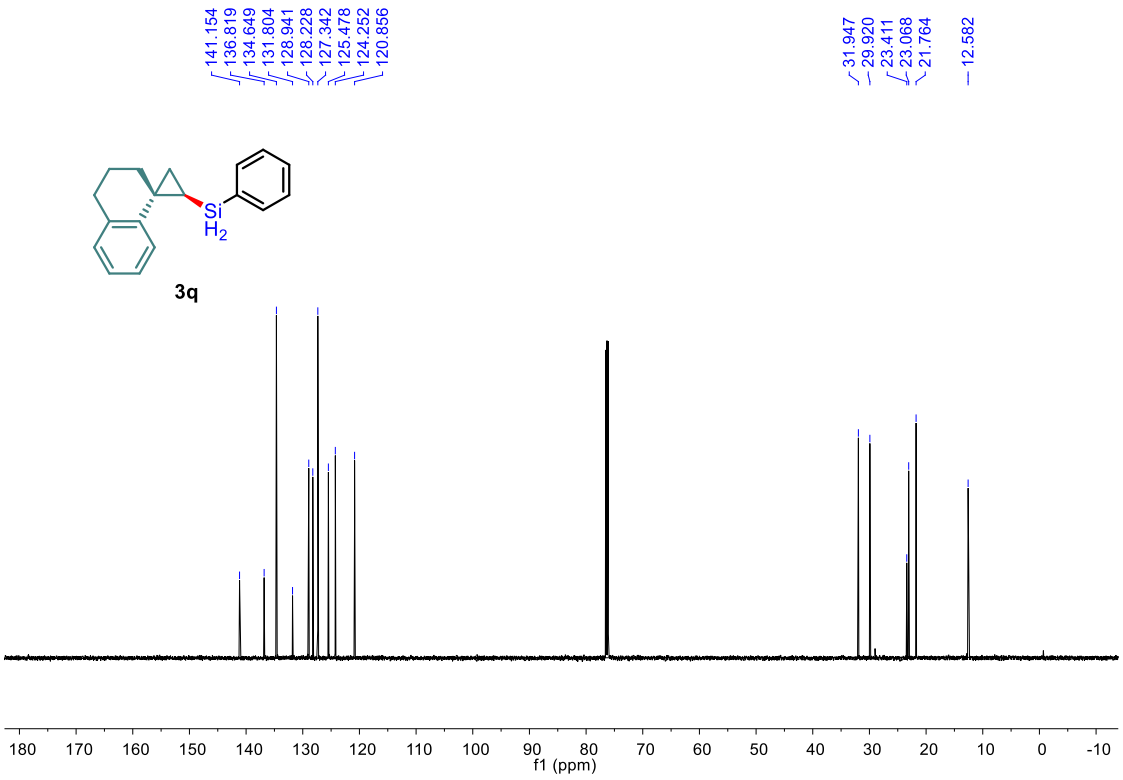
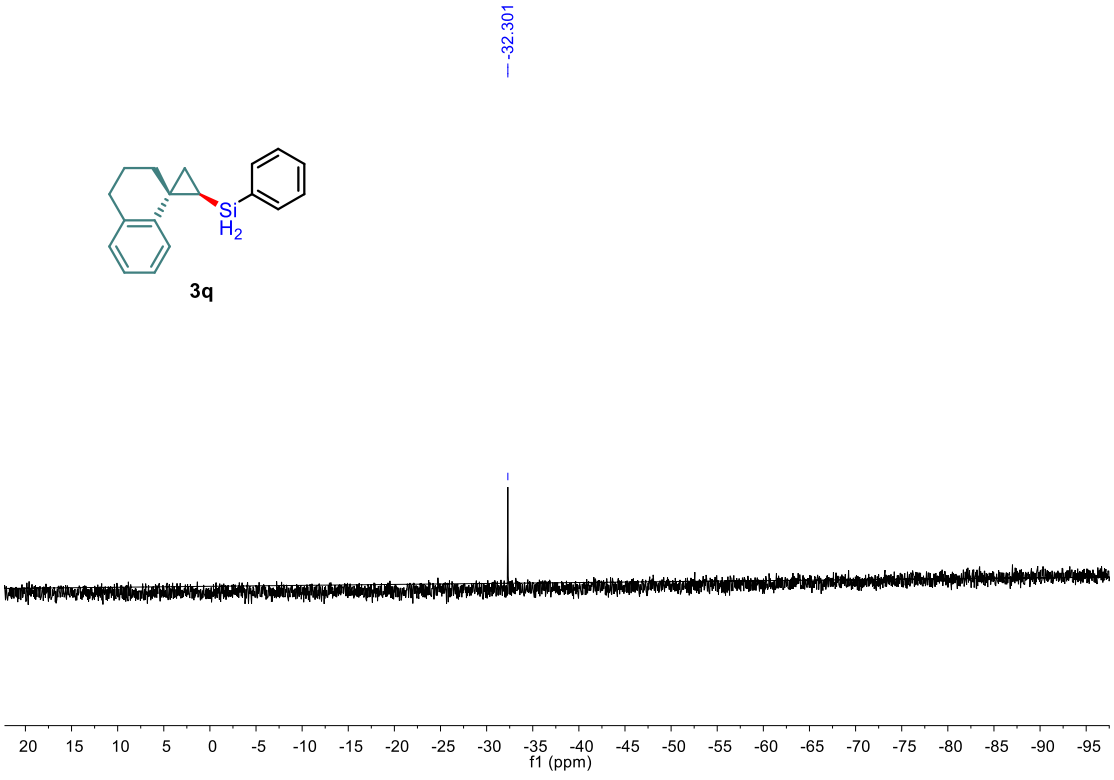
7.355
7.344
7.342
7.091
7.086
7.081
7.076
7.068
7.063
7.053
7.045
7.035
6.760
6.748
4.504
4.499
4.494
4.489
4.399
4.392
4.389
4.382
2.871
2.861
2.851
1.889
1.880
1.877
1.871
1.866
1.856
1.851
1.847
1.842
1.835
1.824
1.473
1.466
1.456
1.449
0.973
0.966
0.960
0.953
0.533
0.528
0.521
0.515
0.510
0.504
0.498
0.492

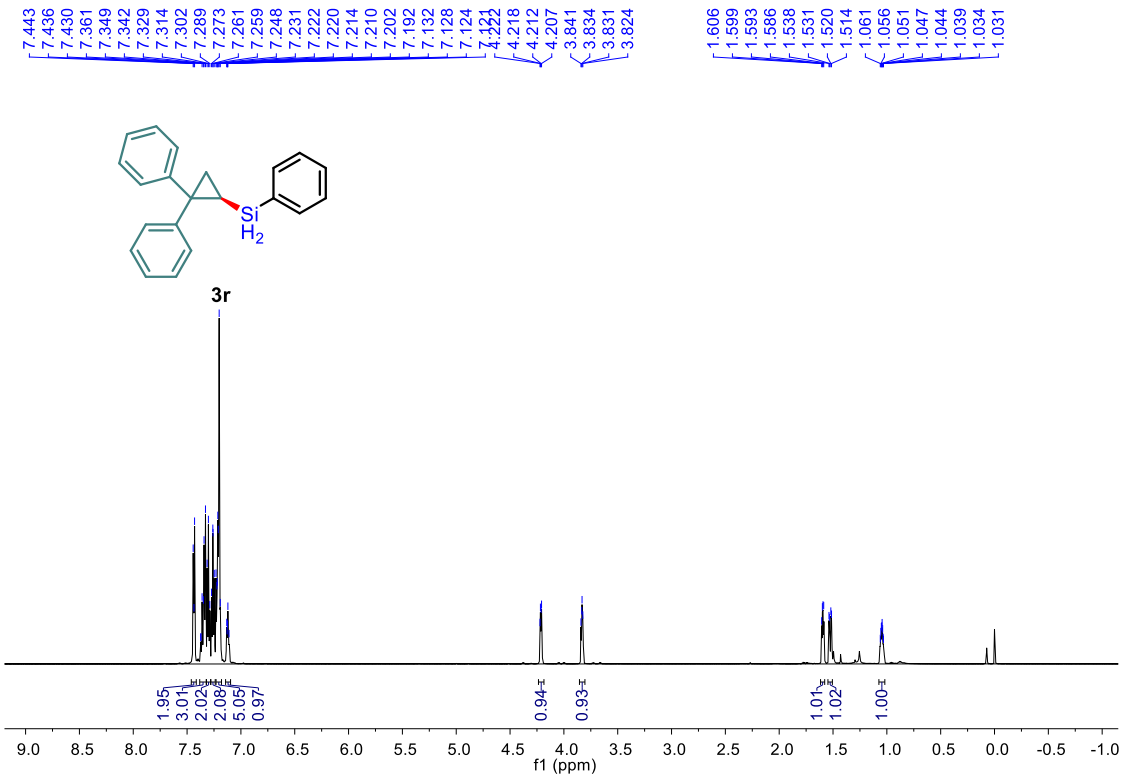


3q


1.96
2.92
2.97
1.01
0.93
0.93
2.01
4.06
1.01
1.02
1.00
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)


141.154
136.819
134.649
131.804
128.941
128.228
127.342
125.478
124.252
120.856
31.947
29.920
23.411
23.068
21.764
12.582
Si
H2
3q
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-32.301
Si
H2
3q
20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95
f1 (ppm)


7.443
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7.430
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7.349
7.342
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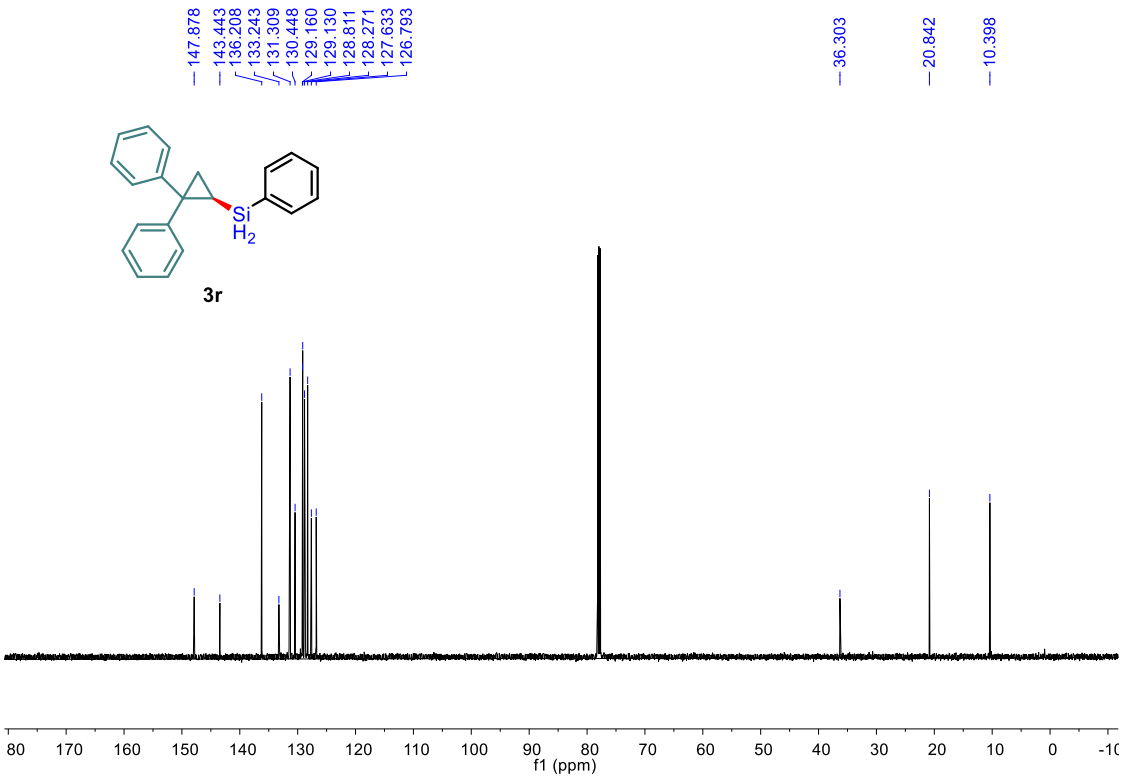
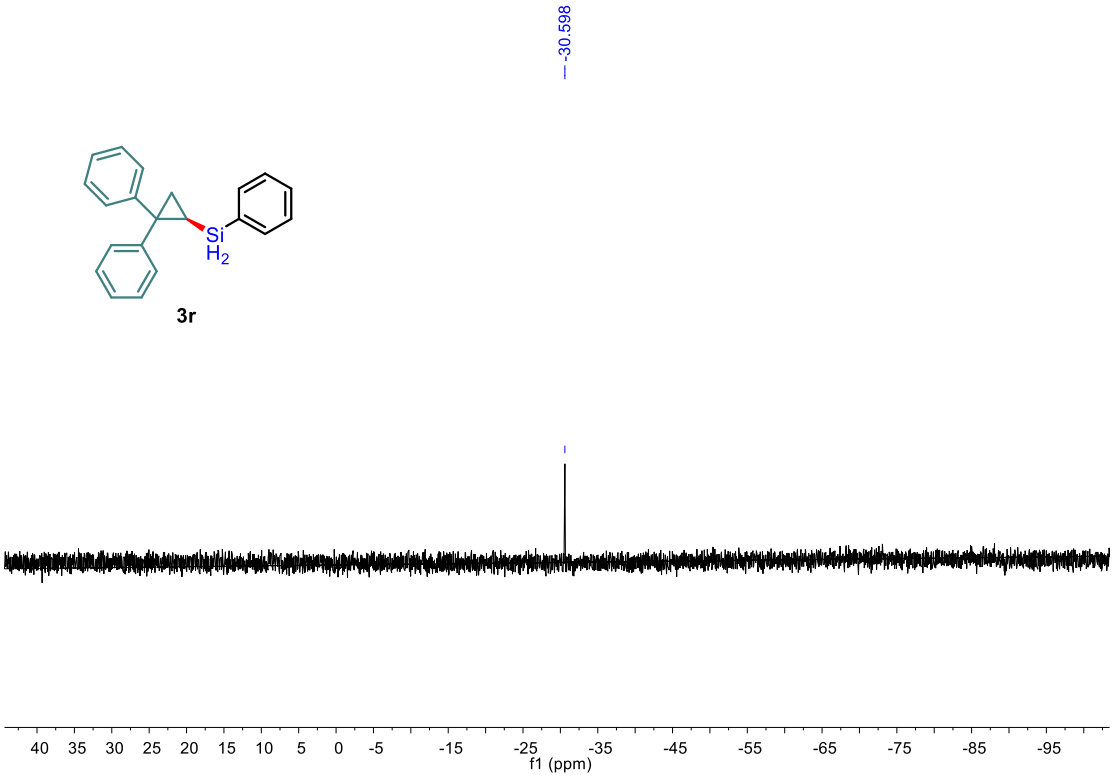
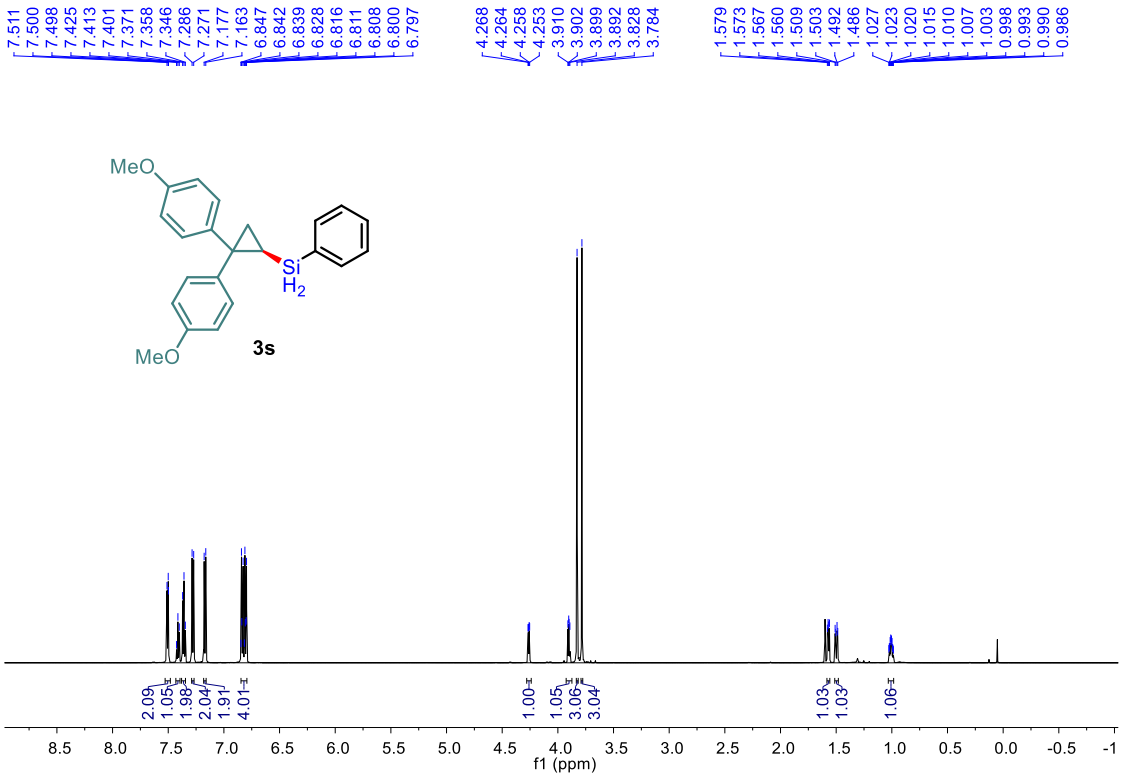
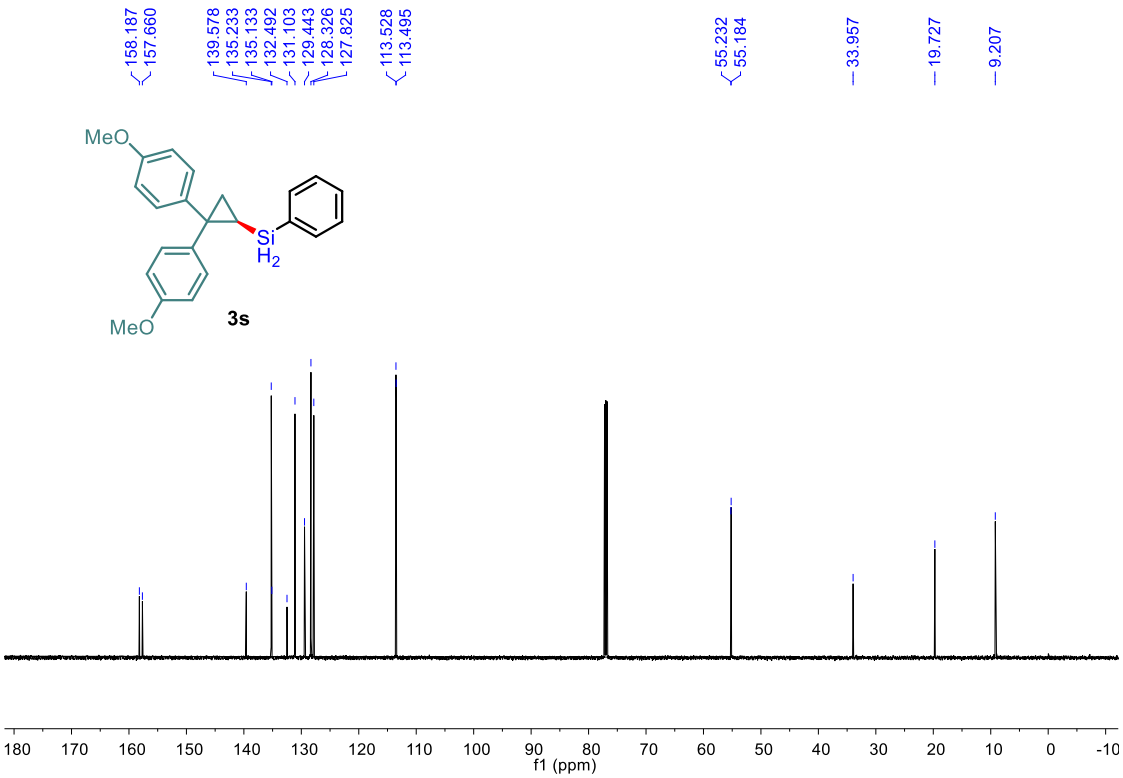
7.314
7.302
7.289
7.273
7.261
7.259
7.248
7.231
7.222
7.220
7.214
7.210
7.202
7.192
7.132
7.128
7.124
4.218
4.212
4.207
3.841
3.834
3.831
3.824
1.606
1.599
1.593
1.586
1.538
1.531
1.520
1.514
1.061
1.056
1.051
1.047
1.044
1.039
1.034
1.031
Si
H2
3r
1.95
3.01
2.02
2.08
5.05
0.97
0.94
0.93
1.01
1.02
1.00
f1 (ppm)


147.878
143.443
136.208
133.243
131.309
130.448
129.160
129.130
128.811
128.271
127.633
126.793
36.303
20.842
10.398
Si
H2
3r
f1 (ppm)


-30.598
Si
H2
3r
40 35 30 25 20 15 10 5 0 -5 -15 -25 -35 -45 -55 -65 -75 -85 -95
f1 (ppm)


7.511 7.500 7.498 7.425 7.413 7.401 7.371 7.358 7.346 7.286 7.271 7.177 7.163 6.847 6.842 6.839 6.828 6.816 6.811 6.808 6.800 6.797
4.268 4.264 4.258 4.253 3.910 3.902 3.899 3.892 3.828 3.784
1.579 1.573 1.567 1.560 1.509 1.503 1.492 1.486 1.027 1.023 1.020 1.015 1.010 1.007 1.003 0.998 0.993 0.990 0.986
MeO
Si
H2
MeO
3s
2.09 1.05 1.98 2.04 1.91 4.01
1.00 1.05 3.06 3.04
1.03 1.03 1.06
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 -1
f1 (ppm)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157.660
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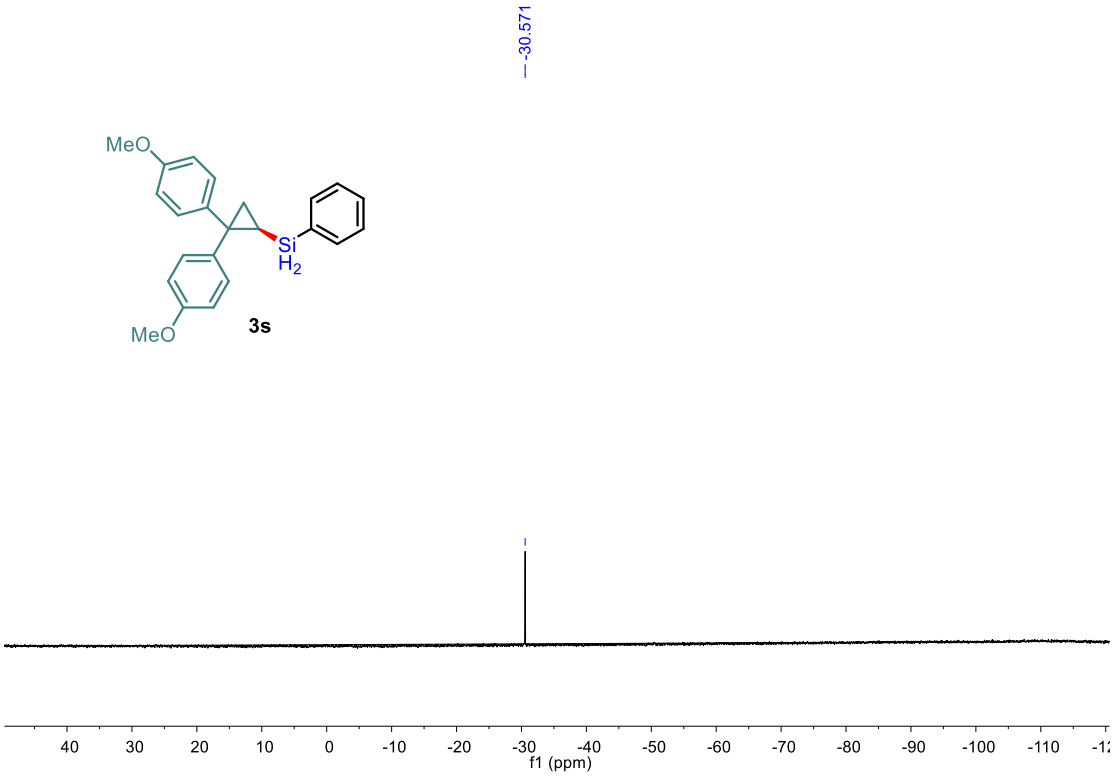
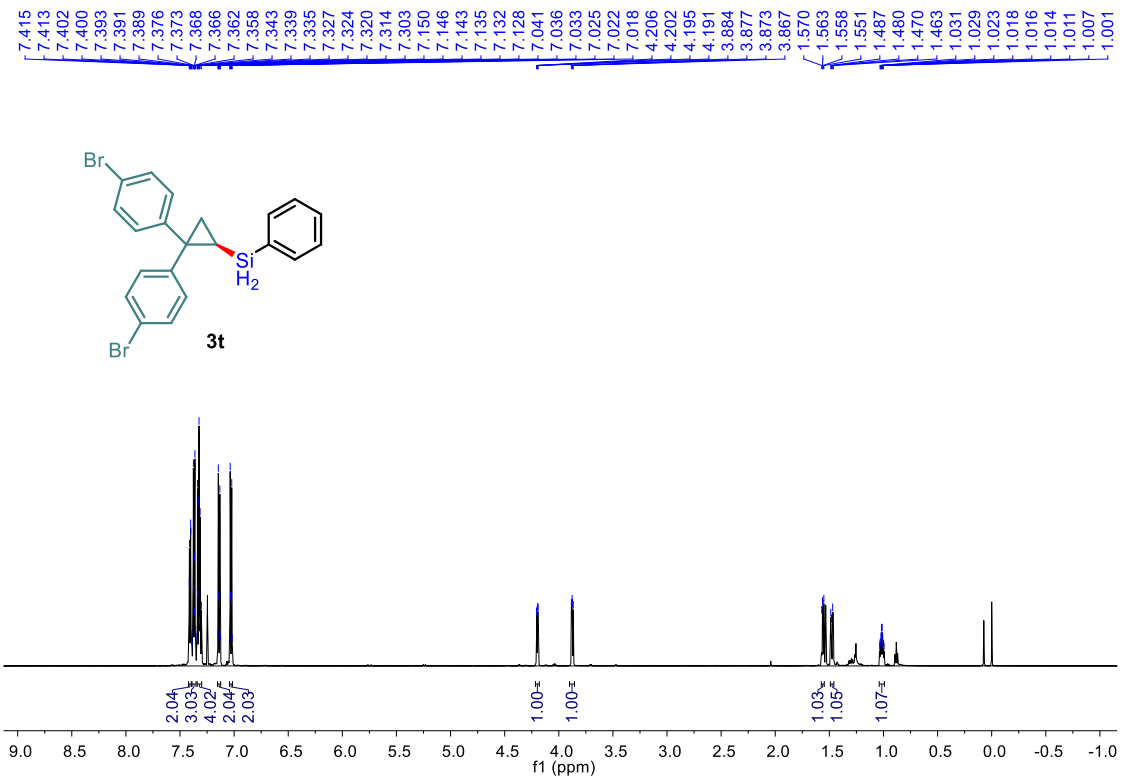
135.233
135.133
132.492
131.103
129.443
128.326
127.825
113.528
113.495
55.232
55.184
33.957
19.727
9.207
MeO
Si
H2
MeO
3s
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-30.571
MeO
Si
H2
MeO
3s
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -12
f1 (ppm)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7.400
7.393
7.391
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7.376
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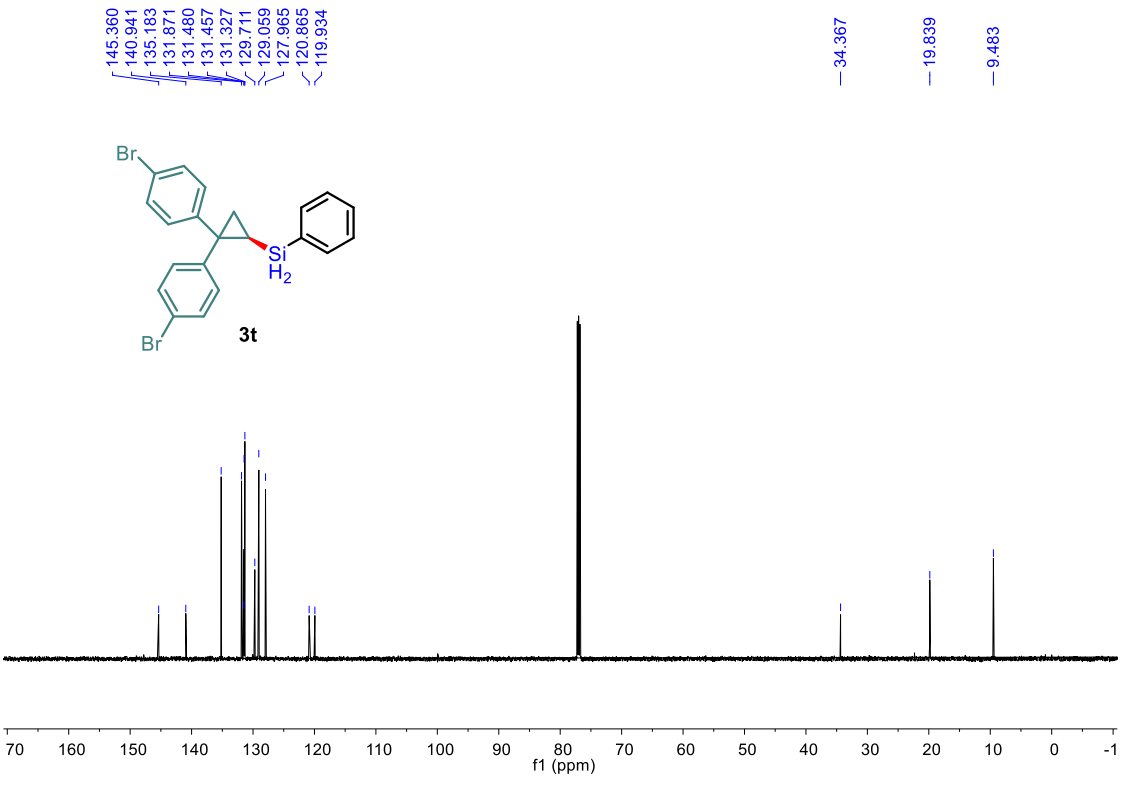
7.366
7.362
7.358
7.343
7.339
7.335
7.327
7.324
7.320
7.314
7.303
7.150
7.146
7.143
7.135
7.132
7.128
7.041
7.036
7.033
7.025
7.022
7.018
4.206
4.202
4.195
4.191
3.884
3.877
3.873
3.867
1.570
1.563
1.558
1.551
1.487
1.480
1.470
1.463
1.031
1.029
1.023
1.018
1.016
1.014
1.011
1.007
1.001
Br
Si
H2
Br
3t
2.04
3.03
4.02
2.04
2.03
1.00
1.00
1.03
1.05
1.07
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 -1.0
f1 (ppm)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129.711
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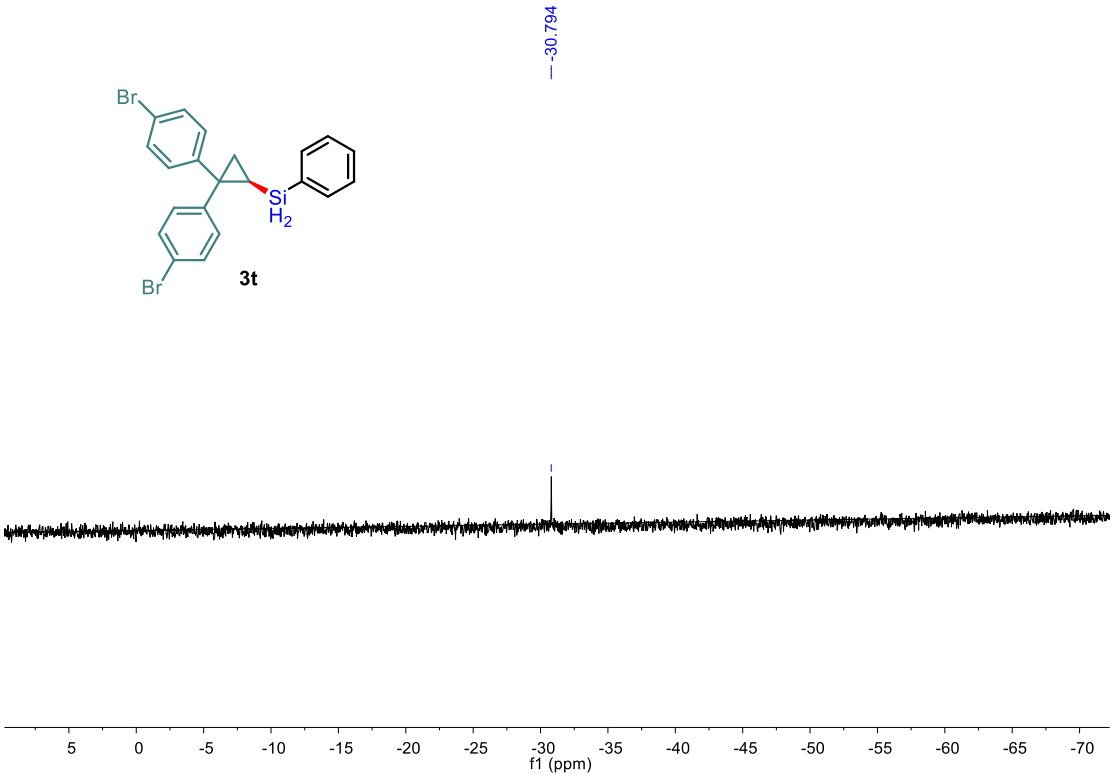
127.965
120.865
119.934
34.367
19.839
9.483
Br
Si
H2
Br
3t
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)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Br
Si
H2
Br
3t
5
0
-5
-10
-15
-20
-25
-30
-35
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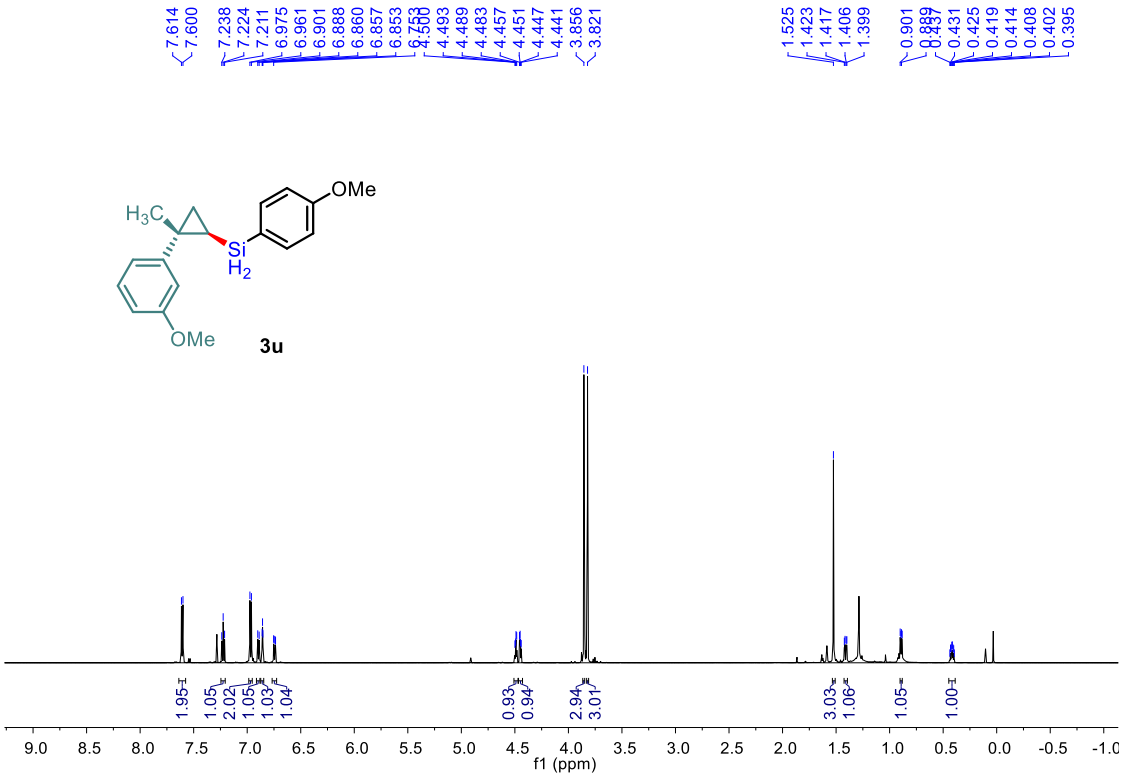
-45
-50
-55
-60
-65
-70
f1 (ppm)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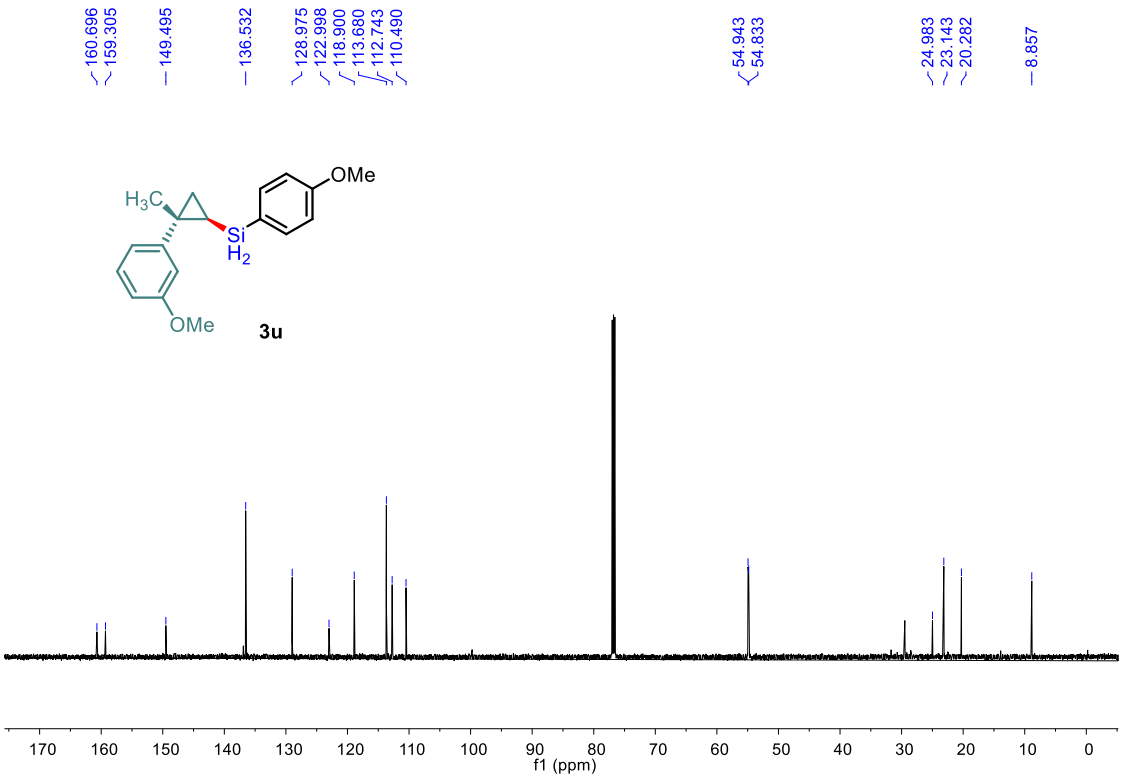
7.600
7.238
7.224
7.211
6.975
6.961
6.901
6.888
6.860
6.857
6.853
4.500
4.493
4.489
4.483
4.457
4.451
4.447
4.441
3.856
3.821
1.525
1.423
1.417
1.406
1.399
0.901
0.889
0.431
0.425
0.419
0.414
0.408
0.402
0.395
H3C
Si
H2
OMe
OMe
3u
1.95
1.05
2.02
1.05
1.03
1.04
0.93
0.94
2.94
3.01
3.03
1.06
1.05
1.00
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
-1.0
f1 (ppm)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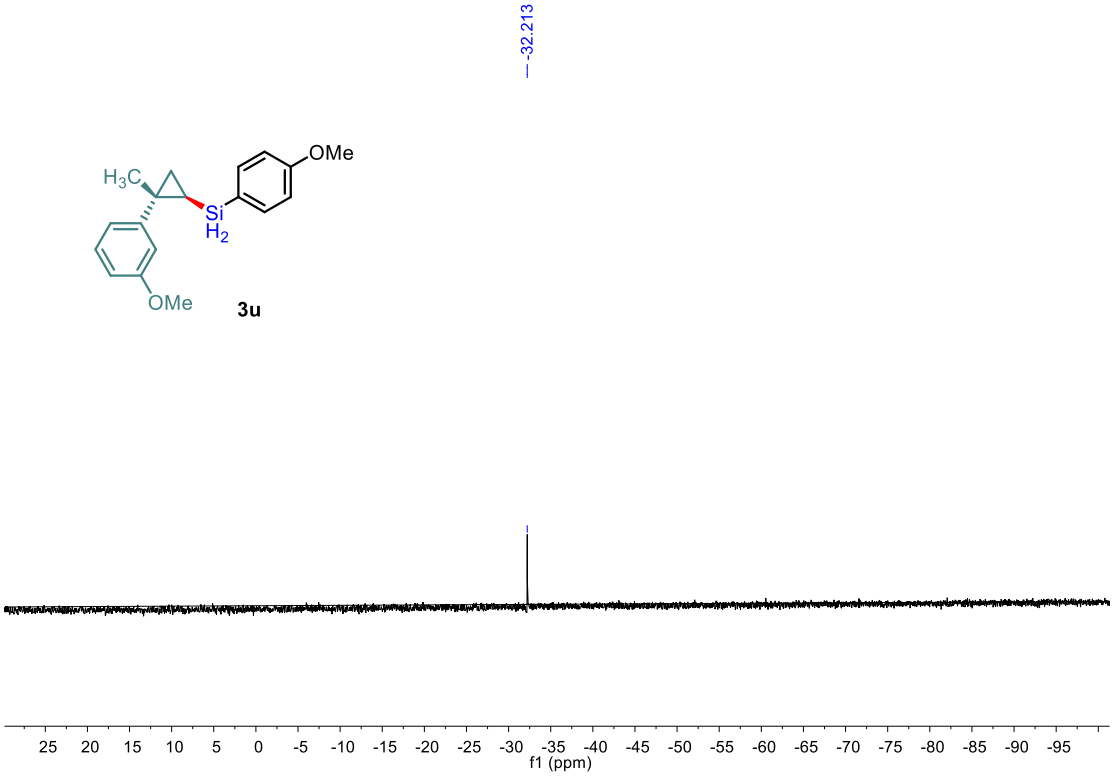
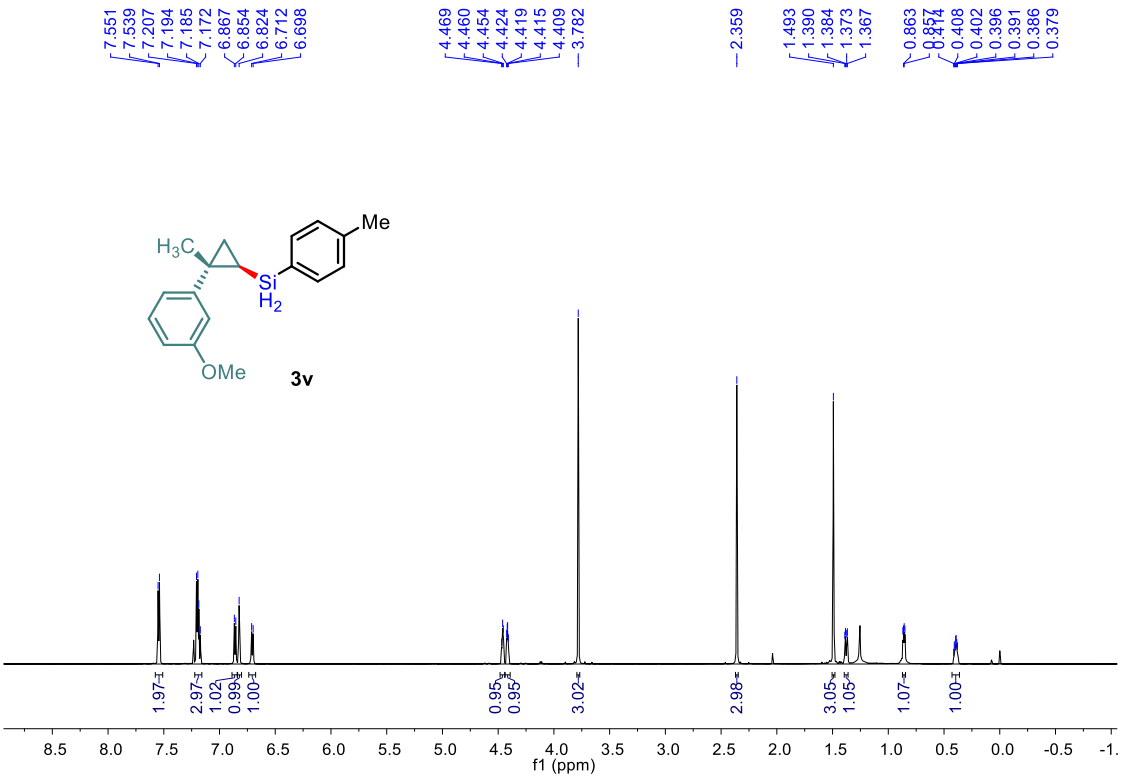
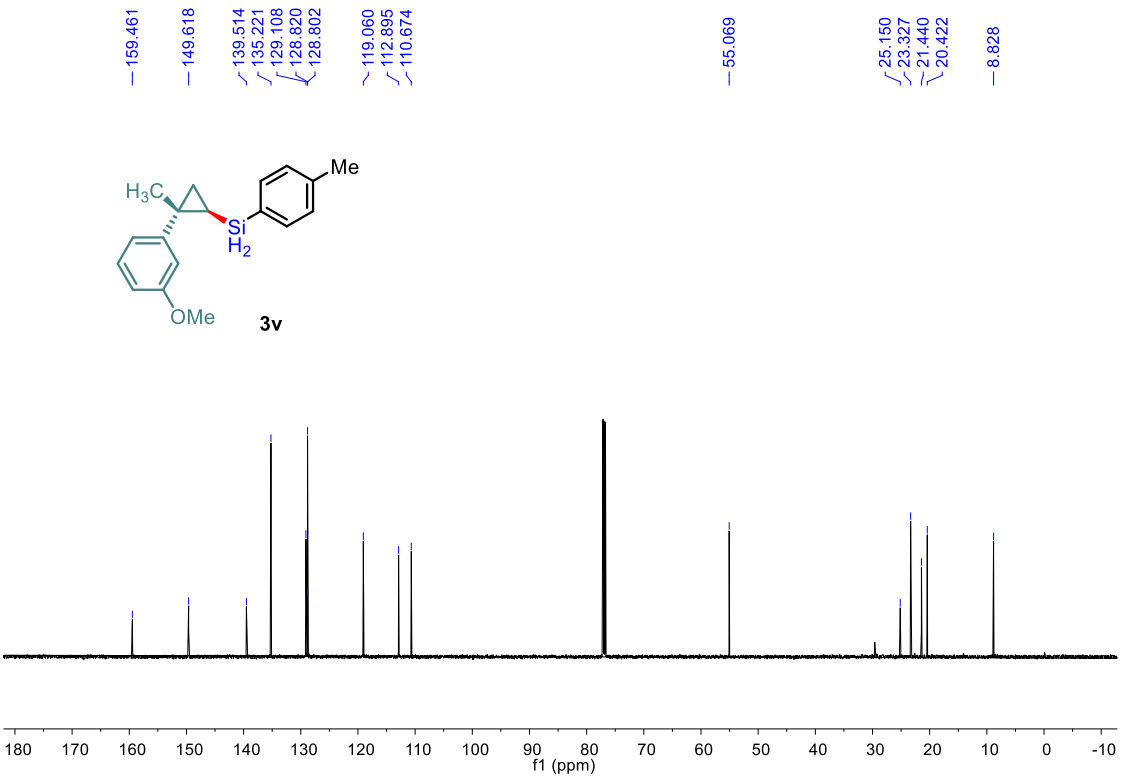
159.305
149.495
136.532
128.975
122.998
118.900
113.680
112.743
110.490
54.943
54.833
24.983
23.143
20.282
8.857
OMe
H3C
Si
H2
OMe
3u
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-32.213
OMe
H3C
Si
H2
OMe
3u
25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95
f1 (ppm)


7.551
7.539
7.207
7.194
7.185
7.172
6.867
6.854
6.824
6.712
6.698
4.469
4.460
4.454
4.424
4.419
4.415
4.409
3.782
2.359
1.493
1.390
1.384
1.373
1.367
0.863
0.857
0.414
0.408
0.402
0.396
0.391
0.386
0.379
Me
H3C
Si
H2
OMe
3v
1.97
2.97
1.02
0.99
1.00
0.95
0.95
3.02
2.98
3.05
1.05
1.07
1.00
f1 (ppm)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149.618
139.514
135.221
129.108
128.820
128.802
119.060
112.895
110.674
55.069
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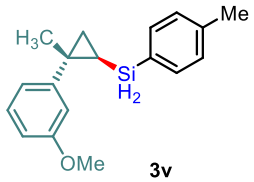
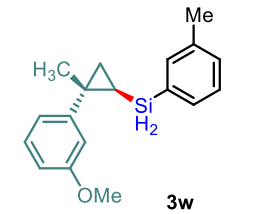
23.327
21.440
20.422
8.828
Me
H3C
Si
H2
OMe
3v
f1 (ppm)


H3C
Si
H2
Me
OMe

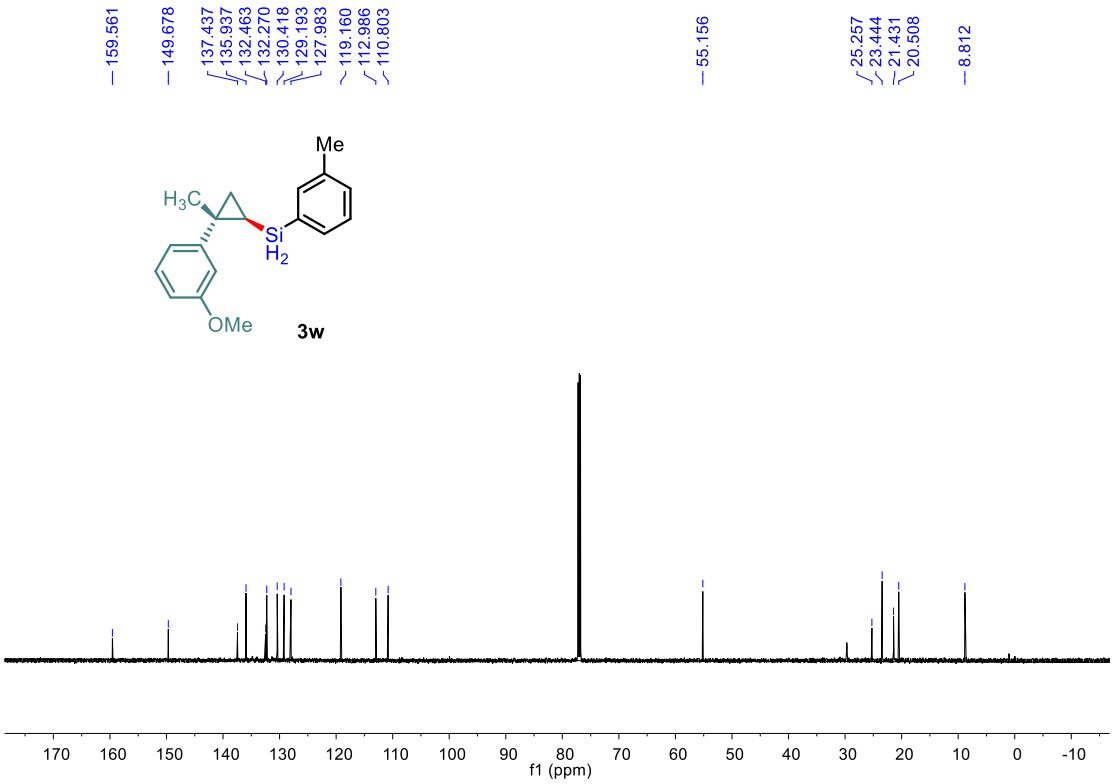
3v

-32.052
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
f1 (ppm)


H3C
Si
H2
Me
OMe

3w

7.468
7.459
7.446
7.290
7.278
7.265
7.225
7.212
7.203
7.190
7.176
6.876
6.863
6.831
6.719
6.716
6.706
6.703
4.472
4.466
4.463
4.456
4.415
4.409
4.406
4.399
3.785
2.361
1.502
1.405
1.399
1.388
1.382
0.872
0.866
0.419
0.413
0.407
0.401
0.396
0.390
0.384
0.377
0.90
1.04
1.09
1.06
1.17
1.01
0.98
0.98
0.95
0.96
3.04
3.08
3.05
1.01
0.97
1.00
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
-1.0
f1 (ppm)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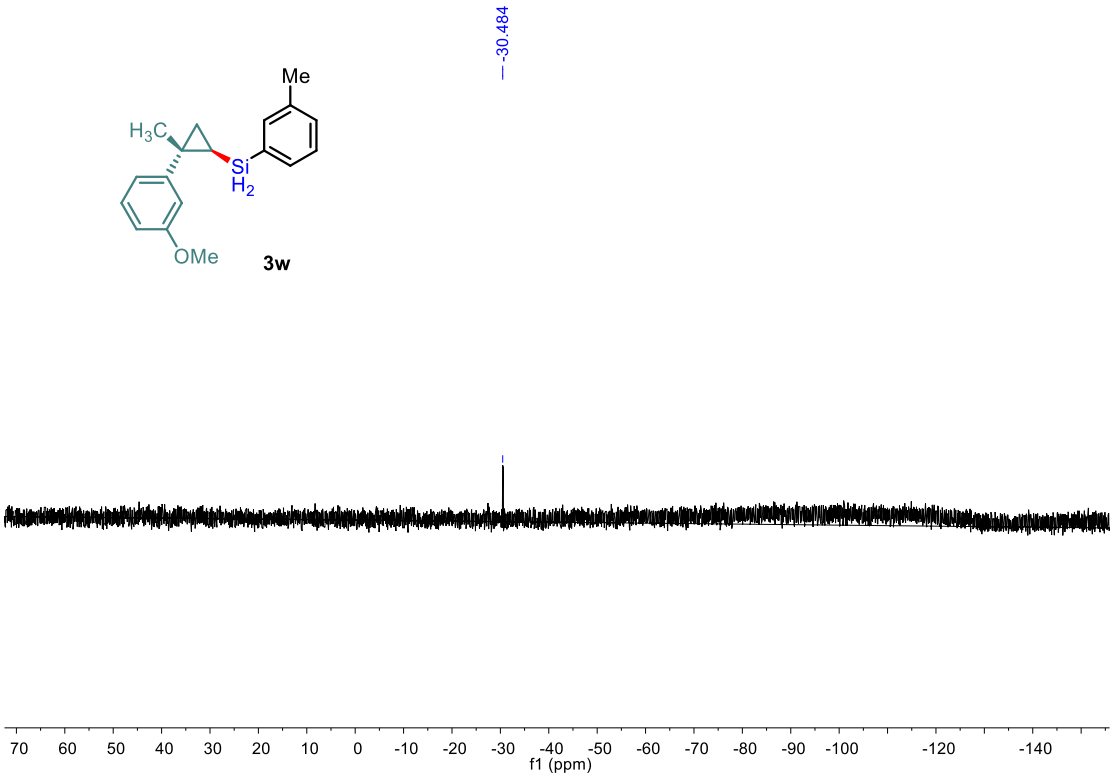
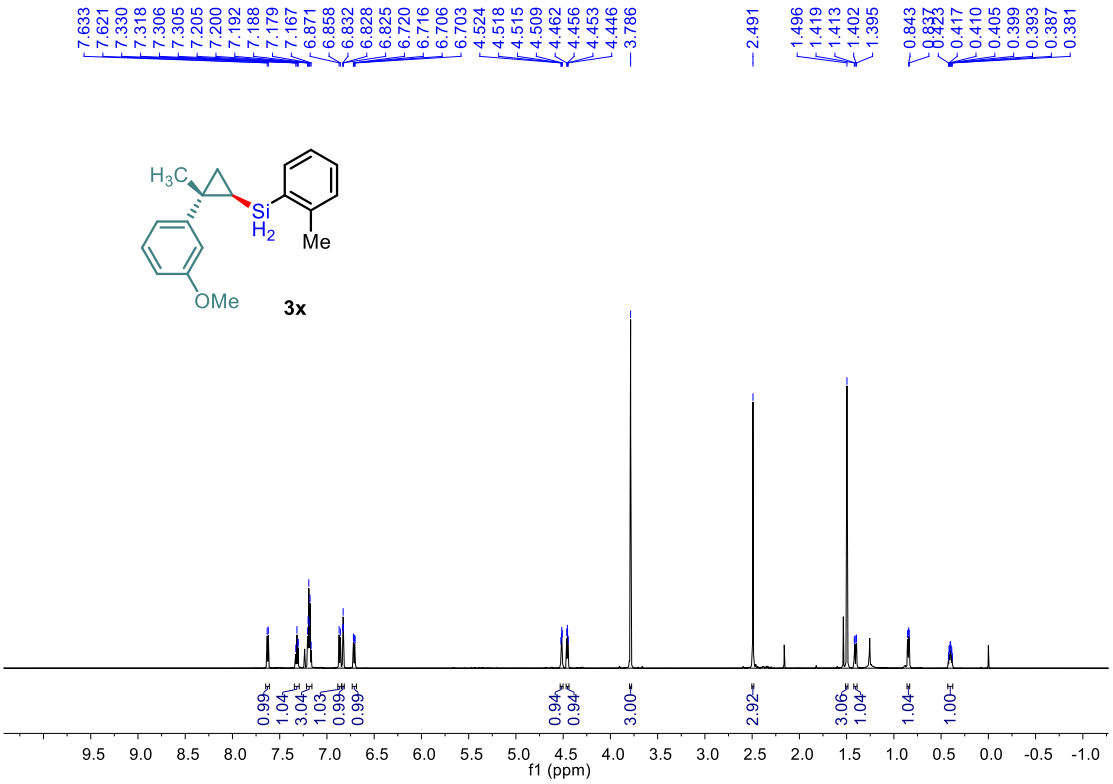
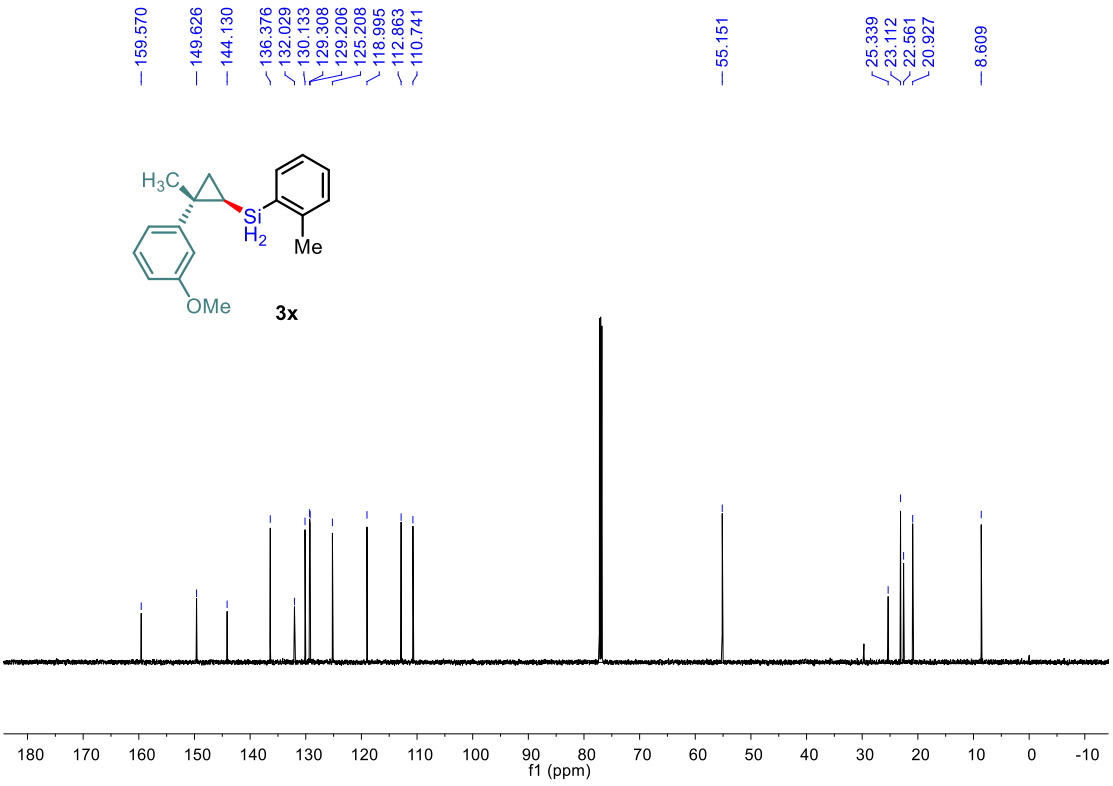
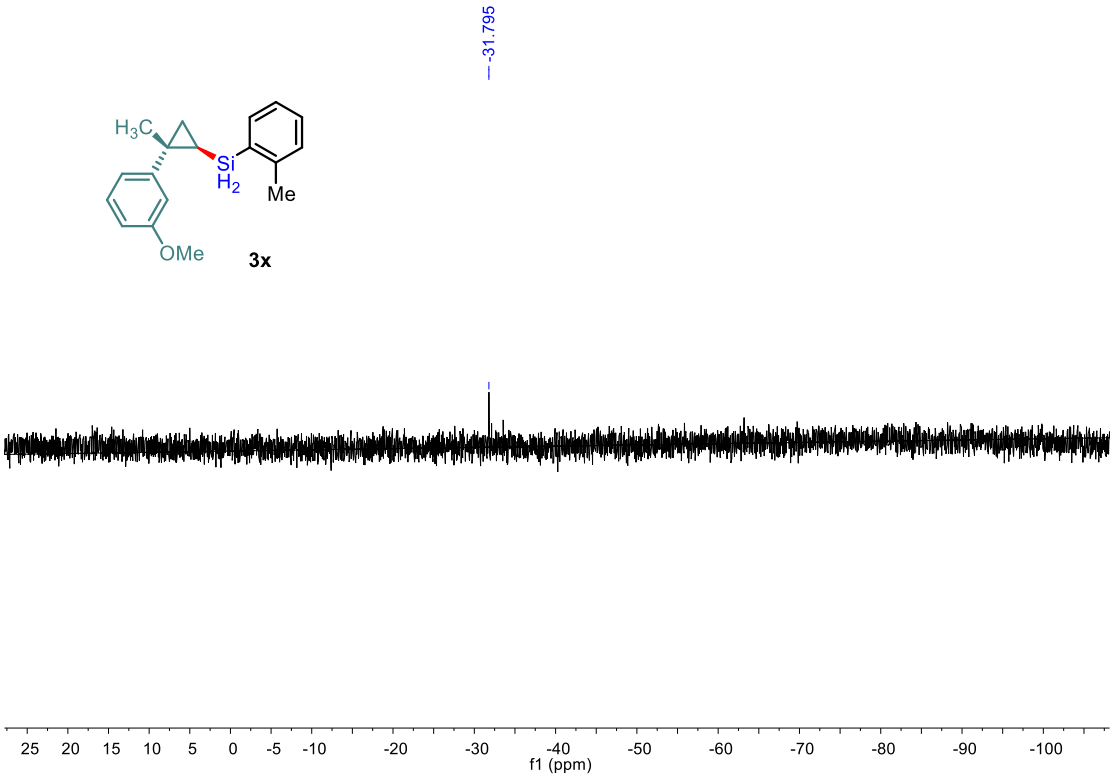
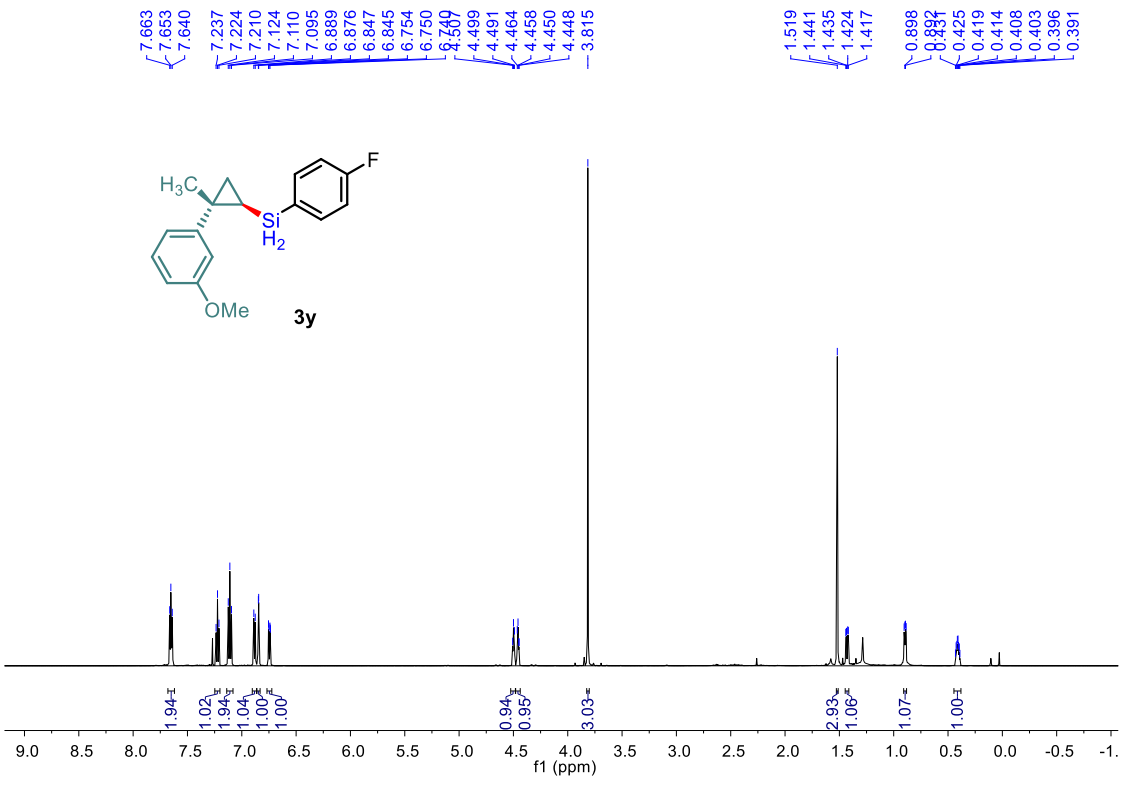
149.678
137.437
135.937
132.463
132.270
130.418
129.193
127.983
119.160
112.986
110.803
55.156
25.257
23.444
21.431
20.508
8.812
Me
H3C
Si
H2
OMe
3w
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

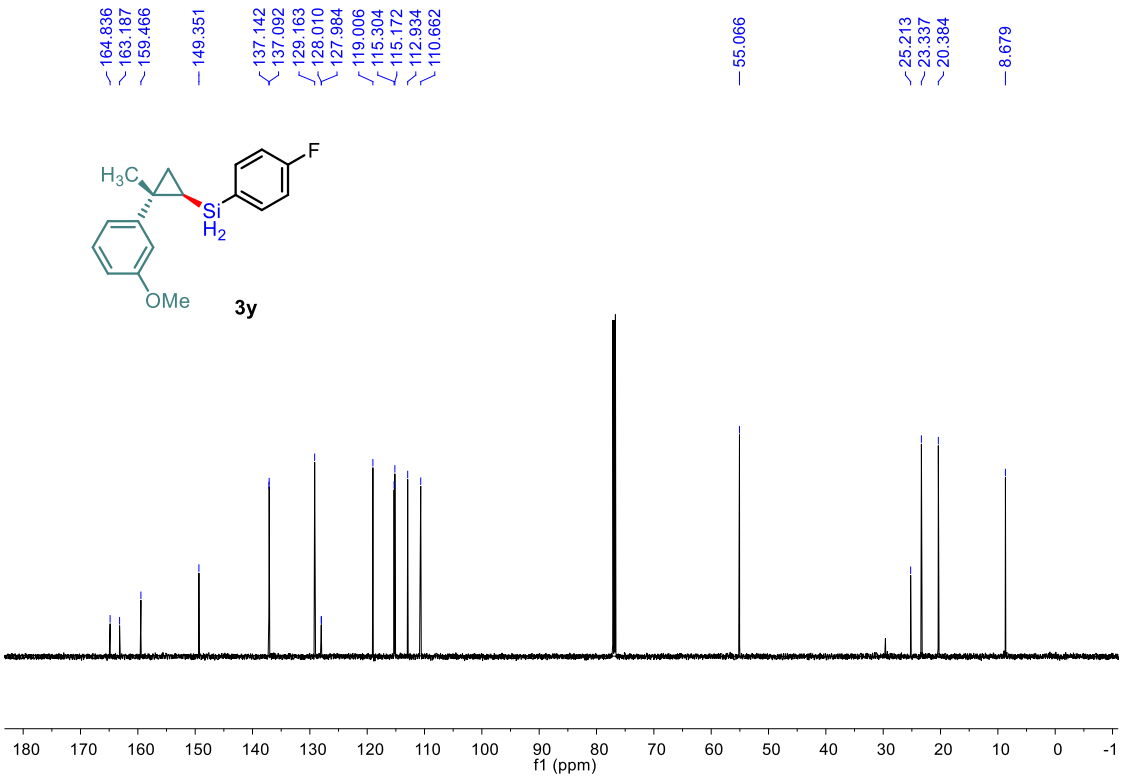

-30.484
Me
H3C
Si
H2
OMe
3w
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140
f1 (ppm)

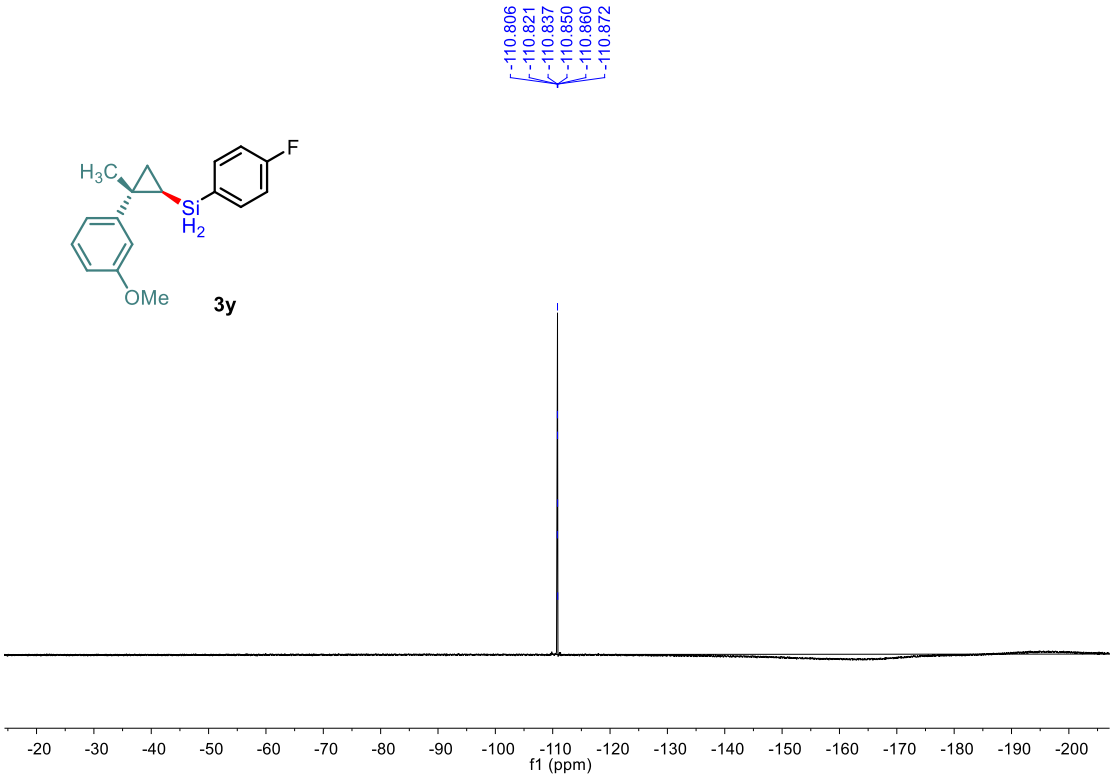

7.633
7.621
7.330
7.318
7.306
7.305
7.205
7.200
7.192
7.188
7.179
7.167
6.871
6.858
6.832
6.828
6.825
6.720
6.716
6.706
6.703
4.524
4.518
4.515
4.509
4.462
4.456
4.453
4.446
3.786
2.491
1.496
1.419
1.413
1.402
1.395
0.843
0.417
0.410
0.405
0.399
0.393
0.387
0.381
H3C
Si
H2
Me
OMe
3x
0.99
1.04
3.04
1.03
0.99
0.99
0.94
0.94
3.00
2.92
3.06
1.04
1.04
1.00
f1 (ppm)

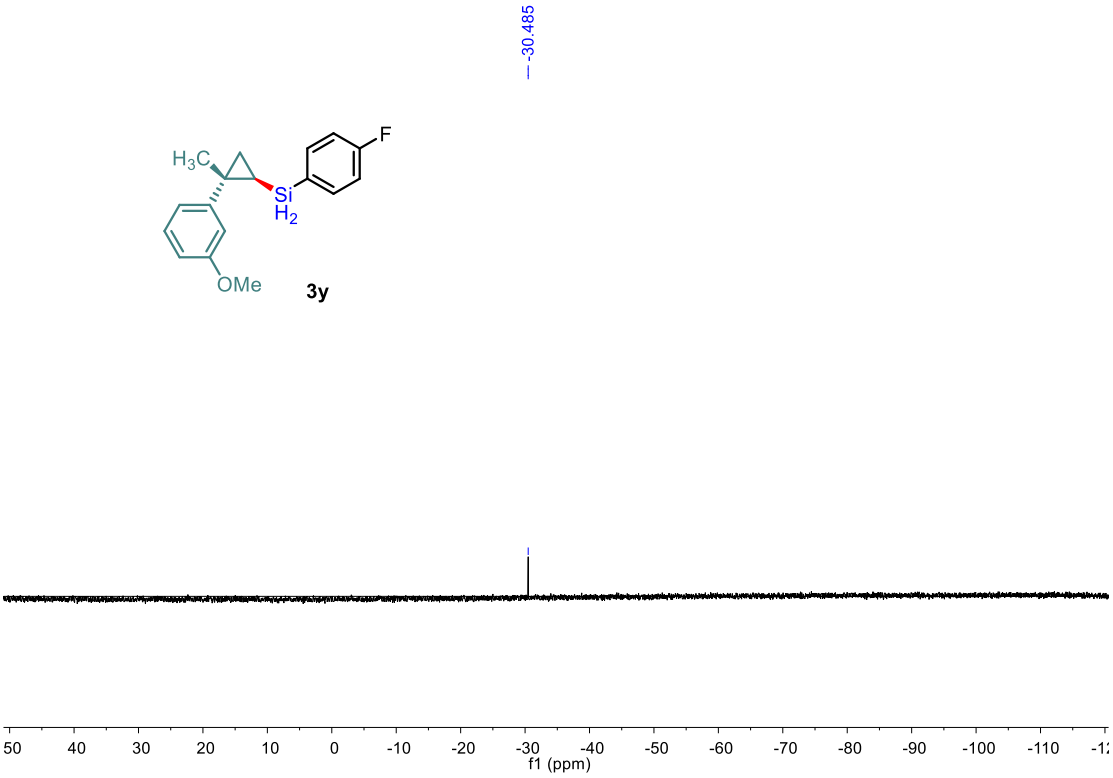

159.570
149.626
144.130
136.376
132.029
130.133
129.308
129.206
125.208
118.995
112.863
110.741
55.151
25.339
23.112
22.561
20.927
8.609
H3C
Si
H2
Me
OMe
3x
f1 (ppm)

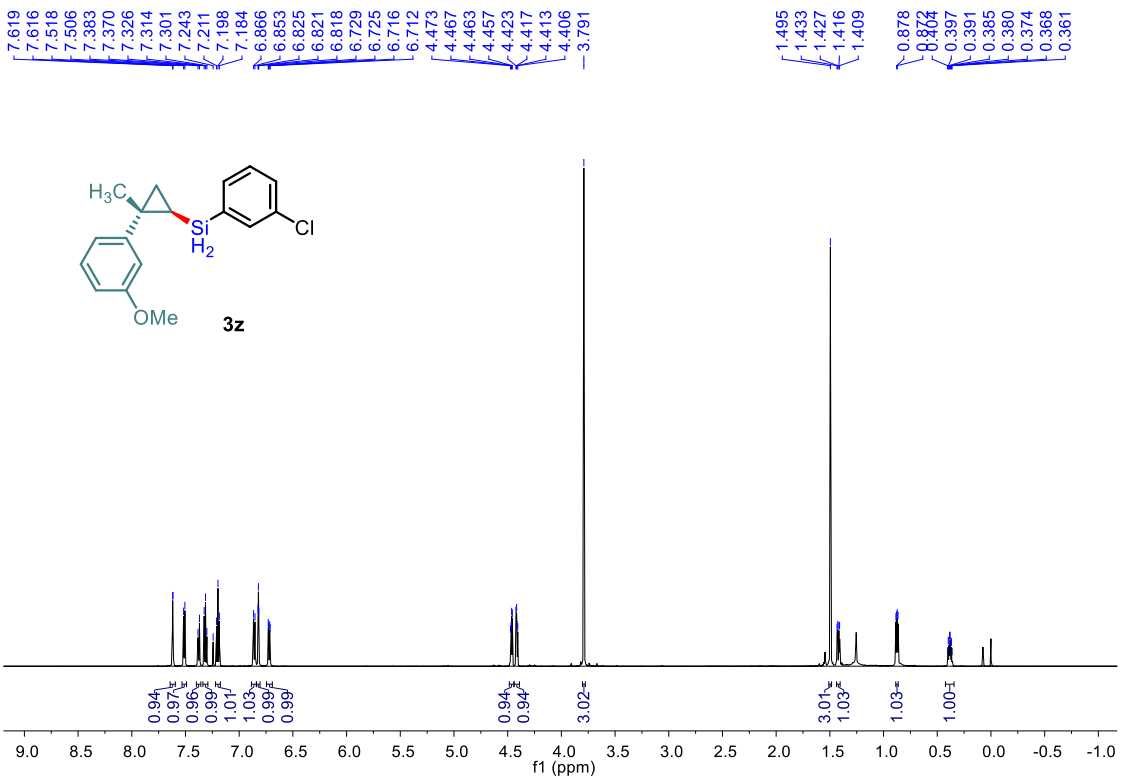

-31.795
H3C
Si
H2
Me
OMe
3x
25 20 15 10 5 0 -5 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

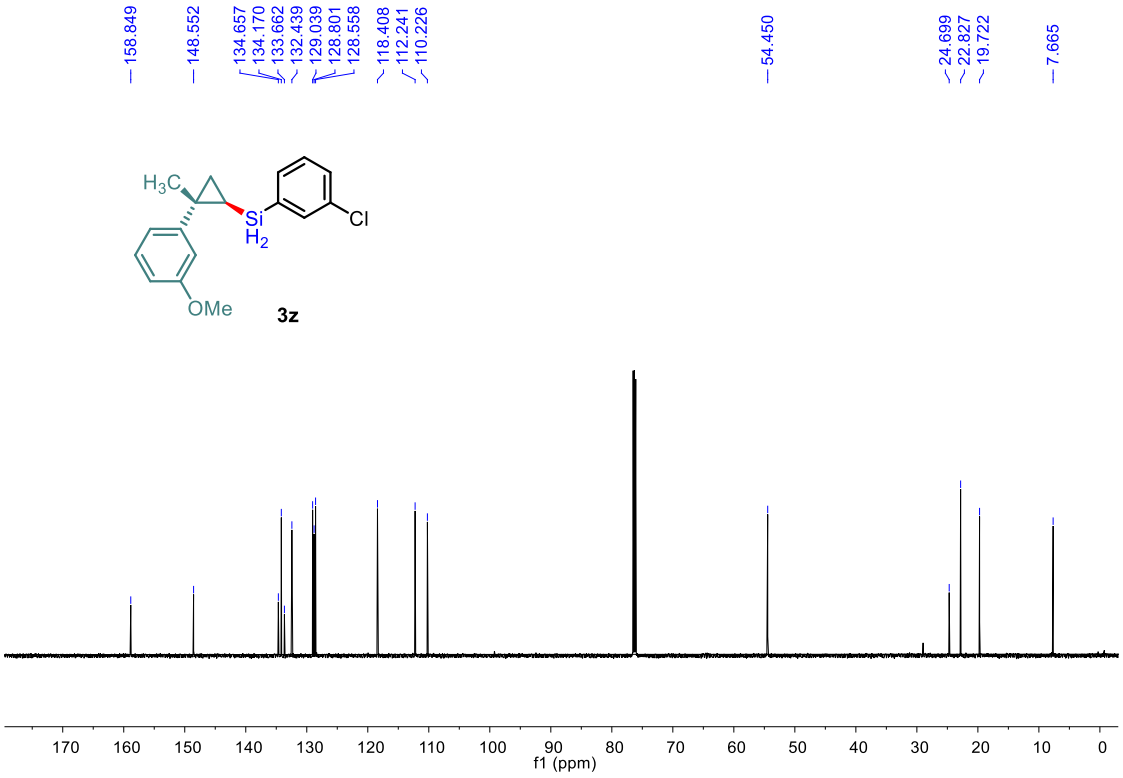

7.663
7.653
7.640
7.237
7.224
7.210
7.124
7.110
7.095
6.889
6.876
6.847
6.845
6.754
6.750
4.499
4.491
4.464
4.458
4.450
4.448
3.815
1.519
1.441
1.435
1.424
1.417
0.898
0.425
0.419
0.414
0.408
0.403
0.396
0.391
F
H3C
Si
H2
OMe
3y
1.94
1.02
1.94
1.04
1.00
1.00
0.94
0.95
3.03
2.93
1.06
1.07
1.00
9.0 8.5 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 -1.
f1 (ppm)


164.836
163.187
159.466
149.351
137.142
137.092
129.163
128.010
127.984
119.006
115.304
115.172
112.934
110.662
55.066
25.213
23.337
20.384
8.679
H3C
Si
H2
F
OMe
3y
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


-110.806
-110.821
-110.837
-110.850
-110.860
-110.872
H3C
Si
H2
F
OMe
3y
-20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


-30.485
H3C
Si
H2
F
OMe
3y
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)


7.619
7.616
7.518
7.506
7.383
7.370
7.326
7.314
7.301
7.243
7.211
7.198
7.184
6.866
6.853
6.825
6.821
6.818
6.729
6.725
6.716
6.712
4.473
4.467
4.463
4.457
4.423
4.417
4.413
4.406
3.791
1.495
1.433
1.427
1.416
1.409
0.878
0.872
0.404
0.397
0.391
0.385
0.380
0.374
0.368
0.361
H3C
Si
H2
Cl
OMe
3z
0.94
0.97
0.96
0.99
1.01
1.03
0.99
0.99
0.94
0.94
3.02
3.01
1.03
1.03
1.00
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 -1.0
f1 (ppm)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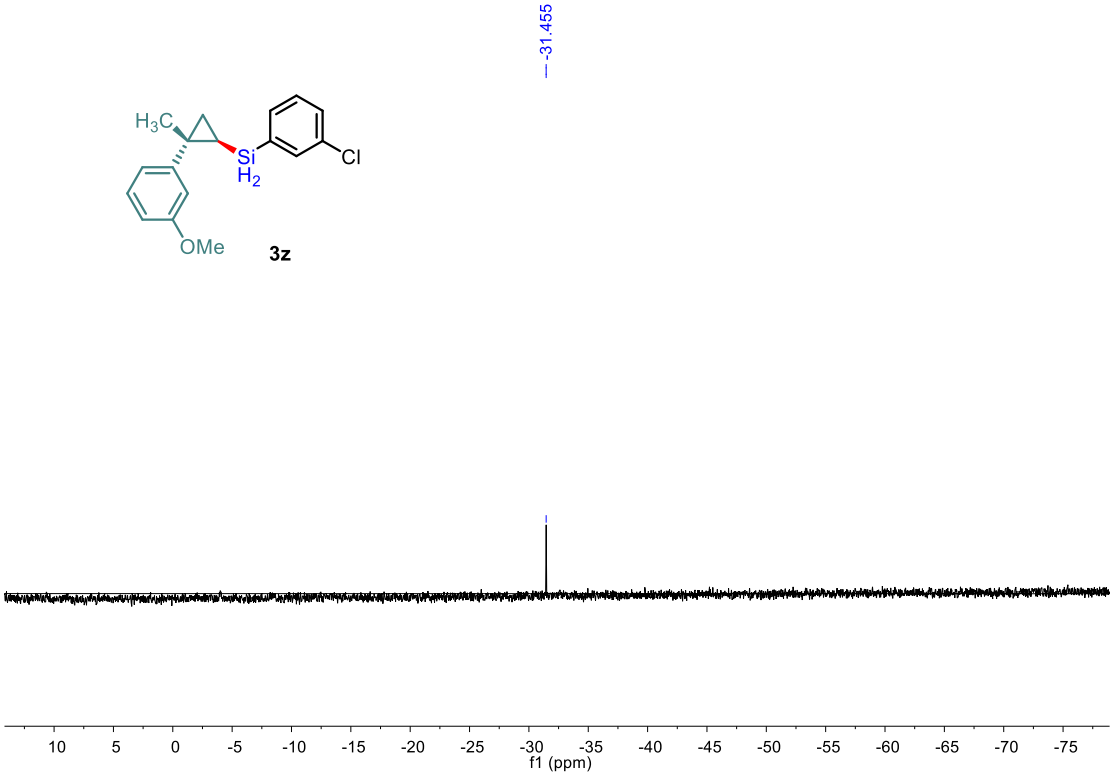
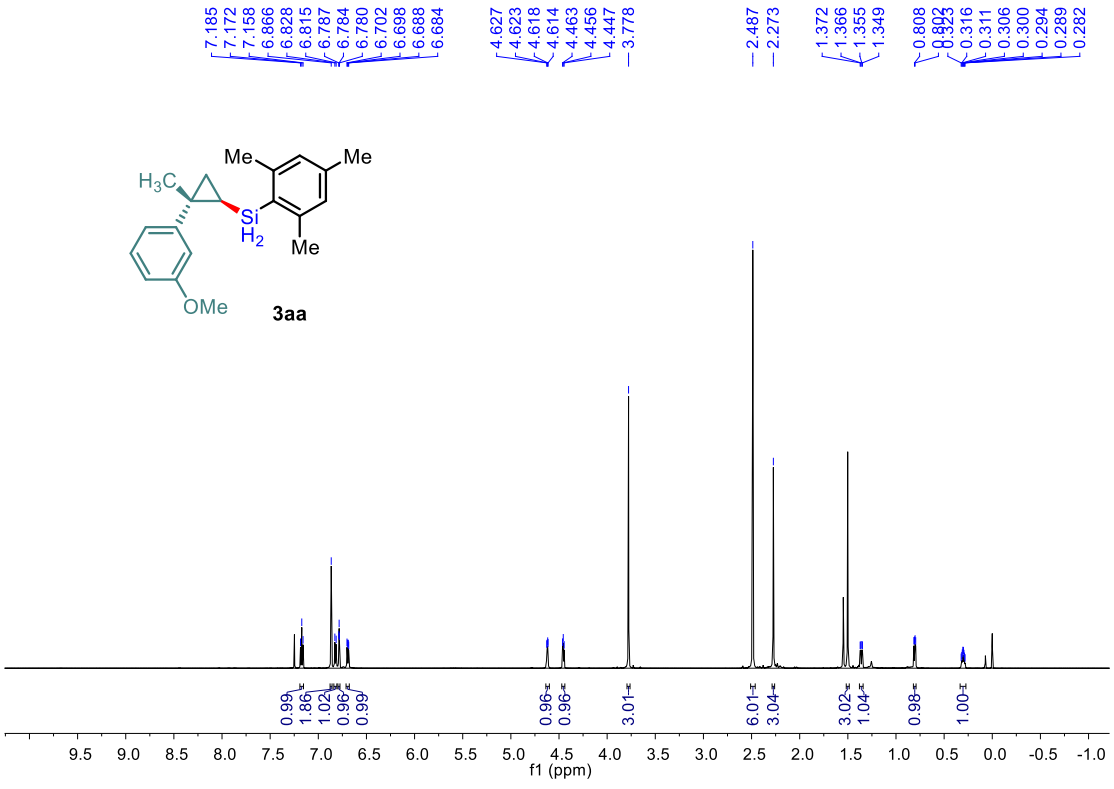
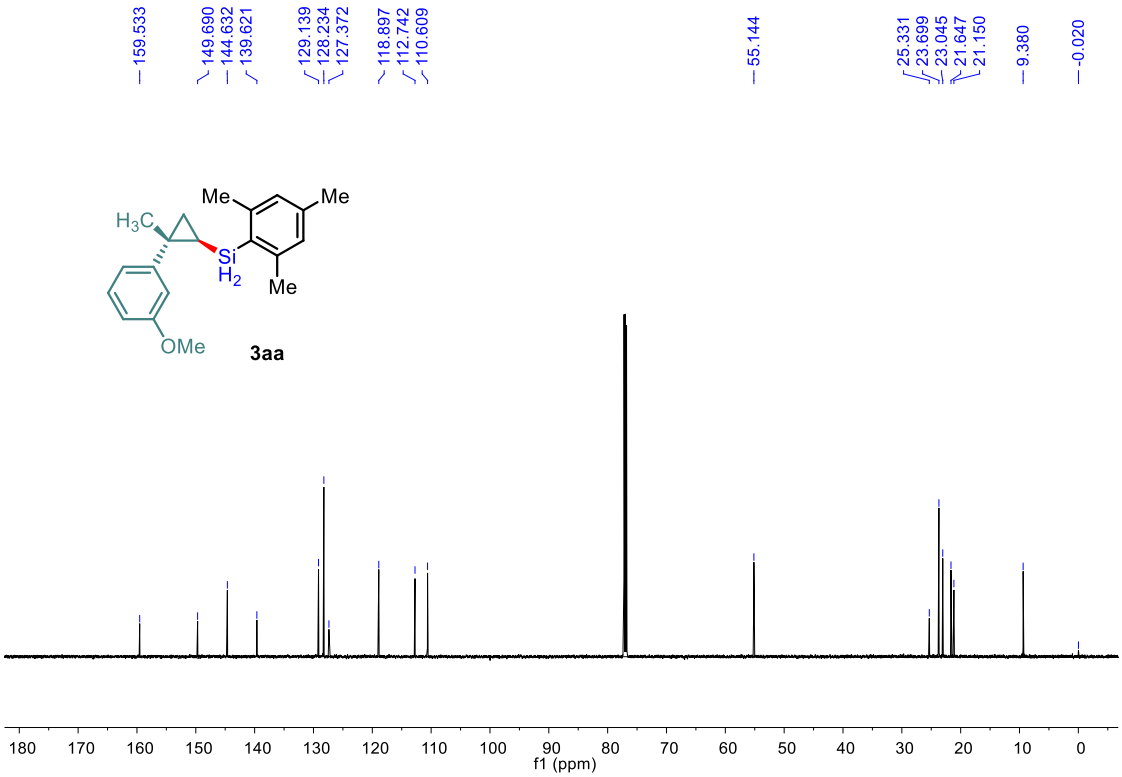
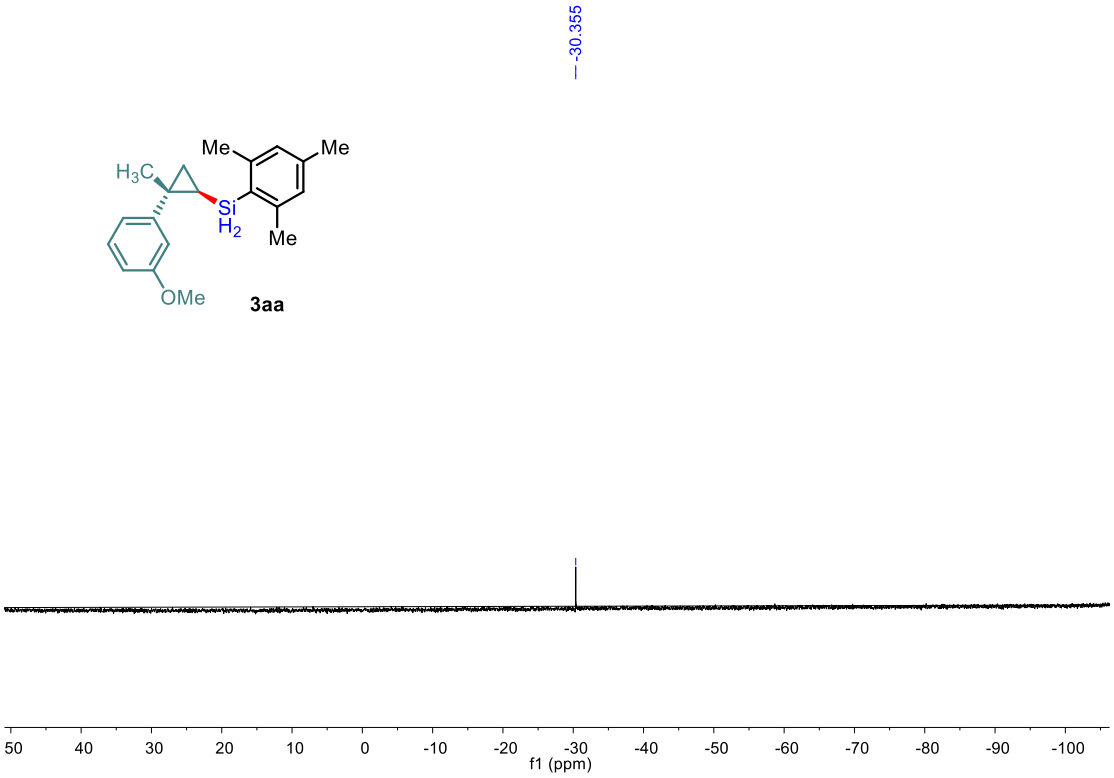
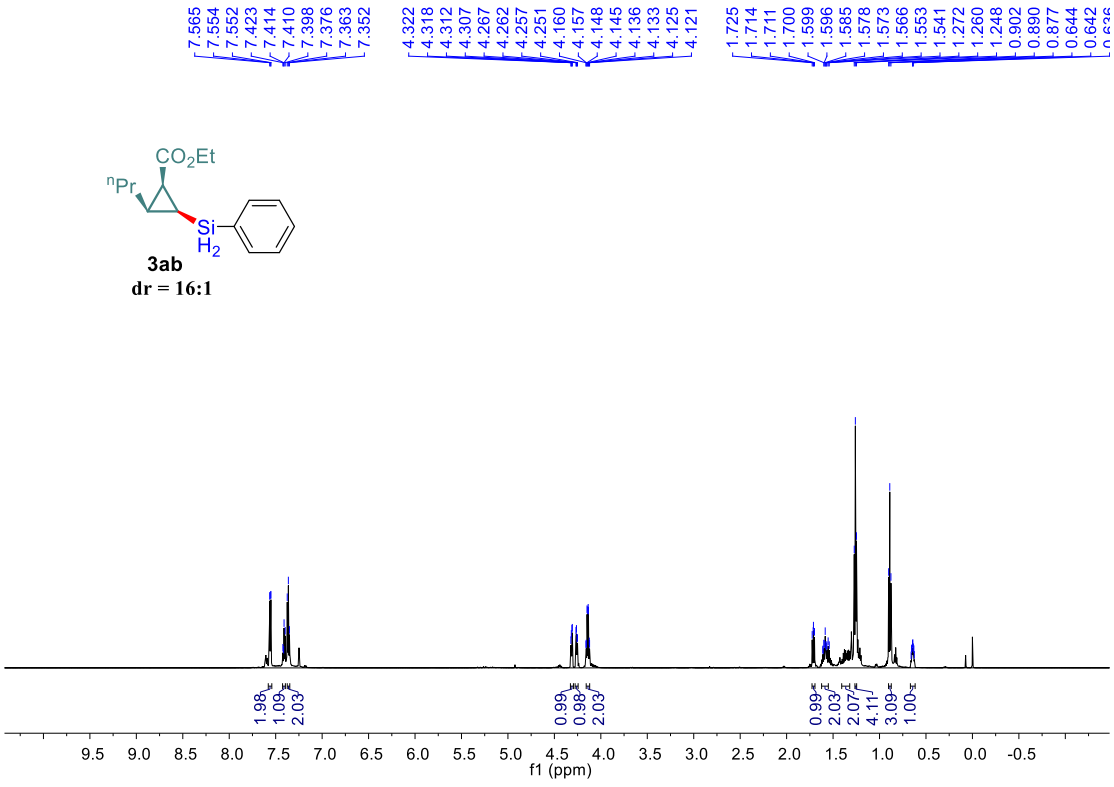
148.552
134.657
134.170
133.662
132.439
129.039
128.801
128.558
118.408
112.241
110.226
54.450
24.699
22.827
19.722
7.665
H3C
Si
H2
Cl
OMe
3z
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

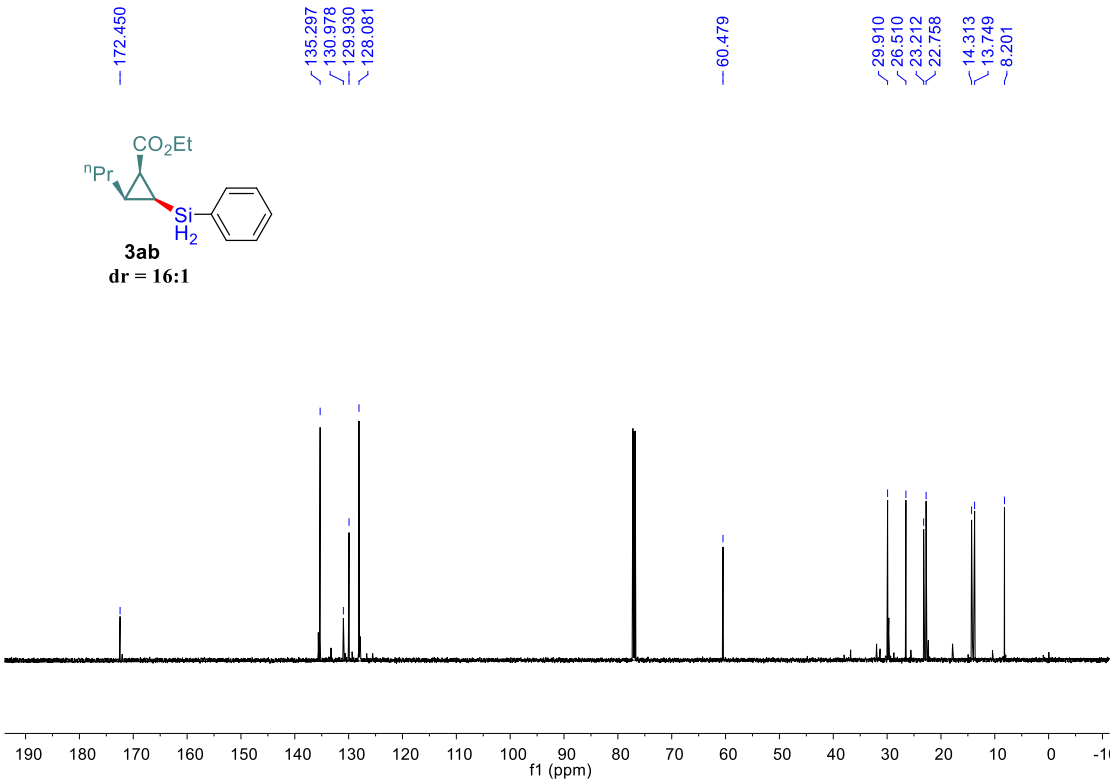

-31.455
H3C
Si
H2
Cl
OMe
3z
10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75
f1 (ppm)

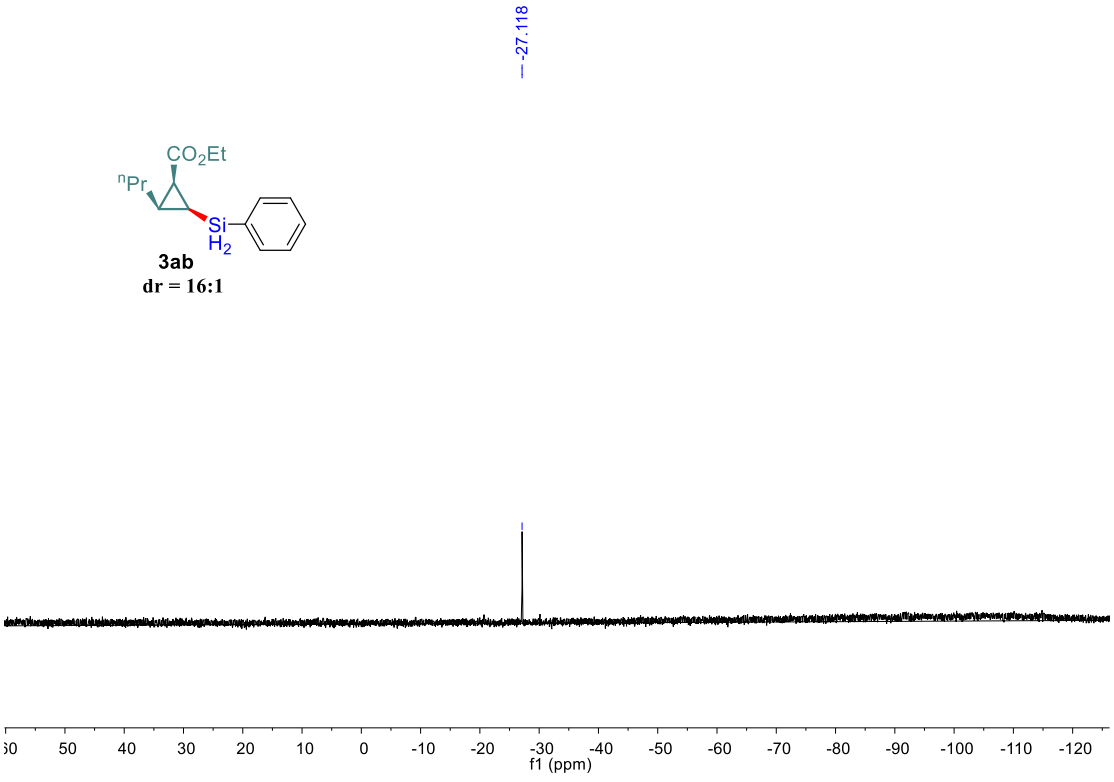

7.185
7.172
7.158
6.866
6.828
6.815
6.787
6.784
6.780
6.702
6.698
6.688
6.684
4.627
4.623
4.618
4.614
4.463
4.456
4.447
3.778
2.487
2.273
1.372
1.366
1.355
1.349
0.808
0.802
0.323
0.316
0.311
0.306
0.300
0.294
0.289
0.282
Me
Me
H3C
Si
H2
Me
OMe
3aa
0.99
1.86
1.02
0.96
0.99
0.96
0.96
3.01
6.01
3.04
3.02
1.04
0.98
1.00
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 -1.0
f1 (ppm)

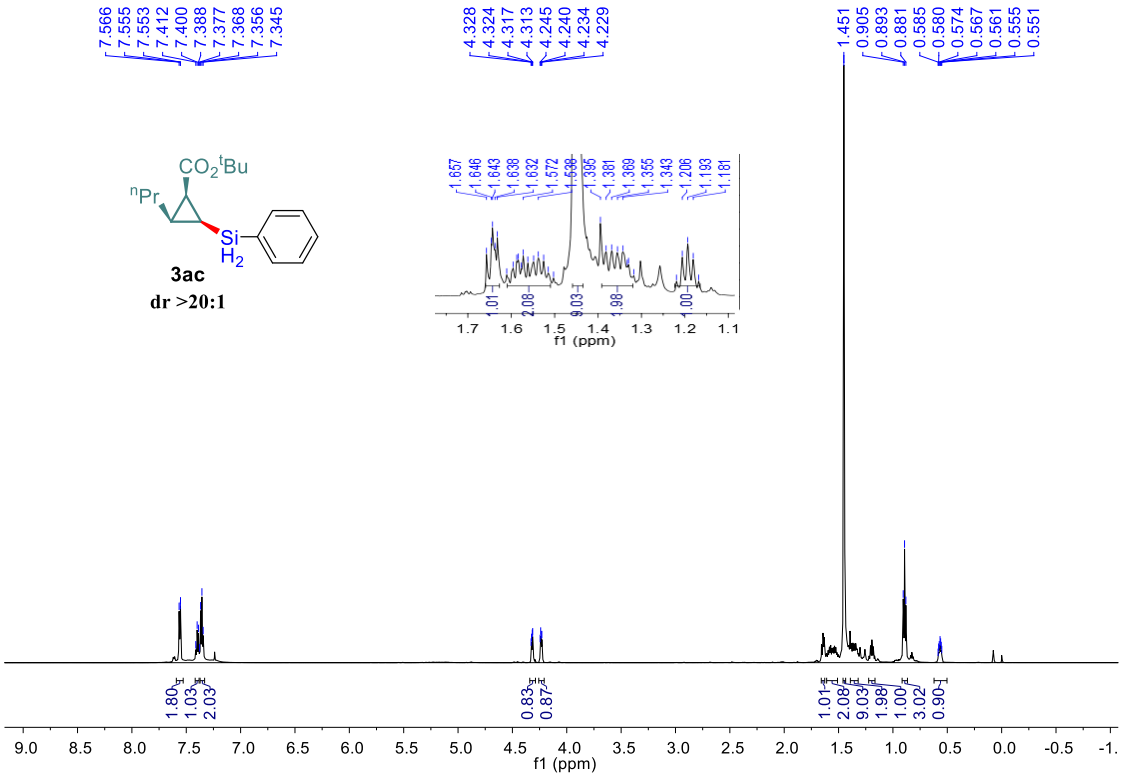

159.533
149.690
144.632
139.621
129.139
128.234
127.372
118.897
112.742
110.609
55.144
25.331
23.699
23.045
21.647
21.150
9.380
-0.020
Me
Me
H3C
Si
H2
Me
OMe
3aa
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-30.355
Me
Me
H3C
Si
H2
Me
OMe
3aa
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)


7.565 7.554 7.552 7.423 7.414 7.410 7.398 7.376 7.363 7.352
4.322 4.318 4.312 4.307 4.267 4.262 4.257 4.251 4.160 4.157 4.148 4.145 4.136 4.133 4.125 4.121
1.725 1.714 1.711 1.700 1.599 1.596 1.585 1.578 1.573 1.566 1.553 1.541 1.272 1.260 1.248 0.902 0.890 0.877 0.644 0.642
CO2Et
nPr
Si
H2
3ab
dr = 16:1
1.98 1.09 2.03
0.99 0.98 2.03
0.99 2.03 2.07 4.11 3.09 1.00
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)


172.450
135.297
130.978
129.930
128.081
60.479
29.910
26.510
23.212
22.758
14.313
13.749
8.201
CO2Et
nPr
Si
H2
3ab
dr = 16:1
f1 (ppm)


-27.118
CO2Et
nPr
Si
H2
3ab
dr = 16:1
f1 (ppm)


7.566
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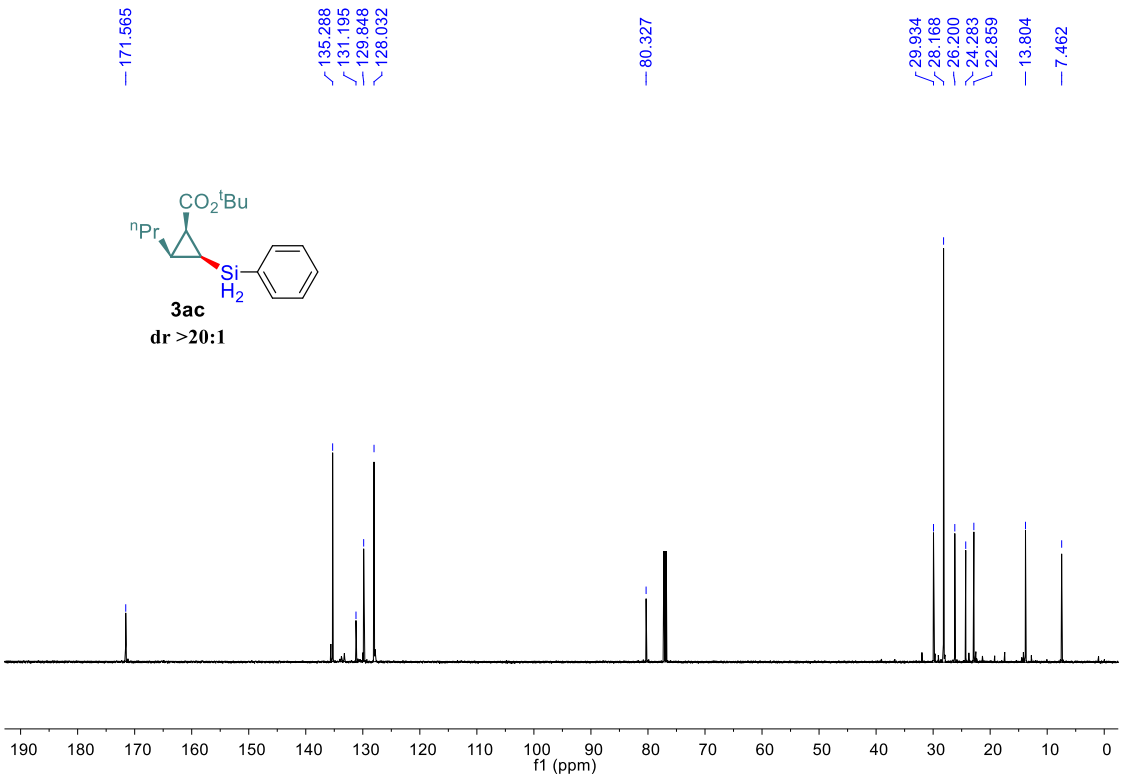
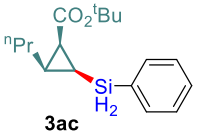
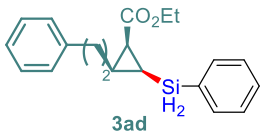
7.553
7.412
7.400
7.388
7.377
7.368
7.356
7.345
4.328
4.324
4.317
4.313
4.245
4.240
4.234
4.229
1.451
0.905
0.893
0.881
0.585
0.580
0.574
0.567
0.561
0.555
0.551
CO2tBu
nPr
Si
H2
3ac
dr >20:1
1.657
1.646
1.643
1.638
1.632
1.572
1.538
1.395
1.381
1.369
1.355
1.343
1.206
1.193
1.181
1.01
2.08
9.03
1.98
1.00
1.7 1.6 1.5 1.4 1.3 1.2 1.1
f1 (ppm)
1.80
1.03
2.03
0.83
0.87
1.01
2.08
9.03
1.98
1.00
3.02
0.90
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 -1.
f1 (ppm)


171.565
135.288
131.195
129.848
128.032
80.327
29.934
28.168
26.200
24.283
22.859
13.804
7.462
CO2tBu
nPr
Si
H2
3ac
dr >20:1
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



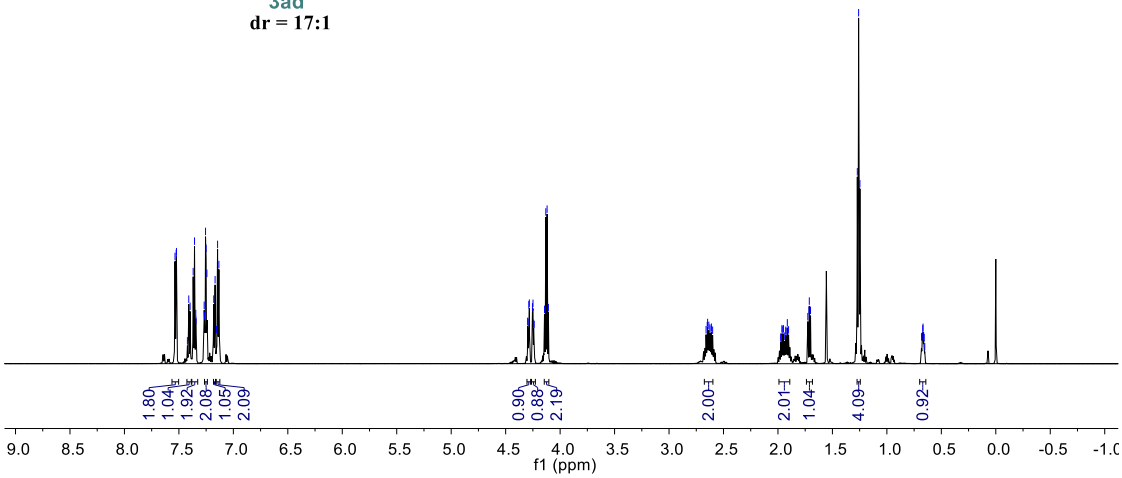
3ac

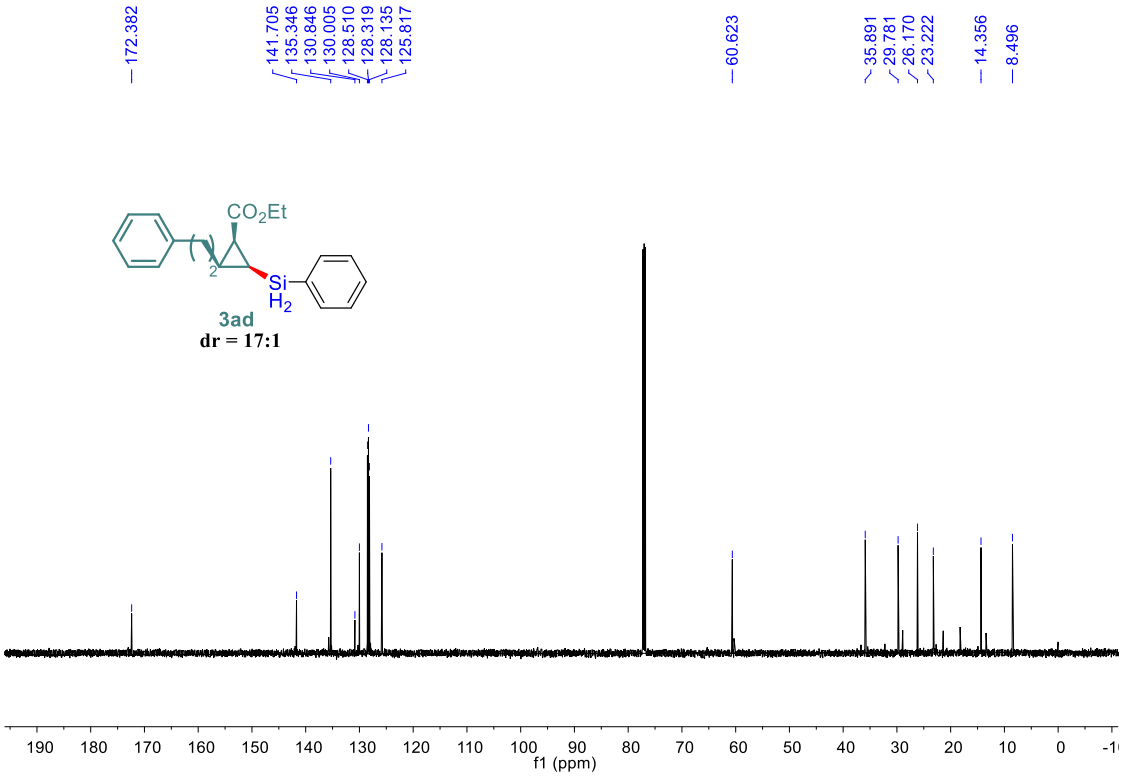
dr >20:1

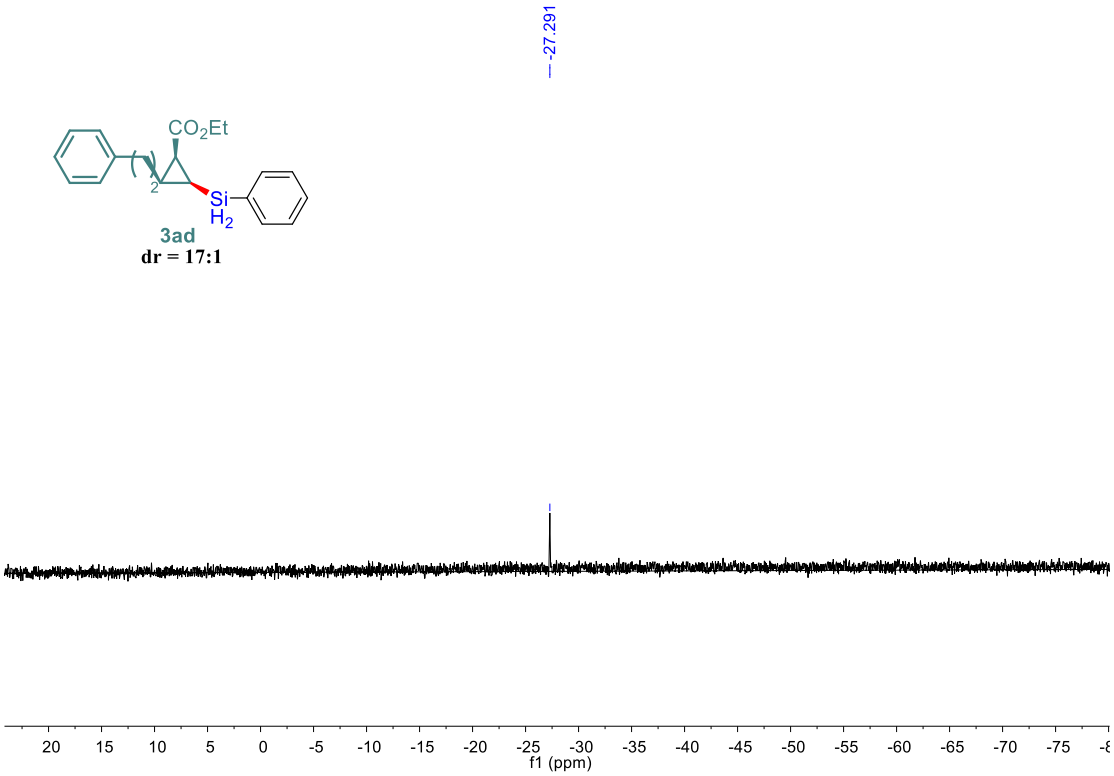


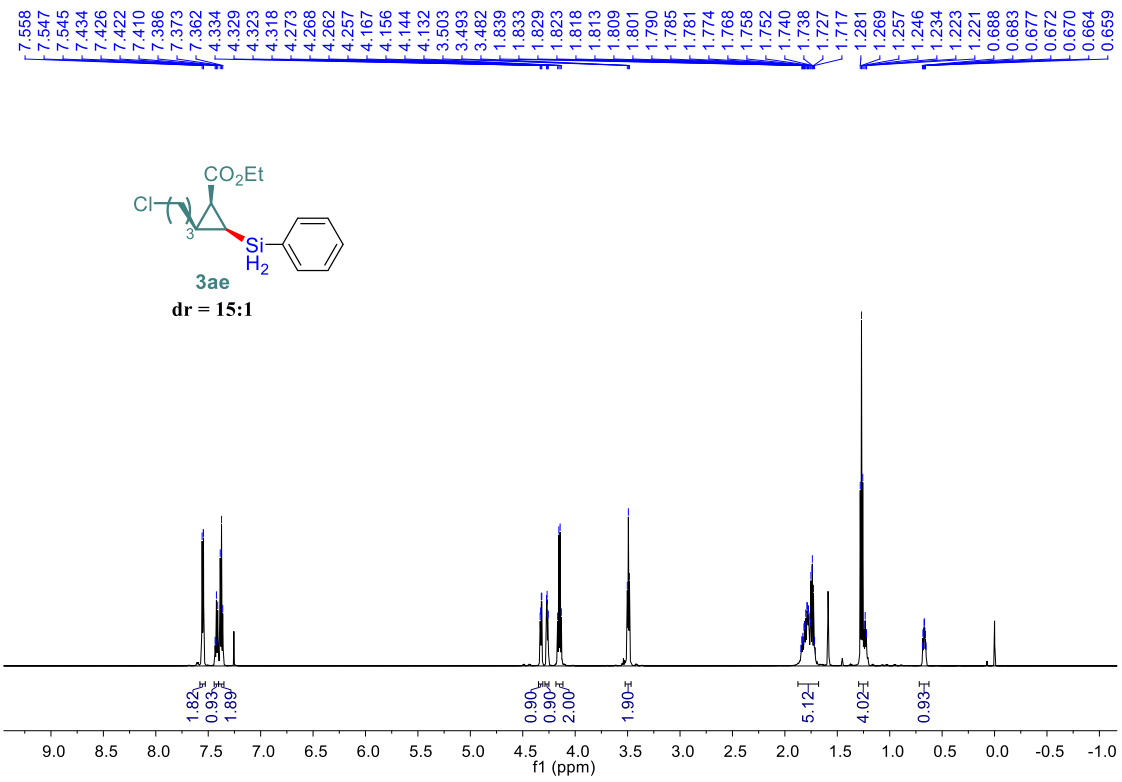
3ad

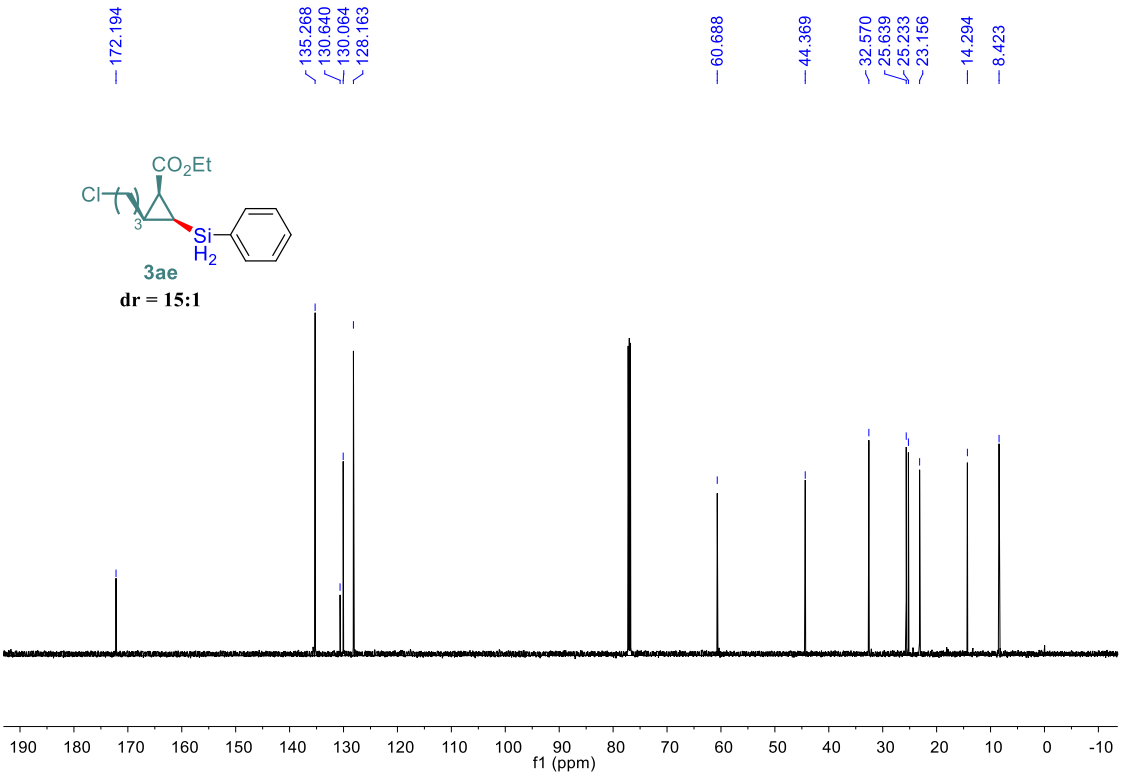
dr = 17:1

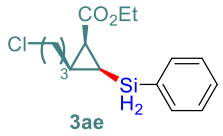



172.382
141.705
135.346
130.846
130.005
128.510
128.319
128.135
125.817
60.623
35.891
29.781
26.170
23.222
14.356
8.496
CO2Et
Si
H2
3ad
dr = 17:1
f1 (ppm)


-27.291
CO2Et
Si
H2
3ad
dr = 17:1
f1 (ppm)

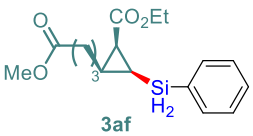

7.558
7.547
7.545
7.434
7.426
7.422
7.410
7.386
7.373
7.362
4.334
4.329
4.323
4.318
4.273
4.268
4.262
4.257
4.167
4.156
4.144
4.132
3.503
3.493
3.482
1.839
1.833
1.829
1.823
1.818
1.813
1.809
1.801
1.790
1.785
1.781
1.774
1.768
1.758
1.752
1.740
1.738
1.727
1.717
1.281
1.269
1.257
1.246
1.234
1.223
1.221
0.688
0.683
0.677
0.672
0.670
0.664
0.659
CO2Et
Cl
3
Si
H2
3ae
dr = 15:1
1.82
0.93
1.89
0.90
0.90
2.00
1.90
5.12
4.02
0.93
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 -1.0
f1 (ppm)


172.194
135.268
130.640
130.064
128.163
60.688
44.369
32.570
25.639
25.233
23.156
14.294
8.423
CO2Et
Cl
3
Si
H2
3ae
dr = 15:1
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



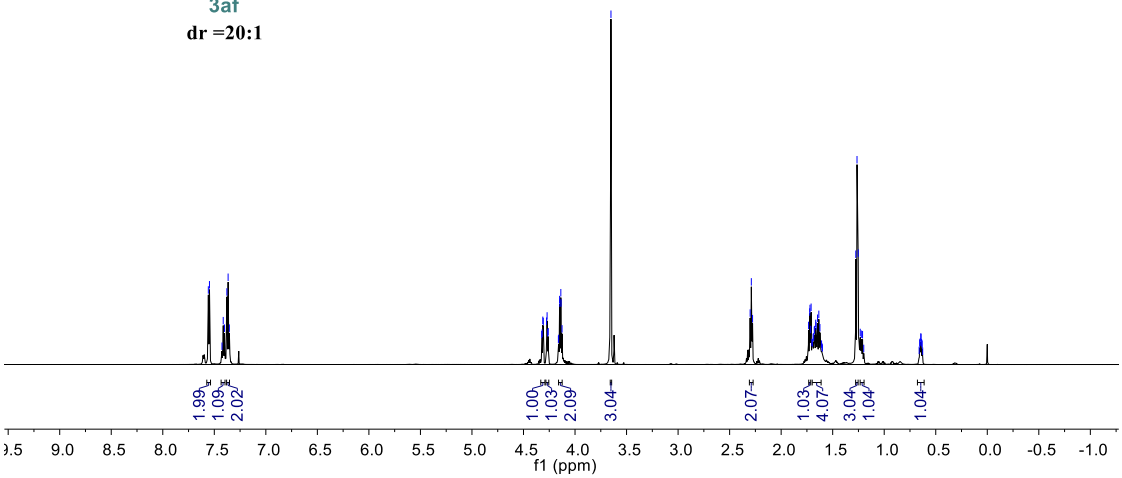
3ae

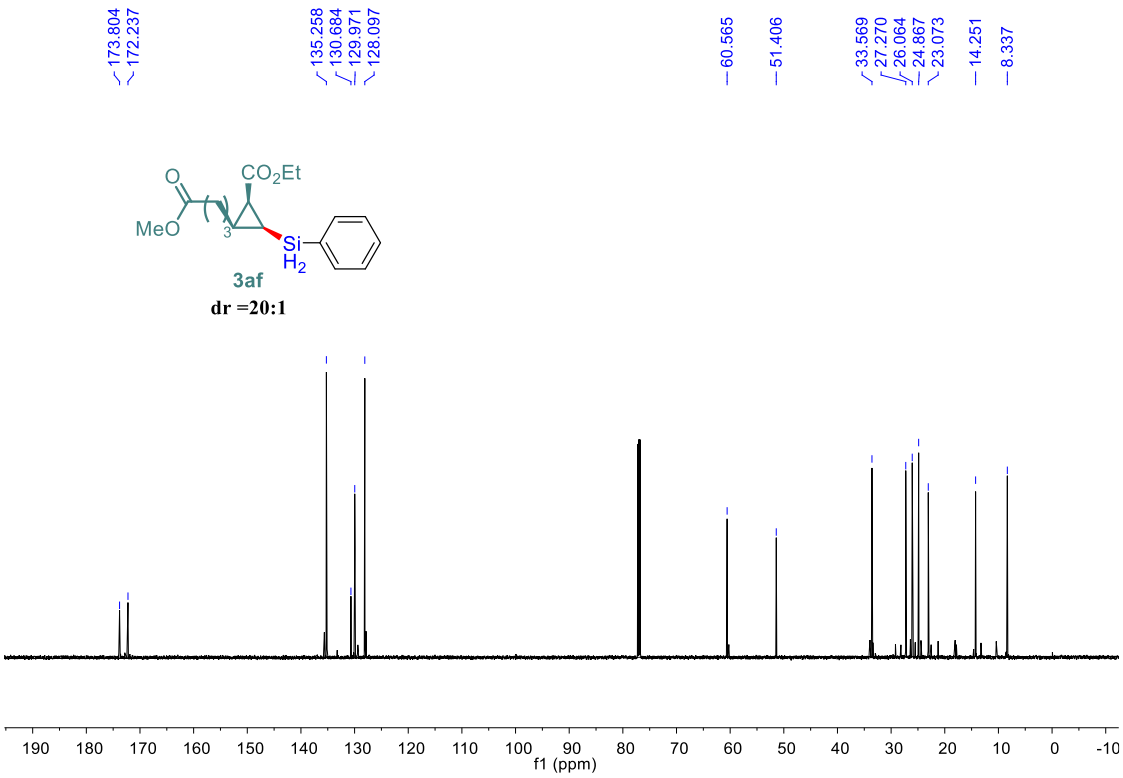
dr = 15:1

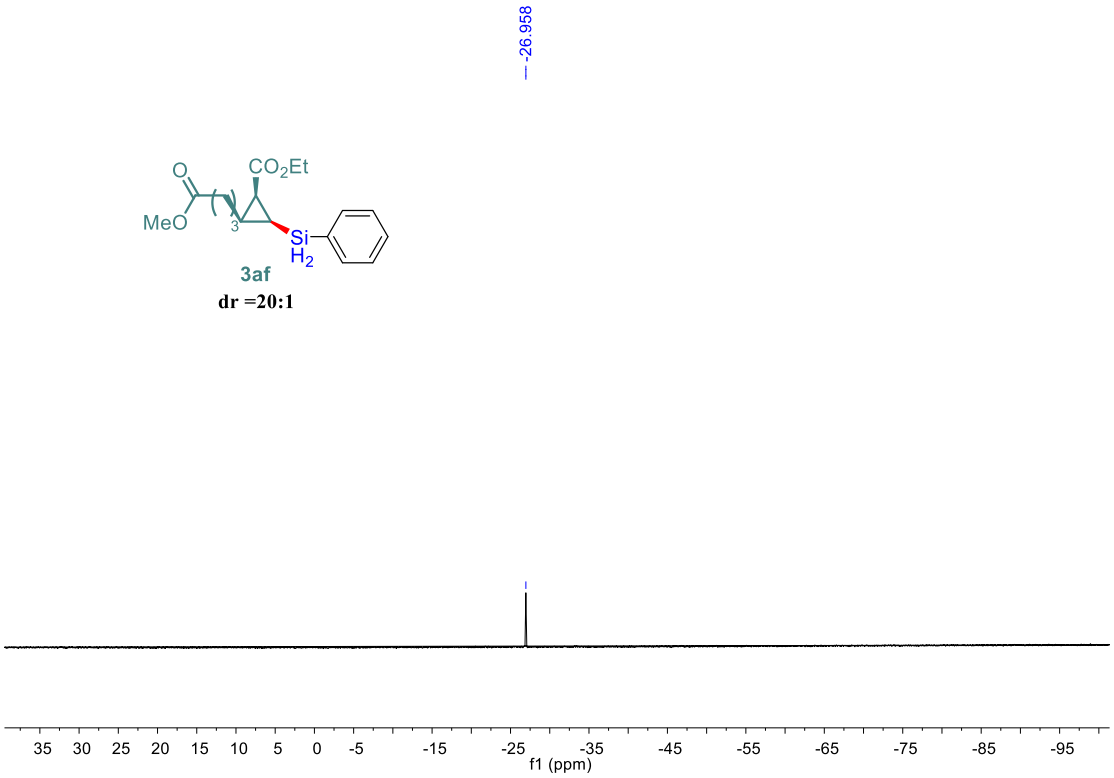


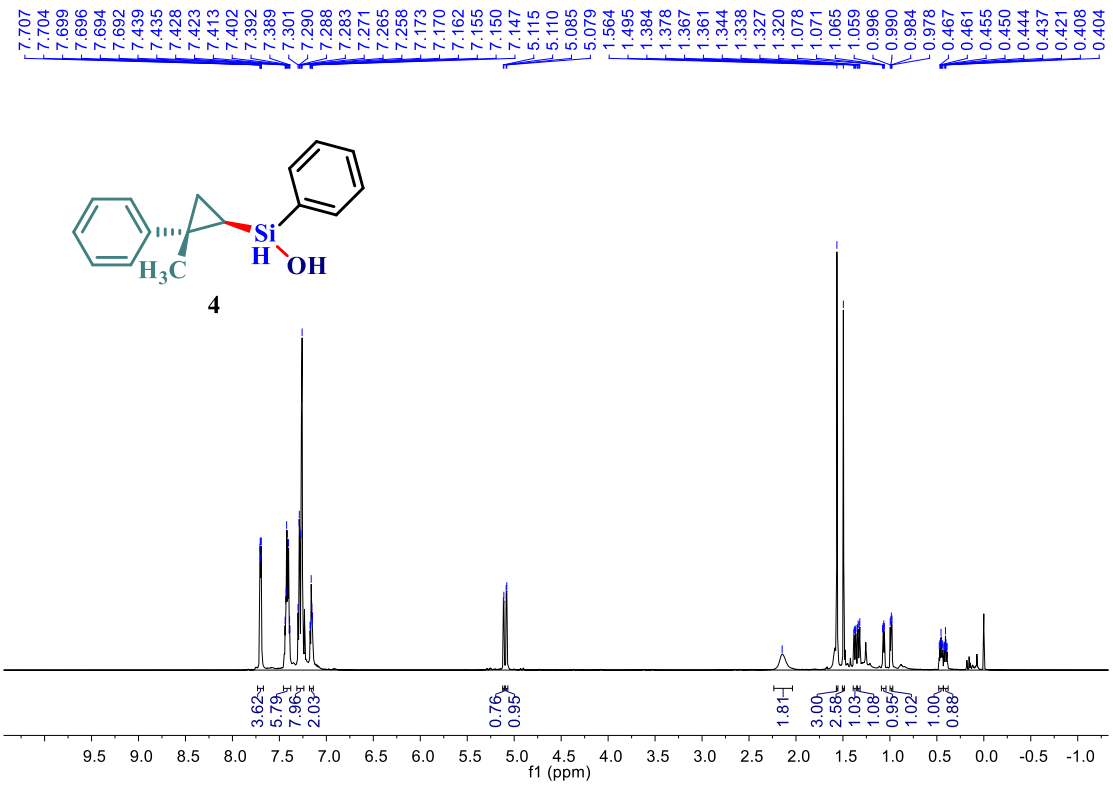
3af

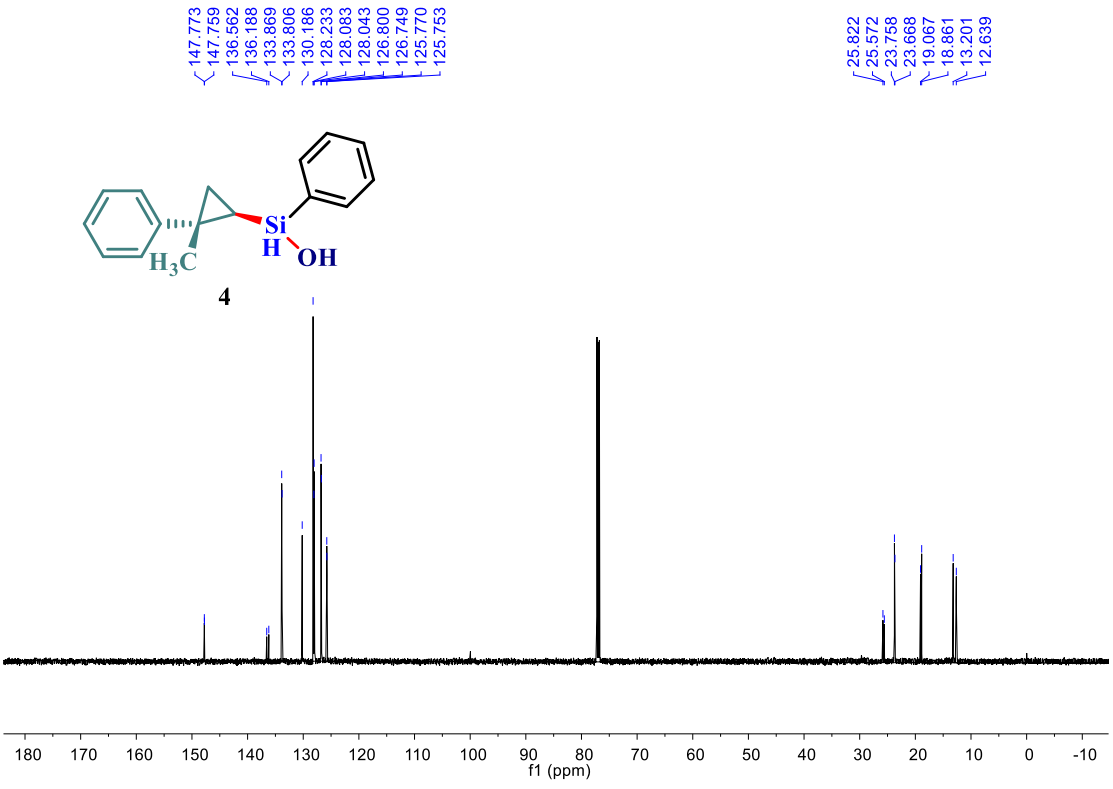
dr =20:1

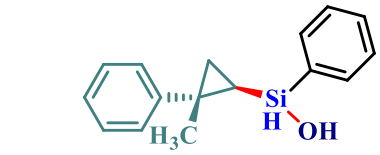



173.804
172.237
135.258
130.684
129.971
128.097
60.565
51.406
33.569
27.270
26.064
24.867
23.073
14.251
8.337
O
CO2Et
MeO
3
Si
H2
3af
dr =20:1
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-26.958
O
CO2Et
MeO
3
Si
H2
3af
dr =20:1
35 30 25 20 15 10 5 0 -5 -15 -25 -35 -45 -55 -65 -75 -85 -95
f1 (ppm)


7.707
7.704
7.699
7.696
7.694
7.692
7.439
7.435
7.428
7.423
7.413
7.402
7.392
7.389
7.301
7.290
7.288
7.283
7.271
7.265
7.258
7.173
7.170
7.162
7.155
7.150
7.147
5.115
5.110
5.085
5.079
1.564
1.495
1.384
1.378
1.367
1.361
1.344
1.338
1.327
1.320
1.078
1.071
1.065
1.059
0.996
0.990
0.984
0.978
0.467
0.461
0.455
0.450
0.444
0.437
0.421
0.408
0.404
Si
H
OH
H3C
4
3.62
5.79
7.96
2.03
0.76
0.95
1.81
3.00
2.58
1.03
1.08
0.95
1.02
1.00
0.88
f1 (ppm)

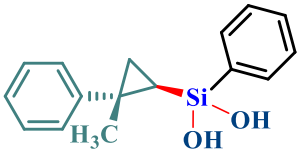

147.773
147.759
136.562
136.188
133.869
133.806
130.186
128.233
128.083
128.043
126.800
126.749
125.770
125.753
25.822
25.572
23.758
23.668
19.067
18.861
13.201
12.639
Si
H
OH
H3C
4
f1 (ppm)


Si
H
OH
H3C

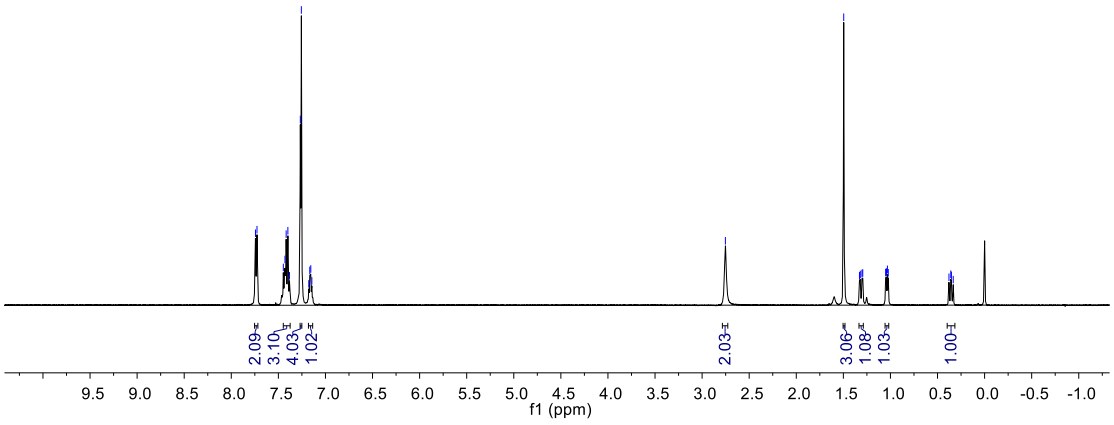
4

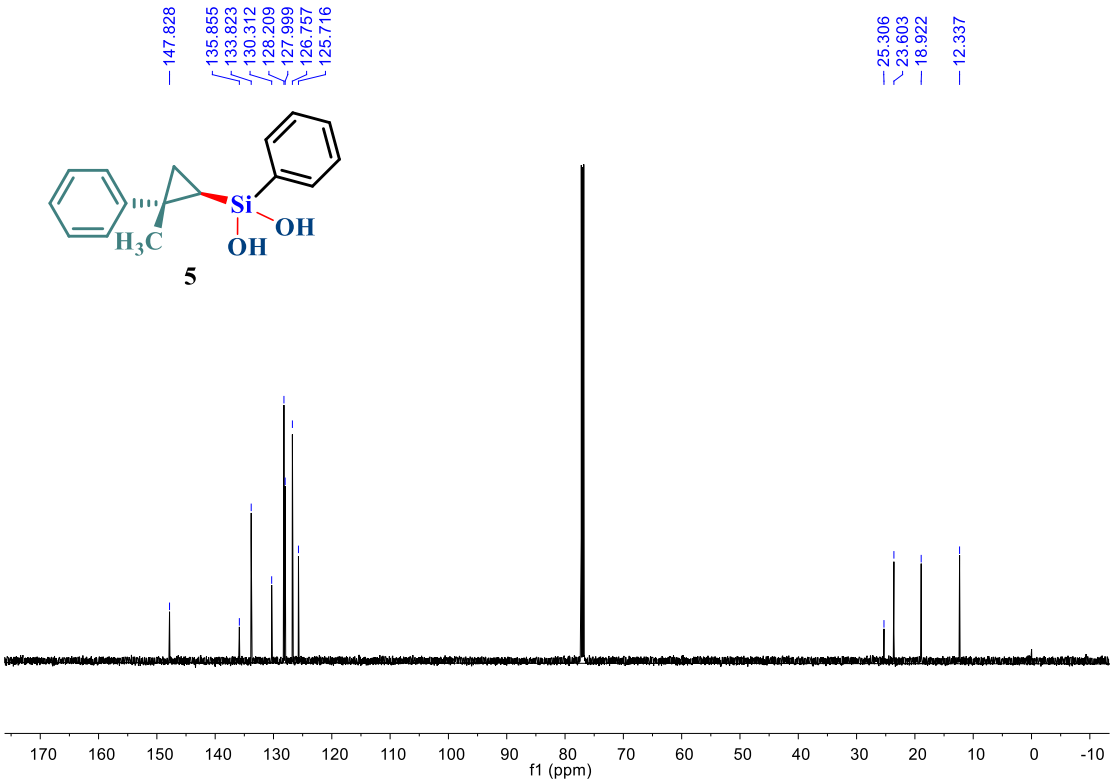
-12.556
-13.081
50 45 40 35 30 25 20 15 10 5 0 -5 -15 -25 -35 -45 -55 -65 -75
f1 (ppm)

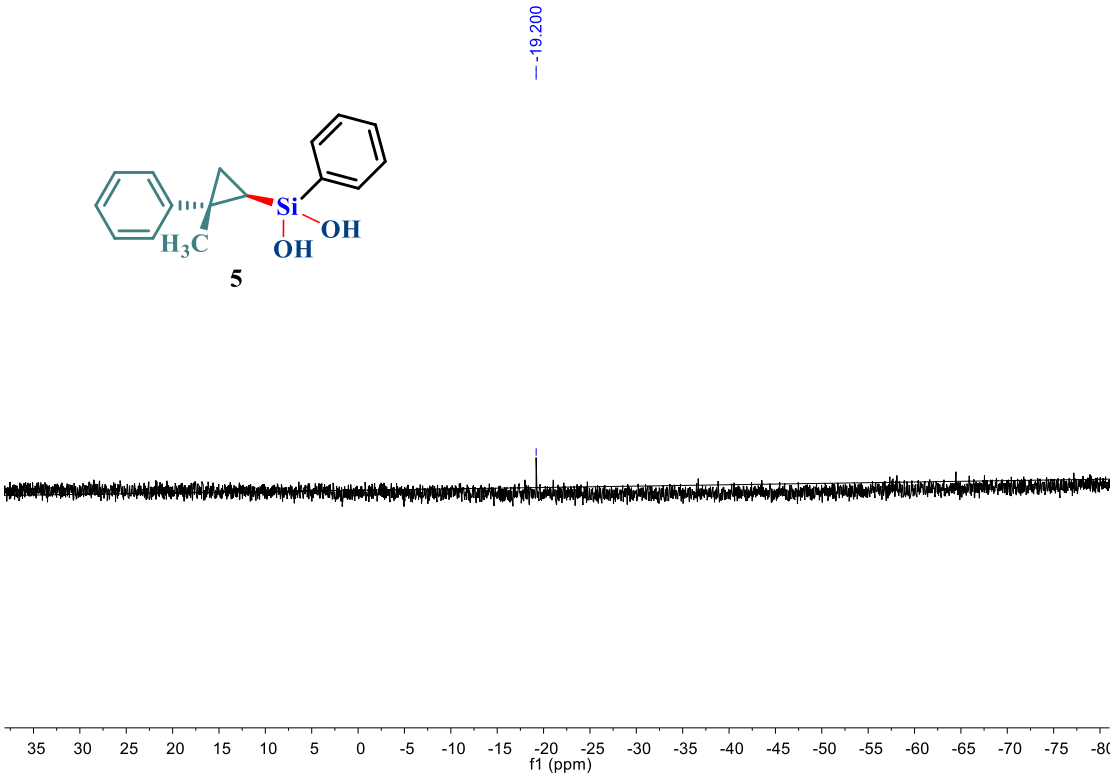

7.743
7.727
7.447
7.430
7.417
7.399
7.382
7.267
7.256
7.177
7.167
7.156
7.144
2.753
1.496
1.329
1.320
1.303
1.294
1.051
1.042
1.032
1.023
0.378
0.359
0.353
0.333

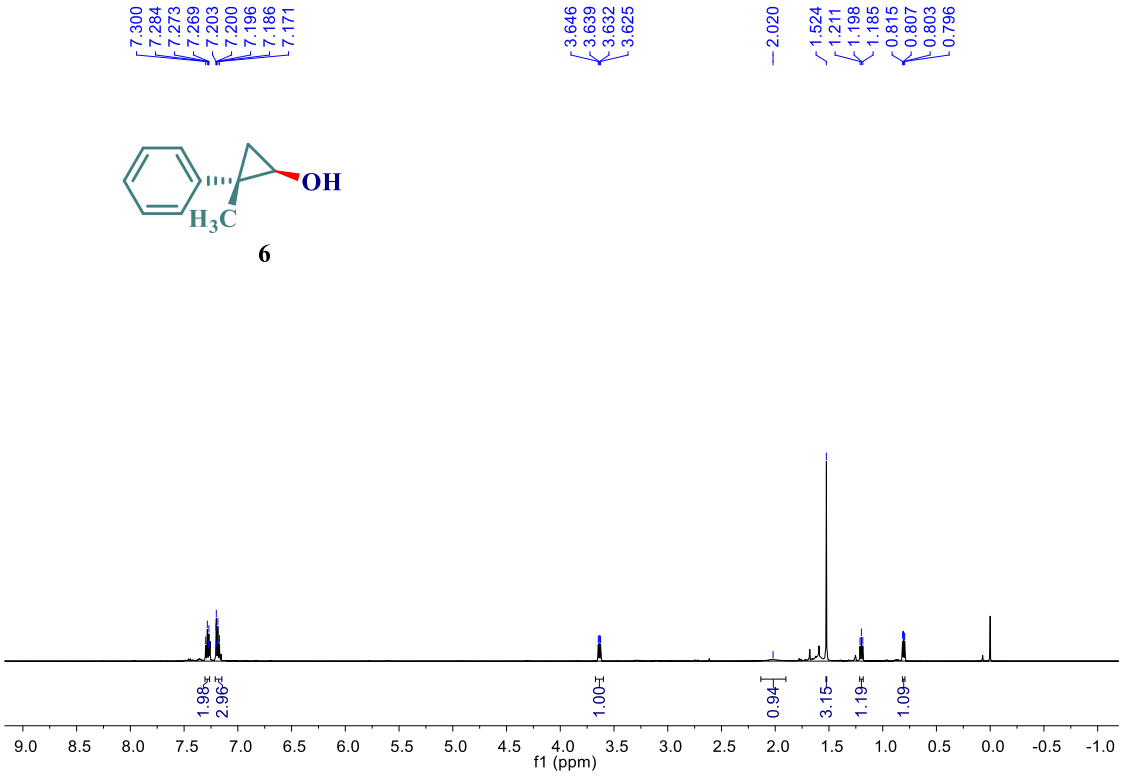

Si
OH
OH
H3C

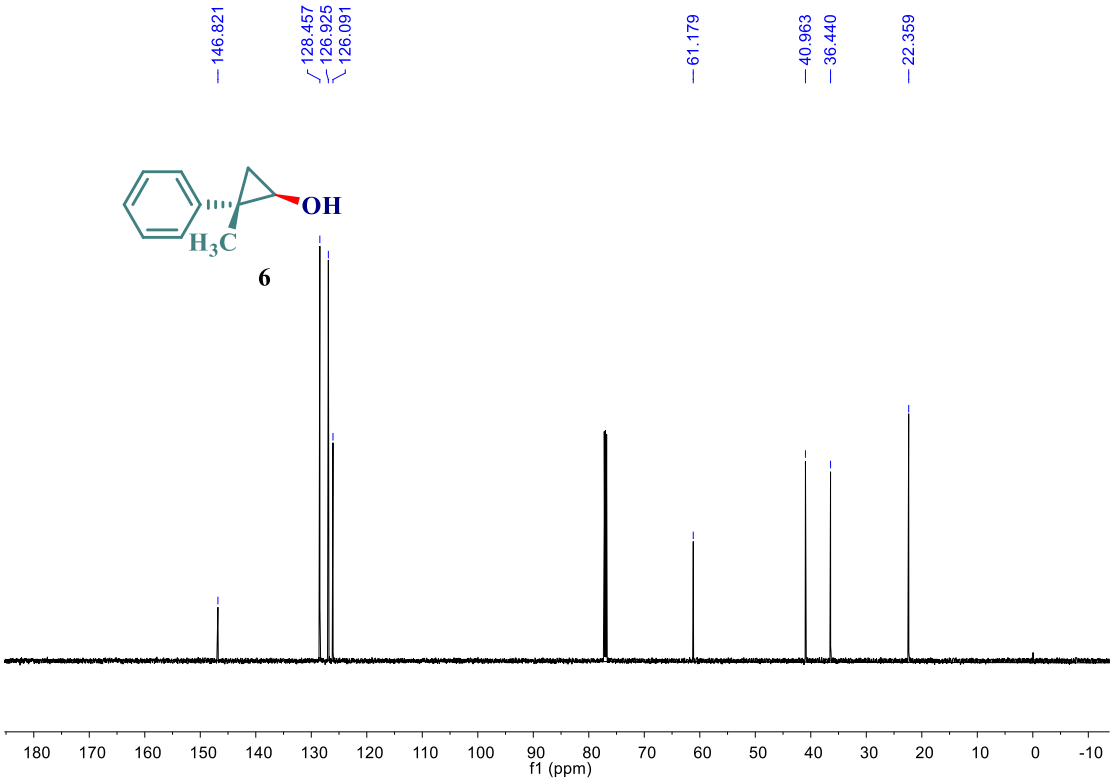
5

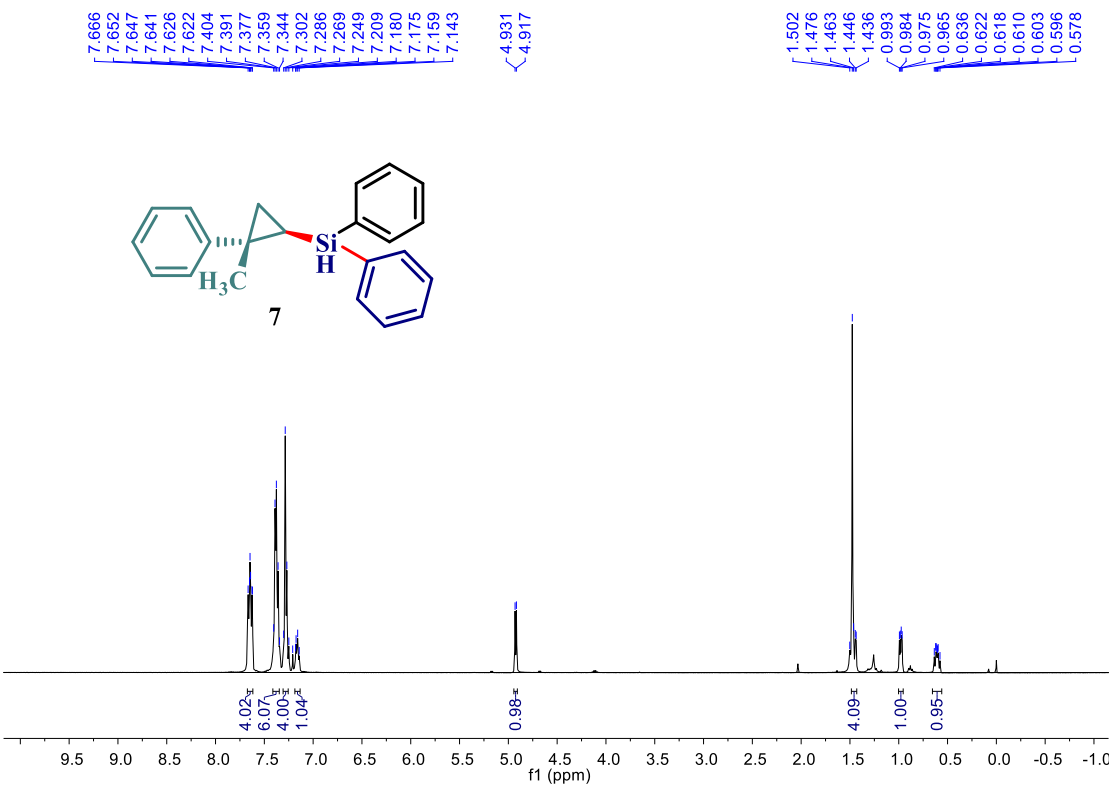

2.09
3.10
4.03
1.02
2.03
3.06
1.08
1.03
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

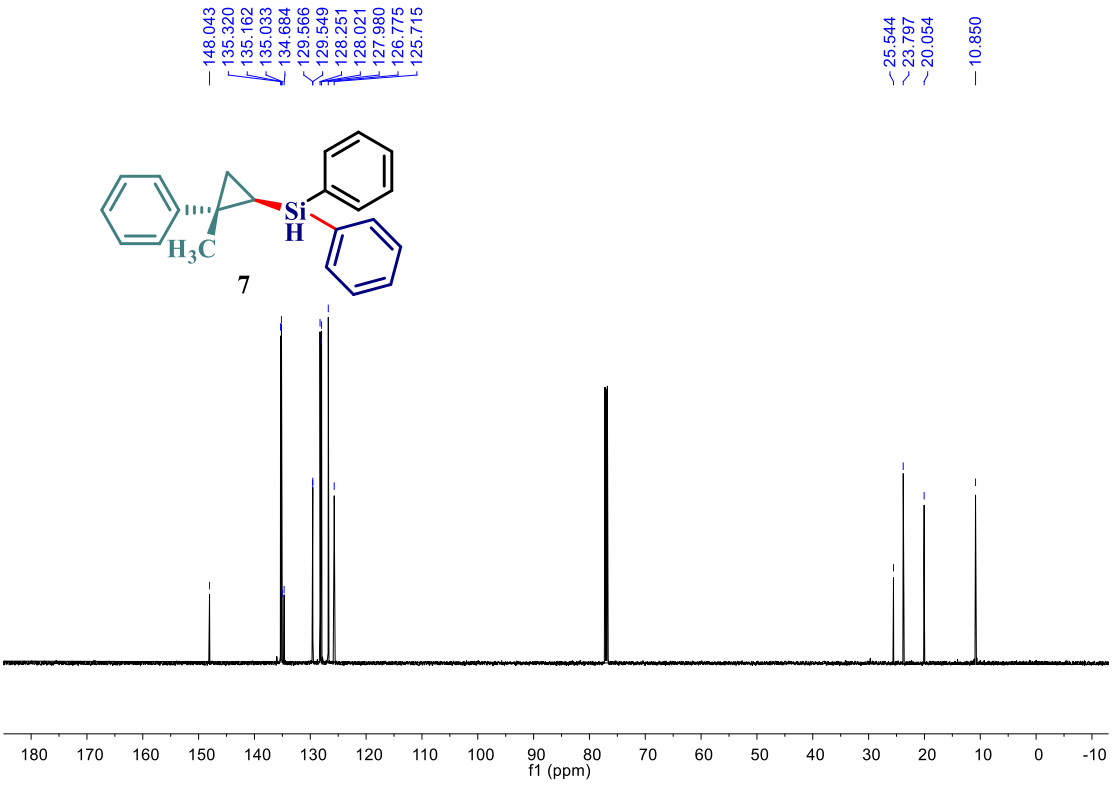

147.828
135.855
133.823
130.312
128.209
127.999
126.757
125.716
25.306
23.603
18.922
12.337
Si
OH
OH
H3C
5
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

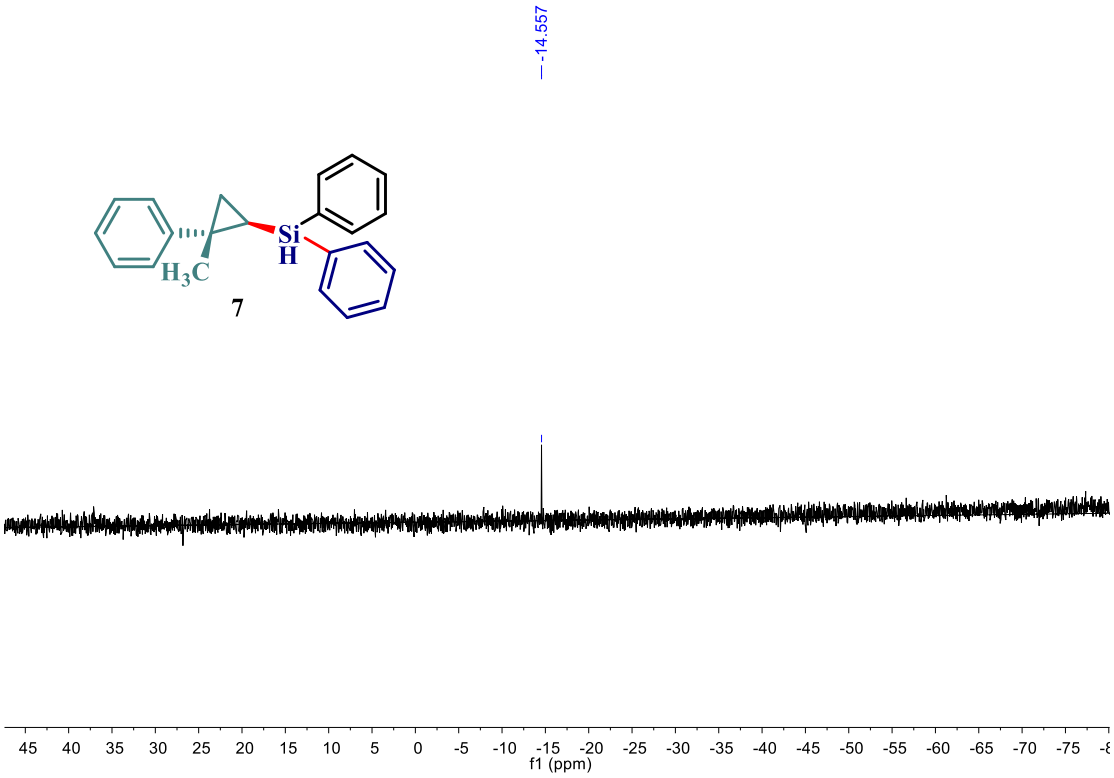

-19.200
Si
OH
OH
H3C
5
35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80
f1 (ppm)

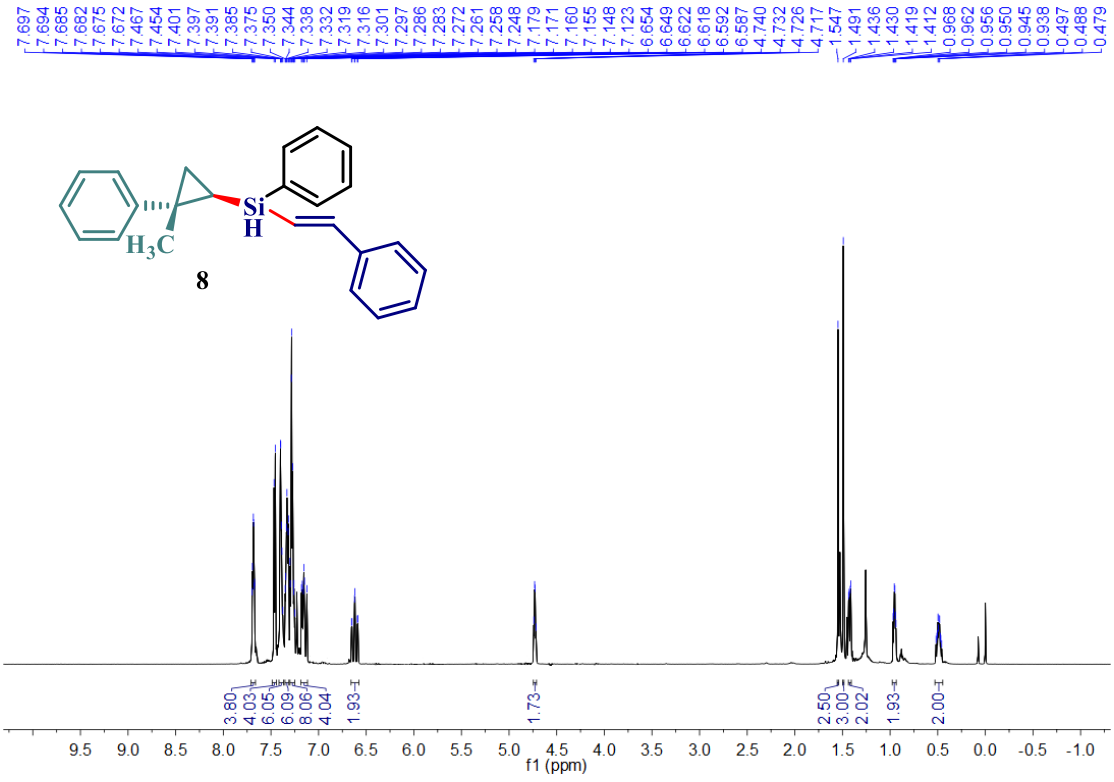

7.300
7.284
7.273
7.269
7.203
7.200
7.196
7.186
7.171
3.646
3.639
3.632
3.625
2.020
1.524
1.211
1.198
1.185
0.815
0.807
0.803
0.796
OH
H3C
6
1.98
2.96
1.00
0.94
3.15
1.19
1.09
f1 (ppm)

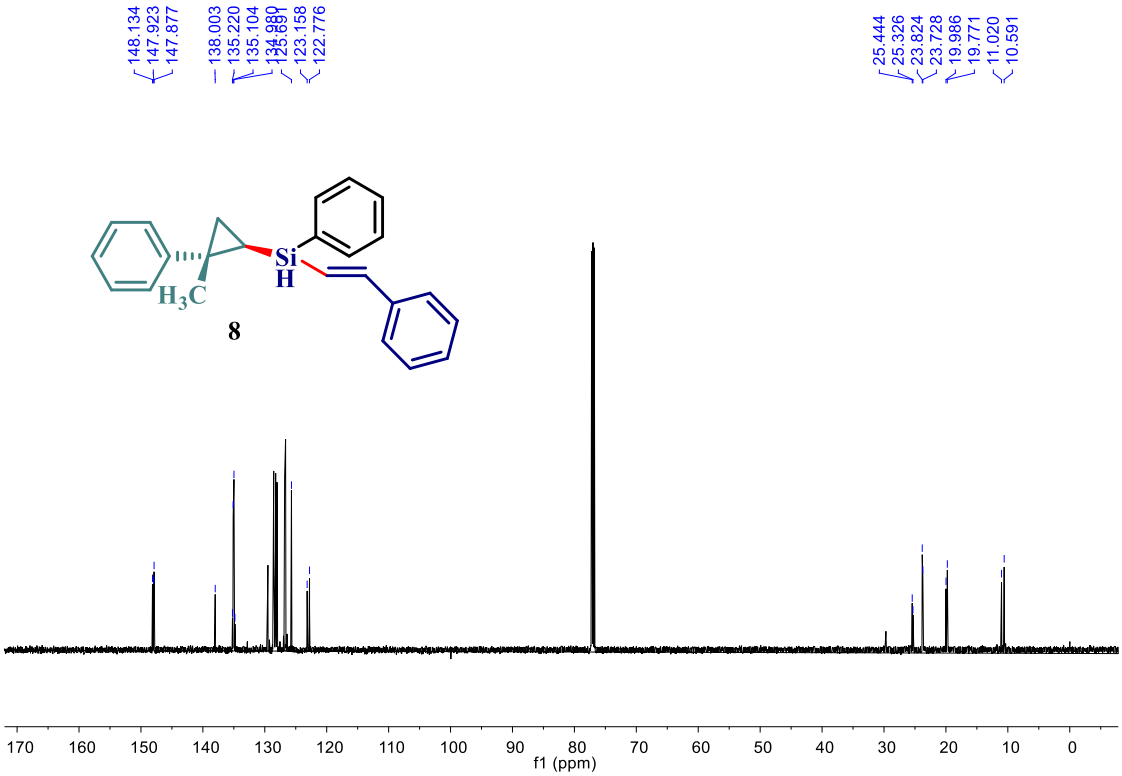

146.821
128.457
126.925
126.091
61.179
40.963
36.440
22.359
OH
H3C
6
f1 (ppm)

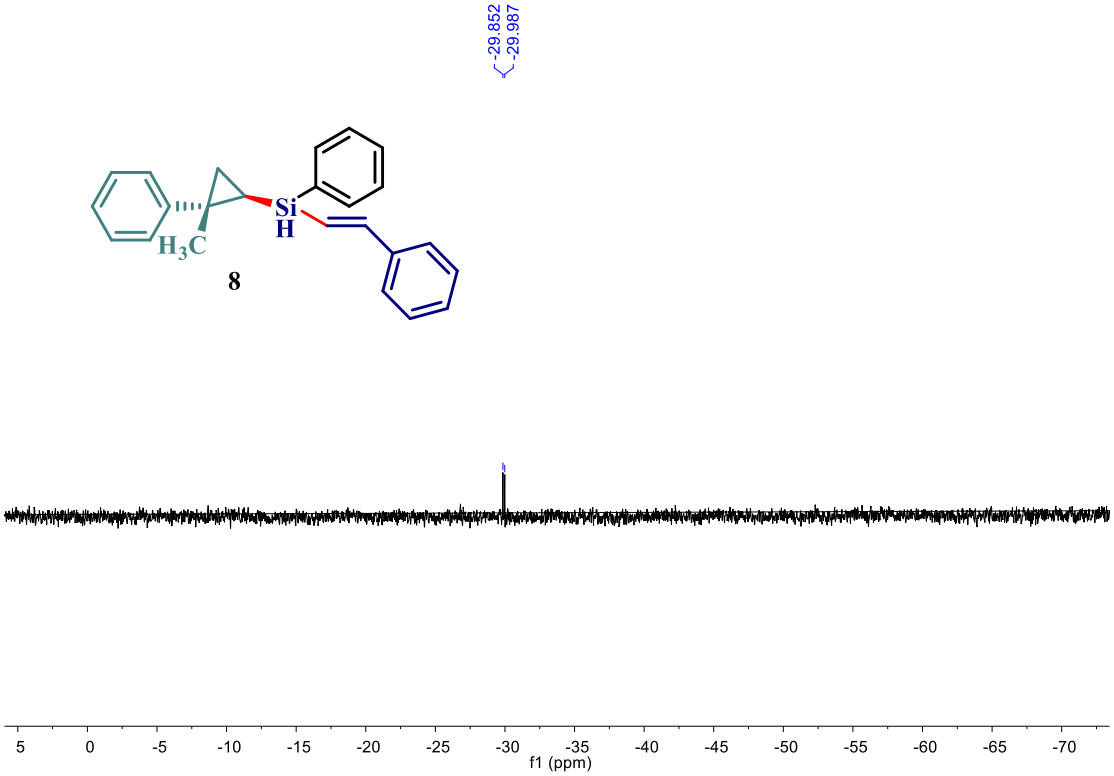

7.666
7.652
7.647
7.641
7.626
7.622
7.404
7.391
7.377
7.359
7.344
7.302
7.286
7.269
7.249
7.209
7.180
7.175
7.159
7.143
4.931
4.917
1.502
1.476
1.463
1.446
1.436
0.993
0.984
0.975
0.965
0.636
0.622
0.618
0.610
0.603
0.596
0.578
Si
H
H3C
7
4.02
6.07
4.00
1.04
0.98
4.09
1.00
0.95
f1 (ppm)


148.043
135.320
135.162
135.033
134.684
129.566
129.549
128.251
128.021
127.980
126.775
125.715
25.544
23.797
20.054
10.850
Si
H
H3C
7
f1 (ppm)


-14.557
Si
H
H3C
7
45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75
f1 (ppm)


7.697
7.694
7.685
7.682
7.675
7.672
7.467
7.454
7.401
7.397
7.391
7.385
7.375
7.350
7.344
7.338
7.332
7.319
7.316
7.301
7.297
7.286
7.283
7.272
7.261
7.258
7.248
7.179
7.171
7.160
7.155
7.148
7.123
6.654
6.649
6.622
6.618
6.592
6.587
4.740
4.732
4.726
4.717
1.547
1.491
1.436
1.430
1.419
1.412
0.968
0.962
0.956
0.950
0.945
0.938
0.497
0.488
0.479
Si
H
H3C
8
3.80
4.03
6.05
6.09
8.06
4.04
1.93
1.73
2.50
3.00
2.02
1.93
2.00
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 -1.0
f1 (ppm)


148.134
147.923
147.877
138.003
135.220
135.104
134.880
134.691
123.881
123.158
122.776
25.444
25.326
23.824
23.728
19.986
19.771
11.020
10.591
Si
H
H3C
8
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-29.852
-29.987
Si
H
H3C
8
5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70
f1 (ppm)