Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Cobalt- and Iron-Catalyzed Regiodivergent Alkene Hydrosilylations

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Supporting Information

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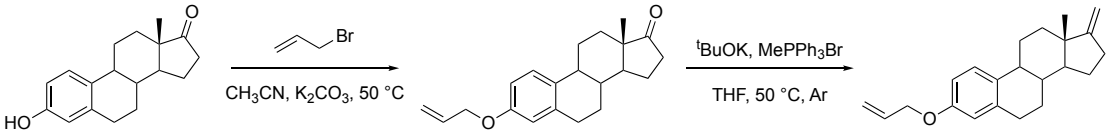
1. General Information

^{1}H NMR and ^{13}C NMR were recorded on a Jeol 400 MHz spectrometer (^{1}H NMR: 400MHz, ^{31}P NMR: 162 MHz, ^{13}C NMR: 100MHz). The chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz respectively. ^{1}H NMR spectra were referenced to the solvent residual peak ($CDCl_3$, δ 7.26 ppm) and ^{13}C{1H} NMR spectra were referenced to the solvent residual peak ($CDCl_3$, δ 77.0 ppm). IR was recorded on Nicolet iS5 FTIR spectrometer. High Resolution mass spectra were obtained using Thermo Scientific Exactive mass spectrometer, Santa Clara, CA with HESI electrospray with 50% acetonitrile water containing either 0.1% Formic acid at infusion rate of 5 μL/min. All solvents were purified and dried according to the standard procedures unless otherwise noted. Commercially substrates was purchased and used directly. Substrates 5-vinylbenzo[*d*][1,3]dioxole (**4n**),[S1] 1-(prop-1-en-2-yl)-3-vinylbenzene (**4u**),[S2] and (S)-4,8-dimethylnona-1,7-diene (**4w**)[S3] were prepared according to the literature procedures.

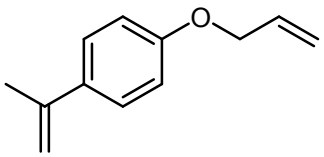
2. General procedure for the synthesis of substrates 4y-4aa (**4aa** as an example)



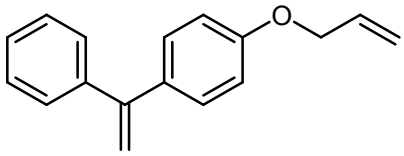
11 **12** **4aa**

To a solution of the estrone **11** (1g, 3.7 mmol) in CH_3CN (10 mL) were added K_2CO_3 (1g, 7.4 mmol) and allyl bromide (640μL, 7.4 mmol). The suspension was stirred at 50 ºC until the starting material was fully consumed, as indicated by TLC (about 3 h). After cooling to r.t., the mixture was filtered through a short pad of Celite, which was subsequently washed with EtOAc (50 mL). After evaporation of the organic solvent, the crude product **12** was obtained, which can be used in the next step without further purification.

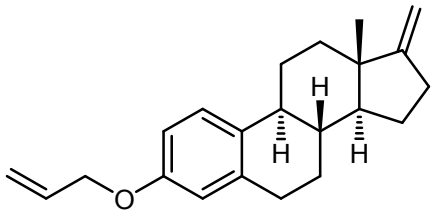
To a suspension of ^{t}BuOK (628 mg, 5.6 mmol, 1.5 equiv.) in anhydrous THF (15 mL) was added $MePPh_3Br$ (2.0 g, 5.6 mmol, 1.5 equiv.) under argon atmosphere. The suspension was stirred at room temperature for 1 h, and then the crude product **12** was added. The resulting mixture was warmed to 50 ºC and stirred for 5 h. After cooling to r.t., the mixture was filtered through a short pad of silica gel, which was subsequently washed with diethyl ether (200 mL). After evaporation of the organic solvent, the residue was purified by silica gel column chromatography (hexane/EtOAc 50/1 followed by hexane/EtOAc 20/1) to provide 1.05 g (92% yield) of **4aa** as a colorless oil.



1-(Allyloxy)-4-(prop-1-en-2-yl)benzene (**4y**): colorless oil, 1.67 g (starting material 10 mmol), 96% yield; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.45-7.42 (d, *J* = 8.8 Hz, 2H), 6.91-6.89 (d, *J* = 9.2 Hz, 2H), 6.13-6.04 (m, 1H), 5.47-5.41 (m, 1H), 5.33-5.30 (m, 2H), 5.03-5.01 (m, 1H), 4.58-4.55 (m, 2H), 2.16-2.15 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 158.0, 142.5, 133.8, 133.2, 126.5, 117.6, 114.3, 110.7, 68.7, 21.9; IR (neat): 3083, 1971, 1604, 1509, 1241, 1179, 1022, 996, 923, 886, 830 cm^{-1}; HRMS: calcd. for $C_{12}H_{14}O$ $[M+H]^+$ 175.1117, found: 175.1116.

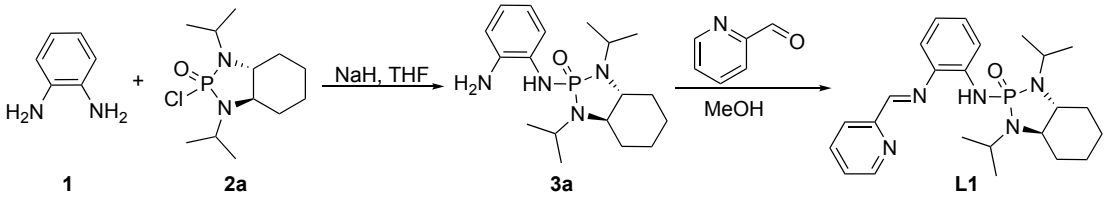


1-(Allyloxy)-4-(1-phenylvinyl)benzene (**4z**): white solid, m.p.: 61-62 ºC, 2.22 g (starting material 10 mmol), 94% yield; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.40-7.36 (m, 5H), 7.33-7.31 (d, *J* = 8.8 Hz, 2H), 6.94-6.92 (d, *J* = 8.8 Hz, 2H), 6.16-6.07 (m, 1H), 5.50-5.40 (m, 3H), 5.36-5.33 (m, 1H), 4.60-4.58 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): 158.3, 149.4, 141.7, 134.0, 133.2, 129.3, 128.3, 128.1, 127.6, 117.7, 114.2, 113.0, 68.7; IR (neat): 2979, 2882, 1505, 1388, 1235, 1178, 939, 840 cm^{-1}; HRMS: calcd. for $C_{17}H_{16}O$ $[M+H]^+$ 237.1274, found: 237.1270.



(8*S,*9*S,*13*S,*14*S*)-3-(allyloxy)-13-methyl-17-methylene-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthrene (**4aa**): colorless oil, 1.05 g, 92% yield; ^{1}H NMR ($CDCl_3$, 400 MHz): 7.25-7.23 (d, *J* = 8.4 Hz, 1H), 6.77-6.74 (dd, *J* = 8.4 Hz, *J* = 2.8 Hz, 1H), 6.68-6.67 (d, *J* = 2.8 Hz, 1H), 6.13-6.03 (m, 1H), 5.46-5.40 (m, 1H), 5.31-5.28 (m, 1H), 4.71-4.70 (t, *J* = 2.0 Hz, 2H), 4.54-4.52 (m, 2H), 2.96-2.83 (m, 2H), 2.61-2.54 (m, 1H), 2.41-2.21 (m, 3H), 2.00-1.94 (m, 2H), 1.88-1.80 (m, 1H), 1.62-1.36 (m, 5H), 1.32-1.23 (m, 1H), 0.85 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 161.7, 156.4, 138.0, 133.6, 132.9, 126.2, 117.4, 114.7, 112.1, 100.8, 68.7, 53.4, 44.3, 44.0, 38.7, 35.7, 29.8, 29.4, 27.6, 26.6, 23.9, 18.5; IR (neat): 2919, 2866, 1607, 1497, 1253, 1231, 1024, 874, 783 cm^{-1}; HRMS: calcd. for $C_{22}H_{28}O$ $[M+H]^+$ 309.2213, found: 309.2207.

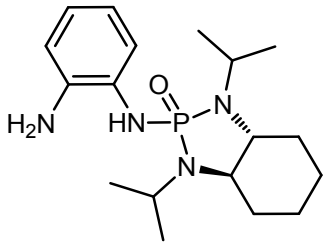
3. General procedure for the synthesis of ligands (**L1** as an example)



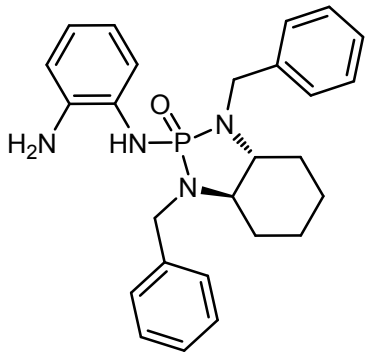
To a 250 mL schlenk flask was added a solution of *o*-Phenylenediamine (**1**) (30 mmol, 3.24g) in anhydrous THF (80 mL) and the solution was cooled to 0 ˚C under argon atmosphere. To the above solution, NaH (60% in mineral oil) (30 mmol, 1.2 g) was added portionwise under argon atmosphere. The resulting solution was warmed to 40 ˚C and stirred at 40 ˚C for 1 hour, then was cooled to 0 ˚C. To the solution was added a solution of **2a**[S4] (20 mmol, 5.57g) in 20 mL anhydrous THF. The resulting solution was warmed to 40 ˚C and stirred at 40 ˚C overnight. To quench the reaction, 50 mL saturated NH_4Cl aqueous solution was slowly added to the reaction mixture. The resulting suspension was extracted with diethyl ether for three times (3×100 mL), and the combined organic phase was dried over anhydrous $MgSO_4$. After filtering $MgSO_4$, the organic solvent was removed under vacuum and the product was purified by silica gel column chromatography (CH_2Cl_2/EtOAc 2/1 followed by EtOAc/MeOH 20/1) to provide 3.7 g (53% yield)

of **3a** as a white solid.

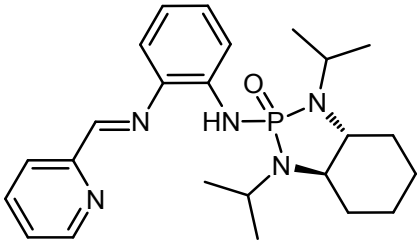
To a solution of **3a** (350mg, 1 mmol) in methanol (5 mL) was added picolinaldehyde (190 μL, 2 mmol). The solution was stirred overnight at room temperature then the solvent was evaporated. The residue was purified by silica gel column chromatography (EtOAc/Hexane/Et_3N 50/50/1 followed by EtOAc/MeOH/Et_3N 100/5/1) to give the corresponding **L1** (431mg, 98% yield).



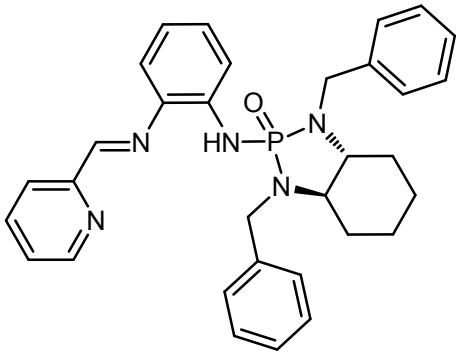
(*3aR,7aR*)-2-((2-Aminophenyl)amino)-1,3-diisopropyloctahydro-1*H*-benzo[*d*][1,3,2]diazaphosphole 2-oxide (**3a**): white solid, m.p.: 216-218 °C; ^{1}H NMR (400MHz, $CDCl_3$): 7.51-7.49 (d, *J* = 8.0 Hz, 1H), 6.79-6.75 (m, 1H), 6.65-6.58 (m, 2H), 6.43-6.41 (d, *J* = 6.0 Hz, 1H), 4.45 (s, 2H), 3.61-3.41 (m, 2H), 3.09-2.99 (m, 2H), 2.13-2.01 (m, 2H), 1.82-1.75 (m, 2H), 1.41-1.39 (d, *J* = 6.8 Hz, 3H), 1.37-1.27 (m, 4H), 1.22-1.20 (d, *J* = 6.4 Hz, 3H), 1.08-1.06 (d, *J* = 6.8 Hz, 3H), 0.95-0.93 (d, *J* = 6.4 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$): 18.8; ^{13}C NMR (100MHz, $CDCl_3$): 138.8 (d, $J_{P\text{-}C}$ = 8.2 Hz), 128.7, 122.3, 120.1 (d, $J_{P\text{-}C}$ = 2.0 Hz), 117.6, 116.1, 60.7 (d, $J_{P\text{-}C}$ = 13.8 Hz), 59.6 (d, $J_{P\text{-}C}$ = 10.6 Hz), 44.6 (d, $J_{P\text{-}C}$ = 2.5 Hz), 43.9 (d, $J_{P\text{-}C}$ = 4.9 Hz), 30.6 (d, $J_{P\text{-}C}$ = 8.2 Hz), 29.7 (d, $J_{P\text{-}C}$ = 11.0 Hz), 24.4, 24.2, 22.6 (d, $J_{P\text{-}C}$ = 2.6 Hz), 21.1 (d, $J_{P\text{-}C}$ = 3.2 Hz), 19.8 (d, $J_{P\text{-}C}$ = 1.2 Hz), 19.7 (d, $J_{P\text{-}C}$ = 2.7 Hz); IR (neat): 3231, 2925, 2852, 1653, 1504, 1281, 1202, 1178, 1018, 946, 751; HRMS: calcd. for $C_{18}H_{31}N_4OP$ $[M+H]^+$ 351.2308, found: 351.2307.



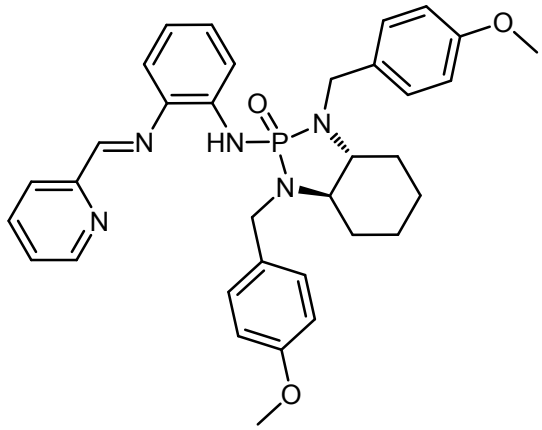
(*3aR,7aR*)-2-((2-Aminophenyl)amino)-1,3-dibenzyloctahydro-1*H*-benzo[*d*][1,3,2]diazaphosphole 2-oxide (**3b**): white solid, m.p.: 190-192 °C; ^{1}H NMR (400MHz, $CDCl_3$): 7.35-7.31 (m, 4H), 7.22-7.16 (m, 7H), 6.93-6.89 (t, *J* = 7.6 Hz, 1H), 6.71-6.65 (m, 2H), 6.03-6.01 (d, *J* = 7.2 Hz, 1H), 4.47-4.33 (m, 2H), 4.08-4.03 (m, 3H), 3.63-3.57 (dd, *J* = 16.4 Hz, *J* = 8.8 Hz, 1H), 2.97-2.88 (m, 2H), 1.75-1.73 (d, *J* = 9.6 Hz, 1H), 1.58-1.53 (m, 3H), 1.16-1.09 (m, 3H), 0.97-0.92 (m, 1H); ^{31}P NMR (162 MHz, $CDCl_3$): 24.3; ^{13}C NMR (100MHz, $CDCl_3$): 140.4 (d, $J_{P\text{-}C}$ = 4.3 Hz), 140.1 (d, $J_{P\text{-}C}$ = 7.1 Hz), 138.9 (d, $J_{P\text{-}C}$ = 4.9 Hz), 128.3, 128.1, 128.0, 127.3, 126.9, 126.8, 126.6, 123.9, 122.4 (d, $J_{P\text{-}C}$ = 2.1 Hz), 118.1, 116.3, 65.0 (d, $J_{P\text{-}C}$ = 10.4 Hz), 63.0 (d, $J_{P\text{-}C}$ = 10.0 Hz), 47.3 (d, $J_{P\text{-}C}$ = 3.0 Hz), 46.4 (d, $J_{P\text{-}C}$ = 4.9 Hz), 30.2 (d, $J_{P\text{-}C}$ = 7.8 Hz), 29.3 (d, $J_{P\text{-}C}$ = 10.4 Hz), 24.2, 24.1; IR (neat): 3413, 3261, 2949, 1589, 1504, 1440, 1279, 1201, 1179, 940, 782; HRMS: calcd. for $C_{26}H_{31}N_4OP$ $[M+H]^+$ 447.2308, found: 447.2302.



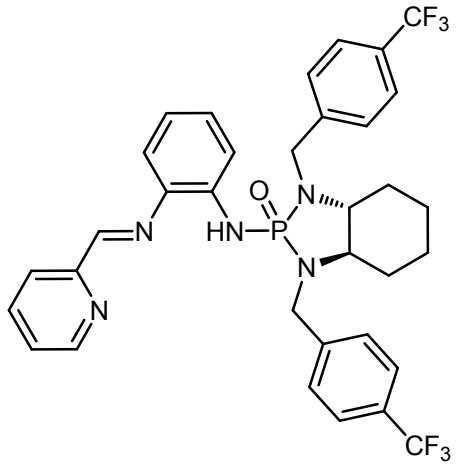
(*3aR,7aR*)-1,3-Diisopropyl-2-((2-((*E*)-(pyridin-2-ylmethylene)amino)phenyl)amino)octahydro-1*H*-benzo[*d*][1,3,2]diazaphosphole 2-oxide (**L1**): yellow solid, m.p.: 137-139 °C; ^{1}H NMR (400MHz, $CDCl_3$): 8.70 (s, 1H), 8.69-8.67 (m, 1H), 8.28-8.26 (d, *J* = 7.6 Hz, 1H), 7.83-7.79 (m, 1H), 7.55-7.53 (dd, *J* = 8.0 Hz, *J* = 0.8 Hz, 1H), 7.38-7.35 (m, 1H), 7.24-7.15 (m, 2H), 6.92-6.88 (m, 1H), 6.29-6.27 (d, *J* = 6.8 Hz, 1H), 3.57-3.40 (m, 2H), 3.19-3.12 (m, 2H), 2.16-2.07 (m, 2H), 1.84-1.81 (m, 2H), 1.40-1.38 (m, 4H), 1.35-1.33 (d, *J* = 6.8 Hz, 3H), 1.21-1.20 (d, *J* = 6.8 Hz, 3H), 1.18-1.16 (d, *J* = 6.8 Hz, 3H), 1.00-0.98 (d, *J* = 6.4 Hz, 3H); ^{31}P NMR (162 MHz, $CDCl_3$): 16.8; ^{13}C NMR (100MHz, $CDCl_3$): 158.6, 154.6, 149.7, 138.2, 137.4 (d, $J_{P\text{-}C}$ = 8.9 Hz), 136.8, 128.3, 125.3, 121.9, 120.7, 117.1 (d, $J_{P\text{-}C}$ = 1.6 Hz), 117.0, 60.8 (d, $J_{P\text{-}C}$ = 10.7 Hz), 59.7 (d, $J_{P\text{-}C}$ = 10.6 Hz), 44.9 (d, $J_{P\text{-}C}$ = 2.4 Hz), 44.2 (d, $J_{P\text{-}C}$ = 4.8 Hz), 30.5 (d, $J_{P\text{-}C}$ = 8.2 Hz), 30.0 (d, $J_{P\text{-}C}$ = 11.3 Hz), 24.5 (d, $J_{P\text{-}C}$ = 1.0 Hz), 24.4 (d, $J_{P\text{-}C}$ = 1.4 Hz), 22.5 (d, $J_{P\text{-}C}$ = 2.8 Hz), 21.6 (d, $J_{P\text{-}C}$ = 4.7 Hz), 20.3 (d, $J_{P\text{-}C}$ = 2.4 Hz), 20.1 (d, $J_{P\text{-}C}$ = 0.8 Hz); IR (neat): 3361, 2970, 2934, 2865, 1585, 1488, 1385, 1201, 1180, 1015, 990, 977, 747; HRMS: calcd. for $C_{24}H_{34}N_5OP$ $[M+H]^+$ 440.2574, found: 440.2563.



(*3aR,7aR*)-1,3-Dibenzyl-2-((2-((*E*)-(pyridin-2-ylmethylene)amino)phenyl)amino)octahydro-1*H*-benzo[*d*][1,3,2]diazaphosphole 2-oxide (**L2**): yellow solid, m.p.: 129-131 °C; ^{1}H NMR (400MHz, $CDCl_3$): 8.69-8.68 (d, *J* = 4.4 Hz, 1H), 8.66 (s, 1H), 8.24-8.22 (d, *J* = 8.0 Hz, 1H), 7.81-7.77 (t, *J* = 7.8 Hz, 1H), 7.40-7.35 (m, 4H), 7.32-7.30 (m, 2H), 7.24-7.19 (m, 4H), 7.15-7.12 (m, 4H), 6.99-6.96 (t, *J* = 7.8 Hz, 1H), 6.40-6.38 (d, *J* = 6.8 Hz, 1H), 4.45-4.36 (m, 2H), 4.02-3.96 (dd, *J* = 15.2 Hz, *J* = 8.8 Hz, 1H), 3.86-3.79 (dd, *J* = 16.4 Hz, *J* = 9.2 Hz, 1H), 3.22-3.09 (m, 2H), 1.84-1.64 (m, 4H), 1.22-1.17 (m, 3H), 1.13-1.07 (m, 1H); ^{31}P NMR (162 MHz, $CDCl_3$): 21.7; ^{13}C NMR (100MHz, $CDCl_3$): 158.6, 154.3, 149.5, 139.5 (d, $J_{P\text{-}C}$ = 3.8 Hz), 138.7 (d, $J_{P\text{-}C}$ = 5.9 Hz), 137.3 (d, $J_{P\text{-}C}$ = 8.9 Hz), 137.0 (d, $J_{P\text{-}C}$ = 0.7 Hz), 136.6, 128.3, 128.12, 128.09, 128.0, 127.5, 126.8 (d, $J_{P\text{-}C}$ = 4.6 Hz), 125.2, 121.9, 121.1, 117.0, 116.6 (d, $J_{P\text{-}C}$ = 1.7 Hz), 64.7 (d, $J_{P\text{-}C}$ = 10.8 Hz), 63.5 (d, $J_{P\text{-}C}$ = 10.0 Hz), 47.4 (d, $J_{P\text{-}C}$ = 2.3 Hz), 46.5 (d, $J_{P\text{-}C}$ = 5.1 Hz), 30.1 (d, $J_{P\text{-}C}$ = 7.7 Hz), 29.5 (d, $J_{P\text{-}C}$ = 11.0 Hz), 24.2, 24.1; IR (neat): 2937, 1587, 1494, 1322, 1211, 1173, 930, 739; HRMS: calcd. for $C_{32}H_{34}N_5OP$ $[M+H]^+$ 536.2574, found: 536.2565.

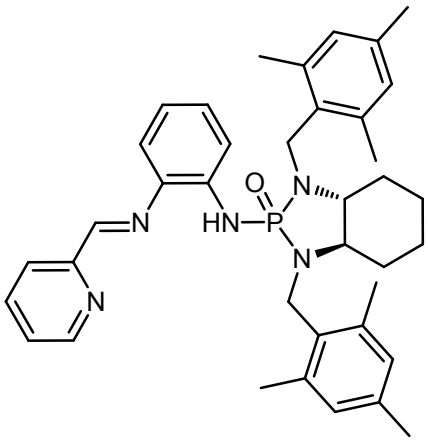


(*3aR,7aR*)-1,3-Bis(4-methoxybenzyl)-2-((2-((*E*)-(pyridin-2-ylmethylene)amino)phenyl)amino)octahydro-1*H*-benzo[*d*][1,3,2]diazaphosphole 2-oxide (**L3**): yellow solid, m.p.: 87-89 ºC; ^{1}H NMR (400MHz, $CDCl_3$): 8.70-8.68 (m, 1H), 8.66 (s, 1H), 8.23-8.21 (d, *J* = 7.6 Hz, 1H), 7.82-7.77 (m, 1H), 7.38-7.32 (m, 2H), 7.25-7.17 (m, 6H), 6.97-6.93 (m, 1H), 6.72-6.70 (d, *J* = 8.8 Hz, 2H), 6.66-6.64 (d, *J* = 8.8 Hz, 2H), 6.34-6.32 (d, *J* = 7.2 Hz, 1H), 4.32-4.25 (m, 2H), 3.98-3.92 (dd, *J* = 14.8 Hz, *J* = 10.0 Hz, 1H), 3.82-3.76 (dd, *J* = 16.0 Hz, *J* = 9.6 Hz, 1H), 3.72 (s, 3H), 3.66 (s, 3H), 3.17-3.03 (m, 2H), 1.88-1.76 (m, 2H), 1.68-1.65 (m, 2H), 1.25-1.17 (m, 3H), 1.14-1.08 (m, 1H); ^{31}P NMR (162 MHz, $CDCl_3$): 21.3; ^{13}C NMR (100MHz, $CDCl_3$): 158.4, 154.3, 149.5, 137.2, 136.6, 131.3 (d, $J_{P\text{-}C}$ = 3.6 Hz), 130.4 (d, $J_{P\text{-}C}$ = 5.3 Hz), 129.5, 128.8, 128.2, 125.2, 121.9, 121.0, 116.9, 116.6 (d, $J_{P\text{-}C}$ = 1.8 Hz), 113.4 (d, $J_{P\text{-}C}$ = 10.4 Hz), 64.5 (d, $J_{P\text{-}C}$ = 10.8 Hz), 63.2 (d, $J_{P\text{-}C}$ = 10.1 Hz), 55.1, 55.0, 46.7 (d, $J_{P\text{-}C}$ = 2.3 Hz), 45.8 (d, $J_{P\text{-}C}$ = 5.2 Hz), 30.1 (d, $J_{P\text{-}C}$ = 7.9 Hz), 29.4 (d, $J_{P\text{-}C}$ = 10.7 Hz), 24.3, 24.2; IR (neat): 3340, 2936, 2832, 1610, 1510, 1490, 1277, 1241, 1171, 1033, 817, 742; HRMS: calcd. for $C_{34}H_{38}N_5O_3P$ $[M+H]^+$ 596.2785, found: 596.2777.



(3*aR*,7*aR*)-2-((2-((*E*)-(Pyridin-2-ylmethylene)amino)phenyl)amino)-1,3-bis(4-(trifluoromethyl)benzyl)octahydro-*1H*-benzo[*d*][1,3,2]diazaphosphole 2-oxide (**L4**): yellow solid, m.p.: 95-97 ºC; ^{1}H NMR (400MHz, $CDCl_3$): 8.69-8.68 (d, *J* = 4.8 Hz, 1H), 8.66 (s, 1H), 8.18-8.16 (d, *J* = 8.0 Hz, 1H), 7.80-7.76 (m, 1H), 7.50-7.45 (m, 4H), 7.43-7.35 (m, 5H), 7.31-7.29 (d, *J* = 8.0 Hz, 1H), 7.25-7.20 (m, 2H), 7.02-6.98 (m, 1H), 6.41-6.39 (d, *J* = 7.2 Hz, 1H), 4.48-4.44 (d, *J* = 13.6 Hz, 1H), 4.41-4.37 (d, *J* = 12.4 Hz, 1H), 4.06-4.00 (dd, *J* = 15.6 Hz, *J* = 9.2 Hz, 1H), 3.91-3.85 (dd, *J* = 16.4 Hz, *J* = 10.0 Hz, 1H), 3.25-3.10 (m, 2H), 1.82-1.69 (m, 4H), 1.29-1.20 (m, 3H), 1.13-1.05 (m, 1H); ^{31}P NMR (162 MHz, $CDCl_3$): 21.4; ^{13}C NMR (100MHz, $CDCl_3$): 158.9, 154.1, 149.6, 143.6 (m), 142.7 (m),

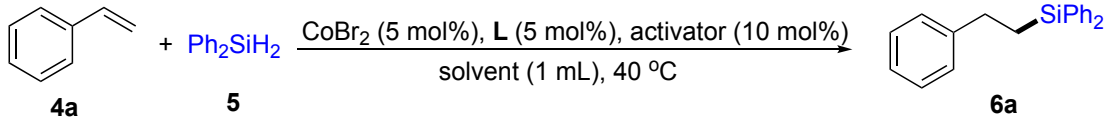
137.3 (d, $J_{P\text{-}C}$ = 8.9 Hz), 136.63, 136.61, 129.2 (m), 128.4, 128.3, 127.7, 125.3, 125.1 (m), 124.1 (m, $J_{F\text{-}C}$ = 270.5 Hz, $J_{P\text{-}C}$ = 7.2 Hz), 121.8, 121.6, 117.2, 116.3 (d, $J_{P\text{-}C}$ = 2.0 Hz), 64.8 (d, $J_{P\text{-}C}$ = 10.5 Hz), 63.5 (d, $J_{P\text{-}C}$ = 9.8 Hz), 47.0 (d, $J_{P\text{-}C}$ = 4.2 Hz), 46.2 (d, $J_{P\text{-}C}$ = 5.1 Hz), 30.1 (d, $J_{P\text{-}C}$ = 7.5 Hz), 29.4 (d, $J_{P\text{-}C}$ = 10.8 Hz), 24.1, 24.0; IR (neat): 3353, 2937, 2865, 1618, 1586, 1492, 1321, 1159, 1105, 1064, 836, 742; HRMS: calcd. for $C_{34}H_{32}F_6N_5OP$ $[M+H]^+$ 672.2321, found: 672.2313.



(*3aR,7aR*)-2-((2-((*E*)-(Pyridin-2-ylmethylene)amino)phenyl)amino)-1,3-bis(2,4,6-trimethylbenzyl)octahydro-*1H*-benzo[*d*][1,3,2]diazaphosphole 2-oxide (**L5**): yellow solid, m.p.: 201-203 ºC; ^{1}H NMR (400MHz, $CDCl_3$): 8.72-8.70 (m, 1H), 8.51 (s, 1H), 8.15-8.13 (d, *J* = 7.6 Hz, 1H), 7.86-7.82 (m, 1H), 7.41-7.38 (m, 1H), 7.14-7.09 (m, 2H), 7.05-7.03 (d, *J* = 7.6 Hz, 1H), 6.88-6.84 (m, 1H), 6.71 (s, 2H), 6.35 (s, 2H), 5.92-5.91 (d, *J* = 6.8 Hz, 1H), 4.25-4.16 (m, 2H), 4.06-4.01 (dd, *J* = 14.0 Hz, *J* = 6.0 Hz 1H), 3.91-3.82 (dd, *J* = 24.0 Hz, *J* = 13.2 Hz, 1H), 3.20-3.05 (m, 2H), 2.34 (s, 6H), 2.24 (s, 6H), 2.18 (s, 3H), 2.16-2.14 (m, 1H), 1.91 (s, 3H), 1.81-1.58 (m, 3H), 1.42-1.25 (m, 3H), 1.08-0.99 (m, 1H); ^{31}P NMR (162 MHz, $CDCl_3$): 23.6; ^{13}C NMR (100MHz, $CDCl_3$): 156.8, 154.6, 149.4, 137.7 (d, $J_{P\text{-}C}$ = 3.8 Hz), 137.4 (d, $J_{P\text{-}C}$ = 1.1 Hz), 136.7, 136.5, 136.4, 136.3, 136.2, 130.8 (d, $J_{P\text{-}C}$ = 7.7 Hz), 130.0 (d, $J_{P\text{-}C}$ = 2.9 Hz), 129.0, 128.6, 128.0, 125.0, 121.7, 120.3, 116.6 (d, $J_{P\text{-}C}$ = 1.7 Hz), 115.9, 65.3 (d, $J_{P\text{-}C}$ = 10.0 Hz), 63.3 (d, $J_{P\text{-}C}$ = 9.4 Hz), 41.9 (d, $J_{P\text{-}C}$ = 4.3 Hz), 41.6, 30.2 (d, $J_{P\text{-}C}$ = 8.0 Hz), 28.6 (d, $J_{P\text{-}C}$ = 11.0 Hz), 24.6 (d, $J_{P\text{-}C}$ = 1.4 Hz), 24.5, 20.8 (d, $J_{P\text{-}C}$ = 17.3 Hz), 20.2 (d, $J_{P\text{-}C}$ = 14.9 Hz); IR (neat): 3330, 2929, 2854, 1585, 1490, 1207, 1102, 941, 756; HRMS: calcd. for $C_{38}H_{46}N_5OP$ $[M+H]^+$ 620.3513, found: 620.3507.

4. Optimization of reaction conditions

Table S1. Cobalt Catalyzed Anti-Markovnikov Hydrosilylation[a]

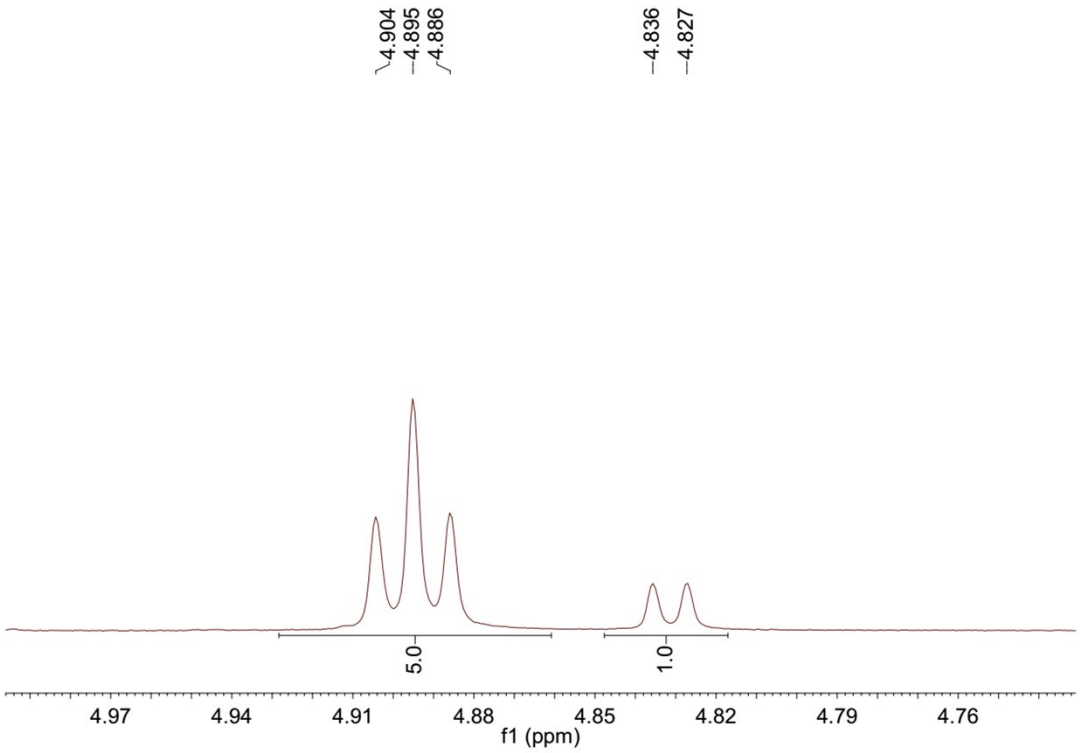


4a **5** **6a**

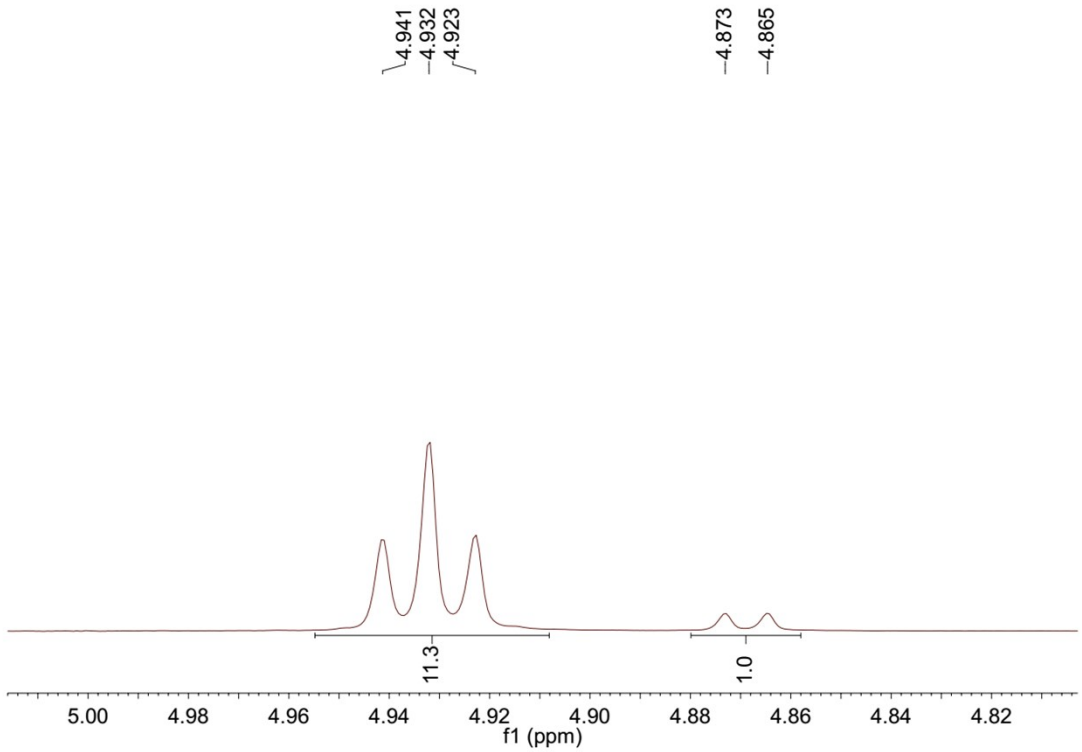
Entry	Ligand	Solvent	Activator	Yield (%)[b]	r.r (l/b)[c]
1	**L1**	THF	^{t}BuONa	52	5/1
2	**L2**	THF	^{t}BuONa	87	11/1
3	**L3**	THF	^{t}BuONa	76	7/1
4	**L4**	THF	^{t}BuONa	64	4/1
5	**L5**	THF	^{t}BuONa	56	4/1
6	**L2**	Toluene	^{t}BuONa	82	10/1
7	**L2**	1,4-dioxane	^{t}BuONa	69	10/1
8	**L2**	THF	$NaHBEt_3$	85	23/1

[a] The reaction of **4a** (0.2 mmol) with **5** (0.3 mmol) was performed in the presence of $CoBr_2$ (5 mol%), **L** (5 mol%) and activator (10 mol%) in solvent (1 mL) at 40 °C for 24 h. [b] Yield of isolated product. [c] The regioisomer ratio (r.r) of the product **6a** was determined by ^{1}H NMR.

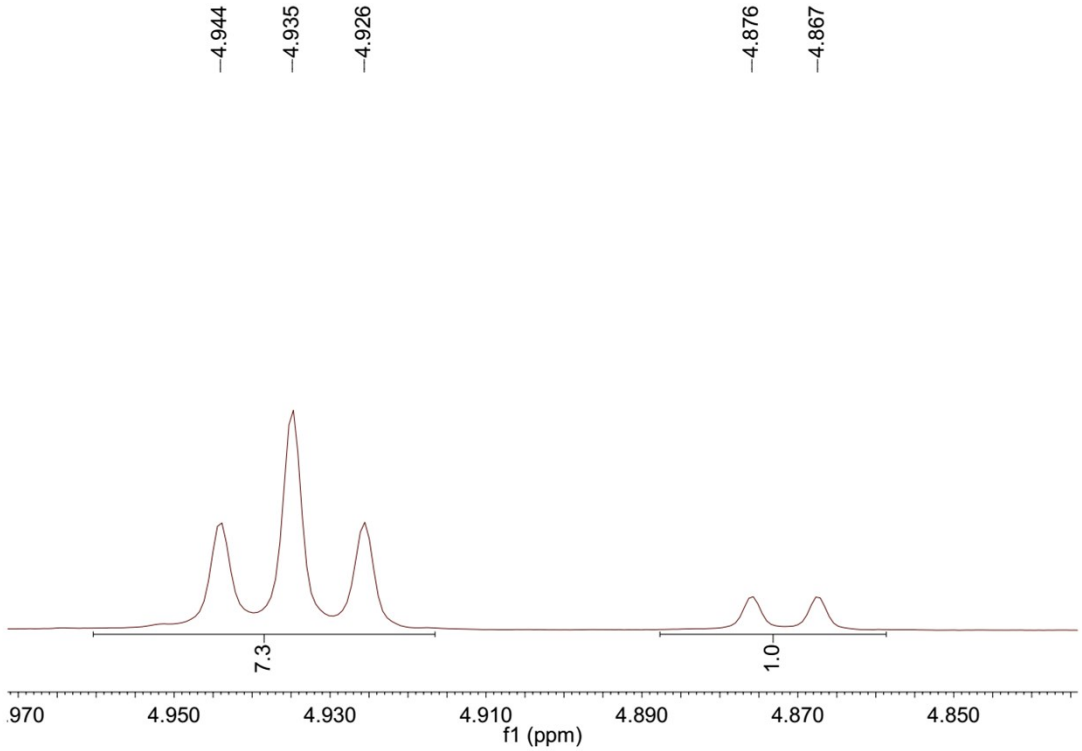
Entry 1



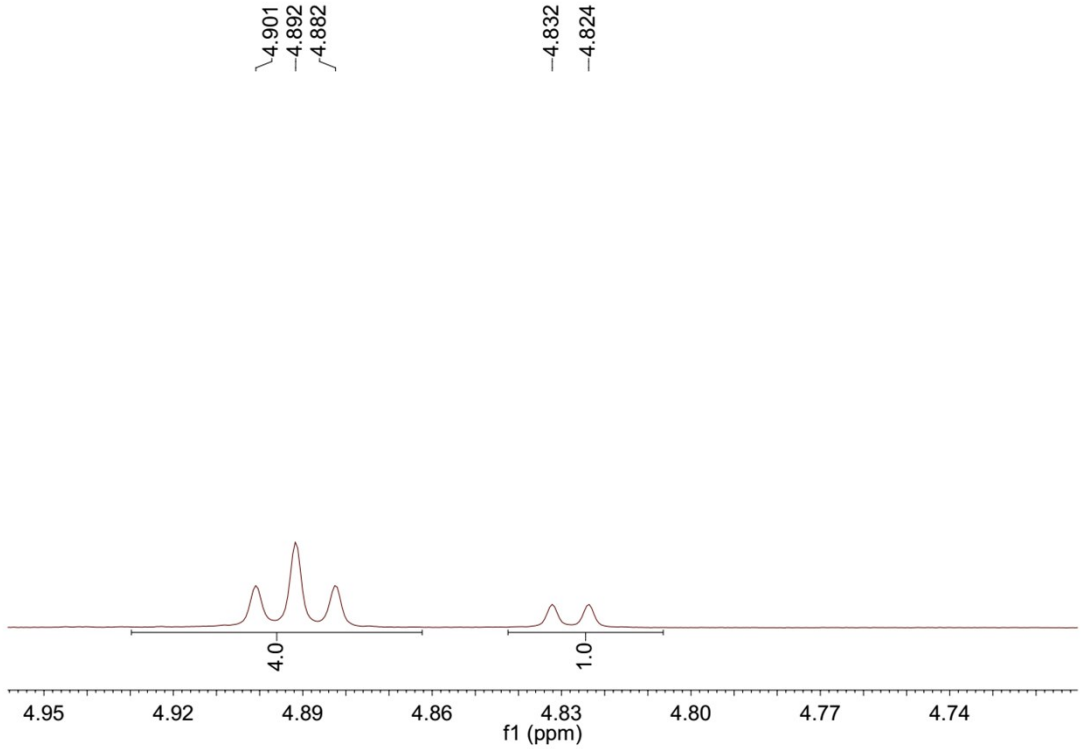
Entry 2



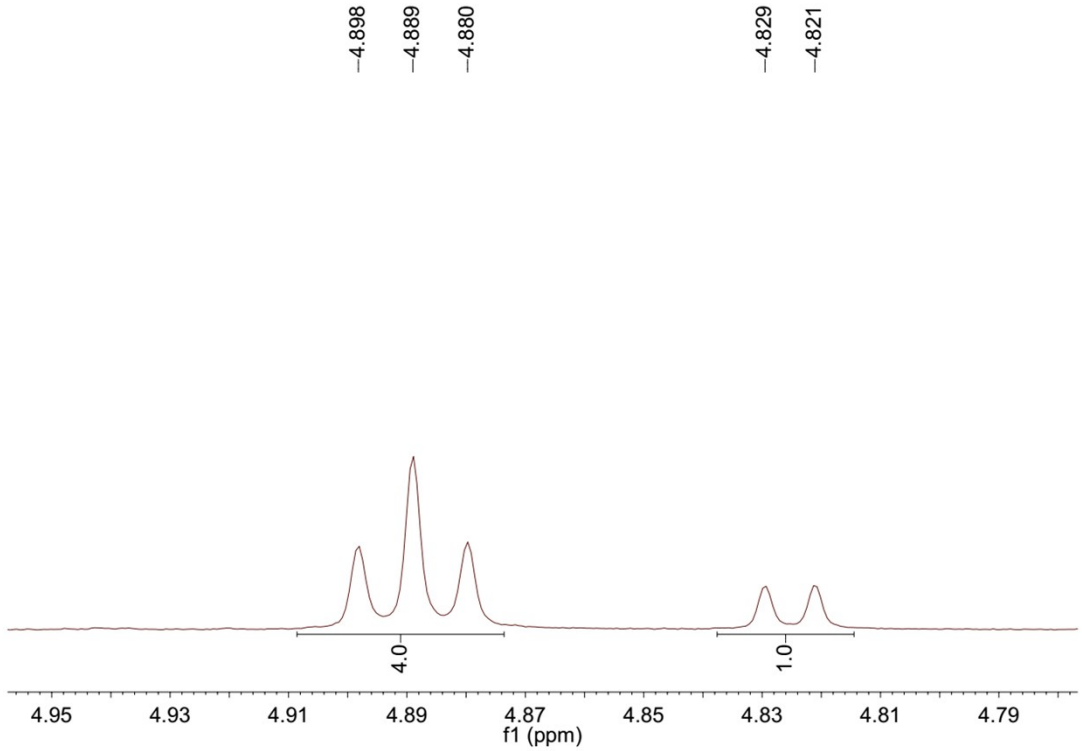
Entry 3



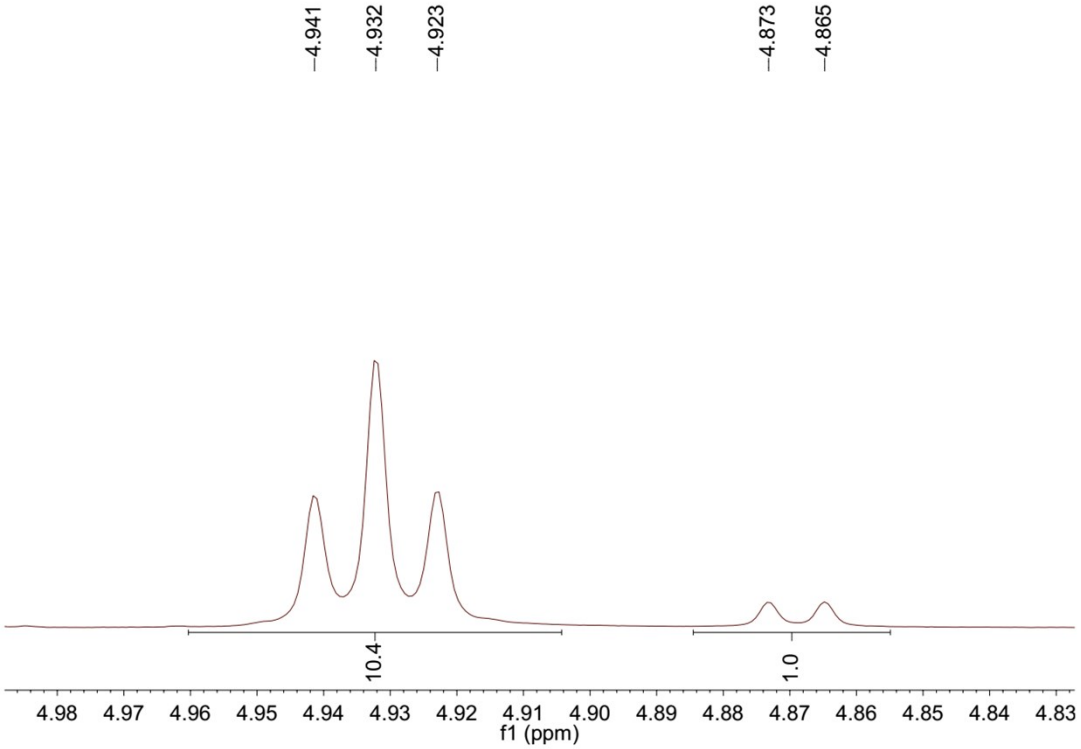
Entry 4



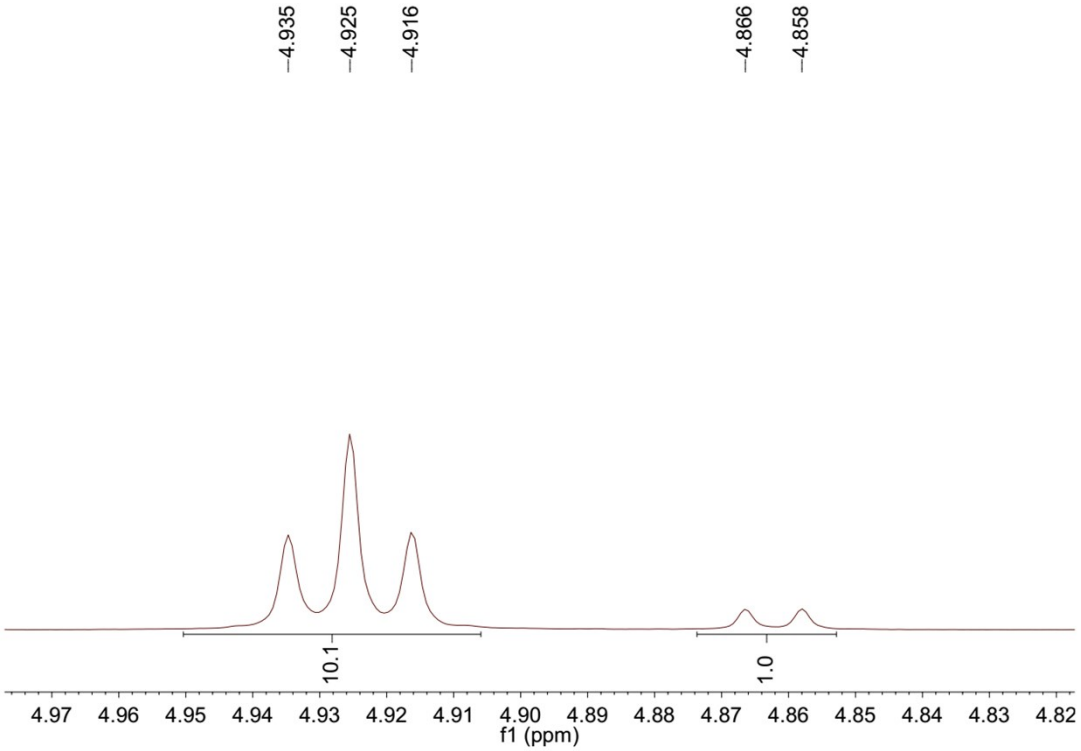
Entry 5



Entry 6



Entry 7



Entry 8

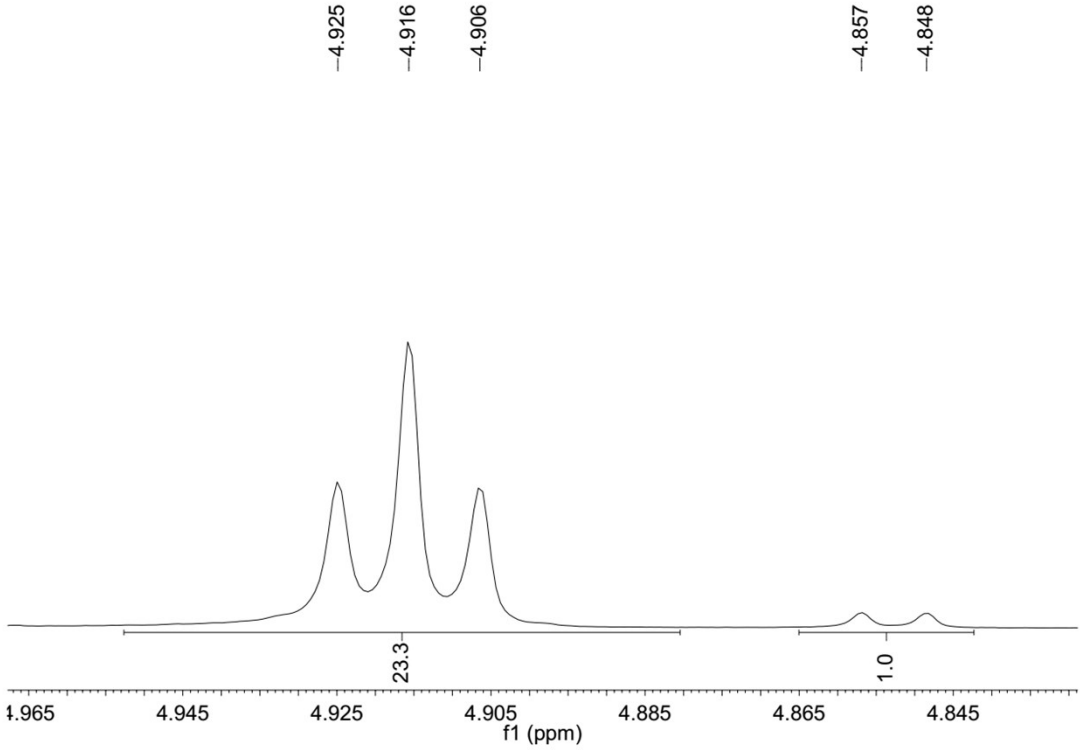
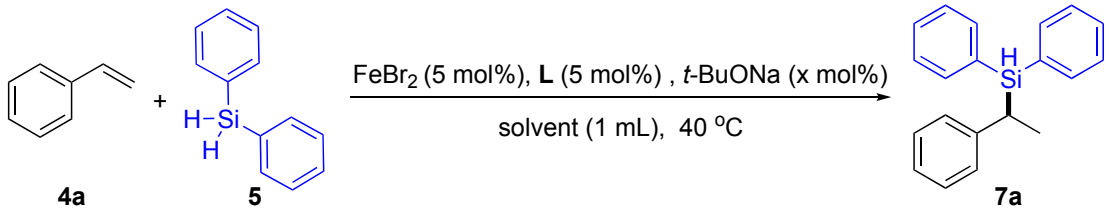


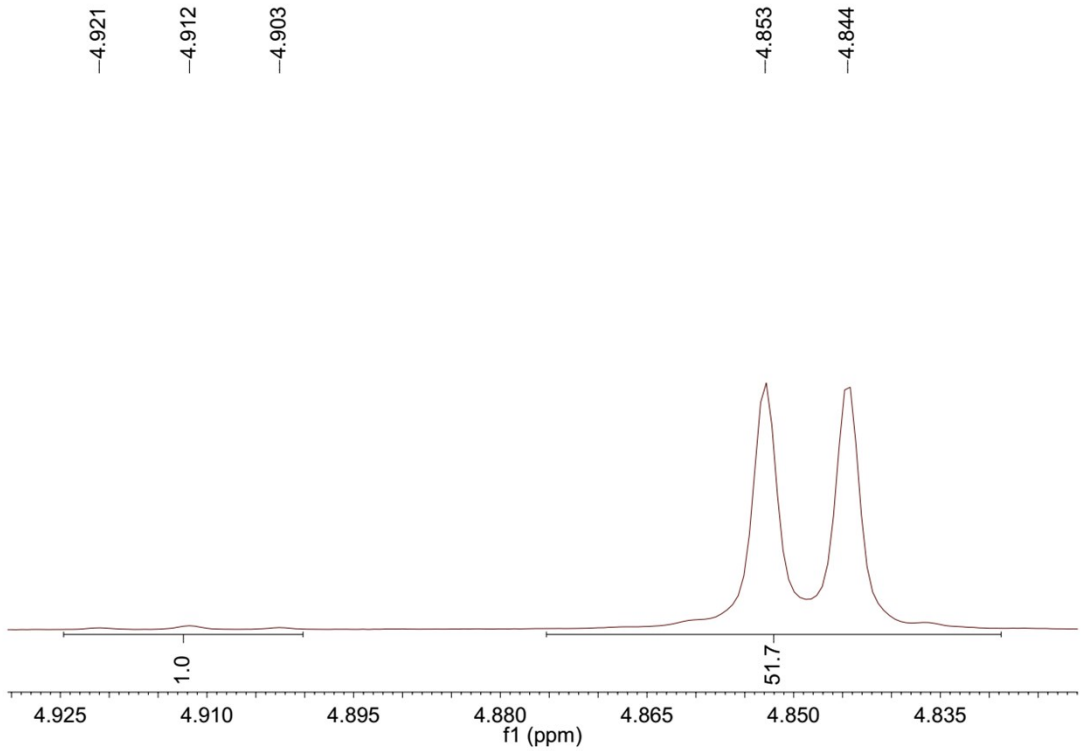
Table S2. Iron Catalyzed Markovnikov Hydrosilylation[a]



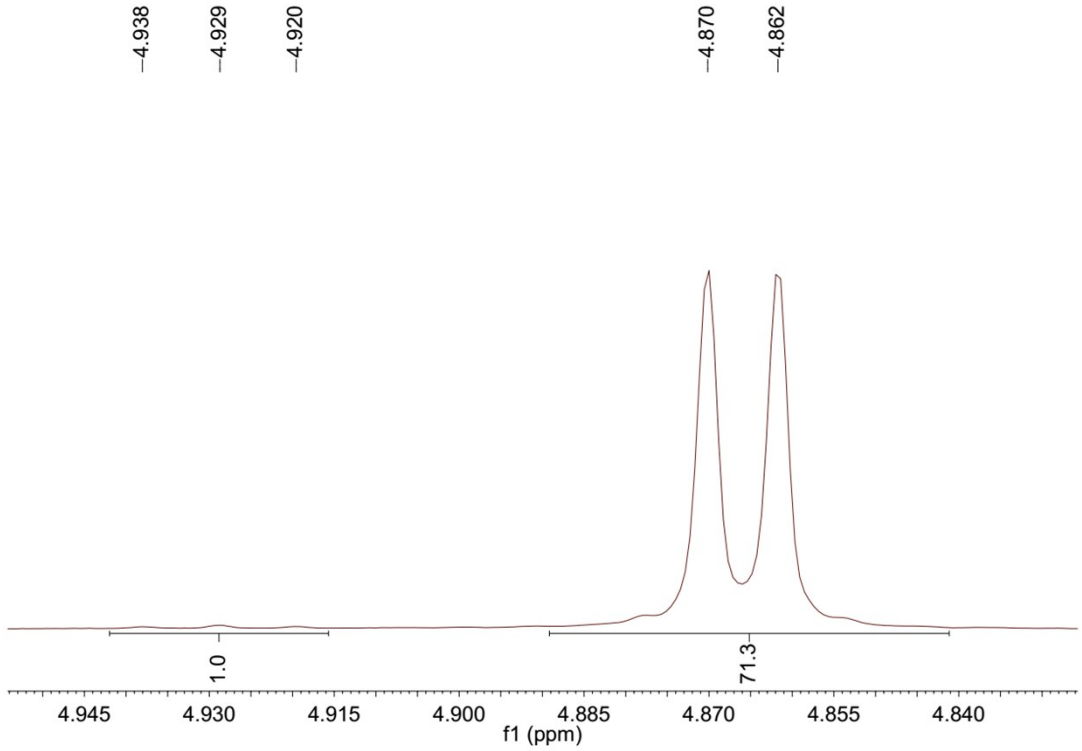
Entry	Ligand	Solvent	x	Yield (%)[b]	r.r (b/l)[c]
1	**L1**	THF	15	trace	n.d
2	**L1**	THF	20	43	52/1
3	**L1**	THF	25	84	71/1
4	**L2**	THF	25	67	44/1
5	**L3**	THF	25	58	30/1
6	**L4**	THF	25	56	11/1
7	**L5**	THF	25	50	29/1
8	**L1**	Toluene	25	62	23/1
9	**L1**	1,4-dioxane	25	82	51/1
10[d]	**L1**	THF	15	98	>99/1

[a] The reaction of **4a** (0.2 mmol) with **5** (0.6 mmol) was performed in the presence of $FeBr_2$ (5 mol%), **L** (5 mol%) and ^{t}BuONa (10 mol%) in solvent (1 mL) at 40 °C for 24 h. [b] Yield of isolated product. [c] The regioisomer ratio (r.r) of the product **7a** was determined by ^{1}H NMR. [d] **L1** was *in-situ* formed in the reaction from **3a** (5 mol%) and picolinaldehyde (5 mol%).

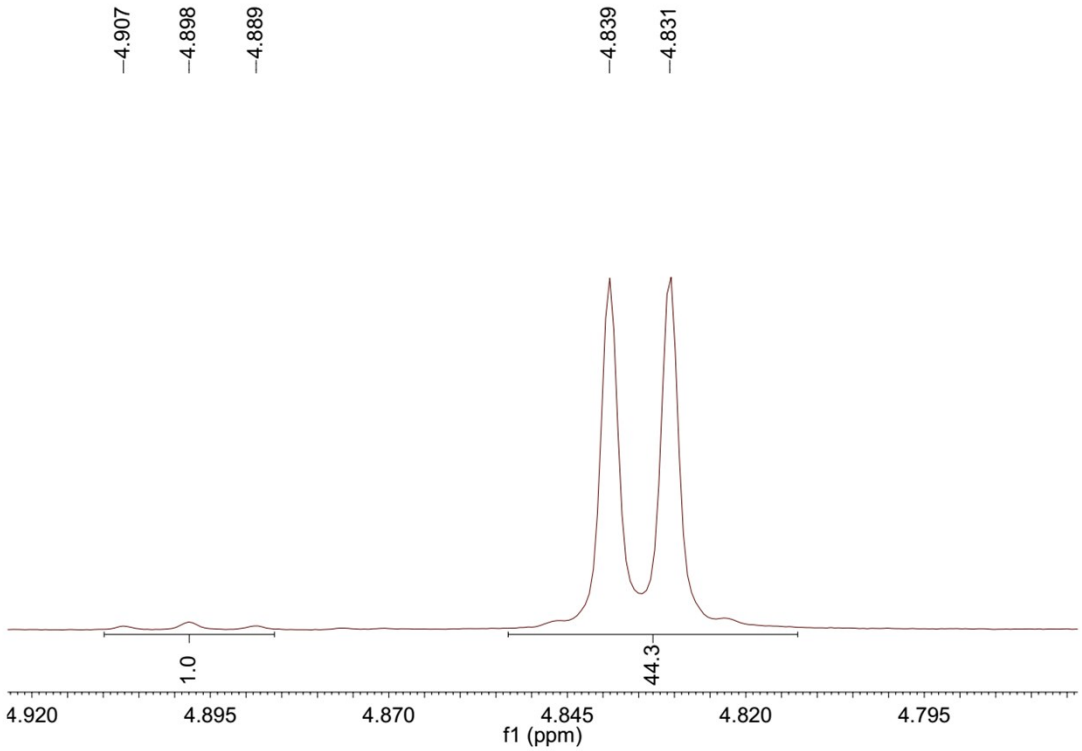
Entry 2



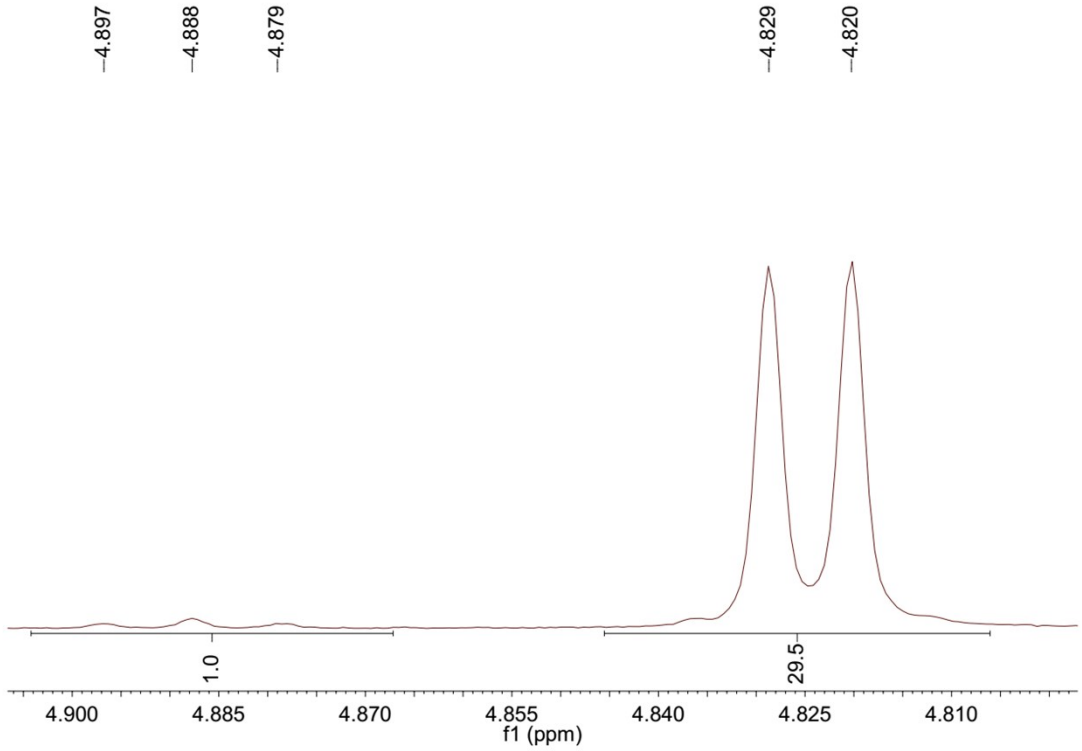
Entry 3



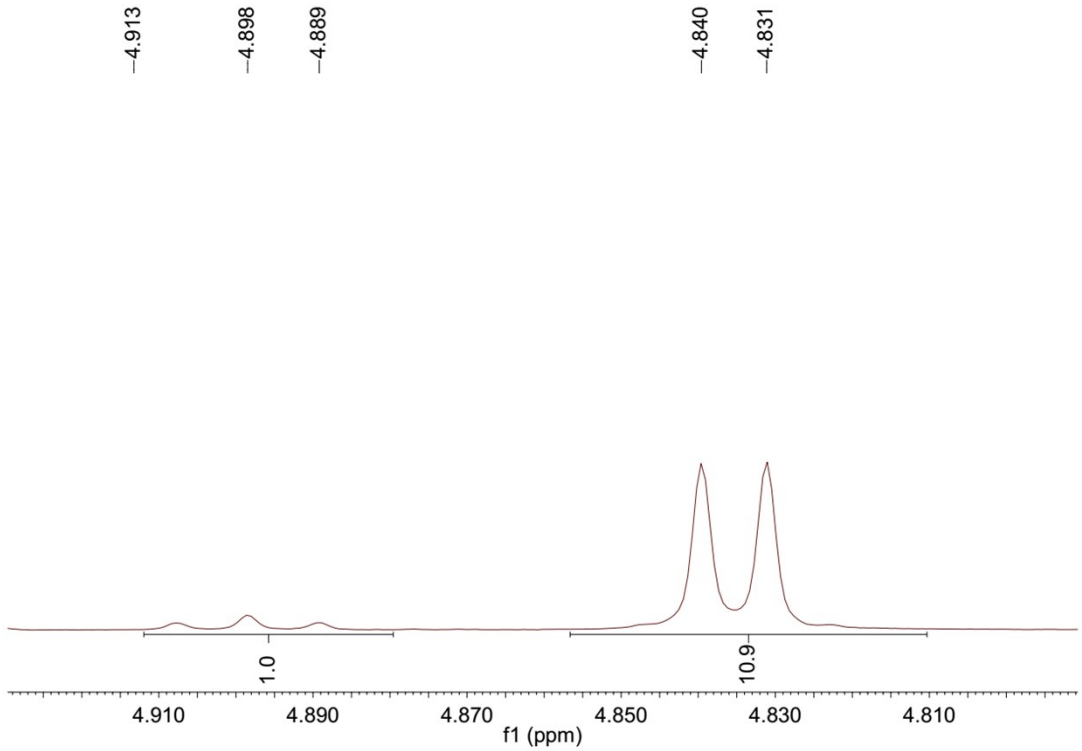
Entry 4



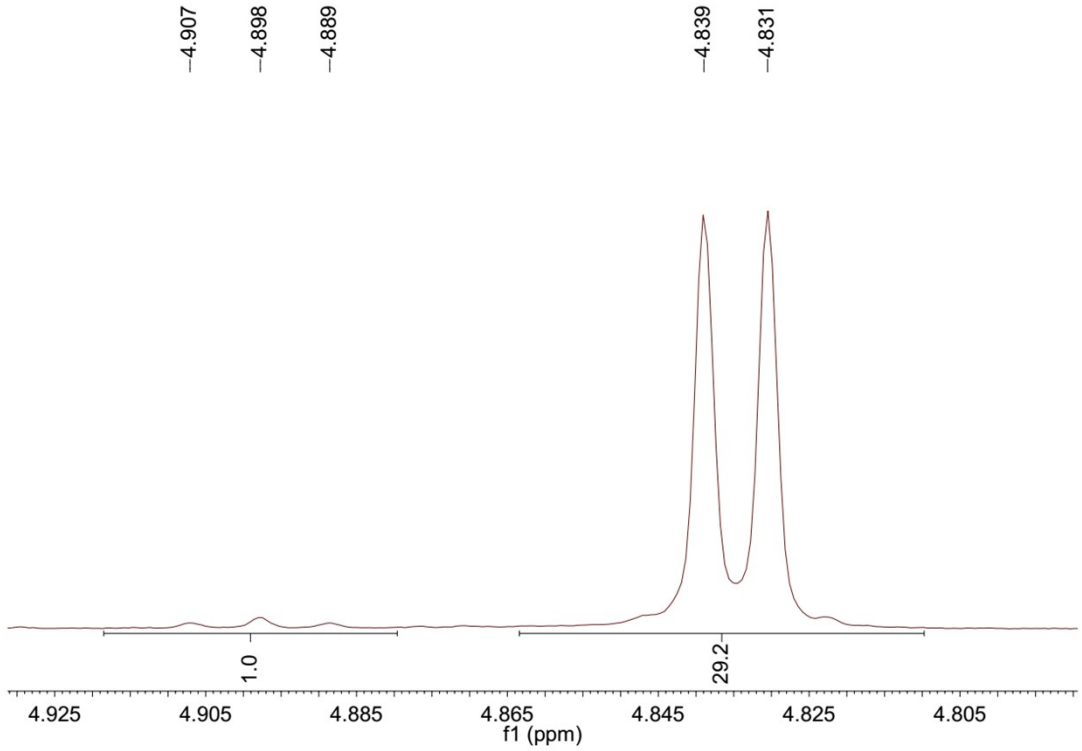
Entry 5



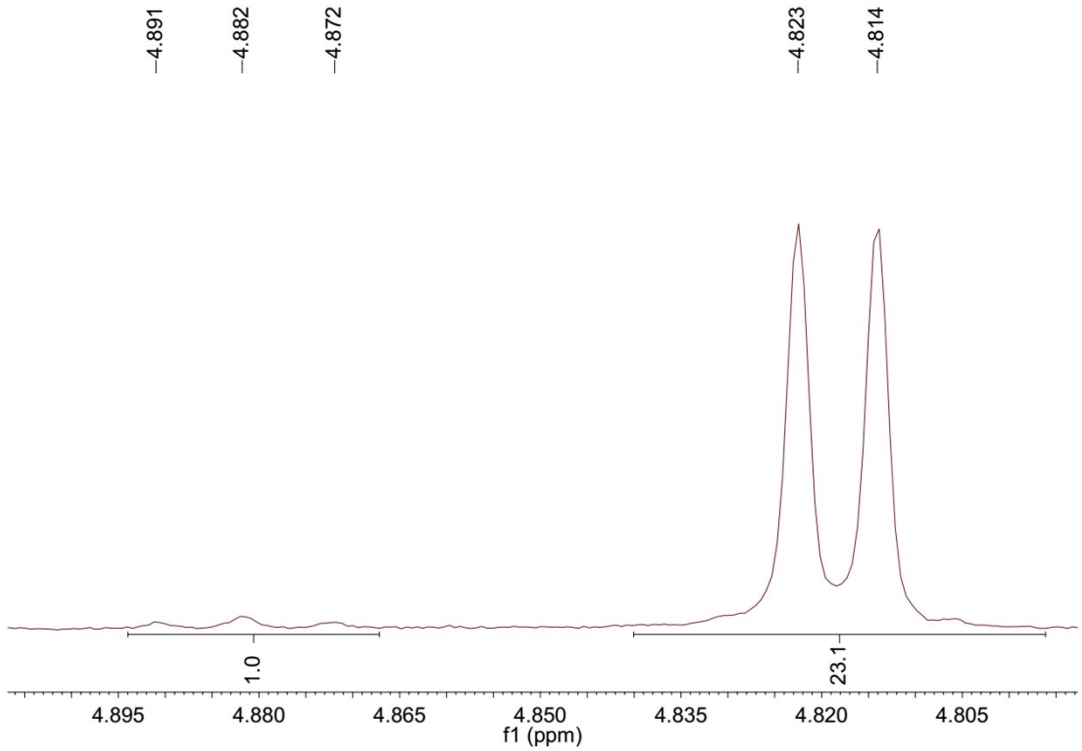
Entry 6



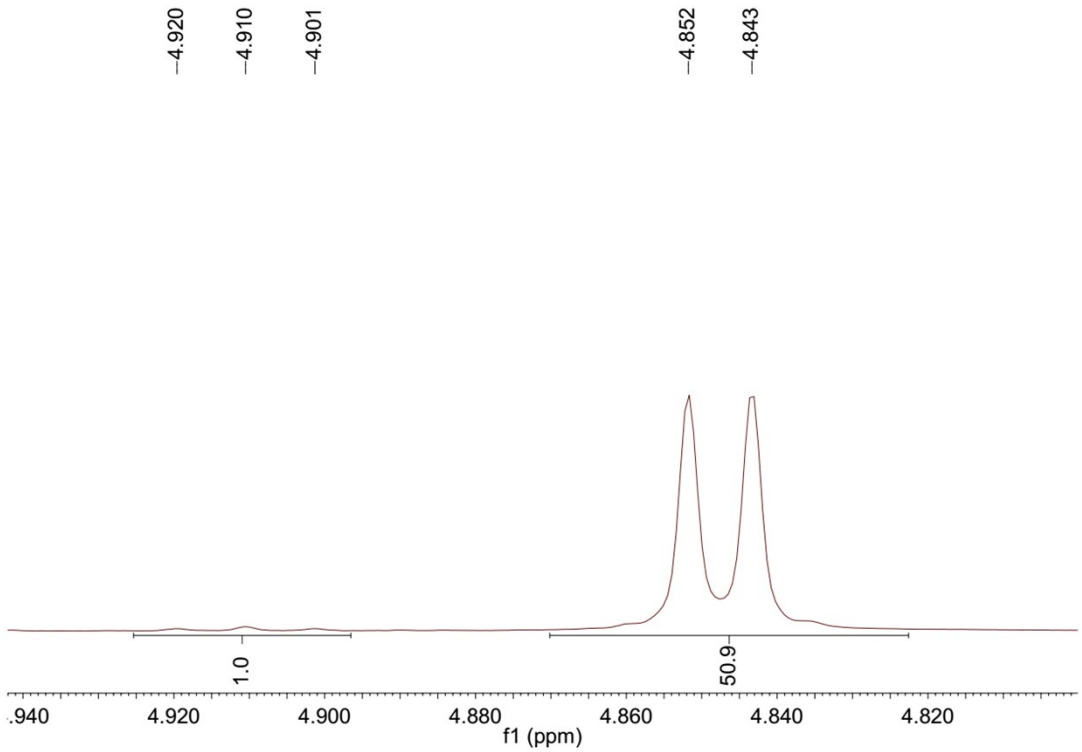
Entry 7



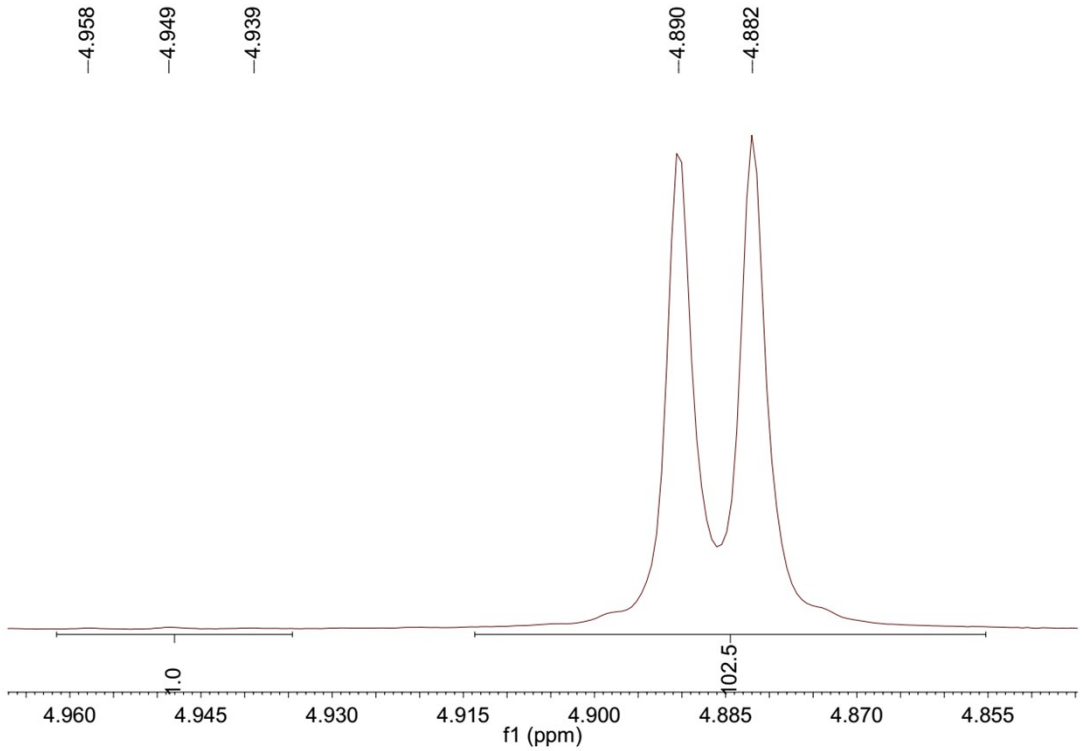
Entry 8



Entry 9



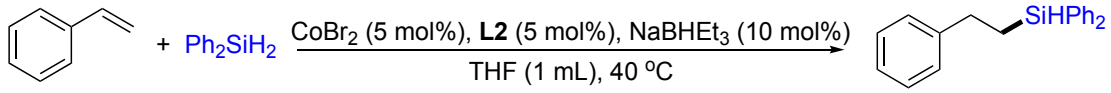
Entry 10



5.General Procedures for Hydrosilylation

5.1 General Procedures for Cobalt Catalyzed Hydrosilylation

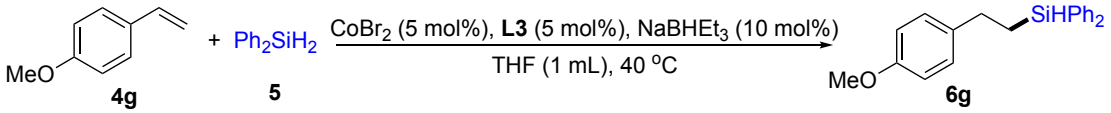
Procedure I (**4a** as an example)



4a **5** **6a**

Inside an argon-atmosphere glovebox, a borosilicate glass vial was charged with $CoBr_2$ (3.2 mg, 0.015 mmol) and **L2** (8.1 mg, 0.015 mmol), with anhydrous THF (1mL) as solvent. Subsequently, $NaBHEt_3$ (30 μL) (1 mol/L in THF) was added as activator. The resulting mixture was stirred at room temperature for 5 hours to form the active catalyst. Subsequently, diphenylsilane **5** (84 μL, 0.45 mmol, 1.5 equiv.) was added and the mixture was stirred for 30 min before adding styrene **4a** (34 μL, 0.3 mmol). The reaction mixture was removed from the glovebox and stirred at 40 °C under an argon atmosphere for 24 hours. The reaction solvent was evaporated in vacuum and the resulting residue was purified by silica gel column chromatography (hexane followed by diethyl ether/hexane = 1/200) affording 73 mg (84% yield) product **6a** as colorless oil.

Procedure II (**4g** as an example)

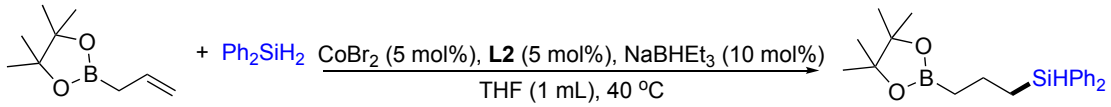


4g **5** **6g**

Inside an argon-atmosphere glovebox, a borosilicate glass vial was charged with $CoBr_2$ (3.2

mg, 0.015 mmol) and **L3** (8.9 mg, 0.015 mmol), with anhydrous THF (1mL) as solvent. Subsequently, $NaBHEt_3$ (30 μL) (1 mol/L in THF) was added as activator. The resulting mixture was stirred at room temperature for 5 hours to form the active catalyst. Subsequently, diphenylsilane **5** (84 μL, 0.45 mmol, 1.5 equiv.) was added and the mixture was stirred for 30 min before adding 4-vinylanisole **4g** (40 μL, 0.3 mmol). The reaction mixture was removed from the glovebox and stirred at 40 °C under an argon atmosphere for 24 hours. The reaction solvent was evaporated in vacuum and the resulting residue was purified by silica gel column chromatography (hexane followed by diethyl ether/hexane = 1/100) affording 87 mg (91% yield) product **6g** as colorless oil.

Procedure III (**4p** as an example)

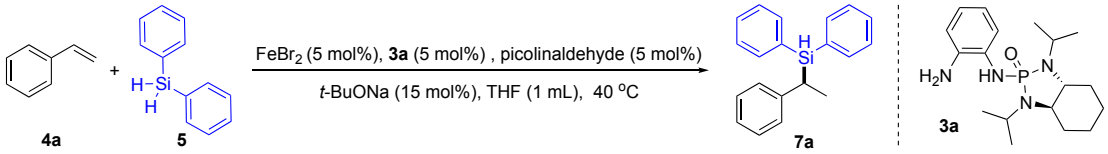


4p **5** **6p**

Inside an argon-atmosphere glovebox, a borosilicate glass vial was charged with $CoBr_2$ (3.2 mg, 0.015 mmol), **L2** (8.1 mg, 0.015 mmol) and NaO^tBu (2.9 mg, 0.03 mmol). Subsequently, anhydrous THF (1mL) was added as solvent. The resulting mixture was stirred at room temperature for 5 hours to form the active catalyst. Subsequently, diphenylsilane **5** (84 μL, 0.45 mmol, 1.5 equiv.) and allylboronic acid pinacol ester **4p** (56 μL, 0.3 mmol) were added. The reaction mixture was removed from the glovebox and stirred at 40 °C under an argon atmosphere for 24 hours. The reaction solvent was evaporated in vacuum and the resulting residue was purified by silica gel column chromatography (diethyl ether/hexane = 1/200 followed by diethyl ether/hexane = 1/50) affording 75 mg (71% yield) product **6p** as colorless oil.

5.2 General Procedures for Iron Catalyzed Hydrosilylation

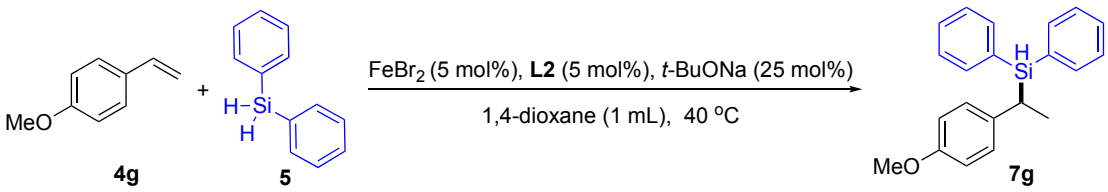
Procedure I (**4a** as an example)



4a **5** **7a** **3a**

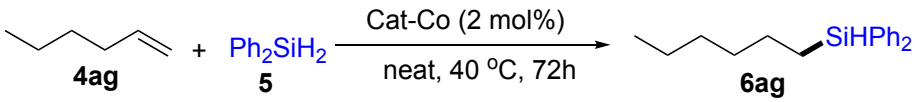
Inside an argon-atmosphere glovebox, a borosilicate glass vial was charged with $FeBr_2$ (3.2 mg, 0.015 mmol), **3a** (5.3 mg, 0.015 mmol), picolinaldehyde (1.4 μL, 0.015 mmol) and ^{t}BuONa (4.3 mg, 0.045 mmol), with anhydrous THF (1mL) as solvent. The resulting mixture was stirred at room temperature for 5 hours to form the active catalyst. Subsequently, diphenylsilane **5** (167 μL, 0.9 mmol, 3.0 equiv.) was added and the mixture was stirred for 30 min before adding styrene **4a** (34 μL, 0.3 mmol). The reaction mixture was removed from the glovebox and stirred at 40 °C under an argon atmosphere for 24 hours. Then the reaction solvent was evaporated in vacuum and the resulting residue was purified by silica gel column chromatography (hexane followed by diethyl ether/hexane = 1/200) affording 84 mg (97% yield) product **7a** as colorless oil.

Procedure II (**4g** as an example)



Inside an argon-atmosphere glovebox, a borosilicate glass vial was charged with $FeBr_2$ (3.2 mg, 0.015 mmol), **L2** (8.1 mg, 0.015 mmol) and ^tBuONa (7.2 mg, 0.075 mmol), with anhydrous 1,4-dioxane (1mL) as solvent. The resulting mixture was stirred at room temperature for 5 hours to form the active catalyst. Subsequently, diphenylsilane **5** (167 μL, 0.9 mmol, 3.0 equiv.) was added and the mixture was stirred for 30 min before adding 1-(trifluoromethoxy)-4-vinylbenzene **4g** (56 mg, 0.3 mmol). The reaction mixture was removed from the glovebox and stirred at 40 °C under an argon atmosphere for 24 hours. Then the reaction solvent was evaporated in vacuum and the resulting residue was purified by silica gel column chromatography (hexane followed by diethyl ether/hexane = 1/100) affording 56 mg (50% yield) product **7g** as colorless oil.

6. Procedure for Gram Scale Hydrosilylation

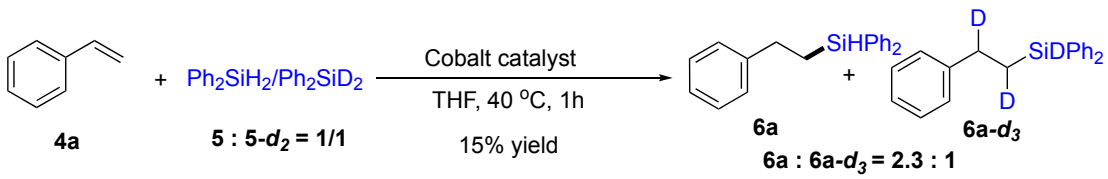


Before performing the reaction, the active catalyst was prepared in the glovebox. A borosilicate glass vial was charged with $CoBr_2$ (26.2 mg, 0.12 mmol), **L2** (64.3 mg, 0.12 mmol) and NaO^tBu (35 mg, 0.36 mmol). Subsequently, anhydrous THF (2 mL) was added as solvent. The resulting mixture was stirred at room temperature for 5 hours to form the active catalyst. The solvent was removed in vacuum and the vial containing the catalyst was removed from the glovebox.

To the above vial was added substrate **4ag** (0.75 mL, 8 mmol) and diphenylsilane (1.11 mL, 6 mmol) under air atmosphere. The reaction mixture was stirred at 40 °C under air atmosphere for 72 hours. Then the reaction mixture was purified by silica gel column chromatography (hexane followed by diethyl ether/hexane = 1/200) affording 1.2 g (75% yield) product **6ag** as colorless oil.

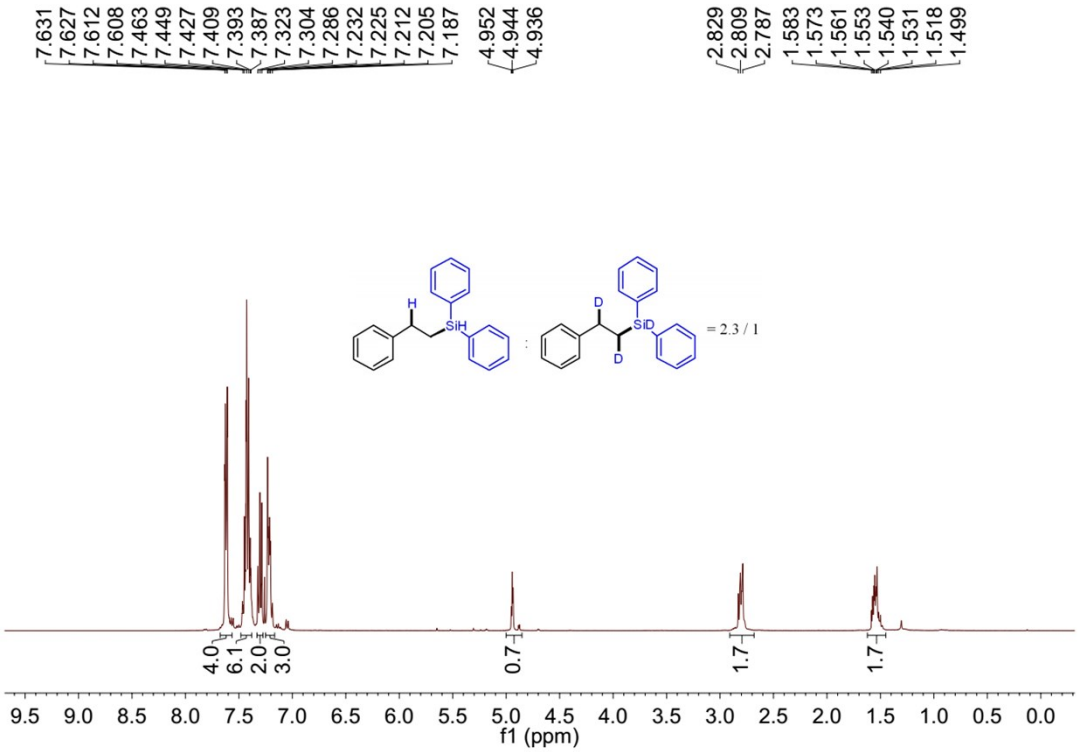
7. Procedure for KIE Study

7.1 Cobalt Catalyzed Hydrosilylation

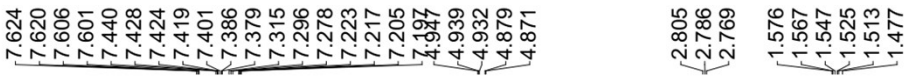


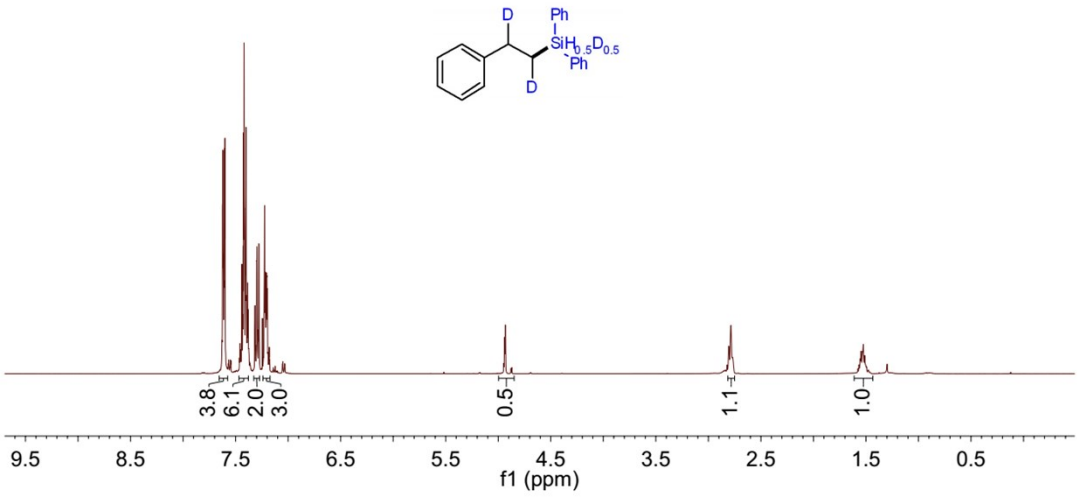
Inside an argon-atmosphere glovebox, a borosilicate glass vial was charged with $CoBr_2$ (3.2 mg, 0.015 mmol) and **L2** (8.1 mg, 0.015 mmol), with anhydrous THF (1mL) as solvent. Subsequently, $NaBHEt_3$ (30 μL) (1 mol/L in THF) was added as activator. The resulting mixture was stirred at room temperature for 5 hours to form the active catalyst. Subsequently, diphenylsilane **5** (42 μL, 0.23 mmol) and d^2-diphenylsilane ***d*²-5** (42 μL, 0.23 mmol) were added and the mixture was stirred for 30 min before adding styrene **4a** (34 μL, 0.3 mmol). The reaction

mixture was removed from the glovebox and stirred at 40 °C under an argon atmosphere for 1 hours. The reaction solvent was evaporated in vacuum and the resulting residue was purified by silica gel column chromatography (hexane followed by diethyl ether/hexane = 1/200) affording 13 mg (15% yield) mixture **6a** and ***d*^{3}-6a** as colorless oil. The ratio of **6a** and ***d*^{3}-6a** was determined by ^{1}H NMR spectra (as shown below).

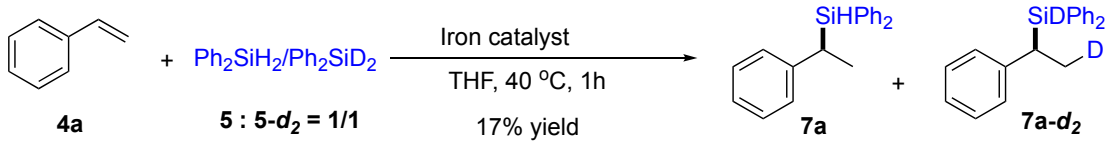


The reaction of *d*^{2}-diphenylsilane (***d*^{2}-5)** (84 μL, 0.45 mmol) with styrene (34 μL, 0.3 mmol) was similar to the above procedure. The deuterated product was determined by ^{1}H NMR spectra (as shown below).



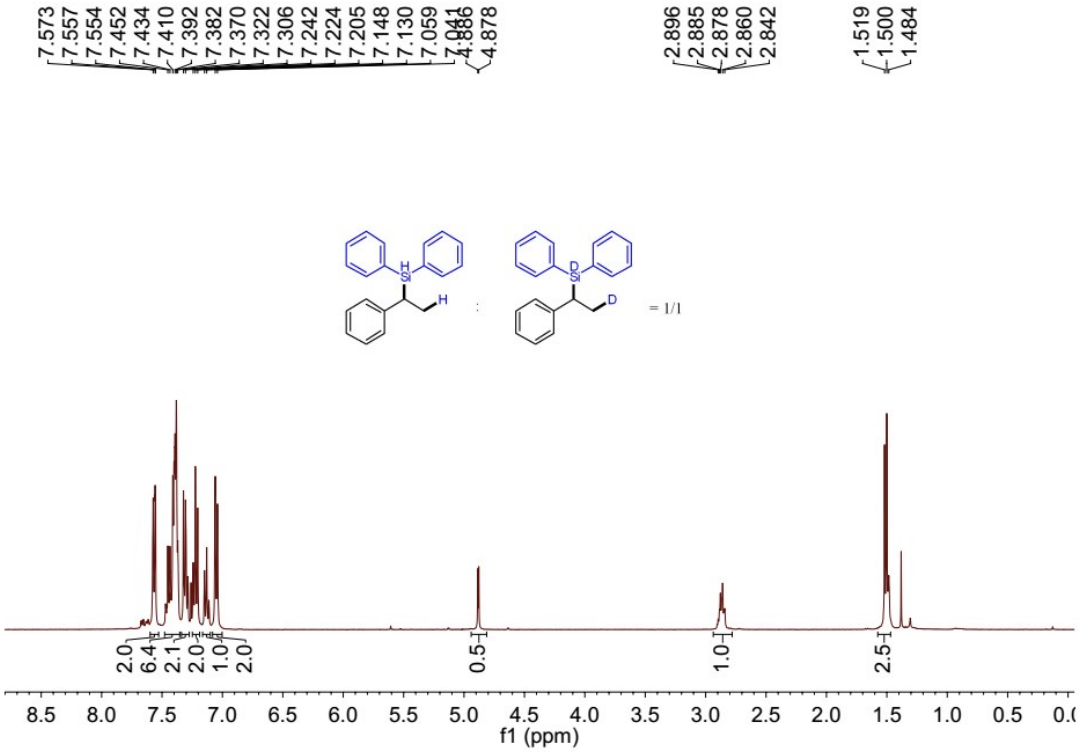


7.2 Iron Catalyzed Hydrosilylation

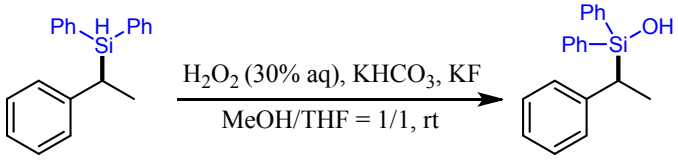


4a **5 : 5-d_2 = 1/1** **7a** **7a-d_2** **7a/7a-d_2 = 1/1**

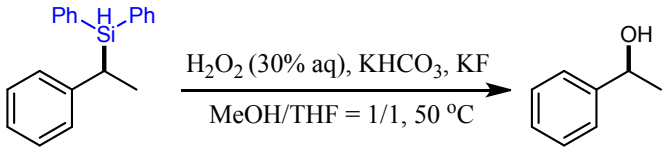
Inside an argon-atmosphere glovebox, a borosilicate glass vial was charged with $FeBr_2$ (3.2 mg, 0.015 mmol), **3a** (5.3 mg, 0.015 mmol), picolinaldehyde (1.4 μL, 0.015 mmol) and ^{t}BuONa (4.3 mg, 0.045 mmol), with anhydrous THF (1mL) as solvent. The resulting mixture was stirred at room temperature for 5 hours to form the active catalyst. Subsequently, diphenylsilane **5** (84 μL, 0.45 mmol) and d^2-diphenylsilane ***d*^{2}-5** (84 μL, 0.45 mmol) were added and the mixture was stirred for 30 min before adding styrene **4a** (34 μL, 0.3 mmol). The reaction mixture was removed from the glovebox and stirred at 40 °C under an argon atmosphere for 1 hours. Then the reaction solvent was evaporated in vacuum and the resulting residue was purified by silica gel column chromatography (hexane followed by diethyl ether/hexane = 1/200) affording 15 mg (17% yield) mixture **7a** and ***d*^{2}-7a** as colorless oil. The ratio of **7a** and ***d*^{2}-7a** was determined by ^{1}H NMR spectra (as shown below).


7.573
7.557
7.554
7.452
7.434
7.410
7.392
7.382
7.370
7.322
7.306
7.242
7.224
7.205
7.148
7.130
7.059
7.041
4.886
4.878
2.896
2.885
2.878
2.860
2.842
1.519
1.500
1.484
H
Si
H
D
Si
D
= 1/1
2.0
6.4
2.1
2.0
1.0
2.0
0.5
1.0
2.5
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
f1 (ppm)

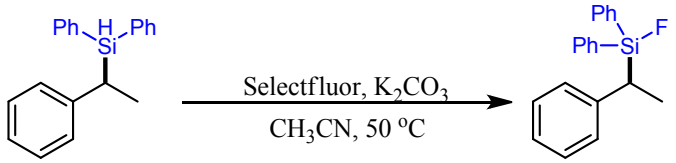
8. Derivatization of hydrosilylation products



To a solution of **7a** (144mg, 0.5 mmol, 1.0 equiv.) in MeOH and THF (6 mL, MeOH/THF = 1/1, v/v), KF (116 mg, 2.0 mmol, 4.0 equiv.), $KHCO_3$ (200 mg, 2.0 mmol, 4 equiv.) and hydrogen peroxide (1.2 ml, 30% aqueous solution) were added. Then the mixture was stirred at room temperature. After 20 h, the mixture was extracted with EtOAc and them the organic layer was separated and washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane/DCM = 1/1 followed by DCM) affording 132 mg (87% yield) of the title compound as a colorless oil.

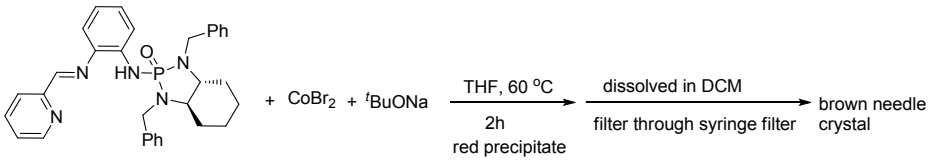


To a solution of **7a** (144mg, 0.5 mmol, 1.0 equiv.) in MeOH and THF (6 mL, MeOH/THF = 1/1, v/v), KF (232 mg, 4.0 mmol, 8.0 equiv.), $KHCO_3$ (250 mg, 2.5 mmol, 5 equiv.) and hydrogen peroxide (1.2 ml, 30% aqueous solution) were added. Then the mixture was stirred at 50 °C. After 20 h, the mixture was extracted with EtOAc and them the organic layer was separated and washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane/EtOAc = 10/1 followed by hexane/EtOAc = 6/1) affording 50 mg (82% yield) of the title compound as a colorless oil.



To a solution of **7a** (144mg, 0.5 mmol, 1.0 equiv.) in CH_3CN (2 mL), Selectfluor (425 mg, 1.2 mmol, 2.4 equiv.) and K_2CO_3 (83 mg, 0.6 mmol, 1.2 equiv.) were added. Then the mixture was stirred at 50 °C. After 20 h, the mixture was filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane followed by hexane/Et_2O = 100/1) affording 112 mg (73% yield) of the title compound as a colorless oil.

9. Preparation of precatalyst single crystals and their solid-state structures



Inside an argon-atmosphere glovebox, a borosilicate glass vial was charged with $CoBr_2$ (43.7 mg, 0.2 mmol) and **L2** (107.1 mg, 0.2 mmol), ^{t}BuONa (19.2 mg, 0.2 mmol), with anhydrous THF (1mL) as solvent. The reaction mixture was removed from the glovebox and stirred at 60 °C under an argon atmosphere for 2 hours. The desired complex precipitated from the solution and it was obtained by filtration in the glovebox. The desired complex was dissolved in the DCM and filtered through a syringe filter to remove the byproduct sodium bromide. The complex DCM solution was covered with toluene. After two or three days, the complex crystals can be been collected from the solution. Air- and moisture-sensitivity of the crystals precluded further analysis.

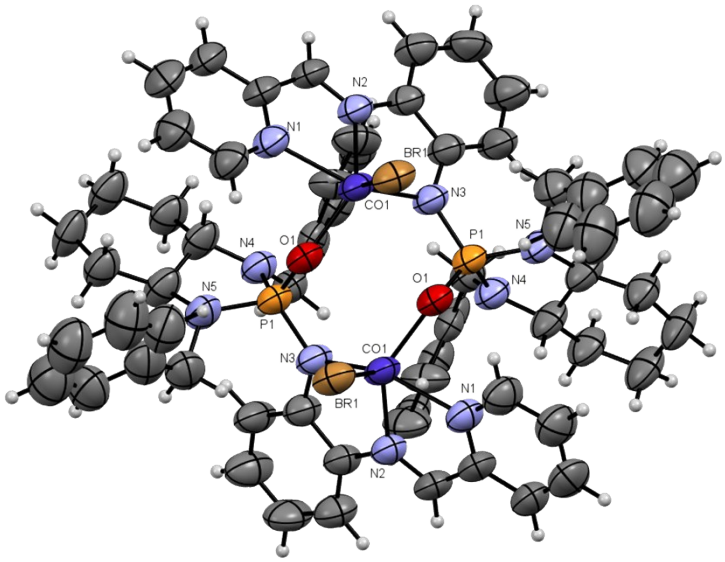
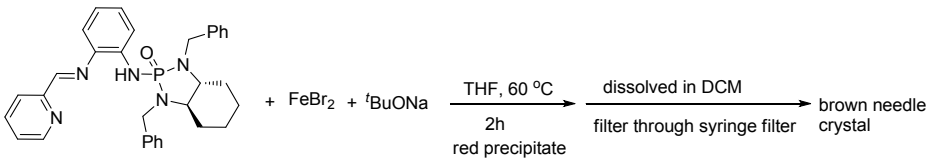


Figure S1. The thermal ellipsoids are represented at 50% probability. Carbon, hydrogen, nitrogen, oxygen, phosphorus, bromine and cobalt atoms are represented by gray, white, light blue, red, light orange, orange and purple ellipsoids, respectively. The B sites of disordered atoms were omitted for clarity.

Table S3. Crystal data and structure refinement for cobalt-precatalyst.

Identification code	fin19_21
Crystal color	red
Crystal habit	needle
Empirical formula	$C_{64}H_{66}Br_2Co_2N_{10}O_2P_2$
Formula weight	1346.88
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	C2/*c*
Unit cell dimensions	a = 21.1593(7) Å alpha = 90 °. b = 21.8994(6) Å beta = 112.926(3) °. c = 20.9154(5) Å gamma = 90 °.
Volume	8926.1(5) $Å^3$
Z	4
Calculated density	1.002 Mg/m^3
Absorption coefficient	4.584 mm^{-1}
F(000)	2760
Crystal size	0.469 x 0.066 x 0.058 mm
Theta range for data collection	3.035 to 77.231 °
Limiting indices	-26<=h<=26, -27<=k<=27, -26<=l<=19
Reflections collected / unique	57024 / 9235 [R(int) = 0.0650]
Completeness to theta = 67.679°	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9235 / 893 / 507
Goodness-of-fit on F^2	1.093
Final R indices [I>2sigma(I)]	R1 = 0.0928, wR2 = 0.2811
R indices (all data)	R1 = 0.1068, wR2 = 0.2950
Extinction coefficient	0.00091(10)
Largest diff. peak and hole	0.992 and -0.428 e.$Å^{-3}$



Inside an argon-atmosphere glovebox, a borosilicate glass vial was charged with $FeBr_2$ (43.1 mg, 0.2 mmol) and **L2** (107.1 mg, 0.2 mmol), ^{t}BuONa (19.2 mg, 0.2 mmol), with anhydrous THF (1mL) as solvent. The reaction mixture was removed from the glovebox and stirred at 60 °C under an argon atmosphere for 2 hours. The desired complex precipitated from the solution and it was obtained by filtration in the glovebox. The desired complex was dissolved in the DCM and filtered through a syringe filter to remove the byproduct sodium bromide. The complex DCM solution

was covered with toluene. After one or two days, the complex crystals can be been collected from the solution. Air- and moisture-sensitivity of the crystals precluded further analysis.

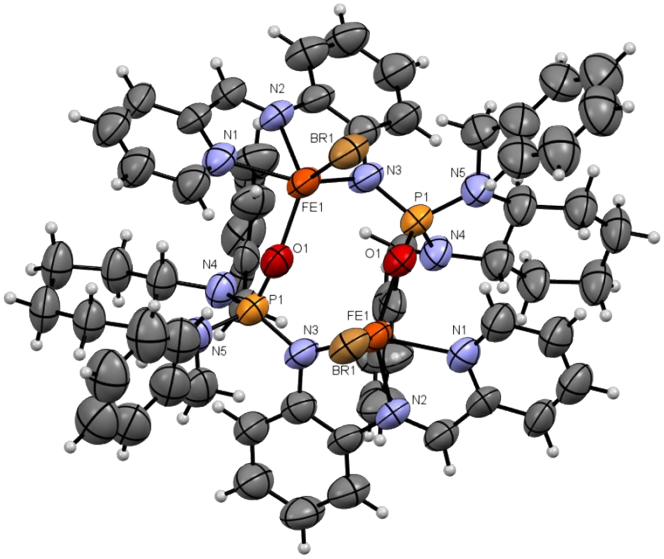


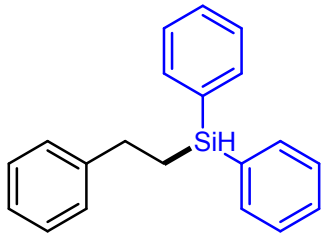
Figure S2. The thermal ellipsoids are represented at 50% probability. Carbon, hydrogen, nitrogen, oxygen, phosphorus, bromine and iron atoms are represented by gray, white, light blue, red, light orange, orange and light red ellipsoids, respectively. The B sites of disordered atoms were omitted for clarity.

Table S4. Crystal data and structure refinement for iron-precatalyst.

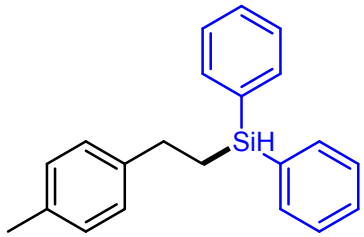
Identification code	fin19_23
Crystal color	red
Crystal habit	needle
Empirical formula	$C_{64}H_{66}Br_2Fe_2N_{10}O_2P_2$
Formula weight	1340.72
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	C2/*c*
Unit cell dimensions	a = 21.2987(13) Å alpha = 90 °. b = 21.5281(13) Å beta = 113.418(7) °. c = 21.0374(11) Å gamma = 90 °.
Volume	8851.5(10) $Å^3$
Z	4
Calculated density	1.006 Mg/m^3
Absorption coefficient	4.315 mm^{-1}
F(000)	2752
Crystal size	0.355 x 0.044 x 0.031 mm
Theta range for data collection	3.054 to 77.265 °
Limiting indices	-26<=h<=26, -26<=k<=26, -20<=l<=26
Reflections collected / unique	30025 / 8928 [R(int) = 0.0649]
Completeness to theta = 67.679°	99.0 %

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8928 / 893 / 507
Goodness-of-fit on F^2	1.281
Final R indices [I>2sigma(I)]	R1 = 0.1055, wR2 = 0.3224
R indices (all data)	R1 = 0.1342, wR2 = 0.3509
Extinction coefficient	0.0022(2)
Largest diff. peak and hole	1.139 and -0.504 e.Å-3

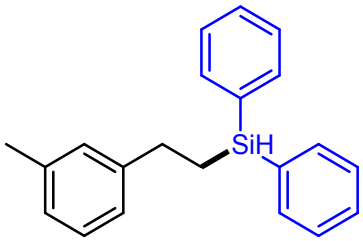
10. Experimental data for hydrosilylation products



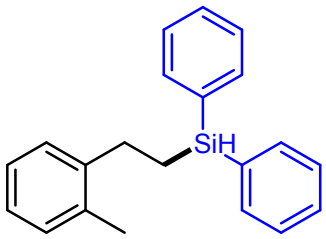
Phenethyldiphenylsilane (**6a**): colorless oil, 73mg, 84% yield, regioselectivity: 24/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.50-7.48 (m, 4H), 7.31-7.25 (m, 6H), 7.19-7.15 (m, 2H), 7.11-7.07 (m, 3H), 4.82-4.81 (t, *J* = 3.6 Hz, 1H), 2.70-2.66 (m, 2H), 1.45-1.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 144.3, 135.1, 134.0, 129.6, 128.3, 128.0, 127.8, 125.7, 30.4, 14.2; These data are in accordance with the literature. [S5]



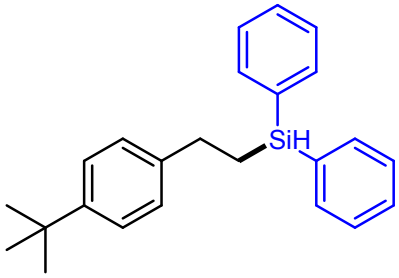
(4-Methylphenethyl)diphenylsilane (**6b**): colorless oil, 73mg, 80% yield, regioselectivity: 11/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.50-7.47 (m, 4H), 7.33-7.25 (m, 6H), 6.99 (s, 4H), 4.82-4.80 (t, *J* = 3.6 Hz, 1H), 2.66-2.62 (m, 2H), 2.22 (s, 3H), 1.43-1.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 141.3, 135.1, 134.1, 129.6, 129.0, 128.0, 127.7, 29.9, 21.0, 14.4; These data are in accordance with the literature.[S5]



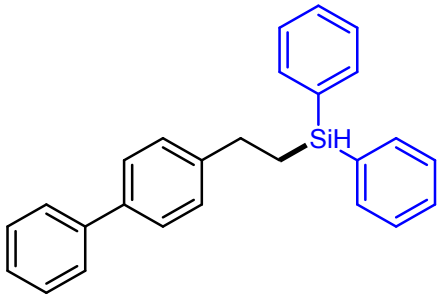
(3-Methylphenethyl)diphenylsilane (**6c**): Colorless oil, 71mg, 78% yield, regioselectivity:11/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.63-7.61 (m, 4H), 7.44-7.38 (m, 6H), 7.22-7.18 (m, 1H), 7.03-7.01 (d, *J* = 7.6 Hz, 3H), 4.95-4.93 (t, *J* = 3.8 Hz, 1H), 2.79-2.75 (m, 2H), 2.35 (s, 3H), 1.57-1.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 144.3, 137.9, 135.1, 134.1, 129.6, 128.6, 128.2, 128.0, 126.4, 124.8, 30.3, 21.4, 14.3; These data are in accordance with the literature.[S5]



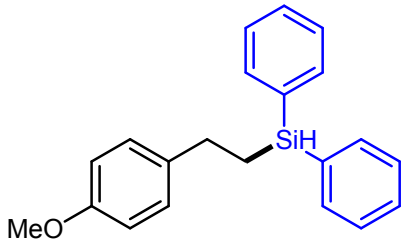
(2-Methylphenethyl)diphenylsilane (**6d**): colorless oil, 67mg, 74%, regioselectivity: 29/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.52-7.49 (m, 4H), 7.32-7.26 (m, 6H), 7.06-7.00 (m, 4H), 4.86-4.84 (t, *J* = 3.8 Hz, 1H), 2.66-2.62 (m, 2H), 2.14 (s, 3H), 1.41-1.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 142.6, 135.4, 135.1, 134.1, 130.1, 129.6, 128.03, 127.99, 126.0, 125.8, 27.8, 19.1, 13.0; IR (neat): 3066, 2924, 2114, 1486, 1427, 1115, 798, 726, 695; HRMS (ESI): cacld. for $C_{21}H_{22}Si$ $[M+H]^+$: 303.1564, found: 303.1566.



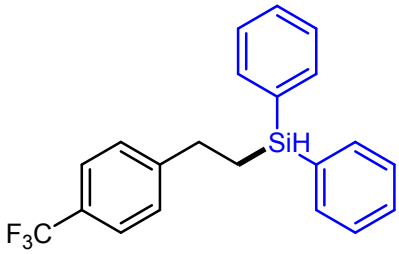
(4-(*tert*-Butyl)phenethyl)diphenylsilane (**6e**): colorless oil, 89mg, 86% yield, regioselectivity: 14/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.68-7.65 (m, 4H), 7.49-7.43 (m, 6H), 7.39-7.37 (d, *J* = 8.4 Hz, 2H), 7.23-7.21 (d, *J* = 8.0 Hz, 2H), 5.02-5.00 (t, *J* = 3.6 Hz, 1H), 2.86-2.82 (m, 2H), 1.64-1.58 (m, 2H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): 148.5, 141.3, 135.1, 134.1, 129.6, 128.0, 127.4, 125.2, 34.3, 31.4, 29.8, 14.1; These data are in accordance with the literature.[S5]



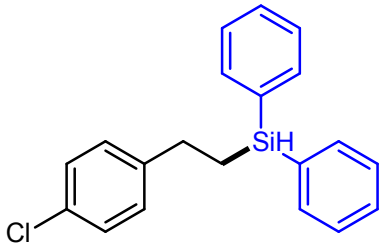
(2-([1,1'-Biphenyl]-4-yl)ethyl)diphenylsilane (**6f**): colorless oil, 100mg, 91% yield, regioselectivity: 9/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.64-7.60 (m, 6H), 7.54-7.52 (d, *J* = 8.4 Hz, 2H), 7.48-7.40 (m, 9H), 7.30-7.28 (d, *J* = 8.4 Hz, 2H), 4.98-4.96 (t, *J* = 3.8 Hz, 1H), 2.87-2.83 (m, 2H), 1.61-1.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 143.5, 141.1, 138.7, 135.5, 135.1, 134.0, 129.6, 128.7, 128.3, 128.0, 127.1, 127.0, 30.1, 14.2; These data are in accordance with the literature.[S5]



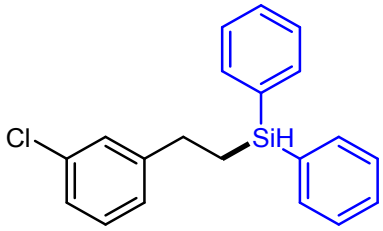
(4-Methoxyphenethyl)diphenylsilane (**6g**): colorless oil, 87mg, 91% yield, regioselectivity: 19/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.61-7.58 (m, 4H), 7.45-7.37 (m, 6H), 7.13-7.11 (d, *J* = 8.8 Hz, 1H), 6.84-6.82 (d, *J* = 8.4 Hz, 1H), 4.92-4.90 (t, *J* = 3.8 Hz, 1H), 3.80 (s, 3H), 2.76-2.72 (m, 2H), 1.54-1.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 157.6, 136.4, 135.1, 134.1, 129.6, 128.7, 128.0, 113.7, 55.2, 29.5, 14.5; These data are in accordance with the literature.[S5]



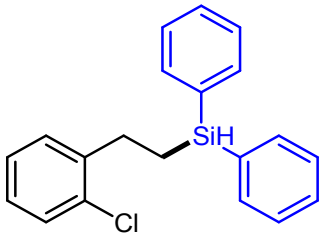
Diphenyl(4-(trifluoromethyl)phenethyl)silane (**6h**): colorless oil, 72mg, 67% yield, regioselectivity: 14/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.59-7.57 (m, 4H), 7.52-5.50 (d, *J* = 8.0 Hz, 2H), 7.43-7.37 (m, 6H), 7.29-7.27 (d, *J* = 8.0 Hz, 2H), 4.93-4.91 (t, *J* = 3.8 Hz, 1H), 2.85-2.81 (m, 2H), 1.55-1.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 148.3, 135.8, 135.1, 133.7, 129.8, 128.2, 128.1, 125.2 (q, $J_{F\text{-}C}$ = 4.3 Hz), 124.3 (q, $J_{F\text{-}C}$ = 270.5 Hz), 30.4, 14.1; IR (neat): 3068, 2925, 2118, 1616, 1428, 1322, 1162, 1115, 1065, 819, 799, 696; HRMS (ESI): cacld. for $C_{21}H_{19}F_3Si$ $[M+H]^+$: 357.1281, found: 357.1274.



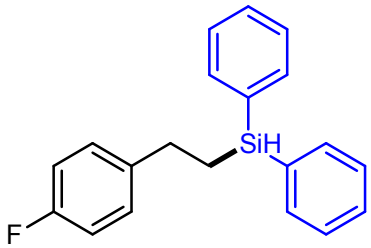
(4-Chlorophenethyl)diphenylsilane (**6i**): colorless oil, 68mg, 70% yield, regioselectivity: 16/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.49-7.46 (m, 4H), 7.32-7.26 (m, 6H), 7.13-7.10 (m, 2H), 7.00-6.98 (m, 2H), 4.80-4.79 (t, *J* = 3.2 Hz, 1H), 2.65-2.61 (t, *J* = 8.4 Hz, 2H), 1.41-1.35 (m, 2H); ^{13}C NMR: 142.7, 135.1, 133.8, 131.3, 129.7, 129.2, 128.4, 128.1, 29.8, 14.2; These data are in accordance with the literature.[S5]



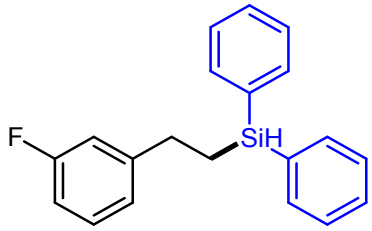
(3-Chlorophenethyl)diphenylsilane (**6j**): colorless oil, 70 mg, 72% yield, regioselectivity: 13/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.61-7.59 (m, 4H), 7.44-7.38 (m, 6H), 7.22-7.15 (m, 3H), 7.10-7.06 (m, 1H), 4.93-4.91 (t, *J* = 3.8 Hz, 1H), 2.78-2.74 (m, 2H), 1.54-1.49 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 146.3, 135.1, 134.0, 133.7, 129.7, 129.5, 128.1, 128.0, 126.1, 125.9, 30.2, 14.0; These data are in accordance with the literature.[S6]



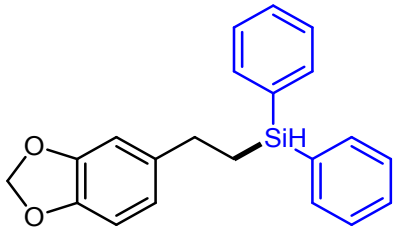
(2-Chlorophenethyl)diphenylsilane (**6k**): colorless oil, 49 mg, 51% yield, regioselectivity: 32/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.61-7.59 (m, 4H), 7.44-7.31 (m, 6H), 7.33-7.31 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.21-7.19 (dd, *J* = 7.6 Hz, *J* = 2.0 Hz, 1H), 7.18-7.14 (m, 1H), 7.13-7.09 (m, 1H), 4.95-4.93 (t, *J* = 3.6 Hz, 1H), 2.88-2.84 (m, 2H), 1.54-1.49 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 141.9, 135.8, 135.1, 133.9, 129.72, 129.67, 129.4, 128.0, 127.2, 126.8, 28.6, 12.7; IR (neat): 3066, 2922, 2116, 1472, 1442, 1115, 791, 728, 695; HRMS (ESI): cacld. for $C_{20}H_{19}ClSi$ $[M-H]^+$: 321.0861, found: 321.0858.



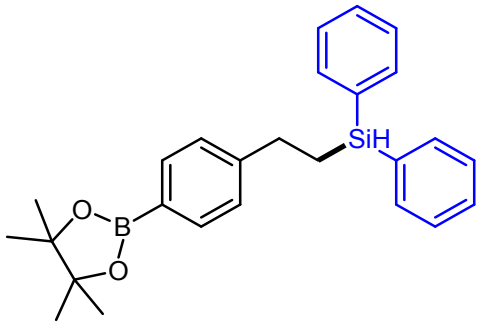
(4-Fluorophenethyl)diphenylsilane (**6l**): colorless oil, 66mg, 72% yield, regioselectivity: 22/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.50-7.47 (m, 4H), 7.33-7.26 (m, 6H), 7.04-7.01 (m, 2H), 6.87-6.83 (t, *J* = 8.6 Hz, 2H), 4.81-4.79 (t, *J* = 3.6 Hz, 1H), 2.67-2.63 (m, 2H), 1.43-1.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 161.1 (d, J_{F-C} = 241.9Hz), 139.8 (d, J_{F-C} = 3.2 Hz), 135.1, 133.9, 129.7, 129.1 (d, J_{F-C} = 7.8 Hz), 128.1, 115.0 (d, J_{F-C} = 21.0 Hz), 29.7, 14.4; These data are in accordance with the literature.[S5]



(3-Fluorophenethyl)diphenylsilane (**6m**): colorless oil, 71 mg, 77% yield, regioselectivity: 15/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.61-7.59 (m, 4H), 7.46-7.38 (m, 6H), 7.25-7.20 (m, 1H), 6.98-6.96 (d, *J* = 7.6 Hz, 1H), 6.92-6.86 (m, 2H), 4.94-4.92 (t, *J* = 3.6 Hz, 1H), 2.80-2.76 (m, 2H), 1.55-1.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 162.9 (d, J_{F-C} = 244.0 Hz), 146.9 (d, J_{F-C} = 7.0 Hz), 135.1, 133.8, 129.7, 129.6, 128.1, 123.5 (d, J_{F-C} = 2.9 Hz), 114.7 (d, J_{F-C} = 20.7 Hz), 112.5 (d, J_{F-C} = 20.9 Hz), 30.2 (d, J_{F-C} = 2.0 Hz), 14.0; These data are in accordance with the literature.[S5]

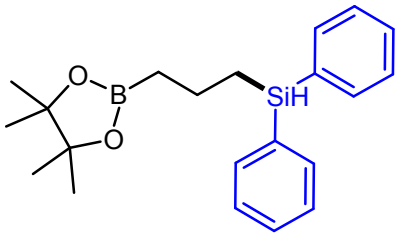


(2-(Benzo[d][1,3]dioxol-5-yl)ethyl)diphenylsilane (**6n**): colorless oil, 70 mg, 70% yield, regioselectivity: 12/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.58-7.56 (m, 4H), 7.42-7.35 (m, 6H), 6.71-6.68 (m, 2H), 6.63-6.61 (d, *J* = 8.8 Hz, 1H), 5.91 (s, 2H), 4.89-4.87 (t, *J* = 3.8 Hz, 1H), 2.71-2.67 (m, 2H), 1.50-1.45 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 147.5, 145.5, 138.3, 135.1, 134.0, 129.6, 128.0, 120.4, 108.4, 108.0, 100.7, 30.2, 14.6; IR (neat): 2883, 2115, 1500, 1487, 1427, 1240, 1114, 1037, 938, 801, 729, 695; HRMS (ESI): cacld. for $C_{21}H_{20}O_2Si$ $[M-H]^+$: 331.1149, found: 331.1146.

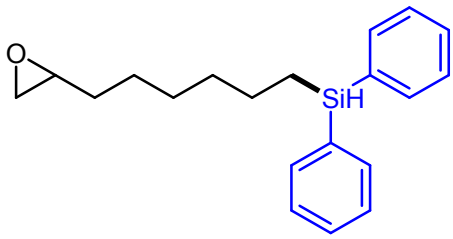


Diphenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenethyl)silane (**6o**): colorless oil, 90mg, 71% yield, regioselectivity: 8/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.77-7.75 (d, *J* = 8.0 Hz, 2H), 7.62-7.59 (m, 4H), 7.44-7.38 (m, 6H), 7.24-7.22 (d, *J* = 8.0 Hz, 2H), 4.93-4.91 (t, *J* = 3.8 Hz, 1H), 2.82-2.78 (m, 2H), 1.56-1.51 (m, 2H), 1.37 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): 147.8, 135.1,

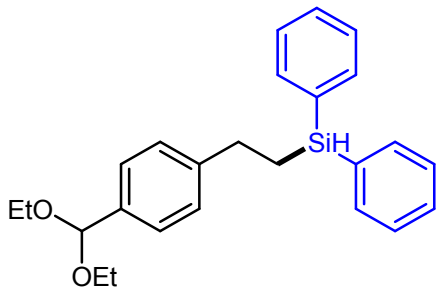
134.9, 133.9, 129.6, 128.0, 127.3, 83.6, 30.6, 24.8, 14.1; IR (neat): 2975, 2117, 1609, 1357, 1142, 1087, 859, 804, 731, 697; HRMS (ESI): cacld. for $C_{26}H_{31}BO_2Si$ $[M+H]^+$: 415.2259, found: 415.2251.



Diphenyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)silane (**6p**): colorless oil, 75mg, 71% yield, regioselectivity: >99/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.56-7.54 (m, 4H), 7.37-7.31 (m, 6H), 4.85-4.83 (t, *J* = 3.6 Hz, 1H), 1.64-1.56 (m, 2H), 1.22-1.16 (m, 14H), 0.91-0.88 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 135.1, 134.7, 129.4, 127.9, 82.9, 24.8, 19.1, 15.2; IR (neat): 2976, 2924, 2112, 1427, 1369, 1311, 1142, 1115, 803, 730, 696; HRMS (ESI): cacld. for $C_{21}H_{29}BO_2Si$ $[M+Na]^+$: 375.1922, found: 375.1924.

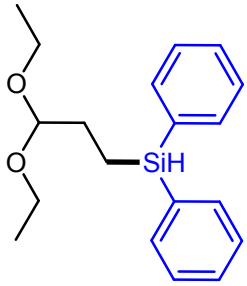


(6-(Oxiran-2-yl)hexyl)diphenylsilane (**6q**): colorless oil, 64mg, 69% yield, regioselectivity: >99/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.57-7.55 (m, 4H), 7.42-7.34 (m, 6H), 4.86-4.85 (t, *J* = 3.6 Hz, 1H), 2.91-2.86 (m, 1H), 2.75-2.73 (t, *J* = 4.6 Hz, 1H), 2.46-2.44 (dd, *J* = 5.2 Hz, *J* = 2.8 Hz, 1H), 1.51-1.33 (m, 10H), 1.18-1.13 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 135.1, 134.6, 129.5, 127.9, 52.4, 47.1, 33.0, 32.5, 29.0, 25.8, 24.3, 12.1; IR (neat): 2921, 2852, 2112, 1427, 1115, 802, 728, 696; HRMS (ESI): cacld. for $C_{20}H_{26}OSi$ $[M+H]^+$: 311.1826, found: 311.1820.

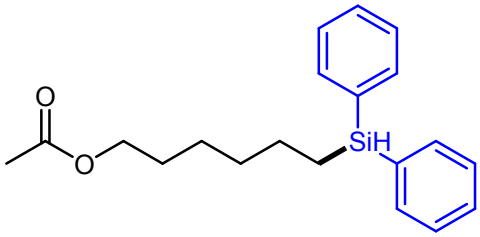


(4-(Diethoxymethyl)phenethyl)diphenylsilane (**6r**): colorless oil, 76mg, 65% yield, regioselectivity: 10/1; ^{1}H NMR (400 MHz, d^6-acetone): 7.60-7.58 (m, 4H), 7.41-7.37 (m, 6H), 7.32-7.30 (d, *J* = 8.0 Hz, 2H), 7.19-7.17 (d, *J* = 8.4 Hz, 2H), 5.43 (s, 1H), 4.85-4.83 (t, *J* = 3.6 Hz, 1H), 3.57-3.51 (m, 2H),

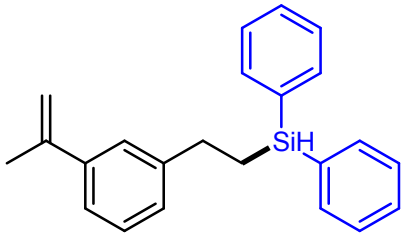
3.47-3.42 (m, 2H), 2.75-2.71 (m, 2H), 1.56-1.51 (m, 2H), 1.15-1.12 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, d^6-acetone): 144.2, 137.2, 135.1, 134.1, 129.7, 128.2, 127.5, 126.7, 101.3, 60.4, 30.1, 14.8, 14.0; IR (neat): 2972, 2878, 2116, 1442, 1332, 1109, 1050, 802, 729, 696; HRMS (ESI): cacld. for $C_{25}H_{30}O_2Si$ [M-H]$^+$: 389.1931, found: 389.1929.



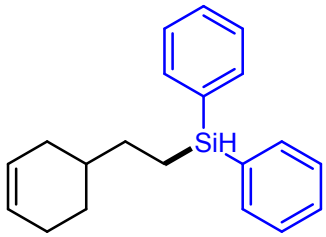
(3,3-Diethoxypropyl)diphenylsilane (**6s**): colorless oil, 58mg, 62% yield, regioselectivity: >99/1; ^{1}H NMR (400 MHz, d^6-acetone): 7.58-7.55 (m, 4H), 7.42-7.34 (m, 6H), 4.84-4.82 (t, *J* = 3.8 Hz, 1H), 4.44-4.41 (t, *J* = 5.4 Hz, 1H), 3.57-3.50 (m, 2H), 3.42-3.35 (m, 2H), 1.67-1.62 (m, 2H), 1.22-1.17 (m, 2H), 1.10-1.06 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, d^6-acetone): 135.7, 135.0, 130.4, 128.8, 104.7, 61.4, 29.1, 15.6, 7.2; IR (neat): 2972, 2876, 2115, 1428, 1116, 1057, 804, 729, 696; HRMS (ESI): cacld. for $C_{19}H_{26}O_2Si$ [M+H]$^+$: 315.1775, found: 315.1769.



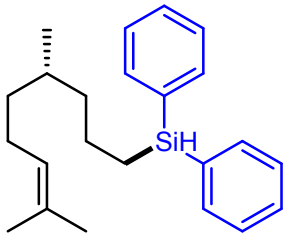
6-(Diphenylsilyl)hexyl acetate (**6t**): colorless oil, 60mg, 61% yield, regioselectivity: >99/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.49-7.46 (m, 4H), 7.33-7.25 (m, 6H), 4.78-4.76 (t, *J* = 3.8 Hz, 1H), 3.96-3.93 (t, *J* = 6.6 Hz, 2H), 1.95 (s,3H), 1.53-1.46 (m, 2H), 1.41-1.24 (m, 6H), 1.09-1.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.2, 135.0, 134.5, 129.5, 127.9, 64.5, 32.7, 28.4, 25.5, 24.3, 21.0, 12.1; IR (neat): 2922, 2854, 2113, 1735, 1427, 1233, 1115, 1035, 803, 729, 696; HRMS (ESI): cacld. for $C_{20}H_{26}O_2Si$ [M-H]$^+$: 325.1618, found: 325.1622.



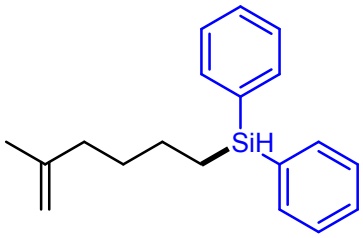
Diphenyl(3-(prop-1-en-2-yl)phenethyl)silane (**6u**): colorless oil, 69mg, 70% yield, regioselectivity: 22/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.51-7.49 (m, 4H), 7.33-7.27 (m, 6H), 7.20-7.13 (m, 3H), 7.03-7.01 (d, *J* = 7.6 Hz, 1H), 5.25 (m, 1H), 4.98-4.97 (m, 1H), 4.83-4.82 (t, *J* = 3.6 Hz, 1H), 2.72-2.67 (m, 2H), 2.05 (s, 3H), 1.47-1.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 144.2, 143.4, 141.3, 135.1, 134.0, 129.6, 128.2, 128.0, 126.9, 125.1, 123.0, 112.3, 30.5, 21.9, 14.3; IR (neat): 3066, 2920, 2116, 1683, 1600, 1427, 1272, 1114, 798, 728, 695; HRMS (ESI): cacld. for $C_{23}H_{24}Si$ $[M+H]^+$: 329.1720, found: 329.1719.



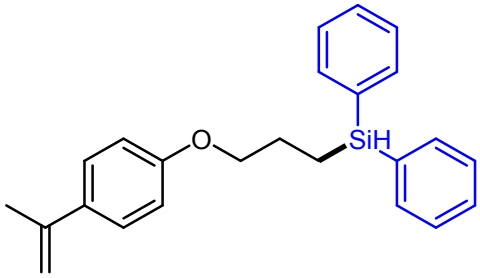
(2-(Cyclohex-3-en-1-yl)ethyl)diphenylsilane (**6v**): colorless oil, 71mg, 81% yield, regioselectivity: >99/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.58-7.55 (m, 4H), 7.43-7.35 (m, 6H), 5.68-5.62 (m, 2H), 4.86-4.85 (t, *J* = 3.6 Hz, 1H), 2.16-2.10 (m, 1H), 2.04-2.00 (m, 2H), 1.79-1.75 (m, 1H), 1.66-1.51 (m, 2H), 1.46-1.40 (m, 2H), 1.24-1.15 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 135.1, 134.6, 129.5, 128.0, 127.1, 126.6, 36.3, 31.5, 31.1, 28.4, 25.3, 9.2; These data are in accordance with the literature. [S5]



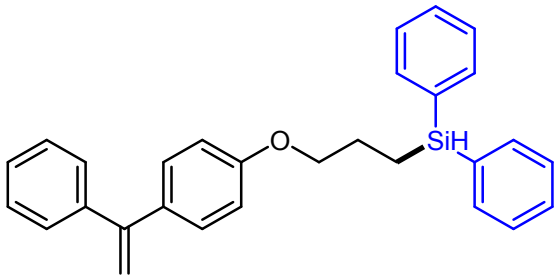
(S)-(4,8-Dimethylnon-7-en-1-yl)diphenylsilane (**6w**): colorless oil, 66mg, 65% yield, regioselectivity: >99/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.57-7.55 (m, 4H), 7.42-7.34 (m, 6H), 5.10-5.06 (m, 1H), 4.86-4.85 (t, *J* = 3.6 Hz, 1H), 2.00-1.87 (m, 2H), 1.68 (s, 3H), 1.59 (s, 3H), 1.42-1.35 (m, 3H), 1.30-1.06 (m, 6H), 0.83-0.81 (d, *J* = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 135.1, 134.7, 131.0, 129.4, 127.9, 125.0, 40.5, 37.0, 32.0, 25.7, 25.5, 21.8, 19.5, 17.6, 12.3; IR (neat): 2960, 2918, 2854, 2114, 1427, 1114, 802, 728, 696; HRMS (ESI): cacld. for $C_{23}H_{32}Si$ $[M+H]^+$: 337.2346, found: 337.2346.



(5-Methylhex-5-en-1-yl)diphenylsilane (**6x**): colorless oil, 54mg, 64% yield, regioselectivity: >99/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.57-7.55 (m, 4H), 7.40-7.34 (m, 6H), 4.87-4.85 (t, *J* = 3.8 Hz, 1H), 4.67-4.63 (m, 2H), 2.01-1.98 (t, *J* = 7.0 Hz, 2H), 1.68 (s, 3H), 1.53-1.45 (m, 4H), 1.19-1.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 146.0, 135.1, 134.6, 129.5, 127.9, 109.6, 37.4, 31.1, 24.1, 22.4, 12.0; IR (neat): 3067, 2924, 2853, 2114, 1647, 1427, 1114, 884, 801, 728, 695; HRMS (ESI): cacld. for $C_{19}H_{24}Si$ $[M+H]^+$: 281.1720, found: 281.1718.

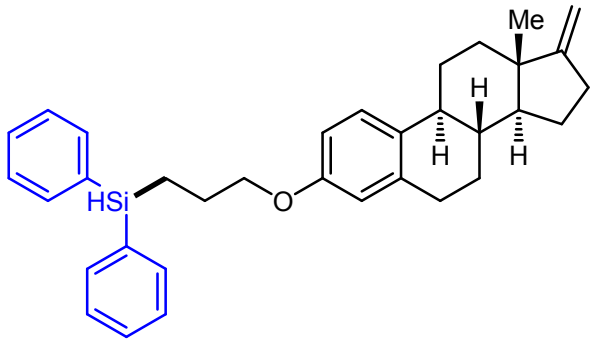


Diphenyl(3-(4-(prop-1-en-2-yl)phenoxy)propyl)silane (**6y**): colorless oil, 90mg, 84% yield, regioselectivity: >99/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.51-7.49 (m, 4H), 7.33-7.28 (m, 8H), 6.75-6.73 (d, *J* = 8.8 Hz, 2H), 5.20 (m, 1H), 4.91-4.90 (m, 1H), 4.85-4.83 (t, *J* = 3.8 Hz, 1H), 3.90-3.86 (t, *J* = 6.4 Hz, 2H), 2.05 (m, 3H), 1.89-1.83 (m, 2H), 1.25-1.19 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 158.4, 142.6, 135.1, 134.0, 133.5, 129.7, 128.0, 126.5, 114.1, 110.5, 69.9, 24.3, 21.9, 8.4; IR (neat): 3066, 2920, 2116, 1605, 1510, 1427, 1243, 1178, 1115, 831, 804, 730, 696; HRMS (ESI): cacld. for $C_{24}H_{26}OSi$ $[M+H]^+$: 359.1826, found: 359.1822.

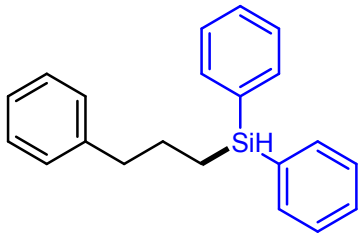


Diphenyl(3-(4-(1-phenylvinyl)phenoxy)propyl)silane (**6z**): colorless oil, 96mg, 76% yield, regioselectivity: >99/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.60-7.57 (m, 4H), 7.43-7.31 (m, 11H), 7.26-7.24 (d, *J* = 9.6 Hz, 2H), 6.83-6.80 (d, *J* = 8.8 Hz, 2H), 5.40-5.39 (d, *J* = 1.2 Hz, 1H), 5.35 (d, *J* = 1.2

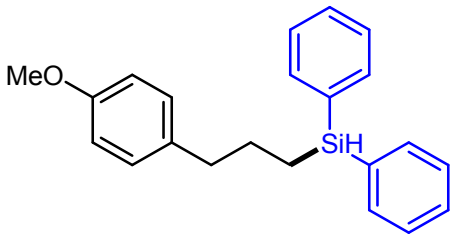
Hz, 1H), 4.93-4.92 (t, *J* = 3.8 Hz, 1H), 3.99-3.95 (t, *J* = 6.6 Hz, 1H), 1.99-1.92 (m, 2H), 1.33-1.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 158.7, 149.5, 141.8, 135.1, 134.0, 133.8, 129.7, 129.3, 128.3, 128.1, 128.0, 127.6, 114.0, 112.8, 69.9, 24.3, 8.5; IR (neat): 3065, 2929, 2115, 1650, 1598, 1507, 1427, 1245, 1172, 1114, 804, 731, 696; HRMS (ESI): cacld. for $C_{29}H_{28}OSi$ $[M+H]^+$: 421.1982, found: 421.1983.



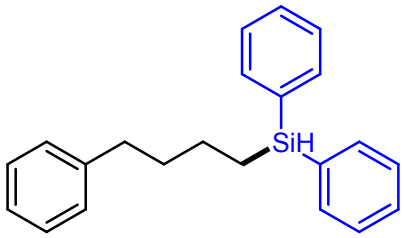
(3-(((8S,9S,13S,14S)-13-Methyl-17-methylene-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)propyl)diphenylsilane (**6aa**): white solid, m.p.: 102-104 °C; 101mg, 68% yield, regioselectivity: >99/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.59-7.56 (m, 4H), 7.42-7.35 (m, 6H), 7.21-7.19 (d, *J* = 8.4 Hz, 1H), 6.68-6.66 (dd, *J* = 8.8 Hz, *J* = 2.8 Hz, 1H), 6.59 (d, *J* = 2.4 Hz, 1H), 4.92-4.90 (t, *J* = 3.8 Hz, 1H), 4.68-4.67 (m, 2H), 3.94-3.91 (t, *J* = 6.6 Hz, 2H), 2.88-2.79 (m, 2H), 2.58-2.51 (m, 1H), 2.38-2.19 (m, 3H), 1.98-1.88 (m, 4H), 1.85-1.78 (m, 1H), 1.55-1.27 (m, 8H), 0.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 161.8, 156.8, 137.9, 135.1, 134.1, 132.7, 129.6, 128.0, 126.3, 114.4, 112.0, 100.8, 69.9, 53.4, 44.4, 44.0, 38.8, 35.7, 29.9, 29.4, 27.6, 26.6, 24.3, 23.9, 18.5, 8.4; IR (neat): 2931, 2854, 2119, 1611, 1499, 1427, 1279, 1249, 1109, 1014, 846, 802, 772, 696; HRMS (ESI): cacld. for $C_{34}H_{40}OSi$ $[M-H]^+$: 491.2765, found: 491.2769.



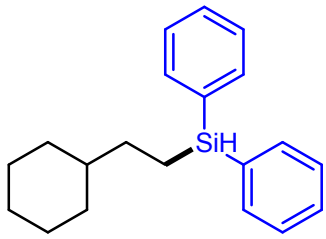
Diphenyl(3-phenylpropyl)silane (**6ab**): colorless oil, 74mg, 82% yield, regioselectivity: >99/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.59-7.57 (m, 4H), 7.45-7.37 (m, 6H), 7.32-7.29 (m, 2H), 7.23-7.17 (m, 3H), 4.93-4.91 (t, *J* = 3.6 Hz, 1H), 2.74-2.70 (t, *J* = 7.6 Hz, 2H), 1.88-1.80 (m, 2H), 1.26-1.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 142.1, 135.1, 134.3, 129.5, 128.5, 128.2, 128.0, 125.7, 39.2, 26.3, 11.8; These data are in accordance with the literature.[S5]



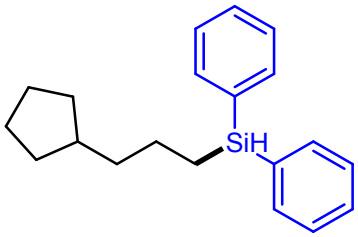
(3-(4-Methoxyphenyl)propyl)diphenylsilane (**6ac**): colorless oil, 93mg, 93% yield, regioselectivity: >99/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.57-7.54 (m, 4H), 7.42-7.31 (m, 6H), 7.08-7.05 (d, *J* = 8.8 Hz, 2H), 6.84-6.82 (d, *J* = 8.8 Hz, 2H), 4.90-4.88 (t, *J* = 4.0 Hz, 1H), 3.79 (s, 3H), 2.65-2.61 (t, *J* = 8.0 Hz, 2H), 1.81-1.73 (m, 2H), 1.21-1.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 157.7, 135.1, 134.4, 134.2, 129.5, 129.4, 127.9, 113.6, 55.2, 38.3, 26.5, 11.7; These data are in accordance with the literature.[S7]



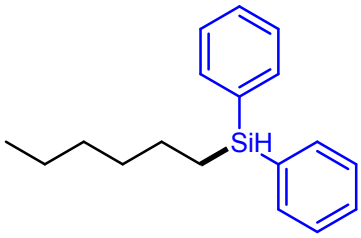
Diphenyl(4-phenylbutyl)silane (**6ad**): colorless oil, 72mg, 76%, regioselectivity: >99/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.48-7.46 (m, 4H), 7.31-7.25 (m, 6H), 7.19-7.15 (m, 2H), 7.10-7.04 (m, 3H), 4.79-4.77 (t, *J* = 3.6 Hz, 1H), 2.53-2.49 (t, *J* = 7.8 Hz, 2H), 1.65-1.58 (m, 2H), 1.48-1.41 (m, 2H), 1.13-1.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 142.6, 135.1, 134.5, 129.5, 128.4, 128.2, 128.0, 125.6, 35.5, 34.9, 24.1, 12.0; These data are in accordance with the literature.[S8]



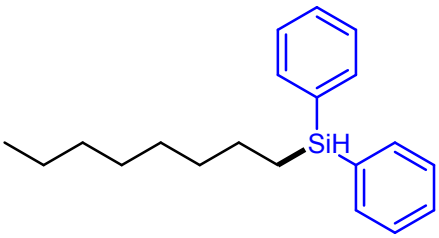
(2-Cyclohexylethyl)diphenylsilane (**6ae**): colorless oil, 70mg, 79% yield, regioselectivity: >99/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.61-7.58 (m, 4H), 7.45-7.37 (m, 6H), 4.89-4.87 (t, *J* = 3.6 Hz, 1H), 1.80-1.66 (m, 5H), 1.41-1.35 (m, 2H), 1.28-1.14 (m, 6H), 0.93-0.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 135.1, 134.7, 129.4, 127.9, 40.5, 32.9, 31.8, 26.7, 26.4, 9.2; These data are in accordance with the literature. [S5]



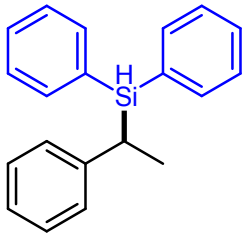
(3-Cyclopentylpropyl)diphenylsilane (**6af**): colorless oil, 62mg, 70% yield, regioselectivity: >99/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.59-7.57 (m, 4H), 7.43-7.35 (m, 6H), 4.89-4.87 (t, *J* = 3.6 Hz, 1H), 1.80-1.67 (m, 3H), 1.60-1.55 (m, 2H), 1.53-1.46 (m, 4H), 1.42-1.37 (m, 2H), 1.19-1.14 (m, 2H), 1.08-0.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 135.1, 134.7, 129.4, 127.9, 39.8, 39.7, 32.6, 25.1, 23.5, 12.3; IR (neat): 2944, 2916, 2113, 1427, 1114, 802, 726, 695; HRMS (ESI): cacld. for $C_{20}H_{26}Si$ $[M+H]^+$: 295.1877, found: 295.1876.



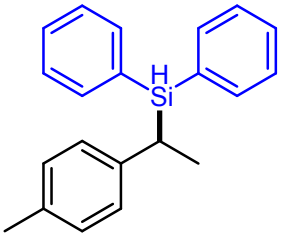
Hexyldiphenylsilane (**6ag**): colorless oil, 51mg, 63% yield, regioselectivity: >99/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.49-7.46 (m, 4H), 7.33-7.25 (m, 6H), 4.78-4.76 (t, *J* = 3.8 Hz, 1H), 1.42-1.34 (m, 2H), 1.32-1.25 (m, 2H), 1.19-1.15 (m, 4H), 1.09-1.04 (m, 2H), 0.80-0.76 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 135.2, 134.8, 129.6, 128.0, 33.0, 31.6, 24.5, 22.7, 14.2, 12.3; These data are in accordance with the literature.[S9]



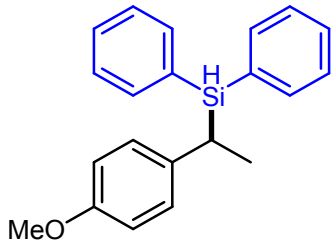
Octyldiphenylsilane (**6ah**): colorless oil, 58mg, 65% yield, regioselectivity: >99/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.49-7.46 (m, 4H), 7.31-7.25 (m, 6H), 4.78-4.76 (t, *J* = 3.8 Hz, 1H), 1.41-1.34 (m, 2H), 1.31-1.26 (m, 2H), 1.20-1.15 (m, 8H), 1.09-1.04 (m, 2H), 0.80-0.77 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 135.1, 134.7, 129.4, 127.9, 33.2, 31.9, 29.20, 29.17, 24.4, 22.7, 14.1, 12.1; These data are in accordance with the literature.[S10]



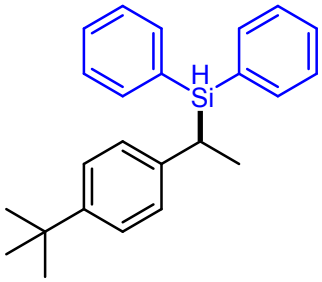
Diphenyl(1-phenylethyl)silane (7a): colorless oil, 84mg, 97% yield, regioselectivity: >99/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.46-7.43 (m, 2H), 7.33-7.25 (m, 6H), 7.20-7.17 (m, 2H), 7.12-7.08 (m, 2H), 7.03-6.99 (m, 1H), 6.94-6.92 (m, 2H), 4.76-4.75 (d, *J* = 3.2 Hz, 1H), 2.78-2.72 (m, 1H), 1.40-1.38 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 144.3, 135.7, 135.5, 133.0, 129.7, 129.5, 128.1, 127.9, 127.7, 127.68, 124.9, 26.9, 16.5. These data are in accordance with the literature.[S5]



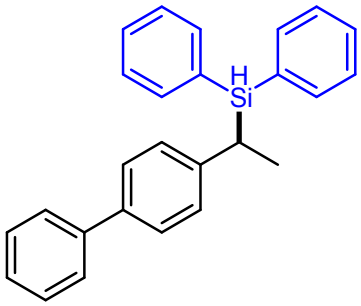
Diphenyl(1-(*p*-tolyl)ethyl)silane (**7b**): colorless oil, 88mg, 97% yield, regioselectivity: 30/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.58-7.55 (m, 2H), 7.46-7.36 (m, 6H), 7.33-7.29 (m, 2H), 7.05-7.03 (d, *J* = 8.0 Hz, 2H), 6.96-6.94 (d, *J* = 8.4 Hz, 2H), 4.88-4.87 (d, *J* = 3.2 Hz, 1H), 2.87-2.80 (m, 1H), 2.32 (s, 3H), 1.49-1.47 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 141.2, 135.7, 135.5, 134.2, 133.17, 133.15, 129.6, 129.5, 128.9, 127.9, 127.7, 127.6, 26.3, 20.9, 16.7; These data are in accordance with the literature. [S5]



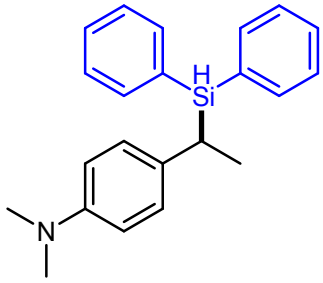
(1-(4-Methoxyphenyl)ethyl)diphenylsilane (**7c**): colorless oil, 95mg, 99% yield, regioselectivity: 39/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.55-7.53 (m, 2H), 7.45-7.35 (m, 6H), 7.31-7.27 (m, 2H), 6.97-6.93 (m, 2H), 6.78-6.75 (m, 2H), 4.85-4.84 (d, *J* = 3.2 Hz, 1H), 3.78 (s, 3H), 2.82-2.76 (m, 1H), 1.46-1.44 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): 157.2, 136.4, 135.8, 135.7, 133.3, 133.26, 129.8, 129.6, 128.7, 128.0, 127.8, 113.7, 55.3, 25.9, 17.0. These data are in accordance with the literature. [S5]



(1-(4-(*tert*-Butyl)phenyl)ethyl)diphenylsilane (**7d**): colorless oil, 101mg, 98 % yield, regioselectivity: >99/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.58-7.56 (m, 2H), 7.47-7.36 (m, 6H), 7.31-7.25 (m, 4H), 7.01-6.99 (d, *J* = 8.0 Hz, 2H), 4.89-4.88 (d, *J* = 3.2 Hz, 1H), 2.89-2.82 (m, 1H), 1.52-1.50 (d, *J* = 7.2 Hz, 3H), 1.35 (s, 9H); ^{13}C NMR ($CDCl_3$, 100MHz): 147.7, 141.1, 135.7, 135.5, 133.21, 133.16, 129.6, 129.5, 127.9, 127.6, 127.3, 125.0, 34.2, 31.4, 26.2, 16.5. These data are in accordance with the literature. [S5]

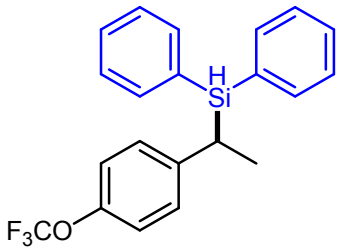


(1-([1,1'-Biphenyl]-4-yl)ethyl)diphenylsilane (**7e**): colorless oil, 80mg,73% yield, regioselectivity: 71/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.61-7.56 (m, 4H), 7.47-7.28 (m, 13H), 7.10-7.08 (d, *J* = 8.4 Hz, 2H), 4.89-4.88 (d, *J* = 3.2 Hz, 1H), 2.94-2.87 (m, 1H), 1.53-1.51 (d, *J* =7.2 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): 143.5, 141.0, 137.6, 135.7, 135.6, 132.9, 129.7, 129.6, 128.7, 128.1, 127.9, 127.7, 126.9, 126.82, 126.77, 26.7, 16.4. These data are in accordance with the literature. [S5]

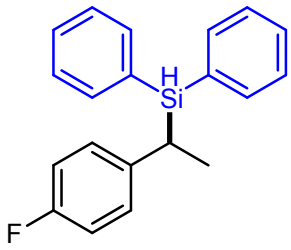


4-(1-(Diphenylsilyl)ethyl)-N,N-dimethylaniline (**7f**): colorless oil, 98mg, 99% yield, regioselectivity: >99/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.59-7.57 (m, 2H), 7.46-7.36 (m, 6H), 7.33-7.29 (m, 2H), 6.97-6.95 (d, *J* = 8.8 Hz, 2H), 6.69-6.67 (d, *J* = 8.8 Hz, 2H), 4.89-4.88 (d, *J* = 3.6 Hz, 1H), 2.93 (s, 6H), 2.81-2.75 (m, 1H), 1.48-1.46 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): 148.4, 135.7, 135.6,

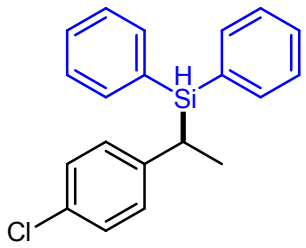
133.54, 133.48, 132.4, 129.5, 129.4, 128.3, 127.8, 127.6, 113.1, 40.9, 25.4, 16.9; IR (neat): 2948, 2863, 2111, 1612, 1515, 1443, 1342, 1113, 803, 730; HRMS (ESI): cacld. for $C_{22}H_{25}NSi$ $[M+H]^+$: 332.1829, found: 332.1819.



Diphenyl(1-(4-(trifluoromethoxy)phenyl)ethyl)silane (**7g**): colorless oil, 56mg, 50% yield, regioselectivity: 75/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.55-53 (m, 2H), 7.46-7.34 (m, 6H), 7.31-7.28 (m, 2H), 7.05-7.03 (d, *J* = 8.4 Hz, 2H), 7.00-6.98 (d, *J* = 8.8 Hz, 2H), 4.84-4.83 (d, *J* = 3.2 Hz, 1H), 2.90-2.83 (m, 1H), 1.49-1.47 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): 146.6 (q, J_{F-C} = 2.1 Hz), 143.2, 135.6, 135.4, 132.5, 132.4, 129.9, 129.7, 128.6, 128.0, 127.8, 120.7 (q, J_{F-C} =1.0 Hz), 120.5 (q, J_{F-C} = 255.1 Hz), 26.5, 16.3; IR (neat): 3069, 2952, 2126, 1505, 1252, 1154, 1111, 795, 730; HRMS (ESI): cacld. for $C_{21}H_{19}F_3OSi$ $[M+H]^+$: 371.1230, found: 371.1245.

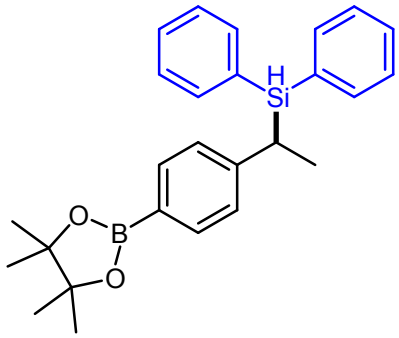


(1-(4-Fluorophenyl)ethyl)diphenylsilane (**7h**): colorless oil, 85mg, 93 % yield, regioselectivity: 37/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.59-7.57 (m, 2H), 7.49-7.45 (m, 1H), 7.43-7.39 (m, 5H), 7.35-7.31 (m, 2H), 7.01-6.90 (m, 4H), 4.89-4.88 (d, *J* = 3.6 Hz, 1H), 2.90-2.83 (m, 1H), 1.51-1.49 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): 160.6 (d, J_{F-C} = 241.3 Hz), 139.9 (d, J_{F-C} = 3.2 Hz), 135.6, 135.5, 132.7, 129.8, 129.7, 128.84, 128.76, 128.0, 127.8, 114.8 (d, J_{F-C} = 20.9 Hz), 26.1, 16.6. These data are in accordance with the literature.[S5]

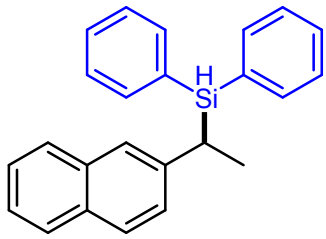


(1-(4-Chlorophenyl)ethyl)diphenylsilane (**7i**): colorless oil, 54mg, 56 % yield, regioselectivity: 71/1;

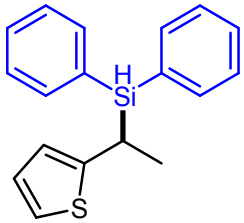
^{1}H NMR (400 MHz, $CDCl_3$): 7.55-7.52 (m, 2H), 7.46-7.42 (m, 1H), 7.40-7.37 (m, 5H), 7.33-7.29 (m, 2H), 7.17-7.15 (d, *J* = 8.4 Hz, 2H), 6.94-6.92 (d, *J* = 8.8 Hz, 2H), 4.84-4.83 (d, *J* = 3.2 Hz, 1H), 2.86-2.79 (m, 1H), 1.47-1.45 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): 142.9, 135.6, 135.5, 132.53, 132.52, 130.4, 129.8, 129.7, 128.9, 128.2, 128.0, 127.8, 26.5, 16.4. IR (neat): 3067, 2955, 2868, 2118, 1488, 1427, 1112, 829, 798, 730; HRMS (ESI): cacld. for $C_{20}H_{19}ClSi$ $[M-H]^+$: 321.0861, found: 321.0858.



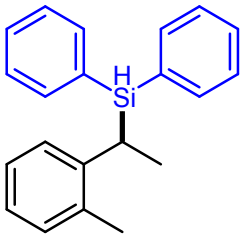
Diphenyl(1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethyl)silane (**7j**): white solid, m.p.: 99-101 °C; 57mg, 46% yield; regioselectivity: 96/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.66-7.64 (d, *J* = 8.4 Hz, 2H), 7.53-7.51 (m, 2H), 7.44-7.34 (m, 6H), 7.30-7.26 (m, 2H), 7.04-7.02 (d, *J* = 8.0 Hz, 2H), 4.85-4.84 (d, *J* = 3.2 Hz, 1H), 2.90-2.84 (m, 1H), 1.48-1.46 (d, *J* = 7.6 Hz, 3H), 1.35 (s, 12H); ^{13}C NMR (100MHz, $CDCl_3$): 148.0, 135.7, 135.5, 134.7, 132.8, 132.7, 129.7, 129.6, 127.9, 127.7, 127.2, 83.6, 27.4, 24.9, 24.8,16.3; IR (neat): 2976, 2923, 2159, 1605, 1397, 1357, 1327, 1140, 1091, 811, 793, 696; HRMS (ESI): cacld. for $C_{26}H_{31}BO_2Si$ $[M+Na]^+$: 437.2079, found: 437.2074.



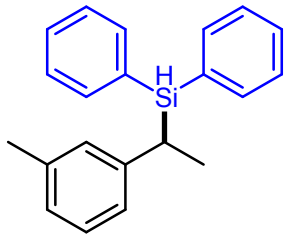
(1-(Naphthalen-2-yl)ethyl)diphenylsilane (**7k**): colorless oil, 72mg, 71 % yield, regioselectivity: 19/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.77-7.75 (m, 1H), 7.67-7.64 (m, 2H), 7.54-7.52 (m, 2H), 7.43-7.32 (m, 9H), 7.27-7.23 (m, 2H), 7.16-7.13 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 1H), 4.91-4.90 (d, *J* = 3.2 Hz, 1H), 3.03-2.97 (m, 1H), 1.56-1.55 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): 142.0, 135.7, 135.6, 133.6, 132.89, 132.87, 131.5, 129.7, 129.6, 127.9, 127.7, 127.51, 127.46, 127.3, 127.2, 125.7, 125.2, 124.7, 27.2, 16.5. These data are in accordance with the literature.[S5]



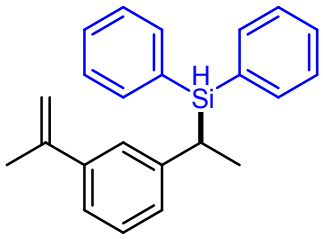
Diphenyl(1-(thiophen-2-yl)ethyl)silane (**7l**): colorless oil, 55mg, 62 % yield, regioselectivity >99/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.57-7.55 (m, 2H), 7.46-7.36 (m, 6H), 7.34-7.30 (m, 2H), 7.03-7.02 (dd, *J* = 5.2 Hz, *J* = 1.2 Hz, 1H), 6.88-6.86 (dd, *J* = 5.2 Hz, *J* = 3.2 Hz, 1H), 6.61-6.59 (m, 1H), 4.93-4.92 (d, *J* = 3.2 Hz, 1H), 3.17-3.11 (m, 1H), 1.53-1.51 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): 148.1, 135.6, 135.5, 132.7, 132.5, 129.83, 129.76, 128.0, 127.8, 126.7, 122.8, 121.8, 22.2, 18.0. These data are in accordance with the literature.[S5]



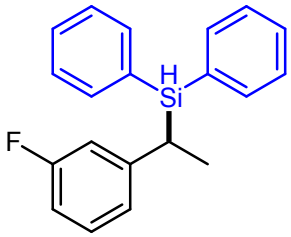
Diphenyl(1-(o-tolyl)ethyl)silane (**7m**): colorless oil, 64mg, 70% yield, regioselectivity: 28/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.47-7.45 (m, 2H), 7.39-7.18 (m, 7H), 7.17-7.15 (d, *J* = 7.2 Hz, 1H), 7.07-7.03 (m, 1H), 6.99-6.93 (m, 3H), 4.72 (d, *J* = 3.2 Hz, 1H), 2.96-2.90 (m, 1H), 2.00 (s, 3H), 1.38-1.36 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): 142.8, 135.8, 135.3, 135.1, 133.3, 132.8, 130.0, 129.7, 129.5, 127.9, 127.7, 126.7, 126.0, 124.7, 21.9, 20.1, 16.5. IR (neat): 3066, 2955, 2118, 1485, 1427, 1107, 796, 729, 695; HRMS (ESI): cacld. for $C_{21}H_{22}Si$ $[M+Na]^+$: 325.1383, found: 325.1378.



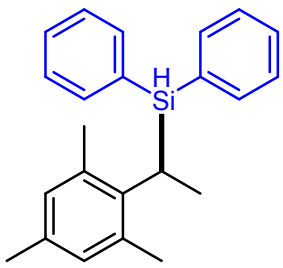
Diphenyl(1-(*m*-tolyl)ethyl)silane (**7n**): colorless oil, 90mg, 99 % yield, regioselectivity >99/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.60-7.57 (m, 2H), 7.49-7.45 (m, 1H), 7.43-7.38 (m, 5H), 7.34-7.31 (m, 2H), 7.16-7.12 (t, *J* = 7.6 Hz, 1H), 6.98-6.96 (d, *J* = 7.2 Hz, 1H), 6.89-6.87 (d, *J* = 8.0 Hz, 1H), 6.85 (s, 1H), 4.90-4.89 (d, *J* = 3.2 Hz, 1H), 2.88-2.82 (m, 1H), 2.29 (s, 3H), 1.52-1.50 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): 144.1, 137.5, 135.7, 135.6, 133.1, 129.6, 129.5, 128.6, 128.0, 127.8, 127.6, 125.6, 124.7, 26.8, 21.4, 16.4. These data are in accordance with the literature.[S%]



Diphenyl(1-(3-(prop-1-en-2-yl)phenyl)ethyl)silane (**7o**): colorless oil, 86mg, 87 % yield, regioselectivity >99/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.57-7.55 (m, 2H), 7.46-7.36 (m, 6H), 7.32-7.28 (m, 2H), 7.25-7.22 (m, 1H), 7.21-7.17 (t, *J* = 7.4 Hz, 1H), 7.05-7.04 (t, *J* = 1.8 Hz, 1H), 6.98-6.96 (m, 1H), 5.19 (m, 1H), 5.02-5.00 (m, 1H), 4.87-4.86 (d, *J* = 3.2 Hz, 1H), 2.91-2.85 (m, 1H), 2.04-2.03 (m, 3H), 1.52-1.50 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): 144.0, 143.5, 140.9, 135.7, 135.6, 133.0, 132.9, 129.7, 129.6, 128.0, 127.9, 127.7, 126.6, 125.2, 122.2, 112.0, 27.0, 21.7, 16.3. IR (neat): 3066, 2955, 2117, 1596, 1452, 1112, 888, 799, 729, 695; HRMS (ESI): cacld. for $C_{23}H_{24}Si$ $[M+H]^+$: 329.1720, found: 329.1716.

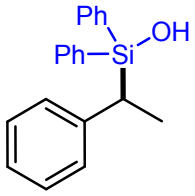


(1-(3-Fluorophenyl)ethyl)diphenylsilane (**7p**): colorless oil, 52 mg, 57 % yield, regioselectivity: 41/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.57-7.54 (m, 2H), 7.47-7.43 (m, 1H), 7.41-7.38 (m, 5H), 7.33-7.29 (m, 2H), 7.17-7.12 (m, 1H), 6.83-6.79 (m, 2H), 6.74-6.71 (m, 1H), 4.87-4.86 (d, *J* = 3.2 Hz, 1H), 2.90-2.84 (m, 1H), 1.49-1.47 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): 162.8 (d, $J_{F\text{-}C}$ = 243.5 Hz), 147.2 (d, $J_{F\text{-}C}$ = 7.2 Hz), 135.6, 135.5, 132.5 (d, $J_{F\text{-}C}$ = 3.2 Hz), 129.9, 129.7, 129.4, 129.3, 128.0, 127.8, 123.3 (d, $J_{F\text{-}C}$ =2.8 Hz), 114.3 (d, $J_{F\text{-}C}$ = 21.3 Hz), 111.7 (d, $J_{F\text{-}C}$ = 21.0 Hz), 27.0 (d, $J_{F\text{-}C}$ = 1.9 Hz), 16.2; These data are in accordance with the literature.[S%]

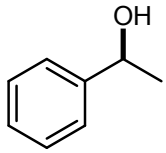


(1-Mesitylethyl)diphenylsilane (**7q**): colorless oil, 30mg, 30% yield, regioselectivity: >99/1; ^{1}H NMR (400 MHz, $CDCl_3$): 7.69-7.67 (m, 2H); 7.45-7.39 (m, 3H), 7.29-7.25 (m, 1H), 7.21-7.15 (m, 4H), 6.78 (s, 1H), 6.75 (s, 1H), 5.11-5.10 (d, *J* = 5.2 Hz, 1H), 3.24-3.17 (m, 1H), 2.36 (s, 3H), 2.23 (s, 3H),

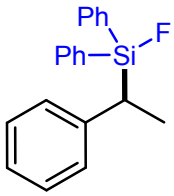
2.12 (s, 3H), 1.47-1.45 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): 138.0, 136.4, 135.8, 135.5, 134.9, 134.6, 134.2, 134.1, 130.5, 129.6, 129.3, 129.0, 128.1, 127.6, 21.9, 21.74, 21.67, 20.6, 15.8; IR (neat): 2920, 2867, 2125, 1459, 1427, 1108, 796, 730, 695; HRMS (ESI): cacld. for $C_{23}H_{26}Si$ $[M+Na]^+$: 353.1696, found: 353.1695.



Diphenyl(1-phenylethyl)silanol (**8**): colorless oil, 132 mg, 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$): 7.58-7.56 (m, 2H), 7.48-7.34 (m, 6H), 7.32-7.30 (m, 2H), 7.22-7.18 (m, 2H), 7.13-7.09 (m, 1H), 7.03-7.00 (m, 2H), 2.88-2.82 (q, *J* = 7.6 Hz, 1H), 2.18 (br, 1H), 1.48-1.46 (d, *J* = 7.6 Hz, 3H); ^{13}CNMR (100 MHz, $CDCl_3$): 143.4, 134.72, 134.67, 134.6, 134.2, 129.93, 129.90, 128.2, 127.9, 127.8, 127.7, 125.0, 29.0, 15.3; These data are in accordance with the literature.[S11]



1-Phenylethanol (**9**): colorless oil, 50 mg, 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$): 7.40-7.34 (m, 4H), 7.30-7.26 (m, 1H), 4.92-4.87 (q, *J* = 6.5 Hz, 1H), 1.95 (br, 1H), 1.51-1.49 (d, *J* = 6.4 Hz, 3H); ^{13}CNMR (100 MHz, $CDCl_3$): 145.8, 128.5, 127.4, 125.3, 70.4, 25.1; These data are in accordance with the literature.[S12]



Fluorodiphenyl(1-phenylethyl)silane (**10**): colorless oil, 112 mg, 73% yield; ^{1}H NMR (400 MHz, $CDCl_3$): 7.58-7.56 (m, 2H), 7.51-7.39 (m, 6H), 7.36-7.32 (t, *J* = 7.6 Hz, 2H), 7.24-7.20 (t, *J* = 7.4 Hz, 2H), 7.17-7.13 (m, 1H), 7.07-7.05 (d, *J* = 7.2 Hz, 2H), 2.96-2.89 (m, 1H), 1.55-1.53 (d, *J* = 7.6 Hz, 3H); ^{13}CNMR (100 MHz, $CDCl_3$): 142.0 (d, J_{F-C} = 0.7 Hz), 134.69, 134.67, 134.5 (d, J_{F-C} = 2.5 Hz), 131.9 (d, J_{F-C} = 9.6 Hz), 131.8 (d, J_{F-C} = 9.9 Hz), 130.5, 128.2, 128.1 (d, J_{F-C} = 0.8 Hz), 127.9, 127.8, 125.3, 28.4 (d, J_{F-C} = 13.4 Hz), 14.9; ^{19}F NMR ($CDCl_3$, 376 MHz): -174.8 (d, *J* = 5.3 Hz); These data are in accordance with the literature.[S11]

11. References:

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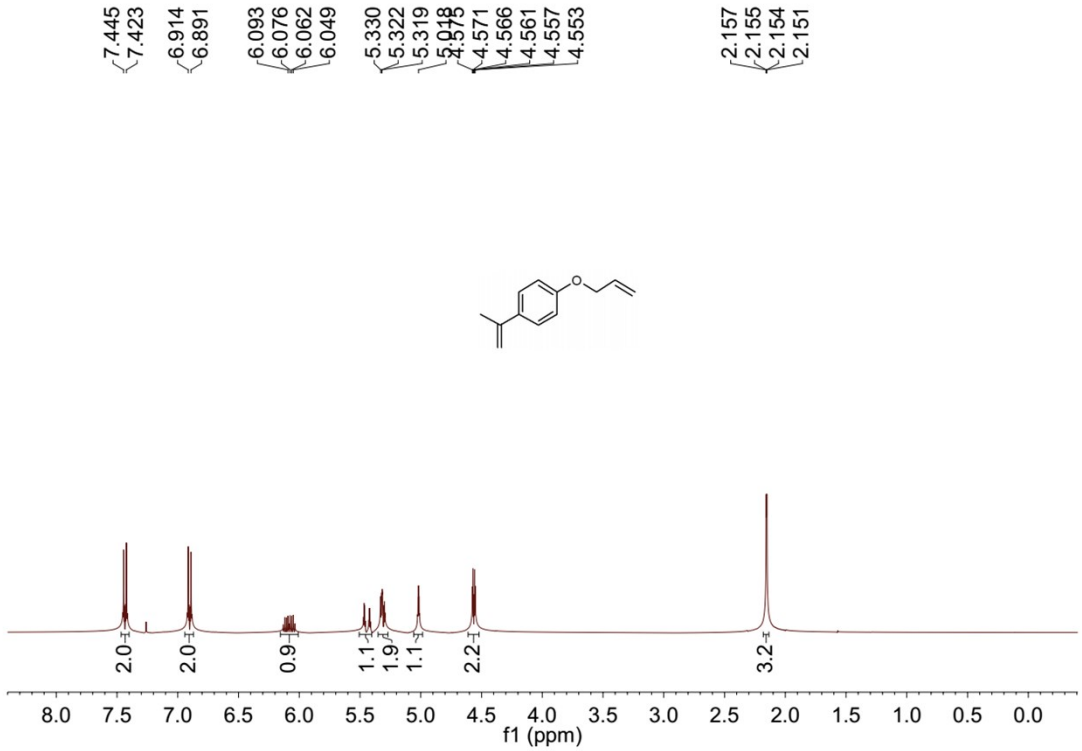
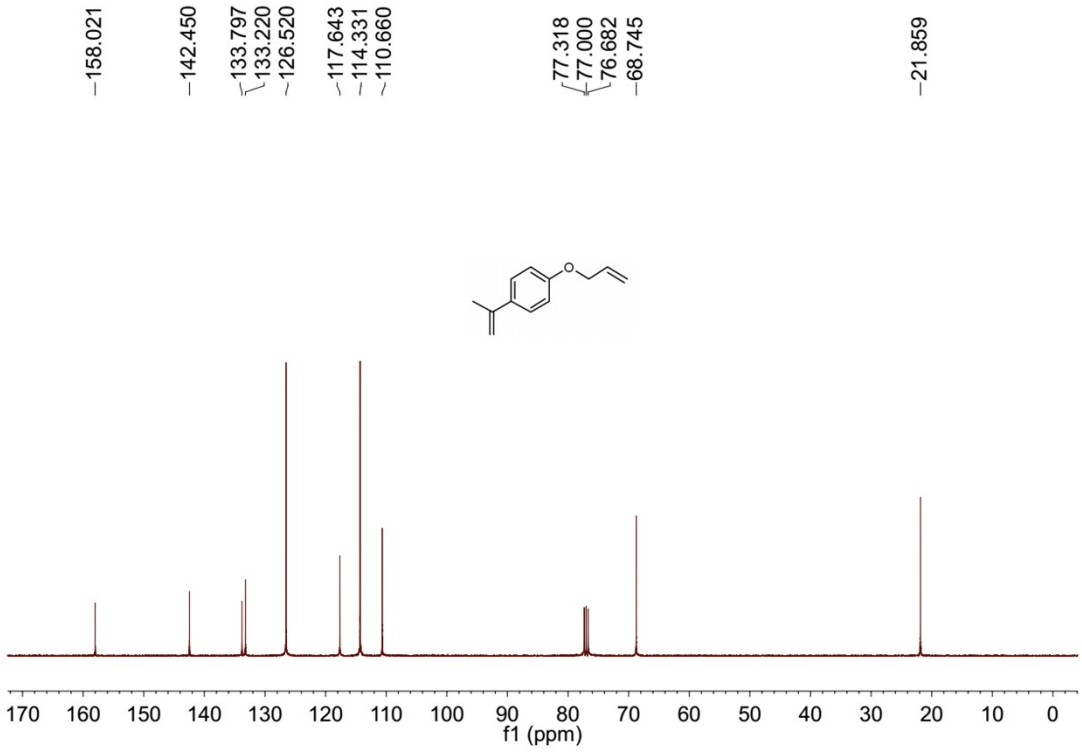
Part II NMR spectra

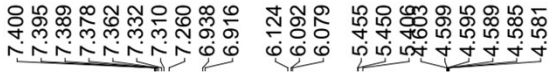
4y ^{1}H NMR

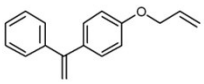


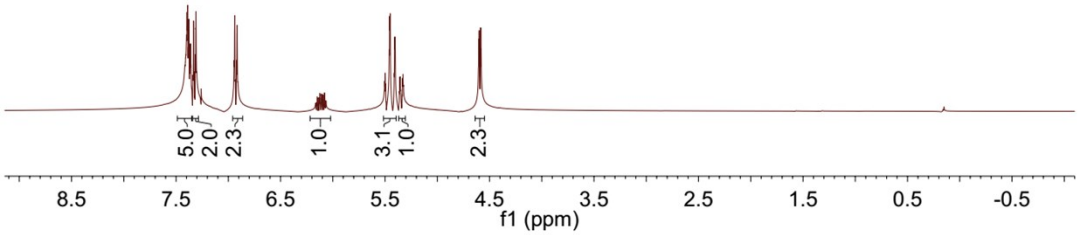
4y ^{13}C NMR



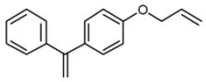
4z ^{1}H NMR

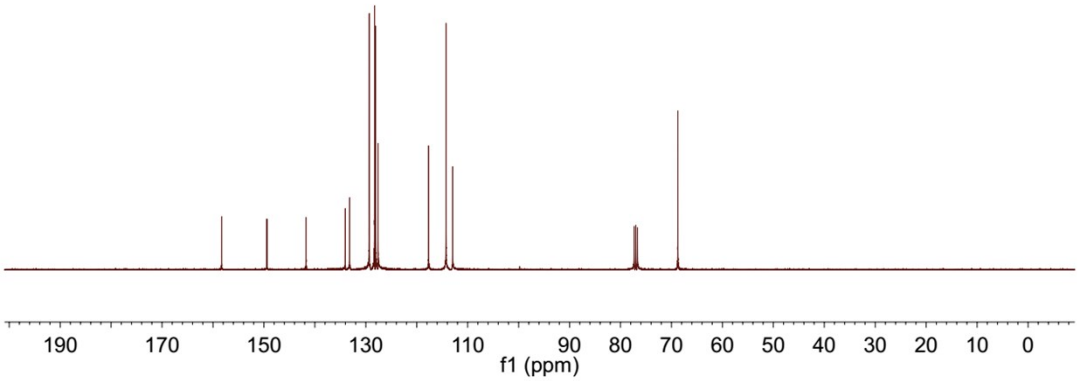




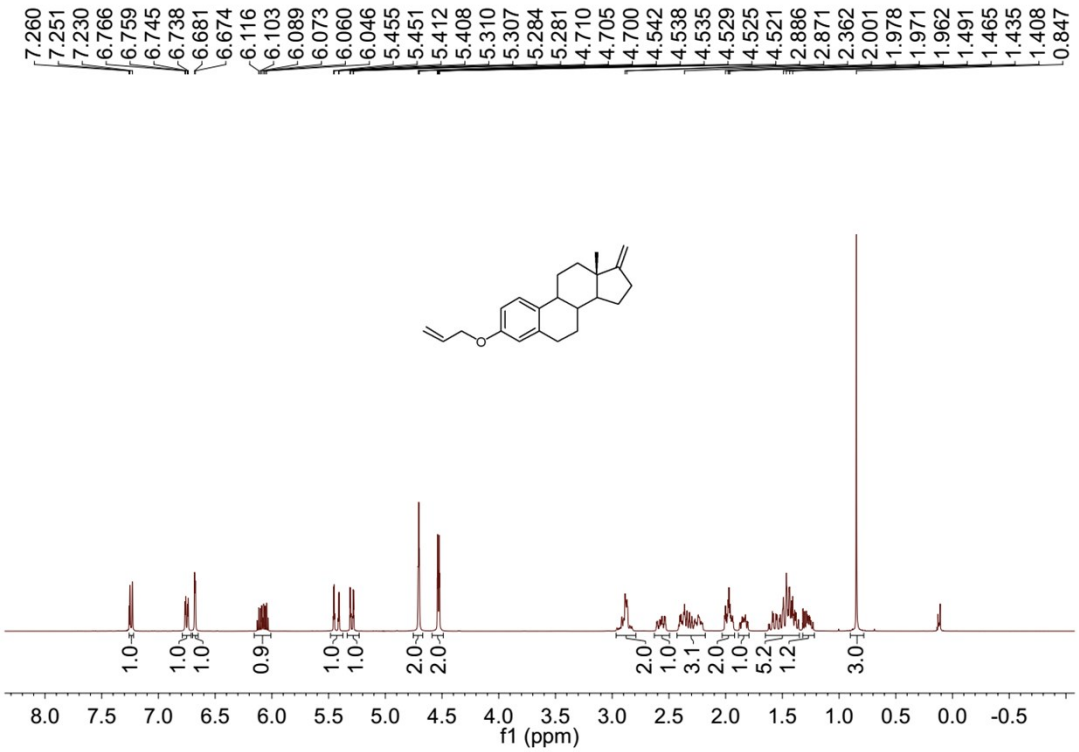


4z ^{13}C NMR

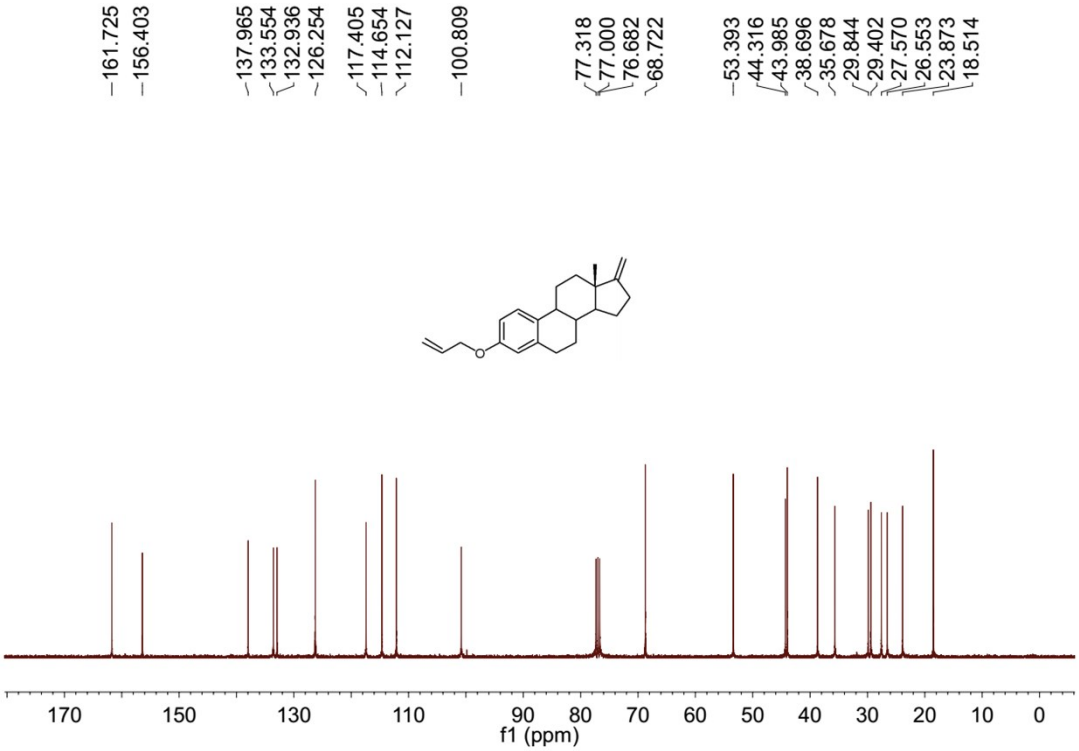




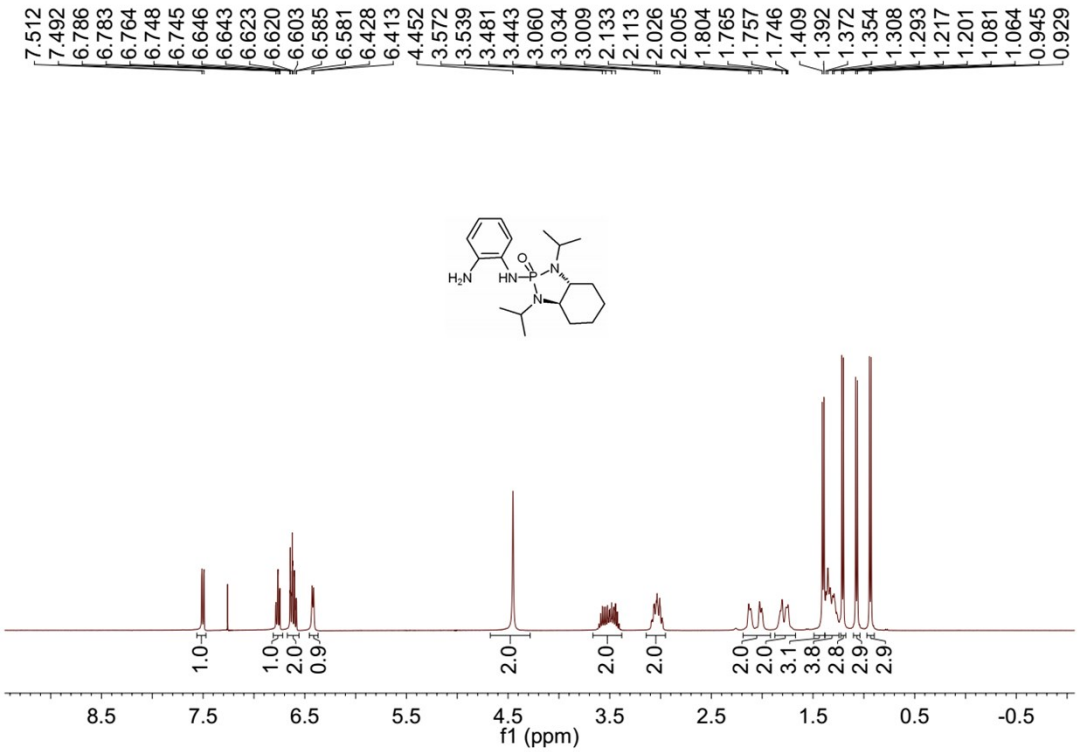
4aa ^{1}H NMR



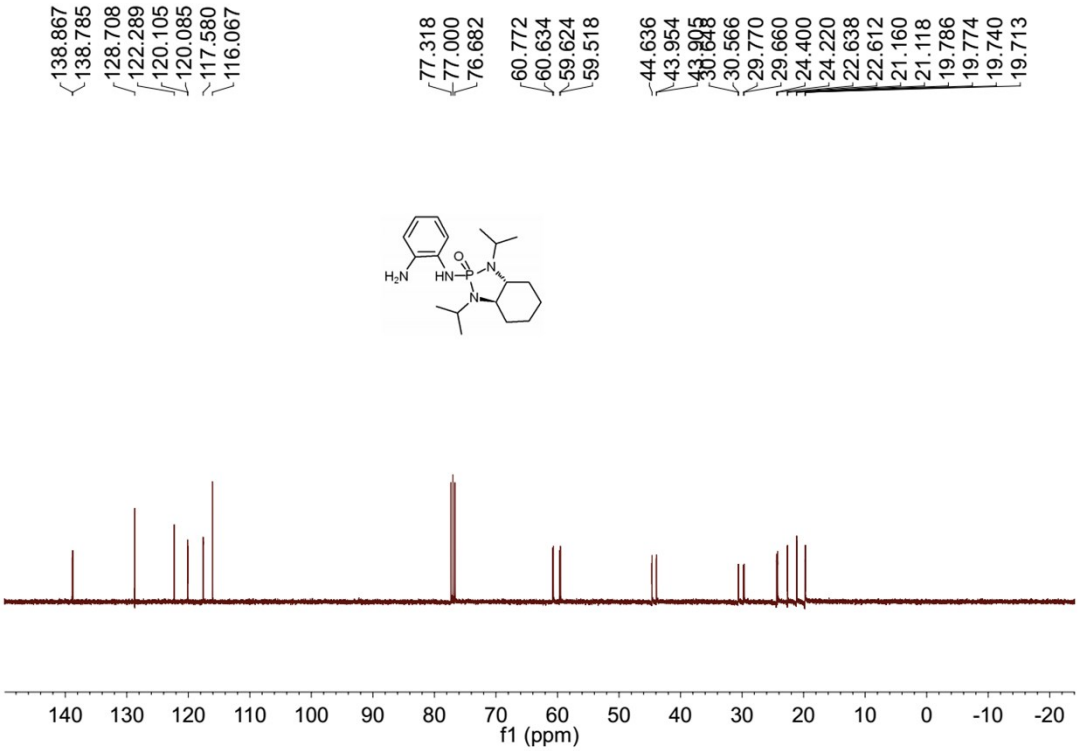
4aa ^{13}C NMR



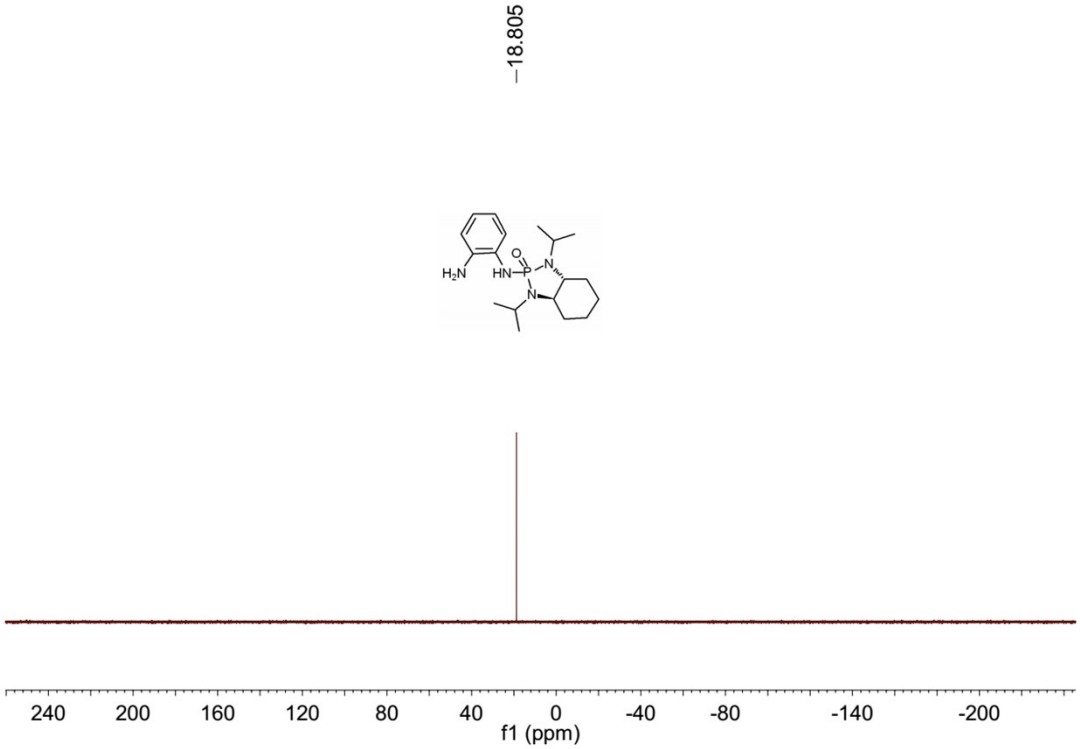
3a ^{1}H NMR



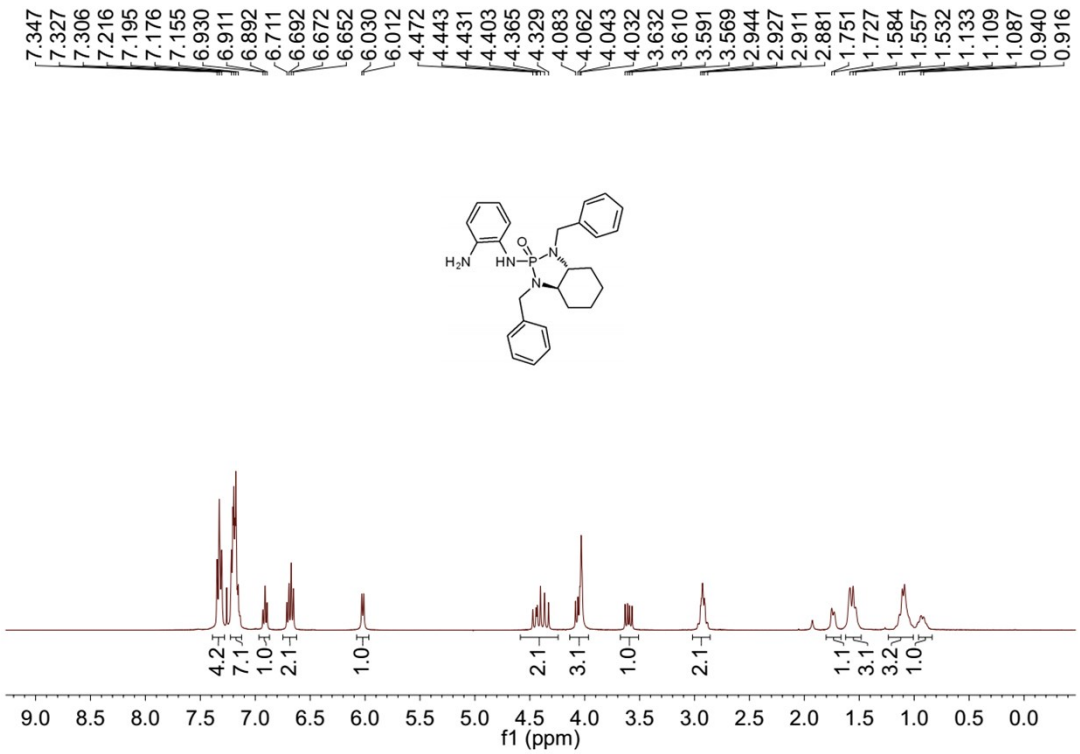
3a ^{13}C NMR



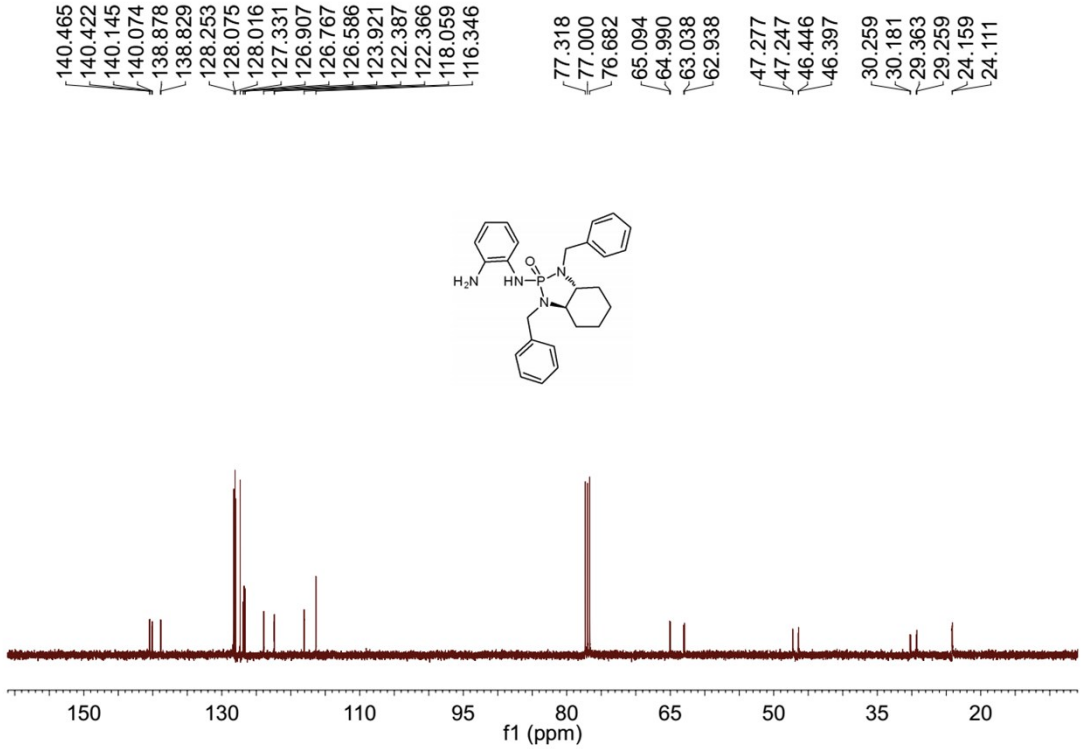
3a ^{31}P NMR



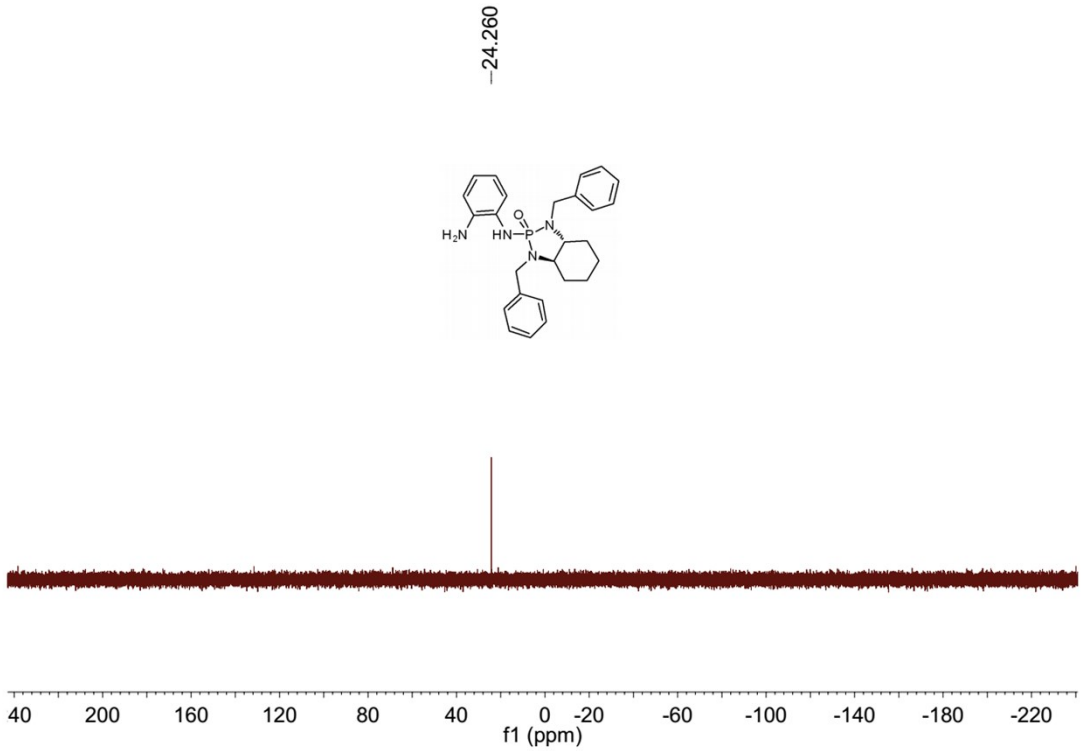
3b ^{1}H NMR



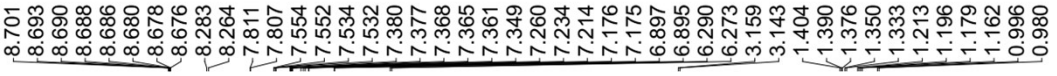
3b ^{13}C NMR

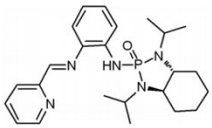


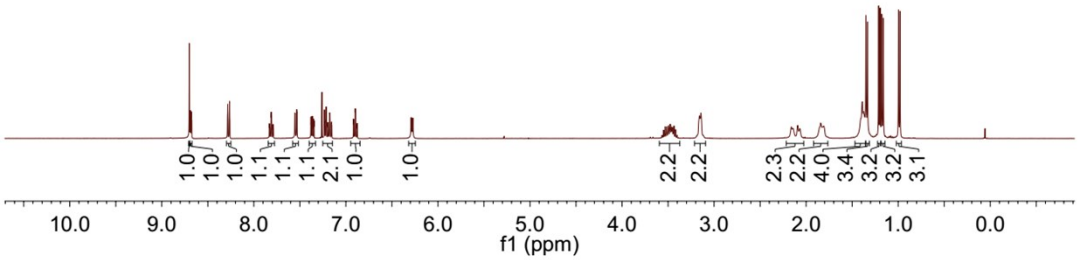
3b ^{31}P NMR



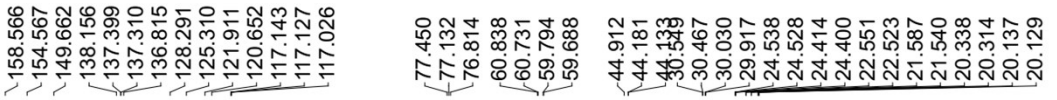
L1 ^{1}H NMR

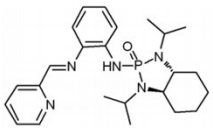


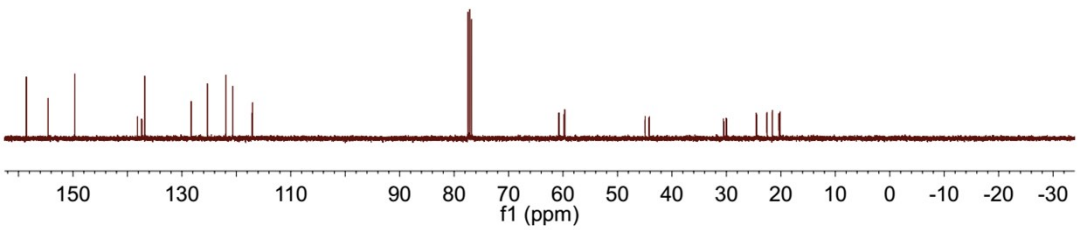




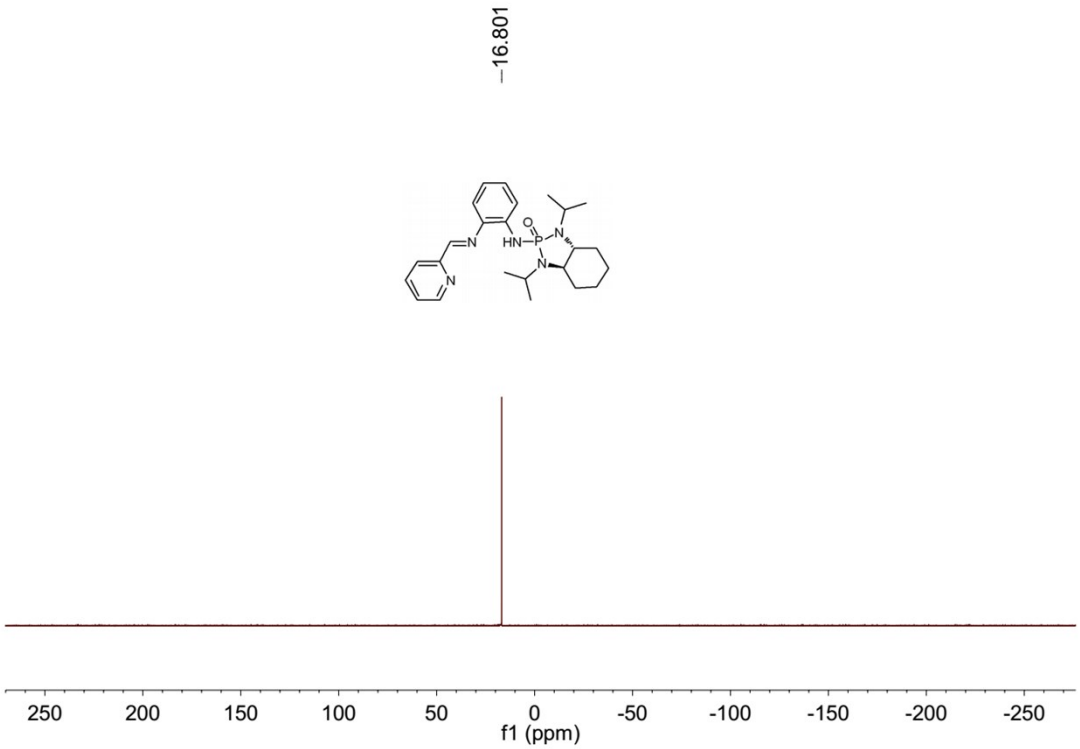
L1 ^{13}C NMR



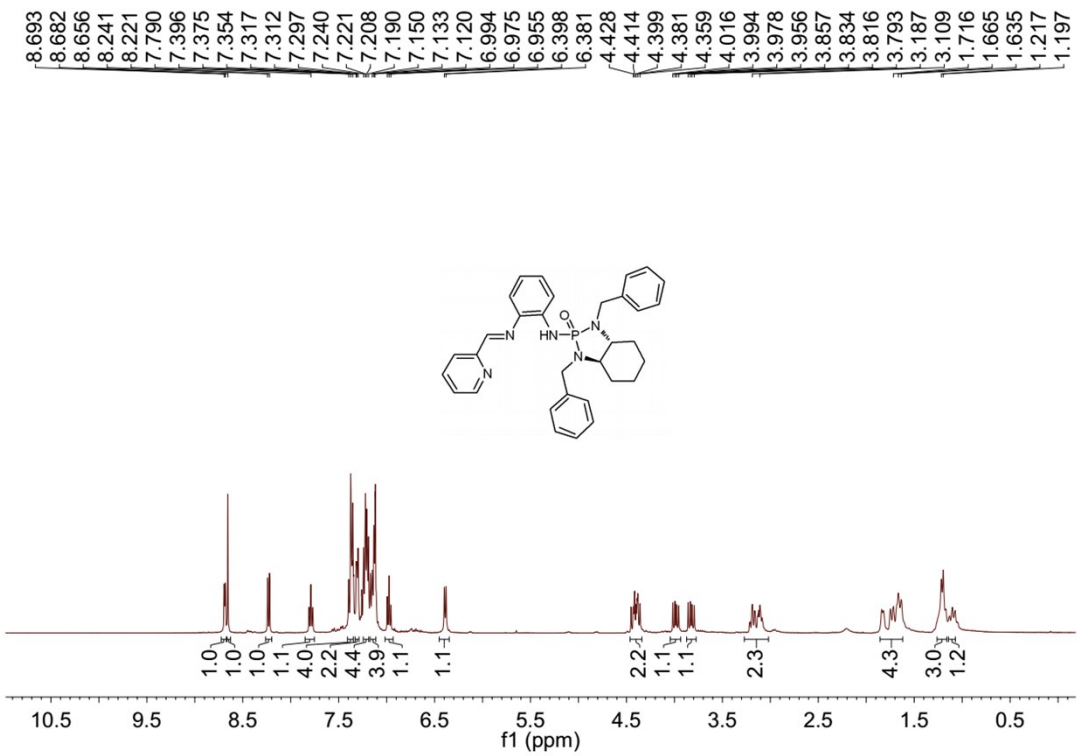




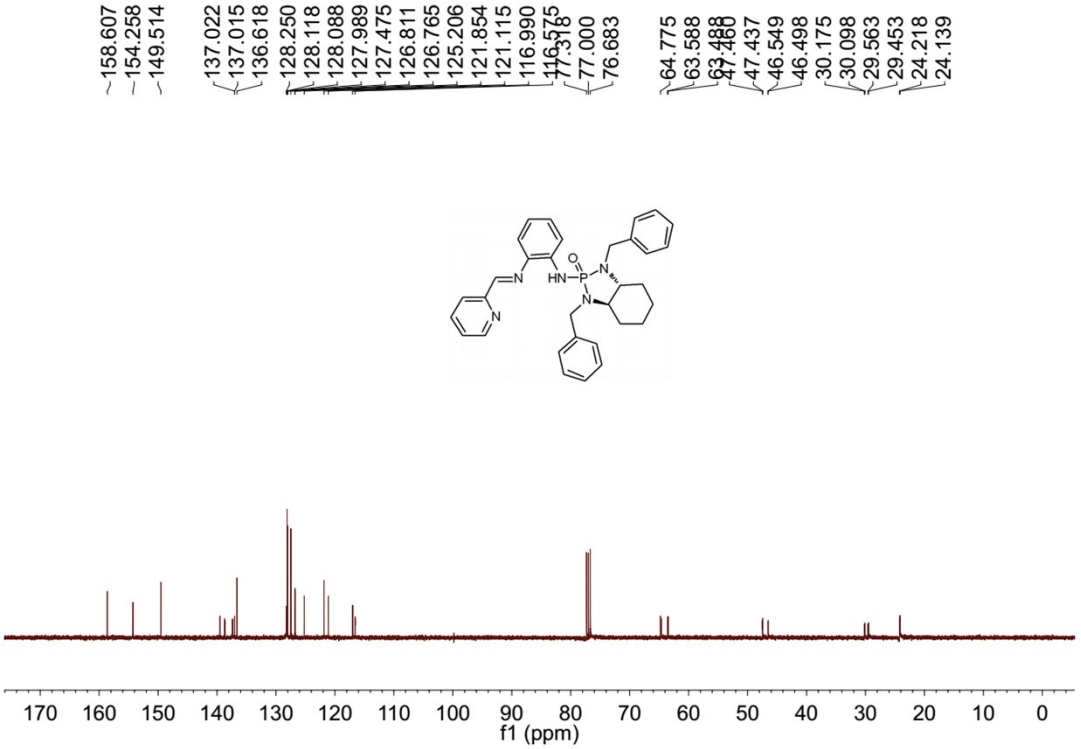
L1 ^{31}P NMR



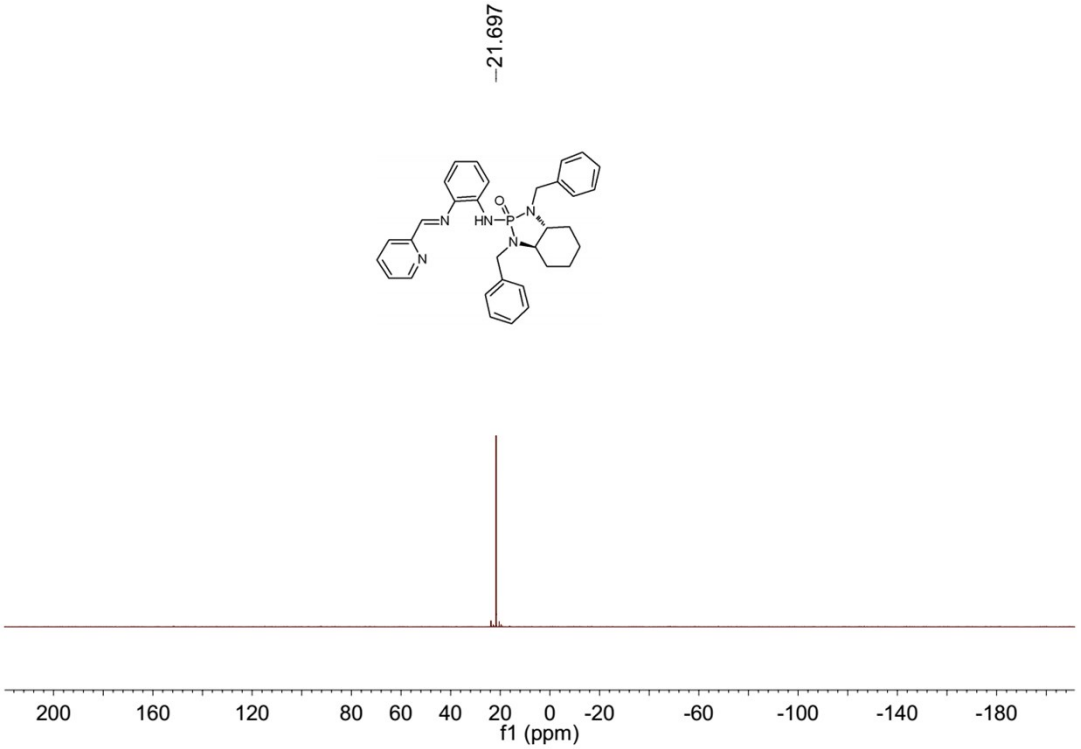
L2 ^{1}H NMR



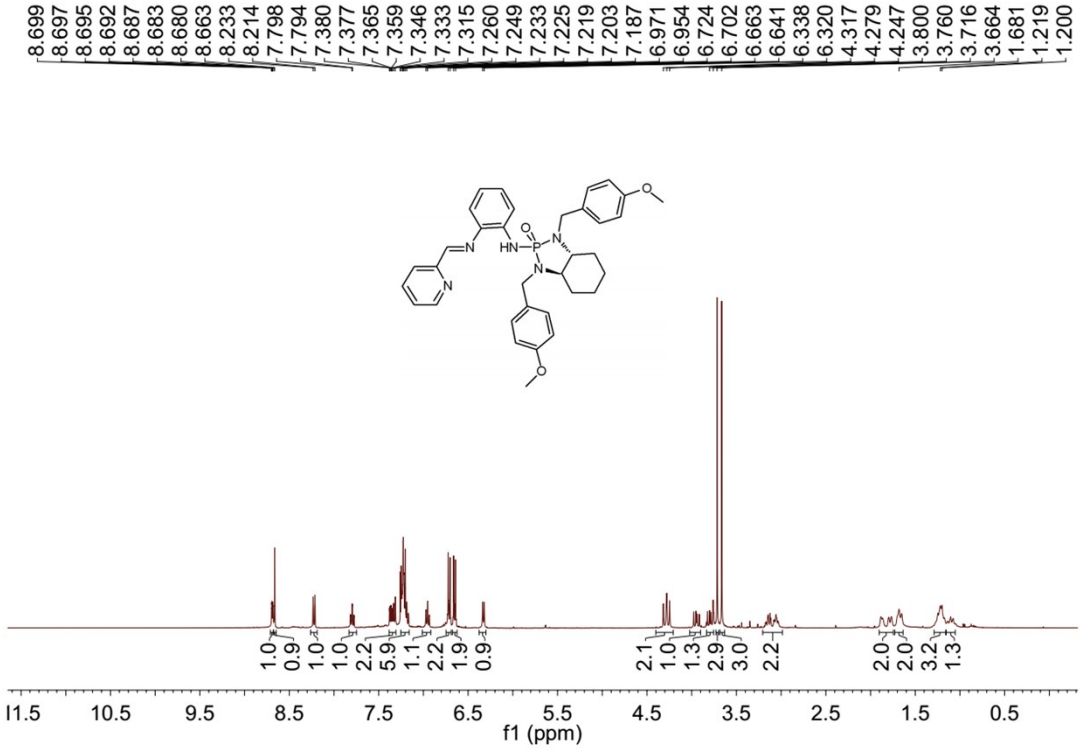
L2 ^{13}C NMR



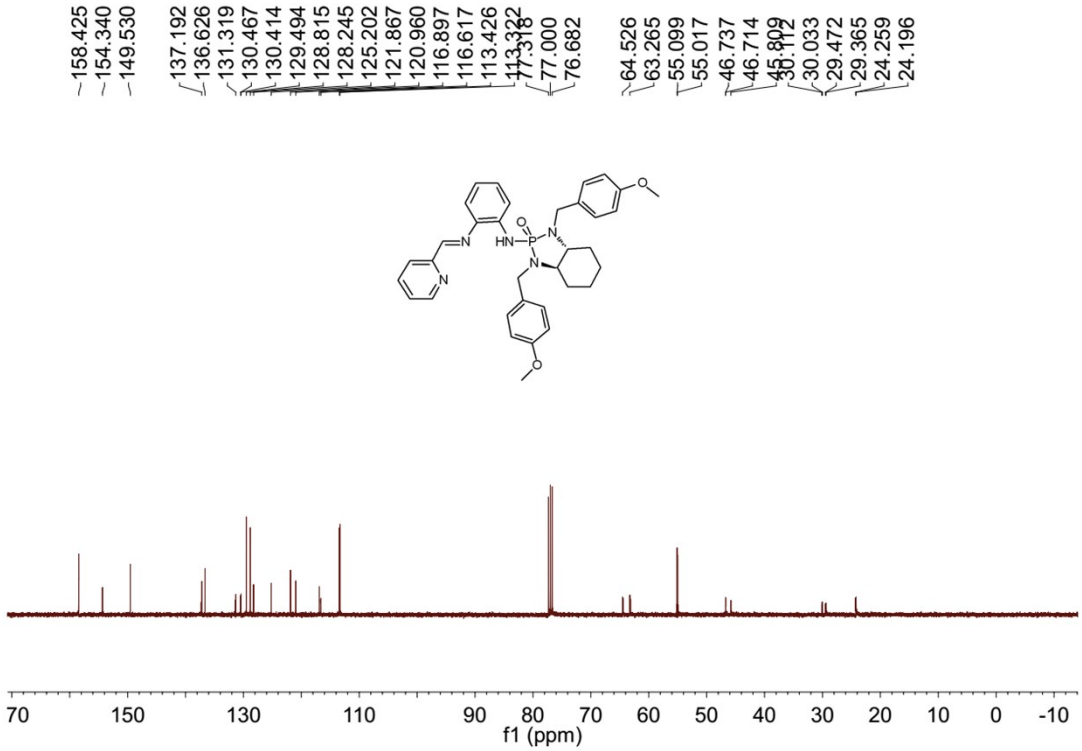
L2 ^{31}P NMR



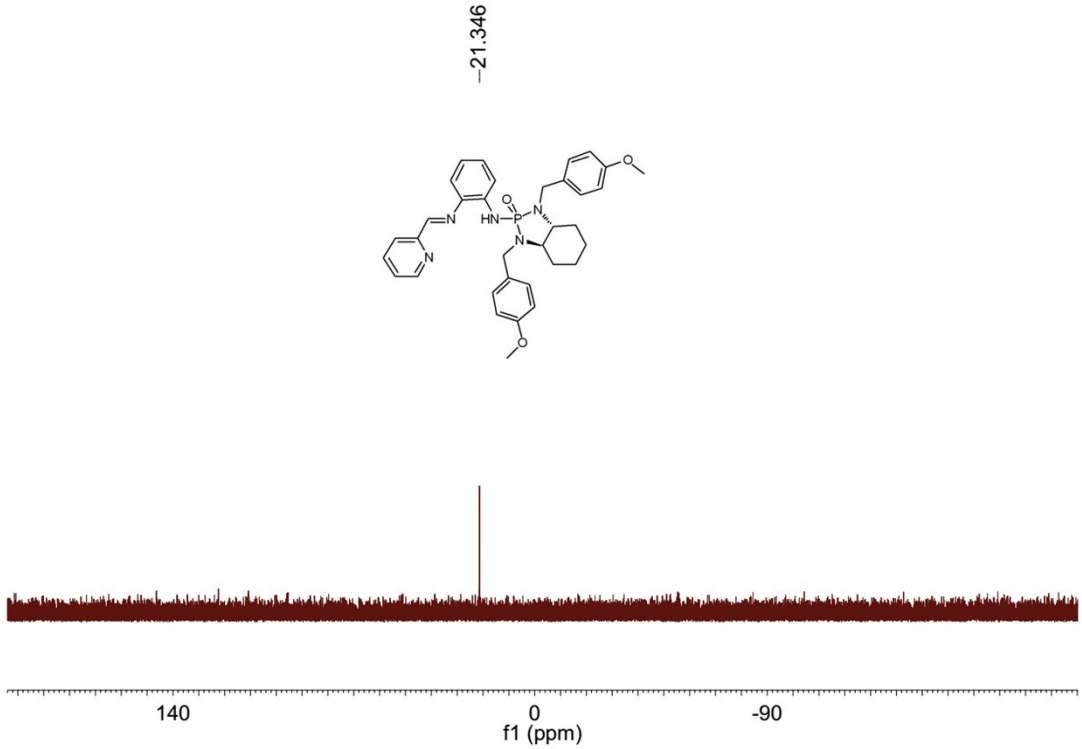
L3 ^{1}H NMR



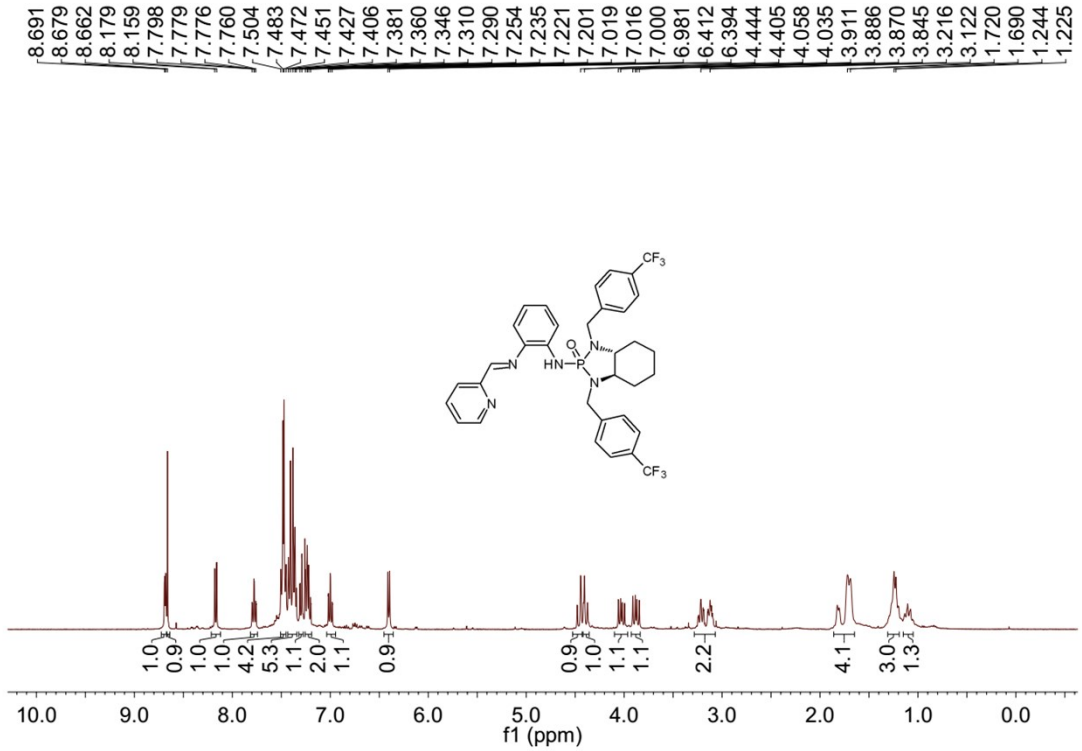
L3 ^{13}C NMR



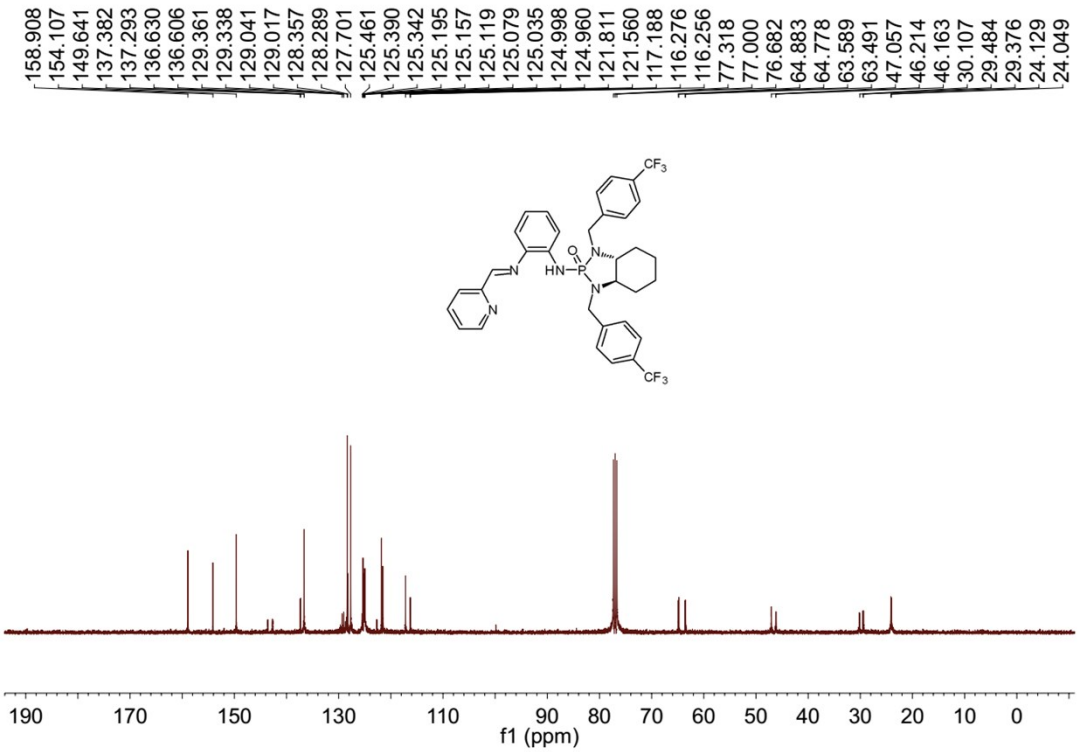
L3 ^{31}P NMR



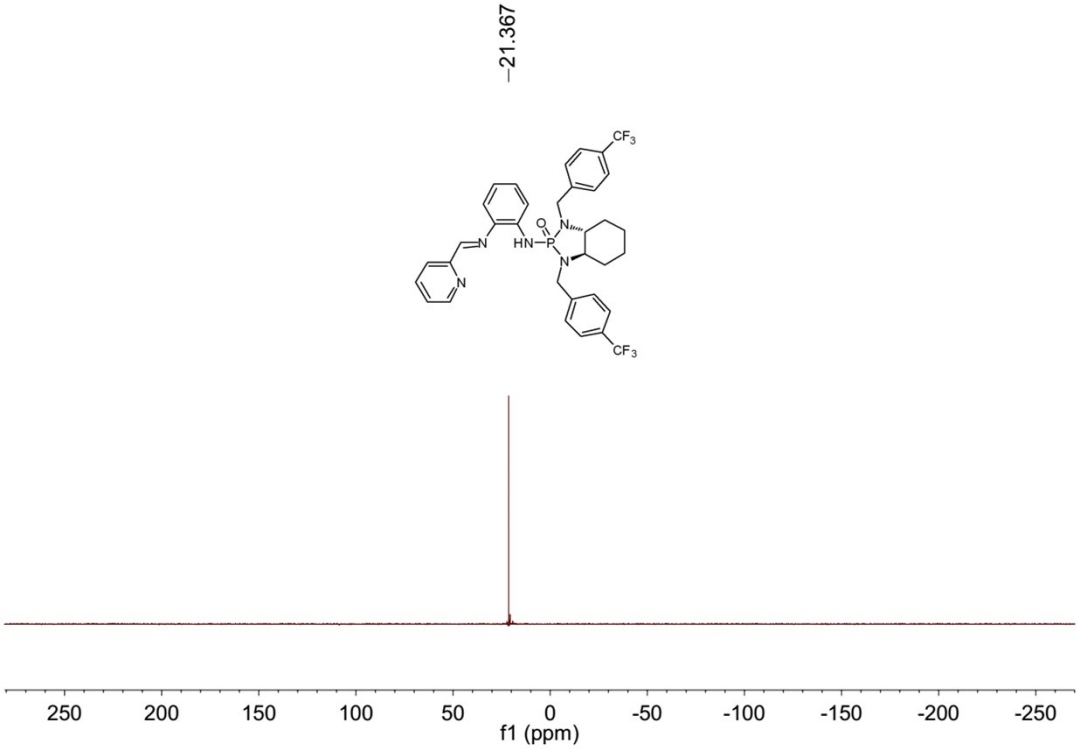
L4 ^{1}H NMR



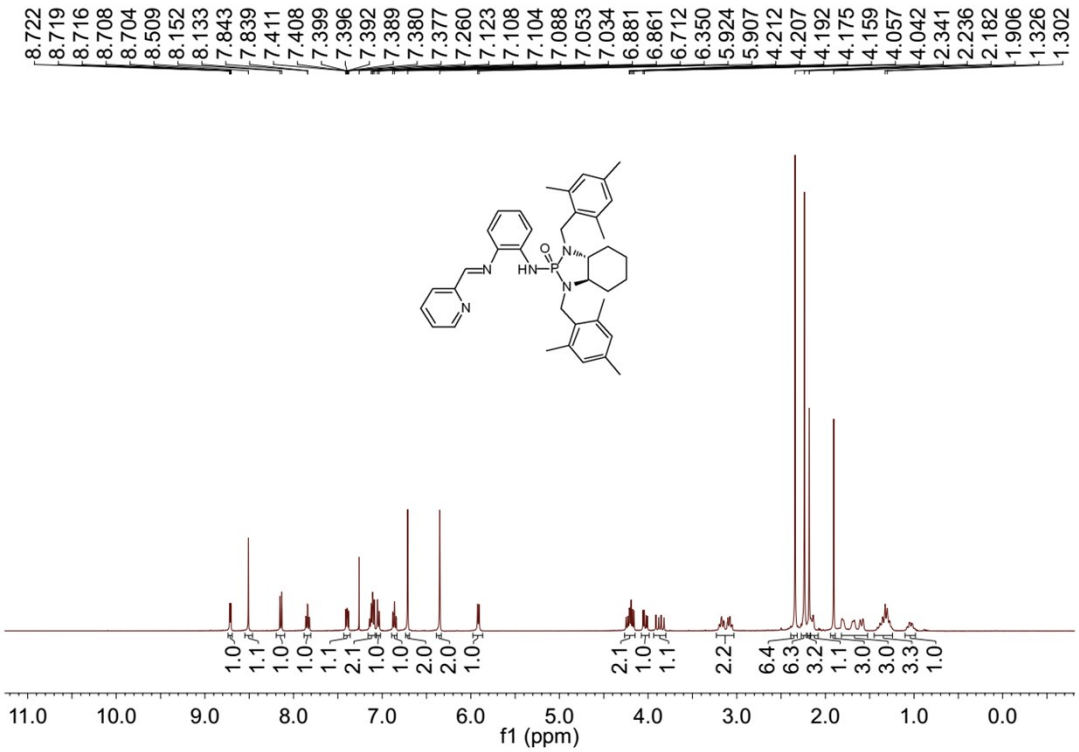
L4 ^{13}C NMR



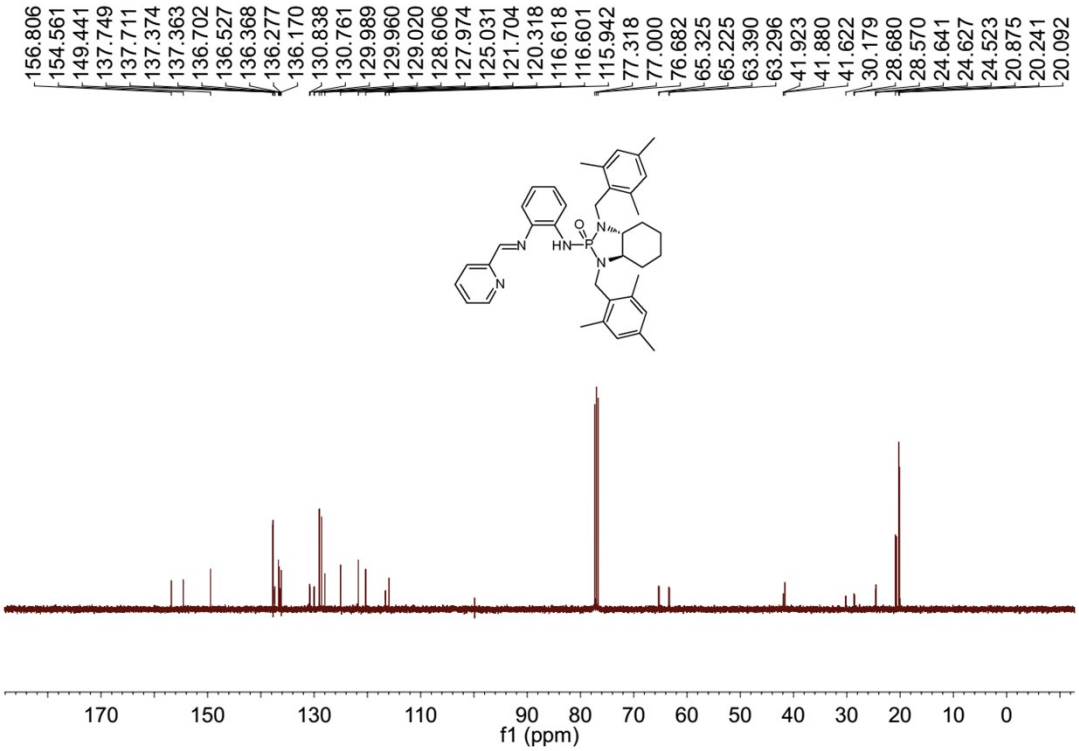
L4 ^{31}P NMR



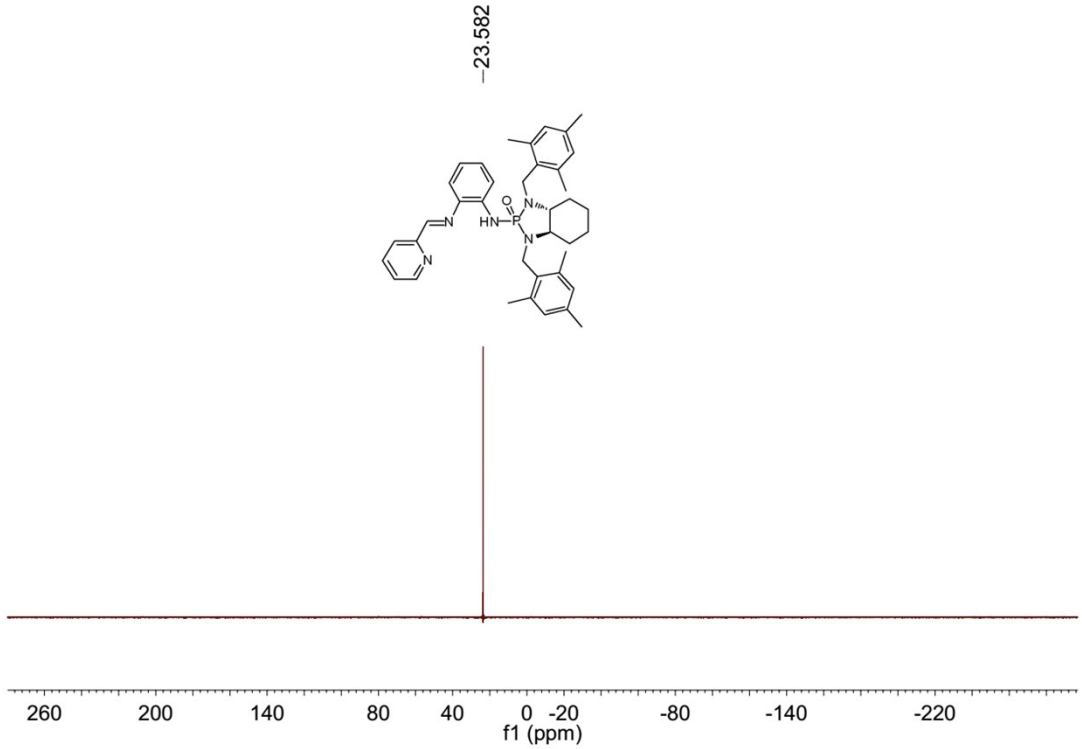
L5 ^{1}H NMR



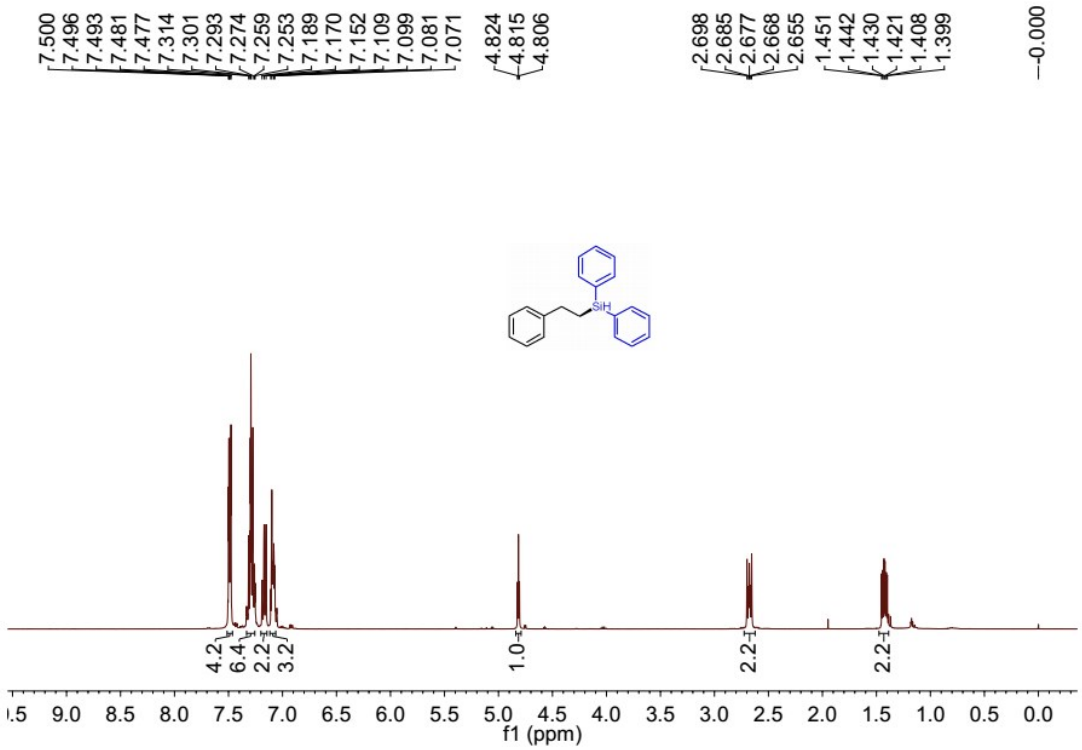
L5 ^{13}C NMR



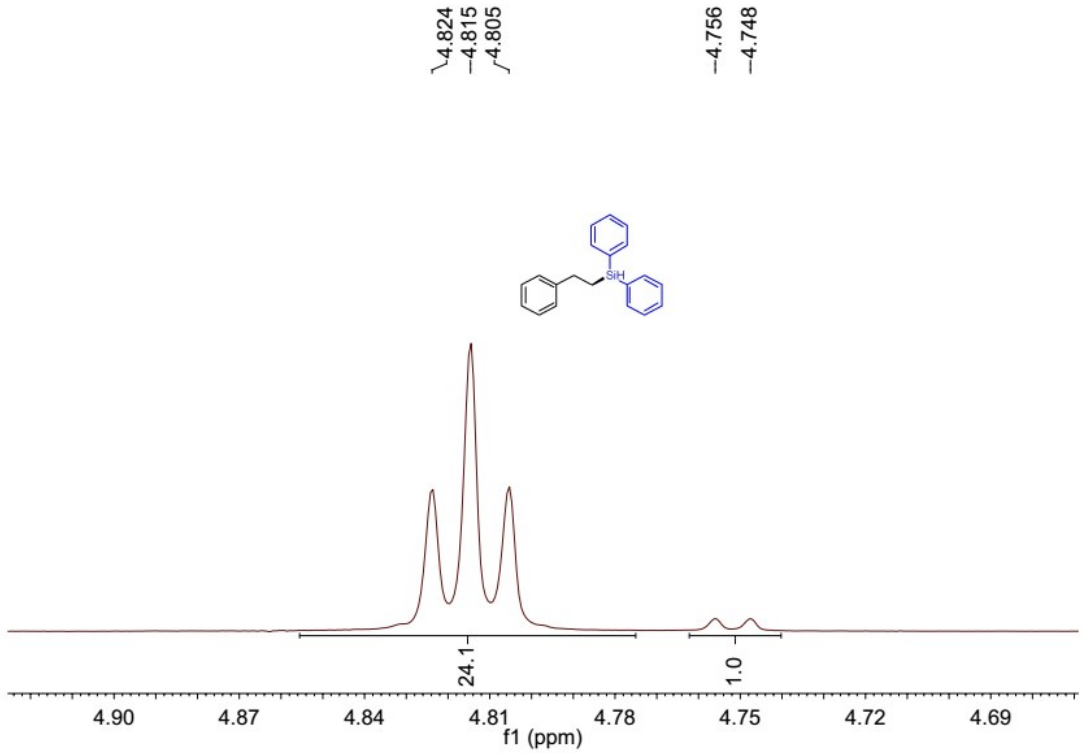
L5 ^{31}P NMR



6a ^{1}H NMR



6a regioselectivity



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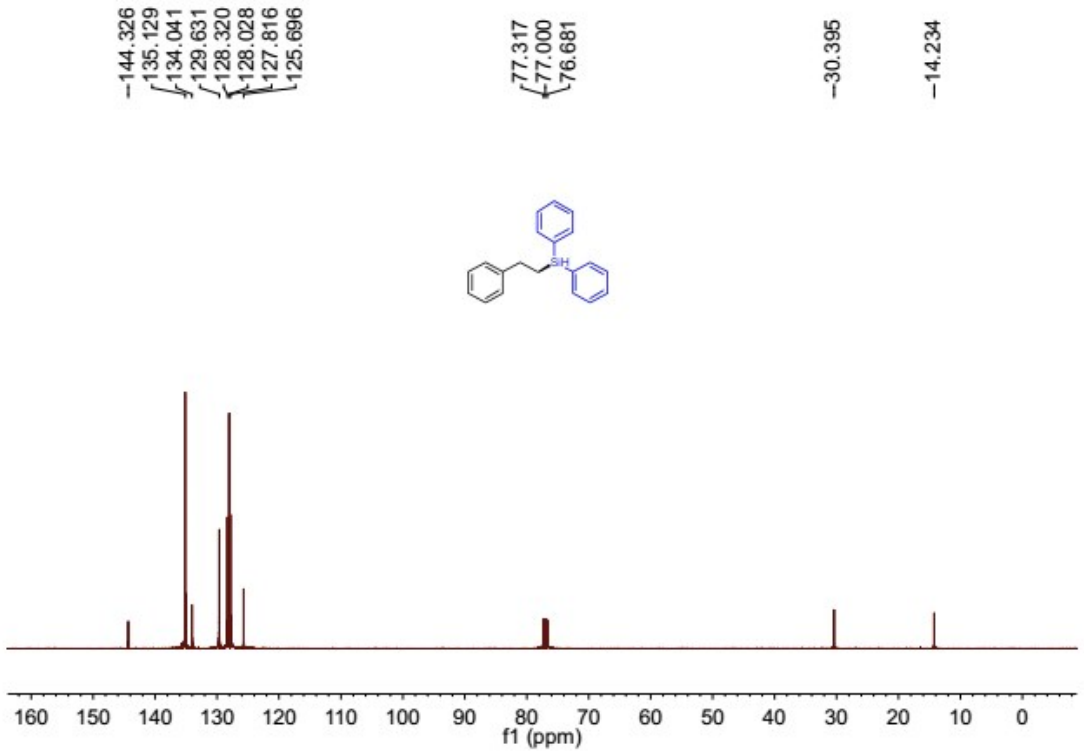

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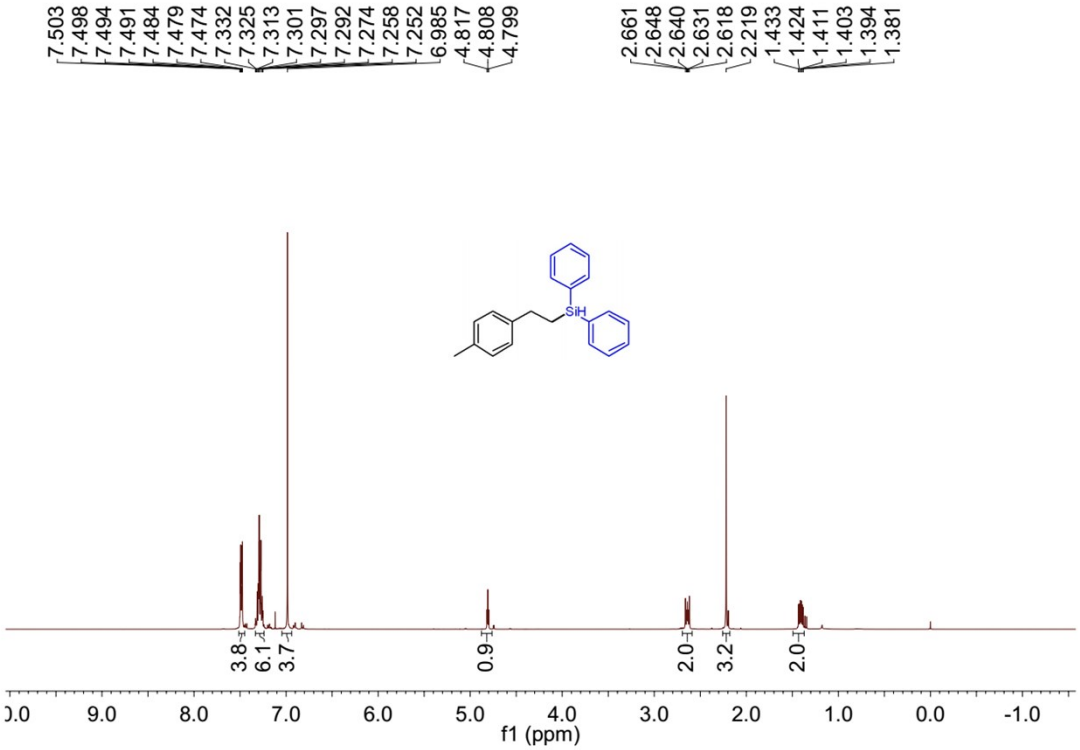
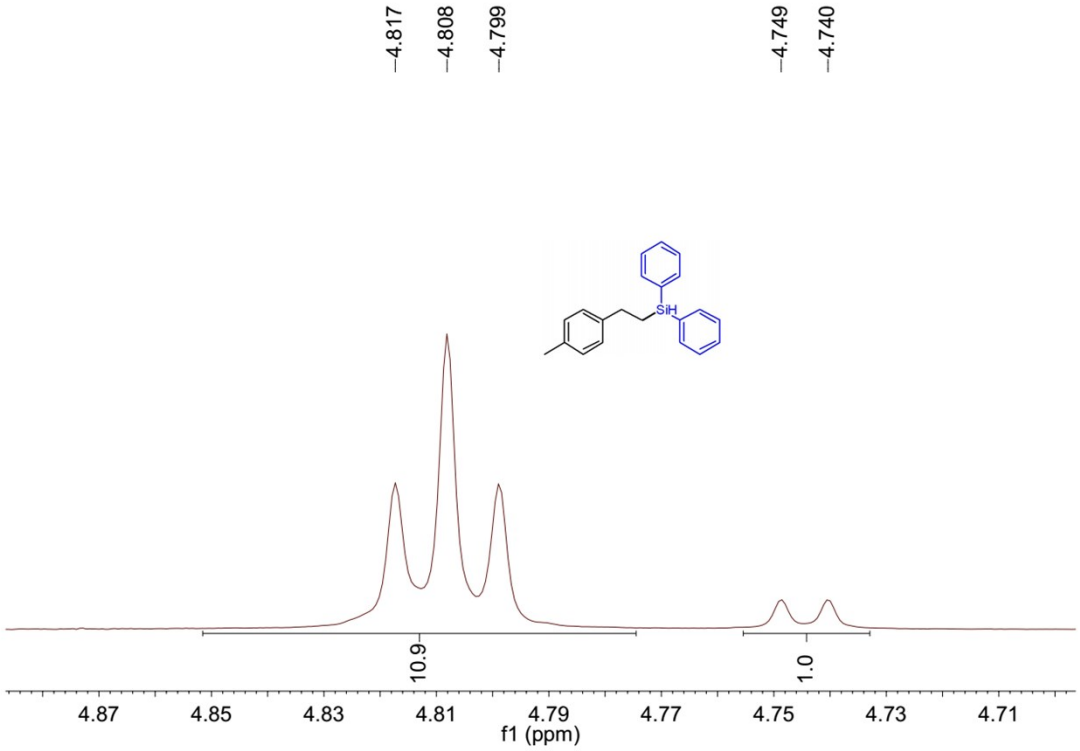


6b regioselectivity



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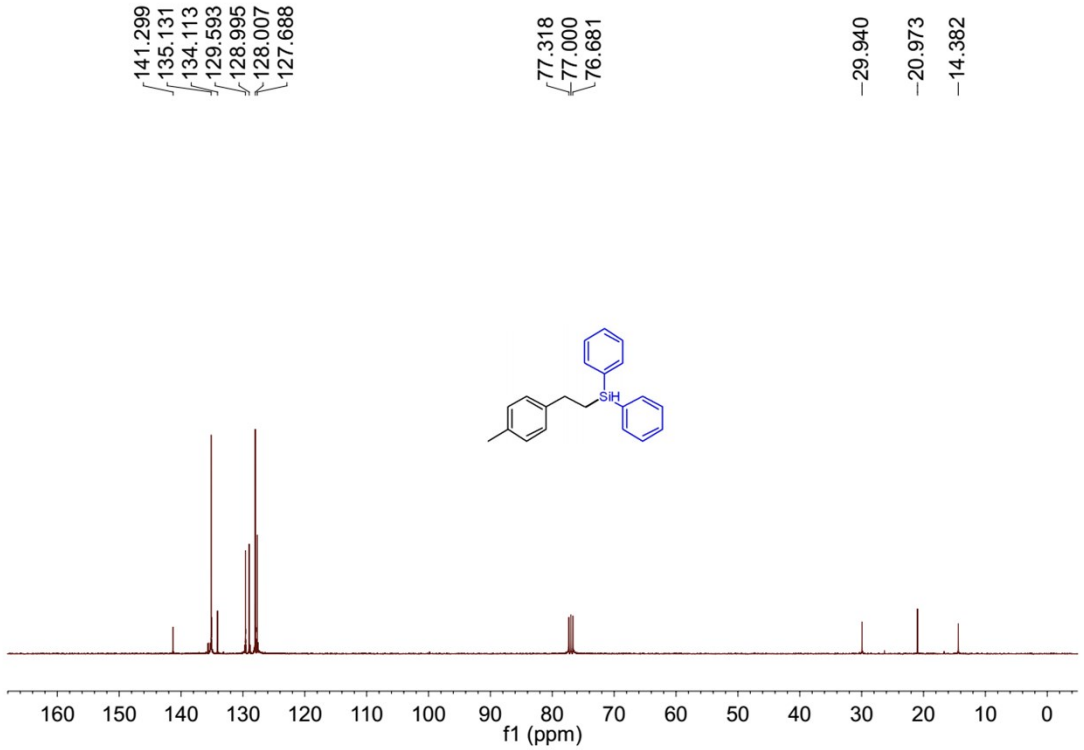

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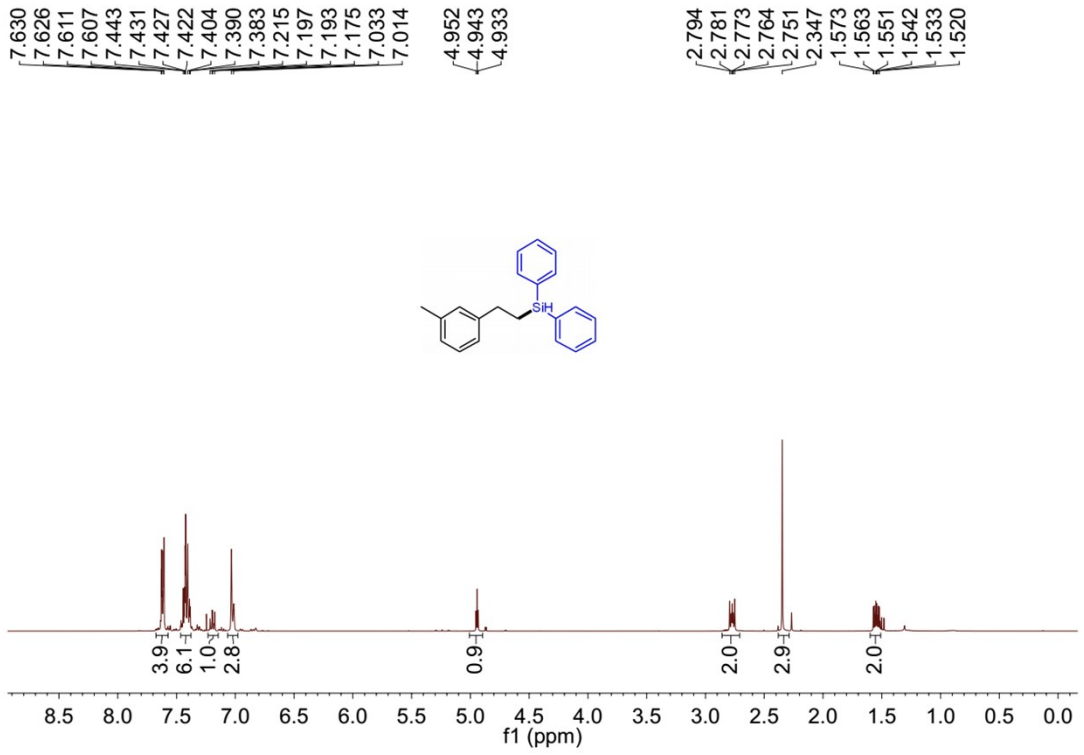
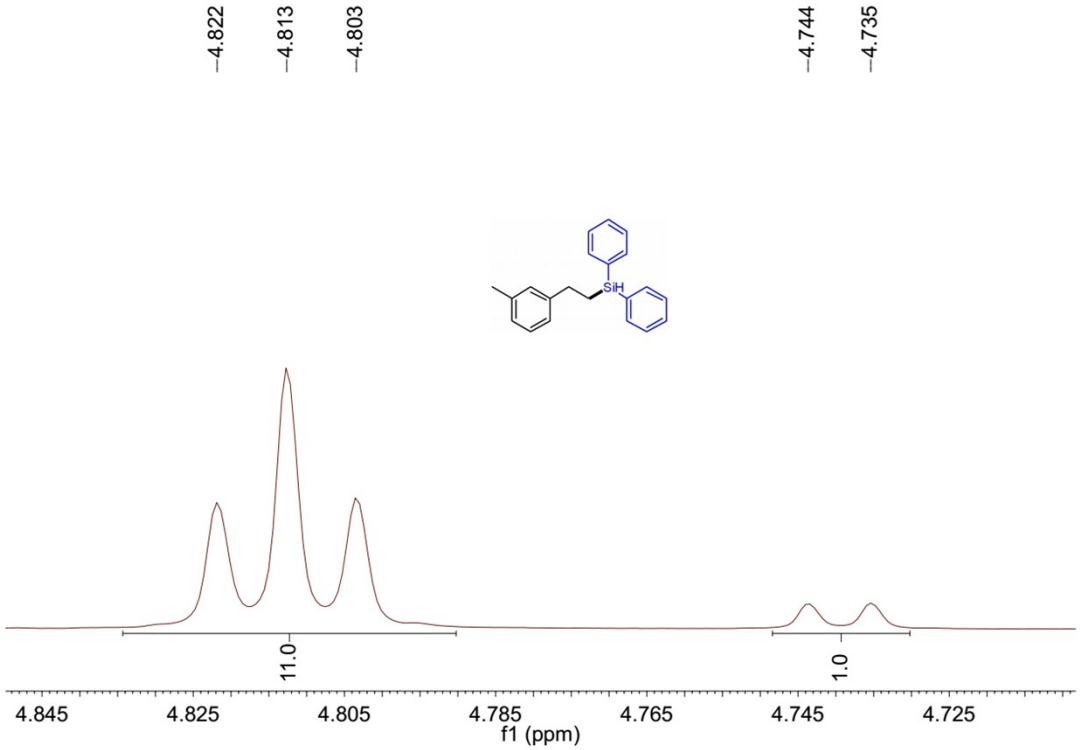


6c regioselectivity



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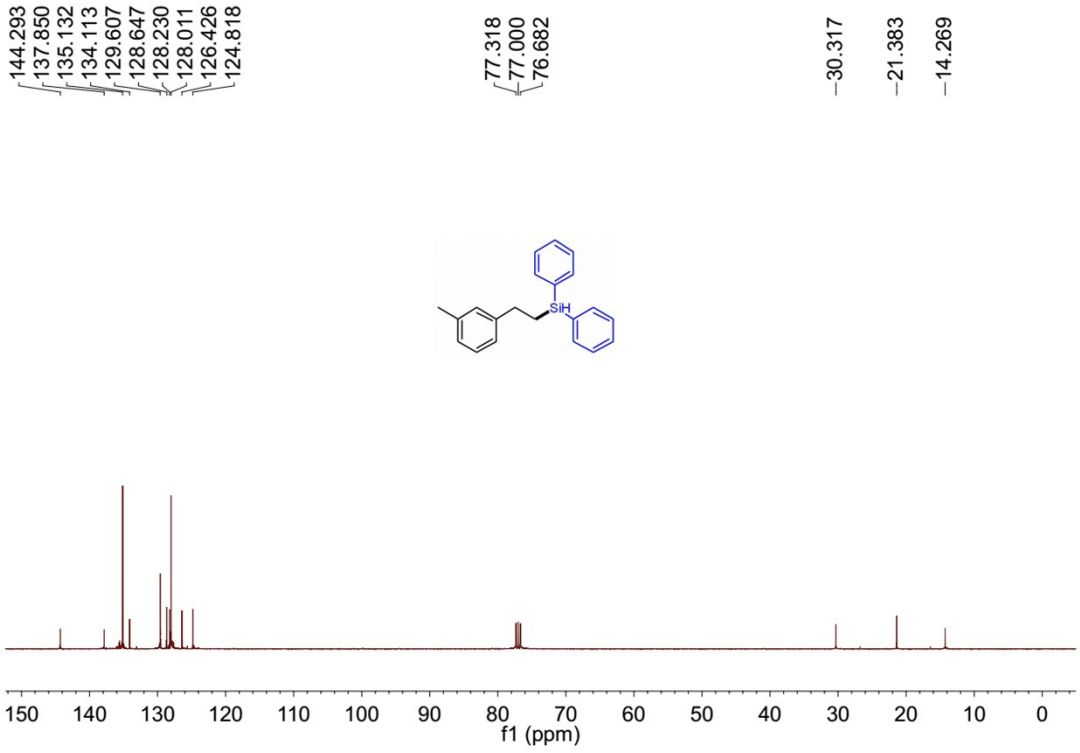

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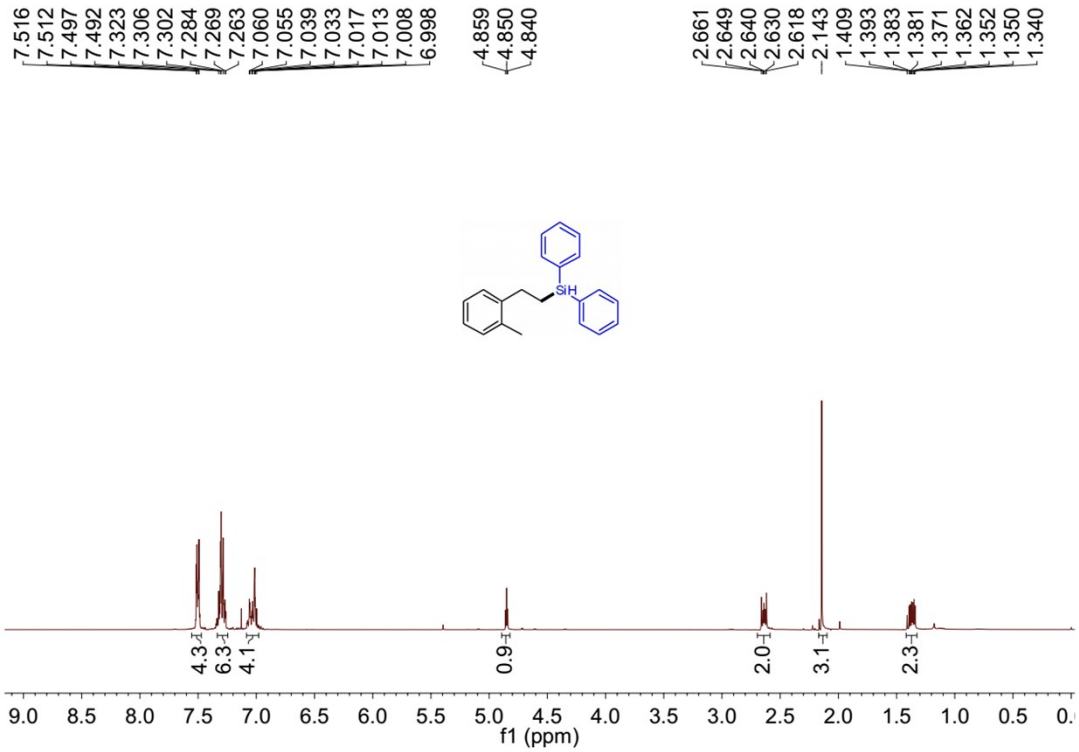

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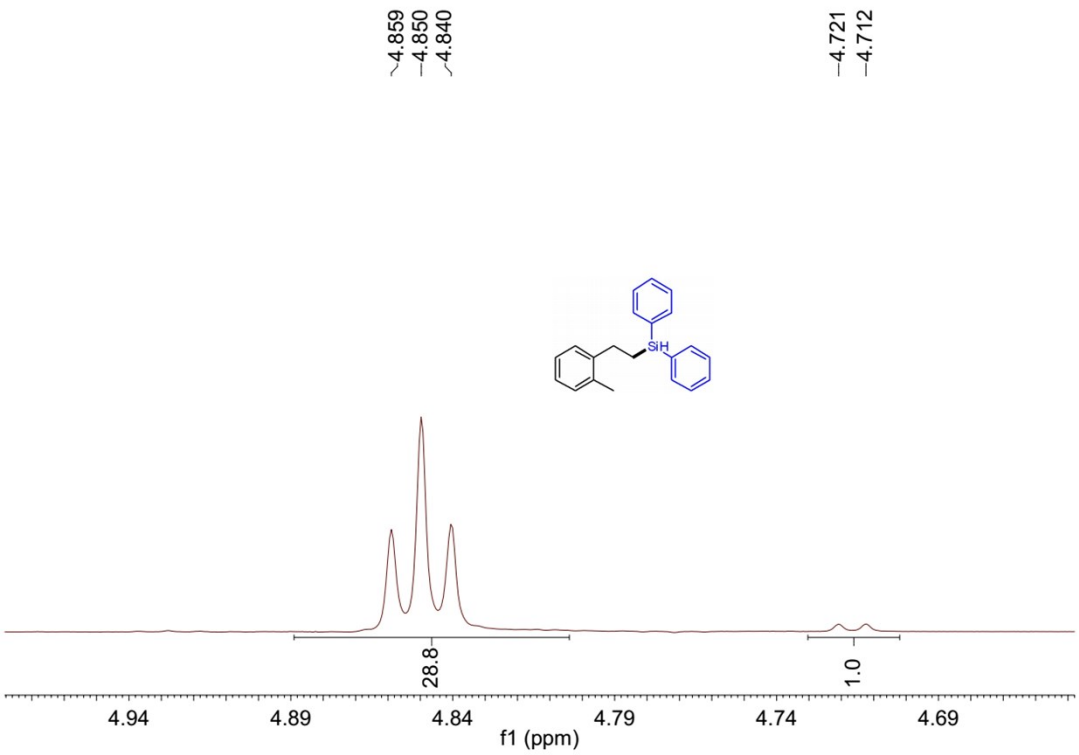
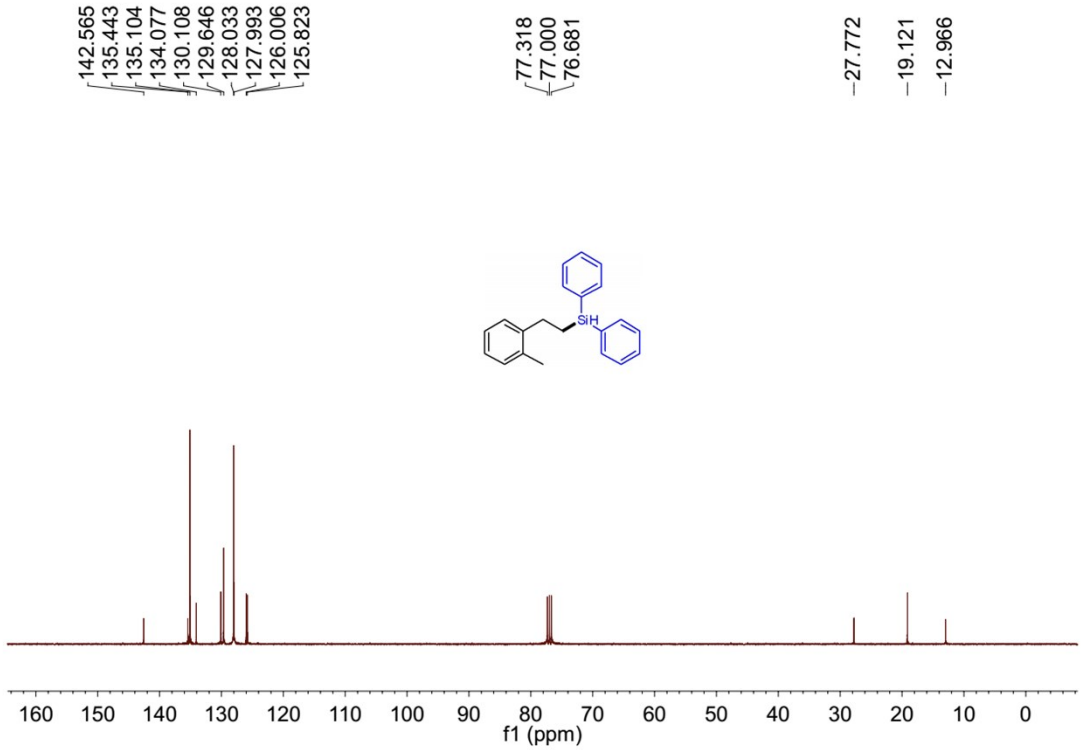
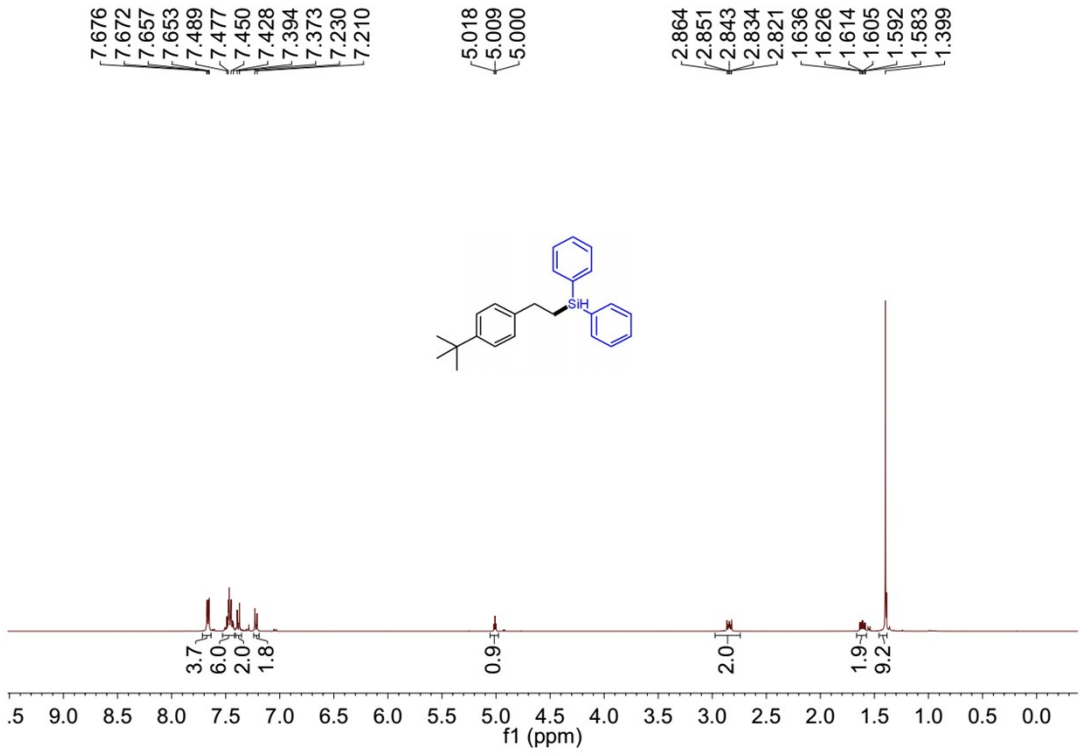


6d ^{13}C NMR



6e ^{1}H NMR



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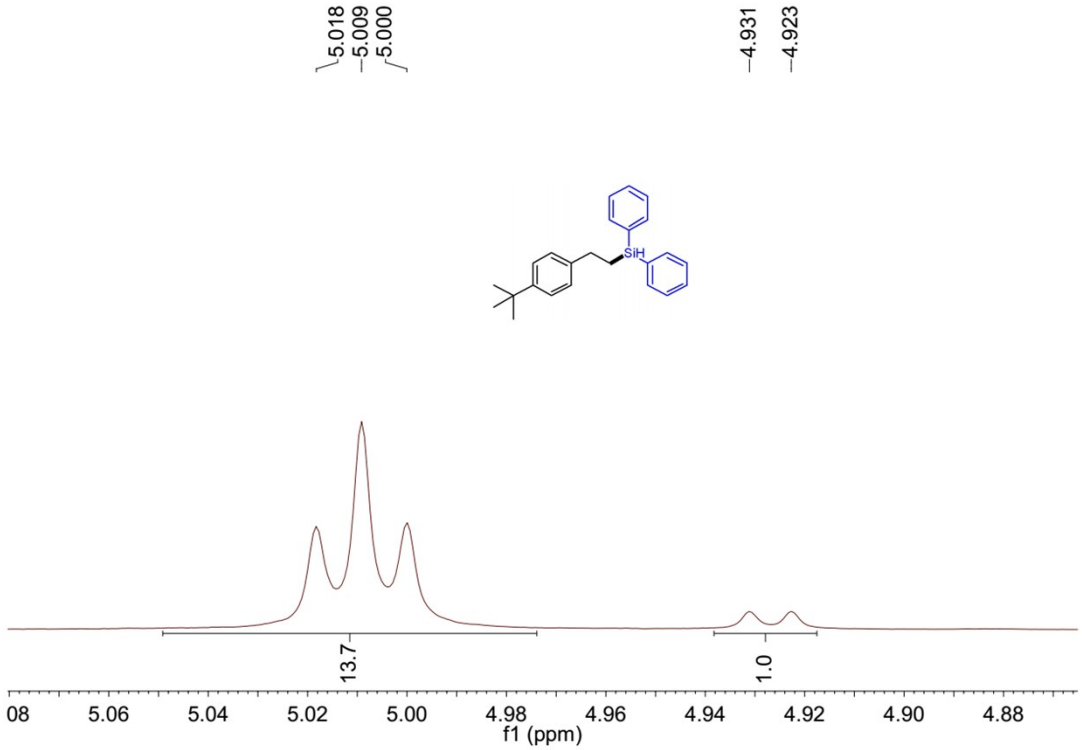
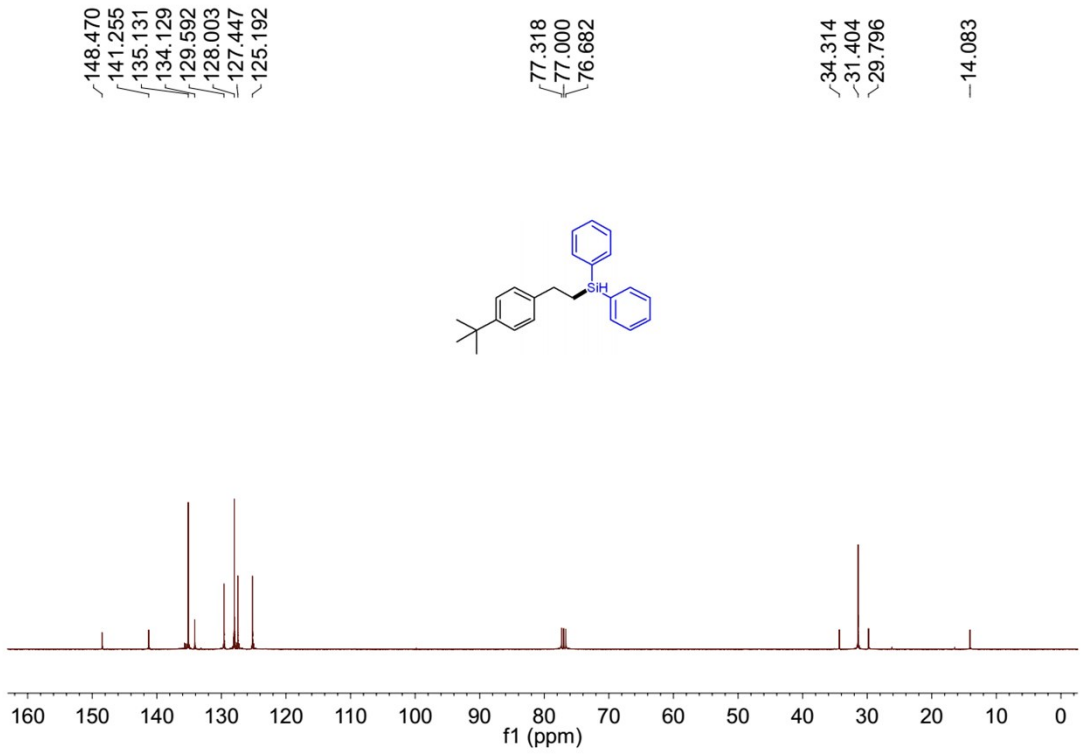
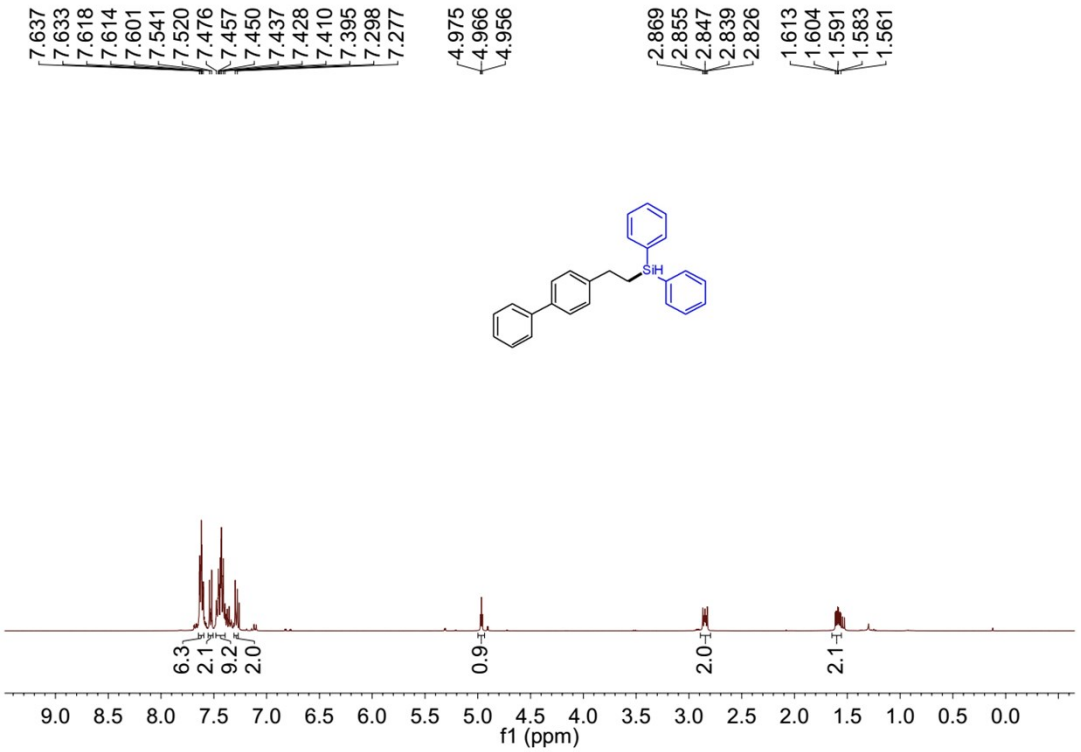


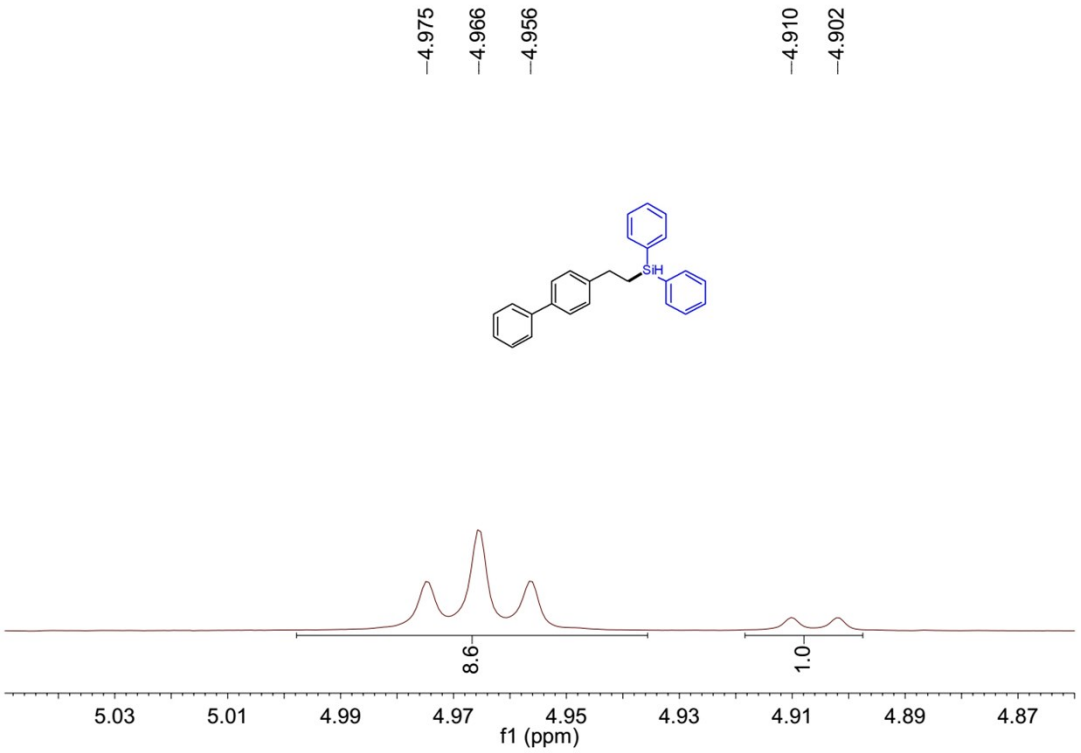
6e ^{13}C NMR



6f ^{1}H NMR



6f regioselectivity



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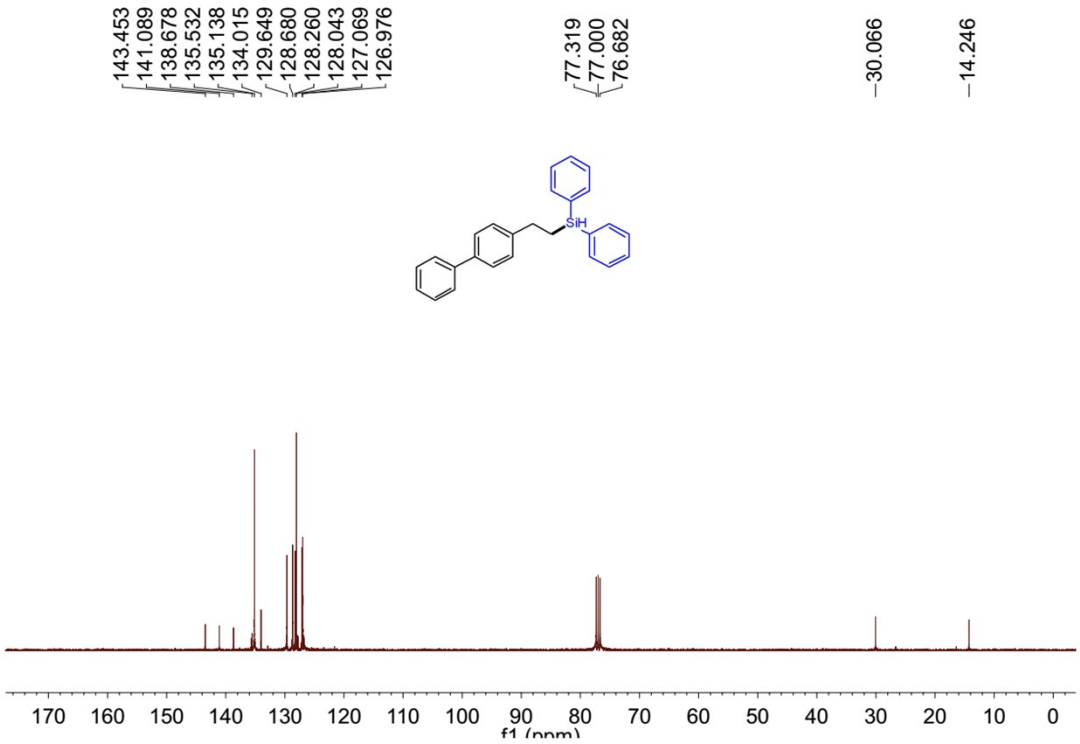
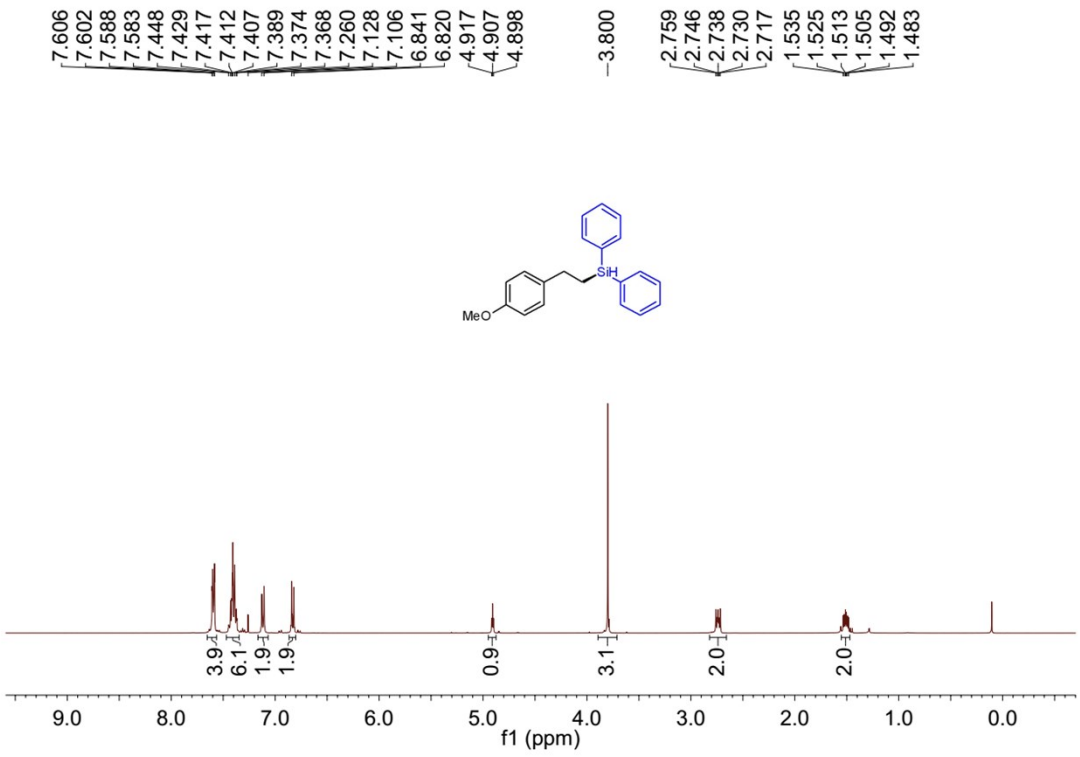
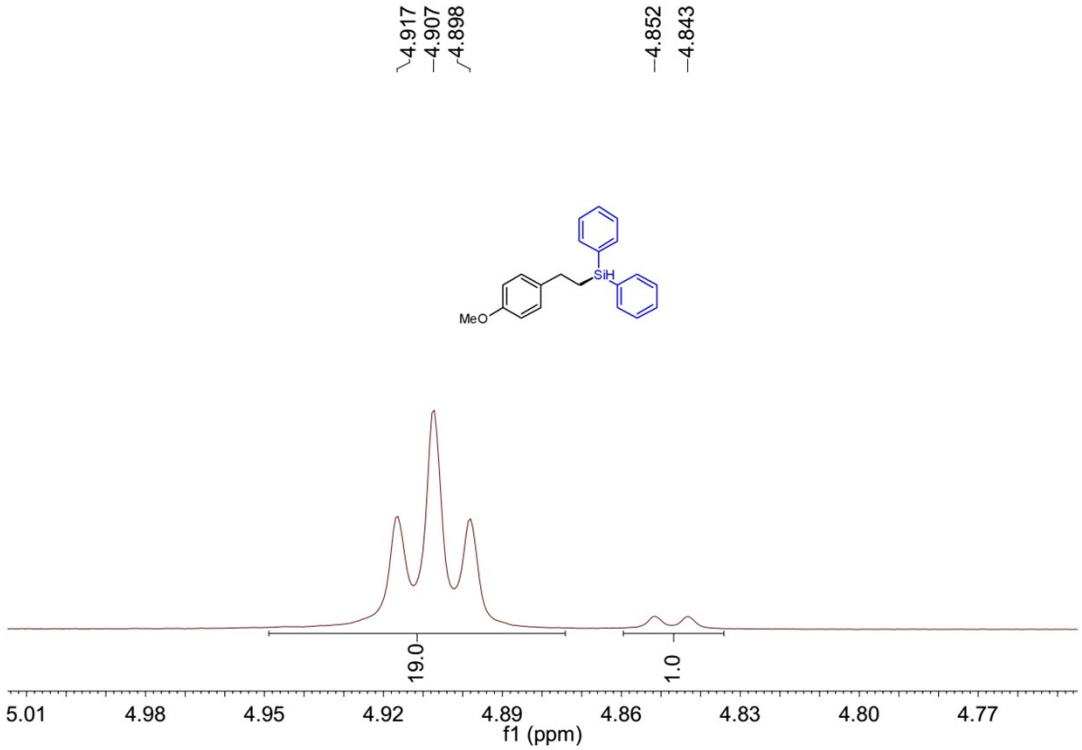


6g ^{1}H NMR



6g regioselectivity



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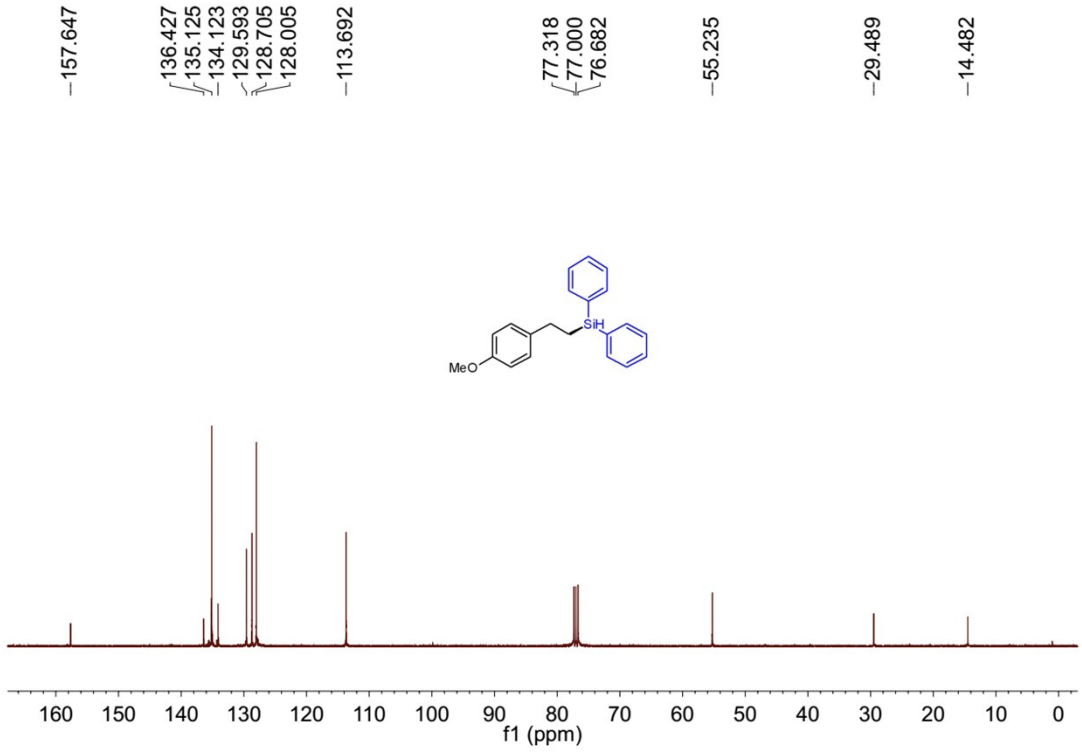
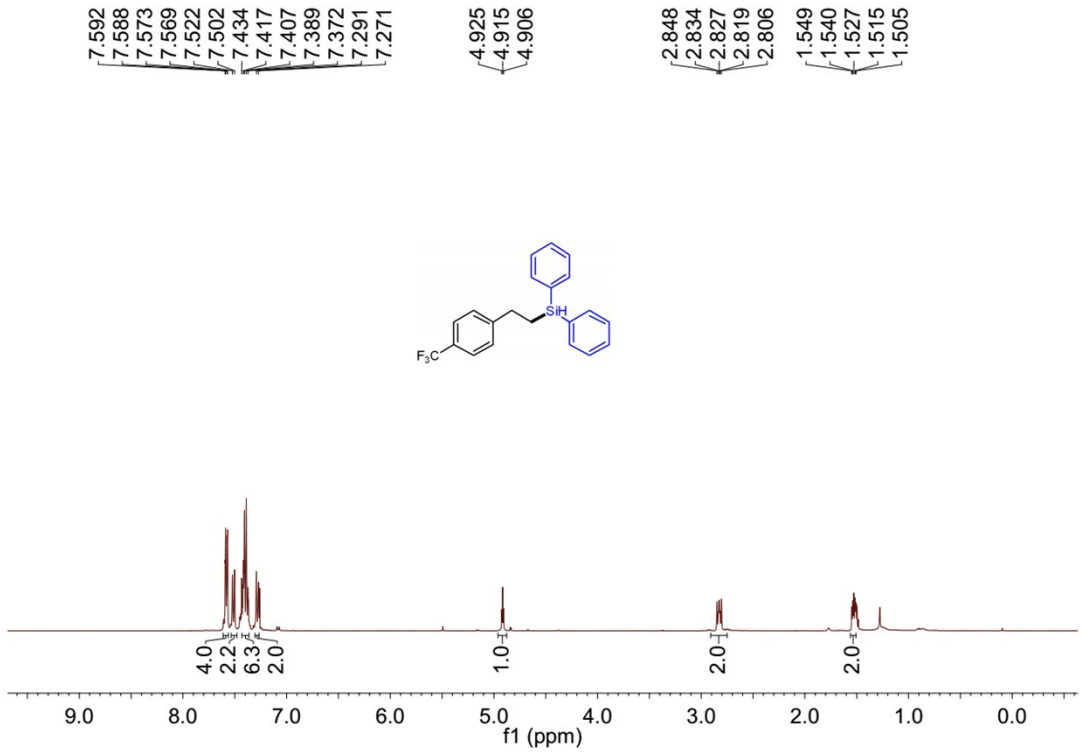


6h ^{1}H NMR



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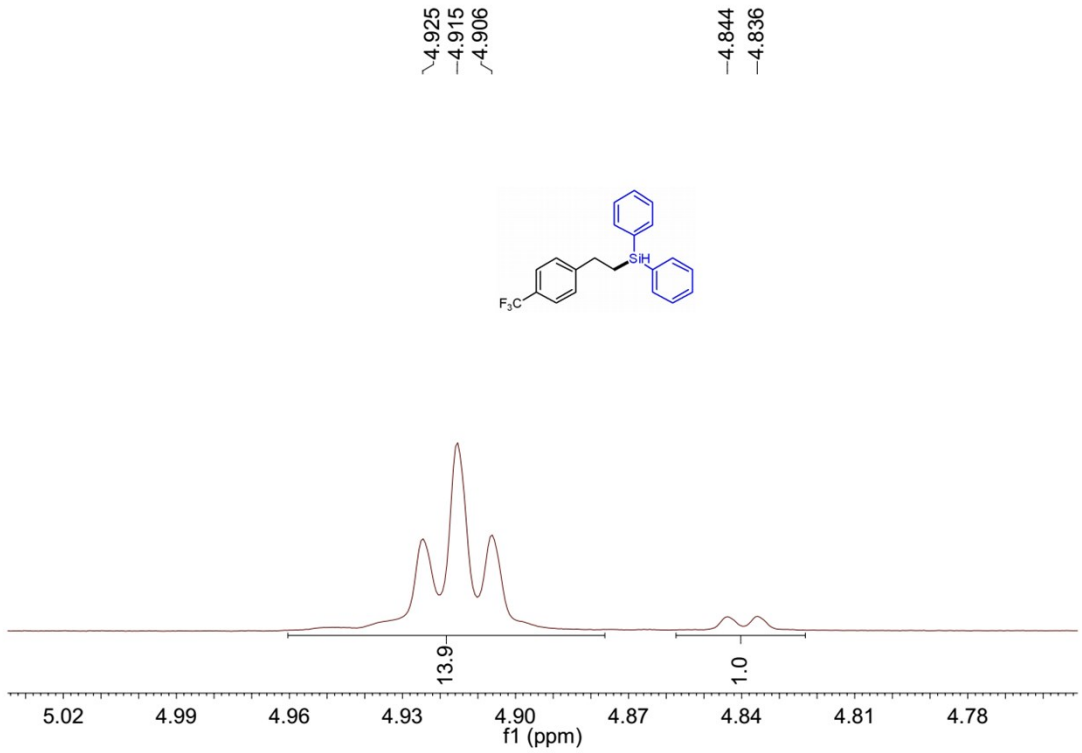
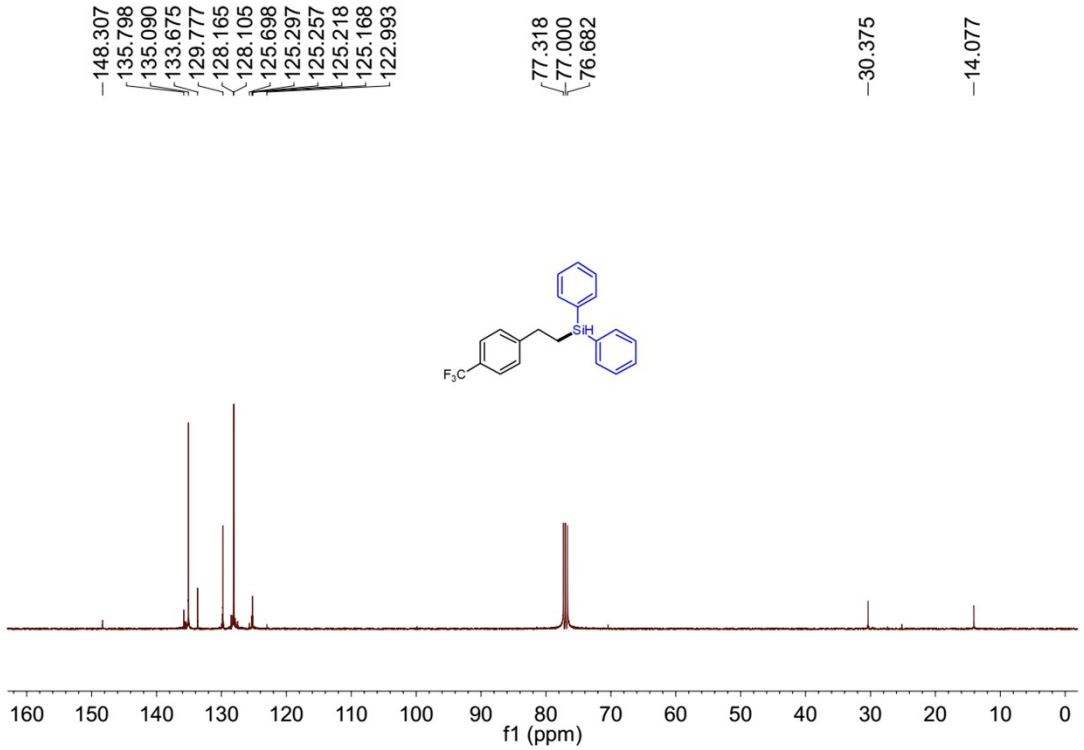
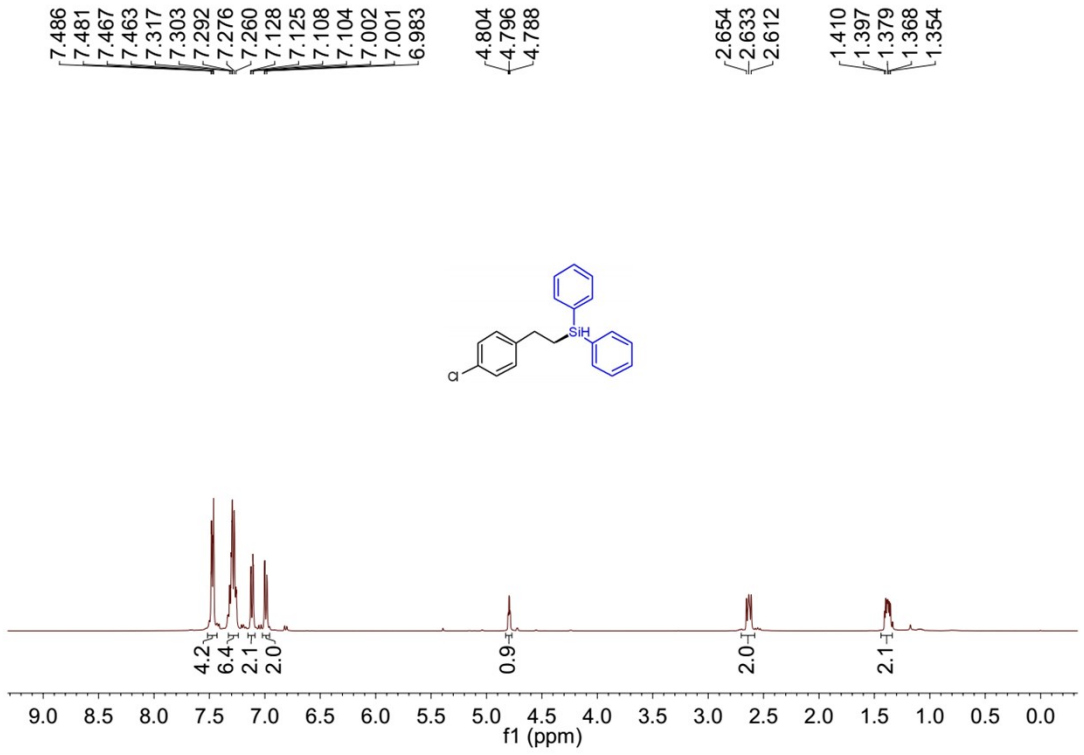


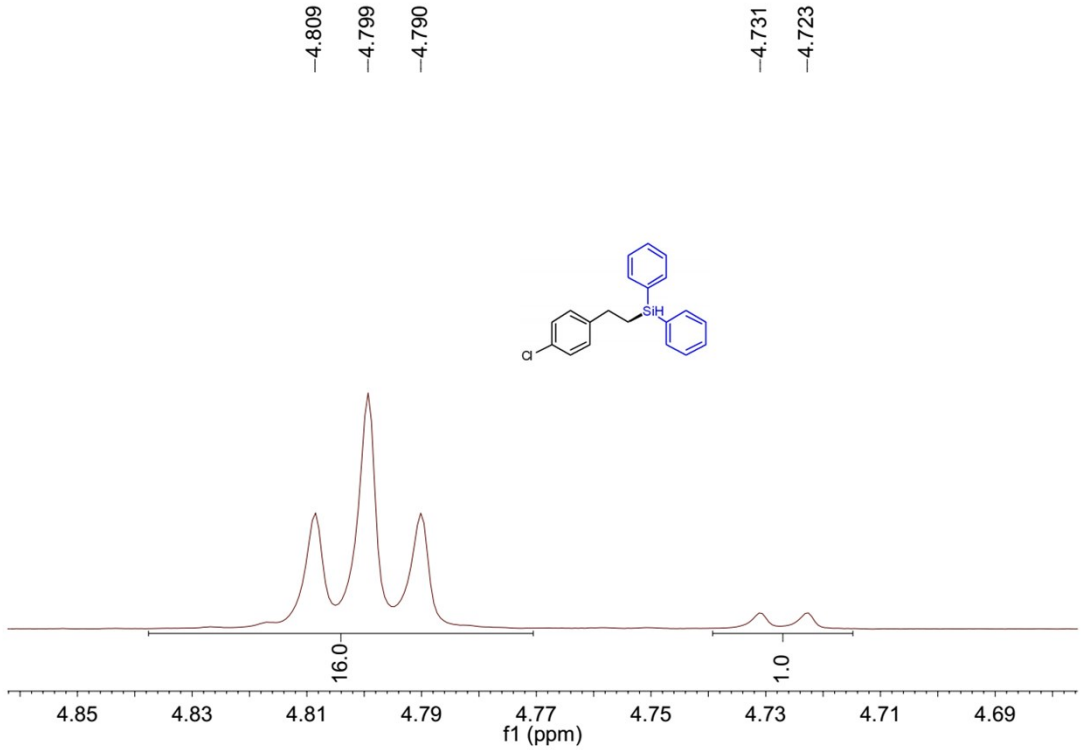
6h ^{13}C NMR



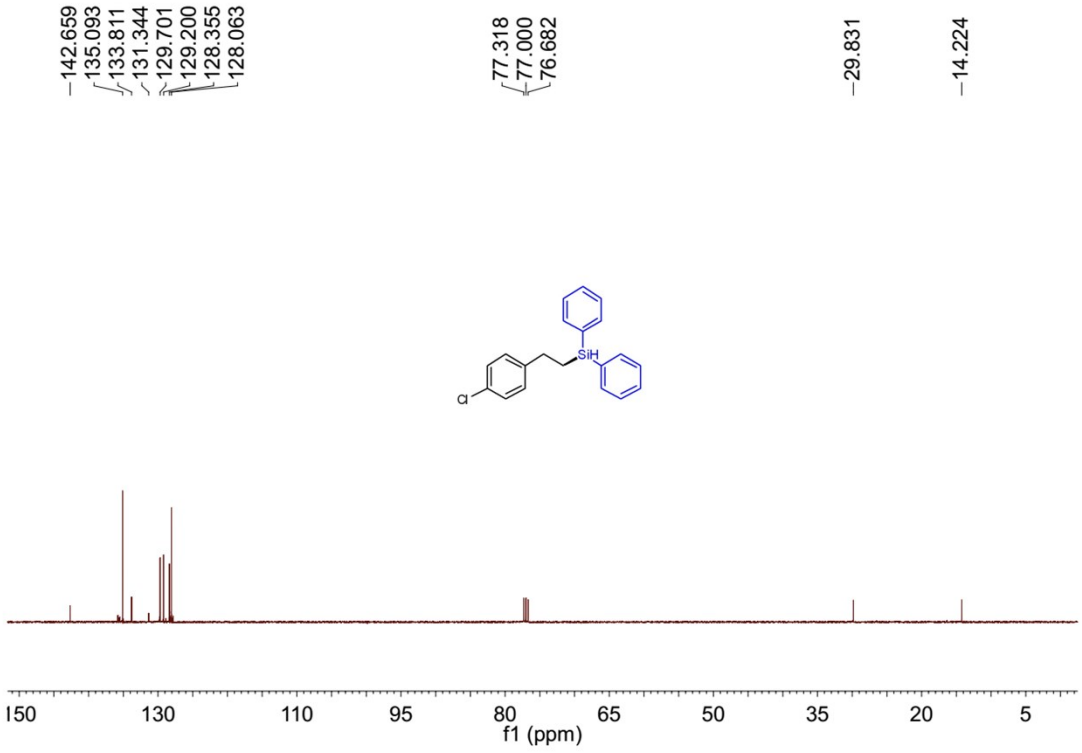
6i ^{1}H NMR



6i regioselectivity



6i ^{13}C NMR



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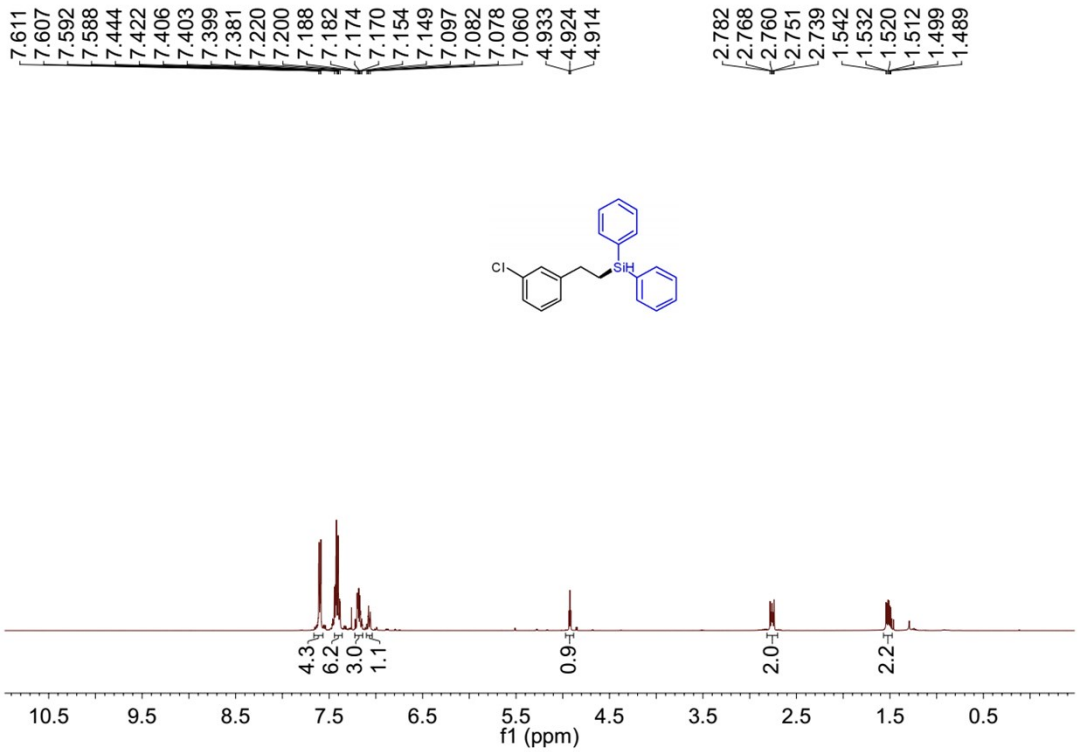

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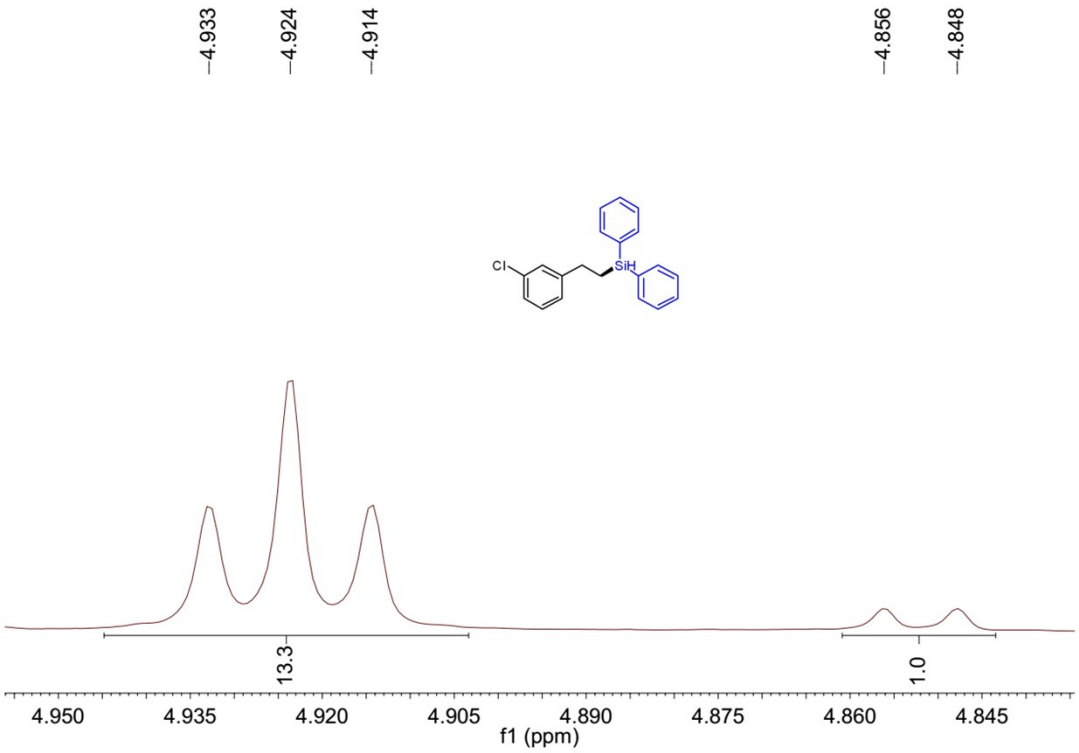
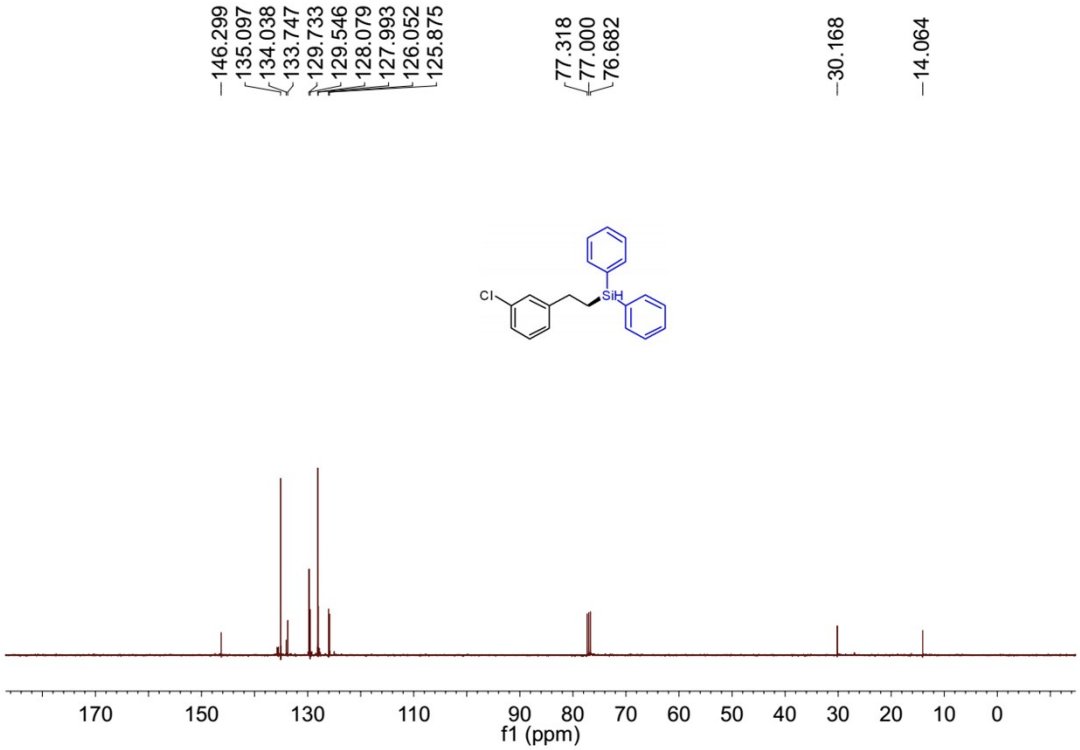
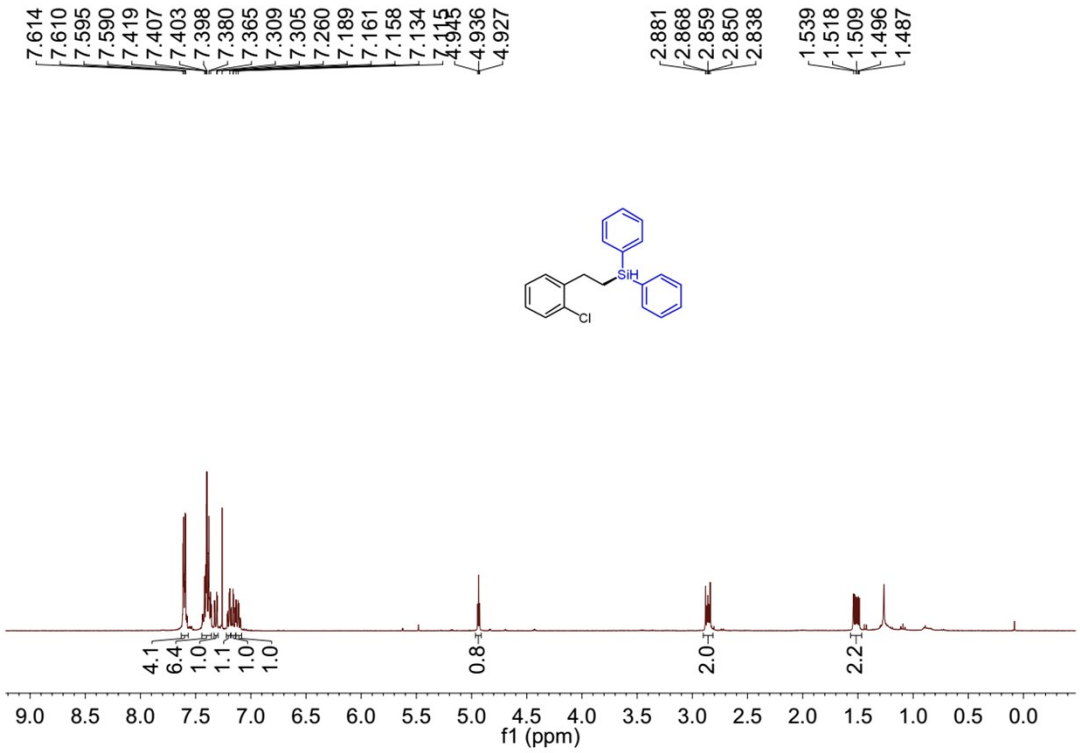


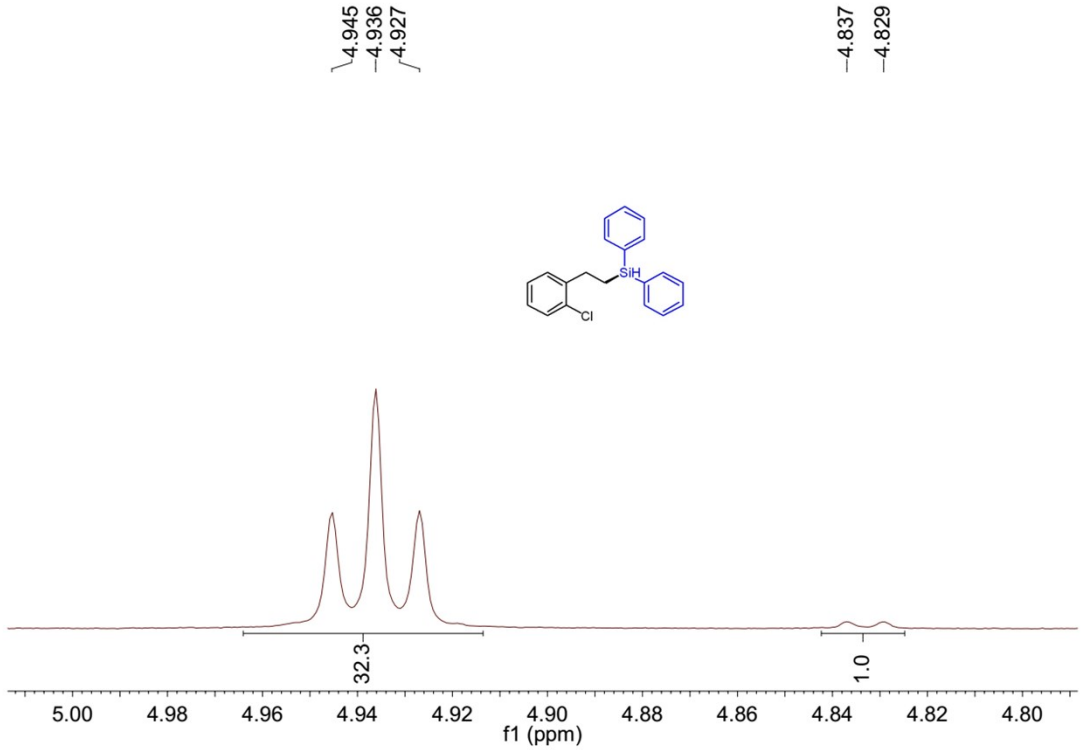
6j ^{13}C NMR



6k ^{1}H NMR



6k regioselectivity



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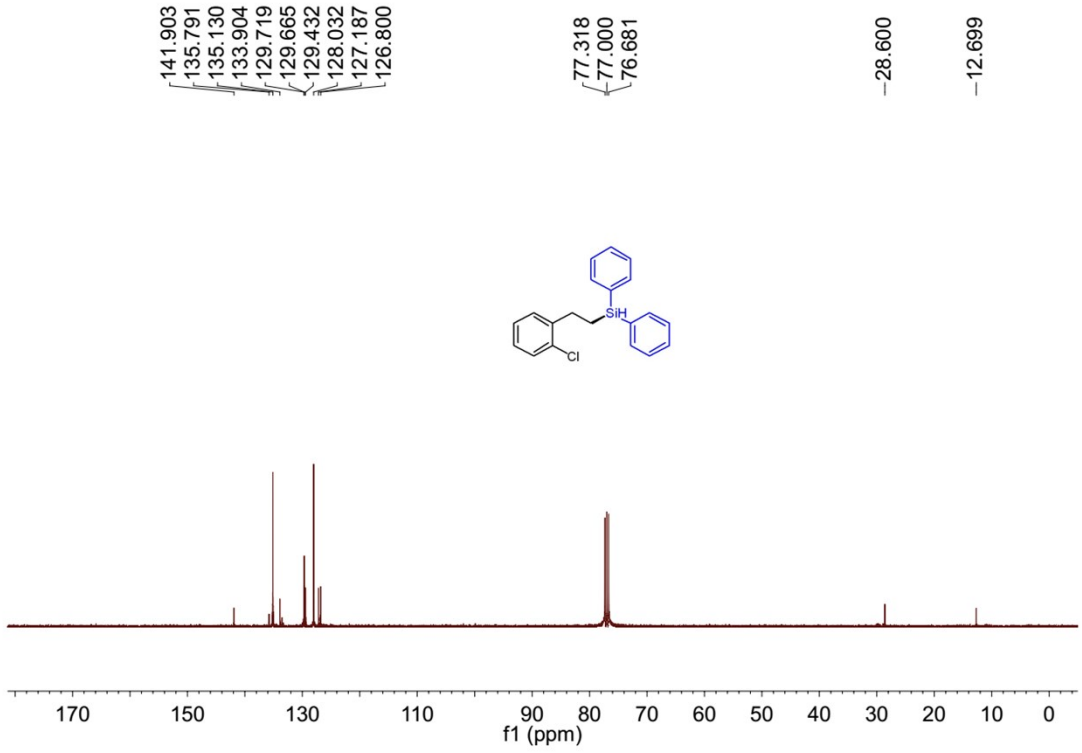

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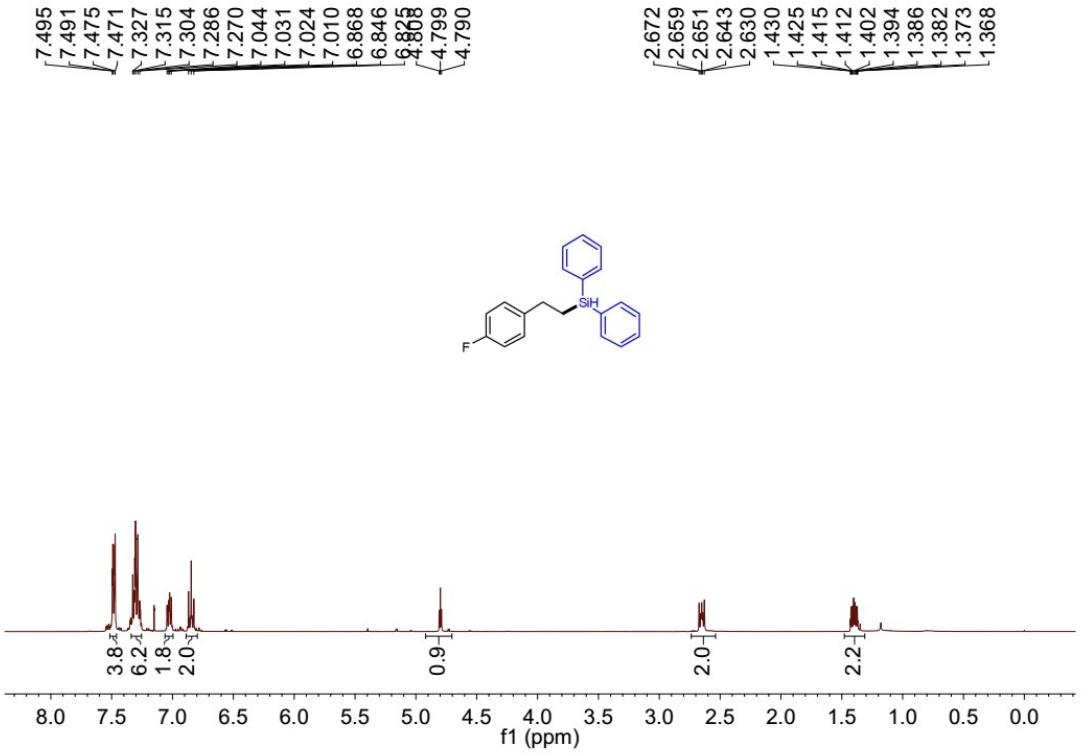

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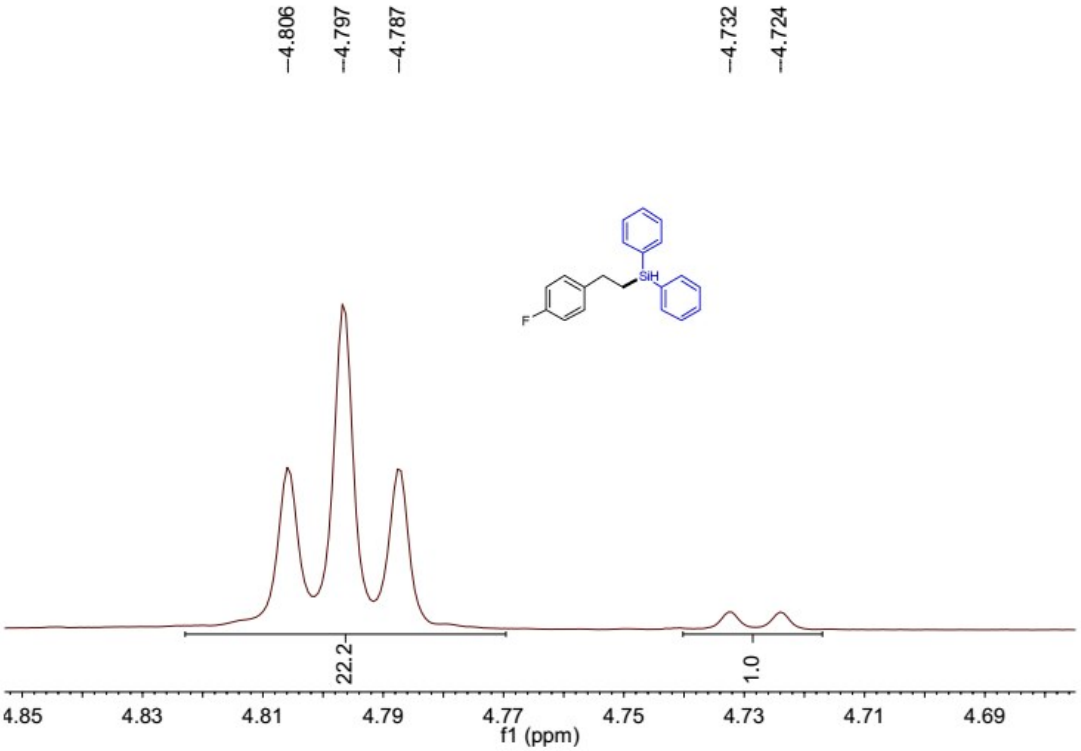

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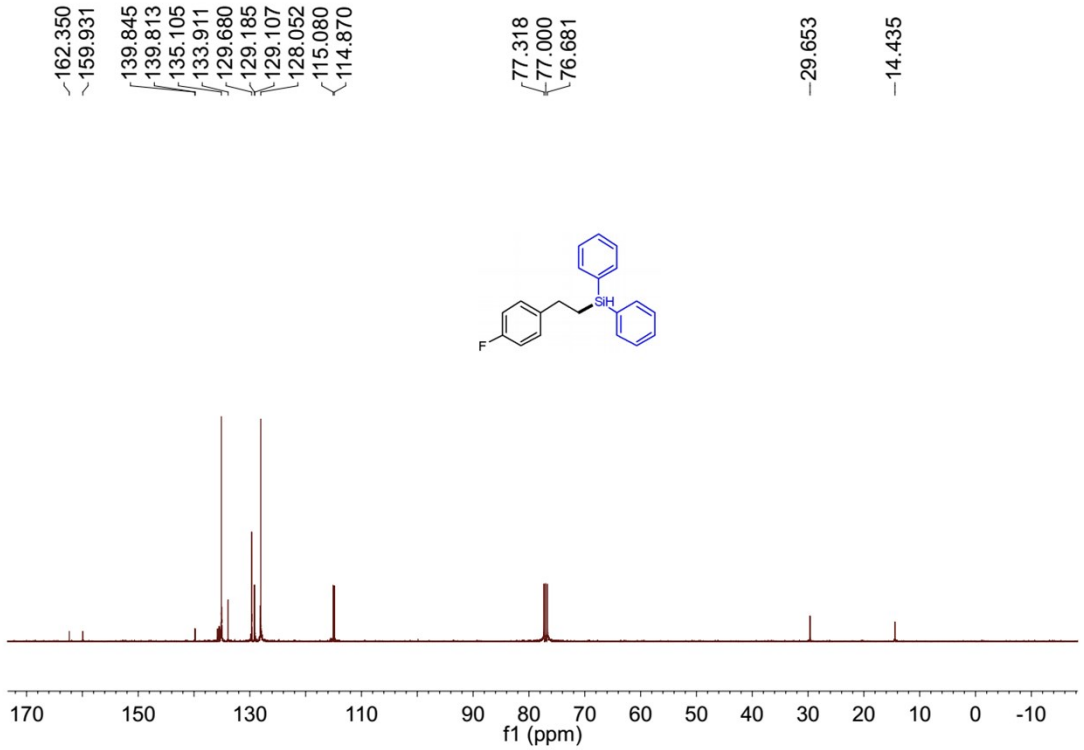
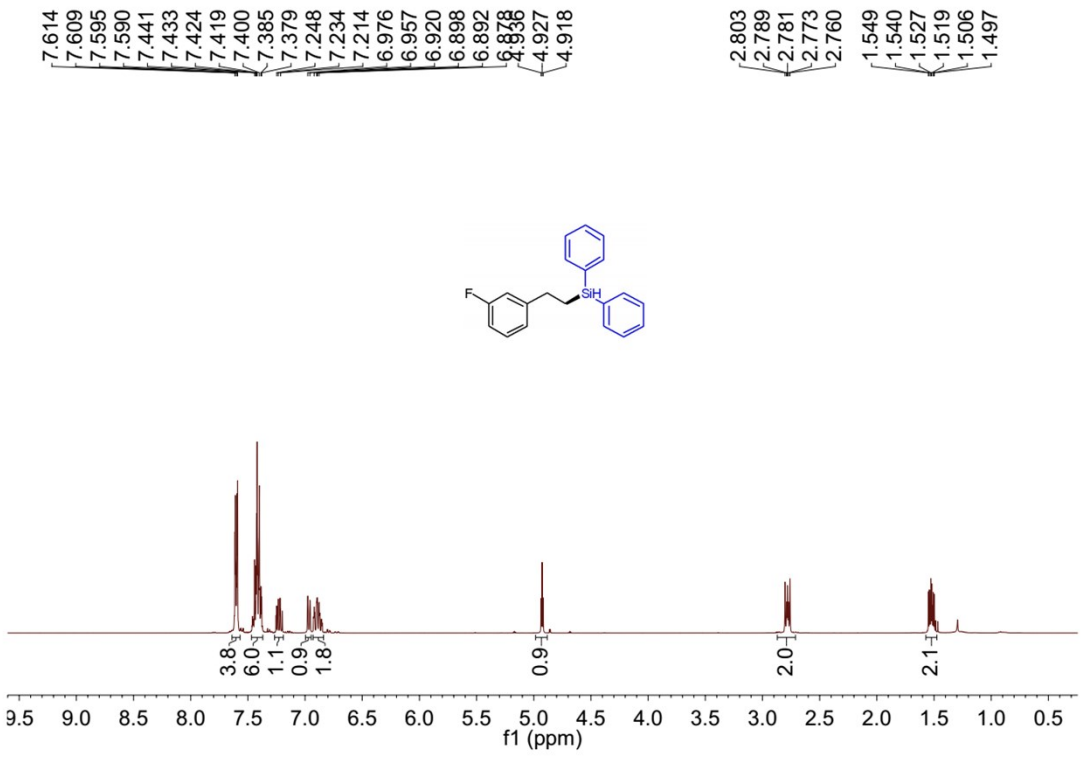
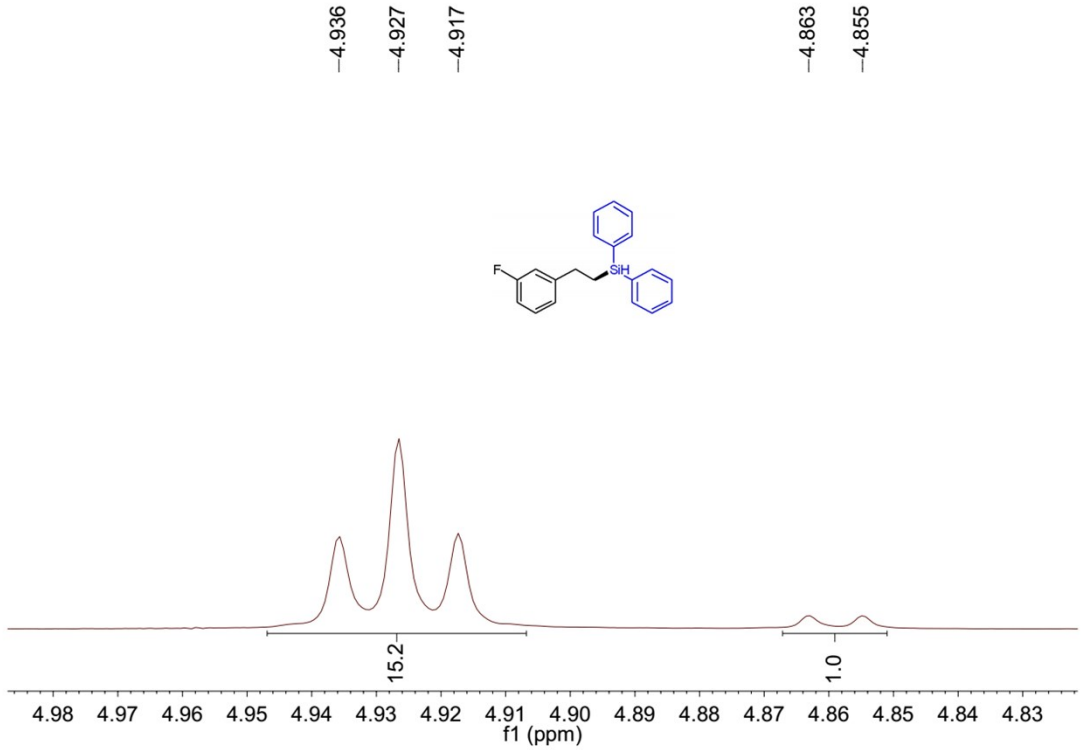


6m ^{1}H NMR



6m regioselectivity



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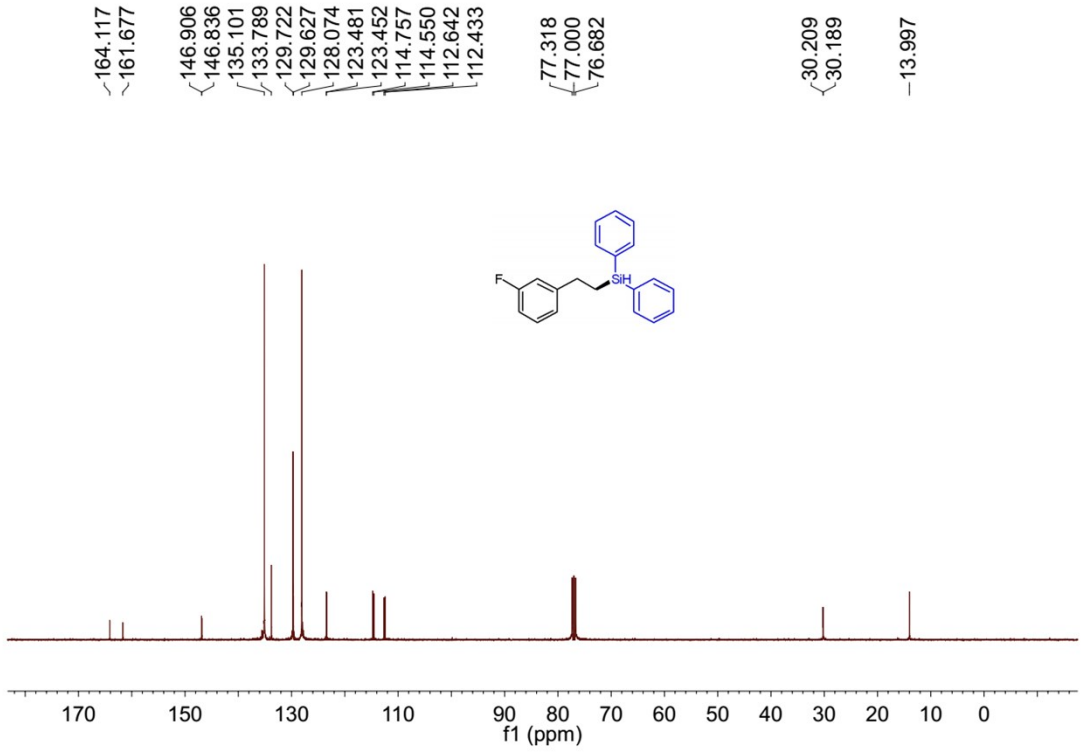

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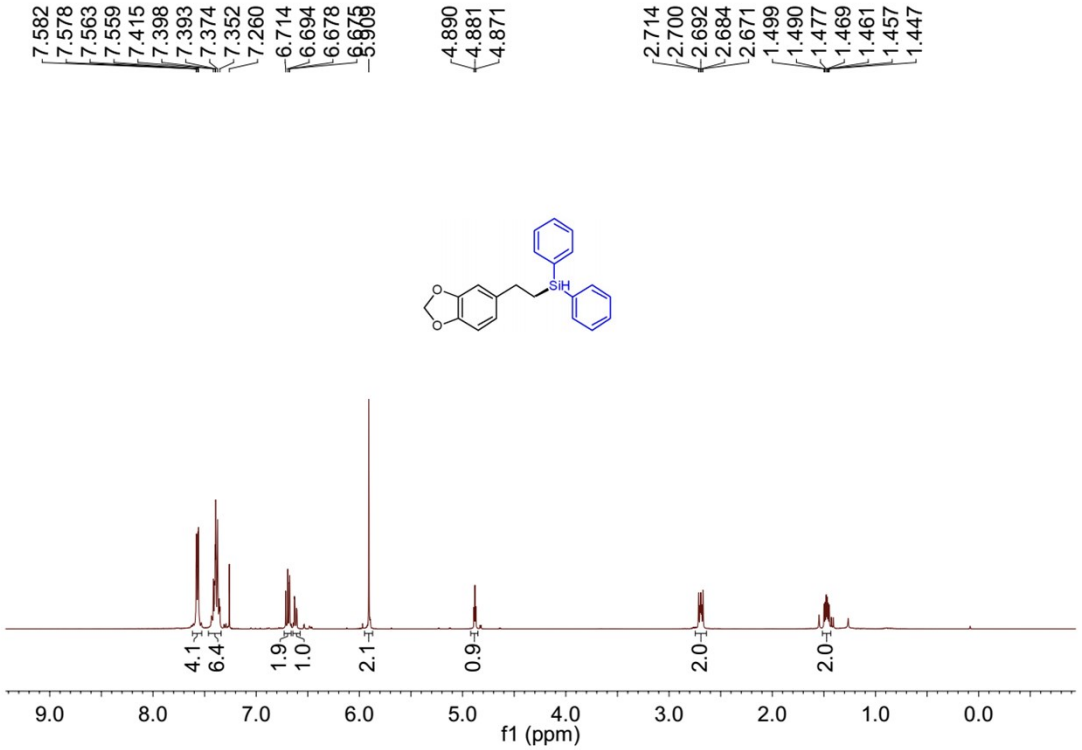
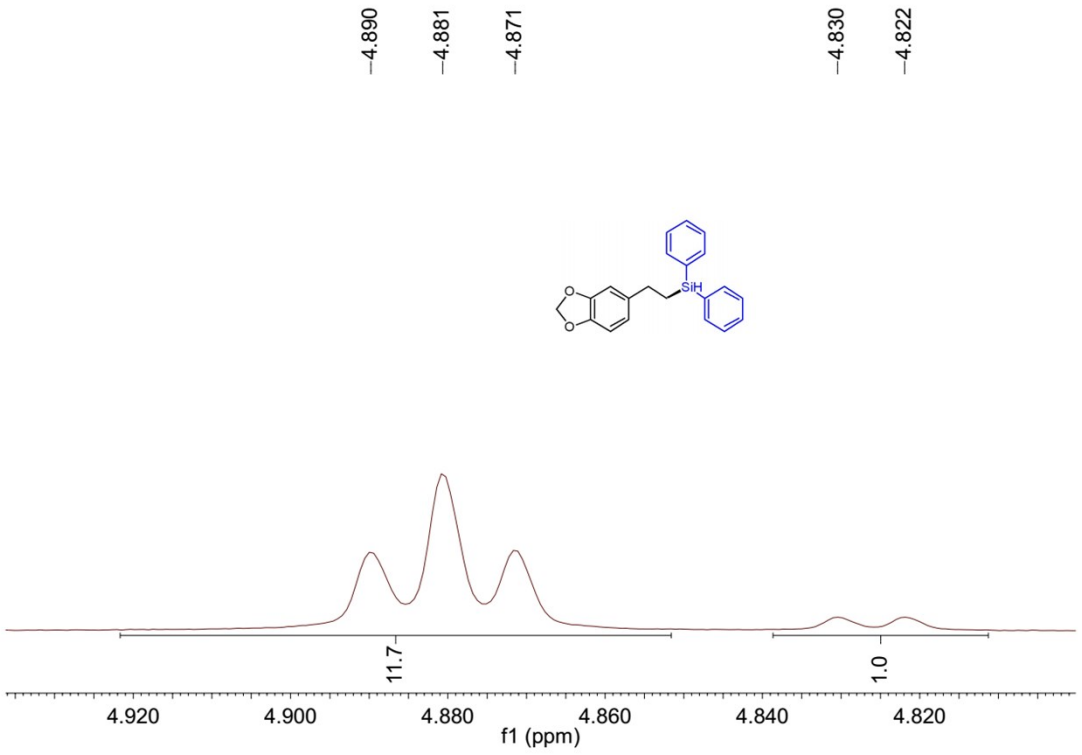


6n regioselectivity



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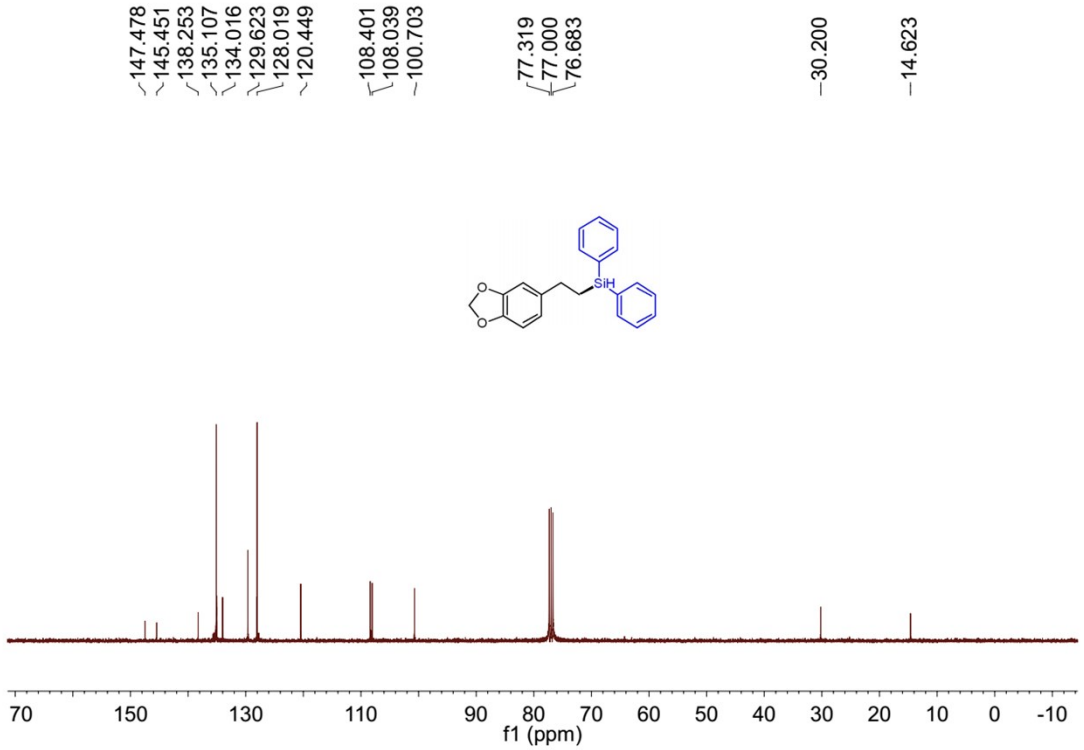

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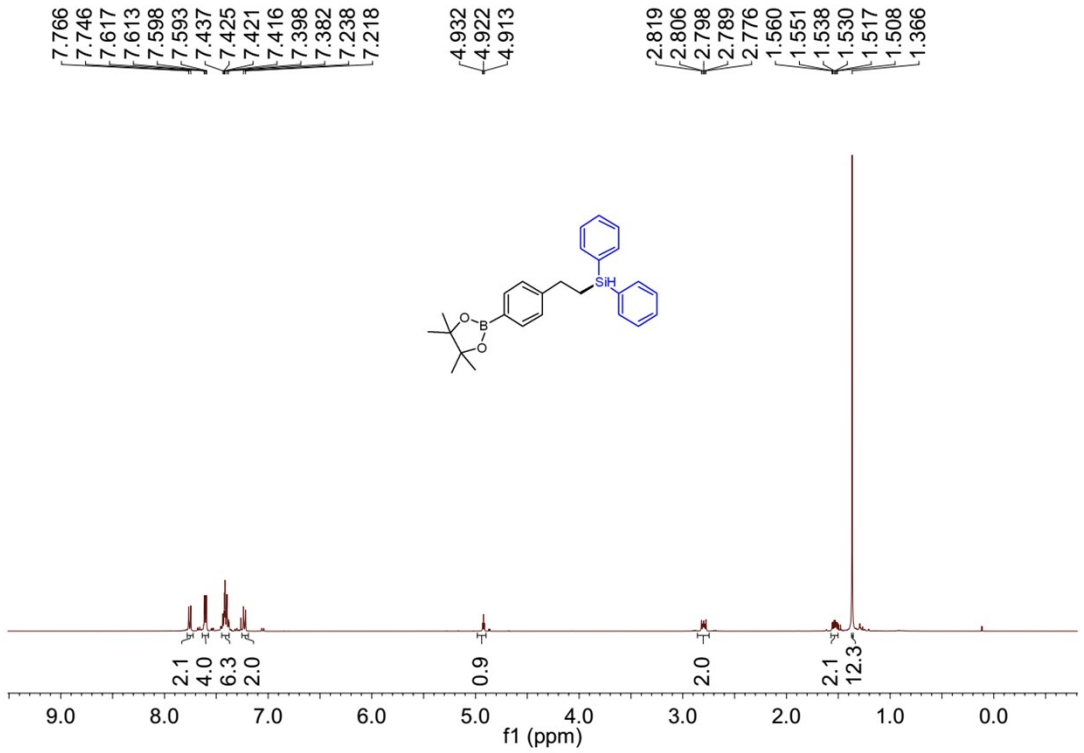
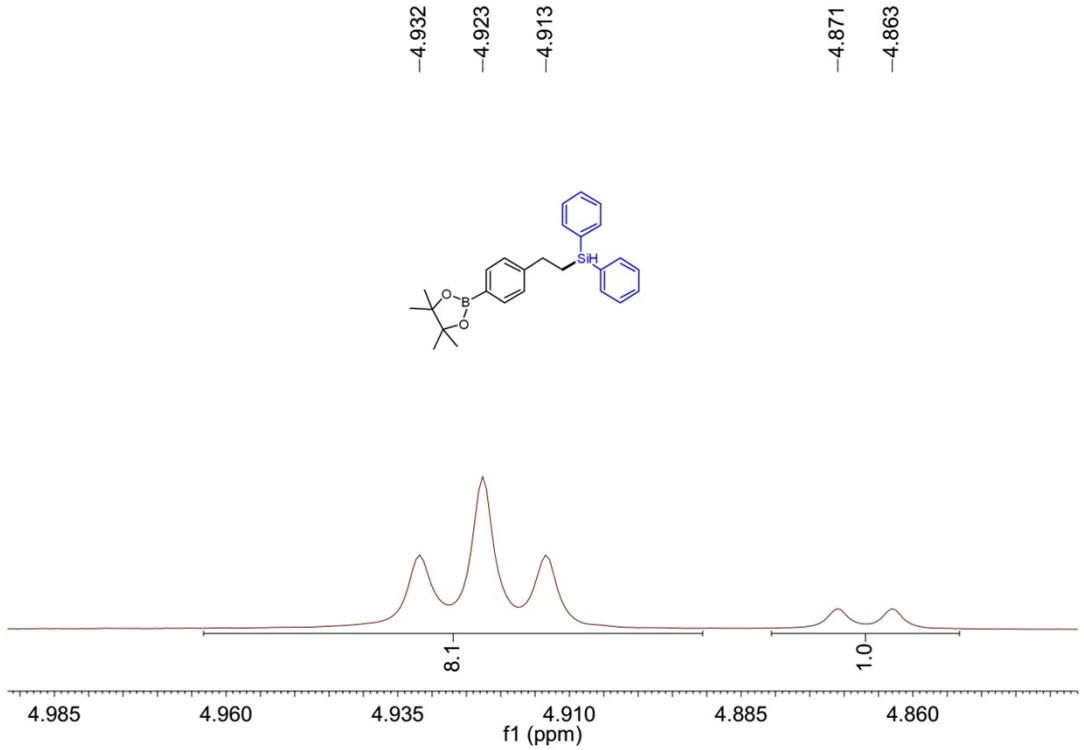
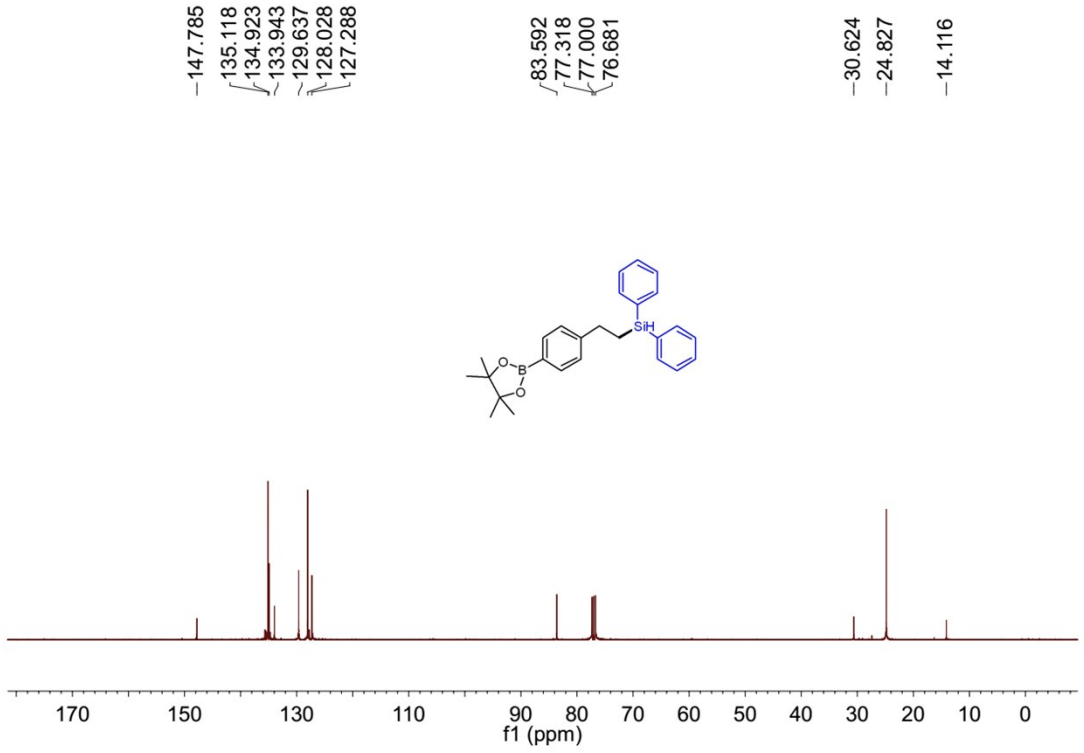


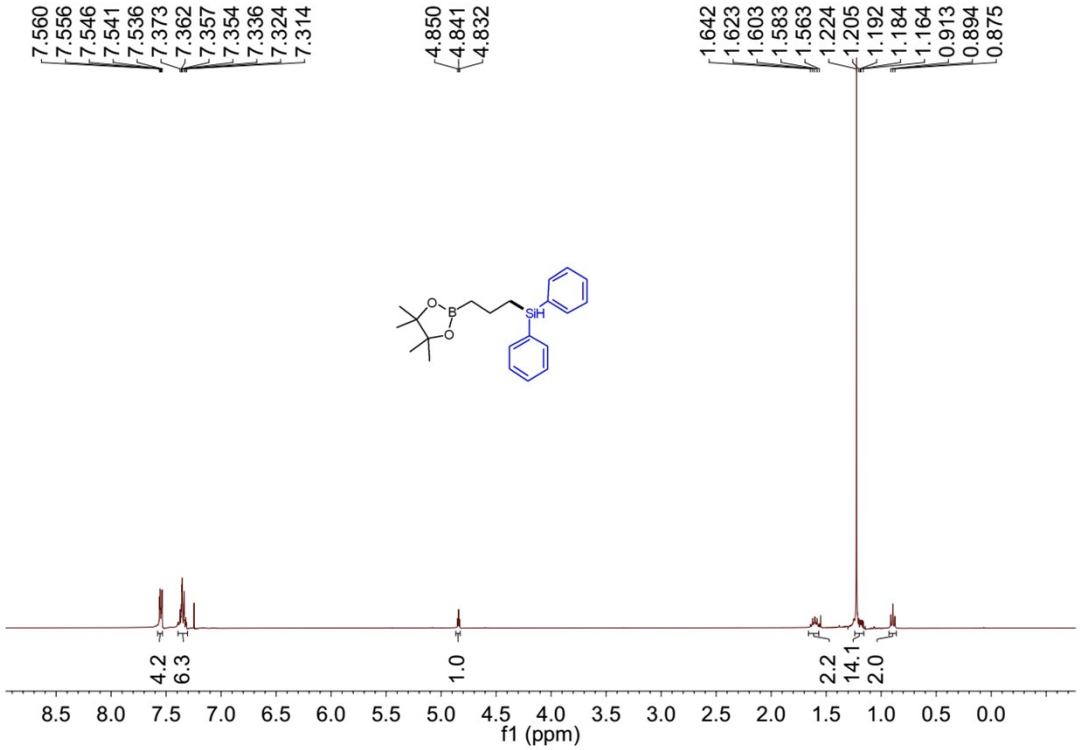
6o regioselectivity



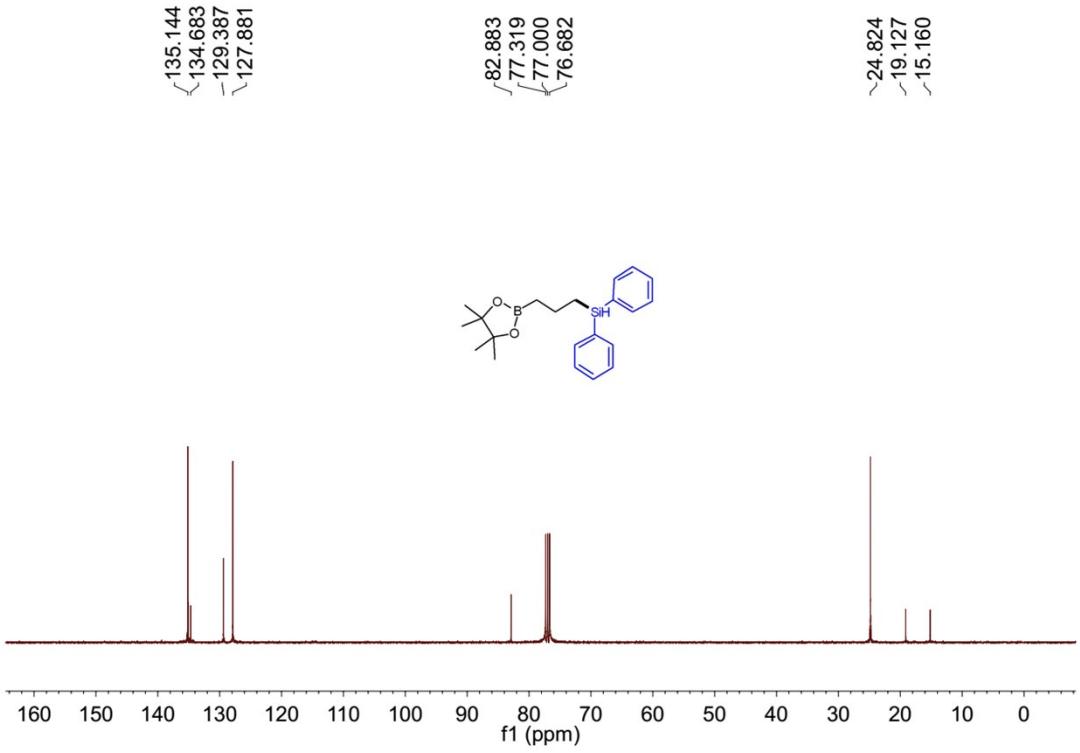
6o ^{13}C NMR



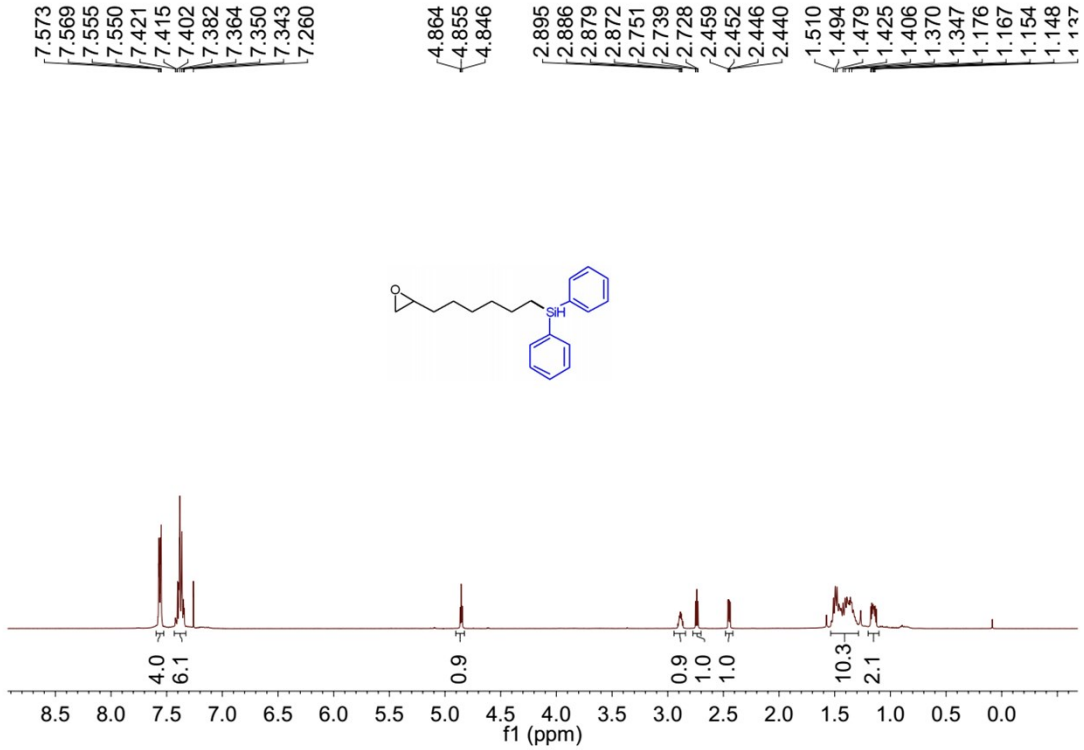
6p ^{1}H NMR



6p ^{13}C NMR



6q ^{1}H NMR



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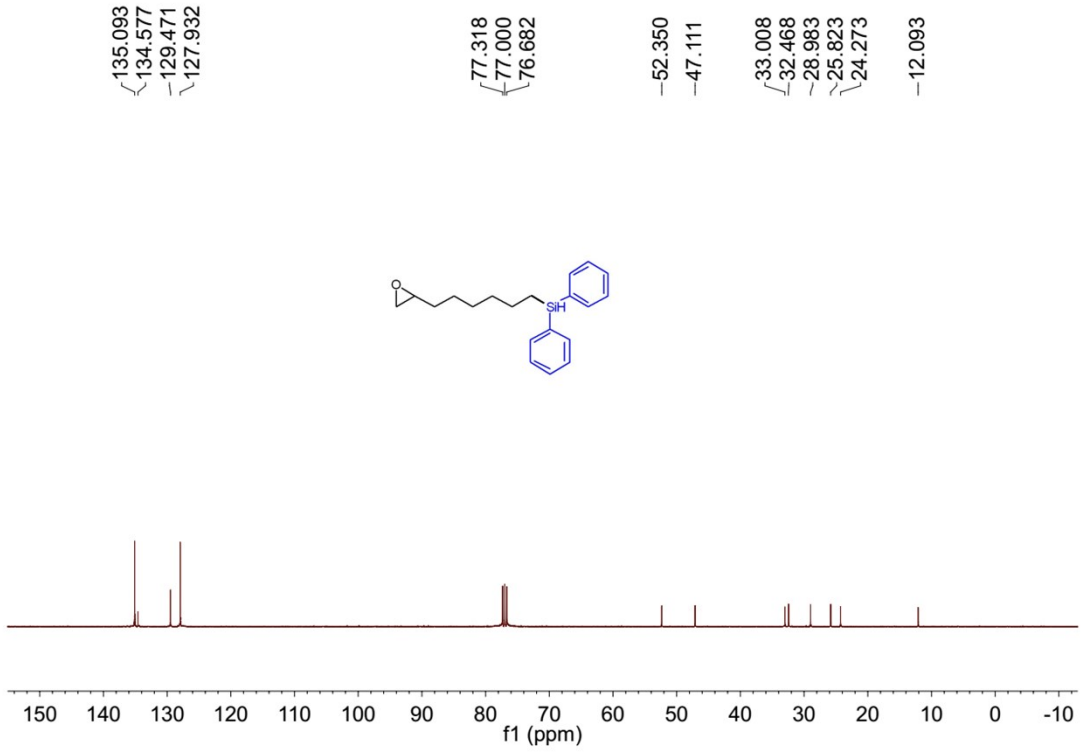

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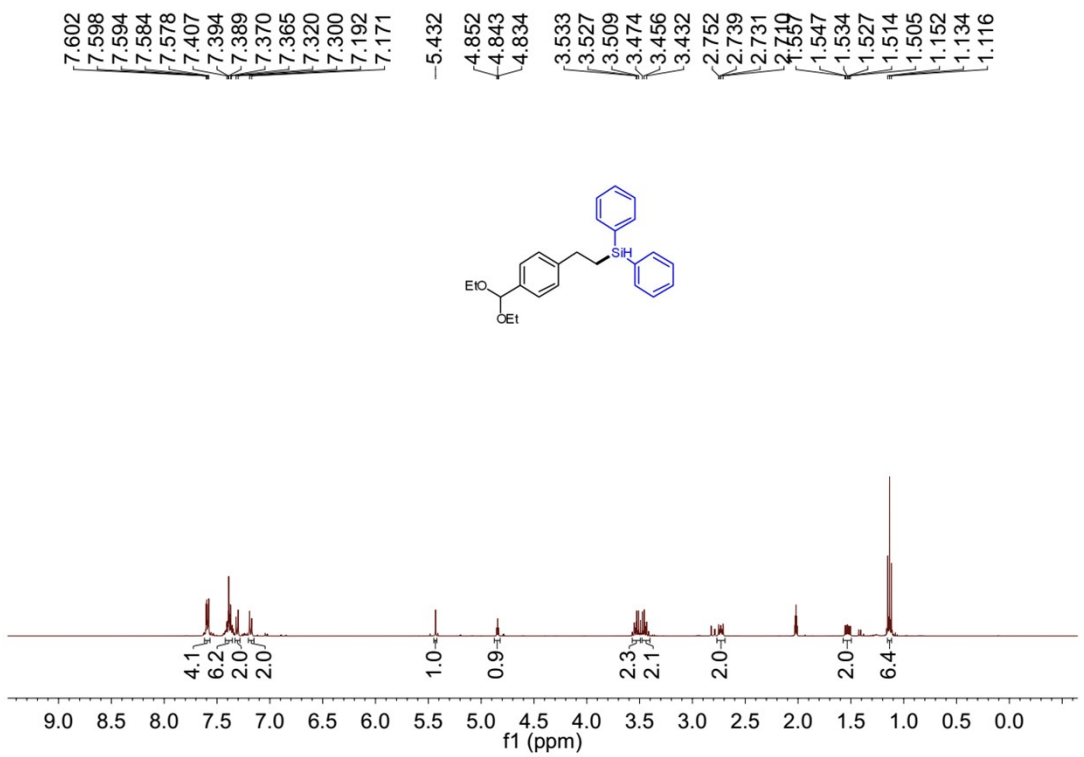
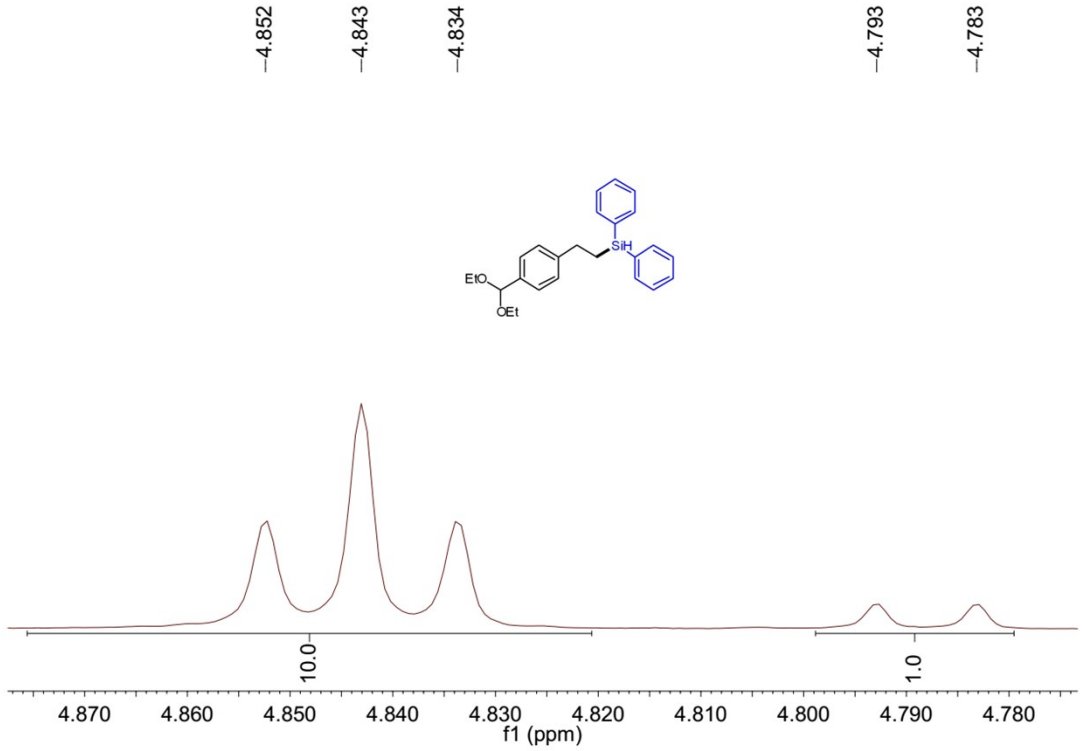


6r regioselectivity



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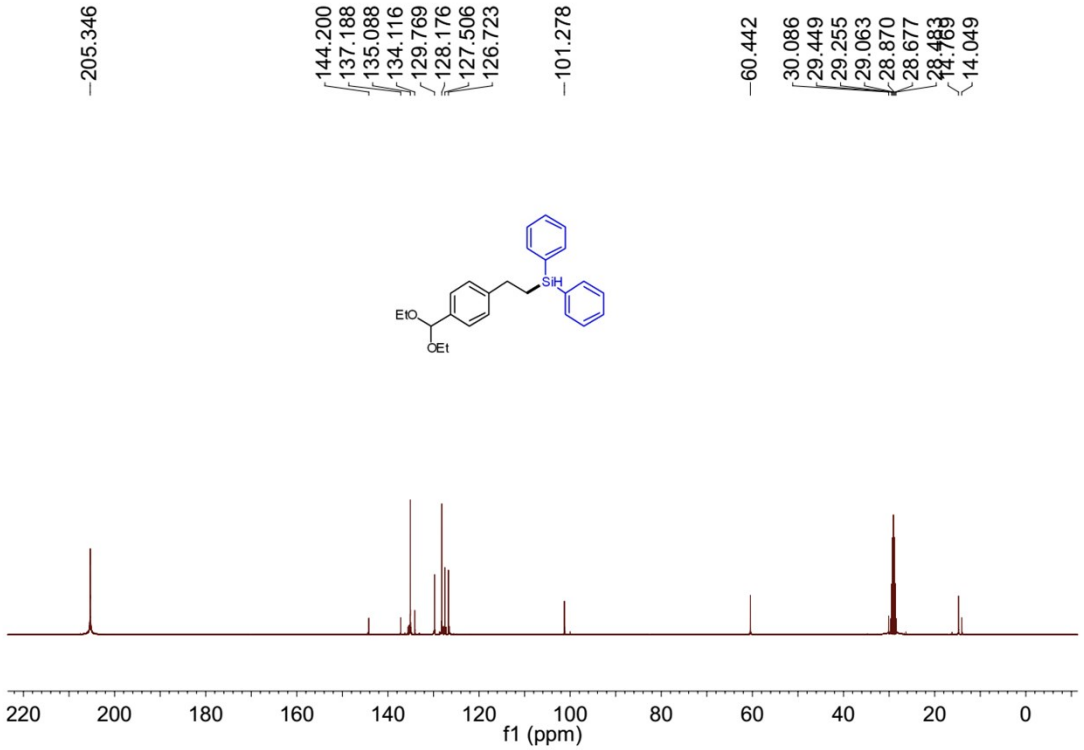
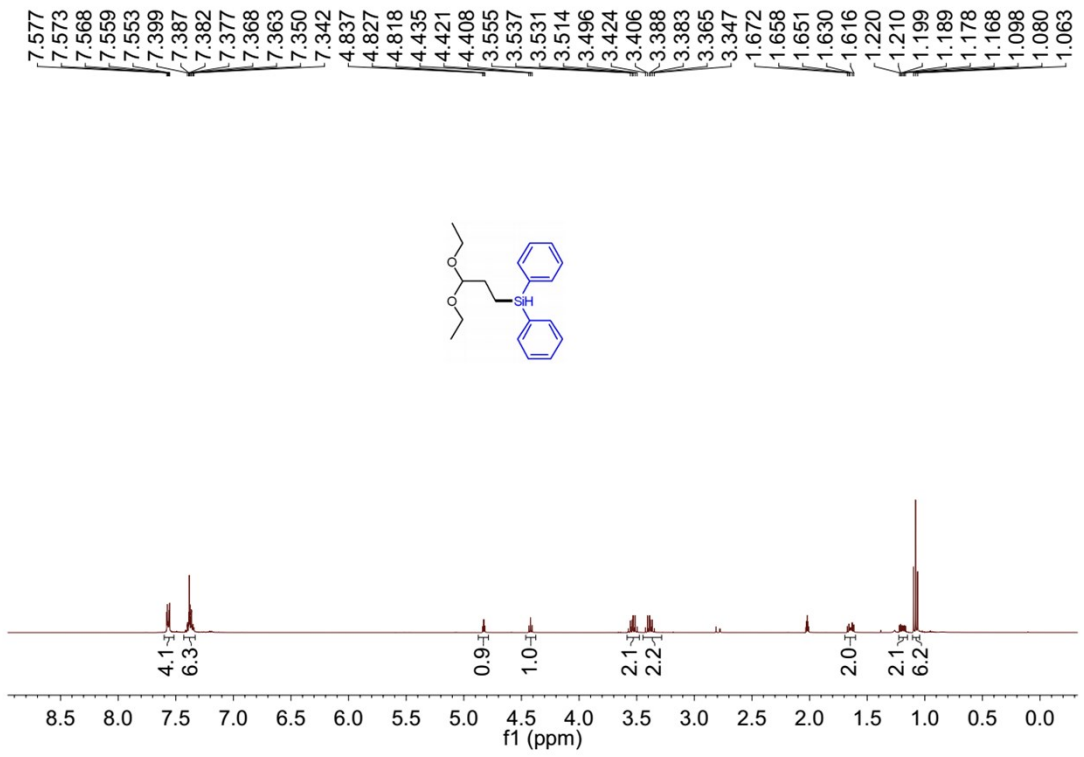
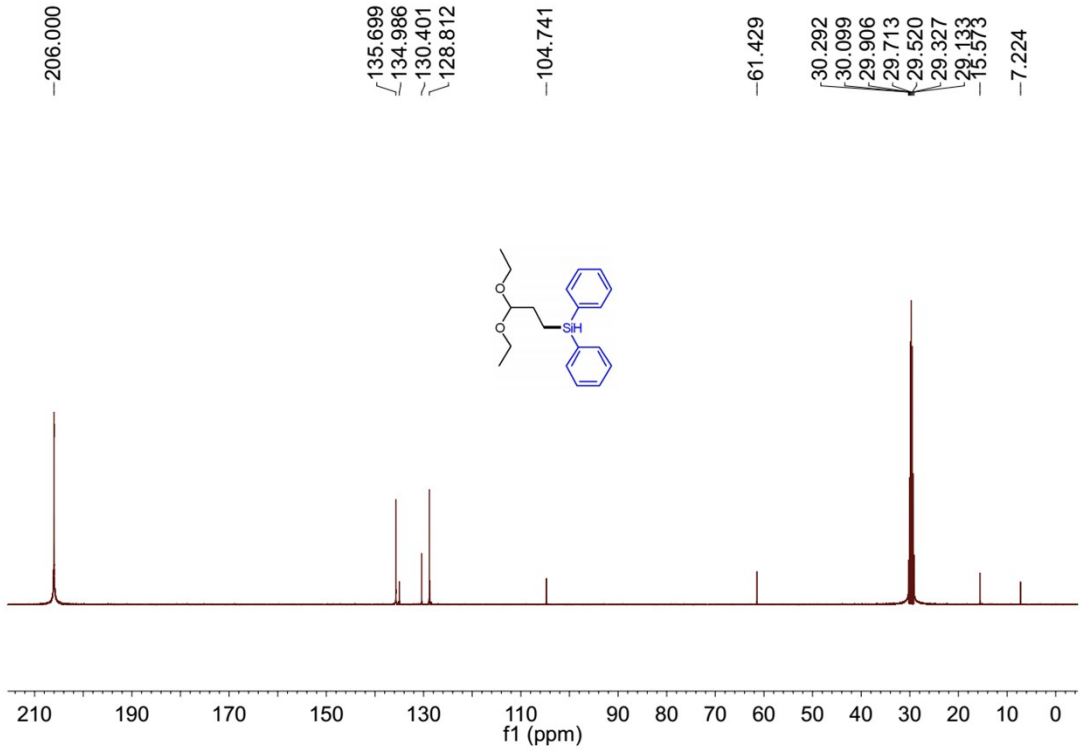


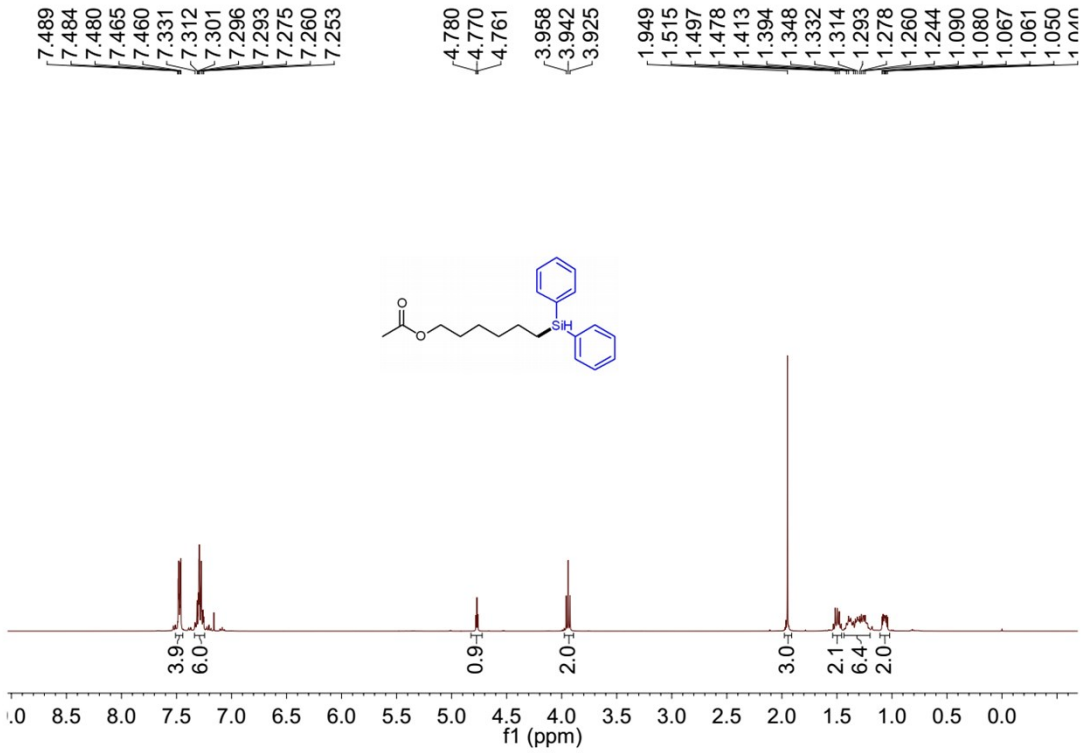
6s ^{1}H NMR



6s ^{13}C NMR



6t ^{1}H NMR



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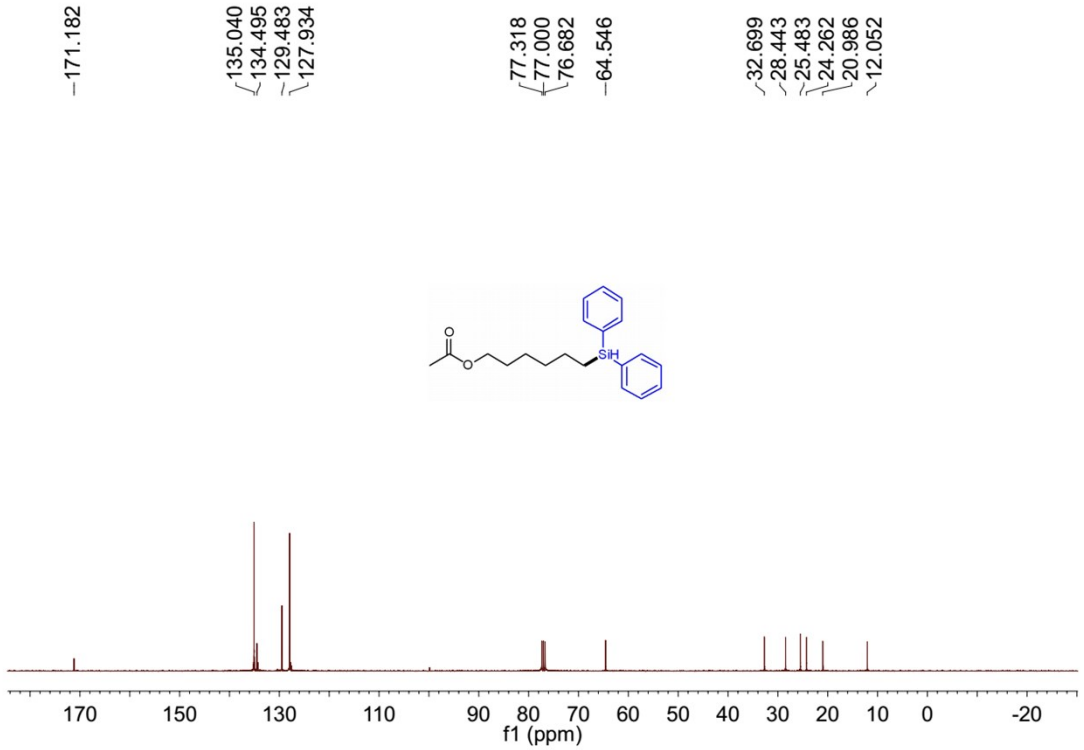
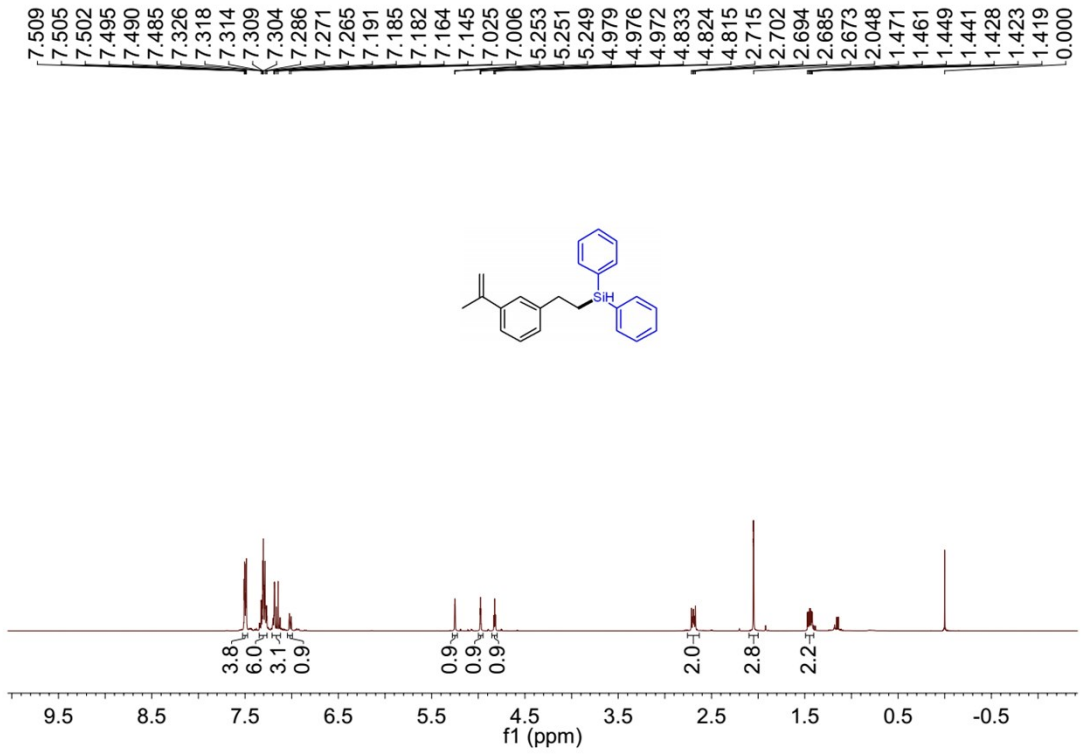
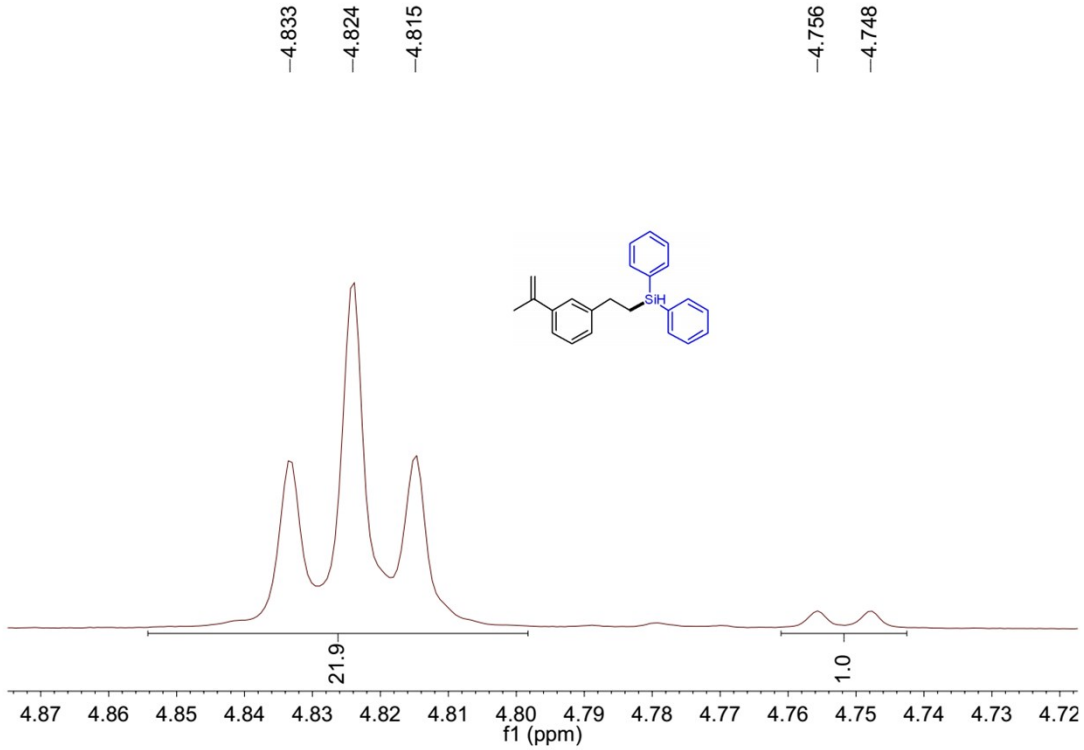


6u ^{1}H NMR



6u regioselectivity



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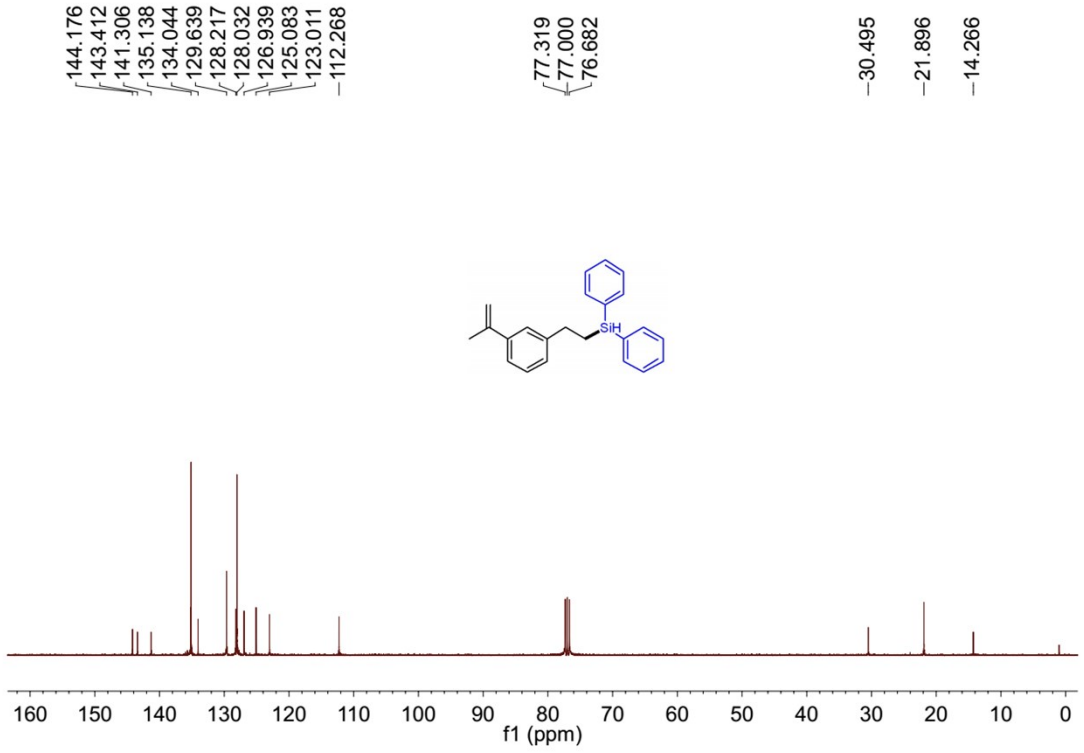

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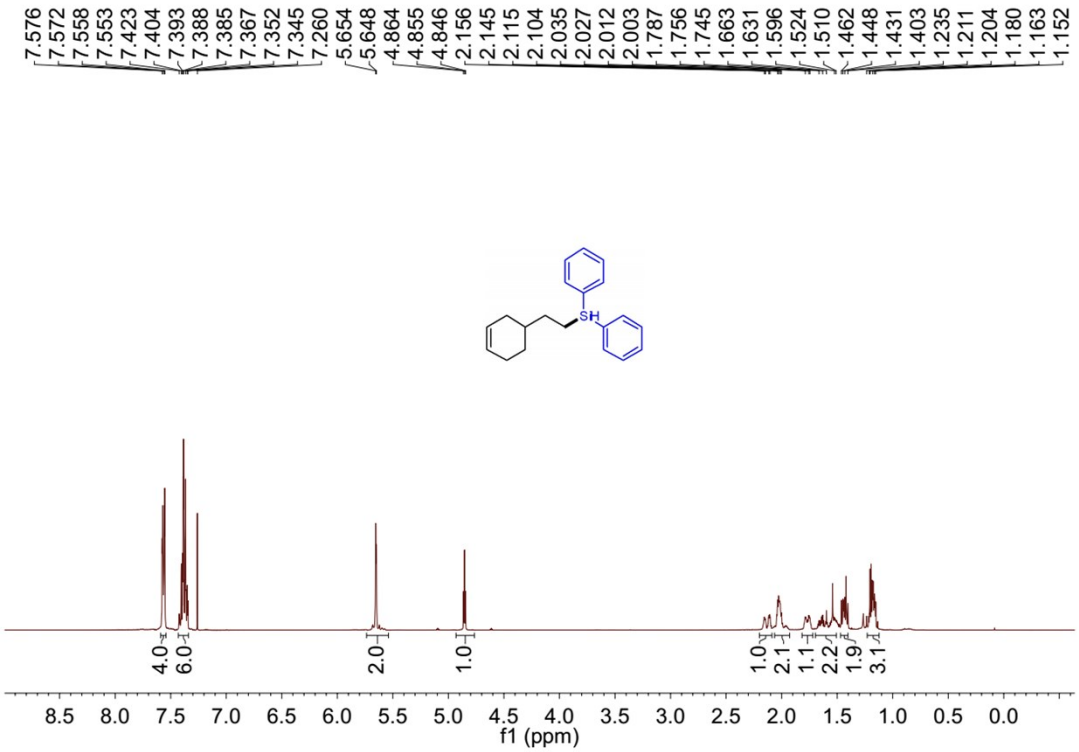
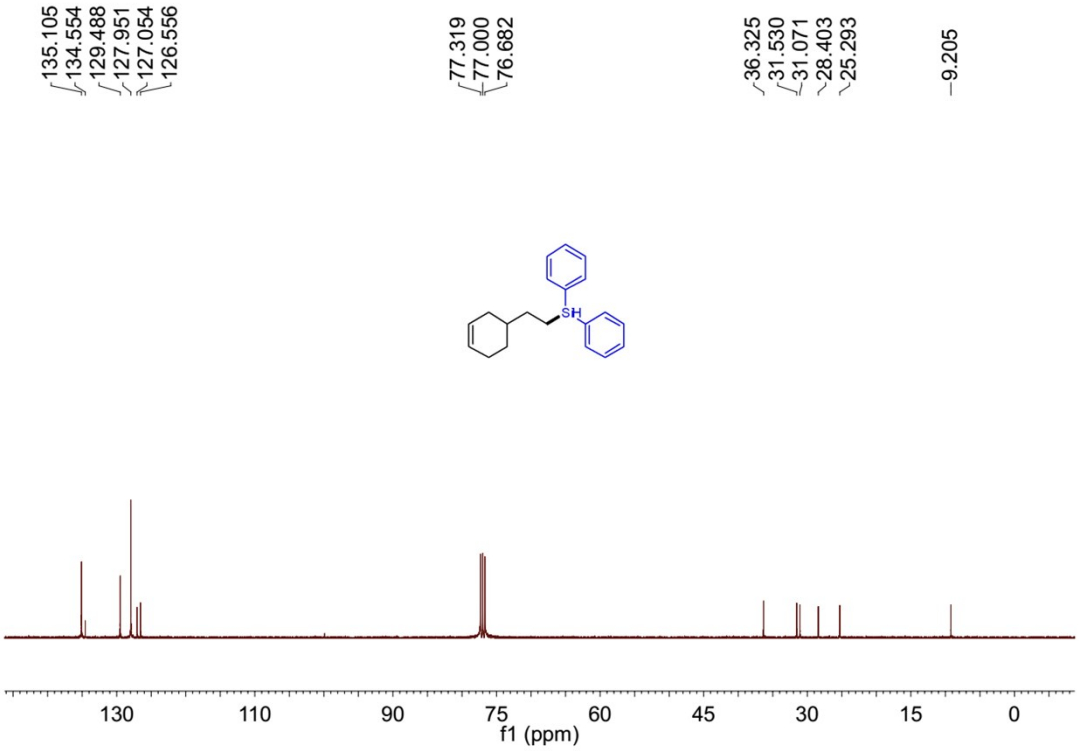
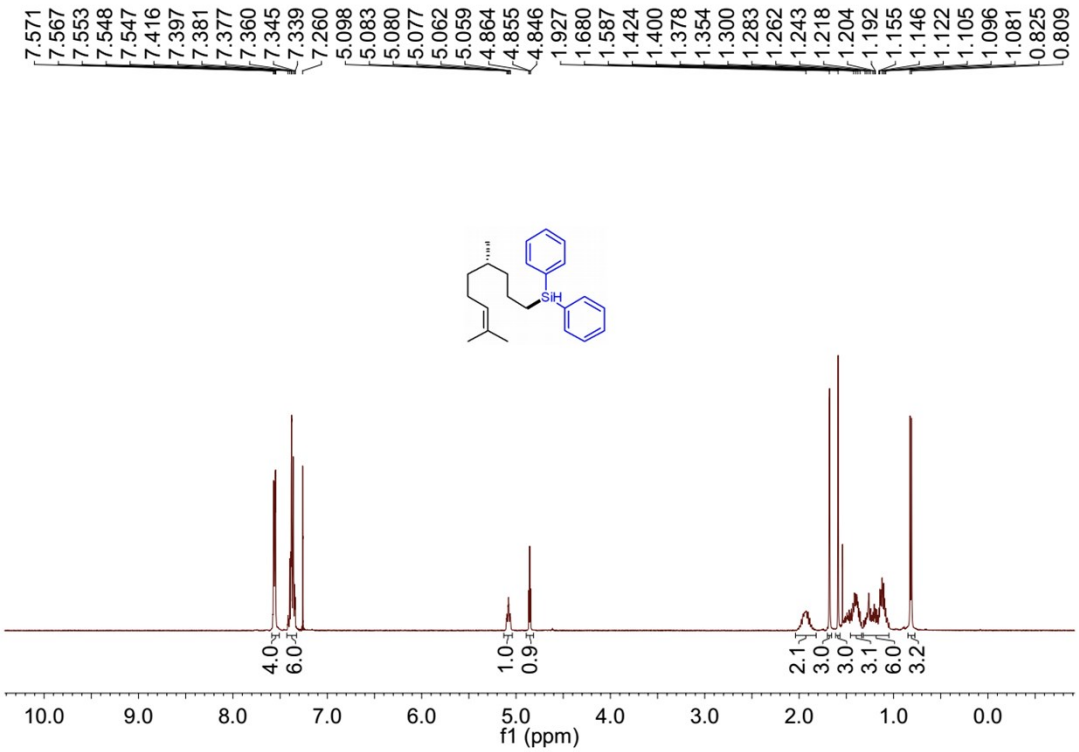


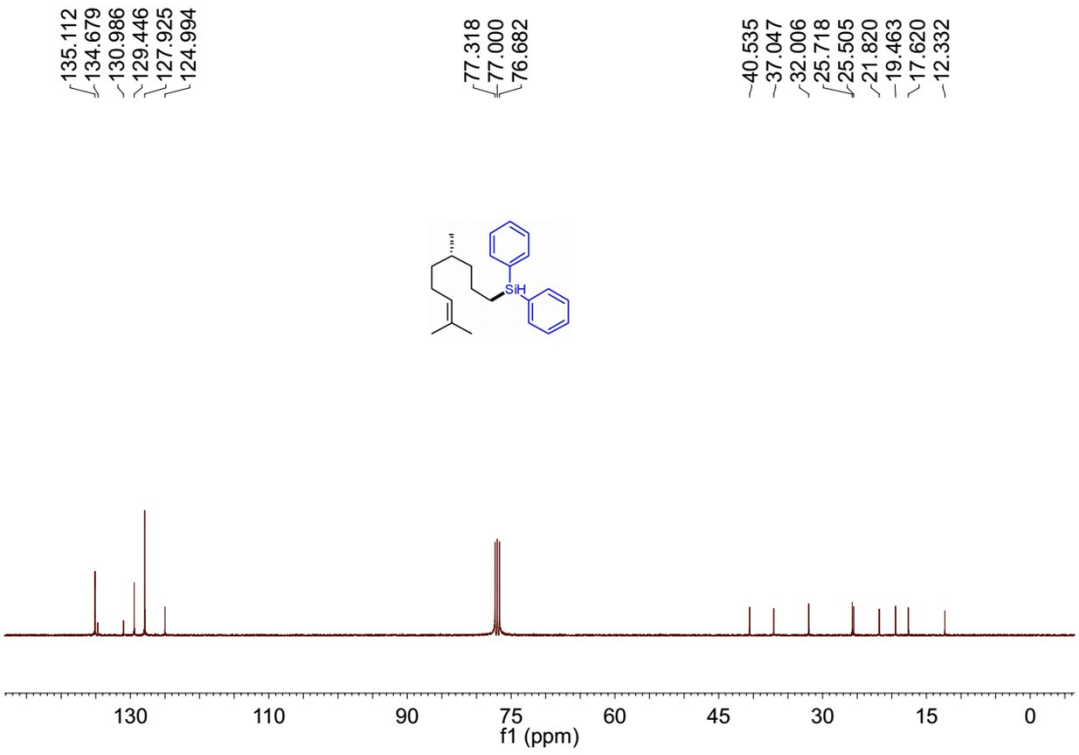
6v ^{13}C NMR



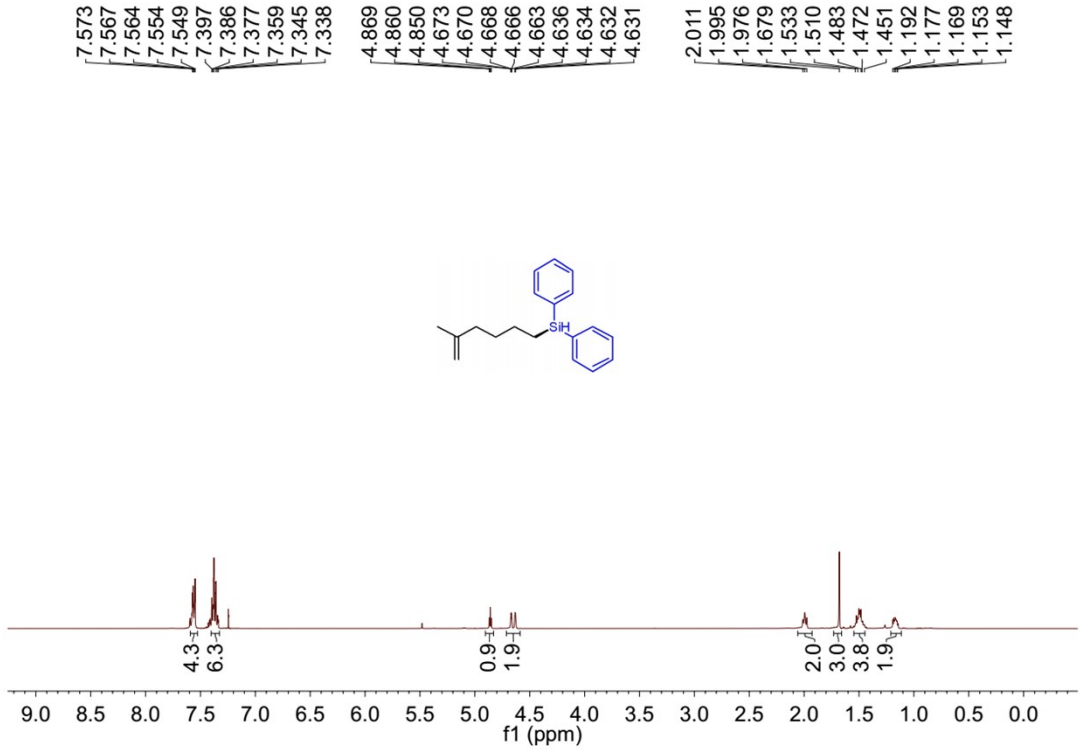
6w ^{1}H NMR



6w ^{13}C NMR



6x ^{1}H NMR



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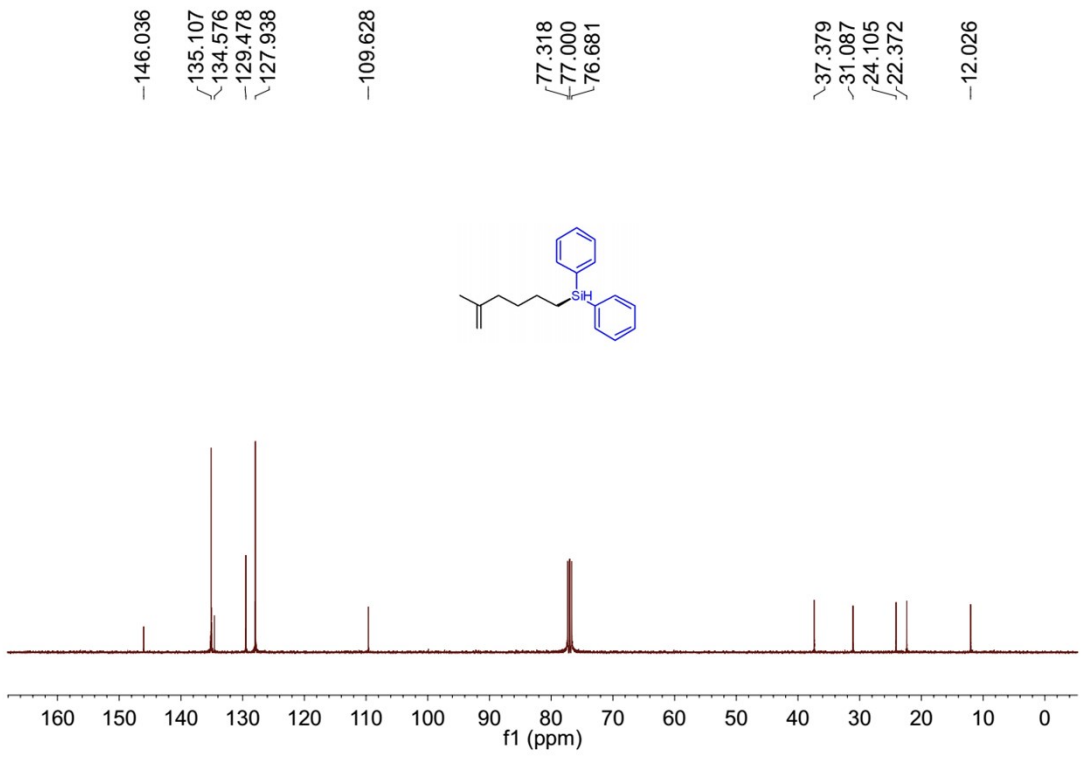

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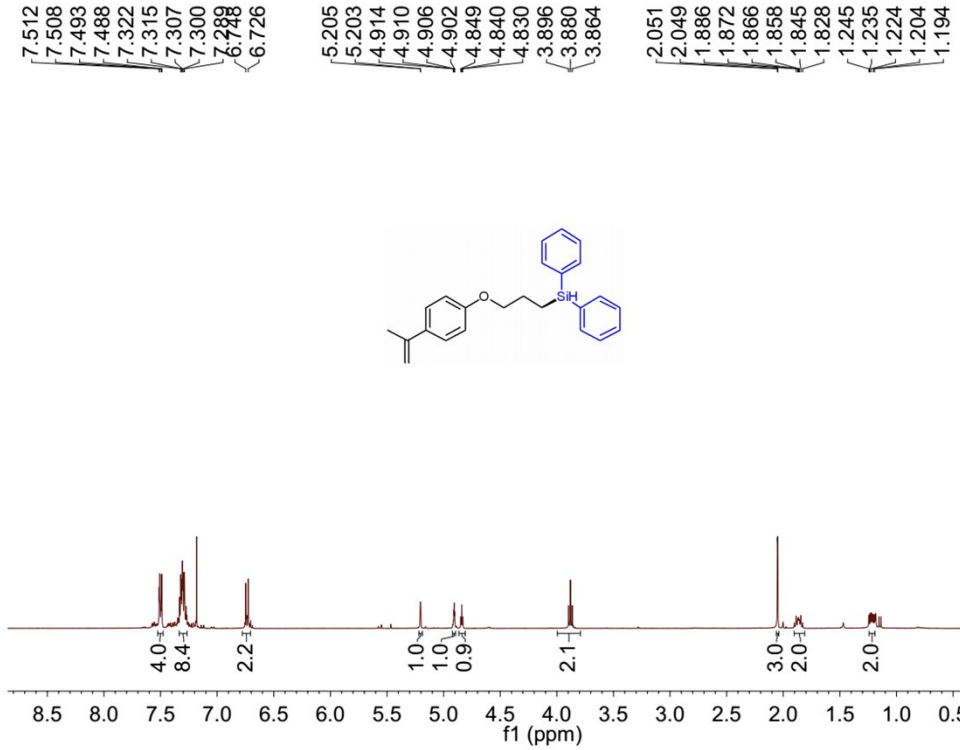

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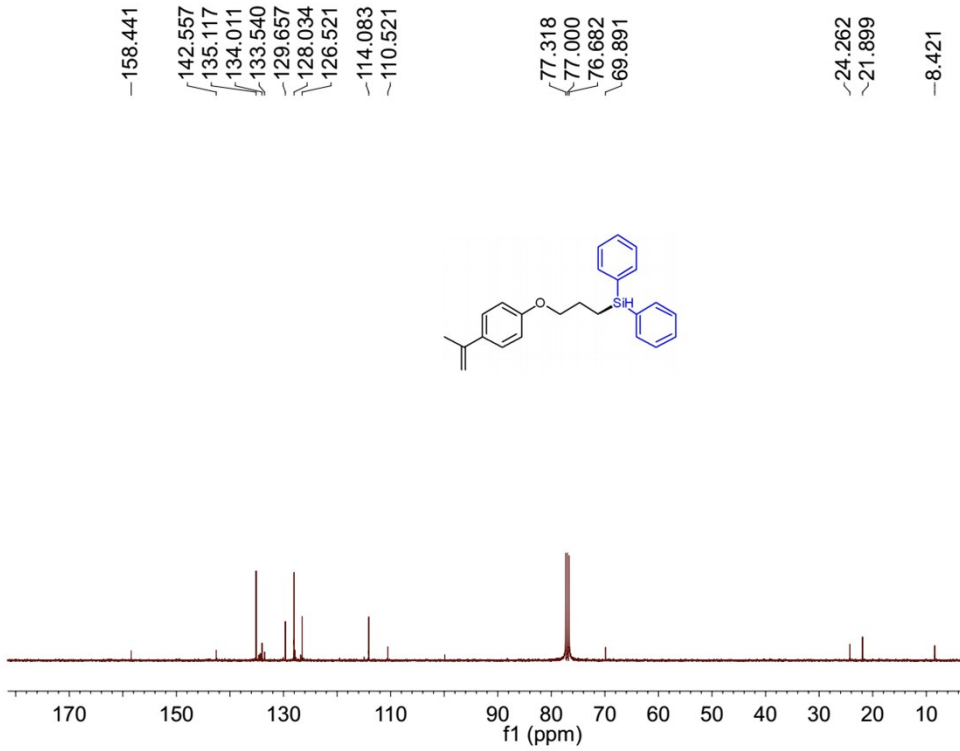
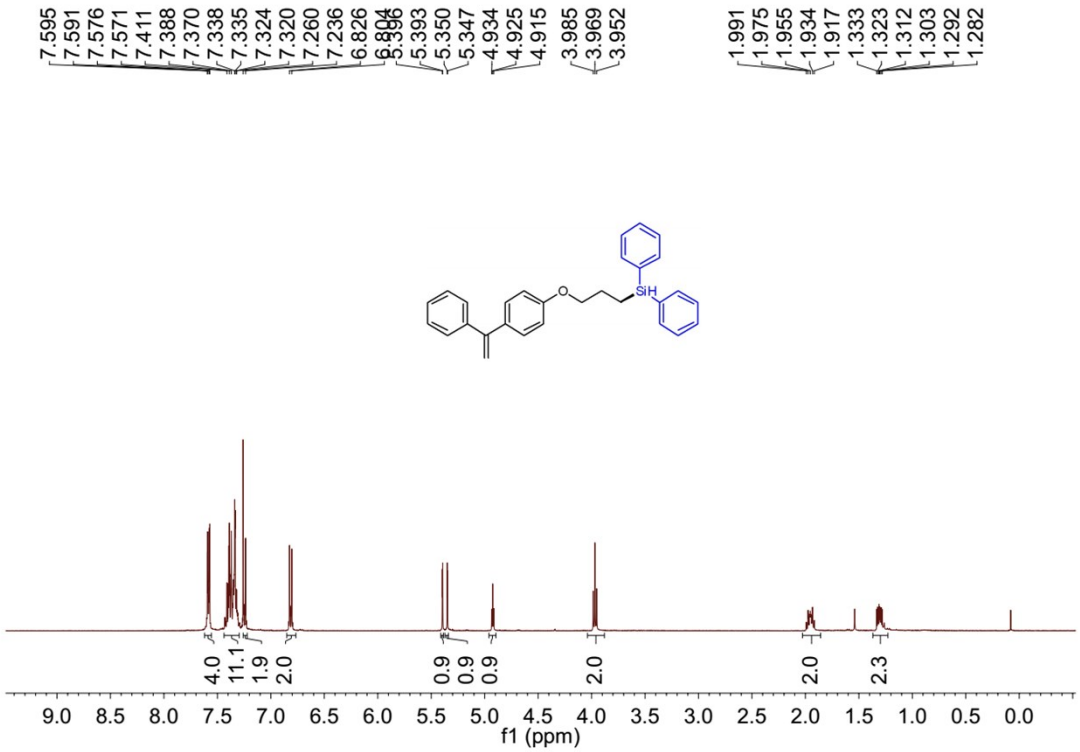


6z ^{1}H NMR



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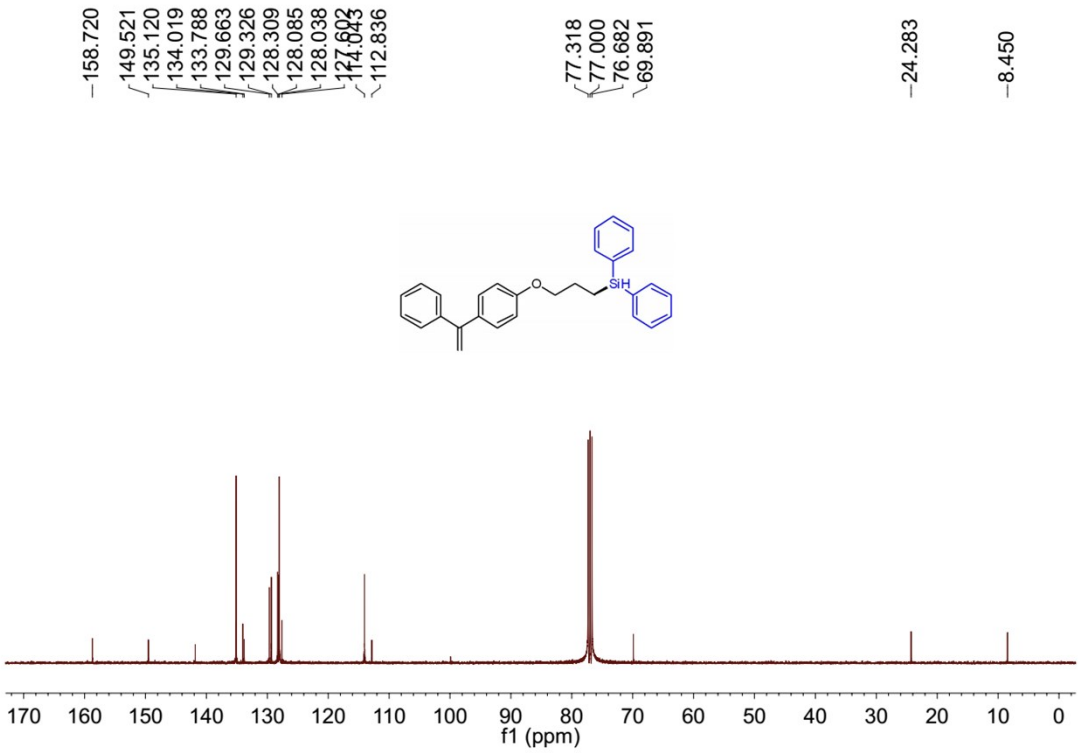
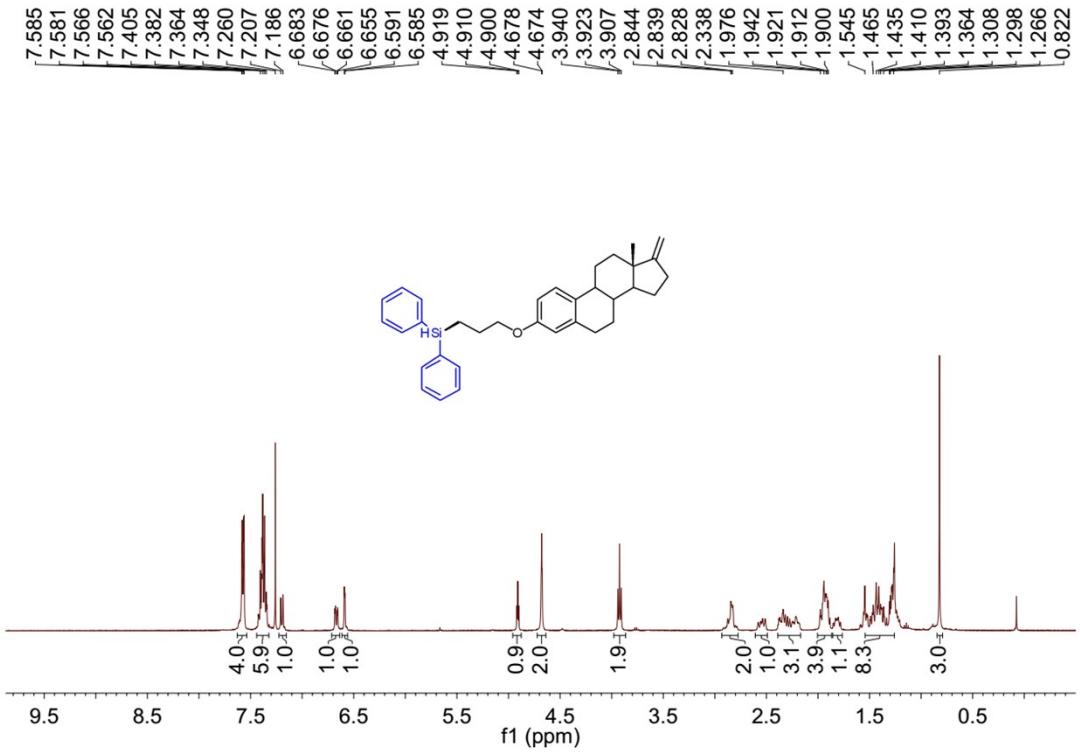


6aa ^{1}H NMR



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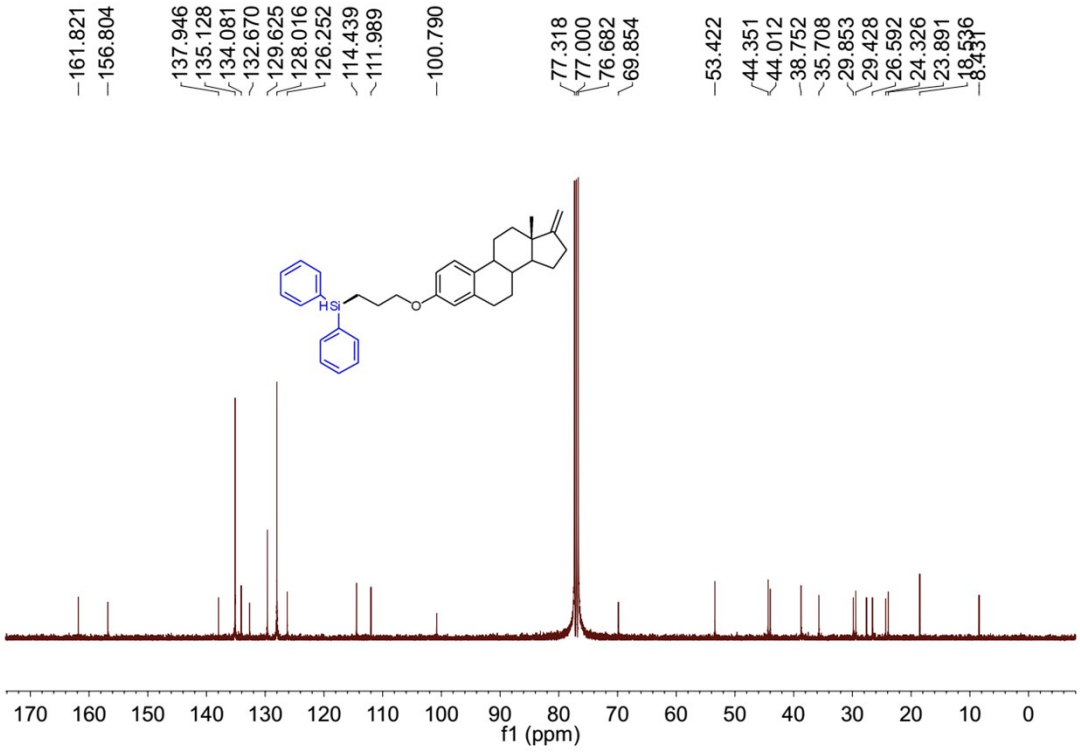

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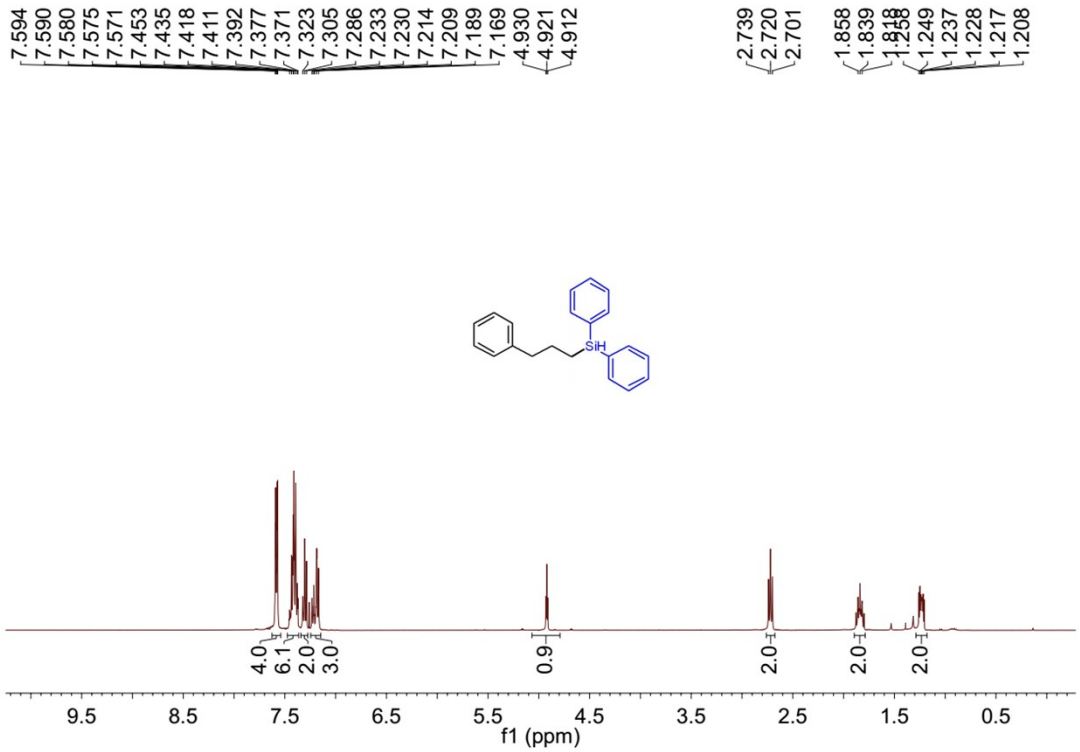
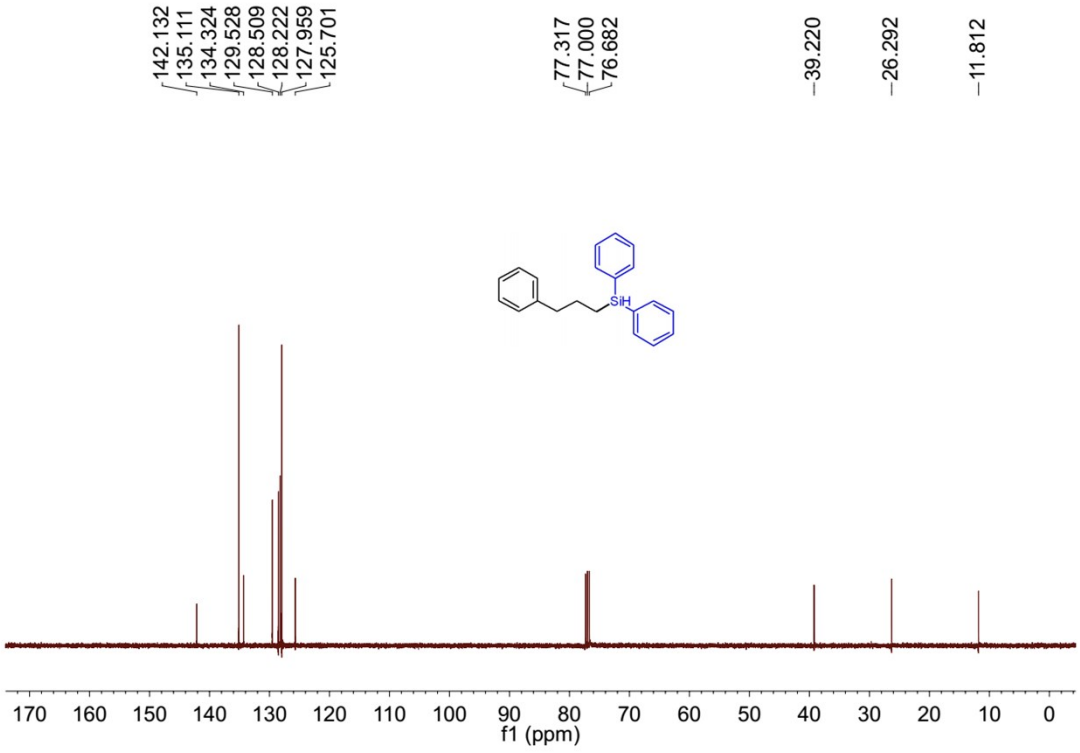
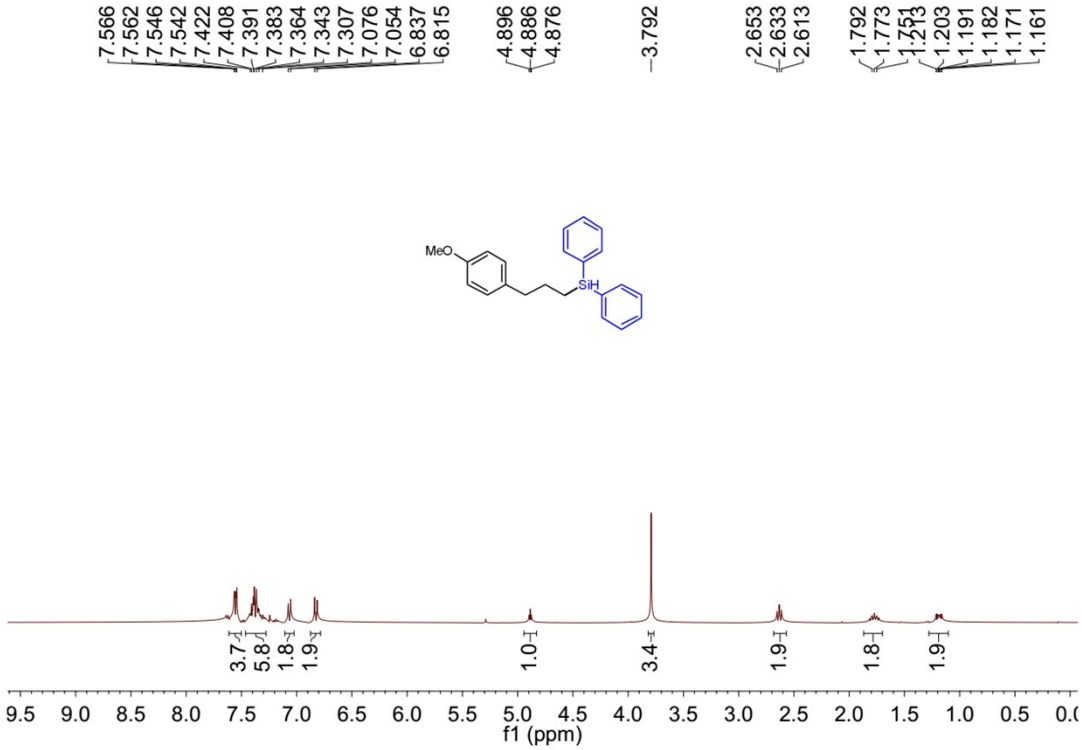


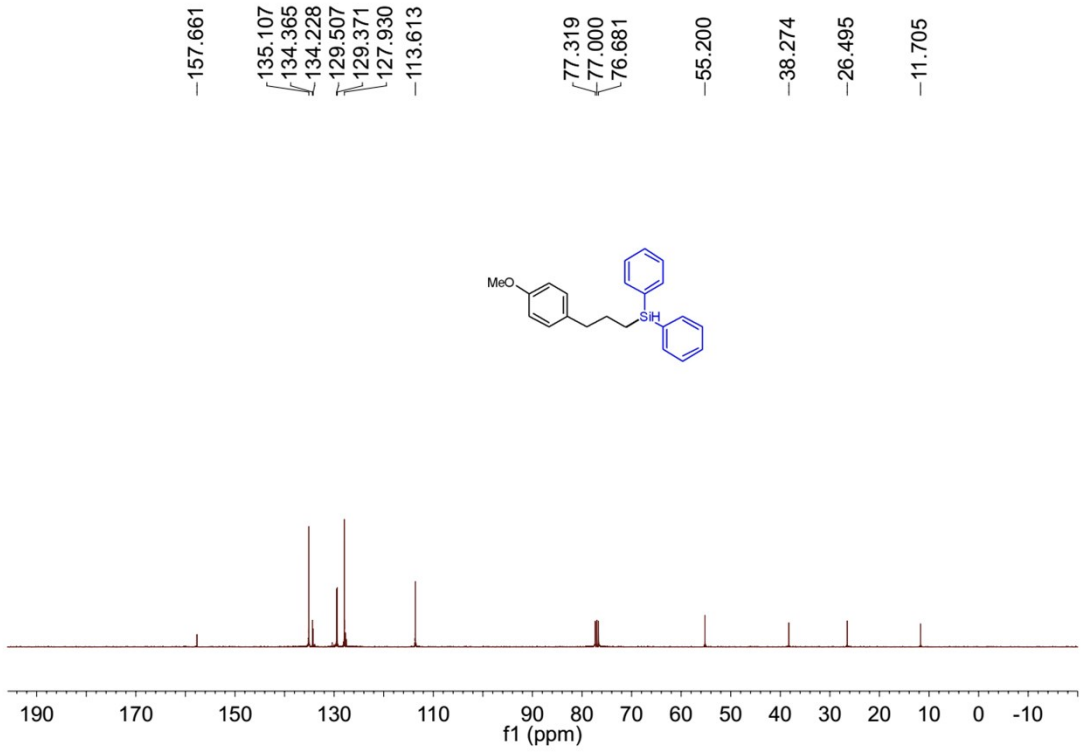
6ab ^{13}C NMR



6ac ^{1}H NMR



6ac ^{13}C NMR



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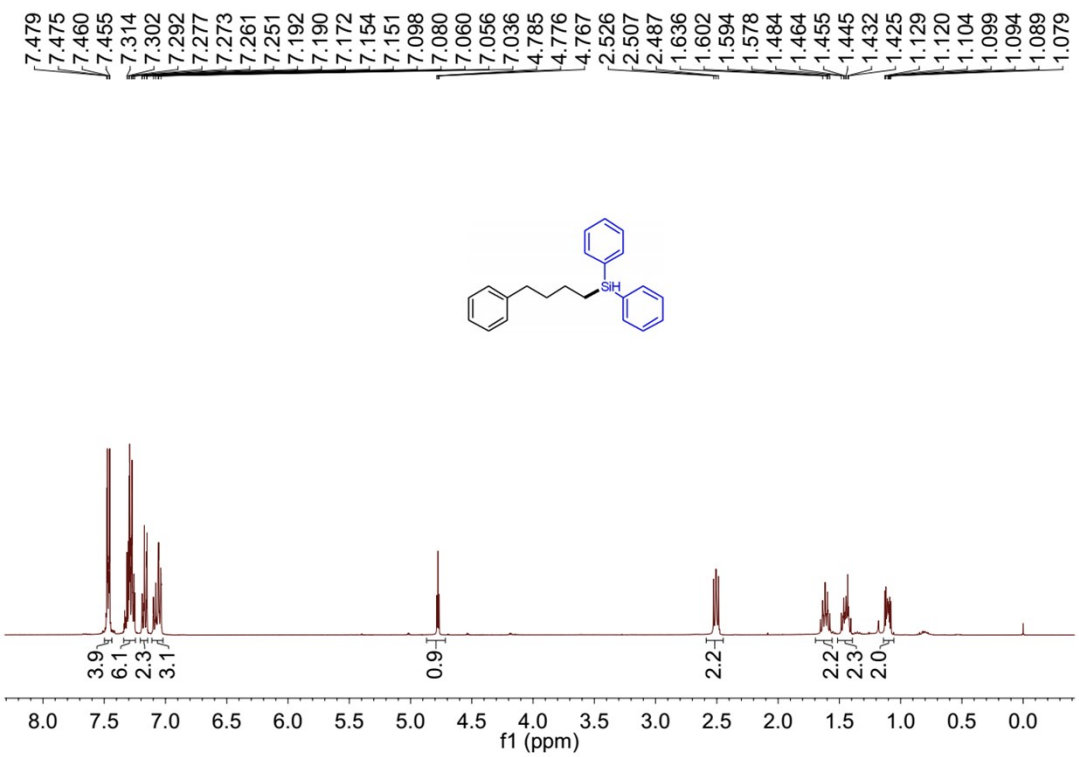
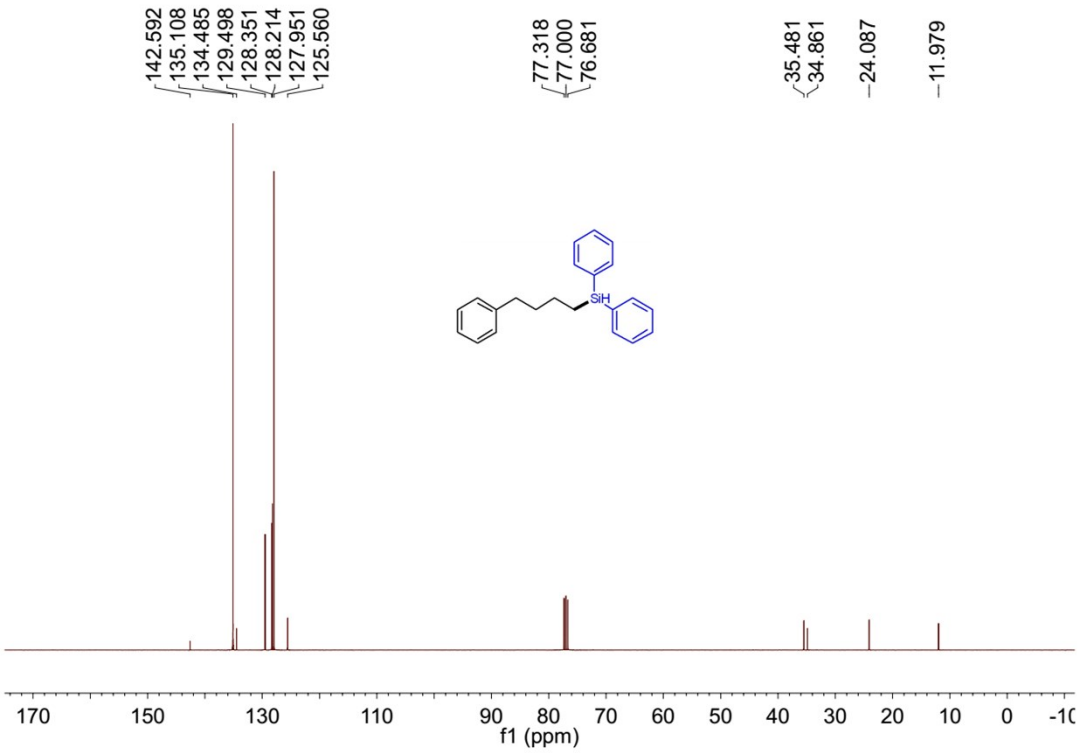
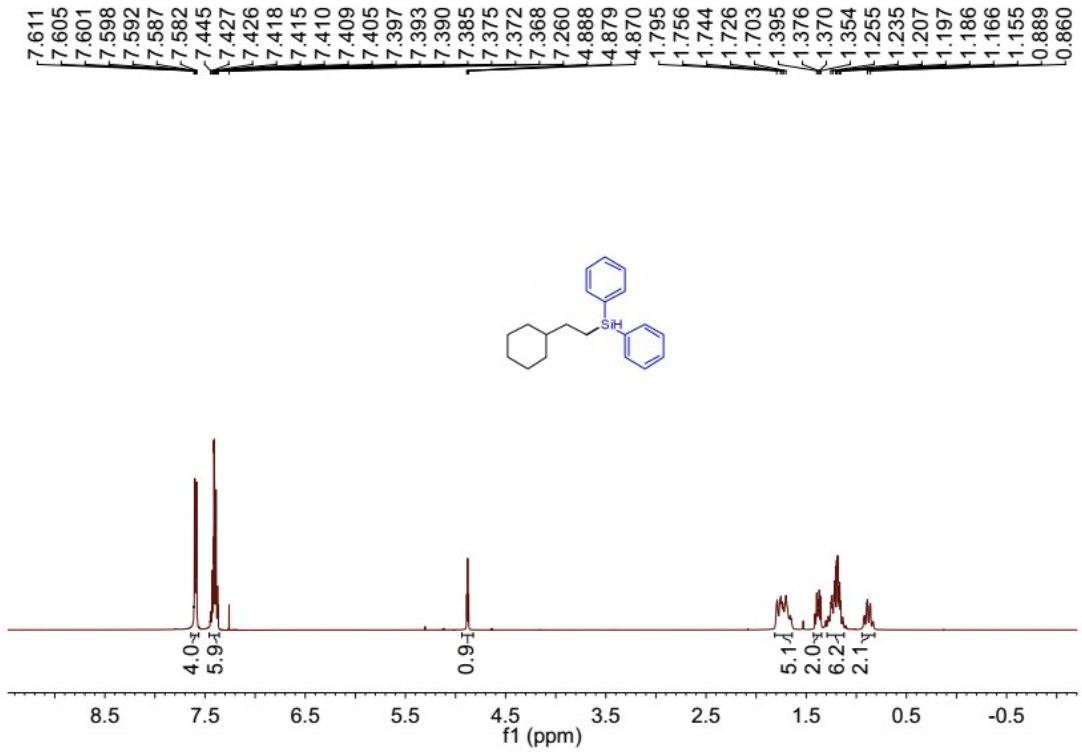


6ad^{13}C NMR



6ae ^{1}H NMR



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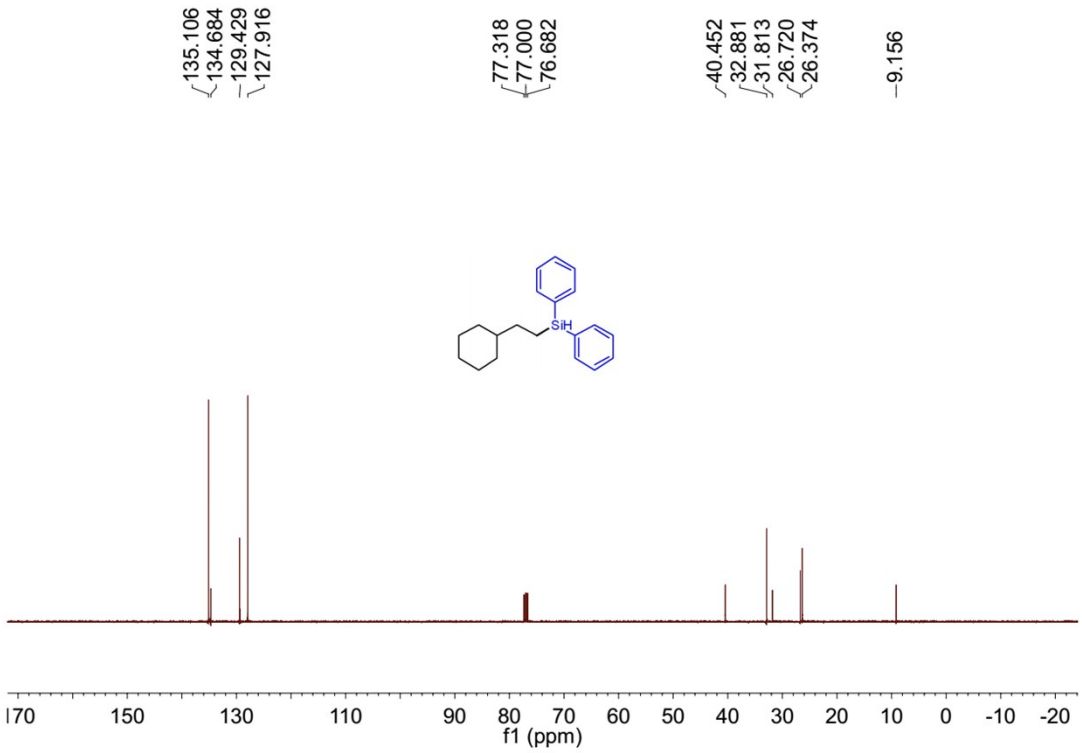

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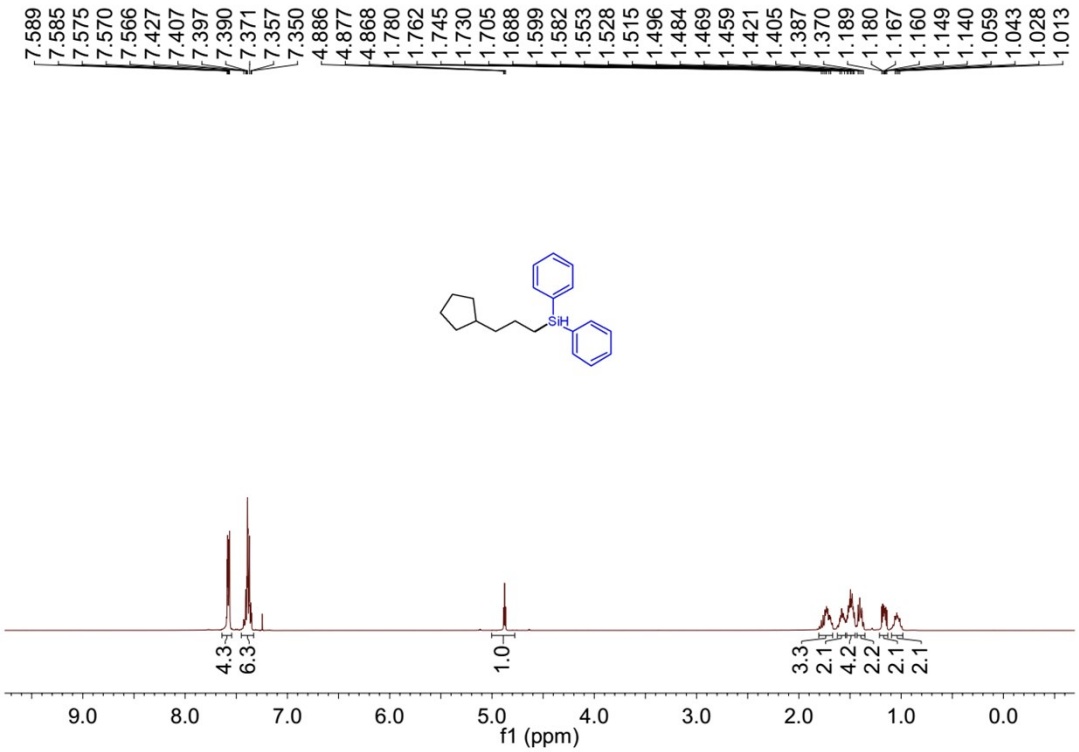

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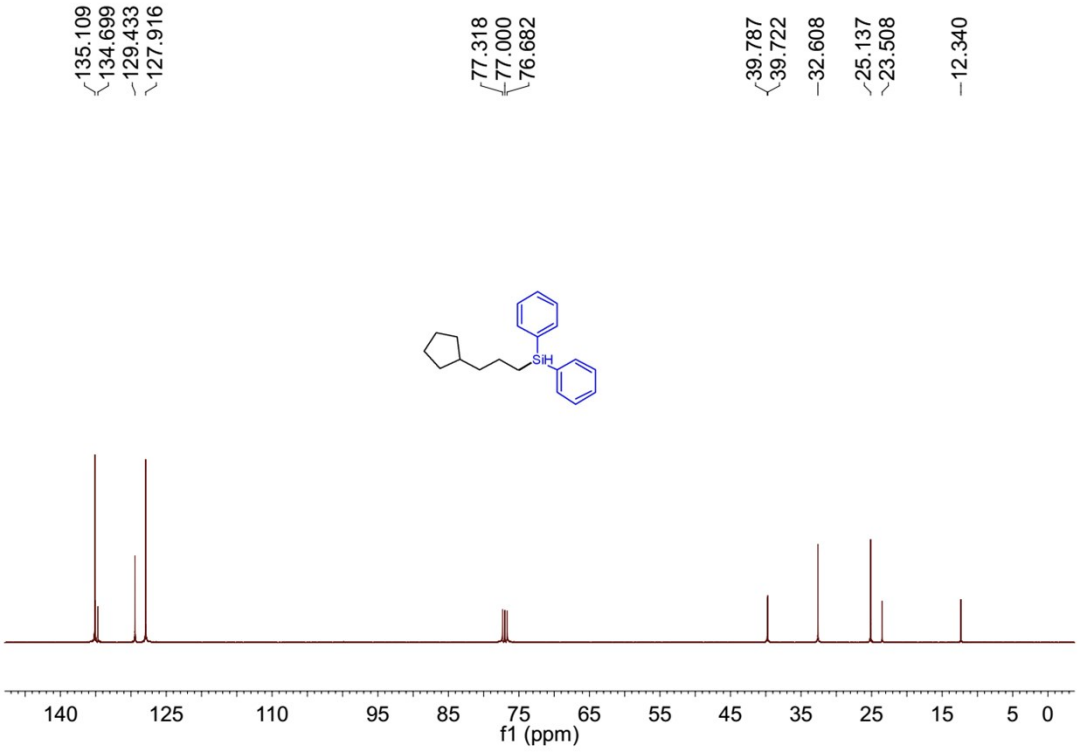

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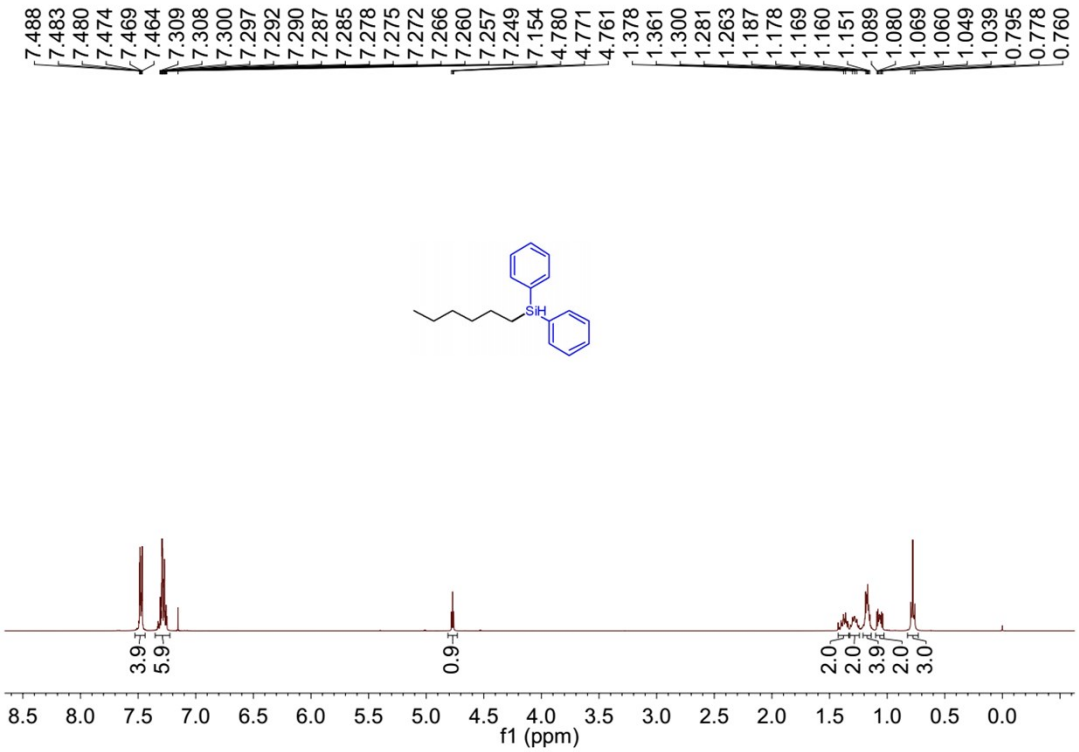

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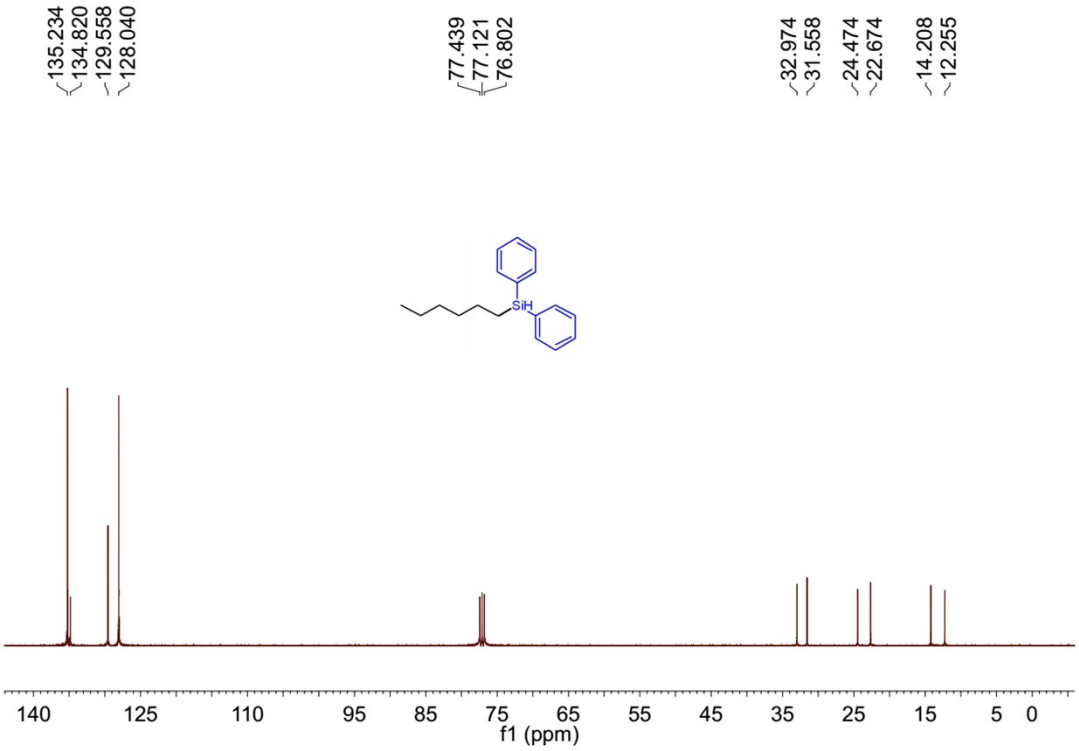

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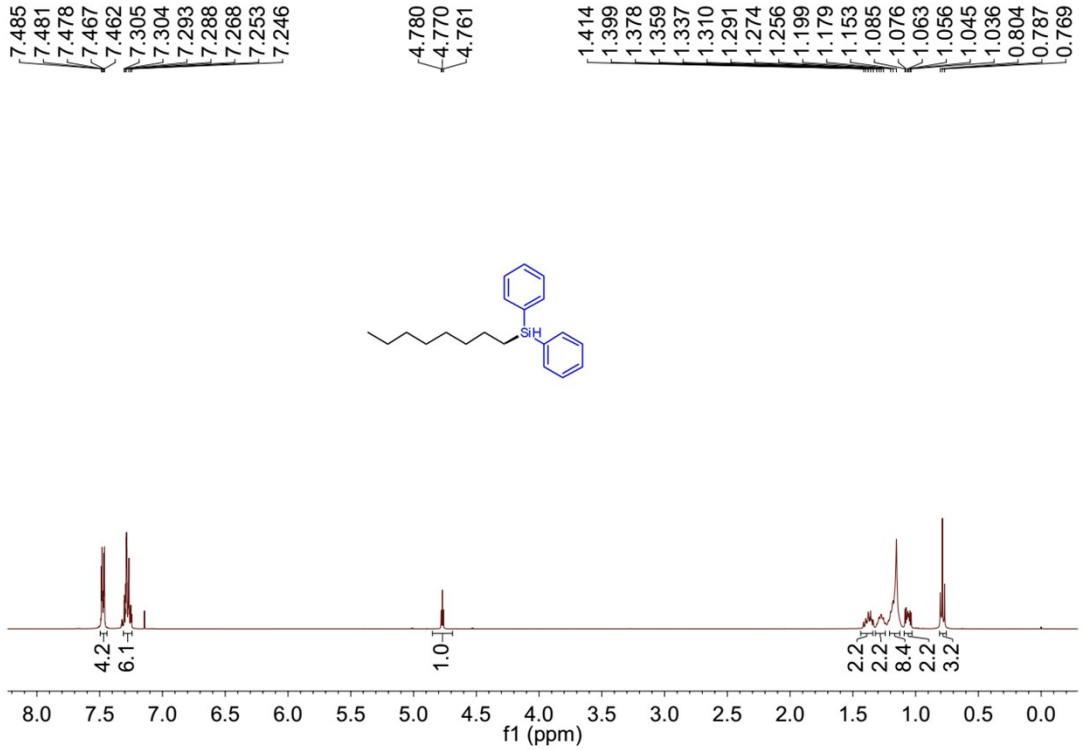
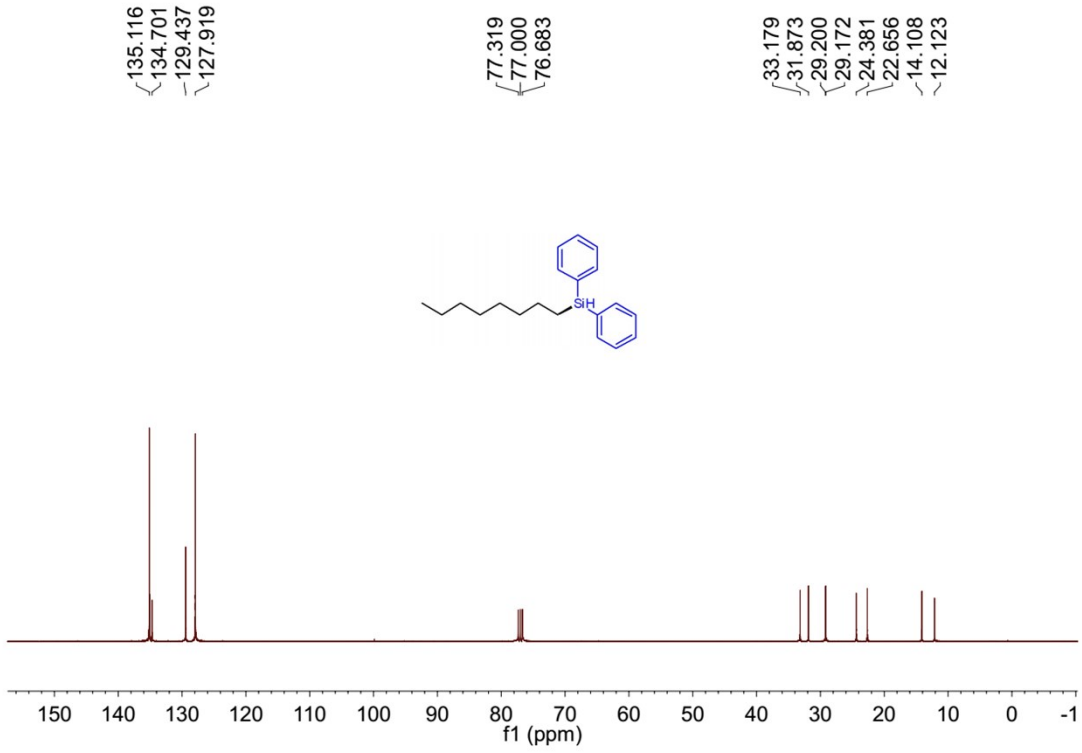
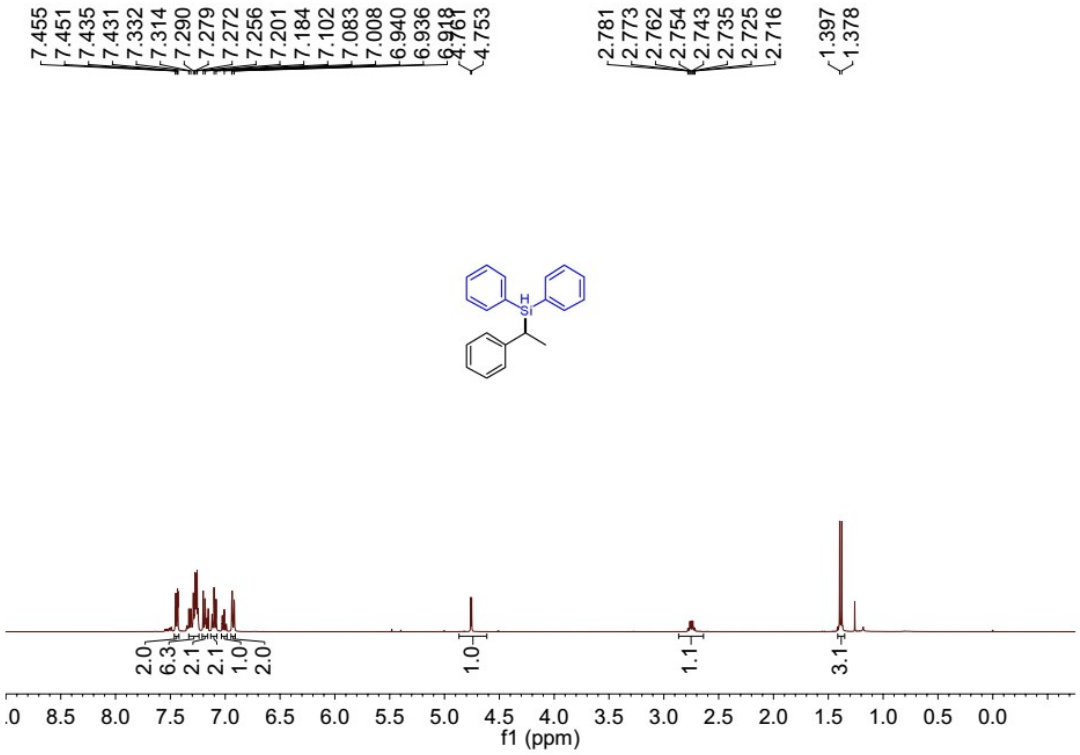


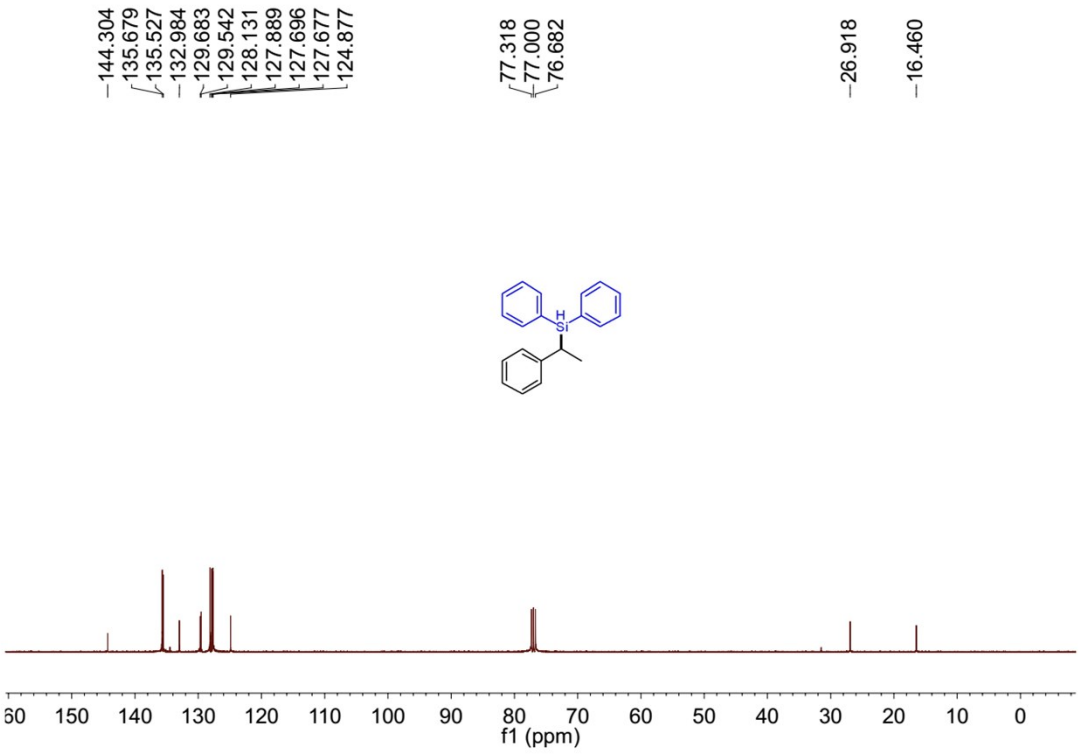
6ah ^{13}C NMR



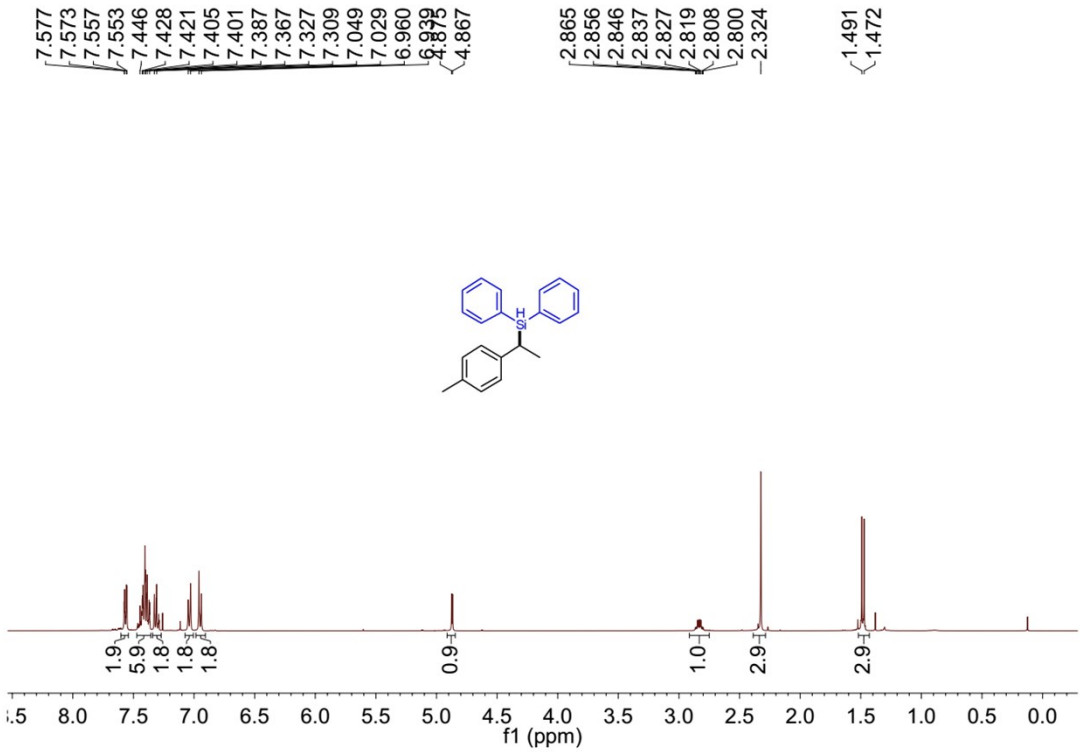
7a ^{1}H NMR



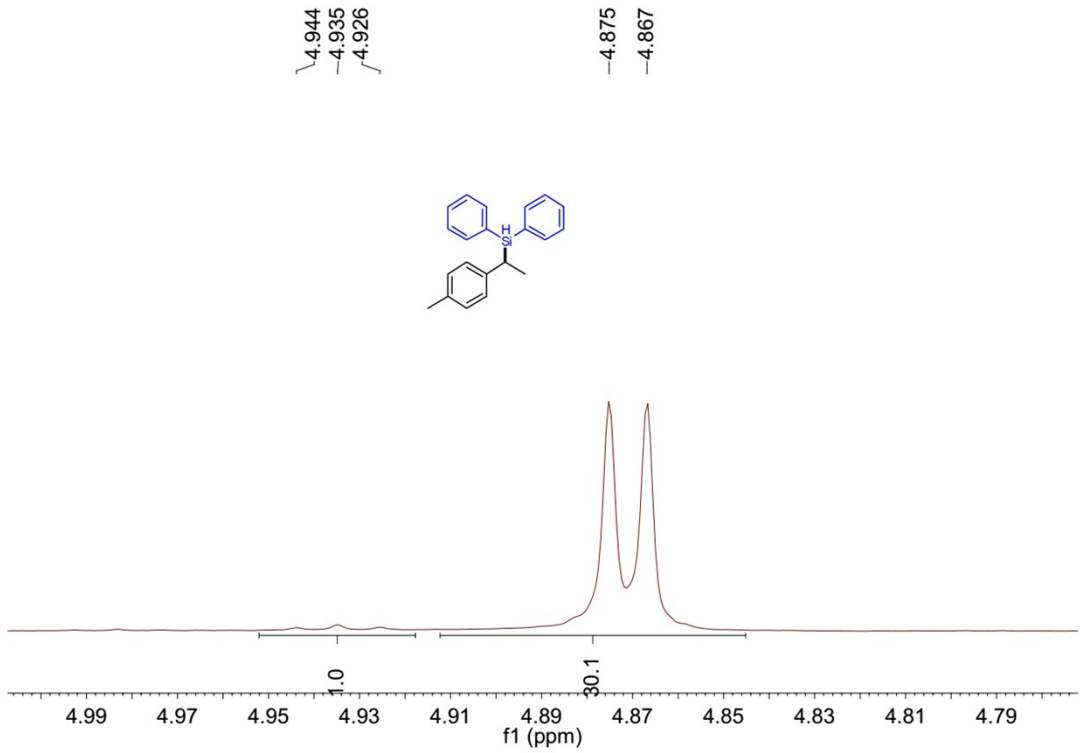
7a ^{13}C NMR



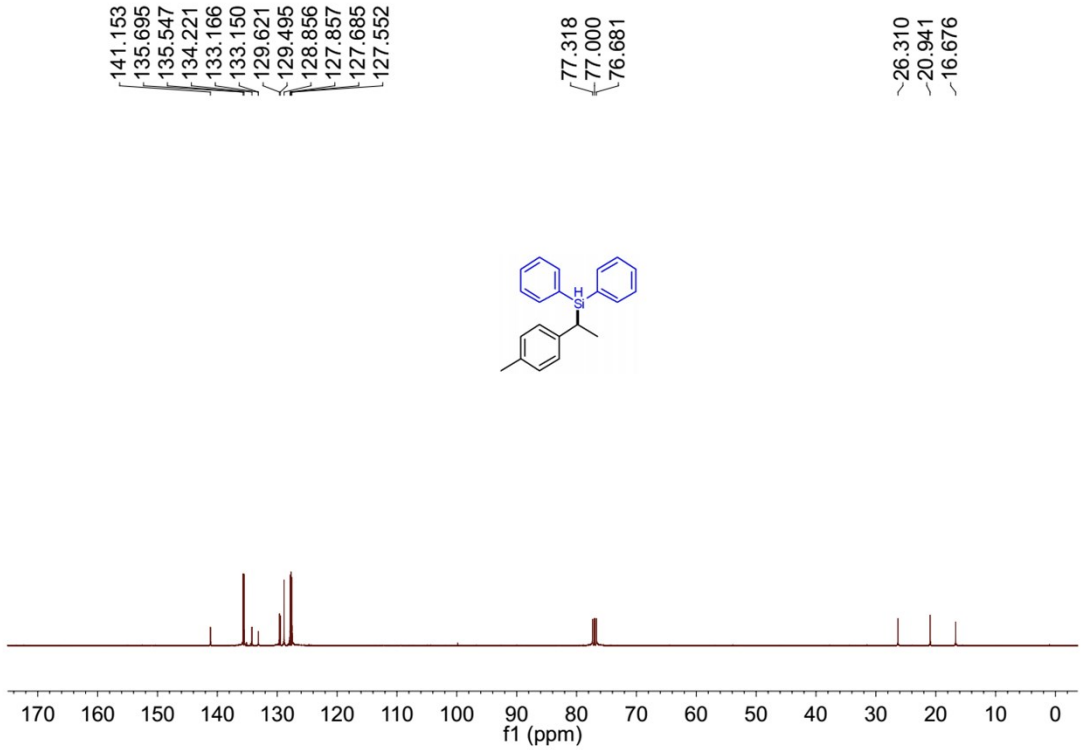
7b ^{1}H NMR



7b regioselectivity



7b ^{13}C NMR



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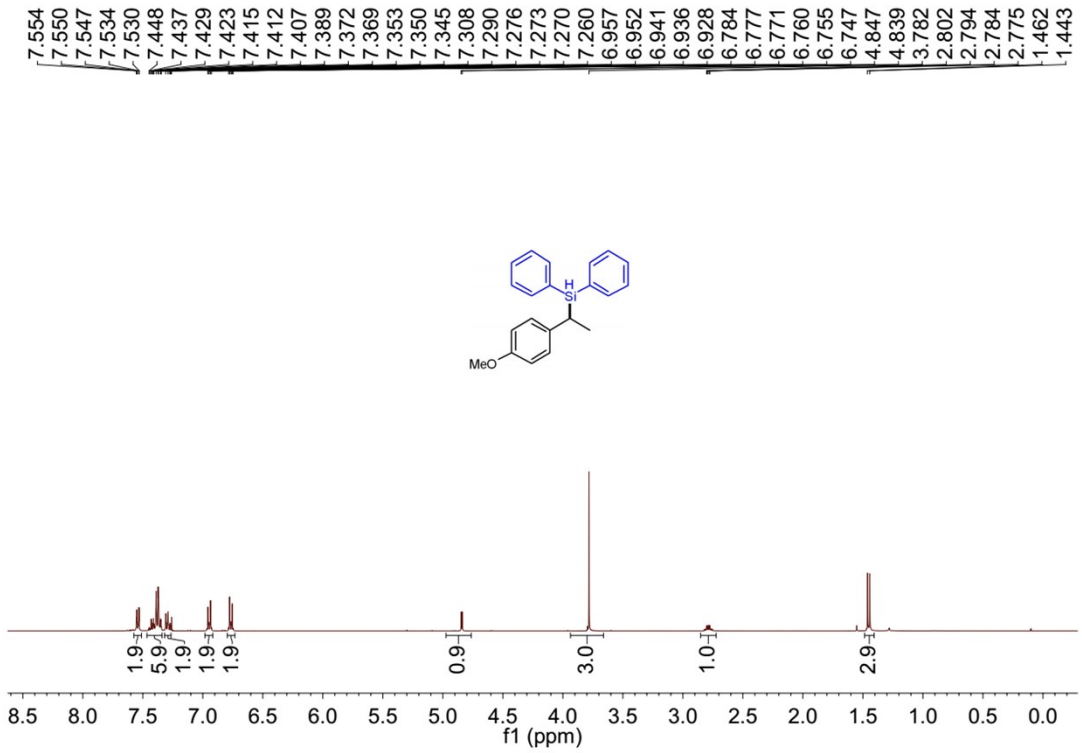

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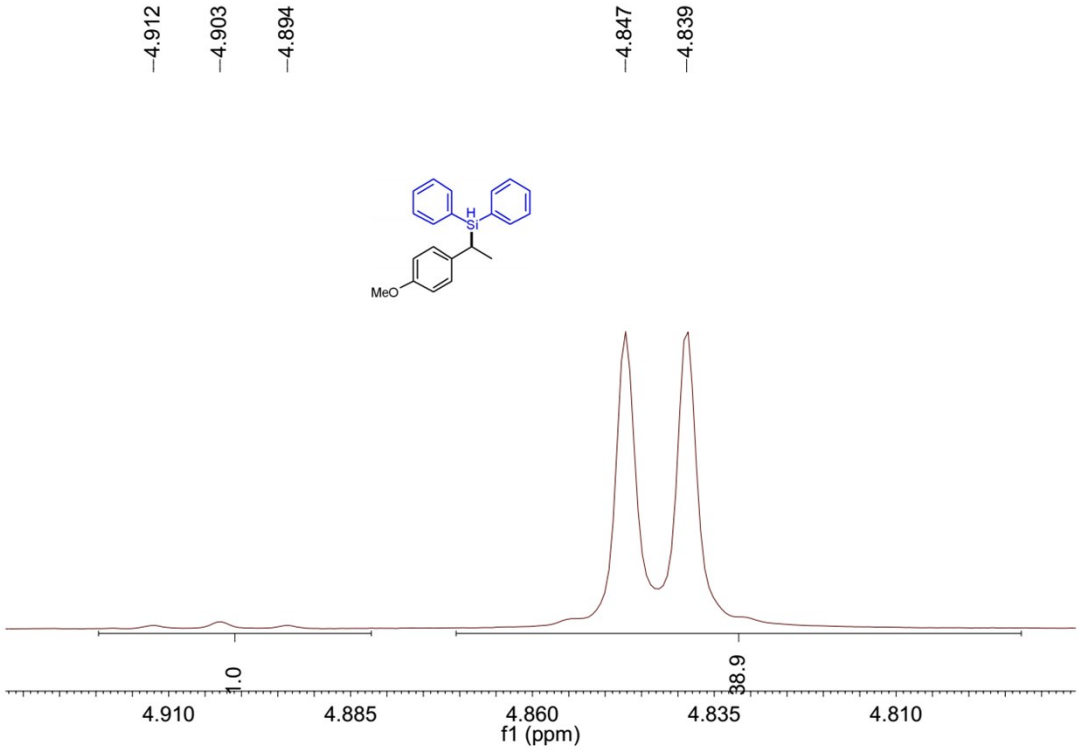

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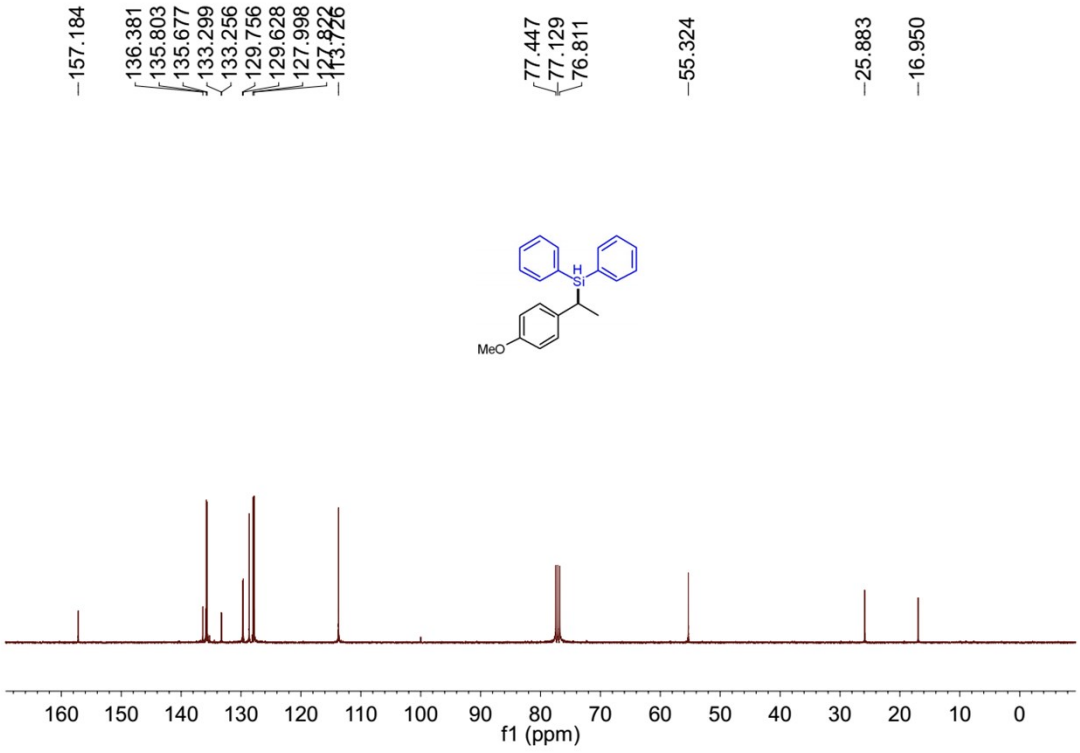

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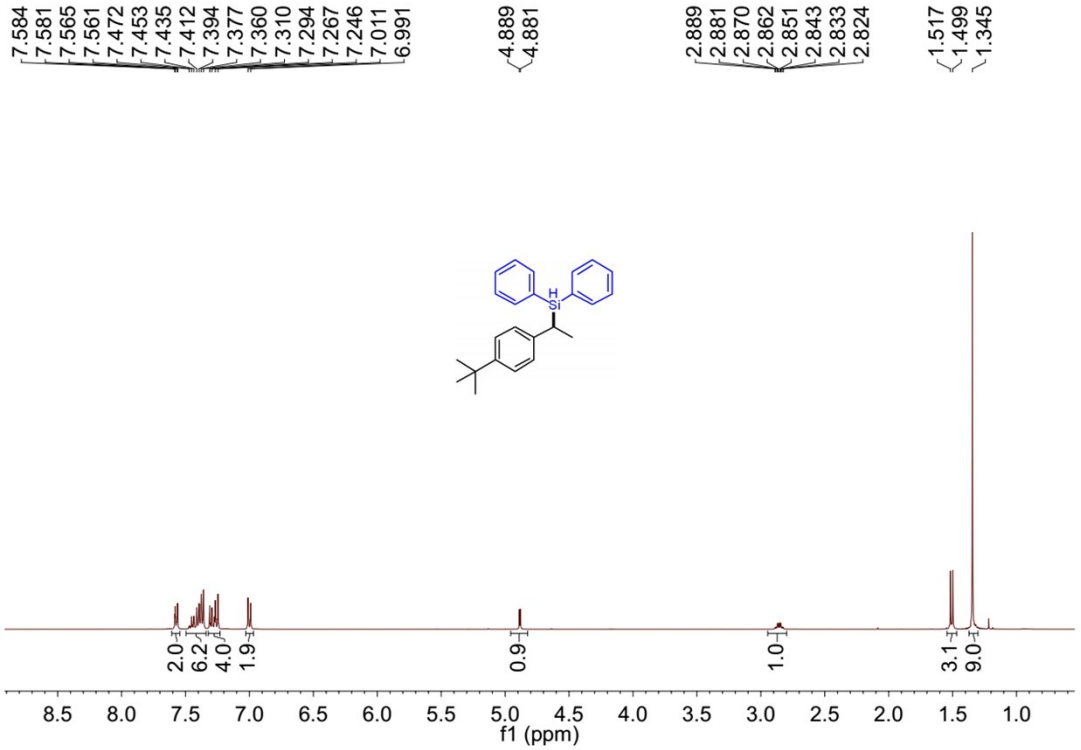

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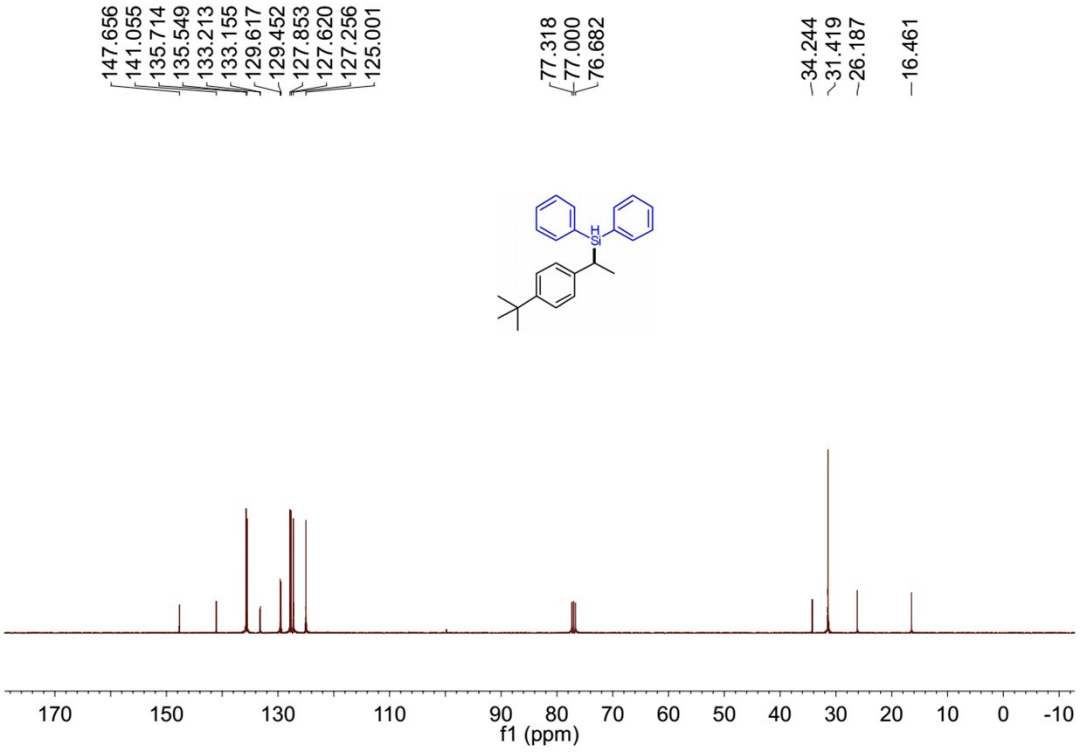

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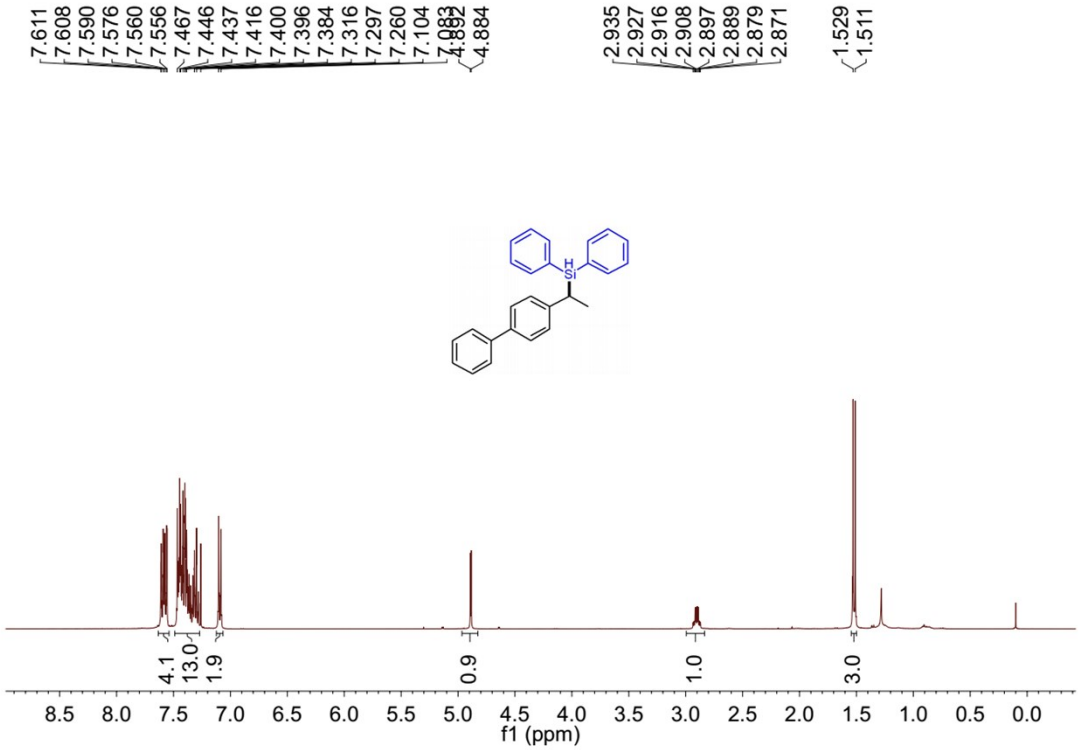

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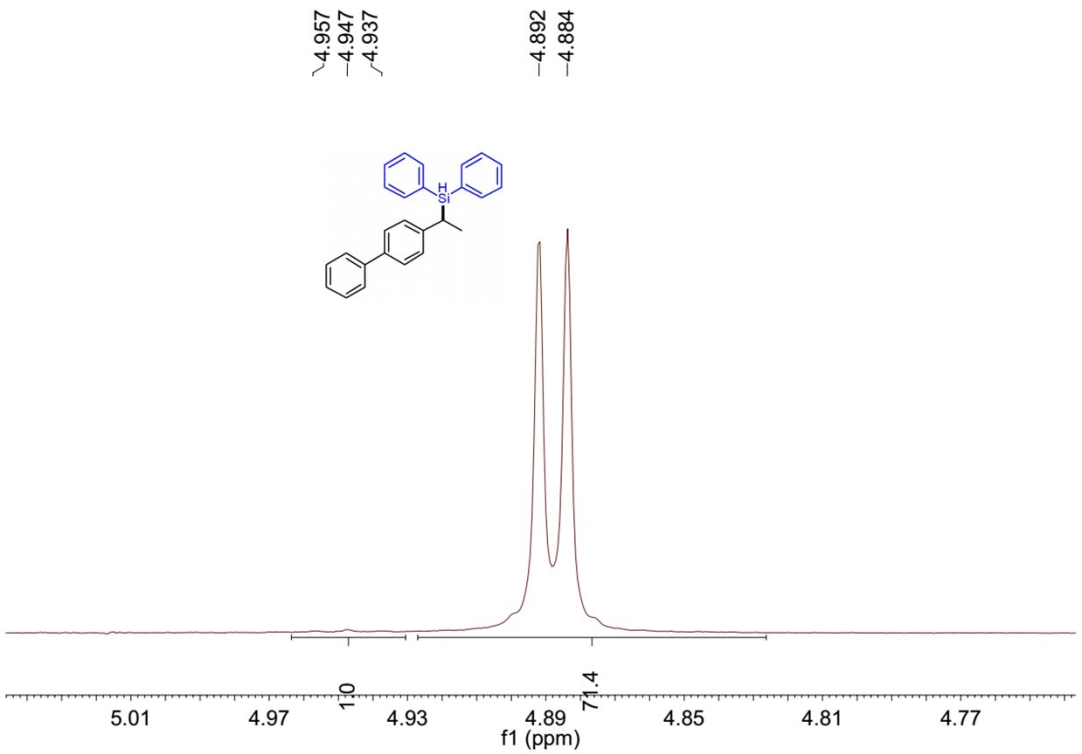

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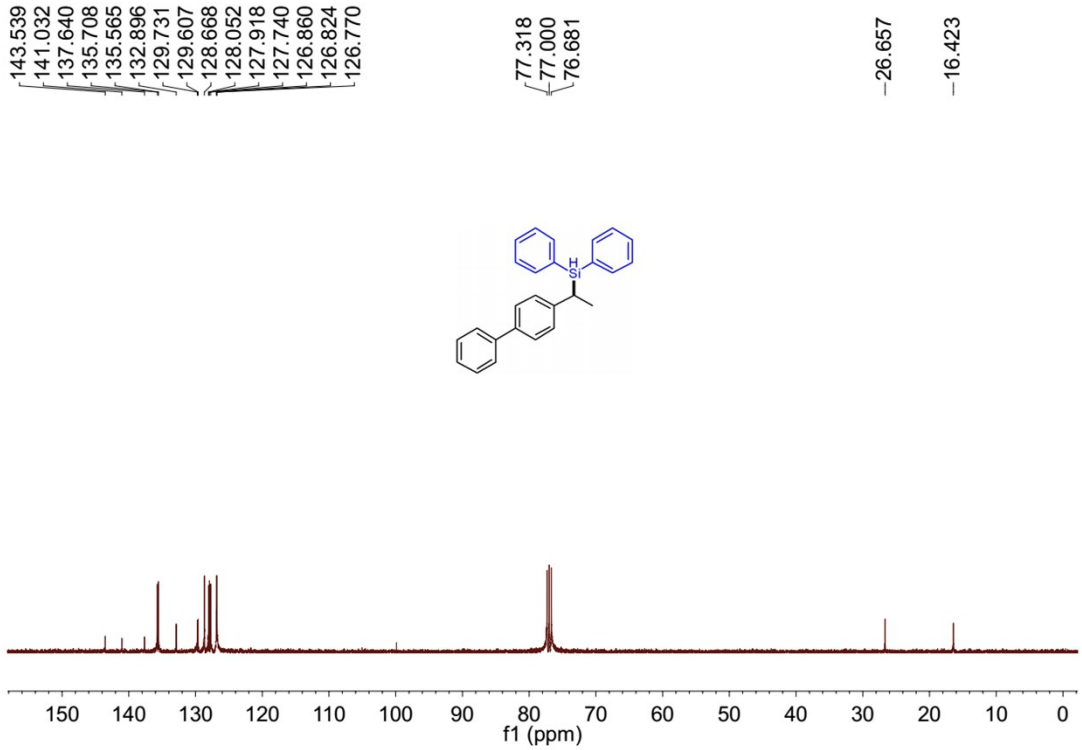

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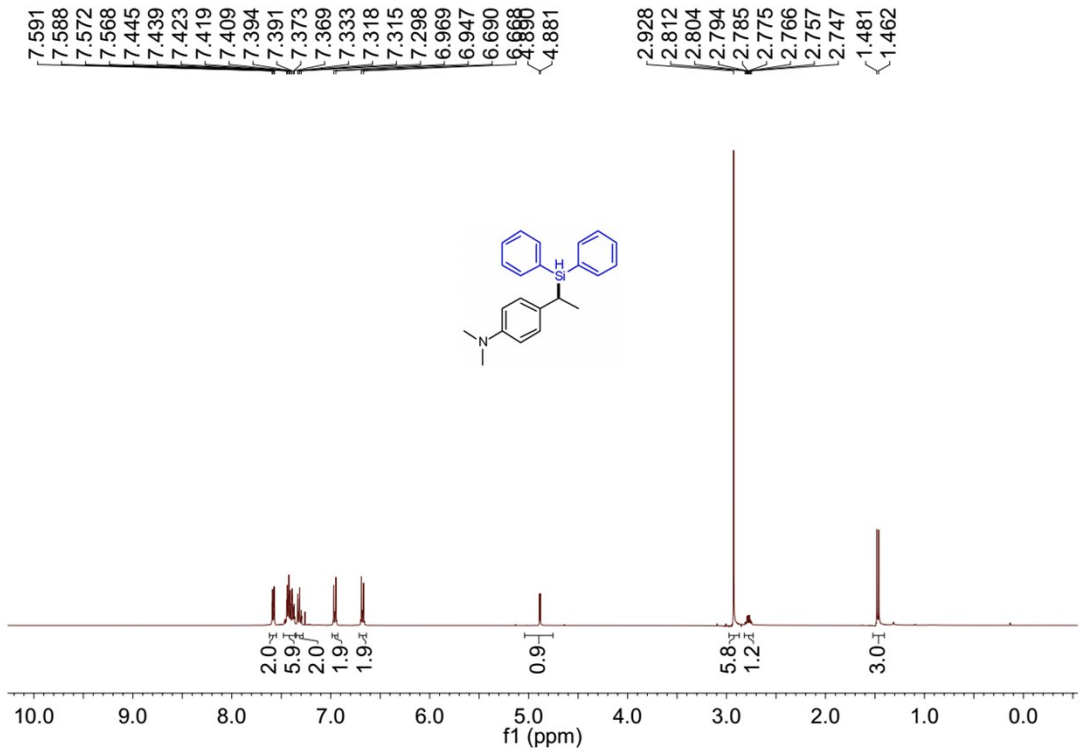
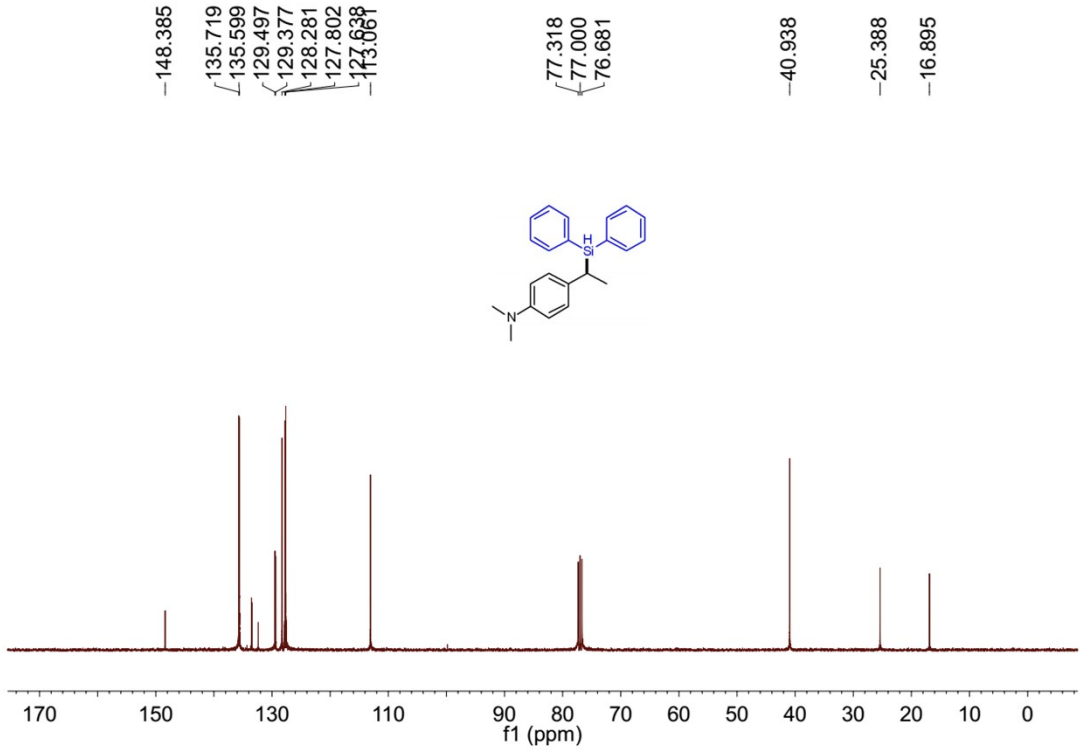
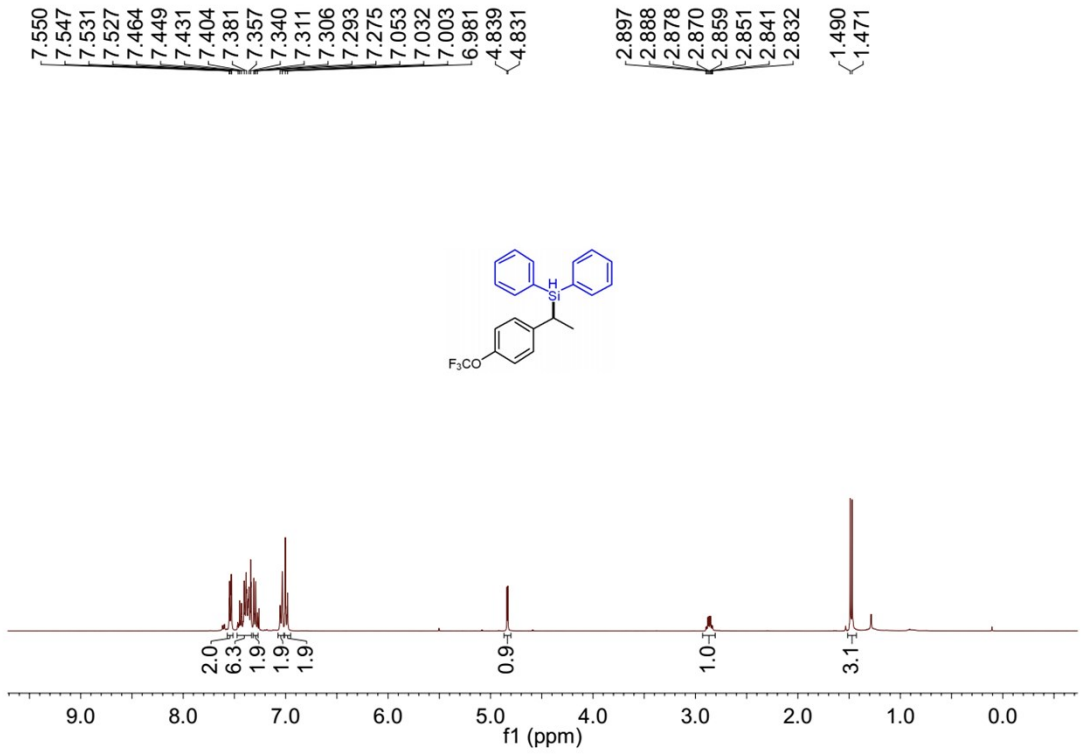


7f ^{13}C NMR



7g ^{1}H NMR



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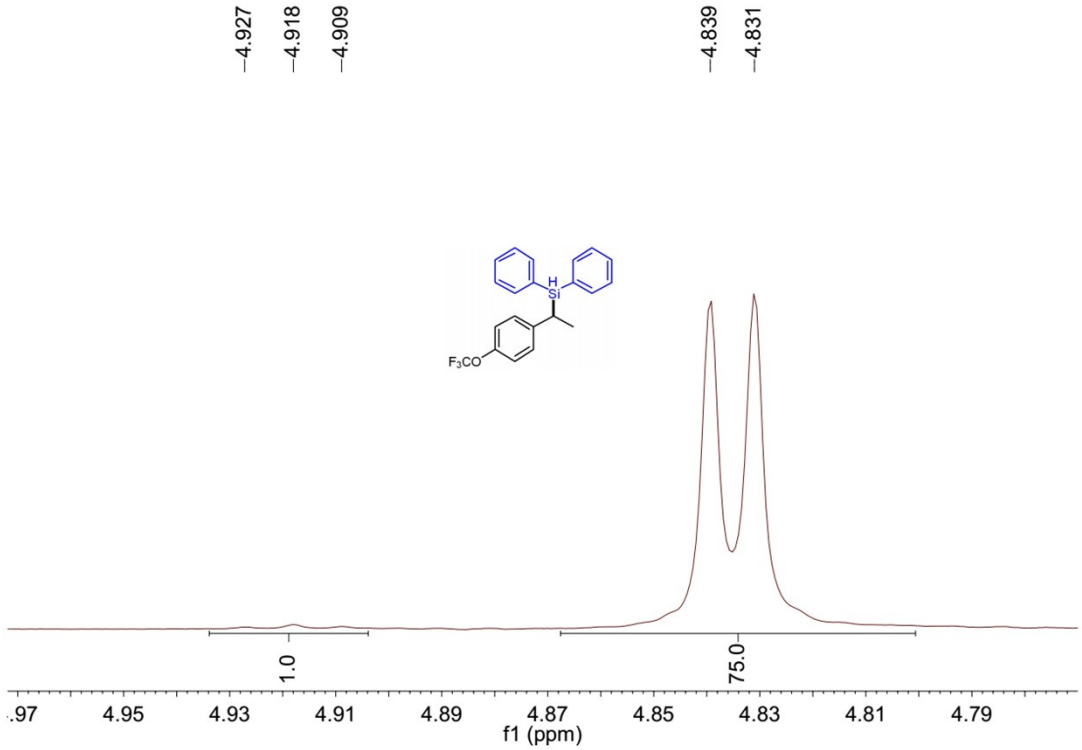

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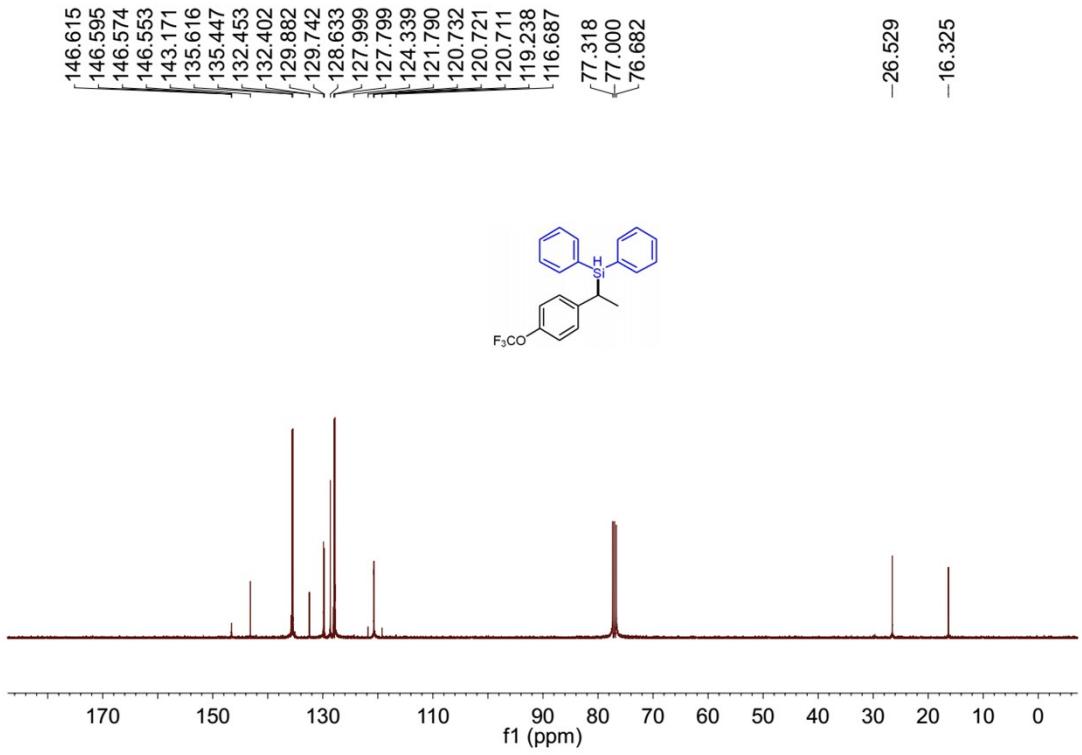

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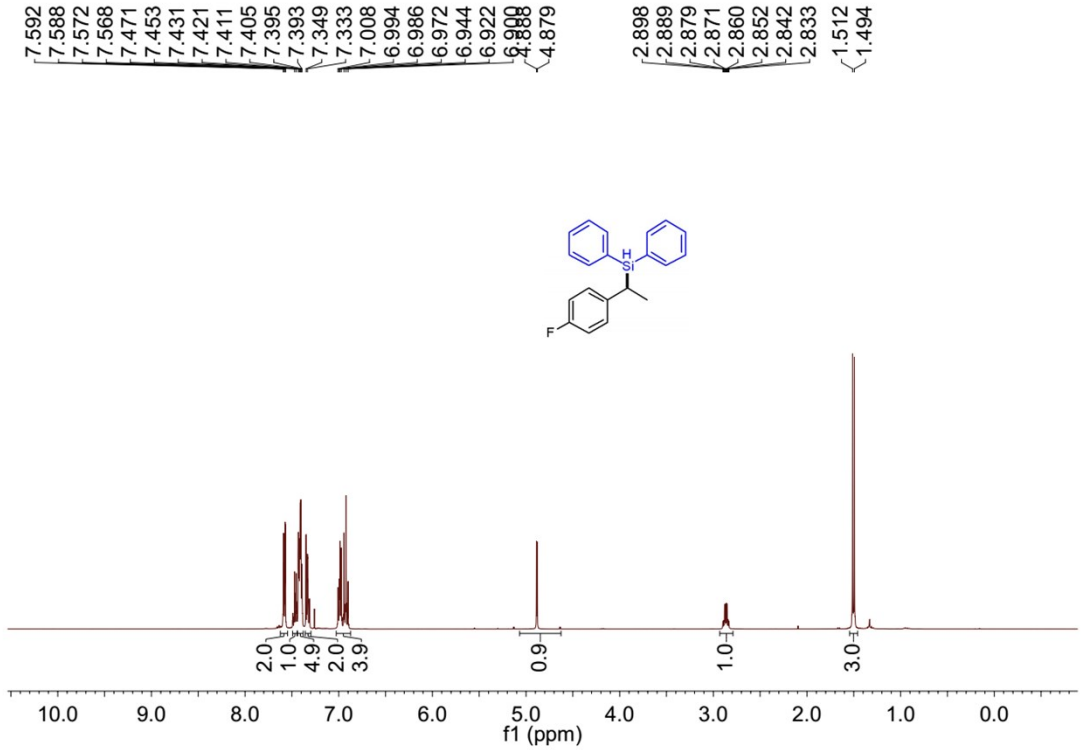

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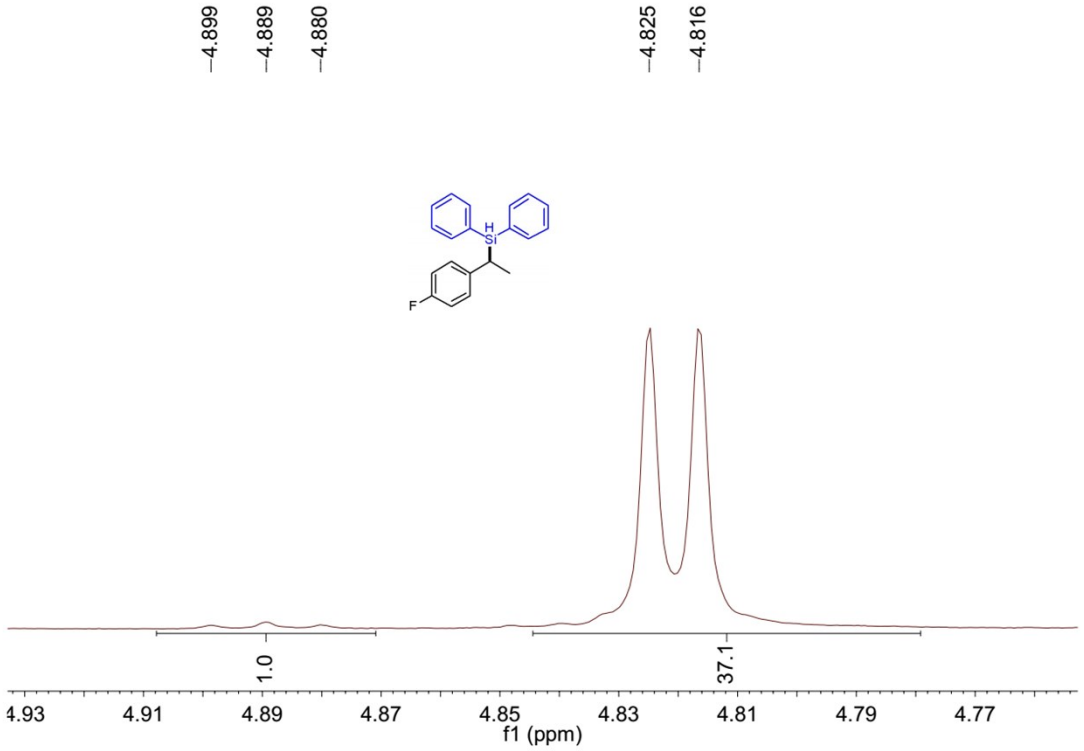

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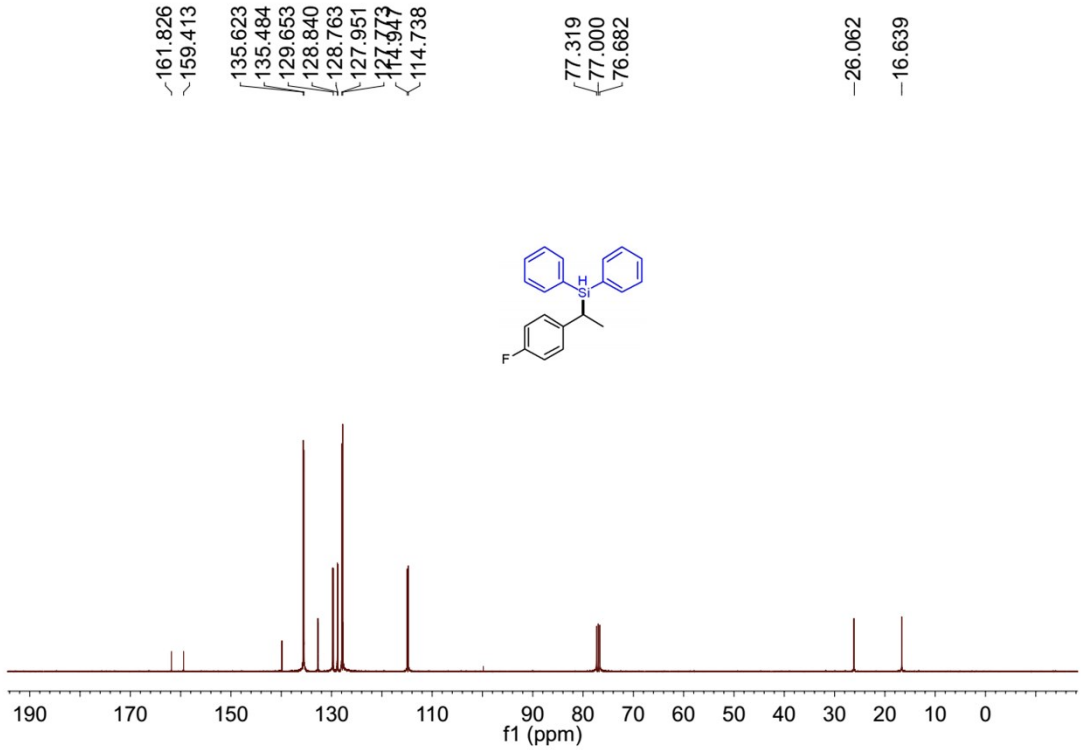

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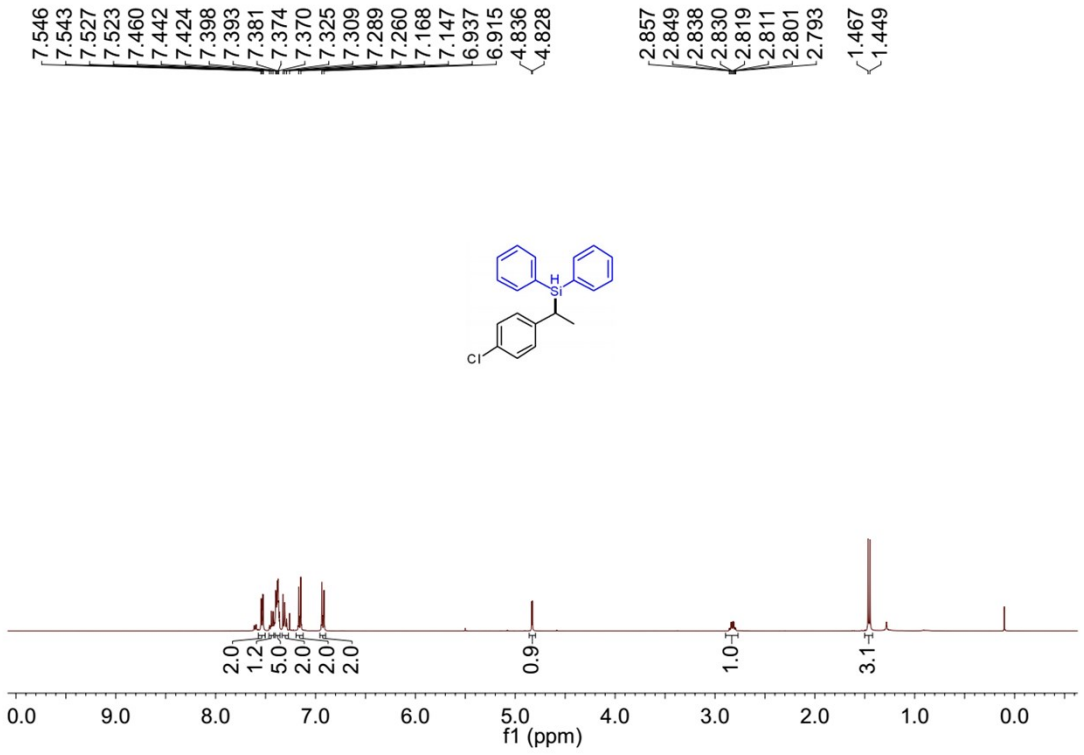

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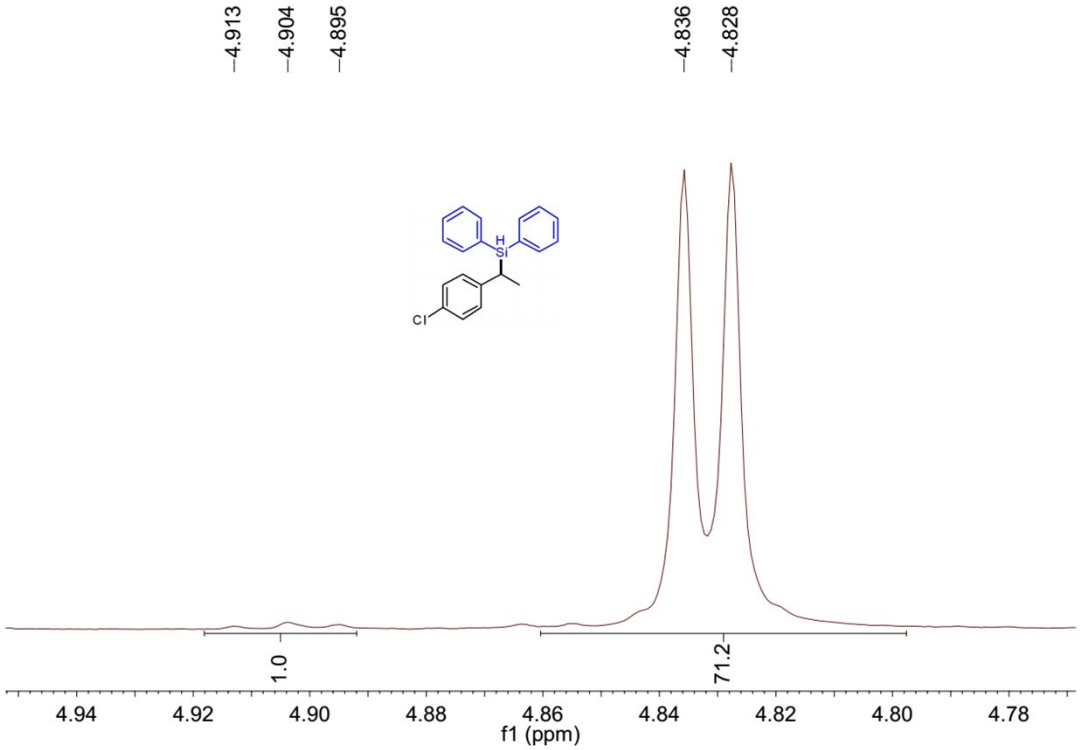

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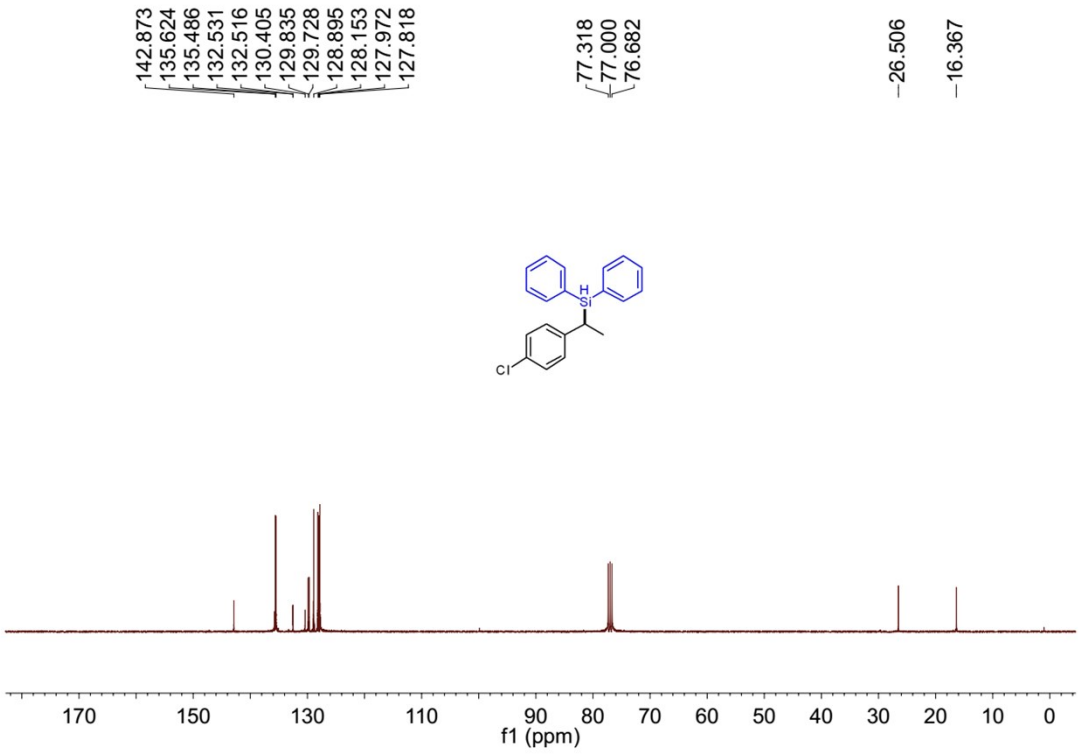

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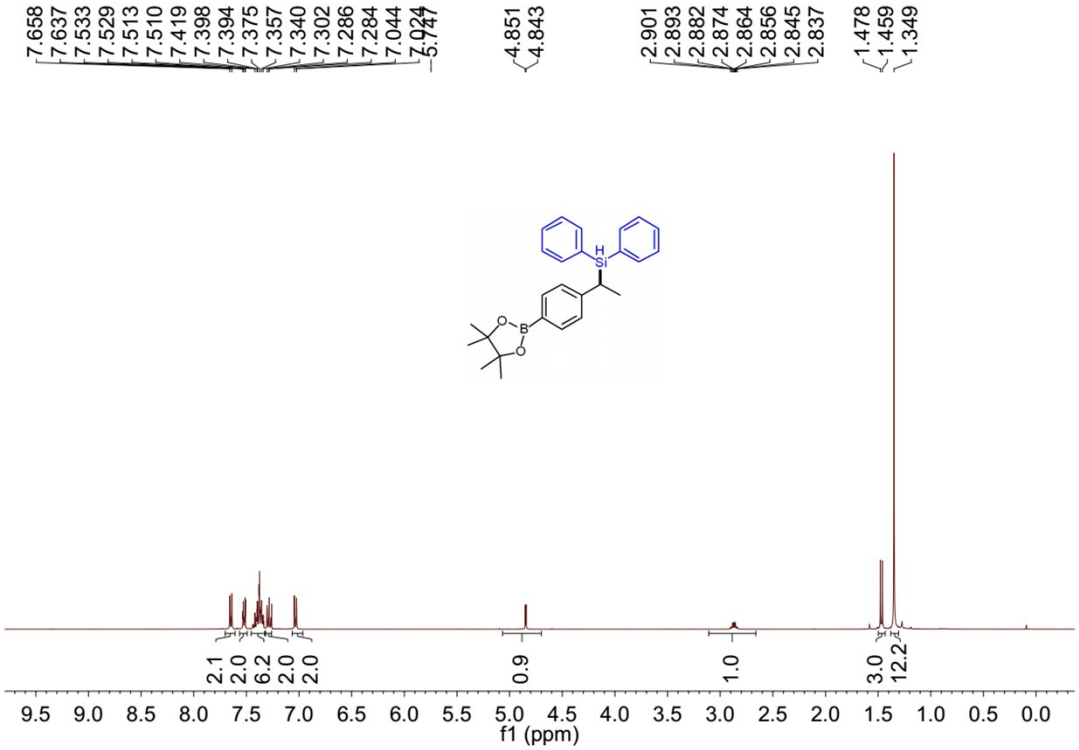

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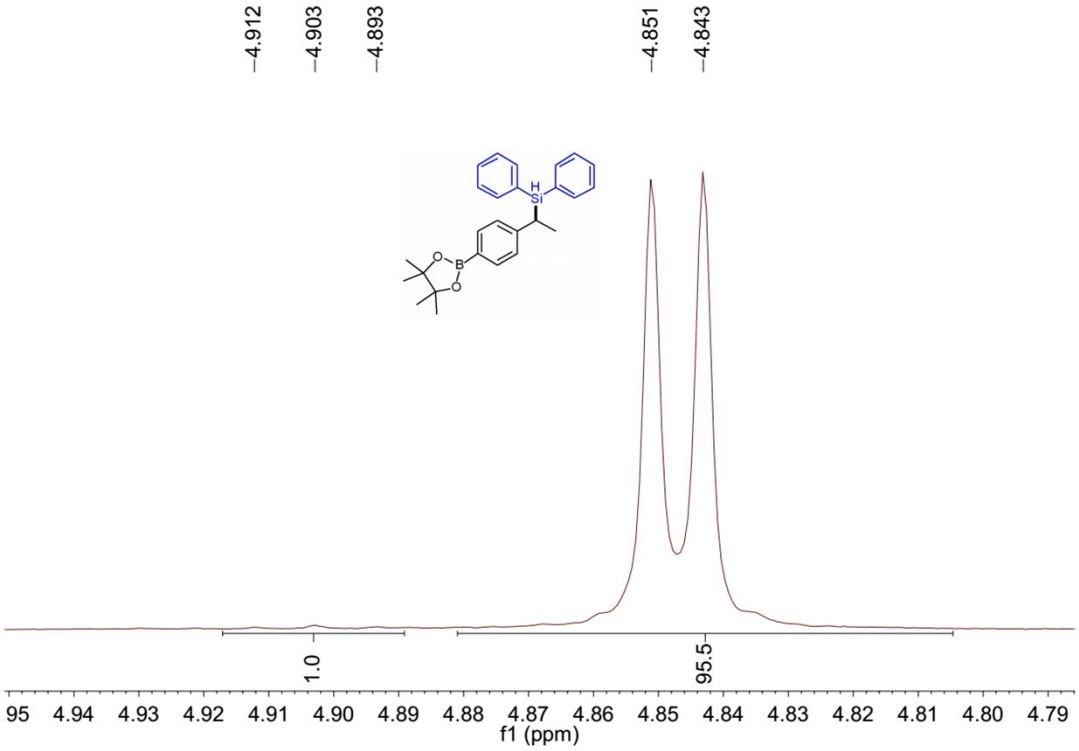

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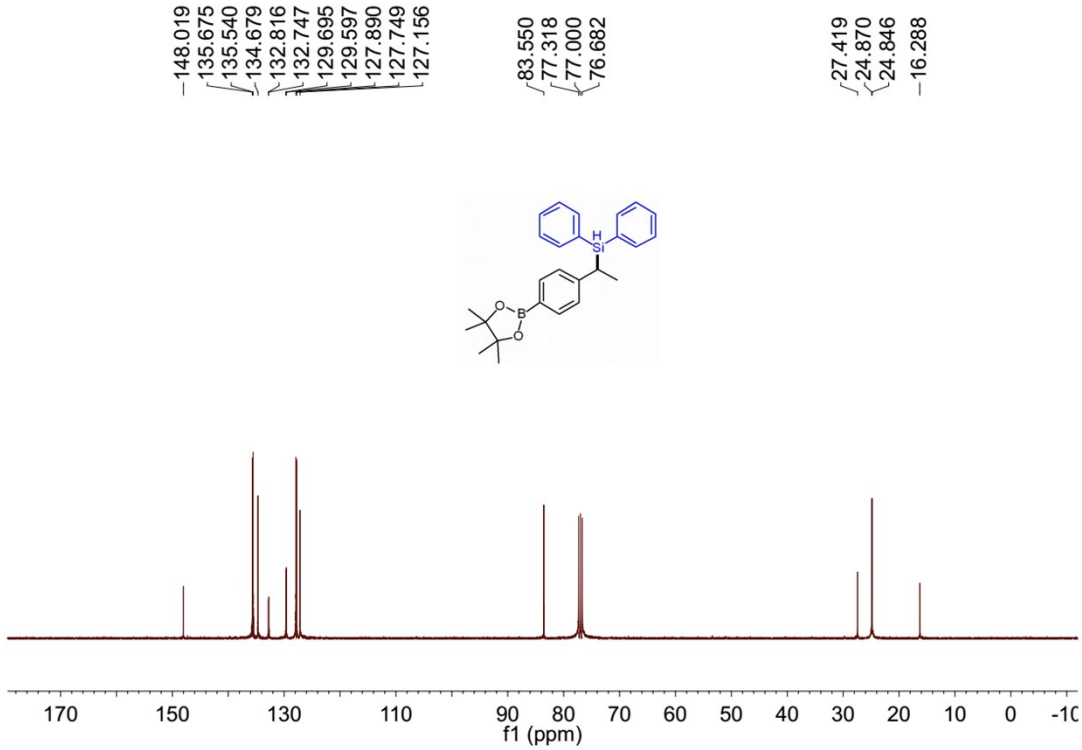

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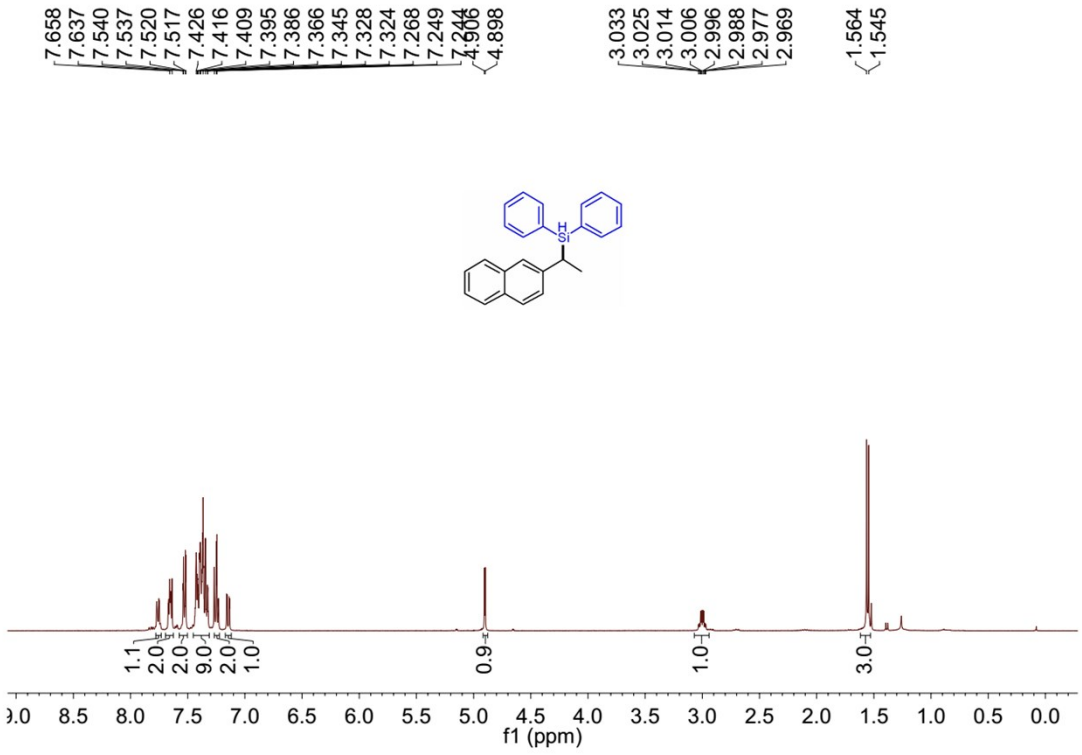

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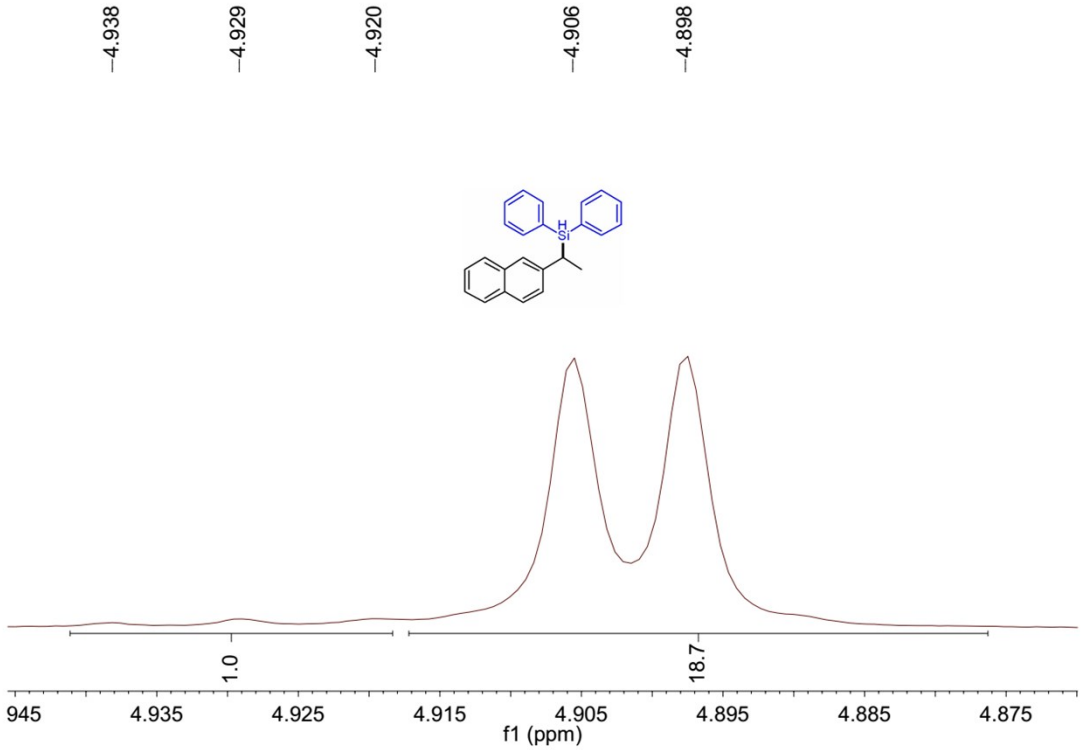

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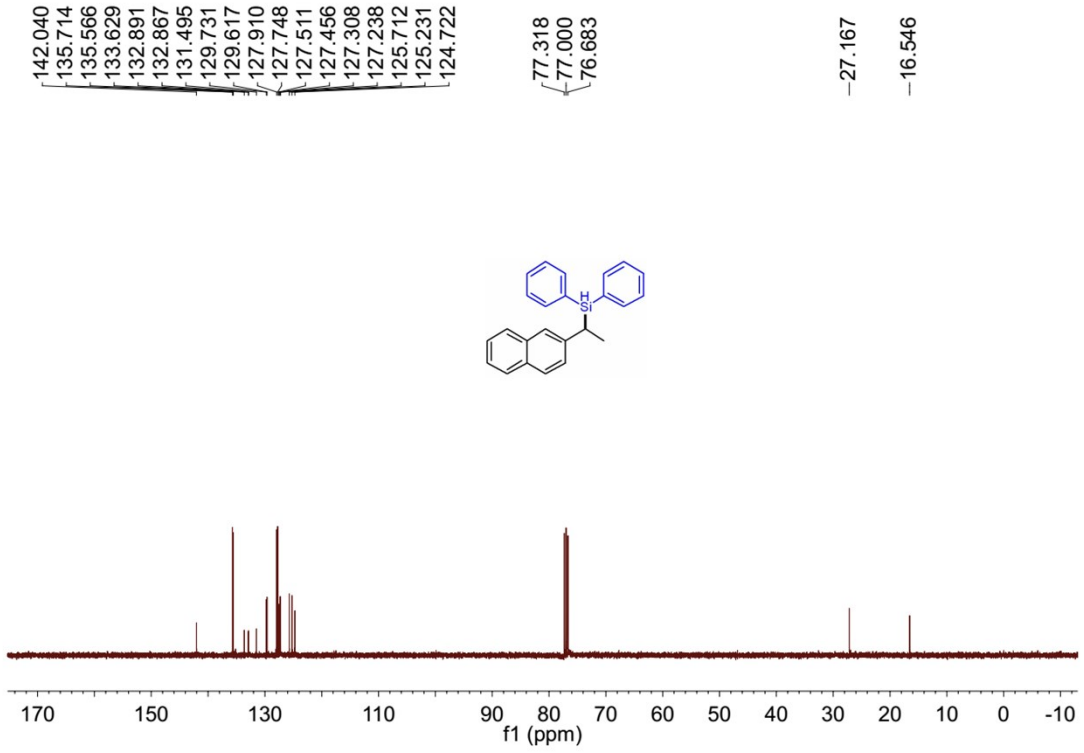

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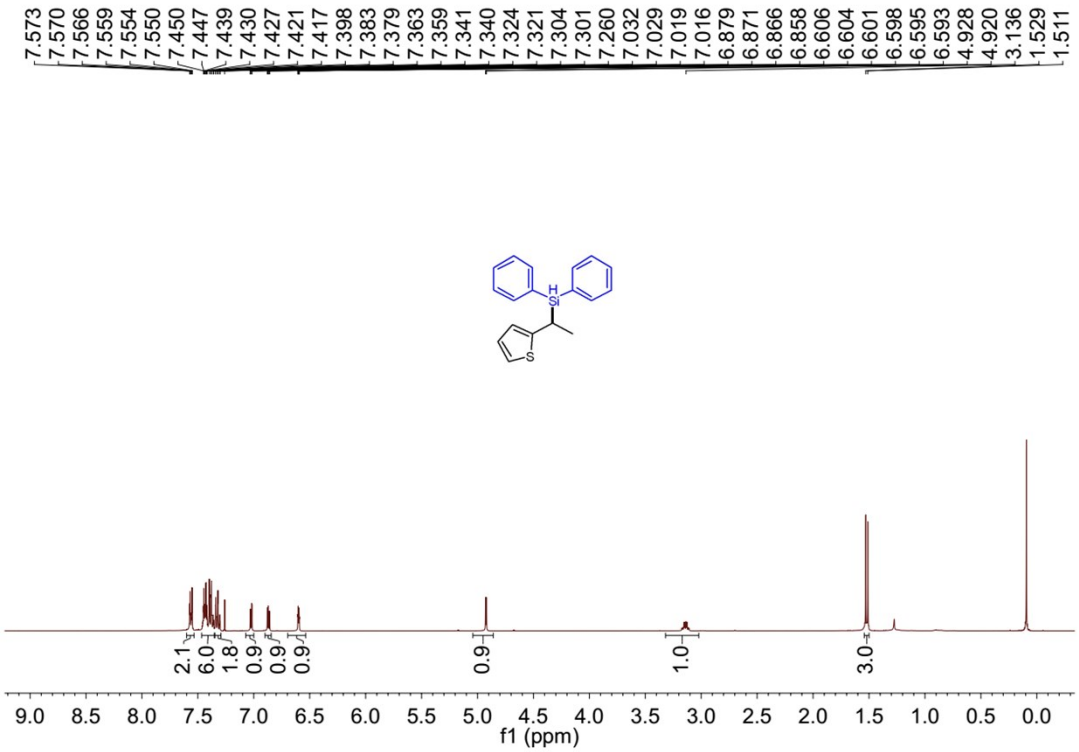

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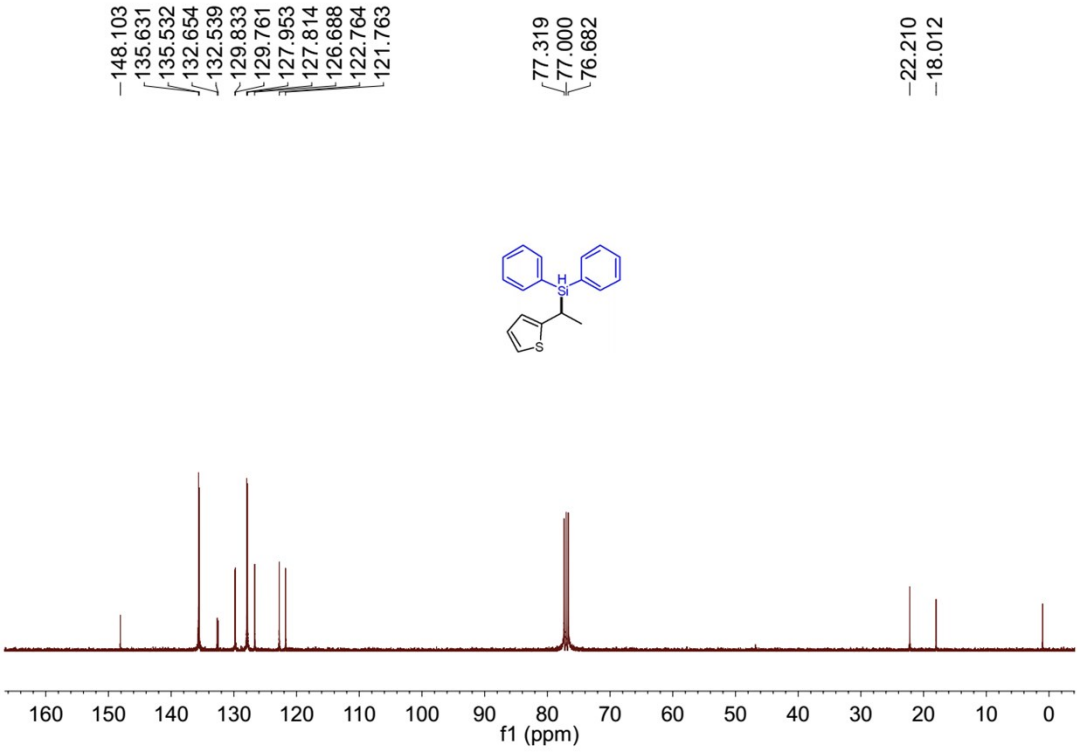

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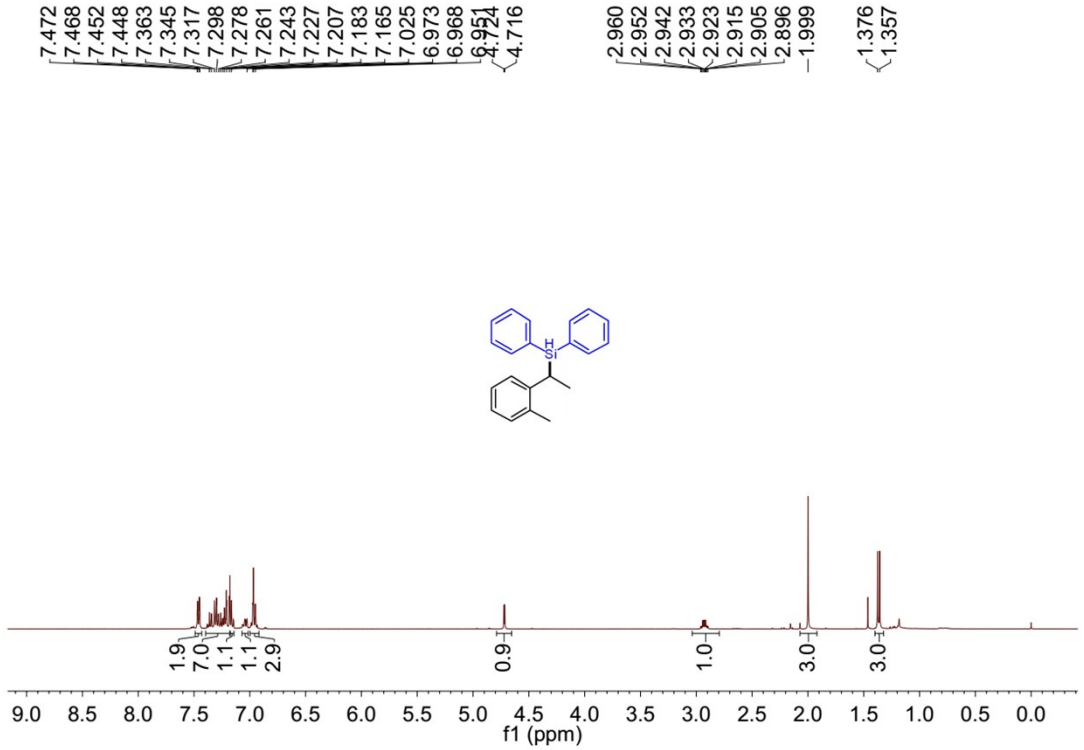
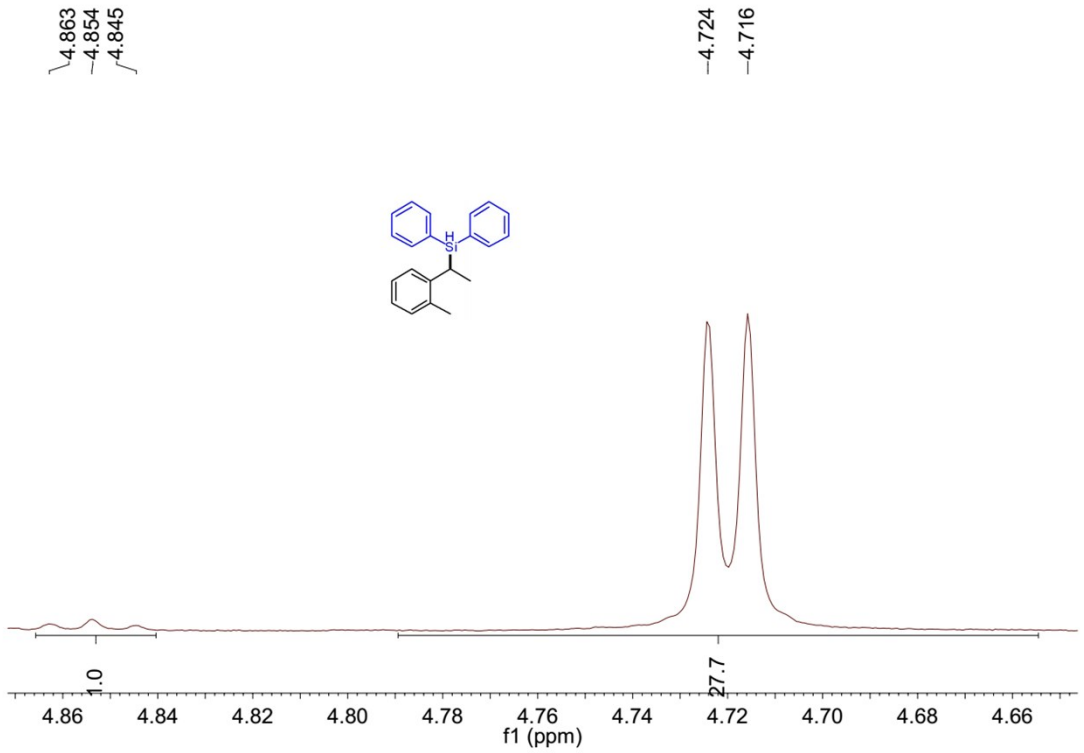


7m regioselectivity



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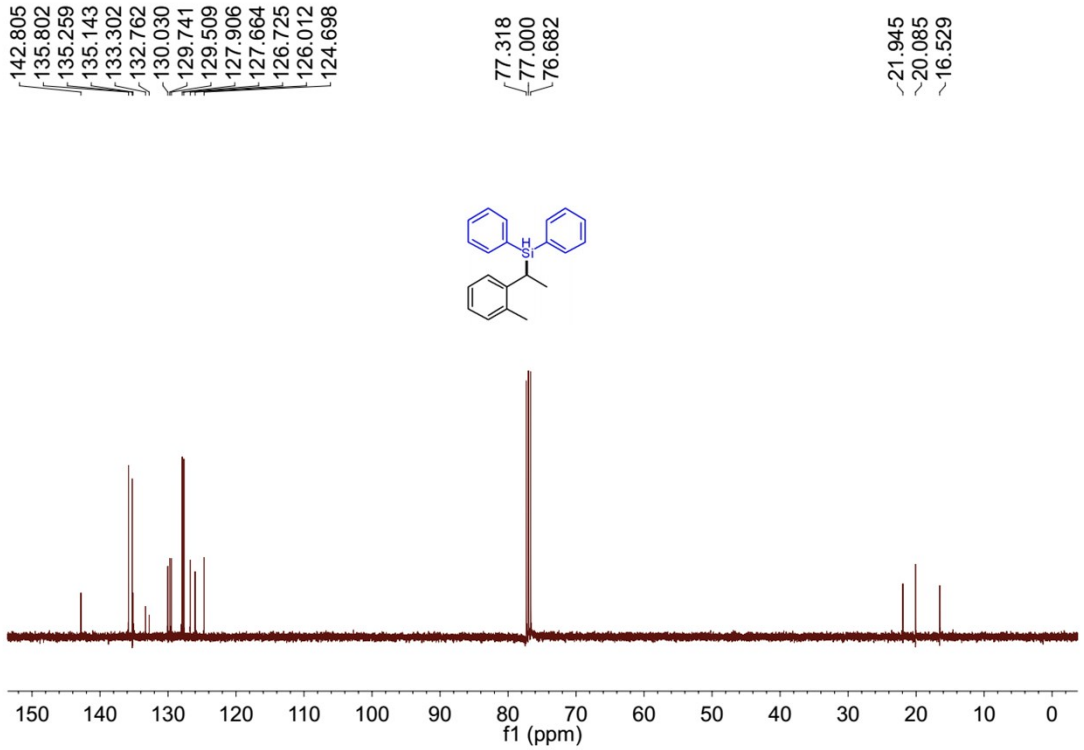

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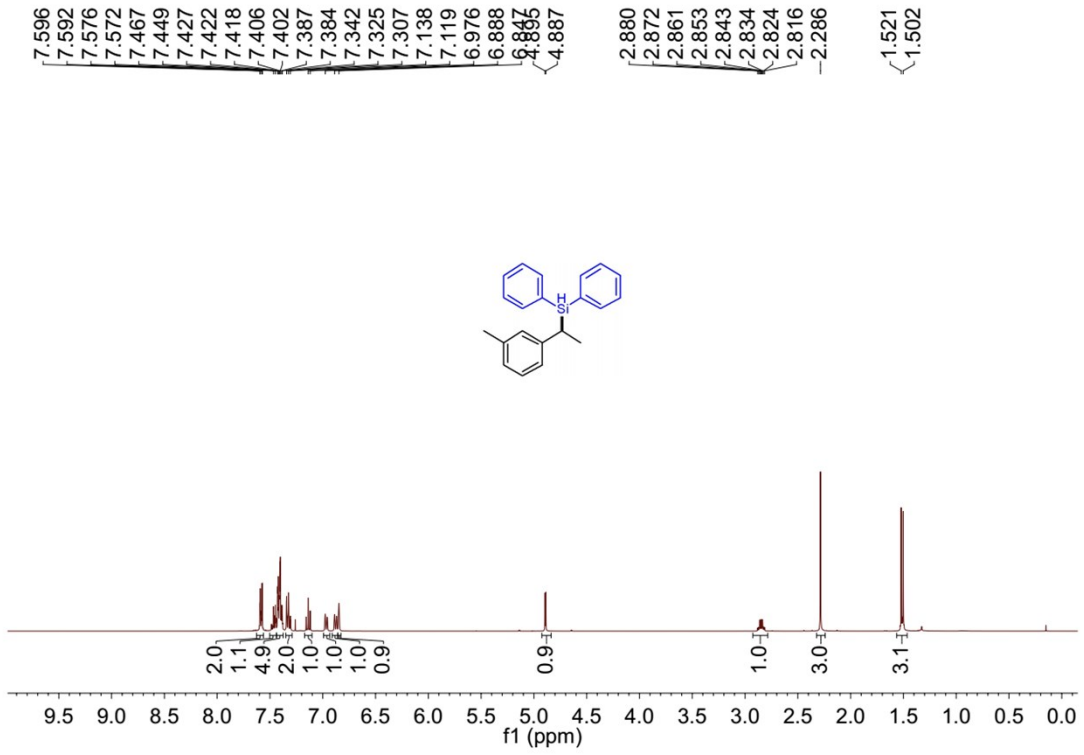

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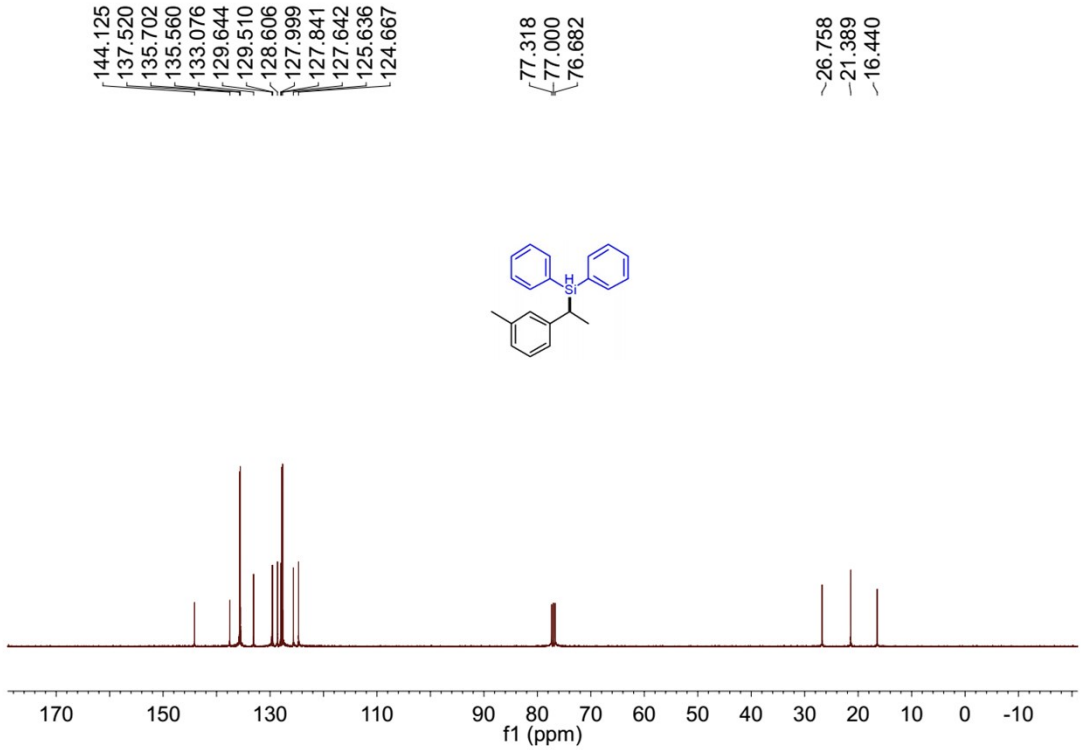

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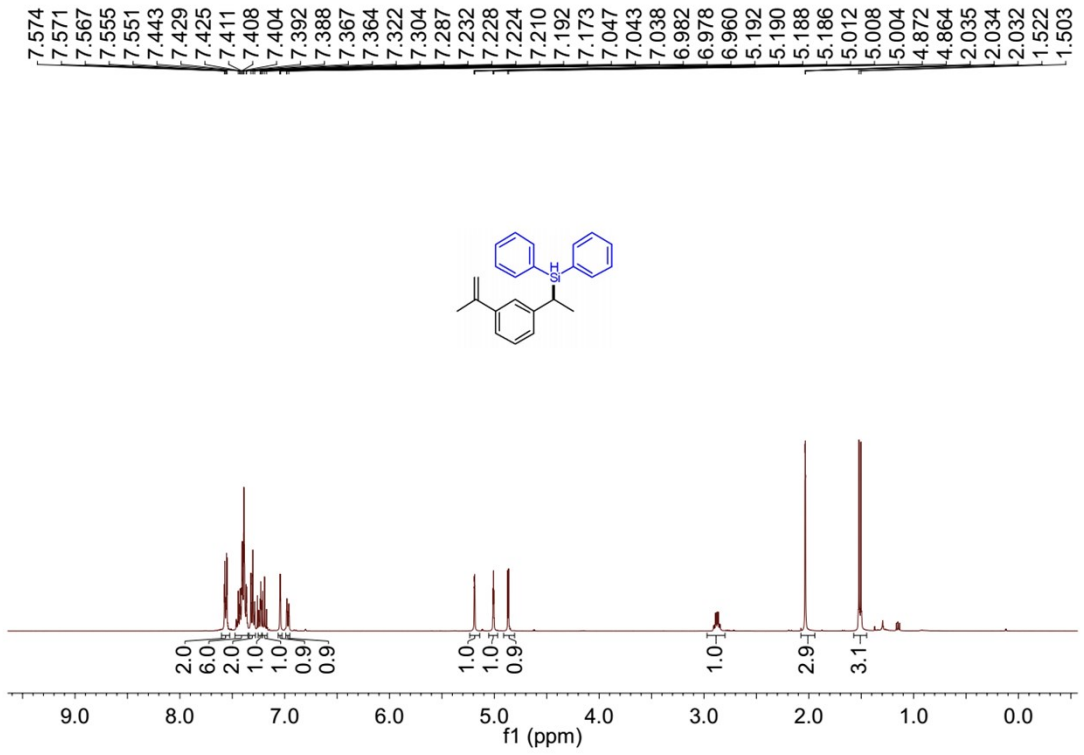
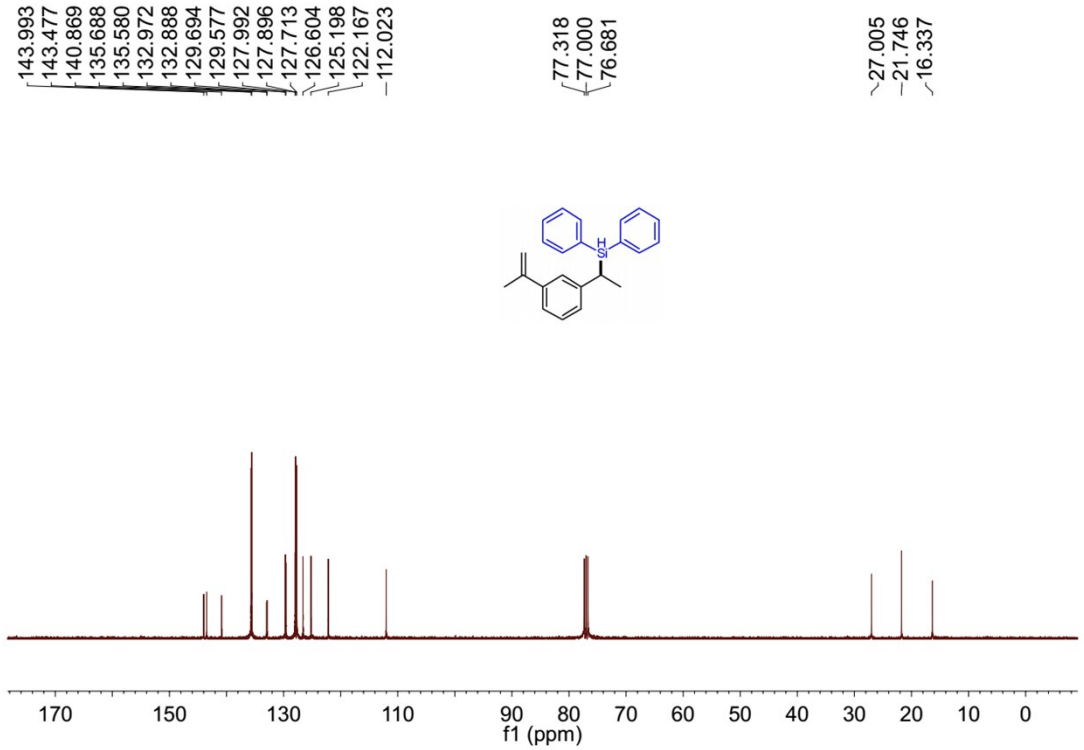


7o ^{13}C NMR



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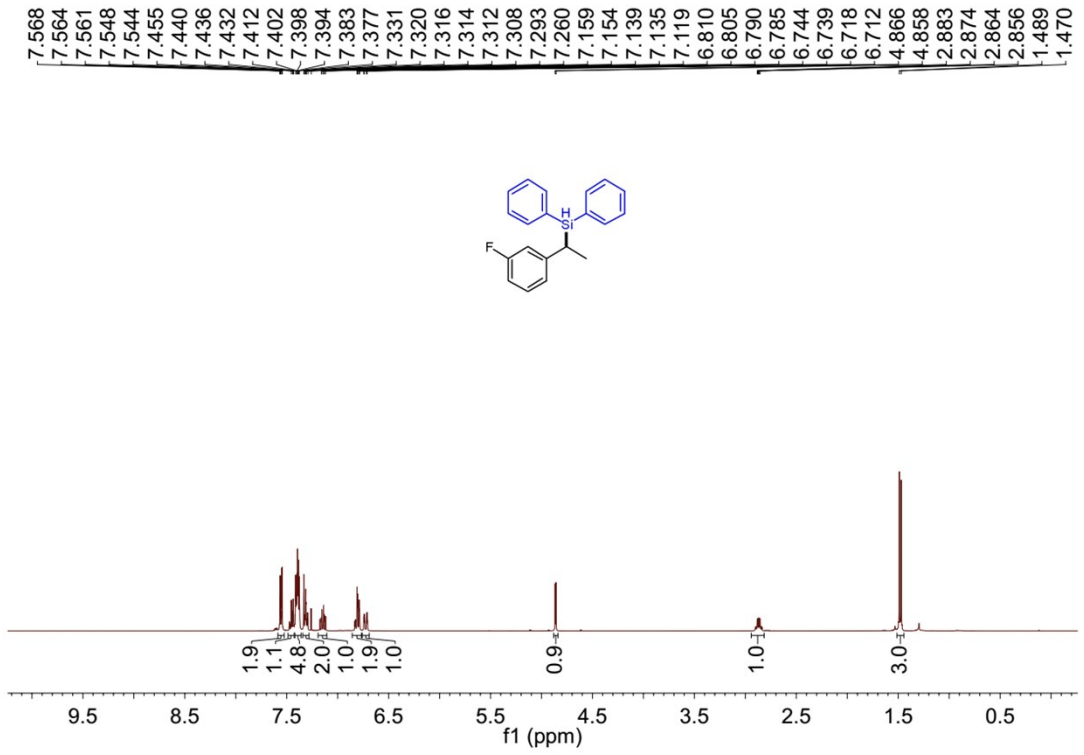
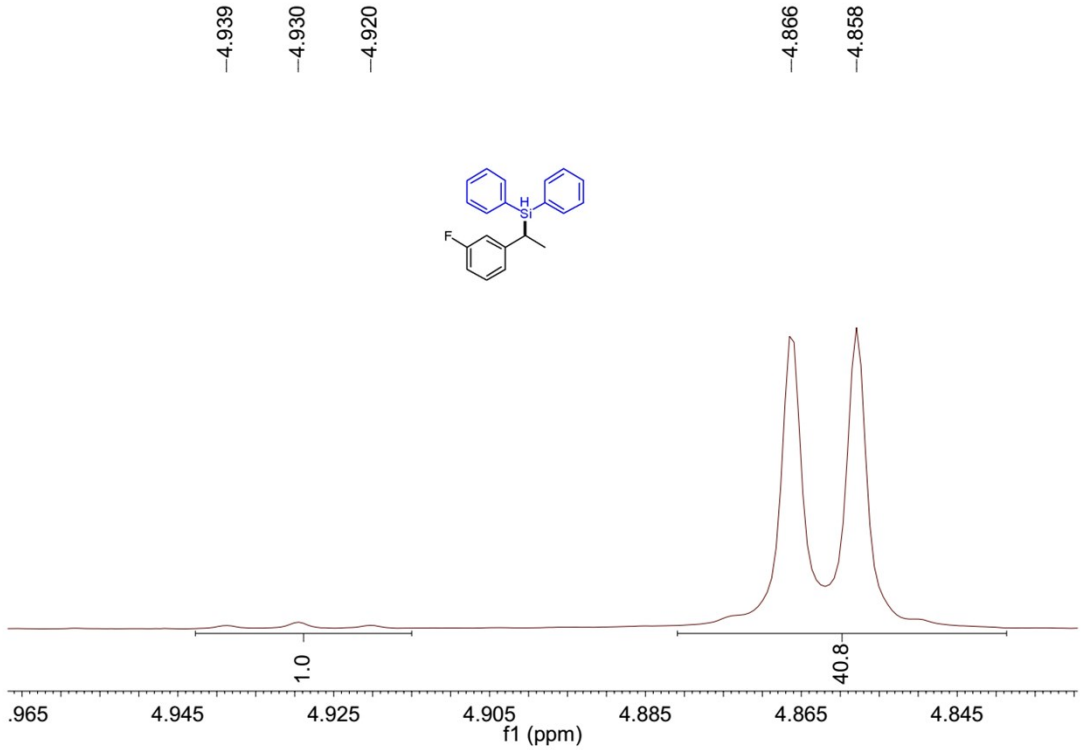


7p regioselectivity



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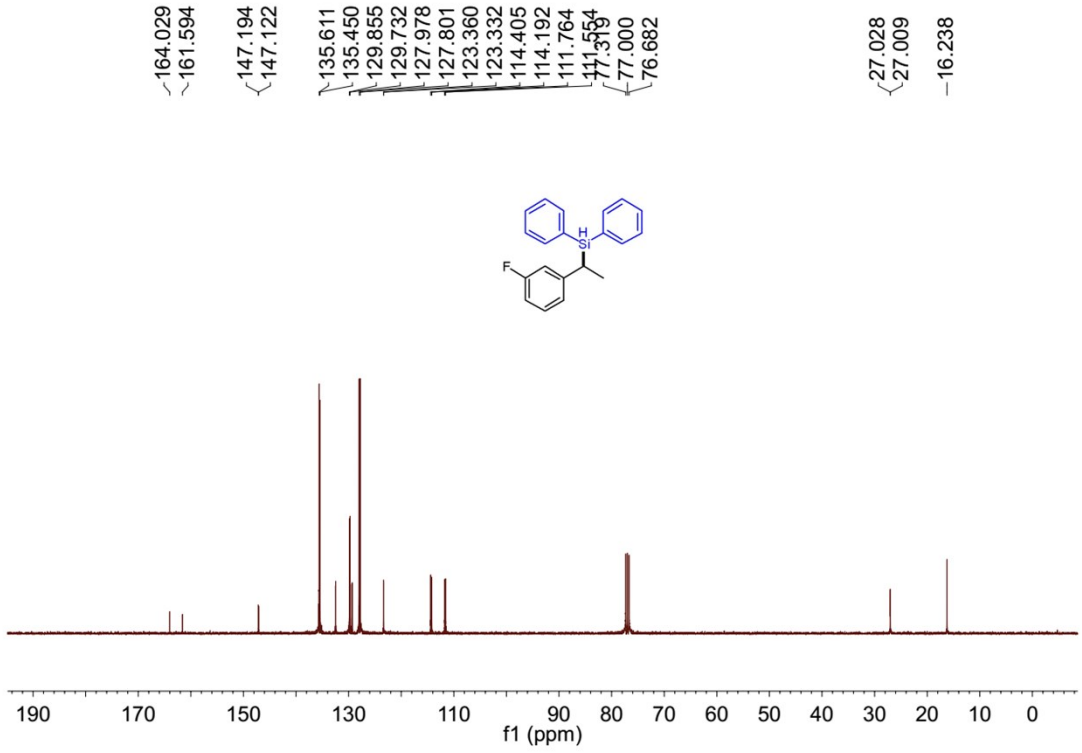

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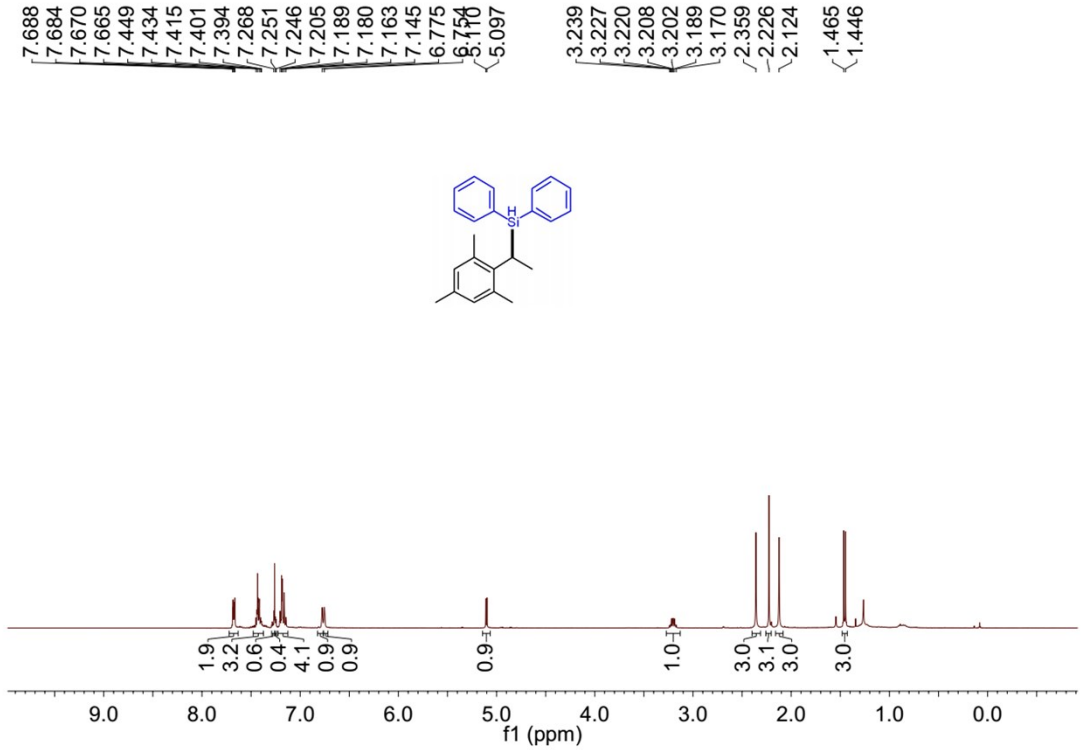
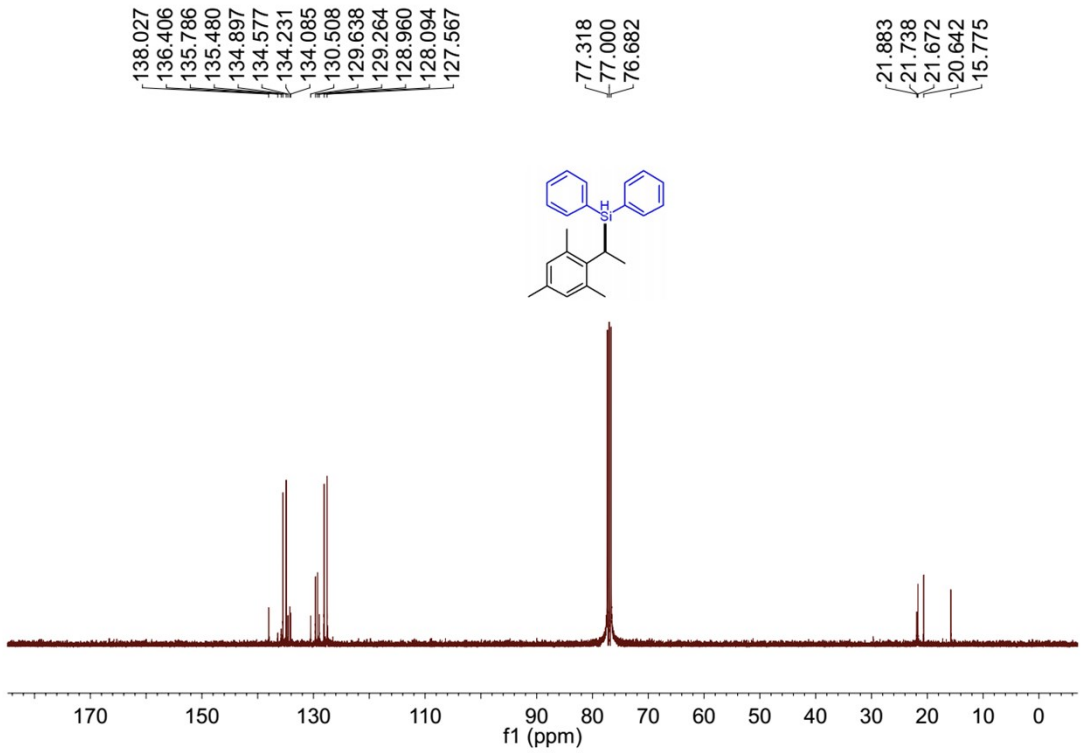


7q ^{13}C NMR



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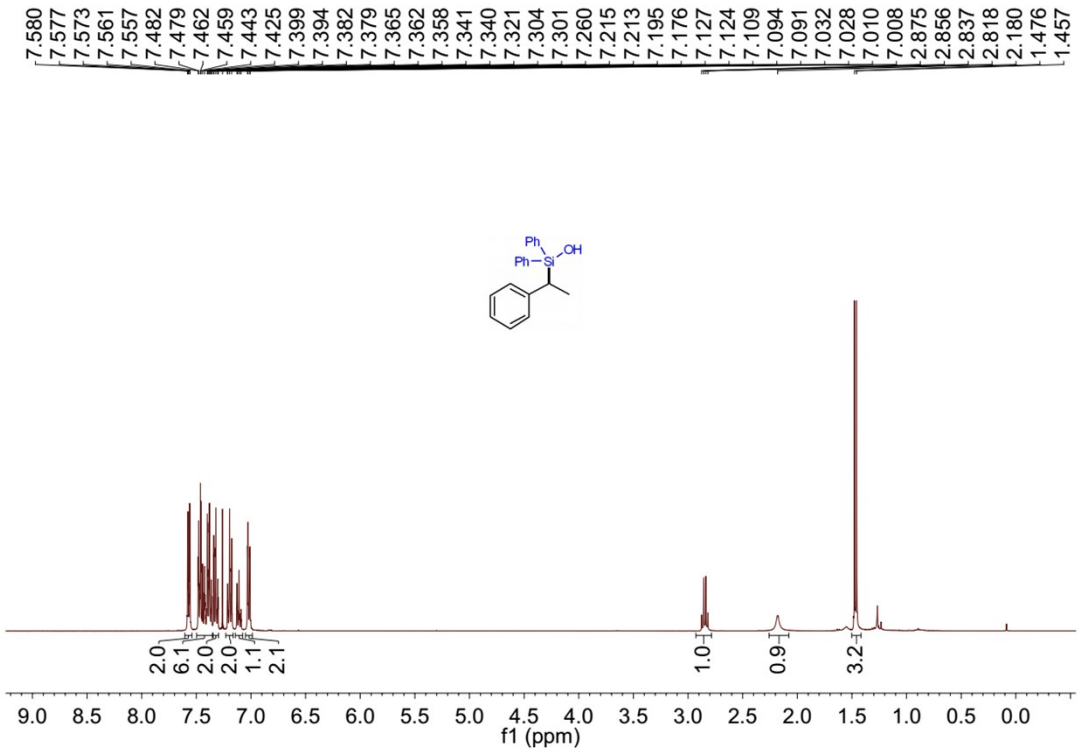

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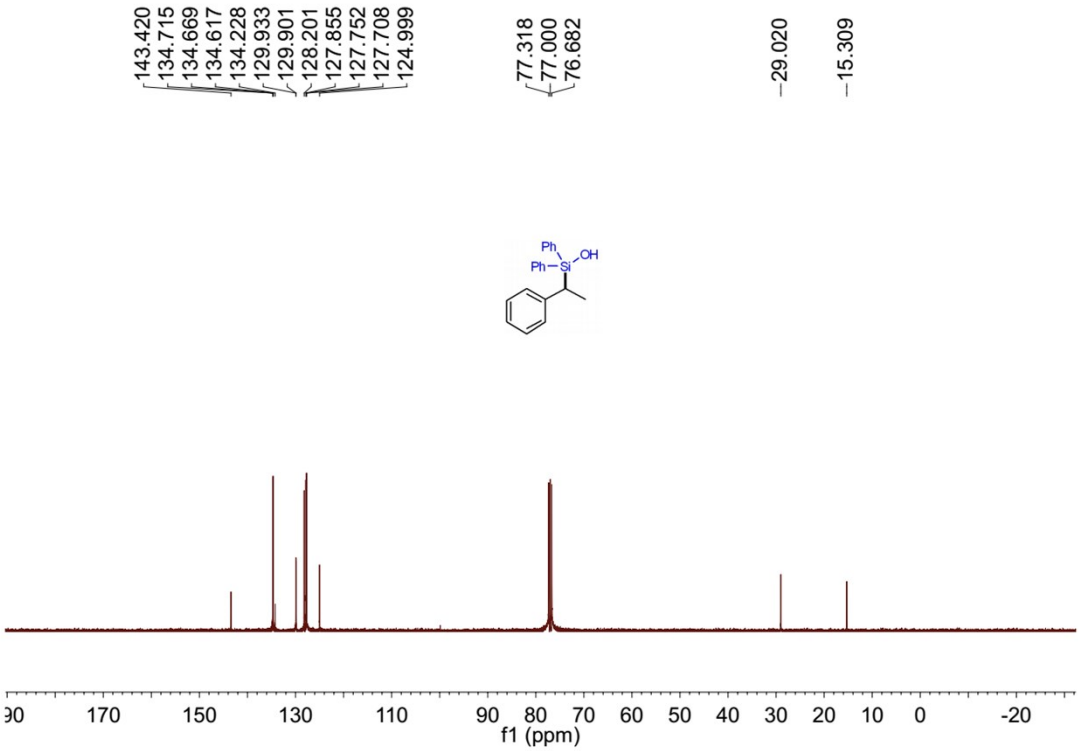
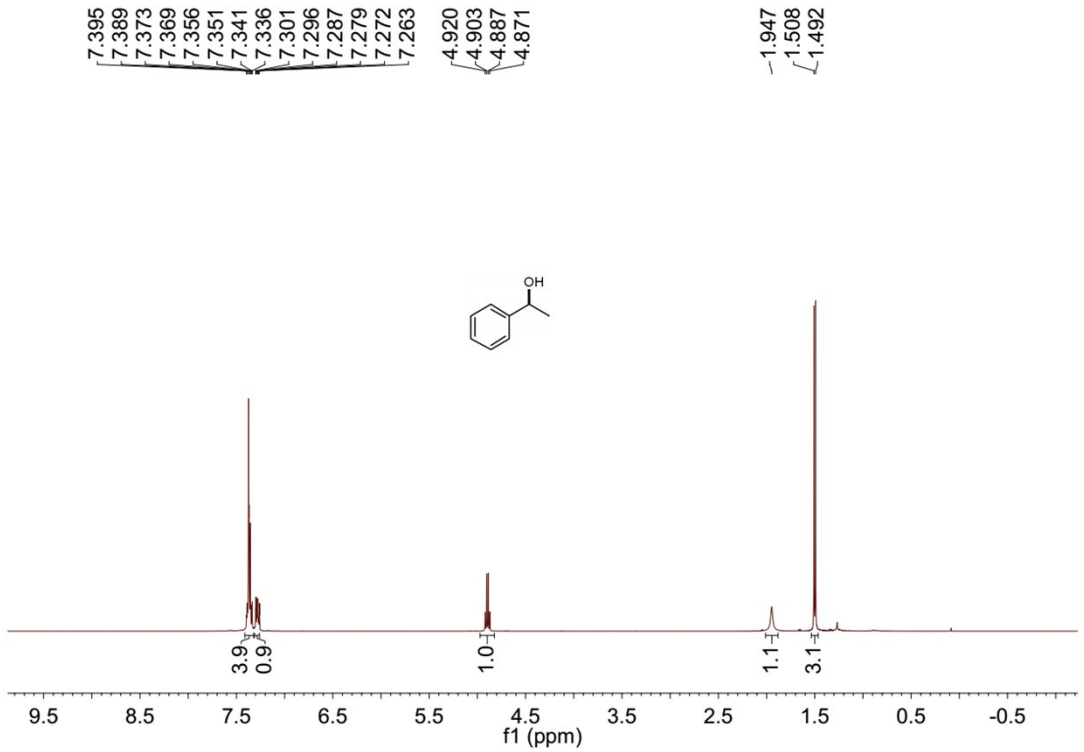
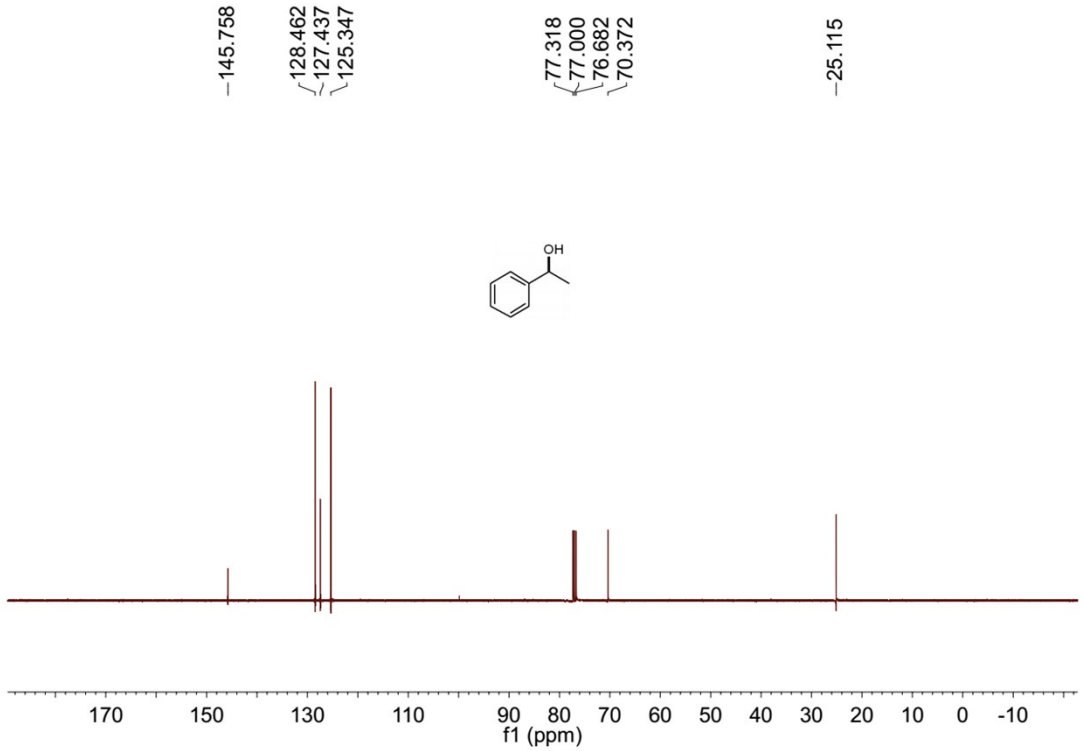


9 ^{1}H NMR



9 ^{13}C NMR



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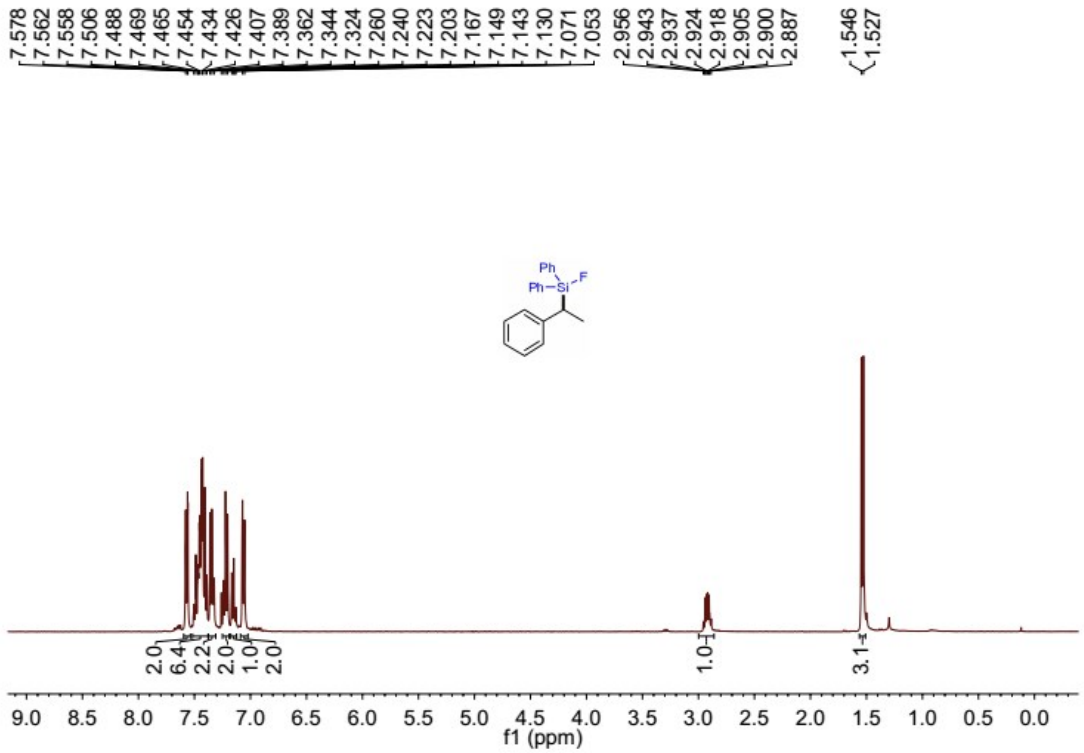
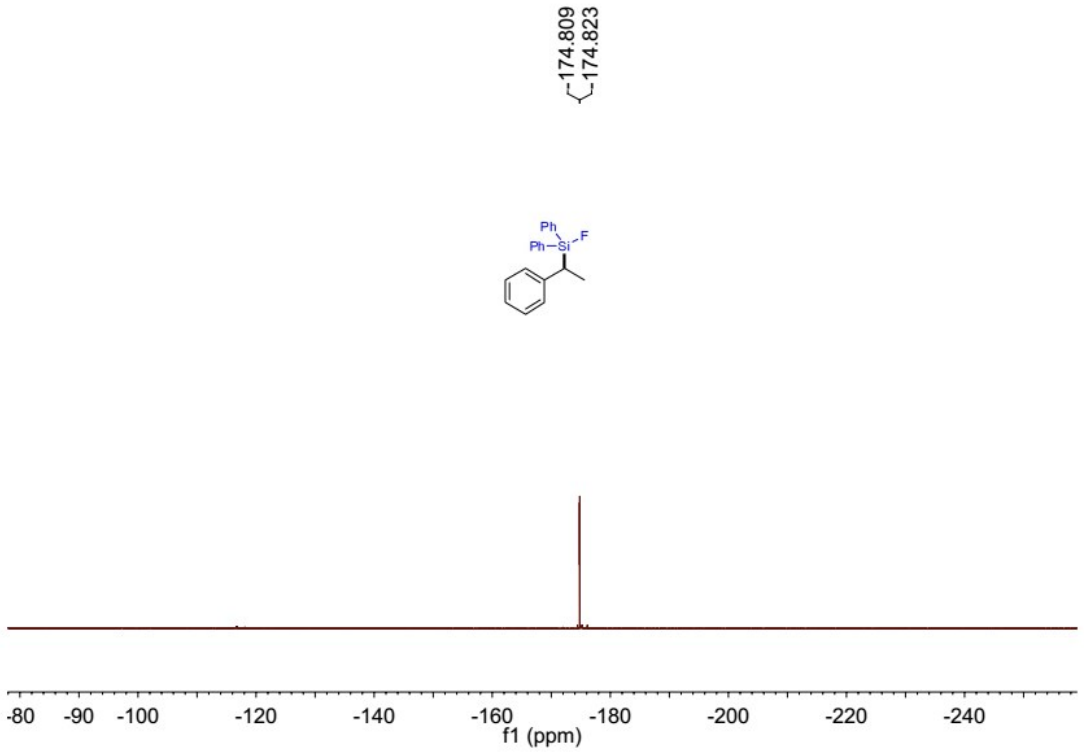


10 ^{19}FNMR



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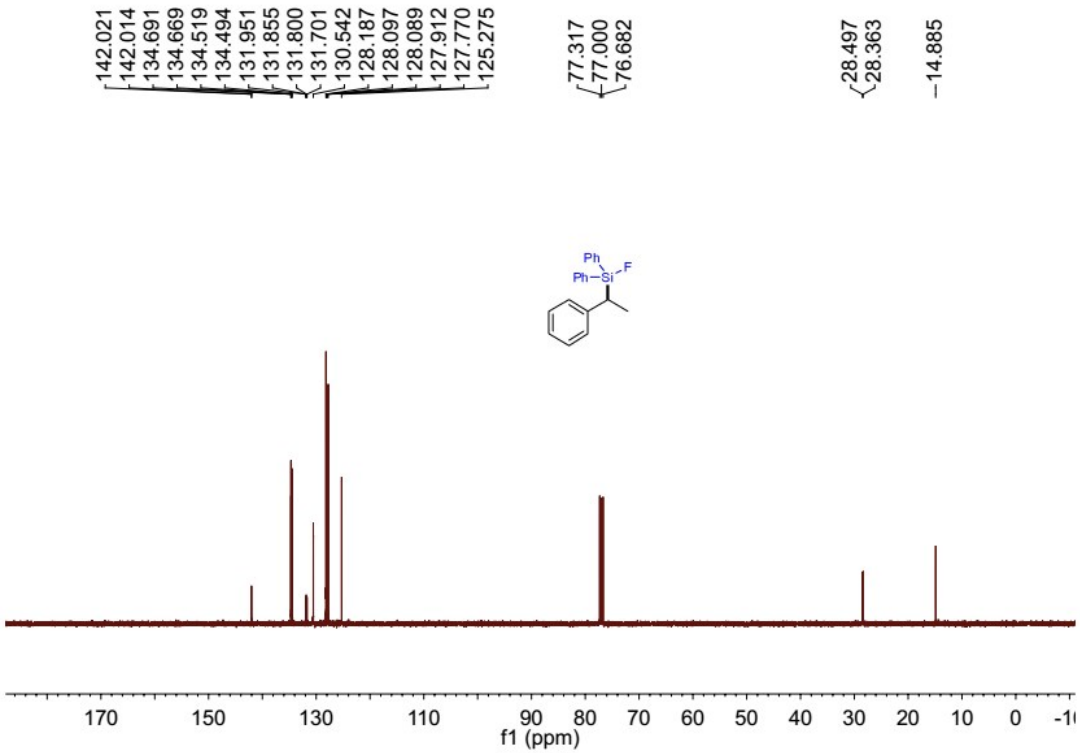
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f1 (ppm)