Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Multifunctional P-ligand -Controlled "Silicon-Centered" Selectivity in Rh/Cu –Catalyzed Si-C bond Cleavage of Silacyclobutanes

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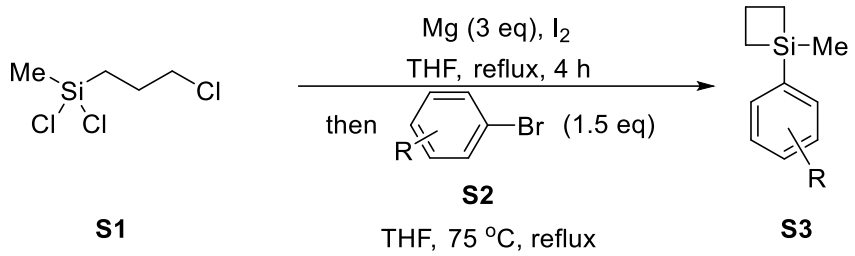
Content

1. General Information

Unless specifically stated, all reagents were commercially obtained and where appropriate, purified prior to use. For example, all the aldehydes recrystallized or distilled prior to use. Dichloromethane, toluene, were freshly distilled from CaH_2, tetrahydrofuran (THF) and 1,4- dioxane were dried and distilled from metal sodium and benzophenone. Et_3N solvents were dried. Other commercially available reagents and solvents were used directly without purification. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica (300-400 mesh). ^1H NMR, ^{13}C NMR spectra were recorded on a Bruker 400 MHz or 500 MHz spectrometer in $CDCl_3$. Multiplicities were given as: s (singlet); d (doublet); dd (doublets of doublet); t (triplet); q (quartet); or m (multiplets). High resolution mass spectra (HRMS) of the products were obtained on a Bruker Daltonics micro TOFspectrometer. HPLC was carried out with a Agilent 1260 infinity, Waters AcQuity HPLC or Waters AcQuity UPLC using a chiralcel AD-H column, a chiralcel OJ-H column, a chiralcel IA column, a chiralcel OD-H column, a chiralcel IC column,or a chiralcel OX-H column, a chiralcel OP column, a chiralcel Phenomenex column.

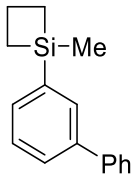
2. Experimental Procedures and Spectral Data of Reactants

2.1. General procedure for the synthesis of Silacyclobutanes (S3).[1]



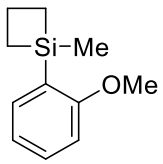
Magnesium (60 mmol), 5 mL solution of the **S1** in THF (3.12 mL of the **S1** was dissolved in 20 mL THF) and a grain of I_2 in dry THF was heated to reflux. The rest of the **S1** solution was added dropwise over a period of 1 h and the resulting solution was refluxed for additional 4 h. **S2** (30 mmol) dissolved in 30 mL THF was added dropwise

over a period of 3 h and the resulting solution was refluxed overnight. The reaction was allowed to cool to room temperature before quenching with 15 mL aq. NH_4Cl. The mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were then dried over Na_2SO_4 and concentrated under reduced vacuum. The residue was purified by silica gel flash column chromatography (eluent: petroleum ether) to afford **S3** as colorless oil.



1-([1,1'-biphenyl]-3-yl)-1-methylsiletane (1x):

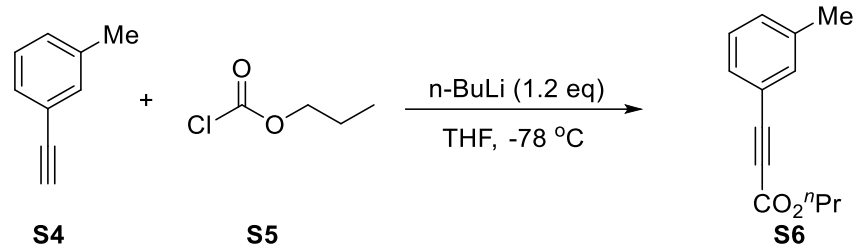
Colorless oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (s, 1H), 7.93-7.85 (m, 4H), 7.77-7.67 (m, 3H), 7.61 (t, *J* = 6.8 Hz, 1H), 2.60-2.45 (m, 2H), 1.74-1.60 (m, 2H), 1.58-1.43 (m, 2H), 0.89 (d, *J* = 1.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.6, 141.9, 140.3, 133.5, 133.4, 129.9, 129.5, 129.4, 128.4, 128.3, 15.6, -0.5. GC MS (EI) m/z: 238.1, 210.1, 195.1, 181.0, 165.1, 152.1.



1-(2-methoxyphenyl)-1-methylsiletane (1aq):

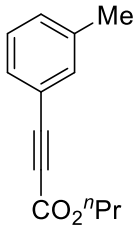
Colorless oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (dd, *J* = 7.1, 1.8 Hz, 1H), 7.50-7.40 (m, 1H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 3.87 (s, 3H), 2.28-2.13 (m, 2H), 1.45-1.32 (m, 2H), 1.29-1.15 (m, 2H), 0.58 (s, 3H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.2, 135.1, 131.4, 126.8, 120.7, 109.7, 55.3, 18.4, 14.5, -0.6. GC MS (EI) m/z: 192.1, 164.1, 149.0, 134.1, 121.1, 105.0, 59.0.

2.2. General procedure for the synthesis of propyl 3-(m-tolyl)propiolate (S6).[2]



S4 **S5** **S6**

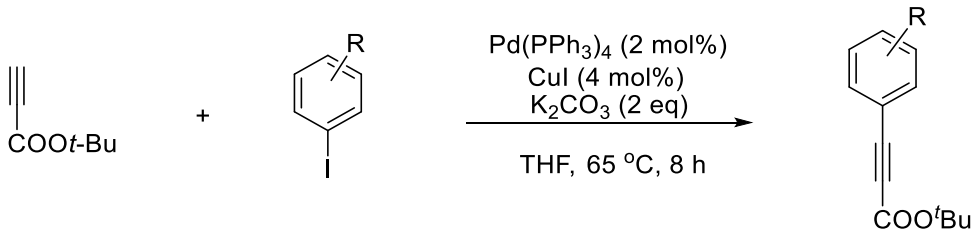
Dry THF (20 mL) was added to the **S4** (1 equiv, 10.0 mmol) in a round-bottom flask equipped with a stir bar. The solution was cooled to −78 °C, and n-BuLi (2.5 M in hexanes, 12.0 mmol) was added dropwise, and the resulting solution was stirred. After 1 hours, **S5** (1.2 equiv, 12.0 mmol) was added dropwise to the mixture at −78 °C and the resulting mixture was stirred for 8 h. The reaction was then diluted with ethyl acetate, and water was added. The organic layer was washed with brine and dried over anhydrous sodium sulfate. Concentration in vacuo yielded a yellow oil which, upon purification by column chromatography, yielded the corresponding ester **S6**.



Propyl 3-(m-tolyl)propiolate (2d):

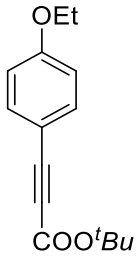
Yellow oil, ^{1}H NMR (400 MHz, Chloroform-d) δ 7.31-7.26 (m, 2H), 7.18-7.11 (m, 2H), 4.09 (t, J = 6.7 Hz, 2H), 2.23 (s, 3H), 1.73-1.51 (m, 2H), 0.89 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 154.2, 138.4, 133.4, 131.5, 130.1, 128.5, 119.4, 86.3, 80.4, 67.5, 21.9, 21.1, 10.3. HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{13}H_{14}NaO_2$: 225.0886, found: 225.0873.

2.3. General procedure for the synthesis of tert-butyl 3-phenylpropiolate (S9).[3]



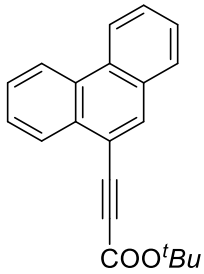
S7 **S8** **S9**

The reaction of **S8** (1.2 eq, 36 mmol) with **S7** (30 mmol) in THF at 65 ºC in the presence of $Pd(PPh_3)_4$ (2 mol%), copper(I) iodide (4 mol %) and K_2CO_3 (2 eq) afforded the ester **S9** after 6 h. The mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were then dried over Na_2SO_4 and concentrated under reduced vacuum. The residue was purified by silica gel flash column chromatography (eluent: EA/PE = 50/1) to afford **S9**.



Tert-butyl 3-(4-ethoxyphenyl)propiolate (2l):

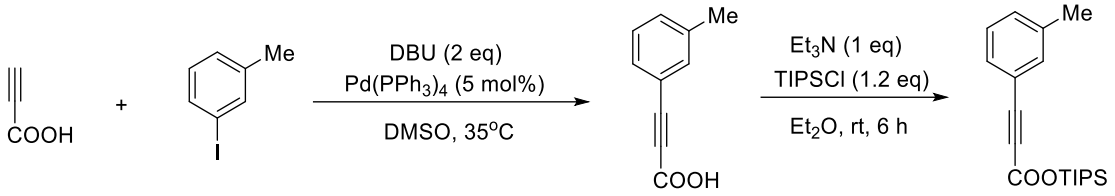
White solid, mp 48 - 51 ºC ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 3.96 (q, *J* = 7.0 Hz, 2H), 1.46 (s, 6H), 1.34 (t, *J* = 7.0 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 159.8, 152.5, 133.9, 113.7, 110.6, 83.8, 82.3, 80.5, 62.7, 27.2, 13.8. HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{15}H_{18}NaO_3$: 269.1148, found: 269.1154.



Tert-butyl 3-(phenanthren-9-yl)propiolate (2ad):

White solid, mp 73 - 76 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 8.58-8.46 (m, 2H), 8.35-8.26 (m, 1H), 8.04 (s, 1H), 7.76-7.70 (m, 1H),, 7.61-7.54 (m, 3H), 7.53-7.44 (m, 1H), 1.51 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 153.4, 135.2, 131.1, 130.8, 130.7, 130.0, 129.1, 128.6, 127.6, 127.5, 127.2, 126.8, 122.9, 122.8, 116.5, 86.3, 83.7, 82.4, 28.2. HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{21}H_{18}NaO_2$:325.1199, found:325.1194.

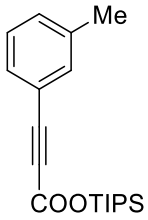
2.4. General procedure for the synthesis of triisopropylsilyl 3-(m-tolyl)propiolate (S13).[4]



S10 **S11** **S12** **S13**

a) An oven dried 25 mL round-bottomed glass flask equipped with a magnetic stirring bar was charged with the **S11** (20 mmol), $Pd(PPh_3)_4$ (1 mmol), and DBU (40 mmol) in dimethyl sulfoxide (40 mL), to which was added **S10** (22 mmol). The reaction mixture was stirred at 35 °C for 12 h. The corresponding **S12** was isolated after addition of 30 mL of saturated Na_2CO_3 solution and extraction with ethyl acetate. The crude product was recrystallized or purified by column chromatography.

b) To a solution of **S12** (10 mmol) and triethylamine (10 mmol) in Et_2O (20 mL) was slowly added TIPSCl (12 mmol) at room temperature. Volatiles were removed under reduced pressure. And then, hexane (20 mL) was added to the crude product and the residue was purified by silica gel flash column chromatography (eluent: EA/PE = 50/1) to afford **S13**.

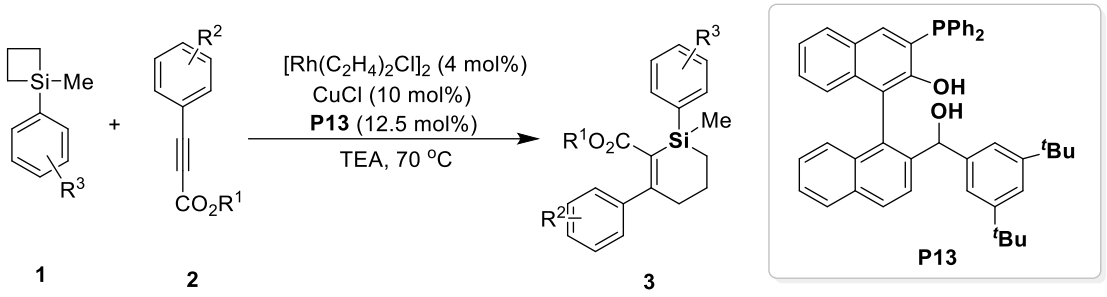


Triisopropylsilyl 3-(m-tolyl)propiolate (2ae):

Yellow oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35-7.27 (m, 2H), 7.19-7.13 (m, 2H), 2.25 (s, 3H), 1.34-1.21 (m, 3H), 1.04 (d, J = 7.5 Hz, 18H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 153.3, 138.4, 133.6, 131.4, 130.2, 128.5, 119.9, 85.5, 82.0, 21.2, 17.8, 12.1. HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{19}H_{28}NaO_2Si$:339.1751, found:339.1760.

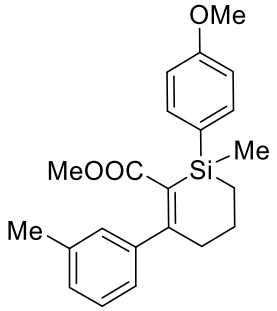
3. Experimental Procedures and Spectral Data of Products

3.1. General procedure for the Rh/Cu-cocatalyzed (3+2) annulation of silacycles with internal alkynes



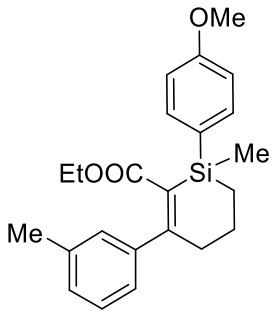
1 2 3

Silacyclobutane **1** (0.2 mmol), $[Rh(C_2H_4)_2Cl]_2$ (3.2 mg, 0.008 mmol), CuCl (2.0 mg, 0.02 mmol) and **P13** (16.8 mg, 0.025 mmol) in TEA (2 mL) was stirred at room temperature for 30 min. Then the substrate **2** (2.5 eq, 0.5 mmol) was added to the reaction mixture, and the reaction was stirred at 70 °C for 14 h. Upon reaction completion, the mixture was concentrated under reduced vacuum. The residue was purified by silica gel flash column chromatography (eluent: PE and EtOAc) to afford **3**.



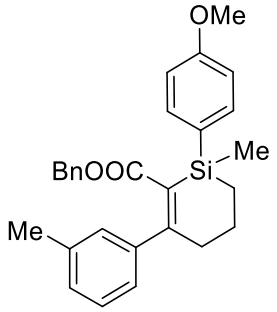
Methyl 1-(4-methoxyphenyl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3a):

Yellow oil (52 mg, 71% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (d, J = 8.4 Hz, 2H), 7.08 (t, J = 7.6 Hz, 1H), 6.99-6.88 (m, 3H), 6.82 (d, J = 8.5 Hz, 2H), 3.68 (s, 3H), 3.21 (s, 3H), 2.59-2.40 (m, 2H), 2.23 (s, 3H), 1.91-1.83 (m, 2H), 1.01-0.91 (m, 1H), 0.84-0.74 (m, 1H), 0.44 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.8, 163.3, 160.7, 144.6, 137.7, 135.8, 129.6, 128.4, 128.1, 127.7, 127.1, 123.7, 113.7, 55.1, 51.1, 37.0, 21.5, 21.3, 11.3, -3.2; IR (KBr, cm $^{-1}$): 2917.8, 1700.0, 1591.9 1502.9, 1277.9, 1245.8, 1181.8, 1110.9, 1028.8, 800.4, 703.9; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{22}H_{26}NaO_3Si$: 389.1543, found: 389.1529.



Ethyl 1-(4-methoxyphenyl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3b):

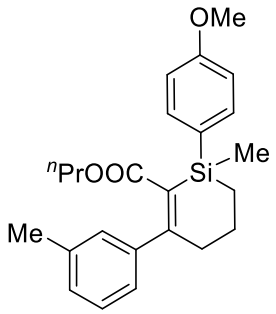
Colorless oil (50 mg, 65% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, J = 8.6 Hz, 2H), 7.10 (t, J = 7.5 Hz, 1H), 7.02-6.90 (m, 3H), 6.83 (d, J = 8.5 Hz, 2H), 3.75-3.67 (m, 5H), 2.61-2.50 (m, 1H), 2.51-2.39 (m, 1H), 2.24 (s, 3H), 1.94-1.85 (m, 2H), 1.04-0.92 (m, 1H), 0.87-0.76 (m, 1H), 0.72 (t, J = 7.1 Hz, 3H), 0.46 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.3, 163.2, 160.7, 144.7, 137.6, 135.8, 129.8, 128.3, 128.0, 127.8, 127.25 , 123.8, 113.6, 59.8, 55.1, 37.1, 21.5, 21.3, 13.8, 11.3, -3.1; IR (KBr, cm $^{-1}$): 2920.9, 1695.5, 1592.3, 1502.9, 1278.2, 1181.2, 1111.1, 805.6, 703.8; HRMS (ESI-TOF) m/z: [M+ Na]+ calculate*d* for $C_{23}H_{28}NaO_3Si$: 403.1700, found: 403.1717.



Benzyl 1-(4-methoxyphenyl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3c):

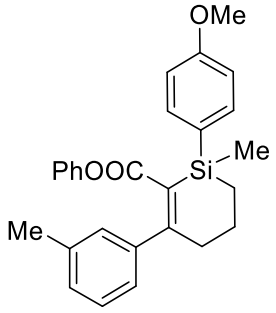
Colorless oil (71.6 mg, 81% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, J = 8.5 Hz, 2H), 7.12-7.04 (m, 4H), 7.00-6.90 (m, 3H), 6.80 (d, J = 8.5 Hz, 2H), 6.72-6.67 (m, 2H), 4.64 (dd, 2H), 3.71 (s, 3H), 2.59-2.41 (m, 2H), 2.20 (s, 3H), 1.94-1.84 (m, 2H), 0.99-0.92 (m, 1H), 0.86-0.75 (m, 1H), 0.43 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.2, 163.4, 160.7, 144.7, 137.8, 135.9, 135.9, 129.5, 128.4, 128.2, 128.2, 127.7, 127.6, 127.2, 123.8, 113.7, 65.9, 55.1, 37.1, 21.5, 21.2, 11.4, -3.3; IR (KBr, cm $^{-1}$):

2918.8, 1696.2, 1592.2, 1502.5, 1278.3, 1180.5, 1111.3, 806.8, 696.9; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{28}H_{30}NaO_3Si$: 465.1856, found: 465.1870.



Propyl 1-(4-methoxyphenyl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3d):

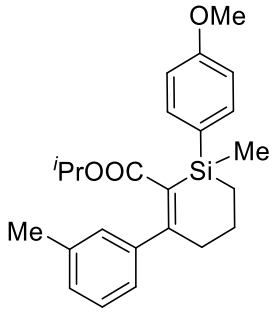
Colorless oil (53 mg, 67% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, J = 8.5 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.01-6.90 (m, 3H), 6.83 (d, J = 8.5 Hz, 2H), 3.72 (s, 3H), 3.64-3.57 (m, 1H), 2.60-2.51 (m, 1H), 2.50-2.39 (m, 1H), 2.24 (s, 3H), 1.97-1.79 (m, 2H), 1.22-1.09 (m, 2H), 1.00-0.91 (m, 1H), 0.85-0.75 (m, 1H), 0.50 (t, J = 7.4 Hz, 3H), 0.46 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-d) δ 171.5, 162.9, 160.7, 144.7, 137.7, 135.8, 129.8, 128.3, 128.1, 127.9, 127.3, 123.7, 113.6, 65.7, 55.1, 37.1, 21.7, 21.5, 21.3, 11.4, 10.3, -3.2; IR (KBr, cm $^{-1}$): 2920.6, 1694.3, 1592.4, 1502.9, 1278.2, 1181.1, 1111.2, 802.0; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{24}H_{30}NaO_3Si$: 417.1856, found: 417.1881.



Phenyl 1-(4-methoxyphenyl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3e):

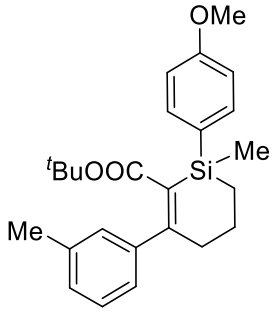
Colorless oil (66 mg, 77% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.10-7.02 (m, 5H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.32 (d, *J* = 7.8 Hz, 2H), 3.71 (s, 3H), 2.73-2.58 (m, 1H), 2.58-2.47 (m, 1H), 2.26 (s, 3H), 2.09-1.82 (m, 2H), 1.10-1.01 (m, 1H), 0.93-0.81 (m, 1H), 0.55

(s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.9, 163.7, 160.9, 150.7, 144.5, 137.9, 136.0, 129.4, 129.1, 128.7, 128.3, 127.4, 127.2, 125.4, 124.0, 121.6, 113.8, 55.1, 36.9, 21.5, 21.3, 11.2, -3.3; IR (KBr, cm $^{-1}$): 2912.1, 1717.1, 1591.4, 1278.2, 1248.1, 1159.0, 1110.7, 971.3, 802.2; HRMS (ESI-TOF) m/z: [M+ Na]+ calculate*d* for $C_{27}H_{28}NaO_3Si$: 451.1700, found: 451.1716.



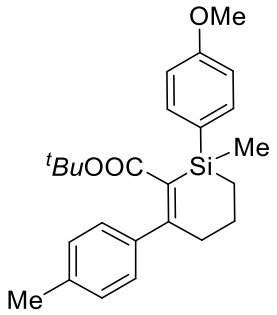
Isopropyl 1-(4-methoxyphenyl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3f):

Colorless oil (59 mg, 75% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.00-6.93 (m, 3H), 6.82 (d, *J* = 8.5 Hz, 2H), 4.66-4.56 (m, 1H), 3.71 (s, 3H), 2.60-2.50 (m, 1H), 2.48-2.38 (m, 1H), 2.23 (s, 3H), 1.94-1.84 (m, 2H), 1.01-0.92 (m, 1H), 0.85-0.78 (m, 1H), 0.75 (d, *J* = 6.3 Hz, 3H), 0.68 (d, *J* = 6.3 Hz, 3H), 0.47 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.8, 162.2, 160.7, 144.6, 137.5, 135.9, 130.2, 128.2, 128.0, 127.8, 127.4, 123.8, 113.6, 67.0, 55.1, 36.9, 21.5, 21.5, 21.3, 21.3, 11.3, -3.2; IR (KBr, cm $^{-1}$): 2919.5, 1692.9, 1592.7, 1503.3, 1278.8, 1245.2, 1181.7, 1109.9, 803.1; HRMS (ESI-TOF) m/z: [M+ Na]+ calculate*d* for $C_{24}H_{30}NaO_3Si$: 417.1856, found: 417.1841.



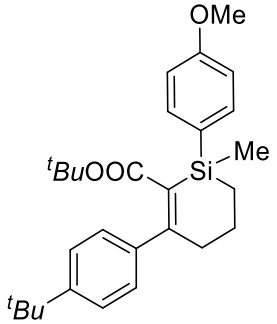
Tert-butyl 1-(4-methoxyphenyl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3g):

Yellow oil (63.4 mg, 78% yield).[1]H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, J = 8.5 Hz, 2H), 7.11 (t, J = 7.6 Hz, 1H), 7.02-6.91 (m, 3H), 6.83 (d, J = 8.6 Hz, 2H), 3.72 (s, 3H), 2.57-2.38 (m, 2H), 2.24 (s, 3H), 1.93-1.84 (m, 2H), 0.97 (s, 10H), 0.83-0.74 (m, 1H), 0.46 (s, 3H); [13]C NMR (100 MHz, Chloroform-*d*) δ 170.6, 161.6, 160.7, 144.8, 137.4, 136.0, 131.3, 128.1 (d, J = 2.8 Hz), 128.0, 127.6, 123.9, 113.5, 79.8, 55.1, 36.8, 27.7, 21.5, 21.3, 11.5, -3.2; IR (KBr, cm $^{-1}$): 2912.9, 1691.3, 1592.9, 1503.2, 1278.5, 1246.2, 1156.6, 1111.3, 806.8, 696.9; HRMS (ESI-TOF) m/z: [M+ Na]+ calculat*ed* for $C_{25}H_{32}NaO_3Si$: 431.2013, found: 431.2026.



Tert-butyl 1-(4-methoxyphenyl)-1-methyl-3-(p-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3h):

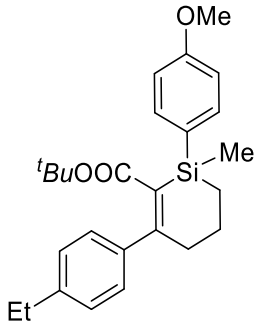
Yellow oil (69.4 mg, 85% yield). [1]H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, J = 8.5 Hz, 2H), 7.07-6.99 (m, 4H), 6.82 (d, J = 8.5 Hz, 2H), 3.71 (s, 3H), 2.57-2.39 (m, 2H), 2.25 (s, 3H), 1.94-1.82 (m, 2H), 0.98 (s, 9H), 0.95-0.89 (m, 1H), 0.83-0.75 (m, 1H), 0.45 (s, 3H); [13]C NMR (100 MHz, Chloroform-*d*) δ 170.5, 161.8, 160.7, 142.0, 137.0, 135.9, 131.1, 128.7, 128.2, 126.8, 113.5, 79.8, 55.1, 37.0, 27.8, 21.4, 21.3, 11.6, -3.2; IR (KBr, cm $^{-1}$): 2920.9, 1689.9, 1592.7, 1503.1, 1365.4, 1278.4, 1245.9, 1156.1, 1111.1, 803.5; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{25}H_{32}NaO_3Si$: 431.2013, found: 431.2001.



Tert-butyl 3-(4-(tert-butyl)phenyl)-1-(4-methoxyphenyl)-1-methyl-1,4,5,6-

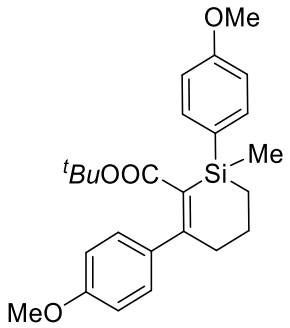
tetrahydrosiline-2-carboxylate (3i):

Yellow oil (83.7 mg, 93% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 8.3 Hz, 2H), 7.08 (d, J = 8.3 Hz, 2H), 6.83 (d, J = 8.5 Hz, 2H), 3.72 (s, 3H), 2.59-2.39 (m, 2H), 1.91-1.85 (m, 2H), 1.23 (s, 9H), 0.94 (s, 9H), 0.90-0.73 (m, 2H), 0.46 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.7, 161.3, 160.7, 150.3, 142.0, 136.0, 131.3, 128.2, 126.7, 124.8, 113.6, 79.8, 55.1, 36.7, 34.6, 31.5, 27.7, 21.4, 11.5, -3.1; IR (KBr, cm $^{-1}$): 2961.9, 1689.4, 1592.7, 1503.1, 1364.8, 1278.3, 1245.8, 1158.1, 1111.2, 801.1; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{28}H_{38}NaO_3Si$: 473.2482, found: 473.2467.



Tert-butyl 3-(4-ethylphenyl)-1-(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-carboxylate (3j):

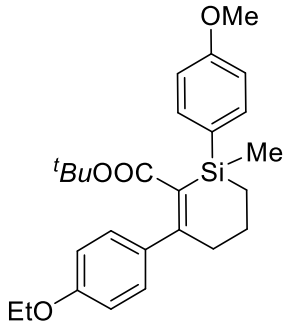
Yellow oil (78.4 mg, 93% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, J = 8.4 Hz, 2H), 7.10-7.02 (m, 4H), 6.83 (d, J = 8.5 Hz, 2H), 3.72 (s, 3H), 2.59-2.49 (m, 3H), 2.47-2.37 (m, 1H), 1.93-1.82 (m, 2H), 1.14 (t, J = 7.6 Hz, 3H), 0.97 (s, 9H), 0.95-0.90 (m, 1H), 0.83-0.75 (m, 1H), 0.46 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.6, 161.7, 160.6, 143.5, 142.2, 136.0, 131.1, 128.2, 127.5, 126.9, 113.5, 79.8, 55.1, 36.9, 28.7, 27.7, 21.3, 15.8, 11.5, -3.2; IR (KBr, cm $^{-1}$): 2965.8, 1690.0, 1592.7, 1503.1, 1365.5, 1278.6, 1246.1, 1156.8, 1111.2, 802.4; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{26}H_{34}NaO_3Si$: 445.2169, found: 445.2175.



Tert-butyl 1,3-bis(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-

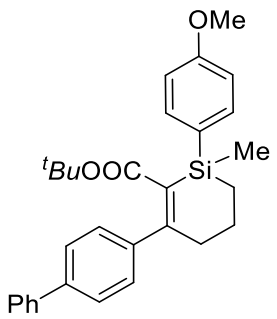
carboxylate (3k):

Colorless oil (74.9 mg, 88% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.5 Hz, 2H), 6.75 (d, J = 8.6 Hz, 2H), 3.72 (d, J = 2.7 Hz, 6H), 2.59-2.35 (m, 2H), 1.93-1.80 (m, 2H), 1.00 (s, 9H), 0.98-0.88 (m, 1H), 0.83-0.74 (m, 1H), 0.46 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.7, 161.1, 160.6, 159.1, 137.3, 136.0, 130.9, 128.2, 128.2, 113.5, 113.4, 79.9, 55.3, 55.1, 36.9, 27.8, 21.4, 11.6, -3.2; IR (KBr, cm $^{-1}$): 2907.6, 1688.3, 1592.6, 1503.9, 1278.6, 1244.5, 1154.9, 1110.5, 1029.7, 802.0; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{25}H_{32}NaO_4Si$: 447.1962, found: 447.1951.



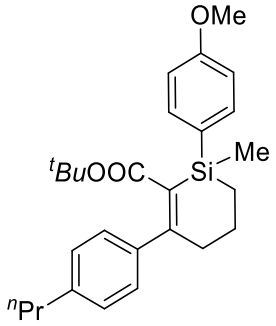
Tert-butyl 3-(4-ethoxyphenyl)-1-(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-carboxylate (3l):

Colorless oil (82.9 mg, 95% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, J = 8.5 Hz, 2H), 7.09 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.5 Hz, 2H), 6.74 (d, J = 8.7 Hz, 2H), 3.94 (q, J = 7.0 Hz, 2H), 3.72 (s, 3H), 2.57-2.37 (m, 2H), 1.91-1.83 (m, 2H), 1.32 (t, J = 7.0 Hz, 3H), 1.00 (s, 9H), 0.99-0.89 (m, 1H), 0.82-0.73 (m, 1H), 0.45 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.8, 161.1, 160.6, 158.4, 137.2, 136.0, 130.9, 128.2, 128.2, 113.9, 113.5, 79.9, 63.5, 55.1, 36.9, 27.8, 21.4, 14.9, 11.6, -3.2; IR (KBr, cm $^{-1}$): 2975.9, 1689.2, 1593.0, 1477.2, 1278.9, 1243.8, 1155.9, 1111.3, 804.2; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{26}H_{34}NaO_4Si$: 461.2119, found: 461.2122.



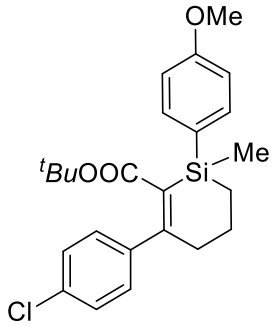
Tert-butyl 3-([1,1'-biphenyl]-4-yl)-1-(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-carboxylate (3m):

Yellow oil (86.8 mg, 92% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52-7.48 (m, 4H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.27-7.20 (m, 3H), 6.83 (d, *J* = 8.5 Hz, 2H), 3.71 (s, 3H), 2.62-2.41 (m, 2H), 1.96-1.85 (m, 2H), 0.97 (s, 9H), 0.95-0.76 (m, 2H), 0.48 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.5, 161.0, 160.7, 143.9, 141.0, 140.2, 136.0, 131.7, 128.8, 127.9, 127.4, 127.3, 127.1, 126.7, 113.5, 80.0, 55.1, 36.8, 27.8, 21.3, 11.5, -3.2; IR (KBr, cm $^{-1}$): 2922.8, 1688.9, 1592.3, 1502.6, 1278.4, 1246.1, 1155.8, 1110.9, 801.2, 759.9, 696.4; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{30}H_{34}NaO_3Si$: 493.2169, found: 493.2154.



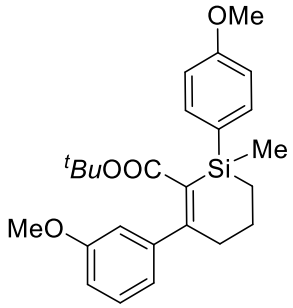
Tert-butyl 1-(4-methoxyphenyl)-1-methyl-3-(4-propylphenyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3ae):

Yellow oil (72.8 mg, 83% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.04 (q, *J* = 8.1 Hz, 4H), 6.83 (d, *J* = 8.4 Hz, 2H), 3.72 (s, 3H), 2.56-2.41 (m, 4H), 1.95-1.82 (m, 2H), 1.54 (q, *J* = 7.5 Hz, 2H), 0.96 (s, 9H), 0.93-0.75 (m, 5H), 0.46 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.7, 161.4, 160.6, 142.2, 141.9, 136.0, 131.1, 128.1, 126.8, 113.5, 79.8, 55.1, 37.9, 36.8, 27.7, 24.7, 21.3, 13.9, 11.5, -3.2; IR (KBr, cm $^{-1}$): 2927.7, 1691.1, 1592.8, 1564.2, 1278.2, 1246.4, 1157.5, 1111.2, 1031.7, 805.5; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{27}H_{36}NaO_3Si$: 459.2326, found: 459.2315.



Tert-butyl 3-(4-chlorophenyl)-1-(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-carboxylate (3o):

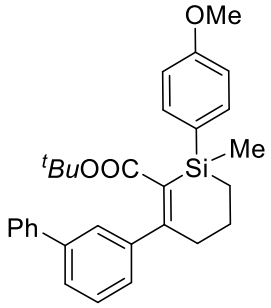
Light yellow oil (69.5 mg, 81% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 3.73 (s, 3H), 2.55-2.35 (m, 2H), 1.93-1.84 (m, 2H), 0.99 (s, 9H), 0.97-0.89 (m, 1H), 0.84-0.75 (m, 1H), 0.46 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.2, 160.7, 160.0, 143.3, 136.0, 133.1, 132.3, 128.3, 128.2, 127.7, 113.6, 80.2, 55.1, 36.8, 27.8, 21.3, 11.4, -3.3; IR (KBr, cm $^{-1}$): 2925.3, 1693.1, 1592.9, 1503.0, 1278.8, 1181.9, 1111.1, 800.6; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{24}H_{29}ClNaO_3Si$: 451.1467, found: 451.1459.



Tert-butyl 3-(3-methoxyphenyl)-1-(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-carboxylate (3p):

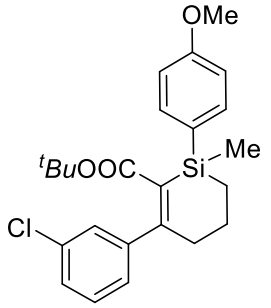
Colorless oil (66.9 mg, 79% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 8.5 Hz, 2H), 7.13 (t, *J* = 7.8 Hz, 1H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.77-6.66 (m, 3H), 3.72 (d, *J* = 5.4 Hz, 6H), 2.59-2.37 (m, 2H), 1.88 (t, *J* = 5.9 Hz, 2H), 0.97 (s, 9H), 0.98-0.89 (m, 1H), 0.86-0.77 (m, 1H), 0.46 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.4, 161.1, 160.7, 159.3, 146.3, 136.0, 131.5, 129.1, 127.9, 119.4, 113.5, 113.0, 112.3, 79.9, 55.3, 55.1, 36.8, 27.7, 21.3, 11.4, -3.2; IR (KBr, cm $^{-1}$): 2924.7, 1690.3, 1592.0, 1503.0, 1278.6, 1246.1, 1156.3, 1110.9, 1031.1, 806.1; HRMS (ESI-TOF) m/z: [M+ Na]+

calculated for $C_{25}H_{32}NaO_4Si$: 447.1962, found: 447.1951.



Tert-butyl 3-([1,1'-biphenyl]-3-yl)-1-(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-carboxylate (3q):

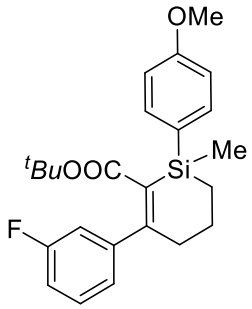
Colorless oil (81.6 mg, 86% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, J = 8.4 Hz, 4H), 7.40 (d, J = 9.1 Hz, 1H), 7.39-7.21 (m, 5H), 7.12 (d, J = 7.7 Hz, 1H), 6.83 (d, J = 8.5 Hz, 2H), 3.71 (s, 3H), 2.65-2.42 (m, 2H), 1.95-1.85 (m, 2H), 1.02-0.95 (m, 1H), 0.92 (s, 9H), 0.87-0.76 (m, 1H), 0.48 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.5, 161.1, 160.7, 145.5, 141.1, 141.0, 136.0, 131.8, 128.8, 128.5, 127.9, 127.4, 127.3, 126.0, 125.8, 125.7, 113.6, 80.0, 55.1, 36.9, 27.7, 21.3, 11.4, -3.2; IR (KBr, cm $^{-1}$): 2924.9, 1691.7, 1592.1, 1502.7, 1246.3, 1155.6, 1111.1, 802.9, 755.3, 703.4; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{30}H_{34}NaO_3Si$: 493.2169, found: 493.2172.



Tert-butyl 3-(3-chlorophenyl)-1-(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-carboxylate (3r):

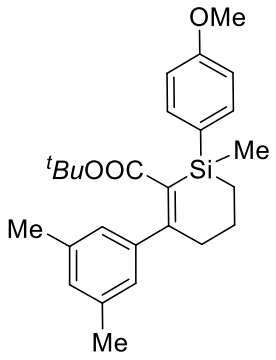
Colorless oil (45.9 mg, 53% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, J = 8.5 Hz, 2H), 7.19-7.15 (m, 3H), 7.07-7.00 (m, 1H), 6.84 (d, J = 8.5 Hz, 2H), 3.73 (s, 3H), 2.57-2.33 (m, 2H), 1.94-1.82 (m, 2H), 0.99 (s, 9H), 0.97-0.90 (m, 1H), 0.85-0.77 (m, 1H), 0.47 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.1, 160.8, 159.3, 146.5, 136.0, 133.9, 132.7, 129.4, 127.6, 127.4, 127.1, 125.0, 113.6, 80.3, 55.2, 36.6, 27.8, 21.2, 11.3, -3.3; IR (KBr, cm $^{-1}$): 2925.2, 1693.4, 1592.0, 1503.0, 1278.8, 1246.3,

1155.6, 1111.2, 803.6, 779.8, 696.0; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{24}H_{29}ClNaO_3Si$: 451.1467, found: 451.1483.



Tert-butyl 3-(3-fluorophenyl)-1-(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-carboxylate (3s):

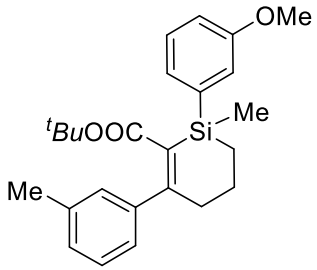
Yellow oil (47.7 mg, 57% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, J = 8.5 Hz, 2H), 7.22-7.16 (m, 1H), 6.95-6.82 (m, 5H), 3.73 (s, 3H), 2.56-2.35 (m, 2H), 1.94-1.84 (m, 2H), 0.99 (s, 9H), 0.96-0.89 (m, 1H), 0.85-0.78 (m, 1H), 0.47 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.2, 163.8, 161.4, 160.8, 159.5, 147.0 (d, J = 7.3 Hz), 136.0, 132.5, 129.6 (d, J = 8.1 Hz), 127.6, 122.6 (d, J = 2.9 Hz), 114.1 (dd, J = 21.3, 11.7 Hz), 113.6, 80.2, 55.2, 36.6, 27.7, 21.2, 11.3, -3.3; IR (KBr, cm $^{-1}$): 2928.3, 1694.0, 1592.8, 1503.4, 1279.3, 1246.8, 1152.9, 1111.9, 945.7, 810.8; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{24}H_{29}FNaO_3Si$: 435.1762, found: 435.1747.



Tert-butyl 3-(3,5-dimethylphenyl)-1-(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-carboxylate (3t):

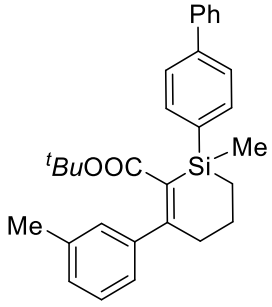
Yellow oil (70.5 mg, 84% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, J = 8.6 Hz, 2H), 6.86-6.81 (m, 3H), 6.77 (d, J = 1.7 Hz, 2H), 3.72 (s, 3H), 2.59-2.37 (m, 2H), 2.20 (s, 6H), 1.92-1.82 (m, 2H), 0.98 (s, 9H), 0.96-0.90 (m, 1H), 0.81-0.75 (m, 1H), 0.46 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.7, 161.8, 160.6, 144.8, 137.4,

136.0, 131.1, 129.0, 128.1, 124.6, 113.5, 79.8, 55.1, 36.8, 27.7, 21.4, 21.3, 11.5, -3.1; IR (KBr, cm $^{-1}$): 2915.8, 1690.9, 1592.6, 1503.1, 1277.8, 1246.3, 1156.3, 1111.4, 804.4; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{26}H_{34}NaO_3Si$: 445.2169, found: 445.2172.



Tert-butyl 1-(3-methoxyphenyl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3u):

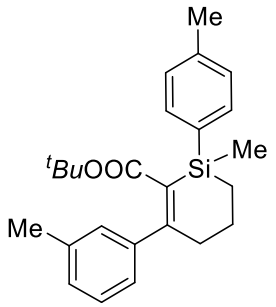
Colorless oil (45 mg, 55% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24-7.19 (m, 1H), 7.18-7.07 (m, 3H), 7.02-6.91 (m, 3H), 6.86-6.78 (m, 1H), 3.74 (s, 3H), 2.60-2.36 (m, 2H), 2.24 (s, 3H), 1.93-1.83 (m, 2H), 0.97 (s, 9H), 0.88-0.74 (m, 2H), 0.48 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.4, 162.3, 159.0, 144.8, 139.0, 137.5, 130.8, 128.9, 128.1, 128.0, 127.6, 126.8, 123.9, 120.0, 114.5, 79.9, 55.2, 36.9, 27.7, 21.5, 21.3, 11.3, -3.3; IR (KBr, cm $^{-1}$): 2922.1, 1690.8, 1570.5, 1282.8, 1245.0, 1228.2, 1155.8, 779.3, 695.2; HRMS (ESI-TOF) m/z: [M+ Na]+ calculate*d* for $C_{25}H_{32}NaO_3Si$: 431.2013, found: 431.2004.



Tert-butyl 1-([1,1'-biphenyl]-4-yl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3v):

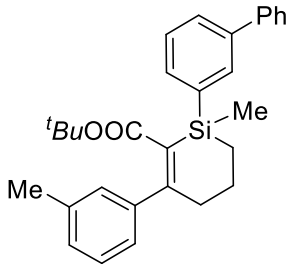
Colorless oil (66.1 mg, 73% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, J = 8.1 Hz, 2H), 7.55-7.47 (m, 4H), 7.34 (t, J = 7.6 Hz, 2H), 7.29-7.20 (m, 1H), 7.16-7.07 (m, 1H), 7.02-6.92 (m, 3H), 2.59-2.43 (m, 2H), 2.24 (s, 3H), 1.95-1.86 (m, 2H), 1.07-1.00 (m, 1H), 0.97 (s, 9H), 0.89-0.77 (m, 1H), 0.51 (s, 3H); ^{13}C NMR (100 MHz,

Chloroform-*d*) δ 170.5, 162.2, 144.8, 142.0, 141.3, 137.5, 136.1, 135.0, 130.9, 128.9, 128.1, 128.0, 127.6, 127.4, 127.3, 126.5, 123.9, 80.0, 36.9, 27.7, 21.5, 21.3, 11.3, -3.3; IR (KBr, cm $^{-1}$): 2921.1, 1689.1, 1365.5, 1246.8, 1156.4, 804.8, 755.9, 697.6; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{30}H_{34}NaO_2Si$: 477.2220, found: 477.2201.



Tert-butyl 1-methyl-3-(m-tolyl)-1-(p-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3w):

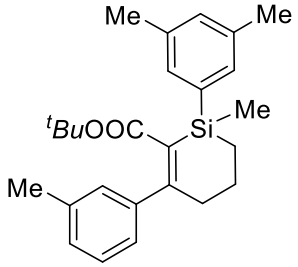
Colorless oil (46 mg, 59% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (d, J = 7.6 Hz, 2H), 7.13-7.07 (m, 3H), 7.02-6.91 (m, 3H), 2.57-2.39 (m, 2H), 2.25 (d, J = 7.7 Hz, 6H), 1.93-1.81 (m, 2H), 0.97 (s, 9H), 0.95-0.92 (m, 1H), 0.83-0.73 (m, 1H), 0.47 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.5, 161.8, 144.9, 139.1, 137.5, 134.5, 133.6, 131.1, 128.6, 128.1, 128.0, 127.6, 123.9, 79.9, 36.9, 27.7, 21.6, 21.5, 21.3, 11.4, -3.2; IR (KBr, cm $^{-1}$): 2917.4, 1691.7, 1246.3, 1157.1, 781.6; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{25}H_{32}NaO_2Si$: 415.2064, found: 415.2052.



Tert-butyl 1-([1,1'-biphenyl]-3-yl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3x):

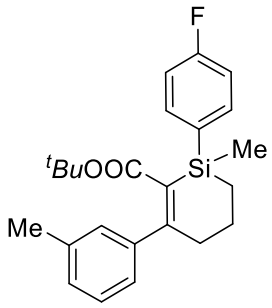
Colorless oil (47.2 mg, 52% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (s, 1H), 7.59-7.46 (m, 4H), 7.40-7.30 (m, 3H), 7.30-7.20 (m, 3H), 7.16-7.07 (m, 1H), 7.02-6.92 (m, 3H), 2.59-2.52 (m, 1H), 2.49-2.40 (m, 1H), 2.24 (s, 3H), 1.94-1.87 (m, 2H), 1.05-0.95 (m, 1H), 0.94 (s, 9H), 0.90-0.77 (m, 1H), 0.53 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.5, 162.4, 144.8, 141.7, 140.5, 137.9, 137.5, 133.5, 133.2, 130.8,

128.8, 128.2, 128.0, 127.7, 127.4, 127.3, 123.9, 80.0, 36.9, 27.7, 21.5, 21.4, 11.4, -3.2; IR (KBr, cm $^{-1}$): 2920.2, 1689.7, 1246.2, 1155.7, 812.9, 752.1, 699.9; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{30}H_{34}NaO_2Si$: 477.2220, found: 477.2222.



Tert-butyl 1-(3,5-dimethylphenyl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3y):

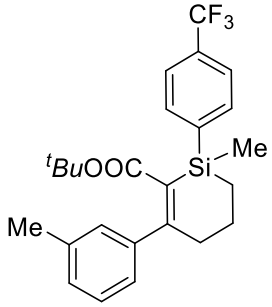
Colorless oil (38 mg, 47% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.17-7.10 (m, 3H), 7.03-6.89 (m, 4H), 2.61-2.52 (m, 1H), 2.45-2.37 (m, 1H), 2.24 (d, J = 4.2 Hz, 9H), 1.93-1.85 (m, 2H), 1.05-1.01 (m, 1H), 0.98 (s, 9H), 0.83-0.77 (m, 1H), 0.48 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.7, 161.7, 144.9, 137.5, 136.9, 136.9, 132.1, 131.2, 131.0, 128.1, 128.0, 127.7, 123.9, 79.8, 36.9, 27.7, 21.5, 21.4, 11.2, 1.2, -2.9; IR (KBr, cm $^{-1}$): 2918.5, 1691.9, 1365.2, 1246.0, 1157.6, 1139.9, 781.2; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{26}H_{34}NaO_2Si$: 429.2220, found: 429.2229.



Tert-butyl 1-(4-fluorophenyl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3z):

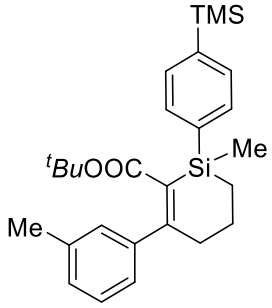
Colorless oil (53.6 mg, 68% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57-7.51 (m, 2H), 7.12 (t, J = 7.5 Hz, 1H), 7.03-6.91 (m, 5H), 2.58-2.51 (m, 1H), 2.48-2.39 (m, 1H), 2.24 (s, 3H), 1.95-1.80 (m, 2H), 0.96 (s, 9H), 0.93-0.90 (m, 1H), 0.85-0.78 (m, 1H), 0.48 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.4, 165.2, 162.7, 162.4, 144.7, 137.5, 136.5, 136.4, 132.8, 132.8, 130.7, 128.2, 128.0, 127.6, 123.8, 115.0, 114.8, 80.0, 36.8, 27.7, 21.5, 21.3, 11.4, -3.3; IR (KBr, cm $^{-1}$): 2922.7, 1689.5, 1587.1, 1231.2,

1160.4, 812.8, 782.1; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{24}H_{29}FNaO_2Si$: 419.1813, found: 419.1802.



Tert-butyl 1-methyl-3-(m-tolyl)-1-(4-(trifluoromethyl)phenyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3aa):

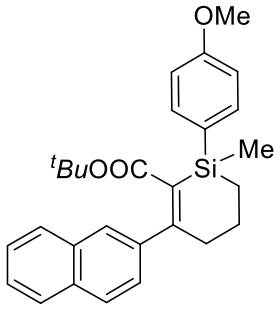
Colorless oil (28 mg, 31% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, J = 7.3 Hz, 2H), 7.52 (d, J = 7.1 Hz, 2H), 7.13 (t, J = 7.5 Hz, 1H), 7.01 (d, J = 7.6 Hz, 1H), 6.95 (d, J = 9.1 Hz, 2H), 2.61-2.41 (m, 2H), 2.26 (s, 3H), 1.97-1.80 (m, 2H), 0.96 (s, 9H), 0.95-0.79 (m, 2H), 0.51 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.2, 163.5, 144.6, 142.7, 137.6, 134.8, 129.9, 128.3, 128.1, 127.6, 124.3, 124.3, 124.3, 124.2, 123.8, 80.3, 36.9, 27.7, 21.5, 21.2, 11.1, -3.5; IR (KBr, cm $^{-1}$): 2924.2, 1688.5, 1323.5, 1158.6, 1124.6, 1059.3, 805.4, 698.3; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{25}H_{29}F_3NaO_2Si$: 469.1781, found: 469.1783.



Tert-butyl 1-methyl-3-(m-tolyl)-1-(4-(trimethylsilyl)phenyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3ab):

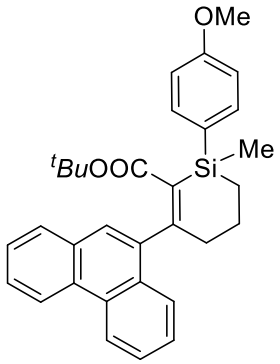
Colorless oil (37.8 mg, 42% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (d, J = 7.2 Hz, 2H), 7.43 (d, J = 7.9 Hz, 2H), 7.12 (t, J = 7.5 Hz, 1H), 7.03-6.89 (m, 3H), 2.58-2.38 (m, 2H), 2.25 (s, 3H), 1.95-1.83 (m, 2H), 1.05-0.97 (m, 1H), 0.96 (s, 9H), 0.86-0.75 (m, 1H), 0.48 (s, 3H), 0.18 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.5, 161.9, 144.9, 141.5, 137.8, 137.5, 133.7, 132.6, 131.0, 128.1, 128.0, 127.6, 123.9, 80.0,

36.9, 27.7, 21.5, 21.3, 11.1, -1.1, -3.4; IR (KBr, cm $^{-1}$): 2954.7, 1692.2, 1247.2, 1157.6, 1134.2, 837.4, 800.5, 782.5, 752.7; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{27}H_{38}NaO_2Si_2$: 473.2303, found: 473.2299.



Tert-butyl 1-(4-methoxyphenyl)-1-methyl-3-(naphthalen-2-yl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3ac):

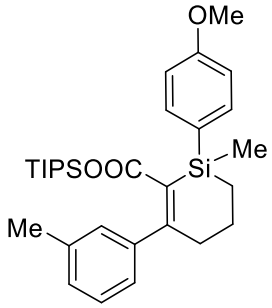
White solid (81.9 mg, 92% yield), mp 79 - 83 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.75-7.66 (m, 3H), 7.61 (s, 1H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.39-7.31 (m, 2H), 7.29 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 2H), 3.71 (s, 3H), 2.66-2.59 (m, 1H), 2.55-2.47 (m, 1H), 1.97-1.88 (m, 2H), 1.03-0.95 (m, 1H), 0.88 (s, 9H), 0.84-0.75 (m, 1H), 0.50 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) *δ* 170.6, 161.2, 160.7, 142.3, 136.0, 133.2, 132.7, 132.1, 128.1, 127.9, 127.7, 127.6, 126.2, 125.9, 125.5, 125.4, 113.6, 80.0, 55.1, 36.8, 27.7, 21.4, 11.5, -3.1. IR (KBr, cm $^{-1}$): 2914.7, 1688.1, 1592.3, 1502.6, 1278.4, 1245.9, 1155.5, 1111.0, 806.5, 745.6; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{28}H_{32}NaO_3Si$: 467.2013, found: 467.2010.



Tert-butyl 1-(4-methoxyphenyl)-1-methyl-3-(phenanthren-9-yl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3ad):

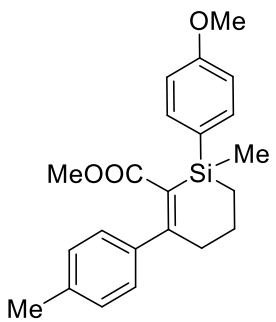
Yellow oil (37.0 mg, 37% yield), mp 104 - 108 °C, ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 8.66-8.53 (m, 2H), 7.85-7.71 (m, 2H), 7.63-7.46 (m, 6H), 7.40 (d, *J* = 11.7 Hz, 1H),

6.92-6.86 (m, 2H), 3.75 (s, 3H), 2.68-2.38 (m, 2H), 2.06-1.92 (m, 2H), 1.13-0.84 (m, 2H), 0.64-0.45 (m, 12H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.8 (d, J = 46.1 Hz), 161.5 (d, J = 37.3 Hz), 160.7, 141.6 (d, J = 24.2 Hz), 136.0, 135.9, 133.4, 131.7 (d, J = 7.2 Hz), 130.4 (d, J = 3.0 Hz), 130.1 , 130.0-129.7 (m), 128.6 (d, J = 3.5 Hz), 128.3, 128.1, 126.9, 126.8 (d, J = 3.7 Hz), 126.7 (d, J = 4.1 Hz), 126.4 (d, J = 4.5 Hz), 124.1, 123.8, 122.9 (d, J = 4.6 Hz), 122.6, 113.7, 79.7, 55.2, 37.3 (d, J = 50.2 Hz), 27.3 (d, J = 7.2 Hz), 21.5, 11.8 (d, J = 10.5 Hz), -2.8 (d, J = 50.5 Hz). IR (KBr, cm $^{-1}$): 2922.6, 1697.2, 1590.8, 1277.7, 1246.9, 1160.6, 1110.4, 1028.3, 810.5, 758.3, 726.9; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{32}H_{34}NaO_3Si$: 517.2169, found: 517.2159.



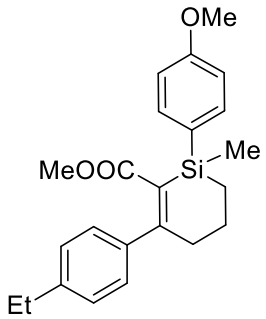
Triisopropylsilyl 1-(4-methoxyphenyl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3ae):

Colorless oil (45.7 mg, 45% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, J = 8.5 Hz, 2H), 7.10 (t, J = 7.9 Hz, 1H), 6.99-6.93 (m, 3H), 6.82 (d, J = 8.5 Hz, 2H), 3.73 (s, 3H), 2.57-2.47 (m, 1H), 2.46-2.36 (m, 1H), 2.23 (s, 3H), 1.91-1.81 (m, 2H), 0.93-0.76 (m, 5H), 0.72-0.64 (m, 18H), 0.51 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.2, 162.4, 160.8, 145.3, 137.8 136.1, 131.1, 128.2, 128.2, 128.1, 127.6, 124.0, 113.7, 55.2, 37.8, 21.5, 21.3, 17.8, 12.2, 12.1, 1.2, -3.4; IR (KBr, cm $^{-1}$): 2923.9, 2865.9, 1686.7, 1593.1, 1502.8, 1279.2, 1245.7, 1111.9, 802.8, 705.0; HRMS (ESI-TOF) m/z: [M+ Na]+ calculate*d* for $C_{30}H_{44}NaO_3Si_2$: 531.2721, found: 531.2725.



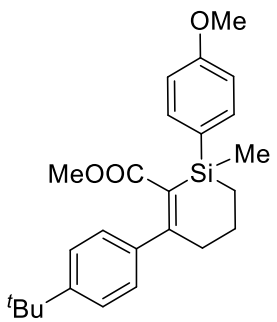
Methyl 1-(4-methoxyphenyl)-1-methyl-3-(p-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3af):

Light yellow oil (52.8 mg, 72% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 8.5 Hz, 2H), 7.13 (s, 4H), 6.94 (d, *J* = 8.5 Hz, 2H), 3.82 (s, 3H), 3.35 (s, 3H), 2.71-2.62 (m, 1H), 2.60-2.51 (m, 1H), 2.35 (s, 3H), 2.04-1.95 (m, 2H), 1.12-1.03 (m, 1H), 0.95-0.86 (m, 1H), 0.55 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.9, 163.4, 160.7, 141.7, 137.4, 135.8, 129.4, 128.9, 127.8, 126.5, 113.7, 55.1, 51.1, 37.1, 21.3 (d, *J* = 4.4 Hz), 11.3, -3.2; IR (KBr, cm $^{-1}$): 2918.3, 1698.2, 1592.0, 1502.9, 1277.9, 1246.1, 1181.8, 1110.8, 798.8; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{22}H_{26}NaO_3Si$: 389.1543, found: 389.1547.



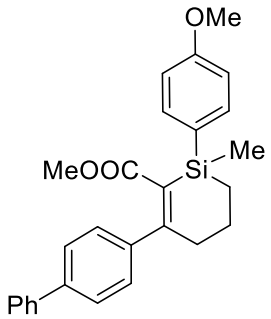
Methyl 3-(4-ethylphenyl)-1-(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-carboxylate (3ag):

Yellow oil (51 mg, 67% yield).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.5 Hz, 2H), 7.16 (s, 4H), 6.94 (d, *J* = 8.5 Hz, 2H), 3.82 (s, 3H), 3.35 (s, 3H), 2.71-2.53 (m, 4H), 2.05-1.95 (m, 2H), 1.25 (t, *J* = 7.6 Hz, 3H), 1.10-1.03 (m, 1H), 0.96-0.86 (m, 1H), 0.56 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.0, 163.2, 160.7, 143.7, 141.9, 135.8, 129.4, 127.8, 127.6, 126.6, 55.1, 51.1, 37.0, 28.6, 21.3, 15.5, 11.3, -3.2; IR (KBr, cm $^{-1}$): 2928.9, 1698.5, 1591.9, 1502.9, 1277.9, 1246.3, 1181.9, 1110.9, 798.8; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{23}H_{28}NaO_3Si$: 403.1700, found:403.1690.



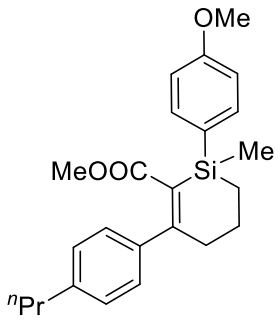
Methyl 3-(4-(tert-butyl)phenyl)-1-(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-carboxylate (3ah):

Yellow oil (51 mg, 62% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, J = 8.6 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 6.93 (d, J = 8.5 Hz, 2H), 3.82 (s, 3H), 3.33 (s, 3H), 2.73-2.52 (m, 2H), 2.05-1.95 (m, 2H), 1.33 (s, 9H), 1.12-1.03 (m, 1H), 0.95-0.88 (m, 1H), 0.56 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.0, 162.9, 160.7, 150.6, 141.5, 135.8, 129.4, 127.8, 126.3, 125.0, 113.7, 55.1, 51.0, 36.9, 34.6, 31.4, 21.3, 11.3, -3.2; IR (KBr, cm $^{-1}$): 2956.8, 1699.9, 1592.1, 1503.2, 1278.1, 1247.1, 1115.2, 798.8; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{25}H_{32}NaO_3Si$: 431.2013, found: 431.2014.



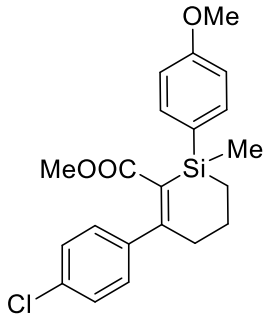
Methyl 3-([1,1'-biphenyl]-4-yl)-1-(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-carboxylate (3ai):

Yellow oil (40 mg, 47% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66-7.55 (m, 6H), 7.49-7.42 (m, 2H), 7.39-7.30 (m, 3H), 6.95 (d, J = 8.6 Hz, 2H), 3.83 (s, 3H), 3.37 (s, 3H), 2.77-2.56 (m, 2H), 2.08-1.98 (m, 2H), 1.15-1.07 (m, 1H), 0.98-0.90 (m, 1H), 0.58 (s, 3H); 13C NMR (100 MHz, Chloroform-*d*) δ 171.9, 162.6, 160.8, 143.6, 140.7, 140.4, 135.8, 130.0, 128.9, 127.6, 127.4, 127.1 (d, J = 2.5 Hz), 126.9, 113.7, 55.1, 51.2, 37.0, 21.3, 11.3, -3.2; IR (KBr, cm $^{-1}$): 2917.7, 1697.8, 1591.4, 1502.4, 1277.8, 1245.9, 1181.9, 1110.5, 761.9, 696.3; HRMS (ESI-TOF) m/z: [M+ Na]+ calculate*d* for $C_{27}H_{28}NaO_3Si$: 451.1700 , found: 451.1688.



Methyl 1-(4-methoxyphenyl)-1-methyl-3-(4-propylphenyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3aj):

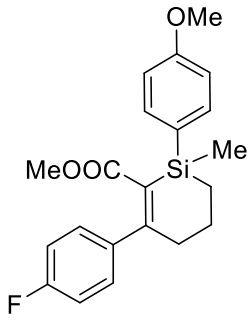
Yellow oil (50.5 mg, 64% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (d, J = 8.5 Hz, 2H), 7.09-6.99 (m, 4H), 6.83 (d, J = 8.6 Hz, 2H), 3.72 (s, 3H), 3.23 (s, 3H), 2.63-2.40 (m, 4H), 1.96-1.84 (m, 2H), 1.64-1.48 (m, 2H), 1.03-0.93 (m, 1H), 0.84 (t, J = 7.3 Hz, 4H), 0.45 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.0, 163.1, 160.7, 142.2, 141.9, 135.8, 129.4, 128.2, 127.8, 126.5, 113.7, 55.1, 51.0, 37.8, 36.9, 24.5, 21.3, 13.9, 11.3, -3.2; IR (KBr, cm $^{-1}$): 2926.1, 1698.8, 1591.9, 1502.8, 1277.9, 1246.0, 1181.8, 1110.8, 798.2; HRMS (ESI-TOF) m/z: [M+ Na]+ calculate*d* for $C_{24}H_{30}NaO_3Si$: 417.1856 , found: 417.1848.



Methyl 3-(4-chlorophenyl)-1-(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-carboxylate (3ak):

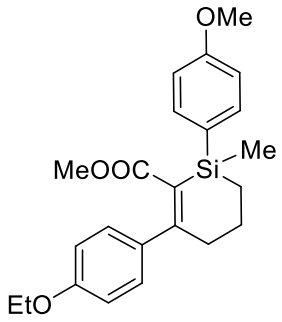
Yellow oil (30.9 mg, 40% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (d, J = 9.0 Hz, 2H), 7.19 (t, J = 5.4 Hz, 2H), 7.06 (d, J = 6.5 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 3.74 (s, 3H), 3.26 (s, 3H), 2.58-2.36 (m, 2H), 1.97-1.85 (m, 2H), 1.05-0.92 (m, 1H), 0.87-0.74 (m, 1H), 0.46 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.5, 161.8, 160.8, 143.0, 135.8, 133.5, 130.7, 128.4, 128.0, 127.4, 113.8, 55.1, 51.2, 37.0, 21.2, 11.2, -3.2; IR (KBr, cm $^{-1}$): 2912.0, 1700.2, 1592.41, 1502.8, 1278.3, 1246.4, 1181.9,

1110.9, 798.4; HRMS (ESI-TOF) m/z: [M+ Na]+ calculate*d* for $C_{21}H_{23}ClNaO_3Si$: 409.0997 , found: 409.0987.



Methyl 3-(4-fluorophenyl)-1-(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-carboxylate (3al):

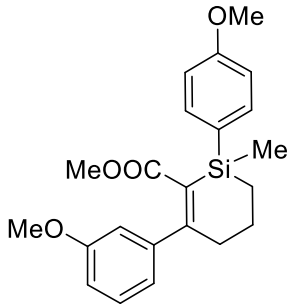
Colorless oil (28.16 mg, 38% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (d, J = 8.5 Hz, 2H), 7.14-7.08 (m, 2H), 6.91 (t, J = 8.7 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 3.73 (s, 3H), 3.25 (s, 3H), 2.61-2.38 (m, 2H), 1.95-1.85 (m, 2H), 1.05-0.93 (m, 1H), 0.86-0.78 (m, 1H), 0.46 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.7, 163.5, 161.9, 161.1, 160.8, 140.6 (d, J = 3.5 Hz), 135.8, 130.4, 128.3 (d, J = 8.1 Hz), 127.5, 115.2, 115.0, 113.7, 55.1, 51.2, 37.2, 21.3, 11.2, -3.2; IR (KBr, cm $^{-1}$): 2911.9, 1699.5, 1593.3, 1503.6, 1278.2, 1246.3, 1182.2, 1110.8, 798.8; HRMS (ESI-TOF) m/z: [M+ Na]+ calculate*d* for $C_{21}H_{23}FNaO_3Si$: 393.1293 , found: 393.1279.



Methyl 3-(4-ethoxyphenyl)-1-(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-carboxylate (3am):

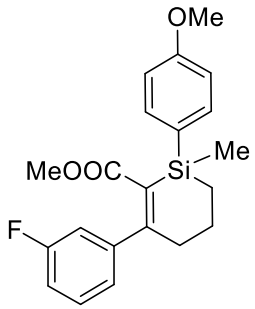
Colorless oil (28.6 mg, 36% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, J = 8.5 Hz, 2H), 7.16 (d, J = 8.7 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 4.02 (q, J = 7.0 Hz, 2H), 3.81 (s, 3H), 3.35 (s, 3H), 2.74-2.48 (m, 2H), 2.04-1.91 (m, 2H), 1.41 (t, J = 7.0 Hz, 3H), 1.10-0.98 (m, 1H), 0.94-0.84 (m, 1H), 0.53 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.2, 162.6, 160.7, 158.6, 136.8, 135.8, 129.1,

128.0, 127.8, 114.0, 113.7, 63.5, 55.1, 51.2, 36.9, 21.3, 15.0, 11.3, -3.2; IR (KBr, cm $^{-1}$): 2924.1, 1697.3, 1592.2, 1503.8, 1242.0, 1179.7, 1110.6, 1044.5, 798.7; HRMS (ESI-TOF) m/z: [M+ Na]+ calculate*d* for $C_{23}H_{28}NaO_4Si$: 419.1649, found: 419.1654.



Methyl 3-(3-methoxyphenyl)-1-(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-carboxylate (3an):

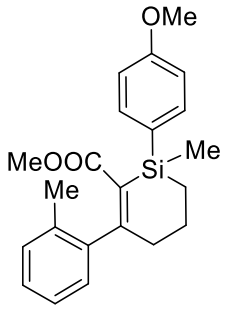
Yellow oil (50 mg, 65% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (d, J = 8.7 Hz, 2H), 7.17-7.08 (m, 1H), 6.83 (d, J = 8.6 Hz, 2H), 6.75-6.66 (m, 3H), 3.70 (d, J = 6.2 Hz, 6H), 3.24 (s, 3H), 2.61-2.39 (m, 2H), 1.94-1.83 (m, 2H), 1.02-0.93 (m, 1H), 0.85-0.76 (m, 1H), 0.45 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.7, 162.5, 160.7, 159.4, 146.0, 135.8, 129.9, 129.2, 127.5, 119.0, 113.7, 113.3, 112.0, 55.3, 55.1, 51.1, 36.8, 21.2, 11.2, -3.2; IR (KBr, cm $^{-1}$): 2910.1, 1699.1, 1591.4, 1502.9, 1278.0, 1245.4, 1181.6, 1110.8, 1033.2, 799.9; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{22}H_{26}NaO_4Si$: 405.1493, found: 405.1498.



Methyl 3-(3-fluorophenyl)-1-(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-carboxylate (3ao):

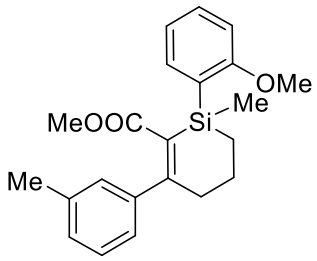
Colorless oil (23.7 mg, 32% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (d, J = 8.5 Hz, 2H), 7.24-7.14 (m, 1H), 6.94-6.78 (m, 5H), 3.74 (s, 3H), 3.26 (s, 3H), 2.62-2.38 (m, 2H), 1.95-1.86 (m, 2H), 1.04-0.93 (m, 1H), 0.88-0.76 (m, 1H), 0.46 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.4, 163.9, 161.4 (d, J = 6.0 Hz), 160.8, 146.8 (d,

J = 7.3 Hz), 135.8, 130.8, 129.7 (d, *J* = 8.4 Hz), 127.3, 122.3 (d, *J* = 2.5 Hz), 114.5 (d, *J* = 21.1 Hz), 113.7 (d, *J* = 3.0 Hz), 113.5, 55.1, 51.2, 36.9, 21.2, 11.2, -3.3; IR (KBr, cm $^{-1}$): 2948.6, 1703.4, 1592.4, 1503.1, 1278.6, 1246.9, 1111.4, 801.1, 697.2; HRMS (ESI-TOF) m/z: [M+ Na]+ calculat*d* for $C_{21}H_{23}FNaO_3Si$: 393..1293, found: 393.1307.



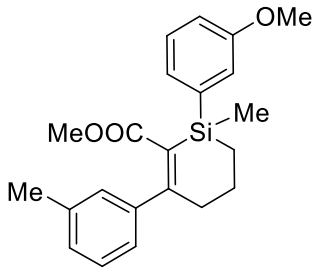
Methyl 1-(4-methoxyphenyl)-1-methyl-3-(o-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3ap):

Yellow oil (33 mg, 45% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49-7.42 (m, 2H), 7.11-7.03 (m, 3H), 6.95-6.83 (m, 3H), 3.74 (s, 3H), 3.20 (d, *J* = 5.4 Hz, 3H), 2.43-2.25 (m, 2H), 2.18 (d, *J* = 24.0 Hz, 3H), 1.95-1.80 (m, 2H), 1.02-0.94 (m, 1H), 0.89-0.77 (m, 1H), 0.47 (d, *J* = 7.8 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.3, 166.4 (d, *J* = 18.3 Hz), 160.7, 144.7 (d, *J* = 13.8 Hz), 135.7 (d, *J* = 6.6 Hz), 133.4 (d, *J* = 60.0 Hz), 129.8 (d, *J* = 10.3 Hz), 129.0 (d, *J* = 24.0 Hz), 128.1 (d, *J* = 21.1 Hz), 127.0 (d, *J* = 5.0 Hz), 126.2 (d, *J* = 60.0 Hz), 125.5 (d, *J* = 10.4 Hz), 113.7 (d, *J* = 3.7 Hz), 55.1 , 51.0 , 37.8 (d, *J* = 21.8 Hz), 21.2 (d, *J* = 11.9 Hz), 19.5 (d, *J* = 27.5 Hz), 11.8 (d, *J* = 20.4 Hz), -3.0 (d, *J* = 8.8 Hz); IR (KBr, cm $^{-1}$): 2909.4, 1716.3, 1591.9, 1502.7, 1277.5, 1246.6, 1181.9, 1110.8, 799.7; HRMS (ESI-TOF) m/z: [M+ Na]+ calculat*d* for $C_{22}H_{26}NaO_3Si$: 389.1543, found: 389.1534.



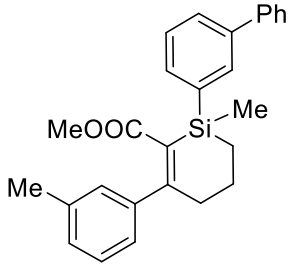
Methyl 1-(2-methoxyphenyl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3aq):

Yellow oil (22 mg, 30% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51-7.44 (m, 1H), 7.32-7.25 (m, 1H), 7.12 (t, J = 7.5 Hz, 1H), 7.04-6.85 (m, 4H), 6.76 (d, J = 8.2 Hz, 1H), 3.72 (s, 3H), 3.27 (s, 3H), 2.53-2.42 (m, 2H), 2.26 (s, 3H), 1.91-1.75 (m, 2H), 1.18-1.07 (m, 1H), 0.82-0.71 (m, 1H), 0.44 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.2, 164.3, 162.8, 144.9, 137.7, 136.6, 131.2, 129.9, 128.3, 128.1, 127.2, 124.9, 123.8, 120.6, 109.6, 55.2, 51.1, 37.1, 21.6, 21.3, 10.8, -2.8; IR (KBr, cm $^{-1}$): 2909.0, 1703.9, 1587.3, 1427.5, 1233.8, 1044.9, 802.6, 756.7; HRMS (ESI-TOF) m/z: [M+ Na]+ calculate*d* for $C_{22}H_{26}NaO_3Si$: 389.1543, found: 389.1563.



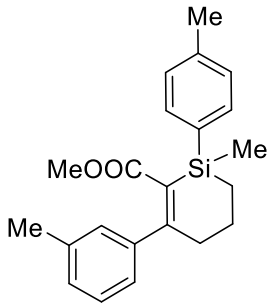
Methyl 1-(3-methoxyphenyl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3ar):

Yellow oil (41.1 mg, 56% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 (t, J = 8.2 Hz, 1H), 7.25-7.17 (m, 3H), 7.13-7.00 (m, 3H), 6.93 (dd, J = 8.2, 2.7 Hz, 1H), 3.83 (s, 3H), 3.35 (s, 3H), 2.71-2.51 (m, 2H), 2.35 (s, 3H), 2.06-1.93 (m, 2H), 1.14-1.05 (m, 1H), 0.96-0.87 (m, 1H), 0.57 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.7, 164.1, 159.0, 144.6, 138.7, 137.7, 129.1, 129.0, 128.5, 128.1, 127.1, 126.6, 123.7, 119.8, 114.6, 55.2, 51.1, 37.1, 21.6, 21.2, 11.1, -3.3; IR (KBr, cm $^{-1}$): 2918.1, 1699.5, 1570.1 1281.7, 1227.4, 1045.3, 782.1, 695.5; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{22}H_{26}NaO_3Si$: 389.1543, found: 389.1561.



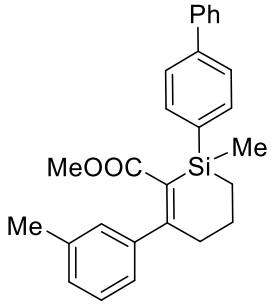
Methyl 1-([1,1'-biphenyl]-3-yl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3as):

Colorless oil (31.4 mg, 38% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (s, 1H), 7.56-7.48 (m, 4H), 7.37 (t, *J* = 8.1 Hz, 3H),7.27 (t, *J* = 10.7 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.04-6.92 (m, 3H), 3.27 (s, 3H), 2.64-2.42 (m, 2H), 2.26 (s, 3H), 1.97-1.87 (m, 2H), 1.10-1.02 (m, 1H), 0.91-0.83 (m, 1H), 0.52 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.8, 164.1, 144.6, 141.7, 140.6, 137.8, 137.7, 133.3, 133.1, 129.1, 128.9, 128.5, 128.3, 128.1, 127.4, 127.3, 127.1, 123.7, 51.2, 37.1, 21.6, 21.3, 11.1, -3.2; IR (KBr, cm $^{-1}$): 2919.6, 1699.2, 1428.6 1228.9, 1046.6, 799.5, 699.6, 646.4; HRMS (ESI-TOF) m/z: [M+ Na]+ calculate*d* for $C_{27}H_{28}NaO_2Si$: 435.1751 , found: 435.1737.



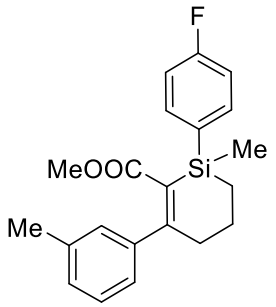
Methyl 1-methyl-3-(m-tolyl)-1-(p-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3at):

Colorless oil (36.5 mg, 52% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 7.9 Hz, 2H), 7.25-7.18 (m, 3H), 7.12-7.01 (m, 3H), 3.35 (s, 3H), 2.70-2.52 (m, 2H), 2.36 (d, *J* = 5.5 Hz, 6H), 2.08-1.93 (m, 2H), 1.15-1.02 (m, 1H), 0.96-0.88 (m, 1H), 0.56 (s, 3H);^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.8, 163.7, 144.7, 139.3, 137.7, 134.3, 133.3, 129.4, 128.8, 128.4, 128.1, 127.1, 123.7, 51.1, 37.1, 21.6, 21.5, 21.3, 11.2, -3.3; IR (KBr, cm $^{-1}$): 2919.1, 1700.6, 1578.8 1429.8, 1229.1, 1106.5, 786.5, 703.9; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{22}H_{26}NaO_2Si$: 373.1594, found: 373.1607.



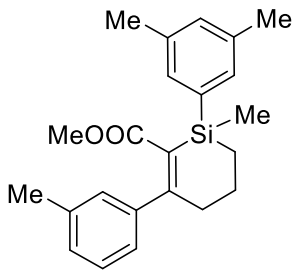
Methyl 1-([1,1'-biphenyl]-4-yl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3au):

Light yellow oil (43 mg, 52% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, J = 8.2 Hz, 2H), 7.52 (d, J = 9.8 Hz, 4H), 7.35 (t, J = 7.6 Hz, 2H), 7.27 (t, J = 7.4 Hz, 1H), 7.12 (t, J = 8.0 Hz, 1H), 7.03-6.91 (m, 3H), 3.26 (s, 3H), 2.64-2.46 (m, 2H), 2.26 (s, 3H), 1.98-1.87 (m, 2H), 1.10-0.98 (m, 1H), 0.90-0.81 (m, 1H), 0.51 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.8, 164.1, 144.6, 142.1, 141.2, 137.8, 135.8, 134.8, 129.1, 128.9, 128.5, 128.1, 127.5, 127.3, 127.1, 126.7, 123.7, 51.1, 37.1, 21.6, 21.3, 11.2, -3.3; IR (KBr, cm $^{-1}$): 2919.2, 1698.9, 1203.1, 1112.9, 798.3, 755.1, 697.2; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{27}H_{28}NaO_2Si$: 435.1751, found: 435.1774.



Methyl 1-(4-fluorophenyl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3av):

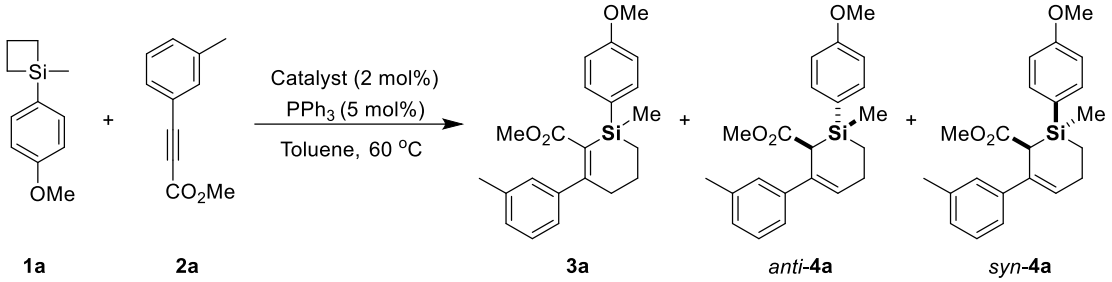
Yellow oil (41.8 mg, 59% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (dd, J = 2.1 Hz, 2H), 7.20 (t, J = 7.5 Hz, 1H), 7.13-6.97 (m, 5H), 3.32 (s, 3H), 2.70-2.49 (m, 2H), 2.35 (s, 3H), 2.04-1.89 (m, 2H), 1.16-0.99 (m, 1H), 0.99-0.87 (m, 1H), 0.56 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.7, 165.2, 164.2, 162.8, 144.5, 137.8, 136.3 (d, J = 7.8 Hz), 132.5 (d, J = 3.7 Hz), 129.0, 128.6, 128.1, 127.1, 123.6, 115.2, 115.0, 51.1, 37.1, 21.6, 21.2, 11.2, -3.3; IR (KBr, cm $^{-1}$): 2919.9, 1699.3, 1586.2 1498.9, 1228.9, 1163.0, 1114.1, 824.5, 798.4, 703.5; HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{21}H_{23}FNaO_2Si$: 377.1344, found: 377.1331.



Methyl 1-(3,5-dimethylphenyl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3aw):

Yellow oil (29.2 mg, 40% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.15-7.08 (m, 3H), 7.03-6.91 (m, 4H), 3.26 (s, 3H), 2.64-2.54 (m, 1H), 2.50-2.40 (m, 1H), 2.25 (d, *J* = 5.9 Hz, 9H), 1.96-1.86 (m,2H), 1.05-0.97 (m, 1H), 0.84-0.77 (m, 1H), 0.46 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.8, 163.6, 144.7, 137.7, 137.1, 136.7, 132.0, 131.2, 129.5, 128.5, 128.1, 127.1, 123.7, 51.1, 37.1, 21.6, 21.3, 11.2, -3.1; IR (KBr, cm $^{-1}$): 2916.9, 1701.3, 1428.9, 1229.0, 1139.3, 856.5, 784.2, 694.9; HRMS (ESI-TOF) m/z: [M+ Na]+ calculate*d* for $C_{23}H_{28}NaO_2Si$: 387.1751 , found: 387.1735.

Table S1. The effect of Rhodium metal salts in this reaction.[a]

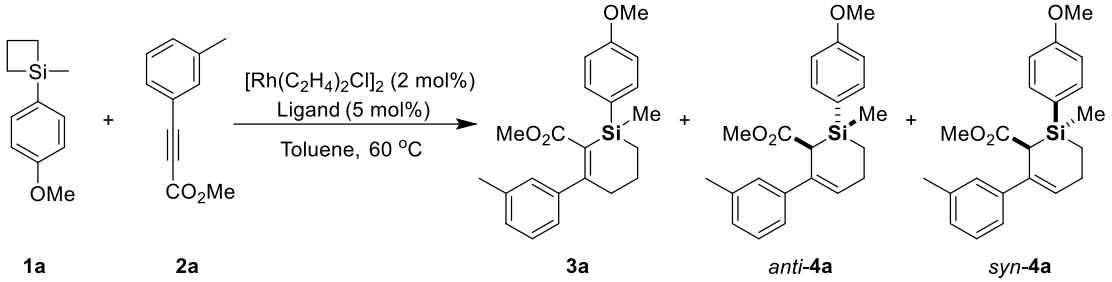


1a **2a** **3a** *anti*-**4a** *syn*-**4a**

Entry	Catalyst	Con.(%)[b]	**3a**:**4a** (%)[b]	*dr* of **4a** (%)[b]
1	$[Rh(nbd)_2Cl]_2$	nr	/	
2	$[Rh(OAc)]_2$	nr	/	
3	$Rh(CO)_4Cl_2$	nr	/	
4	$Rh(acac)(CO)_2$	nr	/	
5	$[Rh(cod)_2Cl]_2$	nr	/	
6	$[Rh(C_2H_4)_2Cl]_2$	15	7:93	32:68
7	$[Rh(cod)_2]BF_4$	nr	/	
8	$Rh(PPh_3)_3Cl$	nr	/	
9	$RhCl_3$	nr	/	

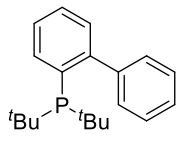
[a]All the reactions were run on a 0.2 mmol scale in 2.0 mL solvents for 14 h. [b]Determined by GC-MS.

Table S2. The effect of P-ligands in this reaction.[a]

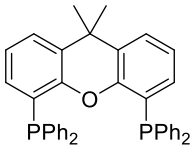


Entry	Ligand	Con.(%)[b]	**3a**:**4a** (%)[b]	*dr* of **4a** (%)[b]
1	DPEphos	15	28:72	17:83
2	JohnPhos	trace	/	/
3	Xantphos	nr	/	/
4	DavePhos	nr	/	/
5	S-Phos	nr	/	/
6	RuPhos	nr	/	/
7	CyJohnPhos	nr	/	/
8	Xphos	nr	/	/
9	Brettphos	nr	/	/
10	**P1**	76	31:69	74:26
11	**P2**	36	11:89	56:44
12	**P3**	19	12:87	59:41
13	**P4**	30	90:10	13:87
14	**P5**	25	24:76	61:39
15	**P6**	nr	/	/
16	**P7**	nr	/	/
17	**P8**	nr	/	/
18	**P9**	nr	/	/
19	**P10**	nr	/	/
20	**P11**	nr	/	/
21	**P12**	nr	/	/

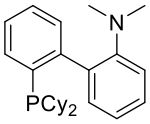
[a]All the reactions were run on a 0.2 mmol scale in 2.0 mL solvents for 14 h. [b]Determined by GC-MS.



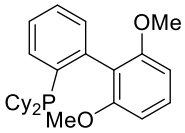
JohnPhos



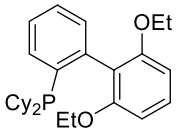
XantPhos



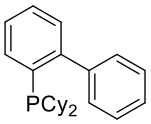
DavePhos



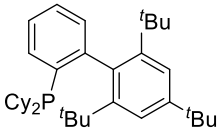
S-Phos



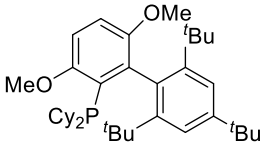
RuPhos



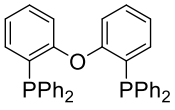
CyJohnPhos



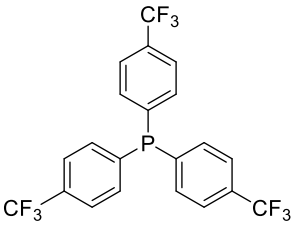
Xphos



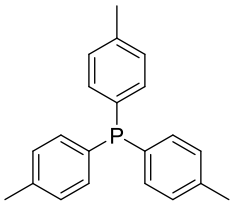
Brettphos



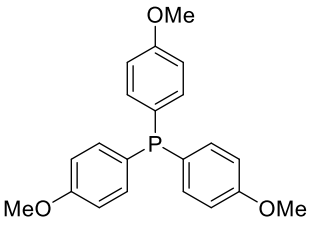
DPEphos



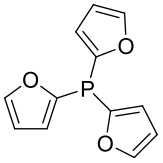
P1



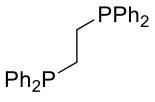
P2



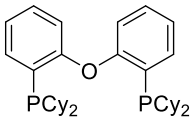
P3



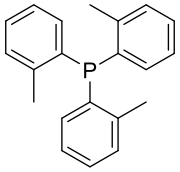
P4



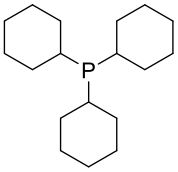
P5



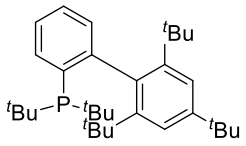
P6



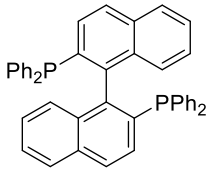
P7



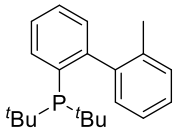
P8



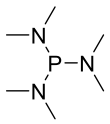
P9



P10

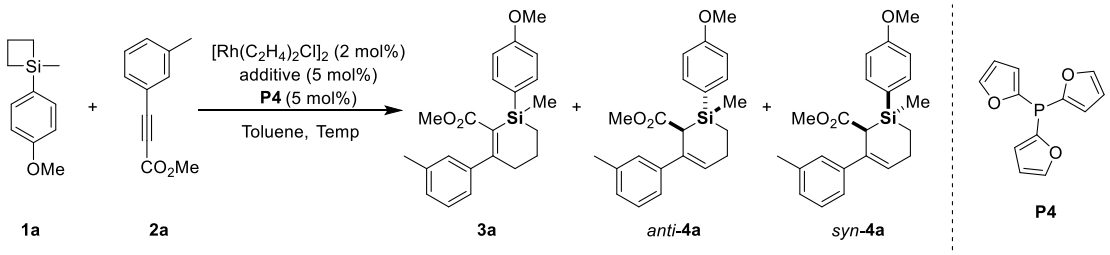


P11



P12

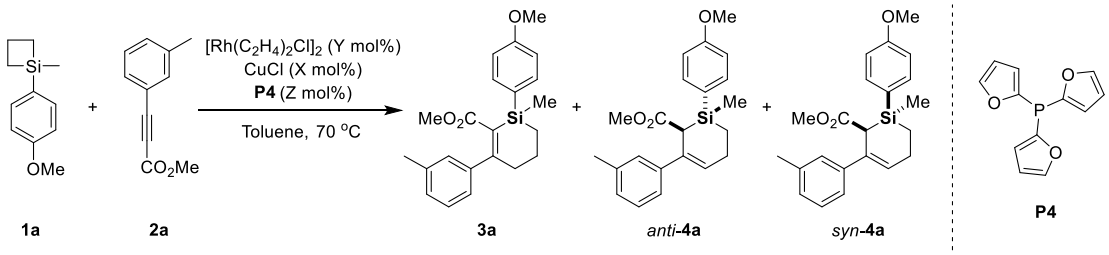
Table S3. The effect of Additive and Temperature in this reaction.[a]



Entry	additive	Temp (°C)	Con.(%)[b]	**3a**:**4a** (%)[b]	*dr* of **4a** (%)[b]	**3a** (%)[c]
1	$Cu(CH_3CN)_4PF_6$	60	nr	/	/	/
2	$Cu(CH_3CN)_4BF_4$	60	35	90:10	20:80	/
3	CuF_2	60	18	94:6	17:83	/
4	$Cu(OTf)_2$	60	nr	/	/	/
5	CuI	60	46	55:45	38:62	/
6	$Cu(acac)_2$	60	23	94:6	13:87	/
7	$Cu(OAc)_2$	60	18	92:8	14:86	/
8	$CuCl_2$	60	43	89:11	9:91	19
9	Cu_2SO_4	60	12	95:5	17:83	/
10	$CuBr_2$	60	48	41:59	55:45	/
11	$CuCl_2$	70	54	88:12	10:90	21
12	$CuCl_2$	80	58	76:24	8:92	18
13	CuCl	70	65	80:20	28:72	28
14	CuCN	70	67	65:35	14:86	15
15	CuBr	70	10	64:36	26:74	6
16	$LiBF_4$	70	21	94:6	21:79	10
17	$ZnCl_2$	70	39	82:18	23:77	16
18	$NaSbF_6$	70	nr	/	/	/
19	$NaBH_4$	70	nr	/	/	/
20	^{t}BuONa	70	nr	/	/	/
21	Et_3NaBH	70	nr	/	/	/
22	^{i}Pr$_2$NH	70	nr	/	/	/
23	^{t}BuOK	70	nr	/	/	/
24	$AgSbF_6$	70	nr	/	/	/
25	$AgBF_4$	70	nr	/	/	/

[a]All the reactions were run on a 0.2 mmol scale in 2.0 mL solvents for 14 h. [b]Determined by GC-MS. [c]Determind by ^{1}H NMR. [c]Yield of the isolated product.

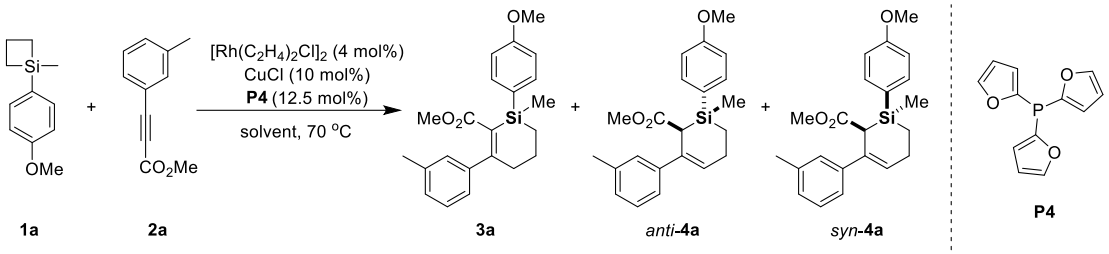
Table S4. The effect of the amount of 2a/catalyst/L8/additive in this reaction.[a]



Entry	**2a**	X	Y	Z	Con.(%)[b]	**3a**:**4a** (%)[b]	*dr* of **4a** (%)[b]	**3a** (%)[c]	**3a** (%)[d]
1	1.2 eq	5	2	5	65	80:20	28:72	28	25
2	2.5 eq	5	2	5	67	85:15	19:81	42	40
3	2.5 eq	10	2	5	85	82:18	22:78	52	48
4	2.5 eq	10	4	5	95	83:17	17:83	62	58
5	2.5 eq	10	4	12.5	96	93:7	22:78	70	65

[a]All the reactions were run on a 0.2 mmol scale in 2.0 mL solvents for 14 h. [b]Determined by GC-MS. [c]Determind by ^{1}H NMR. [c]Determind by ^{1}H NMR. [d]Yield of the isolated product.

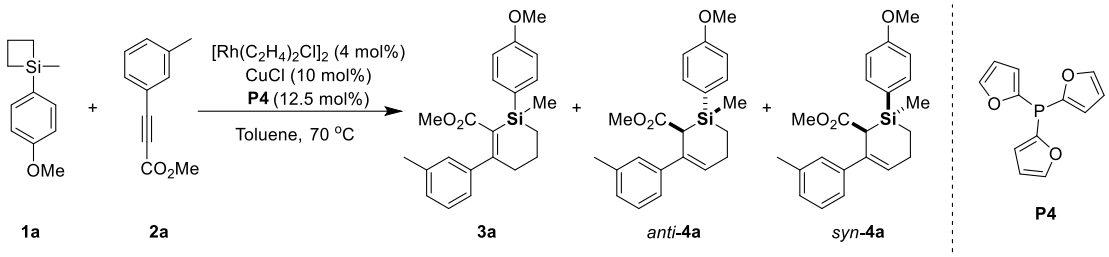
Table S5. The effect of solvent in this reaction.[a]



Entry	Solvent	Con.(%)[b]	**3a**:**4a**(%)[b]	*dr* of **4a** (%)[b]	**3a** (%)[c]	**3a** (%)[d]
1	Tol	96	93:7	22:78	70	65
2	PhCl	92	89:11	17:83	63	51
4	EA	80	92:8	17:83	/	/
5	1,4-Dioxane	80	81:19	10:90	/	/
6	CH_3CN	49	52:48	30:70	/	/
7	*p*-xylene	74	75:25	29:71	/	/
8	Benzotrifluoride	35	95:5	27:73	/	/

[a]All the reactions were run on a 0.2 mmol scale in 2.0 mL solvents for 14 h. [b]Determined by GC-MS. [c]Determind by ^{1}H NMR. [c]Determind by ^{1}H NMR. [d]Yield of the isolated product.

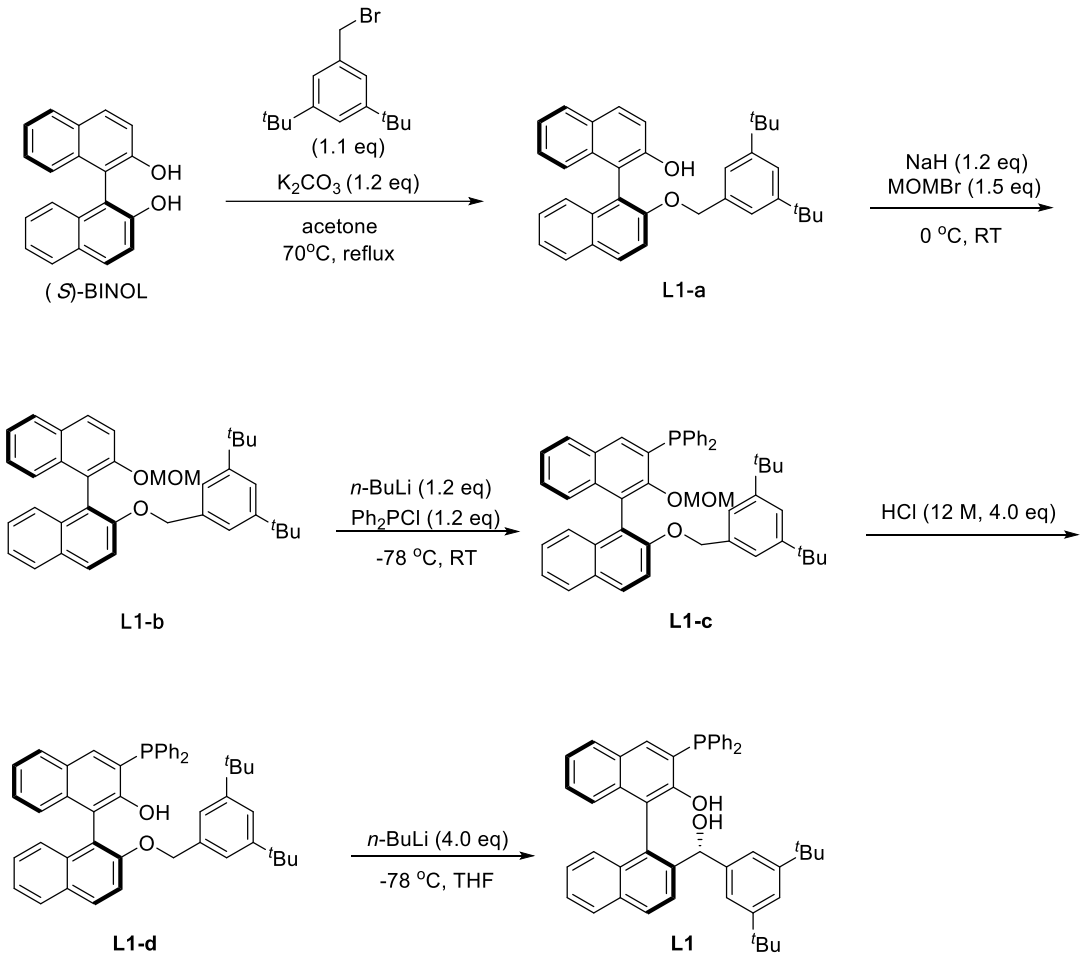
Table S6. Control Experiments.[a]



Entry	Without	Con.(%)[b]	**3a**:**4a** (%)[b]	*dr* of **4a** (%)[b]
1	CuCl and **P4**	nr	/	/
2	$[Rh(C_2H_4)_2Cl]_2$	< 5%	/	/
3	CuCl	30	90:10	13:87

[a]All the reactions were run on a 0.2 mmol scale in 2.0 mL solvents for 14 h. [b]Determined by GC-MS.

3.2. General procedure for the synthesis of Ar-BINMOL-Phos.[5]



a) (*S*)-BINOL (30 mmol, 8.6 g) and K_2CO_3 (1.2 eq, 5g) in acetone solution was heated to reflux and stir for 1 hour. Then 3,5-^{t}Bu-PhCH_2Br (1.1 eq, 8.3 ml) was added to the reaction mixture, and the reaction was stirred at 70 °C for 2 h. After the completion of the reaction was detected by TLC, the reaction flask was removed and cooled to room temperature, and the reactants were suction filtered. Wash with EtOAc. Take the lower layer of filtrate and spin dry under reduced pressure to obtain a concentrated organic phase, which is separated by chromatographic column (PE/EA, 50/1) to obtain **L1-a** (71% yield, 10.40 g)

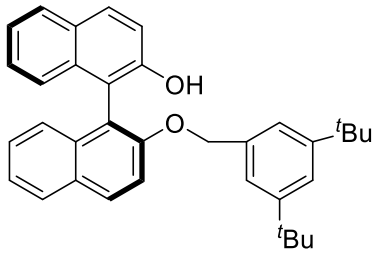
b) Dry THF (20 mL) was added to the NaH (1.5 eq, 0.77g) in a round-bottom flask equipped with a stir bar. The solution was cooled to 0 °C, slowly drop the **L1-a** solution into the flask, continue to stir at 0°C for 1 hour, then extract MOMBr (1.5 eq, 0.90 ml) and slowly drop it into the reaction system, and then add the reaction system Transfer

to room temperature and stir overnight. After the completion of the reaction was detected by TLC, the reaction was quenched with saturated aqueous NH_4Cl at low temperature. After stirring for 5 min, it was extracted with EtOAc. The organic phases were combined and spin-dried under reduced pressure to obtain a concentrated organic phase. Column separation (PE/EA, 50/1) to obtain **L1-b** (67% yield, 7.60 g)

c) 6.85 mL (17.1 mmol) of 2.5M solution n-BuLi in hexanes was added dropwise to a solution of compound **L1-b** (7.6 g, 14.3 mmol) in 30 mL of THF at -78 ºC. The resulting solution was stirred at -78 ºC for 1 h, and then 5 mL of PPh_2Cl (3.08 mL, 17.16 mmol, 1.2 equiv) in THF was added slowly at the same temperature. The reaction mixture was stirred for 6 hours. When the reaction is completed, it was quenched with saturated aqueous NH_4Cl (5 mL) and stirred vigorously for 5 minutes. The aqueous phase was extracted with ethyl acetate (3×20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (PE/EA, 10/1) to give 3.07 g (30% yield, 4.29 mmol) of the compound **L1-c**.

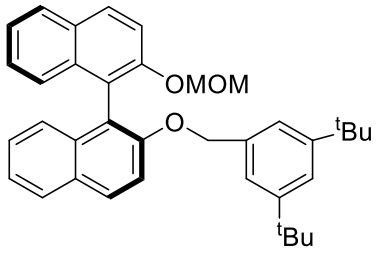
d) To a solution of **L1-c** (3.07 g, 4.29 mmol) in 10 mL of THF, 2 mL of 12M aqueous HCl was added at 40 ºC for 2 h. The organic phase was extracted with water (3×30 mL) and ethyl acetate (3×30 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. the residue was purified by silica gel column chromatography (PE/EA, 10/1 to 5/1) to give 2.59 g (90% yield) of compound **L1-d**.

e) To a solution of **L1-d** (2.59 g, 3.86 mmol) in 10 mL of THF, 6.18 mL (15.44 mmol, 4 equiv) of 2.5M solution n-BuLi in hexanes was added at -78 ºC for 5 min and the color of the mixture turn to jasper. Then the reaction continued to stir at room temperature for additional 2 h. At last, it was quenched with saturated aqueous NH_4Cl (10 mL) and stirred for 5 minutes. The aqueous phase was extracted with ethyl acetate (3×20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (PE/EA, 10/1 to 5/1) to give 1.82 g (2.7 mmol, 70% yield) of **L1**. The synthesis of **L8**/**L9** are similarly to that of **L1**.



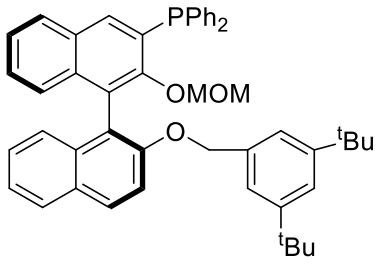
(*S*)-2'-((3,5-di-tert-butylbenzyl)oxy)-[1,1'-binaphthalen]-2-ol (L1-a):

White Solid, mp 67 – 77 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 9.0 Hz, 1H), 7.86-7.73 (m, 3H), 7.47 (d, *J* = 9.1 Hz, 1H), 7.31-7.26 (m, 2H), 7.25-7.16 (m, 2H), 7.18-7.10 (m, 3H), 7.04 (d, *J* = 7.9 Hz, 1H), 6.81 (d, *J* = 1.8 Hz, 2H), 5.06-4.95 (m, 2H), 1.09 (s, 18H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.4, 151.4, 150.9, 135.9, 134.2, 134.0, 131.1, 129.9, 129.8, 129.3, 128.3, 128.2, 127.4, 126.6, 125.2, 125.0, 124.5, 123.4, 121.6, 121.2, 117.7, 116.5, 115.7, 115.3, 71.7, 34.8, 31.5; HRMS (ESI-TOF) m/z: [M+ Na]+ calculat*d* for $C_{35}H_{36}NaO_2$: 511.2608, found: 511.2587.



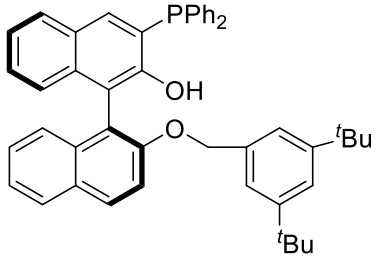
(*S*)-2-((3,5-di-tert-butylbenzyl)oxy)-2'-(methoxymethoxy)-1,1'-binaphthalene (L1-b):

White Solid, mp 92 – 95 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (t, *J* = 9.1 Hz, 2H), 7.77 (dd, *J* = 8.2, 3.7 Hz, 2H), 7.50 (d, *J* = 9.0 Hz, 1H), 7.42 (d, *J* = 9.0 Hz, 1H), 7.27-7.18 (m, 2H), 7.14-7.10 (m, 5H), 6.72 (d, *J* = 1.8 Hz, 2H), 4.99-4.83 (m, 4H), 3.01 (s, 3H), 1.06 (s, 18H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 154.4, 152.8, 150.7, 136.5, 134.3, 134.2, 130.1, 129.5, 129.5, 128.1, 128.0, 126.5, 126.4, 125.7, 125.6, 124.2, 123.8, 121.5, 121.3, 121.1, 120.7, 117.5, 116.0, 95.3, 71.9, 55.9, 34.8, 31.5; HRMS (ESI-TOF) m/z: [M+ Na]+ calculat*d* for $C_{37}H_{40}NaO_3$: 555.2870, found: 555.2852.



(*S*)-(2'-((3,5-di-tert-butylbenzyl)oxy)-2-(methoxymethoxy)-[1,1'-binaphthalen]-3-yl)diphenylphosphane (L1-c):

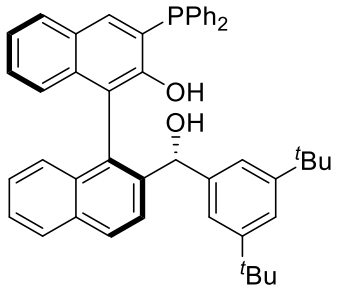
White Solid, mp 113-116 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 9.0 Hz, 1H), 7.72 (d, *J* = 8.0, 1.2 Hz, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 9.0 Hz, 1H), 7.28 (d, *J* = 3.8 Hz, 5H), 7.21-7.06 (m, 11H), 6.84 (t, *J* = 7.7 Hz, 2H), 6.73 (d, *J* = 1.8 Hz, 2H), 5.01 (q, *J* = 11.9 Hz, 2H), 4.62 (d, *J* = 5.4 Hz, 1H), 4.51 (d, *J* = 5.5 Hz, 1H), 2.60 (s, 3H), 1.03 (s, 18H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.2, 155.0, 154.7, 150.7, 137.2, 137.1, 136.8, 136.7, 136.4, 134.7, 134.7, 134.5, 134.4, 134.2, 134.0, 133.9, 132.8, 132.7, 131.1, 129.9, 129.2, 129.0, 128.6, 128.6, 128.5, 128.4, 128.3, 127.9, 126.8, 126.7, 125.8, 125.7, 125.1-124.8 (m), 123.8, 121.5, 121.0, 120.0, 114.8, 99.0 (d, *J* = 6.3 Hz), 71.5, 56.8 (d, *J* = 5.0 Hz), 34.8, 31.5; HRMS (ESI-TOF) m/z: [M+ H]+ calculated for $C_{49}H_{50}O_3P$: 717.3492, found: 717.3461.



(*S*)-2'-((3,5-di-tert-butylbenzyl)oxy)-3-(diphenylphosphanyl)-[1,1'-binaphthalen]-2-ol (L1-d):

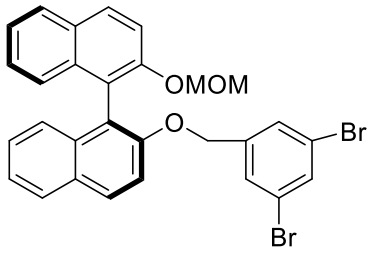
White Solid, mp 127 – 133 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 9.0 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.79-7.72 (m, 1H), 7.62 (d, *J* = 9.1 Hz, 1H), 7.59-7.51 (m, 2H), 7.52-7.27 (m, 14H), 7.08 (t, *J* = 6.8 Hz, 2H), 6.98 (d, *J* = 2.0 Hz, 2H), 5.21 (s, 2H), 1.28 (s, 18H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.3, 152.4, 152.3, 150.8, 136.3, 136.2, 136.2, 136.1, 134.6, 134.5, 134.4, 134.1, 133.9, 133.7, 131.1, 129.7, 129.3, 129.3, 129.1, 128.7, 128.6 (d, *J* = 2.1 Hz), 128.5, 128.4, 128.4, 128.3, 127.4,

127.1, 126.4, 126.3, 125.0, 124.8, 124.4, 123.5, 121.6, 121.0, 116.3, 115.5, 115.3 (d, *J* = 2.0 Hz), 71.7, 34.8, 31.5; HRMS (ESI-TOF) m/z: [M+ H]+ calculated for $C_{47}H_{46}O_2P$: 673.3230, found: 673.3207.



(*S*)-2'-((*R*)-(3,5-di-tert-butylphenyl)(hydroxy)methyl)-3-(diphenylphosphanyl)-[1,1'-binaphthalen]-2-ol (L1):

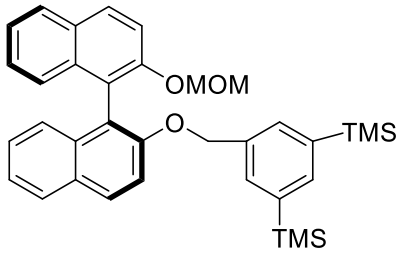
White Solid, mp 93 – 106 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.7 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.58-7.53 (m, 2H), 7.44-7.30 (m, 12H), 7.22-7.18 (m, 1H), 7.16-7.08 (m, 3H), 7.07-7.02 (m, 1H), 6.87 (d, *J* = 1.8 Hz, 2H), 6.81 (d, *J* = 8.3 Hz, 1H), 5.85 (s, 1H), 5.64 (s, 1H), 1.09 (s, 18H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 152.5, 152.4, 150.5, 142.2, 142.0, 135.2, 135.2, 135.0, 134.7, 134.2, 134.1, 134.0, 133.9, 133.5, 132.8, 129.8, 129.6, 129.5, 129.1, 129.1, 129.0, 128.9, 128.9, 128.9, 128.4, 128.3, 127.5, 126.8, 126.5, 126.4, 126.0, 125.7, 125.2, 124.0, 121.2, 120.5, 117.9, 73.8, 34.9, 31.5; ^{31}P NMR (162 MHz, Chloroform-*d*) δ -17.18; HRMS (ESI-TOF) m/z: [M+ H]+ calculated for $C_{47}H_{46}O_2P$: 673.3230, found: 673.3241.



(*S*)-2-((3,5-dibromobenzyl)oxy)-2'-(methoxymethoxy)-1,1'-binaphthalene (L8-a):

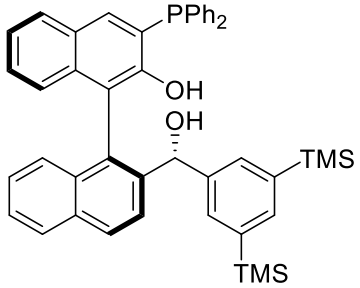
White Solid, mp 68 - 71 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92-7.76 (m, 4H), 7.51 (d, *J* = 9.0 Hz, 1H), 7.34 (s, 1H), 7.29-7.22 (m, 3H), 7.18-7.14 (m, 3H), 7.04 (d, *J* = 9.5 Hz, 1H), 6.91 (d, *J* = 1.7 Hz, 2H), 5.03 (d, *J* = 6.8 Hz, 1H), 4.92-4.87 (m, 2H), 4.82 (d, *J* = 13.0 Hz, 1H), 3.00 (s, 3H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 153.5, 152.8, 141.6, 134.2, 134.0, 133.1, 130.0, 129.9, 129.7, 129.6, 128.4, 128.3, 128.0, 126.7,

126.6, 125.7, 125.3, 124.3, 124.2, 122.9, 121.2, 120.9, 117.3, 115.8, 95.2, 69.8, 55.9. HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{29}H_{22}Br_2NaO_3$: 598.9828, found: 600.9807.



(*S*)-(5-(((2'-(methoxymethoxy)-[1,1'-binaphthalen]-2-yl)oxy)methyl)-1,3-phenylene) bis (trimethylsilane) (L8-b):

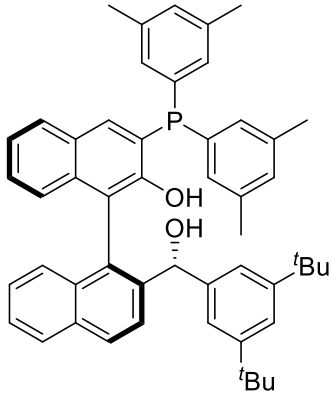
White Solid, mp 87 – 94 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (dd, *J* = 11.0, 9.0 Hz, 2H), 7.76-7.70 (m, 2H), 7.44 (d, *J* = 9.0 Hz, 1H), 7.37 (d, *J* = 9.0 Hz, 1H), 7.31 (s, 1H), 7.22-7.16 (m, 2H), 7.11-7.04 (m, 4H), 6.98 (s, 2H), 4.94-4.80 (m, 4H), 2.96 (s, 3H), -0.00 (s, 18H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.4, 153.8, 140.5, 138.4, 136.6, 135.3, 135.2, 133.4, 131.0, 130.6, 130.5, 129.1, 129.0, 127.5, 126.6, 125.2, 124.9, 122.4, 121.8, 118.5, 117.1, 96.3, 72.9, 56.9, -0.0. HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{35}H_{40}NaO_3Si_2$: 587.2408, found: 587.2427.



(*S*)-2'-((*R*)-(3,5-bis(trimethylsilyl)phenyl)(hydroxy)methyl)-3-(diphenylphosphaneyl)-[1,1'-binaphthalen]-2-ol (L8):

White Solid, mp 92 – 104 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.6 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.47 (dd, *J* = 8.4, 3.5 Hz, 2H), 7.31-7.19 (m, 13H), 7.11-7.04 (m, 5H), 6.96 (t, *J* = 7.1 Hz, 1H), 6.71 (d, *J* = 8.3 Hz, 1H), 5.71 (s, 1H), 5.59 (s, 1H), -0.00 (s, 18H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 153.5, 153.4, 143.0, 142.0, 140.2, 138.0, 136.7, 136.6, 136.5, 136.4, 136.1 (d, *J* = 4.1 Hz), 135.8, 135.2, 135.1, 135.0, 134.9, 134.5, 133.8, 132.8, 130.8, 130.7, 130.3, 130.2, 130.1 (d, *J* = 2.2 Hz),

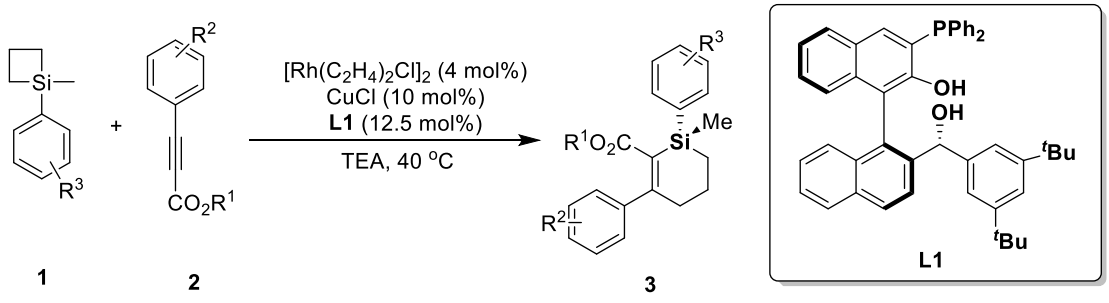
129.9, 129.8 (d, *J* = 2.2 Hz), 129.8, 129.4, 129.3, 128.4, 127.8, 127.5, 126.6, 126.0, 124.9, 118.6, 74.6, 0.0. ^{31}P NMR (162 MHz, Chloroform-*d*) δ -17.57; HRMS (ESI-TOF) m/z: [M+ Na]+ calculat*ed* for $C_{45}H_{45}NaO_2PSi_2$: 727.2588, found: 727.2590.



(*S*)-3-(bis(3,5-dimethylphenyl)phosphaneyl)-2'-((*R*)-(3,5-di-tert-butylphenyl) (hydroxy)methyl)-[1,1'-binaphthalen]-2-ol (L9):

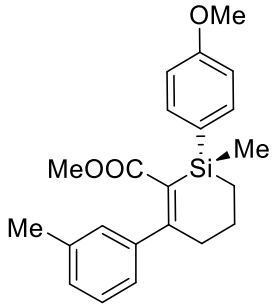
White Solid, mp 99 – 115 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.7 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.59 (dd, *J* = 13.7 Hz, 2H), 7.44-7.30 (m, 2H), 7.21-6.79 (m, 14H), 5.65 (s, 1H), 2.27 (d, *J* = 6.3 Hz, 1H), 2.20 (d, *J* = 5.3 Hz, 11H), 1.09 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 152.3, 150.4, 142.3, 141.9, 138.5, 138.4, 138.4, 138.3, 135.4, 135.4, 135.0, 133.5, 132.8, 131.8, 131.6, 131.6, 131.5, 131.4, 129.8, 129.6, 129.1, 129.1, 128.4, 128.3, 127.4, 126.7, 126.5, 126.3, 125.7, 125.2, 123.9, 121.0, 120.5, 117.9, 73.7, 34.9, 31.5, 21.5. ^{31}P NMR (162 MHz, Chloroform-*d*) δ -16.84; HRMS (ESI-TOF) m/z: [M+ Na]+ calculat*ed* for $C_{51}H_{53}NaO_2P$: 751.3675, found: 751.3665.

3.3. General procedure for the asymmetric version for the Rh/Cu-cocatalyzed (3+2) annulation of silacycles with internal alkynes.



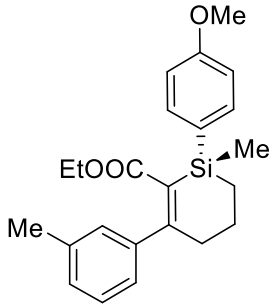
Silacyclobutane **1** (0.2 mmol), $[Rh(C_2H_4)_2Cl]_2$ (3.2 mg, 0.008 mmol), CuCl (2.0 mg,

0.02 mmol) and chiral Ar-BINMOL-Phos (**L1**) (16.8 mg, 0.025 mmol) in TEA (2 mL) was stirred at room temperature for 30 min. Then the substrate **2** (2.5 eq, 0.5 mmol) was added to the reaction mixture, and the reaction was stirred at 40 °C for 14 h. Upon reaction completion, the mixture was concentrated under reduced vacuum. The residue was purified by silica gel flash column chromatography (eluent: PE and EtOAc) to afford **3**. The *er* value was detected by chiral HPLC.



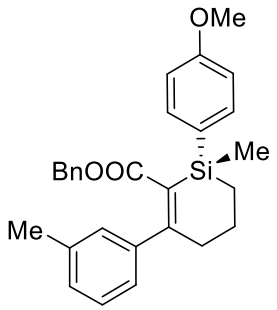
Methyl (*S*)-1-(4-methoxyphenyl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3a):

Yellow oil (38.1 mg, 52% yield),$[\alpha]_D^{25}$ = + 8.3 (c = 1.09, $CHCl_3$). Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 99:1, 0.8 mL/min, 254 nm, 80:20 *er*); major enantiomer t_r =9.558 min, minor enantiomer t_r =8.253 min.



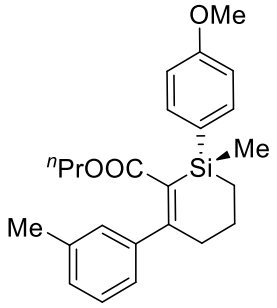
Ethyl (*S*)-1-(4-methoxyphenyl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3b):

Colorless oil (25.1 mg, 33% yield),$[\alpha]_D^{25}$ = + 14.6 (c = 0.67, $CHCl_3$). Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 99:1, 0.8 mL/min, 254 nm, 82:18 *er*); major enantiomer t_r =9.597 min, minor enantiomer t_r =8.538 min.



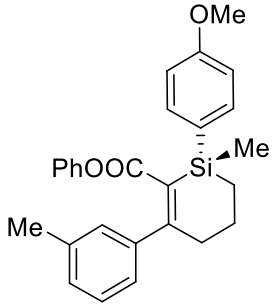
Benzyl (*S*)-1-(4-methoxyphenyl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3c):

Colorless oil (36.3 mg, 41% yield),$[\alpha]_D^{25}$ = + 5.6 (c = 0.97, $CHCl_3$). Enantiomeric excess was determined by HPLC with a Chiralpak OX-H column (hexanes: 2-propanol = 98:2, 0.8 mL/min, 254 nm, 82:18 *er*); major enantiomer t_r =10.021 min, minor enantiomer t_r =8.941 min.



Propyl (*S*)-1-(4-methoxyphenyl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3d):

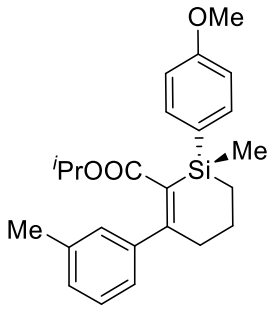
Colorless oil (23.7 mg, 30% yield),$[\alpha]_D^{25}$ = + 9.5 (c = 0.66, $CHCl_3$). Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 95:5, 0.8 mL/min, 254 nm, 83:17 *er*); major enantiomer t_r =6.401 min, minor enantiomer t_r =5.811 min.



Phenyl (*S*)-1-(4-methoxyphenyl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3e):

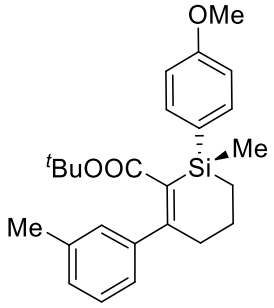
Colorless oil (30.0 mg, 35% yield),$[\alpha]_D^{25}$ = + 16.2 (c = 0.54, $CHCl_3$). Enantiomeric

excess was determined by HPLC with a Chiralpak OX-H column (hexanes: 2-propanol = 99:1, 0.5 mL/min, 254 nm, 85:15 *er*); major enantiomer t_r =13.431 min, minor enantiomer t_r =15.078 min.



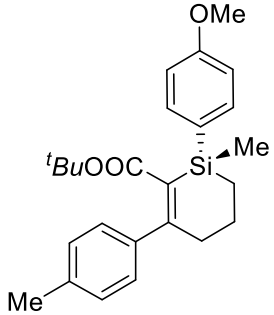
Isopropyl (*S*)-1-(4-methoxyphenyl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3f):

Colorless oil (37.9 mg, 48% yield),$[\alpha]_D^{25}$ = + 10.4 (c = 1.19, $CHCl_3$). Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 98:2, 0.8 mL/min, 254 nm, 86:14 *er*); major enantiomer t_r =9.165 min, minor enantiomer t_r =8.271 min.



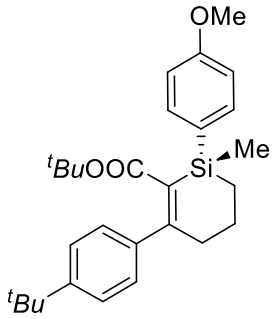
Tert-butyl (*S*)-1-(4-methoxyphenyl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3g):

Yellow oil (36.7 mg, 45% yield),$[\alpha]_D^{25}$ = + 9 (c = 0.91, $CHCl_3$). Enantiomeric excess was determined by HPLC with a Chiralpak OJ-H column (hexanes: 2-propanol = 95:5, 0.6 mL/min, 254 nm, 91:9 *er*); major enantiomer t_r =7.238 min, minor enantiomer t_r =11.427 min.



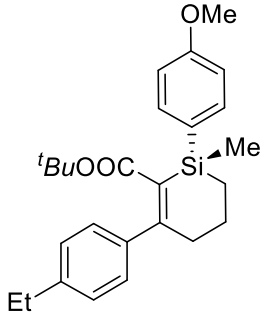
Tert-butyl (*S*)-1-(4-methoxyphenyl)-1-methyl-3-(p-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3h):

Yellow oil (44.5 mg, 52% yield),$[\alpha]_D^{25}$ = + 3.1 (c = 0.64, $CHCl_3$). Enantiomeric excess was determined by HPLC with a Chiralpak OJ-H column (hexanes: 2-propanol = 98:2, 0.8 mL/min, 254 nm, 87:13 *er*); major enantiomer t_r =14.725 min, minor enantiomer t_r =22.732 min.



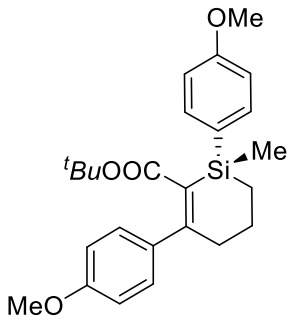
Tert-butyl (*S*)-3-(4-(tert-butyl)phenyl)-1-(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-carboxylate (3i):

Yellow oil (47.7 mg, 53% yield),$[\alpha]_D^{25}$ = + 11.7 (c = 0.44, $CHCl_3$). Enantiomeric excess was determined by HPLC with a Chiralpak OJ-H column (hexanes: 2-propanol = 99:1, 0.4 mL/min, 254 nm, 88:12 *er*); major enantiomer t_r =29.537 min, minor enantiomer t_r =42.964 min.



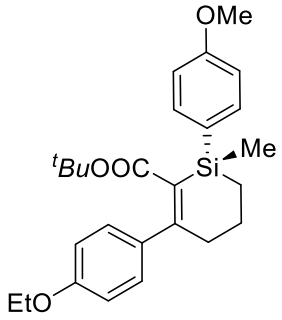
Tert-butyl (*S*)-3-(4-ethylphenyl)-1-(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-carboxylate (3j):

Yellow oil (45.6 mg, 54% yield),$[\alpha]_D^{25}$ = + 13.2 (c = 0.54, $CHCl_3$). Enantiomeric excess was determined by HPLC with a Chiralpak OJ-H column (hexanes: 2-propanol = 99:1, 0.4 mL/min, 254 nm, 87:13 *er*); major enantiomer t_r =45.383 min, minor enantiomer t_r =68.063 min.



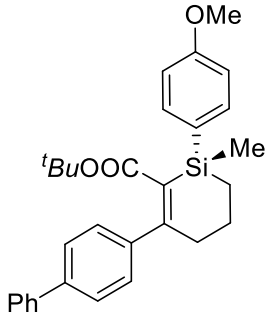
Tert-butyl (*S*)-1,3-bis(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-carboxylate (3k):

Colorless oil (36.5 mg, 43% yield),$[\alpha]_D^{25}$ = + 10.1 (c = 0.47, $CHCl_3$). Enantiomeric excess was determined by HPLC with a Chiralpak OJ-H column (hexanes: 2-propanol = 97:3, 0.6 mL/min, 254 nm, 86:14 *er*); major enantiomer t_r =13.998 min, minor enantiomer t_r =26.843 min.



Tert-butyl (*S*)-3-(4-ethoxyphenyl)-1-(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-carboxylate (3l):

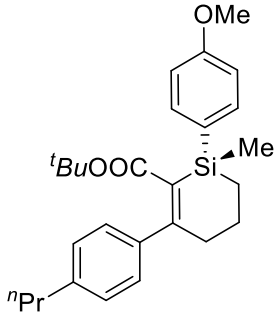
Colorless oil (44.7 mg, 51% yield),$[\alpha]_D^{25}$ = + 8.7 (c = 1.01, $CHCl_3$). Enantiomeric excess was determined by HPLC with a Chiralpak OJ-H column (hexanes: 2-propanol = 99:1, 0.6 mL/min, 254 nm, 94:6 *er*); major enantiomer t_r =16.134 min, minor enantiomer t_r =35.521 min.



Tert-butyl (*S*)-3-([1,1'-biphenyl]-4-yl)-1-(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-carboxylate (3m):

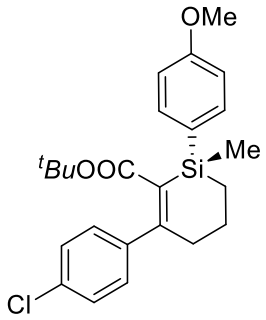
Yellow oil (45.2 mg, 48% yield),$[\alpha]_D^{25}$ = - 6.7 (c = 0.30, $CHCl_3$). Enantiomeric excess

was determined by HPLC with a Chiralpak OD-H + OD-H column (hexanes: 2-propanol = 98:2, 0.8 mL/min, 254 nm, 85:15 *er*); major enantiomer t_r =41.056 min, minor enantiomer t_r =45.257 min.



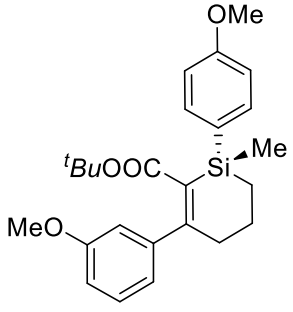
Tert-butyl (*S*)-1-(4-methoxyphenyl)-1-methyl-3-(4-propylphenyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3n):

Yellow oil (42.7 mg, 49% yield),$[\alpha]_D^{25}$ = + 2.3 (c = 0.55, $CHCl_3$). Enantiomeric excess was determined by HPLC with a Chiralpak OJ-H column (hexanes: 2-propanol = 99:1, 0.4 mL/min, 254 nm, 86:14 *er*); major enantiomer t_r =40.847 min, minor enantiomer t_r =59.647 min.



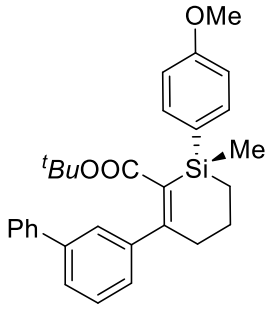
Tert-butyl (*S*)-3-(4-chlorophenyl)-1-(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-carboxylate (3o):

Light yellow oil (35.1 mg, 41% yield),$[\alpha]_D^{25}$ = + 10.5 (c = 0.33, $CHCl_3$). Enantiomeric excess was determined by HPLC with a Chiralpak OJ-H column (hexanes: 2-propanol = 99:1, 0.6 mL/min, 254 nm, 90:10 *er*); major enantiomer t_r =11.111 min, minor enantiomer t_r =26.919 min.



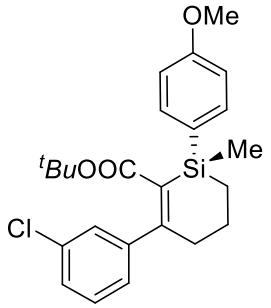
Tert-butyl (*S*)-3-(3-methoxyphenyl)-1-(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-carboxylate (3p):

Colorless oil (38.2 mg, 45% yield),$[\alpha]_D^{25}$ = + 2.3 (c = 0.65, $CHCl_3$). Enantiomeric excess was determined by HPLC with a Chiralpak OJ-H column (hexanes: 2-propanol = 99:1, 0.6 mL/min, 254 nm, 92:8 *er*); major enantiomer t_r =13.94 min, minor enantiomer t_r =29.795 min.



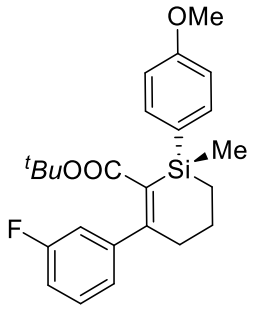
Tert-butyl (*S*)-3-([1,1'-biphenyl]-3-yl)-1-(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-carboxylate (3q):

Yellow oil (45.1 mg, 48% yield),$[\alpha]_D^{25}$ = + 2.84 (c = 0.58, $CHCl_3$). Enantiomeric excess was determined by HPLC with a Chiralpak OP-H column (hexanes: 2-propanol = 99:1, 0.6 mL/min, 254 nm, 86:14 *er*); major enantiomer t_r =21.172 min, minor enantiomer t_r =27.967 min.



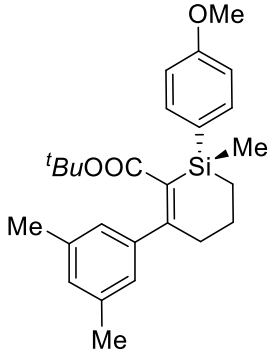
Tert-butyl (*S*)-3-(3-chlorophenyl)-1-(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-carboxylate (3r):

Colorless oil (19.7 mg, 23% yield),$[\alpha]_D^{25}$ = - 27 (c = 0.1, $CHCl_3$). Enantiomeric excess was determined by HPLC with a Chiralpak OJ-H column (hexanes: 2-propanol = 98:2, 0.6 mL/min, 254 nm, 87:13 *er*); major enantiomer t_r =9.685 min, minor enantiomer t_r =19.648 min.



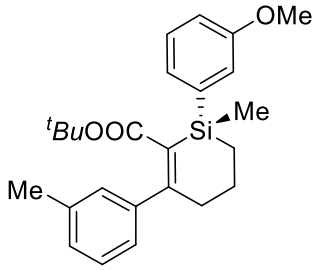
Tert-butyl (*S*)-3-(3-fluorophenyl)-1-(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-carboxylate (3s):

Yellow oil (20.6 mg, 25% yield),$[\alpha]_D^{25}$ = - 7.4 (c = 0.22, $CHCl_3$). Enantiomeric excess was determined by HPLC with a Chiralpak OJ-H column (hexanes: 2-propanol = 98:2, 0.6 mL/min, 254 nm, 87:13 *er*); major enantiomer t_r =9.112 min, minor enantiomer t_r =24.856 min.



Tert-butyl (*S*)-3-(3,5-dimethylphenyl)-1-(4-methoxyphenyl)-1-methyl-1,4,5,6-tetrahydrosiline-2-carboxylate (3t):

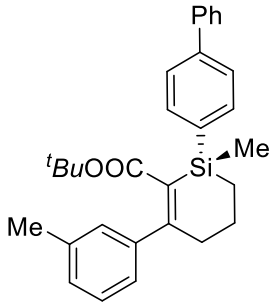
Yellow oil (38.0 mg, 45% yield),$[\alpha]_D^{25}$ = + 5.8 (c = 0.72, $CHCl_3$). Enantiomeric excess was determined by HPLC with a Chiralpak OJ-H column (hexanes: 2-propanol = 99:1, 0.4 mL/min, 254 nm, 90:10 *er*); major enantiomer t_r =43.165 min, minor enantiomer t_r =82.033 min.



Tert-butyl (*S*)-1-(3-methoxyphenyl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3u):

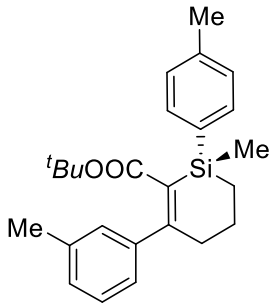
Colorless oil (22.1 mg, 27% yield), $[\alpha]_D^{25}$ = + 8.6 (c = 0.22, $CHCl_3$). Enantiomeric

excess was determined by HPLC with a Chiralpak OJ-H column (hexanes: 2-propanol = 98:2, 0.6 mL/min, 254 nm, 75:25 *er*); major enantiomer t_r =22.798 min, minor enantiomer t_r =30.510 min.



Tert-butyl (*S*)-1-([1,1'-biphenyl]-4-yl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3v):

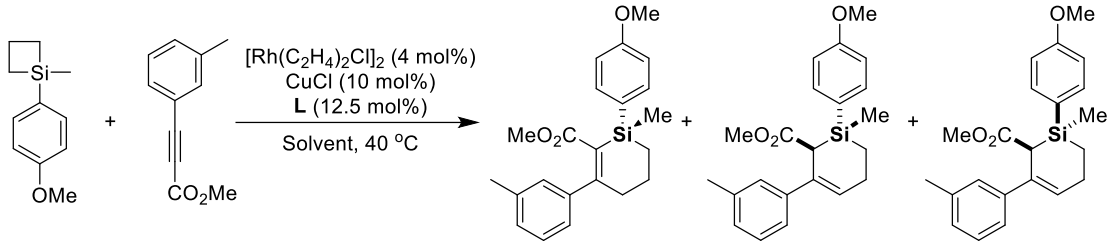
Colorless oil (37.2 mg, 41% yield), $[\alpha]_D^{25}$ = - 5.2 (c = 0.31, $CHCl_3$). Enantiomeric excess was determined by HPLC with a Chiralpak phenomenex column (hexanes: 2-propanol = 99:1, 0.8 mL/min, 254 nm, 84:16 *er*); major enantiomer t_r =5.662 min, minor enantiomer t_r =5.176 min.



Tert-butyl (*S*)-1-methyl-3-(m-tolyl)-1-(p-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylate (3w):

Colorless oil (24.3 mg, 31% yield), $[\alpha]_D^{25}$ = + 7.4 (c = 0.20, $CHCl_3$). Enantiomeric excess was determined by HPLC with a Chiralpak AD-H + OJ-H column (hexanes: 2-propanol = 99.5:0.5, 0.8 mL/min, 254 nm, 83:17 *er*); major enantiomer t_r =53.514 min, minor enantiomer t_r =60.933 min.

Table S7. The effect of chiral phosphoramidite ligands in this reaction.[a]

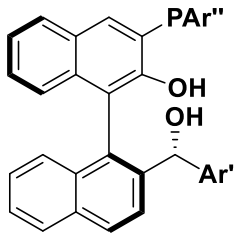


1a **2a** **3a** *anti*-**4a** *syn*-**4a**

Entry	Ligand	solvent	Con.(%)[b]	**3a**:**4a** (%)[b]	*dr* of **4a** (%)[b]	*er* of **3a** (%)[c]
1	**L1**	Tol	17	77:23	73:27	64:36
2	**L2**	Tol	25	63:37	69:31	62:38
3	**L3**	Tol	40	77:23	68:32	64:36
4	**L4**	Tol	36	59:41	55:45	56:44
5	**L5**	Tol	20	79:21	64:36	61:39
6	**L6**	Tol	24	72:68	70:30	64:36
7	**L7**	Tol	52	83:17	59:41	58:42
8	**L10**	Tol	< 5	/	/	67:33
9	**L11**	Tol	nr	/	/	/
10	**L12**	Tol	< 5	/	/	84:16
11	**L13**	Tol	nr	/	/	/
12	**L14**	Tol	nr	/	/	/
13	**L15**	Tol	< 5	/	/	50:50
14	**L16**	Tol	nr	/	/	/
15	**L17**	Tol	< 5	/	/	53:47
16	**L1**	TEA	54	100:0	/	80:20
17	**L2**	TEA	10	100:0	/	81:19
18	**L3**	TEA	9	100:0	/	81:19
19	**L4**	TEA	21	100:0	/	72:22
20	**L5**	TEA	11	100:0	/	81:19
21	**L6**	TEA	10	100:0	/	81:19
22	**L7**	TEA	13	100:0	/	67:33
23	**L8**	TEA	21	100:0	/	79:21
24	**L9**	TEA	56	100:0	/	80:20
25	**L10**	TEA	nr	/	/	/
26	**L11**	TEA	nr	/	/	/
27	**L12**	TEA	nr	/	/	/
28	**L13**	TEA	nr	/	/	/
29	**L14**	TEA	nr	/	/	/
30	**L15**	TEA	nr	/	/	/
31	**L16**	TEA	nr	/	/	/
32	**L17**	TEA	nr	/	/	/
33	**L18**	TEA	nr	/	/	/

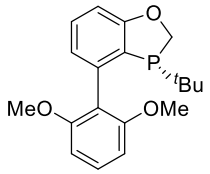
34	**L19**	TEA	nr	/	/	/
35	**L20**	TEA	nr	/	/	/

[a]All the reactions were run on a 0.2 mmol scale in 2.0 mL solvents for 14 h. [b]Determined by GC-MS. [c]*er* of **3a** was determined by chiral HPLC analysis.

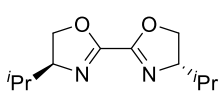


Ar-BINMOL-Phos

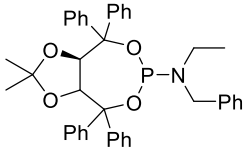
L1 Ar' = 3,5-(*t*-Bu)$_2$-Ph Ar''= Ph
L2 Ar' = 3,5-(C$_6$H$_5$)$_2$-Ph Ar'' = Ph
L3 Ar' = 3,5-(OMe)$_2$-Ph Ar''= Ph
L4 Ar' = 2-SiMe$_3$-Ph Ar'' = Ph
L5 Ar' = 3-OMe-Ph Ar'' = Ph
L6 Ar' = 4-Me-Ph Ar'' = Ph
L7 Ar' = naphthy Ar'' = Ph
L8 Ar' = 3,5-(SiMe$_3$)$_2$-Ph Ar'' = Ph
L9 Ar' = 3,5-(*t*-Bu)$_2$-Ph Ar'' = 3,5-Me-Ph



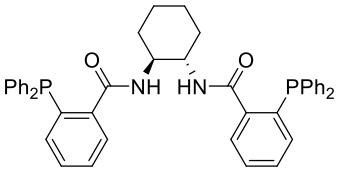
L10



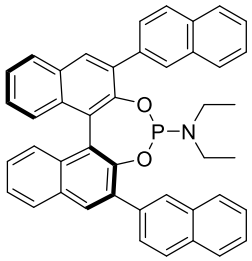
L11



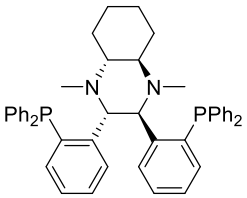
L12



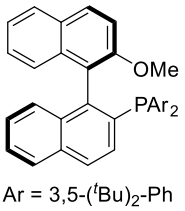
L13



L14

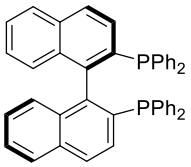


L15

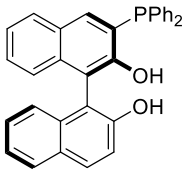


Ar = 3,5-(*t*Bu)$_2$-Ph

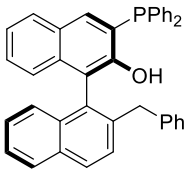
L16



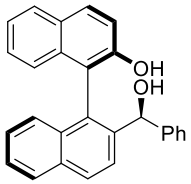
L17



L18

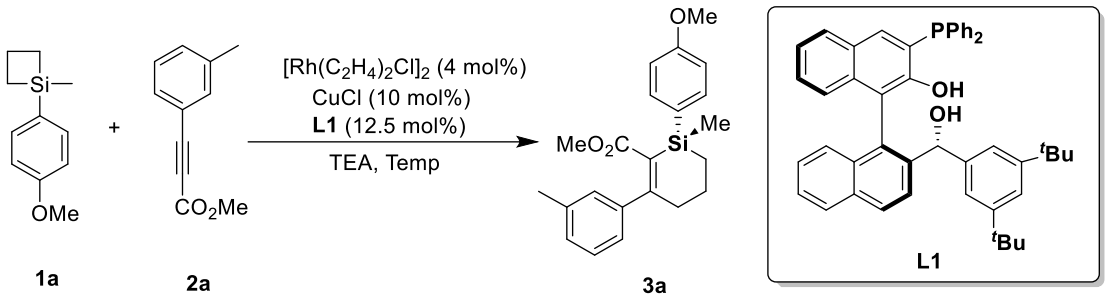


L19



L20

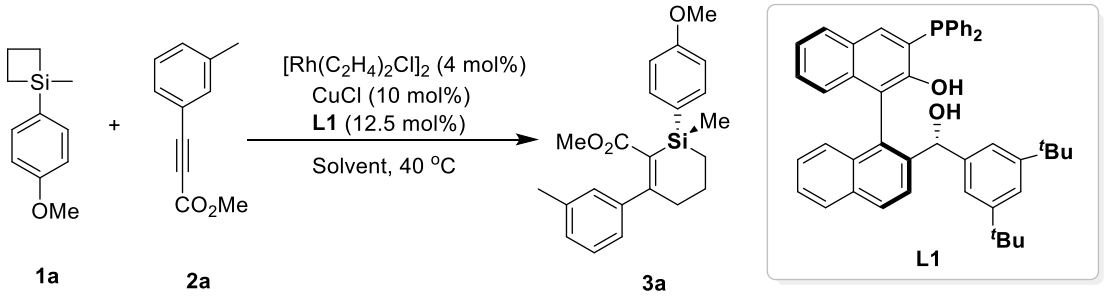
Table S8. The effect of temperature in this reaction.[a]



Entry	Temp	**3a** (%)[b]	*er* of **3a** (%)[c]
1	30	18	83:17
2	40	54	80:20
3	50	55	77:23
4	70	85	74:26

[a]All the reactions were run on a 0.2 mmol scale in 2.0 mL solvents for 14 h. [b]Determind by ^{1}H NMR. [c]*er* of **3a** was determined by chiral HPLC analysis.

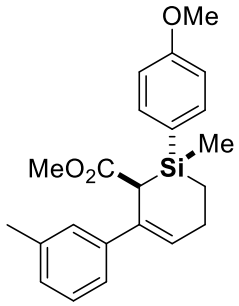
Table S9. Comparative Experiment.[a]



Entry	additive	Solvent	**3a** (%)[b]	*er* of **3a** (%)[c]
1[d]	Without CuCl	TEA	< 10% yield	/
2[e]	KOt-Bu	TEA	38	81:19
3[e]	KOt-Bu	Tol	nr	/

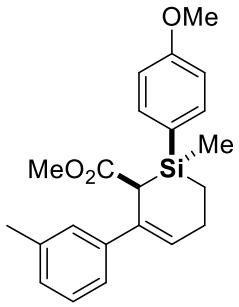
[a]All the reactions were run on a 0.2 mmol scale in 2.0 mL solvents for 14 h. [b]Determind by ^{1}H NMR. [c]*er* of **3a** was determined by chiral HPLC analysis. [d]Without CuCl. [e]KOt-Bu (12.5 mol%).

3.4. General procedure for the synthesis of 4a.



Methyl (1*R*,2*S*)-1-(4-methoxyphenyl)-1-methyl-3-(m-tolyl)-1,2,5,6-tetrahydrosiline-2-carboxylate (*anti*-4a):

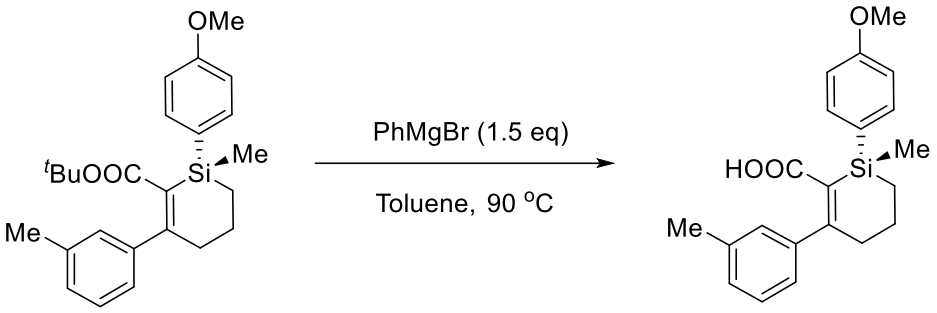
Yellow oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, J = 8.4 Hz, 2H), 7.20-7.07 (m, 3H), 7.02 (d, J = 7.4 Hz, 1H), 6.91 (d, J = 8.3 Hz, 2H), 6.34 (t, J = 4.9 Hz, 1H), 3.81 (s, 3H), 3.65 (s, 3H), 3.51 (s, 1H), 2.76-2.62 (m, 1H), 2.56-2.46 (m, 1H), 2.32 (s, 3H), 1.13-1.01 (m, 2H), 0.39 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.9, 161.0, 144.4, 137.9, 135.3, 134.7, 132.8, 128.3, 127.6, 126.7, 123.0, 114.0, 55.2, 51.7, 37.4, 23.2, 21.7, 7.5, -4.8. HRMS (ESI-TOF) m/z: [M+ Na]+ calculated for $C_{22}H_{26}NaO_3Si$: 389.1543, found: 389.1547.



Methyl (1*S*,2*S*)-1-(4-methoxyphenyl)-1-methyl-3-(m-tolyl)-1,2,5,6-tetrahydrosiline-2-carboxylate (*syn*-4a):

Yellow oil, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, J = 8.6 Hz, 2H), 7.20-7.10 (m, 3H), 7.03 (d, J = 7.2 Hz, 1H), 6.93 (d, J = 8.6 Hz, 2H), 6.34 (t, J = 4.8 Hz, 1H), 3.82 (s, 3H), 3.34 (s, 1H), 3.18 (s, 3H), 2.94-2.82 (m, 1H), 2.64-2.48 (m, 1H), 2.33 (s, 3H), 1.45-1.36 (m, 1H), 0.96-0.87 (m, 1H), 0.44 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.6, 161.1, 144.5, 137.9, 135.8, 134.4, 132.1, 128.3, 127.6, 126.8, 125.6, 123.0, 113.7, 55.2, 51.3, 38.8, 23.7, 21.7, 5.6, -4.3. HRMS (ESI-TOF) m/z: [M+ H]+ calculated for $C_{22}H_{27}O_3Si$: 367.1724, found: 367.1715.

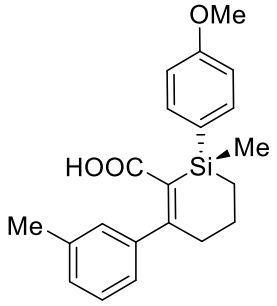
4. Downstream transformation of product 3g.



3g
91:9 *er*

5
68% yield, 91:9 *er*

Add toluene (0.1 mL) solution of **3g** (0.2 mol) to PhMgBr (1.5 eq, 0.3 mol) in toluene (0.1 mL). Reflux the mixture for 6 hours under N_2. After completion of the reaction, pour the mixture into 3% aqueous HCl at 0 °C. Extract the mixture with ethyl acetate. The residue was purified by silica gel flash column chromatography (eluent: PE /EA = 2/1) to afford **5**.



(*S*)-1-(4-methoxyphenyl)-1-methyl-3-(m-tolyl)-1,4,5,6-tetrahydrosiline-2-carboxylic acid (5):

White solid (23.9 mg, 68% yield),mp 112 - 118 °C; $[\alpha]_D^{25}$ = - 2.23 (c = 0.47, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 8.6 Hz, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 7.01-6.89 (m, 3H), 6.82 (d, *J* = 8.5 Hz, 2H), 3.73 (s, 3H), 2.58-2.40 (m, 2H), 2.22 (s, 3H), 1.96-1.80 (m, 2H), 1.01-0.92 (m, 1H), 0.84-0.75 (m, 1H), 0.43 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 175.8, 164.5, 160.8, 144.2, 137.9, 135.9, 128.8, 128.7, 128.2, 127.6, 127.2, 123.8, 113.7, 55.1, 37.3, 21.5, 21.2, 11.4, -3.3. HRMS (ESI-TOF) m/z: [M+ Na]+ calculate*d* for $C_{21}H_{24}NaO_3Si$:375.1387, found:375.1374. Enantiomeric excess was determined by HPLC with a Chiralpak OJ-H column (hexanes: 2-propanol = 90:10, 0.8 mL/min, 254 nm, 91:9 *er*); major enantiomer t_r =8.439 min, minor enantiomer t_r =15.628 min.

5. Supplementary Figures

Figure S1. NOESY spectrum of 3g. The determination of the structure of product 3g

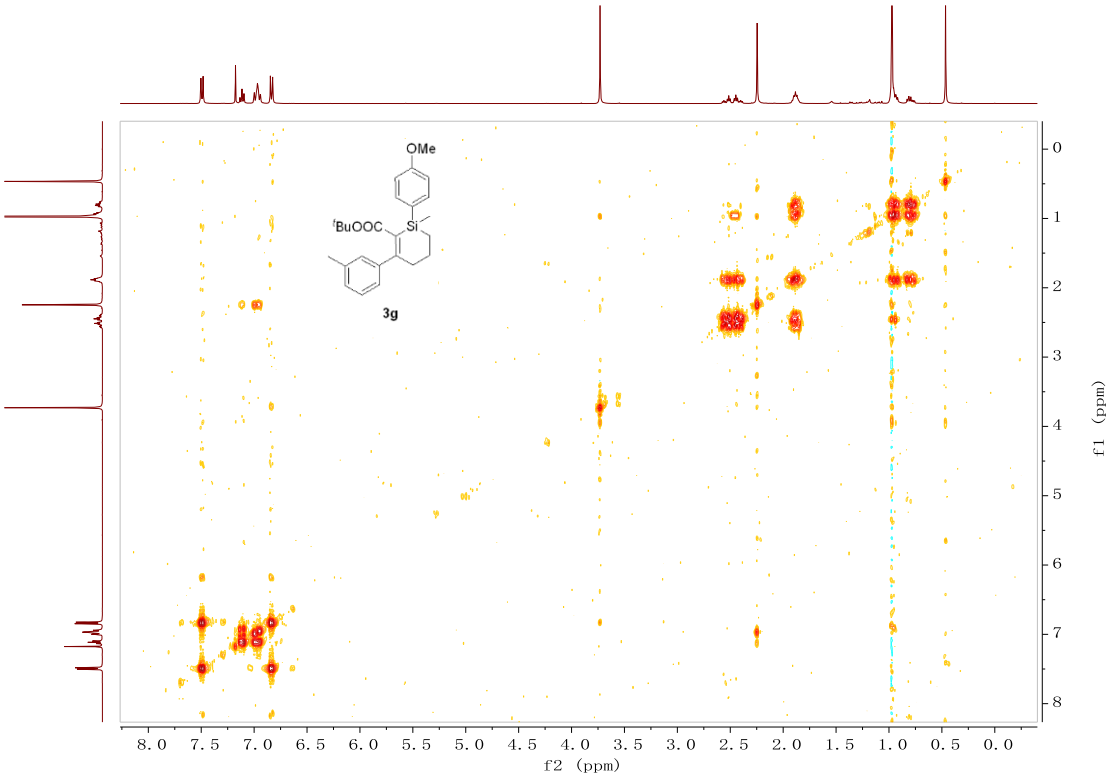
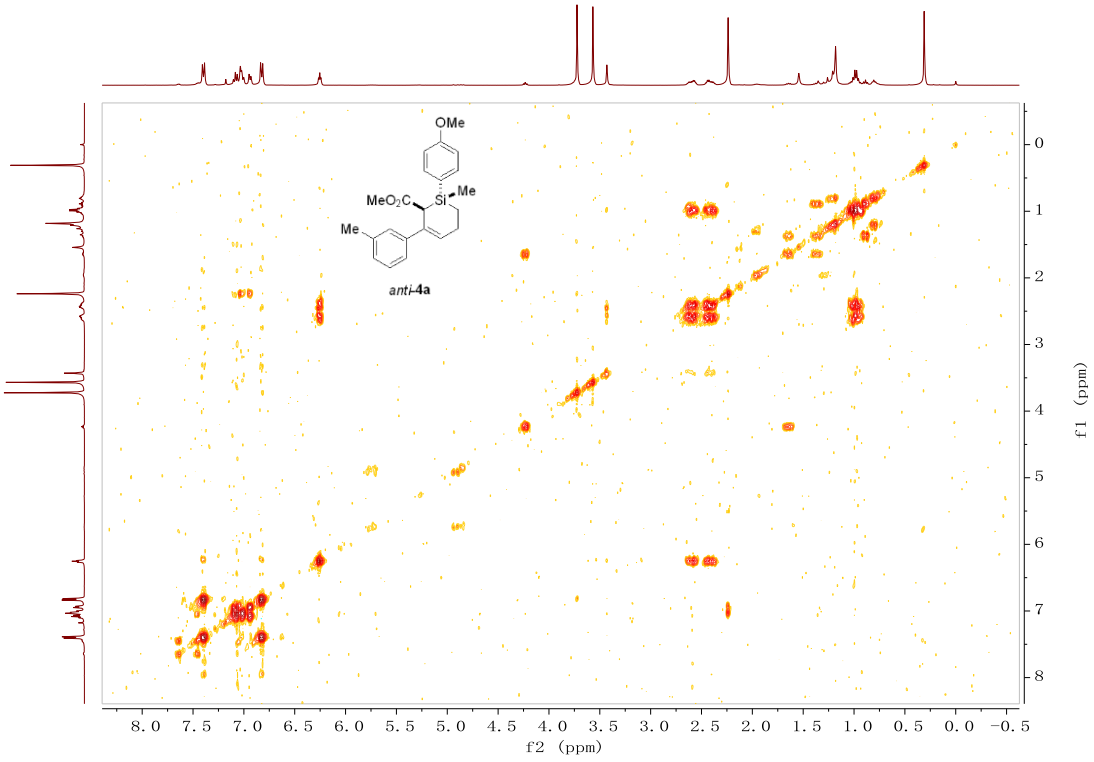


Figure S2. NOESY spectrum of *anti*-4a. The determination of the structure of product *anti*-4a

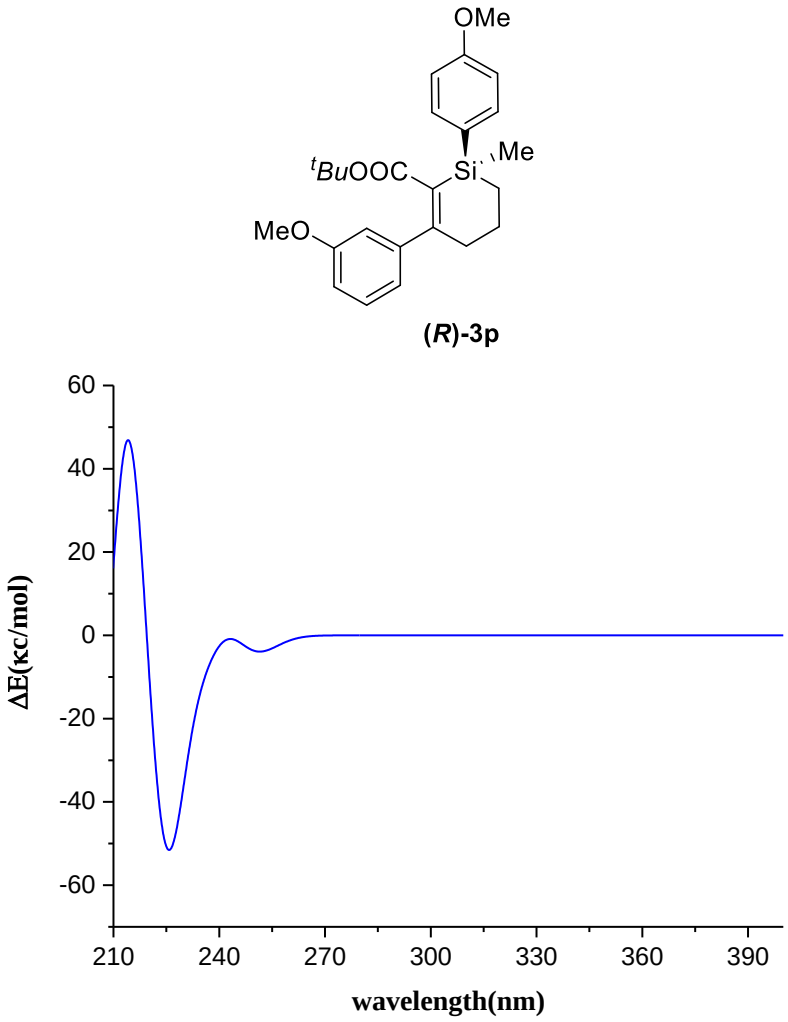


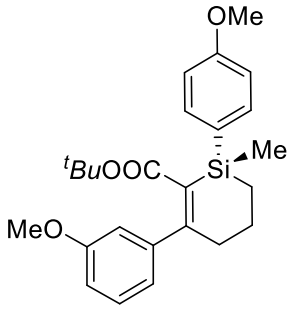
6. Determination of Absolute Configuration by ECD Experiments

ECD experiments: ECD spectra of **3g**, **3p** at a concentration of 1.0×10^{-3} M in acetonitrile, were recorded in a 1 mm pathlength quartz cuvette, using a MOS-450/AF Circular Dichroism Spectrometer (Bio-Logic, France). The experimental conditions were as follows: bandwidth, 1 nm; wavelength range, 200-600 nm; wavelength step size, 1 nm; time-per-point, 1.0 s; temperature, 25 ^{o}C. Acetonitrile was measured under the same conditions to obtain baseline.

ECD computations: Geometry optimization of the conformers were carried out in the framework of density functional theory (DFT) using the M06L hybrid density functional and 6-311G(d,p) basis set, IEFPCM in acetonitrile with Gaussian 09 (Gaussian Inc., Wallingford, CT). Frequency calculations were also carried out to confirm the geometries obtained were true minima of the potential energy surface by exhibiting no imaginary frequencies. Rotatory strengths in velocity form (Rvel) and length form (Rlen), oscillator strengths and excitation energies of the 30 lowest electronic transitions were calculated for each conformer employing time-dependent density functional theory (TD-DFT) at M06l/6-311G(d,p), IEFPCM in acetonitrile. Boltzmann-population-weighted composite ECD spectra were then generated with SpecDis.

Figure S3. DFT calculation for the ECD spectrum of chiral product 3p.




OMe
Me
tBuOOC
Si
MeO

(*S*)-3p

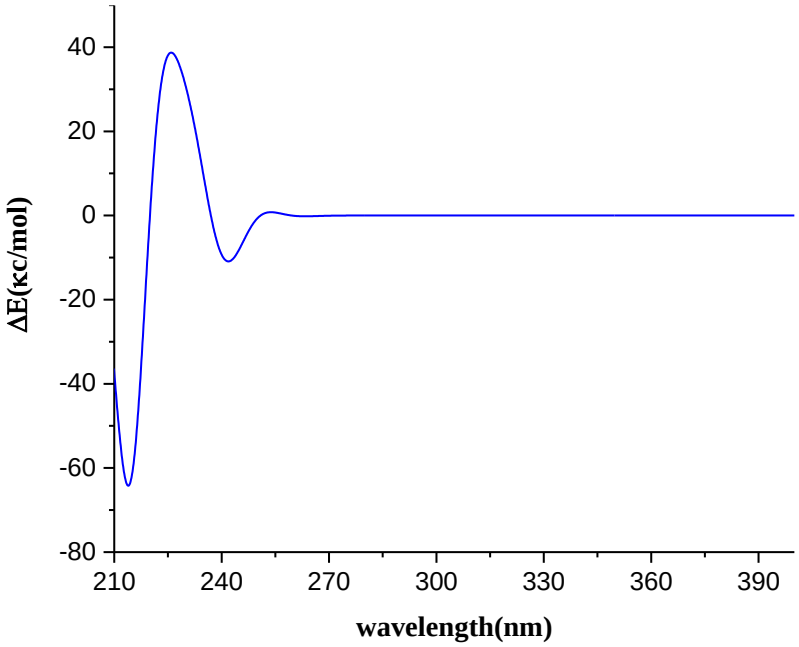

ΔE(κc/mol)
40
20
0
-20
-40
-60
-80
210
240
270
300
330
360
390
wavelength(nm)

Figure S4. Experimentally tested ECD spectrum of chiral product 3p (1.0×10^{-3} M) in CH_3CN.

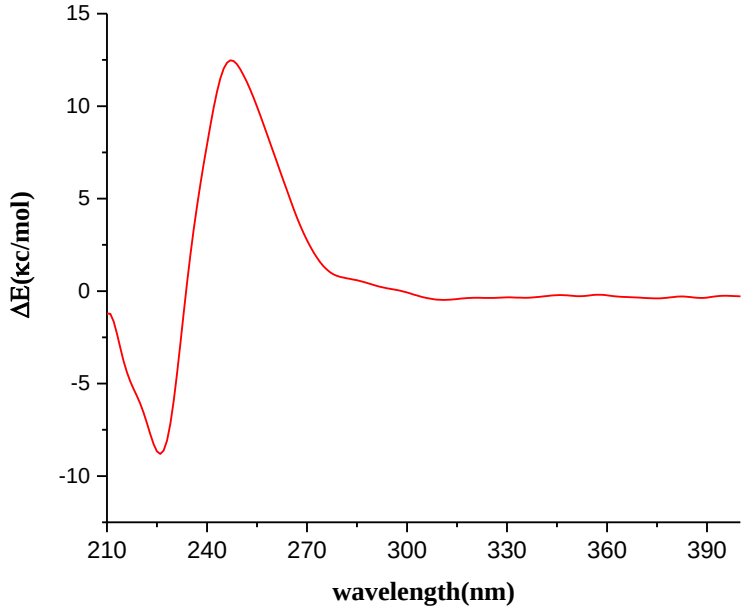


Figure S5. DFT calculation for the ECD spectrum of chiral product 3g.

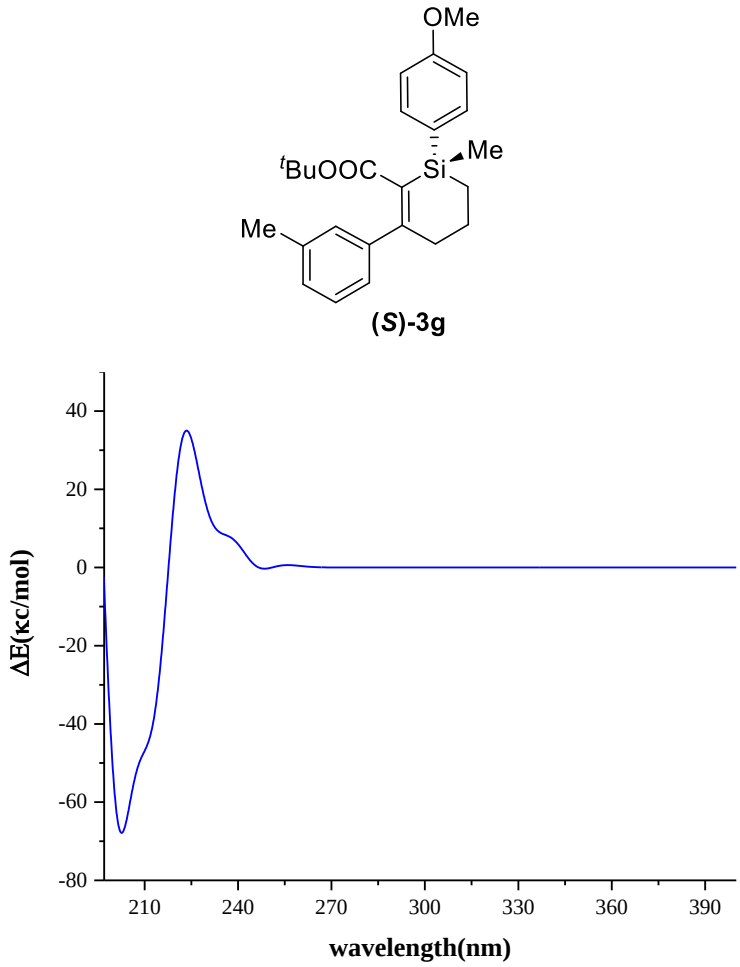
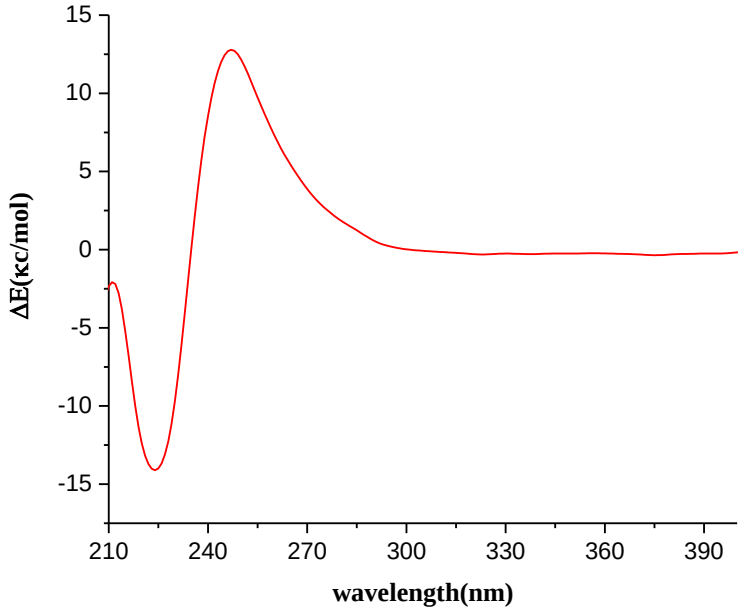


Figure S6. Experimentally tested ECD spectrum of chiral product 3g (1.0×10^{-3} M) in CH_3CN.



7. References

1. Zhen-Lei Song, et al. *Angew. Chem. Int. Ed.* **2019**, 58, 4695-4699.

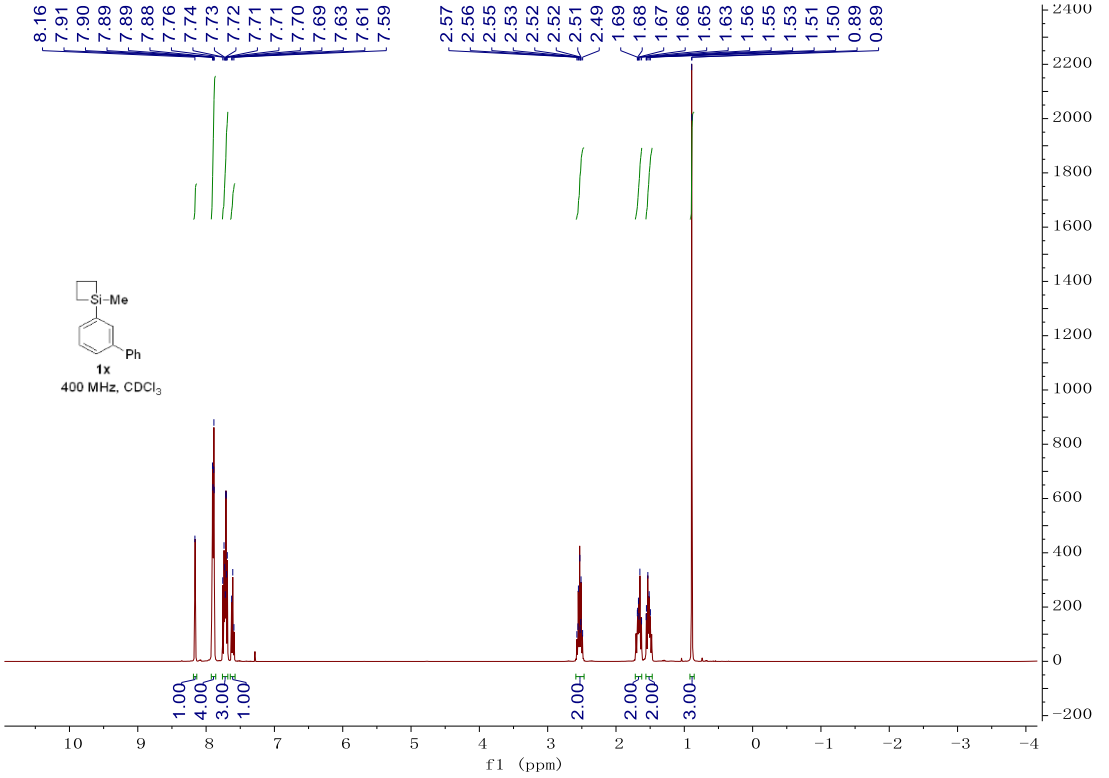
2.Webster L. Santos, et al. *J. Org. Chem*. **2018**, 83, 17, 10436-10444

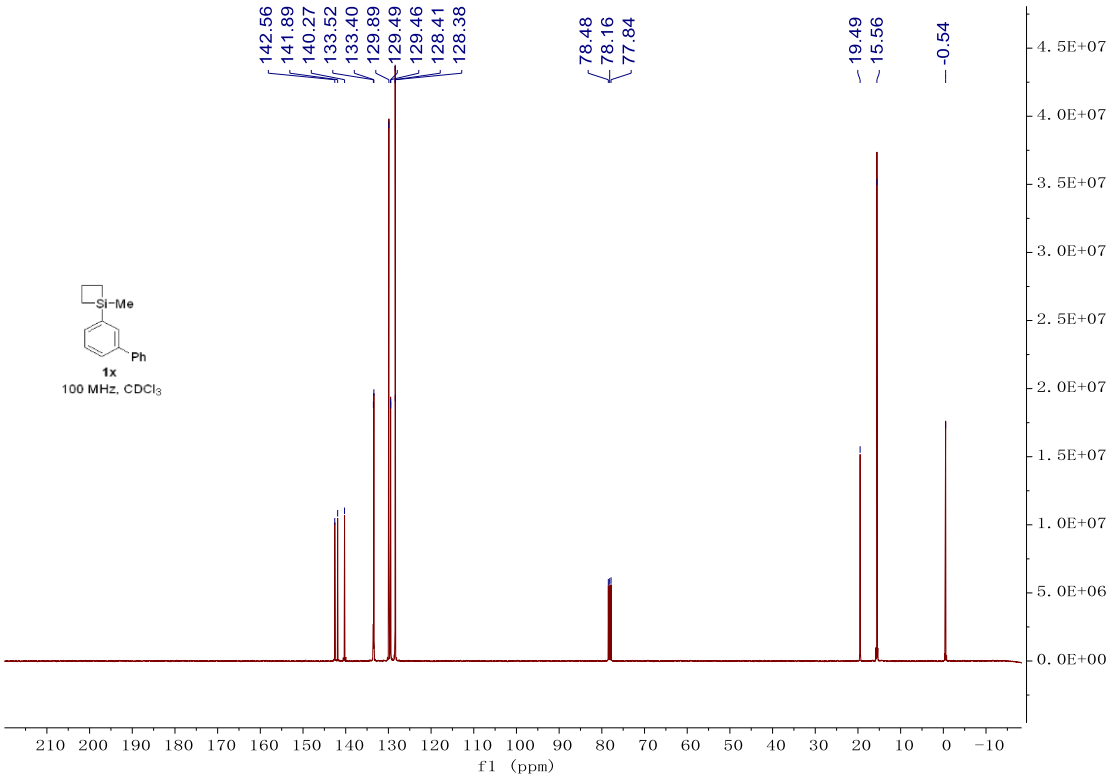
3. Eckert, Thomas, Ipaktschi, Junes, *Synthetic ommunications*. **1998**, 8, 327-335.

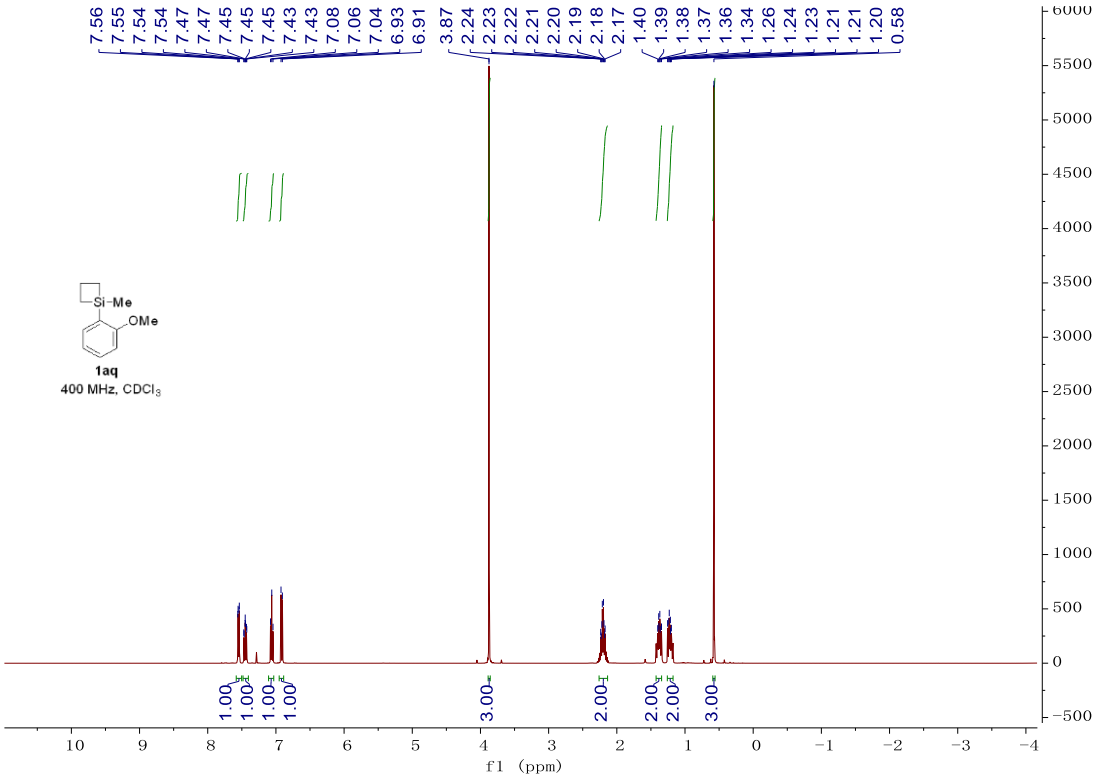
4. Yan-Hong He, et al. *Tetrahedron*. **2019**, 75, 130763

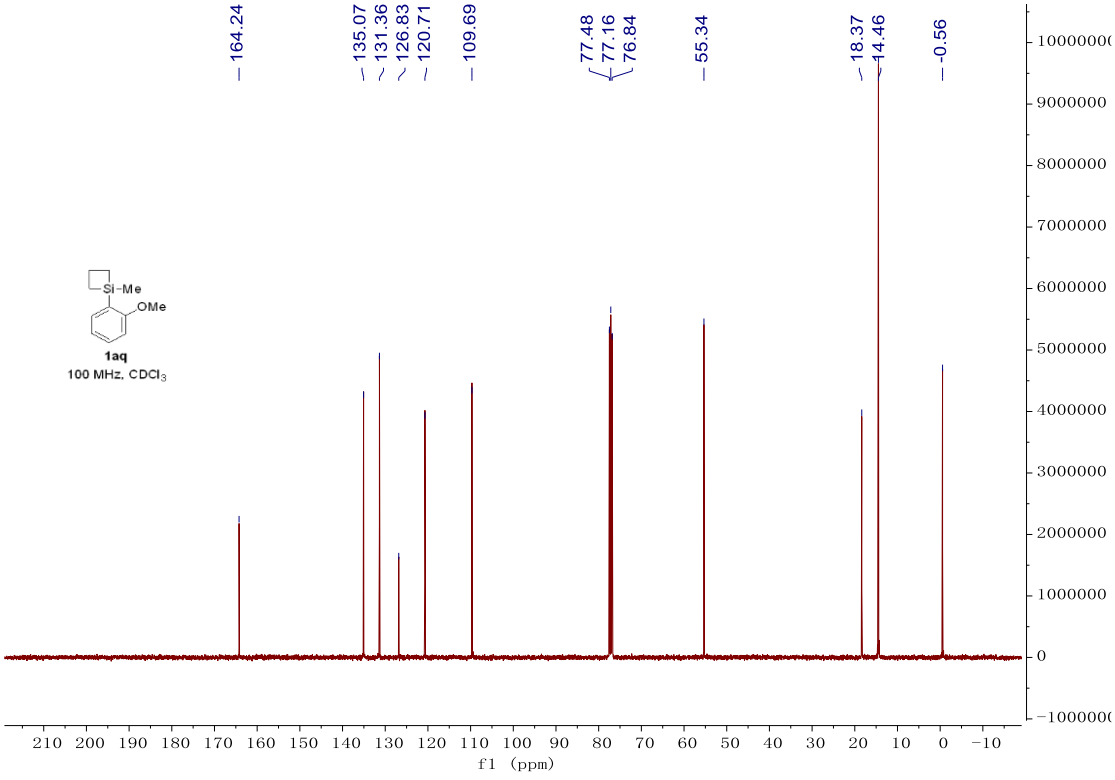
5. Li-Wen Xu, et al. *Org. Lett.* **2019**, 21, 4355–4358

8. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR Spectra






7.56
7.55
7.54
7.54
7.47
7.47
7.45
7.45
7.45
7.43
7.43
7.08
7.06
7.04
6.93
6.91
3.87
2.24
2.23
2.22
2.21
2.20
2.19
2.18
2.17
1.40
1.39
1.38
1.37
1.36
1.34
1.26
1.24
1.23
1.21
1.21
1.20
0.58
Si-Me
OMe
1aq
400 MHz, CDCl3
1.00
1.00
1.00
1.00
3.00
2.00
2.00
2.00
3.00
f1 (ppm)


164.24
135.07
131.36
126.83
120.71
109.69
77.48
77.16
76.84
55.34
18.37
14.46
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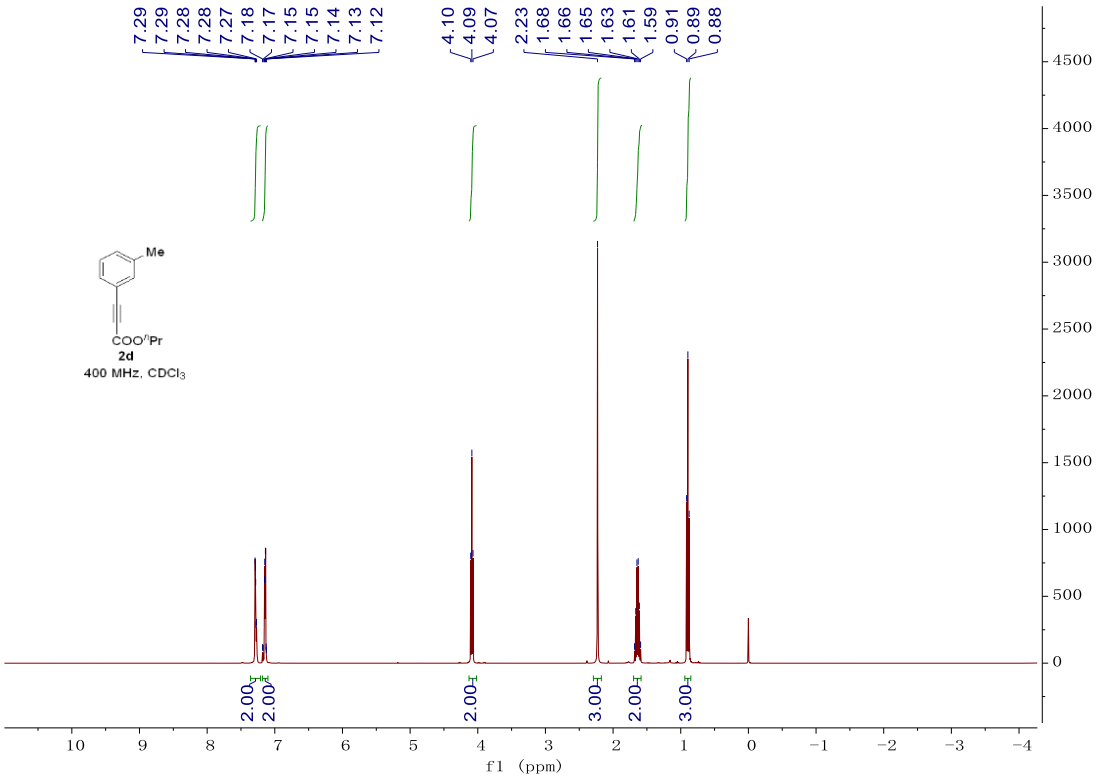
Si-Me
OMe
1aq
100 MHz, CDCl3
f1 (ppm)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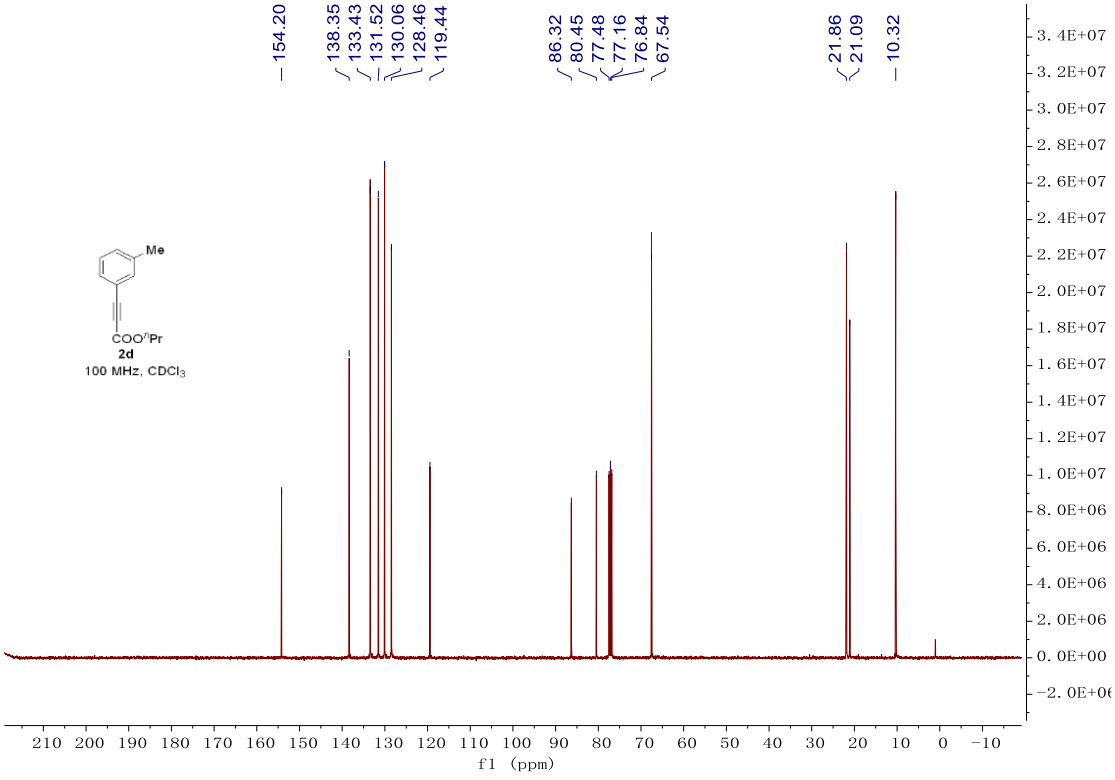
7.28
7.27
7.18
7.17
7.15
7.15
7.14
7.13
7.12
4.10
4.09
4.07
2.23
1.68
1.66
1.65
1.63
1.61
1.59
0.91
0.89
0.88
Me
COO^{n}Pr
2d
400 MHz, CDCl$_3$
2.00
2.00
2.00
3.00
2.00
3.00
f1 (ppm)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128.46
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86.32
80.45
77.48
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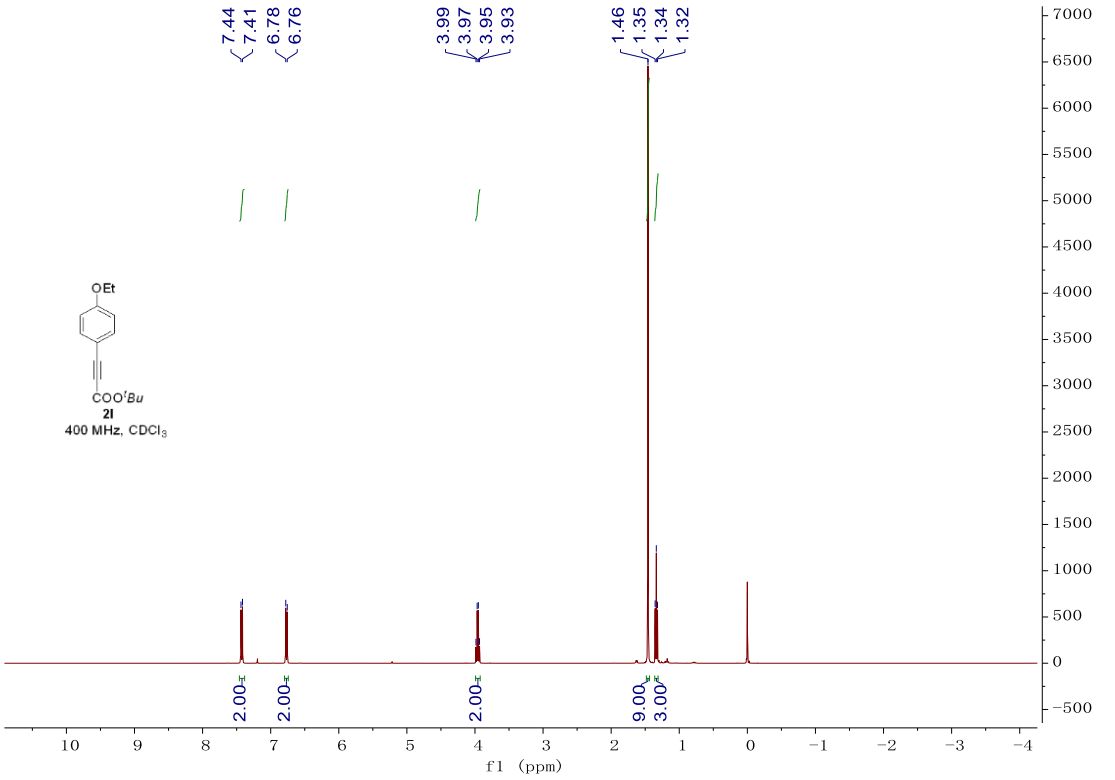
21.86
21.09
10.32
Me
COO^{n}Pr
2d
100 MHz, CDCl$_3$
f1 (ppm)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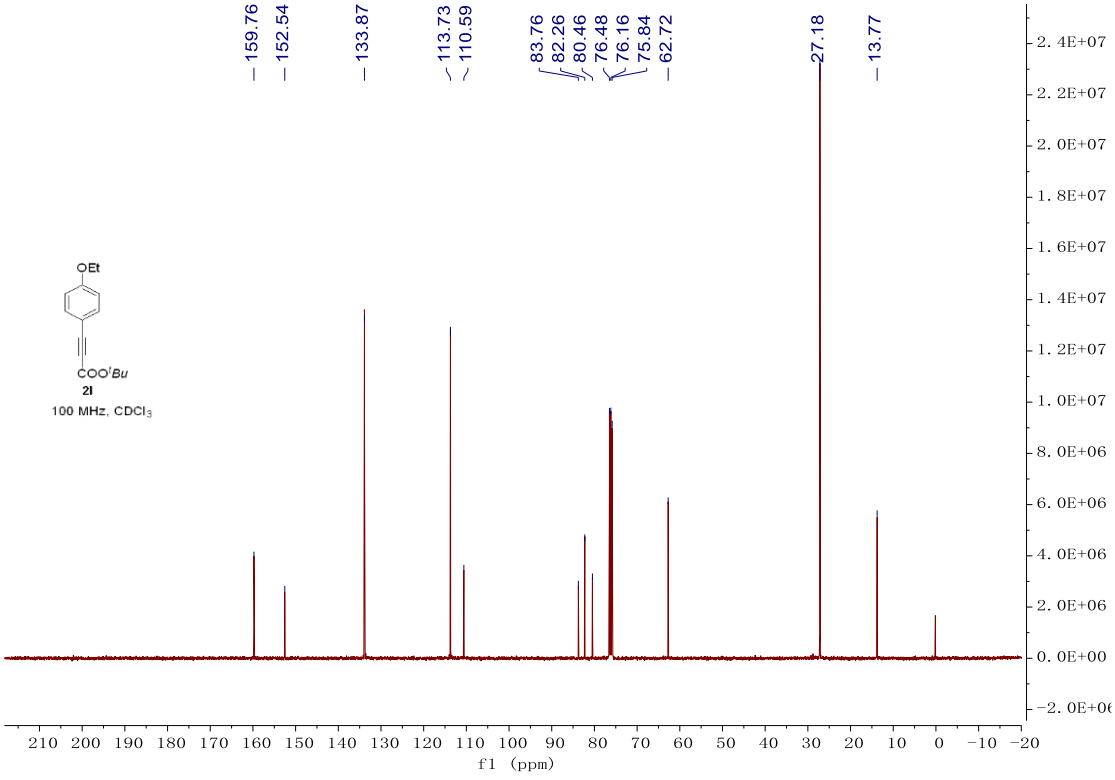
7.41
6.78
6.76
3.99
3.97
3.95
3.93
1.46
1.35
1.34
1.32
OEt
COO'Bu
2l
400 MHz, CDCl3
2.00
2.00
2.00
9.00
3.00
f1 (ppm)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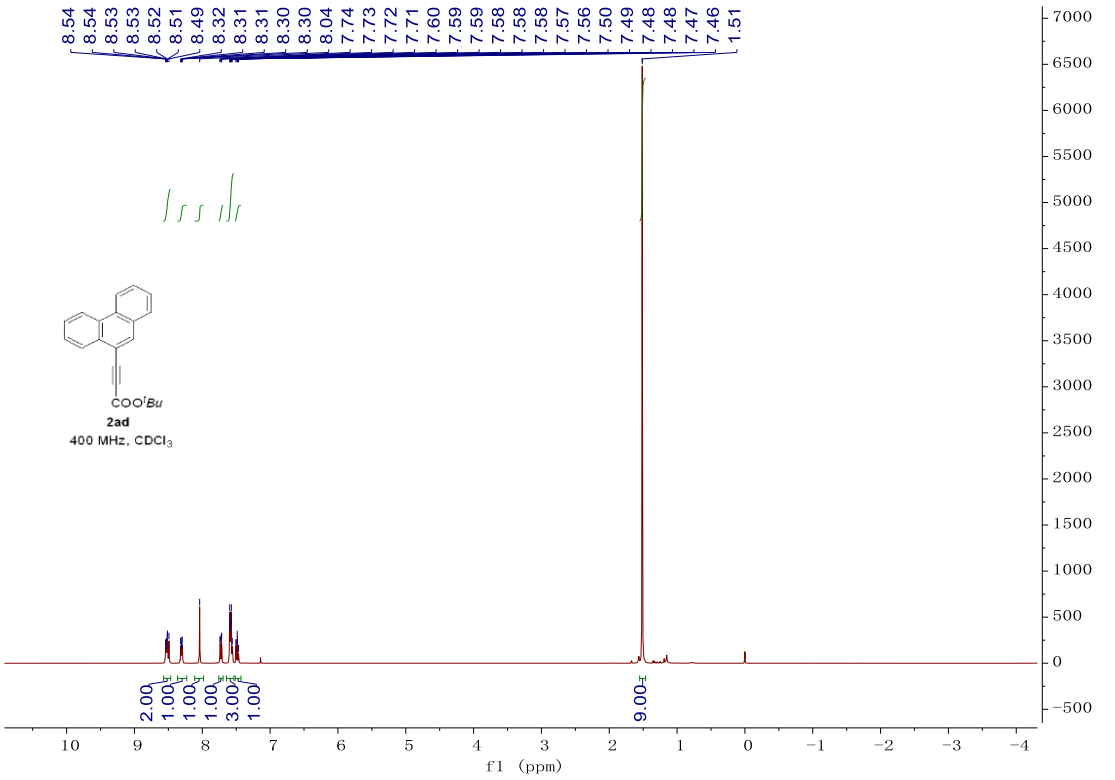
COO'Bu
2l
100 MHz, CDCl3
f1 (ppm)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8.52
8.51
8.49
8.32
8.31
8.31
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8.30
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7.73
7.72
7.71
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7.59
7.58
7.58
7.58
7.57
7.56
7.50
7.49
7.48
7.48
7.47
7.46
1.51
COO^{t}Bu
2ad
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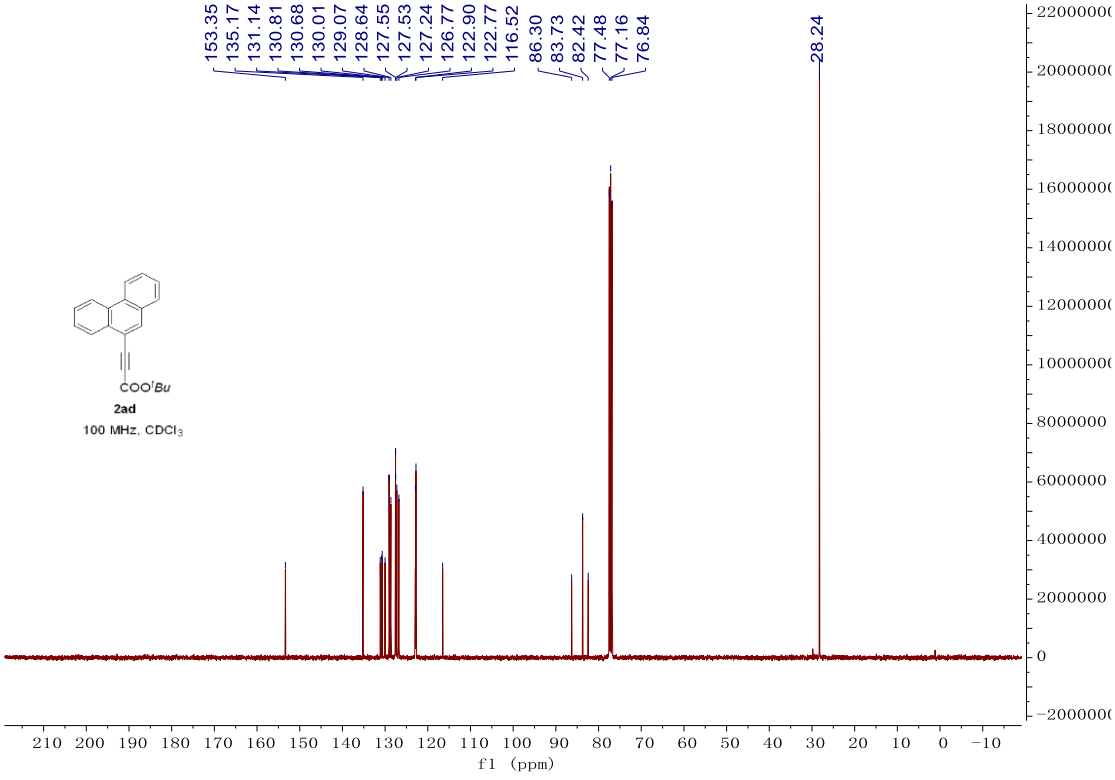
1.00
3.00
1.00
9.00
f1 (ppm)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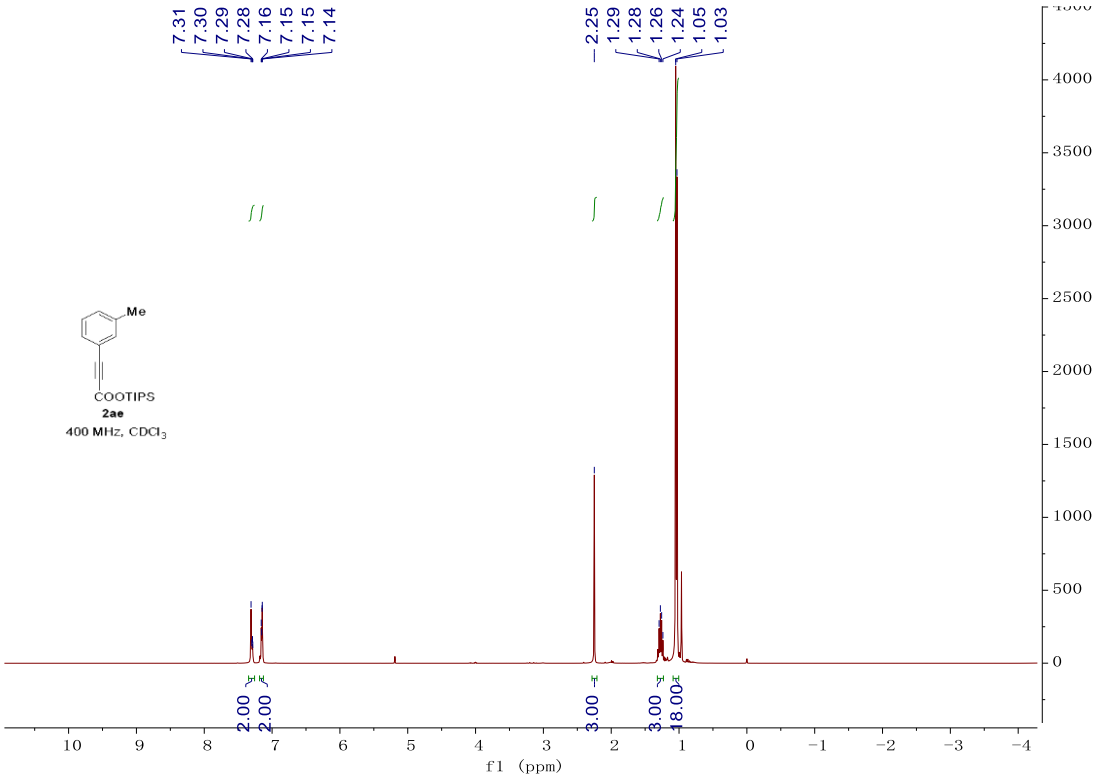
100 MHz, CDCl$_3$
f1 (ppm)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7.30
7.29
7.28
7.16
7.15
7.15
7.14
2.25
1.29
1.28
1.26
1.24
1.05
1.03
Me
COOTIPS
2ae
400 MHz, CDCl3
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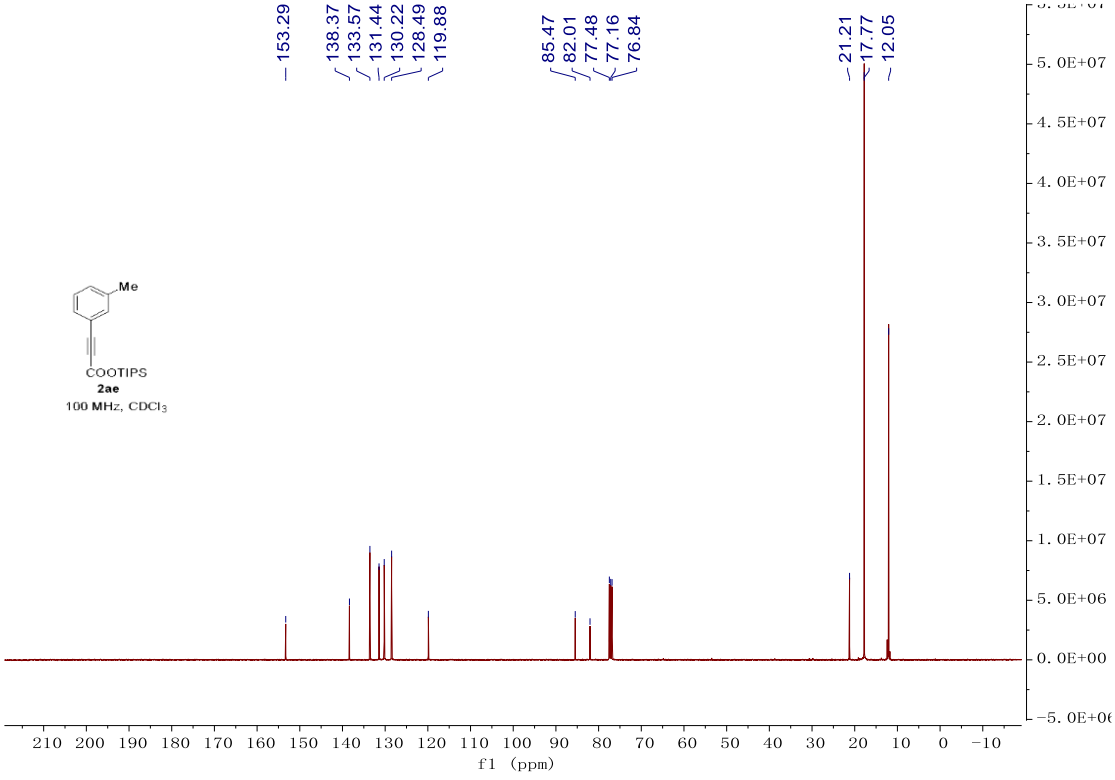
3.00
18.00
f1 (ppm)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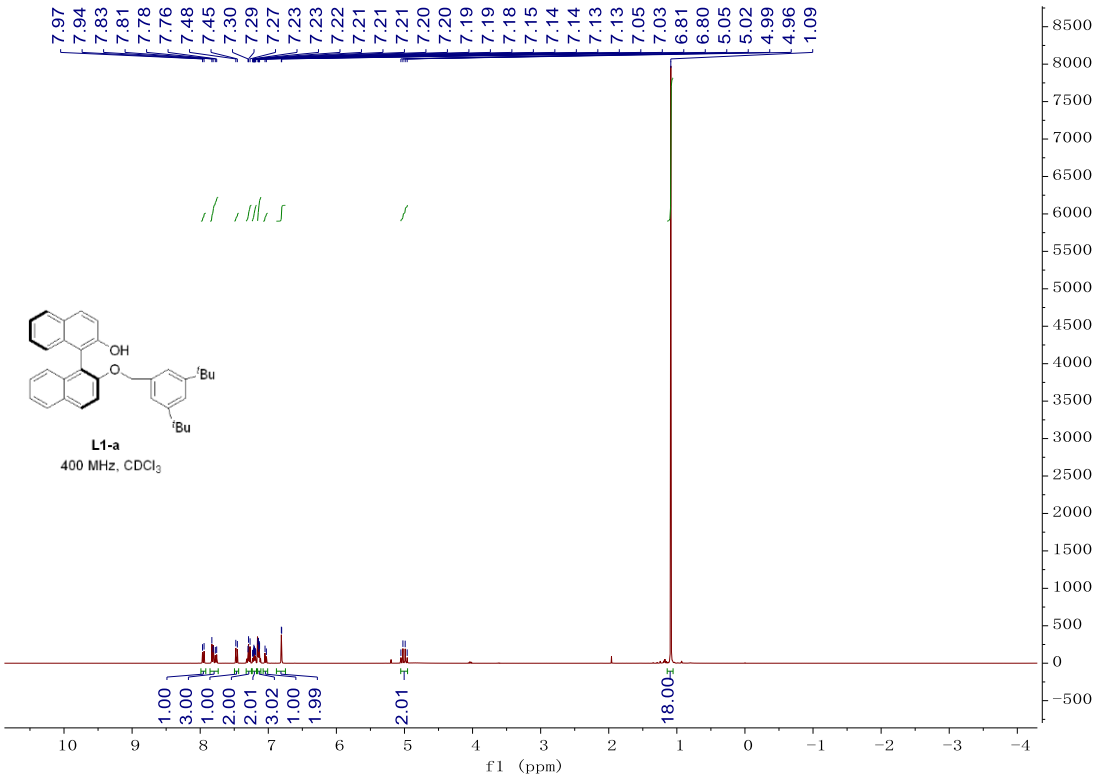
COOTIPS
2ae
100 MHz, CDCl3
f1 (ppm)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7.45
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7.23
7.22
7.21
7.21
7.21
7.20
7.20
7.19
7.19
7.18
7.15
7.14
7.14
7.13
7.13
7.05
7.03
6.81
6.80
5.05
5.02
4.99
4.96
1.09
OH
O
tBu
tBu
L1-a
400 MHz, CDCl3
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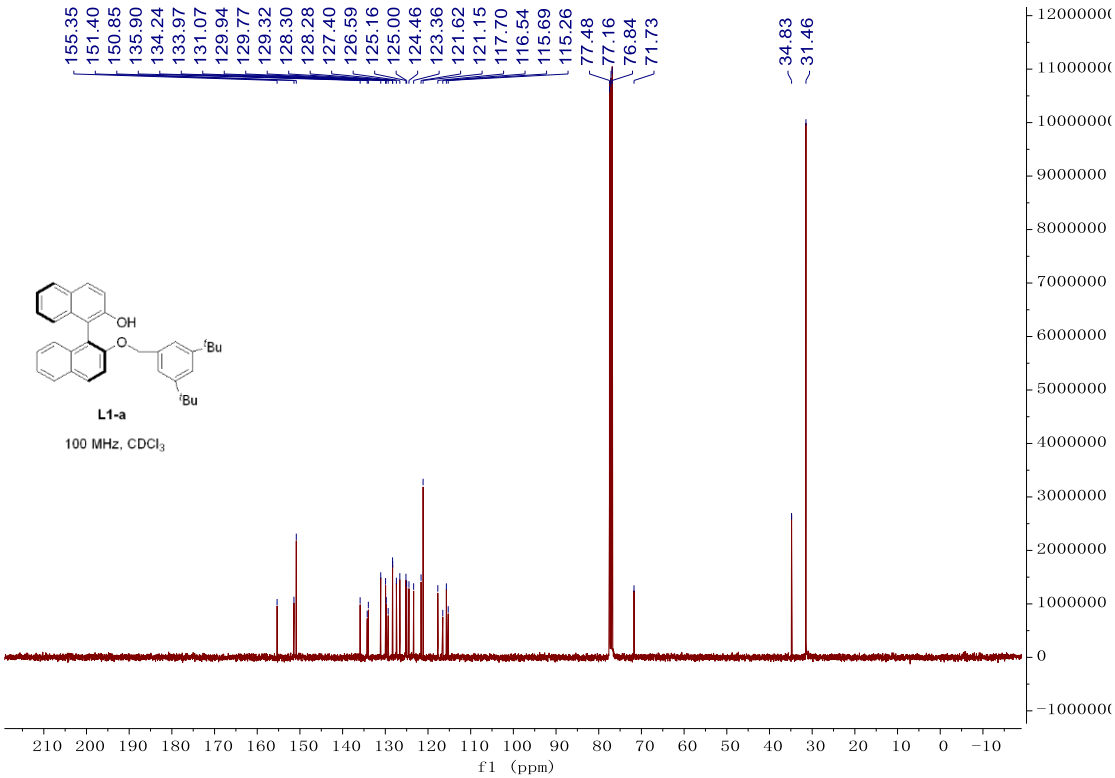
3.02
1.00
1.99
2.01
18.00
f1 (ppm)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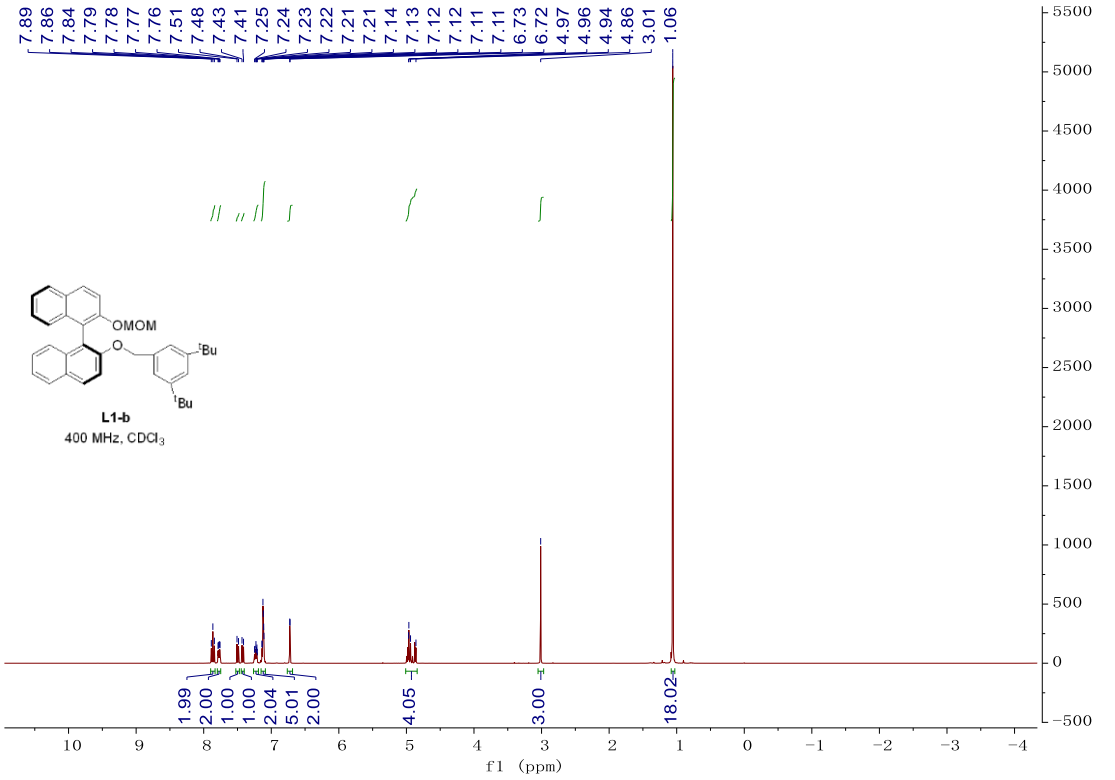
125.16
125.00
124.46
123.36
121.62
121.15
117.70
116.54
115.69
115.26
77.48
77.16
76.84
71.73
34.83
31.46
OH
O
tBu
tBu
L1-a
100 MHz, CDCl3
f1 (ppm)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7.22
7.21
7.21
7.14
7.13
7.12
7.12
7.11
7.11
6.73
6.72
4.97
4.96
4.94
4.86
3.01
1.06
OMOM
tBu
tBu
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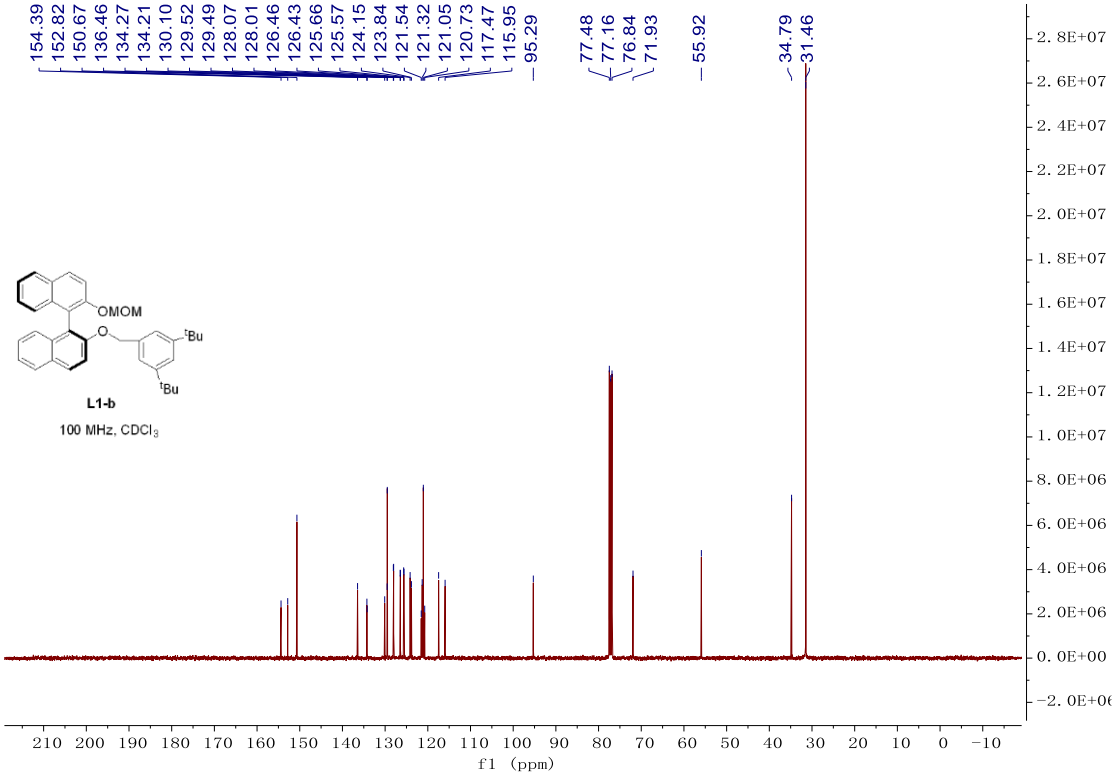
400 MHz, CDCl3
1.99
2.00
1.00
1.00
2.04
5.01
2.00
4.05
3.00
18.02
f1 (ppm)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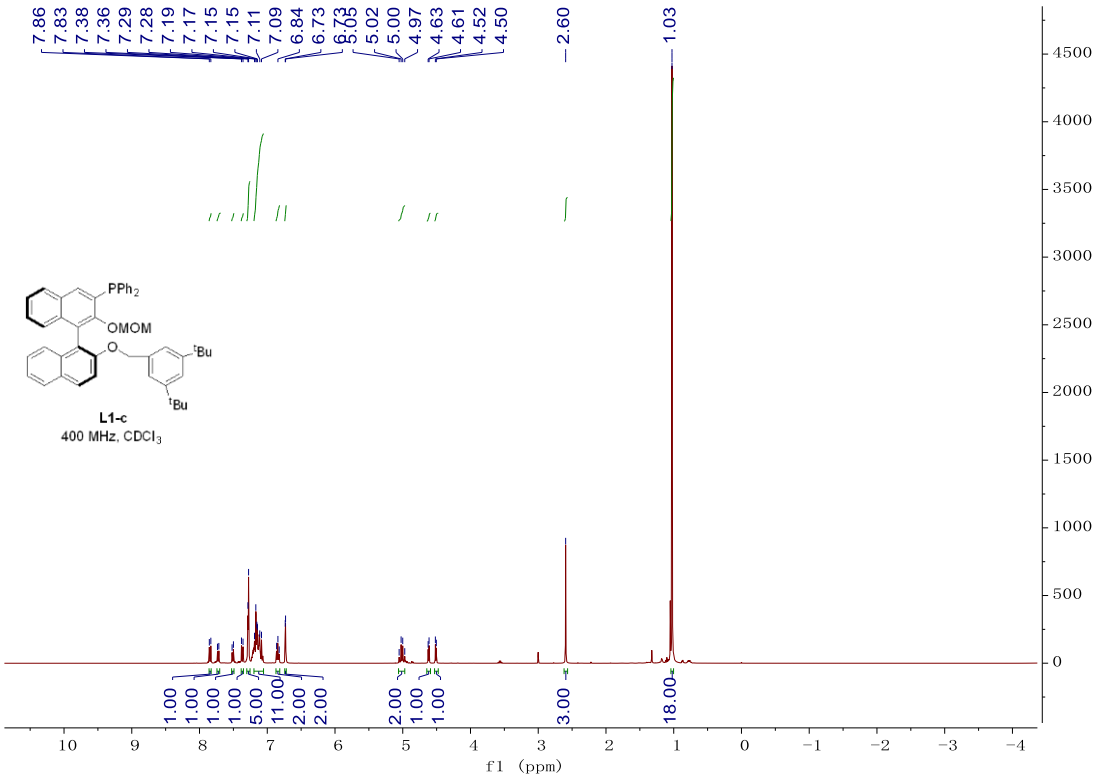
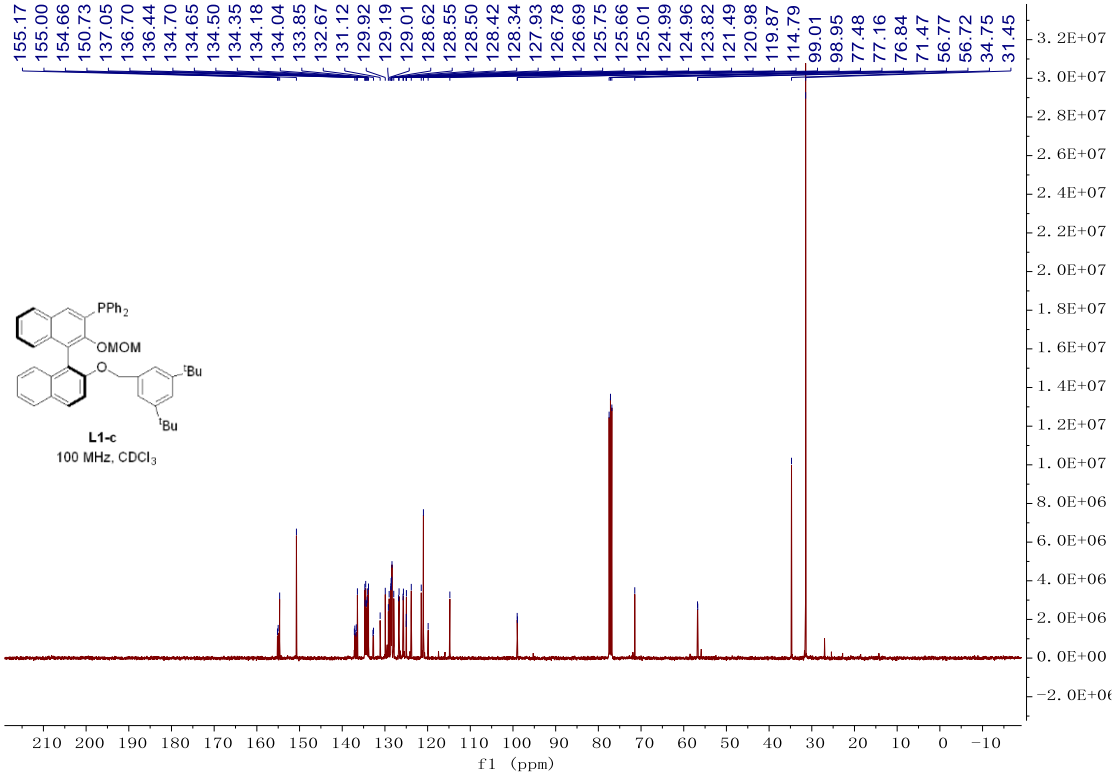
152.82
150.67
136.46
134.27
134.21
130.10
129.52
129.49
128.07
128.01
126.46
126.43
125.66
125.57
124.15
123.84
121.54
121.32
121.05
120.73
117.47
115.95
95.29
77.48
77.16
76.84
71.93
55.92
34.79
31.46
OMOM
tBu
tBu
L1-b
100 MHz, CDCl3
f1 (ppm)


7.86
7.83
7.38
7.36
7.29
7.28
7.19
7.17
7.15
7.15
7.11
7.09
6.84
6.73
6.73
5.05
5.02
5.00
4.97
4.63
4.61
4.52
4.50
2.60
1.03
PPh2
OMOM
tBu
tBu
L1-c
400 MHz, CDCl3
1.00
1.00
1.00
1.00
5.00
11.00
2.00
2.00
2.00
1.00
1.00
3.00
18.00
f1 (ppm)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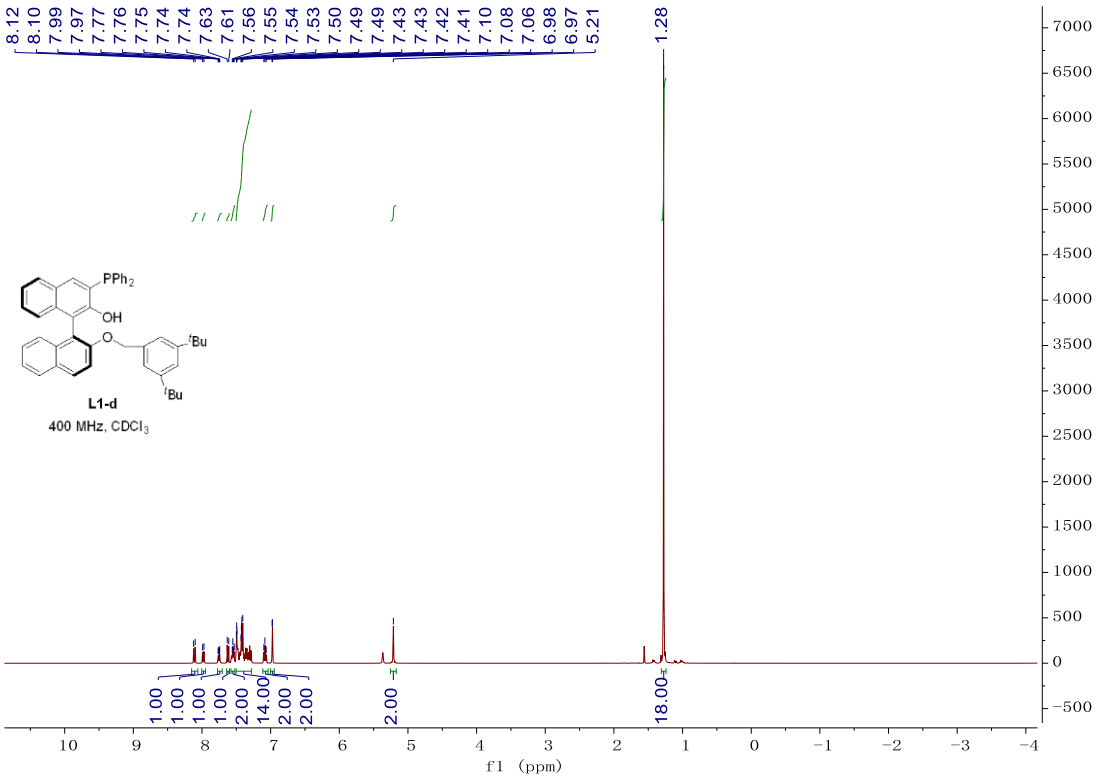
134.70
134.65
134.50
134.35
134.18
134.04
133.85
132.67
131.12
129.92
129.19
129.01
128.62
128.55
128.50
128.42
128.34
127.93
126.78
126.69
125.75
125.66
125.01
124.99
124.96
123.82
121.49
120.98
119.87
114.79
99.01
98.95
77.48
77.16
76.84
71.47
56.77
56.72
34.75
31.45
PPh2
OMOM
tBu
tBu
L1-c
100 MHz, CDCl3
f1 (ppm)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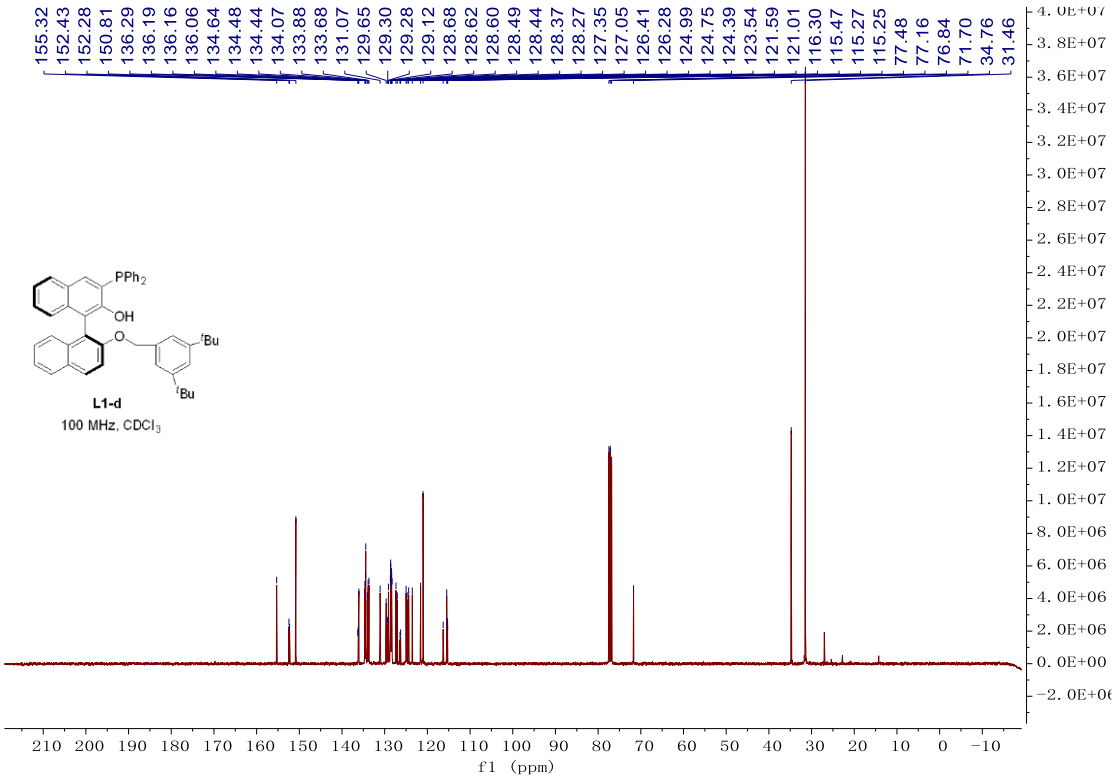
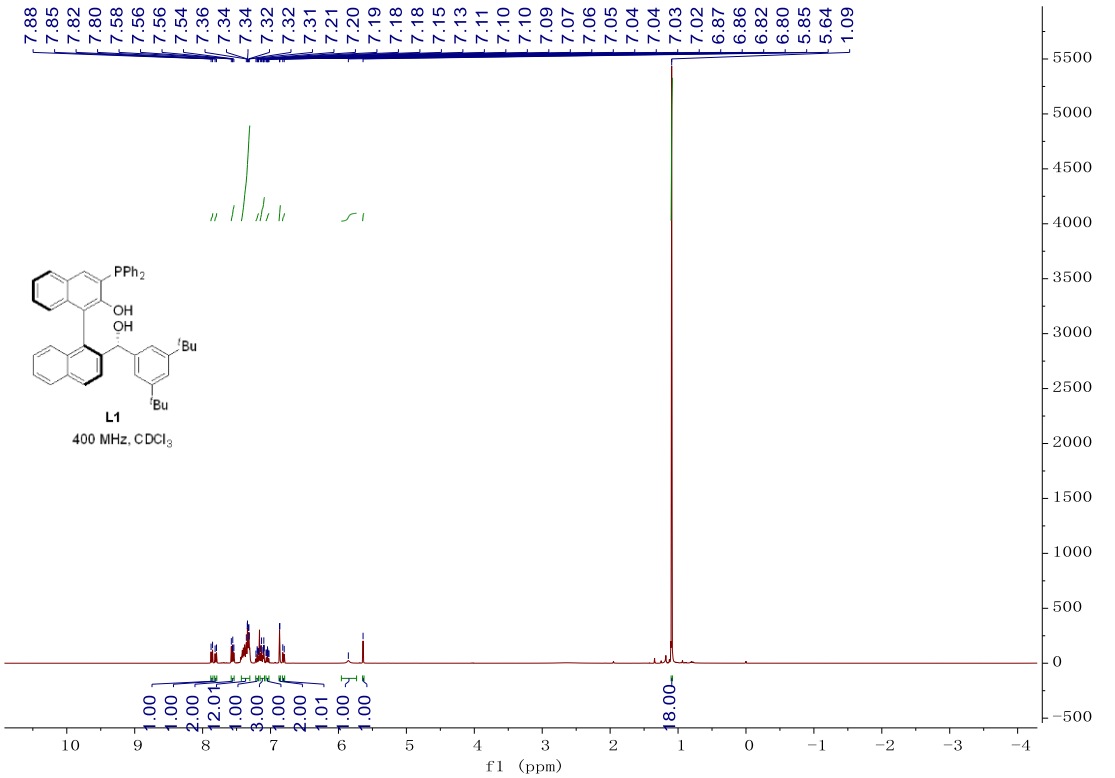
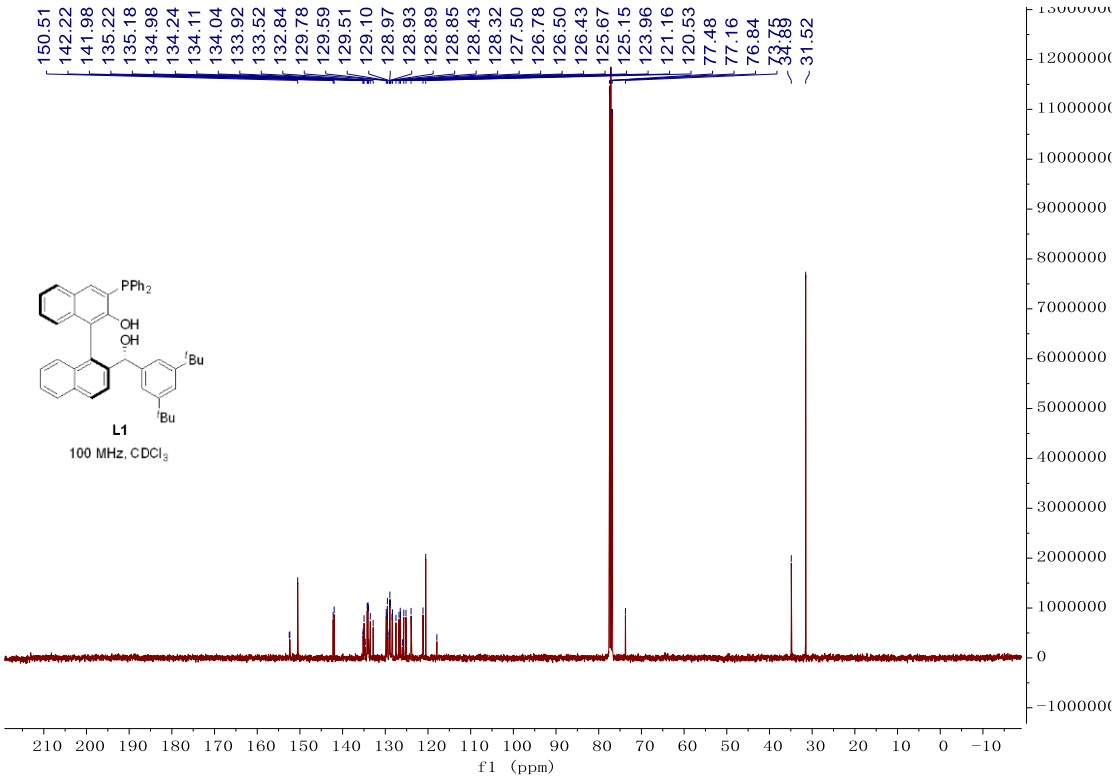
8.10
7.99
7.97
7.77
7.76
7.75
7.74
7.74
7.63
7.61
7.56
7.55
7.54
7.53
7.50
7.49
7.49
7.43
7.43
7.42
7.41
7.10
7.08
7.06
6.98
6.97
5.21
1.28
PPh2
OH
O
tBu
tBu
L1-d
400 MHz, CDCl3
1.00
1.00
1.00
1.00
2.00
14.00
2.00
2.00
2.00
18.00
f1 (ppm)


155.32
152.43
152.28
150.81
136.29
136.19
136.16
136.06
134.64
134.48
134.44
134.07
133.88
133.68
131.07
129.65
129.30
129.28
129.12
128.68
128.62
128.60
128.49
128.44
128.37
128.27
127.35
127.05
126.41
126.28
124.99
124.75
124.39
123.54
121.59
121.01
116.30
115.47
115.27
115.25
77.48
77.16
76.84
71.70
34.76
31.46
PPh2
OH
O
tBu
tBu
L1-d
100 MHz, CDCl3
f1 (ppm)


7.88
7.85
7.82
7.80
7.58
7.56
7.56
7.54
7.36
7.34
7.34
7.32
7.32
7.31
7.21
7.20
7.19
7.18
7.18
7.15
7.13
7.11
7.10
7.10
7.09
7.07
7.06
7.05
7.04
7.04
7.03
7.02
6.87
6.86
6.82
6.80
5.85
5.64
1.09
PPh2
OH
OH
tBu
tBu
L1
400 MHz, CDCl3
1.00
1.00
2.00
12.01
1.00
3.00
1.00
2.00
1.01
1.00
1.00
18.00
f1 (ppm)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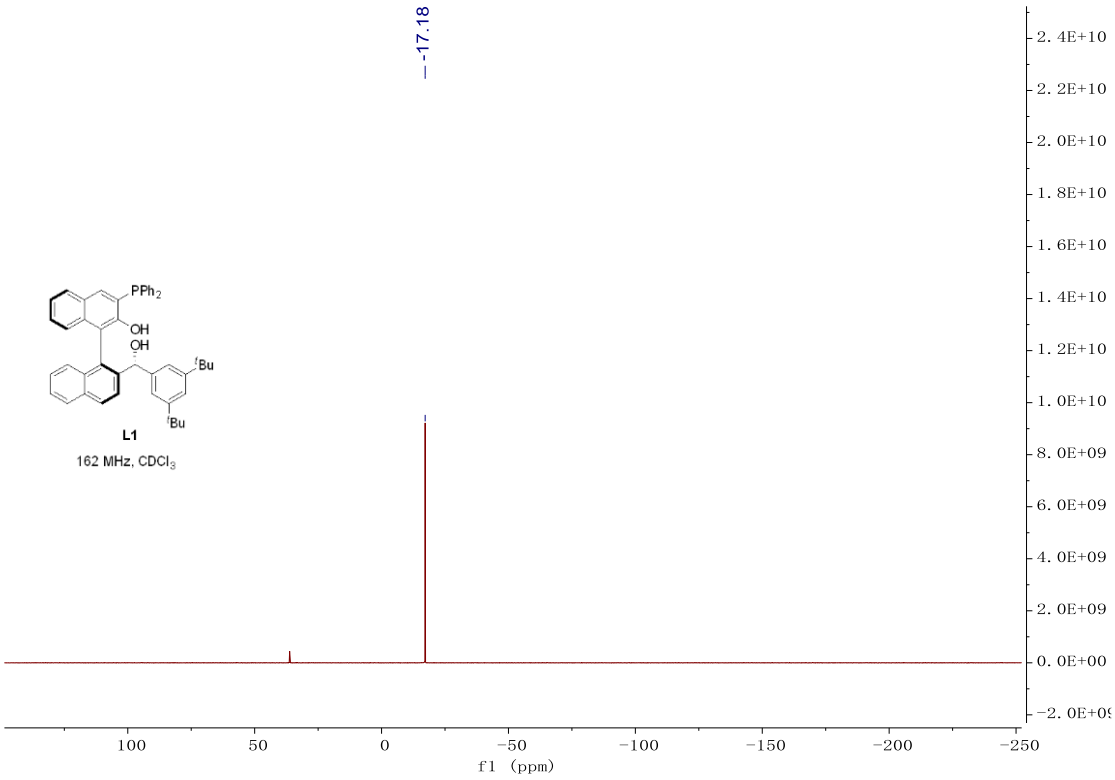
142.22
141.98
135.22
135.18
134.98
134.24
134.11
134.04
133.92
133.52
132.84
129.78
129.59
129.51
129.10
128.97
128.93
128.89
128.85
128.43
128.32
127.50
126.78
126.50
126.43
125.67
125.15
123.96
121.16
120.53
77.48
77.16
76.84
34.89
31.52
PPh2
OH
OH
tBu
tBu
L1
100 MHz, CDCl3
f1 (ppm)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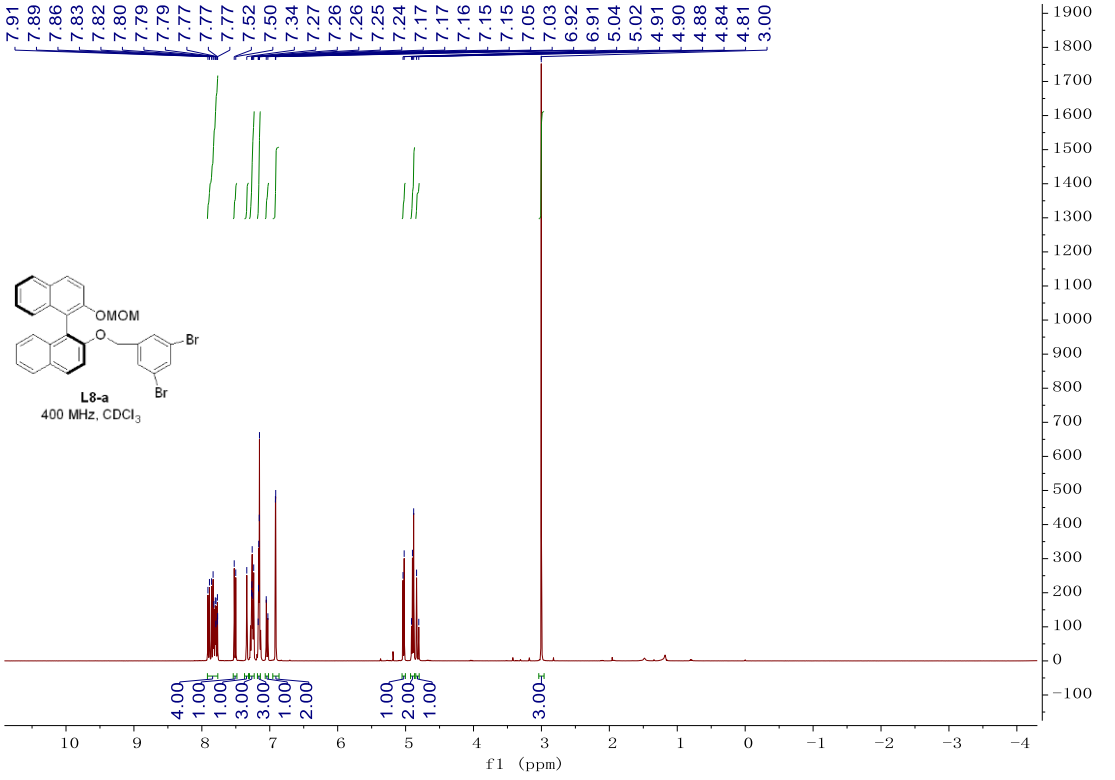
PPh2
OH
OH
tBu
tBu
L1
162 MHz, CDCl3
f1 (ppm)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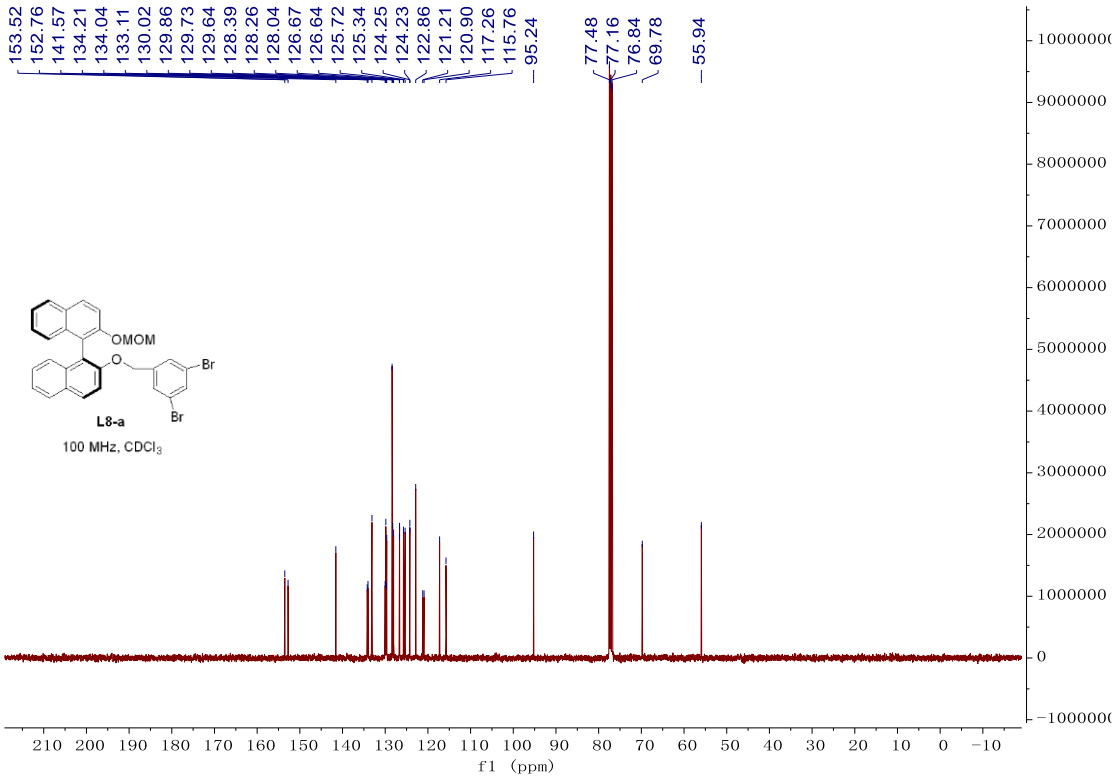
7.89
7.86
7.83
7.82
7.80
7.79
7.79
7.77
7.77
7.77
7.52
7.50
7.34
7.27
7.26
7.26
7.25
7.24
7.17
7.17
7.16
7.15
7.15
7.05
7.03
6.92
6.91
5.04
5.02
4.91
4.90
4.88
4.84
4.81
3.00
OMOM
O
Br
Br
L8-a
400 MHz, CDCl3
4.00
1.00
1.00
3.00
3.00
1.00
2.00
1.00
2.00
1.00
3.00
f1 (ppm)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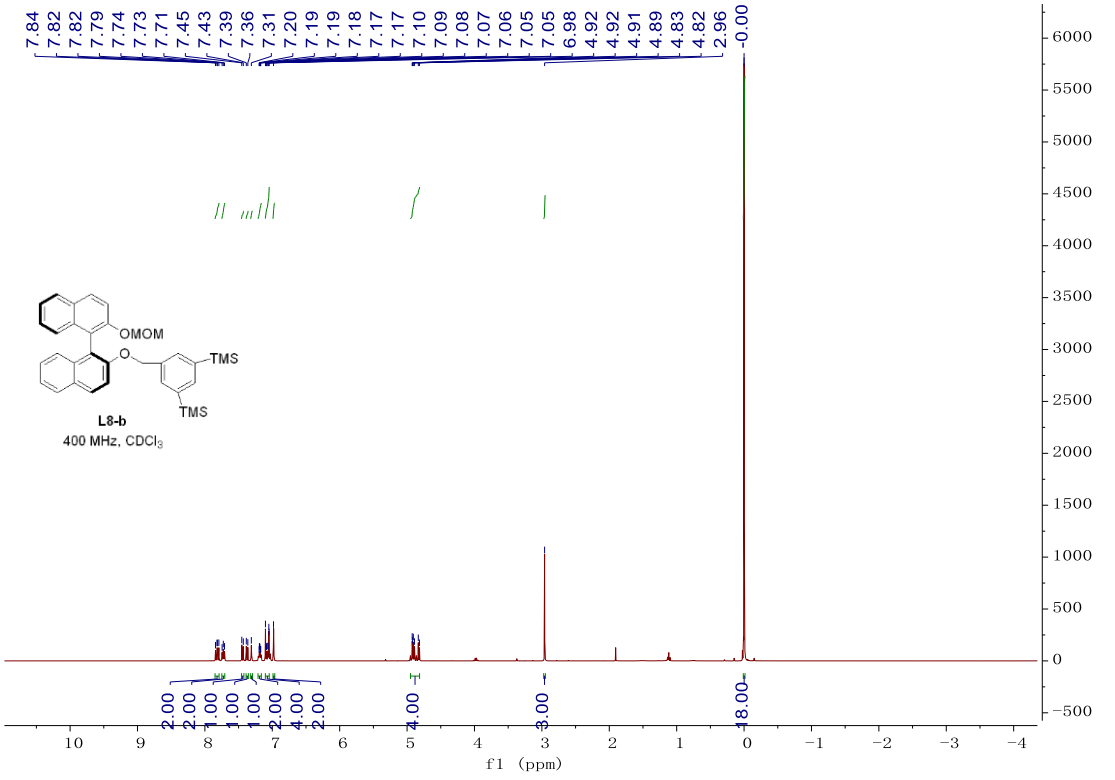
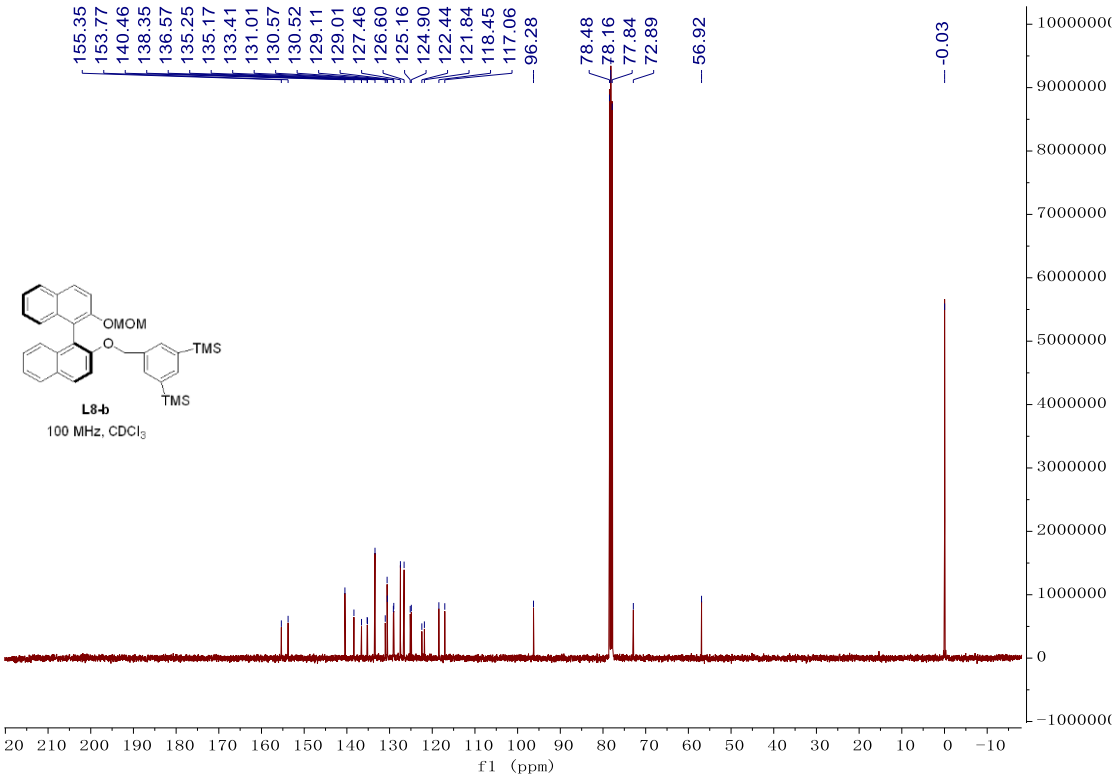
152.76
141.57
134.21
134.04
133.11
130.02
129.86
129.73
129.64
128.39
128.26
128.04
126.67
126.64
125.72
125.34
124.25
124.23
122.86
121.21
120.90
117.26
115.76
95.24
77.48
77.16
76.84
69.78
55.94
OMOM
O
Br
Br
L8-a
100 MHz, CDCl3
f1 (ppm)


7.84
7.82
7.82
7.79
7.74
7.73
7.71
7.45
7.43
7.39
7.36
7.31
7.20
7.19
7.19
7.18
7.17
7.17
7.10
7.09
7.08
7.07
7.06
7.05
7.05
6.98
4.92
4.92
4.91
4.89
4.83
4.82
2.96
0.00
OMOM
O
TMS
TMS
L8-b
400 MHz, CDCl3
2.00
2.00
1.00
1.00
1.00
2.00
4.00
2.00
4.00
3.00
18.00
f1 (ppm)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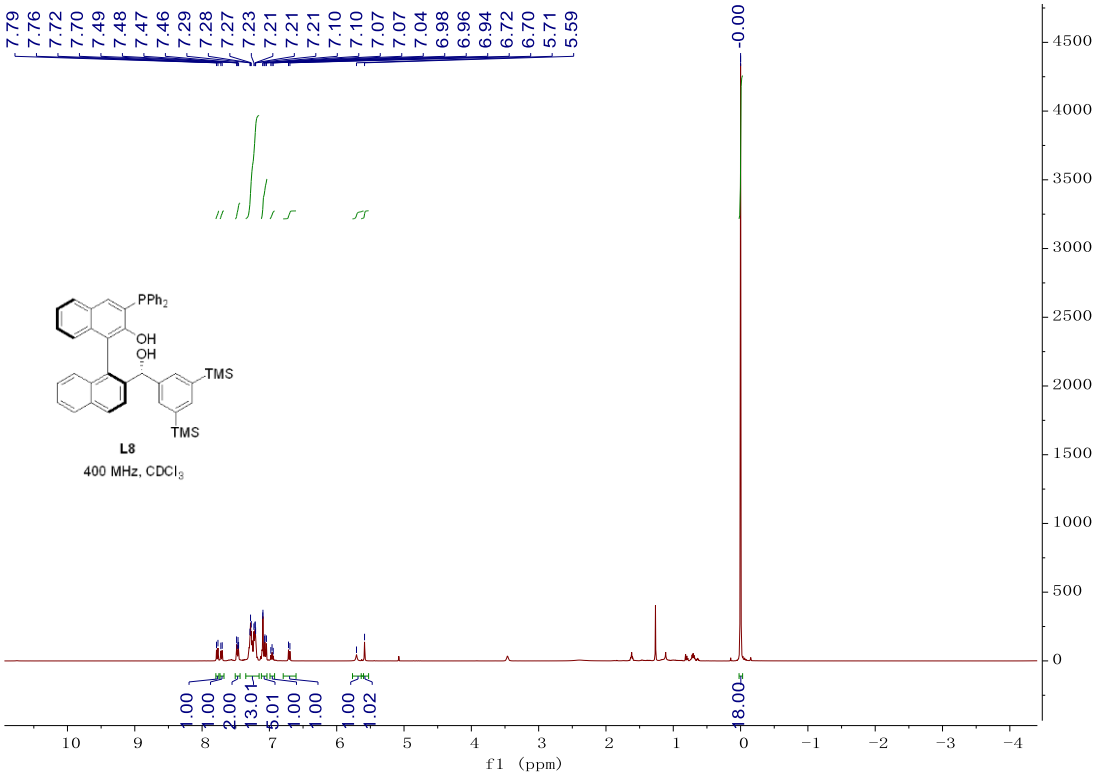
153.77
140.46
138.35
136.57
135.25
135.17
133.41
131.01
130.57
130.52
129.11
129.01
127.46
126.60
125.16
124.90
122.44
121.84
118.45
117.06
96.28
78.48
78.16
77.84
72.89
56.92
-0.03
OMOM
TMS
TMS
L8-b
100 MHz, CDCl3
f1 (ppm)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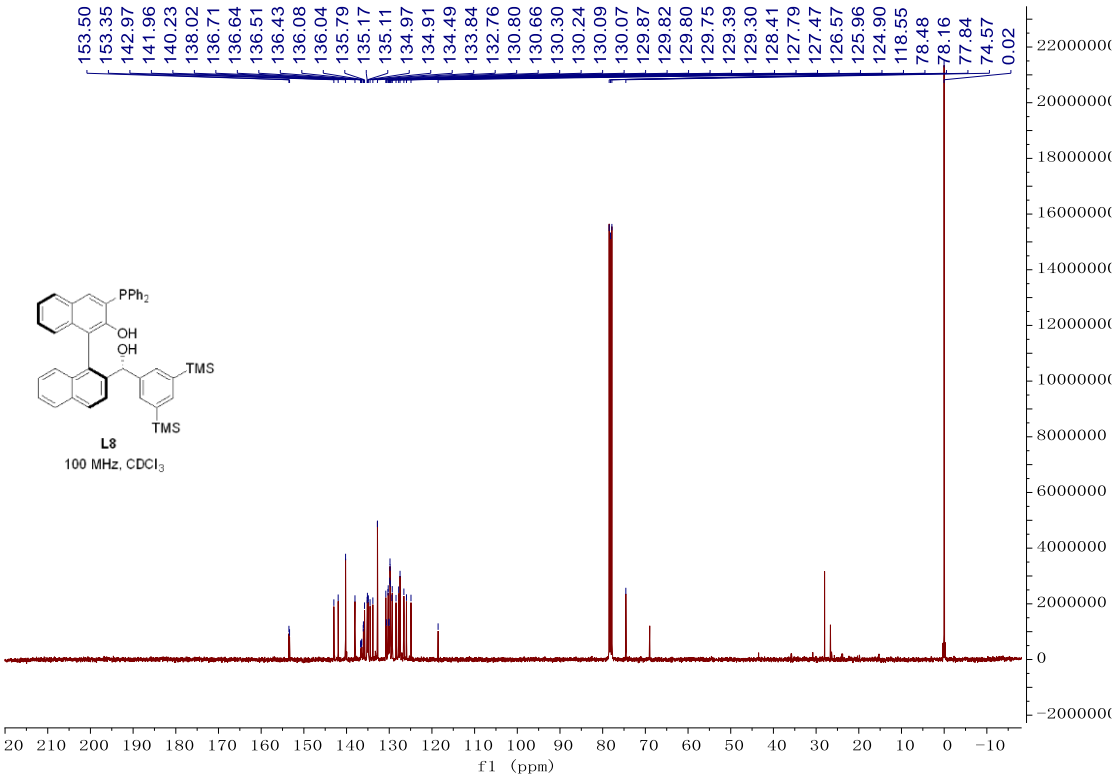
7.76
7.72
7.70
7.49
7.48
7.47
7.46
7.29
7.28
7.27
7.23
7.21
7.21
7.21
7.10
7.10
7.07
7.07
7.04
6.98
6.96
6.94
6.72
6.70
5.71
5.59
-0.00
PPh2
OH
OH
TMS
TMS
L8
400 MHz, CDCl3
1.00
1.00
2.00
13.01
5.01
1.00
1.00
1.00
1.02
18.00
f1 (ppm)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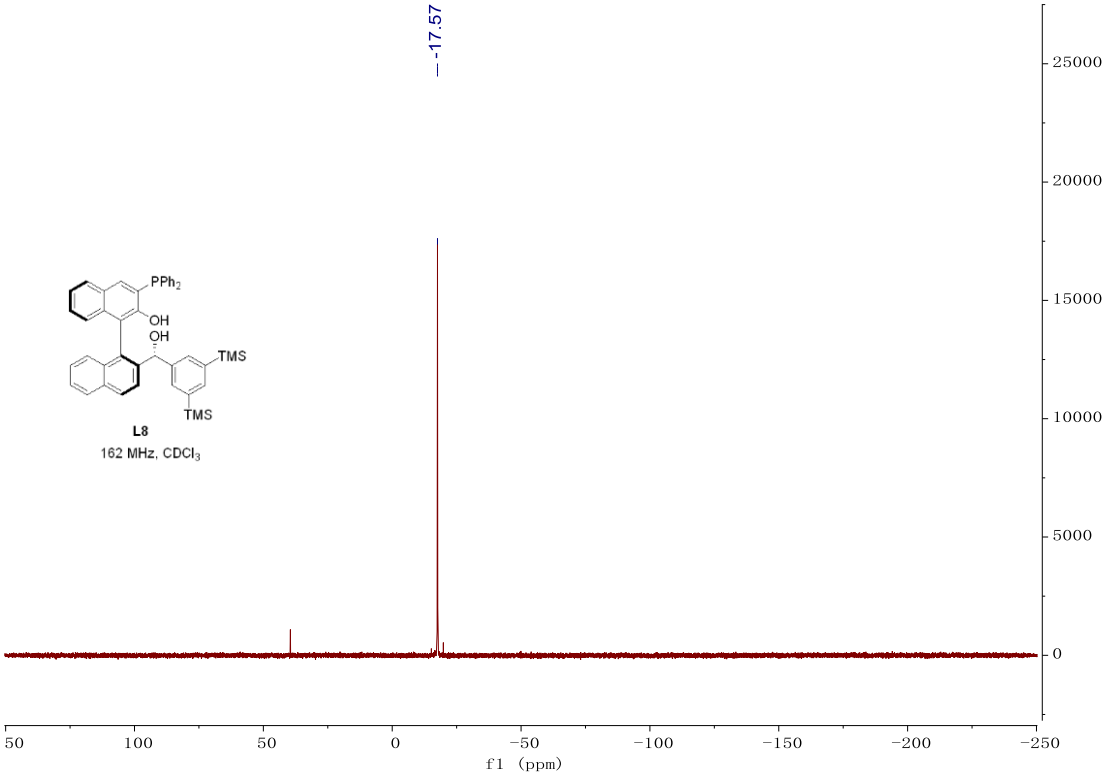
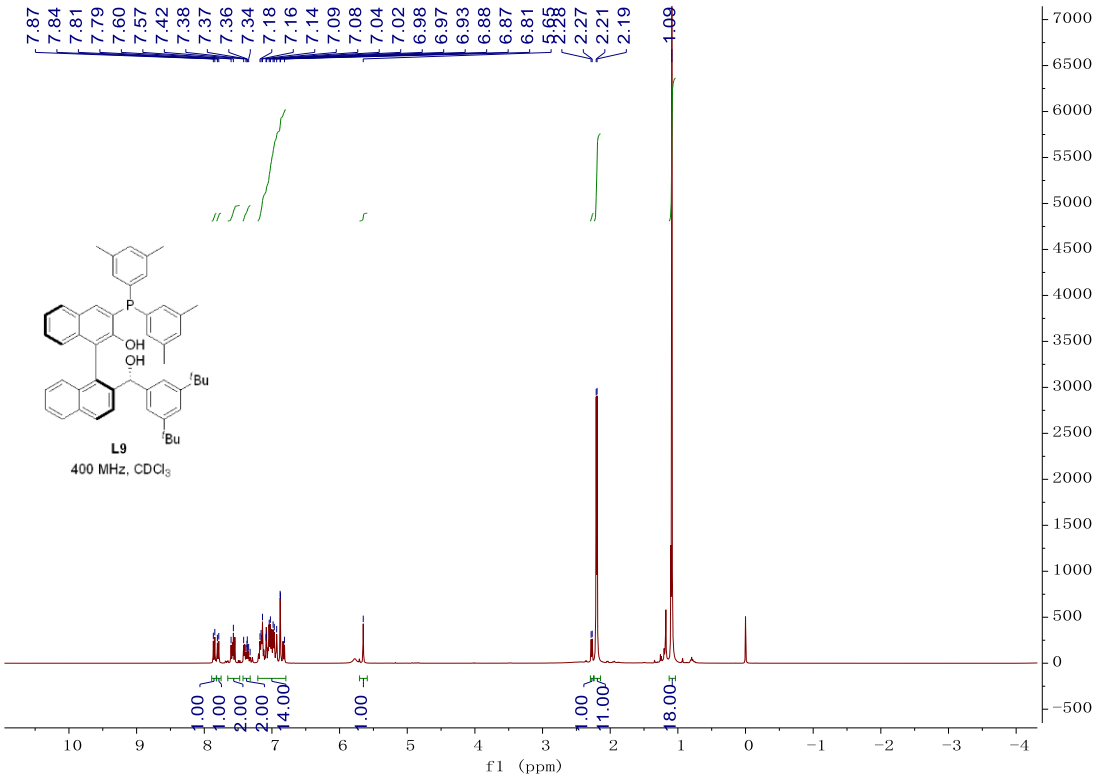
153.35
142.97
141.96
140.23
138.02
136.71
136.64
136.51
136.43
136.08
136.04
135.79
135.17
135.11
134.97
134.91
134.49
133.84
132.76
130.80
130.66
130.30
130.24
130.09
130.07
129.87
129.82
129.80
129.75
129.39
129.30
128.41
127.79
127.47
126.57
125.96
124.90
118.55
78.48
78.16
77.84
74.57
0.02
PPh2
OH
OH
TMS
TMS
L8
100 MHz, CDCl3
f1 (ppm)


-17.57
PPh2
OH
OH
TMS
TMS
L8
162 MHz, CDCl3
f1 (ppm)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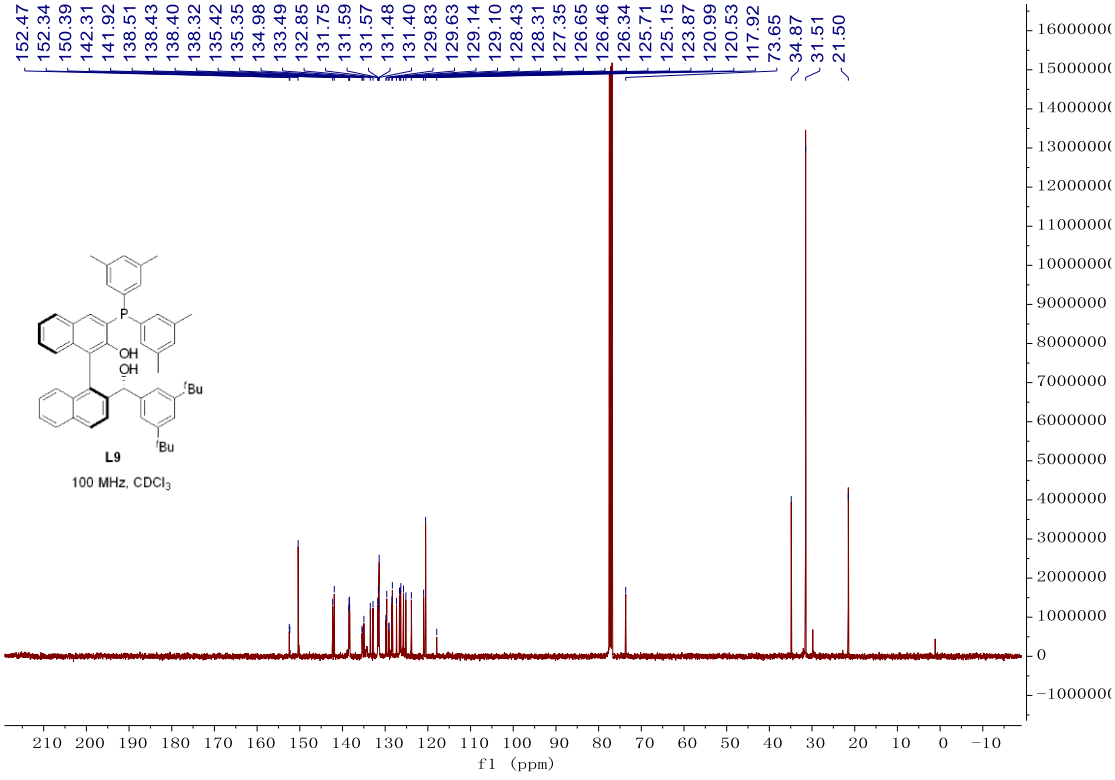
7.84
7.81
7.79
7.60
7.57
7.42
7.38
7.37
7.36
7.34
7.18
7.16
7.14
7.09
7.08
7.04
7.02
6.98
6.97
6.93
6.88
6.87
6.81
5.65
2.28
2.27
2.21
2.19
1.09
OH
OH
tBu
tBu
L9
400 MHz, CDCl3
1.00
1.00
2.00
2.00
14.00
1.00
1.00
11.00
18.00
f1 (ppm)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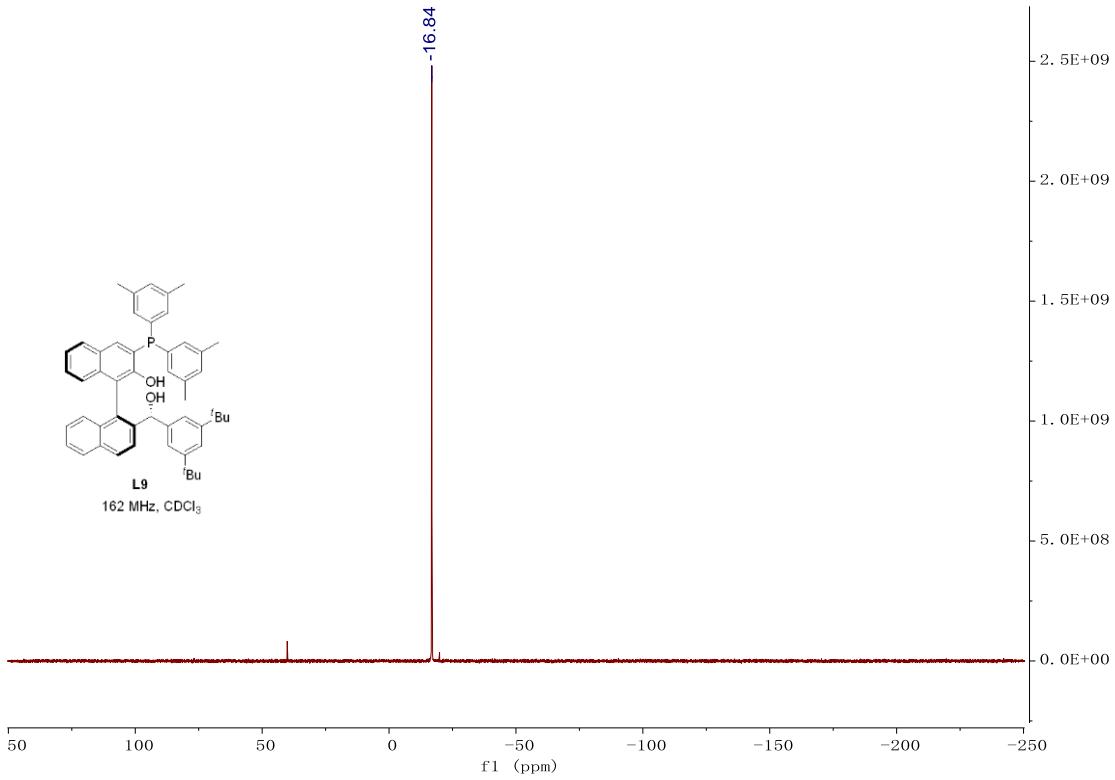
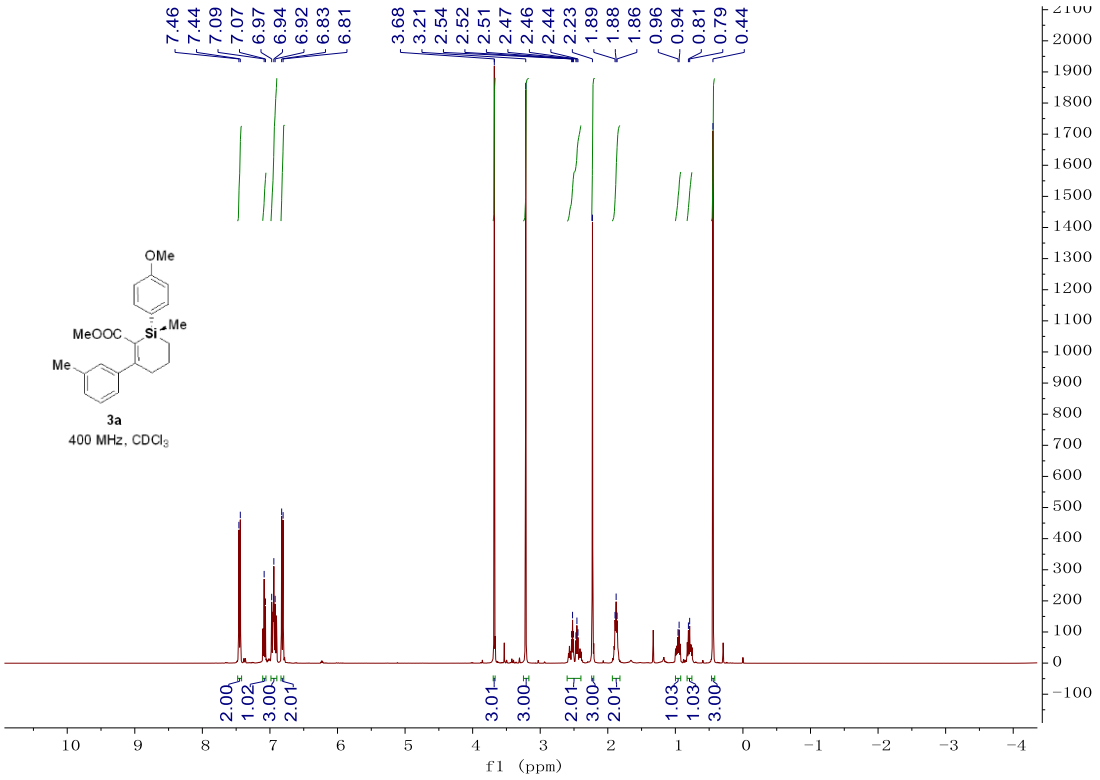
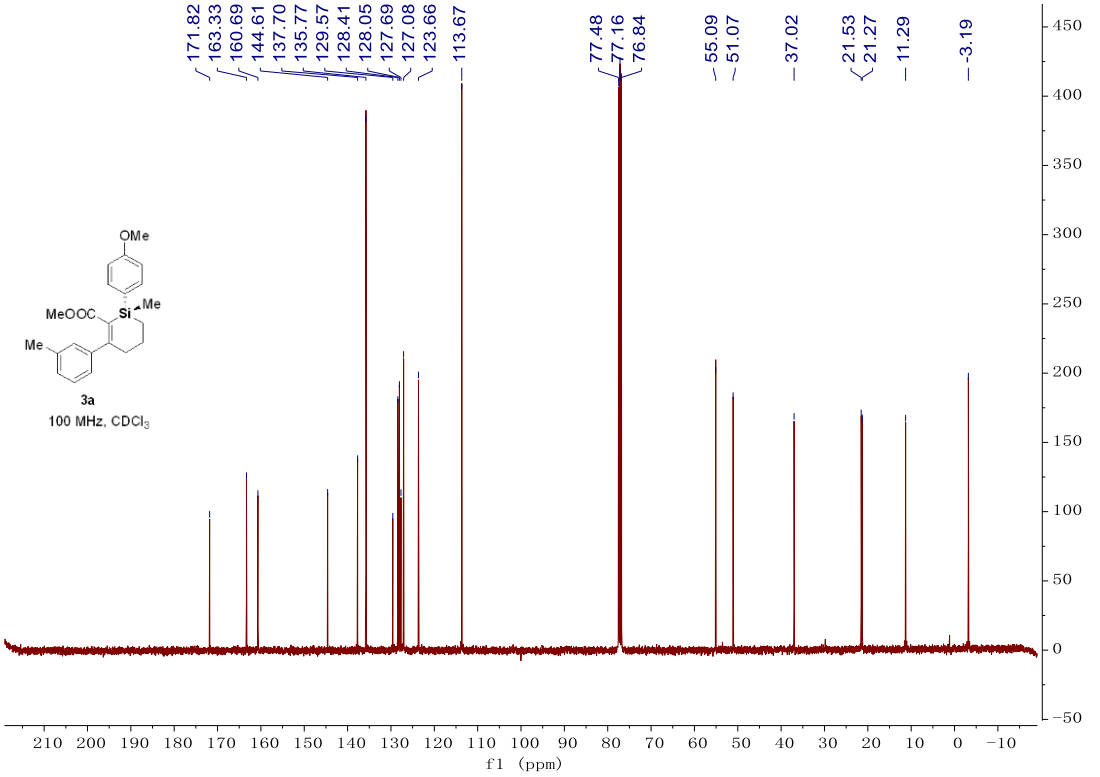
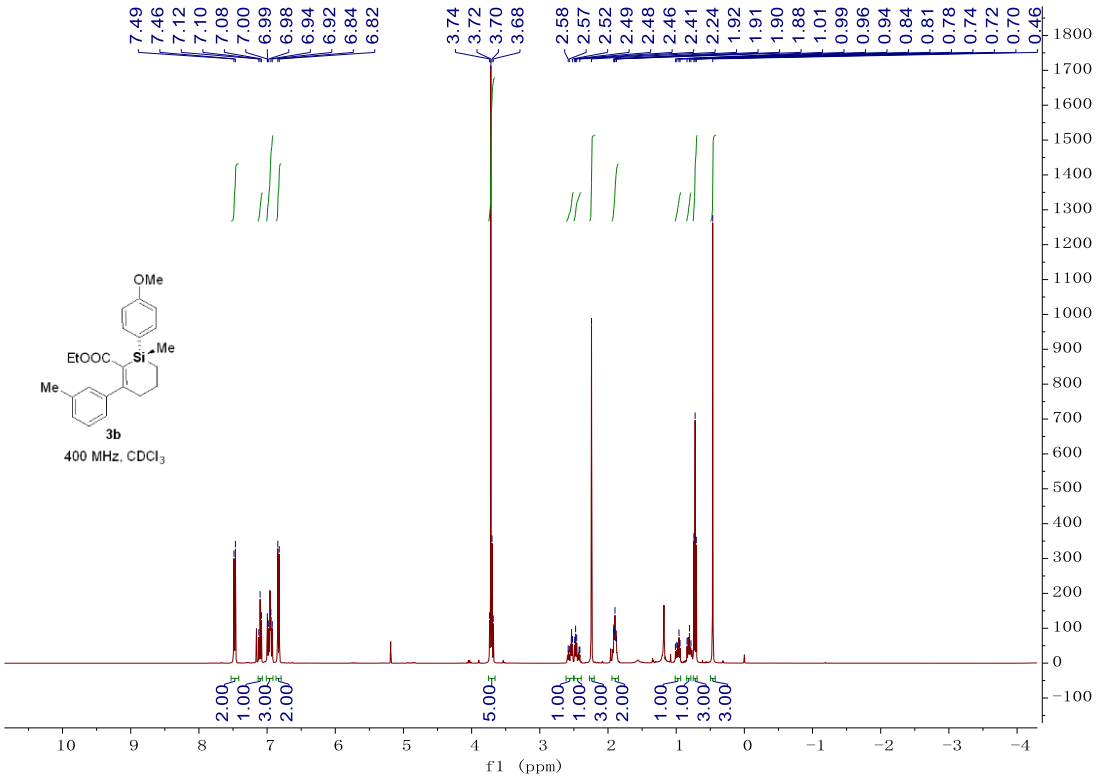
152.34
150.39
142.31
141.92
138.51
138.43
138.40
138.32
135.42
135.35
134.98
133.49
132.85
131.75
131.59
131.57
131.48
131.40
129.83
129.63
129.14
129.10
128.43
128.31
127.35
126.65
126.46
126.34
125.71
125.15
123.87
120.99
120.53
117.92
73.65
34.87
31.51
21.50
OH
OH
tBu
tBu
L9
100 MHz, CDCl3
f1 (ppm)


-16.84
2.5E+09
2.0E+09
1.5E+09
1.0E+09
5.0E+08
0.0E+00
OH
OH
tBu
tBu
L9
162 MHz, CDCl3
50
100
50
0
-50
-100
-150
-200
-250
f1 (ppm)


7.46
7.44
7.09
7.07
6.97
6.94
6.92
6.83
6.81
3.68
3.21
2.54
2.52
2.51
2.47
2.46
2.44
2.23
1.89
1.88
1.86
0.96
0.94
0.81
0.79
0.44
OMe
MeOOC
Si
Me
Me
3a
400 MHz, CDCl3
2.00
1.02
3.00
2.01
3.01
3.00
2.01
3.00
2.01
1.03
1.03
3.00
f1 (ppm)


171.82
163.33
160.69
144.61
137.70
135.77
129.57
128.41
128.05
127.69
127.08
123.66
113.67
77.48
77.16
76.84
55.09
51.07
37.02
21.53
21.27
11.29
-3.19
OMe
MeOOC
Si
Me
Me
3a
100 MHz, CDCl3
f1 (ppm)


7.49
7.46
7.12
7.10
7.08
7.00
6.99
6.98
6.94
6.92
6.84
6.82
3.74
3.72
3.70
3.68
2.58
2.57
2.52
2.49
2.48
2.46
2.41
2.24
1.92
1.91
1.90
1.88
1.01
0.99
0.96
0.94
0.84
0.81
0.78
0.74
0.72
0.70
0.46
OMe
EtOOC
Si
Me
Me
3b
400 MHz, CDCl3
2.00
1.00
3.00
2.00
5.00
1.00
1.00
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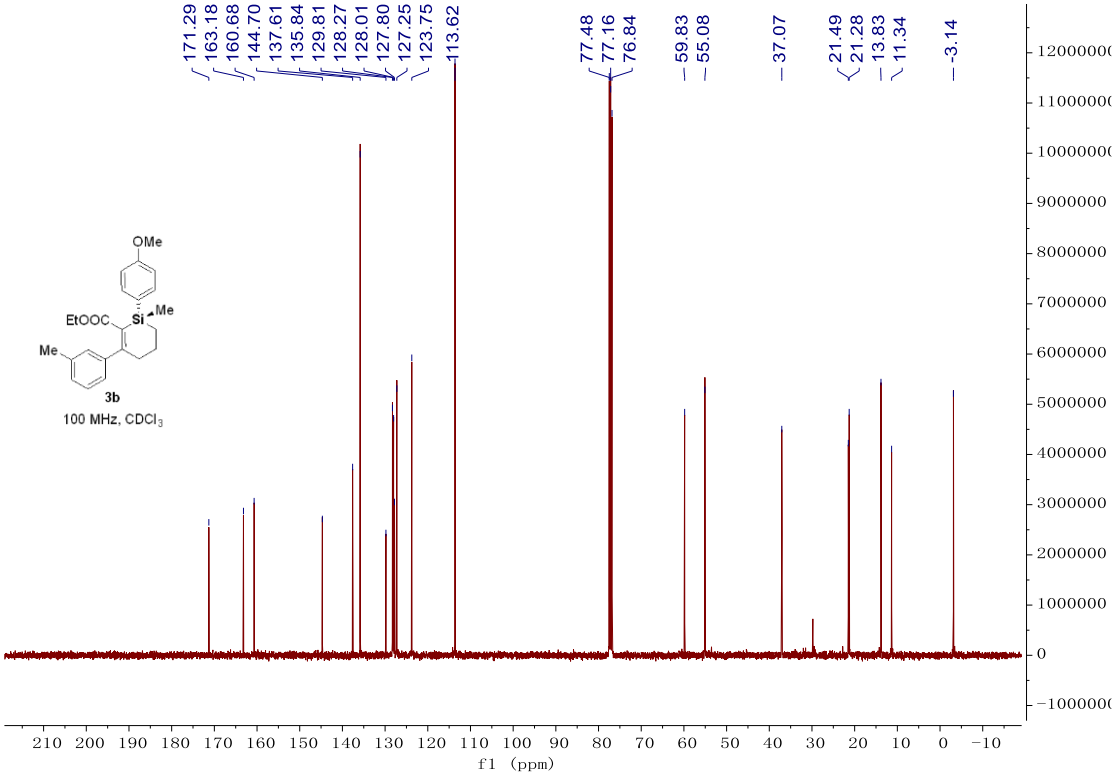
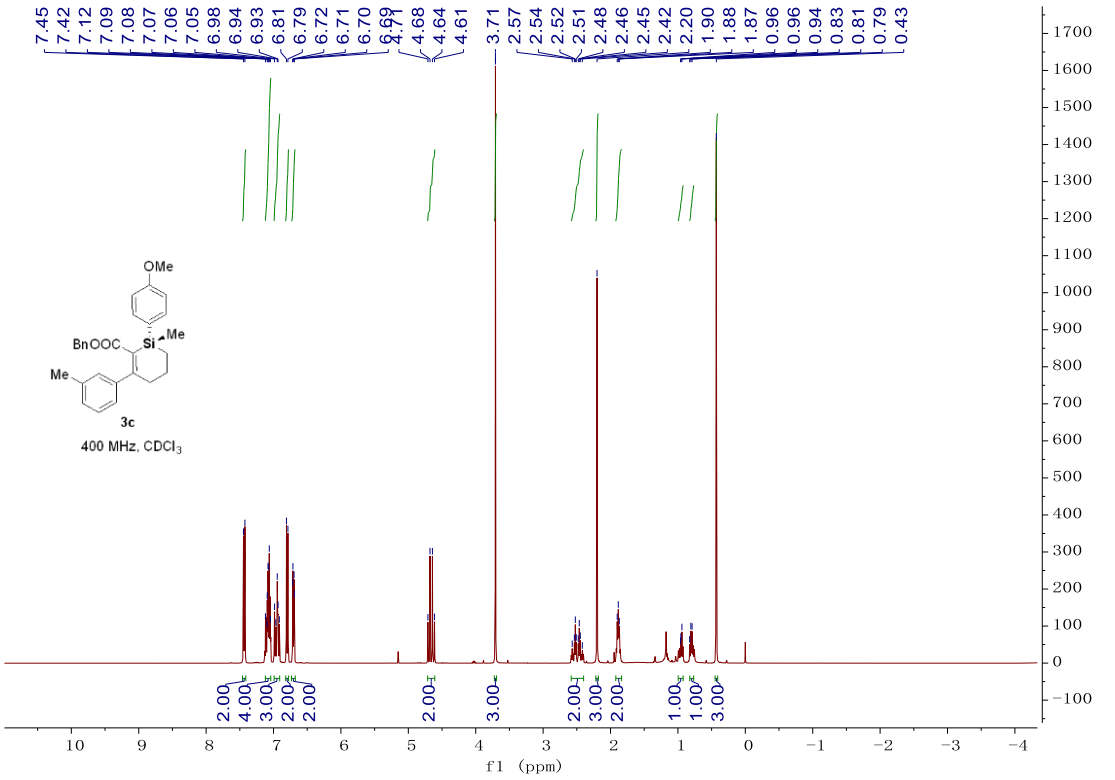
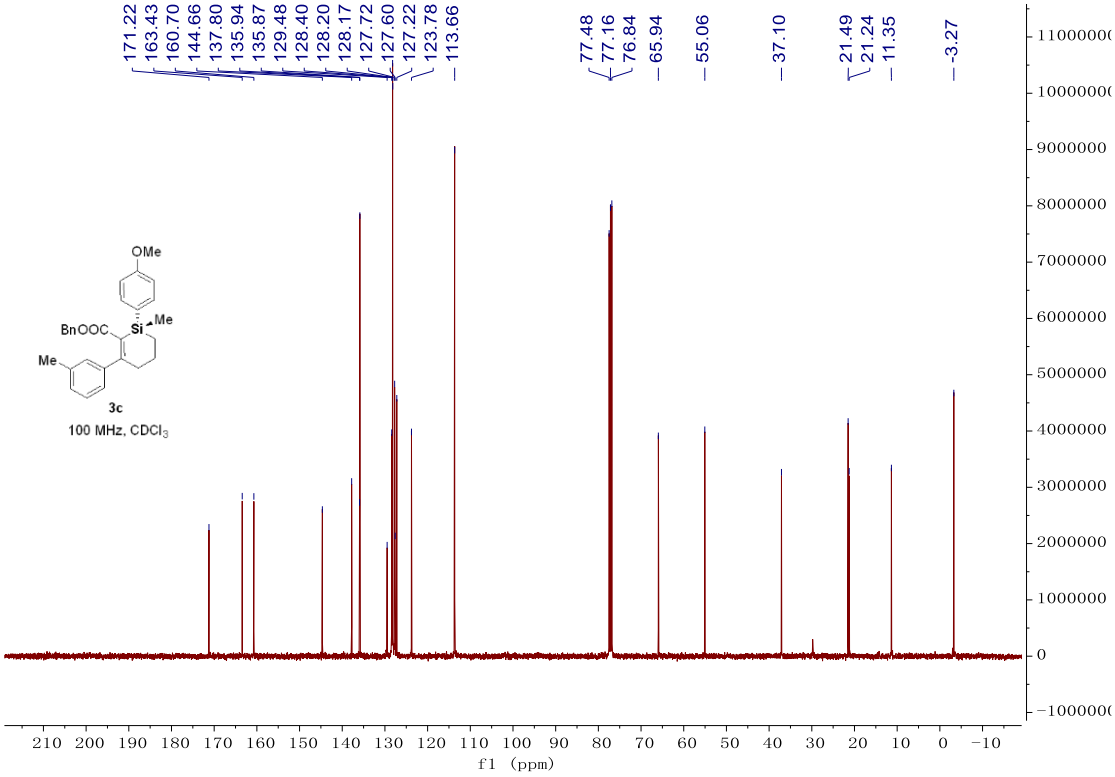
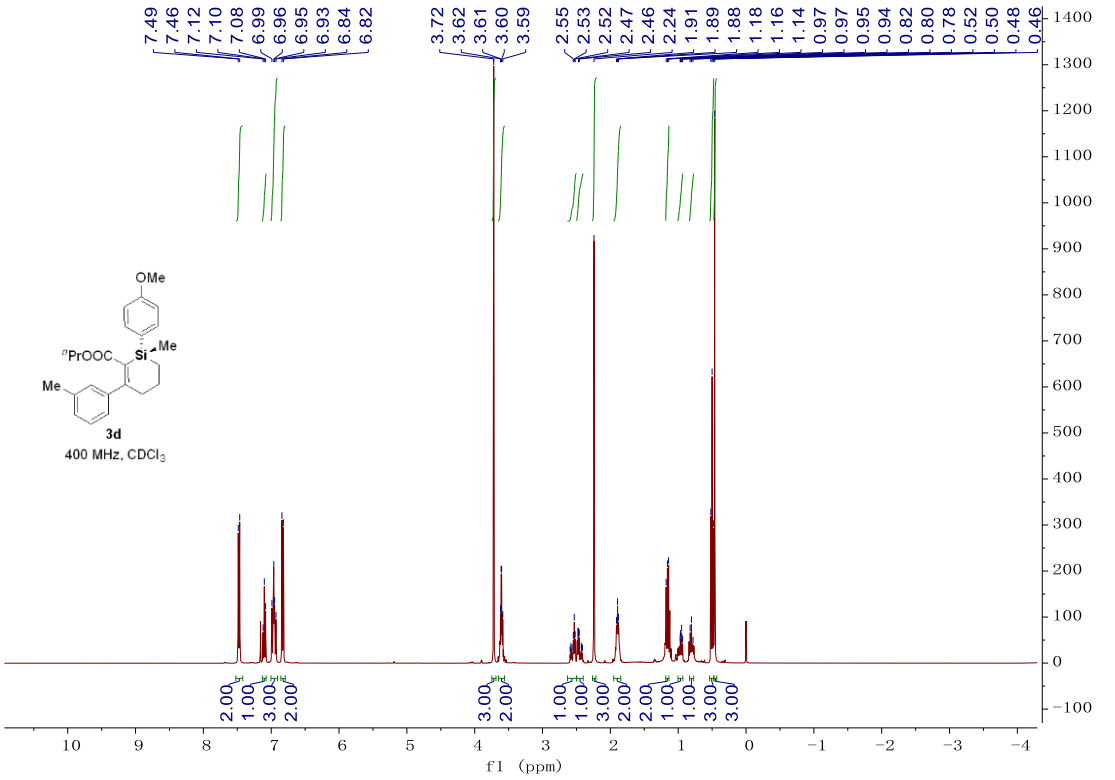
2.00
1.00
1.00
3.00
3.00
f1 (ppm)


171.29
163.18
160.68
144.70
137.61
135.84
129.81
128.27
128.01
127.80
127.25
123.75
113.62
77.48
77.16
76.84
59.83
55.08
37.07
21.49
21.28
13.83
11.34
-3.14
OMe
EtOOC
Si
Me
Me
3b
100 MHz, CDCl3
f1 (ppm)


7.45 7.42 7.12 7.09 7.08 7.07 7.06 7.05 6.98 6.94 6.93 6.81 6.79 6.72 6.71 6.70 4.68 4.64 4.61 3.71 2.57 2.54 2.52 2.51 2.48 2.46 2.45 2.42 2.20 1.90 1.88 1.87 0.96 0.96 0.94 0.83 0.81 0.79 0.43
OMe
BnOOC
Si
Me
Me
3c
400 MHz, CDCl3
2.00 4.00 3.00 2.00 2.00 2.00 3.00 2.00 3.00 2.00 1.00 1.00 3.00
f1 (ppm)


171.22 163.43 160.70 144.66 137.80 135.94 135.87 129.48 128.40 128.20 128.17 127.72 127.60 127.22 123.78 113.66
77.48 77.16 76.84 65.94 55.06 37.10 21.49 21.24 11.35 -3.27
OMe
BnOOC
Si
Me
Me
3c
100 MHz, CDCl3
f1 (ppm)


7.49
7.46
7.12
7.10
7.08
6.99
6.96
6.95
6.93
6.84
6.82
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2.53
2.52
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0.80
0.78
0.52
0.50
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nPrOOC
Si
Me
Me
3d
400 MHz, CDCl3
2.00
1.00
3.00
2.00
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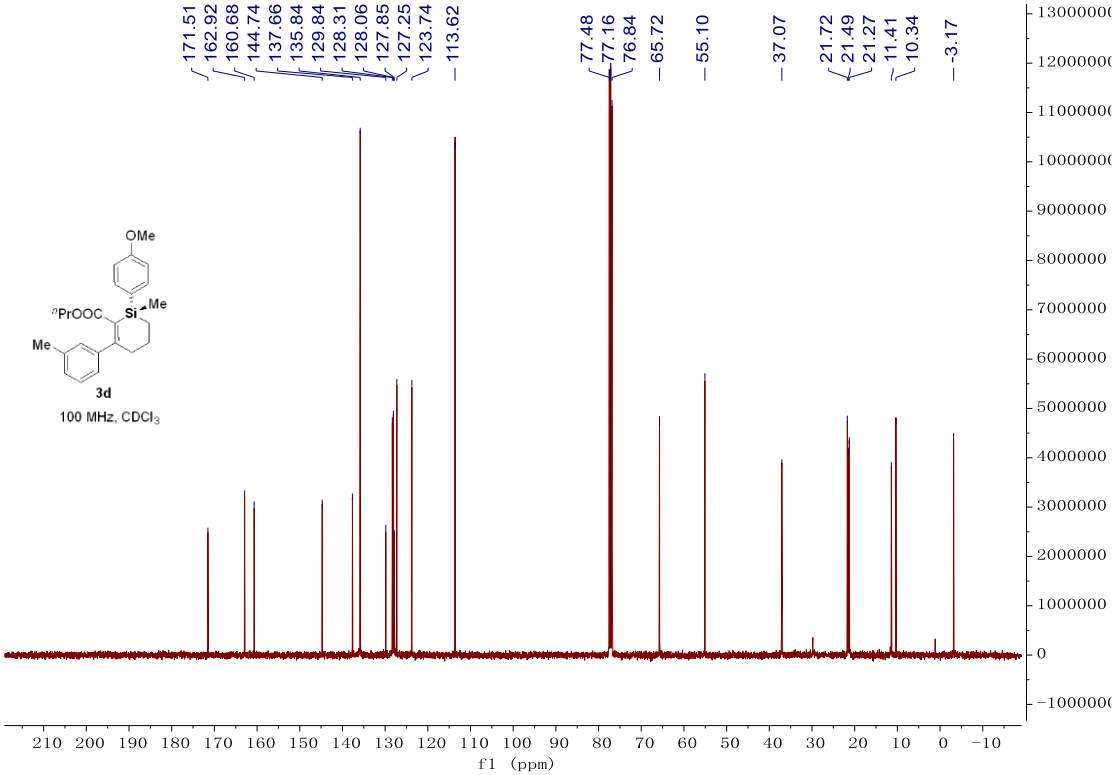
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65.72
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37.07
21.72
21.49
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Me
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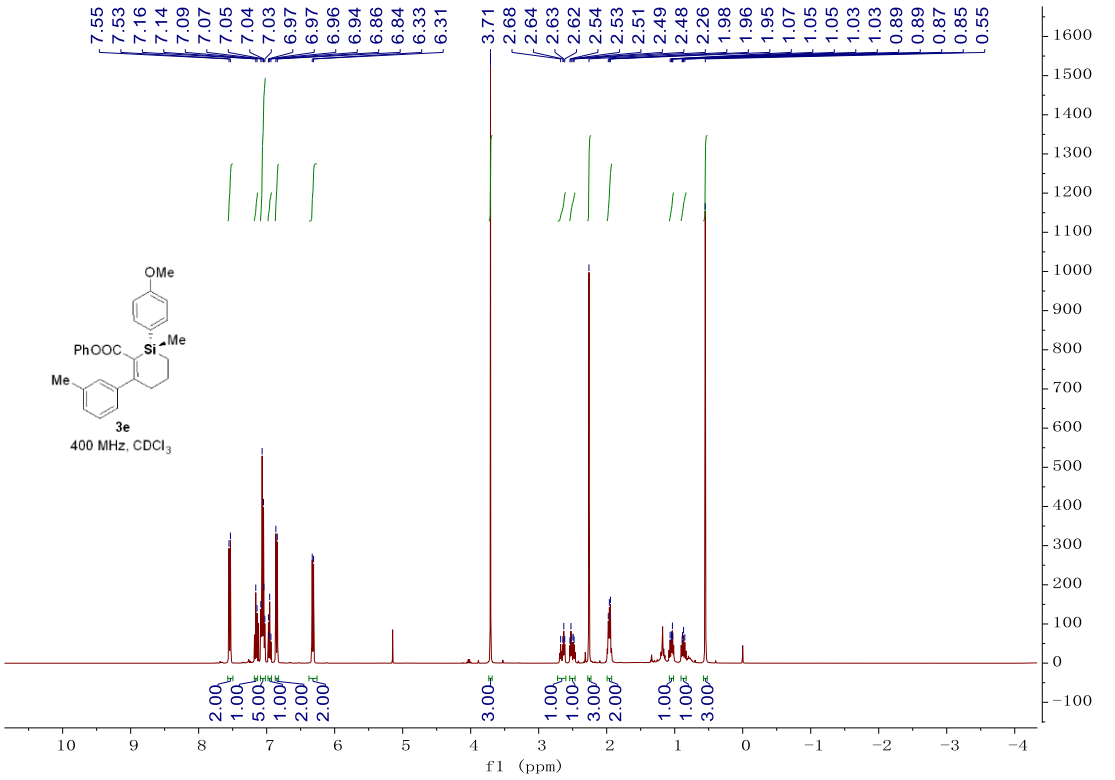
100 MHz, CDCl3
f1 (ppm)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OMe
PhOOC
Si
Me
Me
3e
400 MHz, CDCl3
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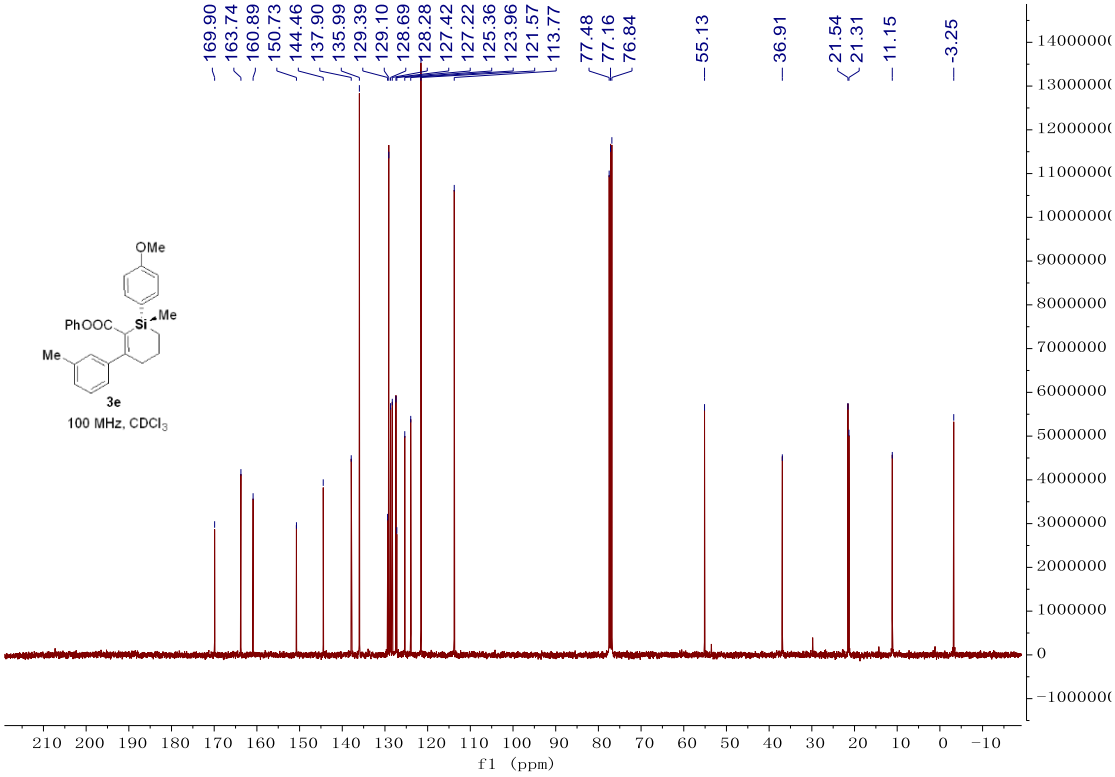
f1 (ppm)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77.48 77.16 76.84
55.13
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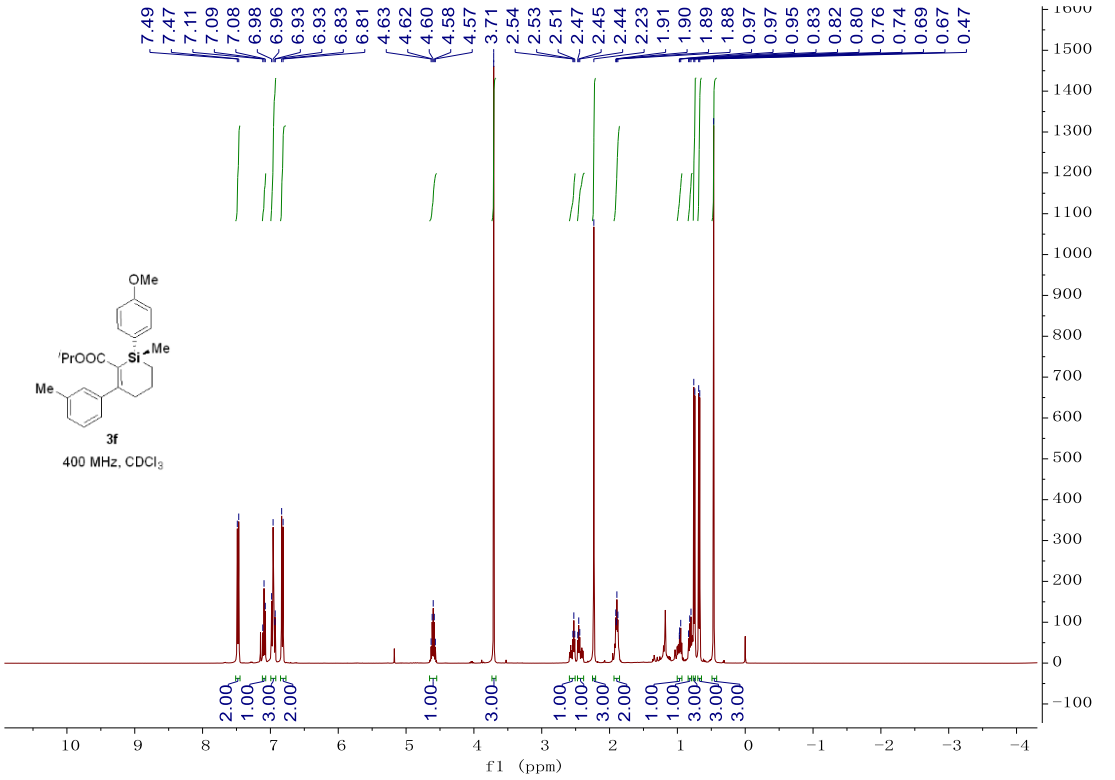
11.15
-3.25
OMe
PhOOC
Si
Me
Me
3e
100 MHz, CDCl3
f1 (ppm)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4.57
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2.45
2.44
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1.89
1.88
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0.97
0.95
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0.82
0.80
0.76
0.74
0.69
0.67
0.47
OMe
iPrOOC
Si
Me
Me
3f
400 MHz, CDCl3
2.00
1.00
3.00
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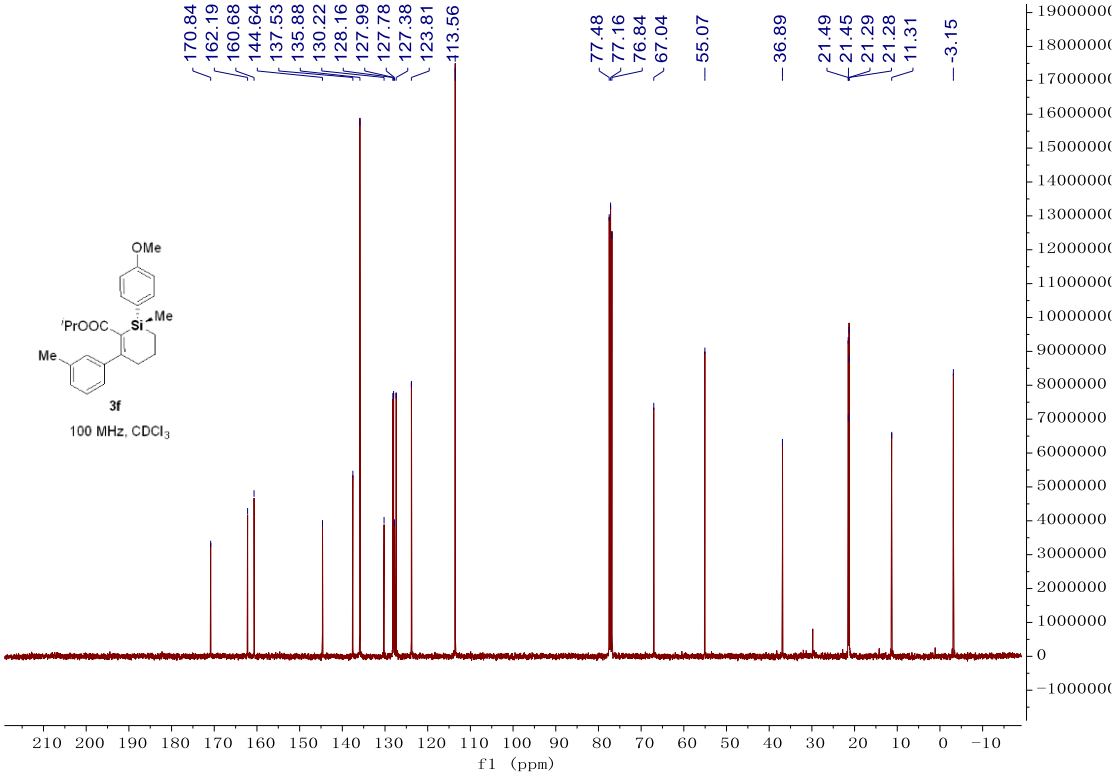
f1 (ppm)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55.07
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21.45
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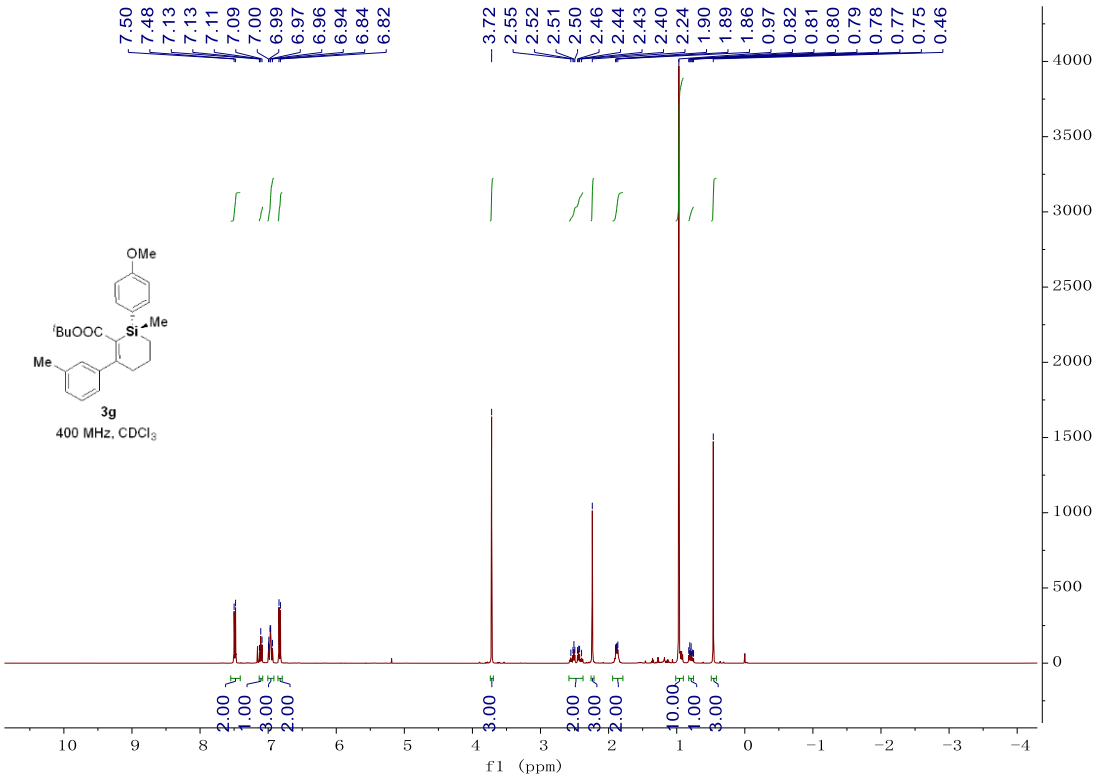
iPrOOC
Si
Me
Me
3f
100 MHz, CDCl3
f1 (ppm)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2.50
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2.24
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1.89
1.86
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0.46
OMe
tBuOOC
Si
Me
Me
3g
400 MHz, CDCl3
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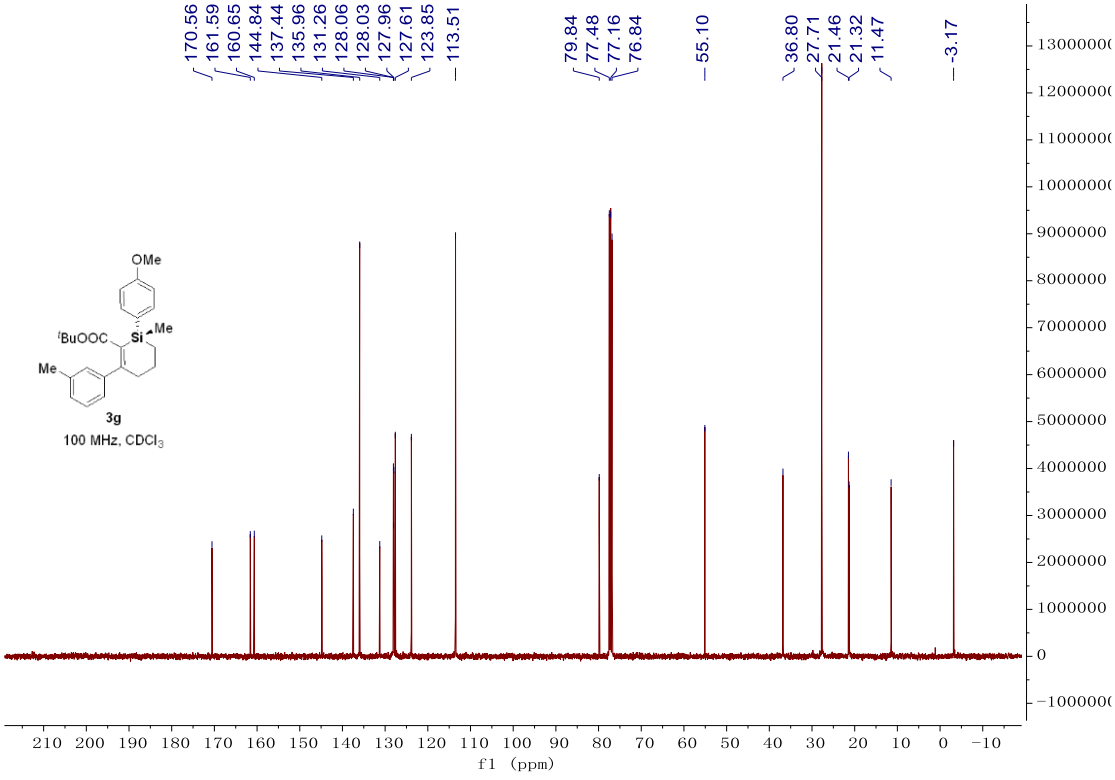
f1 (ppm)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76.84
55.10
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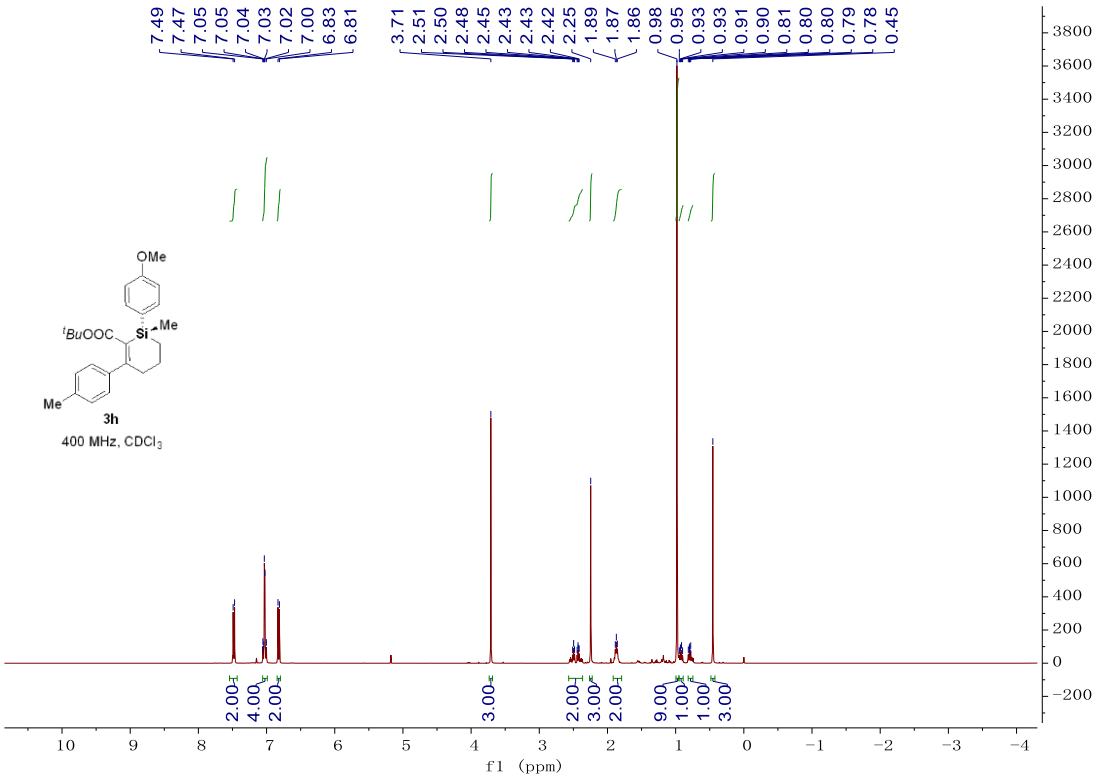
Si
Me
Me
3g
100 MHz, CDCl3
f1 (ppm)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1.86
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0.90
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0.80
0.80
0.79
0.78
0.45
OMe
tBuOOC
Si
Me
Me
3h
400 MHz, CDCl3
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2.00
3.00
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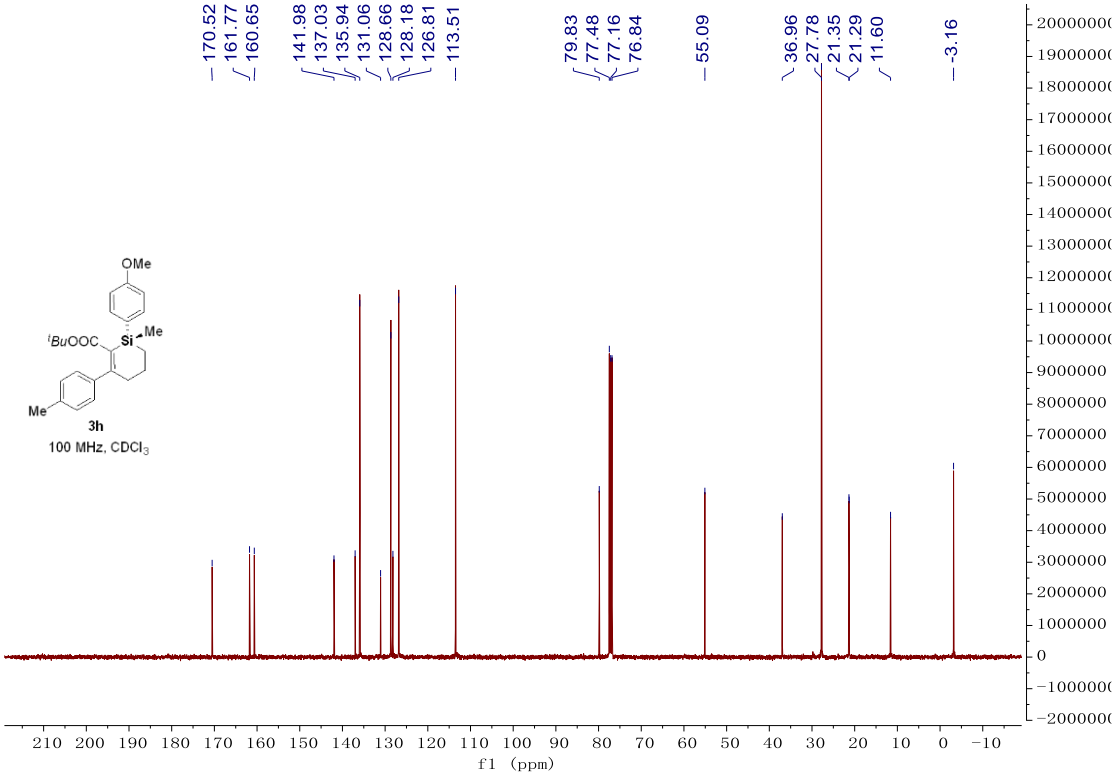
3.00
f1 (ppm)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55.09
36.96
27.78
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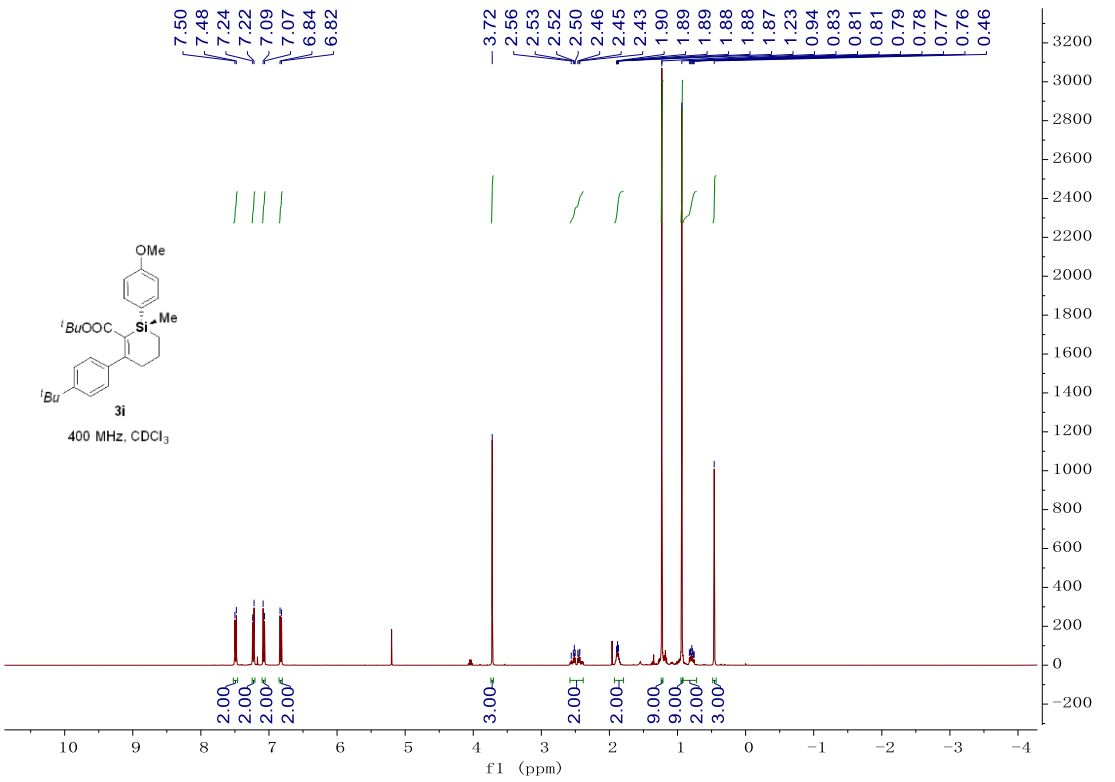
tBuOOC
Si
Me
Me
3h
100 MHz, CDCl3
f1 (ppm)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1.89
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0.81
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OMe
tBuOOC
Si
Me
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3i
400 MHz, CDCl3
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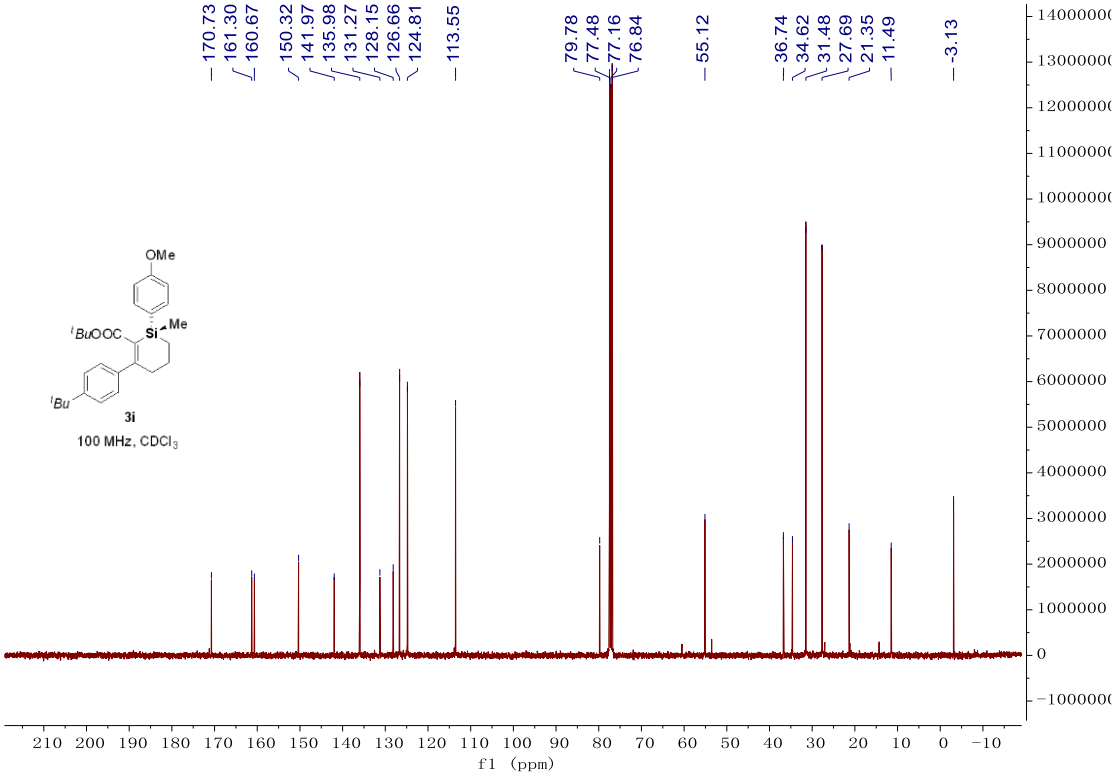
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31.48
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-3.13
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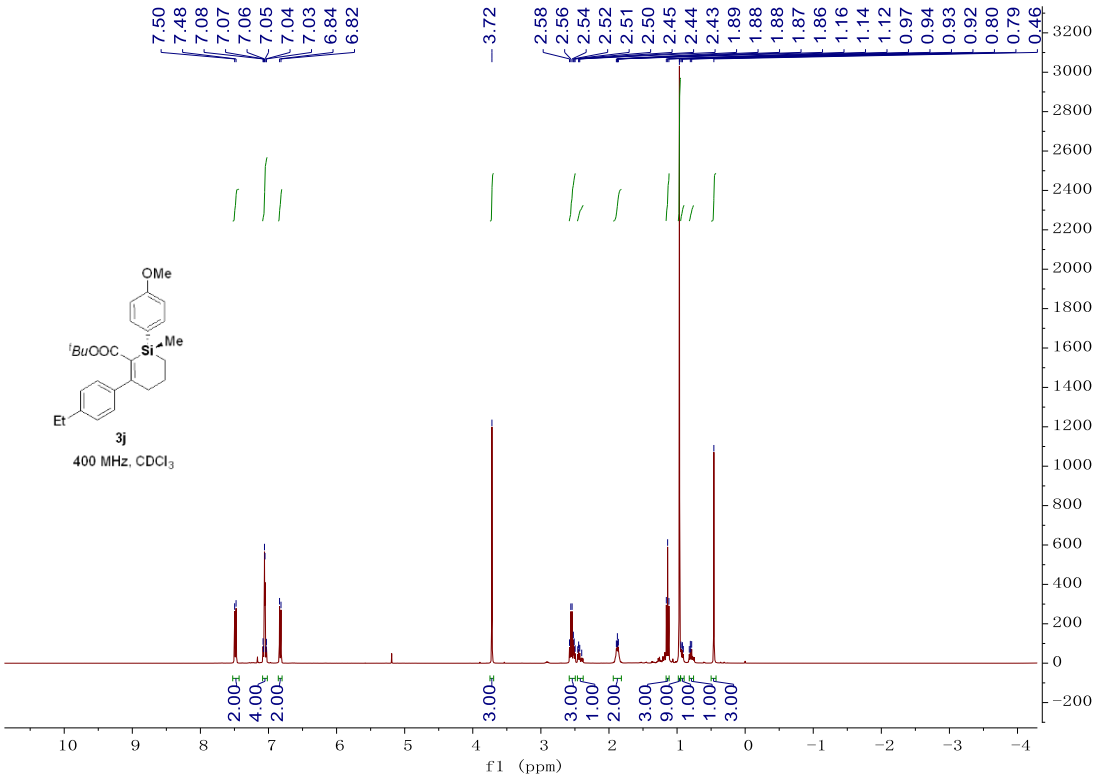
tBuOOC
Si
Me
tBu
3i
100 MHz, CDCl3
f1 (ppm)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OMe
tBuOOC
Si
Me
Et
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400 MHz, CDCl3
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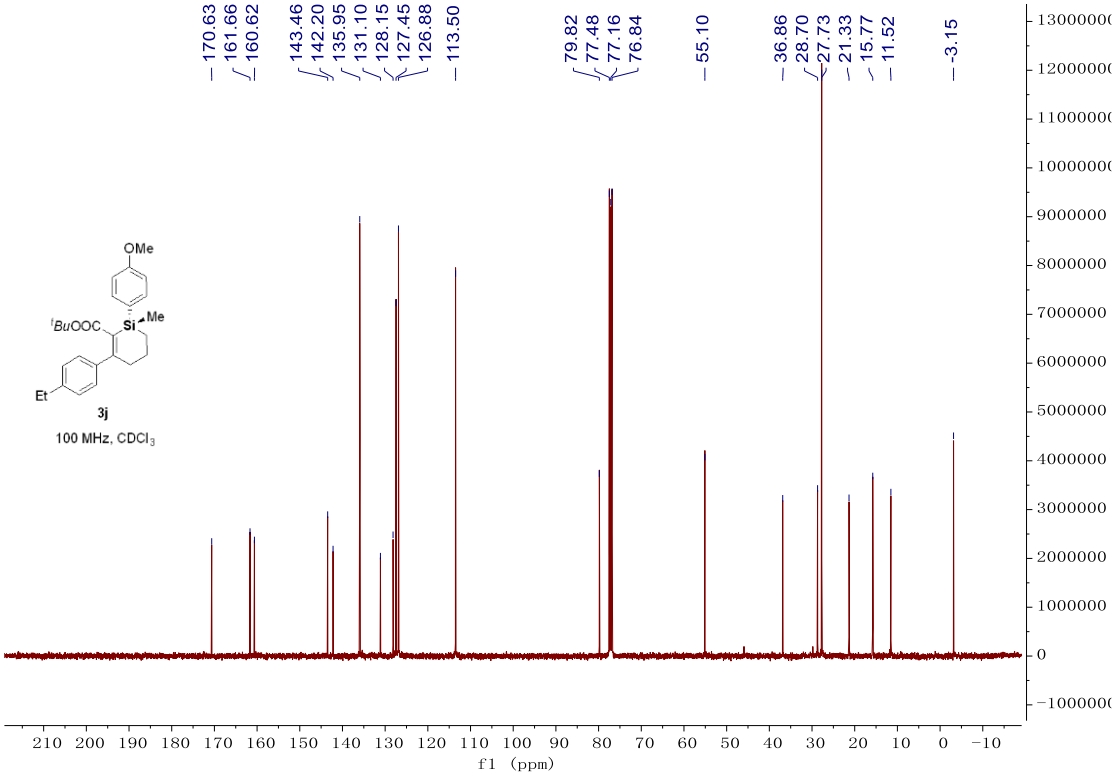
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27.73
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-3.15
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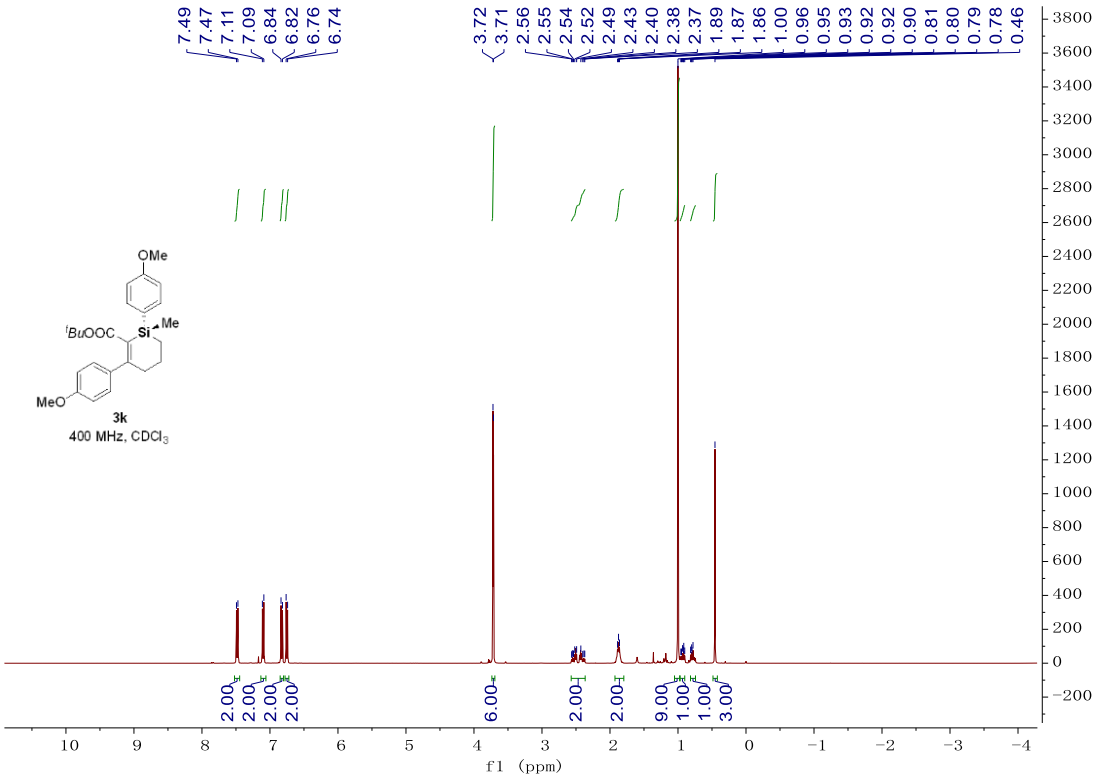
Si
Me
Et
3j
100 MHz, CDCl3
f1 (ppm)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MeO
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400 MHz, CDCl3
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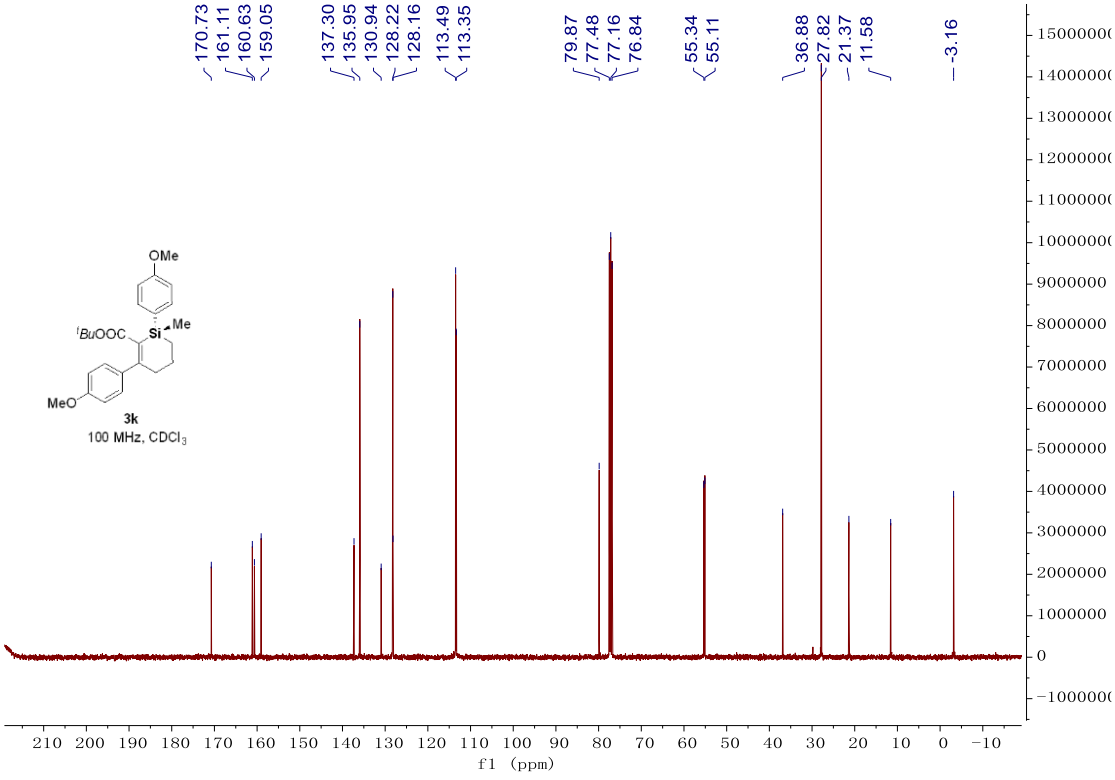
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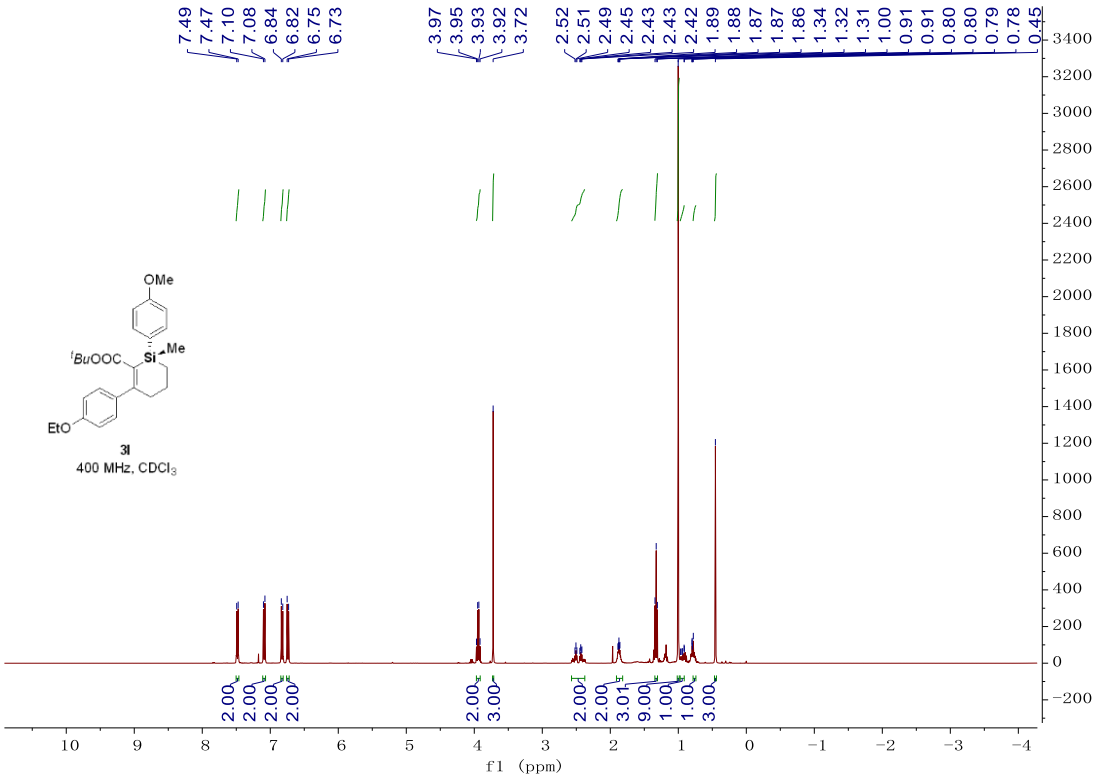
Si
Me
MeO
3k
100 MHz, CDCl3
f1 (ppm)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OMe
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EtO
3l
400 MHz, CDCl3
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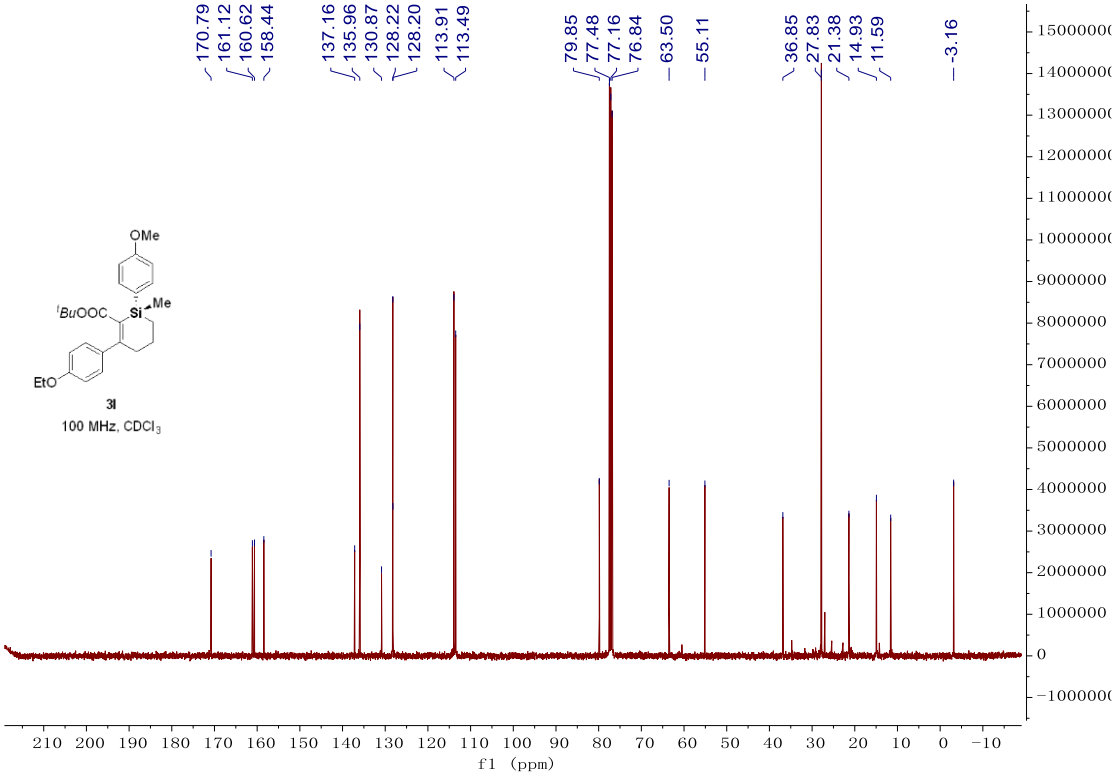
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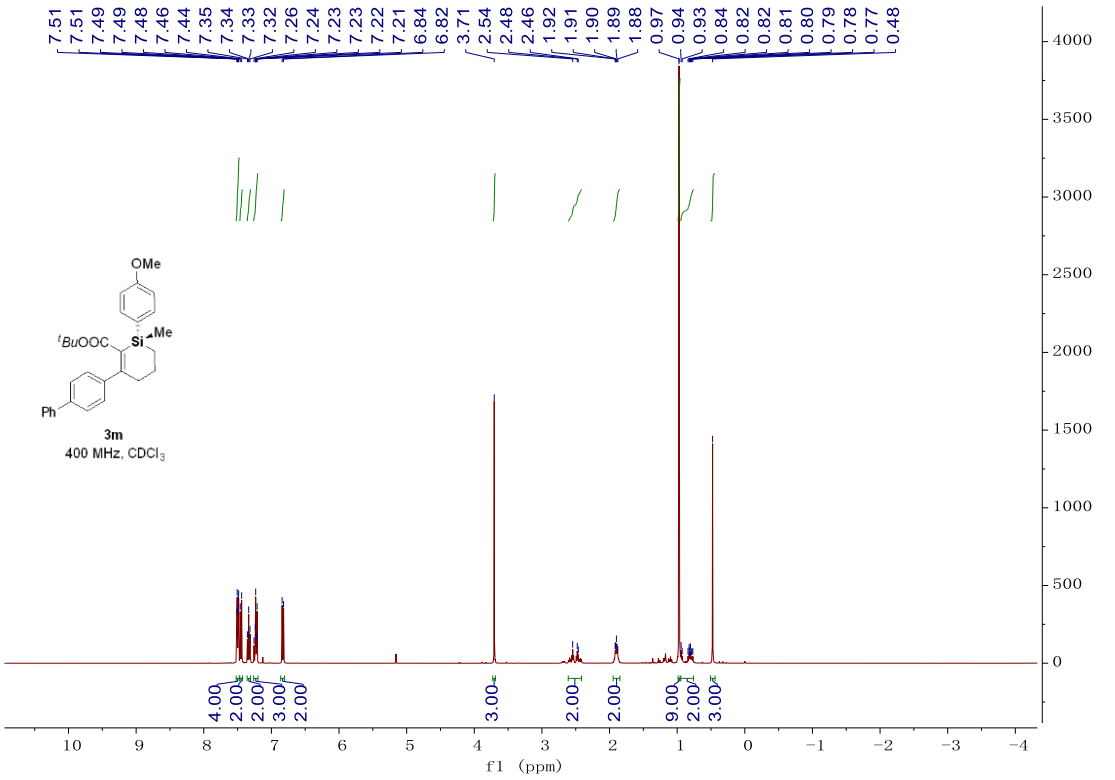
Me
EtO
3l
100 MHz, CDCl3
f1 (ppm)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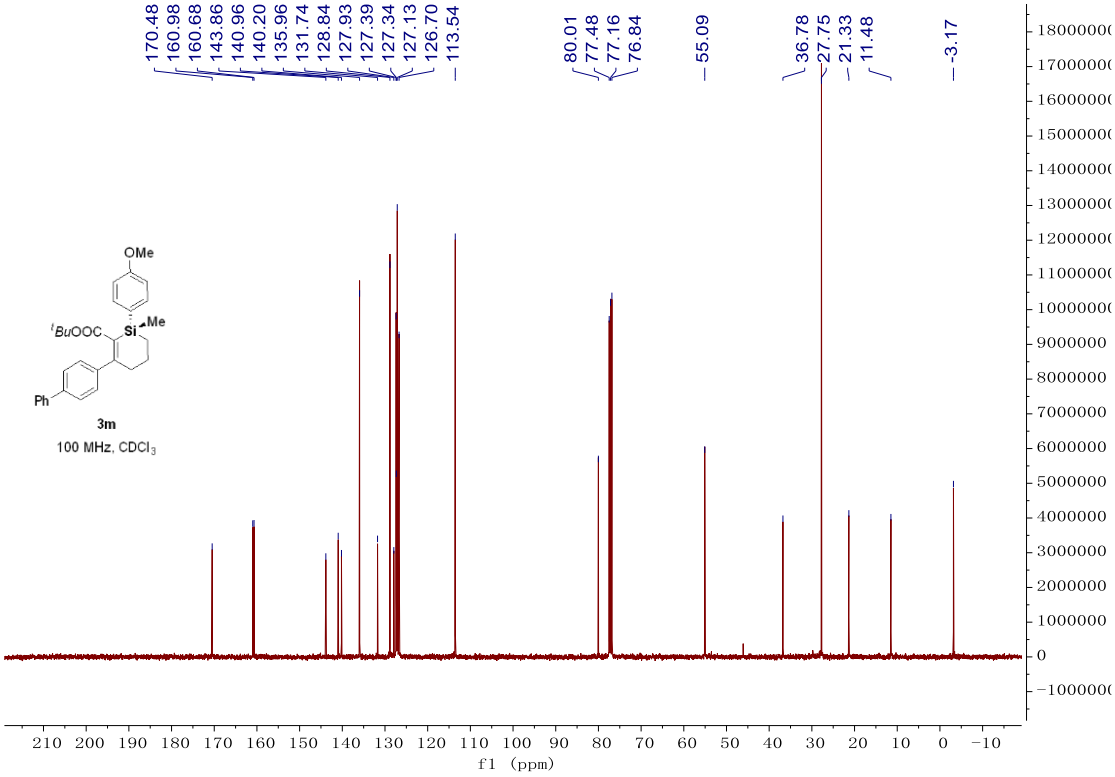
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Me
Ph
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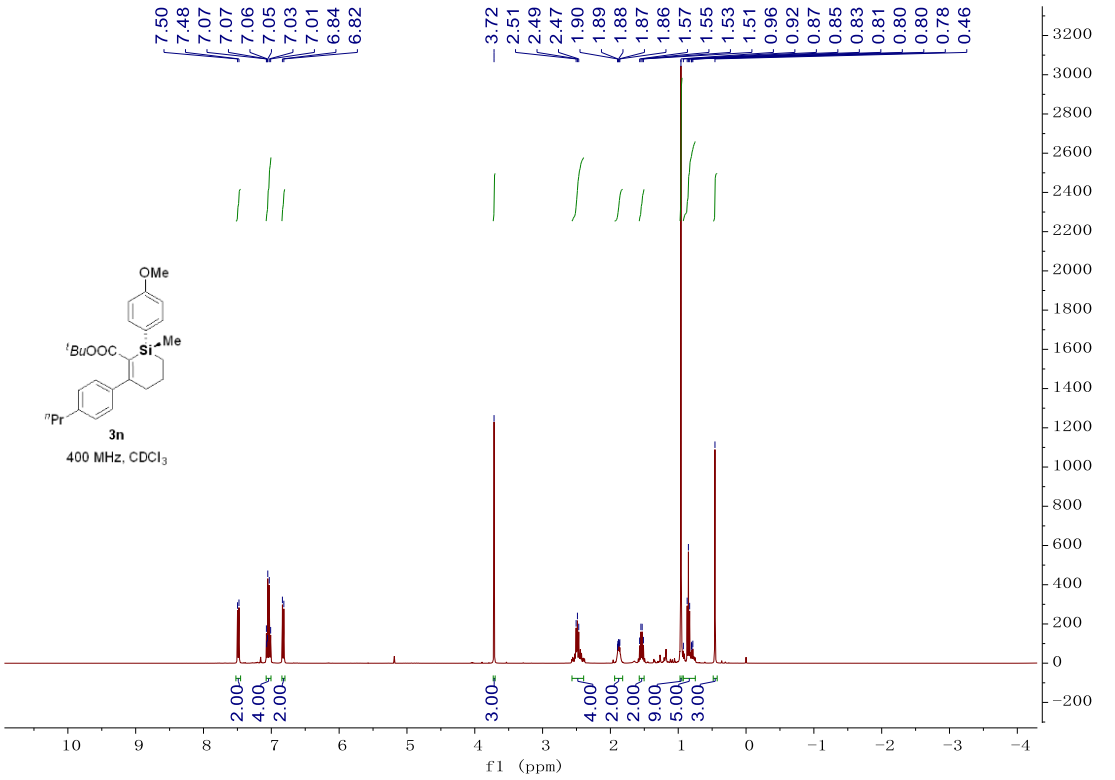
100 MHz, CDCl3
f1 (ppm)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OMe
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Si
Me
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400 MHz, CDCl3
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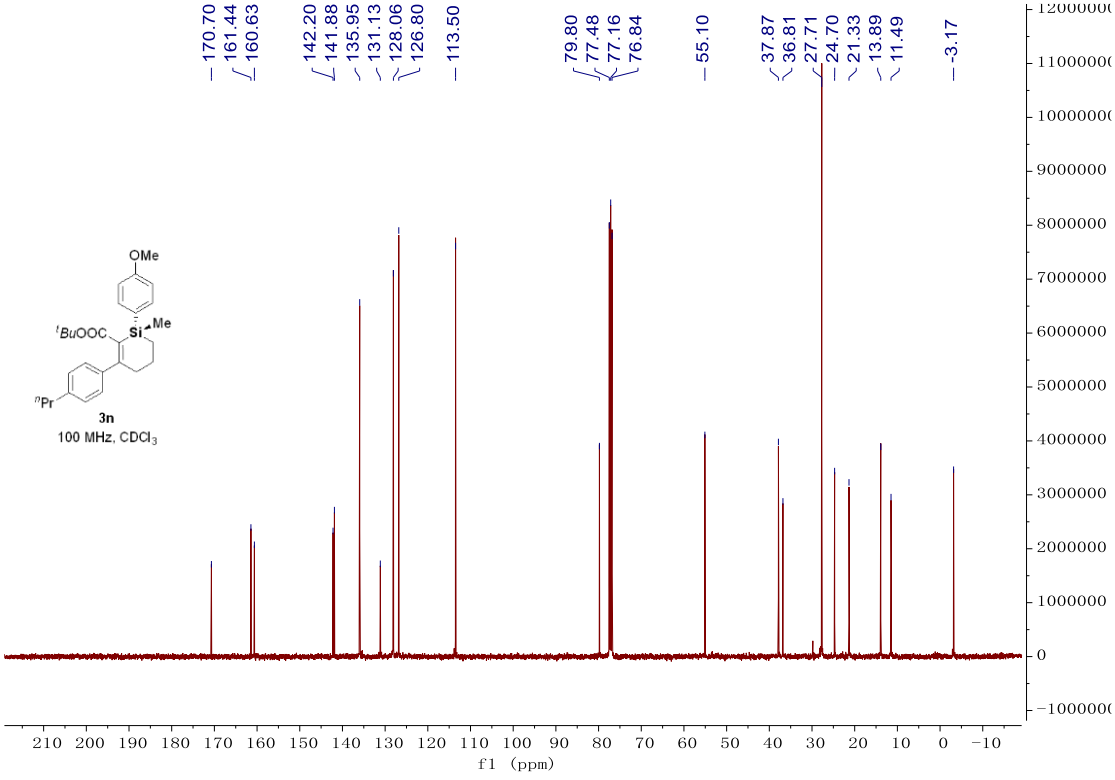
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Me
nPr
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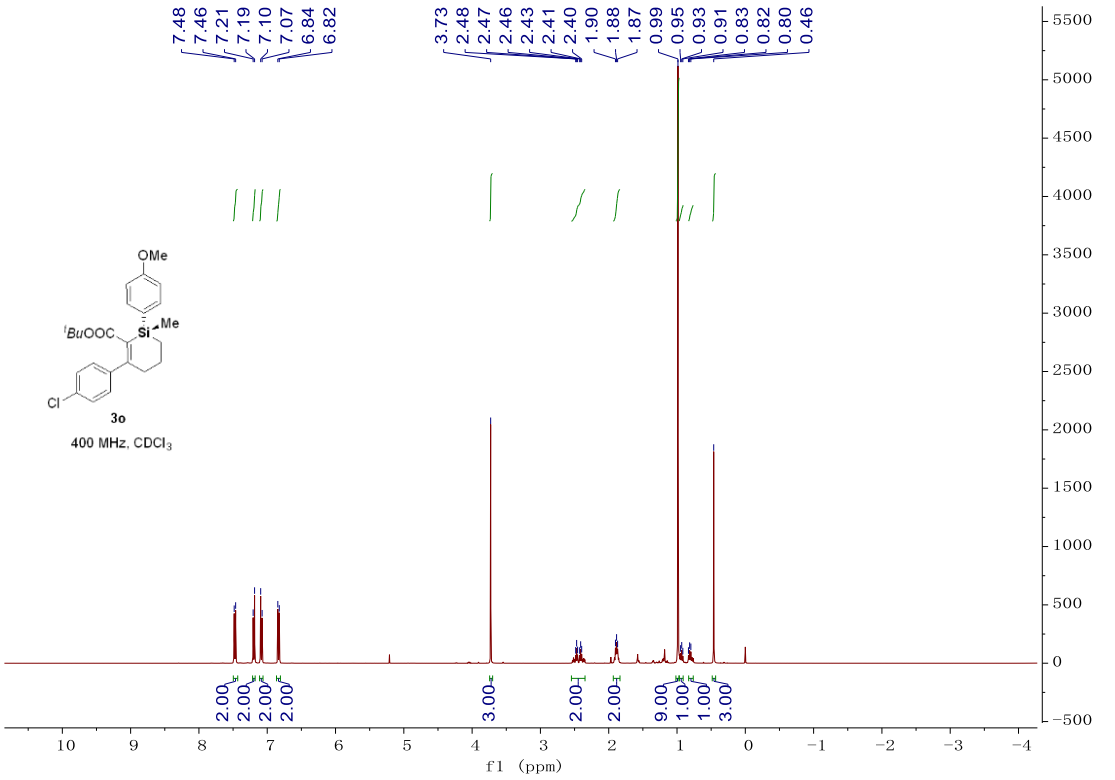
100 MHz, CDCl3
f1 (ppm)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2.40
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1.88
1.87
0.99
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0.93
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0.80
0.46
OMe
tBuOOC
Si
Me
Cl
3o
400 MHz, CDCl3
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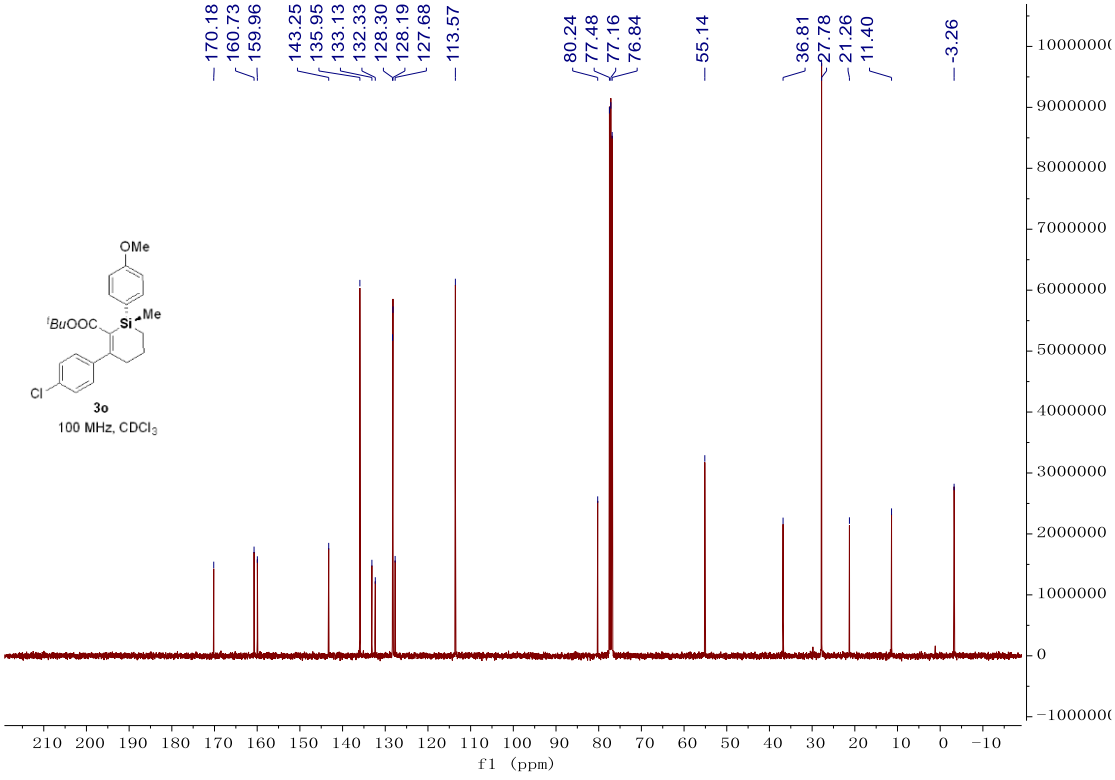
f1 (ppm)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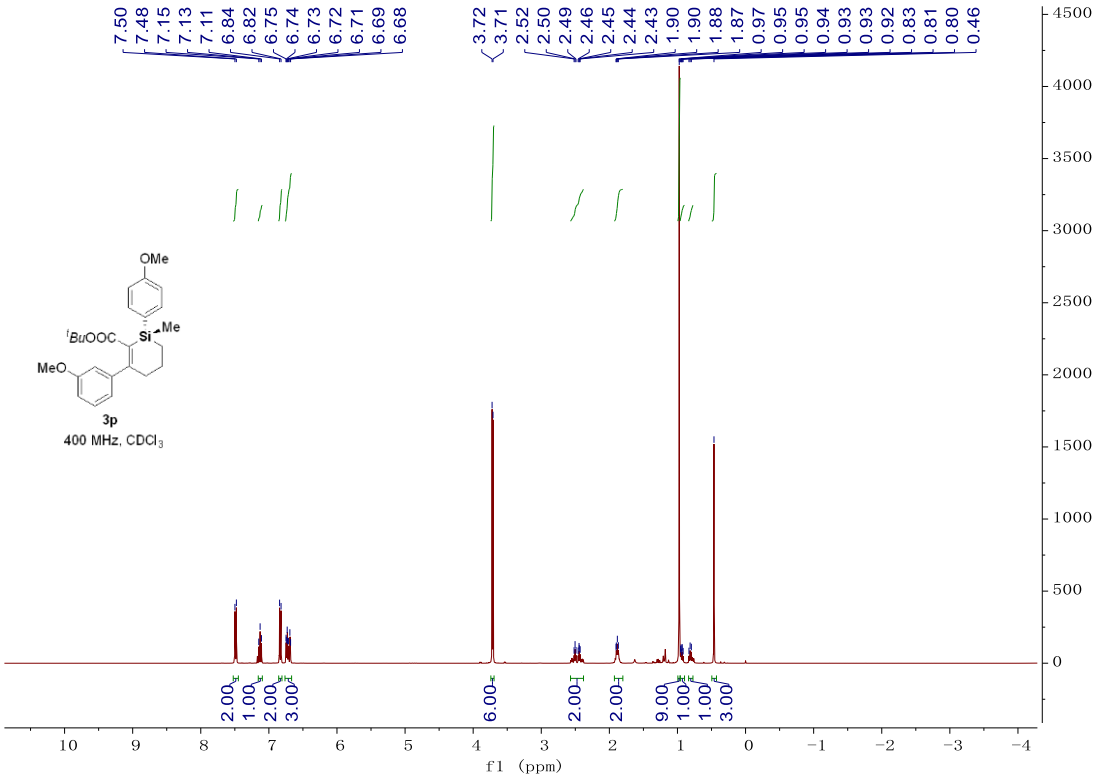
Me
Cl
3o
100 MHz, CDCl3
f1 (ppm)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2.50
2.49
2.46
2.45
2.44
2.43
1.90
1.90
1.88
1.87
0.97
0.95
0.95
0.94
0.93
0.93
0.92
0.83
0.81
0.80
0.46
OMe
tBuOOC
Si
Me
MeO
3p
400 MHz, CDCl3
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6.00
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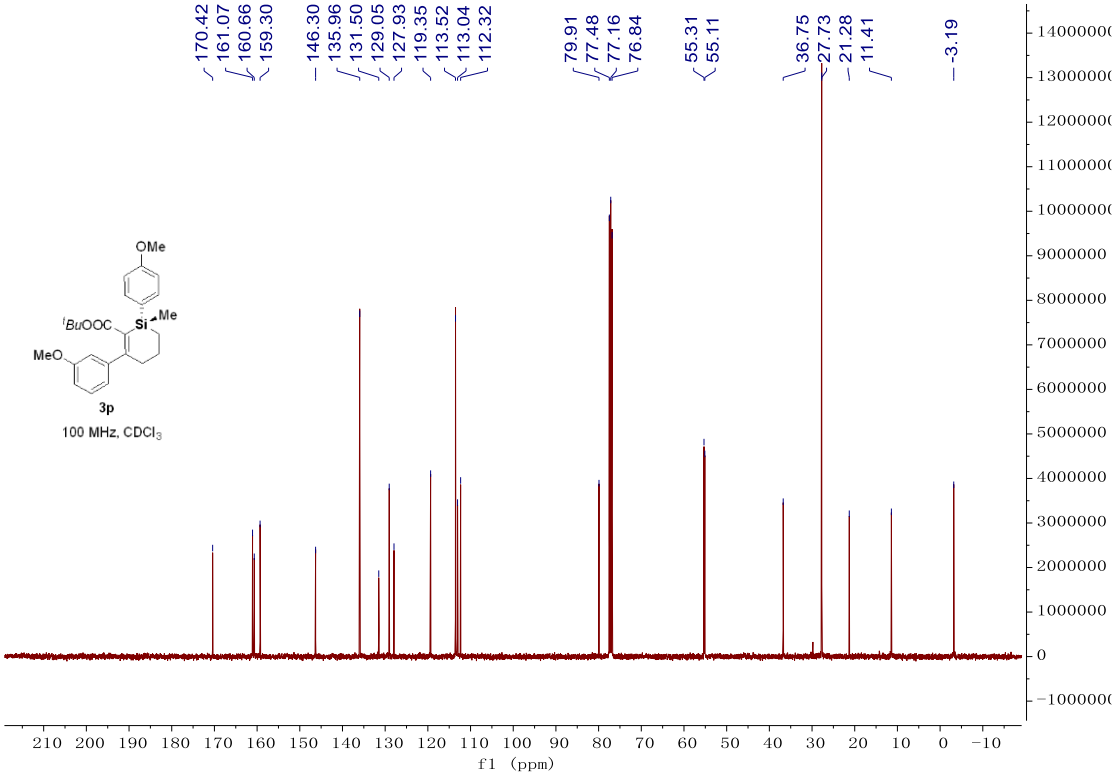
9.00
1.00
1.00
3.00
f1 (ppm)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119.35
113.52
113.04
112.32
79.91
77.48
77.16
76.84
55.31
55.11
36.75
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-3.19
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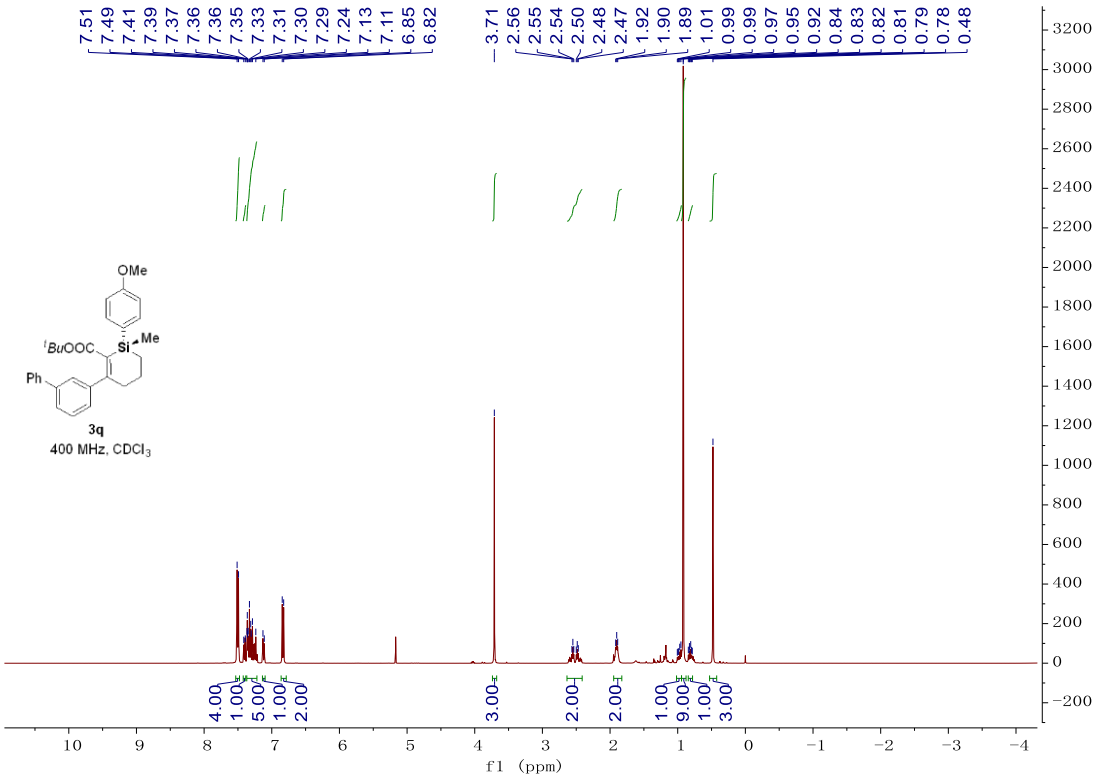
tBuOOC
Si
Me
MeO
3p
100 MHz, CDCl3
f1 (ppm)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7.24
7.13
7.11
6.85
6.82
3.71
2.56
2.55
2.54
2.50
2.48
2.47
1.92
1.90
1.89
1.01
0.99
0.99
0.97
0.95
0.92
0.84
0.83
0.82
0.81
0.79
0.78
0.48
OMe
tBuOOC
Si
Me
Ph
3q
400 MHz, CDCl3
4.00
1.00
5.00
1.00
2.00
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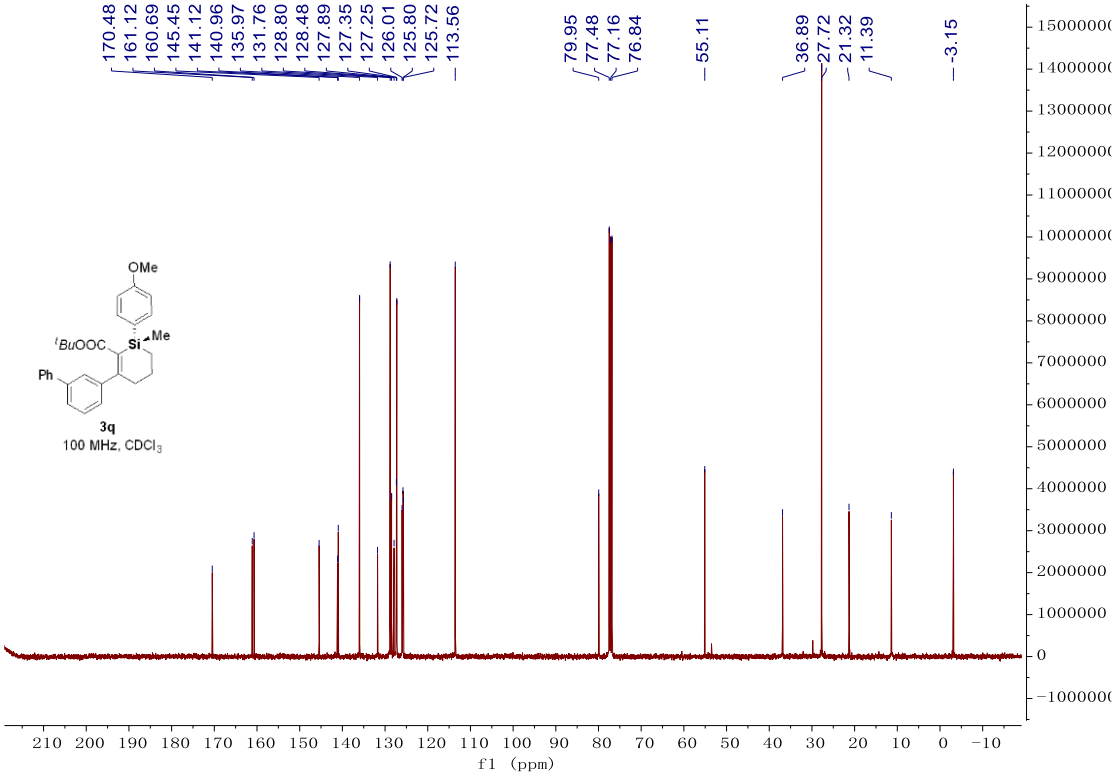
1.00
9.00
1.00
3.00
f1 (ppm)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127.25
126.01
125.80
125.72
113.56
79.95
77.48
77.16
76.84
55.11
36.89
27.72
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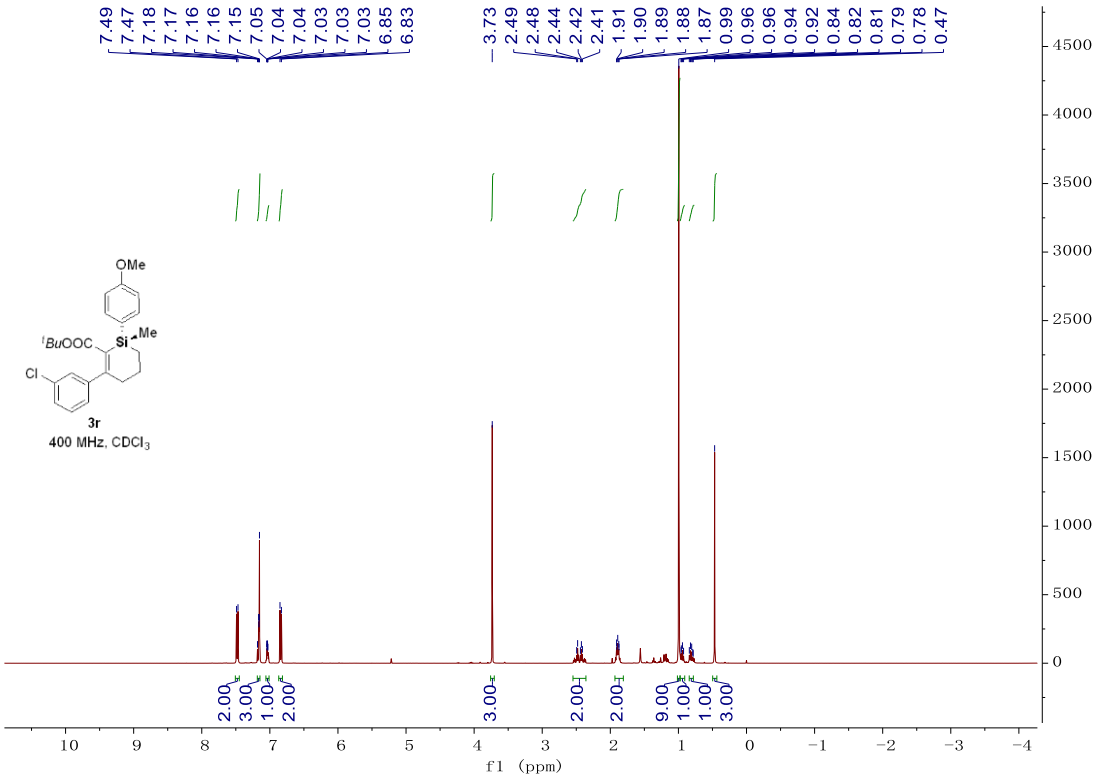
11.39
-3.15
OMe
tBuOOC
Si
Me
Ph
3q
100 MHz, CDCl3
f1 (ppm)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7.04
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7.03
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6.83
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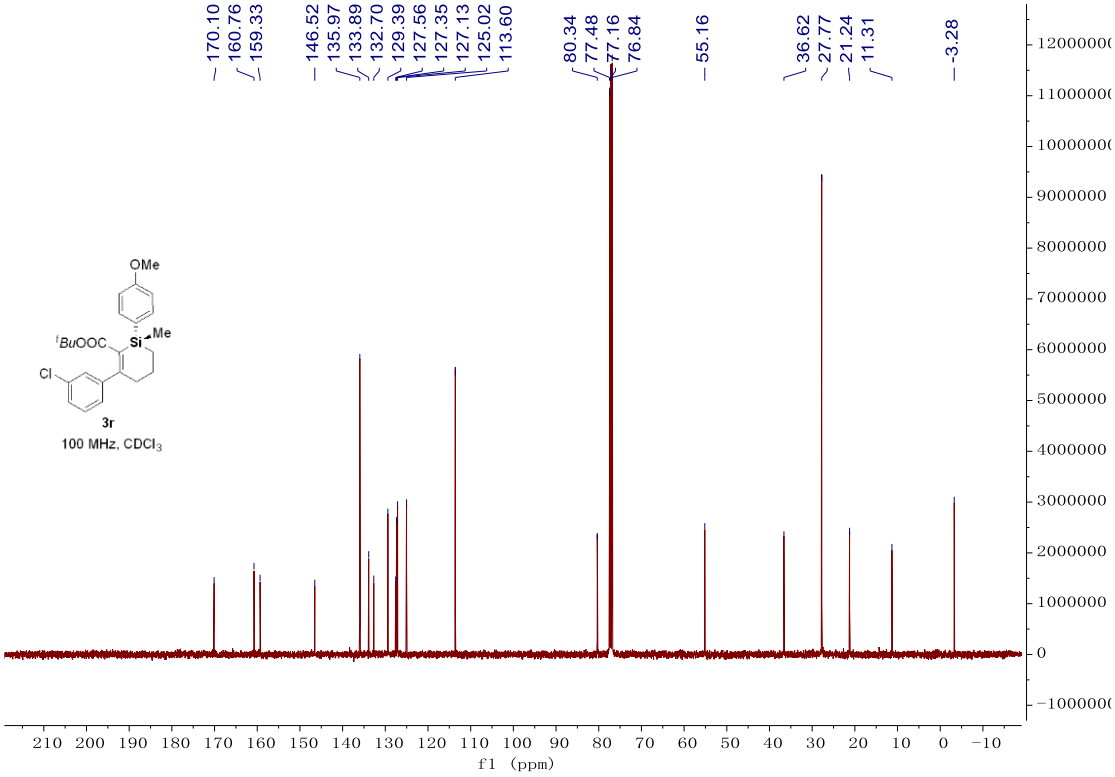
2.48
2.44
2.42
2.41
1.91
1.90
1.89
1.88
1.87
0.99
0.96
0.96
0.94
0.92
0.84
0.82
0.81
0.79
0.78
0.47
OMe
tBuOOC
Si
Me
Cl
3r
400 MHz, CDCl3
2.00
3.00
1.00
2.00
3.00
2.00
2.00
9.00
1.00
1.00
3.00
f1 (ppm)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127.13
125.02
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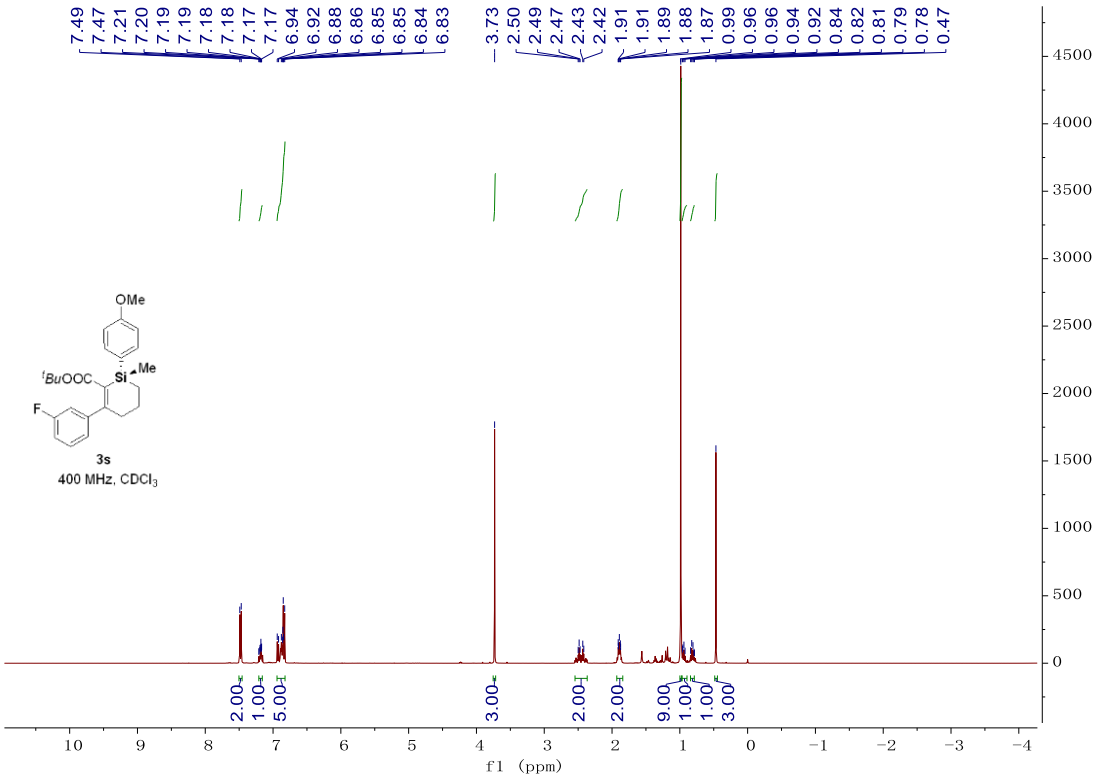
80.34
77.48
77.16
76.84
55.16
36.62
27.77
21.24
11.31
-3.28
OMe
tBuOOC
Si
Me
Cl
3r
100 MHz, CDCl3
f1 (ppm)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7.19
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7.18
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7.17
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6.92
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6.85
6.85
6.84
6.83
3.73
2.50
2.49
2.47
2.43
2.42
1.91
1.91
1.89
1.88
1.87
0.99
0.96
0.96
0.94
0.92
0.84
0.82
0.81
0.79
0.78
0.47
OMe
tBuOOC
Si
Me
F
3s
400 MHz, CDCl3
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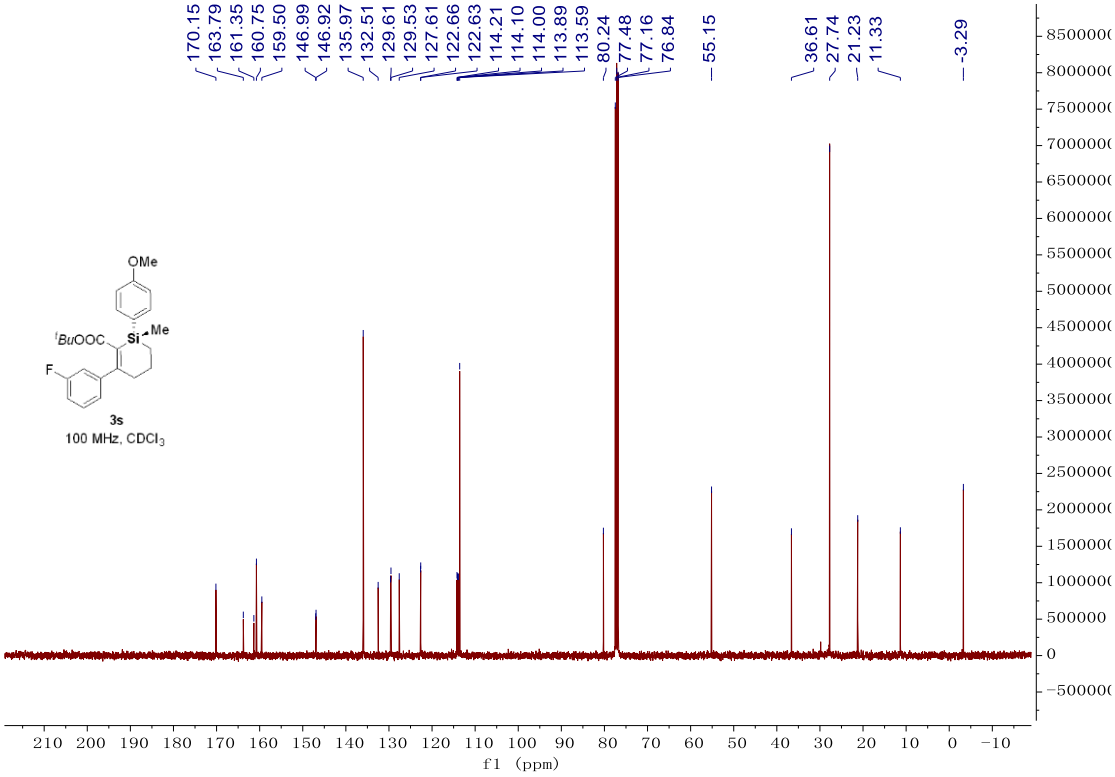
1.00
5.00
3.00
2.00
2.00
9.00
1.00
1.00
3.00
f1 (ppm)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129.61
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127.61
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122.63
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113.89
113.59
80.24
77.48
77.16
76.84
55.15
36.61
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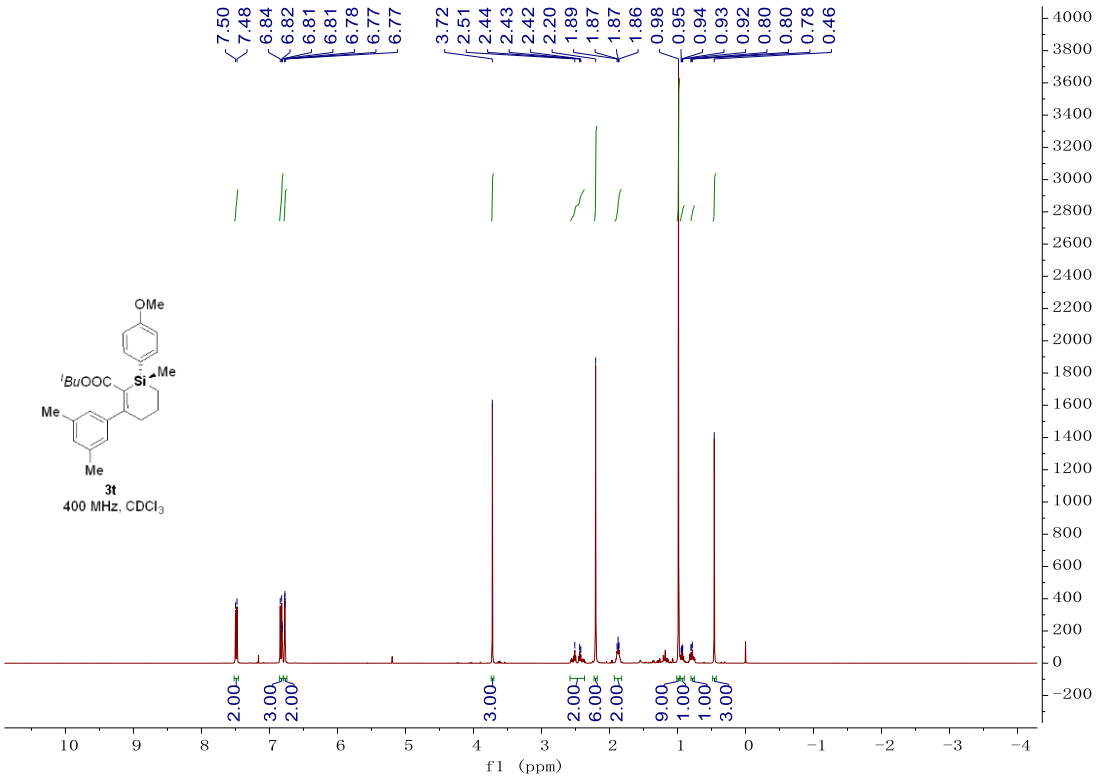
11.33
-3.29
OMe
tBuOOC
Si
Me
F
3s
100 MHz, CDCl3
f1 (ppm)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6.84
6.82
6.81
6.81
6.78
6.77
6.77
3.72
2.51
2.44
2.43
2.42
2.20
1.89
1.87
1.87
1.86
0.98
0.95
0.94
0.93
0.92
0.80
0.80
0.78
0.46
OMe
tBuOOC
Si
Me
Me
Me
3t
400 MHz, CDCl3
2.00
3.00
2.00
3.00
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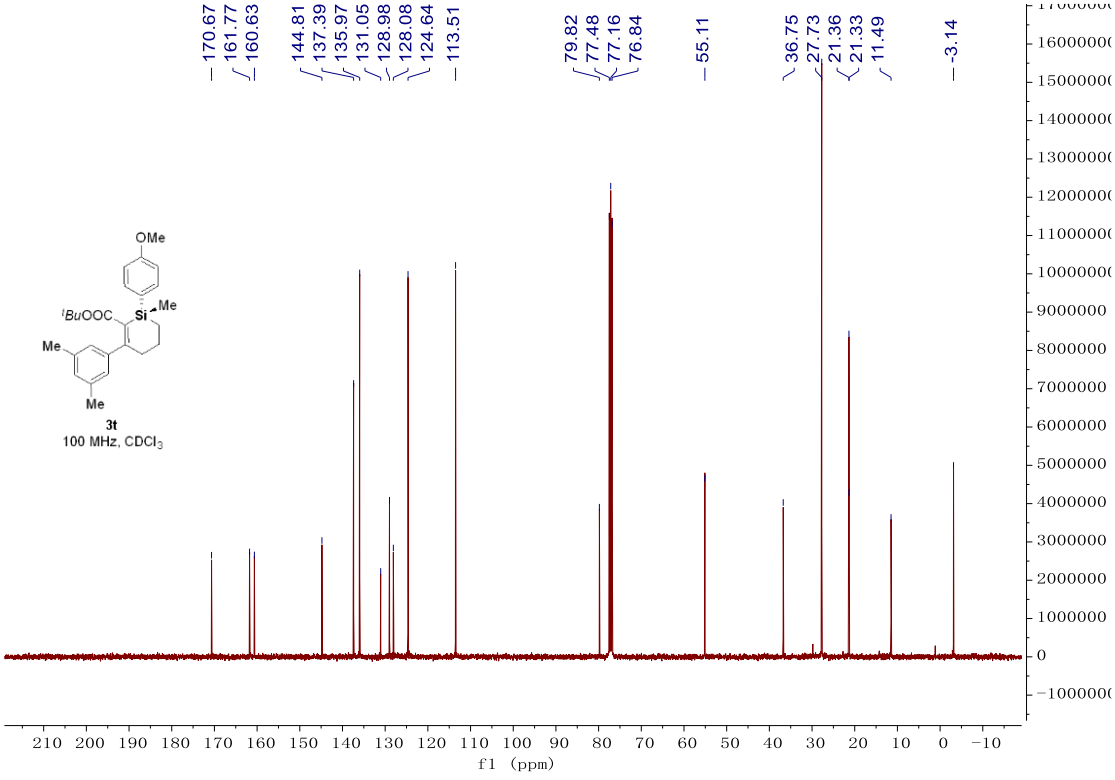
9.00
1.00
1.00
3.00
f1 (ppm)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124.64
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79.82
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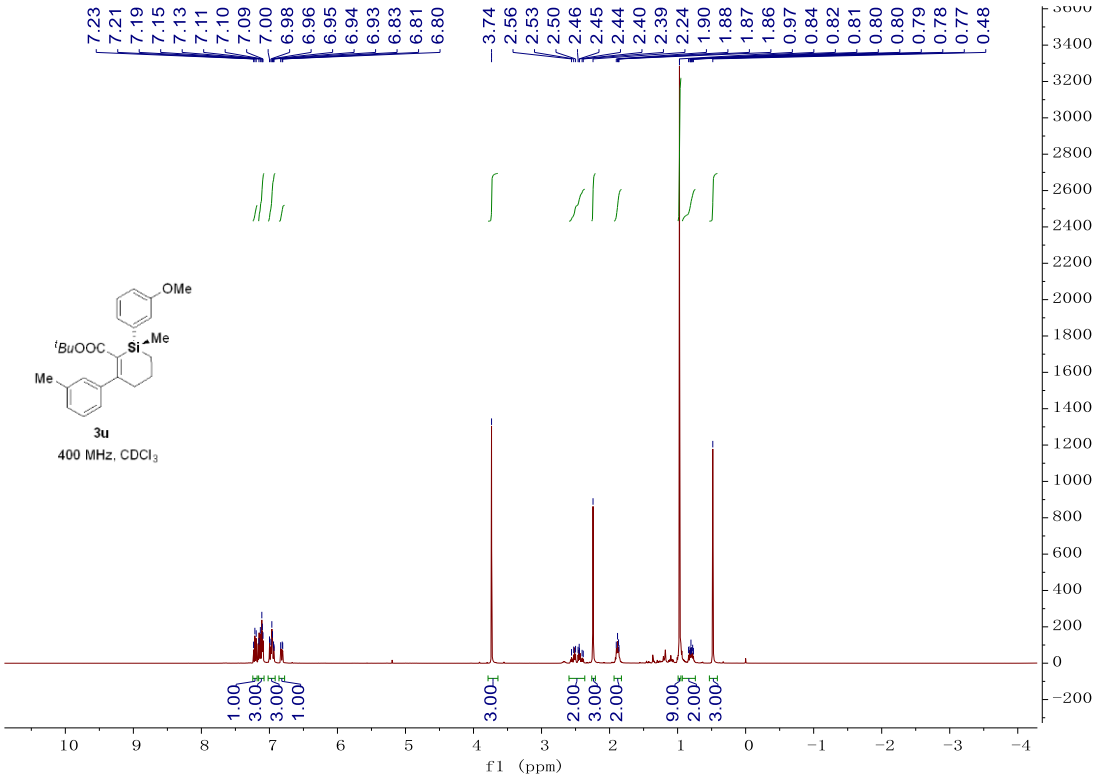
77.16
76.84
55.11
36.75
27.73
21.36
21.33
11.49
-3.14
OMe
tBuOOC
Si
Me
Me
Me
3t
100 MHz, CDCl3
f1 (ppm)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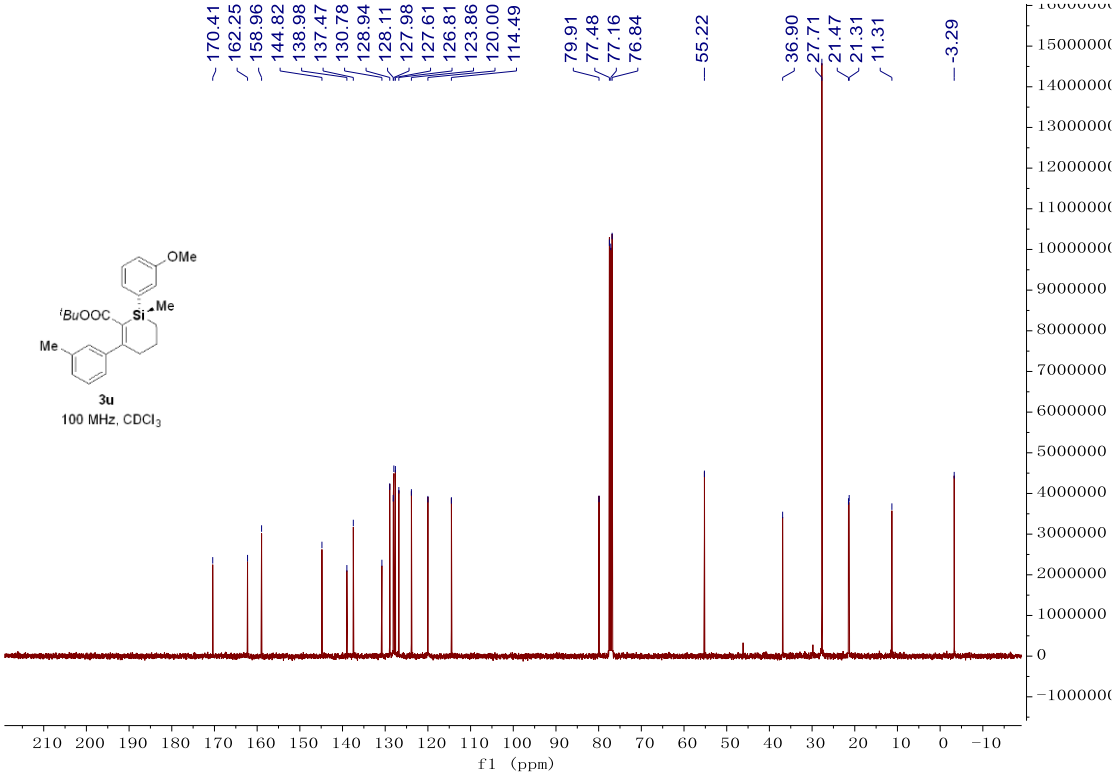
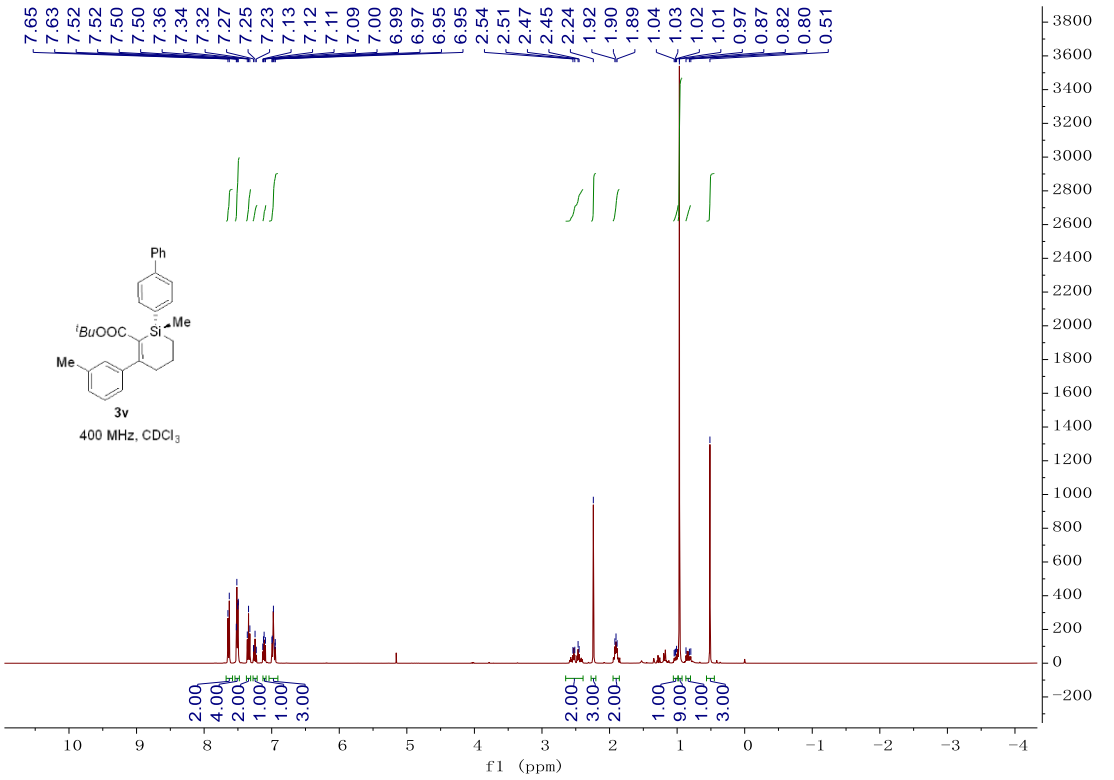
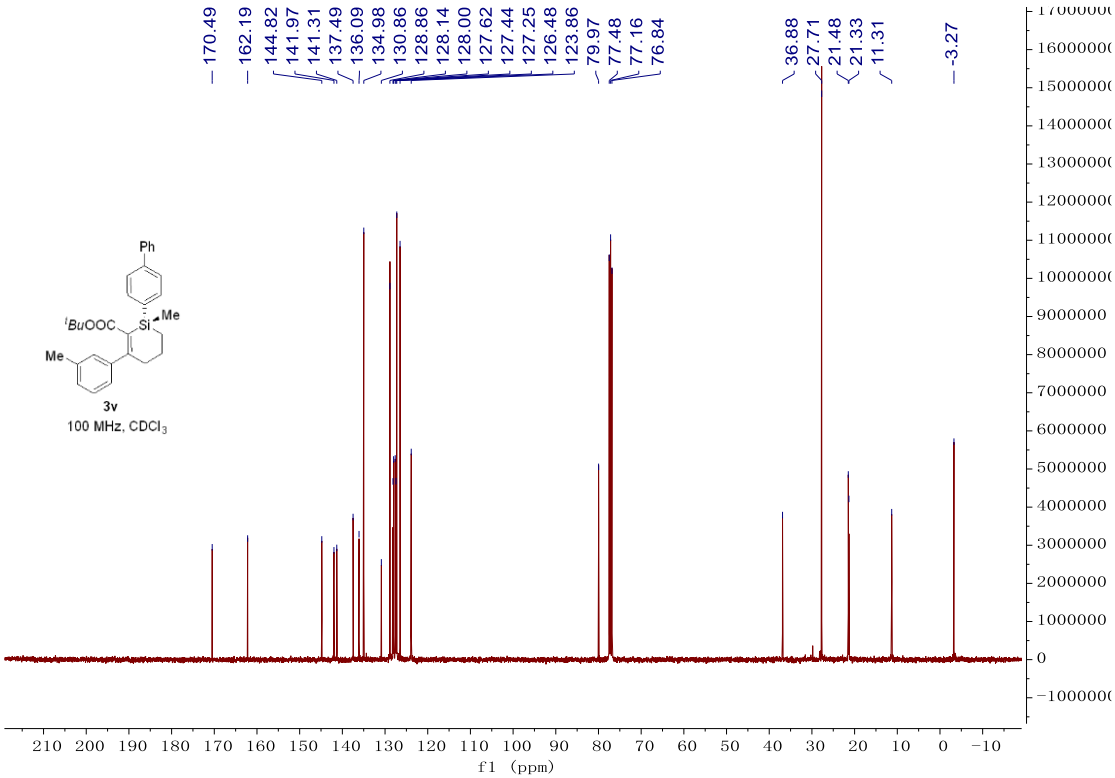
3.74 2.56 2.53 2.50 2.46 2.45 2.44 2.40 2.39 2.24 1.90 1.88 1.87 1.86 0.97 0.84 0.82 0.81 0.80 0.80 0.79 0.78 0.77 0.48
OMe
tBuOOC
Si
Me
Me
3u
400 MHz, CDCl3
1.00 3.00 3.00 1.00 3.00 2.00 3.00 2.00 9.00 2.00 3.00
f1 (ppm)


170.41 162.25 158.96 144.82 138.98 137.47 130.78 128.94 128.11 127.98 127.61 126.81 123.86 120.00 114.49
79.91 77.48 77.16 76.84
55.22
36.90 27.71 21.47 21.31 11.31
-3.29
OMe
tBuOOC
Si
Me
Me
3u
100 MHz, CDCl3
f1 (ppm)


7.65 7.63 7.52 7.52 7.50 7.50 7.36 7.34 7.32 7.27 7.25 7.23 7.13 7.12 7.11 7.09 7.00 6.99 6.97 6.95 6.95 2.54 2.51 2.47 2.45 2.24 1.92 1.90 1.89 1.04 1.03 1.02 1.01 0.97 0.87 0.82 0.80 0.51
Ph
tBuOOC
Si
Me
Me
3v
400 MHz, CDCl3
2.00 4.00 2.00 1.00 1.00 3.00 2.00 3.00 2.00 1.00 9.00 1.00 3.00
f1 (ppm)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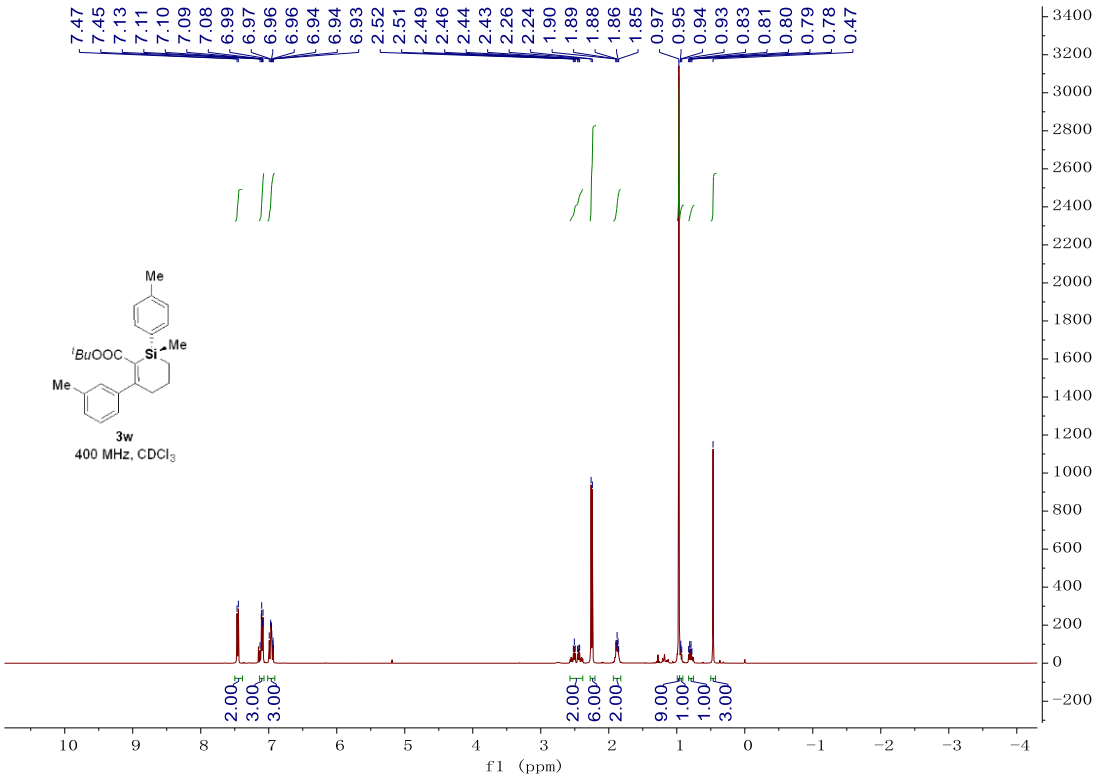
Ph
tBuOOC
Si
Me
Me
3v
100 MHz, CDCl3
f1 (ppm)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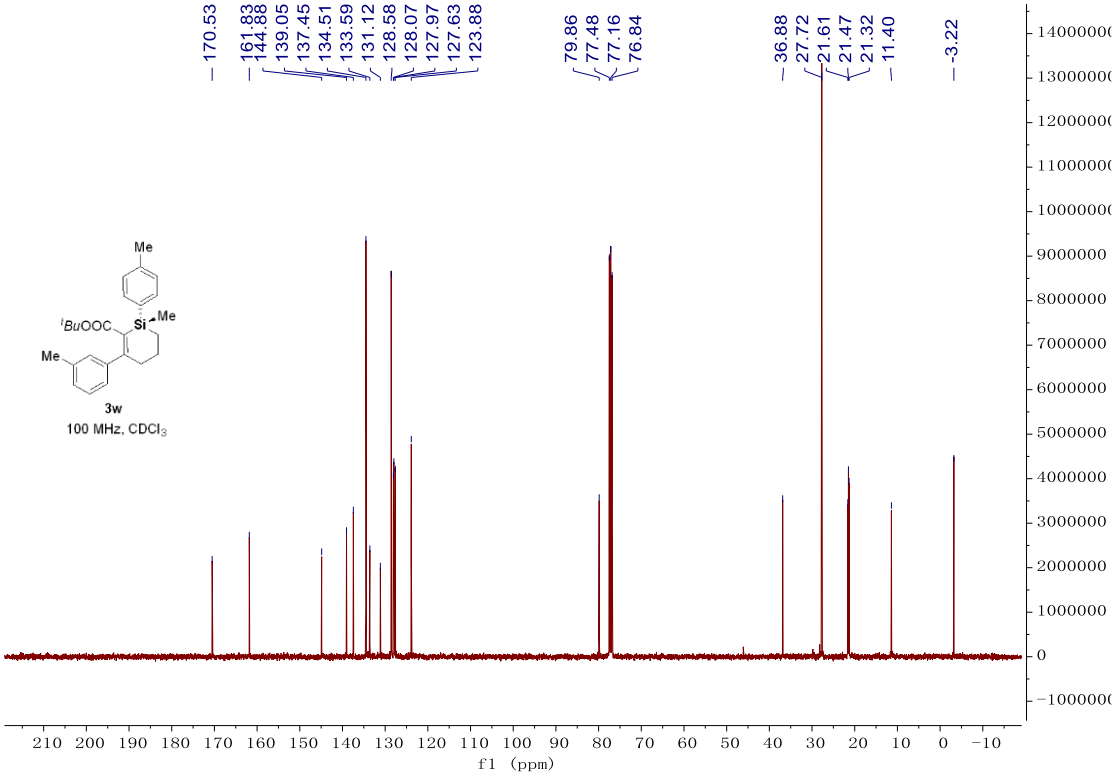
7.09
7.08
6.99
6.97
6.96
6.96
6.94
6.94
6.93
2.52
2.51
2.49
2.46
2.44
2.43
2.26
2.24
1.90
1.89
1.88
1.86
1.85
0.97
0.95
0.94
0.93
0.83
0.81
0.80
0.79
0.78
0.47
2.00
3.00
3.00
2.00
6.00
2.00
9.00
1.00
1.00
3.00
f1 (ppm)
Me
tBuOOC
Si
Me
Me
3w
400 MHz, CDCl3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139.05
137.45
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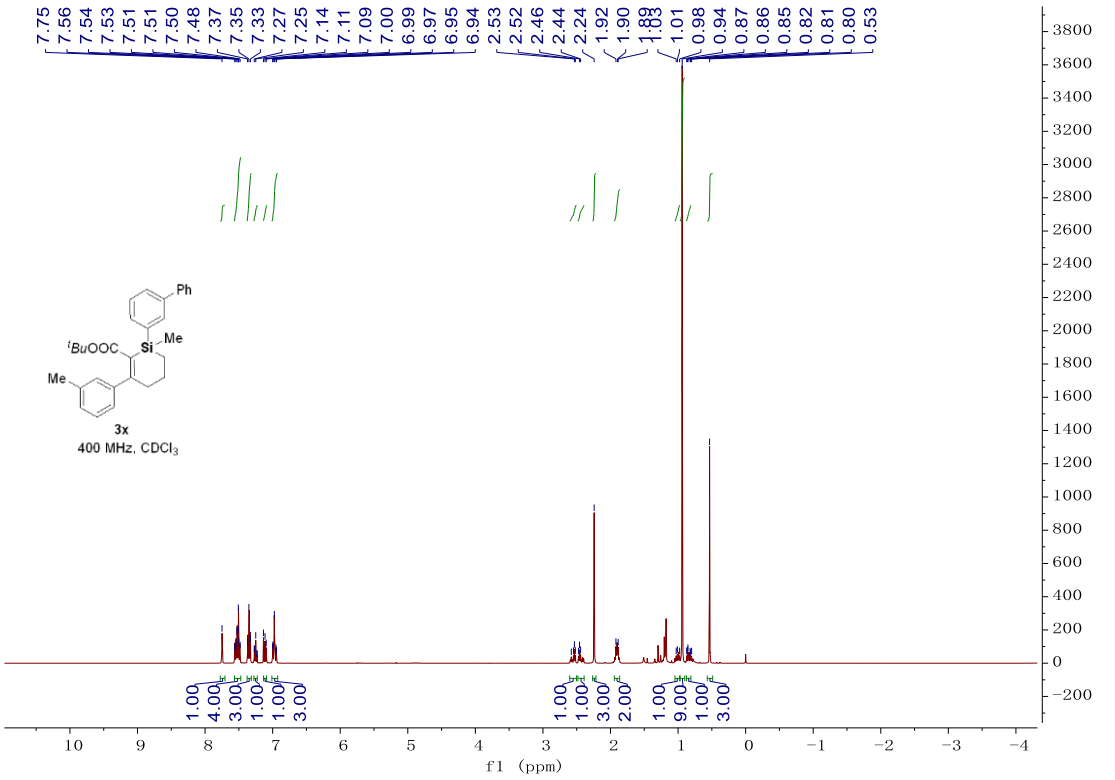
128.58
128.07
127.97
127.63
123.88
79.86
77.48
77.16
76.84
36.88
27.72
21.61
21.47
21.32
11.40
-3.22
f1 (ppm)
Me
tBuOOC
Si
Me
Me
3w
100 MHz, CDCl3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Ph
Me
tBuOOC
Si
Me
3x
400 MHz, CDCl3
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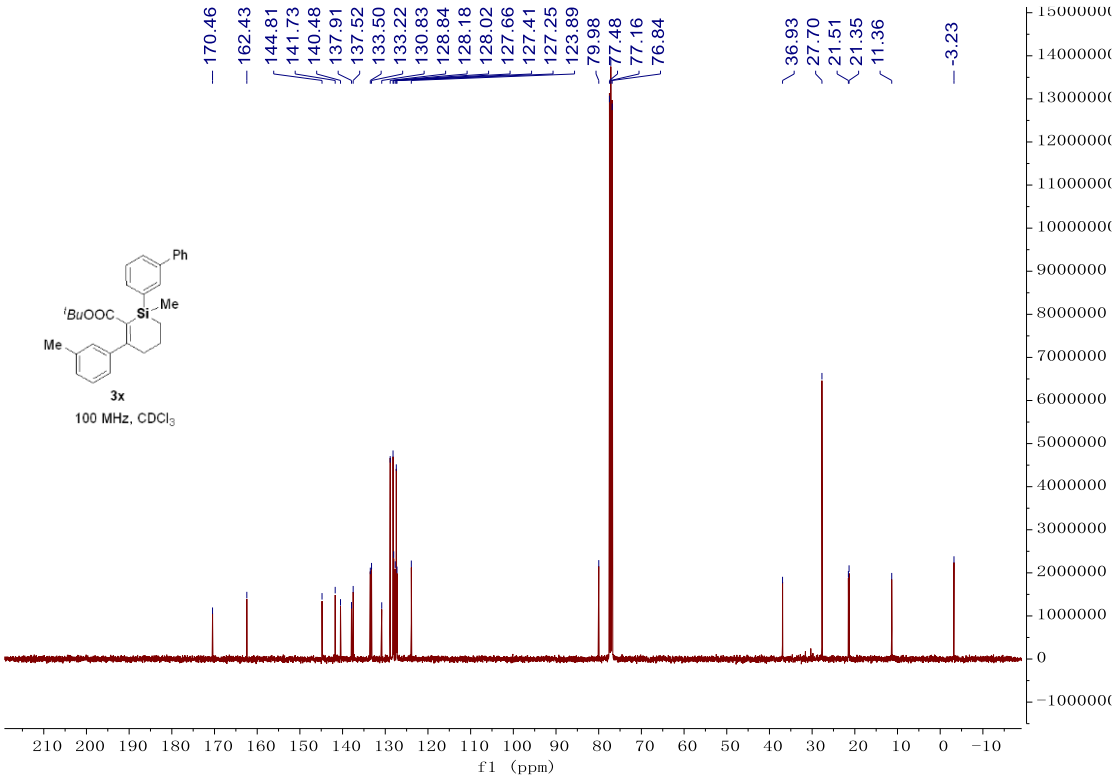
f1 (ppm)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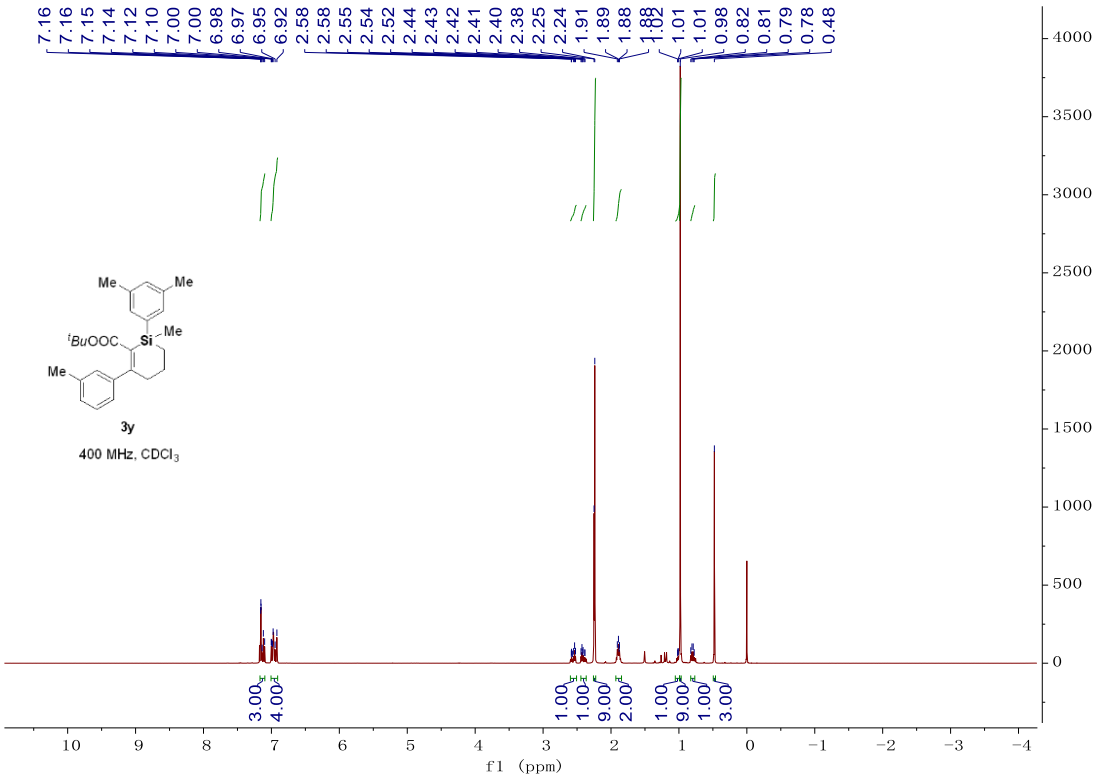
Ph
Me
tBuOOC
Si
Me
3x
100 MHz, CDCl3
f1 (ppm)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7.00
6.98
6.97
6.95
6.92
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2.58
2.55
2.54
2.52
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2.41
2.40
2.38
2.25
2.24
1.91
1.89
1.88
1.02
1.01
1.01
0.98
0.82
0.81
0.79
0.78
0.48
Me
Me
Me
tBuOOC
Si
Me
3y
400 MHz, CDCl3
3.00
4.00
1.00
1.00
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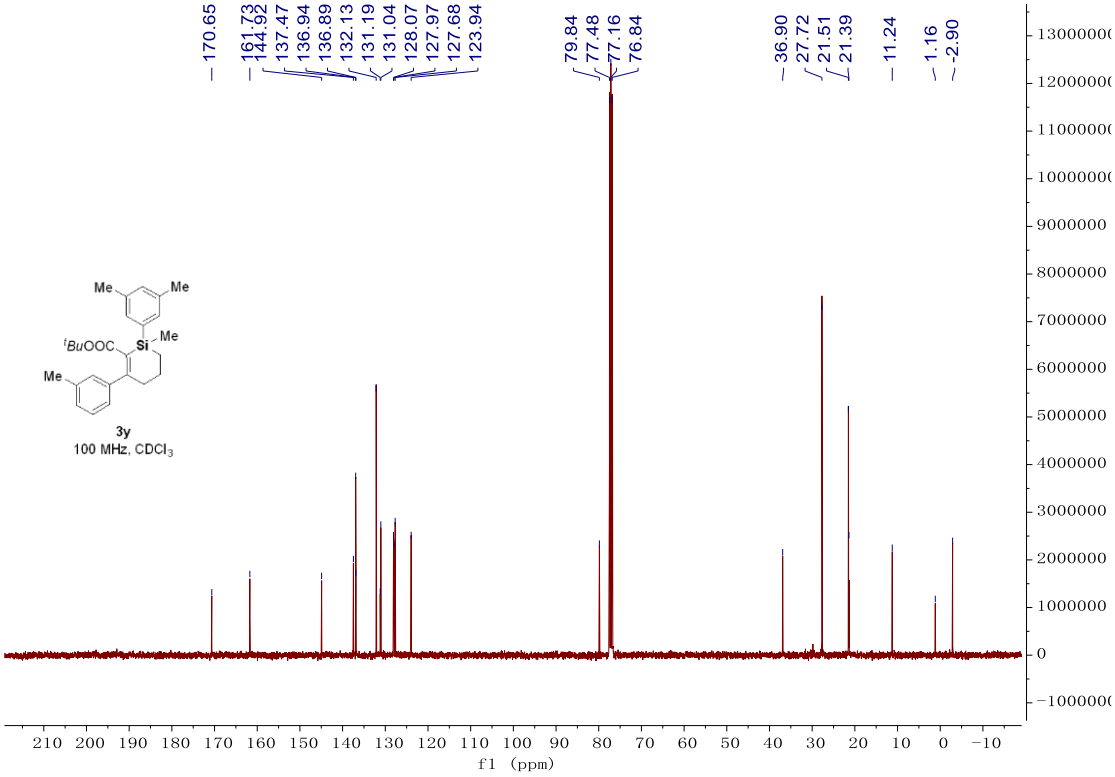
1.00
9.00
1.00
3.00
f1 (ppm)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131.19
131.04
128.07
127.97
127.68
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79.84
77.48
77.16
76.84
36.90
27.72
21.51
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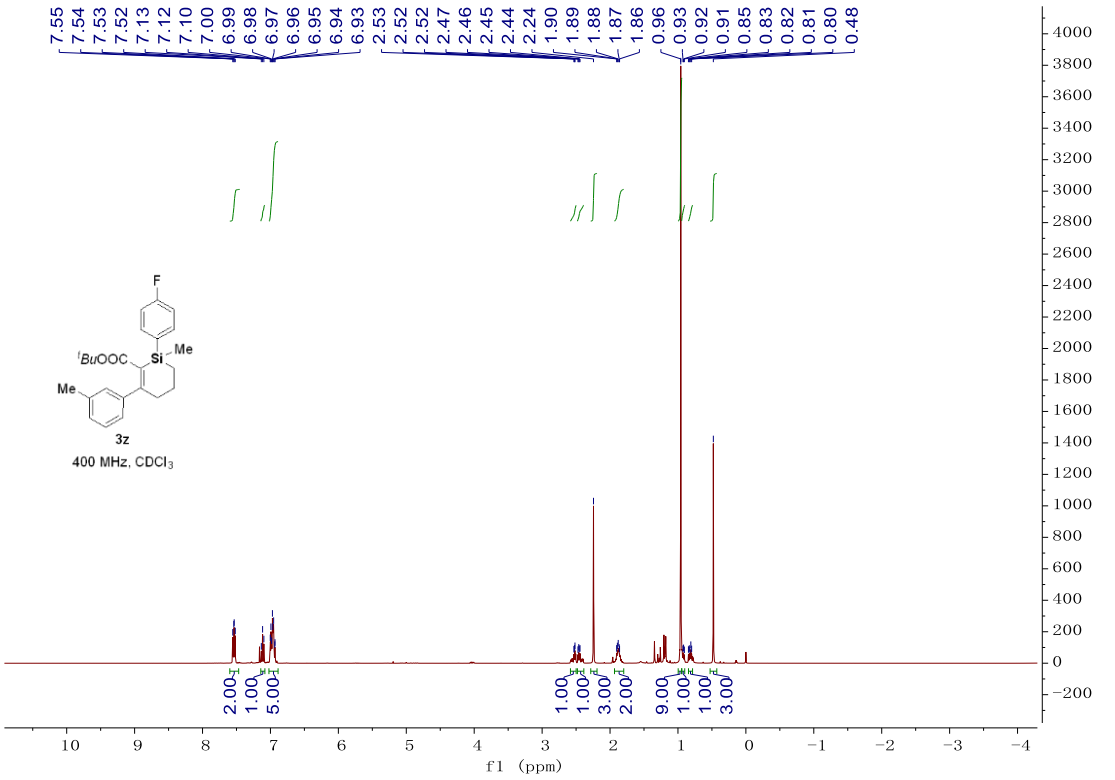
-2.90
Me
Me
Me
tBuOOC
Si
Me
3y
100 MHz, CDCl3
f1 (ppm)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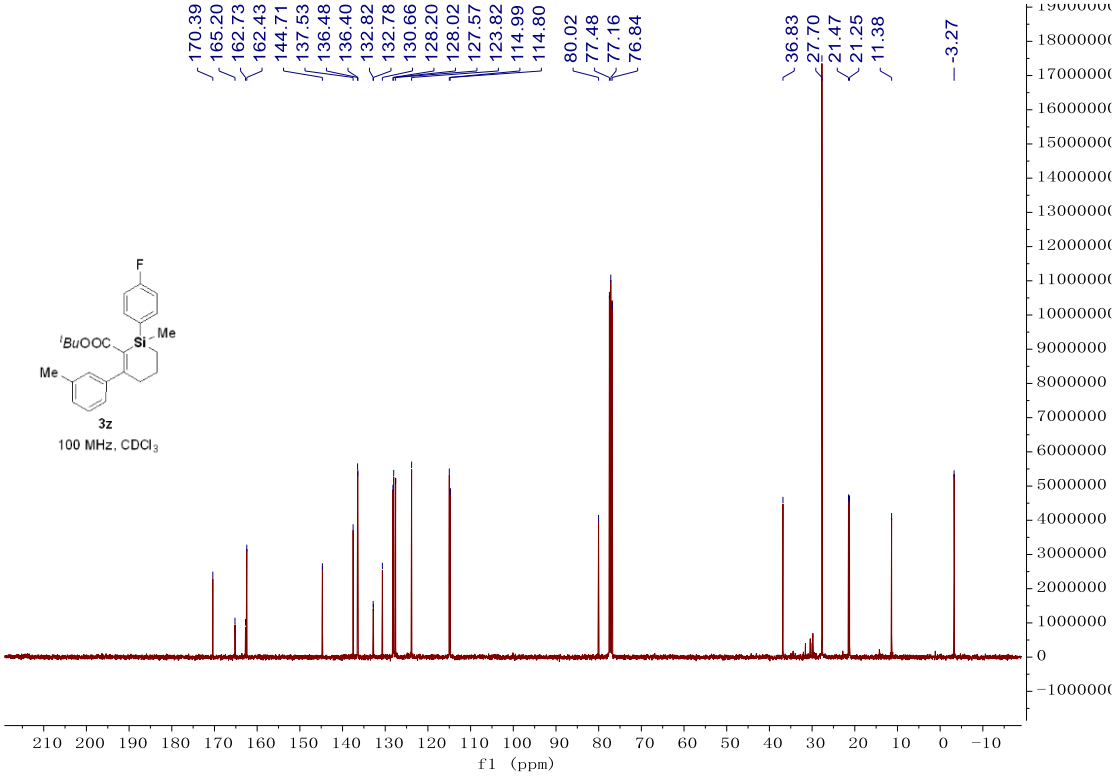
F
tBuOOC
Si
Me
Me
3z
400 MHz, CDCl3
2.00 1.00 5.00 1.00 1.00 3.00 2.00 9.00 1.00 1.00 3.00
f1 (ppm)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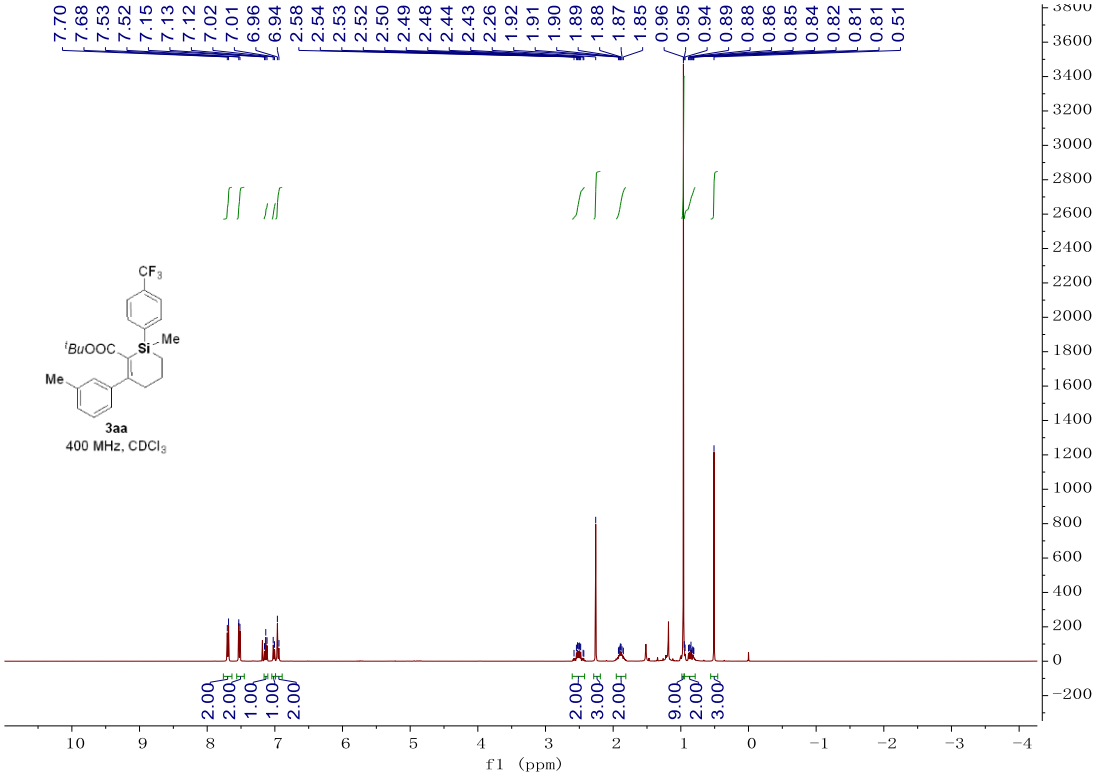
F
tBuOOC
Si
Me
Me
3z
100 MHz, CDCl3
f1 (ppm)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6.94
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2.53
2.52
2.50
2.49
2.48
2.44
2.43
2.26
1.92
1.91
1.90
1.89
1.88
1.87
1.85
0.96
0.95
0.94
0.89
0.88
0.86
0.85
0.84
0.82
0.81
0.81
0.51
CF3
tBuOOC
Si
Me
Me
3aa
400 MHz, CDCl3
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2.00
1.00
1.00
2.00
2.00
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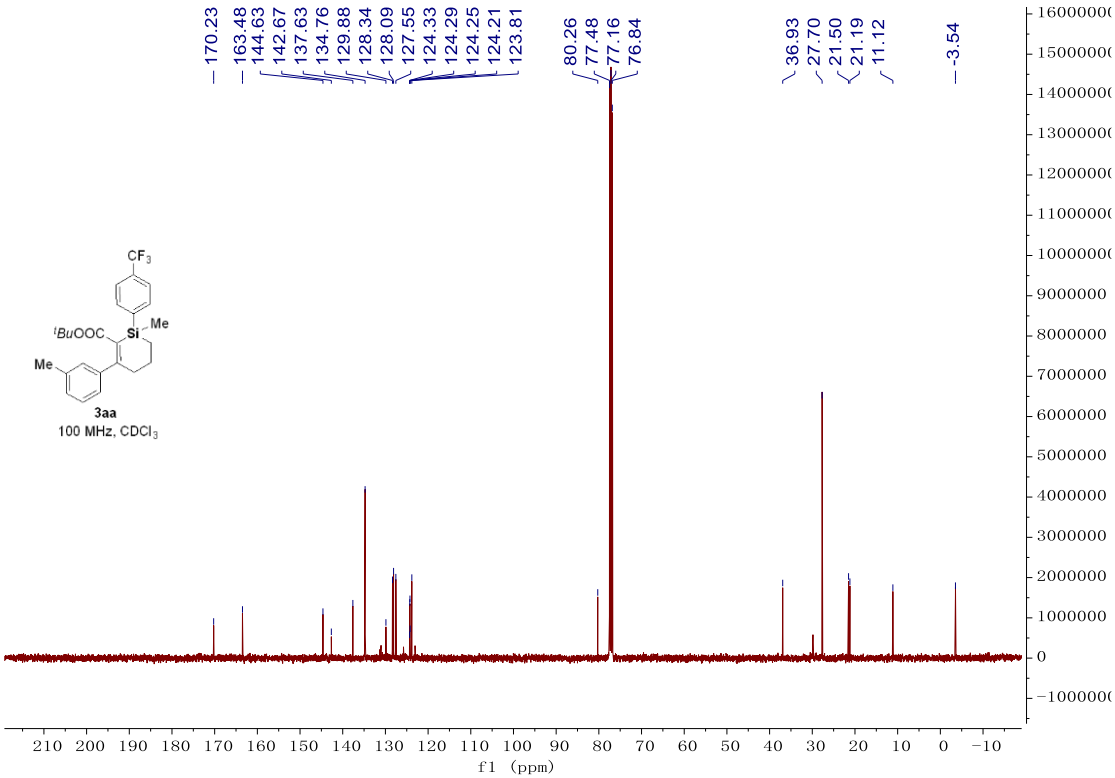
2.00
9.00
2.00
3.00
f1 (ppm)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142.67
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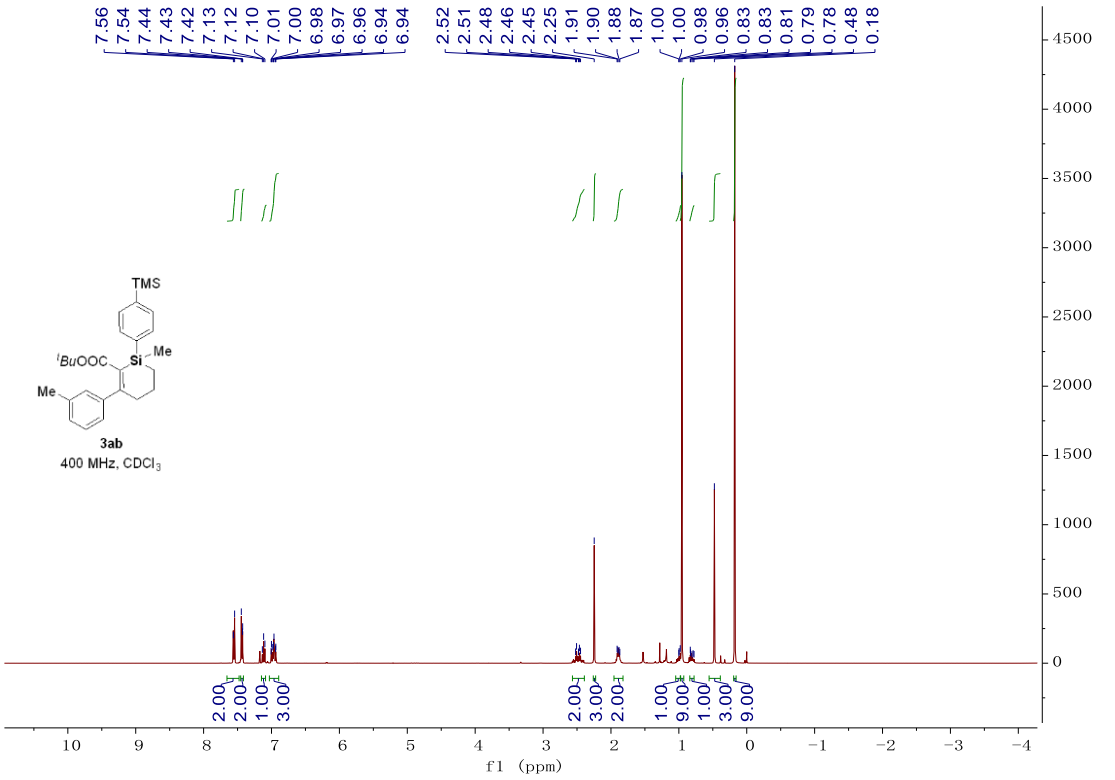
128.34
128.09
127.55
124.33
124.29
124.25
124.21
123.81
80.26
77.48
77.16
76.84
36.93
27.70
21.50
21.19
11.12
-3.54
CF3
tBuOOC
Si
Me
Me
3aa
100 MHz, CDCl3
f1 (ppm)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2.52 2.51 2.48 2.46 2.45 2.25 1.91 1.90 1.88 1.87
1.00 1.00 0.98 0.96 0.83 0.83 0.81 0.79 0.78 0.48 0.18
TMS
tBuOOC
Si
Me
Me
3ab
400 MHz, CDCl3
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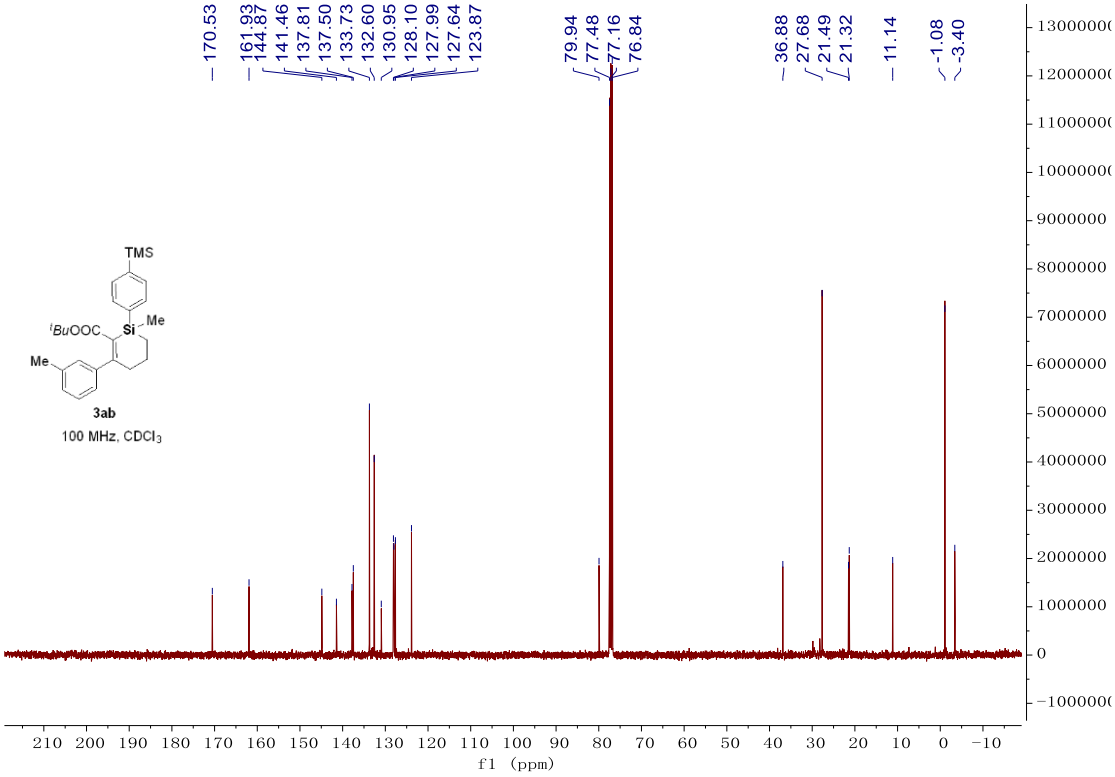
f1 (ppm)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79.94 77.48 77.16 76.84
36.88 27.68 21.49 21.32 11.14 -1.08 -3.40
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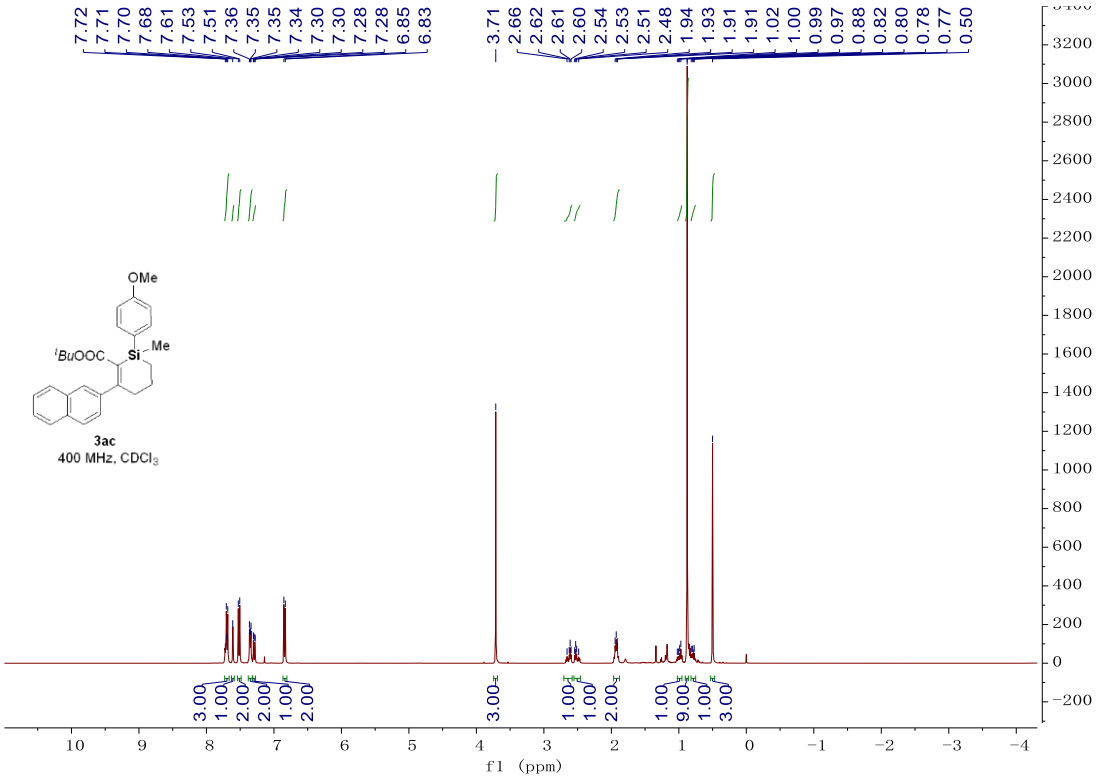
tBuOOC
Si
Me
Me
3ab
100 MHz, CDCl3
f1 (ppm)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3.71 2.66 2.62 2.61 2.60 2.54 2.53 2.51 2.48 1.94 1.93 1.91 1.91 1.02 1.00 0.99 0.97 0.88 0.82 0.80 0.78 0.77 0.50
OMe
tBuOOC
Si
Me
3ac
400 MHz, CDCl3
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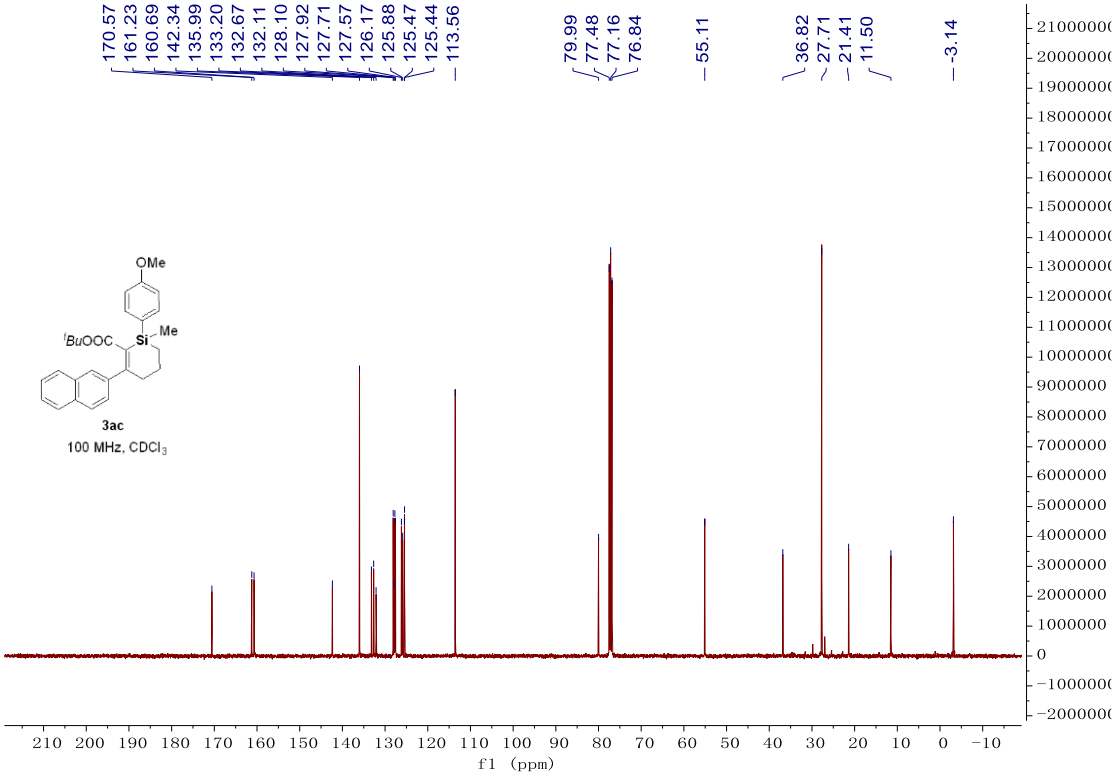
f1 (ppm)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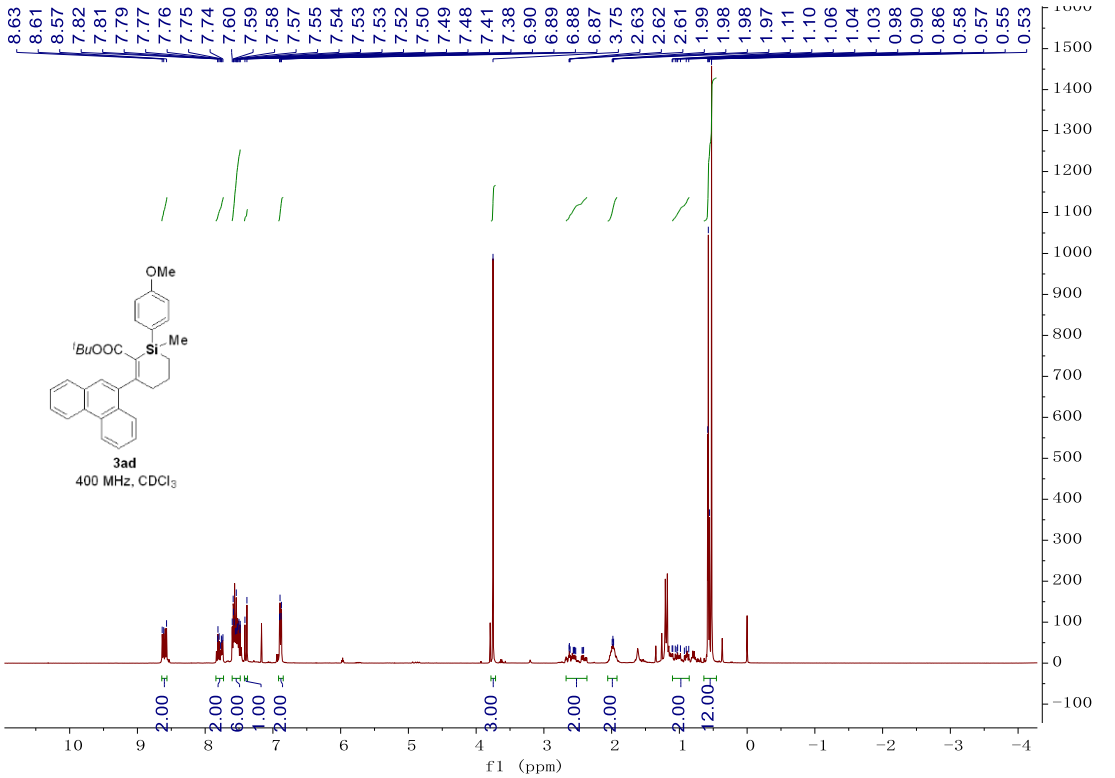
79.99 77.48 77.16 76.84
55.11
36.82 27.71 21.41 11.50
-3.14
OMe
tBuOOC
Si
Me
3ac
100 MHz, CDCl3
f1 (ppm)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OMe
Me
Si
tBuOOC
3ad
400 MHz, CDCl3
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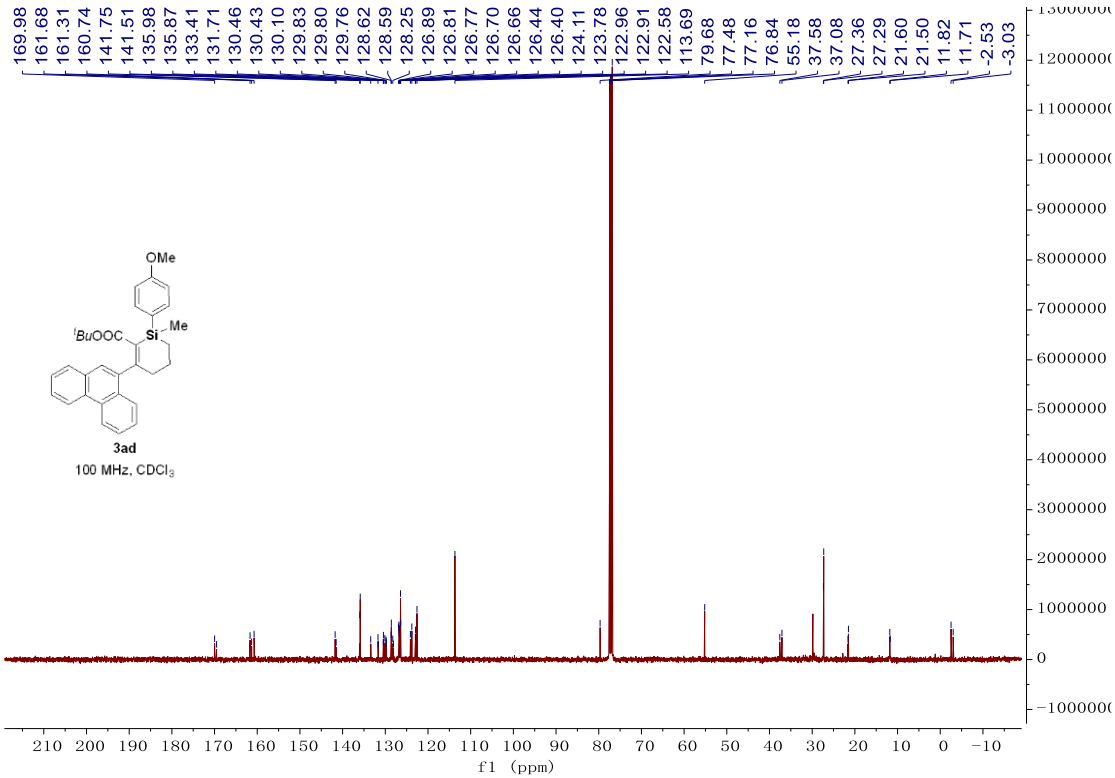
f1 (ppm)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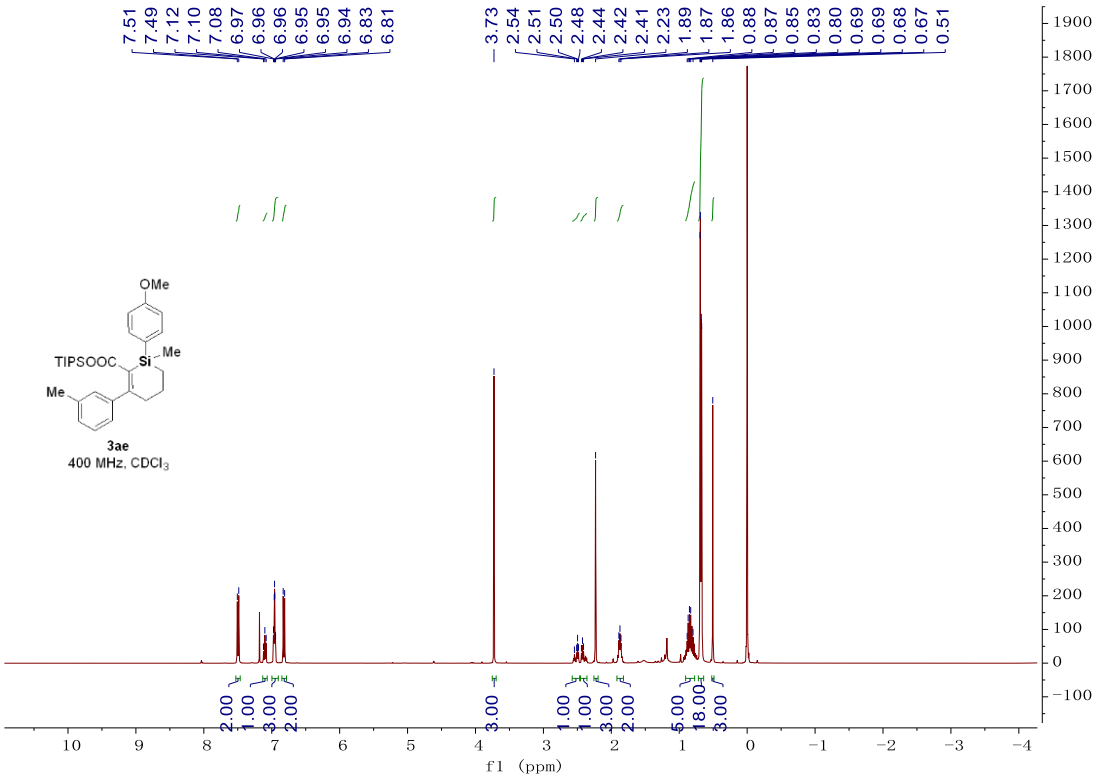
OMe
Me
Si
tBuOOC
3ad
100 MHz, CDCl3
f1 (ppm)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6.96
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6.95
6.94
6.83
6.81
3.73
2.54
2.51
2.50
2.48
2.44
2.42
2.41
2.23
1.89
1.87
1.86
0.88
0.87
0.85
0.83
0.80
0.69
0.69
0.68
0.67
0.51
OMe
TIPSOOC
Si
Me
Me
3ae
400 MHz, CDCl3
2.00
1.00
3.00
2.00
3.00
1.00
1.00
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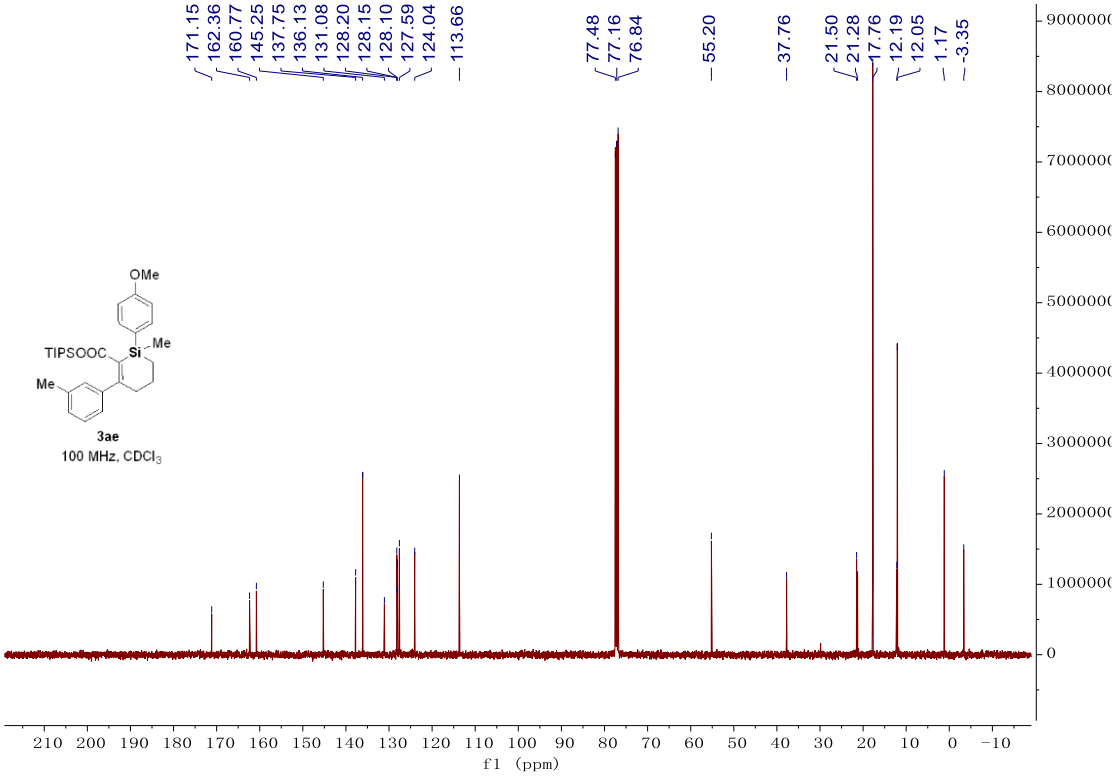
2.00
5.00
18.00
3.00
f1 (ppm)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136.13
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128.20
128.15
128.10
127.59
124.04
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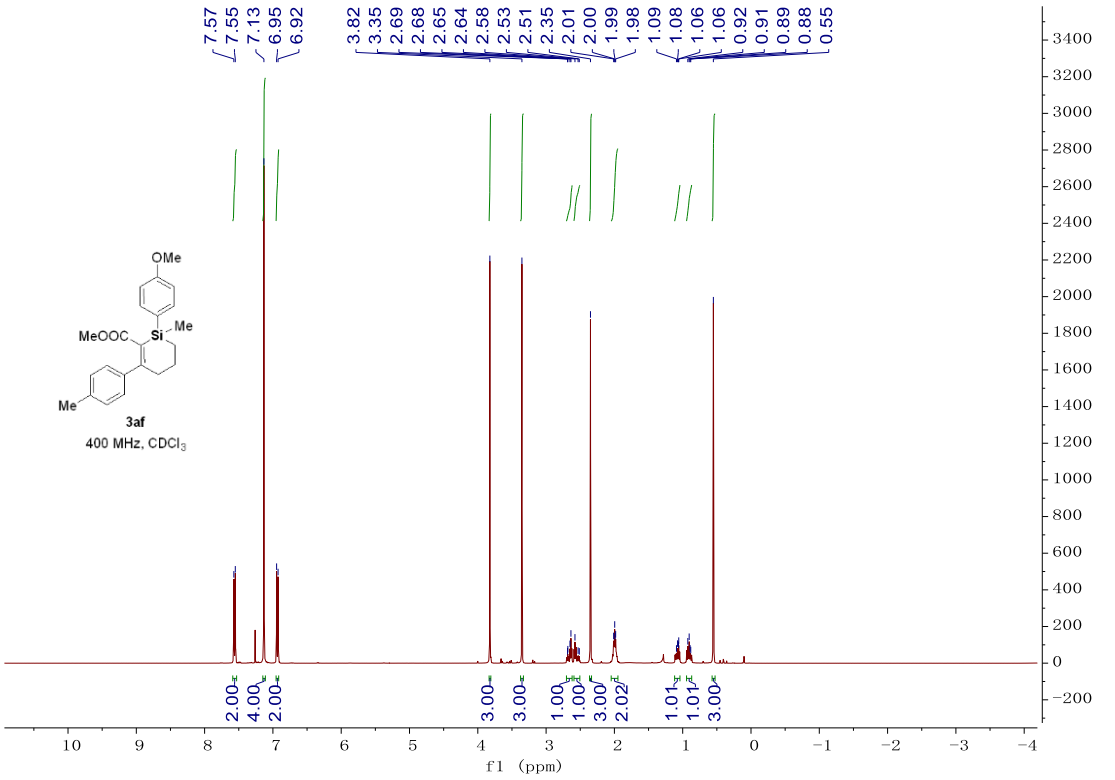
77.48
77.16
76.84
55.20
37.76
21.50
21.28
17.76
12.19
12.05
1.17
-3.35
OMe
TIPSOOC
Si
Me
Me
3ae
100 MHz, CDCl3
f1 (ppm)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3.82
3.35
2.69
2.68
2.65
2.64
2.58
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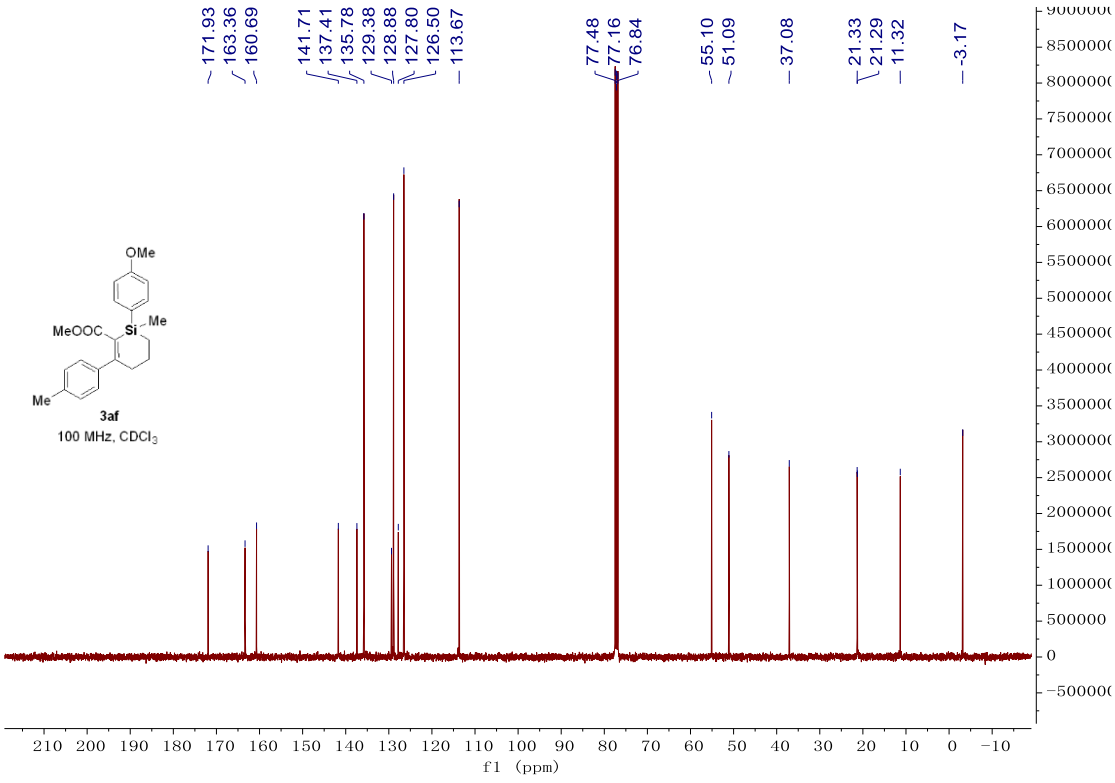
2.51
2.35
2.01
2.00
1.99
1.98
1.09
1.08
1.06
1.06
0.92
0.91
0.89
0.88
0.55
OMe
MeOOC
Si
Me
Me
3af
400 MHz, CDCl3
2.00
4.00
2.00
3.00
3.00
1.00
1.00
3.00
2.02
1.01
1.01
3.00
f1 (ppm)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137.41
135.78
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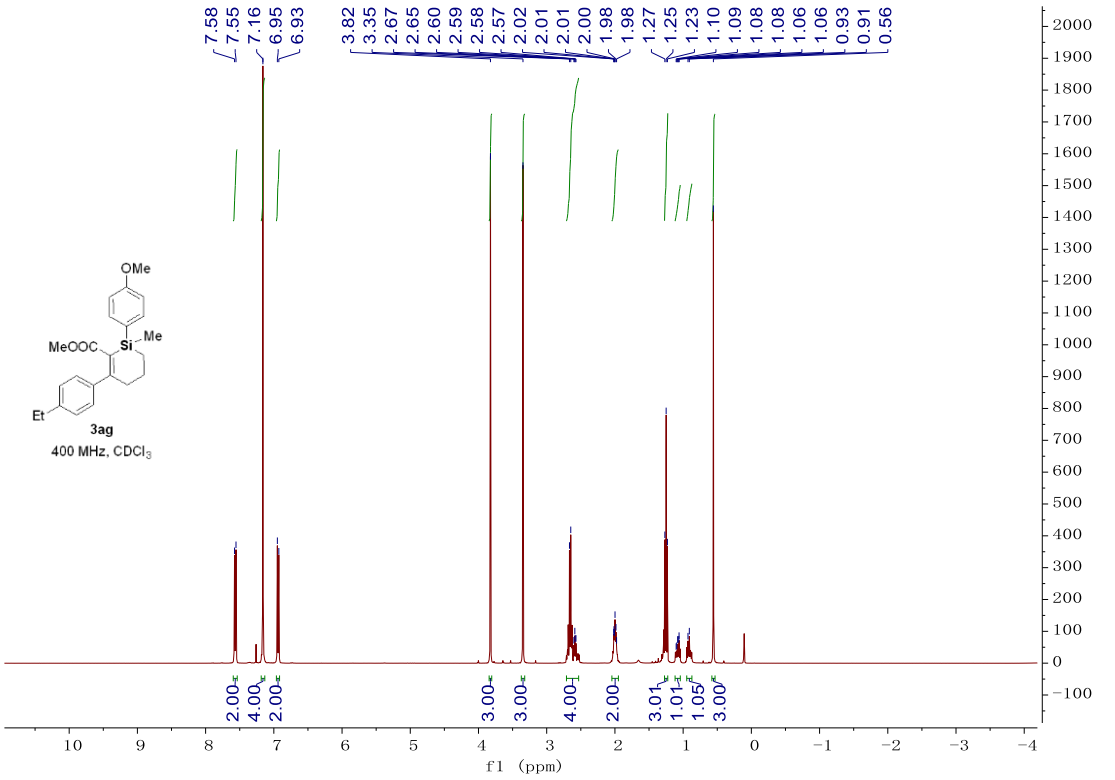
128.88
127.80
126.50
113.67
77.48
77.16
76.84
55.10
51.09
37.08
21.33
21.29
11.32
-3.17
OMe
MeOOC
Si
Me
Me
3af
100 MHz, CDCl3
f1 (ppm)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3.82
3.35
2.67
2.65
2.60
2.59
2.58
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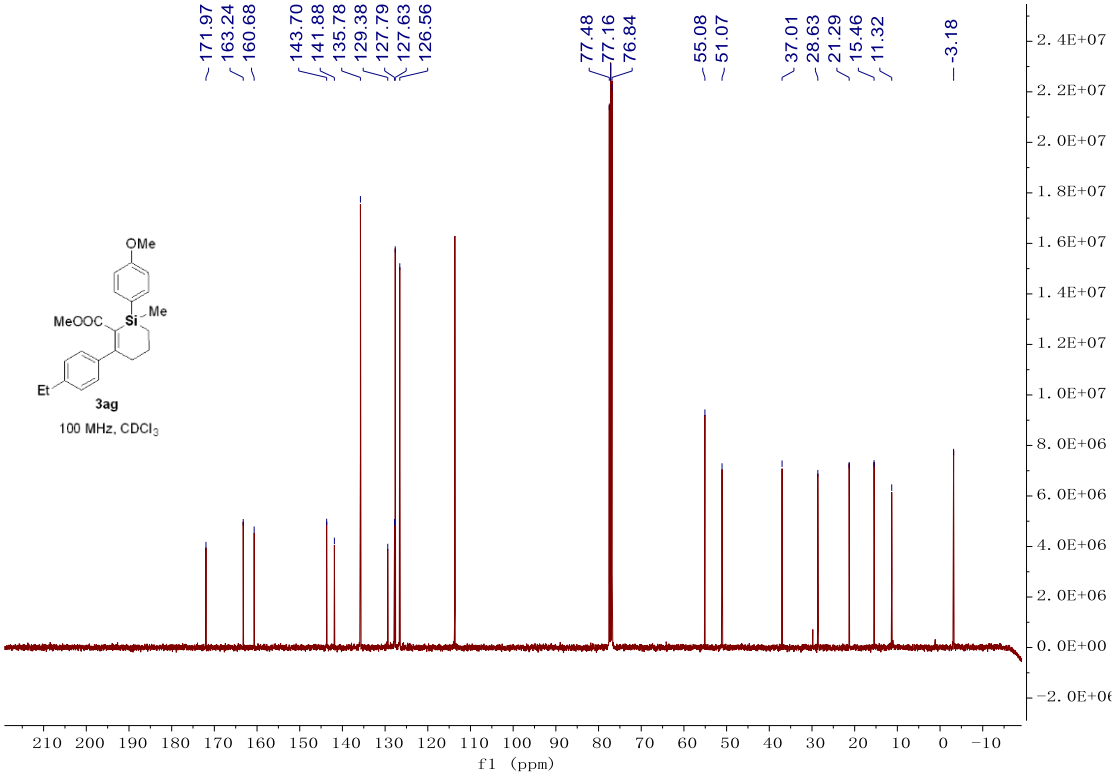
2.02
2.01
2.01
2.00
1.98
1.98
1.27
1.25
1.23
1.10
1.09
1.08
1.08
1.06
1.06
0.93
0.91
0.56
OMe
MeOOC
Si
Me
Et
3ag
400 MHz, CDCl3
2.00
4.00
2.00
3.00
3.00
4.00
2.00
3.01
1.01
1.05
3.00
f1 (ppm)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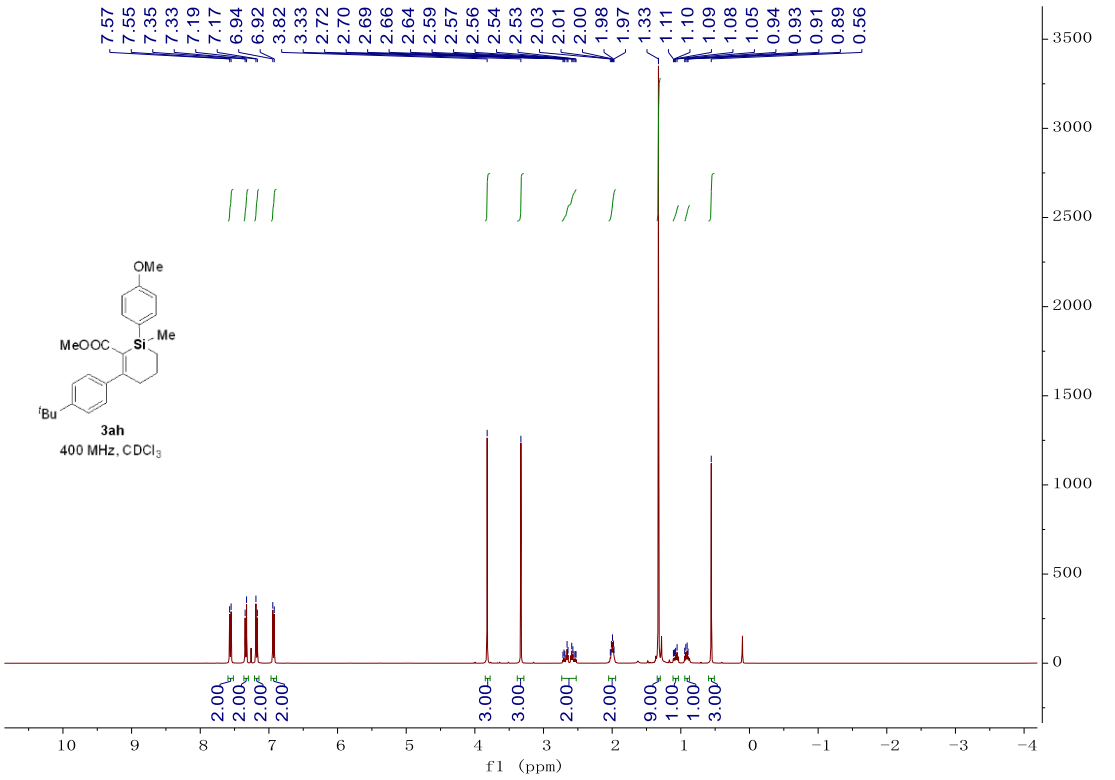
127.63
126.56
77.48
77.16
76.84
55.08
51.07
37.01
28.63
21.29
15.46
11.32
-3.18
OMe
MeOOC
Si
Me
Et
3ag
100 MHz, CDCl3
f1 (ppm)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6.92
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3.33
2.72
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2.69
2.66
2.64
2.59
2.57
2.56
2.54
2.53
2.03
2.01
2.00
1.98
1.97
1.33
1.11
1.10
1.09
1.08
1.05
0.94
0.93
0.91
0.89
0.56
OMe
MeOOC
Si
Me
tBu
3ah
400 MHz, CDCl3
2.00
2.00
2.00
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3.00
3.00
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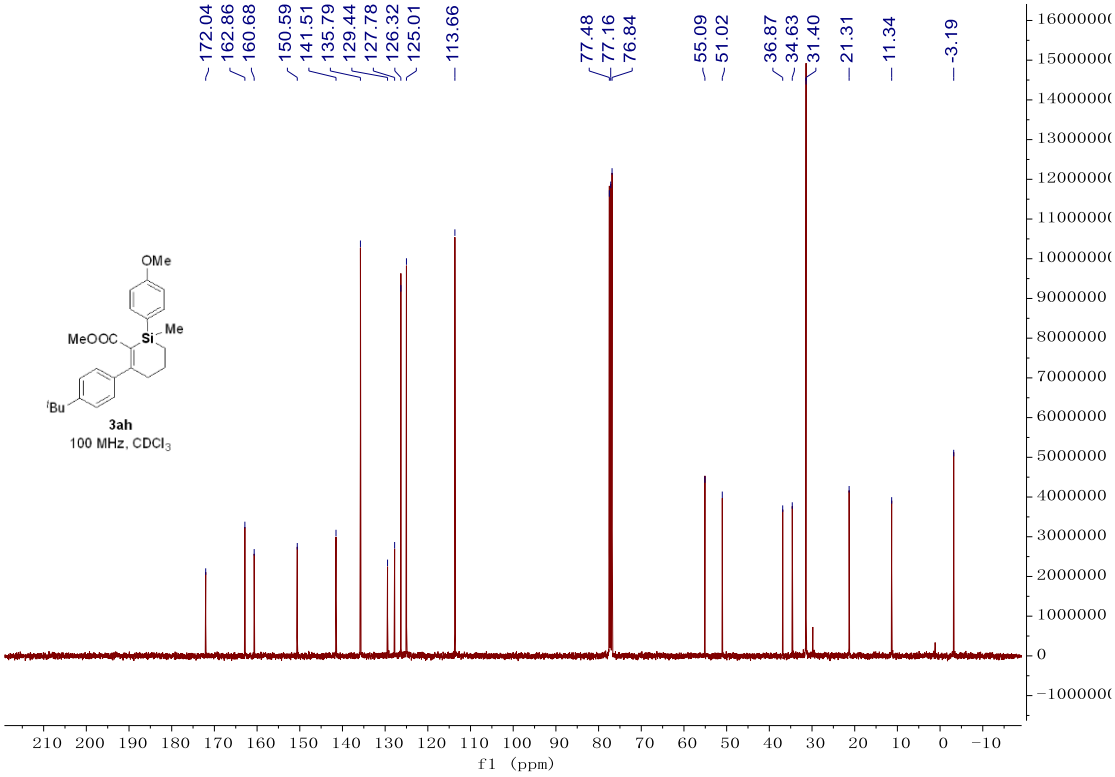
9.00
1.00
1.00
3.00
f1 (ppm)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135.79
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127.78
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125.01
113.66
77.48
77.16
76.84
55.09
51.02
36.87
34.63
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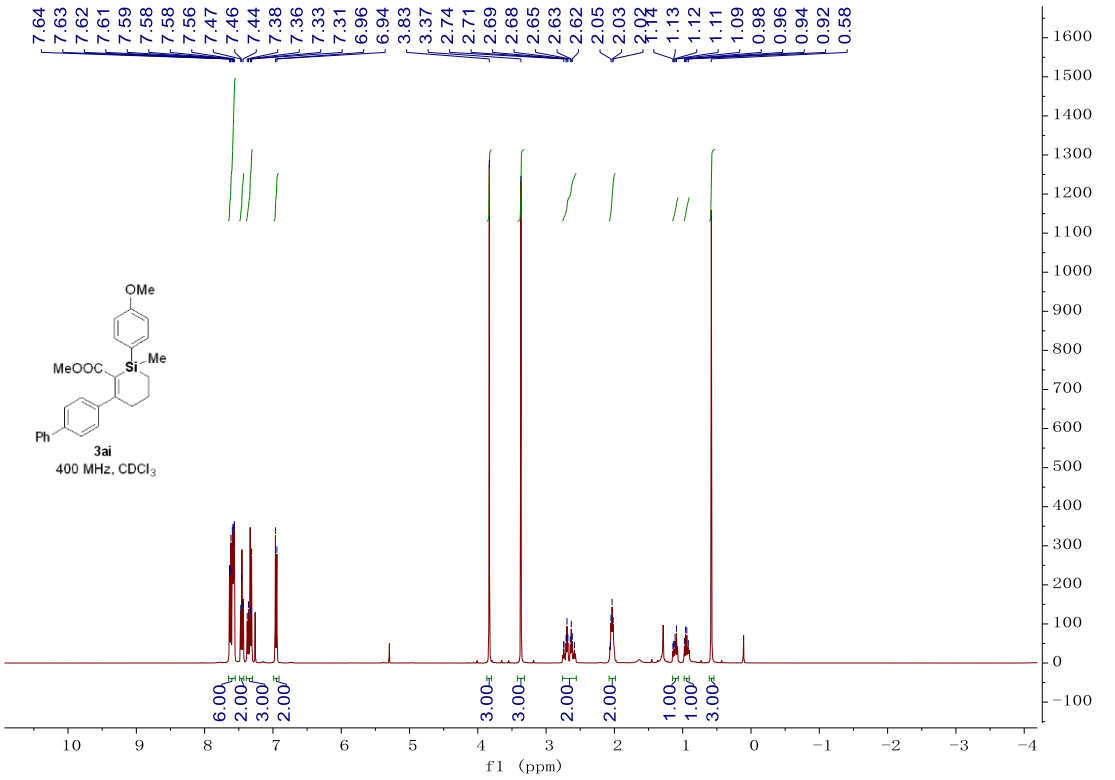
11.34
-3.19
OMe
MeOOC
Si
Me
tBu
3ah
100 MHz, CDCl3
f1 (ppm)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7.58
7.56
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7.38
7.36
7.33
7.31
6.96
6.94
3.83
3.37
2.74
2.71
2.69
2.68
2.65
2.63
2.62
2.05
2.03
2.02
1.14
1.13
1.12
1.11
1.09
0.98
0.96
0.94
0.92
0.58
OMe
MeOOC
Si
Me
Ph
3ai
400 MHz, CDCl3
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2.00
3.00
3.00
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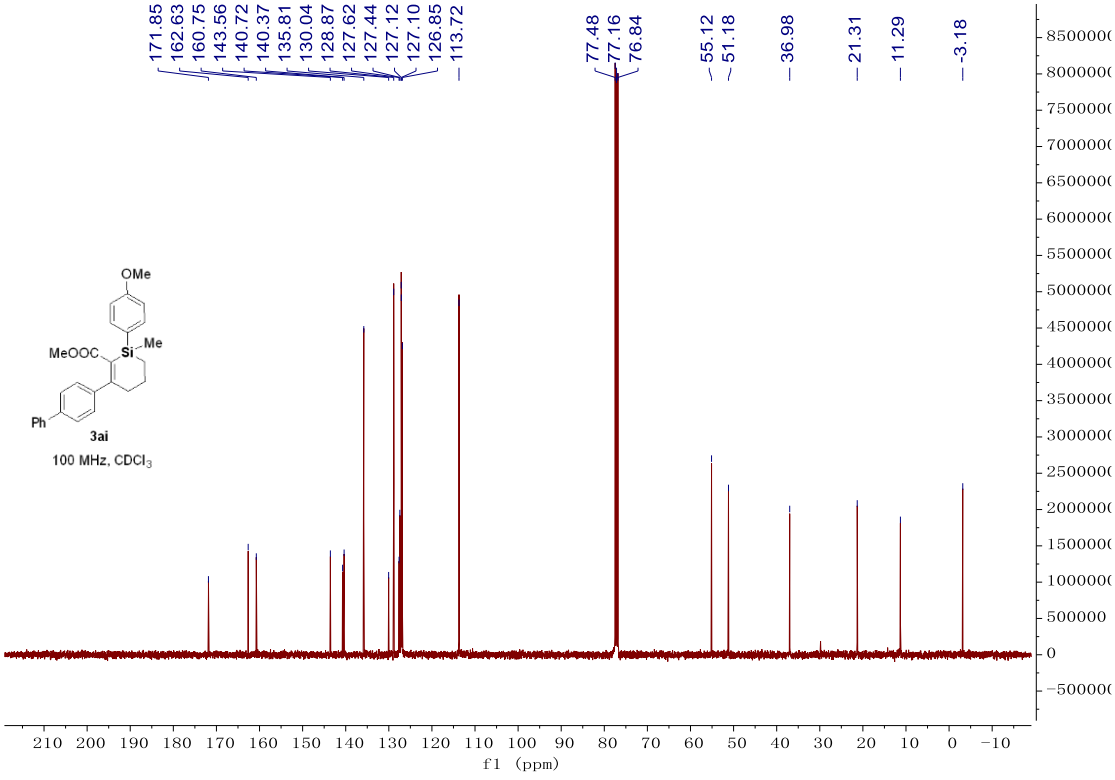
1.00
1.00
3.00
f1 (ppm)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127.44
127.12
127.10
126.85
113.72
77.48
77.16
76.84
55.12
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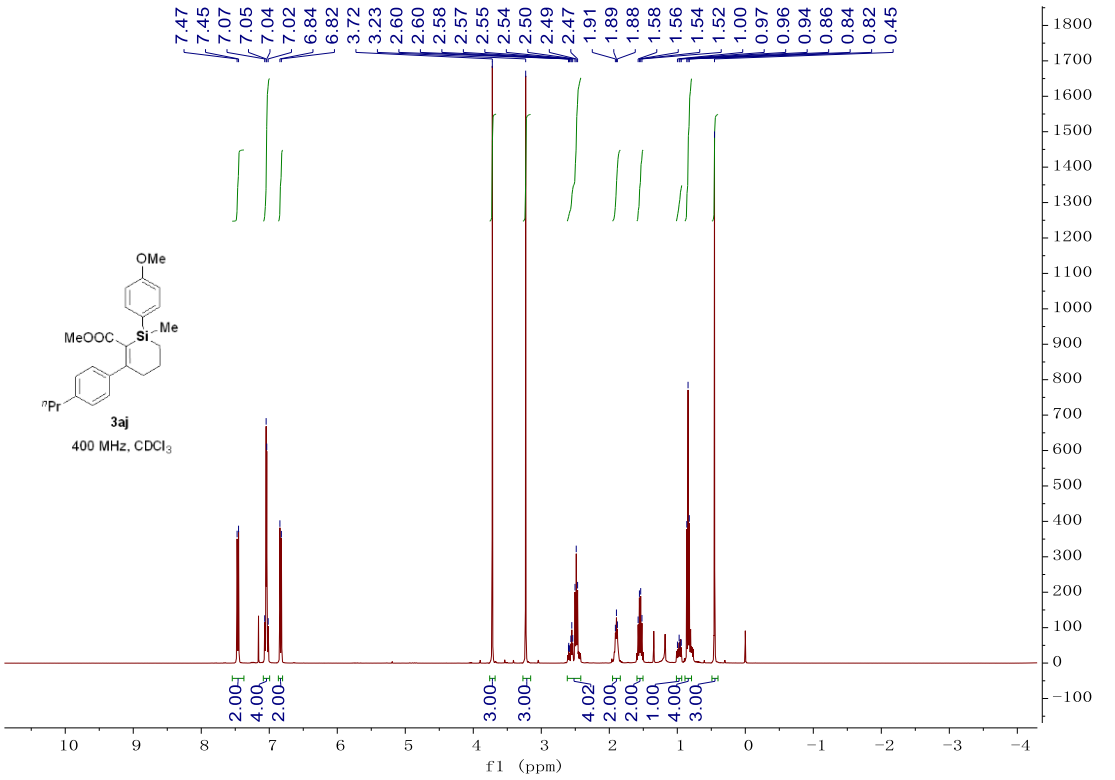
11.29
-3.18
OMe
MeOOC
Si
Me
Ph
3ai
100 MHz, CDCl3
f1 (ppm)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7.02
6.84
6.82
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2.60
2.58
2.57
2.55
2.54
2.50
2.49
2.47
1.91
1.89
1.88
1.58
1.56
1.54
1.52
1.00
0.97
0.96
0.94
0.86
0.84
0.82
0.45
OMe
MeOOC
Si
Me
nPr
3aj
400 MHz, CDCl3
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4.02
2.00
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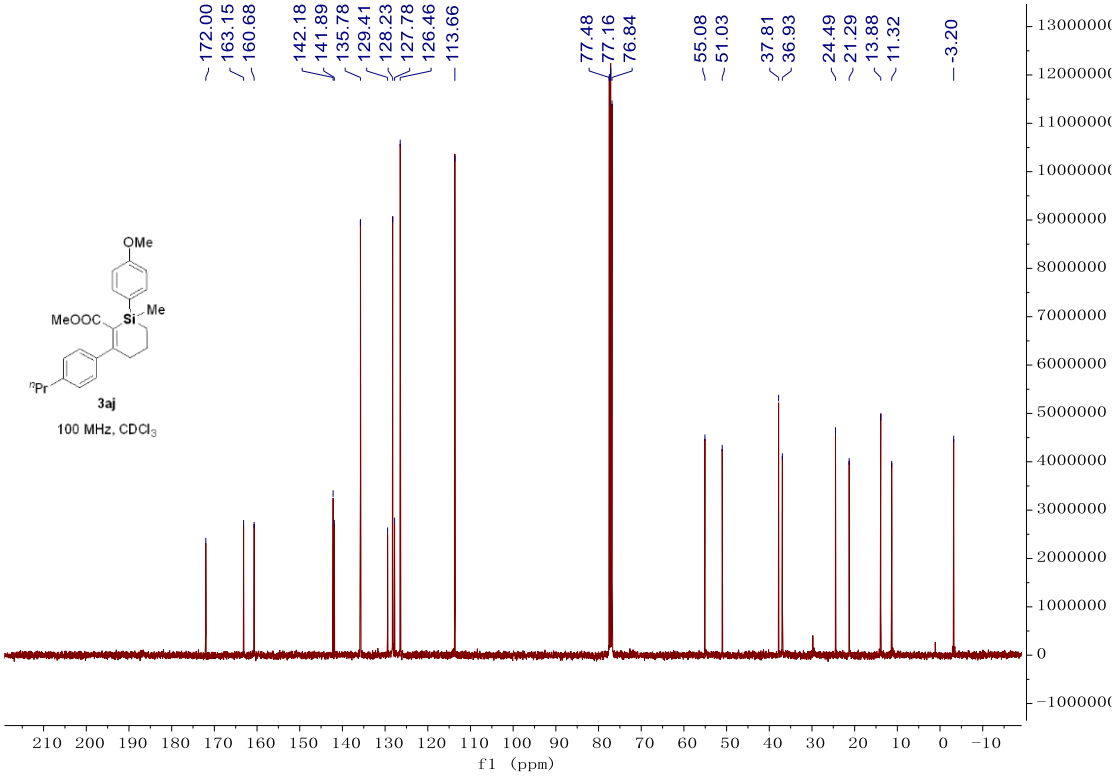
3.00
f1 (ppm)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77.48
77.16
76.84
55.08
51.03
37.81
36.93
24.49
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11.32
-3.20
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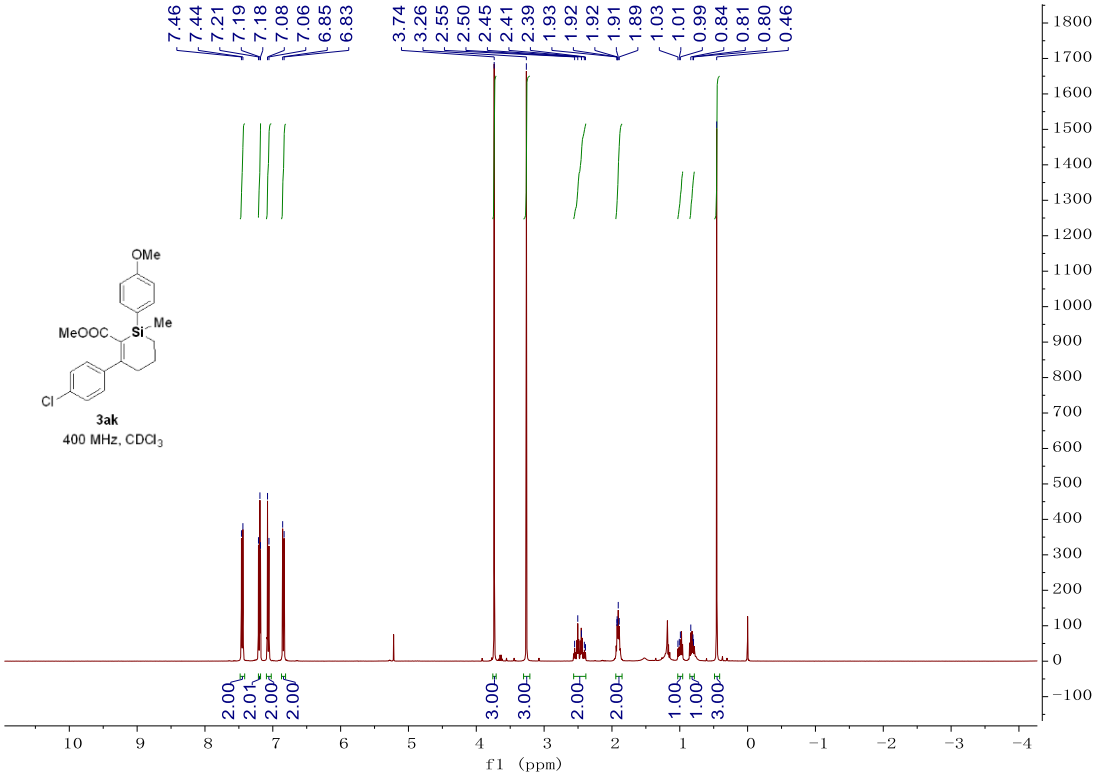
MeOOC
Si
Me
nPr
3aj
100 MHz, CDCl3
f1 (ppm)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6.83
3.74
3.26
2.55
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2.45
2.41
2.39
1.93
1.92
1.92
1.91
1.89
1.03
1.01
0.99
0.84
0.81
0.80
0.46
OMe
MeOOC
Si
Me
Cl
3ak
400 MHz, CDCl3
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3.00
3.00
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1.00
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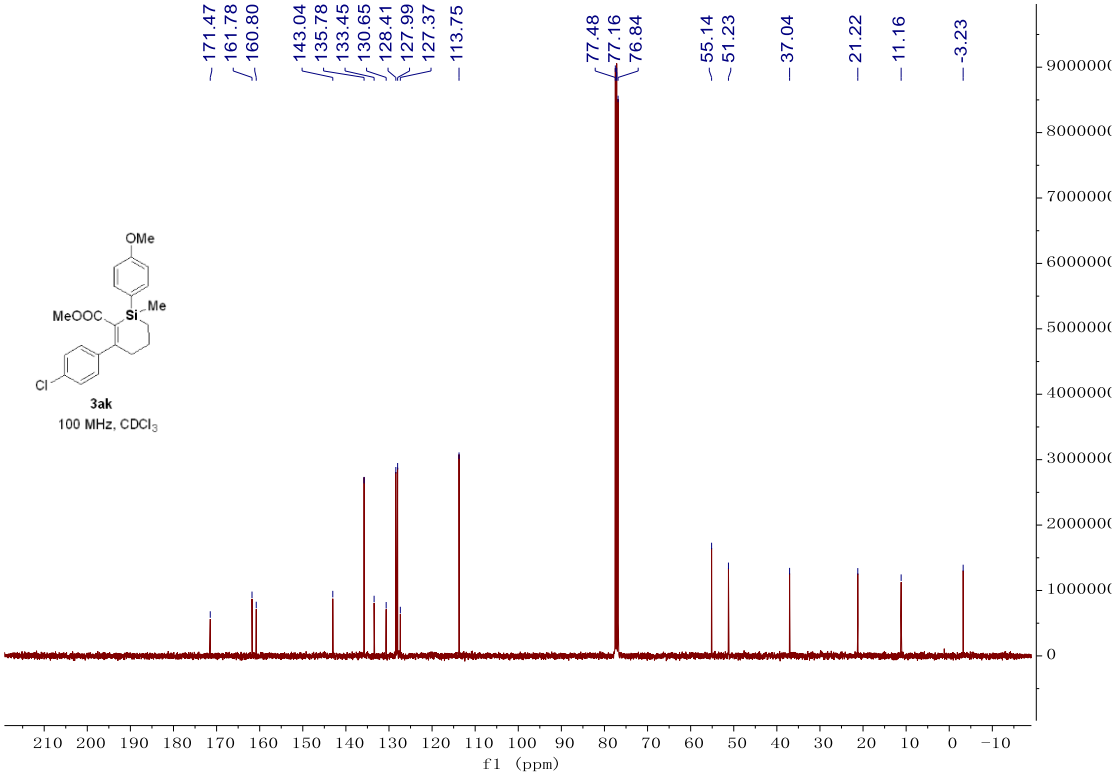
3.00
f1 (ppm)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127.37
113.75
77.48
77.16
76.84
55.14
51.23
37.04
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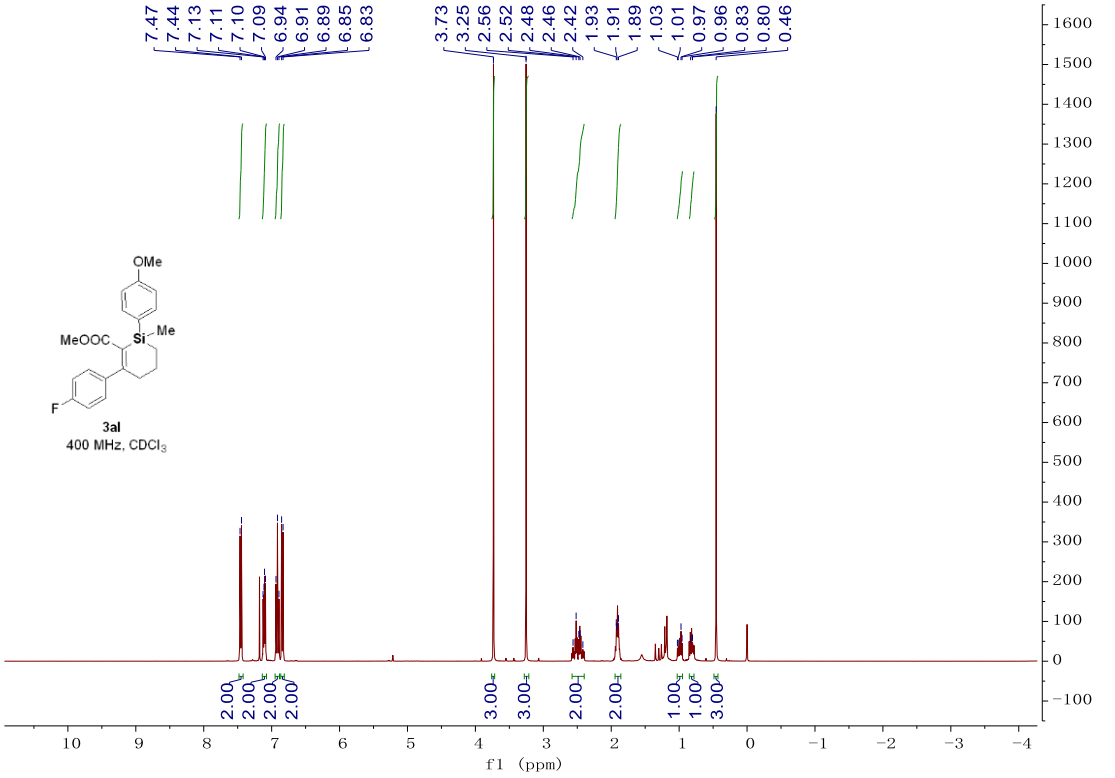
11.16
-3.23
OMe
MeOOC
Si
Me
Cl
3ak
100 MHz, CDCl3
f1 (ppm)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7.09
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6.91
6.89
6.85
6.83
3.73
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2.56
2.52
2.48
2.46
2.42
1.93
1.91
1.89
1.03
1.01
0.97
0.96
0.83
0.80
0.46
OMe
MeOOC
Si
Me
F
3al
400 MHz, CDCl3
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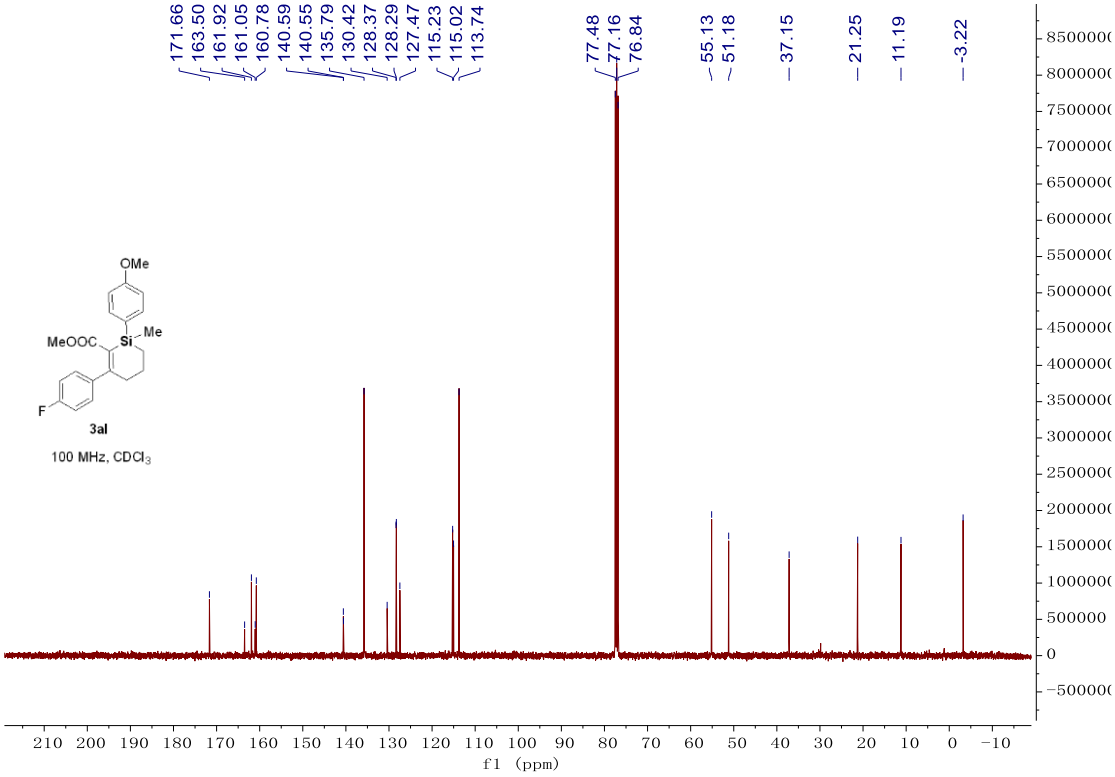
2.00
2.00
2.00
3.00
3.00
2.00
2.00
1.00
1.00
3.00
f1 (ppm)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161.05
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135.79
130.42
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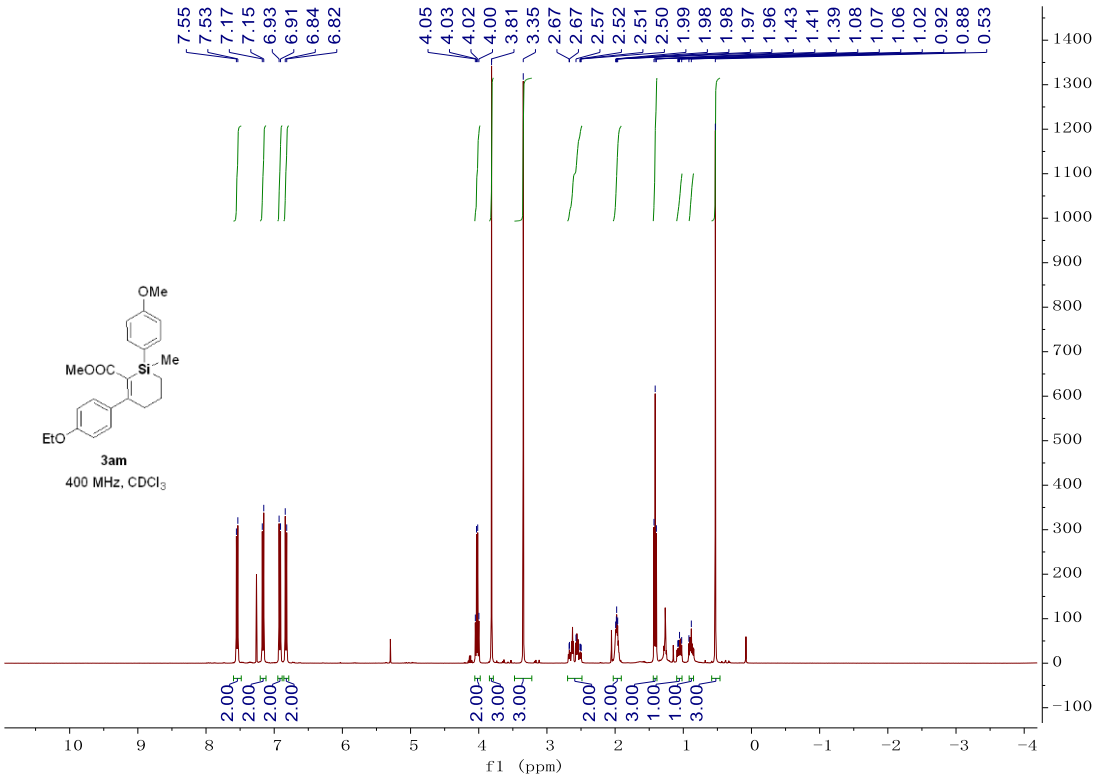
128.29
127.47
115.23
115.02
113.74
77.48
77.16
76.84
55.13
51.18
37.15
21.25
11.19
-3.22
OMe
MeOOC
Si
Me
F
3al
100 MHz, CDCl3
f1 (ppm)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6.82
4.05
4.03
4.02
4.00
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1.98
1.97
1.96
1.43
1.41
1.39
1.08
1.07
1.06
1.02
0.92
0.88
0.53
OMe
MeOOC
Si
Me
EtO
3am
400 MHz, CDCl3
2.00
2.00
2.00
2.00
2.00
3.00
3.00
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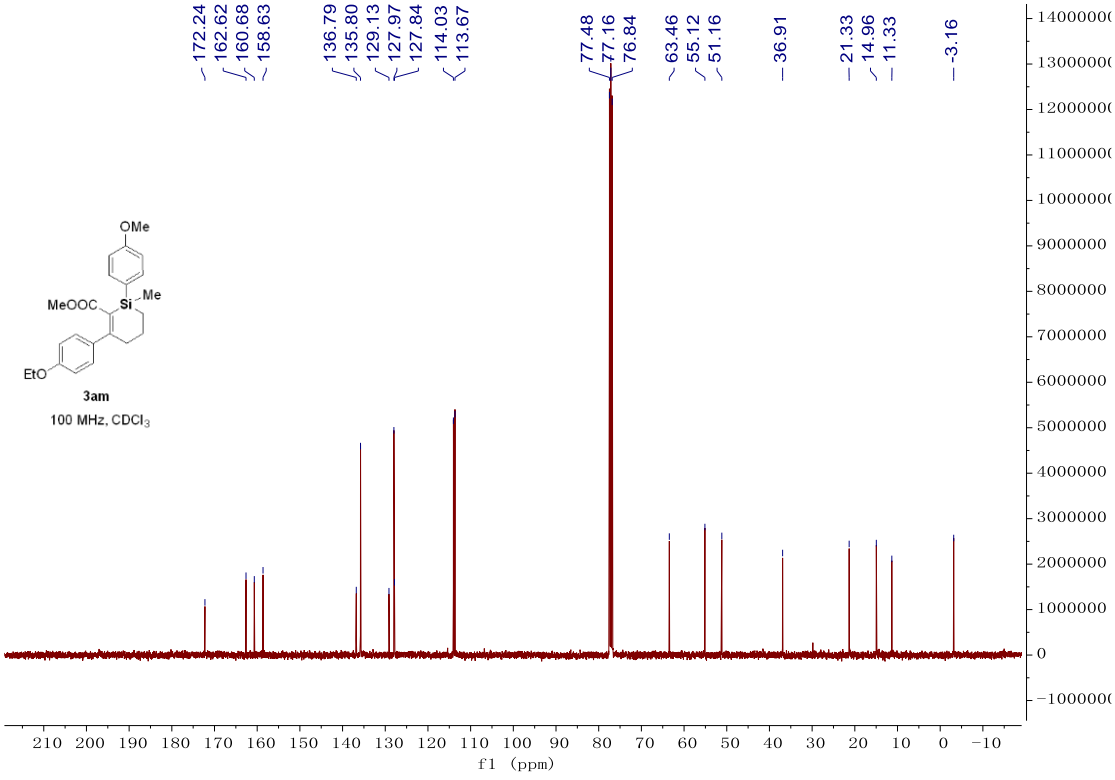
3.00
1.00
1.00
3.00
f1 (ppm)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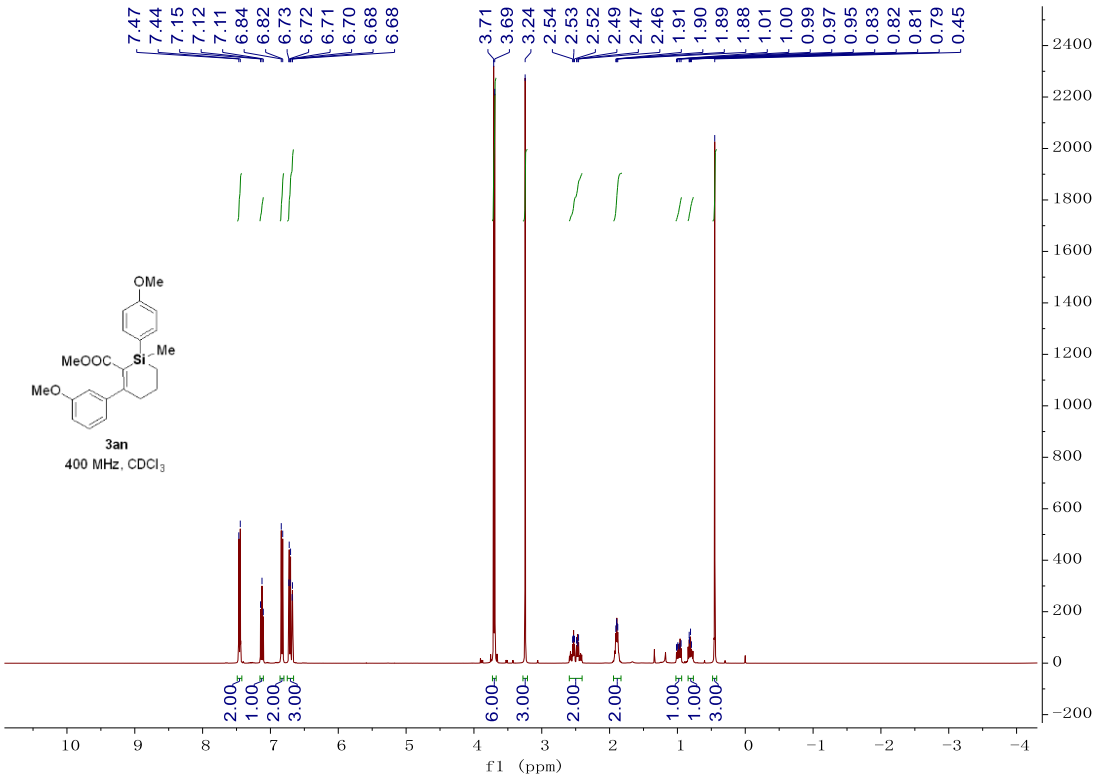
77.48
77.16
76.84
63.46
55.12
51.16
36.91
21.33
14.96
11.33
-3.16
OMe
MeOOC
Si
Me
EtO
3am
100 MHz, CDCl3
f1 (ppm)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7.12
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6.82
6.73
6.72
6.71
6.70
6.68
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3.71
3.69
3.24
2.54
2.53
2.52
2.49
2.47
2.46
1.91
1.90
1.89
1.88
1.01
1.00
0.99
0.97
0.95
0.83
0.82
0.81
0.79
0.45
OMe
MeOOC
Si
Me
MeO
3an
400 MHz, CDCl3
2.00
1.00
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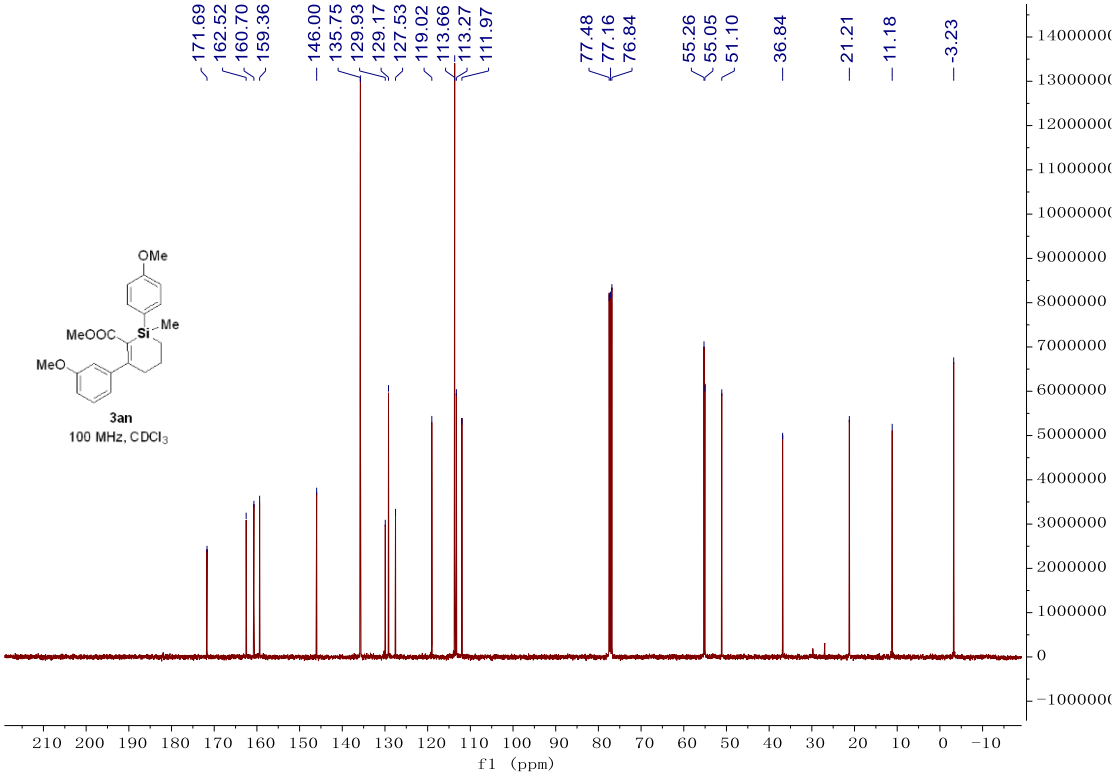
3.00
6.00
3.00
2.00
2.00
1.00
1.00
3.00
f1 (ppm)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127.53
119.02
113.66
113.27
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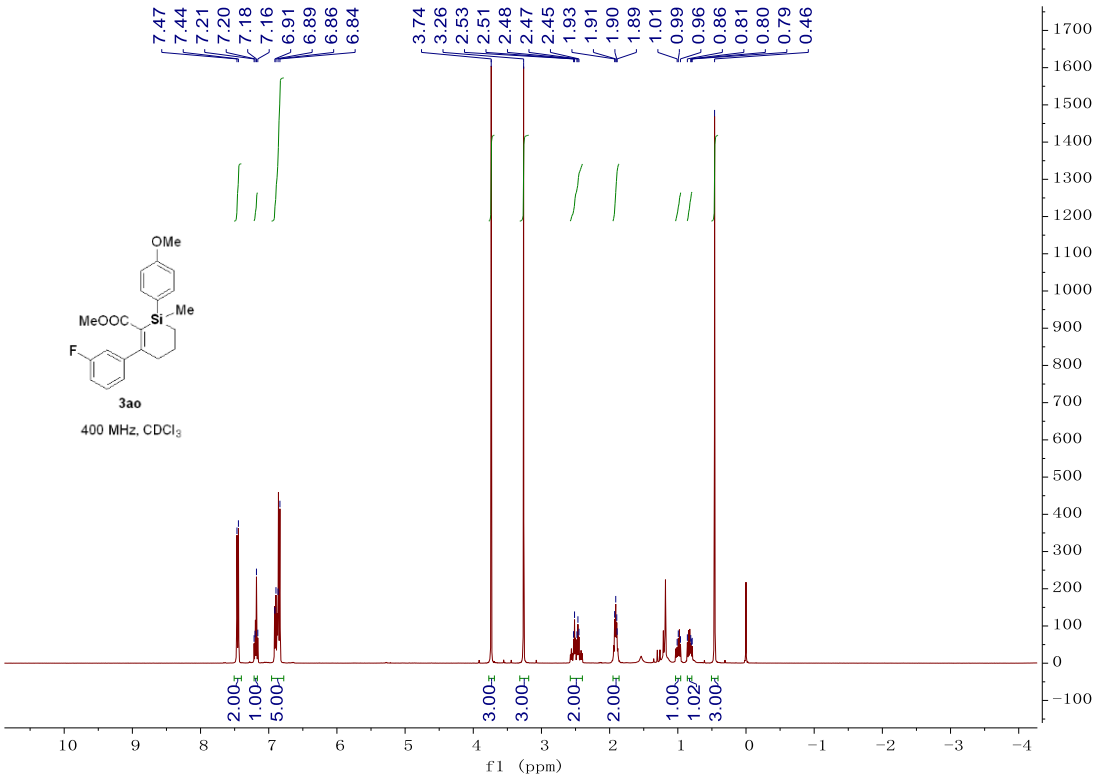
77.48
77.16
76.84
55.26
55.05
51.10
36.84
21.21
11.18
-3.23
OMe
MeOOC
Si
Me
MeO
3an
100 MHz, CDCl3
f1 (ppm)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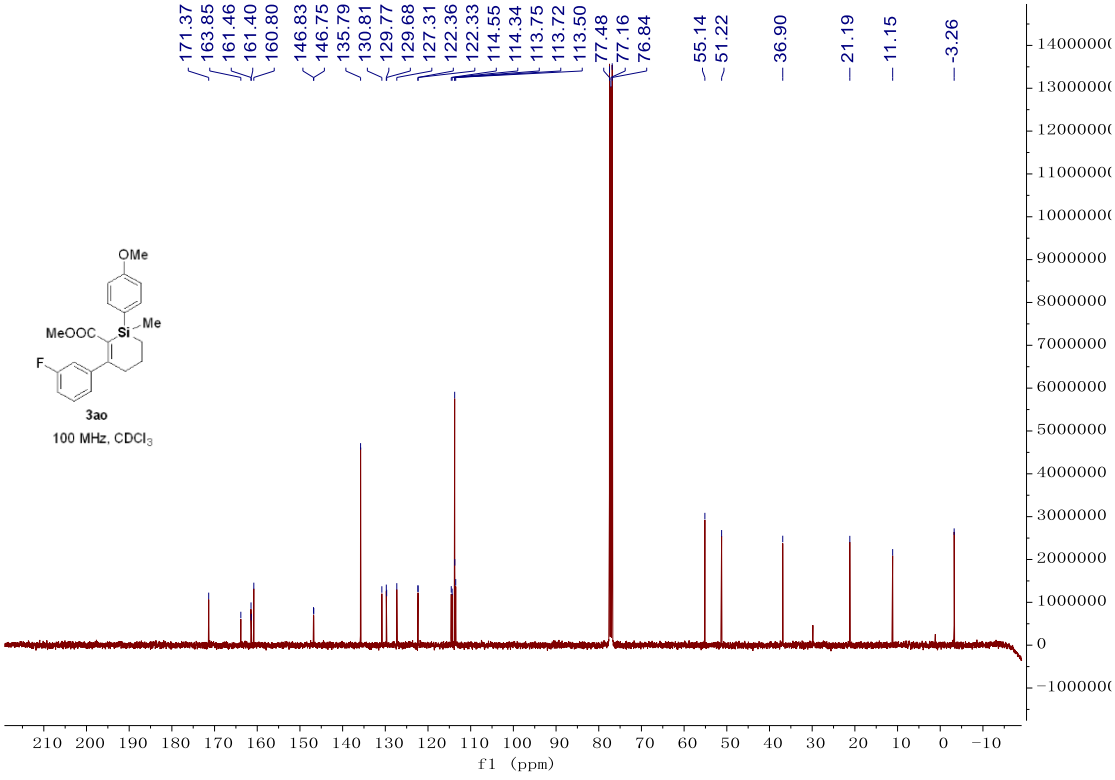
7.44
7.21
7.20
7.18
7.16
6.91
6.89
6.86
6.84
3.74
3.26
2.53
2.51
2.48
2.47
2.45
1.93
1.91
1.90
1.89
1.01
0.99
0.96
0.86
0.81
0.80
0.79
0.46
OMe
MeOOC
Si
Me
F
3ao
400 MHz, CDCl3
2.00
1.00
5.00
3.00
3.00
2.00
2.00
1.00
1.02
3.00
f1 (ppm)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163.85
161.46
161.40
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146.83
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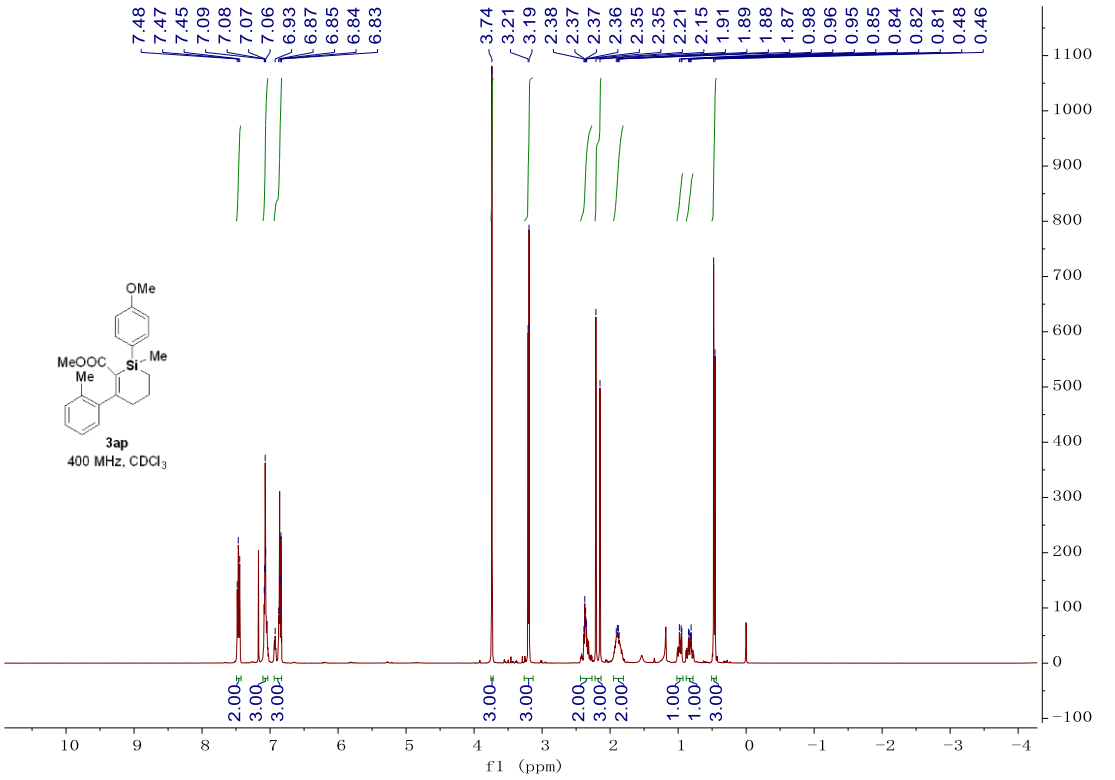
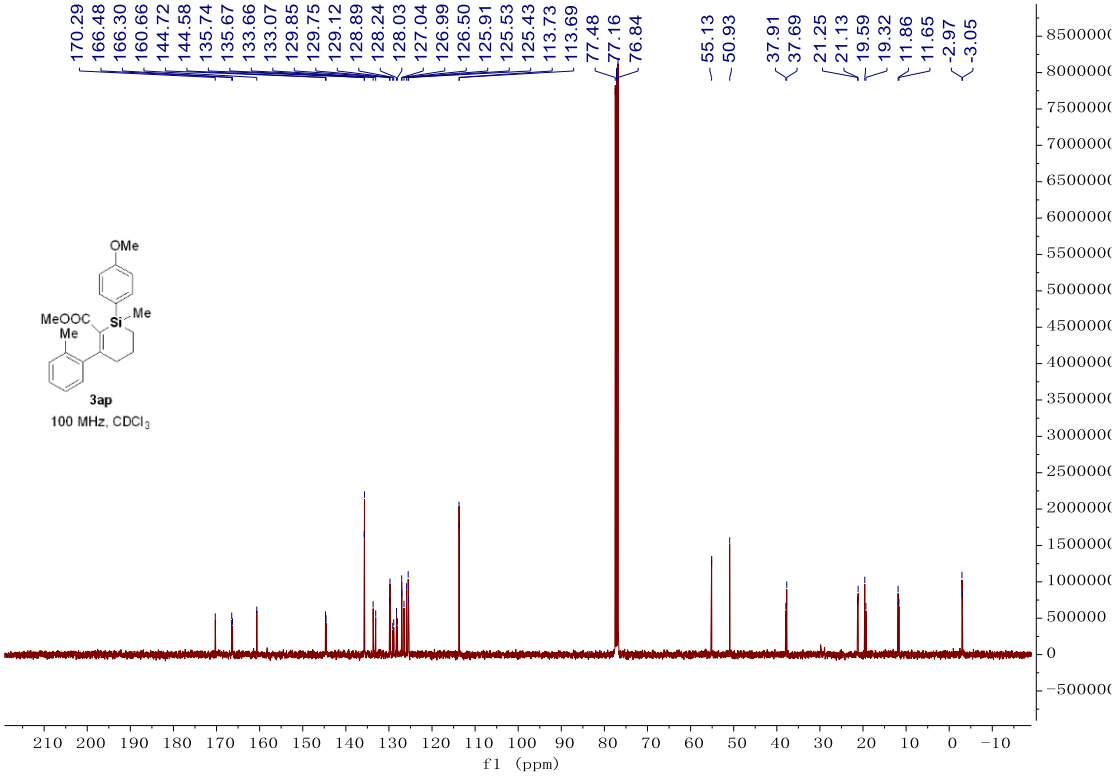
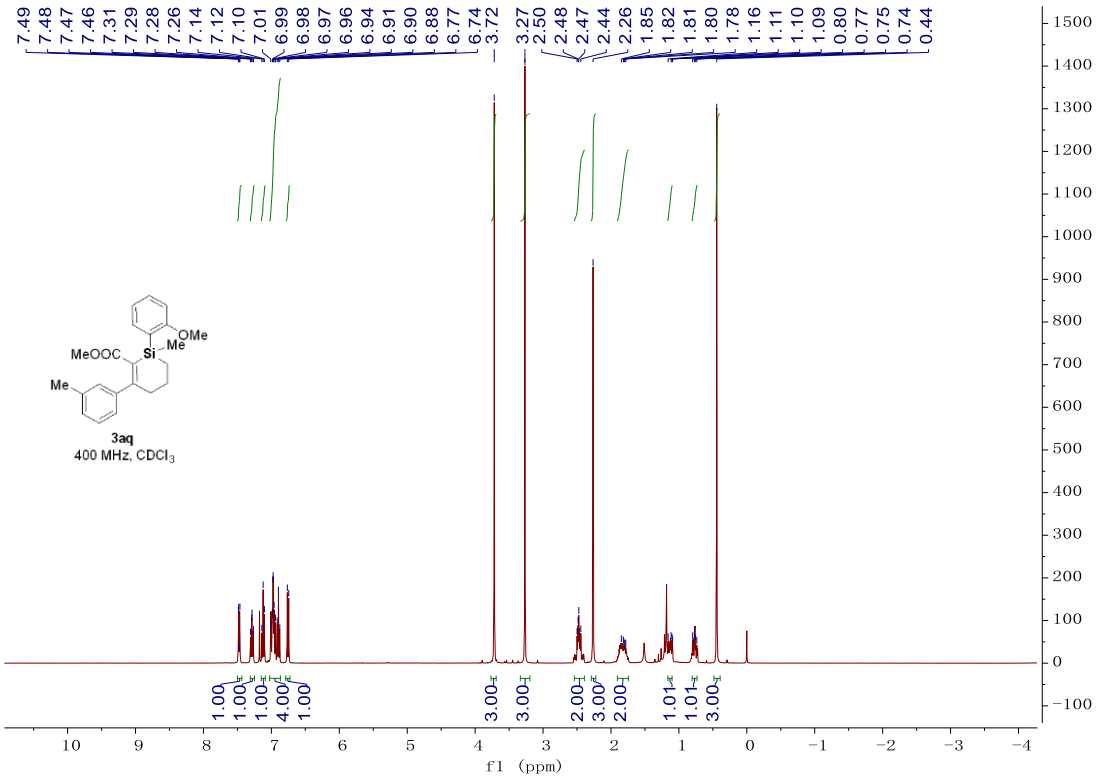
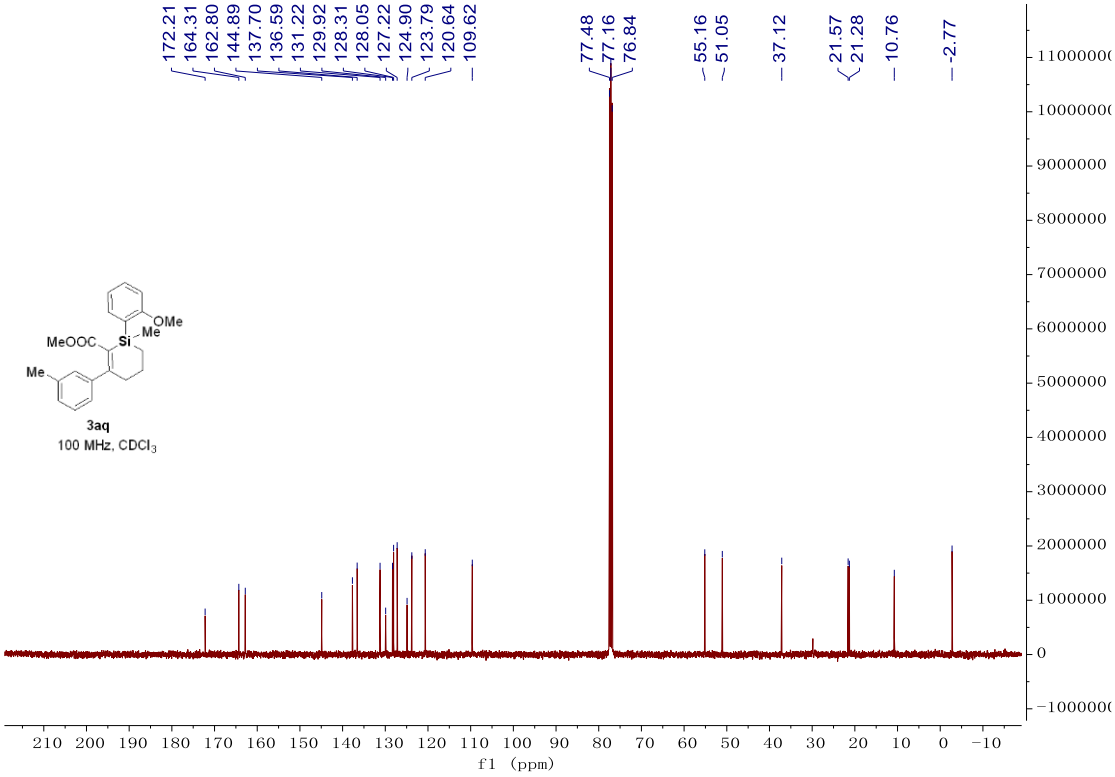
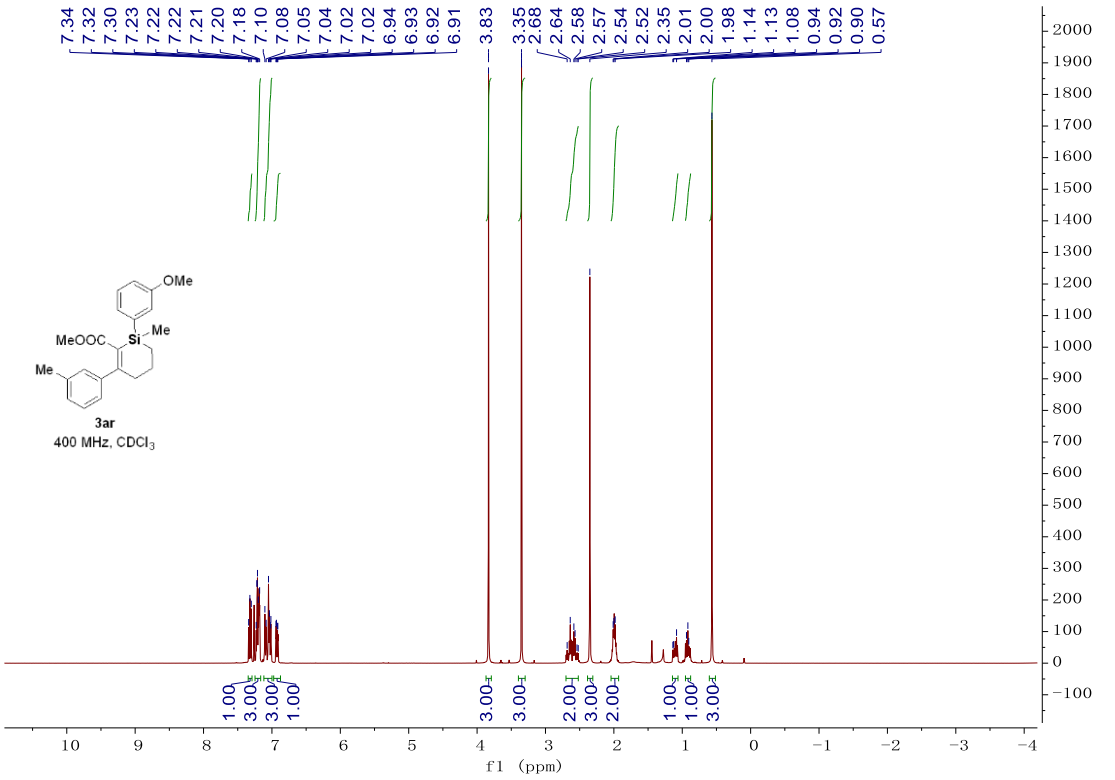
135.79
130.81
129.77
129.68
127.31
122.36
122.33
114.55
114.34
113.75
113.72
113.50
77.48
77.16
76.84
55.14
51.22
36.90
21.19
11.15
-3.26
OMe
MeOOC
Si
Me
F
3ao
100 MHz, CDCl3
f1 (ppm)


7.48 7.47 7.45 7.09 7.08 7.07 7.06 6.93 6.87 6.85 6.84 6.83
3.74 3.21 3.19 2.38 2.37 2.37 2.36 2.35 2.35 2.21 2.15 1.91 1.89 1.88 1.87 0.98 0.96 0.95 0.85 0.84 0.82 0.81 0.48 0.46
OMe
MeOOC
Me
Si
Me
Me
3ap
400 MHz, CDCl3
2.00 3.00 3.00 3.00 3.00 2.00 3.00 2.00 1.00 1.00 3.00
f1 (ppm)


170.29 166.48 166.30 160.66 144.72 144.58 135.74 135.67 133.66 133.07 129.85 129.75 129.12 128.89 128.24 128.03 127.04 126.99 126.50 125.91 125.53 125.43 113.73 113.69 77.48 77.16 76.84
55.13 50.93 37.91 37.69 21.25 21.13 19.59 19.32 11.86 11.65 -2.97 -3.05
OMe
MeOOC
Me
Si
Me
Me
3ap
100 MHz, CDCl3
f1 (ppm)


7.49 7.48 7.47 7.46 7.31 7.29 7.28 7.26 7.14 7.12 7.10 7.01 6.99 6.98 6.97 6.96 6.94 6.91 6.90 6.88 6.77 6.74 3.72 3.27 2.50 2.48 2.47 2.44 2.26 1.85 1.82 1.81 1.80 1.78 1.16 1.11 1.10 1.09 0.80 0.77 0.75 0.74 0.44
OMe
Me
MeOOC
Si
Me
3aq
400 MHz, CDCl3
1.00 1.00 1.00 4.00 1.00 3.00 3.00 2.00 3.00 2.00 1.01 1.01 3.00
f1 (ppm)


172.21 164.31 162.80 144.89 137.70 136.59 131.22 129.92 128.31 128.05 127.22 124.90 123.79 120.64 109.62 77.48 77.16 76.84 55.16 51.05 37.12 21.57 21.28 10.76 -2.77
OMe
Me
MeOOC
Si
Me
3aq
100 MHz, CDCl3
f1 (ppm)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7.32
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7.23
7.22
7.22
7.21
7.20
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7.10
7.08
7.05
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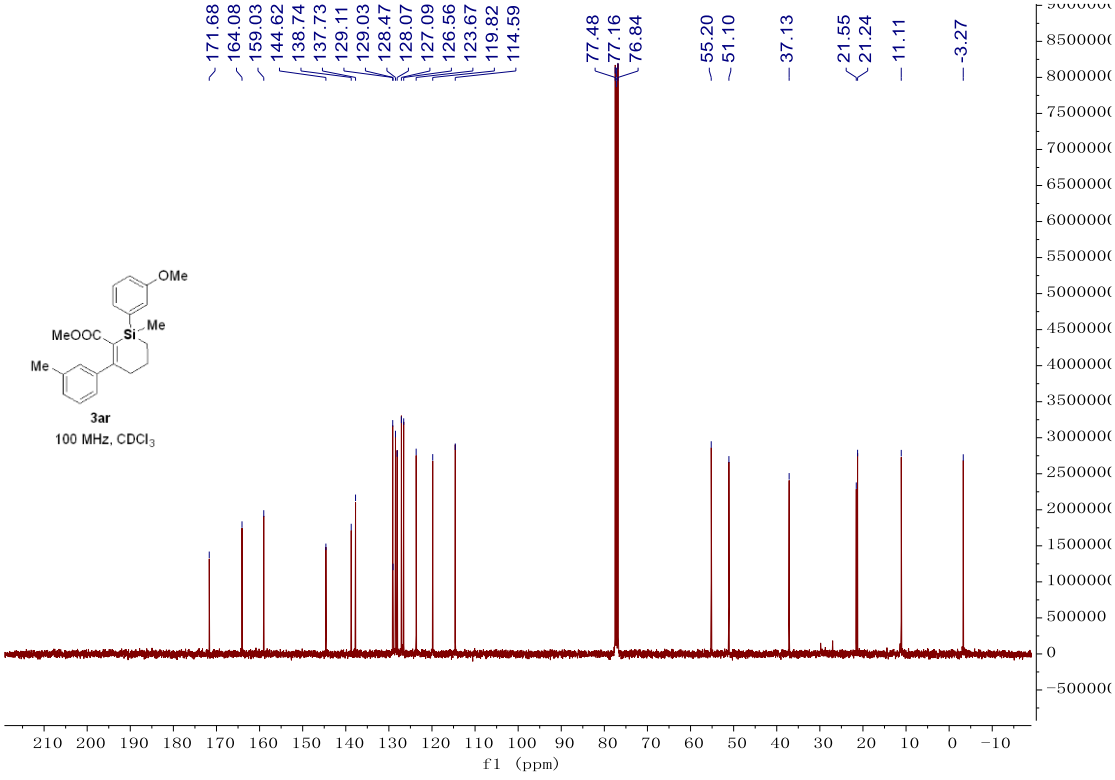
7.02
7.02
6.94
6.93
6.92
6.91
3.83
3.35
2.68
2.64
2.58
2.57
2.54
2.52
2.35
2.01
2.00
1.98
1.14
1.13
1.08
0.94
0.92
0.90
0.57
OMe
MeOOC
Si
Me
Me
3ar
400 MHz, CDCl3
1.00
3.00
3.00
1.00
3.00
3.00
2.00
3.00
2.00
1.00
1.00
3.00
f1 (ppm)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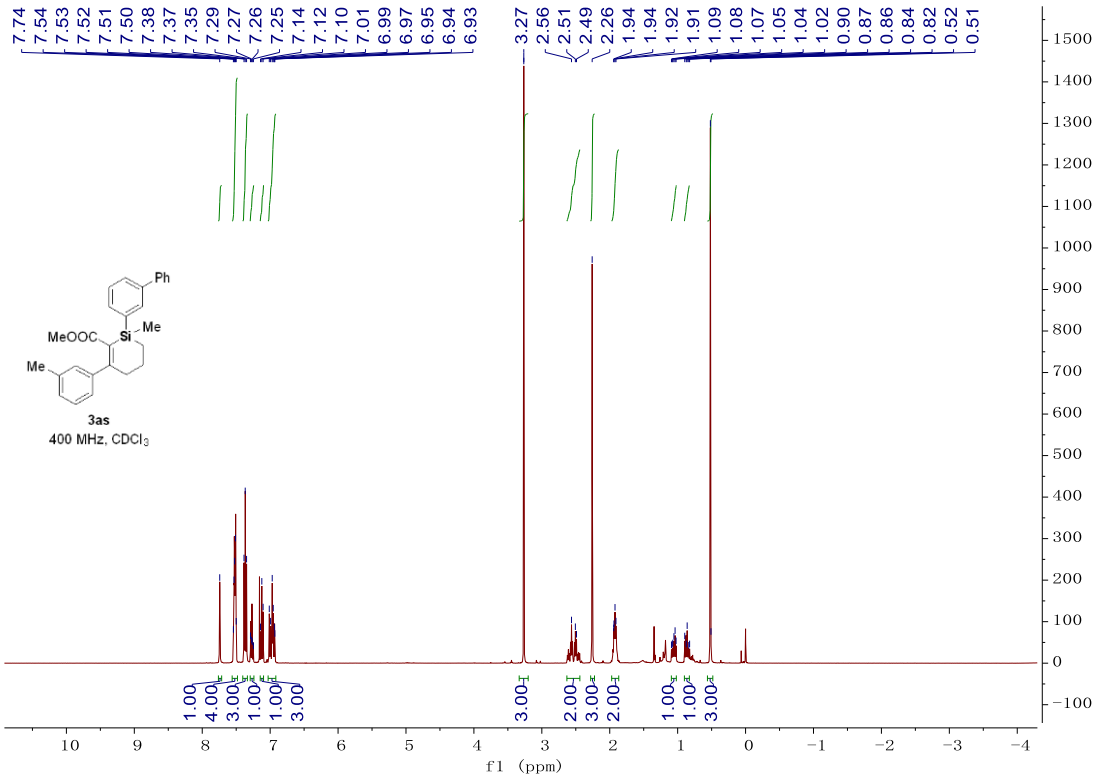
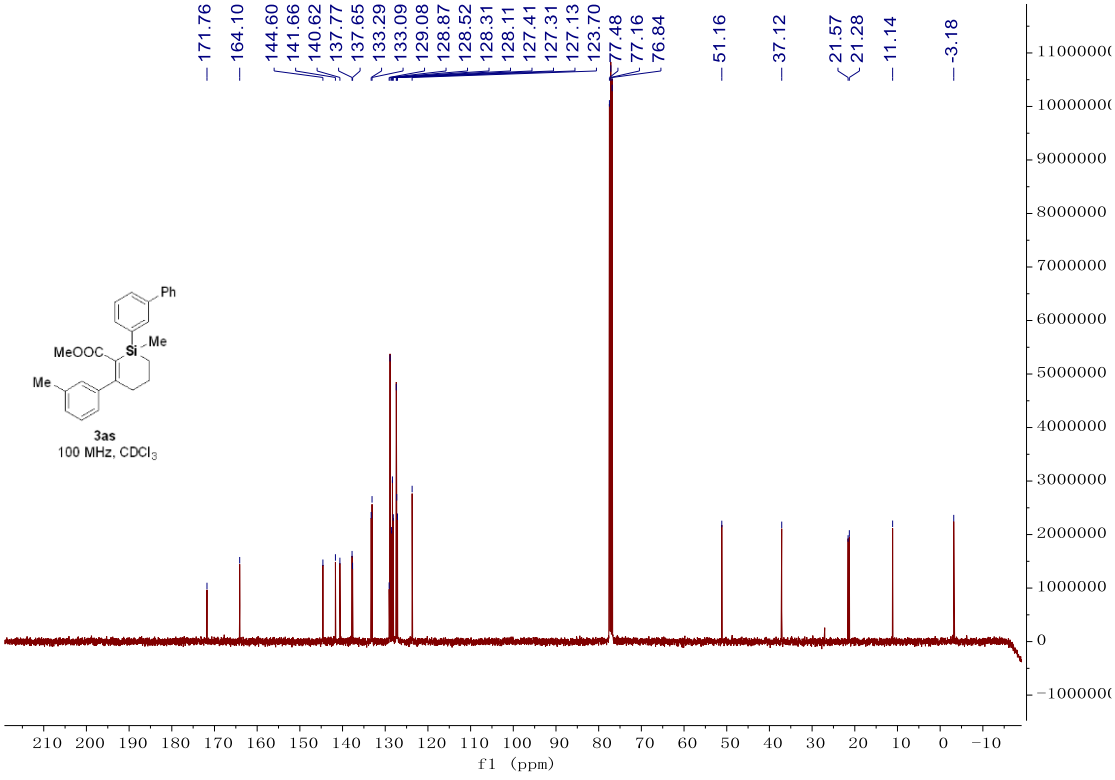
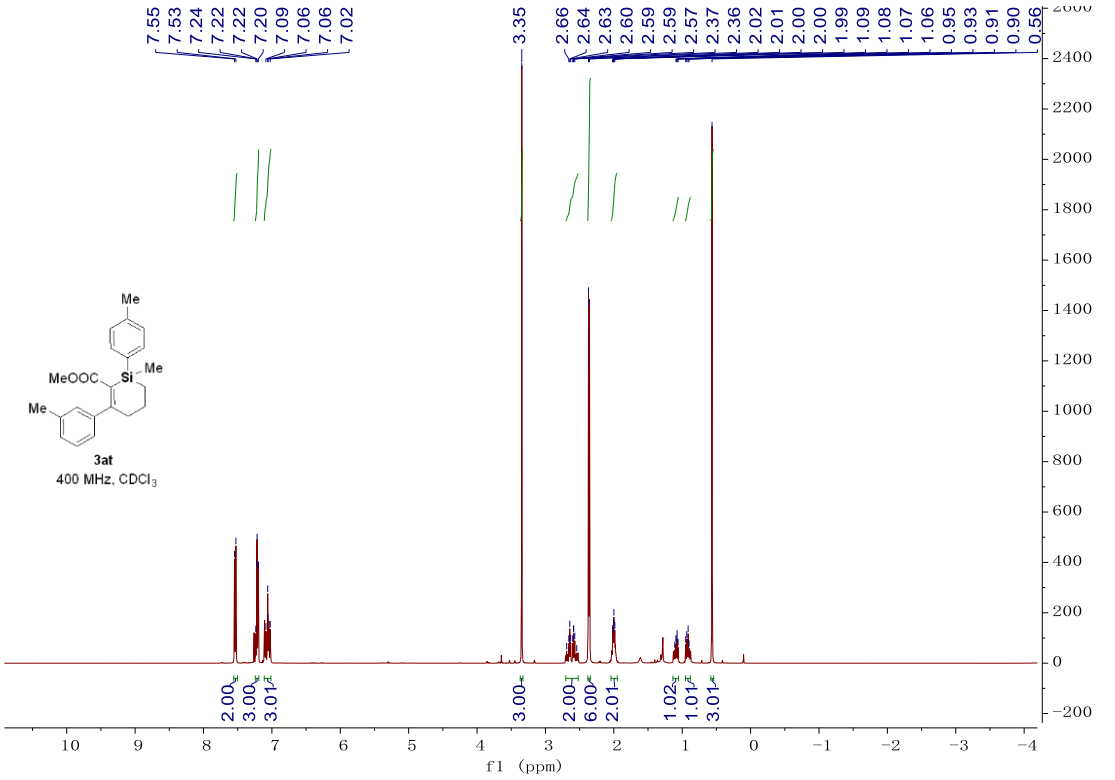
164.08
159.03
144.62
138.74
137.73
129.11
129.03
128.47
128.07
127.09
126.56
123.67
119.82
114.59
77.48
77.16
76.84
55.20
51.10
37.13
21.55
21.24
11.11
-3.27
OMe
MeOOC
Si
Me
Me
3ar
100 MHz, CDCl3
f1 (ppm)


7.74 7.54 7.53 7.52 7.51 7.50 7.38 7.37 7.35 7.29 7.27 7.26 7.25 7.14 7.12 7.10 7.01 6.99 6.97 6.95 6.94 6.93
3.27 2.56 2.51 2.49 2.26 1.94 1.94 1.92 1.91 1.09 1.08 1.07 1.05 1.04 1.02 0.90 0.87 0.86 0.84 0.82 0.52 0.51
Ph
MeOOC
Si
Me
Me
3as
400 MHz, CDCl3
1.00 4.00 3.00 1.00 1.00 3.00 3.00 2.00 3.00 2.00 1.00 1.00 3.00
f1 (ppm)


171.76 164.10 144.60 141.66 140.62 137.77 137.65 133.29 133.09 129.08 128.87 128.52 128.31 128.11 127.41 127.31 127.13 123.70 77.48 77.16 76.84 51.16 37.12 21.57 21.28 11.14 -3.18
Ph
MeOOC
Si
Me
Me
3as
100 MHz, CDCl3
f1 (ppm)


7.55
7.53
7.24
7.22
7.22
7.20
7.09
7.06
7.06
7.02
3.35
2.66
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2.63
2.60
2.59
2.59
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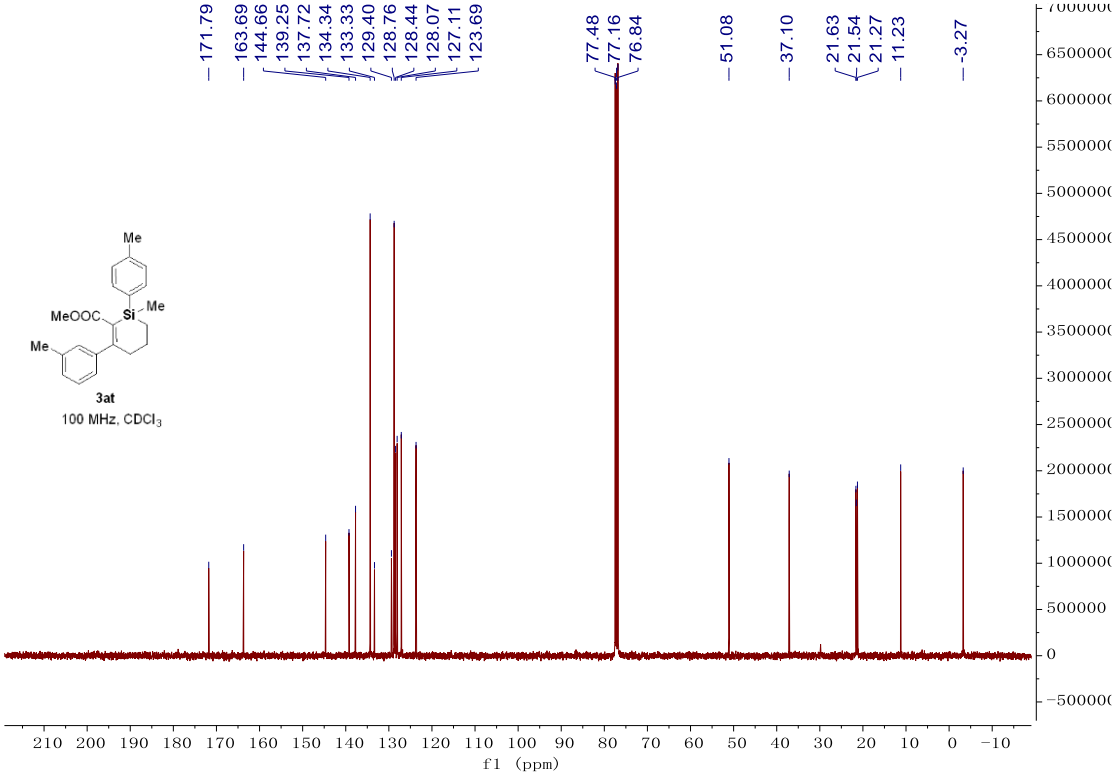
2.36
2.02
2.01
2.00
2.00
1.99
1.09
1.08
1.07
1.06
0.95
0.93
0.91
0.90
0.56
Me
MeOOC
Si
Me
Me
3at
400 MHz, CDCl3
2.00
3.00
3.01
3.00
2.00
6.00
2.01
1.02
1.01
3.01
f1 (ppm)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139.25
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134.34
133.33
129.40
128.76
128.44
128.07
127.11
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77.48
77.16
76.84
51.08
37.10
21.63
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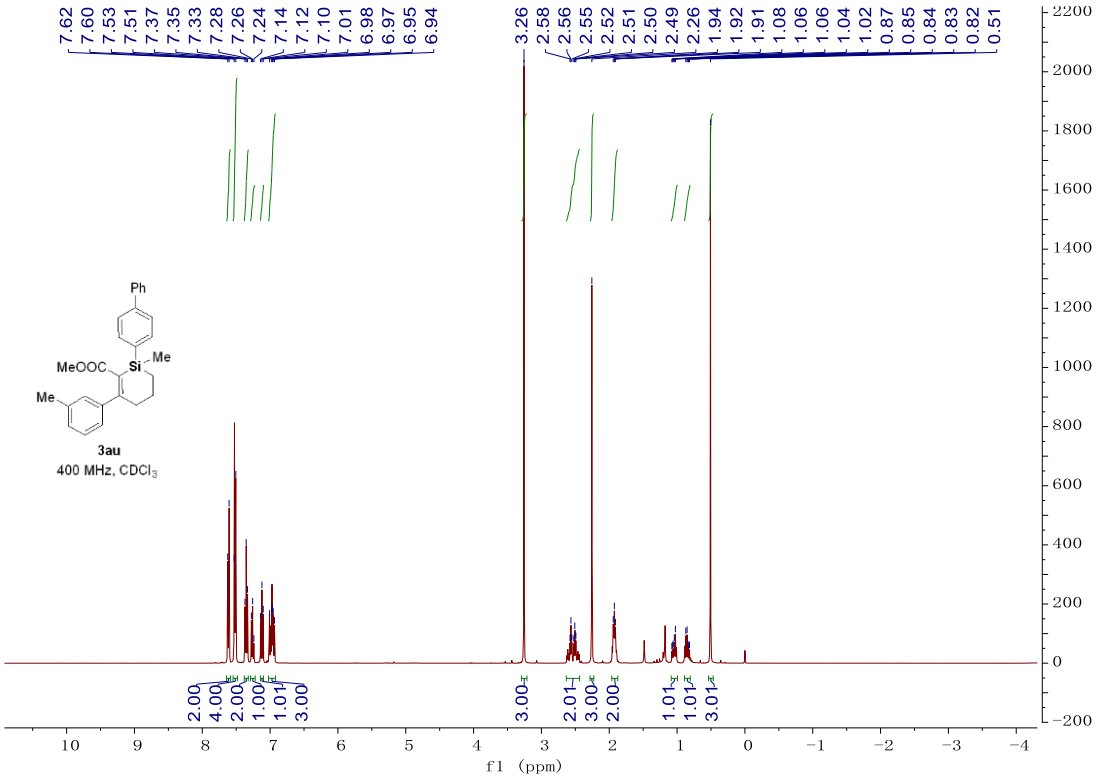
21.27
11.23
-3.27
Me
MeOOC
Si
Me
Me
3at
100 MHz, CDCl3
f1 (ppm)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7.60
7.53
7.51
7.37
7.35
7.33
7.28
7.26
7.24
7.14
7.12
7.10
7.01
6.98
6.97
6.95
6.94
3.26
2.58
2.56
2.55
2.52
2.51
2.50
2.49
2.26
1.94
1.92
1.91
1.08
1.06
1.06
1.04
1.02
0.87
0.85
0.84
0.83
0.82
0.51
Ph
MeOOC
Si
Me
Me
3au
400 MHz, CDCl3
2.00
4.00
2.00
1.00
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3.00
3.00
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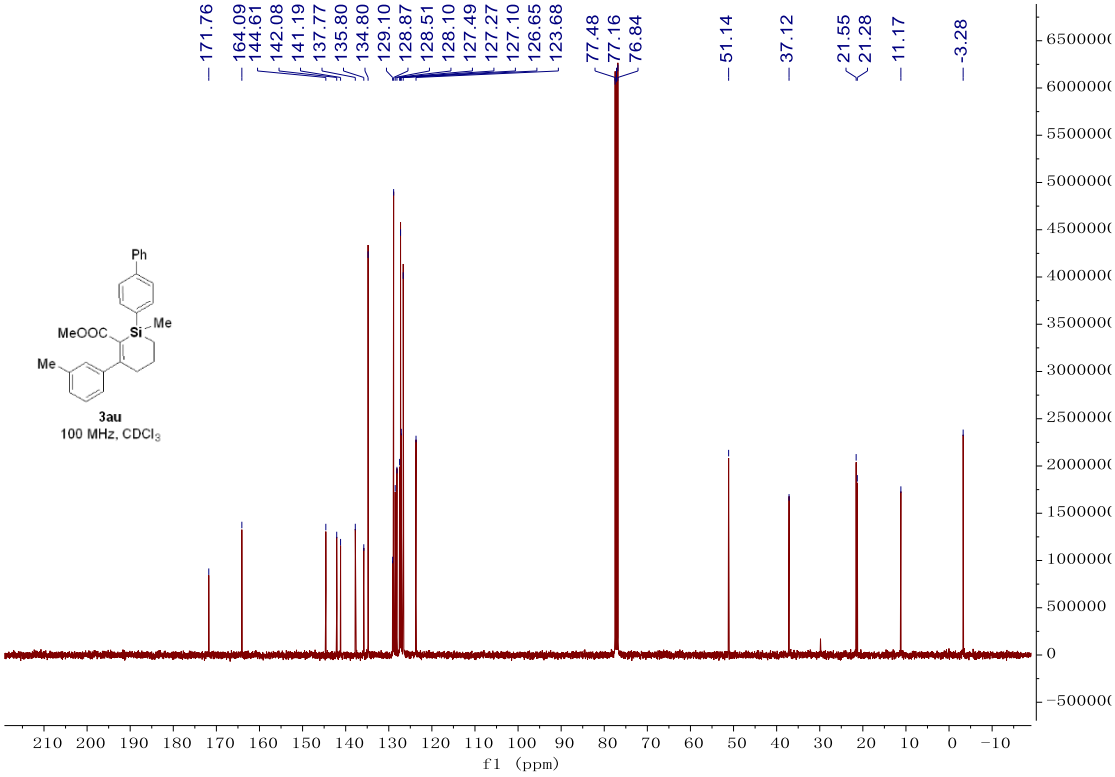
2.00
1.01
1.01
3.01
f1 (ppm)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142.08
141.19
137.77
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134.80
129.10
128.87
128.51
128.10
127.49
127.27
127.10
126.65
123.68
77.48
77.16
76.84
51.14
37.12
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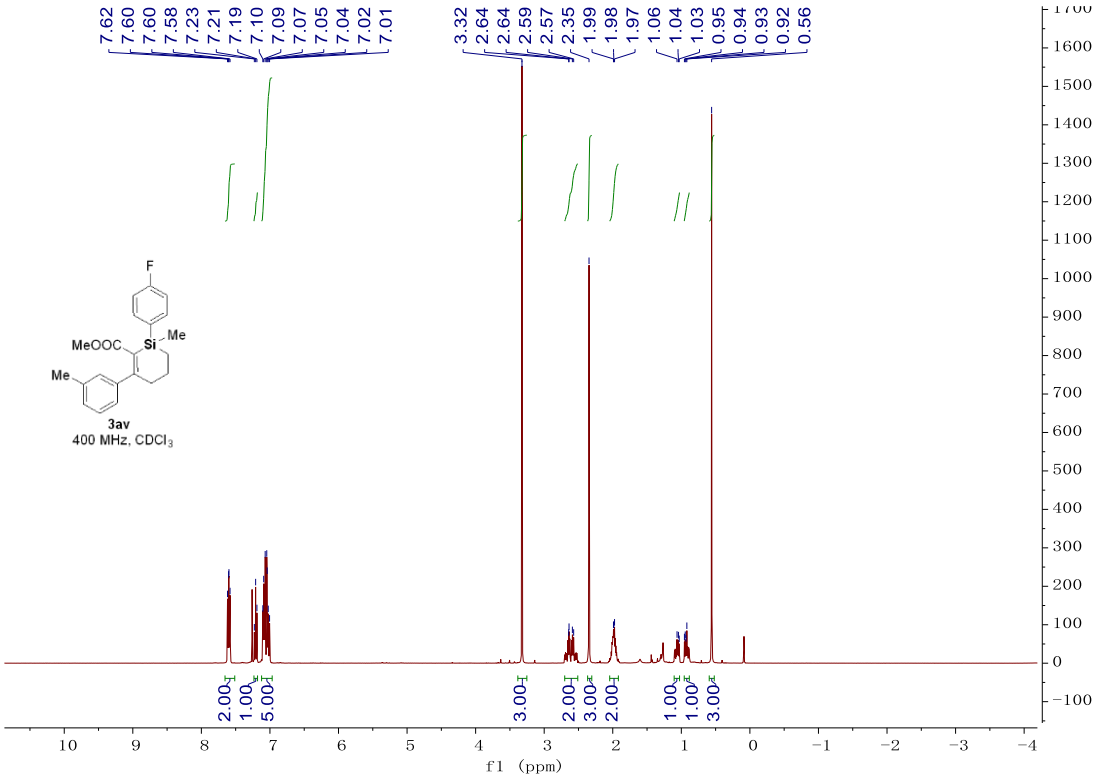
11.17
-3.28
Ph
MeOOC
Si
Me
Me
3au
100 MHz, CDCl3
f1 (ppm)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7.60
7.60
7.58
7.23
7.21
7.19
7.10
7.09
7.07
7.05
7.04
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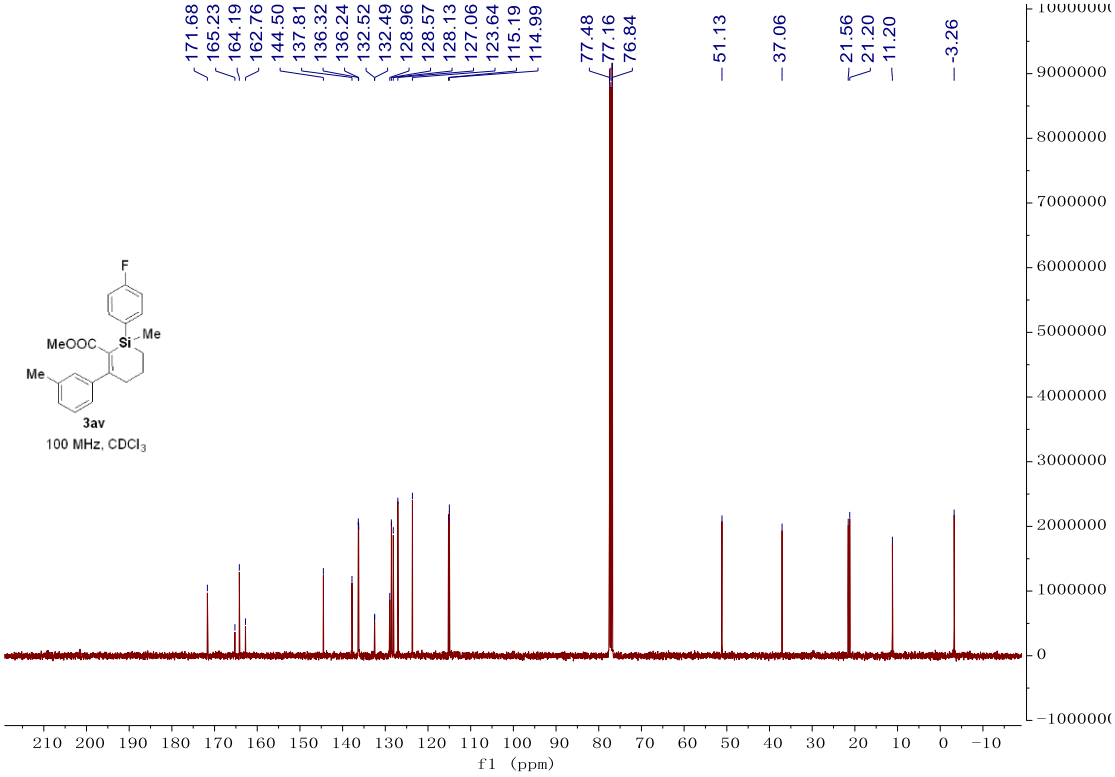
7.01
3.32
2.64
2.64
2.59
2.57
2.35
1.99
1.98
1.97
1.06
1.04
1.03
0.95
0.94
0.93
0.92
0.56
F
MeOOC
Si
Me
Me
3av
400 MHz, CDCl3
2.00
1.00
5.00
3.00
2.00
3.00
2.00
1.00
1.00
3.00
f1 (ppm)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136.24
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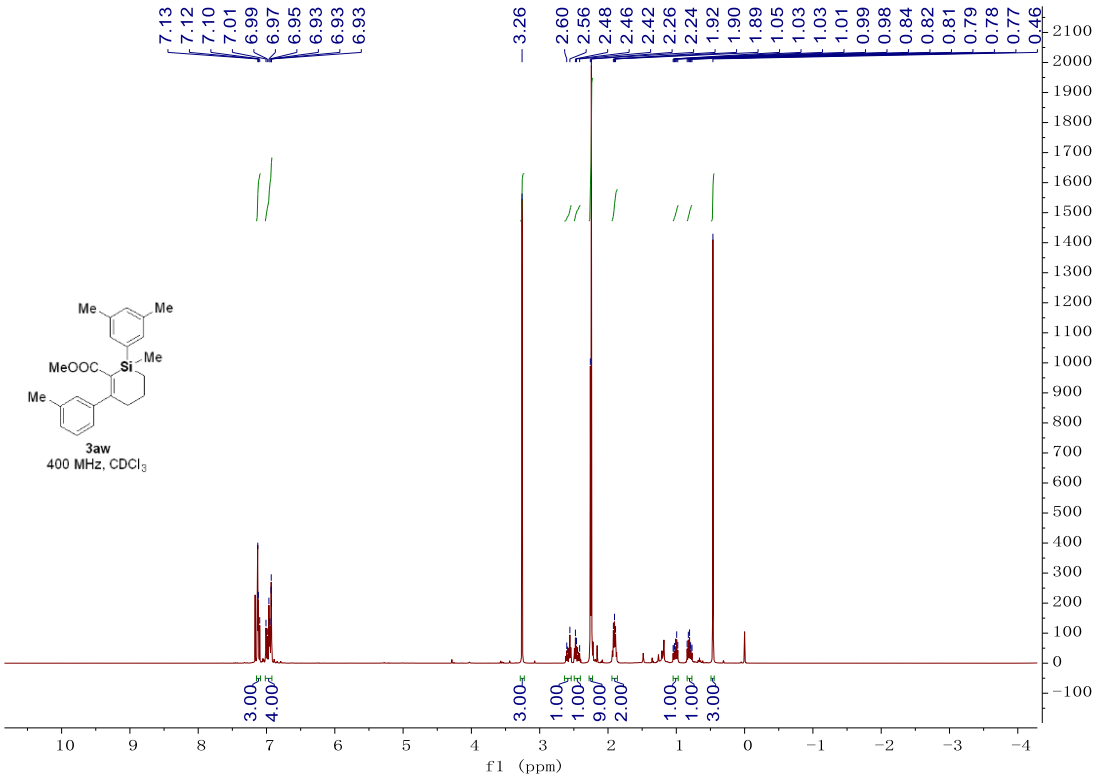
132.49
128.96
128.57
128.13
127.06
123.64
115.19
114.99
77.48
77.16
76.84
51.13
37.06
21.56
21.20
11.20
-3.26
F
MeOOC
Si
Me
Me
3av
100 MHz, CDCl3
f1 (ppm)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7.12
7.10
7.01
6.99
6.97
6.95
6.93
6.93
6.93
3.26
2.60
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2.48
2.46
2.42
2.26
2.24
1.92
1.90
1.89
1.05
1.03
1.03
1.01
0.99
0.98
0.84
0.82
0.81
0.79
0.78
0.77
0.46
Me
Me
MeOOC
Si
Me
Me
3aw
400 MHz, CDCl3
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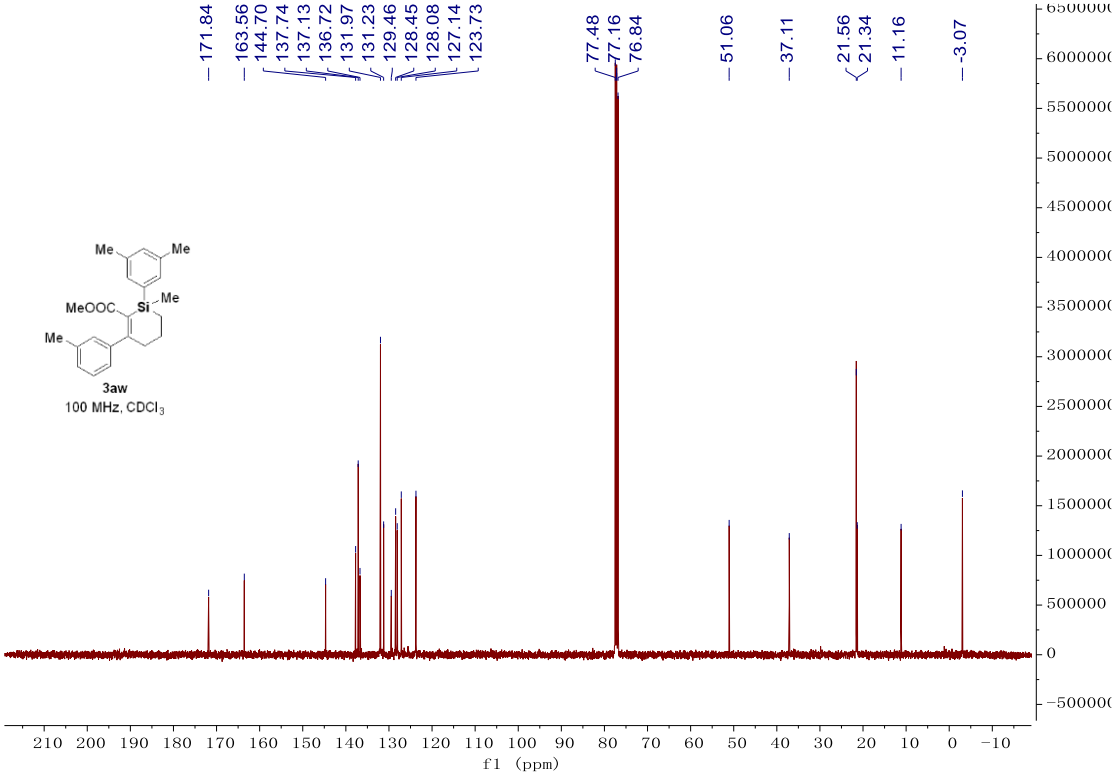
2.00
1.00
1.00
3.00
f1 (ppm)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131.23
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128.45
128.08
127.14
123.73
77.48
77.16
76.84
51.06
37.11
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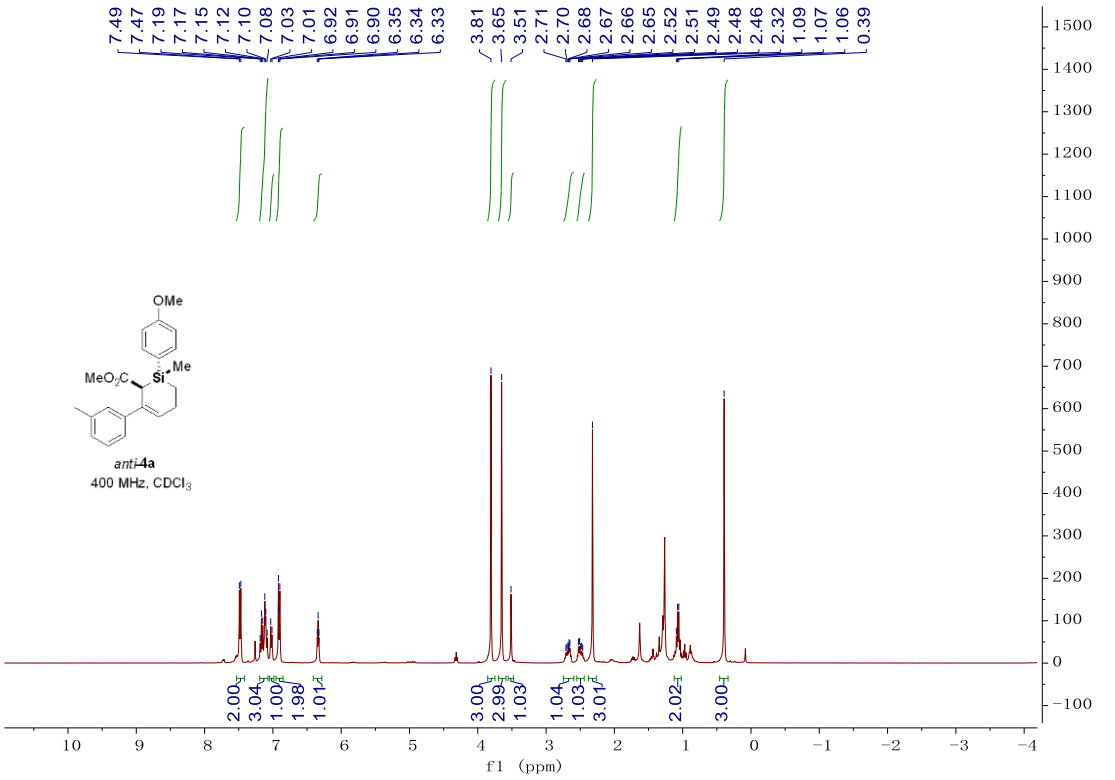
11.16
-3.07
Me
Me
MeOOC
Si
Me
Me
3aw
100 MHz, CDCl3
f1 (ppm)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7.19
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7.10
7.08
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7.01
6.92
6.91
6.90
6.35
6.34
6.33
3.81
3.65
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2.67
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2.51
2.49
2.48
2.46
2.32
1.09
1.07
1.06
0.39
OMe
MeO2C
Si
Me
anti-4a
400 MHz, CDCl3
2.00
3.04
1.00
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1.01
3.00
2.99
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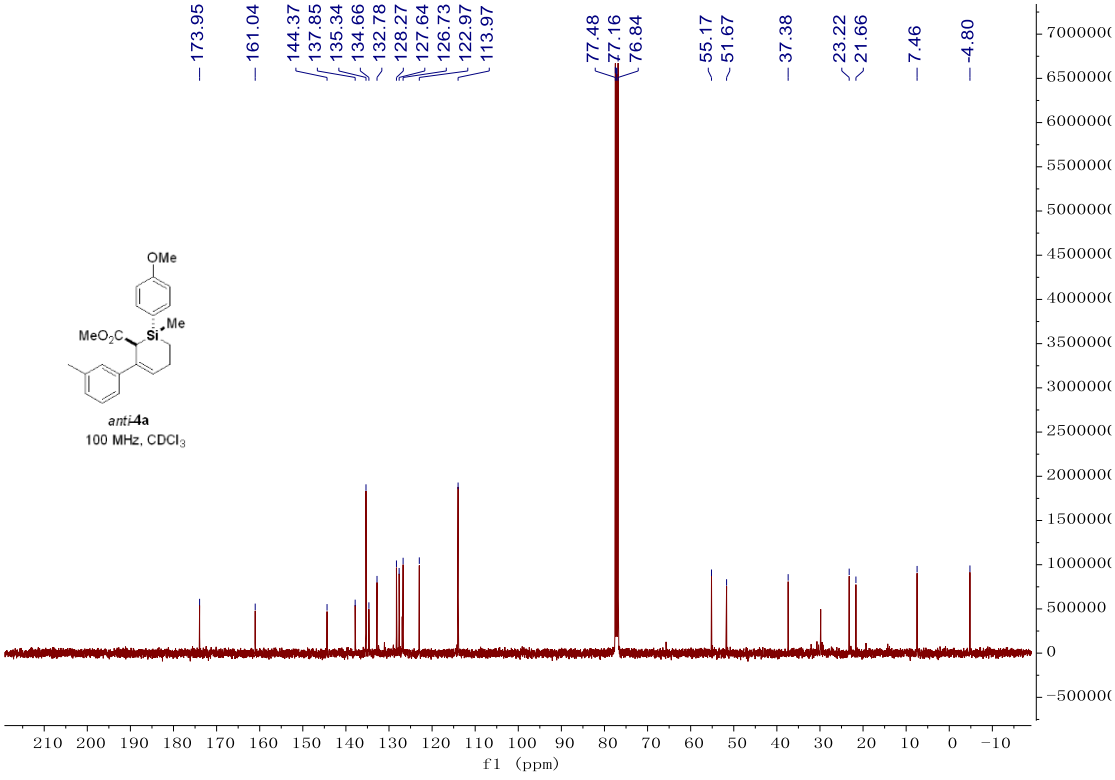
1.03
3.01
2.02
3.00
f1 (ppm)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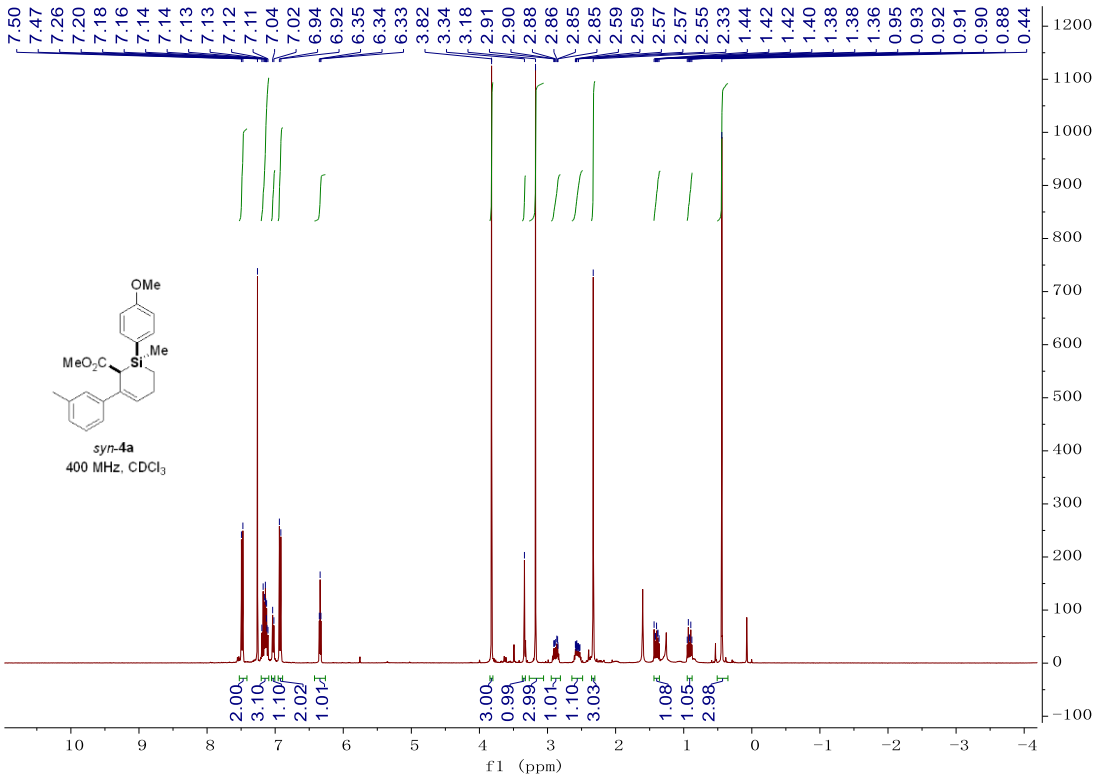
127.64
126.73
122.97
113.97
77.48
77.16
76.84
55.17
51.67
37.38
23.22
21.66
7.46
-4.80
OMe
MeO2C
Si
Me
anti-4a
100 MHz, CDCl3
f1 (ppm)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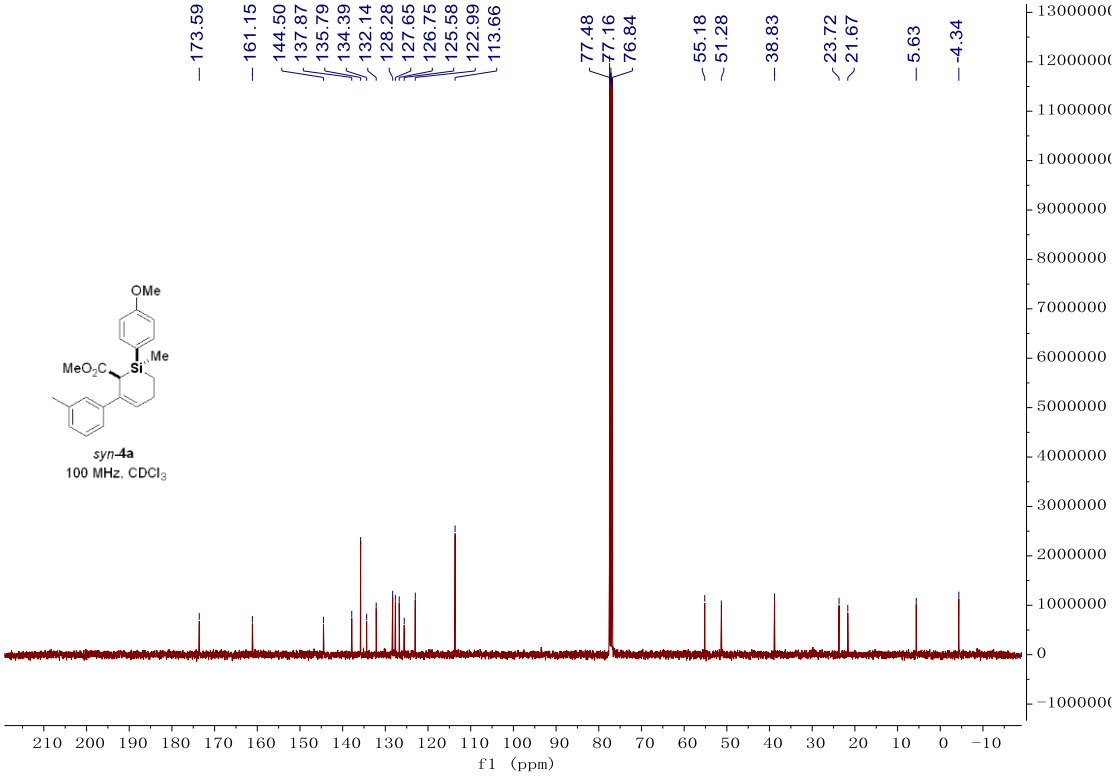
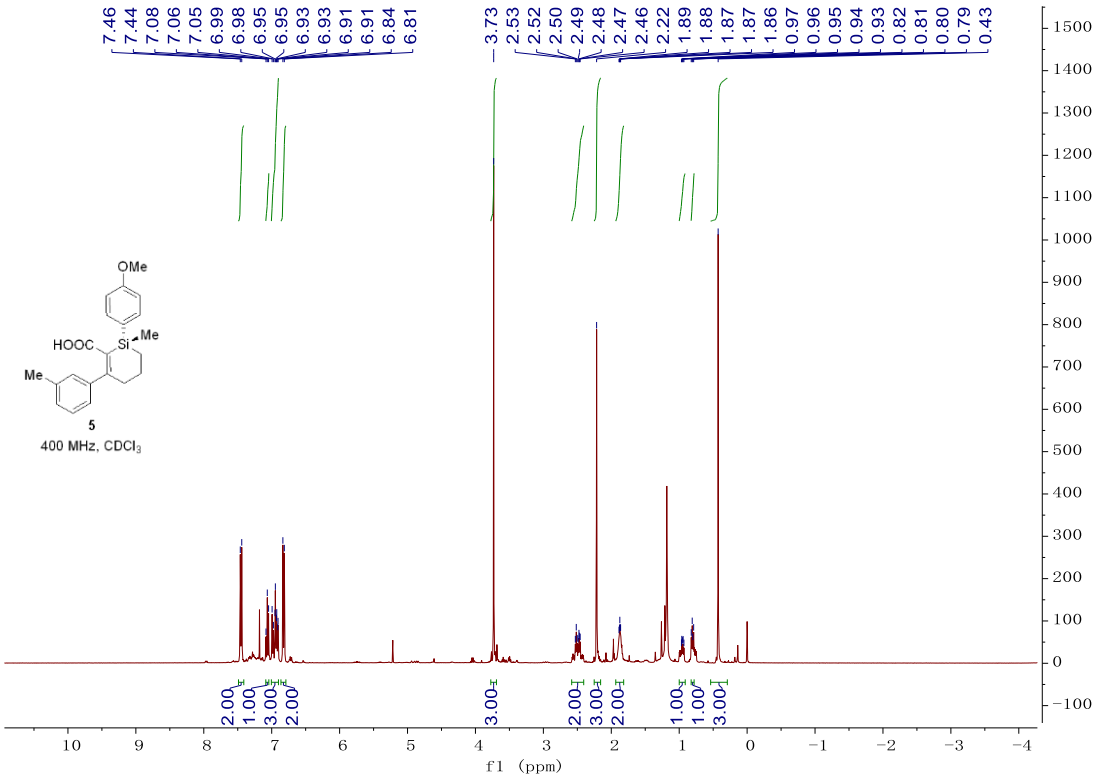
3.82 3.34 3.18 2.91 2.90 2.88 2.86 2.85 2.85 2.59 2.59 2.57 2.57 2.55 2.33 1.44 1.42 1.42 1.40 1.38 1.38 1.36 0.95 0.93 0.92 0.91 0.90 0.88 0.44
OMe
MeO2C
Si
Me
syn-4a
400 MHz, CDCl3
2.00 3.10 1.10 2.02 1.01 3.00 0.99 2.99 1.01 1.10 3.03 1.08 1.05 2.98
f1 (ppm)


173.59 161.15 144.50 137.87 135.79 134.39 132.14 128.28 127.65 126.75 125.58 122.99 113.66
77.48 77.16 76.84
55.18 51.28 38.83 23.72 21.67 5.63 -4.34
OMe
MeO2C
Si
Me
syn-4a
100 MHz, CDCl3
f1 (ppm)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6.99
6.98
6.95
6.95
6.93
6.93
6.91
6.91
6.84
6.81
3.73
2.53
2.52
2.50
2.49
2.48
2.47
2.46
2.22
1.89
1.88
1.87
1.87
1.86
0.97
0.96
0.95
0.94
0.93
0.82
0.81
0.80
0.79
0.43
OMe
HOOC
Si
Me
Me
5
400 MHz, CDCl3
2.00
1.00
3.00
2.00
3.00
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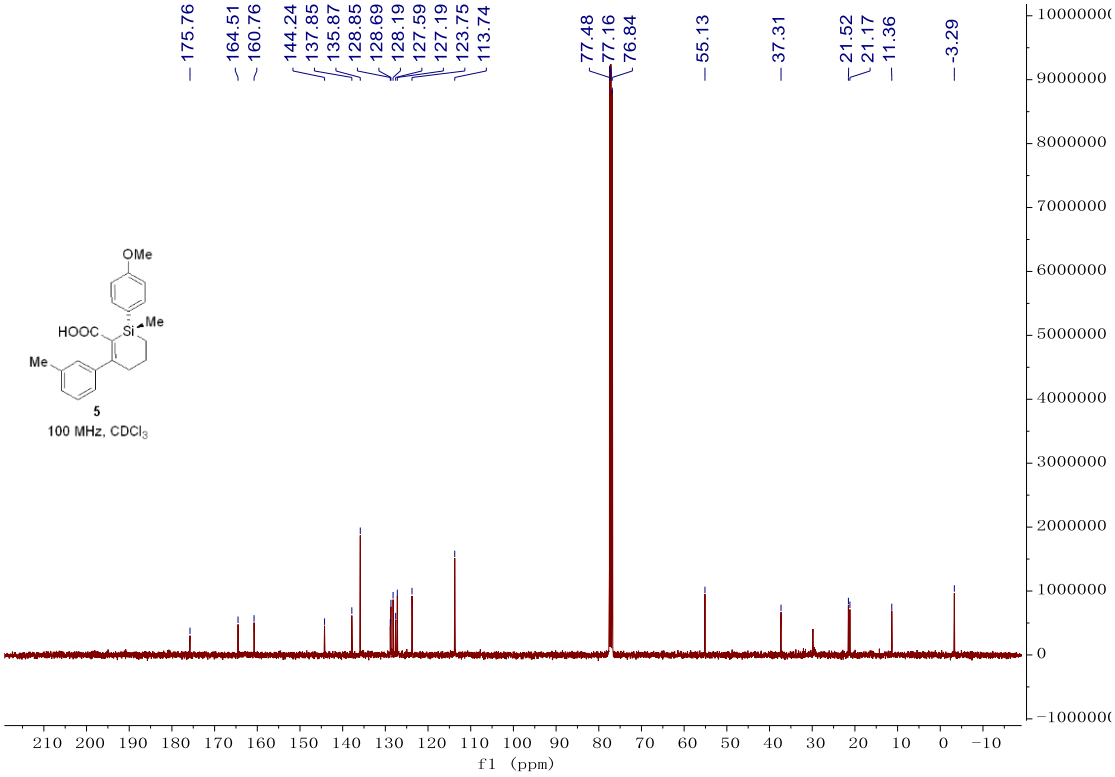
2.00
1.00
1.00
3.00
f1 (ppm)


175.76
164.51
160.76
144.24
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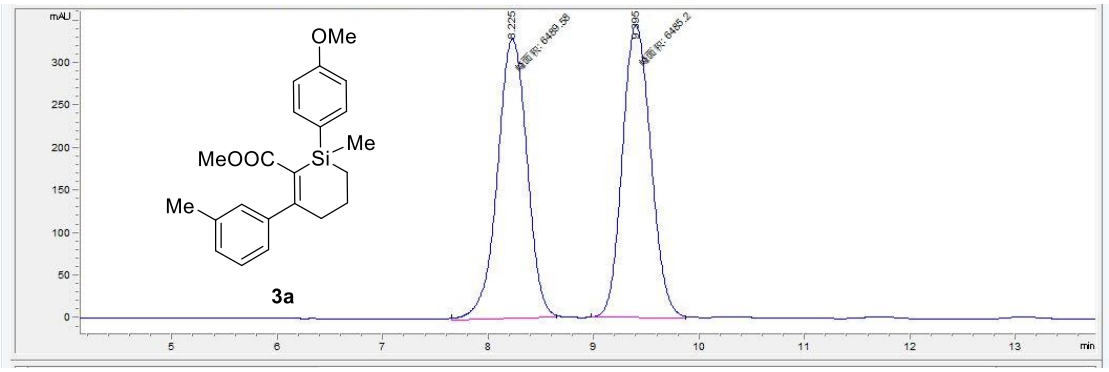
135.87
128.85
128.69
128.19
127.59
127.19
123.75
113.74
77.48
77.16
76.84
55.13
37.31
21.52
21.17
11.36
-3.29
OMe
HOOC
Si
Me
Me
5
100 MHz, CDCl3
f1 (ppm)

9. HPLC Spectra



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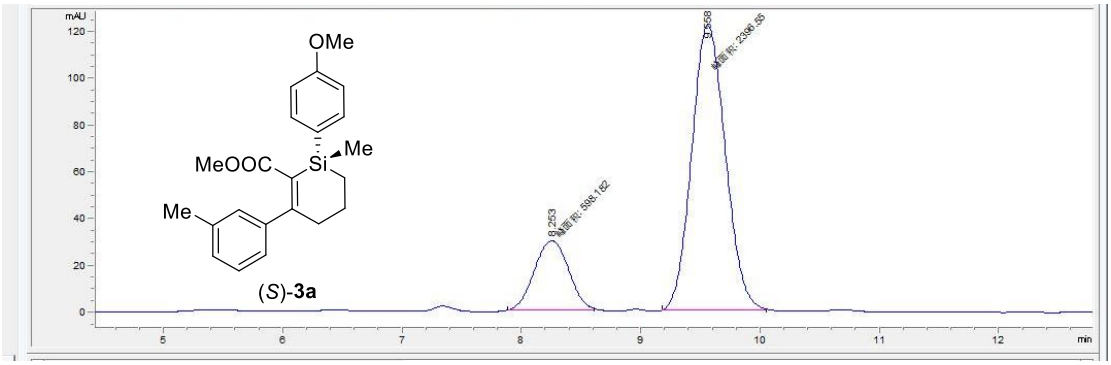
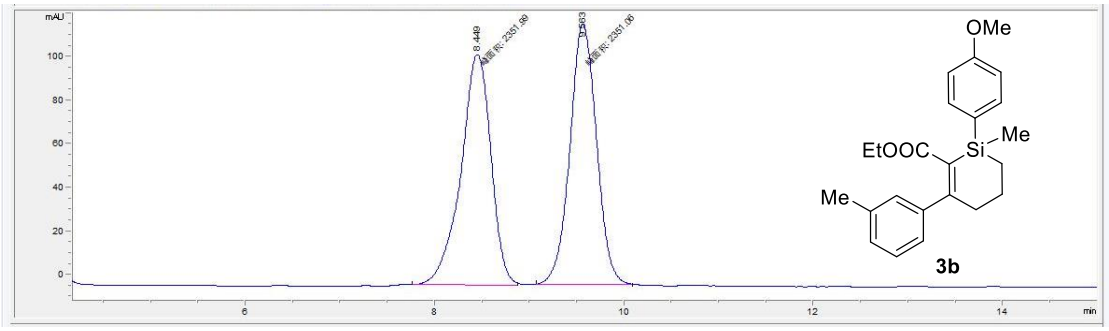
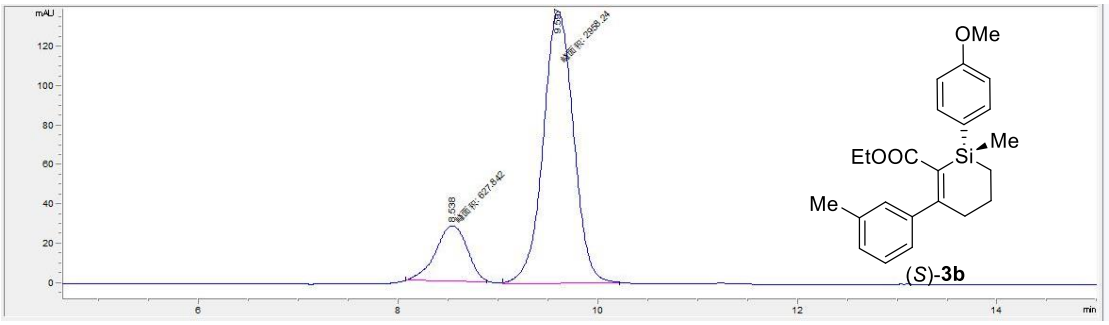
1	8.225	6489.6	329.0	50.017
2	9.395	6485.2	344.8	49.983



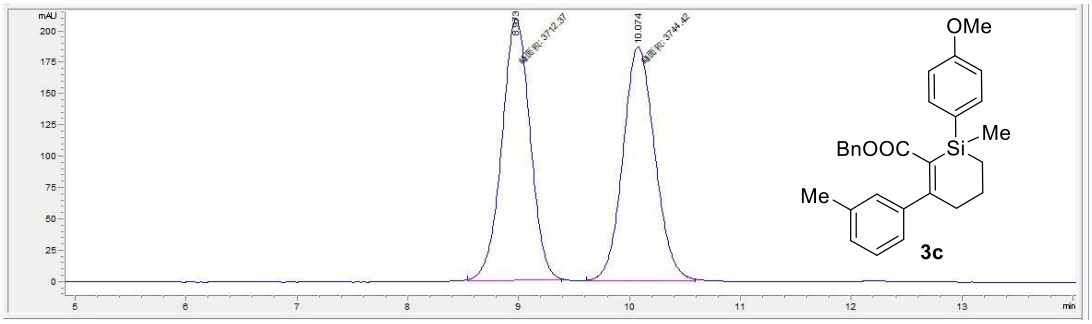
	Time/min	Area	Height	Area%
1	8.253	598.2	29.8	19.974
2	9.558	2396.6	122.0	80.026



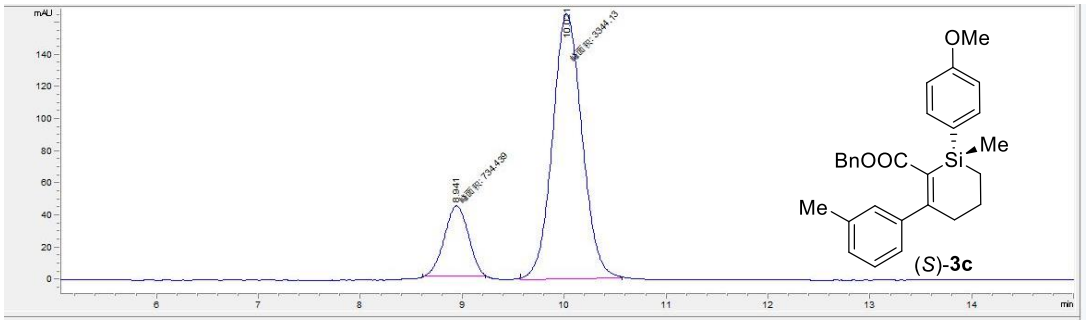
	Time/min	Area	Height	Area%
1	8.449	2352	105.9	50.010
2	9.563	2351.1	119.7	49.990



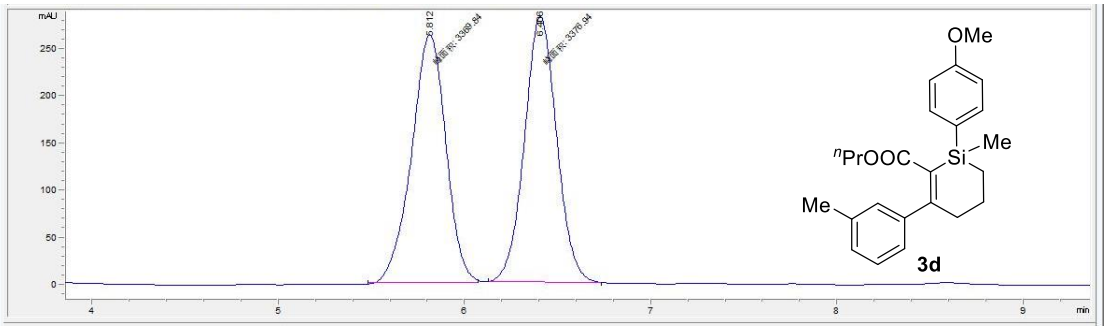
	Time/min	Area	Height	Area%
1	8.538	627.8	28.2	17.508
2	9.597	2958.2	138.9	82.492



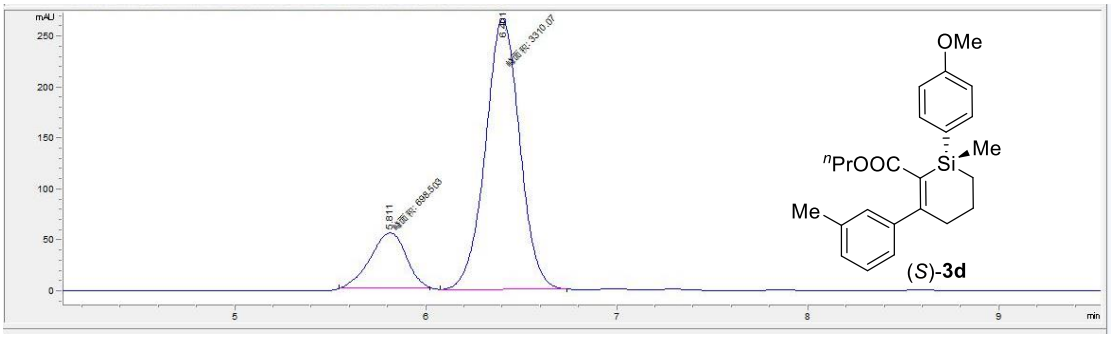
	Time/min	Area	Height	Area%
1	8.973	3712.4	209.4	49.785
2	10.074	3744.4	186.8	50.215



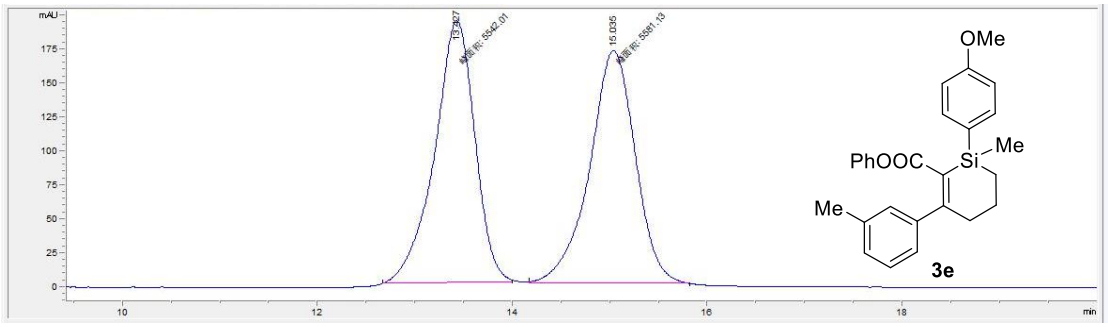
	Time/min	Area	Height	Area%
1	8.941	734.4	44.3	18.007
2	10.021	3344.1	165.4	81.993



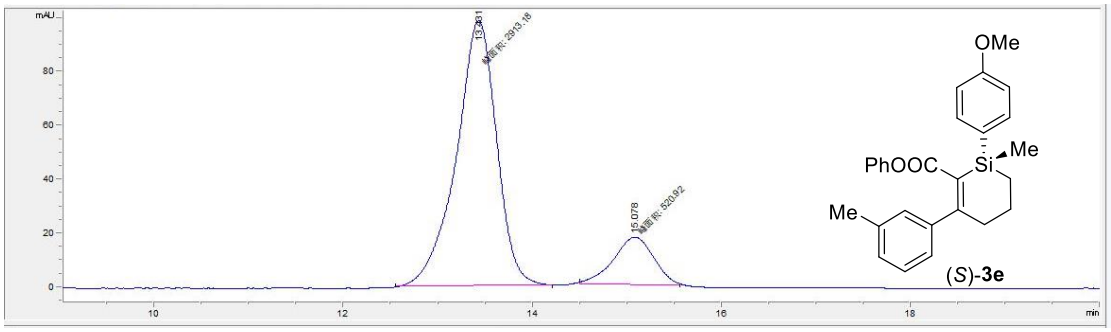
	Time/min	Area	Height	Area%
1	5.812	3369.8	262.8	49.947
2	6.406	3376.9	281.4	50.053



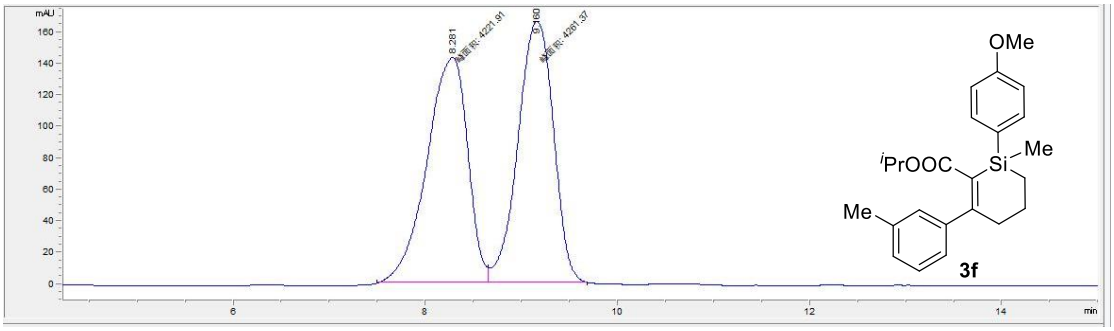
	Time/min	Area	Height	Area%
1	5.811	698.5	53.9	17.425
2	6.401	3310.1	265.8	82.575



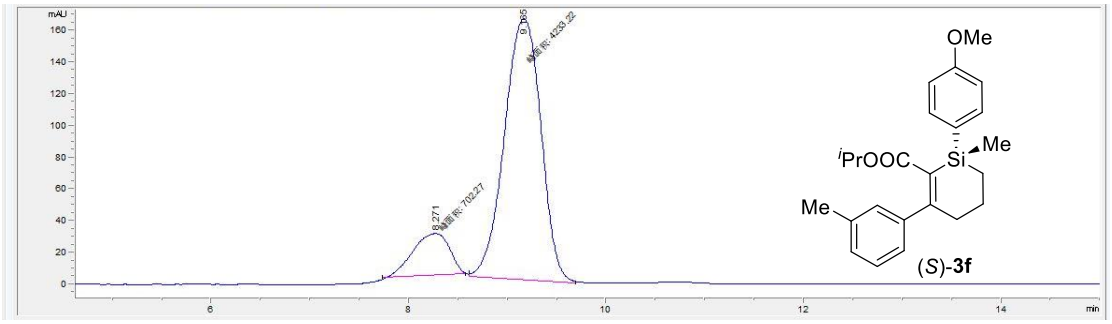
	Time/min	Area	Height	Area%
1	13.427	5542	192.7	49.824
2	15.035	5581.1	171.1	50.176



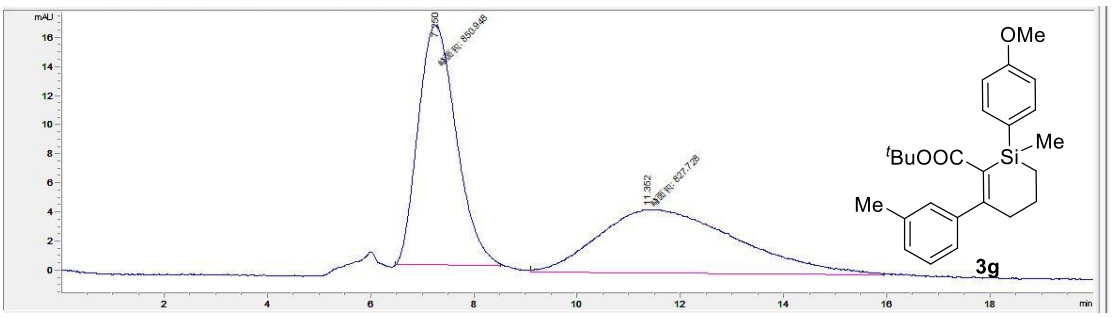
	Time/min	Area	Height	Area%
1	13.431	2913.2	98.5	84.831
2	15.078	520.9	17.5	15.169



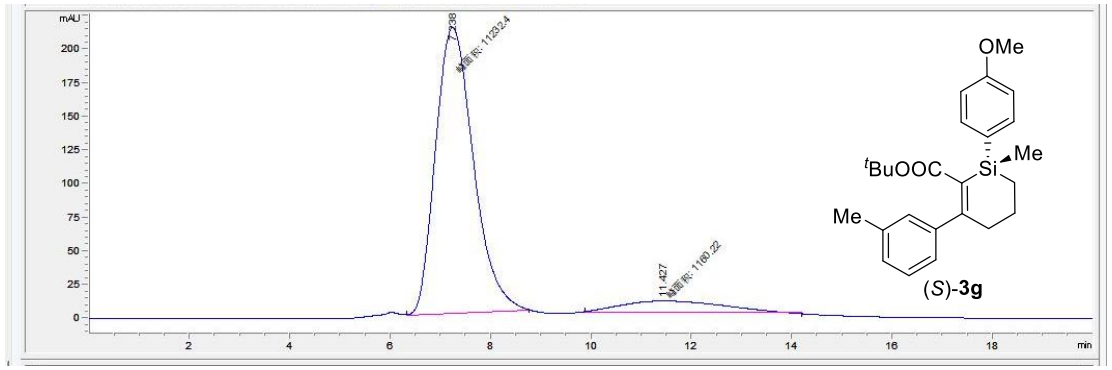
	Time/min	Area	Height	Area%
1	8.281	4221.9	142.9	49.767
2	9.16	4261.4	165.7	50.233



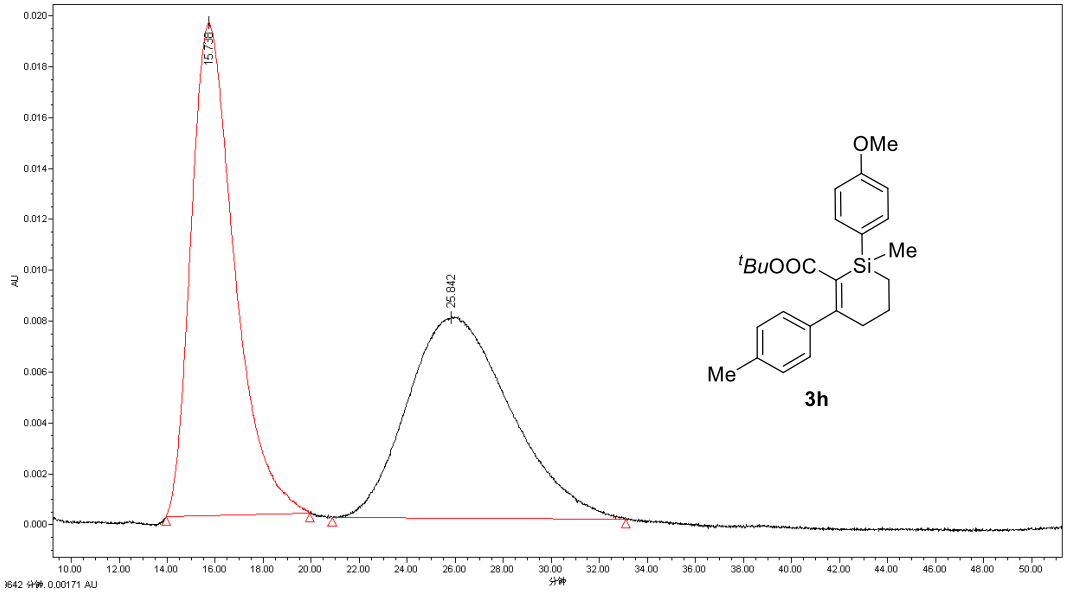
	Time/min	Area	Height	Area%
1	8.271	702.3	26.7	14.299
2	9.165	4233.2	164.5	85.771



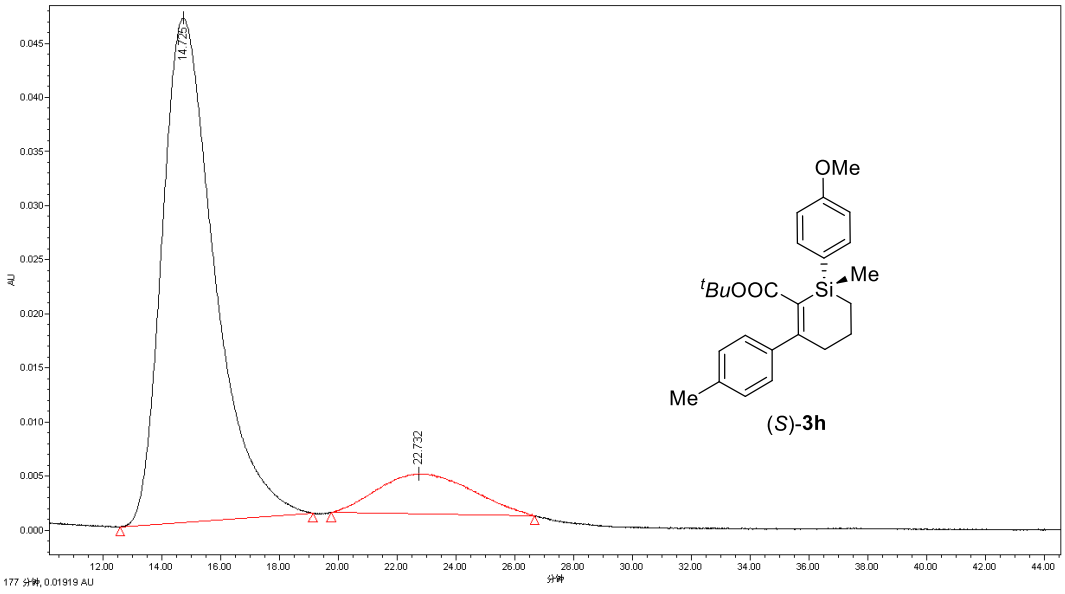
	Time/min	Area	Height	Area%
1	7.25	850.9	16.5	50.692
2	11.352	827.7	4.4	49.308



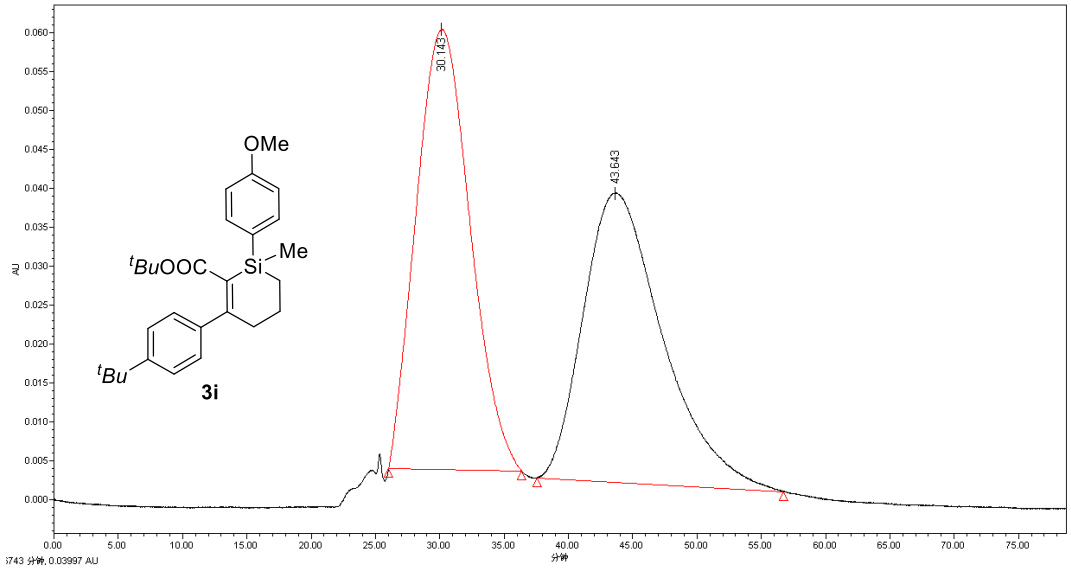
	Time/min	Area	Height	Area%
1	7.238	11232.4	212.9	90.638
2	11.427	1160.2	8.4	9.362



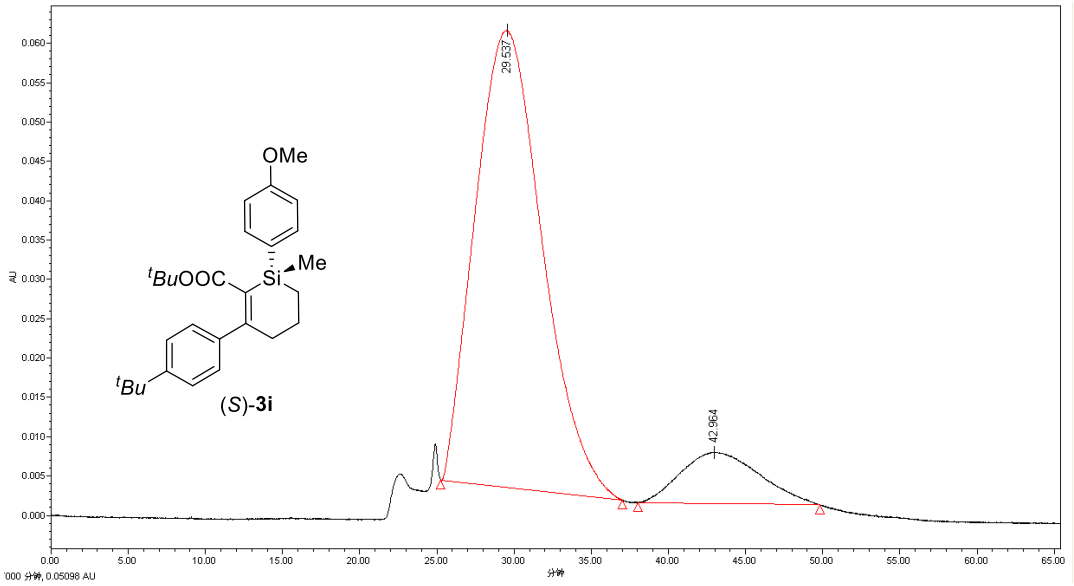
	Time/min	Area	Height	Area%
1	15.738	2444349	19374	50.86
2	25.842	2362113	7904	49.14



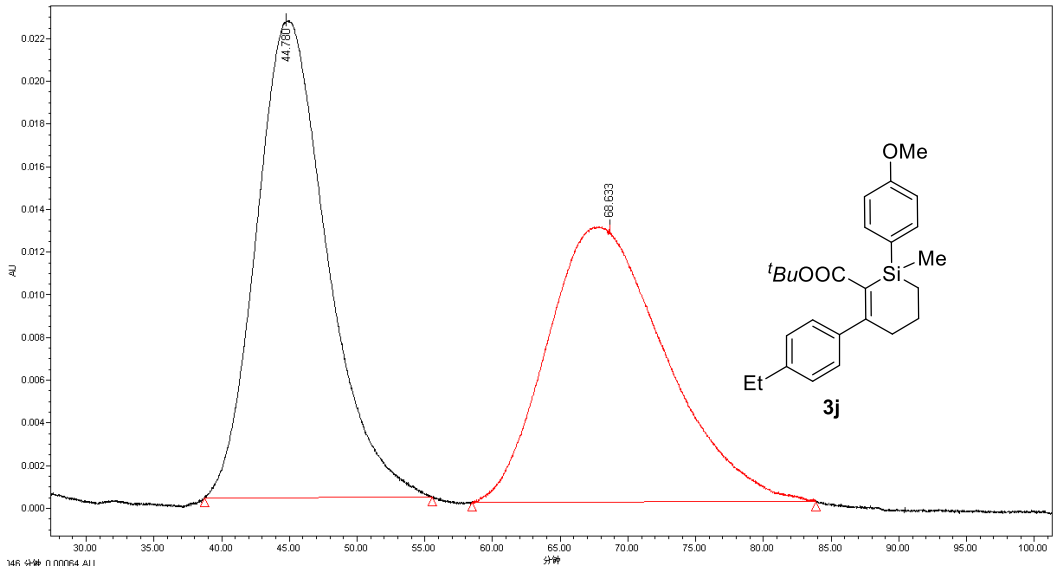
	Time/min	Area	Height	Area%
1	14.725	5758452	46581	87.42
2	22.732	828617	3721	12.58



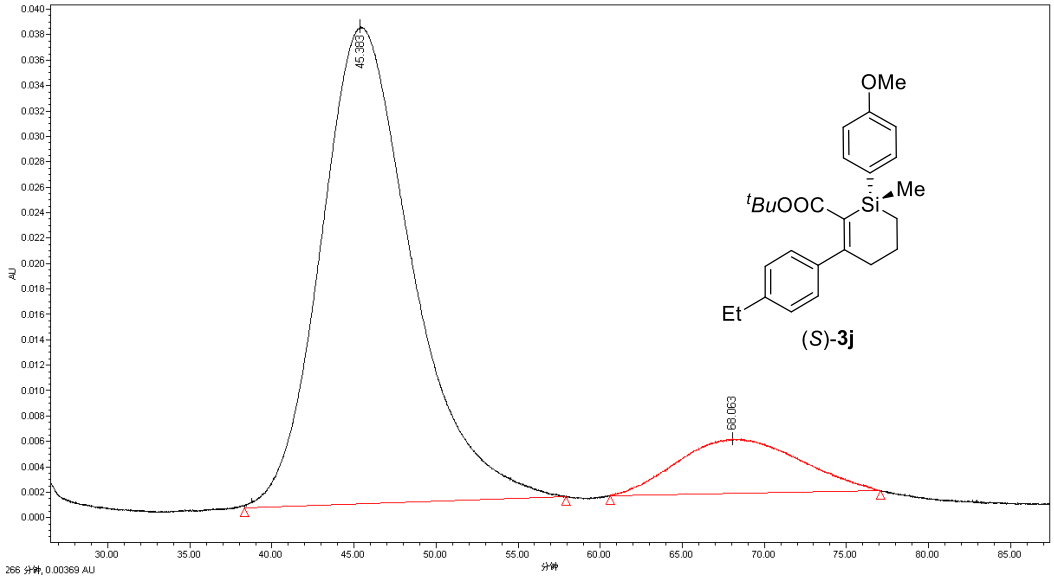
	Time/min	Area	Height	Area%
1	30.143	16479937	56507	50.82
2	43.643	15946264	37134	49.18



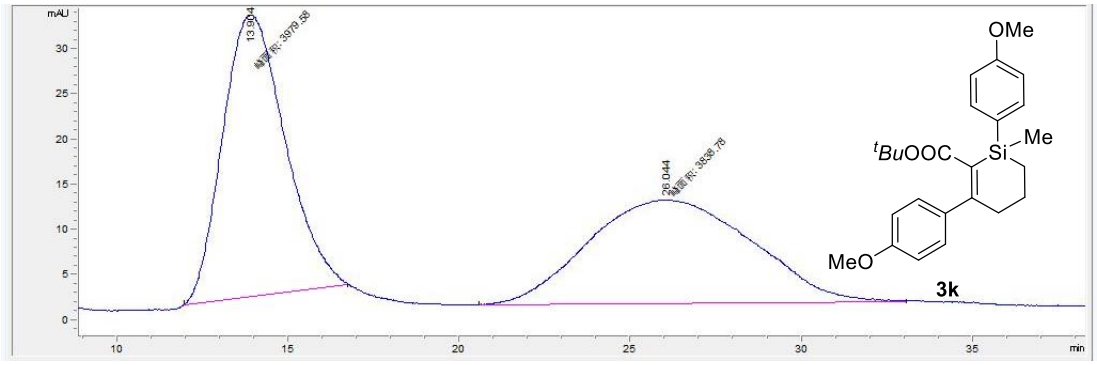
	Time/min	Area	Height	Area%
1	29.537	17631221	58071	88.44
2	42.964	2303590	6516	11.56



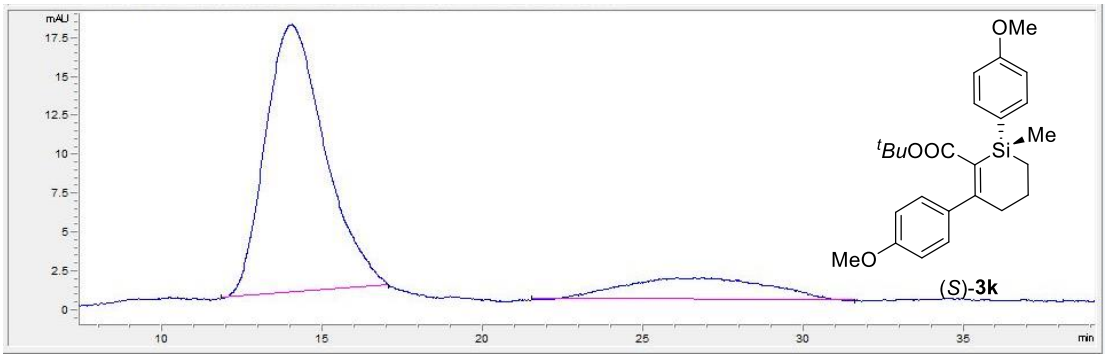
	Time/min	Area	Height	Area%
1	44.780	8116999	22361	50.81
2	68.633	7858572	12782	49.19



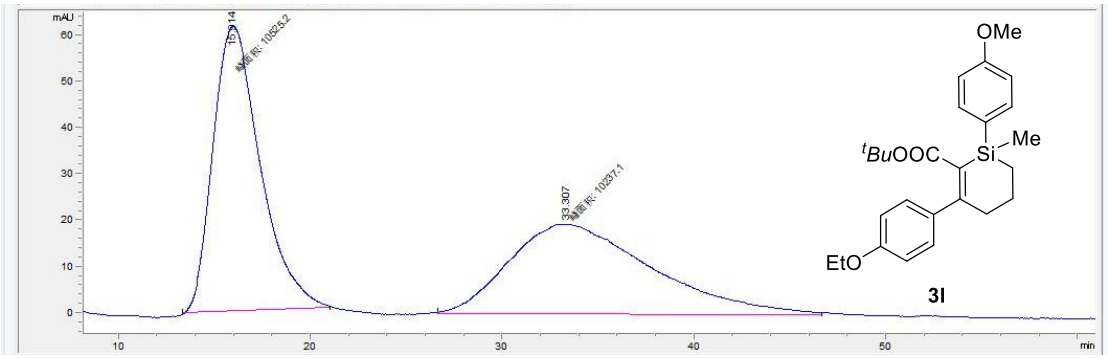
	Time/min	Area	Height	Area%
1	45.383	14452558	37538	86.68
2	68.063	2220516	4306	13.32



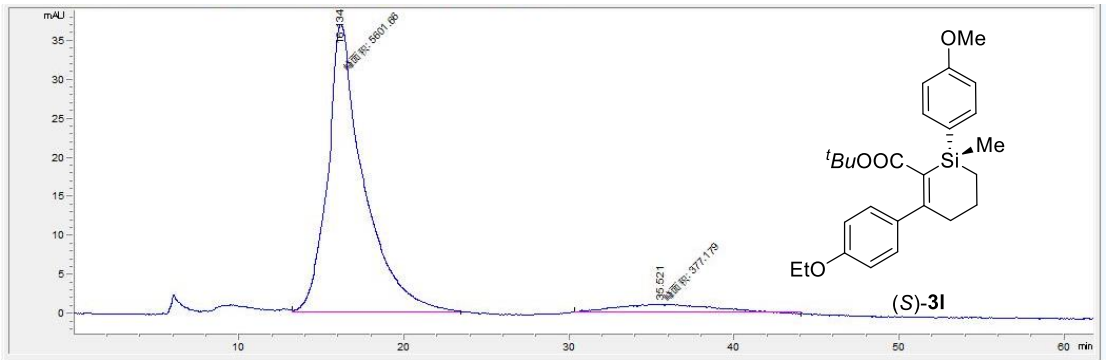
	Time/min	Area	Height	Area%
1	13.904	3979.6	31.2	50.900
2	26.044	3838.8	11.5	49.100



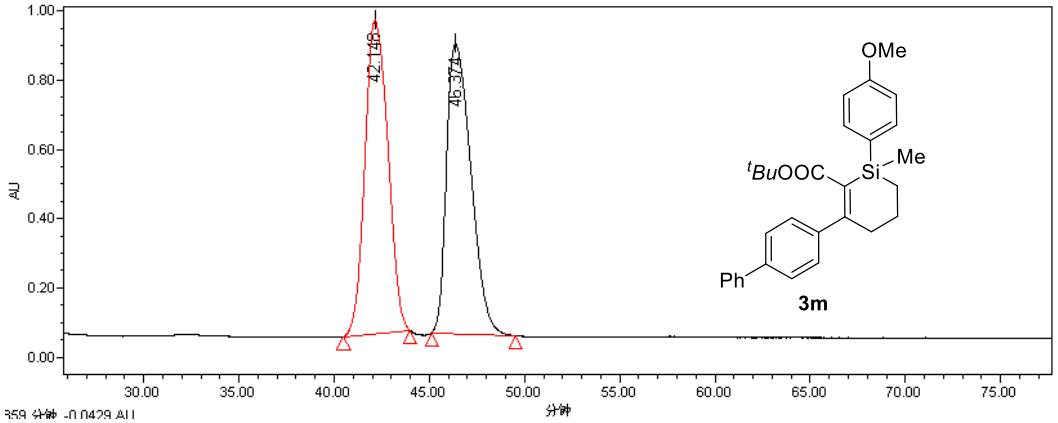
	Time/min	Area	Height	Area%
1	13.989	2231.9	17.3	83.072
2	26.844	545.8	1.4	16.928



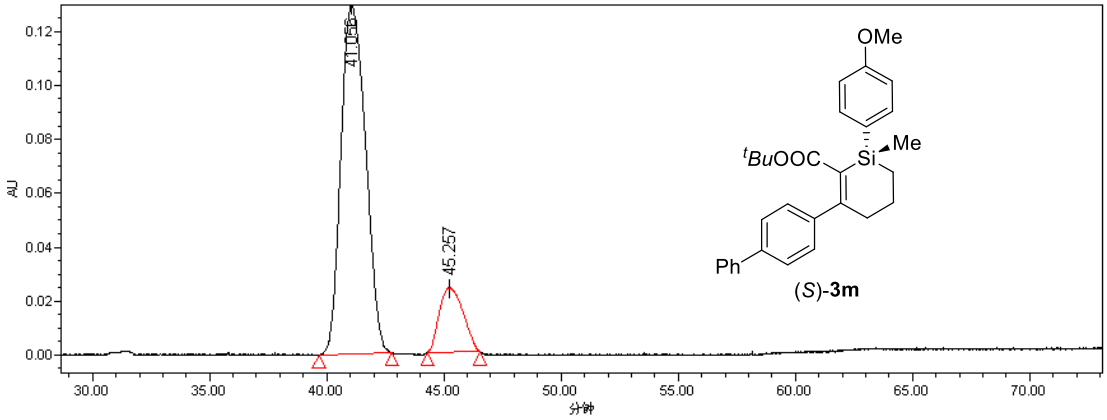
	Time/min	Area	Height	Area%
1	15.914	10525.2	61.5	50.694
2	33.307	10237.1	19.6	49.306



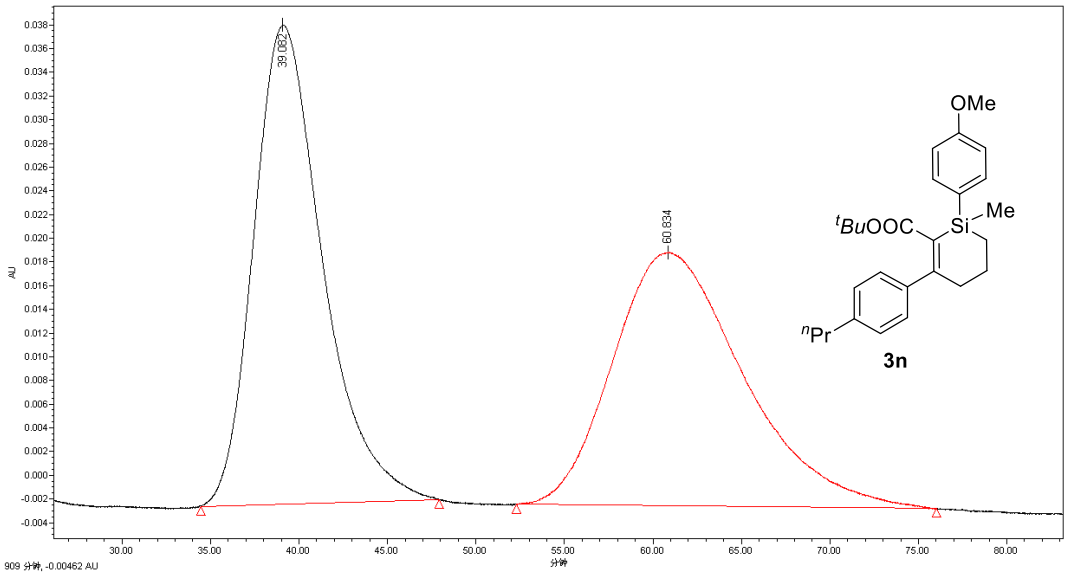
	Time/min	Area	Height	Area%
1	16.134	5601.7	36.8	93.691
2	35.521	377.2	1	6.309



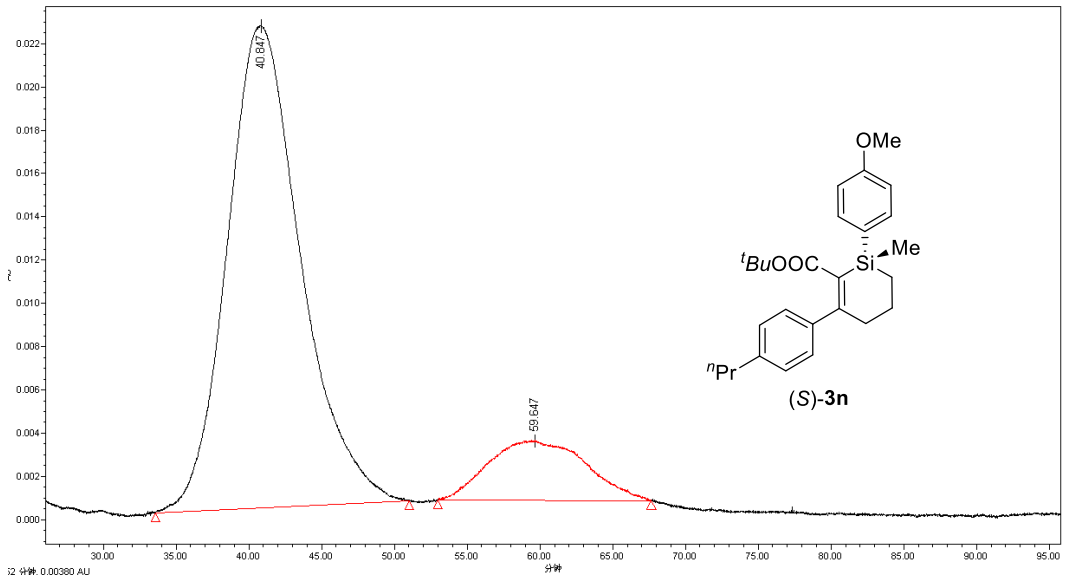
	Time/min	Area	Height	Area%
1	42.148	75976378	905869	50.47
2	46.374	74565047	837239	49.53



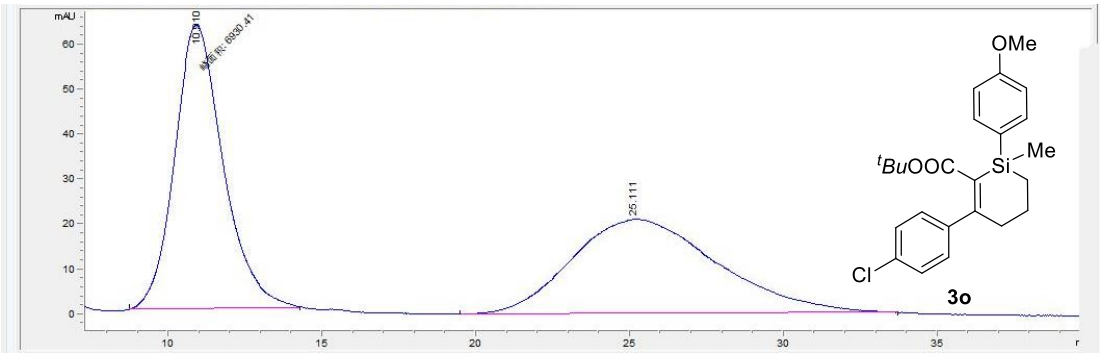
	Time/min	Area	Height	Area%
1	41.056	9461729	129353	84.94
2	45.257	1677055	23642	15.06



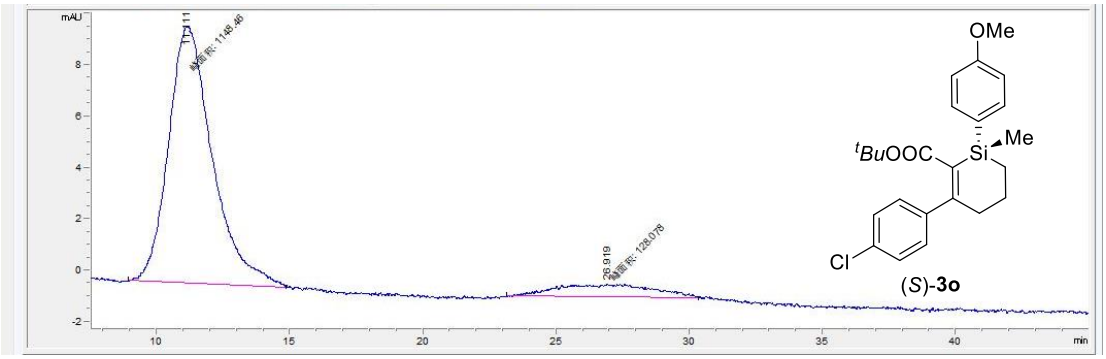
	Time/min	Area	Height	Area%
1	39.082	10929952	40379	49.94
2	60.834	10956851	21384	50.06



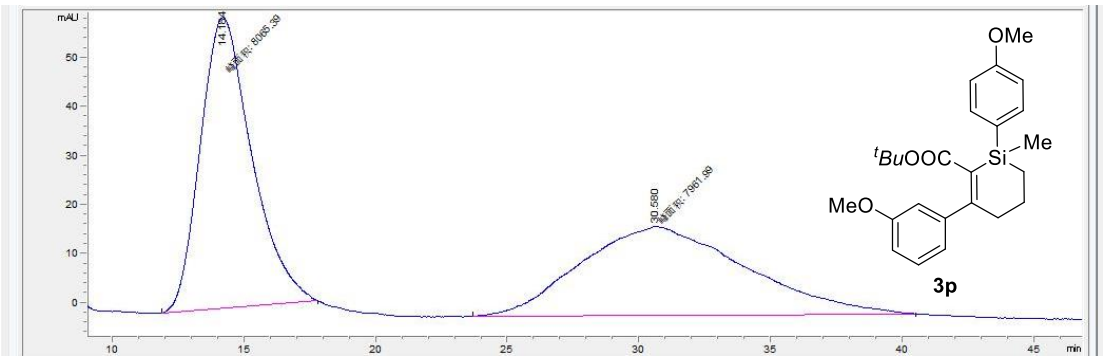
	Time/min	Area	Height	Area%
1	40.847	7830199	22268	85.92
2	59.647	1283308	2758	14.08



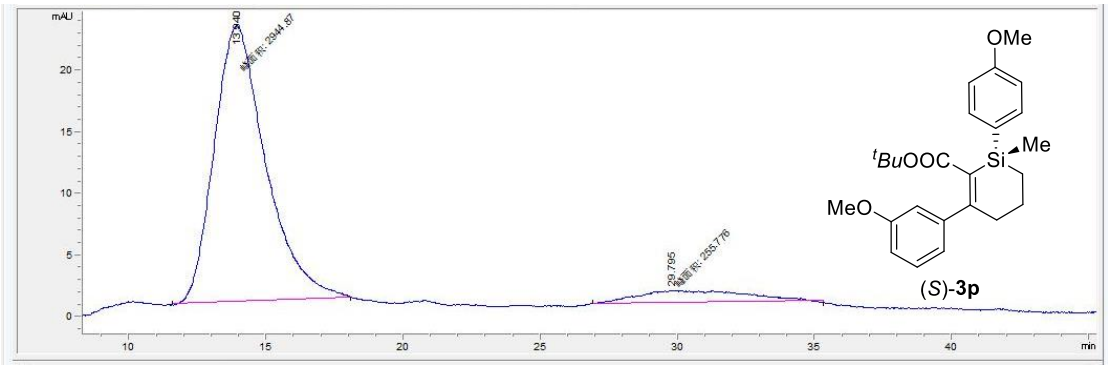
	Time/min	Area	Height	Area%
1	10.91	6930.4	63	50.036
2	25.111	6920.5	21	49.964



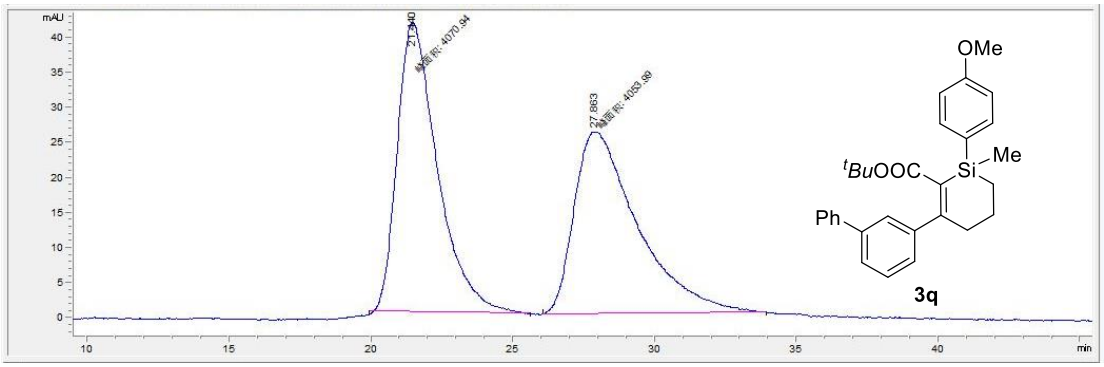
	Time/min	Area	Height	Area%
1	11.111	1148.5	10	89.967
2	26.919	128.1	0.52	10.033



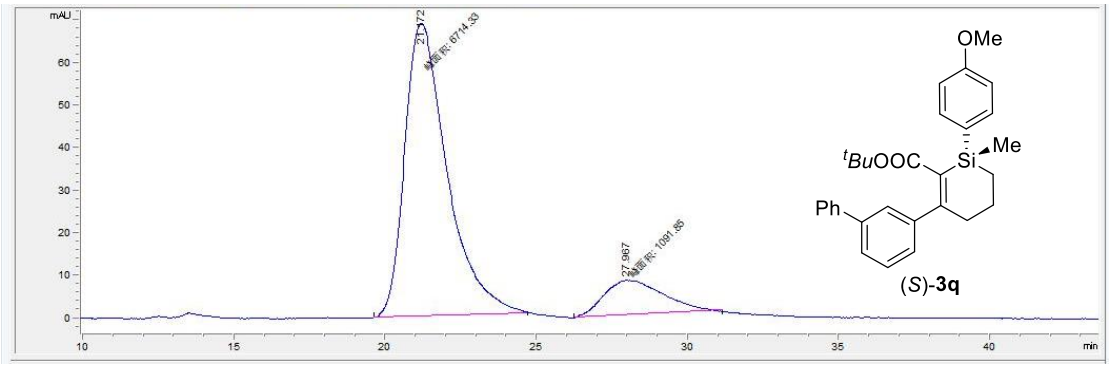
	Time/min	Area	Height	Area%
1	14.184	8065.4	59.4	50.323
2	30.58	7962	18.2	49.677



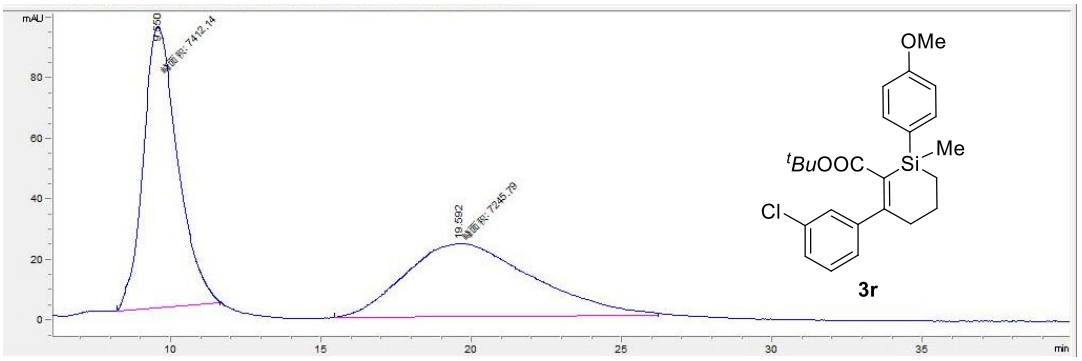
	Time/min	Area	Height	Area%
1	13.94	2944.9	22.5	92.009
2	29.795	255.8	0.95	7.991



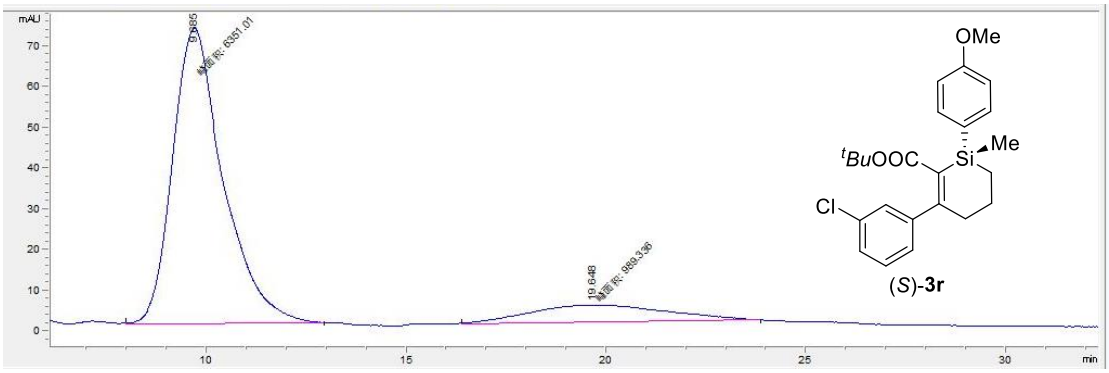
	Time/min	Area	Height	Area%
1	21.44	4070.9	41.2	50.104
2	27.863	4054	26	49.896



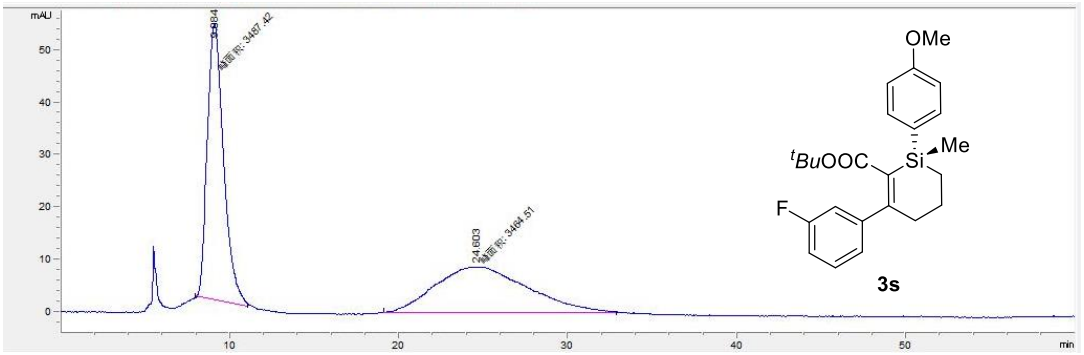
	Time/min	Area	Height	Area%
1	21.172	6714.3	68.8	86.013
2	27.967	1091.8	8.1	13.987



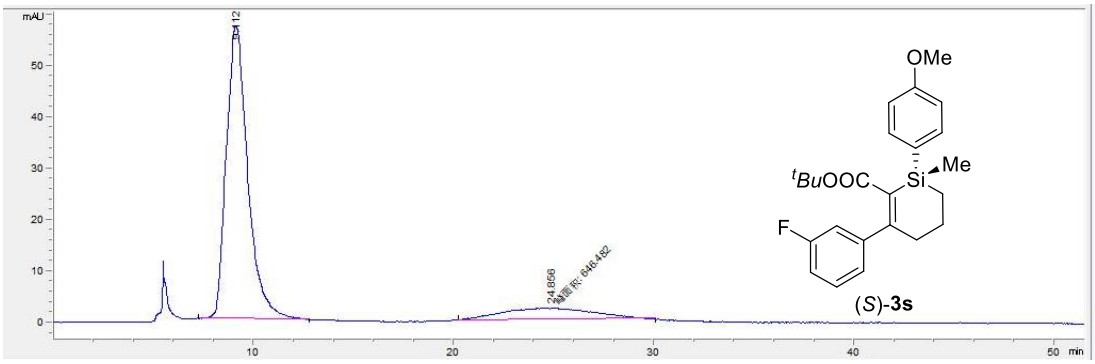
	Time/min	Area	Height	Area%
1	9.55	7412.1	92.6	50.567
2	19.592	7245.8	24.3	49.433



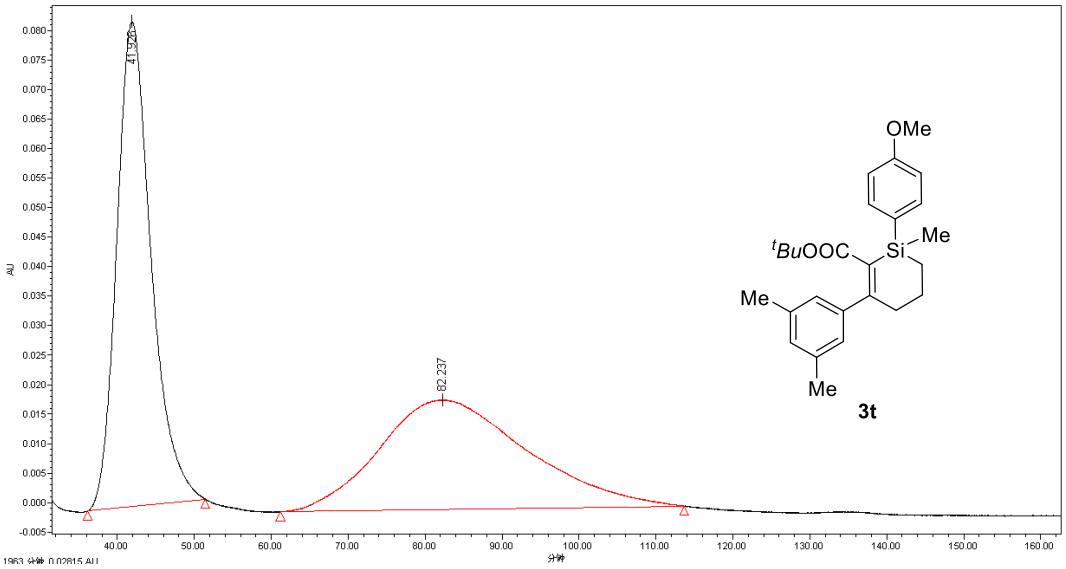
	Time/min	Area	Height	Area%
1	9.685	6351	72.4	86.522
2	19.648	989.3	4.2	13.478



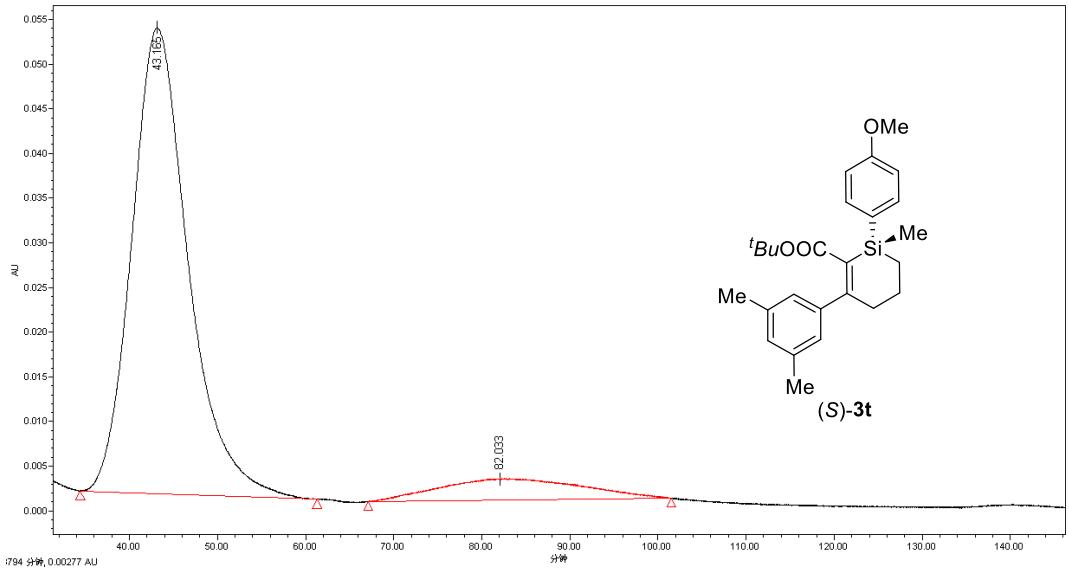
	Time/min	Area	Height	Area%
1	9.084	3487.4	52.5	50.165
2	24.603	3464.5	8.9	49.835



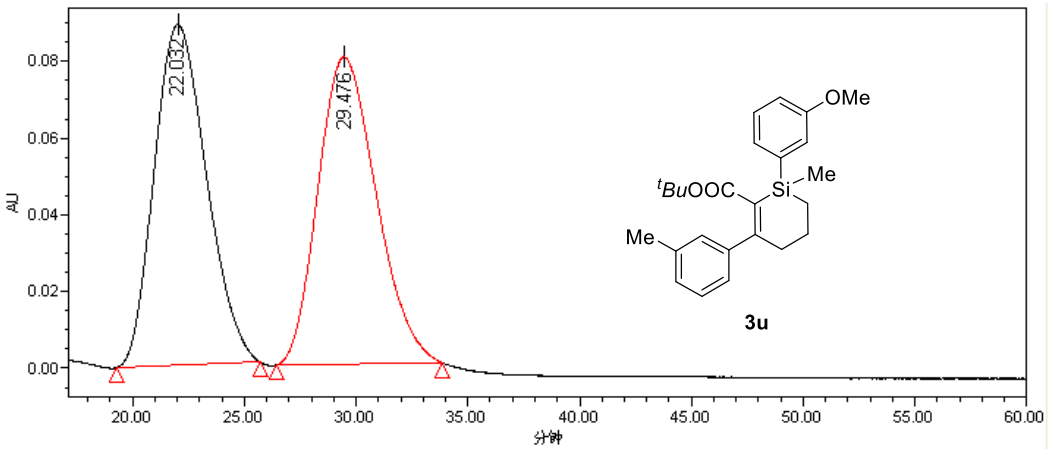
	Time/min	Area	Height	Area%
1	9.112	4255.9	57.1	86.813
2	24.856	646.5	2.1	13.187



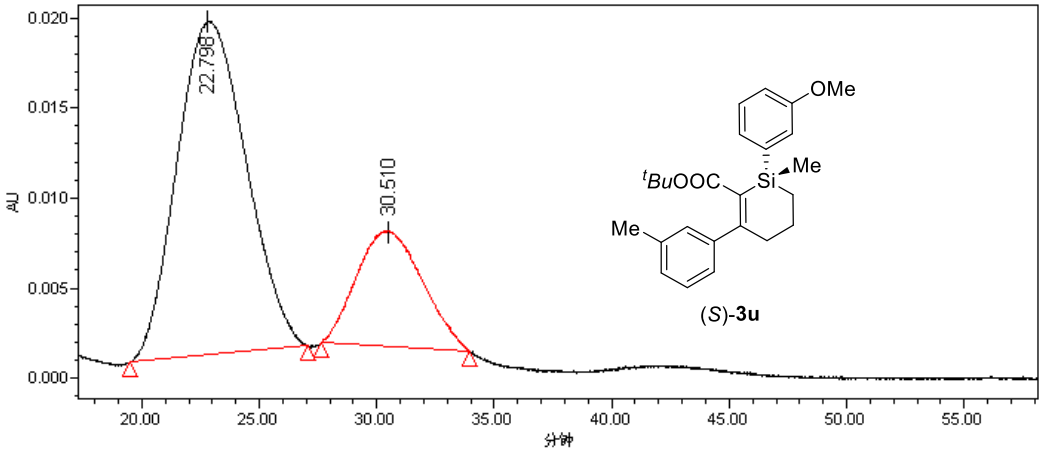
	Time/min	Area	Height	Area%
1	41.926	25630447	82270	50.88
2	82.237	24747592	18608	49.12



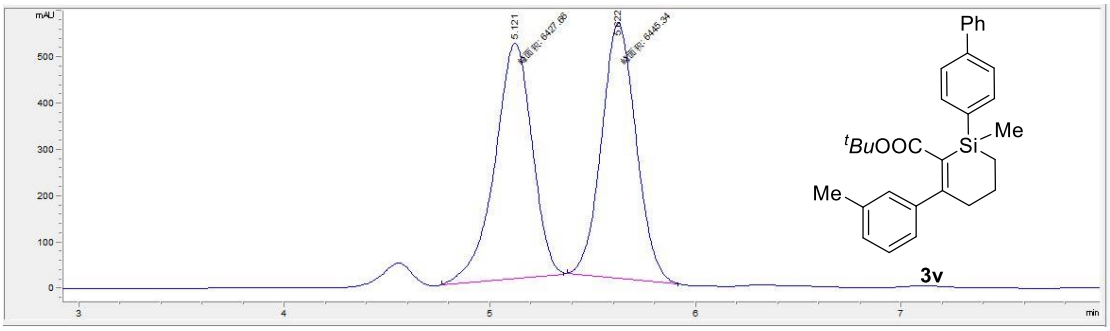
	Time/min	Area	Height	Area%
1	43.165	23231254	52155	89.63
2	82.033	2688343	2384	10.37



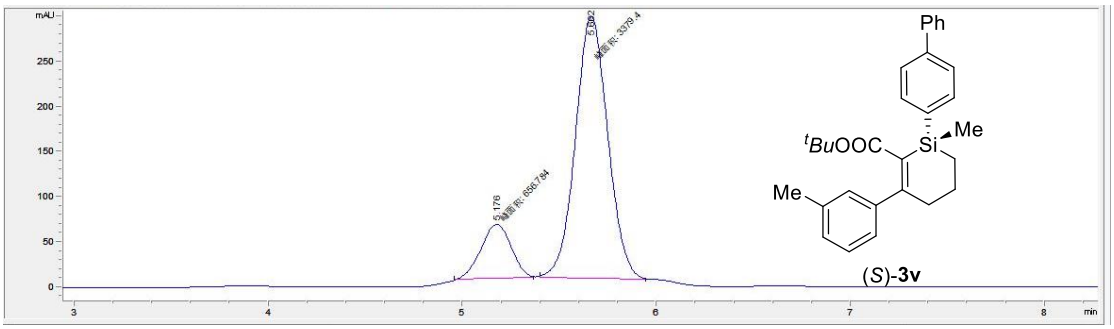
	Time/min	Area	Height	Area%
1	22.032	14425751	88890	49.84
2	29.476	14520231	80056	50.16



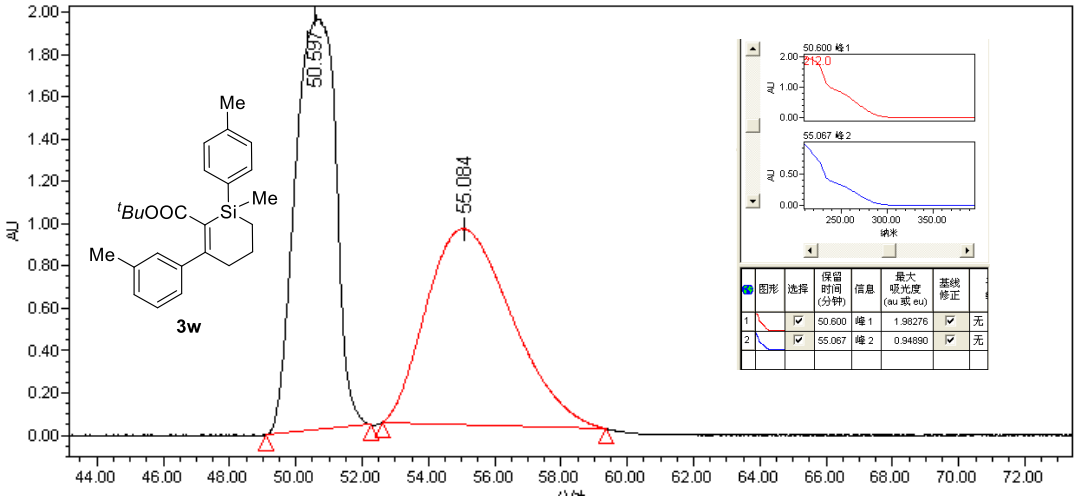
	Time/min	Area	Height	Area%
1	22.798	3787257	18481	75.25
2	30.510	1245375	6381	24.75



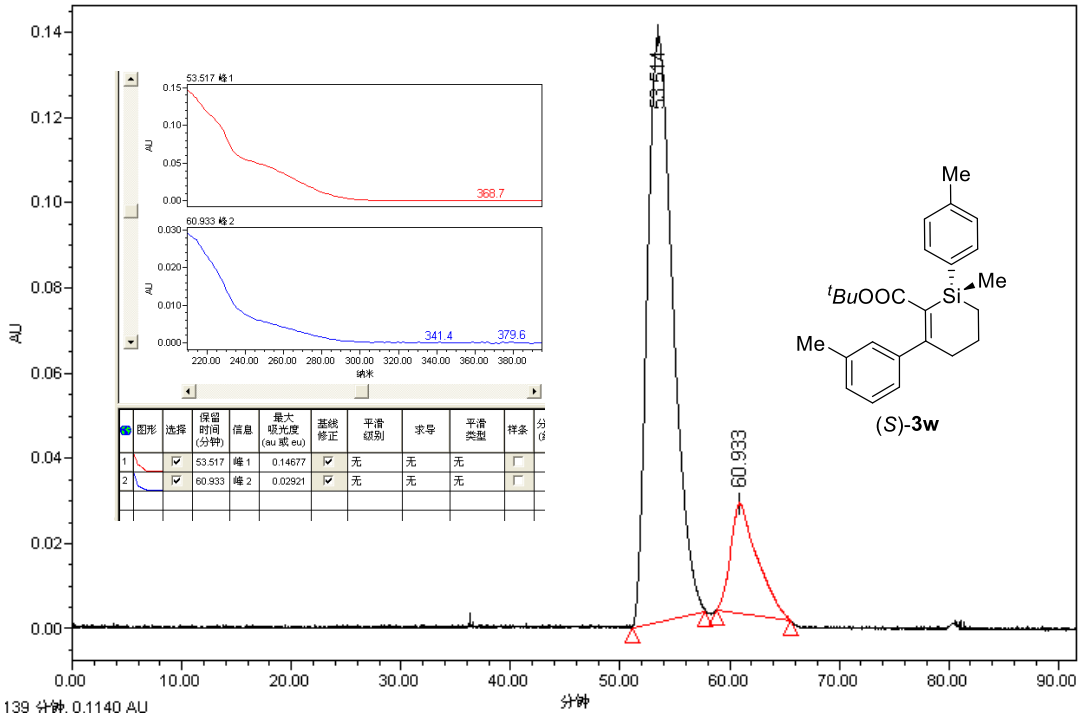
	Time/min	Area	Height	Area%
1	5.121	6427.7	509.8	49.931
2	5.622	6445.3	551.3	50.069



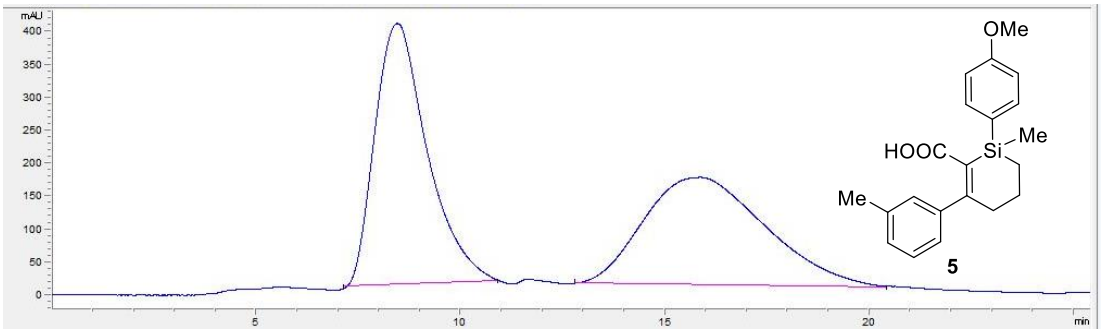
	Time/min	Area	Height	Area%
1	5.176	656.8	60.2	16.272
2	5.662	3379.4	291.4	83.728



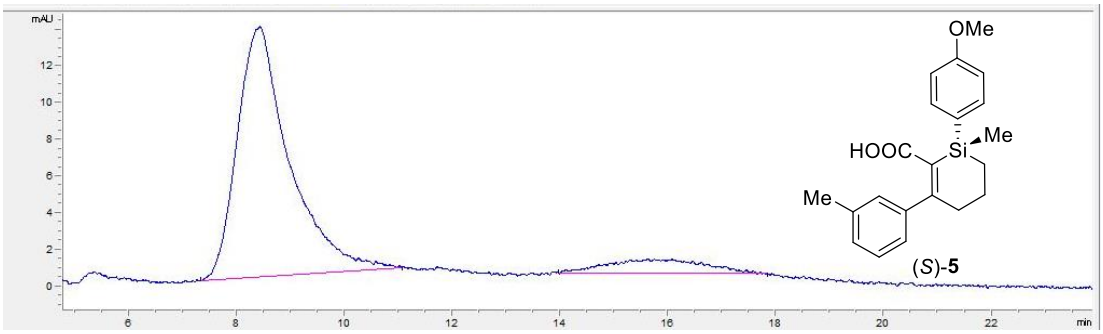
	Time/min	Area	Height	Area%
1	50.597	166515097	1957671	49.91
2	55.084	167112889	926944	50.09



	Time/min	Area	Height	Area%
1	53.514	22397903	137505	83.59
2	60.933	4397811	25834	16.41



	Time/min	Area	Height	Area%
1	8.452	35371.5	397	50.935
2	15.879	34072.7	164	49.065



	Time/min	Area	Height	Area%
1	8.439	911.7	13.7	90.555
2	15.628	95.1	0.78	9.445