Supporting Information for:

Rhodium(I)-Catalyzed Highly Enantioselective Insertion of Carbenoid into Si-H: Efficient Access to Functional Chiral Silanes

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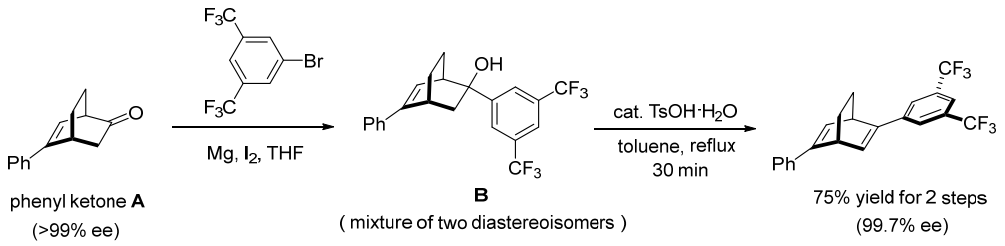
Contents:

1.General

All reactions were carried out in flame-dried glassware with magnetic stirring under an atmosphere of argon. Solvents were dried and distilled by standard procedures. NMR spectra were recorded on a Varian spectrometer (300 MHz, 400 MHz for ^{1}H; 100 MHz, 126 MHz for ^{13}C; and 202 MHz for ^{31}P). Chemical shifts are reported in δ ppm referenced to an internal $SiMe_4$ standard for ^{1}H NMR and chloroform-d (δ 77.16) for ^{13}C NMR. HPLC was performed on a JASCO 2000 instrument by using Daicel column with hexane/2-propanol as the eluent. High Resolution Mass Spectra (HRMS) were recorded on an Orbitrap mass spectrometer with ESI resource. Optical rotation were measured using a Rudolph Autopol VI Automatic Polarimeter. The α-diazoesters[1], α-diazophosphonates[2] and $PhSiDMe_2$[3] were prepared according to the known literature.

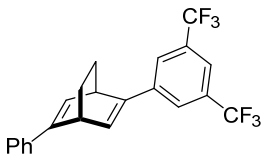
2. Synthesis of C_1-symmetric chiral diene L7 , $[Rh(L7)Cl]_2$ and $[Rh(L7)(OH)]_2$



The phenyl ketone **A** was prepared according to the literature procedures[4]

Under Ar atmosphere, 3.5-bis(trifluoromethyl)-phenyl magnesium bromide (1 M, 20 mL) was added to a solution of phenyl ketone A (1.98 g, 10 mmol) in THF in an ice bath dropwise. The mixture was allowed to warm to room temperature and stirred for another 2 h. The reaction was quenched by water with cooling. The aqueous layer was extracted with EA. The combined organic phases were washed with water, dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give the corresponding crude product **B** as a solid (quant. 4.1 g).

The above obtained crude **B** (200 mg, 0.48 mmol) was dissolved in 20 mL of toluene. To this solution was added *p*-toluene sulfonic acid monohydrate (9.3 mg, 0.048 mmol) and then the resulting mixture was heated to reflux for 30 minutes. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography to give the corresponding C_1-symmetric chiral diene ligand **L7** (143 mg, 75% yield, 99.7% ee).



L7

White solid, 99.7% ee

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (s, 2H), 7.72 (s, 1H), 7.51-7.39 (m, 2H), 7.35 (t, J = 7.4 Hz, 2H), 7.27-7.25 (m, 1H), 6.85 (dd, J = 6.5, 2.0 Hz, 1H), 6.65 (dd, J = 6.5, 2.0 Hz, 1H), 4.31 (d, J = 6.3 Hz, 1H), 4.23 (d, J = 6.3 Hz, 1H), 1.61-1.56 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.9, 144.9, 140.3, 137.8, 133.3, 131.9 (d, J_{C-F} = 34.0 H_Z), 128.74, 128.67, 127.3, 124.9, 124.8, 124.7, 122.5, 120.3, 40.4, 40.0, 25.8, 25.5. EI-MS (*m/z*, %) 394 $[M]^+$; EI-HRMS calcd for $C_{22}H_{16}F_6$ $[M]^+$ 394.1156, found 394.1147.

The synthesis of [Rh(**L7**)Cl]$_2$:

Under Ar atmosphere, **L7** (100 mg, 0.25 mmol) and [Rh(C_2H_4)$_2$Cl]$_2$ (58 mg, 1.2 equiv, 0.3 mmol Rh) were mixed in 15 mL DCM stirred at 40 ^oC for 12 h. The color of the solution was changed from yellow to red. The solvent was evaporated in vacuo, the resulting residue was then purified by silica gel column chromatography to afford the corresponding [Rh(**L7**)Cl]$_2$ (117 mg, 83% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73-7.62 (m, 10H), 7.40 (s, 6H), 4.91 (s, 2H), 4.71 (s, 2H), 3.86 (s, 2H), 3.25 (s, 2H), 1.16 (s, 8H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.7, 137.7, 131.7 (d, J_{C-F} = 32.4 Hz), 128.6, 128.2, 127.2, 126.5, 124.5, 122.3, 120.6, 120.2, 67.3, 60.7, 45.9, 45.09, 45.01, 42.8, 42.7, 25.6, 25.2.

The synthesis of [Rh(**L7**)(OH)]$_2$:

Under Ar atmosphere, [Rh(**L7**)Cl]$_2$ (80 mg, 0.15 mmol Rh) was dissolved in 2 mL acetone and keep stirring. 1.5 mL KOH (1M) was added into the solution and the resulting mixture was stirred in room temperature for another 2 hours. The red solid precipated from the system was filtered, washed three times by water (3*1 mL) and dried to afford the corresponding [Rh(**L7**)(OH)]$_2$ (43 mg, 56% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.71 – 7.69 (m, 4H), 7.57 (s, 1H), 7.50 – 7.39 (m, 8H), 7.34 – 7.23 (m, 2H), 4.86 (s, 2H), 4.47 (s, 2H), 3.60 (d, J = 5.2 Hz, 2H), 2.79 (s, 2H), 2.17 (s, 1H), 1.17 (s, 8H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.3, 139.5, 131.8 (q, J_{C-F} = 32.8 Hz), 129.4, 128.9, 127.2, 125.6, 125.4, 124.4, 122.3, 119.7, 60.5, 60.4, 55.0, 54.9, 42.5, 42.4, 42.1, 42.0, 40.6, 40.5, 25.5, 24.7.

3. General procedure for Rh(I)-Catalyzed asymmetric Si-H insertion of α-diazoesters

Under Ar atmosphere, a solution of [Rh(C_2H_4)$_2$Cl]$_2$ (0.6 mg, 0.0015mmol, 1.5 mol%), **L7 (**1.3 mg, 0.0033 mmol, 3.3 mol%**)** in 1mL of DCM was stirred at room temperature for 30 min. The color of the solution was changed from yellow to red. The α-diazoester **1** (0.1 mmol) and trisubstituted silanes (0.15 mmol) dissolved in another 1mL of DCM was introduced into the system subsequently. The resulting mixture was stirred at room temperature for 6 hours until the diazo compound disappeared. The solvent was evaporated in vacuo, the resulting residue was then purified by silica gel column chromatography to afford the corresponding insertion product **3**.

4. General procedure for Rh(I)-Catalyzed asymmetric Si-H insertion of α-diazophosphonates

Under Ar atmosphere, [Rh(**L7**)$_2$Cl]$_2$ (1.8 mg, 0.0015mmol, 1.5 mol%) was solute in 1 mL of DCM keep stirring at room temperature. The α-diazophosphonates **4** (0.1 mmol) and trisubstituted silanes (0.15 mmol) dissolved in another 1 mL of DCM was introduced into the system subsequently. The resulting mixture was stirred at 40 ^oC for 12 hours until the diazo compound disappeared. The solvent was evaporated in vacuo, the resulting residue was then purified by silica gel column chromatography to afford the corresponding insertion product **5**.

References:

(1) a). M. Hu, C. Ni, J. Hu, *J. Am. Chem. Soc.* **2012**, *134*, 15257-15260. b). Q.-H. Deng, H.-W. Xu, A. W. Yuen, X.-J. Xu, C.-M. Che, *Org. Lett.* **2008**, *10*, 1529-1532.

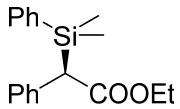
(2) a). D. Seyferth, R. S. Marmor, P. Hilbert, *J. Org. Chem.* **1971**, *36*, 1379-1385. b). H. Tomioka, K. Hirai, Y. Tanimoto, *J. Chem. Soc., Perkin Trans.* **1994**, *2*, 633-641. c). N. Gurudata, C. Benezra, H. Cohen, *Can. J. Chem.* **1973**, *51*, 1142-1147.

(3) M. Yan, T. Jin, Y. Ishikawa, T. Minato, T. Fujita, L.-Y. Chen, M. Bao, N. Asao, M.-W. Chen, Y. Yamamoto, *J. Am. Chem. Soc.* **2012**, *134*, 17536-17542.

(4) S. Abele, R. Inauen, D. Spielvogel, C. Moessner, *J. Org. Chem.* **2012**, *77*, 4765-4773.

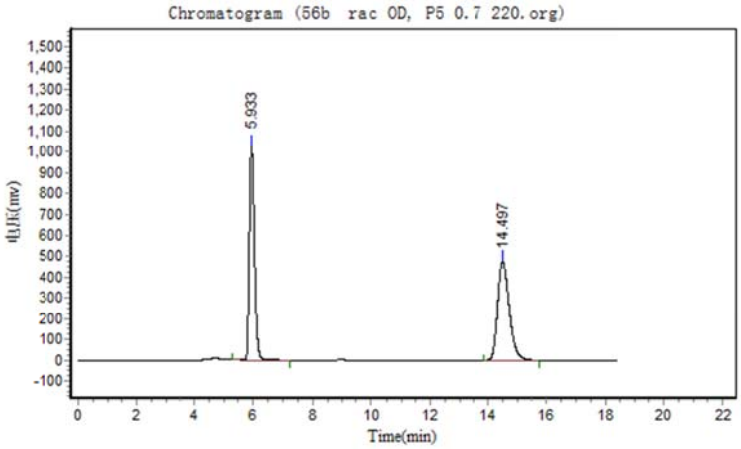
5. Characterization data and HPLC chromatogram of Si-H insertion products 3 and 5

Ethyl (R)-2-(dimethyl(phenyl)silyl)-2-phenylacetate (3b)



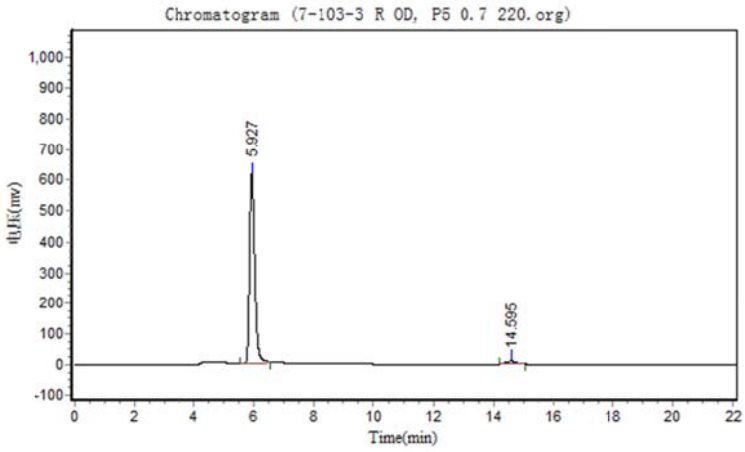
colorless oil, 84%, 94% ee;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 - 7.30 (m, 5H), 7.27 – 7.15 (m, 5H), 4.11 – 3.89 (q, *J* = 7.1 Hz, 2H), 3.60 (s, 1H), 1.12 (t, *J* = 7.1 Hz, 3H), 0.37 (s, 3H), 0.32 (s, 3H); $[\alpha]_D^{25}$ = +26.9 (***c*** 1.9, $CHCl_3$). [lit: $[\alpha]_D^{20}$ = +29.0 (*c* 1.9, $CHCl_3$) for (*R*) with 98% ee.] (*Angew. Chem. Int. Ed.* **2008**, *47*, 8496.)

HPLC: Chiralcel OD-H column (250 mm); detected at 230 nm; hexane/*i*-propanol = 97/3; flow = 0.7 mL/min; Retention time: 6.0 min (major), 13.3 min.



Results

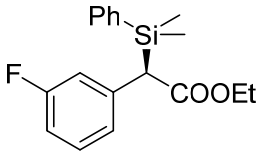
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.933	1021227.188	12189644.000	48.1551
2		14.497	476497.969	13123660.000	51.8449
Total			1497725.156	25313304.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.927	615209.813	7337626.000	97.0563
2		14.595	9259.204	222552.000	2.9437
Total			624469.017	7560178.000	100.0000

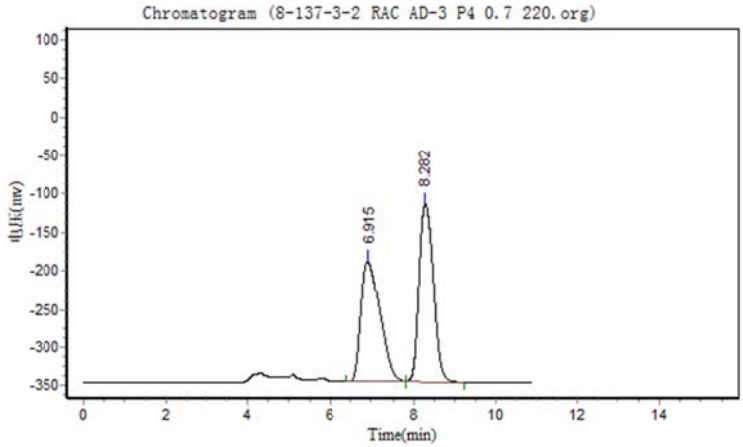
Ethyl (R)-2-(dimethyl(phenyl)silyl)-2-(3-fluorophenyl)acetate (3e)



colorless oil, 75%, 95% ee;

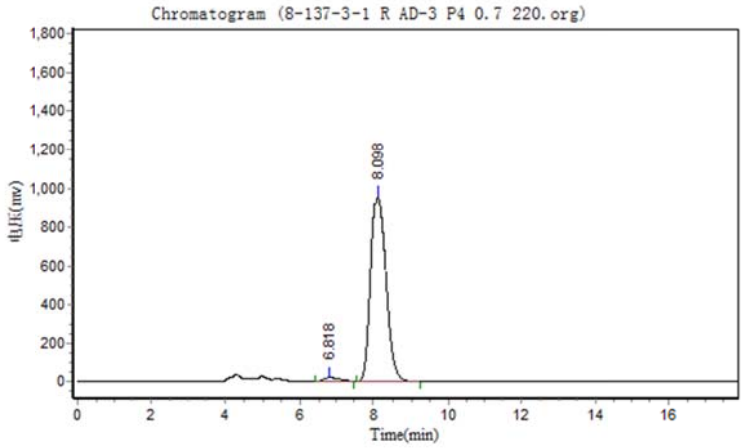
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.40-7.31 (m, 5H), 7.16 (dt, *J* = 7.8, 6.3 Hz, 1H), 7.04 (dt, *J* = 7.8, 2.6 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.85 (td, *J*= 8.4, 2.6 Hz, 1H), 4.02 (qd, *J* = 7.1, 2.1 Hz, 2H), 3.60 (s, 1H), 1.12 (t, *J* = 7.1 Hz, 3H), 0.38 (s, 3H), 0.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.3, 162.7 (d, $J_{C\text{-}F}$ = 244.4 Hz), 138.8 (d, $J_{C\text{-}F}$ = 8.0 Hz), 135.2, 134.1, 129.9, 129.3 (d, $J_{C\text{-}F}$ = 8.5 Hz), 127.9, 124.2 (d, $J_{C\text{-}F}$ = 2.5 Hz), 115.3 (d, $J_{C\text{-}F}$ = 21.4 Hz), 112.6 (d, $J_{C\text{-}F}$ = 21.4 Hz), 60.5, 46.2, 14.3, -4.1, -4.5. ESI-MS (*m/z*, %) 339 $[M+Na]^+$; ESI-HRMS calcd for $C_{18}H_{21}O_2FNaSi$ $[M+Na]^+$ 339.1187, found 339.1179. $[\alpha]_D^{25}$ = +24.5 (*c* 0.6, $CHCl_3$).

HPLC: Chiralpak AD-3 column (250 mm); detected at 220 nm; hexane/*i*-propanol = 99/1; flow = 0.7 mL/min; Retention time: 6.9 min, 8.2 min (major).



Results

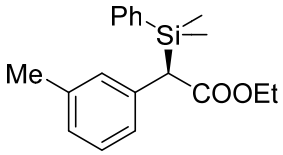
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.915	156323.203	4885475.500	46.6960
2		8.282	230471.750	5576827.000	53.3040
Total			386794.953	10462302.500	100.0000



Results

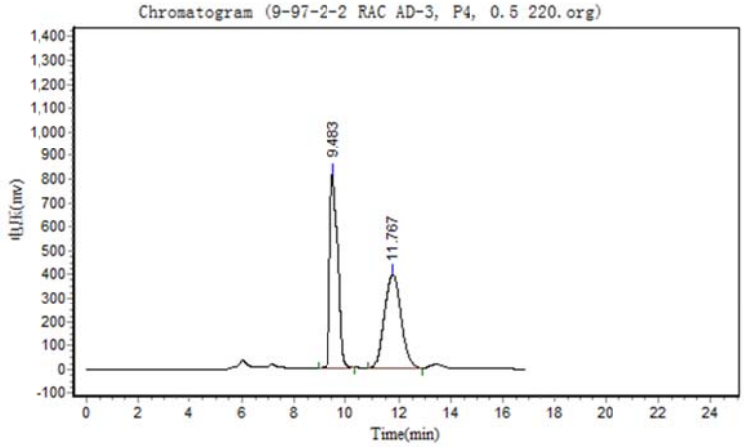
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.818	18142.711	569150.000	2.1430
2		8.098	949719.750	25989410.000	97.8570
Total			967862.461	26558560.000	100.0000

Ethyl (R)-2-(dimethyl(phenyl)silyl)-2-(m-tolyl)acetate (3f)



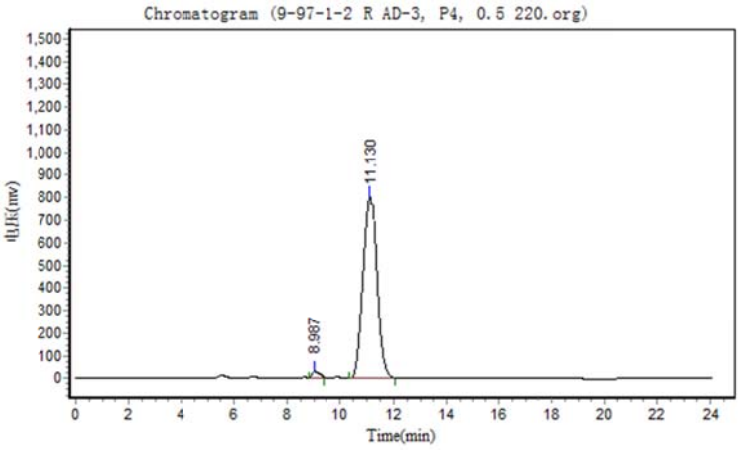
colorless oil, 80%, 96% ee;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.31 (m, 5H), 7.15 – 6.96 (m, 4H), 4.00 (dq, *J* = 7.1, 1.2 Hz, 2H), 3.56 (s, 1H), 2.27 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H), 0.37 (s, 3H), 0.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.8, 137.6, 136.0, 135.9, 134.2, 129.7, 129.3, 128.0, 127.7, 126.5, 125.6, 60.3, 46.1, 21.6, 14.3, -3.9, -4.5. ESI-MS (*m/z*, %) 335 $[M+Na]^+$; ESI-HRMS calcd for $C_{19}H_{24}O_2NaSi$ $[M+Na]^+$ 335.1438, found 335.1428. $[\alpha]_D^{25}$ = +18.5 (*c* 0.6, $CHCl_3$).

HPLC: Chiralpak AD-3 column (250 mm); detected at 220 nm; hexane/*i*-propanol = 99/1; flow = 0.5 mL/min; Retention time: 9.5 min, 11.8 min (major).



Results

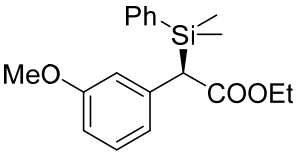
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.483	811348.375	17485344.000	49.8871
2		11.767	397203.250	17564476.000	50.1129
Total			1208551.625	35049820.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.987	28240.766	528750.313	1.8735
2		11.130	801409.438	27694066.000	98.1265
Total			829650.203	28222816.313	100.0000

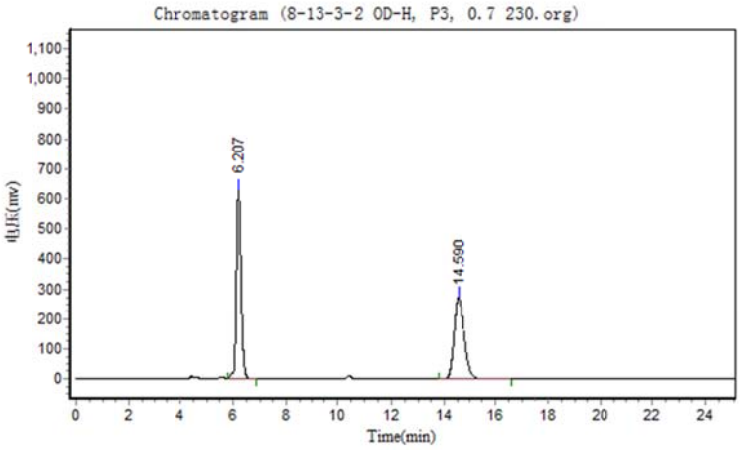
Ethyl (R)-2-(dimethyl(phenyl)silyl)-2-(3-methoxyphenyl)acetate (3g)



colorless oil, 75%, 96% ee;

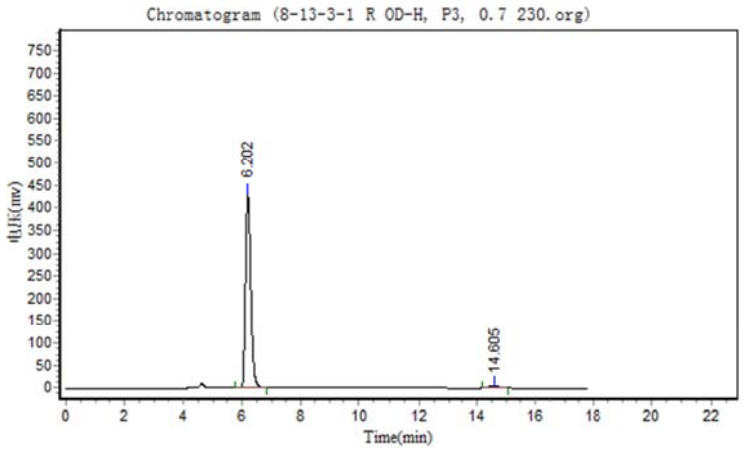
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 – 7.32 (m, 5H), 7.15 (t, *J* = 7.9 Hz, 1H), 6.89 – 6.64 (m, 3H), 4.03 (m, *J* = 7.1, 2.0 Hz, 2H), 3.71 (s, 3H), 3.60 (s, 1H), 1.15 (t, *J* = 7.1 Hz, 3H), 0.40 (s, 3H), 0.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 159.4, 137.7, 135.7, 134.3, 129.7, 129.0, 127.8, 121.0, 113.7, 111.8, 60.4, 55.1, 46.3, 14.3, -3.9, -4.4. ESI-MS (*m/z*, %) 351 $[M+Na]^+$; ESI-HRMS calcd for $C_{19}H_{24}O_3NaSi$ $[M+Na]^+$ 351.1387, found 351.1379. $[\alpha]_D^{25}$ = +21.7 (*c* 0.4, $CHCl_3$).

HPLC: Chiralcel OD-H column (250 mm); detected at 230 nm; hexane/*i*-propanol = 95/5; flow = 0.7 mL/min; Retention time: 6.2 min (major), 14.6 min.



Results

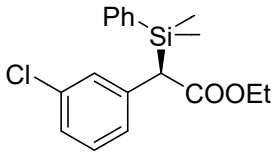
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.207	627564.375	7936988.000	51.0704
2		14.590	272911.500	7604279.000	48.9296
Total			900475.875	15541267.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.202	427099.406	5341770.500	97.8837
2		14.605	4613.881	115494.648	2.1163
Total			431713.287	5457265.148	100.0000

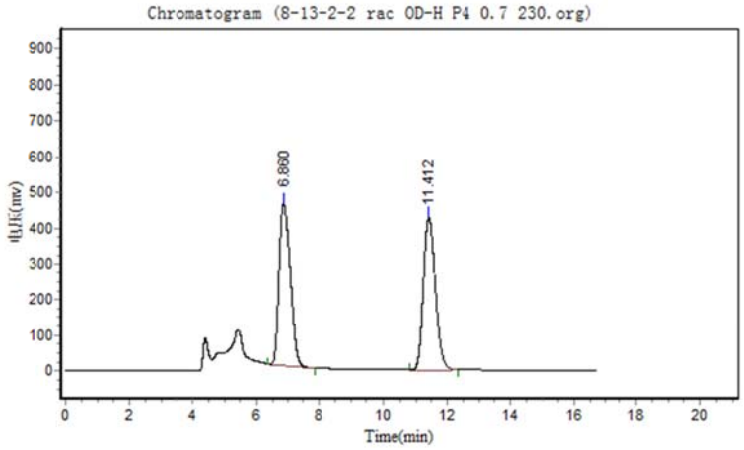
Ethyl (R)-2-(3-chlorophenyl)-2-(dimethyl(phenyl)silyl)acetate (3h)



Colorless oil, 90%, 96% ee;

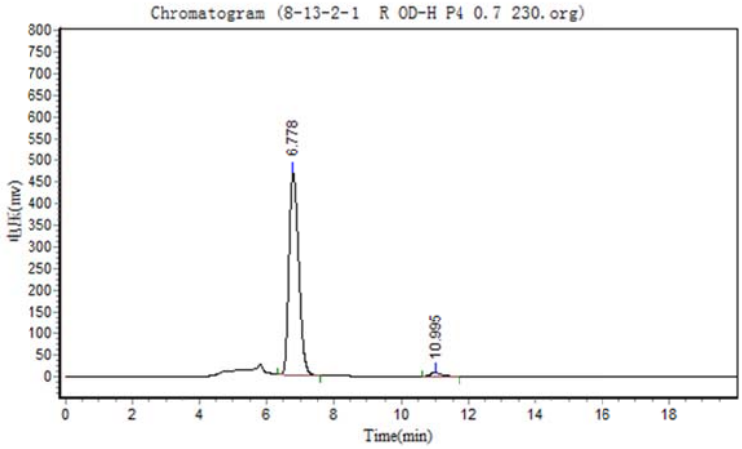
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.39 – 7.24 (m, 5H), 7.14 – 6.98 (m, 4H), 4.02 (q, *J* = 7.1 Hz, 2H), 3.56 (s, 1H), 1.13 (t, *J* = 7.1 Hz, 3H), 0.38 (s, 3H), 0.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.3, 138.3, 135.1, 134.2, 133.9, 129.9, 129.2, 128.5, 127.9, 126.7, 125.9, 60.5, 46.0, 14.3, -4.1, -4.5. ESI-MS (*m/z*, %) 355 $[M+Na]^+$; ESI-HRMS calcd for $C_{18}H_{21}O_2ClNaSi$ $[M+Na]^+$ 355.0892, found 355.0889. $[\alpha]_D^{25}$ = +21.8 (*c* 1.2, $CHCl_3$).

HPLC: Chiralcel OD-H column (250 mm); detected at 230 nm; hexane/*i*-propanol = 99/1; flow = 0.7 mL/min; Retention time: 6.8 min (major), 11.4 min.



Results

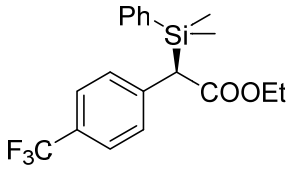
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.860	452265.781	11189010.000	49.4349
2		11.412	427738.438	11444824.000	50.5651
Total			880004.219	22633834.000	100.0000



Results

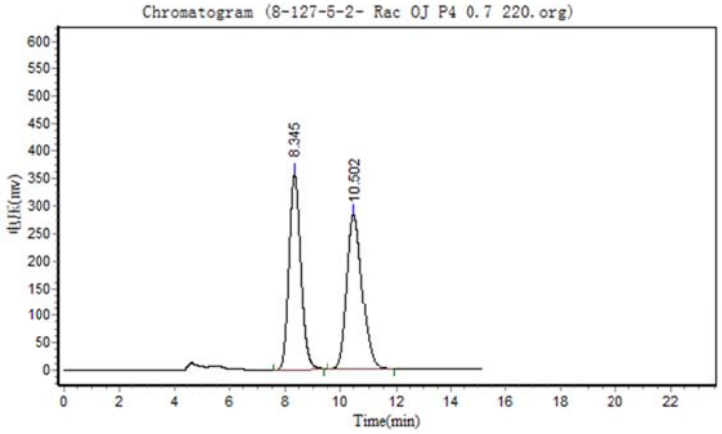
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.778	464011.313	9291710.000	97.9187
2		10.995	8974.988	197500.547	2.0813
Total			472986.301	9489210.547	100.0000

Ethyl (R)-2-(dimethyl(phenyl)silyl)-2-(4-(trifluoromethyl)phenyl)acetate (3i)



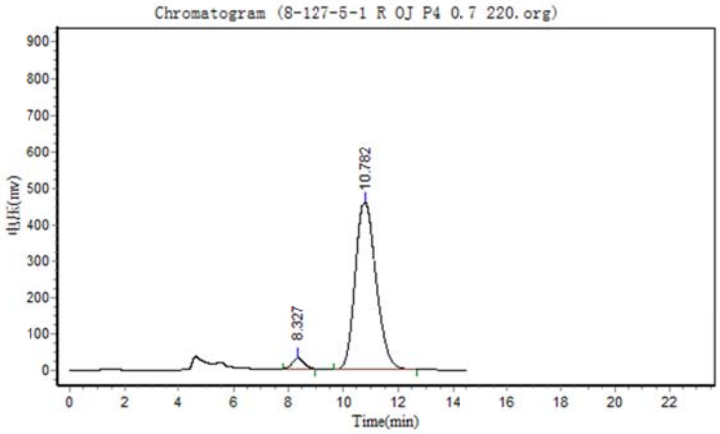
Colorless oil, 72%, 93% ee;
^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.48 – 7.26 (m, 9H), 4.04 (dq, *J* = 7.2, 3.6 Hz, 2H), 3.67 (s, 1H), 1.14 (t, *J* = 7.1 Hz, 3H), 0.37 (s, 3H), 0.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.1, 140.6, 134.9, 134.2, 130.0, 128.6, 128.1, 127.9, 125.0 (d, $J_{C\text{-}F}$ = 3.7 Hz), 60.6, 46.5, 14.3, -4.1, -4.5. ESI-MS (*m/z*, %) 389 $[M+Na]^+$; ESI-HRMS calcd for $C_{19}H_{21}O_2F_3NaSi$ $[M+Na]^+$ 389.1155, found 389.1163. $[\alpha]_D^{25}$ = +22.0 (*c* 1.1, $CHCl_3$).

HPLC: Chiralcel OJ-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 99/1; flow = 0.7 mL/min; Retention time: 8.3 min, 10.5 min (major).



Results

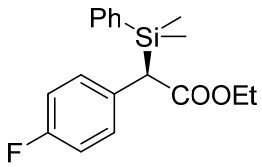
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.345	354052.594	10433139.000	49.1978
2		10.502	281238.094	10773387.000	50.8022
Total			635290.688	21206526.000	100.0000



Results

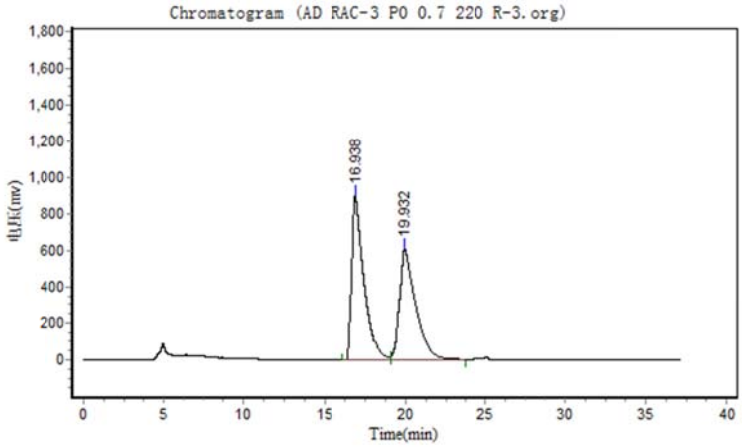
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.327	29563.189	870847.625	3.6309
2		10.782	456326.625	23113480.000	96.3691
Total			485889.814	23984327.625	100.0000

Ethyl (R)-2-(dimethyl(phenyl)silyl)-2-(4-fluorophenyl)acetate (3j)



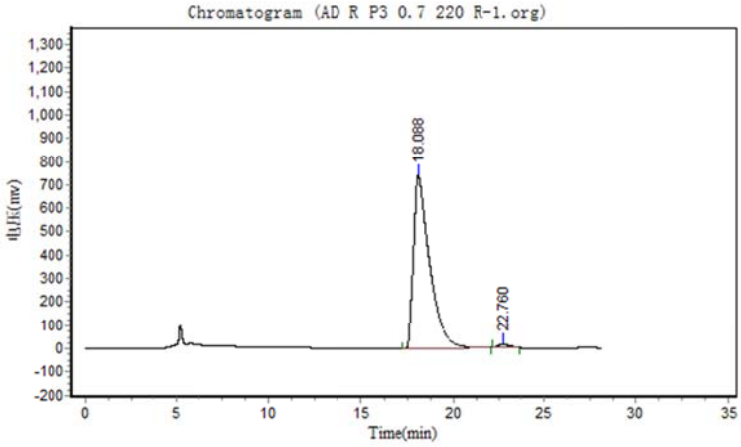
Colorless oil, 85%, 97% ee;
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41 – 7.33 (m, 5H), 7.19 (dd, *J* = 8.6, 5.5 Hz, 2H), 6.93 (t, *J* = 8.6 Hz, 2H), 4.05 (dq, *J* = 7.2, 3.6 Hz, 2H), 3.61 (s, 1H), 1.14 (q, *J* = 7.5 Hz, 3H), 0.38 (s, 3H), 0.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.8, 161.3 (d, *J* = 244.4 Hz), 135.4, 134.2, 131.9, 129.86 (d, *J* = 7.6 Hz), 128.3 (d, *J* = 49.1 Hz), 127.8, 114.9 (d, *J* = 21.4 Hz), 60.5, 45.4, 14.3, -4.1, -4.4. ESI-MS (*m/z*, %) 339 $[M+Na]^+$; ESI-HRMS calcd for $C_{18}H_{21}O_2FNaSi$ $[M+Na]^+$ 339.1187, found 339.1187. $[\alpha]_D^{25}$ = +29.2 (*c* 0.2, $CHCl_3$).

HPLC: Chiralpak AD-H column (250 mm); detected at 230 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 16.9 min (major), 19.9 min.



Results

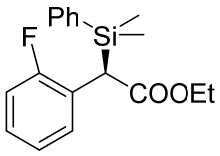
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.938	894887.063	46267676.000	52.4514
2		19.932	605280.438	41942860.000	47.5486
Total			1500167.500	88210536.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.088	738978.438	45026056.000	98.5941
2		22.760	15004.716	642055.750	1.4059
Total			753983.153	45668111.750	100.0000

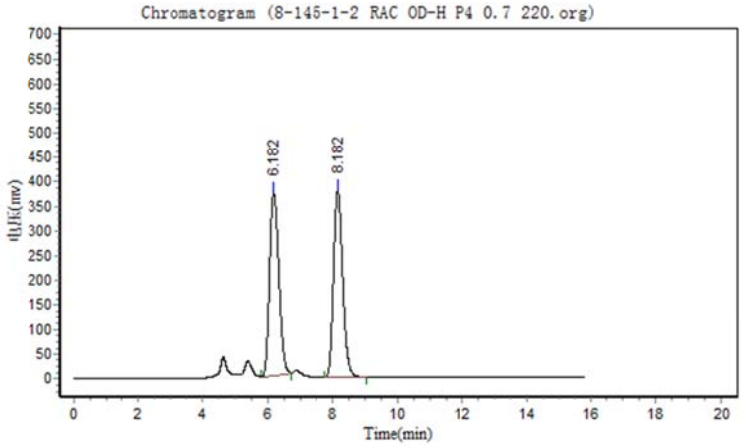
Ethyl (R)-2-(dimethyl(phenyl)silyl)-2-(2-fluorophenyl)acetate (3k)



Colorless oil, 68%, 91% ee;

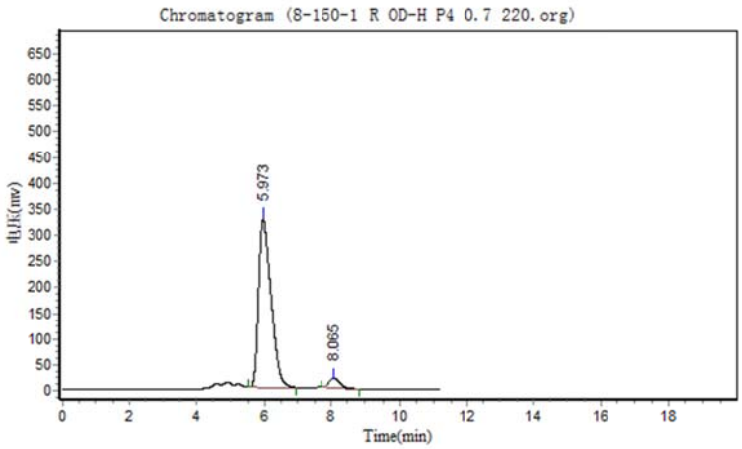
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (td, J = 7.5, 1.4 Hz, 1H), 7.45 – 7.31 (m, 5H), 7.14 – 7.04 (m, 2H), 7.00 – 6.90 (m, 1H), 4.09 (s, 3H), (dq, J = 7.1, 1.2 Hz, 2H), 1.13 (t, J = 7.1 Hz, 3H), 0.39 (s, 3H), 0.37 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.2, 159.5 (d, $J_{C\text{-}F}$ = 244.4 Hz), 135.5, 134.1, 130.3 (d, $J_{C\text{-}F}$ = 2.8 Hz), 129.8, 127.8, 127.1 (d, $J_{C\text{-}F}$ = 8.3 Hz), 123.8 (d, $J_{C\text{-}F}$ = 3.8 Hz), 123.7, 114.9 (d, $J_{C\text{-}F}$ = 23.9 Hz) , 60.5, 36.6, 14.3, -3.7, -4.5. ESI-MS (*m/z*, %) 339 $[M+Na]^+$; ESI-HRMS calcd for $C_{18}H_{21}O_2FNaSi$ $[M+Na]^+$ 339.1187, found 339.1179. $[\alpha]_D^{25}$ = +29.4 (*c* 0.4, $CHCl_3$).

HPLC: Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 99/1; flow = 0.7 mL/min; Retention time: 6.1 min (major), 8.1 min.



Results

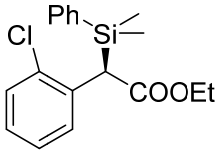
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.182	373658.250	7516313.000	50.1194
2		8.182	378560.250	7480509.500	49.8806
Total			752218.500	14996822.500	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.973	323646.906	8296205.500	95.2763
2		8.065	17870.402	411320.500	4.7237
Total			341517.309	8707526.000	100.0000

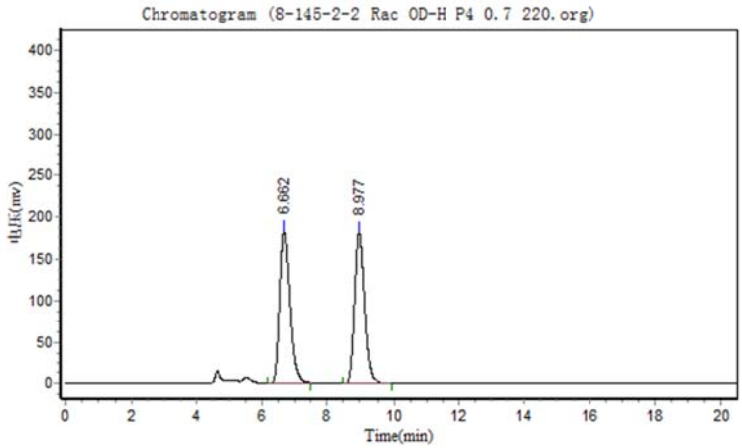
Ethyl (R)-2-(2-chlorophenyl)-2-(dimethyl(phenyl)silyl)acetate (3l)



Colorless oil, 68%, 93% ee;

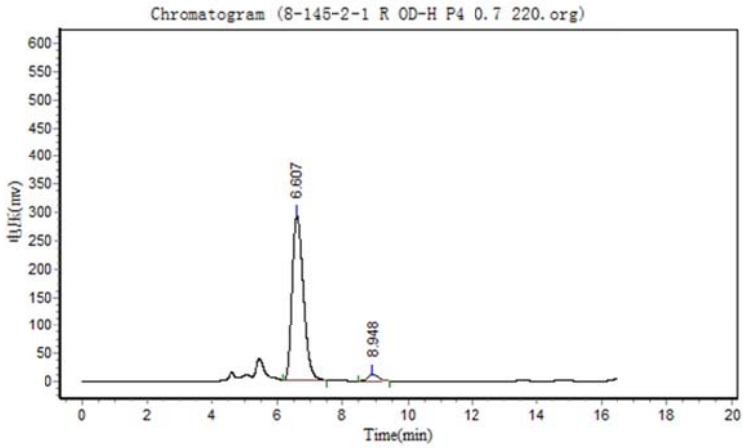
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.8 Hz, 1H), 7.49 – 7.24 (m, 6H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 4.41 (s, 1H), 4.02 (q, *J* = 7.1 Hz, 2H), 1.13 (t, *J* = 7.1, 3H), 0.37 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.2, 135.5, 134.3, 134.2, 133.0, 130.6, 129.8, 129.3, 127.8, 126.9, 126.5, 60.6, 40.9, 14.3, -3.3, -4.5. ESI-MS (*m/z*, %) 332 $[M+Na]^+$; ESI-HRMS calcd for $C_{18}H_{21}O_2ClNaSi$ $[M+Na]^+$ 355.0892, found 355.0888. $[\alpha]_D^{25}$ = +85.5 (*c* 0.6, $CHCl_3$).

HPLC: Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 99/1; flow = 0.7 mL/min; Retention time: 6.6 min (major), 8.9 min.



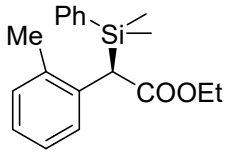
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.662	181433.656	3863769.500	50.1103
2		8.977	180940.000	3846763.000	49.8897
Total			362373.656	7710532.500	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.607	290709.375	6963540.500	96.5648
2		8.948	11320.113	247719.391	3.4352
Total			302029.488	7211259.891	100.0000

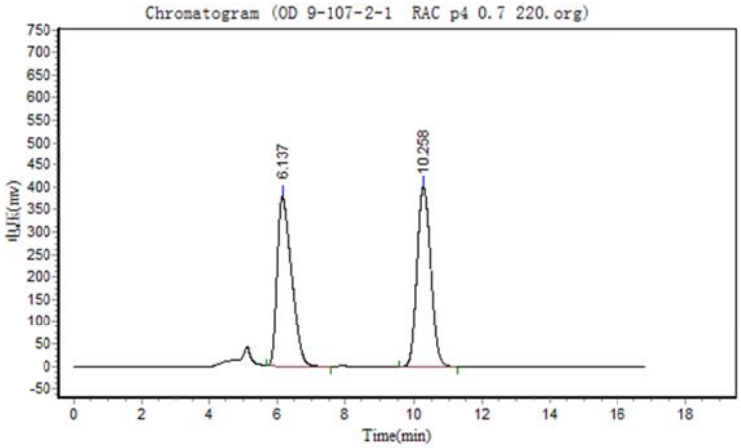


Ethyl (R)-2-(dimethyl(phenyl)silyl)-2-(o-tolyl)acetate (3m)

Colorless oil, 70%, 94% ee;

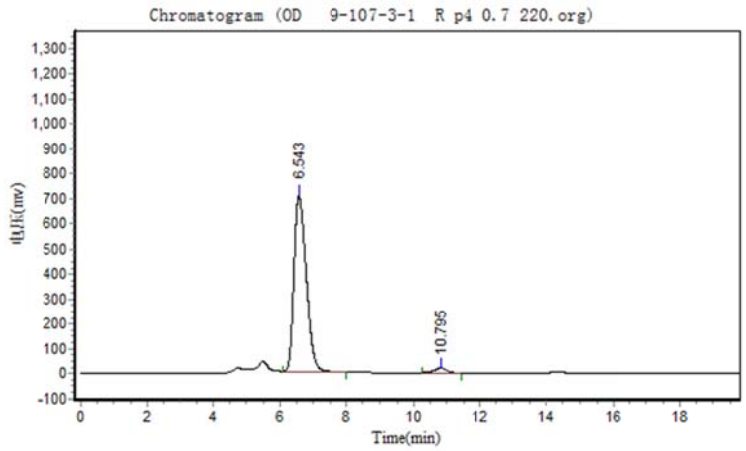
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.7 Hz, 1H), 7.38 – 7.26 (m, 6H), 7.13 – 7.01 (m, 2H), 4.06 (dq, *J* = 7.1, 1.2 Hz, 2H), 3.88 (s, 1H), 2.06 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H), 0.42 (s, 3H), 0.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9, 136.1, 135.1, 134.6, 134.1, 130.3, 129.7, 129.1, 127.8, 125.9, 125.7, 60.4, 40.7, 20.5, 14.4, -3.6, -4.1. ESI-MS (*m/z*, %) 335 $[M+Na]^+$; ESI-HRMS calcd for $C_{19}H_{24}O_2NaSi$ $[M+Na]^+$ 335.1438, found 335.1435. $[\alpha]_D^{25}$ = +45.6 (*c* 0.7, $CHCl_3$).

HPLC: Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 99/1; flow = 0.7 mL/min; Retention time: 6.1 min (major), 10.3 min.



Results

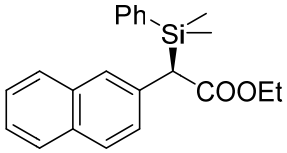
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.137	376192.531	10966141.000	49.2241
2		10.258	400683.156	11311858.000	50.7759
Total			776875.688	22277999.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.543	701812.813	18059000.000	97.2019
2		10.795	19145.736	519861.000	2.7981
Total			720958.549	18578861.000	100.0000

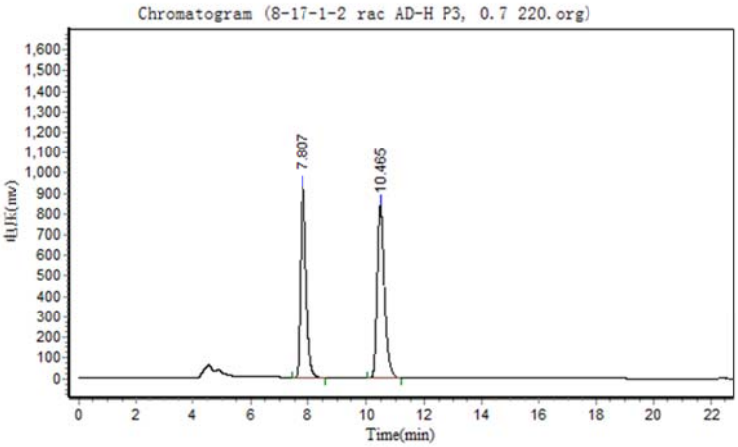
Ethyl (R)-2-(dimethyl(phenyl)silyl)-2-(naphthalen-2-yl)acetate (3n)



Colorless oil, 90%, 93% ee;

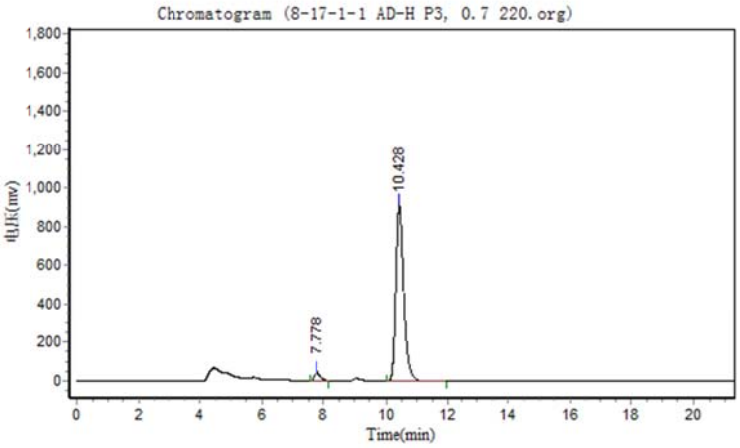
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 – 7.66 (m, 4H), 7.53 – 7.27 (m, 8H), 4.05 (dq, J = 7.1, 1.1 Hz, 2H), 3.78 (s, 1H), 1.14 (t, J = 7.1 Hz, 3H), 0.40 (s, 3H), 0.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.7, 135.6, 134.1, 133.7, 133.4, 131.8, 129.7, 127.7, 127.48, 127.41, 126.5, 125.8, 125.2, 60.3, 46.3, 14.2, -3.9, -4.5. ESI-MS (*m/z*, %) 371 $[M+Na]^+$; ESI-HRMS calcd for $C_{22}H_{24}O_2NaSi$ $[M+Na]^+$ 371.1438, found 371.1427. $[\alpha]_D^{25}$ = +23.9 (*c* 0.9, $CHCl_3$).

HPLC: Chiralpak AD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 95/5; flow = 0.7 mL/min; Retention time: 7.8 min, 10.4 min (major).



Results

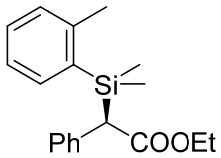
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.807	928064.813	13575847.000	47.6430
2		10.465	835519.500	14919077.000	52.3570
Total			1763584.313	28494924.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.778	44664.789	621539.188	3.6855
2		10.428	907273.813	16243134.000	96.3145
Total			951938.602	16864673.188	100.0000

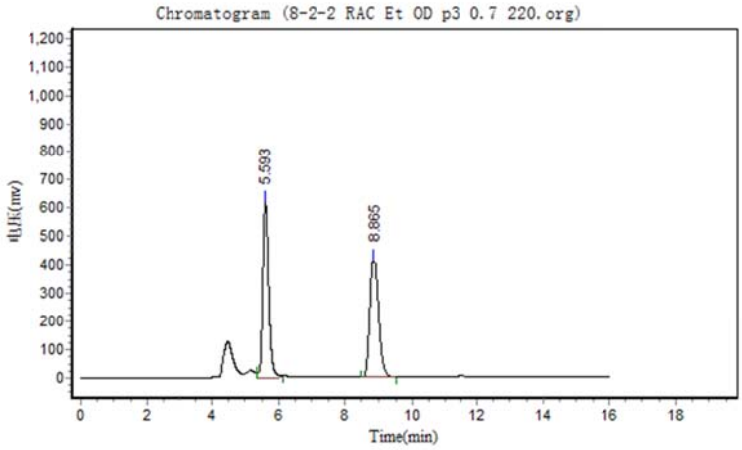
Ethyl (R)-2-(dimethyl(o-tolyl)silyl)-2-phenylacetate (3o)



Colorless oil, 50%, 95% ee;

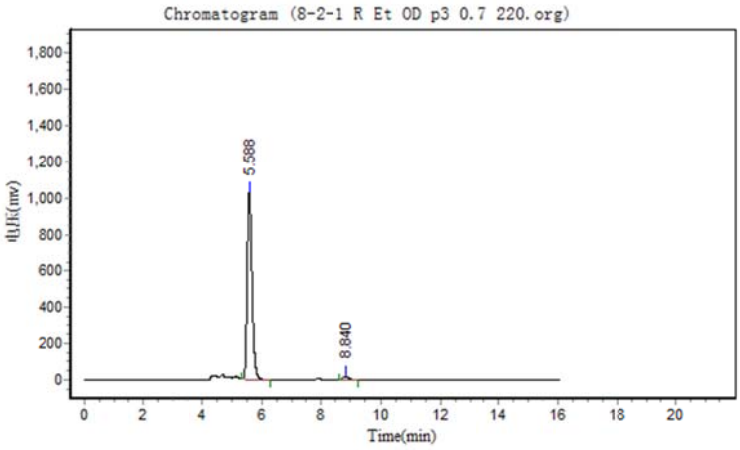
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.12 (m, 9H), 3.95 (dq, *J* = 7.1, 1.2 Hz, 2 H), 3.78 (s, 1H), 2.41 (s, 3H), 1.07 (t, *J* = 7.1 Hz, 3H), 0.46 (s, 3H), 0.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.8, 144.1, 136.3, 135.4, 134.2, 130.1, 130.0, 128.4, 128.1, 125.7, 125.0, 60.3, 45.8, 23.5, 14.2, -2.2, -2.5. ESI-MS (*m/z*, %) 335 $[M+Na]^+$; ESI-HRMS calcd for $C_{19}H_{24}O_2NaSi$ $[M+Na]^+$ 335.1438, found 335.1433. $[\alpha]_D^{25}$ = +50.5 (*c* 0.2, $CHCl_3$).

HPLC: Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 95/5; flow = 0.7 mL/min; Retention time: 5.6 min (major), 8.8 min.



Results

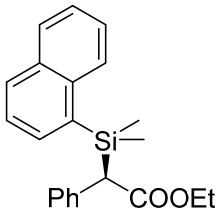
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.593	617940.625	7583399.500	51.9615
2		8.865	419599.438	7010870.000	48.0385
Total			1037540.063	14594269.500	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.588	1024859.438	11620715.000	97.4515
2		8.840	19821.902	303904.281	2.5485
Total			1044681.340	11924619.281	100.0000

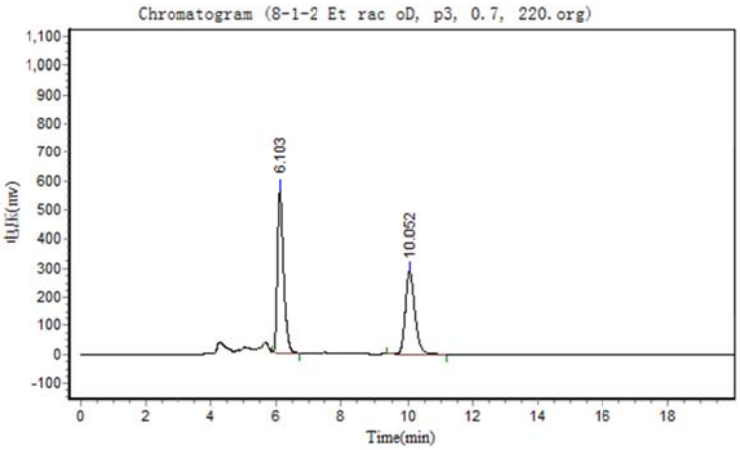
Ethyl (R)-2-(dimethyl(naphthalen-1-yl)silyl)-2-phenylacetate (3p)



Colorless oil, 60%, 96% ee;

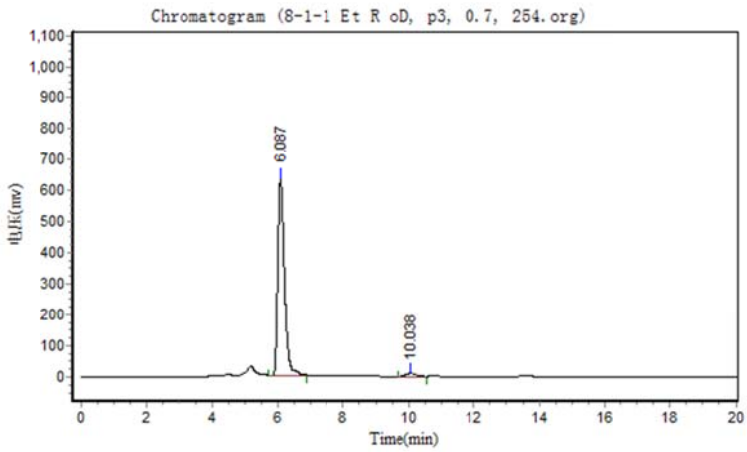
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.0 Hz, 2H), 7.66 – 7.51 (m, 3H), 7.51 – 7.35 (m, 1H), 7.35 – 7.11 (m, 5H), 3.99 (s, 1H), 3.96 – 3.80 (m, 2H), 0.91 (t, J = 7.1 Hz, 3H), 0.62 (s, 3H), 0.49 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9, 137.0, 136.3, 134.8, 134.0, 133.5, 130.7, 129.3, 128.4, 128.13, 128.09, 126.0, 125.7, 125.6, 125.0, 60.3, 45.9, 14.0, -2.1, -2.2. ESI-MS (*m/z*, %) 371 $[M+Na]^+$; ESI-HRMS calcd for $C_{22}H_{24}O_2NaSi$ $[M+Na]^+$ 371.1438, found 371.1433. $[\alpha]_D^{25}$ = -7.0 (*c* 1.0, $CHCl_3$).

HPLC: Chiralcel OD-H column (250 mm); detected at 254 nm; hexane/*i*-propanol = 95/5; flow = 0.7 mL/min; Retention time: 6.1 min (major), 10.0 min.



Results

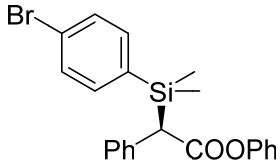
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.103	556283.438	7316135.500	55.3937
2		10.052	289986.844	5891397.000	44.6063
Total			846270.281	13207532.500	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.087	629939.313	8834940.000	97.7821
2		10.038	9962.264	200392.609	2.2179
Total			639901.576	9035332.609	100.0000

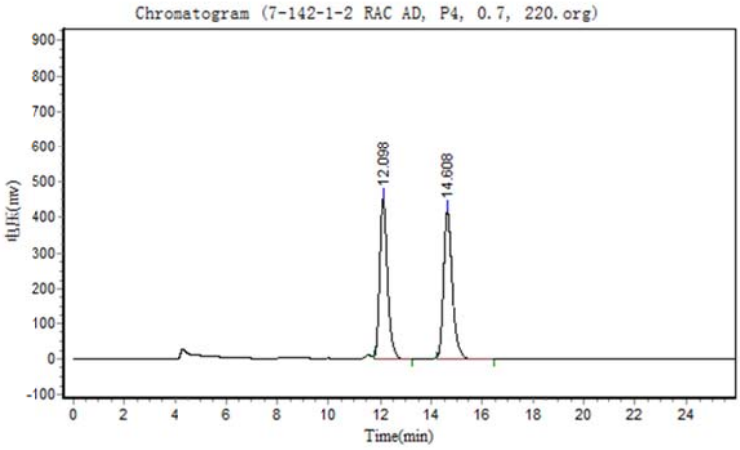
Phenyl (R)-2-((4-bromophenyl)dimethylsilyl)-2-phenylacetate (3q)



Colorless oil, 82%, 95% ee;

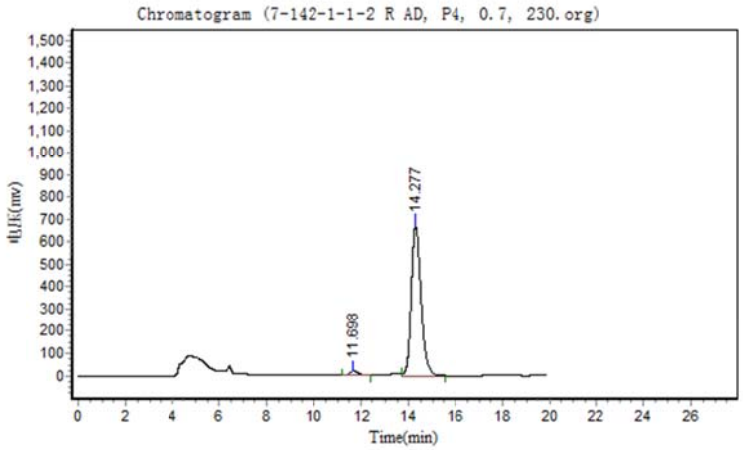
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.37 – 7.21 (m, 10H), 6.86 (d, *J* = 8.1 Hz, 2H), 3.87 (s, 1H), 0.49 (s, 3H), 0.43 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.2, 150.7, 135.9, 135.3, 134.1, 131.2, 129.4, 128.45, 128.40, 126.2, 125.8, 125.0, 121.7, 45.8, -3.8, -4.4. ESI-MS (*m/z*, %) 447 $[M+Na]^+$; ESI-HRMS calcd for $C_{22}H_{21}O_2BrNaSi$ $[M+Na]^+$ 447.0386, found 447.0387. $[\alpha]_D^{25}$ = +29.5 (*c* 1.5, $CHCl_3$).

HPLC: Chiralpak AD-H column (250 mm); detected at 230 nm; hexane/*i*-propanol = 99/1; flow = 0.7 mL/min; Retention time: 11.7 min, 14.3 min (major).



Results

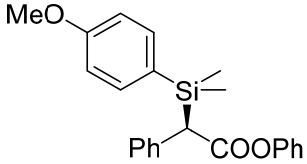
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.098	453167.906	9783982.000	49.2812
2		14.608	416930.344	10069392.000	50.7188
Total			870098.250	19853374.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.698	18759.945	520709.094	2.6000
2		14.277	672046.688	19506482.000	97.4000
Total			690806.633	20027191.094	100.0000

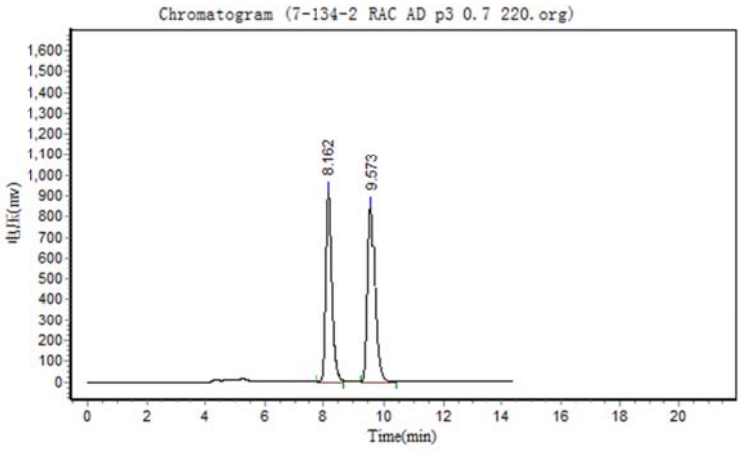
Phenyl (*R*)-2-((4-methoxyphenyl)dimethylsilyl)-2-phenylacetate (3r)



Colorless oil, 70%, 96% ee;

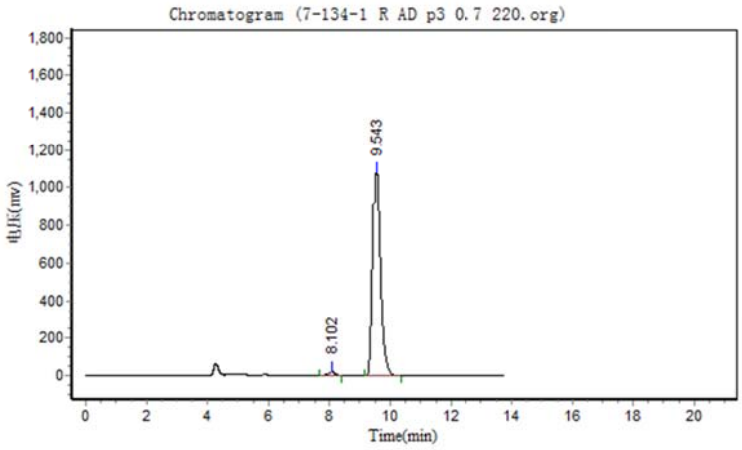
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.5 Hz, 2H), 7.34 – 7.26 (m, 6H), 7.24 – 7.17 (m, 2H), 6.92 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 7.6 Hz, 2H), 3.85 (s, 1H), 3.83 (s, 3H), 0.44 (s, 3H), 0.39 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.4, 161.2, 150.9, 135.9, 135.8, 129.4, 128.5, 128.3, 126.03, 125.95, 125.7, 121.9, 113.8, 55.2, 46.3, -3.5, -4.3. ESI-MS (*m/z*, %) 399 $[M+Na]^+$; ESI-HRMS calcd for $C_{23}H_{24}O_3NaSi$ $[M+Na]^+$ 399.1387, found 399.1376. $[\alpha]_D^{25}$ = +32.6 (*c* 1.4, $CHCl_3$).

HPLC: Chiralpak AD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 95/5; flow = 0.7 mL/min; Retention time: 8.1 min, 9.5 min (major).



Results

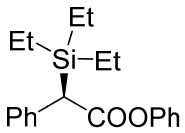
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.162	913131.500	13248474.000	49.1614
2		9.573	842072.250	13700483.000	50.8386
Total			1755203.750	26948957.000	100.0000



Results

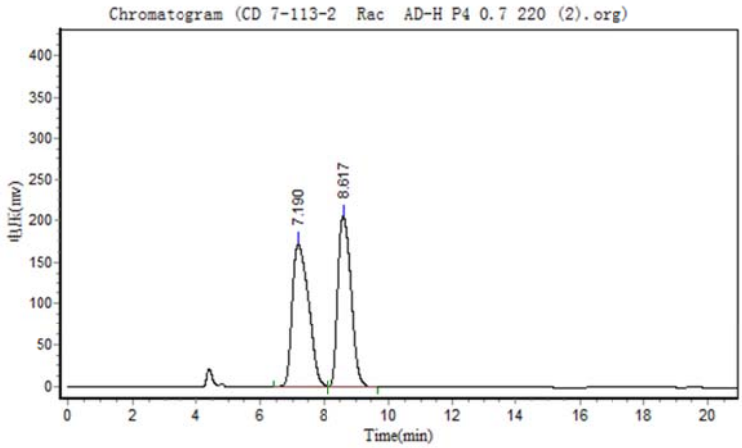
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.102	20434.502	362647.031	1.9925
2		9.543	1078777.750	17837704.000	98.0075
Total			1099212.252	18200351.031	100.0000

Phenyl (*R*)-2-phenyl-2-(triethylsilyl)acetate (3s)



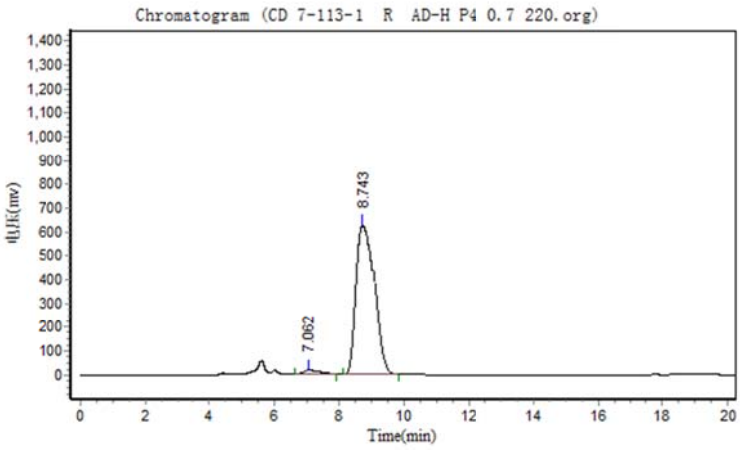
Colorless oil, 82%, 95% ee;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.27 (m, 6H), 7.27 – 7.17 (m, 2H), 7.12 (s, 2H), 3.80 (s, 1H), 0.99 (t, *J* = 7.8 Hz, 9H), 0.81 – 0.64 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.9, 151.0, 129.5, 128.6, 128.4, 125.9, 125.7, 121.8, 42.9, 7.3, 3.0. ESI-MS (*m/z*, %) 349 $[M+Na]^+$; ESI-HRMS calcd for $C_{20}H_{26}O_2NaSi$ $[M+Na]^+$ 349.1594, found 349.1588. $[\alpha]_D^{25}$ = +26.3 (*c* 1.1, $CHCl_3$).

HPLC: Chiralpak AD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 99/1; flow = 0.7 mL/min; Retention time: 7.2 min, 8.6 min (major).



Results

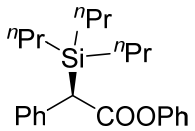
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.190	172567.797	6098436.500	50.5494
2		8.617	206161.953	5965880.500	49.4506
Total			378729.750	12064317.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.062	15707.504	590505.063	2.4094
2		8.743	625200.813	23917926.000	97.5906
Total			640908.316	24508431.063	100.0000

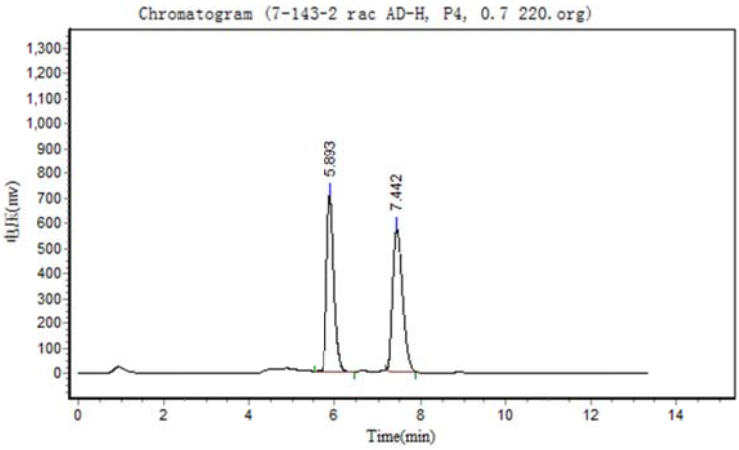
Phenyl (*R*)-2-phenyl-2-(tripropylsilyl)acetate (3t)



Colorless oil, 75%, 97% ee;

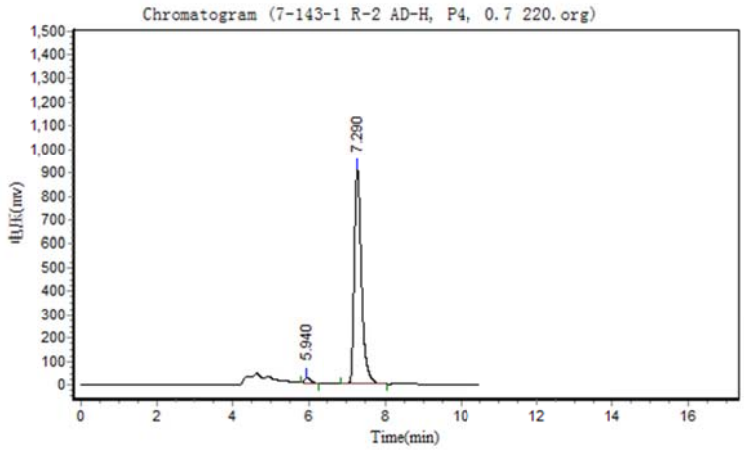
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.38 (m, 4H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.22 (m, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 3.79 (s, 1H), 1.42 – 1.32 (m, 6H), 0.97 (t, *J* = 7.2 Hz, 9H), 0.79 – 0.63 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.1, 151.2, 136.4, 129.6, 128.7, 128.5, 126.0, 125.8, 121.9, 43.6, 18.8, 17.3, 14.7. ESI-MS (*m/z*, %) 391 $[M+Na]^+$; ESI-HRMS calcd for $C_{23}H_{32}O_2NaSi$ $[M+Na]^+$ 391.2064, found 391.2061. $[\alpha]_D^{25}$ = +26.0 (*c* 1.0, $CHCl_3$).

HPLC: Chiralpak AD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 99/1; flow = 0.7 mL/min; Retention time: 5.9 min, 7.3 min (major).



Results

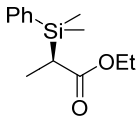
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.893	710356.625	8591166.000	48.3955
2		7.442	569625.188	9160845.000	51.6045
Total			1279981.813	17752011.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.940	20095.855	216755.844	1.7609
2		7.290	908836.438	12092349.000	98.2391
Total			928932.293	12309104.844	100.0000

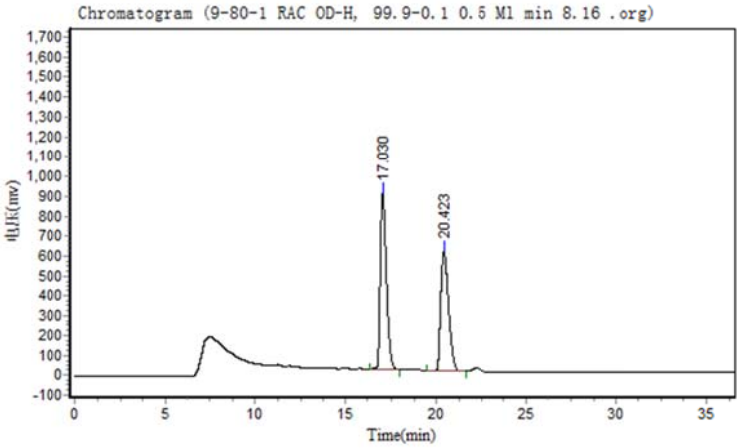
Ethyl (*R*)-2-(dimethyl(phenyl)silyl)propanoate (3u)



Colorless oil, 45%, 77% ee;

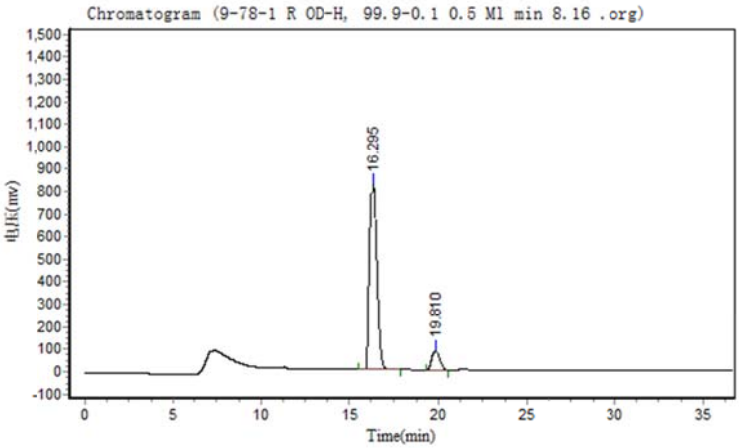
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (s, 2H), 7.37 (s, 3H), 4.01 (q, J = 6.9 Hz, 2H), 2.44 – 2.16 (m, 1H), 1.15 – 1.10 (m, 6H), 0.37 (s, 6H); $[\alpha]_D^{25}$ = +38.8 (*c* 1.0, $CHCl_3$). [lit: $[\alpha]_D^{20}$ = +18.5 (*c* 1.0, $CHCl_3$) for (*R*) with 35% ee] (*Angew. Chem. Int. Ed.* **2008**, *47*, 8496.)

HPLC: Chiralcel OD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 99.9/0.1; flow = 0.5 mL/min; Retention time: 17.0 min (major), 20.4 min.



Results

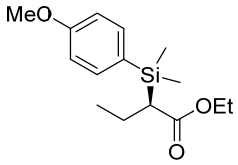
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.030	881419.563	20806276.000	53.3503
2		20.423	599700.563	18193100.000	46.6497
Total			1481120.125	38999376.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.295	818724.250	21106818.000	88.3839
2		19.810	85945.781	2774028.500	11.6161
Total			904670.031	23880846.500	100.0000

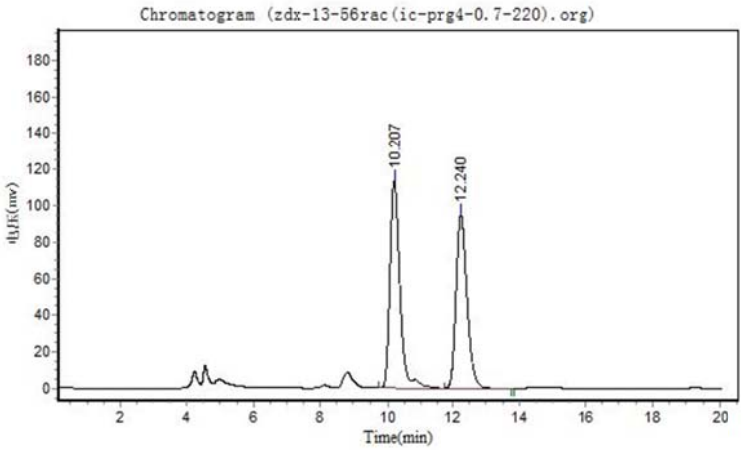
Ethyl (R)-2-((4-methoxyphenyl)dimethylsilyl)butanoate (3v)



Colorless oil, 34% yield, 70% ee

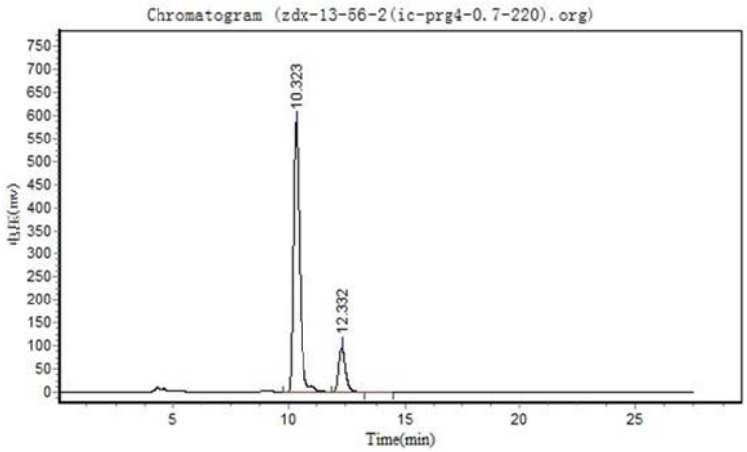
^{1}HNMR (300 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.4 Hz, 2H), 6.90(d, *J* = 8.4 Hz, 2H), 4.07 – 3.99(m, 2H), 3.81 (s, 3H), 2.08 – 2.03(m, 1H), 1.82 – 1.71(m, 1H), 1.44 – 1.36(m, 1H), 1.15 (t, *J* = 6.9 Hz, 3H), 0.88 (t, *J* = 7.5 Hz, 3H), 0.33(s, 3H), 0.32(s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 175.4, 160.9, 135.4, 127.4, 113.7, 59.8, 55.1, 39.9, 20.6, 15.1, 14.5, -3.6, -4.4. EI/MS (*m/z*, %): 280(M^+), 165 (100). HRMS-EI calcd for $C_{15}H_{24}O_3Si$ (M^+) 280.1495.1464, found 280.1496; $[\alpha]_D^{25}$ = +13.0(c 0.6, $CHCl_3$).

HPLC: Chiralpak IC-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 99/1; flow = 0.7 mL/min; Retention time: 10.2 min(major), 12.2 min.



Results

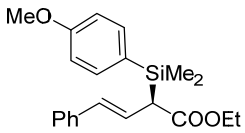
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.207	113294.500	2399387.500	52.6484
2		12.240	94949.297	2157989.000	47.3516
Total			208243.797	4557376.500	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.323	584081.563	11298448.000	84.9706
2		12.332	96850.539	1998447.250	15.0294
Total			680932.102	13296895.250	100.0000

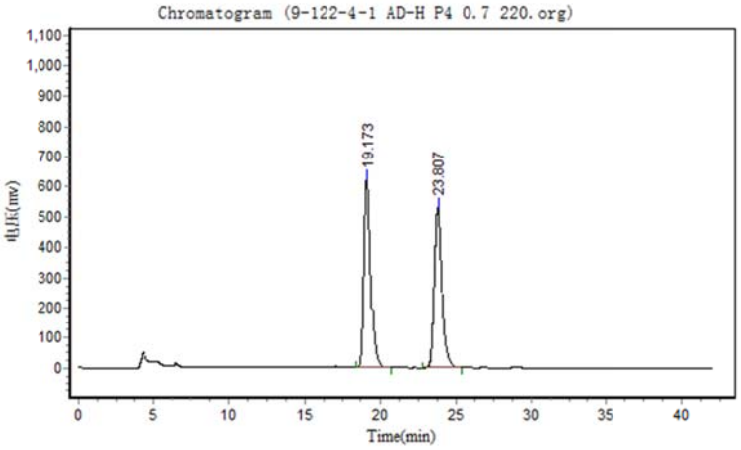
Ethyl (*R*,*E*)-2-((4-methoxyphenyl)dimethylsilyl)-4-phenylbut-3-enoate (3w)



Colorless oil, 41%, 90% ee.

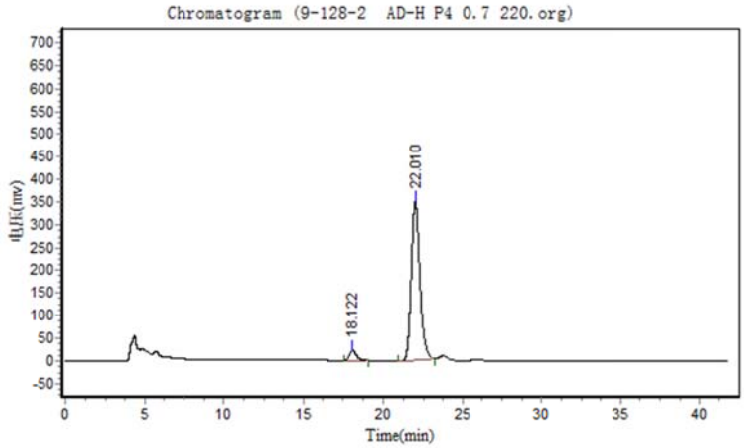
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.20 – 7.16 (m, 5H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.38 (dd, *J*=16.0, 10.0 Hz, 1H), 6.10 (d, *J*=16.0 Hz, 1H), 4.11 – 3.92 (m, 2H), 3.81 (s, 3H), 3.20 (d, *J* = 10.0 Hz, 1H), 1.13 (t, *J* = 7.1 Hz, 3H), 0.40 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9, 161.1, 137.8, 135.8, 128.8, 128.6, 127.0, 126.3, 126.1, 125.4, 113.7, 60.3, 55.2, 44.7, 14.4, -4.10, -4.15. ESI-MS (*m/z*, %) 377 $[M+Na]^+$; ESI-HRMS calcd for $C_{21}H_{16}O_3NaSi$ $[M+Na]^+$ 377.1549, found 377.1558. $[\alpha]_D^{25}$ = -56.2 (*c* 0.5, $CHCl_3$).

HPLC: Chiralpak AD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 99/1; flow = 0.7 mL/min; Retention time: 19.1 min, 23.8 min (major).



Results

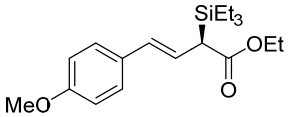
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.173	623159.313	18849628.000	49.7423
2		23.807	528741.500	19044958.000	50.2577
Total			1151900.813	37894586.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.122	21769.746	686783.500	4.9345
2		22.010	348688.656	13231088.000	95.0655
Total			370458.402	13917871.500	100.0000

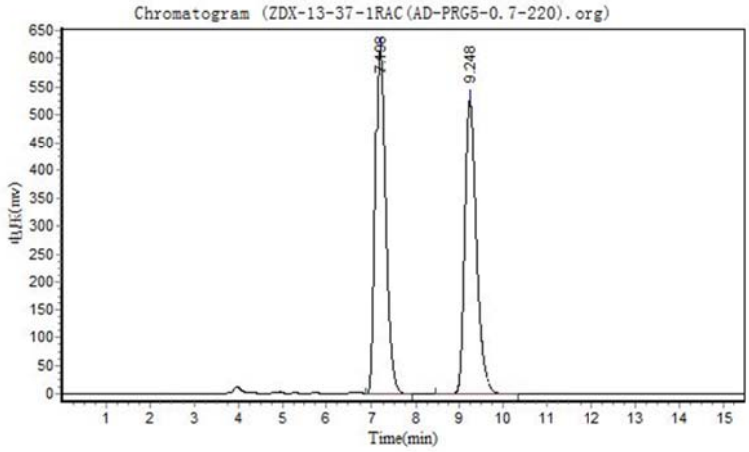
Ethyl (R,E)-4-(4-methoxyphenyl)-2-(triethylsilyl)but-3-enoate (3x)



Colorless oil, 36% yield, 89% ee.

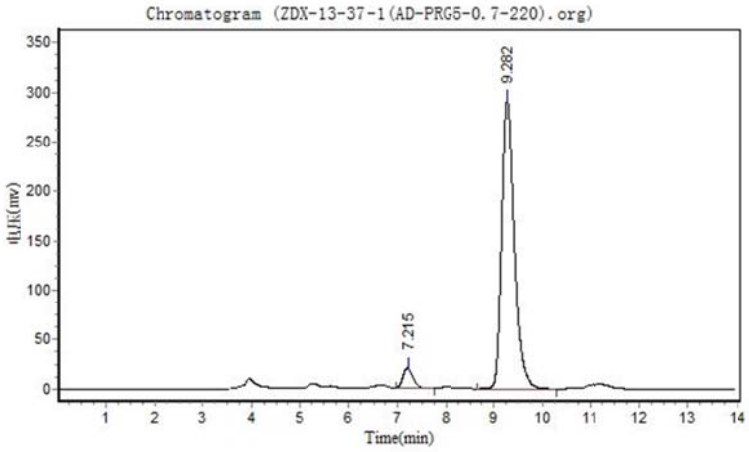
^{1}HNMR (300 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.4, 2H), 6.83(d, *J* = 8.4, 2H), 6.33(dd, *J* = 16.3, 9.9 Hz, 1H), 6.18 (d, *J* = 16.3 Hz, 1H), 4.13 (q, *J* = 13.8 Hz, 2H), 3.79 (s, 3H), 3.14 (d, *J* = 9.6 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H), 0.98(t, *J* = 8.1 Hz, 9H), 0.66(q, *J* = 15.6 Hz, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 173.5, 158.8, 130.7, 127.8, 127.1, 123.6, 114.1, 60.2, 55.4, 41.5, 14.5, 7.3, 2.7. EI/MS (*m/z*, %): 334(M^+), 174 (100). HRMS-EI calcd for $C_{19}H_{30}O_3Si$ (M^+) 334.1464, found 334.1465; $[\alpha]_D^{25}$ = -45.9 (c 0.5, $CHCl_3$).

HPLC: Chiralpak AD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 97/3; flow = 0.7 mL/min; Retention time: 7.2 min, 9.2 min (major).



Results

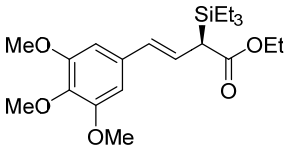
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.198	614510.250	9521864.000	49.5637
2		9.248	525579.625	9689508.000	50.4363
Total			1140089.875	19211372.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.215	20813.188	316583.594	5.6563
2		9.282	291278.281	5280383.000	94.3437
Total			312091.469	5596966.594	100.0000

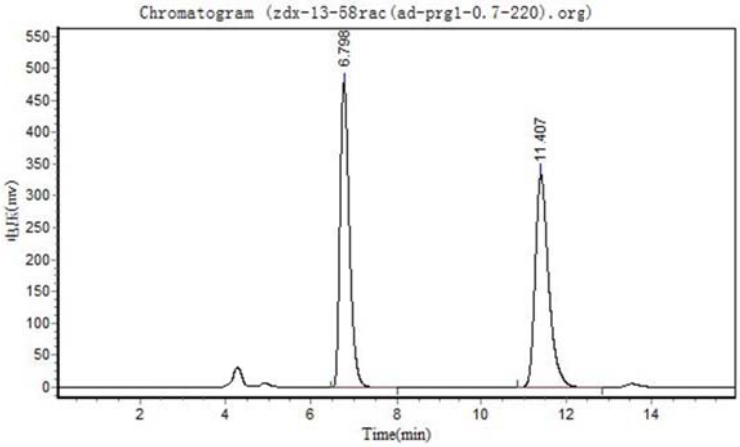
Ethyl (R,E)-2-(triethylsilyl)-4-(3,4,5-trimethoxyphenyl)but-3-enoate (3y)



Colorless oil, 28% yield, 94% ee.

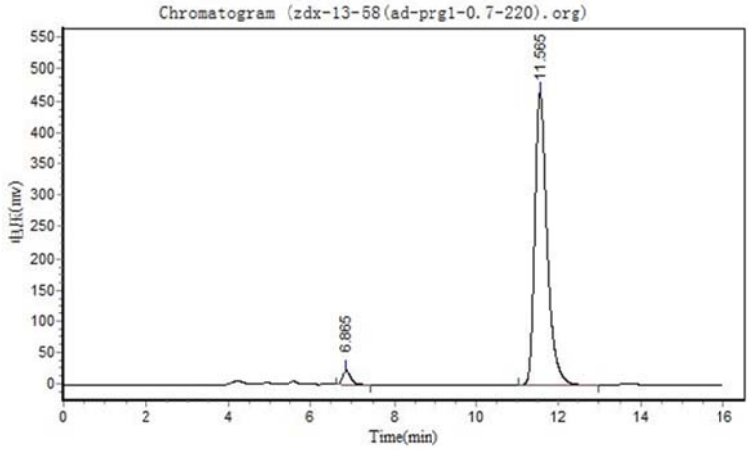
^{1}HNMR (300 MHz, $CDCl_3$): δ 6.56 (s, 2H), 6.40 (dd, *J* = 16.6, 10.5 Hz, 1H), 6.16 (d, *J* = 16.6 Hz, 1H), 4.15 (q, *J* = 13.8 Hz, 2H), 3.88 (s, 6H), 3.84 (s, 3H), 3.18 (d, *J* = 10.5 Hz, 1H), 1.29 (t, *J* = 6.9 Hz, 3H), 1.00(t, *J* = 7.8 Hz, 9H), 0.68(q, *J* = 15.9 Hz, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 175.2, 155.2, 135.3, 129.9, 127.0, 104.8, 62.8, 62.1, 58.0, 55.4, 43.2, 16.3, 9.1, 4.5. ESI-MS (*m/z*, %) 417 $[M+Na]^+$. HRMS-ESI calcd for $C_{21}H_{35}O_5Si$ $[M+H]^+$395.2176, found 395.2248; $[\alpha]_D^{25}$ = -82.2 (c 0.5, $CHCl_3$).

HPLC: Chiralpak AD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 6.8 min, 11.4 min (major).



Results

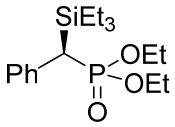
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.798	477031.156	7308015.500	50.1201
2		11.407	332654.000	7272984.000	49.8799
Total			809685.156	14580999.500	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.865	22199.410	310305.781	3.1466
2		11.565	463824.906	9551403.000	96.8534
Total			486024.316	9861708.781	100.0000

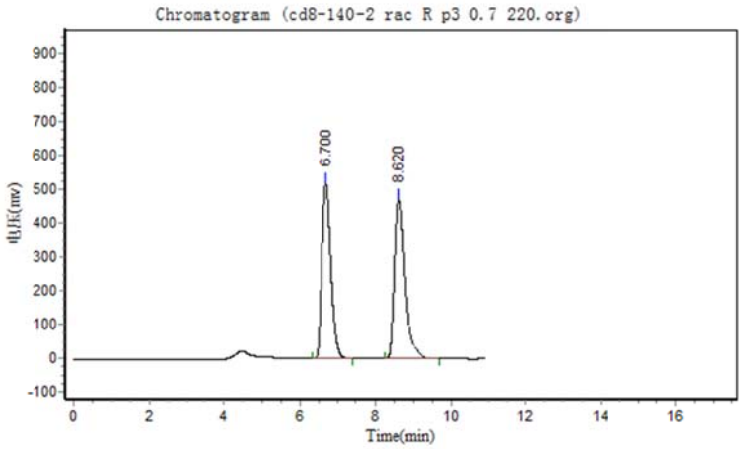
Diethyl (*S*)-(phenyl(triethylsilyl)methyl)phosphonate (5a)



Colorless oil, 59%, 93% ee;

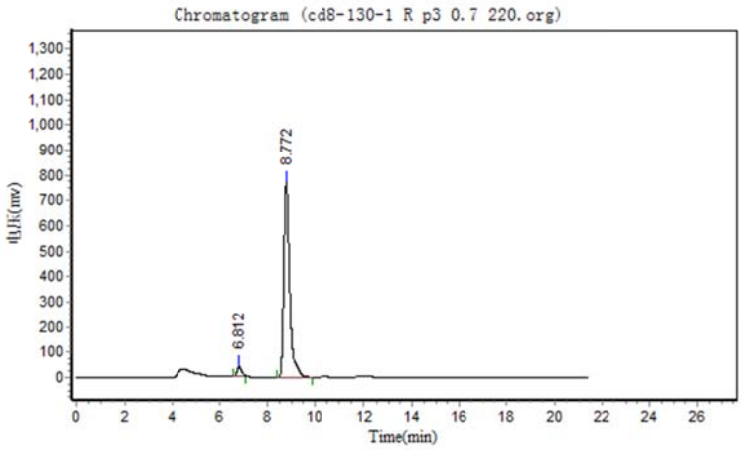
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.16 (m, 5H), 4.10 – 3.93 (m, 2H), 3.89 – 3.74 (m, 2H), 2.77 (d, *J* = 27.0 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.8 Hz, 9H), 0.73 – 0.62 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.1 (d, *J* = 7.6 Hz), 129.6 (d, *J* = 8.2 Hz), 128.4 (d, *J* = 1.6 Hz), 125.7 (d, *J* = 2.6 Hz), 61.8 (dd, *J* = 175.1, 7.6 Hz), 34.5 (d, *J* = 126.0 Hz), 16.2 (dd, *J* = 8.8, 6.5 Hz), 7.4, 3.4 (d, *J* = 2.3 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 29.5. ESI-MS (*m/z*, %) 343 $[M+H]^+$; ESI-HRMS calcd for $C_{17}H_{32}O_3PSi$ $[M+H]^+$ 343.1853, found 343.1844. $[\alpha]_D^{25}$ = -17.8 (*c* 0.8, $CHCl_3$).

HPLC: Chiralpak AD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 95/5; flow = 0.7 mL/min; Retention time: 6.5 min, 8.4 min (major).



Results

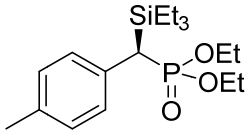
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.700	516683.594	8614942.000	49.0242
2		8.620	467911.844	8957891.000	50.9758
Total			984595.438	17572833.000	100.0000



Results

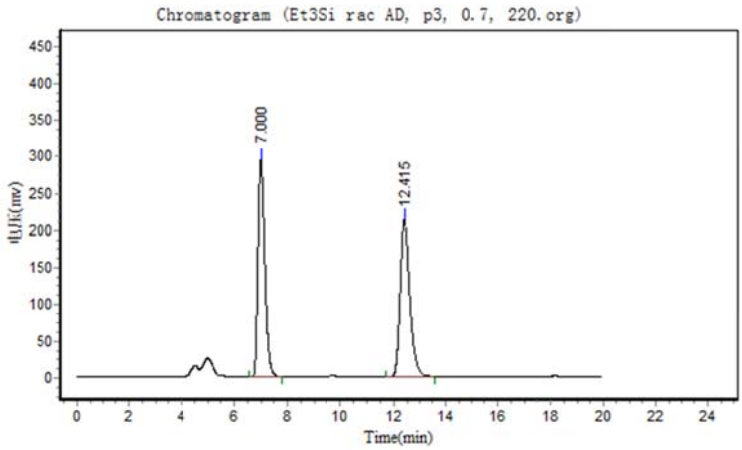
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.812	37308.750	468487.500	3.4494
2		8.772	769031.063	13113177.000	96.5506
Total			806339.813	13581664.500	100.0000

Diethyl (*S*)-(p-tolyl(triethylsilyl)methyl)phosphonate (5b)



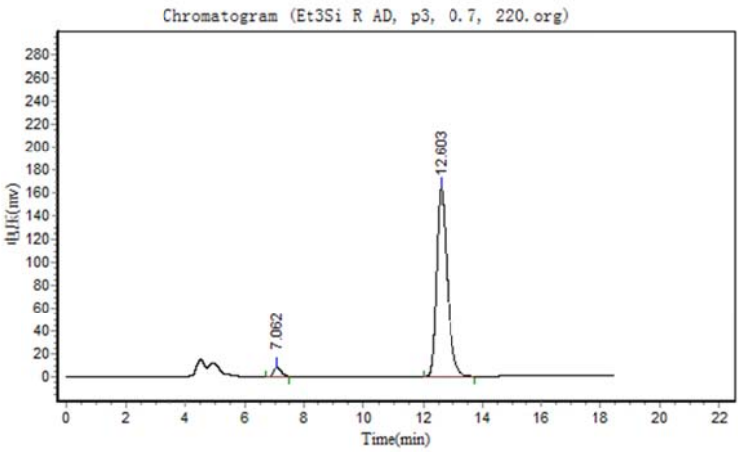
Colorless oil, 53%, 93% ee;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (dd, *J* = 23.0, 7.4 Hz, 4H), 4.15 – 3.96 (m, 2H), 3.90 – 3.75 (m, 2H), 2.73 (d, *J* = 27.0 Hz, 1H), 2.29 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.0 Hz, 3H), 0.91 (t, *J* = 7.8 Hz, 9H), 0.75 – 0.51 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.1, 131.7 (d, *J* = 7.7 Hz), 129.4 (d, *J* = 8.1 Hz), 129.1 (d, *J* = 1.8 Hz), 61.6 (dd, *J* = 175.1, 6.3 Hz), 33.5 (d, *J* = 126.0 Hz), 21.0, 16.3 (t, *J* = 6.5 Hz), 7.3, 3.4 (d, *J* = 2.3 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 29.7. ESI-MS (*m/z*, %) 357 $[M+H]^+$; ESI-HRMS calcd for $C_{18}H_{34}O_3PSi$ $[M+H]^+$ 357.2009, found 357.2003. $[\alpha]_D^{25}$ = -17.3 (*c* 0.5, $CHCl_3$).

HPLC: Chiralpak AD-H column (250 mm); detected at 220 nm; hexane/i-propanol = 95/5; flow = 0.7 mL/min; Retention time: 7.1 min, 12.6 min (major).



Results

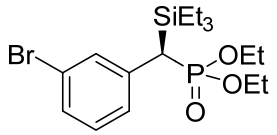
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.000	293031.156	5286316.000	49.6029
2		12.415	211851.797	5370954.500	50.3971
Total			504882.953	10657270.500	100.0000



Results

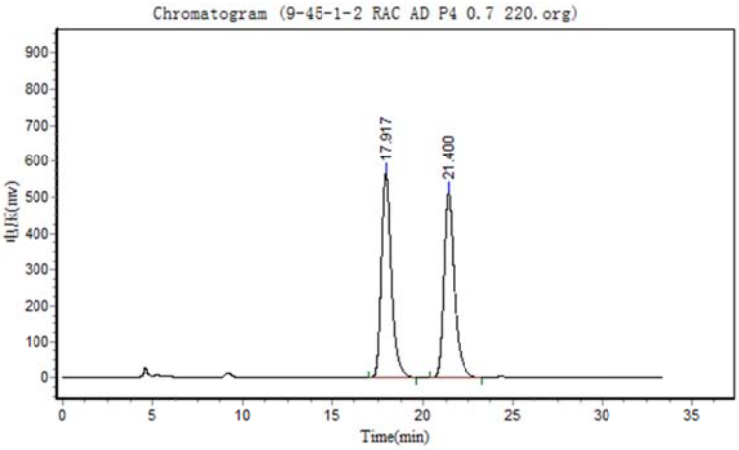
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.062	8049.962	152333.406	3.5027
2		12.603	162867.688	4196738.000	96.4973
Total			170917.649	4349071.406	100.0000

Diethyl (*S*)-((3-bromophenyl)(triethylsilyl)methyl)phosphonate (5c)



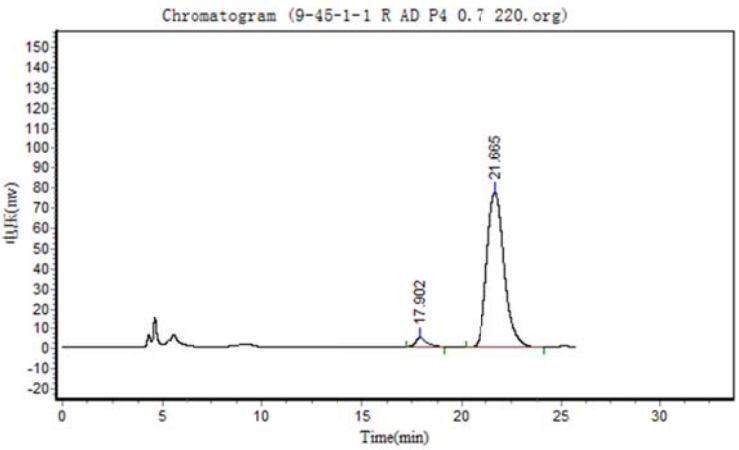
colorless oil, 63%, 92% ee;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.05 (m, 4H), 4.20 – 3.95 (m, 2H), 3.95 – 3.76 (m, 2H), 2.73 (d, *J* = 27.0 Hz, 1H), 1.28 (d, *J* = 7.1 Hz, 3H), 1.12 (t, *J* = 7.0 Hz, 3H), 0.92 (t, *J* = 7.8 Hz, 9H), 0.74 – 0.55 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.8 (d, *J* = 7.5 Hz), 132.4 (d, *J* = 8.6 Hz), 130.0, 128.9, 128.2 (d, *J* = 7.7 Hz), 122.5, 62.0 (dd, *J* = 153.7, 6.3 Hz), 33.5 (d, *J* = 127.3 Hz), 16.4, 7.4, 3.5 (d, *J* = 2.2 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 28.5. ESI-MS (*m/z*, %) 421 $[M+H]^+$; ESI-HRMS calcd for $C_{17}H_{31}O_3BrPSi$ $[M+H]^+$ 421.0958, found 421.0946. $[\alpha]_D^{25}$ = -18.8 (*c* 0.5, $CHCl_3$).

HPLC: Chiralpak AD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 99/1; flow = 0.7 mL/min; Retention time: 17.9 min, 21.7 min (major).



Results

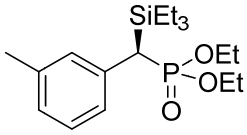
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.917	563696.063	22002022.000	51.1404
2		21.400	511959.156	21020768.000	48.8596
Total			1075655.219	43022790.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.902	4669.872	185405.313	3.7764
2		21.665	77007.875	4724108.500	96.2235
Total			81677.747	4909513.813	100.0000

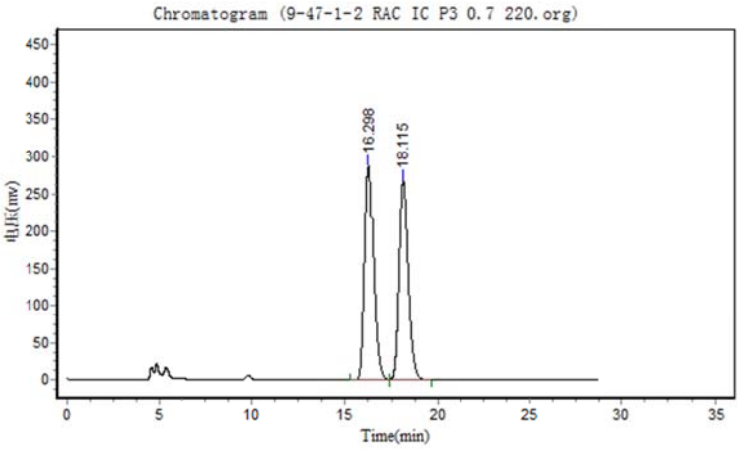
Diethyl (S)-(m-tolyl(triethylsilyl)methyl)phosphonate (5d)



Colorless oil, 57%, 97% ee;

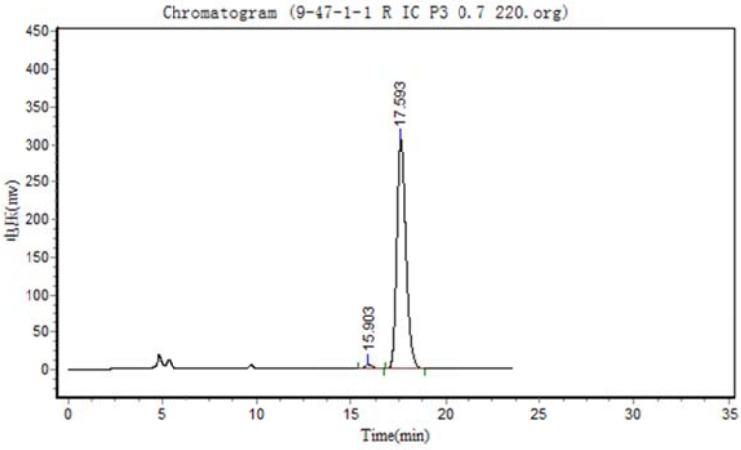
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 (t, *J* = 7.7 Hz, 1H), 7.05 (s, 2H), 6.96 (d, *J* = 7.3 Hz, 1H), 4.15 – 3.96 (m, 2H), 3.97 – 3.65 (m, 2H), 2.73 (d, *J* = 25.4 Hz, 1H), 2.31 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.07 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.8 Hz, 9H), 0.77 – 0.57 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 134.9 (d, *J* = 7.5 Hz), 130.4 (d, *J* = 8.2 Hz), 128.3, 126.7 (d, *J* = 8.1 Hz), 126.5 (d, *J* = 2.02 Hz), 61.8 (dd, *J* = 139.4, 6.1 Hz), 33.9 (d, *J* = 121.2 Hz), 21.6, 16.3 (dd, *J* = 8.1, 6.1 Hz), 7.5, 3.6 (d, *J* = 2.3 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 29.6. ESI-MS (*m/z*, %) 379 $[M+Na]^+$; ESI-HRMS calcd for $C_{18}H_{33}O_3NaPSi$ $[M+Na]^+$ 379.1829, found 379.1823. $[\alpha]_D^{25}$ = -19.2 (*c* 0.6, $CHCl_3$).

HPLC: Chiralpak IC column (250 mm); detected at 220 nm; hexane/*i*-propanol = 95/5; flow = 0.7 mL/min; Retention time: 16.2 min, 18.1 min (major).



Results

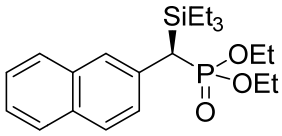
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.298	286252.344	9177831.000	49.5654
2		18.115	266716.938	9338770.000	50.4346
Total			552969.281	18516601.000	100.0000



Results

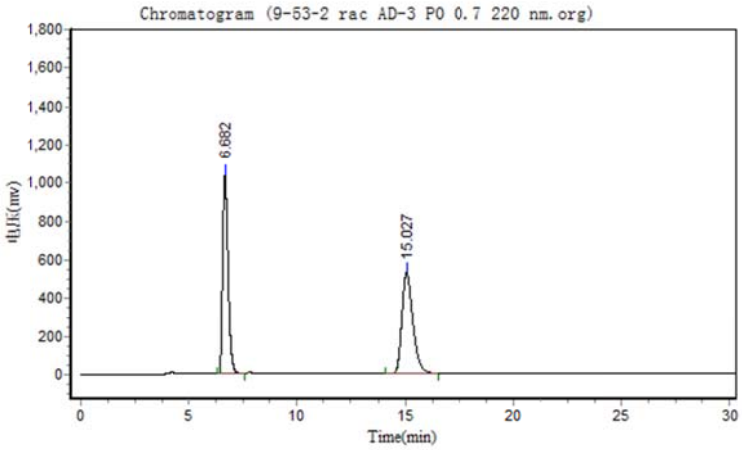
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.903	5315.992	155162.000	1.4852
2		17.593	305659.094	10292025.000	98.5148
Total			310975.086	10447187.000	100.0000

Diethyl (S)-(naphthalen-2-yl(triethylsilyl)methyl)phosphonate (5e)



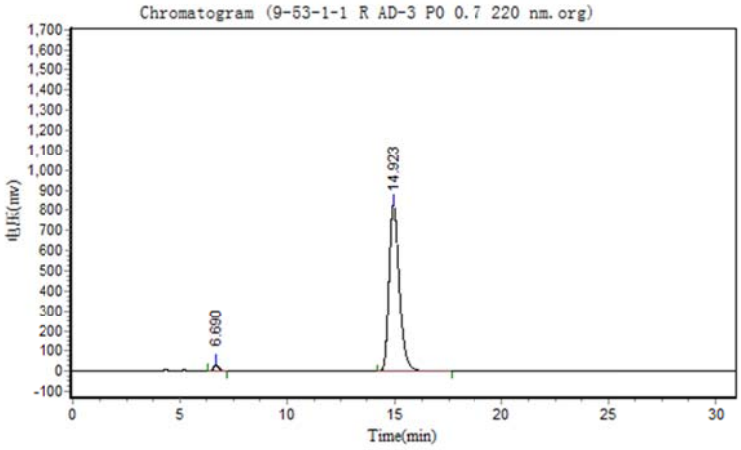
Colorless oil, 46%, 97% ee;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 – 7.70 (m, 4H), 7.45 – 7.41 (m, 3H), 4.11 – 4.00 (m, 2H), 4.00 – 3.69 (m, 2H), 2.97 (d, *J* = 25.3 Hz, 1H), 1.27 (t, *J* = 7.0 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H), 0.93 (t, *J* = 7.8 Hz, 9H), 0.81 – 0.56 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.6, 132.9 (d, *J* = 7.8 Hz), 131.8, 128.4, 128.0, 127.73 (d, *J* = 5.0 Hz), 127.68 (d, *J* = 3.8 Hz), 126.1, 125.4, 61.9 (dd, *J* = 171.0, 6.3 Hz), 34.3 (d, *J* = 126.0 Hz), 16.4 (t, *J* = 6.7 Hz), 7.5, 3.6 (d, *J* = 2.5 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 29.3. ESI-MS (*m/z*, %) 393 $[M+H]^+$; ESI-HRMS calcd for $C_{21}H_{34}O_3PSi$ $[M+H]^+$ 393.2009, found 393.2007. $[\alpha]_D^{25}$ = -14.8 (*c* 0.4, $CHCl_3$).

HPLC: Chiralpak AD-3 column (250 mm); detected at 220 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 6.7 min, 15.0 min (major).



Results

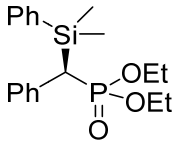
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.682	1037099.000	17996966.000	48.6967
2		15.027	532805.688	18960304.000	51.3033
Total			1569904.688	36957270.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.690	32176.023	499140.438	1.7483
2		14.923	831594.563	28050914.000	98.2517
Total			863770.586	28550054.438	100.0000

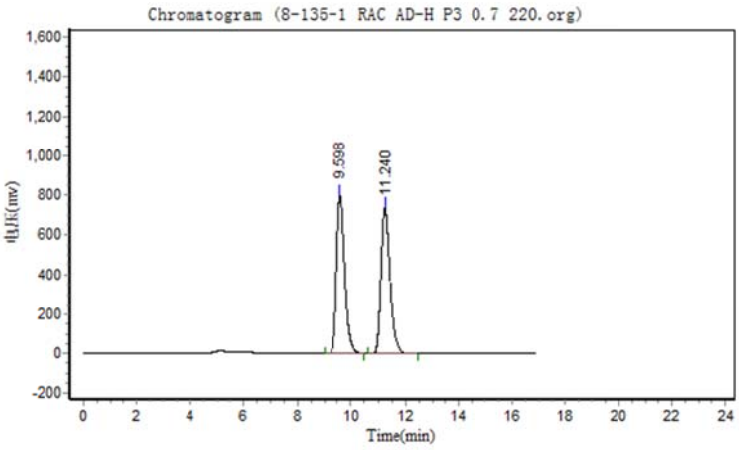
Diethyl (S)-((dimethyl(phenyl)silyl)(phenyl)methyl)phosphonate (5f)



Colorless oil, 48%, 95% ee;

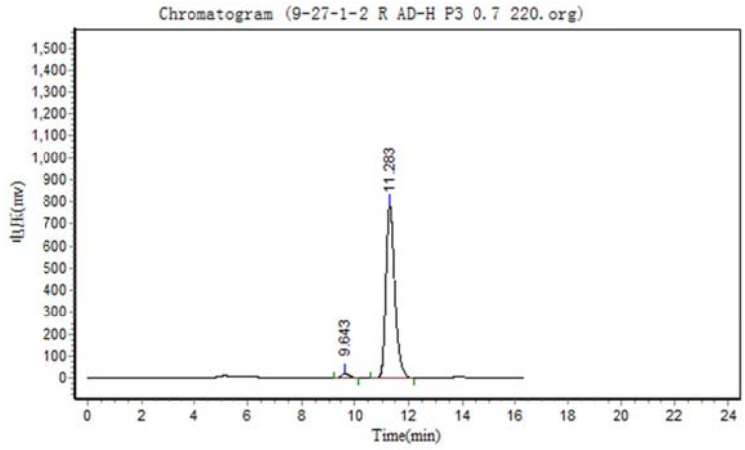
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 – 7.24 (m, 5H), 7.24 – 7.01 (m, 5H), 3.92 - 3.72 (m, 4H), 2.87 (d, *J* = 24.4 Hz, 1H), 1.12 (t, *J* = 7.0 Hz, 3H), 1.02 (t, *J* = 7.0 Hz, 3H), 0.52 (s, 3H), 0.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.7 (d, *J* = 4.1 Hz), 134.7 (d, *J* = 7.1 Hz), 134.3, 129.6 (d, *J* = 8.3 Hz), 129.4, 128.3, 127.6, 125.8 (d, *J* = 2.3 Hz), 61.7 (dd, *J* = 161.3, 7.6 Hz), 37.2 (d, *J* = 126.0 Hz), 16.2 (dd, *J* = 5.0, 1.3 Hz), -2.9, -3.1 (d, *J* = 2.2 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 28.5. ESI-MS (*m/z*, %) 385 $[M+Na]^+$; ESI-HRMS calcd for $C_{19}H_{27}O_3NaPSi$ $[M+H]^+$ 385.1359, found 385.1350. $[\alpha]_D^{25}$ = -31.3 (*c* 0.4, $CHCl_3$).

HPLC: Chiralpak AD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 95/5; flow = 0.7 mL/min; Retention time: 9.6 min, 11.2 min (major).



Results

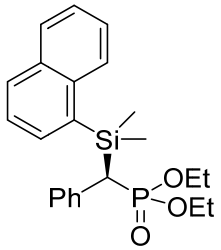
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.598	796271.625	17332908.000	50.0374
2		11.240	729951.188	17306980.000	49.9626
Total			1526222.813	34639888.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.643	19886.186	414557.438	2.2247
2		11.283	782270.563	18220066.000	97.7753
Total			802156.748	18634623.438	100.0000

Diethyl (S)-((dimethyl(naphthalen-1-yl)silyl)(phenyl)methyl)phosphonate (5g)

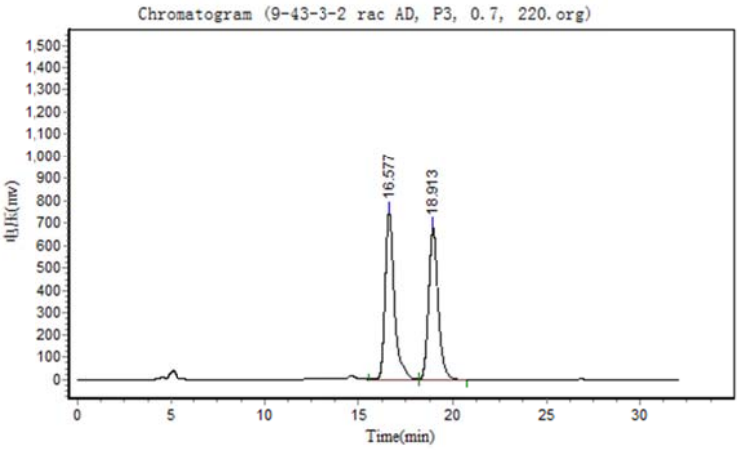


5g

Colorless oil, 58%, 99% ee;

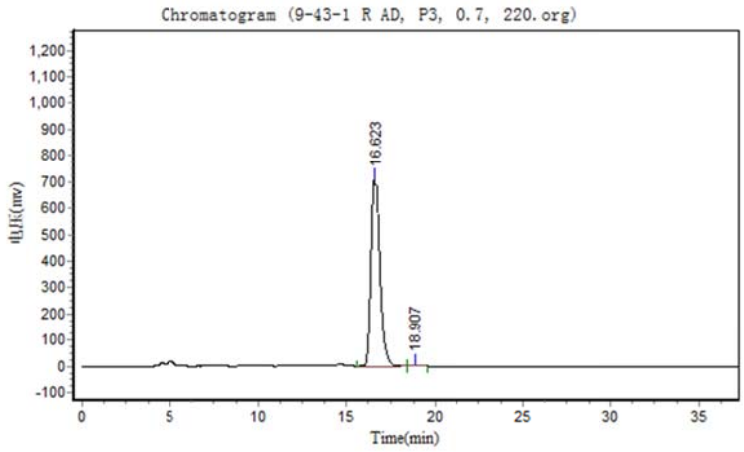
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.6 Hz, 1H), 7.87 – 7.83 (m, 2H), 7.57 – 7.39 (m, 3H), 7.36 (d, *J* = 15.0 Hz, 1H), 7.13 – 7.08 (m, 5H), 3.93 – 3.64 (m, 4H), 3.29 (d, *J* = 24.9 Hz, 1H), 0.97 (dd, *J* = 12.9, 6.8 Hz, 6H), 0.79 (s, 3H), 0.44 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.8, 134.8, 133.5, 130.3, 129.5, 129.42, 129.35, 128.3, 128.0, 125.9, 125.8, 125.4, 125.04 (s), 61.8 (dd, *J* = 195.3, 3.8 Hz), 36.8 (d, *J* = 126.0 Hz), 16.1 (dd, *J* = 14.6, 6.5 Hz), -0.7, -1.5 (d, *J* = 2.9 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 28.5. ESI-MS (*m/z*, %) 435 $[M+Na]^+$; ESI-HRMS calcd for $C_{23}H_{29}O_3NaPSi$ $[M+Na]^+$ 435.1516, found 435.1504. $[\alpha]_D^{25}$ = -87.7 (*c* 0.8, $CHCl_3$).

HPLC: Chiralpak AD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 95/5; flow = 0.7 mL/min; Retention time: 16.6 min (major), 18.9 min.



Results

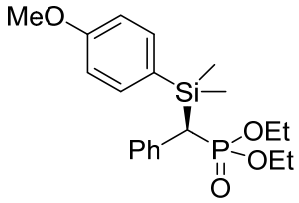
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.577	752456.250	25740554.000	51.6765
2		18.913	675875.250	24070380.000	48.3235
Total			1428331.500	49810934.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.623	709063.000	22480690.000	99.3181
2		18.907	4945.635	154357.094	0.6819
Total			714008.635	22635047.094	100.0000

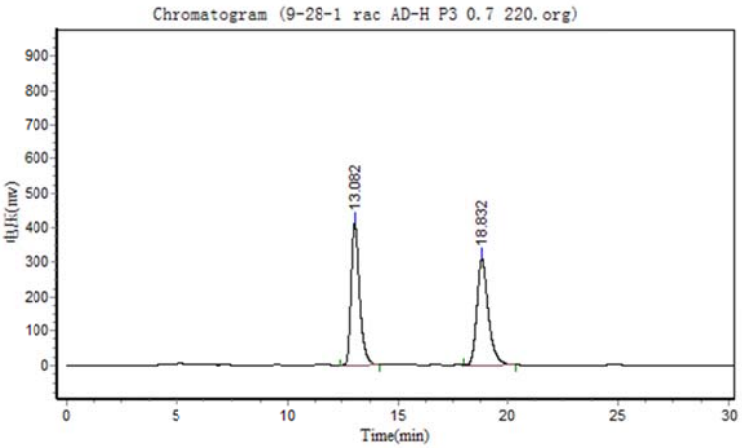
Diethyl (S)-(((4-methoxyphenyl)dimethylsilyl)(phenyl)methyl)phosphonate (5h)



Colorless oil, 55%, 97% ee;

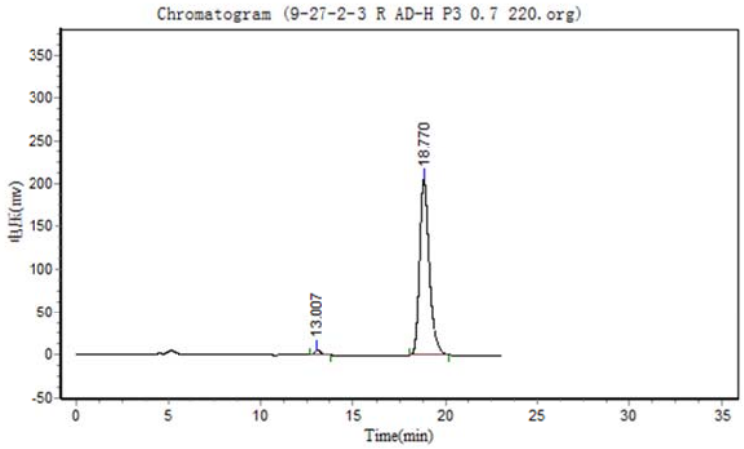
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 2H), 7.22 – 7.00 (m, 5H), 6.83 (d, *J* = 8.5 Hz, 2H), 4.03 – 3.65 (m, 7H), 2.84 (d, *J* = 24.3 Hz, 1H), 1.14 (t, *J* = 7.0 Hz, 3H), 1.03 (t, *J* = 7.0 Hz, 3H), 0.48 (s, 3H), 0.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 135.9, 134.8 (d, *J* = 7.1 Hz), 129.6 (d, *J* = 8.3 Hz), 128.3, 127.5 (d, *J* = 4.1 Hz), 125.7, 113.3, 61.8 (dd, *J* = 157.5, 8.8 Hz), 55.1, 37.5 (d, *J* = 163.8 Hz), 16.2 (dd, *J* = 7.6, 5.0 Hz), -2.7, -2.8. ^{31}P NMR (202 MHz, $CDCl_3$) δ 28.6. ESI-MS (*m/z*, %) 415 $[M+Na]^+$; ESI-HRMS calcd for $C_{20}H_{29}O_4NaPSi$ $[M+Na]^+$ 415.1465, found 415.1453. $[\alpha]_D^{25}$ = -42.5 (*c* 0.4, $CHCl_3$).

HPLC: Chiralpak AD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 95/5; flow = 0.7 mL/min; Retention time: 13.0 min, 18.8 min (major).



Results

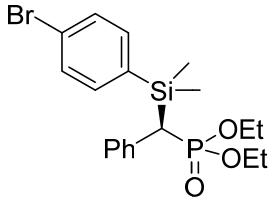
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.082	412105.594	11035258.000	49.7837
2		18.832	310032.188	11131159.000	50.2163
Total			722137.781	22166417.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.007	5418.510	136267.250	1.7985
2		18.770	204377.266	7440335.500	98.2015
Total			209795.775	7576602.750	100.0000

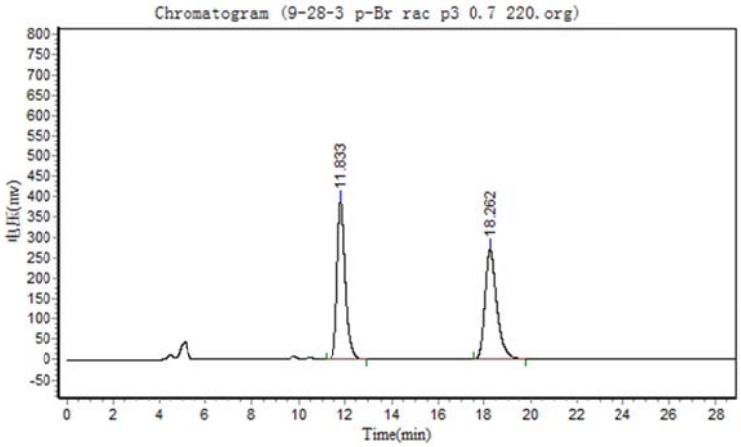
Diethyl (S)-(((4-bromophenyl)dimethylsilyl)(phenyl)methyl)phosphonate (5i)



Colorless oil, 52%, 92% ee;

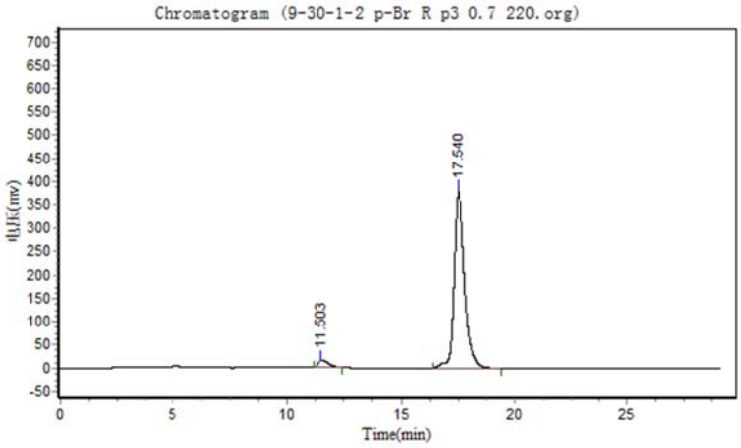
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.1 Hz, 2H), 7.26 – 7.13 (m, 5H), 7.06 (d, *J* = 6.7 Hz, 2H), 4.03 – 3.65 (m, 4H), 2.84 (d, *J* = 24.4 Hz, 1H), 1.14 (t, *J* = 7.0 Hz, 3H), 1.02 (t, *J* = 7.0 Hz, 3H), 0.48 (s, 3H), 0.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.0, 135.6, 134.4 (d, *J* = 7.0 Hz), 130.7, 129.6 (d, *J* = 8.2 Hz), 128.4, 125.9, 124.3, 61.9 (dd, *J* = 170.1, 6.3 Hz), 37.2 (d, *J* = 126.0 Hz), 16.3 (dd, *J* = 6.2, 3.6 Hz), -2.9, -3.0. ^{31}P NMR (202 MHz, $CDCl_3$) δ 28.0. ESI-MS (*m/z*, %) 441 $[M+H]^+$; ESI-HRMS calcd for $C_{19}H_{27}O_3BrPSi$ $[M+H]^+$ 441.0645, found 441.0637. $[\alpha]_D^{25}$ = -30.5 (*c* 0.5, $CHCl_3$).

HPLC: Chiralpak AD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 95/5; flow = 0.7 mL/min; Retention time: 11.5 min, 17.5 min (major).



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.833	388304.781	9686532.000	50.2737
2		18.262	270580.250	9581060.000	49.7263
Total			658885.031	19267592.000	100.0000



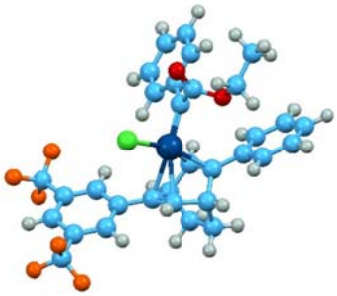
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.503	14348.884	501859.563	3.8068
2		17.540	378160.156	12681523.000	96.1932
Total			392509.040	13183382.563	100.0000

6. The calculated cartesian coordinates for the minima

The coordinates, total free energies (Hartree/Particle) of strucure for the minima were calculated at by Guassian09 at the B3LYP level of theory. In these calculations, the lanl2dz basis set was used to rhodium atom and the 6-31+G** basis were used to other atoms.

Intermediate A_vac



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C	6.11101100	3.35901600	22.22852400
C	5.33238500	4.52260200	
C	5.53546100	5.53568500	23.18153800
C	8.62670700	6.60284400	
C	7.23018400	6.05698700	24.18093500
C	6.50577800	5.39841200	
C	6.72337100	6.46937900	24.23034100
O	8.20453900	6.84272100	
O	6.72188100	5.13180300	23.29927000
H	10.54688900	5.76047800	
H	9.28660500	4.54773900	18.10578200
H	10.04432600	5.43332700	
H	7.99848000	4.06391400	19.95739600
H	7.67705700	2.29952300	
H	5.95648100	2.57111100	22.27784600
H	4.56619100	4.63295800	
H	4.92920200	6.43532700	21.31714000
C	9.78127900	7.29662800	
C	11.86016100	6.86308900	19.47791100
C	7.02298200	8.60172600	
C	8.08646000	8.94002800	19.35010400
C	8.05330800	10.44176000	
C	6.64578500	10.76299100	18.66089300
C	5.65749200	10.47305400	
C	6.21658700	9.80467500	18.32412800
C	7.20748300	10.80663800	
C	8.29918600	11.21180600	16.98999800
C	4.24601400	10.90409300	

C	3.43023500	11.00308500	21.44485700
C	2.11466200	11.46185300	
C	1.25844900	11.60372900	23.13813800
C	1.58182800	11.83137400	
C	2.38791100	11.73175000	24.91278600
C	3.69827100	11.26949800	
C	1.79401400	12.10338300	24.99200700
C	9.37341400	8.20064200	
C	10.24490600	8.42020500	23.31674400
C	11.47248900	7.76361800	
C	11.00594200	6.63092300	23.56358800
Cl	4.62970400	8.39920500	
F	2.72838700	12.22594700	22.39689100
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F	0.89175200	11.18417200	23.54200900
F	1.06241300	12.90887900	
F	0.02665600	11.06368800	22.67236100
F	1.80719600	11.00536400	
Rh	6.31156300	8.28671600	22.34317800
H	9.14540500	7.12275800	
H	12.81748500	6.35373100	21.87346900
H	7.04473700	7.70977900	
H	8.79558100	10.71734100	22.77200200
H	6.48024400	11.32334300	
H	5.43468500	9.48832500	24.02960100
H	7.64925400	10.32158500	
H	6.65626400	11.68249900	24.71110600
H	9.30152500	10.97085900	
H	8.27432100	12.28819500	23.68534400
H	3.81341700	10.73638400	
H	0.56029200	12.18777200	22.65216000
H	4.28285500	11.16127800	
H	9.94827600	9.09119900	23.79026100
H	12.12637600	7.95271200	
H	11.29725500	5.94152800	23.69073400
H	9.01577500	7.57054400	
H	7.74516500	6.34945600	24.92346300
			22.45671200
			21.31889200
			21.40740600

19.98144400
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20.68263400
20.55264400
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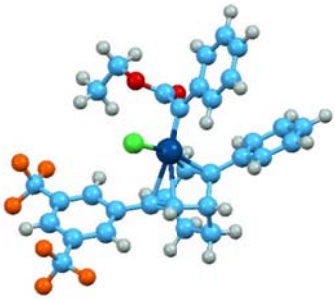
17.78164600
17.51290000

Zero-point correction=	0.509140 (Hartree/Particle)
Thermal correction to Energy=	0.548146
Thermal correction to Enthalpy=	0.549090
Thermal correction to Gibbs Free Energy=	0.430517
Sum of electronic and zero-point Energies=	-2553.884885
Sum of electronic and thermal Energies=	-2553.845878
Sum of electronic and thermal Enthalpies=	-2553.844934
Sum of electronic and thermal Free Energies=	-2553.963507

Intermediate B_vac

Atomic type	Corrdinates (Angstroms)		
			
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C	8.95197000	4.71999000	18.59194900
C	8.54670600	6.03877700	18.35604100
C	7.82256500	6.72927100	19.32222400
C	4.14007700	4.80343700	23.32361100
C	6.09327300	6.01948700	22.65052500
C	7.47087400	6.10225400	20.54332900
C	6.69830900	6.81683300	21.53535900
O	4.89450900	5.52773700	22.31016600
O	6.64206800	5.84999800	23.72948800
H	2.59754000	6.31749400	23.46026800
H	3.86485700	6.45486000	24.70153400
H	2.64206800	5.17660100	24.82120500
H	7.63315900	4.26528000	21.69055100
H	8.93808000	3.06077600	19.97623600
H	9.52096800	4.18464000	17.83678800
H	8.79238500	6.52390400	17.41619300
H	7.47810900	7.74097900	19.14126100
C	9.87729200	7.66506100	23.51171000
C	11.86489700	7.15625800	22.22090800
C	7.14904100	9.04030500	23.62658600
C	8.17452200	9.33761100	22.69822000
C	8.12462100	10.82121800	22.29915200
C	6.69662200	11.09966200	21.85867300
C	5.74201600	10.84841600	22.80882800

C	6.35546900	10.26230500	24.08276900
C	7.35821300	11.30807100	24.67129700
C	8.41117200	11.66213400	23.58823800
C	4.32459500	11.27040800	22.72648100
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C	2.25654700	11.92597600	23.83421400
C	1.47417200	12.17815600	25.09803600
C	1.65338600	12.19073900	22.60558600
C	2.39263500	11.98866700	21.43629700
C	3.70687700	11.53023900	21.48793900
C	1.72048300	12.24289400	20.10838500
C	9.43647800	8.56967800	22.52826300
C	10.24094000	8.74752200	21.38696100
C	11.44026900	8.05123000	21.23447400
C	11.07538300	6.96542100	23.35829800
Cl	4.89378300	8.78765800	19.77587900
F	2.59667300	12.29916800	19.08327300
F	1.03824900	13.42044000	20.11749100
F	0.81275300	11.27854500	19.81065900
F	1.32120900	13.50811500	25.33950900
F	0.22434200	11.65480600	25.03335100
F	2.07179700	11.64888200	26.19330900
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H	9.28178200	7.50801600	24.40454800
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H	7.16995900	8.15556700	24.25410800
H	8.83774100	11.06273300	21.51128900
H	6.49282500	11.61494800	20.92630200
H	5.60260800	9.97656400	24.81755600
H	7.83313300	10.87668500	25.55881000
H	6.81211000	12.19963500	24.99825900
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H	8.37302500	12.72605000	23.33183900
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H	9.91876200	9.42164300	20.59923600
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Zero-point correction= 0.509111 (Hartree/Particle)

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Thermal correction to Enthalpy=	0.549155
Thermal correction to Gibbs Free Energy=	0.430180
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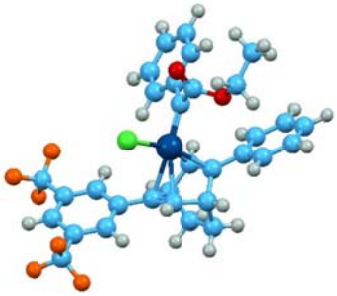
Sum of electronic and thermal Energies=	-2553.854889
Sum of electronic and thermal Enthalpies=	-2553.853945
Sum of electronic and thermal Free Energies=	-2553.972920

Intermediate A_Sol



Atomic type	Corrdinates (Angstroms)		
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C	5.18862200	4.68363200	24.23356800
C	5.48062400	5.70219900	23.33413300
C	9.10009800	6.25003300	18.47798800
C	7.24803500	6.13483700	19.99468100
C	6.37754700	5.48632700	22.25683300
C	6.68208000	6.55270500	21.32217100
O	8.50569700	6.52478600	19.78564500
O	6.55469000	5.52836100	19.19066900
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H	7.65570600	4.00407700	21.30906400
H	7.16105800	2.22016500	22.93201600
H	5.57525000	2.63649400	24.80129000
H	4.48829200	4.86059100	25.04382300
H	5.00826100	6.67384700	23.42911300
C	9.85040900	7.37619800	23.31109200
C	11.94284800	7.08879600	22.12047800
C	7.12342100	8.71353100	23.48656500
C	8.14320000	9.08403600	22.57992000

C	8.04204800	10.57880600	22.24174700
C	6.60867500	10.82963800	21.81136300
C	5.65899400	10.50927300	22.74706600
C	6.28788900	9.88612300	23.99535400
C	7.25606900	10.93718900	24.63116600
C	8.29589600	11.37360800	23.56778400
C	4.22848700	10.89094700	22.66975300
C	3.38790300	10.78681200	23.78608400
C	2.04783800	11.18890800	23.71820700
C	1.20247000	11.08563000	24.96045600
C	1.51353400	11.70098500	22.54110400
C	2.34845200	11.80473700	21.42055700
C	3.67879500	11.40692400	21.47710900
C	1.76064800	12.33775300	20.13952400
C	9.43922800	8.37579000	22.40795600
C	10.31636200	8.71692700	21.36124600
C	11.55237600	8.08478000	21.21959800
C	11.08326300	6.73670000	23.16632100
Cl	4.56982300	8.49034800	19.82089800
F	2.68764900	12.53587000	19.17529300
F	1.12754500	13.52735900	20.33092600
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F	1.59034900	11.97972200	25.91326600
F	-0.10972400	11.31476300	24.72365100
F	1.29298300	9.85812200	25.53848000
Rh	6.30484500	8.39969600	21.52017800
H	9.21334400	7.10403000	24.14609400
H	12.90559400	6.59764600	22.01263100
H	7.19120100	7.82290000	24.10182200
H	8.74279500	10.88361800	21.46652200
H	6.40232100	11.38306000	20.90235300
H	5.55173100	9.54212300	24.71961700
H	7.74279900	10.47985300	25.49846800
H	6.67664300	11.79153200	24.99571100
H	9.31889100	11.18037100	23.90648900
H	8.21877200	12.44397500	23.35249300
H	3.76578600	10.39808800	24.72351400
H	0.47670700	12.01164200	22.49172700
H	4.28869600	11.48449200	20.58756300
H	10.02704100	9.46893700	20.63471400
H	12.20839300	8.36762800	20.40114800
H	11.37713200	5.97246600	23.88036900
H	9.81873400	7.06055400	18.34727100
H	8.31890100	6.32958000	17.71980600

Zero-point correction=	0.508447 (Hartree/Particle)
Thermal correction to Energy=	0.547643
Thermal correction to Enthalpy=	0.548587
Thermal correction to Gibbs Free Energy=	0.429345
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Sum of electronic and thermal Energies=	-2553.872291
Sum of electronic and thermal Enthalpies=	-2553.871346
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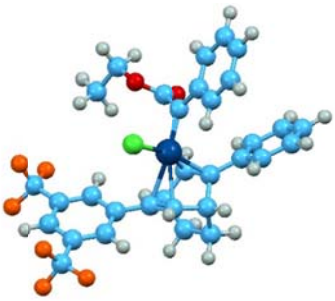
Intermediate B_Sol



Atomic type	Corrdinates (Angstroms)		
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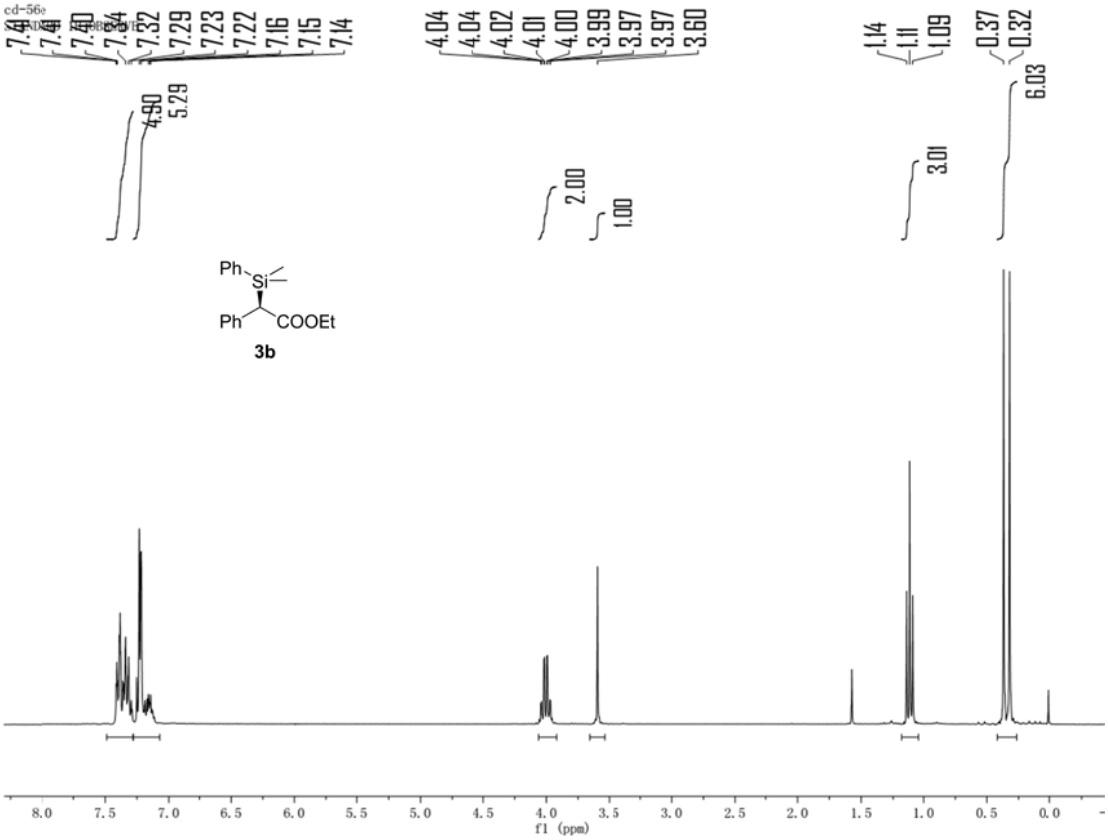
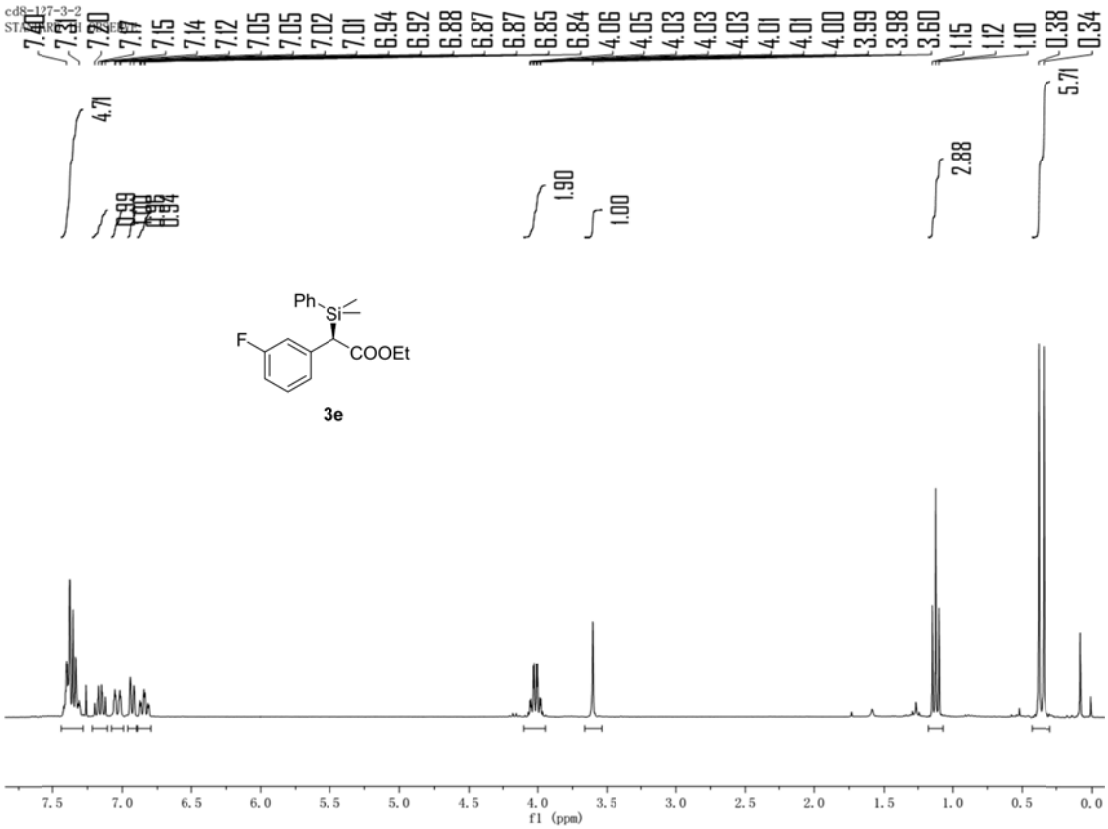
C	8.42263200	3.98890300	19.72944000
C	8.92155100	4.66530200	18.60762000
C	8.69895400	6.04013300	18.45182800
C	7.98483500	6.74120000	19.41625700
C	4.03496000	4.93567700	23.35140600
C	6.05510400	6.02846500	22.64271100
C	7.46411100	6.07781300	20.55767800
C	6.69698800	6.80887100	21.53682500
O	4.80046600	5.67143100	22.34463300
O	6.63275400	5.76786100	23.68953100
H	2.62329800	6.54272400	23.69712600
H	3.97952900	6.50548200	24.84966400
H	2.67743500	5.30768800	24.96954900
H	7.31916500	4.15040600	21.55798100
H	8.59848300	2.92427700	19.84637100
H	9.48187700	4.11975800	17.85395400
H	9.08338400	6.55785300	17.57871500
H	7.79786900	7.80263700	19.30193600
C	9.92115700	7.70259200	23.49129200
C	11.90969300	7.20950100	22.19414000
C	7.17915900	9.04491900	23.61157800
C	8.19631300	9.35092700	22.67647200
C	8.12984000	10.83107800	22.27241600

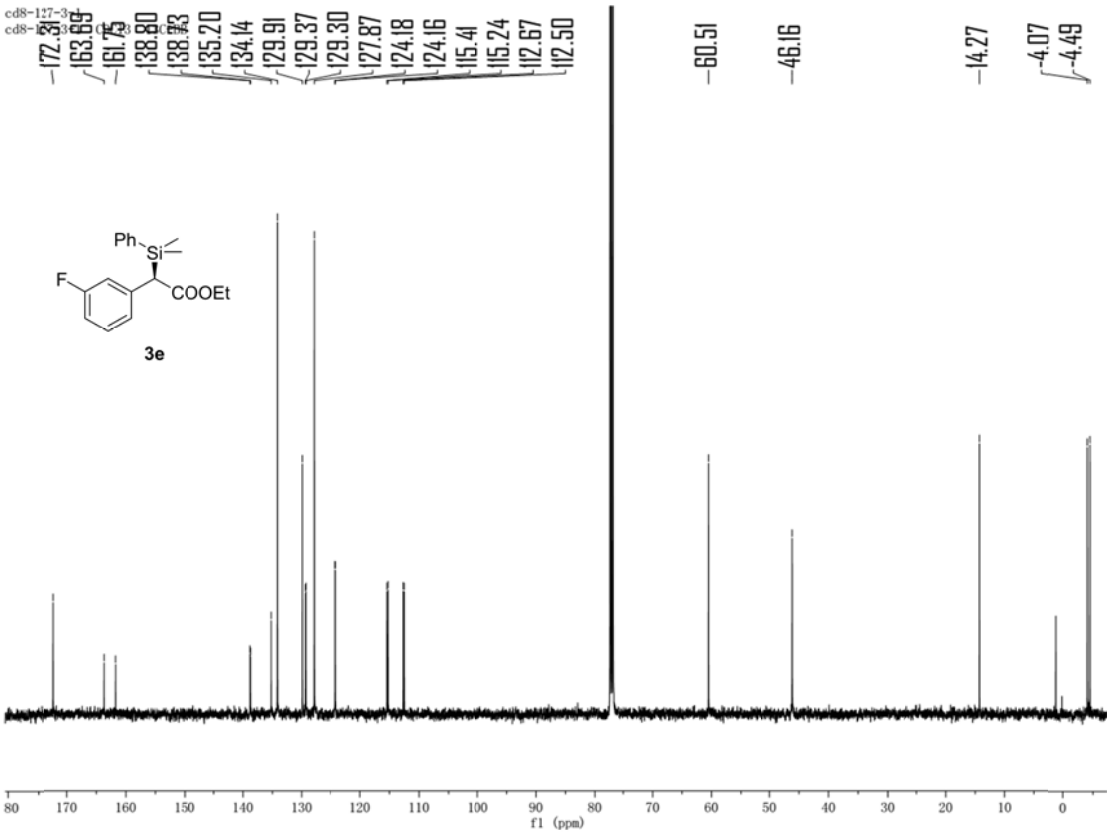
C	6.69652700	11.09154100	21.84202000
C	5.75036400	10.83383900	22.80093700
C	6.37691700	10.25875700	24.07343700
C	7.37578400	11.31460300	24.65042400
C	8.41377100	11.67924900	23.55804800
C	4.32867300	11.24449900	22.72222500
C	3.55548300	11.37742100	23.88836300
C	2.23119600	11.81411000	23.82164400
C	1.42263800	11.99464800	25.08004300
C	1.63882200	12.12518800	22.59709400
C	2.40286300	11.99313300	21.43511600
C	3.72634100	11.55805500	21.49016200
C	1.76571600	12.27019800	20.09747100
C	9.46441300	8.59478200	22.50266000
C	10.26455500	8.78095200	21.35917100
C	11.47210000	8.09752800	21.20583300
C	11.12740300	7.01560500	23.33722300
Cl	4.83598300	8.72696800	19.75535900
F	2.66252700	12.69388400	19.17389400
F	0.79848400	13.21882100	20.17596900
F	1.17139200	11.16006900	19.57734000
F	1.21212300	13.31104500	25.36332800
F	0.19054800	11.42968300	24.97973700
F	2.01714900	11.45437400	26.16972700
Rh	6.36805300	8.66998200	21.64786300
H	9.33859000	7.55341900	24.39422100
H	12.85001800	6.67876000	22.07687400
H	7.21625300	8.16484000	24.24474900
H	8.83292100	11.07910300	21.47852200
H	6.48854400	11.61582800	20.91578900
H	5.63625800	9.96570900	24.81635100
H	7.86194300	10.88554000	25.53241900
H	6.82211000	12.19879600	24.98247100
H	9.43591000	11.47938800	23.89555000
H	8.35773700	12.74028400	23.29508200
H	3.98227700	11.15524500	24.85742300
H	0.60979100	12.46229000	22.54758000
H	4.28366900	11.43919100	20.57000200
H	9.93672900	9.45347000	20.57282600
H	12.06869100	8.25643900	20.31200200
H	11.45992200	6.33601300	24.11682900
H	4.71855600	4.28791100	23.90315700
H	3.35103900	4.32449000	22.76060000

Zero-point correction=	0.508293(Hartree/Particle)
Thermal correction to Energy=	0.547526
Thermal correction to Enthalpy=	0.548470
Thermal correction to Gibbs Free Energy=	0.429572
Sum of electronic and zero-point Energies=	-2553.917179
Sum of electronic and thermal Energies=	-2553.877946
Sum of electronic and thermal Enthalpies=	-2553.877001
Sum of electronic and thermal Free Energies=	-2553.995899

7. Copies of ^{1}H NMR and ^{13}C NMR spectra of products and catalyst



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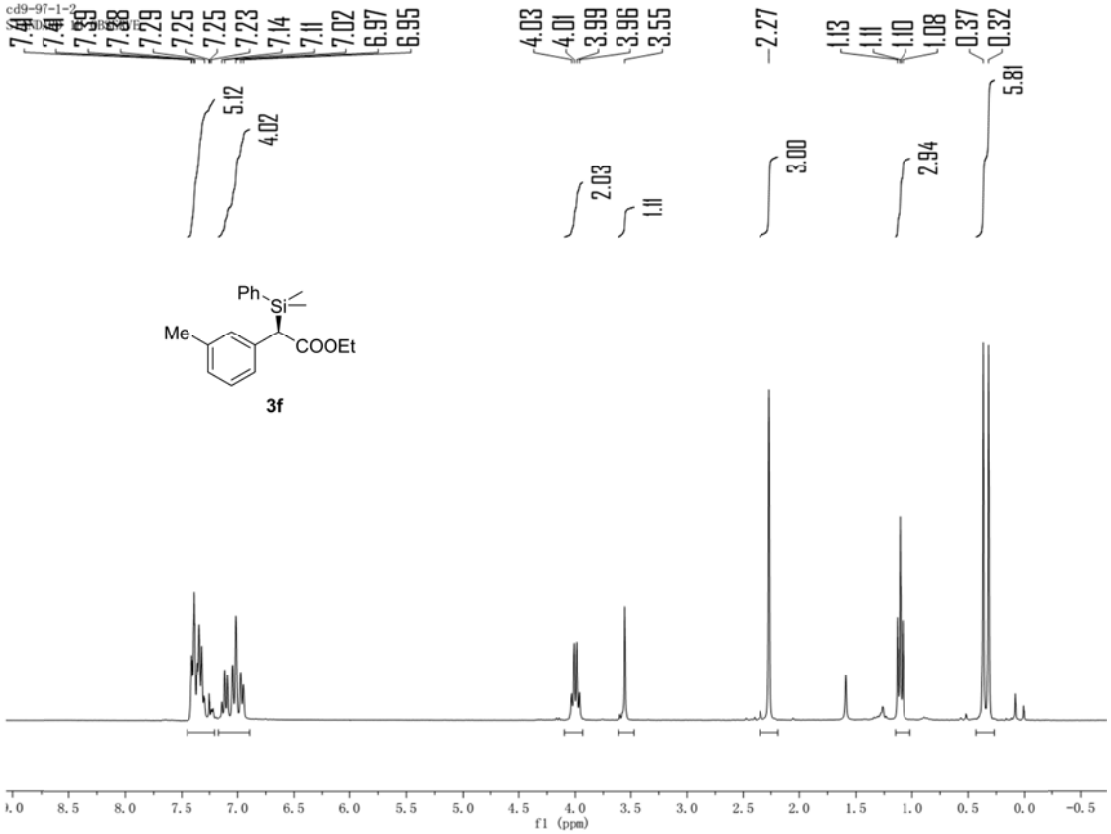
161.75
138.80
138.43
135.20
134.14
129.91
129.37
129.30
127.87
124.18
124.16
115.41
115.24
112.67
112.50
60.51
46.16
14.27
-4.07
-4.49
Ph
Si
F
COOEt
3e
f1 (ppm)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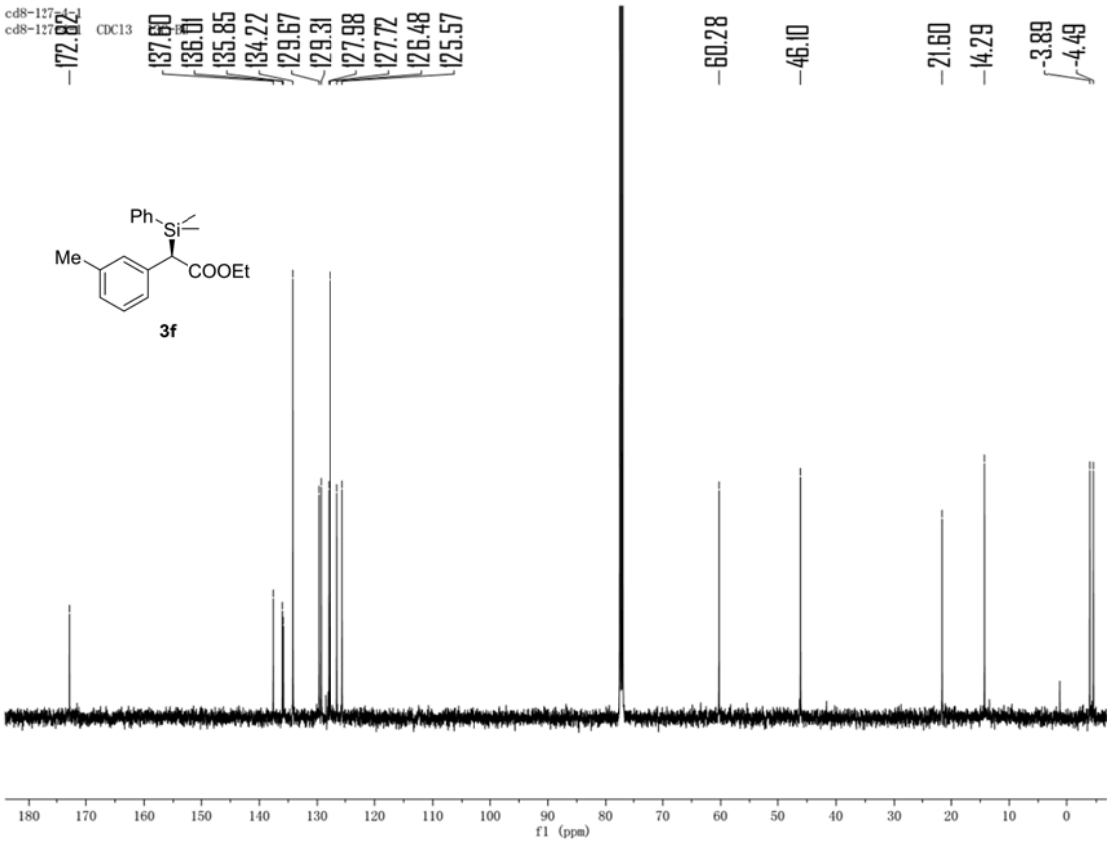
7.39
7.29
7.25
7.23
7.14
7.11
7.02
6.97
6.95
4.03
4.01
3.99
3.96
3.55
2.27
1.13
1.11
1.10
1.08
0.37
0.32
5.12
4.02
2.03
1.11
3.00
2.94
5.81
Ph
Si
Me
COOEt
3f
f1 (ppm)


cd8-127
cd8-127
CDCl3
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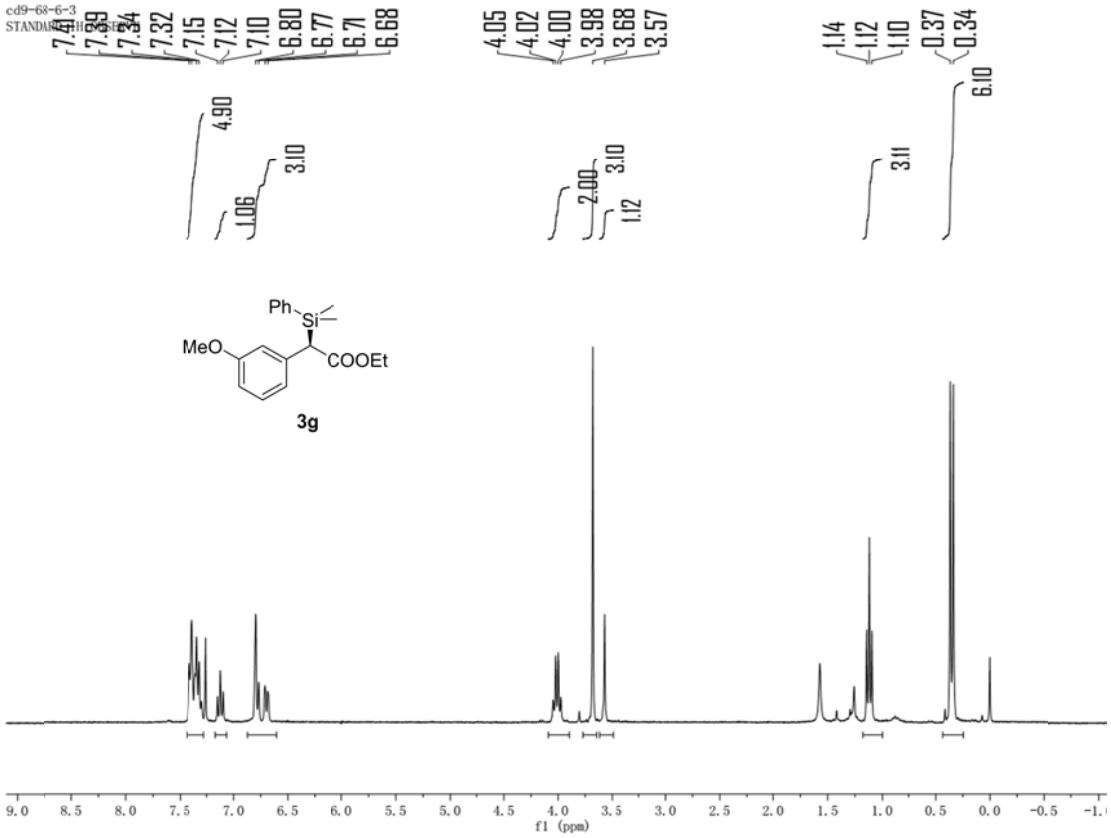
137.60
136.01
135.85
134.22
129.67
129.31
127.98
127.72
126.48
125.57
60.28
46.10
21.60
14.29
3.89
-4.49
Ph
Si
Me
COOEt
3f
f1 (ppm)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7.41
7.39
7.34
7.32
7.15
7.12
7.10
6.80
6.77
6.71
6.68
4.05
4.02
4.00
3.98
3.68
3.57
1.14
1.12
1.10
0.37
0.34
4.90
3.10
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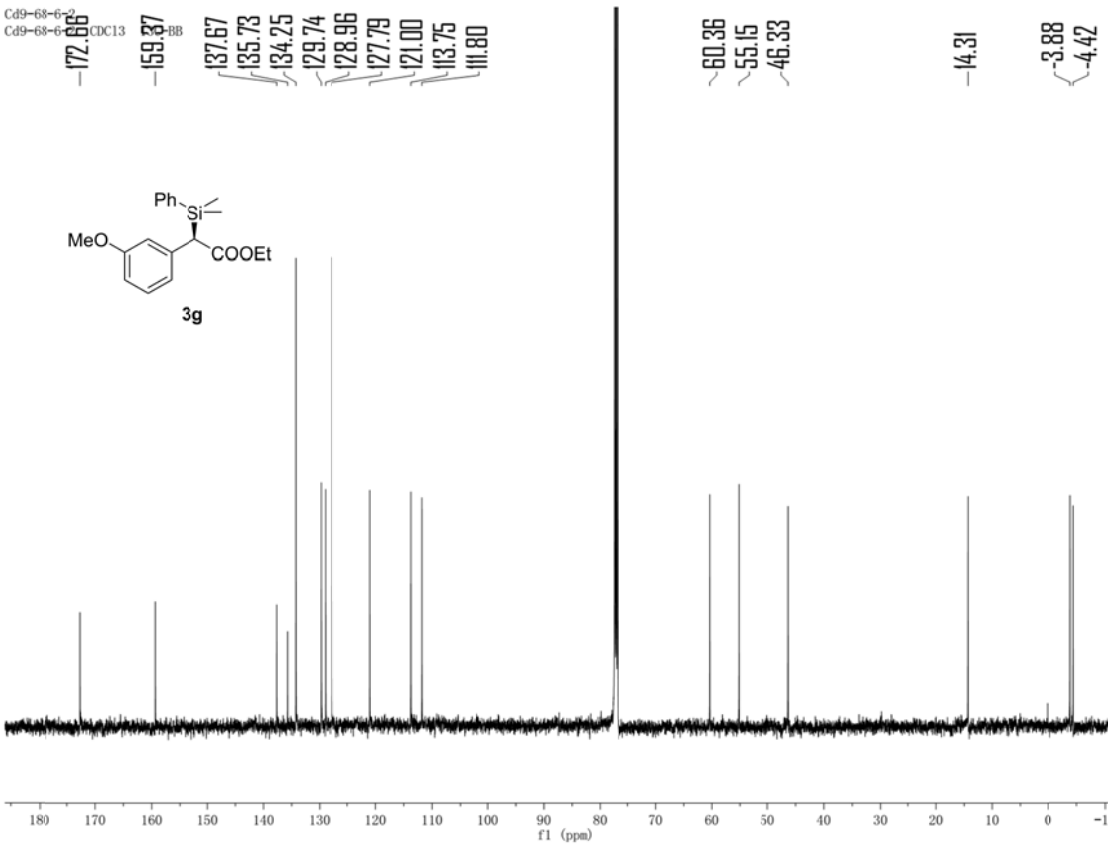
3.10
1.12
3.11
6.10
Ph
Si
MeO
COOEt
3g
f1 (ppm)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137.67
135.73
134.25
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127.79
121.00
113.75
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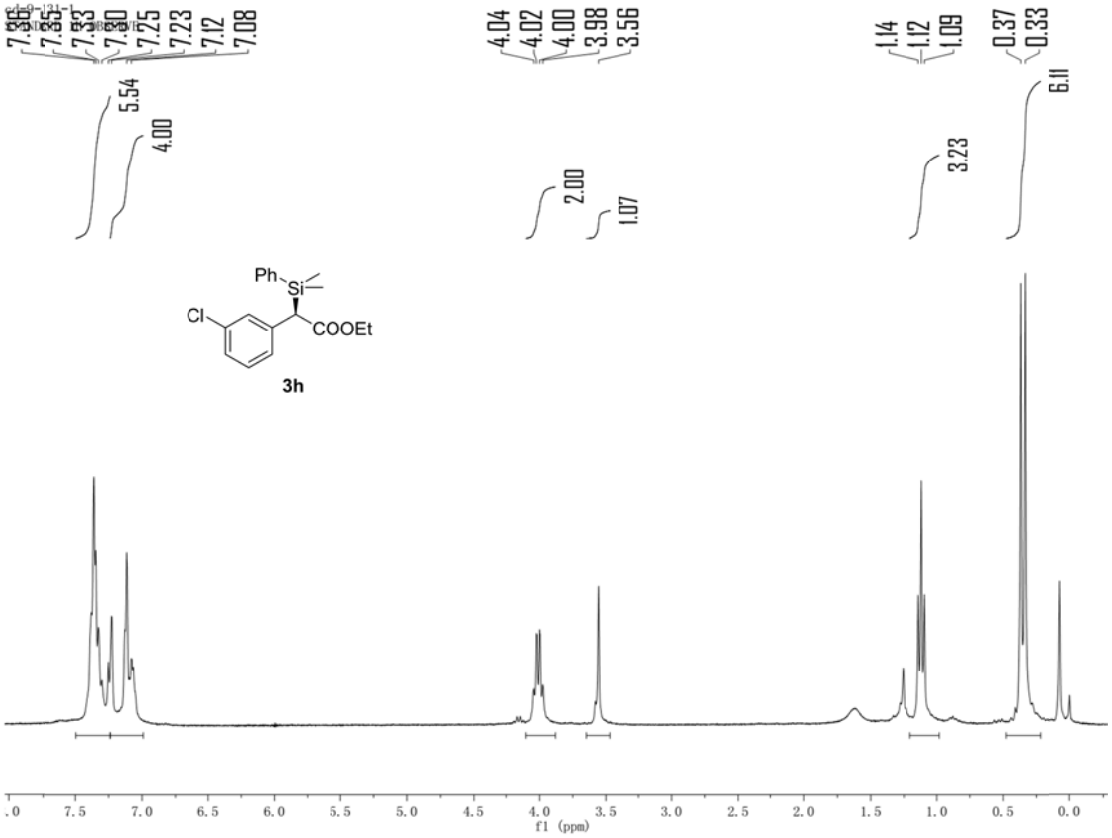
46.33
14.31
-3.88
-4.42
Ph
Si
MeO
COOEt
3g
f1 (ppm)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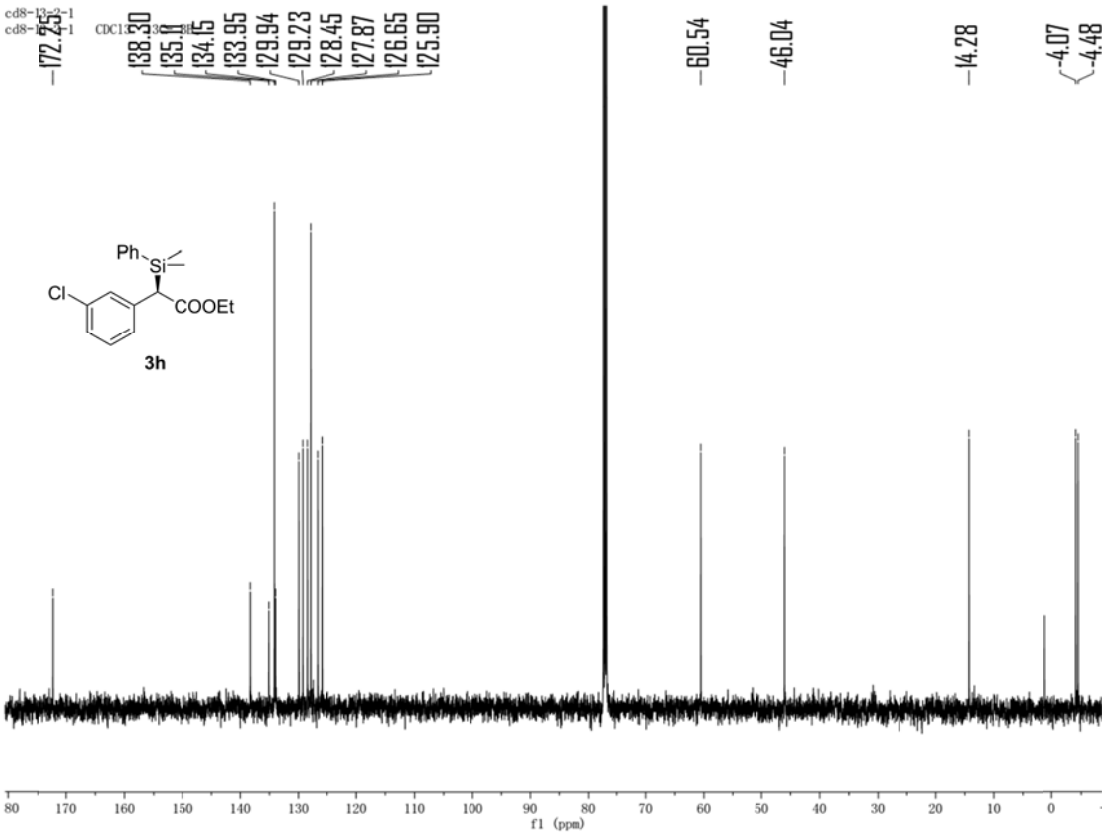
7.35
7.33
7.30
7.25
7.23
7.12
7.08
4.04
4.02
4.00
3.98
3.56
1.14
1.12
1.09
0.37
0.33
5.54
4.00
2.00
1.07
3.23
6.11
Ph
Si
Cl
COOEt
3h
f1 (ppm)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135.11
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133.95
129.94
129.23
128.45
127.87
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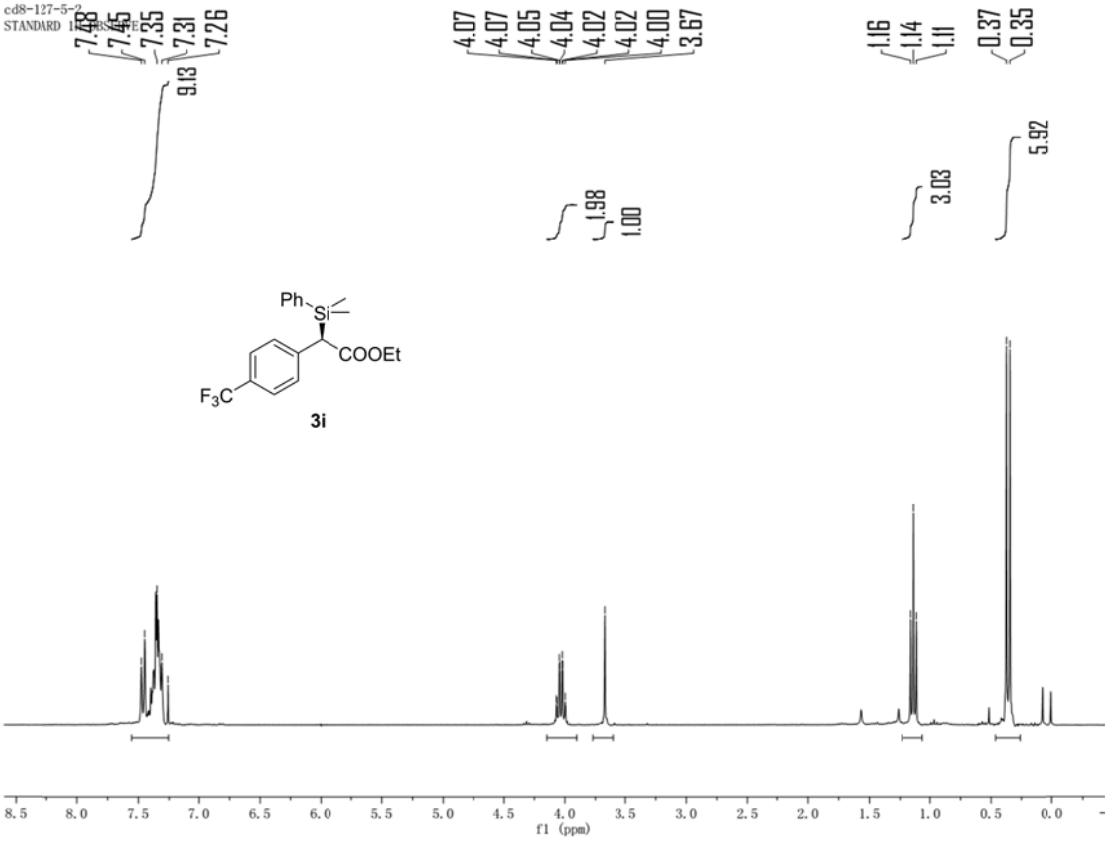
125.90
60.54
46.04
14.28
-4.07
-4.48
Ph
Si
Cl
COOEt
3h
f1 (ppm)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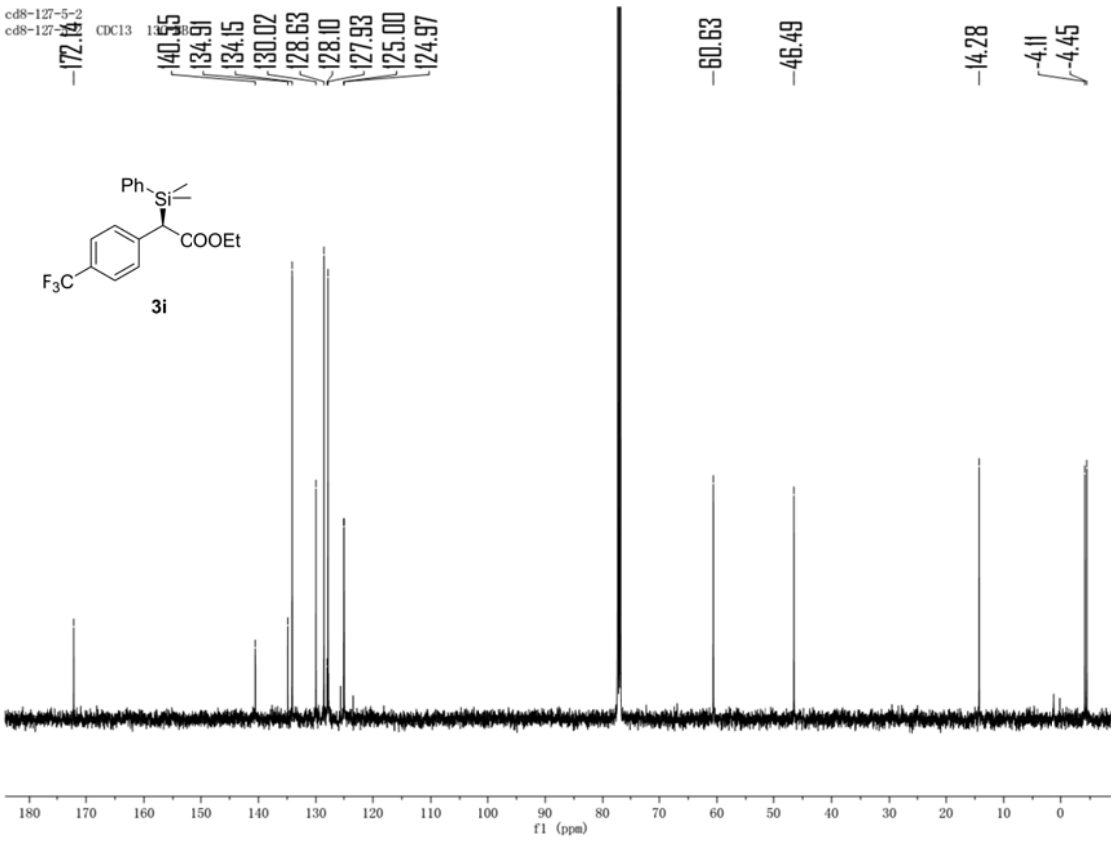
7.35
7.31
7.26
9.13
4.07
4.07
4.05
4.04
4.02
4.02
4.00
3.67
1.98
1.00
1.16
1.14
1.11
3.03
0.37
0.35
5.92
Ph
Si
COOEt
F3C
3i
f1 (ppm)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130.02
128.63
128.10
127.93
125.00
124.97
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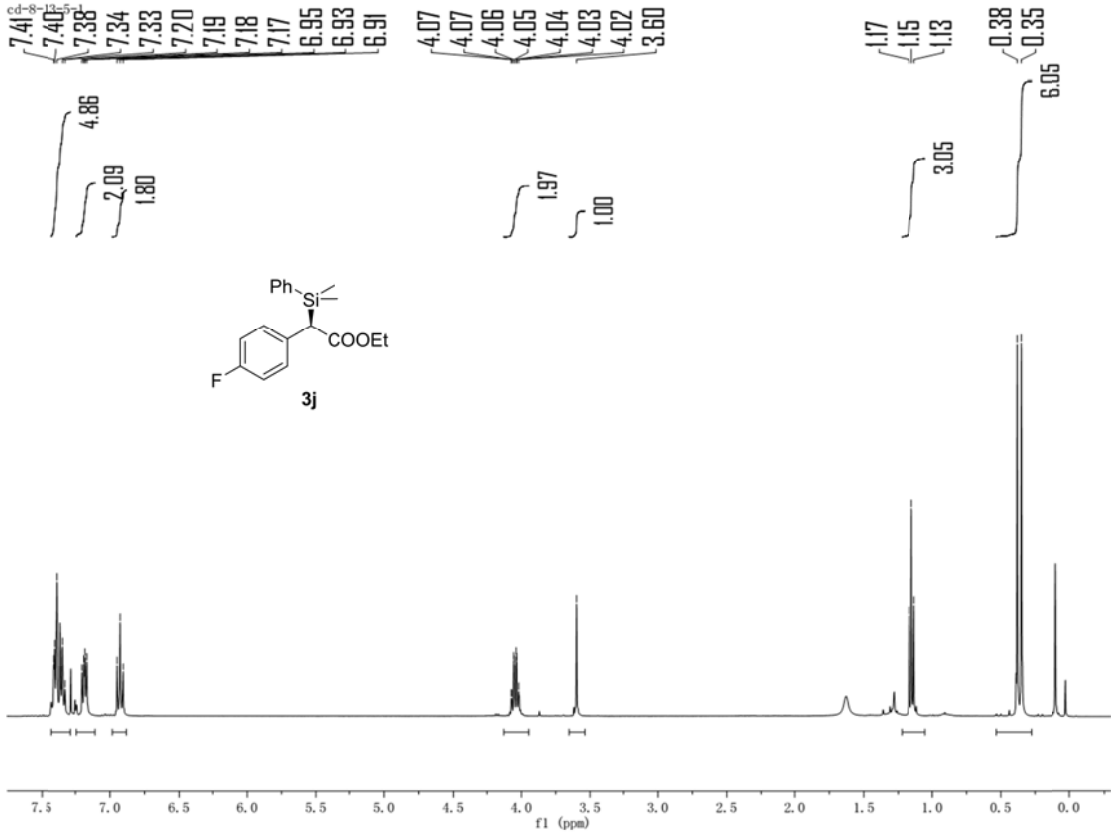
46.49
14.28
-4.11
-4.45
Ph
Si
COOEt
F3C
3i
f1 (ppm)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7.20
7.19
7.18
7.17
6.95
6.93
6.91
4.07
4.07
4.06
4.05
4.04
4.03
4.02
3.60
1.17
1.15
1.13
0.38
0.35
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1.80
1.97
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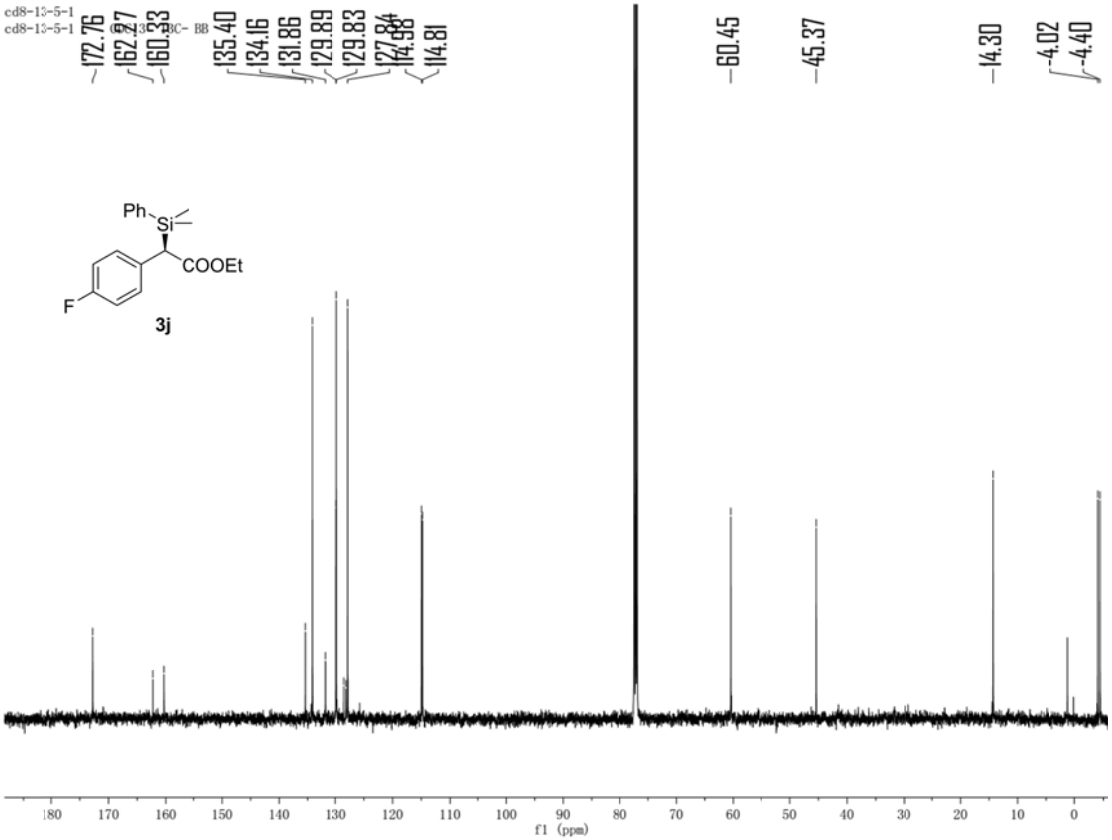
6.05
Ph
Si
COOEt
F
3j
f1 (ppm)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cd8-13-5-1
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135.40
134.16
131.86
129.89
129.83
127.84
114.81
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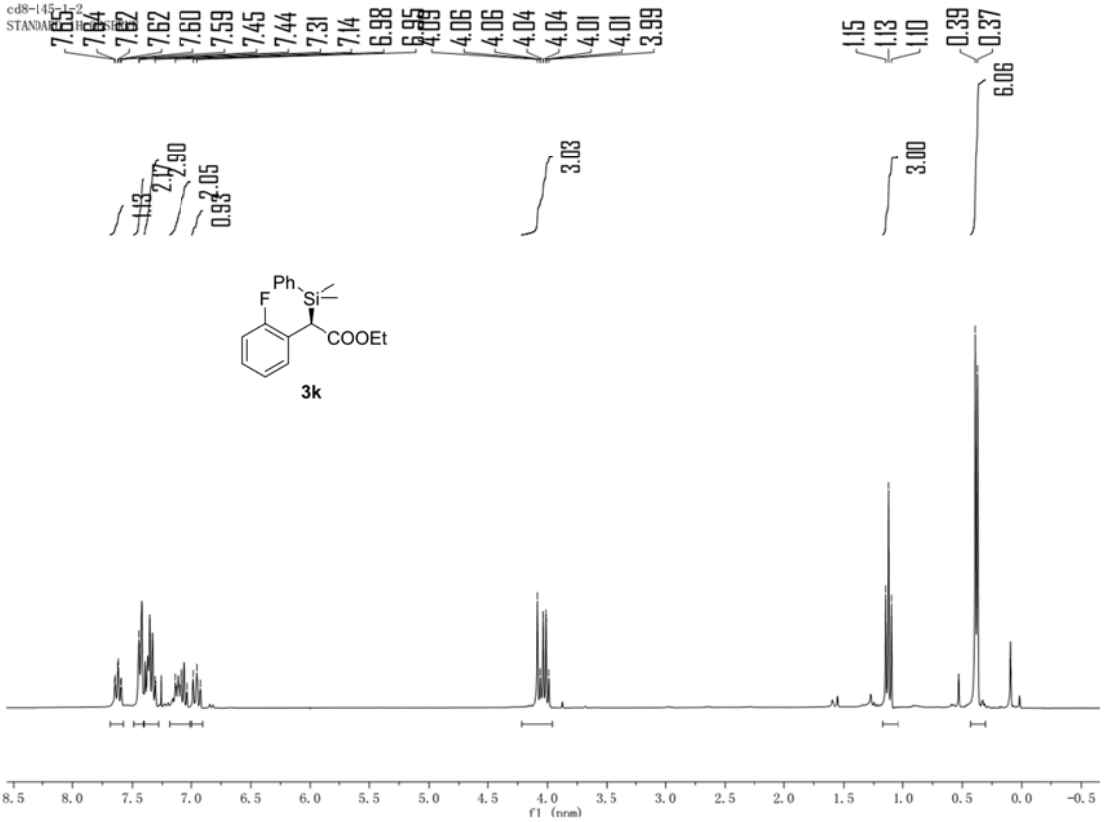
45.37
14.30
-4.02
-4.40
Ph
Si
COOEt
F
3j
f1 (ppm)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7.64
7.62
7.60
7.59
7.45
7.44
7.31
7.14
6.98
4.06
4.04
4.01
3.99
1.15
1.13
1.10
0.39
0.37
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3.03
3.00
2.90
2.05
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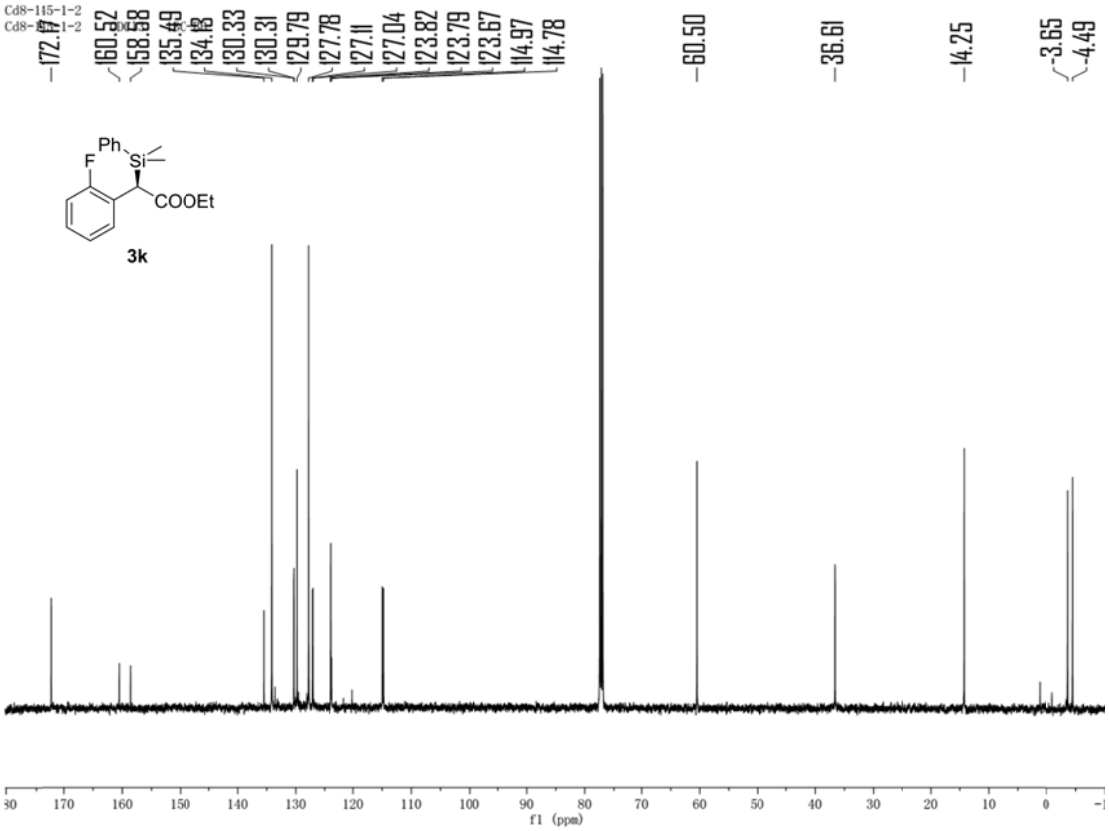
Ph
Si
F
COOEt
3k
f1 (ppm)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135.49
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130.33
130.31
129.79
127.78
127.11
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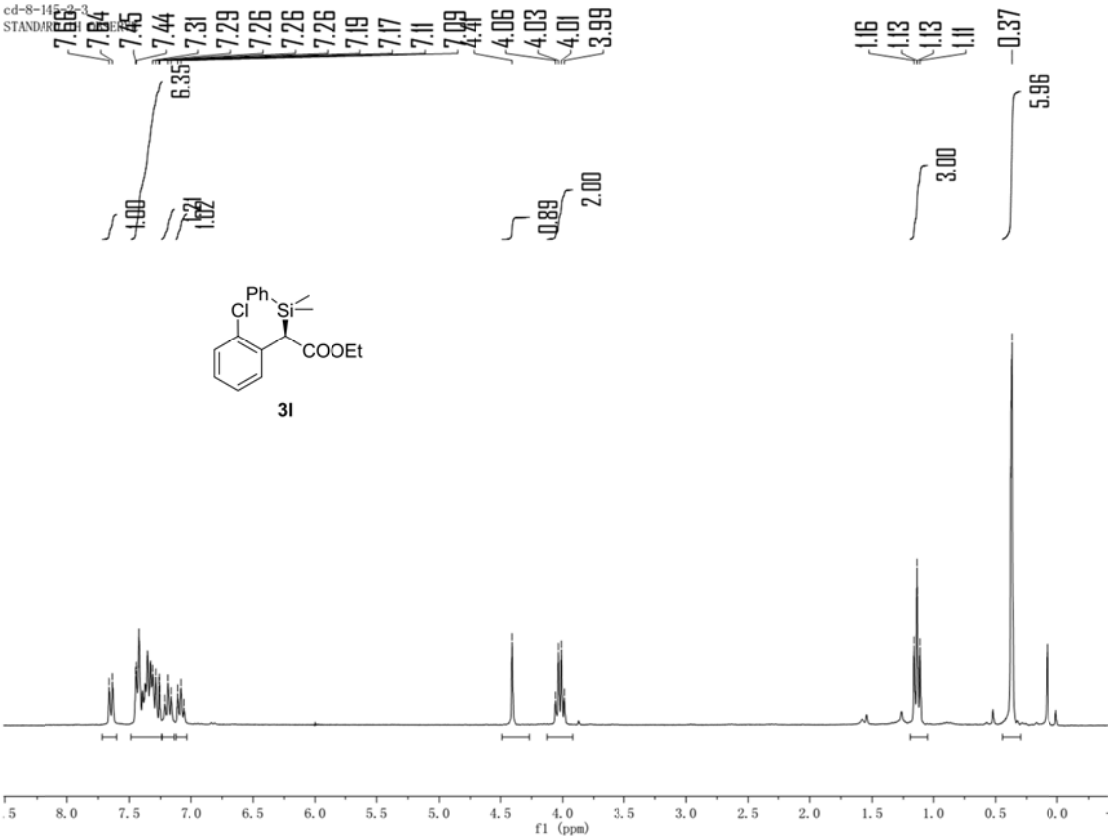
123.82
123.79
123.67
114.97
114.78
60.50
36.61
14.25
-3.65
-4.49
Ph
Si
F
COOEt
3k
f1 (ppm)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7.64
7.45
7.44
7.31
7.29
7.26
7.26
7.26
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7.17
7.11
7.09
4.41
4.06
4.03
4.01
3.99
1.16
1.13
1.13
1.11
0.37
6.35
5.96
3.00
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1.00
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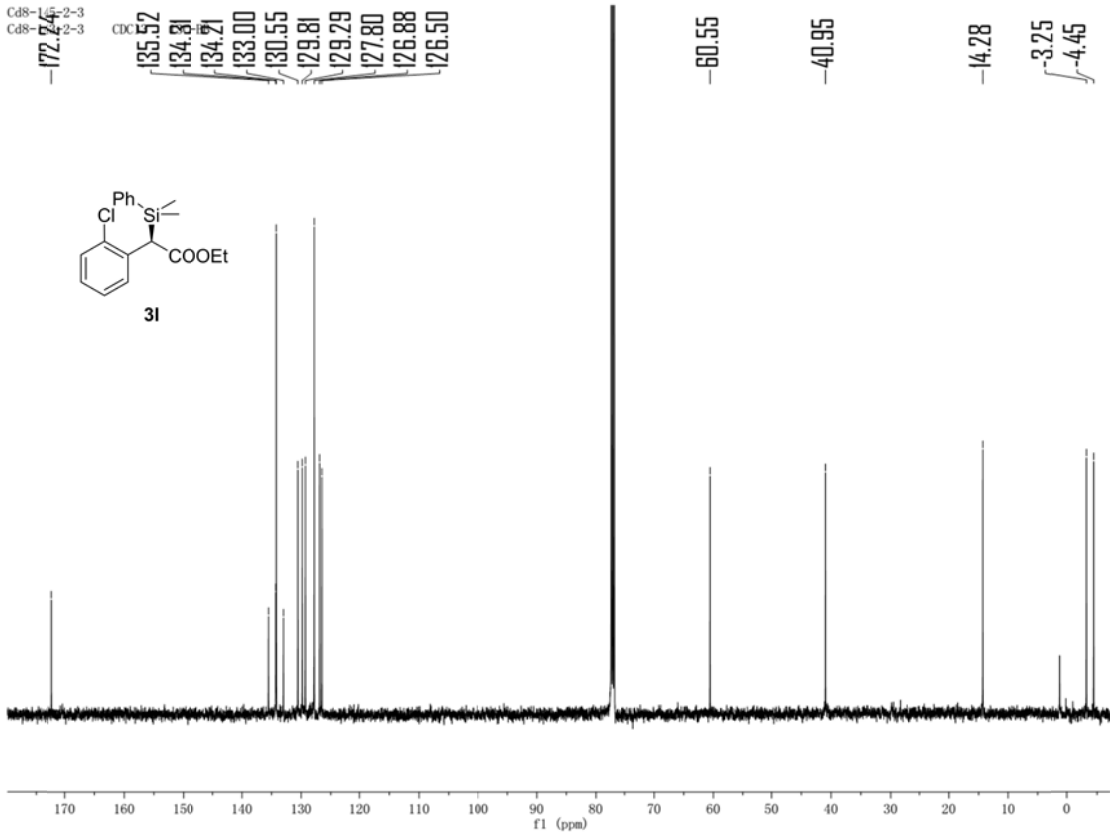
Ph
Si
Cl
COOEt
3l
f1 (ppm)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Cd8-1j5-2-3
CDCl3
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134.21
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129.81
129.29
127.80
126.88
126.50
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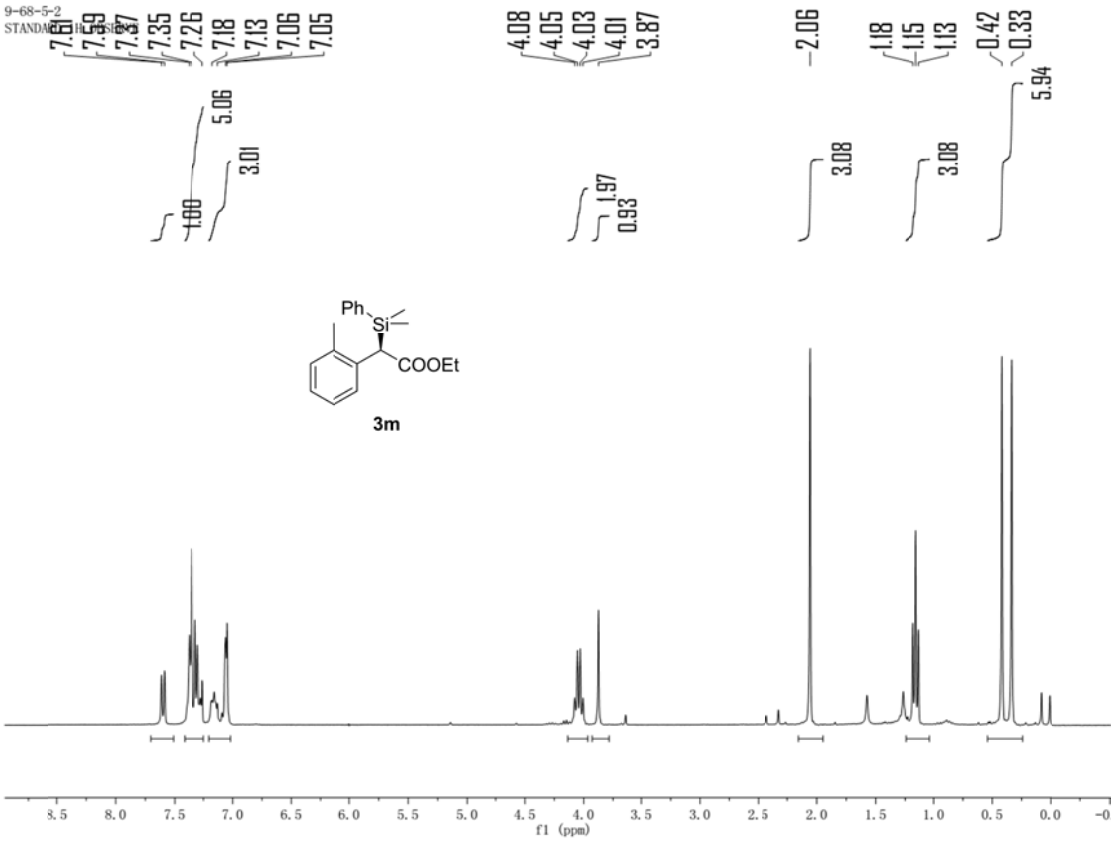
40.95
14.28
-3.25
-4.45
Ph
Si
Cl
COOEt
3l
f1 (ppm)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7.59
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7.35
7.26
7.18
7.13
7.06
7.05
4.08
4.05
4.03
4.01
3.87
2.06
1.18
1.15
1.13
0.42
0.33
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1.97
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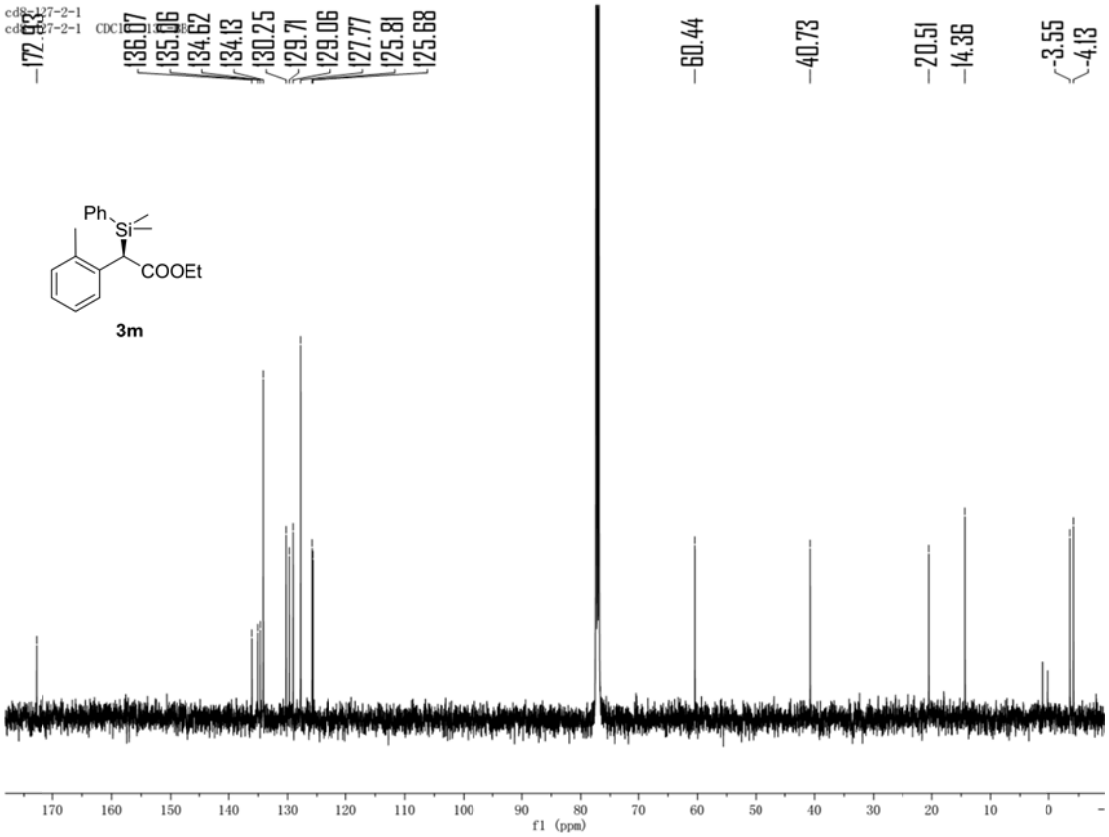
3.08
3.08
5.94
Ph
Si
COOEt
3m
f1 (ppm)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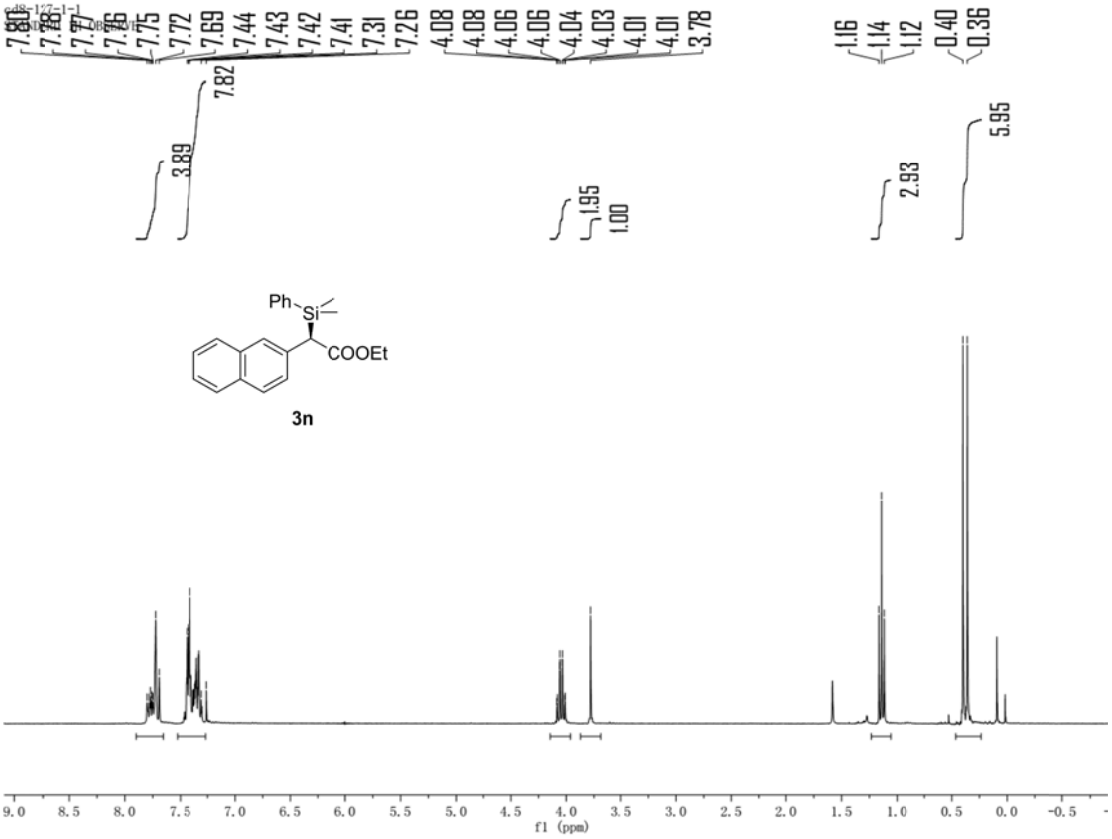
Ph
Si
COOEt
3m
f1 (ppm)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7.26
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4.08
4.06
4.06
4.04
4.03
4.01
4.01
3.78
1.16
1.14
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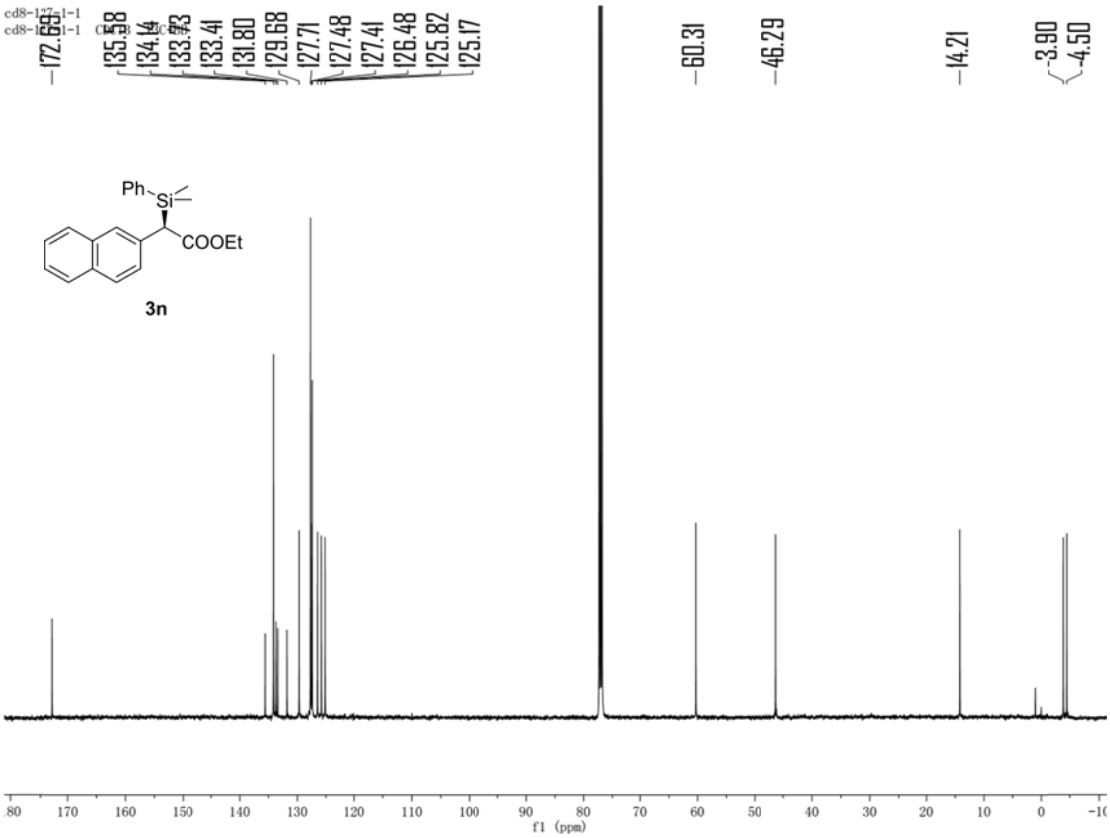
Ph
Si
COOEt
3n
f1 (ppm)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46.29
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Si
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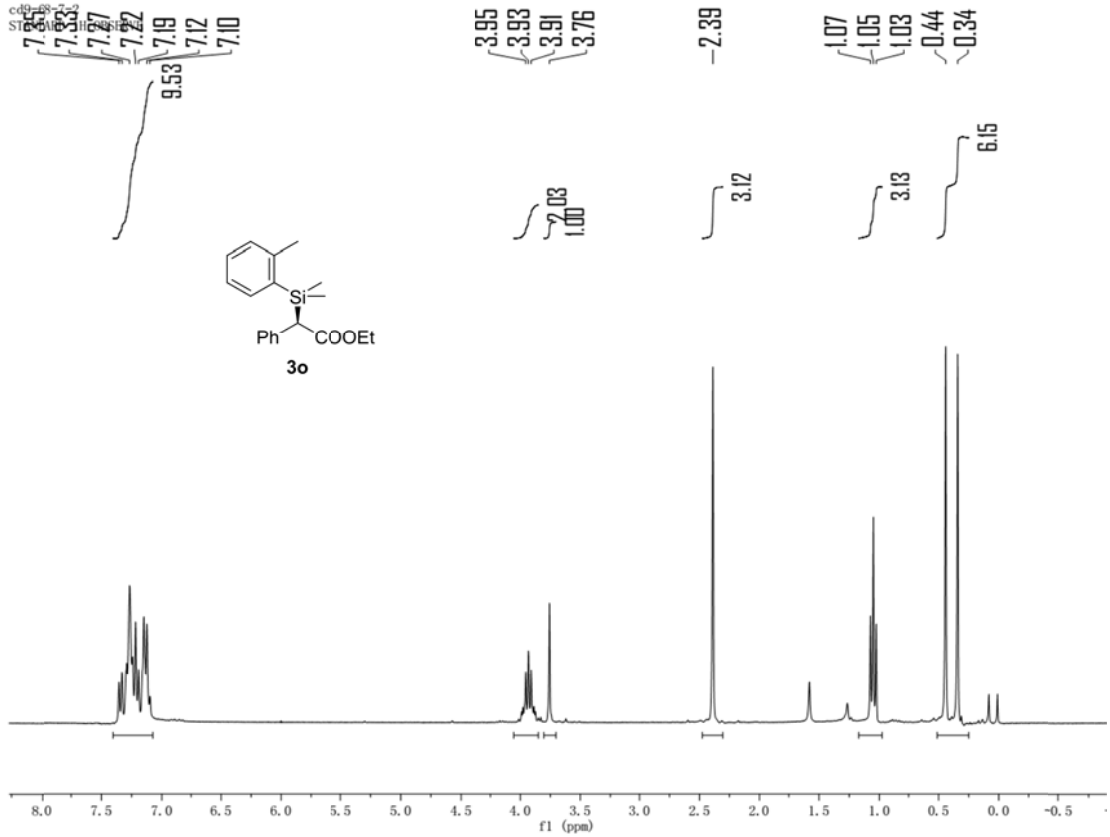
3n
f1 (ppm)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2.03
1.00
2.39
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6.15
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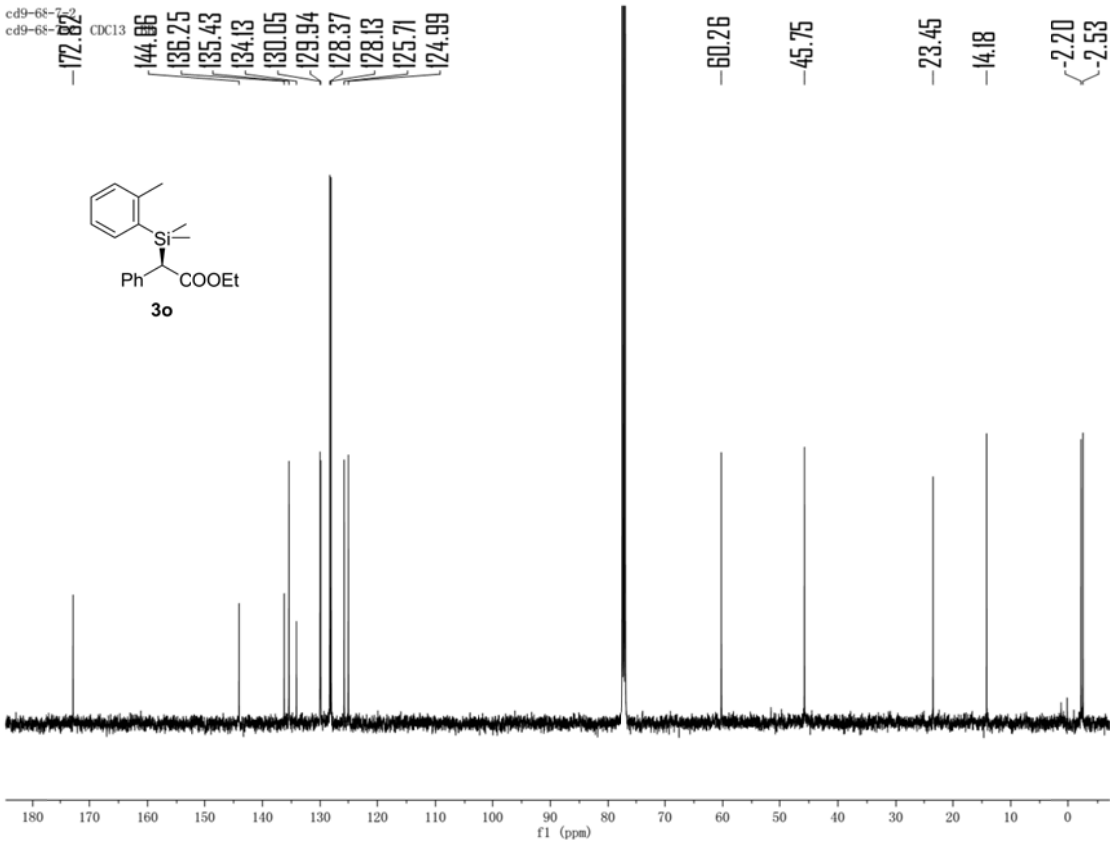
Ph
COOEt
3o
f1 (ppm)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cd9-68-7-2 CDC13
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128.13
125.71
124.99
60.26
45.75
23.45
14.18
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-2.53
Si
Ph
COOEt
3o
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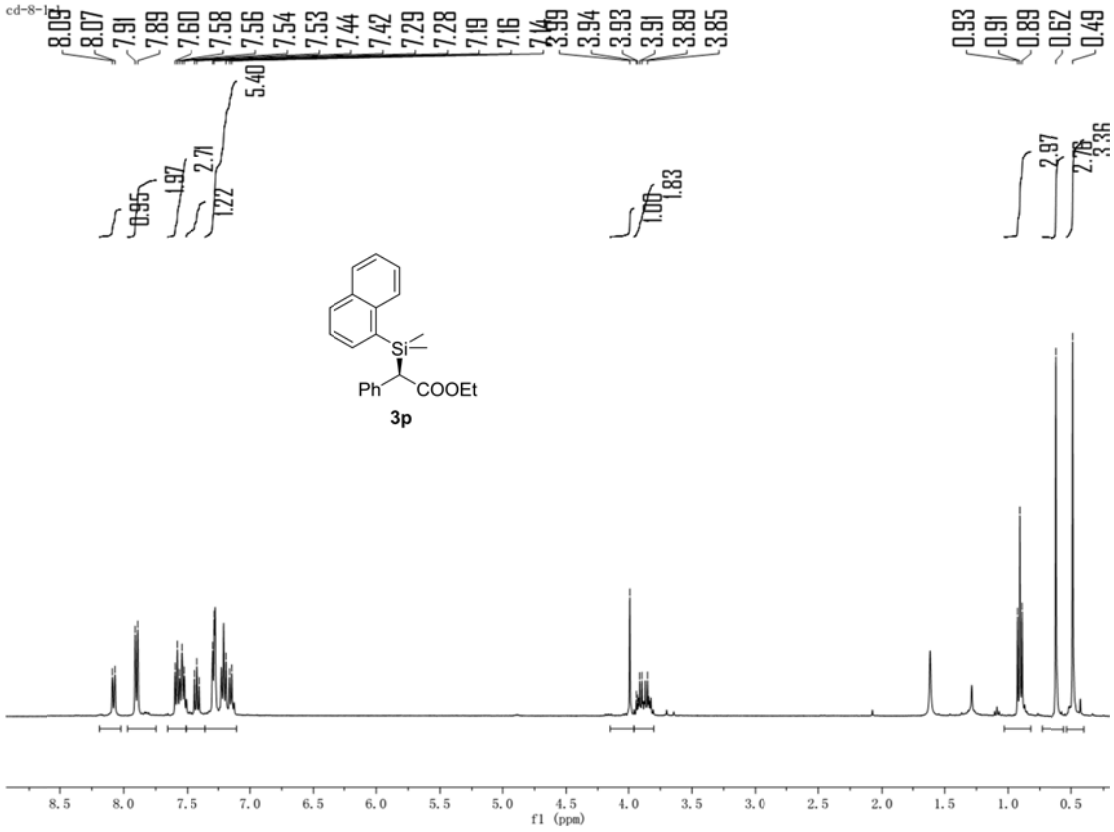
f1 (ppm)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7.29
7.28
7.19
7.16
3.99
3.94
3.93
3.91
3.89
3.85
0.93
0.91
0.89
0.62
0.49
5.40
0.95
1.97
2.71
1.22
1.06
1.83
2.97
2.76
3.36
Si
Ph
COOEt
3p
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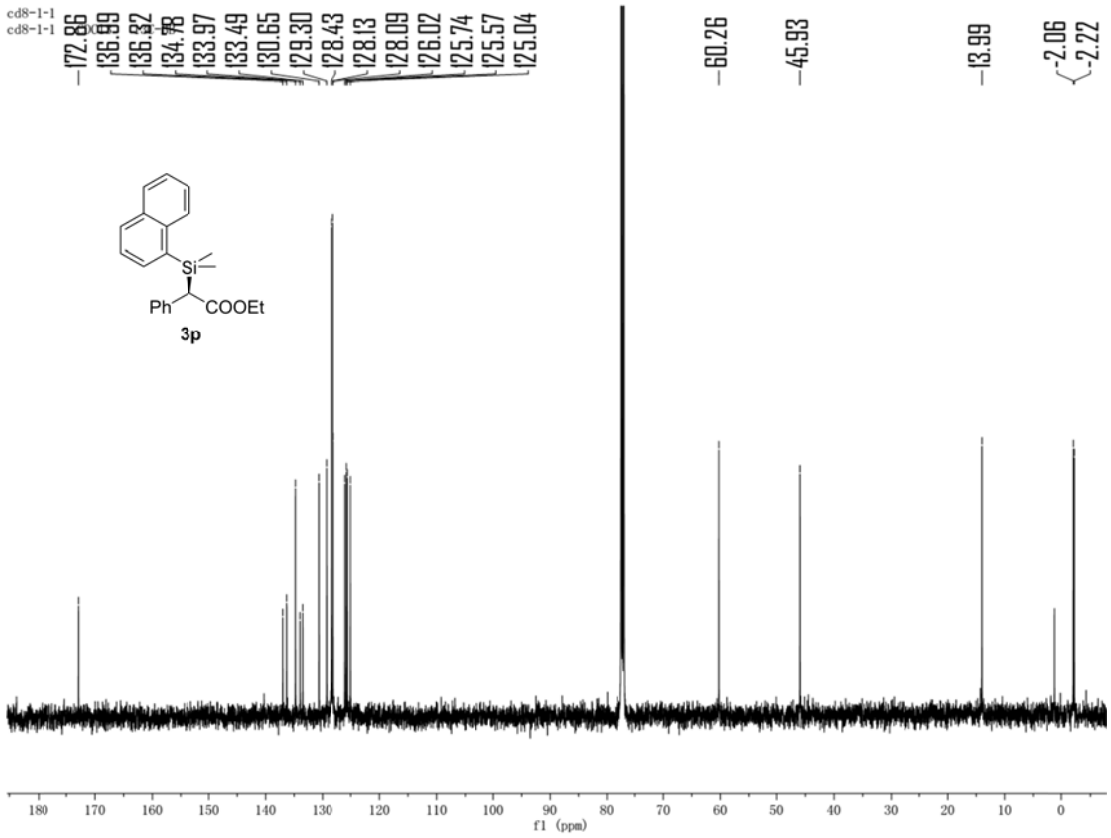
f1 (ppm)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cd8-1-1
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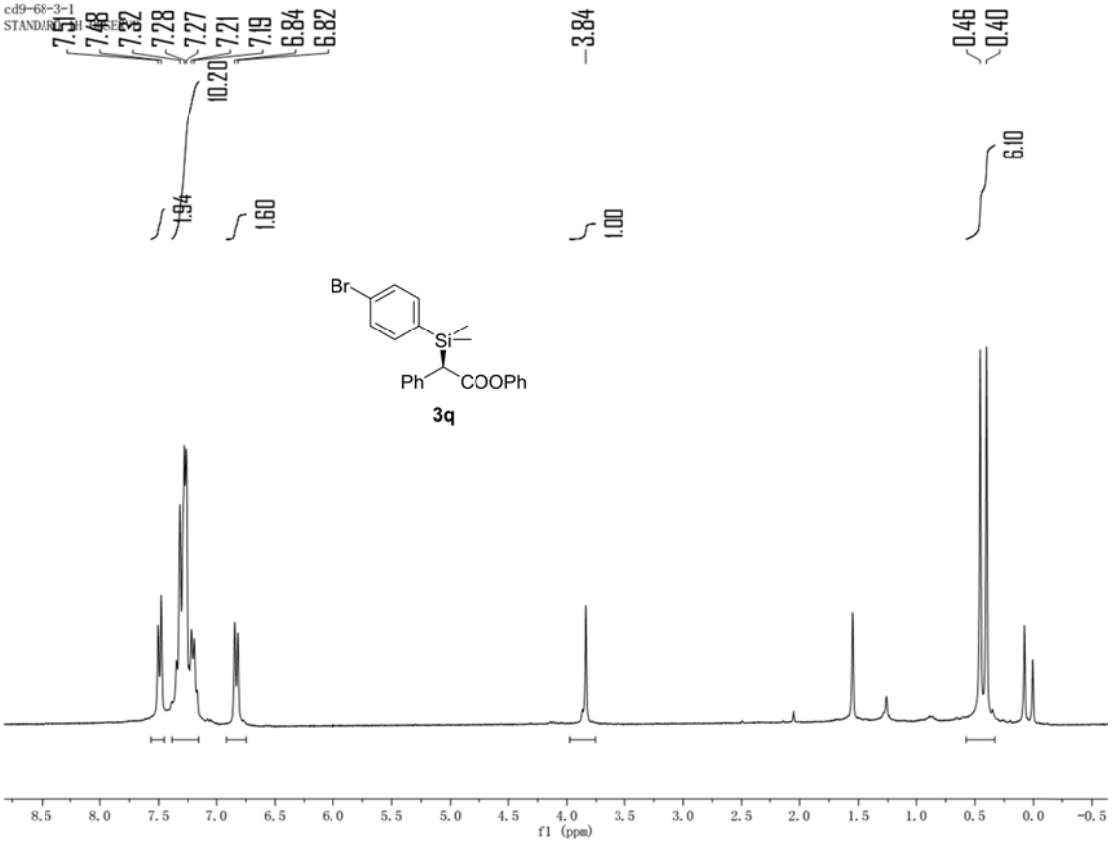
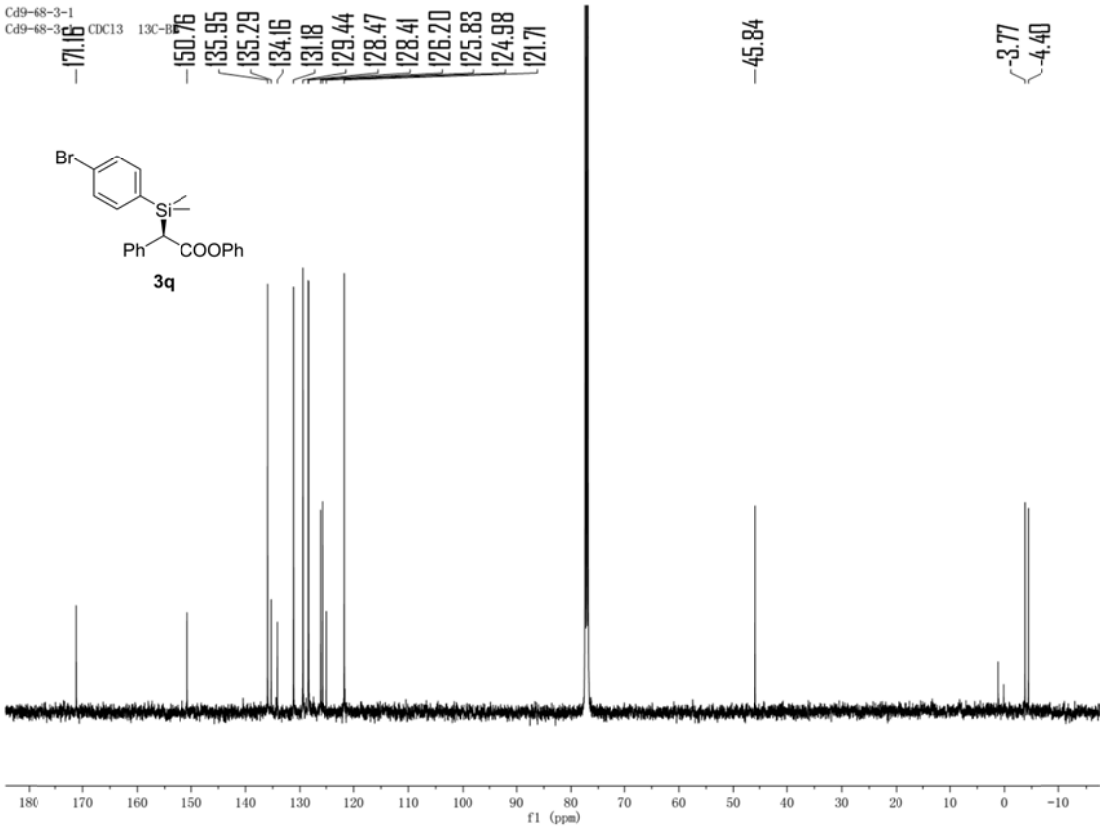
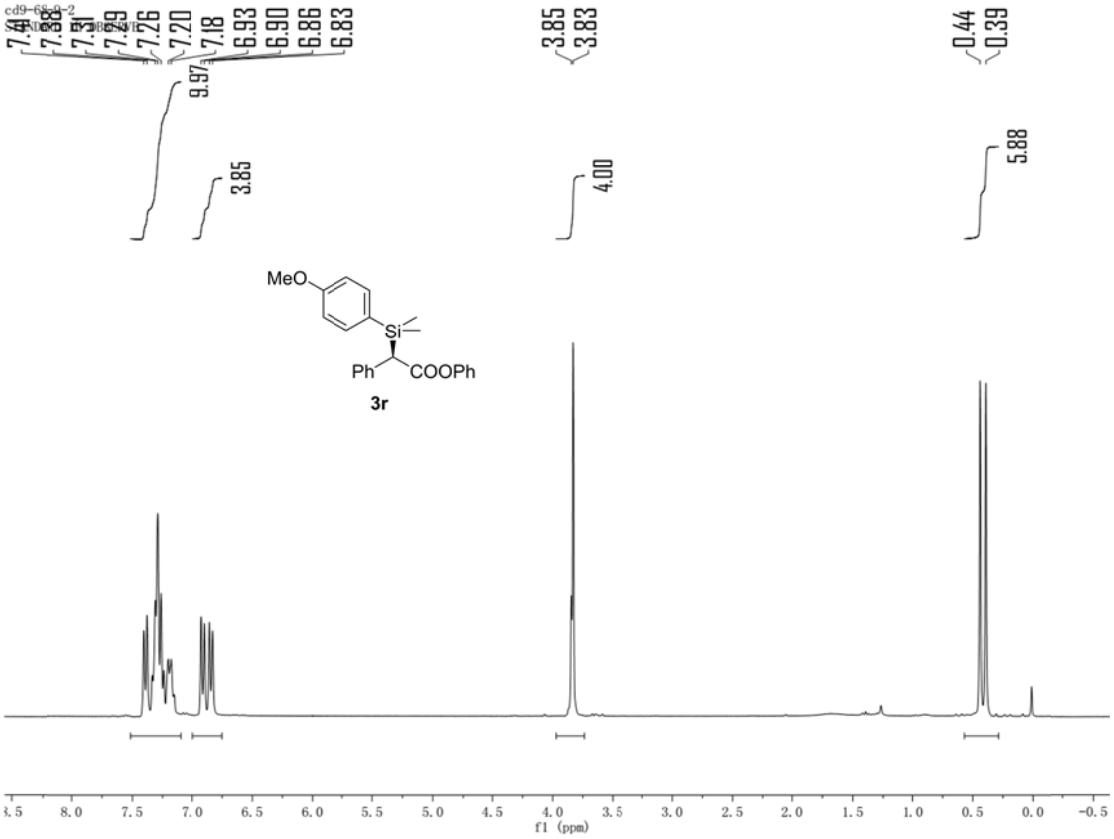
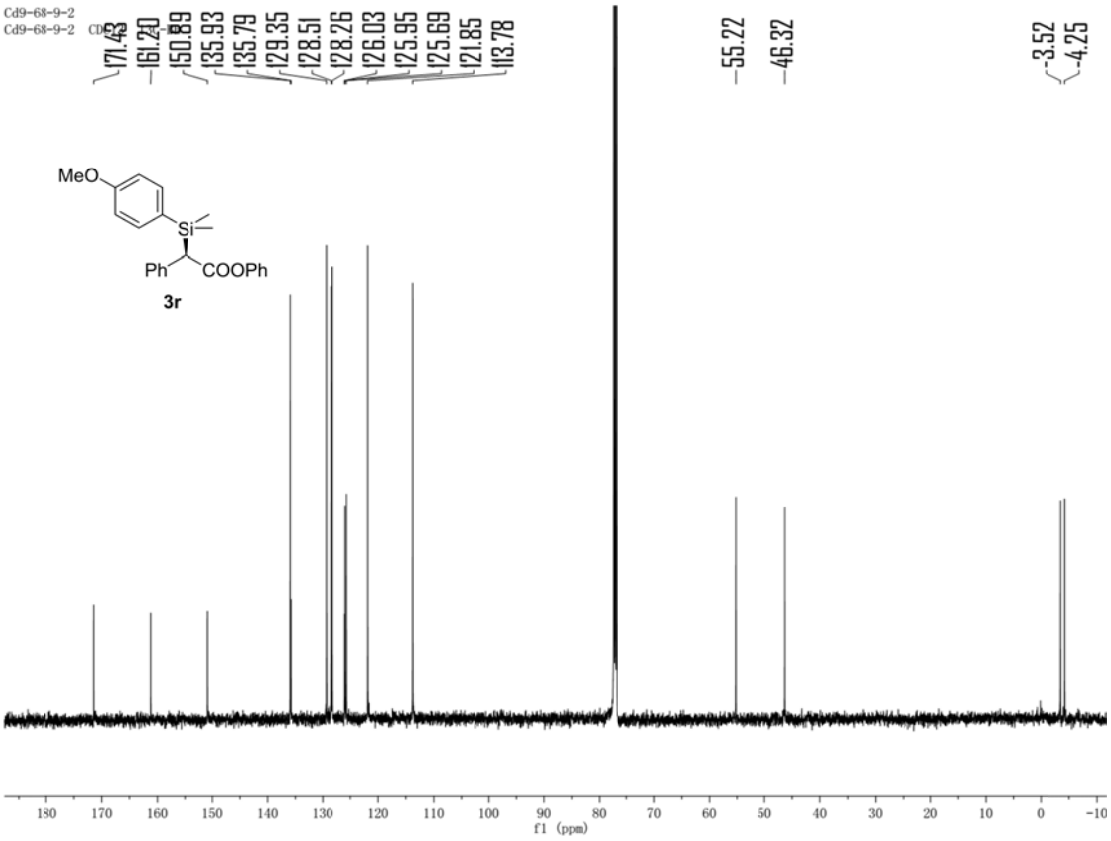
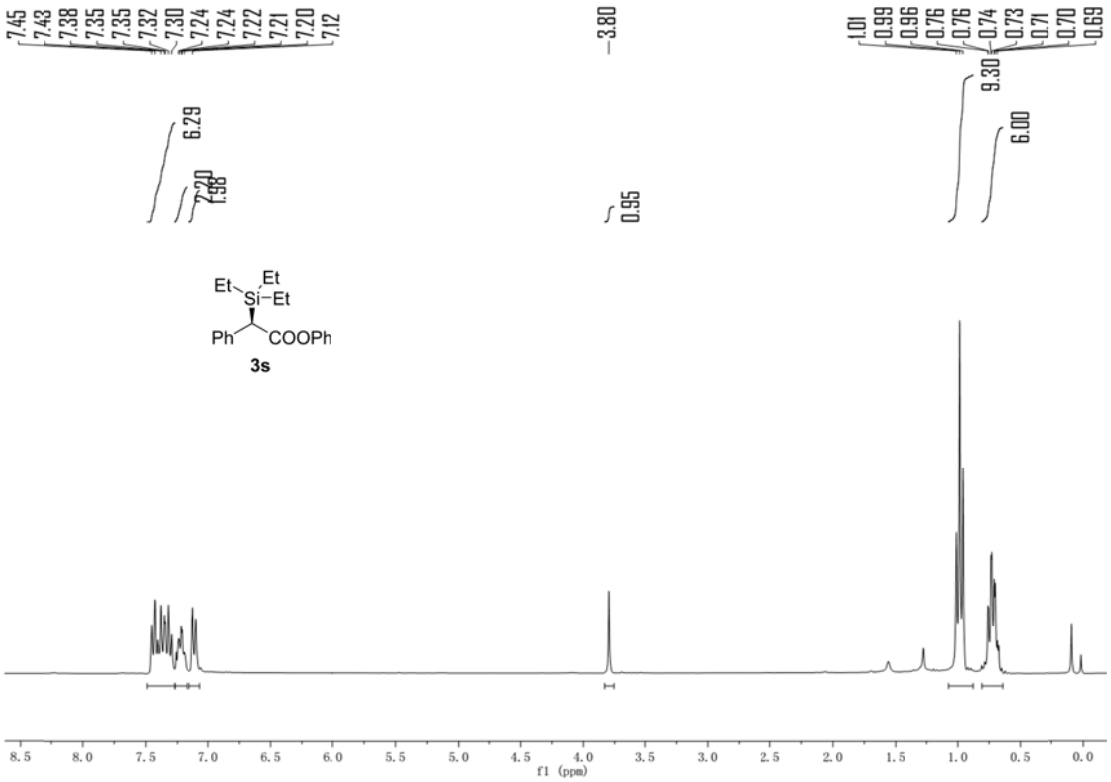
136.32
134.78
133.97
133.49
130.65
129.30
128.43
128.13
128.09
126.02
125.74
125.57
125.04
60.26
45.93
13.99
-2.06
-2.22
Si
Ph
COOEt
3p
f1 (ppm)

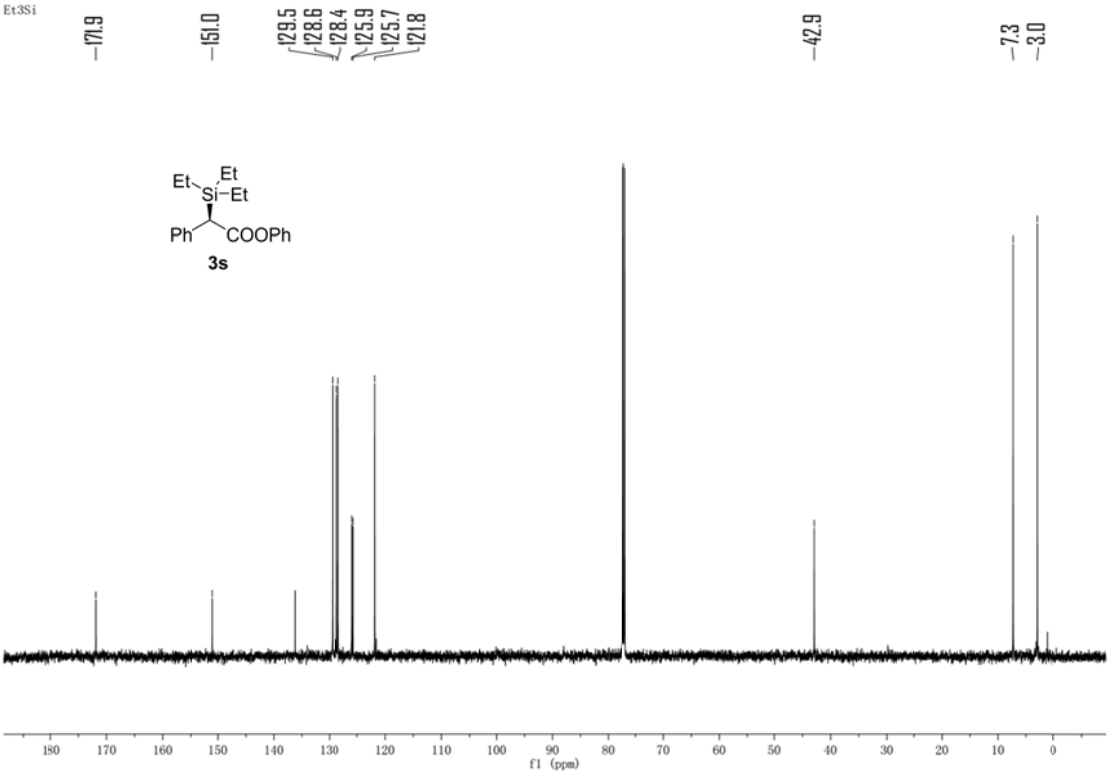

cd9-68-3-1
7.50
7.48
7.32
7.28
7.27
7.21
7.19
6.84
6.82
10.20
1.94
1.60
3.84
1.00
0.46
0.40
6.10
Br
Si
Ph
COOPh
3q
f1 (ppm)

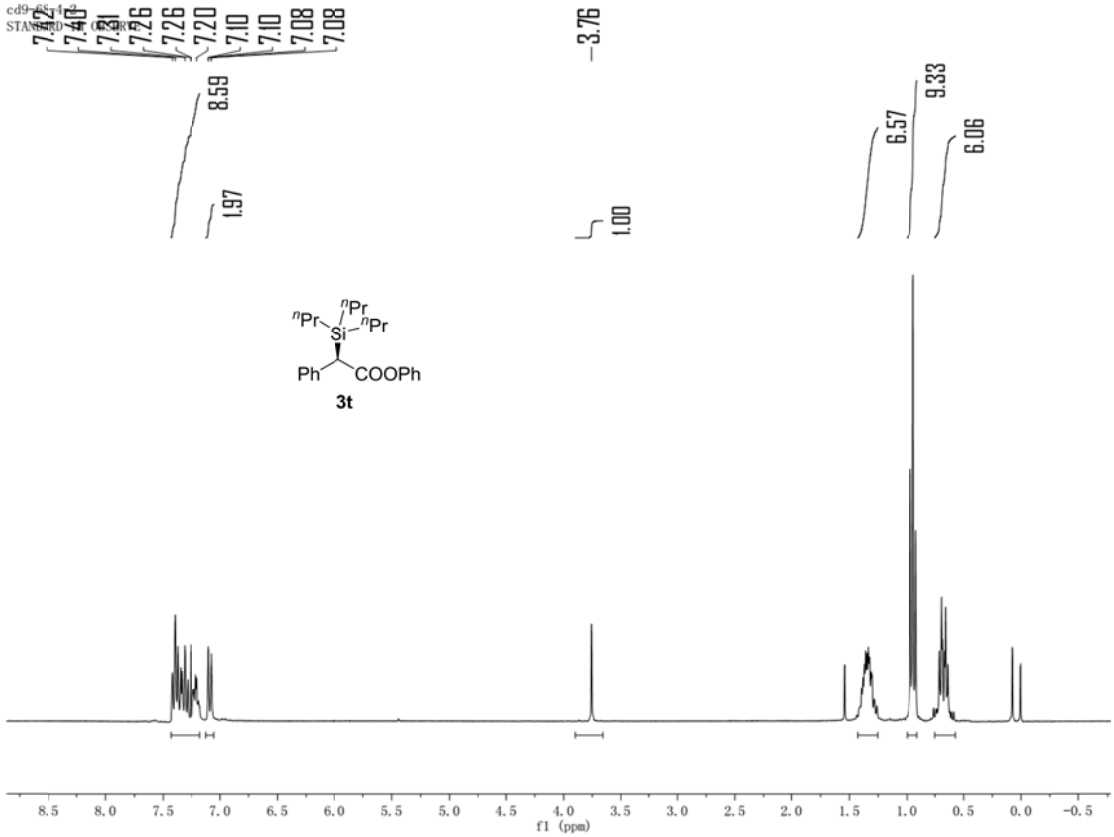

Cd9-68-3-1
171.16
150.76
135.95
135.29
134.16
131.18
129.44
128.47
128.41
126.20
125.83
124.98
121.71
45.84
3.77
4.40
Br
Si
Ph
COOPh
3q
f1 (ppm)

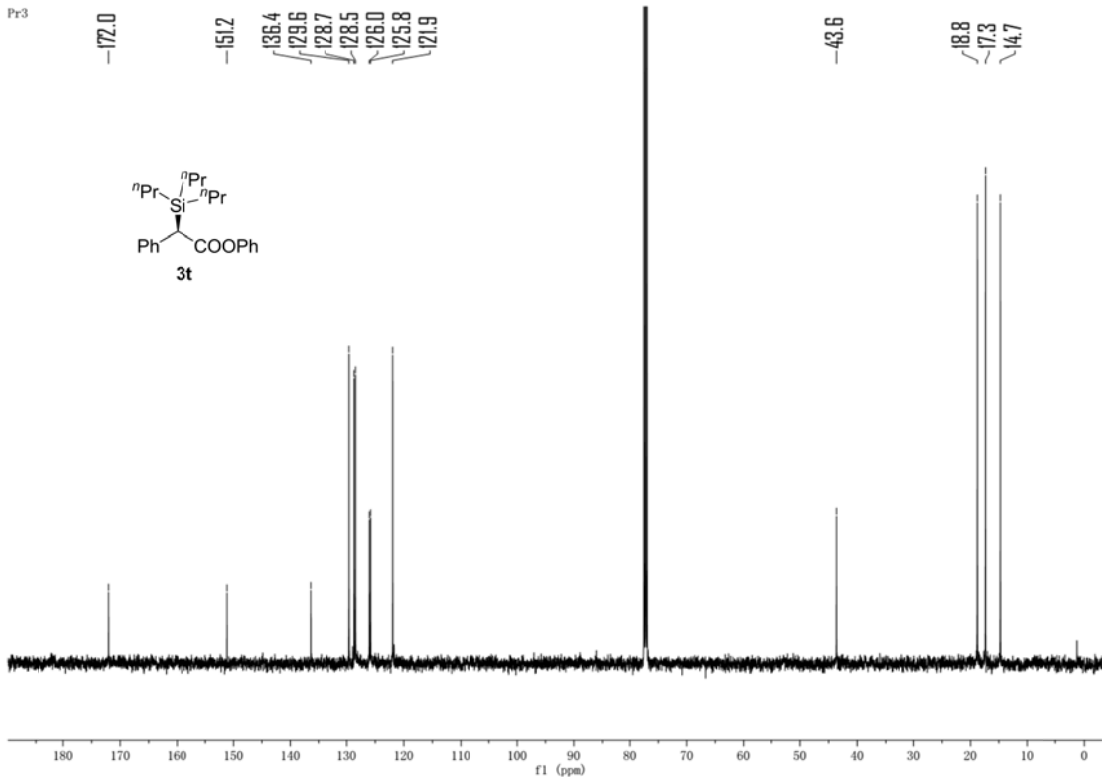

7.26
7.20
7.18
6.93
6.90
6.86
6.83
3.85
3.83
0.44
0.39
9.97
3.85
4.00
5.88
MeO
Si
Ph
COOPh
3r
f1 (ppm)

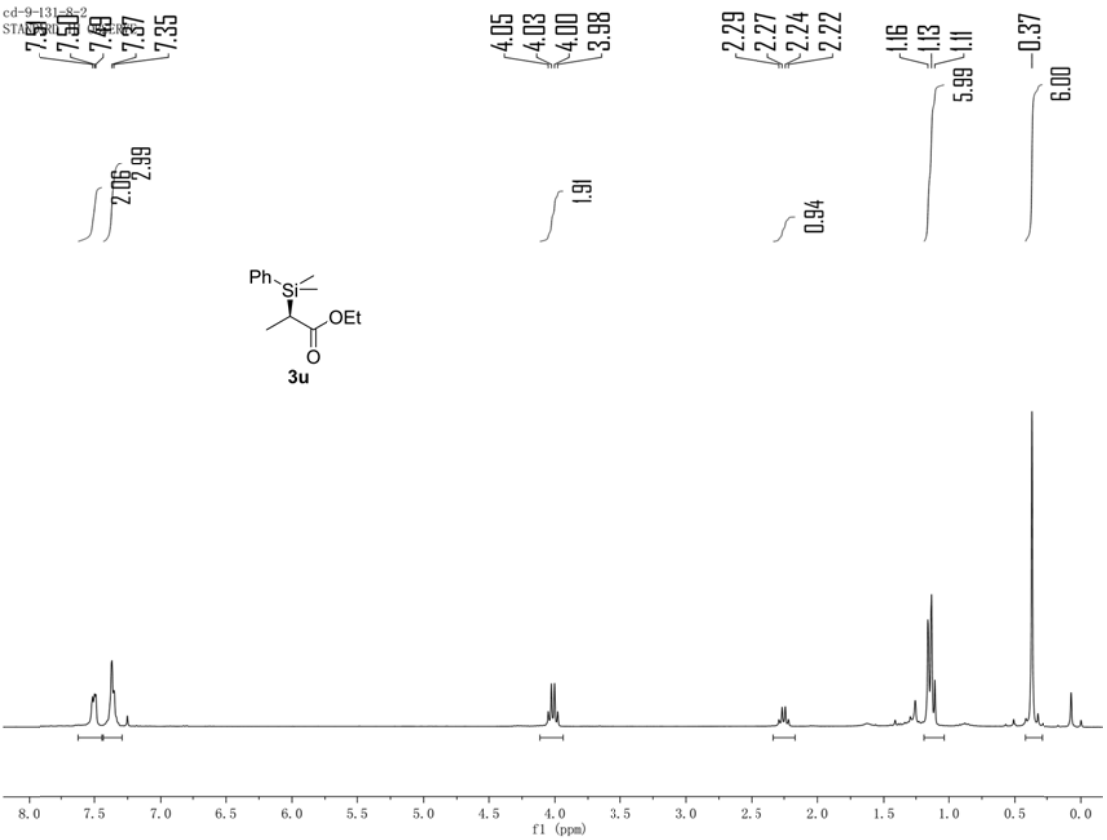

Cd9-68-9-2
171.43
161.20
150.89
135.93
135.79
129.35
128.51
128.26
126.03
125.95
125.69
121.85
113.78
55.22
46.32
-3.52
-4.25
MeO
Si
Ph
COOPh
3r
f1 (ppm)

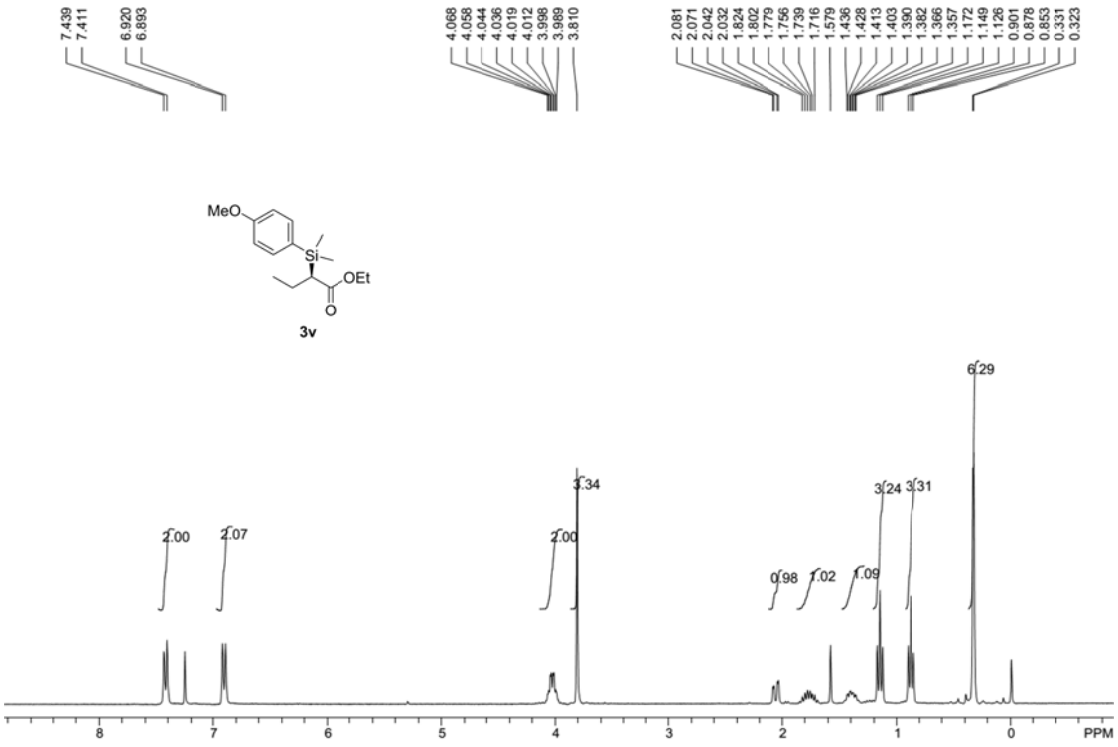

7.45
7.43
7.38
7.35
7.35
7.32
7.30
7.24
7.24
7.22
7.21
7.20
7.12
3.80
1.01
0.99
0.96
0.76
0.76
0.74
0.73
0.71
0.70
0.69
6.29
7.20
7.98
0.95
9.30
6.00
Et
Et
Si
Et
Ph
COOPh
3s
f1 (ppm)

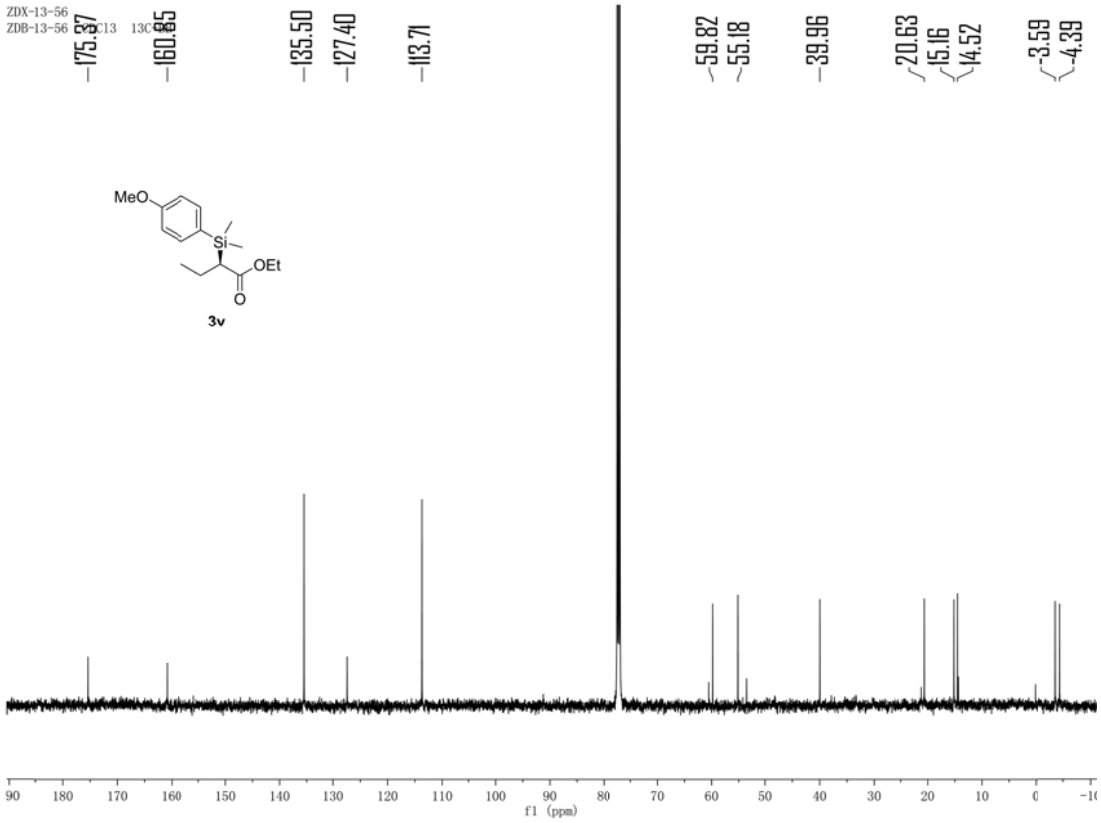

Et3Si
171.9
151.0
129.5
128.6
128.4
125.9
125.7
121.8
42.9
7.3
3.0
Et
Et
Si
Et
Ph
COOPh
3s
f1 (ppm)

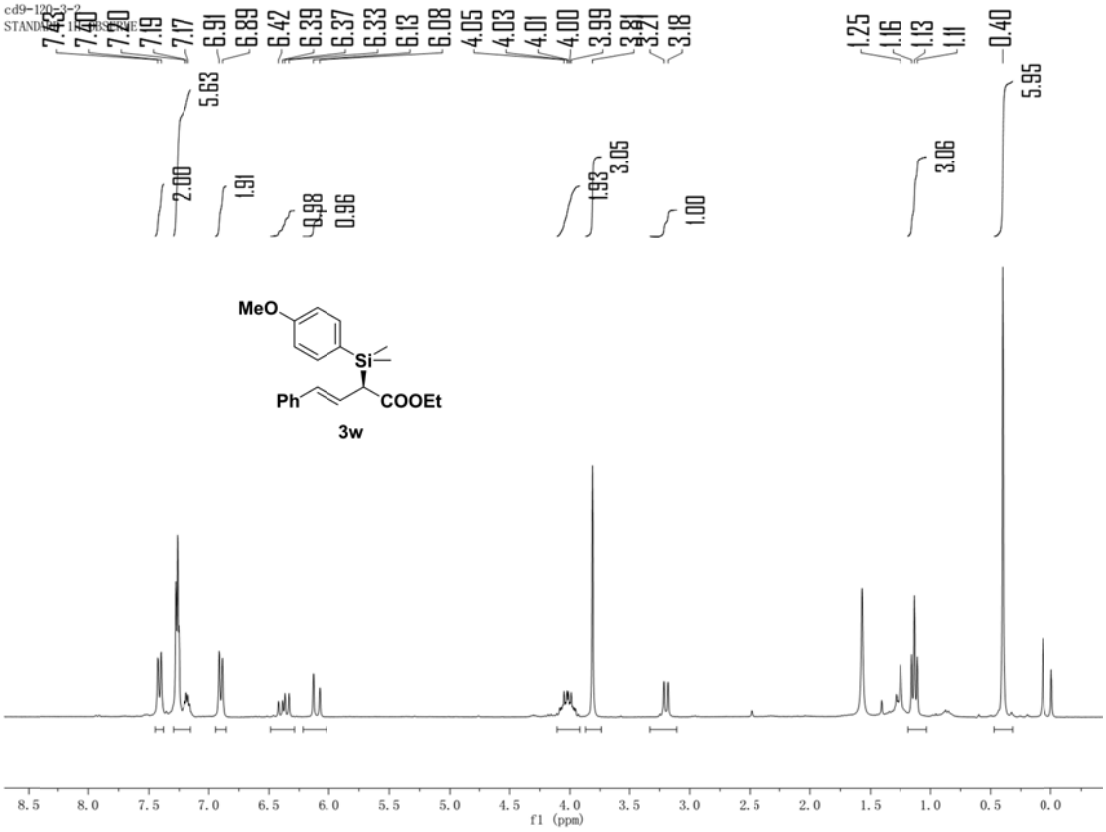

cd9-c6d6
STANDARD
7.26
7.20
7.10
7.08
3.76
8.59
1.97
1.00
6.57
9.33
6.06
nPr
nPr
Si
nPr
Ph
COOPh
3t
f1 (ppm)

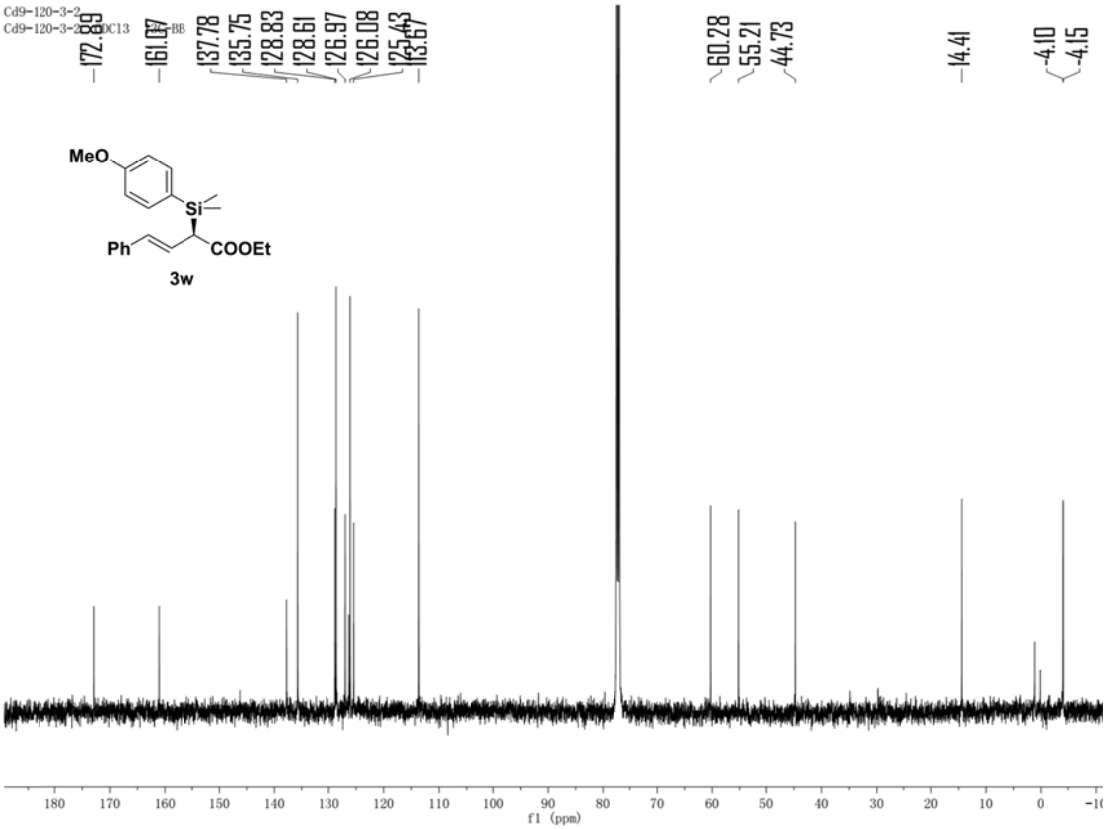

Pr3
172.0
151.2
136.4
129.6
128.7
128.5
126.0
125.8
121.9
43.6
18.8
17.3
14.7
Ph
COOPh
3t
f1 (ppm)

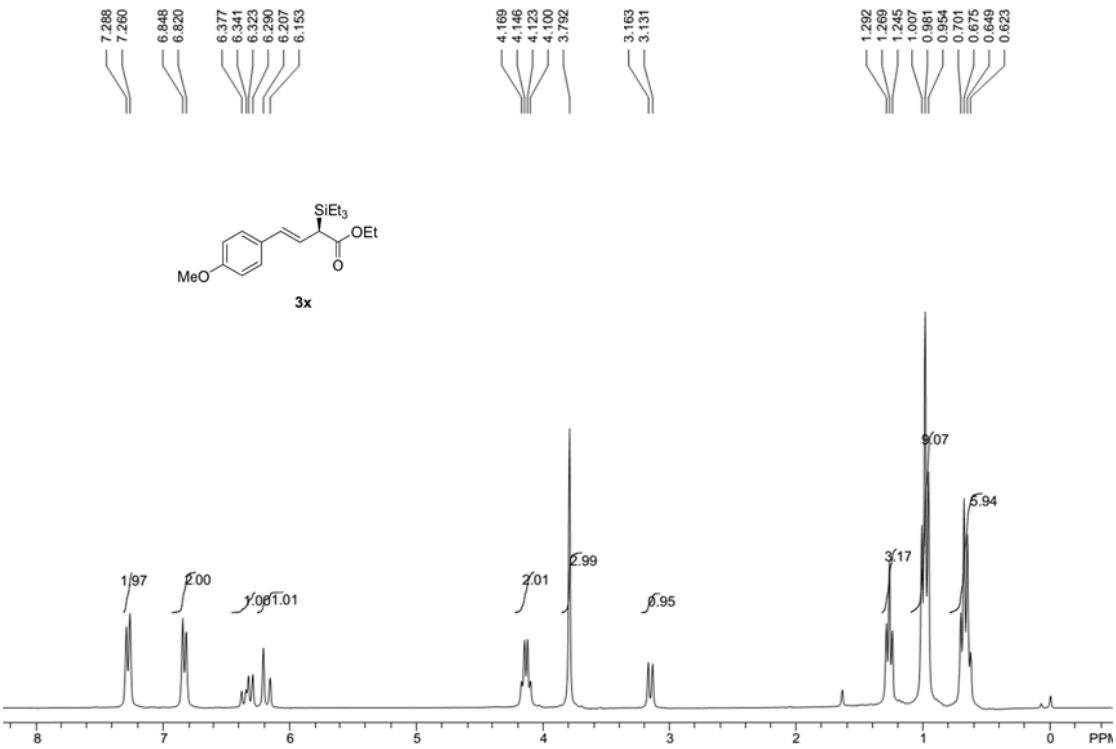

7.50
7.49
7.37
7.35
4.05
4.03
4.00
3.98
2.29
2.27
2.24
2.22
1.16
1.13
1.11
-0.37
2.06
2.99
1.91
0.94
5.99
6.00
Ph
OEt
O
3u
f1 (ppm)

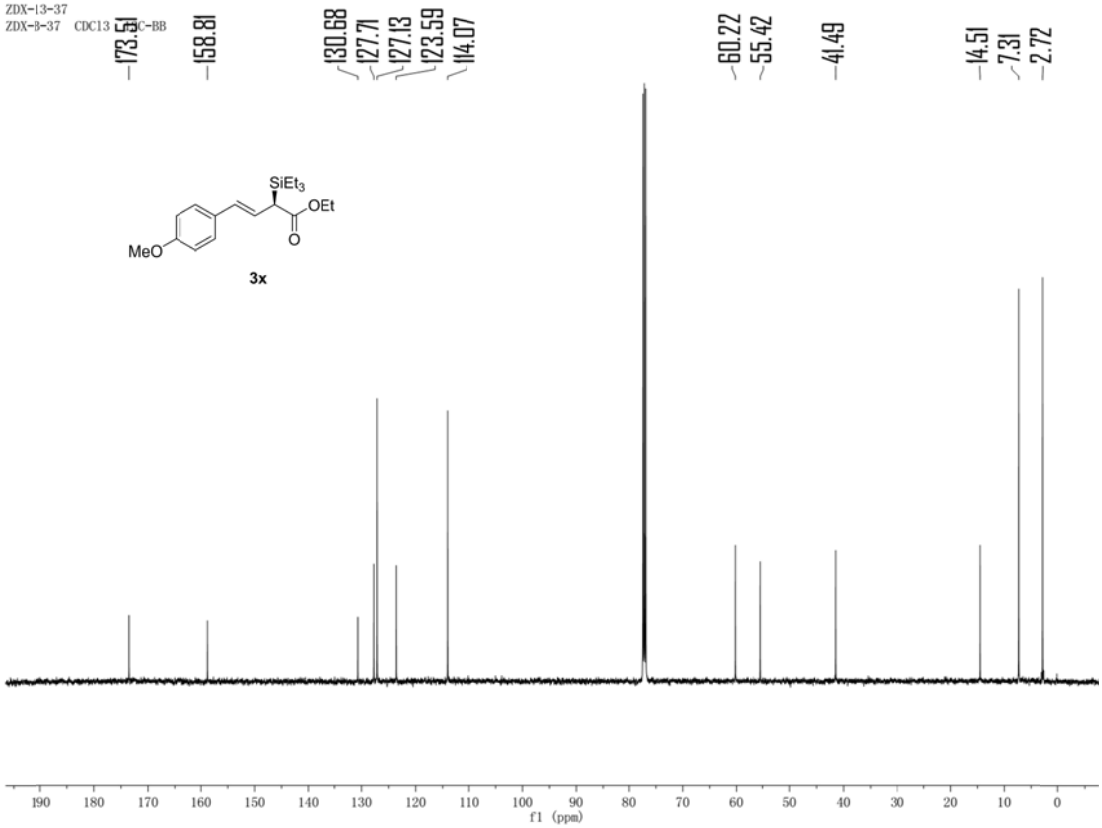

7.439
7.411
6.920
6.893
4.068
4.058
4.044
4.036
4.019
4.012
3.998
3.989
3.810
2.081
2.071
2.042
2.032
1.824
1.802
1.779
1.756
1.739
1.716
1.579
1.436
1.428
1.413
1.403
1.390
1.382
1.366
1.357
1.172
1.149
1.126
0.901
0.878
0.853
0.331
0.323
MeO
Si
OEt
O
3v
6.29
3.34
3.24
3.31
2.00
2.07
2.00
0.98
1.02
1.09
PPM

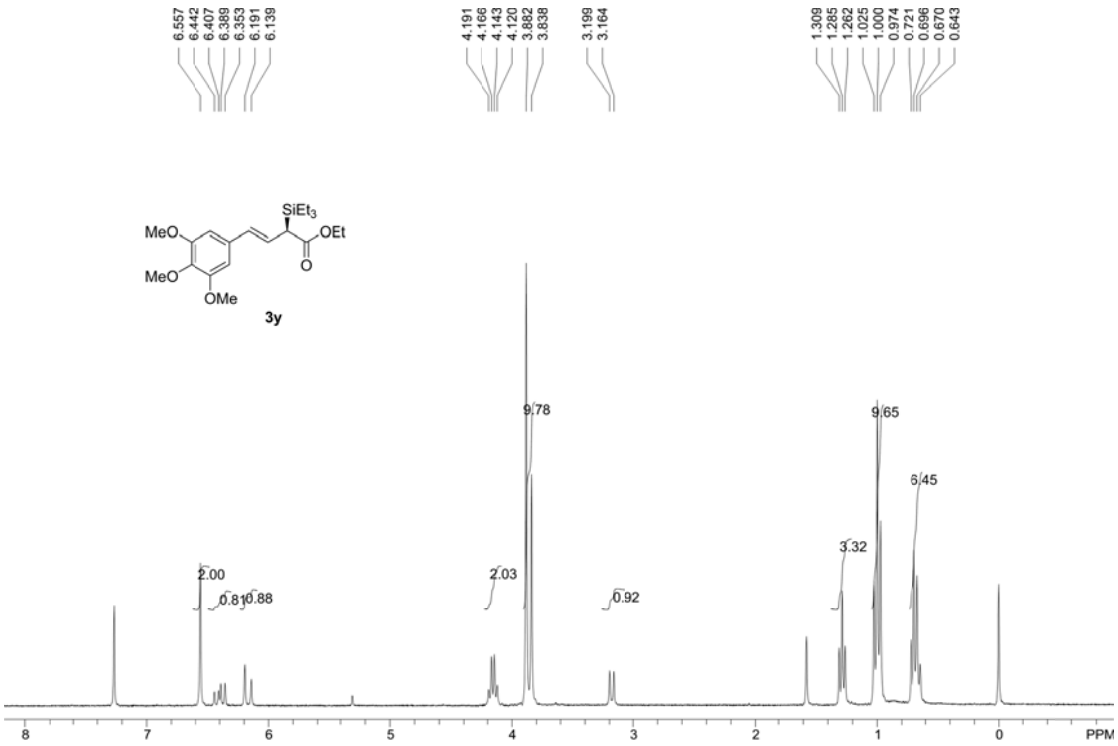

ZDX-13-56
ZDB-13-56
175.37
160.85
135.50
127.40
113.71
59.82
55.18
39.96
20.63
15.16
14.52
-3.59
-4.39
MeO
Si
OEt
O
3v
f1 (ppm)

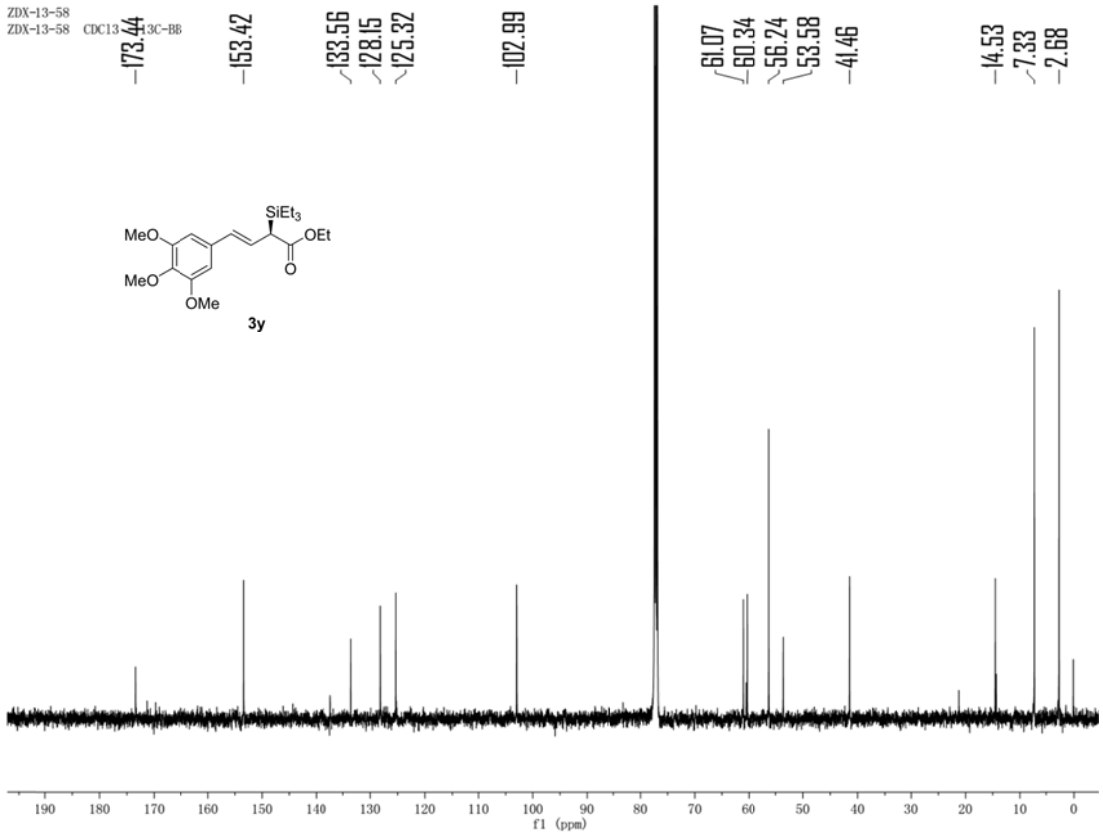

cd9-120-3-2
7.43
7.40
7.20
7.19
7.17
6.91
6.89
6.42
6.39
6.37
6.33
6.13
6.08
4.05
4.03
4.01
4.00
3.99
3.81
3.21
3.18
1.25
1.16
1.13
1.11
-0.40
5.63
5.95
2.00
1.91
0.98
0.96
1.93
3.05
1.00
3.06
MeO
Si
Ph
COOEt
3w
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

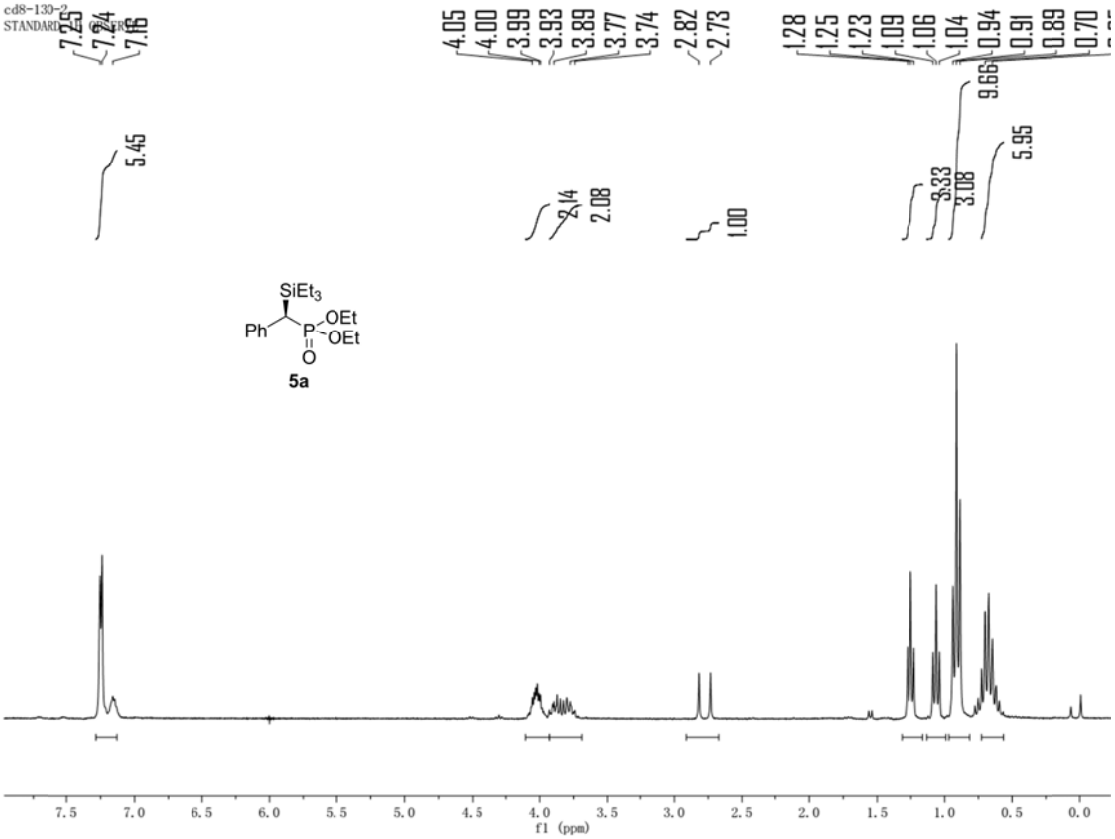

Cd9-120-3-2
Cd9-120-3-2 DC13
172.89
161.07
137.78
135.75
128.83
128.61
126.97
126.08
125.43
113.67
60.28
55.21
44.73
14.41
-4.10
-4.15
MeO
Si
Ph
COOEt
3w
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

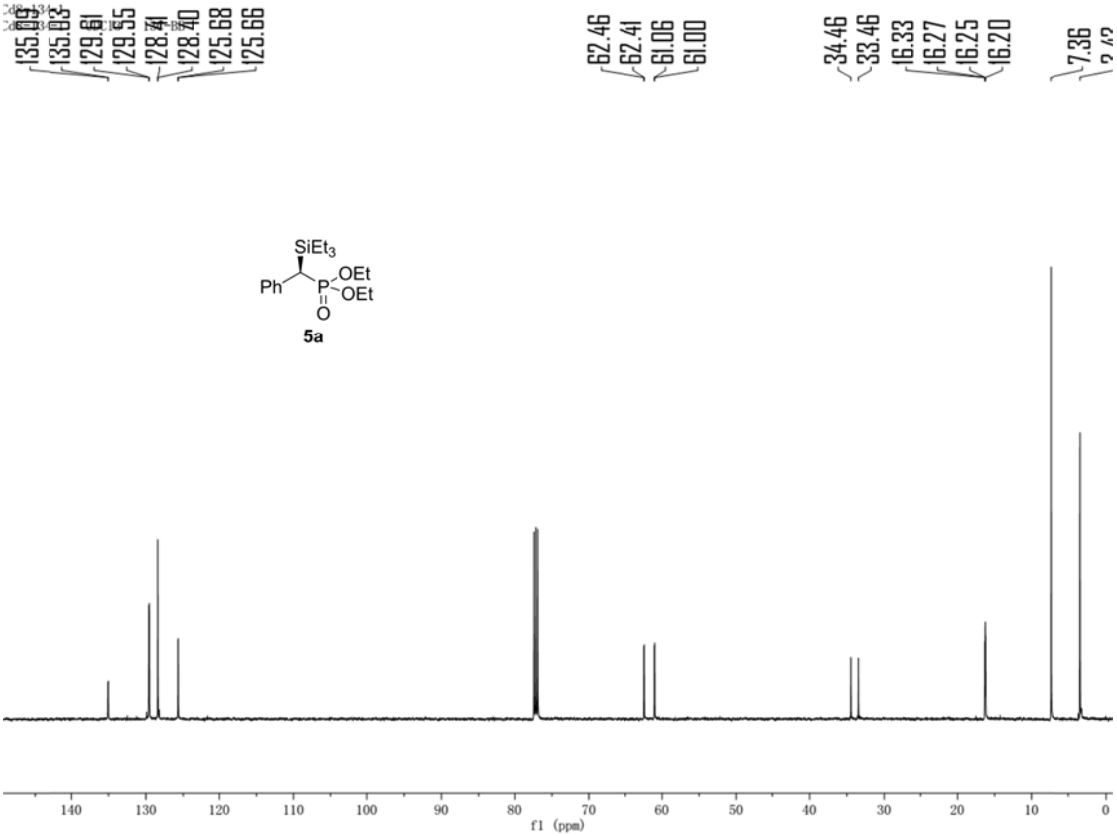

7.288
7.260
6.848
6.820
6.377
6.341
6.323
6.290
6.207
6.153
4.169
4.146
4.123
4.100
3.792
3.163
3.131
1.292
1.269
1.245
1.007
0.981
0.954
0.701
0.675
0.649
0.623
SiEt3
OEt
MeO
O
3x
1.97
2.00
1.06
1.01
2.01
2.99
0.95
3.17
9.07
5.94
8
7
6
5
4
3
2
1
0
PPM

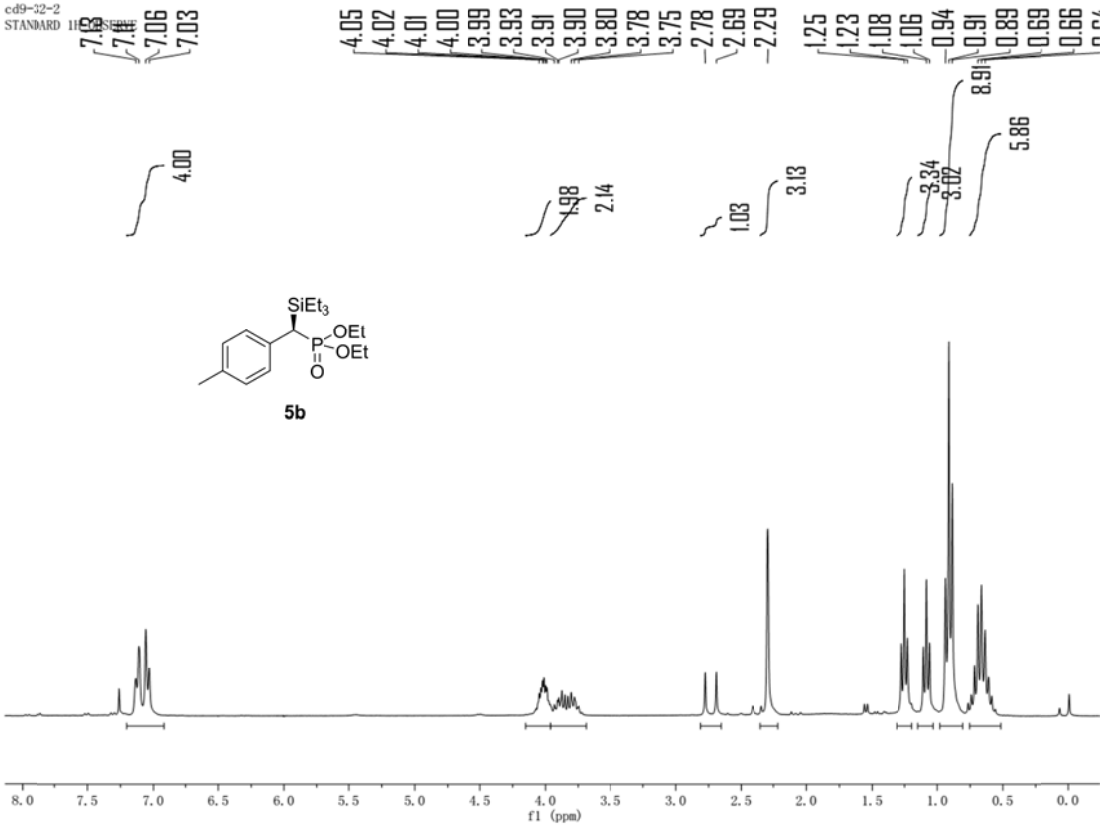

ZDX-13-37
ZDX-8-37 CDCl3
173.51
158.81
130.68
127.71
127.13
123.59
114.07
60.22
55.42
41.49
14.51
7.31
2.72
SiEt3
OEt
MeO
O
3x
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

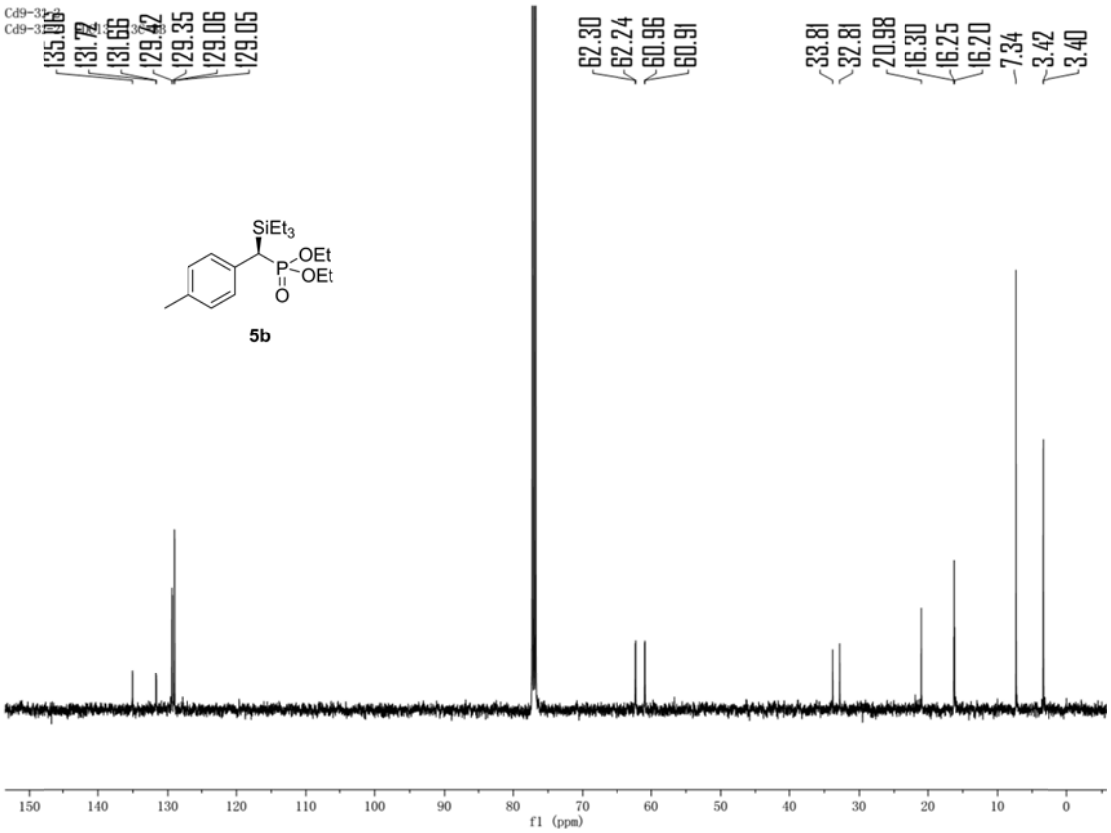

6.557
6.442
6.407
6.389
6.353
6.191
6.139
4.191
4.166
4.143
4.120
3.882
3.838
3.199
3.164
1.309
1.285
1.262
1.025
1.000
0.974
0.721
0.696
0.670
0.643
SiEt3
MeO
MeO
OMe
OEt
O
3y
9.78
9.65
6.45
3.32
2.00
0.81
0.88
2.03
0.92
8
7
6
5
4
3
2
1
0
PPM

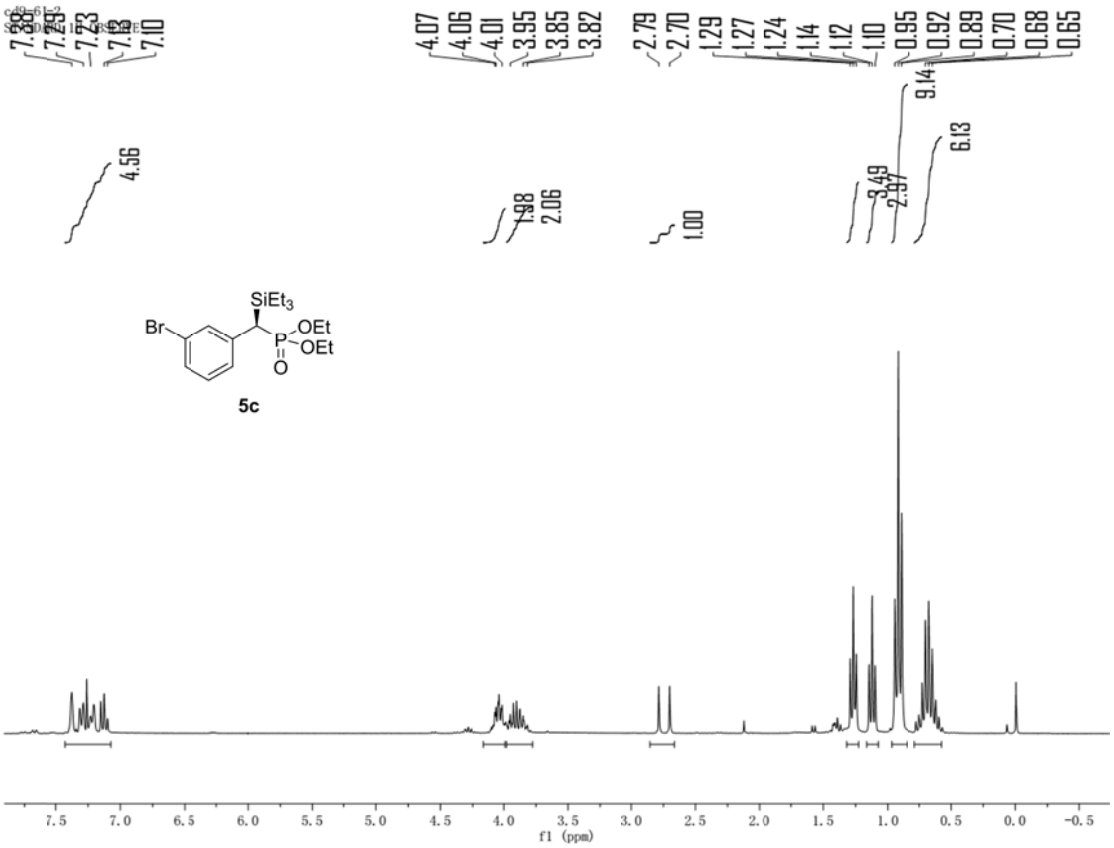

ZDX-13-58
ZDX-13-58 CDCl3 13C-BB
173.44
153.42
133.56
128.15
125.32
102.99
61.07
60.34
56.24
53.58
41.46
14.53
7.33
2.68
SiEt3
MeO
MeO
OMe
OEt
O
3y
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

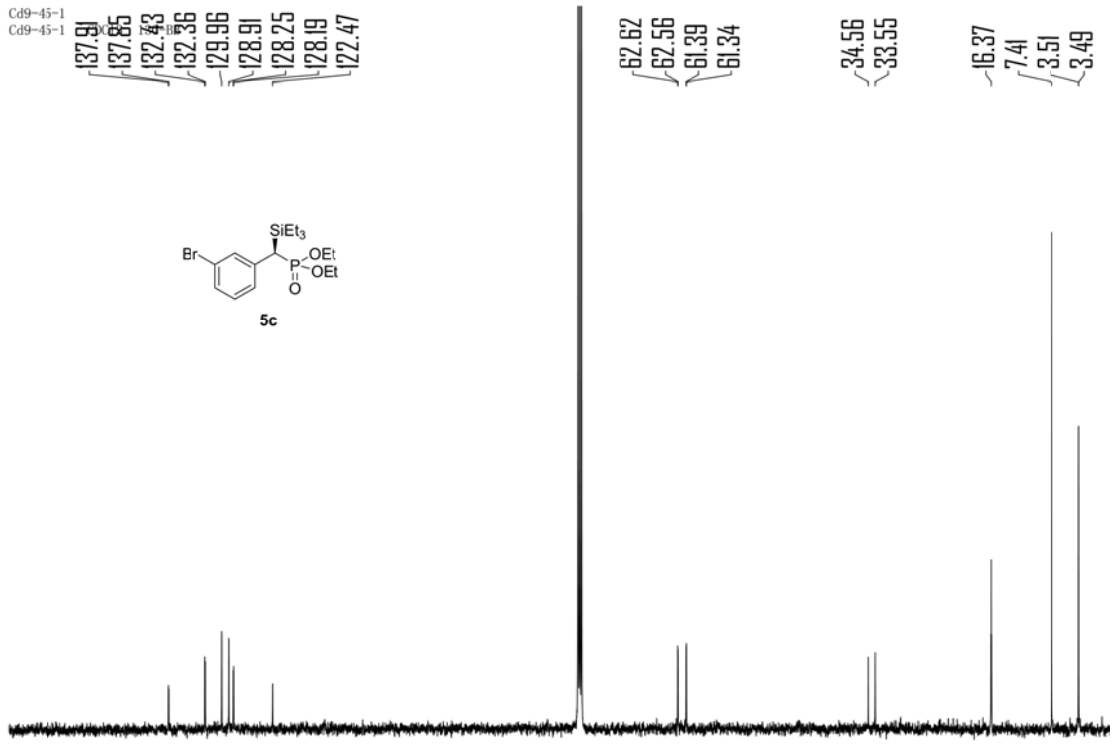

cd8-130-2
STANDARD
7.25
7.24
7.16
5.45
4.05
4.00
3.99
3.93
3.89
3.77
3.74
2.82
2.73
2.14
2.08
1.00
1.28
1.25
1.23
1.09
1.06
1.04
0.94
0.91
0.89
0.70
9.66
3.33
3.08
5.95
SiEt3
Ph
P
OEt
OEt
O
5a
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

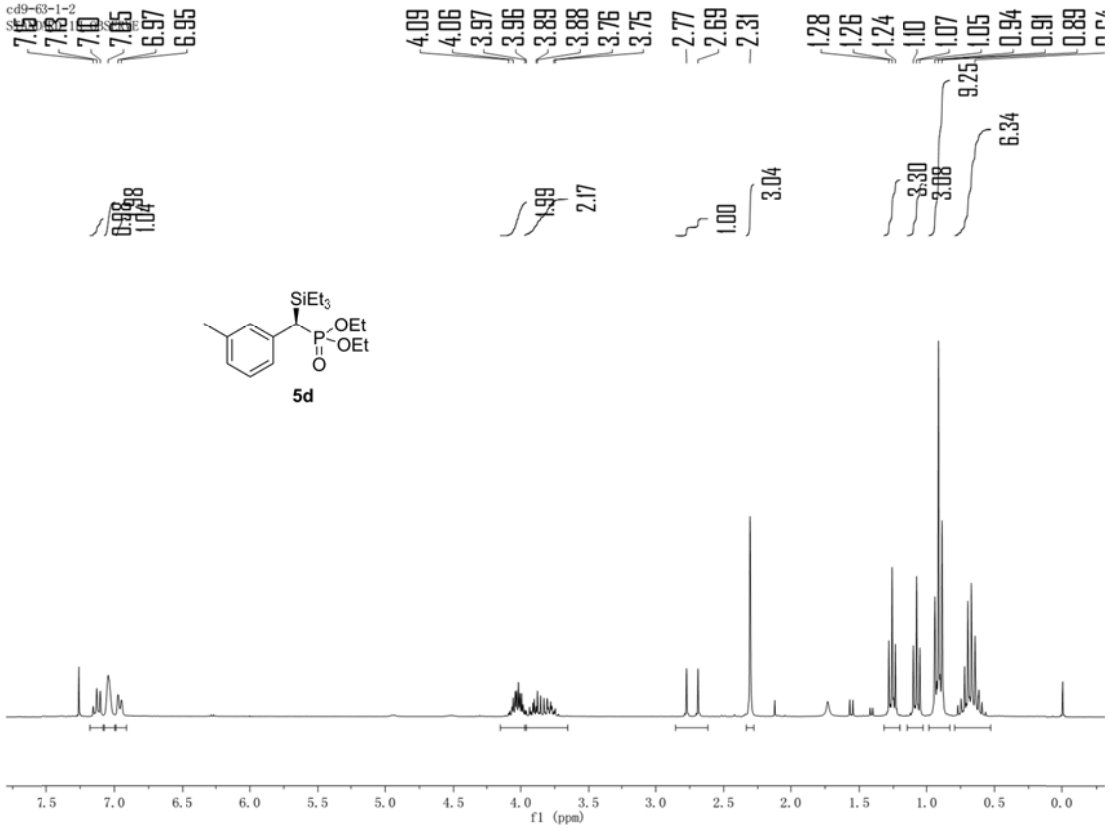

135.09
135.03
129.61
129.55
128.74
128.40
125.68
125.66
62.46
62.41
61.06
61.00
34.46
33.46
16.33
16.27
16.25
16.20
7.36
SiEt3
Ph
P
OEt
OEt
O
5a
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

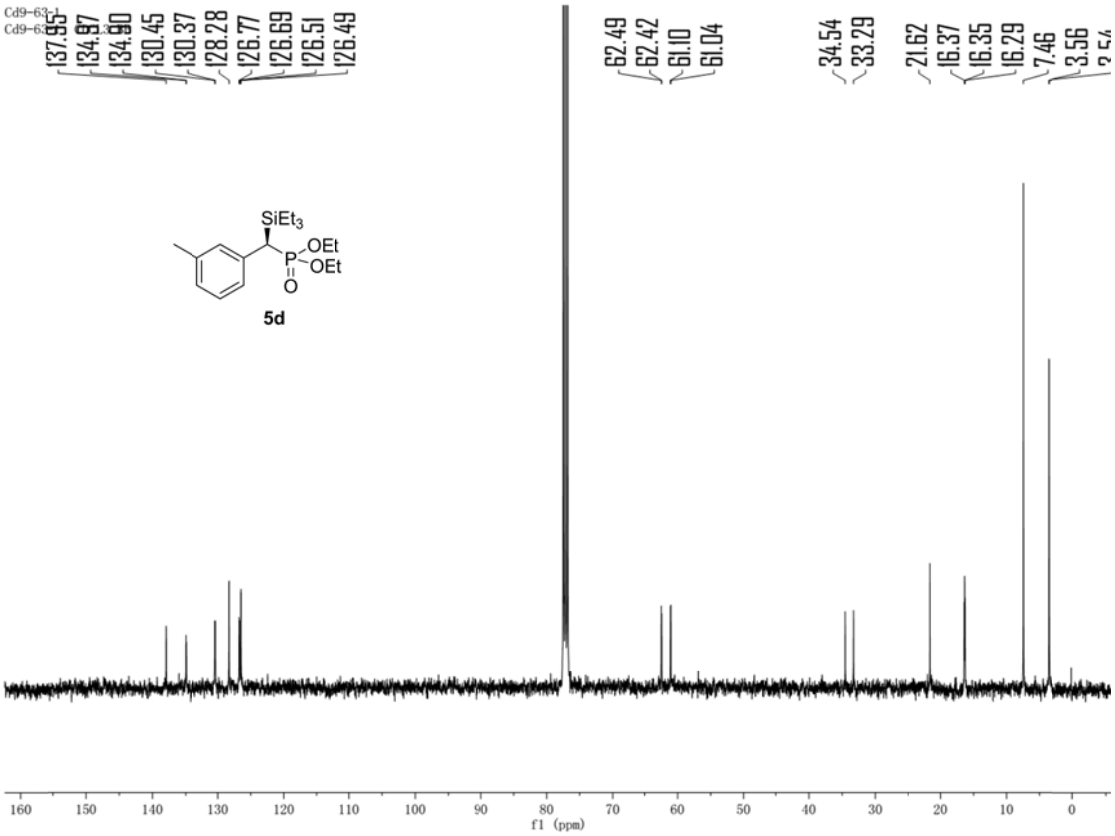

cd9-32-2
7.06
7.03
4.05
4.02
4.01
4.00
3.99
3.93
3.91
3.90
3.80
3.78
3.75
2.78
2.69
2.29
1.25
1.23
1.08
1.06
0.94
0.91
0.89
0.69
0.66
4.00
1.98
2.14
1.03
3.13
3.34
3.02
8.91
5.86
SiEt3
OEt
OEt
P
O
5b
f1 (ppm)

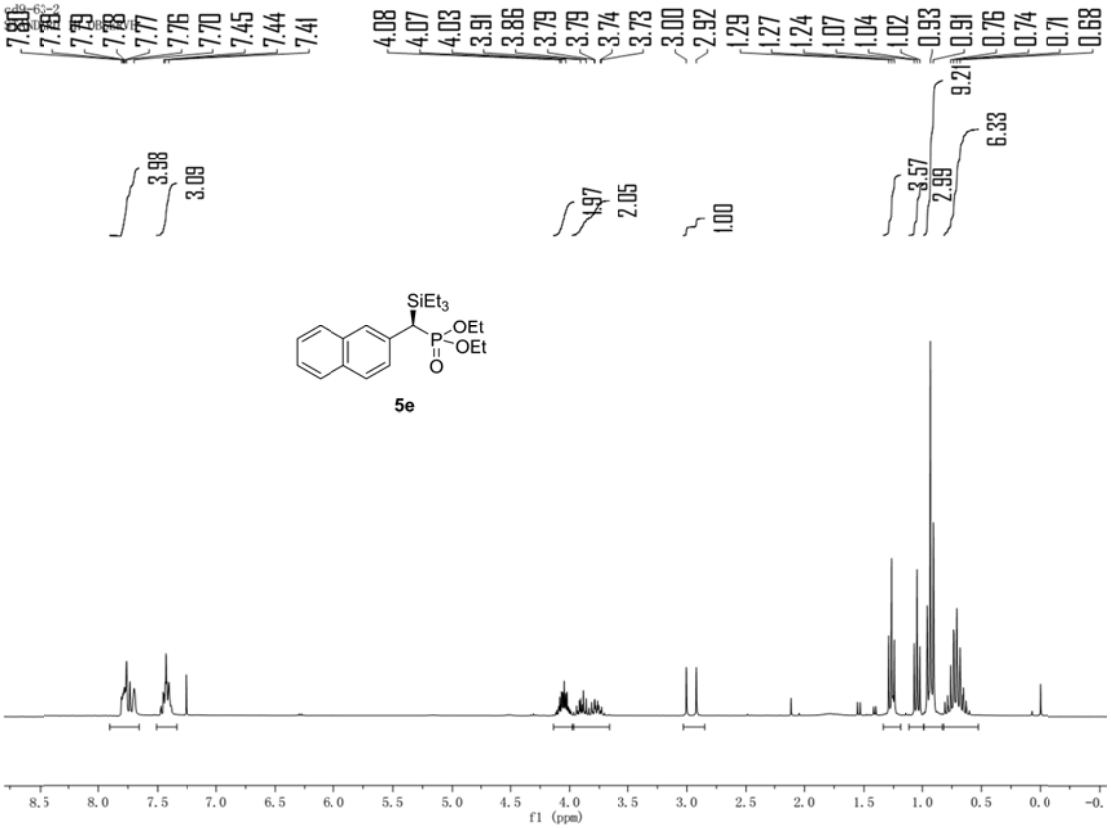

135.06
131.72
131.65
129.42
129.35
129.06
129.05
62.30
62.24
60.96
60.91
33.81
32.81
20.98
16.30
16.25
16.20
7.34
3.42
3.40
SiEt3
OEt
OEt
P
O
5b
f1 (ppm)

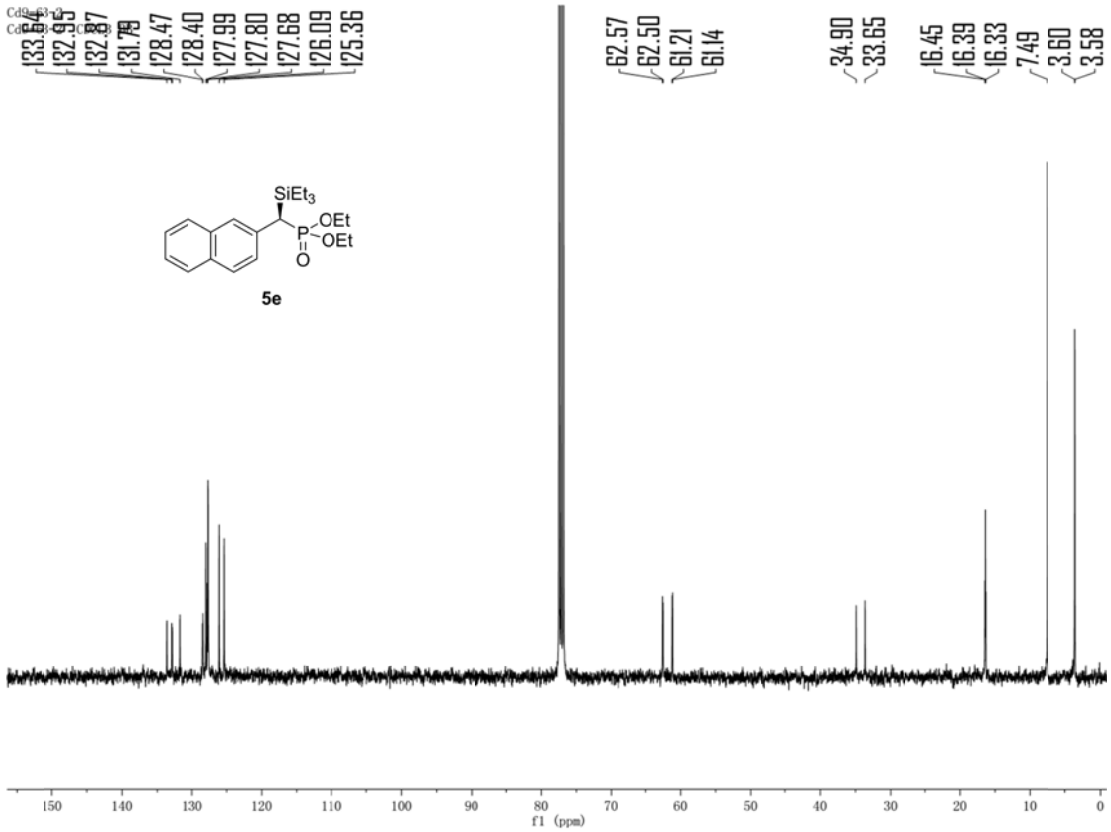

7.38
7.29
7.23
7.19
7.10
4.07
4.06
4.01
3.95
3.85
3.82
2.79
2.70
1.29
1.27
1.24
1.14
1.12
1.10
0.95
0.92
0.89
0.70
0.68
0.65
4.56
1.98
2.06
1.00
3.49
2.97
9.14
6.13
SiEt3
Br
OEt
OEt
P
O
5c
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


Cd9-45-1
Cd9-45-1
137.91
137.85
132.43
132.36
129.96
128.91
128.25
128.19
122.47
62.62
62.56
61.39
61.34
34.56
33.55
16.37
7.41
3.51
3.49
SiEt3
Br
OEt
OEt
P
O
5c


cd9-63-1-2
7.15
7.13
7.10
7.05
6.97
6.95
4.09
4.06
3.97
3.96
3.89
3.88
3.76
3.75
2.77
2.69
2.31
1.28
1.26
1.24
1.10
1.07
1.05
0.94
0.91
0.89
9.25
6.34
3.30
3.08
3.04
2.17
1.99
1.00
1.04
SiEt3
OEt
OEt
P
O
5d
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Cd9-63-1
137.95
134.97
134.90
130.45
130.37
128.28
126.77
126.69
126.51
126.49
62.49
62.42
61.10
61.04
34.54
33.29
21.62
16.37
16.35
16.29
7.46
3.56
SiEt3
OEt
OEt
P
O
5d
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.80
7.78
7.77
7.76
7.70
7.45
7.44
7.41
4.08
4.07
4.03
3.91
3.86
3.79
3.79
3.74
3.73
3.00
2.92
1.29
1.27
1.24
1.07
1.04
1.02
0.93
0.91
0.76
0.74
0.71
0.68
3.98
3.09
4.97
2.05
1.00
3.57
2.99
9.21
6.33
SiEt3
OEt
OEt
P
O
5e
f1 (ppm)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132.95
132.87
131.79
128.47
128.40
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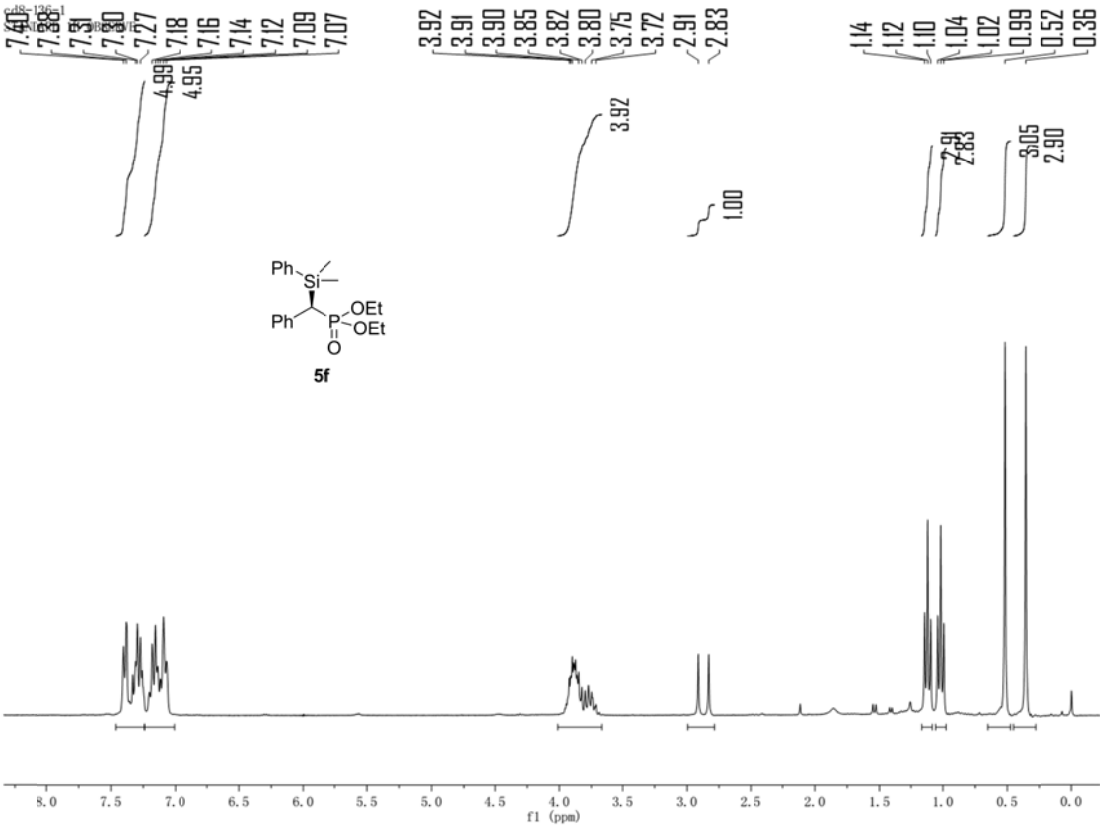
127.80
127.68
126.09
125.36
62.57
62.50
61.21
61.14
34.90
33.65
16.45
16.39
16.33
7.49
3.60
3.58
SiEt3
OEt
OEt
P
O
5e
f1 (ppm)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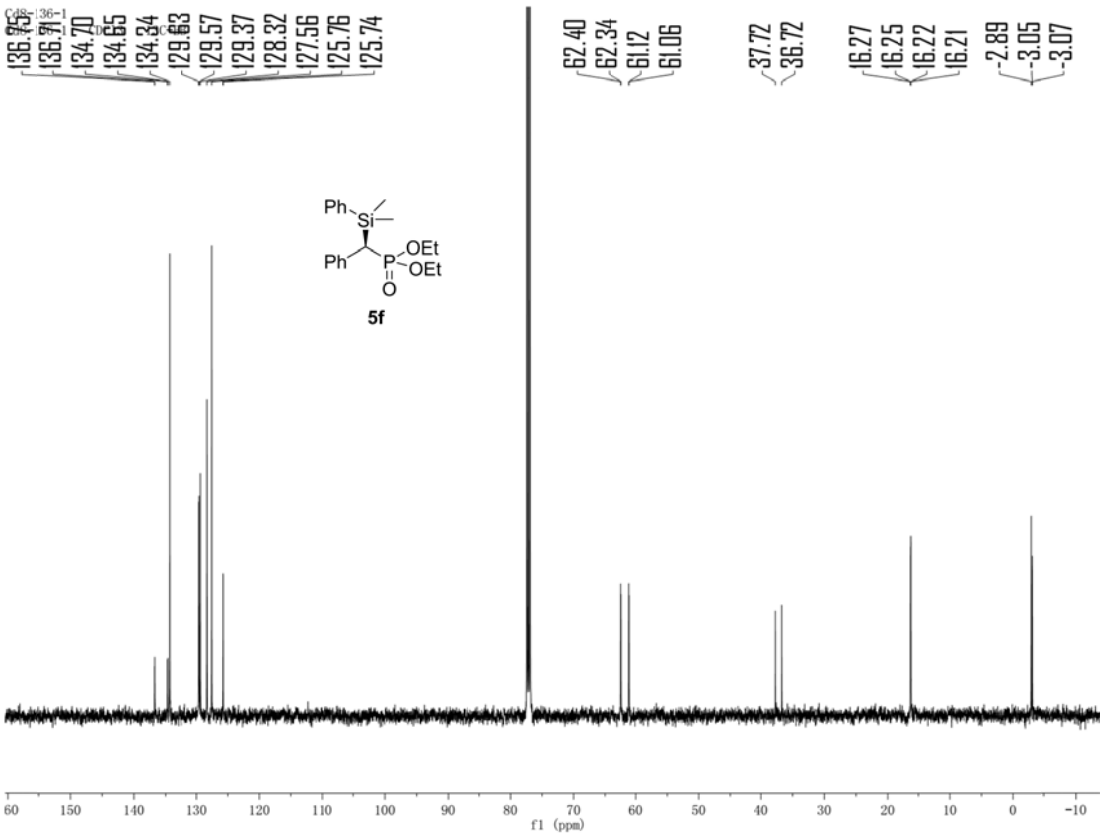
7.38
7.31
7.30
7.27
7.18
7.16
7.14
7.12
7.09
7.07
4.99
4.95
3.92
3.91
3.90
3.85
3.82
3.80
3.75
3.72
2.91
2.83
1.14
1.12
1.10
1.04
1.02
0.99
0.52
0.36
3.92
1.00
2.91
2.83
3.05
2.90
Ph
Si
Ph
P
OEt
OEt
O
5f
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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134.65
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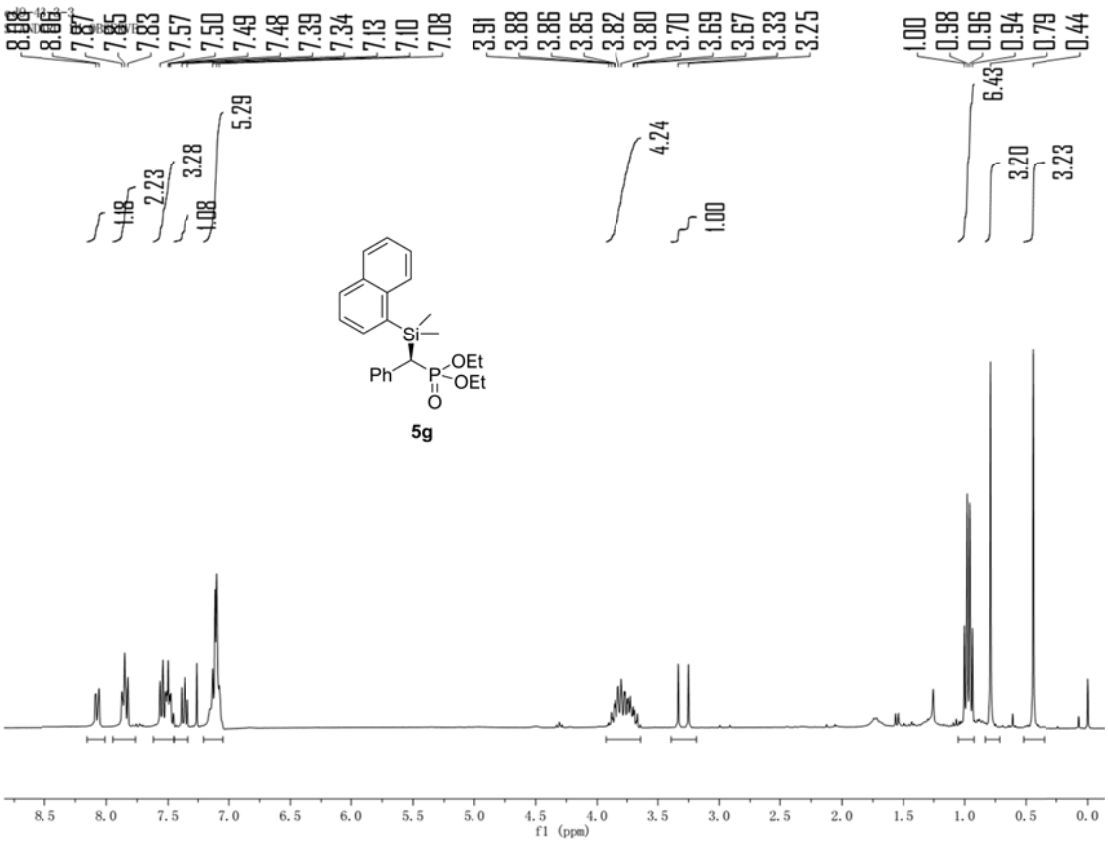
129.63
129.57
129.37
128.32
127.56
125.76
125.74
62.40
62.34
61.12
61.06
37.72
36.72
16.27
16.25
16.22
16.21
-2.89
-3.05
-3.07
Ph
Si
Ph
P
OEt
OEt
O
5f
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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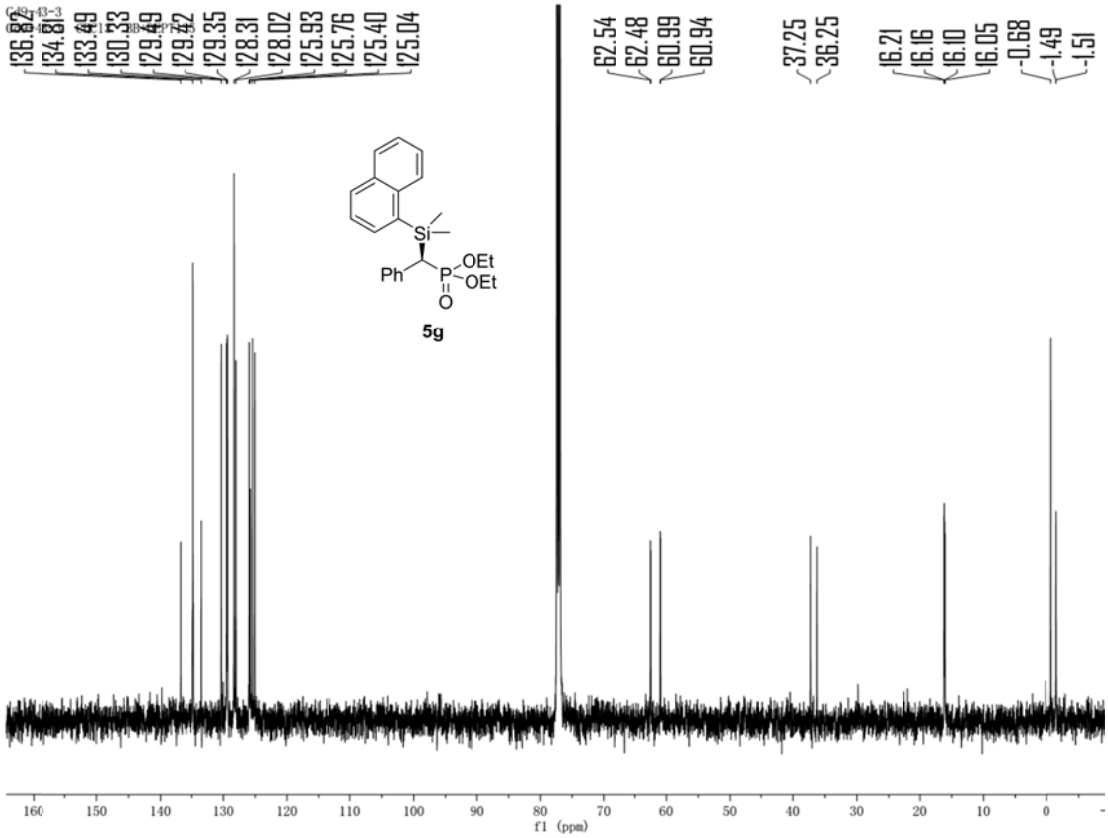
8.06
7.87
7.85
7.83
7.57
7.50
7.49
7.48
7.39
7.34
7.13
7.10
7.08
3.91
3.88
3.86
3.85
3.82
3.80
3.70
3.69
3.67
3.33
3.25
1.00
0.98
0.96
0.94
0.79
0.44
1.18
2.23
3.28
5.29
4.24
1.00
6.43
3.20
3.23
Si
Ph
P
OEt
OEt
O
5g
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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134.81
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130.33
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129.42
129.35
128.31
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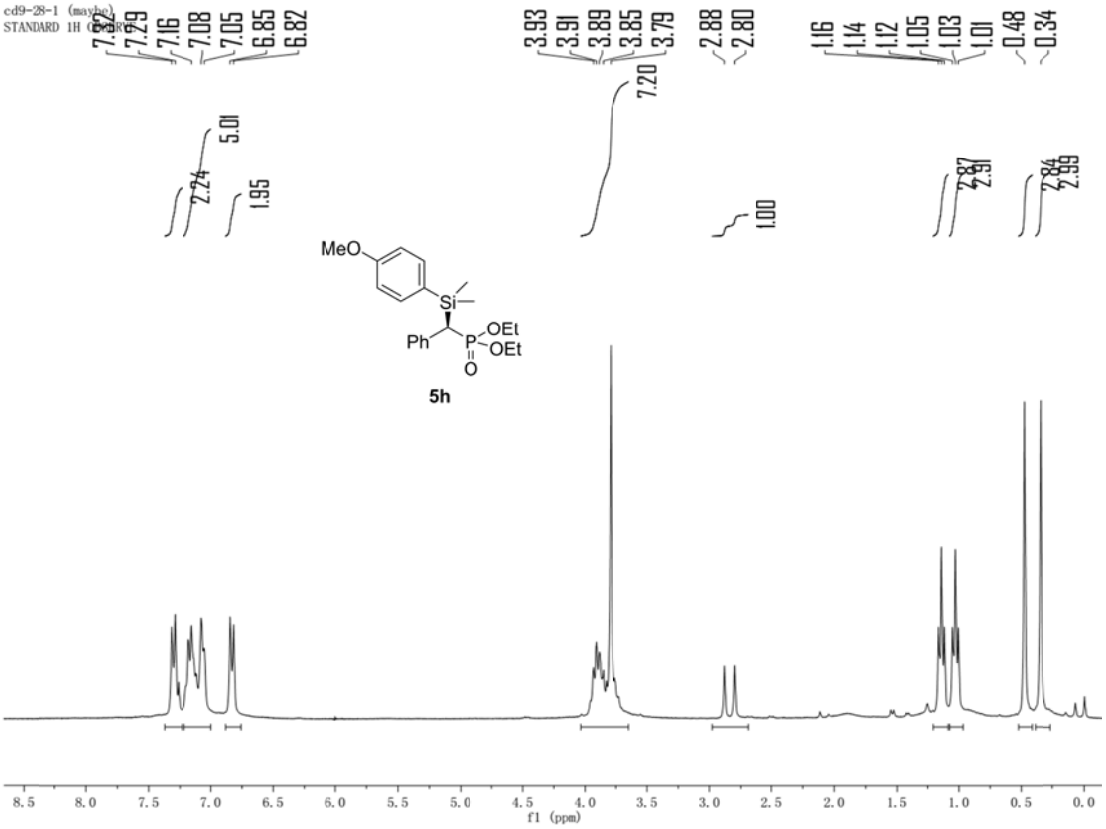
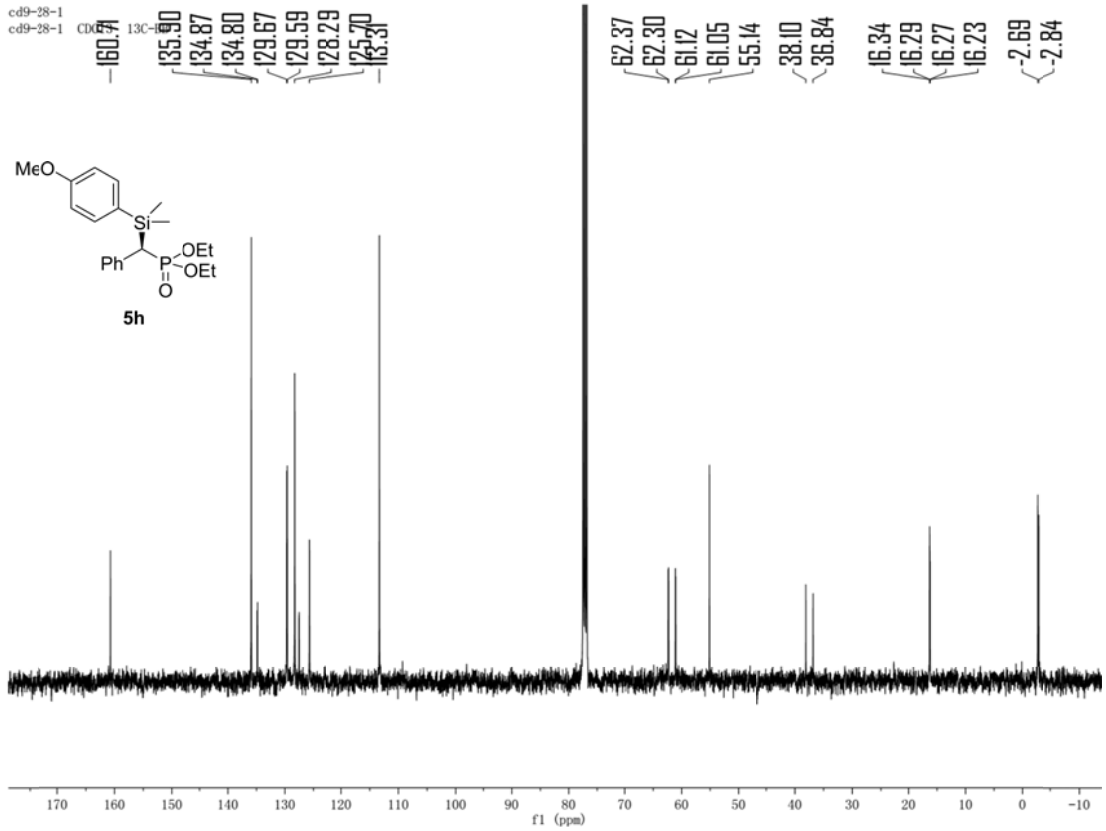
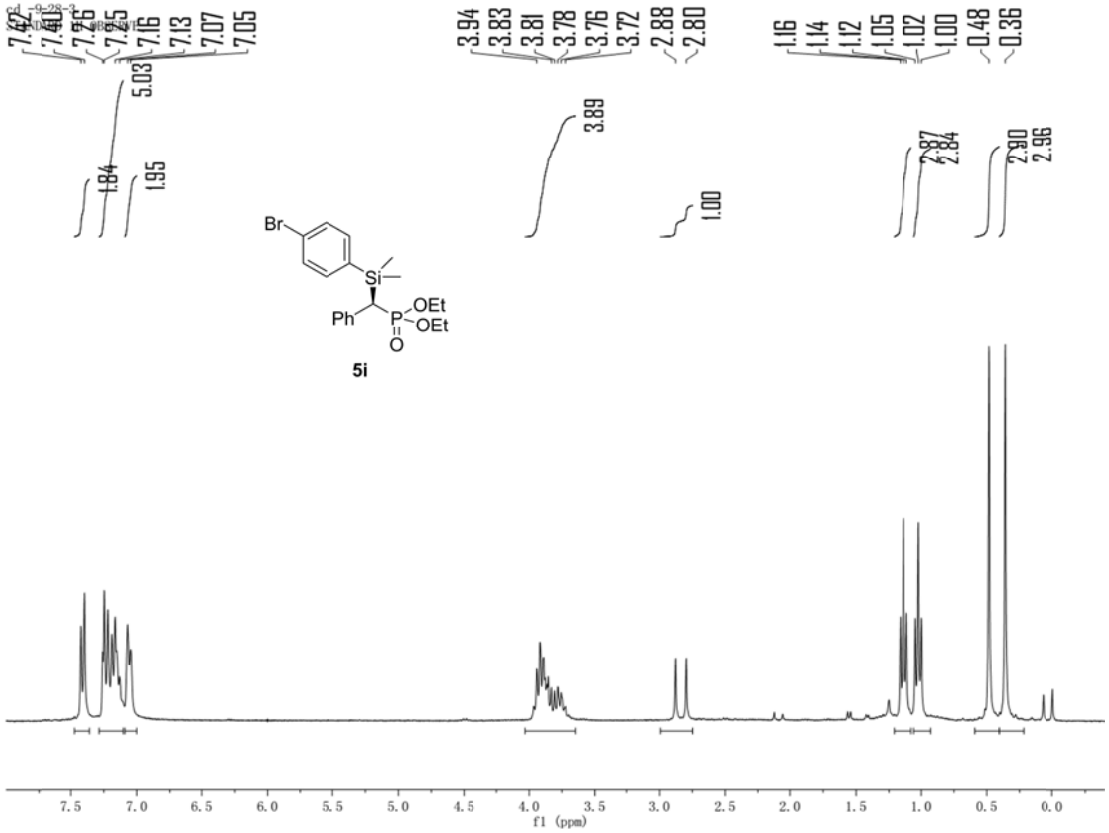
125.93
125.76
125.40
125.04
62.54
62.48
60.99
60.94
37.25
36.25
16.21
16.16
16.10
16.05
-0.68
-1.49
-1.51
Si
Ph
P
OEt
OEt
O
5g
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


cd9-28-1 (maybe)
STANDARD 1H CDCl3
7.29
7.16
7.08
7.05
6.85
6.82
3.93
3.91
3.89
3.85
3.79
2.88
2.80
1.16
1.14
1.12
1.05
1.03
1.01
0.48
0.34
7.20
5.01
7.24
1.95
1.00
2.87
2.91
2.34
2.39
MeO
Si
Ph
P
OEt
OEt
O
5h
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


cd9-28-1
cd9-28-1 CDCl3 13C-BB
160.71
135.90
134.87
134.80
129.67
129.59
128.29
125.70
113.31
62.37
62.30
61.12
61.05
55.14
38.10
36.84
16.34
16.29
16.27
16.23
-2.69
-2.84
MeO
Si
Ph
P
OEt
OEt
O
5h
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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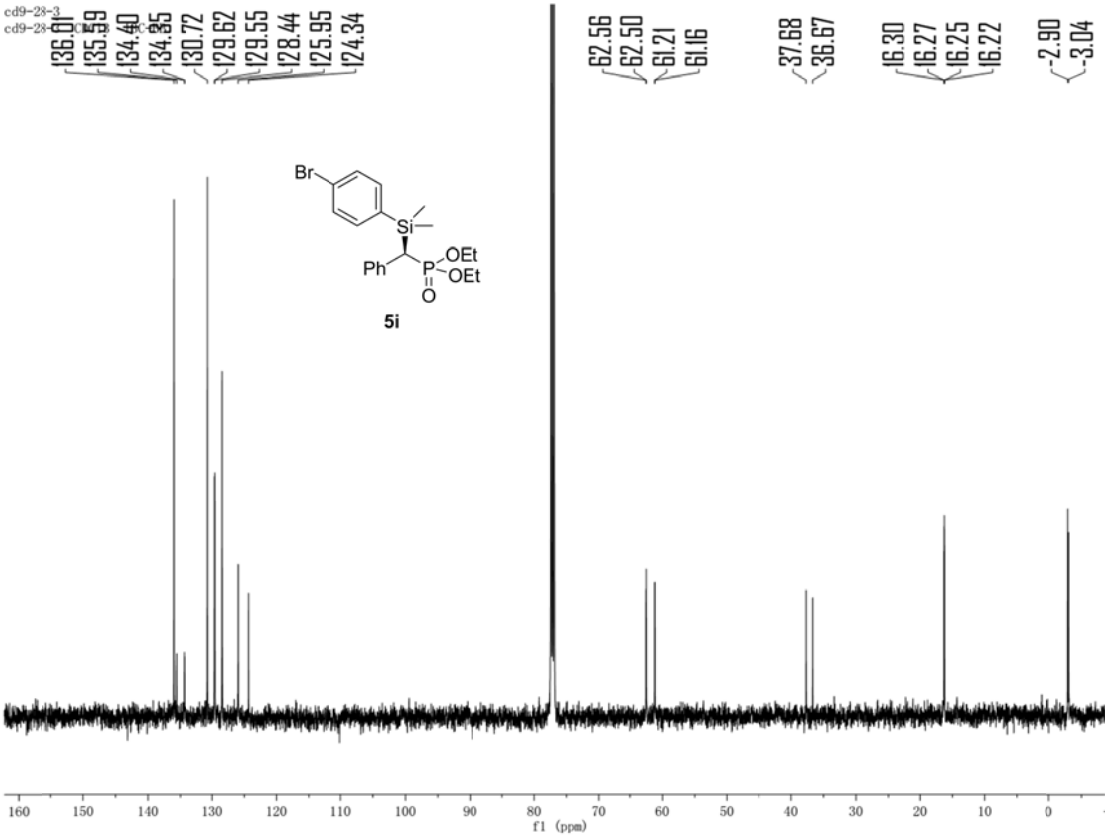
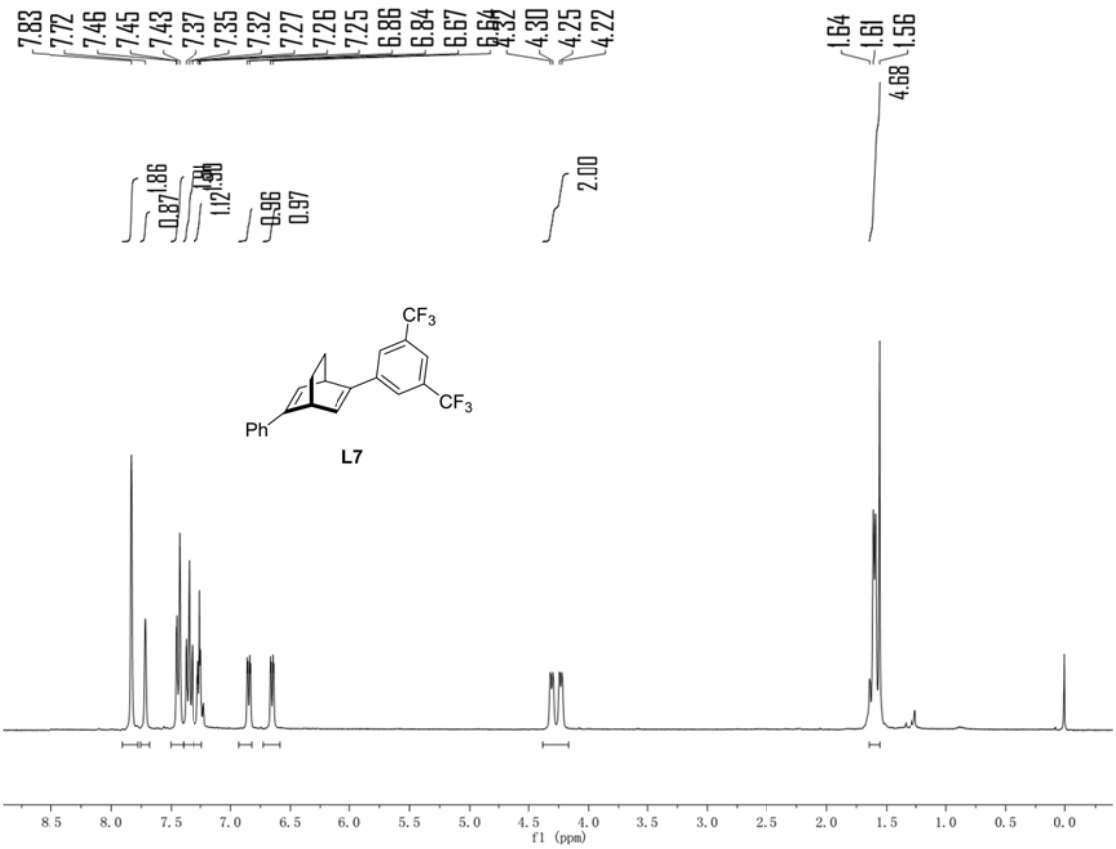
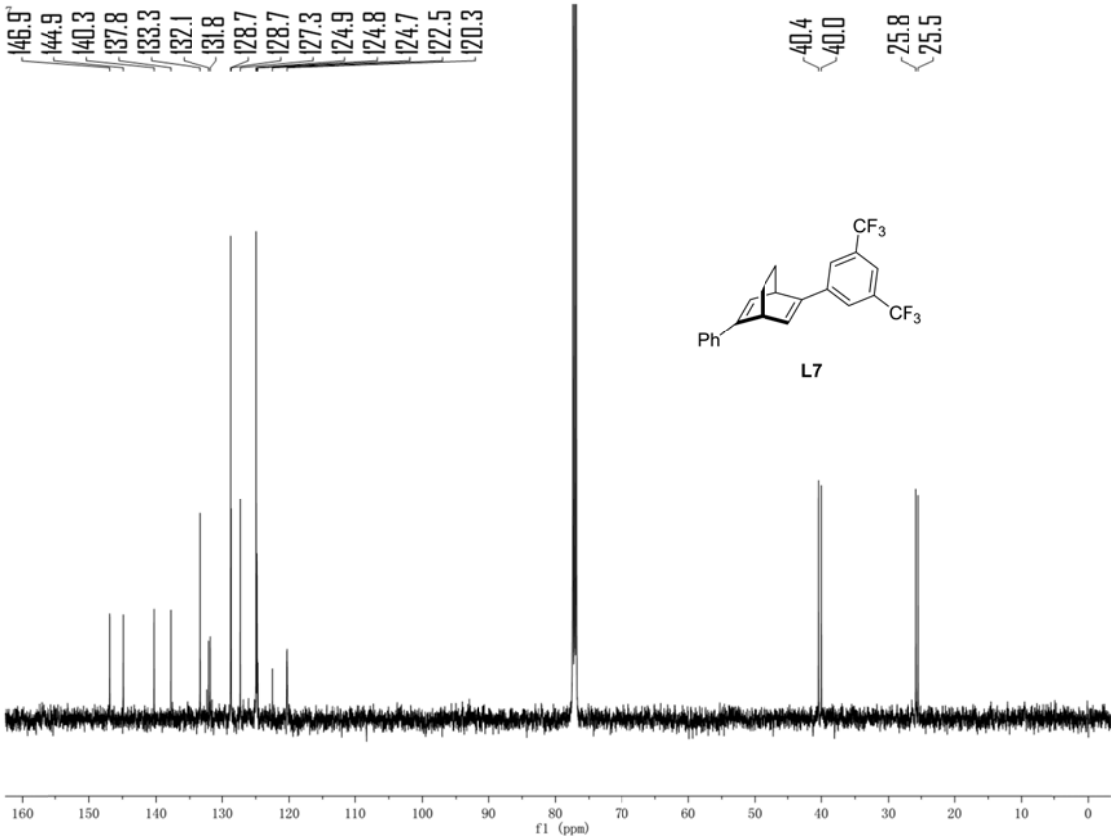
7.40
7.26
7.25
7.16
7.13
7.07
7.05
5.03
1.84
1.95
3.94
3.83
3.81
3.78
3.76
3.72
2.88
2.80
3.89
1.00
1.16
1.14
1.12
1.05
1.02
1.00
0.48
0.36
2.87
2.84
2.90
2.96
Br
Si
Ph
P
OEt
OEt
O
5i
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


cd9-23-3
136.01
135.59
134.40
134.35
130.72
129.62
129.55
128.44
125.95
124.34
62.56
62.50
61.21
61.16
37.68
36.67
16.30
16.27
16.25
16.22
-2.90
-3.04
Br
Si
Ph
P
OEt
OEt
O
5i
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.83
7.72
7.46
7.45
7.43
7.37
7.35
7.32
7.27
7.26
7.25
6.86
6.84
6.67
4.30
4.25
4.22
1.64
1.61
1.56
4.68
1.86
0.87
1.12
0.96
0.97
2.00
CF3
CF3
Ph
L7
f1 (ppm)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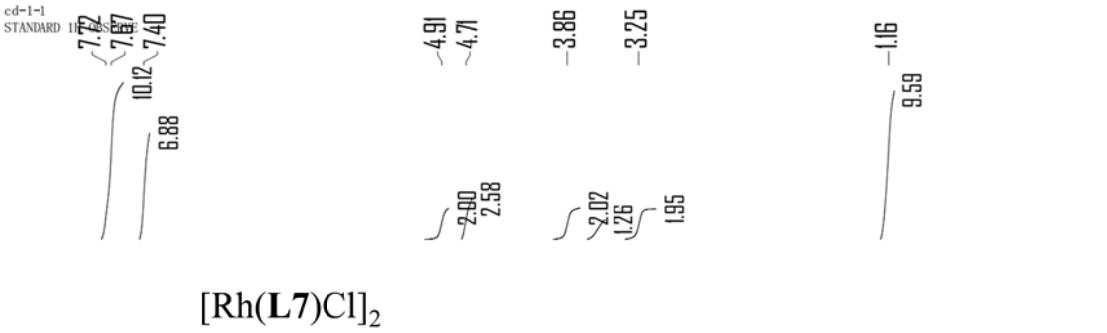
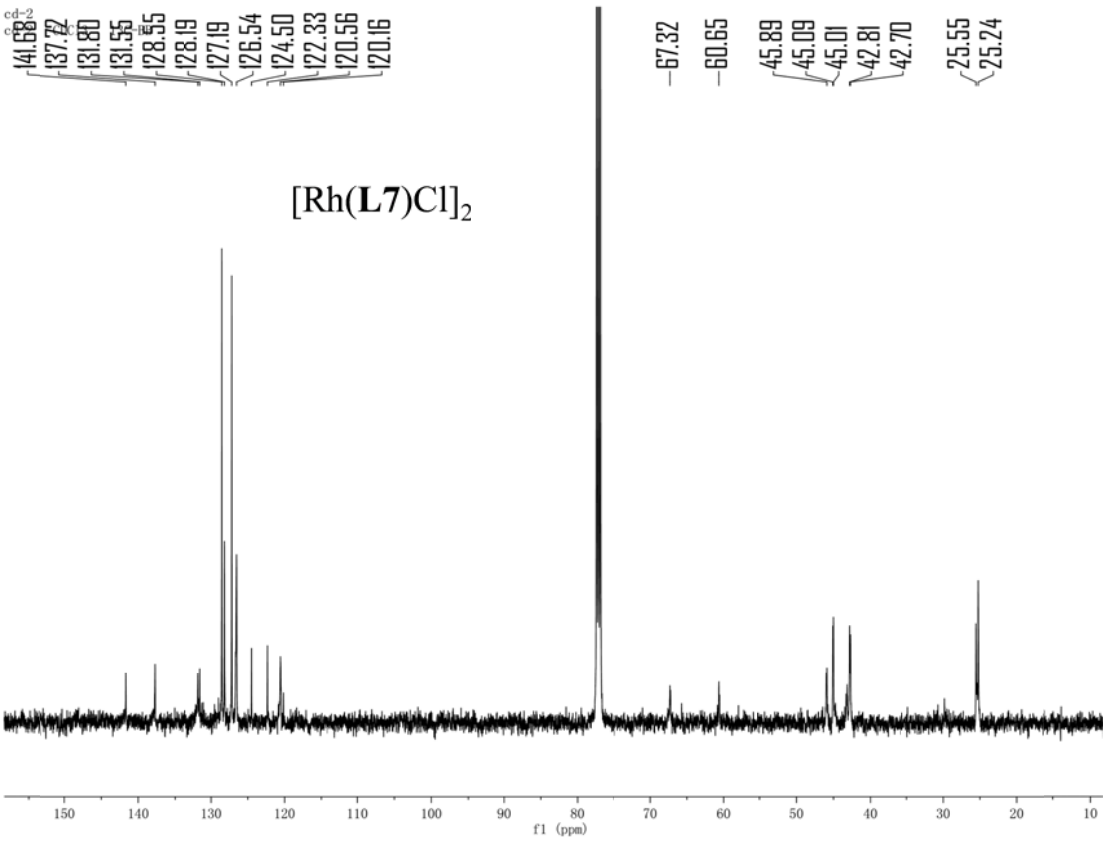
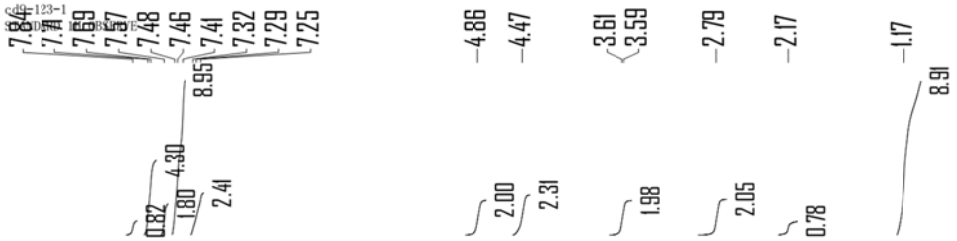
144.9
140.3
137.8
133.3
132.1
131.8
128.7
128.7
127.3
124.9
124.8
124.7
122.5
120.3
40.4
40.0
25.8
25.5
CF3
CF3
Ph
L7
f1 (ppm)



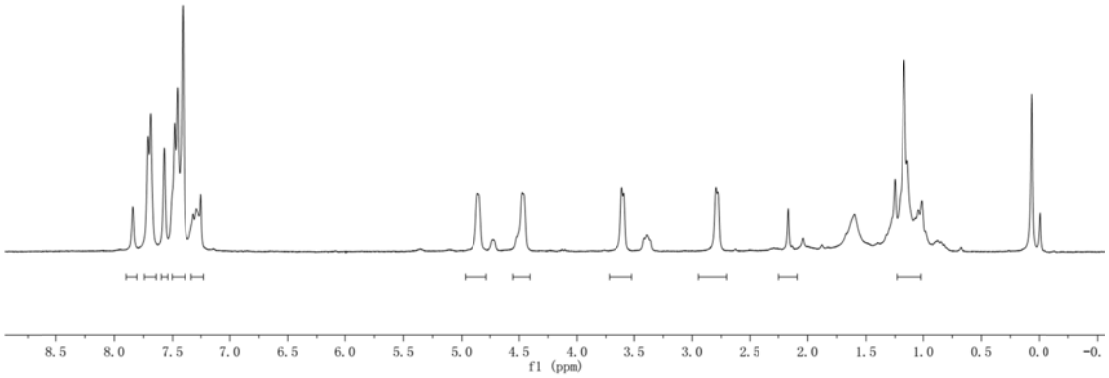
$[Rh(\mathbf{L7})Cl]_2$

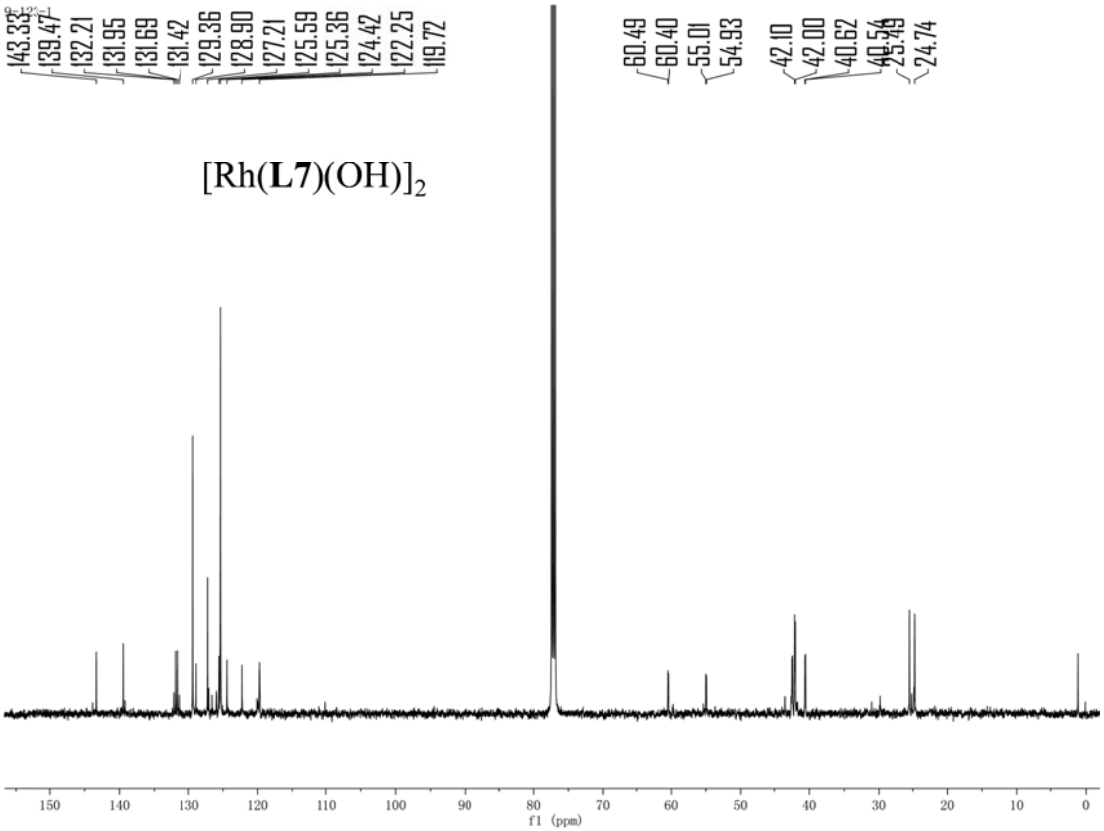


$[Rh(\mathbf{L7})Cl]_2$



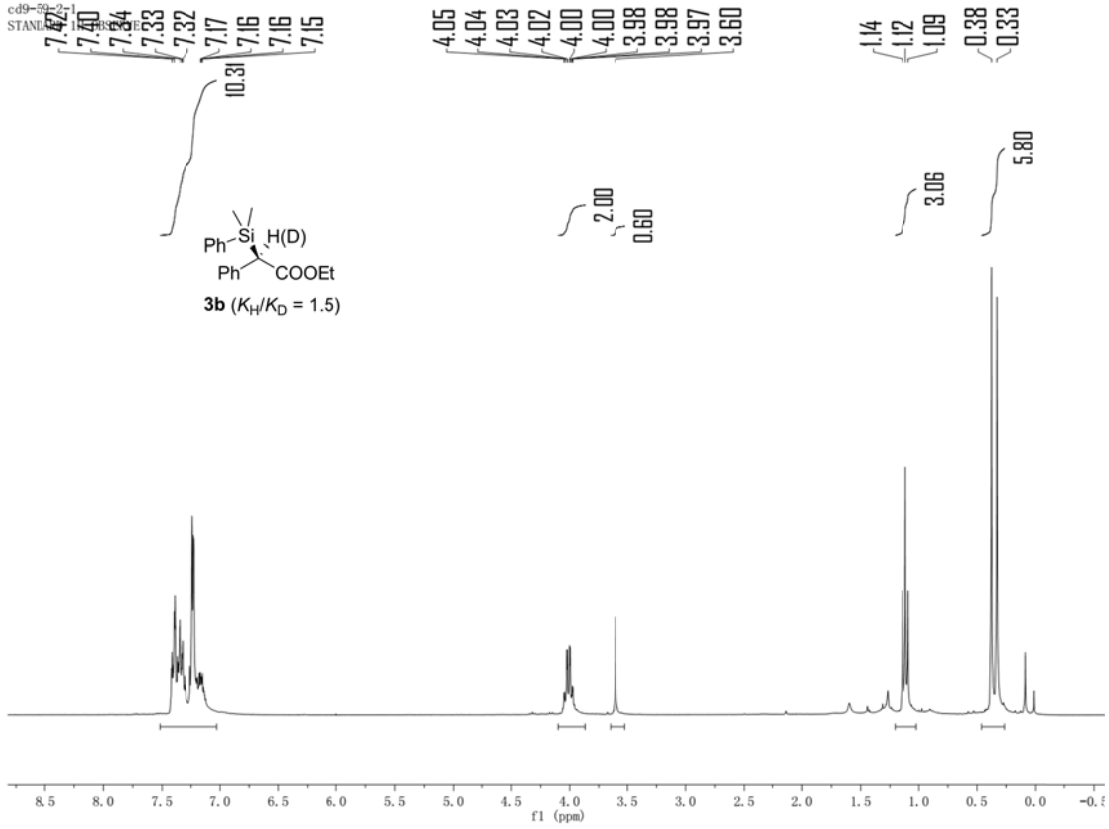
$[Rh(\mathbf{L7})(OH)]_2$

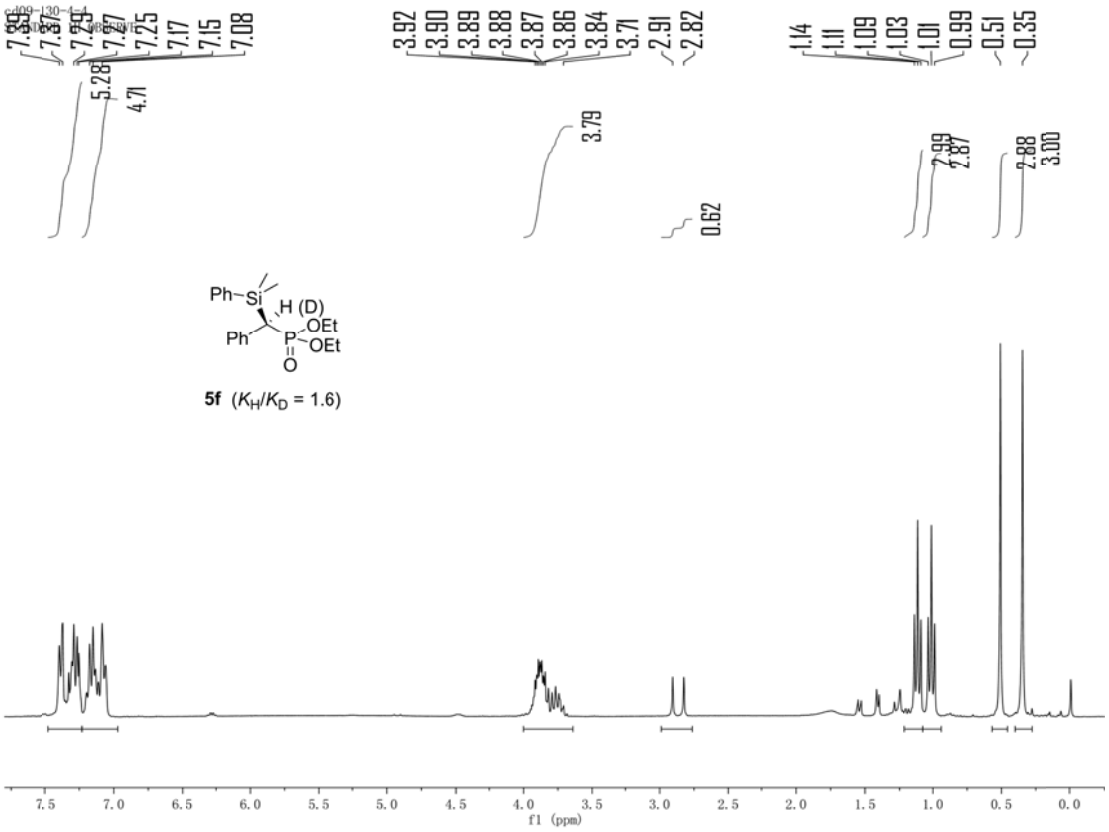




$[Rh(\mathbf{L7})(OH)]_2$

8. Copies of ^{1}H NMR spectra of products in KIE experiments





9. X-ray structures of catalyst $[Rh(L7)Cl]_2$