Supporting Information

Palladium-Catalyzed Si-C bond-forming Silylation of Aryl Iodides with Hydrosilanes: An Enhanced Enantioselective Synthesis of Silicon-stereogenic Silanes by Desymmetrization

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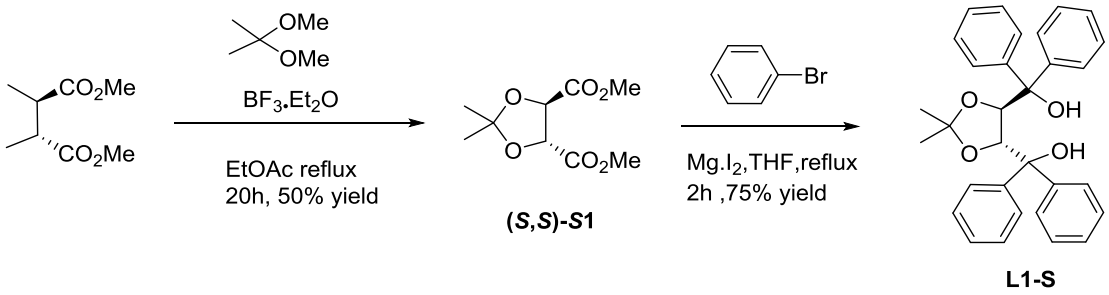
S-1. General information

All reagents and solvents were dried and purified before use by the usual procedures. Reactions were monitored by thin layer chromatography using silica gel. All the reactions dealing with air or moisture sensitive compounds were carried out in a dry reaction vessel under positive pressure of argon. Air- and moisture-sensitive liquids and solutions were transferred via a syringe or a stainless steel cannula. ^{1}H NMR was recorded at 400 MHz or 500 MHz: chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$ at 7.26 ppm). ^{13}C NMR was recorded at 100 MHz or 126 MHz: chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.20 ppm). ^{31} P NMR were recorded at 202 MHz: chemical shifts for phosphorous are reported in parts per million (ppm, δ = scale) referenced to the phosphorous resonance of phosphoric acid ($\delta = 0$). The ESI - MS analysis of the samples was operated on an LCQ advantage mass spectrometer (ThermoFisher Company, USA), equipped with an ESI ion source in the positive ionization mode, with data acquisition using the Xcalibur software (Version 1.4). high resolution mass spectral analyses (LRMS and HRMS) were performed at Chemical Instrument Center, HangZhou Normal University (Bruker Daltonics micrOTOF-QII). Tetrahydrofuran (with Na and benzophenone) were freshly distilled in prior to use.

S-2 .Synthesis of TADDOL

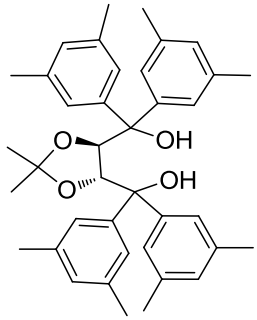


(4*S*,5*S*)-dimethyl-2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylate (S1): To a 500-mL bottom flask equipped with reflux condenser was added a ethyl acetate solution (202 mL, 0.60M) of (*S*,*S*)-dimethyl-D-tatrate (21.6g, 121mmol).Then, 2,2-dimethoxypropa ne (17.9ml, 146 mmol, 1.2 equiv) and BF_3•Et_2O (37.4 mL, 303 mmol, 2.5 equiv) wer

e added and the reaction mixture was heated to reflux for 20 h. The reaction mixture was then cooled to ambient temperature and poured into a 1-L Erlenmeyer flask. Satur ated aqueous $NaHCO_3$ (600 mL) was slowly added with stirring until gas evolution ce ased. The phases were separated and the aqueous layer was extracted with ethyl acetat e (2 x 100 mL). The combined organic extracts were washed with brine (50 mL), drie d over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by column chromatography (5:1 hexanes/ethyl acetate) to afford the methylen ated tartrate S1 as an amber oil (13.2 g, 50% yield).

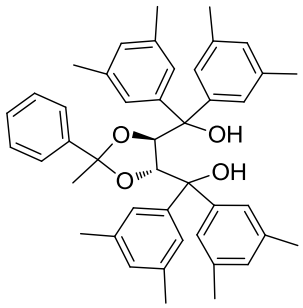
Procedure for preparation of L1-S: Dimethyl ketal *para*-methylphenyl-TADDOL was prepared according to the literature procedure[1] with slight modification. To a flame dried 250 mL 2-neck round-bottom flask equipped with a magnetic stir bar and reflux condenser was added freshly crushed magnesium turnings (4.37 g, 179.9 mmol) under N_2. The apparatus was flame dried, and a single crystal of I_2 was added as a solution in THF (180 mL). 4-Bromotoluene (30.76 g, 179.9 mmol) was slowly added to the magnesium mixture at room temperature via syringe. The reaction was cautiously allowed to reflux at 80 ℃ in an oil bath for 2 h, at which time the reaction was cooled to 0 ℃, and a solution of (4*S*,5*S*)-dimethyl-2,2-dimethyl-1,3-dioxolane -4,5-dicarboxylate (8.53 g, 39.10 mmol) in tetrahydrofuran (20 mL) was added slowly via syringe. The reaction was allowed to reflux for 12 h, after which it was cooled to 0 ℃ and quenched with sat. NH_4Cl (aq.) (100 mL). The organic and aqueous layers were separated and the aqueous layer was extracted with ethyl acetate (3 x 50 mL). The combined organics were dried over Na_2SO_4(s), filtered, and concentrated in vacuo. The crude material was recrystallized from hot methanol. The crystallized solid was isolated by filtration, washed with cold methanol, and dried under vacuum to afford the product as a white solid (15.3 g, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.46 (d, J = 6.6 Hz,4H), 7.23 (ddt, J = 21.6, 15.4, 4.8 Hz,18H), 4.53 (s,2H), 0.96 (s,3H).

Charcterazition of L2-S- L8-S:



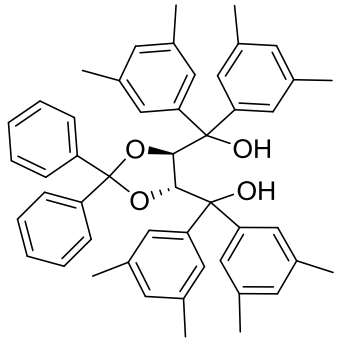
L2-S

((4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(bis(3,5-dimethylphenyl)methanol)(L2-S): White solid; 76% yield; $[\alpha]^{22}_{D}$ = -32.7 (c =2.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.07 (s, 4H), 6.85 (d, *J* = 6.3 Hz, 6H), 6.76 (s, 2H), 4.47 (s, 2H), 2.18 (d, *J* = 39.4 Hz, 24H), 0.98 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 145.97, 142.75, 137.42, 136.44, 129.26, 128.79, 126.41, 125.38, 109.34, 81.18 ,78.01, 27.18, 21.26, 1.12. HR-MS calcd for $C_{39}H_{46}O_4[M+Na]^+$: 601.3396. Found: 601.3312.



L3-S

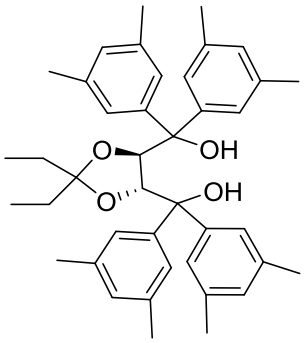
((4*R*,5*R*)-2-methyl-2-phenyl-1,3-dioxolane-4,5-diyl)bis(bis(3,5-dimethylphenyl)methanol)(L3-S): White solid; 42% yield; $[\alpha]^{22}_{D}$ = -73.7 (c =2.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.26 (s, 5H), 7.19 (s, 2H), 6.98 (s, 2H), 6.91 (s, 1H), 6.84 (s, 2H), 6.76 (d, *J* = 13.0 Hz, 3H), 6.70 (s, 1H), 6.62 (s, 1H), 5.07 (dd, *J* = 19.2, 4.8 Hz, 2H), 2.33 (s, 6H), 2.16 (m,18H), 1.44 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 145.71, 145.39, 144.48, 144.24, 142.98, 136.98 (d, *J* = 3.8 Hz), 136.86, 128.91, 128.77 (d, *J* = 8.3 Hz), 128.51, 128.35, 128.00, 125.76, 125.01, 124.82, 124.62, 123.93, 110.77, 83.62 , 81.97, 78.65 (d, *J* = 5.4 Hz), 30.32, 21.82 – 21.51 (m). HR-MS calcd for $C_{44}H_{48}O_4[M+Na]^+$: 663.3553. Found: 663.3464.



L4-S

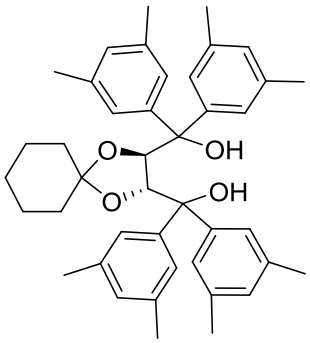
((4*R*,5*R*)-2,2-diphenyl-1,3-dioxolane-4,5-diyl)bis(bis(3,5-dimethylphenyl)methanol)(L4-S): White solid; 45% yield; $[\alpha]^{22}_{D}$ = +76.1 (c =2.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.28 (d, J = 3.6 Hz, 4H), 7.17 (s, 6H), 7.11 (s, 4H), 6.84 (s, 2H), 6.67 (s, 4H), 6.54 (s, 2H), 5.43 (s, 2H),

2.29 (s, 12H), 2.05 (s, 12H).^{13}C NMR (126 MHz, $CDCl_3$) δ = 146.20, 144.89, 141.91, 137.01, 136.64, 128.53 , 128.35, 127.91, 125.01, 124.66, 123.31, 111.57, 84.14, 21.64. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 146.20, 144.89, 141.95, 137.01, 136.64, 128.53 (d, *J* = 4.3 Hz), 128.35, 127.91, 125.01, 124.66, 123.31, 111.57, 84.14, 79.48, 21.64. HR-MS calcd for $C_{49}H_{50}O_4[M+Na]^+$:725. 3709.Found: 725.3634.



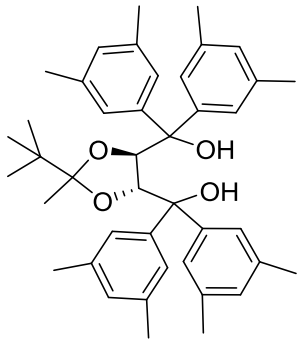
L5-S

((4*R*,5*R*)-2,2-diethyl-1,3-dioxolane-4,5-diyl)bis(bis(3,5-dimethylphenyl)methanol)(L5-S): White solid; 73% yield; $[\alpha]^{22}_D$ =+143 (c =2.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.12 (s, 4H), 6.96 (s, 4H), 6.91 (s, 2H), 6.86 (s, 2H), 4.35 (s, 2H), 2.26 (d, *J* = 30.4 Hz, 24H), 1.41 – 1.27 (m, 4H), 0.74 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 146.33, 142.60, 137.35, 136.27, 129.13, 128.71, 126.41, 125.51, 112.00, 80.57, 78.07, 29.67, 21.60, 8.28. HR-MS calcd for $C_{41}H_{50}O_4[M+Na]^+$: 629.3709. Found: 629.3619.



L6-S

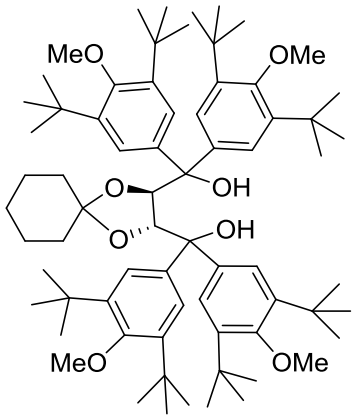
((2*R*,3*R*)-1,4-dioxaspiro[4.5]decane-2,3-diyl)bis(bis(3,5-dimethylphenyl)methanol)(L6-S): White solid; 60% yield; $[\alpha]^{22}_D$ = -54.6 (c =-2.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.15 (s, 4H), 6.99 (s, 4H), 6.91 (s, 2H), 6.85 (s, 2H), 4.47 (s, 2H), 2.26 (d, *J* = 27.9 Hz, 24H), 1.48 (d, *J* = 6.3 Hz, 4H), 1.26 (d, *J* = 19.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 146.34, 142.76, 137.36, 136.28, 129.12, 128.68, 126.40, 125.48, 109.61, 80.68, 78.10, 36.69, 25.18, 24.10, δ = 21.61 (d, J = 3.6 Hz).



L7-S

((4*R*,5*R*)-2-(tert-butyl)-2-methyl-1,3-dioxolane-4,5-diyl)bis(bis(3,5-dimethylphenyl)methanol)(L7-S): White solid; 50% yield; $[\alpha]^{22}_D$ = -95.4 (c =2.3, $CHCl_3$). ^{1}H NMR (500 M

Hz, $CDCl_3$) δ = 7.15 (s, 4H), 6.99 (s, 4H), 6.91 (s, 2H), 6.85 (s, 2H), 4.47 (s, 2H), 2.26 (d, J = 27.9 Hz, 24H), 1.48 (d, J = 6.3 Hz, 4H), 1.26 (d, J = 19.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 146.84, 146.68, 142.63, 142.33, 137.33, 136.21, 129.04, 128.68, 126.83, 126.53, 125.72, 125.36, 112.70, 81.33, 79.30, 78.42, 77.83, 39.13, 25.08, 21.74 – 21.46 (m), 19.82. HR-MS calcd for $C_{42}H_{52}O_4$[M+Na]$^+$: 643.3866. Found: 643.3778.



L8-S

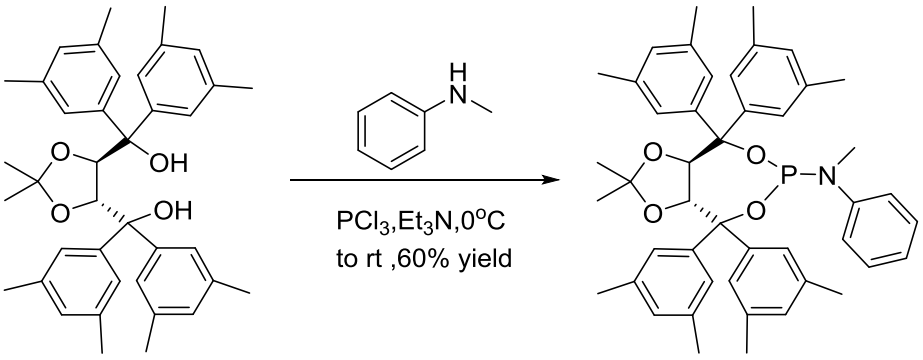
((2*R*,3*R*)-1,4-dioxaspiro[4.5]decane-2,3-diyl)bis(bis(4-methoxy-3,5-di-tert-butylphenyl)methanol)(L8-S): White solid; 35% yield; $[\alpha]^{22}_D$ = -89.6 (c =3.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.30 (s, 4H), 7.25 (d, J = 7.3 Hz, 4H), 4.75 (s, 2H), 3.63 (d, J = 10.3 Hz, 12H), 1.44 (s, 4H), 1.37 (s, 36H), 1.30 (s, 36H), 1.23 (d, J = 12.2 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 158.38 (d, J = 17.9 Hz), 142.33, 141.50, 126.06, 81.48, 64.24 (d, J = 13.5 Hz), 36.67, 35.81 (d, J = 3.4 Hz), 32.12 (d,J= 19.2 Hz), 31.45, 24.14. HR-MS calcd for $C_{70}H_{106}O_8$[M+Na]$^+$: 1097.7888. Found: 1097.7774.

S-3. Synthesis of TADDOL-derived phosphoramidite ligands

(***R***,***R***)-**L1** were prepared according to the literature procedure[2] with slight modification. To a 25 mL round-bottomed flask equipped with a magnetic stir bar was added the diol (0.60, mmol). THF (3 mL) followed by Et_3N (0.29 mL, 0.95 mmol) were added *via* syringe, and the resulting solution was cooled to 0 ℃ before the dropwise addition of phosphorous trichloride (58μL, 0.66 mmol). The reaction mixture was stirred for 1 hour and the amine (2.70 mmol) wasthen slowly added at 0 ℃. The reaction was warmed to room temperature and stirred overnight.The reaction was then diluted with Et_2O (15 mL) and filtered through a pad of Celite. The filtrate was concentrated *in vacuo* and the resulting crude mixture was purified by flash silica column chromatography (0-2% EtOAc/1% Et_3N/Hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.9 Hz, 2H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.42 (d, *J* = 7.7 Hz, 2H), 7.37 – 7.13 (m, 14H), 5.

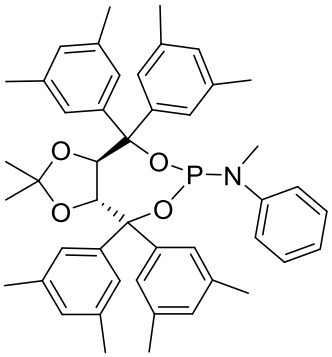
18 (dd, *J* = 8.5, 2.8 Hz, 1H), 4.81 (d, *J* = 8.5 Hz, 1H), 2.72 (d, *J* = 10.6 Hz, 6H), 1.27 (s,3H), 0.28 (s,3H).

Preparation of (TADDOL)PN(Me)$_2$ (L2):



L2-S **(*R*,*R*)-L2**

Preparation of (TADDOL)PN(Me)Ph (L2)[3]: To a cooled (0 °C) solution of N-meth ylaniline (98.6 mg, 0.92 mmol) in dry THF (30 mL) was added PCl_3 (82 µL, 0.92 mm ol) dropwise. The resulting clear solution was stirred at room temperature for 1 h and t hen cooled to -78 °C, subsequently, TEA (130 µL, 0.92 mmol) was added dropwise. After stirring at -78 °C for 0.5 h, a solution of TADDOL **L2-S** (531.8 mg, 0.92 mmol) and triethylamine (300 µL, 2.12 mmol) in dry THF (2 mL) was slowly added. The res ulting milky white suspension was stirred at room temperature overnight and then filte red under nitrogen through a pad of celite. The celite was further washed with dry TH F and the volatile solvents were removed via rotovap. The residue was dried on a vacu um line. Flash chromatography (90:10 hexanes:ethyl acetate) afforded the title compo und **(*R*,*R*)-L2**(300.8 mg, 46%) as a white foamy solid: mp 130.0–131.5 °C;

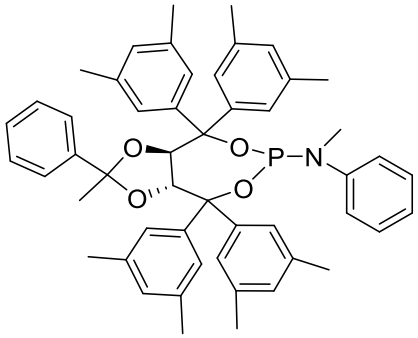


(*R*,*R*)- L2

Charcterazition of L2- L8

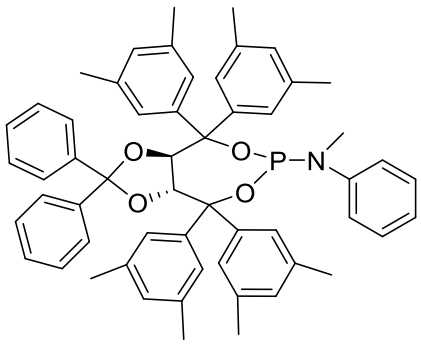
(*R*,*R*)-L2: White solid; 46% yield; $[\alpha]^{22}_D$ = -27.9 (c =2.3, $CHCl_3$). $[\alpha]^{22}_D$ = -87.1 (c =2.3, $CHCl_3$). ^{1}H NMR (400 M

Hz, $CDCl_3$) δ = 7.34 (s, 2H), 7.14 – 7.05 (m, 5H), 6.99 (t, J = 10.9 Hz, 6H), 6.76 (d, J = 16.2 Hz, 4H), 5.07 (dd, J = 8.2, 3.0 Hz, 1H), 4.78 – 4.43 (m, 1H), 3.24 (d, J = 3.4 Hz, 3H), 2.18 (d, J = 2.9 Hz, 18H), 2.13 (s, 6H), 1.33 (s, 3H), 0.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 147.07, 146.82, 146.47, 146.03 (d, J = 2.2 Hz), 141.43, 141.12, 137.04, 136.58, 136.48, 136.03, 128.88, 128.77, 128.64, 128.48, 126.66, 126.19 (d, J = 3.5 Hz), 124.77 (d, J = 15.9 Hz), 121.26, 119.46 (d, J = 16.1 Hz), 111.33, 82.99 (d, J = 3.5 Hz), 82.70, 82.49, 81.66 (d, J = 3.8 Hz), 81.56, 31.42, 27.48, 25.18, 21.35 (t, J = 6.0 Hz).^{31}P NMR (202 MHz, $CDCl_3$) δ = 136.74 .HR-MS calcd for $C_{46}H_{52}NO_4P$[M+Na]$^+$: 736.3634. Found: 736.3564.



(***R*,*R***)-L3

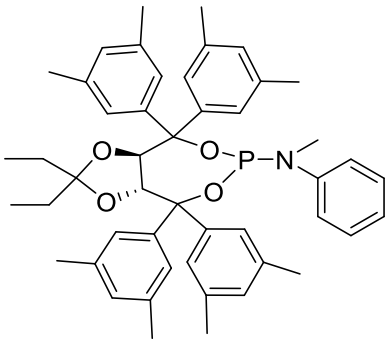
(*R*,*R*)-L3: White solid; 45% yield; $[\alpha]^{22}_D$ = -139 (c =2.3, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.53 (d, J = 7.1 Hz, 2H), 7.45 – 7.33 (m, 3H), 7.29 (s, 2H), 7.23 – 7.15 (m, 5H), 7.10 (d, J = 8.8 Hz, 5H), 6.97 – 6.82 (m, 4H), 6.69 (s, 1H), 5.36 (dd, J = 8.5, 3.6 Hz, 1H), 4.78 (d, J = 8.5 Hz, 1H), 3.46 (d, J = 4.0 Hz, 3H), 2.33 – 2.21 (m, 18H), 1.86 (s, 6H), 0.54 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 147.27, 147.03, 146.60, 146.09 (d, J = 2.9 Hz), 144.48, 141.63 (d, J = 1.3 Hz), 141.03, 137.33, 136.88 (d, J = 13.9 Hz), 136.33, 129.13, 128.84 (dd, J = 12.1, 3.3 Hz), 128.11 , 127.75, 127.01, 126.01 (d, J = 2.1 Hz), 124.97, 124.76, 121.60 (d, J = 1.8 Hz), 119.76 (d, J = 16.0 Hz), 112.00, 84.09 (d, J = 3.2 Hz), 83.43, 83.20, 81.91 (d, J = 8.4 Hz), 80.83 (d, J = 4.5 Hz), 31.80, 28.03, 21.68 (d, J = 7.9 Hz), 21.08. ^{31}P NMR (202 MHz, $CDCl_3$) δ = 137.08. HR-MS calcd for $C_{51}H_{54}NO_4P$[M+Na]$^+$: 798.3790. Found: 798.3701.



(***R*,*R***)-L4

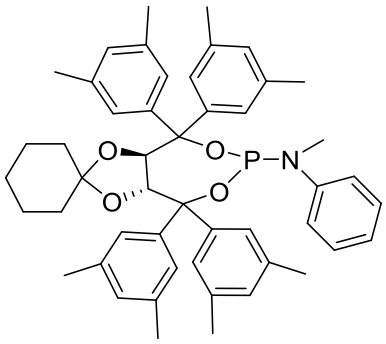
(*R*,*R*)-L4: White solid; 38% yield; $[\alpha]^{22}_D$ = -65.0 (c =2.3, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.39 (d, J = 6.4 Hz, 2H), 7.31 (d, J = 12.4 Hz, 5H), 7.20 – 7.11 (m, 6H), 7.07 (d, J = 8.1 Hz, 2H), 6.89 (dd, J = 16.1, 9.8 Hz, 6H), 6.79 (s, 2H), 6.74 (s, 1H), 6.63 (d, J = 6.0 Hz, 2H), 6.38 (s, 1H), 5.48 (d, J = 8.8 Hz, 1H),

5.10 (dd, J = 8.8, 2.3 Hz, 1H), 3.31 (s, 3H), 2.32 (s, 6H), 2.25 (s, 6H), 2.02 (s, 6H), 1.95 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 147.33, 147.08, 146.54, 146.38 (d, J = 3.2 Hz), 143.79, 142.39, 141.30, 140.99, 137.40, 137.01 (d, J = 2.8 Hz), 135.77, 129.27, 129.12 (d, J = 1.1 Hz), 128.98 , 128.81, 128.04 (d, J = 14.6 Hz), 127.17, 126.79, 126.63, 126.50 (d, J = 2.4 Hz), 125.88, 125.15 (d, J = 3.9 Hz), 125.04, 121.56, 119.71, 119.55, 111.26 , 85.14 (d, J = 3.6 Hz), 84.58, 84.38, 82.18 (d, J = 8.7 Hz), 81.03 (d, J = 4.5 Hz), 31.50, 21.74 (d, J = 6.0 Hz), 21.57, 21.31 . ^{31}P NMR (202 MHz, $CDCl_3$) δ = 132.05. HR-MS calcd for $C_{56}H_{56}NO_4P[M+Na]^+$: 860.3947. Found:860.3866.



(*R*,*R*)-L5

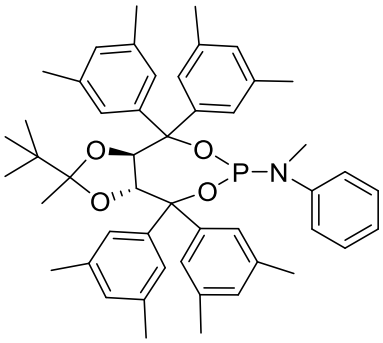
(*R*,*R*)-L5: White solid; 56% yield; $[\alpha]^{22}_D$ = -39.7 (c = 2.3, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27 (s, 2H), 7.18 (dd, J = 17.9, 9.5 Hz, 7H), 7.09 (d, J = 8.2 Hz, 2H), 7.01 (s, 2H), 6.85 (d, J = 16.2 Hz, 4H), 5.04 (d, J = 8.5 Hz, 1H), 4.87 (d, J = 8.6 Hz, 1H), 3.11 (s, 3H), 2.24 (t, J = 5.6 Hz, 24H), 1.36 (ddd, J = 46.3, 14.6, 6.4 Hz, 4H), 0.69 (t, J = 7.4 Hz, 3H), 0.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 147.43 (s), 147.17 (s), 146.64 (d, J = 7.8 Hz), 142.04 (d, J = 2.6 Hz), 141.56 (d, J = 1.2 Hz), 137.32, 136.83, 136.39 , 136.14, 129.20, 128.69 (dd, J = 11.1, 3.2 Hz), 127.00 – 126.54, 125.03 (d, J = 10.1 Hz), 121.33, 119.43 (d, J = 16.8 Hz), 115.57, 83.62 (d, J = 3.0 Hz), 82.35 – 81.70 (m), 31.63, 29.67, 28.54, 21.58 (t, J = 4.3 Hz), 8.27 (d, J = 8.6 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ = 134.77. HR-MS calcd for $C_{48}H_{56}NO_4P[M+Na]^+$: 764.3947. Found: 764.3870.



(*R*,*R*)-L6

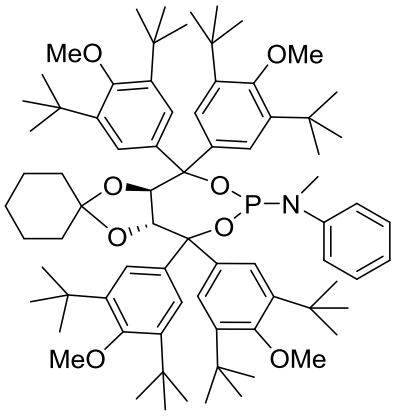
(*R*,*R*)-6: White solid; 53% yield; $[\alpha]^{22}_D$ = -134 (c =2.3, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39 (s, 2H), 7.25 – 7.14 (m, 4H), 7.14 – 7.08 (m, 4H), 7.06 (s, 2H), 6.92 (t, J = 7.2 Hz, 1H), 6.84 (t, J = 8.9 Hz, 4H), 5.07 (dd, J = 8.4, 3.2 Hz, 1H), 4.81 (d, J = 8.4 Hz, 1H), 3.25 (d, J = 3.7 Hz, 3H), 2.25 (dd, J = 12.2, 6.1 Hz, 24H), 1.48 (d, J = 20.7 Hz, 4H), 1.22 (d, J = 29.3 Hz, 4H), 0.55 (s, 1H), 0.32 (s, 1H). ^{13}C NMR (101 MH

z, $CDCl_3$) δ = 147.39, 147.14,146.72, 146.49 (d, J = 1.6 Hz), 141.74, 141.30, 137.32, 136.86, 136.58, 136.18, 129.16, 128.92, 128.83 – 128.59 (m), 126.86, 126.55 (d, J = 4. 4 Hz), 125.02, 121.41, 119.49 (d, J = 16.6 Hz), 82.89 – 82.18 (m), 81.96 (d, J = 8.1 H z), 77.41, 77.09, 76.77, 37.28,35.41, 31.60, 25.21, 24.38, 24.11, 21.65. ^{31}P NMR (202 MHz, $CDCl_3$) δ = 136.76. HR-MS calcd for $C_{49}H_{56}NO_4P[M+Na]^+$: 776.3947. Found: 776.3872.



(*R*,*R*)-L7

(*R*,*R*)-L7: White solid; 47% yield; $[\alpha]^{22}_D$ = -158 (c =2. 3, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.19 (d, J = 6.3 Hz, 5H), 7.15 (s, 2H), 7.11 (s, 2H), 7.05 (s, 1 H), 7.00 (s, 1H), 6.95 (s, 1H), 6.89 (d, J = 16.9 Hz, 3 H), 6.82 – 6.76 (m, 2H), 4.99 (dd, J = 16.6, 8.5 Hz, 1 H), 4.86 (d, J = 8.8 Hz, 1H), 2.88 (dd, J = 6.0, 3.0 Hz, 3H), 2.22 (dd, J = 18.8, 11.5 Hz, 24H), 0.57 (d, J = 9. 2 Hz, 6H), 0.46 (d, J = 12.2 Hz, 4H), 0.32 (s, 2H) ^{13}C NMR (101 MHz, $CDCl_3$) δ = 147.53, 147.27, 147.07, 146.51 (d, J = 13.7 Hz), 142.17 (d, J = 16.4 Hz), 141.83, 141.54, 137.47, 136.93, 136.07, 129.36 (d, J = 11.9 Hz), 128. 77, 128.51, 127.41, 127.04 (d, J = 23.6 Hz), 125.32, 121.24 (d, J = 6.3 Hz), 119.19, 11 6.45, 86.01, 84.91, 82.52 (d, J = 8.5 Hz), 81.49 (s), 80.28 (d, J = 14.2 Hz), 79.89 (d, J = 3.8 Hz), 38.82, 38.59, 31.69, 24.80, 24.54, 21.87 –21.37(m),19.47, 18.45. ^{31}P NMR (202 MHz, $CDCl_3$) δ = 136.41 .HR-MS calcd for $C_{49}H_{58}NO_4P[M+H]^+$: 756.4103. Fou nd:756.4195

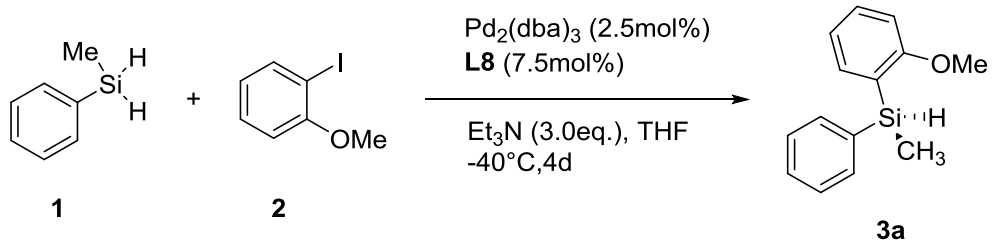


(*R*,*R*)-L8

(*R*,*R*)-L8: Pale yellow solid; 28% yield; $[\alpha]^{22}_D$ = -21.1 (c =1.6, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54 (d, J = 11.1 Hz, 4H), 7.25 (d, J = 6.4 Hz, 4H), 7.13 (dd, J = 17.1, 7.8 Hz, 4H), 6.87 (t, J = 7.1 Hz, 1H), 5.20 (d, J = 10.6 Hz, 1H), 4.73 (d, J = 8.7 Hz, 1H), 3.63 – 3.57 (m, 12H), 3.35 (d, J = 2.9 Hz, 3H), 1.38 – 1.27 (m, 82H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 158.57, 158.12, 142.41, 141.73 (d, J = 9.4 Hz),

141.22, 140.21, 136.33, 135.69, 127.43, 125.51, 121.14, 119.16 (d, J = 16.7 Hz), 110.60 , 82.73 (dd, J = 19.0, 9.2 Hz), 77.33, 77.02, 76.70, 64.12, 37.17, 35.82 (t, J = 8.5 Hz), 32.14 (dd, J = 12.8, 3.8 Hz), 31.06, 24.96, 23.92, 23.71.^{31}P NMR (202 MHz, $CDCl_3$) δ = 137.50 .

S-4 . Experimental Procedure for palladium-catalyzed asymmetric arylation reaction:

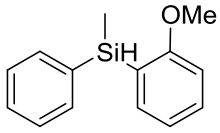


1 **2** **3a**

Typical experimental procedure[4] for palladium-catalyzed asymmetric arylation reaction at -40 ℃.

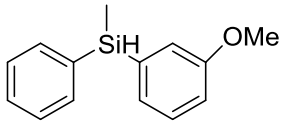
A mixture of $Pd_2(dba)_3$ (23 mg, 0.025 mmol) and phosphoramidite ligand (90 mg, 0.075 mmol) was stirred in THF (2 mL) for 2 hours at room temperature. The reaction mixture was cooled to -40 ℃ and stirred for 10 minutes. To the reaction mixture were added triethylamine (418 μL, 3.0 mmol), aryl iodide **2** (203 μL, 1.0 mmol) and secondary silane **1** (256 μL, 1.5 mmol,). After stirring for 3-10 days at -40 ^{o}C, the reaction mixture was quenched with water, extracted with dichloromethane three times, and the extracts dried over sodium sulfate. The solvent was then evaporated under a reduced pressure and crude product purified by preparative TLC (silica gel). Enantiomeric excess of the arylated product was determined by HPLC analysis employing a chiral stationary phase.

S-5. Characterization data of Products 3a-3l



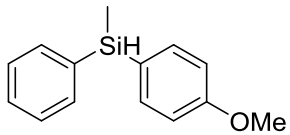
3a

(2-methoxyphenyl)(methyl)(phenyl)silane(3a): Yield 50%; Colo rless oil. 85% *ee*. HPLC conditions: chiralcel OJ-H, n-hexane/2-pr opanol = 99/1, 1 mL/min. minor enantiomer t_1 = 7.075 min, major enantiomer t_2 = 8.096 min; $[\alpha]^{22}_D$ = -27.9 (c =12.4, $CHCl_3$). ^{1}H NM R (400 MHz, $CDCl_3$) δ = 7.63 – 7.46 (m, 2H), 7.34 (dd, J = 11.7, 6.4 Hz, 5H), 6.92 (t, J = 7.3 Hz, 1H), 6.80 (d, J = 8.3 Hz, 1H), 4.92 (d, J = 3.2 Hz, 1H), 3.73 (s, 3H), 0.61 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 164.45, 136.78, 136.04, 134.99, 131.70, 129. 29, 127.86, 123.81, 120.78, 109.81, 55.29, -4.94. HR-MS calcd for $C_{14}H_{16}OSi$ $[M+H]^+$: 229.0970. Found: 229.1046.



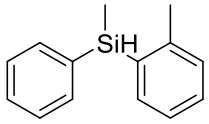
3b

(3-methoxyphenyl)methylphenylsilane(3b): Yield 45%; Col orless oil. 35% *ee*. HPLC conditions: chiralcel OJ-H, n-hexan e/2-propanol = 80/20, 1 mL/min. major enantiomer t_1 = 8.829 min, mnor enantiomer t_2 = 9.54 min; $[\alpha]^{22}_D$ = -12 (c =15.1, C HCl_3). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 (d, J = 6.7 Hz, 2H), 7.32 – 7.19 (m, 4H), 7.08 – 6.99 (m, 2H), 6.85 (d, J = 9.8 Hz, 1H), 4.98 – 4.58 (m, 1H), 3.70 (s, 3H), 0.54 (d, J = 3.7 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.10, 136.94, 135.23, 134.86, 129.59, 129.26, 128.02, 127.13, 120.19, 114.96, 55.14, -4.96. HR-MS calcd for $C_{14}H_{16}OSi$ $[M+Na]^+$: 251.0970. Found: 251.0877.



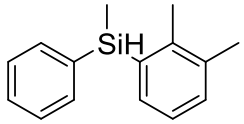
3c

(4-methoxyphenyl)methylphenylsilane (3c): Yield 42%;Co lorless oil. 14% *ee*. HPLC conditions: chiralcel OJ-H, n-hexa ne/2-propanol = 99/1, 1 mL/min. major enantiomer t_1 = 12.33 1 min, minor enantiomer t_2 =13.02 min; $[\alpha]^{22}_D$ = -4.94 (c =5.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54 (d, J = 6.3 Hz, 2H), 7.48 (d, J = 6.7 H z, 2H), 7.41 – 7.30 (m, 3H), 6.91 (d, J = 6.9 Hz, 2H), 5.01 – 4.83 (m, 1H), 3.79 (s, 3 H), 0.59 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.79, 135.28, 134.78, 133.73, 12 8.38, 126.89, 124.94, 112.75, 53.98, -5.80. HR-MS calcd for $C_{14}H_{16}OSi$[M+H]+: 229. 0970. Found : 229.1049.



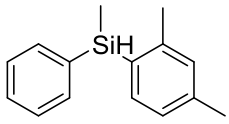
3d

Methyl(2-methylphenyl)phenylsilane (3d): Yield 62%; Col orless oil. 78%ee. HPLC conditions: chiralcel OJ-H, n-hexane/2-pro panol = 99/1, 1 mL/min, minor t1 = 6.234 min, major enantiomer t_2 = 6.814 min; $[\alpha]^{22}_D$ = -24.96 (c =12.4, $CHCl_3$). ^{1}H NMR (500 MH z, $CDCl_3$) δ= 7.52 (dd, J = 17.2, 7.7 Hz, 3H), 7.35 (dd, J = 19.3, 7.3 Hz, 4H), 7.19 (d, J = 9.0 Hz, 2H), 5.04 (s, 1H), 2.37 (d, J = 10.5 Hz, 3H), 0.64 (dd, J = 10.4, 3.8 Hz, 3 H). δ = ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.29, 135.77, 135.62, 134.82, 134.06, 130.0 2 , 129.64, 129.42, 128.01, 125.15, 22.67, -4.75. HR-MS calcd for $C_{14}H_{16}Si$[[M+Na] $^+$: 235.1021 Found: 235.0915.



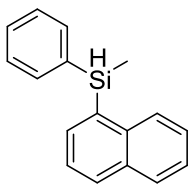
3e

(2,3-dimethylphenyl)methylphenylsilane (3e): Yield 32%; Col orless oil. 69% *ee*. HPLC conditions: chiralcel OJ-H, n-hexane/2 -propanol = 99/1, 1 mL/min. minor enantiomer t_1 = 4.485 min, m ajor enantiomer t_2 = 5.503 min; $[\alpha]^{22}_D$ = -28.1 (c =4.65, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58 – 7.45 (m, 2H), 7.42 – 7.25 (m, 4H), 7.20 (d, J = 7.4 Hz, 1H), 7.10 (t, J = 7.4 Hz, 1H), 5.06 (q, J = 3.8 Hz, 1H), 2.26 (d, J = 12.0 Hz, 6H), 0.62 (d, J = 3.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 142.67, 136.52, 136.0 5, 134.85, 134.16, 133.81, 131.82, 129.40, 128.04, 125.42, 20.51, 19.82, -4.34. HR-M S calcd for $C_{15}H_{18}Si$ [M+Na]+: 249.1178. Found: 249.1073.



3f

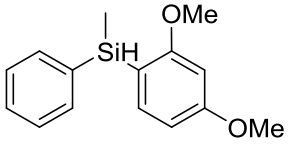
(2,4-dimethylphenyl)methylphenylsilane (3f): Yield 48%; Colorless oil. 86% *ee*. HPLC conditions: chiralcel OJ-H, n-hexane, 0.8 mL/min. minor enantiomer t_1 = 15.342 min, major enantiomer t_2 = 16.777 min; $[\alpha]^{22}_D$ = +19.84 (c =5.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.50 (d, J = 8.6 Hz, 2H), 7.40 – 7.22 (m, 4H), 6.99 (s, 2H), 5.02 (s, 1H), 2.31 (d, J = 9.9 Hz, 6H), 0.68 – 0.46 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 1 44.31, 139.99, 135.99, 134.87, 130.74, 130.45, 129.41, 128.06, 126.04, 22.61, 21.46, -4.62. HR-MS calcd for $C_{15}H_{18}Si$[M+Na]$^+$: 249.1178. Found: 249.10 95.



3g

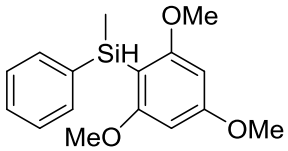
Methyl(naphthalen-1-yl)phenylsilane(3g): Yield

53% ;Colorless solid. 75% *ee*. HPLC conditions: chiralcel OJ-H, n-hexane/2-propanol = 99/1, 1 mL/min. minor enantiomer t_1 = 7.535 min, major enantiomer t_2 = 9.764 min; $[\alpha]^{22}_D$ = -9.4 (c =3.8, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 – 8.02 (m, 1H), 7.84 (d, J = 8.3 Hz, 1H), 7.80 (dd, J = 6.8, 2.7 Hz, 1H), 7.71 (dd, J = 6.7, 1.2 Hz, 1H), 7.55 (dd, J = 7.8, 1.5 Hz, 2H), 7.43 – 7.35 (m, 3H), 7.33 – 7.24 (m, 3H), 5.36 (q, J = 3.9 Hz, 1H), 0.73 (d, J = 3.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ =137.33 (s), 135.50 (d, J = 19.5 Hz), 135.09, 133.55, 133.47, 130.69, 129.70, 129.09, 128.22, 128.17, 126.26, 125.83, 125.42, -4.29. HR-MS calcd for $C_{17}H_{16}Si$ $[M+Na]^+$: 271.1021. Found: 271.0923.



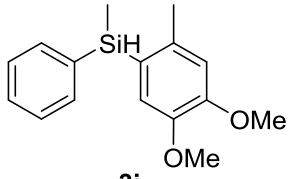
3h

(2,4-dimethoxyphenyl)(methyl)(phenyl)silane(3h): Yield 47%;Colorless solid. 22% *ee*. HPLC conditions: chiralcel OJ-H, n-hexane/2-propanol = 95/5, 1 mL/min. major enantiomer t_1 = 8.736 min, minor enantiomer t_2 = 11.121 min; $[\alpha]^{22}_D$ = -9.3 (c =14.5, $CHCl_3$). ^{1}HNMR (400 MHz, $CDCl_3$) δ = 7.50 (dd, J = 7.0, 2.4 Hz, 2H), 7.29 – 7.21 (m, 3H), 7.18 (d, J = 8.0 Hz, 1H), 6.38 (dd, J = 8.0, 2.0 Hz, 1H), 6.33 (d, J = 1.7 Hz, 1H), 4.80 (q, J = 3.7 Hz, 1H), 3.67 (d, J = 18.8 Hz, 6H), 0.50 (d, J = 3.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.83, 163.16, 137.59, 136.42, 134.84, 129.10, 127.75, 115.01, 104.86, 97.91, 55.28, 25.41, -4.86. HR-MS calcd for $C_{15}H_{18}O_2Si$ $[M+Na]^+$:281.1076. Found: 281.0982.



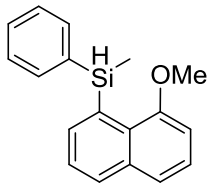
3i

Methyl(phenyl)(2,4,6-trimethoxyphenyl)silane(3i): Yield 28% ;Colorless solid. 36% *ee*. HPLC conditions: chiralcel OJ-H, n-hexane/2-propanol = 99/1, 1 mL/min. minor enantiomer t_1 = 21.367 min, major enantiomer t_2 = 36. 92 min; $[\alpha]^{22}_D$ = +14.5 (c =4.65, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50 (dd, J = 6.4, 3.0 Hz, 2H), 7.24 – 7.16 (m, 3H), 6.01 (s, 2H), 4.93 (s, 1H), 3.72 (s, 3H), 3.62 (s, 6H), 0.50 (d, J = 3.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.51, 163.93, 141.16, 137.78, 134.57, 128.61, 127.47, 108.00, 102.13, 90.72, 55.50, 55.25, 44.52, -3.88. HR-MS calcd for $C_{16}H_{20}O_3Si[M+Na]^+$: 311.1182. Found: 311.1092.



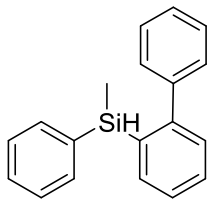
3j

(2,4-dimethoxy-6-methylphenyl)(methyl)(phenyl)silane(3j): Yield 37% ;Colorless solid. 36% *ee*. HPLC conditions: chiralcel OJ-H, n-hexane/2-propanol = 99/1, 1 mL/min. minor t_1 =11.603 min, minor enantiomer t_2 =14.074 min; $[\alpha]^{22}_D$ = +27 (c =14, 8 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52 (dd, J = 7.3, 1.8 Hz, 2H), 7.36 (t, J = 6.7 Hz, 3H), 6.97 (s, 1H), 6.73 (s, 1H), 5.00 (q, J = 3.8 Hz, 1H), 3.85 (d, J = 21.6 Hz, 6H), 2.31 (s, 3H), 0.63 (d, J = 3.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.34, 146.49, 137.66, 135.85, 134.71, 129.35, 127.96, 124.44, 118.69, 113.47, 56.08, 55.70, 22.13, -4.88. HR-MS calcd for $C_{16}H_{20}O_2Si[M+Na]^+$: 295.1223. Found: 295.1140.



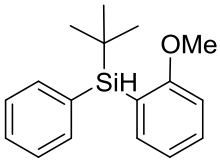
3K

(8-methoxynaphthalen-1-yl)(methyl)(phenyl)silane(3k): Yield 50% ;Colorless solid. 71% *ee*. HPLC conditions: chiralcel OJ-H, n-hexane/2-propanol = 99/1, 1 mL/min. minor enantiomer t_1 = 8.269 min, major enantiomer t_2 =17.565 min; $[\alpha]^{22}_D$ = - 21.3 (c =11, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.31 (d, J = 8.6 Hz, 1H), 7.81 (d, J = 9.0 Hz, 1H), 7.70 (d, J = 8.1 Hz, 1H), 7.52 (dd, J = 6.3, 3.1 Hz, 2H), 7.39 – 7.32 (m, 1H), 7.23 (dd, J = 16.0, 7.3 Hz, 4H), 7.11 (d, J = 8.7 Hz, 1H), 5.46 (q, J = 3.8 Hz, 1H), 3.66 (s, 3H), 0.65 (d, J = 3.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.60, 138.59, 136.73, 134.68, 132.6, 129.55, 128.96, 128.66, 127.69, 127.17, 126.60, 123.42, 117.07, 113.09, 56.25, -4.35. EI-MS calcd for $C_{18}H_{18}OSi[M+H]^+$: 278.



3l

[1,1'-biphenyl]-2-yl(methyl)(phenyl)silane(3l): Yield 41%; Colorless oil. 70% *ee*. HPLC conditions: chiralcel OJ-H, n-hexane/2-propanol = 99/1, 1 mL/min. major enantiomer t_1 = 5.865 min, minor enantiomer t_2 = 6.925 min; $[\alpha]^{22}_D$ = -26.6 (c =2.3, $CHCl_3$). ^{1}H NMR(500 MHz, $CDCl_3$) δ = 7.59 (d, J = 7.2 Hz, 1H), 7.42 (dd, J = 18.8, 7.2 Hz, 3H), 7.31 (d, J = 14.4 Hz, 8H), 7.21 (d, J = 15.6 Hz, 2H), 4.79 (d, J = 3.2 Hz, 1H), 0.24 (d, J = 3.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 149.76, 143.47, 136.38, 134.82, 134.20, 129.56, 129.46, 129.40, 129.34, 129.25, 127.91, 127.87, 127.20, 126.48, -4.62. HR-MS calcd for $C_{19}H_{18}OSi$ $[M-H]^-$: 273.1178. Found: 273.1091.



3m

Tert-butyl(2-methoxyphenyl)(phenyl)silane(3m): Yield 30%; Colorless oil. 25% *ee*. HPLC conditions: chiralcel OJ-H, n-hexane/2-propanol = 99/1, 0.7 mL/min. minor enantiomer t_1 = 7.429 min, major enantiomer t_2 = 8.17 min; $[\alpha]^{22}_D$ = + 6.11 (c =1.8, 1$CHCl_3$). ^{1}H NMR(500 MHz, $CDCl_3$) δ = 7.71 (d, J = 6.8 Hz, 2H), 7.36 – 7.27 (m, 5H), 6.91 (d, J = 11.0 Hz, 1H), 6.81 (d, J = 11.5 Hz, 1H), 4.61 (d, J = 4.6 Hz, 1H), 3.75 (d, J = 4.0 Hz, 3H), 1.06 (d, J = 4.8 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 163.89, 138.29, 136.02, 135.26, 134.99, 131.55, 129.17, 127.64, 122.94, 120.71, 109.75, 54.78, 28.35, 18.29. HR-MS calcd for $C_{17}H_{22}OSi$ $[M+Na]^+$: 293.1440. Found: 269.1342.

S-6. References

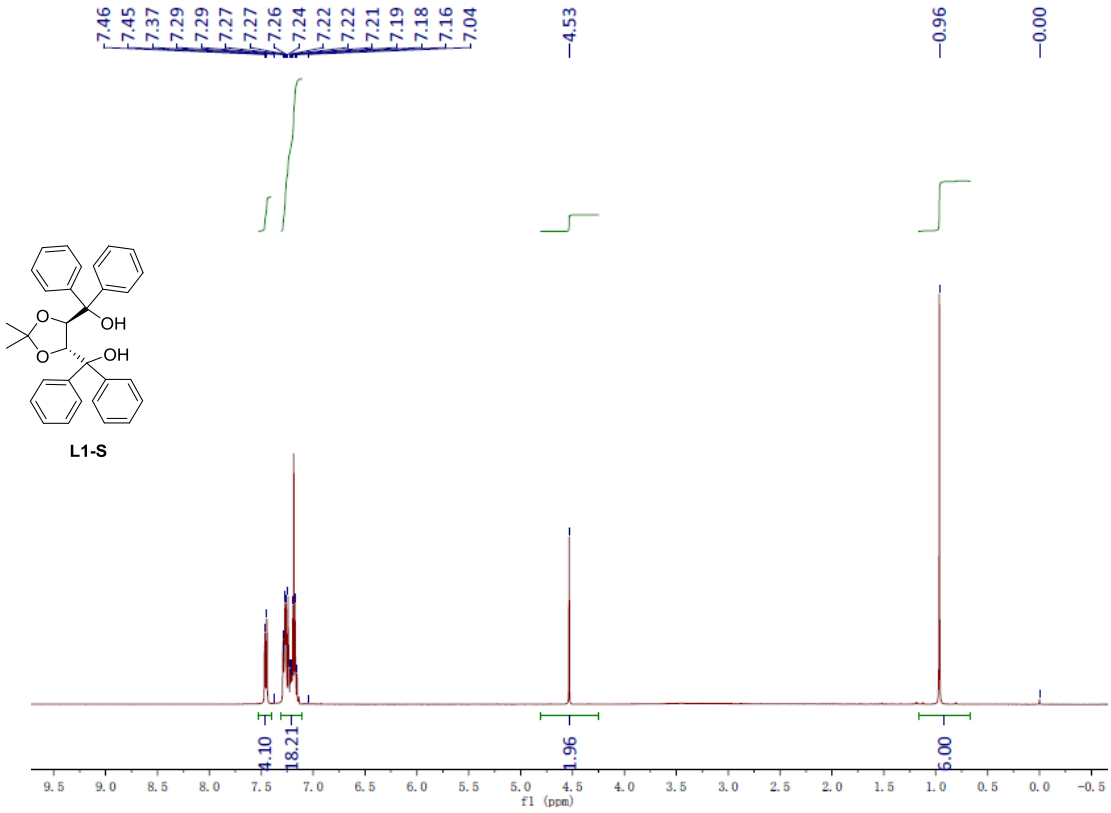
1. For synthesis of L1-S, please see: a) Ho-Yan Sun, Koji Kubota, and Dennis G. Hall, *Chem. Eur. J*, **2015**, 20, 1-10; b) Sieber, J. D.; Morken, J. P. *J. Am. Chem. Soc*. **2008**, 130, 4978.
2. For synthesis of L1, please see: a) Julia Pedroni, Michele Boghi, Tanguy Saget, and Nicolai Cramer, *Angew. Chem. Int. Ed.*, 2014, 53, 9064-9067; b) Angela R. Woodward, Heather E. Burks, Louis M. Chan, and James P. Morken, *Org. Lett*, **2005**, 24, 5505-5507; c) Chunrui Sun, Bowman Potter and James P. Morken, *J. Am. Chem. Soc*, **2014**, 45, 93-116.
3. For synthesis of L2-L8, please see: a) Shin A. Moteki, Di Wu, Kusum L. Chandra, D. Sahadeva Reddy, and James M. Takacs, *Org. Lett*, **2005**, 14, 3097-3100; b)Sean M. Smith and James M. Takacs, *Org. Lett*, **2010**, 20, 4612-4615.
4. For synthesis of 3a-3l, please see: a) Yu Kurihara, Michihiro Nishikawa, Yoshinori Yamanoi and Hiroshi Nishihara, *Chem. Commun.*, **2012,** 48, 11564–11566 **;** b) Yoshinori Yamanoi, Takafumi Taira, Jun-ichi Sato, Ikuse Nakamula, andHiroshi Nishihara, *Org. Lett*, **2007**, 22, 4543-4547.

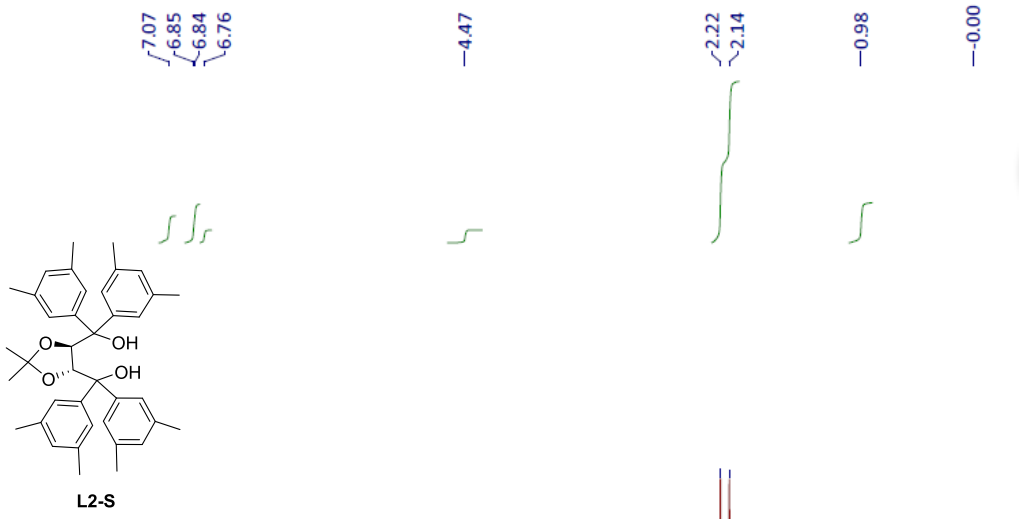
Table S1. The effect of other solvents, palladium salts, and bases, on the Pd/**L8**-catalyzed Si-C bond-forming silylation of **2a** with **1a**.

Run a	**Solvent (1-8)** [a]	**Yield (%)**	**Ee (%)**
1	DME	45	65
2	Et_2O	40	79
3	CH_2Cl_2	48	70
4	PhMe	57	75
5	$CHCl_3$	53	57
6	DMF	80	17
7	MeOH	0	-
8	CH_3CN	73	47
Run b	**Pd (9-13)**[a]	**Yield (%)**	**Ee (%)**
9	$PdCl_2$	45	51
10	$Pd(PPh_3)_2Cl_2$	51	9
11	$Pd(PPh_3)_4$	<5	-
12	$Pd(OAc)_2$	60	45
13	$[(\eta\text{-}C_3H_5)PdCl]_2$	<5	-
Run c	**Base (14-17)**[a]	**Yield (%)**	**Ee (%)**
14	DBU	<5	-
15	DIPEA	<5	-
16	K_2CO_3	48	80
17	TMEDA	45	76

Note: [a] The reaction was carried out similarly to that of Table 1, except the alternated factors.

S-7. NMR Spectrum

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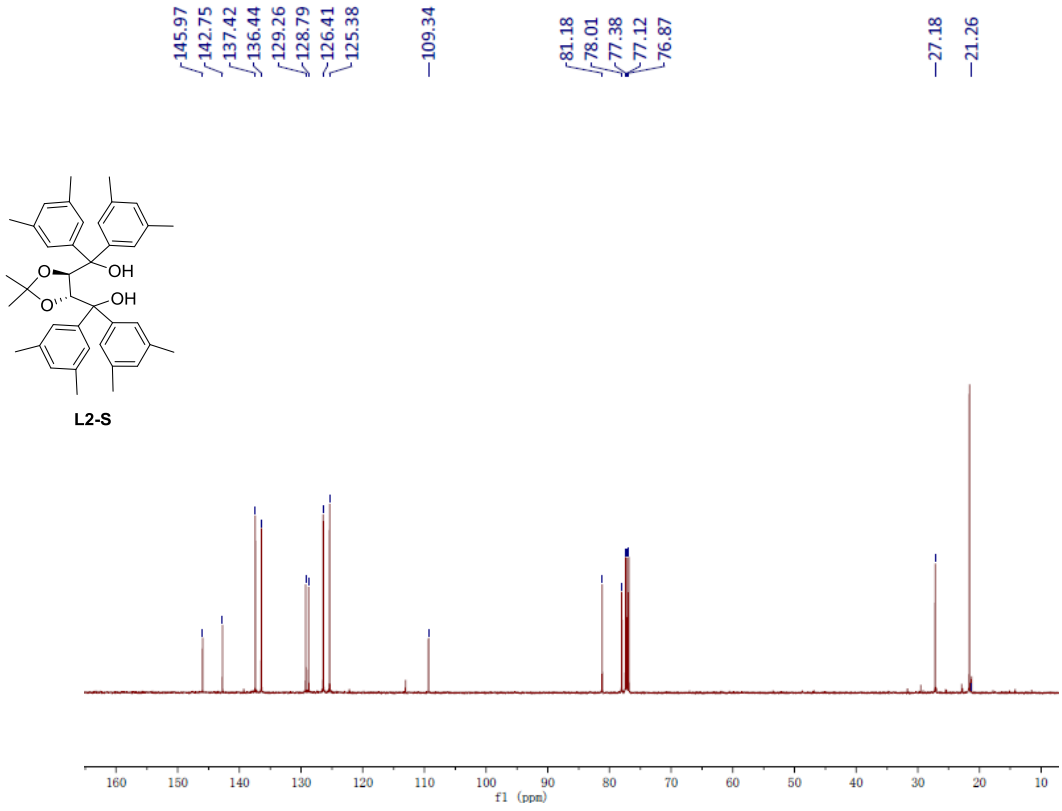
6.85
6.84
6.76
4.47
2.22
2.14
0.98
0.00
OH
OH
O
O
4.02
5.77
1.91
1.92
24.04
6.00
f1 (ppm)

L2-S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142.75
137.42
136.44
129.26
128.79
126.41
125.38
109.34
81.18
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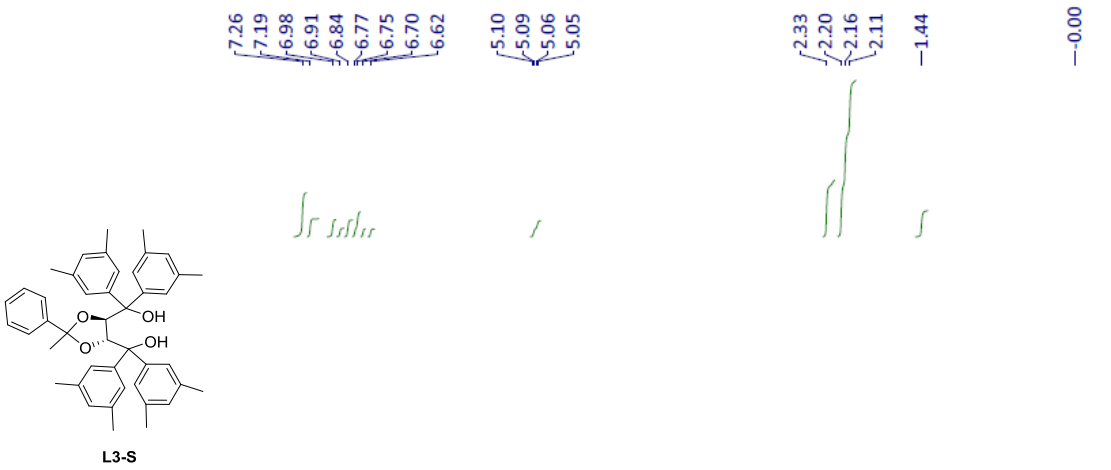
77.38
77.12
76.87
27.18
21.26
OH
OH
O
O
f1 (ppm)

L2-S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6.75
6.70
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5.10
5.09
5.06
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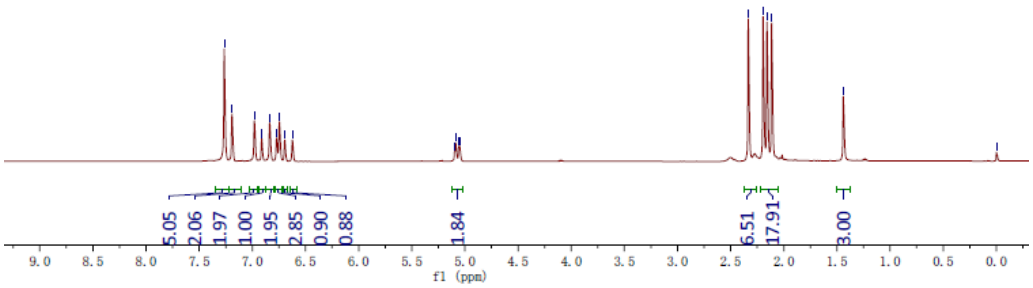
2.33
2.20
2.16
2.11
1.44
0.00
OH
OH
O
O

L3-S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2.06
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1.95
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1.84
6.51
17.91
3.00
f1 (ppm)


145.71
145.39
144.48
144.24
142.98
136.99
136.96
136.86
128.91
128.80
128.74
128.51
128.35
128.00
125.76
125.01
124.82
124.62
123.93
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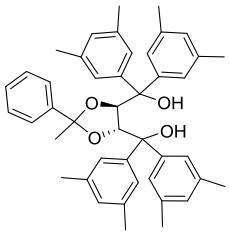
76.88
30.32
21.72
21.68
21.61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OH
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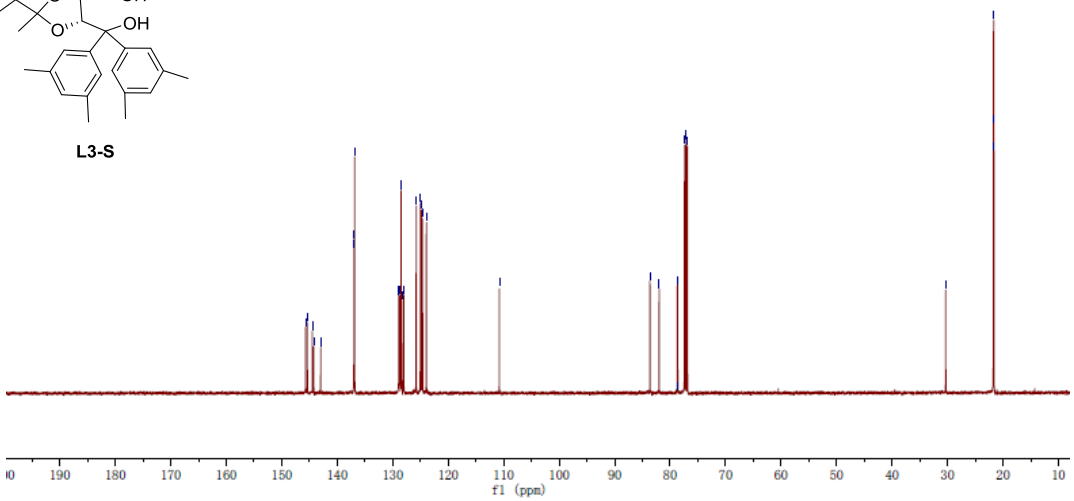
O

L3-S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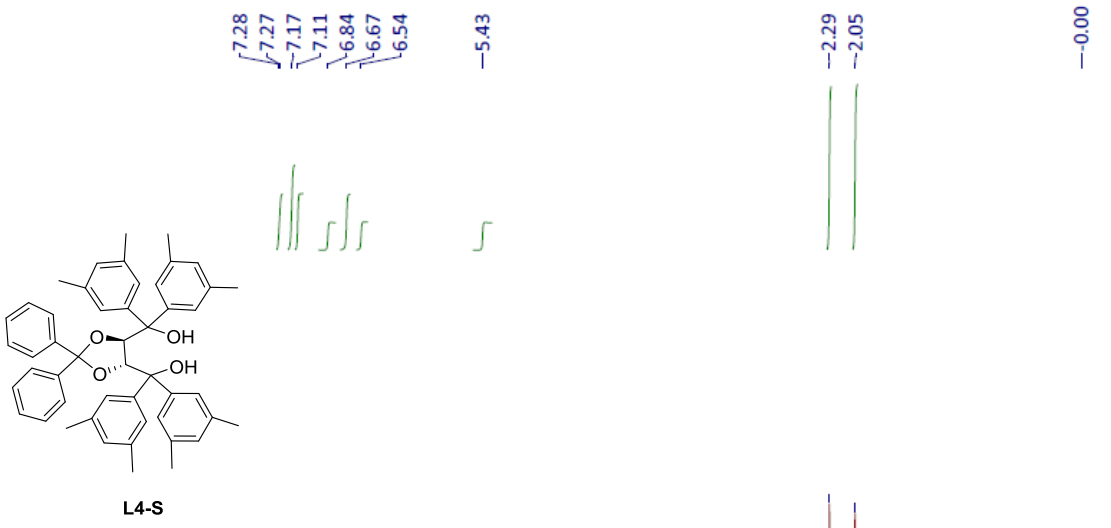
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OH
OH
O
O
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2.03
1.98
12.00
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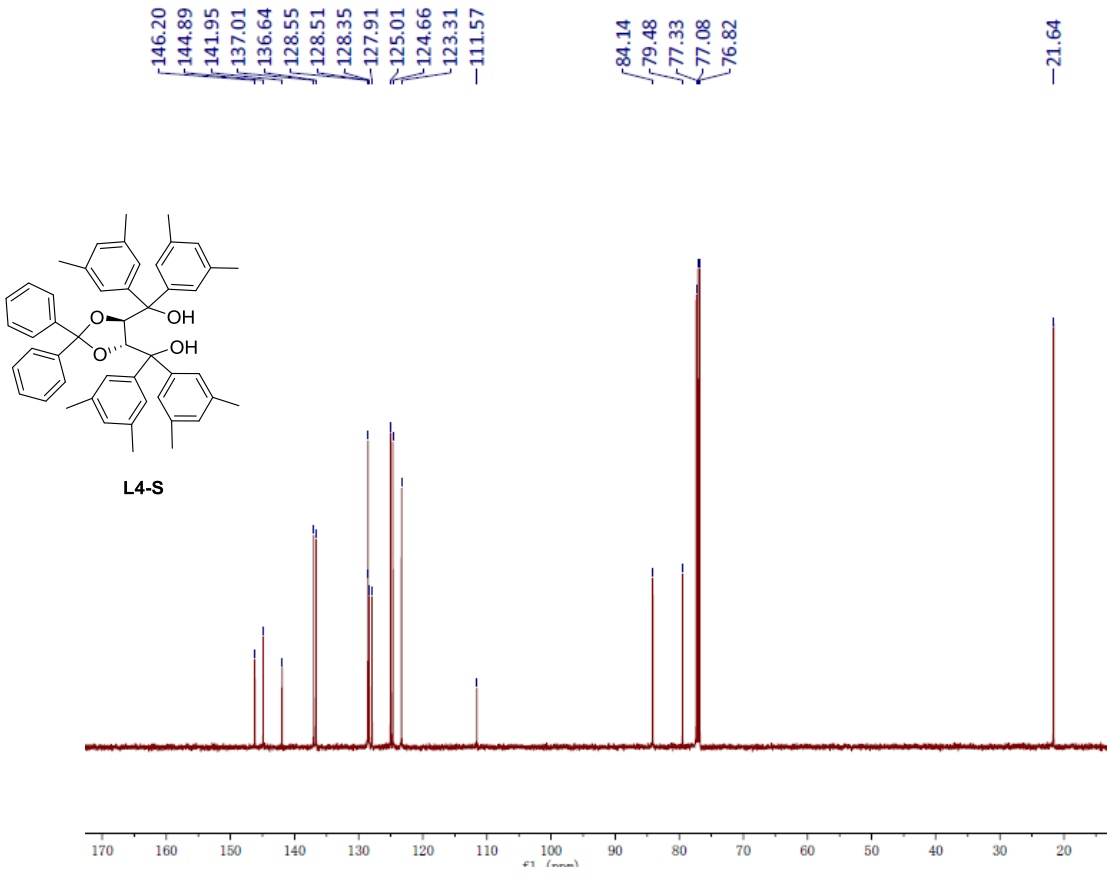
f1 (ppm)

L4-S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128.35
127.91
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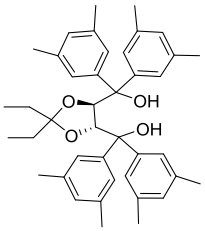
76.82
21.64
OH
OH
O
O

L4-S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OH
O
OH

L5-S

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2.23
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1.35
1.33
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0.74
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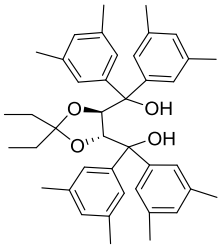
4.13
6.00
f1 (ppm)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OH
O
OH

L5-S

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29.67
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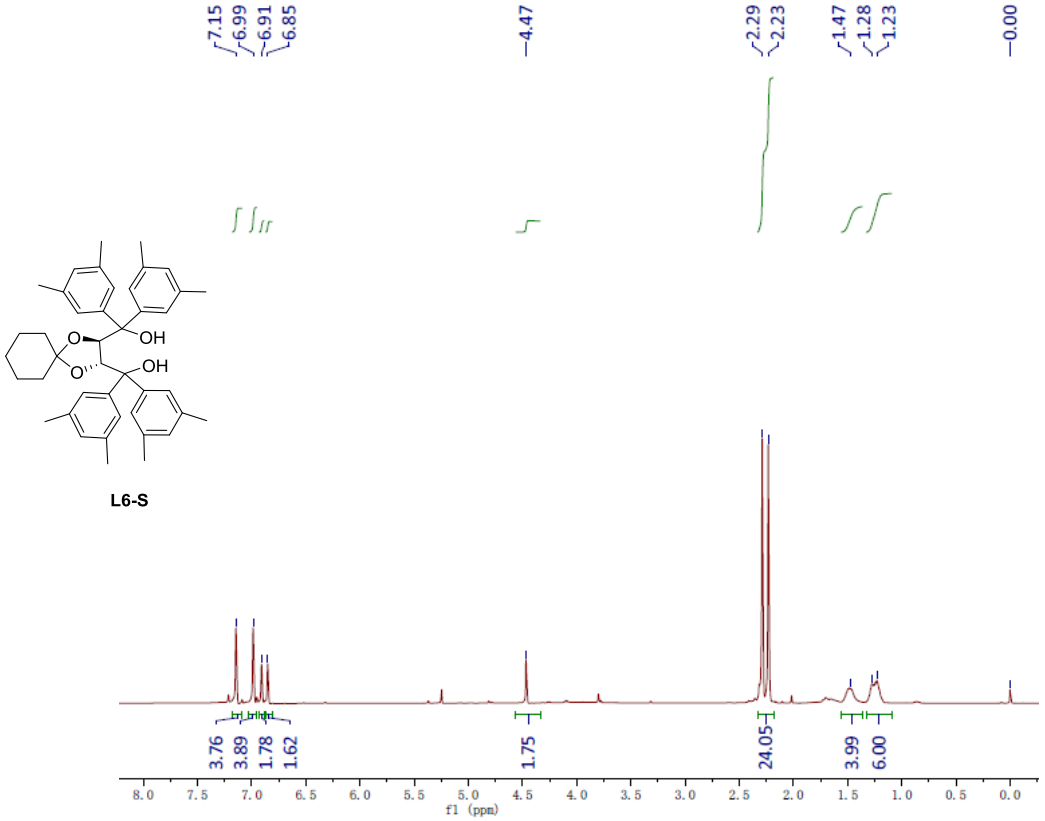
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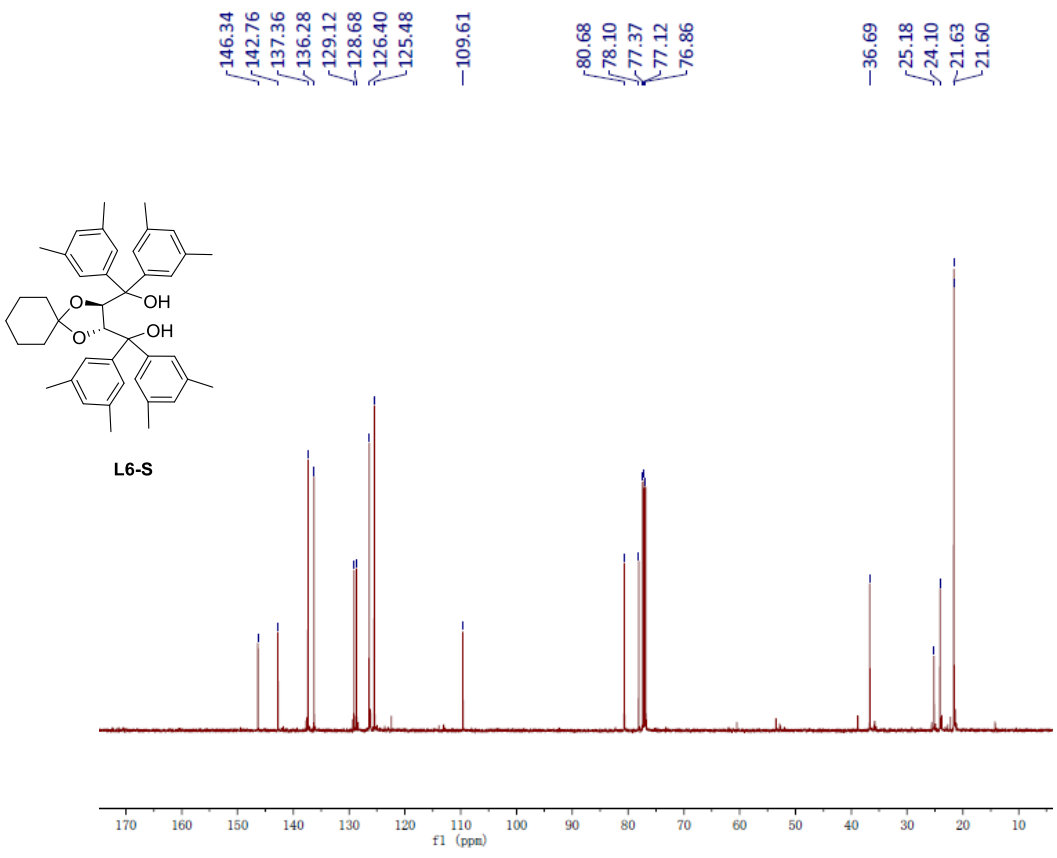
f1 (ppm)

L6-S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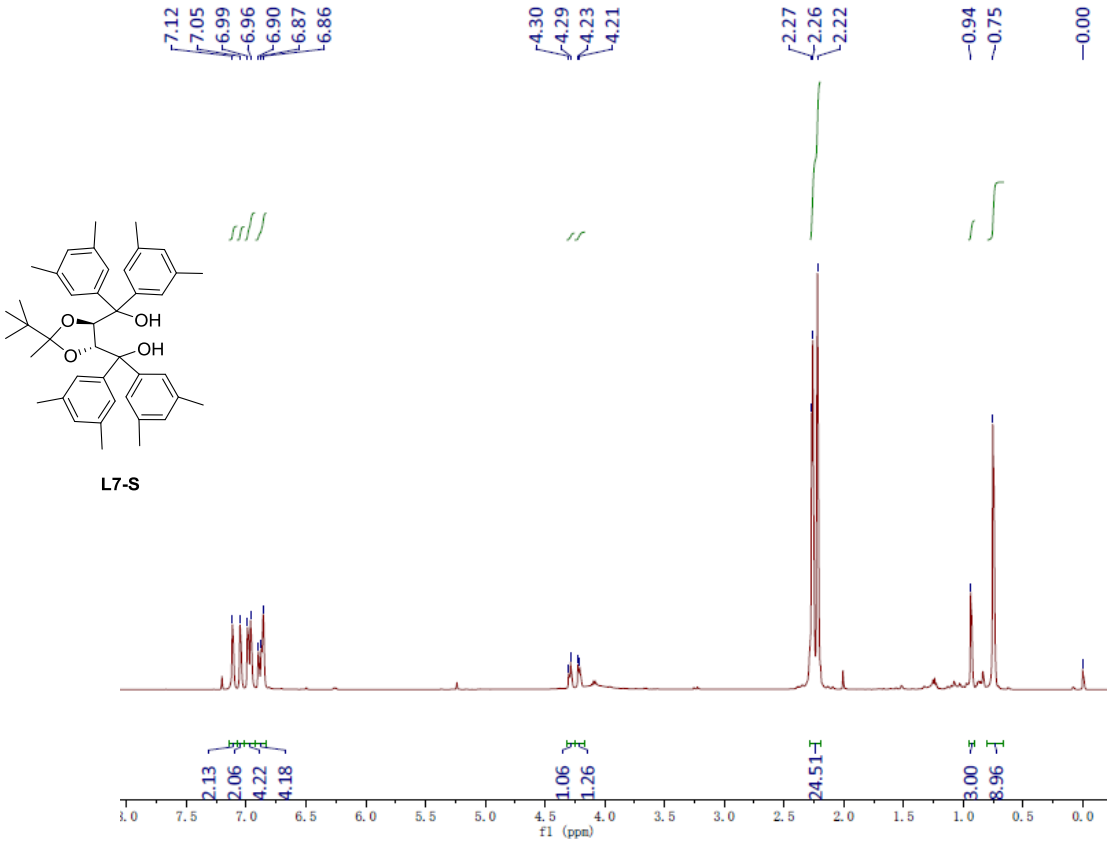
OH
OH
O
O
f1 (ppm)

L6-S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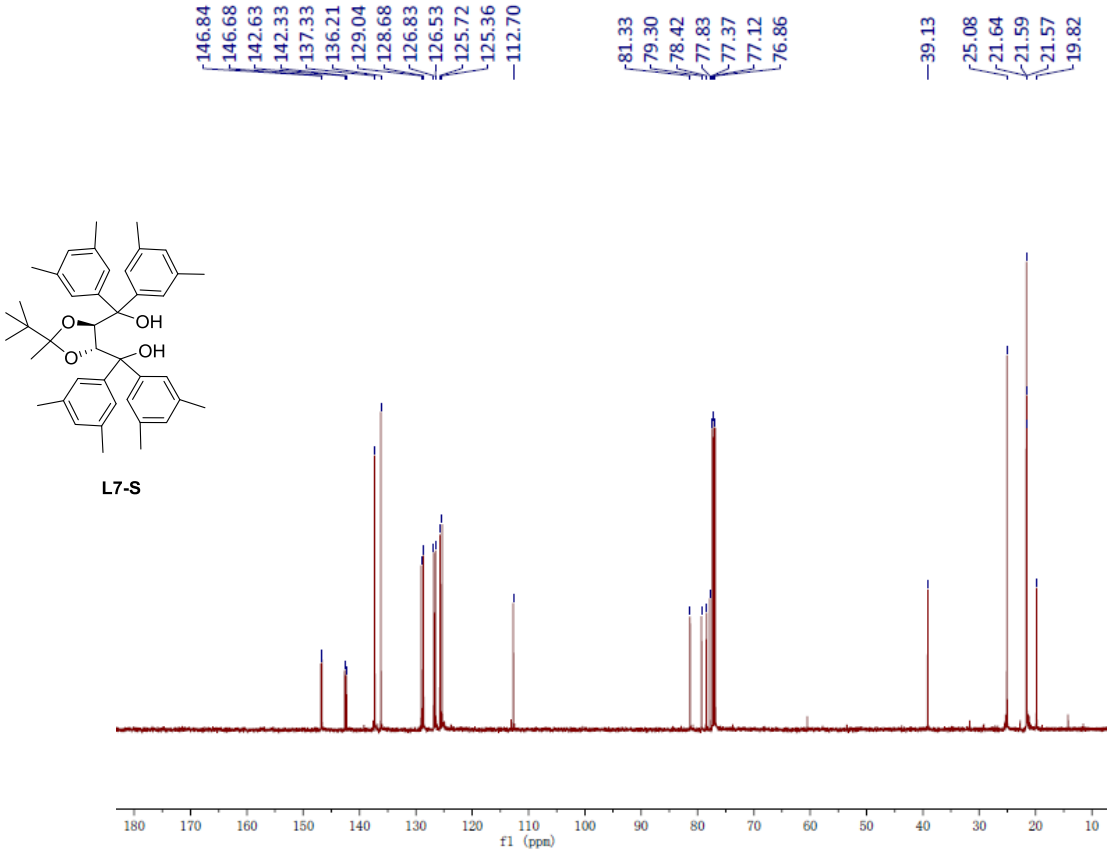
f1 (ppm)

L7-S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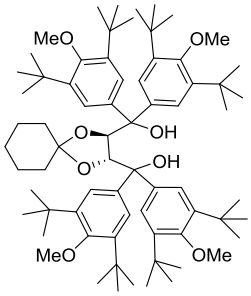
O
f1 (ppm)

L7-S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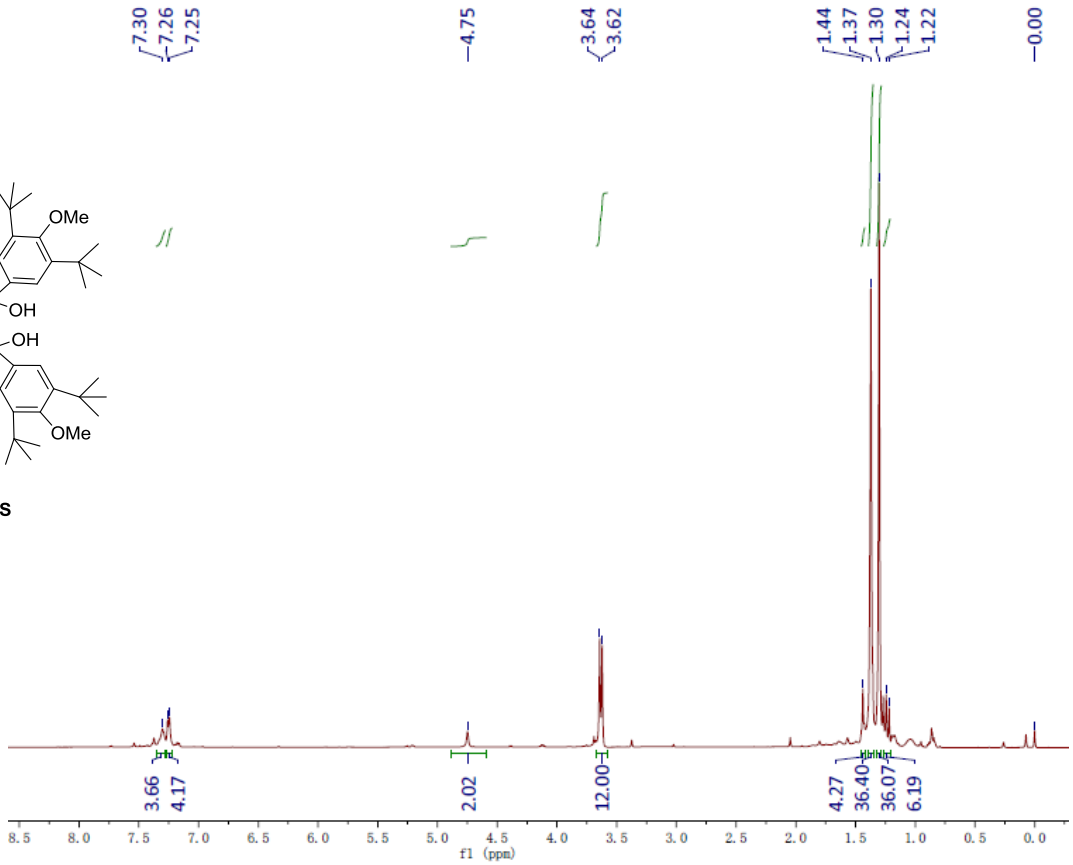
OMe

L8-S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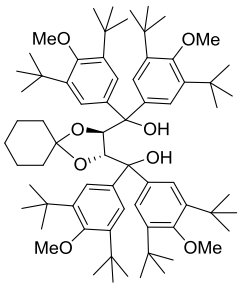
f1 (ppm)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OH
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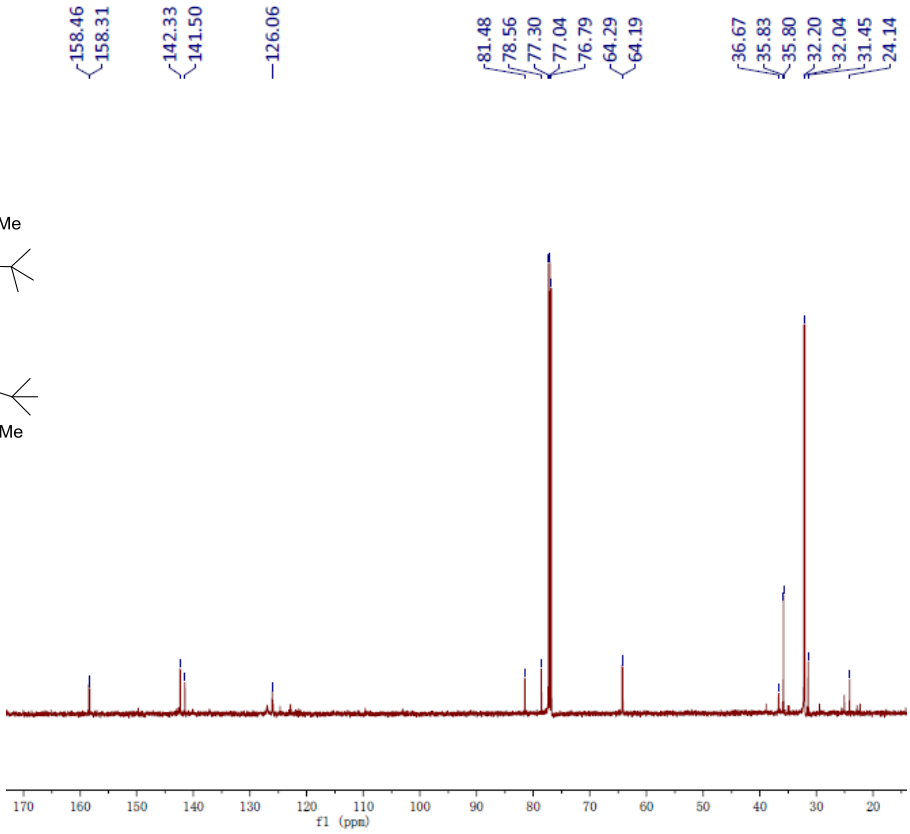
L8-S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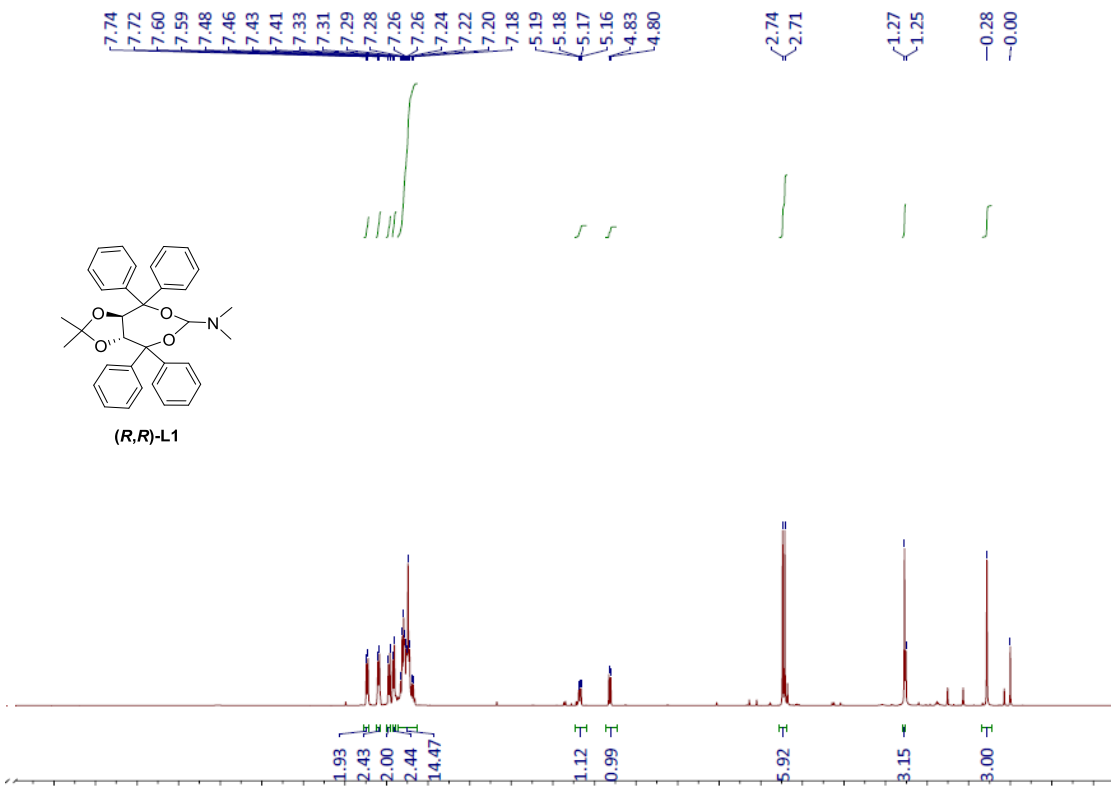
f1 (ppm)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1.25
0.28
0.00
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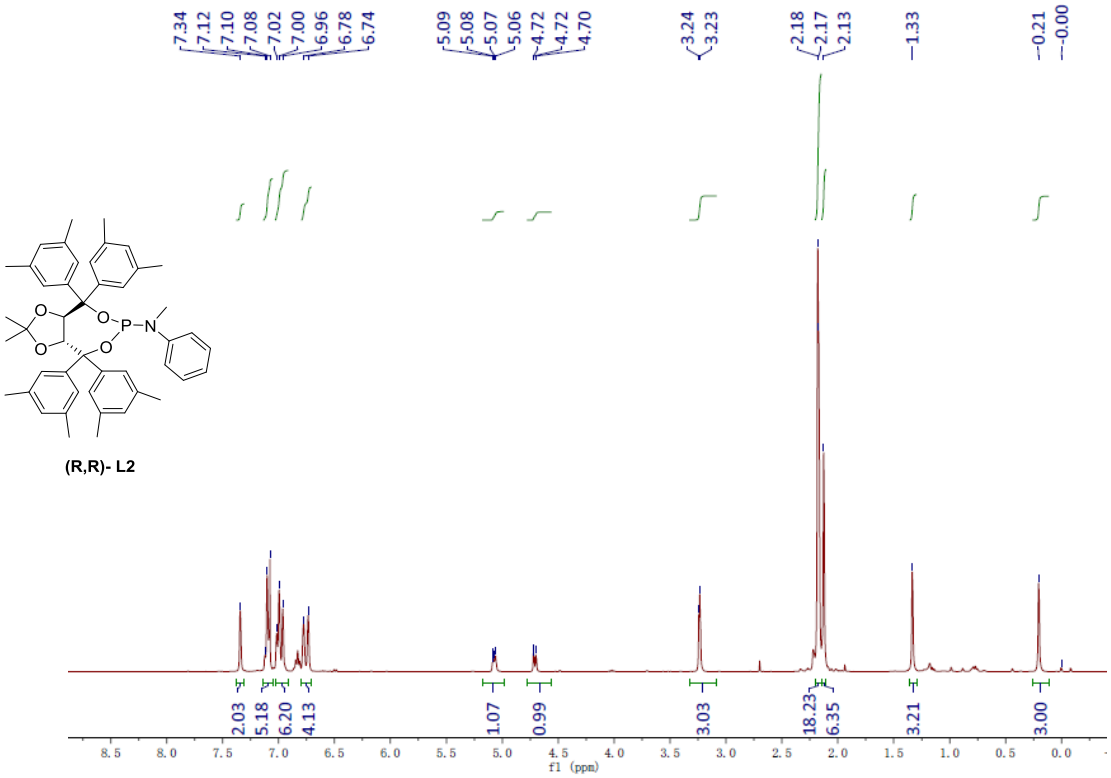
3.00

(*R*,*R*)-L1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5.06
4.72
4.72
4.70
3.24
3.23
2.18
2.17
2.13
1.33
0.21
0.00
2.03
5.18
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18.23
6.35
3.21
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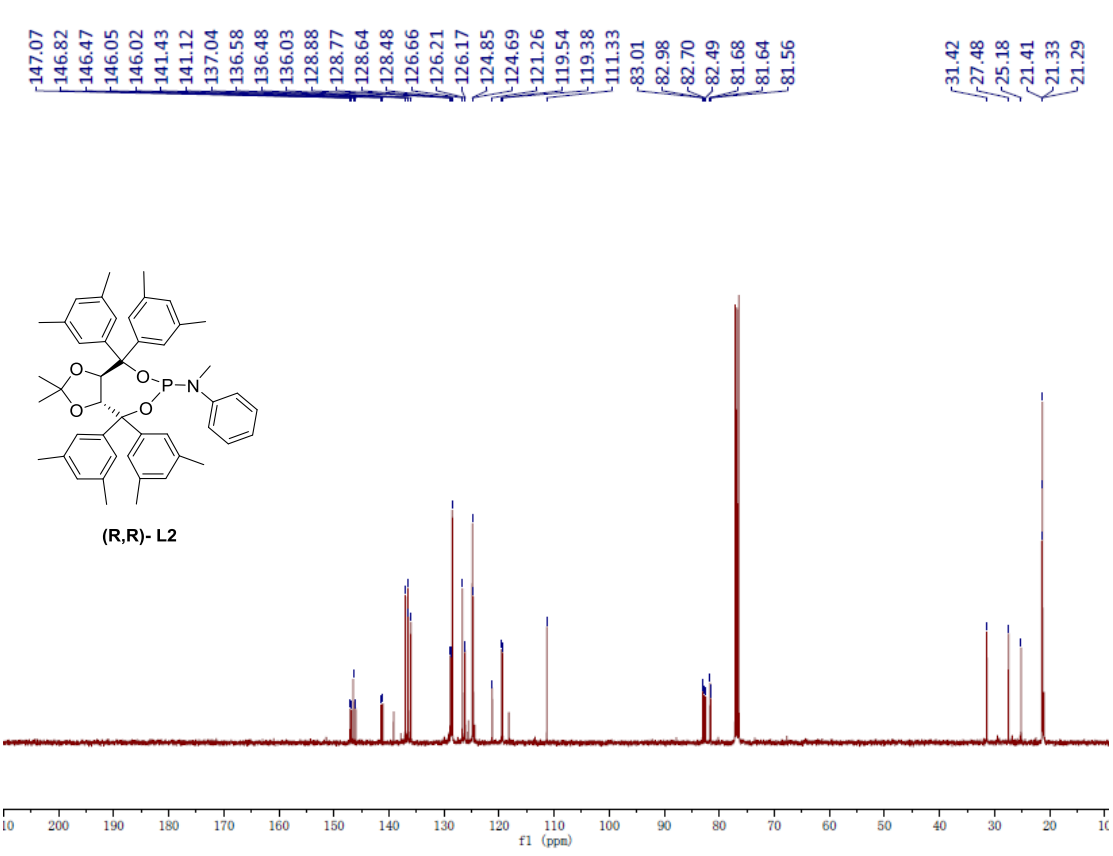
f1 (ppm)

(R,R)- L2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111.33
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82.70
82.49
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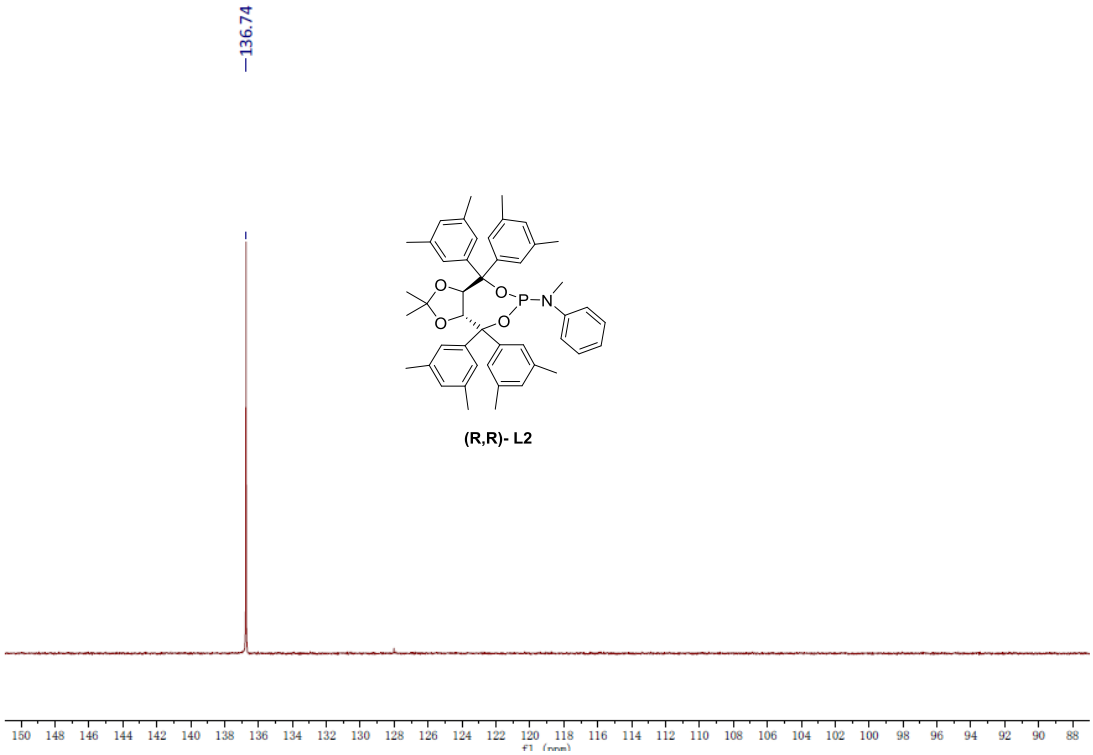
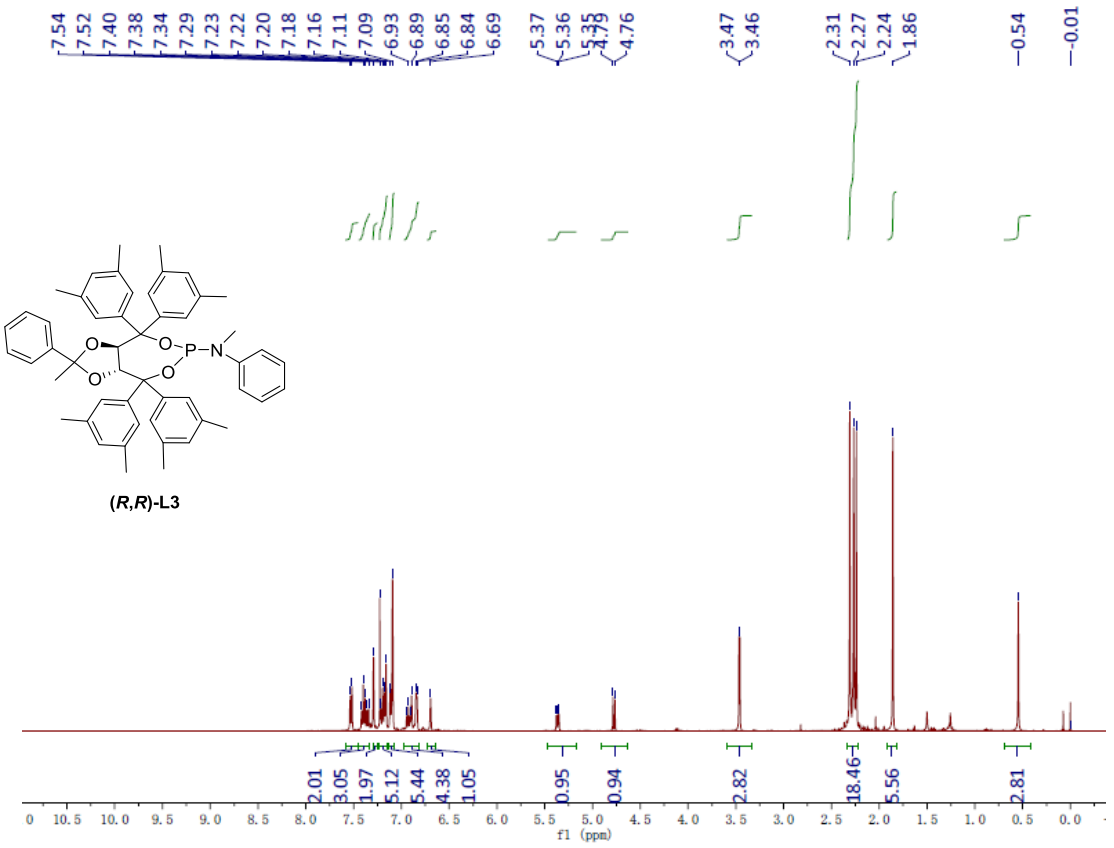
f1 (ppm)

(R,R)- L2


136.74
150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110 108 106 104 102 100 98 96 94 92 90 88

(R,R)- L2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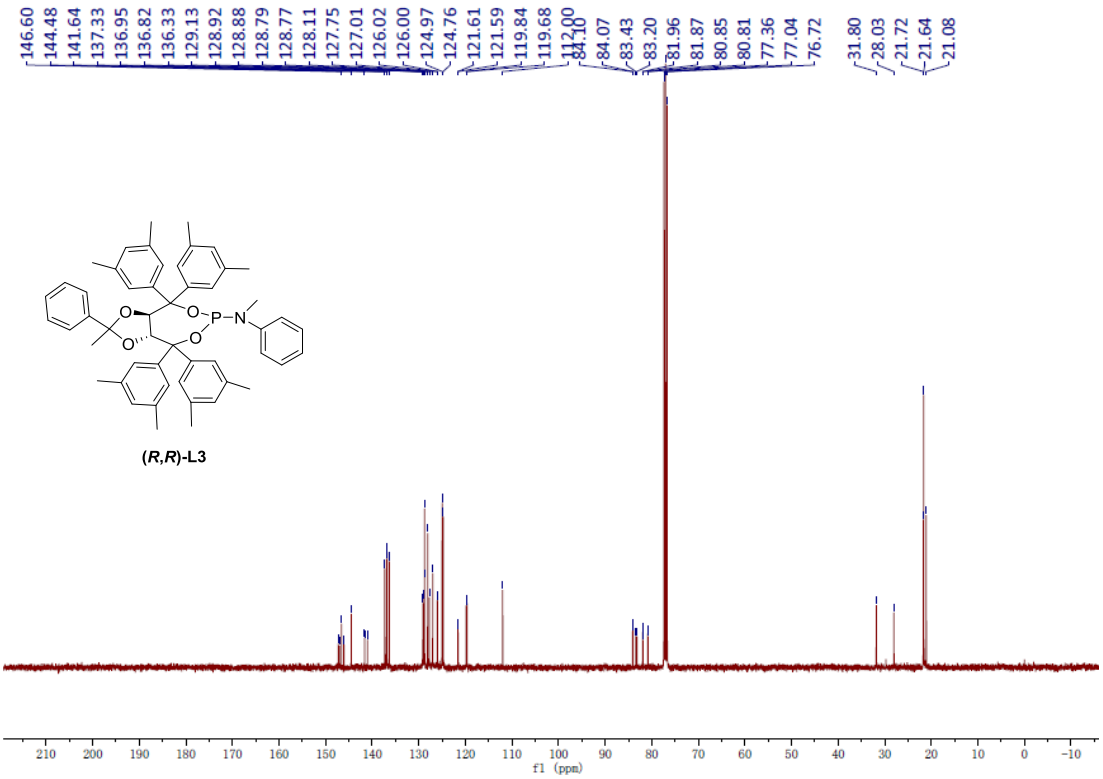
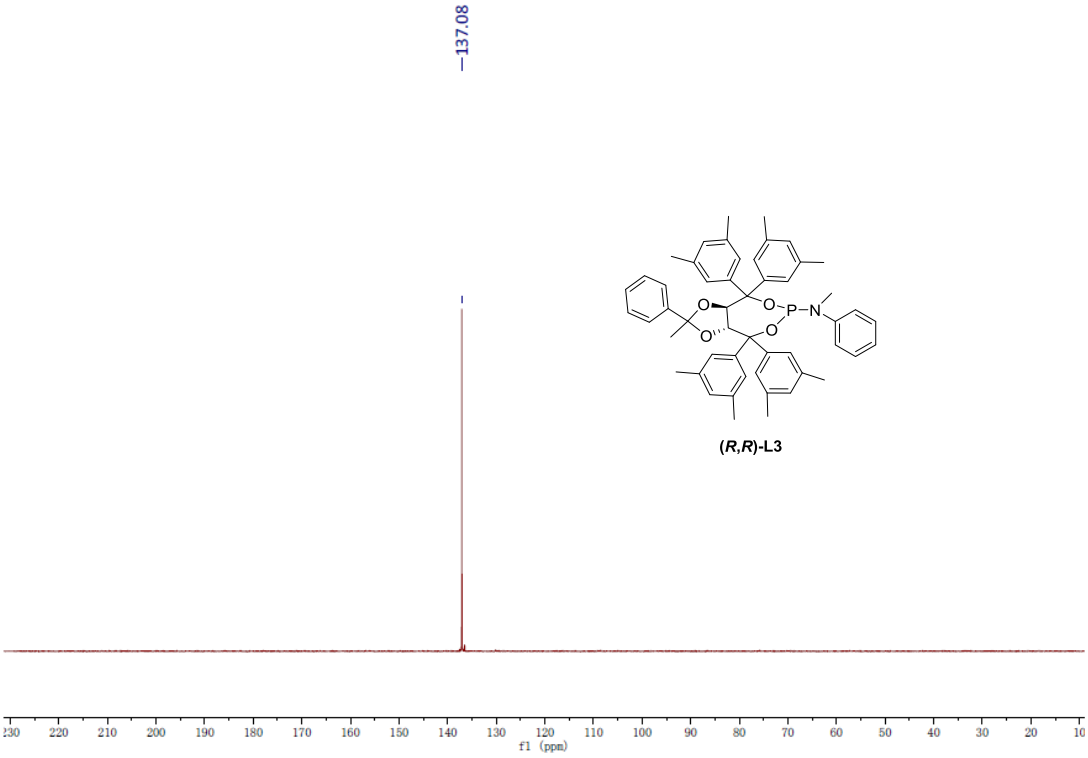
6.93
6.89
6.85
6.84
6.69
5.37
5.36
4.79
4.76
3.47
3.46
2.31
2.27
2.24
1.86
0.54
0.01
2.01
3.05
1.97
5.12
5.44
4.38
1.05
0.95
0.94
2.82
18.46
5.56
2.81
f1 (ppm)

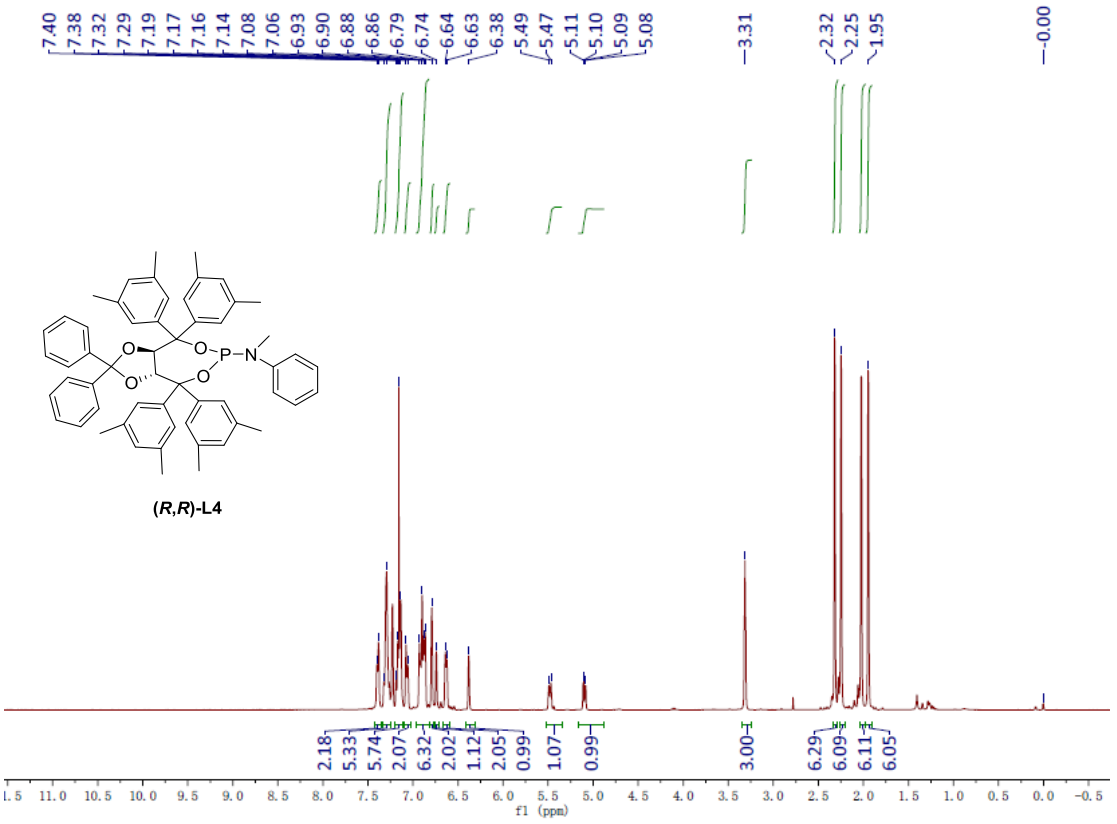
(*R*,*R*)-L3


146.60
144.48
141.64
137.33
136.95
136.82
136.33
129.13
128.92
128.88
128.79
128.77
128.11
127.75
127.01
126.02
126.00
124.97
124.76
121.61
121.59
119.84
119.68
112.00
84.10
84.07
83.43
83.20
81.96
81.87
80.85
80.81
77.36
77.04
76.72
31.80
28.03
21.72
21.64
21.08
f1 (ppm)

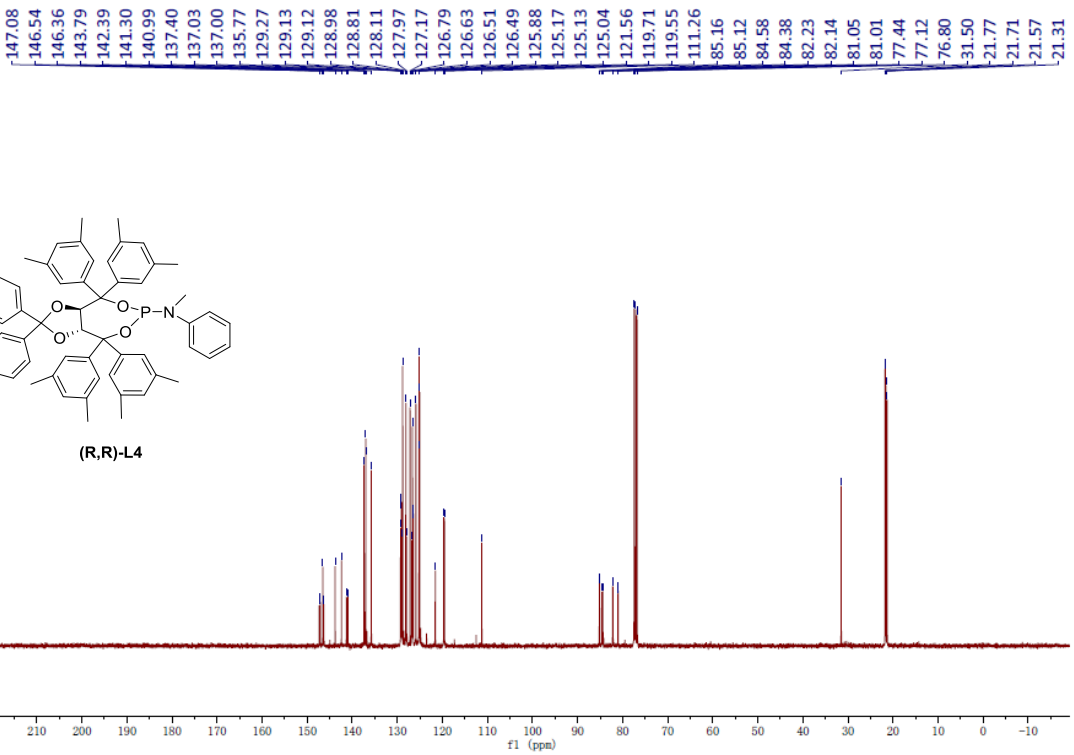
(*R*,*R*)-L3



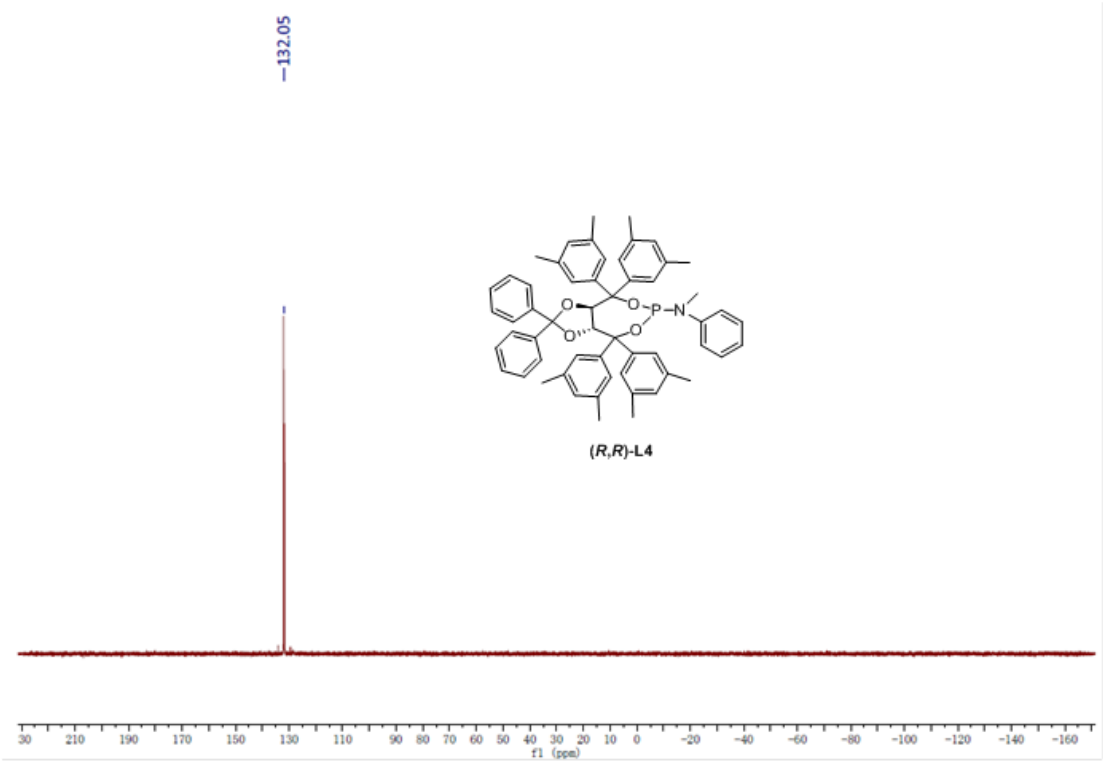
(*R*,*R*)-L3

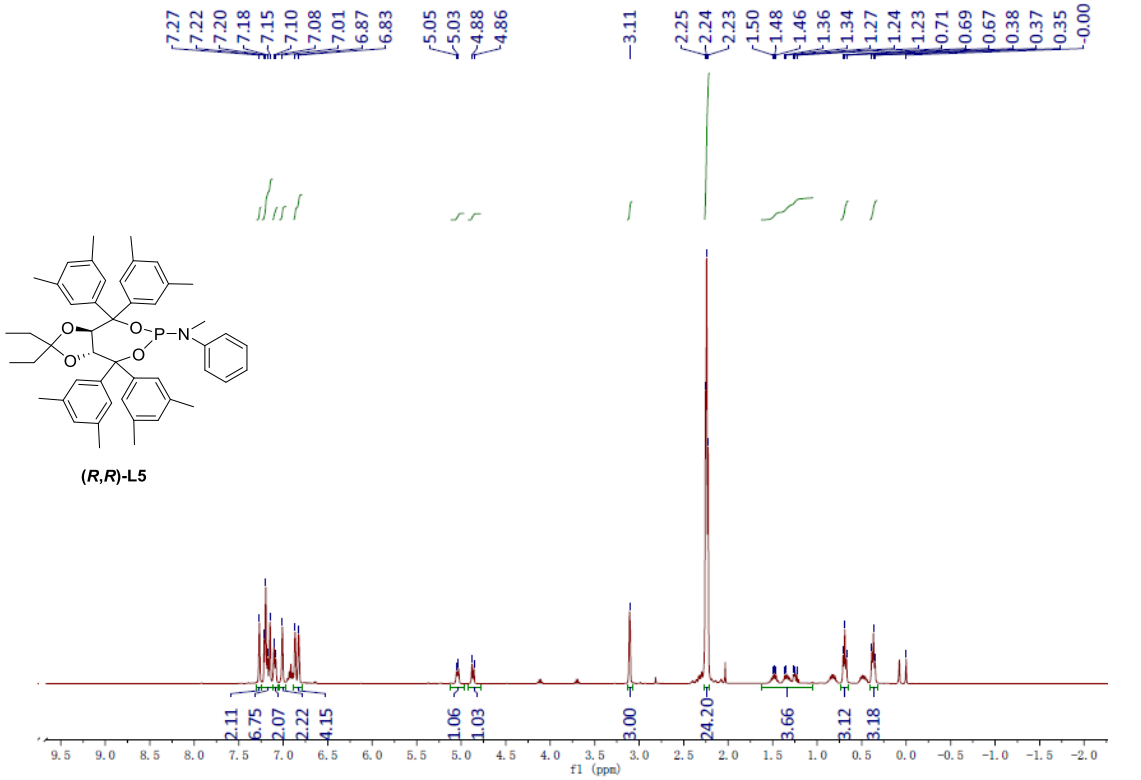

7.40
7.38
7.32
7.29
7.19
7.17
7.16
7.14
7.08
7.06
6.93
6.90
6.88
6.86
6.79
6.74
6.64
6.63
6.38
5.49
5.47
5.11
5.10
5.09
5.08
3.31
2.32
2.25
1.95
0.00
2.18
5.33
5.74
2.07
6.32
2.02
1.12
2.05
0.99
1.07
0.99
3.00
6.29
6.09
6.11
6.05
f1 (ppm)

(*R*,*R*)-L4

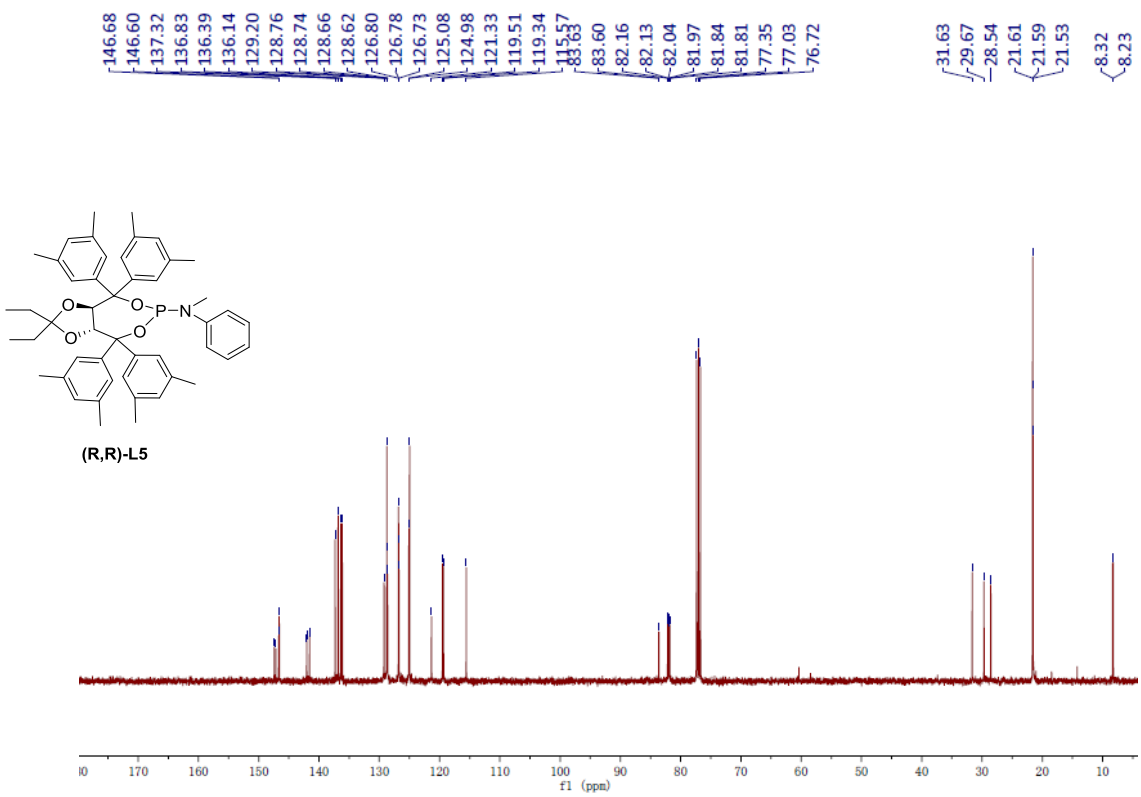

147.08
146.54
146.36
143.79
142.39
141.30
140.99
137.40
137.03
137.00
135.77
129.27
129.13
129.12
128.98
128.81
128.11
127.97
127.17
126.79
126.63
126.51
126.49
125.88
125.17
125.13
125.04
121.56
119.71
119.55
111.26
85.16
85.12
84.58
84.38
82.23
82.14
81.05
81.01
77.44
77.12
76.80
31.50
21.77
21.71
21.57
21.31
f1 (ppm)

(R,R)-L4

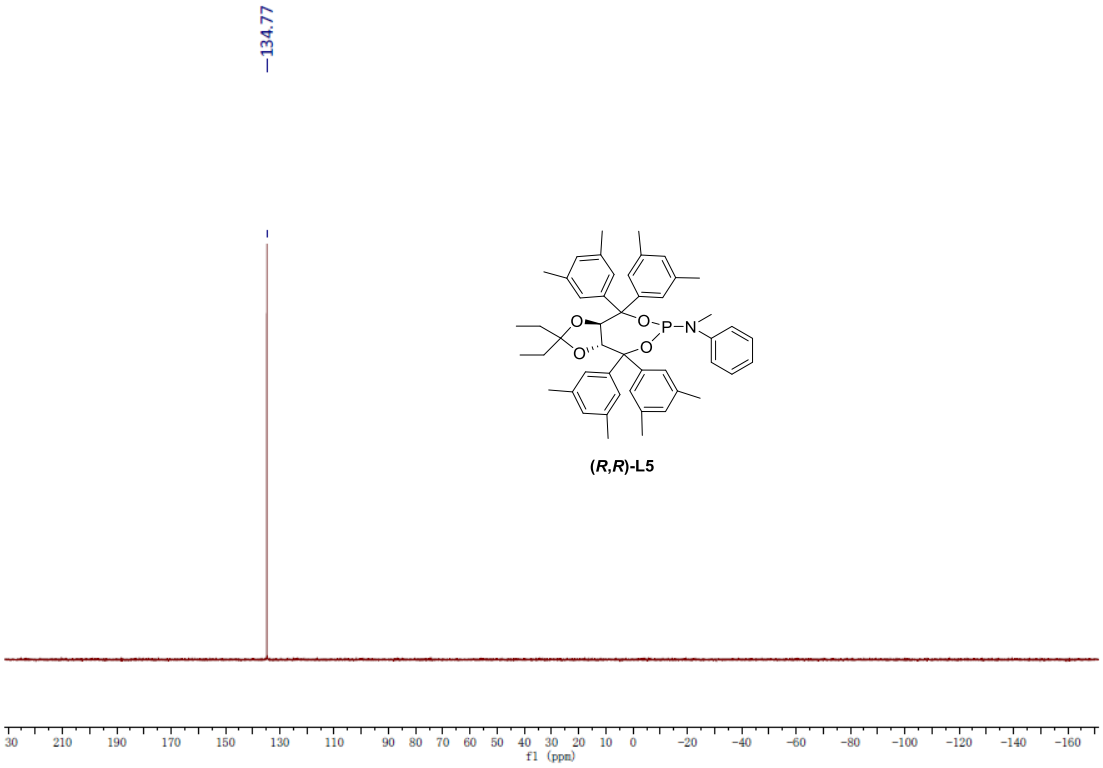

132.05
(R,R)-L4
30 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160
f1 (ppm)


7.27
7.22
7.20
7.18
7.15
7.10
7.08
7.01
6.87
6.83
5.05
5.03
4.88
4.86
3.11
2.25
2.24
2.23
1.50
1.48
1.46
1.36
1.34
1.27
1.24
1.23
0.71
0.69
0.67
0.38
0.37
0.35
0.00
2.11
6.75
2.07
2.22
4.15
1.06
1.03
3.00
24.20
3.66
3.12
3.18
f1 (ppm)

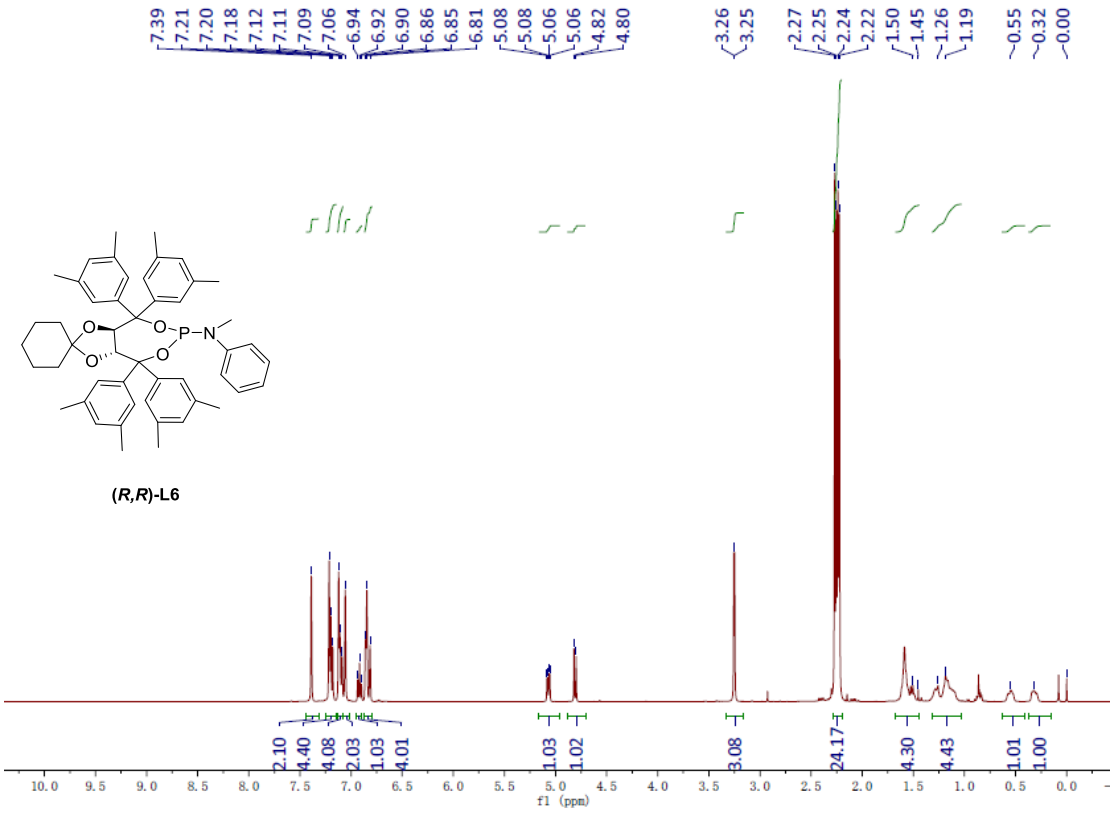
(*R*,*R*)-L5


146.68
146.60
137.32
136.83
136.39
136.14
129.20
128.76
128.74
128.66
128.62
126.80
126.78
126.73
125.08
124.98
121.33
119.51
119.34
115.57
83.63
83.60
82.16
82.13
82.04
81.97
81.84
81.81
77.35
77.03
76.72
31.63
29.67
28.54
21.61
21.59
21.53
8.32
8.23
f1 (ppm)

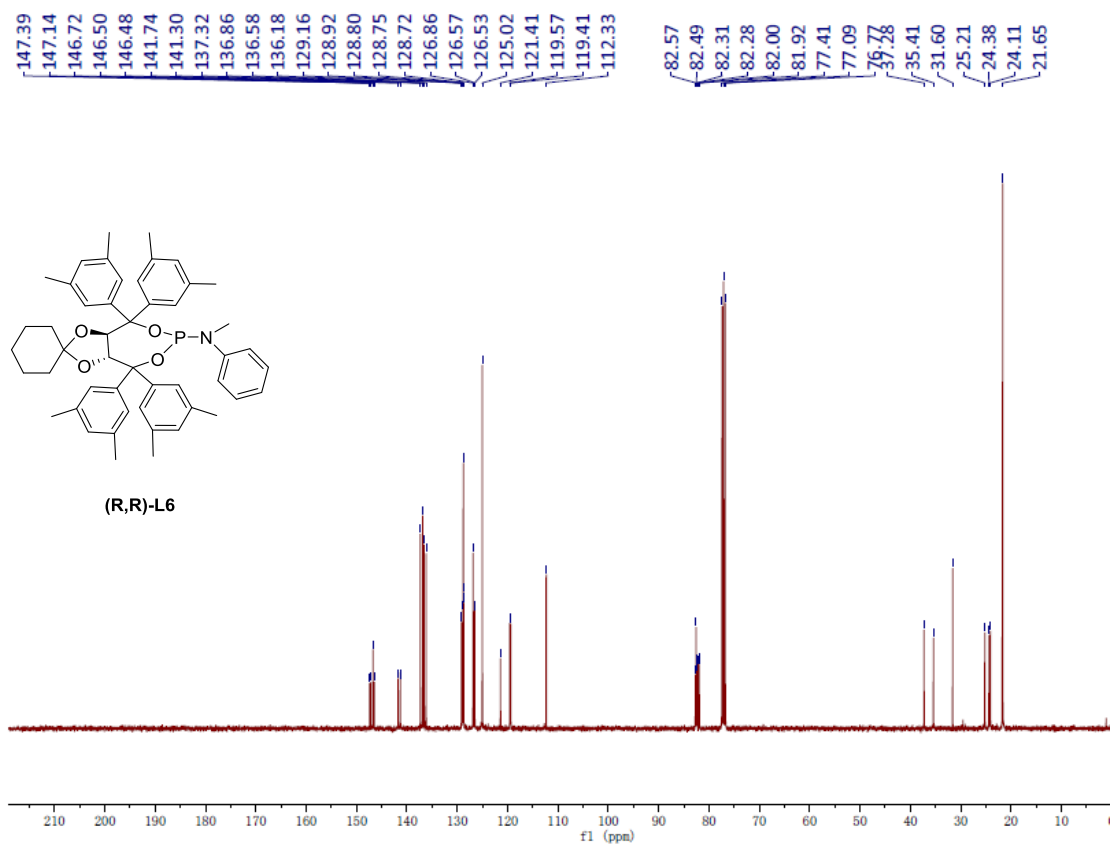
(R,R)-L5


134.77
O
O
P
N
O
O
30 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160
f1 (ppm)

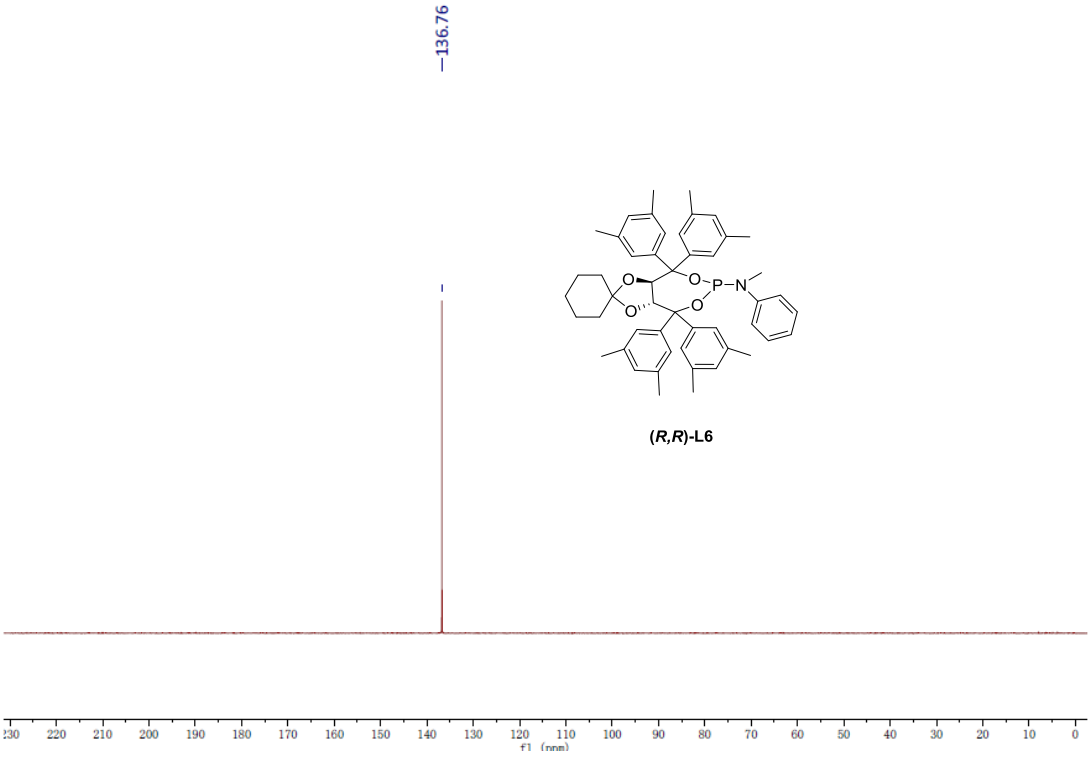
(*R*,*R*)-L5


7.39
7.21
7.20
7.18
7.12
7.11
7.09
7.06
6.94
6.92
6.90
6.86
6.85
6.81
5.08
5.08
5.06
5.06
4.82
4.80
3.26
3.25
2.27
2.25
2.24
2.22
1.50
1.45
1.26
1.19
0.55
0.32
0.00
2.10
4.40
4.08
2.03
1.03
4.01
1.03
1.02
3.08
24.17
4.30
4.43
1.01
1.00
f1 (ppm)

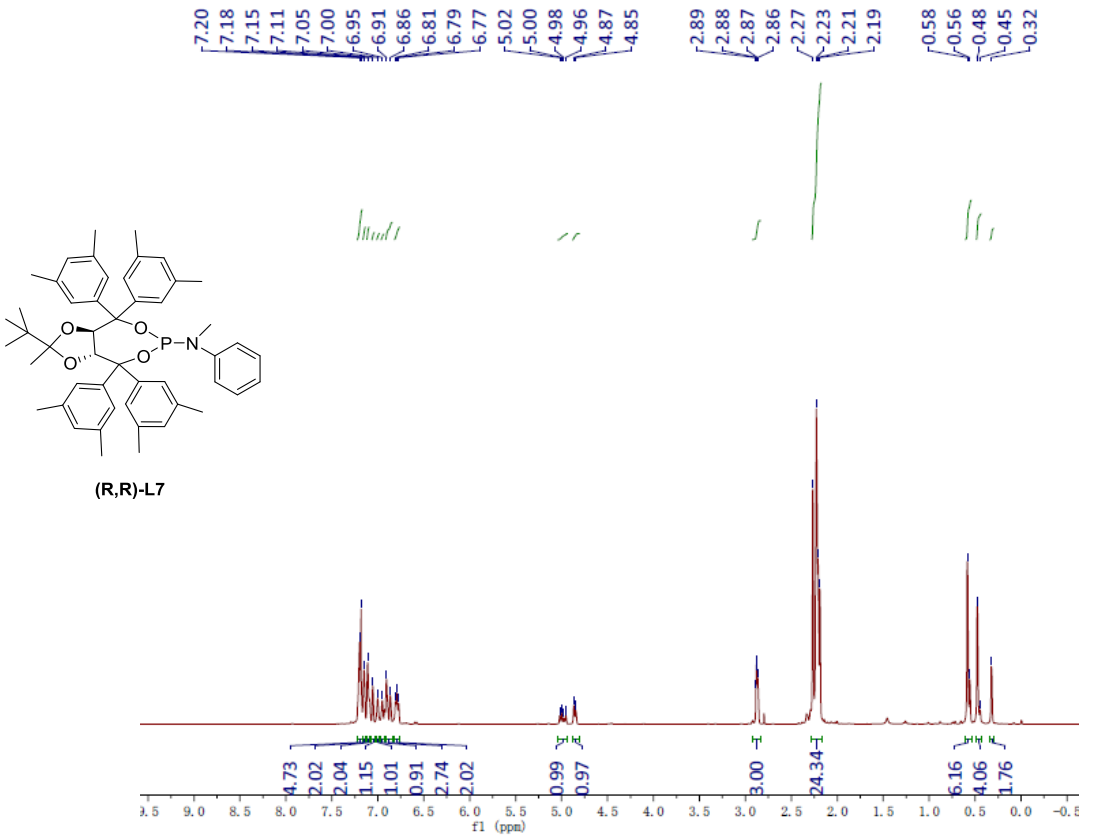
(*R*,*R*)-L6


147.39
147.14
146.72
146.50
146.48
141.74
141.30
137.32
136.86
136.58
136.18
129.16
128.92
128.80
128.75
128.72
126.86
126.57
126.53
125.02
121.41
119.57
119.41
112.33
82.57
82.49
82.31
82.28
82.00
81.92
77.41
77.09
76.77
37.28
35.41
31.60
25.21
24.38
24.11
21.65
f1 (ppm)

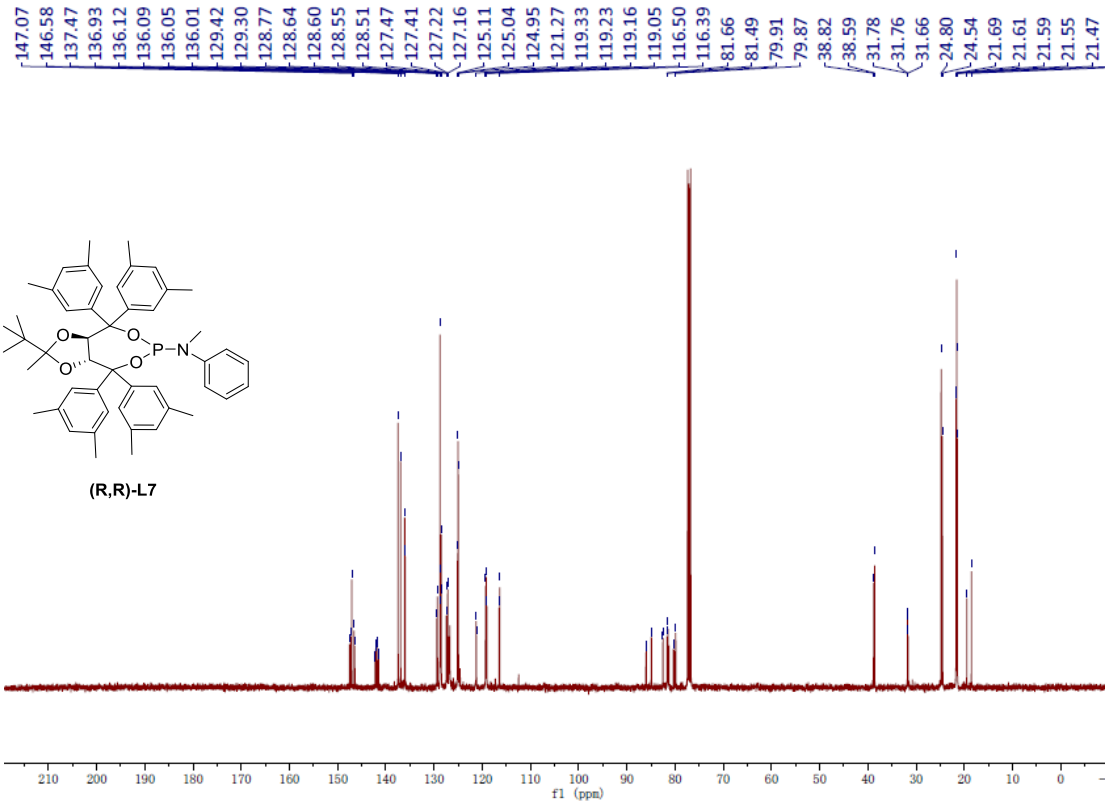
(R,R)-L6


136.76
O
O
O
P
N
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

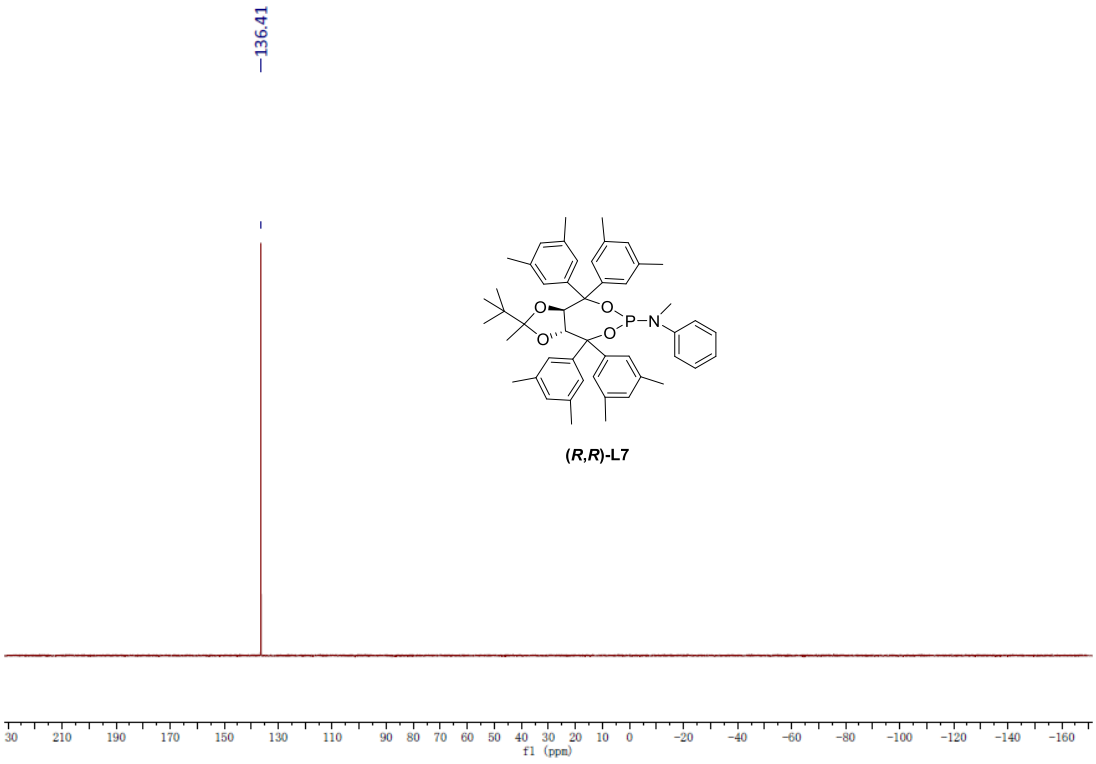
(*R*,*R*)-L6


7.20
7.18
7.15
7.11
7.05
7.00
6.95
6.91
6.86
6.81
6.79
6.77
5.02
5.00
4.98
4.96
4.87
4.85
2.89
2.88
2.87
2.86
2.27
2.23
2.21
2.19
0.58
0.56
0.48
0.45
0.32
4.73
2.02
2.04
1.15
1.01
0.91
2.74
2.02
0.99
0.97
3.00
24.34
6.16
4.06
1.76
f1 (ppm)

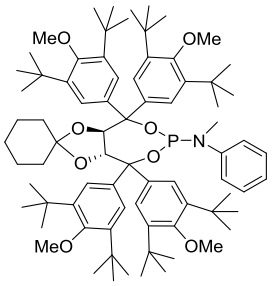
(R,R)-L7


147.07
146.58
137.47
136.93
136.12
136.09
136.05
136.01
129.42
129.30
128.77
128.64
128.60
128.55
128.51
127.47
127.41
127.22
127.16
125.11
125.04
124.95
121.27
119.33
119.23
119.16
119.05
116.50
116.39
81.66
81.49
79.91
79.87
38.82
38.59
31.78
31.76
31.66
24.80
24.54
21.69
21.61
21.59
21.55
21.47
f1 (ppm)

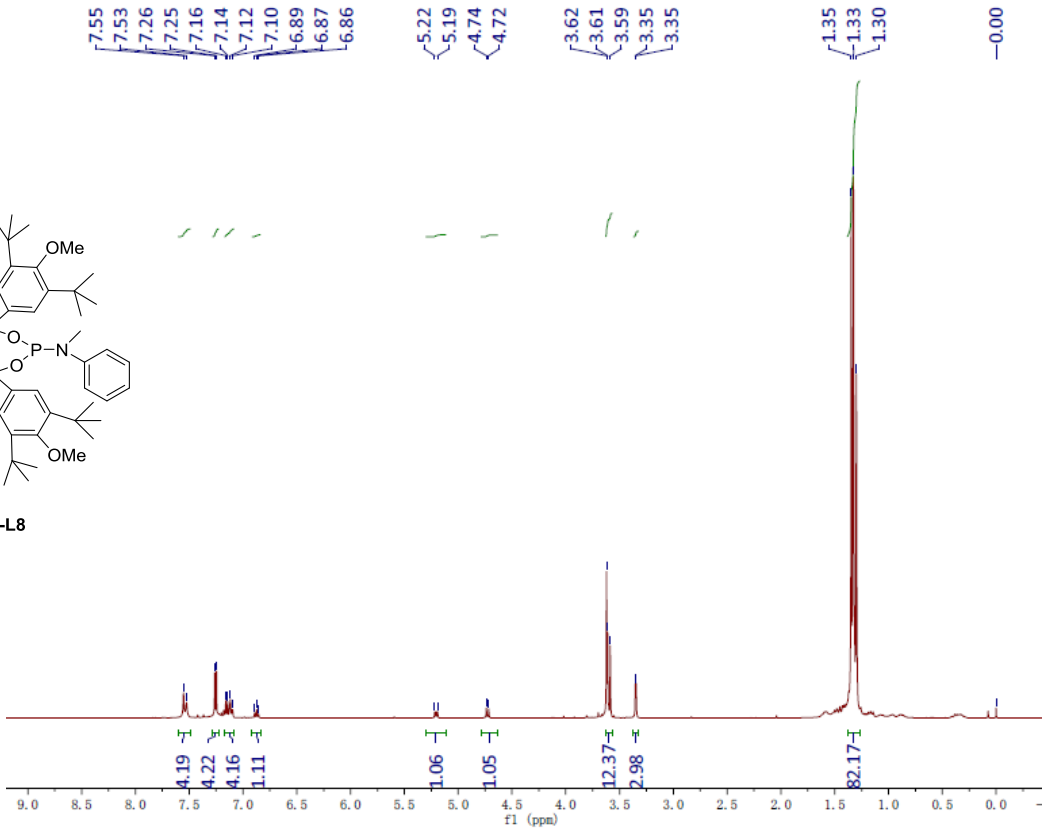
(R,R)-L7

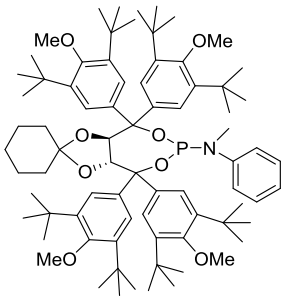

136.41
O
O
O
O
P
N
30 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160
f1 (ppm)

(*R*,*R*)-L7


MeO
OMe
O
O
P
N
O
O
MeO
OMe

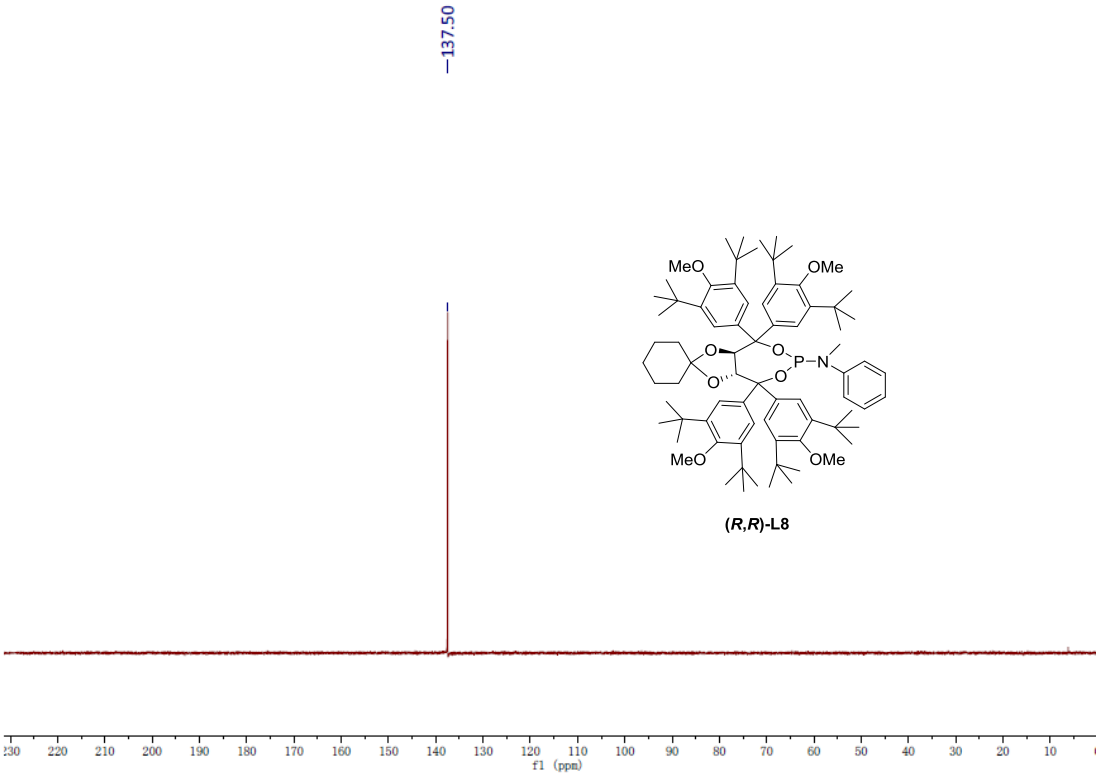
(R,R)-L8


7.55
7.53
7.26
7.25
7.16
7.14
7.12
7.10
6.89
6.87
6.86
5.22
5.19
4.74
4.72
3.62
3.61
3.59
3.35
3.35
1.35
1.33
1.30
0.00
4.19
4.22
4.16
1.11
1.06
1.05
12.37
2.98
82.17
f1 (ppm)

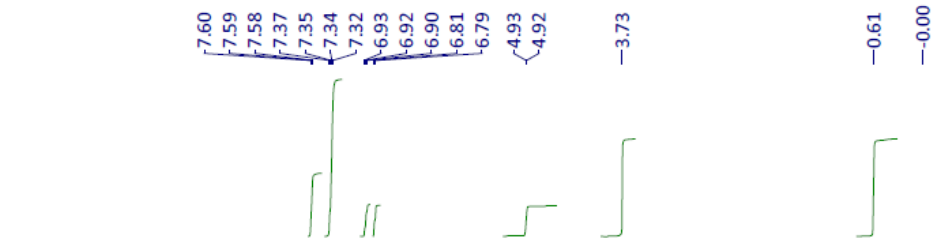

MeO
OMe
O
O
P
N
O
O
MeO
OMe

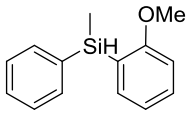
(R,R)-L8

158.59
158.54
158.18
158.07
142.41
141.78
141.69
141.22
140.21
127.43
125.51
121.14
119.24
119.07
110.60
82.86
82.58
77.33
77.02
37.17
35.91
35.79
35.74
32.24
32.18
32.09
32.07
31.06
24.96
23.92
f1 (ppm)

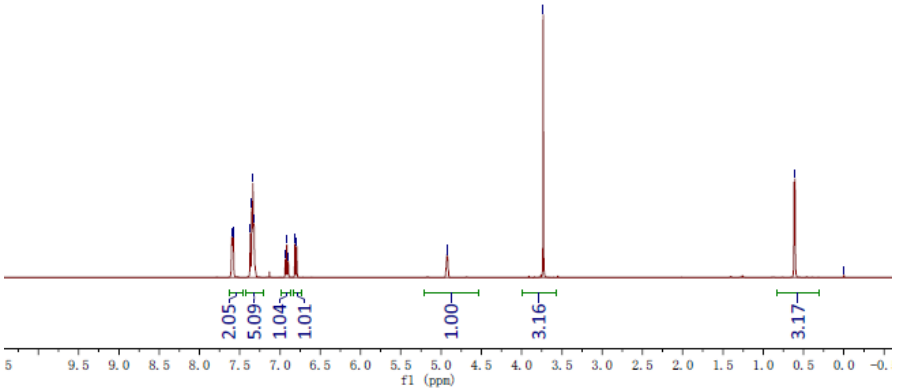

137.50
MeO
OMe
O
O
O
P
N
MeO
OMe
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

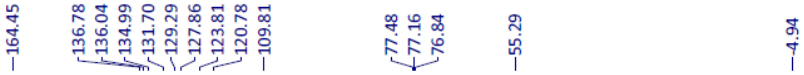
(*R*,*R*)-L8

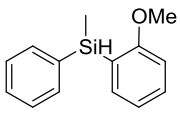

7.60
7.59
7.58
7.37
7.35
7.34
7.32
6.93
6.92
6.90
6.81
6.79
4.93
4.92
3.73
0.61
0.00


OMe
SiH

3a

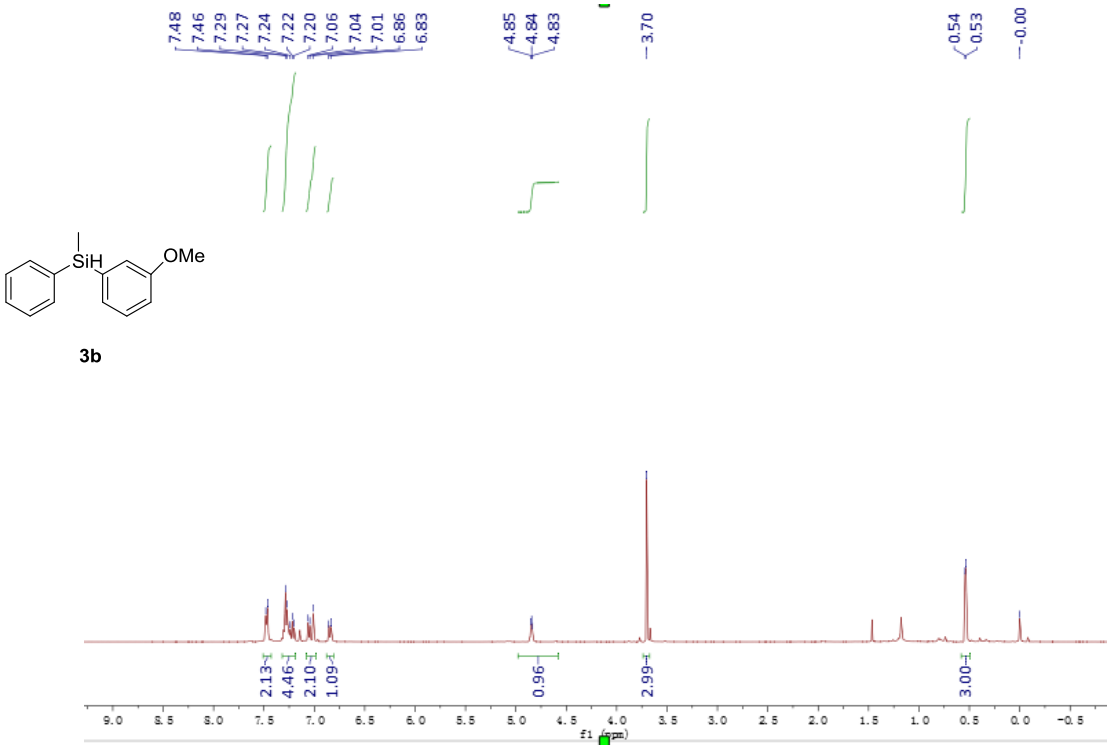

2.05
5.09
1.04
1.01
1.00
3.16
3.17
f1 (ppm)


164.45
136.78
136.04
134.99
131.70
129.29
127.86
123.81
120.78
109.81
77.48
77.16
76.84
55.29
4.94

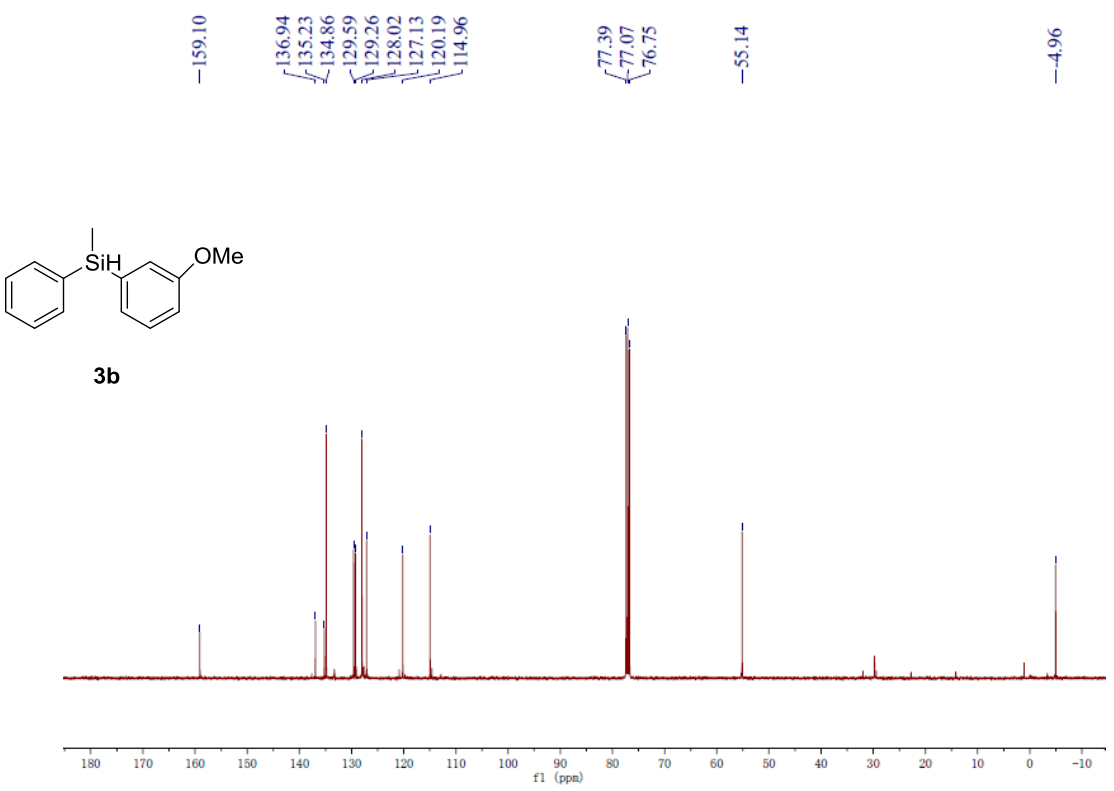

OMe
SiH

3a

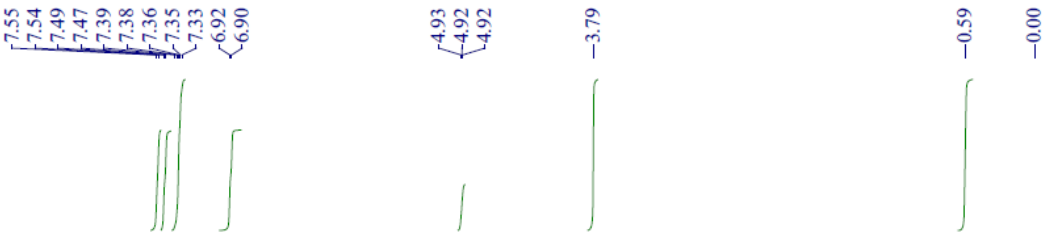
f1 (ppm)

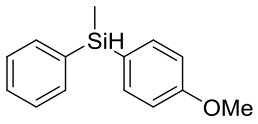

7.48
7.46
7.29
7.27
7.24
7.22
7.20
7.06
7.04
7.01
6.86
6.83
4.85
4.84
4.83
3.70
0.54
0.53
0.00
SiH
OMe
2.13
4.46
2.10
1.09
0.96
2.99
3.00
f1 (ppm)

3b

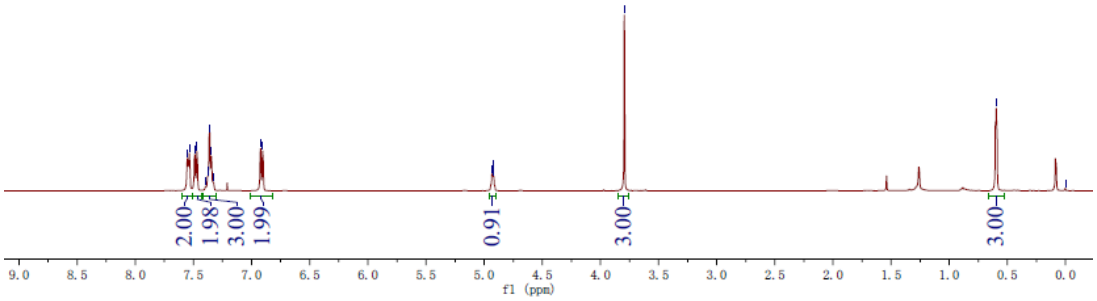

159.10
136.94
135.23
134.86
129.59
129.26
128.02
127.13
120.19
114.96
77.39
77.07
76.75
55.14
4.96
SiH
OMe
f1 (ppm)

3b

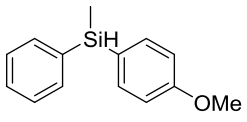

7.55
7.54
7.49
7.47
7.39
7.38
7.36
7.35
7.33
6.92
6.90
4.93
4.92
4.92
3.79
0.59
0.00


SiH
OMe

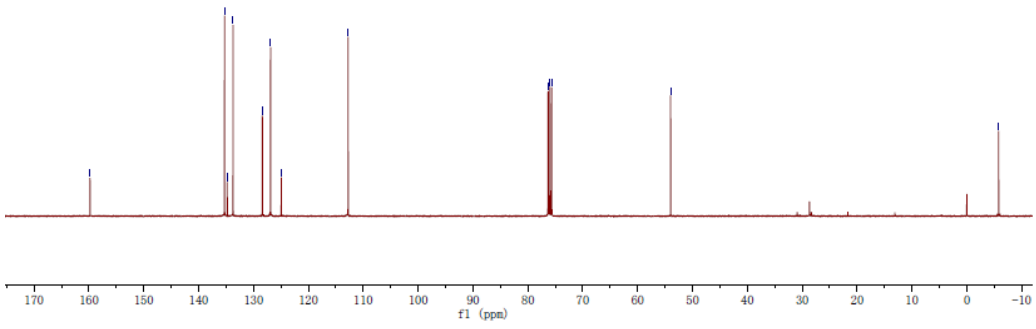
3c

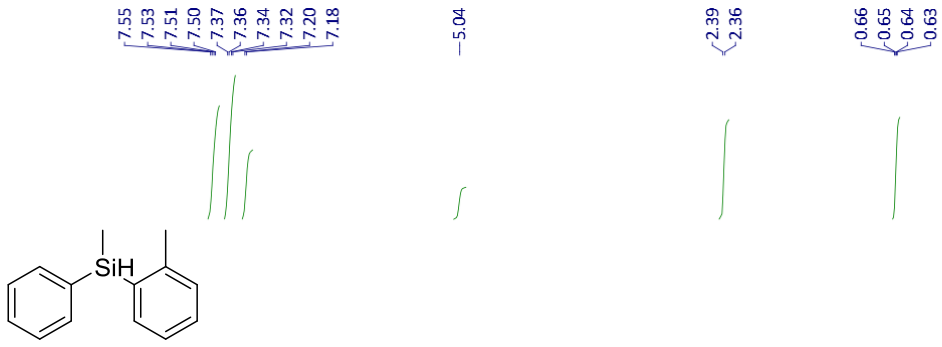

2.00
1.98
3.00
1.99
0.91
3.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


159.79
135.28
134.78
133.73
128.38
126.89
124.94
112.75
76.30
75.99
75.67
53.98
5.80

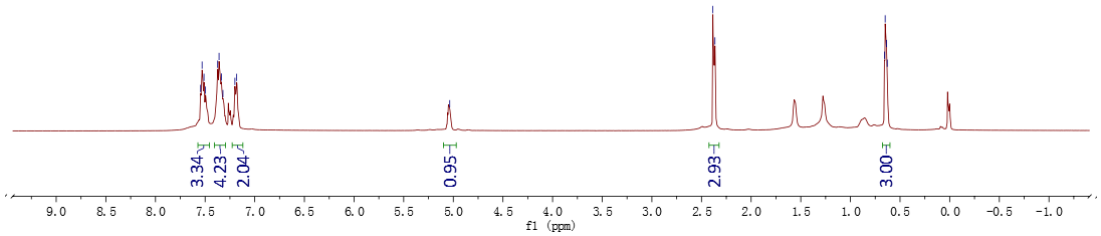

SiH
OMe

3c

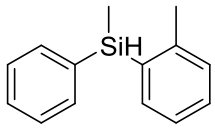

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.55
7.53
7.51
7.50
7.37
7.36
7.34
7.32
7.20
7.18
5.04
2.39
2.36
0.66
0.65
0.64
0.63
SiH

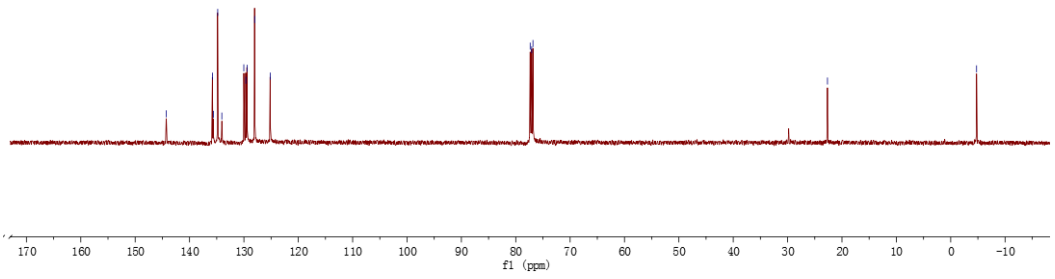
3d

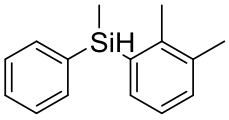

3.34
4.23
2.04
0.95
2.93
3.00
f1 (ppm)


144.29
135.77
135.62
134.82
134.06
130.02
129.64
129.42
128.01
125.15
77.35
77.07
76.84
22.67
-4.75

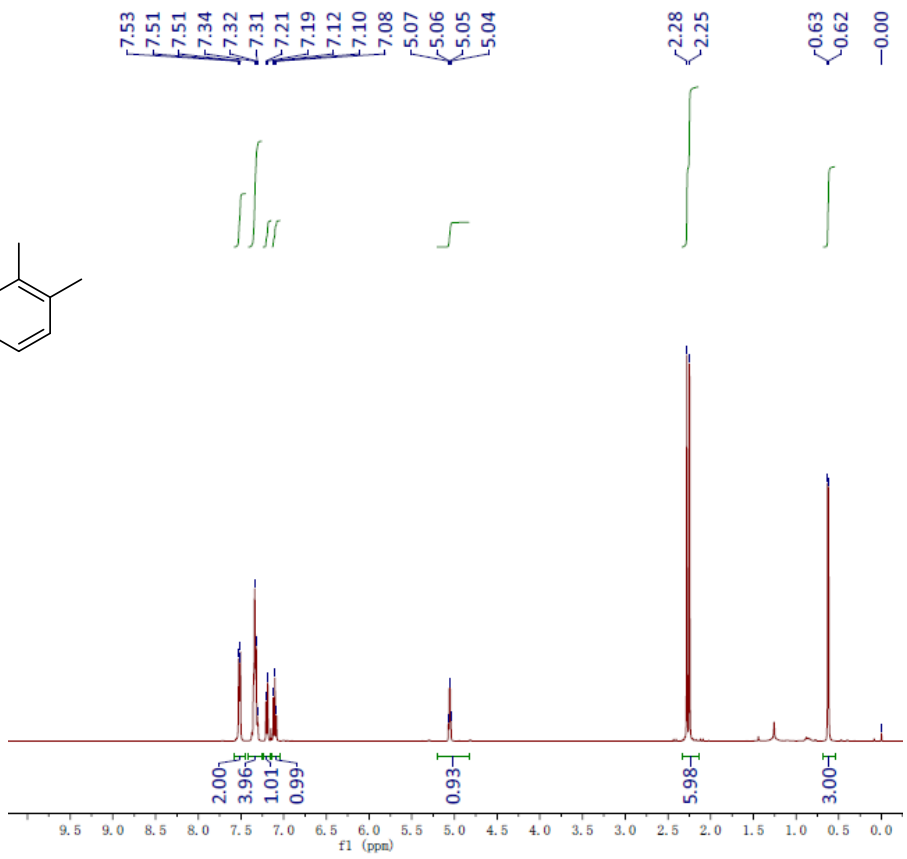

SiH

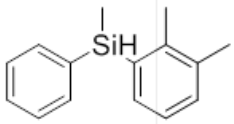
3d


f1 (ppm)

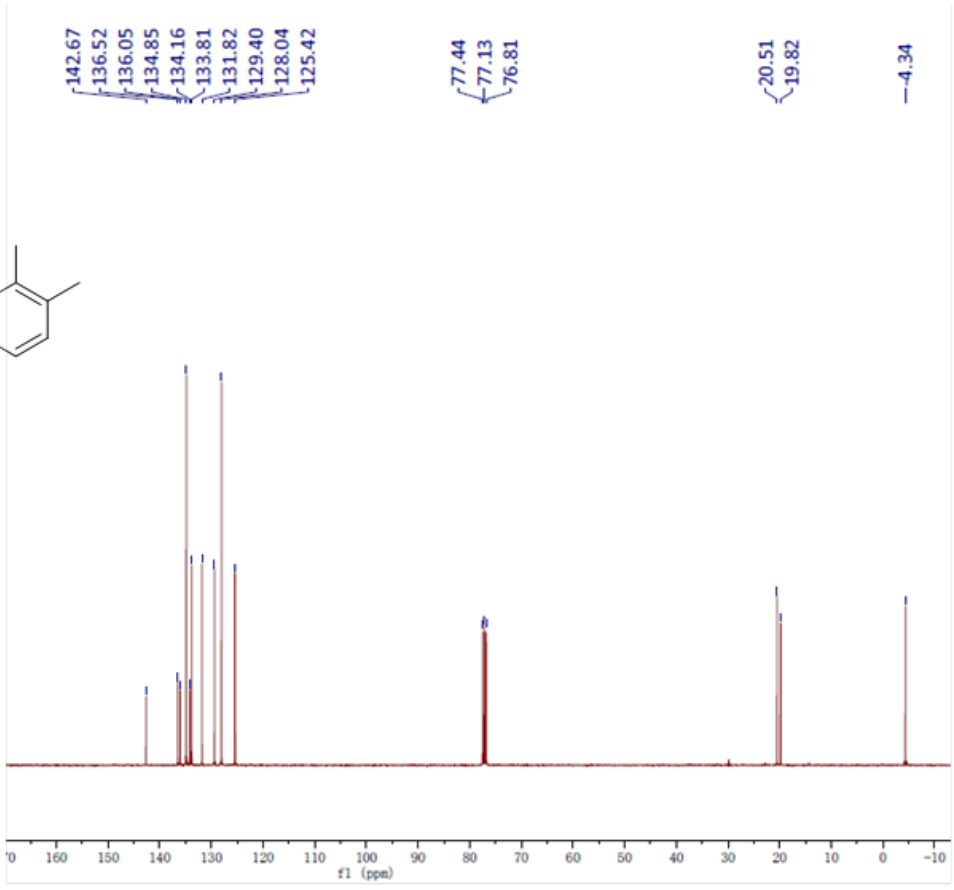

SiH

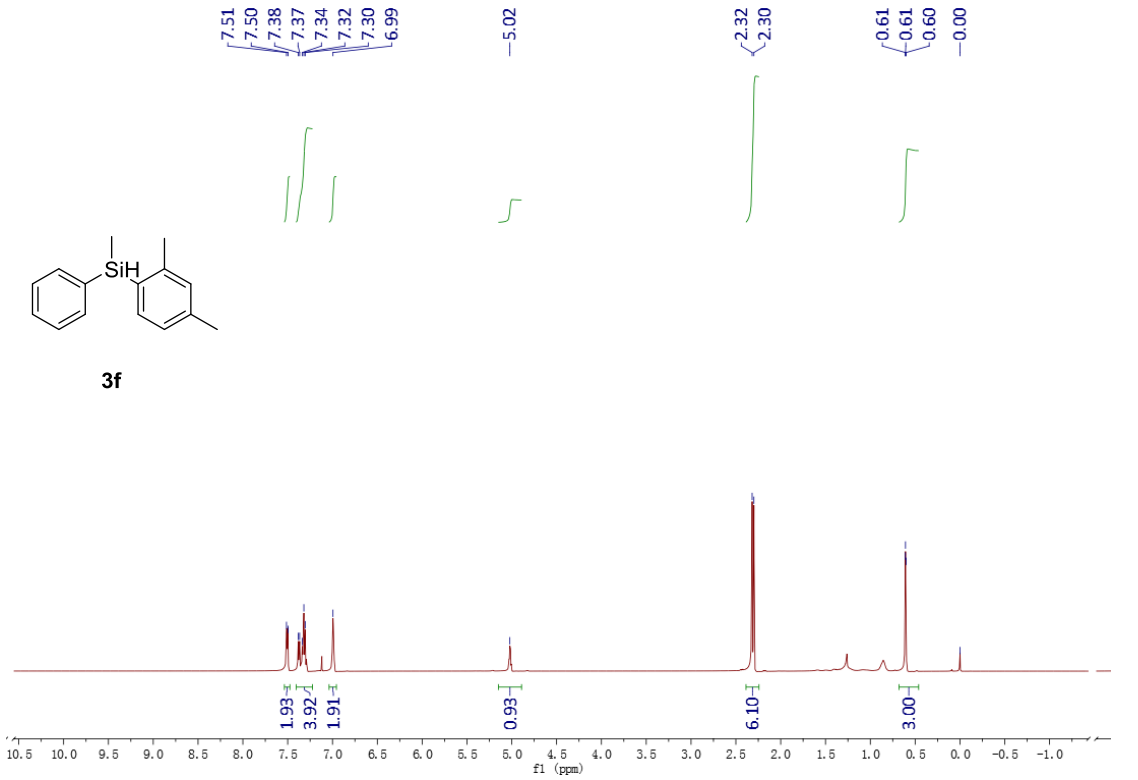
3e


7.53
7.51
7.51
7.34
7.32
7.31
7.21
7.19
7.12
7.10
7.08
5.07
5.06
5.05
5.04
2.28
2.25
0.63
0.62
0.00
2.00
3.96
1.01
0.99
0.93
5.98
3.00
f1 (ppm)

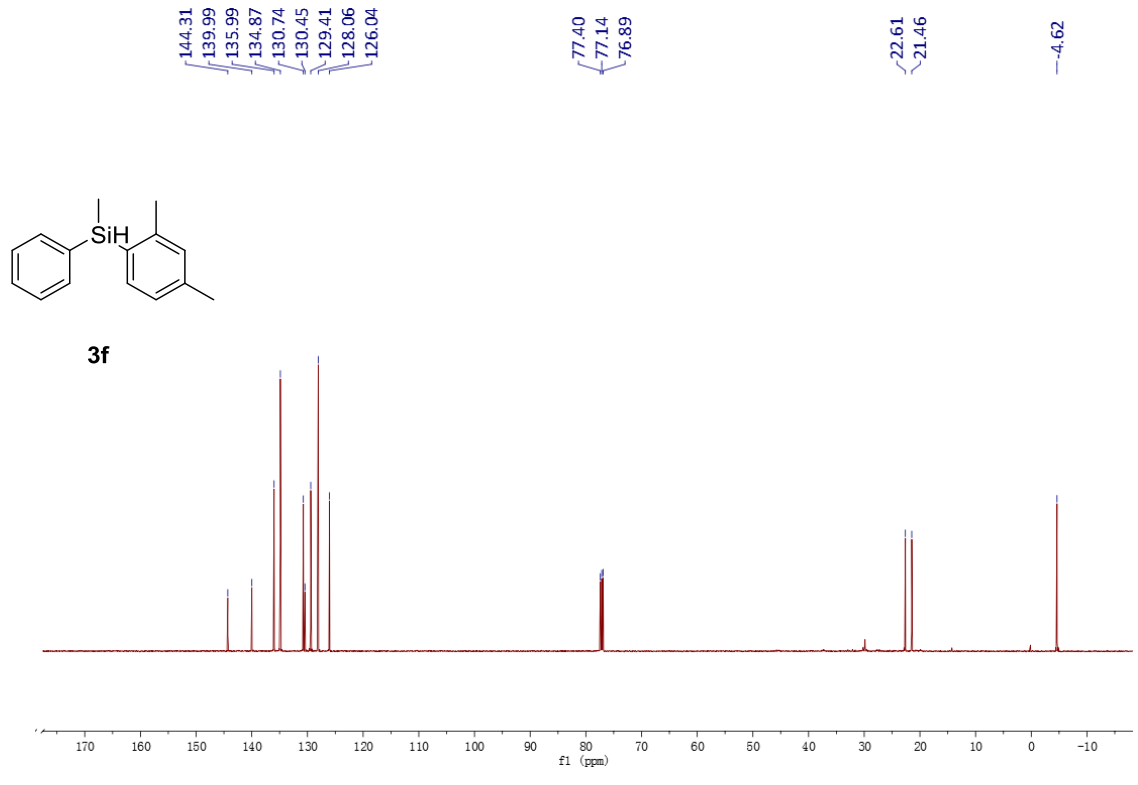

SiH

3e

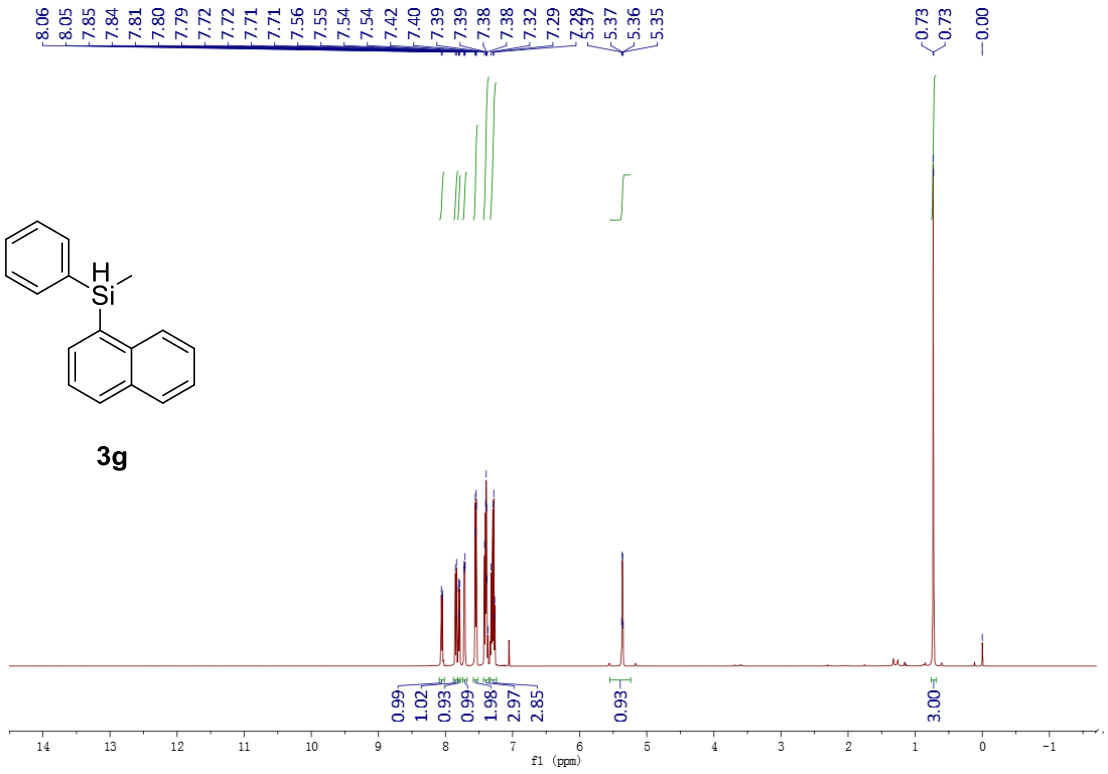

142.67
136.52
136.05
134.85
134.16
133.81
131.82
129.40
128.04
125.42
77.44
77.13
76.81
20.51
19.82
-4.34
f1 (ppm)


7.51
7.50
7.38
7.37
7.34
7.32
7.30
6.99
5.02
2.32
2.30
0.61
0.61
0.60
0.00
SiH
1.93
3.92
1.91
0.93
6.10
3.00
f1 (ppm)

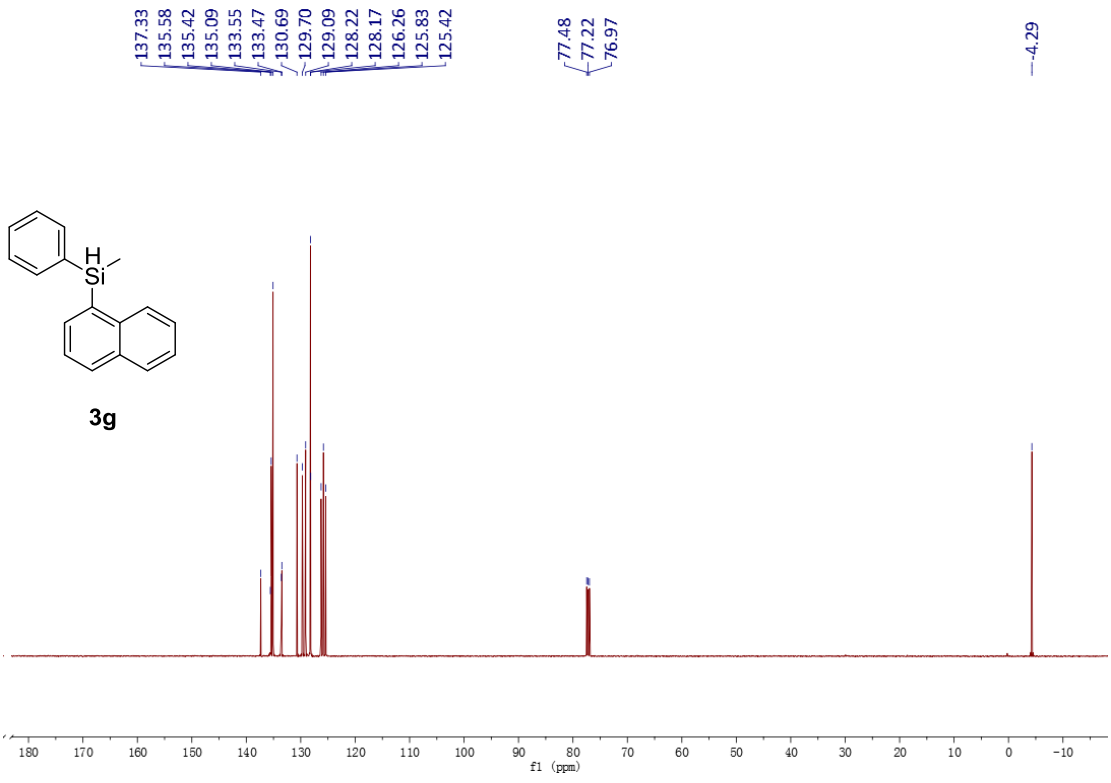
3f


144.31
139.99
135.99
134.87
130.74
130.45
129.41
128.06
126.04
77.40
77.14
76.89
22.61
21.46
-4.62
SiH
f1 (ppm)

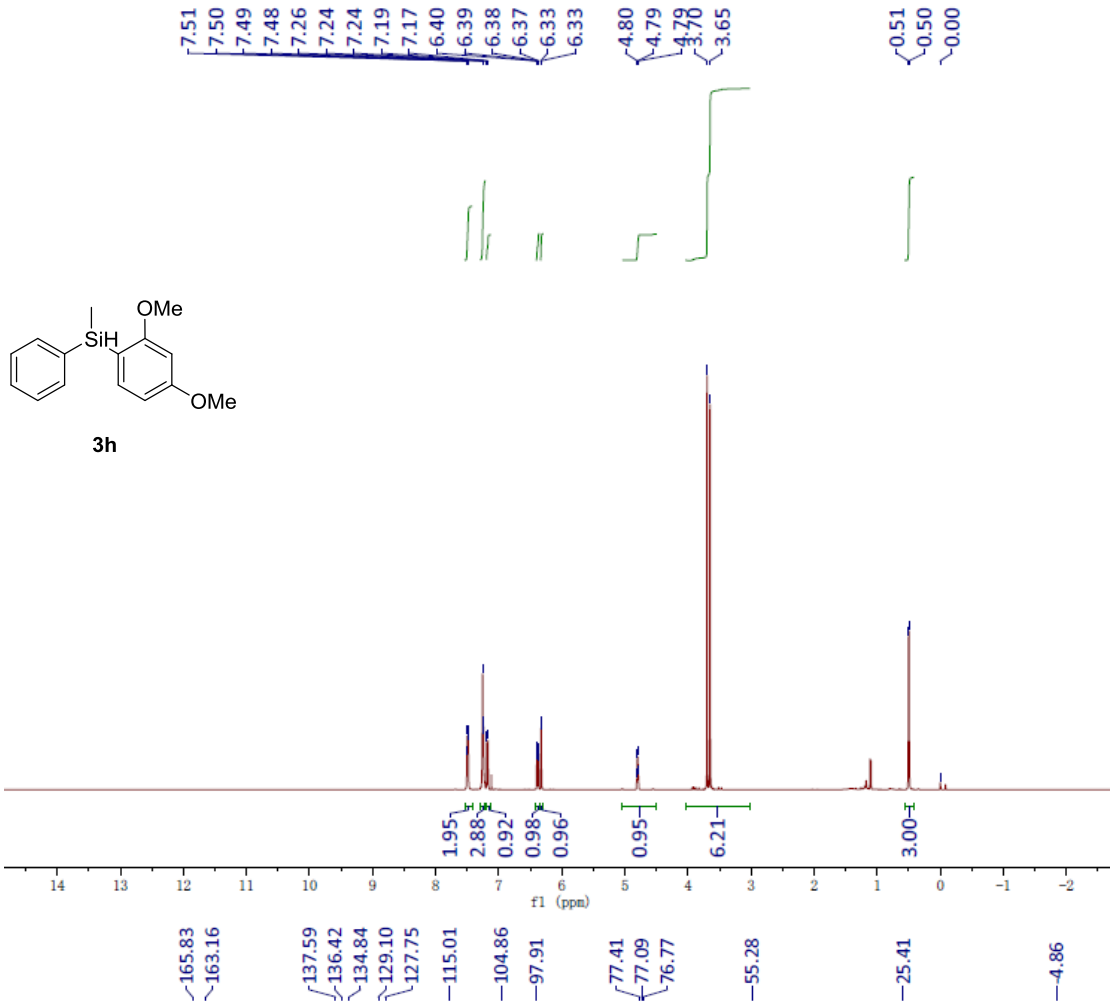
3f


8.06
8.05
7.85
7.84
7.81
7.80
7.79
7.72
7.72
7.71
7.71
7.56
7.55
7.54
7.54
7.42
7.40
7.39
7.39
7.38
7.38
7.32
7.29
5.37
5.36
5.35
0.73
0.73
0.00
H
Si
0.99
1.02
0.93
0.99
1.98
2.97
2.85
0.93
3.00
f1 (ppm)

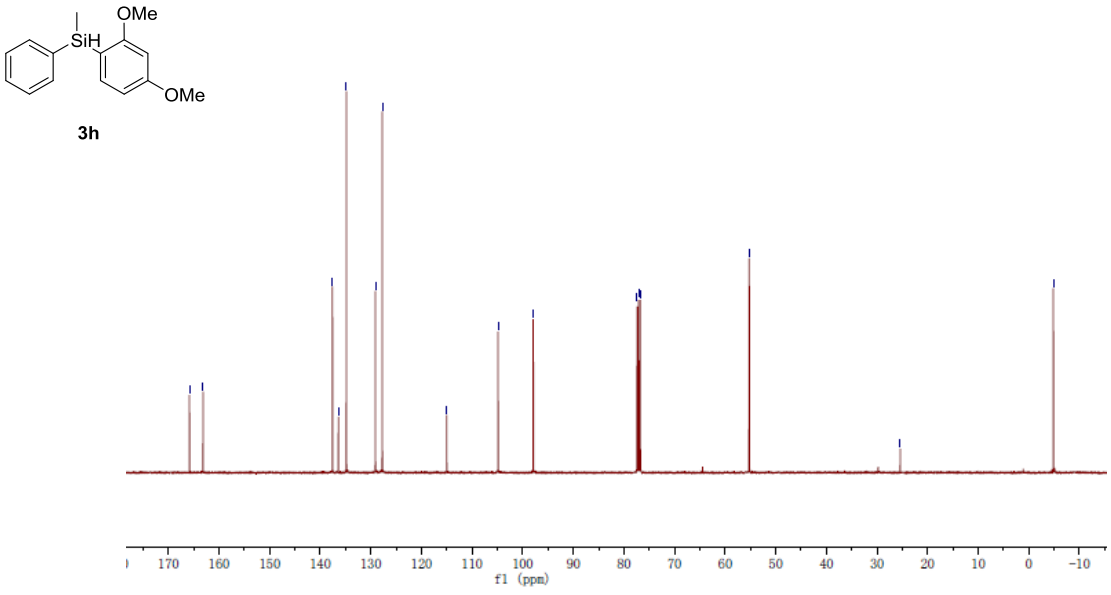
3g


137.33
135.58
135.42
135.09
133.55
133.47
130.69
129.70
129.09
128.22
128.17
126.26
125.83
125.42
77.48
77.22
76.97
-4.29
H
Si
f1 (ppm)

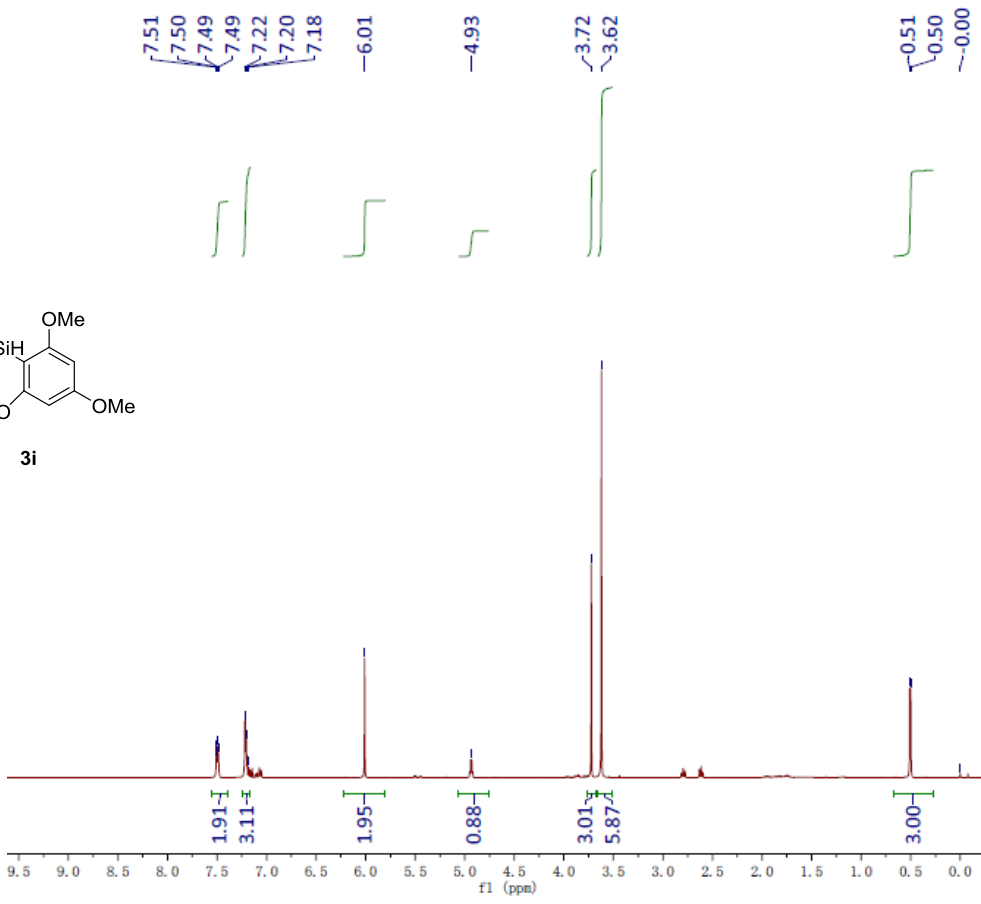
3g


7.51
7.50
7.49
7.48
7.26
7.24
7.24
7.19
7.17
6.40
6.39
6.38
6.37
6.33
6.33
4.80
4.79
4.79
3.70
3.65
0.51
0.50
0.00
OMe
SiH
OMe
1.95
2.88
0.92
0.98
0.96
0.95
6.21
3.00
f1 (ppm)

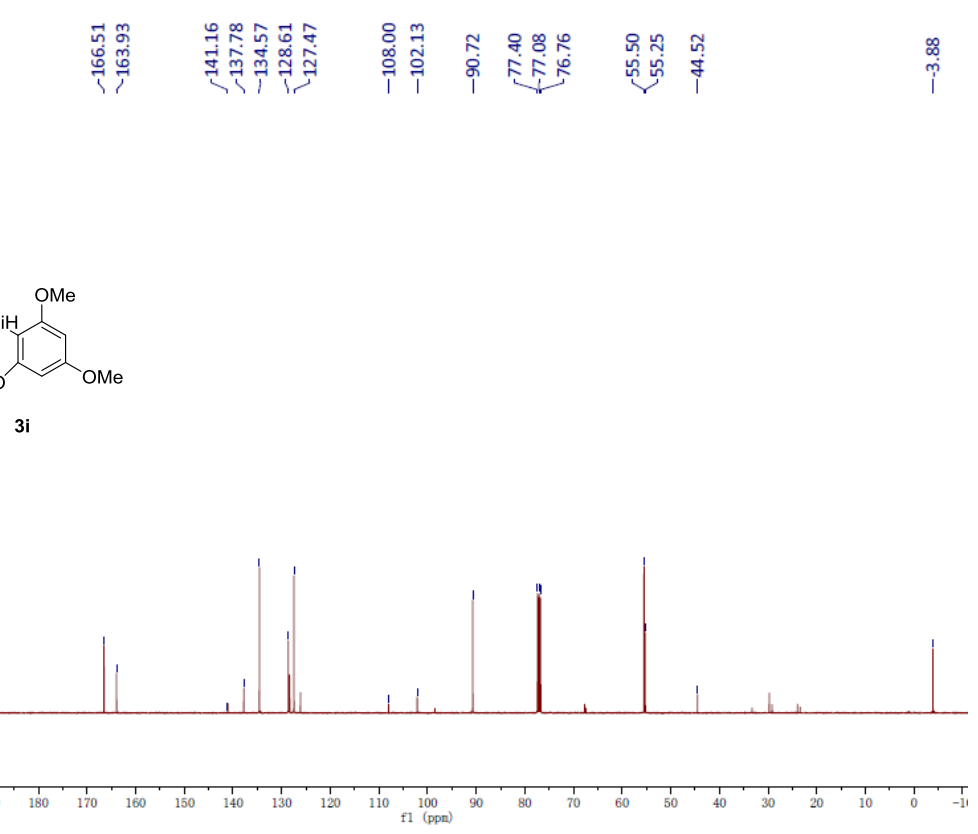
3h


OMe
SiH
OMe
165.83
163.16
137.59
136.42
134.84
129.10
127.75
115.01
104.86
97.91
77.41
77.09
76.77
55.28
25.41
4.86
f1 (ppm)

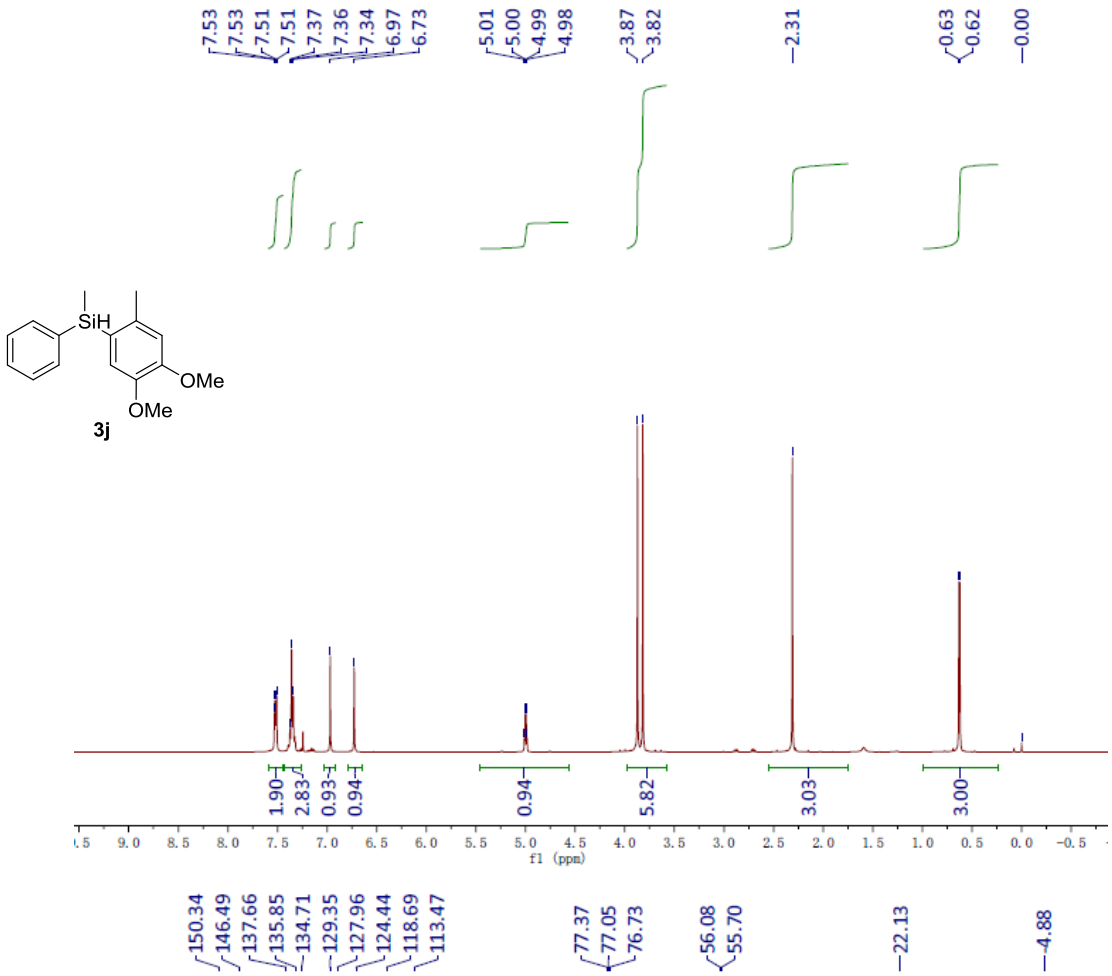
3h

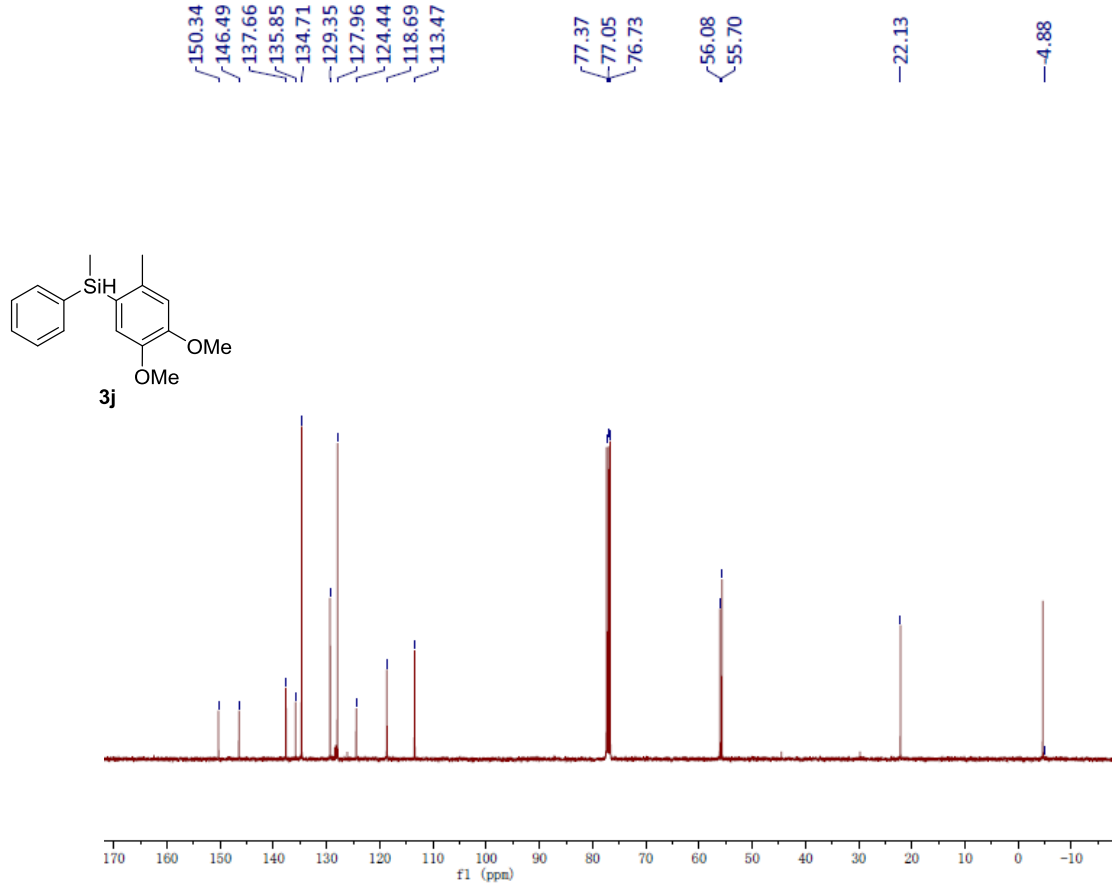

7.51
7.50
7.49
7.49
7.22
7.20
7.18
6.01
4.93
3.72
3.62
0.51
0.50
-0.00
OMe
SiH
MeO
OMe
1.91
3.11
1.95
0.88
3.01
5.87
3.00
f1 (ppm)

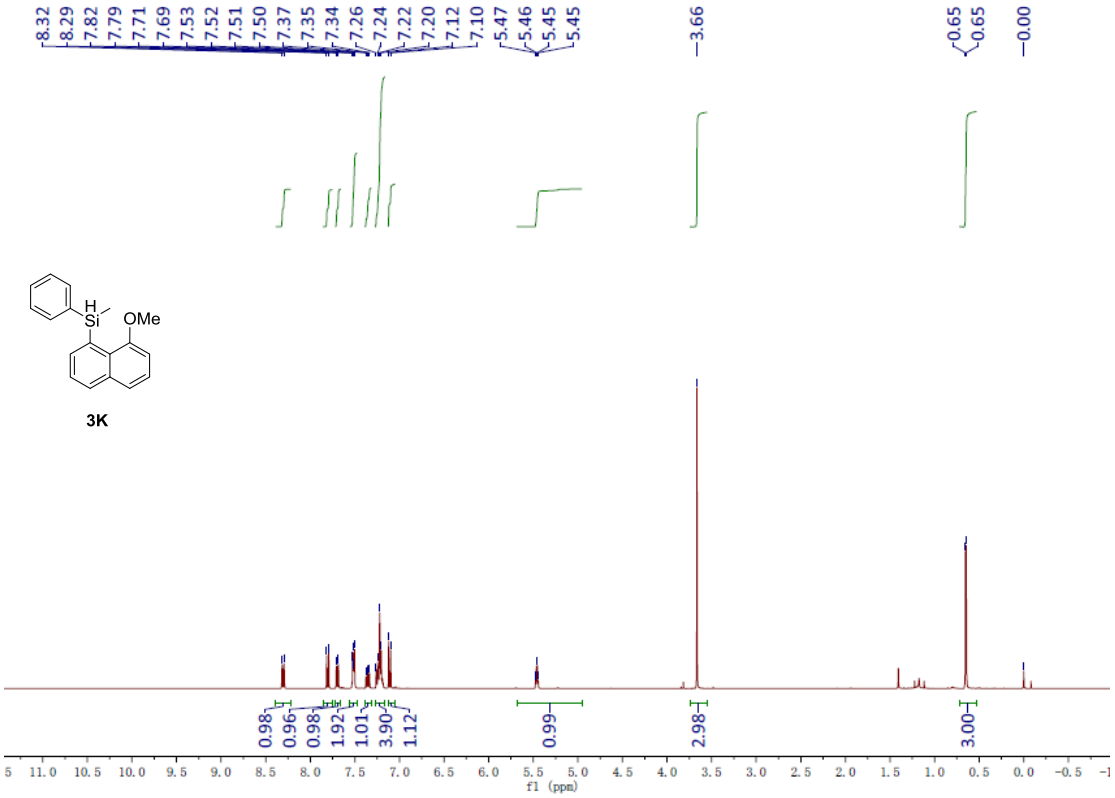
3i


166.51
163.93
141.16
137.78
134.57
128.61
127.47
108.00
102.13
90.72
77.40
77.08
76.76
55.50
55.25
44.52
3.88
OMe
SiH
MeO
OMe
f1 (ppm)

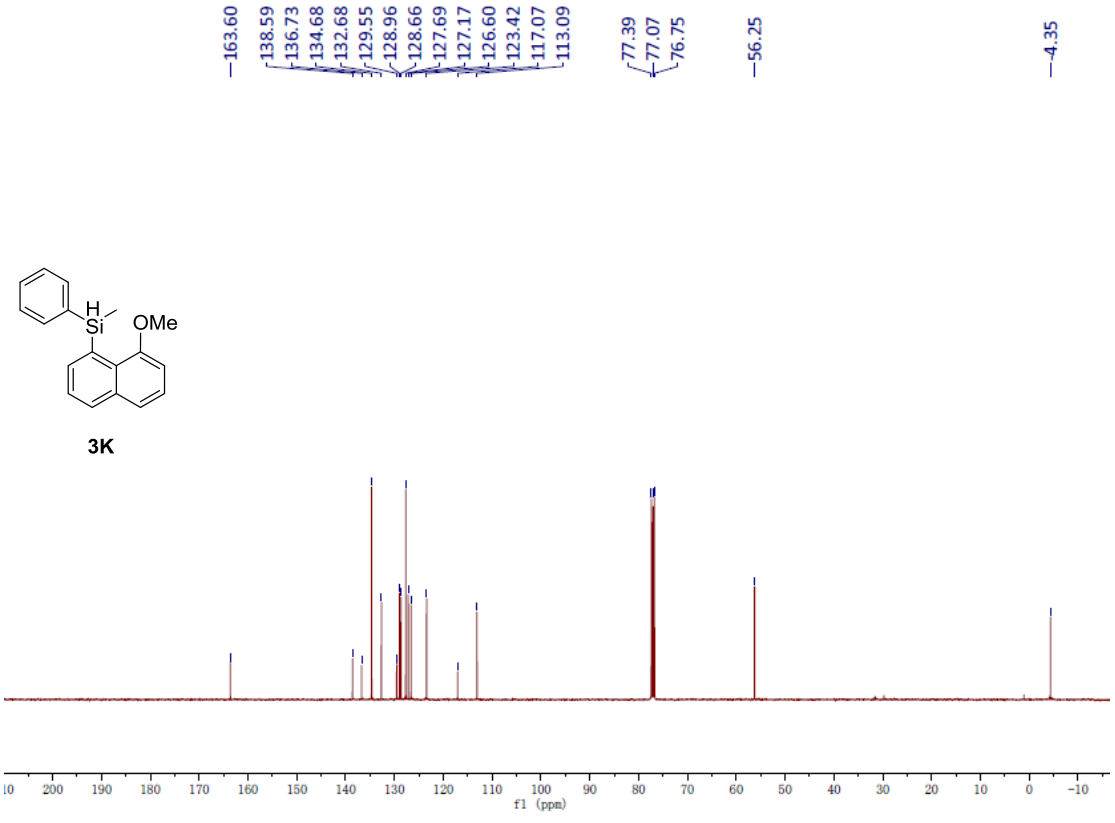
3i


7.53
7.53
7.51
7.51
7.37
7.36
7.34
6.97
6.73
5.01
5.00
4.99
4.98
3.87
3.82
2.31
0.63
0.62
0.00
SiH
OMe
OMe
3j
1.90
2.83
0.93
0.94
0.94
5.82
3.03
3.00
f1 (ppm)

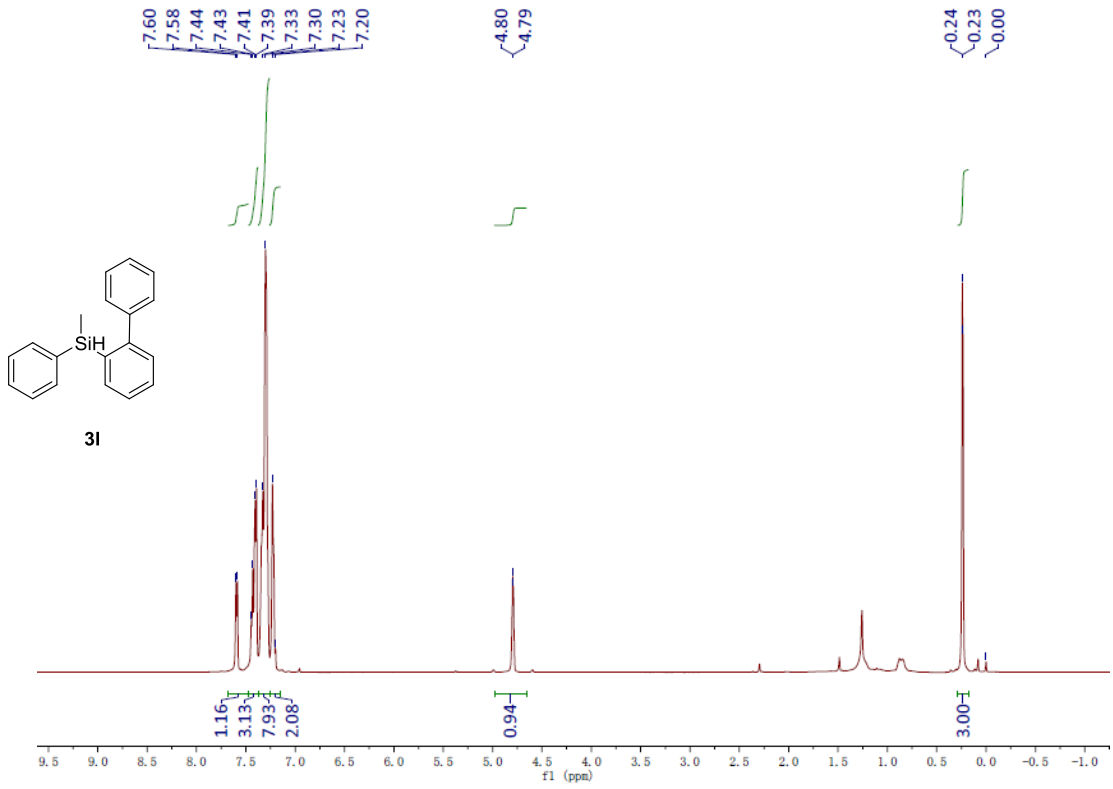

150.34
146.49
137.66
135.85
134.71
129.35
127.96
124.44
118.69
113.47
77.37
77.05
76.73
56.08
55.70
22.13
4.88
SiH
OMe
OMe
3j
f1 (ppm)

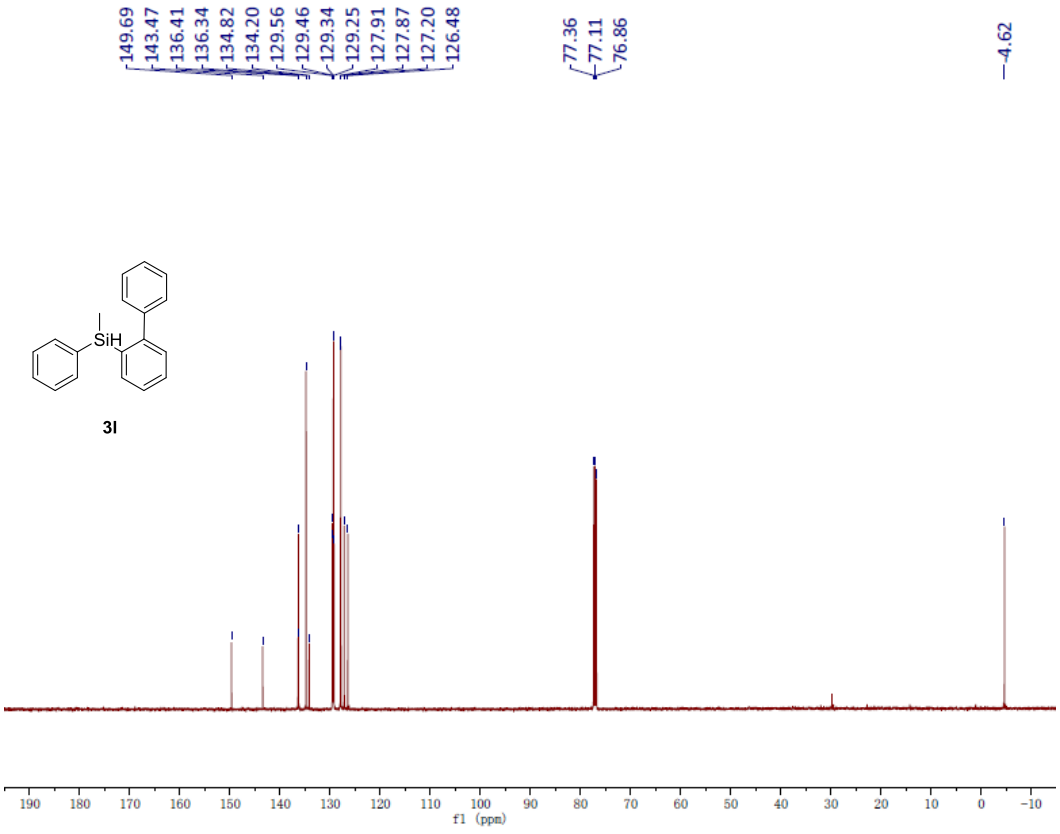

8.32
8.29
7.82
7.79
7.71
7.69
7.53
7.52
7.51
7.50
7.37
7.35
7.34
7.26
7.24
7.22
7.20
7.12
7.10
5.47
5.46
5.45
5.45
3.66
0.65
0.65
0.00
H
Si
OMe
0.98
0.96
0.98
1.92
1.01
3.90
1.12
0.99
2.98
3.00
f1 (ppm)

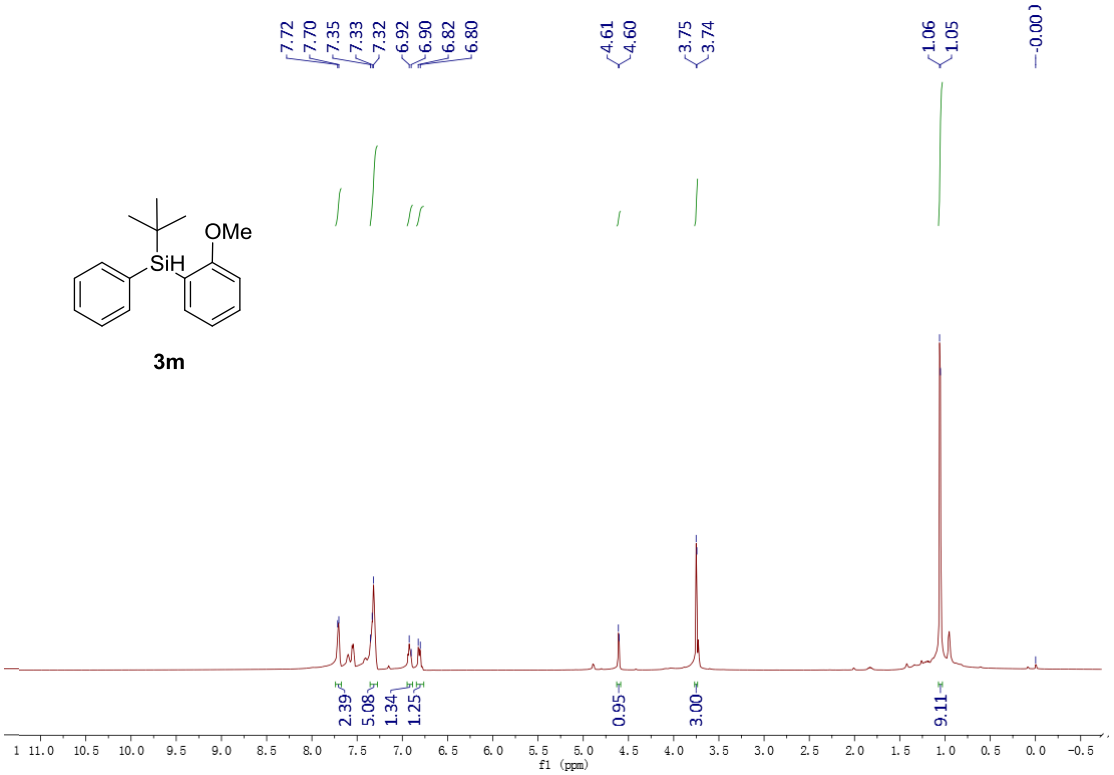
3K


163.60
138.59
136.73
134.68
132.68
129.55
128.96
128.66
127.69
127.17
126.60
123.42
117.07
113.09
77.39
77.07
76.75
56.25
4.35
H
Si
OMe
f1 (ppm)

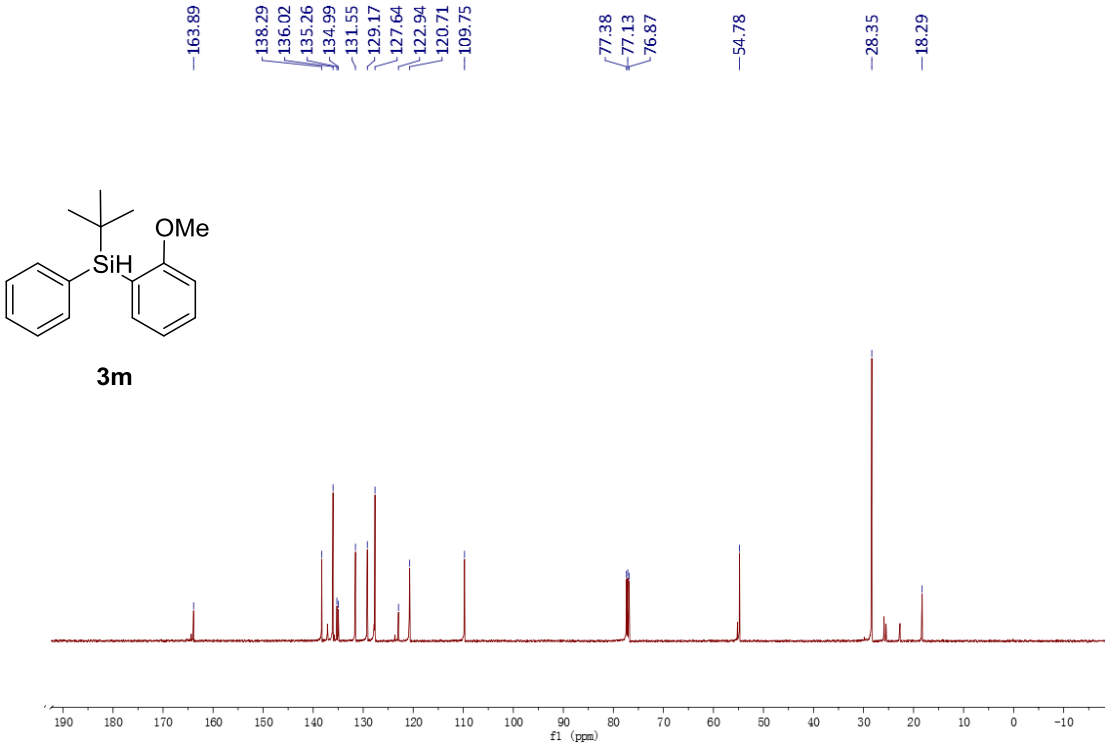
3K


7.60
7.58
7.44
7.43
7.41
7.39
7.33
7.30
7.23
7.20
4.80
4.79
0.24
0.23
0.00
SiH
3l
1.16
3.13
7.93
2.08
0.94
3.00
f1 (ppm)


149.69
143.47
136.41
136.34
134.82
134.20
129.56
129.46
129.34
129.25
127.91
127.87
127.20
126.48
77.36
77.11
76.86
-4.62
SiH
3l
f1 (ppm)

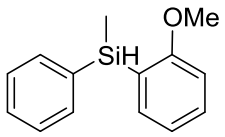

7.72
7.70
7.35
7.33
7.32
6.92
6.90
6.82
6.80
4.61
4.60
3.75
3.74
1.06
1.05
-0.00
OMe
SiH
2.39
5.08
1.34
1.25
0.95
3.00
9.11
f1 (ppm)

3m

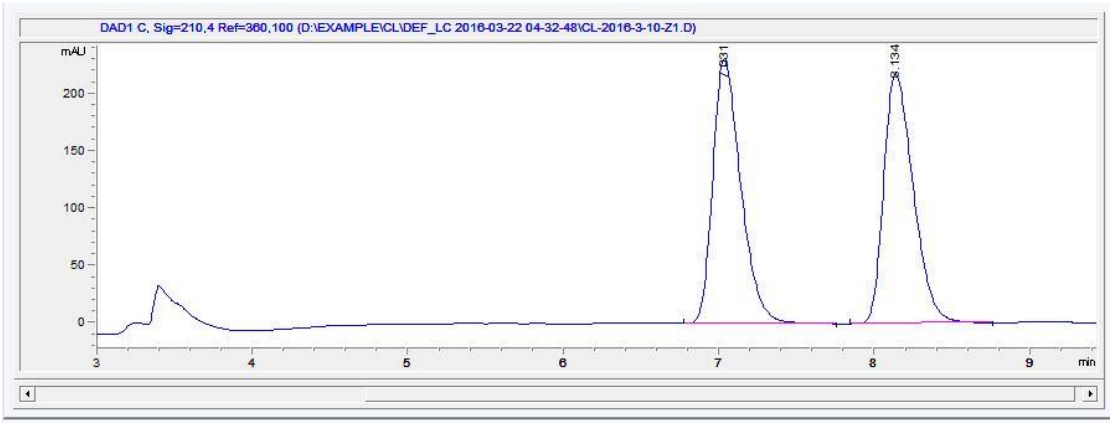

163.89
138.29
136.02
135.26
134.99
131.55
129.17
127.64
122.94
120.71
109.75
77.38
77.13
76.87
54.78
28.35
18.29
OMe
SiH
f1 (ppm)

3m

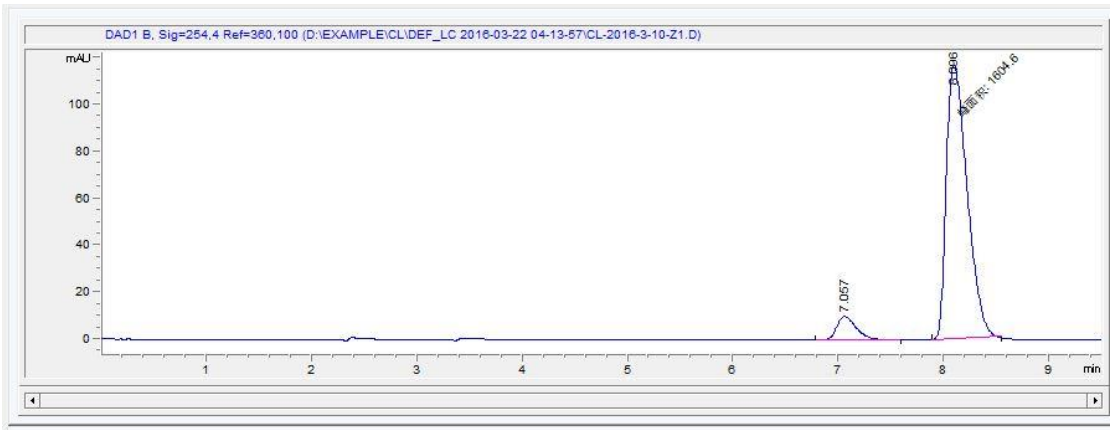
S-8. HPLC spectra of product 3a-3l



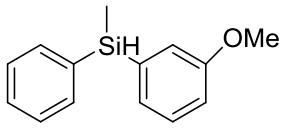
3a 85%ee



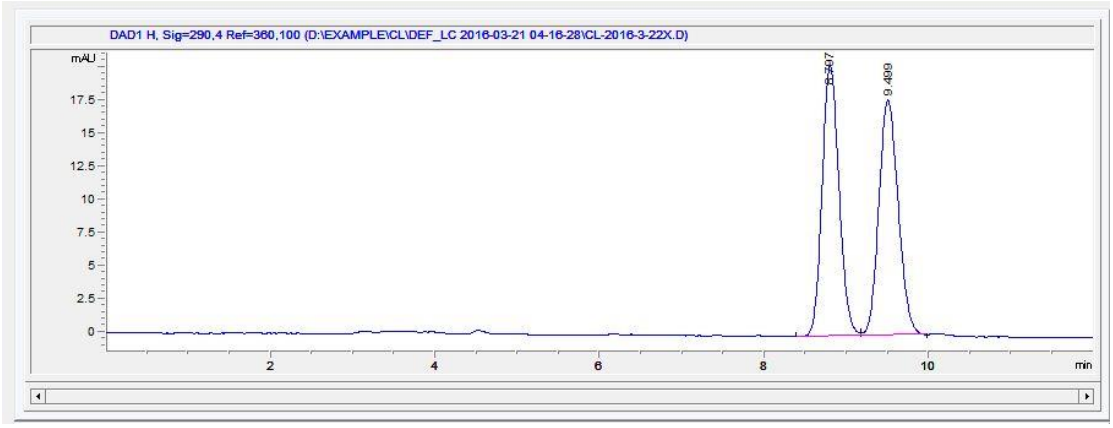
#	Time	Area	Height	Width	Symmetry	Area%
1	7.031	2886.8	230.9	0.1918	0.638	50.047
2	8.134	2881.4	217.5	0.2006	0.632	49.953



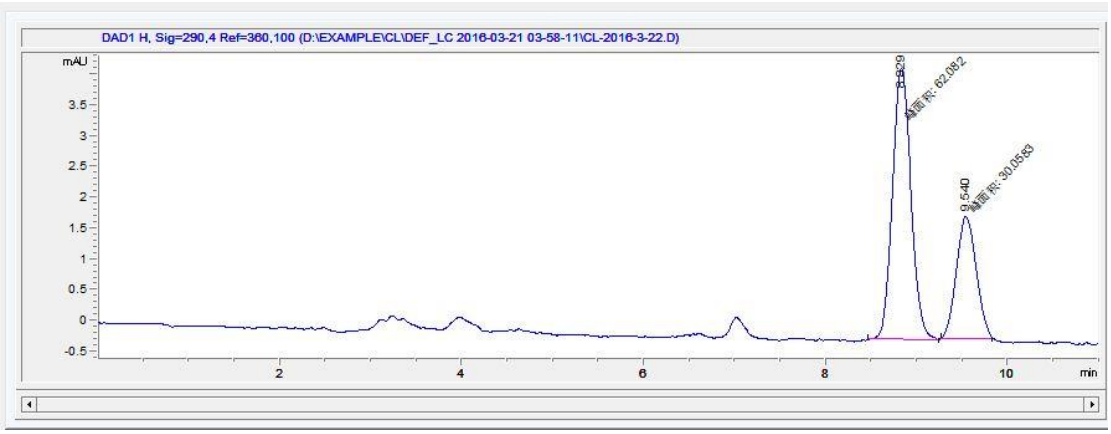
#	Time	Area	Height	Width	Symmetry	Area%
1	7.075	127.2	10	0.1921	0.631	7.343
2	8.096	1604.6	116.7	0.2291	0.561	92.657



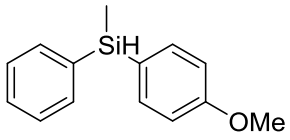
3b 35%ee



#	Time	Area	Height	Width	Symmetry	Area%
1	8.797	291.5	20.4	0.2247	0.855	50.164
2	9.499	289.6	17.7	0.2565	0.832	49.836



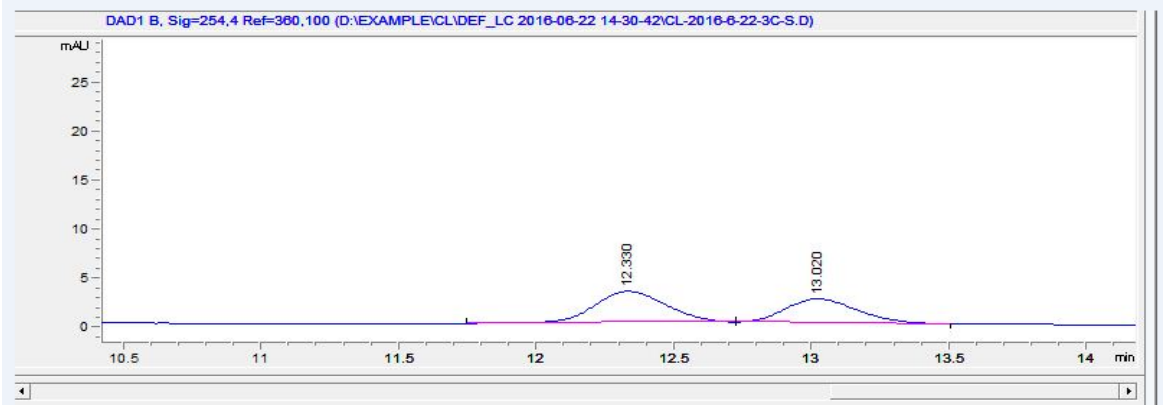
#	Time	Area	Height	Width	Symmetry	Area%
1	8.829	62.1	4.4	0.2352	0.849	67.378
2	9.54	30.1	2	0.2529	0.892	32.622



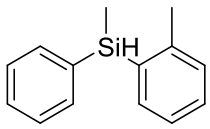
3c

14%ee

#	Time	Area	Height	Width	Symmetry	Area%
1	12.512	850	42.5	0.3076	0.777	49.771
2	13.19	857.8	40.2	0.3271	0.763	50.229

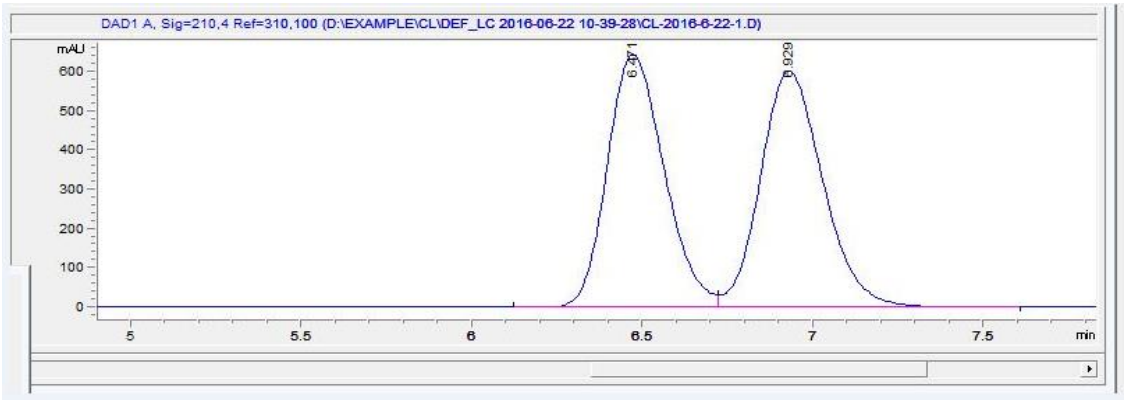


#	Time	Area	Height	Width	Symmetry	Area%
1	12.33	57.9	3.2	0.2787	0.872	56.910
2	13.02	43.9	2.4	0.2719	0.773	43.090

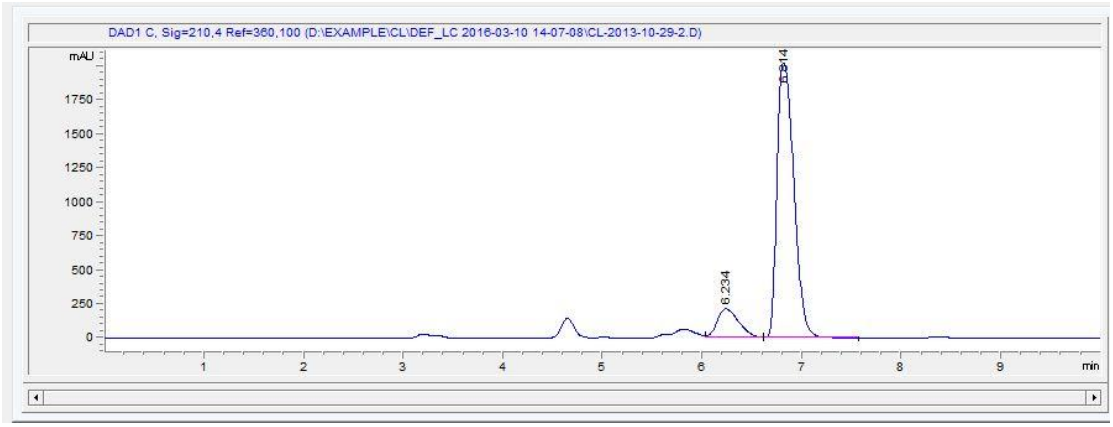


3d

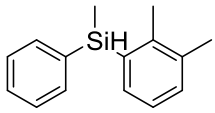
78%ee



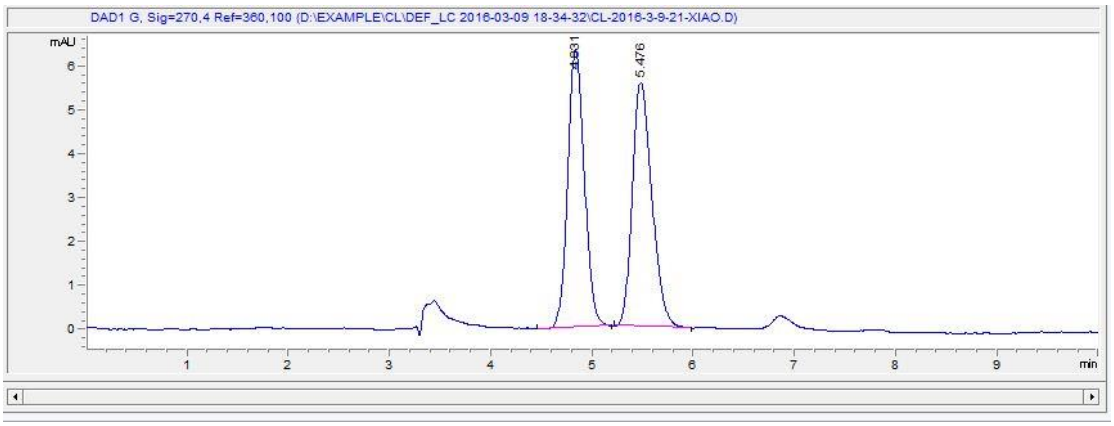
#	Time	Area	Height	Width	Symmetry	Area%
1	6.471	7481	644.6	0.1814	0.779	49.376
2	6.929	7670.1	603.2	0.1964	0.797	50.624



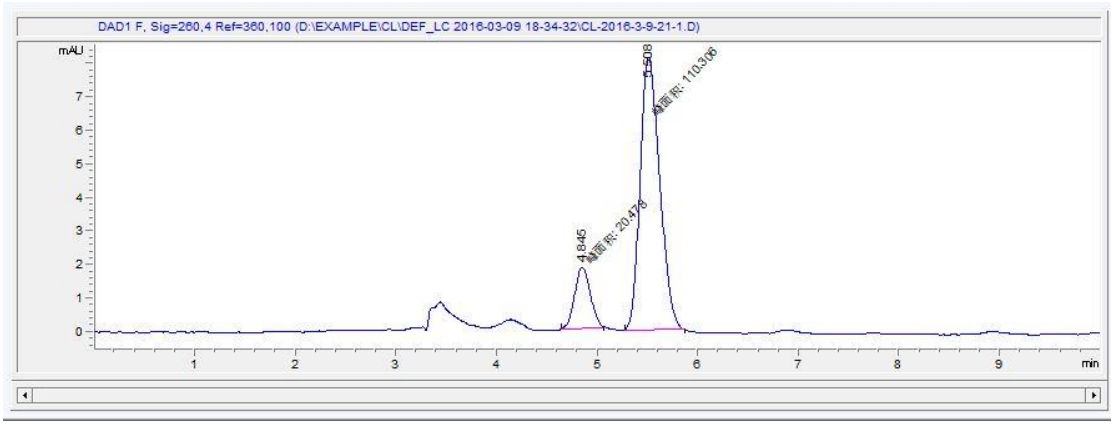
#	Time	Area	Height	Width	Symmetry	Area%
1	6.234	3194.4	212.4	0.2334	0.656	11.173
2	6.814	23711.2	2018.4	0.1891	0605	88.827



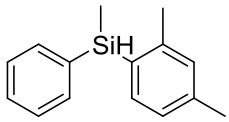
3e 69%ee



#	Time	Area	Height	Width	Symmetry	Area%
1	4.831	72.2	6.3	0.1749	0.832	49.145
2	5.476	74.7	5.6	0.2046	0.71	50.855

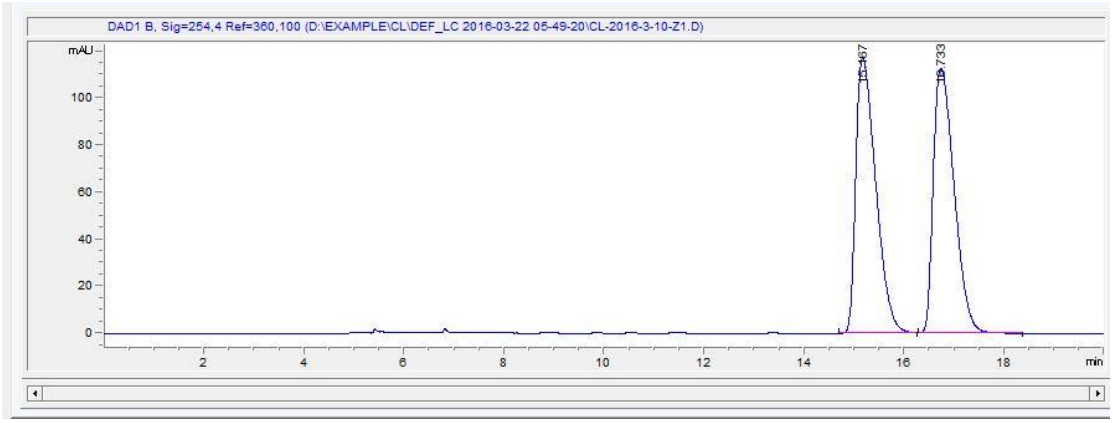


#	Time	Area	Height	Width	Symmetry	Area%
1	4.485	20.5	1.9	0.1841	0.85	15.658
2	5.508	110.3	8.1	0.2257	00.746	84.342

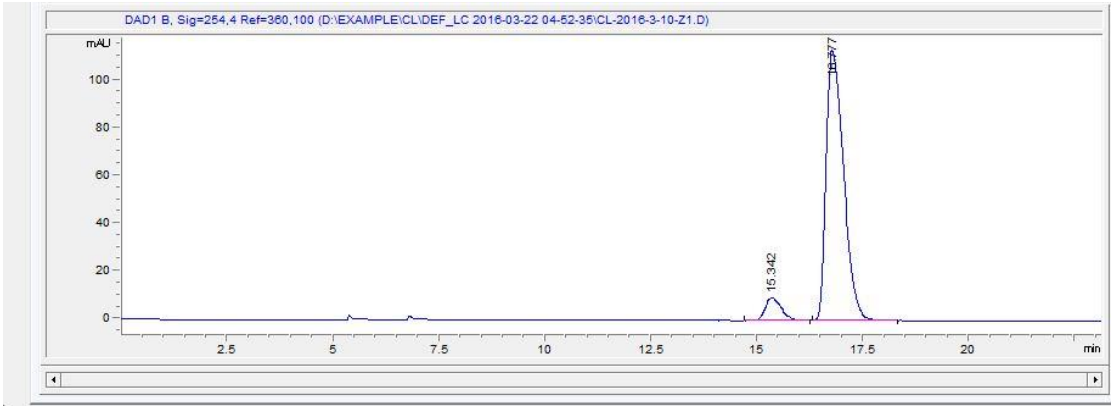


3f

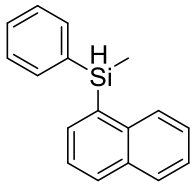
86%ee



#	Time	Area	Height	Width	Symmetry	Area%
1	15.167	3249.3	117.3	0.4311	0.495	49.930
2	16.733	3258.4	112.6	0.4555	0.54	50.070



#	Time	Area	Height	Width	Symmetry	Area%
1	15.342	252.7	9.5	0.4102	0.671	7.181
2	16.777	3266.3	113.1	0.457	0.549	92.819



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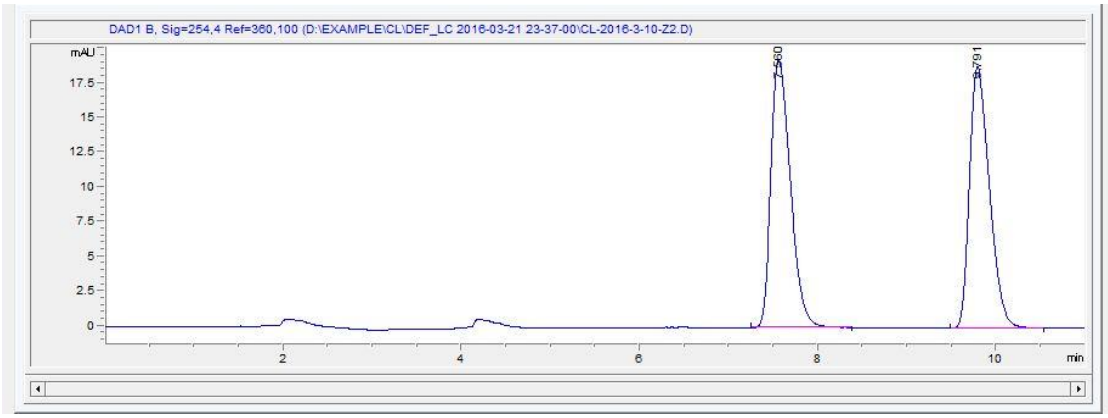
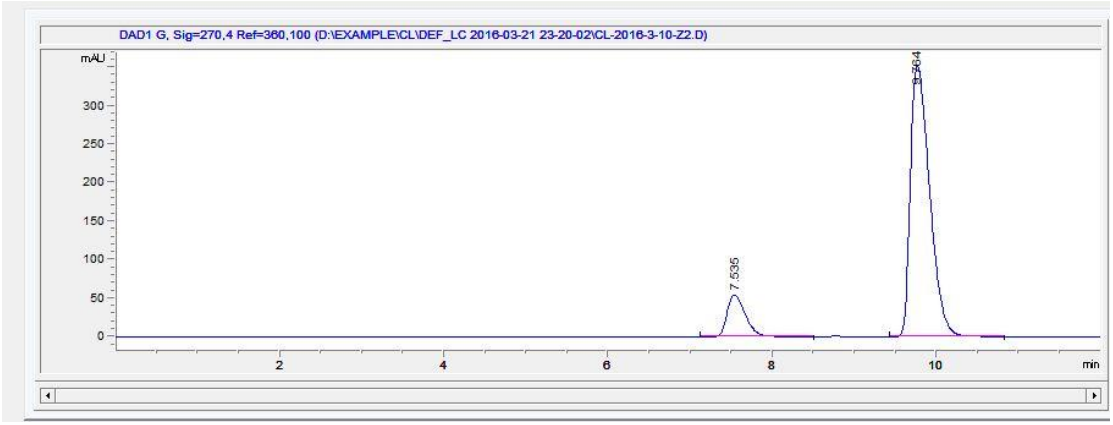
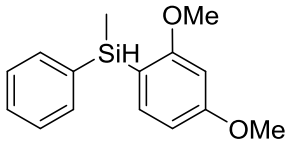


#	Time	Area	Height	Width	Symmetry	Area%
1	7.56	294	19.3	0.2356	0.631	50.007
2	9.791	293.9	18.8	0.244	0.624	49.993



#	Time	Area	Height	Width	Symmetry	Area%
1	7.535	830.4	54.3	0.2366	0.625	12.624
2	9.764	5747.8	352.6	0.2542	0.538	87.376



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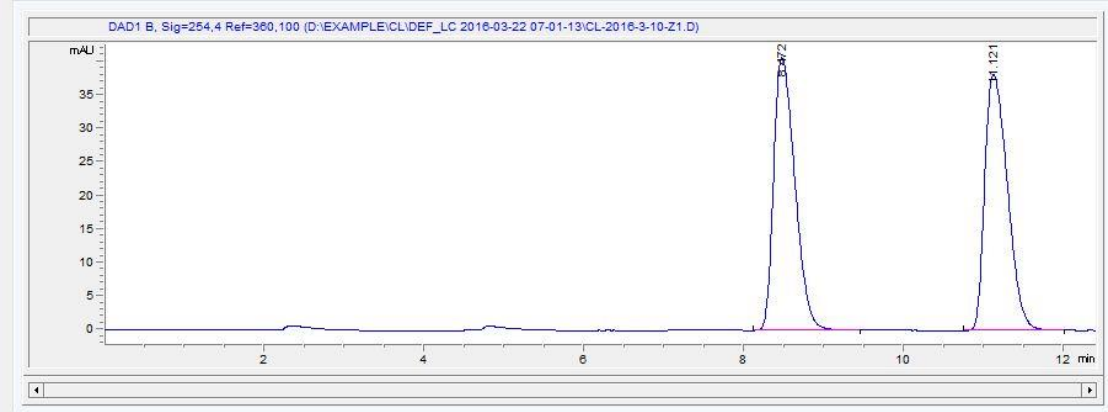
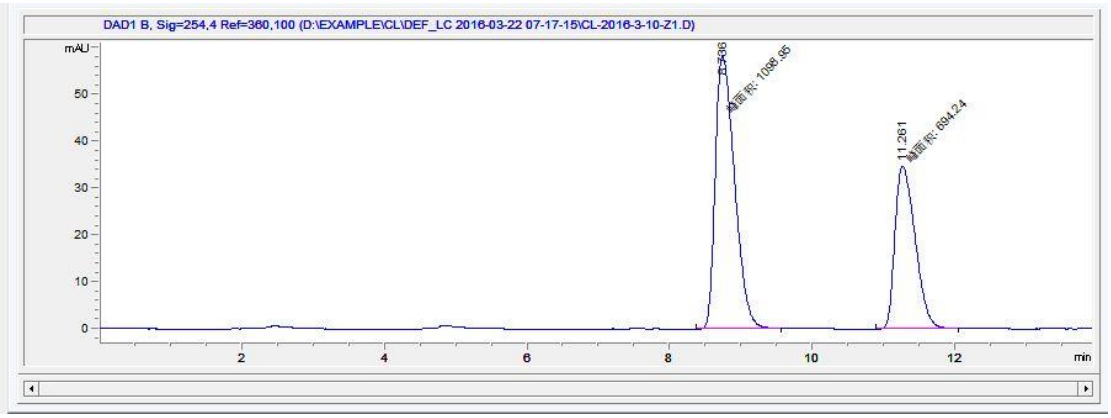
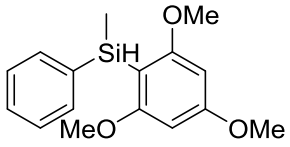


#	Time	Area	Height	Width	Symmetry	Area%
1	8.472	752.8	40.7	0.2936	0.597	49.923
2	11.121	755.1	38.3	0.3181	0.583	50.077



#	Time	Area	Height	Width	Symmetry	Area%
1	8.736	1098.9	58.4	0.3141	0.583	61.285
2	11.261	694.2	34.8	0.3324	0.581	37.715



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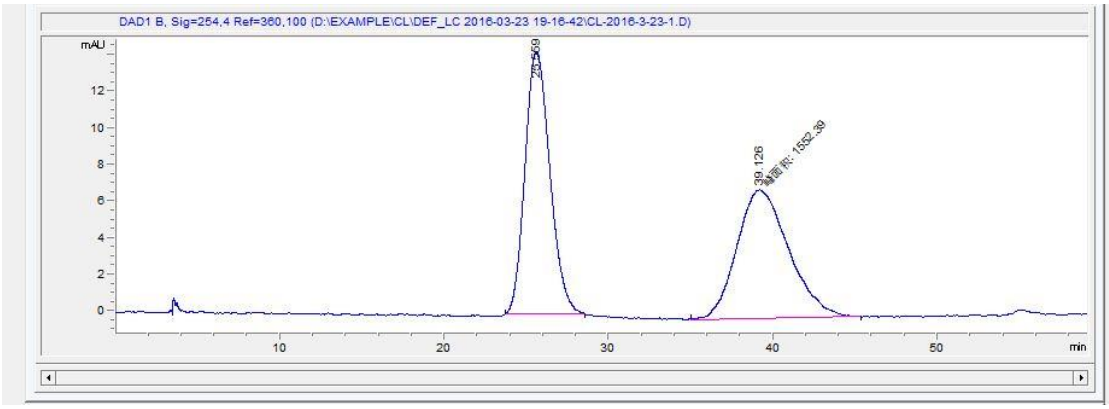
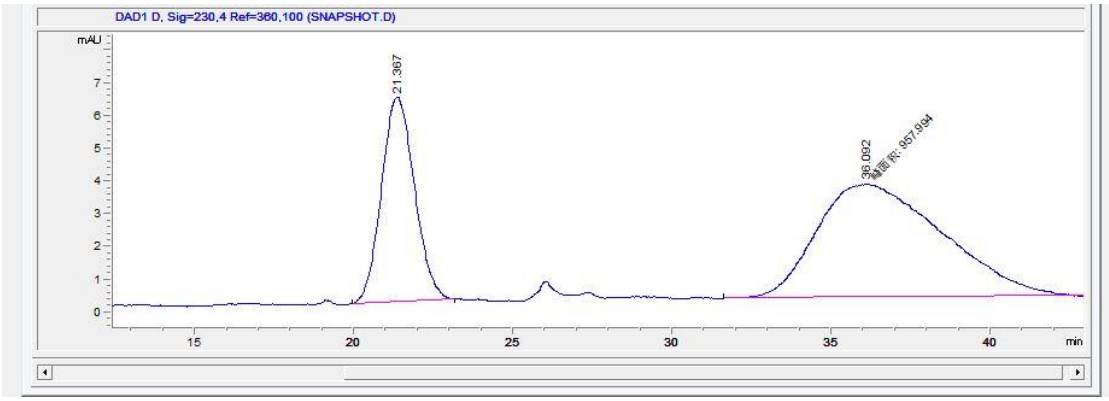
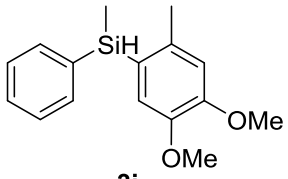


#	Time	Area	Height	Width	Symmetry	Area%
1	25.559	1516.4	14.3	1.2465	0.776	49.414
2	39.126	1552.4	7	3.6794	0.715	50.587



#	Time	Area	Height	Width	Symmetry	Area%
1	21.367	450.3	6.2	0.8551	0.944	31.967
2	36.092	958	3.5	4.6014	0.641	68.024



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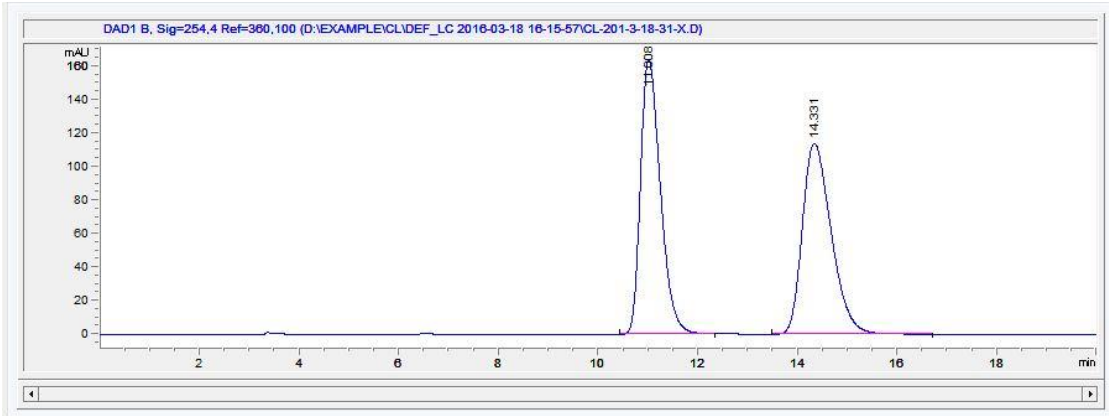
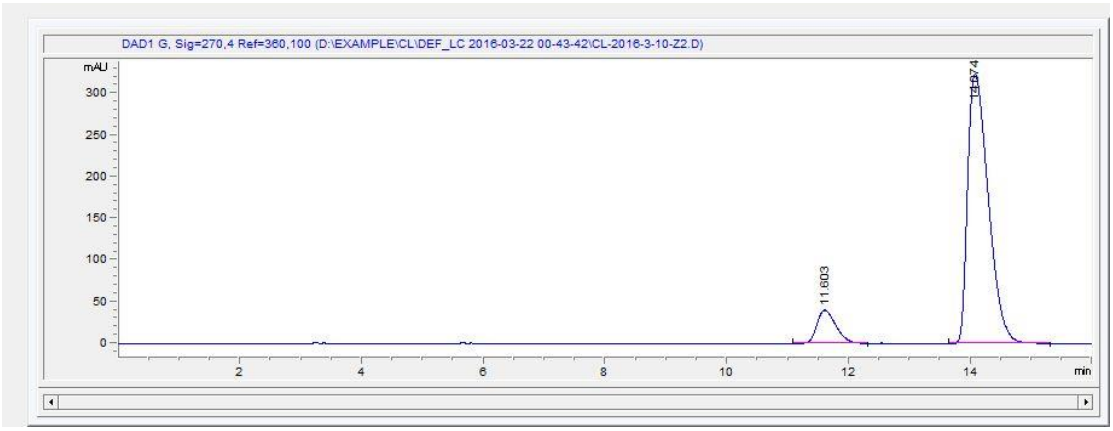
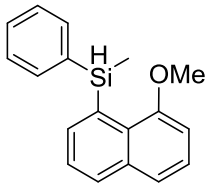


#	Time	Area	Height	Width	Symmetry	Area%
1	11.088	4551.1	164	0.4278	0.650	49.760
2	14.331	14595	114	0,6241	0.666	50.240



#	Time	Area	Height	Width	Symmetry	Area%
1	11.603	869.3	39.9	0.3359	0.678	10.169
2	14.074	7679.9	4323.4	40.3731	0.532	89.831



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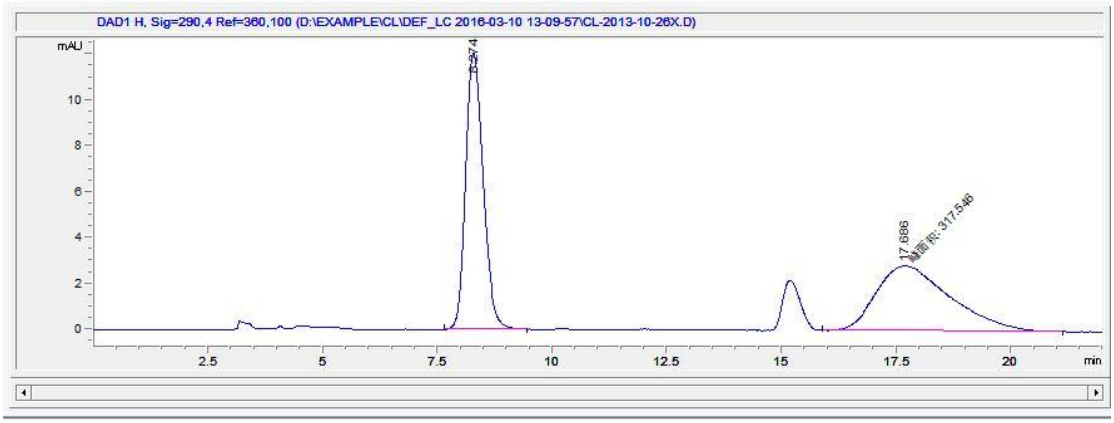
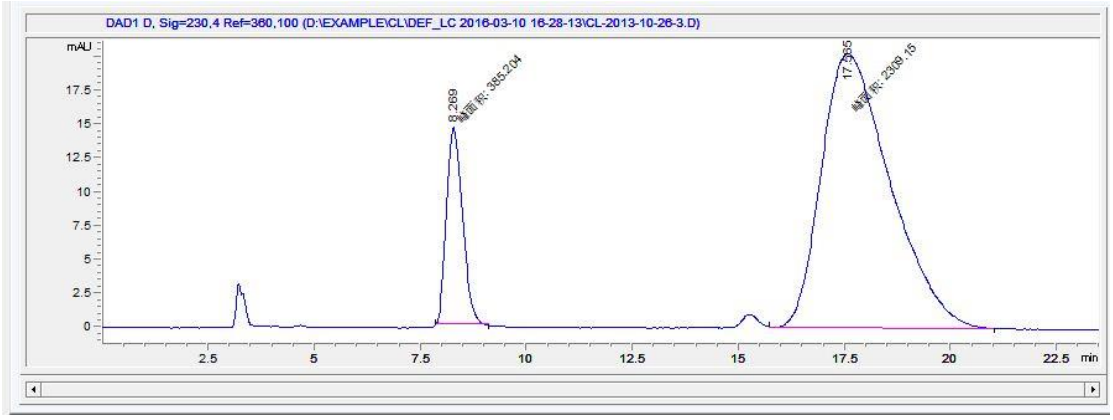
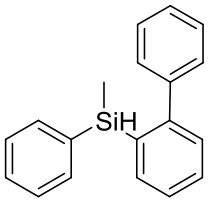


#	Time	Area	Height	Width	Symmetry	Area%
1	8.274	317.7	12	0.4056	0.751	50.012
2	17.686	317.5	2.8	1.873	0.609	49.988



#	Time	Area	Height	Width	Symmetry	Area%
1	8.269	385.2	14.6	0.4396	0.769	14.297
2	17.565	2309.2	20.3	1.8948	0.606	85.703



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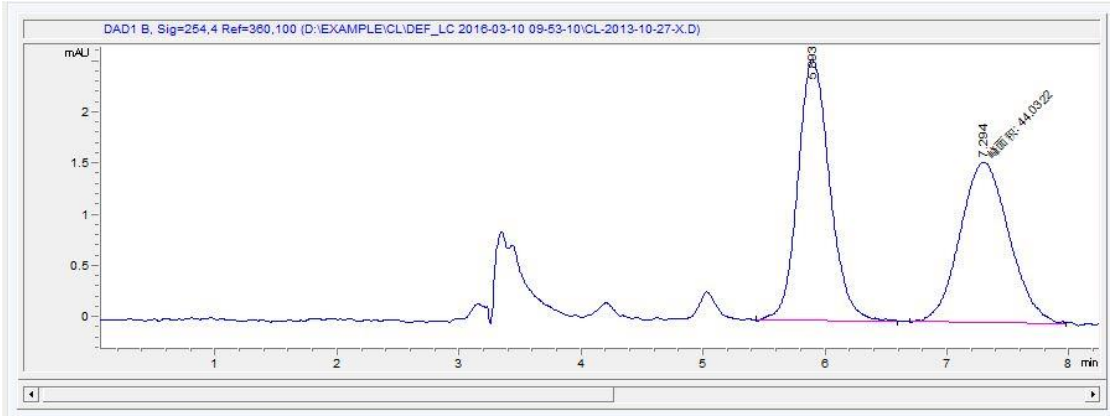
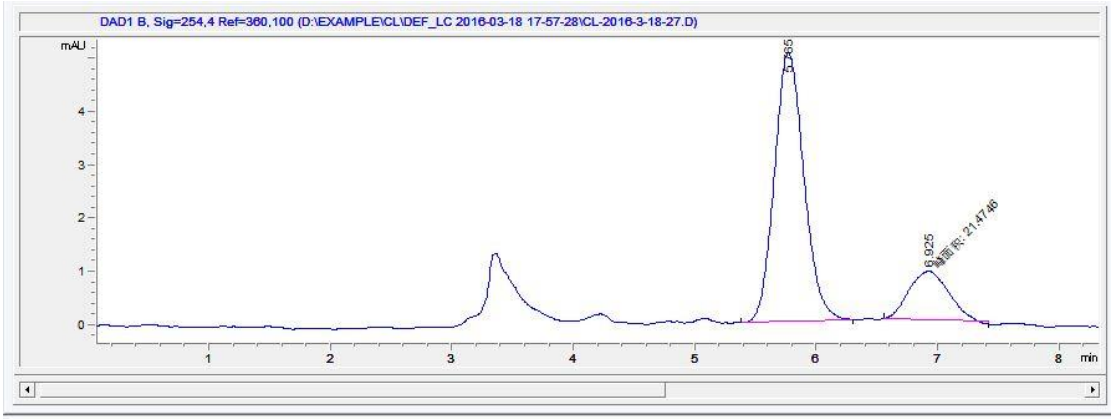
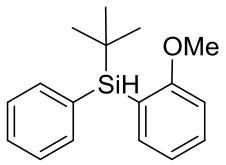


#	Time	Area	Height	Width	Symmetry	Area%
1	5.893	46.6	2.6	0.2792	0.841	51.413
2	7.294	44	1.6	0.4673	0.881	48.569



#	Time	Area	Height	Width	Symmetry	Area%
1	5.865	85.3	5	0.2635	0.844	79.894
2	6.925	21.5	0.93	0.3855	0.992	20.106



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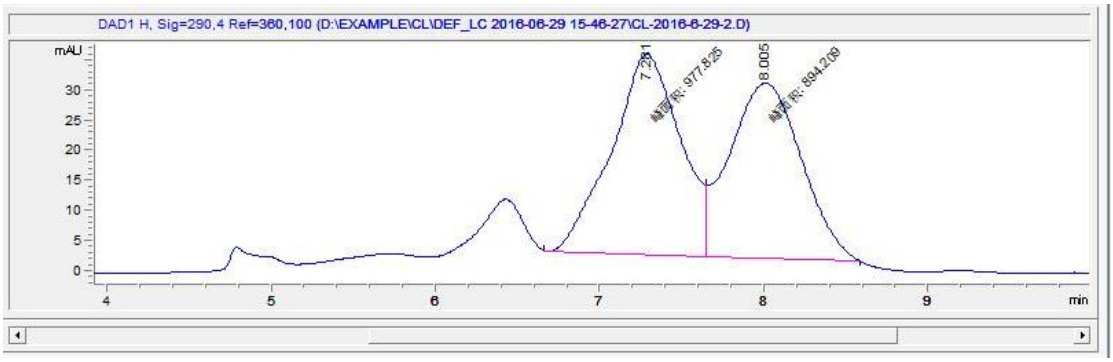
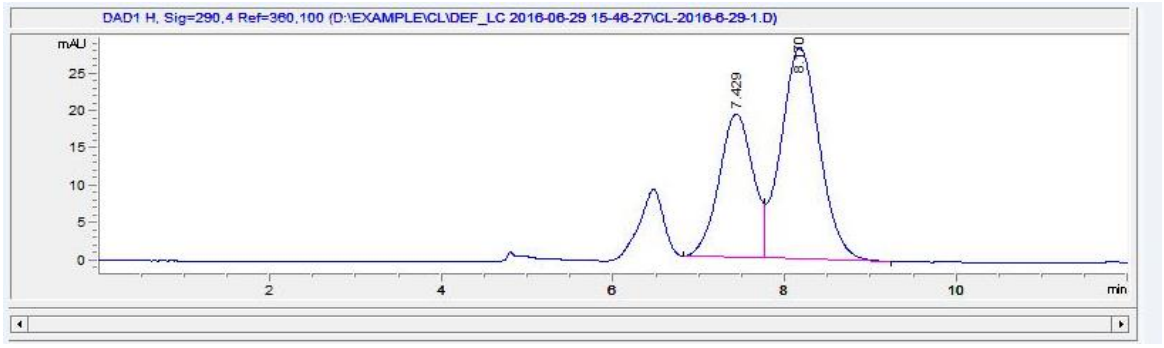


#	Time	Area	Height	Width	Symmetry	Area%
1	7.281	977.8	33.4	0.4882	1.005	52.223
2	8.005	894.2	29.2	0.5102	0.947	47.767



#	Time	Area	Height	Width	Symmetry	Area%
1	7.429	536	19.2	0.4231	0.999	37.744
2	8.17	884.1	28.4	0.4731	0.891	62.256