

Supporting Information

Enantioselective Construction of Six- and Seven-Membered Triorgano-Substituted Silicon-Stereogenic Heterocycles

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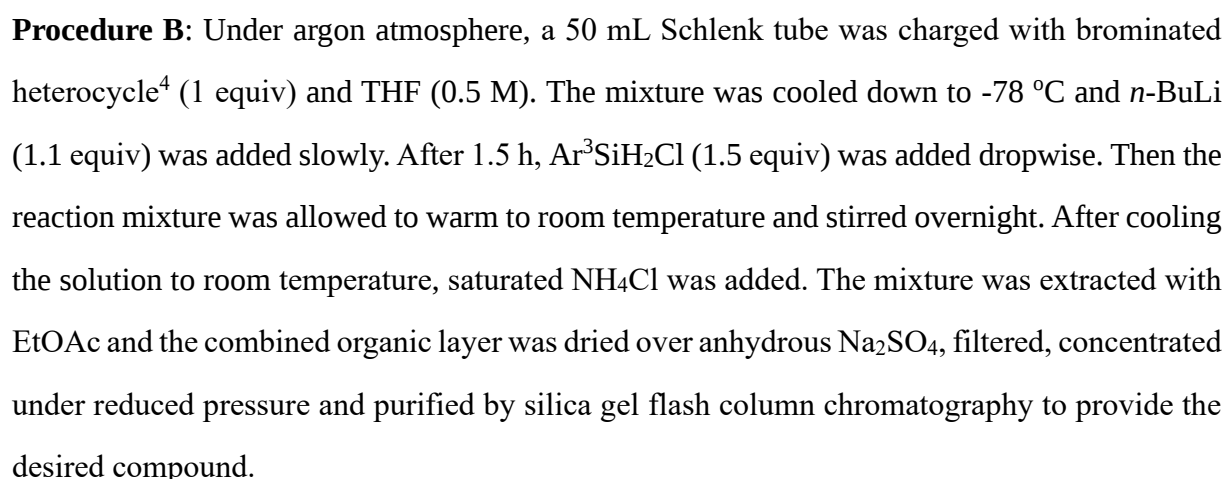
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I. General Information

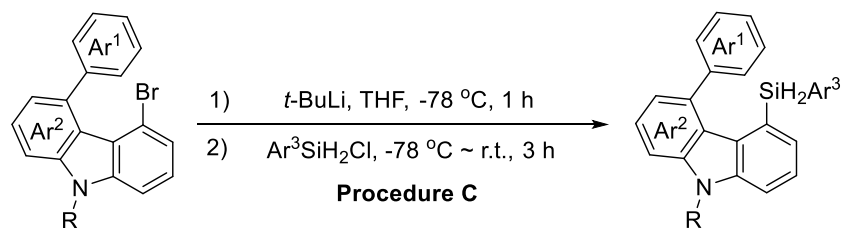
Regular reactions were carried out under argon atmosphere with magnetic stirring. Catalysis reactions were performed in colorless 5 mL microwave reaction tube under an inert atmosphere of argon. Anhydrous solvents were obtained from Inert Pure Solv solvent purification system or purchased from Energy Chemical. TLC were performed on silica gel Huanghai HSGF254 plates and visualization of the developed chromatogram was performed by fluorescence quenching ($\lambda_{\text{max}} = 254 \text{ nm}$). Column chromatography was performed using GENERAL-REAGENT silica gel (200-300 mesh). Unless otherwise noted, all reagents were obtained from commercial suppliers (Bide Pharmatech, Aladdin, Energy Chemical, Adamas, and TCI) and used without further purification.

NMR spectra were obtained on Bruker DPX 400 (400 MHz) or Bruker DPX 600 (600 MHz) instruments. The ^1H NMR (400 or 600 MHz) chemical shifts were measured relative to CDCl_3 as the internal reference (CDCl_3 : δ 7.26 ppm). The ^{13}C NMR (100 or 150 MHz) chemical shifts were given using CDCl_3 as the internal standard (CDCl_3 : δ 77.0 ppm). High resolution mass spectra (HRMS) were obtained with an Agilent Technologies 6230 TOF LC/MS or Waters Premier GC-TOF MS by electrospray ionization (ESI) or electron impact ionization (EI). X-Ray single-crystal diffraction data were collected on Bruker D8 VENTURE. Absorption spectra were measured with a UV-Vis spectrophotometer (Shimadzu, UV3600). Emission spectra were measured with a Shimadzu RF-6000 spectrometer. Circular polarized luminescence (CPL) spectra were measured on a JASCO CPL-300 spectrometer. Circular dichroism (CD) spectra were measured on an APPLIED PHOTOPHYSICS Chirascan CD Spectrometer. Chiral HPLC chromatograms were obtained from an Agilent 1260 system. Optical rotation was measured on Rudolph Automatic Polarmeter at concentrations of 0.1 g/100 mL in CHCl_3 .

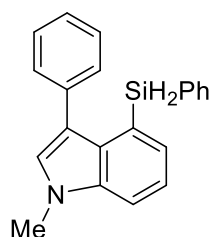
1. Indole Dihydrosilane Substrates^{1,2,3}



2. Carbazole Dihydrosilane Substrates^{1,7}

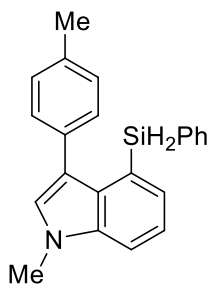


Procedure C: Under argon atmosphere, a 50 mL Schlenk tube was charged with brominated heterocycle⁸ (1 equiv) and THF (0.1 M). The mixture was cooled down to -78 °C and *t*-BuLi (2.2 equiv) was added slowly. After 1 h, Ar³SiH₂Cl (1.5 equiv) was added dropwise. Then the reaction mixture was allowed to warm to room temperature and stirred for additional 3 h. Then, saturated NH₄Cl was added. The mixture was extracted with EtOAc and the combined organic layer was dried over anhydrous Na₂SO₄, filtered, concentrated under reduced pressure and purified by silica gel flash column chromatography to provide the desired compound.



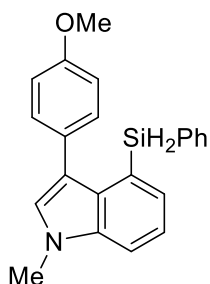
1-Methyl-3-phenyl-4-(phenylsilyl)-1H-indole (**1a**)

The reaction was performed at 3 mmol scale according to procedure A. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 40/1, v/v) afforded the product **1a** as a white solid (526 mg, 56% yield). ¹H NMR (400 MHz, CDCl₃): δ = 7.47 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.36 (dd, *J* = 6.9, 1.0 Hz, 1H), 7.32 – 7.25 (m, 6H), 7.25 – 7.18 (m, 5H), 7.04 (s, 1H), 4.64 (s, 2H), 3.84 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 136.0, 135.8, 135.5, 132.7, 131.7, 131.0, 131.0, 129.1, 128.1, 127.8, 127.6, 126.7, 123.0, 121.2, 119.4, 111.7, 32.8 ppm. HRMS (ESI): calcd for C₂₁H₂₀NSi [M+H]⁺ 314.1360, found 314.1357.



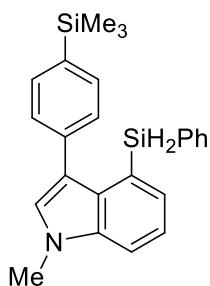
1-Methyl-4-(phenylsilyl)-3-(*p*-tolyl)-1*H*-indole (**1b**)

The reaction was performed at 3.7 mmol scale according to procedure A. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 40/1, v/v) afforded the product **1b** as a white solid (556 mg, 46% yield). ^1H NMR (400 MHz, CDCl_3): δ = 7.45 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 6.9 Hz, 1H), 7.31 – 7.17 (m, 6H), 7.15 (d, J = 7.9 Hz, 2H), 7.04 (d, J = 7.8 Hz, 2H), 7.01 (s, 1H), 4.65 (s, 2H), 3.82 (s, 3H), 2.38 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 136.4, 135.8, 135.5, 132.9, 132.8, 131.8, 130.9, 130.8, 129.1, 128.5, 128.1, 127.5, 123.0, 121.1, 119.3, 111.6, 32.7, 21.2 ppm. HRMS (ESI): calcd for $\text{C}_{22}\text{H}_{22}\text{NSi}$ $[\text{M}+\text{H}]^+$ 328.1516, found 328.1513.



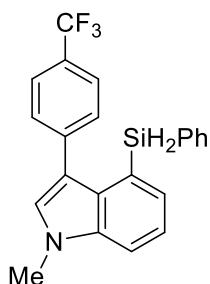
3-(4-Methoxyphenyl)-1-methyl-4-(phenylsilyl)-1*H*-indole (**1c**)

The reaction was performed at 3.6 mmol scale according to procedure A. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 80/1, v/v) afforded the product **1c** as a white solid (501 mg, 40% yield). ^1H NMR (400 MHz, CDCl_3): δ = 7.46 (d, J = 8.2 Hz, 1H), 7.39 – 7.32 (m, 1H), 7.32 – 7.25 (m, 3H), 7.25 – 7.18 (m, 3H), 7.15 (dd, J = 8.5, 2.0 Hz, 2H), 7.00 (s, 1H), 6.77 (dd, J = 8.5, 1.9 Hz, 2H), 4.64 (d, J = 2.6 Hz, 2H), 3.88 – 3.80 (m, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 158.8, 135.7, 135.4, 132.8, 132.1, 132.0, 130.8, 129.1, 128.1, 128.1, 127.5, 122.9, 121.1, 118.9, 113.2, 111.6, 55.3, 32.7 ppm. HRMS (ESI): calcd for $\text{C}_{22}\text{H}_{22}\text{NOSi}$ $[\text{M}+\text{H}]^+$ 344.1465, found 344.1462.



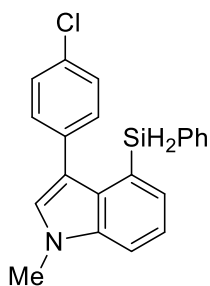
1-Methyl-4-(phenylsilyl)-3-(4-(trimethylsilyl)phenyl)-1H-indole (1d)

The reaction was performed at 1.7 mmol scale according to procedure A. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 40/1, v/v) afforded the product **1d** as a pale yellow oil (332 mg, 50% yield). ^1H NMR (400 MHz, CDCl_3): δ = 7.47 (d, J = 8.2 Hz, 1H), 7.41 (dd, J = 6.9, 0.9 Hz, 1H), 7.36 (d, J = 7.9 Hz, 2H), 7.30 – 7.25 (m, 2H), 7.21 (d, J = 7.9 Hz, 2H), 7.19 – 7.11 (m, 4H), 7.02 (s, 1H), 4.68 (s, 2H), 3.83 (s, 3H), 0.31 (s, 9H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 138.2, 136.3, 135.9, 135.3, 132.8, 132.8, 131.6, 131.2, 130.2, 129.0, 128.1, 127.5, 123.0, 121.2, 119.5, 111.7, 32.8, -1.0 ppm. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{28}\text{NSi}_2$ $[\text{M}+\text{H}]^+$ 386.1755, found 386.1749.



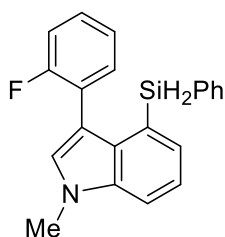
1-Methyl-4-(phenylsilyl)-3-(4-(trifluoromethyl)phenyl)-1H-indole (1e)

The reaction was performed at 1.5 mmol scale according to procedure A. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 80/1, v/v) afforded the product **1e** as a white solid (184 mg, 32% yield). ^1H NMR (400 MHz, CDCl_3): δ = 7.50 (dd, J = 8.3, 0.9 Hz, 1H), 7.47 (dd, J = 7.0, 1.0 Hz, 1H), 7.41 (d, J = 8.0 Hz, 2H), 7.34 – 7.24 (m, 4H), 7.15 (t, J = 7.6 Hz, 2H), 7.09 (dd, J = 8.0, 1.4 Hz, 2H), 7.03 (s, 1H), 4.71 (s, 2H), 3.85 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 139.9, 136.0, 135.1, 132.1, 131.7, 131.2, 130.8, 129.2, 128.6 (q, $J_{\text{C-F}}$ = 32.1 Hz), 128.4, 127.6, 124.6 (q, $J_{\text{C-F}}$ = 3.7 Hz), 124.5 (q, $J_{\text{C-F}}$ = 270.2 Hz), 122.7, 121.6, 118.1, 112.0, 32.9 ppm. ^{19}F NMR (565 MHz, CDCl_3): δ = -62.32 ppm. HRMS (ESI): calcd for $\text{C}_{22}\text{H}_{19}\text{F}_3\text{NSi}$ $[\text{M}+\text{H}]^+$ 382.1233, found 382.1229.



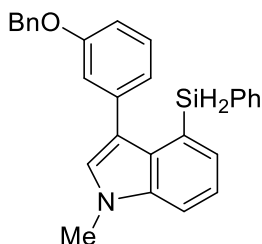
3-(4-Chlorophenyl)-1-methyl-4-(phenylsilyl)-1H-indole (**1f**)

The reaction was performed at 1.4 mmol scale according to procedure B. Purification via silica gel column chromatography (petroleum ether) afforded the product **1f** as a white solid (208 mg, 43% yield). ^1H NMR (400 MHz, CDCl_3): δ = 7.47 (dd, J = 8.2, 0.9 Hz, 1H), 7.41 (dd, J = 7.0, 1.0 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.23 – 7.17 (m, 4H), 7.16 – 7.09 (m, 4H), 7.00 (s, 1H), 4.69 (s, 2H), 3.83 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 135.9, 135.3, 134.4, 132.7, 132.3, 132.1, 131.5, 131.3, 129.2, 128.2, 127.8, 127.6, 122.8, 121.4, 118.1, 111.8, 32.8 ppm. HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{19}\text{ClNSi}$ $[\text{M}+\text{H}]^+$ 348.0970, found 348.0967.



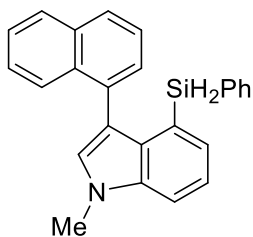
3-(2-Fluorophenyl)-1-methyl-4-(phenylsilyl)-1H-indole (**1g**)

The reaction was performed at 3.3 mmol scale according to procedure A. Purification via silica gel column chromatography (petroleum ether/ethyl acetate = 100/1, v/v) afforded the product **1g** as a pale yellow oil (624 mg, 57% yield). ^1H NMR (600 MHz, CDCl_3): δ = 7.47 (d, J = 8.2 Hz, 1H), 7.36 (d, J = 6.9 Hz, 1H), 7.30 – 7.22 (m, 3H), 7.22 – 7.16 (m, 5H), 7.07 (s, 1H), 7.02 – 6.93 (m, 2H), 4.65 (s, 2H), 3.83 (s, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 161.2 (d, $J_{\text{C-F}}$ = 243.5 Hz), 135.9, 135.4, 133.9 (d, $J_{\text{C-F}}$ = 2.4 Hz), 132.3, 132.0, 130.9, 129.1, 128.9, 128.9, 127.5, 123.6 (d, $J_{\text{C-F}}$ = 16.5 Hz), 123.3 (d, $J_{\text{C-F}}$ = 3.5 Hz), 122.9, 121.3, 115.2 (d, $J_{\text{C-F}}$ = 22.4 Hz), 111.8, 111.4, 32.9 ppm. ^{19}F NMR (565 MHz, CDCl_3): δ = -113.21 ppm. HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{19}\text{FNSi}$ $[\text{M}+\text{H}]^+$ 332.1265, found 332.1262.



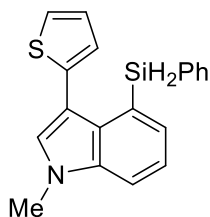
3-(3-(Benzyloxy)phenyl)-1-methyl-4-(phenylsilyl)-1H-indole (**1h**)

The reaction was performed at 2.0 mmol scale according to procedure A. Purification via silica gel column chromatography (petroleum ether/ethyl acetate =40/1, v/v) afforded the product **1h** as a white solid (433 mg, 52% yield). ^1H NMR (400 MHz, CDCl_3): δ = 7.47 (d, J = 8.2 Hz, 1H), 7.44 – 7.34 (m, 5H), 7.34 – 7.24 (m, 4H), 7.24 – 7.13 (m, 4H), 7.03 (s, 1H), 6.90 (t, J = 9.5 Hz, 2H), 6.85 (s, 1H), 4.88 (s, 2H), 4.69 (d, J = 1.6 Hz, 2H), 3.83 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 158.3, 137.4, 137.2, 135.8, 135.4, 132.7, 131.6, 131.1, 129.0, 128.8, 128.5, 128.1, 127.8, 127.6, 127.5, 123.9, 122.9, 121.3, 119.3, 116.7, 113.9, 111.7, 69.6, 32.8 ppm. HRMS (ESI): calcd for $\text{C}_{28}\text{H}_{26}\text{NOSi}$ $[\text{M}+\text{H}]^+$ 420.1778, found 420.1772.



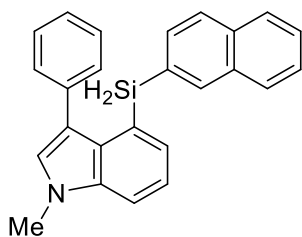
1-Methyl-3-(naphthalen-1-yl)-4-(phenylsilyl)-1H-indole (**1i**)

The reaction was performed at 3.3 mmol scale according to procedure A. Purification via silica gel column chromatography (petroleum ether/ethyl acetate =80/1, v/v) afforded the product **1i** as a white solid (740 mg, 62% yield). ^1H NMR (400 MHz, CDCl_3): δ = 7.84 – 7.77 (m, 2H), 7.61 (d, J = 8.5 Hz, 1H), 7.47 (dd, J = 8.1, 1.1 Hz, 1H), 7.39 – 7.34 (m, 1H), 7.33 – 7.23 (m, 4H), 7.22 – 7.17 (m, 1H), 7.15 – 7.09 (m, 1H), 7.05 (s, 1H), 7.05 – 6.97 (m, 4H), 4.22 – 4.09 (m, 2H), 3.80 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 135.8, 135.1, 134.5, 133.4, 133.4, 133.0, 132.4, 130.6, 129.7, 129.1, 128.8, 127.8, 127.6, 127.3, 126.9, 125.6, 125.5, 125.1, 123.4, 121.3, 116.1, 111.6, 32.8 ppm. HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{22}\text{NSi}$ $[\text{M}+\text{H}]^+$ 364.1516, found 364.1513.



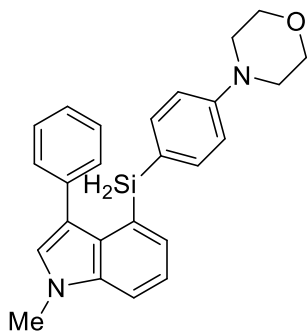
1-Methyl-4-(phenylsilyl)-3-(thiophen-2-yl)-1H-indole (**1j**)

The reaction was performed at 2.0 mmol scale according to procedure A. Purification via silica gel column chromatography (petroleum ether/ethyl acetate =80/1, v/v) afforded the product **1j** as a brown oil (224 mg, 35% yield). ^1H NMR (600 MHz, CDCl_3): δ = 7.46 (d, J = 8.2 Hz, 1H), 7.35 – 7.31 (m, 4H), 7.28 – 7.25 (m, 4H), 7.15 (s, 1H), 7.00 – 6.98 (m, 1H), 6.86 (d, J = 2.7 Hz, 1H), 4.65 (s, 2H), 3.83 (s, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 136.3, 135.7, 135.5, 132.8, 132.6, 131.1, 129.7, 129.1, 129.1, 127.6, 126.9, 125.6, 123.2, 121.5, 111.7, 110.3, 32.9 ppm. HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{18}\text{NSSi}$ $[\text{M}+\text{H}]^+$ 320.0924, found 320.0921.



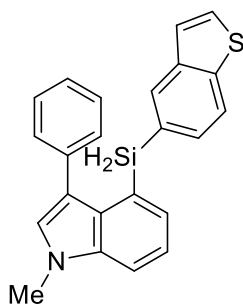
1-Methyl-4-(naphthalen-2-ylsilyl)-3-phenyl-1H-indole (**1k**)

The reaction was performed at 2.5 mmol scale according to procedure A. Purification via silica gel column chromatography (petroleum ether/ethyl acetate =40/1, v/v) afforded the product **1k** as a colorless oil (618 mg, 68% yield). ^1H NMR (600 MHz, CDCl_3): δ = 7.75 (d, J = 7.7 Hz, 1H), 7.72 (s, 1H), 7.69 (d, J = 7.7 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.47 – 7.40 (m, 4H), 7.30 – 7.24 (m, 5H), 7.20 – 7.17 (m, 2H), 7.01 (s, 1H), 4.78 (s, 2H), 3.80 (s, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 136.5, 136.0, 135.9, 133.7, 132.8, 131.7, 131.3, 131.1, 131.0, 130.3, 128.2, 128.1, 127.8, 127.6, 126.8, 126.7, 126.3, 125.7, 122.9, 121.2, 119.4, 111.7, 32.8 ppm. HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{22}\text{NSi}$ $[\text{M}+\text{H}]^+$ 364.1516, found 364.1510.



4-(4-((1-Methyl-3-phenyl-1H-indol-4-yl)silyl)phenyl)morpholine (**1l**)

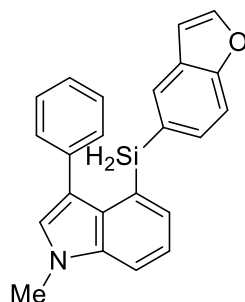
The reaction was performed at 1.0 mmol scale according to procedure A. Purification via silica gel column chromatography (petroleum ether/ethyl acetate =20/1, v/v) afforded the product **1l** as a white solid (251 mg, 63% yield). ^1H NMR (600 MHz, CDCl_3): δ = 7.43 (d, J = 8.1 Hz, 1H), 7.33 – 7.23 (m, 7H), 7.18 (d, J = 8.5 Hz, 2H), 7.03 (s, 1H), 6.77 (d, J = 8.5 Hz, 2H), 4.59 (s, 2H), 3.84 – 3.82 (m, 4H), 3.81 (s, 3H), 3.15 – 3.13 (m, 4H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 151.8, 136.7, 136.2, 135.8, 131.6, 131.0, 130.7, 128.1, 127.8, 126.7, 123.8, 121.9, 121.2, 119.5, 114.7, 111.4, 66.8, 48.7, 32.7 ppm. HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{27}\text{N}_2\text{OSi}$ $[\text{M}+\text{H}]^+$ 399.1887, found 399.1884.



4-(Benzo[*b*]thiophen-5-ylsilyl)-1-methyl-3-phenyl-1H-indole (**1m**)

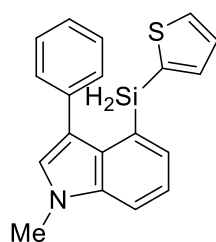
The reaction was performed at 2.5 mmol scale according to procedure A. Purification via silica gel column chromatography (petroleum ether/ethyl acetate =80/1, v/v) afforded the product **1m** as an orange solid (240 mg, 26% yield). ^1H NMR (600 MHz, CDCl_3): δ = 7.53 (d, J = 2.1 Hz, 1H), 7.44 (t, J = 4.0 Hz, 2H), 7.38 (d, J = 6.7 Hz, 1H), 7.34 (d, J = 8.2 Hz, 1H), 7.27 – 7.23 (m, 4H), 7.21 – 7.18 (m, 2H), 7.14 (d, J = 8.2 Hz, 1H), 6.99 (s, 1H), 6.62 (d, J = 1.5 Hz, 1H), 4.74 (s, 2H), 3.78 (s, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 155.8, 144.6, 136.0, 135.9, 131.6, 131.2, 131.0, 128.9, 128.2, 127.7, 127.1, 126.7, 126.0, 123.5, 121.2, 119.4, 111.7, 110.8, 106.3,

32.7 ppm. HRMS (ESI): calcd for $C_{23}H_{20}NSSi$ $[M+H]^+$ 370.1080, found 370.1077.



4-(Benzofuran-5-ylsilyl)-1-methyl-3-phenyl-1H-indole (1n)

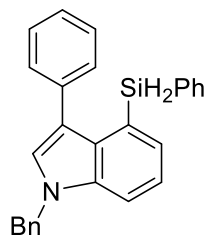
The reaction was performed at 2.5 mmol scale according to procedure A. Purification via silica gel column chromatography (petroleum ether/ethyl acetate =80/1, v/v) afforded the product **1n** as an orange solid (274 mg, 31% yield). 1H NMR (600 MHz, $CDCl_3$): δ = 7.56 (d, J = 2.1 Hz, 1H), 7.47 (d, J = 8.2 Hz, 1H), 7.45 (s, 1H), 7.38 (d, J = 6.9 Hz, 1H), 7.35 (d, J = 8.2 Hz, 1H), 7.29 – 7.23 (m, 4H), 7.21 – 7.19 (m, 2H), 7.14 (d, J = 8.2 Hz, 1H), 7.02 (s, 1H), 6.65 (d, J = 2.0 Hz, 1H), 4.73 (s, 2H), 3.83 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 155.8, 144.6, 136.1, 135.9, 131.6, 131.2, 131.0, 131.0, 129.0, 128.2, 127.7, 127.1, 126.7, 126.1, 123.5, 121.2, 119.4, 111.7, 110.8, 106.4, 32.8 ppm. HRMS (ESI): calcd for $C_{23}H_{20}NOSi$ $[M+H]^+$ 354.1309, found 354.1304.



4-(Thiophen-2-ylsilyl)-1-methyl-3-phenyl-1H-indole (1o)

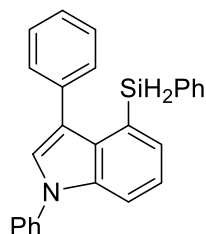
The reaction was performed at 2.5 mmol scale according to procedure A. Purification via silica gel column chromatography (petroleum ether/ethyl acetate =80/1, v/v) afforded the product **1o** as a pale yellow solid (176 mg, 22% yield). 1H NMR (600 MHz, $CDCl_3$): δ = 7.57 (d, J = 4.5 Hz, 1H), 7.47 (d, J = 8.2 Hz, 1H), 7.37 – 7.31 (m, 6H), 7.26 (d, J = 7.4 Hz, 1H), 7.10 – 7.08 (m, 2H), 7.06 (s, 1H), 4.72 (s, 2H), 3.84 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 137.5, 136.1, 135.8, 131.9, 131.6, 130.9, 130.5, 128.2, 128.1, 127.9, 126.9, 122.6, 121.3, 119.3, 111.8,

32.8 ppm. HRMS (ESI): calcd for $C_{19}H_{18}NSSi$ $[M+H]^+$ 320.0924, found 320.0921.



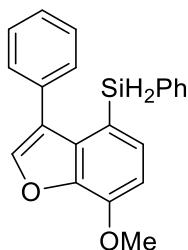
1-Benzyl-3-phenyl-4-(phenylsilyl)-1*H*-indole (**1p**)

The reaction was performed at 2.6 mmol scale according to procedure A. Purification via silica gel column chromatography (petroleum ether) afforded the product **1p** as a white solid (428 mg, 42% yield). 1H NMR (400 MHz, $CDCl_3$): δ = 7.43 (dd, J = 8.3, 0.9 Hz, 1H), 7.36 – 7.14 (m, 17H), 7.11 (s, 1H), 5.35 (s, 2H), 4.64 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.1, 136.0, 135.5, 135.5, 132.7, 132.0, 131.2, 131.0, 129.1, 128.8, 127.8, 127.7, 127.6, 127.5, 127.0, 126.8, 123.2, 121.4, 120.0, 112.1, 50.1 ppm. HRMS (ESI): calcd for $C_{27}H_{24}NSi$ $[M+H]^+$ 390.1673, found 390.1668.



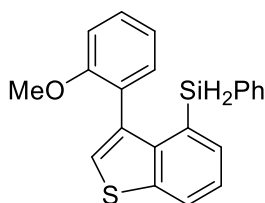
1,3-Diphenyl-4-(phenylsilyl)-1*H*-indole (**1q**)

The reaction was performed at 1.3 mmol scale according to procedure A. Purification via silica gel column chromatography (petroleum ether) afforded the product **1q** as a white solid (243 mg, 50% yield). 1H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, J = 8.3 Hz, 1H), 7.57 – 7.48 (m, 4H), 7.43 – 7.20 (m, 14H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.4, 135.5, 135.5, 135.2, 132.6, 132.6, 131.9, 131.0, 129.7, 129.2, 127.9, 127.6, 127.2, 127.1, 126.8, 124.7, 123.4, 122.0, 121.6, 112.9 ppm. HRMS (ESI): calcd for $C_{26}H_{22}NSi$ $[M+H]^+$ 376.1516, found 376.1515.



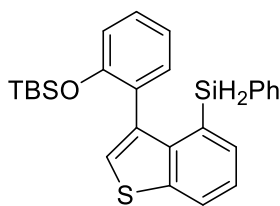
(7-Methoxy-3-phenylbenzofuran-4-yl)(phenyl)silane (1r)

The reaction was performed at 1.0 mmol scale according to procedure A. Purification via silica gel column chromatography (petroleum ether/ethyl acetate =80/1, v/v) afforded the product **1r** as a white solid (220 mg, 67% yield). ^1H NMR (400 MHz, CDCl_3): δ = 7.59 (s, 1H), 7.40 (d, J = 7.9 Hz, 1H), 7.37 – 7.16 (m, 10H), 6.85 (d, J = 7.9 Hz, 1H), 4.59 (s, 2H), 4.05 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 147.5, 144.2, 142.6, 135.3, 134.9, 134.1, 132.2, 131.8, 130.5, 129.3, 128.1, 127.9, 127.7, 124.8, 115.1, 106.2, 56.0 ppm. HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{19}\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 331.1149, found 331.1146.



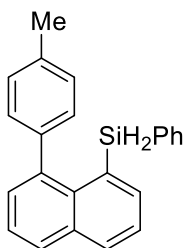
(3-(2-Methoxyphenyl)benzo[b]thiophen-4-yl)(phenyl)silane (1s)

The reaction was performed at 3.1 mmol scale according to procedure A. Purification via silica gel column chromatography (petroleum ether/ethyl acetate =80/1, v/v) afforded the product **1s** as a colorless viscous oil (717 mg, 67% yield). ^1H NMR (400 MHz, CDCl_3): δ = 7.99 (dd, J = 8.1, 1.1 Hz, 1H), 7.50 (dd, J = 7.0, 1.1 Hz, 1H), 7.41 – 7.27 (m, 4H), 7.26 – 7.22 (m, 4H), 7.10 (dd, J = 7.4, 1.8 Hz, 1H), 6.85 (td, J = 7.4, 1.0 Hz, 1H), 6.79 (d, J = 8.3 Hz, 1H), 4.39 – 4.31 (m, 2H), 3.48 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 158.3, 143.4, 140.3, 136.5, 135.7, 135.5, 133.0, 132.5, 129.8, 129.2, 127.6, 126.8, 125.6, 125.5, 125.1, 123.2, 120.0, 110.5, 54.9 ppm. HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{19}\text{OSSi}$ $[\text{M}+\text{H}]^+$ 347.0920, found 347.0918.



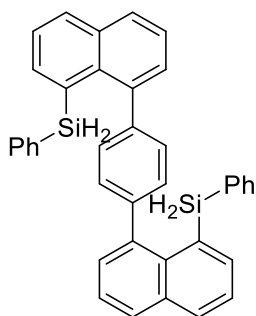
***tert*-Butyldimethyl(2-(4-(phenylsilyl)benzo[*b*]thiophen-3-yl)phenoxy)silane (**1t**)**

The reaction was performed at 1.6 mmol scale according to procedure A. Purification via silica gel column chromatography (petroleum ether/ethyl acetate =80/1, v/v) afforded the product **1t** as a colorless oil (350 mg, 45% yield). ^1H NMR (400 MHz, CDCl_3): δ = 7.95 (dd, J = 8.1, 1.1 Hz, 1H), 7.44 (dd, J = 7.1, 1.1 Hz, 1H), 7.35 – 7.22 (m, 8H), 7.12 – 7.07 (m, 1H), 6.87 – 6.80 (m, 2H), 4.54 – 4.30 (m, 2H), 0.50 (s, 9H), 0.04 (s, 3H), -0.10 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 154.8, 143.5, 140.1, 137.2, 135.6, 135.3, 132.9, 132.7, 129.5, 129.3, 128.7, 127.7, 127.2, 125.4, 124.8, 123.1, 120.8, 119.1, 25.0, 17.6, -4.2, -4.8 ppm. HRMS (ESI): calcd for $\text{C}_{26}\text{H}_{31}\text{OSSi}_2$ $[\text{M}+\text{H}]^+$ 447.1629, found 447.1627.



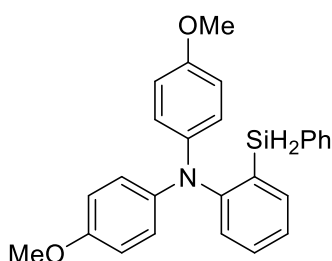
Phenyl(8-(*p*-tolyl)naphthalen-1-yl)silane (1u**)**

The reaction was performed at 3.4 mmol scale according to literature^{1,2,9}. Purification via silica gel column chromatography (petroleum ether) afforded the product **1u** as a white solid (648 mg, 64% yield). ^1H NMR (600 MHz, CDCl_3): δ = 7.96 (d, J = 8.1 Hz, 1H), 7.87 (dd, J = 8.1, 1.1 Hz, 1H), 7.72 (dd, J = 6.8, 1.2 Hz, 1H), 7.49 (t, J = 7.8 Hz, 1H), 7.41 (t, J = 7.8 Hz, 1H), 7.36 (dd, J = 7.0, 1.3 Hz, 1H), 7.33 – 7.29 (m, 1H), 7.26 – 7.19 (m, 4H), 7.14 (d, J = 7.9 Hz, 2H), 7.09 (d, J = 7.7 Hz, 2H), 4.16 (s, 2H), 2.41 (s, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 142.0, 139.8, 139.5, 137.6, 136.6, 135.3, 134.7, 134.5, 131.3, 131.2, 129.9, 129.4, 129.1, 129.1, 128.7, 127.6, 124.9, 124.7, 21.3 ppm.



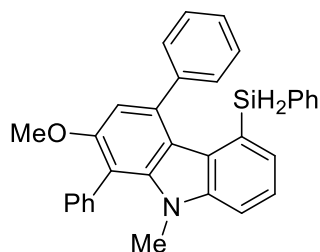
1,4-Bis(8-(phenylsilyl)naphthalen-1-yl)benzene (**1v**)

The reaction was performed at 1.0 mmol scale according to literature^{1,2,9}. Purification via silica gel column chromatography (petroleum ether) afforded the product **1v** as a white solid (266 mg, 49% yield). ¹H NMR (400 MHz, CDCl₃): δ = 8.04 (d, J = 8.0 Hz, 2H), 7.97 (d, J = 7.9 Hz, 2H), 7.82 (d, J = 6.5 Hz, 2H), 7.62 (t, J = 7.5 Hz, 2H), 7.54 (d, J = 6.8 Hz, 2H), 7.49 (t, J = 7.4 Hz, 2H), 7.33 – 7.27 (m, 10H), 7.20 (s, 4H), 4.34 (s, 4H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 142.2, 141.8, 140.0, 136.4, 135.2, 134.5, 131.5, 131.2, 129.8, 129.8, 129.2, 129.0, 127.7, 125.0, 124.8 ppm.



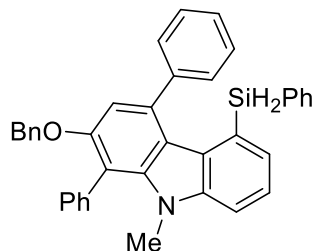
N,N-Bis(4-methoxyphenyl)-2-(phenylsilyl)aniline (**1w**)

The reaction was performed at 5.5 mmol scale according to literature^{1,2,10}. Purification via silica gel column chromatography (petroleum ether) afforded the product **1w** as a pale yellow solid (766 mg, 34% yield). ¹H NMR (400 MHz, CDCl₃): δ = 7.40 (dd, J = 7.3, 1.2 Hz, 1H), 7.34 (d, J = 6.6 Hz, 2H), 7.26 – 7.18 (m, 2H), 7.15 (t, J = 7.1 Hz, 2H), 6.98 (t, J = 7.3 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 6.67 (d, J = 9.0 Hz, 4H), 6.58 (d, J = 9.0 Hz, 4H), 4.39 (s, 2H), 3.60 (s, 6H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 154.7, 154.4, 142.4, 138.7, 135.6, 132.0, 131.7, 130.9, 129.4, 127.8, 127.7, 124.2, 124.2, 114.2, 55.3 ppm. HRMS (ESI): calcd for C₂₆H₂₆NO₂Si [M+H]⁺ 412.1727, found 412.1719.



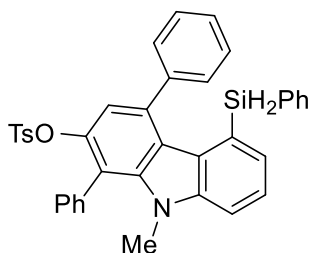
2-Methoxy-9-methyl-1,4-diphenyl-5-(phenylsilyl)-9H-carbazole (**3a**)

The reaction was performed at 3.0 mmol scale according to procedure C. Purification via silica gel column chromatography (petroleum ether/ethyl acetate =80/1, v/v) afforded the product **3a** as a white solid (985 mg, 70% yield). ^1H NMR (400 MHz, CDCl_3): δ = 7.64 – 7.58 (m, 2H), 7.51 – 7.46 (m, 4H), 7.45 – 7.40 (m, 3H), 7.40 – 7.34 (m, 1H), 7.32 – 7.18 (m, 7H), 7.05 (dd, J = 6.9, 1.0 Hz, 1H), 6.76 (s, 1H), 3.97 (s, 2H), 3.81 (s, 3H), 3.22 (s, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 155.7, 143.0, 142.3, 141.5, 137.8, 135.9, 135.7, 134.8, 131.6, 130.1, 129.9, 129.4, 129.0, 127.9, 127.7, 127.6, 127.3, 125.0, 123.8, 116.7, 112.2, 110.0, 107.5, 56.6, 32.6 ppm. HRMS (ESI): calcd for $\text{C}_{32}\text{H}_{28}\text{NOSi}$ $[\text{M}+\text{H}]^+$ 470.1935, found 470.1922.



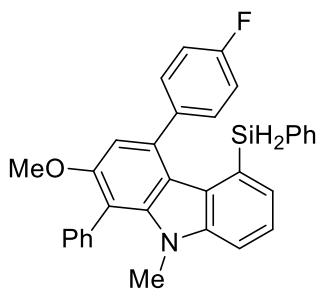
2-(Benzyloxy)-9-methyl-1,4-diphenyl-5-(phenylsilyl)-9H-carbazole (**3b**)

The reaction was performed at 1.0 mmol scale according to procedure C. Purification via silica gel column chromatography (petroleum ether/ethyl acetate =80/1, v/v) afforded the product **3b** as a white solid (283 mg, 52% yield). ^1H NMR (600 MHz, CDCl_3): δ = 7.58 (d, J = 7.3 Hz, 2H), 7.51 (d, J = 6.9 Hz, 2H), 7.48 (t, J = 7.4 Hz, 2H), 7.45 – 7.40 (m, 3H), 7.36 (t, J = 7.3 Hz, 1H), 7.32 – 7.24 (m, 6H), 7.23 – 7.19 (m, 4H), 7.12 (d, J = 7.1 Hz, 2H), 7.07 (d, J = 7.0 Hz, 1H), 6.83 (s, 1H), 5.08 (s, 2H), 3.97 (s, 2H), 3.27 (s, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 154.7, 142.9, 142.3, 141.4, 137.8, 137.5, 135.9, 135.7, 134.8, 131.6, 130.1, 130.0, 129.4, 129.0, 128.2, 127.9, 127.7, 127.60, 127.4, 127.3, 126.7, 125.1, 123.9, 117.1, 113.4, 110.0, 109.7, 71.3, 32.6 ppm. HRMS (ESI): calcd for $\text{C}_{38}\text{H}_{32}\text{NOSi}$ $[\text{M}+\text{H}]^+$ 546.2248, found 546.2249.



9-Methyl-1,4-diphenyl-5-(phenylsilyl)-9H-carbazol-2-yl 4-methylbenzenesulfonate (**3c**)

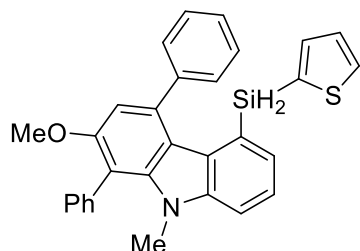
The reaction was performed at 1.0 mmol scale according to procedure C. Purification via silica gel column chromatography (petroleum ether/ethyl acetate =40/1, v/v) afforded the product **3c** as a white solid (340 mg, 56% yield). ^1H NMR (600 MHz, CDCl_3): δ = 7.50 (d, J = 7.8 Hz, 2H), 7.42 – 7.34 (m, 8H), 7.34 – 7.26 (m, 5H), 7.24 – 7.20 (m, 4H), 7.17 – 7.12 (m, 3H), 7.01 (d, J = 2.1 Hz, 1H), 3.96 (d, J = 1.9 Hz, 2H), 3.21 (s, 3H), 2.41 (s, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 145.0, 144.7, 142.5, 141.7, 140.4, 137.7, 135.7, 134.4, 133.8, 133.2, 131.5, 130.6, 130.0, 129.5, 129.4, 129.1, 128.3, 127.9, 127.8, 127.7, 127.6, 126.8, 126.4, 125.0, 121.0, 117.6, 116.6, 110.5, 32.6, 21.6 ppm. HRMS (ESI): calcd for $\text{C}_{38}\text{H}_{32}\text{NO}_3\text{SSi}$ $[\text{M}+\text{H}]^+$ 610.1867, found 610.1865.



4-(4-Fluorophenyl)-2-methoxy-9-methyl-1-phenyl-5-(phenylsilyl)-9H-carbazole (**3d**)

The reaction was performed at 1.2 mmol scale according to procedure C. Purification via silica gel column chromatography (petroleum ether/ethyl acetate =80/1, v/v) afforded the product **3d** as a white solid (380 mg, 65% yield). ^1H NMR (600 MHz, CDCl_3): δ = 7.58 – 7.52 (m, 2H), 7.51 – 7.45 (m, 4H), 7.45 – 7.41 (m, 1H), 7.33 – 7.21 (m, 7H), 7.15 – 7.05 (m, 3H), 6.69 (s, 1H), 4.03 (s, 2H), 3.81 (s, 3H), 3.21 (s, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 162.7 (d, $J_{\text{C-F}}$ = 245.4 Hz), 155.6, 142.3, 141.5, 139.0 (d, $J_{\text{C-F}}$ = 2.7 Hz), 136.6, 135.8, 135.7, 134.3, 131.7 (d, $J_{\text{C-F}}$ = 7.8 Hz), 131.5, 130.1, 129.1, 128.0, 127.7, 127.6, 127.4, 124.6, 124.0, 116.7, 116.3

(d, $J_{C-F} = 21.5$ Hz), 112.4, 110.1, 107.5, 56.6, 32.5 ppm. ^{19}F NMR (565 MHz, CDCl_3): $\delta = -114.88$ ppm. HRMS (ESI): calcd for $\text{C}_{32}\text{H}_{27}\text{FNOSi}$ $[\text{M}+\text{H}]^+$ 488.1840, found 488.1839.



2-Methoxy-9-methyl-1,4-diphenyl-5-(thiophen-2-ylsilyl)-9H-carbazole (**3e**)

The reaction was performed at 1.0 mmol scale according to procedure C. Purification via silica gel column chromatography (petroleum ether/ethyl acetate =80/1, v/v) afforded the product **3e** as a white solid (190 mg, 40% yield). ^1H NMR (600 MHz, CDCl_3): $\delta = 7.64$ (d, $J = 7.4$ Hz, 2H), 7.54 (d, $J = 4.5$ Hz, 1H), 7.50 – 7.42 (m, 7H), 7.40 (t, $J = 7.4$ Hz, 1H), 7.31 (d, $J = 8.0$ Hz, 1H), 7.27 (t, $J = 7.5$ Hz, 1H), 7.14 (d, $J = 6.9$ Hz, 1H), 7.11 (d, $J = 2.9$ Hz, 1H), 7.08 (t, $J = 3.9$ Hz, 1H), 6.77 (s, 1H), 4.07 (s, 2H), 3.82 (s, 3H), 3.21 (s, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3): $\delta = 155.7, 142.8, 142.2, 141.5, 137.7, 137.4, 135.9, 133.0, 131.9, 131.6, 130.1, 129.5, 129.5, 128.0, 128.0, 127.8, 127.4, 127.3, 124.6, 123.9, 116.6, 112.3, 110.2, 107.5, 56.6, 32.6$ ppm. HRMS (ESI): calcd for $\text{C}_{30}\text{H}_{26}\text{NOSSi}$ $[\text{M}+\text{H}]^+$ 476.1499, found 476.1501.

III. Optimization for 7-Membered Si-Stereogenic Heterocycles

A 5 mL microwave tube was charged with dihydrosilanes **3a** (0.1 mmol, 46.9 mg, 1.0 equiv), [Rh(cod)Cl]₂ (0.5 mg, 1 mol%), ligand (3 mol%), and toluene (1 mL) in glovebox. The tube was capped, then removed from the glovebox and stirred at indicated temperature for 12 h. After the system was cooled to room temperature, the reaction mixture was concentrated *in vacuo*, the crude residue was dissolved in 1 mL of deuterated chloroform for ¹H NMR analysis. The yields were determined by crude ¹H NMR analysis using dibromomethane as an internal standard. The *ee* value of desired compound **4a** was determined by HPLC analysis on a chiral stationary phase. The result of optimization of reaction conditions was listed in **Table S1**.

Table S1. Optimization of Reaction Conditions^a

Josiphos-type

L1, R = *t*Bu, R' = Ph
L2, R = *t*Bu, R' = Cy
L3, R = Ph, R' = *t*Bu
L4, R = Cy, R' = Ph
L5, R = Cy, R' = Cy

L6, (*R*)-BINAP

L7

Entry	Ligand	T (°C)	Yield (%) ^b	<i>ee</i> (%) ^d
1	L1	70	50	69
2	L1	100	72	76
3	L1	120	70	72
4	L2	100	35	42
5	L3	100	83 (78^c)	90
6	L4	100	76	10
7	L5	100	67	3

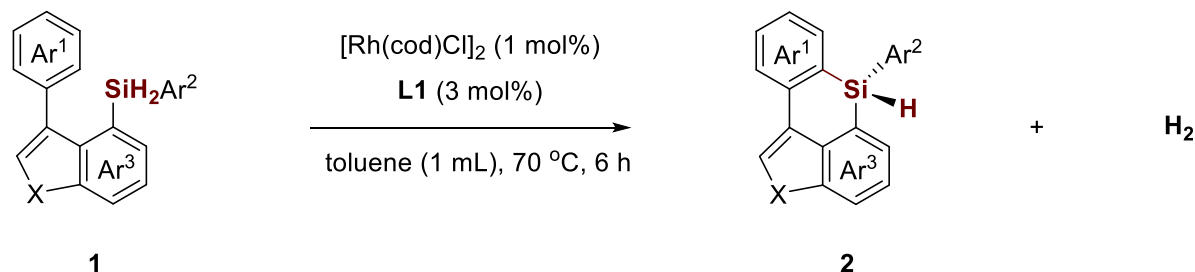
8	L6	100	16	36
9	L7	100	25	29

^aReaction conditions: **3a** (46.9 mg, 0.1 mmol), [Rh(cod)Cl]₂ (0.5 mg, 1 mol%) and chiral ligand (3 mol%) in anhydrous toluene (1.0 mL) at indicated temperature for 12 h. ^bNMR yield.

^cIsolated yield. ^d*ee* value was based on chiral HPLC analysis: AD-3 column, wavelength = 250 nm, eluents: hexane/isopropanol = 95/5, flow rate = 1.0 mL/min, temperature = 28 °C.

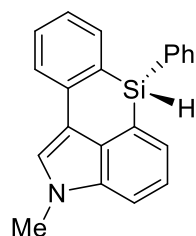
IV. Enantioselective Construction of Si-Stereogenic Heterocycles

1. Scope of Six-Membered Silicon-Stereogenic Heterocycles



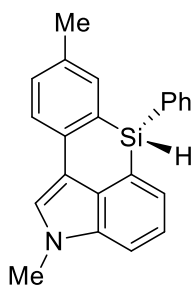
X = NR, O, S

A 5 mL microwave tube was charged with **1** (0.1 mmol, 1 equiv), $[\text{Rh}(\text{cod})\text{Cl}]_2$ (0.5 mg, 1 mol%), **L1** (1.6 mg, 3 mol%), and toluene (1 mL) in glovebox. The tube was sealed, then removed from the glovebox, and the mixture was stirred at 70 °C for 6 h. After the completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to give the product.



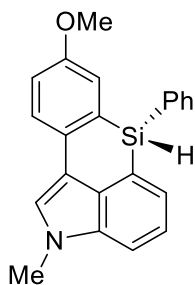
(S)-2-Methyl-6-phenyl-2,6-dihydrobenzo[5,6]silino[4,3,2-cd]indole (**2a**)

The product **2a** was purified via silica gel column chromatography (petroleum ether/ethyl acetate = 80/1, v/v) as a white solid (25.9 mg, 83% yield). ^1H NMR (600 MHz, CDCl_3): δ = 7.77 (d, J = 7.9 Hz, 1H), 7.64 – 7.59 (m, 3H), 7.58 (s, 1H), 7.45 (d, J = 6.8 Hz, 1H), 7.41 – 7.35 (m, 3H), 7.34 – 7.30 (m, 3H), 7.13 (t, J = 7.3 Hz, 1H), 5.71 (s, 1H), 3.84 (s, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 139.5, 136.6, 135.7, 135.5, 135.4, 131.8, 129.9, 129.6, 128.0, 127.0, 126.7, 125.5, 124.7, 122.7, 122.5, 122.4, 115.7, 110.7, 33.0 ppm. HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{18}\text{Si}$ $[\text{M}+\text{H}]^+$ 312.1203, found 312.1201. HPLC (Chiralpak OD-3) *i*-PrOH/hexane = 5/95, 1.0 mL/min, T = 28 °C, λ = 250 nm, t_r (major) = 11.7 min, t_r (minor) = 15.5 min, 96% *ee*. $[\alpha]_{\text{D}}^{28.3}$ = +132 (c = 0.1, CHCl_3).



(S)-2,8-Dimethyl-6-phenyl-2,6-dihydrobenzo[5,6]silino[4,3,2-*cd*]indole (2b)

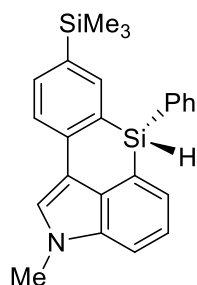
The product **2b** was purified via silica gel column chromatography (petroleum ether/ethyl acetate = 80/1, v/v) as a white solid (25.4 mg, 78% yield). ^1H NMR (400 MHz, CDCl_3): δ = 7.68 (d, J = 8.0 Hz, 1H), 7.65 – 7.59 (m, 2H), 7.53 (s, 1H), 7.45 – 7.40 (m, 2H), 7.39 – 7.28 (m, 5H), 7.20 (dd, J = 8.1, 1.6 Hz, 1H), 5.69 (s, 1H), 3.83 (s, 3H), 2.30 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 136.9, 136.8, 135.9, 135.5, 134.0, 131.8, 130.9, 129.6, 128.0, 126.9, 126.6, 125.0, 122.6, 122.5, 115.7, 110.6, 33.0, 21.1 ppm. HRMS (ESI): calcd for $\text{C}_{22}\text{H}_{20}\text{NSi}$ $[\text{M}+\text{H}]^+$ 326.1360, found 326.1361. HPLC (Chiralpak OD-3) *i*-PrOH/hexane = 5/95, 1.0 mL/min, T = 28 $^\circ\text{C}$, λ = 250 nm, t_r (major) = 8.2 min, t_r (minor) = 8.9 min, 96% *ee*. $[\alpha]_{\text{D}}^{29.7}$ = +69 (c = 0.1, CHCl_3).



(S)-8-Methoxy-2-methyl-6-phenyl-2,6-dihydrobenzo[5,6]silino[4,3,2-*cd*]indole (2c)

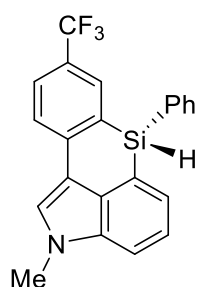
The product **2c** was purified via silica gel column chromatography (petroleum ether/ethyl acetate = 80/1, v/v) as a white solid (26.0 mg, 76% yield). ^1H NMR (400 MHz, CDCl_3): δ = 7.71 (d, J = 8.7 Hz, 1H), 7.62 (dd, J = 7.7, 1.6 Hz, 2H), 7.46 (s, 1H), 7.43 (d, J = 6.7 Hz, 1H), 7.39 – 7.28 (m, 5H), 7.13 (d, J = 2.8 Hz, 1H), 6.96 (dd, J = 8.7, 2.8 Hz, 1H), 5.70 (s, 1H), 3.81 (s, 3H), 3.78 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 156.6, 135.6, 135.4, 135.4, 132.5, 131.6, 129.6, 128.4, 128.0, 126.5, 124.5, 123.9, 122.6, 122.1, 120.5, 116.5, 115.5, 110.6, 55.3, 32.9 ppm. HRMS (ESI): calcd for $\text{C}_{22}\text{H}_{20}\text{NOSi}$ $[\text{M}+\text{H}]^+$ 342.1309, found 342.1305. HPLC

(Chiralpak AD-3) *i*-PrOH/hexane = 1/99, 1.0 mL/min, T = 28 °C, λ = 250 nm, t_r (major) = 30.7 min, t_r (minor) = 48.3 min, 96% *ee*. $[\alpha]_D^{28.8} = +47$ (c = 0.1, CHCl₃).



(S)-2-Methyl-6-phenyl-8-(trimethylsilyl)-2,6-dihydrobenzo[5,6]silino[4,3,2-*cd*]indole (2d)

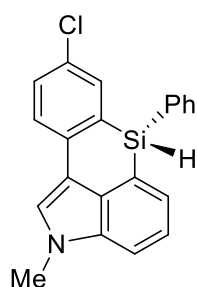
The product **2d** was purified via silica gel column chromatography (petroleum ether/ethyl acetate = 40/1, v/v) as a colorless oil (27.2 mg, 71% yield). ¹H NMR (400 MHz, CDCl₃): δ = 7.79 (s, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.62 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.57 (s, 1H), 7.54 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.46 (d, *J* = 6.2 Hz, 1H), 7.38 – 7.29 (m, 5H), 5.73 (s, 1H), 3.81 (s, 3H), 0.24 (s, 9H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 141.8, 140.0, 135.9, 135.8, 135.5, 135.3, 134.9, 131.9, 129.5, 127.9, 126.7, 126.0, 125.7, 122.7, 122.6, 121.7, 115.7, 110.6, 33.0, -1.1 ppm. HRMS (ESI): calcd for C₂₄H₂₆NSi₂ [M+H]⁺ 384.1598, found 384.1595. HPLC (Chiralpak AD-3) *i*-PrOH/hexane = 1/99, 1.0 mL/min, T = 28 °C, λ = 280 nm, t_r (major) = 7.8 min, t_r (minor) = 9.1 min, 97% *ee*. $[\alpha]_D^{29.6} = +23$ (c = 0.1, CHCl₃).



(S)-2-Methyl-6-phenyl-8-(trifluoromethyl)-2,6-dihydrobenzo[5,6]silino[4,3,2-*cd*]indole (2e)

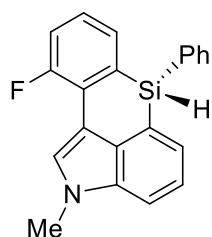
The product **2e** was purified via silica gel column chromatography (petroleum ether/ethyl acetate = 10/1, v/v) as a white solid (26.5 mg, 70% yield). ¹H NMR (400 MHz, CDCl₃): δ = 7.82 (s, 1H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.63 – 7.54 (m, 4H), 7.47 (d, *J* = 6.7 Hz, 1H), 7.42 – 7.31 (m, 5H), 5.74 (s, 1H), 3.83 (s, 3H) ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 142.9, 135.6, 135.4,

134.8, 133.2 (q, $J_{C-F} = 3.9$ Hz), 131.7, 130.0, 128.2, 127.7, 127.3, 126.7, 126.6 (q, $J_{C-F} = 3.8$ Hz), 126.2 (q, $J_{C-F} = 32.1$ Hz), 124.5 (q, $J_{C-F} = 269.9$ Hz), 123.1, 122.4, 121.7, 114.7, 111.0, 33.2 ppm. ^{19}F NMR (565 MHz, CDCl_3): $\delta = -62.20$ ppm. HRMS (ESI): calcd for $\text{C}_{22}\text{H}_{17}\text{F}_3\text{NSi}$ $[\text{M}+\text{H}]^+$ 380.1077, found 380.1082. HPLC (Chiralpak AD-3) *i*-PrOH/hexane = 5/95, 1.0 mL/min, $T = 28$ °C, $\lambda = 250$ nm, t_r (major) = 7.3 min, t_r (minor) = 8.6 min, 92% *ee*. $[\alpha]_{\text{D}}^{29.7} = +196$ ($c = 0.1$, CHCl_3).



(S)-8-Chloro-2-methyl-6-phenyl-2,6-dihydrobenzo[5,6]silino[4,3,2-cd]indole (2f)

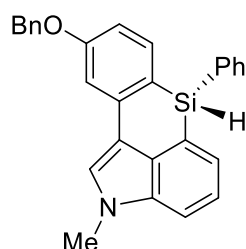
L5 (1.8 mg, 3 mol%) was used as ligand, the product **2f** was purified via silica gel column chromatography (petroleum ether/ethyl acetate = 40/1, v/v) as a white solid (25.4 mg, 74% yield). ^1H NMR (600 MHz, CDCl_3): $\delta = 7.57$ (d, $J = 8.5$ Hz, 1H), 7.51 (d, $J = 7.9$ Hz, 2H), 7.45 (d, $J = 2.1$ Hz, 1H), 7.42 (s, 1H), 7.36 (d, $J = 6.8$ Hz, 1H), 7.32 – 7.28 (m, 2H), 7.28 – 7.20 (m, 4H), 5.61 (s, 1H), 3.72 (s, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3): $\delta = 137.8$, 135.8, 135.5, 135.4, 135.0, 131.6, 130.2, 130.0, 129.9, 129.4, 128.1, 126.9, 125.7, 123.9, 122.9, 121.6, 114.8, 110.9, 33.0 ppm. HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{17}\text{ClNSi}$ $[\text{M}+\text{H}]^+$ 346.0813, found 346.0819. HPLC (Chiralpak OD-3) *i*-PrOH/hexane = 5/95, 1.0 mL/min, $T = 28$ °C, $\lambda = 250$ nm, t_r (major) = 9.0 min, t_r (minor) = 9.5 min, 92% *ee*. $[\alpha]_{\text{D}}^{29.7} = +77$ ($c = 0.1$, CHCl_3).



(R)-10-Fluoro-2-methyl-6-phenyl-2,6-dihydrobenzo[5,6]silino[4,3,2-cd]indole (2g)

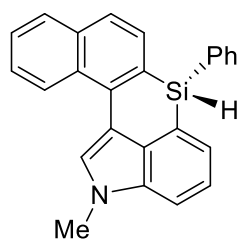
The product **2g** was purified via silica gel column chromatography (petroleum ether/ethyl acetate = 40/1, v/v) as a white solid (26.2 mg, 80% yield). ^1H NMR (400 MHz, CDCl_3): $\delta =$

7.84 (d, $J = 3.4$ Hz, 1H), 7.62 – 7.57 (m, 2H), 7.48 – 7.30 (m, 7H), 7.18 – 7.06 (m, 2H), 5.73 (s, 1H), 3.86 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 159.6$ (d, $J_{\text{C-F}} = 248.9$ Hz), 135.4, 134.7, 132.2 (d, $J_{\text{C-F}} = 3.3$ Hz), 132.0, 130.6, 130.4, 130.2 (d, $J_{\text{C-F}} = 2.0$ Hz), 129.8, 128.0, 127.4 (d, $J_{\text{C-F}} = 11.2$ Hz), 126.9, 125.2 (d, $J_{\text{C-F}} = 7.8$ Hz), 122.7, 121.7, 116.9 (d, $J_{\text{C-F}} = 22.3$ Hz), 110.8, 110.1, 33.0 ppm. ^{19}F NMR (565 MHz, CDCl_3): $\delta = -111.36$ ppm. HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{17}\text{FNSi}$ $[\text{M}+\text{H}]^+$ 330.1109, found 330.1106. HPLC (Chiralpak OD-3) *i*-PrOH/hexane = 5/95, 1.0 mL/min, $T = 28$ °C, $\lambda = 220$ nm, t_r (major) = 5.5 min, t_r (minor) = 6.4 min, 92% *ee*. $[\alpha]_{\text{D}}^{29.5} = +152$ ($c = 0.1$, CHCl_3).



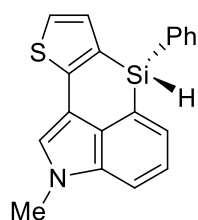
(S)-9-(Benzyloxy)-2-methyl-6-phenyl-2,6-dihydrobenzo[5,6]silino[4,3,2-*cd*]indole (2h)

The product **2h** was purified via silica gel column chromatography (petroleum ether/ethyl acetate = 40/1, v/v) as a white solid (34.2 mg, 82% yield). ^1H NMR (400 MHz, CDCl_3): $\delta = 7.61$ (dd, $J = 7.7, 1.6$ Hz, 2H), 7.52 (t, $J = 4.1$ Hz, 2H), 7.45 (t, $J = 7.5$ Hz, 3H), 7.42 – 7.28 (m, 9H), 6.80 (dd, $J = 8.2, 2.4$ Hz, 1H), 5.68 (s, 1H), 5.12 (s, 2H), 3.82 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 160.4, 141.2, 138.0, 137.0, 136.1, 135.5, 135.4, 131.9, 129.5, 128.6, 128.0, 127.9, 127.6, 126.8, 125.6, 122.7, 118.7, 115.6, 111.7, 110.6, 108.9, 69.8, 33.0$ ppm. HRMS (ESI): calcd for $\text{C}_{28}\text{H}_{24}\text{NOSi}$ $[\text{M}+\text{H}]^+$ 418.1622, found 418.1615. HPLC (Chiralpak OD-3) *i*-PrOH/hexane = 15/85, 1.0 mL/min, $T = 28$ °C, $\lambda = 250$ nm, t_r (minor) = 21.0 min, t_r (major) = 26.8 min, 97% *ee*. $[\alpha]_{\text{D}}^{29.3} = +98$ ($c = 0.1$, CHCl_3).



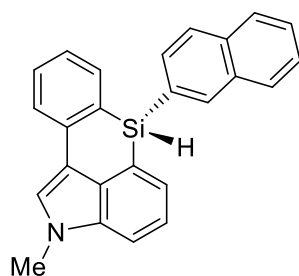
(S)-2-Methyl-6-phenyl-2,6-dihydronaphtho[1',2':5,6]silino[4,3,2-*cd*]indole (2i)

The product **2i** was purified via silica gel column chromatography (petroleum ether/ethyl acetate = 40/1, v/v) as a pale yellow solid (10.9 mg, 30% yield). ^1H NMR (400 MHz, CDCl_3): δ = 8.77 (d, J = 8.6 Hz, 1H), 8.06 (s, 1H), 7.84 (d, J = 7.9 Hz, 1H), 7.69 – 7.55 (m, 5H), 7.52 (t, J = 7.1 Hz, 2H), 7.43 (d, J = 7.5 Hz, 1H), 7.40 – 7.28 (m, 4H), 5.82 (s, 1H), 3.91 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 138.1, 136.0, 135.5, 135.4, 134.8, 133.1, 132.1, 130.4, 130.3, 129.7, 129.0, 128.0, 126.9, 126.0, 126.0, 125.9, 124.4, 123.0, 122.7, 114.8, 110.6, 33.1 ppm. HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{20}\text{NSi}$ $[\text{M}+\text{H}]^+$ 362.1360, found 362.1355. HPLC (Chiralpak OD-3) *i*-PrOH/hexane = 5/95, 1.0 mL/min, T = 28 °C, λ = 250 nm, t_r (major) = 12.1 min, t_r (minor) = 21.7 min, 87% *ee*. $[\alpha]_{\text{D}}^{29.4}$ = +120 (c = 0.1, CHCl_3).



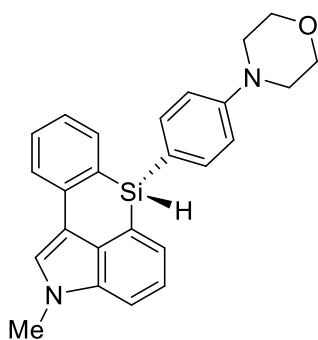
(R)-2-Methyl-6-phenyl-2,6-dihydrothieno[2',3':5,6]silino[4,3,2-cd]indole (2j)

The product **2j** was purified via silica gel column chromatography (petroleum ether/ethyl acetate = 80/1, v/v) as a dark green solid (29.0 mg, 91% yield). ^1H NMR (600 MHz, CDCl_3): δ = 7.61 – 7.59 (m, 2H), 7.49 – 7.48 (m, 1H), 7.36 – 7.30 (m, 6H), 7.16 (d, J = 4.9 Hz, 1H), 7.14 (d, J = 5.0 Hz, 1H), 5.77 (s, 1H), 3.74 (s, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 145.5, 135.5, 135.2, 135.1, 132.2, 131.3, 129.6, 128.0, 127.5, 125.7, 124.9, 123.1, 122.2, 121.1, 112.0, 110.7, 32.8 ppm. HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{16}\text{NSSi}$ $[\text{M}+\text{H}]^+$ 318.0767, found 318.0763. HPLC (Chiralpak OD-3) *i*-PrOH/hexane = 5/95, 1.0 mL/min, T = 28 °C, λ = 250 nm, t_r (major) = 11.7 min, t_r (minor) = 12.5 min, 91% *ee*. $[\alpha]_{\text{D}}^{25.0}$ = +242 (c = 0.1, CHCl_3).



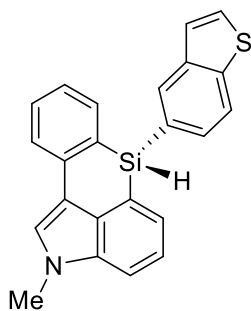
(S)-2-Methyl-6-(naphthalen-2-yl)-2,6-dihydrobenzo[5,6]silino[4,3,2-cd]indole (2k)

The product **2k** was purified via silica gel column chromatography (petroleum ether/ethyl acetate = 40/1, v/v) as a white solid (27.1 mg, 75% yield). ^1H NMR (600 MHz, CDCl_3): δ = 8.18 (s, 1H), 7.82 – 7.73 (m, 4H), 7.62 (d, J = 7.6 Hz, 2H), 7.57 (s, 1H), 7.49 – 7.41 (m, 3H), 7.41 – 7.34 (m, 2H), 7.31 (t, J = 6.9 Hz, 1H), 7.11 (t, J = 7.0 Hz, 1H), 5.84 (s, 1H), 3.82 (s, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 139.6, 136.7, 136.6, 135.5, 134.0, 133.2, 133.0, 131.8, 131.2, 130.0, 128.2, 127.7, 127.3, 127.0, 126.8, 126.6, 125.9, 125.6, 124.7, 122.7, 122.5, 122.4, 115.7, 110.7, 33.0 ppm. HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{20}\text{NSi}$ $[\text{M}+\text{H}]^+$ 362.1360, found 362.1355. HPLC (Chiralpak OD-3) *i*-PrOH/hexane = 5/95, 1.0 mL/min, T = 28 °C, λ = 254 nm, t_r (major) = 13.5 min, t_r (minor) = 21.6 min, 96% *ee*. $[\alpha]_{\text{D}}^{25.0}$ = +133 (c = 0.1, CHCl_3).



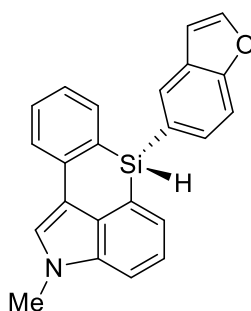
(S)-4-(4-(2-Methyl-2,6-dihydrobenzo[5,6]silino[4,3,2-*cd*]indol-6-yl)phenyl)morpholine (2l)

The product **2l** was purified via silica gel column chromatography (petroleum ether/ethyl acetate = 40/1, v/v) as a white solid (30.9 mg, 78% yield). ^1H NMR (600 MHz, CDCl_3): δ = 7.76 (d, J = 7.9 Hz, 1H), 7.59 (d, J = 7.2 Hz, 1H), 7.57 (s, 1H), 7.52 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 6.8 Hz, 1H), 7.36 (t, J = 7.6 Hz, 2H), 7.32 – 7.30 (m, 1H), 7.12 (t, J = 7.3 Hz, 1H), 6.87 (d, J = 8.4 Hz, 2H), 5.67 (s, 1H), 3.84 (s, 3H), 3.83 – 3.81 (m, 4H), 3.17 – 3.15 (m, 4H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 139.5, 136.7, 136.6, 135.5, 131.8, 129.7, 127.7, 126.7, 125.4, 124.6, 123.1, 122.7, 122.4, 115.8, 114.8, 110.5, 66.8, 48.5, 33.0 ppm. HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{25}\text{N}_2\text{OSi}$ $[\text{M}+\text{H}]^+$ 397.1731, found 397.1727. HPLC (Chiralpak AD-3) *i*-PrOH/hexane = 50/50, 1.0 mL/min, T = 28 °C, λ = 250 nm, t_r (major) = 8.7 min, t_r (minor) = 51.5 min, 93% *ee*. $[\alpha]_{\text{D}}^{25.0}$ = +77 (c = 0.1, CHCl_3).



(S)-6-(Benzo[*b*]thiophen-5-yl)-2-methyl-2,6-dihydrobenzo[5,6]silino[4,3,2-*cd*]indole (2m)

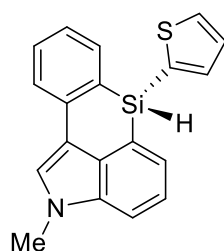
The product **2m** was purified via silica gel column chromatography (petroleum ether/ethyl acetate = 80/1, v/v) as a pale yellow solid (8.8 mg, 24% yield). ^1H NMR (600 MHz, CDCl_3): δ = 7.87 (s, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.62 – 7.59 (m, 2H), 7.58 (d, J = 2.1 Hz, 1H), 7.55 (d, J = 8.2 Hz, 1H), 7.48 (d, J = 8.2 Hz, 1H), 7.44 (d, J = 6.8 Hz, 1H), 7.40 – 7.37 (m, 2H), 7.33 – 7.31 (m, 1H), 7.12 (t, J = 7.2 Hz, 1H), 6.70 (d, J = 1.6 Hz, 1H), 5.79 (s, 1H), 3.86 (s, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 156.1, 144.8, 139.5, 136.7, 135.5, 131.8, 131.2, 129.9, 129.4, 129.0, 127.5, 126.8, 125.5, 124.7, 122.9, 122.7, 122.5, 115.7, 111.3, 110.6, 106.5, 33.0 ppm. HRMS (ESI): calcd for $\text{C}_{23}\text{H}_{18}\text{NSSi}$ $[\text{M}+\text{H}]^+$ 368.0924, found 368.0922. HPLC (Chiralpak OD-3) *i*-PrOH/hexane = 5/95, 1.0 mL/min, T = 28 °C, λ = 254 nm, t_r (major) = 14.9 min, t_r (minor) = 22.2 min, 90% *ee*. $[\alpha]_{\text{D}}^{25.0}$ = +176 (c = 0.1, CHCl_3).



(S)-6-(Benzofuran-5-yl)-2-methyl-2,6-dihydrobenzo[5,6]silino[4,3,2-*cd*]indole (2n)

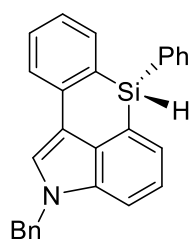
The product **2n** was purified via silica gel column chromatography (petroleum ether/ethyl acetate = 80/1, v/v) as a pale yellow solid (17.6 mg, 50% yield). ^1H NMR (600 MHz, CDCl_3): δ = 8.09 (s, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.62 – 7.60 (m, 2H), 7.55 (d, J = 8.0 Hz, 1H), 7.45 (d, J = 6.8 Hz, 1H), 7.40 – 7.37 (m, 3H), 7.33 – 7.31 (m, 1H), 7.28 (d, J = 5.4 Hz, 1H), 7.12 (t, J = 7.3 Hz, 1H), 5.81 (s, 1H), 3.86 (s, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 141.3, 139.5, 139.4, 136.7, 135.5, 131.8, 131.3, 131.0, 130.5, 130.0, 127.2, 126.8,

126.1, 125.6, 124.7, 123.9, 122.7, 122.6, 122.5, 122.2, 115.7, 110.7, 33.0 ppm. HRMS (ESI): calcd for $C_{23}H_{18}NOSi$ $[M+H]^+$ 352.1152, found 352.1150. HPLC (Chiralpak OD-3) *i*-PrOH/hexane = 5/95, 1.0 mL/min, $T = 28\text{ }^{\circ}C$, $\lambda = 254\text{ nm}$, t_r (major) = 14.6 min, t_r (minor) = 23.4 min, 94% *ee*. $[\alpha]_D^{25.0} = +81$ ($c = 0.1$, $CHCl_3$).



(S)-2-Methyl-6-(thiophen-2-yl)-2,6-dihydrobenzo[5,6]silino[4,3,2-*cd*]indole (2o)

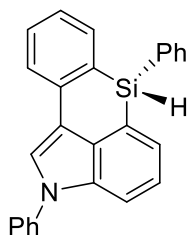
The product **2o** was purified via silica gel column chromatography (petroleum ether/ethyl acetate = 80/1, v/v) as a white solid (19.7 mg, 62% yield). 1H NMR (600 MHz, $CDCl_3$): $\delta = 7.76$ (d, $J = 7.9$ Hz, 1H), 7.69 (d, $J = 7.3$ Hz, 1H), 7.65 (d, $J = 4.6$ Hz, 1H), 7.58 (s, 1H), 7.52 (d, $J = 6.8$ Hz, 1H), 7.40 (t, $J = 8.0$ Hz, 3H), 7.36 – 7.34 (m, 1H), 7.19 – 7.18 (m, 1H), 7.16 (d, $J = 7.3$ Hz, 1H), 5.85 (s, 1H), 3.85 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 139.4$, 137.1, 136.6, 135.5, 134.3, 132.3, 131.7, 130.1, 128.4, 126.8, 126.5, 125.7, 124.8, 122.7, 122.5, 121.8, 115.5, 110.9, 33.0 ppm. HRMS (ESI): calcd for $C_{19}H_{16}NSSi$ $[M+H]^+$ 318.0767, found 318.0765. HPLC (Chiralpak OD-3) *i*-PrOH/hexane = 5/95, 1.0 mL/min, $T = 28\text{ }^{\circ}C$, $\lambda = 254\text{ nm}$, t_r (major) = 13.1 min, t_r (minor) = 17.3 min, 90% *ee*. $[\alpha]_D^{25.0} = +156$ ($c = 0.1$, $CHCl_3$).



(S)-2-Benzyl-6-phenyl-2,6-dihydrobenzo[5,6]silino[4,3,2-*cd*]indole (2p)

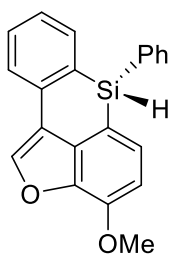
The product **2p** was purified via silica gel column chromatography (petroleum ether/ethyl acetate = 80/1, v/v) as a white solid (28.5 mg, 74% yield). 1H NMR (400 MHz, $CDCl_3$): $\delta = 7.75$ (d, $J = 7.9$ Hz, 1H), 7.67 – 7.58 (m, 4H), 7.45 (d, $J = 6.7$ Hz, 1H), 7.40 – 7.23 (m, 9H), 7.20 – 7.11 (m, 3H), 5.72 (s, 1H), 5.34 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 139.4$,

137.1, 136.6, 135.6, 135.5, 135.2, 132.0, 129.9, 129.6, 128.9, 128.0, 127.8, 127.1, 127.0, 126.9, 124.8, 122.9, 122.6, 122.6, 116.3, 111.1, 50.3 ppm. HRMS (ESI): calcd for $C_{27}H_{22}NSi$ $[M+H]^+$ 388.1516, found 388.1513. HPLC (Chiralpak OD-3) *i*-PrOH/hexane = 5/95, 1.0 mL/min, T = 28 °C, λ = 250 nm, t_r (major) = 16.7 min, t_r (minor) = 27.5 min, 91% *ee*. $[\alpha]_D^{29.3}$ = +72 (*c* = 0.1, $CHCl_3$).



(S)-2,6-Diphenyl-2,6-dihydrobenzo[5,6]silino[4,3,2-*cd*]indole (2q)

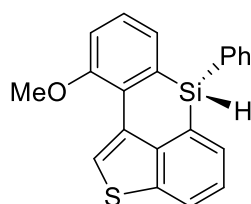
The product **2q** was purified via silica gel column chromatography (petroleum ether) as a white solid (26.8 mg, 72% yield). 1H NMR (400 MHz, $CDCl_3$): δ = 7.88 (s, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.69 – 7.60 (m, 4H), 7.59 – 7.49 (m, 5H), 7.44 – 7.29 (m, 6H), 7.18 (td, *J* = 7.4, 1.0 Hz, 1H), 5.74 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.5, 139.0, 136.6, 135.5, 134.7, 132.6, 130.0, 129.7, 129.7, 128.0, 127.8, 127.4, 126.7, 125.2, 124.4, 124.1, 123.5, 122.9, 122.9, 117.8, 112.0 ppm. HRMS (ESI): calcd for $C_{26}H_{20}NSi$ $[M+H]^+$ 374.1360, found 374.1356. HPLC (Chiralpak OD-3) *i*-PrOH/hexane = 5/95, 1.0 mL/min, T = 28 °C, λ = 250 nm, t_r (major) = 6.7 min, t_r (minor) = 7.3 min, 95% *ee*. $[\alpha]_D^{29.6}$ = +90 (*c* = 0.1, $CHCl_3$).



(S)-3-Methoxy-6-phenyl-6H-benzo[5,6]silino[4,3,2-*cd*]benzofuran (2r)

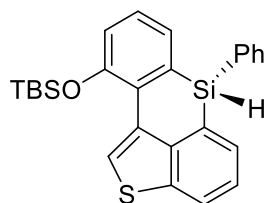
The product **2r** was purified via silica gel column chromatography (petroleum ether/ethyl acetate = 80/1, v/v) as a white solid (19.8 mg, 60% yield). 1H NMR (400 MHz, $CDCl_3$): δ = 8.16 (s, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.66 (d, *J* = 7.1 Hz, 1H), 7.59 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.44 (td, *J* = 7.8, 1.3 Hz, 1H), 7.41 – 7.31 (m, 3H), 7.27 (dd, *J* = 7.4,

0.9 Hz, 1H). 6.95 (d, $J = 7.8$ Hz, 1H), 5.65 (s, 1H), 4.06 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 146.7, 142.9, 141.0, 136.7, 136.1, 135.4, 135.1, 133.9, 131.2, 130.0, 129.9, 129.4, 128.1, 126.8, 124.3, 121.4, 114.2, 108.6, 56.2$ ppm. HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{17}\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 329.0992, found 329.0989. HPLC (Chiralpak OD-3) *i*-PrOH/hexane = 1/99, 1.0 mL/min, $T = 28^\circ\text{C}$, $\lambda = 250$ nm, t_r (minor) = 11.5 min, t_r (major) = 13.5 min, 95% *ee*. $[\alpha]_{\text{D}}^{29.6} = +112$ ($c = 0.1$, CHCl_3).



(S)-10-Methoxy-6-phenyl-6H-2-thia-6-silaaceanthrylene (2s)

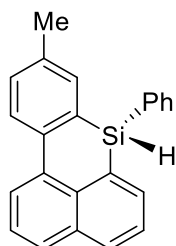
$[\text{Rh}(\text{cod})\text{Cl}]_2$ (2.0 mg, 4 mol%), **L1** (4.5 mg, 8 mol%) was used, the product **2s** was purified via silica gel column chromatography (petroleum ether) as a colorless oil (18.3 mg, 53% yield). ^1H NMR (400 MHz, CDCl_3): $\delta = 8.99$ (s, 1H), 7.98 (dd, $J = 8.0, 0.7$ Hz, 1H), 7.66 (dd, $J = 6.9, 0.5$ Hz, 1H), 7.61 – 7.56 (m, 2H), 7.41 – 7.26 (m, 6H), 7.12 (dd, $J = 7.1, 2.4$ Hz, 1H), 5.67 (s, 1H), 4.04 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 157.6, 143.3, 138.0, 135.5, 135.2, 131.4, 131.1, 130.3, 129.9, 129.3, 128.6, 128.4, 128.1, 127.2, 125.8, 124.6, 123.9, 113.4, 55.4$ ppm. HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{17}\text{OSSi}$ $[\text{M}+\text{H}]^+$ 345.0764, found 345.0762. HPLC (Chiralpak OD-3) *i*-PrOH/hexane = 1/99, 1.0 mL/min, $T = 28^\circ\text{C}$, $\lambda = 250$ nm, t_r (minor) = 6.8 min, t_r (major) = 7.7 min, 94% *ee*. $[\alpha]_{\text{D}}^{29.5} = +87$ ($c = 0.1$, CHCl_3).



(S)-10-((*tert*-Butyldimethylsilyl)oxy)-6-phenyl-6H-2-thia-6-silaaceanthrylene (2t)

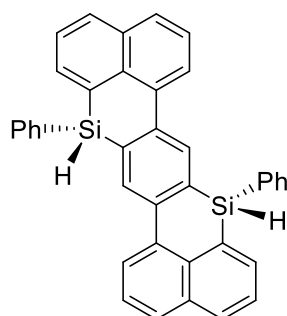
The product **2t** was purified via silica gel column chromatography (petroleum ether) as a colorless oil (26.9 mg, 61% yield). ^1H NMR (400 MHz, CDCl_3): $\delta = 8.93$ (s, 1H), 7.98 (d, $J = 8.0$ Hz, 1H), 7.66 (d, $J = 6.9$ Hz, 1H), 7.58 (dd, $J = 7.8, 1.4$ Hz, 2H), 7.42 – 7.31 (m, 4H), 7.28 (d, $J = 7.1$ Hz, 1H), 7.15 (t, $J = 7.6$ Hz, 1H), 7.05 (dd, $J = 8.0, 1.1$ Hz, 1H), 5.66 (s, 1H), 1.05

(s, 9H), 0.35 (s, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 153.8, 143.2, 138.0, 135.5, 135.2, 131.4, 131.4, 130.4, 130.2, 129.9, 129.4, 128.7, 128.1, 126.8, 125.9, 124.5, 123.9, 122.3, 26.2, 18.8, -3.4, -3.4 ppm. HRMS (ESI): calcd for $\text{C}_{26}\text{H}_{31}\text{OSSi}_2$ $[\text{M}+\text{H}]^+$ 445.1472, found 445.1469. HPLC (Chiralpak IB) *i*-PrOH/hexane = 0/100, 1.0 mL/min, T = 28 °C, λ = 250 nm, t_r (minor) = 8.6 min, t_r (major) = 15.1 min, 95% *ee*. $[\alpha]_{\text{D}}^{29.4}$ = +96 (c = 0.1, CHCl_3).



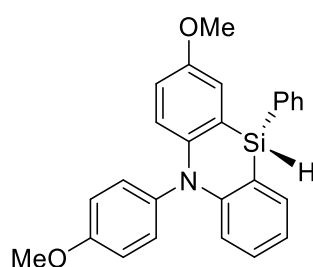
(S)-9-Methyl-7-phenyl-7H-benzo[e]naphtho[1,8-bc]siline (2u)

The reaction was performed with $[\text{Rh}(\text{cod})\text{Cl}]_2$ (1.0 mg, 2 mol%), **L1** (2.2 mg, 4 mol%), and toluene (1 mL) at 60 °C for 8 h. The product **2u** was purified via silica gel column chromatography (petroleum ether) as a colorless oil (24.6 mg, 76% yield). ^1H NMR (400 MHz, CDCl_3): δ = 8.32 (d, J = 7.6 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.1 Hz, 1H), 7.83 (t, J = 7.4 Hz, 2H), 7.63 – 7.54 (m, 3H), 7.52 – 7.44 (m, 2H), 7.42 – 7.31 (m, 4H), 5.59 (s, 1H), 2.35 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 140.7, 136.5, 136.4, 135.7, 135.6, 135.0, 134.4, 134.3, 134.0, 131.7, 131.3, 129.9, 129.5, 129.0, 128.1, 127.6, 126.4, 125.9, 125.0, 124.7, 20.9 ppm. HRMS (ESI): calcd for $\text{C}_{23}\text{H}_{19}\text{Si}$ $[\text{M}+\text{H}]^+$ 323.1251, found 323.1249. HPLC (Chiralpak OD-3) *i*-PrOH/hexane = 1/99, 1.0 mL/min, T = 28 °C, λ = 250 nm, t_r (minor) = 5.6 min, t_r (major) = 8.0 min, 97% *ee*. $[\alpha]_{\text{D}}^{29.6}$ = +30 (c = 0.1, CHCl_3).



The reaction was performed with **1v** (27.1 mg, 0.05 mmol), $[\text{Rh}(\text{cod})\text{Cl}]_2$ (0.5 mg, 2 mol%), **L1** (1.6 mg, 6 mol%), and toluene (1 mL) at 70 °C for 12 h. The product **2v** was purified via silica

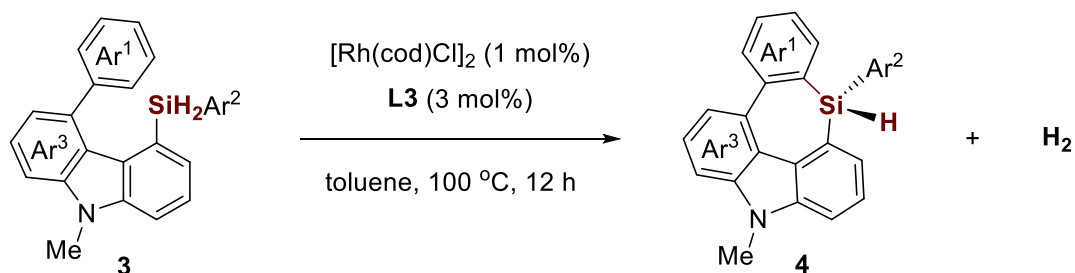
gel column chromatography (petroleum ether) as a pale yellow solid (11.2 mg, 42% yield). ^1H NMR (600 MHz, CDCl_3): δ = 8.46 (s, 2H), 8.30 (d, J = 7.4 Hz, 2H), 7.96 (d, J = 8.1 Hz, 2H), 7.86 (d, J = 8.1 Hz, 4H), 7.67 (d, J = 7.1 Hz, 4H), 7.57 (t, J = 7.7 Hz, 2H), 7.52 (t, J = 7.2 Hz, 2H), 7.43 – 7.41 (m, 2H), 7.38 (t, J = 7.2 Hz, 4H), 5.71 (s, 2H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 141.4, 135.9, 135.7, 134.5, 134.0, 133.9, 133.7, 131.6, 131.4, 130.1, 130.0, 128.2, 127.3, 126.0, 125.4, 125.2 ppm. HRMS (EI): calcd for $\text{C}_{38}\text{H}_{26}\text{Si}_2$ $[\text{M}]^+$ 538.1573, found 538.1574. HPLC (Chiralpak OD-3) *i*-PrOH/hexane = 1/99, 1.0 mL/min, T = 28 °C, λ = 250 nm, t_r (major) = 7.5 min, t_r (minor) = 8.2 min, 99% *ee*. $[\alpha]_{\text{D}}^{25.0}$ = -172 (c = 0.1, CHCl_3).



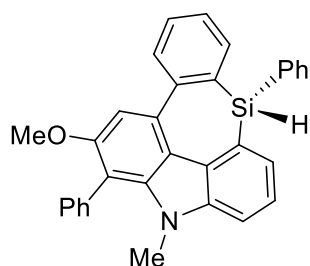
(R)-2-Methoxy-5-(4-methoxyphenyl)-10-phenyl-5,10-dihydrodibenzo[*b,e*][1,4]azasiline (2w)

L7 (1.8 mg, 3 mol%) was used as ligand, the product **2w** was purified via silica gel column chromatography (petroleum ether) as a white solid (18.3 mg, 45% yield). ^1H NMR (600 MHz, CDCl_3): δ = 7.67 (d, J = 6.5 Hz, 2H), 7.49 (d, J = 7.2 Hz, 1H), 7.44 – 7.37 (m, 3H), 7.21 (d, J = 8.7 Hz, 2H), 7.11 – 7.17 (m, 3H), 7.00 (d, J = 3.0 Hz, 1H), 6.86 (t, J = 7.1 Hz, 1H), 6.76 (dd, J = 9.3, 3.0 Hz, 1H), 6.41 (t, J = 6.6 Hz, 2H), 5.69 (s, 1H), 3.92 (s, 3H), 3.71 (s, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 159.0, 152.7, 150.2, 144.6, 136.3, 136.1, 135.6, 135.4, 132.2, 130.5, 129.9, 128.1, 119.2, 118.9, 118.8, 117.6, 116.9, 116.1, 114.3, 112.1, 55.6, 55.5 ppm. HRMS (ESI): calcd for $\text{C}_{26}\text{H}_{24}\text{NO}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 410.1571, found 410.1566. HPLC (Chiralpak OD-H) *i*-PrOH/hexane = 0.5/99.5, 1.0 mL/min, T = 28 °C, λ = 250 nm, t_r (major) = 15.9 min, t_r (minor) = 21.9 min, 58% *ee*. $[\alpha]_{\text{D}}^{29.9}$ = -23 (c = 0.1, CHCl_3).

2. Scope of Seven-Membered Silicon-Stereogenic Heterocycles

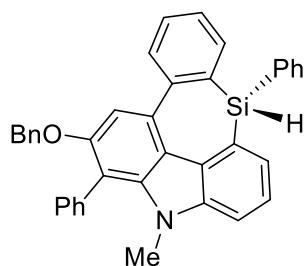


A 5 mL microwave tube was charged with **3** (0.1 mmol, 1 equiv), $[\text{Rh}(\text{cod})\text{Cl}]_2$ (0.5 mg, 1 mol%), **L3** (1.6 mg, 3 mol%), and toluene (1 mL) in glovebox. The tube was sealed, then removed from the glovebox, and the mixture was stirred at 100 °C for 12 h. After the completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to give the product.



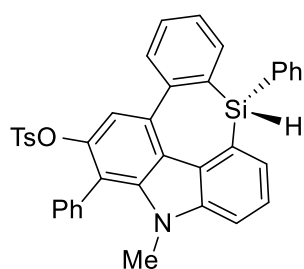
(S)-11-Methoxy-1-methyl-5,12-diphenyl-1,5-dihydrobenzo[6,7]silepino[2,3,4,5-def]carbazole (**4a**)

The product **4a** was purified via silica gel column chromatography ((petroleum ether/ethyl acetate = 80/1, v/v) as a white solid (36.3 mg, 78% yield). ^1H NMR (400 MHz, CDCl_3): δ = 7.89 (dd, J = 7.3, 1.4 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.55 (td, J = 7.7, 1.6 Hz, 1H), 7.51 – 7.39 (m, 10H), 7.34 (s, 1H), 7.32 – 7.27 (m, 2H), 7.25 – 7.22 (m, 2H), 5.62 (s, 1H), 3.90 (s, 3H), 3.19 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 155.7, 145.8, 141.3, 141.0, 137.4, 136.8, 135.7, 135.3, 133.6, 133.2, 132.5, 131.5, 131.4, 130.2, 129.6, 127.9, 127.9, 127.4, 127.2, 127.1, 125.3, 125.1, 116.9, 113.4, 109.4, 106.4, 56.7, 32.6 ppm. HRMS (ESI): calcd for $\text{C}_{32}\text{H}_{26}\text{NOSi}$ $[\text{M}+\text{H}]^+$ 468.1778, found 468.1767. HPLC (Chiralpak AD-3) *i*-PrOH/hexane = 5/95, 1.0 mL/min, T = 28 °C, λ = 250 nm, t_r (major) = 7.3 min, t_r (minor) = 9.2 min, 90% *ee*. $[\alpha]_D^{29.6}$ = +71 (c = 0.1, CHCl_3).



(S)-11-(Benzyloxy)-1-methyl-5,12-diphenyl-1,5-dihydrobenzo[6,7]silepino[2,3,4,5-def]carbazole (4b)

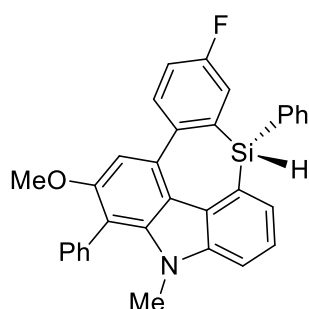
The product **4b** was purified via silica gel column chromatography ((petroleum ether/ethyl acetate = 80/1, v/v) as a white solid (29.6 mg, 55% yield). ^1H NMR (600 MHz, CDCl_3): δ = 7.88 (d, J = 7.1 Hz, 1H), 7.58 (d, J = 7.9 Hz, 1H), 7.53 (d, J = 7.4 Hz, 1H), 7.51 – 7.43 (m, 7H), 7.43 – 7.38 (m, 3H), 7.37 (s, 1H), 7.32 – 7.24 (m, 5H), 7.23 – 7.17 (m, 4H), 5.62 (s, 1H), 5.21 – 5.12 (m, 2H), 3.23 (s, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 154.6, 145.7, 141.3, 140.8, 137.6, 137.4, 136.7, 135.7, 135.3, 133.6, 133.2, 132.5, 131.6, 131.5, 130.2, 129.6, 128.3, 127.9, 127.8, 127.5, 127.4, 127.3, 127.0, 126.9, 125.3, 125.1, 117.2, 114.6, 109.4, 109.1, 71.5, 32.6 ppm. HRMS (ESI): calcd for $\text{C}_{38}\text{H}_{30}\text{NOSi}$ $[\text{M}+\text{H}]^+$ 544.2091, found 544.2088. HPLC (Chiralpak AD-3) *i*-PrOH/hexane = 2/98, 0.5 mL/min, T = 28 $^\circ\text{C}$, λ = 250 nm, t_r (major) = 14.0 min, t_r (minor) = 20.3 min, 85% *ee*. $[\alpha]_{\text{D}}^{29.8}$ = +27 (c = 0.1, CHCl_3).



(S)-1-Methyl-5,12-diphenyl-1,5-dihydrobenzo[6,7]silepino[2,3,4,5-def]carbazol-11-yl 4-methylbenzenesulfonate (4c)

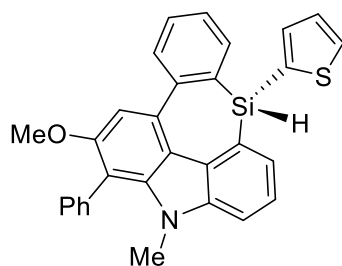
The product **4c** was purified via silica gel column chromatography ((petroleum ether/ethyl acetate = 40/1, v/v) as a white solid (41.2 mg, 68% yield). ^1H NMR (600 MHz, CDCl_3): δ = 7.90 (d, J = 7.2 Hz, 1H), 7.80 (s, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.59 – 7.51 (m, 3H), 7.45 (t, J = 7.3 Hz, 1H), 7.40 (d, J = 7.6 Hz, 2H), 7.38 – 7.33 (m, 3H), 7.32 – 7.26 (m, 5H), 7.25 – 7.21 (m, 2H), 7.06 (d, J = 8.1 Hz, 2H), 7.03 (d, J = 7.6 Hz, 1H), 5.65 (s, 1H), 3.16 (s, 3H), 2.37 (s,

3H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 145.3, 144.7, 144.6, 141.6, 140.0, 137.6, 136.8, 135.2, 133.4, 133.3, 133.1, 132.9, 132.9, 131.5, 131.3, 130.5, 129.7, 129.5, 128.9, 128.2, 127.9, 127.8, 127.7, 127.7, 127.4, 127.0, 126.4, 125.7, 120.9, 118.0, 115.5, 109.9, 32.7, 21.6 ppm. HRMS (ESI): calcd for $\text{C}_{38}\text{H}_{30}\text{NO}_3\text{SSi}$ $[\text{M}+\text{H}]^+$ 608.1710, found 608.1702. HPLC (Chiralpak AD-H) *i*-PrOH/hexane = 10/90, 1.0 mL/min, $T = 28\text{ }^\circ\text{C}$, $\lambda = 250\text{ nm}$, t_r (major) = 9.7 min, t_r (minor) = 14.4 min, 90% *ee*. $[\alpha]_{\text{D}}^{29.7} = +78$ ($c = 0.1$, CHCl_3).



(S)-7-Fluoro-11-methoxy-1-methyl-5,12-diphenyl-1,5-dihydrobenzo[6,7]silepino[2,3,4,5-def]carbazole (4d)

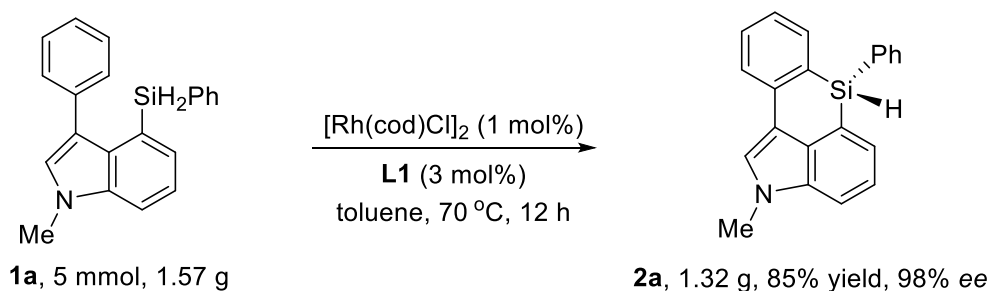
The product **4d** was purified via silica gel column chromatography ((petroleum ether/ethyl acetate = 80/1, v/v) as a white solid (38.6 mg, 80% yield). ^1H NMR (600 MHz, CDCl_3): δ = 7.79 – 7.75 (m, 1H), 7.55 (dd, $J = 8.4, 2.7\text{ Hz}$, 1H), 7.50 – 7.41 (m, 9H), 7.35 – 7.31 (m, 2H), 7.29 – 7.20 (m, 4H), 5.57 (s, 1H), 3.90 (s, 3H), 3.20 (s, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 162.0 (d, $J_{\text{C-F}} = 249.5\text{ Hz}$), 155.7, 141.9 (d, $J_{\text{C-F}} = 3.2\text{ Hz}$), 141.3, 141.0, 136.4, 135.9 (d, $J_{\text{C-F}} = 4.1\text{ Hz}$), 135.6, 135.3, 134.6 (d, $J_{\text{C-F}} = 6.9\text{ Hz}$), 132.7, 131.4 (d, $J_{\text{C-F}} = 10.4\text{ Hz}$), 129.9, 128.1, 127.9 (d, $J_{\text{C-F}} = 1.7\text{ Hz}$), 127.8, 127.4, 126.3, 125.4, 125.2, 122.6 (d, $J_{\text{C-F}} = 19.1\text{ Hz}$), 117.0 (d, $J_{\text{C-F}} = 20.7\text{ Hz}$), 116.7, 113.4, 109.6, 106.4, 56.7, 32.6 ppm. ^{19}F NMR (565 MHz, CDCl_3): δ = -116.27 ppm. HRMS (ESI): calcd for $\text{C}_{32}\text{H}_{25}\text{FNOSi}$ $[\text{M}+\text{H}]^+$ 486.1684, found 486.1679. HPLC (Chiralpak AD-3) *i*-PrOH/hexane = 5/95, 1.0 mL/min, $T = 28\text{ }^\circ\text{C}$, $\lambda = 250\text{ nm}$, t_r (major) = 6.2 min, t_r (minor) = 8.8 min, 91% *ee*. $[\alpha]_{\text{D}}^{29.8} = +69$ ($c = 0.1$, CHCl_3).



(S)-11-Methoxy-1-methyl-12-phenyl-5-(thiophen-2-yl)-1,5-dihydrobenzo[6,7]silepino[2,3,4,5-*def*]carbazole (4e)

The product **4e** was purified via silica gel column chromatography ((petroleum ether/ethyl acetate = 80/1, v/v) as a white solid (18.7 mg, 40% yield). ^1H NMR (600 MHz, CDCl_3): δ = 7.92 (d, J = 7.3 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 7.6 Hz, 1H), 7.55 (d, J = 4.8 Hz, 1H), 7.53 – 7.42 (m, 8H), 7.36 (s, 1H), 7.33 (d, J = 7.8 Hz, 1H), 7.20 (d, J = 3.2 Hz, 1H), 7.08 (t, J = 3.9 Hz, 1H), 5.75 (s, 1H), 3.92 (s, 3H), 3.21 (s, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 155.8, 145.6, 141.3, 141.0, 137.4, 137.1, 136.3, 135.6, 133.1, 132.5, 132.3, 131.9, 131.5, 131.5, 130.4, 128.3, 127.9, 127.4, 127.1, 127.0, 125.4, 124.8, 116.8, 113.4, 109.6, 106.4, 56.7, 32.6 ppm. HRMS (ESI): calcd for $\text{C}_{30}\text{H}_{24}\text{NOSSi}$ $[\text{M}+\text{H}]^+$ 474.1342, found 474.1339. HPLC (Chiralpak AD-3) *i*-PrOH/hexane = 5/95, 1.0 mL/min, T = 28 $^\circ\text{C}$, λ = 250 nm, t_r (major) = 7.7 min, t_r (minor) = 10.2 min, 86% *ee*. $[\alpha]_{\text{D}}^{29.7}$ = +59 (c = 0.1, CHCl_3).

V. Gram-Scale Reaction



A 250 mL Schlenk tube was charged with **1a** (1.57 g, 5 mmol), $[\text{Rh}(\text{cod})\text{Cl}]_2$ (24.7 mg, 1 mol%), **L1** (83.5 mg, 3 mol%), and toluene (50 mL) in glovebox. The tube was sealed, then removed from the glovebox, and the mixture was stirred at 70 °C for 12 h. After the completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80/1, v/v) afforded the product **2a** as a white solid (1.32 g, 85% yield). HPLC (Chiralpak OD-3) *i*-PrOH/hexane = 5/95, 1.0 mL/min, $T = 28\text{ }^\circ\text{C}$, $\lambda = 220\text{ nm}$, t_r (major) = 11.6 min, t_r (minor) = 16.4 min, 98% ee. $[\alpha]_{\text{D}}^{25.0} = +188$ ($c = 0.1$, CHCl_3).

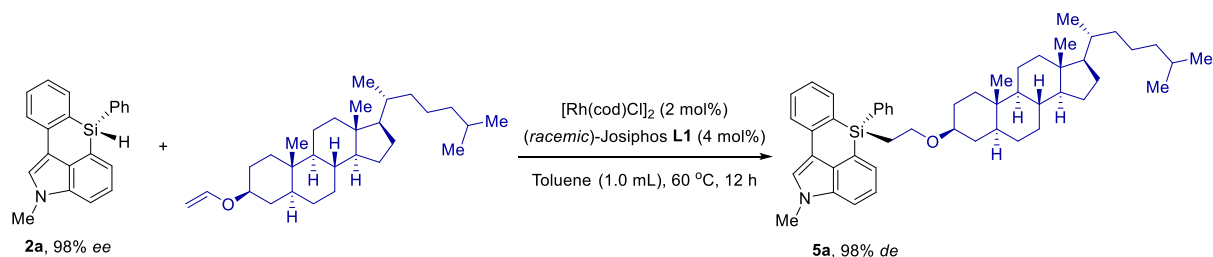
VI. Photophysical Data of Selected Si-Stereogenic Heterocycles

Table S2. Absorption Maxima, Emission Maxima, and Stokes Shifts of Si-Stereogenic Heterocycles

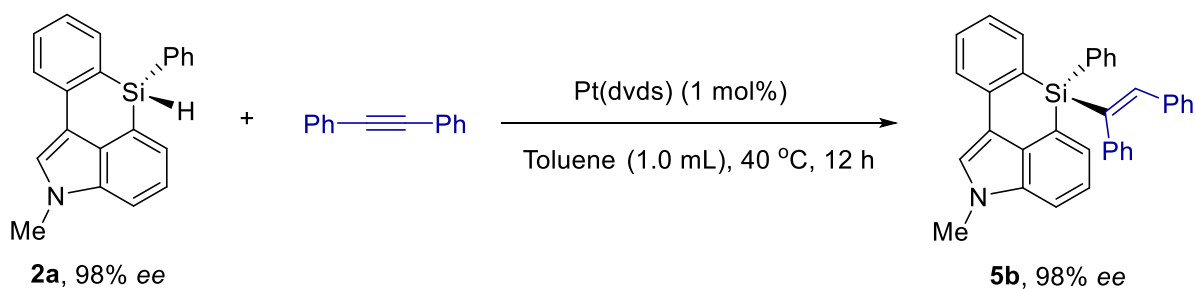
Compound	λ_{abs} (nm) ^a	λ_{em} (nm) ^b	Stokes Shift (cm ⁻¹)
2i	367	417	3268
2u	333, 348	378	3575
2v	365, 382	396, 416	2140
4b	339	409	5049
4c	376	400	1596
4d	339	405	4807

^aAbsorption maximum in CHCl₃ at 10⁻⁵ mol/L. ^bEmission maximum in CHCl₃ at 10⁻⁵ mol/L.

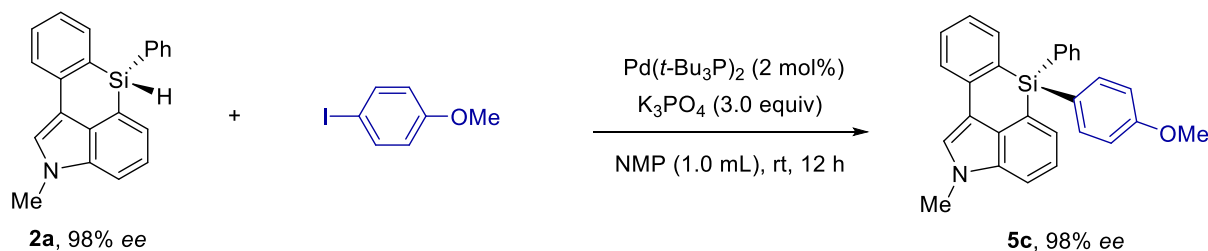
VII. Derivatization of Si-Stereogenic Heterocycles



To a 5 mL tube containing **2a** (0.1 mmol, 31.1 mg, 1.0 equiv), vinyl ether (0.2 mmol, 82.9 mg, 2.0 equiv), $[\text{Rh}(\text{cod})\text{Cl}]_2$ (1.0 mg, 2 mol%) and (*racemic*)-Josiphos **L1** (2.2 mg, 4 mol%) was added toluene (1.0 mL) under argon atmosphere (in glovebox). Then the tube was sealed with a screw cap and taken out of the glovebox. The reaction mixture stirred at 60 °C for 12 h. After the completion of the reaction, the mixture was filtered through a plug of celite with CH_2Cl_2 . The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel to give **5a** as a white solid (56.1 mg, 77% yield). ^1H NMR (600 MHz, CDCl_3) δ = 7.75 (d, J = 7.8 Hz, 1H), 7.63 (d, J = 7.2 Hz, 1H), 7.58 – 7.52 (m, 3H), 7.45 (d, J = 6.6 Hz, 1H), 7.38 – 7.22 (m, 6H), 7.13 (t, J = 7.8 Hz, 1H), 3.82 (s, 3H), 3.54 – 3.45 (m, 2H), 3.03 – 2.95 (m, 1H), 1.92 (d, J = 12.6 Hz, 1H), 1.84 – 1.73 (m, 3H), 1.64 – 1.55 (m, 2H), 1.54 – 1.47 (m, 2H), 1.44 – 1.17 (m, 11H), 1.16 – 0.90 (m, 12H), 0.90 – 0.82 (m, 10H), 0.70 (s, 3H), 0.61 (s, 3H), 0.55 – 0.46 (m, 1H) ppm. ^{13}C NMR (150 MHz, CDCl_3) δ = 139.4, 137.1, 135.6, 135.3, 134.8, 131.7, 129.5, 129.3, 129.1, 127.8, 126.0, 125.2, 124.7, 124.4, 122.6, 122.3, 115.7, 110.3, 77.9, 64.2, 56.5, 56.3, 54.4, 44.8, 42.6, 40.0, 39.5, 36.9, 36.2, 35.8, 35.7, 35.4, 34.6, 33.0, 32.1, 28.8, 28.2, 28.2, 28.0, 24.2, 23.8, 22.80, 22.5, 21.2, 18.6, 17.3, 12.2, 12.0. ppm. HRMS (ESI): calcd for $\text{C}_{50}\text{H}_{68}\text{NOSi}$ $[\text{M}+\text{H}]^+$ 726.5065, found 726.5083. HPLC (Chiralpak OD-3) *i*-PrOH/hexane = 15/85, 1.0 mL/min, T = 28 °C, λ = 230 nm, t_r (minor) = 11.0 min, t_r (major) = 40.4 min, 98% *de*. $[\alpha]_{\text{D}}^{29.7}$ = +17 (c = 0.1, CHCl_3).

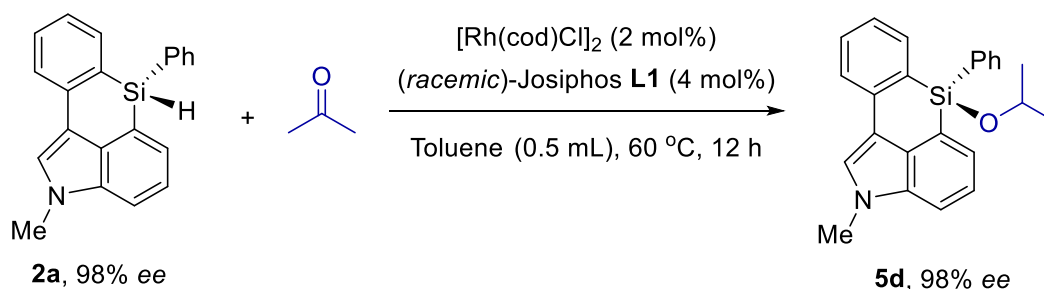


To a 5 mL tube containing **2a** (0.1 mmol, 31.1 mg, 1.0 equiv), 1,2-diphenylacetylene (0.2 mmol, 35.6 mg, 2.0 equiv), and $\text{Pt}(\text{dvds})$ (10 μL , 0.1 M in xylene) was added toluene (1.0 mL) under argon atmosphere (in glovebox). Then the tube was sealed with a screw cap and taken out of the glovebox. The reaction mixture stirred at 40 °C for 12 h. After the completion of the reaction, the mixture was filtered through a plug of celite with CH_2Cl_2 . The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel to give **5b** as a white solid (34.0 mg, 70% yield).¹¹ ^1H NMR (600 MHz, CDCl_3) δ = 7.74 (d, J = 7.9 Hz, 1H), 7.71 (dd, J = 7.4, 1.8 Hz, 2H), 7.61 (d, J = 6.8 Hz, 1H), 7.50 (s, 1H), 7.39 – 7.37 (m, 1H), 7.35 – 7.33 (m, 2H), 7.32 – 7.28 (m, 4H), 7.11 – 7.03 (m, 8H), 6.90 (dd, J = 7.4, 2.0 Hz, 2H), 6.87 (dd, J = 7.5, 1.8 Hz, 2H), 3.77 (s, 3H) ppm. ^{13}C NMR (150 MHz, CDCl_3) δ = 143.0, 141.9, 141.6, 139.7, 137.2, 136.8, 135.8, 135.7, 135.4, 131.6, 129.7, 129.6, 129.2, 128.5, 128.2, 127.9, 127.8, 127.8, 127.2, 126.9, 125.7, 125.3, 124.2, 123.7, 122.5, 122.4, 115.6, 110.3, 32.9 ppm. HRMS (ESI): calcd for $\text{C}_{35}\text{H}_{28}\text{NSi}$ $[\text{M}+\text{H}]^+$ 490.1986, found 490.1981. HPLC (Chiralpak AD-3) *i*-PrOH/hexane = 5/95, 1.0 mL/min, T = 28 °C, λ = 250 nm, t_r (major) = 7.4 min, t_r (minor) = 17.0 min, 98% ee. $[\alpha]_{\text{D}}^{25.0}$ = -35 (c = 0.1, CHCl_3).



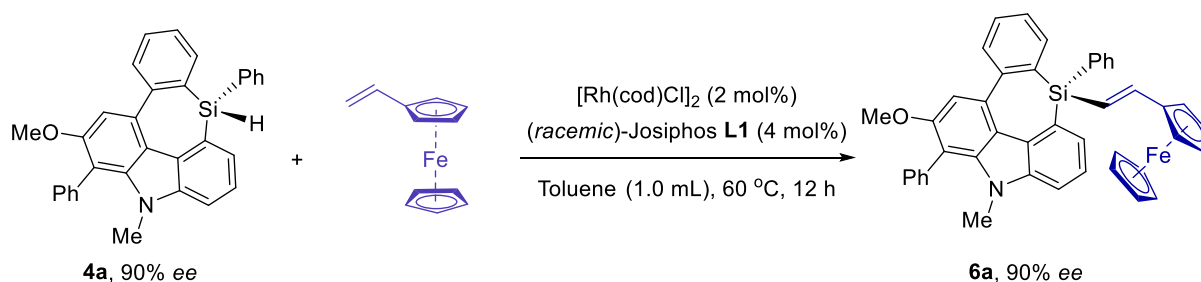
To a 5 mL tube containing **2a** (0.1 mmol, 31.1 mg, 1.0 equiv), 1-iodo-4-methoxybenzene (0.2 mmol, 46.8 mg, 2.0 equiv), $\text{Pd}(t\text{-Bu}_3\text{P})_2$ (1.0 mg, 2 mol%) and K_3PO_4 (0.3 mmol, 63.7 mg, 3.0 equiv) was added 1-Methyl-2-pyrrolidinone (NMP, 1.0 mL) under argon atmosphere (in glovebox). Then the tube was sealed with a screw cap and taken out of the glovebox. The

reaction mixture stirred at room temperature for 12 h. The mixture was quenched with H₂O and extracted with ethyl acetate. The organic layer was washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give **5c** as a white solid (30.1 mg, 72% yield). ¹H NMR (600 MHz, CDCl₃) δ = 7.79 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 7.4 Hz, 1H), 7.61 (d, *J* = 7.7 Hz, 2H), 7.57 (s, 1H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 6.6 Hz, 1H), 7.40 – 7.26 (m, 6H), 7.14 (t, *J* = 7.3 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 2H), 3.82 (s, 3H), 3.76 (s, 3H) ppm. ¹³C NMR (150 MHz, CDCl₃) δ = 160.7, 139.6, 137.4, 136.5, 136.5, 135.8, 135.4, 131.7, 129.6, 129.2, 127.8, 126.9, 126.4, 125.4, 124.8, 124.6, 122.7, 122.4, 115.7, 113.6, 110.4, 55.0, 33.0 ppm. HRMS (ESI): calcd for C₂₈H₂₄NOSi [M+H]⁺ 418.1622, found 418.1617. HPLC (Chiralpak OD-3) *i*-PrOH/hexane = 5/95, 1.0 mL/min, T = 28 °C, λ = 210 nm, *t_r* (minor) = 16.4 min, *t_r* (major) = 21.3 min, 98% *ee*. [α]_D^{29.6} = -18 (*c* = 0.1, CHCl₃).



To a 5 mL tube containing **2a** (0.05 mmol, 15.6 mg, 1.0 equiv), acetone (0.1 mmol, 82.9 mg, 2.0 equiv), [Rh(cod)Cl]₂ (0.5 mg, 2 mol%) and (*racemic*)-Josiphos **L1** (1.1 mg, 4 mol%) was added toluene (0.5 mL) under argon atmosphere (in glovebox). Then the tube was sealed with a screw cap and taken out of the glovebox. The reaction mixture stirred at 60 °C for 12 h. After the completion of the reaction, the mixture was filtered through a plug of celite with CH₂Cl₂. The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel to give **5d** as a white solid (11.0 mg, 60% yield). ¹H NMR (600 MHz, CDCl₃) δ = 7.79 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 7.4 Hz, 1H), 7.66 – 7.64 (m, 2H), 7.61 (s, 1H), 7.56 (d, *J* = 6.8 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.41 – 7.39 (m, 1H), 7.36 (d, *J* = 7.0 Hz, 1H), 7.34 – 7.29 (m, 3H), 7.16 (t, *J* = 7.3 Hz, 1H), 3.99 (dt, *J* = 12.1, 6.0 Hz, 1H), 3.86 (s, 3H), 1.06 (d, *J* = 1.7 Hz, 3H), 1.05 (d, *J* = 1.7 Hz, 3H) ppm. ¹³C NMR (150 MHz, CDCl₃) δ =

140.1, 136.6, 135.8, 135.5, 134.9, 132.1, 130.0, 129.9, 129.5, 127.6, 126.3, 125.7, 125.0, 124.5, 122.5, 122.2, 115.1, 110.9, 65.9, 33.0, 25.5, 25.4 ppm. HRMS (ESI): calcd for $C_{24}H_{24}NOSi$ $[M+H]^+$ 370.1622, found 370.1616. HPLC (Chiralpak AD-3) *i*-PrOH/hexane = 5/95, 1.0 mL/min, $T = 28\text{ }^{\circ}\text{C}$, $\lambda = 250\text{ nm}$, t_r (major) = 4.9 min, t_r (minor) = 15.8 min, 98% *ee*. $[\alpha]_D^{25.0} = +88$ ($c = 0.1$, $CHCl_3$).



To a 5 mL tube containing **4a** (0.05 mmol, 23.4 mg, 1.0 equiv), vinyl ferrocene (0.1 mmol, 22.7 mg, 2.0 equiv), $[Rh(cod)Cl]_2$ (0.5 mg, 2 mol%) and (*racemic*)-Josiphos **L1** (1.1 mg, 4 mol%) was added toluene (1.0 mL) under argon atmosphere (in glovebox). Then the tube was sealed with a screw cap and taken out of the glovebox. The reaction mixture stirred at $60\text{ }^{\circ}\text{C}$ for 12 h. After the completion of the reaction, the mixture was filtered through a plug of celite with CH_2Cl_2 . The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel to give **6a** as an orange solid (16.8 mg, 50% yield). 1H NMR (600 MHz, $CDCl_3$) $\delta = 7.83$ (d, $J = 8.0$ Hz, 1H), 7.70 (dd, $J = 7.4$, 1.2 Hz, 1H), 7.64 (d, $J = 6.7$ Hz, 2H), 7.56 (td, $J = 7.8$, 1.2 Hz, 1H), 7.49 – 7.42 (m, 4H), 7.41 – 7.35 (m, 7H), 7.35 – 7.31 (m, 2H), 6.46 (d, $J = 18.8$ Hz, 1H), 6.21 (d, $J = 18.8$ Hz, 1H), 4.30 (s, 1H), 4.26 (s, 1H), 4.17 (d, $J = 1.2$ Hz, 2H), 3.89 (s, 3H), 3.80 (s, 5H), 3.20 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) $\delta = 155.7$, 148.2, 146.4, 141.4, 140.8, 138.0, 136.7, 136.4, 135.8, 134.8, 134.0, 132.7, 131.5, 131.5, 129.9, 129.5, 129.4, 128.3, 127.8, 127.8, 127.8, 127.3, 126.8, 125.5, 124.9, 118.7, 117.2, 113.3, 109.1, 106.5, 83.7, 69.3, 69.2, 69.1, 67.3, 67.0, 56.8, 32.6 ppm. HRMS (ESI): calcd for $C_{44}H_{35}FeNOSi$ $[M]^+$ 677.1837, found 677.1821. HPLC (Chiralpak AD-3) *i*-PrOH/hexane = 5/95, 1.0 mL/min, $T = 28\text{ }^{\circ}\text{C}$, $\lambda = 250\text{ nm}$, t_r (minor) = 4.7 min, t_r (major) = 6.6 min, 90% *ee*. $[\alpha]_D^{29.7} = +114$ ($c = 0.1$, $CHCl_3$).

VIII. Single Crystal X-Ray Diffraction

Single crystal suitable for X-ray diffraction of compound **2j** was obtained from a solution of the compound **2j** (91% *ee*) in dichloromethane layered with hexane. The X-ray crystal structure is deposited in the Cambridge Crystallographic Data Centre under reference number CCDC 2031952. Diffraction Data were collected on a BrukerD8 venture employing Mo-K α radiation ($\lambda = 0.71073$ Å). The crystal structure was shown in **Figure S1**. The detailed information was listed in the **Tables S3**.

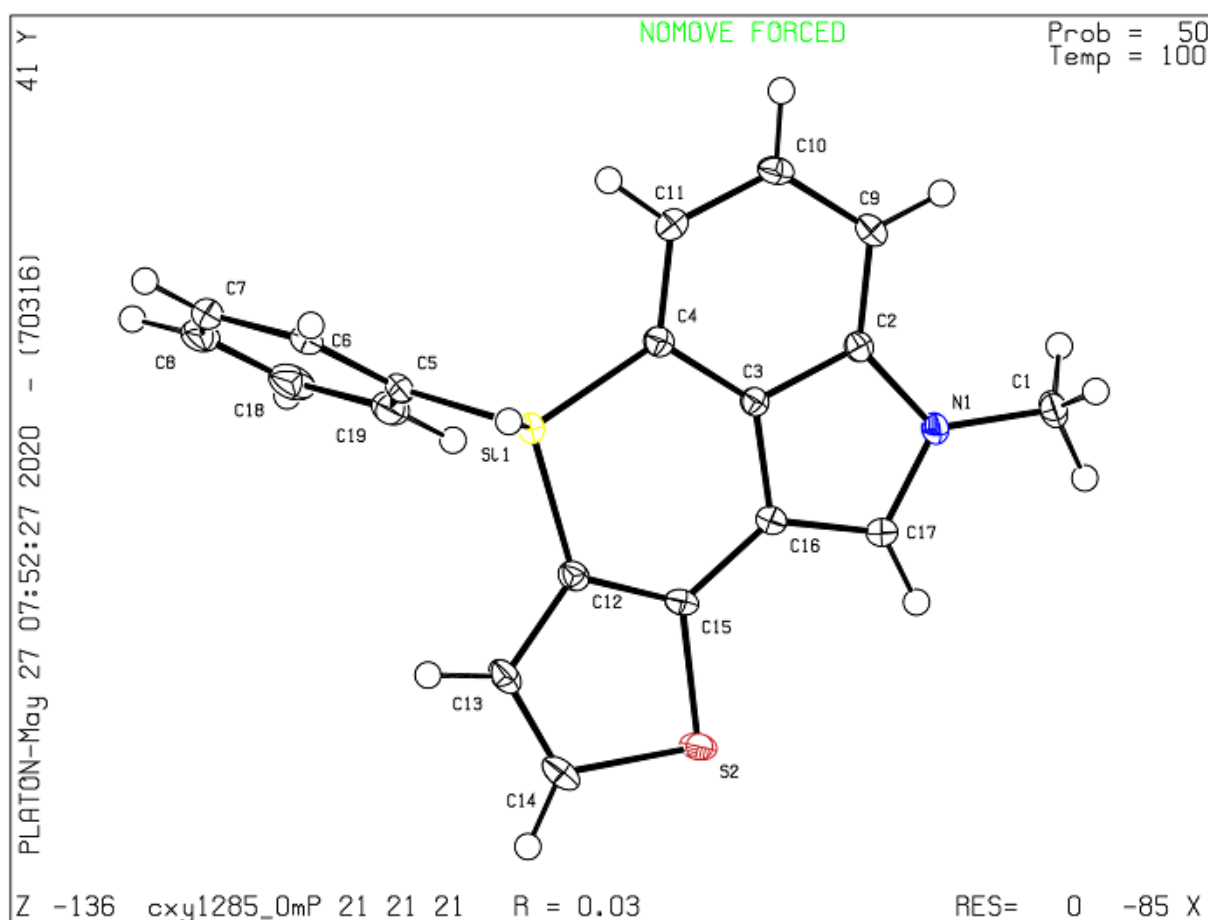


Figure S1. Crystal structure of **2j** (CCDC 2031952).

Table S3. Crystallographic Data and Structure Refinement for compound **2j**.

Compound	2j
CCDC deposition No.	2031952
Empirical formula	C ₁₉ H ₁₅ NSSi
Formula weight	317.47
Temperature	100 K
Crystal system, space group	orthorhombic, P2 ₁ 2 ₁ 2 ₁
Unit cell dimensions	$a = 7.3548(3) \text{ \AA}$ $\alpha = 90^\circ$ $b = 8.2124(3) \text{ \AA}$ $\beta = 90^\circ$ $c = 26.1737(9) \text{ \AA}$ $\gamma = 90^\circ$
Volume	1580.91(10) Å ³
Z, Calculated density	4, 1.334 g/cm ³
Absorption coefficient	0.276 mm ⁻¹
F(000)	664.0
Crystal size	0.35 × 0.31 × 0.23 mm ³
Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection	5.198 to 61.068°
Index ranges	$-7 \leq h \leq 10$, $-11 \leq k \leq 10$, $-37 \leq l \leq 31$
Reflections collected	16195
Independent reflections	4773 [$R_{\text{int}} = 0.0374$, $R_{\text{sigma}} = 0.0403$]
Data / restraints / parameters	4773/0/201
Goodness-of-fit on F ²	1.043
Final R indices [$I \geq 2\sigma(I)$]	$R_I = 0.0345$, $wR_2 = 0.0748$
R indices (all data)	$R_I = 0.0412$, $wR_2 = 0.0776$
Largest diff. peak/hole	0.34 / -0.17 e Å ⁻³
Flack parameter	-0.02(3)

Single crystal suitable for X-ray diffraction of compound **6a** was obtained from a solution of the compound **6a** (90% *ee*) in dichloromethane layered with methyl alcohol. The X-ray crystal structure is deposited in the Cambridge Crystallographic Data Centre under reference number CCDC 2031700. Diffraction Data were collected on a BrukerD8 venture employing Cu-K α radiation ($\lambda = 1.54178$ Å). The crystal structure was shown in **Figure S2**. The detailed information was listed in the **Tables S4**.

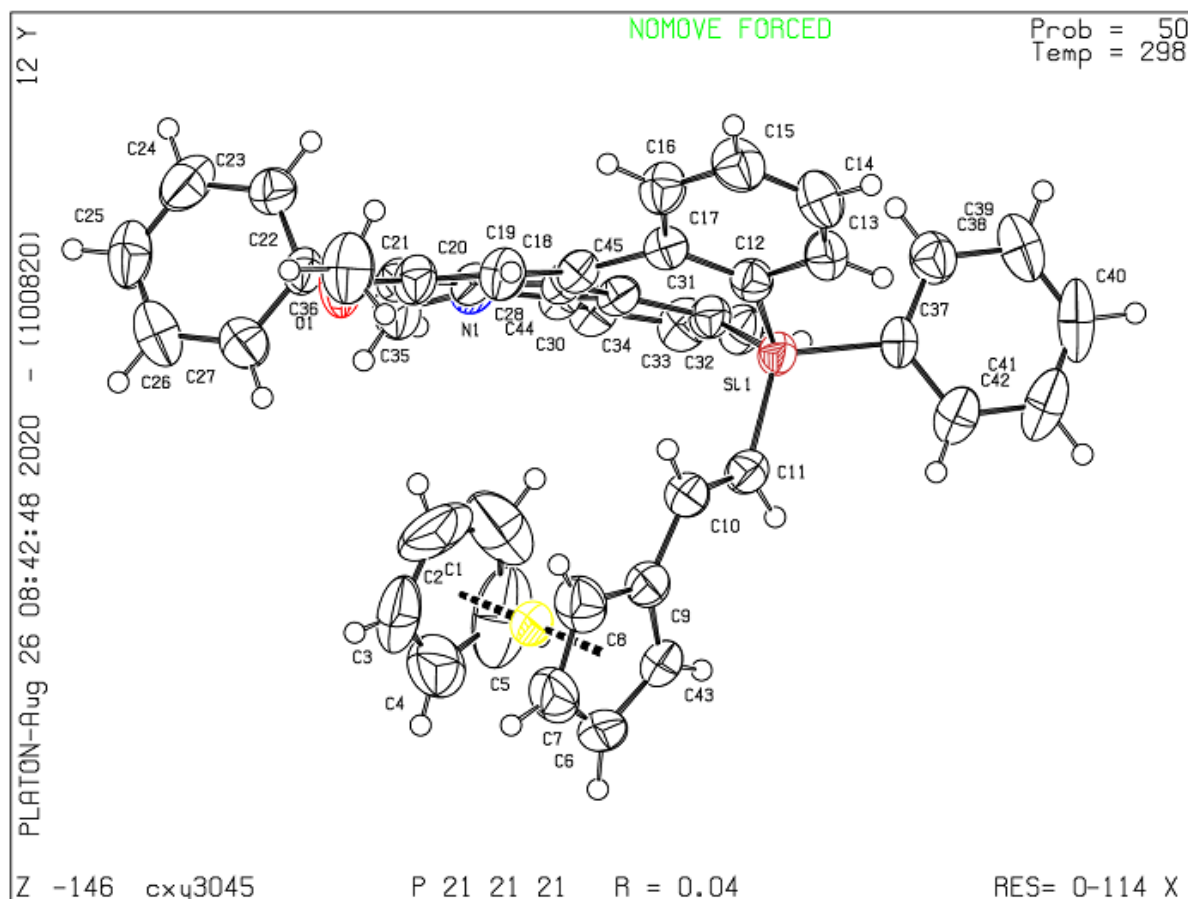


Figure S2. Crystal structure of **6a** (CCDC 2031700).

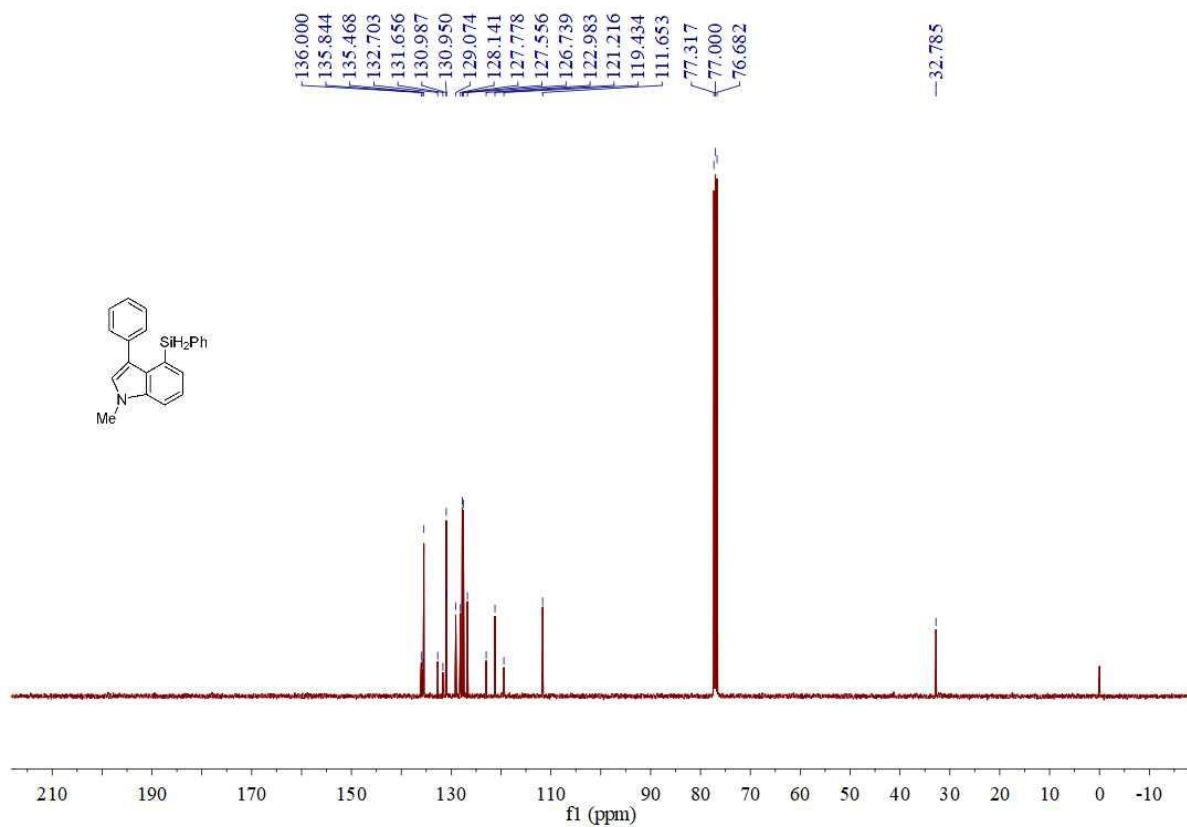
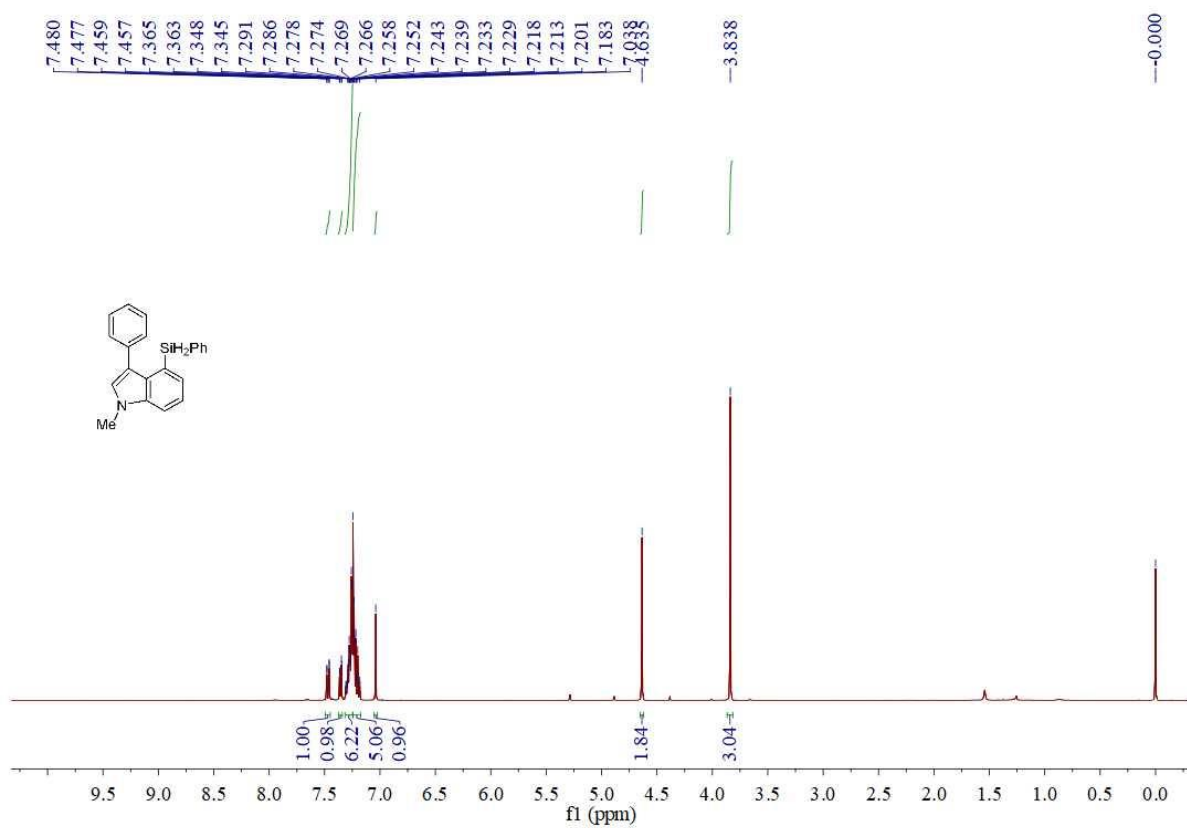
Table S4. Crystallographic Data and Structure Refinement for compound **6a**.

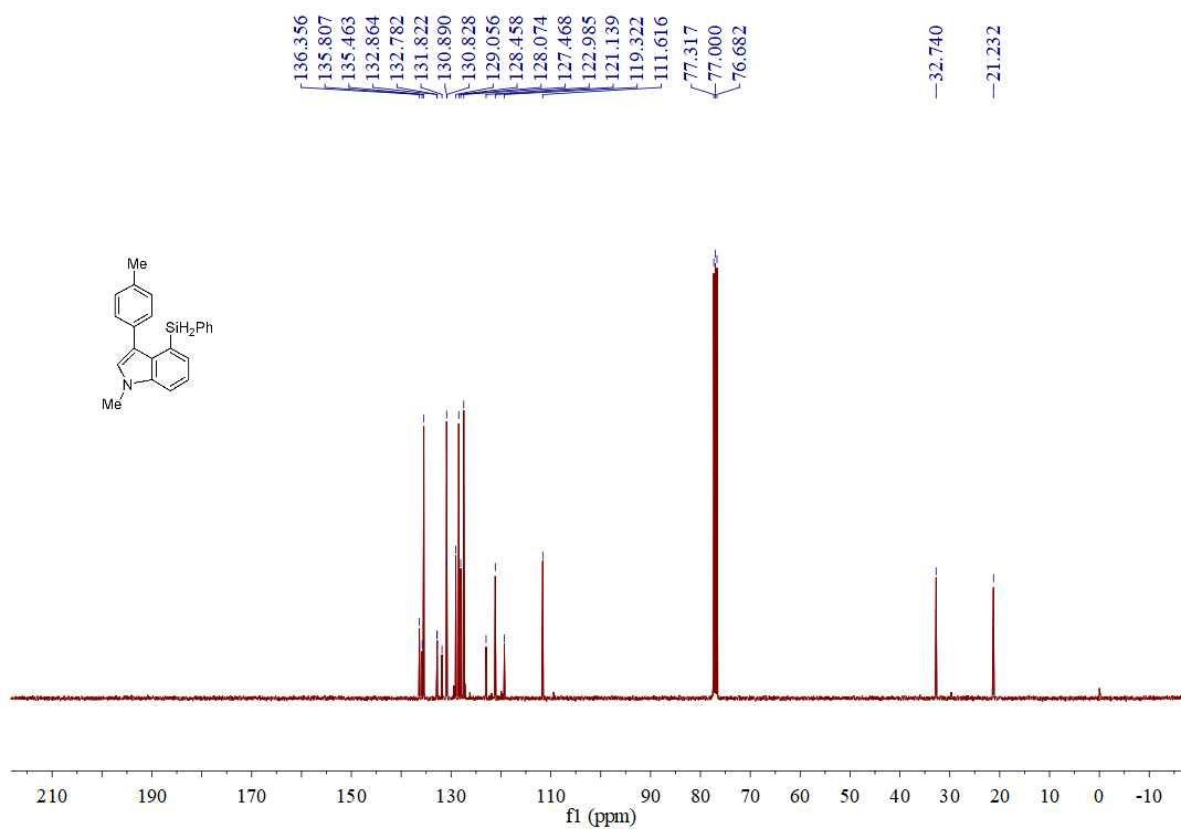
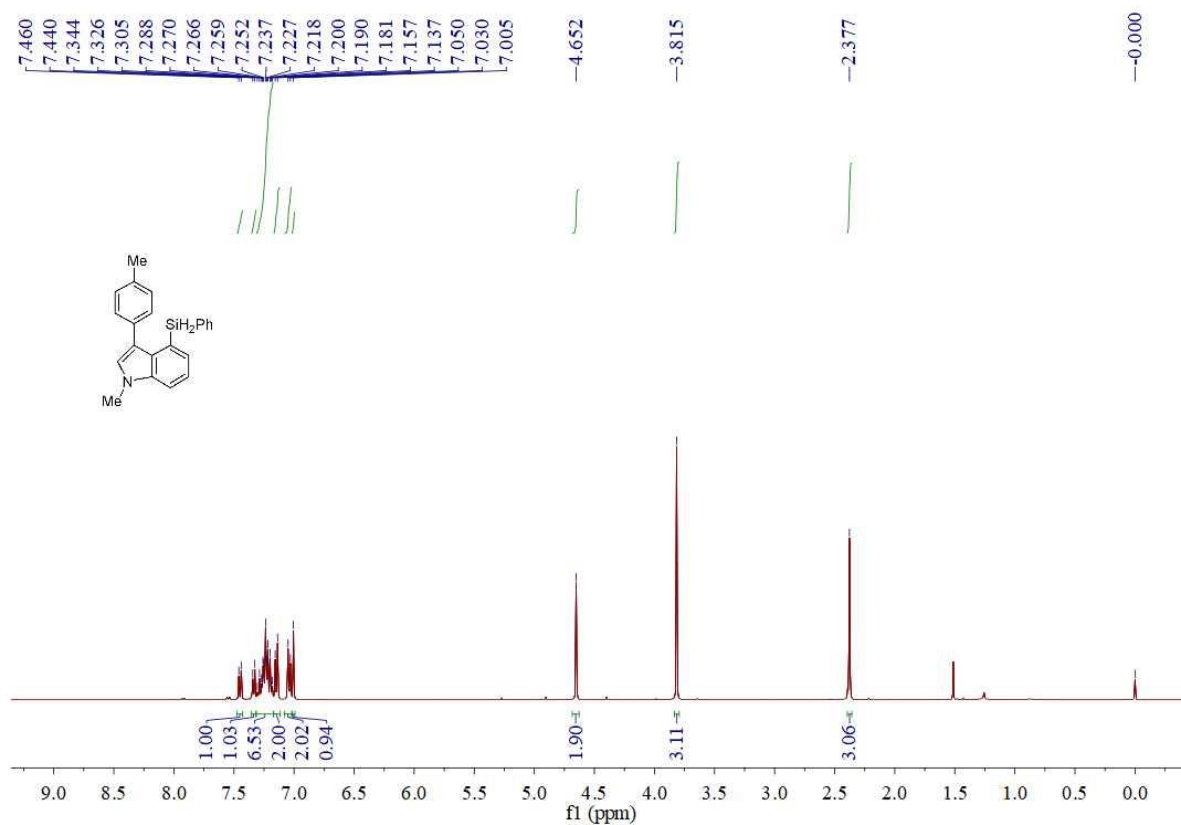
Compound	6a
CCDC deposition No.	2031700
Empirical formula	C ₄₄ H ₃₅ FeNOSi
Formula weight	677.67
Temperature	298 K
Crystal system, space group	orthorhombic, P2 ₁ 2 ₁ 2 ₁
Unit cell dimensions	$a = 10.5746(7) \text{ \AA}$ $\alpha = 90^\circ$ $b = 15.7664(9) \text{ \AA}$ $\beta = 90^\circ$ $c = 20.3486(12) \text{ \AA}$ $\gamma = 90^\circ$
Volume	3392.60(4) Å ³
Z, Calculated density	4, 1.327 g/cm ³
Absorption coefficient	4.177 mm ⁻¹
F(000)	1416.0
Crystal size	0.35 × 0.32 × 0.31 mm ³
Radiation	CuKα ($\lambda = 1.54178$)
2 θ range for data collection	7.092 to 136.874°
Index ranges	$-12 \leq h \leq 12$, $-18 \leq k \leq 18$, $-24 \leq l \leq 22$
Reflections collected	34876
Independent reflections	6213 [$R_{\text{int}} = 0.0858$, $R_{\text{sigma}} = 0.0573$]
Data / restraints / parameters	6213/0/436
Goodness-of-fit on F ²	0.979
Final R indices [$I \geq 2\sigma(I)$]	$R_I = 0.0373$, $wR_2 = 0.0891$
R indices (all data)	$R_I = 0.0430$, $wR_2 = 0.0914$
Largest diff. peak/hole	0.28 / -0.28 e Å ⁻³
Flack parameter	-0.034(5)

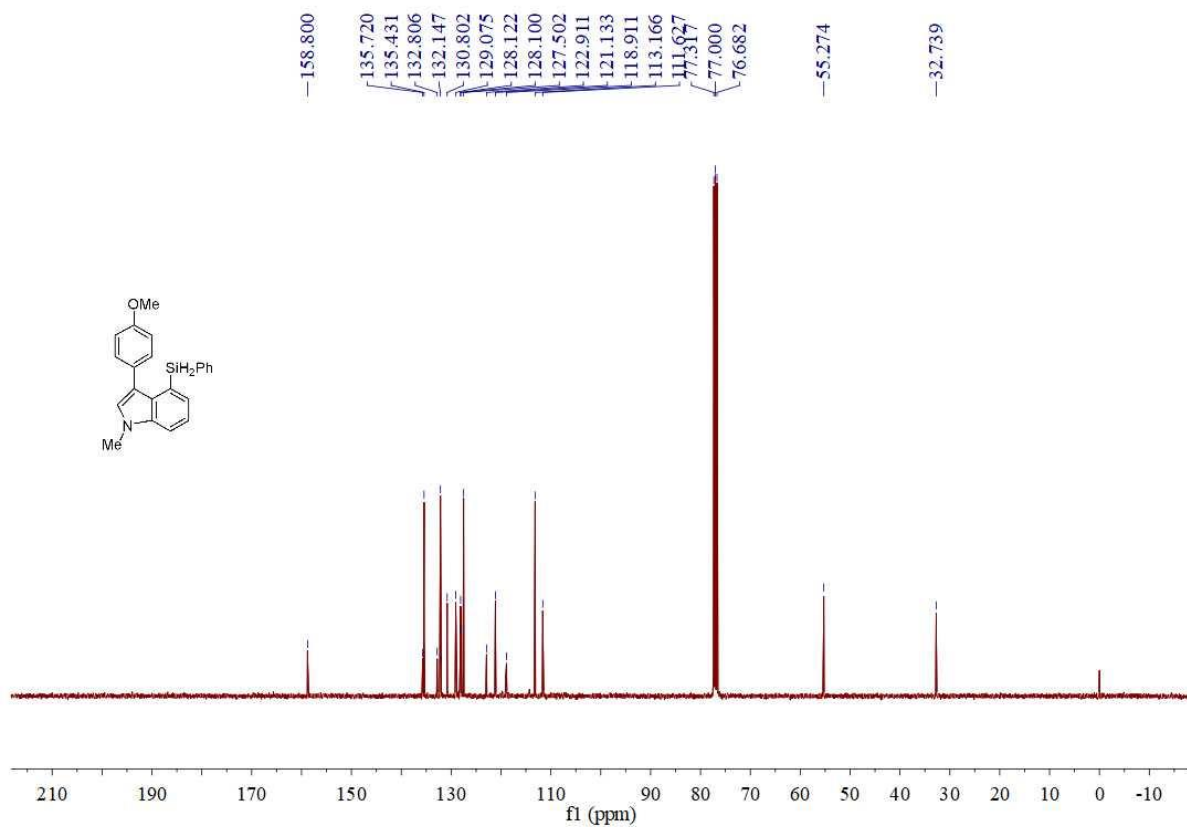
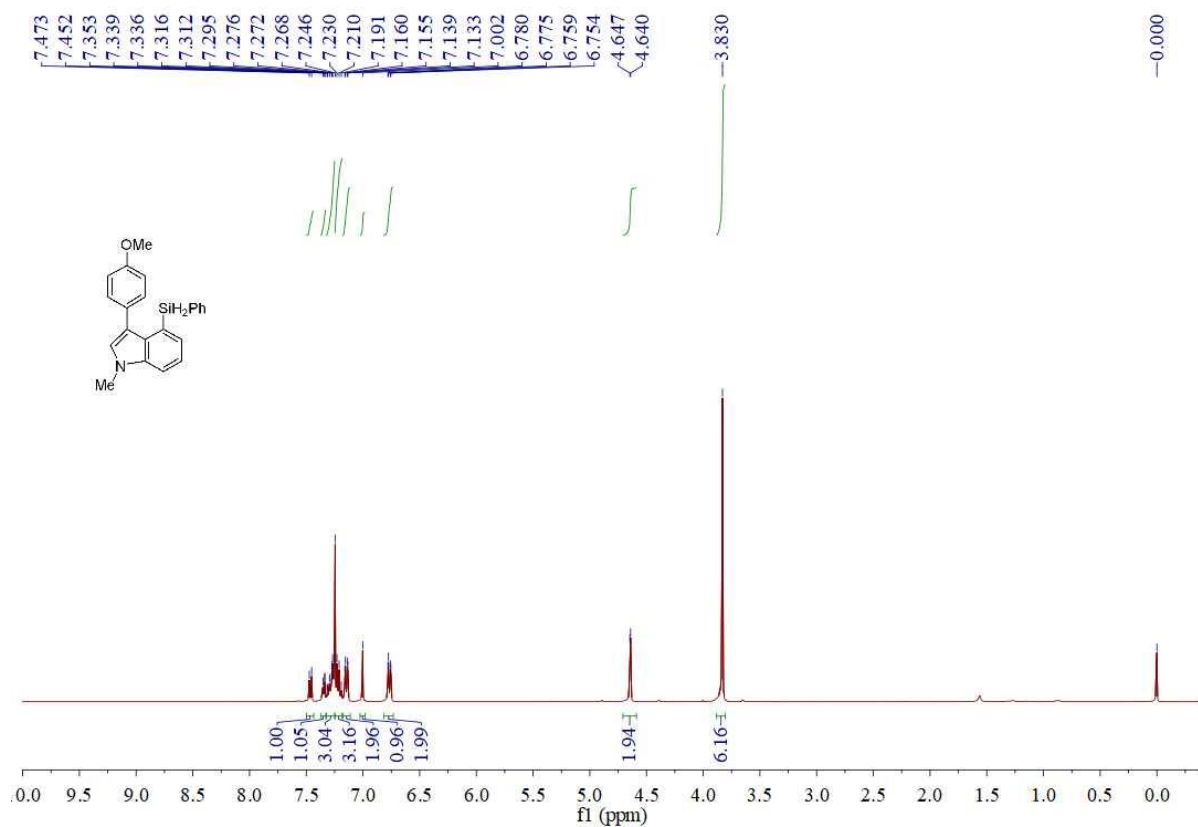
IX. References

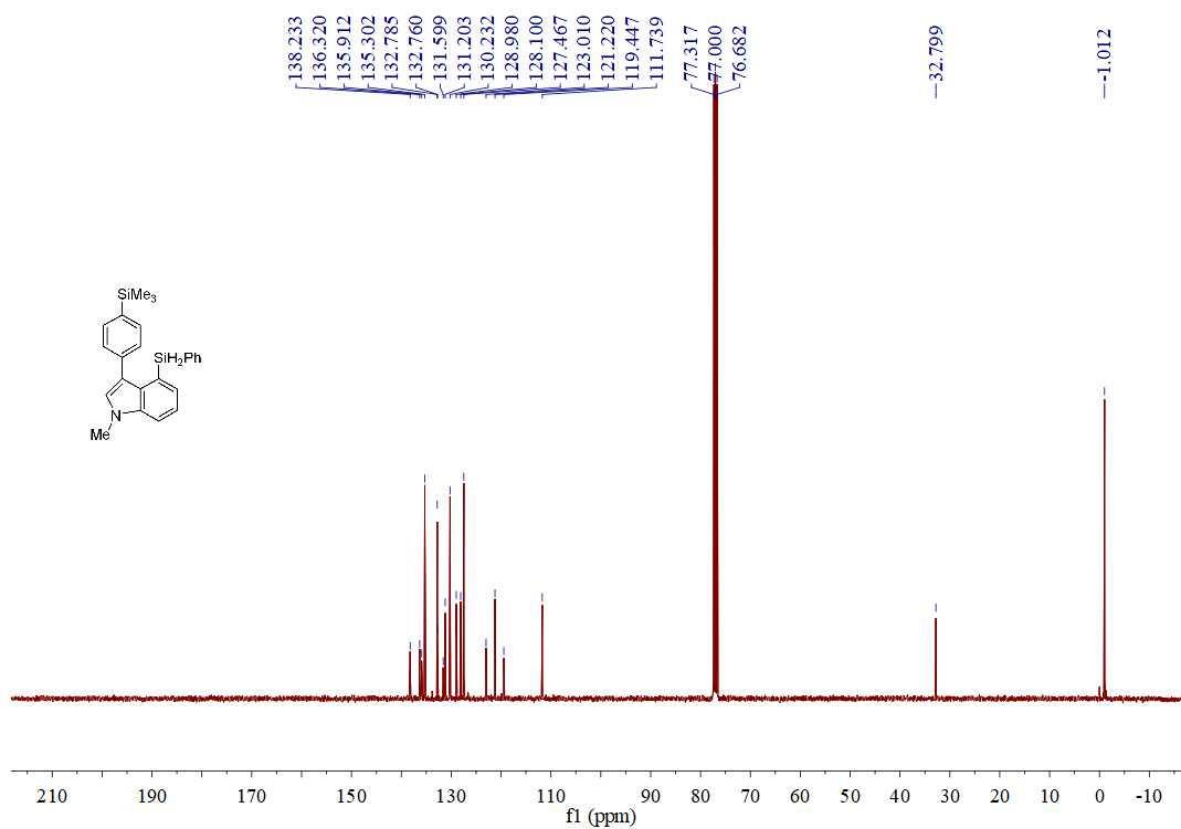
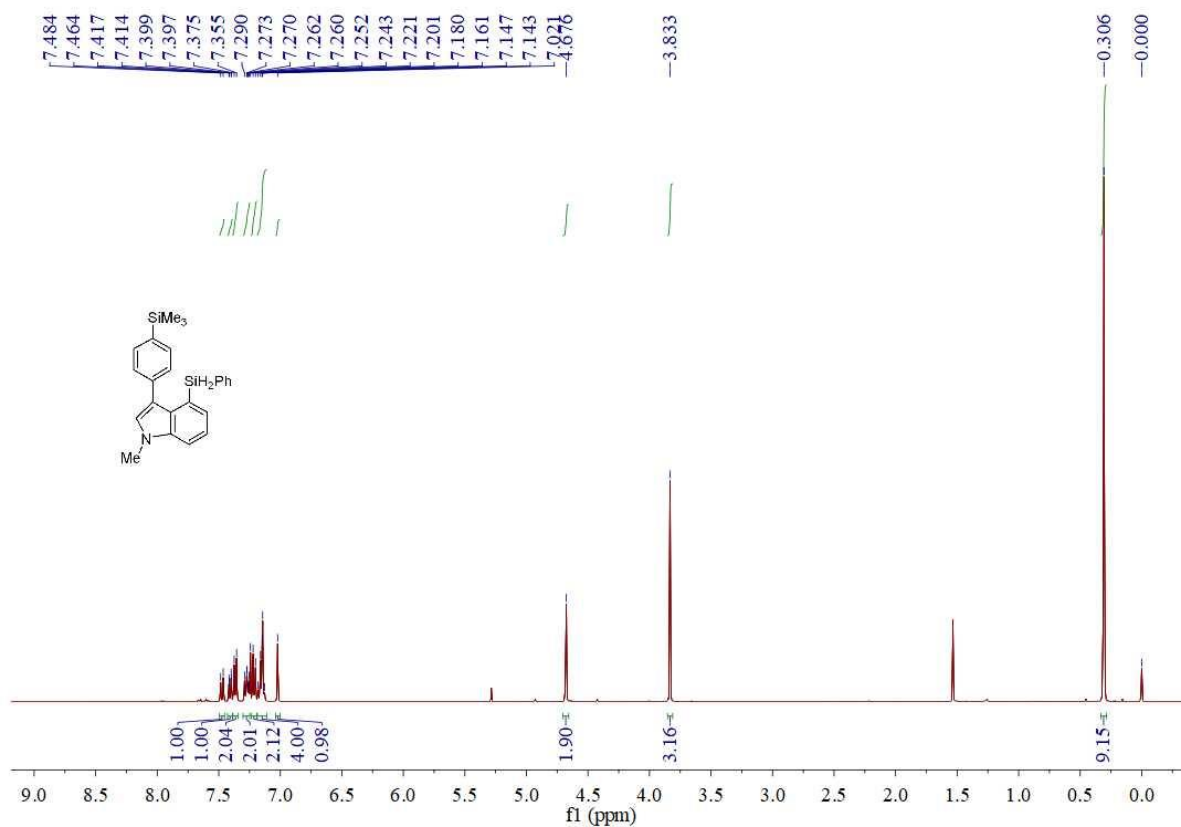
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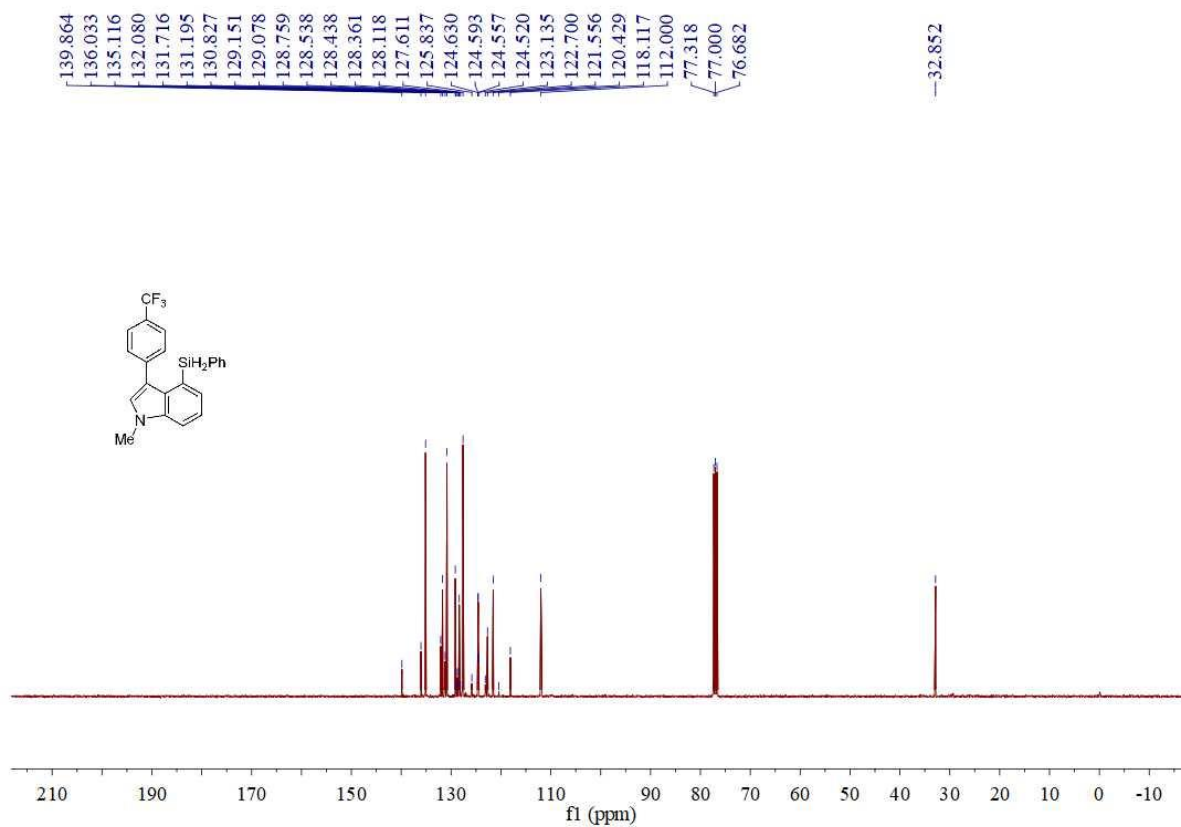
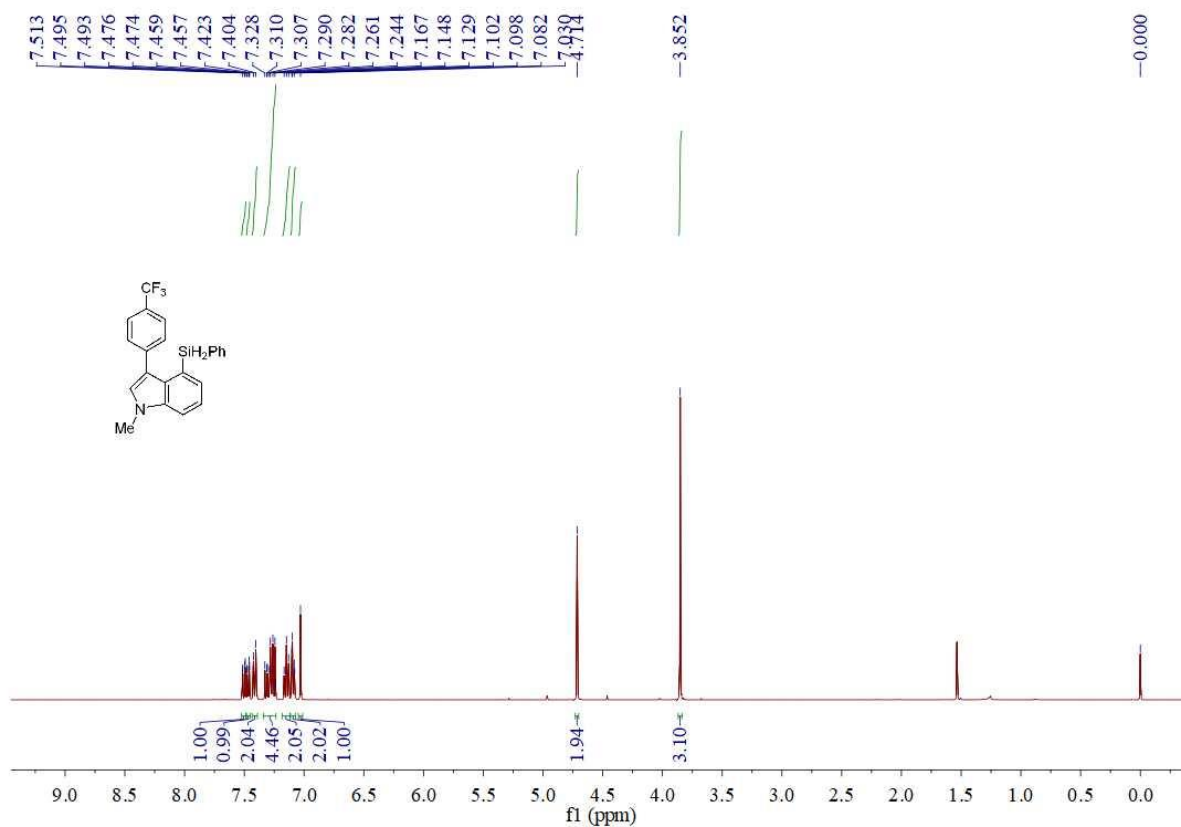
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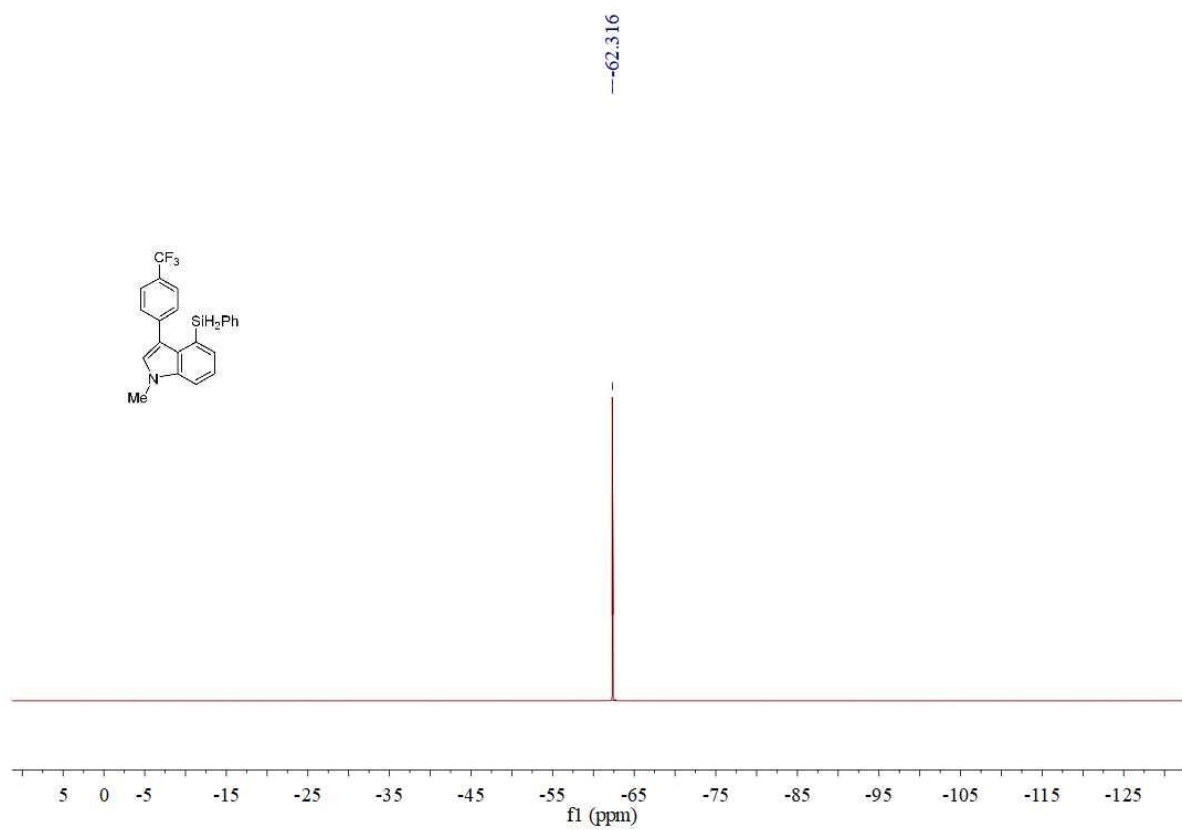


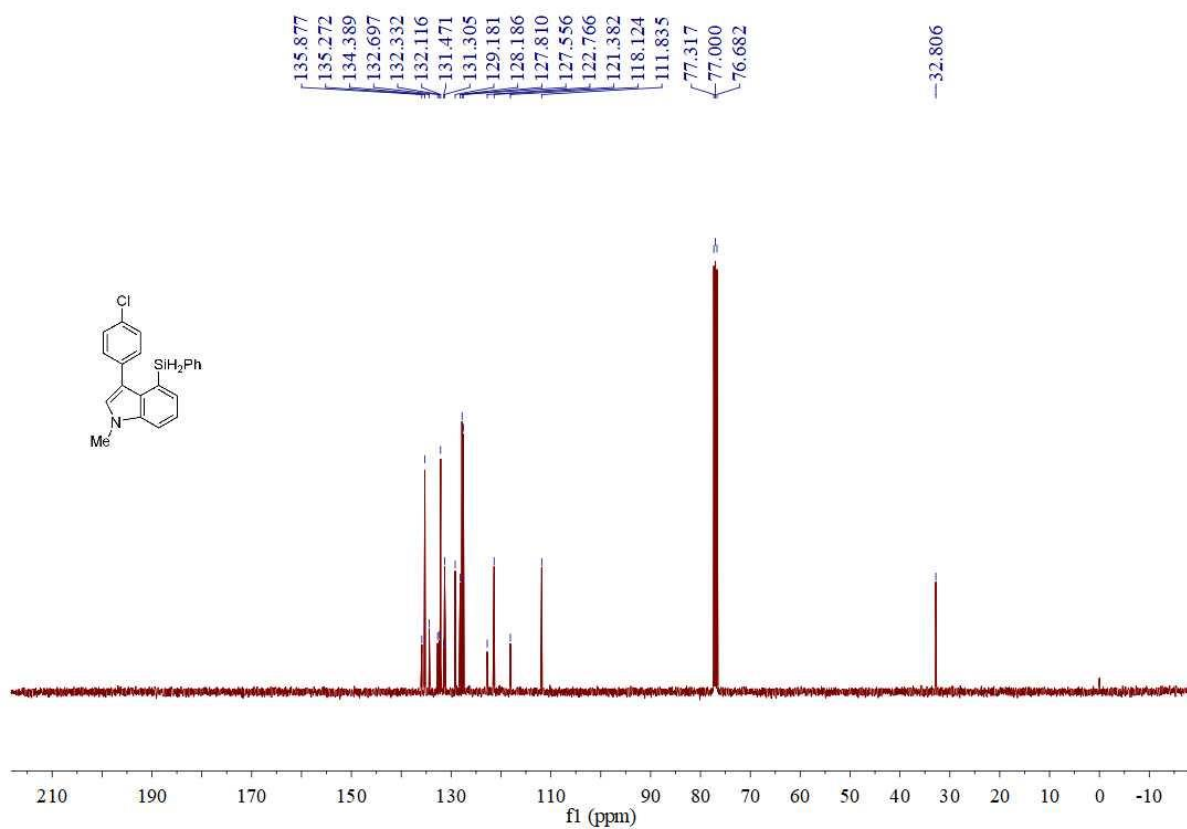
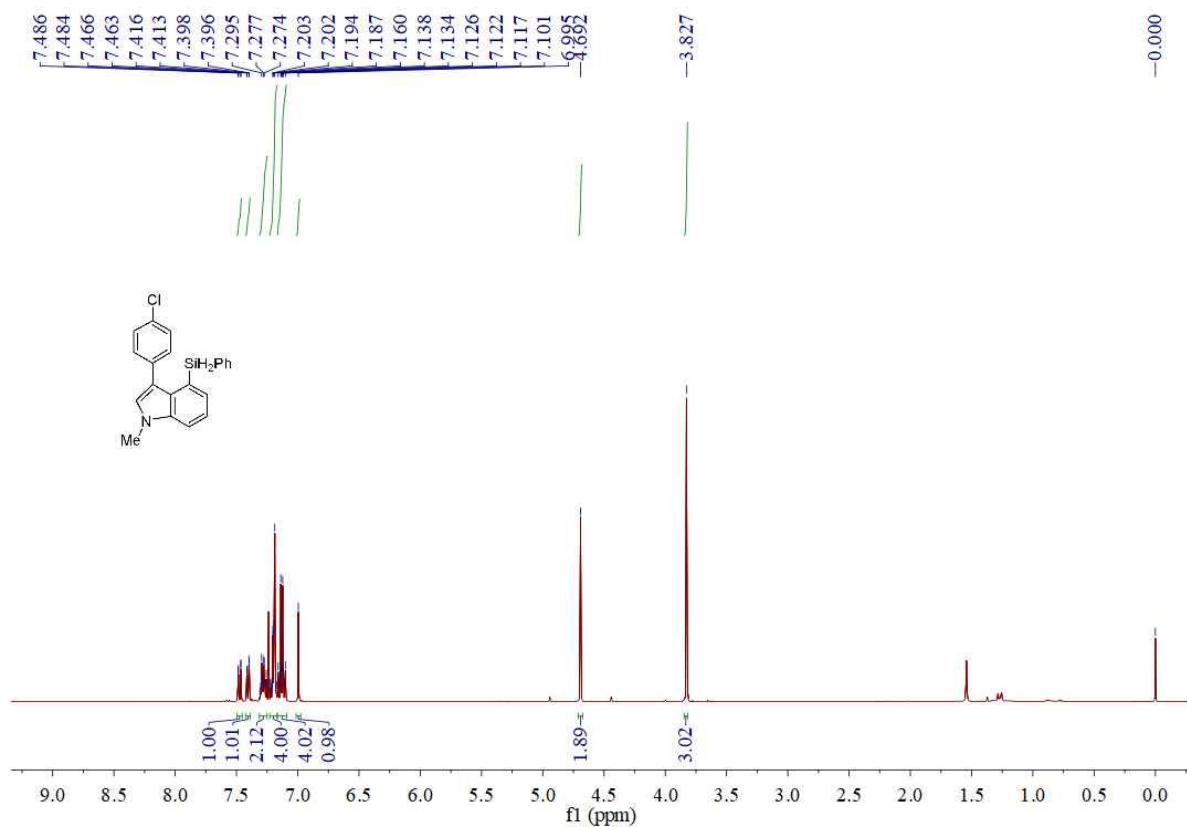


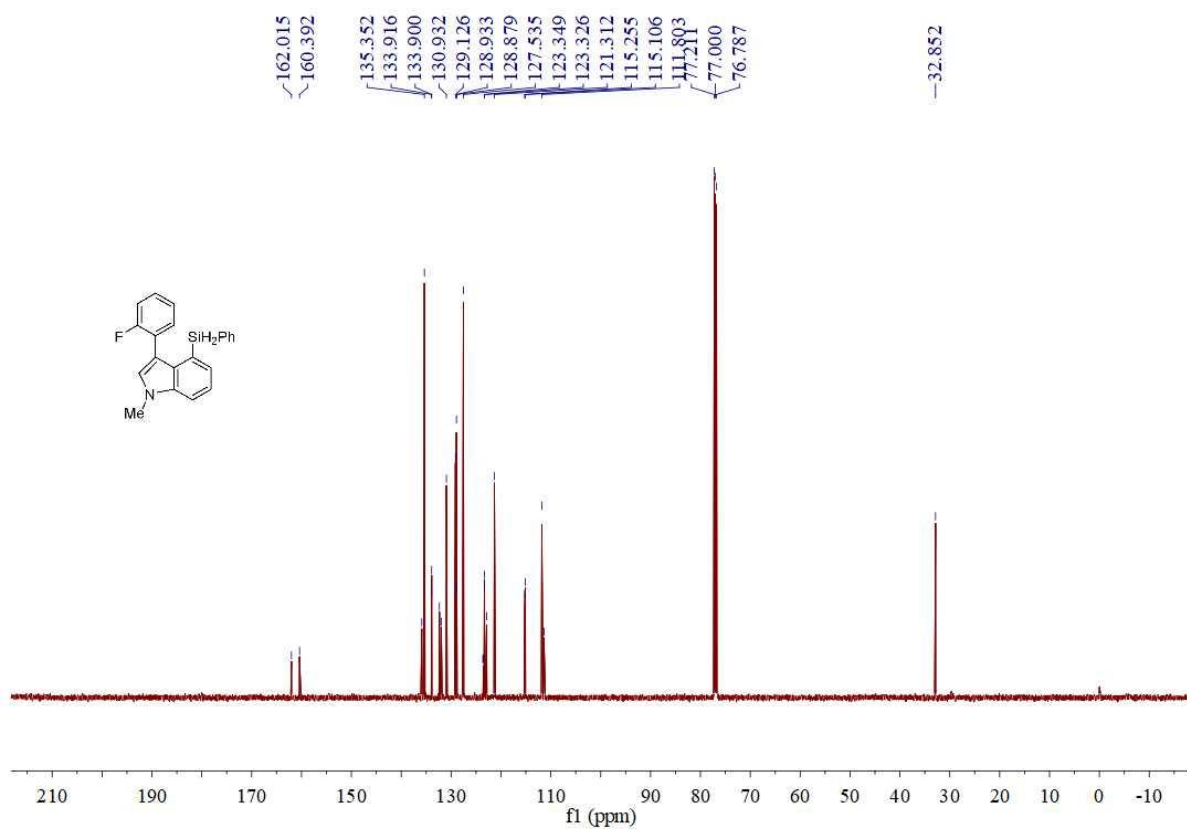
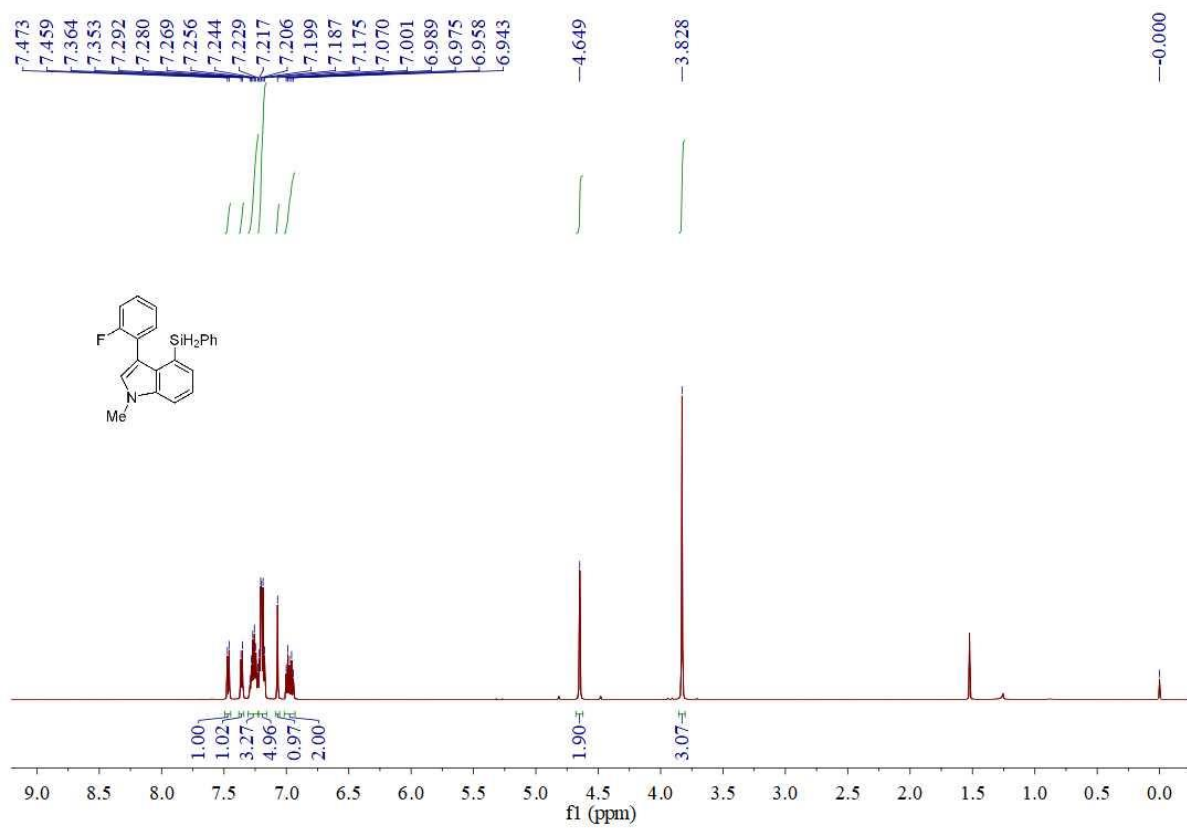


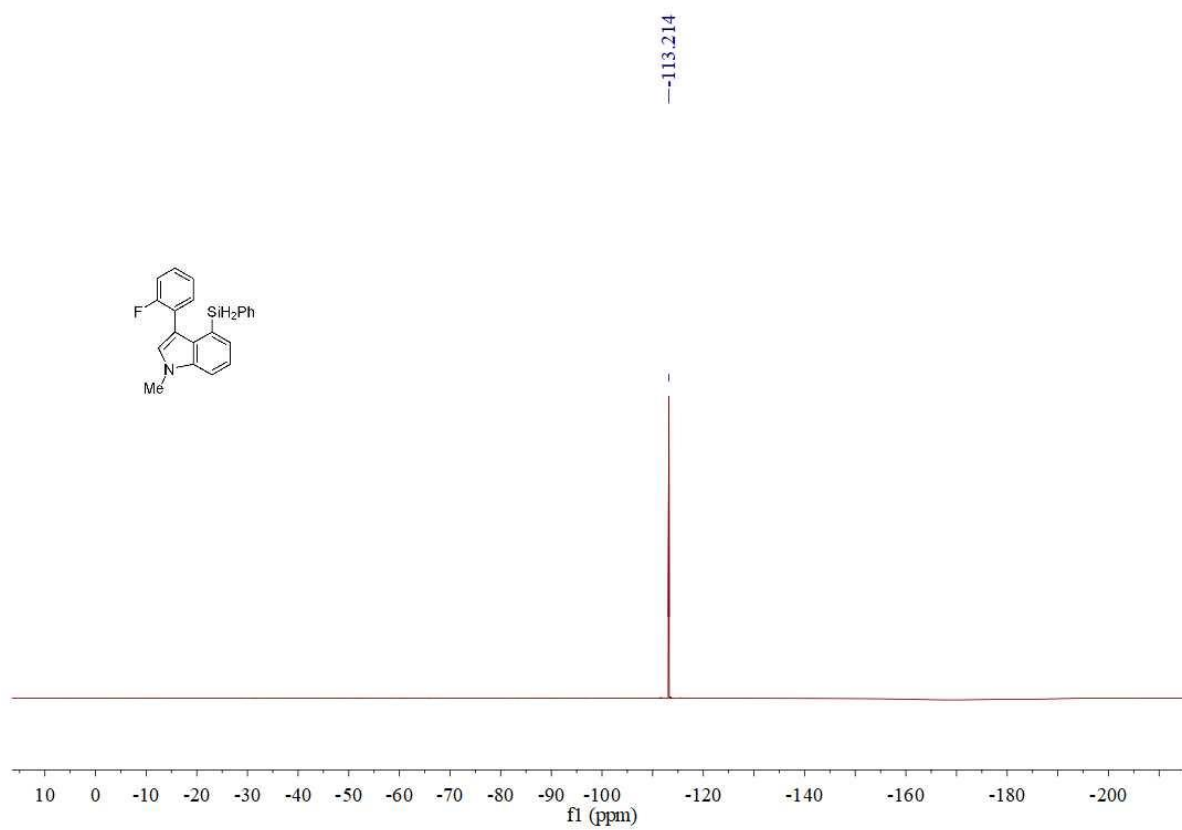


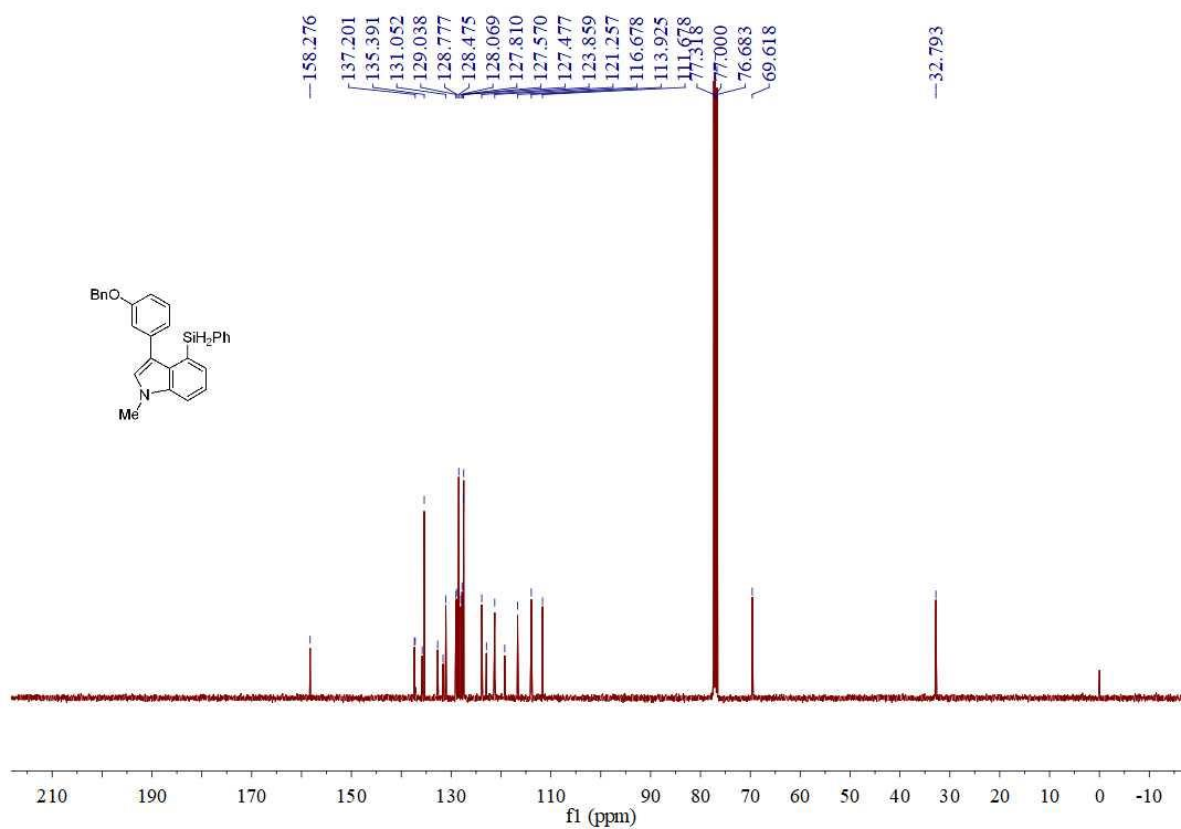
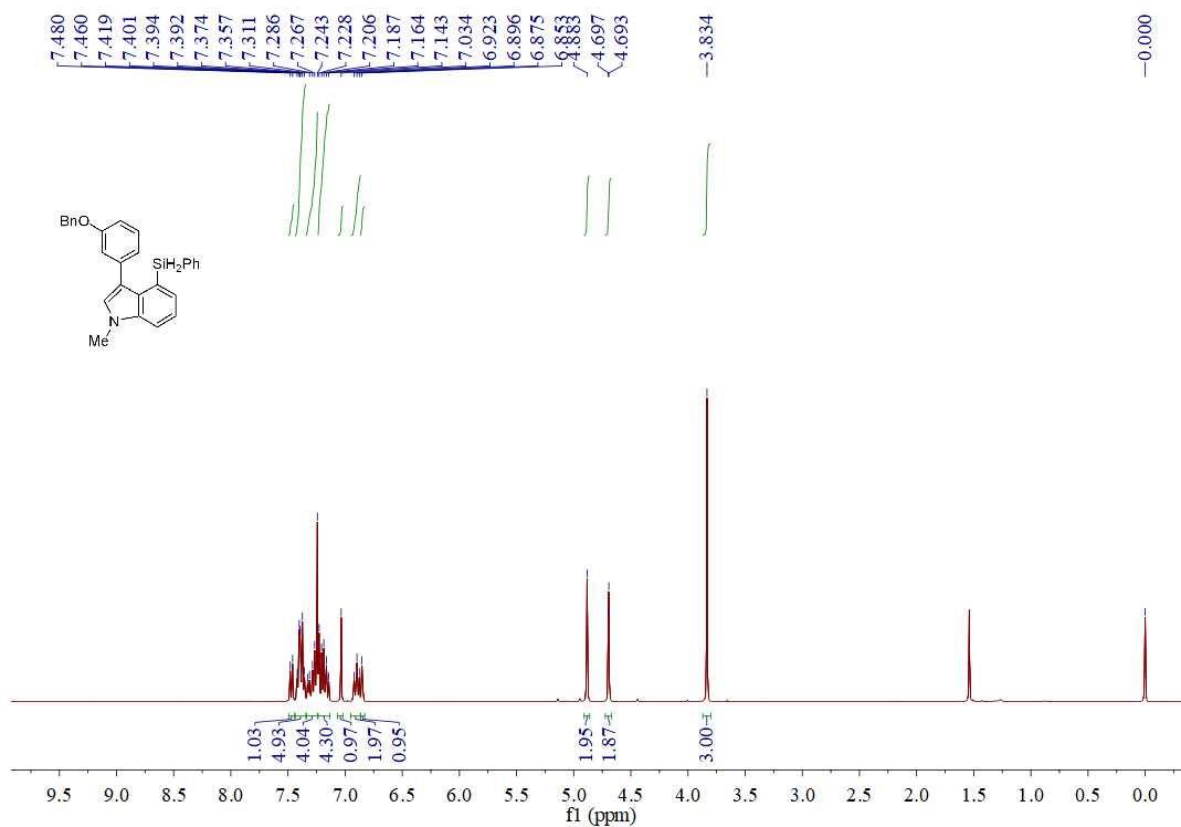


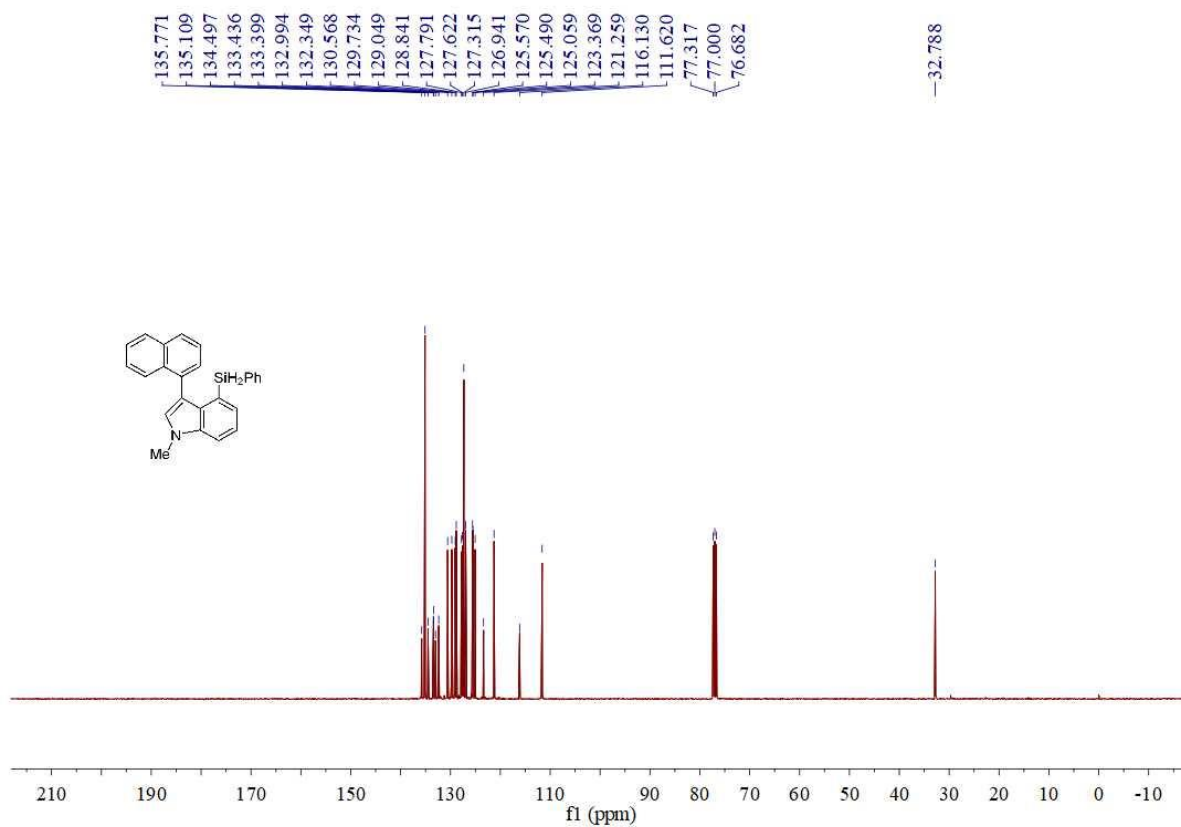
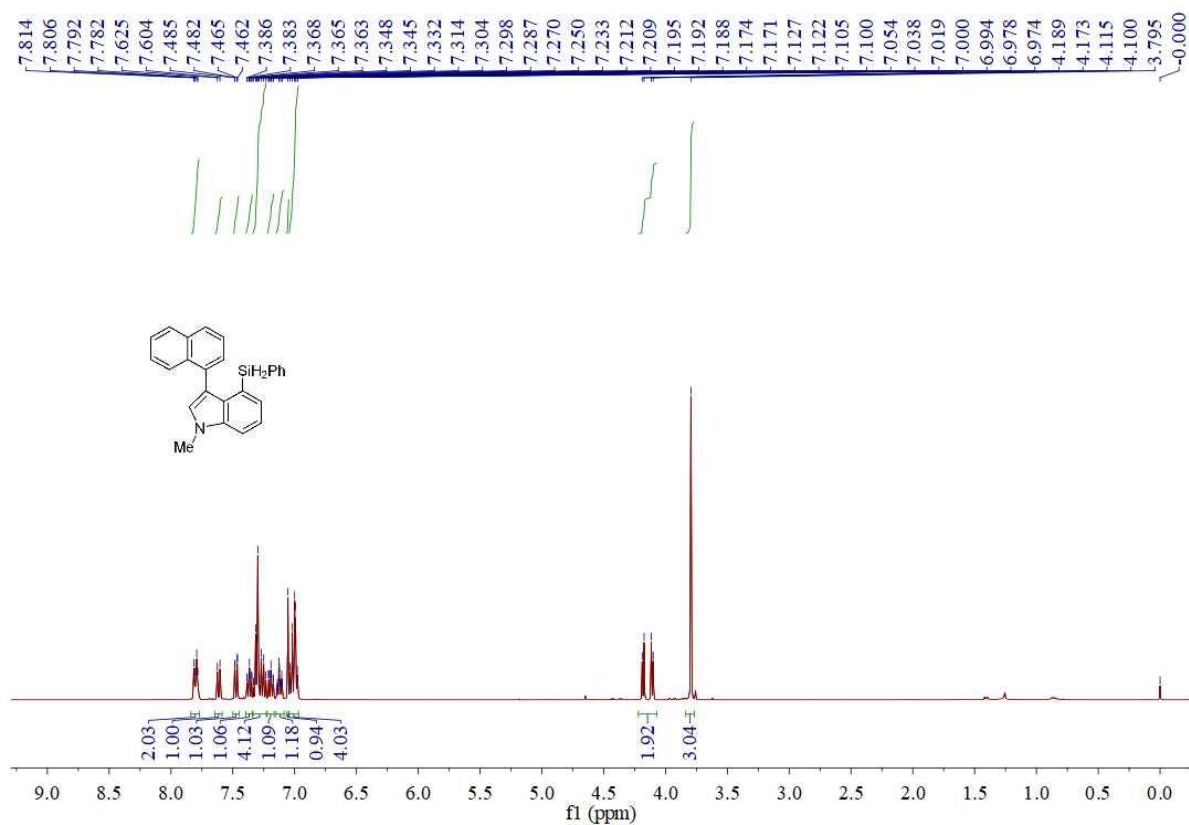


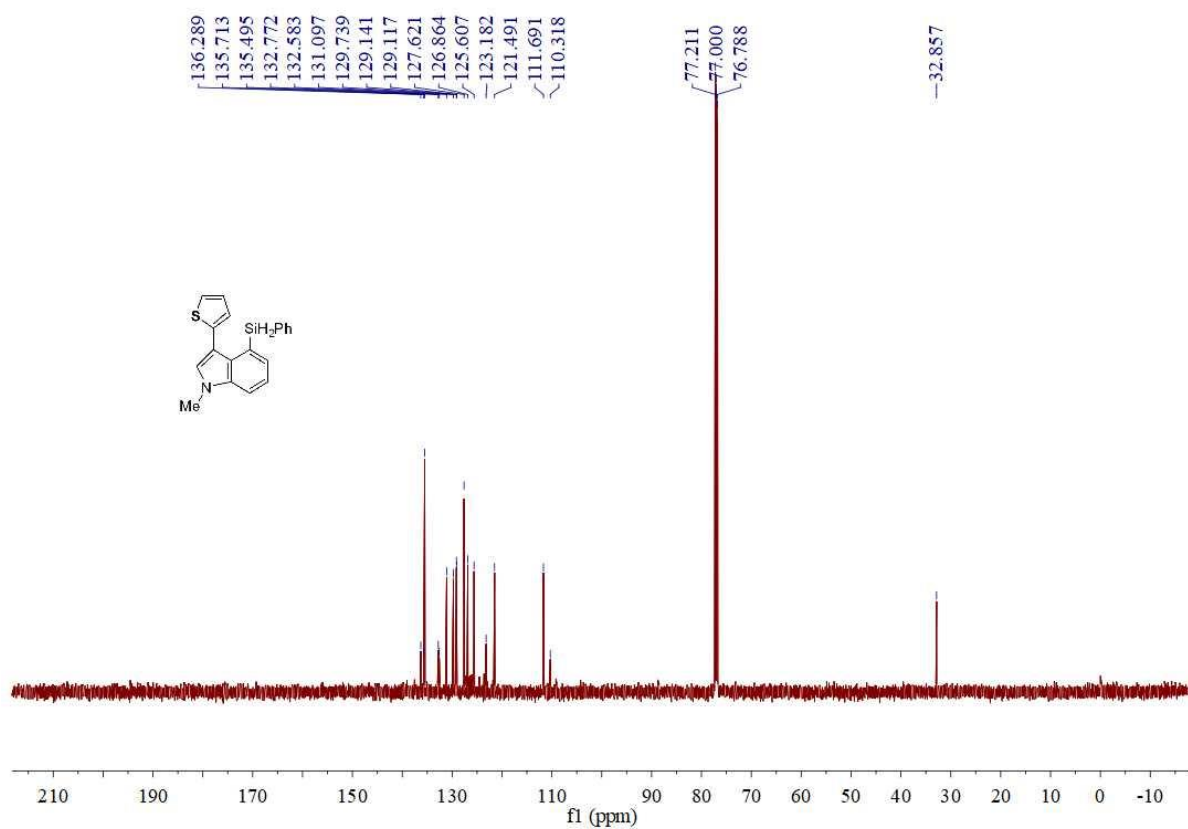
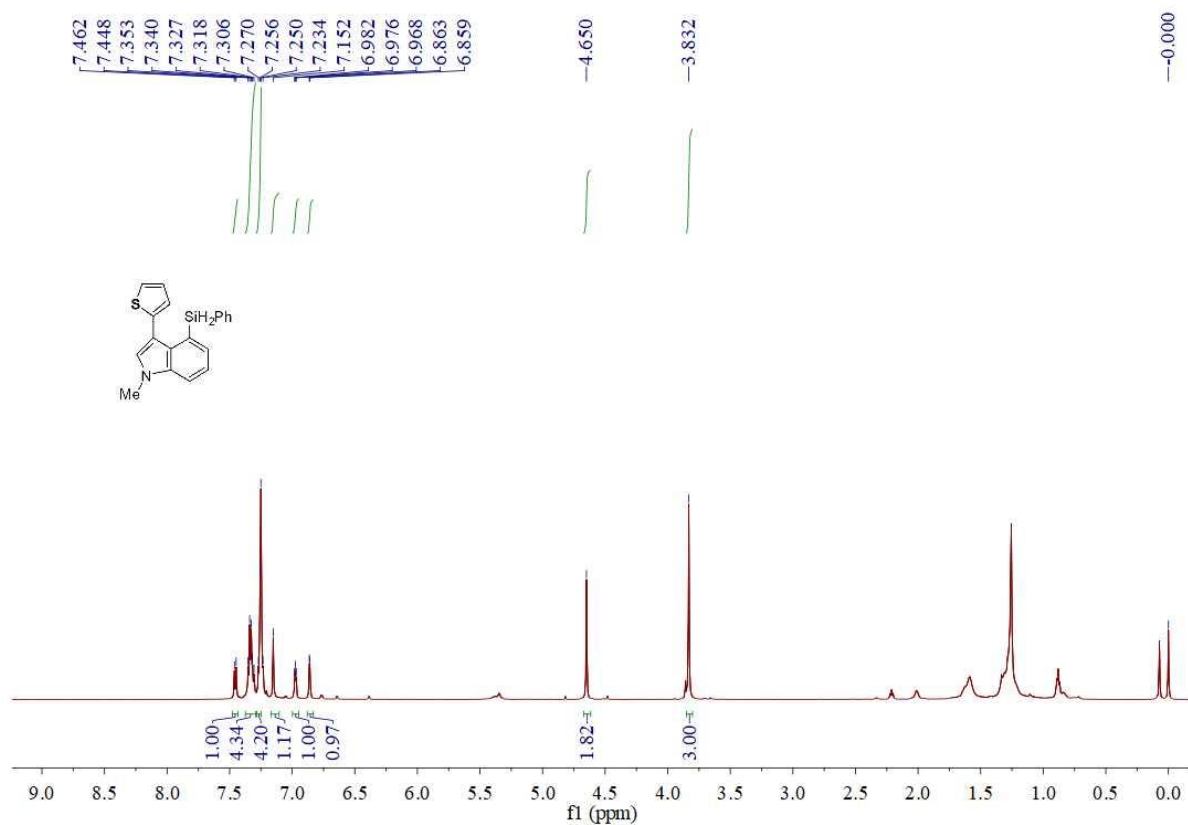


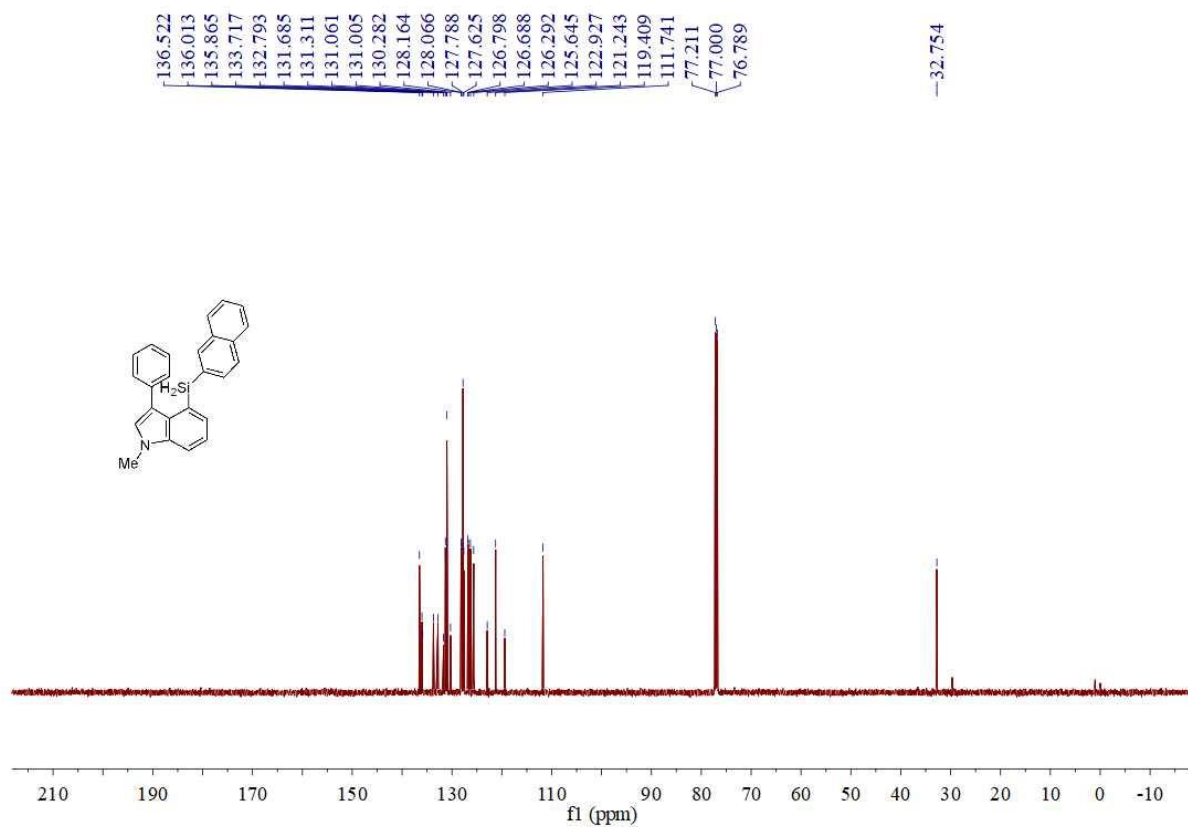
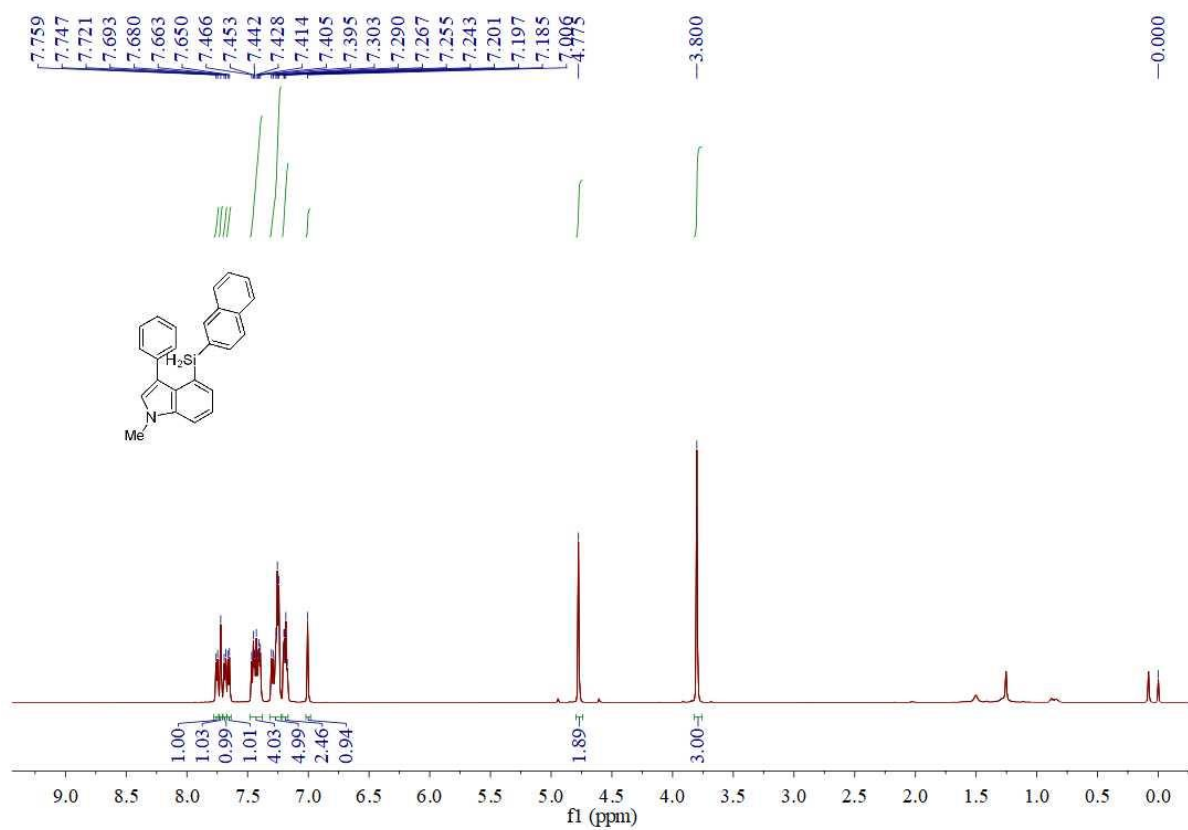


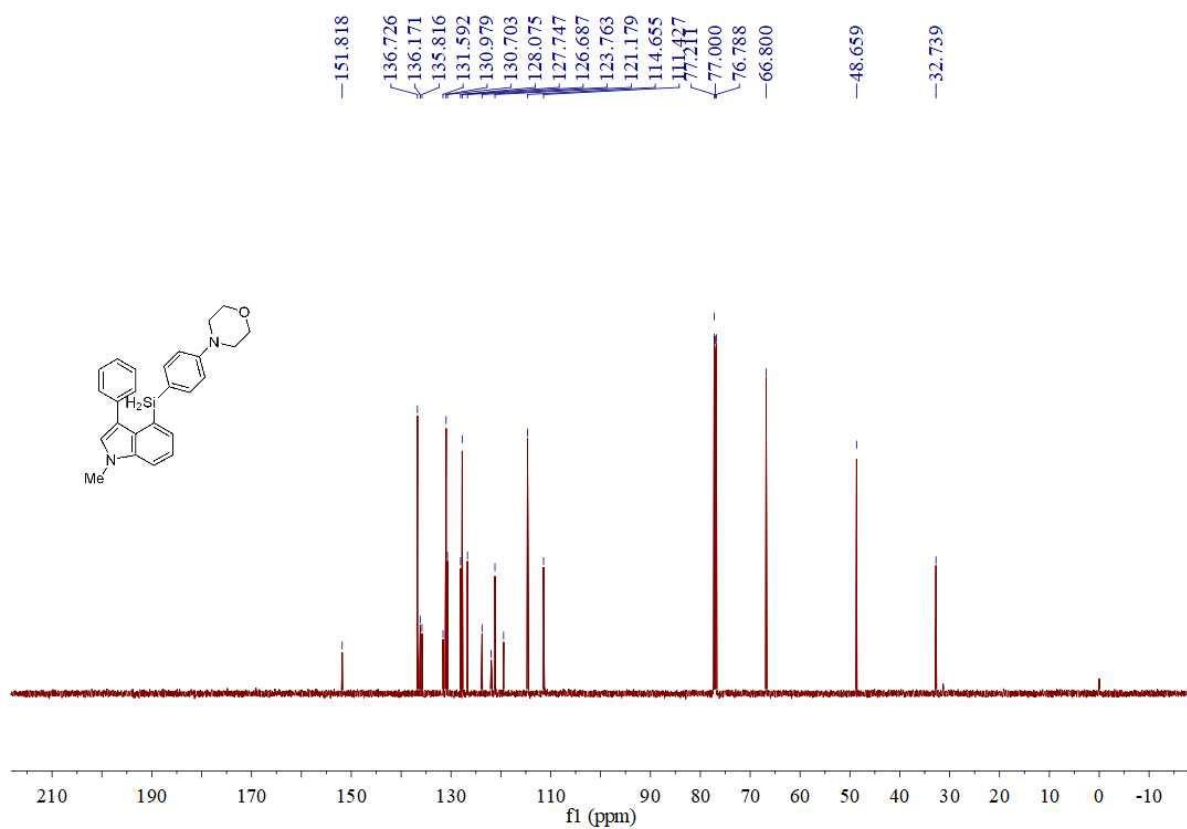
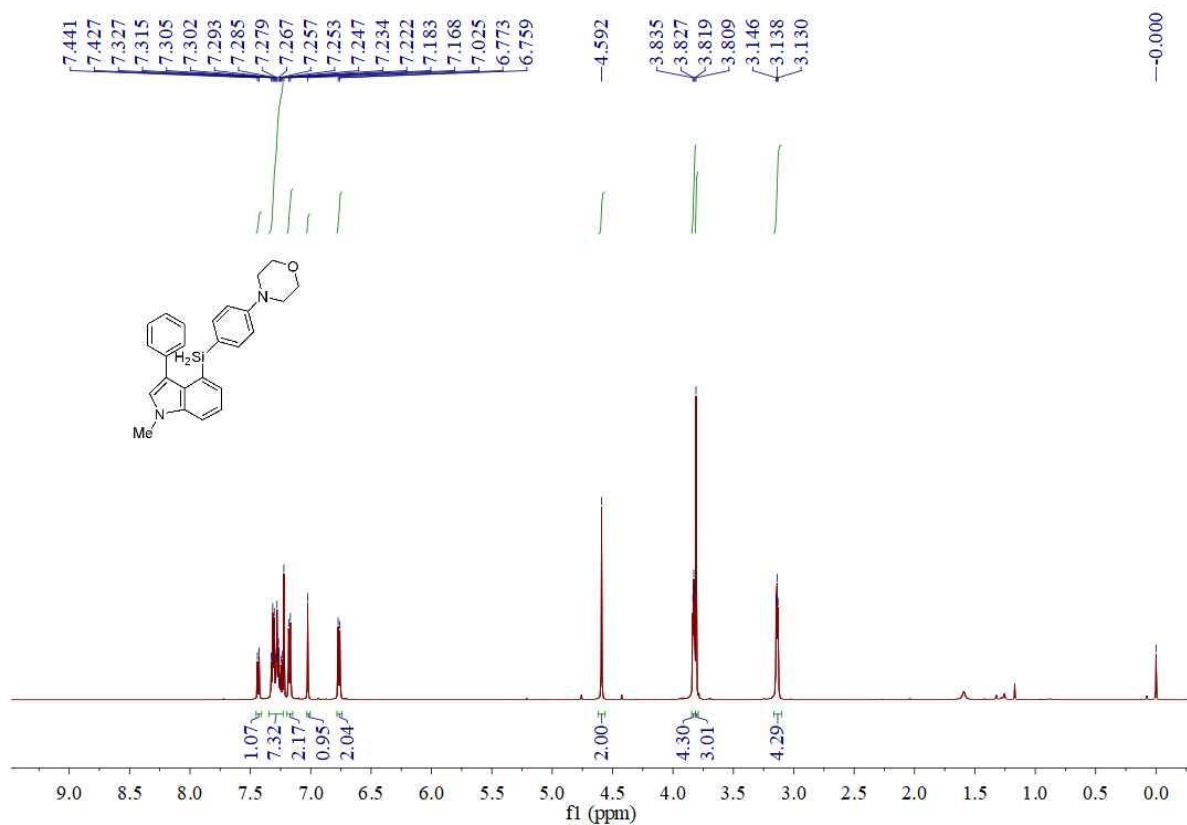


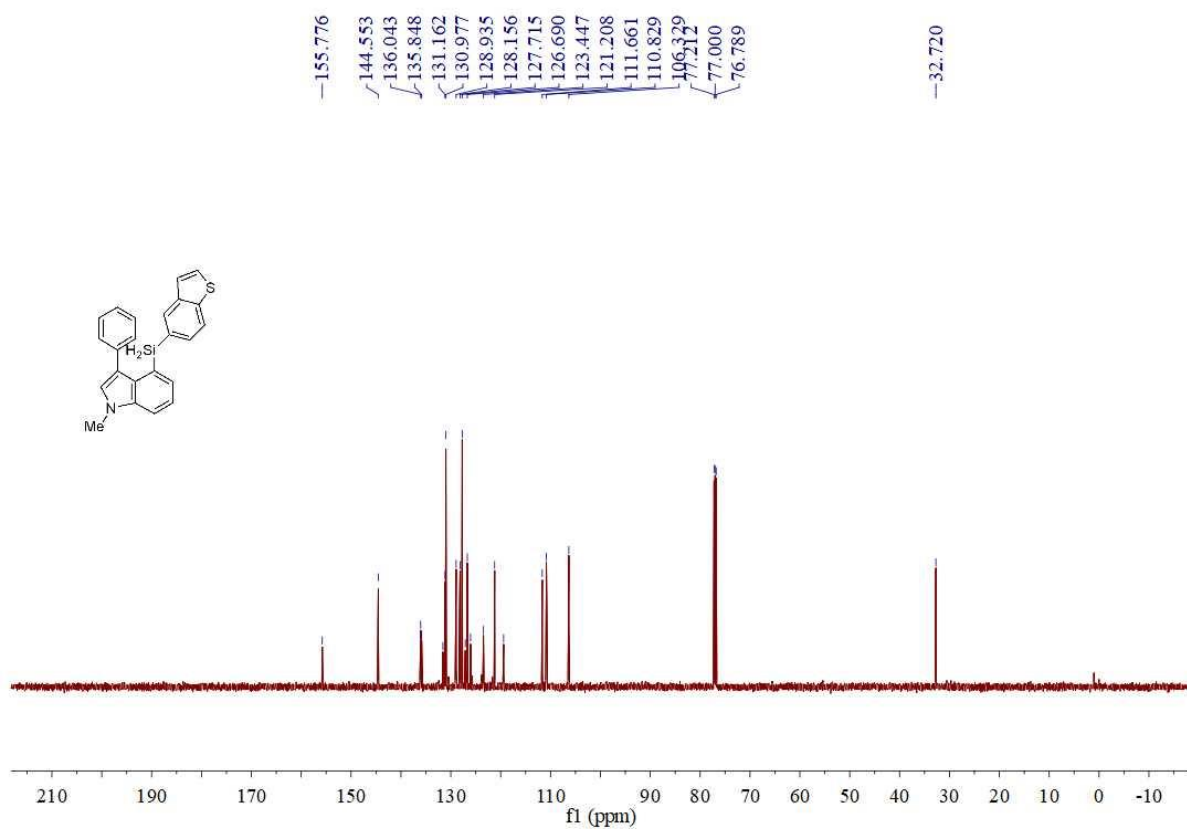
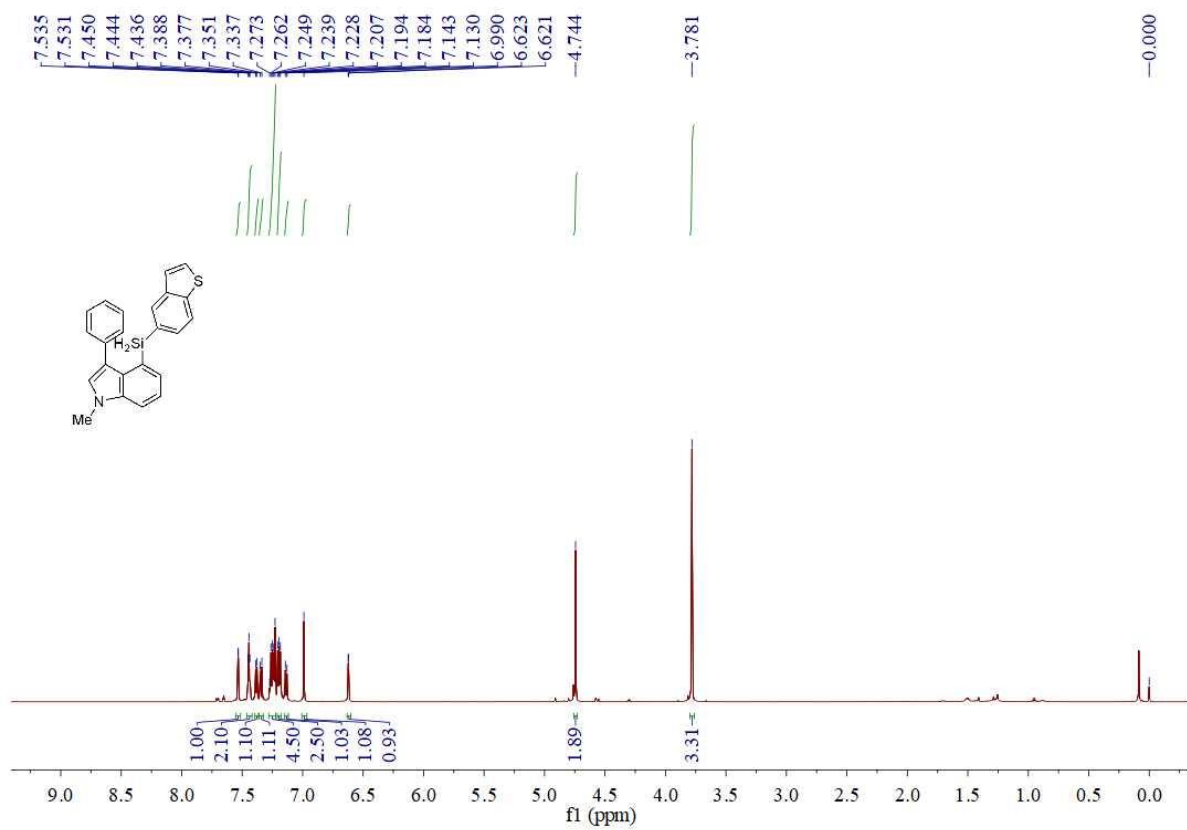


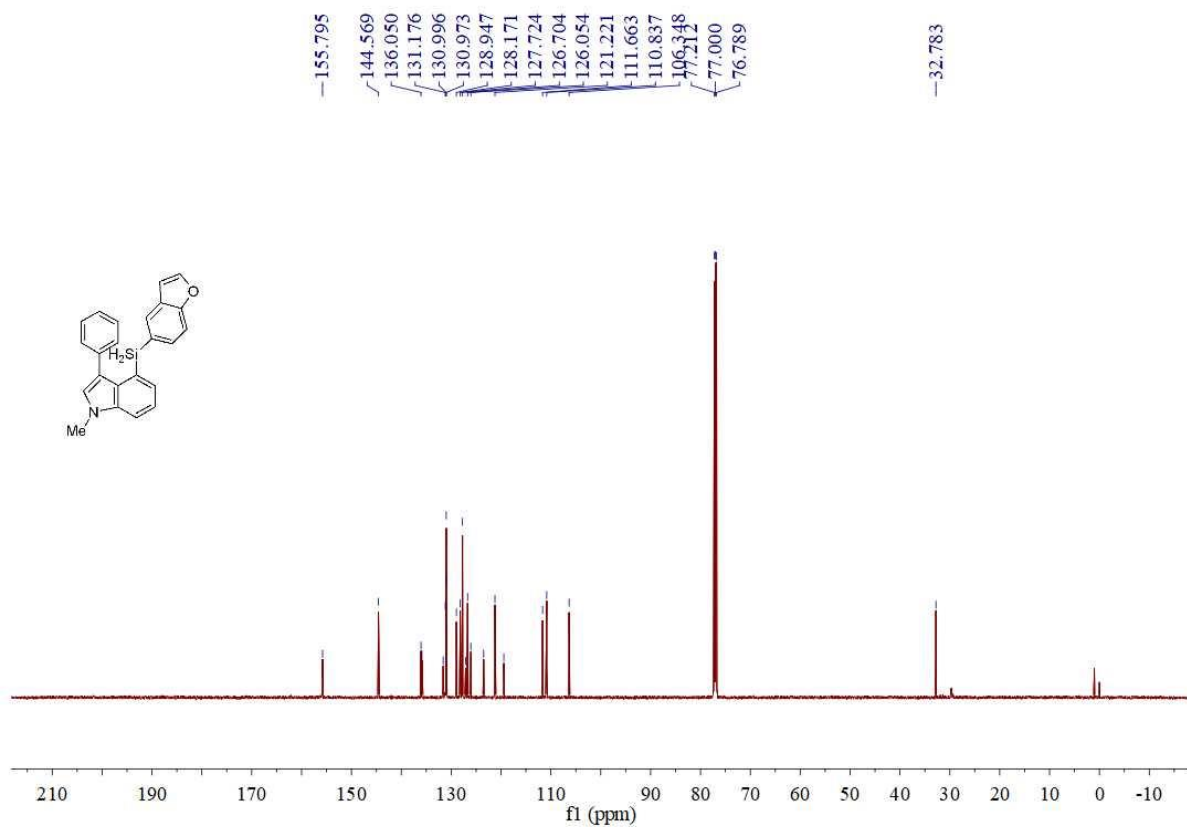
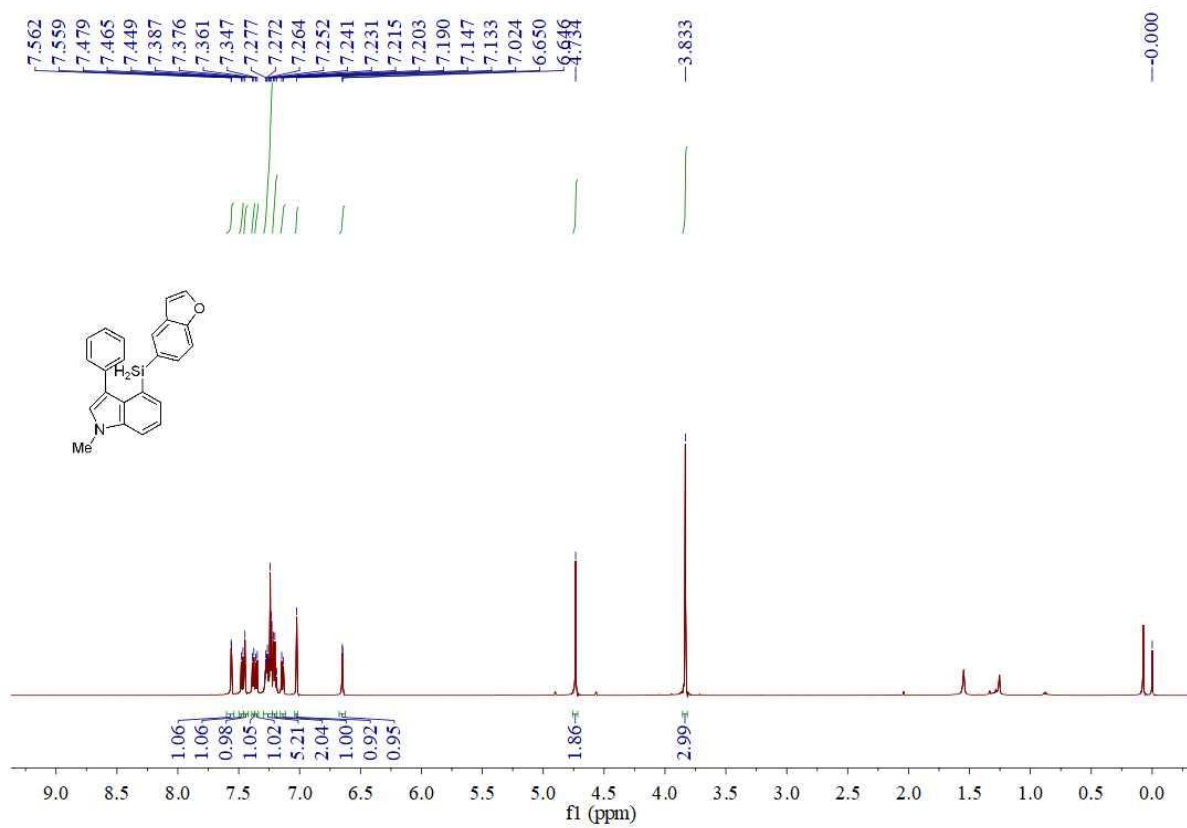


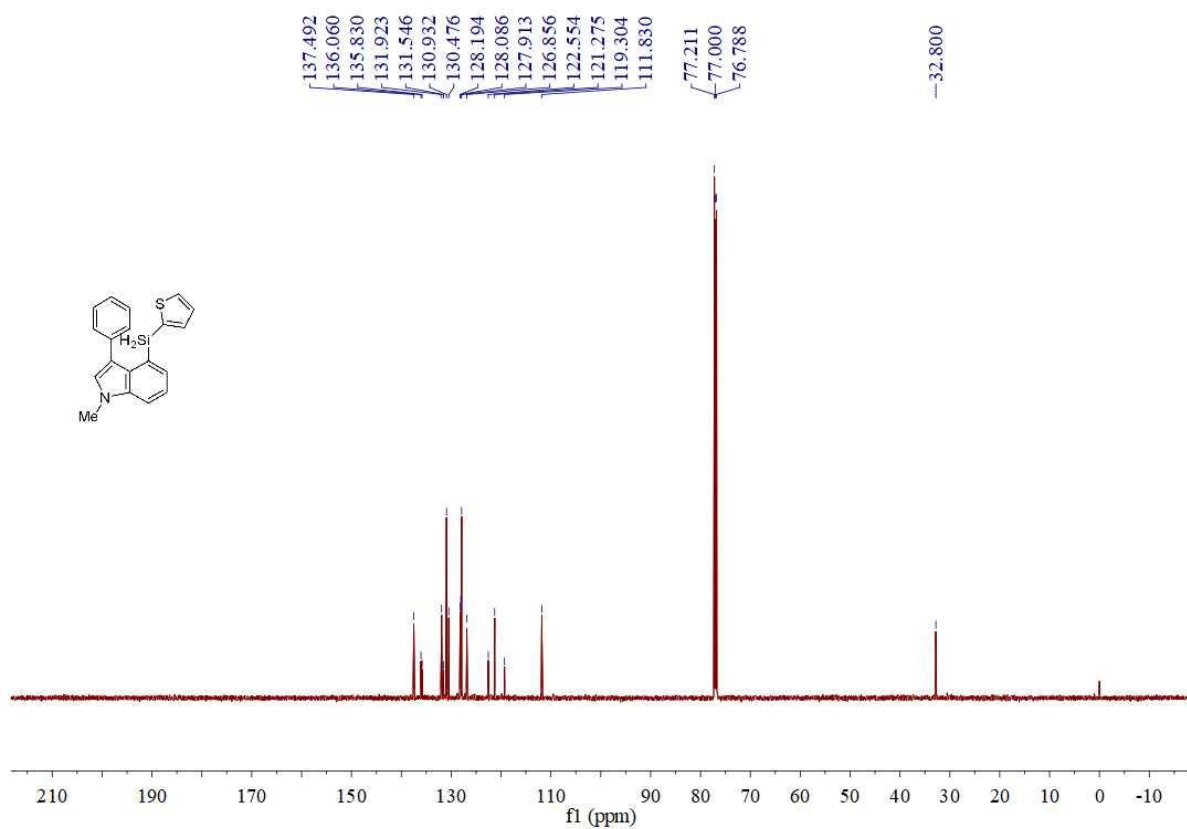
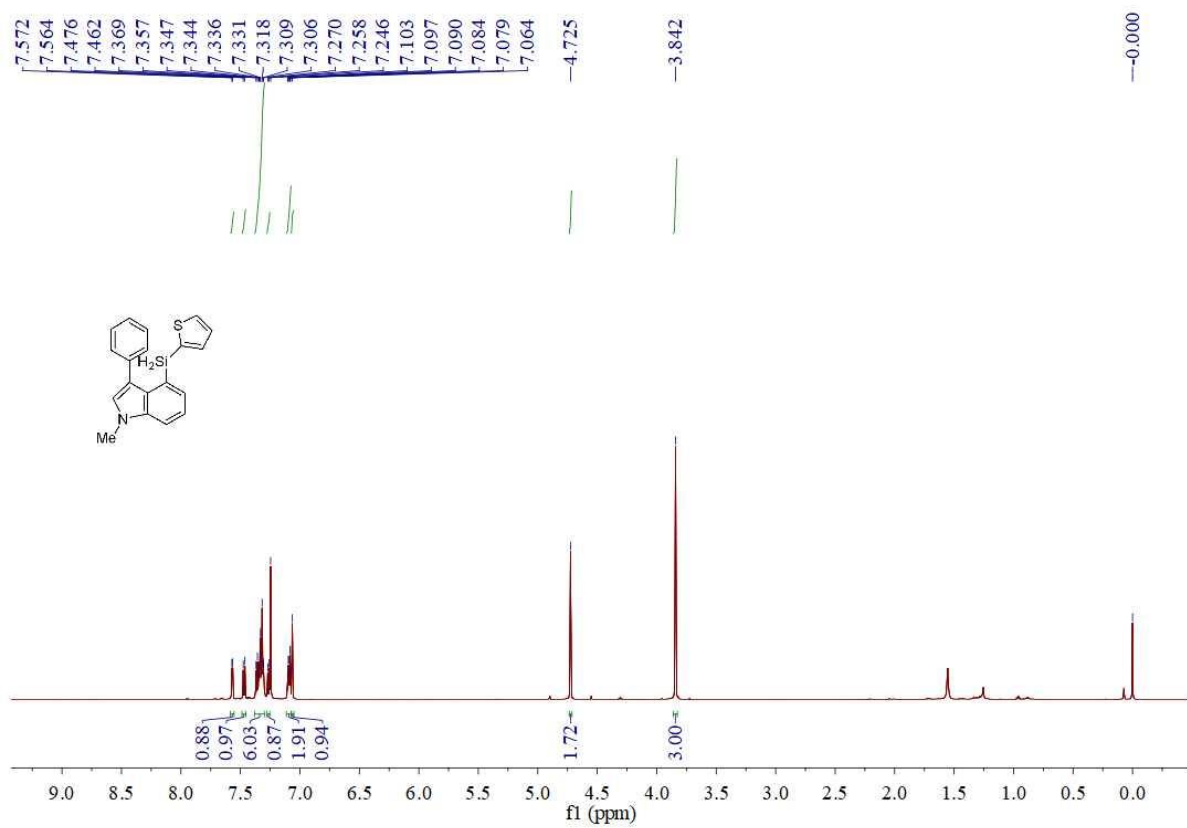


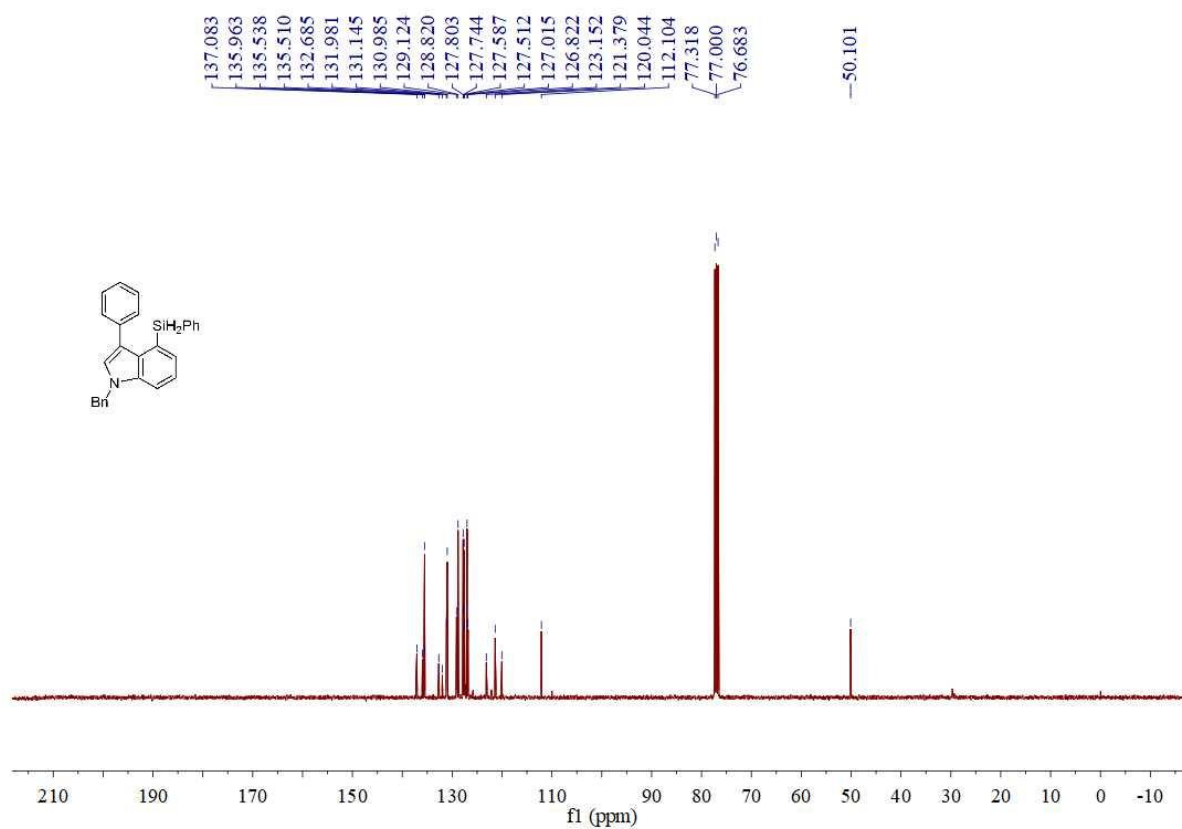
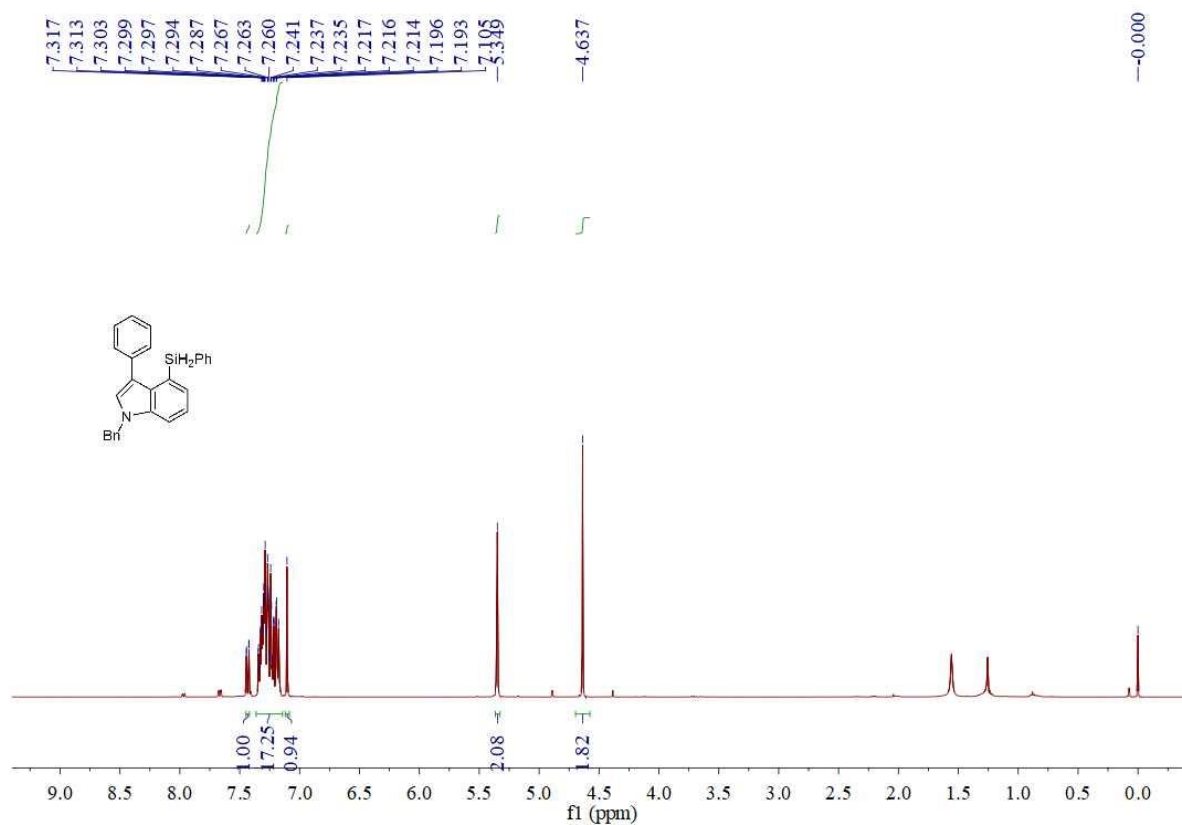


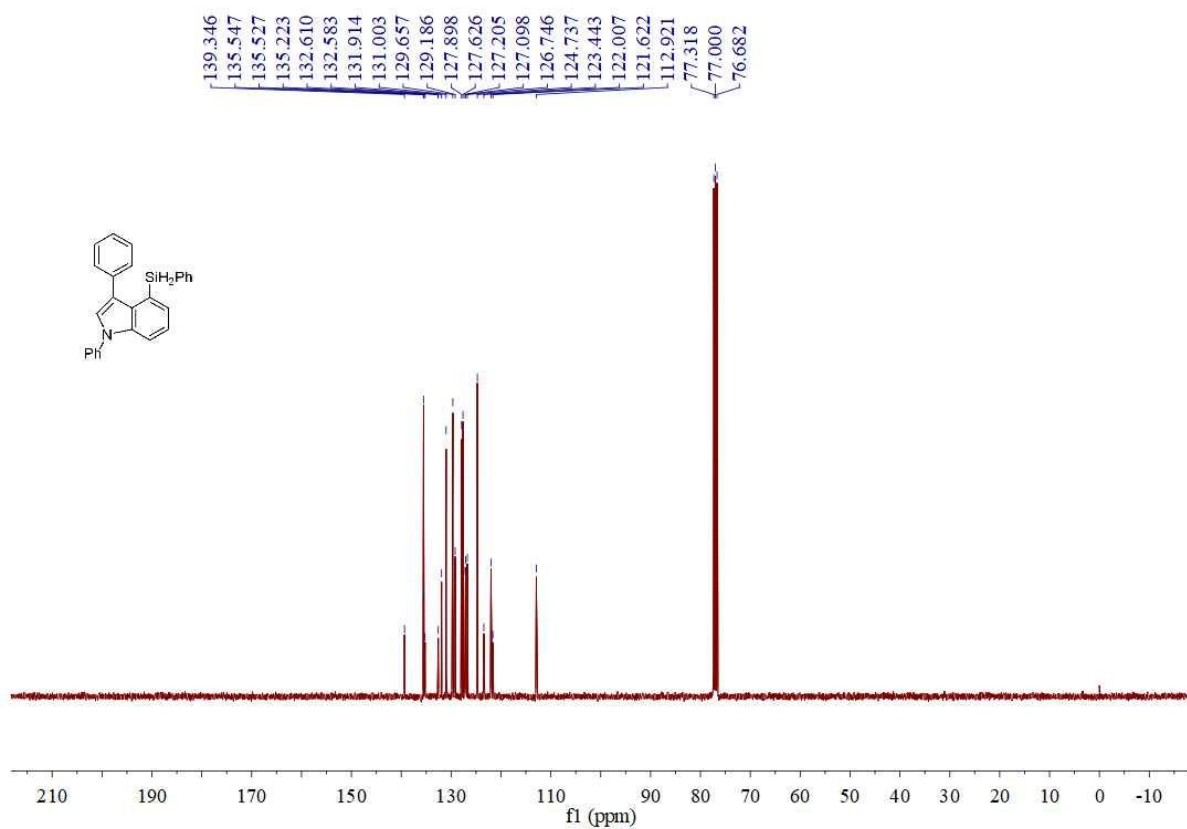
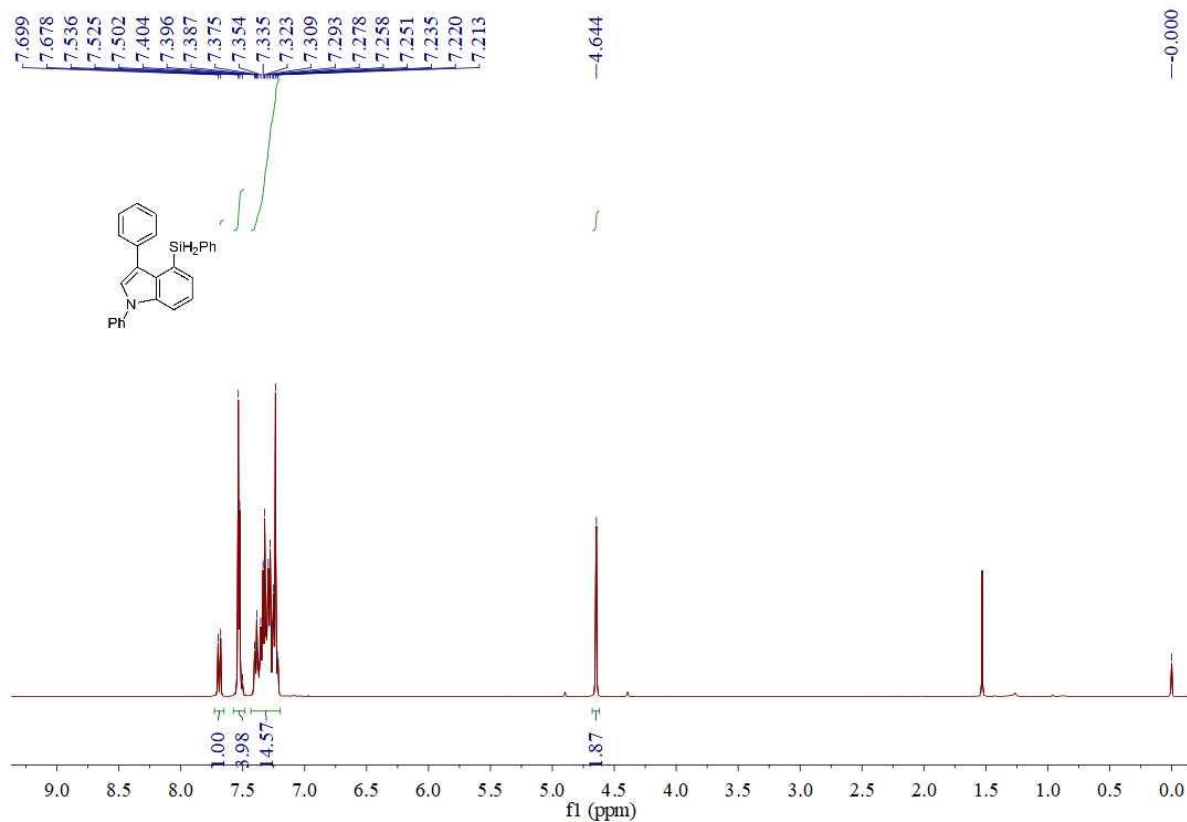


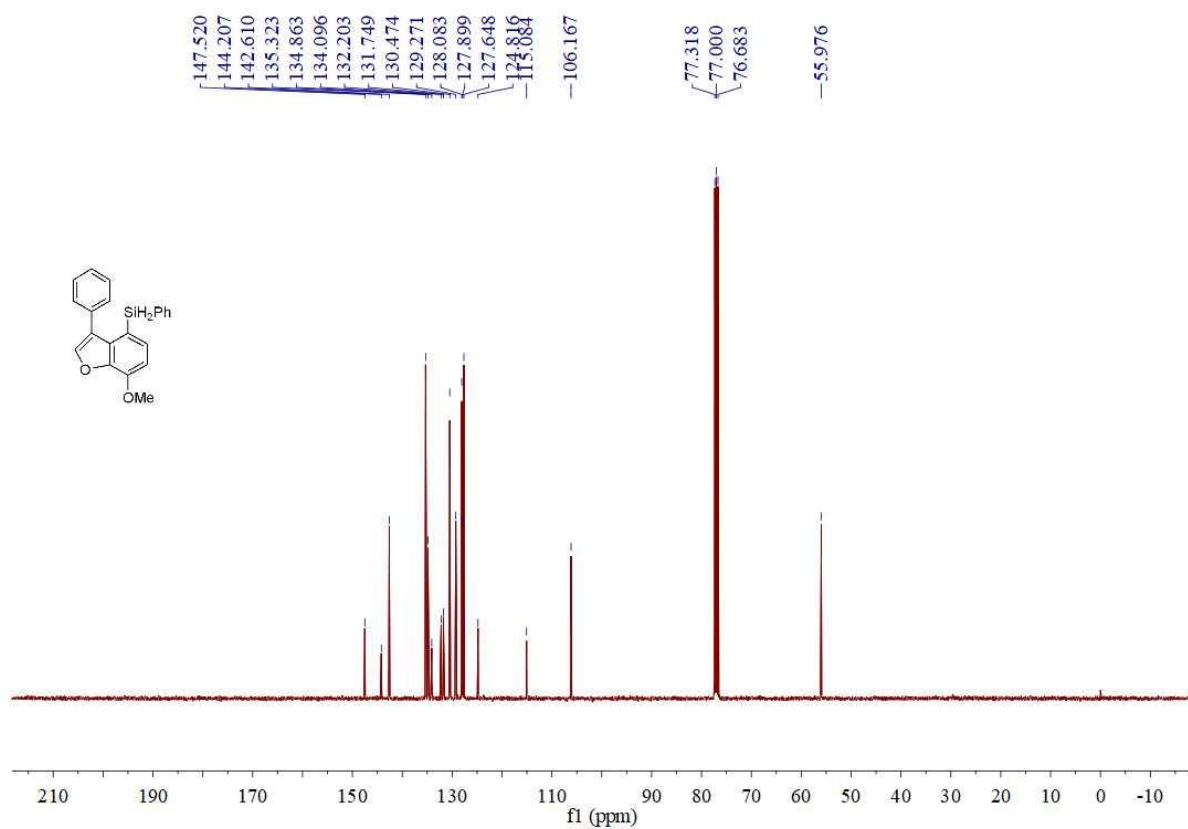
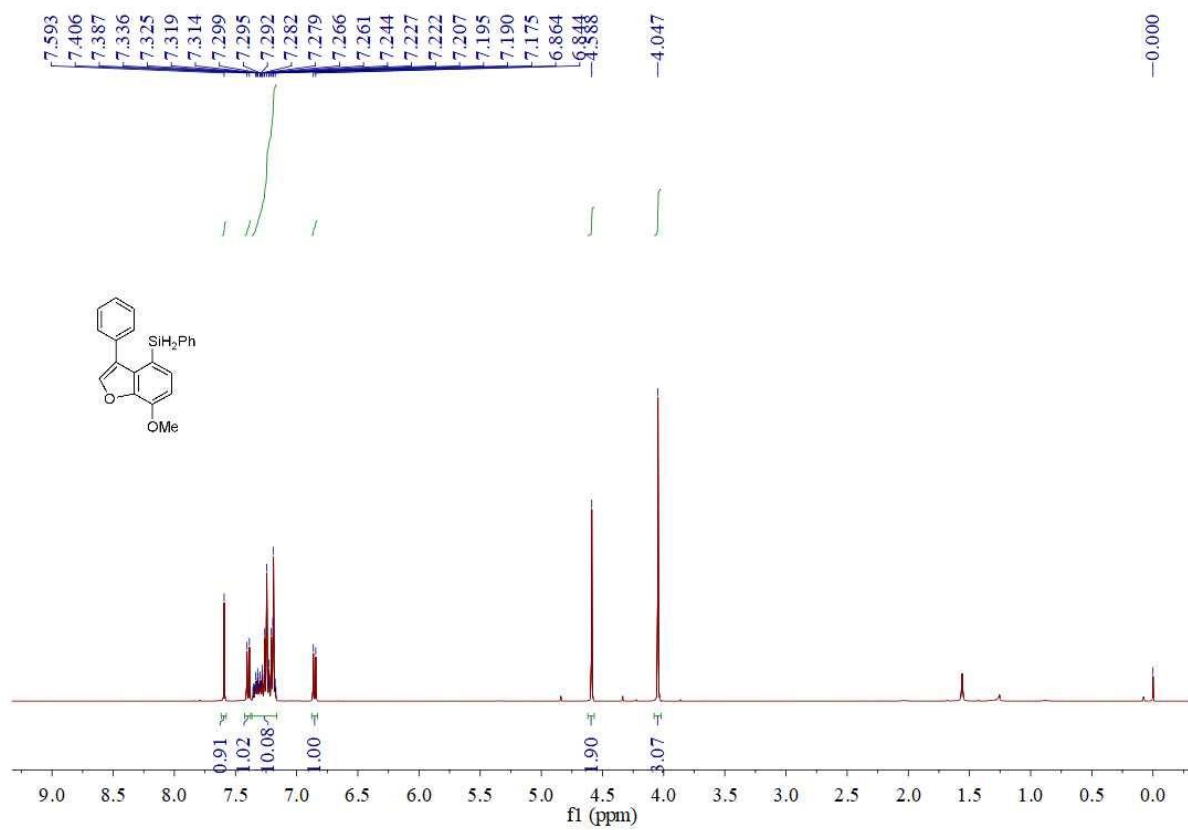


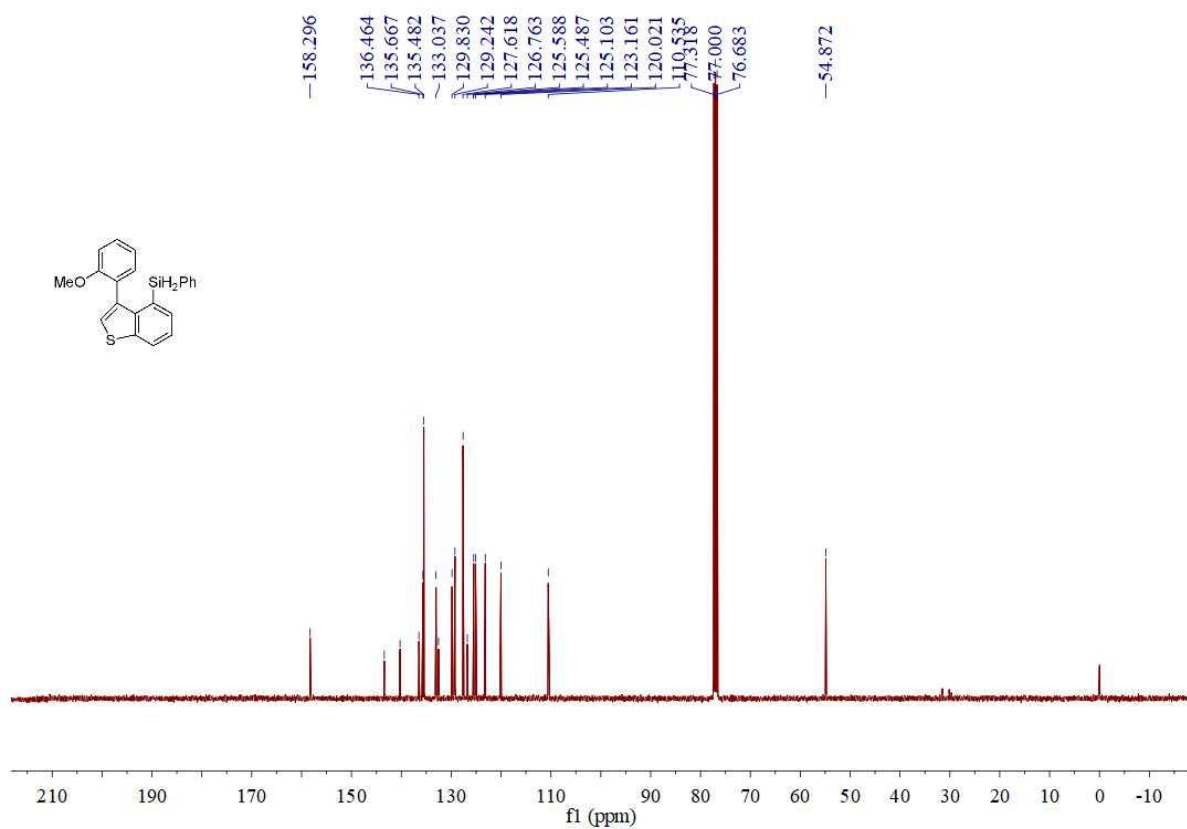
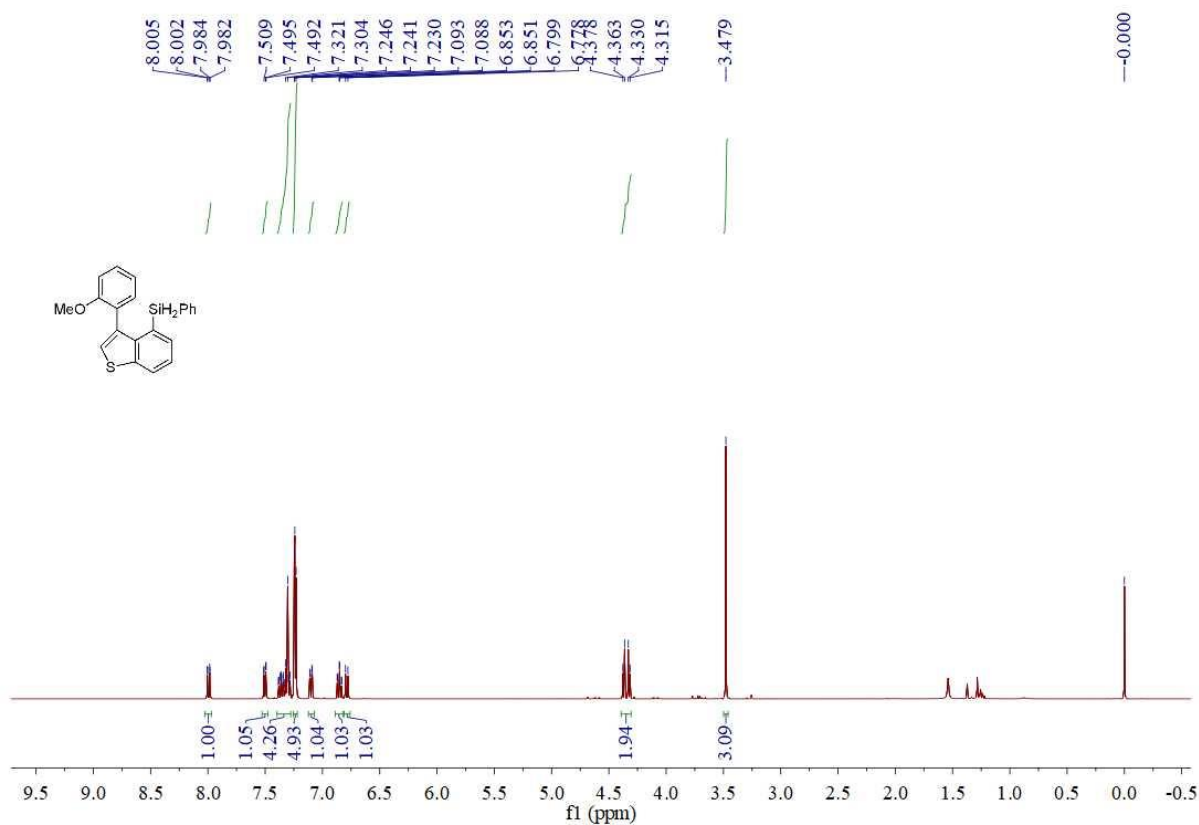


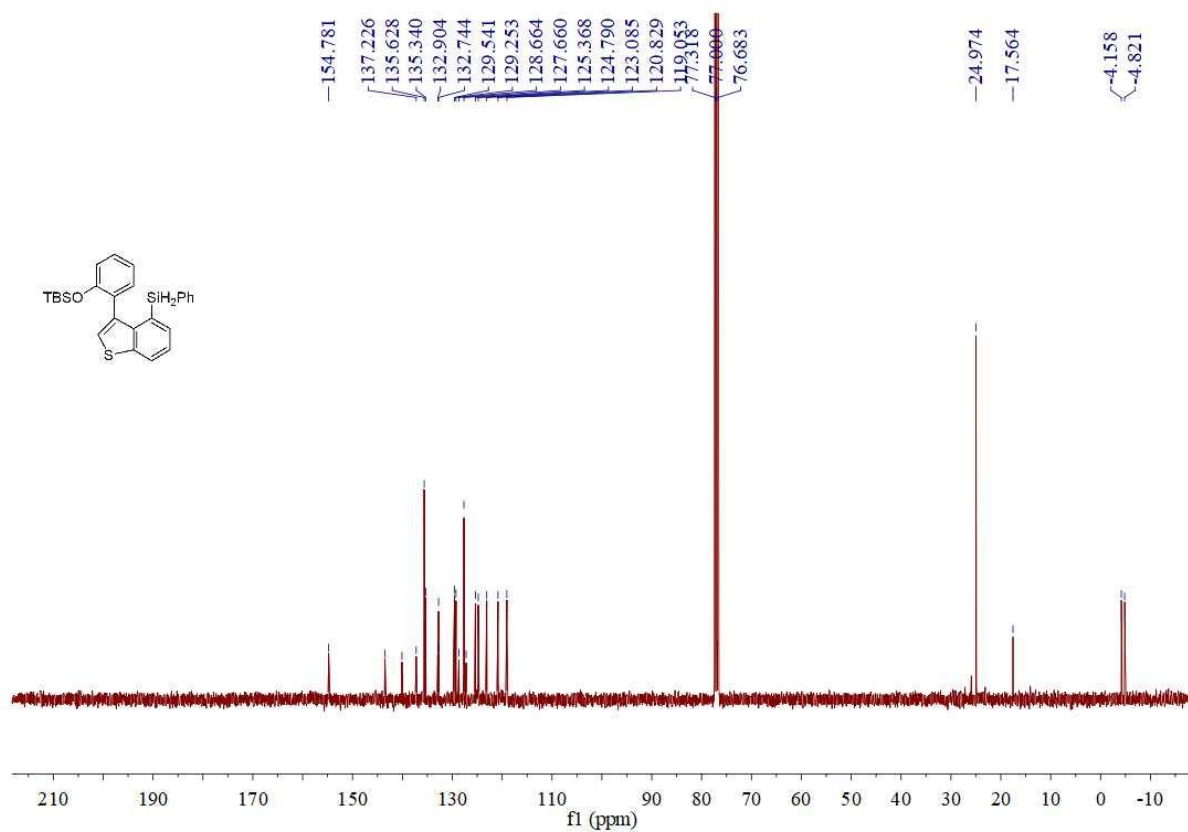
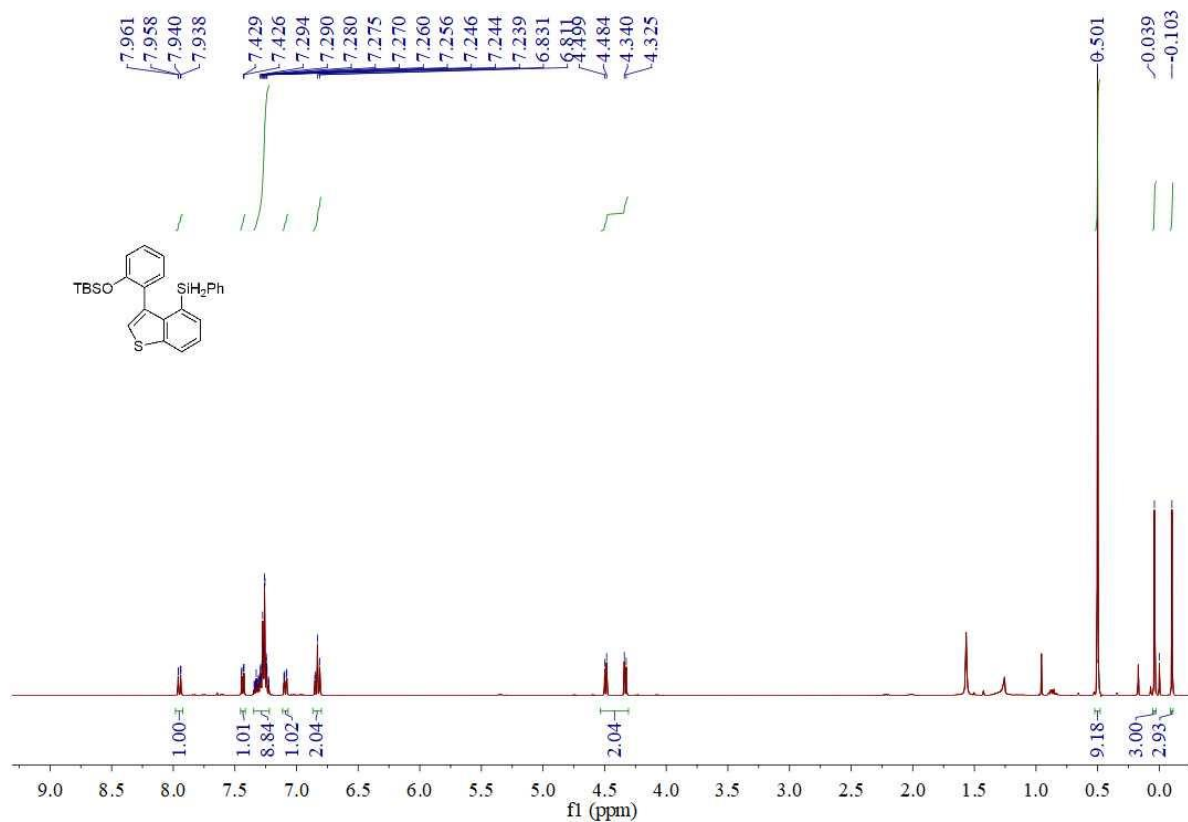


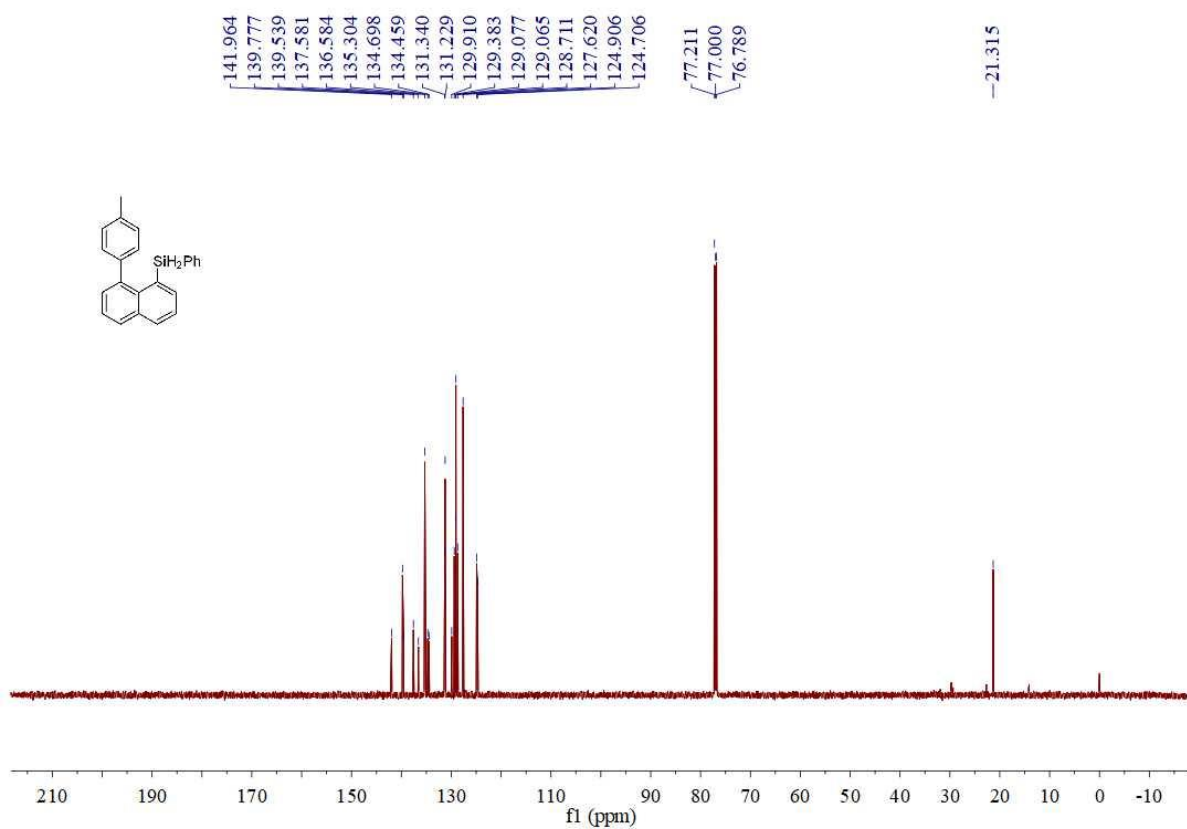
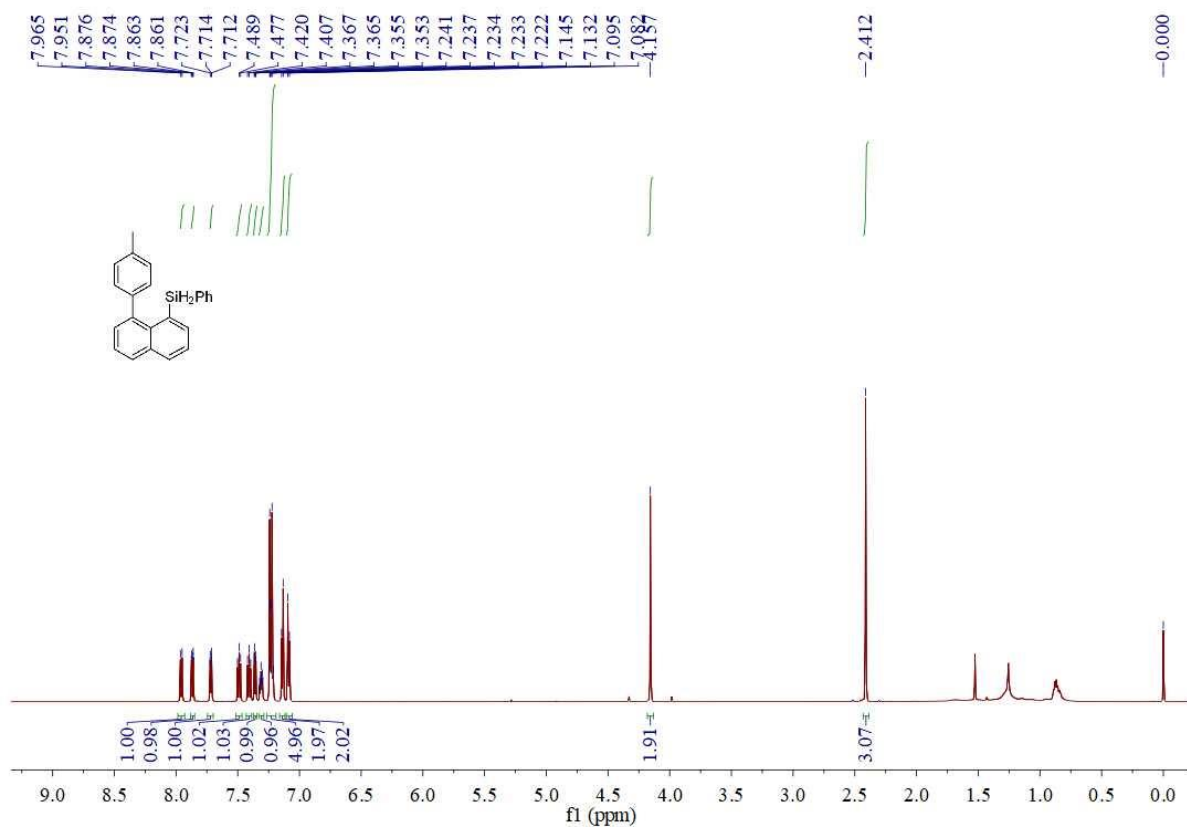


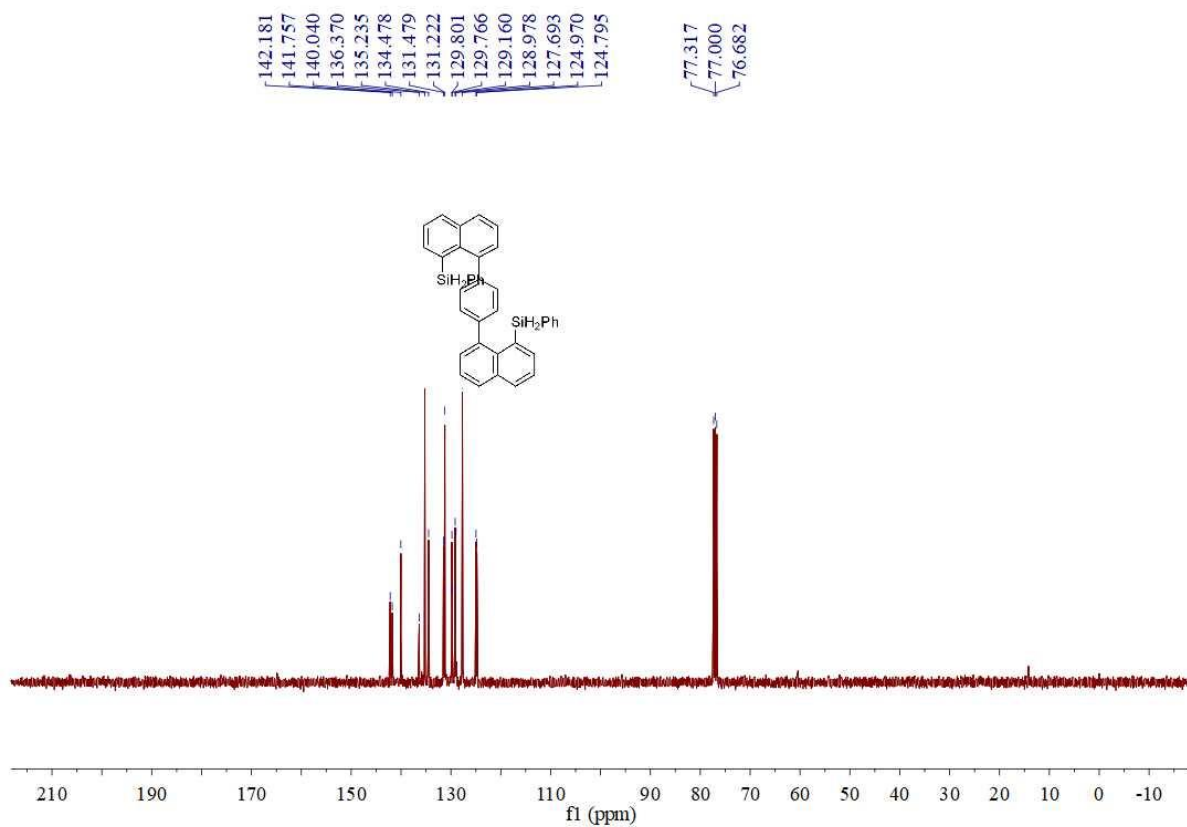
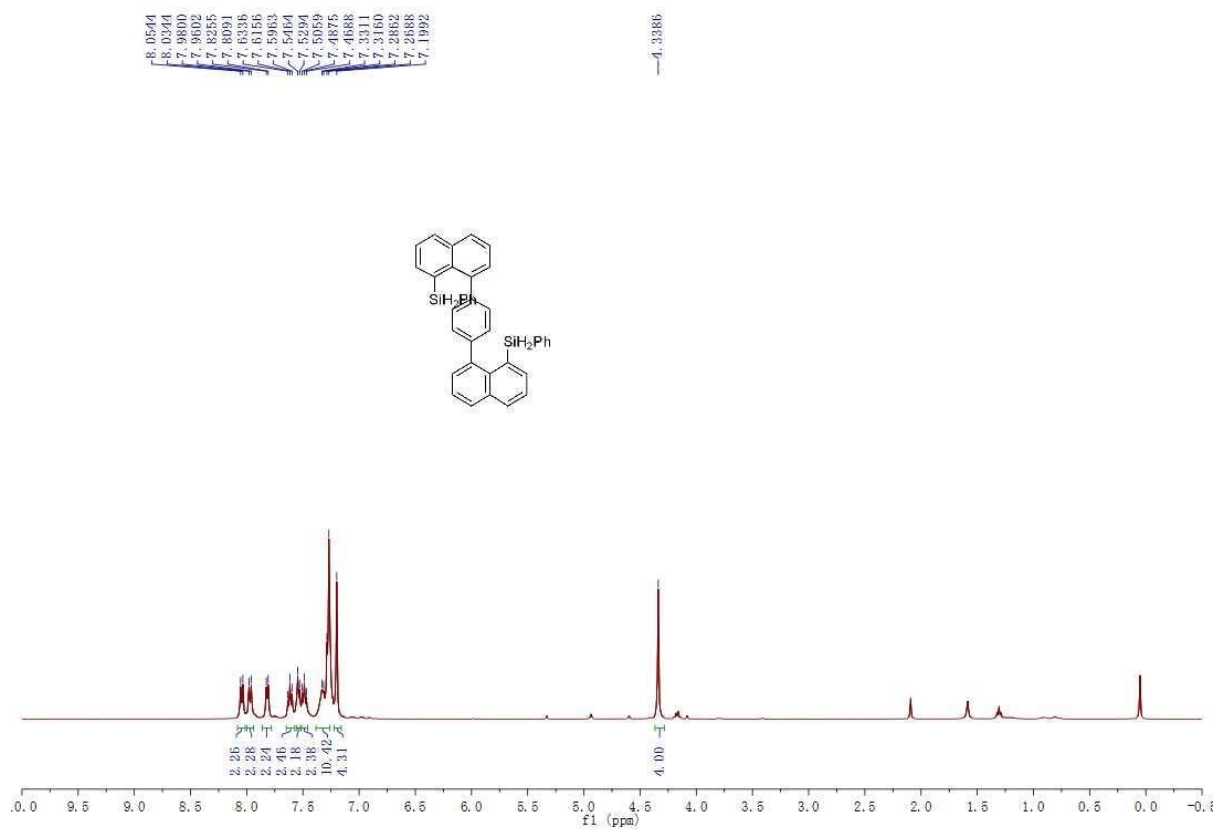


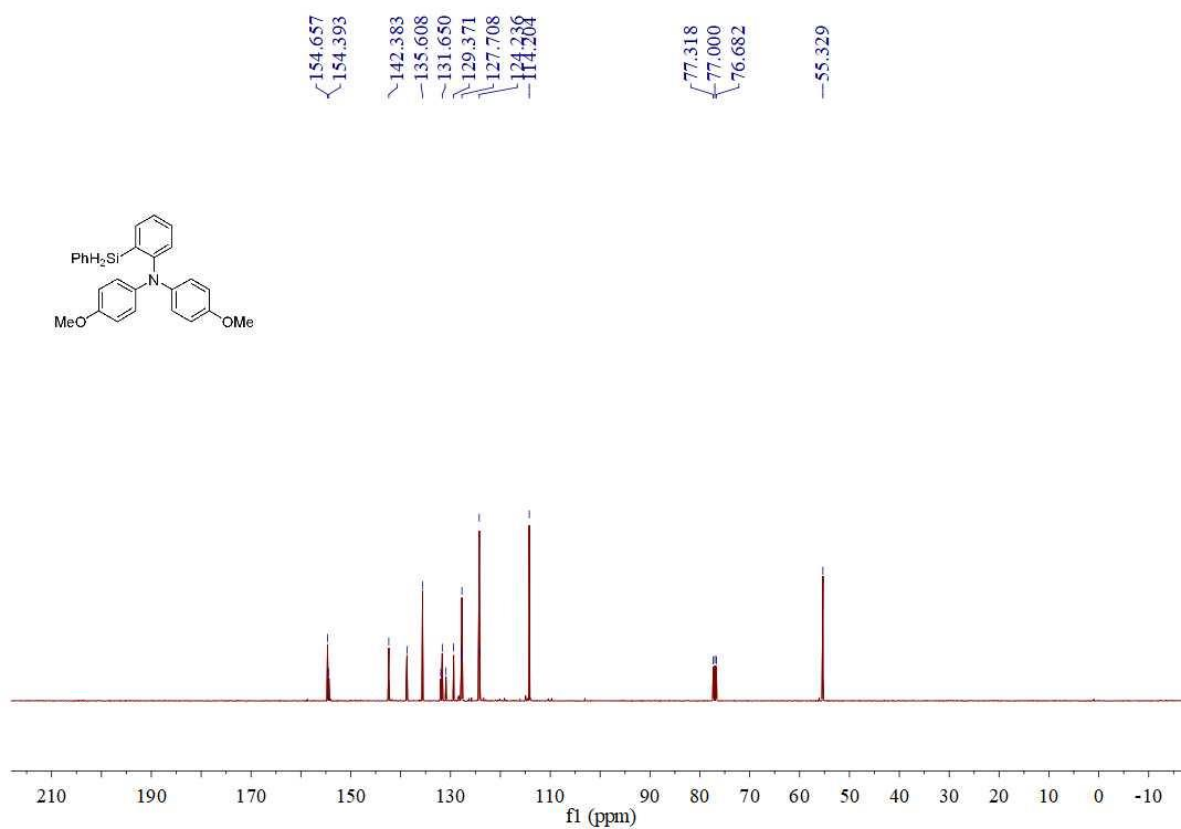
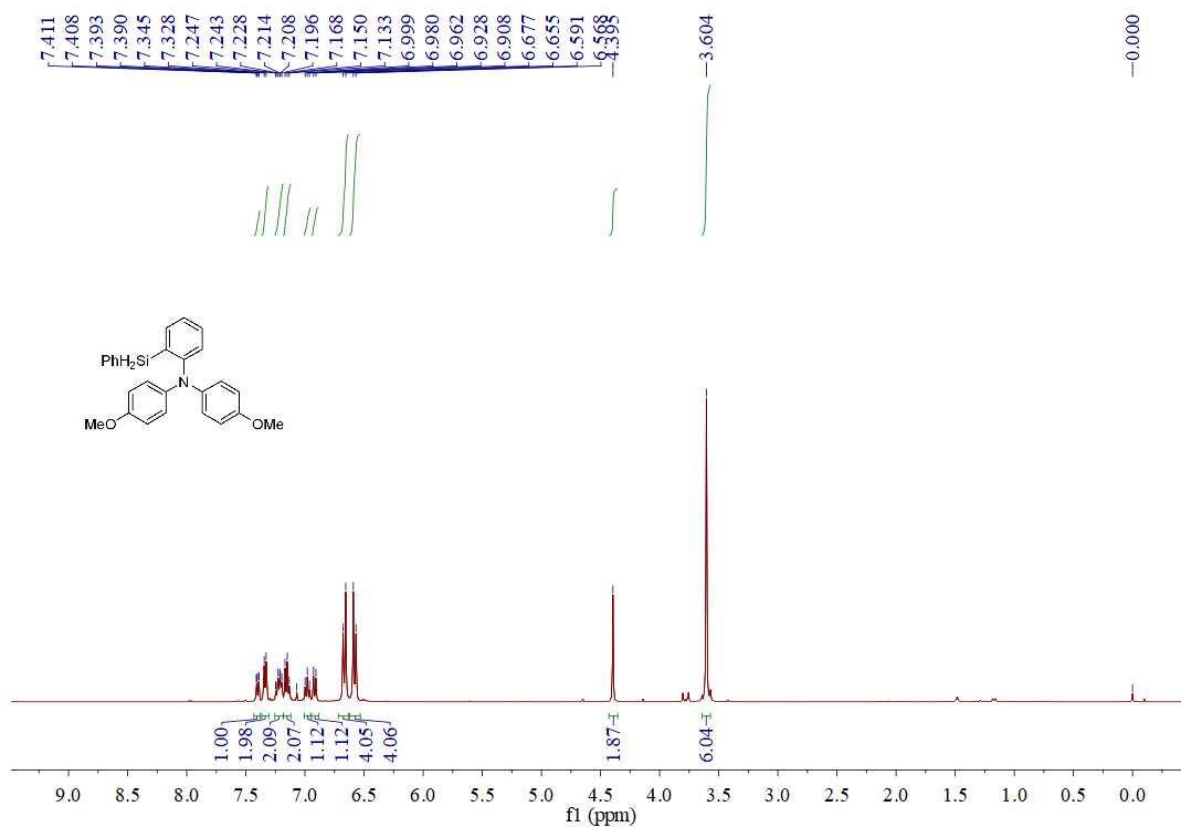


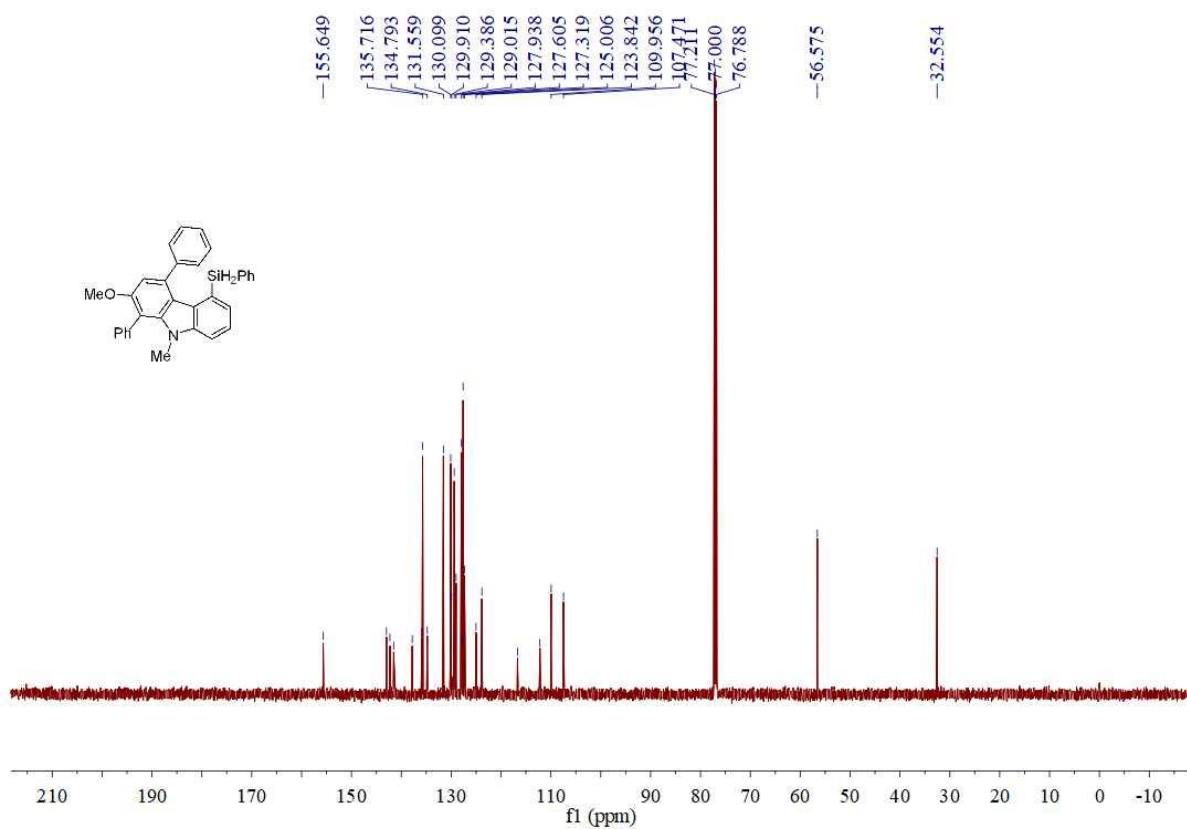
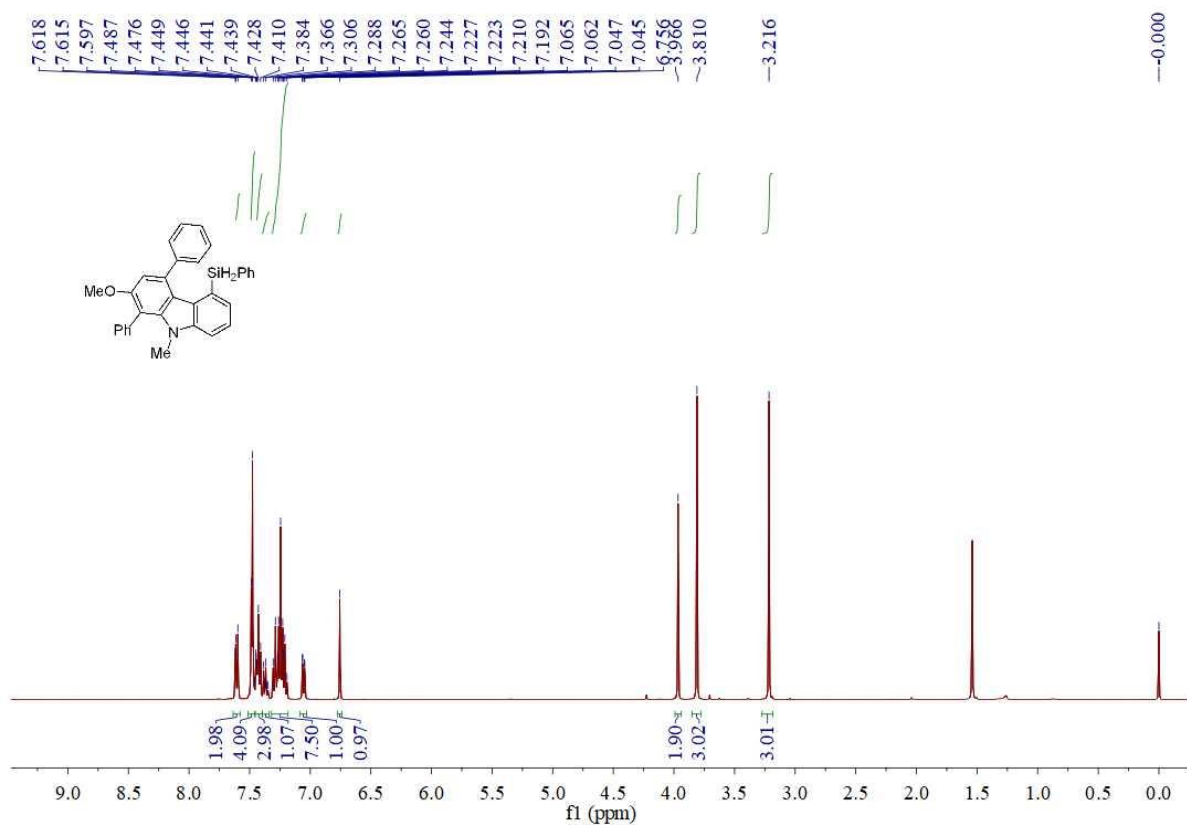


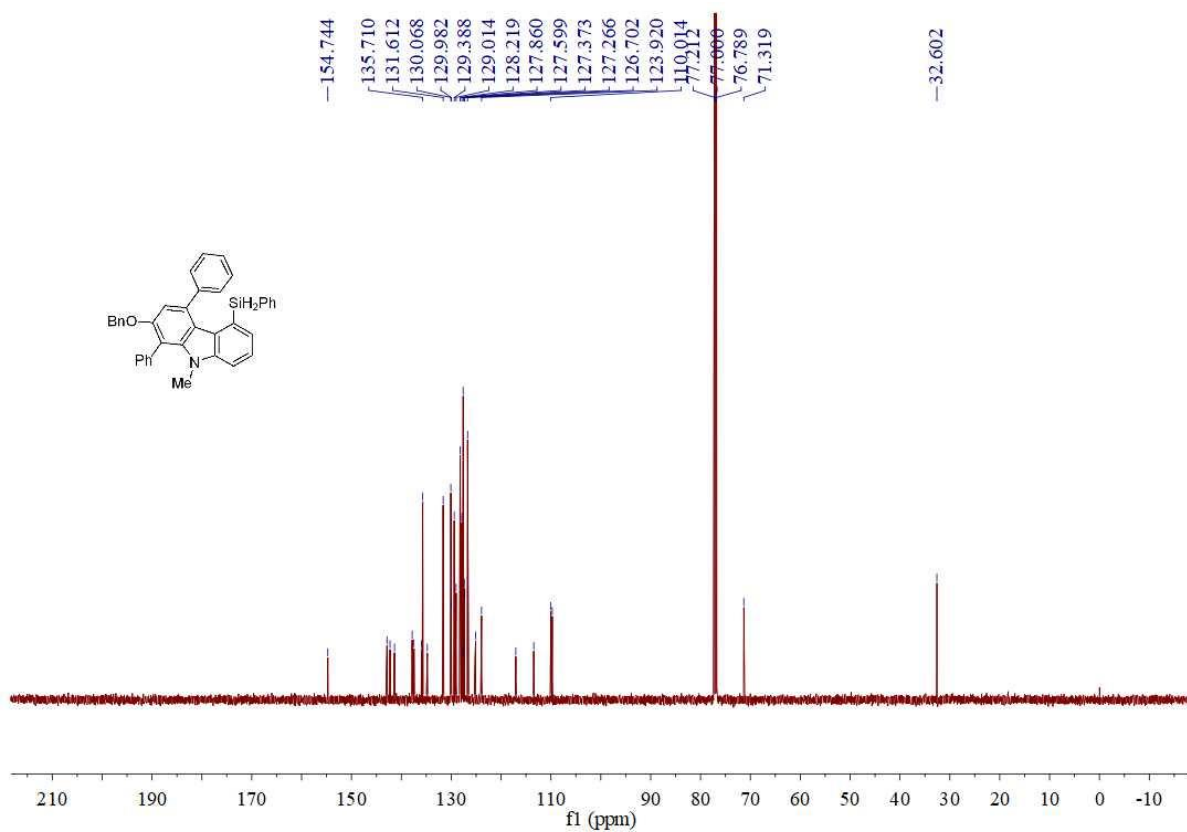
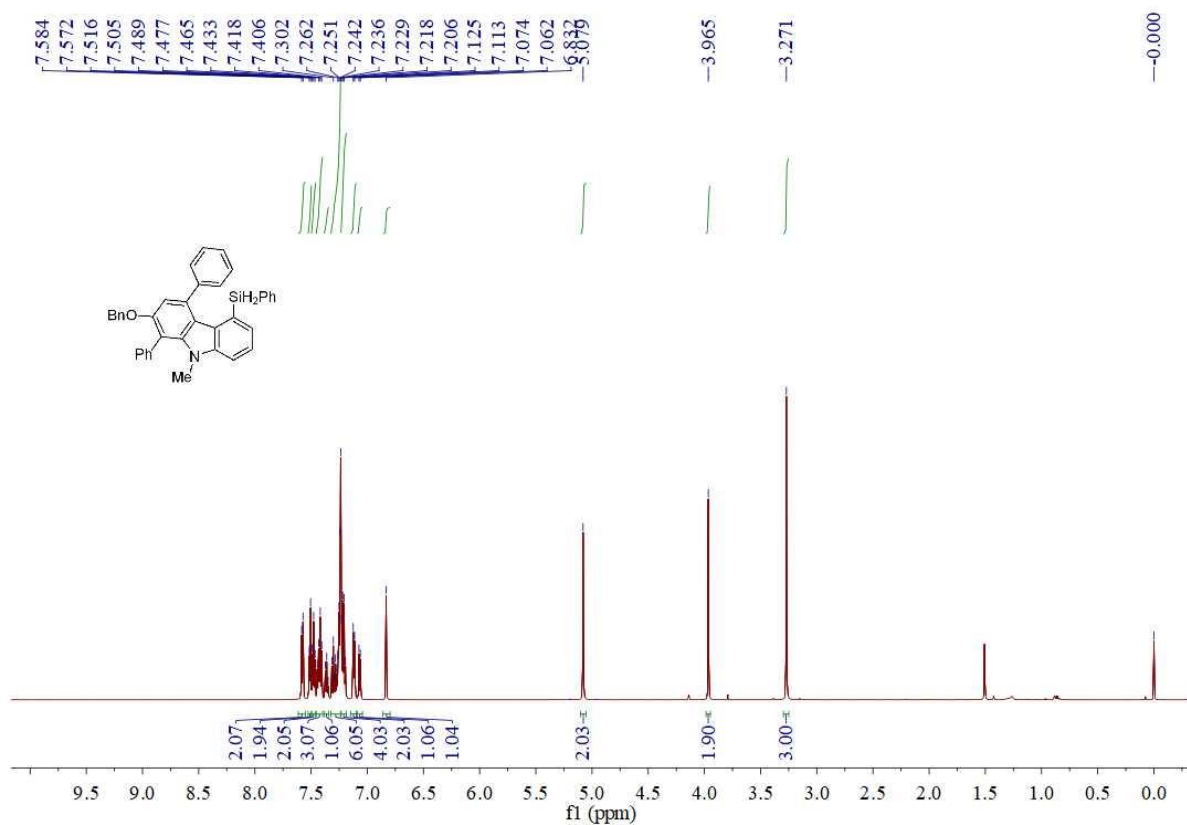


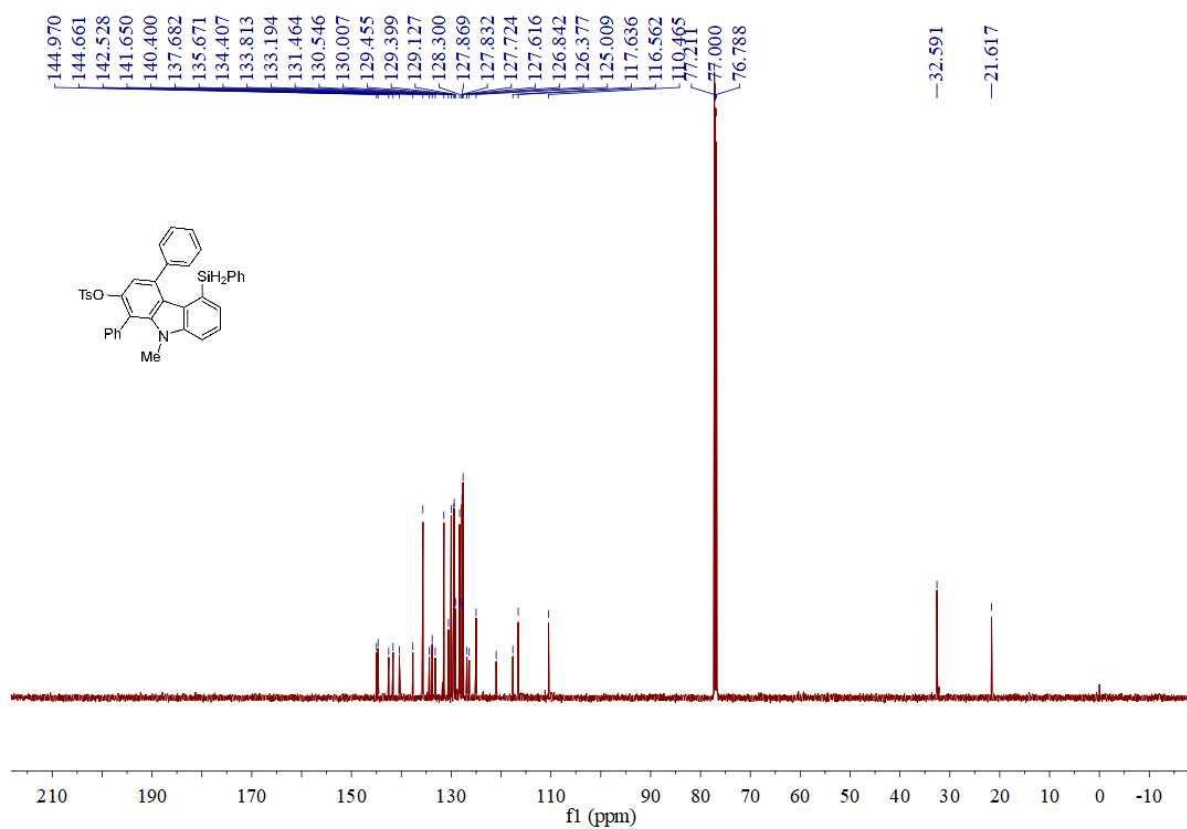
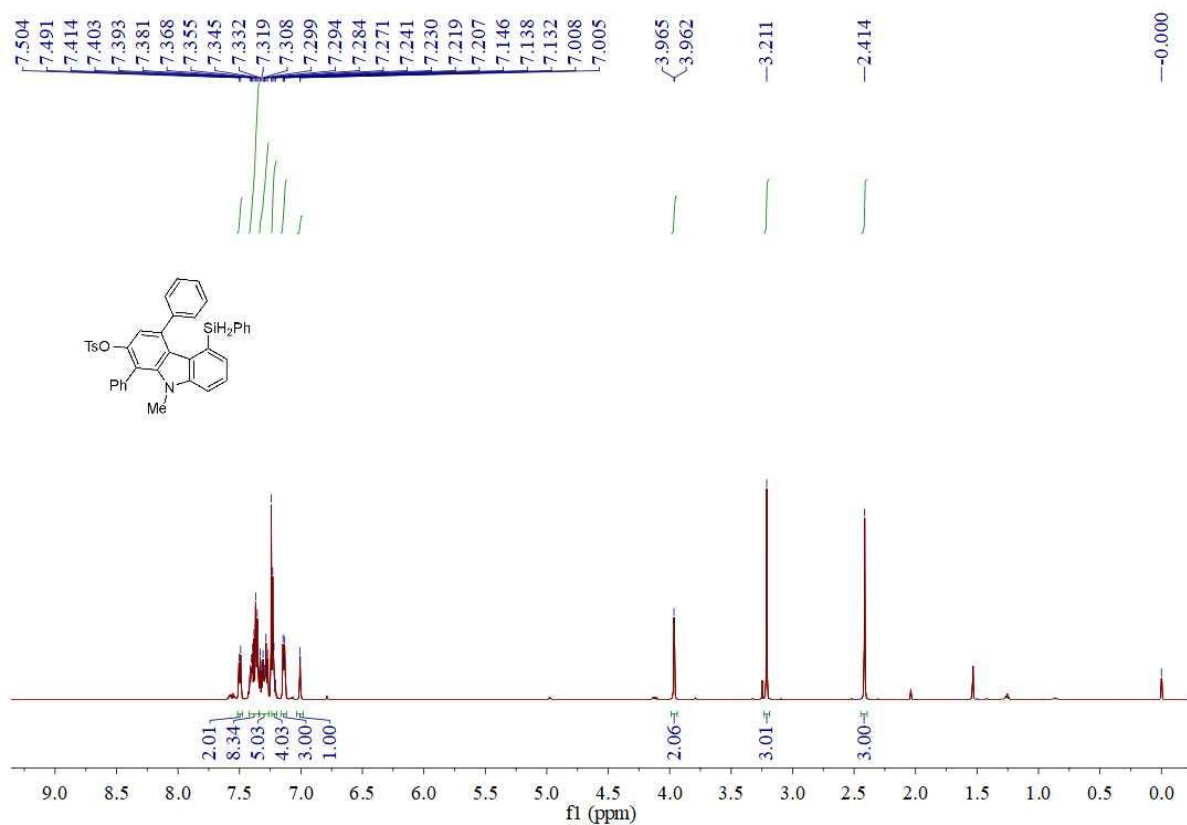


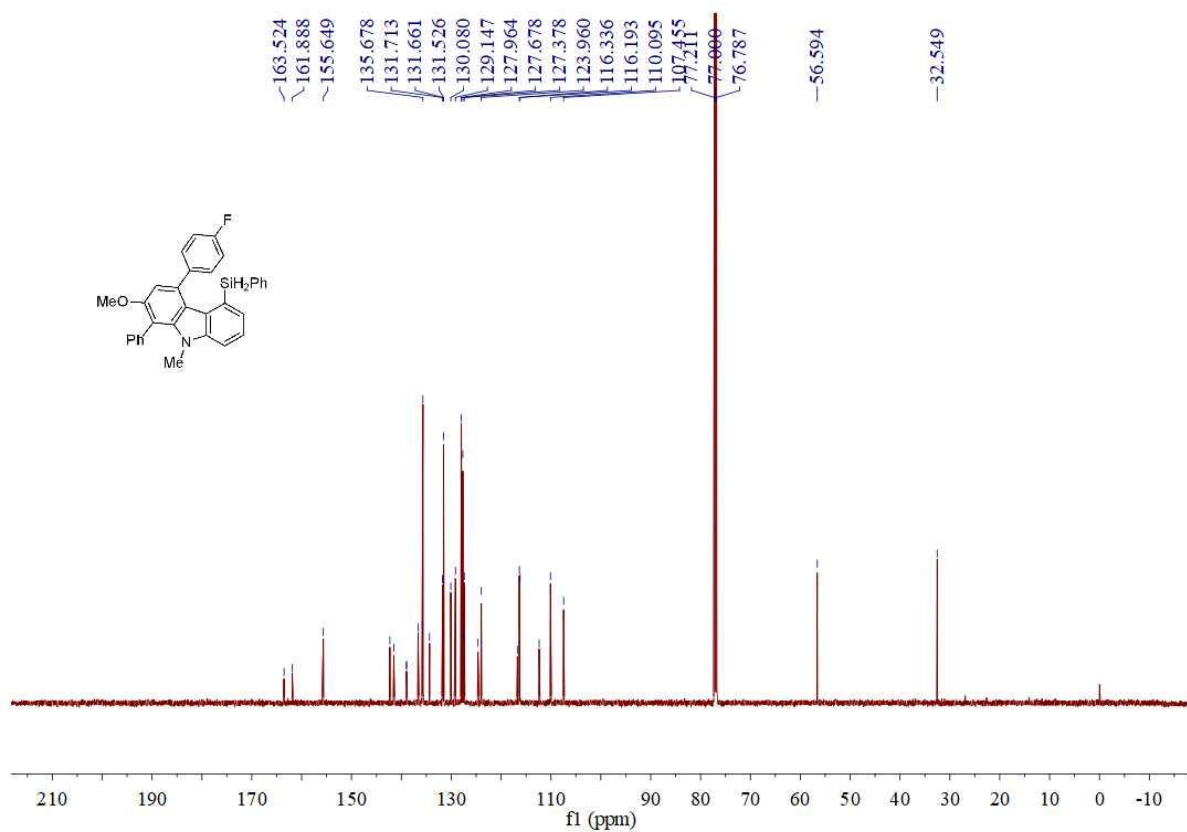
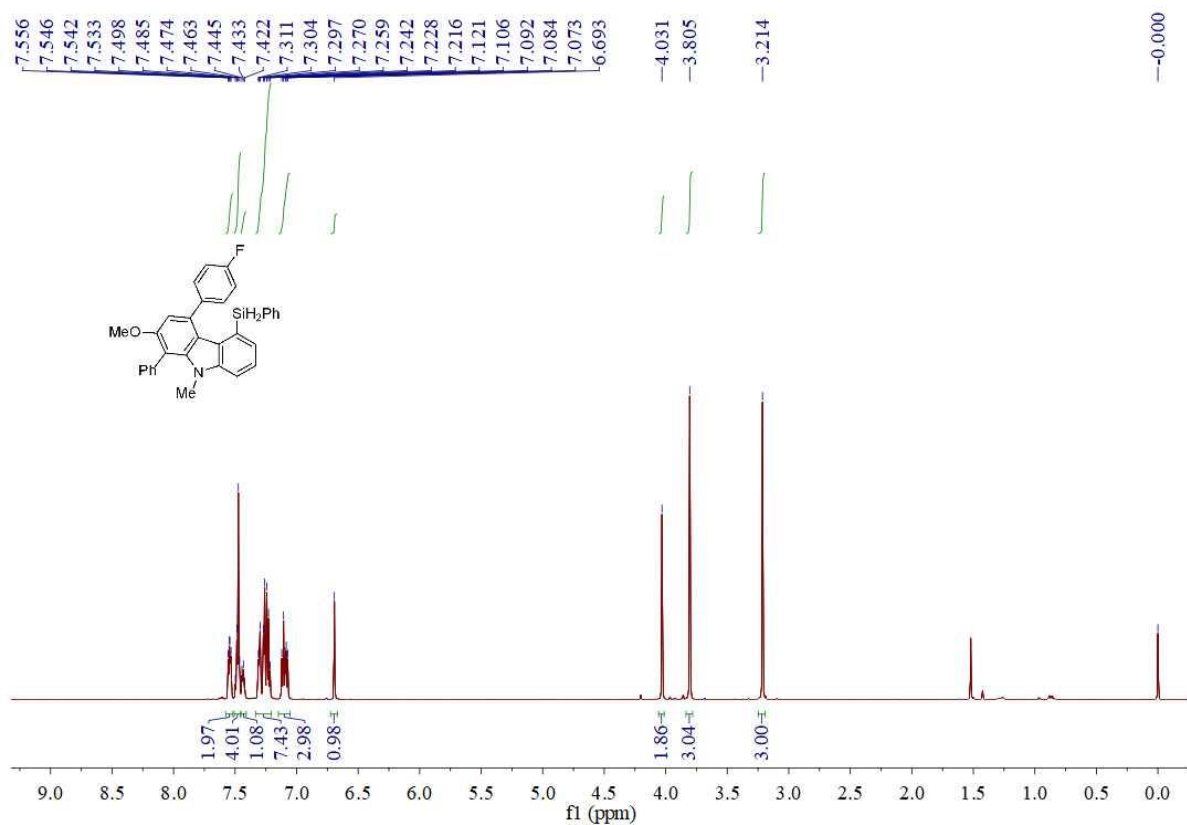


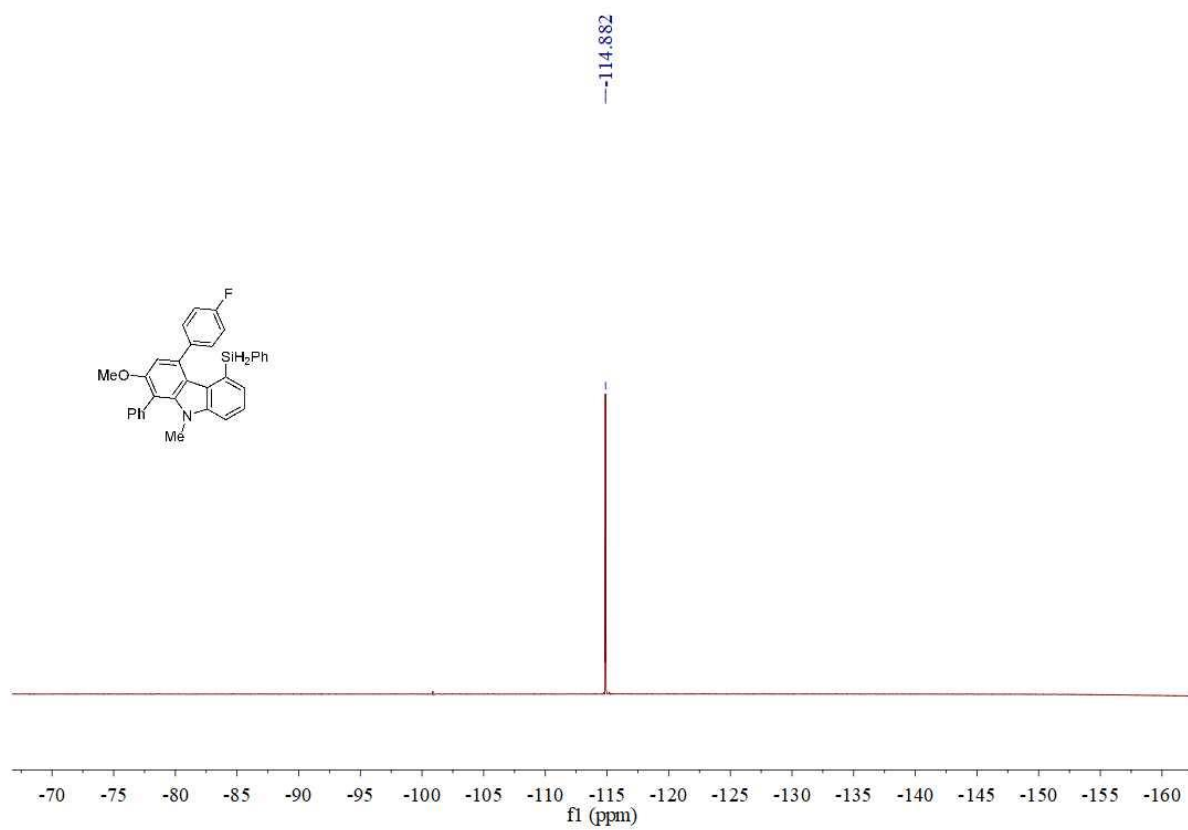


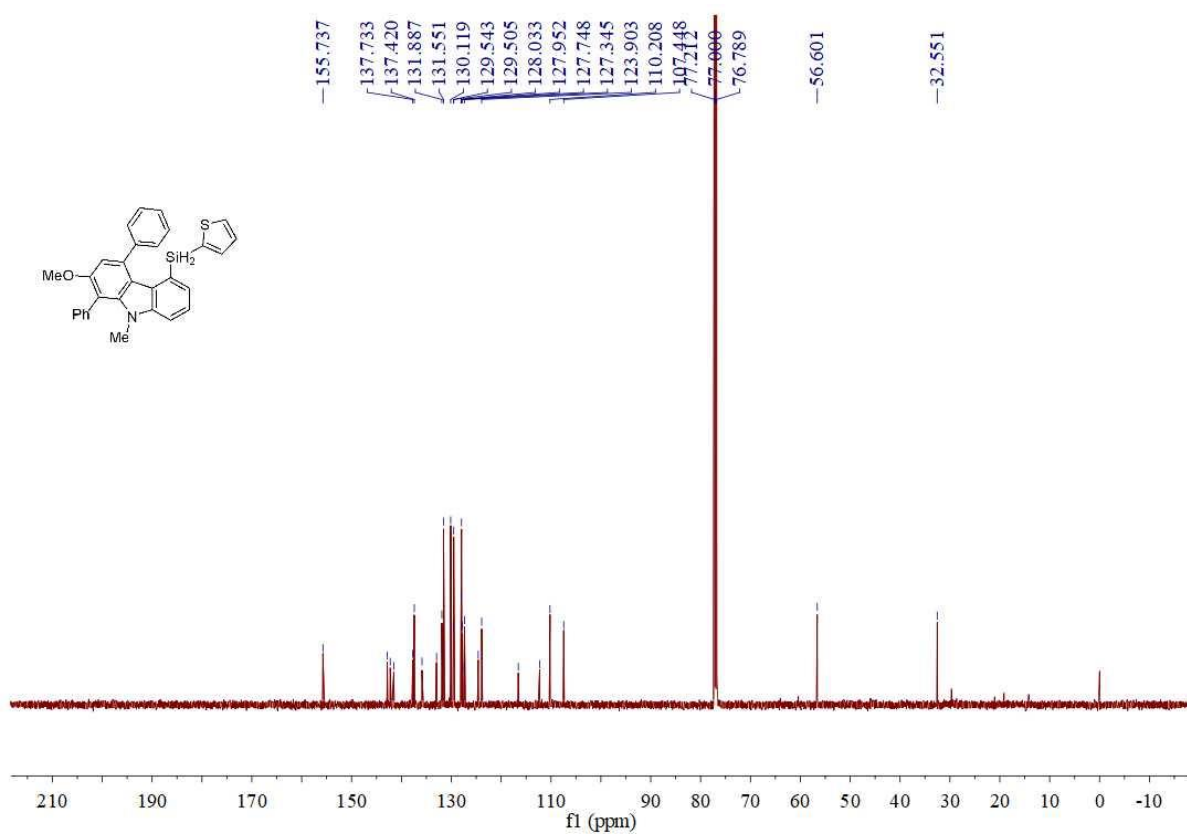
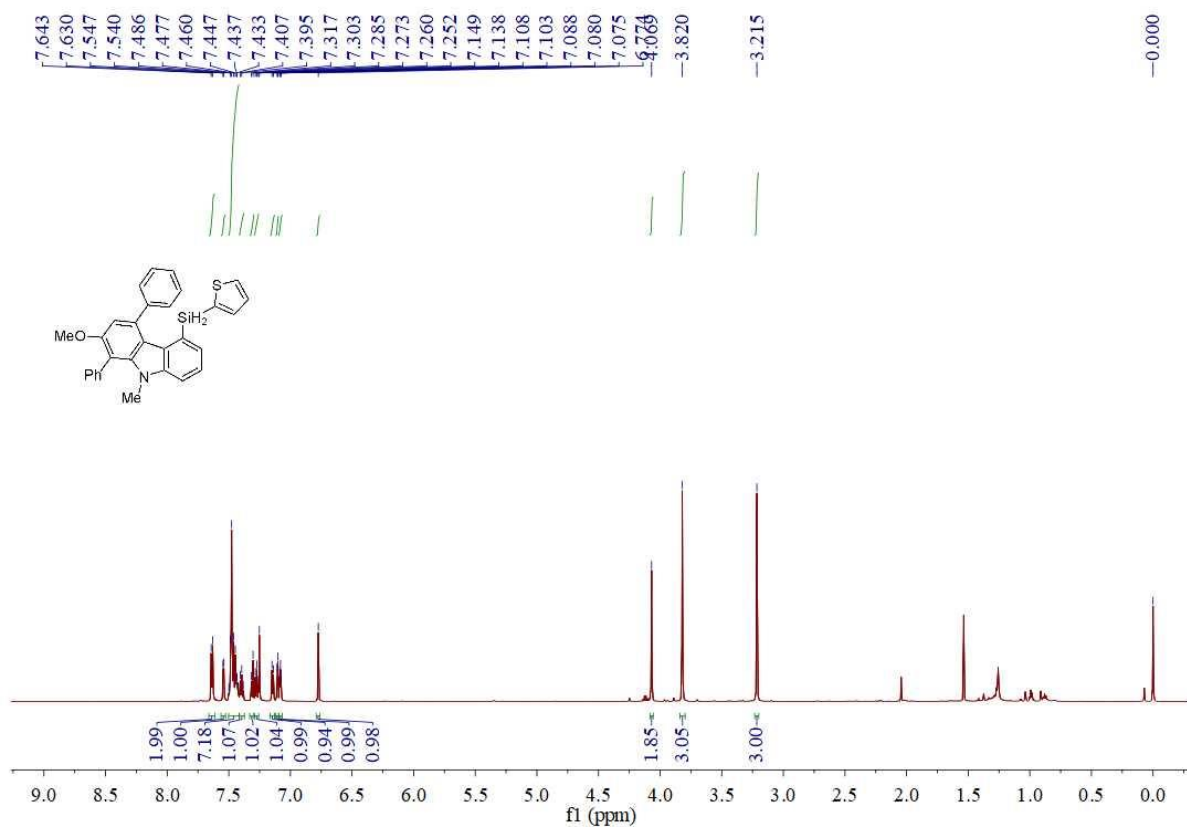


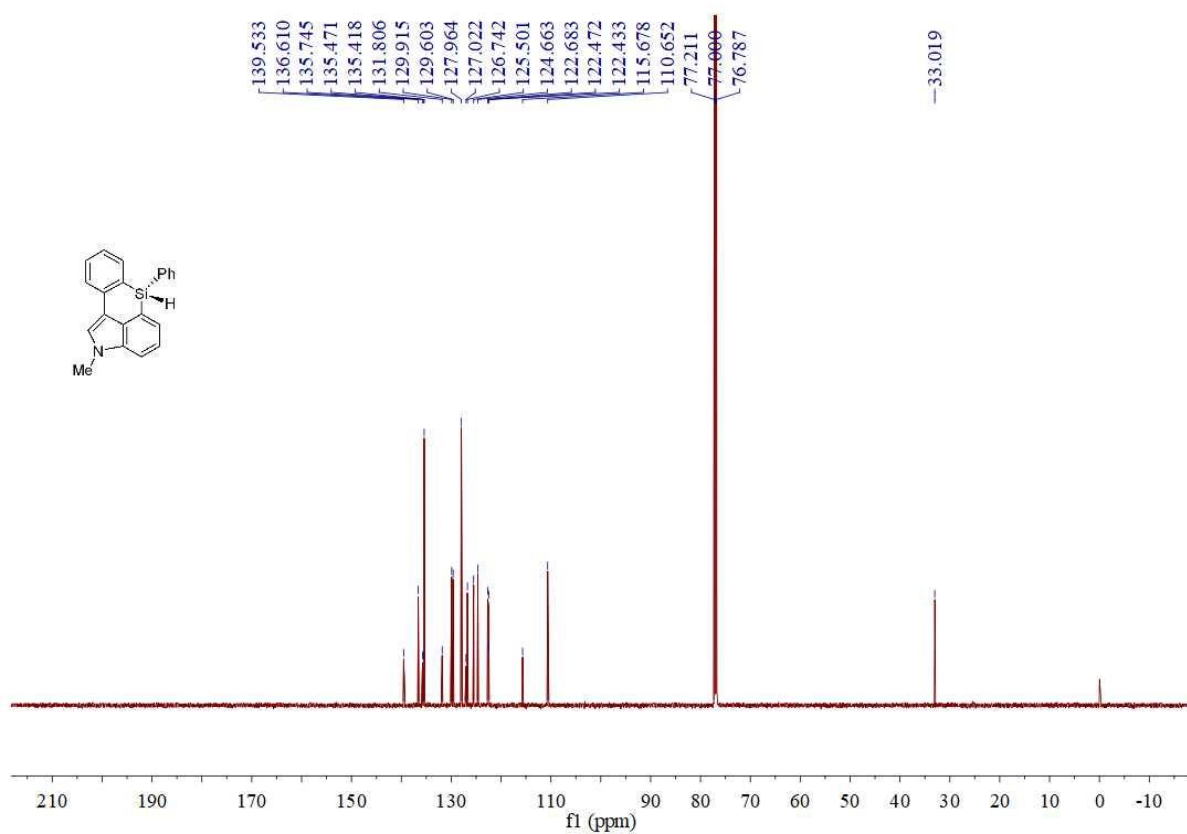
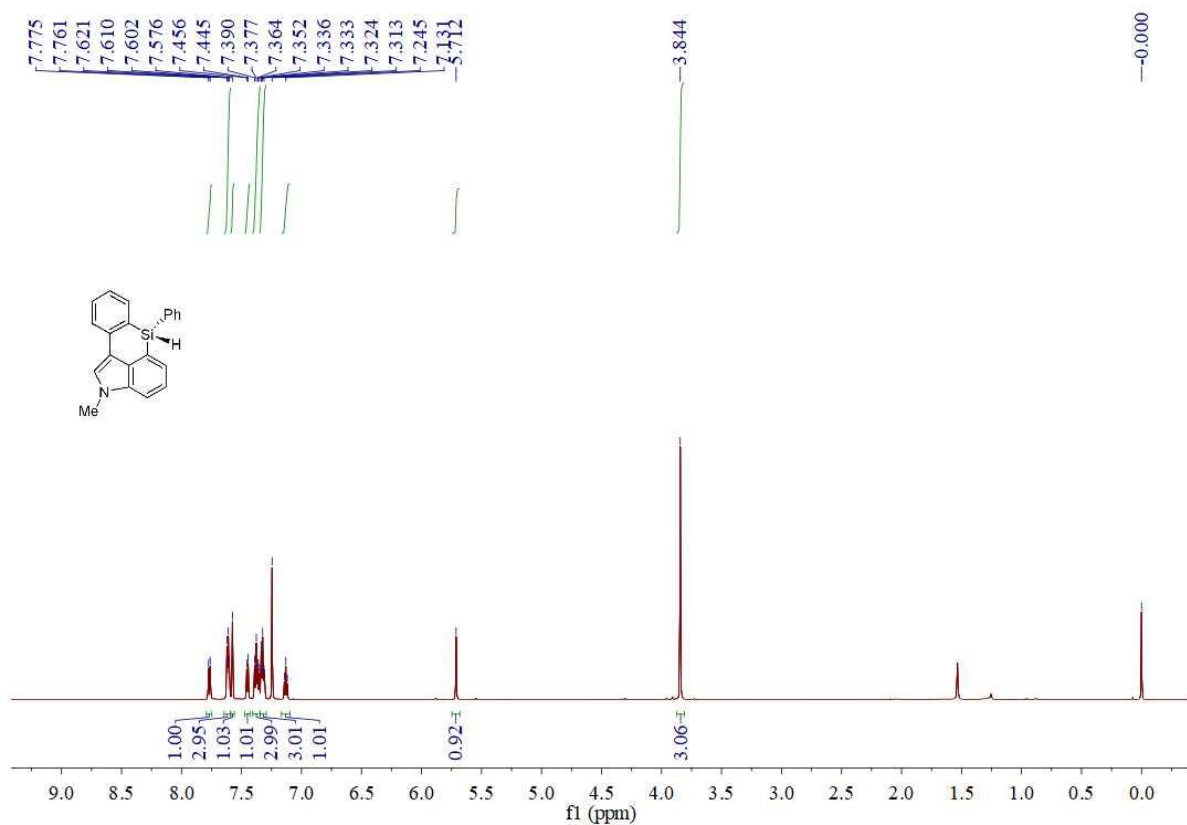


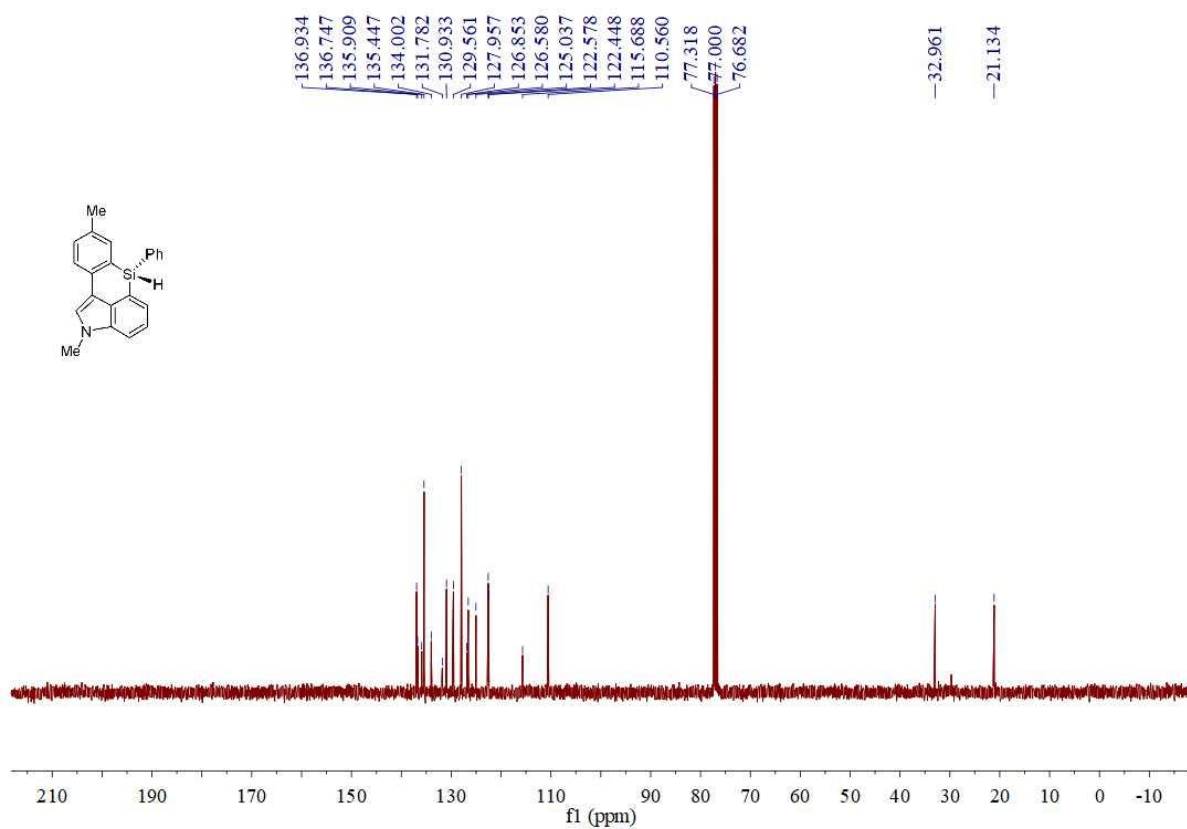
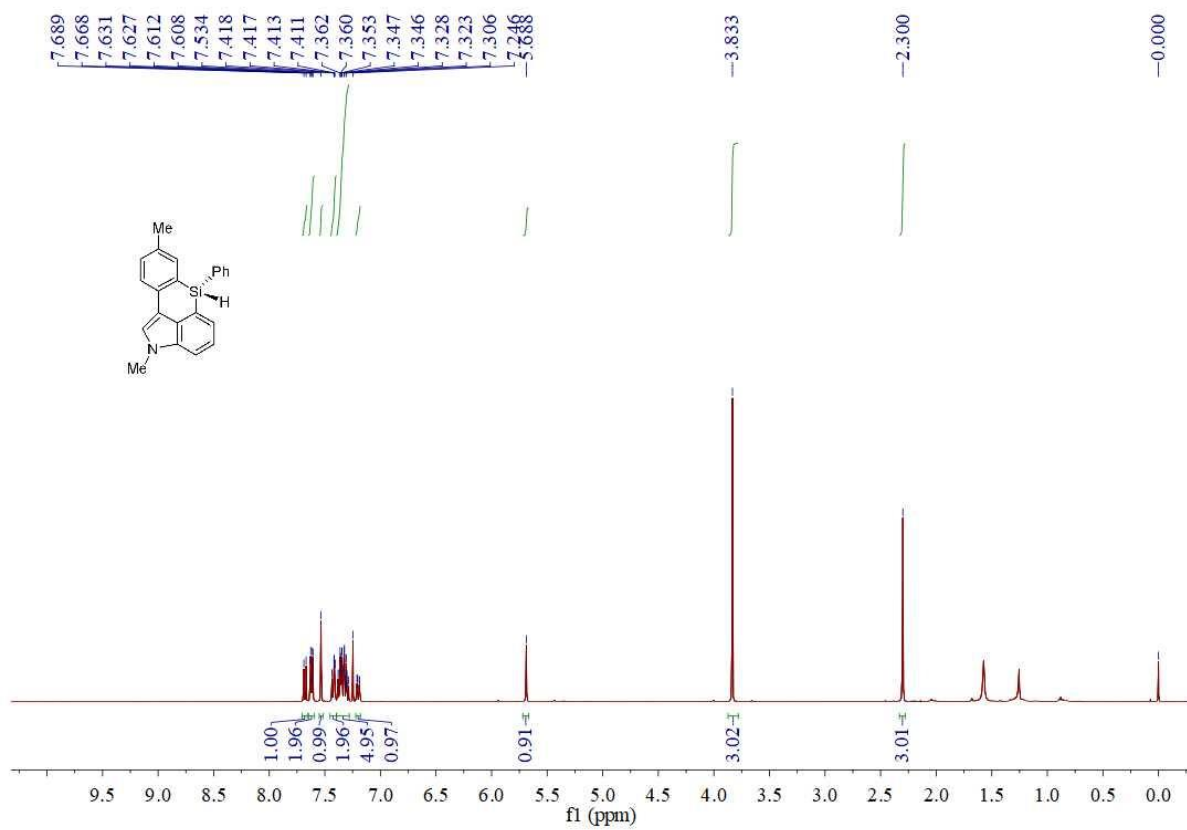


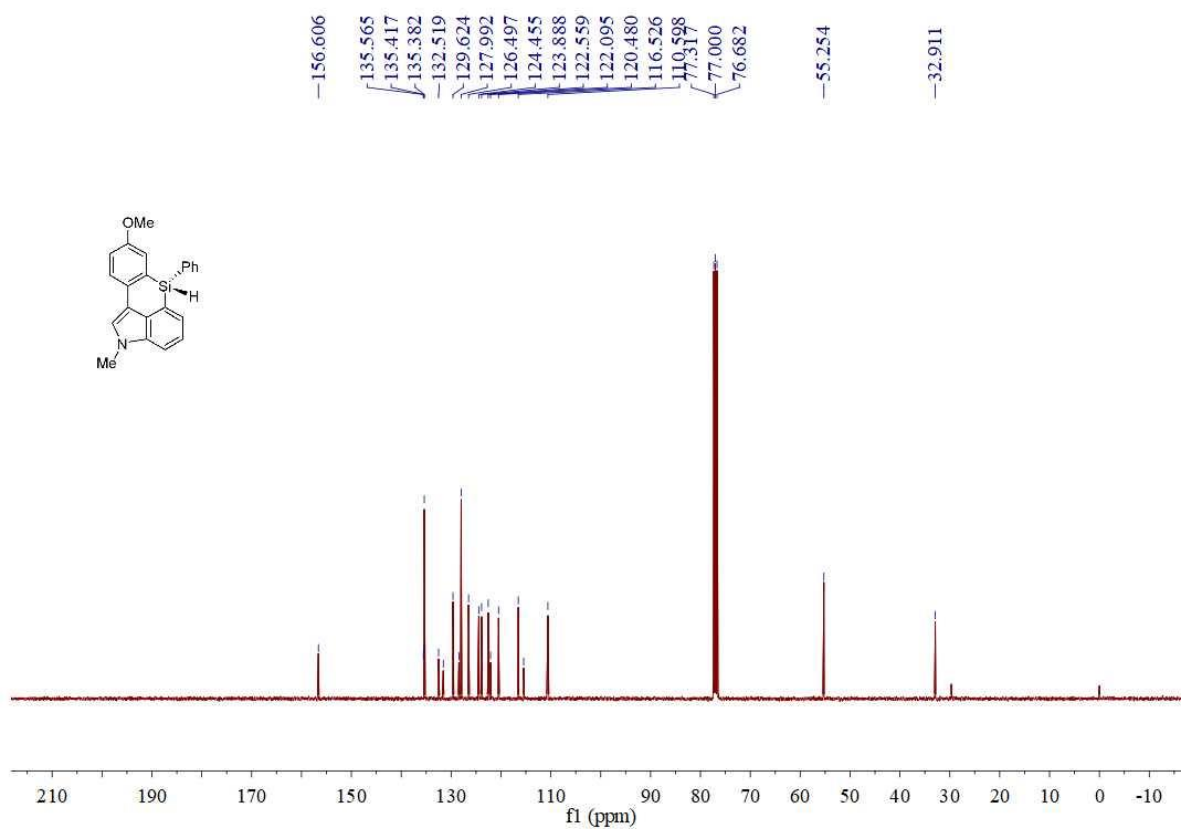
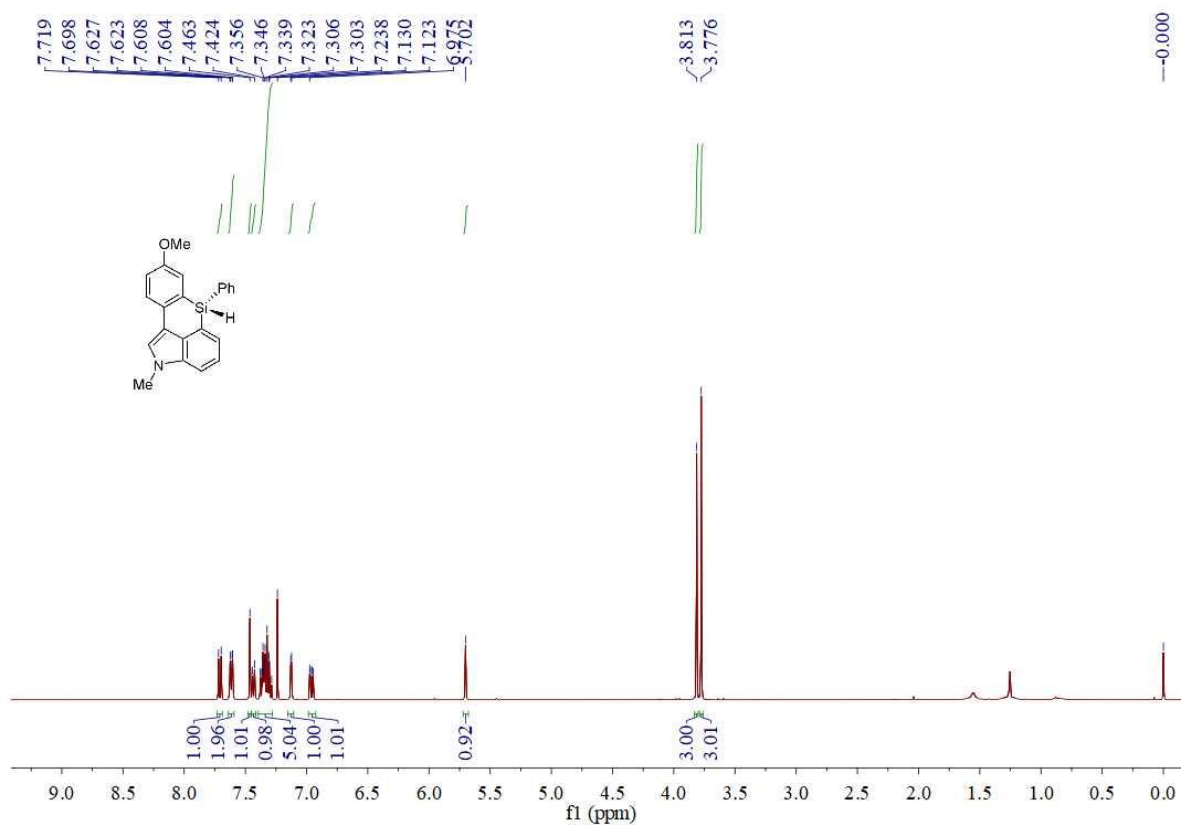


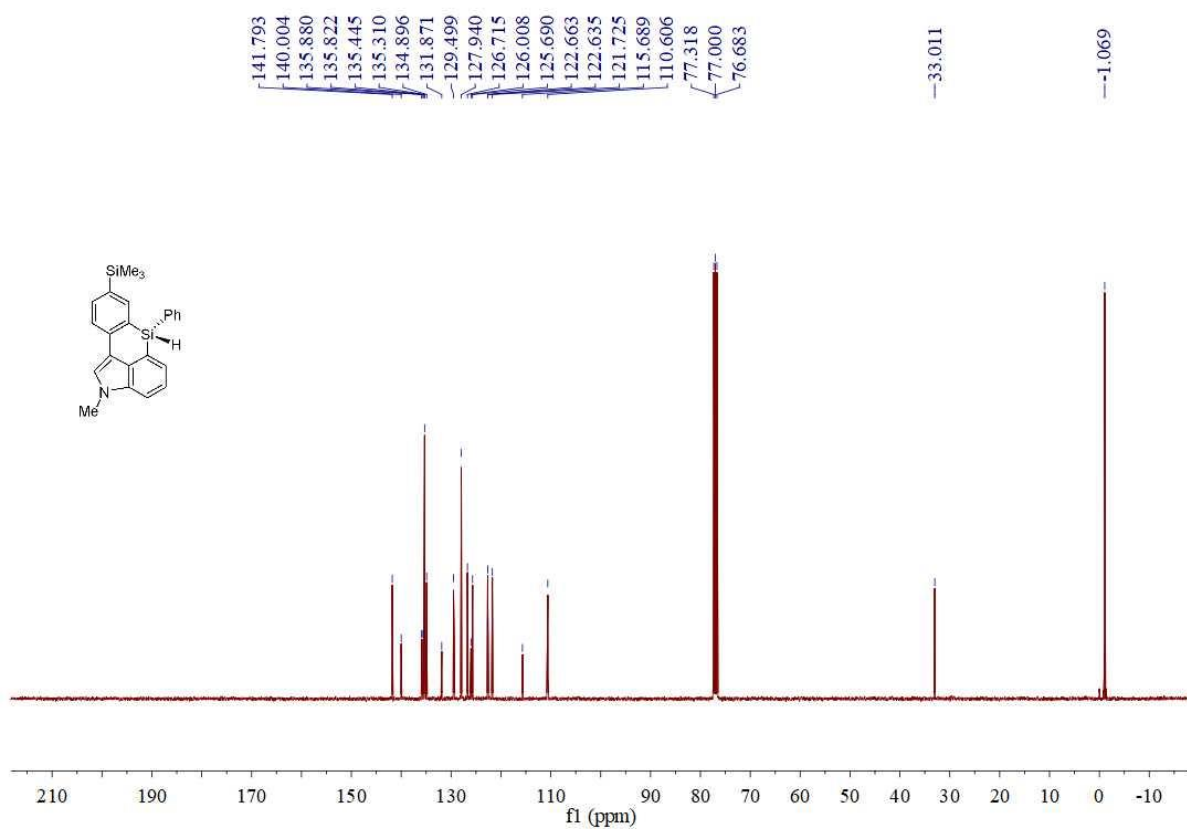
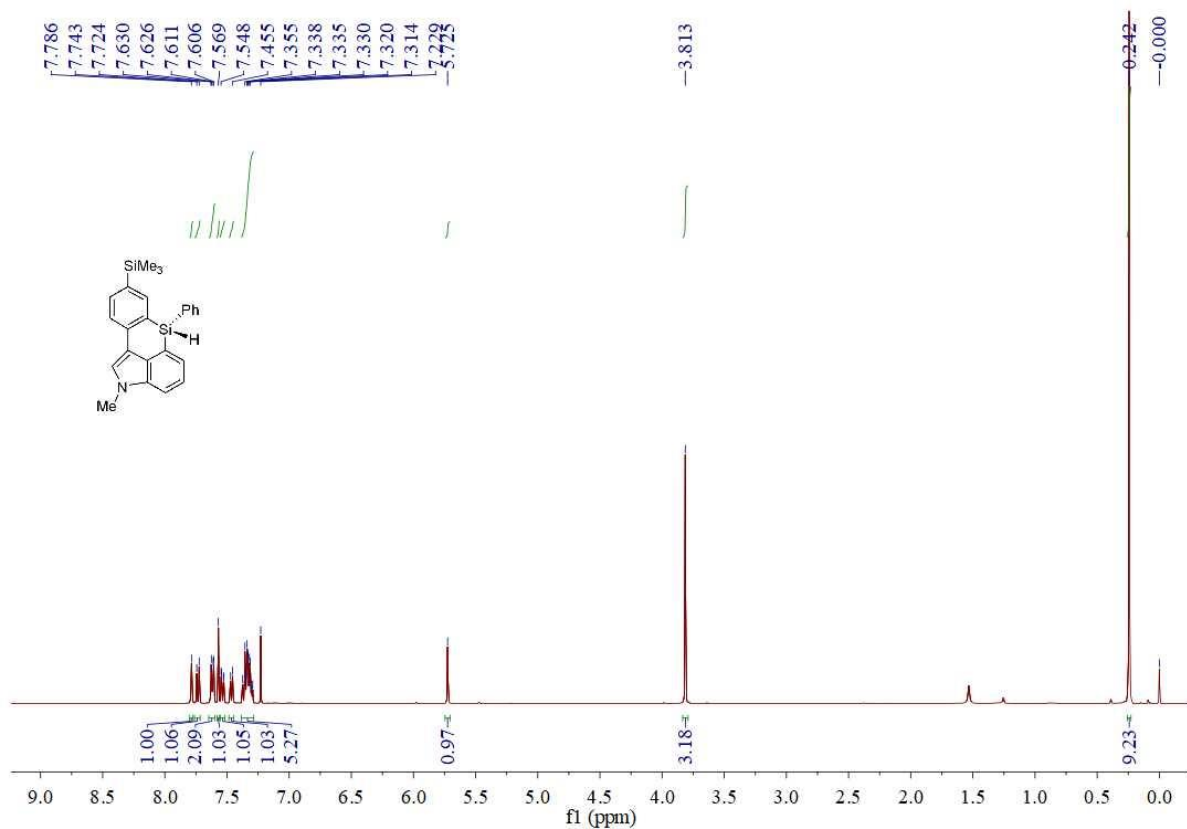


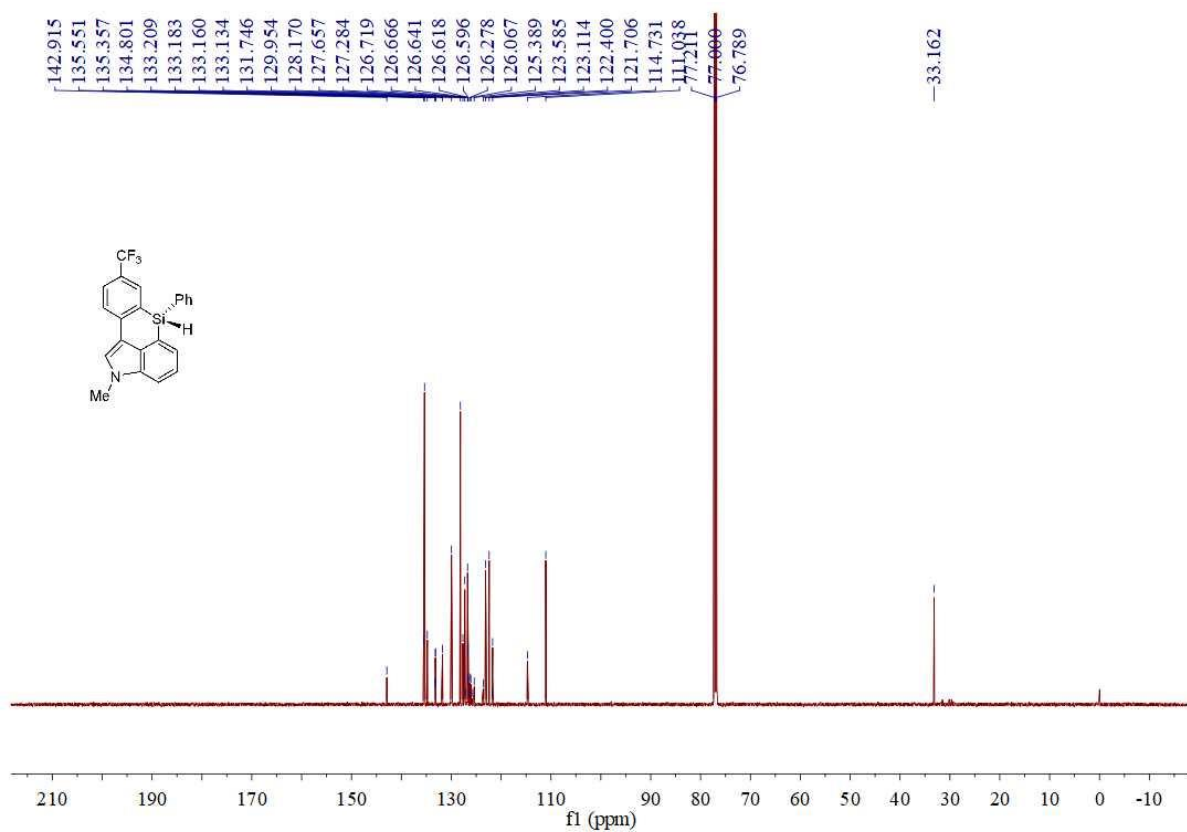
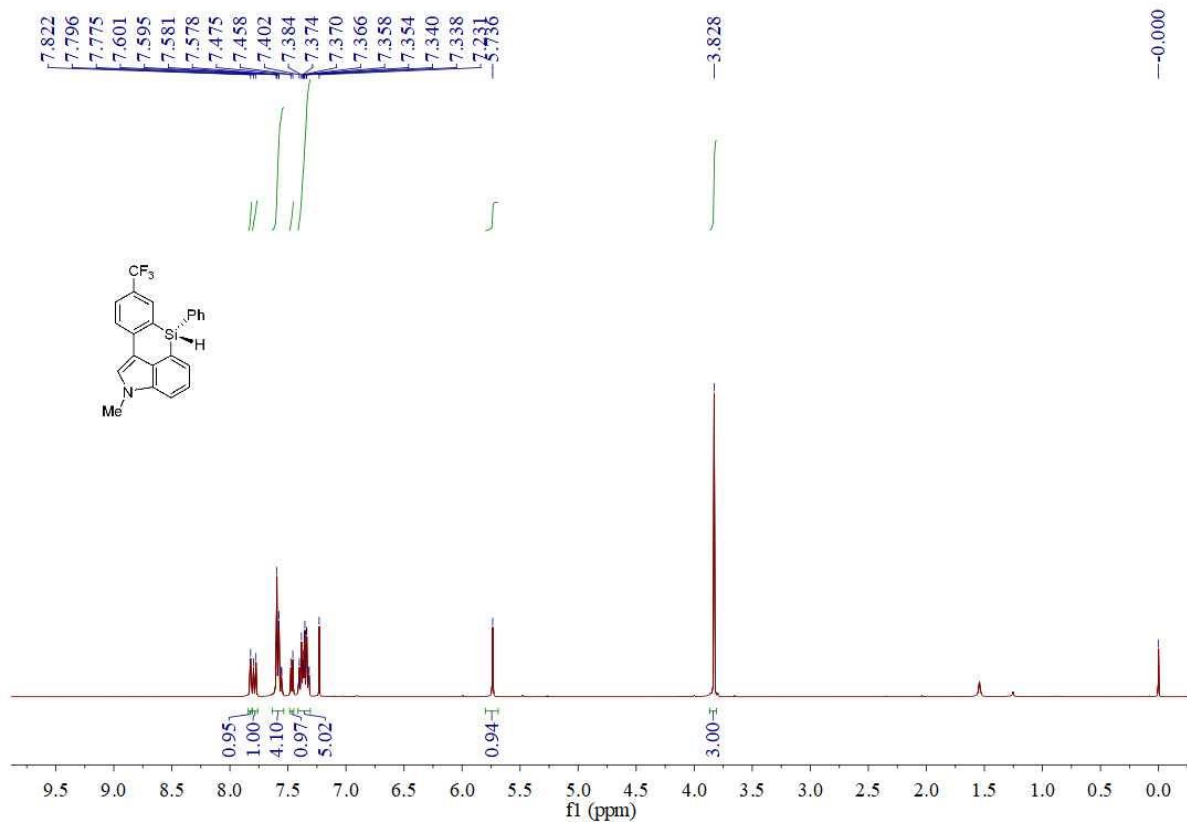


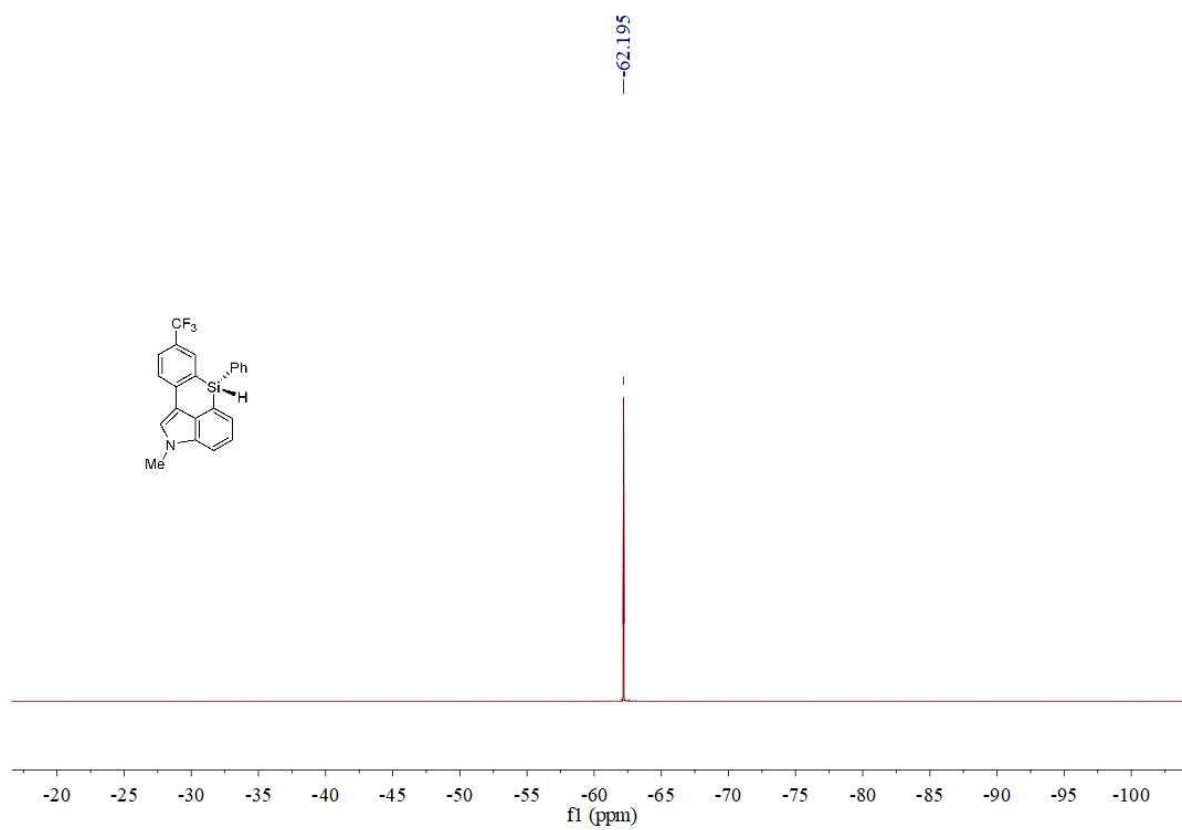


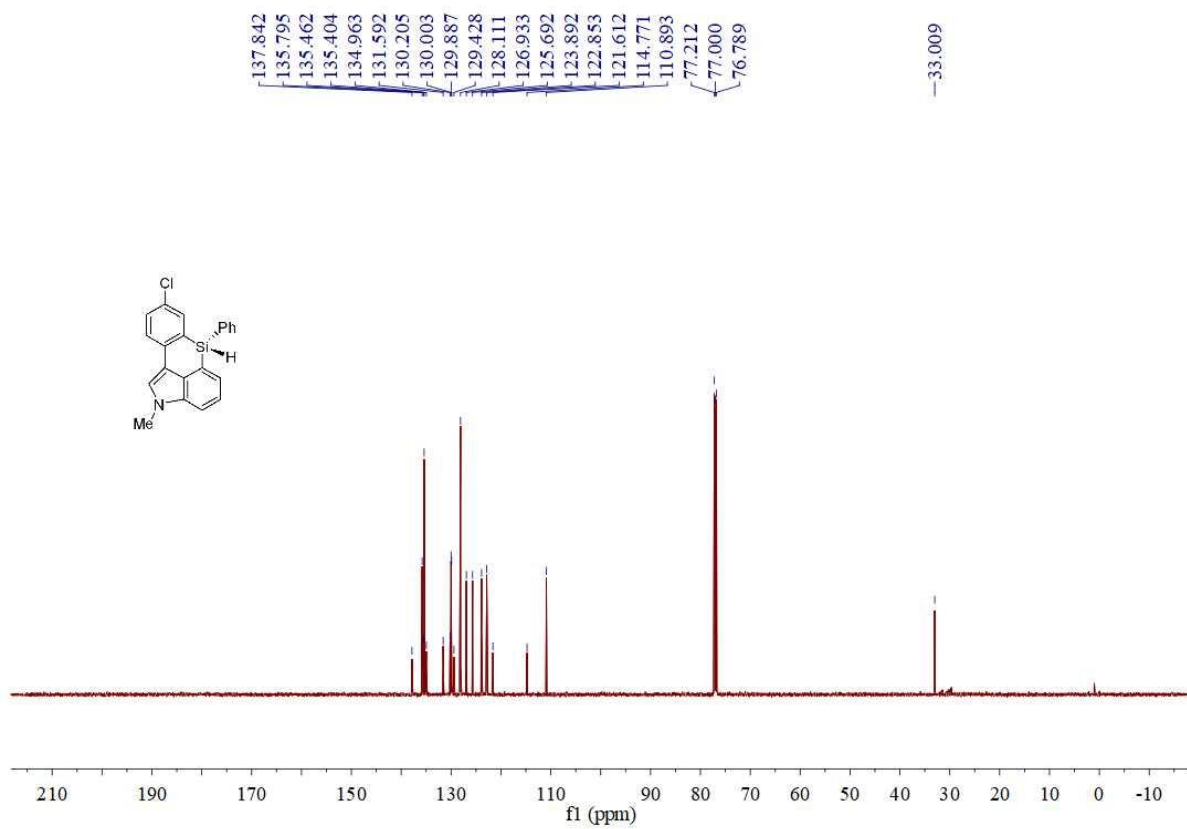
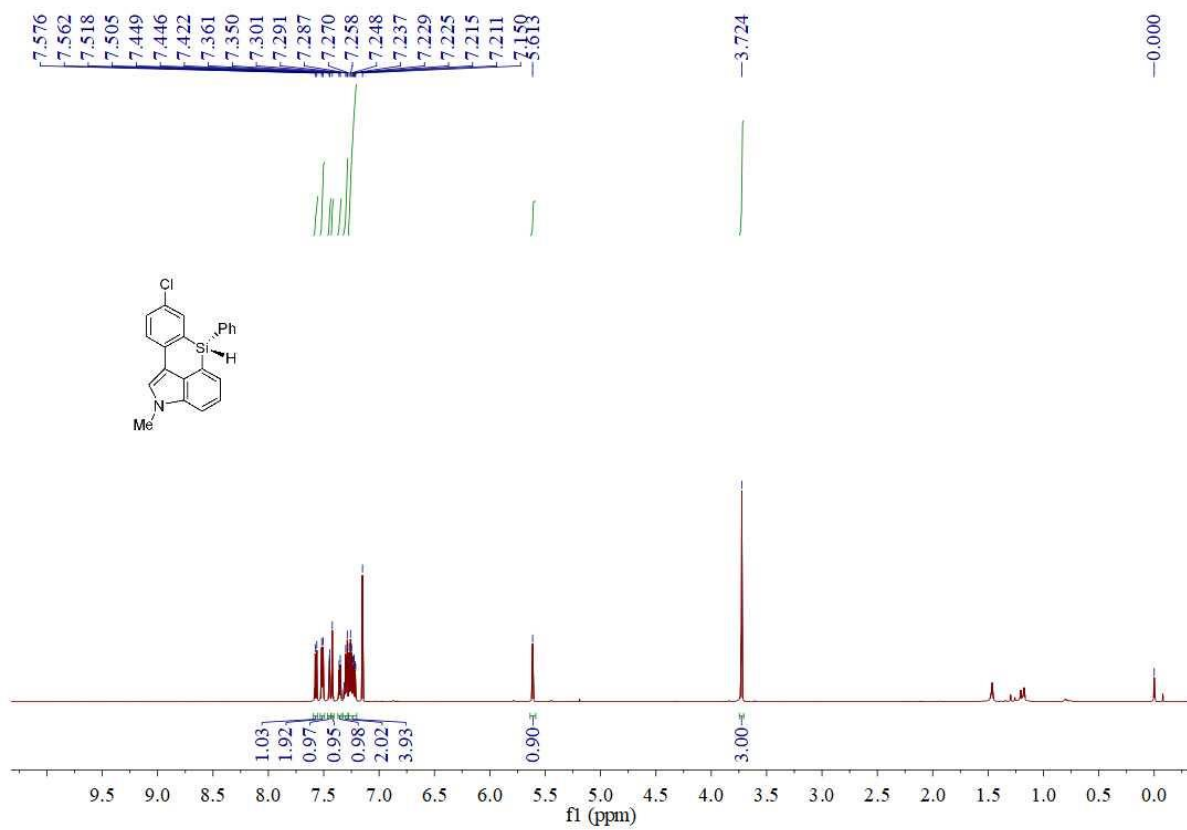


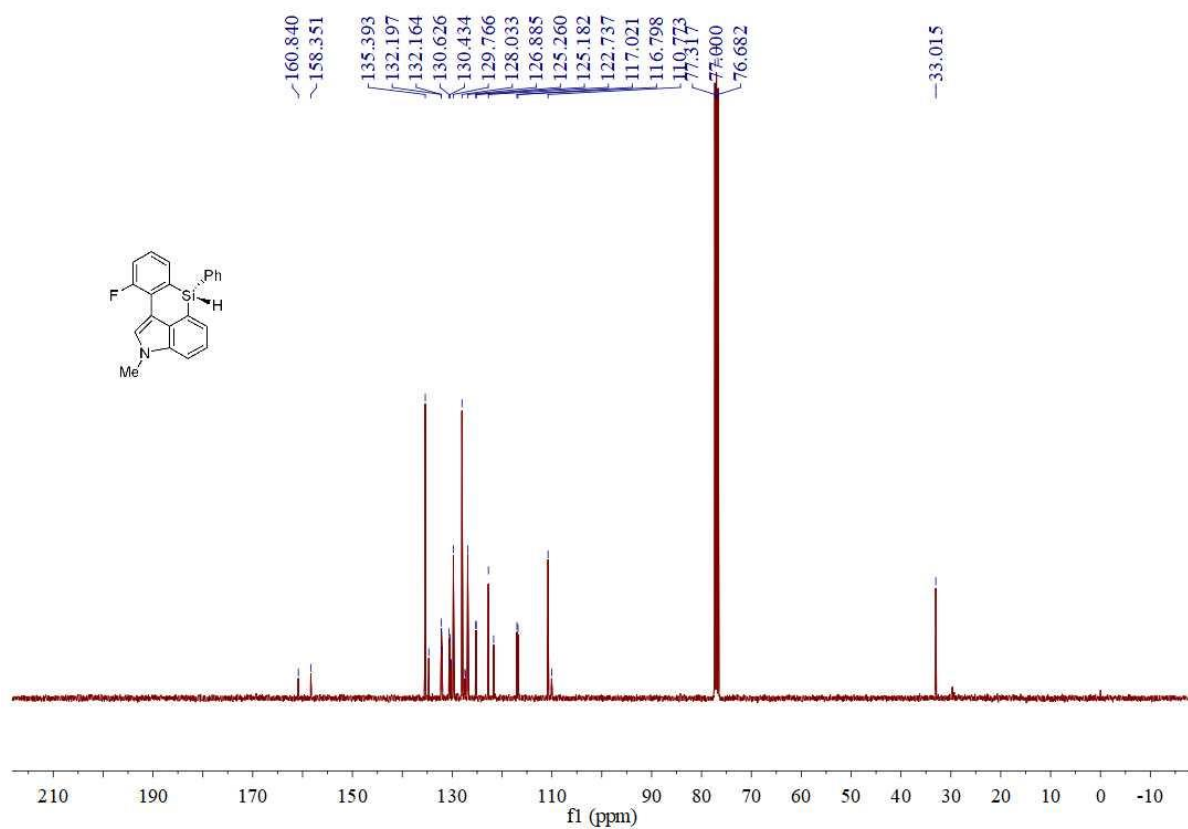
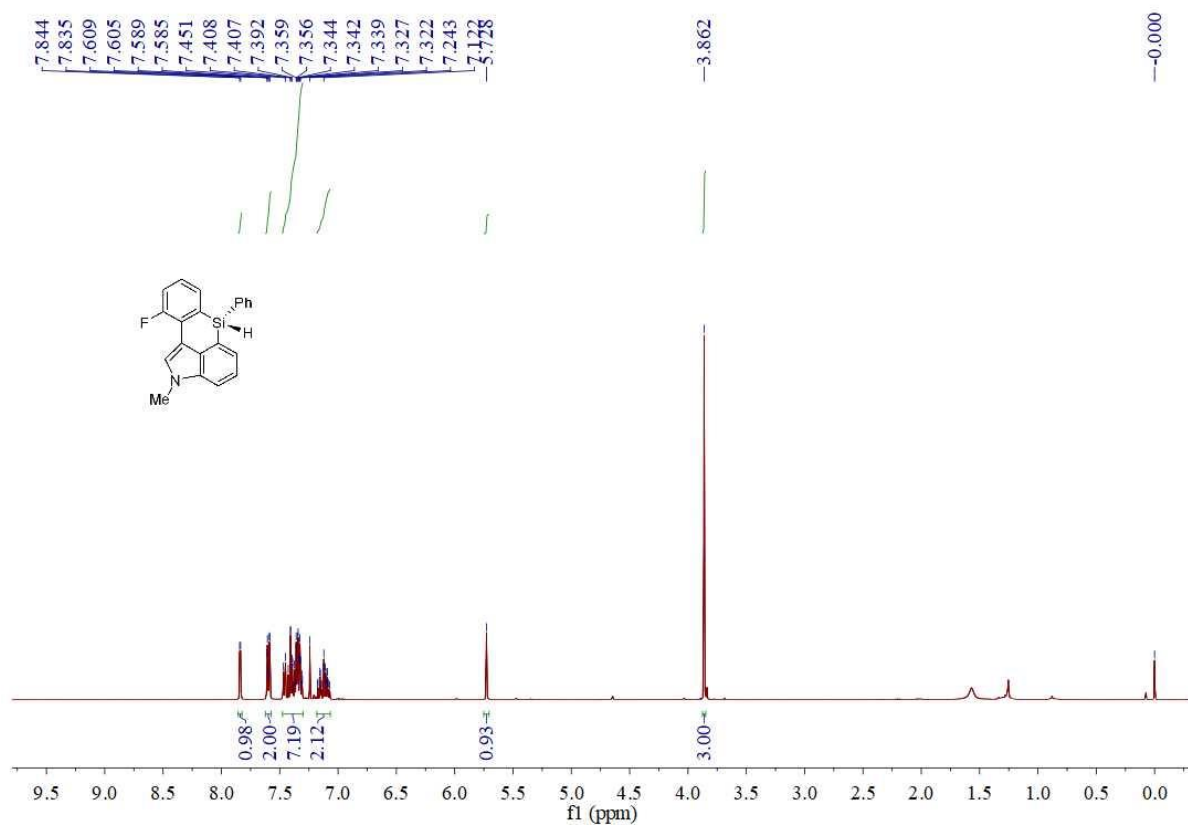


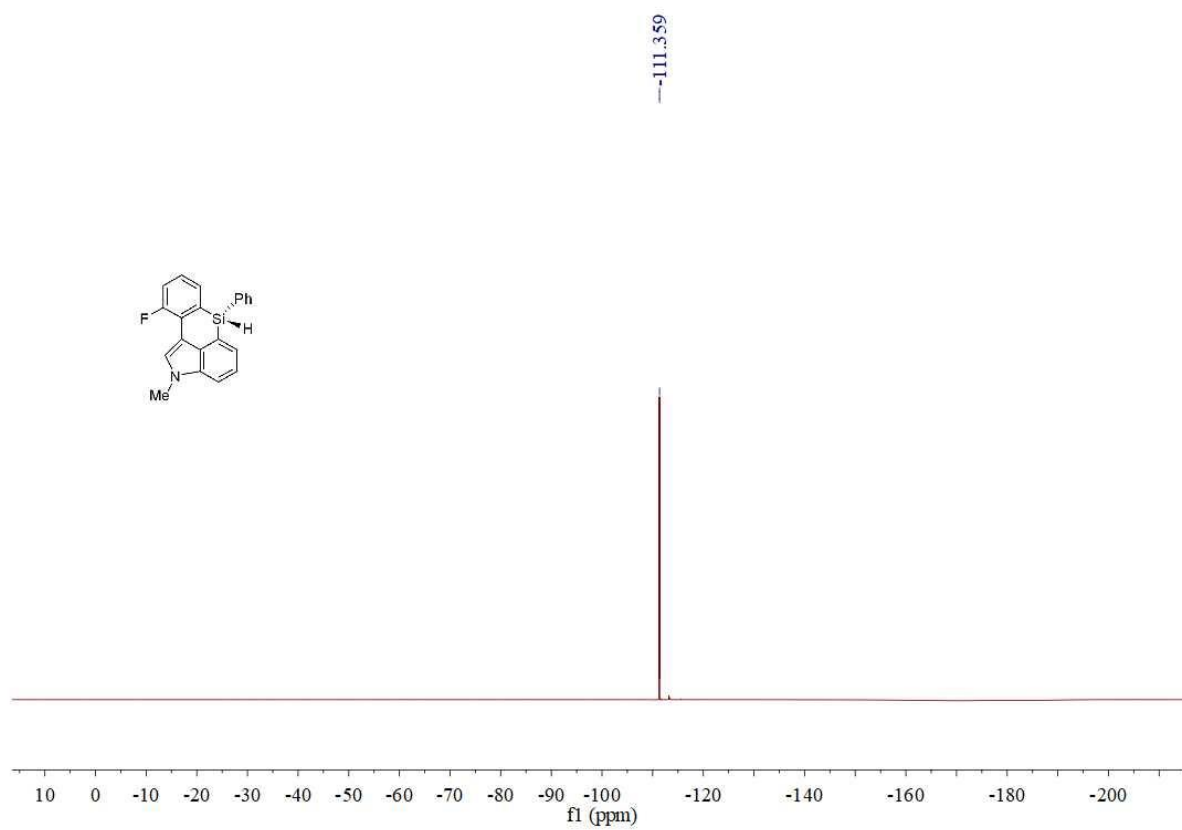


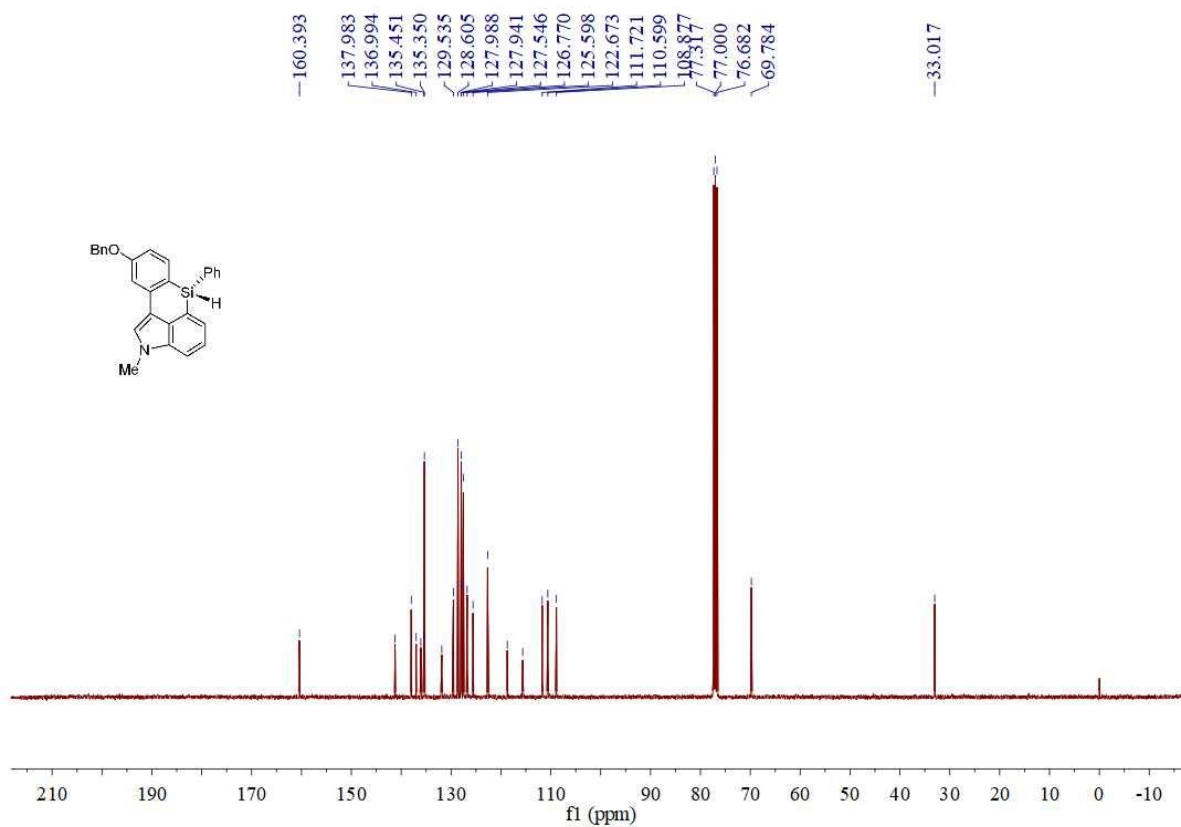
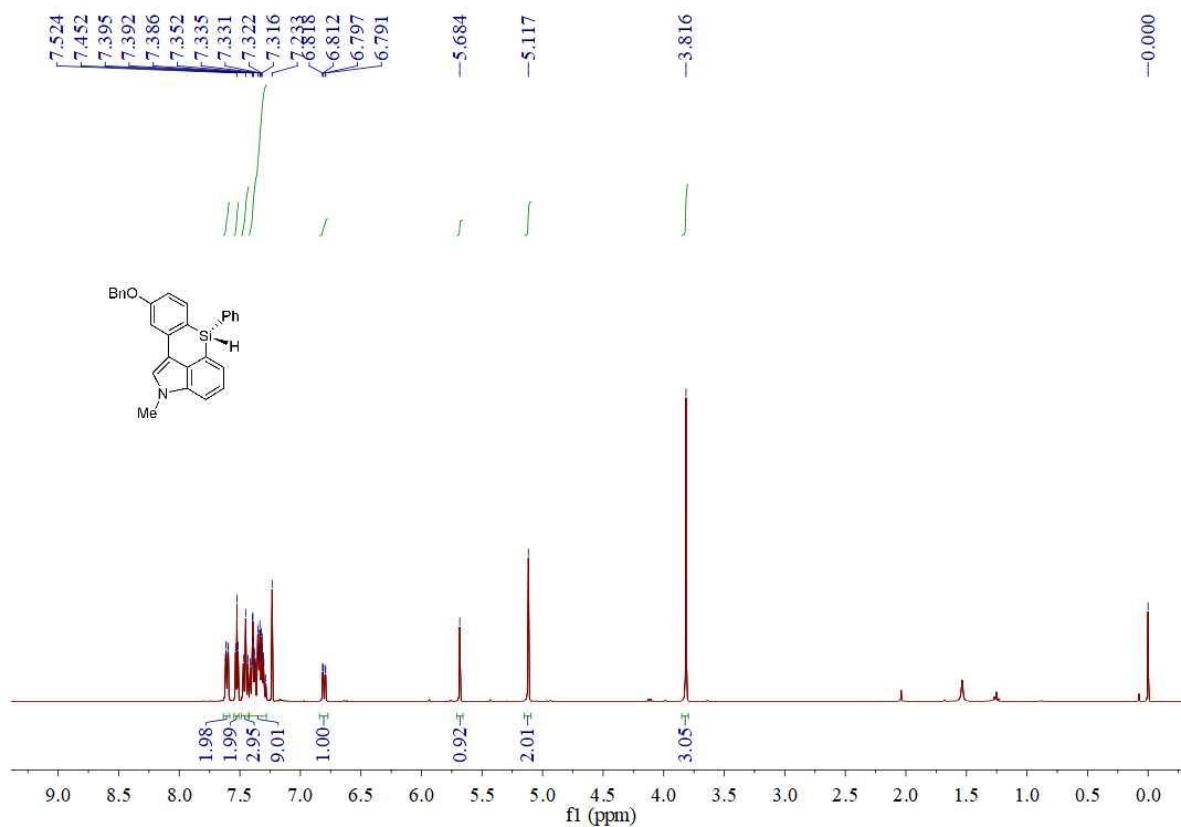


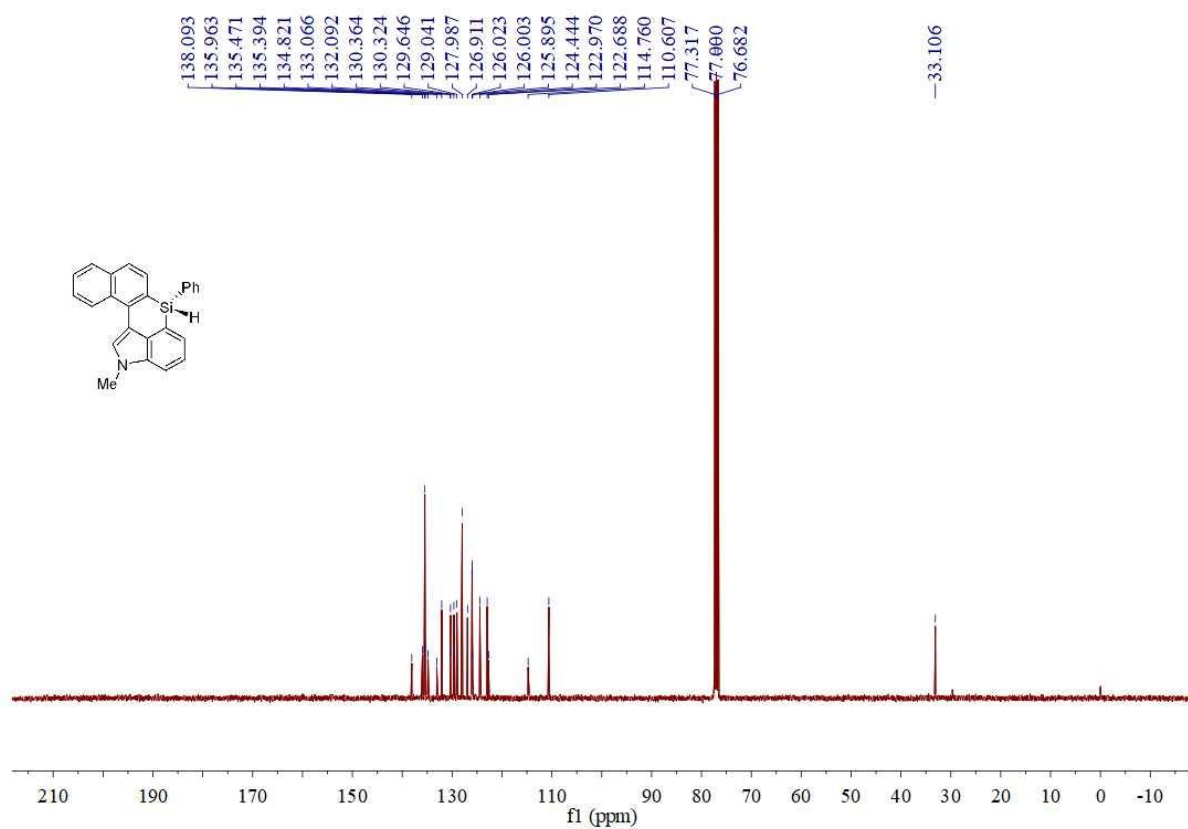
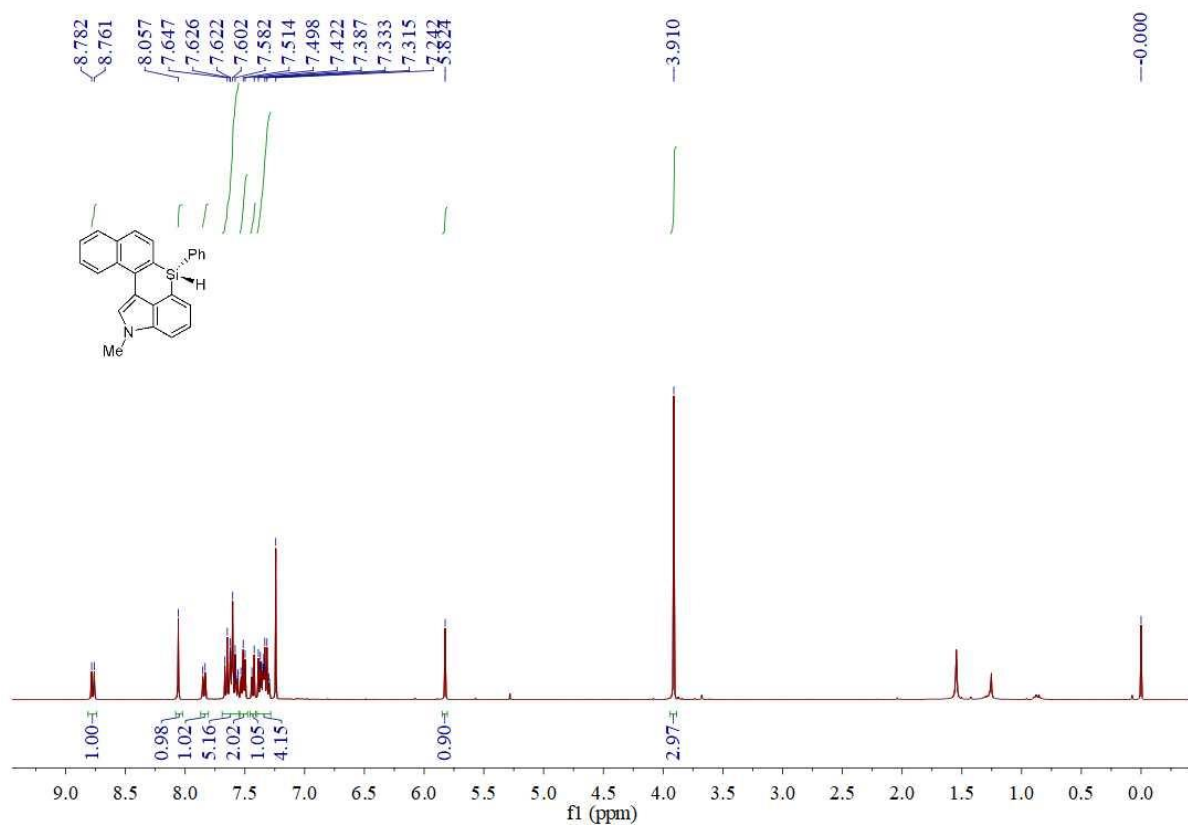


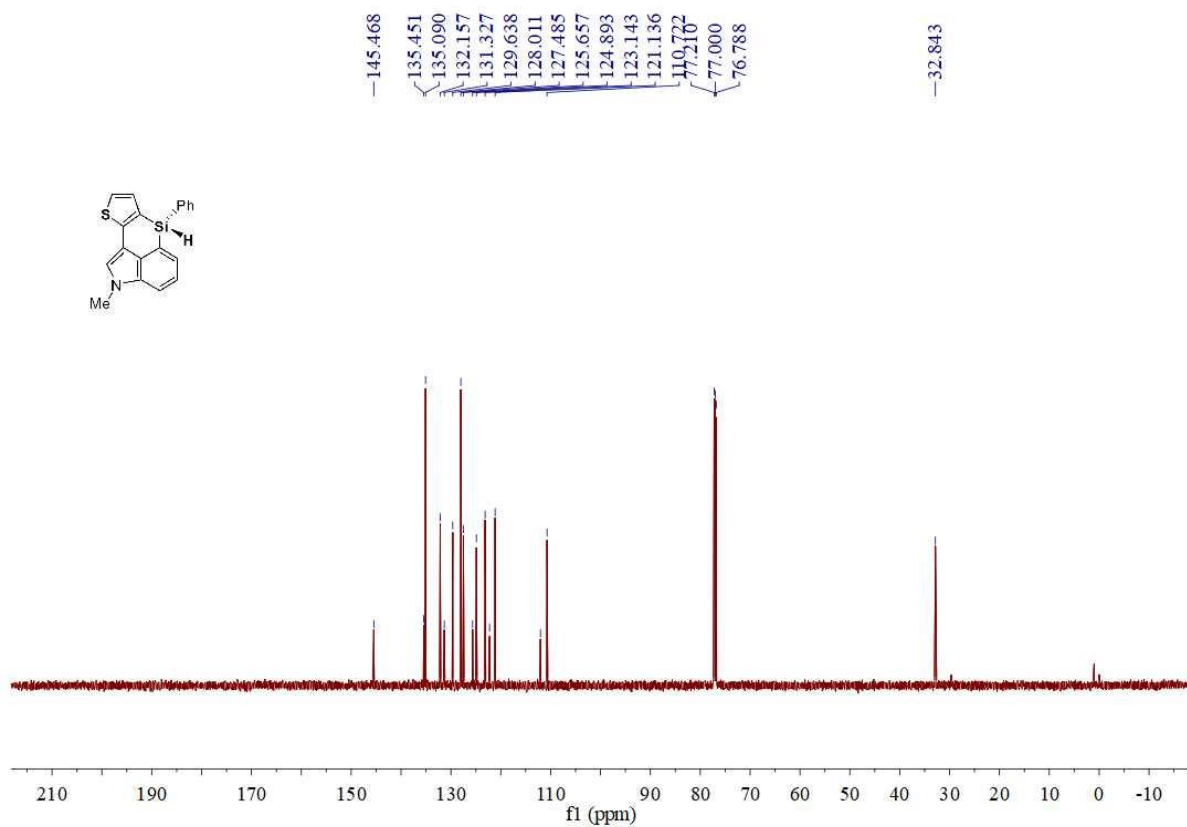
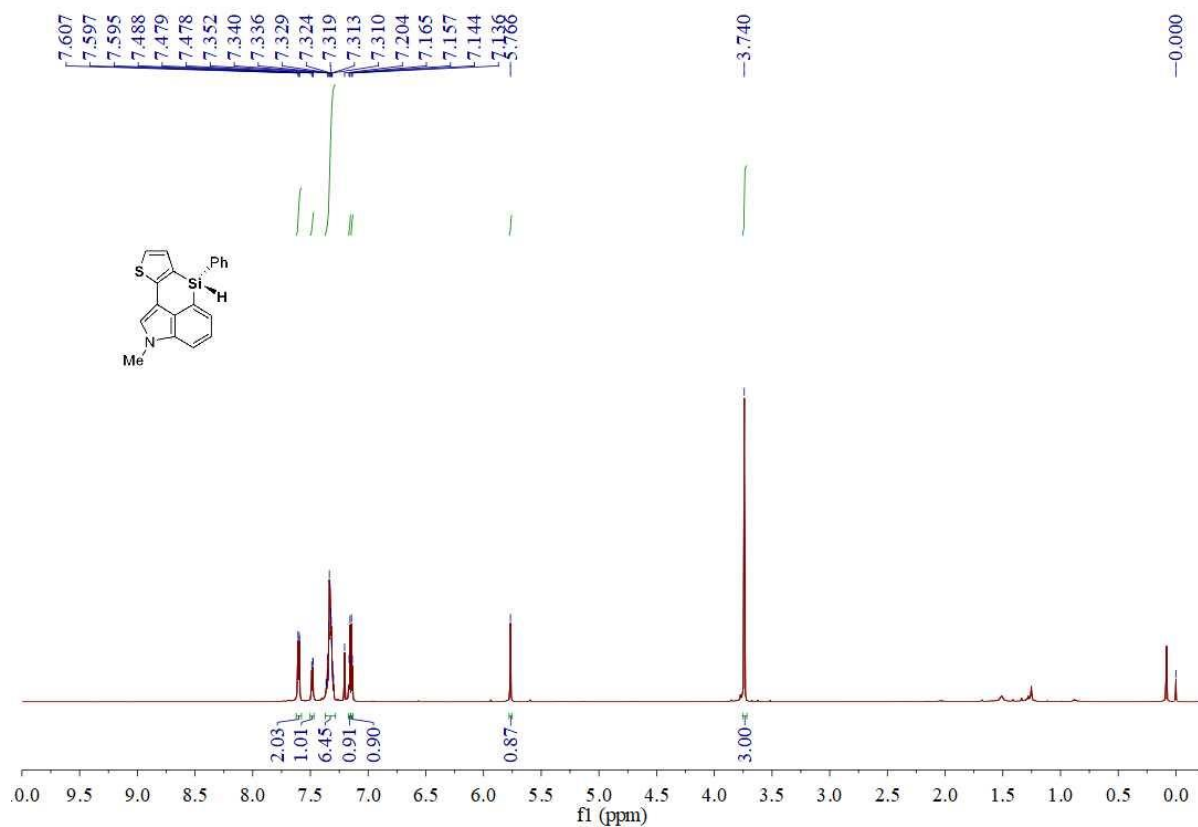


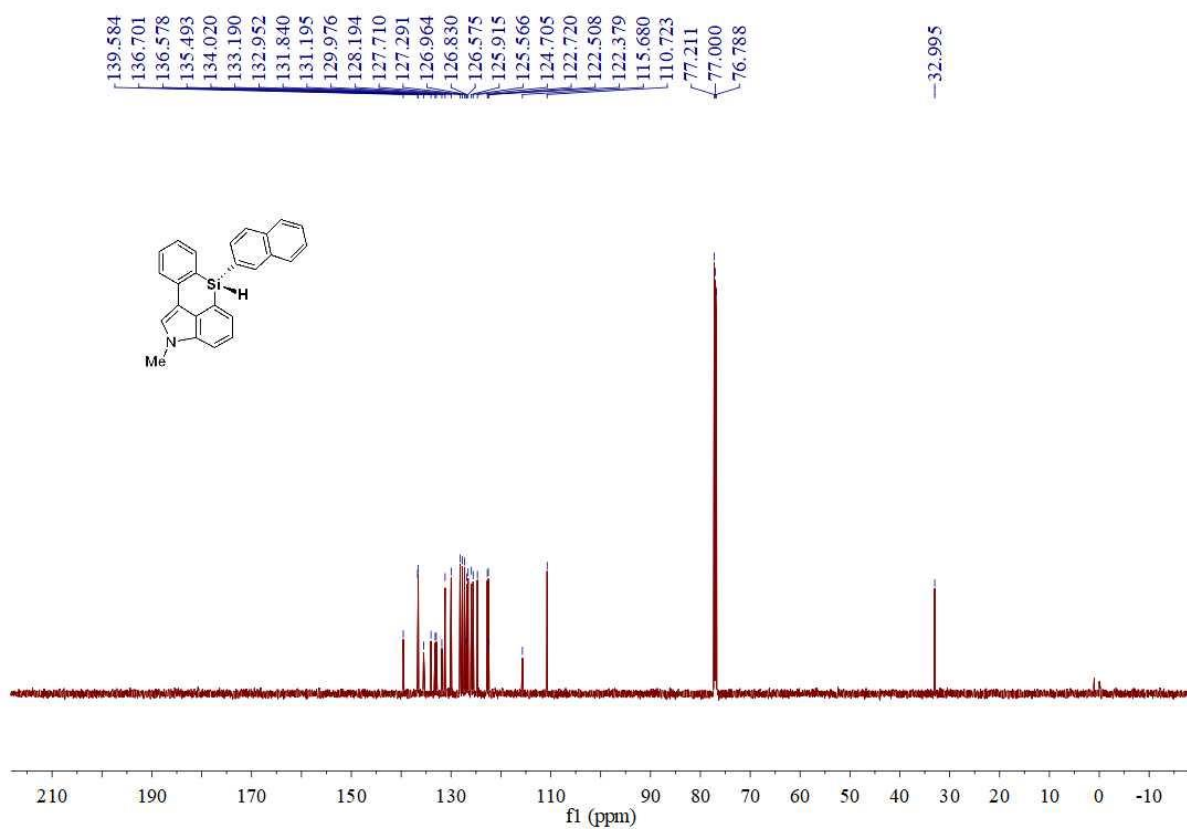
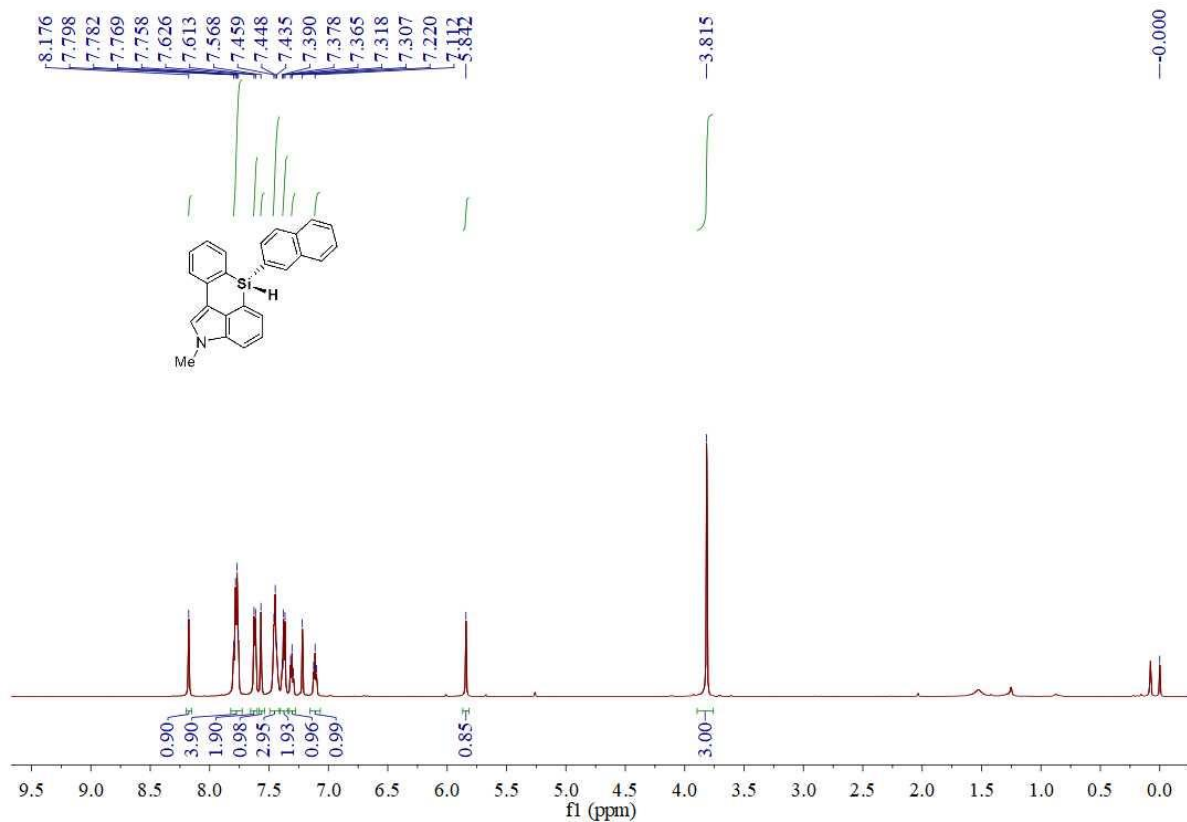


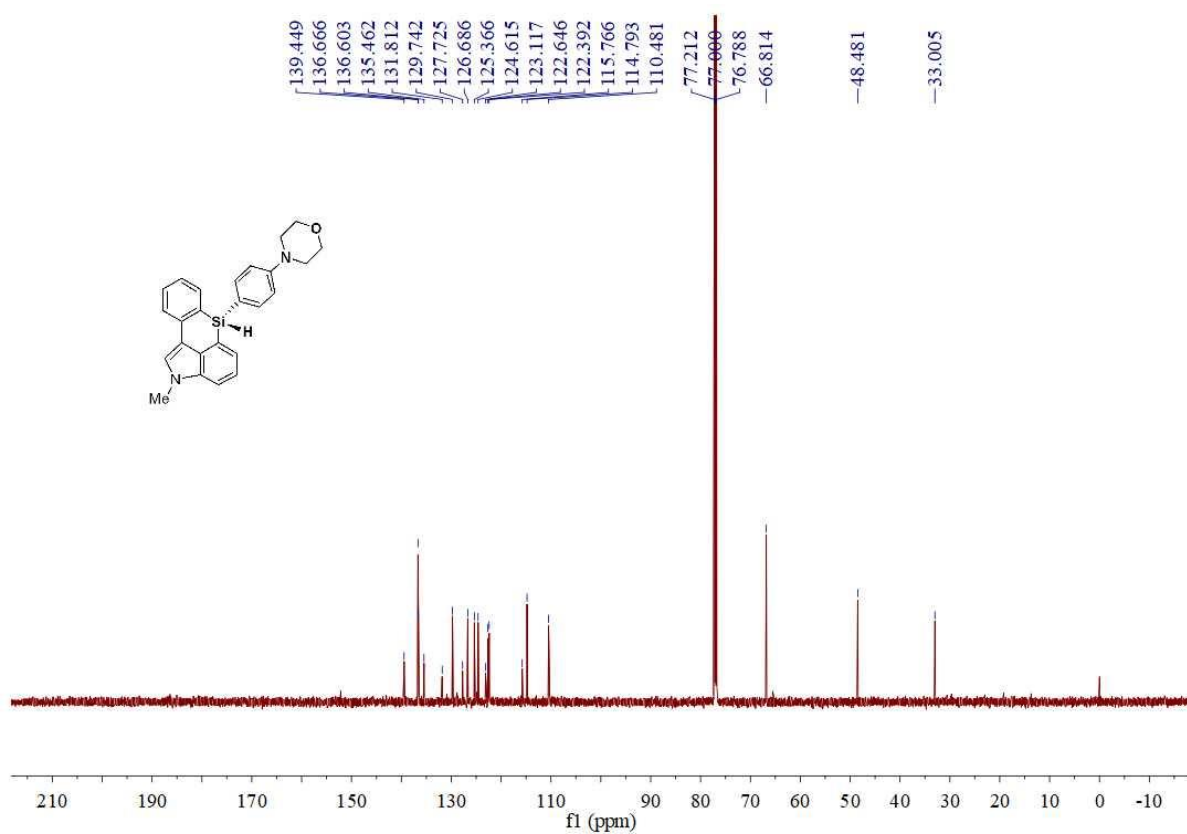
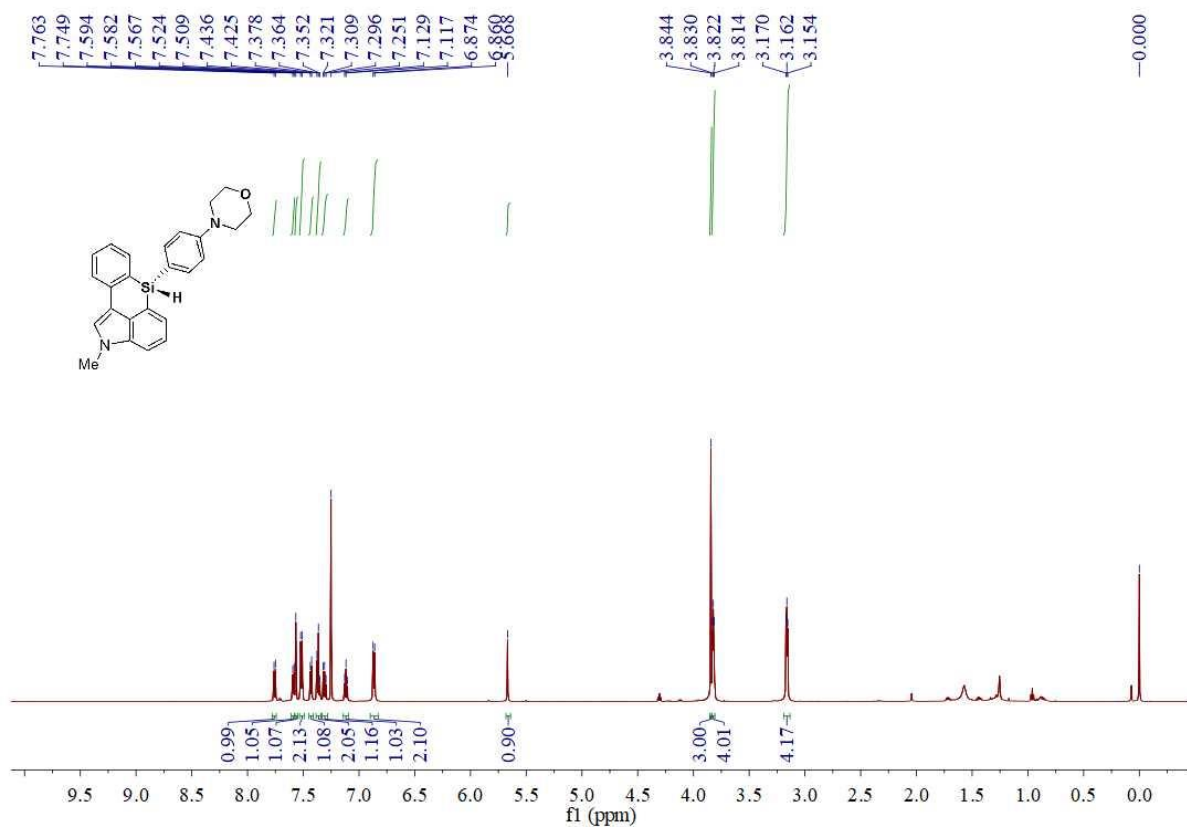


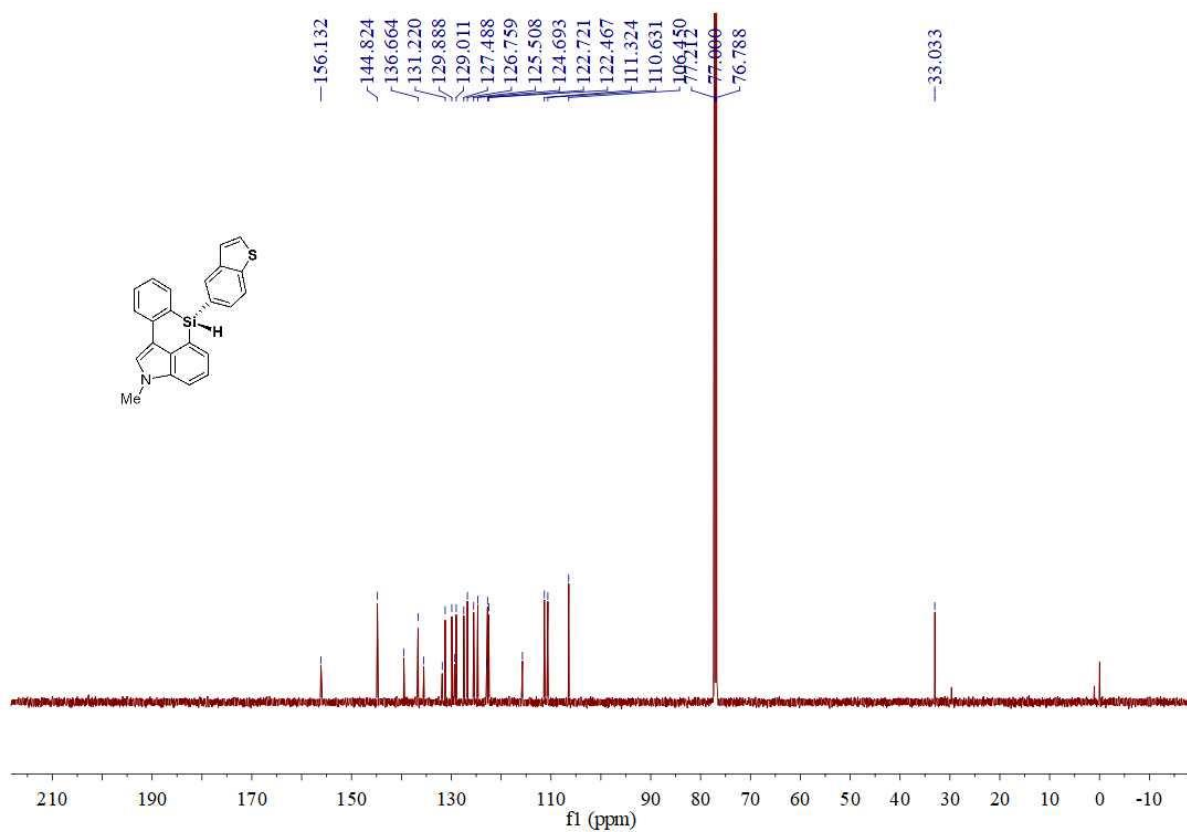
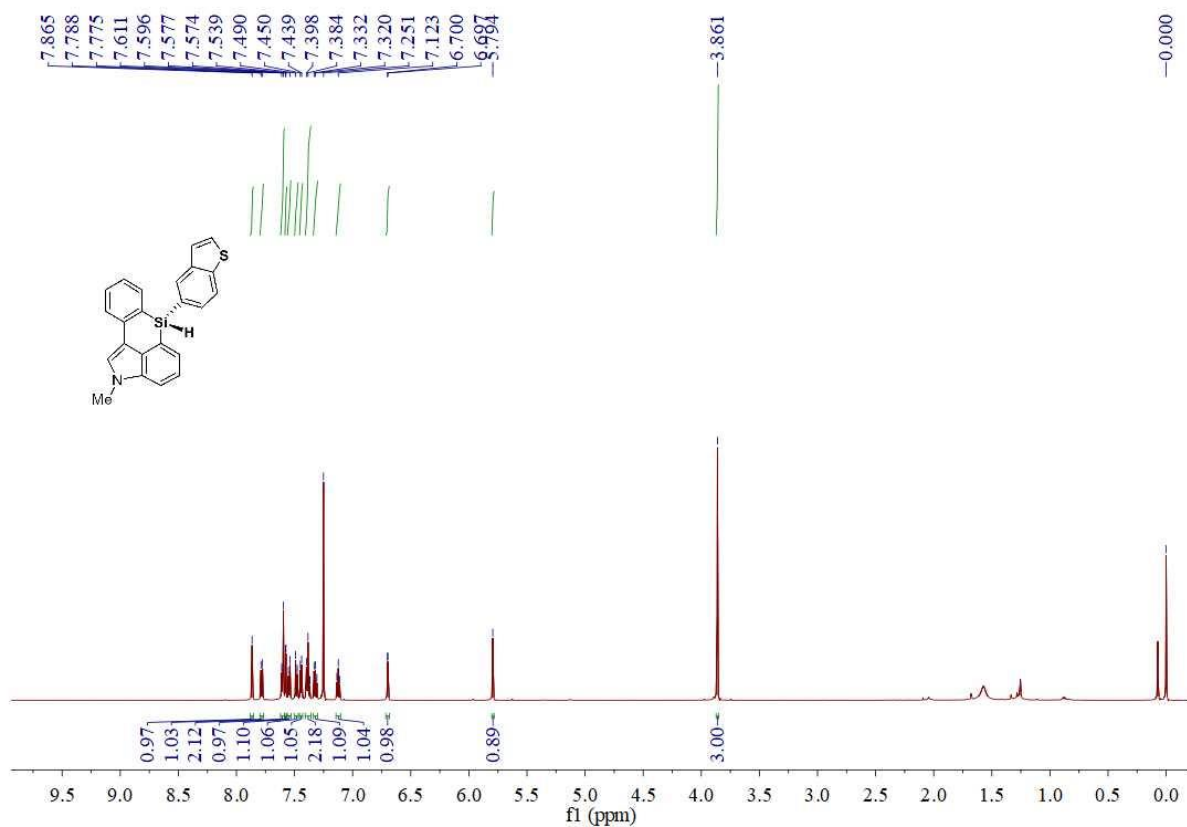


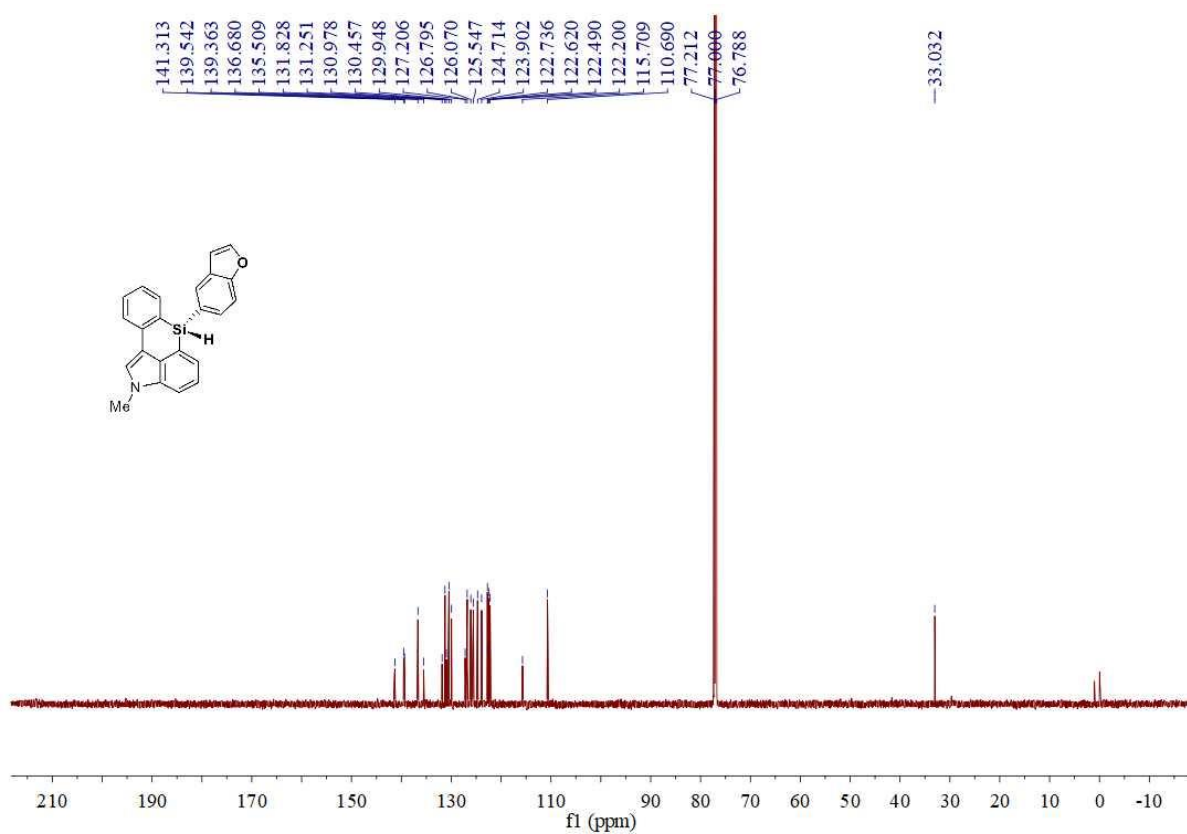
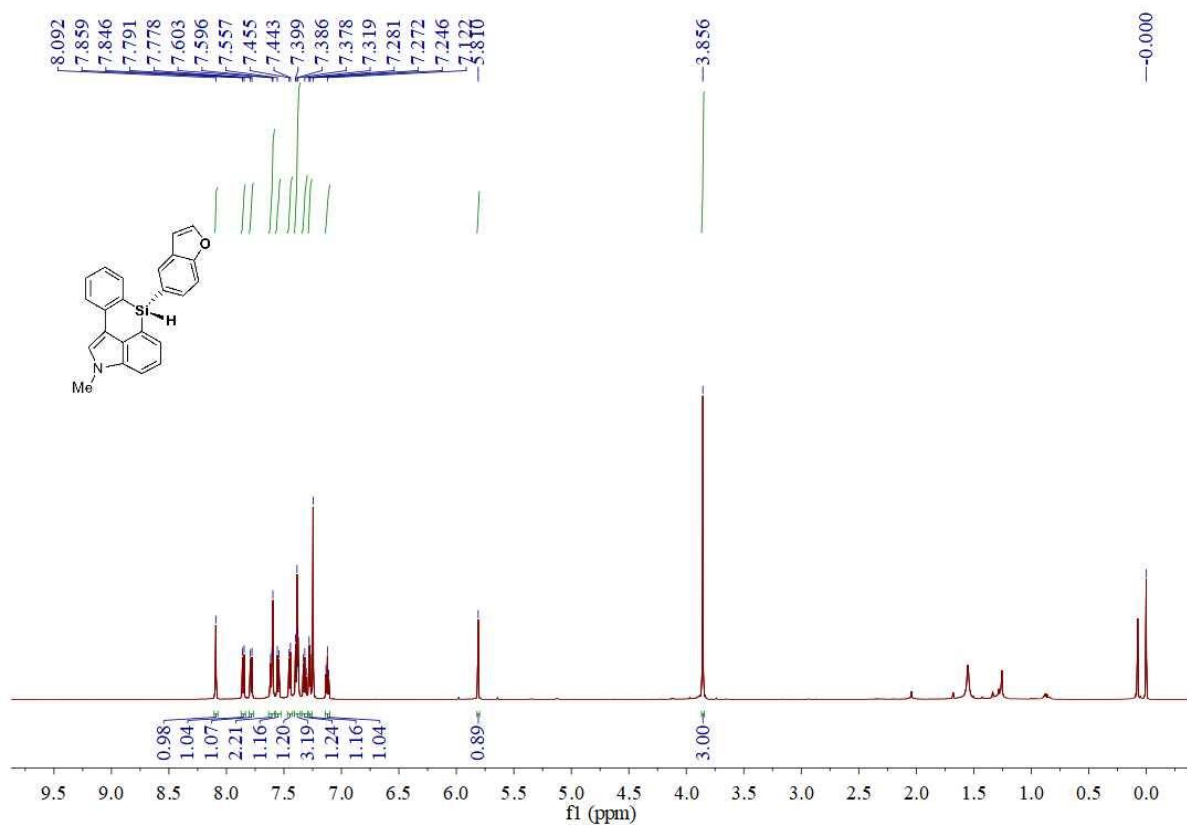


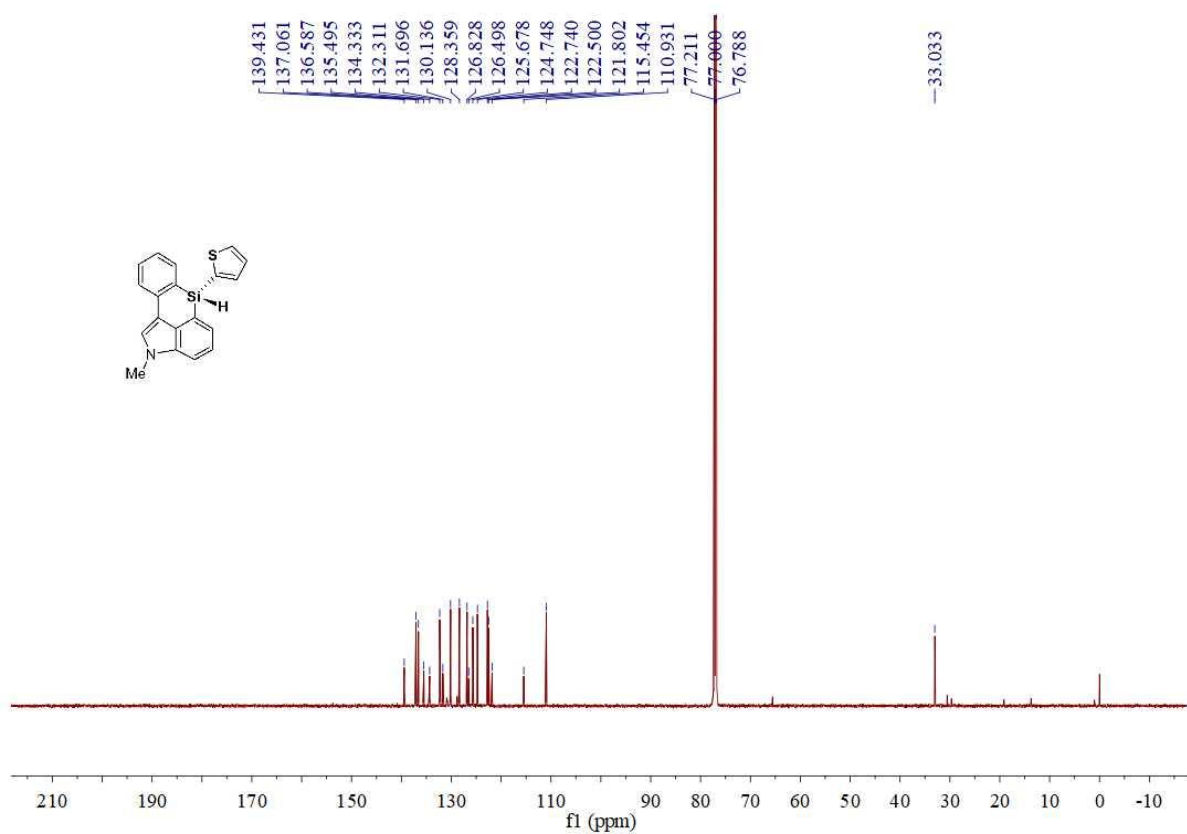
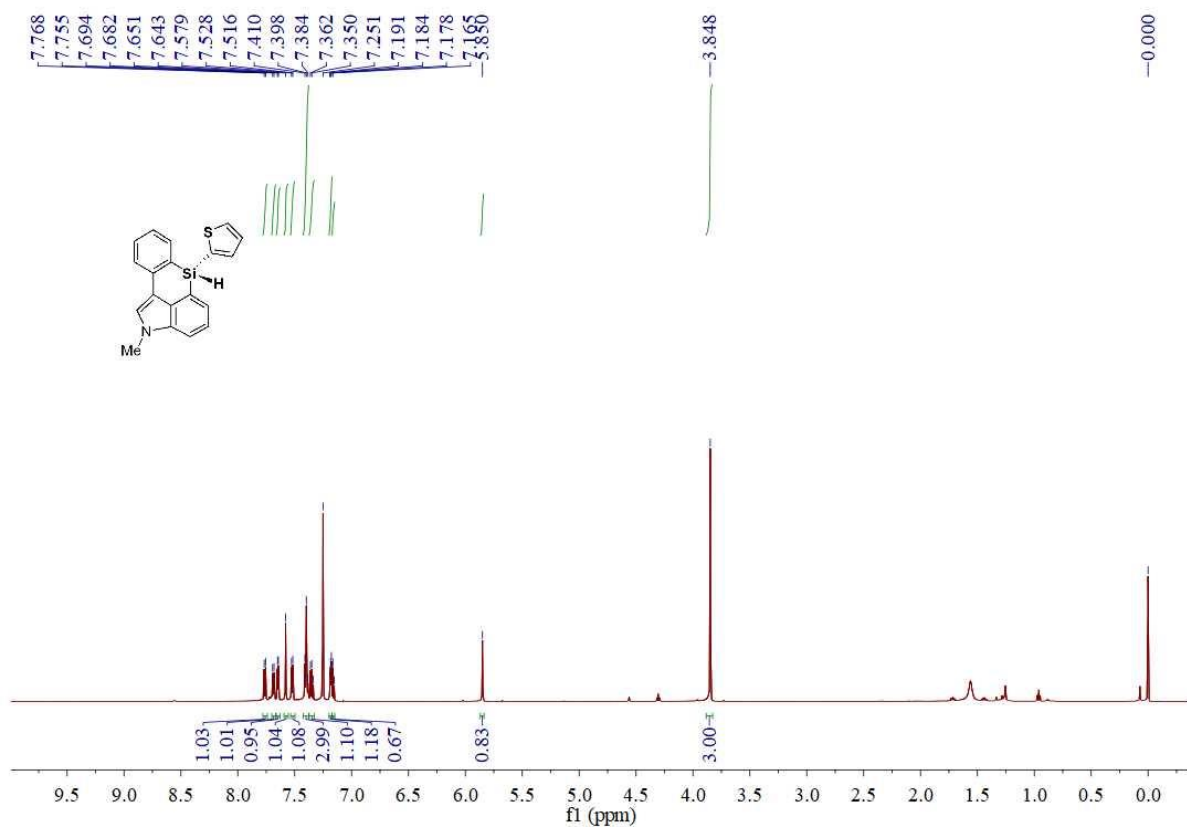


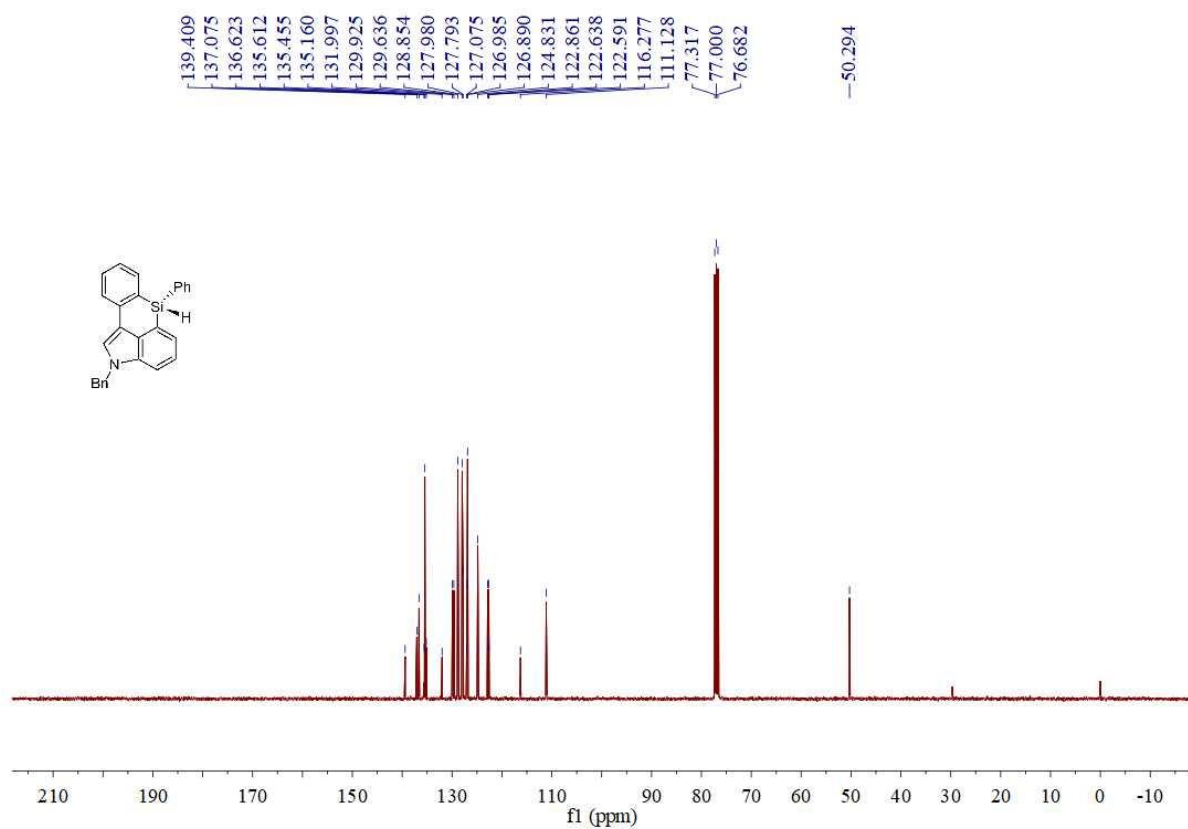
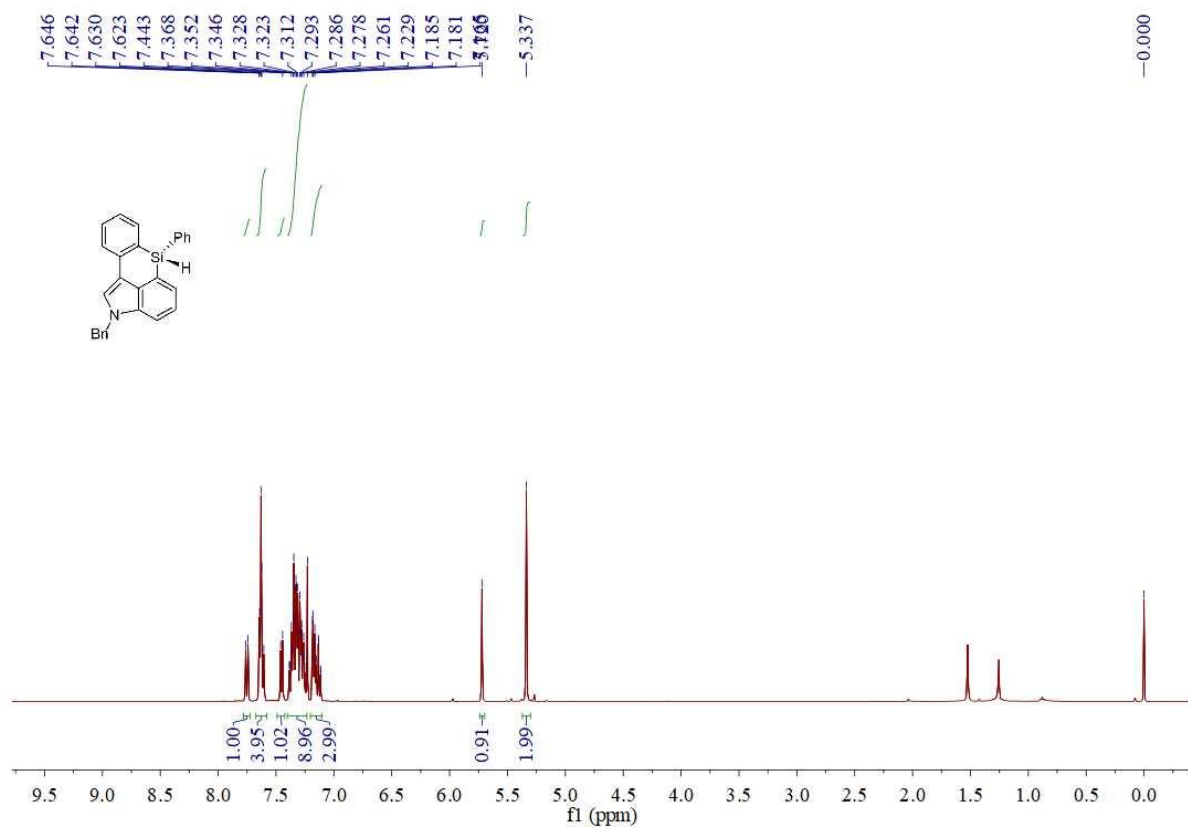


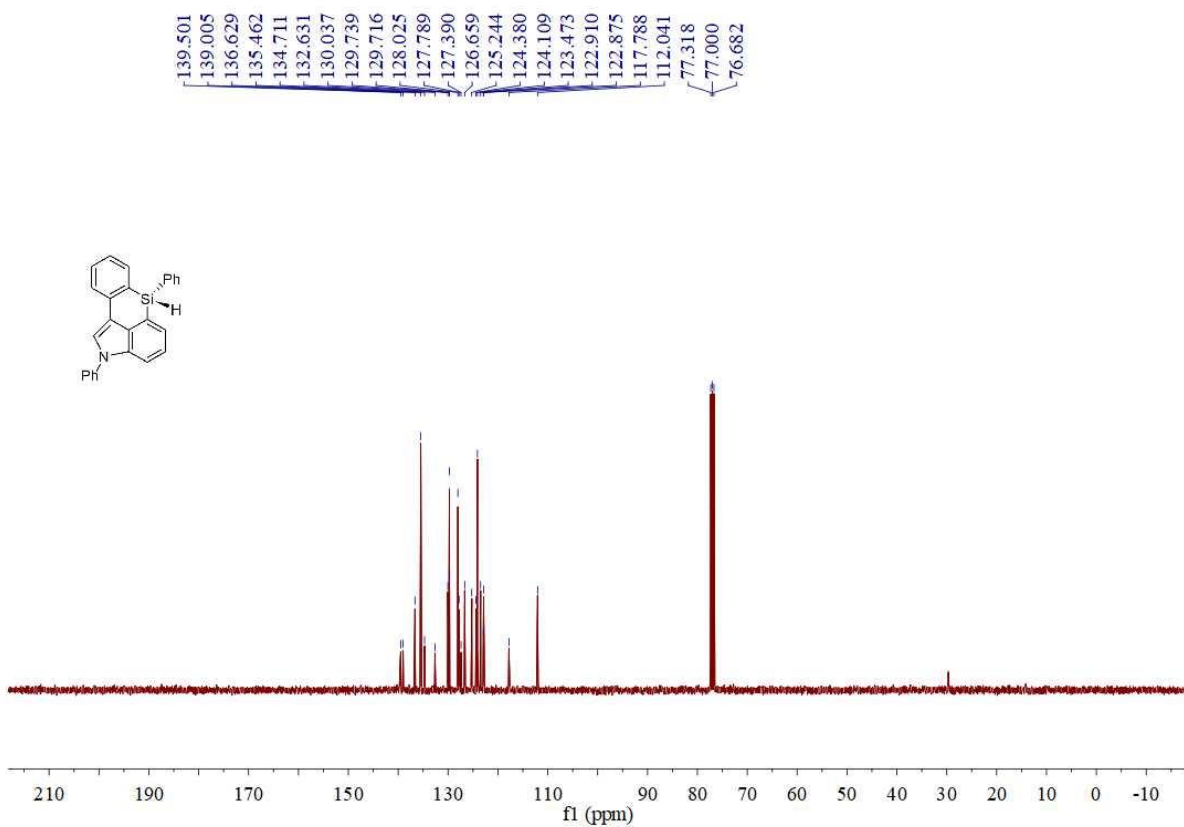
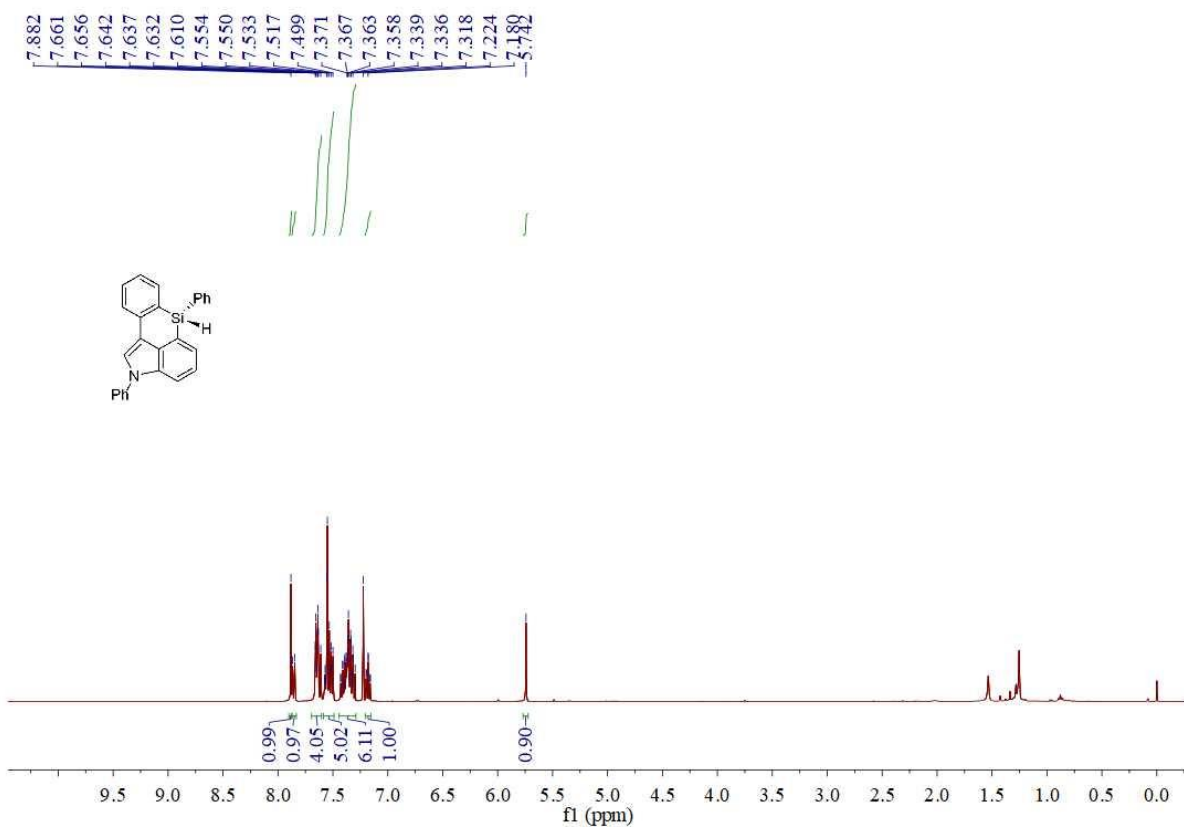


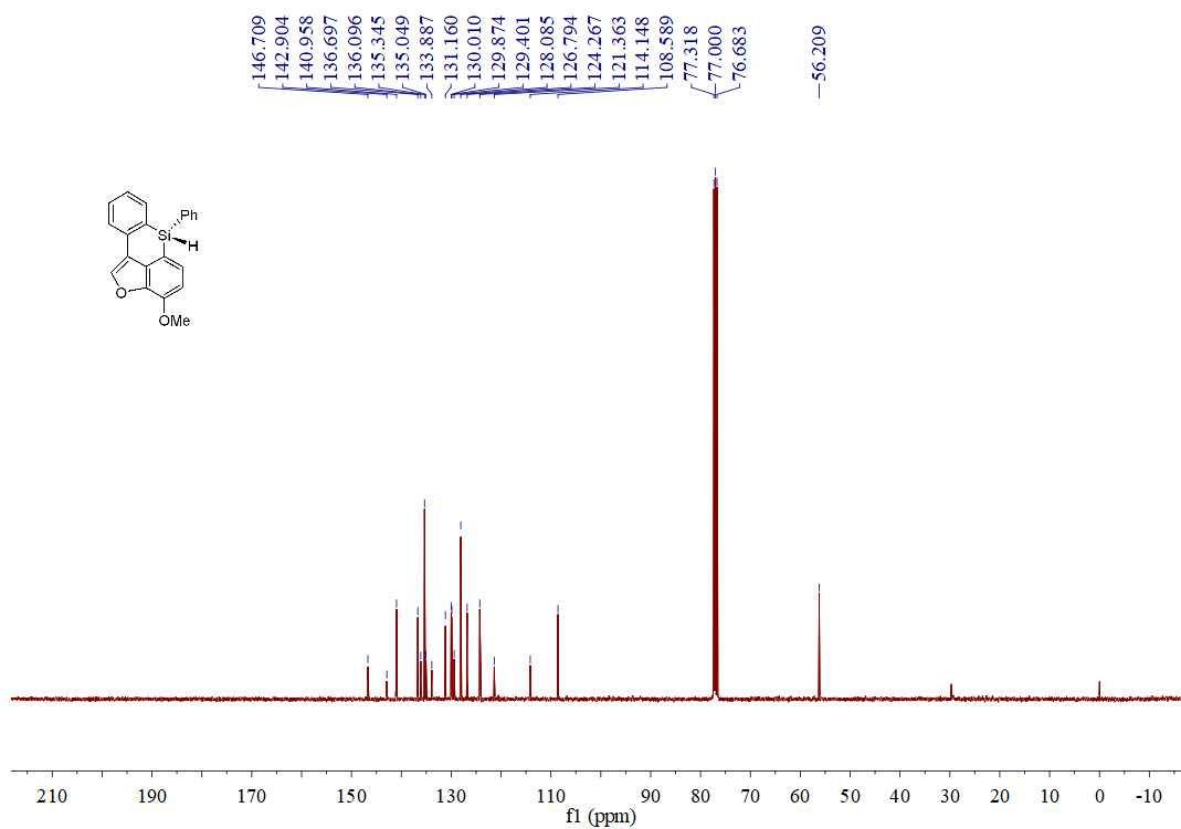
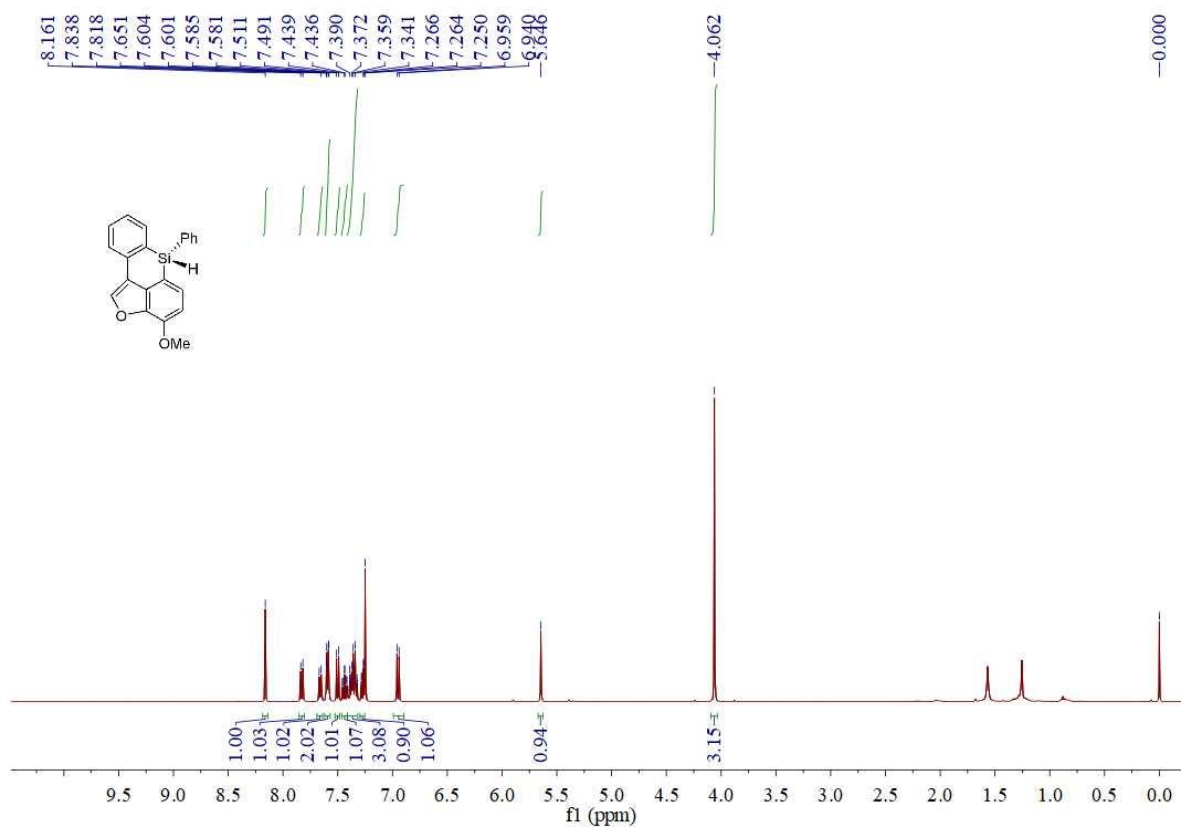


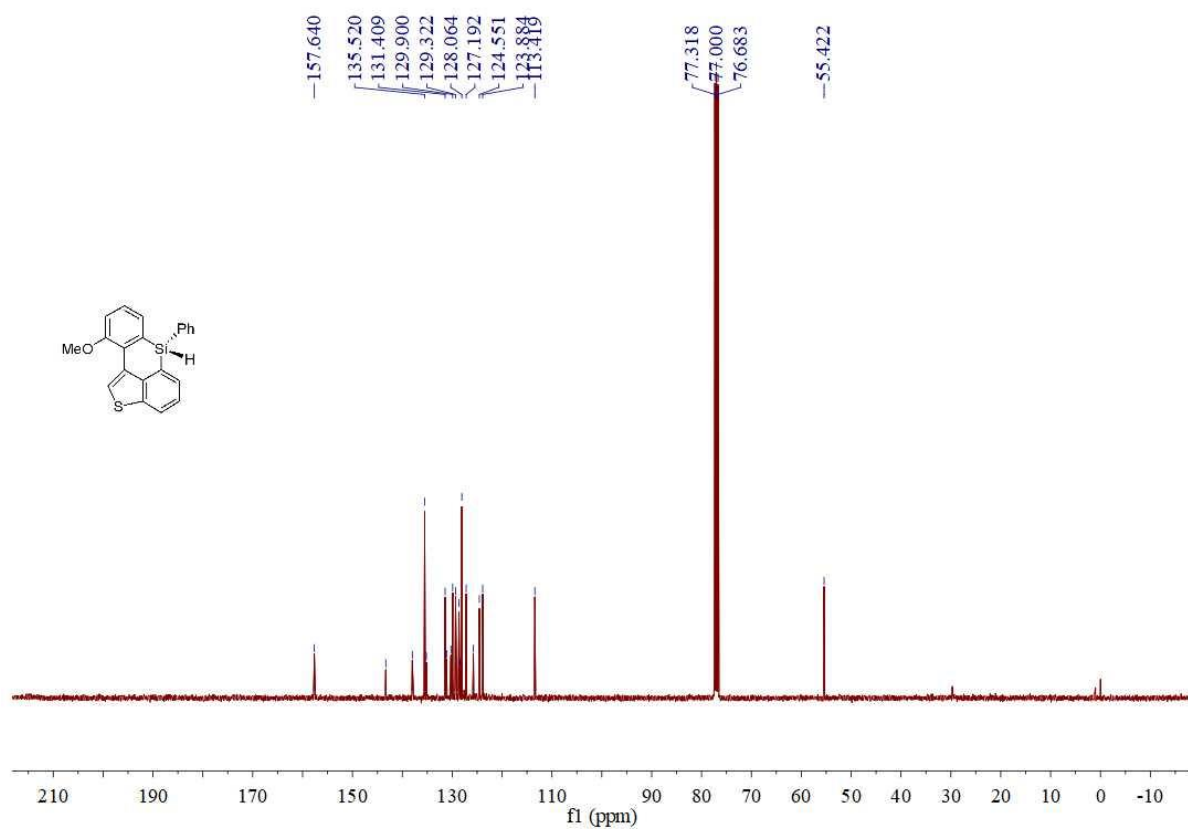
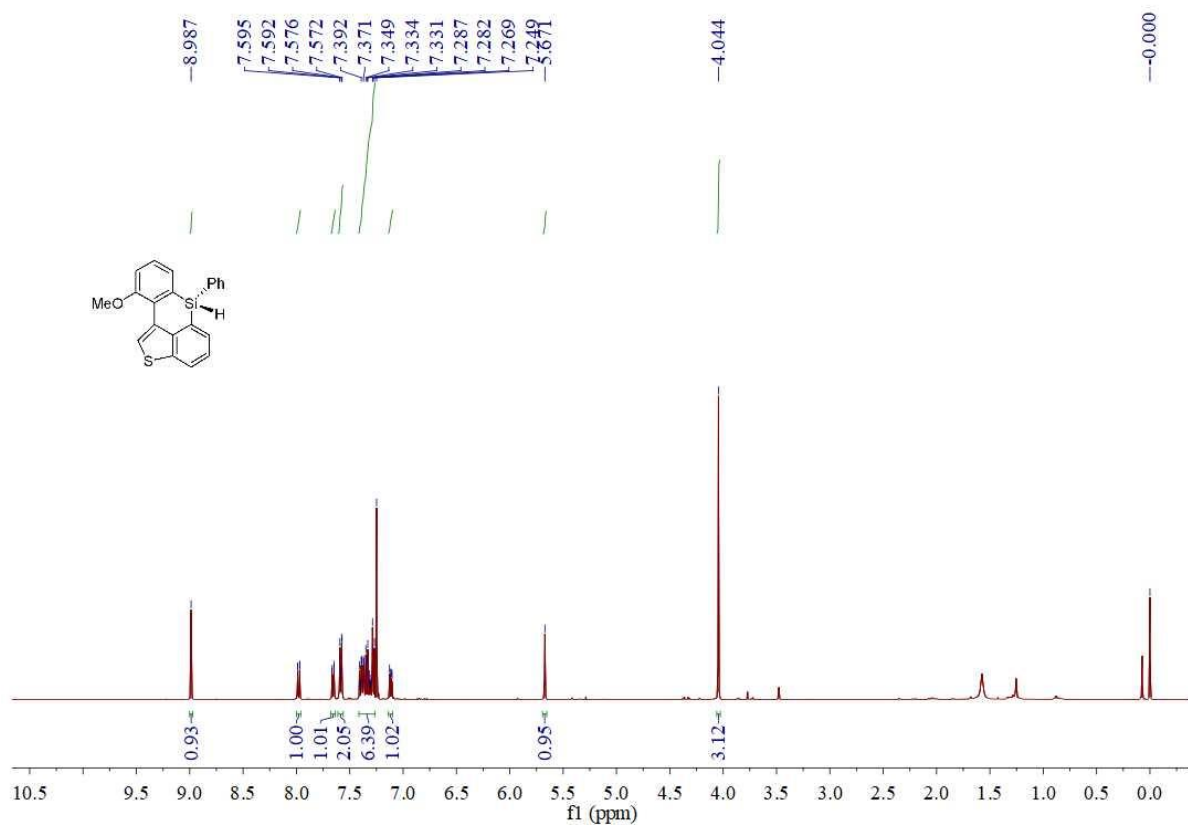


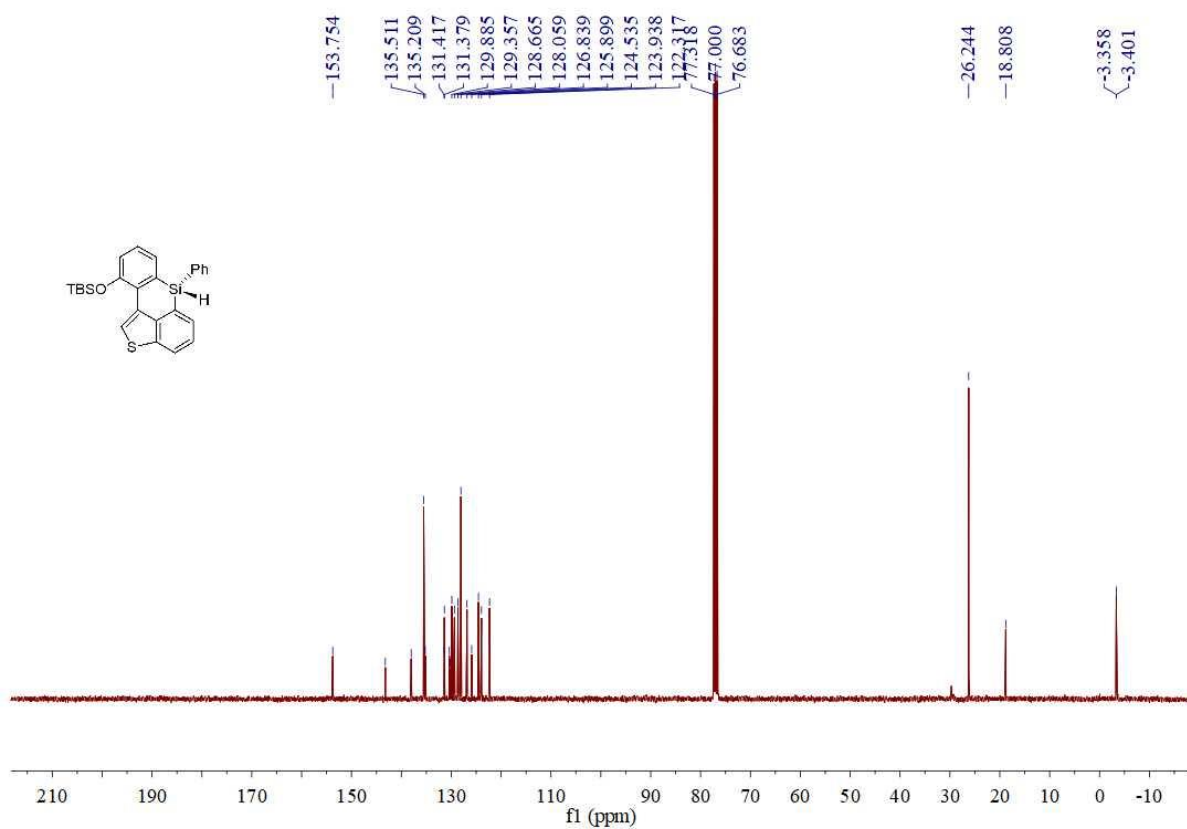
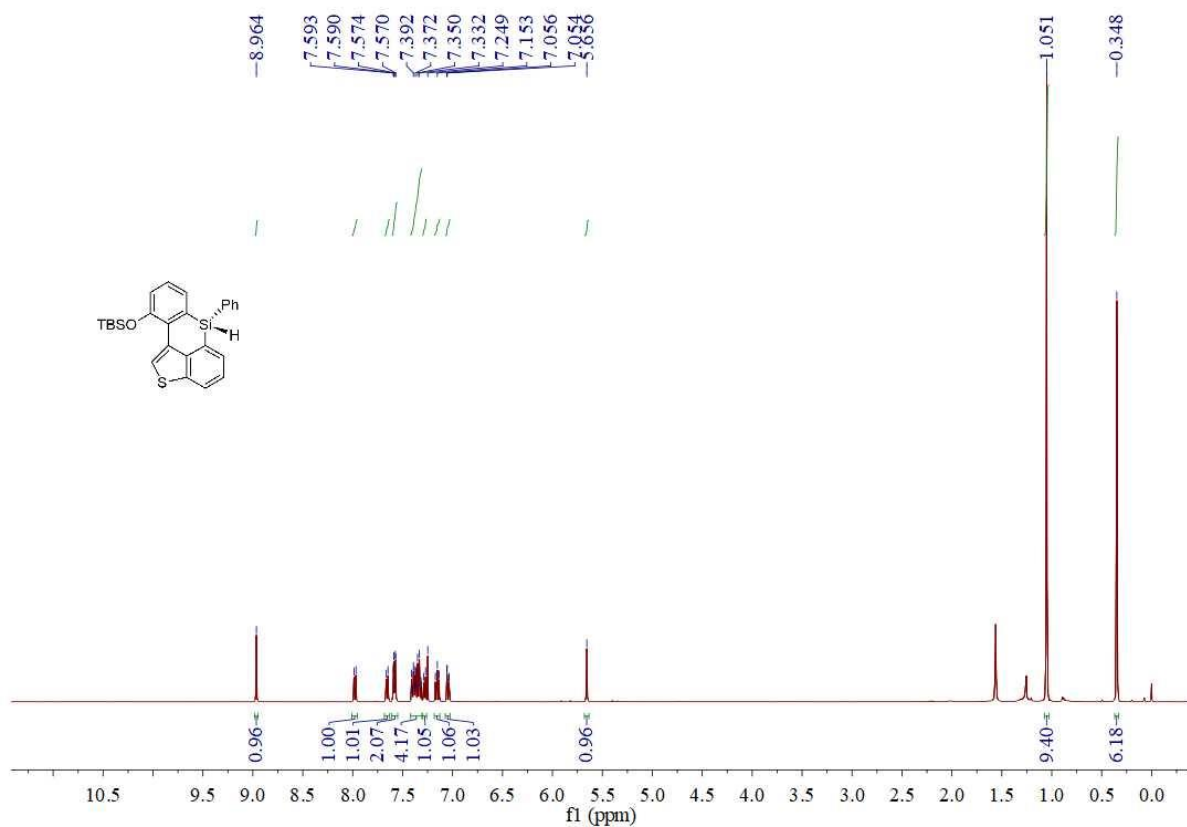


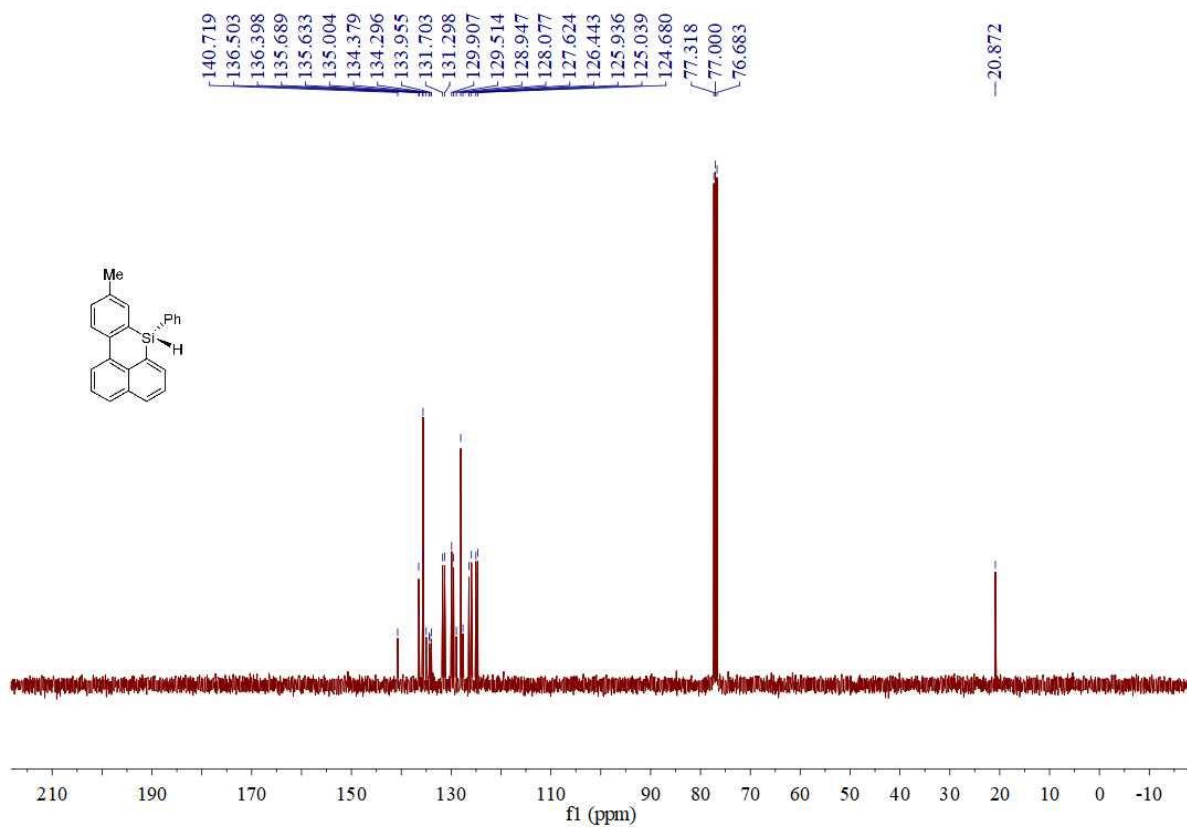
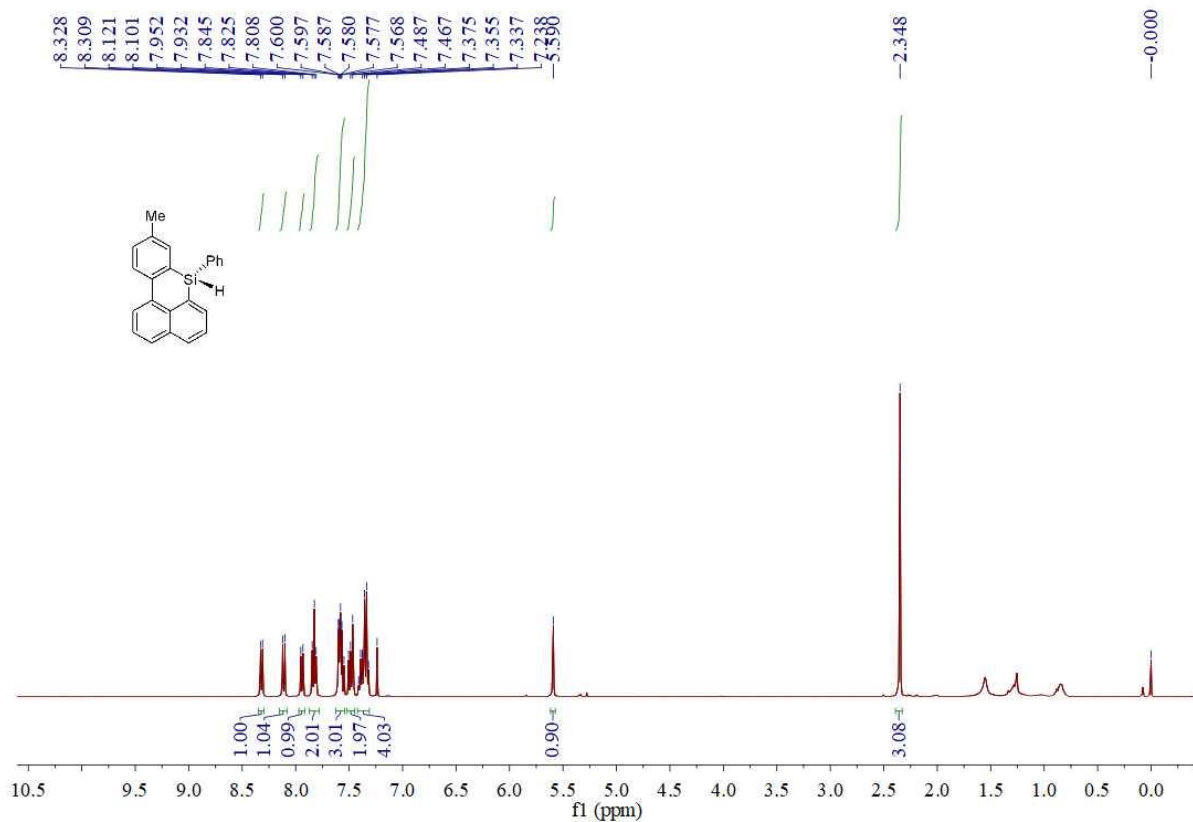


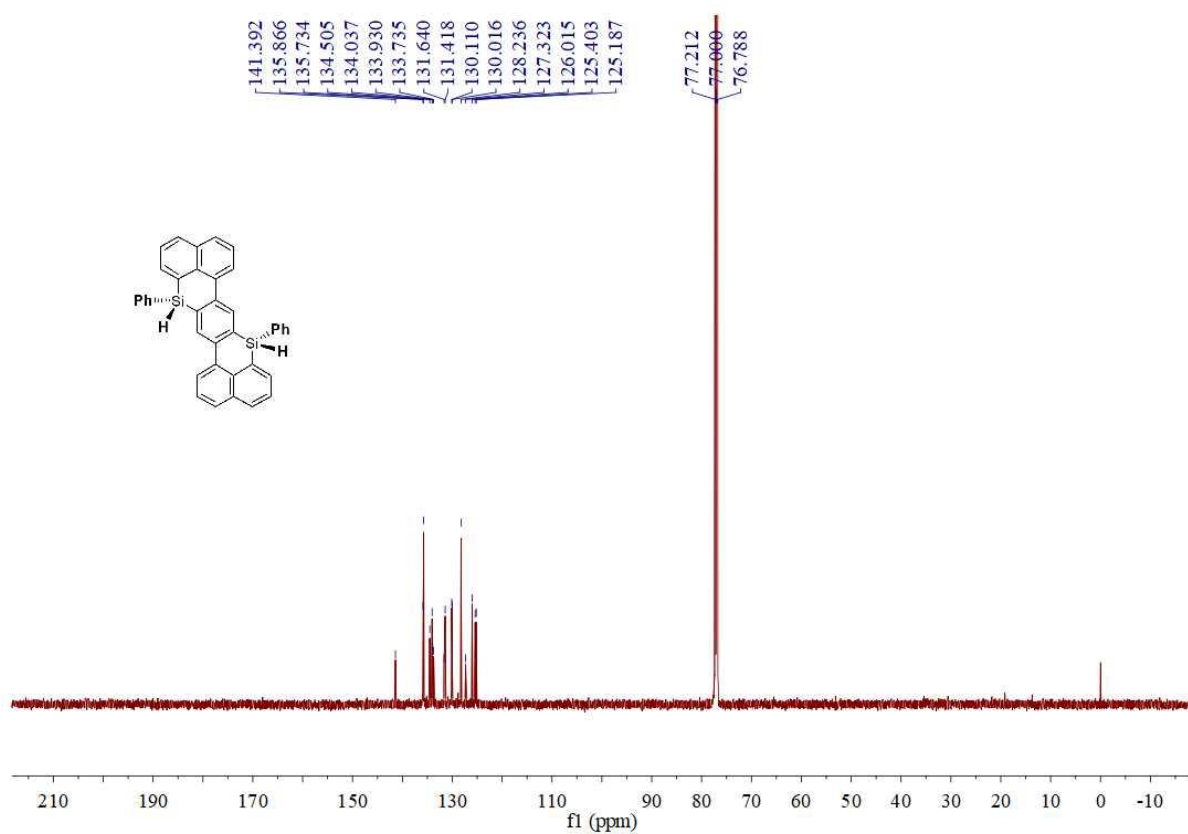
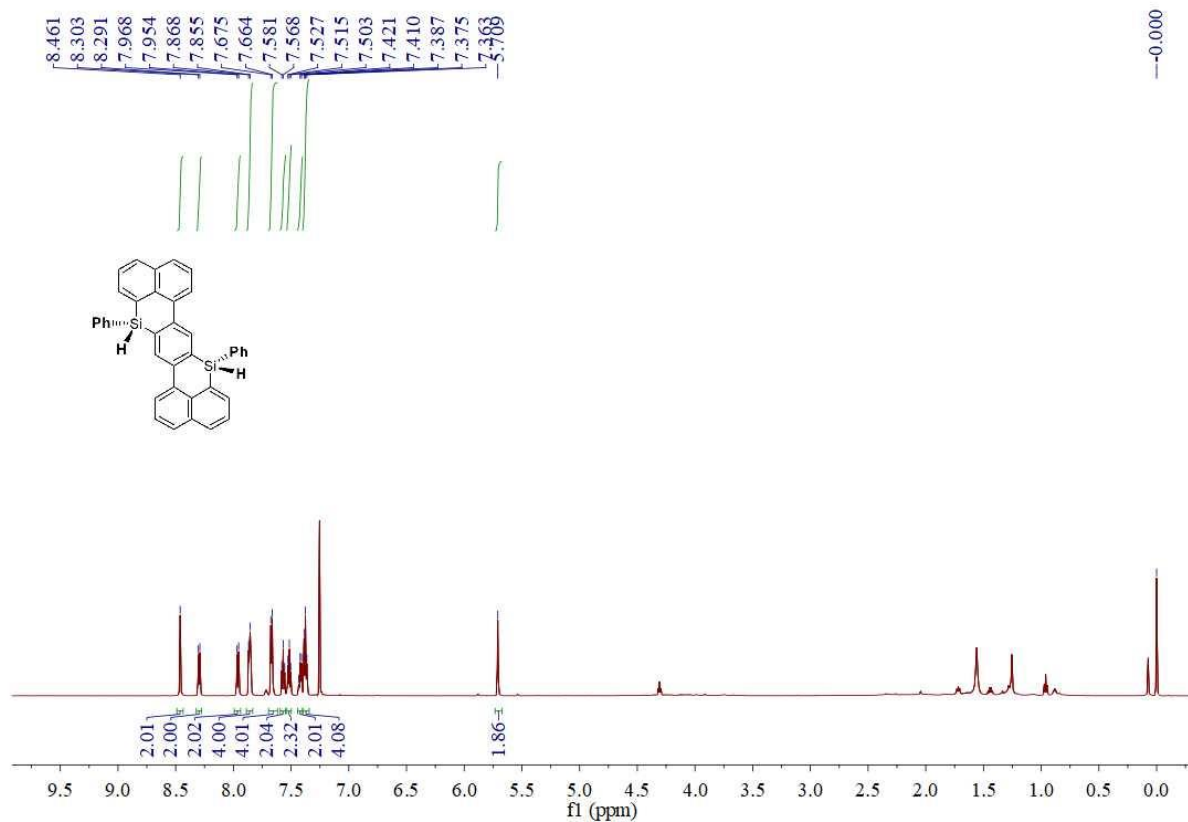


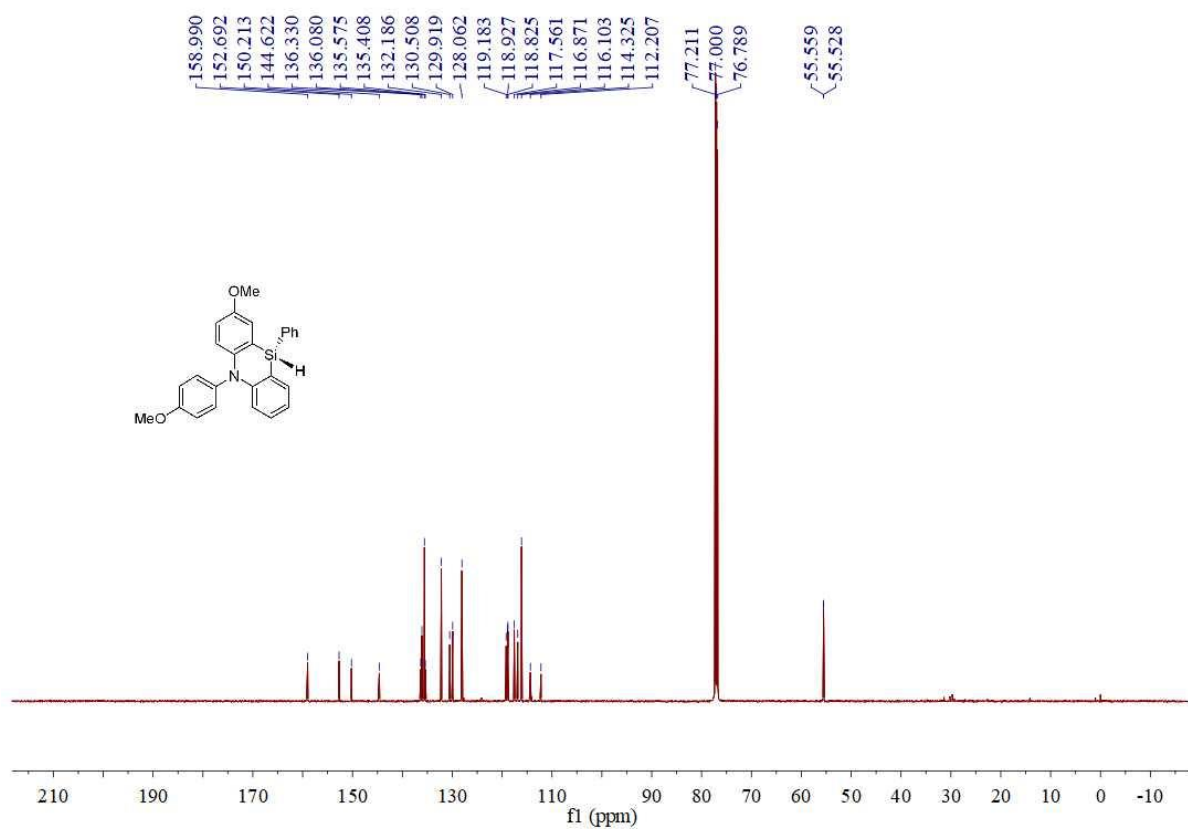
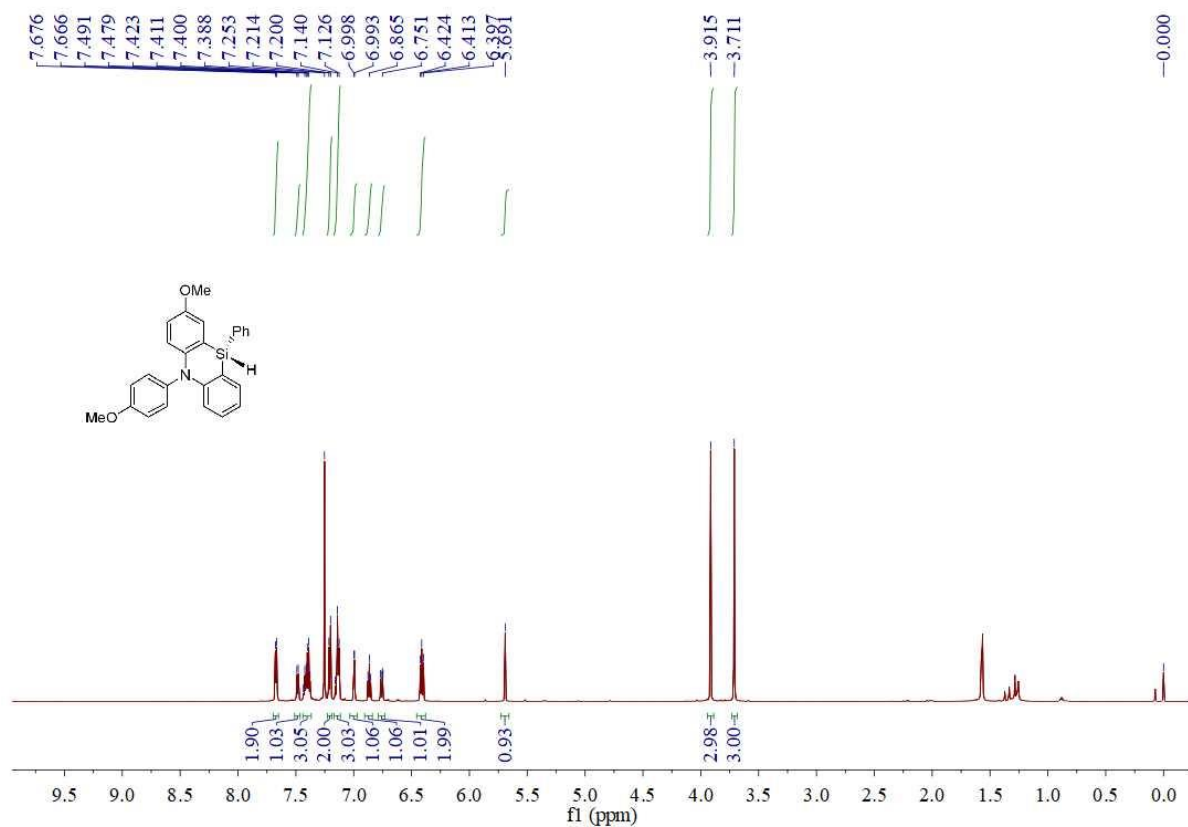


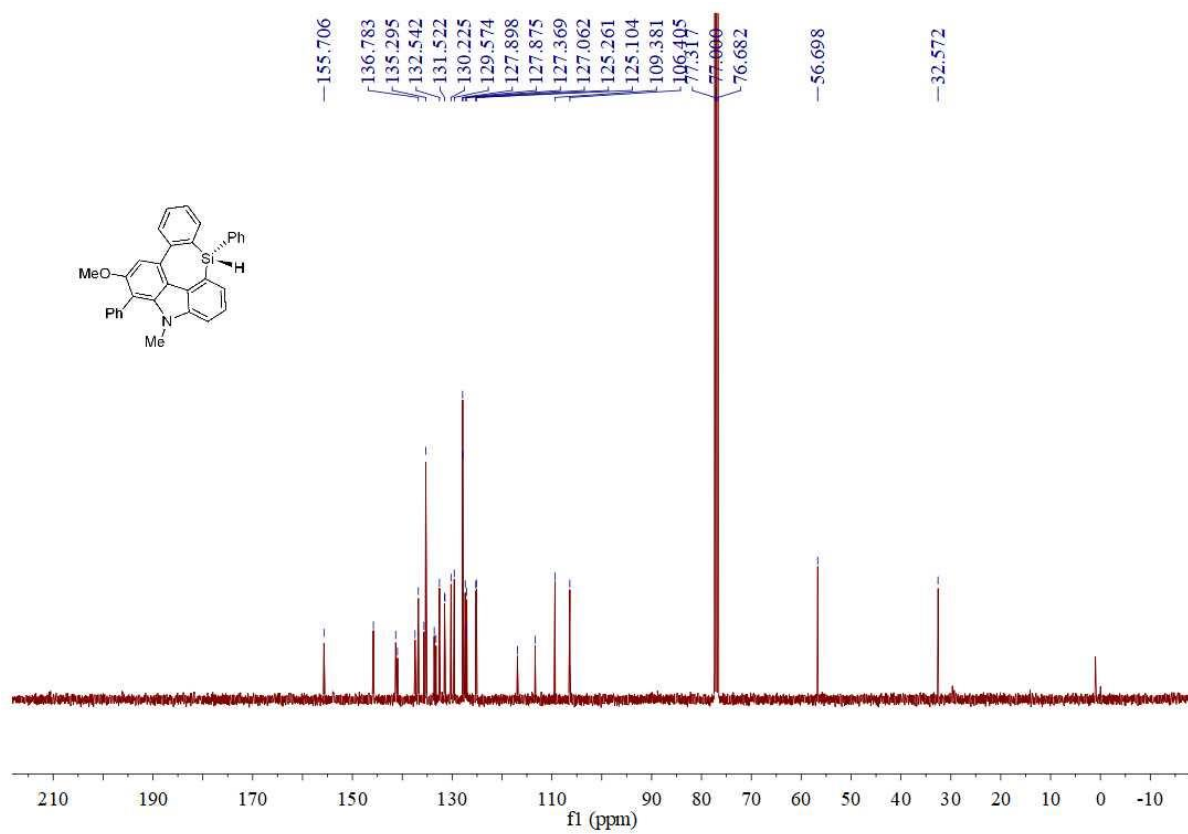
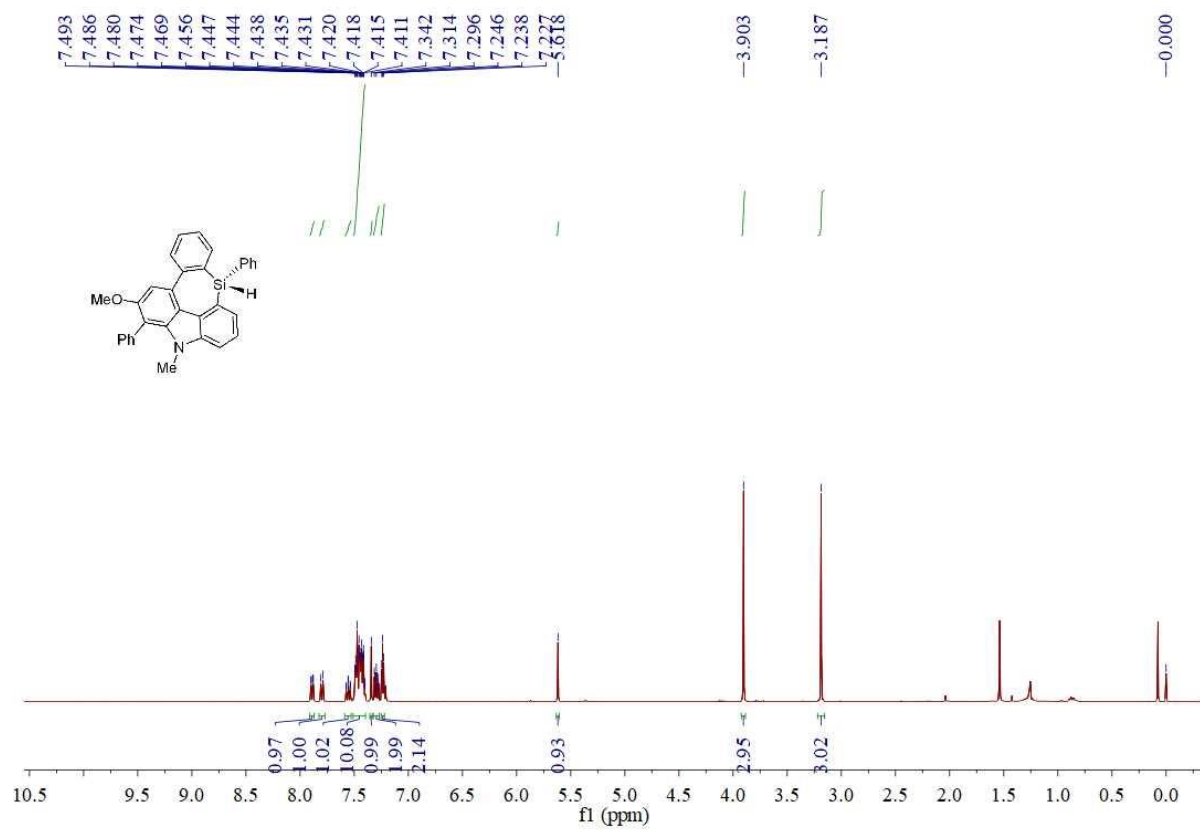


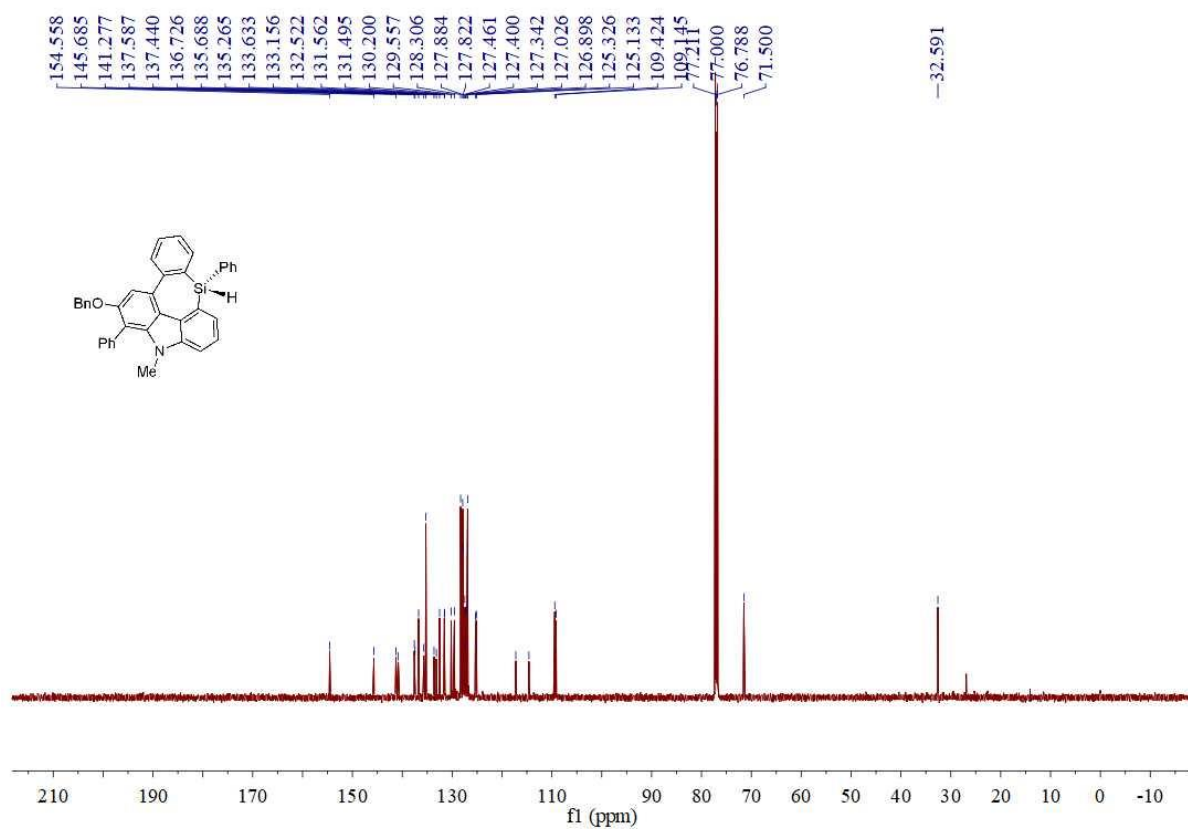
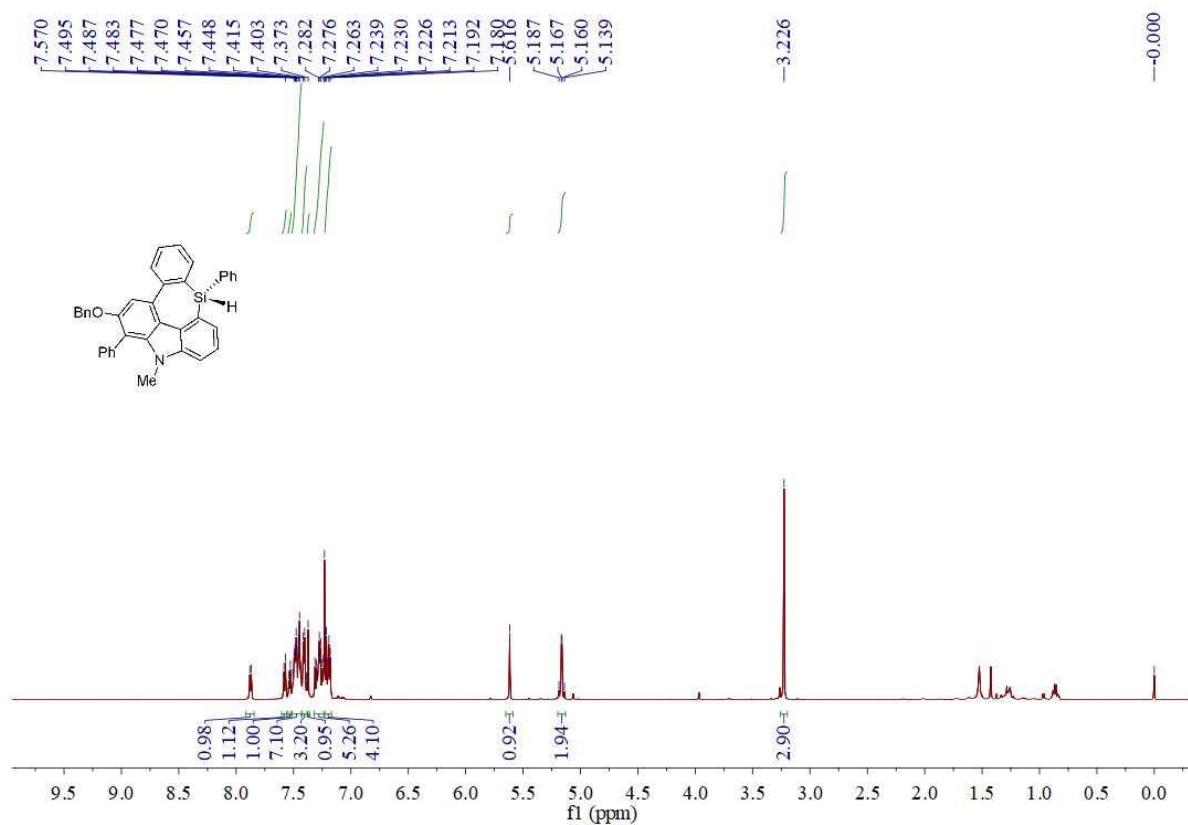


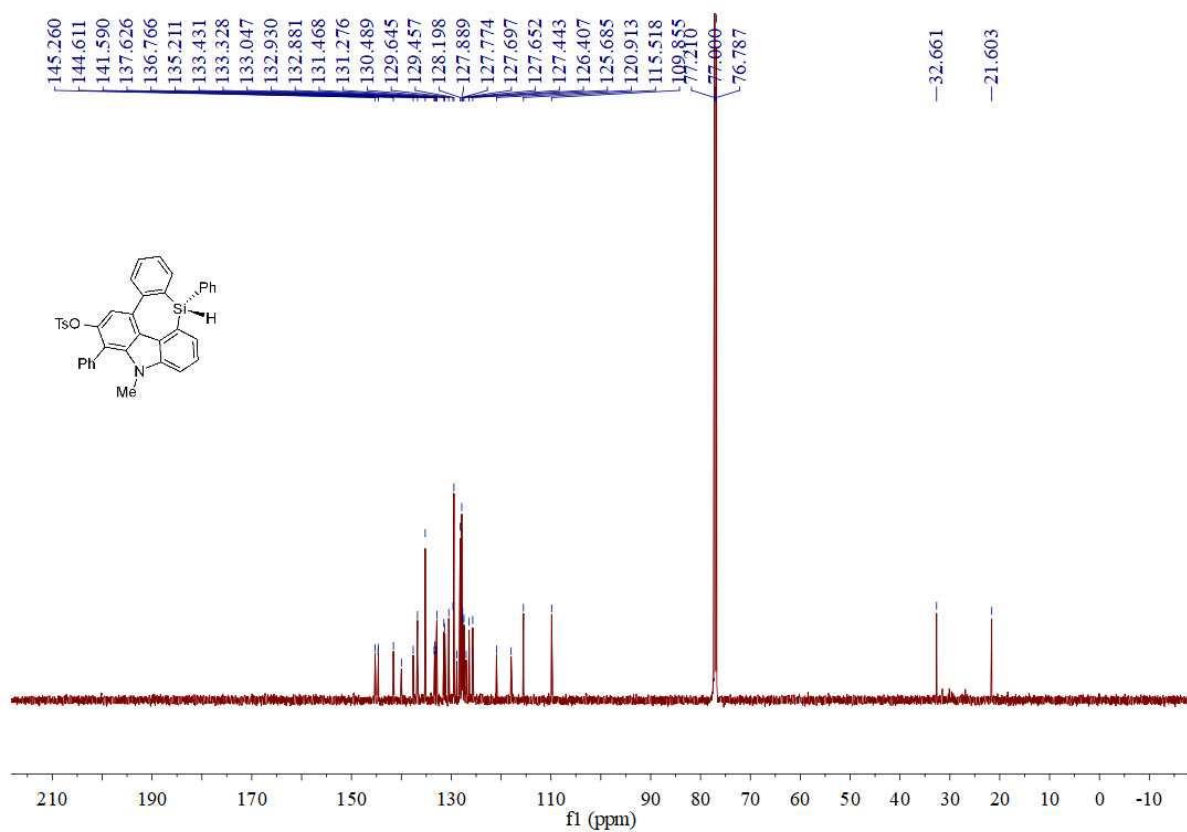
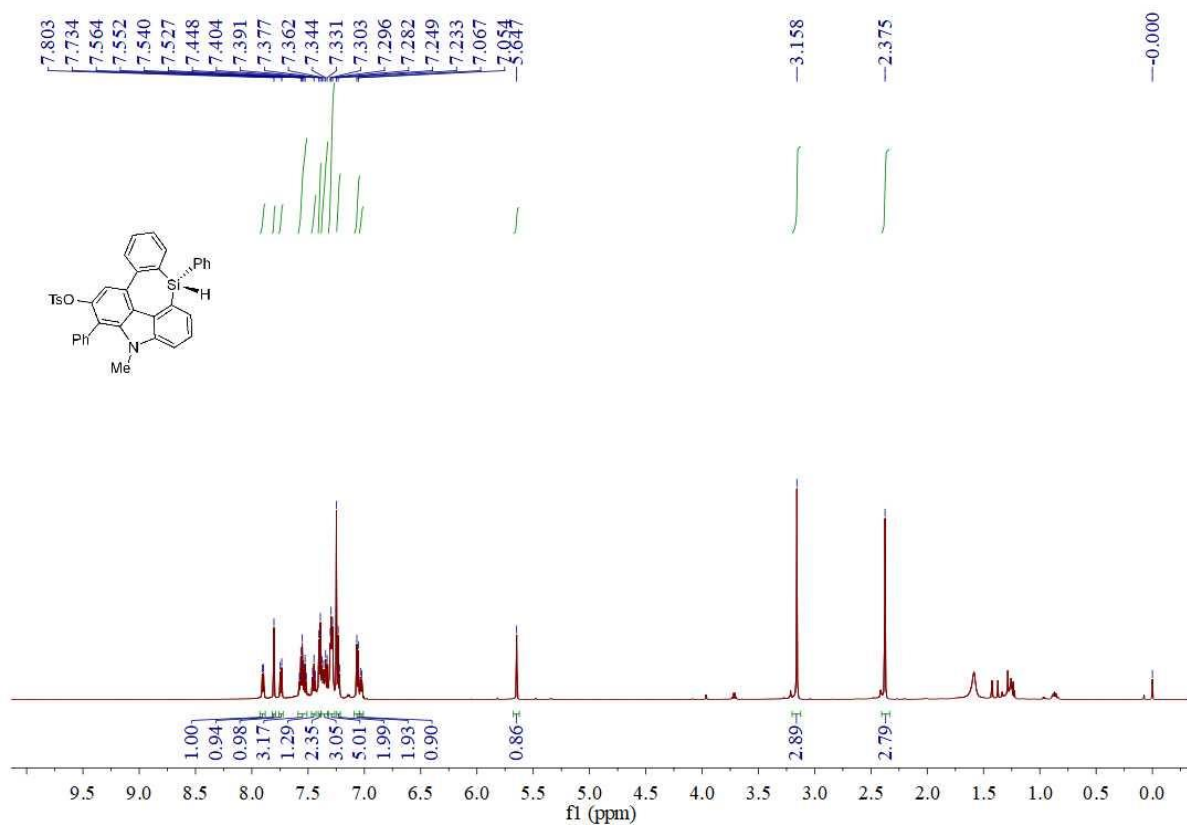


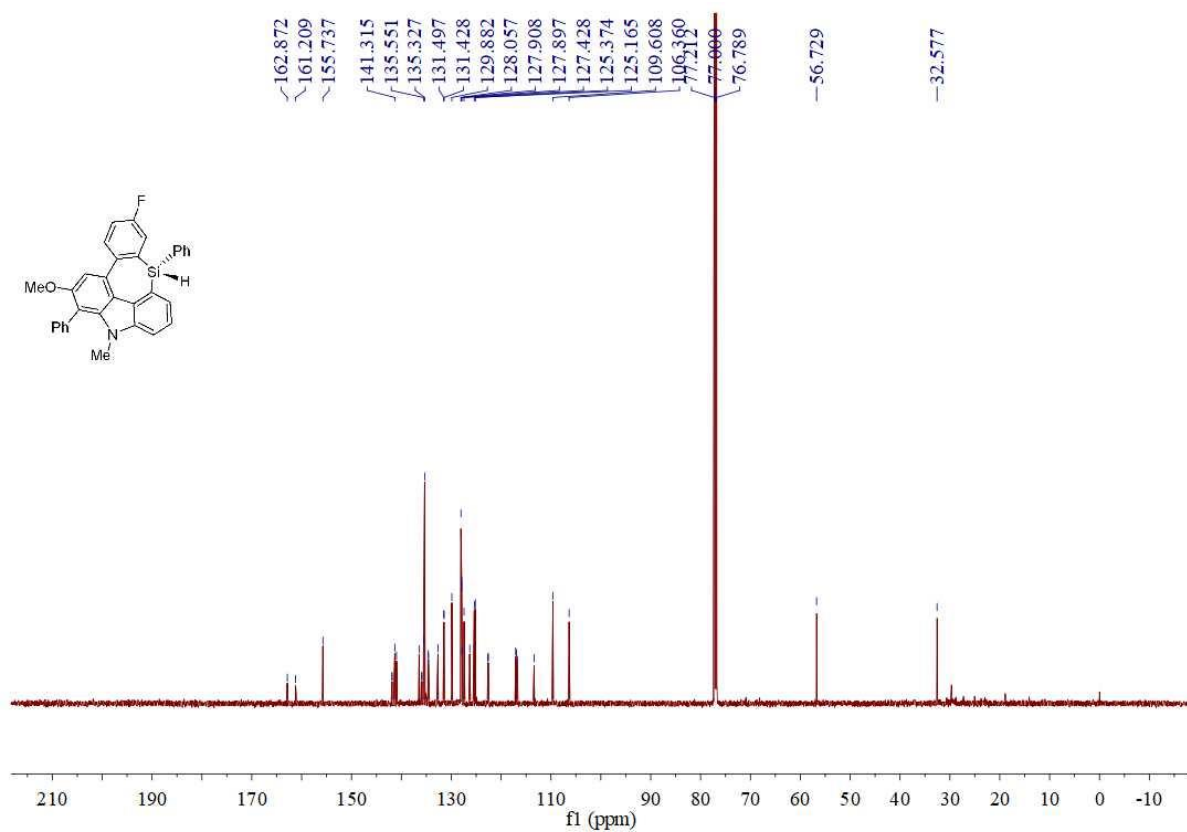
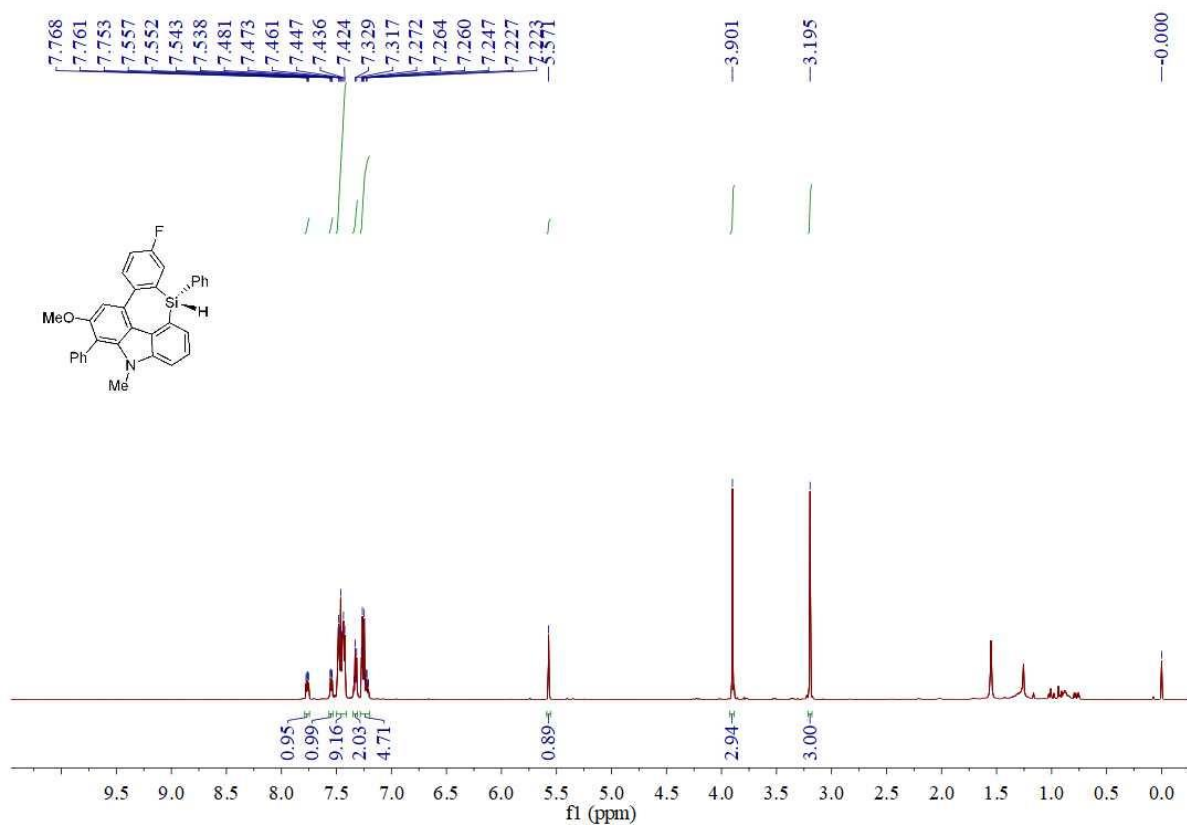


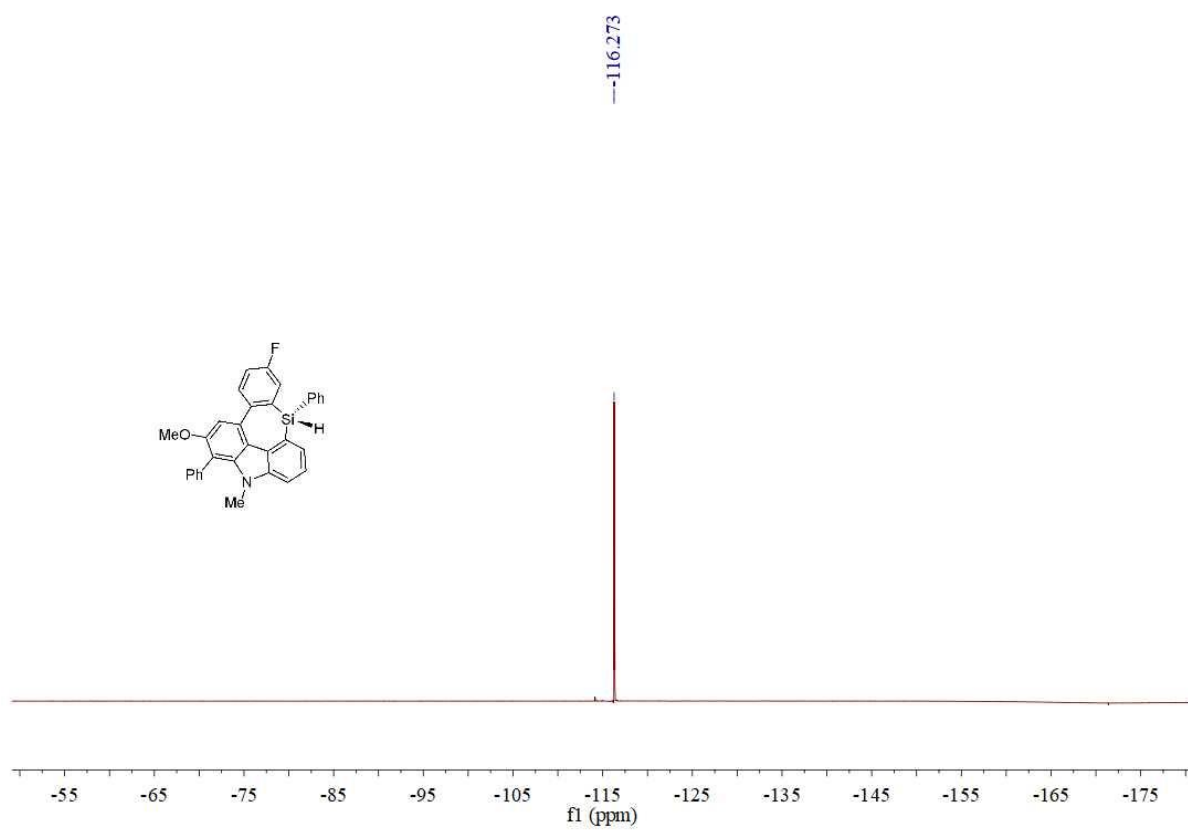


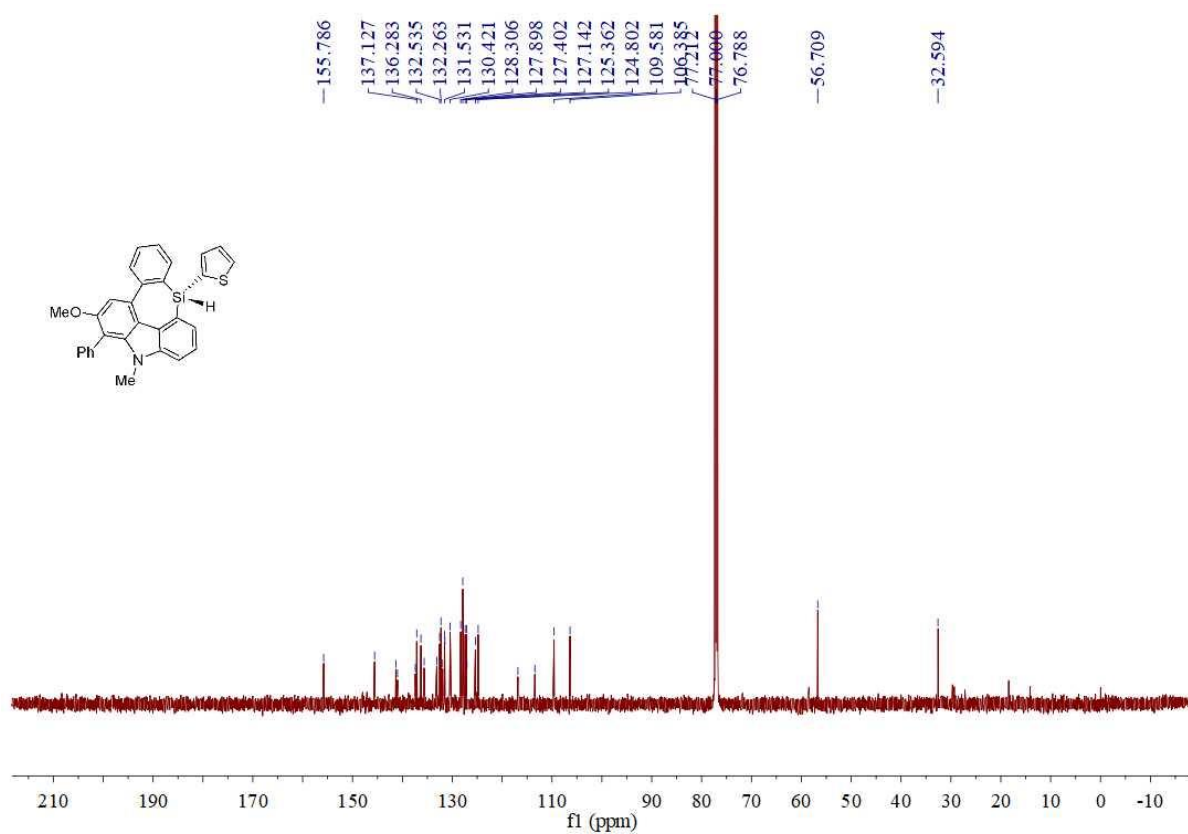
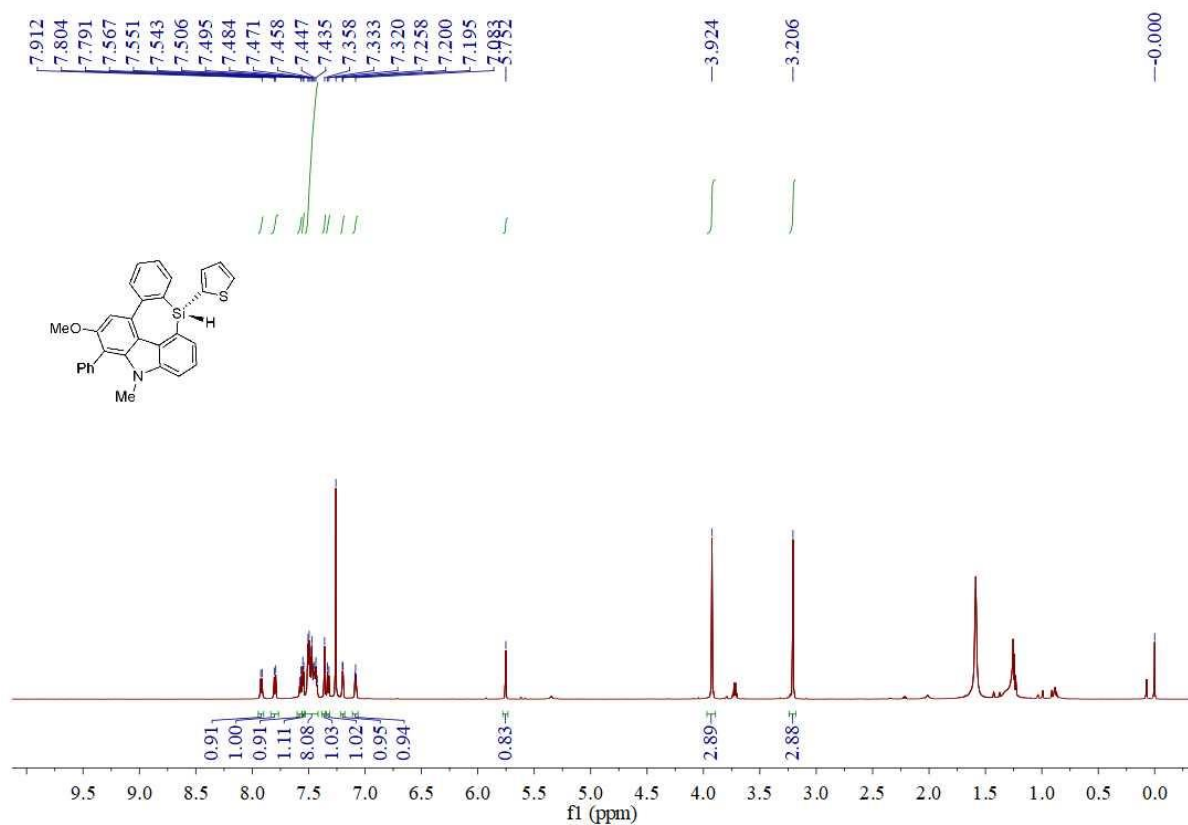


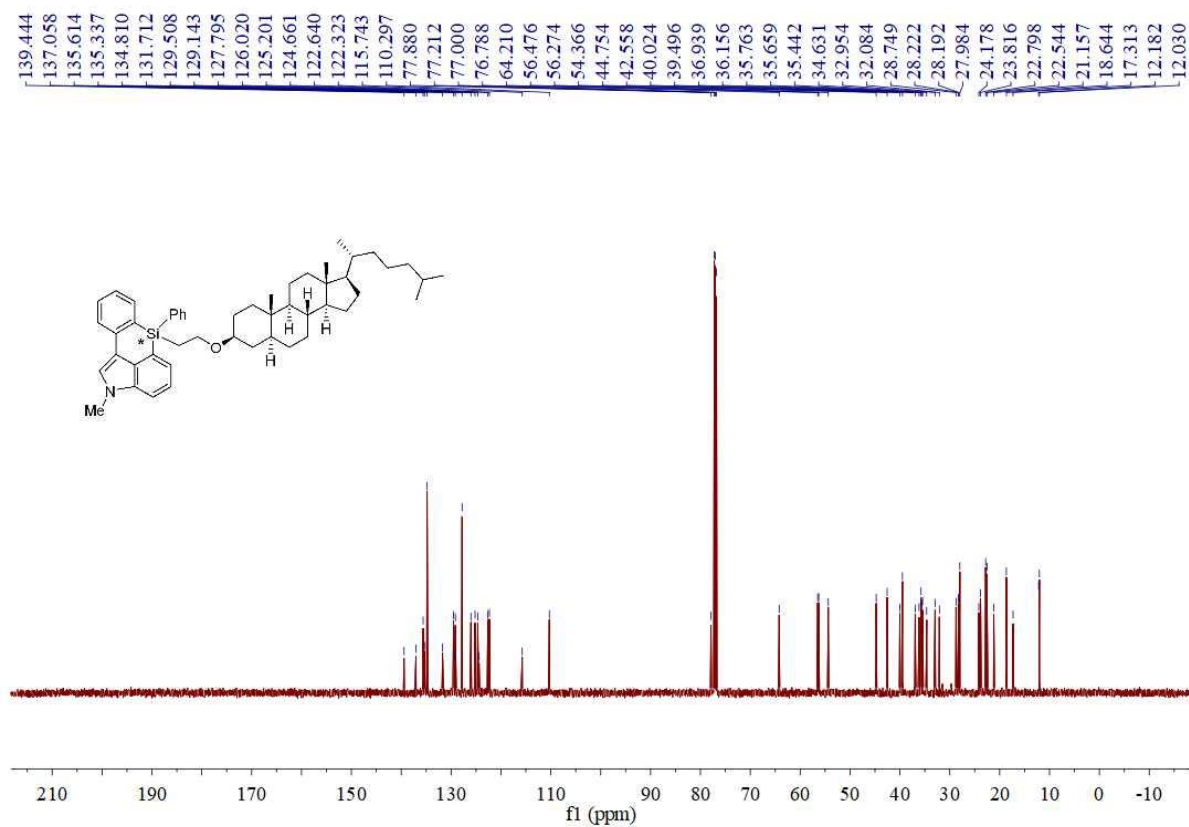
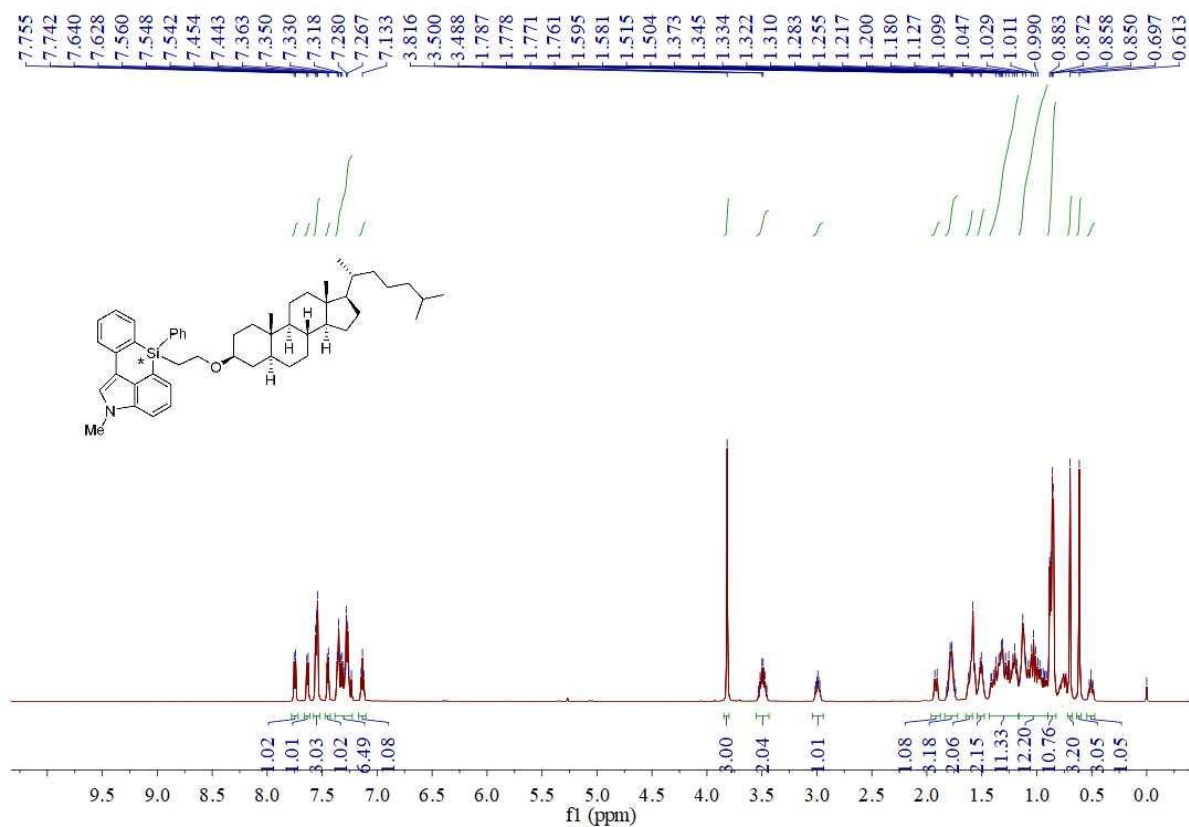


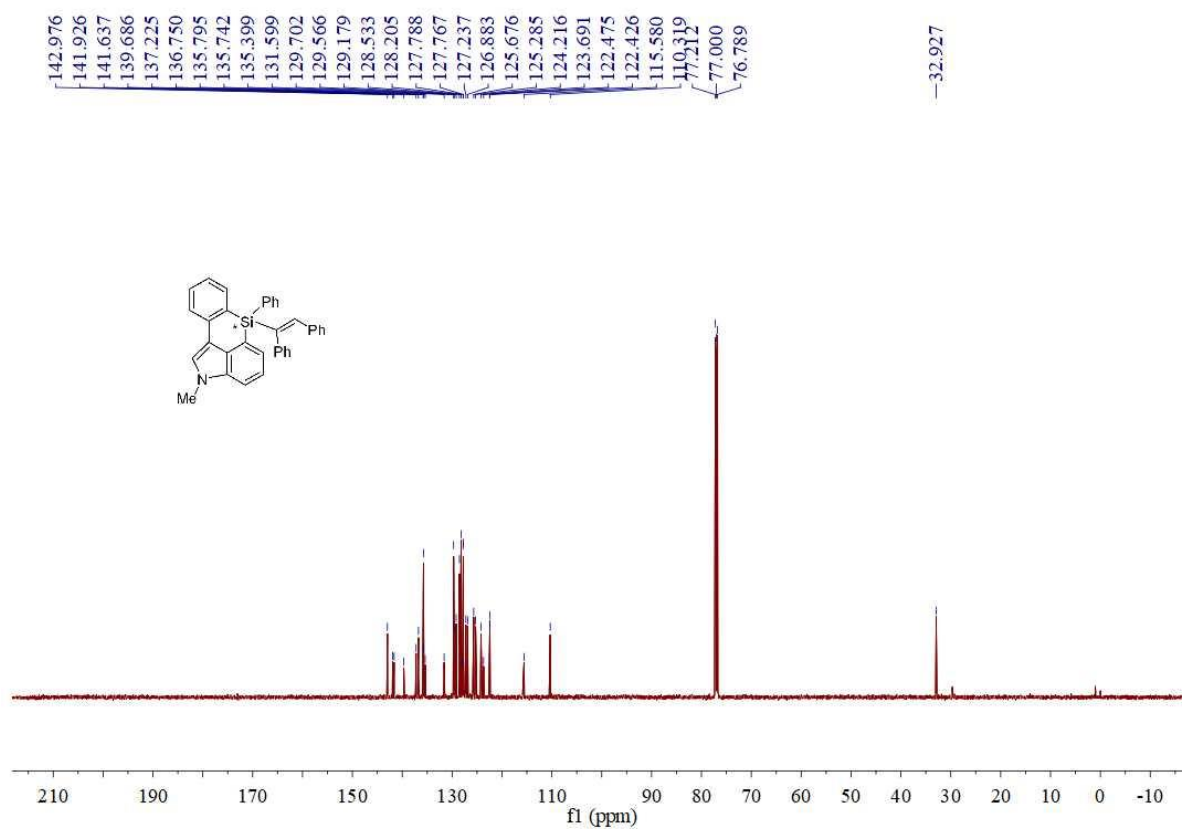
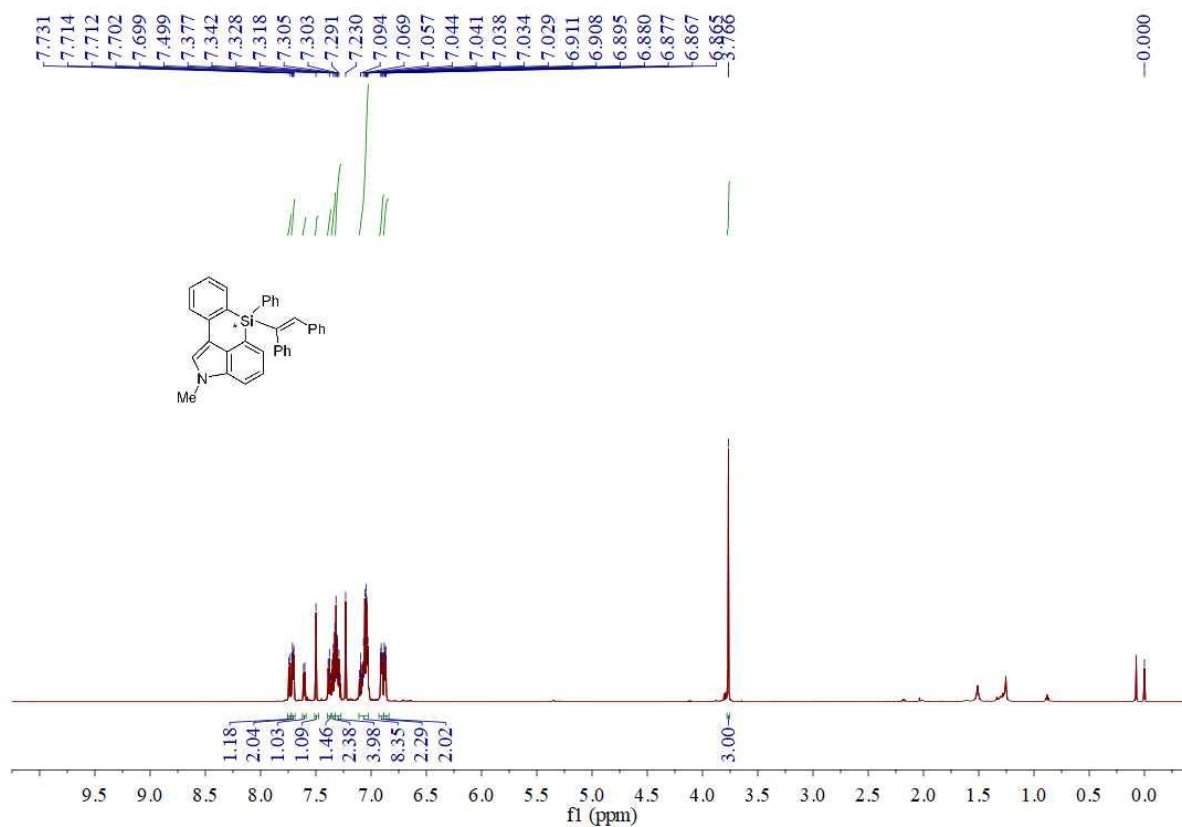


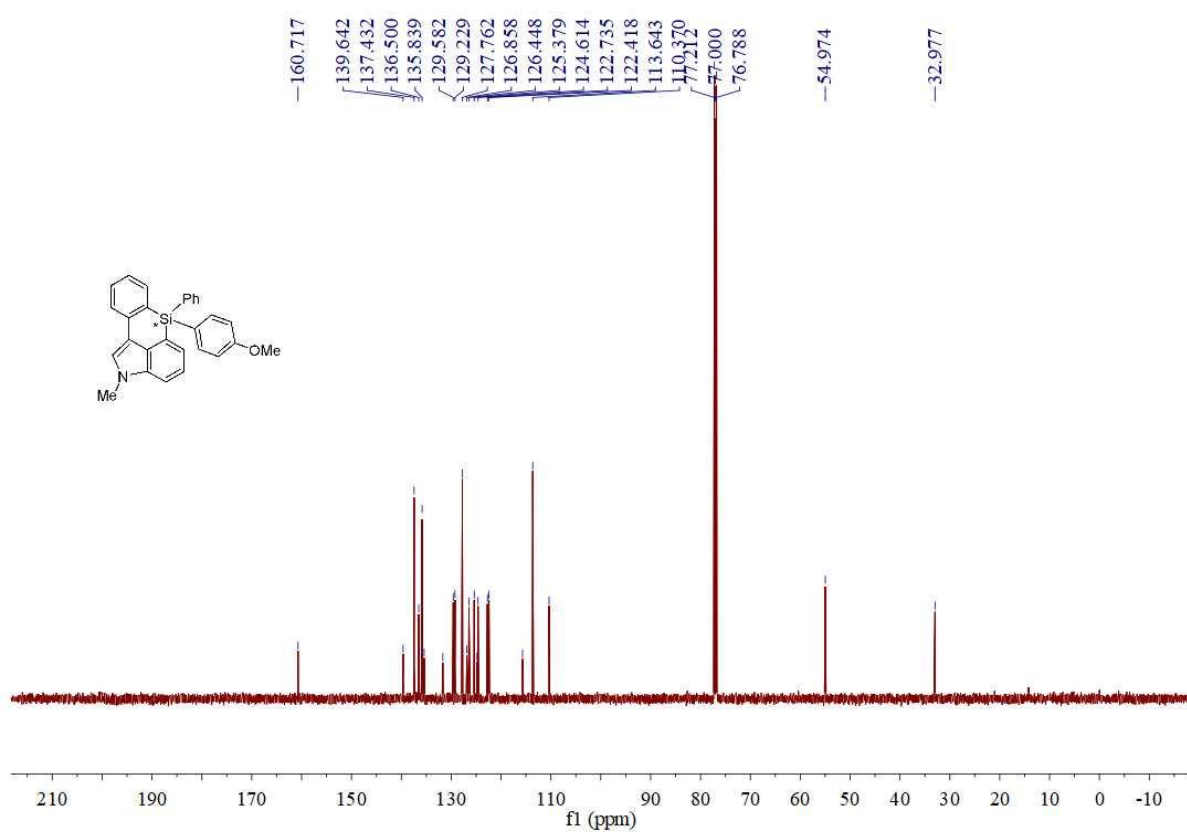
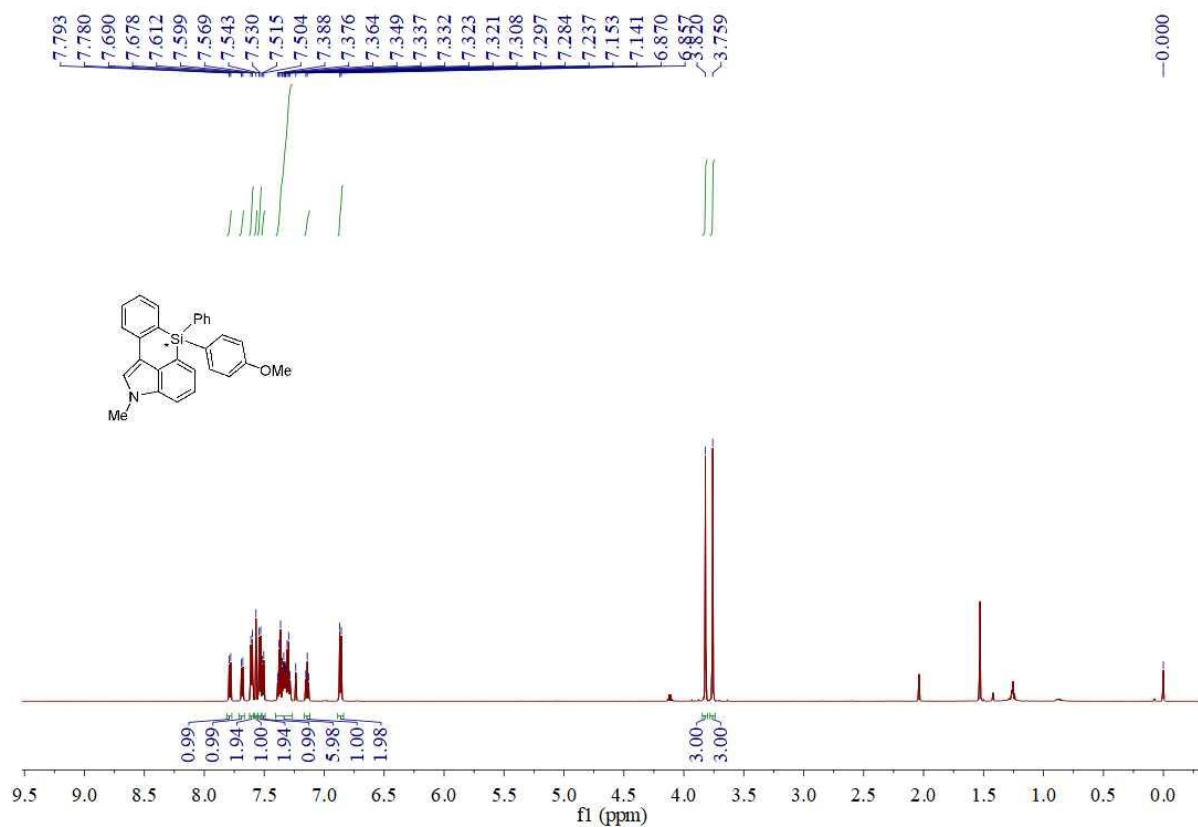


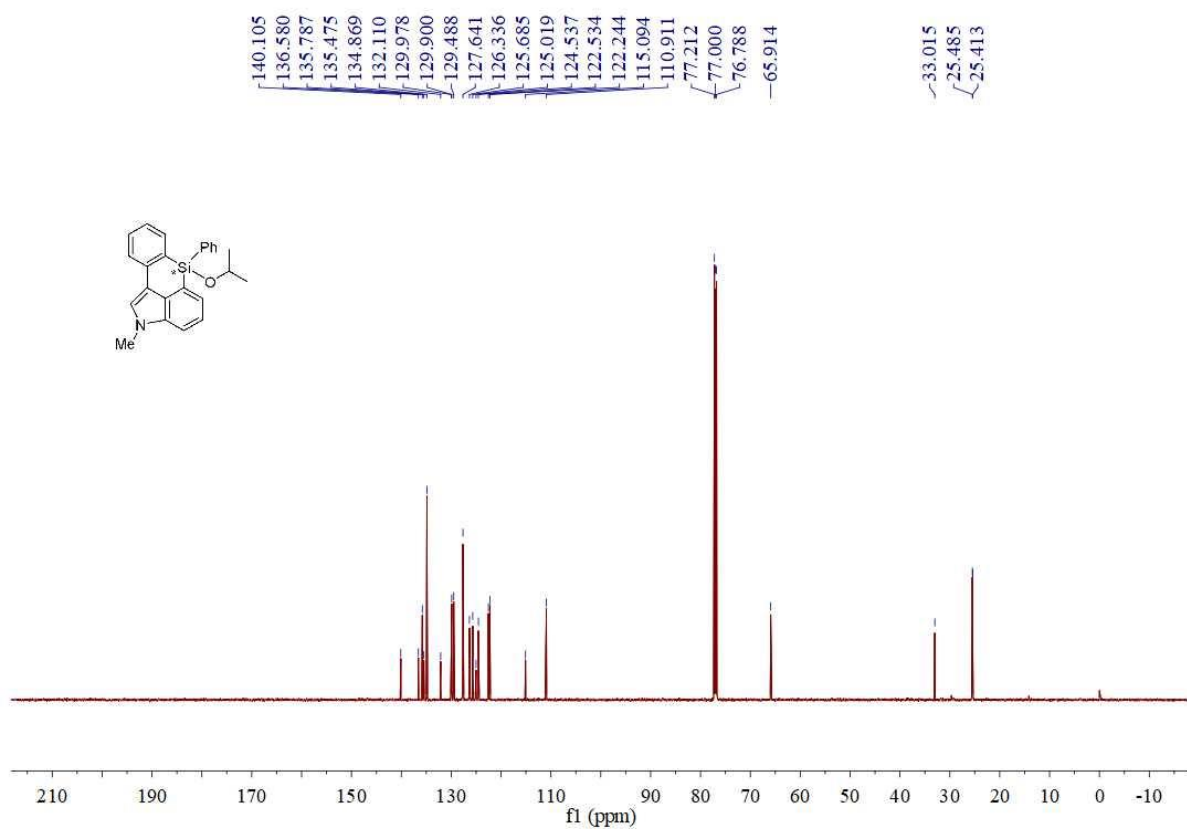
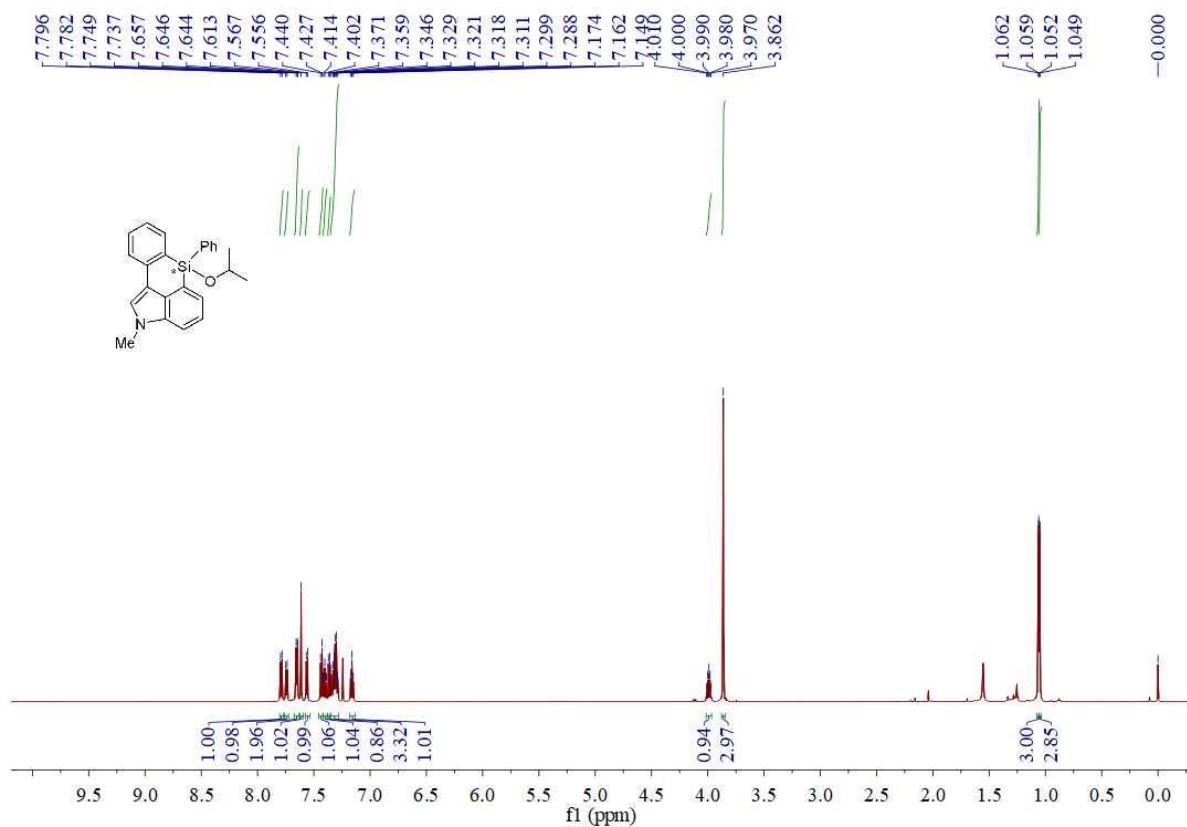


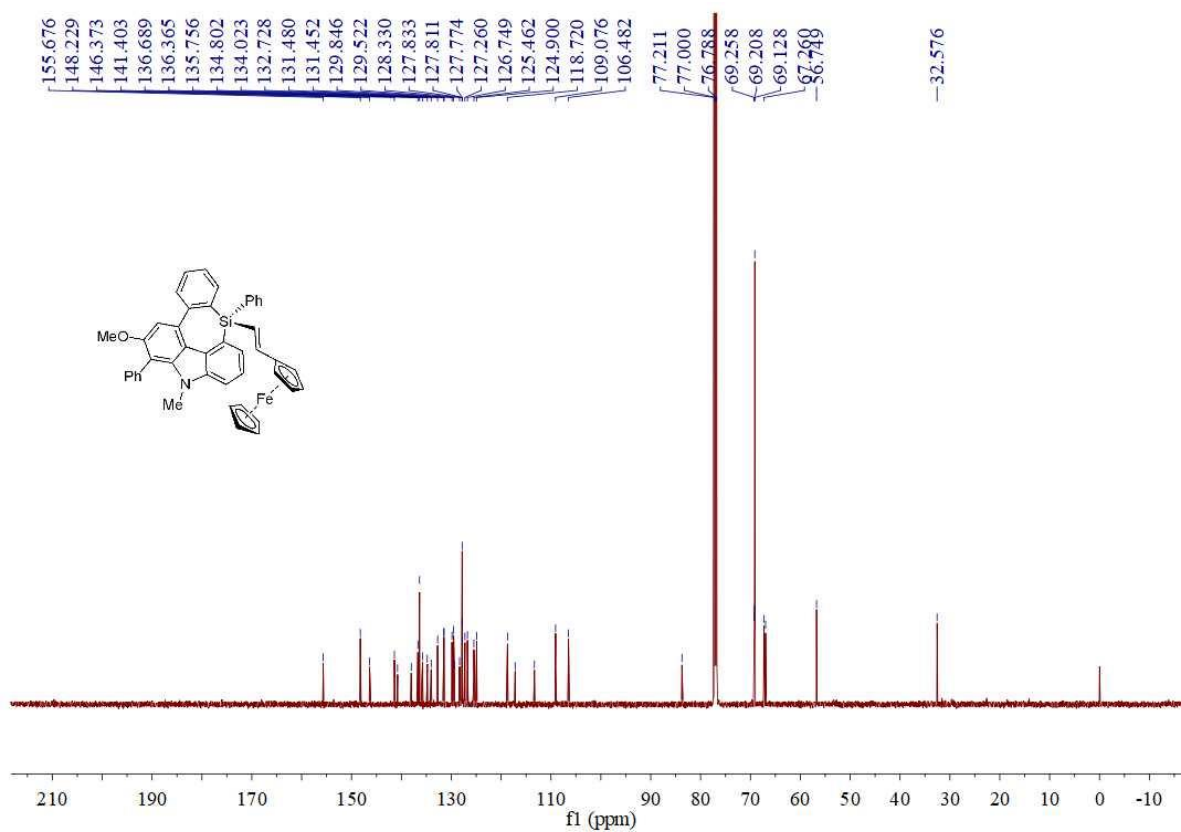
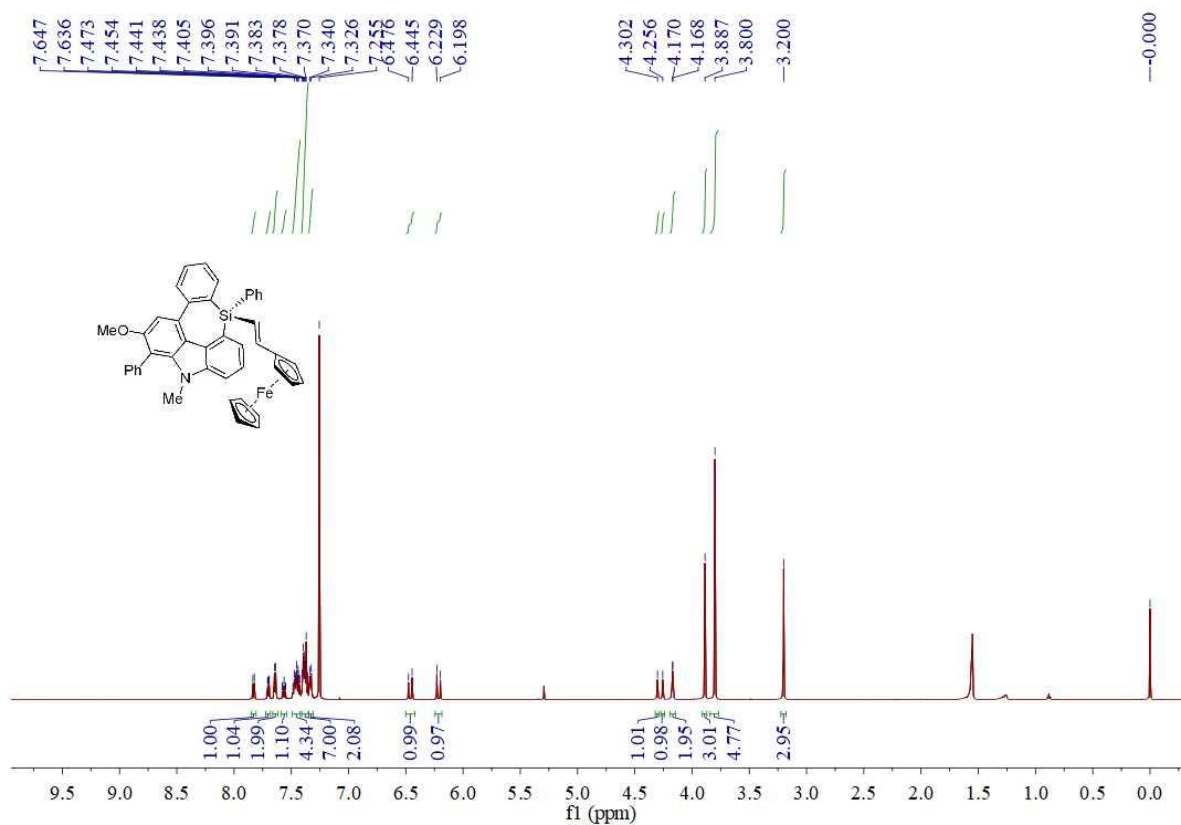




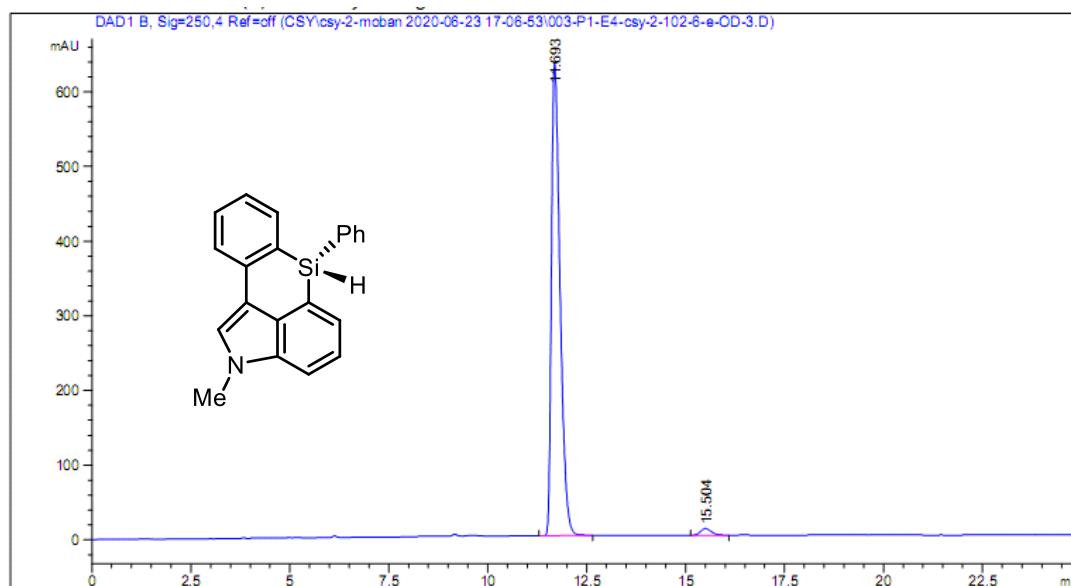
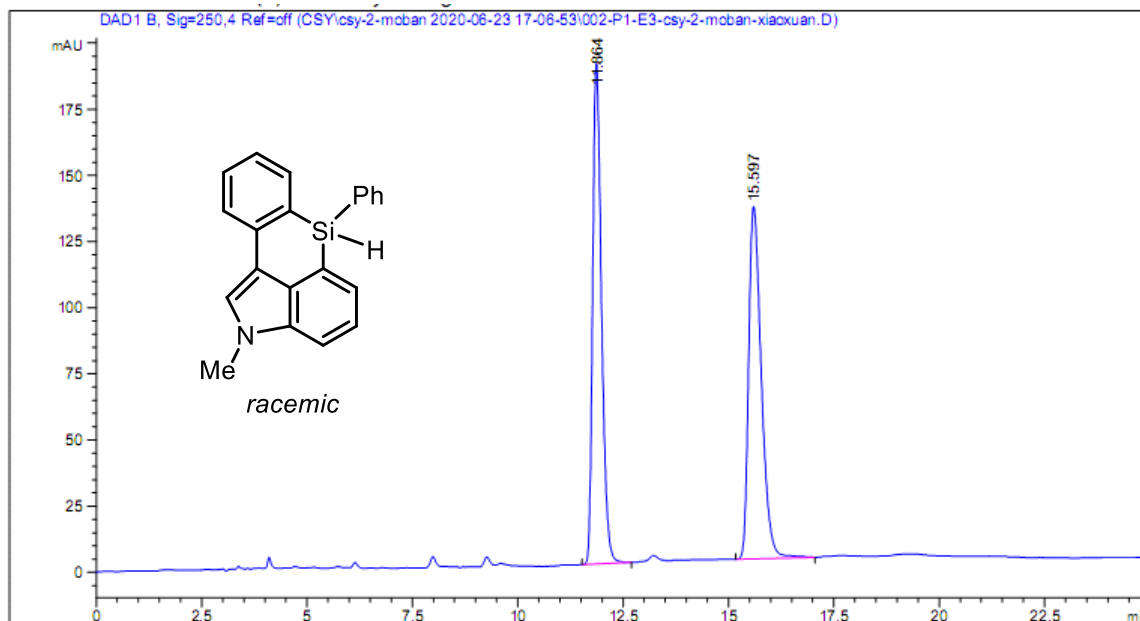


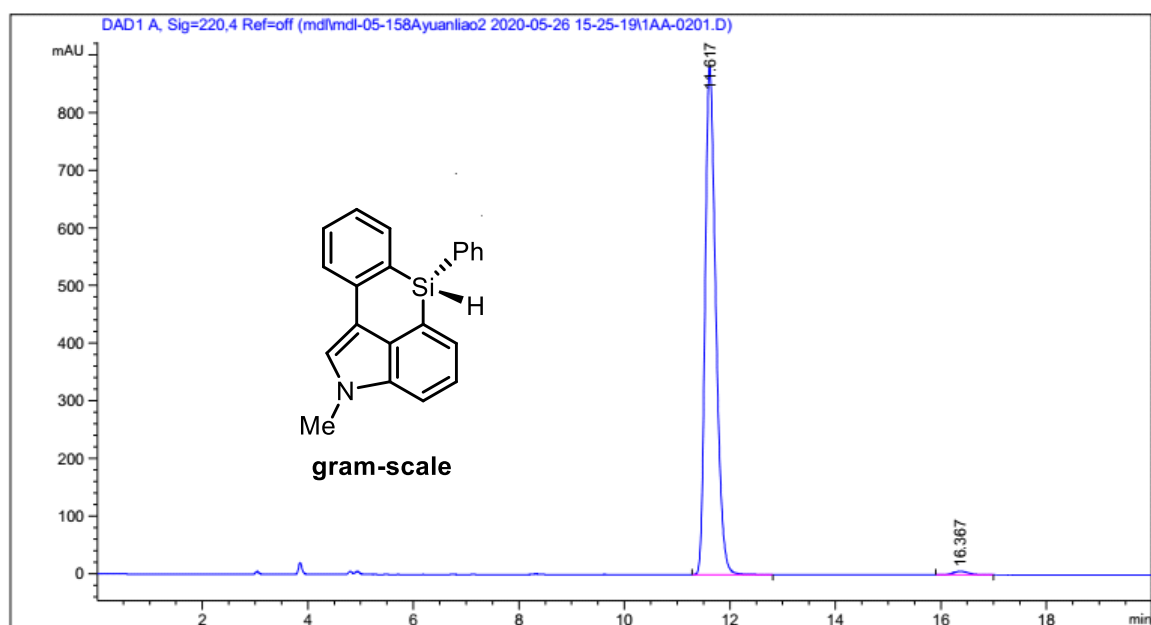
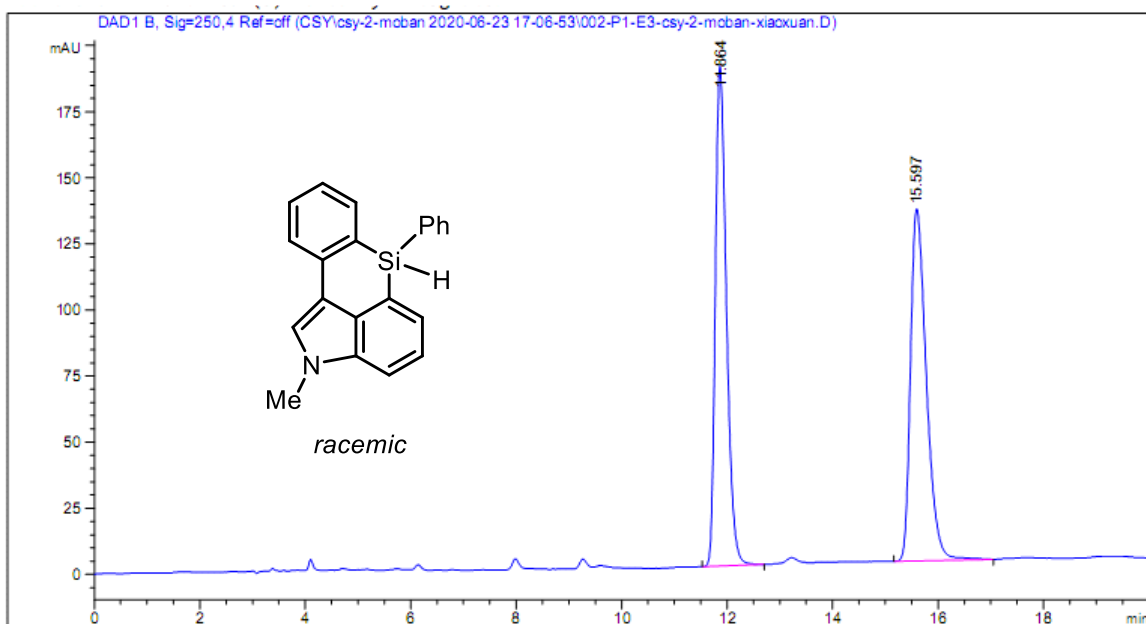


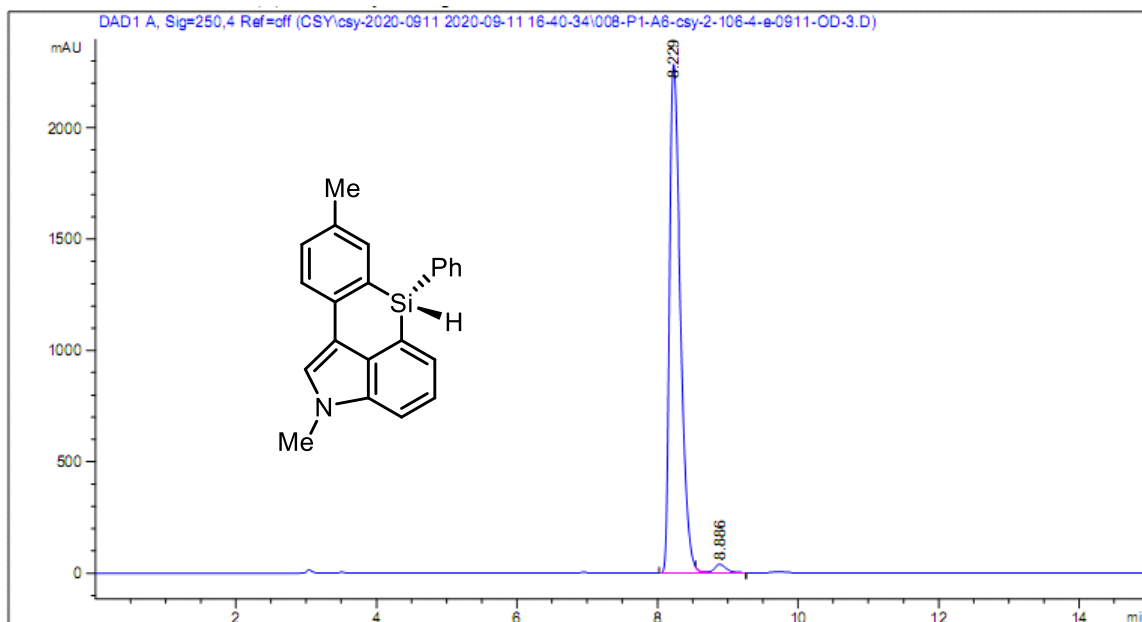
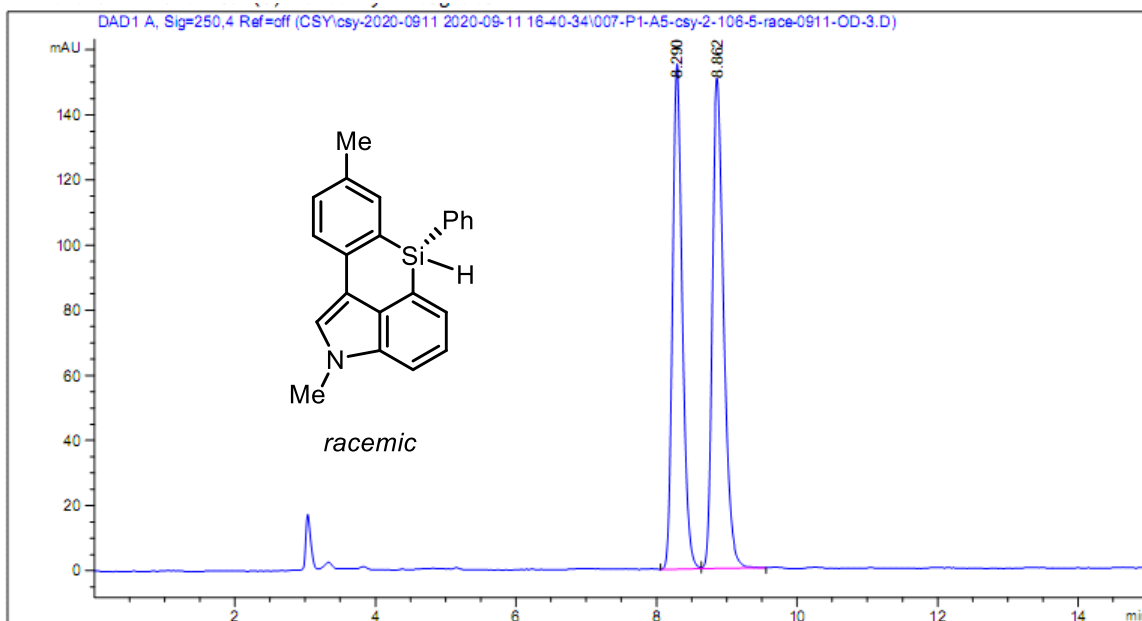


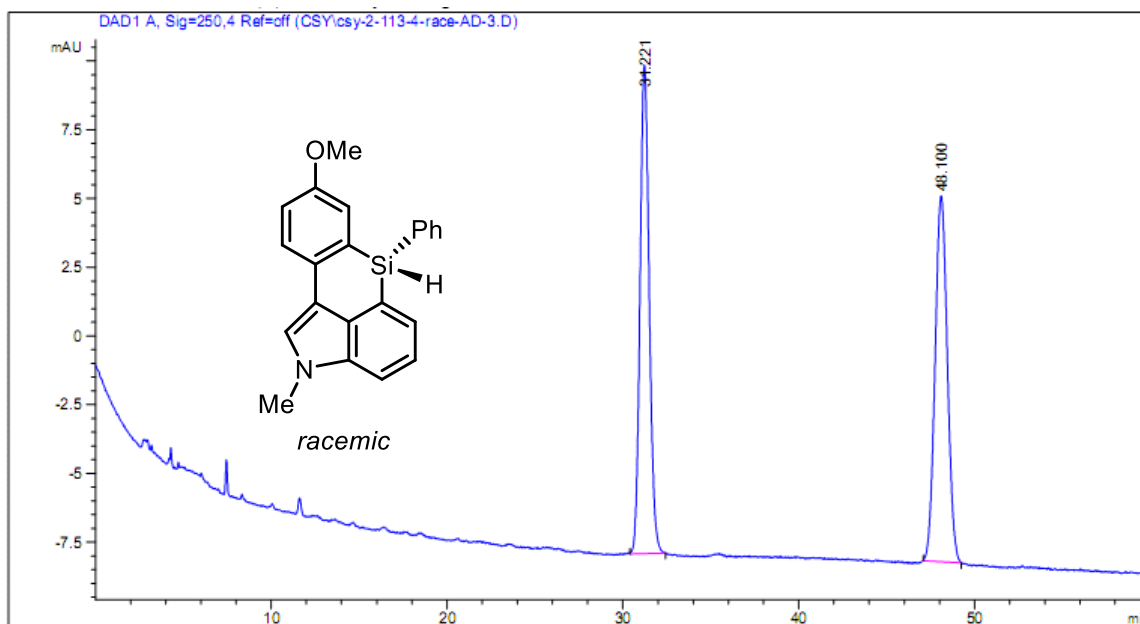


XI. Chiral HPLC Spectra

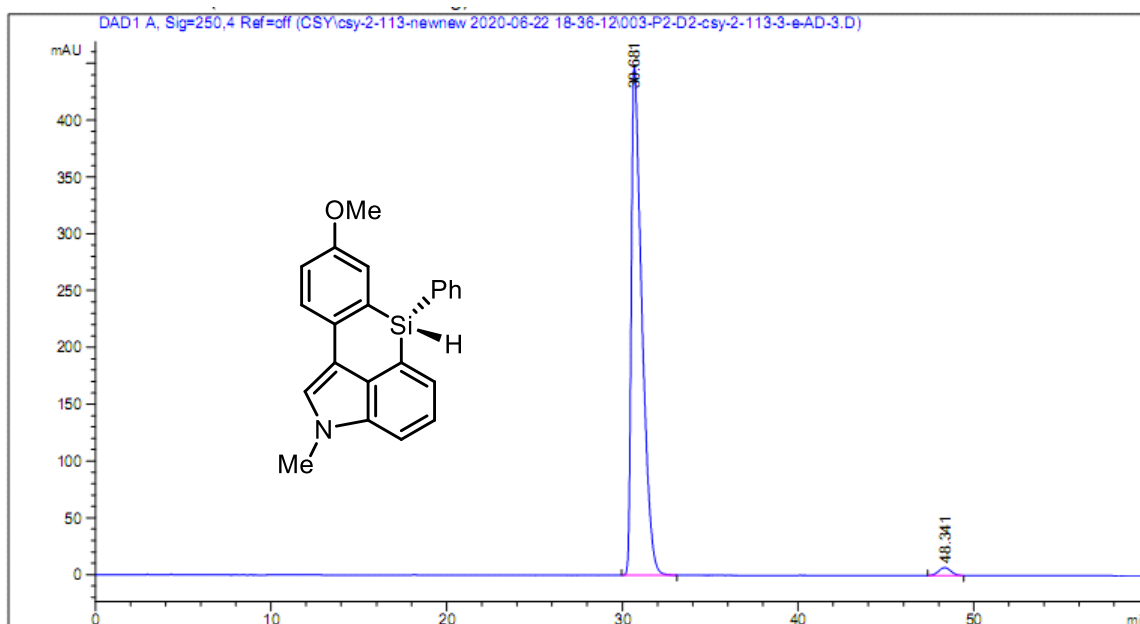




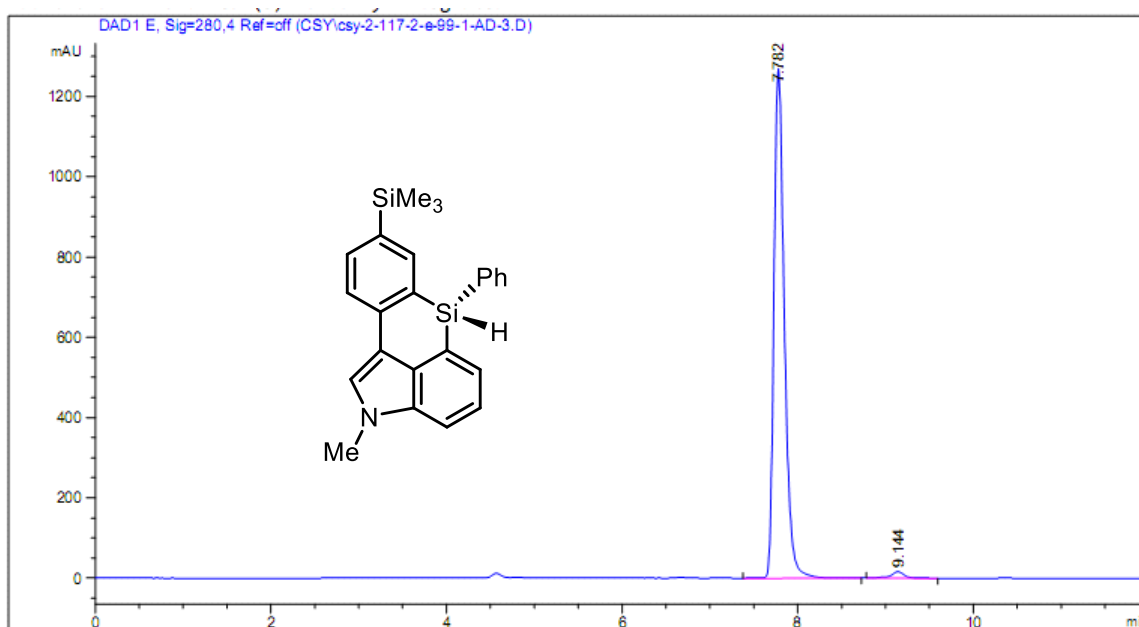
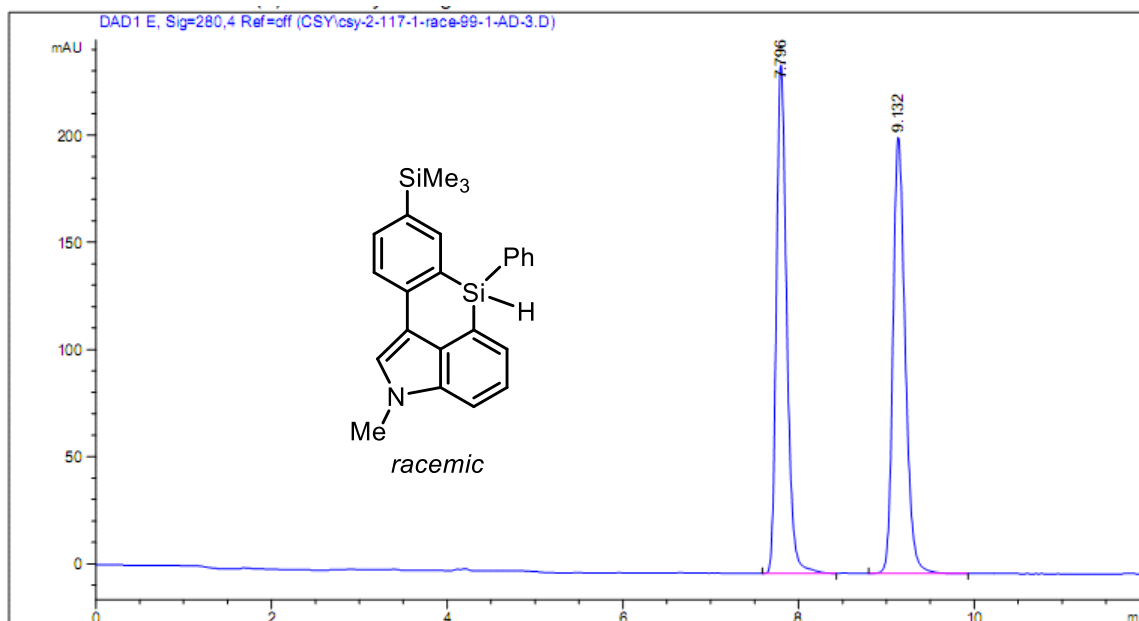


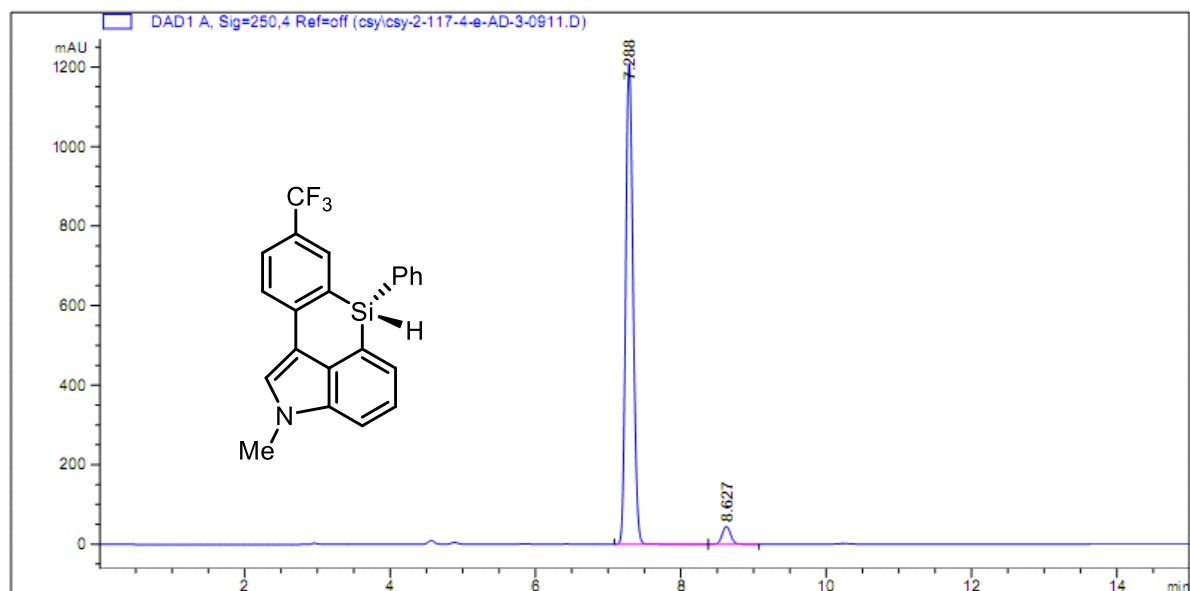
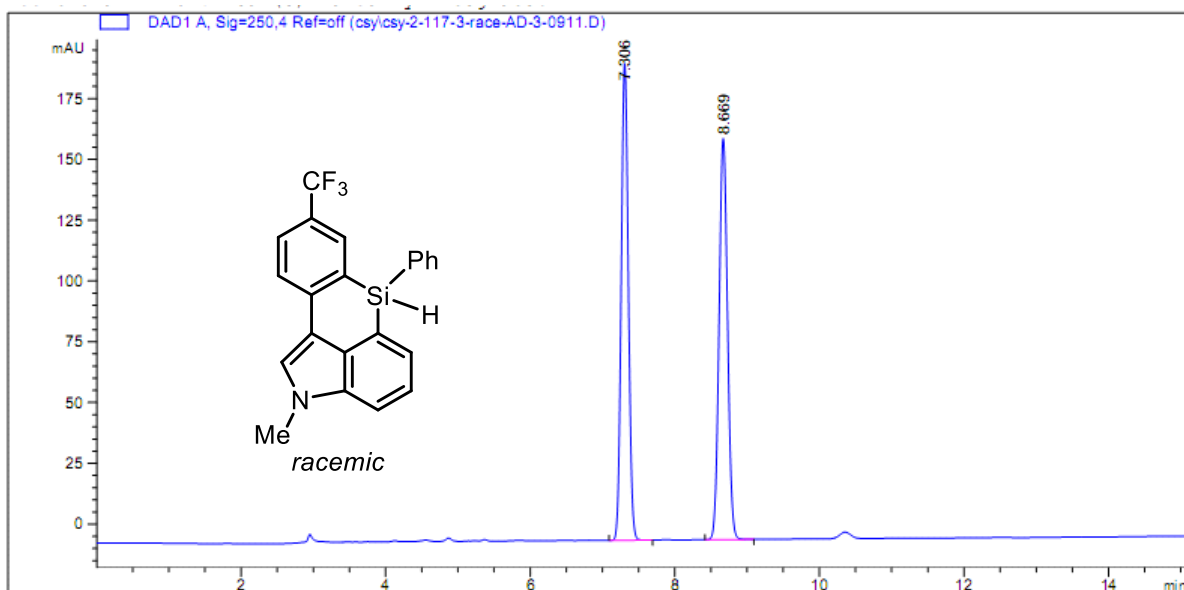


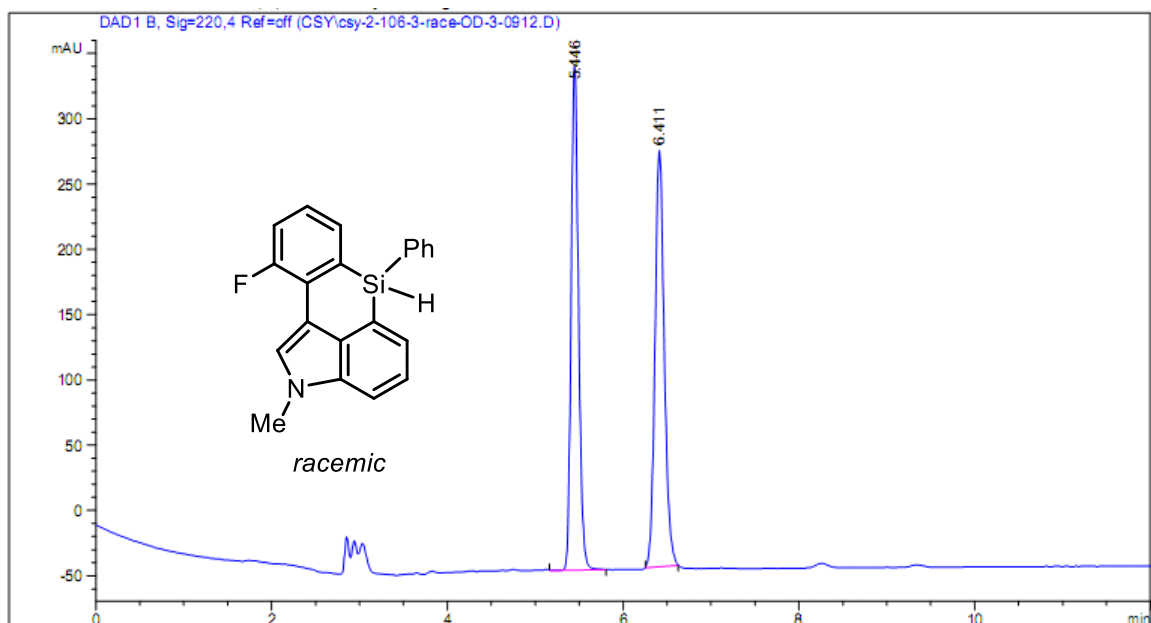
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.221	BB	0.5425	643.61505	17.77425	50.0317
2	48.100	BB	0.6218	642.79919	13.30128	49.9683



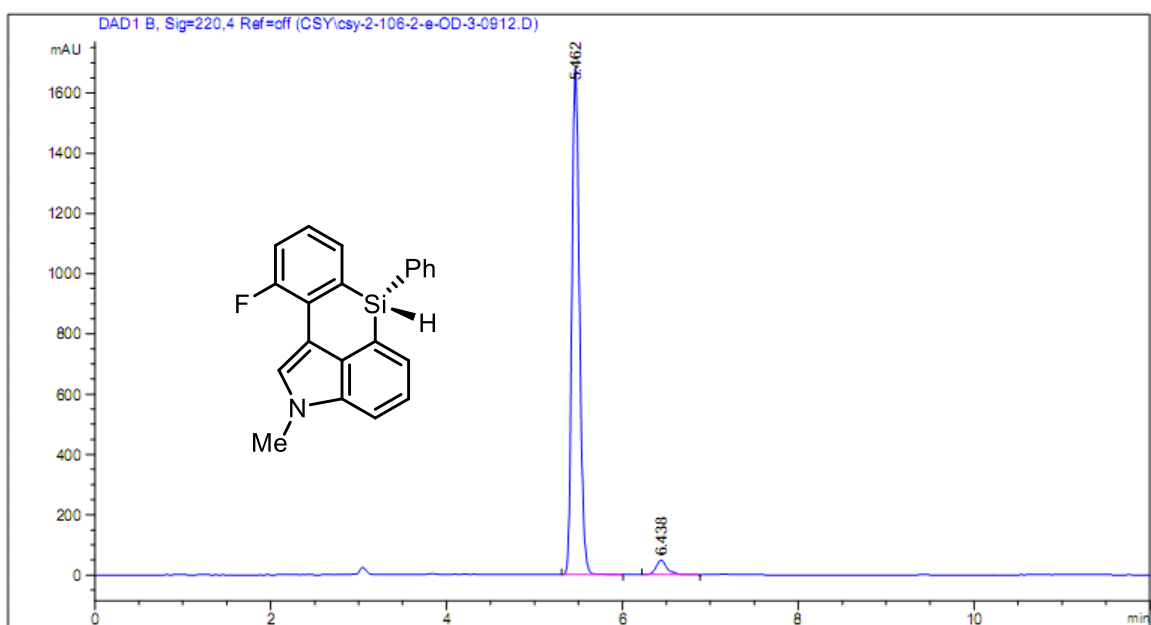
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.681	BB	0.6181	1.87256e4	447.62598	98.1724
2	48.341	BB	0.5916	348.59680	7.21593	1.8276



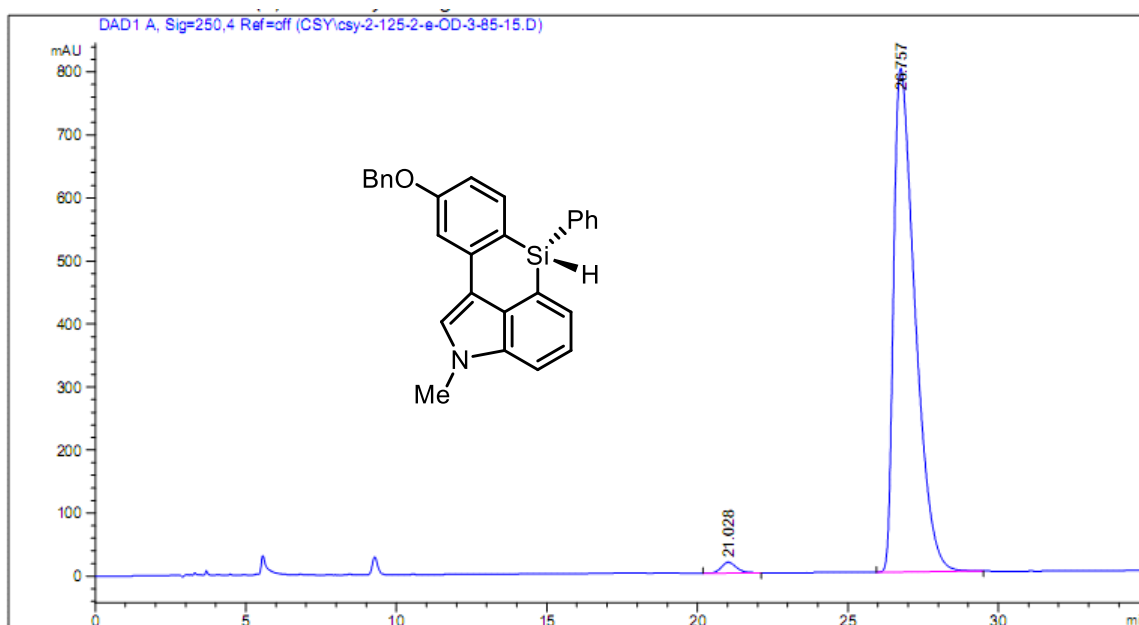
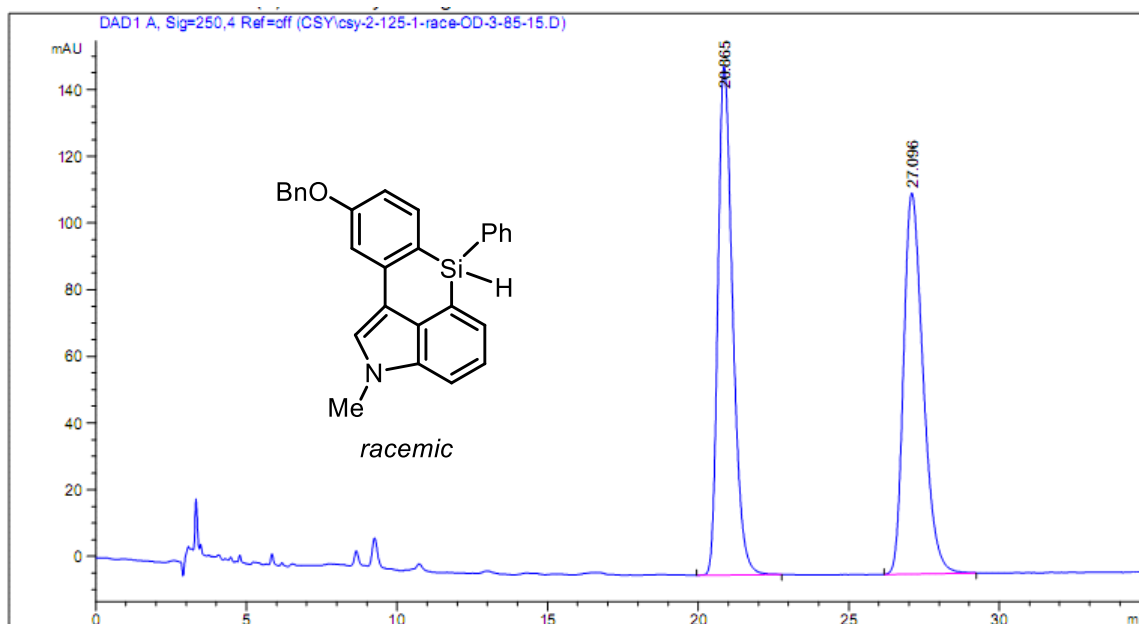


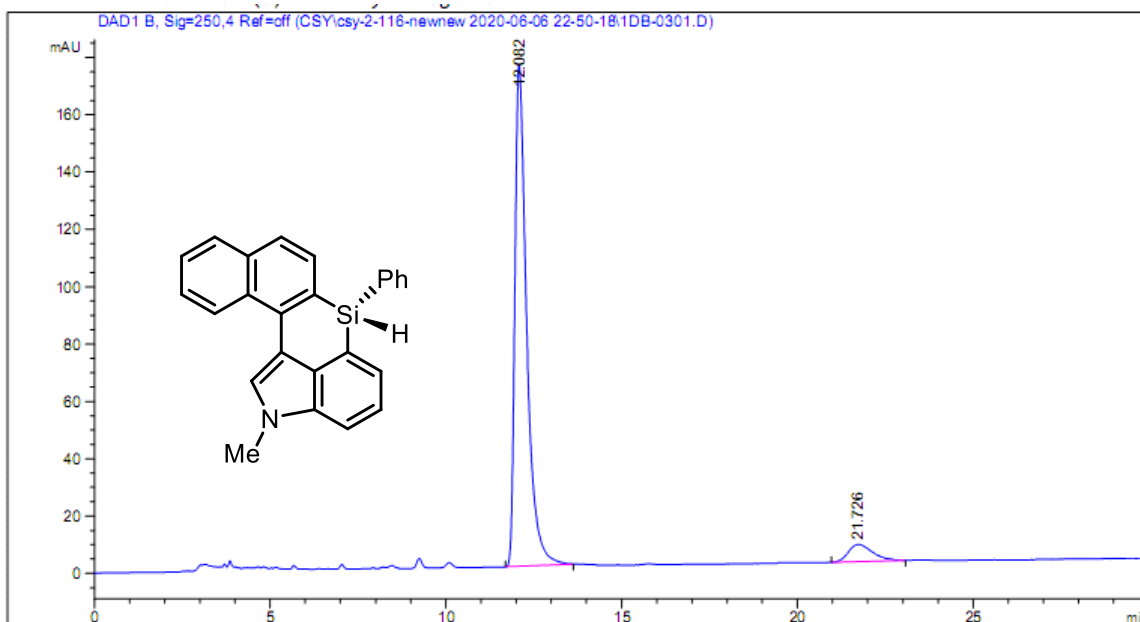
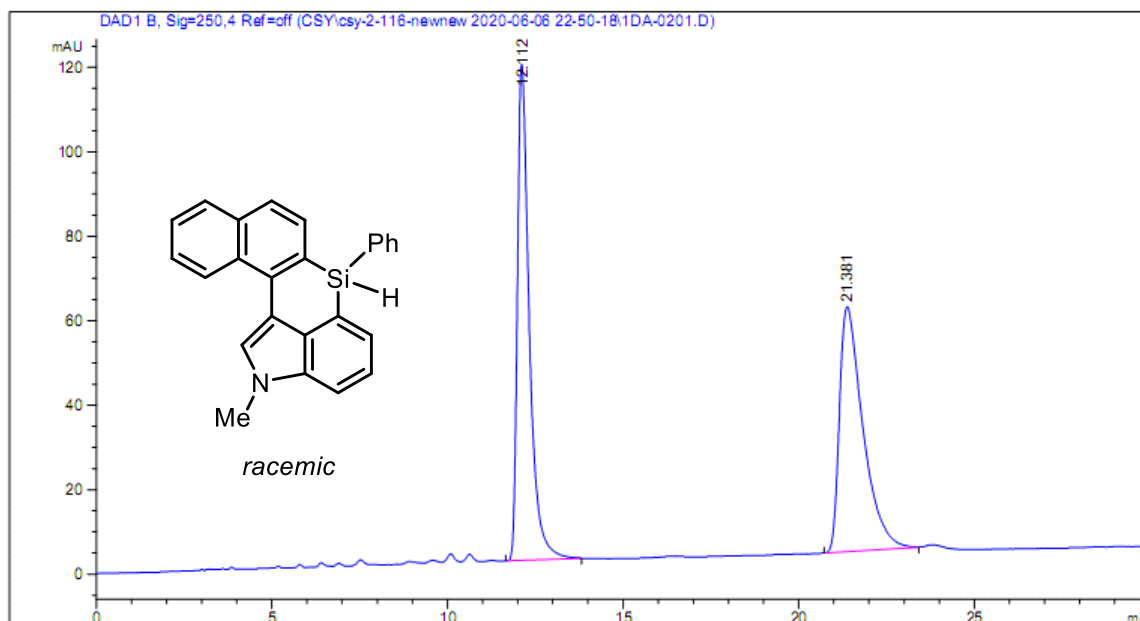


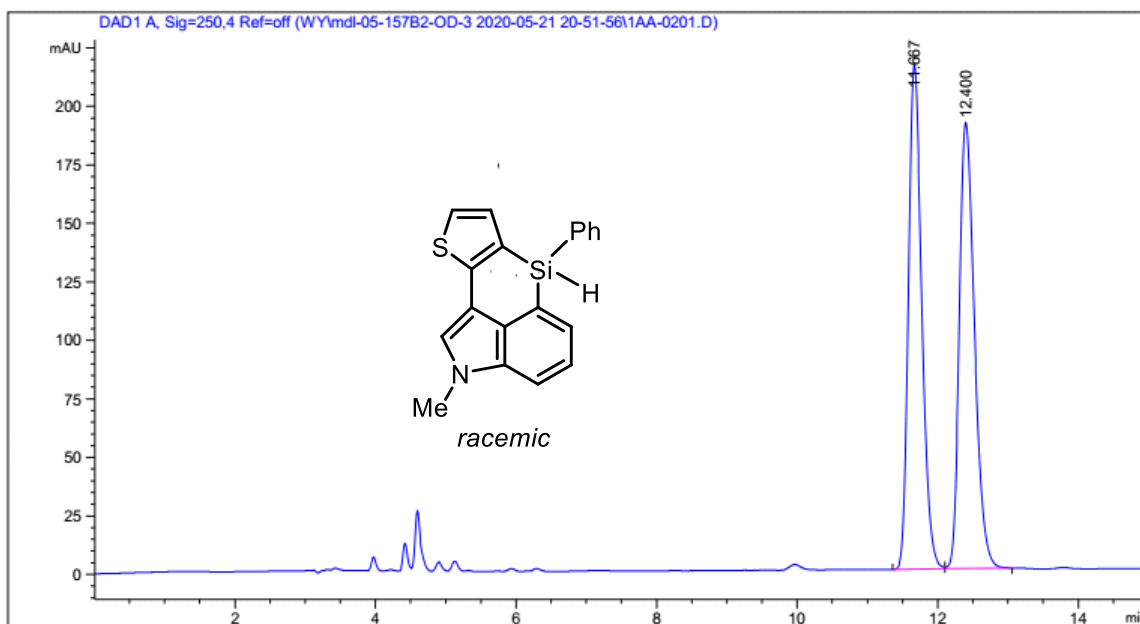
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.446	MM R	0.0968	2248.72388	387.00912	49.0353
2	6.411	MM R	0.1220	2337.20654	319.32523	50.9647



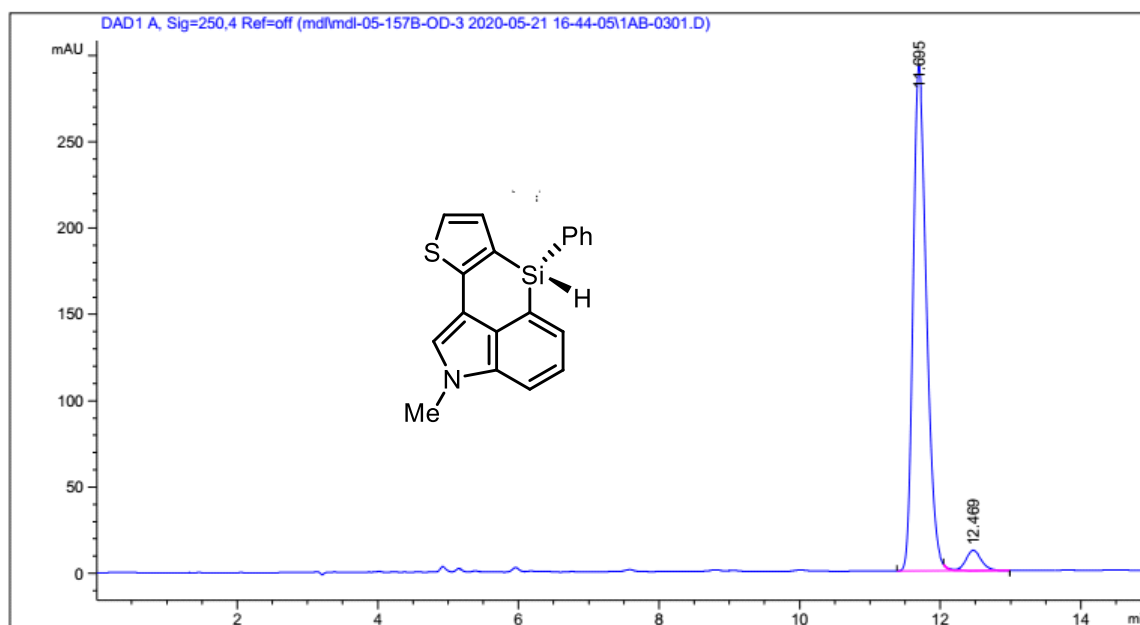
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.462	BB	0.0937	1.00798e4	1687.49207	95.8970
2	6.438	BB	0.1289	431.26443	48.88698	4.1030



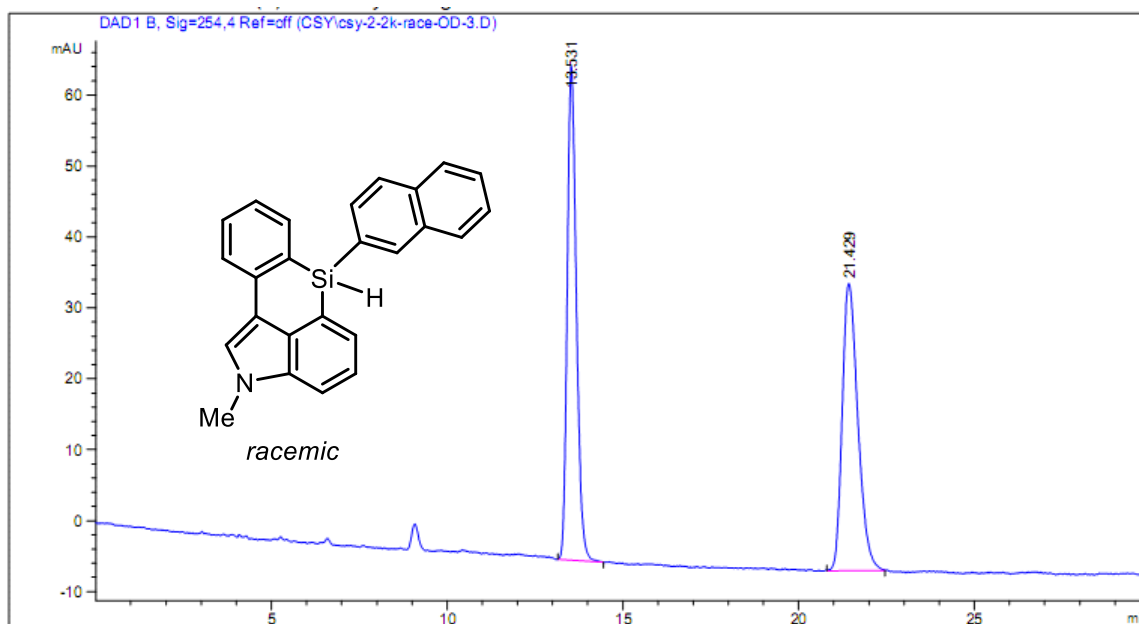




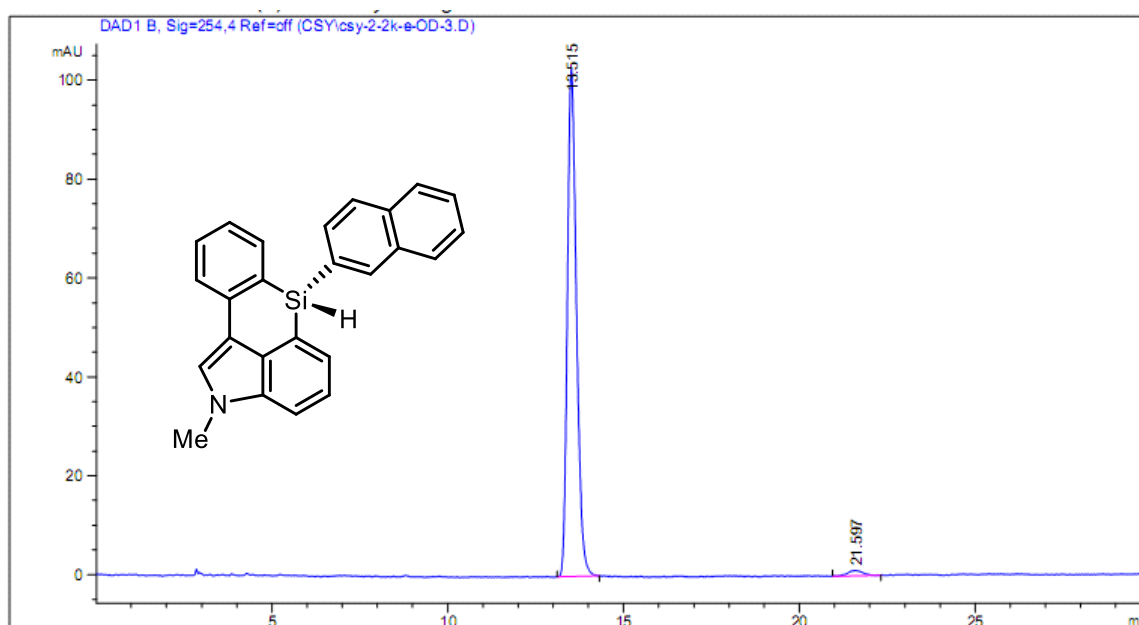
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.667	BV	0.2031	2829.31519	215.60249	49.8782
2	12.400	VB	0.2301	2843.13696	190.57463	50.1218



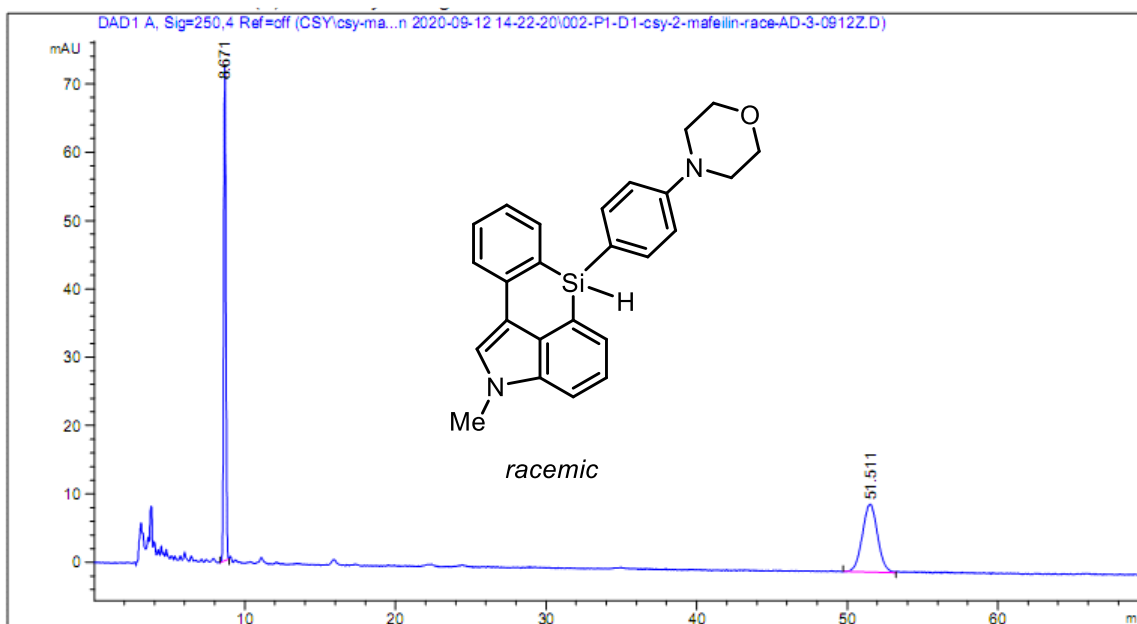
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.695	BV R	0.2074	3896.50171	292.56125	95.5281
2	12.469	VB E	0.2378	182.40567	11.83558	4.4719



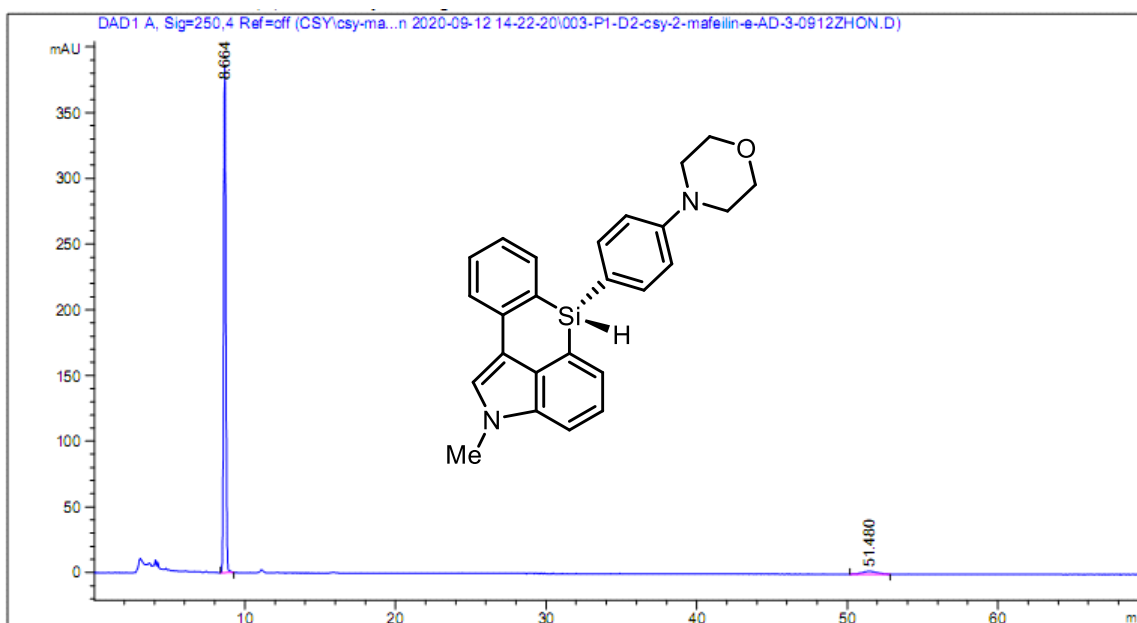
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.531	BB	0.2790	1260.36267	69.68239	50.2162
2	21.429	BB	0.4580	1249.51074	40.49051	49.7838



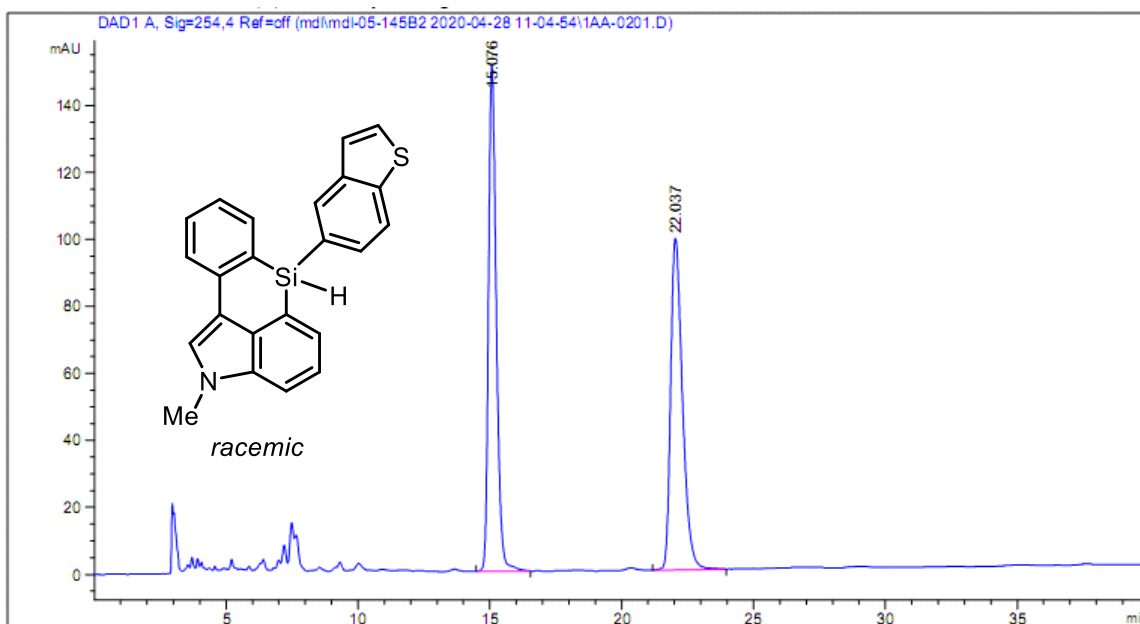
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.515	BB	0.2776	1843.20288	102.61981	98.2482
2	21.597	MM R	0.4971	32.86547	1.10195	1.7518



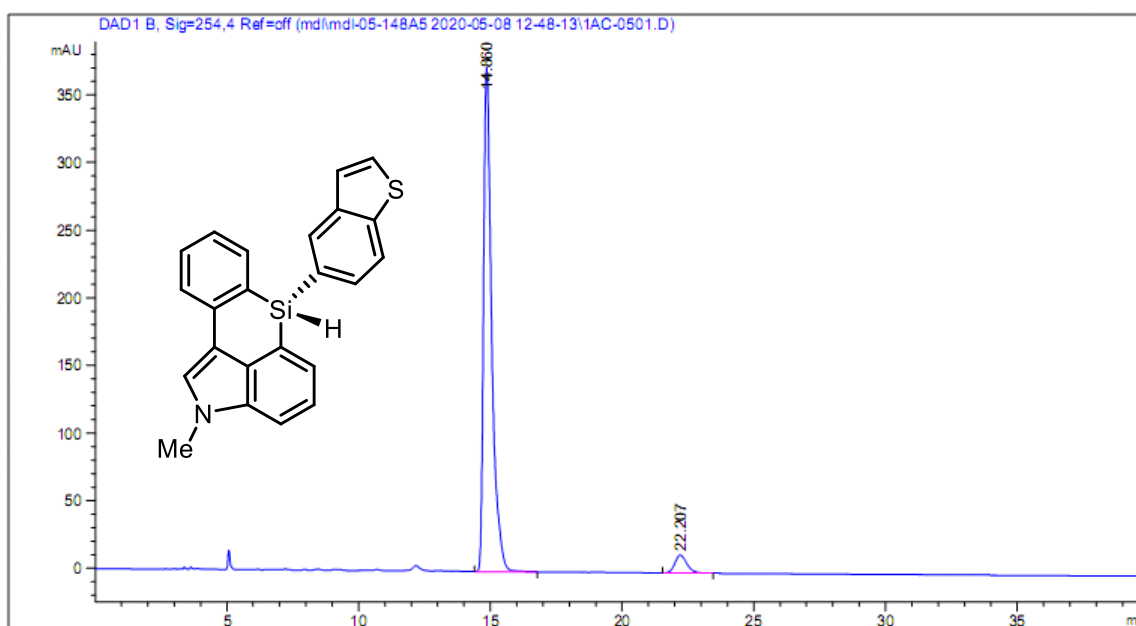
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.671	MM R	0.1631	708.26599	72.36091	50.4486
2	51.511	MM R	1.1708	695.66937	9.90293	49.5514



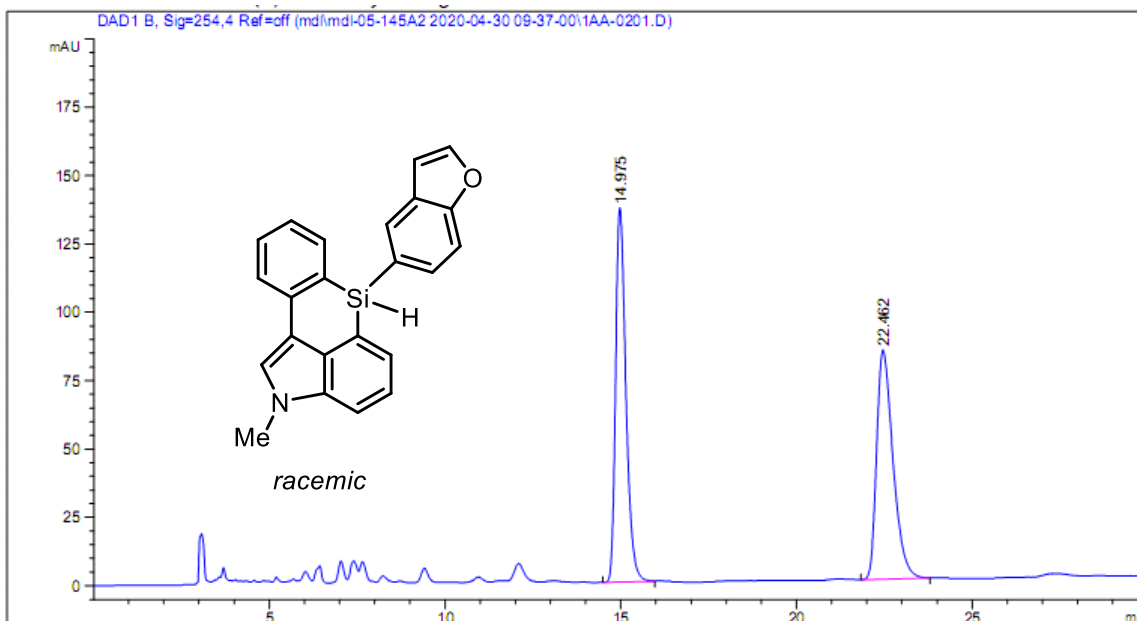
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.664	BB	0.1537	3819.60596	385.18637	96.2729
2	51.480	MM R	1.1735	147.87158	2.10011	3.7271



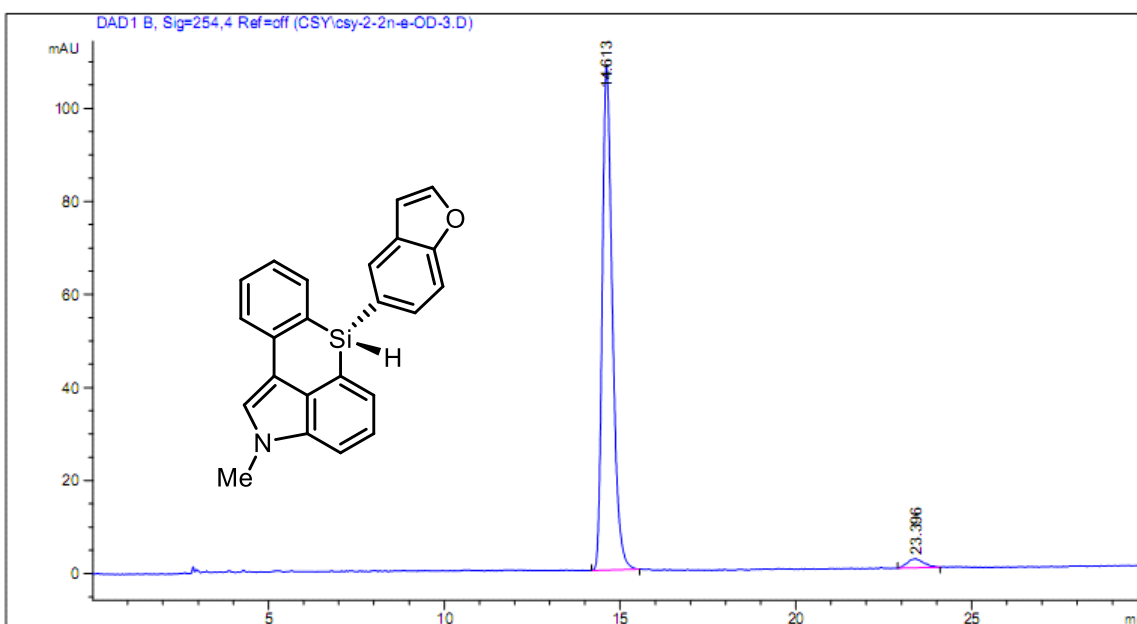
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.076	BB	0.3155	3098.71362	150.94339	50.1961
2	22.037	BB	0.4763	3074.50757	98.99536	49.8039



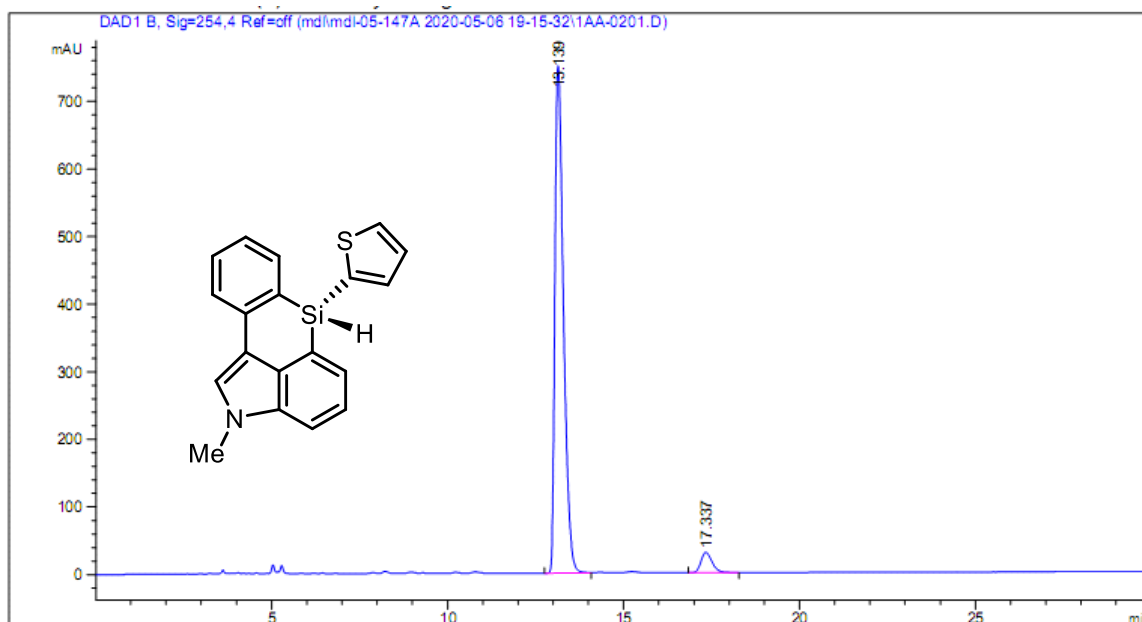
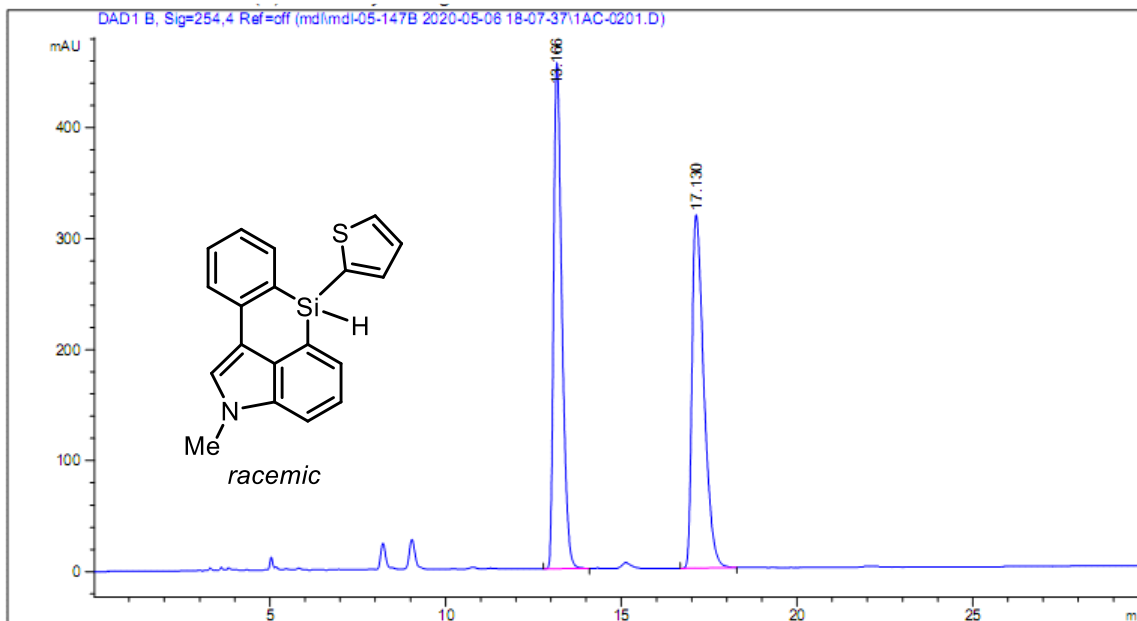
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.860	BB	0.3220	7994.50732	373.00394	95.0263
2	22.207	BB	0.4742	418.43558	13.25923	4.9737

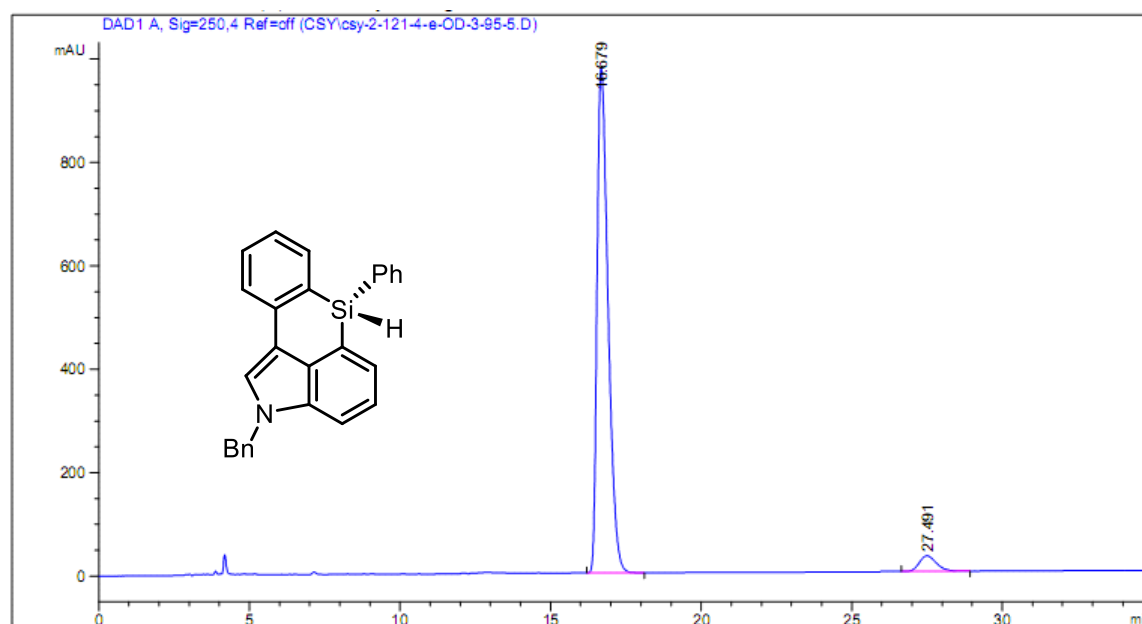
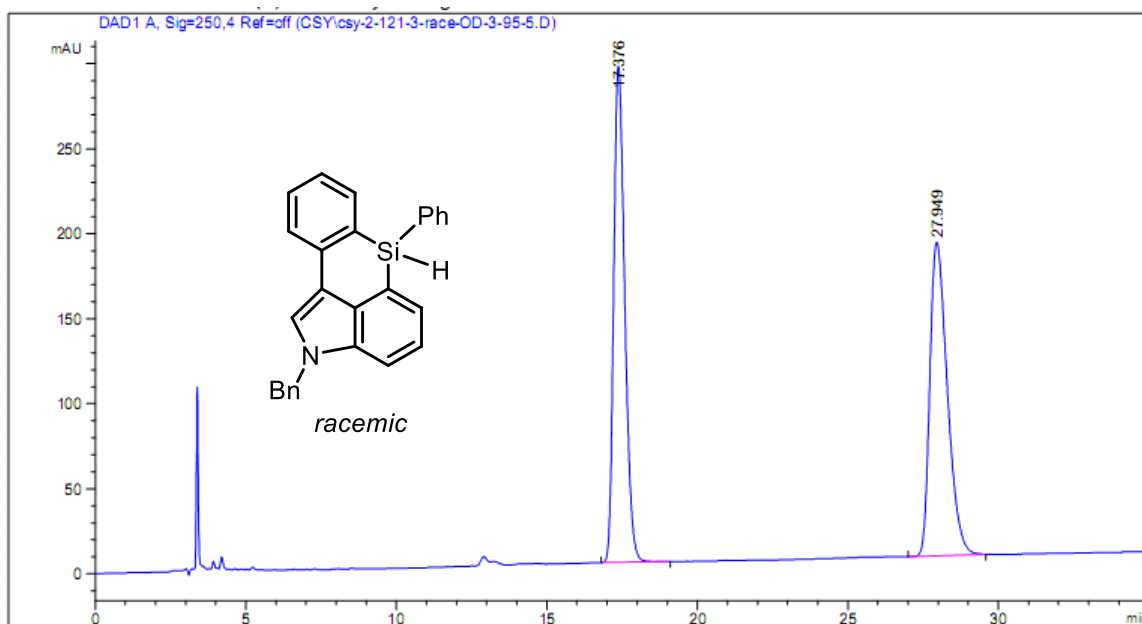


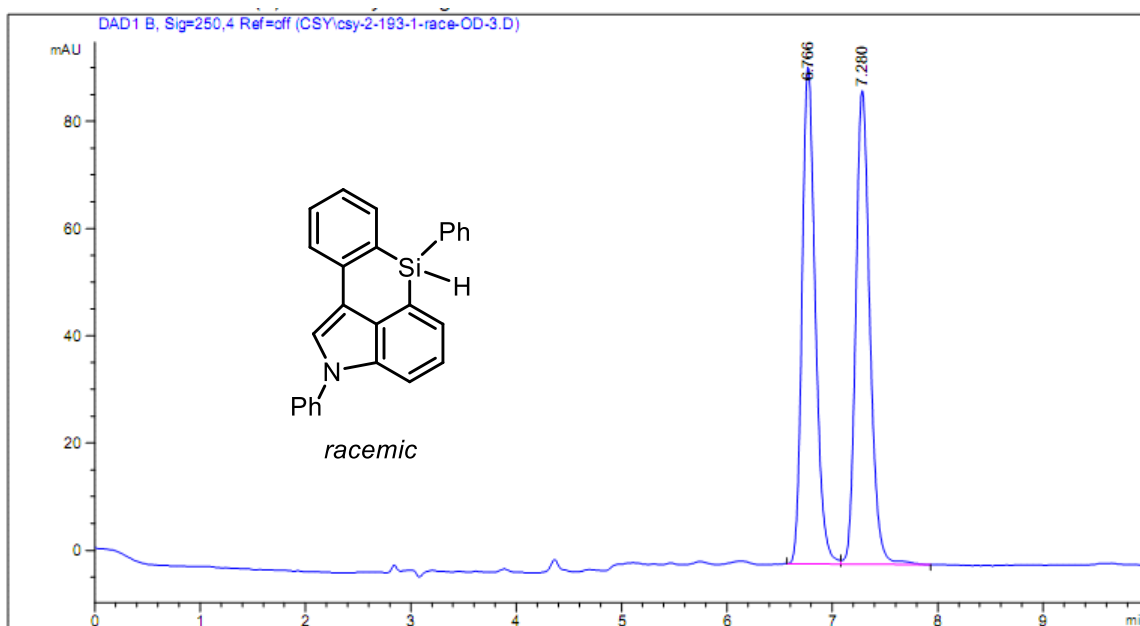
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.975	BB	0.3114	2784.14429	136.82396	50.6694
2	22.462	BB	0.4975	2710.58203	83.77981	49.3306



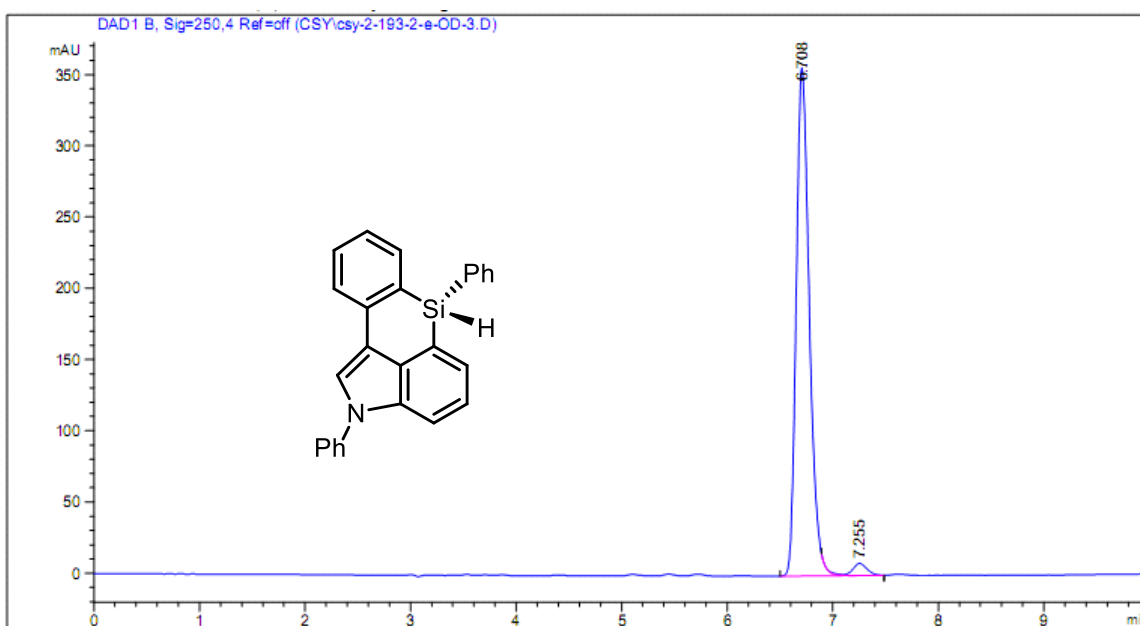
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.613	BB	0.3126	2177.18628	108.29329	97.2273
2	23.396	BB	0.3937	62.08735	1.89794	2.7727



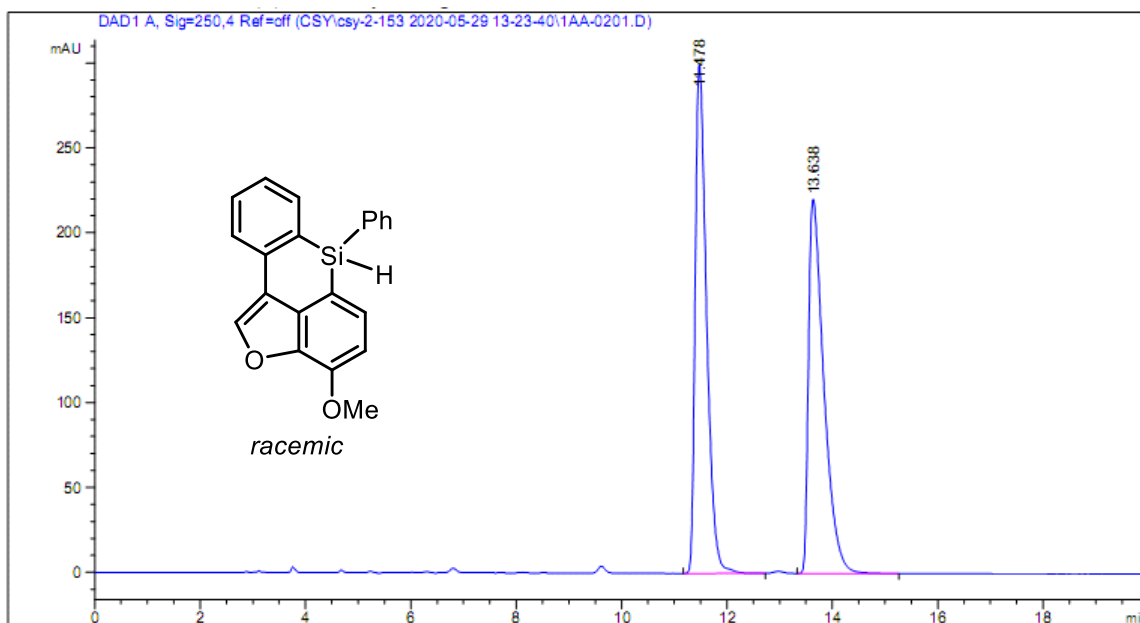




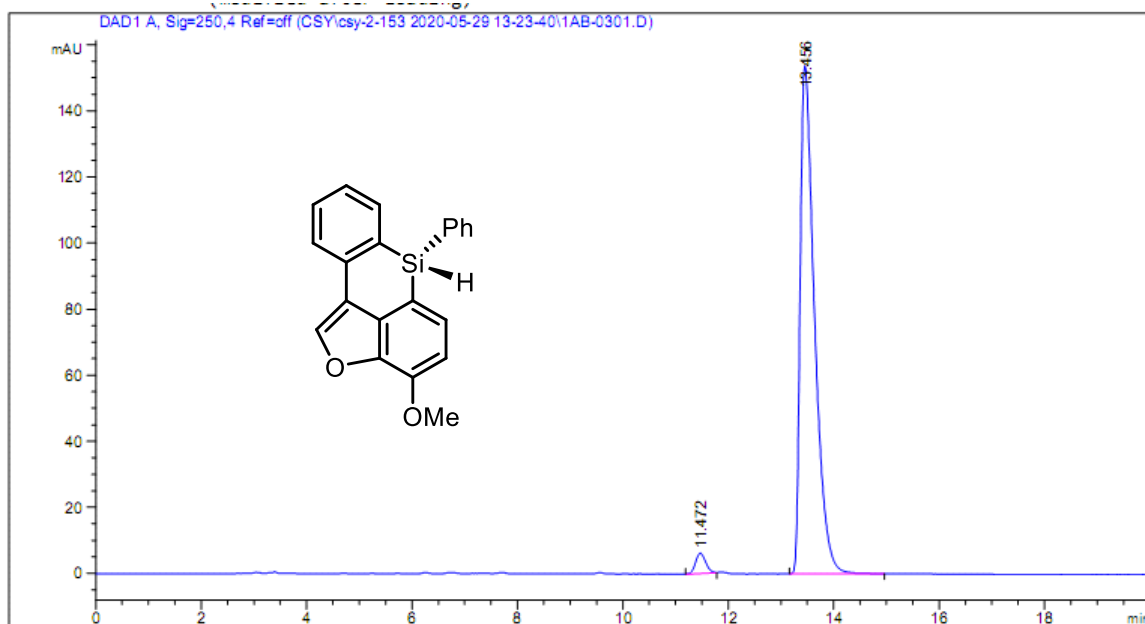
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.766	BV	0.1338	808.83246	92.67847	49.6423
2	7.280	VB	0.1423	820.48962	88.41254	50.3577



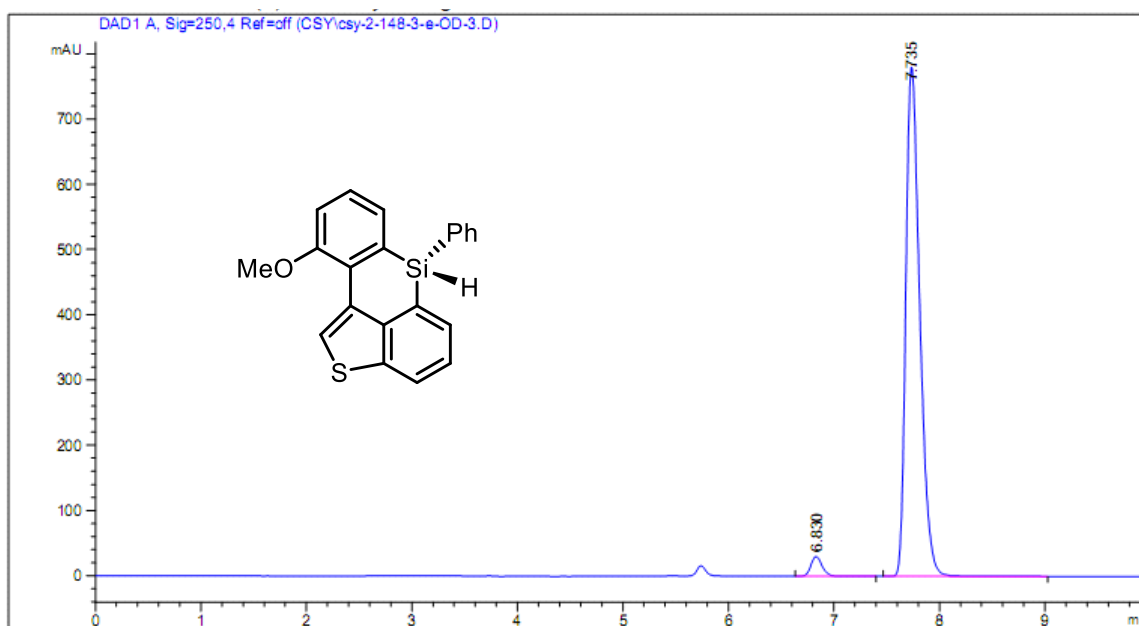
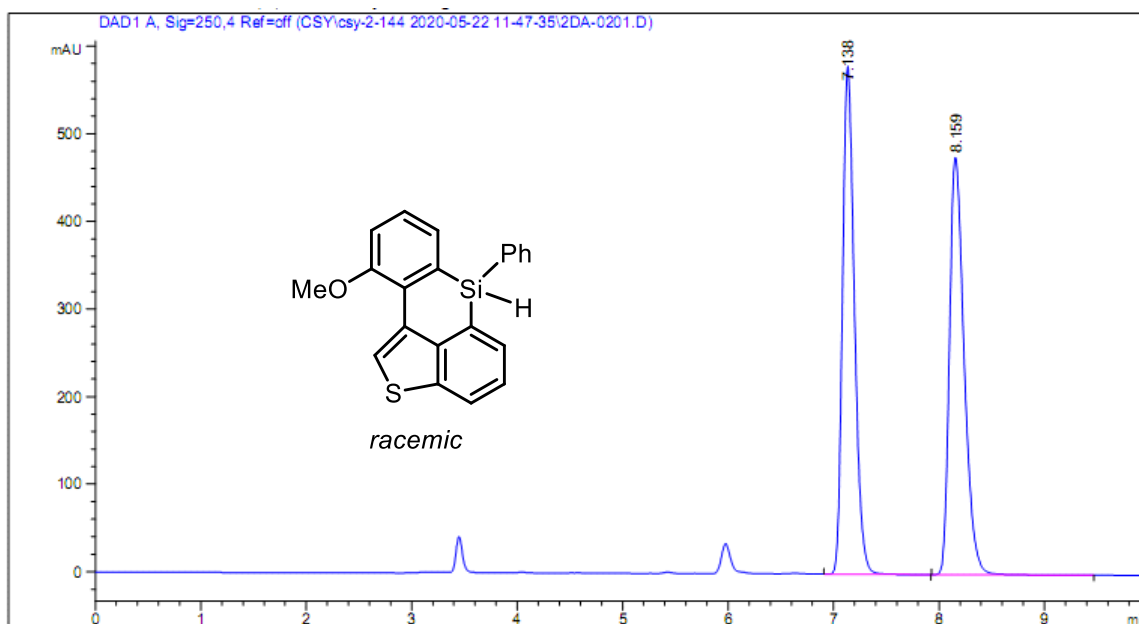
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.708	BV R	0.1326	3074.99512	356.76843	97.3233
2	7.255	VB E	0.1483	84.57084	8.48608	2.6767

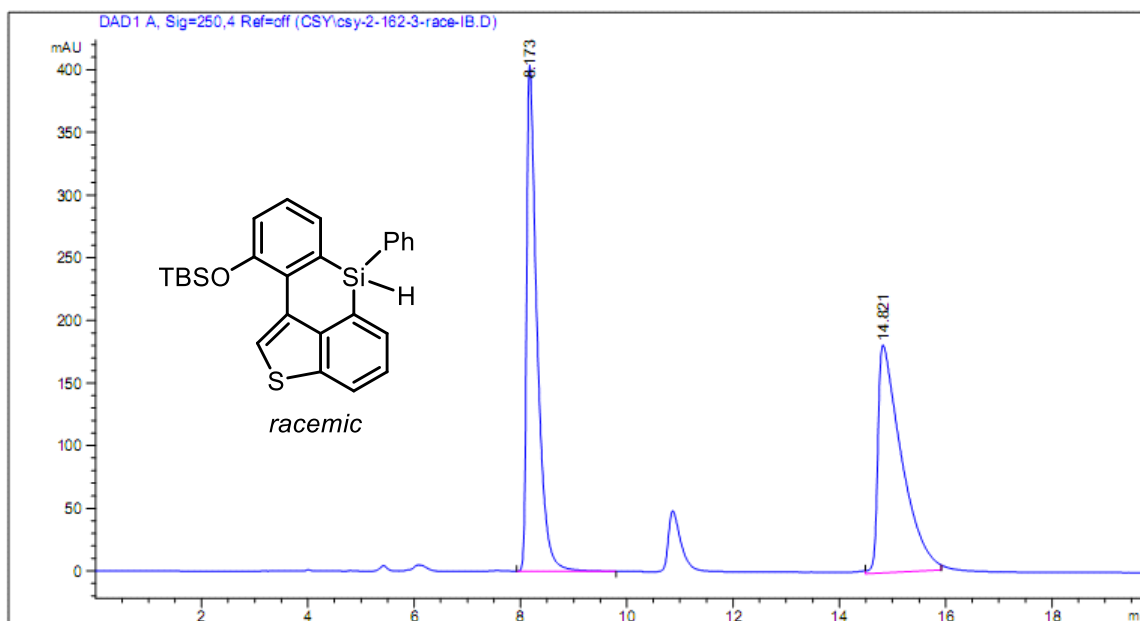


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.478	BB	0.2282	4472.62305	299.61514	50.1170
2	13.638	BB	0.3015	4451.73389	220.51158	49.8830

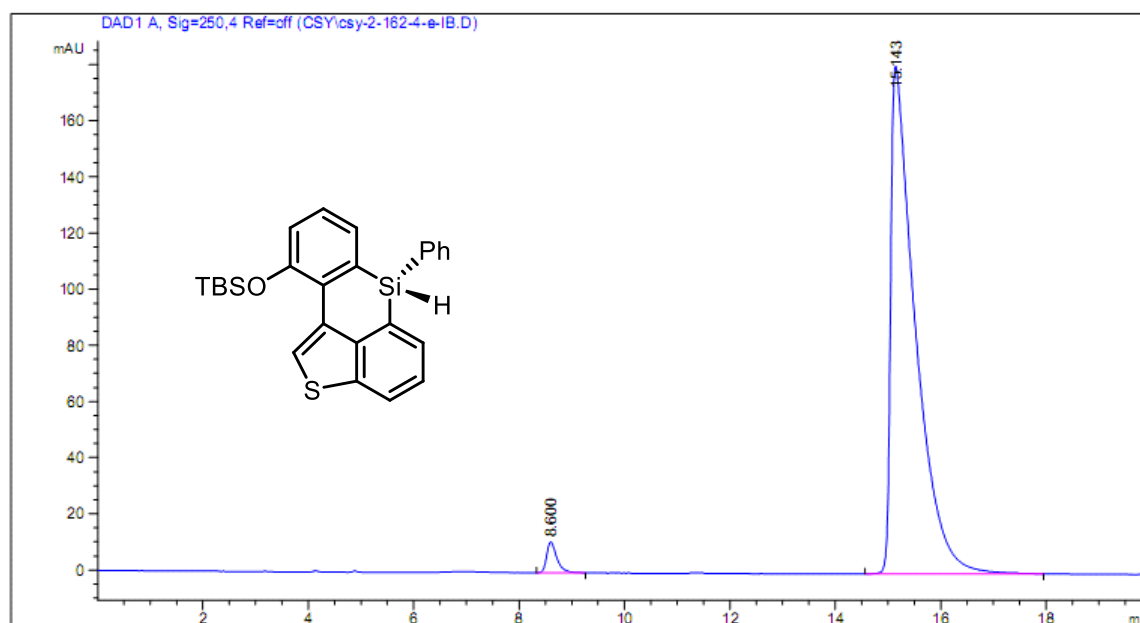


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.472	BB	0.2029	80.39582	6.13331	2.7024
2	13.456	BB	0.2836	2894.57349	153.77072	97.2976

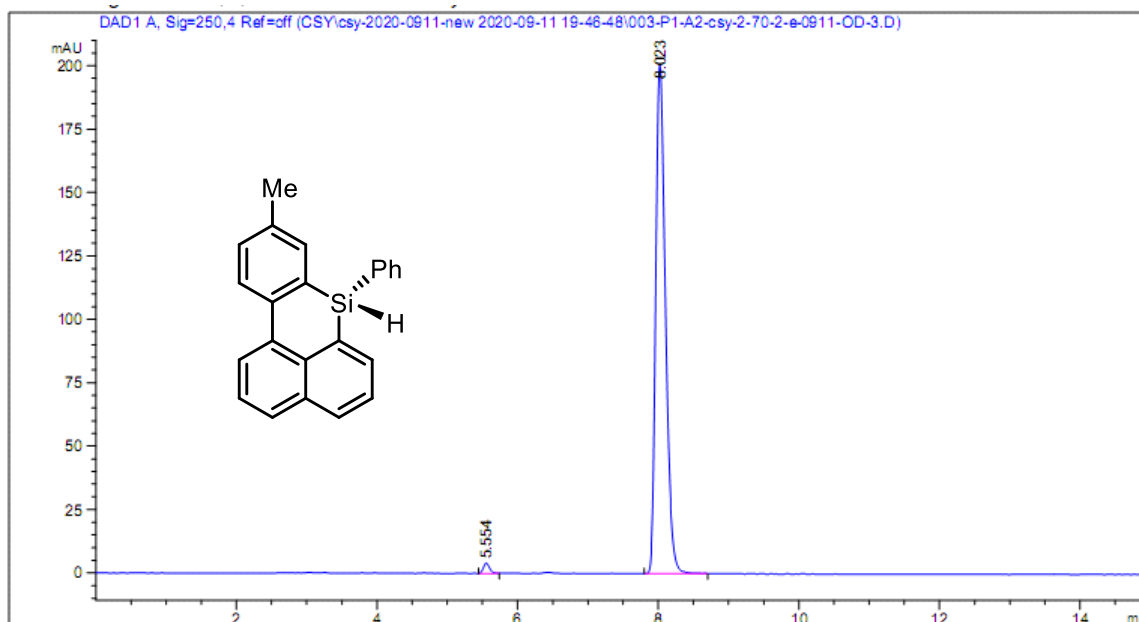
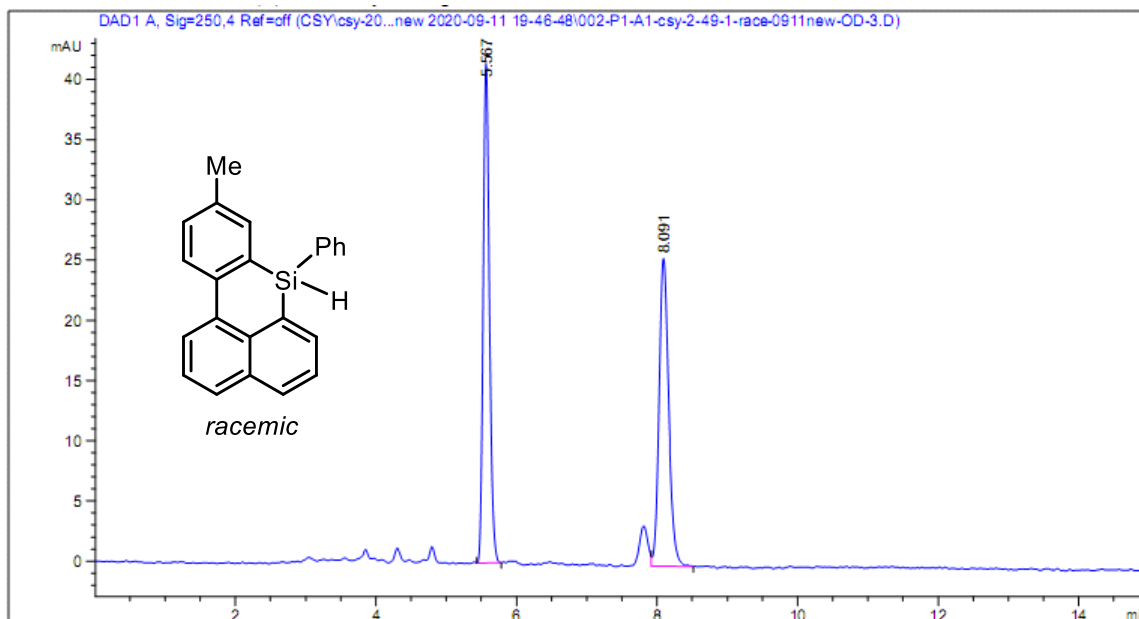


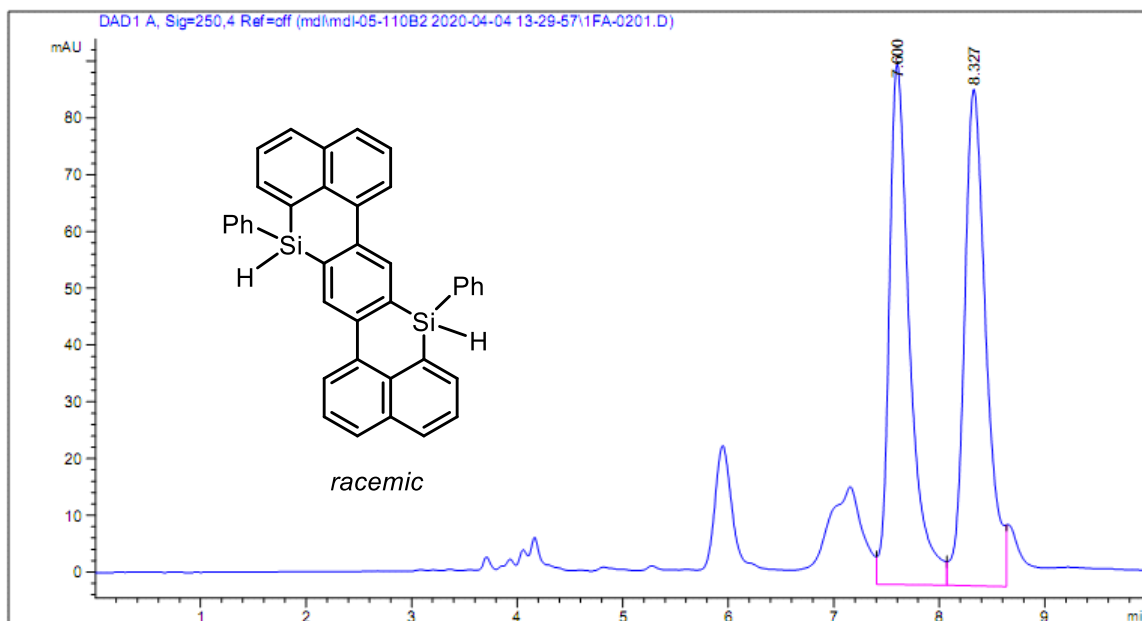


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.173	BB	0.1990	5510.95605	404.31238	49.6637
2	14.821	MM R	0.5120	5585.59717	181.81107	50.3363

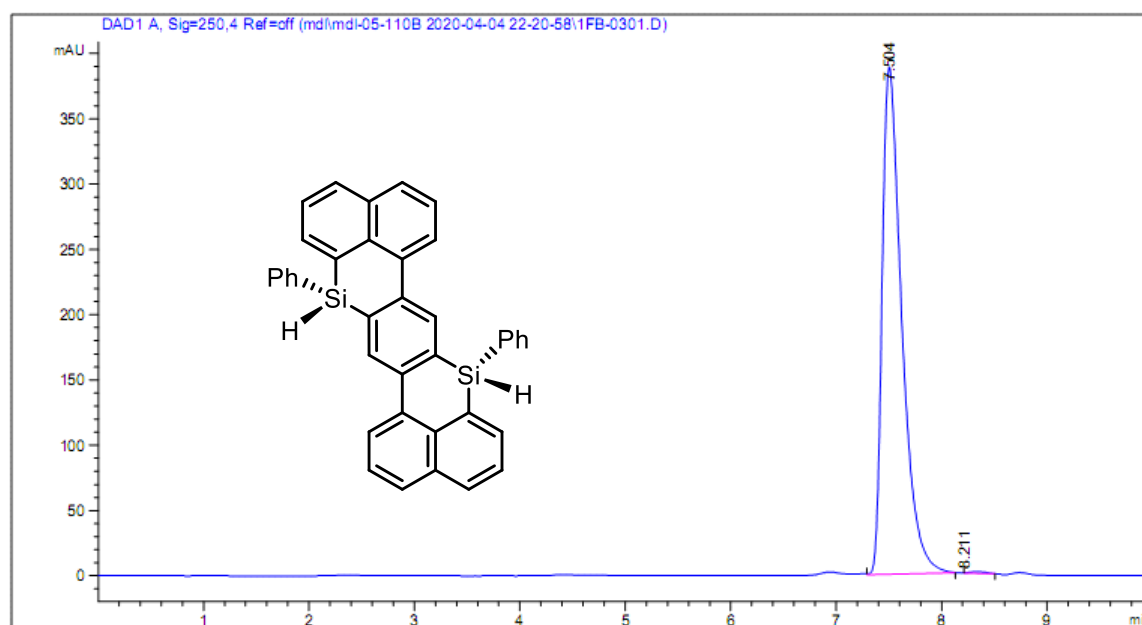


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.600	BB	0.2040	149.46031	11.03790	2.4953
2	15.143	BB	0.4549	5840.26318	180.78598	97.5047

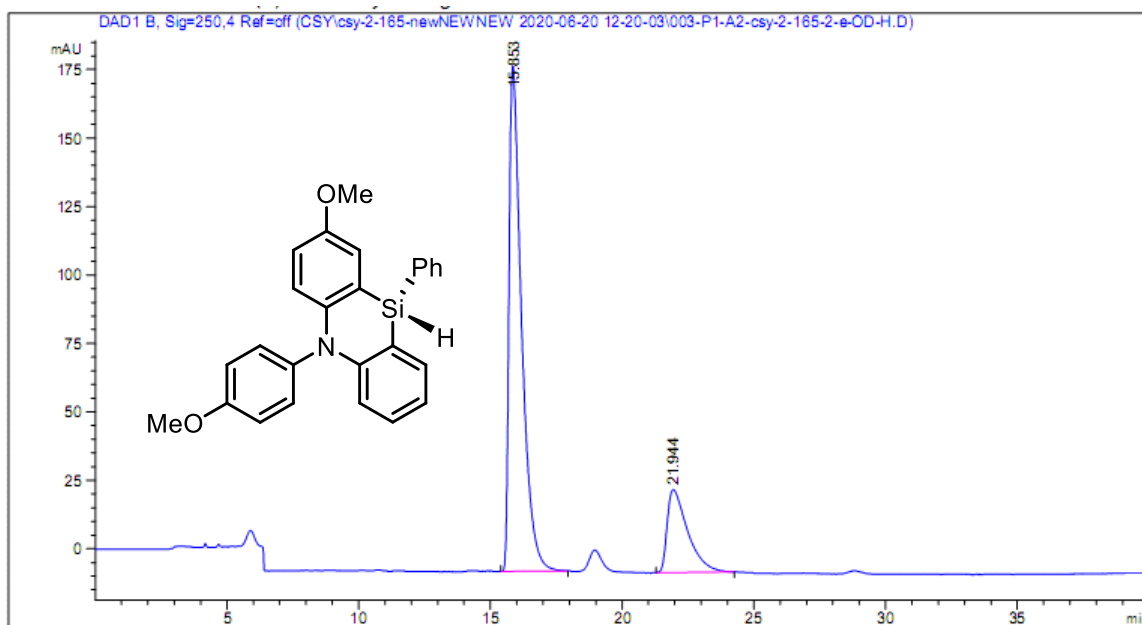
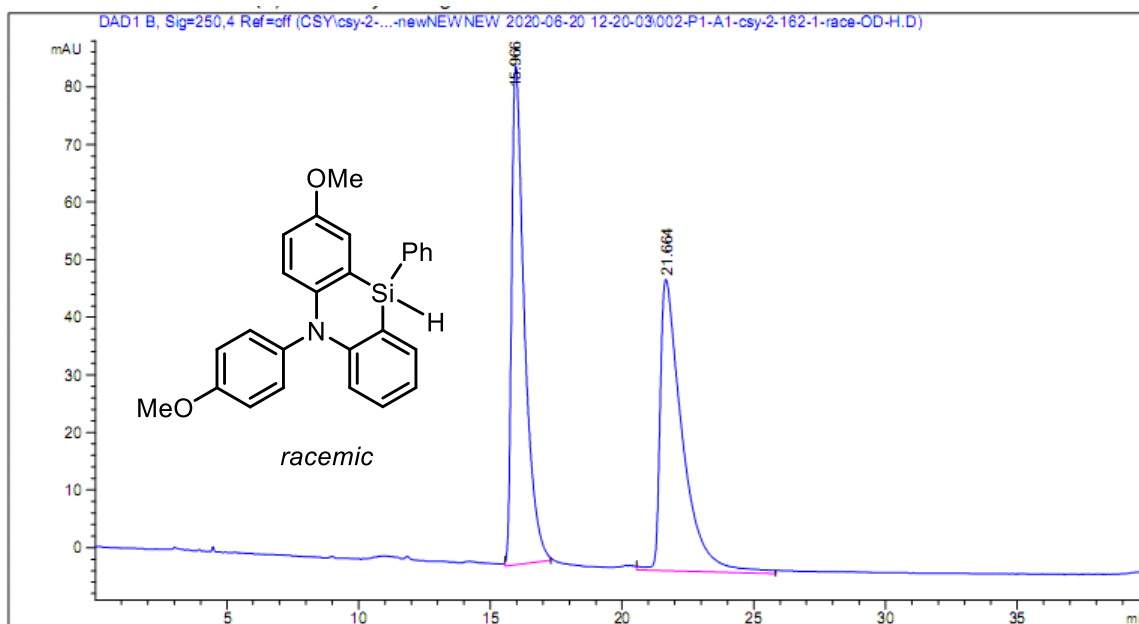


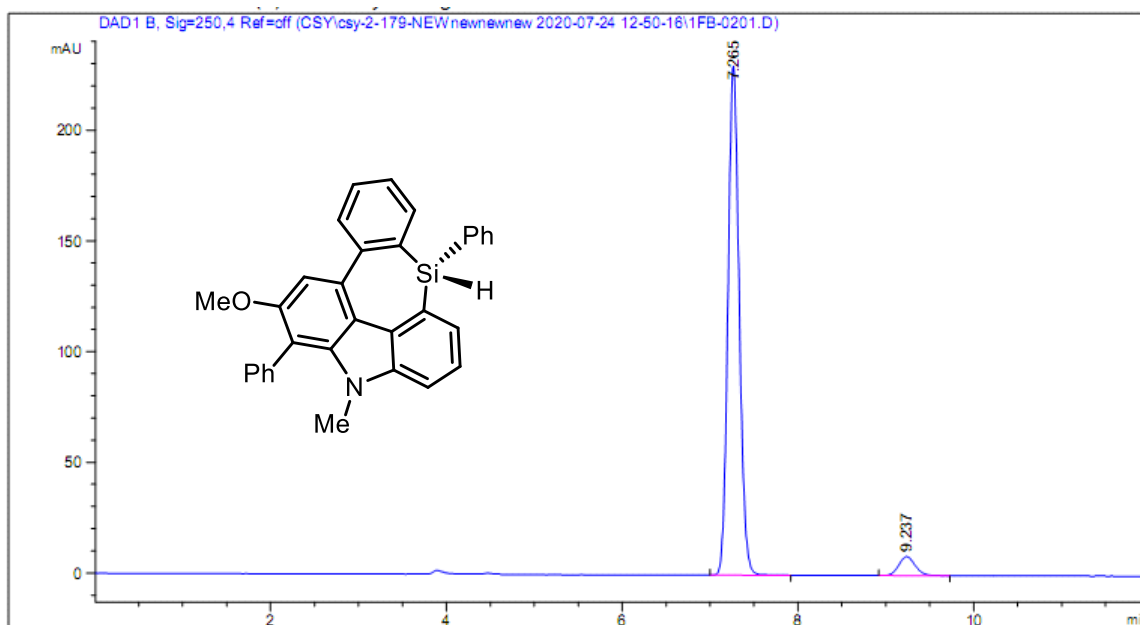
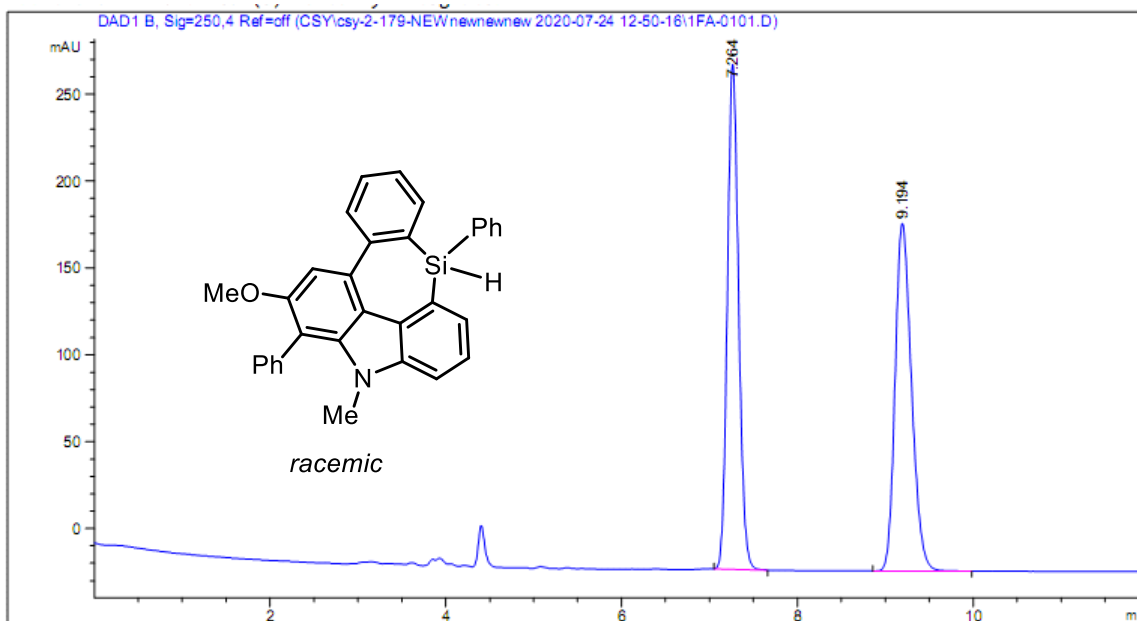


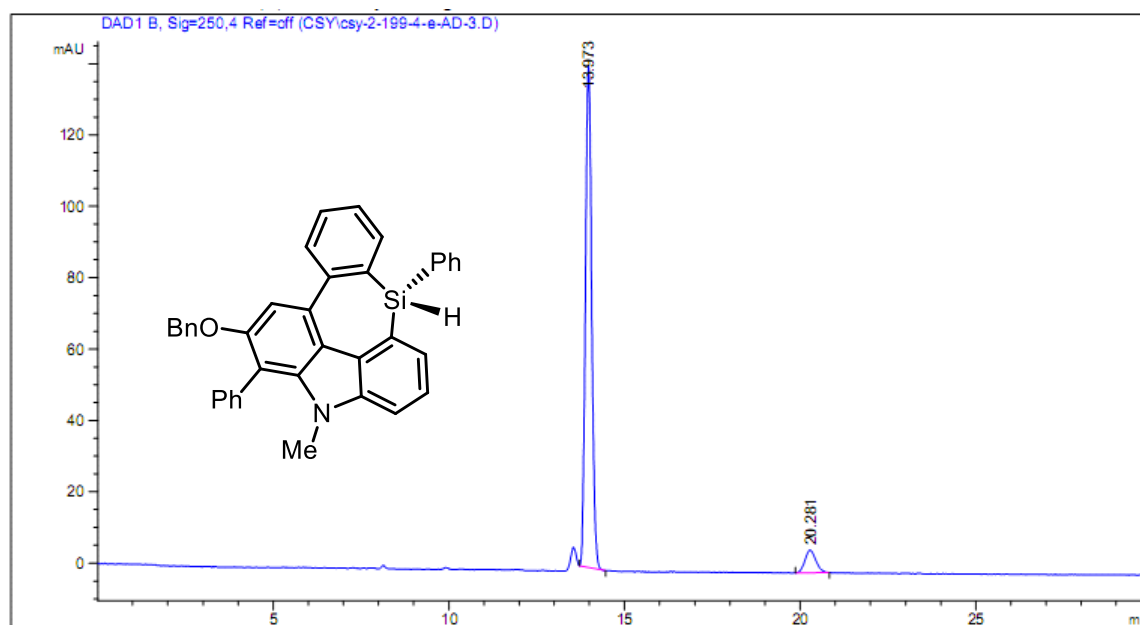
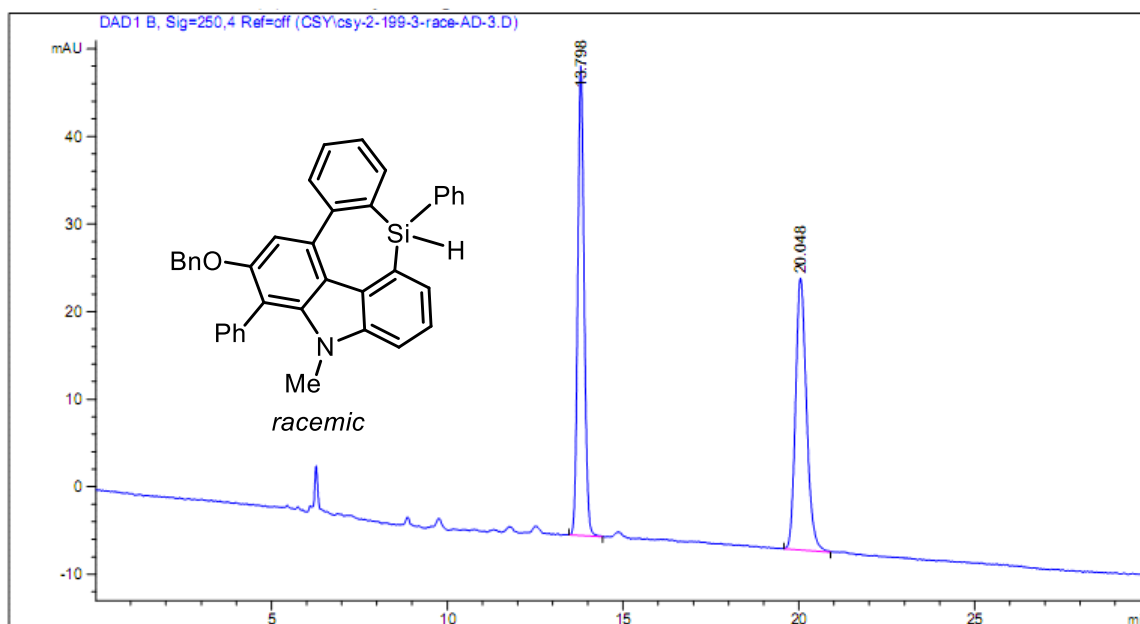
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.600	MF R	0.2258	1243.04468	91.74100	49.8210
2	8.327	FM R	0.2385	1251.97571	87.49155	50.1790

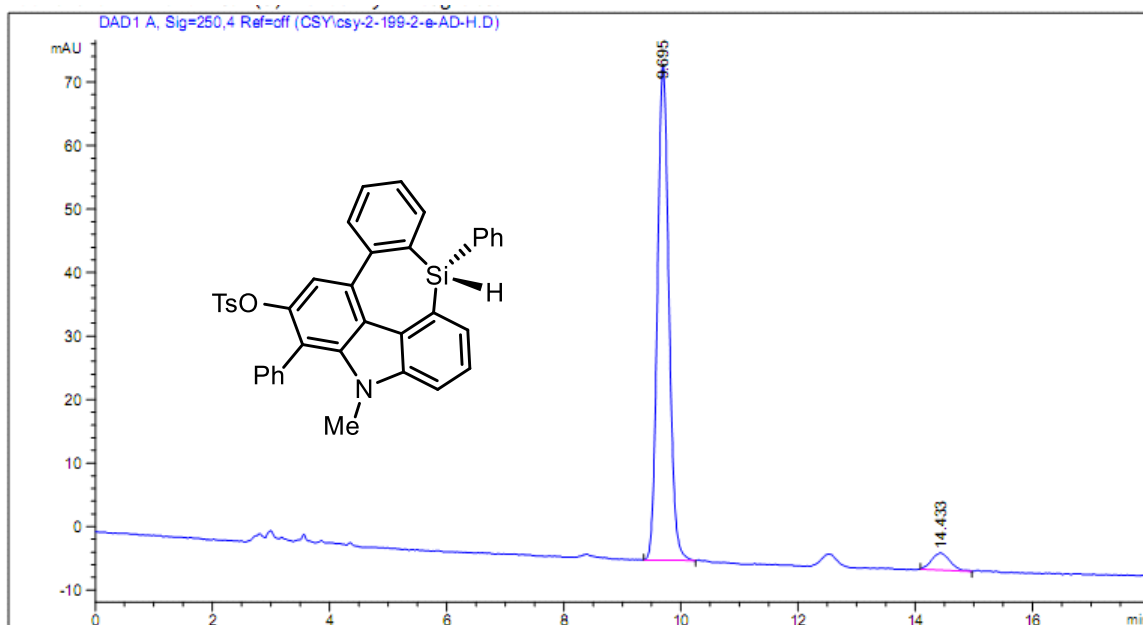
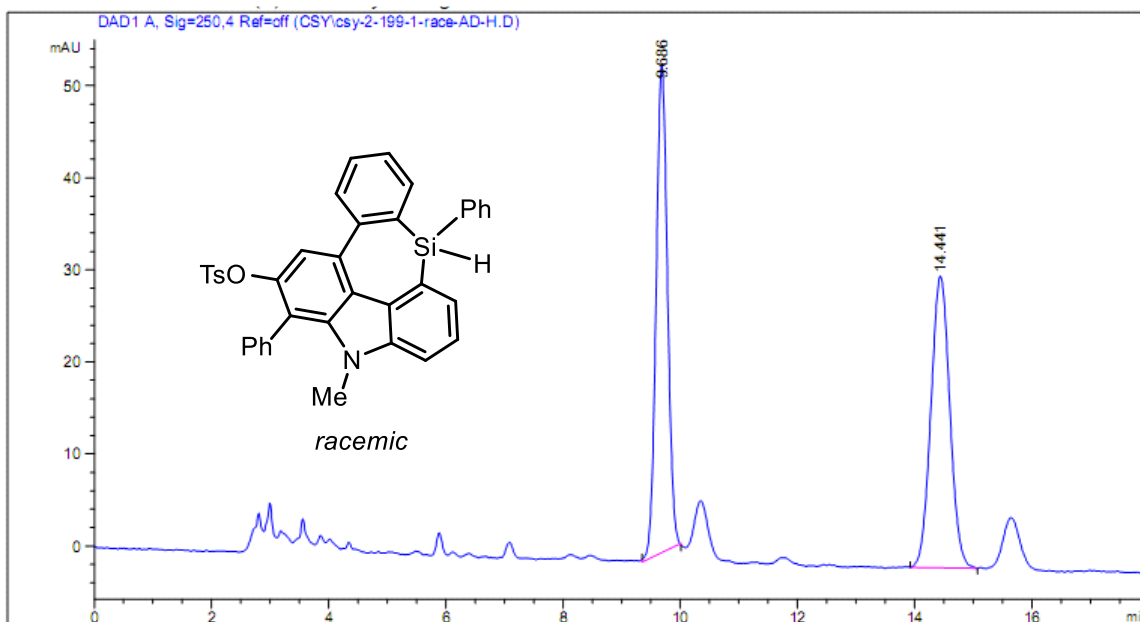


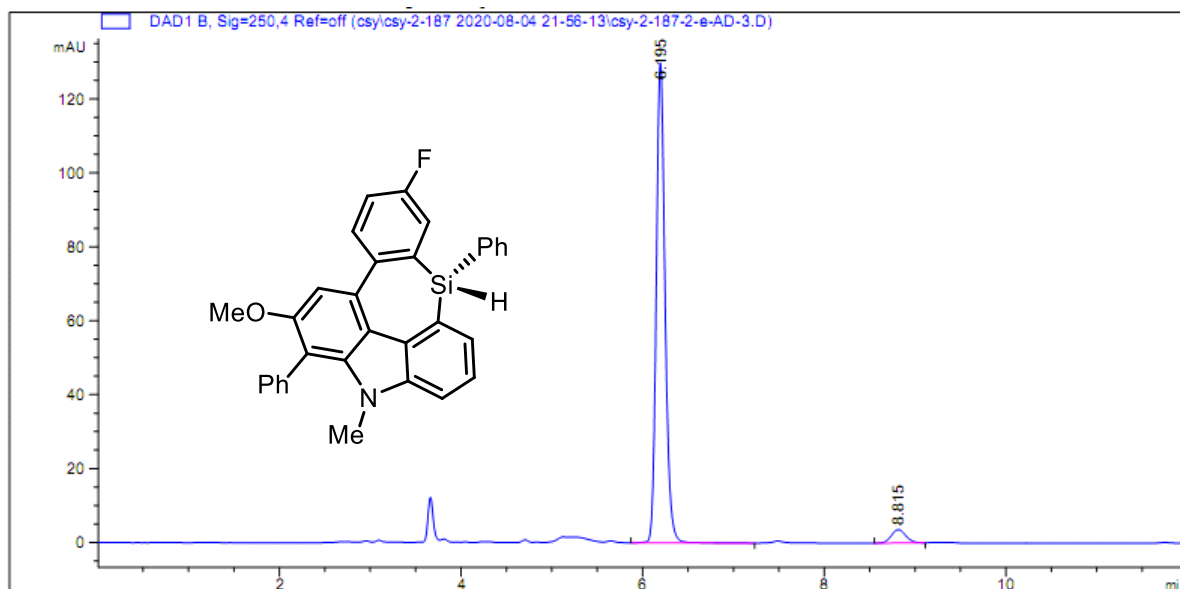
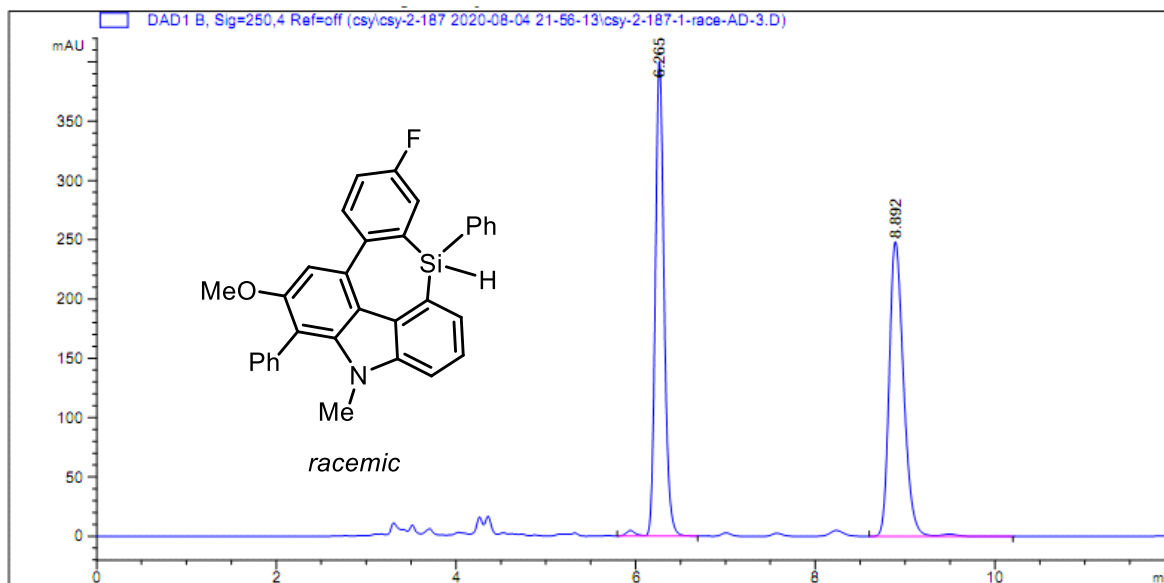
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.504	MM R	0.2155	5024.80908	388.55637	99.6710
2	8.211	MM R	0.1878	16.58517	3.91149e-1	0.3290

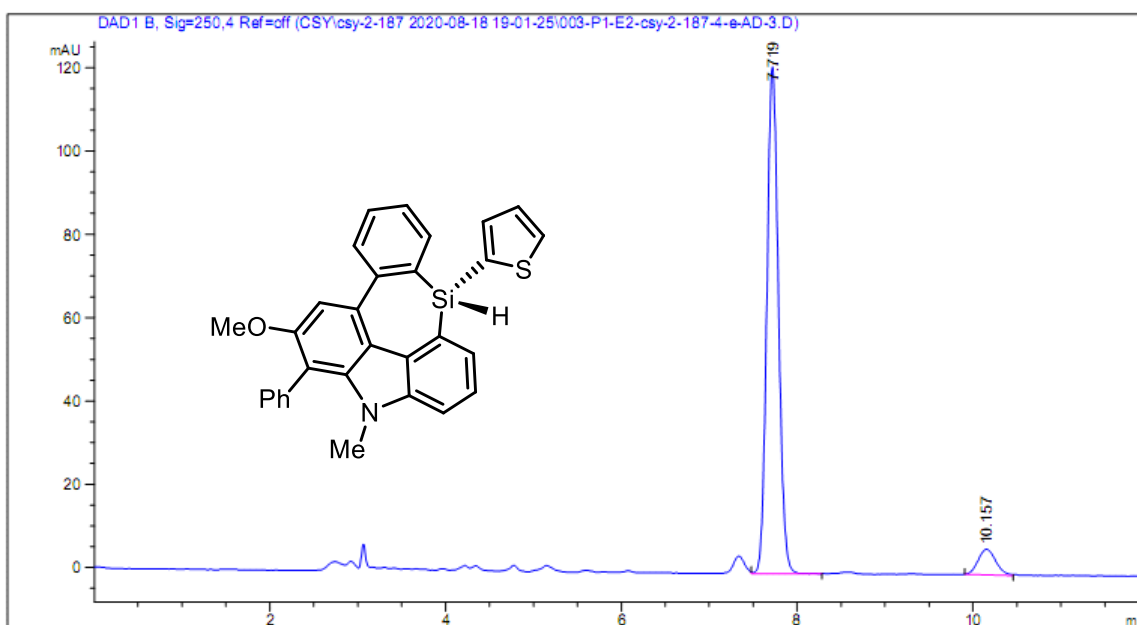
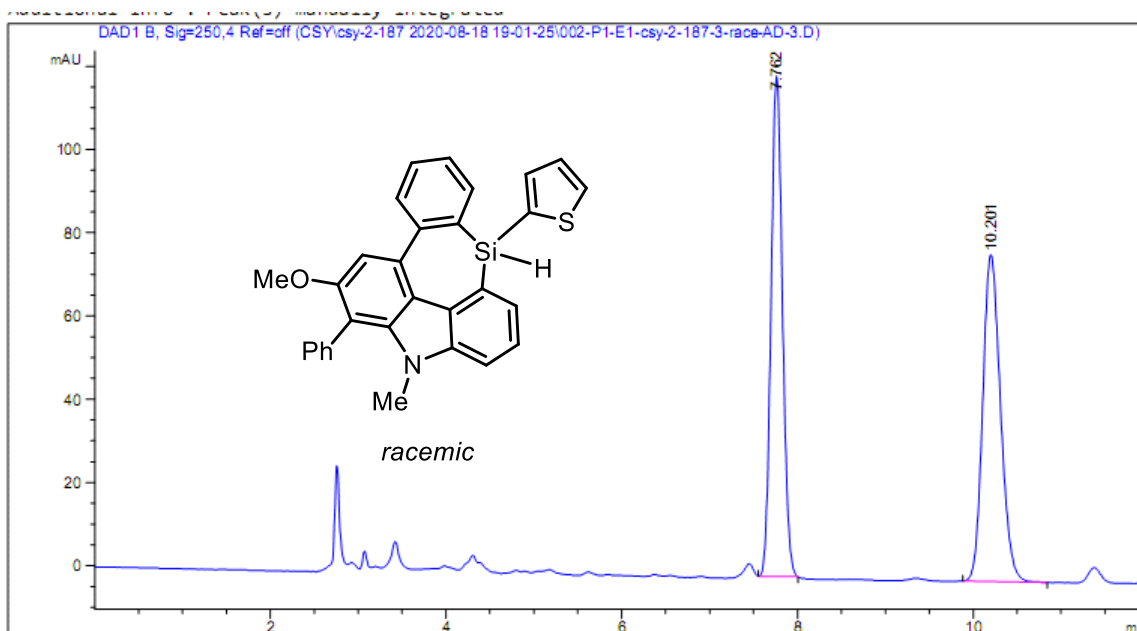


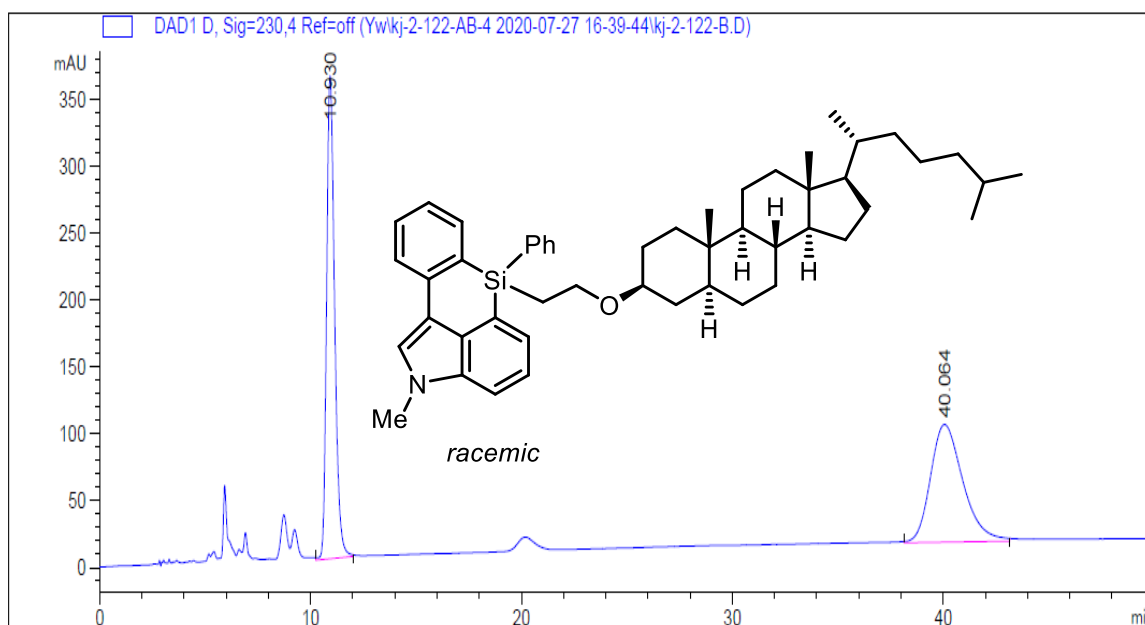




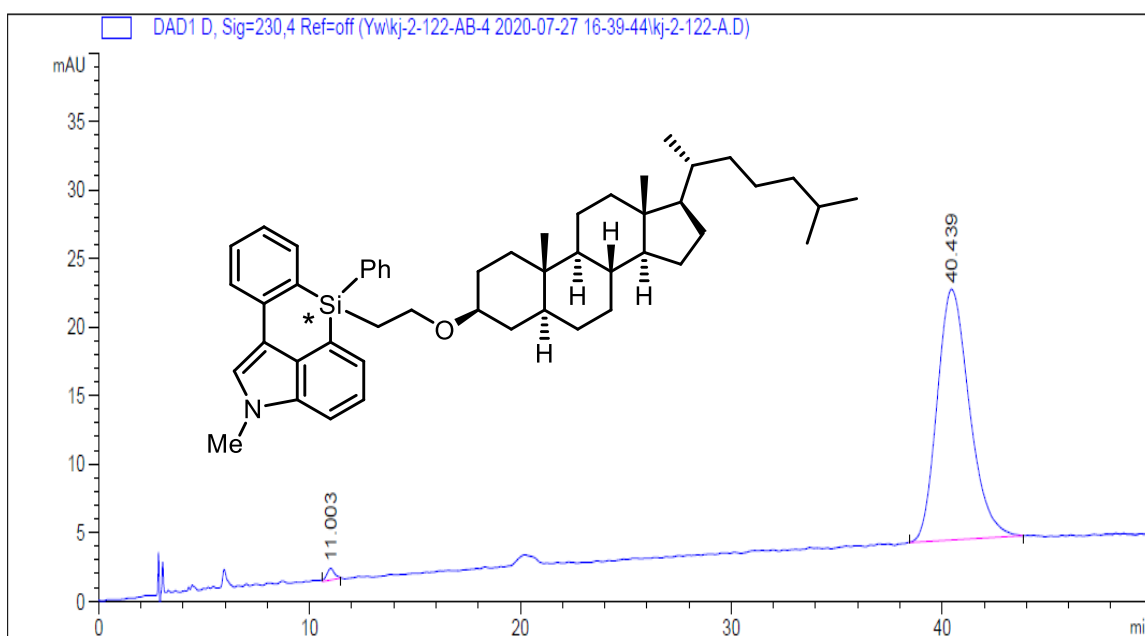




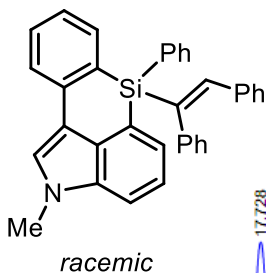




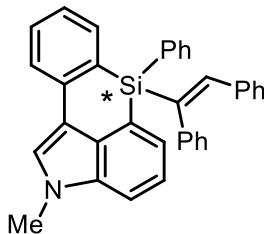
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.930	MM R	0.4386	9499.81543	361.00558	50.1861
2	40.064	MM R	1.7867	9429.35449	87.95641	49.8139



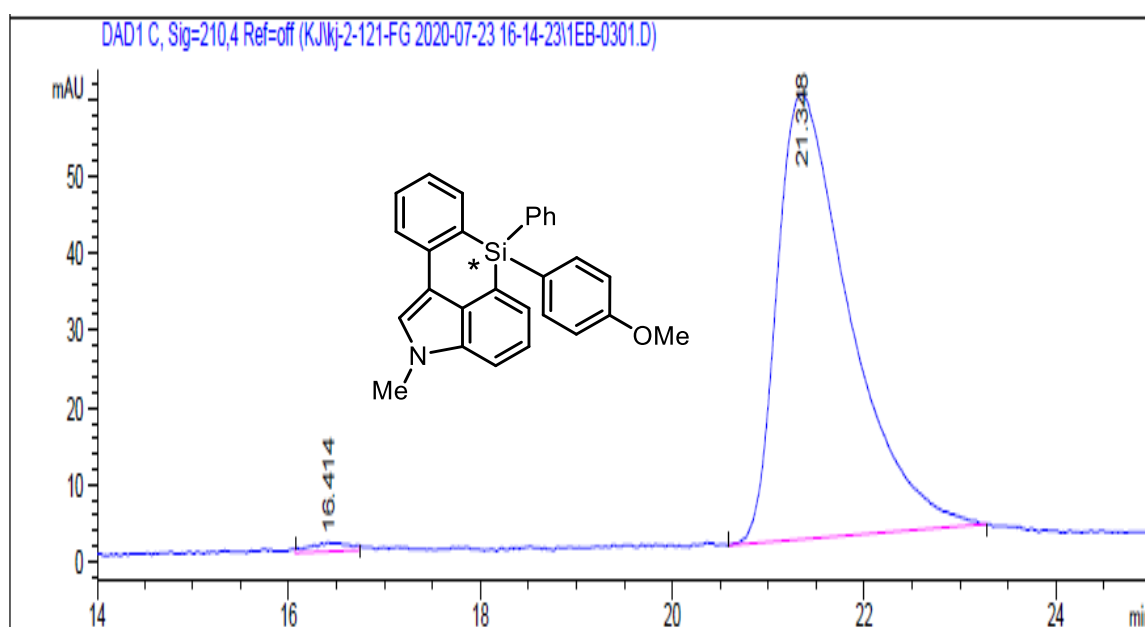
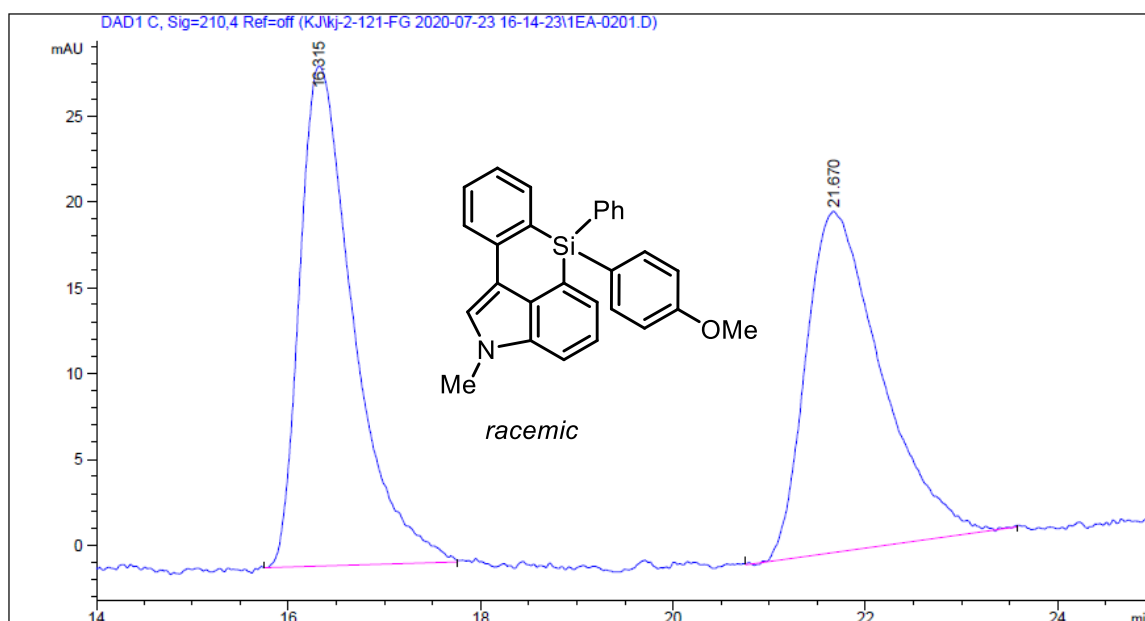
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.003	MM R	0.4205	21.30786	8.44549e-1	1.0829
2	40.439	BB	1.4579	1946.41211	18.28441	98.9171

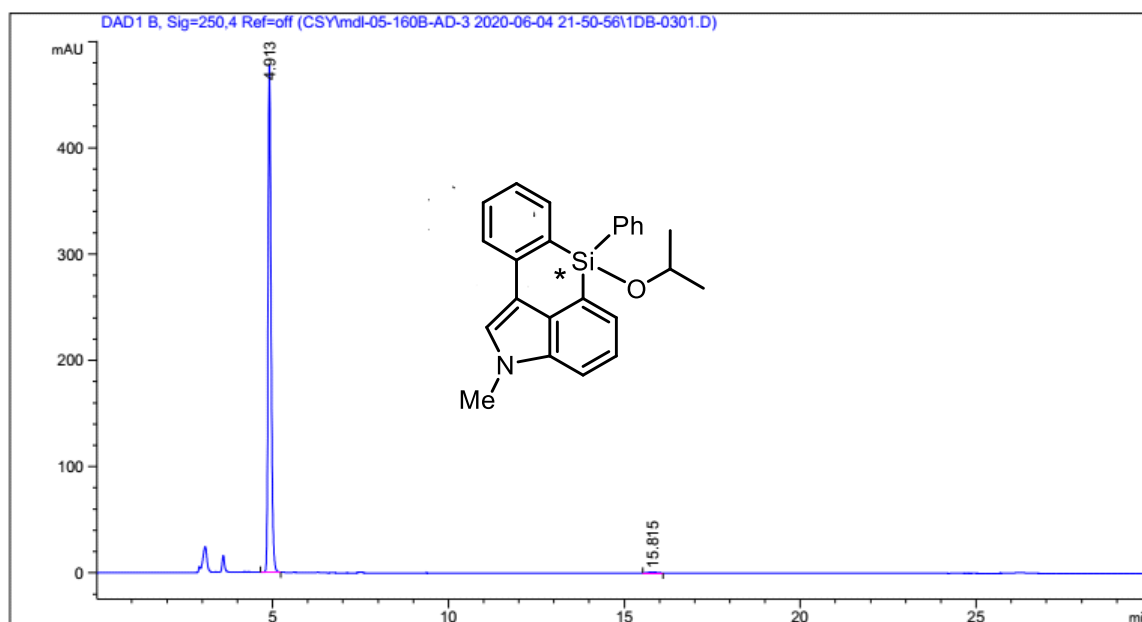
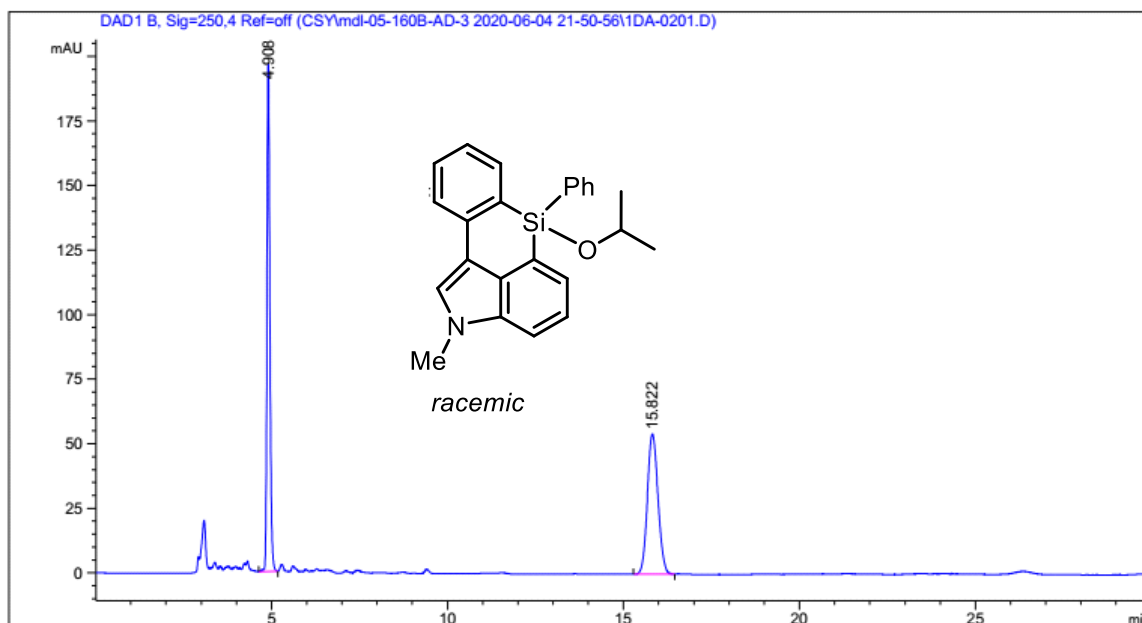


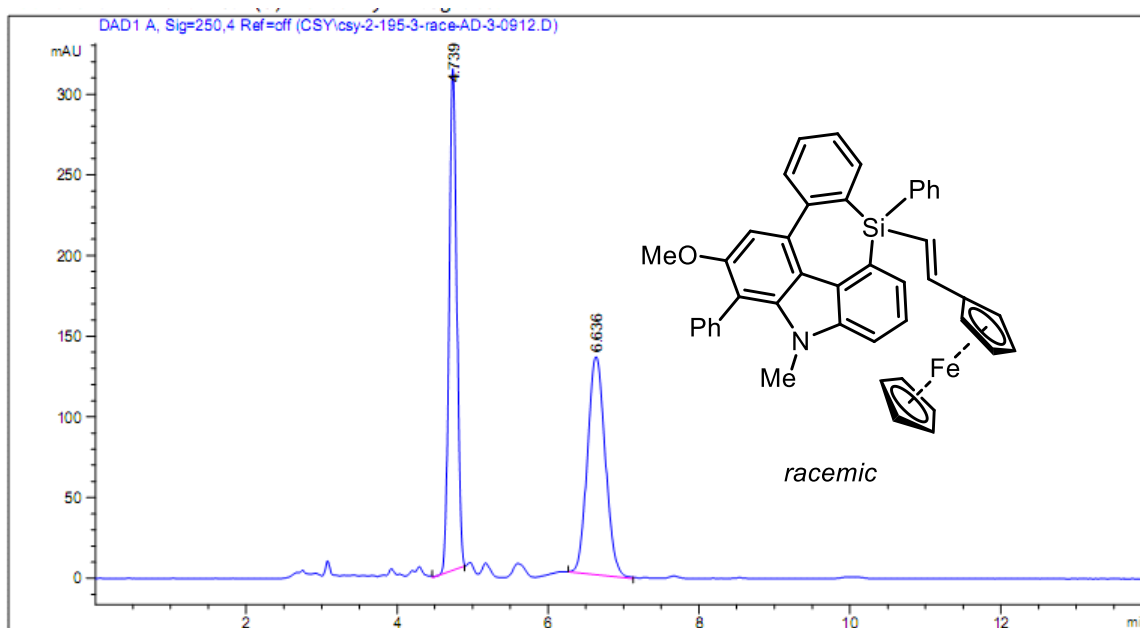
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.647	BB	0.1497	2750.28198	282.18976	50.5670
2	17.728	BB	0.3964	2688.60645	105.81007	49.4330



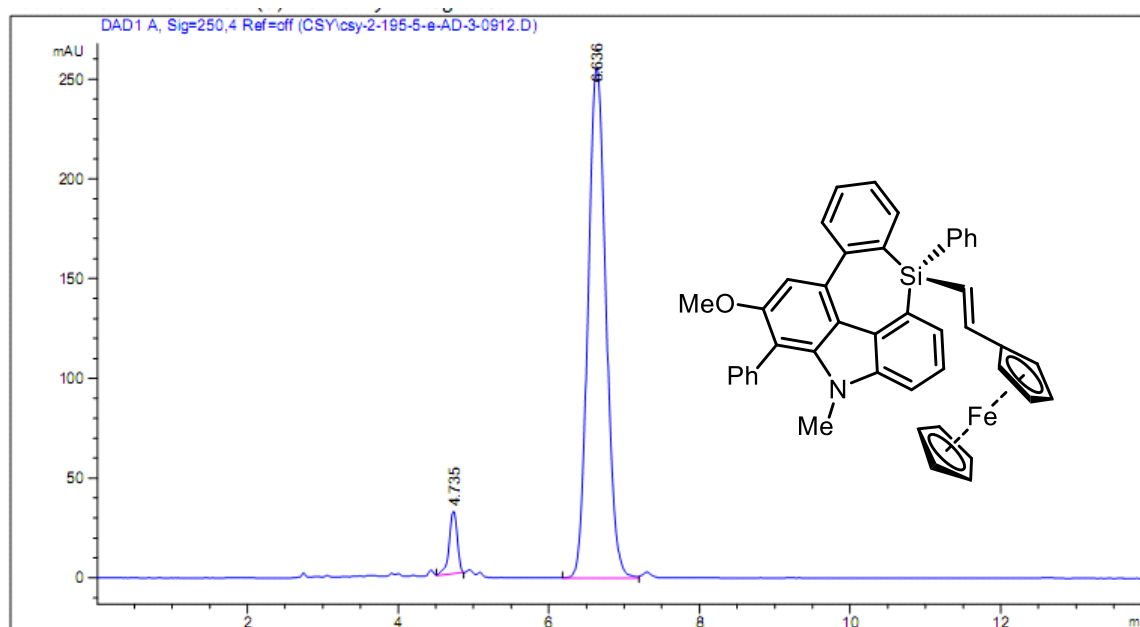
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.414	BB	0.1487	2537.22363	267.49890	98.8358
2	17.027	MM R	0.3863	29.88544	1.28938	1.1642







Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.739	MM R	0.1182	2208.51758	311.33322	49.9800
2	6.636	MM R	0.2730	2210.28101	134.95793	50.0200



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.735	MM R	0.1234	233.05380	31.46772	5.2382
2	6.636	MM R	0.2751	4216.07861	255.40259	94.7618