

## Supporting Information

### **B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-Catalyzed Cyclization of alkynes: Direct Synthesis of 3-Silyl Hetero Cyclic Compounds**

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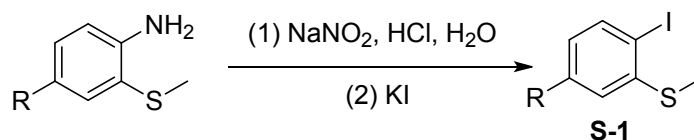
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## General remark

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on Bruker 400M and Mercury 300M in  $\text{CDCl}_3$ . All chemical shifts are given as  $\delta$  value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. All compounds were further characterized by HRMS; copies of  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were provided. Products were purified by flash chromatography on 200-300 mesh silica gels. All melting points were determined without correction. All reactions were carried out under argon atmosphere in oven-dried glassware, unless otherwise noted. All reagents were purchased commercially and used as received, unless otherwise noted.

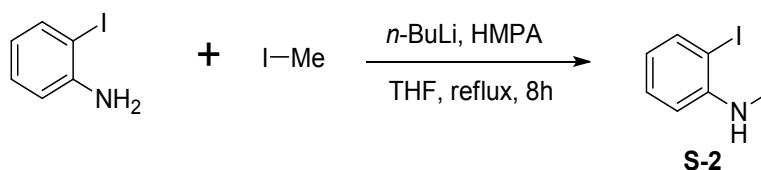
## Experimental section

### General Procedure for the Synthesis of S-1<sup>[1]</sup>



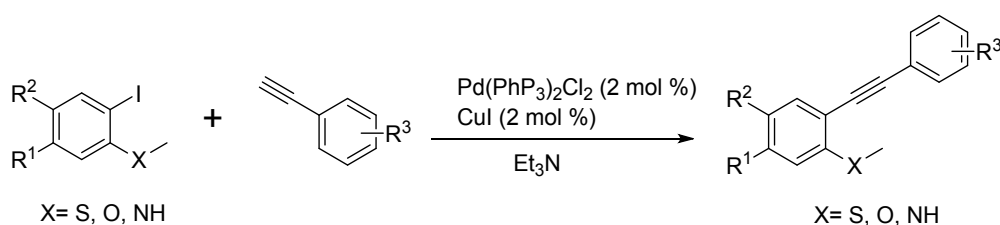
A mixture of 2-(methylthio)aniline (0.21 g, 1.5 mmol), aqueous  $\text{HCl}$  (37%, 0.3 mL) and water (1.3 mL) was cooled to  $0^\circ\text{C}$ . A solution of  $\text{NaNO}_2$  (0.11 g, 1.6 mmol) in water (0.3 mL) was added dropwise and stirred for 10 min. The resulting diazonium salt was treated with a solution of  $\text{KI}$  (0.29 g, 1.7 mmol) in water (0.3 mL). The resulting brown foamy mixture was stirred for 30 min at room temperature and heated at reflux for 15 min. After cooling to ambient temperature, the reaction was diluted with water (10 mL) and neutralized by slow addition of aqueous  $\text{Na}_2\text{S}_2\text{O}_3$ . The mixture was extracted with dichloromethane (10 mL  $\times$  2). The combined organic layer was dried over  $\text{Na}_2\text{SO}_4$ , filtered and evaporated in vacuo. The residue was purified by silica gel column chromatography to afford (2-iodophenyl)(methyl)sulfane as colorless oil (0.3 g, 81%).

### General Procedure for the Synthesis of S-2<sup>[3]</sup>



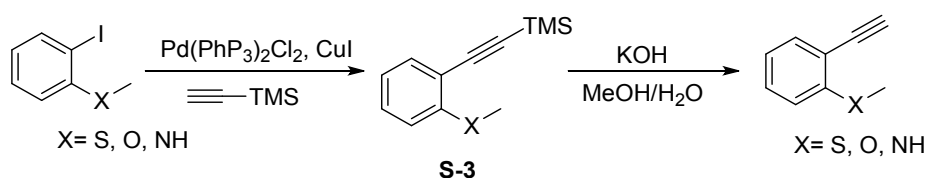
To a THF (30 mL) solution of 2-iodoaniline (1.09 g, 5 mmol) was added *n*-butyllithium (2.5 M, 9.4 mL, 23.5 mmol) at -40 °C. After stirring in this temperature for 30 min, HMPA (1 mL, 5.5 mmol) was added and the reaction was allowed to warm up to room temperature in 20 min. Then iodomethane (1.07 g, 7.5 mmol) was added to the solution and the resulting solution was heated to reflux for 8 h. The reaction was then quenched with a saturated aqueous NH<sub>4</sub>Cl solution. The aqueous solution was extracted with ether, and the organic phase was dried over MgSO<sub>4</sub>, and evaporated to dryness. The residues were eluted through a silica gel column to afford substrate **S-2** (0.87 g, 75%).

### General procedure for the synthesis of 1a-1m, 1s-1u, 3a-3g, 3i-3m



To a solution of (2-iodophenyl)(methyl)sulfane (5 mmol), CuI (2 mol %), and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (2 mol %) in triethylamine (100 mL) was added drop-wise an alkyne (6 mmol) under N<sub>2</sub>. The reaction mixture was stirred for 5-10 h at room temperature. Upon completion, the mixture was diluted with diethyl ether and then washed with water and brine successively. The organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under vacuum. The residue was purified through silica gel flash chromatography to give the desired product in mostly > 90% yield.

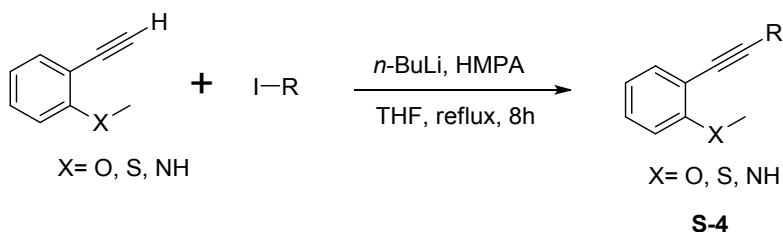
### General Procedure for the Synthesis of 1n-1r, 3h, 3o<sup>[2] [3]</sup>



**S-3** was synthesized using a literature procedure<sup>[2]</sup>.

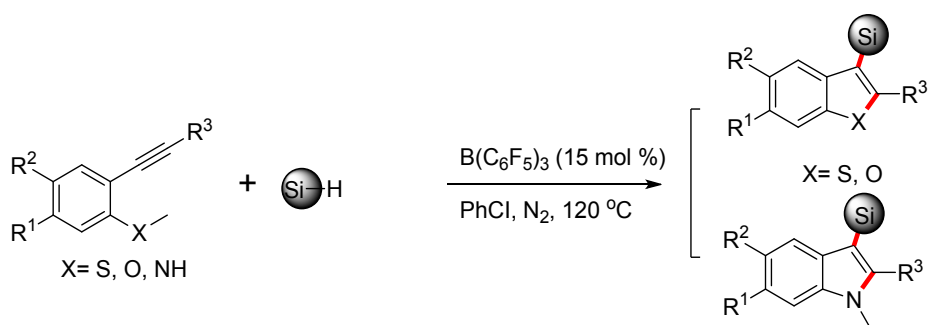
A solution of KOH (0.45 g, 8.0 mmol, 2 equiv) in 2 mL of water was added dropwise to *o*-(trimethylsilylethynyl)thioanisole (0.88 g, 4.0 mmol) in 20 mL of CH<sub>3</sub>OH under an argon atmosphere at 25 °C. The mixture was stirred for another 0.5

h at 25 °C, and the CH<sub>3</sub>OH was removed under vacuum. The residue was added to 20 mL of brine, and the mixture was extracted with EtOAc (3 × 20 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), filtered, and the solvent removed under vacuum. Purification by flash chromatography afforded the **1p** (yield = 96%) as a yellow oil.



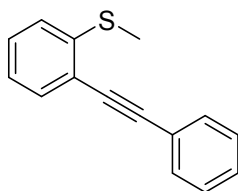
**S-4** was synthesized using a literature procedure<sup>[3]</sup>.

### General procedure for the synthesis of silylated heteroaromatic compounds



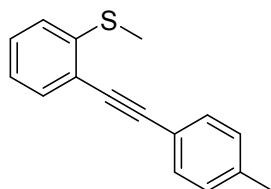
To a flame dried transparent Schlenk tube equipped with a stirring bar was added methyl(2-(phenylethynyl)phenyl)sulfane (0.2 mmol), chlorobenzene (2 mL), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (15 mol %), Diphenylsilane (0.4 mmol, 2 equiv). The reaction mixture was stirred under N<sub>2</sub> at 120 °C for 24 h. Upon completion, the reaction mixture was concentrated under vacuum. The residue was purified by silicagel column chromatography using a petroleum ether to afford the corresponding products.

**The data of substrates:**



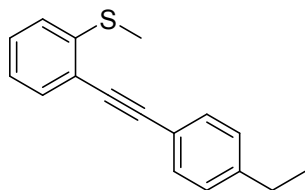
**methyl(2-(phenylethynyl)phenyl)sulfane (1a)**

Yellow solid (1.06 g, 95% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.59\text{--}7.56$  (m, 2 H), 7.49–7.47 (m, 1 H), 7.37–7.27 (m, 4 H), 7.17–7.15 (d,  $J = 7.6$  Hz, 1 H), 7.12–7.08 (m, 1 H), 2.50 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 141.7, 132.2, 131.5, 128.7, 128.3, 128.2, 124.2, 124.1, 123.1, 121.3, 95.8, 86.9, 15.0$ .



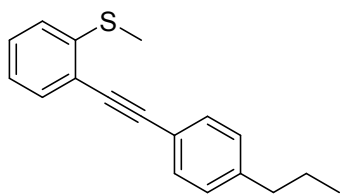
**methyl(2-(*p*-tolylethynyl)phenyl)sulfane (1b)**

Yellow solid (0.96 g, 81% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.50\text{--}7.48$  (d,  $J = 7.2$  Hz, 3 H), 7.31–7.25 (m, 1 H), 7.18–7.16 (d,  $J = 8.0$  Hz, 3 H), 7.13–7.09 (m, 1 H), 2.51 (s, 3 H), 2.37 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 141.5, 138.5, 132.1, 131.5, 129.1, 128.6, 124.2, 124.0, 121.5, 120.1, 96.1, 86.2, 21.5, 15.1$ .



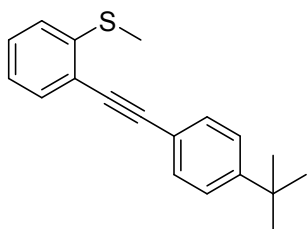
**(2-((4-ethylphenyl)ethynyl)phenyl)(methyl)sulfane (1c)**

Yellow oil (1.059 g, 83% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.50\text{--}7.45$  (m, 3 H), 7.28–7.24 (m, 1 H), 7.17–7.13 (m, 3 H), 7.10–7.06 (m, 1 H), 2.67–2.61 (m, 2 H), 2.47 (s, 3 H), 1.24–1.20 (m, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 144.8, 141.5, 132.0, 131.5, 128.5, 127.8, 124.1, 123.9, 121.4, 120.3, 96.1, 86.2, 28.8, 15.3, 15.0$



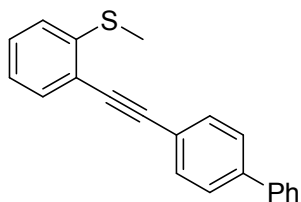
**methyl(2-((4-propylphenyl)ethynyl)phenyl)sulfane (1d)**

Yellow solid (1.13 g, 85% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.50\text{-}7.45$  (m, 3 H), 7.29-7.25 (m, 1 H), 7.16-7.14 (d,  $J = 8.0$  Hz, 3 H), 7.10-7.06 (m, 1 H), 2.60-2.56 (m, 2 H), 2.48 (s, 3 H), 1.68-1.58 (m, 2 H), 0.95-0.91 (m, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 143.3, 141.5, 132.1, 131.4, 128.5, 128.4, 124.2, 124.0, 121.5, 120.3, 96.1, 86.2, 37.9, 24.3, 15.0, 13.7$ .



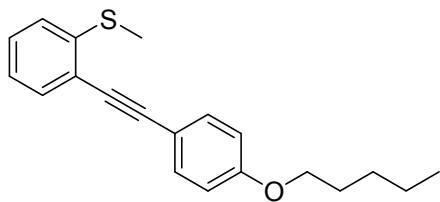
**(2-((4-(tert-butyl)phenyl)ethynyl)phenyl)(methyl)sulfane (1e)**

Yellow solid (1.01 g, 76% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.54\text{-}7.46$  (m, 3 H), 7.39-7.33 (m, 2 H), 7.31-7.25 (m, 1 H), 7.17-7.06 (m, 2 H), 2.50-2.49 (d,  $J = 2.8$  Hz, 3 H), 1.32 (s, 9 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 151.6, 141.6, 132.1, 131.3, 128.5, 125.3, 124.1, 124.0, 121.5, 120.1, 96.0, 86.2, 34.8, 31.1, 15.0$ .



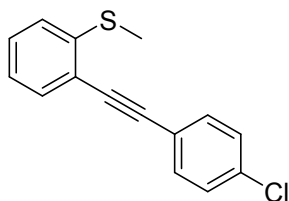
**(2-([1,1'-biphenyl]-4-ylethynyl)phenyl)(methyl)sulfane (1f)**

Yellow solid (1.35 g, 90% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.65\text{-}7.63$  (m, 2 H), 7.61-7.57 (m, 4 H), 7.50-7.48 (m, 1 H), 7.45-7.42 (m, 2 H), 7.37-7.32 (m, 1 H), 7.31-7.27 (m, 1 H), 7.18-7.16 (d,  $J = 8.0$  Hz, 1 H), 7.13-7.09 (m, 1 H), 2.50 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 141.7, 141.1, 140.3, 132.2, 132.0, 128.8, 128.7, 127.6, 127.0, 124.2, 124.1, 122.0, 121.3, 95.8, 87.6, 15.0$ .



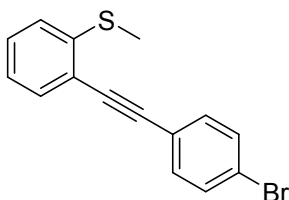
**methyl(2-((4-(pentyloxy)phenyl)ethynyl)phenyl)sulfane (1g)**

Yellow solid (1.24 g, 80% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.51-7.42 (m, 3 H), 7.29-7.24 (m, 1 H), 7.16-7.07 (m, 2 H), 6.87-6.81 (m, 2 H), 3.96-3.93 (m, 2 H), 2.49 (s, 3 H), 1.80-1.76 (m, 2 H), 1.45-1.37 (m, 4 H), 0.95-0.91 (m, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 159.3, 141.3, 133.9, 133.0, 131.9, 128.3, 124.1, 123.9, 121.6, 114.4, 96.0, 85.5, 68.0, 28.8, 28.1, 22.4, 15.0, 14.0.



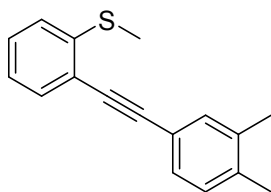
**(2-((4-chlorophenyl)ethynyl)phenyl)(methyl)sulfane (1h)**

Yellow solid (1.09 g, 85% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.50-7.45 (m, 3 H), 7.32-7.27 (m, 3 H), 7.17-7.15 (d, *J* = 8.0 Hz, 1 H), 7.12-7.08 (m, 1 H), 2.49 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 141.7, 134.3, 132.7, 132.2, 128.9, 128.6, 124.2, 123.9, 121.6, 120.8, 94.6, 87.8, 15.0.



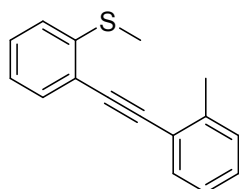
**(2-((4-bromophenyl)ethynyl)phenyl)(methyl)sulfane (1i)**

yellow oil (1.18 g, 86% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.49-7.45 (m, 3 H), 7.43-7.41 (m, 2 H), 7.33-7.29 (m, 1 H), 7.18-7.16 (d, *J* = 7.6 Hz, 1 H), 7.12-7.09 (m, 1 H), 2.50 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 141.8, 133.0, 132.2, 131.6, 129.0, 124.2, 124.0, 122.6, 122.1, 120.9, 94.7, 88.0, 15.0.



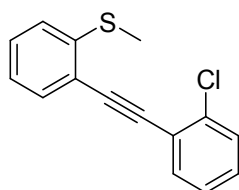
**(2-((3,4-dimethylphenyl)ethynyl)phenyl)(methyl)sulfane (1j)**

Yellow solid (1.1 g, 80% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.47-7.44 (m, 1 H), 7.35 (s, 1 H), 7.33-7.28 (m, 1 H), 7.26-7.23 (m, 1 H), 7.15-7.13 (d, *J* = 9.6 Hz, 1 H), 7.11-7.05 (m, 2 H), 2.48 (s, 3 H), 7.25-7.24 (d, *J* = 4.0 Hz, 6 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 141.5, 137.3, 136.6, 132.5, 132.0, 129.6, 129.0, 128.4, 124.1, 124.0, 121.5, 120.3, 96.2, 86.0, 19.7, 19.5, 15.0.



**methyl(2-(*o*-tolylethynyl)phenyl)sulfane (1k)**

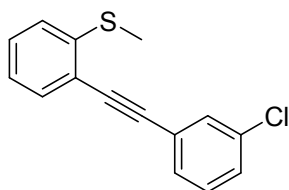
Yellow oil (0.86 g, 72% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.48-7.46 (m, 1 H), 7.40-7.37 (m, 2 H), 7.30-7.21 (m, 2 H), 7.17-7.08 (m, 3 H), 2.50 (s, 3 H), 2.35 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 141.6, 138.0, 132.1, 132.0, 129.3, 128.6, 128.2, 124.2, 124.0, 122.9, 121.3, 96.0, 86.5, 21.2, 15.0.



**(2-((2-chlorophenyl)ethynyl)phenyl)(methyl)sulfane (1l)**

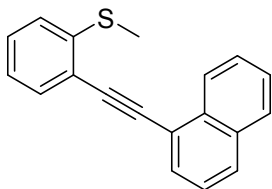
Yellow solid (1.09 g, 84% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.62-7.60 (m, 1 H), 7.55-7.53 (m, 1 H), 7.44-7.42 (m, 1 H), 7.34-7.30 (m, 1 H), 7.27-7.24 (m, 2 H), 7.20-7.18 (d, *J* = 8.0 Hz, 1 H), 7.14-7.10 (m, 1 H), 2.52 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 141.9, 135.8, 133.4, 132.6, 129.3, 129.2, 129.1, 126.4, 124.3, 124.2, 123.2, 121.0, 92.4, 91.9, 15.2.





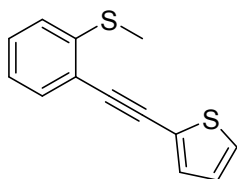
**2-((3-chlorophenyl)ethynyl)phenyl(methyl)sulfane (1m)**

Yellow solid (1.03 g, 80% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.56-7.55 (m, 1 H), 7.47-7.42 (m, 2 H), 7.31-7.27 (m, 2 H), 7.25-7.23 (d, *J* = 8.8 Hz, 1 H), 7.17-7.15 (d, *J* = 8.0 Hz, 1 H), 7.12-7.08 (m, 1 H), 2.49 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 141.9, 134.1, 132.2, 131.3, 129.6, 129.5, 129.1, 128.6, 124.8, 124.2, 124.0, 120.7, 94.2, 88.0, 15.0.



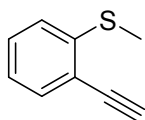
**methyl(2-(naphthalen-1-ylethynyl)phenyl)sulfane (1n)**

Yellow solid (1.10 g, 91% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.65-6.62 (d, *J* = 11.2 Hz, 1 H), 7.86-7.81 (m, 3 H), 7.61-6.59 (d, *J* = 8.8 Hz, 2 H), 7.54-7.42 (m, 2 H), 7.34-7.28 (m, 1 H), 7.21-7.12 (m, 2 H), 2.53 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 141.6, 133.2, 132.4, 130.5, 128.9, 128.8, 128.2, 126.8, 126.5, 126.4, 125.2, 124.3, 124.2, 121.5, 120.9, 94.0, 91.7, 15.2.



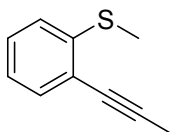
**2-((2-(methylthio)phenyl)ethynyl)thiophene (1o)**

Yellow solid (1.035 g, 90% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.47-7.45 (d, *J* = 7.6 Hz, 1 H), 7.32-7.27 (m, 3 H), 7.18-7.16 (d, *J* = 8.0 Hz, 1 H), 7.12-7.08 (m, 1 H), 7.02-7.00 (m, 1 H), 2.50 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 141.5, 132.1, 132.0, 128.9, 127.5, 127.1, 124.2, 124.1, 123.0, 121.0, 90.5, 88.9, 15.1.



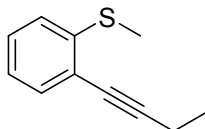
**(2-ethynylphenyl)(methyl)sulfane (1p)**

Yellow oil (1.14 g, 96% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.46\text{-}6.44$  (m, 1 H), 7.33-7.28 (m, 1 H), 7.16-7.14 (d,  $J = 7.6$  Hz, 1 H), 7.10-7.06 (m, 1 H), 3.47 (s, 1 H), 2.48 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 141.8, 133.1, 129.2, 124.2, 120.2, 83.5, 81.0, 15.1$ .



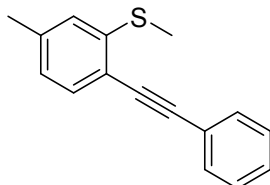
**methyl(2-(prop-1-yn-1-yl)phenyl)sulfane (1q)**

Yellow oil (0.61 g, 75% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.36\text{-}6.35$  (d,  $J = 7.6$  Hz, 1 H), 7.26-7.22 (m, 1 H), 7.13-7.11 (d,  $J = 8.0$  Hz, 1 H), 7.07-7.03 (m, 1 H), 2.48-2.47 (d,  $J = 2.4$  Hz, 3 H), 2.14-2.13 (d,  $J = 1.6$  Hz, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 140.9, 132.1, 127.9, 123.9, 123.6, 121.6, 92.5, 77.1, 14.8, 4.4$ .



**(2-(but-1-yn-1-yl)phenyl)(methyl)sulfane(1r)**

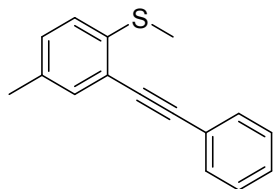
Yellow oil (0.66 g, 75% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.36\text{-}7.34$  (m, 1 H), 7.25-7.21 (m, 1 H), 7.11-7.09 (d,  $J = 8.0$  Hz, 1 H), 7.06-7.02 (m, 1 H), 2.52-2.48 (m, 2 H), 2.46 (s, 3 H), 1.29-1.25 (m, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 141.0, 132.1, 128.0, 124.0, 123.7, 121.9, 98.5, 83.4, 14.9, 13.8, 13.3$ .



**methyl(5-methyl-2-(phenylethynyl)phenyl)sulfane(1s)**

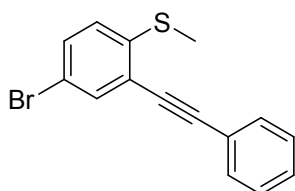
Yellow oil (0.95 g, 85% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.57\text{-}7.55$  (m,

2 H), 7.38-7.32 (m, 4 H), 6.98-6.90 (m, 2 H), 2.50 (s, 3 H), 2.36 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 141.3, 134.0, 132.1, 131.5, 128.3, 128.2, 125.3, 125.0, 123.4, 118.5, 95.1, 87.0, 21.7, 15.1$ .



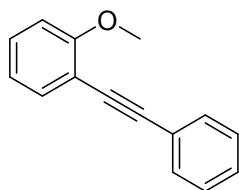
**methyl(4-methyl-2-(phenylethynyl)phenyl)sulfane(1t)**

Yellow oil (0.95 g, 85% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.57$ -7.55 (m, 2 H), 7.36-7.30 (m, 4 H), 7.08 (s, 2 H), 2.48 (s, 3 H), 2.29 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 140.0, 134.2, 132.9, 131.5, 129.7, 128.3, 124.9, 123.3, 121.6, 95.2, 87.2, 21.6, 15.5$ .



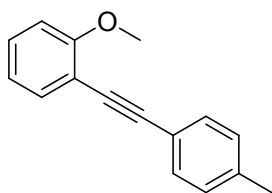
**(4-bromo-2-(phenylethynyl)phenyl)(methyl)sulfane (1u)**

Yellow oil (1.36 g, 90% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.61$ -7.60 (d,  $J = 2.0$  Hz, 1 H), 7.58-7.55 (m, 2 H), 7.41-7.38 (m, 1 H), 7.37-7.34 (m, 3 H), 7.03-7.01 (d,  $J = 8.4$  Hz, 1 H), 2.48 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 141.0, 134.5, 132.7, 131.6, 128.7, 128.4, 125.6, 123.1, 122.7, 117.4, 97.0, 85.5, 15.2$ .



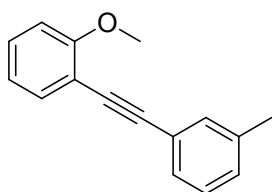
**1-methoxy-2-(phenylethynyl)benzene (3a)**

Yellow oil (0.88 g, 85% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.57$ -7.55 (m, 2 H), 7.51-7.49 (m, 1 H), 7.35-7.27 (m, 4 H), 6.95-6.87 (m, 2 H), 3.89 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 159.8, 135.5, 131.6, 129.7, 128.2, 128.1, 123.5, 120.4, 112.3, 110.6, 93.4, 85.7, 55.8$ .



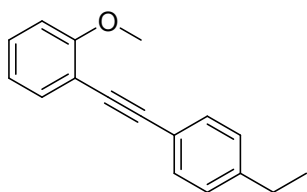
### 1-methoxy-2-(p-tolylethynyl)benzene (3b)

Yellow oil (0.94 g, 85% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.50-7.44 (m, 3 H), 7.27-7.25 (m, 1 H), 7.14-7.12 (d,  $J$  = 8 Hz, 2 H), 6.94-6.86 (m, 2 H), 3.89 (s, 3 H), 2.34 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 159.8, 138.1, 133.5, 131.5, 129.5, 129.0, 120.4, 112.6, 110.6, 93.6, 85.0, 55.8, 21.5.



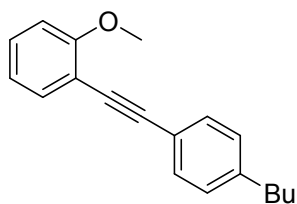
### 1-methoxy-2-(m-tolylethynyl)benzene (3c)

Yellow solid (0.99 g, 89% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.50-7.48 (m, 1 H), 7.39-7.36 (m, 2 H), 7.31-7.20 (m, 2 H), 7.13-7.11 (d,  $J$ =7.6 Hz 1 H), 6.95-6.88 (m, 2 H), 3.90 (s, 3 H), 2.34 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 159.9, 137.8, 133.5, 132.2, 129.6, 129.0, 128.7, 128.1, 123.3, 120.4, 112.5, 110.6, 93.6, 85.3, 55.8, 21.2.



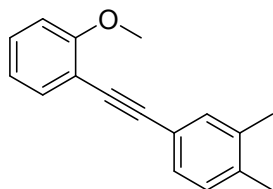
### 1-((4-ethylphenyl)ethynyl)-2-methoxybenzene (3d)

Yellow solid (1.04 g, 88% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.50-7.47 (m, 3 H), 7.30-7.26 (m, 1 H), 7.17-7.15 (d,  $J$ =8 Hz, 2 H), 6.94-6.87 (m, 2 H), 3.90 (s, 3 H), 2.68-2.62 (m, 2 H), 1.25-1.21 (m, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 159.8, 144.5, 133.5, 131.6, 129.5, 127.8, 120.7, 120.4, 112.6, 110.6, 93.6, 84.9, 55.8, 28.8, 15.3.



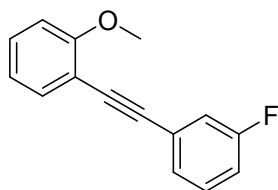
**1-((4-butylphenyl)ethynyl)-2-methoxybenzene (3e)**

Yellow oil (1.15 g, 87% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.50-7.45 (m, 3 H), 7.30-7.26 (m, 1 H), 7.15-7.13 (d,  $J$  = 8 Hz, 2 H), 6.94-6.87 (m, 2 H), 3.89 (s, 3 H), 2.62-2.58 (m, 2 H), 1.62-1.55 (m, 2 H), 1.39-1.29 (m, 2 H), 0.94-0.90 (m, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 159.8, 143.1, 133.5, 131.5, 129.5, 128.3, 120.6, 120.4, 112.6, 110.6, 93.6, 85.0, 55.8, 35.6, 33.4, 22.3, 13.9.



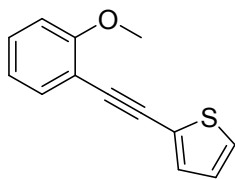
**4-((2-methoxyphenyl)ethynyl)-1,2-dimethylbenzene (3f)**

Yellow solid (0.99 g, 84% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.50-7.47 (m, 1 H), 7.35-7.26 (m, 3 H), 7.10-7.08 (d,  $J$ =7.6 Hz, 1 H), 6.94-6.87 (m, 2 H), 3.90 (s, 3 H), 2.26-2.25 (d,  $J$ =5.6 Hz, 6 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 159.8, 137.0, 136.5, 133.5, 132.7, 129.5, 129.4, 129.1, 120.7, 120.4, 112.7, 110.6, 93.8, 84.7, 55.8, 19.7, 19.5.



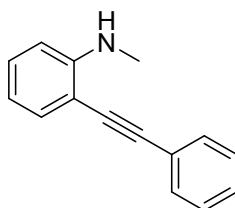
**1-((3-fluorophenyl)ethynyl)-2-methoxybenzene (3g)**

Yellow oil (0.90 g, 80% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.50-7.48 (m, 1 H), 7.34-7.24 (m, 4 H), 7.04-7.00 (m, 1 H), 6.96-6.88 (m, 2 H), 3.90 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 163.5, 161.1, 159.9, 133.6, 130.1, 129.8, 129.7, 127.5, 127.4, 125.4, 125.3, 125.3, 120.5, 118.4, 118.2, 115.5, 115.3, 111.8, 110.6, 92.1, 92.0, 86.7, 55.8.



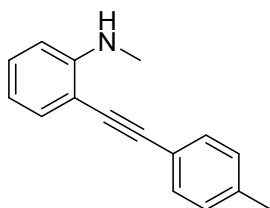
### 2-((2-methoxyphenyl)ethynyl)thiophene (3h)

Yellow oil (0.91 g, 85% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.49\text{-}7.46$  (m, 1 H),  $7.32\text{-}7.24$  (m, 3 H),  $7.00\text{-}6.98$  (m, 1 H),  $6.95\text{-}6.88$  (m, 2 H),  $3.90$  (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 159.8, 133.4, 131.8, 130.0, 127.1, 127.0, 123.5, 120.4, 112.1, 110.6, 89.4, 86.4, 55.8$ .



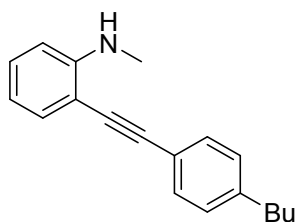
### N-methyl-2-(phenylethynyl)aniline (3i)

Yellow solid (0.88 g, 85% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.53\text{-}7.50$  (m, 2 H),  $7.38\text{-}7.30$  (m, 4 H),  $7.25\text{-}7.21$  (m, 1 H),  $6.67\text{-}6.59$  (m, 2 H),  $4.68$  (s, 1 H),  $2.90$  (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 149.8, 132.0, 131.4, 130.0, 128.3, 128.1, 123.3, 116.2, 109.0, 107.2, 94.9, 86.0, 30.3$ .



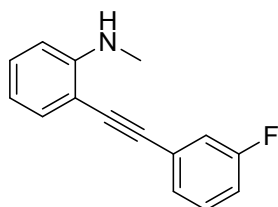
### N-methyl-2-(p-tolyethynyl)aniline (3j)

Yellow solid (0.90 g, 81% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.42\text{-}7.32$  (m, 3 H),  $7.24\text{-}7.20$  (m, 1 H),  $7.15\text{-}7.11$  (m, 2H),  $6.75\text{-}6.58$  (m, 2 H),  $4.68$  (s, 1 H),  $2.92\text{-}2.90$  (m, 3 H),  $2.35$  (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 149.7, 138.3, 132.0, 131.3, 129.8, 129.1, 120.2, 116.2, 108.9, 107.5, 95.0, 85.2, 30.3, 21.5$ .



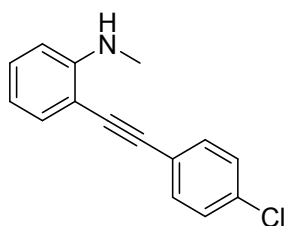
### 2-((4-butylphenyl)ethynyl)-N-methylaniline (3k)

Yellow oil (1.12 g, 85% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.44-7.42 (d,  $J$  = 8 Hz, 2 H), 7.37-7.35 (m, 1 H), 7.24-7.20 (m, 1 H), 7.16-7.14 (d,  $J$  = 8 Hz, 2 H), 6.67-6.59 (m, 2 H), 4.68 (s, 1 H), 2.93-2.91 (d,  $J$  = 8 Hz, 3 H), 2.63-2.59 (m, 2 H), 1.63-1.55 (m, 2 H), 1.39-1.30 (m, 2 H), 0.94-0.91 (m, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 149.7, 143.3, 132.0, 131.4, 129.8, 128.5, 120.4, 116.2, 108.9, 107.5, 95.1, 85.2, 35.6, 33.4, 30.3, 22.3, 13.9.



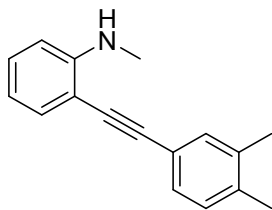
### 2-((3-fluorophenyl)ethynyl)-N-methylaniline (3l)

Yellow oil (0.89 g, 79% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.37-7.19 (m, 5 H), 7.04-7.02 (m, 1 H), 6.75-6.59 (m, 2 H), 4.64 (s, 1 H), 2.92-2.91 (d,  $J$  = 2.4 Hz, 4 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 163.6, 161.1, 149.8, 132.2, 130.4, 130.0, 129.9, 127.3, 125.2, 115.1, 118.2, 118.0, 116.0, 115.5, 115.3, 109.0, 106.6, 93.6, 30.3.



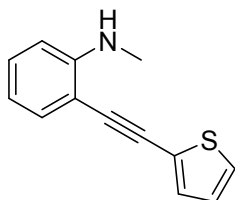
### 2-((4-chlorophenyl)ethynyl)-N-methylaniline (3m)

Yellow solid (0.94 g, 78% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.45-7.43 (m, 2 H), 7.36-7.30 (m, 3 H), 7.27-7.23 (m, 1 H), 6.68-6.60 (m, 2 H), 4.64 (s, 1 H), 2.92 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 149.8, 134.1, 132.6, 132.1, 130.3, 128.7, 121.8, 116.3, 109.1, 106.9, 93.8, 87.0, 30.3.



**2-((3,4-dimethylphenyl)ethynyl)-N-methylaniline (3n)**

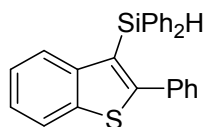
Yellow solid (0.92 g, 78% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.37-7.20 (m, 4 H), 7.11-7.09 (d, *J*=7.6 Hz, 1 H), 6.67-6.59 (m, 2 H), 4.69 (s, 1 H), 2.92-2.91 (d, *J*=3.6 Hz, 3 H), 2.27-2.25 (d, *J*=5.6 Hz, 6 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 149.7, 137.1, 136.7, 132.5, 131.9, 129.8, 129.6, 128.9, 120.5, 116.1, 108.9, 107.6, 95.2, 85.0, 30.3, 19.8, 19.6.



**N-methyl-2-(thiophen-2-ylethynyl)aniline (3o)**

Yellow solid (0.91 g, 85% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.35-7.34 (d, *J*=7.6 Hz, 1 H), 7.28-7.22 (m, 3 H), 7.01-6.99 (m, 1 H), 6.67-6.58 (m, 2 H), 4.63 (s, 1 H), 2.93-2.90 (m, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 149.8, 132.1, 131.6, 130.3, 127.1, 127.0, 123.3, 116.2, 109.0, 106.8, 89.6, 87.8, 30.3.

**The data of products:**

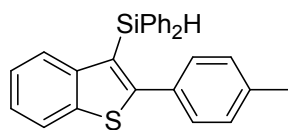


**diphenyl(2-phenylbenzo[*b*]thiophen-3-yl)silane (2a)<sup>[4]</sup>**

Yellow solid (68.99 mg, 88% yield). melting point: 97-98 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.88-7.86 (d, *J* = 8.0 Hz, 1 H), 7.63-7.61 (d, *J* = 8.0 Hz, 1 H), 7.55-7.52 (m, 4 H), 7.44-7.42 (m, 2 H), 7.39-7.34 (m, 2 H), 7.32-7.24 (m, 8 H), 7.18-7.14 (m, 1 H), 5.43 (s, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 155.8, 145.1, 141.0, 135.7, 135.4, 132.8, 130.1, 129.7, 128.5, 128.0, 127.9, 125.7, 125.4, 124.2, 124.0,

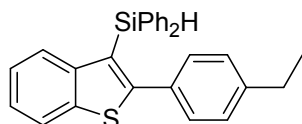


121.8; HRMS calcd for C<sub>26</sub>H<sub>20</sub>SSi [M+H]<sup>+</sup> 393.1128; found: 393.1113.



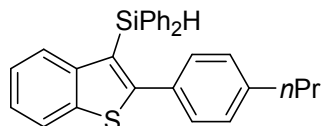
**diphenyl(2-(*p*-tolyl)benzo[*b*]thiophen-3-yl)silane (2b)**

White solid (73.08 mg, 90% yield). melting point: 133-135 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.86-7.83 (d, *J* = 8.4 Hz, 1 H), 7.61-7.59 (d, *J* = 8.0 Hz, 1 H), 7.54-7.52 (m, 4 H), 7.38-7.22 (m, 9 H), 7.16-7.14 (m, 1 H), 7.08-7.06 (d, *J* = 8.0 Hz, 2 H), 5.44 (s, 1 H), 2.32 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 156.0, 145.2, 140.9, 138.4, 135.7, 133.0, 132.5, 130.0, 129.7, 128.7, 128.0, 125.3, 124.1, 123.9, 121.7, 21.2; HRMS calcd for C<sub>27</sub>H<sub>22</sub>SSi [M+H]<sup>+</sup> 407.1284; found: 407.1298.



**(2-(4-ethylphenyl)benzo[*b*]thiophen-3-yl)diphenylsilane (2c)**

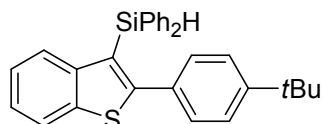
White solid (79.8 mg, 95% yield). melting point: 137-139 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.85-7.83 (d, *J* = 8.0 Hz, 1 H), 7.62-7.60 (d, *J* = 8.4 Hz, 1 H), 7.54-7.52 (m, 4 H), 7.36-7.32 (m, 4 H), 7.29-7.21 (m, 5 H), 7.16-7.12 (m, 1 H), 7.09-7.07 (d, *J* = 8.0 Hz, 2 H), 5.47 (s, 1 H), 2.64-2.59 (m, 2 H), 1.23-1.19 (m, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 156.1, 145.2, 144.6, 140.9, 135.7, 132.9, 132.7, 130.0, 129.7, 128.0, 127.5, 125.3, 124.1, 123.9, 121.7, 28.6, 15.4; HRMS calcd for C<sub>28</sub>H<sub>24</sub>SSi [M+H]<sup>+</sup> 421.1441; found: 421.1447.



**diphenyl(2-(4-propylphenyl)benzo[*b*]thiophen-3-yl)silane (2d)**

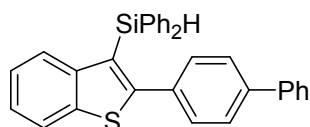
White solid (59.2 mg, 68% yield). melting point: 105-107 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.87-7.85 (d, *J* = 8.0 Hz, 1 H), 7.62-7.60 (d, *J* = 8.0 Hz, 1 H), 7.54-7.52 (m, 4 H), 7.38-7.24 (m, 9 H), 7.17-7.13 (m, 1 H), 7.08-7.06 (d, *J* = 8.0 Hz, 2 H), 5.46 (s, 1 H), 2.59-2.55 (m, 2 H), 1.66-1.60 (m, 2 H), 0.96-0.92 (m, 3 H); <sup>13</sup>C NMR

(100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 156.1, 145.2, 143.2, 141.0, 135.7, 132.9, 132.7, 130.0, 129.7, 128.1, 128.0, 125.3, 125.2, 124.1, 123.9, 121.7, 37.8, 24.4, 13.9; HRMS calcd for C<sub>29</sub>H<sub>26</sub>SSi [M+H]<sup>+</sup> 435.1597; found: 435.1603.



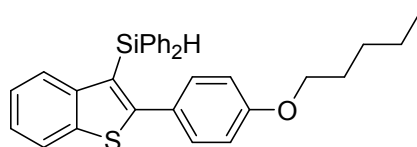
**(2-(4-(*tert*-butyl)phenyl)benzo[*b*]thiophen-3-yl)diphenylsilane (2e)**

White solid (58.24 mg, 65% yield). melting point: 131-133 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 7.89-7.87 (d, *J* = 8.0 Hz, 1 H), 7.64-7.62 (d, *J* = 8.0 Hz, 1 H), 7.53-7.50 (m, 4 H), 7.38-7.23 (m, 11 H), 7.19-7.15 (m, 1 H), 5.50 (s, 1 H), 1.30 (s, 9 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 156.0, 151.5, 145.3, 140.9, 135.8, 132.9, 132.4, 129.8, 129.7, 128.1, 128.0, 125.3, 124.9, 124.1, 123.9, 121.7, 34.6, 31.3; HRMS calcd for C<sub>30</sub>H<sub>28</sub>SSi [M+H]<sup>+</sup> 449.1754; found: 449.1760.



**(2-([1,1'-biphenyl]-4-yl)benzo[*b*]thiophen-3-yl)diphenylsilane (2f)**

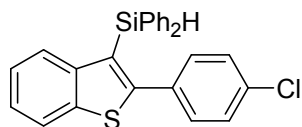
Yellow oil (53.35 mg, 57% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 7.90-7.88 (d, *J* = 8.0 Hz, 1 H), 7.66-7.64 (d, *J* = 8.0 Hz, 1 H), 7.58-7.53 (m, 6 H), 7.47-7.42 (m, 6 H), 7.39-7.27 (m, 8 H), 7.22-7.17 (m, 1 H), 5.53 (s, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 155.4, 145.2, 141.2, 141.0, 140.5, 135.8, 134.3, 132.8, 130.5, 129.7, 128.8, 128.1, 127.5, 127.1, 126.6, 125.8, 125.4, 124.2, 124.0, 121.8; HRMS calcd for C<sub>32</sub>H<sub>24</sub>SSi [M+H]<sup>+</sup> 469.1441; found: 469.1450.



**(2-(4-(pentyloxy)phenyl)benzo[*b*]thiophen-3-yl)diphenylsilane (2g)**

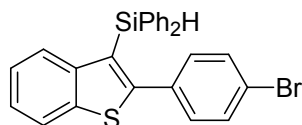
White oil (41.19 mg, 43% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 7.86-7.84 (d, *J* = 8.0 Hz, 1 H), 7.59-7.52 (m, 5 H), 7.39-7.23 (m, 9 H), 7.16-7.13 (m, 1 H), 6.80-6.77 (m, 2 H), 5.45 (s, 1 H), 3.95-3.92 (m, 2 H), 1.81-1.74 (m, 2 H), 1.46-1.35 (m, 4 H)

0.95-0.92 (m, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 159.5, 155.9, 145.2, 140.9, 135.7, 133.0, 131.3, 129.7, 128.0, 127.6, 125.2, 125.0, 124.1, 123.8, 121.7, 113.9, 68.0, 28.9, 28.2, 22.4, 14.0$ ; HRMS calcd for  $\text{C}_{31}\text{H}_{30}\text{SSi}$   $[\text{M}+\text{H}]^+$  479.1860; found: 479.1867.



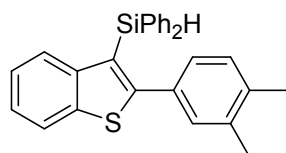
**(2-(4-chlorophenyl)benzo[*b*]thiophen-3-yl)diphenylsilane (2h)**

Yellow solid (65.76 mg, 77% yield). melting point: 154-156 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.89\text{-}7.87$  (d,  $J = 7.6$  Hz, 1 H), 7.64-7.62 (d,  $J = 8.4$  Hz, 1 H), 7.51-7.49 (m, 4 H), 7.41-7.37 (m, 2 H), 7.32-7.28 (m, 7 H), 7.23-7.17 (m, 3 H), 5.44 (s, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 154.1, 145.0, 140.9, 135.7, 134.6, 133.8, 132.5, 131.3, 129.8, 128.1, 126.4, 125.4, 124.4, 124.2, 121.8$ ; HRMS calcd for  $\text{C}_{27}\text{H}_{22}\text{SSi}$   $[\text{M}+\text{H}]^+$  427.0738; found: 427.0742.



**(2-(4-bromophenyl)benzo[*b*]thiophen-3-yl)diphenylsilane (2i)**

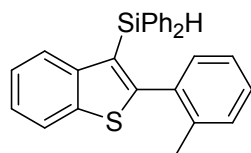
Yellow oil (48.98 mg, 52% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.89\text{-}7.87$  (d,  $J = 8.0$  Hz, 1 H), 7.64-7.62 (d,  $J = 8.2$  Hz, 1H), 7.51-7.49 (m, 4 H), 7.41-7.35 (m, 4 H), 7.32-7.28 (m, 5 H), 7.26-7.22 (m, 2 H), 7.21-7.17 (m, 1 H), 5.45 (s, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 154.1, 145.0, 140.9, 135.7, 134.3, 132.5, 131.6, 131.1, 129.8, 128.1, 126.5, 125.4, 124.4, 124.3, 122.9, 121.8$ ; HRMS calcd for  $\text{C}_{26}\text{H}_{19}\text{BrSSi}$   $[\text{M}+\text{H}]^+$  471.0233; found: 471.0239.



**(2-(3,4-dimethylphenyl)benzo[*b*]thiophen-3-yl)diphenylsilane (2j)**

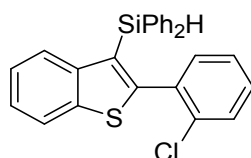
Yellow solid (67.2 mg, 80% yield). melting point: 135-137 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.86\text{-}7.84$  (d,  $J = 8.0$  Hz, 1 H), 7.61-7.59 (d,  $J = 8.0$  Hz, 1 H), 7.54-

7.52 (d,  $J = 6.8$  Hz, 4 H), 7.38-7.23 (m, 7 H), 7.19-7.13 (m, 3 H), 7.05-7.03 (m, 1 H), 5.44 (s, 1 H), 2.23 (s, 3 H), 2.15 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 156.2, 145.2, 140.9, 137.1, 136.1, 135.7, 133.1, 132.9, 131.3, 129.6, 129.2, 128.0, 127.5, 125.3, 125.2, 124.1, 123.8, 121.7, 19.6, 19.5$ ; HRMS calcd for  $\text{C}_{28}\text{H}_{24}\text{SSi}$   $[\text{M}+\text{H}]^+$  421.1441; found: 421.1448.



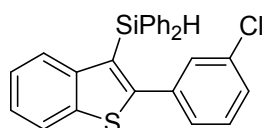
**diphenyl(2-(*o*-tolyl)benzo[*b*]thiophen-3-yl)silane (2k)**

Yellow oil (23.3 mg, 49% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.89$ -7.87 (d,  $J = 8.0$  Hz, 1 H), 7.63-7.61 (d,  $J = 8.0$  Hz, 1 H), 7.54-7.52 (d,  $J = 6.8$  Hz, 4 H), 7.40-7.28 (m, 7 H), 7.23-7.10 (m, 5 H), 5.43 (s, 1 H), 2.26 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 156.0, 145.2, 141.0, 137.6, 135.7, 135.3, 133.1, 130.9, 129.7, 129.2, 128.0, 127.9, 127.2, 125.6, 125.4, 124.2, 123.9, 121.8, 21.3$ ; HRMS calcd for  $\text{C}_{27}\text{H}_{22}\text{SSi}$   $[\text{M}+\text{H}]^+$  407.1084; found: 407.1298.



**(2-(2-chlorophenyl)benzo[*b*]thiophen-3-yl)diphenylsilane (2l)**

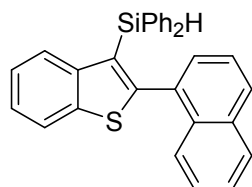
White solid (45.21 mg, 56% yield). melting point: 180-181 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.91$ -7.89 (d,  $J = 8.0$  Hz, 1 H), 7.67-7.65 (d,  $J = 8.0$  Hz, 1 H), 7.51-7.49 (m, 4 H), 7.37-7.27 (m, 8 H), 7.25-7.20 (m, 3 H), 7.16-7.12 (m, 1 H), 5.24 (s, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 151.3, 144.1, 141.2, 135.8, 134.4, 134.3, 132.5, 132.2, 130.0, 129.7, 129.4, 128.6, 127.9, 126.1, 125.3, 124.3, 121.9$ ; HRMS calcd for  $\text{C}_{26}\text{H}_{19}\text{SSi}$   $[\text{M}+\text{H}]^+$  427.0738; found: 427.0754.



**(2-(3-chlorophenyl)benzo[*b*]thiophen-3-yl)diphenylsilane (2m)**

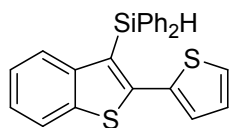
Yellow oil (66.54 mg, 78% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.89$ -7.87

(d,  $J = 8.0$  Hz, 1 H), 7.67-7.65 (d,  $J = 8.4$  Hz, 1 H), 7.53-7.51 (m, 4 H), 7.40-7.36 (m, 3 H), 7.33-7.24 (m, 7 H), 7.22-7.14 (m, 2 H), 5.46 (s, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 153.6, 145.0, 140.9, 137.1, 135.7, 133.8, 132.4, 130.1, 129.9, 129.1, 128.5, 128.3, 128.1, 126.8, 125.5, 124.4, 124.3, 121.8$ ; HRMS calcd for  $\text{C}_{27}\text{H}_{22}\text{SSi}$   $[\text{M}+\text{H}]^+$  427.0738; found: 427.0742.



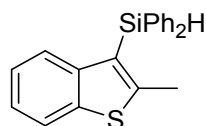
### (2-(naphthalen-1-yl)benzo[b]thiophen-3-yl)diphenylsilane (2n)

Yellow oil (59.2 mg, 67% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.93$ -7.91 (m, 1 H), 7.80-7.73 (m, 4 H), 7.44-7.21 (m, 14 H), 7.15-7.11 (m, 2 H), 5.07 (s, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 153.0, 144.5, 141.5, 135.7, 135.5, 133.1, 132.9, 132.5, 129.6, 129.1, 128.8, 127.9, 127.8, 127.6, 126.3, 126.2, 125.9, 125.1, 124.6, 124.3, 124.2, 121.8$ ; HRMS calcd for  $\text{C}_{30}\text{H}_{20}\text{SSi}$   $[\text{M}+\text{H}]^+$  443.1284; found: 443.1292.



### diphenyl(2-(thiophen-2-yl)benzo[b]thiophen-3-yl)silane (2o)

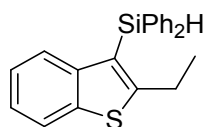
Yellow oil (44.58 mg, 56% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.85$ -7.83 (d,  $J = 8.0$  Hz, 1 H), 7.60-7.55 (m, 5 H), 7.41-7.37 (m, 2 H), 7.34-7.25 (m, 6 H), 7.17-7.14 (m, 1 H), 7.05-7.04 (d,  $J = 3.2$  Hz, 1 H), 6.93-6.91 (m, 1 H), 5.63 (s, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 147.1, 145.1, 141.1, 136.5, 135.7, 132.6, 129.8, 129.0, 128.1, 127.5, 127.3, 127.2, 125.5, 124.3, 121.7$ ; HRMS calcd for  $\text{C}_{24}\text{H}_{18}\text{S}_2\text{Si}$   $[\text{M}+\text{H}]^+$  399.0692; found: 399.0700.



### (2-methylbenzo[b]thiophen-3-yl)diphenylsilane (2q)

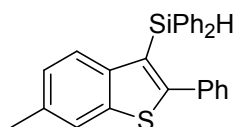
Yellow oil (33.0 mg, 50% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.80$ -7.78 (d,

$J = 8.0$  Hz, 1 H), 7.60-7.57 (m, 5 H), 7.43-7.33 (m, 6 H), 7.23-7.13 (m, 2 H), 5.80 (s, 1 H), 2.55 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 151.9, 145.3, 140.0, 135.8, 132.5, 129.9, 128.2, 124.3, 124.1, 123.9, 123.3, 121.6, 17.3$ ; HRMS calcd for  $\text{C}_{21}\text{H}_{18}\text{SSi}$   $[\text{M}+\text{H}]^+$  331.0971; found: 331.0980.



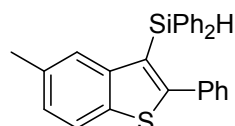
**(2-ethylbenzo[*b*]thiophen-3-yl)diphenylsilane (2r)**

Yellow oil (27.52 mg, 40% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.83\text{-}7.81$  (d,  $J = 7.6$  Hz, 1 H), 7.61-7.57 (m, 5 H), 7.44-7.39 (m, 2 H), 7.37-7.33 (m, 4 H), 7.22-7.20 (m, 1 H), 7.17-7.13 (m, 1 H), 5.79 (s, 1 H), 3.01-2.95 (m, 2 H), 1.24-1.20 (m, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 160.0, 145.0, 139.9, 135.8, 132.6, 129.9, 128.1, 124.3, 123.9, 123.3, 123.2, 121.8, 25.1, 16.9$ ; HRMS calcd for  $\text{C}_{22}\text{H}_{20}\text{SSi}$   $[\text{M}+\text{H}]^+$  345.1128; found: 345.1135.



**(6-methyl-2-phenylbenzo[*b*]thiophen-3-yl)diphenylsilane (2s)**

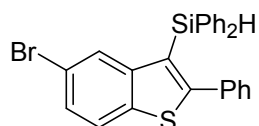
Yellow solid (60.9 mg, 75% yield). melting point: 139-140 °C  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.66$  (s, 1 H), 7.54-7.52 (d,  $J = 7.2$  Hz, 4 H), 7.49-7.47 (d,  $J = 8.4$  Hz, 1 H), 7.43-7.41 (m, 2 H), 7.37-7.34 (m, 2 H), 7.30-7.25 (m, 7 H), 6.99-6.97 (m,  $J = 8.4$  Hz, 1 H), 5.42 (s, 1 H), 2.40 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 154.7, 142.9, 141.3, 135.7, 135.5, 133.9, 133.0, 130.1, 129.7, 128.3, 128.0, 127.9, 125.9, 125.4, 125.0, 121.6, 21.4$ ; HRMS calcd for  $\text{C}_{27}\text{H}_{22}\text{SSi}$   $[\text{M}+\text{H}]^+$  407.1284; found: 407.1288.



**(5-methyl-2-phenylbenzo[*b*]thiophen-3-yl)diphenylsilane (2t)**

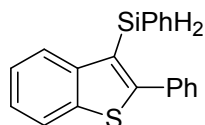
Yellow oil (47.9 mg, 59% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.76\text{-}7.34$  (d,

$J = 8$  Hz, 1 H), 7.53-7.51 (m, 4 H), 7.41-7.35 (m, 5 H), 7.32-7.22 (m, 7 H), 7.12-7.10 (m, 1 H), 5.44 (s, 1 H), 2.25 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 155.9, 145.6, 138.2, 135.8, 135.6, 133.8, 133.0, 130.1, 129.7, 128.4, 128.0, 127.9, 125.7, 125.4, 125.3, 121.3, 21.5$ ; HRMS calcd for  $\text{C}_{27}\text{H}_{22}\text{SSi}$   $[\text{M}+\text{H}]^+$  407.1284; found: 407.1288.



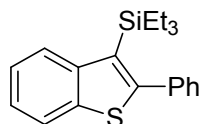
**(5-bromo-2-phenylbenzo[*b*]thiophen-3-yl)diphenylsilane (2u)**

Yellow oil (67.8 mg, 72% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.73$  (m, 2 H), 7.51-7.49 (m, 4 H), 7.41-7.22 (m, 12 H), 5.44 (s, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 157.4, 146.9, 139.6, 135.7, 134.9, 132.3, 130.0, 129.9, 128.7, 128.2, 128.0, 127.9, 127.1, 125.4, 123.0, 118.3$ ; HRMS calcd for  $\text{C}_{26}\text{H}_{19}\text{SSi}$   $[\text{M}+\text{H}]^+$  471.0233; found: 471.0239.



**phenyl(2-phenylbenzo[*b*]thiophen-3-yl)silane (5)**

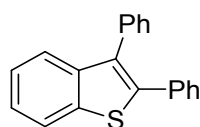
Yellow oil (43.11 mg, 68% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.91$ -7.88 (m, 2 H), 7.54-7.48 (m, 4 H), 7.38-7.28 (m, 8 H), 4.97 (s, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 155.3, 145.4, 141.0, 135.4, 135.3, 131.4, 129.9, 129.8, 128.7, 128.3, 128.2, 124.7, 124.6, 124.3, 124.0, 121.9$ ; HRMS calcd for  $\text{C}_{20}\text{H}_{16}\text{SSi}$   $[\text{M}+\text{H}]^+$  317.0815; found: 317.0820.



**triethyl(2-phenylbenzo[*b*]thiophen-3-yl)silane (6)**

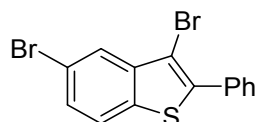
White oil (28.6 mg, 44% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 7.99$ -7.97 (d,  $J = 8.4$  Hz, 1 H), 7.85-7.83 (d,  $J = 7.6$  Hz, 1 H), 7.46-7.28 (m, 7 H), 0.84-0.80 (m, 9 H), 0.69-0.64 (m, 6 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 152.7, 145.6, 141.2,$

136.9, 130.3, 130.0, 128.4, 127.6, 124.8, 123.9, 123.6, 121.7, 7.5, 4.5; HRMS calcd for  $C_{20}H_{24}SSi$   $[M+H]^+$  325.1441; found: 325.1445.



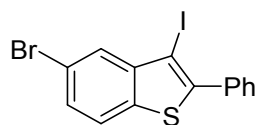
### 2,3-diphenylbenzo[b]thiophene (7)

White solid (32.03 mg, 56% yield). melting point: 113-114 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ , ppm):  $\delta$  = 7.87-7.85 (m, 1 H), 7.60-7.58 (m, 1 H), 7.41-7.31 (m, 9 H), 7.25-7.22 (m, 3 H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ , ppm):  $\delta$  = 140.9, 139.6, 138.9, 135.5, 134.3, 133.3, 130.4, 129.6, 128.6, 128.3, 127.7, 127.4, 124.5, 124.4, 123.4, 122.1; HRMS calcd for  $C_{20}H_{14}S$   $[M+H]^+$  287.0898; found: 287.0901.



### 3,5-dibromo-2-phenylbenzo[b]thiophene (8)

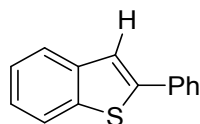
White solid (67.34 mg, 92% yield). melting point: 131-133 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ , ppm):  $\delta$  = 8.01-8.00 (d,  $J$  = 2 Hz, 1 H), 7.74-7.72 (m, 2 H), 7.66-7.64 (m, 1 H), 7.49-7.41 (m, 4 H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ , ppm):  $\delta$  = 140.8, 140.1, 136.3, 132.6, 129.6, 129.1, 128.7, 128.5, 126.4, 123.5, 119.4, 103.9; HRMS calcd for  $C_{14}H_8Br_2S$   $[M+H]^+$  366.8786; found: 366.8790.



### 5-bromo-3-iodo-2-phenylbenzo[b]thiophene (9)

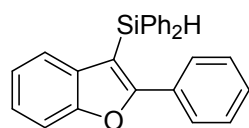
White solid (66.24 mg, 80% yield). melting point: 117-119 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ , ppm):  $\delta$  = 7.99-7.98 (d,  $J$  = 1.6 Hz, 1 H), 7.68-7.63 (m, 3 H), 7.51-7.45 (m, 4 H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ , ppm):  $\delta$  = 144.1, 143.7, 137.6, 134.2, 129.9, 129.2, 129.0, 128.6, 123.4, 119.6, 78.0; HRMS calcd for  $C_{14}H_8BrIS$   $[M+H]^+$  414.8648; found: 414.8653.





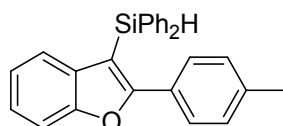
### 2-phenylbenzo[b]thiophene (10)

White solid (37.98 mg, 90% yield). melting point: 236-237 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.82-7.80 (d, *J* = 7.6 Hz, 1 H), 7.76-7.69 (m, 3 H), 7.52 (s, 1 H), 7.42-7.38 (m, 2 H), 7.35-7.27 (m, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 144.2, 140.7, 139.5, 134.3, 128.9, 128.2, 126.5, 124.5, 124.3, 123.5, 122.2, 119.4; HRMS calcd for C<sub>14</sub>H<sub>10</sub>S [M+H]<sup>+</sup> 211.0576; found: 211.0579.



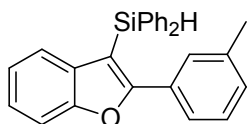
### diphenyl(2-phenylbenzofuran-3-yl)silane (4a)

White oil (52.64 mg, 70% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.92 (s, 1 H), 7.73-7.66 (m, 5H), 7.46-7.33 (m, 8 H), 7.24-7.15 (m, 4 H), 7.02-6.98 (m, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 159.7, 138.3, 137.8, 135.4, 131.7, 131.0, 130.9, 129.7, 128.4, 128.2, 128.1, 120.9, 120.8, 115.6; HRMS calcd for C<sub>26</sub>H<sub>20</sub>OSi [M+H]<sup>+</sup> 377.1356; found: 377.1360.



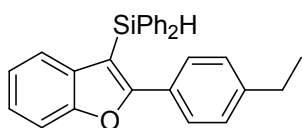
### diphenyl(2-(p-tolyl)benzofuran-3-yl)silane (4b)

Yellow solid (60.08 mg, 77% yield). melting point: 139-140 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.90 (s, 1 H), 7.72-7.67 (m, 5 H), 7.46-7.42 (m, 2 H), 7.37-7.30 (m, 6 H), 7.21-7.17 (m, 1 H), 7.01-6.95 (m, 4 H), 2.24 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 159.6, 138.2, 137.8, 135.5, 134.3, 131.2, 131.0, 130.4, 130.0, 129.4, 129.1, 128.3, 128.2, 127.7, 120.8, 115.5, 21.2; HRMS calcd for C<sub>27</sub>H<sub>22</sub>OSi [M+H]<sup>+</sup> 391.1513; found: 391.1517.



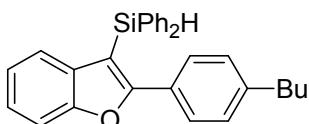
**diphenyl(2-(m-tolyl)benzofuran-3-yl)silane (4c)**

White oil (53.04 mg, 68% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.80 (s, 1 H), 7.72-7.66 (m, 5H), 7.45-7.33 (m, 6 H), 7.23-7.18 (m, 3 H), 7.09-6.96 (m, 4 H), 2.08 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 159.7, 138.2, 138.0, 137.9, 135.4, 131.4, 131.1, 131.0, 130.9, 128.6, 128.3, 128.1, 125.7, 120.9, 120.8, 115.6, 21.0; HRMS calcd for  $\text{C}_{27}\text{H}_{22}\text{OSi}$   $[\text{M}+\text{H}]^+$  391.1513; found: 391.1517.



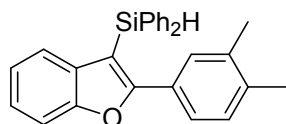
**(2-(4-ethylphenyl)benzofuran-3-yl)diphenylsilane (4d)**

Yellow oil (54.16 mg, 67% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.90 (s, 1 H), 7.72-7.67 (m, 5H), 7.45-7.41 (m, 2 H), 7.37-7.33 (m, 6 H), 7.21-7.16 (m, 1 H), 7.01-6.95 (m, 4 H), 2.57-2.51 (m, 2 H), 1.16-1.13 (m, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 159.7, 144.8, 138.0, 135.8, 135.6, 134.5, 131.4, 131.1, 130.2, 129.6, 128.5, 128.3, 128.1, 121.0, 115.7, 28.7, 15.5; HRMS calcd for  $\text{C}_{28}\text{H}_{24}\text{OSi}$   $[\text{M}+\text{H}]^+$  405.1669; found: 405.1675.



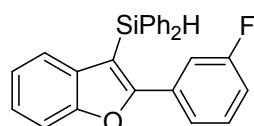
**(2-(4-butylphenyl)benzofuran-3-yl)diphenylsilane (4e)**

White oil (63.07 mg, 73% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 7.90 (s, 1 H), 7.72-7.66 (m, 5H), 7.46-7.42 (m, 2 H), 7.37-7.32 (m, 6 H), 7.21-7.17 (m, 1 H), 7.01-6.96 (m, 4 H), 2.53-2.49 (m, 2 H), 1.55-1.47 (m, 2 H), 1.32-1.22 (m, 2 H), 0.90-0.86 (m, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  = 159.6, 143.3, 137.9, 135.7, 135.5, 131.3, 131.0, 130.9, 130.3, 129.4, 128.5, 128.2, 128.1, 120.8, 115.5, 35.3, 33.4, 22.2, 13.9; HRMS calcd for  $\text{C}_{30}\text{H}_{28}\text{OSi}$   $[\text{M}+\text{H}]^+$  433.1982; found: 433.1990.



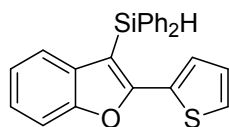
**(2-(3,4-dimethylphenyl)benzofuran-3-yl)diphenylsilane (4f)**

White oil (63.02 mg, 78% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.87 (s, 1 H), 7.70-7.68 (m, 5H), 7.61-7.59 (d, *J* = 6.8 Hz, 1 H), 7.45-7.41 (m, 2 H), 7.37-7.33 (m, 3 H), 7.30-7.26 (m, 1 H), 7.18-7.14 (m, 2 H), 7.02-6.92 (m, 3 H), 2.15 (s, 3 H), 1.99 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 159.6, 137.9, 137.0, 136.6, 135.8, 135.4, 134.3, 131.3, 131.1, 130.9, 130.4, 129.7, 129.3, 128.1, 127.7, 126.1, 120.8, 115.5, 19.5, 19.3; HRMS calcd for C<sub>28</sub>H<sub>24</sub>OSi [M+H]<sup>+</sup> 405.1669; found: 405.1674



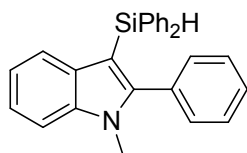
**(2-(3-fluorophenyl)benzofuran-3-yl)diphenylsilane (4g)**

White solid (42.55 mg, 54% yield). melting point: 162-163 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.67-7.62 (m, 5 H), 7.48-7.44 (m, 2H), 7.41-7.37 (m, 4 H), 7.30-7.28 (m, 1 H), 7.23-7.16 (m, 2 H), 7.08-6.98 (m, 4 H), 6.92-6.87 (m, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 164.2, 161.8, 152.9, 143.8, 143.7, 143.1, 135.2, 133.3, 131.6, 131.3, 130.8, 130.1, 130.0, 128.2, 124.0, 122.9, 122.8, 121.4, 119.3, 114.0, 113.8, 113.4, 113.2; HRMS calcd for C<sub>26</sub>H<sub>19</sub>FOSi [M+H]<sup>+</sup> 395.1262; found: 395.1268.



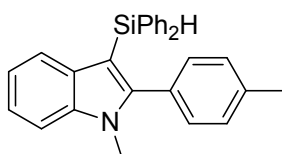
**diphenyl(2-(thiophen-2-yl)benzofuran-3-yl)silane (4h)**

White oil (51.18 mg, 67% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 8.02 (s, 1 H), 7.79-7.77 (d, *J* = 7.2 Hz, 4H), 7.67-7.66 (d, *J* = 7.6 Hz, 1 H), 7.48-7.36 (m, 6 H), 7.20-7.17 (m, 1 H), 7.08-7.07 (d, *J* = 4.4 Hz, 2 H), 7.00-6.95 (m, 2 H), 6.88-6.85 (m, 1 H),; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 159.6, 143.2, 135.8, 134.3, 131.1, 130.9, 130.3, 129.5, 129.4, 128.5, 128.1, 127.5, 126.3, 120.9, 120.7, 115.6; HRMS calcd for C<sub>24</sub>H<sub>18</sub>OSSi [M+H]<sup>+</sup> 383.0921; found: 383.0926.



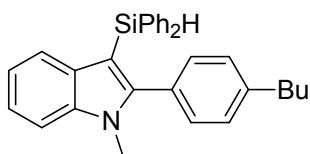
### 3-(diphenylsilyl)-1-methyl-2-phenyl-1H-indole (4i)

Yellow oil (48.23 mg, 62% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.93 (s, 1 H), 7.69-7.60 (m, 5H), 7.40-7.29 (m, 8 H), 7.23-7.17 (m, 1 H), 7.09-7.07 (m, 3 H), 6.78-6.73 (m, 1 H), 6.62-6.60 (d, *J* = 10.4 Hz, 1H), 2.78 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 152.8, 138.6, 137.4, 135.7, 131.5, 130.3, 130.1, 129.3, 128.4, 128.1, 128.0, 127.6, 120.3, 116.7, 108.6, 29.5; HRMS calcd for C<sub>27</sub>H<sub>23</sub>NSi [M+H]<sup>+</sup> 390.1673; found: 390.1679



### 3-(diphenylsilyl)-1-methyl-2-(p-tolyl)-1H-indole (4j)

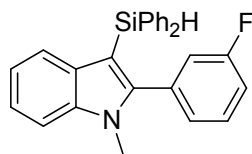
Yellow oil (54.00 mg, 67% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.91 (s, 1 H), 7.68-7.62 (m, 5 H), 7.44-7.39 (m, 2 H), 7.36-7.32 (m, 4 H), 7.28-7.26 (d, *J* = 8 Hz, 2 H), 7.20-7.16 (m, 1 H), 6.92-6.90 (d, *J* = 8 Hz, 2 H), 6.77-6.73 (m, 1 H), 6.61-6.59 (d, *J* = 8 Hz, 1 H), 2.78 (s, 3 H), 2.22 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 152.6, 137.6, 137.5, 135.8, 131.6, 131.0, 130.3, 130.2, 129.1, 128.8, 128.4, 128.0, 120.2, 116.7, 108.6, 29.5, 21.2; HRMS calcd for C<sub>28</sub>H<sub>25</sub>NSi [M+H]<sup>+</sup> 404.1829; found: 404.1834.



### 2-(4-butylphenyl)-3-(diphenylsilyl)-1-methyl-1H-indole (4k)

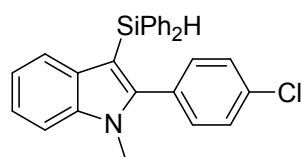
Yellow oil (51.62 mg, 58% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.91 (s, 1 H), 7.67-7.61 (m, 5H), 7.42-7.38 (m, 2 H), 7.35-7.27 (m, 6 H), 7.21-7.16 (m, 1 H), 6.92-6.90 (d, *J* = 8 Hz, 2 H), 6.77-6.73 (m, 1 H), 6.61-6.59 (d, *J* = 8 Hz, 1 H), 2.78 (s, 3 H), 2.50-2.46 (m, 2 H), 1.52-1.44 (m, 2 H), 1.29-1.20 (m, 2 H), 0.89-0.85 (m, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 152.6, 142.7, 137.6, 136.1, 135.7, 131.6,

131.3, 130.3, 129.1, 128.4, 128.2, 128.0, 120.2, 116.7, 108.5, 35.3, 33.4, 29.5, 22.2, 13.9; HRMS calcd for C<sub>31</sub>H<sub>31</sub>NSi [M+H]<sup>+</sup> 446.2309; found: 446.2315



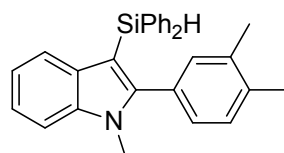
### 3-(diphenylsilyl)-2-(3-fluorophenyl)-1-methyl-1H-indole (4l)

Yellow oil (57.79 mg, 71% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.86 (s, 1 H), 7.66-7.60 (m, 5H), 7.42-7.38 (m, 2 H), 7.35-7.32 (m, 4 H), 7.23-7.19 (m, 1 H), 7.12-7.10 (d, *J* = 7.6 Hz, 1 H), 7.06-7.02 (m, 2 H), 6.77-6.73 (m, 2 H), 6.62-6.60 (d, *J* = 8 Hz, 1 H), 2.77-2.76 (d, *J* = 2 Hz, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 163.8, 161.3, 152.9, 141.1, 141.0, 135.8, 135.7, 134.7, 131.0, 130.5, 129.8, 129.6, 129.5, 128.1, 124.2, 120.5, 116.8, 114.8, 114.6, 114.4, 114.2, 108.8, 29.4; HRMS calcd for C<sub>27</sub>H<sub>22</sub>FNSi [M+H]<sup>+</sup> 408.1579; found: 408.1584.



### 2-(4-chlorophenyl)-3-(diphenylsilyl)-1-methyl-1H-indole (4m)

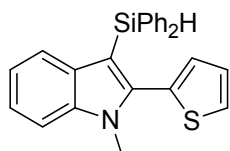
Yellow solid (60.91 mg, 72% yield). melting point: 128-129 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.85 (s, 1 H), 7.66-7.59 (m, 5H), 7.42-7.40 (d, *J* = 7.2 Hz, 2 H), 7.36-7.33 (m, 4 H), 7.28-7.18 (m, 4 H), 7.06-7.04 (d, *J* = 8.2 Hz, 2 H), 6.77-6.73 (m, 1 H), 6.62-6.60 (d, *J* = 8 Hz, 1 H), 2.77 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 152.8, 137.2, 135.8, 135.7, 134.3, 133.7, 133.2, 131.1, 130.5, 129.8, 129.6, 128.3, 128.2, 120.4, 116.8, 108.8, 29.4; HRMS calcd for C<sub>27</sub>H<sub>22</sub>ClNSi [M+H]<sup>+</sup> 424.1283; found: 424.1288



### 2-(3,4-dimethylphenyl)-3-(diphenylsilyl)-1-methyl-1H-indole (4n)

Yellow oil (50.87 mg, 61% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ = 7.89 (s, 1 H), 7.67-7.63 (m, 5 H), 7.42-7.39 (m, 2 H), 7.35-7.32 (m, 4 H), 7.23-7.22 (m, 1 H),

7.20-7.17 (m, 2 H), 7.12-7.10 (d,  $J = 7.6$  Hz, 1 H), 6.90-6.88 (d,  $J = 8$  Hz, 1 H), 6.77-6.73 (m, 1 H), 6.61-6.60 (d,  $J = 7.6$  Hz, 1H), 2.79-2.78 (d,  $J = 1.6$  Hz, 3H), 2.13 (s, 3 H), 1.97 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 152.6, 137.6, 136.4, 136.2, 136.1, 135.7, 134.6, 131.7, 130.7, 130.2, 129.4, 129.0, 128.0, 126.3, 120.1, 116.7, 108.5, 29.5, 19.5, 19.3$ ; HRMS calcd for  $\text{C}_{29}\text{H}_{27}\text{NSi}$   $[\text{M}+\text{H}]^+$  418.1986; found: 418.1990.

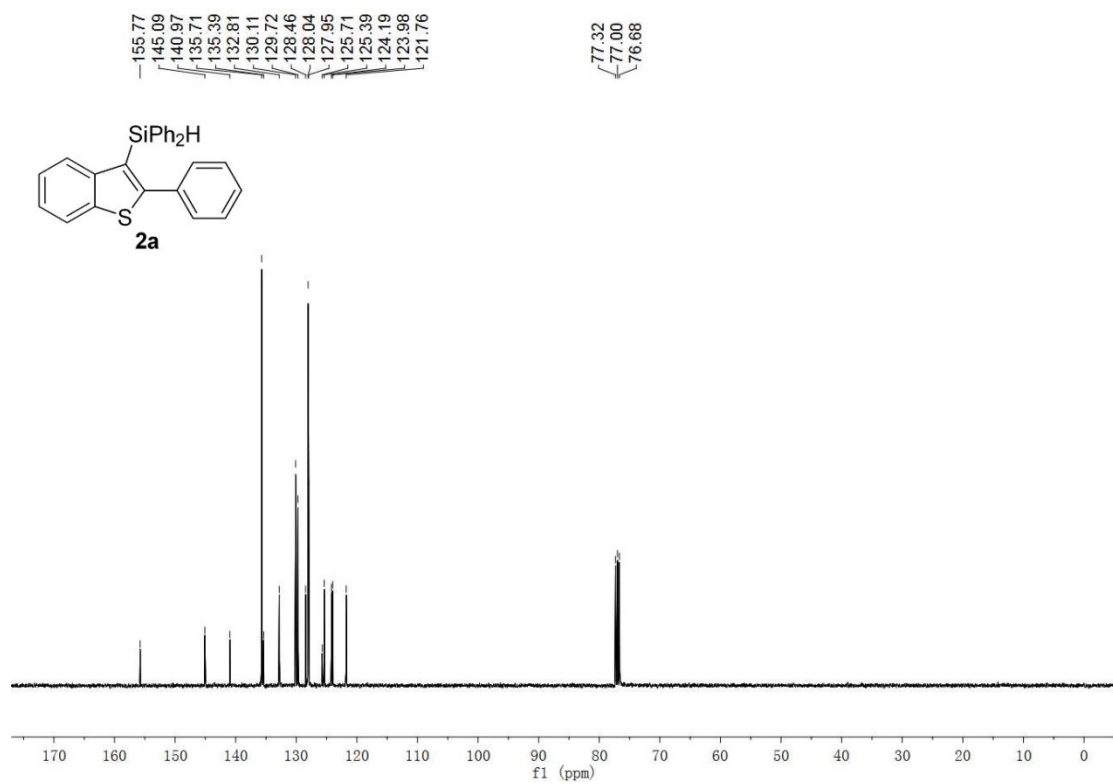
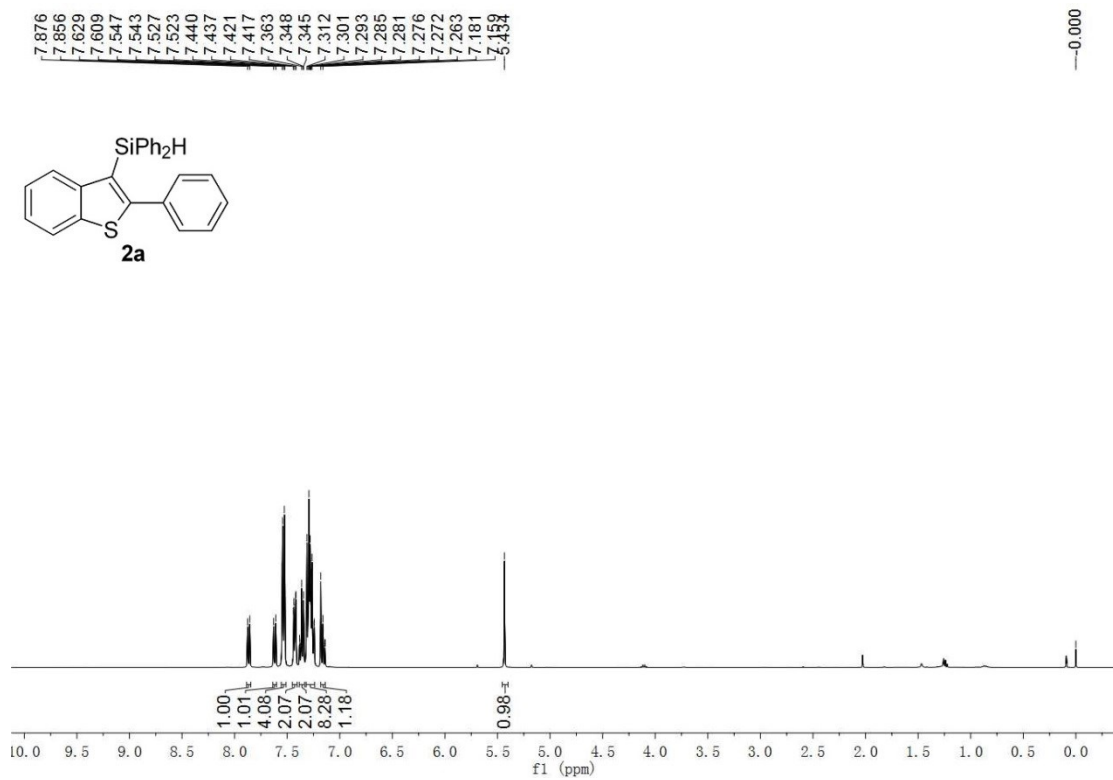


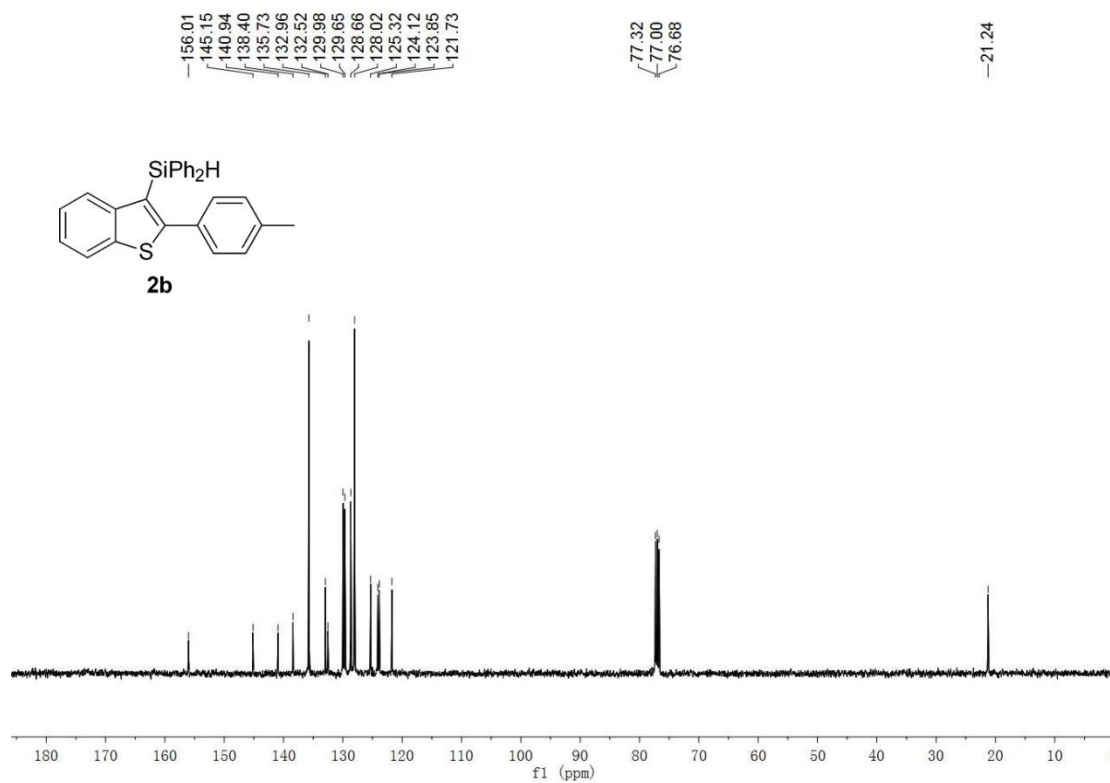
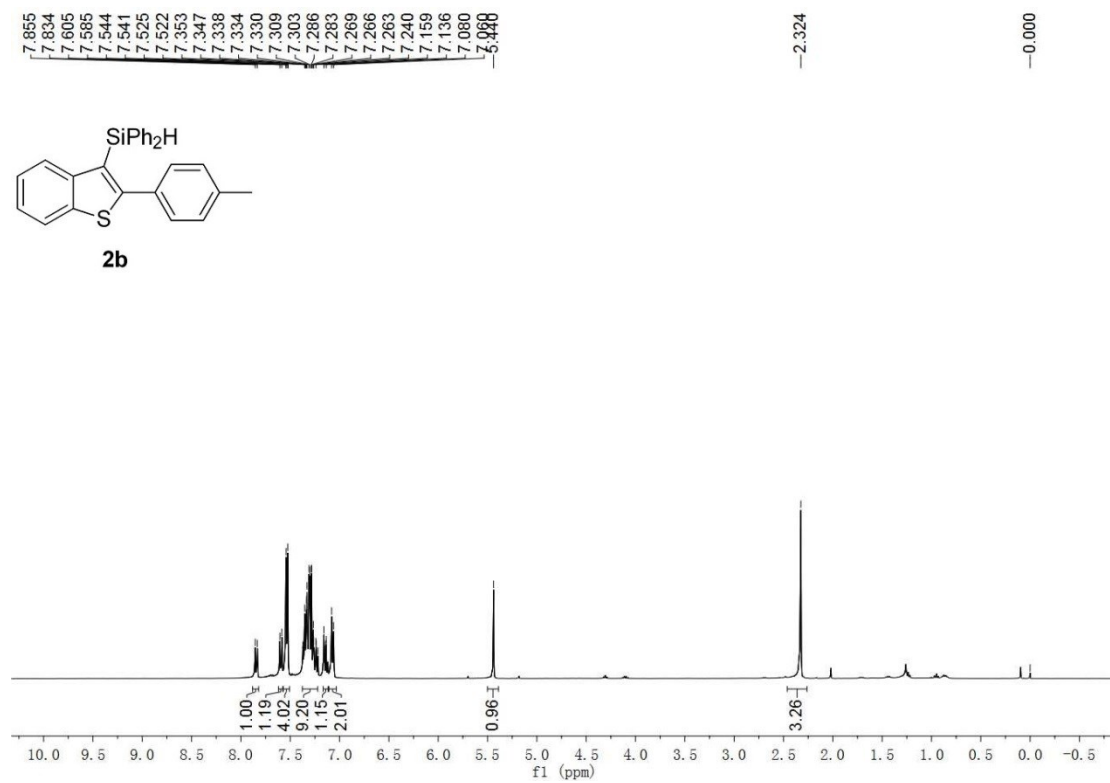
### 3-(diphenylsilyl)-1-methyl-2-(thiophen-2-yl)-1H-indole (4o)

Yellow solid (33.97 mg, 43% yield). melting point: 198-200 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 8.02$  (s, 1 H), 7.74-7.72 (m, 4 H), 7.64-7.62 (m, 1 H), 7.46-7.42 (m, 2 H), 7.39-7.35 (m, 4 H), 7.20-7.16 (m, 1 H), 7.05-7.02 (m, 2 H), 6.83-6.81 (m, 1 H), 6.76-6.72 (m, 1 H), 6.60-6.58 (d,  $J = 7.6$  Hz, 1 H), 2.76 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 152.8, 143.4, 136.0, 130.9, 130.7, 130.4, 129.8, 129.2, 128.9, 128.0, 127.2, 126.0, 120.1, 116.7, 108.6, 29.3$ ; HRMS calcd for  $\text{C}_{25}\text{H}_{21}\text{NSi}$   $[\text{M}+\text{H}]^+$  396.1237; found: 396.1241.

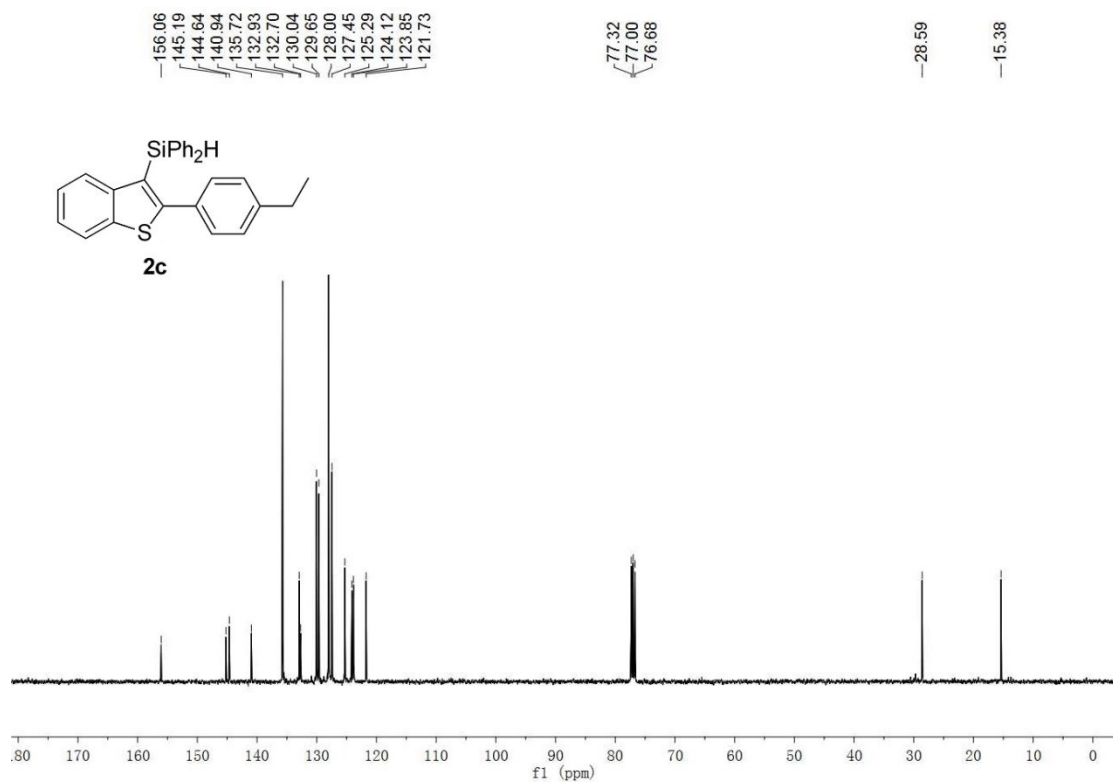
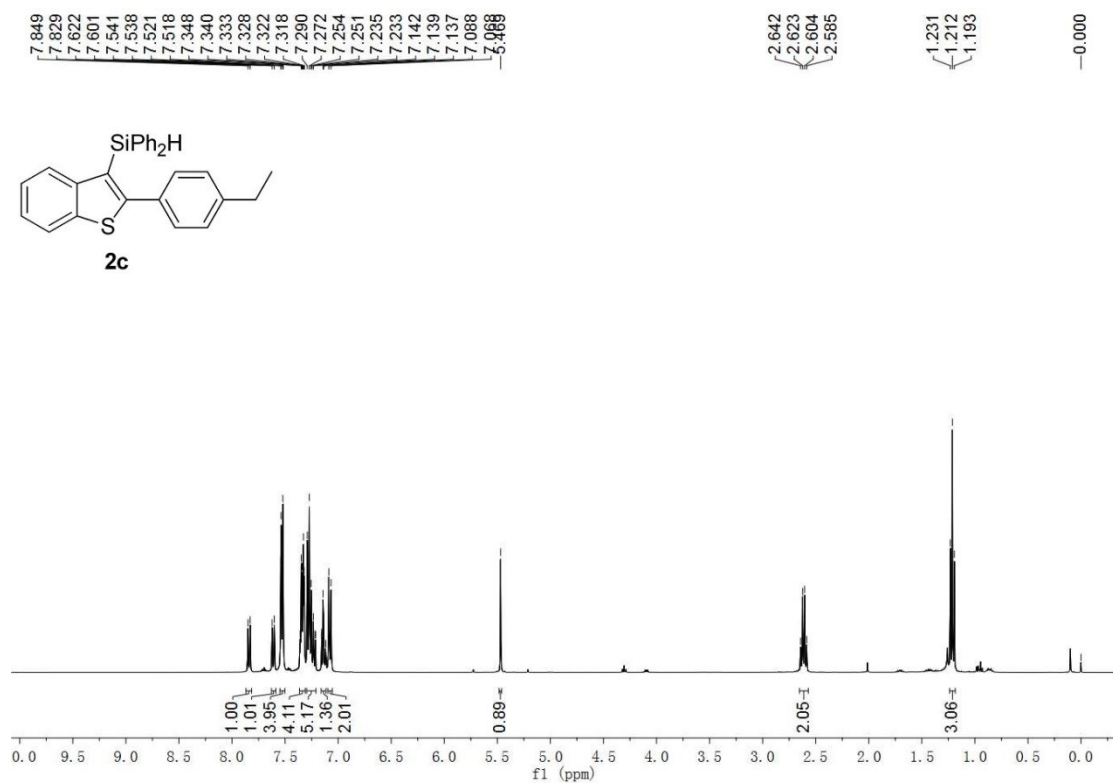
### Reference:

- (1) Yan, J. X.; Xu, J.; Zhou, Y.; Chen, J. L.; Song, Q. L. *Org. Chem. Front.* **2018**, *5*, 1483-1487.
- (2) Mehta, S.; Waldo, J. P.; Larock, R. C. *J. Org. Chem.* **2009**, *74*, 1141-1147.
- (3) Ting, C.-M.; Hsu, Y.-L.; Liu, R.-S. *Chem. Commun.* **2012**, *48*, 6577-6579.
- (4) Mitsudo, K.; Tanaka, S.; Isobuchi, R.; Inada, T.; Mandai, H.; Korenaga, T.; Wakamiya, A.; Murata, Y.; Suga, S. *Org. Lett.* **2017**, *19*, 2564-2567.

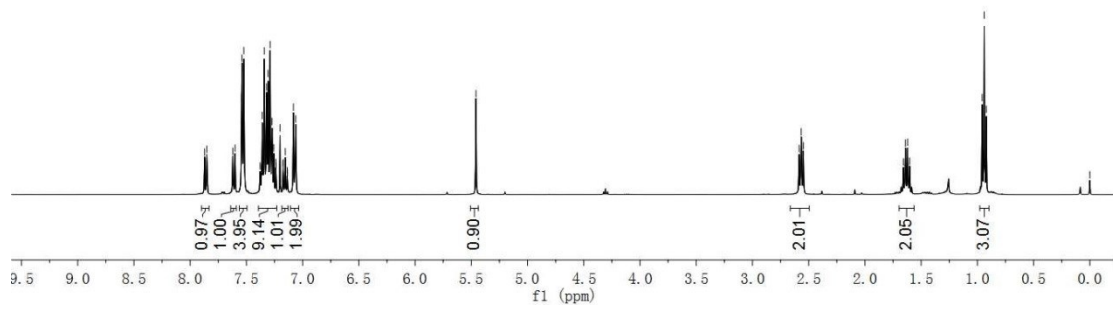
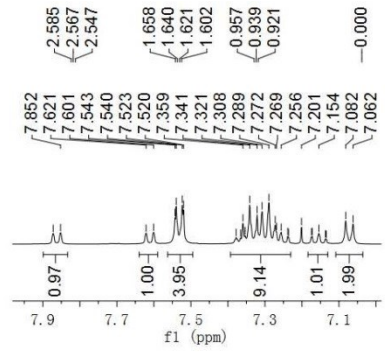
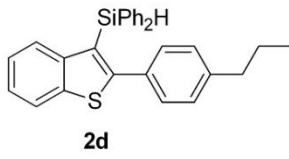




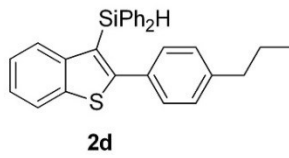




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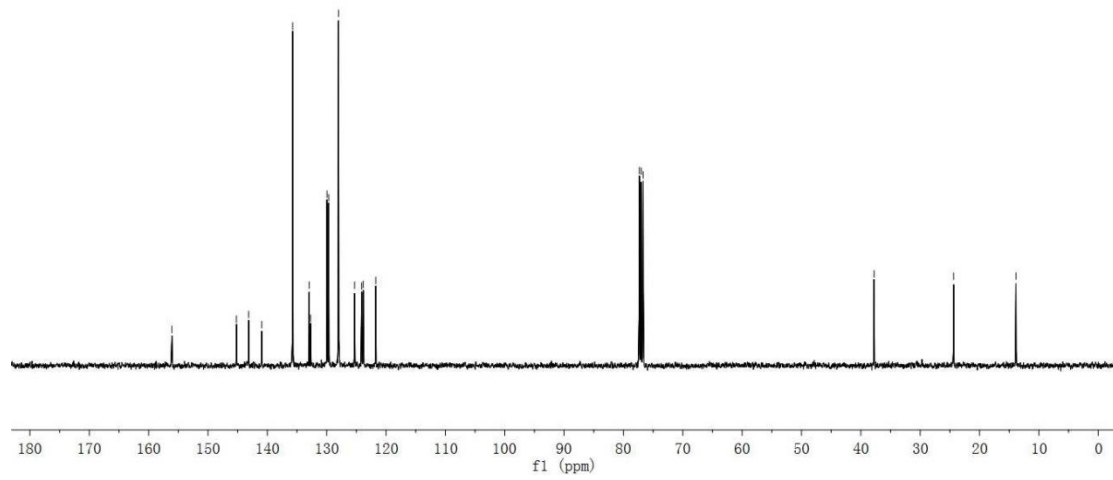


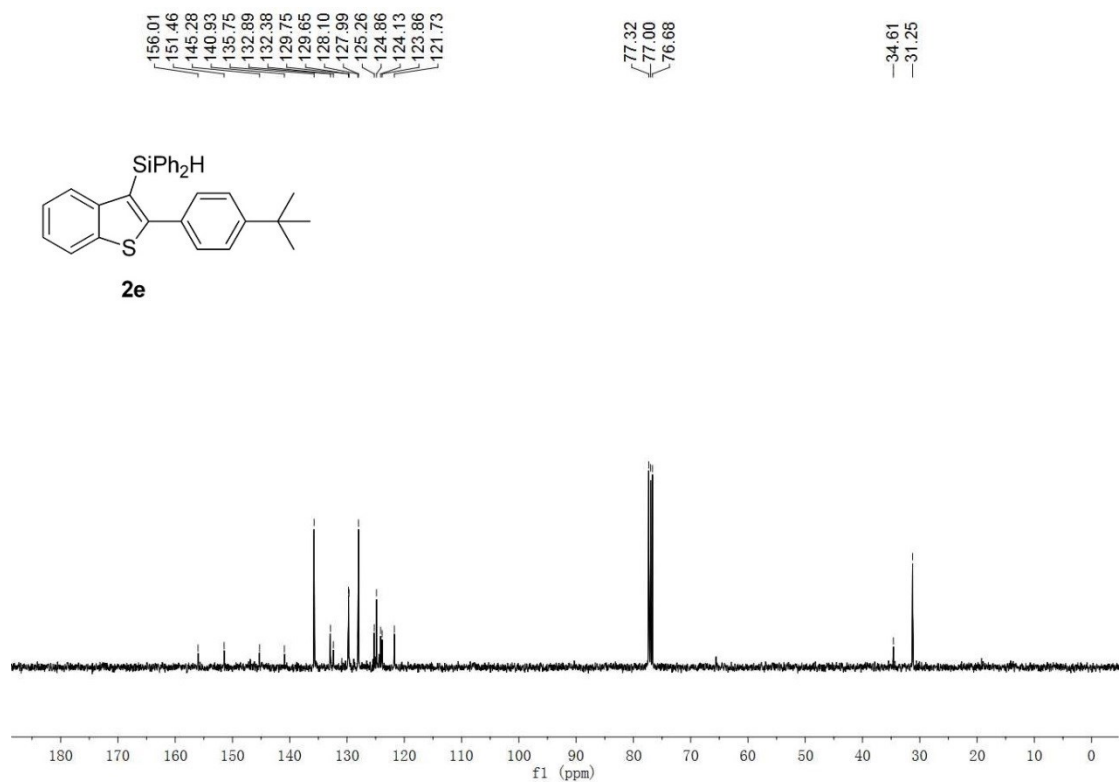
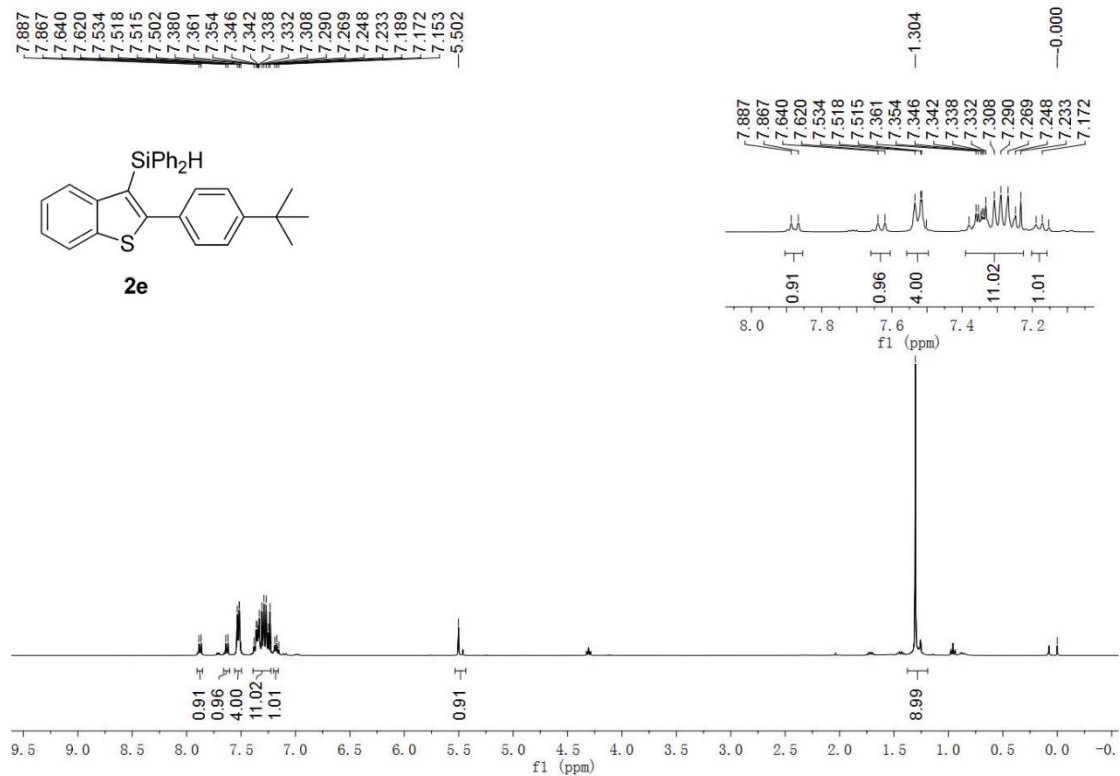
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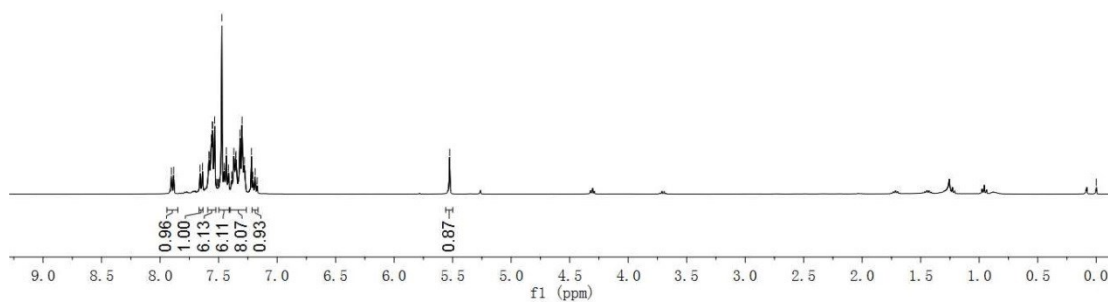
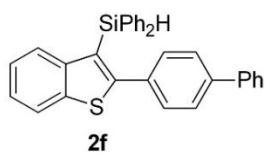
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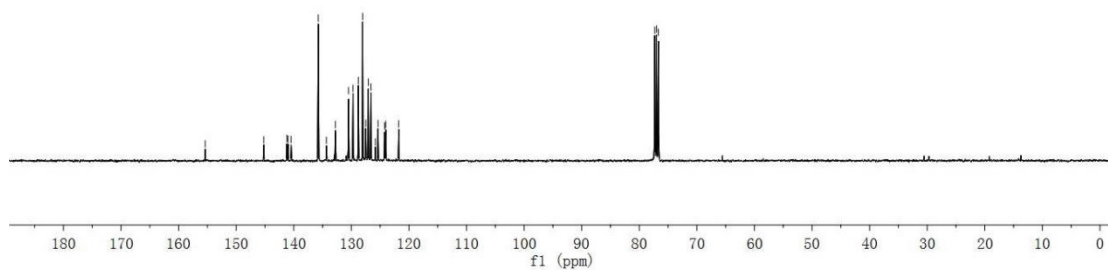
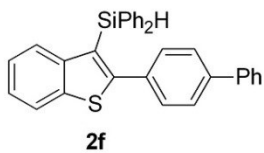
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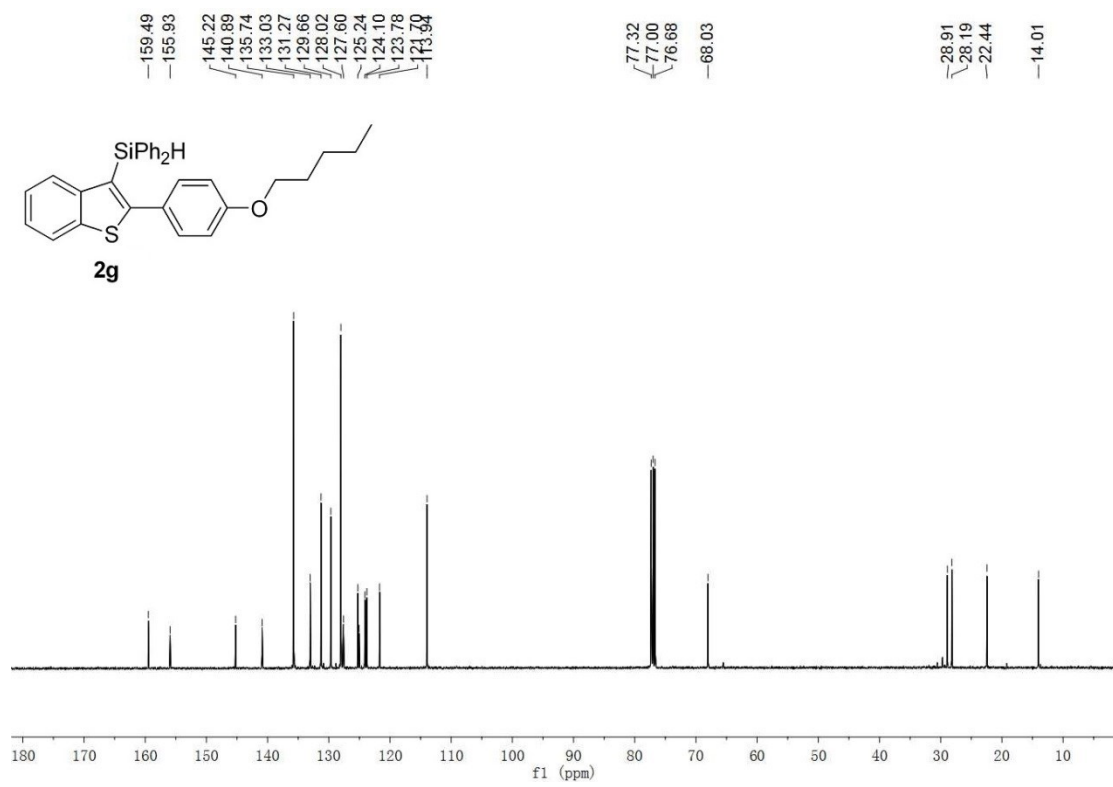
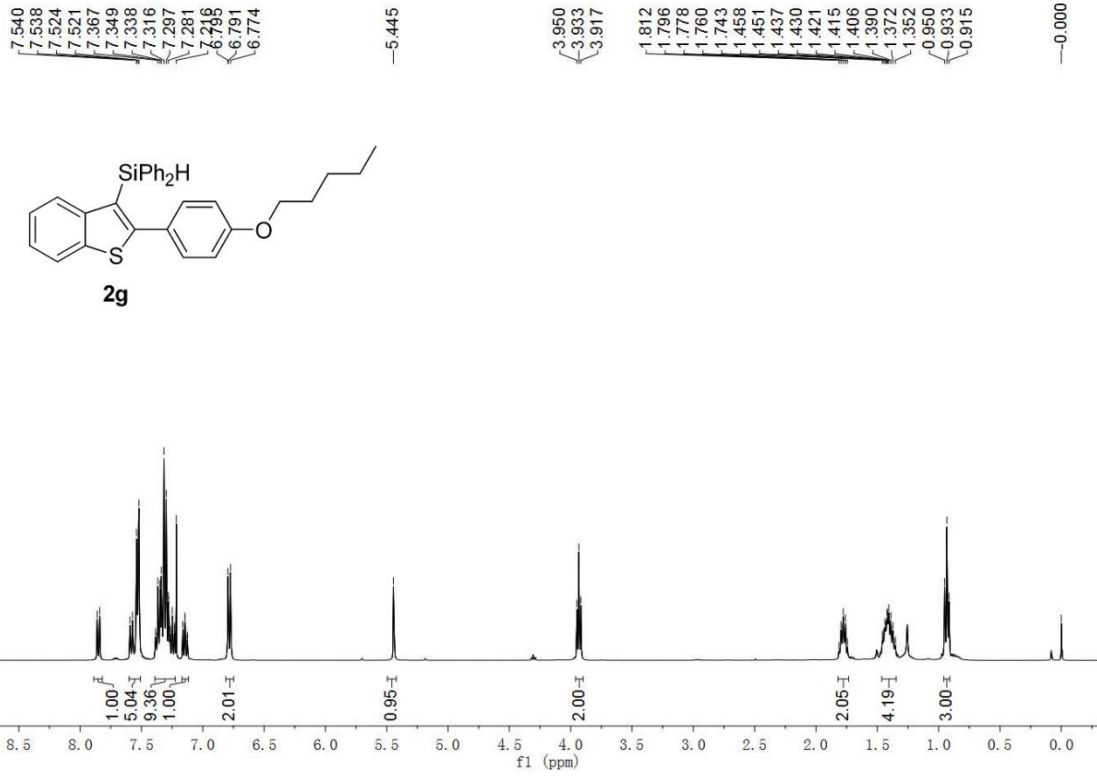
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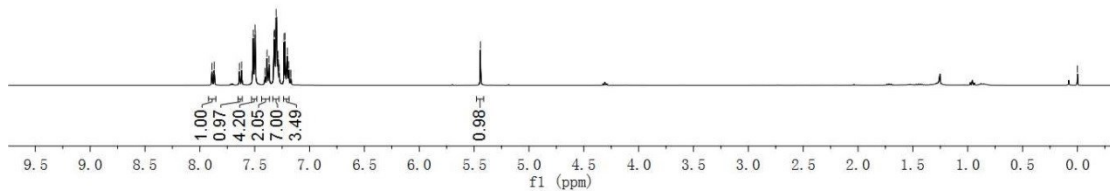
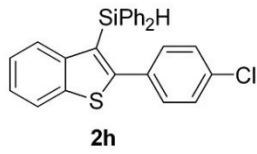
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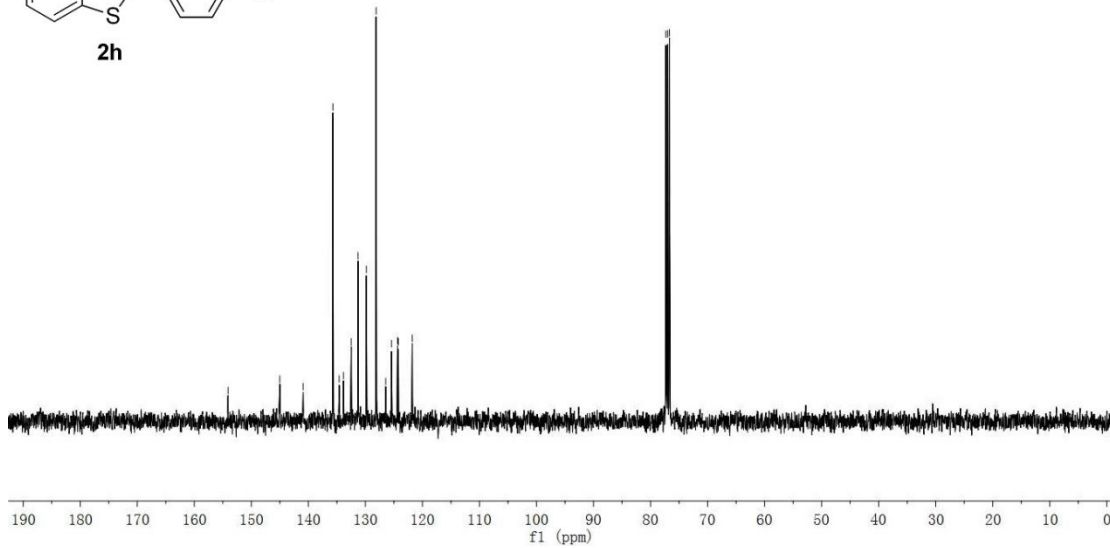
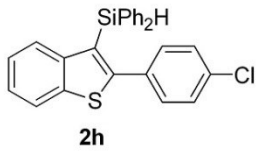


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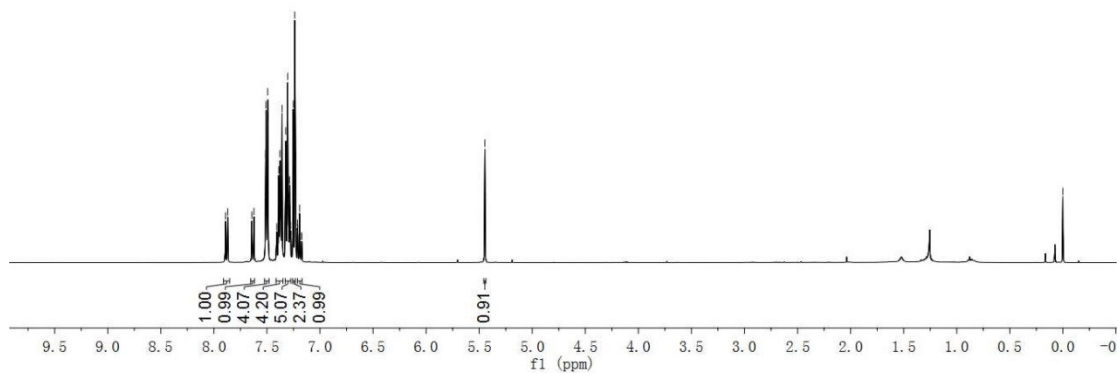
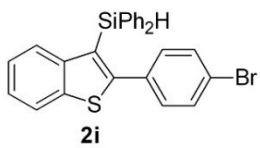


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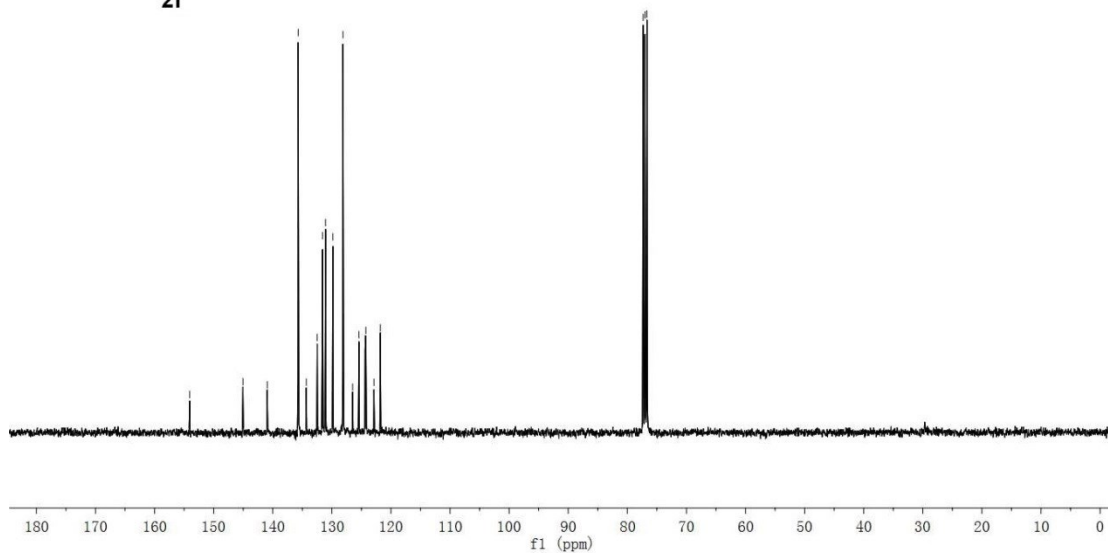
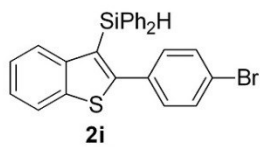


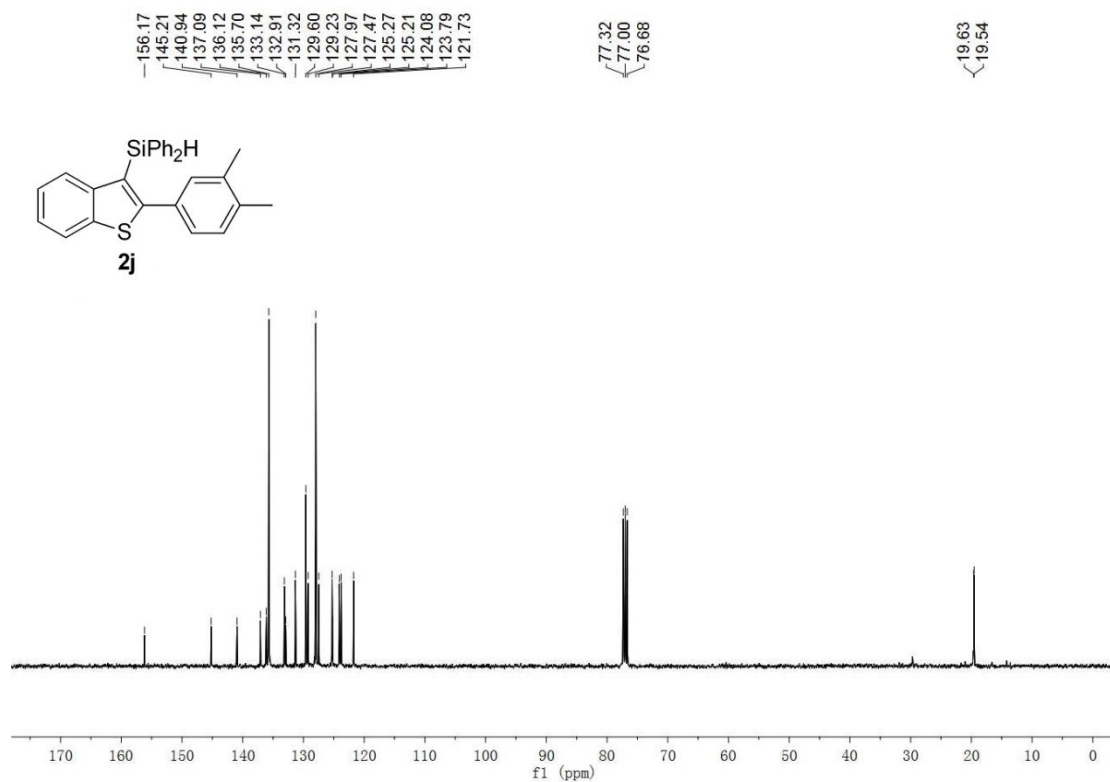
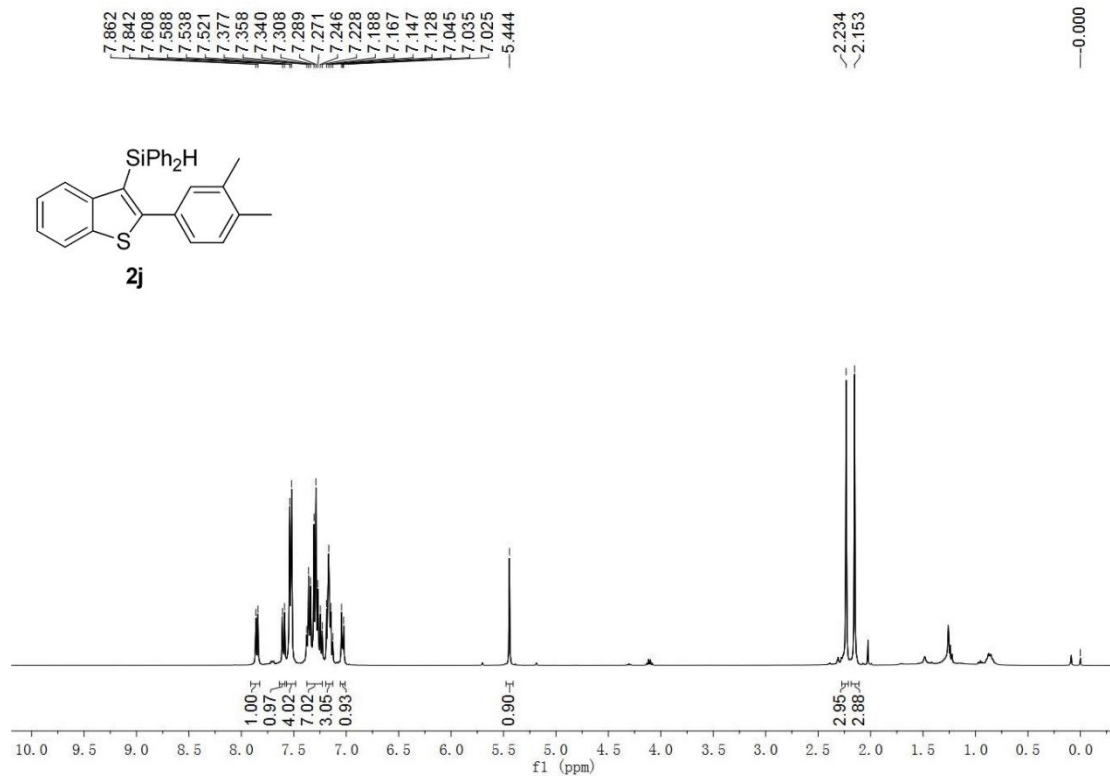
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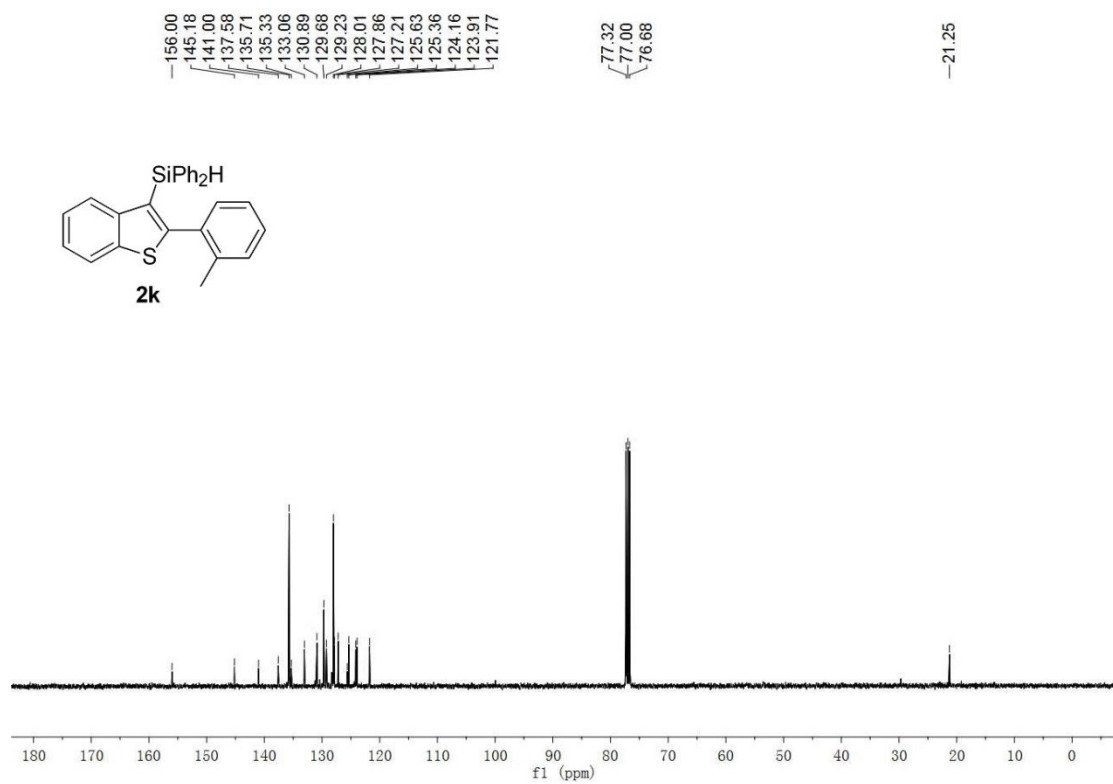
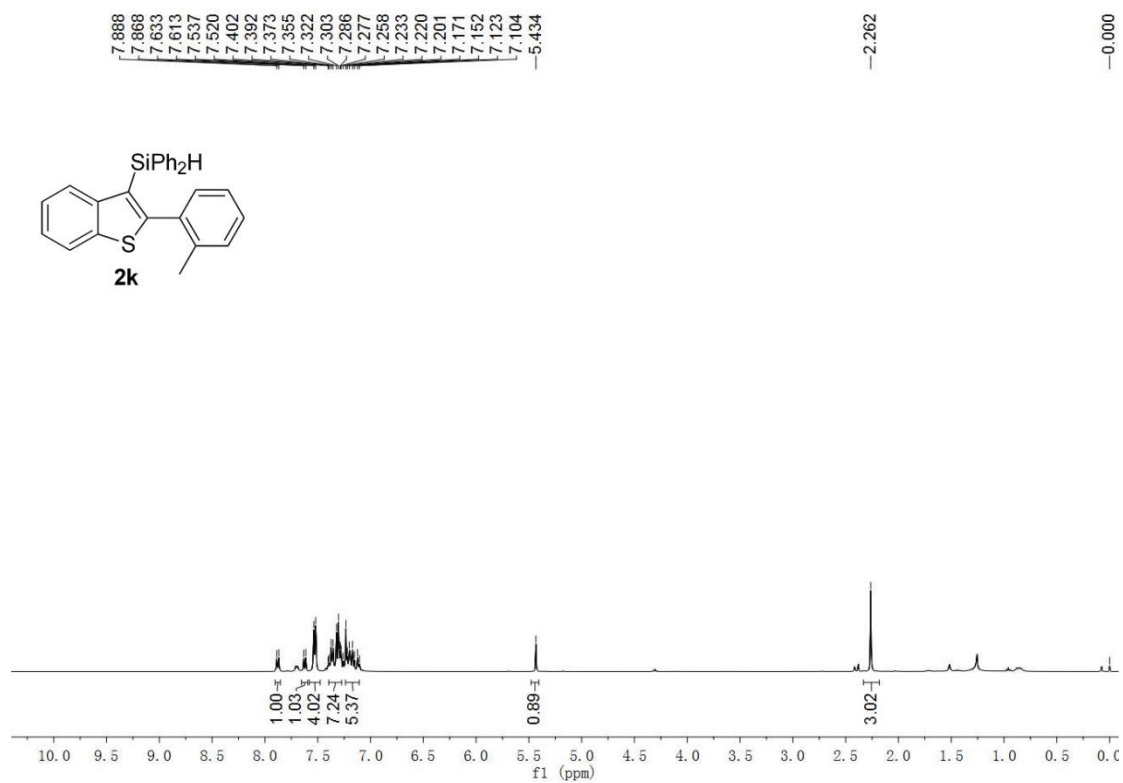
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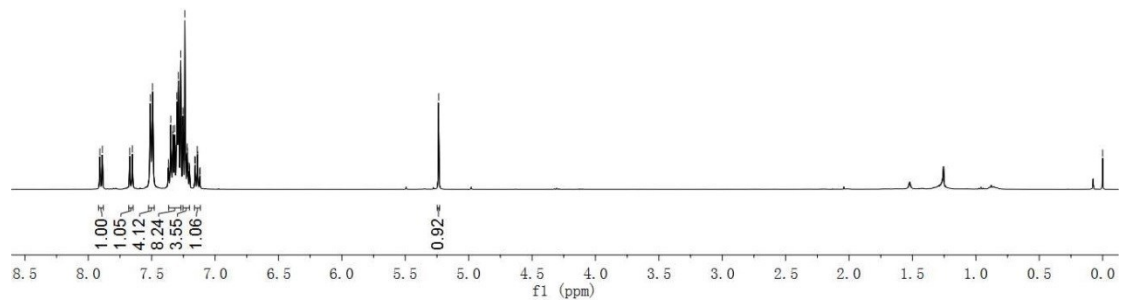
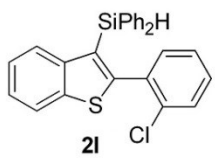




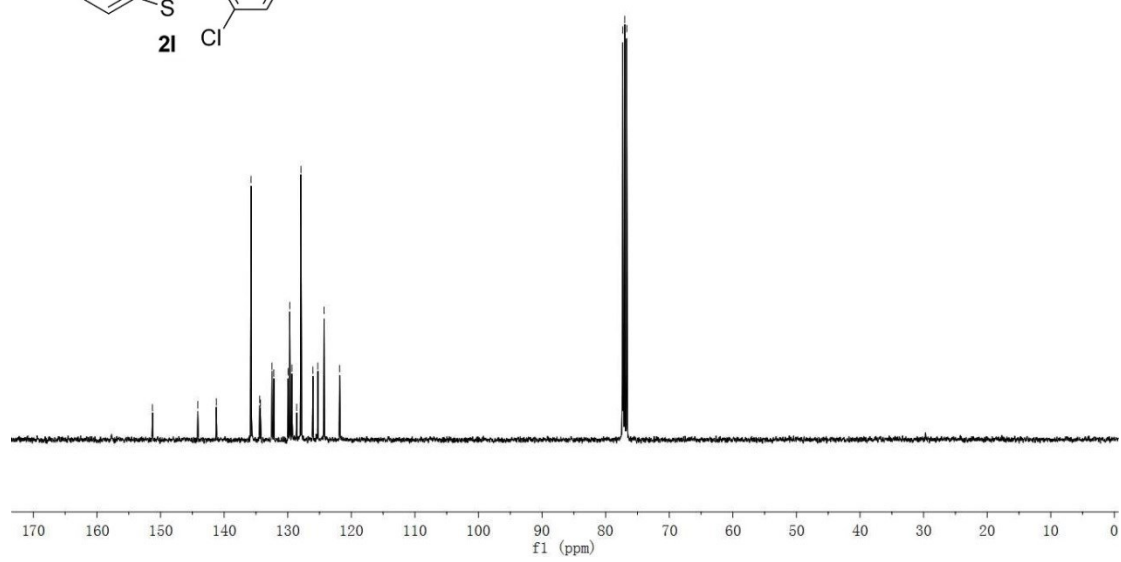
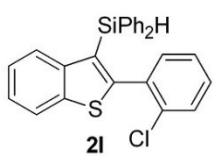


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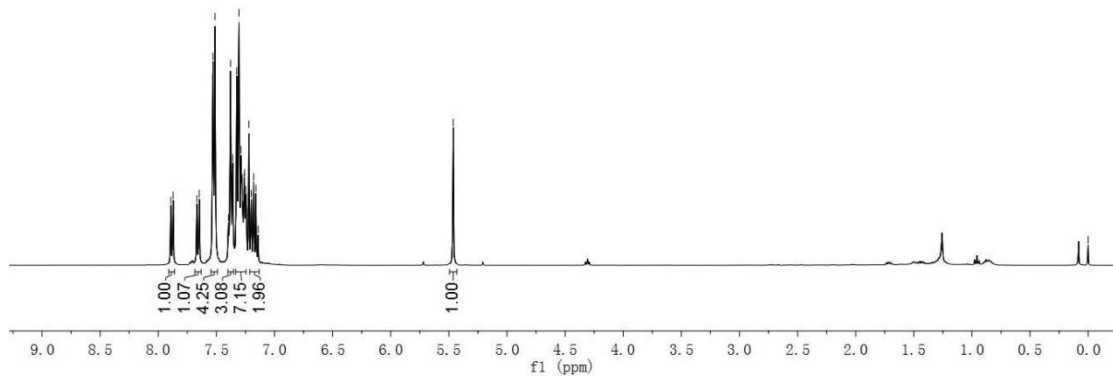
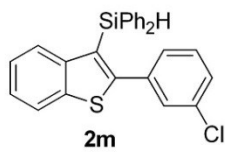


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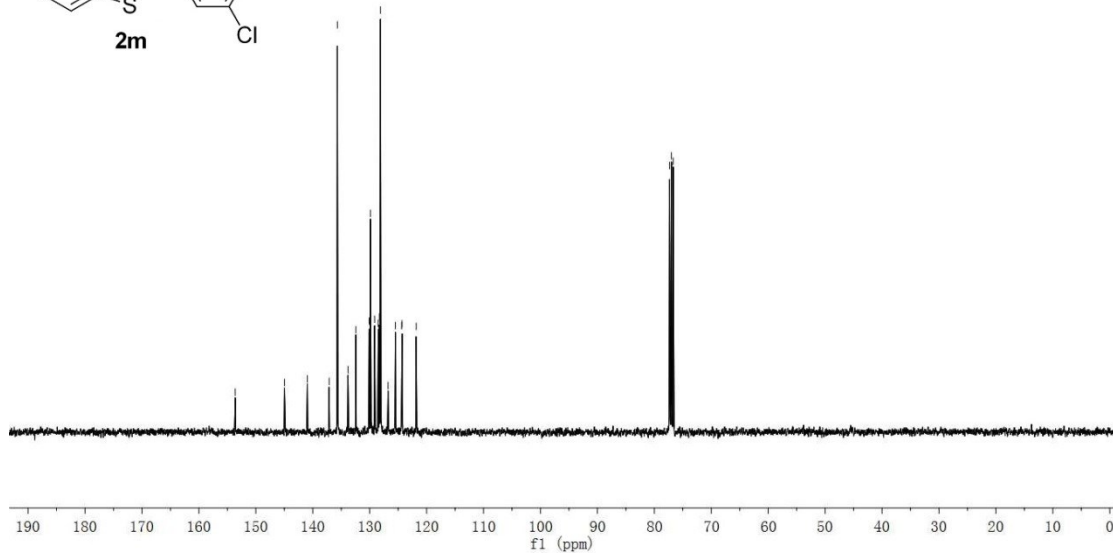
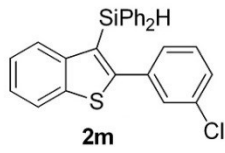
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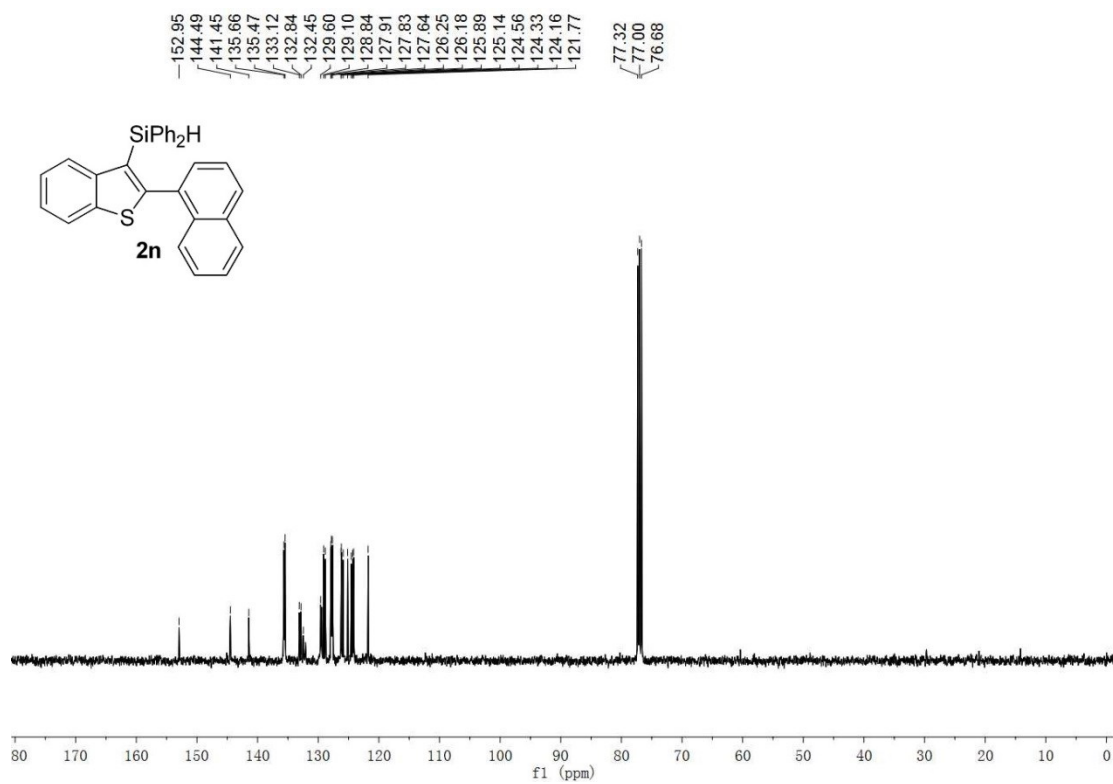
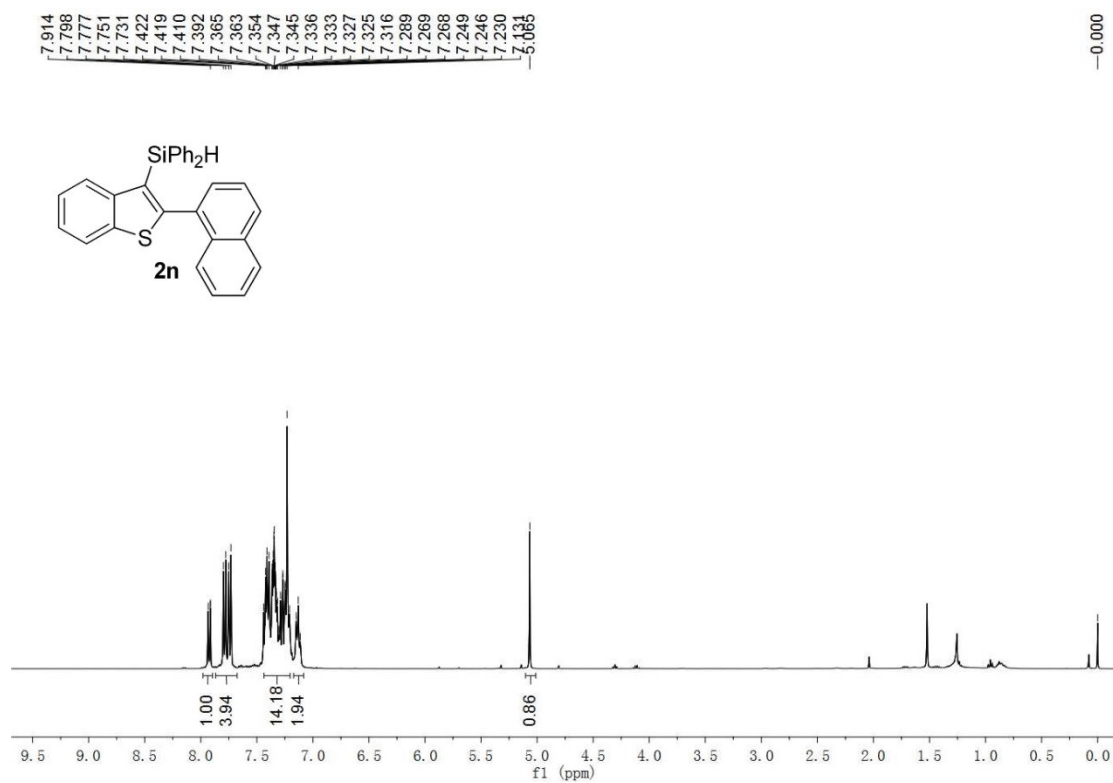
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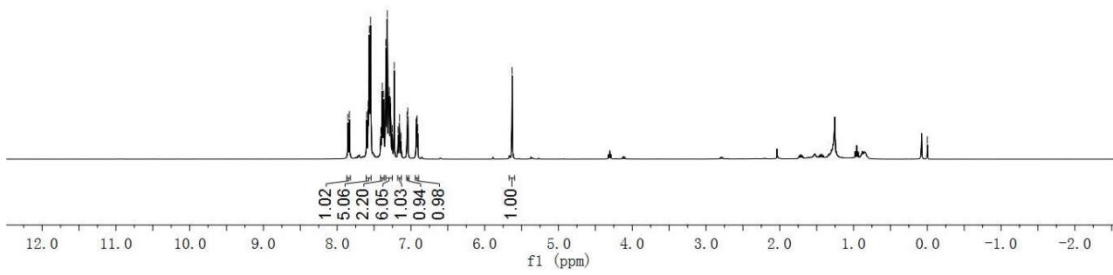
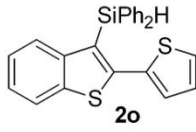
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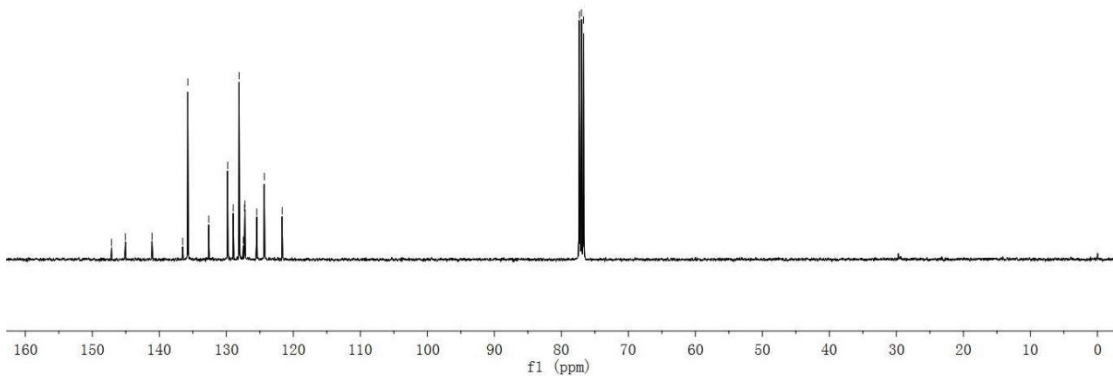
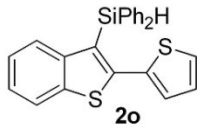
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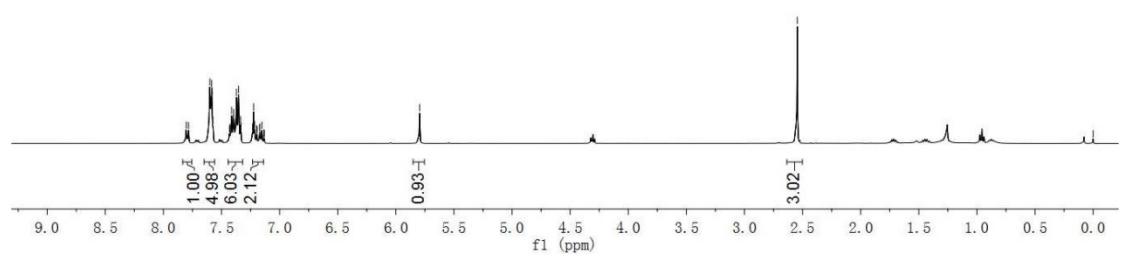
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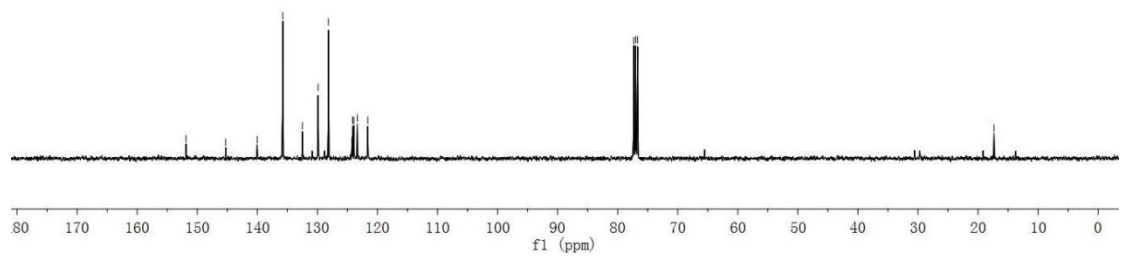
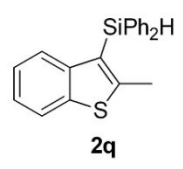
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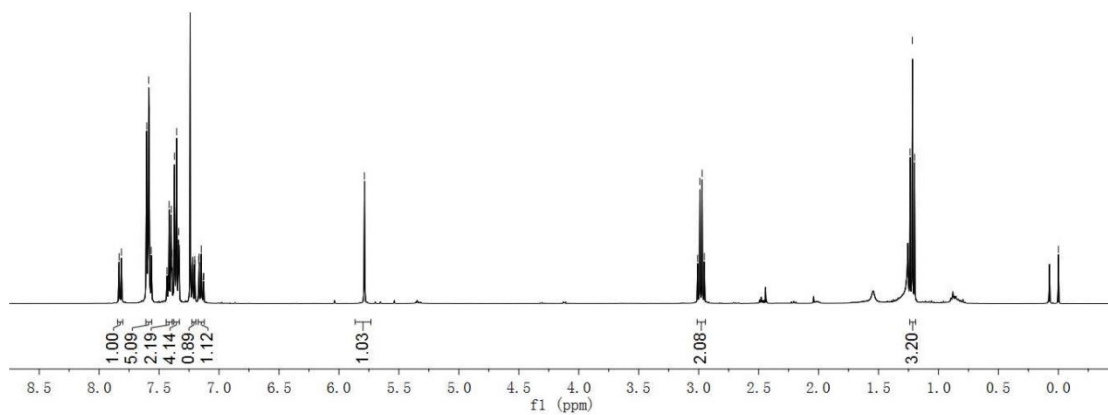
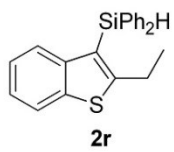


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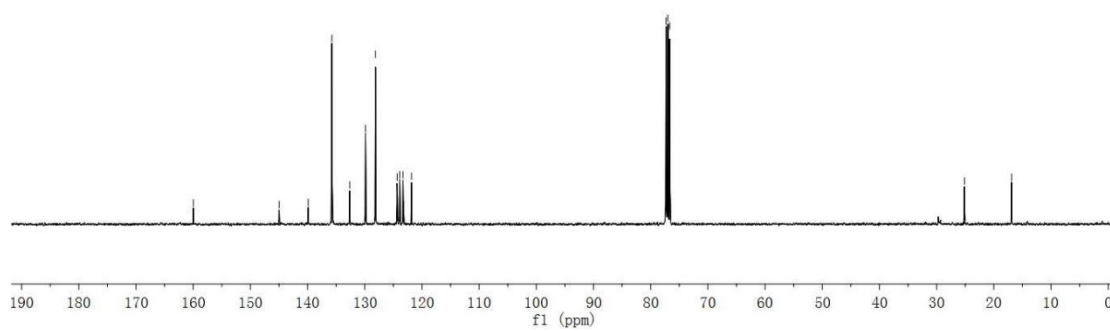
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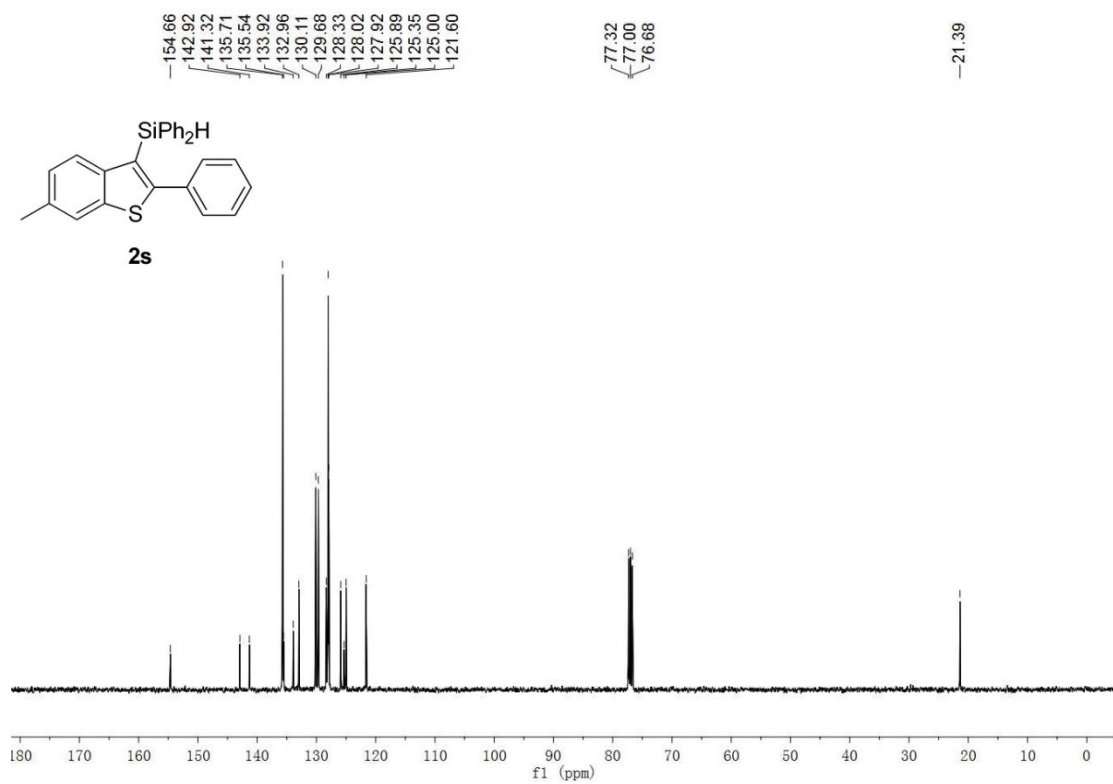
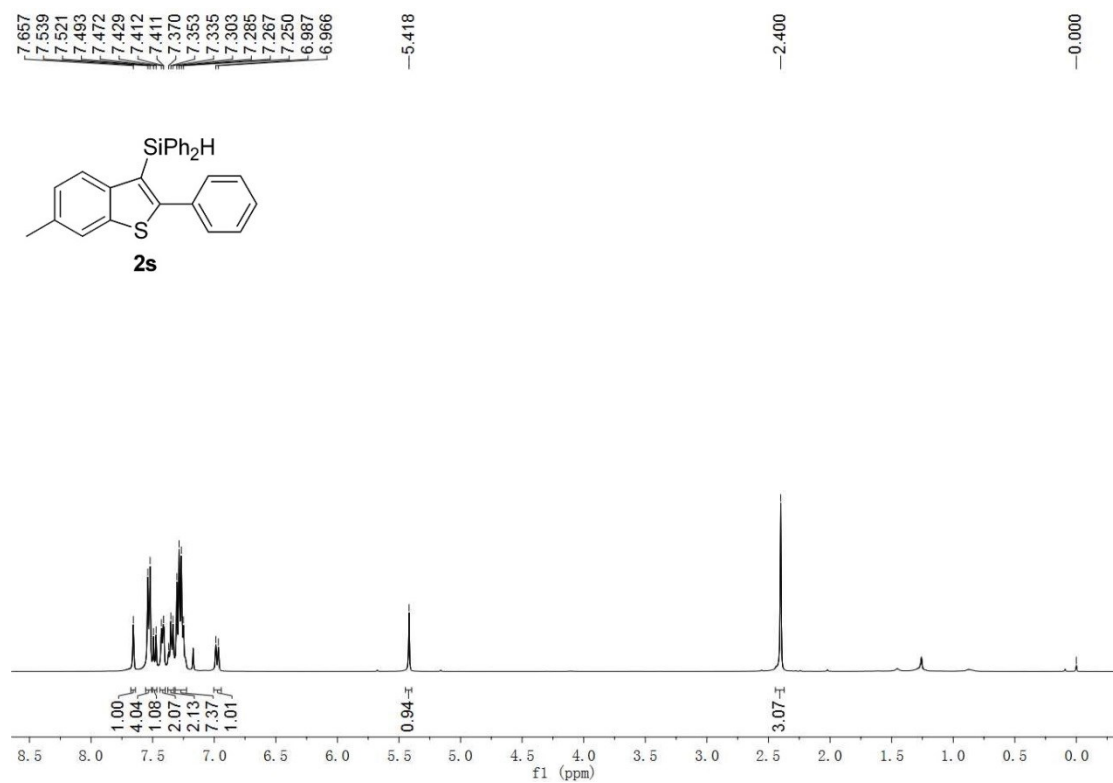


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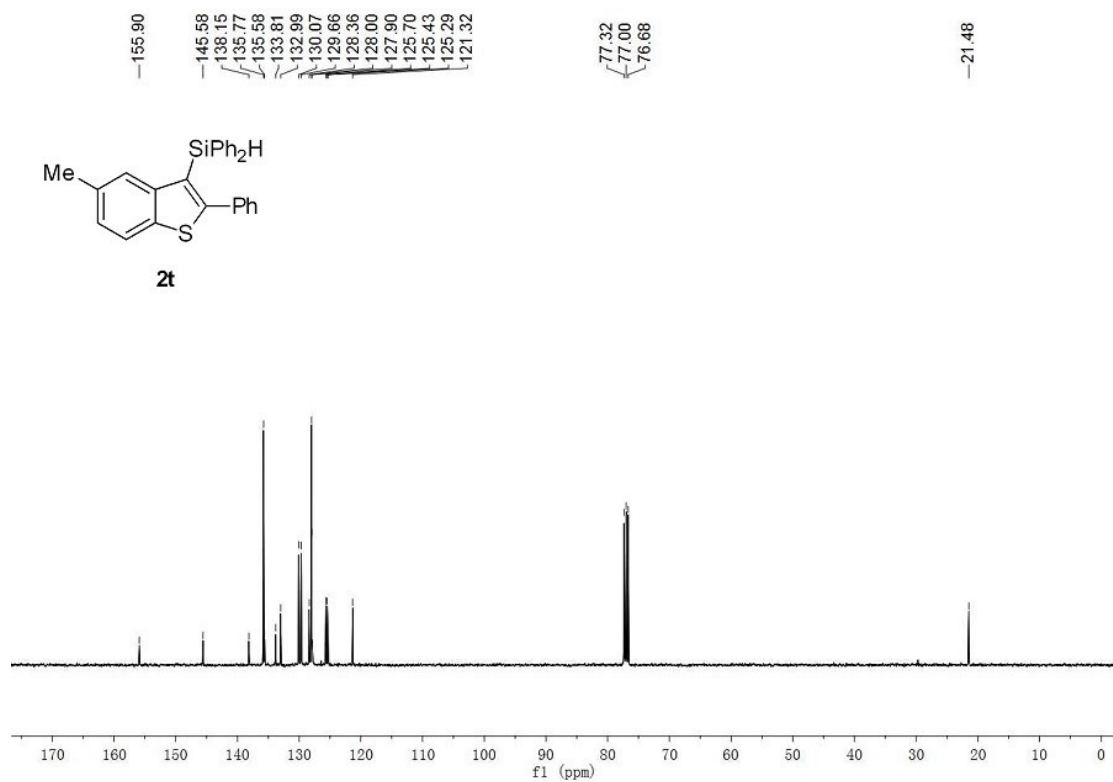
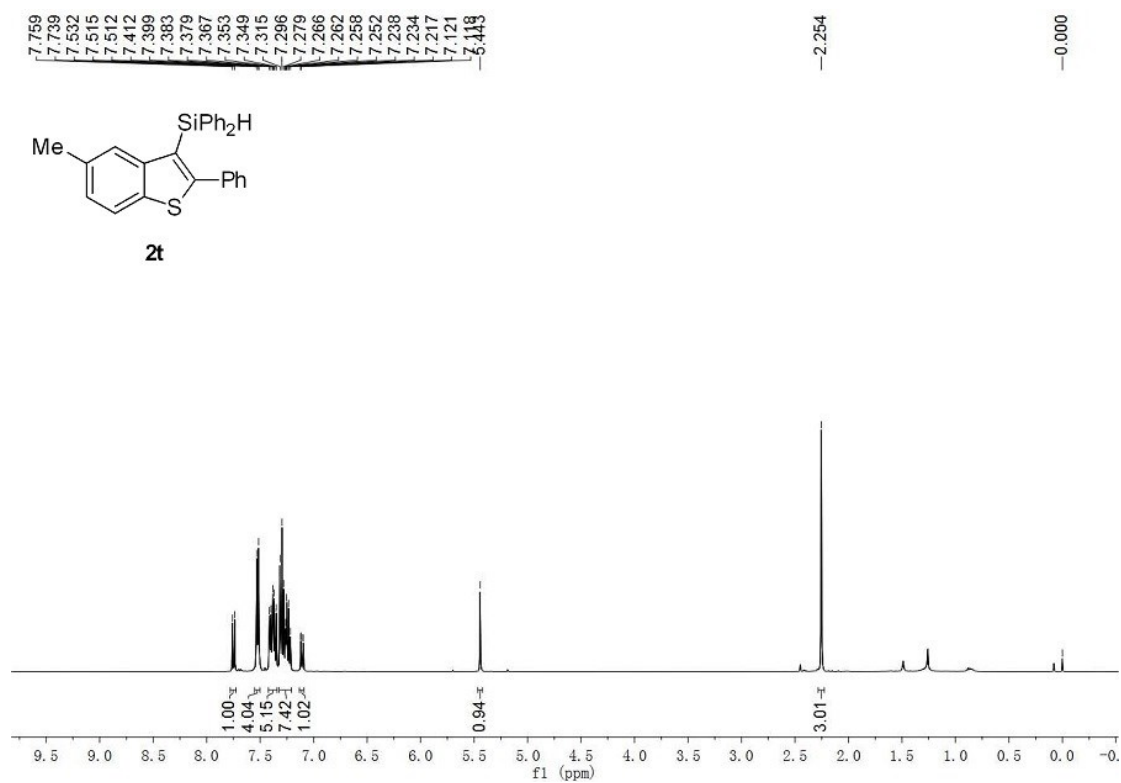
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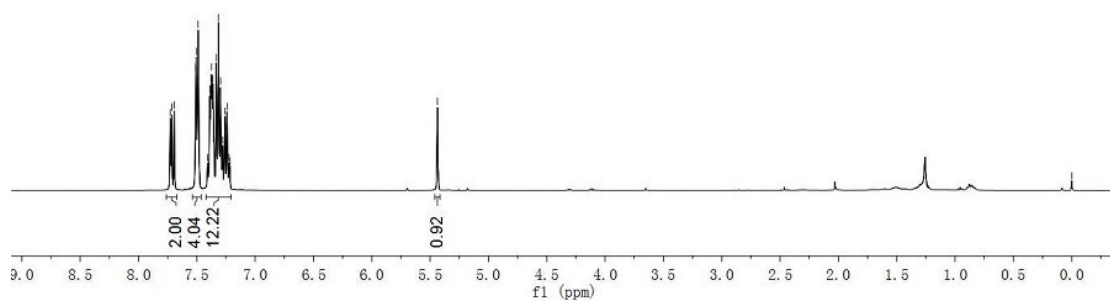




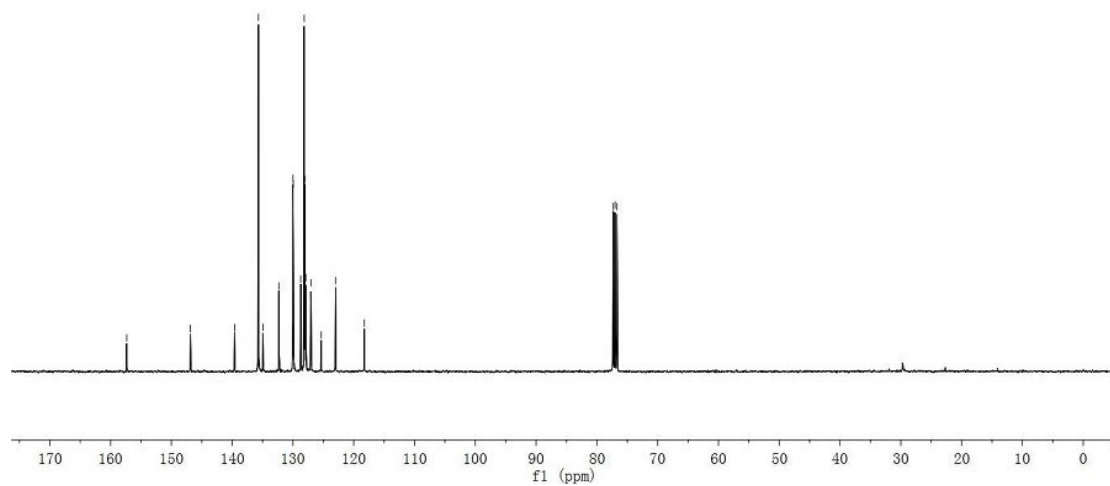
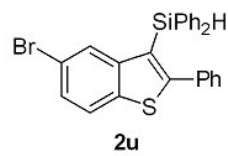


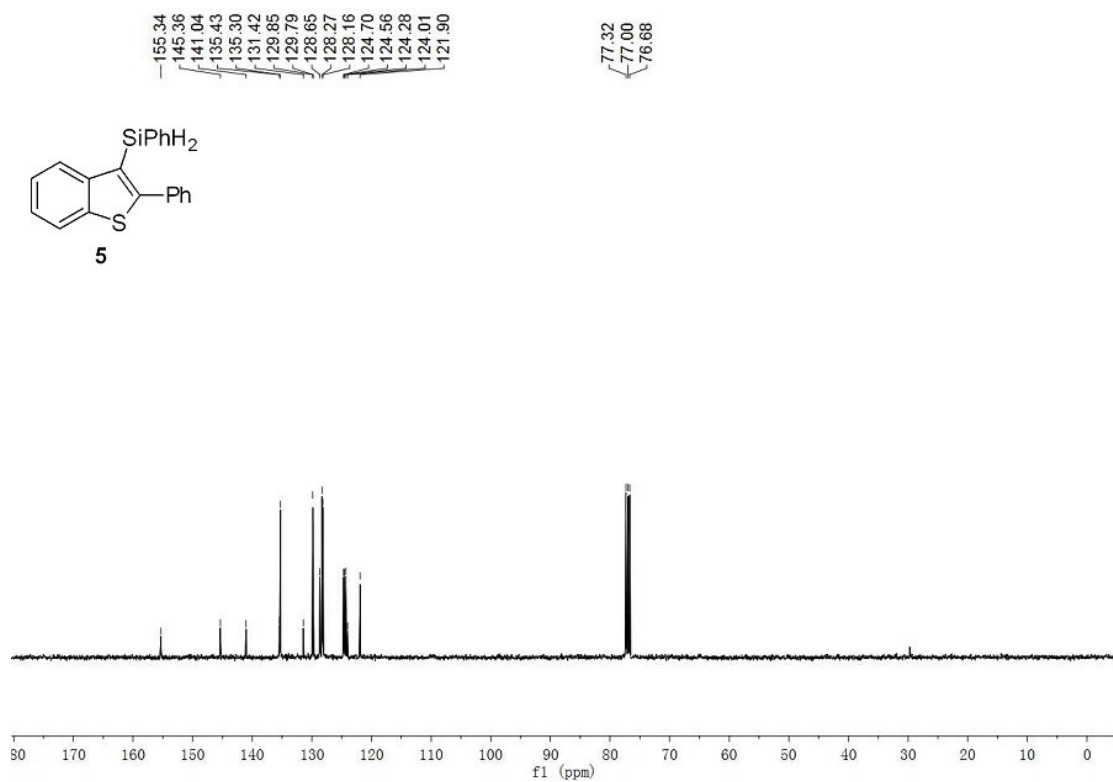
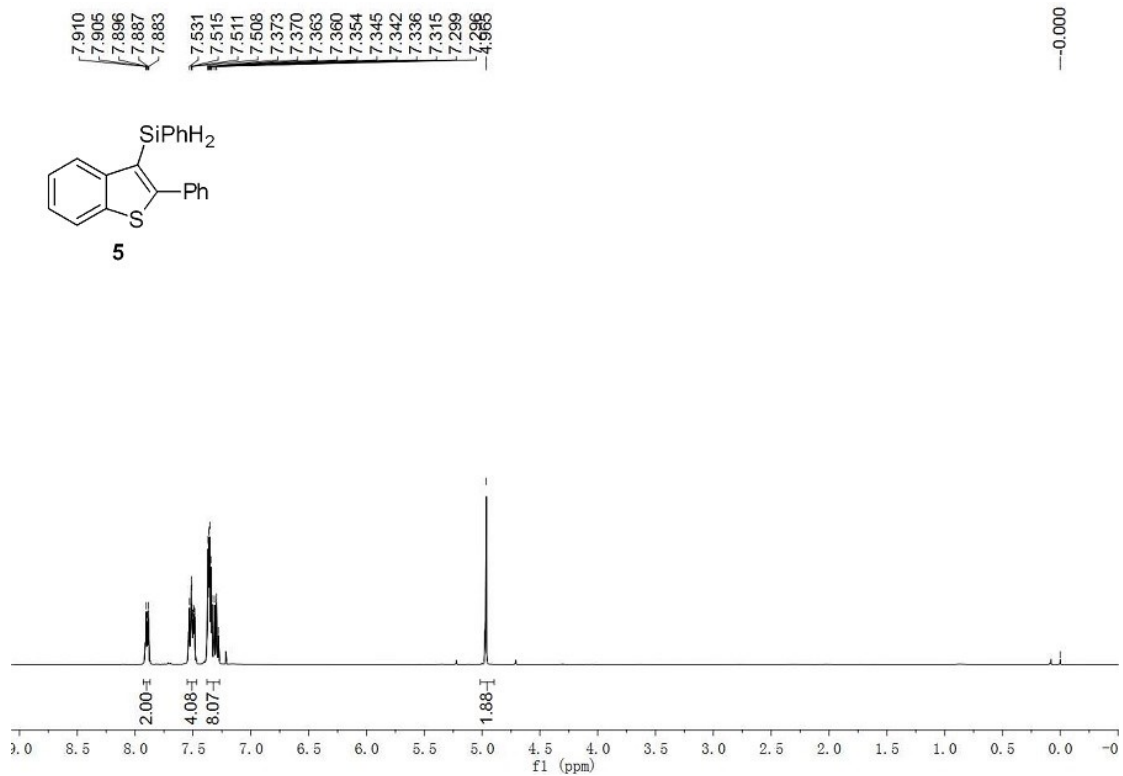
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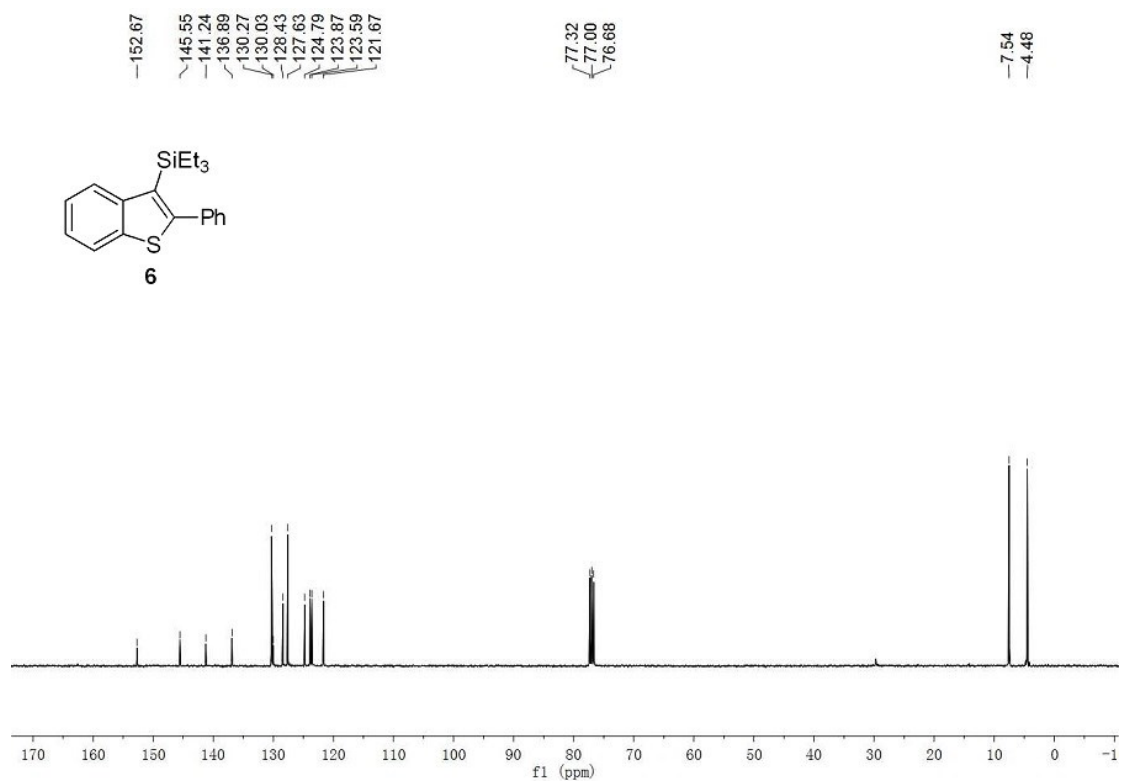
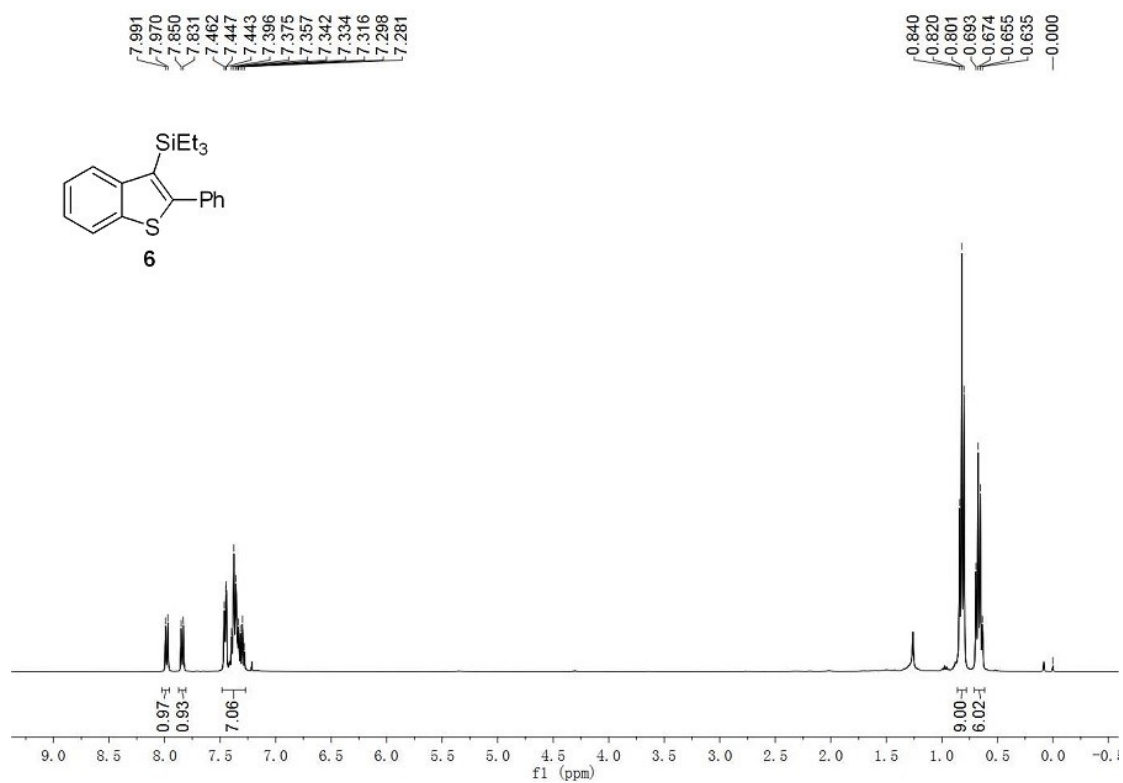
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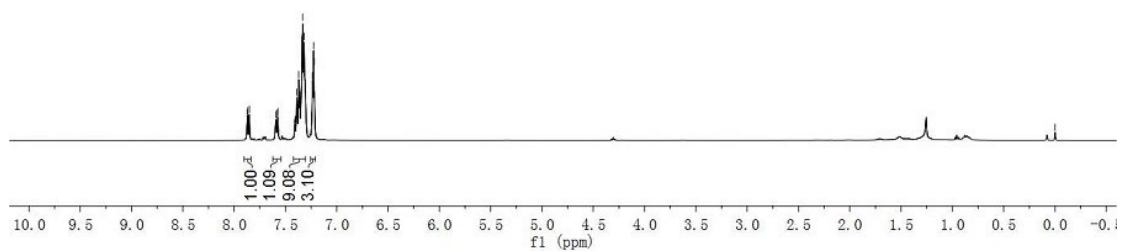
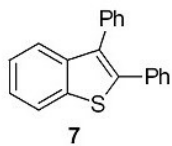






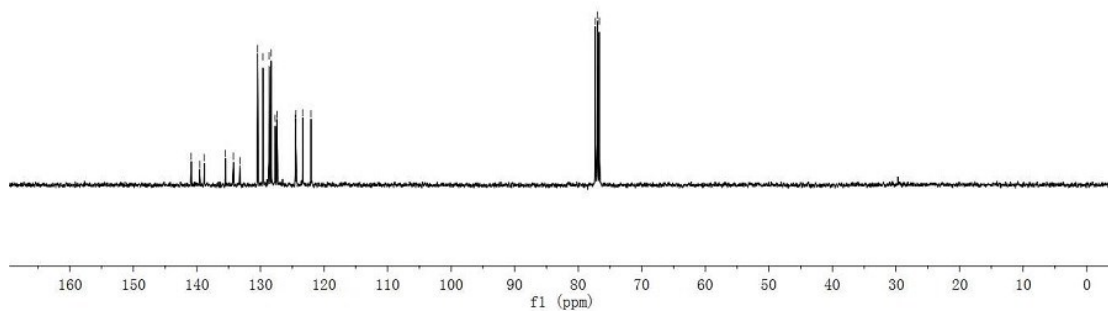
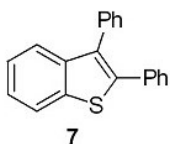
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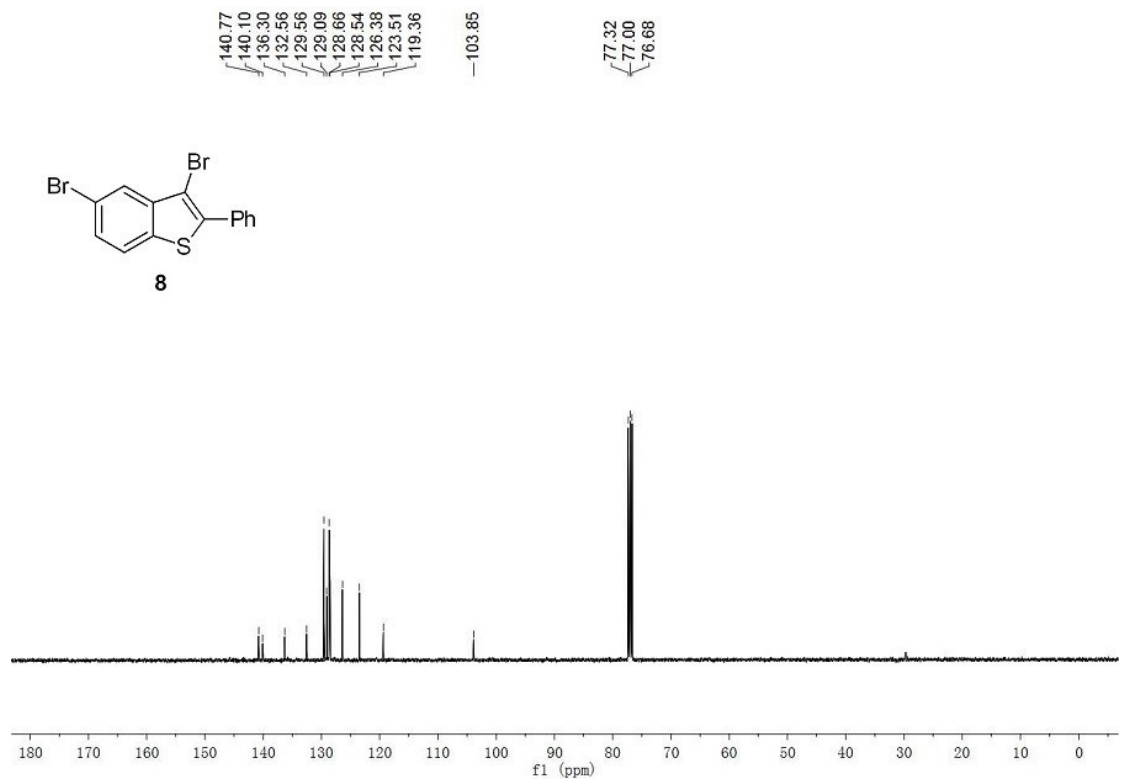
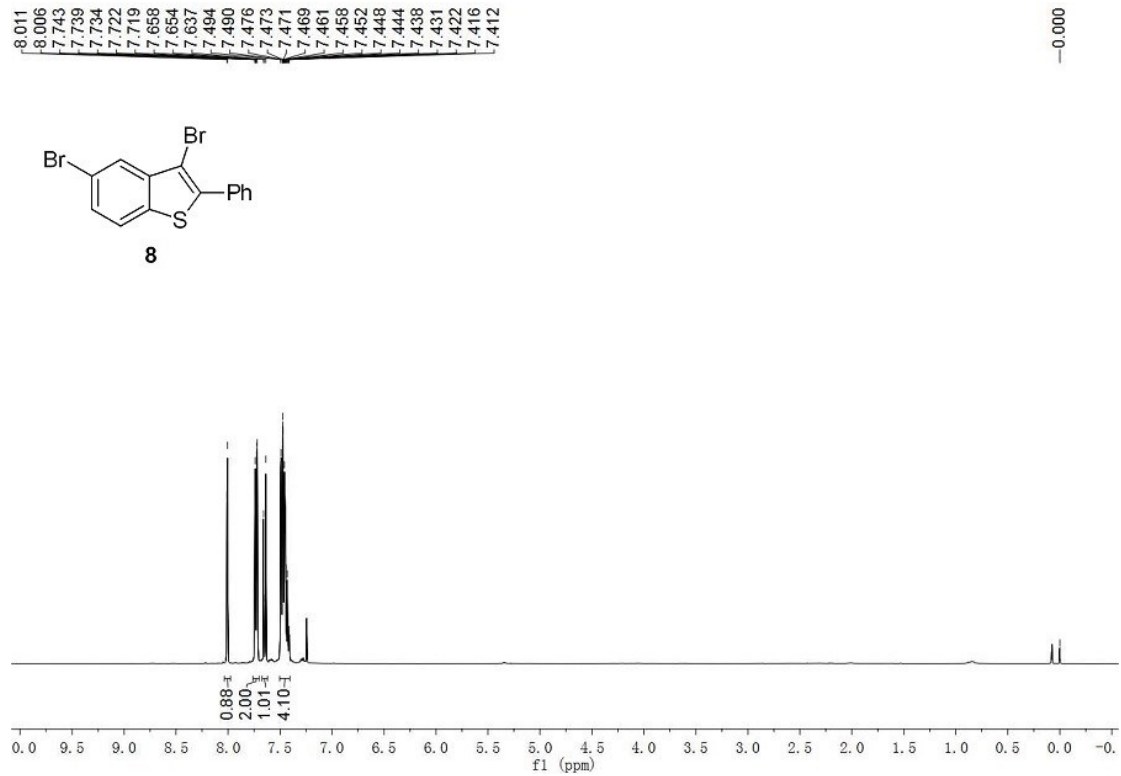
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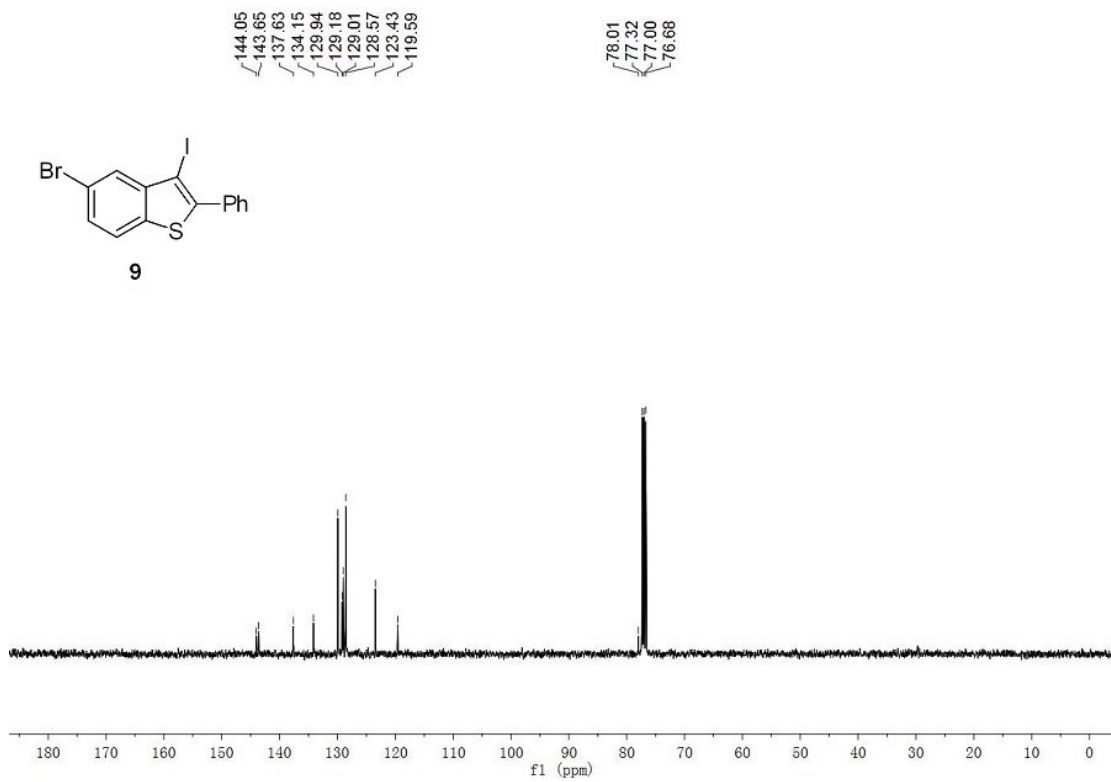
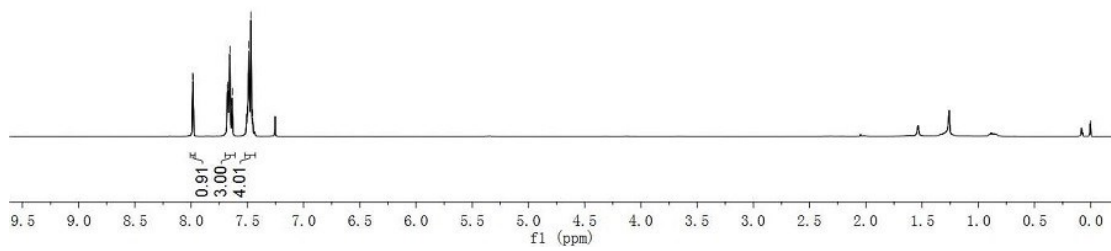


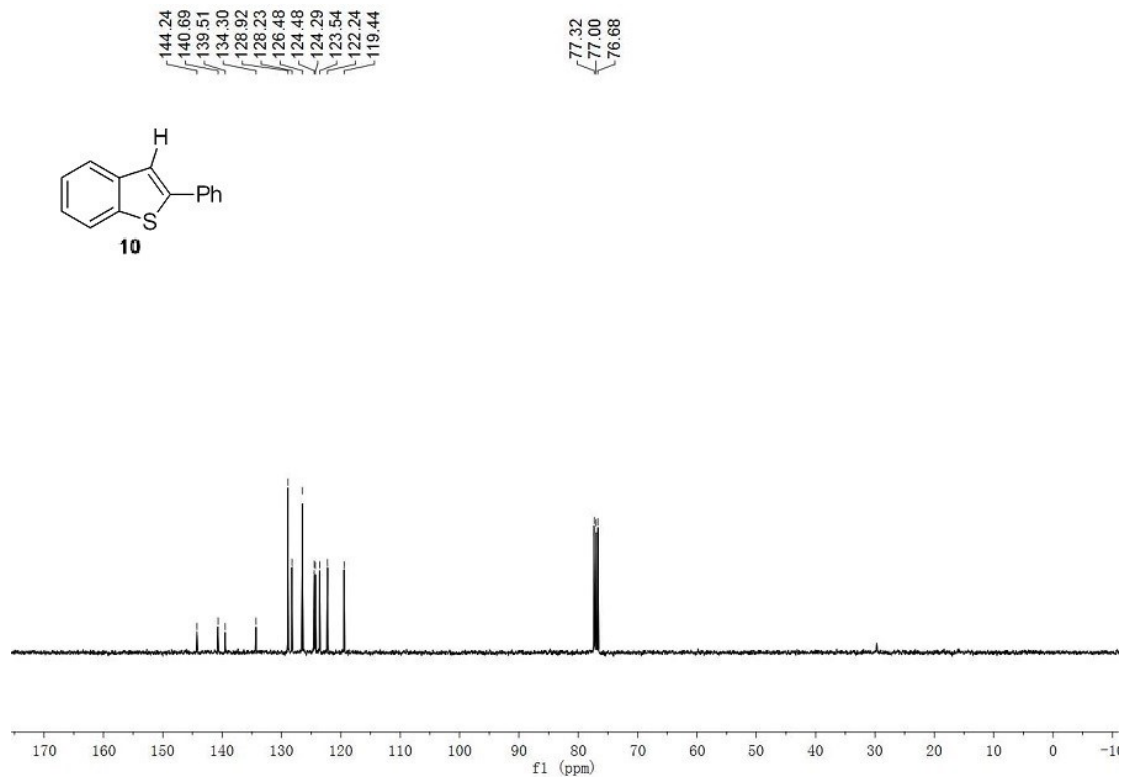
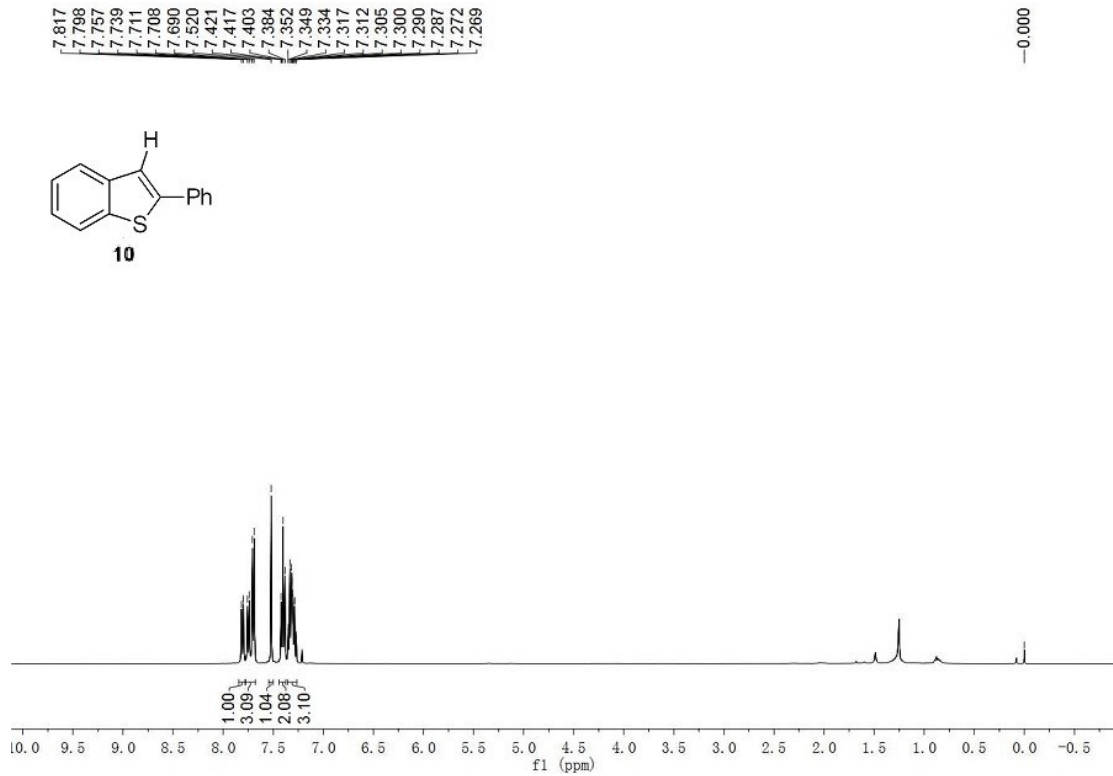
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138.86  
135.53  
134.25  
133.25  
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128.63  
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127.37  
124.52  
124.43  
123.35  
122.05

77.32  
77.00  
76.68





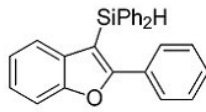




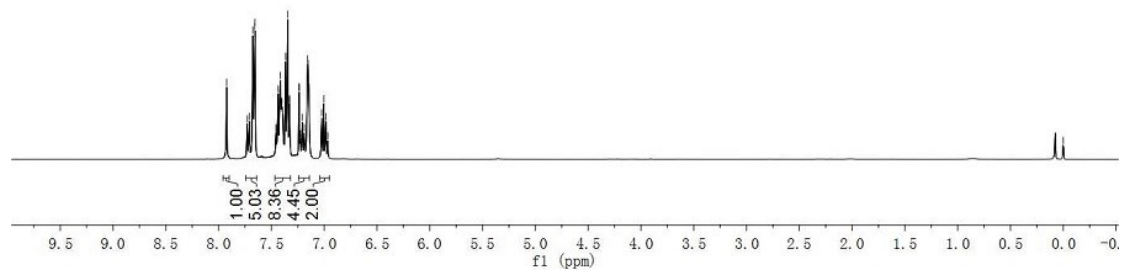


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7.729  
7.710  
7.676  
7.659  
7.656  
7.458  
7.455  
7.437  
7.417  
7.408  
7.404  
7.401  
7.366  
7.348  
7.330  
7.328  
7.242  
7.239  
7.237  
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7.189  
7.157  
7.153  
7.145  
7.024  
7.004  
6.986  
6.967

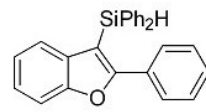
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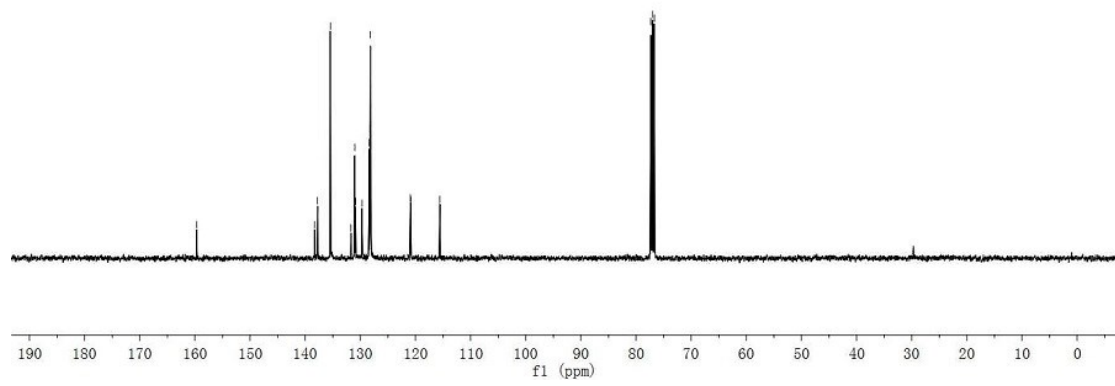
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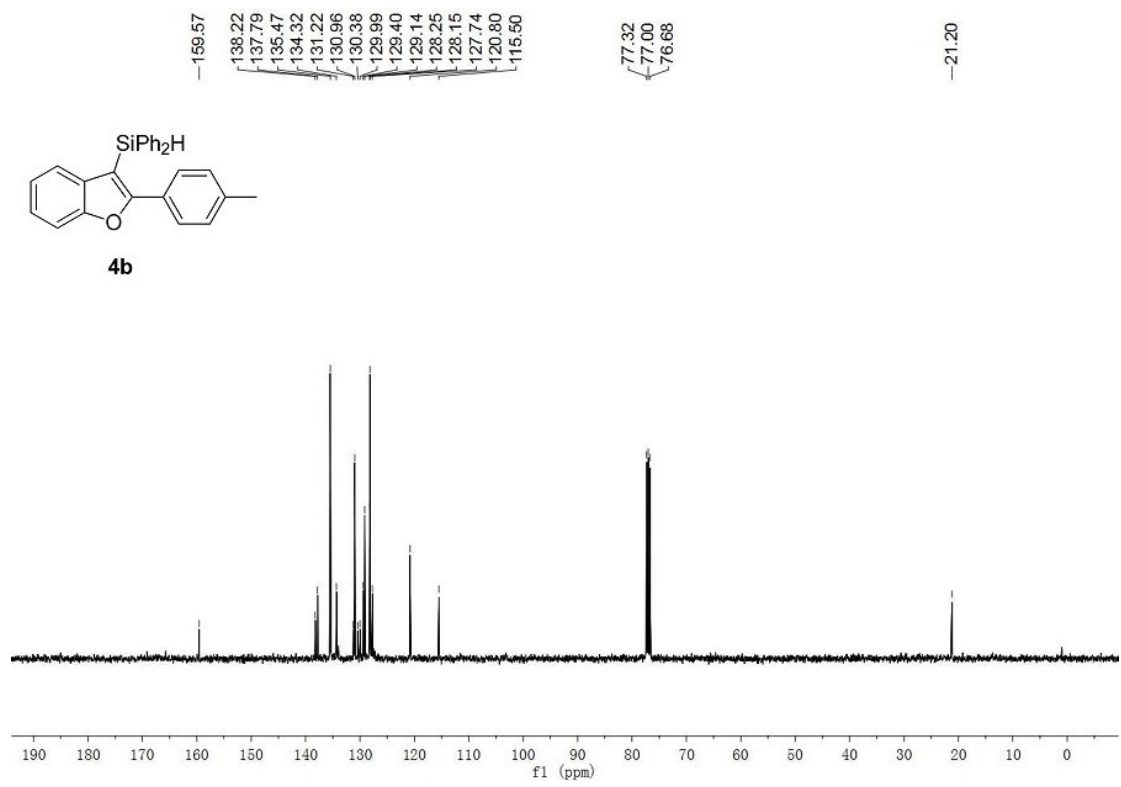
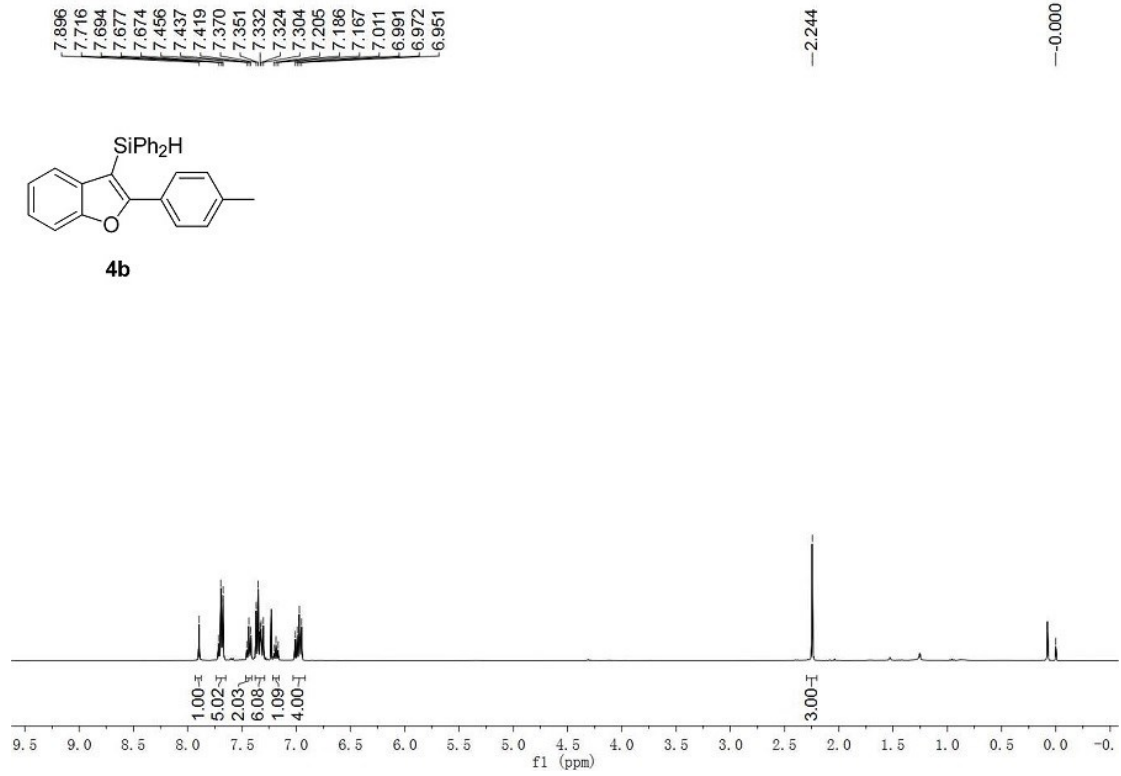


159.71  
138.29  
137.75  
135.43  
131.02  
130.86  
129.70  
128.41  
128.22  
128.05  
120.85  
115.58  
77.32  
77.00  
76.68



4a



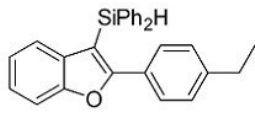


7.901  
7.718  
7.716  
7.694  
7.691  
7.674  
7.671  
7.450  
7.431  
7.415  
7.412  
7.409  
7.365  
7.348  
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7.202  
7.185  
7.167  
7.164  
7.013  
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6.974  
6.954

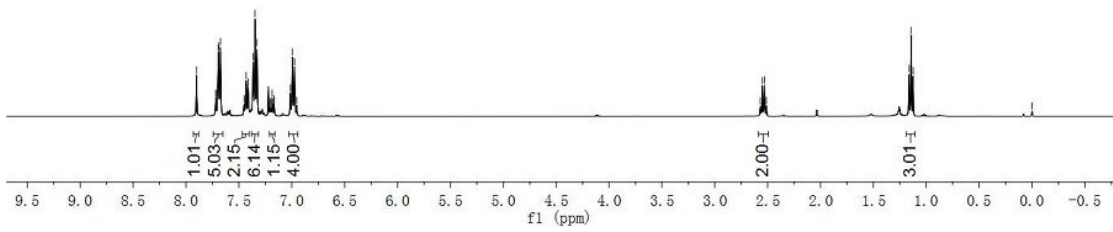
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2.551  
2.532  
2.513

1.163  
1.144  
1.125

-0.000



4d

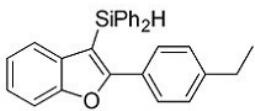


159.56  
144.61  
137.83  
135.63  
135.46  
134.32  
131.23  
130.96  
130.08  
129.40  
128.32  
128.15  
127.93  
120.80  
115.51

77.32  
77.00  
76.68

28.55

15.35



4d

