Supporting Information

General Strategy toward Aromatic 1,2-Ambiphilic Synthons: Pd-Catalyzed Ortho C–H Halogenation of PyDipSi-Arenes

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General Information

NMR spectra were recorded on Bruker Avance DRX-500 (500 MHz) and DPX-400 (400 MHz) instruments. GC/MS analyses were performed on a Hewlett Packard Model 6890 GC interfaced to a Hewlett Packard Model 5973 mass selective detector (15 m × 0.25 mm capillary column, HP-5MS). Column chromatography was carried out employing Merck silica gel (Kieselgel 60, 63-200 μm), ICN silica gel (ICN SiliTech, 63-200 μm), and SiliCycle silica gel (40-63 μm). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated Silica gel plates (60 F_{254}).

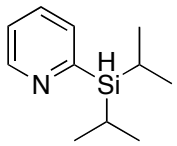
All manipulations with transition metal catalysts were conducted under inert atmosphere using a combination of glovebox and standard Schlenk techniques. Anhydrous tetrahydrofuran, ether, and 1,2-dichloroethane purchased from Aldrich were additionally purified on PureSolv PS-400-4 by Innovative Technology, Inc. purification system and/or stored over calcium hydride. All other reagents were purchased from various commercial sources and used without additional purification.

Synthesis of Starting Materials

Synthesis of 2-(diisopropylsilyl)pyridine 19:

To a solution of 2-bromopyridine (16.05 ml, 26.01 g, 164.6 mmol) in diethyl ether (85 ml) was added dropwise a solution of *n*-butyllithium (63.56 ml, 2.59 M in hexanes, 164.6 mmol) at -78 °C under argon atmosphere. The reaction mixture was stirred at -78 °C for 40 min and then was transferred via cannula to a solution of chlorodiisopropylsilane (24.81 g, 164.6 mmol) in diethyl ether (160 ml) at -78 °C. After being stirred for 2 h at -78 °C, the solution was allowed to warm to rt overnight. The mixture was then filtered through celite and concentrated under a reduced pressure. Subsequent fractional distillation of the residual oil at ca. 1 Torr afforded the 2-(diisopropylsilyl)pyridine as a colorless liquid in 91% yield.

19:



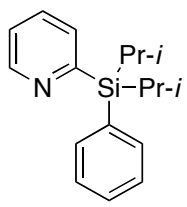
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.77 (ddd, J = 4.77, 1.65, 1.10 Hz, 1 H), 7.57 (td, J = 7.52, 1.83 Hz, 1 H), 7.51 (dt, J = 7.52, 1.28 Hz, 1 H), 7.20 (ddd, J = 7.57, 4.91, 1.47 Hz, 1 H), 4.01 (tt, J = 3.30 Hz; $^{1}J_{Si\text{-}H}$ = 92.25 Hz, 1 H), 1.25 - 1.40 (m, 2 H), 1.10 (d, J = 7.34 Hz, 6 H), 1.02 (d, J = 7.52 Hz, 6 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.9, 150.2, 133.6, 131.4, 122.8, 18.6, 18.6, 10.6

Synthesis of 2-(diisopropyl(phenyl)silyl)pyridine 1a:

To a solution of phenyllithium (5.5 ml, 1.9 M in dibutyl ether, 11.0 mmol) in THF (15 ml) was added dropwise neat 2-(diisopropylsilyl)pyridine **19** (1.93 g, 10.0 mmol) at -78 °C under argon atmosphere. The reaction mixture was stirred at -78 °C for 1 h and then was allowed to warm to rt. The mixture was then poured into 150 ml of hexanes containing small amount of water to neutralize LiH. The resulting solution was dried over anhydrous sodium sulfate, filtered, and concentrated under a reduced pressure. The residual oil was purified by flash column chromatography (silica gel, eluent: EtOAc/Hexanes = 1/10) to provide 2-(diisopropyl(phenyl)silyl)pyridine (2.48 g, 92%).

1a:

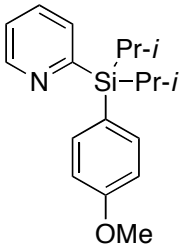


^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.86 (ddd, J = 4.91, 1.7, 1.1 Hz, 1 H), 7.54 - 7.60 (m, 3 H), 7.50 (dt, J = 7.57, 1.26 Hz, 1 H), 7.35 - 7.44 (m, 3 H), 7.24 (ddd, J = 7.66, 4.91, 1.38 Hz, 1 H), 1.63 - 1.74 (sept, J = 7.34 Hz, 2 H), 0.98 - 1.03 (m, J = 7.34 Hz, 12 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.5, 150.2, 136.0, 133.4, 133.0, 132.0, 129.1, 127.6, 122.7, 17.7, 17.6, 10.1

General procedure for the preparation of aryl pyridyl silanes:

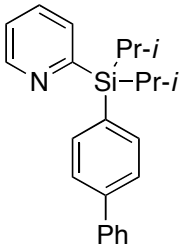
To a solution of aryl bromide or -iodide (10 mmol) in THF (15 ml) was added dropwise a solution of *n*-butyllithium (3.86 ml, 2.59 M in hexanes, 10 mmol) at -78 °C under argon atmosphere. The reaction mixture was stirred at -78 °C for 15 – 40 min and then neat 2-(diisopropylsilyl)pyridine **19** (1.934 g, 10.0 mmol) was added dropwise. The resulting solution was stirred at -78 °C for 1 h and then was allowed to warm to -30 °C. Upon completion of the reaction, the mixture was poured into 150 ml of hexanes containing small amount of water to neutralize LiH. The resulting solution was dried over anhydrous sodium sulfate, filtered, and concentrated under a reduced pressure. The residue was purified by flash column chromatography (silica gel, eluent: EtOAc/Hexanes) to provide aryl pyridyl silane.



1b: (92%, from 4-bromoanisole)

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.82 - 8.87 (m, 1 H), 7.56 (td, *J* = 7.52, 1.83 Hz, 1 H), 7.47 - 7.51 (m, 3 H), 7.22 (ddd, *J* = 7.61, 4.86, 1.47 Hz, 1 H), 6.92 - 6.96 (m, 2 H), 3.83 (s, 3 H), 1.60 - 1.70 (sept, *J* = 7.38 Hz, 2 H), 1.00 (t, *J* = 7.43 Hz, 12 H)

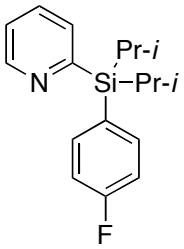
^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.9, 160.5, 150.1, 137.4, 133.3, 131.9, 123.7, 122.6, 113.5, 55.0, 17.7, 17.6, 10.2



1c: (95%, from 4-bromobiphenyl)

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.86 - 8.91 (m, 1 H), 7.53 - 7.67 (m, 8 H), 7.43 - 7.49 (m, 2 H), 7.33 - 7.39 (m, 1 H), 7.23 - 7.27 (m, 1 H), 1.67 - 1.78 (sept, *J* = 7.34 Hz, 2 H), 1.04 - 1.08 (m, 12 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.5, 150.2, 141.8, 141.1, 136.5, 133.5, 132.0, 131.8, 128.8, 127.4, 127.1, 126.3, 122.7, 17.7, 17.6, 10.2

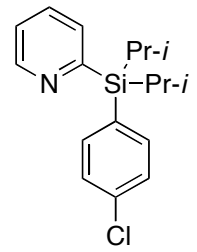


1d: (73%, from 4-fluoroiodobenzene)

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.85 (ddd, *J* = 4.86, 1.74, 1.10 Hz, 1 H), 7.59 (td, *J* = 7.61, 1.83 Hz, 1 H), 7.51 - 7.56 (m, 2 H), 7.48 (dt, *J* = 7.52, 1.19 Hz, 1 H), 7.24 (ddd, *J* = 7.70, 4.86, 1.38 Hz, 1 H), 7.06 - 7.11 (m, 2 H), 1.60 - 1.70 (sept, *J* = 7.38 Hz, 2 H), 0.98 - 1.02 (m, 12 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.2 (br. s.), 163.9 (d, J_{CF} = 248.8 Hz), 150.2, 137.8 (d, J_{CF} = 7.4 Hz), 133.5, 131.8, 128.5 (br. s.), 122.8, 114.9 (d, J_{CF} = 19.4 Hz), 17.6, 17.5, 10.2

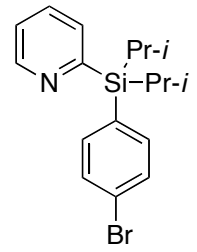
1e: (87%, from 1-chloro-4-iodobenzene)



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.85 (ddd, *J* = 4.91, 1.70, 1.10 Hz, 1 H), 7.59 (td, *J* = 7.61, 1.65 Hz, 1 H), 7.45 - 7.51 (m, 3 H), 7.34 - 7.38 (m, 2 H), 7.24 (ddd, *J* = 7.66, 4.91, 1.38 Hz, 1 H), 1.60 - 1.71 (m, *J* = 7.38 Hz, 2 H), 1.00 (m, *J* = 7.34, 12 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 162.9, 150.3, 137.2, 135.6, 133.5, 131.8, 131.4, 127.9, 122.9, 17.6, 17.5, 10.1

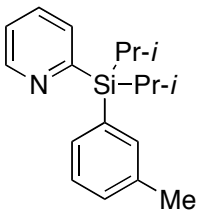
1f: (72%, from 1,4-dibromobenzene)



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.85 (ddd, *J* = 4.58, 1.47, 1.28 Hz, 1 H), 7.59 (td, *J* = 7.61, 1.65 Hz, 1 H), 7.50 - 7.54 (m, 2 H), 7.45 - 7.49 (m, 1 H), 7.40 - 7.44 (m, 2 H), 7.24 (ddd, *J* = 7.57, 4.91, 1.10 Hz, 1 H), 1.59 - 1.72 (sept, *J* = 7.34 Hz, 2 H), 0.96 - 1.02 (m, 12 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 162.8, 150.2, 137.5, 133.6, 132.0, 131.9, 130.9, 124.2, 122.9, 17.6, 17.5, 10.1

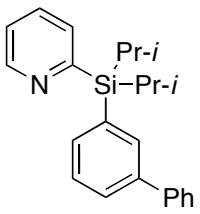
1i: (94%, from 3-bromotoluene)



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.84 - 8.87 (m, 1 H), 7.57 (dt, *J* = 7.52, 1.65 Hz, 1 H), 7.50 (td, *J* = 7.52, 1.10 Hz, 1 H), 7.33 - 7.37 (m, 2 H), 7.27 (t, *J* = 7.52 Hz, 1 H), 7.20 - 7.25 (m, 2 H), 2.36 (s, 3 H), 1.62 - 1.74 (sept, *J* = 7.38 Hz, 2 H), 1.01 (m, *J* = 7.34 Hz, 12 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.7, 150.1, 136.8, 136.5, 133.3, 133.0, 132.8, 132.0, 130.0, 127.5, 122.6, 21.6, 17.7, 17.6, 10.1

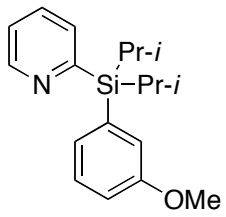
1j: (93%, from 3-bromobiphenyl)



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.87 (d, *J* = 4.77 Hz, 1 H), 7.75 - 7.80 (m, 1 H), 7.51 - 7.67 (m, 6 H), 7.41 - 7.49 (m, 3 H), 7.32 - 7.37 (m, 1 H), 7.23 - 7.27 (m, 1 H), 1.68 - 1.79 (sept, *J* = 7.34 Hz, 2 H), 1.00 - 1.09 (m, 12 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 159.3, 150.2, 141.6, 140.3, 135.0, 134.7, 133.5, 132.0, 128.7, 128.1, 128.0, 127.3, 127.1, 122.8, 17.7, 17.6, 10.1

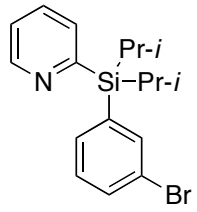
1k: (91%, from 3-bromoanisole)



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.85 (ddd, *J* = 4.91, 1.70, 1.10 Hz, 1 H), 7.57 (td, *J* = 7.52, 1.83 Hz, 1 H), 7.51 (dt, *J* = 7.52, 1.28 Hz, 1 H), 7.32 (dd, *J* = 8.07, 7.52 Hz, 1 H), 7.23 (ddd, *J* = 7.61, 4.86, 1.47 Hz, 1 H), 7.14 (dt, *J* = 7.24, 0.96 Hz, 1 H), 7.10 (dd, *J* = 2.57, 0.55 Hz, 1 H), 6.95 (ddd, *J* = 8.25, 2.75, 0.92 Hz, 1 H), 3.80 (s, 3 H), 1.60 - 1.73 (sept, *J* = 7.38 Hz, 2 H), 1.01 (m, 12 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.4, 158.8, 150.1, 134.7, 133.4, 132.0, 128.8, 128.3, 122.7, 121.7, 114.2, 55.1, 17.7, 17.6, 10.2

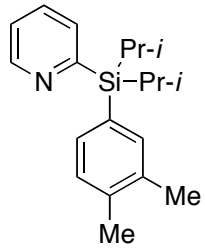
1l: (50%, from 1,3-dibromobenzene)



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.85 (d, *J* = 4.77 Hz, 1 H), 7.64 - 7.67 (m, 1 H), 7.61 (t, *J* = 7.43 Hz, 1 H), 7.53 (ddd, *J* = 8.02, 2.06, 1.10 Hz, 1 H), 7.49 (d, *J* = 7.52 Hz, 1 H), 7.46 (dt, *J* = 7.34, 1.01 Hz, 1 H), 7.25 (t, *J* = 7.61 Hz, 2 H), 1.60 - 1.72 (sept, *J* = 7.34 Hz, 2 H), 0.98 - 1.03 (m, 12 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 162.2, 150.3, 138.2, 134.3, 133.6, 132.2, 131.9, 129.4, 123.0, 122.8, 17.6, 17.5, 10.1

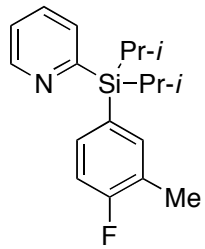
1m: (58%, from 1-iodo-3,4-dimethylbenzene)



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.83 - 8.88 (m, 1 H), 7.54 - 7.60 (m, 1 H), 7.48 - 7.52 (m, 1 H), 7.28 - 7.32 (m, 2 H), 7.22 (ddd, *J* = 7.57, 4.91, 1.28 Hz, 1 H), 7.16 (d, *J* = 7.15 Hz, 1 H), 2.29 (s, 3 H), 2.28 (s, 3 H), 1.62 - 1.74 (sept, *J* = 7.34 Hz, 2 H), 0.98 - 1.04 (m, 12 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.9, 150.1, 137.7, 137.2, 135.7, 133.7, 133.3, 132.0, 129.8, 129.0, 122.6, 19.9, 19.8, 17.7, 17.6, 10.1

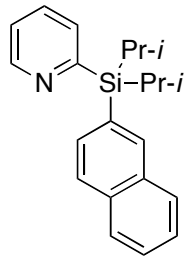
1n: (96%, from 5-bromo-2-fluorotoluene)



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.82 - 8.88 (m, 1 H), 7.59 (dt, *J* = 7.61, 1.28 Hz, 1 H), 7.49 (dt, *J* = 7.57, 1.17 Hz, 1 H), 7.31 - 7.37 (m, 2 H), 7.21 - 7.26 (m, 1 H), 6.99 - 7.06 (m, 1 H), 2.28 (d, *J* = 1.65 Hz, 3 H), 1.59 - 1.71 (sept, *J* = 7.34 Hz, 2 H), 0.97 - 1.02 (m, 12 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.3 (br. s.), 162.5 (d, J_{CF} = 246.9 Hz), 150.2, 139.2 (d, J_{CF} = 4.6 Hz), 135.2 (d, J_{CF} = 7.4 Hz), 133.5 (br. s.), 131.9, 126.2 (d, J_{CF} = 30.5 Hz), 124.1 (d, J_{CF} = 15.7 Hz), 122.8, 114.5 (d, J_{CF} = 21.3 Hz), 17.6, 17.6, 14.6, 10.2

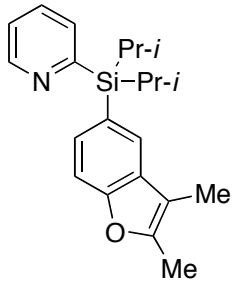
1o: (97%, from 2-bromonaphthalene)



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.86 - 8.93 (m, 1 H), 8.09 (s, 1 H), 7.82 - 7.89 (m, 3 H), 7.61 - 7.64 (m, 1 H), 7.59 (dt, *J* = 7.52, 1.65 Hz, 1 H), 7.47 - 7.56 (m, 3 H), 7.26 (ddd, *J* = 6.83, 5.46, 1.47 Hz, 1 H), 1.73 - 1.84 (sept, *J* = 7.38 Hz, 2 H), 1.06 (m, 12 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.5, 150.2, 136.9, 133.9, 133.5, 132.9, 132.0, 130.8, 128.2, 127.7, 126.7, 126.4, 125.8, 122.8, 17.7, 17.7, 10.3

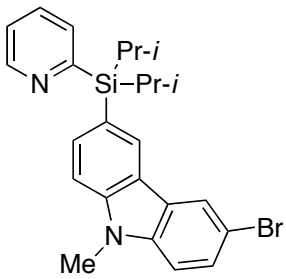
1t: (95%, from 5-bromo-2,3-dimethylbenzo[*b*]furan[1])



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.86 - 8.88 (m, 1 H), 7.55 - 7.60 (m, 2 H), 7.53 (dt, *J* = 7.52, 1.28 Hz, 1 H), 7.40 (dd, *J* = 8.07, 0.55 Hz, 1 H), 7.38 (dd, *J* = 8.07, 1.10 Hz, 1 H), 7.24 (ddd, *J* = 7.43, 4.95, 1.38 Hz, 1 H), 2.39 (s, 3 H), 2.15 (s, 3 H), 1.67 - 1.77 (sept, *J* = 7.38 Hz, 2 H), 0.99 - 1.05 (m, 12 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 164.0, 154.8, 150.2, 150.1, 133.4, 132.1, 130.7, 130.2, 126.4, 125.1, 122.7, 110.0, 109.6, 17.7, 17.6, 11.8, 10.2, 8.0

1u: (50%, from 3,6-dibromo-9-methyl-9H-carbazole[2])



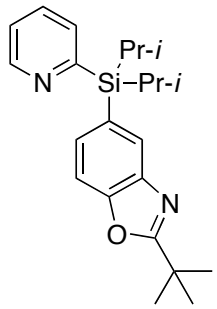
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.89 (ddd, *J* = 4.81, 1.70, 1.01 Hz, 1 H), 8.23 - 8.25 (m, 1 H), 8.20 (d, *J* = 1.65 Hz, 1 H), 7.67 (dd, *J* = 8.25, 1.10 Hz, 1 H), 7.60 (td, *J* = 7.52, 1.83 Hz, 1 H), 7.53 - 7.57 (m, 2 H), 7.44 (d, *J* = 8.25 Hz, 1 H), 7.24 - 7.31 (m, 2 H), 3.85 (s, 3 H), 1.72 - 1.83 (sept, *J* = 7.38 Hz, 2 H), 1.01 - 1.08 (m, 12 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.9, 150.2, 142.1, 139.5, 133.8, 133.5, 132.1, 128.4, 128.3, 124.5, 123.0, 122.7, 121.9, 121.7, 111.9, 109.9, 108.3, 29.2, 17.8, 17.7, 10.3

[1] Kawase, Y.; Hori, S. *Bull. Chem. Soc. Jpn.* **1970**, *43* , 3496.

[2] Patrick, D. A.; Boykin, D. W.; Wilson, W. D.; Tanious, F. A.; Spychala, J.; Bender, B. C.; Hall, J. E.; Dykstra, C. C.; Ohemeng, K. A.; Tidwell, R. R. *Eur. J. Med. Chem.* **1997**, *32*, 781.

1w: (87%, from 5-bromo-2-tert-butylbenzo[d]oxazole[3])



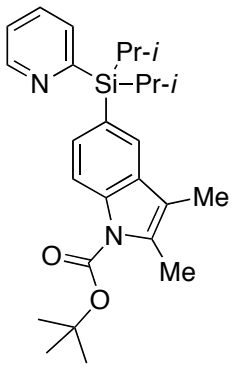
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.80 - 8.87 (m, 1 H), 7.91 - 7.93 (m, 1 H), 7.56 (td, *J* = 7.52, 1.65 Hz, 1 H), 7.52 (dd, *J* = 8.07, 0.55 Hz, 1 H), 7.50 (dt, *J* = 7.52, 1.28 Hz, 1 H), 7.47 (dd, *J* = 8.07, 0.92 Hz, 1 H), 7.22 (ddd, *J* = 7.61, 4.86, 1.47 Hz, 1 H), 1.64 - 1.75 (sept, *J* = 7.38 Hz, 2 H), 1.50 (s, 9 H), 0.97 - 1.06 (m, 12 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 173.3, 163.3, 151.7, 150.2, 141.0, 133.5, 132.0, 132.0, 128.3, 127.4, 122.8, 110.0, 34.2, 28.5, 17.7, 17.6, 10.2

Synthesis of 1v:

To a solution of NaH (142 mg, 5.9 mmol) in THF (10 ml) was added a solution of 5-bromo-2,3-dimethyl-1*H*-indole[4] (1.008 g, 4.5 mmol) in THF (10 ml) at 0 °C under argon atmosphere. The solution was stirred at room temperature for 20 min and then cooled to -78 °C. To this reaction mixture was added dropwise a solution of *t*-butyllithium (5.2 ml, 1.8 M in pentane, 9.4 mmol) at -78 °C. The reaction mixture was stirred at -78 °C for 25 min and then neat 2-(diisopropylsilyl)pyridine **19** (4.5 mmol) was added dropwise. The resulting solution was stirred at -78 °C for 1 h and then was allowed to warm to -30 °C. After being stirred for 1 h at -30 °C, Boc_2O (2.4 ml, 10.34 mmol) was added and the solution was allowed to warm to rt overnight. The reaction was quenched with 10 ml of saturated $KHCO_3$ solution and extracted with EtOAc (3×40 ml). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under a reduced pressure. The residue was purified by flash column chromatography (silica gel, eluent: EtOAc/Hexanes).

1v: (77%, from 5-bromo-2,3-dimethyl-1*H*-indole)



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.81 - 8.93 (m, 1 H), 8.10 (d, *J* = 8.18 Hz, 1 H), 7.61 (s, 1 H), 7.57 (td, *J* = 7.45, 1.75 Hz, 1 H), 7.49 - 7.54 (m, 1 H), 7.42 (dd, *J* = 8.26, 0.80 Hz, 1 H), 7.24 (ddd, *J* = 7.27, 4.93, 1.53 Hz, 1 H), 2.54 (s, 3 H), 2.18 (s, 3 H), 1.64 - 1.79 (m, 11 H), 0.96 - 1.07 (m, 12 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 164.1, 150.9, 150.1, 136.4, 133.4, 132.8, 132.1, 130.9, 130.4, 125.7, 125.4, 122.7, 114.7, 113.8, 83.3, 28.3, 17.8, 17.7, 13.8, 10.2, 8.7

Synthesis of 1g and 1h:

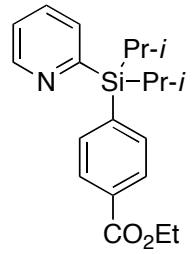
To a solution of aryl bromide **1f** (3 mmol) in THF (8 ml) was added dropwise a solution of *n*-butyllithium (1.19 ml, 2.53 M in hexanes, 3 mmol) at -78 °C under argon atmosphere. The reaction

[3] Goldstein, S. W.; Dambek, P. J. *J. Heterocycl. Chem.* **1990**, *27*, 335

[4] Takemoto, M.; Iwakiri, Y.; Tanaka, K. *Heterocycles* **2007**, *72*, 373.

mixture was stirred at -78 °C for 25 min and then was transferred via cannula to a solution of an appropriate electrophile (9 mmol) in THF (8 ml) at -78 °C. After being stirred for 2 h at -78 °C, the solution was allowed to warm to rt overnight. The reaction was quenched with 10 ml of saturated $KHCO_3$ solution and extracted with EtOAc (3×40 ml). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under a reduced pressure. The residue was purified by flash column chromatography (silica gel, eluent: EtOAc/Hexanes) to provide the corresponding *p*-substituted aryl pyridyl silane.

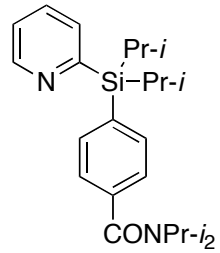
1g: (74%, with diethyl pyrocarbonate)



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.85 (ddd, *J* = 4.81, 1.79, 1.10 Hz, 1 H), 8.01 - 8.05 (m, 2 H), 7.62 - 7.66 (m, 2 H), 7.59 (td, *J* = 7.66, 1.74 Hz, 1 H), 7.47 (dt, *J* = 7.52, 1.19 Hz, 1 H), 7.25 (ddd, *J* = 7.66, 4.81, 1.47 Hz, 1 H), 4.39 (q, *J* = 7.03 Hz, 2 H), 1.64 - 1.74 (sept, *J* = 7.40 Hz, 2 H), 1.39 (t, *J* = 7.03 Hz, 3 H), 0.98 - 1.03 (m, 12 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 166.8, 162.8, 150.3, 139.7, 135.9, 133.5, 131.9, 131.0, 128.3, 122.9, 60.9, 17.6, 17.5, 14.3, 10.1

1h: (98%, with diisopropylcarbamyl chloride)



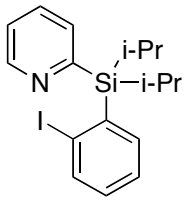
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.84 (ddd, *J* = 4.81, 1.70, 1.01 Hz, 1 H), 7.60 (td, *J* = 7.52, 1.65 Hz, 1 H), 7.53 - 7.57 (m, 2 H), 7.51 (dt, *J* = 7.57, 1.26 Hz, 1 H), 7.29 - 7.33 (m, 2 H), 7.24 (ddd, *J* = 7.66, 4.81, 1.47 Hz, 1 H), 3.98 (br. s., 1 H), 3.52 (br. s., 1 H), 1.59 - 1.71 (sept, *J* = 7.34 Hz, 2 H), 1.54 (br. s., 6 H), 1.16 (br. s., 6 H), 0.96 - 1.04 (m, 12 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 171.1, 163.1, 150.2, 139.5, 136.0, 133.9, 133.5, 131.9, 124.8, 122.8, 50.7, 45.9, 20.8, 17.6, 17.5, 10.2

Halogenation of Aryl Pyridyl Silanes

General procedure:

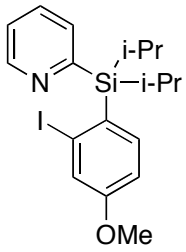
An oven dried 10 ml Wheaton V-vial, containing a stirring bar, was charged with 2-(diisopropyl-(aryl)silyl)pyridine (0.5 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), $PhI(OAc)_2$ (241.6 mg, 0.75 mmol), and NIS (225 mg, 1 mmol) or NBS (178 mg, 1.0 mmol) or NCS (133.5 mg, 1.0 mmol) under N_2 atmosphere. Dry DCE (5 ml) or butyronitrile (10 ml) was added and the reaction vessel was capped with pressure screw cap. Reaction mixture was heated at 60 – 70 °C (DCE) or 100 °C (PrCN) for 45 min – 4 h until judged complete by GC/MS analysis. The resulting mixture was cooled down to room temperature and filtered through a layer of silica gel with the aid of EtOAc. The filtrate was concentrated under a reduced pressure and the residue was purified by column chromatography on a silica gel (eluent: hexanes/EtOAc) affording the corresponding halogenated product.



2a: (91%, 0.1M, DCE, 70 ºC, 45 min)

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.83 (ddd, *J* = 4.91, 1.70, 1.10 Hz, 1 H), 7.89 (dd, *J* = 7.89, 1.10 Hz, 1 H), 7.58 (td, *J* = 7.60, 1.83 Hz, 1 H), 7.52 (dt, *J* = 7.60, 1.28 Hz, 1 H), 7.34 (dd, *J* = 7.34, 1.83 Hz, 1 H), 7.30 (td, *J* = 7.34, 1.10 Hz, 1 H), 7.23 (ddd, *J* = 7.52, 4.95, 1.47 Hz, 1 H), 7.02 (ddd, *J* = 7.89, 7.34, 1.83 Hz, 1 H), 1.89 - 2.02 (sept, *J* = 7.34 Hz, 2 H), 1.19 (d, *J* = 7.34 Hz, 6 H), 1.06 (d, *J* = 7.34 Hz, 6 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.8, 150.1, 140.9, 140.8, 139.3, 133.4, 131.9, 130.7, 126.6, 122.6, 105.0, 18.5, 18.4, 11.5



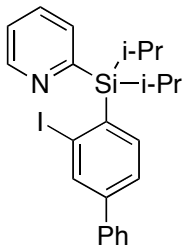
2b: (70%, 0.1M, DCE, 70 ºC, 1 h)

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.81 - 8.83 (m, 1 H), 7.55 - 7.59 (m, 1 H), 7.50 - 7.53 (m, 1 H), 7.46 (d, *J* = 2.38 Hz, 1 H), 7.20 - 7.23 (m, 1 H), 7.22 (d, *J* = 8.25 Hz, 1 H), 6.86 (dd, *J* = 8.34, 2.48 Hz, 1 H), 3.78 (s, 3 H), 1.87 - 1.96 (sept, *J* = 7.43 Hz, 2 H), 1.17 (d, *J* = 7.34 Hz, 6 H), 1.04 (d, *J* = 7.34 Hz, 6 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 164.2, 160.4, 150.0, 140.0, 133.4, 131.9, 131.3, 126.6, 122.5, 113.0, 105.0, 55.2, 18.5, 18.3, 11.6

HRMS (EI) calcd. for $C_{18}H_{24}INOSi$ $[M]^+$: 425.06718. Found: 425.06885.

2c: (88%, 0.1M, DCE, 65 ºC, 1.5 h)

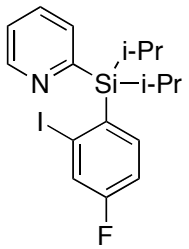


^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.85 (ddd, *J* = 4.77, 1.65, 1.10 Hz, 1 H), 8.14 (d, *J* = 1.83 Hz, 1 H), 7.61 (td, *J* = 7.52, 1.83 Hz, 1 H), 7.56 - 7.58 (m, 2 H), 7.55 - 7.56 (m, 1 H), 7.53 (dd, *J* = 7.79, 1.74 Hz, 1 H), 7.42 - 7.46 (m, 1 H), 7.44 (t, *J* = 7.52 Hz, 1 H), 7.40 (d, *J* = 7.70 Hz, 1 H), 7.35 - 7.39 (m, 1 H), 7.25 (ddd, *J* = 7.38, 4.91, 1.65 Hz, 1 H), 1.94 - 2.03 (sept, *J* = 7.43 Hz, 2 H), 1.22 (d, *J* = 7.34 Hz, 6 H), 1.10 (d, *J* = 7.34 Hz, 6 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.8, 150.1, 143.5, 139.6, 139.4, 139.3, 139.2, 133.5, 131.9, 128.9, 127.9, 127.1, 125.3, 122.7, 105.4, 18.5, 18.4, 11.6

HRMS (EI) calcd. for $C_{23}H_{26}INSi$ $[M]^+$: 471.08792. Found: 471.08686.

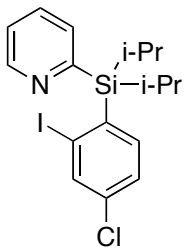
2d: (87%, 0.1M, DCE, 70 ºC, 2.5 h)



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.81 - 8.84 (m, 1 H), 7.64 (dd, *J* = 8.62, 2.38 Hz, 1 H), 7.59 (td, *J* = 7.60, 1.83 Hz, 1 H), 7.52 (dt, *J* = 7.70, 1.19 Hz, 1 H), 7.29 (dd, *J* = 8.44, 6.79 Hz, 1 H), 7.23 (ddd, *J* = 7.61, 4.86, 1.28 Hz, 1 H), 7.03 (td, *J* = 8.34, 2.57 Hz, 1 H), 1.88 - 1.97 (sept, *J* = 7.43 Hz, 2 H), 1.17 (d, *J* = 7.34 Hz, 6 H), 1.05 (d, *J* = 7.52 Hz, 6 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.6, 161.5, 150.2, 140.4 (d, J_{CF} = 7.4 Hz), 136.4, 133.5, 131.8, 128.1 (d, J_{CF} = 21.3 Hz), 122.7, 114.1 (d, J_{CF} = 18.5 Hz), 103.9 (d, J_{CF} = 6.5 Hz), 18.4, 18.3, 11.6

2e: (84%, 0.1M, DCE, 70 ºC, 1.2 h)

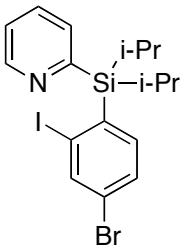


^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.80 - 8.83 (m, *J* = 4.77, 1.10, 0.83, 0.83 Hz, 1 H), 7.91 (d, *J* = 2.02 Hz, 1 H), 7.59 (td, *J* = 7.60, 1.83 Hz, 1 H), 7.51 (dt, *J* = 7.57, 1.26 Hz, 1 H), 7.29 (dd, *J* = 8.10, 1.83 Hz, 1 H), 7.22 - 7.25 (m, 2 H), 1.88 - 1.97 (sept, *J* = 7.43 Hz, 2 H), 1.17 (d, *J* = 7.52 Hz, 6 H), 1.05 (d, *J* = 7.52 Hz, 6 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.3, 150.2, 140.1, 139.9, 139.3, 135.8, 133.6, 131.8, 127.0, 122.8, 104.4, 18.4, 18.3, 11.5

HRMS (EI) calcd. for $C_{17}H_{20}ClINSi$ $[M-1]^+$: 428.00985. Found: 428.00792.

2f: (75%, 0.1M, DCE, 70 ºC, 1.2 h)

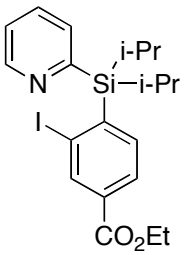


^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.80 - 8.83 (m, 1 H), 8.06 (d, *J* = 1.83 Hz, 1 H), 7.59 (td, *J* = 7.60, 1.83 Hz, 1 H), 7.51 (d, *J* = 7.52 Hz, 1 H), 7.43 (dd, *J* = 8.07, 1.83 Hz, 1 H), 7.24 (ddd, *J* = 7.66, 4.81, 1.28 Hz, 1 H), 7.18 (d, *J* = 8.07 Hz, 1 H), 1.88 - 1.97 (sept, *J* = 7.43 Hz, 2 H), 1.17 (d, *J* = 7.52 Hz, 6 H), 1.05 (d, *J* = 7.34 Hz, 6 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.3, 150.2, 142.7, 140.2, 139.8, 133.6, 131.8, 129.8, 124.2, 122.8, 104.8, 18.4, 18.3, 11.5

HRMS (EI) calcd. for $C_{17}H_{21}BrINSi$ $[M]^+$: 472.96716. Found: 472.96781.

2g: (76%, 0.1M, DCE, 60 ºC, 2 h)

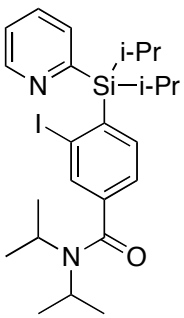


^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.81 (ddd, *J* = 4.77, 1.65, 1.10 Hz, 1 H), 8.51 (d, *J* = 1.65 Hz, 1 H), 7.93 (dd, *J* = 7.79, 1.56 Hz, 1 H), 7.59 (td, *J* = 7.60, 1.83 Hz, 1 H), 7.50 (dt, *J* = 7.61, 1.24 Hz, 1 H), 7.41 (d, *J* = 7.89 Hz, 1 H), 7.24 (ddd, *J* = 7.61, 4.86, 1.47 Hz, 1 H), 4.36 (q, *J* = 7.15 Hz, 2 H), 1.92 - 2.01 (sept, *J* = 7.43 Hz, 2 H), 1.38 (t, *J* = 7.15 Hz, 3 H), 1.18 (d, *J* = 7.34 Hz, 6 H), 1.05 (d, *J* = 7.52 Hz, 6 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 165.1, 163.2, 150.2, 147.1, 141.2, 139.1, 133.6, 132.4, 131.8, 127.1, 122.8, 104.1, 61.3, 18.4, 18.3, 14.3, 11.5

HRMS (EI) calcd. for $C_{20}H_{26}INO_2Si$ $[M]^+$: 467.07775. Found: 467.07658.

2h: (78%, 0.1M, DCE, 60 ºC, 2 h)

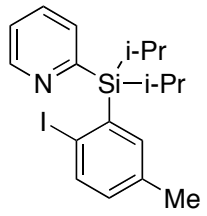


^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.80 - 8.84 (m, 1 H), 7.83 (d, *J* = 1.32 Hz, 1 H), 7.62 (dt, *J* = 7.60, 1.61 Hz, 1 H), 7.54 - 7.58 (m, 1 H), 7.31 (d, *J* = 7.60 Hz, 1 H), 7.21 - 7.27 (m, 2 H), 3.92 (br. s., 1 H), 3.49 (br. s., 1 H), 1.87 - 1.99 (sept, *J* = 7.41 Hz, 2 H), 1.51 (br. s., 6 H), 1.18 (d, *J* = 7.45 Hz, 12 H), 1.04 (d, *J* = 7.45 Hz, 6 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 168.9, 163.3, 150.1, 141.4, 140.9, 139.3, 137.8, 133.8, 131.9, 123.7, 122.9, 104.8, 51.0, 46.0, 20.7, 18.4, 18.2, 11.5

HRMS (EI) calcd. for $C_{24}H_{35}IN_2OSi$ $[M]^+$: 522.15633. Found: 522.15473.

2i: (93%, 0.1M, DCE, 70 ºC, 1 h)

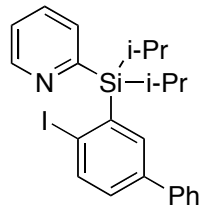


^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.82 (dt, *J* = 4.86, 1.42 Hz, 1 H), 7.75 (d, *J* = 8.07 Hz, 1 H), 7.58 (td, *J* = 7.60, 1.83 Hz, 1 H), 7.53 (dt, *J* = 7.52, 1.19 Hz, 1 H), 7.23 (ddd, *J* = 7.57, 4.81, 1.56 Hz, 1 H), 7.15 (d, *J* = 2.20 Hz, 1 H), 6.85 (dd, *J* = 8.07, 2.38 Hz, 1 H), 2.24 (s, 3 H), 1.91 - 2.00 (sept, *J* = 7.46 Hz, 2 H), 1.19 (d, *J* = 7.52 Hz, 6 H), 1.06 (d, *J* = 7.52 Hz, 6 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 164.0, 150.0, 140.6, 140.3, 140.2, 136.2, 133.4, 131.9, 131.9, 122.6, 100.9, 21.2, 18.5, 18.4, 11.5

HRMS (EI) calcd. for $C_{18}H_{24}INSi$ $[M]^+$: 409.07227. Found: 409.07056.

2j: (90%, 0.1M, DCE, 65 ºC, 1.5 h)

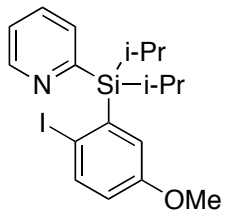


^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.85 (dt, *J* = 4.91, 1.31 Hz, 1 H), 7.96 (d, *J* = 8.07 Hz, 1 H), 7.56 - 7.62 (m, 3 H), 7.47 - 7.51 (m, 2 H), 7.42 (t, *J* = 7.52 Hz, 2 H), 7.35 (tt, *J* = 7.52, 1.28 Hz, 1 H), 7.25 (dd, *J* = 7.79, 2.11 Hz, 2 H), 1.95 - 2.03 (sept, *J* = 7.43 Hz, 2 H), 1.23 (d, *J* = 7.52 Hz, 6 H), 1.11 (d, *J* = 7.52 Hz, 6 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.7, 150.1, 141.2, 141.1, 140.4, 139.4, 138.1, 133.5, 131.9, 129.6, 128.9, 127.5, 126.9, 122.7, 103.8, 18.6, 18.4, 11.6

HRMS (EI) calcd. for $C_{23}H_{26}INSi$ $[M]^+$: 471.08792. Found: 471.08722.

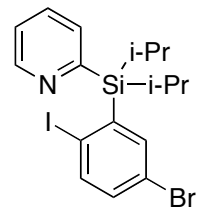
2k: (85%, 0.1M, DCE, 70 ºC, 1.2 h)



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.82 (ddd, *J* = 4.86, 1.74, 1.10 Hz, 1 H), 7.75 (d, *J* = 8.80 Hz, 1 H), 7.56 - 7.60 (m, 1 H), 7.51 - 7.54 (m, 1 H), 7.22 (ddd, *J* = 7.57, 4.91, 1.47 Hz, 1 H), 6.92 (d, *J* = 3.12 Hz, 1 H), 6.61 (dd, *J* = 8.71, 3.21 Hz, 1 H), 3.71 (s, 3 H), 1.90 - 1.99 (sept, *J* = 7.46 Hz, 2 H), 1.20 (d, *J* = 7.52 Hz, 6 H), 1.06 (d, *J* = 7.34 Hz, 6 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.8, 158.4, 150.1, 141.8, 141.5, 133.4, 131.9, 125.9, 122.7, 116.3, 93.1, 55.1, 18.5, 18.4, 11.5

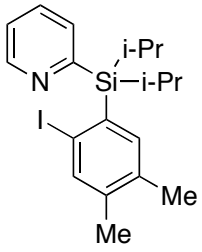
2l: (88%, 0.1M, DCE, 70 ºC, 2 h)



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.81 - 8.83 (m, *J* = 4.77, 1.10, 0.83 Hz, 1 H), 7.71 (d, *J* = 8.25 Hz, 1 H), 7.60 (td, *J* = 7.52, 1.83 Hz, 1 H), 7.52 (dt, *J* = 7.57, 1.26 Hz, 1 H), 7.42 (d, *J* = 2.57 Hz, 1 H), 7.24 (ddd, *J* = 7.66, 4.81, 1.47 Hz, 1 H), 7.14 (dd, *J* = 8.44, 2.57 Hz, 1 H), 1.90 - 1.99 (sept, *J* = 7.46 Hz, 2 H), 1.19 (d, *J* = 7.52 Hz, 6 H), 1.07 (d, *J* = 7.52 Hz, 6 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.0, 150.2, 144.1, 142.4, 141.6, 133.8, 133.6, 131.8, 122.9, 122.4, 102.4, 18.5, 18.3, 11.5

2m: (86%, 0.1M, DCE, 65 ºC, 2 h)

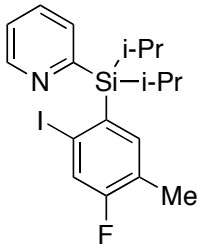


^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.82 (ddd, *J* = 4.77, 1.65, 1.10 Hz, 1 H), 7.68 (s, 1 H), 7.57 (td, *J* = 7.52, 1.83 Hz, 1 H), 7.52 (dt, *J* = 7.52, 1.28 Hz, 1 H), 7.22 (ddd, *J* = 7.52, 4.95, 1.47 Hz, 1 H), 7.08 (s, 1 H), 2.19 (s, 3 H), 2.15 (s, 3 H), 1.90 - 1.99 (sept, *J* = 7.43 Hz, 2 H), 1.18 (d, *J* = 7.52 Hz, 6 H), 1.06 (d, *J* = 7.34 Hz, 6 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 164.2, 150.0, 141.7, 140.5, 139.9, 137.3, 135.1, 133.3, 131.9, 122.5, 101.5, 19.5, 19.1, 18.5, 18.4, 11.5

HRMS (EI) calcd. for $C_{19}H_{26}INSi$ $[M]^+$: 423.08792. Found: 423.08934.

2n: (84%, 0.1M, DCE, 65 ºC, 2 h)

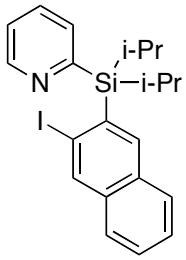


^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.82 (ddd, *J* = 4.81, 1.70, 1.01 Hz, 1 H), 7.59 (td, *J* = 7.52, 1.83 Hz, 1 H), 7.55 (d, *J* = 9.35 Hz, 1 H), 7.52 (dt, *J* = 7.52, 1.28 Hz, 1 H), 7.23 (ddd, *J* = 7.61, 4.86, 1.47 Hz, 1 H), 7.12 (d, *J* = 8.80 Hz, 1 H), 2.17 (d, *J* = 1.47 Hz, 3 H), 1.88 - 1.97 (sept, *J* = 7.46 Hz, 2 H), 1.18 (d, *J* = 7.52 Hz, 6 H), 1.05 (d, *J* = 7.52 Hz, 6 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.7, 161.4 (d, J_{CF} = 253.4 Hz), 150.1, 141.9 (d, J_{CF} = 4.6 Hz), 135.8, 133.5, 131.8, 127.5 (d, J_{CF} = 23.1 Hz), 123.6 (d, J_{CF} = 14.8 Hz), 122.7, 100.0 (d, J_{CF} = 6.5 Hz), 18.5, 18.3, 14.4, 11.6

HRMS (EI) calcd. for $C_{18}H_{23}FINSi$ $[M+1]^+$: 427.06285. Found: 427.06116.

2o: (87%, 0.1M, DCE, 65 ºC, 1.5 h)

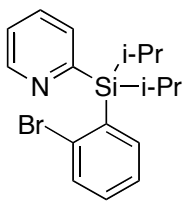


^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.84 - 8.86 (m, 1 H), 8.44 (s, 1 H), 7.88 (s, 1 H), 7.71 - 7.74 (m, 1 H), 7.67 - 7.70 (m, 1 H), 7.60 (td, *J* = 7.60, 1.83 Hz, 1 H), 7.54 - 7.57 (m, 1 H), 7.45 - 7.52 (m, *J* = 7.22, 7.22, 7.11, 6.88, 1.47 Hz, 2 H), 7.24 - 7.27 (m, 1 H), 2.01 - 2.11 (sept, *J* = 7.43 Hz, 2 H), 1.25 (d, *J* = 7.34 Hz, 6 H), 1.13 (d, *J* = 7.34 Hz, 6 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 164.2, 150.1, 140.0, 139.4, 137.5, 135.1, 133.5, 131.9, 131.4, 128.2, 127.3, 126.4, 126.3, 122.7, 100.2, 18.7, 18.5, 11.8

HRMS (EI) calcd. for $C_{21}H_{24}INSi$ $[M]^+$: 445.07227. Found: 445.07169.

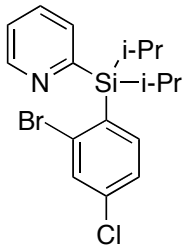
2p: (80%, 0.1M, DCE, 60 ºC, 3 h)



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.81 - 8.84 (m, 1 H), 7.51 - 7.61 (m, 3 H), 7.34 (dd, *J* = 7.24, 2.11 Hz, 1 H), 7.19 - 7.26 (m, 3 H), 1.86 - 1.95 (sept, *J* = 7.43 Hz, 2 H), 1.16 (d, *J* = 7.34 Hz, 6 H), 1.03 (d, *J* = 7.52 Hz, 6 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.9, 150.0, 139.2, 136.2, 133.4, 131.6, 131.1, 130.8, 126.0, 122.6, 18.3, 18.2, 11.5
HRMS (EI) calcd. for $C_{17}H_{22}BrNSi$ $[M]^+$: 347.07049. Found: 347.06867.

2q: (75%, 0.1M, DCE, 70 ºC, 3.5 h)

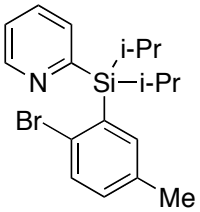


^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.82 (ddd, *J* = 4.91, 1.70, 1.10 Hz, 1 H), 7.58 - 7.62 (m, 2 H), 7.51 (dt, *J* = 7.61, 1.24 Hz, 1 H), 7.22 - 7.27 (m, 3 H), 1.83 - 1.92 (sept, *J* = 7.43 Hz, 2 H), 1.15 (d, *J* = 7.52 Hz, 6 H), 1.01 (d, *J* = 7.34 Hz, 6 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.4, 150.1, 139.9, 136.2, 134.7, 133.5, 133.0, 131.6, 131.1, 126.5, 122.8, 18.3, 18.1, 11.5

HRMS (EI) calcd. for $C_{17}H_{21}BrClN^{81}Si$ $[M]^+$: 383.02947. Found: 383.02772.

2r: (91%, 0.1M, DCE, 60 ºC, 3 h)

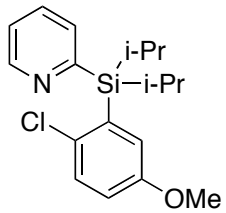


^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.82 (d, *J* = 4.77 Hz, 1 H), 7.59 (td, *J* = 7.52, 1.83 Hz, 1 H), 7.51 - 7.54 (m, 1 H), 7.43 (d, *J* = 8.07 Hz, 1 H), 7.22 (ddd, *J* = 7.47, 5.00, 1.10 Hz, 1 H), 7.14 (d, *J* = 2.20 Hz, 1 H), 7.02 (dd, *J* = 8.16, 2.29 Hz, 1 H), 2.23 (s, 3 H), 1.85 - 1.94 (sept, *J* = 7.43 Hz, 2 H), 1.16 (d, *J* = 7.52 Hz, 6 H), 1.03 (d, *J* = 7.52 Hz, 6 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 164.1, 150.0, 139.9, 135.7, 135.5, 133.4, 133.1, 131.8, 131.6, 127.7, 122.6, 21.0, 18.4, 18.2, 11.5

HRMS (EI) calcd. for $C_{18}H_{24}BrNSi$ $[M]^+$: 361.08614. Found: 361.08550.

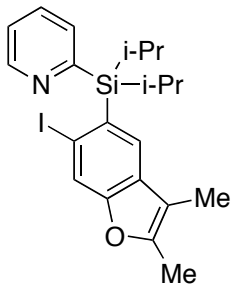
2s: (69%, 0.05M, PrCN, 100 ºC, 4 h)



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.83 (d, *J* = 4.77 Hz, 1 H), 7.60 (td, *J* = 7.60, 1.83 Hz, 1 H), 7.51 - 7.55 (m, 1 H), 7.27 (d, *J* = 8.62 Hz, 1 H), 7.23 (ddd, *J* = 7.47, 4.91, 1.19 Hz, 1 H), 6.90 (d, *J* = 3.12 Hz, 1 H), 6.84 (dd, *J* = 8.62, 3.12 Hz, 1 H), 3.71 (s, 3 H), 1.80 - 1.89 (sept, *J* = 7.43 Hz, 2 H), 1.14 (d, *J* = 7.52 Hz, 6 H), 1.01 (d, *J* = 7.52 Hz, 6 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 163.5, 157.2, 150.0, 134.4, 133.5, 132.7, 131.7, 130.5, 124.4, 122.7, 115.7, 55.3, 18.3, 18.1, 11.3

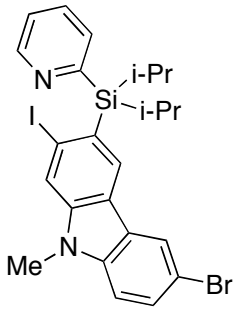
2t: (77%, 0.1M, DCE, 65 ºC, 1.5 h)



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.83 (ddd, *J* = 4.91, 1.70, 1.10 Hz, 1 H), 7.93 (s, 1 H), 7.57 (td, *J* = 7.52, 1.83 Hz, 1 H), 7.52 - 7.55 (m, 1 H), 7.43 (s, 1 H), 7.22 (ddd, *J* = 7.38, 4.81, 1.56 Hz, 1 H), 2.34 (d, *J* = 0.73 Hz, 3 H), 2.06 (d, *J* = 0.92 Hz, 3 H), 1.96 - 2.05 (sept, *J* = 7.34 Hz, 2 H), 1.22 (d, *J* = 7.52 Hz, 6 H), 1.09 (d, *J* = 7.34 Hz, 6 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 164.7, 155.0, 150.9, 150.0, 133.4, 132.1, 131.8, 129.7, 129.2, 123.0, 122.5, 109.6, 96.2, 18.7, 18.5, 11.9, 11.8, 7.7

2u: (69%, 0.1M, DCE, 60 ºC, 2 h)

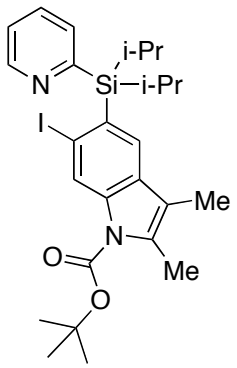


^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.84 - 8.88 (m, 1 H), 8.07 (d, *J* = 1.75 Hz, 1 H), 8.04 (s, 1 H), 7.98 (s, 1 H), 7.54 - 7.63 (m, 3 H), 7.24 (d, *J* = 8.62 Hz, 1 H), 7.22 - 7.28 (m, 1 H), 3.76 (s, 3 H), 1.99 - 2.10 (sept, *J* = 7.41 Hz, 2 H), 1.24 (d, *J* = 7.45 Hz, 6 H), 1.11 (d, *J* = 7.31 Hz, 6 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 164.6, 150.1, 142.7, 139.5, 133.5, 131.9, 131.1, 129.0, 128.8, 124.0, 123.0, 122.7, 121.5, 121.0, 112.4, 110.1, 101.0, 29.3, 18.7, 18.5, 11.9

HRMS (ESI) calcd. for $C_{24}H_{27}BrIN_2Si$ $[M+1]^+$: 577.0172. Found: 577.0177.

2v: (74%, 0.1M, DCE, 70 ºC, without $PhI(OAc)_2$, 1.5 h)

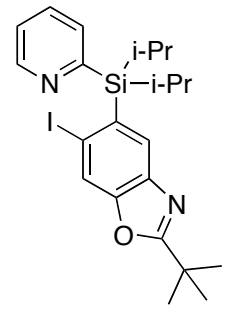


^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.83 (ddd, *J* = 4.77, 1.65, 1.10 Hz, 1 H), 8.68 (s, 1 H), 7.56 (td, *J* = 7.52, 1.83 Hz, 1 H), 7.52 (dt, *J* = 7.52, 1.28 Hz, 1 H), 7.43 (s, 1 H), 7.22 (ddd, *J* = 7.43, 4.86, 1.47 Hz, 1 H), 2.49 (d, *J* = 0.37 Hz, 3 H), 2.08 (d, *J* = 0.55 Hz, 3 H), 1.96 - 2.07 (sept, *J* = 7.52 Hz, 2 H), 1.67 (s, 9 H), 1.22 (d, *J* = 7.52 Hz, 6 H), 1.10 (d, *J* = 7.52 Hz, 6 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 164.8, 150.4, 150.0, 137.1, 133.4, 133.3, 132.5, 131.9, 129.6, 128.6, 127.6, 122.5, 113.5, 97.7, 83.8, 28.2, 18.7, 18.6, 13.8, 11.9, 8.4

HRMS (ESI) calcd. for $C_{26}H_{36}IN_2O_2Si$ $[M+1]^+$: 563.1591. Found: 563.1594.

2w: (72%, 0.1M, DCE, 70 ºC, 5 h)



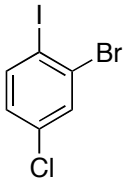
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.80 (ddd, *J* = 4.77, 1.65, 1.10 Hz, 1 H), 8.06 (s, 1 H), 7.73 (s, 1 H), 7.57 (td, *J* = 7.52, 1.83 Hz, 1 H), 7.51 (dt, *J* = 7.52, 1.28 Hz, 1 H), 7.22 (ddd, *J* = 7.61, 4.86, 1.47 Hz, 1 H), 1.93 - 2.03 (sept, *J* = 7.44 Hz, 2 H), 1.46 (s, 9 H), 1.20 (d, *J* = 7.52 Hz, 6 H), 1.06 (d, *J* = 7.34 Hz, 6 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 173.6, 164.0, 152.1, 150.2, 140.9, 135.6, 133.6, 131.7, 130.5, 122.9, 122.7, 97.1, 34.2, 28.4, 18.6, 18.4, 11.8

Further Transformations of Halogenated Products

Synthesis of 3:

An oven dried 2.5 ml Wheaton vial was charged with AgF (104 mg, 0.80 mmol), NIS (180 mg, 0.80 mmol) and a solution of **2q** in anhydrous THF (1.43 ml, 0.14 M, 0.20 mmol) under argon atmosphere. The mixture was stirred overnight in the dark at room temperature. After completion, the mixture was filtered through a short silica plug and concentrated. The residue was purified by silica gel chromatography (hexane) to afford the product (60.2 mg, 95%).



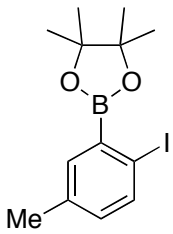
3:[5]

^{1}H NMR (500 MHz; $CDCl_3$): δ 7.76 (d, *J* = 8.46 Hz, 1H), 7.62 (d, *J* = 2.38 Hz, 1H), 7.00 (dd, *J* = 8.46, 2.38 Hz, 1H).

^{13}C NMR (126 MHz; $CDCl_3$): δ 140.8, 135.0, 132.4, 130.4, 128.8, 98.6.

Synthesis of 4:

An oven-dried 10 ml two-neck flask was charged with **2i** (81.8 mg, 0.20 mmol) and dry DCM (0.50 ml) under argon atmosphere. BCl_3 (0.88 ml, 1.0 M solution in heptane) was added dropwise to the mixture at 0 ºC. The resultant mixture was allowed to warm up to room temperature and kept for 6 h. A solution of pinacol (335 mg, 2.84 mmol) and triethylamine (0.50 ml) in dry DCM (0.50 ml) was injected to the above mixture and stirred overnight at room temperature. After completion, saturated aqueous $NaHCO_3$ (2 ml) was added. The mixture was extracted with DCM (5 ml × 3). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by silica gel chromatography (hexane/EtOAc = 20/1) to afford the product (59.8 mg, 87%) as colorless liquid.



4:

^{1}H NMR (500 MHz; $CDCl_3$): δ 7.70 (d, *J* = 8.05 Hz, 1H), 7.34 (d, *J* = 2.25 Hz, 1H), 6.89 (ddd, *J* = 8.05, 2.40, 0.64 Hz, 1H), 2.27 (s, 3H), 1.38 (s, 12H).

^{13}C NMR (126 MHz; $CDCl_3$): δ 139.2, 137.0, 136.7, 132.8, 96.4, 84.4, 24.8, 20.8.

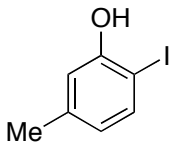
HRMS (EI) calcd. For $C_{13}H_{18}BIO_2$ $[M]^+$: 344.04449. Found: 344.04327.

[5] Jensen, T.; Pedersen, H.; Bang-Andersen, B.; Madsen, R.; Jørgensen, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 888.

Synthesis of 5:

An oven-dried 10 ml flask was charged with **2i** (81.8 mg, 0.20 mmol) and dry DCM (0.50 ml) under argon atmosphere. BCl_3 (0.88 ml, 1.0 M solution in heptane) was added dropwise to the mixture at 0 ºC. The resultant mixture was allowed to warm to room temperature and kept for 6 h. To the mixture was added slowly 30 % hydrogen peroxide (0.3 ml) and 3 % aqueous sodium hydroxide solution (1.0 ml) at room temperature. After stirring overnight, the mixture was diluted with water and extracted with DCM. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by silica gel chromatography (hexane/EtOAc = 5/1) to afford the product (37.3 mg, 80%) as pale brown oil.

5:[6]



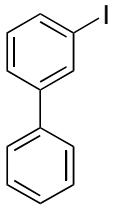
^{1}H NMR (500 MHz; $CDCl_3$): δ 7.50 (d, *J* = 8.07 Hz, 1H), 6.83 (dd, *J* = 2.01, 0.69 Hz, 1H), 6.52 (ddd, *J* = 8.07, 2.01, 0.67 Hz, 1H), 5.20 (s, 1H), 2.29 (s, 3H).

^{13}C NMR (126 MHz; $CDCl_3$): δ 154.5, 140.7, 137.7, 123.6, 115.8, 81.6, 21.0

Synthesis of *m*-iodobiphenyl 6:[7]

An oven dried 2.5 ml Wheaton vial was charged with **2c** (94.2 mg, 0.20 mmol), AgF (104 mg, 0.80 mmol), THF (1.0 ml) and H_2O (22 μL) under argon atmosphere. The mixture was stirred overnight in the dark at room temperature. After completion, the mixture was filtered through a short silica plug and concentrated. The residue was purified by silica gel chromatography (hexane) to afford the product (54.6 mg, 97%) as colorless oil.

6:



^{1}H NMR (500 MHz; $CDCl_3$): δ 7.96 (t, *J* = 1.73 Hz, 1H), 7.69 (ddd, *J* = 7.86, 1.74, 1.03 Hz, 1H), 7.57-7.55 (m, 3H), 7.46 (t, *J* = 7.49 Hz, 2H), 7.40-7.37 (m, 1H), 7.19 (t, *J* = 7.81 Hz, 1H).

^{13}C NMR (126 MHz; $CDCl_3$): δ 143.5, 139.6, 136.19, 136.15, 130.4, 128.9, 127.8, 127.1, 126.4, 94.8.

Synthesis of 7:

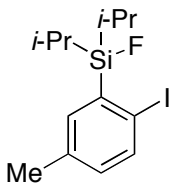
To a solution of **2i** (204.5 mg, 0.5 mmol) in THF (2 ml) was added HF (100 μL, 48% solution in water) at room temperature. After stirring for 1 h at the same temperature, the mixture was

[6] Sogawa, A.; Tsukayama, M.; Nozaki, H.; Nakayama, M. *Heterocycles* **1996**, *43*, 101.

[7] Dektar, J. L.; Hacker, N. P. *J. Org. Chem.* **1990**, *55*, 639.

neutralized with saturated aqueous $NaHCO_3$, extracted with EtOAc (20 ml × 3), dried ($MgSO_4$) and concentrated. The residue was purified by silica gel chromatography (hexane) to afford the product (164 mg, 94%) as colorless oil.

7:



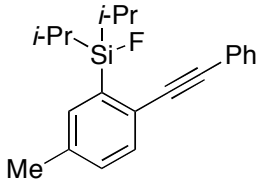
^{1}H NMR (500 MHz; $CDCl_3$): δ 7.70 (d, J = 8.07 Hz, 1 H), 7.35 (d, J = 2.57 Hz, 1 H), 6.93 (dd, J = 8.07, 1.83 Hz, 1 H), 2.32 (s, 3 H), 1.57 - 1.79 (m, 2 H), 1.21 (d, J = 7.70 Hz, 6 H), 1.02 (d, J = 7.34 Hz, 6 H).

^{13}C NMR (126 MHz; $CDCl_3$): δ 141.4 (d, J_{CF} = 12.9 Hz), 139.1, 138.3 (d, J_{CF} = 6.8 Hz), 136.8, 132.6, 97.1 (d, J_{CF} = 3.7 Hz), 21.1, 17.8, 17.1, 13.0.

Synthesis of 8:

Potassium (phenylethynyl)trifluoroborate (128 mg, 0.61 mmol), **7** (143.3 mg, 0.41 mmol), $PdCl_2$(dppf)•CH_2Cl_2 (32.8 mg, 10 mol %), and Cs_2CO_3 (401 mg, 3 equiv) were mixed with anhydrous THF (4 ml) under argon atmosphere. The mixture was heated at reflux for 2 days. After cooling, water (8 ml) was added to the flask. The resulting mixture was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by silica gel chromatography (hexane) to afford the product (87.1 mg, 66%) as colorless oil.

8:



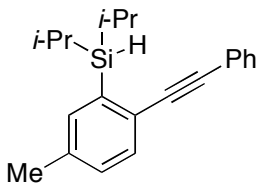
^{1}H NMR (500 MHz; $CDCl_3$): δ 7.44 - 7.51 (m, 4 H), 7.34 - 7.41 (m, 3 H), 7.22 (dd, J = 8.07, 1.83 Hz, 1 H), 2.40 (s, 3 H), 1.49 - 1.61 (m, 2 H), 1.16 (d, J = 7.34 Hz, 6 H), 1.05 (d, J = 7.70 Hz, 6 H).

^{13}C NMR (126 MHz; $CDCl_3$): δ 137.6, 136.4, 135.5, 132.4, 131.2, 130.5, 128.5, 128.3, 124.4, 123.4, 91.0, 90.5, 21.6, 17.4, 17.0, 13.1 (d, J = 12.9 Hz).

Synthesis of 9:

To a suspension of $LiAlH_4$ (16.0 mg, 0.42 mmol) in THF (4 ml) was added **8** (54.6 mg, 0.17 mmol) at room temperature. The mixture was refluxed for 10 h. After cooling, the mixture was poured into ice, extracted with Et_2O, dried over $MgSO_4$, and concentrated. The residue was purified by silica gel chromatography (hexane) to afford the product (48.0 mg, 92%) as colorless oil.

9:



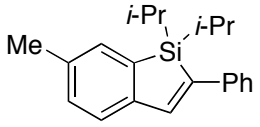
^{1}H NMR (500 MHz; $CDCl_3$): δ 7.52 (dd, *J* = 7.89, 1.65 Hz, 2 H), 7.48 (d, *J* = 7.70 Hz, 1 H), 7.31 - 7.41 (m, 4 H), 7.18 (dd, *J* = 7.89, 1.28 Hz, 1 H), 4.11 (t, *J* = 3.85 Hz, 1 H), 2.38 (s, 3 H), 1.42 - 1.52 (m, 2 H), 1.14 (d, *J* = 7.34 Hz, 6 H), 1.03 (d, *J* = 7.34 Hz, 6 H).

^{13}C NMR (126 MHz; $CDCl_3$): δ 137.6, 137.3, 137.1, 132.3, 131.3, 129.8, 128.4, 128.0, 126.0, 123.8, 91.4, 90.4, 21.6, 19.2, 11.2.

Synthesis of 10:

A suspension of potassium hydride (7 mg, 1.4 equiv) in 1,2-dimethoxyethane (DME, 0.2 ml) was added a solution of **9** (37.7 mg, 0.12 mmol) in DME (1.0 ml) at 0 ºC. The resulting yellow mixture was allowed to warm up to room temperature and stirred for 5 h. The excess KH was quenched with aqueous ammonium chloride at 0 ºC. The organic layer was extracted with Et_2O, washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by silica gel chromatography (hexane) to afford the product (27.8 mg, 74%) as a white solid.

10:



^{1}H NMR (500 MHz; $CDCl_3$): δ 7.54 (s, 1 H), 7.43 - 7.49 (m, 2 H), 7.32 - 7.39 (m, 3 H), 7.19 - 7.27 (m, 2 H), 7.13 - 7.17 (m, 1 H), 2.38 (s, 3 H), 1.43 - 1.51 (m, 2 H), 1.14 (d, *J* = 7.70 Hz, 6 H), 0.97 (d, *J* = 7.34 Hz, 6 H).

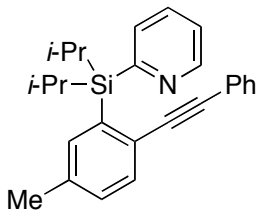
^{13}C NMR (126 MHz; $CDCl_3$): δ 147.7, 143.2, 142.4, 140.3, 135.8, 135.3, 134.0, 130.4, 128.6, 126.7, 124.0, 21.5, 18.2, 18.1, 11.7.

Synthesis of 11:

Phenyl acetylene (24 μl, 0.22 mmol), **2i** (82 mg, 0.2 mmol), $PdCl_2(MeCN)_2$ (1.5 mg, 3 mol %), CuI (0.8 mg, 2 mol %), *t*-Bu_3P (2.5 mg, 6 mol %), and *i*-Pr_2NH (43 μl, 1.5 equiv) were mixed with anhydrous 1,4-dioxane (0.4 ml) under argon atmosphere. The mixture was heated at 60 ^{o}C for 12 hours. After cooling, water (1 ml) was added to the reaction mixture. The resulting mixture was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, and

concentrated. The residue was purified by silica gel chromatography (hexane/EtOAc) to afford the product (69%) as light brown oil.

11:



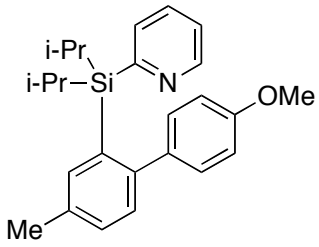
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81 - 8.84 (m, 1 H), 7.46 - 7.56 (m, 3 H), 7.10 - 7.31 (m, 8 H), 2.35 (s, 3 H), 1.86 - 1.97 (sept, *J* = 7.40 Hz, 2 H), 1.11 (d, *J* = 7.45 Hz, 6 H), 1.04 (d, *J* = 7.31 Hz, 6 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.9, 149.8, 137.8, 136.9, 135.4, 133.4, 133.2, 132.1, 131.1, 129.9, 128.1, 127.8, 126.9, 123.5, 122.5, 92.3, 91.1, 21.7, 18.2, 18.0, 11.0

Synthesis of 12:

4-Methoxyphenyl boronic acid (33.4 mg, 0.22 mmol), **2i** (82 mg, 0.2 mmol), $Pd_2(dba)_3$ (3.0 mg, 2.5 mol %), K_3PO_4 (127.4 mg, 3 equiv), and *t*-Bu_3P (4.1 mg, 10 mol %) were mixed with anhydrous 1,4-dioxane (0.4 ml) under argon atmosphere. The mixture was heated at 70 ^{o}C for 12 hours. After cooling, water (1 ml) was added to the reaction mixture. The resulting mixture was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by silica gel chromatography (hexane/EtOAc) to afford the product in 89% yield.

12:



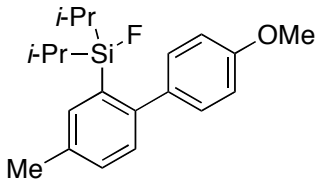
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 - 8.74 (m, 1 H), 7.38 - 7.45 (m, 2 H), 7.16 - 7.23 (m, 2 H), 7.08 - 7.13 (m, 2 H), 6.99 - 7.03 (m, 2 H), 6.62 - 6.69 (m, 2 H), 3.79 (s, 3 H), 2.37 (s, 3 H), 1.28 - 1.39 (sept, *J* = 7.40 Hz, 2 H), 0.99 - 1.03 (m, 12 H)

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9, 158.5, 149.6, 146.8, 138.0, 136.7, 134.9, 133.0, 132.6, 131.4, 130.6, 129.5, 122.0, 112.5, 55.2, 21.4, 18.8, 18.7, 11.7

Synthesis of 13:

To a solution of **12** (266 mg, 0.68 mmol) in THF (3.0 ml) was added HF (136 μL, 48% solution in water) at room temperature. After stirring for 1 h at the same temperature, the mixture was neutralized with saturated aqueous $NaHCO_3$, extracted with EtOAc (20 ml × 3), dried ($MgSO_4$) and concentrated. The residue was purified by silica gel chromatography (hexane/EtOAc = 15/1) to afford the product (229 mg, 100%) as colorless oil.

13:



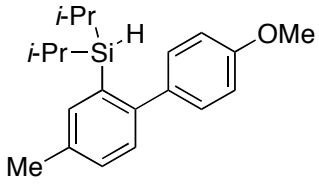
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.54 (s, 1 H), 7.22 - 7.32 (m, 3 H), 7.19 (d, J = 7.60 Hz, 1 H), 6.94 (d, J = 8.77 Hz, 2 H), 3.88 (s, 3 H), 2.44 (s, 3 H), 1.01 (d, J = 5.85 Hz, 6 H), 0.80 - 0.93 (m, 8 H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 159.0, 145.3, 136.4, 135.6 (d, J_{CF} = 5.5 Hz), 135.5, 132.7 (d, J_{CF} = 12.9 Hz), 130.3, 130.2, 129.9, 113.3, 55.3, 30.3, 17.5, 17.2, 13.6 (d, J_{CF} = 14.8 Hz).

Synthesis of 14:

To a suspension of $LiAlH_4$ (64.6 mg, 1.7 mmol) in diethyl ether (5 ml) was added a solution of **13** (229 mg, 0.68 mmol) in diethyl ether (2.5 ml) at room temperature. The mixture was refluxed for 72 h. After cooling, the mixture was poured into ice, extracted with diethyl ether, dried over $MgSO_4$, and concentrated. The residue was purified by silica gel chromatography (hexane/EtOAc = 20/1) to afford the product (166.8 mg, 79%) as light yellow oil.

14:



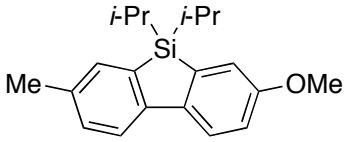
^{1}H NMR (500 MHz; $CDCl_3$): δ 7.39 (d, J = 1.83 Hz, 1 H), 7.16 - 7.25 (m, 4 H), 6.93 (d, J = 8.80 Hz, 2 H), 3.87 (s, 3 H), 3.73 (t, J = 3.67 Hz, 1 H), 2.42 (s, 3 H), 1.04 (s, 2 H), 0.97 - 1.00 (m, 6 H), 0.93 (d, J = 6.97 Hz, 6 H).

^{13}C NMR (126 MHz; $CDCl_3$): δ 158.6, 146.6, 136.8, 136.6, 135.1, 133.6, 130.7, 129.6, 129.6, 112.9, 55.3, 21.3, 19.3, 19.1, 11.6.

Synthesis of 15:

To a solution of **14** (0.2 mmol) in DCM (1 ml) was added 2,6-lutidine (47 μL, 0.4 mmol) and a solution of $Ph_3CB(C_6F_5)_4$ (370 mg, 0.4 mmol) in DCM (1.4 ml) at room temperature. The reaction was completed within 1 h, monitored by GC/MS. Water was added to the reaction mixture. The mixture was extracted with DCM. Combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by silica gel chromatography (hexane to hexane/EtOAc = 100/1) to afford the product (43.9 mg, 71%) as colorless oil.

15:



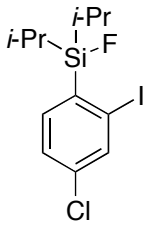
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.71 (d, J = 8.18 Hz, 1 H), 7.62 (d, J = 7.60 Hz, 1 H), 7.38 (s, 1 H), 7.21 (dd, J = 7.89, 1.46 Hz, 1 H), 7.13 (d, J = 2.34 Hz, 1 H), 6.94 (dd, J = 8.48, 2.63 Hz, 1 H), 3.86 (s, 3 H), 2.38 (s, 3 H), 1.31 - 1.42 (m, 2 H), 1.05 (dd, J = 7.31, 1.46 Hz, 12 H).

^{13}C NMR (101 MHz; $CDCl_3$): δ 158.5, 146.3, 142.0, 137.9, 135.4, 134.3, 130.8, 121.4, 119.9, 119.2, 114.7, 55.3, 21.4, 18.2, 11.1.

Synthesis of 2e':

To a solution of **2e** (1.59 g, 3.7 mmol) in THF (10 ml) was added HF (740 μL, 48% solution in water) at room temperature. After stirring for 1 h at the same temperature, the mixture was neutralized with saturated aqueous $NaHCO_3$, extracted with Et_2O, dried over $MgSO_4$, and concentrated. The residue was purified by silica gel chromatography (hexane) to afford the product (1.26 g, 92%) as colorless oil.

2e':



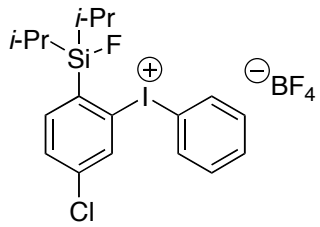
^{1}H NMR (500 MHz; $CDCl_3$): δ 7.85 (d, J = 1.47 Hz, 1 H), 7.40 - 7.45 (m, 1 H), 7.35 - 7.40 (m, 1 H), 1.57 - 1.67 (m, 2 H), 1.18 (d, J = 7.70 Hz, 6 H), 0.99 (d, J = 7.70 Hz, 6 H).

^{13}C NMR (126 MHz; $CDCl_3$): δ 140.2 (d, J_{CF} = 14.8 Hz), 138.7, 138.2 (d, J_{CF} = 7.4 Hz), 136.6, 127.6, 100.6 (d, J_{CF} = 3.7 Hz), 17.7, 17.0, 12.8 (d, J_{CF} = 14.8 Hz).

Synthesis of 16:

m-Chloroperbenzoic acid (76%, 270 mg, 1.2 equiv) was dissolved in DCM (3 ml). To the solution was added a solution of **2e'** (370 mg, 1.0 mmol) in DCM (1 mL) and then BF_3•Et_2O (202 μL, 2.5 equiv) at room temperature. The resulting mixture was stirred at the same temperature for 1 h. After cooling to 0 ºC, phenylboronic acid (134 mg, 1.1 equiv) was added. After stirring for another 30 min at room temperature, the crude reaction mixture was applied to a silica plug (2 g) and eluted with DCM (25 ml) and followed by DCM/MeOH (90 ml, 20:1) to elute the product. The combined solution was concentrated, and Et_2O (3 ml) was added. The flask was stored in the freezer for 1 h to induce precipitation. The ether phase was decanted, and the solid was washed twice with cold ether and then dried under vacuum to give diaryliodonium salts (365.8 mg, 68%, pure enough for the following benzyne chemistry). Analytical pure sample was obtained by further washing the crude

salts with ether. The solids were collected by filtration. Then, the filter cake was washed twice with ether and dried under vacuum.



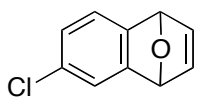
16:

^{1}H NMR (500 MHz; DMSO-d_6): δ 8.24 (d, J = 6.97 Hz, 2 H), 7.80 (t, J = 7.52 Hz, 1 H), 7.52 - 7.67 (m, 4 H), 6.80 (d, J = 1.83 Hz, 1 H), 1.19 - 1.34 (m, 2 H), 1.06 (d, J = 7.34 Hz, 6 H), 0.90 (d, J = 7.34 Hz, 6 H).

^{13}C NMR (126 MHz; DMSO-d_6): δ 139.0, 138.5, 137.9, 137.2, 133.2, 132.5, 130.4, 129.9, 124.7, 114.7, 17.4, 17.2, 13.2.

Synthesis of 18:

To a solution of diaryliodonium salt **16** (83 mg, 0.155 mmol) in DCM (0.6 mL) was added furan (56.5 μL, 5 equiv) and followed by TBAF (0.19 mL, 1.0 M solution in THF, 1.2 equiv) at room temperature. The reaction mixture was stirred for 1 h at the same temperature. Then solvent was evaporated and the residue was applied to silica gel chromatography (eluent: hexane/EtOAc = 9:1) to afford the product (24.6 mg, 89%) as a colorless liquid.



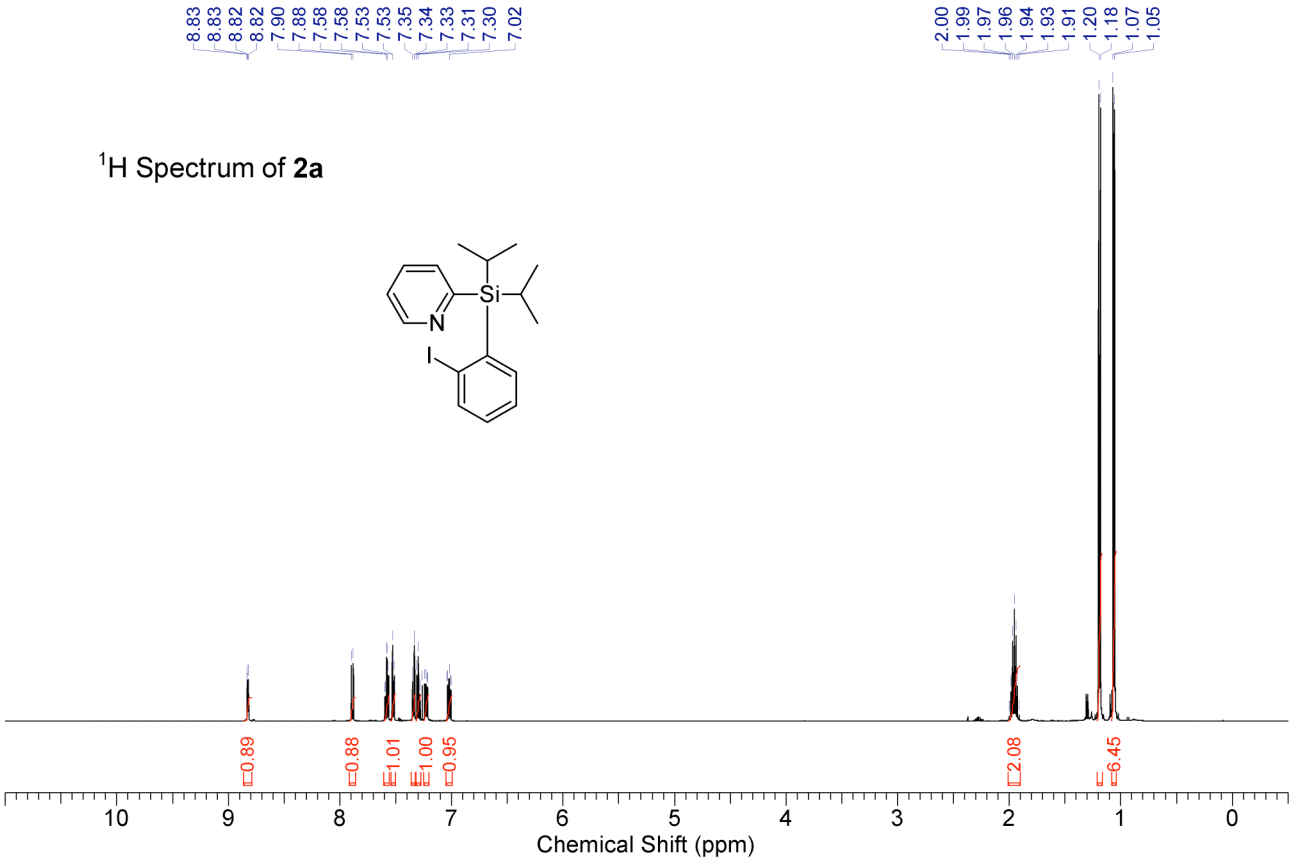
18:[8]

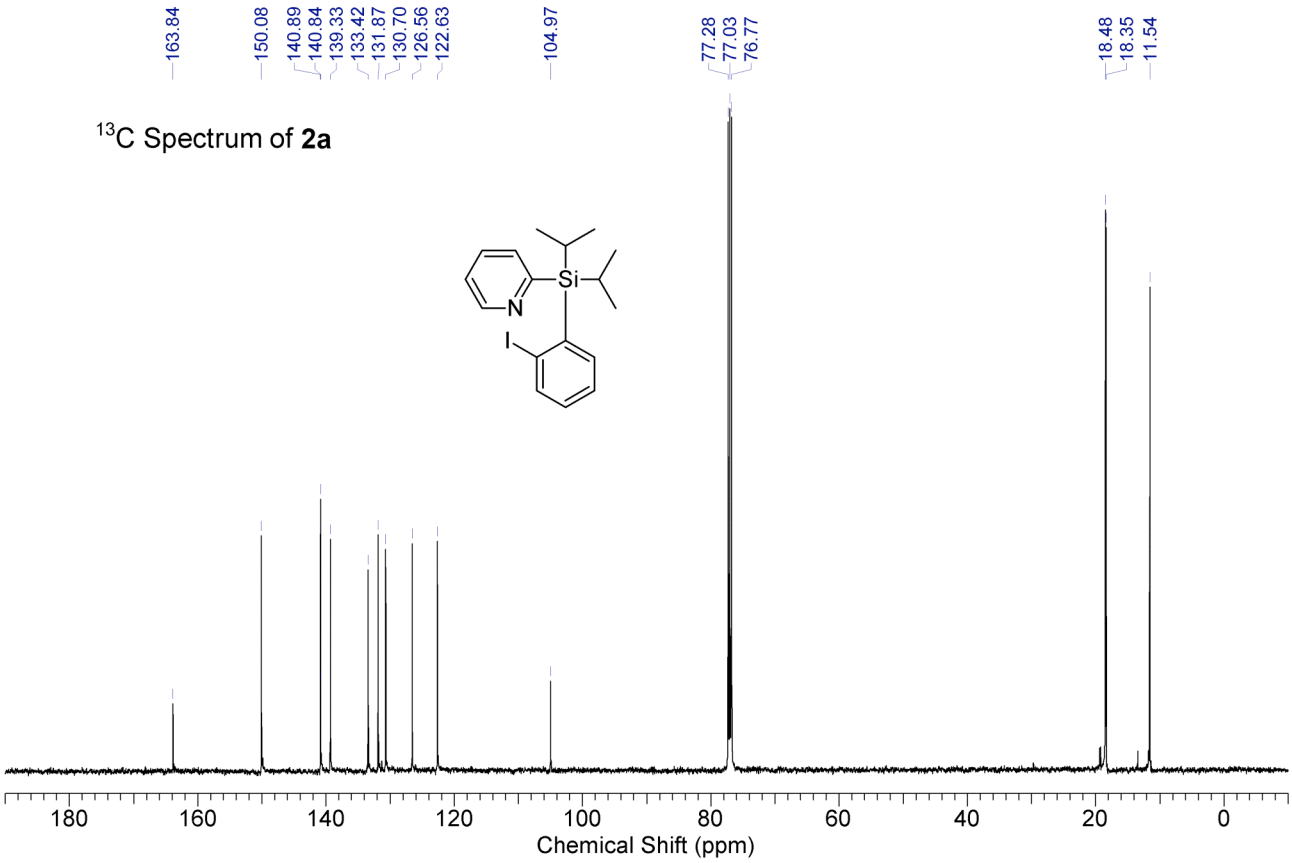
^{1}H NMR (500 MHz; $CDCl_3$): δ 7.23 (d, J = 1.47 Hz, 1 H), 7.15 (d, J = 7.70 Hz, 1 H), 6.99 - 7.07 (m, 2 H), 6.96 (dd, J = 7.70, 1.83 Hz, 1 H), 5.70 (dd, J=3.12, 1.65 Hz, 2 H).

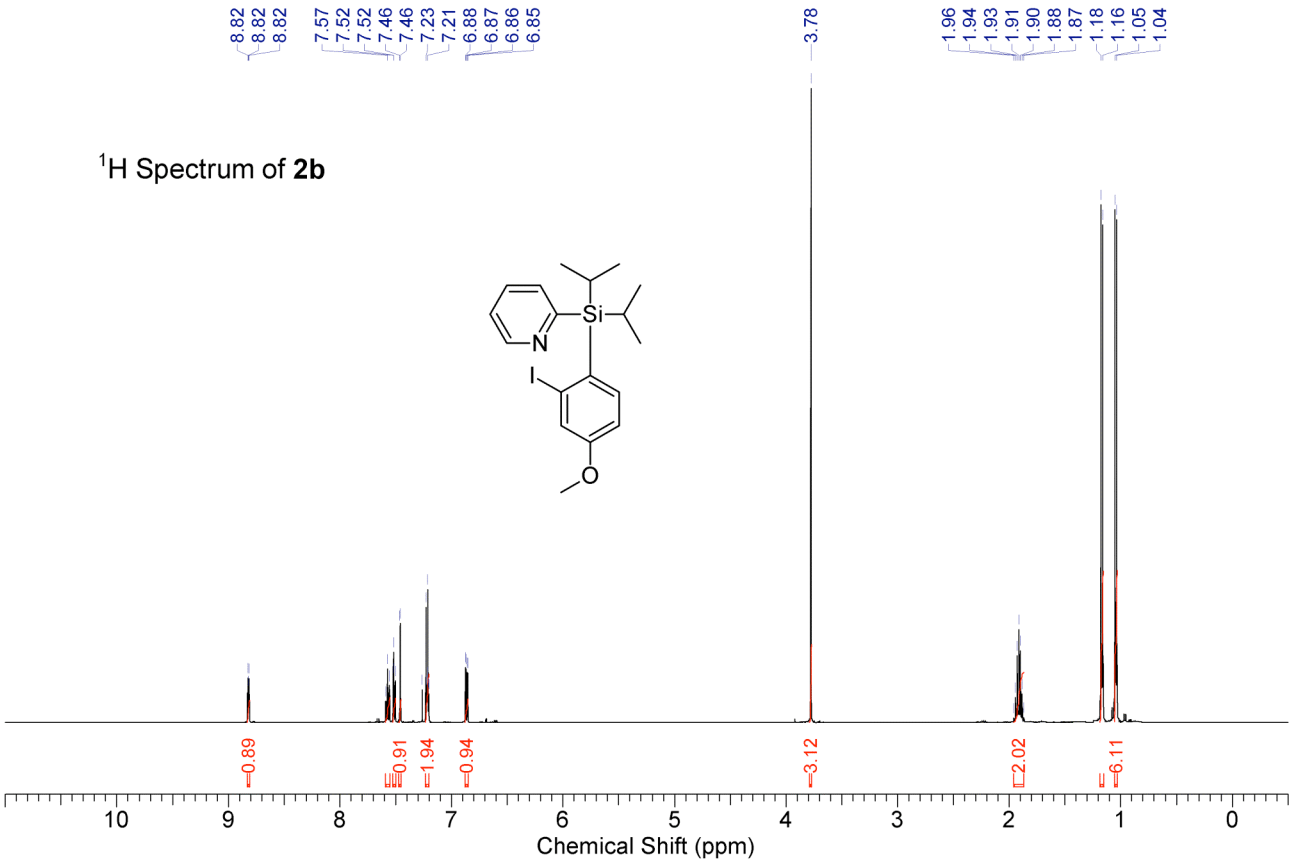
^{13}C NMR (126 MHz; $CDCl_3$): δ 151.4, 147.6, 143.2, 142.6, 130.7, 124.6, 121.3, 121.0, 82.1, 82.0.

[8] Caster, K. C.; Keck, C. G.; Walls, R. D. *J. Org. Chem.* **2001,** *66,* 2932.

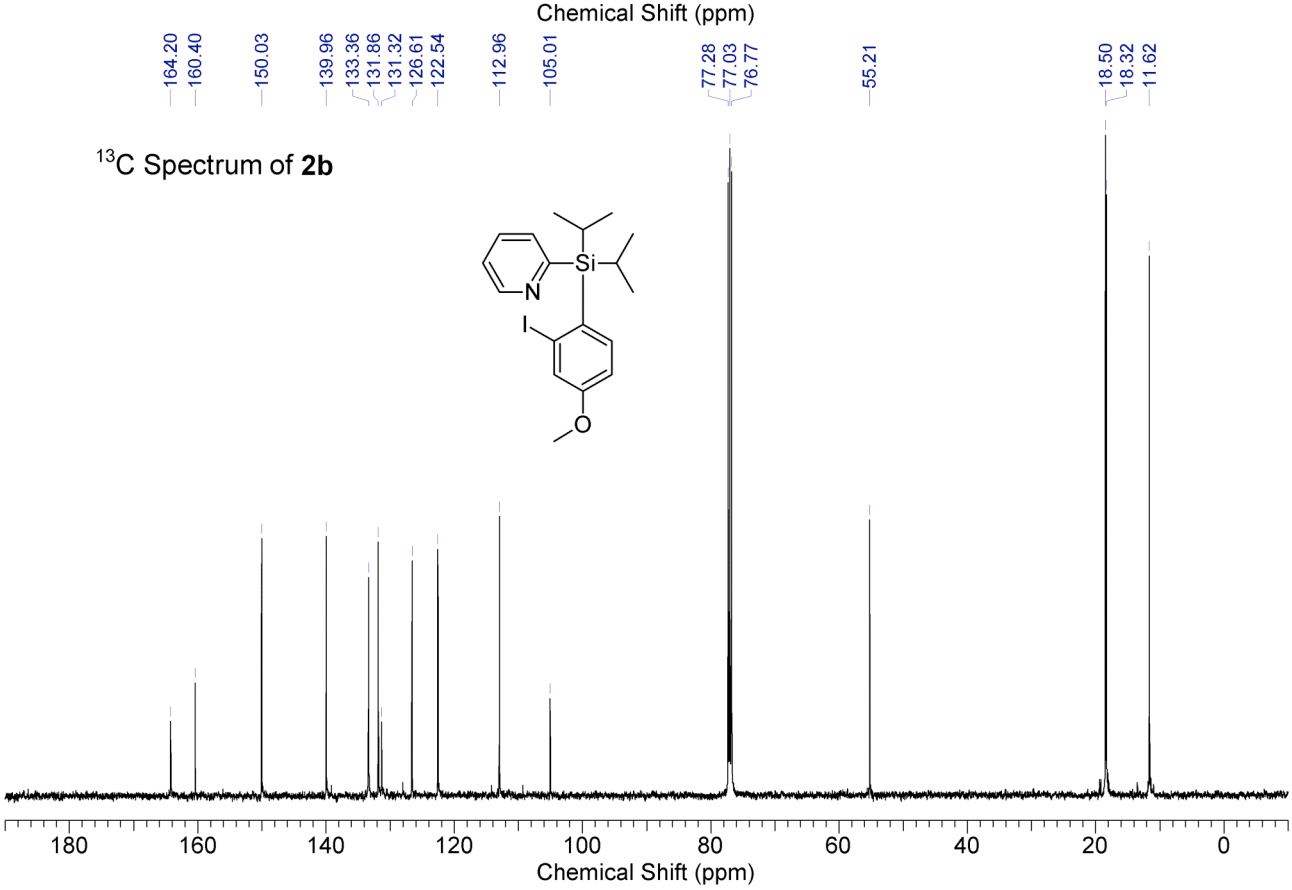
Spectral Charts



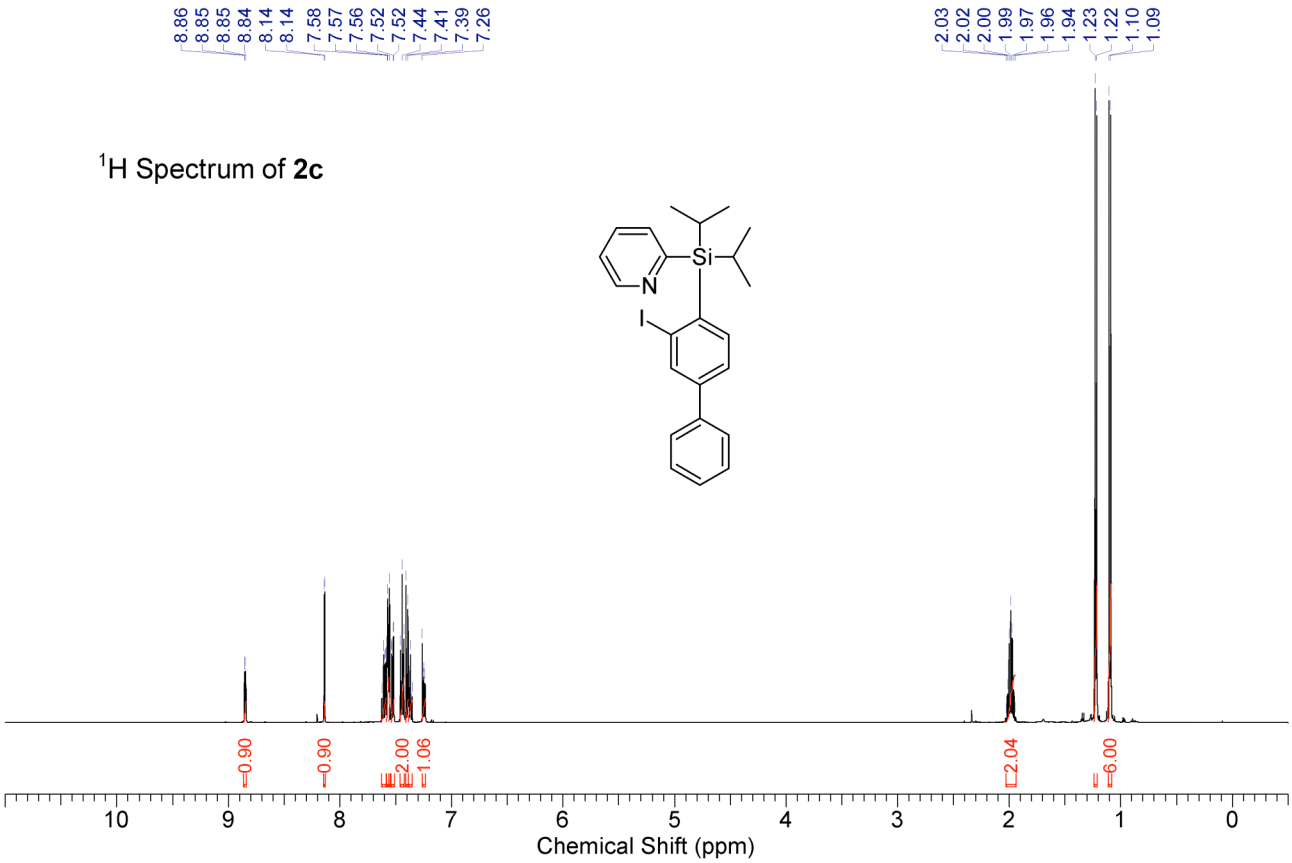




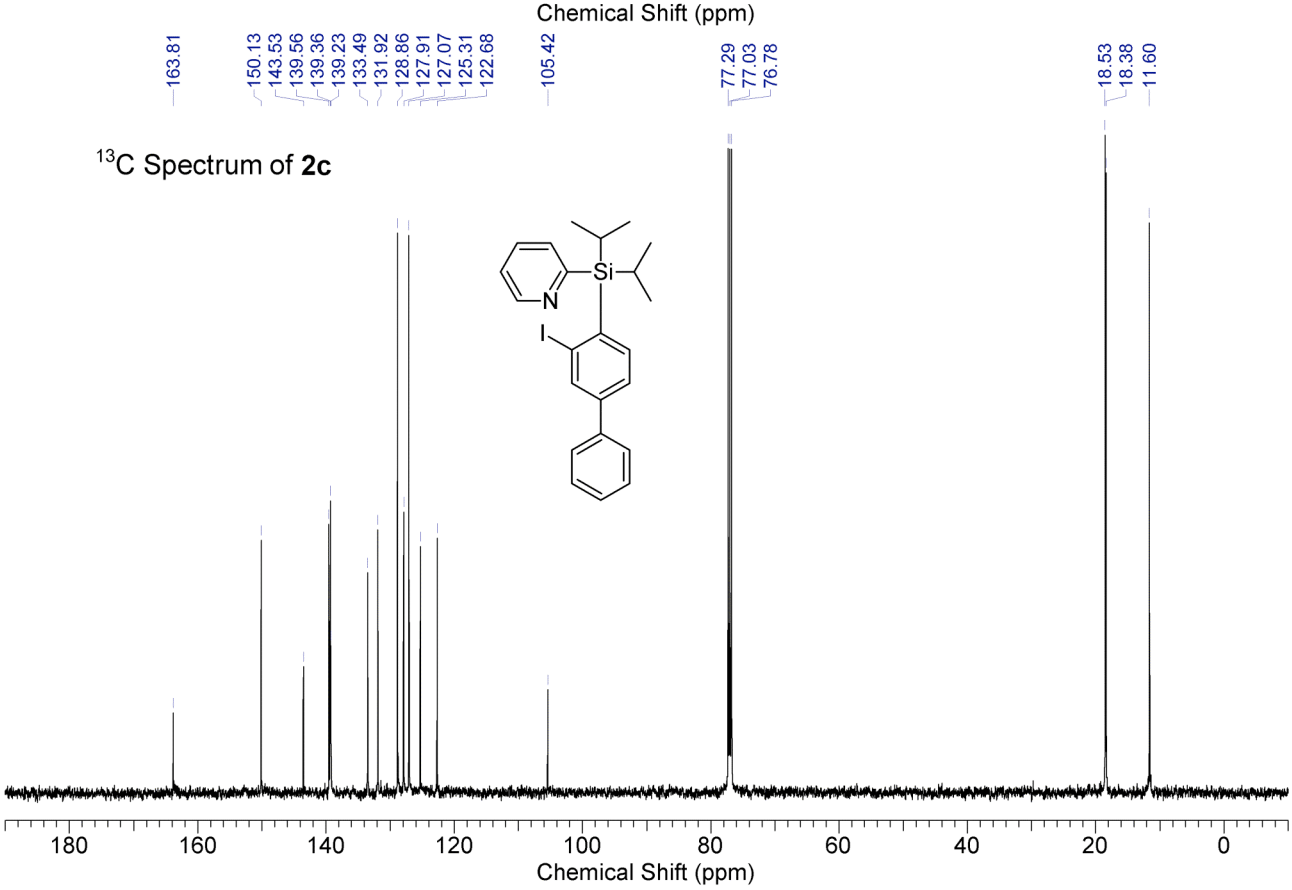
^{1}H Spectrum of **2b**



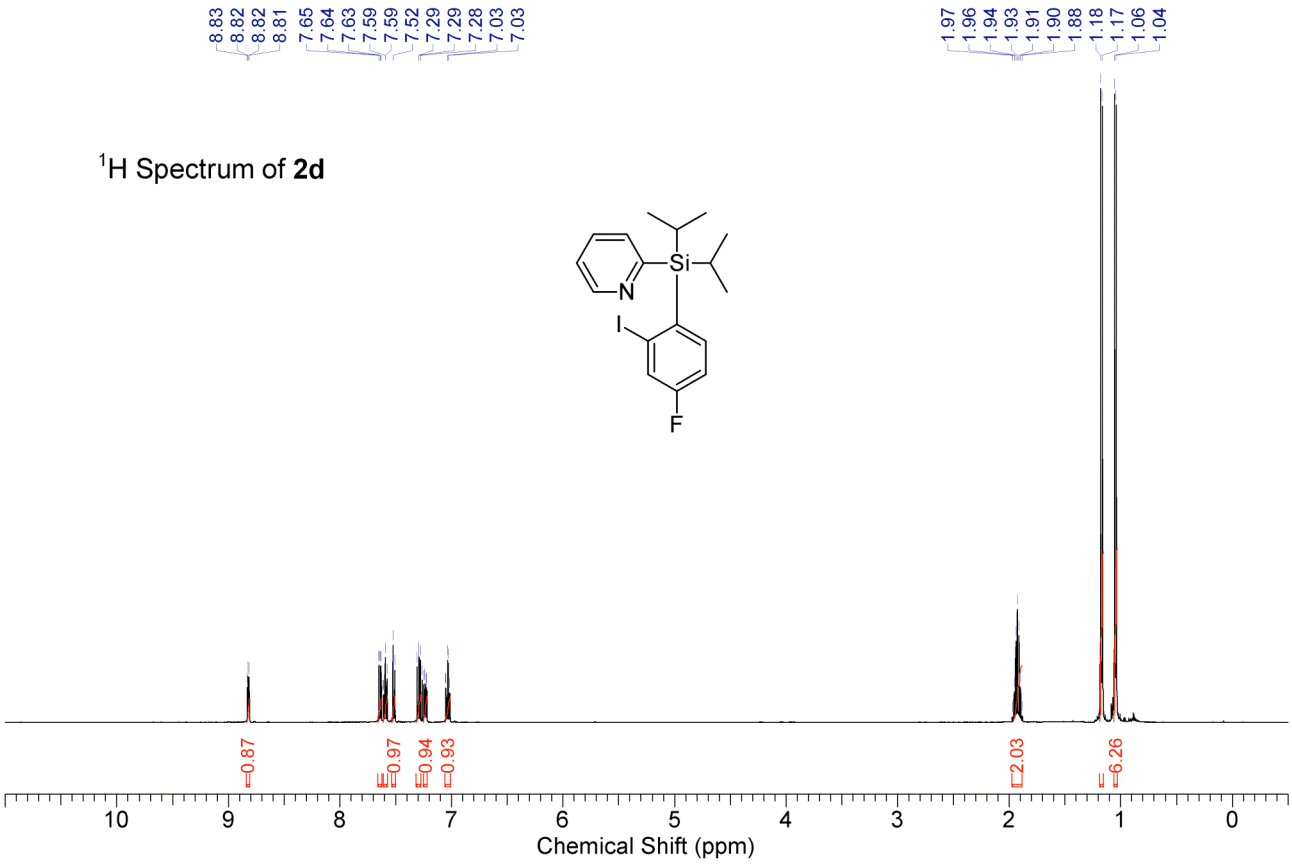
^{13}C Spectrum of **2b**



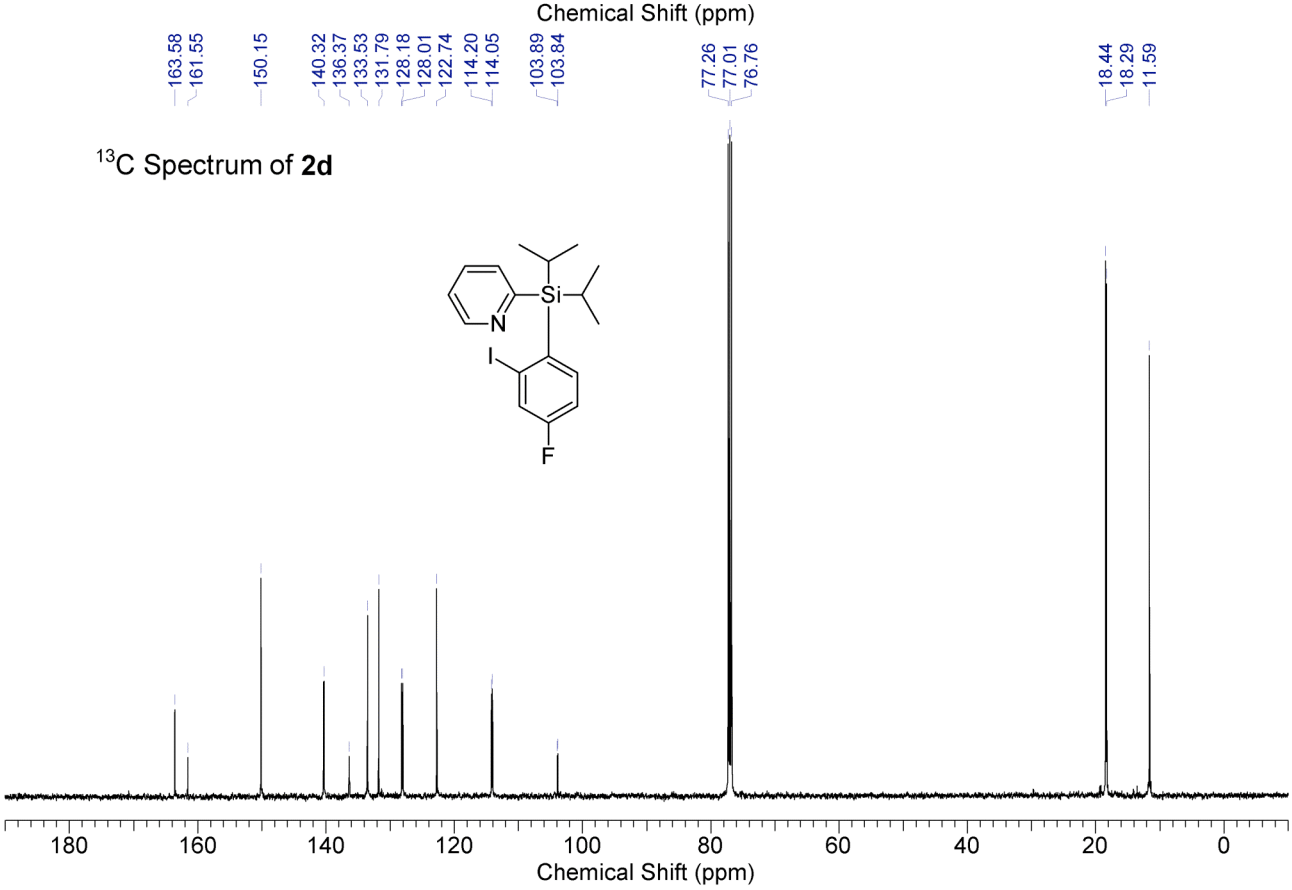
^{1}H Spectrum of **2c**



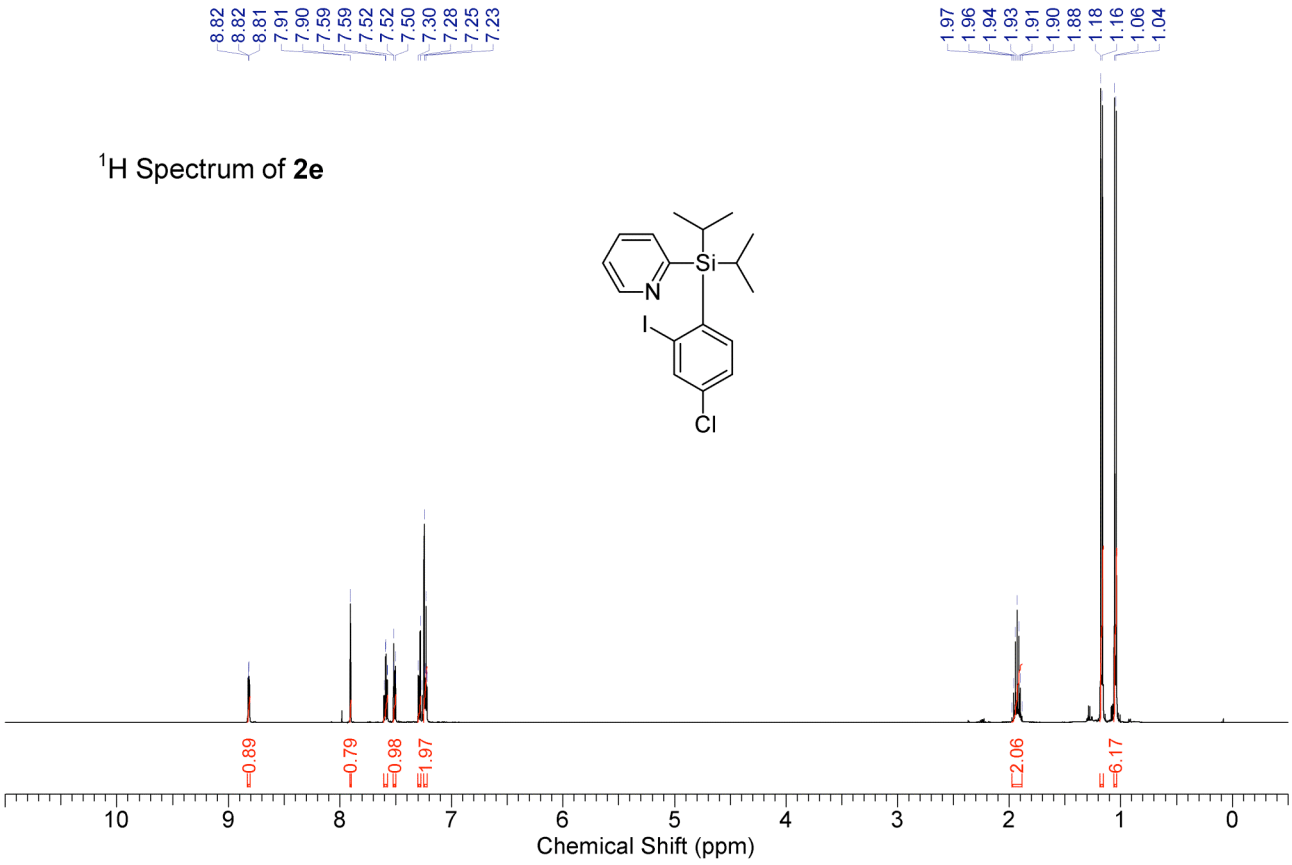
^{13}C Spectrum of **2c**



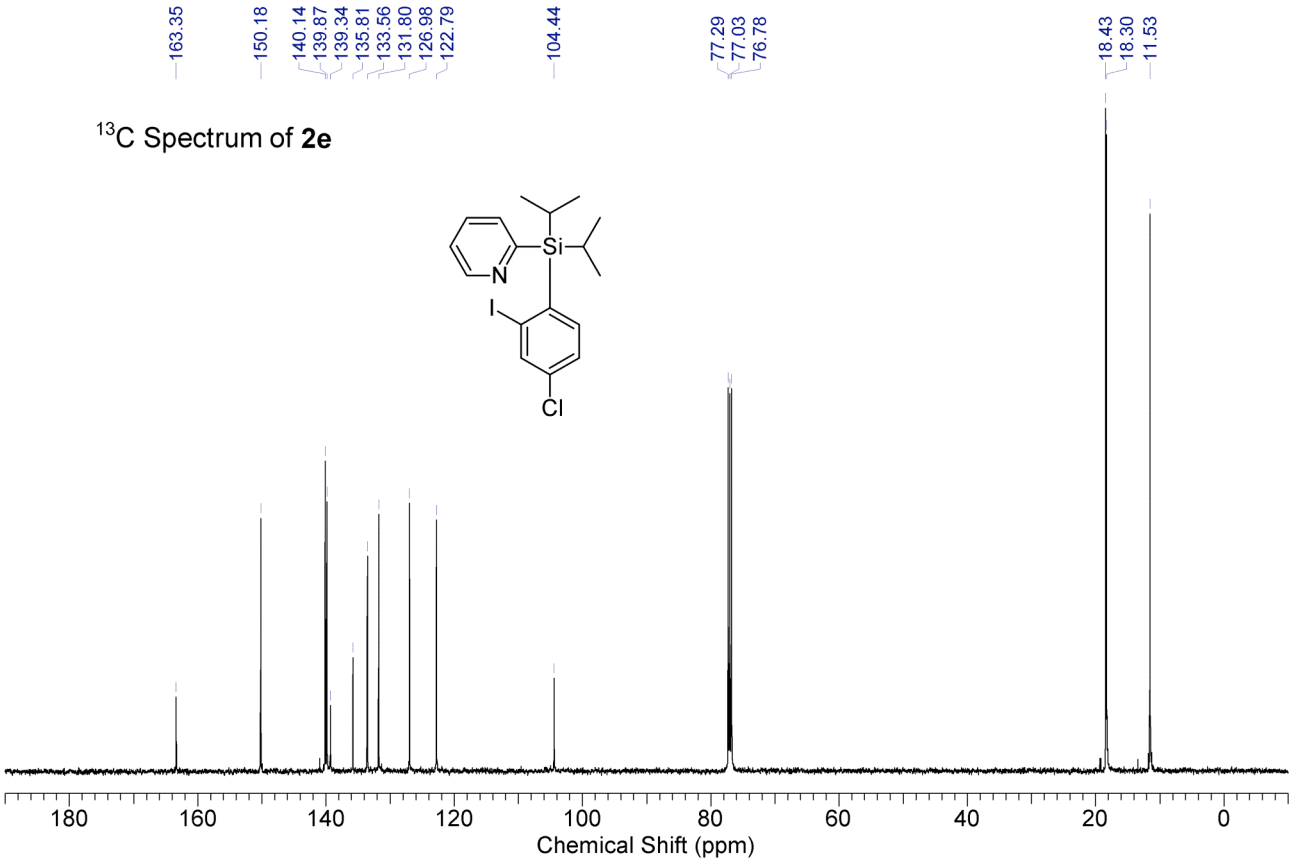
^{1}H Spectrum of **2d**



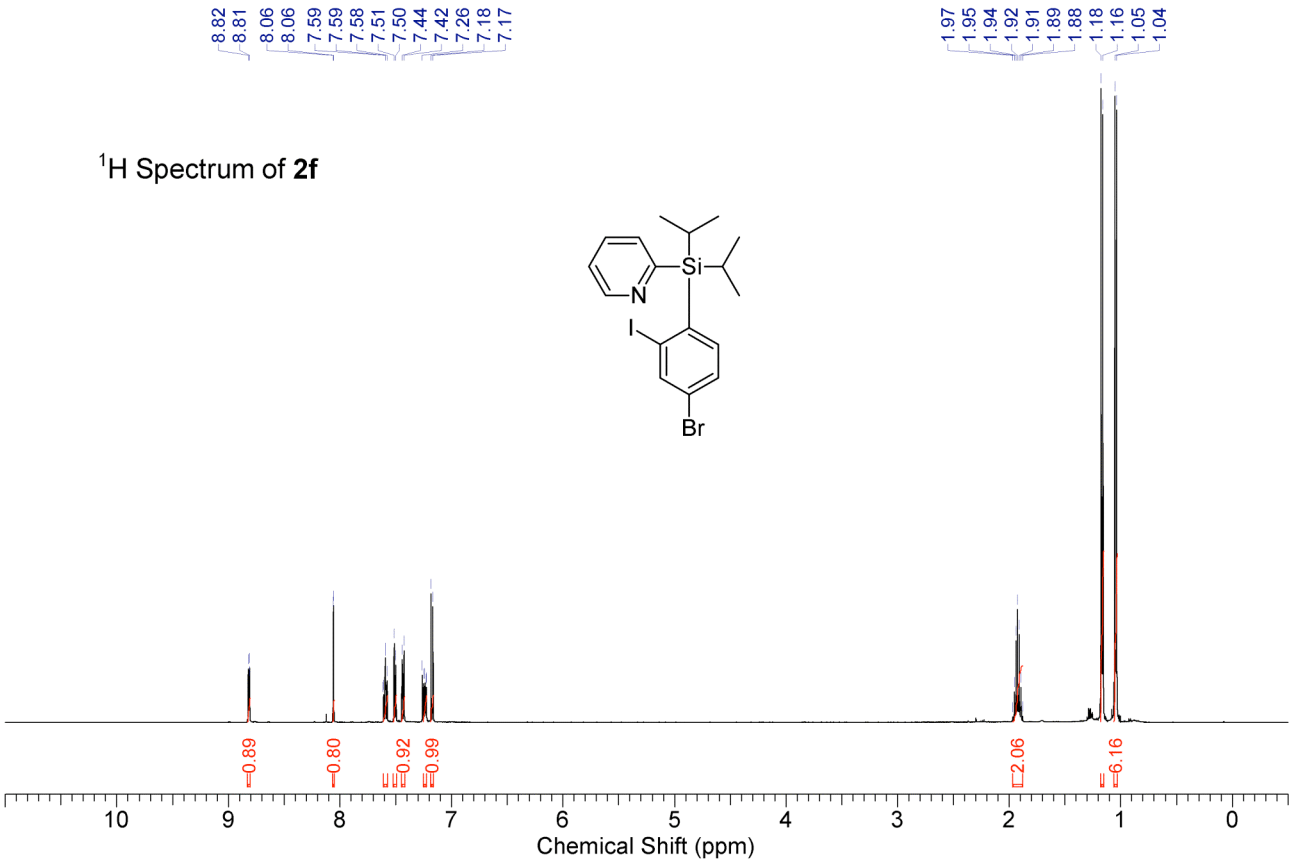
^{13}C Spectrum of **2d**



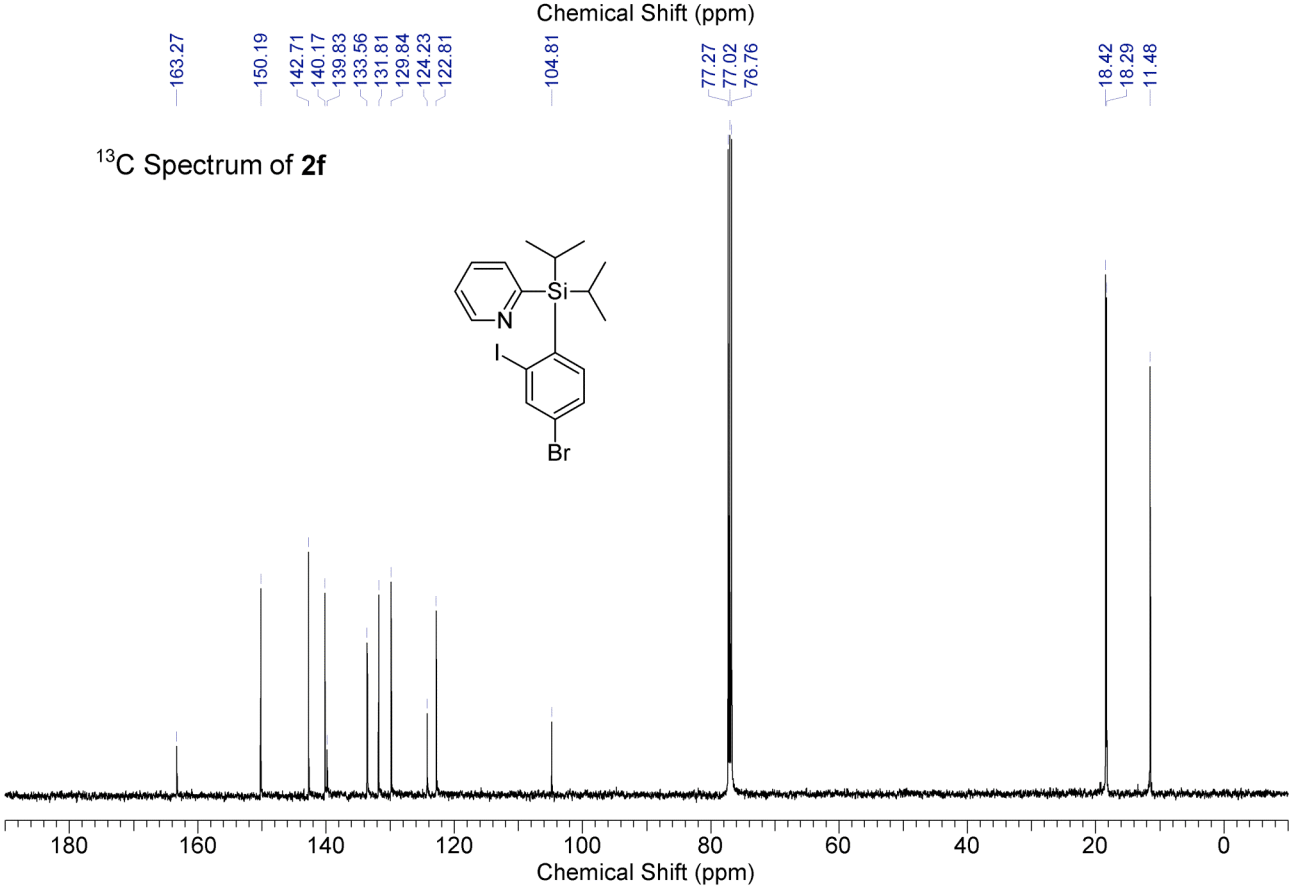
^{1}H Spectrum of **2e**



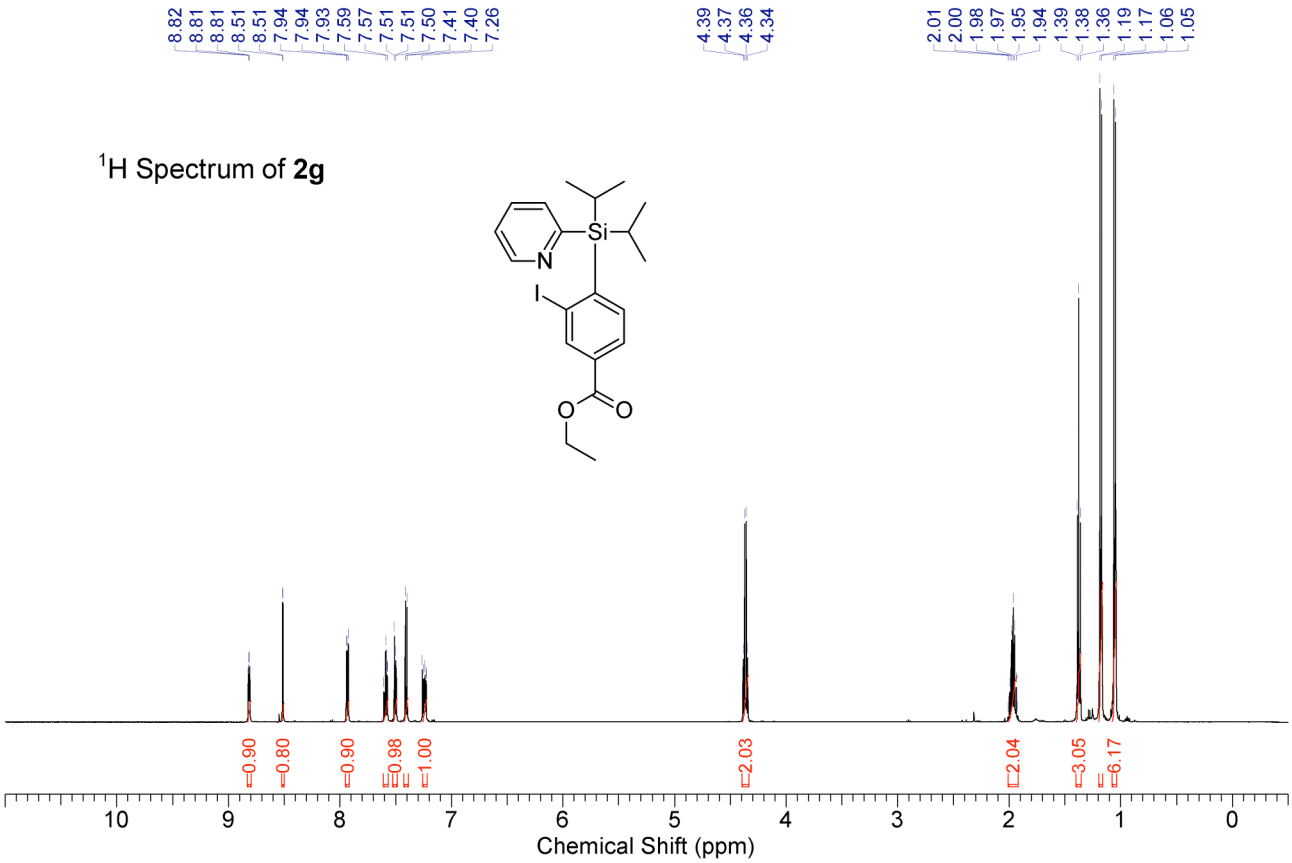
^{13}C Spectrum of **2e**

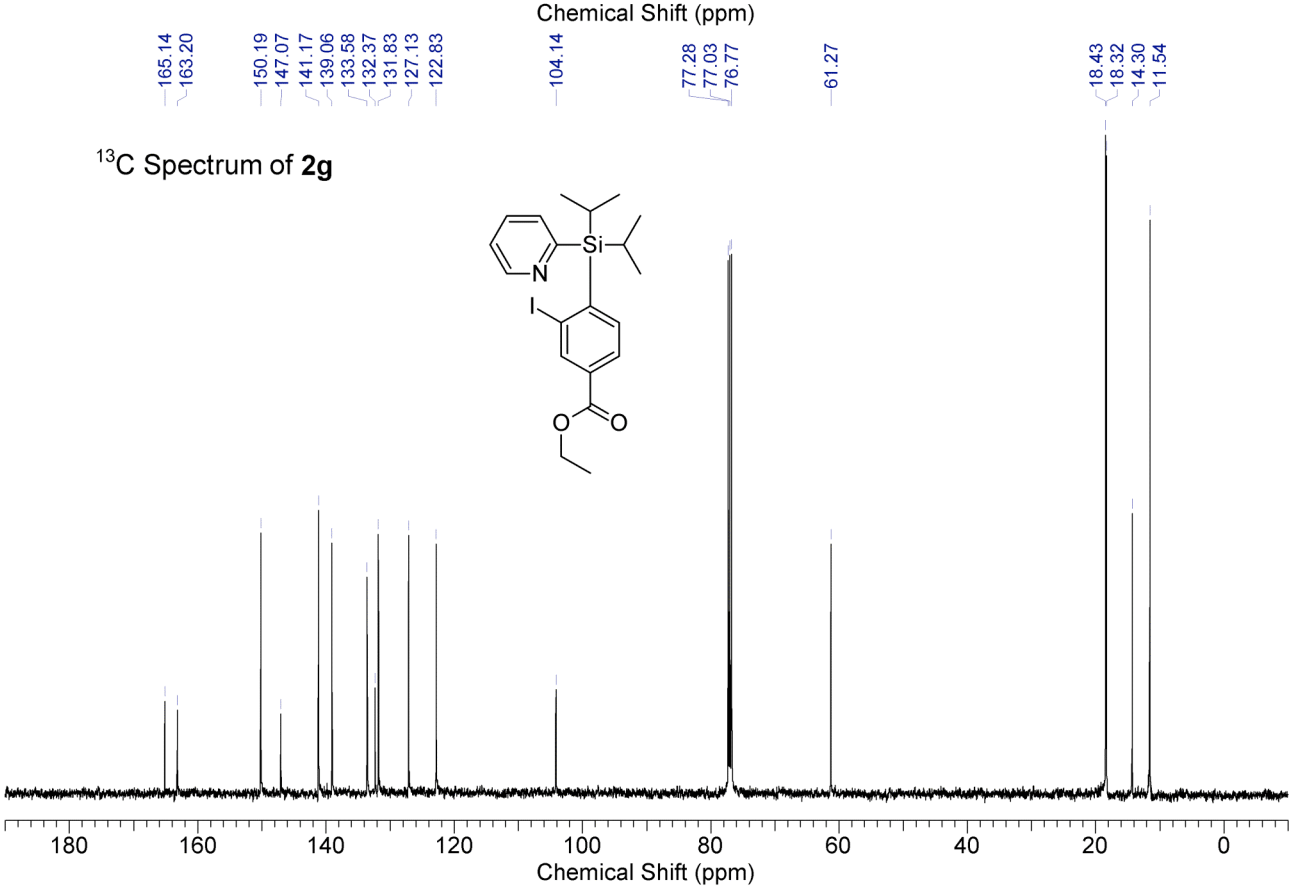


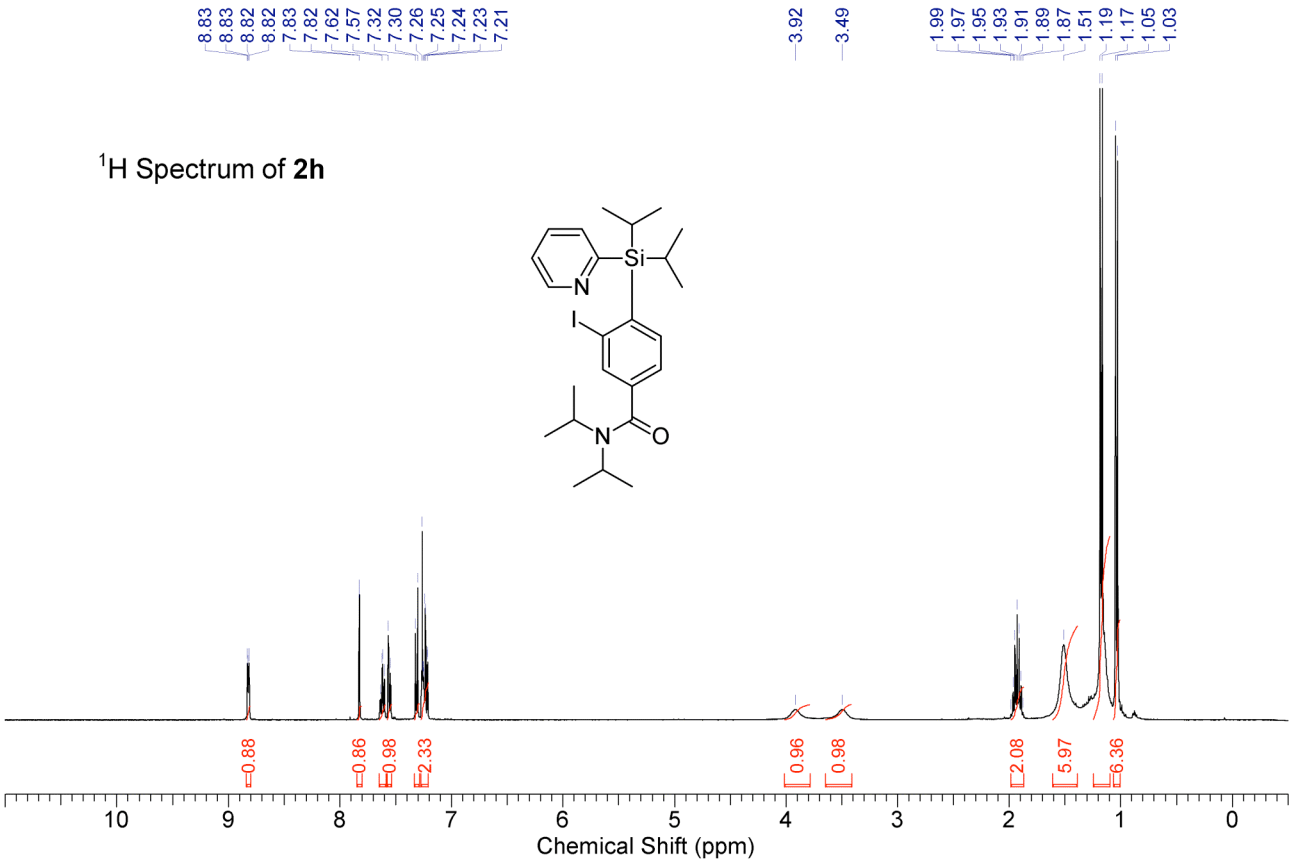
^{1}H Spectrum of **2f**

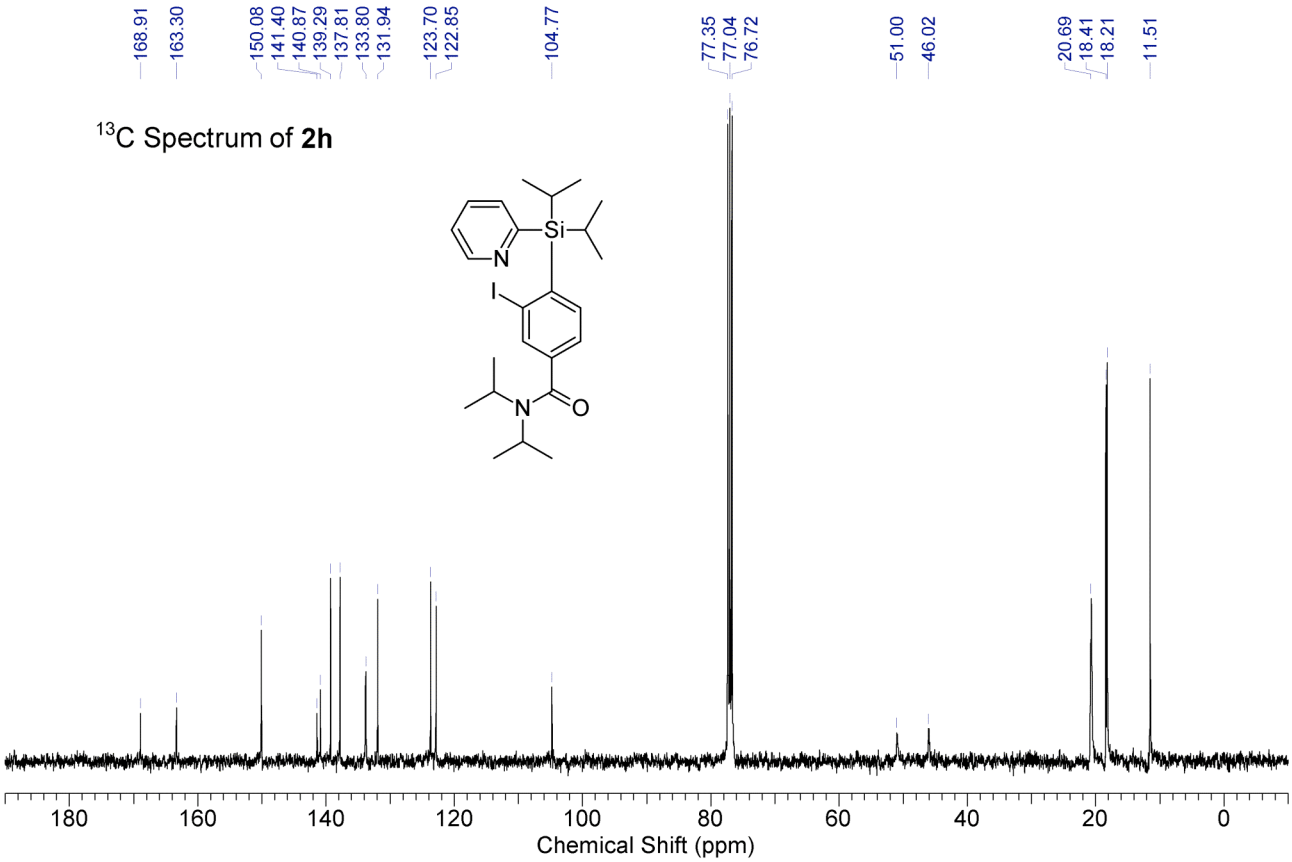


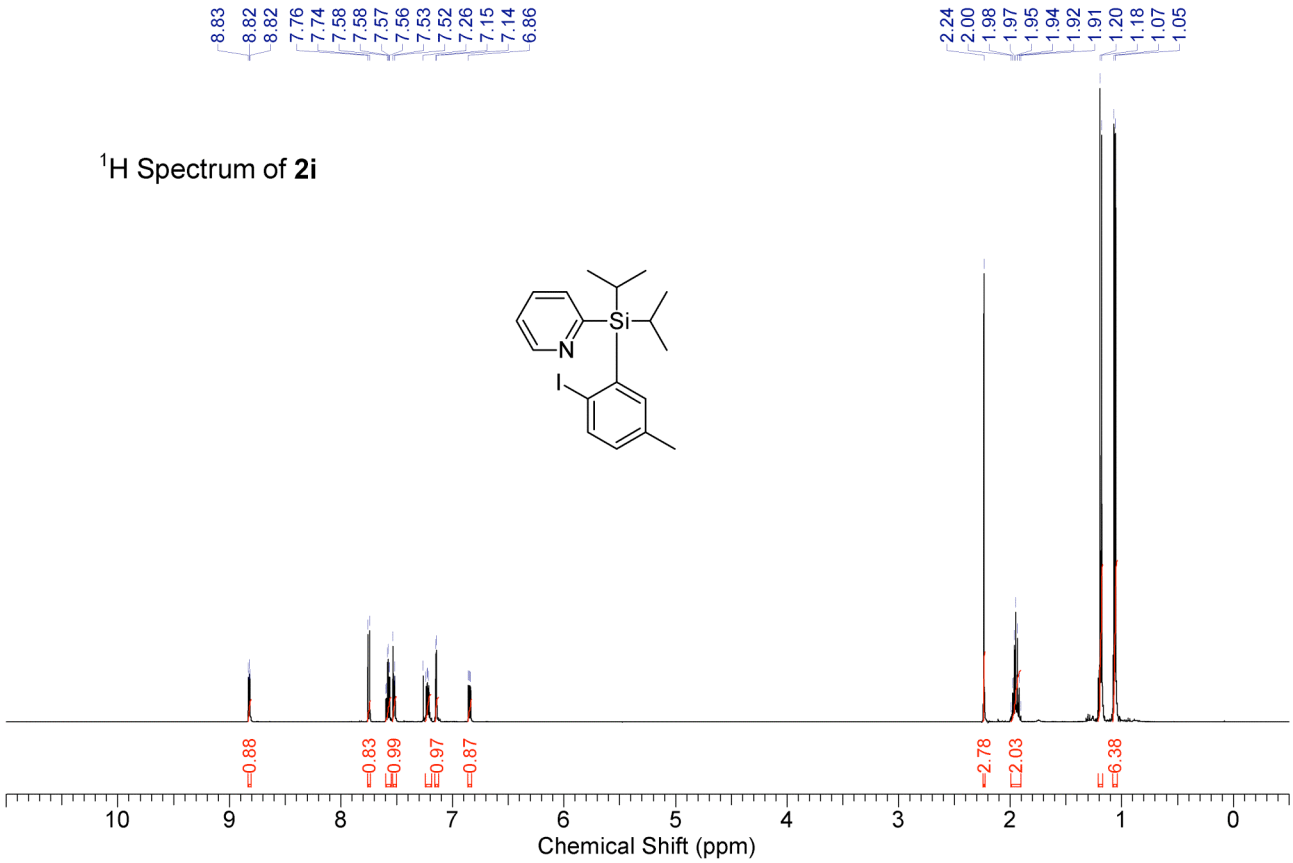
^{13}C Spectrum of **2f**


8.82
8.81
8.81
8.51
8.51
7.94
7.94
7.93
7.59
7.57
7.51
7.51
7.50
7.41
7.40
7.26
4.39
4.37
4.36
4.34
2.01
2.00
1.98
1.97
1.95
1.94
1.39
1.38
1.36
1.19
1.17
1.06
1.05
¹H Spectrum of 2g
Si
N
I
O
O
0.90
0.80
0.90
0.98
1.00
2.03
2.04
3.05
6.17
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

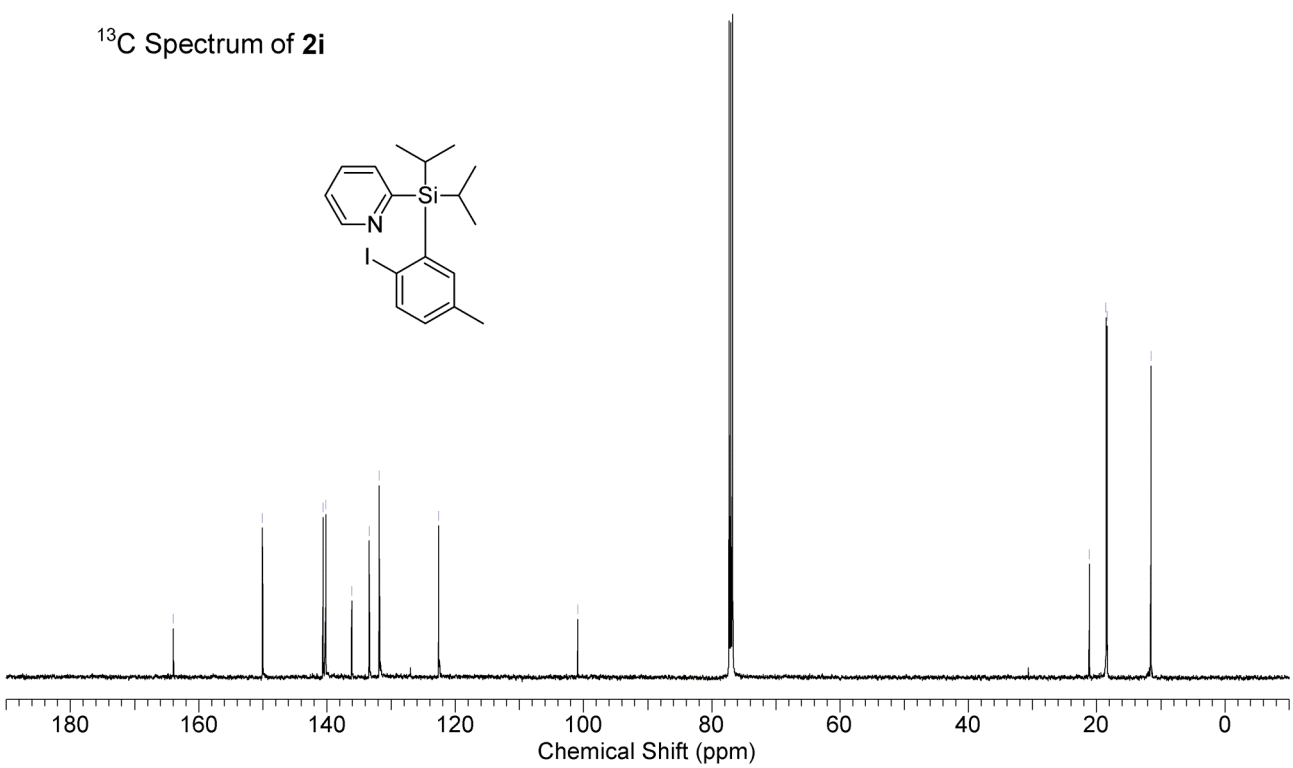

165.14
163.20
150.19
147.07
141.17
139.06
133.58
132.37
131.83
127.13
122.83
104.14
77.28
77.03
76.77
61.27
18.43
18.32
14.30
11.54
¹³C Spectrum of 2g
Si
N
I
O
O
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


8.83
8.83
8.82
8.82
7.83
7.82
7.62
7.57
7.32
7.30
7.26
7.25
7.24
7.23
7.21
3.92
3.49
1.99
1.97
1.95
1.93
1.91
1.89
1.87
1.51
1.19
1.17
1.05
1.03
1H Spectrum of 2h
Si
N
I
N
O
0.88
0.86
0.98
2.33
0.96
0.98
2.08
5.97
6.36
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

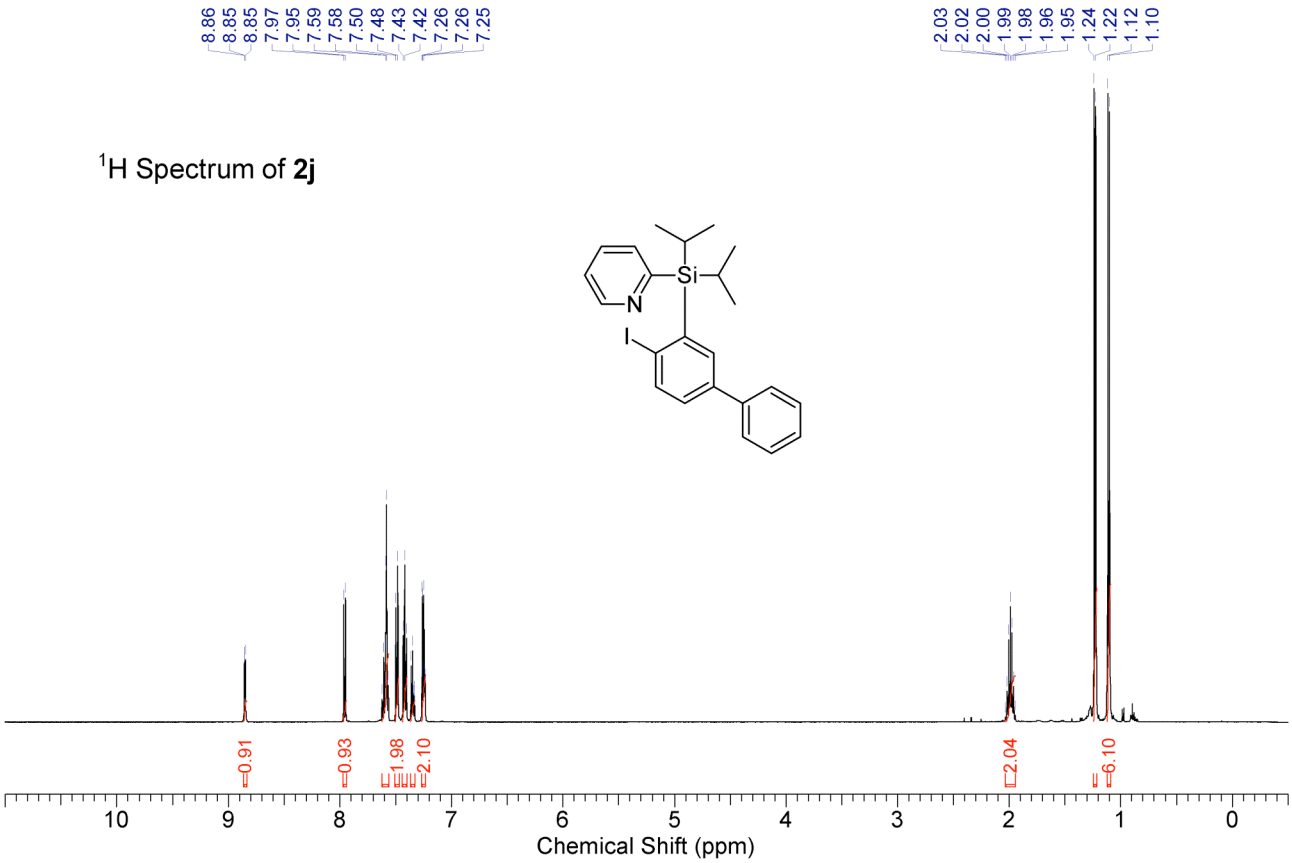

168.91
163.30
150.08
141.40
140.87
139.29
137.81
133.80
131.94
123.70
122.85
104.77
77.35
77.04
76.72
51.00
46.02
20.69
18.41
18.21
11.51
13C Spectrum of 2h
Si
N
I
N
O
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)



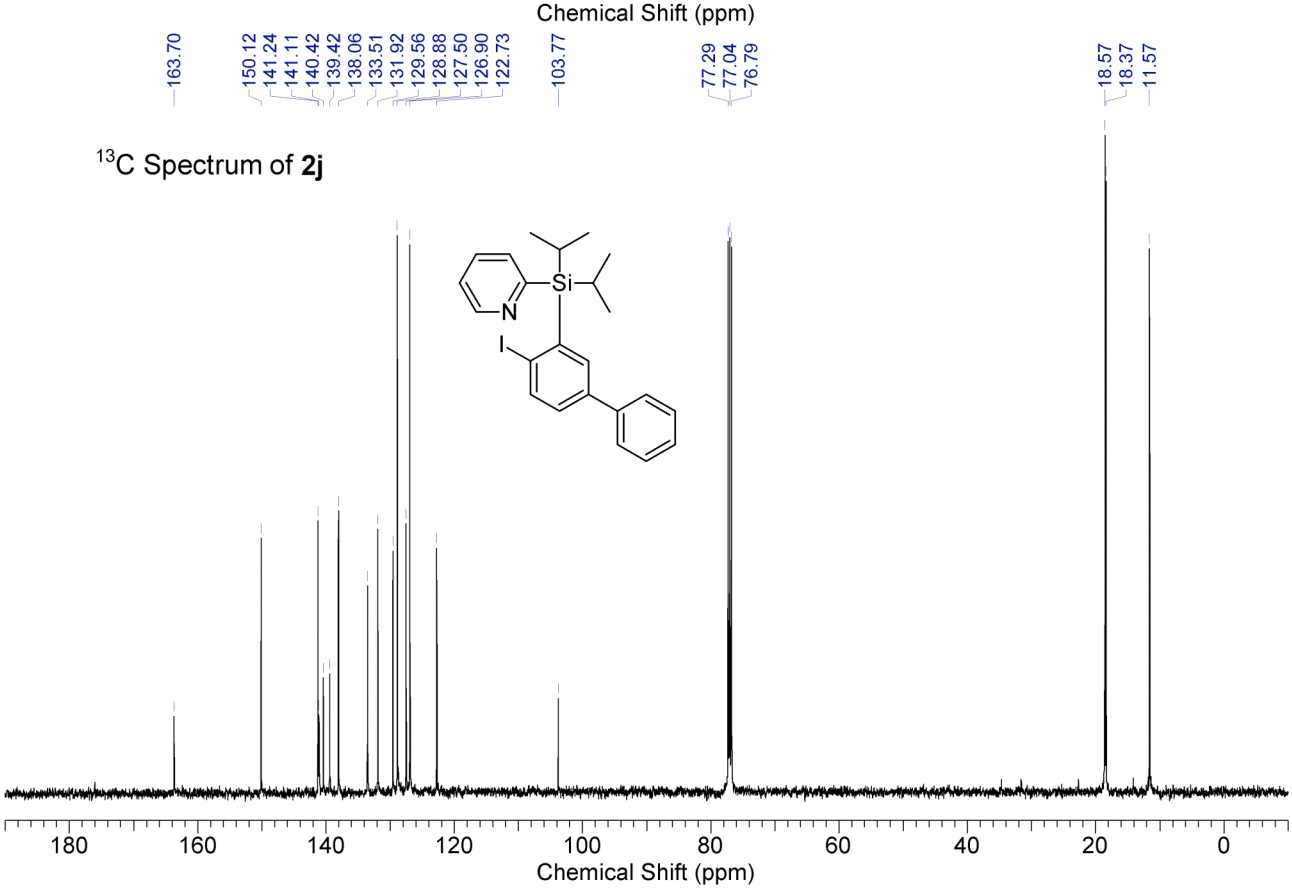
^{1}H Spectrum of **2i**



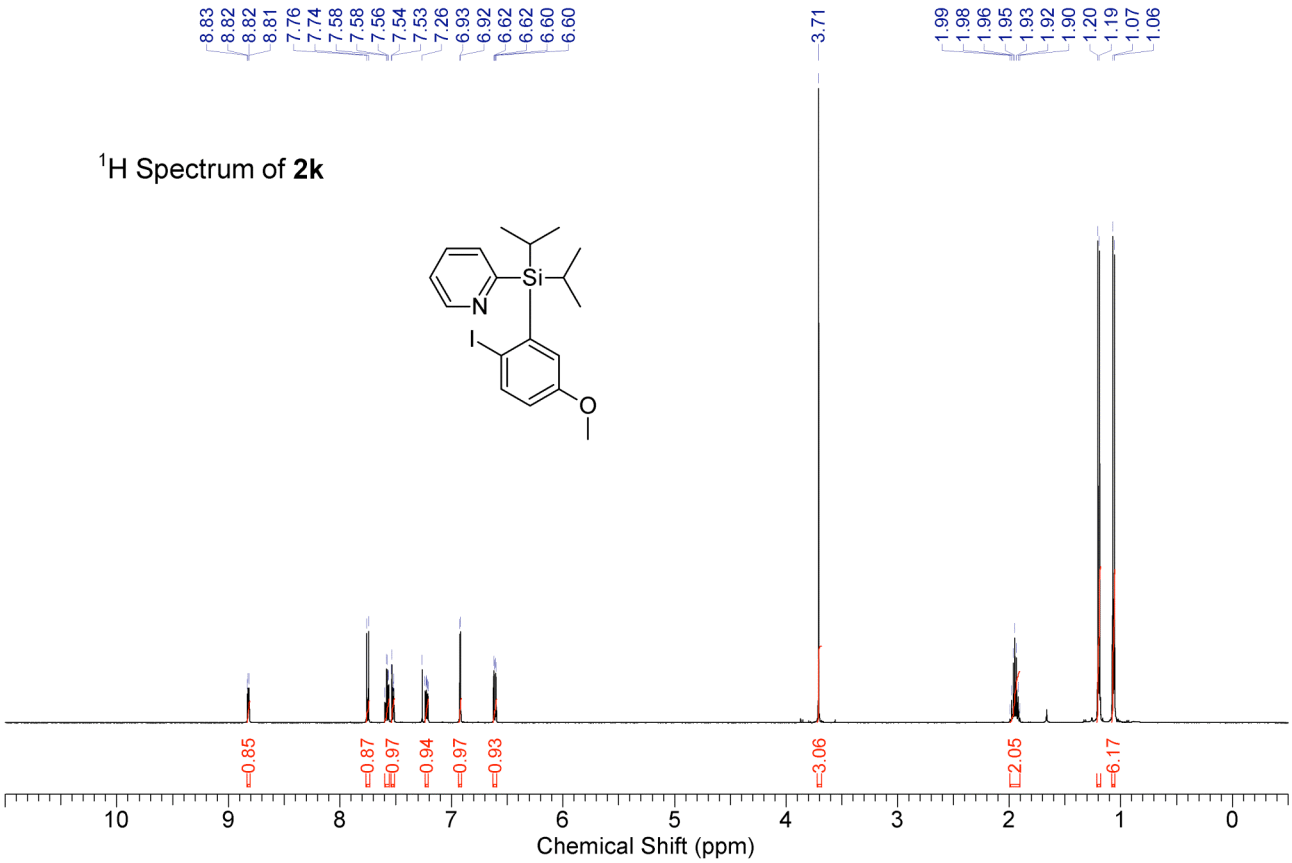
^{13}C Spectrum of **2i**

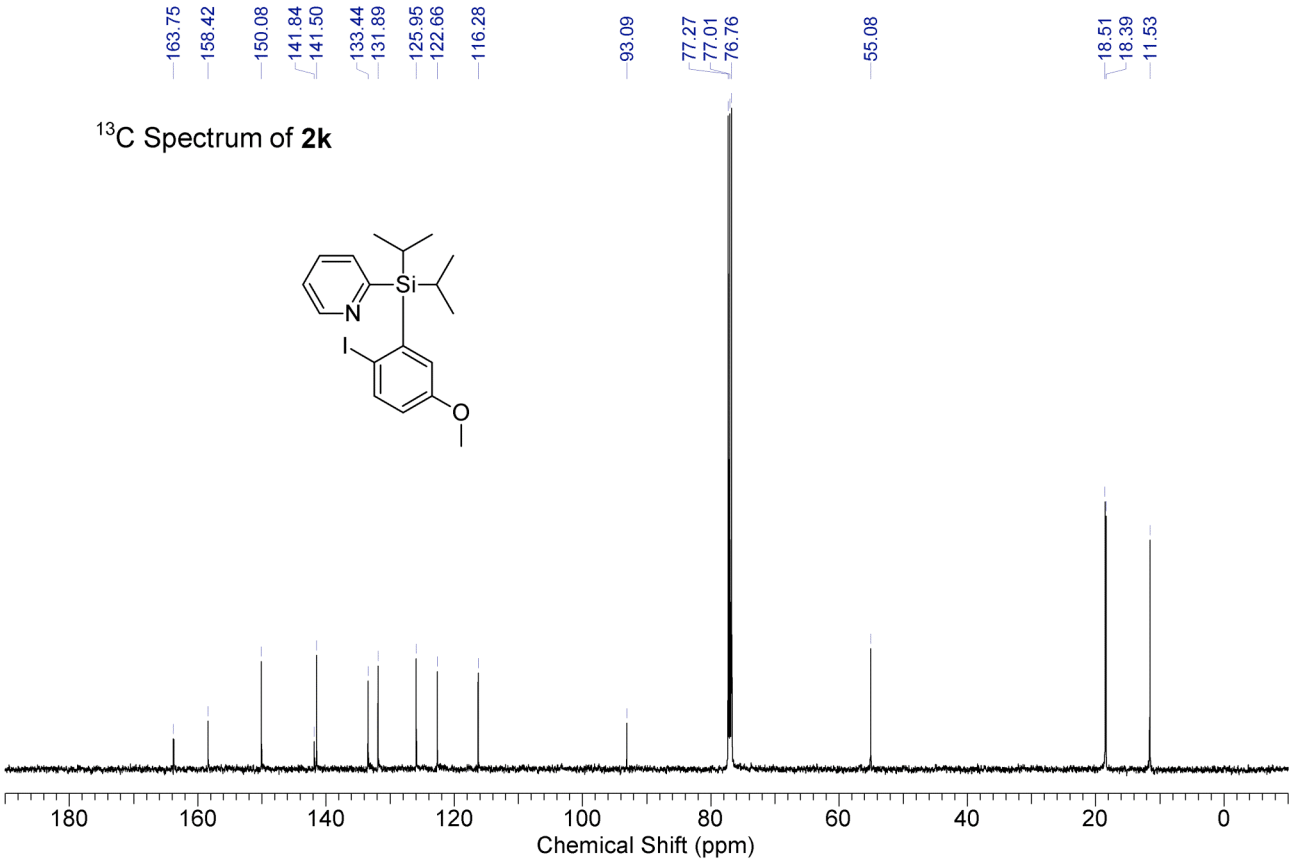


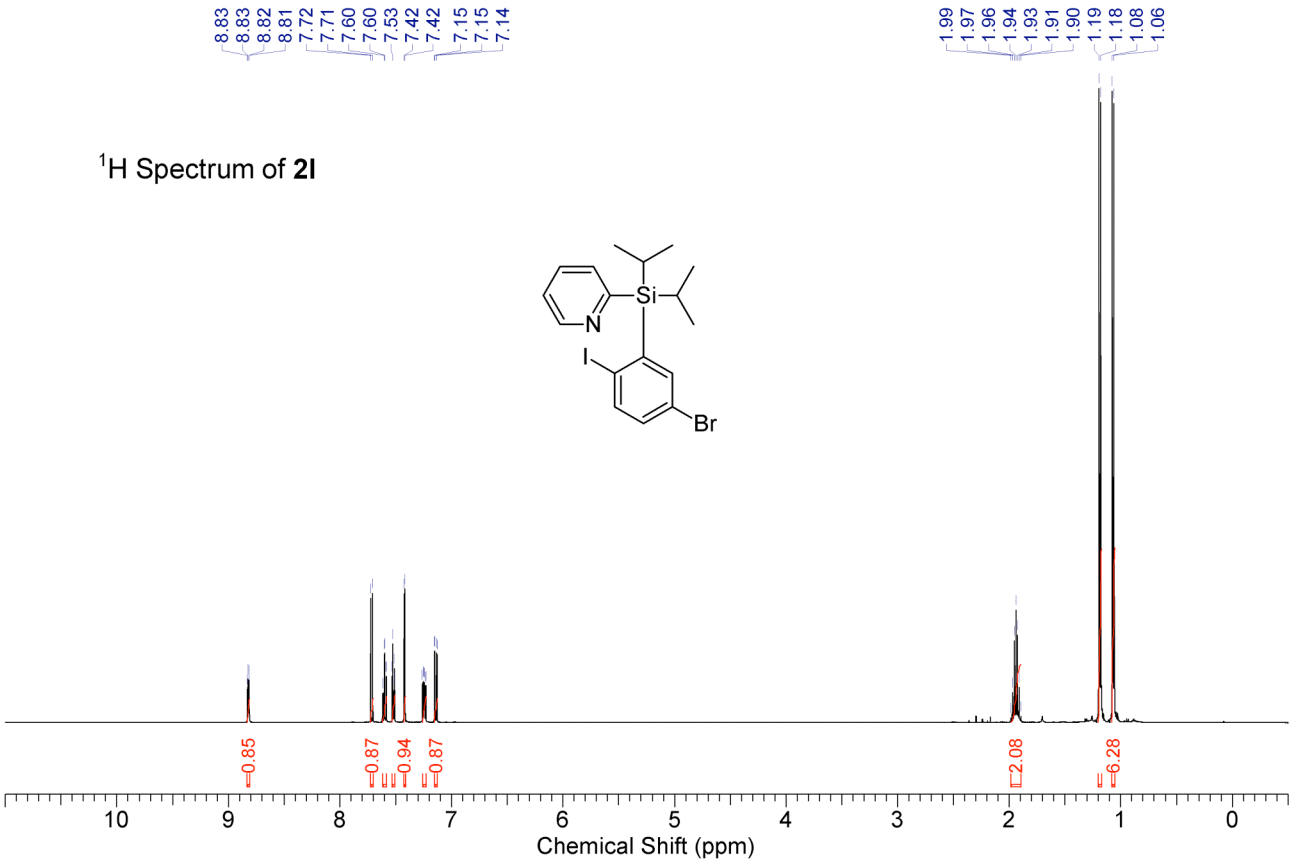
^{1}H Spectrum of **2j**



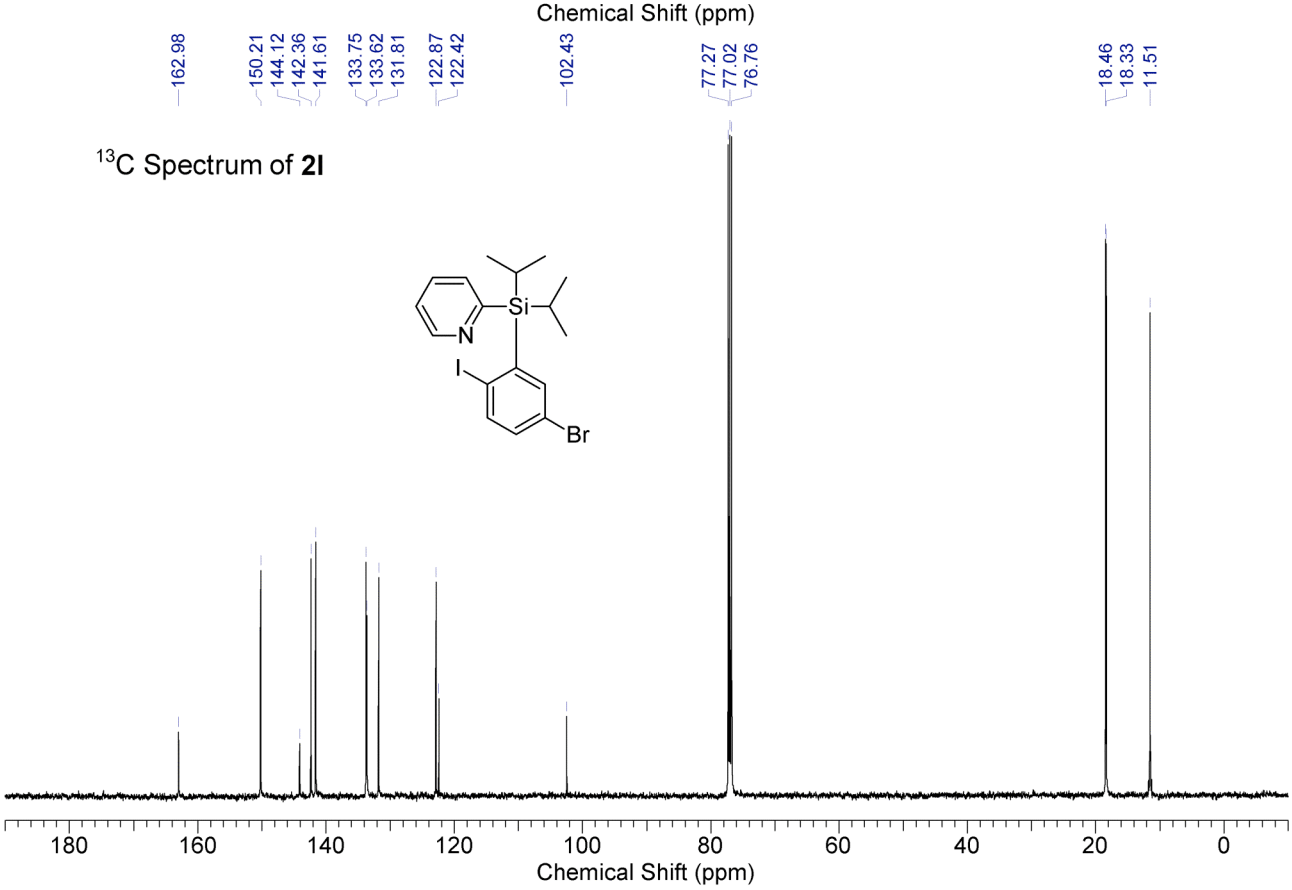
^{13}C Spectrum of **2j**


8.83
8.82
8.82
8.81
7.76
7.74
7.58
7.58
7.56
7.54
7.53
7.26
6.93
6.92
6.62
6.62
6.60
6.60
3.71
1.99
1.98
1.96
1.95
1.93
1.92
1.90
1.20
1.19
1.07
1.06
¹H Spectrum of 2k
Si
N
I
O
0.85
0.87
0.97
0.94
0.97
0.93
3.06
2.05
6.17
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

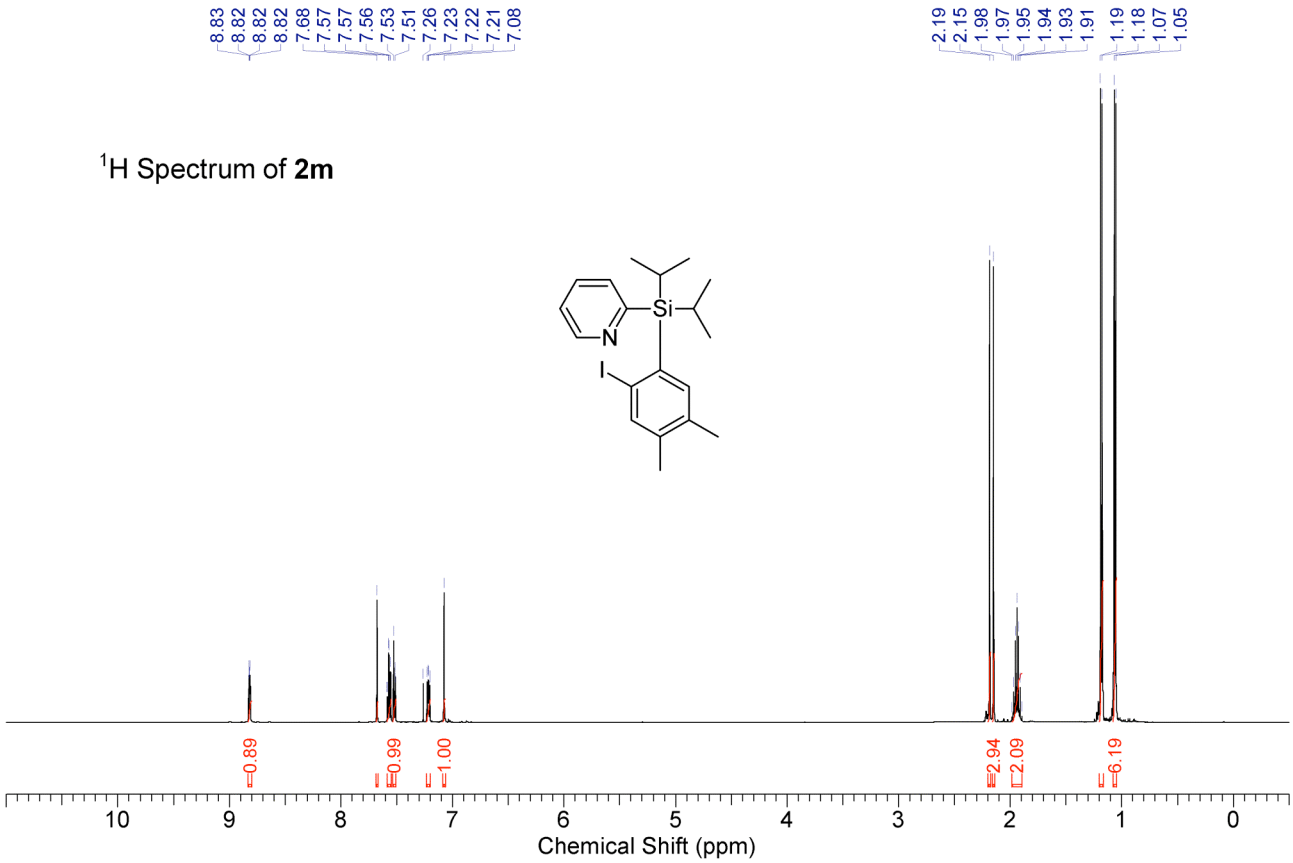

163.75
158.42
150.08
141.84
141.50
133.44
131.89
125.95
122.66
116.28
93.09
77.27
77.01
76.76
55.08
18.51
18.39
11.53
¹³C Spectrum of 2k
Si
N
I
O
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)



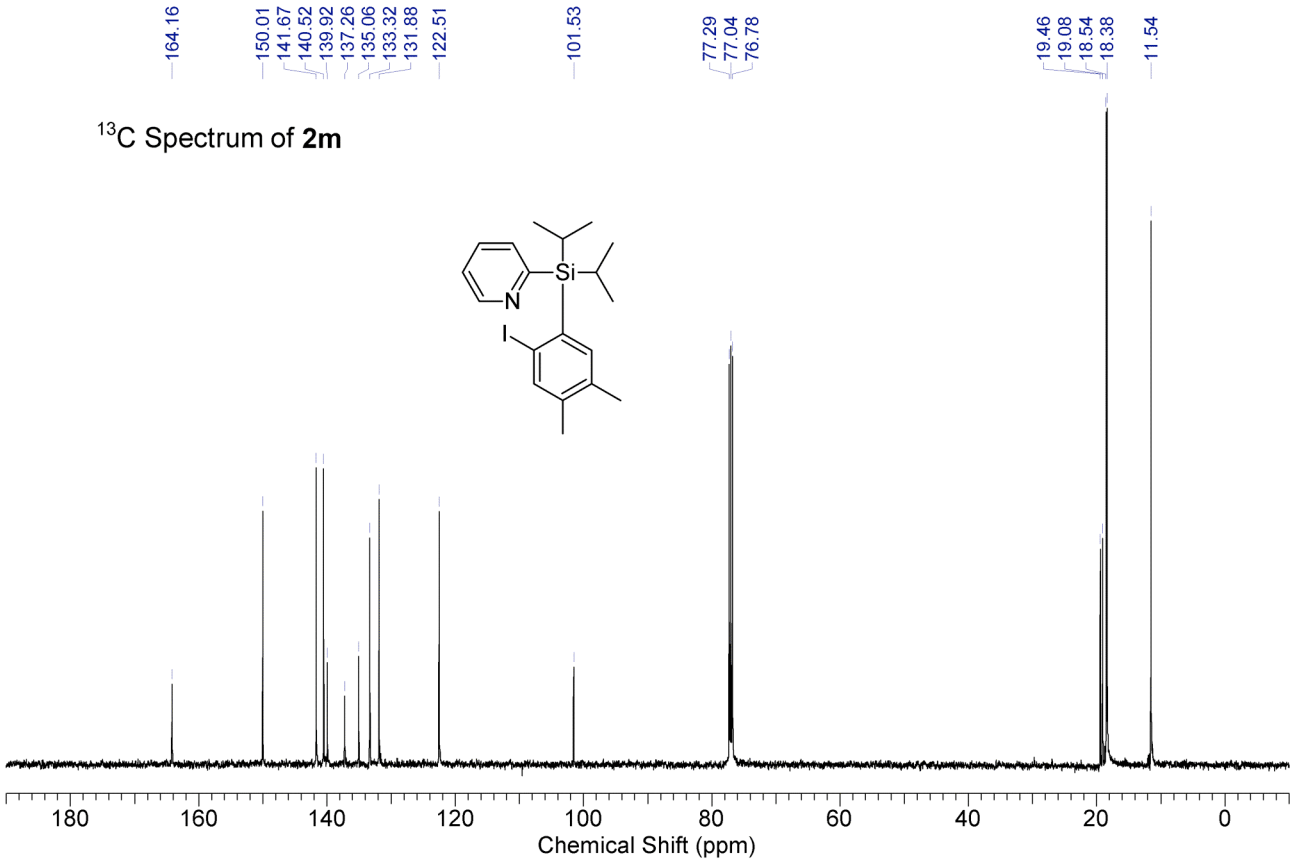
^{1}H Spectrum of **2l**



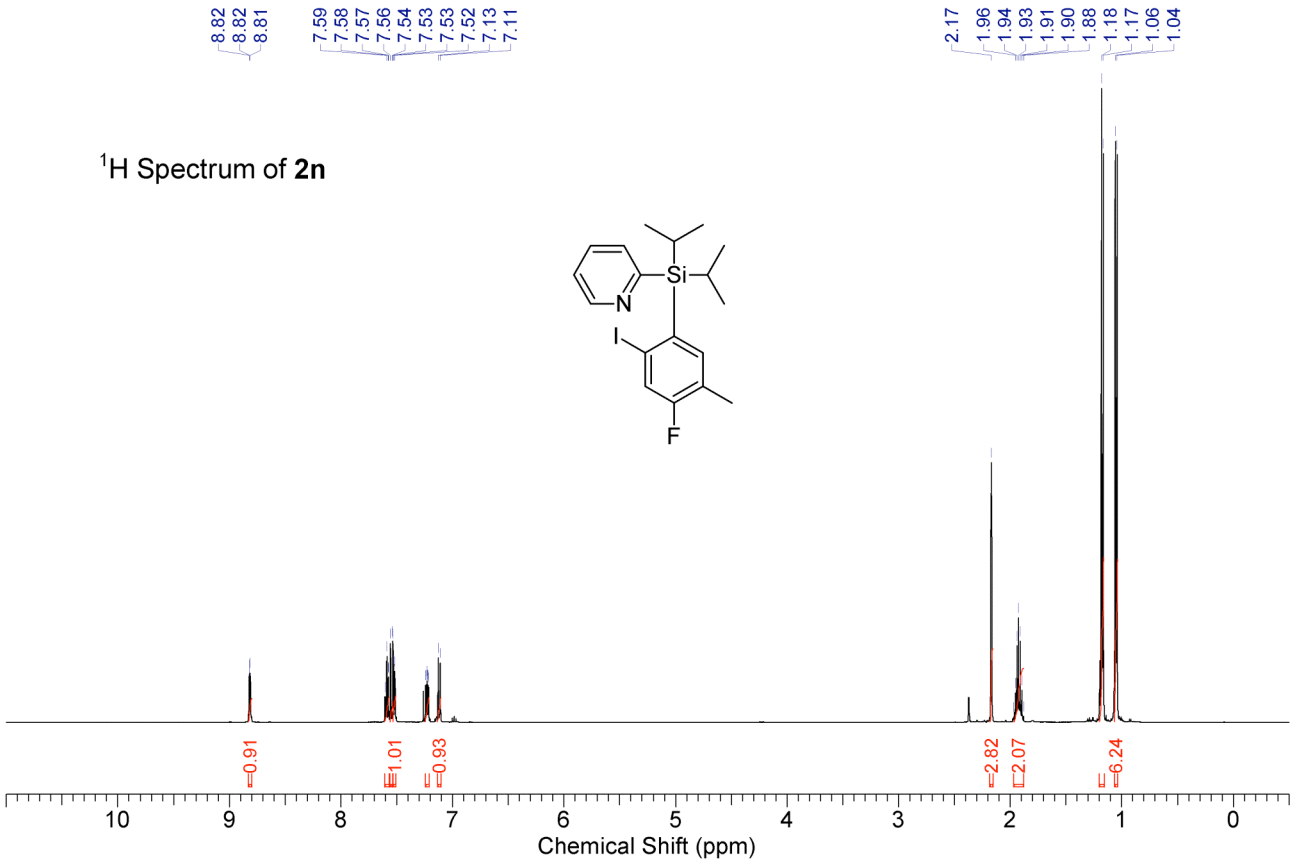
^{13}C Spectrum of **2l**



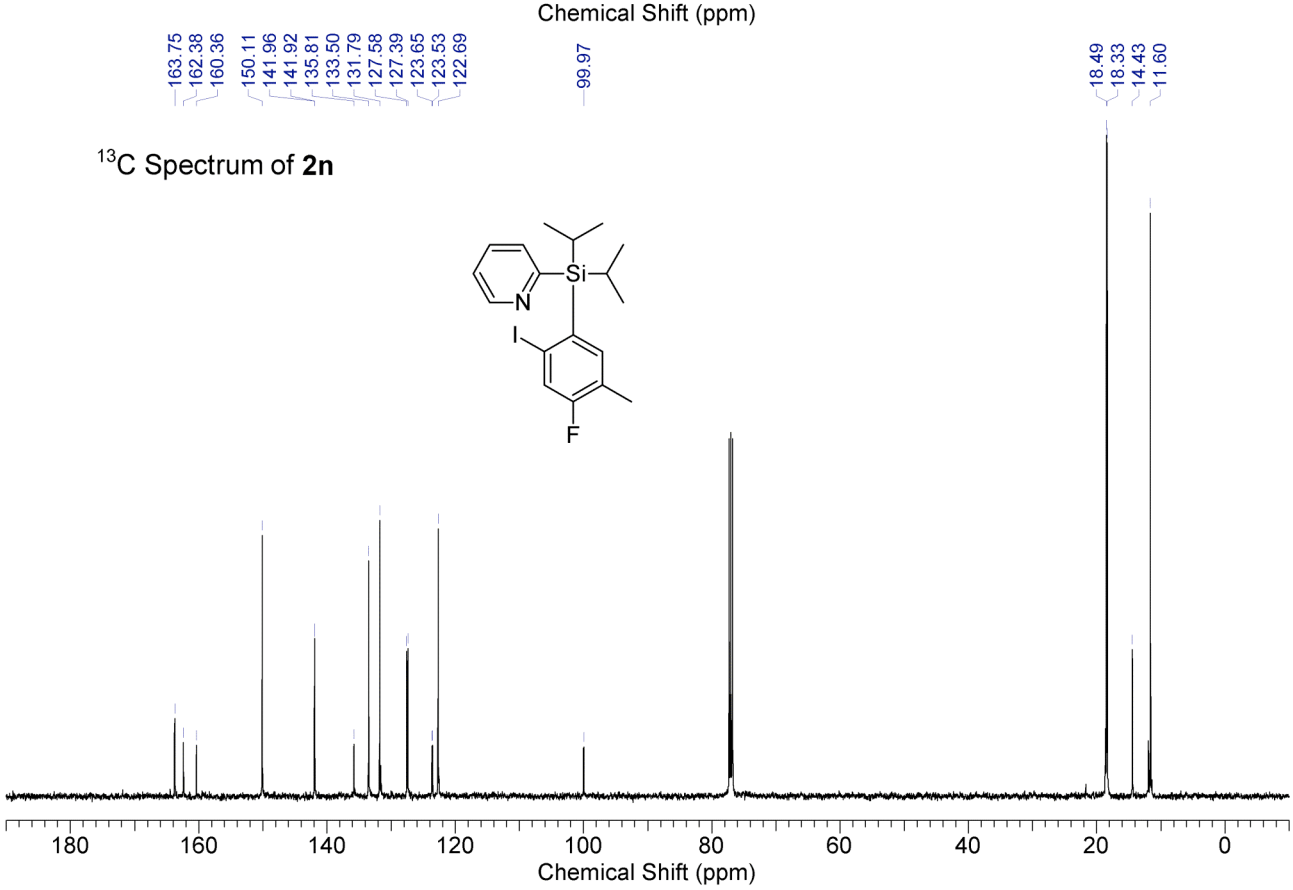
^{1}H Spectrum of **2m**



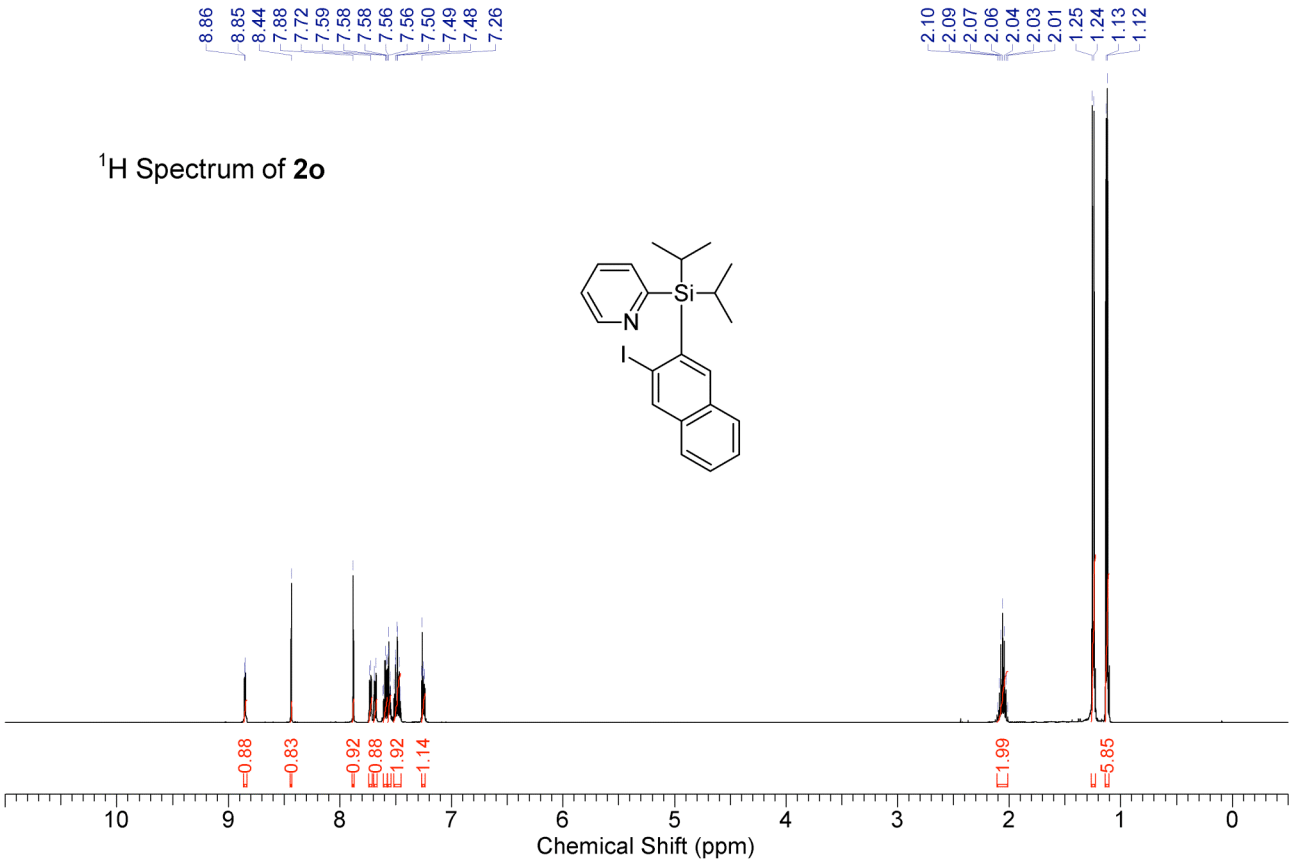
^{13}C Spectrum of **2m**



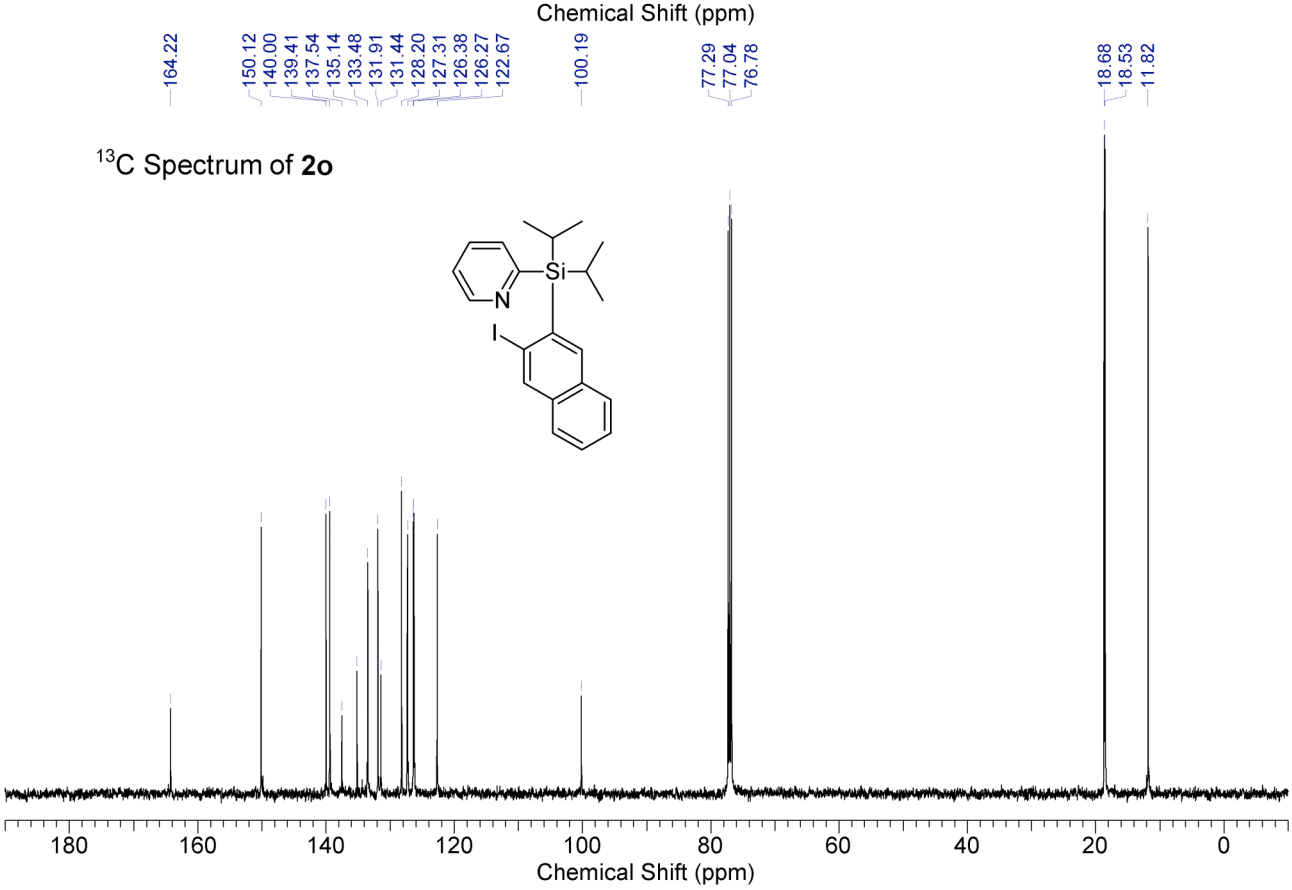
^{1}H Spectrum of **2n**



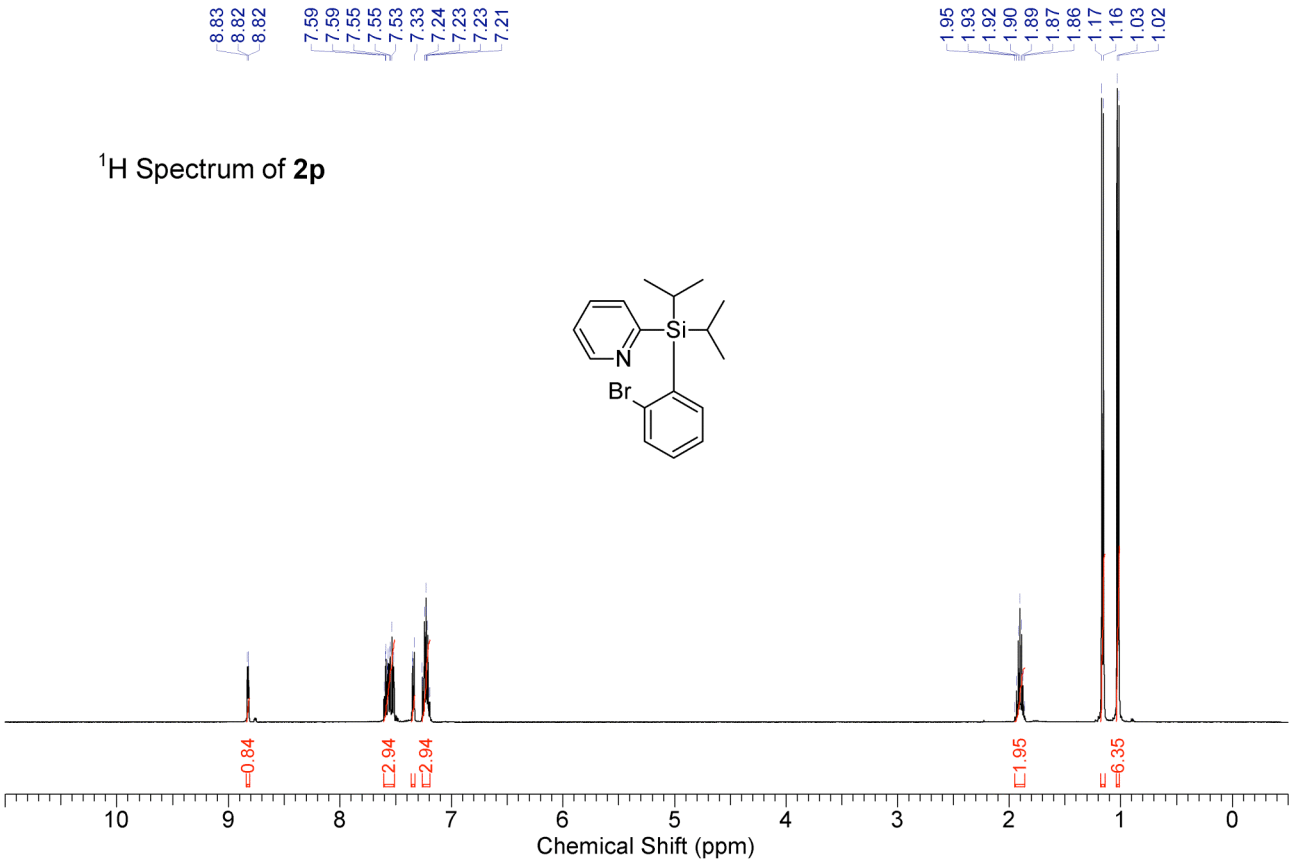
^{13}C Spectrum of **2n**



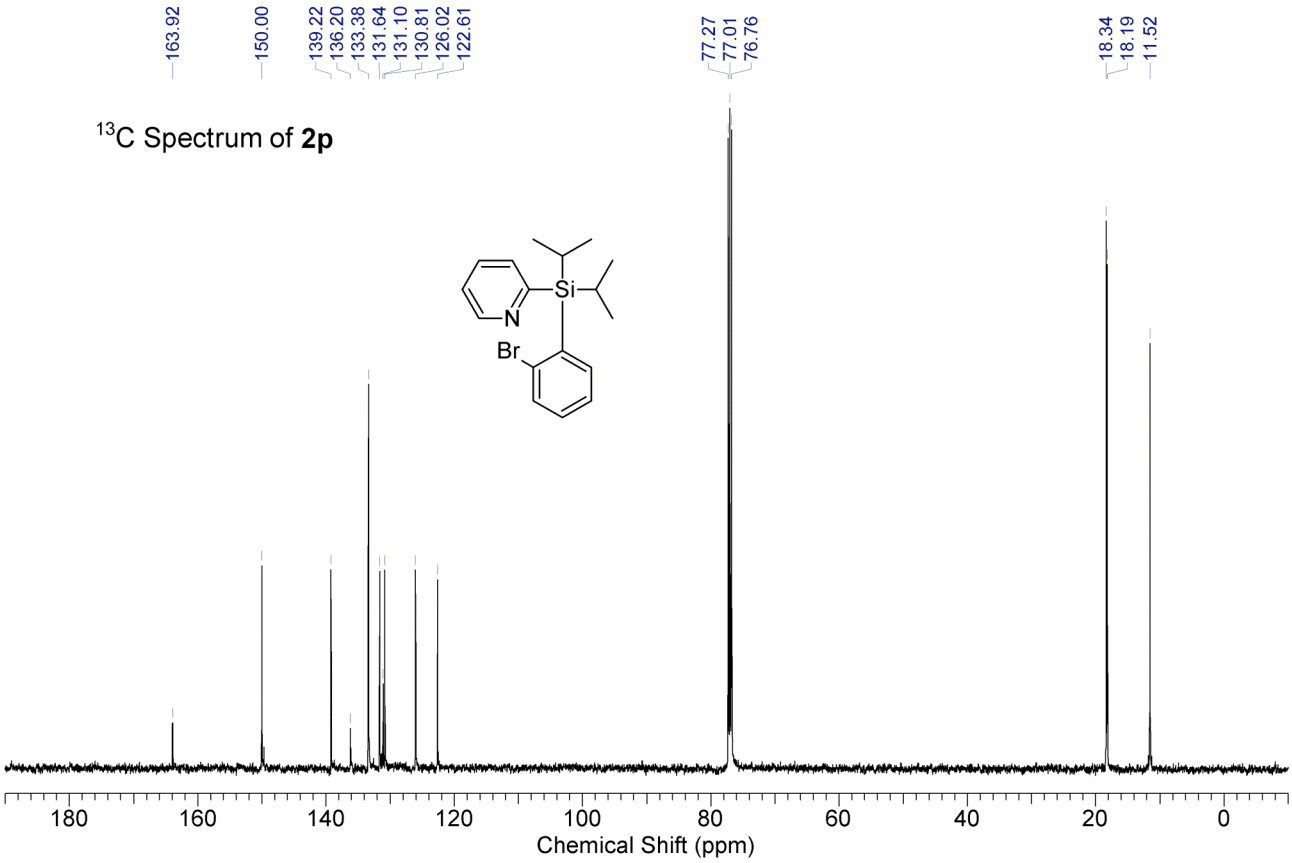
^{1}H Spectrum of **2o**



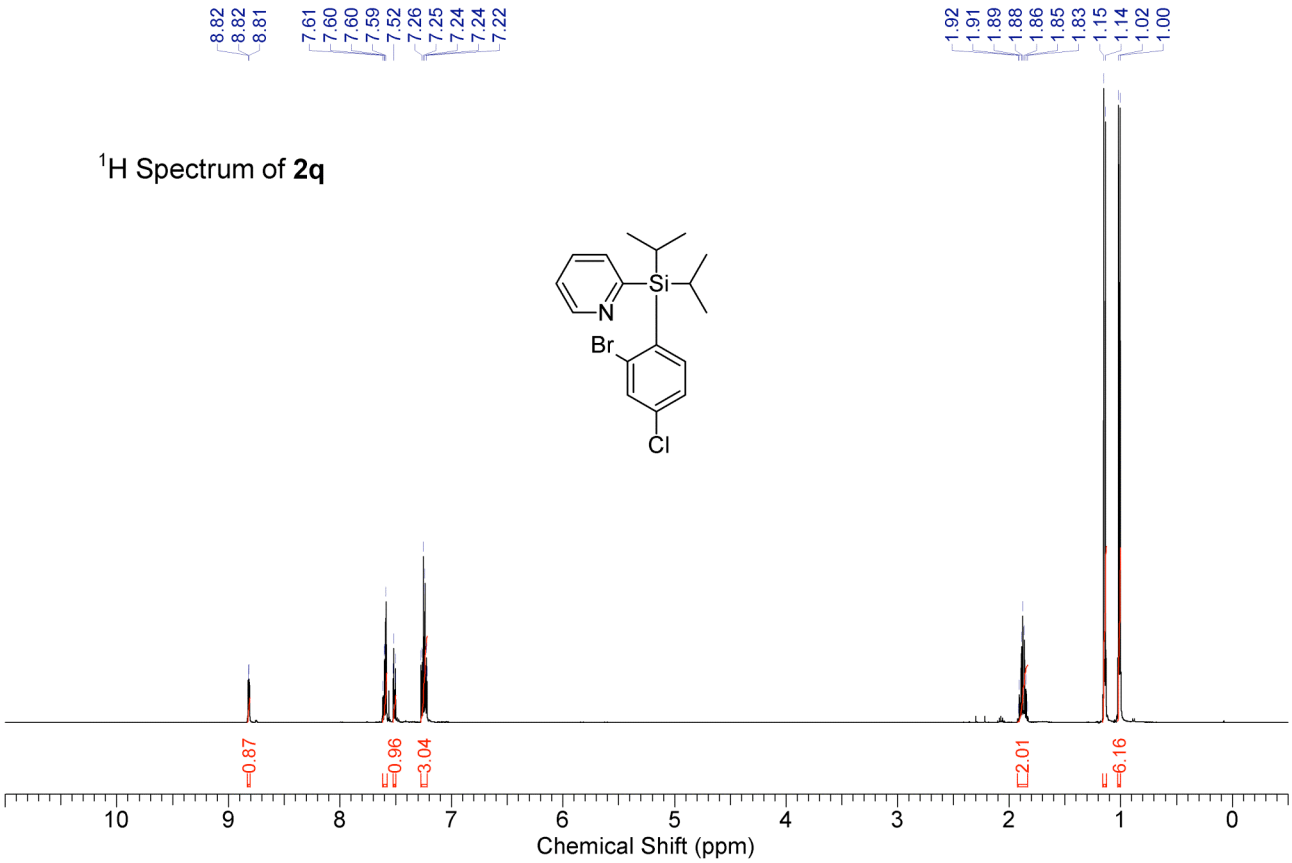
^{13}C Spectrum of **2o**



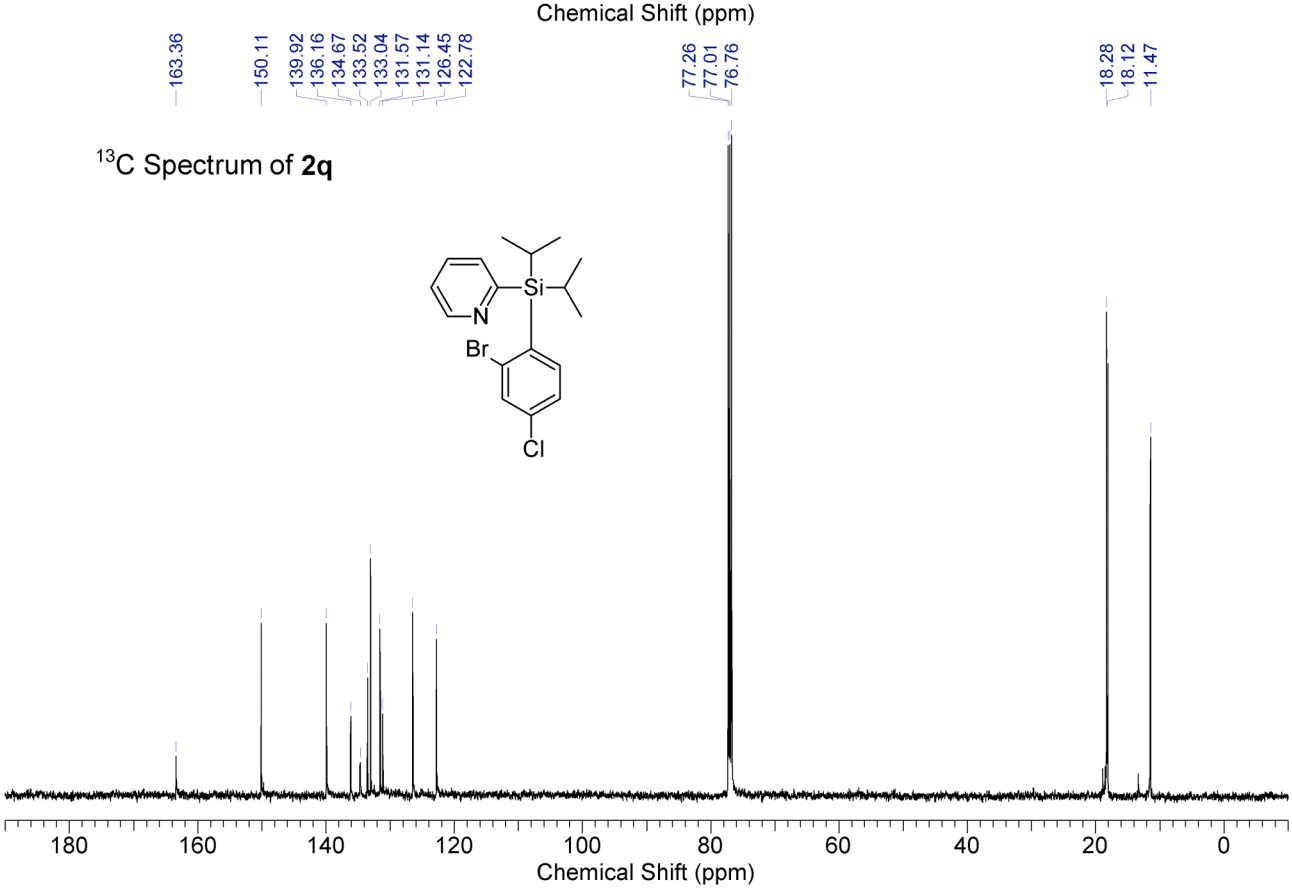
^{1}H Spectrum of **2p**



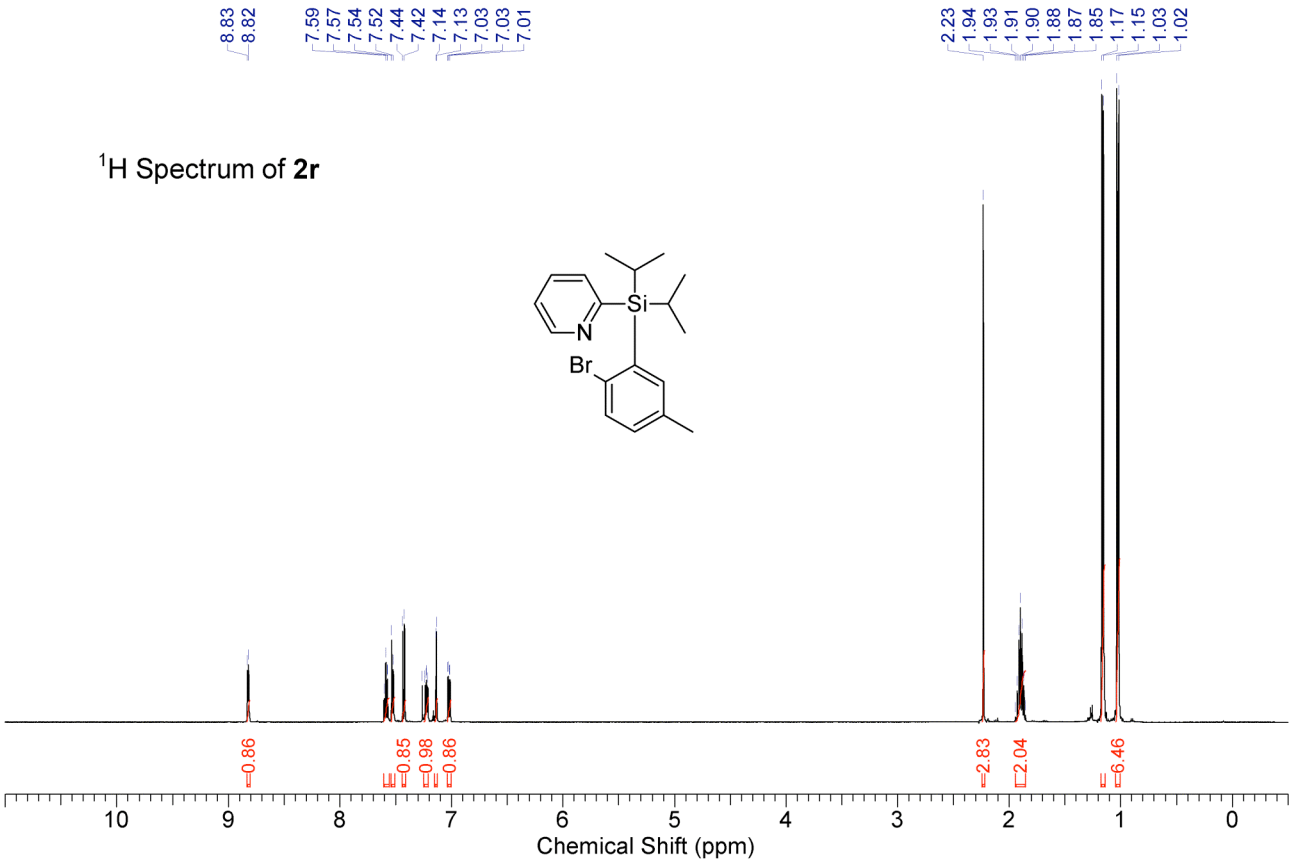
^{13}C Spectrum of **2p**

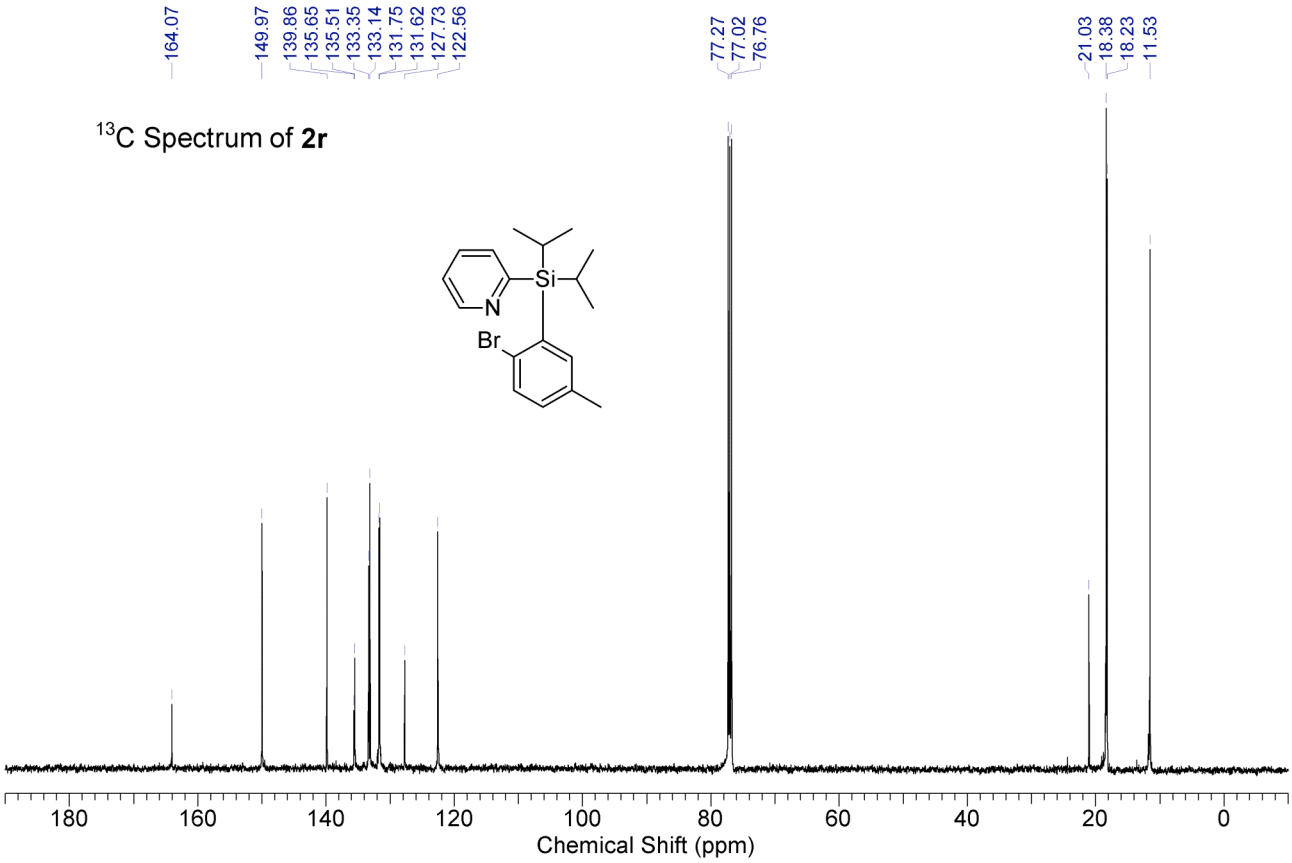


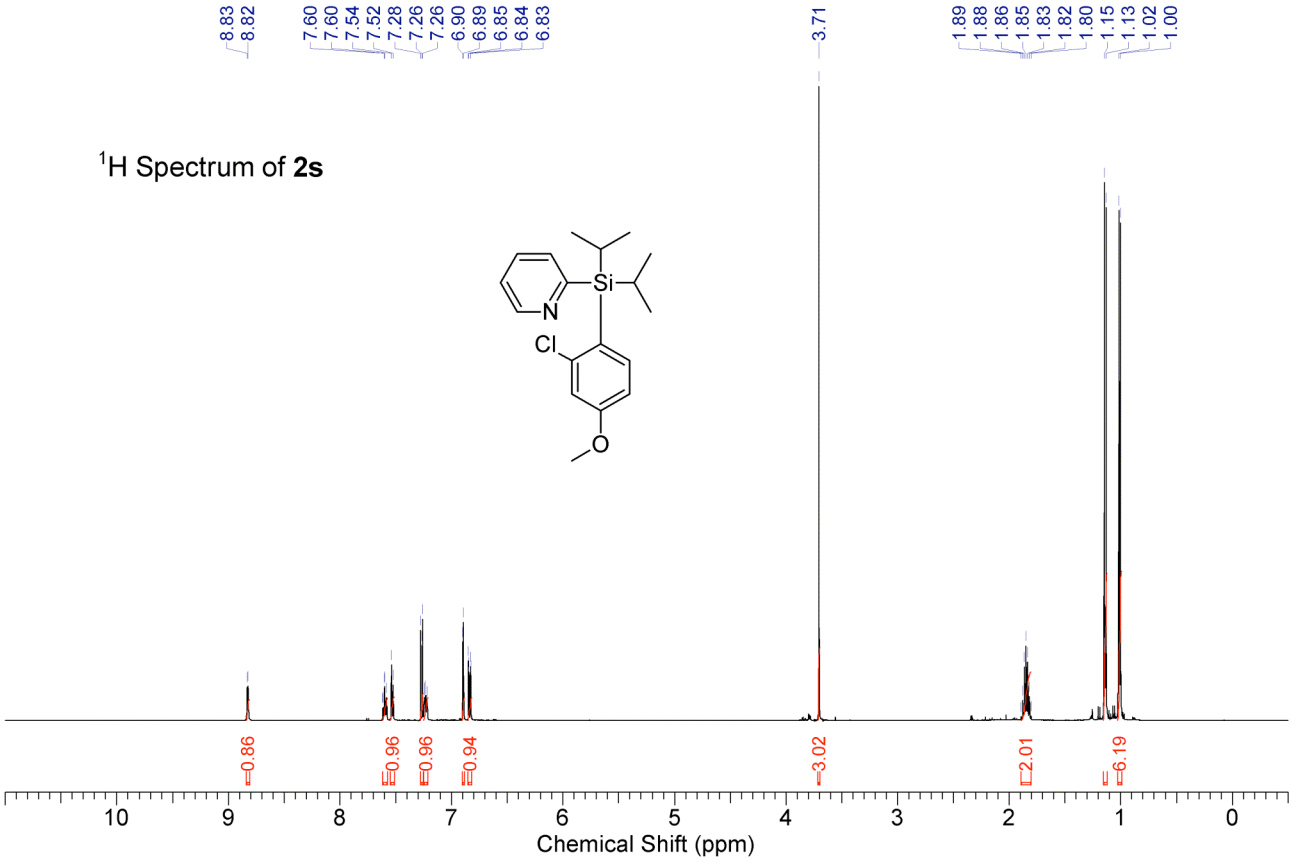
^{1}H Spectrum of **2q**



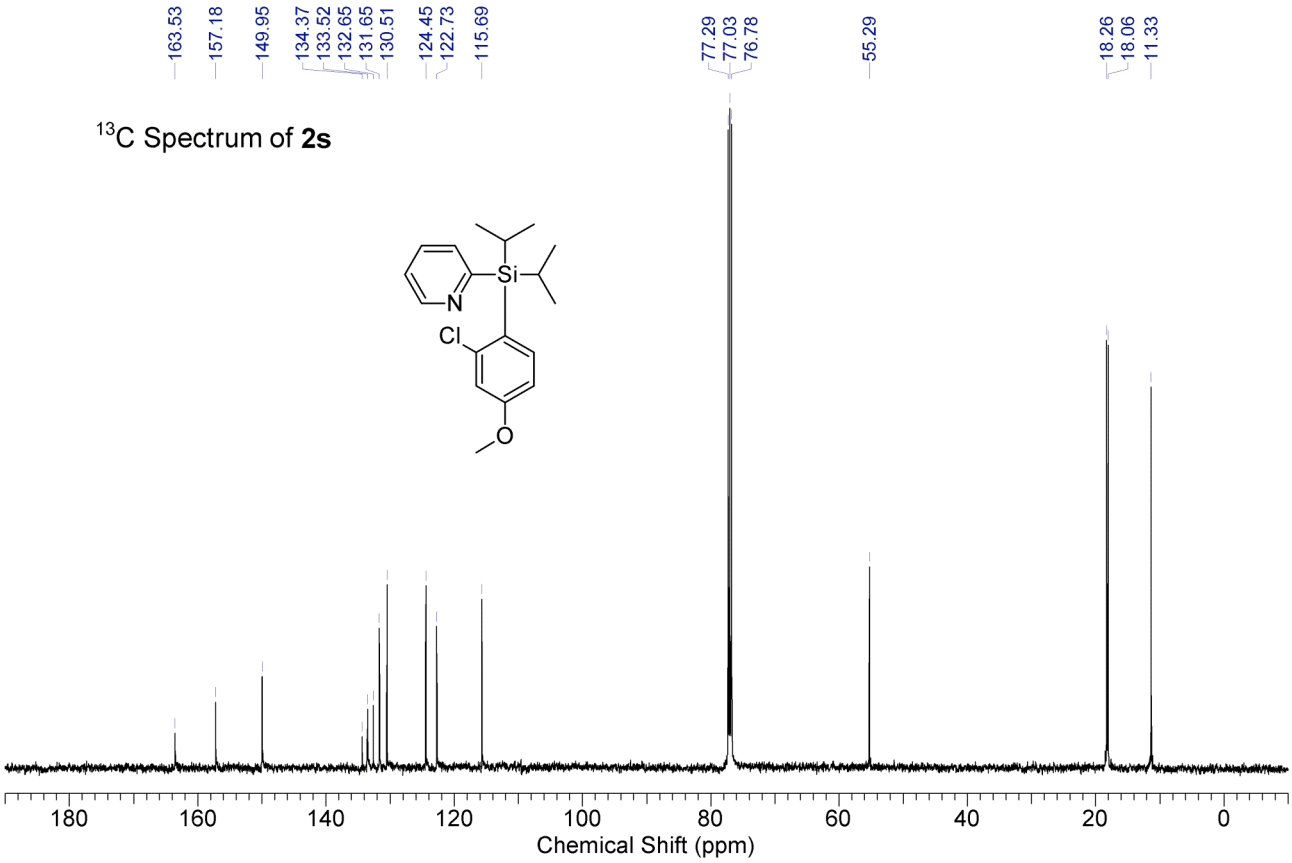
^{13}C Spectrum of **2q**


8.83
8.82
7.59
7.57
7.54
7.52
7.44
7.42
7.14
7.13
7.03
7.03
7.01
2.23
1.94
1.93
1.91
1.90
1.88
1.87
1.85
1.17
1.15
1.03
1.02
1H Spectrum of 2r
Si
N
Br
0.86
0.85
0.98
0.86
2.83
2.04
6.46
Chemical Shift (ppm)

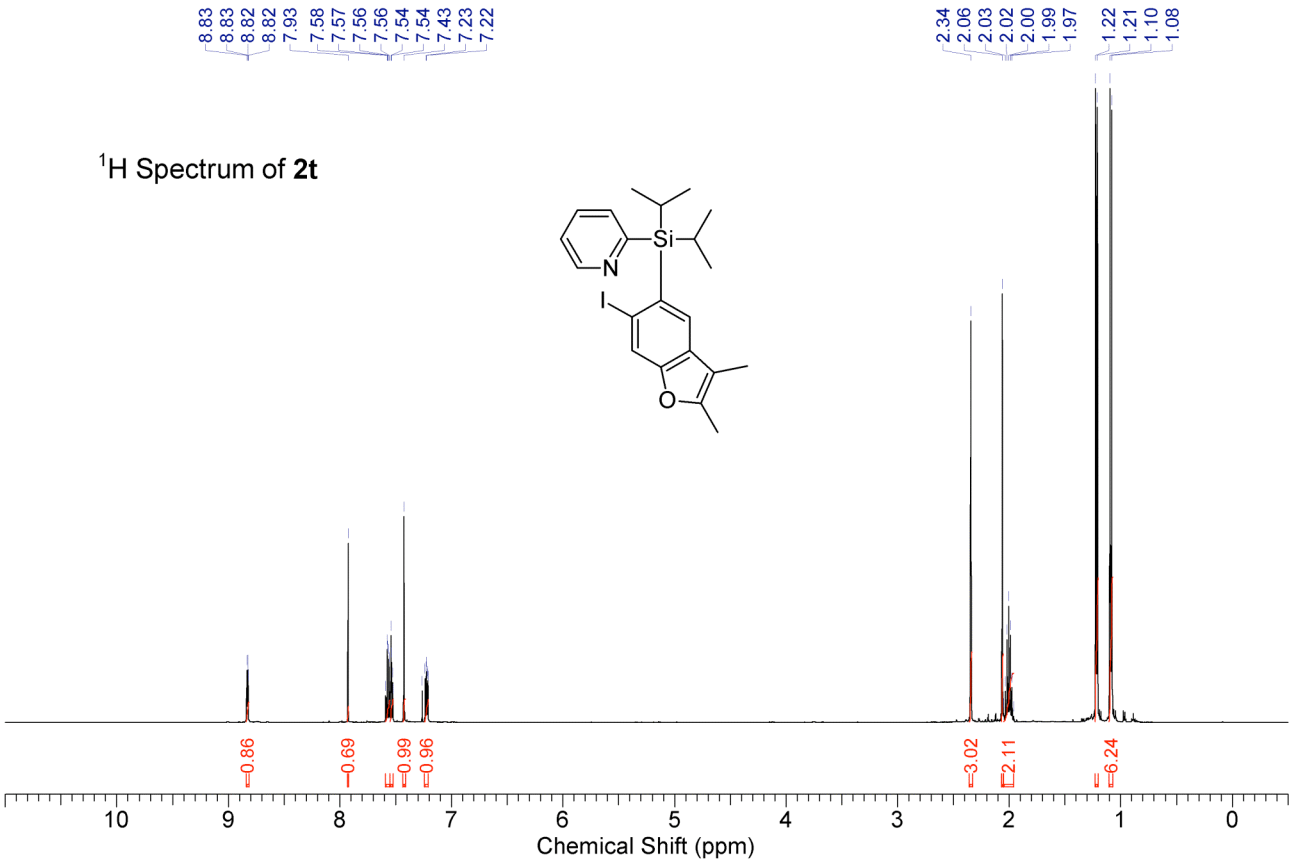

164.07
149.97
139.86
135.65
135.51
133.35
133.14
131.75
131.62
127.73
122.56
77.27
77.02
76.76
21.03
18.38
18.23
11.53
13C Spectrum of 2r
Si
N
Br
Chemical Shift (ppm)



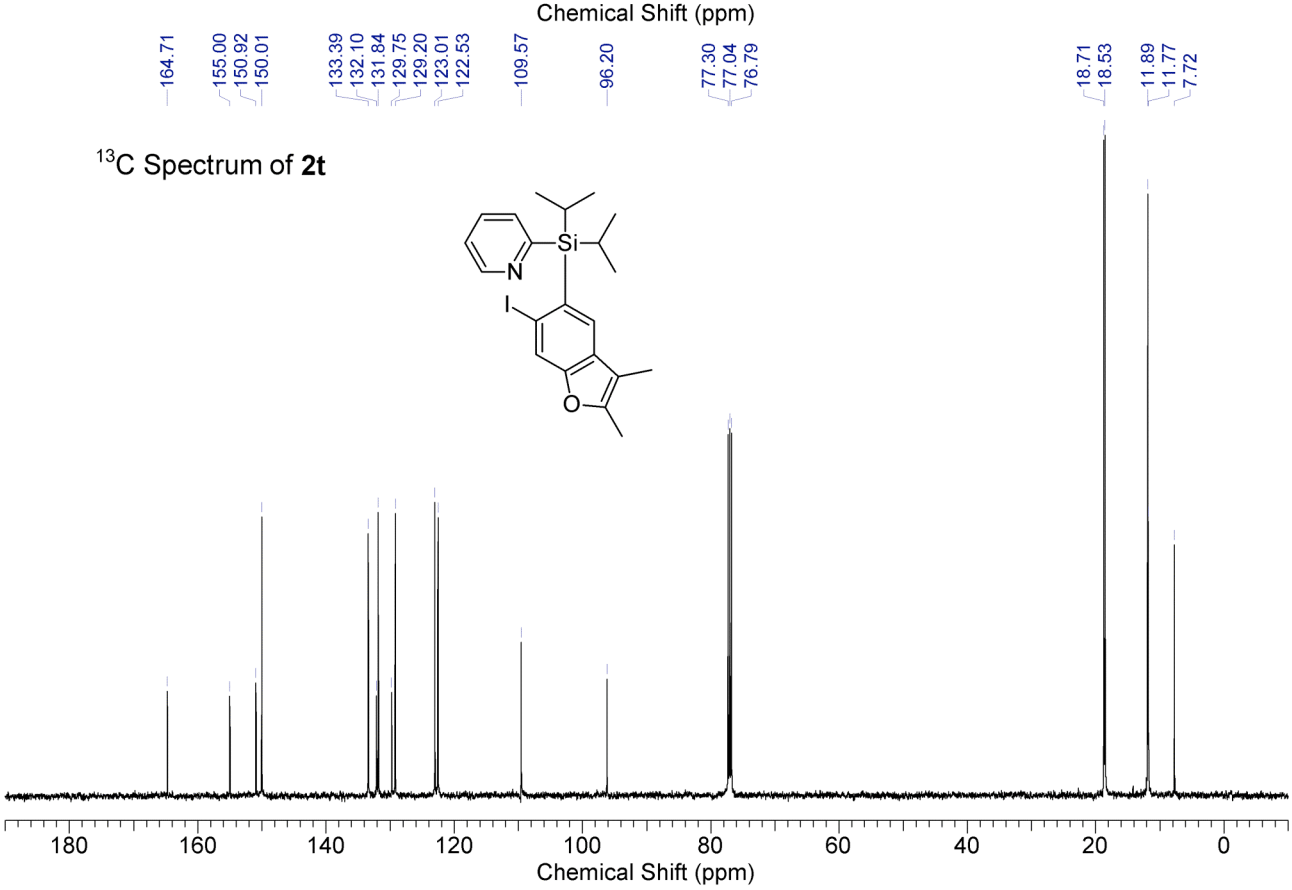
^{1}H Spectrum of **2s**



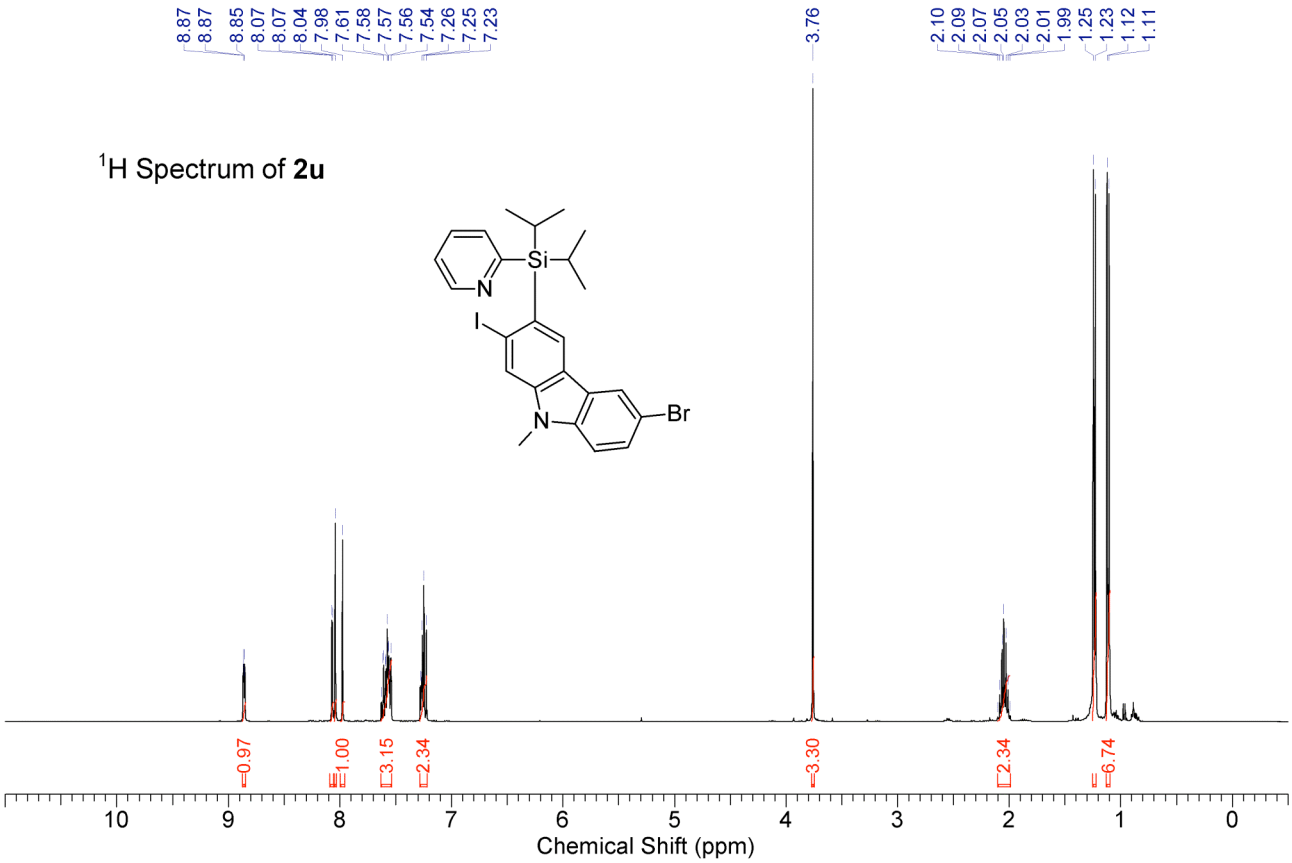
^{13}C Spectrum of **2s**

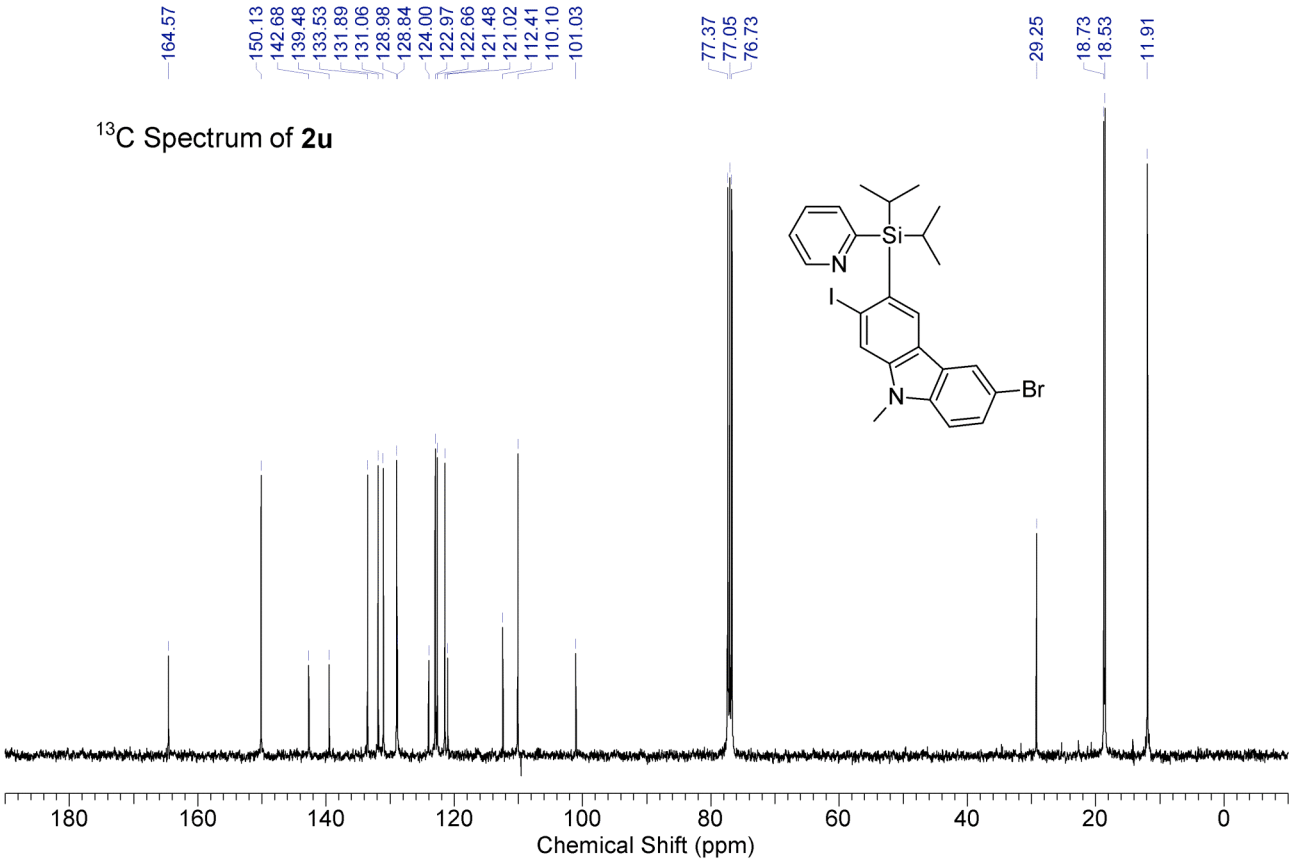


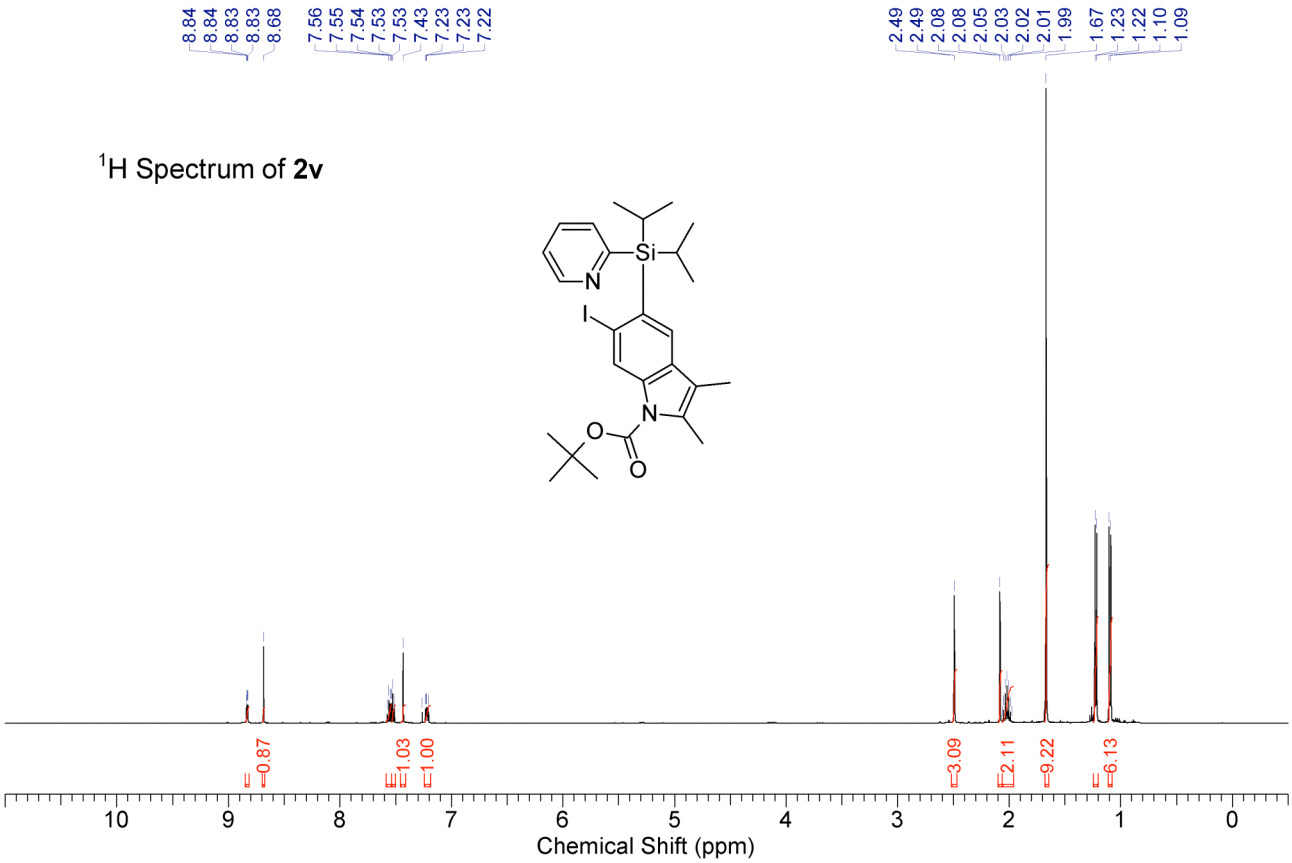
^{1}H Spectrum of **2t**



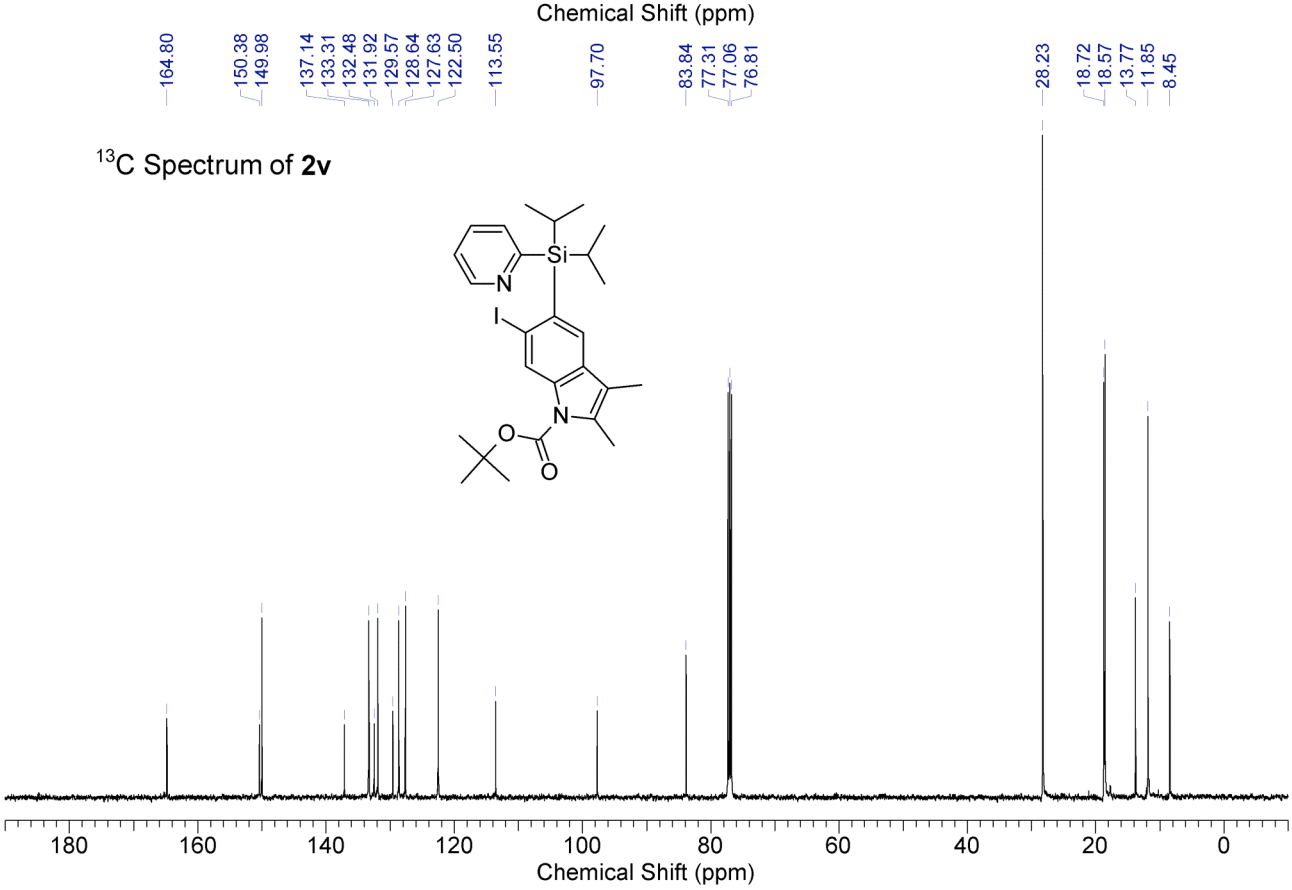
^{13}C Spectrum of **2t**


8.87
8.87
8.85
8.07
8.07
8.04
7.98
7.61
7.58
7.57
7.56
7.54
7.26
7.25
7.23
3.76
2.10
2.09
2.07
2.05
2.03
2.01
1.99
1.25
1.23
1.12
1.11
1H Spectrum of 2u
Si
N
I
N
Br
0.97
1.00
3.15
2.34
3.30
2.34
6.74
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

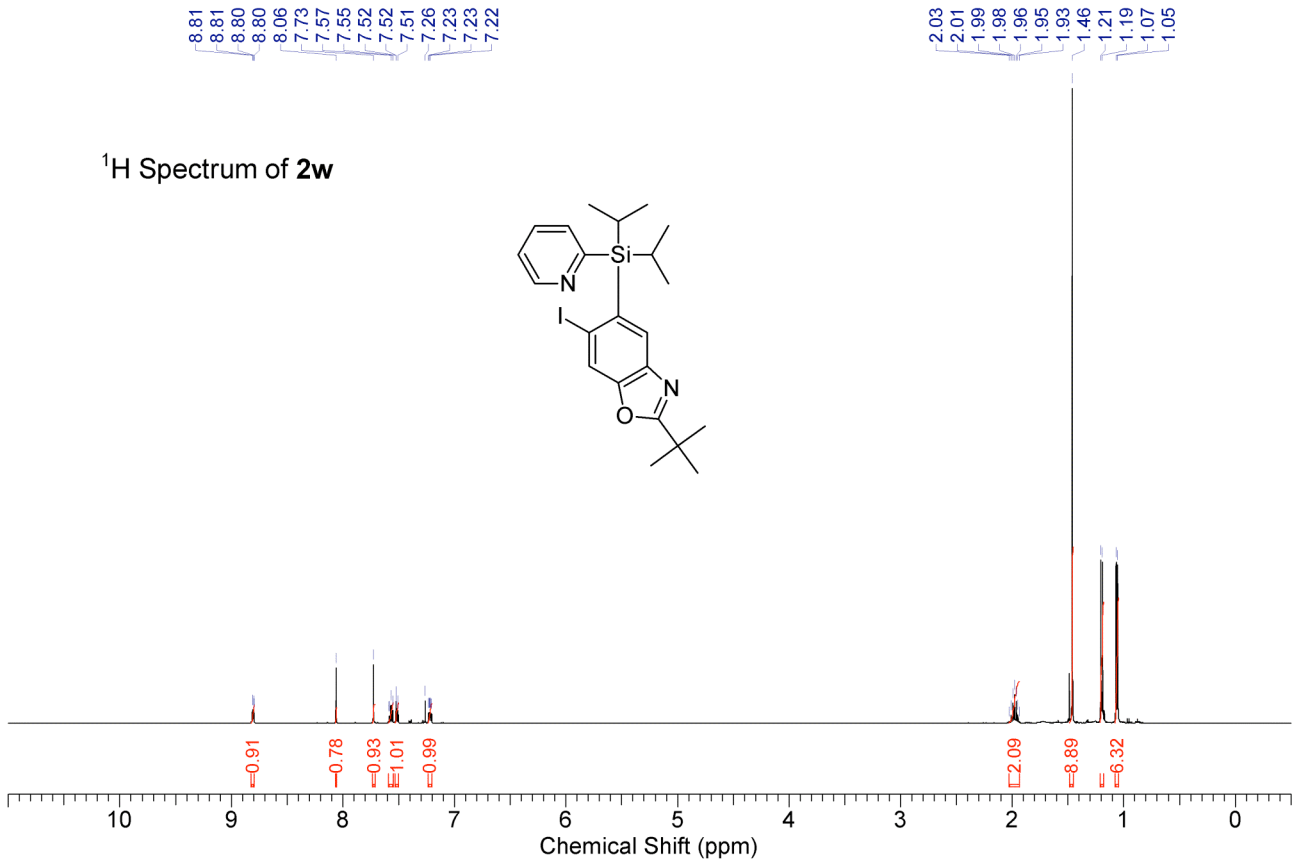

164.57
150.13
142.68
139.48
133.53
131.89
131.06
128.98
128.84
124.00
122.97
122.66
121.48
121.02
112.41
110.10
101.03
77.37
77.05
76.73
29.25
18.73
18.53
11.91
13C Spectrum of 2u
Si
N
I
N
Br
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)



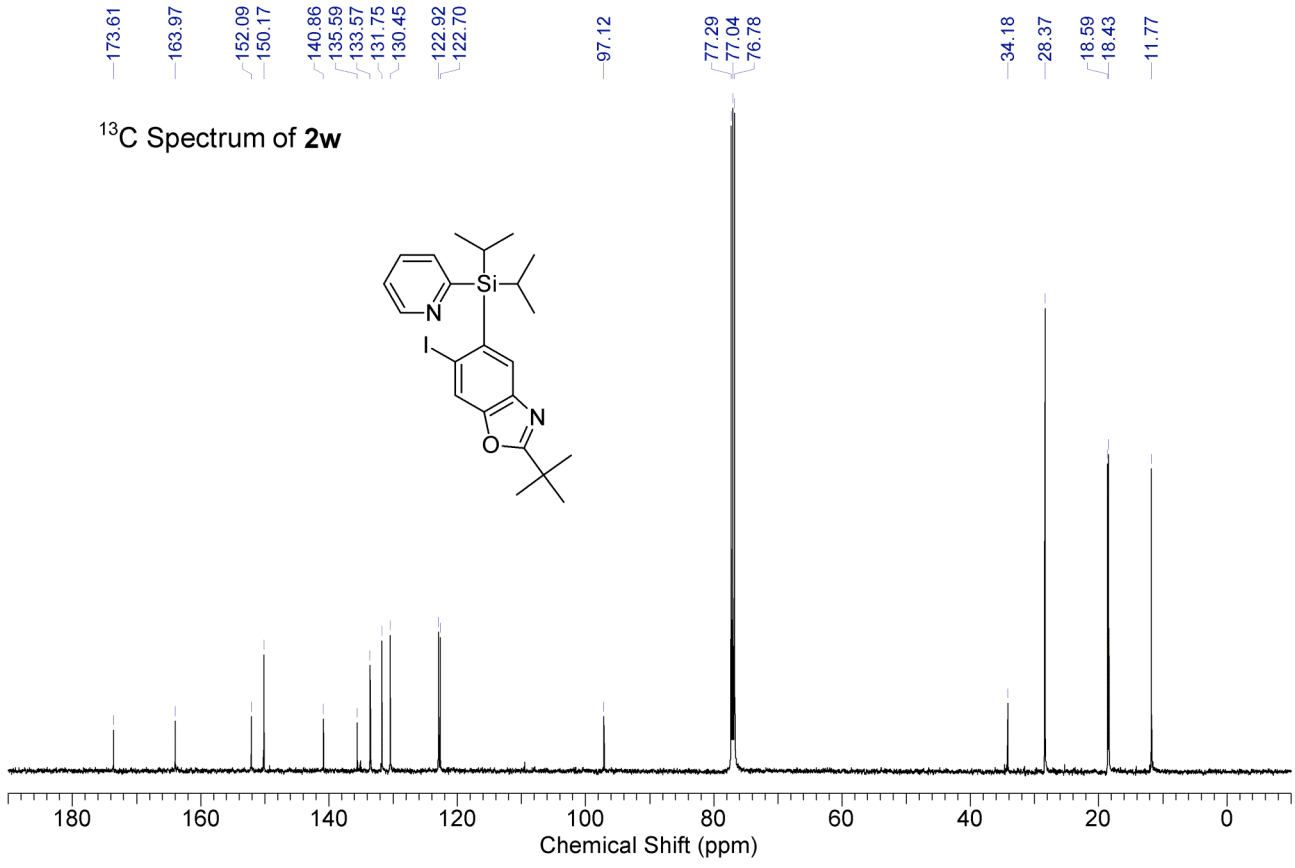
^{1}H Spectrum of **2v**



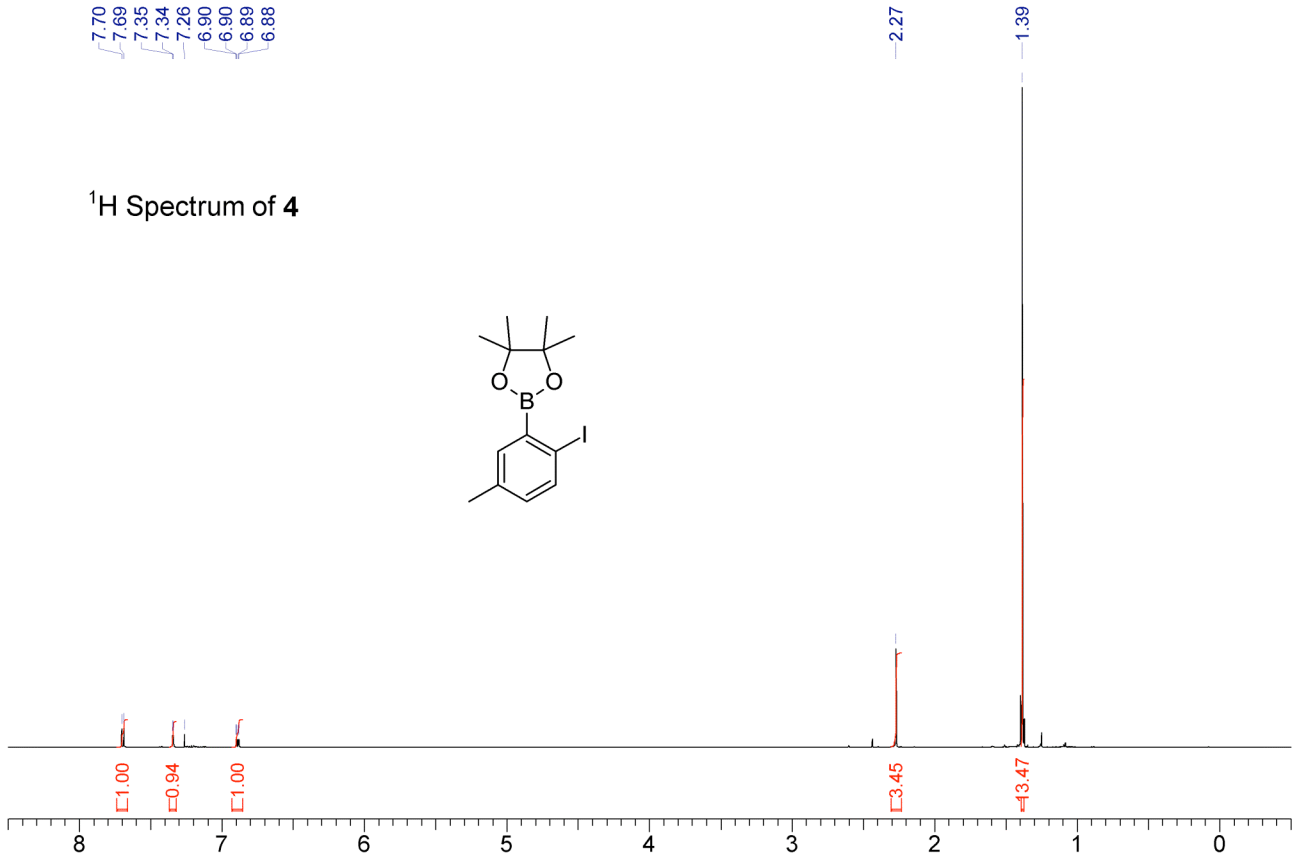
^{13}C Spectrum of **2v**

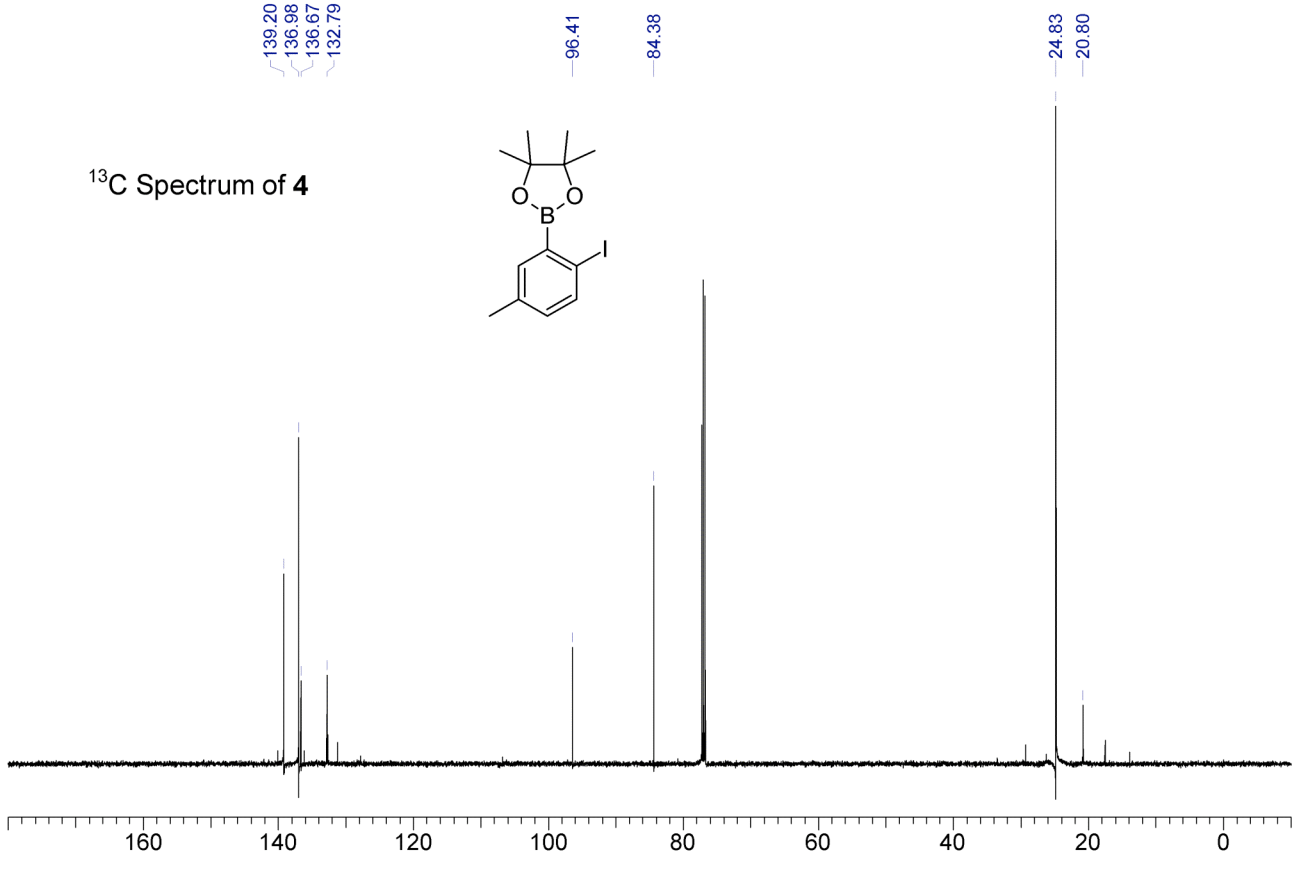


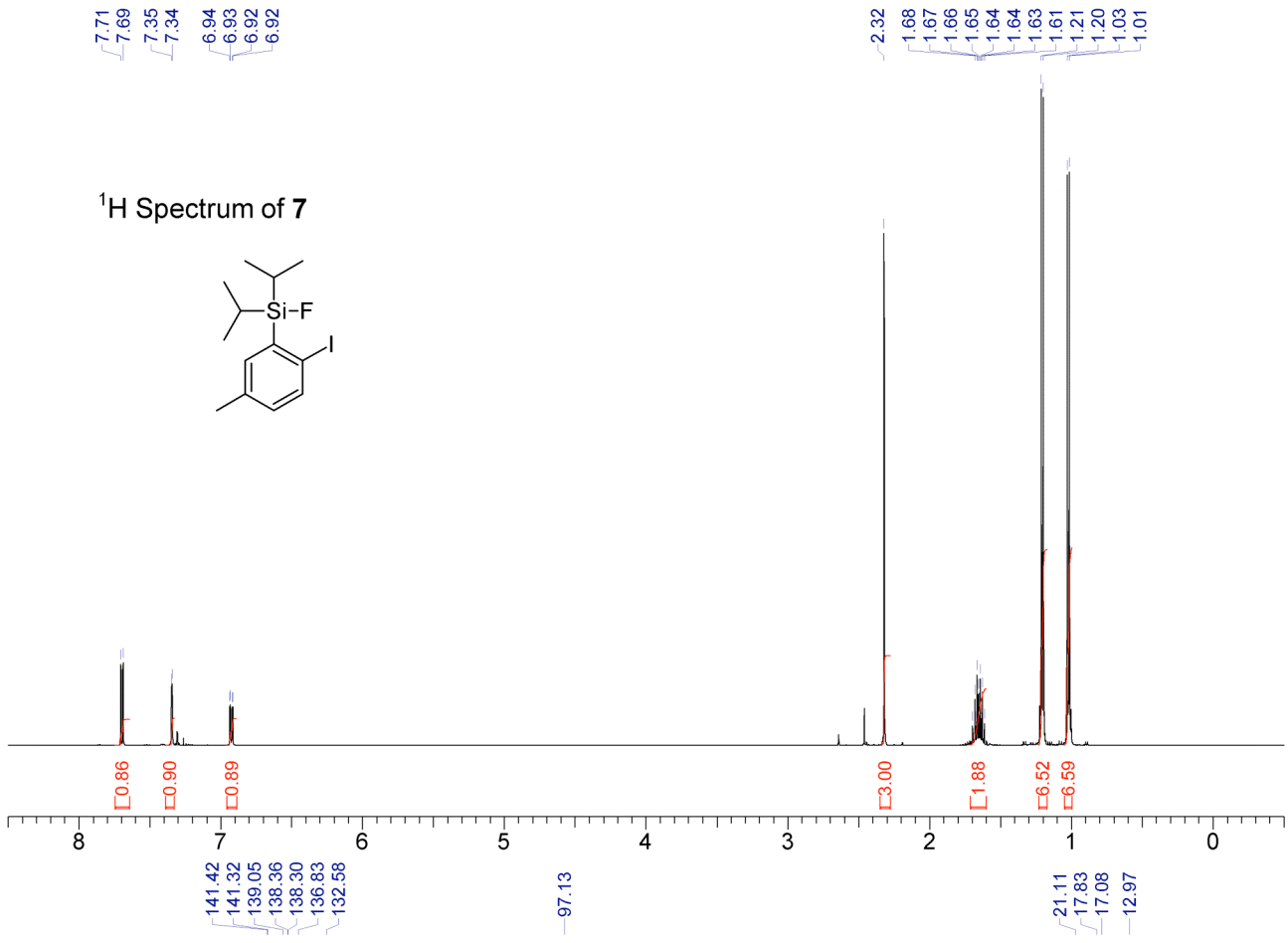
^{1}H Spectrum of **2w**



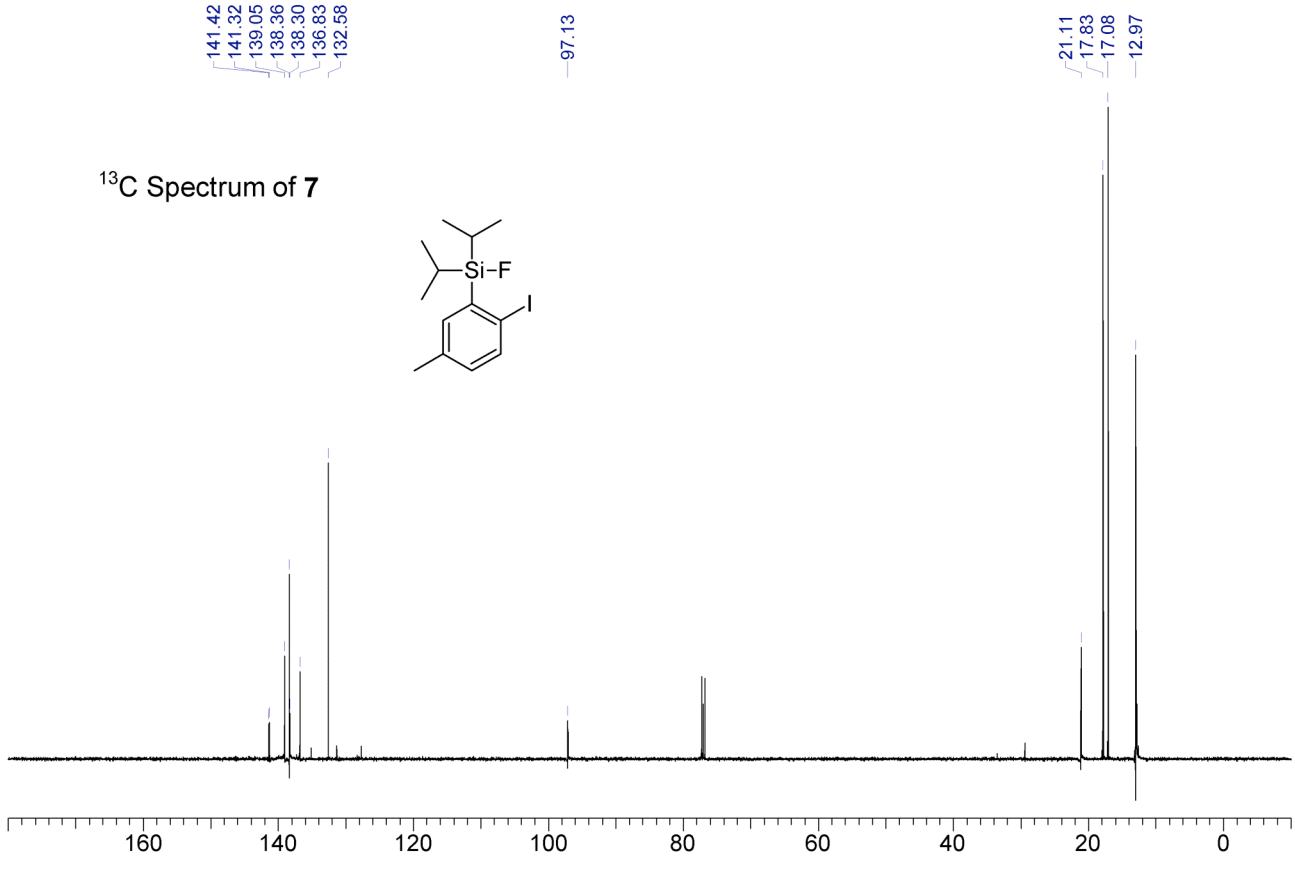
^{13}C Spectrum of **2w**


7.70
7.69
7.35
7.34
7.26
6.90
6.90
6.89
6.88
2.27
1.39
1H Spectrum of 4
O
B
O
I
1.00
0.94
1.00
3.45
3.47
8
7
6
5
4
3
2
1
0

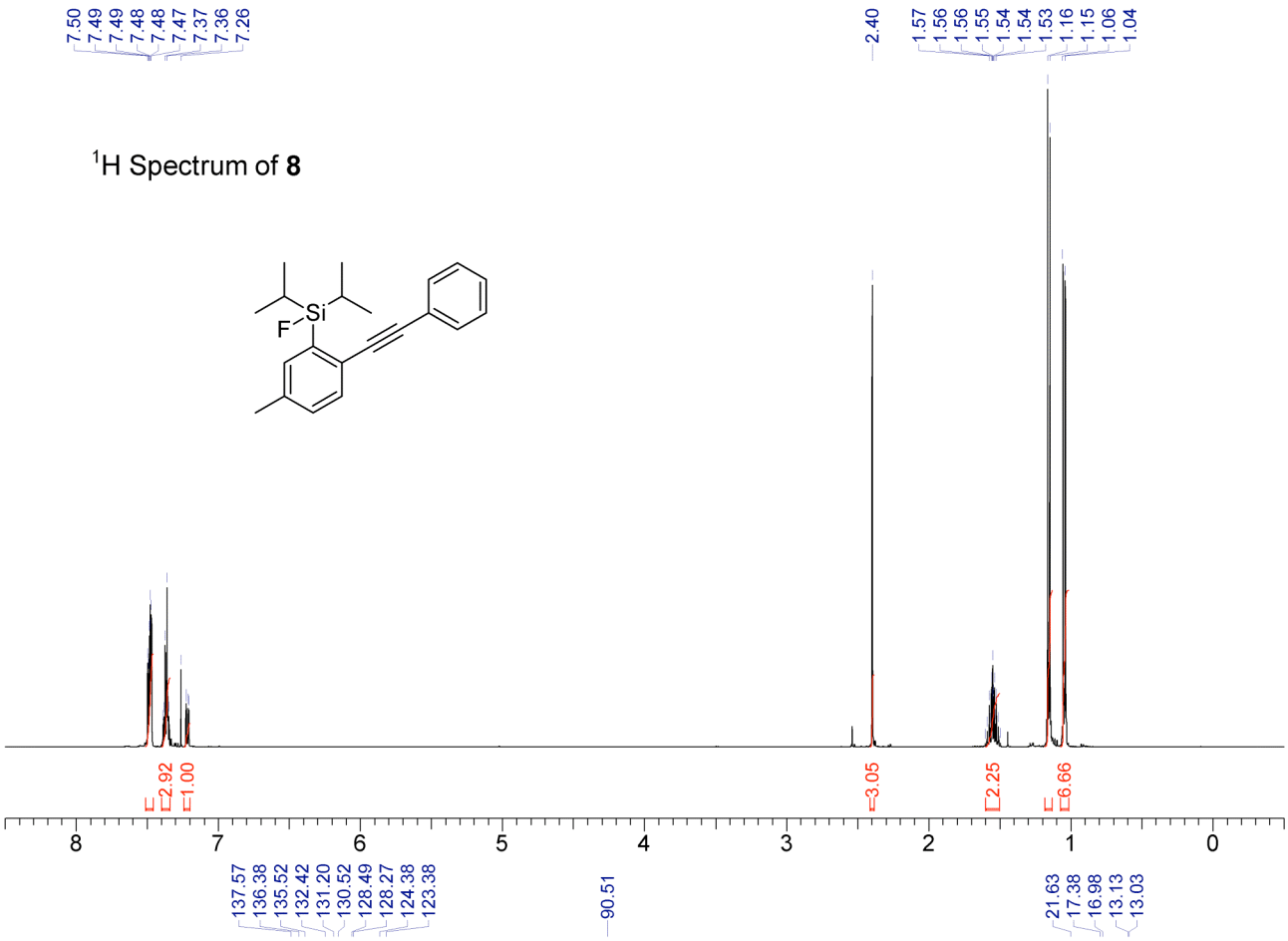

139.20
136.98
136.67
132.79
96.41
84.38
24.83
20.80
13C Spectrum of 4
O
B
O
I
160
140
120
100
80
60
40
20
0



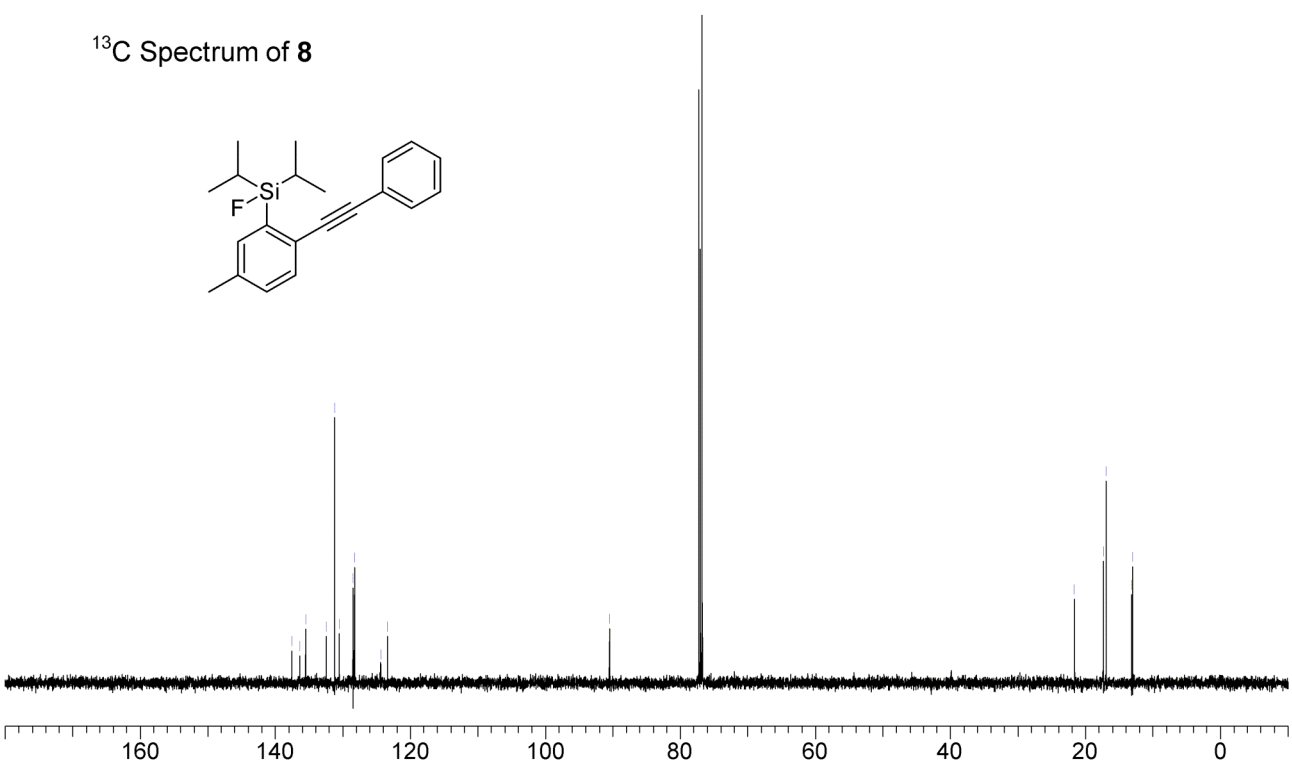
^{1}H Spectrum of **7**



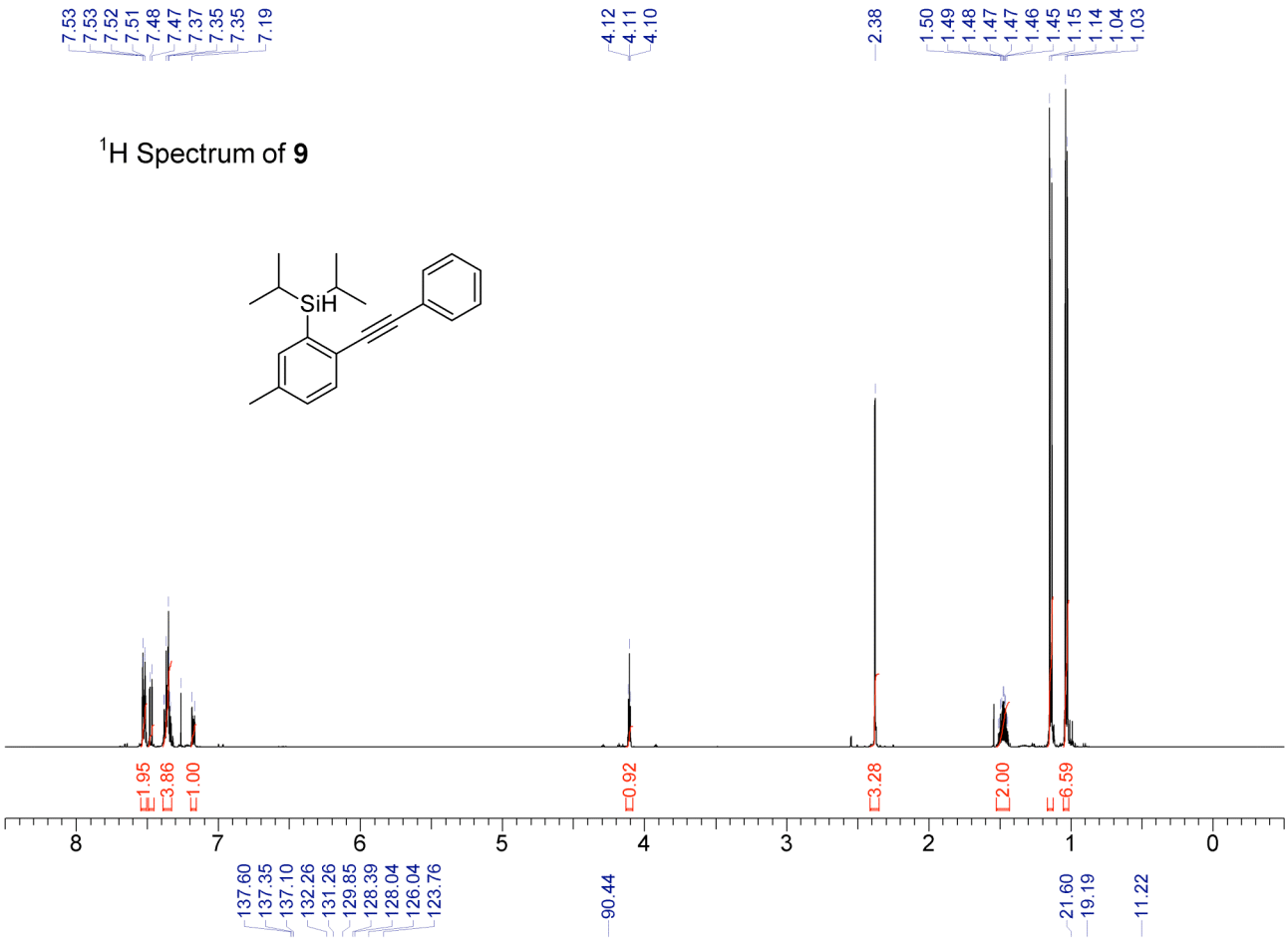
^{13}C Spectrum of **7**

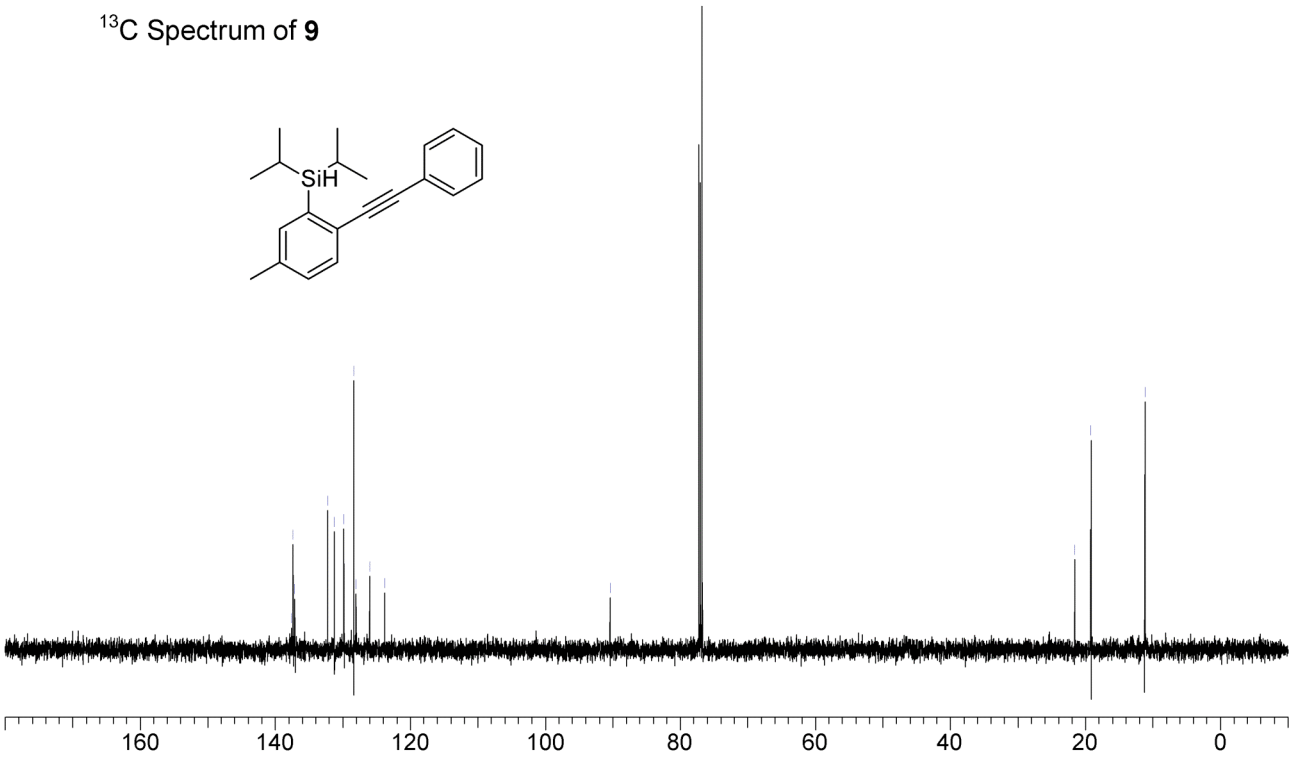


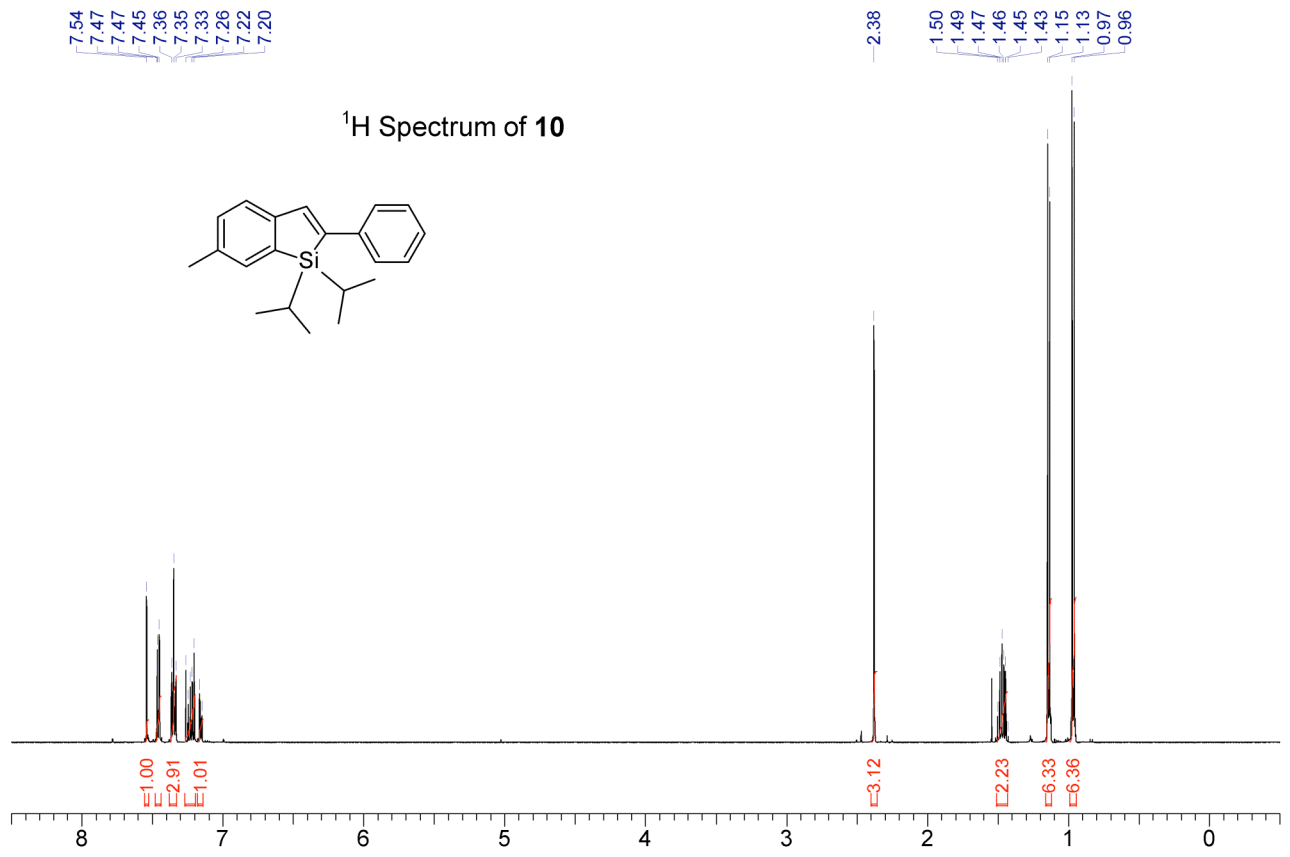
^{1}H Spectrum of **8**

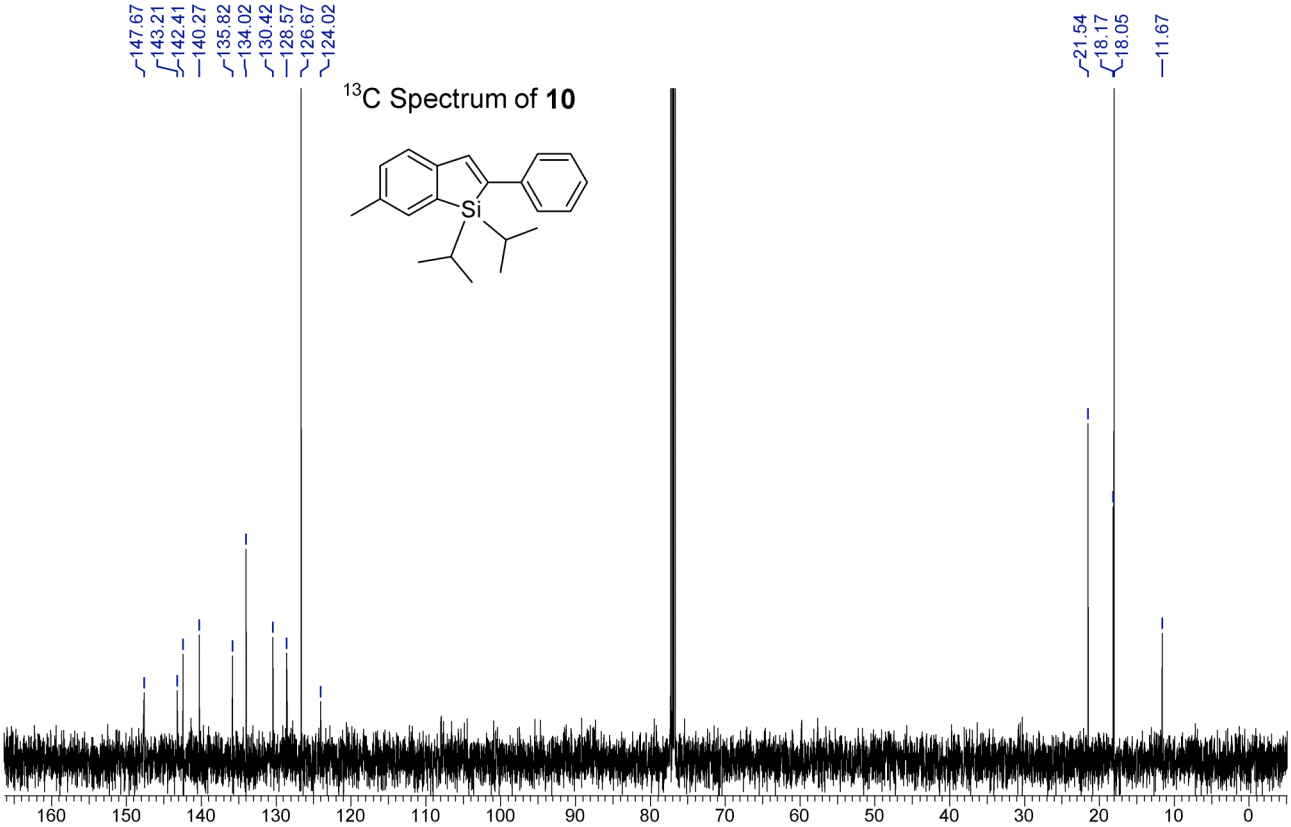


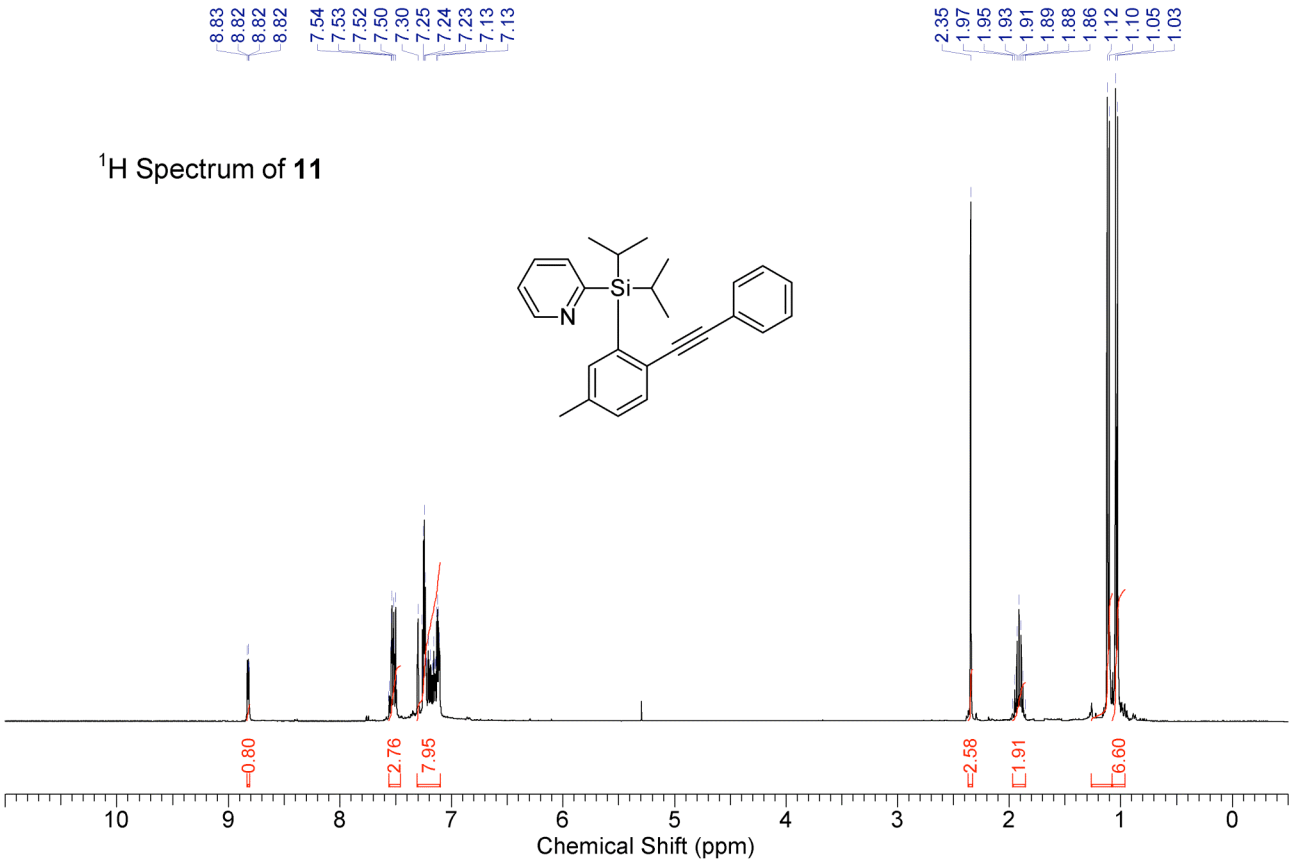
^{13}C Spectrum of **8**

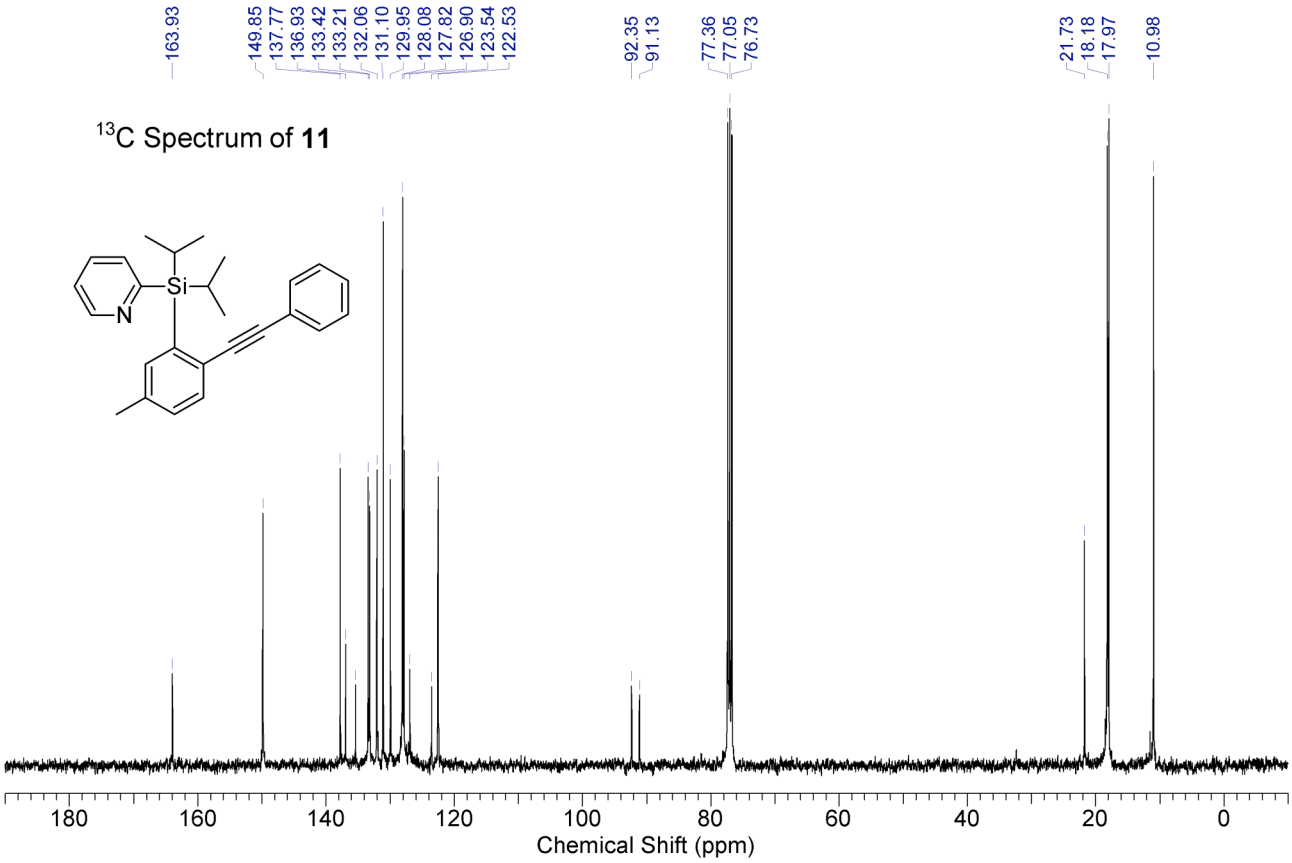

7.53
7.53
7.52
7.51
7.48
7.47
7.37
7.35
7.35
7.19
4.12
4.11
4.10
2.38
1.50
1.49
1.48
1.47
1.47
1.46
1.45
1.15
1.14
1.04
1.03
1H Spectrum of 9
SiH
1.95
3.86
1.00
0.92
3.28
2.00
6.59
8
7
6
5
4
3
2
1
0
137.60
137.35
137.10
132.26
131.26
129.85
128.39
128.04
126.04
123.76
90.44
21.60
19.19
11.22

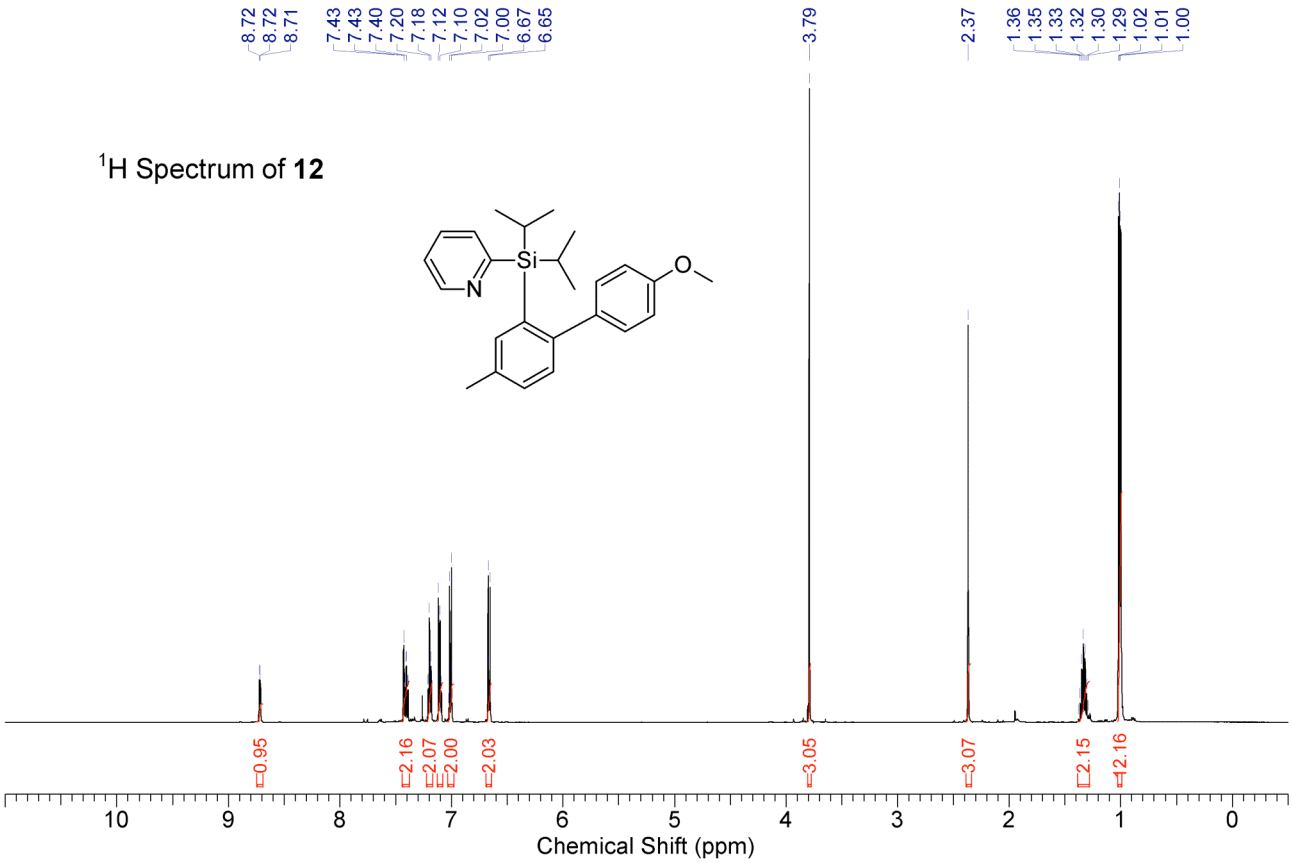

13C Spectrum of 9
SiH
160
140
120
100
80
60
40
20
0

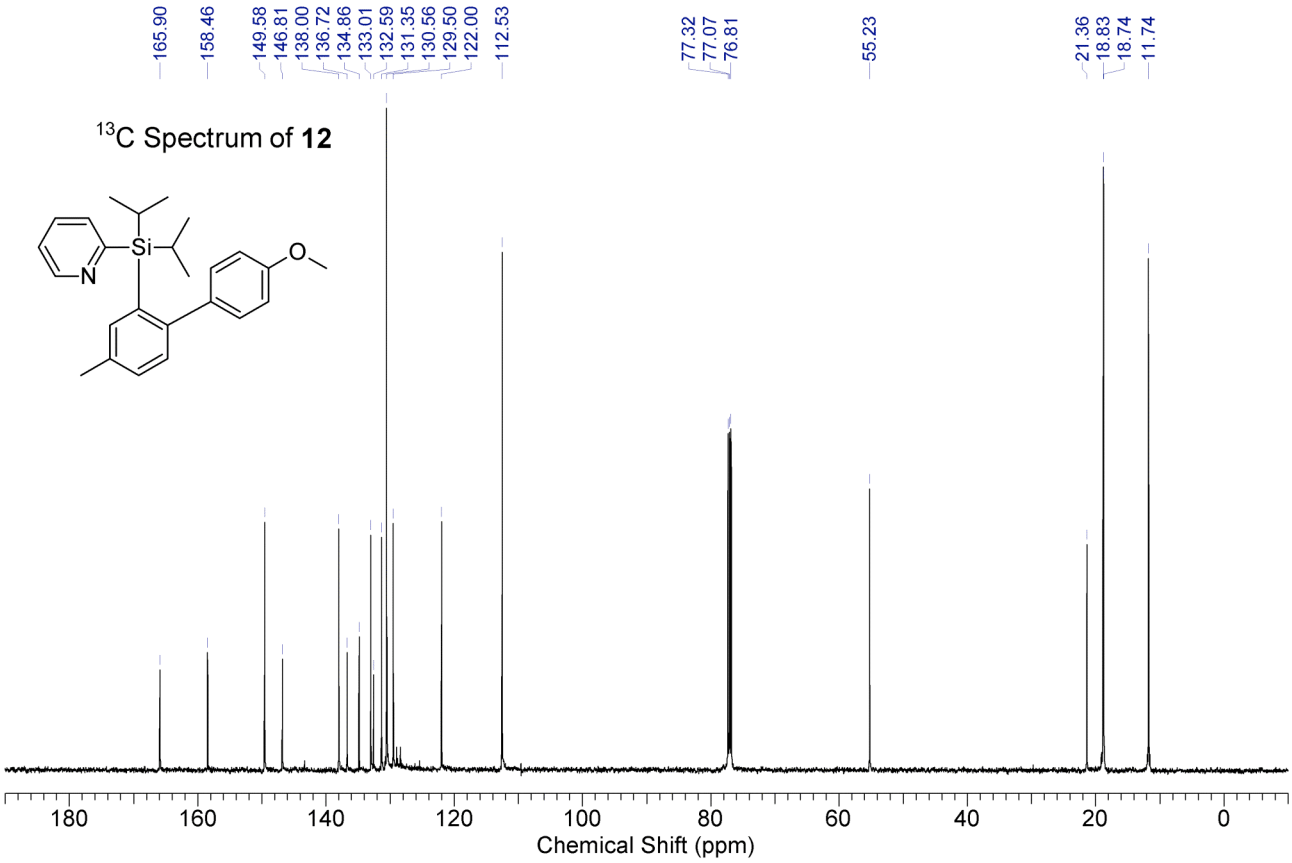

7.54
7.47
7.47
7.45
7.36
7.35
7.33
7.26
7.22
7.20
2.38
1.50
1.49
1.47
1.46
1.45
1.43
1.15
1.13
0.97
0.96
^{1}H Spectrum of **10**
Si
1.00
2.91
1.01
3.12
2.23
6.33
6.36
8
7
6
5
4
3
2
1
0

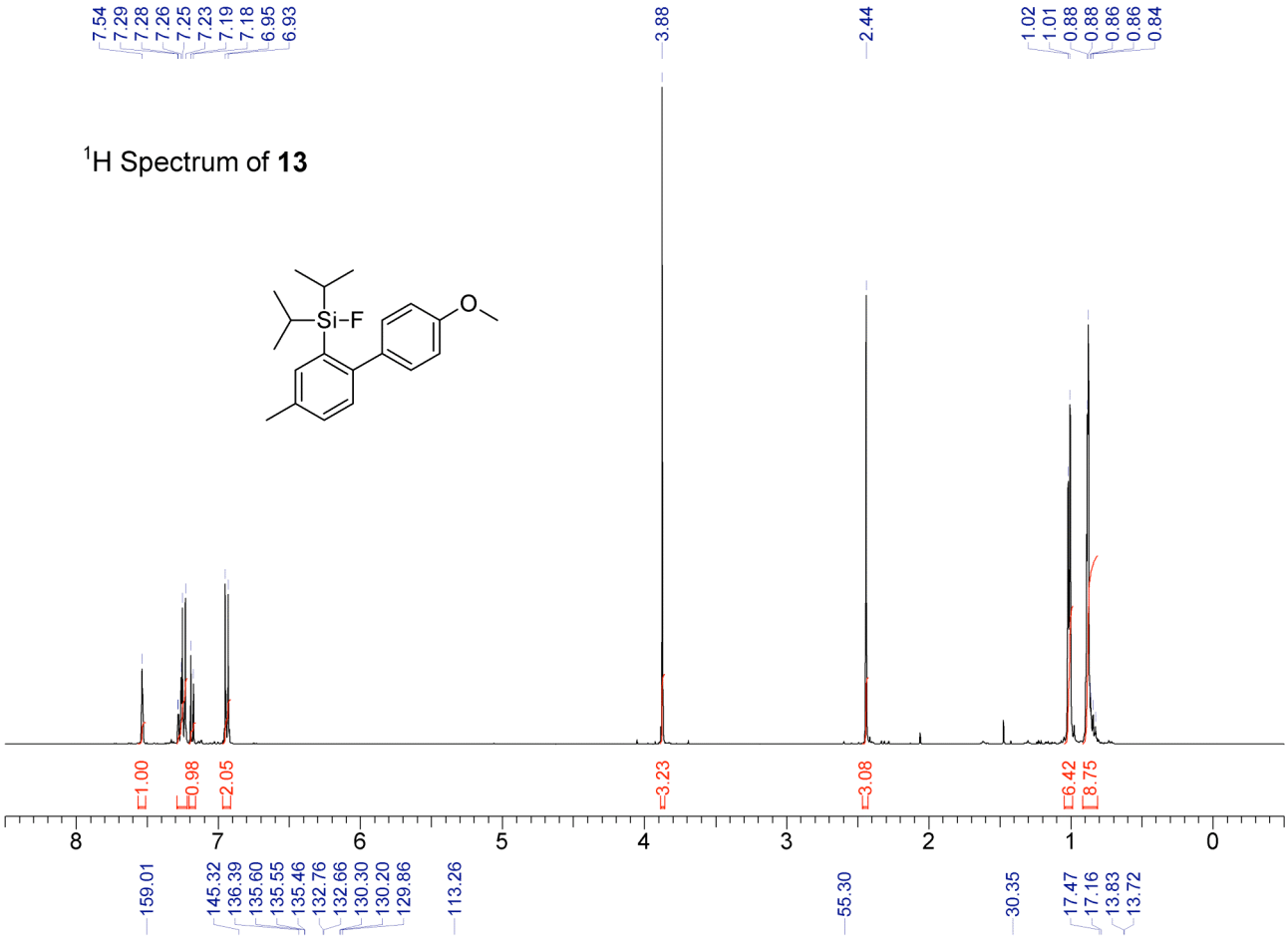

147.67
143.21
142.41
140.27
135.82
134.02
130.42
128.57
126.67
124.02
21.54
18.17
18.05
11.67
^{13}C Spectrum of **10**
Si
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


8.83
8.82
8.82
8.82
7.54
7.53
7.52
7.50
7.30
7.25
7.24
7.23
7.13
7.13
2.35
1.97
1.95
1.93
1.91
1.89
1.88
1.86
1.12
1.10
1.05
1.03
^{1}H Spectrum of **11**
Si
N
0.80
2.76
7.95
2.58
1.91
6.60
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

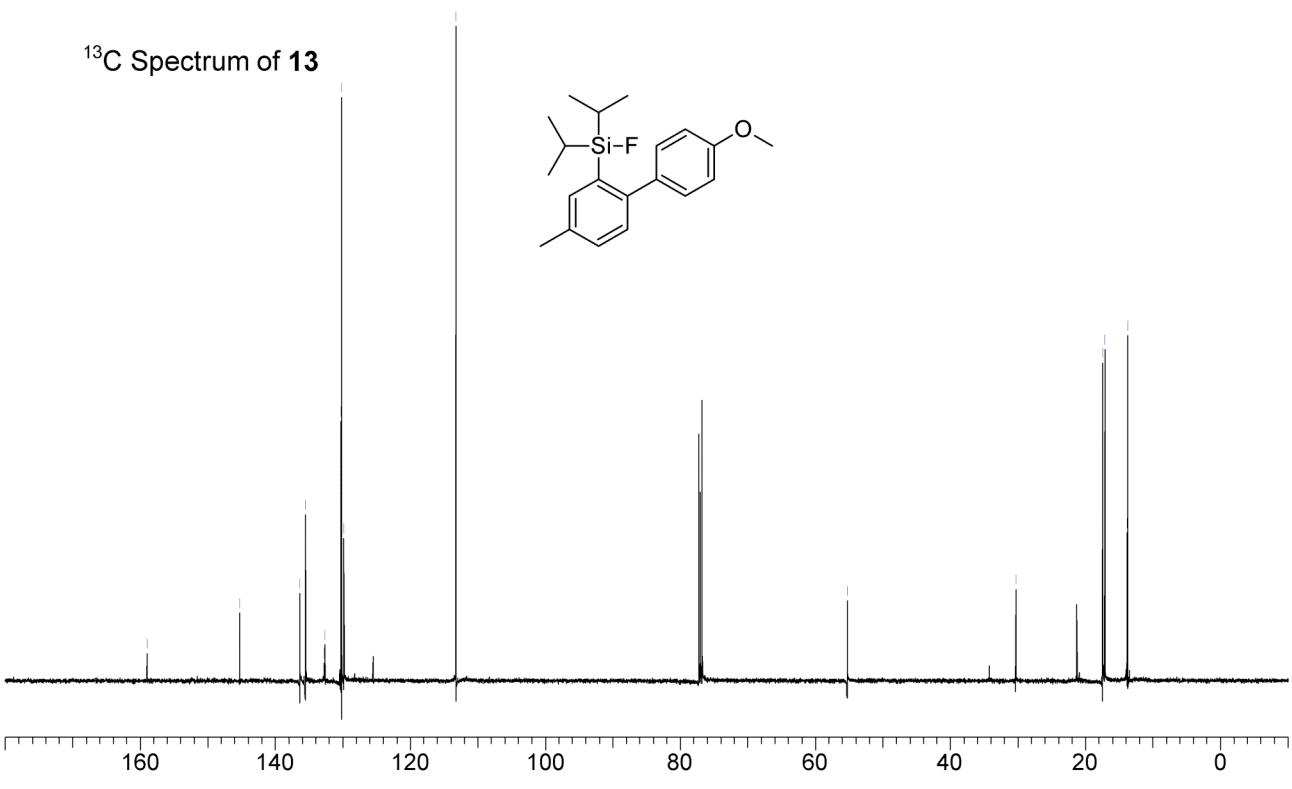

163.93
149.85
137.77
136.93
133.42
133.21
132.06
131.10
129.95
128.08
127.82
126.90
123.54
122.53
92.35
91.13
77.36
77.05
76.73
21.73
18.18
17.97
10.98
^{13}C Spectrum of **11**
Si
N
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


8.72
8.72
8.71
7.43
7.43
7.40
7.20
7.18
7.12
7.10
7.02
7.00
6.67
6.65
3.79
2.37
1.36
1.35
1.33
1.32
1.30
1.29
1.02
1.01
1.00
1H Spectrum of 12
Si
N
O
0.95
2.16
2.07
2.00
2.03
3.05
3.07
2.15
12.16
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

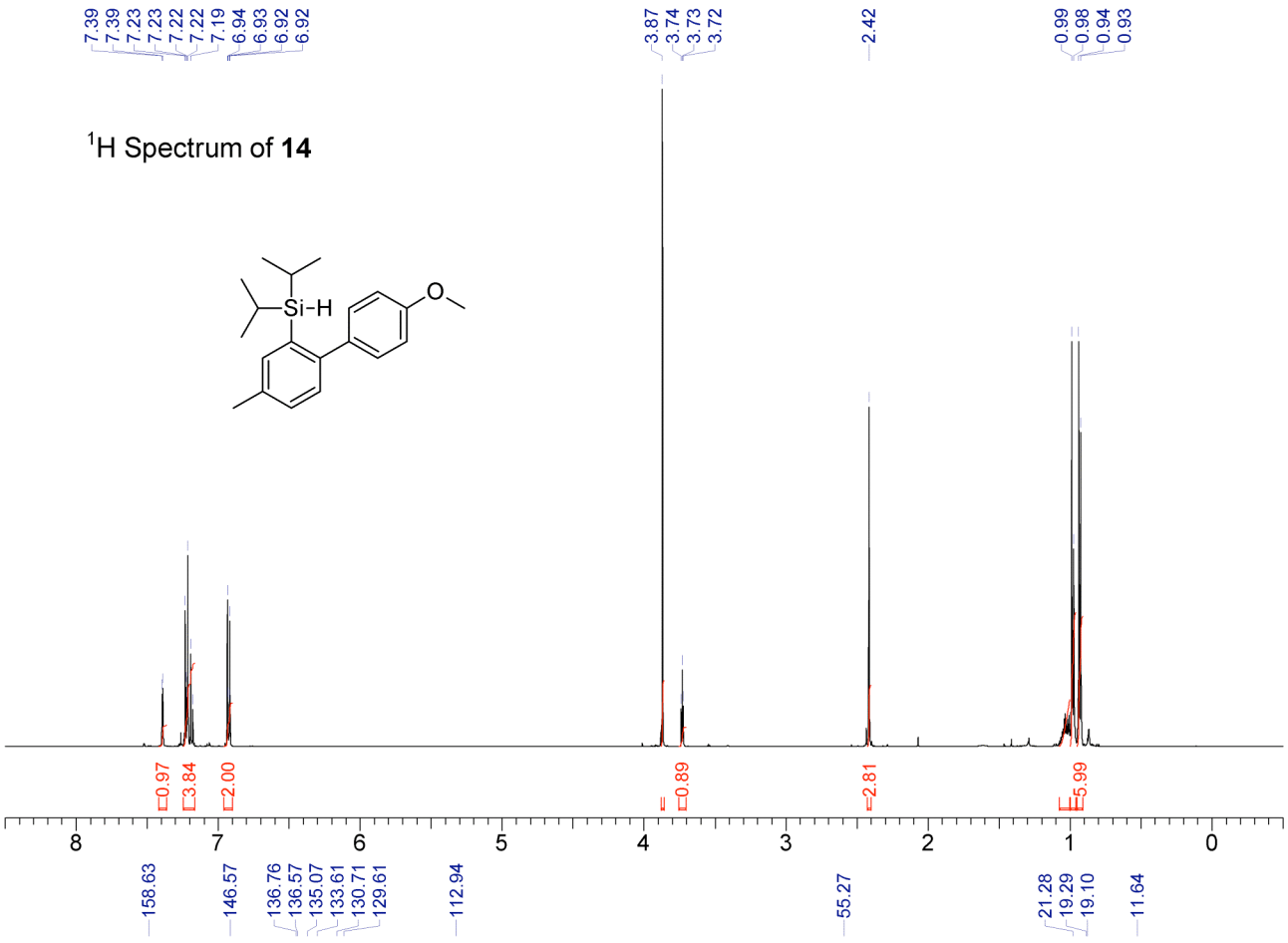

165.90
158.46
149.58
146.81
138.00
136.72
134.86
133.01
132.59
131.35
130.56
129.50
122.00
112.53
77.32
77.07
76.81
55.23
21.36
18.83
18.74
11.74
13C Spectrum of 12
Si
N
O
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

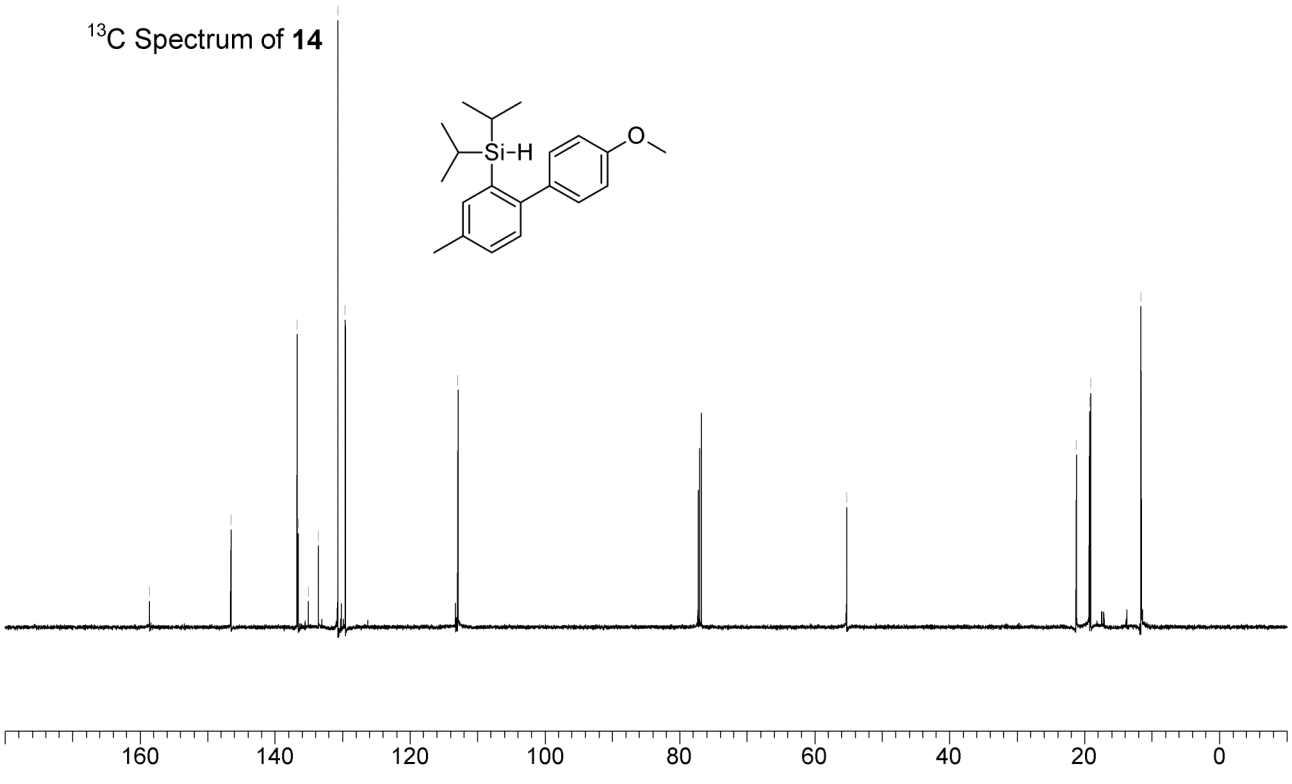


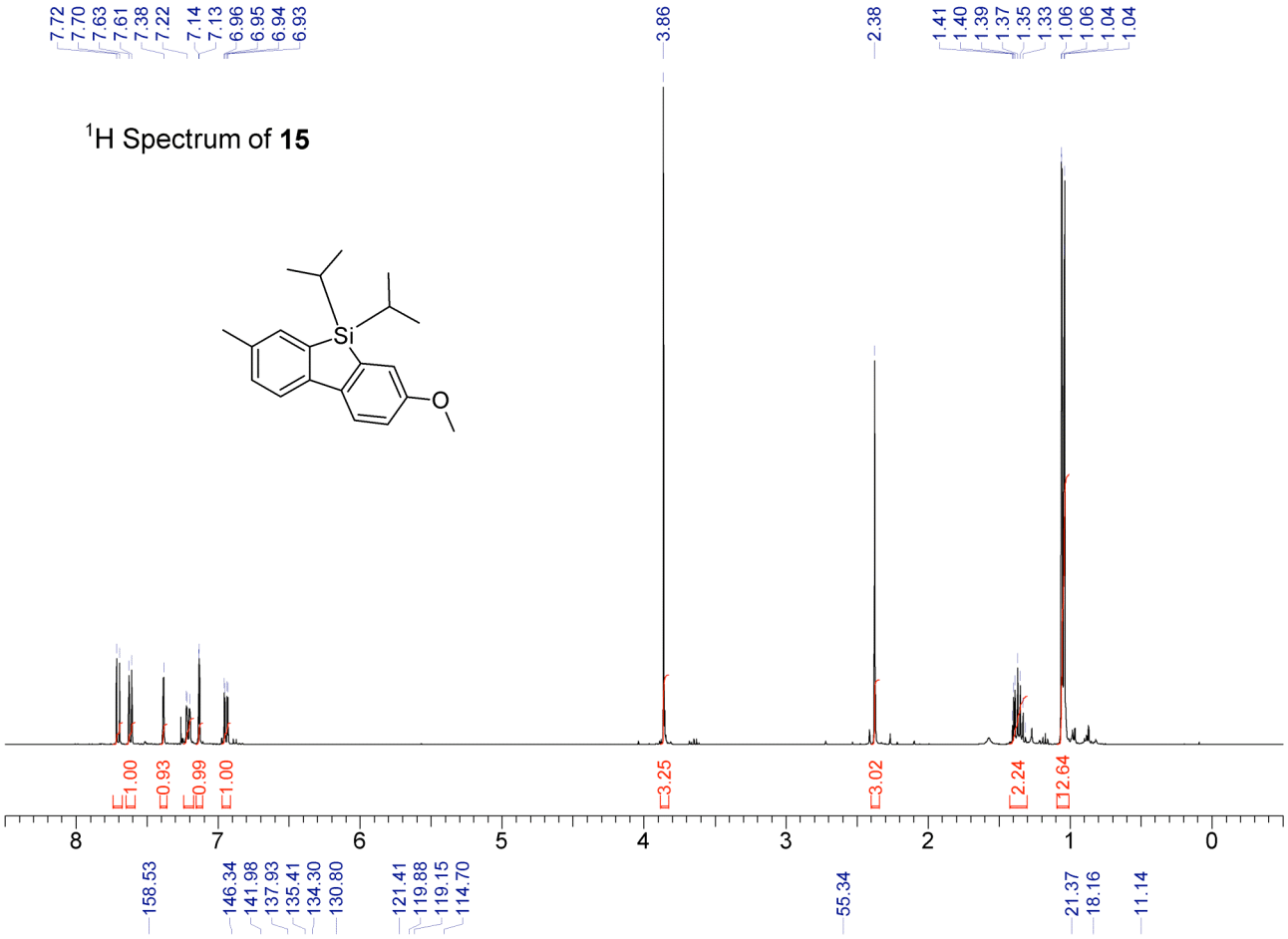
^{1}H Spectrum of **13**

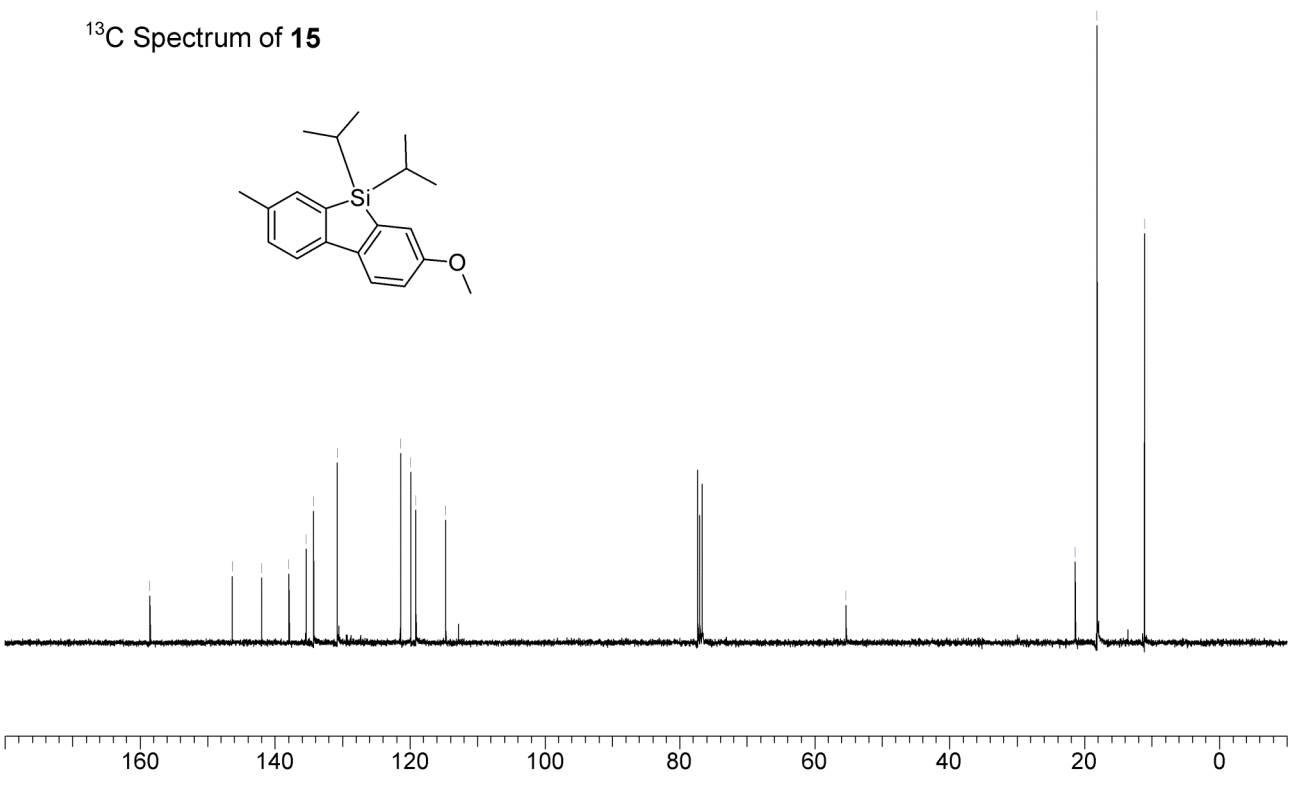


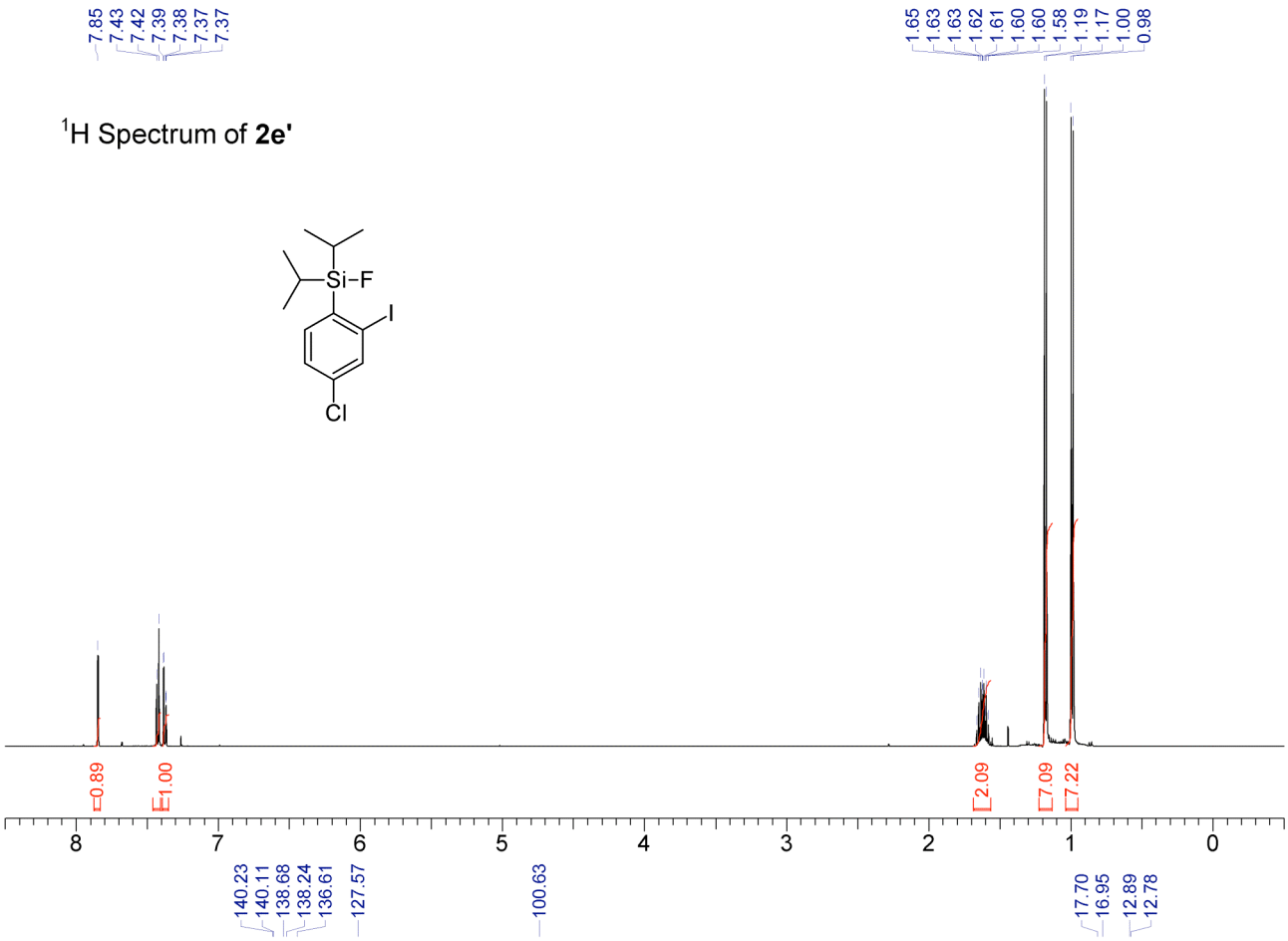
^{13}C Spectrum of **13**


7.39
7.39
7.23
7.23
7.22
7.22
7.19
6.94
6.93
6.92
6.92
3.87
3.74
3.73
3.72
2.42
0.99
0.98
0.94
0.93
1H Spectrum of 14
Si-H
O
0.97
3.84
2.00
0.89
2.81
5.99
8
7
6
5
4
3
2
1
0

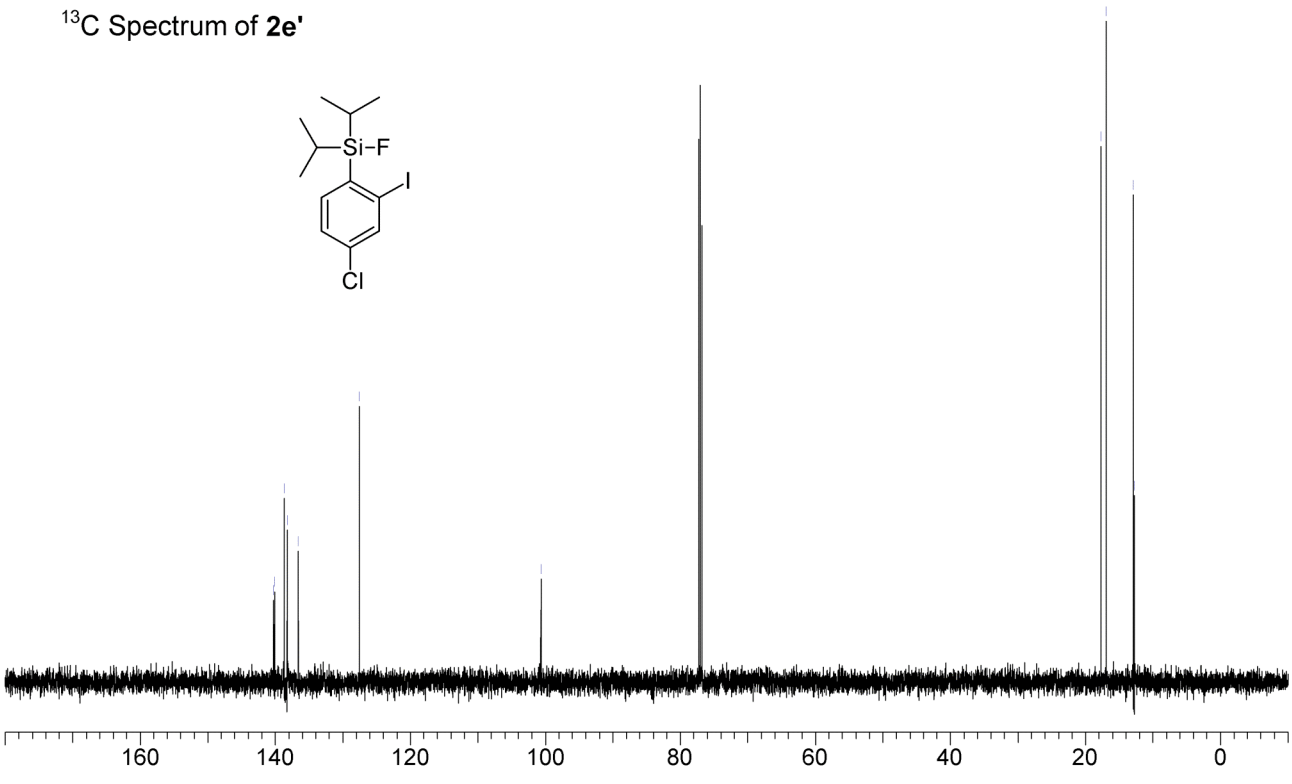

158.63
146.57
136.76
136.57
135.07
133.61
130.71
129.61
112.94
55.27
21.28
19.29
19.10
11.64
13C Spectrum of 14
Si-H
O
160
140
120
100
80
60
40
20
0


7.72
7.70
7.63
7.61
7.38
7.22
7.14
7.13
6.96
6.95
6.94
6.93
3.86
2.38
1.41
1.40
1.39
1.37
1.35
1.33
1.06
1.06
1.04
1.04
1H Spectrum of 15
Si
O
1.00
0.93
0.99
1.00
3.25
3.02
2.24
12.64
8
7
6
5
4
3
2
1
0

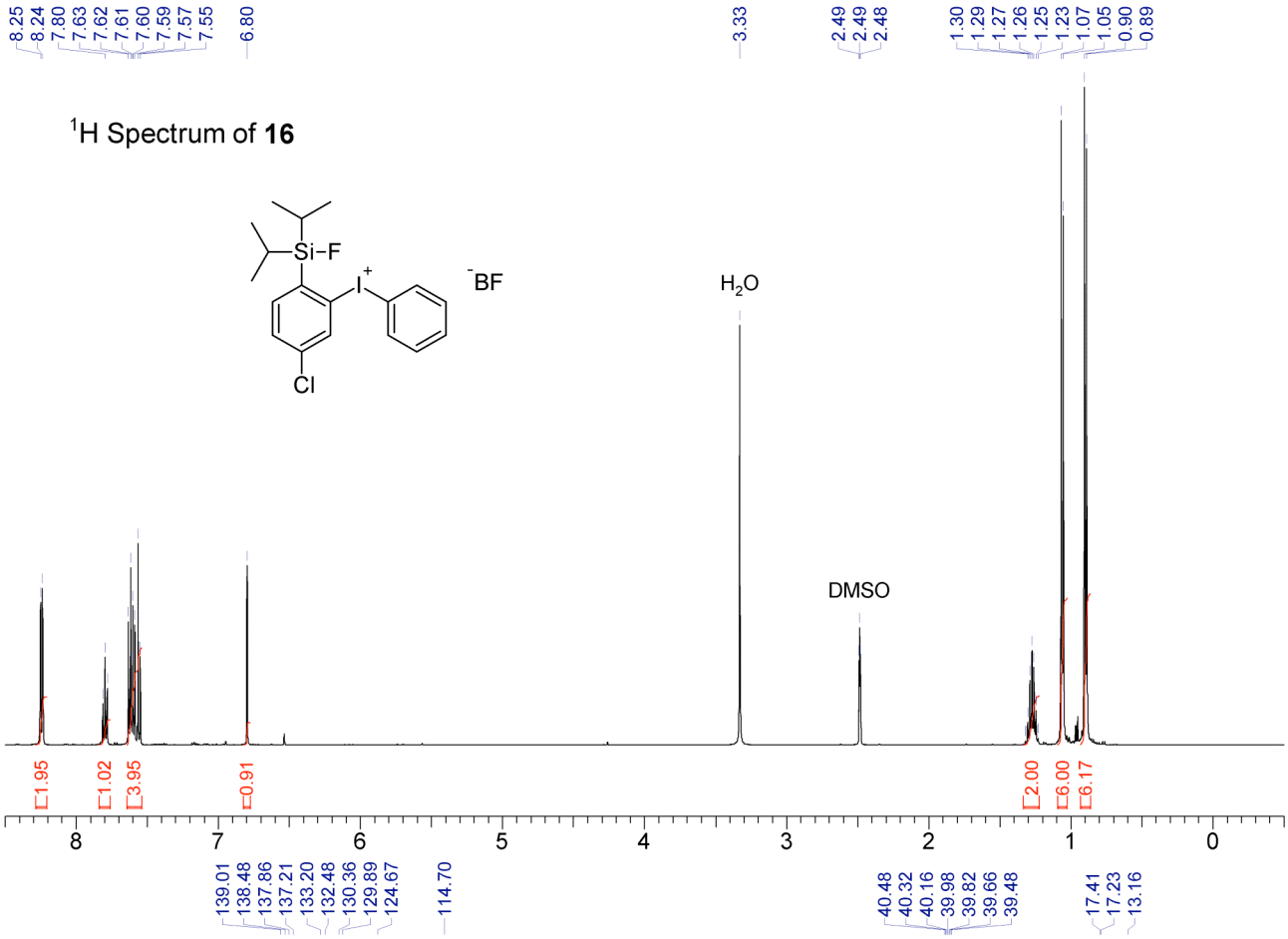

158.53
146.34
141.98
137.93
135.41
134.30
130.80
121.41
119.88
119.15
114.70
55.34
21.37
18.16
11.14
13C Spectrum of 15
Si
O
160
140
120
100
80
60
40
20
0

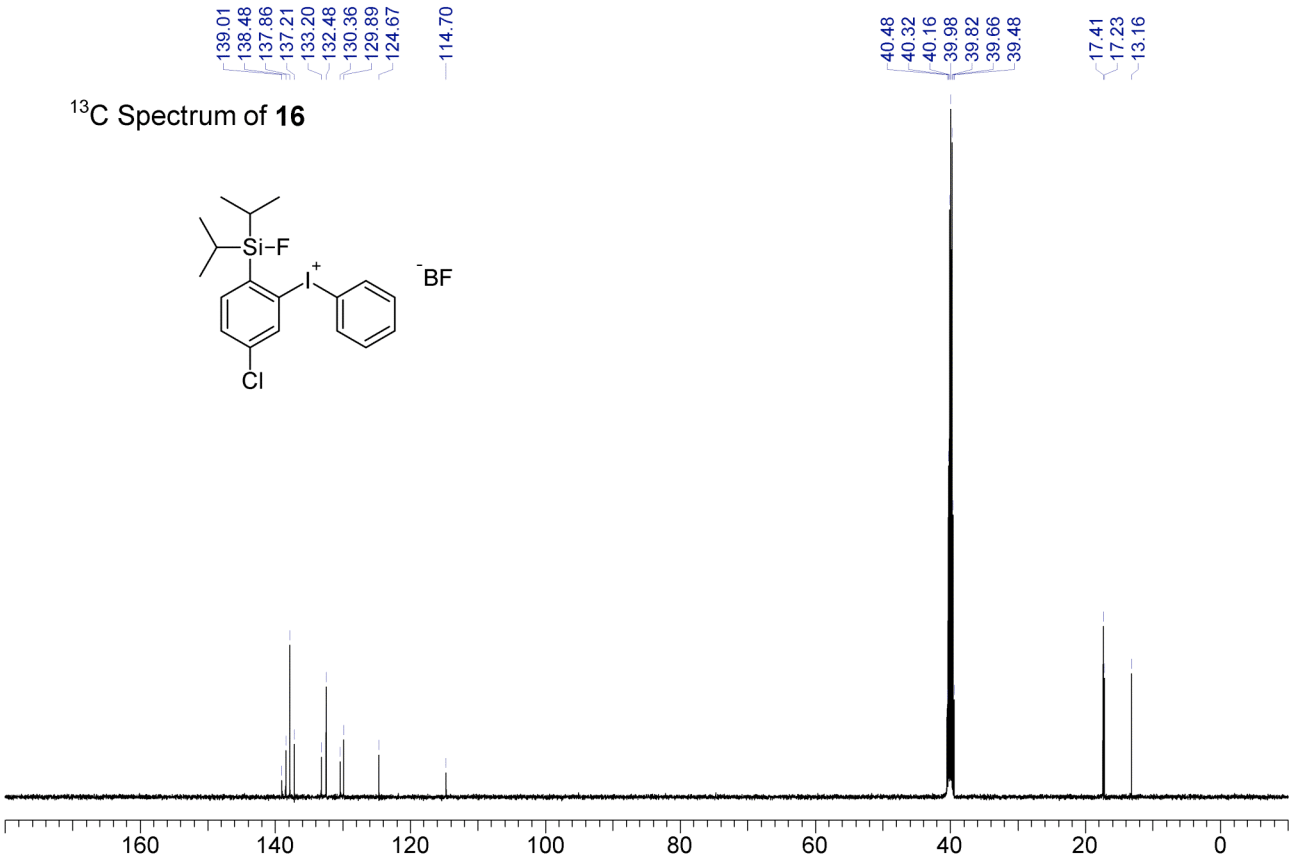


^{1}H Spectrum of **2e'**



^{13}C Spectrum of **2e'**


8.25
8.24
7.80
7.63
7.62
7.61
7.60
7.59
7.57
7.55
6.80
3.33
2.49
2.49
2.48
1.30
1.29
1.27
1.26
1.25
1.23
1.07
1.05
0.90
0.89
1H Spectrum of 16
Si–F
I+
Cl
BF
H2O
DMSO
1.95
1.02
3.95
0.91
2.00
6.00
6.17
8
7
6
5
4
3
2
1
0


139.01
138.48
137.86
137.21
133.20
132.48
130.36
129.89
124.67
114.70
40.48
40.32
40.16
39.98
39.82
39.66
39.48
17.41
17.23
13.16
13C Spectrum of 16
Si–F
I+
Cl
BF
160
140
120
100
80
60
40
20
0