Supporting Information

Fused Heteroaromatic Dihydrosiloles: Synthesis and Double-Fold Modification

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Content

General Information

GC/MS analysis was performed on a Hewlett Packard Model 6890 GC interfaced to a Hewlett Packard Model 5973 mass selective detector (15 m x 0.25 mm capillary column, HP-5MS). Column chromatography was carried out employing Silicycle Silica-P flash silica gel (40-63 μm). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography. NMR spectra were recorded on Bruker Avance DRX-500 (500 MHz) or DPX-400 (400 MHz) instrument. LRMS and HRMS analyses were performed on Micromass 70 VSE mass spectrometer. All manipulations with transition metal catalysts were conducted in oven-dried glassware under inert atmosphere using a combination of glovebox and standard Schlenk techniques unless otherwise noted. Anhydrous solvents purchased from Sigma-Aldrich were additionally purified on PureSolv PS-400-4 by Innovative Technology, Inc. purification system and/or stored over calcium hydride. The starting materials were purchased from Sigma-Aldrich, Alfa Aesar, Strem Chemicals, and AK Scientific.[1] Abbreviations used: dppe - 1,2-Bis(diphenylphosphino)ethane; dppf - 1,2-Bis(diphenylphosphino)ferrocene; dppbe - 1,2-Bis(diphenylphosphino)benzene; TMEDA – *N-N-N'-N'*-tetramethylethylenediamine; SIPr - 1,3-Bis(2,6-di-i-propylphenyl)imidazolidin-2-ylidene; IPr - 1,3-Bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene; IMes - 1,3-Bis(2,4,6-trimethylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene; dtbpy - 4,4′-Di-tert-butyl-2,2′-dipyridyl; tp - 2,2′:6′,2″-terpyridine; pnen – 1,10-phenantroline.

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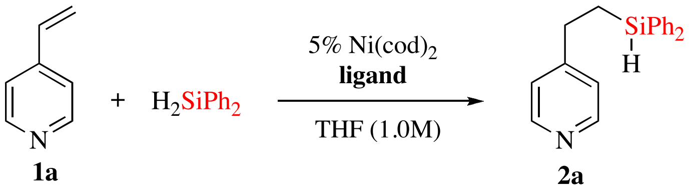
[1] Heteroaromatic styrenes if not commercially available were synthesized from the corresponding bromides using published procedure: Nie, H.-J.; Yao, J.; Zhong, Y.-W. *J. Org. Chem.* **2011**, *76*, 4771.

Part I. Synthesis of Fused Heteroaromatic Dihydrosiloles

Part IA. Hydrosilylation Reaction

<u>Optimization of the hydrosilylation reaction of 4-vinylpyridine **1a** with diphenylsilane</u>



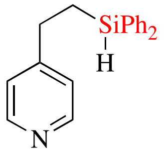
In a glovebox, 1 mL Wheaton microreactor was charged with a catalyst/ligand and THF (0.1 mL, 1.0M). To the resulting solution, diphenylsilane (0.11 mmol, 1.10 equiv, 20.4 µL) was added followed by 4-vinylpyridine (**1a**, 0.1 mmol, 1 equiv, 11.5µL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated (80°C) aluminum block. The reaction mixture was stirred for 2 h at this temperature and after that analyzed by GC/MS.

Optimization table

entry	ligand	**2a** yield, %[a]
1	10% dppe	-
2	10% dppf	-
3	10% dppbe	47
4	10% TMEDA	32
5	20% SIPr	<5
6	20% IPr	-
7	20% IMes	-
8	10% dtbpy	34
9	10% tp	29
10	20% PCy_3	-
11	20% PPh_3	76
12[b]	20% PPh_3	89 (83)[c]
13[d]	20% PPh_3	65

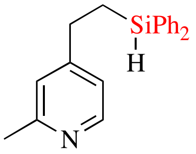
[a]GC Yield. [b] Reaction was carried out at 90°C during 1h. [c]Isolated yield is given in paranthesis. [d]Reaction was carried out at room T during 24h.

General procedure for the hydrosilylation reaction of heteroaromatic styrenes with diphenylsilane. In a glovebox, a 3 mL Wheaton microreactor vial was charged with $Ni(cod)_2$ (27.5 mg, 5 mol%), PPh_3 (52.4 mg, 20 mol%), and THF (1.0 mL, 1.0M). To the resulting solution, Ph_2SiH_2 (1.02 mmol, 1.02 equiv, 189 µL) was added, followed by heteroaromatic styrene **1** (1.0 mmol, 1 equiv). The microreactor was capped with a Teflon pressure cap and placed into pre-heated (90°C) aluminum block. The reaction mixture was stirred for 1 h at this temperature. After completion of the reaction (as determined by GC/MS analysis), microreactor, containing hydrosilylation product **2**, was cooled down and the solvent was evaporated. The product was purified using flash silica gel column chromatography.



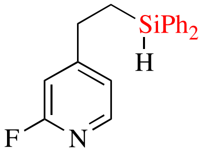
2a: (84%, eluent: Hexanes/EtOAc = 7/1)

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.48 (d, *J* = 5.9 Hz, 2H), 7.59-7.58 (m, 4H), 7.46-7.39 (m, 6H), 7.11 (d, *J* = 5.7 Hz, 2H), 4.92 (t, *J* = 3.7 Hz, 1H), 2.77-2.74 (m, 2H), 1.53-1.49 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 152.9, 149.7, 135.0, 133.4, 129.8, 128.1, 123.2, 29.8, 13.0. HRMS (EI+) calc.d for $C_{20}H_{20}Si$: 289.12868, measured: 289.12774.



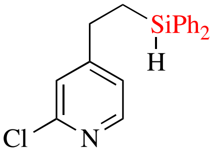
2b: (86%, eluent: Hexanes/EtOAc = 10/1)

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.34 (d, *J* = 5.3 Hz, 1H), 7.58-7.56 (m, 4H), 7.43-7.37 (m, 6H), 6.95 (s, 1H), 6.91 (d, *J* = 5.3 Hz, 1H), 4.90 (t, *J* = 3.5 Hz, 1H), 2.72-2.68 (m, 2H), 2.50 (s, 3H), 1.51-1.46 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 158.3, 153.2, 149.0, 135.1, 133.6, 129.8, 128.1, 122.8, 120.4, 29.8, 24.4, 13.1. HRMS (EI+) calcd. for $C_{20}H_{21}SiN$: 303.14433, measured: 303.14505.



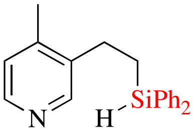
2c: (86%, eluent: Hexanes/EtOAc = 25/1)

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.08 (d, *J* = 5.3 Hz, 1H), 7.59-7.57 (m, 4H), 7.46-7.38 (m, 6H), 6.98 (d, *J* = 5.3 Hz, 1H), 6.74 (s, 1H), 4.92 (t, *J* = 3.5 Hz, 1H), 2.80-2.76 (m, 2H), 1.52-1.48 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 164.2 (d, $J_{C\text{-}F}$ = 237.7 Hz), 159.1 (d, $J_{C\text{-}F}$ = 8.3 Hz), 147.3 (d, *J* = 14.8 Hz), 135.1, 133.3, 130.0, 128.2, 121.1, 108.5 (d, $J_{C\text{-}F}$ = 37.0 Hz), 29.8, 13.0. HRMS (ES+) calcd. for $C_{19}H_{19}SiNF$: 308.1271, measured: 308.1266.



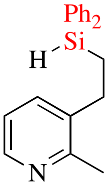
2d: (61%, eluent: Hexanes/EtOAc = 25/1)

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.24 (d, *J* = 5.1 Hz, 1H), 7.59-7.58 (m, 4H), 7.47-7.39 (m, 6H), 7.15 (s, 1H), 7.02 (d, *J* = 5.1 Hz, 1H), 4.93 (t, *J* = 3.7 Hz, 1H), 2.76-2.73 (m, 2H), 1.52-1.48 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 156.3, 151.5, 149.3, 135.0, 133.1, 129.1, 128.1, 123.5, 122.1, 29.6, 12.9. HRMS (EI+) calcd. for $C_{19}H_{19}SiNCl$: 323.08970, measured: 323.08922.



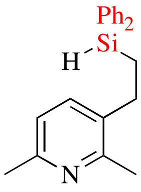
2e: (95%, eluent: Hexanes/EtOAc = 7/1)

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.32 (s, 1H), 8.28 (d, *J* = 5.3 Hz, 1H), 7.59-7.57 (m, 4H), 7.44-7.36 (m, 6H), 6.99 (d, *J* = 4.7 Hz, 1H), 4.95 (t, *J* = 3.5 Hz, 1H), 2.75-2.70 (m, 2H), 2.22 (s, 3H), 1.46-1.41 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 149.4, 147.3, 144.5, 135.1, 133.6, 129.8, 128.1, 125.1, 25.2, 18.5, 13.0. HRMS (EI+) calcd. for $C_{20}H_{21}SiN$: 303.14433, measured: 303.14438.



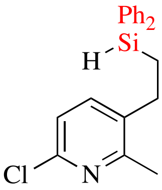
2f: (93%, eluent: Hexanes/EtOAc = 7/1)

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.33 (d, *J* = 4.8 Hz, 1H), 7.61-7.59 (m, 4H), 7.46-7.39 (m, 7H), 7.05 (dd, *J* = 7.7, 4.9 Hz, 1H), 4.95 (m, 1H), 2.76-2.73 (m, 2H), 2.48 (s, 3H), 1.48-1.44 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 156.2, 146.5, 137.5, 135.5, 135.0, 133.6, 129.8, 128.1, 121.3, 27.3, 22.0, 12.5. HRMS (EI+) calcd. for $C_{20}H_{20}SiN$: 302.13650, measured: 302.13617.



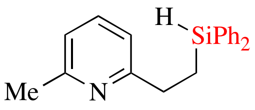
2g: (90%, eluent: Hexanes/EtOAc = 25/1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61-7.59 (m, 4H), 7.45-7.39 (m, 6H), 7.31 (d, J = 8.1 Hz, 1H), 6.91 (d, J = 7.7 Hz, 1H), 4.95 (t, J = 3.7 Hz, 1H), 2.74-2.70 (m, 2H), 2.50 (s, 3H), 2.46 (s, 3H), 1.46-1.43 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.3, 154.8, 136.0, 135.0, 134.0, 133.7, 129.7, 128.1, 120.7, 27.0, 24.0, 22.0, 12.7. HRMS (EI+) calcd. for $C_{21}H_{22}SiN$: 316.15215, measured: 316.15241.



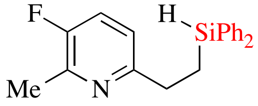
2h: (83%, eluent: Hexanes/EtOAc = 10/1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61-7.59 (m, 4H), 7.47-7.40 (m, 6H), 7.37 (d, J = 8.1 Hz, 1H), 7.07 (d, J = 7.7 Hz, 1H), 4.96 (t, J = 3.7 Hz, 1H), 2.75-2.71 (m, 2H), 2.45 (s, 3H), 1.47-1.43 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 147.5, 138.5, 136.1, 135.0, 133.3, 129.8, 128.1, 121.4, 26.6, 21.7, 12.6. HRMS (EI+) calcd. for $C_{20}H_{19}SiNCl$: 336.09753, measured: 336.09712.



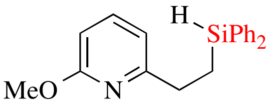
2j: (48%, eluent: Hexanes/EtOAc = 25/1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59-7.58 (m, 4H), 7.44-7.34 (m, 7H), 6.93 (d, J = 7.6 Hz, 2H), 4.94 (t, J = 4.1 Hz, 1H), 2.93-2.89 (m, 2H), 2.51 (s, 3H), 1.62-1.57 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.8, 157.7, 136.5, 135.4, 129.6, 128.0, 120.4, 118.8, 33.0, 24.5, 12.6. HRMS (EI+) calcd. for $C_{20}H_{22}SiN$: 304.1522, measured: 304.1527.



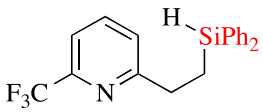
2k: (76%, eluent: Hexanes/EtOAc = 10/1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57-7.56 (m, 4H), 7.40-7.38 (m, 6H), 7.15 (t, J = 8.8 Hz, 1H), 6.91 (dd, J = 8.2, 3.5 Hz, 1H), 4.90 (t, J = 4.1 Hz, 1H), 2.91-2.87 (m, 2H), 2.45 (d, J = 2.9 Hz, 3H), 1.59-1.55 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.2 (d, $J_{C\text{-}F}$ = 5.2 Hz), 156.2 (d, $J_{C\text{-}F}$ = 252.3 Hz), 146.0 (d, $J_{C\text{-}F}$ = 17.0 Hz), 135.2, 134.0, 129.6, 128.0, 122.4, (d, $J_{C\text{-}F}$ = 19.6 Hz), 120.5 (d, $J_{C\text{-}F}$ = 3.7 Hz), 32.3, 17.9, 12.7. HRMS (EI+) calcd. for $C_{20}H_{20}SiNF$: 321.13490, measured: 321.13408.



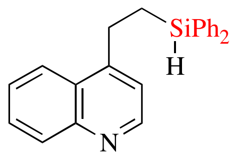
2l: (67%, eluent: Hexanes/EtOAc = 25/1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62-7.60 (m, 4H), 7.44-7.35 (m, 7H), 6.69 (d, J = 7.0 Hz, 1H), 6.54 (d, J = 8.2 Hz, 1H), 4.94 (t, J = 3.5 Hz, 1H), 3.93 (s, 3H), 2.89-2.85 (m, 2H), 1.68-1.62 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.1, 138.7, 135.2, 134.5, 129.6, 128.0, 127.8, 114.5, 107.4, 53.2, 32.4, 11.8. HRMS (ES+) calcd. for $C_{20}H_{22}SiNO$: 320.1471, measured: 320.1462.



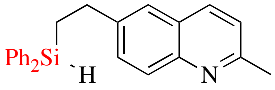
2m: (76%, eluent: Hexanes/EtOAc = 25/1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61-7.59 (m, 4H), 7.47-7.40 (m, 6H), 7.37 (d, J = 8.1 Hz, 1H), 7.07 (d, J = 7.7 Hz, 1H), 4.96 (t, J = 3.7 Hz, 1H), 2.75-2.71 (m, 2H), 2.45 (s, 3H), 1.47-1.43 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.3, 147.6 (q, $J_{C\text{-}F}$ = 33.2 Hz), 137.4, 135.2, 133.7, 129.7, 128.0, 125.0, 121.6 (q, $J_{C\text{-}F}$ = 273.7 Hz), 117.6, 32.8, 12.1. HRMS (EI+) calcd. for $C_{20}H_{17}SiNF_3$: 356.10824, measured: 356.10913.



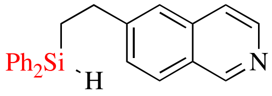
2n (97%, eluent: Hexanes/EtOAc = 10/1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 (d, J = 4.7 Hz, 1H), 8.10 (d, J = 8.8 Hz, 1H), 7.68 (t, J = 7.0 Hz, 1H), 7.62-7.60 (m, 4H), 7.51 (t, J = 8.2 Hz, 1H), 7.44-7.38 (m, 6H), 7.23 (d, J = 4.7 Hz, 1H), 5.00 (t, J = 3.5 Hz, 1H), 3.22-3.18 (m, 2H), 1.65-1.60 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.3, 150.0, 148.3, 135.1, 133.5, 130.0, 129.9, 129.0, 128.2, 127.1, 126.3, 123.3, 120.0, 26.8, 13.1. HRMS (EI+) calcd. for $C_{23}H_{20}SiN$: 338.13650, measured: 338.13727.



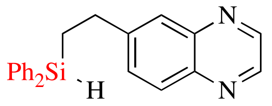
2o: (96%, eluent: Hexanes/EtOAc = 10/1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (t, J = 8.8 Hz, 2H), 7.60-7.58 (m, 4H), 7.54-7.51 (m, 2H), 7.42-7.35 (m, 6H), 7.24 (d, J = 8.2 Hz, 1H), 4.92 (t, J = 3.5 Hz, 1H), 2.96-2.91 (m, 2H), 2.73 (s, 3H), 1.63-1.57 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.1, 146.7, 141.6, 135.7, 135.2, 134.0, 130.5, 129.8, 128.6, 128.1, 126.5, 125.2, 122.0, 30.4, 25.3, 14.1. HRMS (EI+) calcd. for $C_{24}H_{23}SiN$: 353.15998, measured: 353.16029.



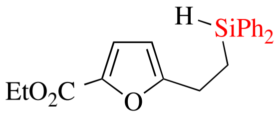
2p: (90%, eluent: Hexanes/EtOAc = 4/1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.26 (s, 1H), 8.53 (d, J = 5.8 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.67-7.63 (m, 5H), 7.55-7.50 (m, 2H), 7.46-7.40 (m, 6H), 5.02 (t, J = 3.7 Hz, 1H), 3.22-3.18 (m, 2H), 1.66-1.61 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.2, 143.0, 139.6, 135.1, 134.1, 133.7, 129.8, 129.1, 128.1, 126.9, 125.9, 116.5, 26.9, 13.7. HRMS (ES+) calcd. for $C_{23}H_{22}SiN$: 340.1522, measured: 340.1509.



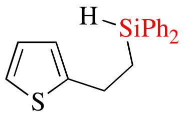
2q: (94%, eluent: Hexanes/EtOAc = 4/1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81-8.79 (m, 2H), 8.01 (d, J = 8.4 Hz, 1H), 7.91 (s, 1H), 7.64-7.61 (m, 5H), 7.44-7.38 (m, 6H), 4.98 (t, J = 3.7 Hz, 1H), 3.05-3.01 (m, 2H), 1.68-1.63 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 144.9, 144.1, 143.1, 141.7, 135.1, 133.6, 131.3, 129.7, 129.2, 128.1, 127.0, 30.6, 13.9. HRMS (ES+) calcd. for $C_{22}H_{21}SiN_2$: 341.1474, measured: 341.1476.



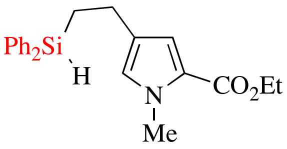
2aa: (93%, eluent: Hexanes/EtOAc = 10/1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59-7.58 (m, 4H), 7.43-7.37 (m, 6H), 7.06 (d, J = 3.5 Hz, 1H), 6.11 (d, J = 3.5 Hz, 1H), 4.92 (t, J = 3.5 Hz, 1H), 4.36 (q, J = 7.0 Hz, 2H), 2.87-2.83 (m, 2H), 1.60-1.55 (m, 2H), 1.39 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2, 158.9, 143.2, 135.1, 133.3, 129.8, 128.1, 119.0, 107.2, 60.7, 23.3, 14.4, 10.5. HRMS (EI+) calcd. for $C_{21}H_{22}SiO_3$: 350.13383, measured: 350.13480.



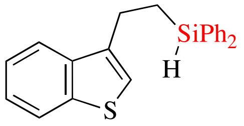
2bb: (70%, eluent: Hexanes/EtOAc = 200/1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62-7.60 (m, 4H), 7.46-7.37 (m, 6H), 7.12 (d, J = 5.1 Hz, 1H), 6.93-6.91 (m, 1H), 6.81-6.80 (m, 1H), 4.94 (t, J = 3.7 Hz, 1H), 3.02-2.99 (m, 2H), 1.66-1.62 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8, 135.1, 133.7, 129.7, 128.1, 126.6, 123.4, 122.8, 24.8, 14.8. HRMS (EI+) calcd. for $C_{18}H_{18}SiS$: 294.08985, measured: 294.09050.



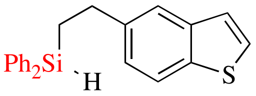
2cc: (91%, eluent: Hexanes/EtOAc = 25/1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60-7.58 (m, 4H), 7.43-7.38 (m, 6H), 6.82 (d, J = 2.0 Hz, 1H), 6.54 (d, J = 1.8 Hz, 1H), 4.91 (t, J = 3.7 Hz, 1H), 4.29 (q, J = 7.0 Hz, 2H), 3.86 (s, 3H), 2.64-2.61 (m, 2H), 1.51-1.47 (m, 2H), 1.37 (t, J = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.3, 135.1, 134.2, 129.5, 127.9, 127.1, 125.6, 122.1, 116.7, 59.6, 36.5, 21.3, 14.4, 13.8. HRMS (EI+) calcd. for $C_{22}H_{25}SiNO_2$: 363.16546, measured: 363.16622.



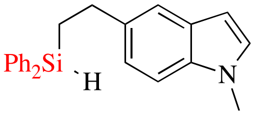
2dd: (94%, eluent: Hexanes/EtOAc = 200/1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89-7.87 (m, 1H), 7.71-7.69 (m, 1H), 7.66-7.64 (m, 4H), 7.48-7.42 (m, 6H), 7.38-7.35 (m, 2H), 7.13 (s, 1H), 5.02 (t, J = 3.3 Hz, 1H), 3.05-3.02 (m, 2H), 1.72-1.68 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.6, 138.6, 135.1, 133.9, 129.7, 128.5, 128.1, 124.1, 123.7, 122.9, 121.6, 120.7, 23.4, 11.9. HRMS (EI+) calcd. for $C_{22}H_{20}SiS$: 344.10550, measured: 344.10636.



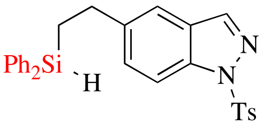
2ee: (92%, eluent: Hexanes/EtOAc = 200/1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 8.1 Hz, 1H), 7.65-7.62 (m, 5H), 7.47-7.38 (m, 7H), 7.30-7.29 (m, 1H), 7.22 (d, J = 8.1 Hz, 1H), 4.98-4.96 (m, 1H), 2.95-2.92 (m, 2H), 1.64-1.60 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.5, 139.9, 137.2, 135.1, 134.2, 129.6, 128.0, 126.4, 124.9, 123.6, 122.3, 122.2, 30.4, 14.7. HRMS (EI+) calcd. for $C_{22}H_{20}SiS$: 344.10550, measured: 344.10597.



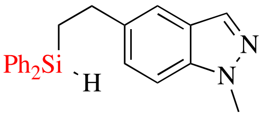
2ff: (89%, eluent: Hexanes/EtOAc = 25/1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60-7.58 (m, 4H), 7.42-7.36 (m, 7H), 7.22 (d, J = 8.2 Hz, 1H), 7.06 (d, J = 8.8 Hz, 1H), 7.02 (d, J = 2.9 Hz, 1H), 6.40 (d, J = 2.9 Hz, 1H), 4.91 (t, J = 3.5 Hz, 1H), 2.89-2.85 (m, 2H), 1.60-1.56 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.4, 135.2, 134.4, 129.6, 128.9, 128.7, 128.0, 122.1, 119.4, 109.0, 100.5, 32.9, 30.5, 15.2. HRMS (EI+) calcd. for $C_{23}H_{23}SiN$: 341.15998, measured: 341.16011.



2gg: (85%, eluent: Hexanes/EtOAc = 4/1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, J = 9.2 Hz, 1H), 8.09 (s, 1H), 7.87 (d, J = 8.4 Hz, 2H), 7.59-7.57 (m, 4H), 7.43-7.35 (m, 8H), 7.24 (d, J = 8.1 Hz, 1H), 4.92 (t, J = 3.7 Hz, 1H), 4.07 (s, 3H), 2.91-2.88 (m, 2H), 2.35 (s, 3H), 1.57-1.53 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.2, 141.0, 140.4, 138.9, 135.0, 134.6, 133.7, 130.0, 129.72, 129.67, 128.0, 127.4, 126.1, 119.4, 123.9, 30.1, 21.5, 14.4. HRMS (ES+) calcd. for $C_{28}H_{27}SiN_2O_2S$: 483.1563, measured: 483.1561.

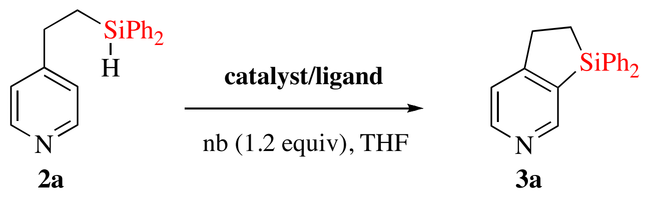


2hh: (84%, eluent: Hexanes/EtOAc = 4/1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.63-7.61 (m, 4H), 7.51 (s, 1H), 7.46-7.39 (m, 6H), 7.31 (d, J = 8.4 Hz, 1H), 7.26 (dd, J = 8.8, 1.5 Hz, 1H), 4.95 (t, J = 3.7 Hz, 1H), 4.07 (s, 3H), 2.94-2.90 (m, 2H), 1.62-1.59 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.7, 136.4, 135.1, 134.1, 132.1, 129.6, 128.0 127.3, 124.2, 118.8, 108.7, 35.5, 30.3, 14.8. HRMS (ES+) calcd. for $C_{22}H_{23}SiN_2$: 343.1631, measured: 343.1628.

Part IB. Dehydrogenative Cyclization

Optimization of the dehydrogenative cyclization reaction of 4-(2-(diphenylsilyl)ethyl)pyridine 2a



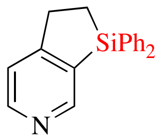
In a 3 mL Wheaton microreactor vial, to a solution of a catalyst/ligand and 2-norbornene (nb) (0.24 mmol, 1.2 equiv, 22.6 mg) in THF (1.0 mL, 0.2M) was added a solution of 4-(2-(diphenylsilyl)ethyl)pyridine (**2a**, 0.2 mmol, 57.8 mg). The microreactor was capped with a Teflon pressure cap and placed into pre-heated (90°C) aluminum block. The reaction mixture was stirred at 90°C until completion as judged by GC/MS analysis.

Optimization table

entry	**catalyst/ligand**	T, h	**2a** yield, %[a]
1	5% $[Ir(OMe)(cod)]_2$/10% dtbpy	6	47
2	5% $[Ir(OMe)(cod)]_2$/10% dtbpy	24	15
3	5% $[Ir(OMe)(cod)]_2$/10% phen	6	63
4[b]	5% $[Ir(OMe)(cod)]_2$/10% phen	6	67
4	5% $[Ir(OMe)(cod)]_2$/10% phen + 20% PPh_3	6	traces
5	5% $[Ir(OMe)(cod)]_2$/ --	6	<5
6	-- /10% phen	6	NR
7	5% $[Ir(OMe)(cod)]_2$/20% PPh_3	24	NR
8	5% $[IrCl(cod)]_2$/10% phen	12	51
9	5% $RhCl(PPh_3)_3$/10% phen	4	41
10[b]	4% $[Ir(OMe)(cod)]_2$/8% phen	6	72
11[b]	3% $[Ir(OMe)(cod)]_2$/6% phen	8	78
12[b]	2% $[Ir(OMe)(cod)]_2$/4% phen	12	83 (79)[b]
13[b]	1% $[Ir(OMe)(cod)]_2$/2% phen	24	81

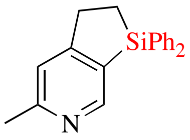
[a]GC Yield. [b]0.5 M concentration was used. [c]Isolated yield is given in paranthesis.

General procedure for dehydrogenative cyclization reaction of heteroaromatic diphenylsilanes 2. In a 3 mL Wheaton microreactor vial, to a solution of $[Ir(cod)OMe]_2$ (0.01 mmol, 2 mol%, 6.6 mg,), 1,10-phenantroline (0.02 mmol, 4 mol%, 3.6 mg), nb (0.6 mmol, 1.2 equiv, 50.4 mg,), and THF (1.0 mL, 0.5M), heteroaromatic dihydrosilole **2** (0.5 mmol, 1.0 equiv) was added. The microreactor was capped with a Teflon pressure cap and placed into pre-heated (90°C) aluminum block. The reaction mixture was stirred for 12 h at this temperature. After completion of the reaction (as determined by GC/MS analysis), microreactor containing cyclization product **3**, was cooled down and the solvent was evaporated. The product was purified using flash silica gel column chromatography.



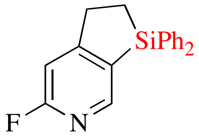
3a: (83%, eluent hexanes/EtOAc = 7/1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.54 (d, J = 5.1 Hz, 1H), 7.60-7.59 (m, 4H), 7.46-7.38 (m, 6H), 7.26 (d, J = 5.1 Hz, 1H), 3.24-3.21 (m, 2H), 1.57-1.54 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4, 154.2, 150.1, 135.0, 134.2, 132.2, 130.0, 128.2, 121.6, 31.7, 10.0. HRMS (EI) calcd. for $C_{20}H_{18}Si$ [M]+: 287.11303. Found: 287.11354.



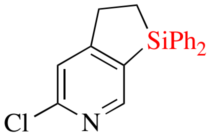
3b: (87%, eluent: Hexanes/EtOAc = 10/1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 (s, 1H), 7.58-7.57 (m, 4H), 7.44-7.36 (m, 6H), 7.13 (s, 1H), 3.18-3.14 (m, 2H), 2.56 (s, 3H), 1.54-1.50 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.2, 159.0, 153.8, 135.0, 134.2, 129.8, 128.6, 128.1, 121.0, 31.5, 24.5, 10.3. HRMS (EI+) calcd. for $C_{20}H_{19}SiN$: 301.12868, measured: 301.12807.



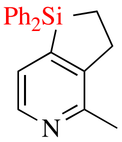
3c: (68% (5:1), eluent: Hexanes/EtOAc = 25/1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.60-7.58 (m, 4H), 7.48-7.40 (m, 6H), 6.89 (s, 1H), 3.25-3.23 (m, 2H), 1.64-1.61 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5 (d, $J_{C\text{-}F}$ = 7.4 Hz), 165.6 (d, $J_{C\text{-}F}$ = 238.6 Hz), 152.1 (d, $J_{C\text{-}F}$ = 14.8 Hz), 135.0, 133.5, 130.2, 129.9 (d, $J_{C\text{-}F}$ = 3.7 Hz), 128.2, 106.7 ($J_{C\text{-}F}$, J = 35.1 Hz), 31.6, 10.9. HRMS (EI+) calcd. for $C_{19}H_{16}SiNF$: 305.10360, measured: 305.10378.



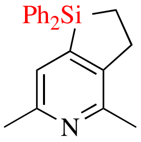
3d: (64%, eluent: Hexanes/EtOAc = 25/1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.58-7.56 (m, 4H), 7.46-7.38 (m, 6H), 7.30 (s, 1H), 3.21-3.18 (m, 2H), 1.60-1.57 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 153.8, 153.0, 135.0, 133.3, 131.4, 130.2, 128.3, 121.8, 31.4, 10.5. HRMS (EI+) calcd. for $C_{19}H_{16}SiNCl$: 321.07405, measured: 321.07480.



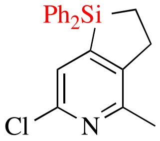
3f: (79%, eluent: Hexanes/EtOAc = 7/1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, J = 4.8 Hz, 1H), 7.57-7.55 (m, 4H), 7.45-7.37 (m, 7H), 3.20-3.17 (m, 2H), 2.55 (s, 3H), 1.57-1.54 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.0, 146.7, 146.0, 145.9, 134.9, 133.7, 129.9, 128.1, 125.2, 29.6, 22.4, 9.0. HRMS (EI+) calcd. for $C_{20}H_{19}SiN$: 301.12868, measured: 301.12914.



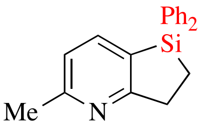
2g: (86%, eluent: Hexanes/EtOAc = 7/1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58-7.57 (m, 4H), 7.45-7.38 (m, 6H), 7.29 (s, 1H), 3.16-3.14 (m, 2H), 2.54 (s, 3H), 2.53 (s, 3H), 1.57-1.54 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 154.0, 146.5, 143.5, 134.9, 133.9, 129.9, 128.0, 124.4, 29.1, 24.0, 22.3, 9.2. HRMS (EI+) calcd. for $C_{21}H_{21}SiN$: 315.14433, measured: 315.14347.



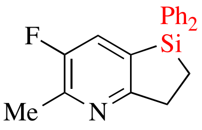
3h: (75%, eluent: Hexanes/EtOAc = 10/1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56-7.54 (m, 4H), 7.48-7.45 (m, 2H), 7.42-7.39 (m, 5H), 3.15-3.13 (m, 2H), 2.52 (s, 3H), 1.62-1.59 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.9, 150.8, 147.9, 145.4, 135.0, 132.9, 130.3, 128.3, 125.0, 28.9, 22.1, 9.5. HRMS (EI+) calcd. for $C_{20}H_{18}SiNCl$: 335.08970, measured: 335.08938.



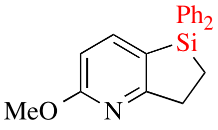
3j: (36%, eluent: Hexanes/EtOAc = 25/1)

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.86 (d, *J* = 7.3 Hz, 1H), 7.57-7.55 (m, 4H), 7.44-7.36 (m, 6H), 7.04 (d, *J* = 7.3 Hz, 1H), 3.34-3.31 (m, 2H), 2.57 (s, 3H), 1.58-1.55 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 172.8, 160.1, 141.8, 135.0, 134.6, 129.8, 128.1, 125.9, 121.0, 34.2, 24.7, 8.6. HRMS (EI+) calcd. for C$_{20}$H$_{20}$SiN: 302.1365, measured: 302.1361.



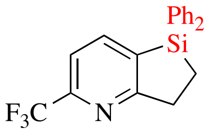
3k: (73%, eluent: Hexanes/EtOAc = 10/1)

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.56-7.51 (m, 5H), 7.46-7.37 (m, 6H), 3.30-3.27 (m, 2H), 2.54 (d, *J* = 2.9 Hz, 3H), 1.63-1.59 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 167.5 (d, $J_{\text{C-F}}$ = 5.2 Hz), 157.2 (d, $J_{\text{C-F}}$ = 253.6 Hz), 148.4 (d, $J_{\text{C-F}}$ = 17.7 Hz), 134.9, 133.9, 130.1, 129.0, 128.2, 126.5 (d, $J_{\text{C-F}}$ = 17.7 Hz), 33.3, 18.3, 9.4. HRMS (EI+) calcd. for C$_{20}$H$_{18}$SiNF: 319.11925, measured: 319.11858.



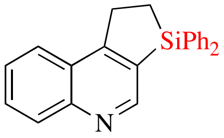
3l: (72%, eluent: Hexanes/EtOAc = 25/1)

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.84 (d, *J* = 8.1 Hz, 1H), 7.58-7.57 (m, 4H), 7.44-7.37 (m, 6H), 6.65 (d, *J* = 8.1 Hz, 1H), 3.99 (s, 3H), 3.28-3.25 (m, 2H), 1.58-1.55 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 172.3, 165.9, 143.4, 135.1, 134.9, 129.7, 128.0, 120.3, 108.9, 53.3, 34.0, 8.6. HRMS (ES+) calcd. for C$_{20}$H$_{20}$SiNO: 318.1314, measured: 318.1313.



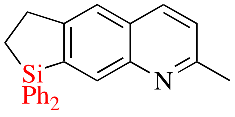
3m: (77%, eluent: Hexanes/EtOAc = 25/1)

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.14 (d, *J* = 7.7 Hz, 1H), 7.57-7.53 (m, 5H), 7.48-7.39 (m, 6H), 3.46-3.43 (m, 2H), 1.68-1.65 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 173.7, 149.4 (q, $J_{\text{C-F}}$ = 33.3 Hz), 143.1, 135.0, 134.3, 133.1, 130.3, 128.3, 121.7 (q, $J_{\text{C-F}}$ = 274.7 Hz), 117.7, 34.0, 8.7. HRMS (EI+) calcd. for C$_{20}$H$_{16}$SiNF$_3$: 355.10041, measured: 355.10021.



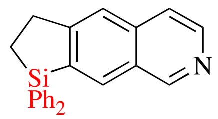
3n: (74%, eluent: Hexanes/EtOAc = 10/1)

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.12 (s, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 8.01 (t, *J* = 8.2 Hz, 1H), 7.76 (t, *J* = 8.2 Hz, 1H), 7.63-7.58 (m, 5H), 7.45-7.37 (m, 6H), 3.69-3.65 (m, 2H), 1.70-1.67 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 162.3, 153.4, 148.4, 135.1, 134.3, 130.0, 129.9, 129.4, 128.2, 126.7, 126.5, 124.0, 29.4, 9.2. HRMS (EI+) calcd. for C$_{23}$H$_{19}$SiN: 337.12868, measured: 337.12800.



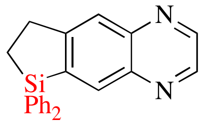
3o: (78%, eluent: Hexanes/EtOAc = 10/1)

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.39 (s, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.68 (s, 1H), 7.65-7.63 (m, 4H), 7.42-7.34 (m, 6H), 7.27-7.26 (m, 1H), 3.39-3.36 (m, 2H), 2.73 (s, 1H), 1.67-1.64 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 158.2, 149.9, 146.7, 140.1, 135.9, 1351, 134.43, 134.40, 129.8, 128.0, 127.6, 122.8, 122.4, 31.4, 25.3, 11.4. HRMS (EI+) calcd. for C$_{24}$H$_{21}$SiN: 351.14433, measured: 351.14493.



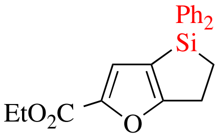
3p: (74%, eluent: Hexanes/EtOAc = 4/1)

^{1}H NMR (500 MHz, CDCl$_3$) δ 9.30 (s, 1H), 8.64 (d, *J* = 5.9 Hz, 1H), 7.88 (s, 2H), 7.79 (d, *J* = 5.9 Hz, 1H), 7.63-7.61 (m, 4H), 7.46-7.38 (m, 6H), 3.66-3.62 (m, 2H), 1.72-1.69 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 152.9, 150.8, 143.5, 135.0, 134.5, 133.2, 130.3, 129.8, 129.4, 128.1, 128.0, 125.7, 117.0, 29.0, 9.1. HRMS (ES+) calcd. For $C_{23}H_{20}SiN$: 338.1365, measured: 338.1361.



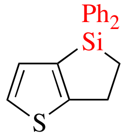
3q: (56%, eluent: Hexanes/EtOAc = 4/1)

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.82 (d, *J* = 13.6 Hz, 2H), 8.48 (s, H), 8.04 (s, 1H), 7.67-7.65 (m, 4H), 7.46-7.38 (m, 6H), 3.50-3.47 (m, 2H), 1.73-1.70 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 154.9, 145.3, 144.2, 143.9, 141.8, 141.7, 135.2, 135.1, 133.7, 130.0, 128.1, 124.7, 31.7, 11.5. HRMS (ES+) calcd. for $C_{22}H_{19}SiN_2$: 339.1318, measured: 339.1313.



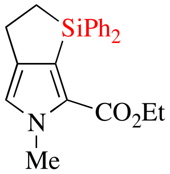
3aa: (88%, eluent: Hexanes/EtOAc = 10/1)

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.59-7.57 (m, 4H), 7.46-7.39 (m, 6H), 7.34 (s, 1H), 4.40 (q, *J* = 7.0 Hz, 2H), 3.09-3.06 (m, 2H), 1.83-1.80 (m, 2H), 1.41-1.39 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 176.3, 158.9, 148.6, 134.7, 134.6, 129.9, 128.0, 120.7, 117.0, 60.8, 23.8, 14.3, 12.0. HRMS (ES+) calcd. for $C_{21}H_{21}SiO_3$: 349.1260, measured: 349.1262.



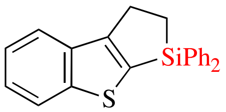
3bb: (67%, eluent: Hexanes/EtOAc = 200/1)

δ 7.63-7.61 (m, 4H), 7.46-7.38 (m, 6H), 7.20 (d, *J* = 4.8 Hz, 1H), 3.31-3.28 (m, 2H), 1.90-1.87 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 161.8, 137.6, 135.6, 134.9, 129.6, 128.3, 127.9, 27.0, 14.7. HRMS (EI+) calcd. for $C_{18}H_{16}SiS$: 292.07420, measured: 292.07477.



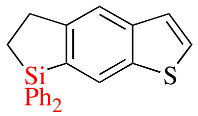
3cc: (84%, eluent: Hexanes/EtOAc = 25/1)

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.63-7.61 (m, 4H), 7.48-7.41 (m, 6H), 6.87 (s, 1H), 4.31 (q, *J* = 7.3 Hz, 2H), 3.90 (s, 3H), 2.93-2.91 (m, 2H), 1.78-1.75 (m, 2H), 1.38 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 161.5, 143.1, 141.6, 135.1, 134.2, 130.1, 129.9, 128.1, 113.4, 59.8, 37.9, 22.4, 14.4. HRMS (EI+) calcd. for $C_{22}H_{23}SiNO_2$: 361.14981, measured: 361.15047.



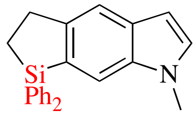
3dd: (63%, eluent: Hexanes/EtOAc = 200/1)

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.91 (d, *J* = 7.3 Hz, 1H), 7.79 (d, *J* = 7.0 Hz, 1H), 7.67-7.65 (m, 4H), 7.46-7.38 (m, 8H), 3.33-3.30 (m, 2H), 1.93-1.91 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 156.8, 149.2, 137.2, 135.0, 134.7, 133.9, 129.9, 124.8, 123.9, 123.2, 122.3, 25.7, 13.1. HRMS (EI+) calcd. for $C_{22}H_{18}SiS$: 342.08985, measured: 342.08904.



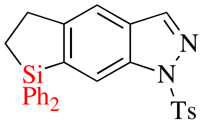
3ee: (61% (10:1), eluent: Hexanes/EtOAc = 200/1)

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.18 (s, 1H), 7.79 (s, 1H), 7.64-7.62 (m, 4H), 7.48 (d, *J* = 5.1 Hz, 1H), 7.44-7.37 (m, 6H), 7.31 (d, *J* = 5.5 Hz, 1H), 3.37-3.34 (m, 2H), 1.65-1.62 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 149.8, 141.5, 138.3, 135.2, 133.2, 129.7, 128.0, 127.5, 127.3, 123.5, 120.2, 31.4, 11.7. HRMS (EI+) calcd. for $C_{22}H_{18}SiS$: 342.08985, measured: 342.09064.



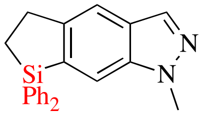
3ff: (94% (10:1), eluent: Hexanes/EtOAc = 25/1)

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.68-7.66 (m, 4H), 7.61 (d, *J* = 9.9 Hz, 2H), 7.44-7.38 (m, 6H), 7.08 (d, *J* = 3.1 Hz, 1H), 6.46 (d, *J* = 3.1 Hz, 1H), 3.79 (s, 3H), 3.37-3.34 (m, 2H), 1.63-1.60 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 144.4, 136.6, 135.9, 135.3, 131.0, 129.9, 129.4, 129.0, 127.8, 117.0, 113.6, 100.3, 32.9, 31.2, 12.1. HRMS (EI+) calcd. for $C_{23}H_{21}SiN$: 339.14433, measured: 339.14480.



3gg: (52% (7:1), eluent: Hexanes/EtOAc = 4/1)

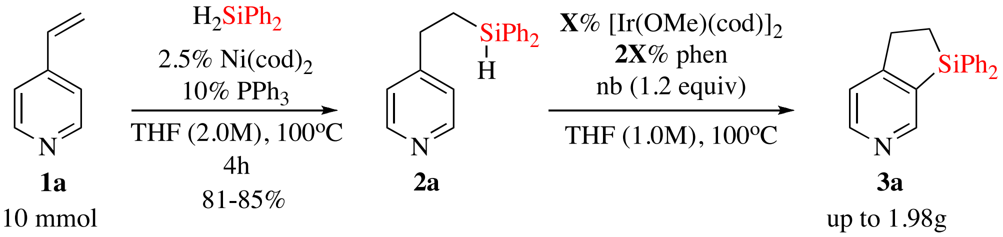
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.46 (s, 1H), 8.14 (s, 1H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.63-7.60 (m, 4H), 7.58 (s, 1H), 7.47-7.39 (m, 6H), 7.20 (d, *J* = 8.1 Hz, 2H), 3.31-3.28 (m, 2H), 2.36 (s, 3H), 1.66-1.63 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 149.2, 145.2, 141.4, 140.2, 135.2, 134.6, 134.0, 130.0, 129.8, 129.7, 128.1, 128.0, 127.5, 117.5, 117.3, 31.2, 21.6, 11.8. HRMS (ES+) calcd. for $C_{28}H_{25}SiN_2O_2S$: 481.1406, measured: 481.1414.



3hh: (59%, eluent: Hexanes/EtOAc = 4/1)

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.94 (s, 1H), 7.68 (s, 1H), 7.65-7.63 (m, 5H), 7.45-7.38 (m, 6H), 4.08 (s, 3H), 3.35-3.31 (m, 2H), 1.67-1.63 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 145.0, 139.8, 136.1, 135.2, 134.7, 132.0, 129.8, 128.0, 126.2, 116.5, 113.5, 35.6, 31.0, 12.2. HRMS (ES+) calcd. for $C_{22}H_{21}SiN_2$: 341.1474, measured: 341.1479.

Part IC. Gram-Scale Synthesis of Dihydropyridinosilole from 4-Vinylpyridine



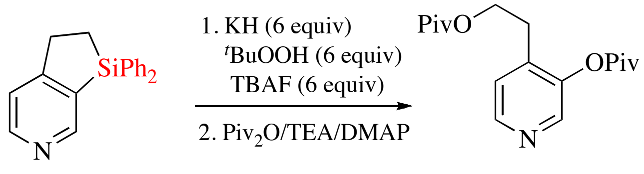
X	time, d	3a, yield
0.5	2	82%
0.25	6	74%

Hydrosilylation. A 10 mL Wheaton microreactor was charged with $Ni(cod)_2$ (68.8 mg, 2.5 mol%), PPh_3 (262.0 mg, 10 mol%), and THF (5.0 mL, 2.0M) and stirred for 5 min. To the resulting solution, Ph_2SiH_2 (10.2 mmol, 1.02 equiv, 1.89 mL) was added, followed by 4-vinylpyridine (**1a**, 10 mmol, 1.05 g, 1.08 mL). The microreactor was capped with a Teflon pressure cap and placed into pre-heated (100°C) aluminum block. The reaction mixture was stirred for 4 h at this temperature. After completion (as determined by GC/MS analysis), microreactor, containing hydrosilylation product **2a**, was cooled down and the solvent was evaporated. The product was purified using flash silica gel column chromatography (2.33-2.45g, 81-85%, eluent Hexanes/EtOAc = 7/1).

Dehydrogenative cyclization. In a 10 mL Wheaton microreactor, to a solution of $[Ir(cod)OMe]_2$ (0.25-0.5 mol%), 1,10-phenantroline (0.5-1.0 mol%), 2-norbornene (1.2 equiv), and THF (1.0M), was added pyridinosilane **2**. The microreactor was capped with a Teflon pressure cap and placed into pre-heated (100°C) aluminum block. The reaction mixture was stirred at this temperature for 2-6 days. After completion (as determined by GC/MS), microreactor, containing dihydropyridinosilole **3**, was cooled down, and the solvent was evaporated. The product was purified using flash silica gel column chromatography (1.71-1.98g, 74-82%, eluent Hexanes/EtOAc = 7/1).

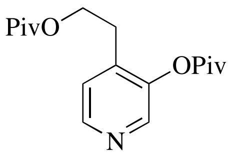
Part II. Further Transformations of Dihydropyridinosylole

Part IIa. Oxidation of Dihydropyridinosylole



3a **4**

To an ice-cooled (0°C) stirred suspension of KH (2.4 mmol, 6 equiv, 96.0 mg) in THF (4 mL), *tert*-butyl hydroperoxide (2.4 mmol, 6 equiv, 0.44 mL 5.5 M in decane) was added. After 10 min, a solution of **3a** (0.4 mmol, 114.8 mg) in THF (0.5 mL) was added to the obtained slurry. To the resulted clear solution, TBAF (2.4 mmol, 6 equiv, 2.4 mL 1.0 M solution in THF) was added and the reaction mixture was allowed warm up to room temperature and stirred for 3h. After that, the reaction mixture was cooled down (ice bath) and 1.0 g of $Na_2S_2O_3$•$5H_2O$ in water (5.0 mL) was added. The mixture was stirred for 30 min and 50 mL of saturated NH_4Cl was added. The resulted solution was extracted with diethyl ether (3 x 10 mL), and the combined organic layers were dried (Na_2SO_4) and concentrated. To the crude, DCM (3mL), Piv_2O (2 mmol, 5 equiv, 189 μL) Et_3N (2 mmol, 5 equiv, 278 μL), and DMAP (0.02 mmol, 0.1 equiv, 4.9 mg) were added and reaction mixture was stirred at room temperature for 2h. Then, a saturated NH_4Cl was added and the organic layer was separated. The aqueous solution was extracted with diethyl ether (3 x 10 mL), and the combined organic layers were dried (Na_2SO_4) and concentrated. The product was purified using flash silica gel column chromatography.

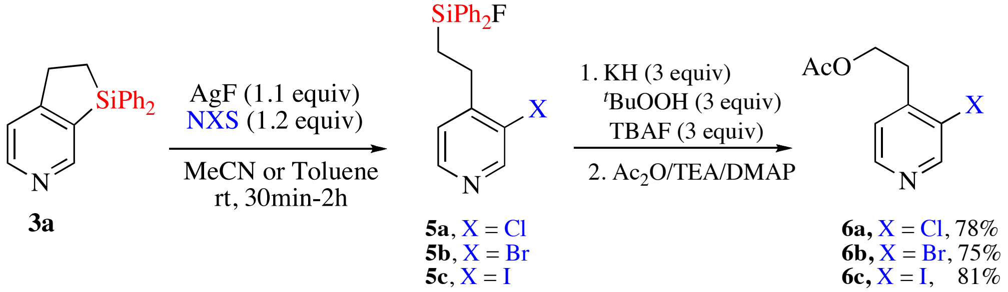


4: (85%, eluent Hexanes/EtOAc = 3/1).

^{1}H NMR (500 MHz, CDCl3): δ ppm 8.40 (d, *J* = 5.0 Hz, 1H), 8.30 (s, 1H), 7.22 (d, *J* = 5.0 Hz, 1H), 4.27-4.25 (t, *J* = 6.6 Hz, 2H), 2.86-2.83 (t, *J* = 6.6 Hz, 2H), 1.39 (s, 9H), 1.13 (s, 9H). ^{13}C NMR (116 MHz, CDCl3): δ ppm 178.1, 176.4, 146.9, 146.5, 144.1, 139.1, 125.0, 62.2, 39.3, 38.7, 28.8, 27.1, 27.0. HRMS (ES+) calcd. for $C_{17}H_{25}NO_4$: 307.17836, measured: 307.17906.

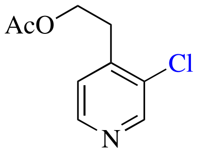
Part IIb. Double-fold Modification of Dihydropyridinosylole

1. Halogenation/Oxygenation

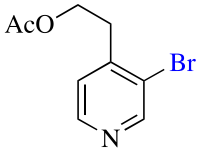


Halogenation. To a 3mL Wheaton vial containing NXS (X = Cl, Br, I) (1.2 equiv), AgF (1.1 equiv), and dihydropyridinosylole (**3a**, 0.4 mmol, 114.8 mg), was added toluene (2 mL, 0.2M). The reaction mixture was vigorously stirred in dark for 2h. After completion (monitored by GC/MS) reaction mixture was filtered through small silica gel column (140 mm x 15 mm) using Hexanes/EtOAc = 4/1 as eluent. Evaporation of the solvent gave **5a**/**5c** as colorless oil.

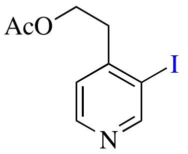
Oxidation. To an ice-cooled (0°C) stirred suspension of KH (1.2 mmol, 3 equiv, 48 mg) in THF (2 mL), *tert*-butyl hydroperoxide (1.2 mmol, 3 equiv, 0.22 mL 5.5 M in decane over MS) was added. After 10 min, a solution of **5a/5c** in THF (0.5 mL) was added to the obtained slurry. To the resulted clear yellowish solution, TBAF (1.2 mmol, 3 equiv, 1.2 mL 1.0 M solution in THF) was added and the reaction mixture was allowed warmed up to room temperature and stirred for 3h. Then, the reaction mixture was cooled down (ice bath) and 1.0 g of $Na_2S_2O_3{\bullet}5H_2O$ in water (5.0 mL) was added. The mixture was stirred for 30 min and 50 mL of saturated NH_4Cl was added. The resulted solution was extracted with diethyl ether (3 x 10 mL), and the combined organic layers were dried (Na_2SO_4) and concentrated. To the crude, DCM (3mL), Ac_2O (2 mmol, 5 equiv, 189 μL) Et_3N (2 mmol, 5 equiv, 278 μL), and DMAP (0.02 mmol, 0.1 equiv, 4.9 mg) were added and the reaction mixture was stirred at room temperature for 2h. Next, a saturated NH_4Cl was added and organic layer was separated. The aqueous solution was extracted with diethyl ether (3 x 10 mL), and the combined organic layers were dried (Na_2SO_4) and concentrated. The product was purified using flash silica gel column chromatography.



6a: (78%, eluent Hexanes/EtOAc = 3/1).
^{1}H NMR (500 MHz, CDCl3): δ ppm 8.56 (s, 1H), 8.42 (d, *J* = 4.8 Hz, 1H), 7.19 (d, *J* = 4.8 Hz, 1H), 4.35-4.32 (t, *J* = 6.6 Hz, 2H), 3.09-3.06 (t, *J* = 6.6 Hz, 2H), 2.02 (s, 3H).^{13}C NMR (116 MHz, CDCl3): δ ppm 170.7, 149.4, 147.7, 144.5, 132.3, 125.2, 62.0, 32.0, 20.8. HRMS (EI+) calcd. for $C_9H_{10}ClNO_2$: 199.04000, measured: 199.03950.



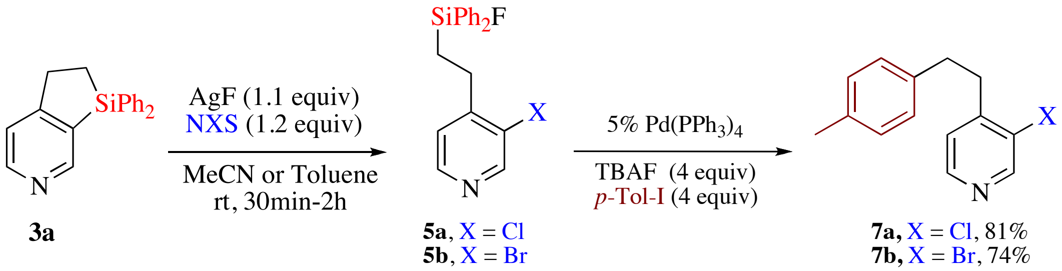
6b: (75%, eluent Hexanes/EtOAc = 3/1).
^{1}H NMR (500 MHz, CDCl3): δ ppm 8.70 (s, 1H), 8.45 (d, *J* = 4.9 Hz, 1H), 7.19 (dd, *J* = 4.9, 0.4 Hz, 1H), 4.36-4.32 (t, *J* = 6.7 Hz, 2H), 3.10-3.07 (t, *J* = 6.7 Hz, 2H), 2.04 (s, 3H). ^{13}C NMR (116 MHz, CDCl3): δ ppm 170.7, 152.1, 148.2, 146.2, 125.5, 123.2, 62.1, 34.5, 20.8. HRMS (EI+) calcd. for $C_9H_{10}BrNO_2$: 242.98948, measured: 242.99033.



6c: (81%, eluent Hexanes/EtOAc = 3/1).

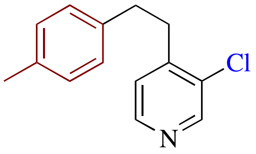
^{1}H NMR (500 MHz, CDCl3): δ ppm 8.90 (s, 1H), 8.43 (d, *J* = 4.8 Hz, 1H), 7.19 (d, *J* = 4.9 Hz, 1H), 4.32-4.29 (t, *J* = 6.6 Hz, 2H), 3.06-3.03 (t, *J* = 6.8 Hz, 2H), 2.04 (s, 3H). ^{13}C NMR (116 MHz, CDCl3): δ ppm 170.7, 157.6, 149.5, 148.9, 125.2, 100.2, 62.2, 38.9, 20.8. HRMS (EI+) calcd. for $C_9H_{10}INO_2$: 290.97565, measured: 290.97616.

2. Halogenation/Arylation



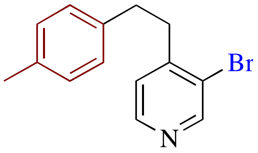
Halogenation. To a 3 mL Wheaton vial containing NXS (X = Cl, Br, I) (1.2 equiv), AgF (0.44 mmol, 1.1 equiv, 55.9 mg), and dihydropyridinosylole (**3a**, 0.4 mmol, 114.8 mg), was added toluene (2 mL, 0.2M). The reaction mixture was vigorously stirred in dark for 2h. After completion (monitored by GC/MS) the reaction mixture was filtered through small silica gel column (140 mm x 15 mm) with Hexanes/EtOAc = 4/1 as eluent. Evaporation of the solvent gave **5a** or **5b** as colorless oil.

Arylation. To a solution of $Pd(PPh_3)_4$ (0.02 mmol, 5 mol%, 23.1 mg) in THF (0.5mL), *p*-tolyliodide (1.6 mmol, 4 equiv, 349 mg) was added. After 10 min, a solution of **7a** or **7b** in 0.5 mL of THF, followed by TBAF (1.6 mmol, 4 equiv, 1.6 mL, 1.0 M solution in THF) was added. The reaction mixture was stirred at 90°C for 24h, and then cooled down. The solvent was evaporated. The product was purified using flash silica gel column chromatography.



7a: (79%, eluent Hexanes/EtOAc = 10/1).

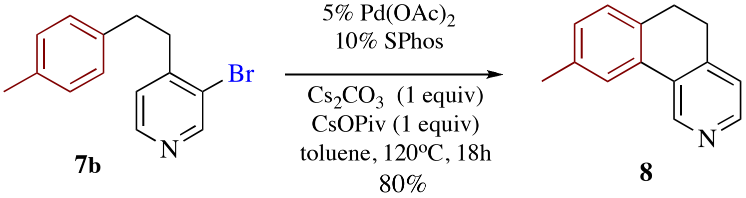
^{1}H NMR (500 MHz, CDCl3): δ ppm 8.56 (s, 1H), 8.35 (d, *J* = 4.8 Hz, 1H), 7.13-7.06 (m, 5H), 3.04-3.01 (m, 2H), 2.92-2.89 (m, 2H), 2.34 (s, 3H). ^{13}C NMR (116 MHz, CDCl3): δ ppm 149.3, 127.9, 147.6, 137.3, 135.8, 132.0, 129.1, 128.2, 124.9, 34.9, 34.3, 21.0. HRMS (EI+) calcd. for $C_{14}H_{15}ClN$: 232.0893, measured: 232.0891.



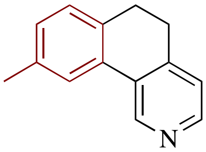
7b: (74%, eluent Hexanes/EtOAc = 10/1).

^{1}H NMR (500 MHz, CDCl3): δ ppm 8.68 (s, 1H), 8.38 (d, *J* = 5.0 Hz, 1H), 7.12-7.06 (m, 5H), 3.02-2.99 (m, 2H), 2.90-2.87 (m, 2H), 2.34 (s, 3H). ^{13}C NMR (116 MHz, CDCl3): δ ppm 151.9, 149.6, 148.2, 137.3, 135.8, 129.2, 128.2, 125.2, 123.0, 37.5, 34.5, 21.0. HRMS (EI+) calcd. for $C_{14}H_{14}BrN$: 275.03095, measured: 275.03042.

Intramolecular direct arylation of 3-bromo-4-(4-methylphenethyl)pyridine



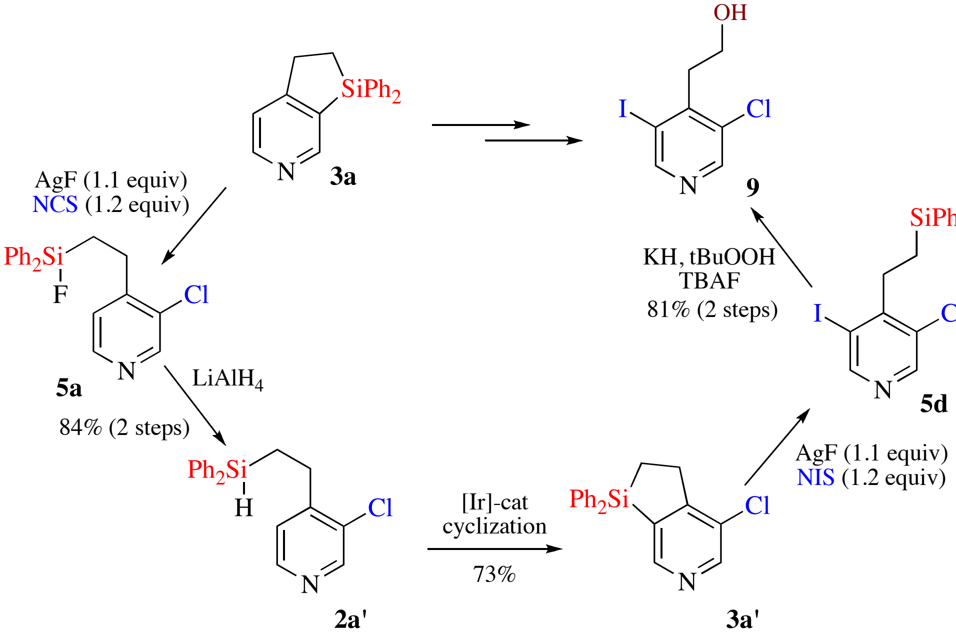
A suspension of $Pd(OAc)_2$ (0.01 mmol, 5 mol%, 2.2 mg), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (SPhos, 0.02 mmol, 10 mol%, 8.2 mg), Cs_2CO_3 (0.2 mmol, 1 equiv, 32.6 mg), CsOPiv (0.2 mmol, 1 equiv, 23.4 mg), **7b** (0.2 mmol, 55 mg), and toluene (1.0 mL) was heated at 120°C for 18h. After completion, as determined by GC/MS analysis, the reaction mixture was cooled down, filtered through Celite and the product was purified using flash silica gel column chromatography.



8: (80%, eluent Hexanes/EtOAc = 7/1).

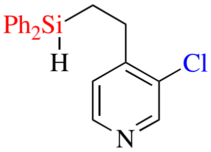
^{1}H NMR (500 MHz, CDCl3): δ ppm 8.96 (s, 1H), 8.43 (d, *J* = 4.8 Hz, 1H), 7.63 (s, 1H), 7.15-7.13 (m, 2H), 7.10 (d, *J* = 7.7 Hz, 1H), 2.84 (s, 4H), 2.42 (s, 3H). ^{13}C NMR (116 MHz, CDCl3): δ ppm 148.3, 145.7, 144.9, 136.8, 134.2, 131.5, 130.5, 129.0, 128.2, 124.0, 122.9, 28.4, 27.6, 21.3. HRMS (EI+) calcd. for $C_{14}H_{13}N$: 195.10480, measured: 195.10409.

Part IIc. Synthesis of Highly Functionalized Pyridine Ring through Double-Fold Modification – C-H Activation Sequence



Halogenation: To a 5 mL Wheaton vial containing NCS (1.2 mmol, 1.2 equiv, 160.2 mg), AgF (1.1 mmol, 1.1 equiv, 139.7 mg), and dihydropyridinosylole (**3a**, 1.0 mmol, 287.4 mg), was added toluene (5.0 mL, 0.2M). The reaction mixture was vigorously stirred in dark for 2h. After completion (monitored by GC/MS) the reaction mixture was filtered through small silica gel column (150 mm x 18 mm) using Hexanes:EtOAc = 4:1 as an eluent. Evaporation of the solvent gave **5a** (318.2 mg, 0.93 mmol, 93%) as colorless oil.

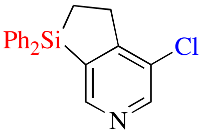
Reduction: To an ice-cooled (0°C) stirred suspension of $LiAlH_4$ (0.65 mmol, 0.6 equiv, 24.7 mg) in Et_2O (5.0 mL), a solution of **5a** (0.93 mmol, 317.2 mg) in Et_2O (1.0 mL) was added. The reaction mixture was allowed to warm up and stirred at room temperature for 2h. After completion of the reaction (determined by GC/MS), reaction mixture was cooled down (ice bath) and EtOH (0.1 mL) was added. The resulting mixture was filtered through Celite and concentrated. The product was purified using flash silica gel column chromatography.



2a': (84% (2 steps), eluent Hexanes/EtOAc = 7/1).

^{1}H NMR (500 MHz, CDCl3): δ ppm 8.50 (s, 1H), 8.36 (d, J = 5.0 Hz, 1H), 7.62-7.60 (m, 4H), 7.46-7.38(m, 6H), 7.14 (d, J = 5.0 Hz, 1H), 4.97 (t, J = 3.7 Hz, 1H), 2.87-2.84 (m, 2H), 1.52-1.48 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.4, 149.2, 147.8, 135.1, 133.3, 131.6, 129.9, 128.1, 124.2, 27.9, 11.7. HRMS (EI+) calcd. for $C_{19}H_{18}ClNSi$: 323.08970, measured: 323.09011

Dehydrogenative Cyclization: in a 5 mL Wheaton microreactor, to a solution of $[Ir(cod)OMe]_2$ (4 mol%), 1,10-phenantroline (8 mol%), 2-norbornene (1.2 equiv), and THF (1.0 mL), was added 3-chloropyridinosilane **2a'** (161.8 mg, 0.5 mmol). The microreactor was capped with a Teflon pressure cap and placed into pre-heated (100°C) aluminum block. The reaction mixture was stirred at this temperature for 3h. After completion (as determined by GC/MS analysis), microreactor, containing dihydropyridinosilole **3a'**, was cooled down, and the solvent was evaporated. The product was purified using flash silica gel column chromatography.

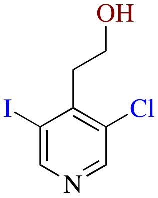


3a': (73%, eluent Hexanes/EtOAc = 7/1).

^{1}H NMR (500 MHz, CDCl3): δ ppm 8.72 (s, 1H), 8.54 (s, 1H), 7.59-7.58 (m, 4H), 7.48-7.39(m, 6H), 3.31-3.28 (m, 2H), 1.61-1.58 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2, 151.7, 149.2, 134.9, 134.5, 133.3, 130.8, 130.2, 128.2, 30.4, 8.8. HRMS (ES+) calcd. for $C_{19}H_{17}ClNSi$: 322.0819, measured: 322.0819.

Halogenation: To a 3 mL Wheaton vial containing NIS (0.24 mmol, 1.2 equiv, 54.0 mg), AgF (0.22 mmol, 1.1 equiv, 27.9 mg), and 3-chlorodihydropyridinosylole (**3a'**, 0.2 mmol, 64.3mg), was added CH_3CN (1.0 mL, 0.2M). The reaction mixture was vigorously stirred in dark for 1h. After completion (monitored by GC/MS) reaction mixture was diluted with acetone, filtered through Celite and concentrated. The product **5d** was purified using flash silica gel column chromatography (80.3 mg, 87%, eluent Hexanes/EtOAc = 7/1).

Oxidation: To an ice-cooled (0°C) stirred suspension of KH (0.6 mmol, 3 equiv, 24.0 mg) in THF (1 mL), *tert*-butyl hydroperoxide (0.6 mmol, 3 equiv, 0.11 mL 5.5 M in decane) was added. After 10 min, a solution of **5d** in THF (0.5 mL) was added to the obtained slurry. To the resulted clear yellowish solution, TBAF (1.2 mmol, 3 equiv, 1.2 mL 1.0 M solution in THF) was added and the reaction mixture was allowed to warmed up to room temperature and stirred for 3h. Then, the reaction mixture was cooled down (ice bath) and 1.0 g of $Na_2S_2O_3$•$5H_2O$ in water (5.0 mL) was added. The mixture was stirred for 30 min and 50 mL of saturated NH_4Cl was added. The resulted solution was extracted with diethyl ether (3 x 10 mL), and the combined organic layers were dried (Na_2SO_4) and concentrated. The product was purified using flash silica gel column chromatography.



9: (81% (2 steps), eluent Hexanes/EtOAc = 2/1).

^{1}H NMR (500 MHz, CDCl3): δ ppm 8.76 (s, 1H), 8.43 (s, 1H), 3.91-3.87 (m, 2H), 3.31-3.26 (m, 2H), 1.94 (broad, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.7, 148.7, 147.6, 132.4, 100.7, 60.2, 41.1. HRMS (EI+) calcd. for C_7H_7ClINO [M]+: 282.92612, measured: 282.92555.

Part III. ^{1}H and ^{13}C NMR Spectra Copies for all Compounds

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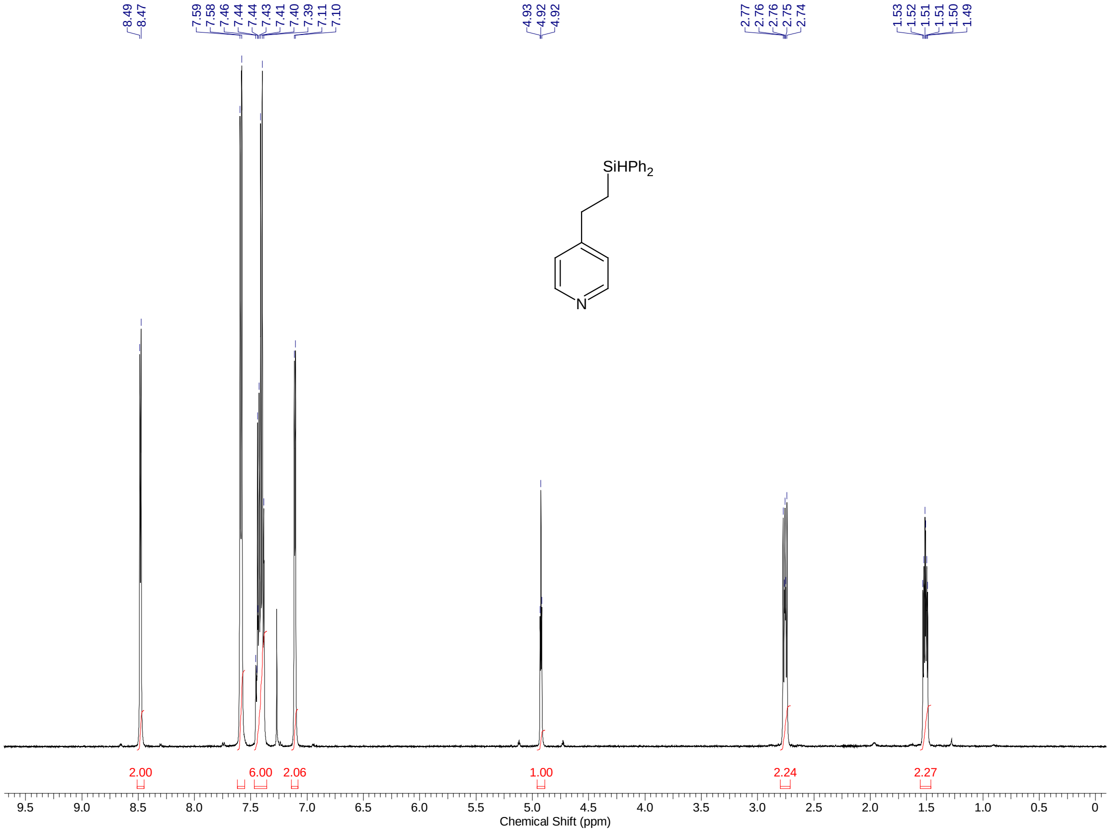

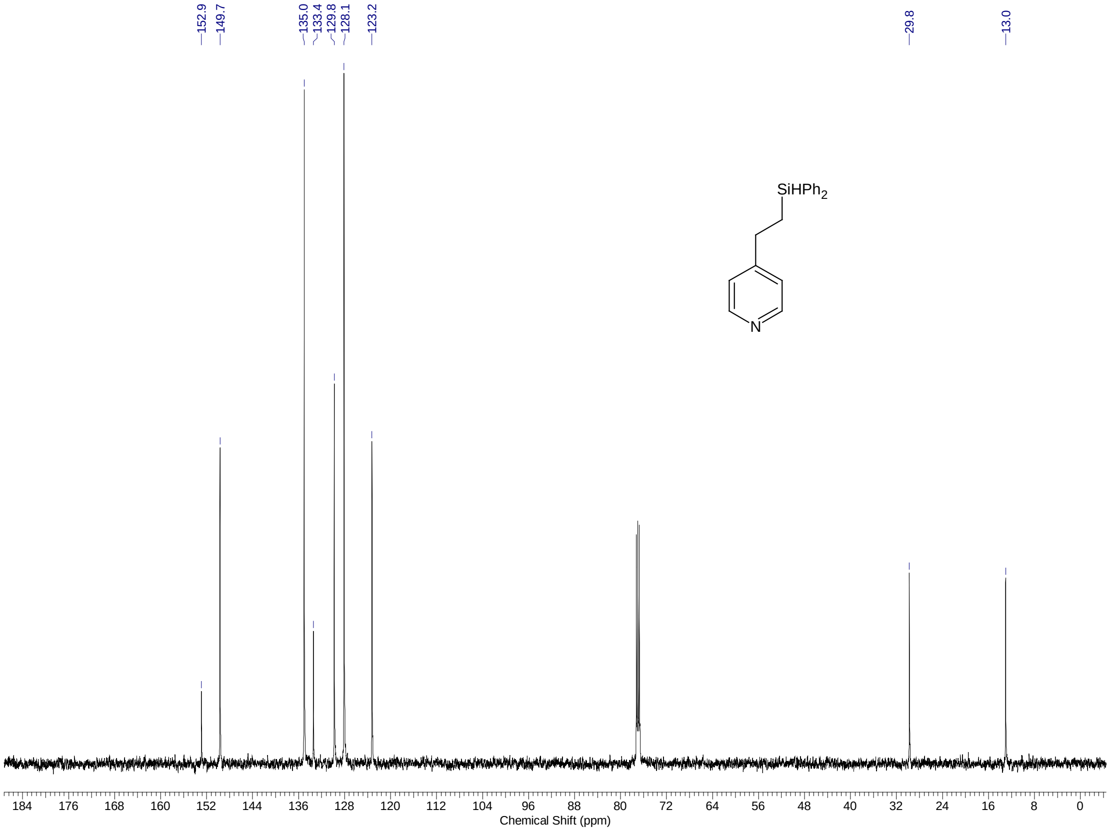

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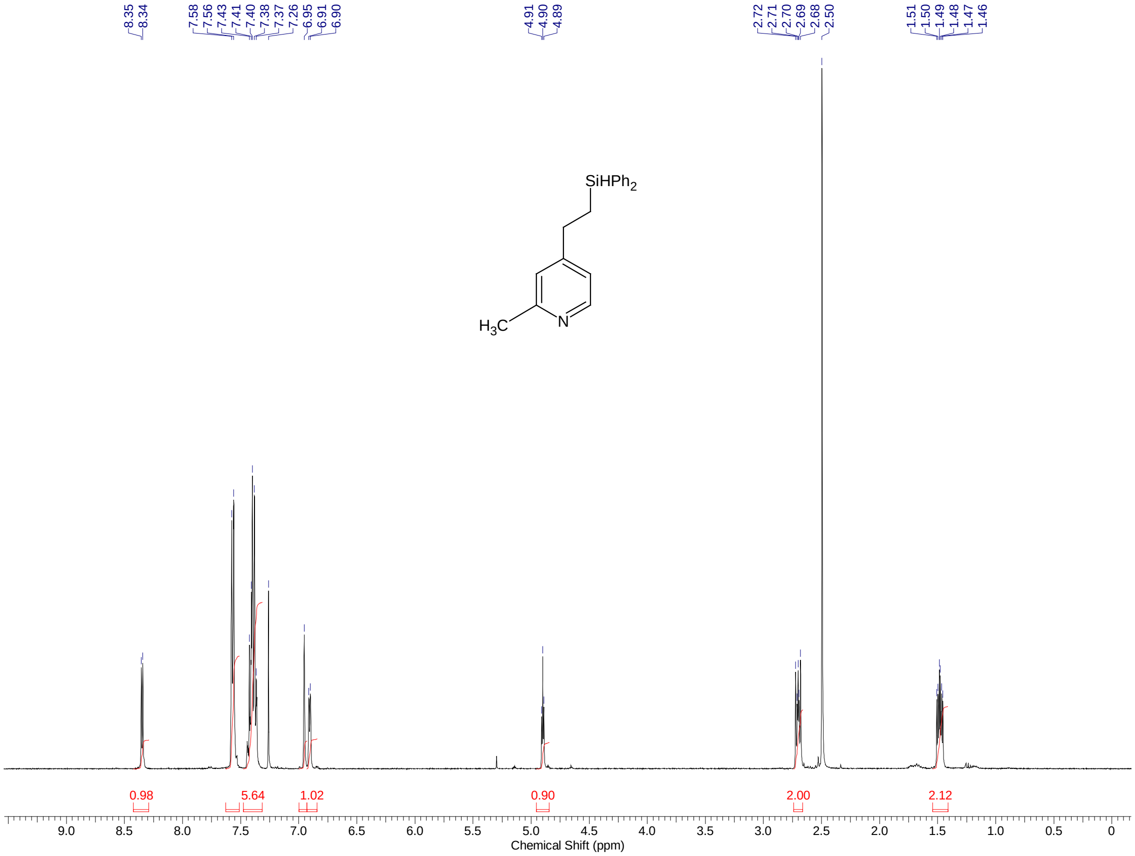
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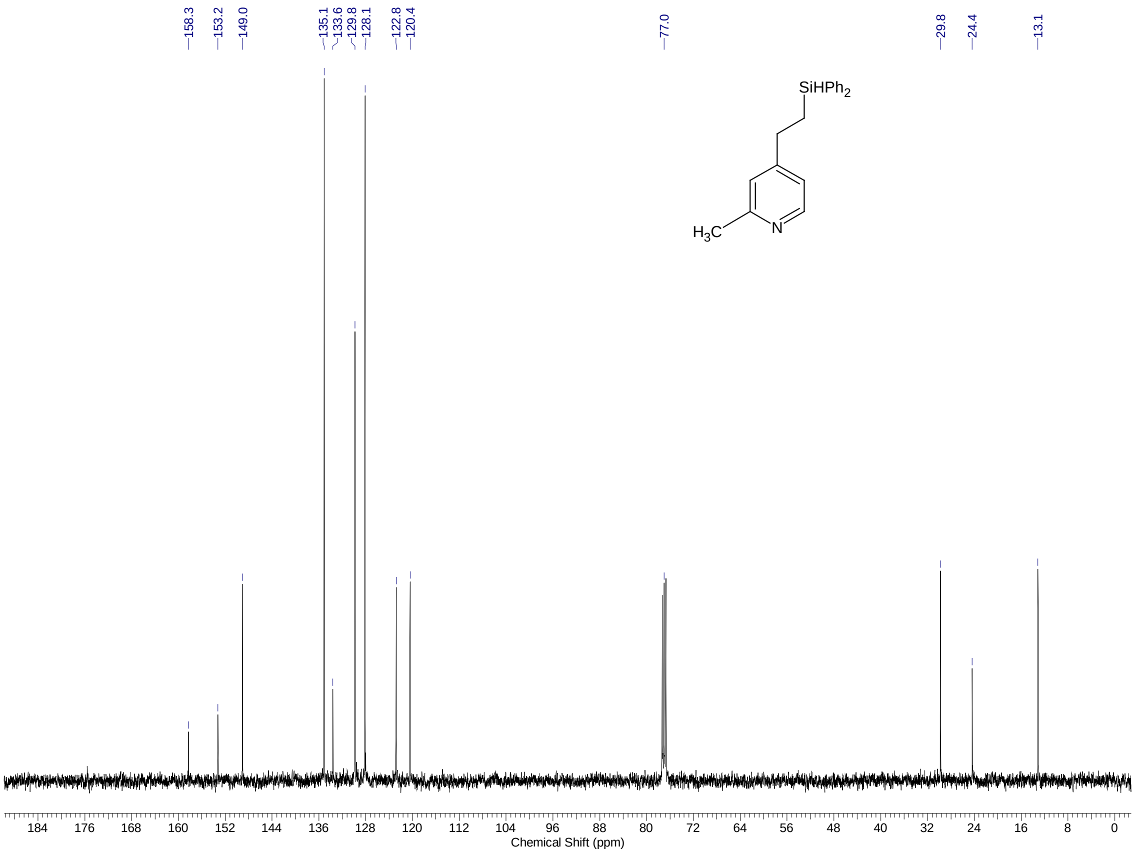
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168
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144
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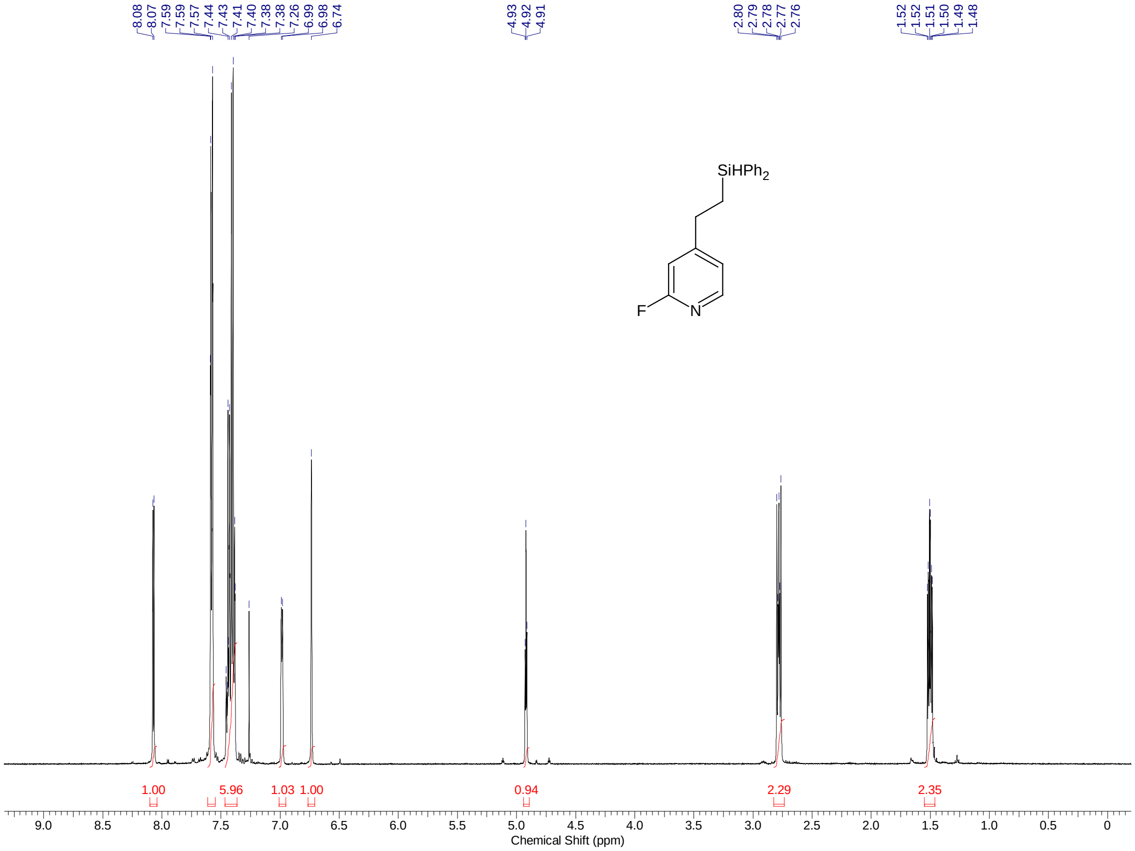

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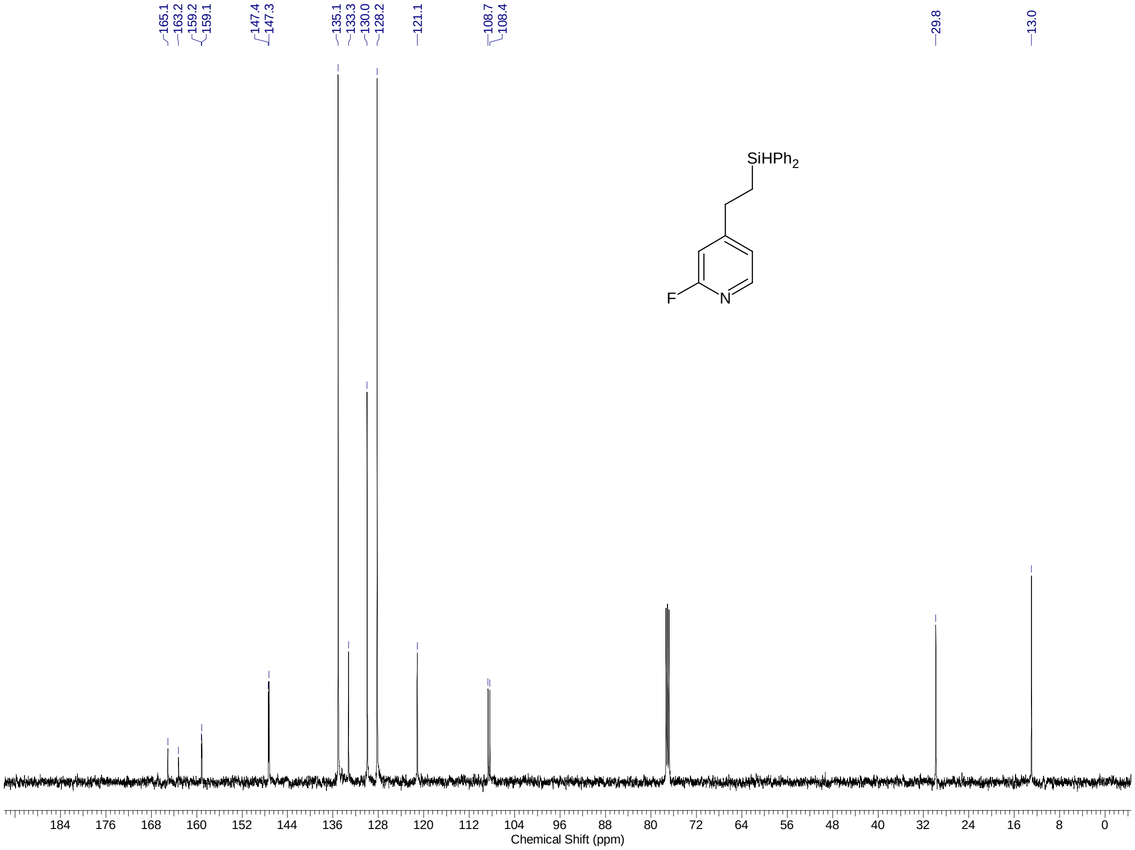

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SiHPh2
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N
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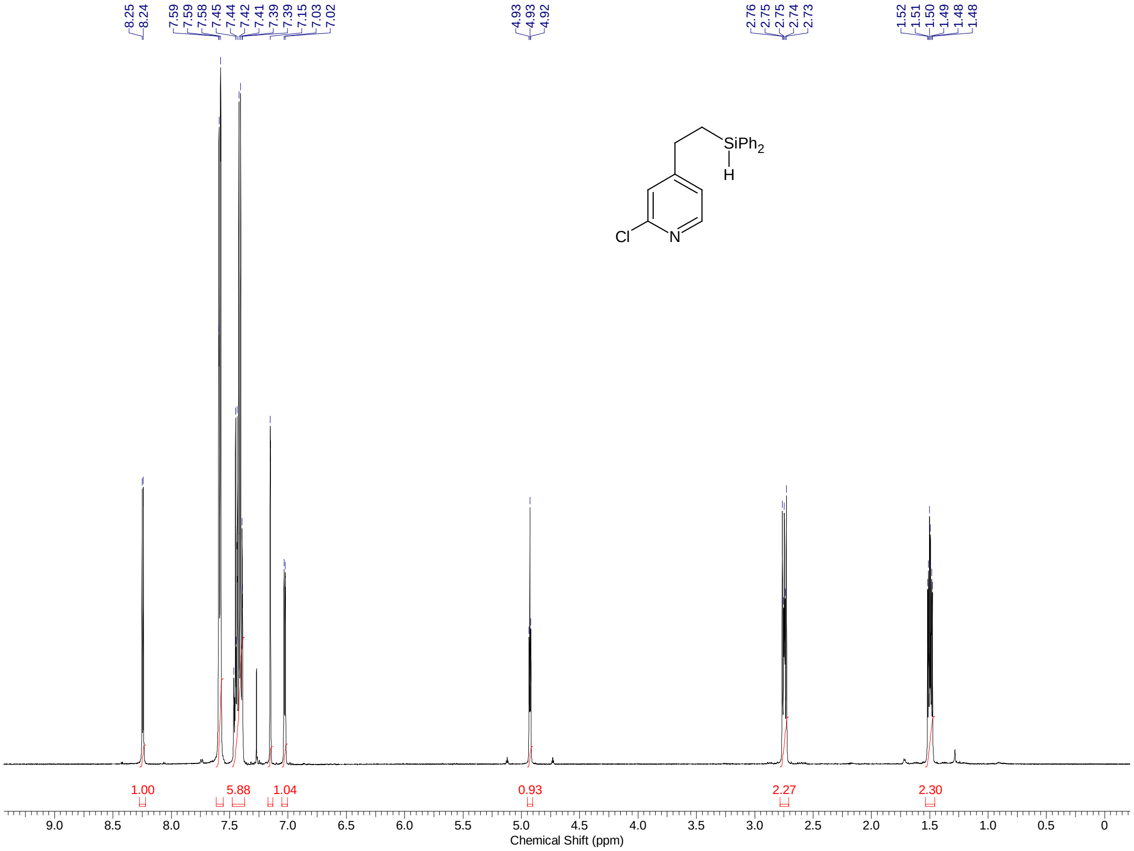
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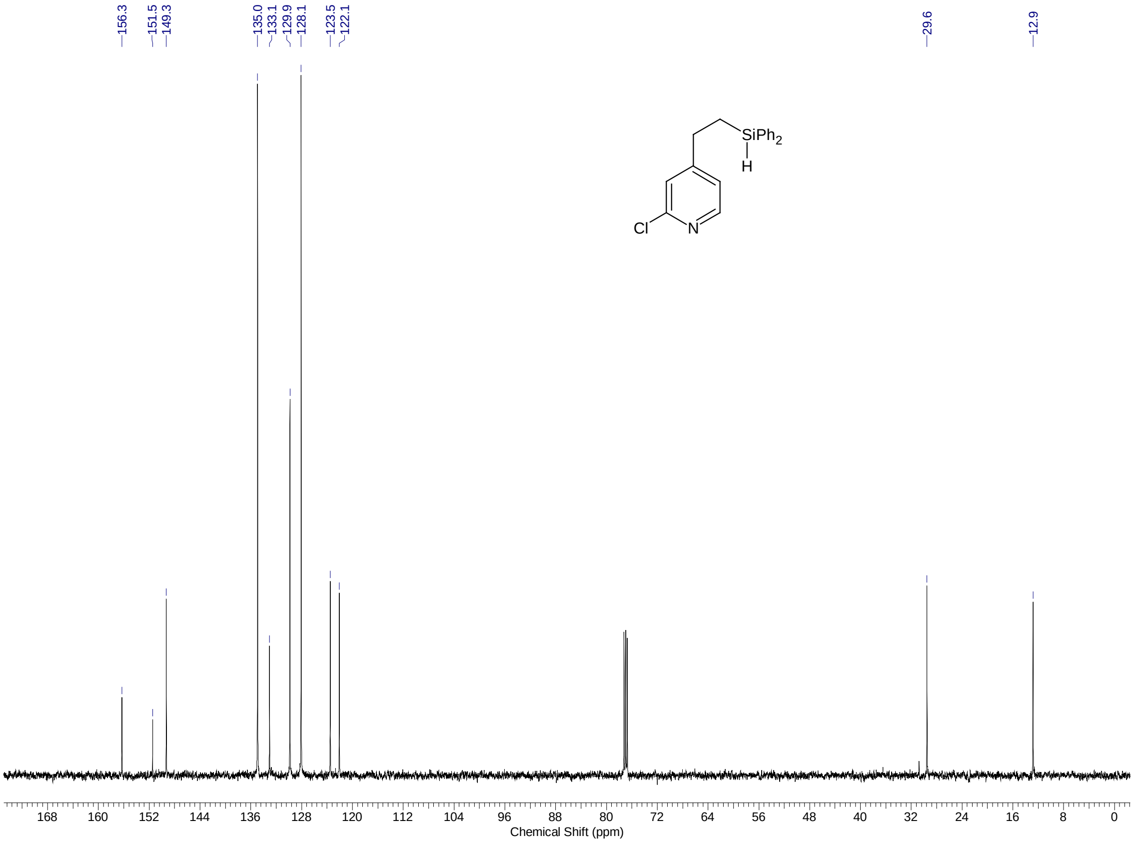
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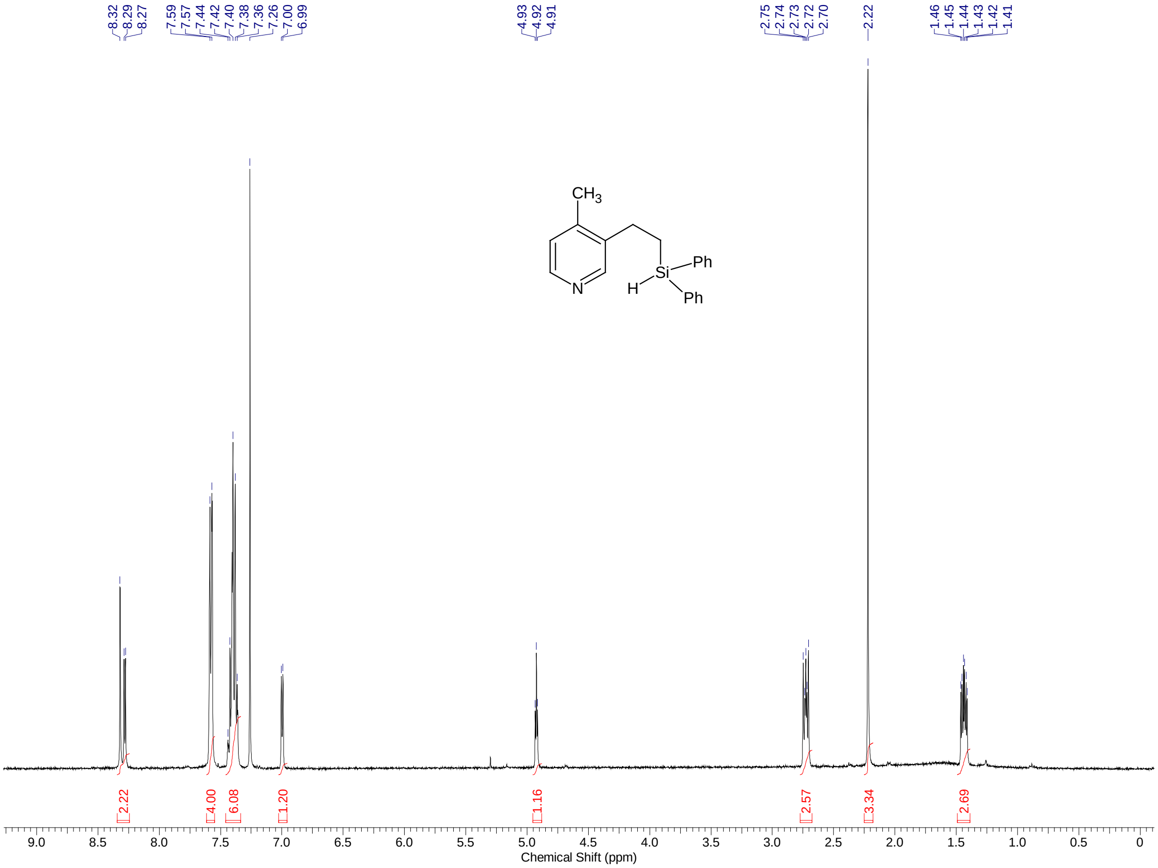
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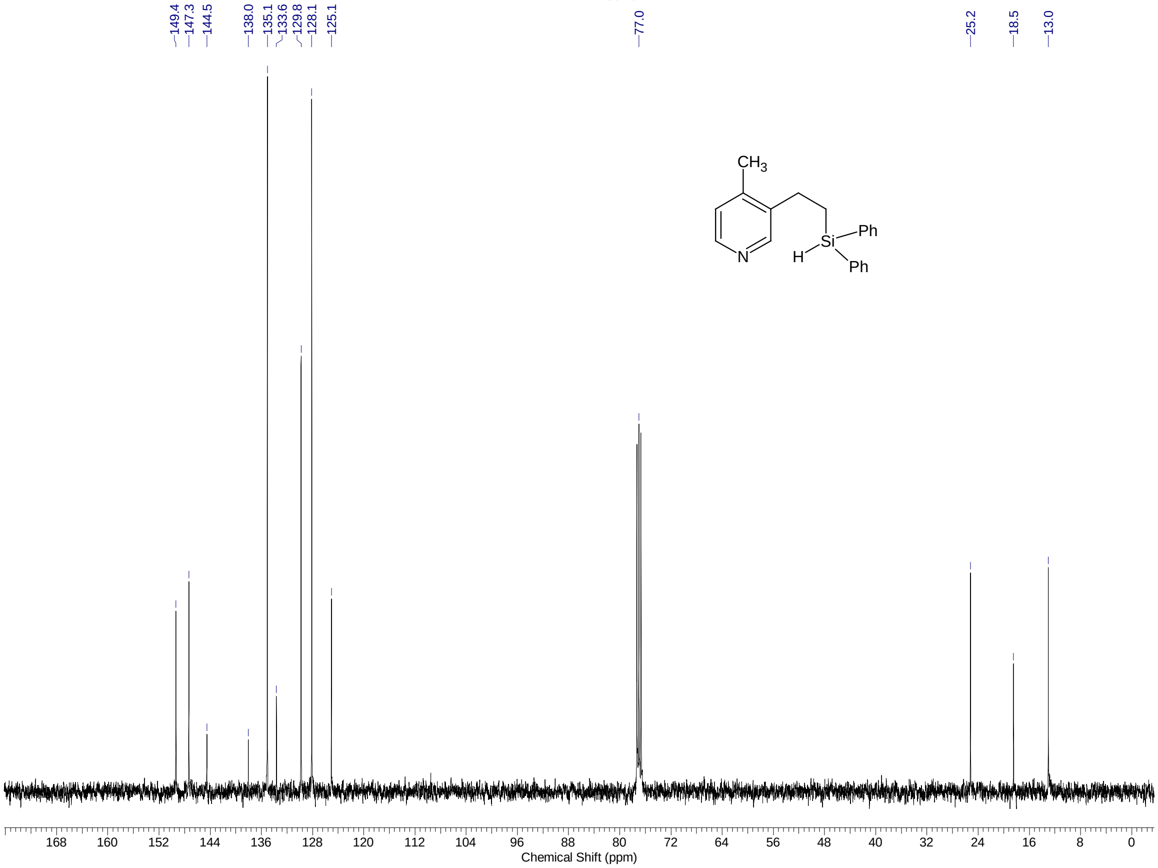
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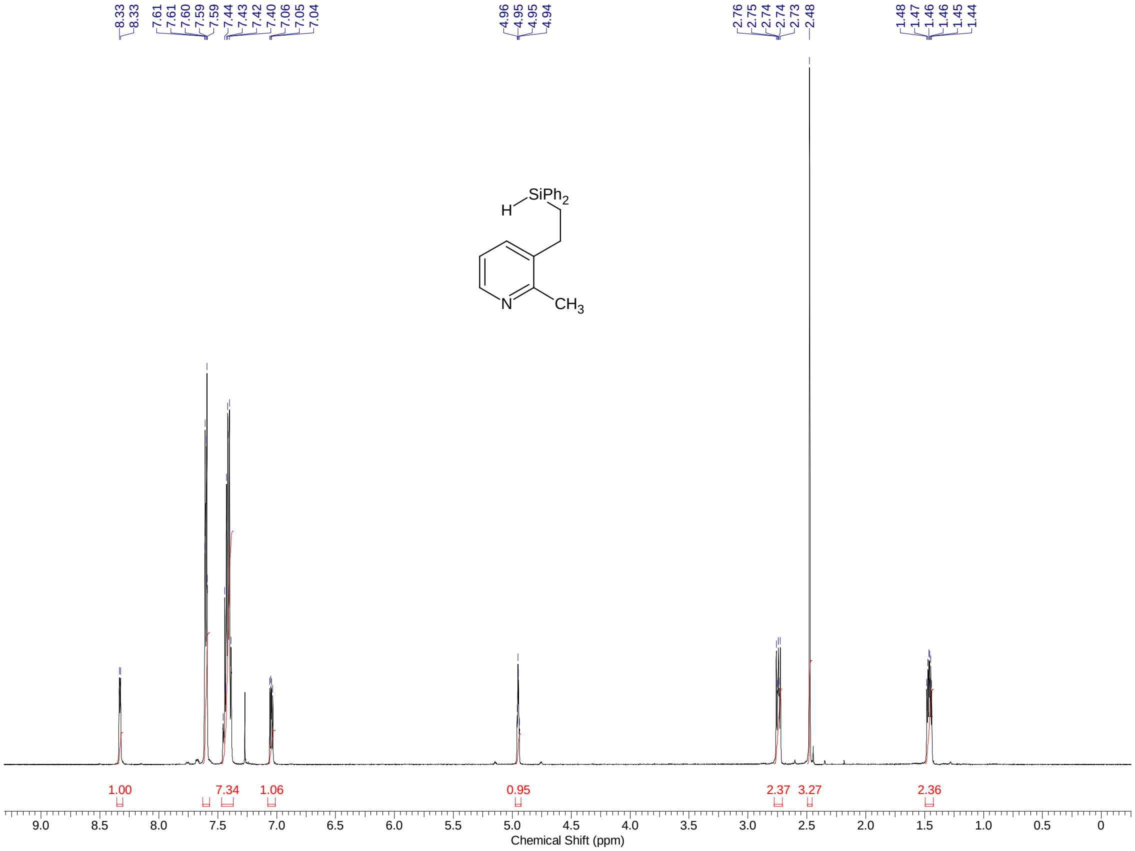
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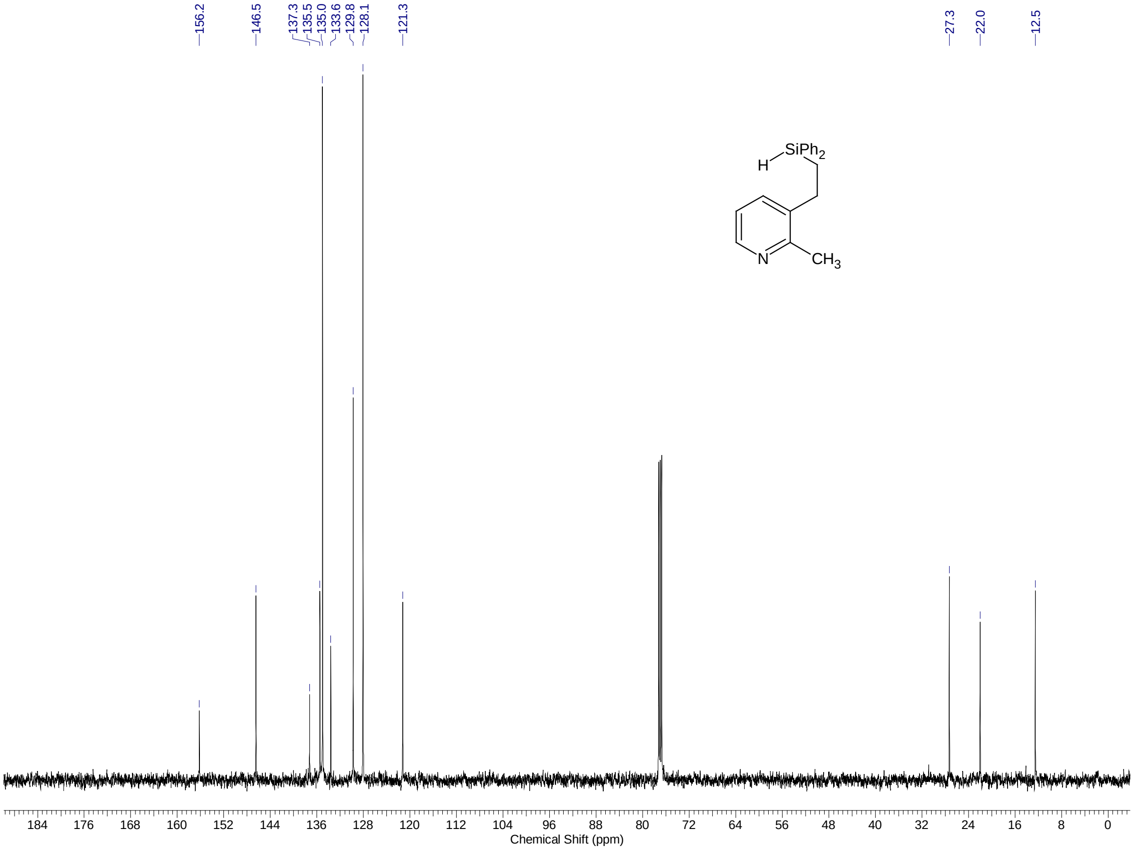
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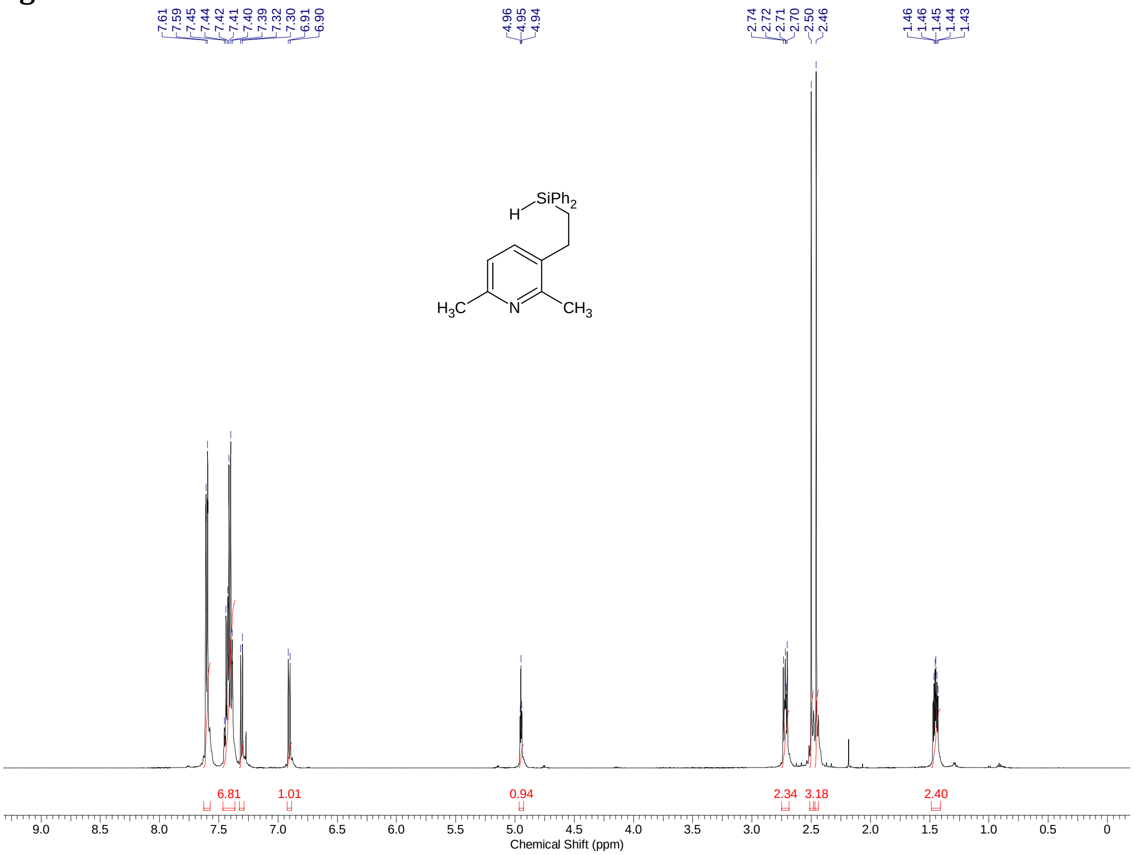
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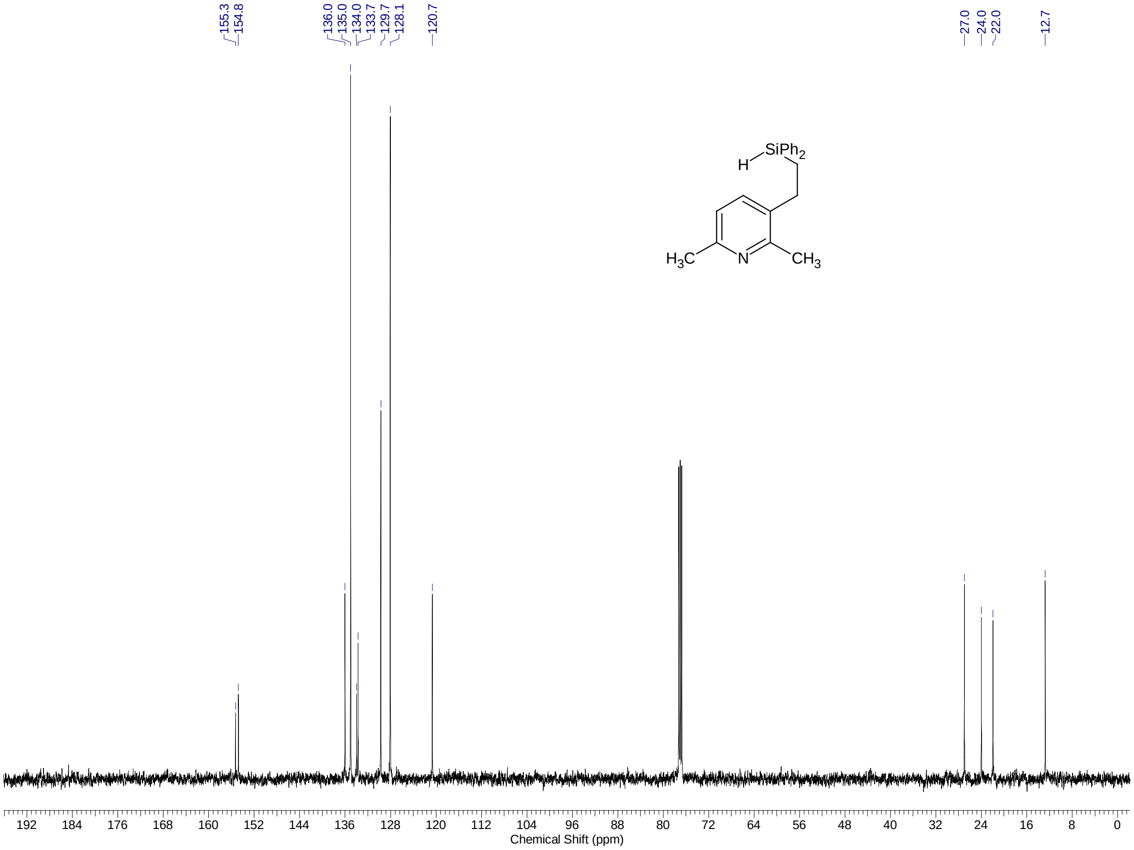
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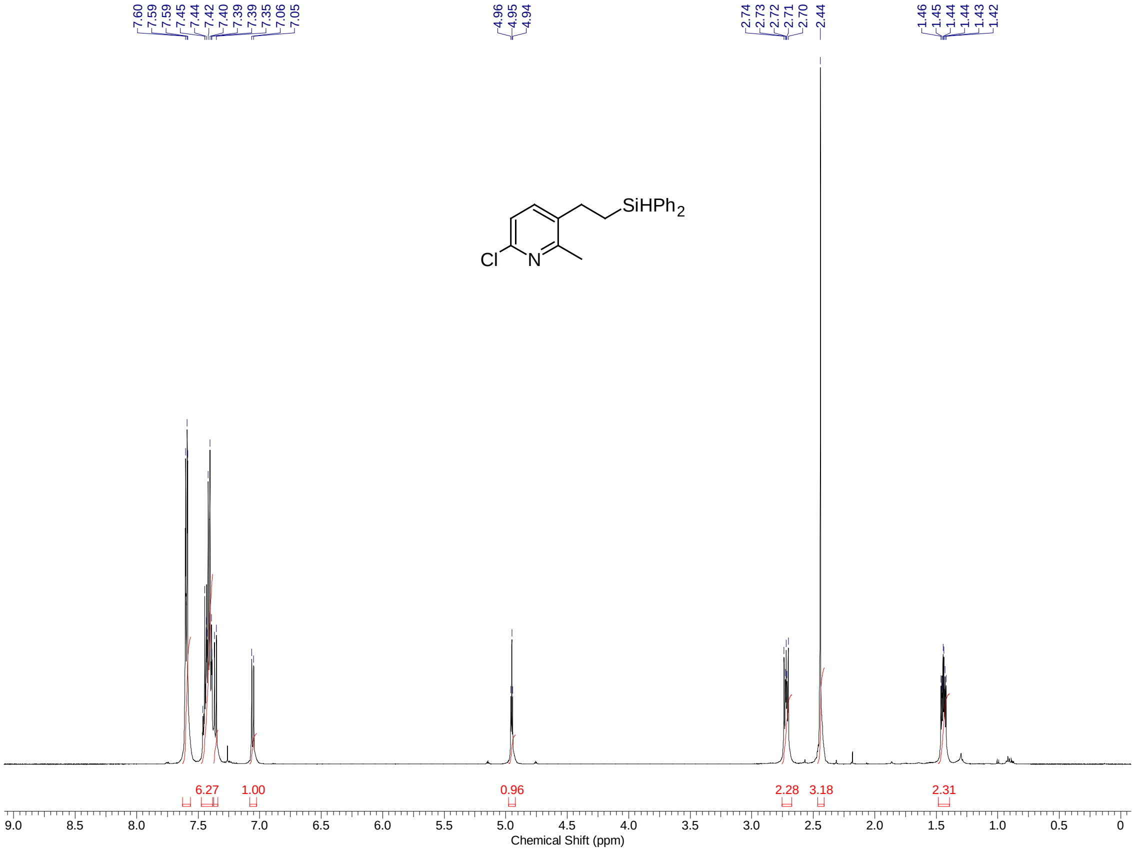
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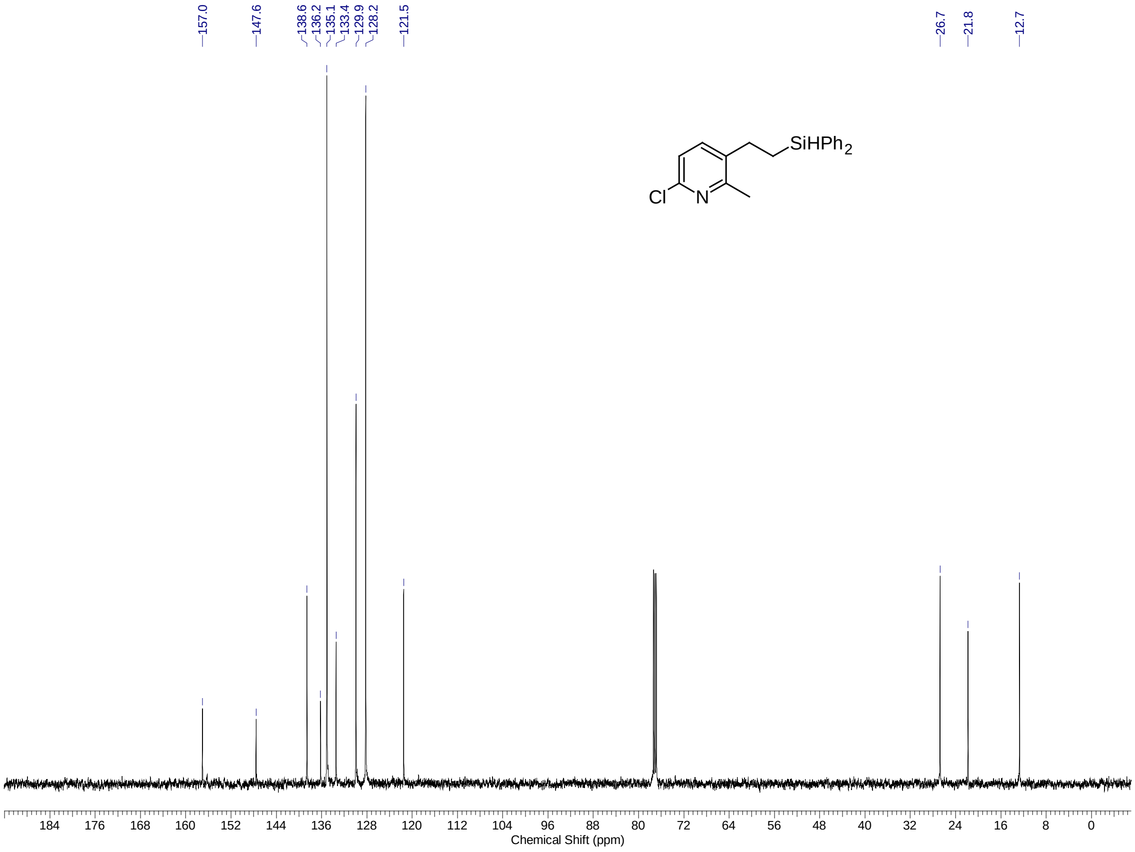
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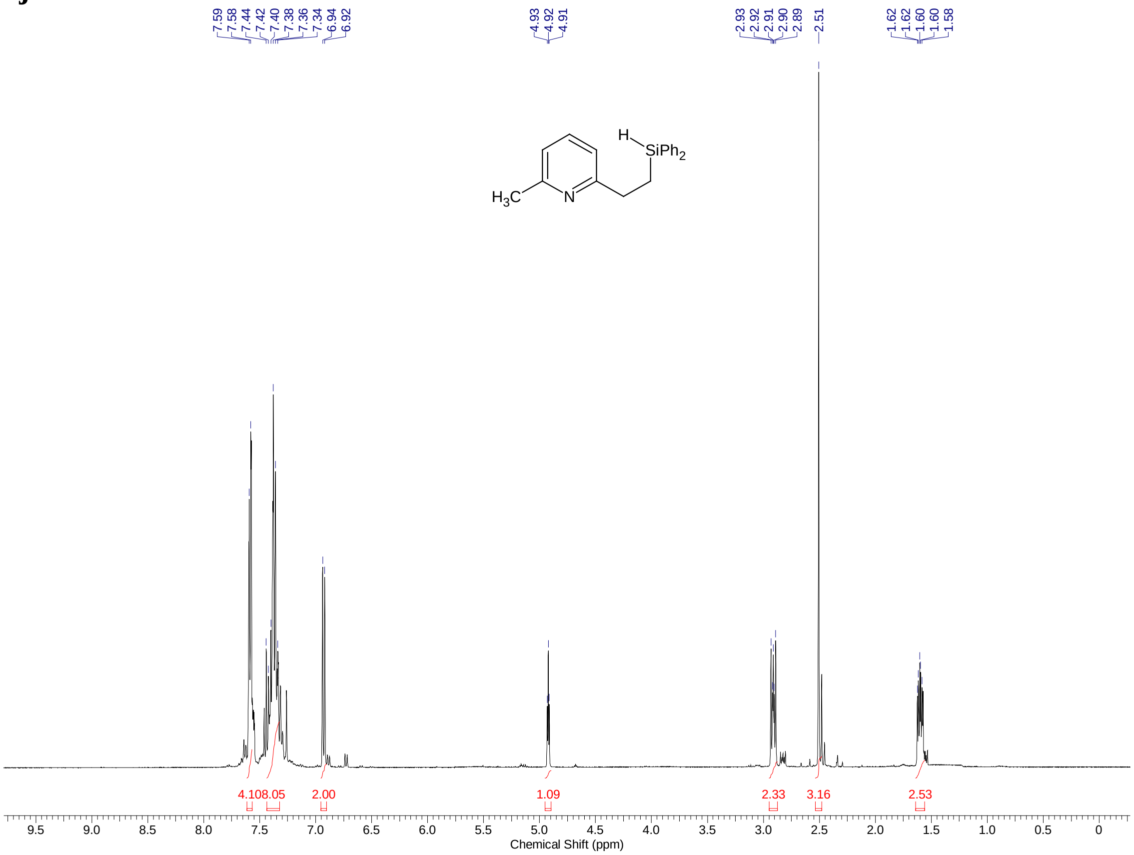
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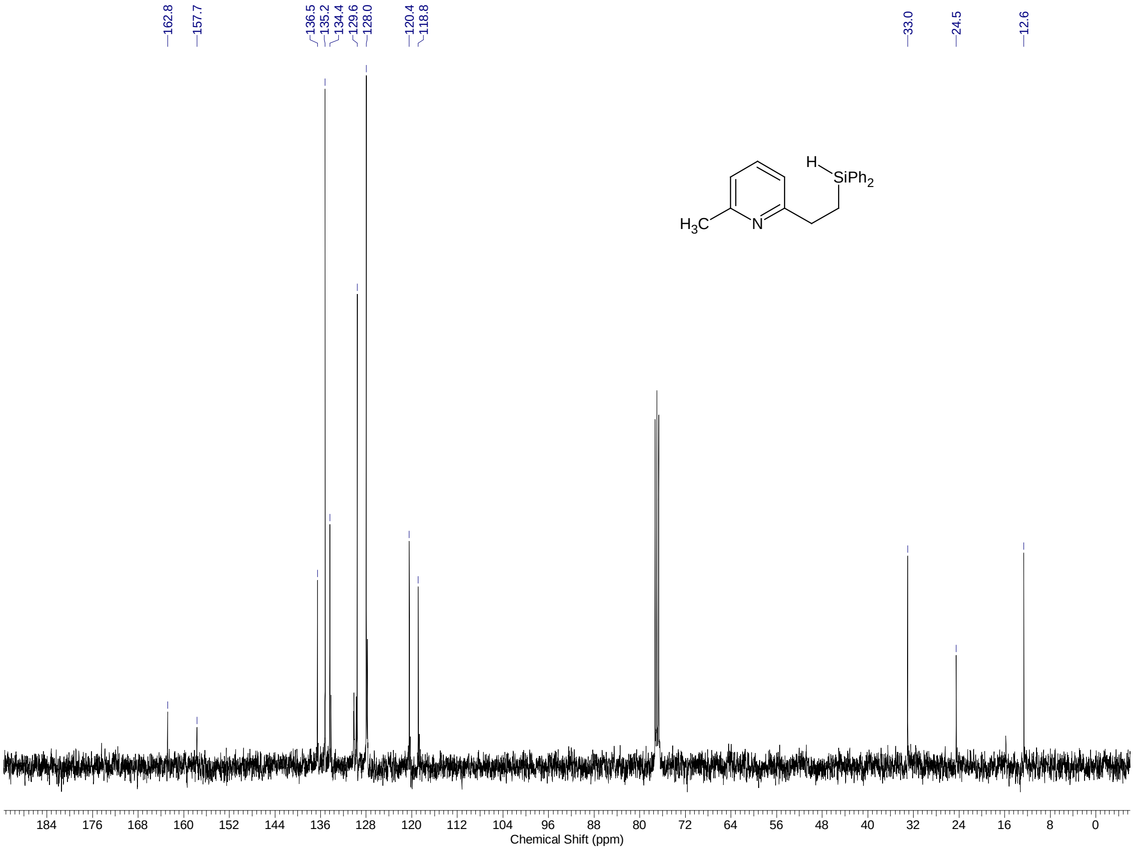
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Chemical Shift (ppm)

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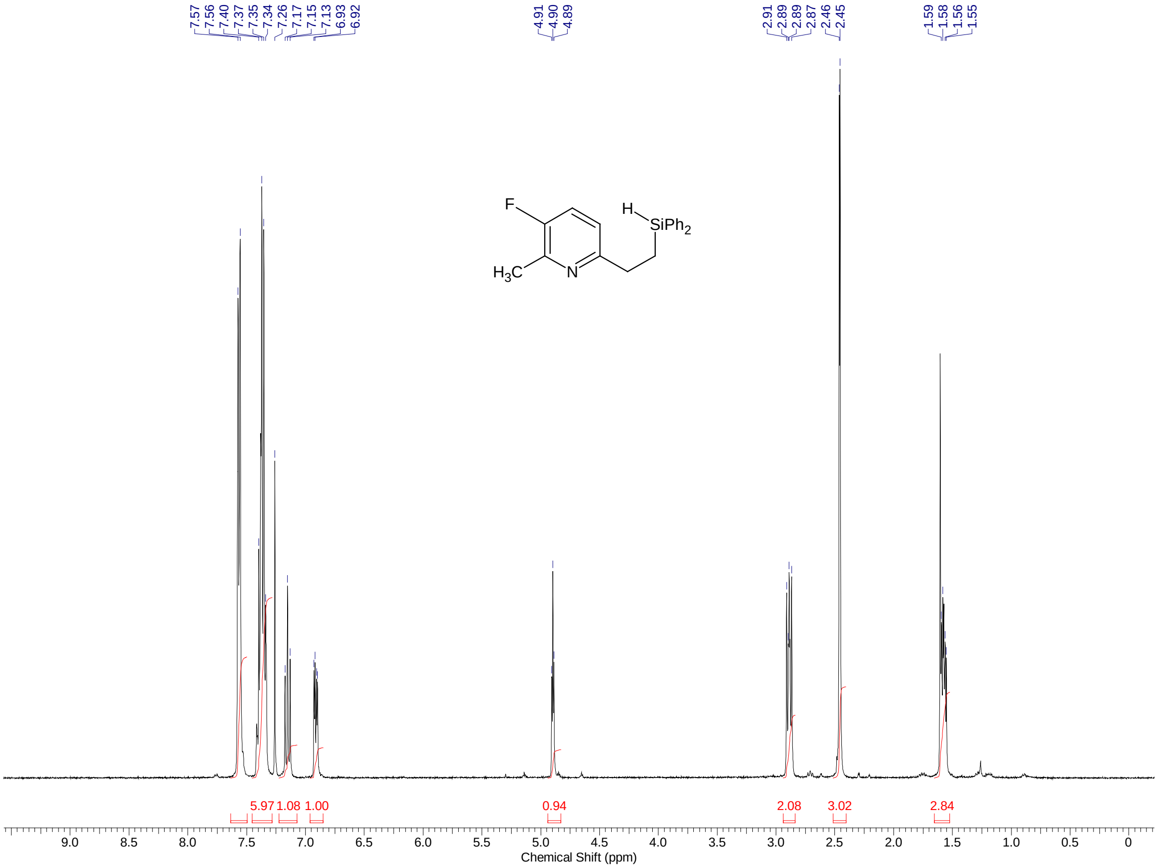

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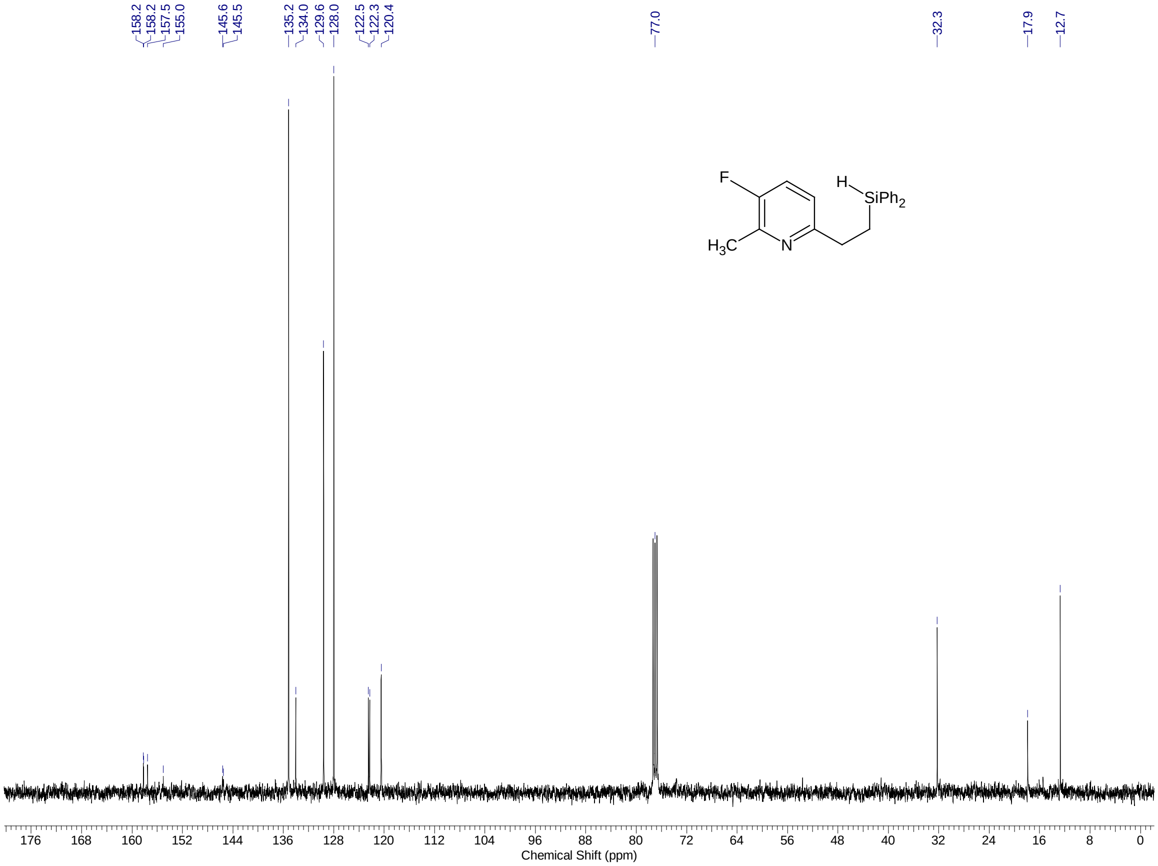
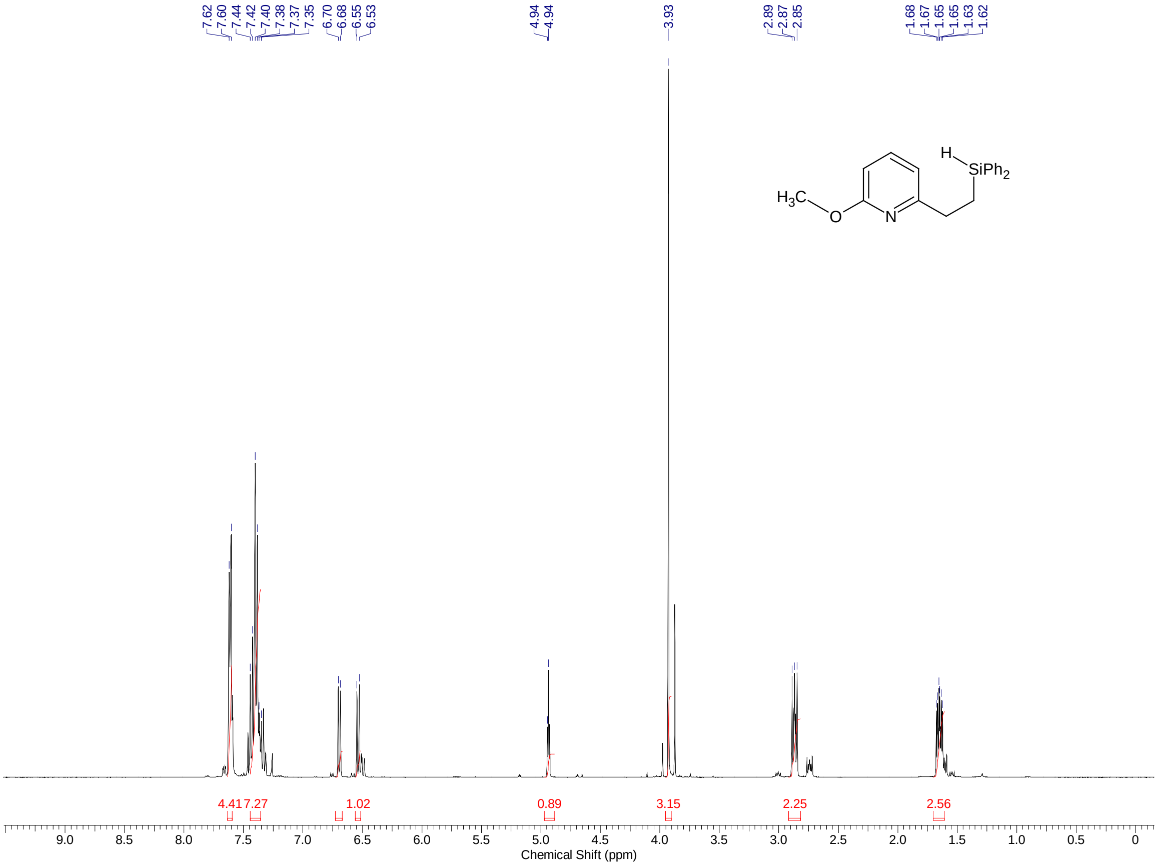
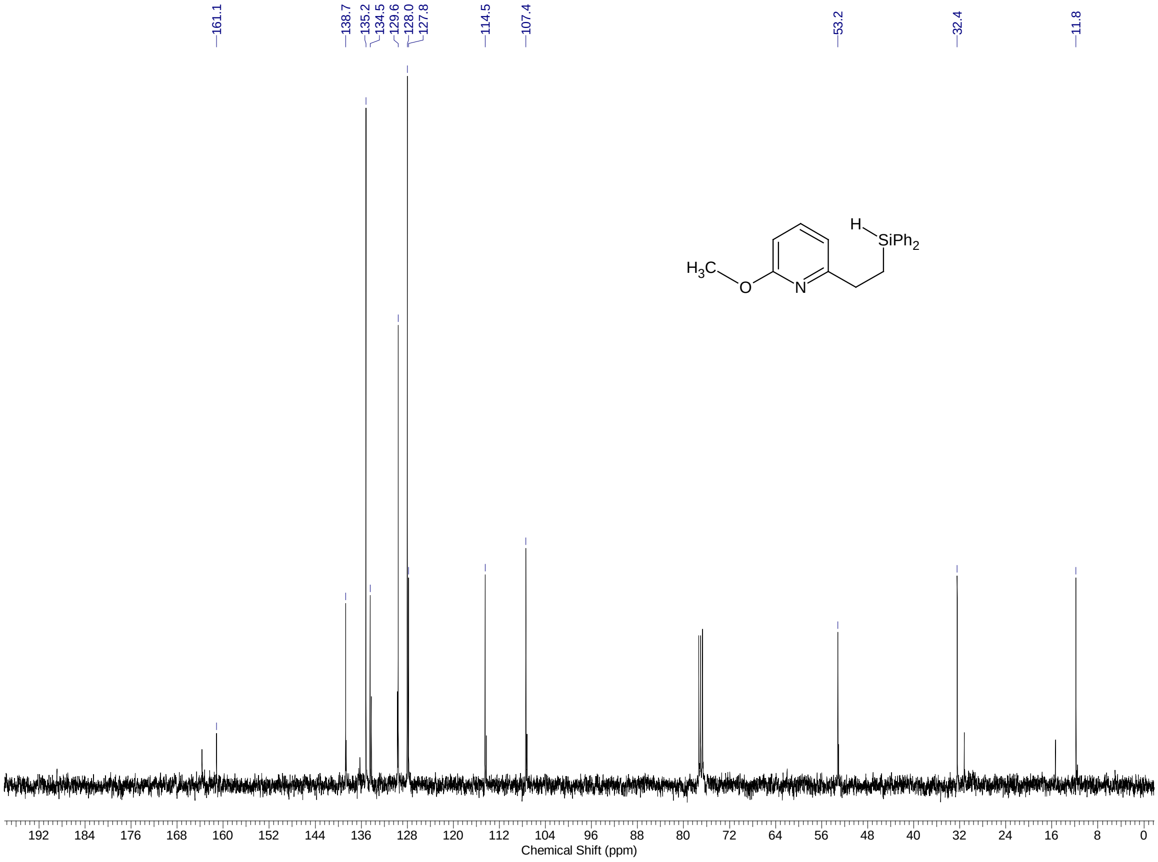
2.08
3.02
2.84
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)



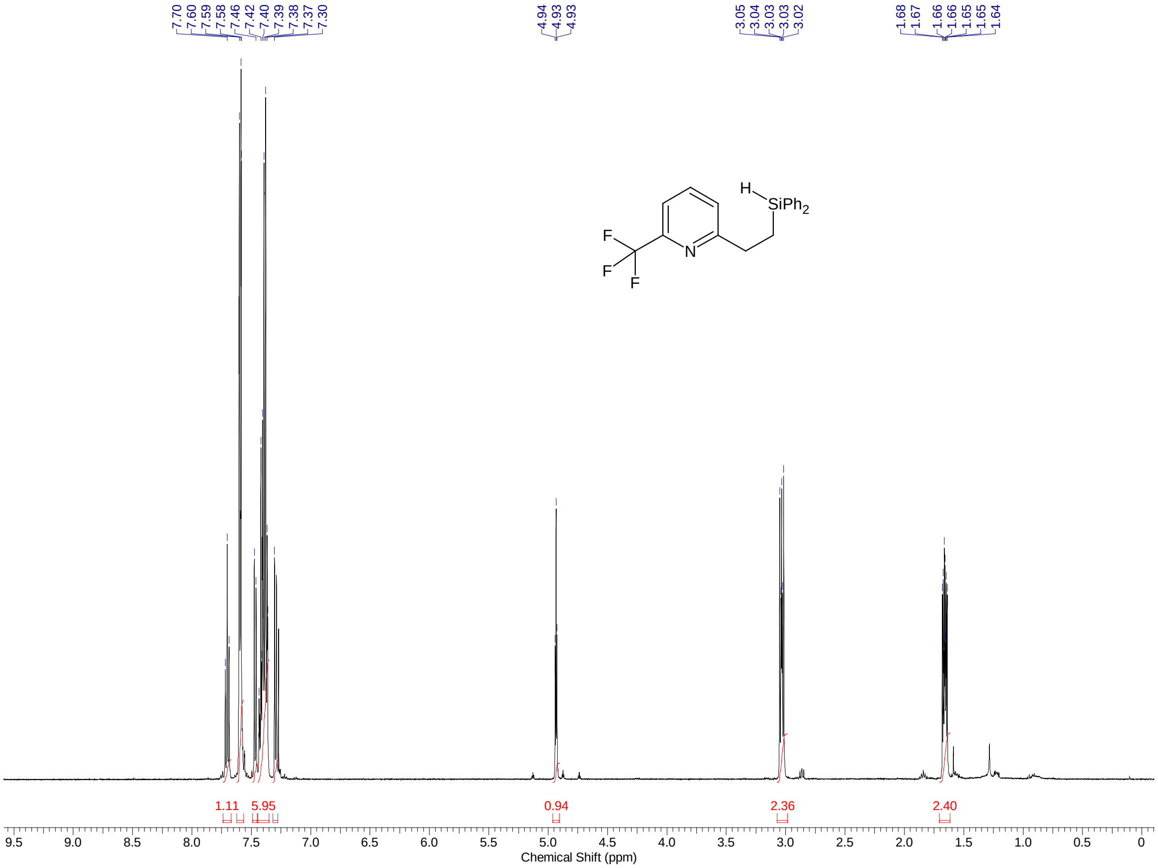
158.2
158.2
157.5
155.0
145.6
145.5
135.2
134.0
129.6
128.0
122.5
122.3
120.4
77.0
32.3
17.9
12.7
F
H
SiPh2
H3C
N
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

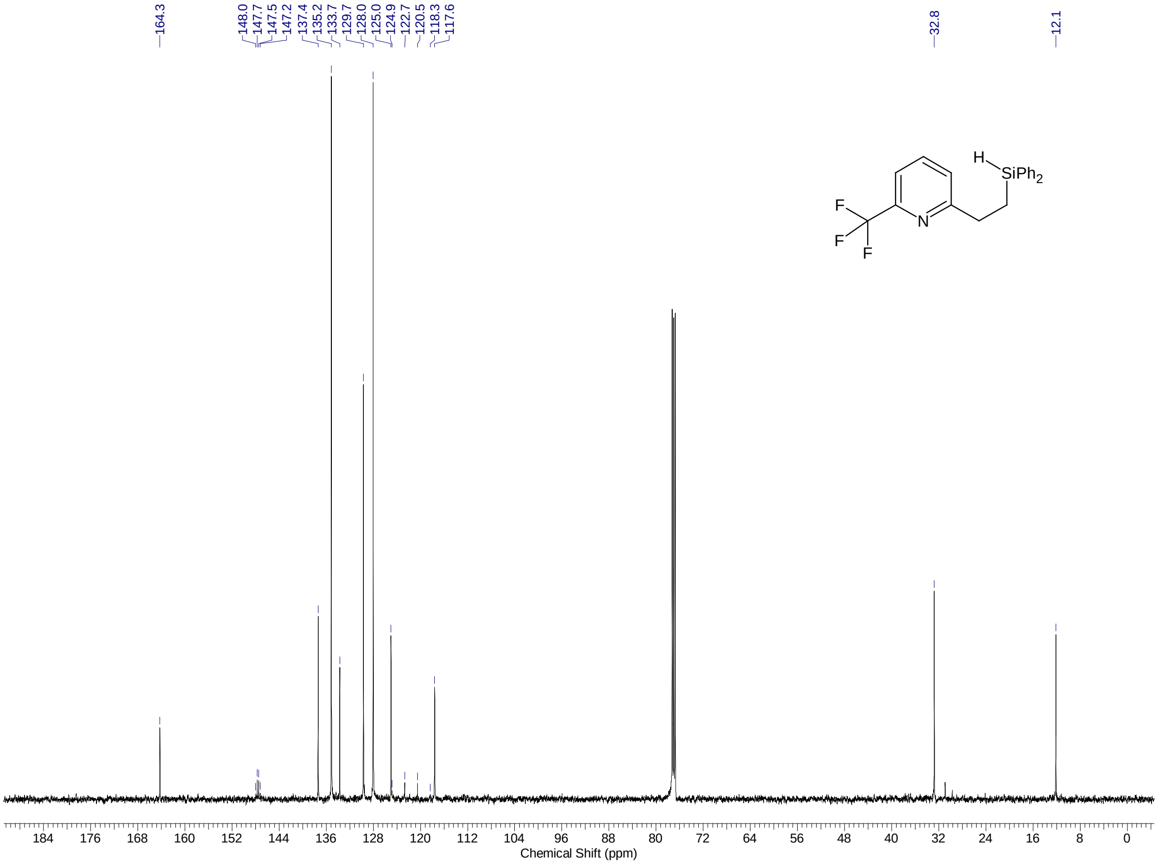
2l:


7.62
7.60
7.44
7.42
7.40
7.38
7.37
7.35
6.70
6.68
6.55
6.53
4.94
4.94
3.93
2.89
2.87
2.85
1.68
1.67
1.65
1.65
1.63
1.62
H
SiPh2
H3C
O
N
4.41
7.27
1.02
0.89
3.15
2.25
2.56
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

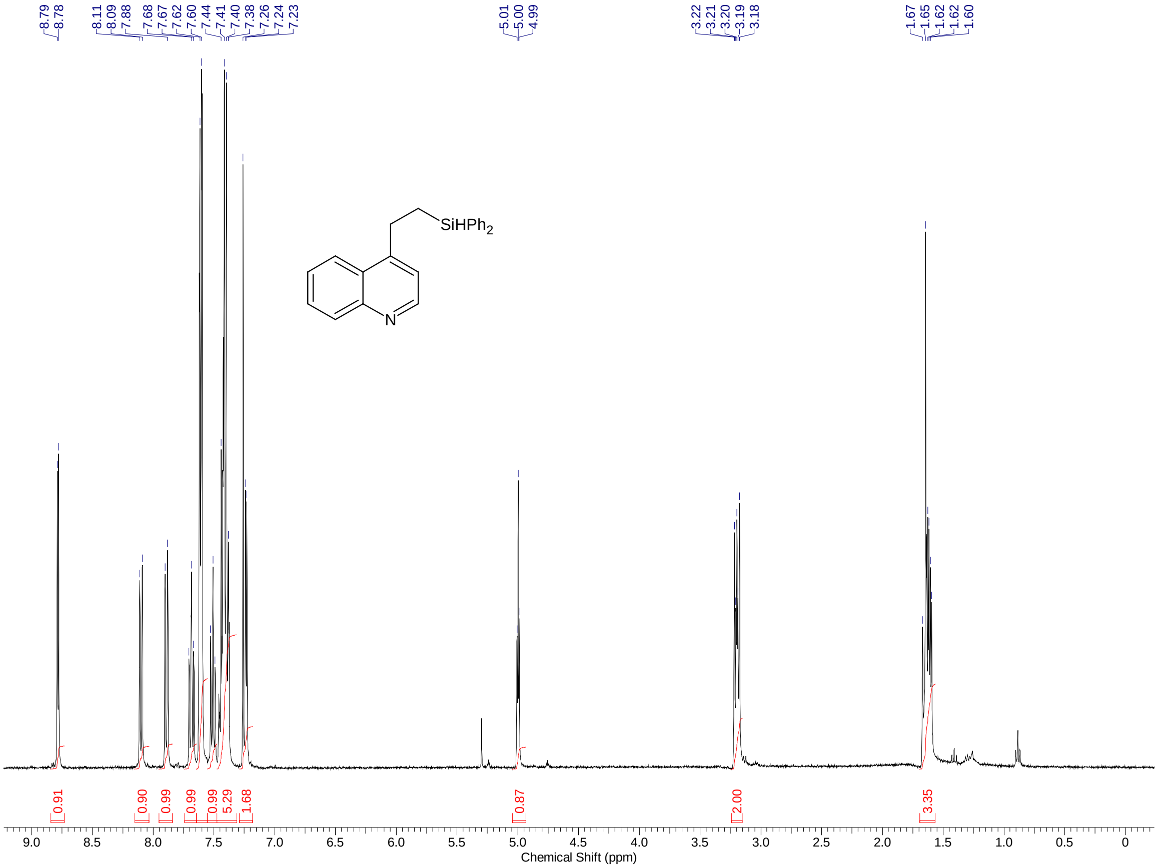

161.1
138.7
135.2
134.5
129.6
128.0
127.8
114.5
107.4
53.2
32.4
11.8
H
SiPh2
H3C
O
N
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

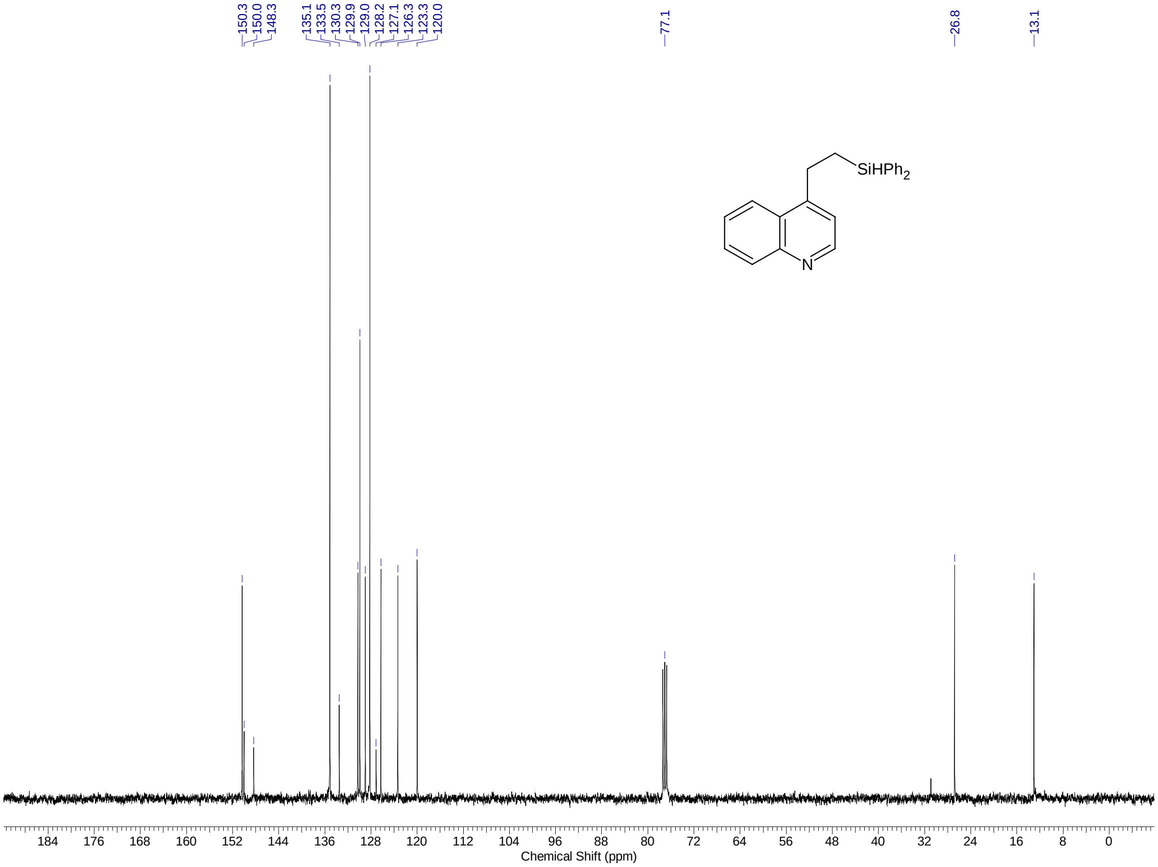
2m:


7.70
7.60
7.59
7.58
7.46
7.42
7.40
7.39
7.38
7.37
7.30
4.94
4.93
4.93
3.05
3.04
3.03
3.03
3.02
1.68
1.67
1.66
1.66
1.65
1.64
1.11
5.95
0.94
2.36
2.40
H
SiPh2
F
F
F
N
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

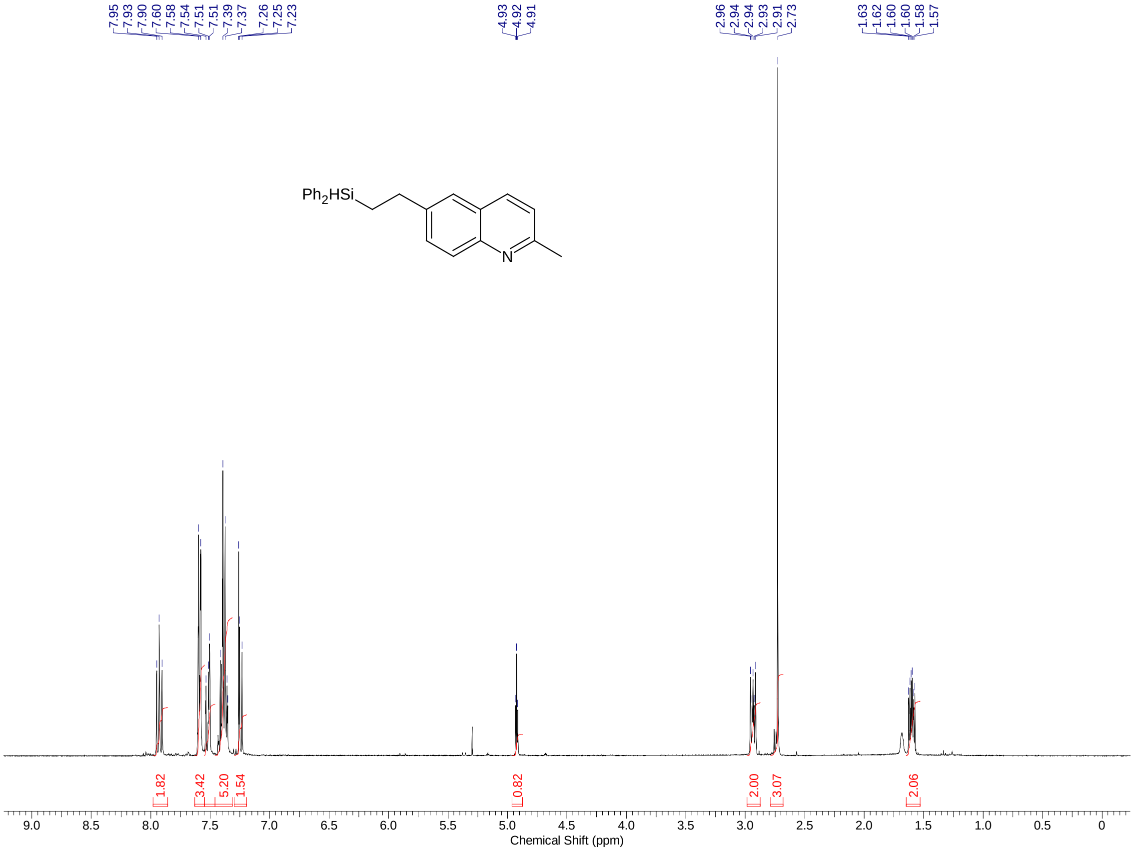

164.3
148.0
147.7
147.5
147.2
137.4
135.2
133.7
129.7
128.0
125.0
124.9
122.7
120.5
118.3
117.6
32.8
12.1
H
SiPh2
F
F
F
N
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

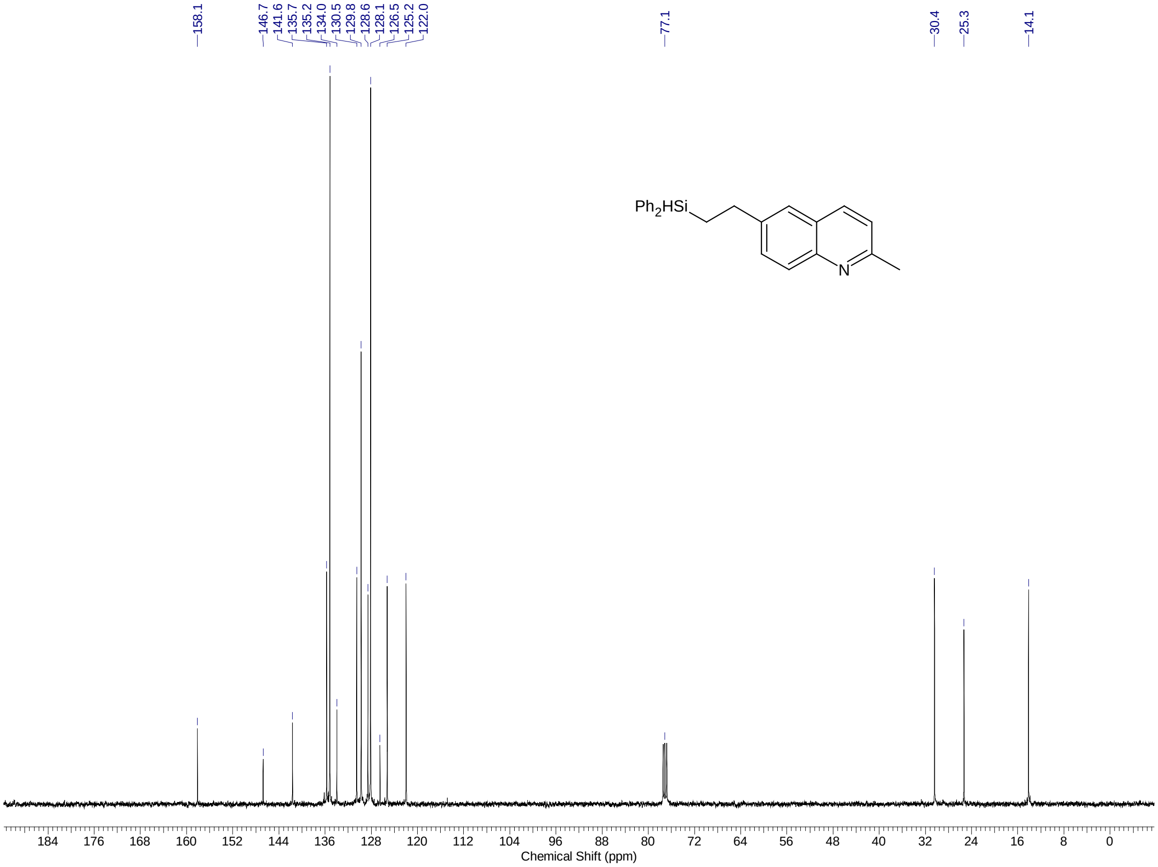
2n:


8.79
8.78
8.11
8.09
7.88
7.68
7.67
7.62
7.60
7.44
7.41
7.40
7.38
7.26
7.24
7.23
5.01
5.00
4.99
3.22
3.21
3.20
3.19
3.18
1.67
1.65
1.62
1.62
1.60
SiHPh2
N
0.91
0.90
0.99
0.99
0.99
5.29
1.68
0.87
2.00
3.35
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

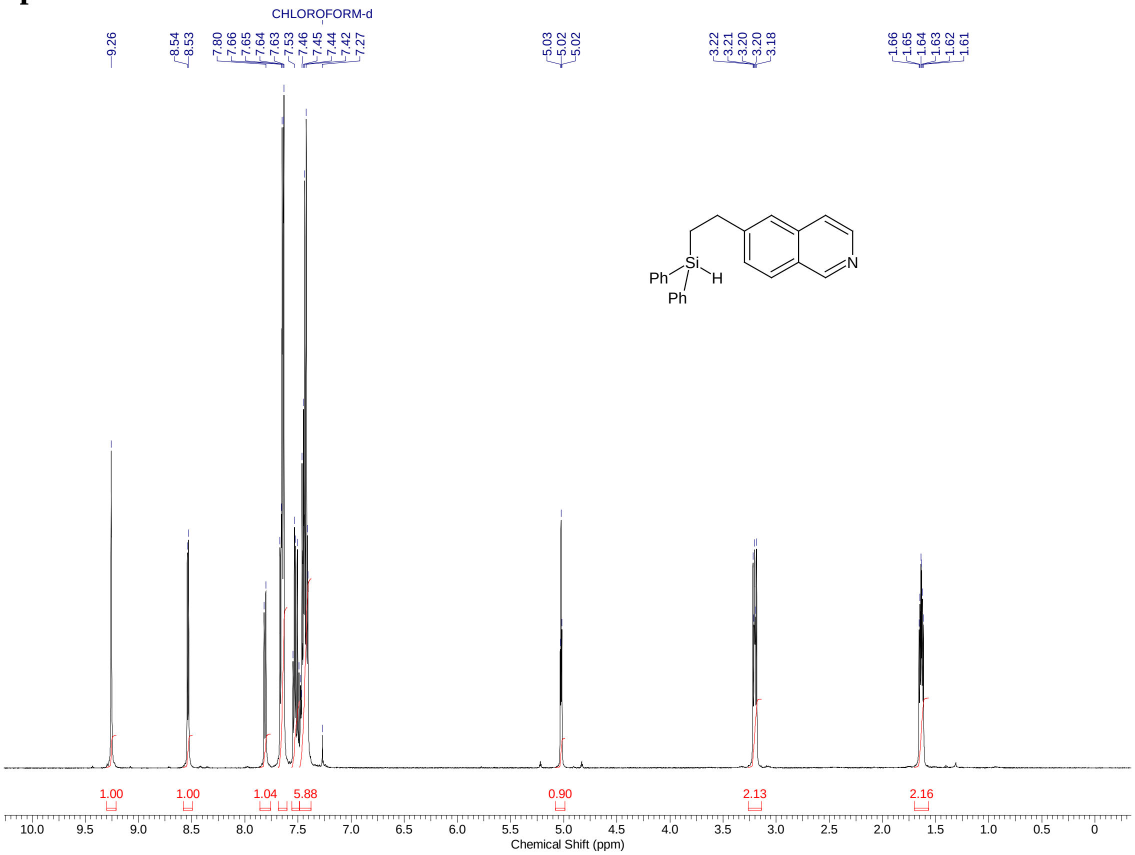

150.3
150.0
148.3
135.1
133.5
130.3
129.9
129.0
128.2
127.1
126.3
123.3
120.0
77.1
26.8
13.1
SiHPh2
N
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

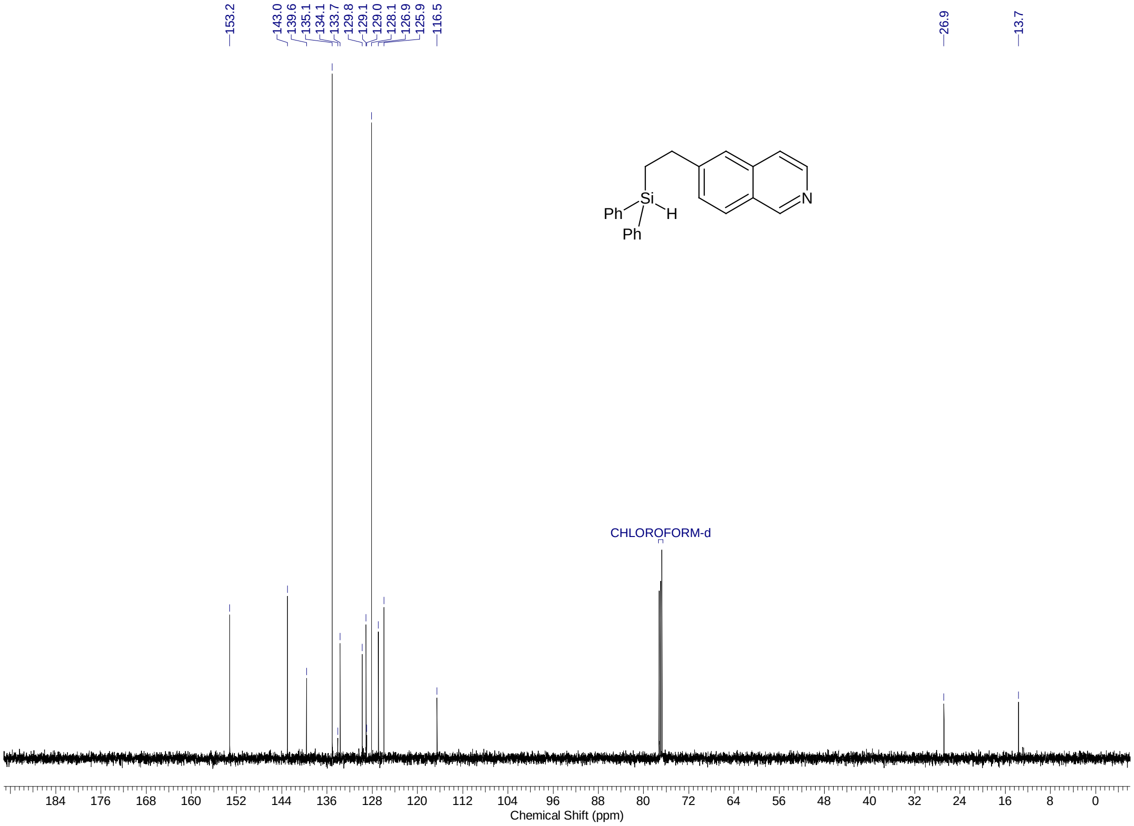
2o:


7.95
7.93
7.90
7.60
7.58
7.54
7.51
7.51
7.39
7.37
7.26
7.25
7.23
4.93
4.92
4.91
2.96
2.94
2.94
2.93
2.91
2.73
1.63
1.62
1.60
1.60
1.58
1.57
Ph2HSi
N
1.82
3.42
5.20
1.54
0.82
2.00
3.07
2.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

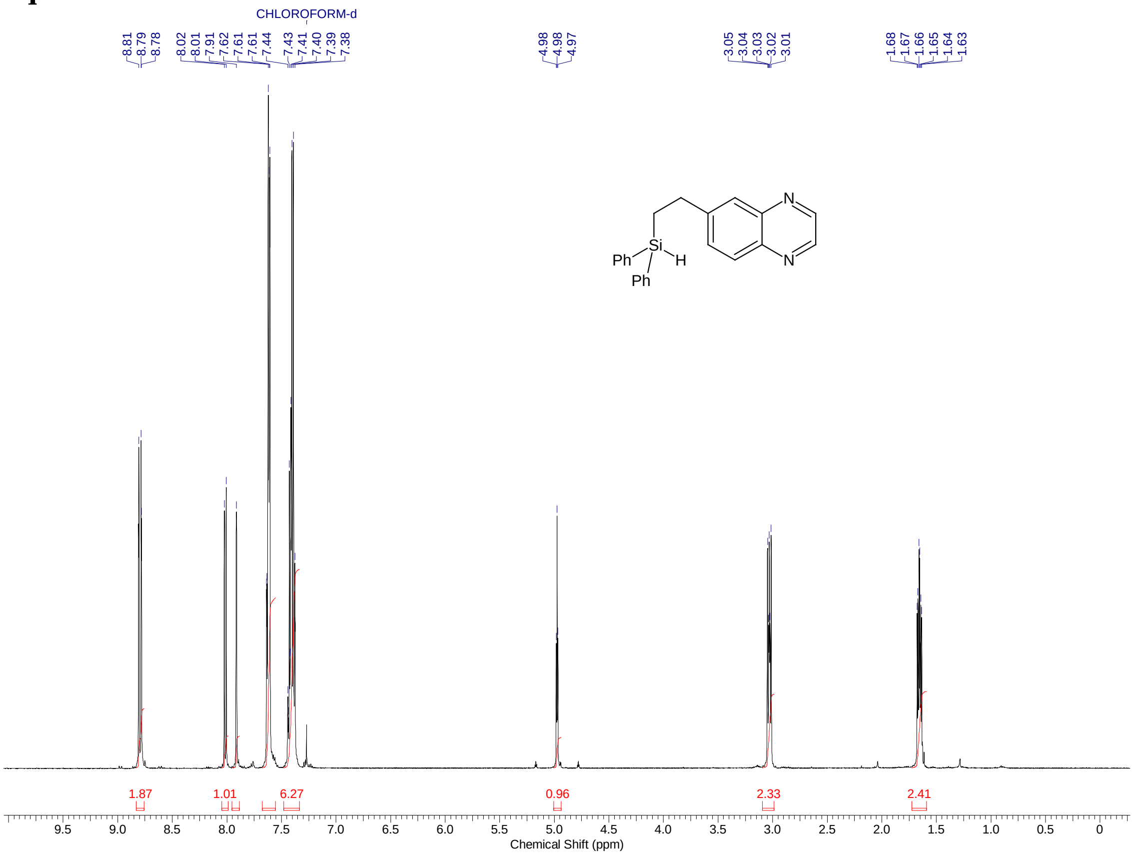

158.1
146.7
141.6
135.7
135.2
134.0
130.5
129.8
128.6
128.1
126.5
125.2
122.0
77.1
30.4
25.3
14.1
Ph2HSi
N
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

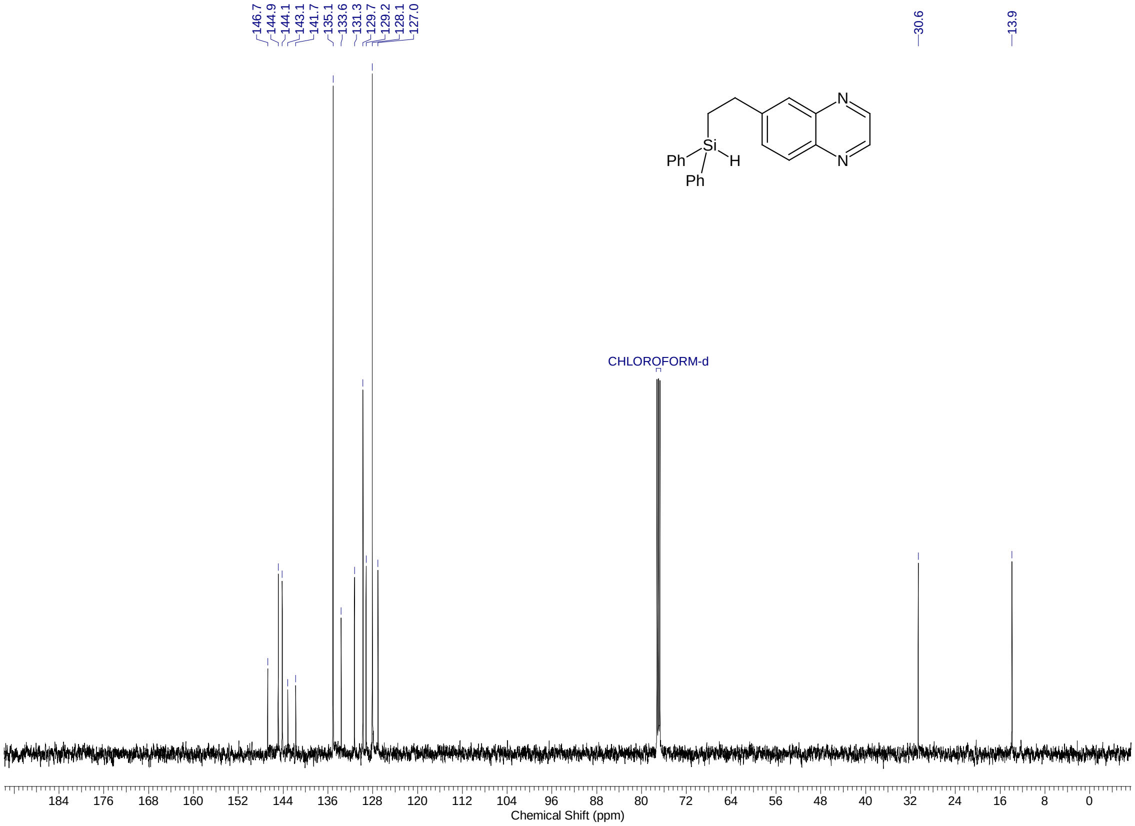
2p:


CHLOROFORM-d
9.26
8.54
8.53
7.80
7.66
7.65
7.64
7.63
7.53
7.46
7.45
7.44
7.42
7.27
5.03
5.02
5.02
3.22
3.21
3.20
3.20
3.18
1.66
1.65
1.64
1.63
1.62
1.61
Ph
Si
H
Ph
N
1.00
1.00
1.04
5.88
0.90
2.13
2.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

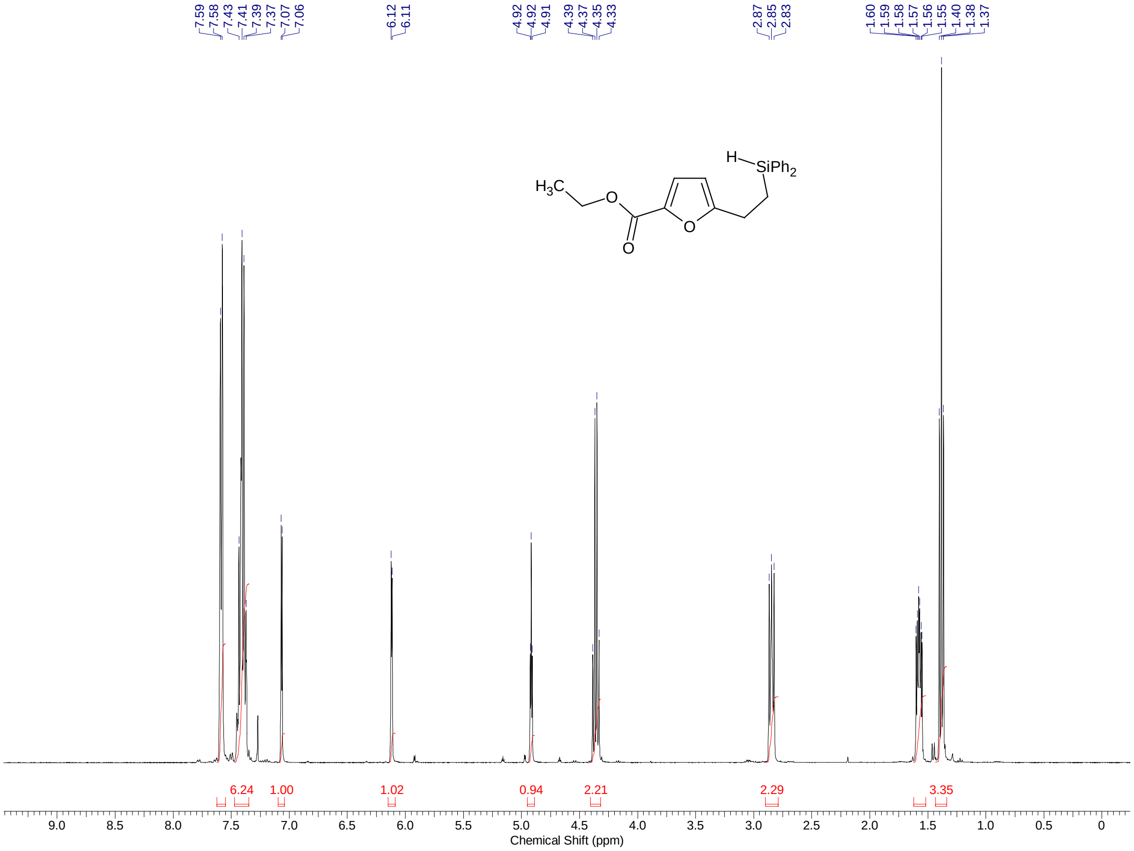

153.2
143.0
139.6
135.1
134.1
133.7
129.8
129.1
129.0
128.1
126.9
125.9
116.5
26.9
13.7
Ph
Si
H
Ph
N
CHLOROFORM-d
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

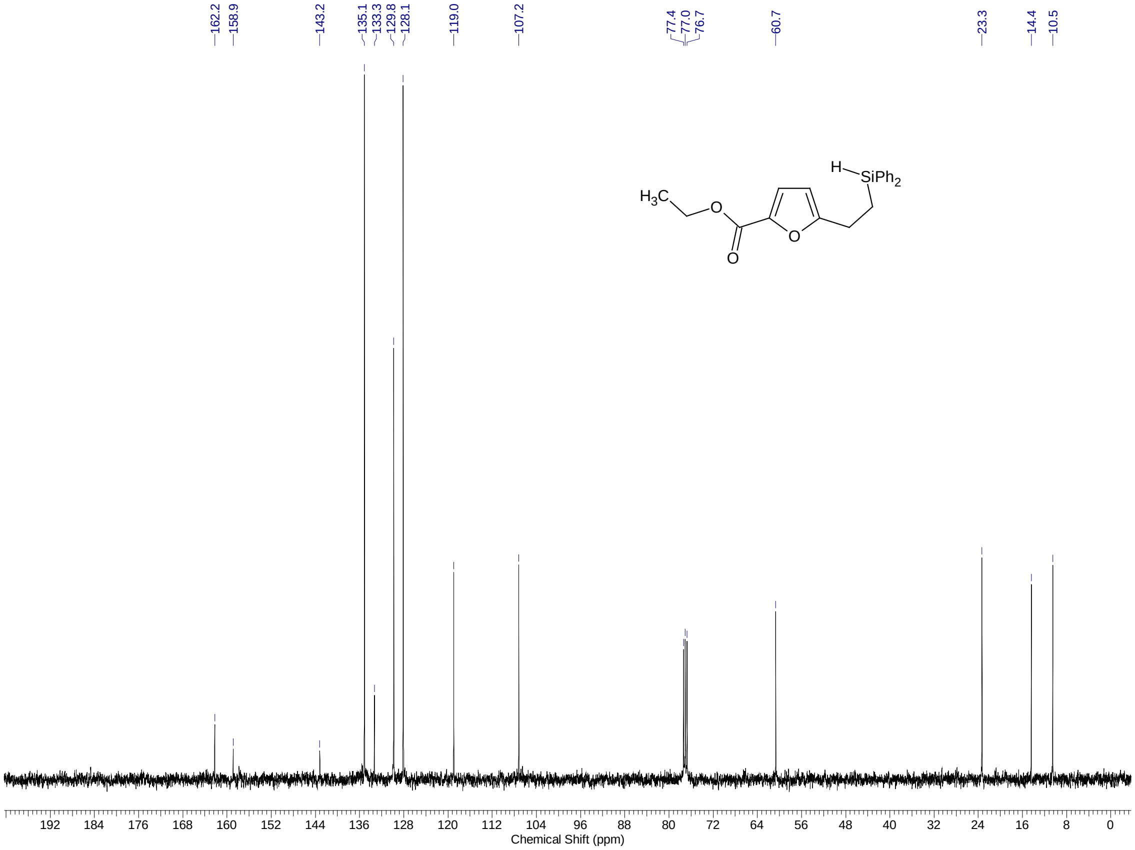
2q:


CHLOROFORM-d
8.81
8.79
8.78
8.02
8.01
7.91
7.62
7.61
7.44
7.43
7.41
7.40
7.39
7.38
4.98
4.98
4.97
3.05
3.04
3.03
3.02
3.01
1.68
1.67
1.66
1.65
1.64
1.63
N
N
Si
H
Ph
Ph
1.87
1.01
6.27
0.96
2.33
2.41
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

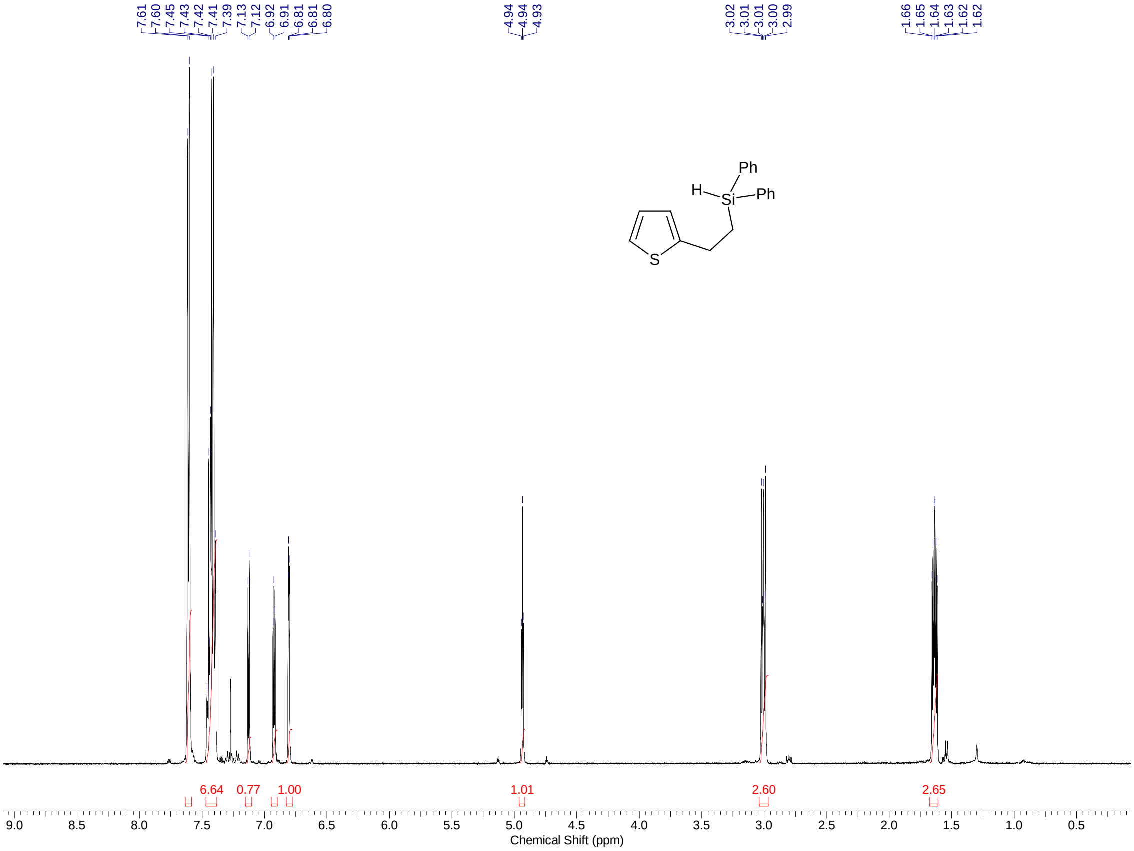

146.7
144.9
144.1
143.1
141.7
135.1
133.6
131.3
129.7
129.2
128.1
127.0
30.6
13.9
N
N
Si
H
Ph
Ph
CHLOROFORM-d
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

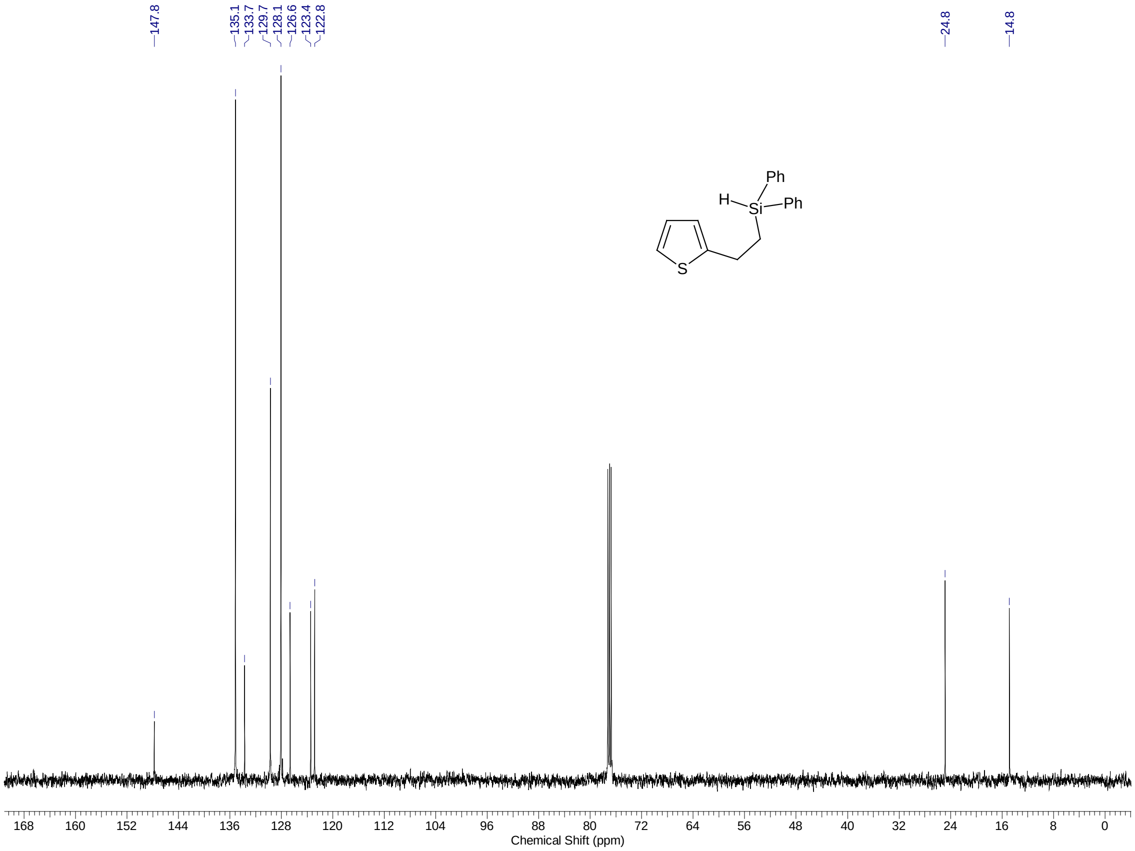
2aa:


7.59
7.58
7.43
7.41
7.39
7.37
7.07
7.06
6.12
6.11
4.92
4.92
4.91
4.39
4.37
4.35
4.33
2.87
2.85
2.83
1.60
1.59
1.58
1.57
1.56
1.55
1.40
1.38
1.37
H
SiPh2
H3C
O
O
O
6.24
1.00
1.02
0.94
2.21
2.29
3.35
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

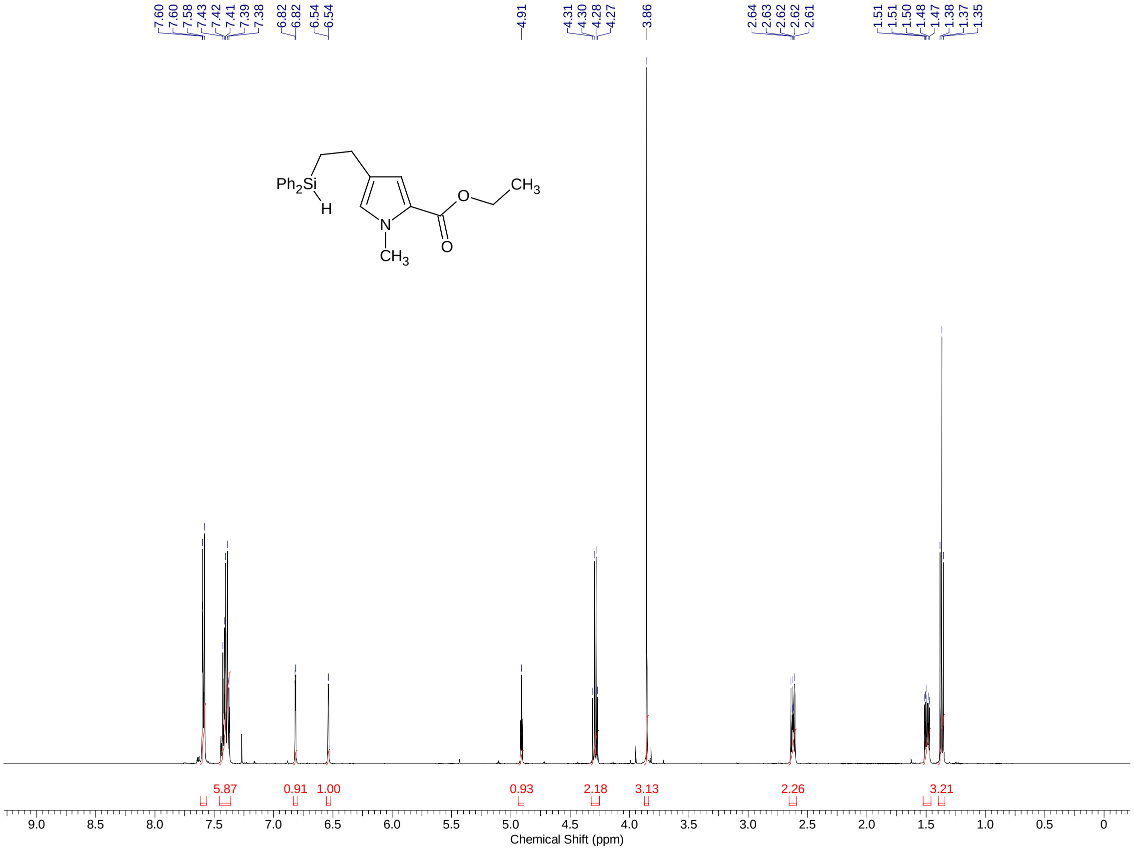

162.2
158.9
143.2
135.1
133.3
129.8
128.1
119.0
107.2
77.4
77.0
76.7
60.7
23.3
14.4
10.5
H
SiPh2
H3C
O
O
O
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

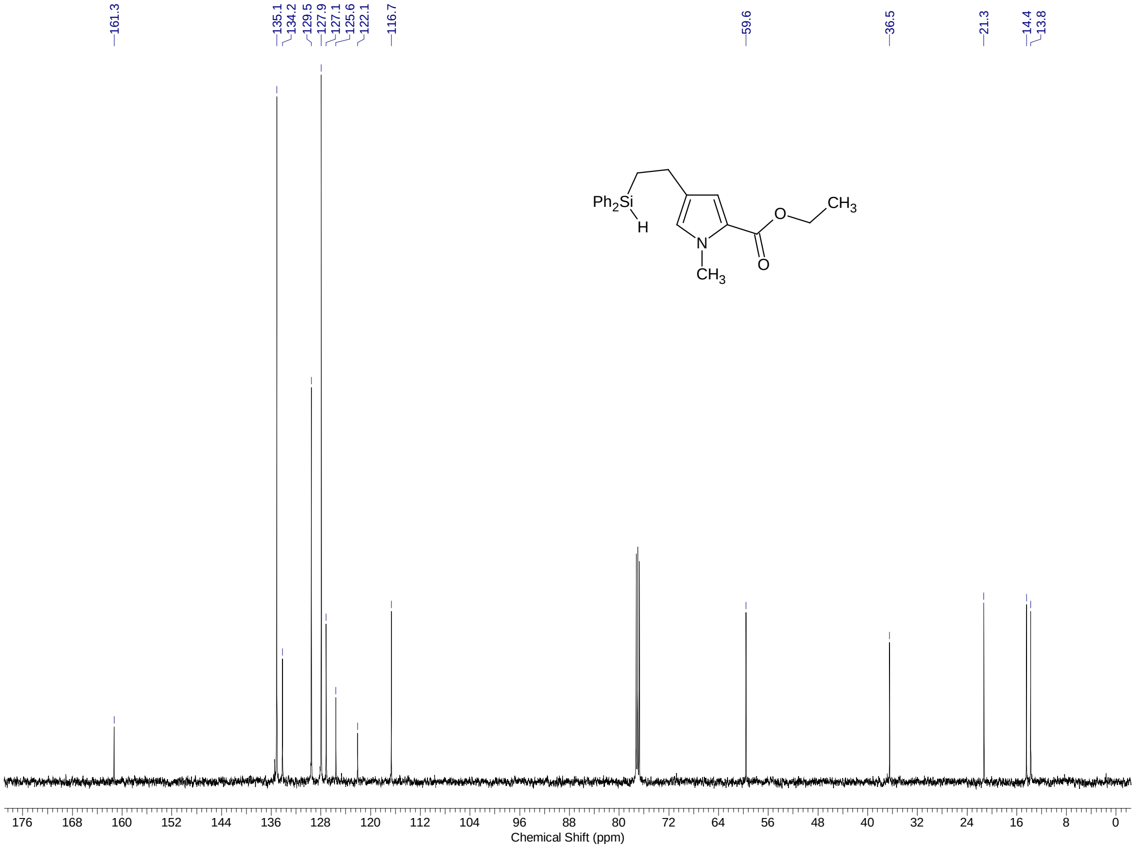
2bb:


7.61
7.60
7.45
7.43
7.42
7.41
7.39
7.13
7.12
6.92
6.91
6.81
6.81
6.80
4.94
4.94
4.93
3.02
3.01
3.01
3.00
2.99
1.66
1.65
1.64
1.63
1.62
1.62
Ph
H
Si
Ph
S
6.64
0.77
1.00
1.01
2.60
2.65
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

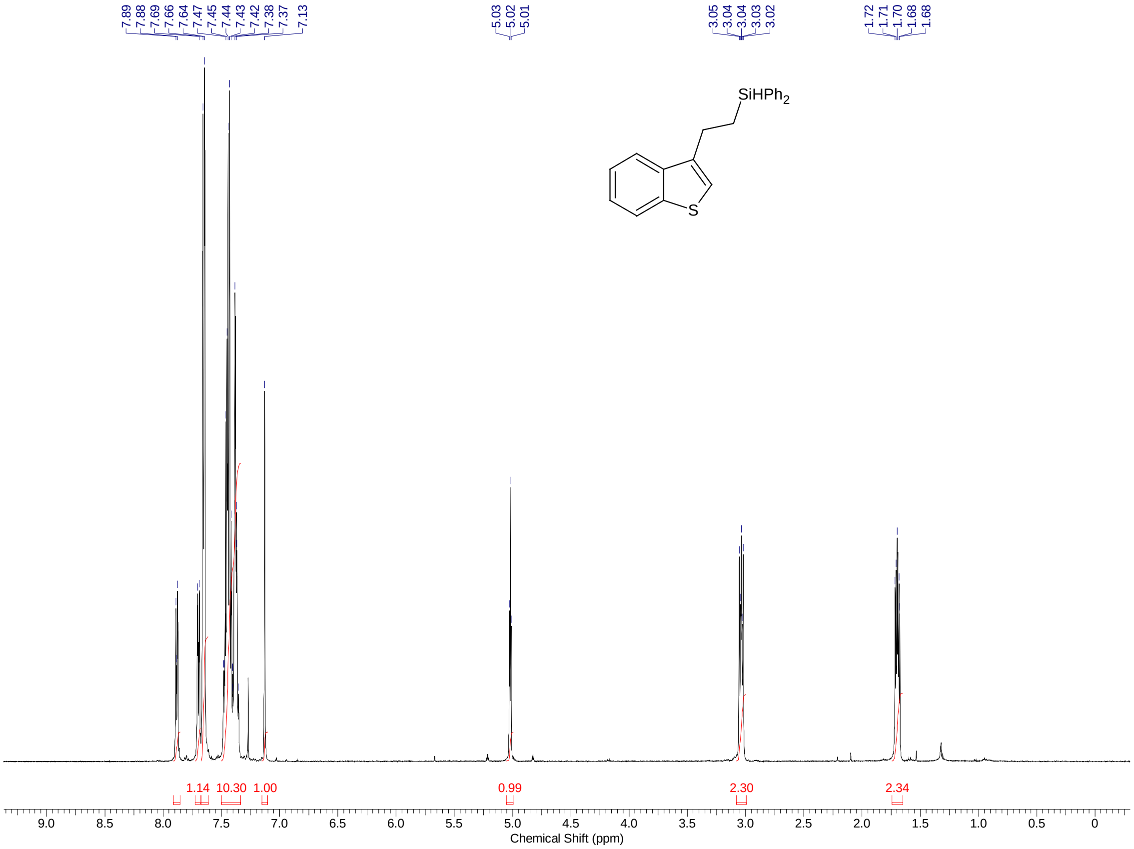

147.8
135.1
133.7
129.7
128.1
126.6
123.4
122.8
24.8
14.8
Ph
H
Si
Ph
S
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

2cc:

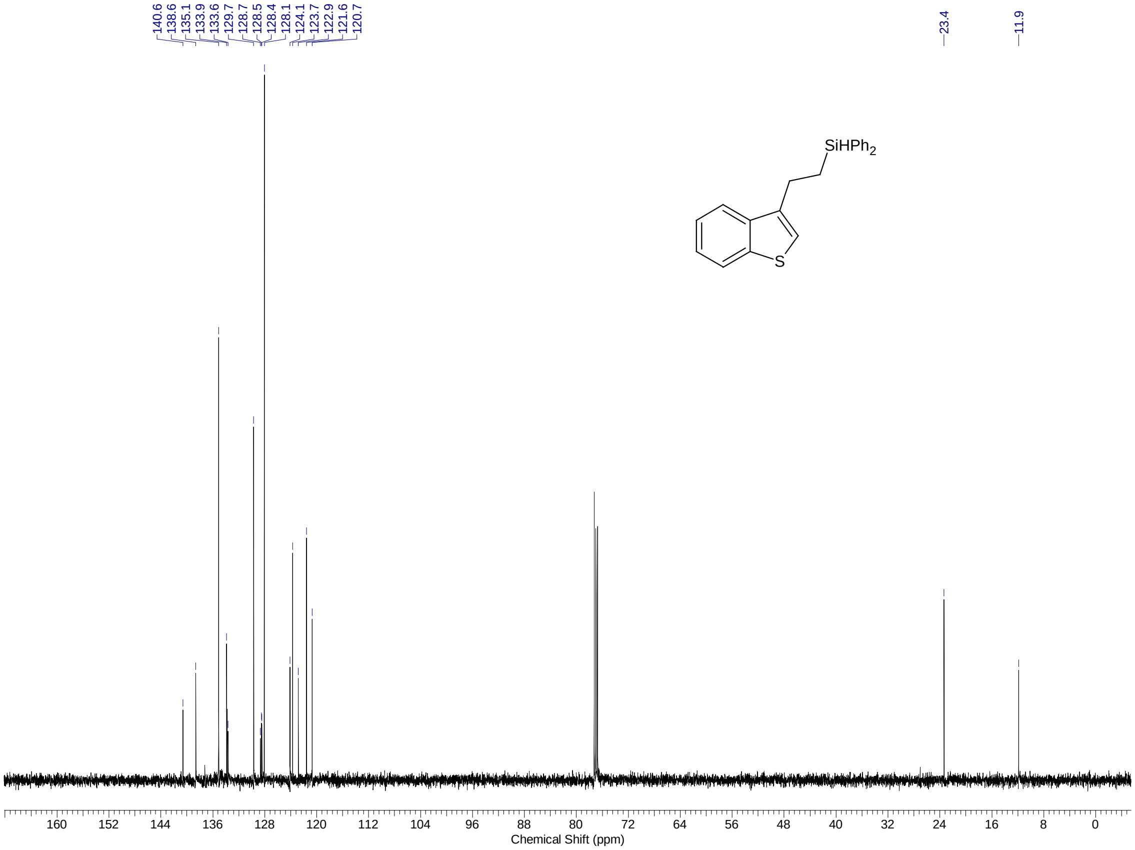

7.60
7.60
7.58
7.43
7.42
7.41
7.39
7.38
6.82
6.82
6.54
6.54
4.91
4.31
4.30
4.28
4.27
3.86
2.64
2.63
2.62
2.62
2.61
1.51
1.51
1.50
1.48
1.47
1.38
1.37
1.35
Ph2Si
H
N
CH3
O
O
CH3
5.87
0.91
1.00
0.93
2.18
3.13
2.26
3.21
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


161.3
135.1
134.2
129.5
127.9
127.1
125.6
122.1
116.7
59.6
36.5
21.3
14.4
13.8
Ph2Si
H
N
CH3
O
O
CH3
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

2dd:

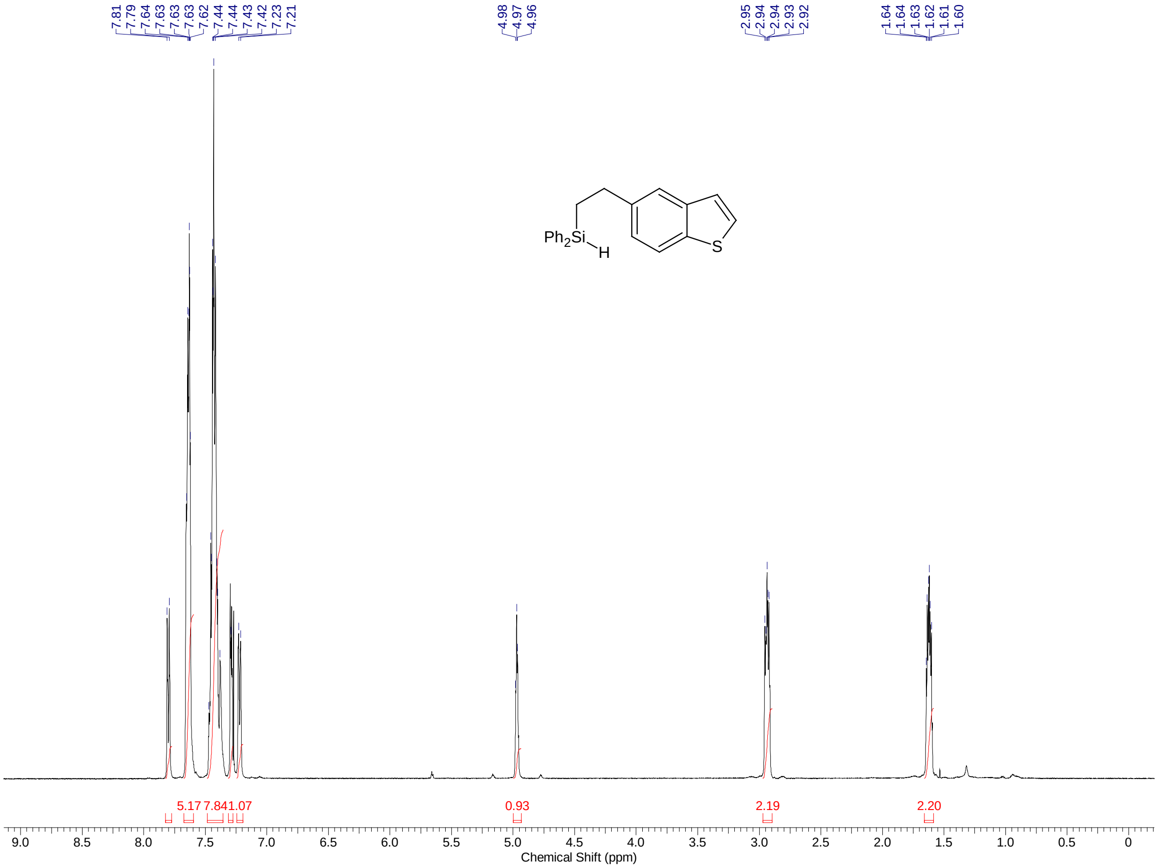


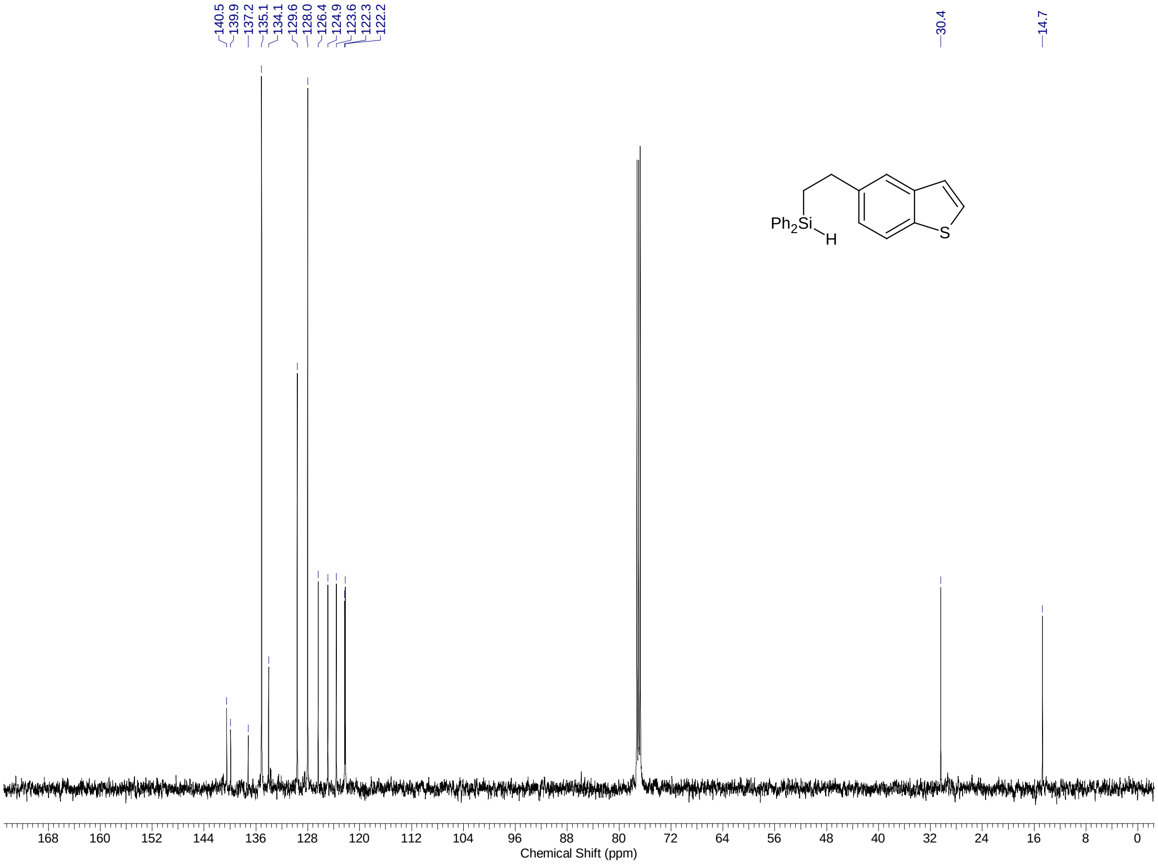
7.89
7.88
7.69
7.66
7.64
7.47
7.45
7.44
7.43
7.42
7.38
7.37
7.13
5.03
5.02
5.01
3.05
3.04
3.04
3.03
3.02
1.72
1.71
1.70
1.68
1.68
SiHPh$_2$
S
1.14
10.30
1.00
0.99
2.30
2.34
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)



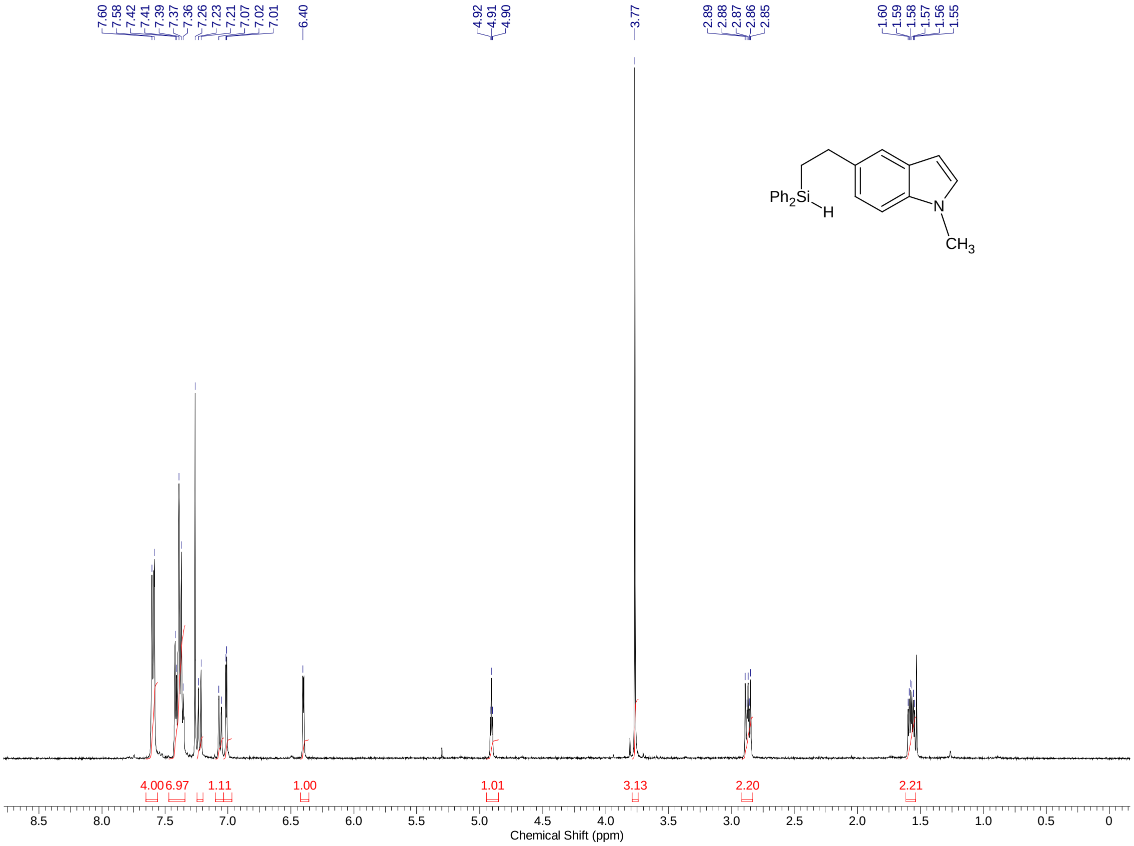
140.6
138.6
135.1
133.9
133.6
129.7
128.7
128.5
128.4
128.1
124.1
123.7
122.9
121.6
120.7
23.4
11.9
SiHPh$_2$
S
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

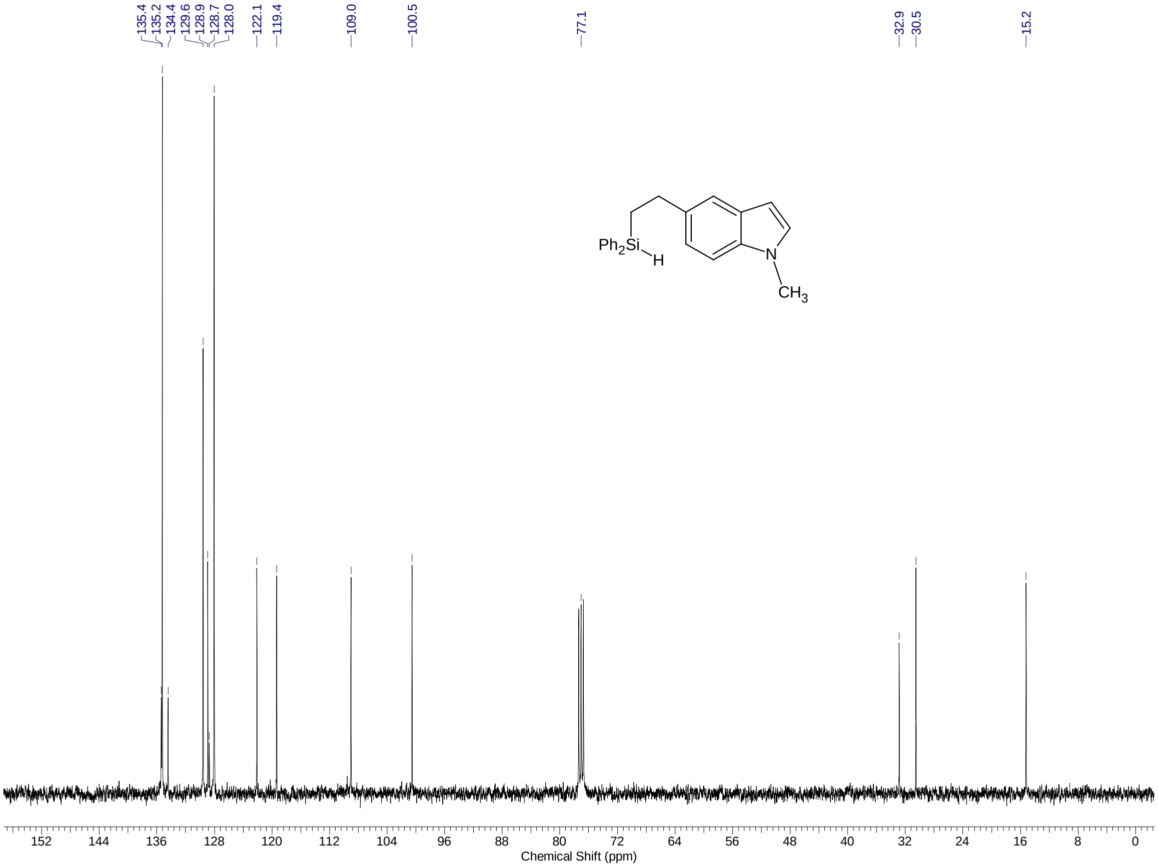
2ee:


7.81
7.79
7.64
7.63
7.63
7.63
7.62
7.44
7.44
7.43
7.42
7.23
7.21
4.98
4.97
4.96
2.95
2.94
2.94
2.93
2.92
1.64
1.64
1.63
1.62
1.61
1.60
Ph2Si
H
S
5.17
7.84
1.07
0.93
2.19
2.20
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

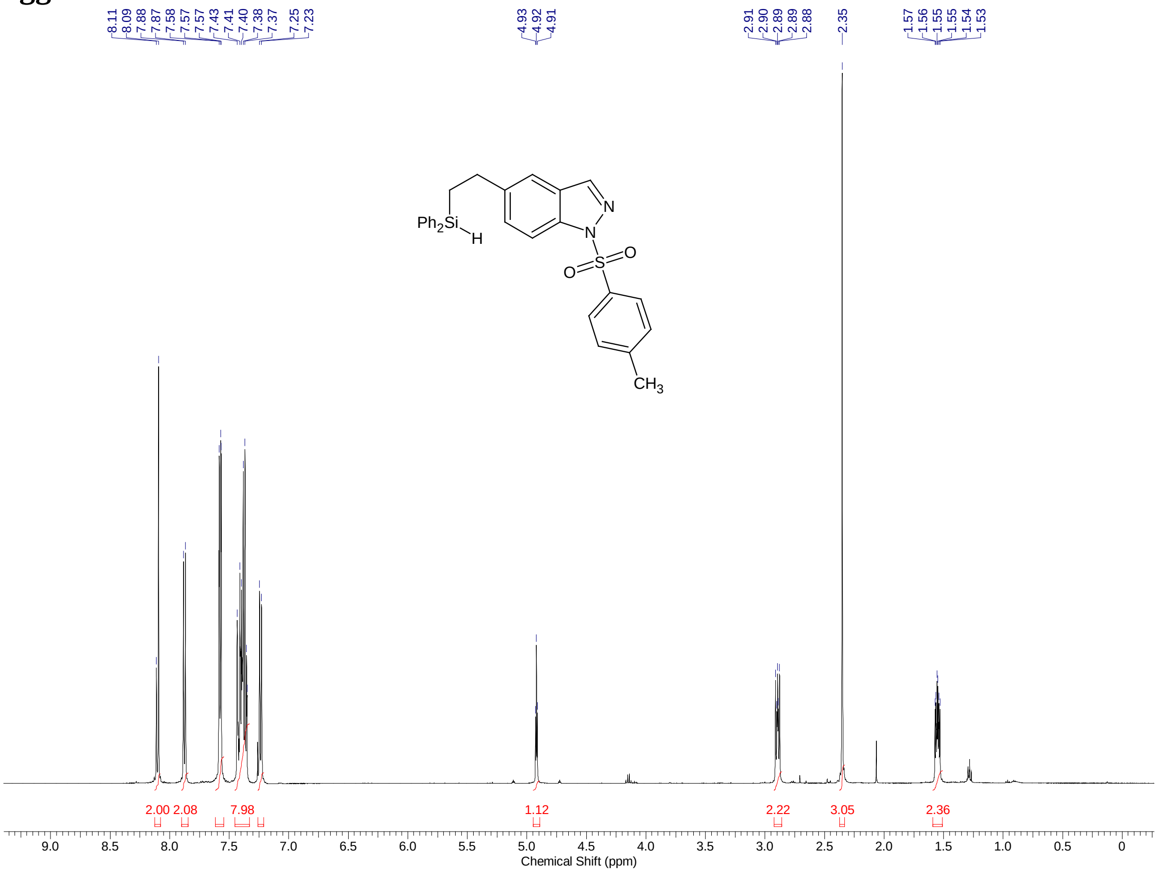

140.5
139.9
137.2
135.1
134.1
129.6
128.0
126.4
124.9
123.6
122.3
122.2
30.4
14.7
Ph2Si
H
S
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

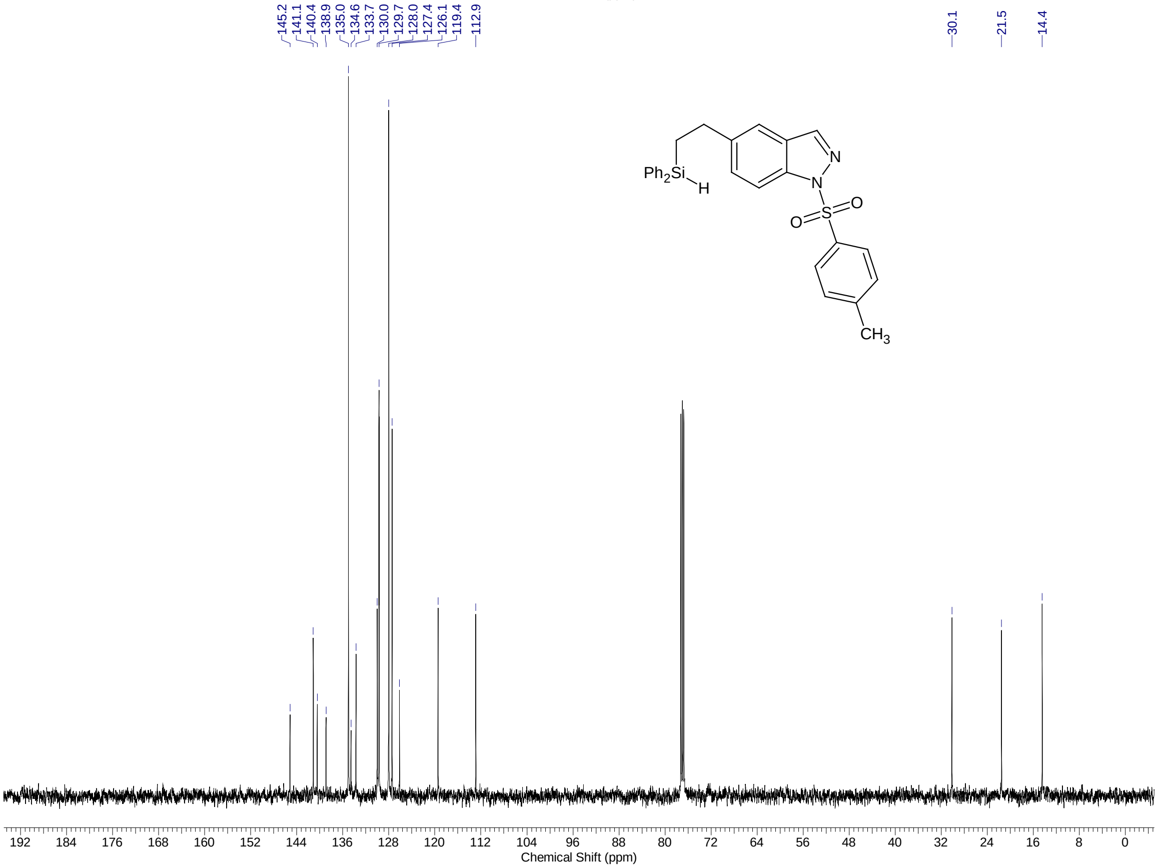
2ff:


7.60
7.58
7.42
7.41
7.39
7.37
7.36
7.26
7.23
7.21
7.07
7.02
7.01
6.40
4.92
4.91
4.90
3.77
2.89
2.88
2.87
2.86
2.85
1.60
1.59
1.58
1.57
1.56
1.55
Ph2Si
H
N
CH3
4.00
6.97
1.11
1.00
1.01
3.13
2.20
2.21
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

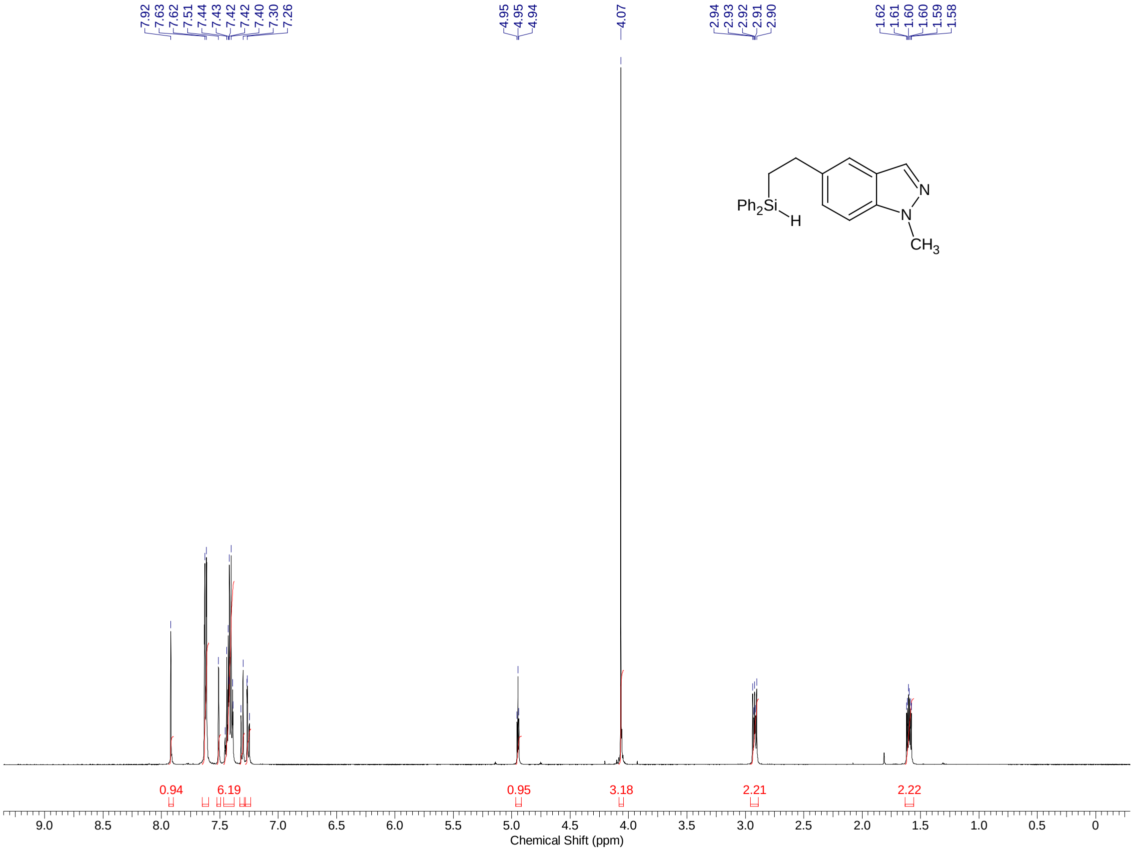

135.4
135.2
134.4
129.6
128.9
128.7
128.0
122.1
119.4
109.0
100.5
77.1
32.9
30.5
15.2
Ph2Si
H
N
CH3
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

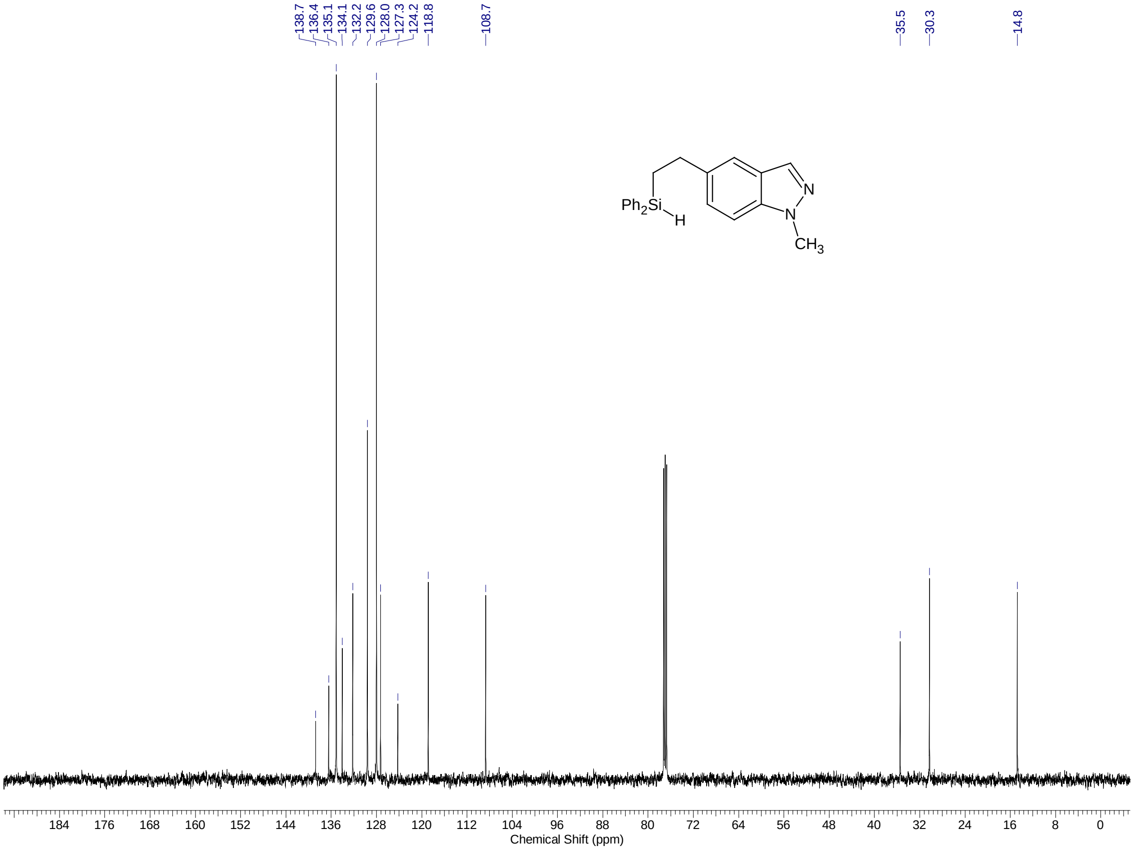
2gg:


8.11
8.09
7.88
7.87
7.58
7.57
7.57
7.43
7.41
7.40
7.38
7.37
7.25
7.23
4.93
4.92
4.91
2.91
2.90
2.89
2.89
2.88
2.35
1.57
1.56
1.55
1.55
1.54
1.53
Ph$_2$Si
H
N
N
S
O
O
CH$_3$
2.00
2.08
7.98
1.12
2.22
3.05
2.36
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

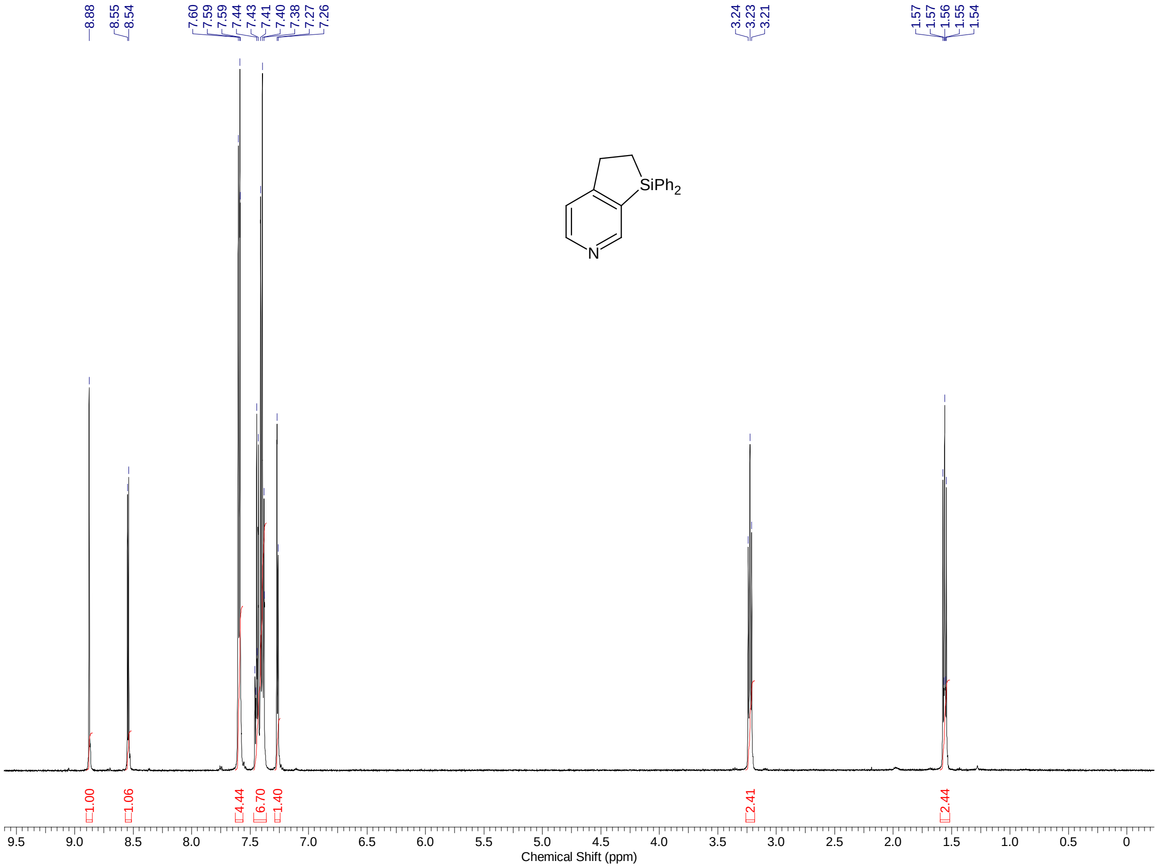

145.2
141.1
140.4
138.9
135.0
134.6
133.7
130.0
129.7
128.0
127.4
126.1
119.4
112.9
30.1
21.5
14.4
Ph$_2$Si
H
N
N
S
O
O
CH$_3$
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

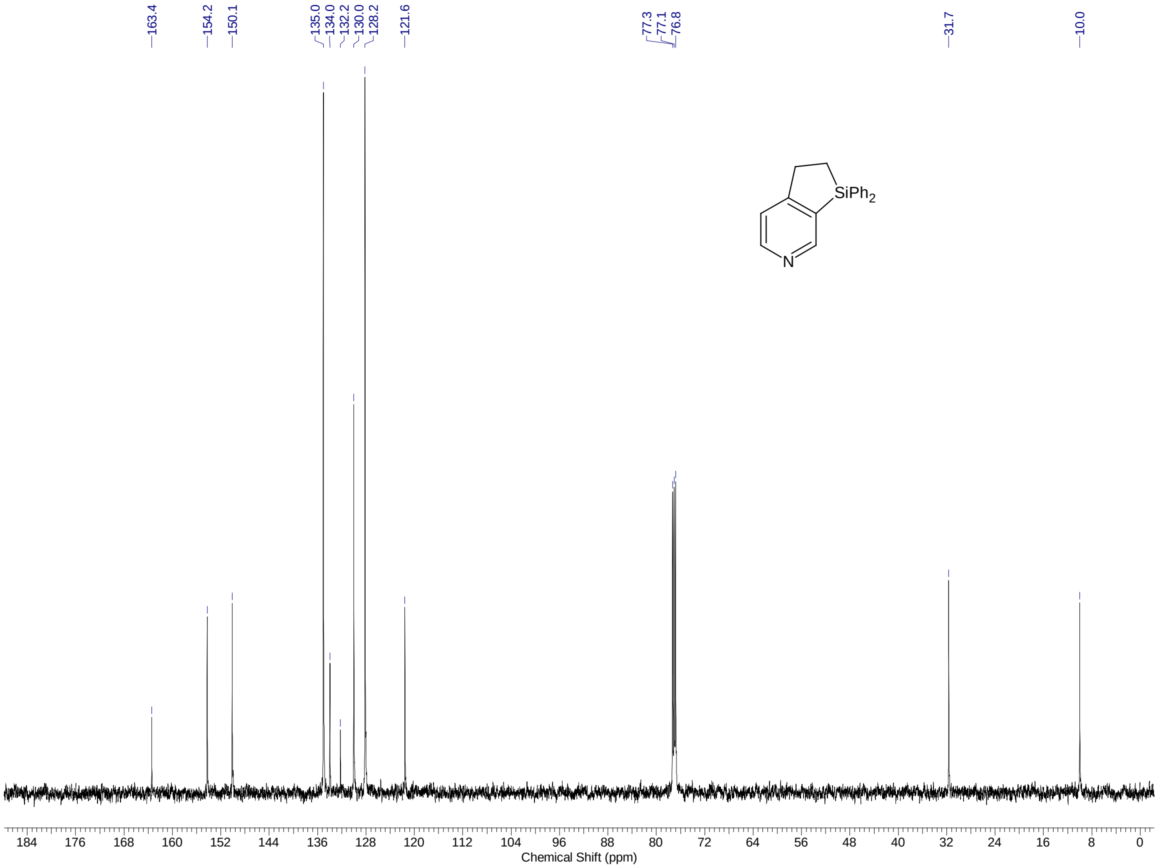
2hh:


7.92
7.63
7.62
7.51
7.44
7.43
7.42
7.42
7.40
7.30
7.26
4.95
4.95
4.94
4.07
2.94
2.93
2.92
2.91
2.90
1.62
1.61
1.60
1.60
1.59
1.58
Ph2Si
H
N
N
CH3
0.94
6.19
0.95
3.18
2.21
2.22
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

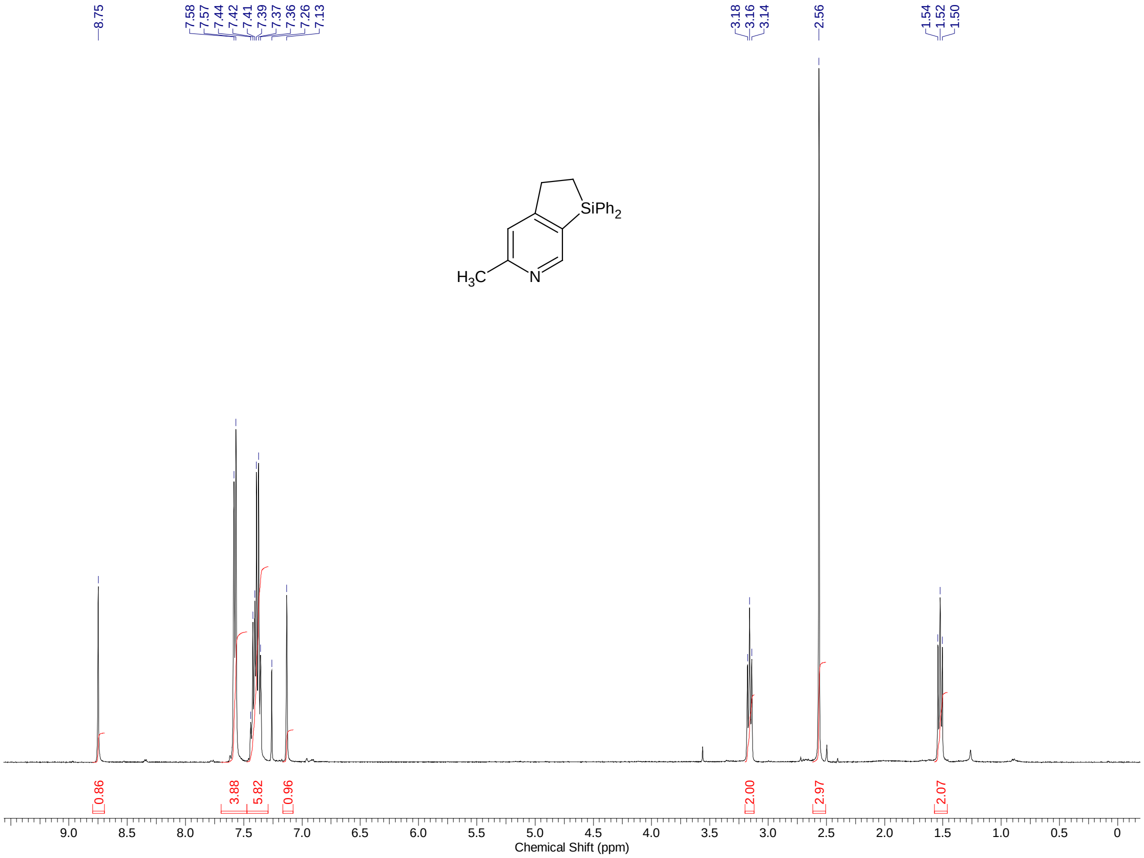

138.7
136.4
135.1
134.1
132.2
129.6
128.0
127.3
124.2
118.8
108.7
35.5
30.3
14.8
Ph2Si
H
N
N
CH3
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

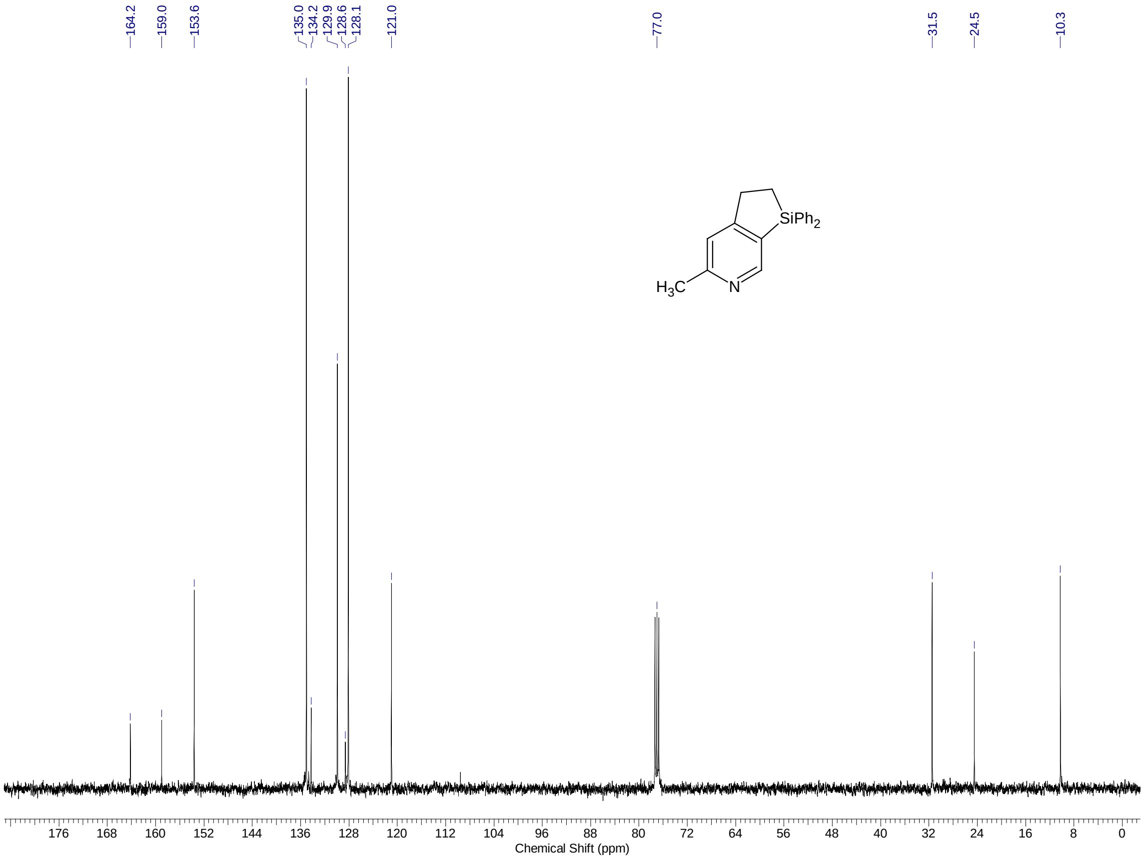
3a:


8.88
8.55
8.54
7.60
7.59
7.59
7.44
7.43
7.41
7.40
7.38
7.27
7.26
3.24
3.23
3.21
1.57
1.57
1.56
1.55
1.54
SiPh2
N
1.00
1.06
4.44
6.70
1.40
2.41
2.44
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

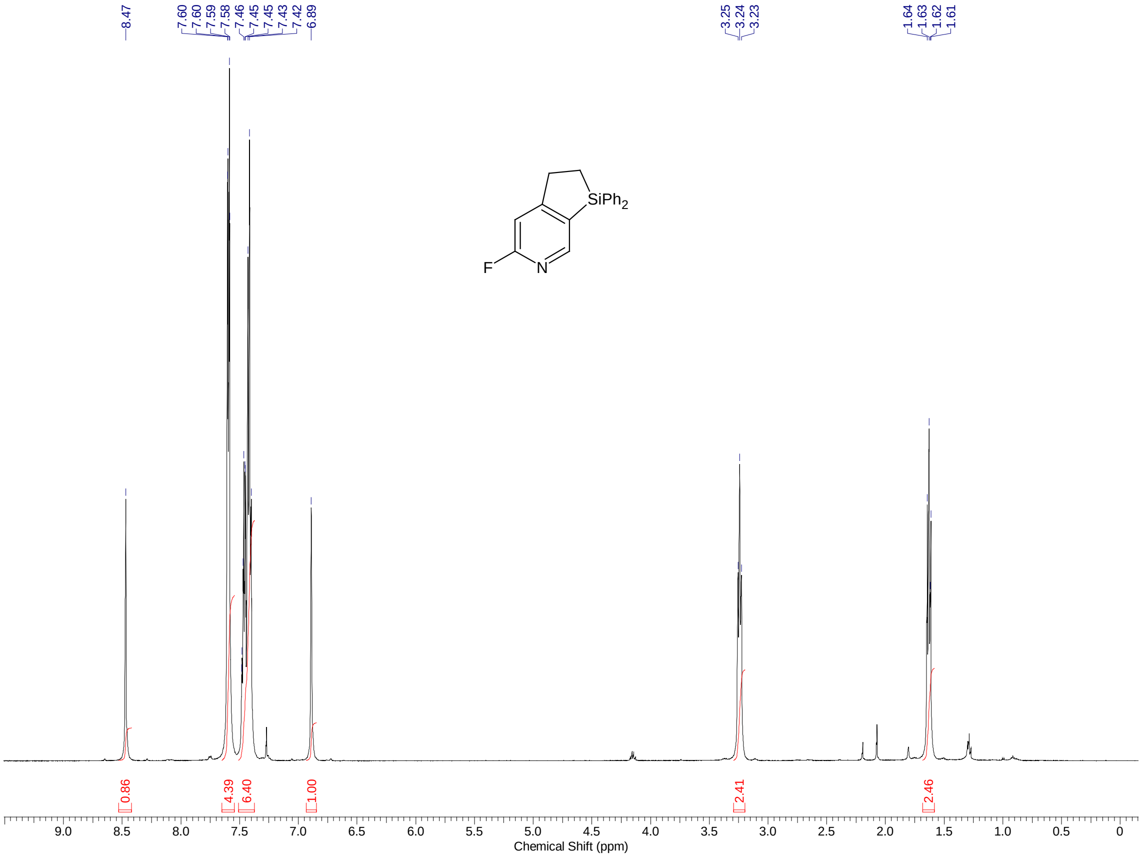

163.4
154.2
150.1
135.0
134.0
132.2
130.0
128.2
121.6
77.3
77.1
76.8
31.7
10.0
SiPh2
N
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

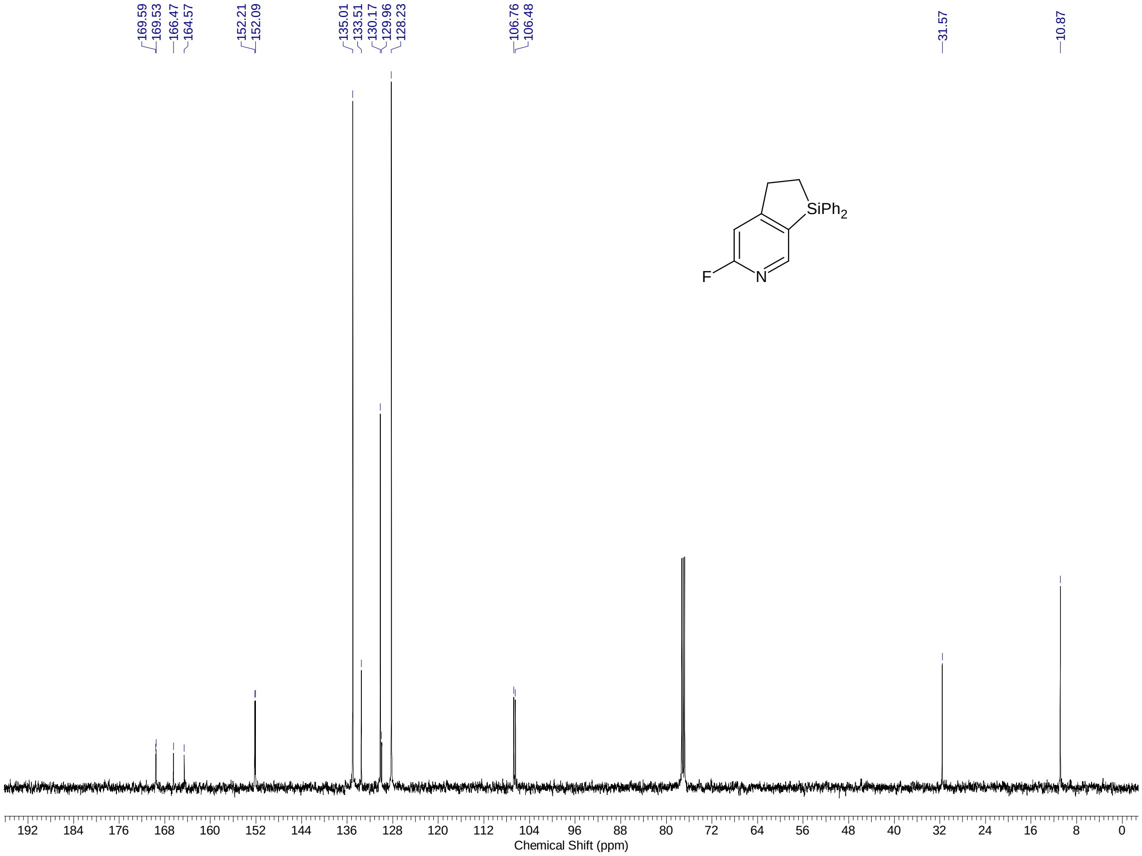
3b:


8.75
7.58
7.57
7.44
7.42
7.41
7.39
7.37
7.36
7.26
7.13
3.18
3.16
3.14
2.56
1.54
1.52
1.50
SiPh2
H3C
N
0.86
3.88
5.82
0.96
2.00
2.97
2.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

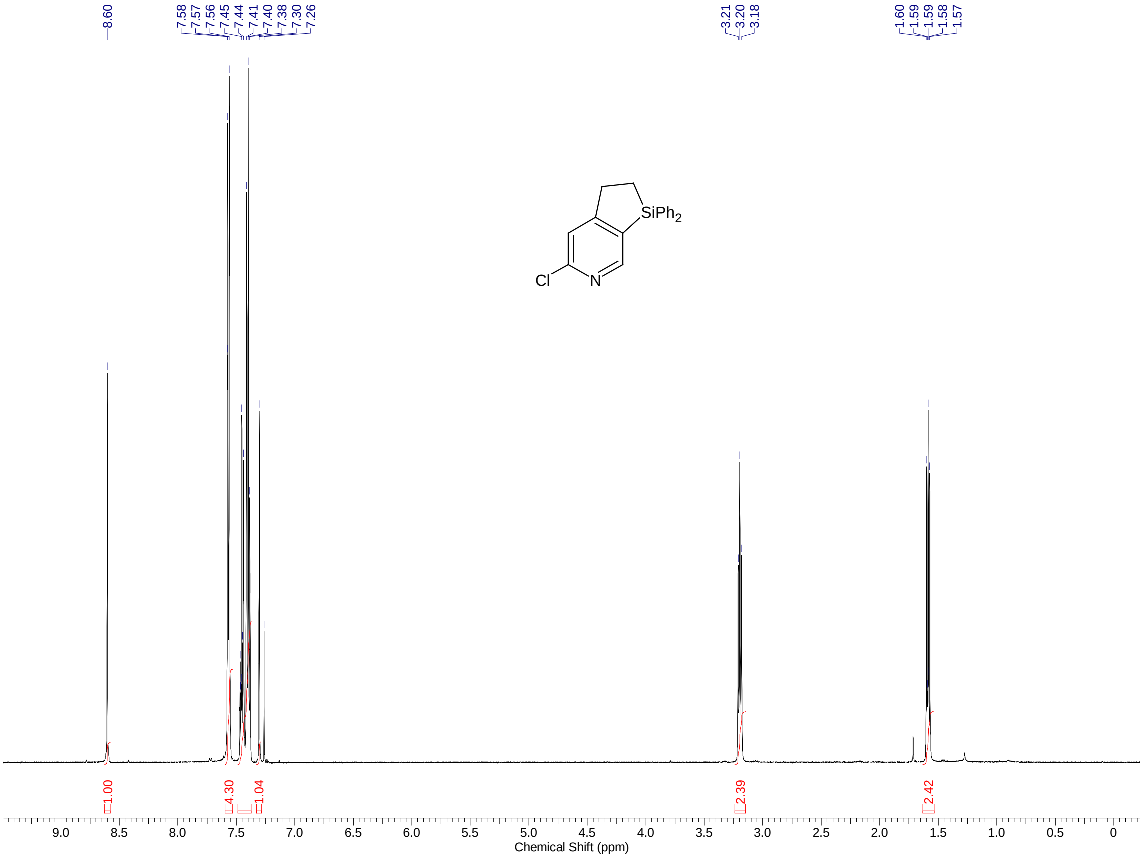

164.2
159.0
153.6
135.0
134.2
129.9
128.6
128.1
121.0
77.0
31.5
24.5
10.3
SiPh2
H3C
N
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

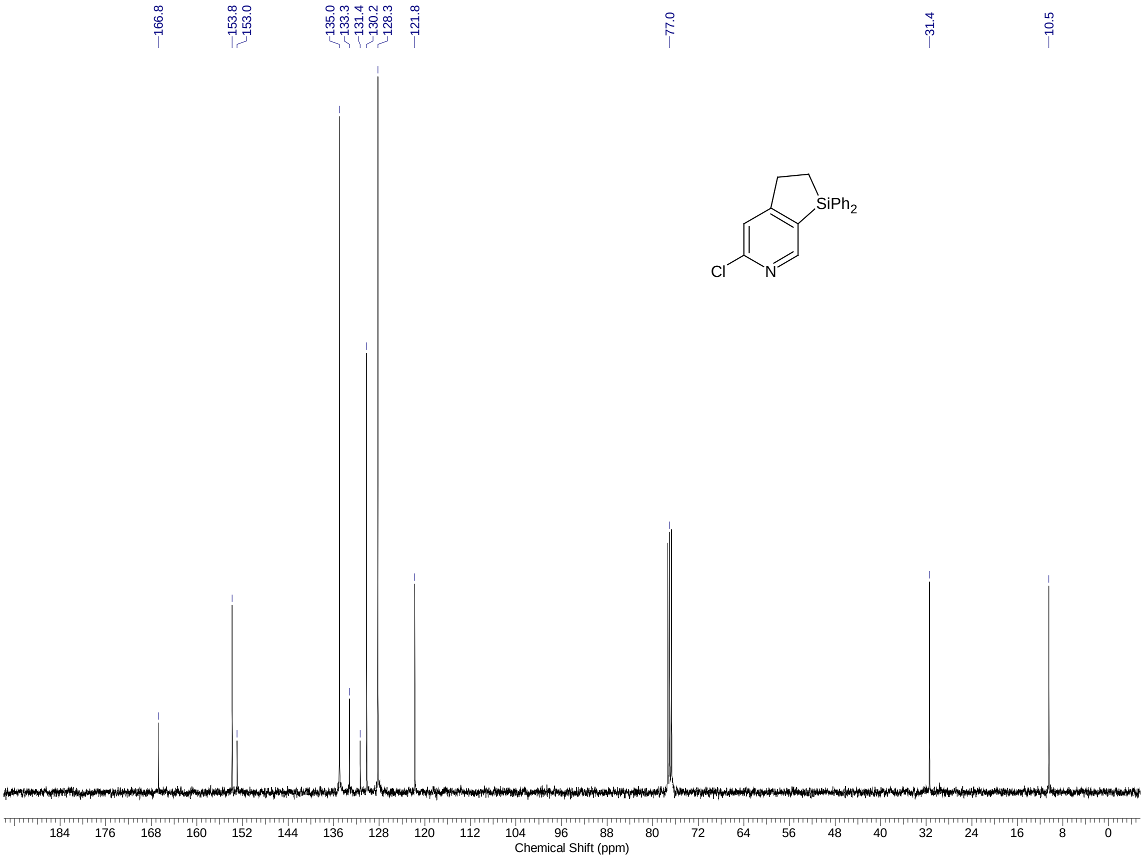
3c:


8.47
7.60
7.60
7.59
7.58
7.46
7.45
7.45
7.43
7.42
6.89
3.25
3.24
3.23
1.64
1.63
1.62
1.61
SiPh$_2$
F
N
0.86
4.39
6.40
1.00
2.41
2.46
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

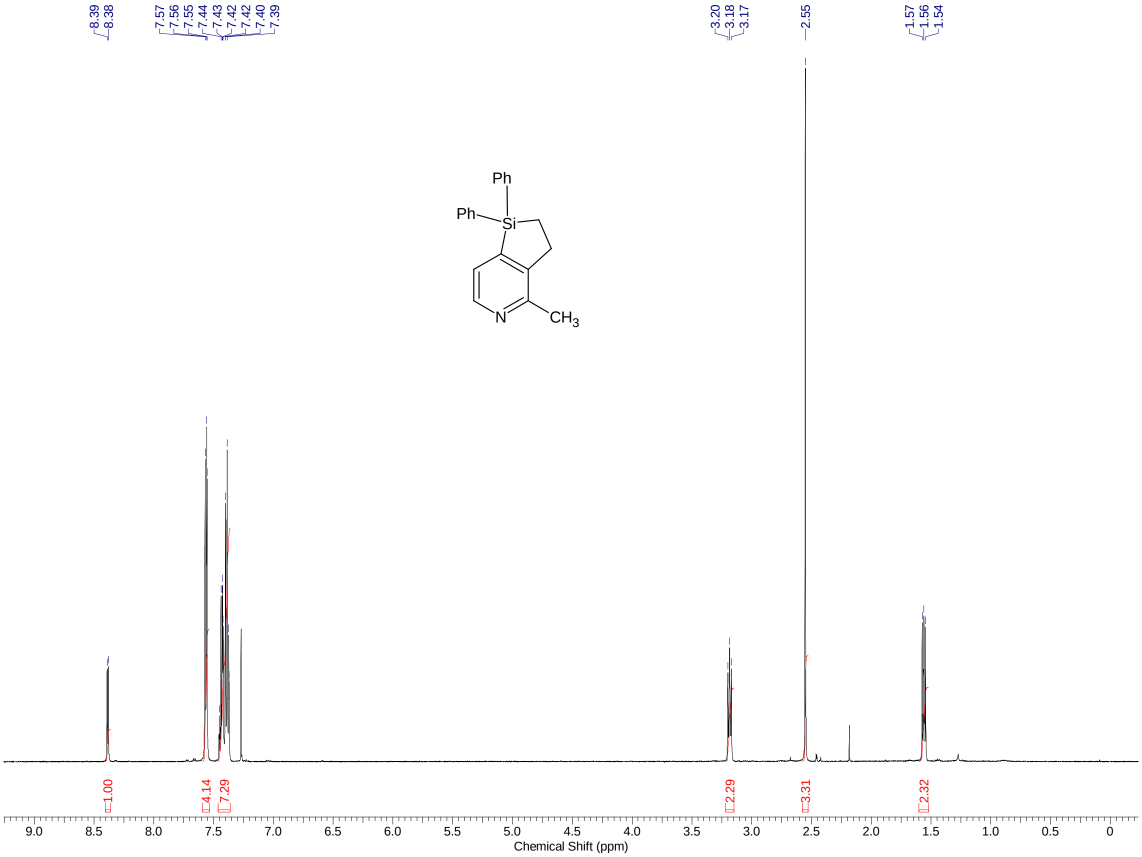

169.59
169.53
166.47
164.57
152.21
152.09
135.01
133.51
130.17
129.96
128.23
106.76
106.48
31.57
10.87
SiPh$_2$
F
N
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

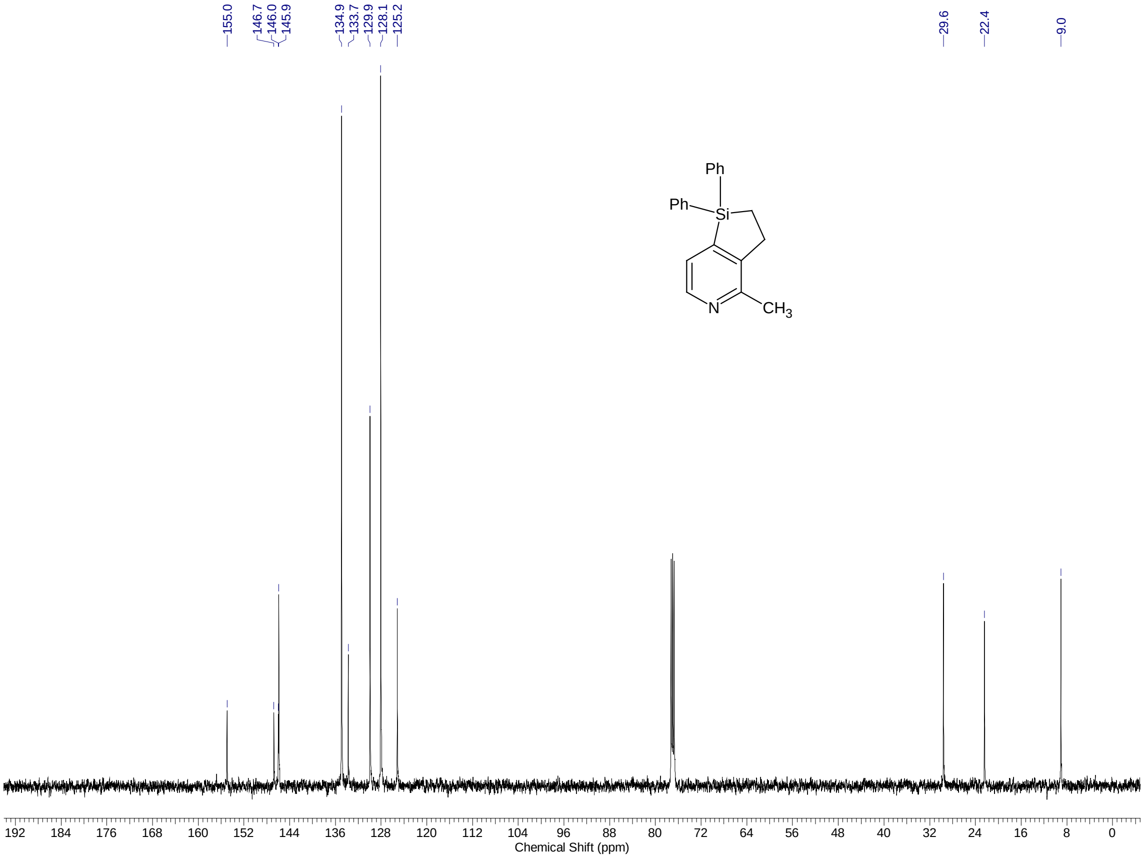
3d:


8.60
7.58
7.57
7.56
7.45
7.44
7.41
7.40
7.38
7.30
7.26
3.21
3.20
3.18
1.60
1.59
1.59
1.58
1.57
SiPh2
Cl
N
1.00
4.30
1.04
2.39
2.42
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

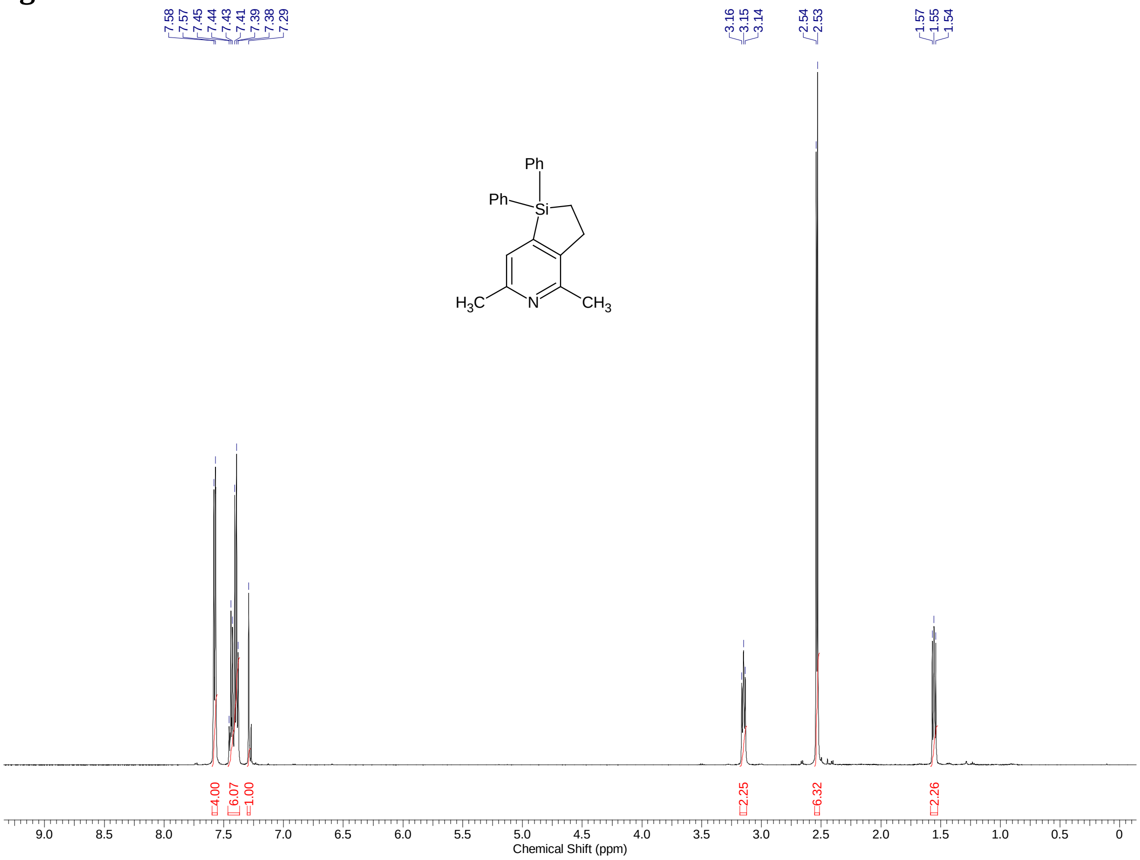

166.8
153.8
153.0
135.0
133.3
131.4
130.2
128.3
121.8
77.0
31.4
10.5
SiPh2
Cl
N
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

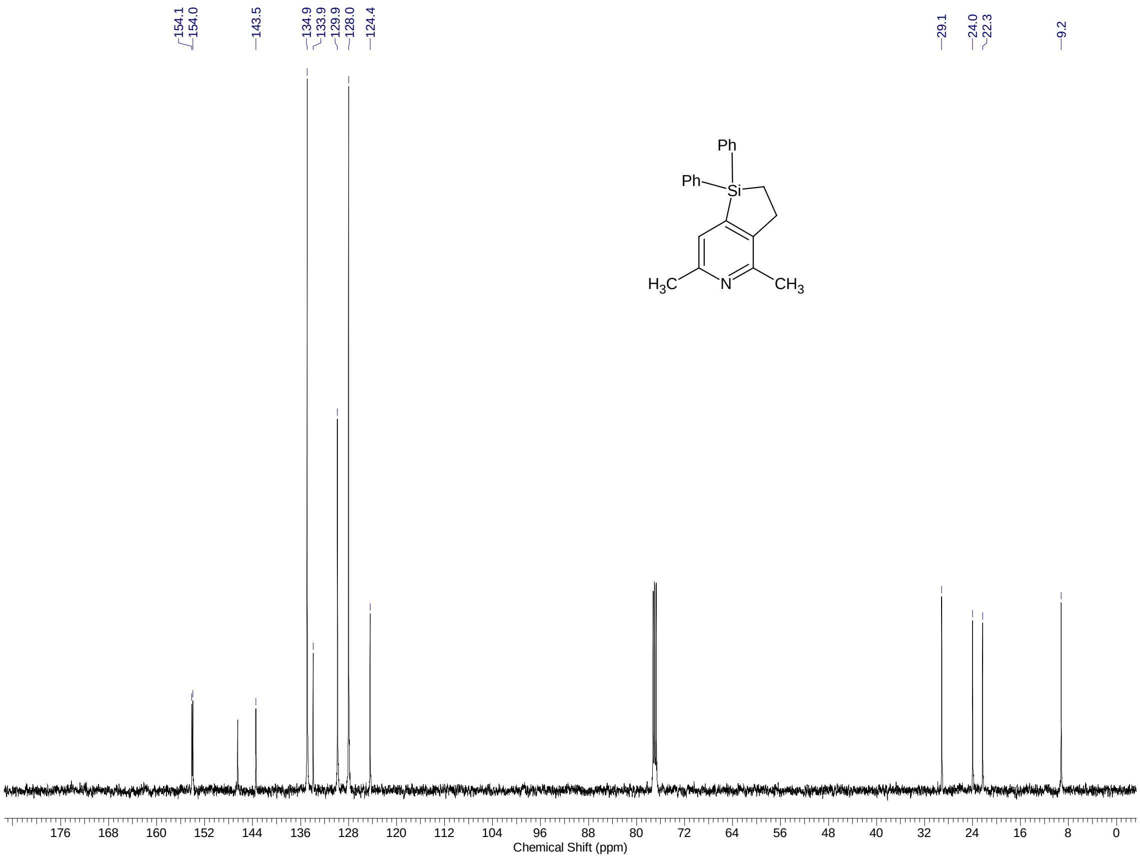
3f:


8.39
8.38
7.57
7.56
7.55
7.44
7.43
7.42
7.42
7.40
7.39
3.20
3.18
3.17
2.55
1.57
1.56
1.54
Ph
Ph
Si
N
CH3
1.00
4.14
7.29
2.29
3.31
2.32
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

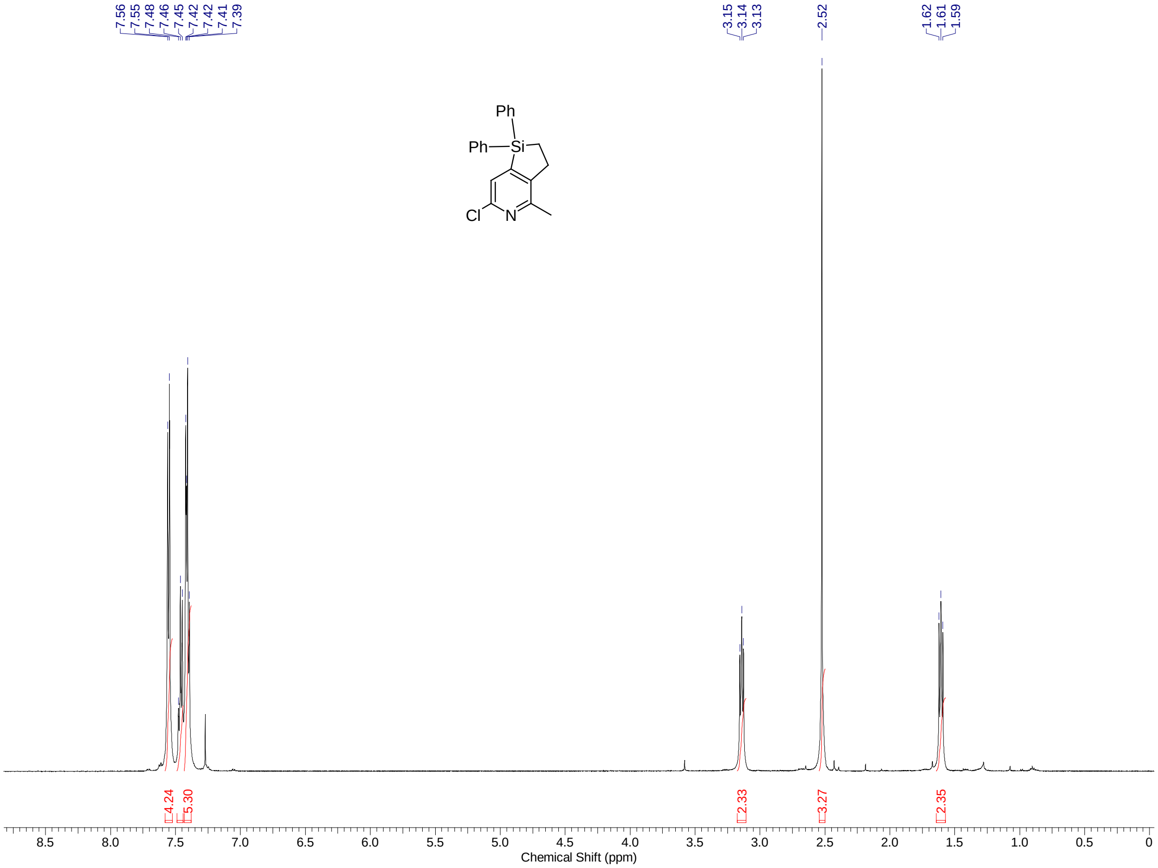

155.0
146.7
146.0
145.9
134.9
133.7
129.9
128.1
125.2
29.6
22.4
9.0
Ph
Ph
Si
N
CH3
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

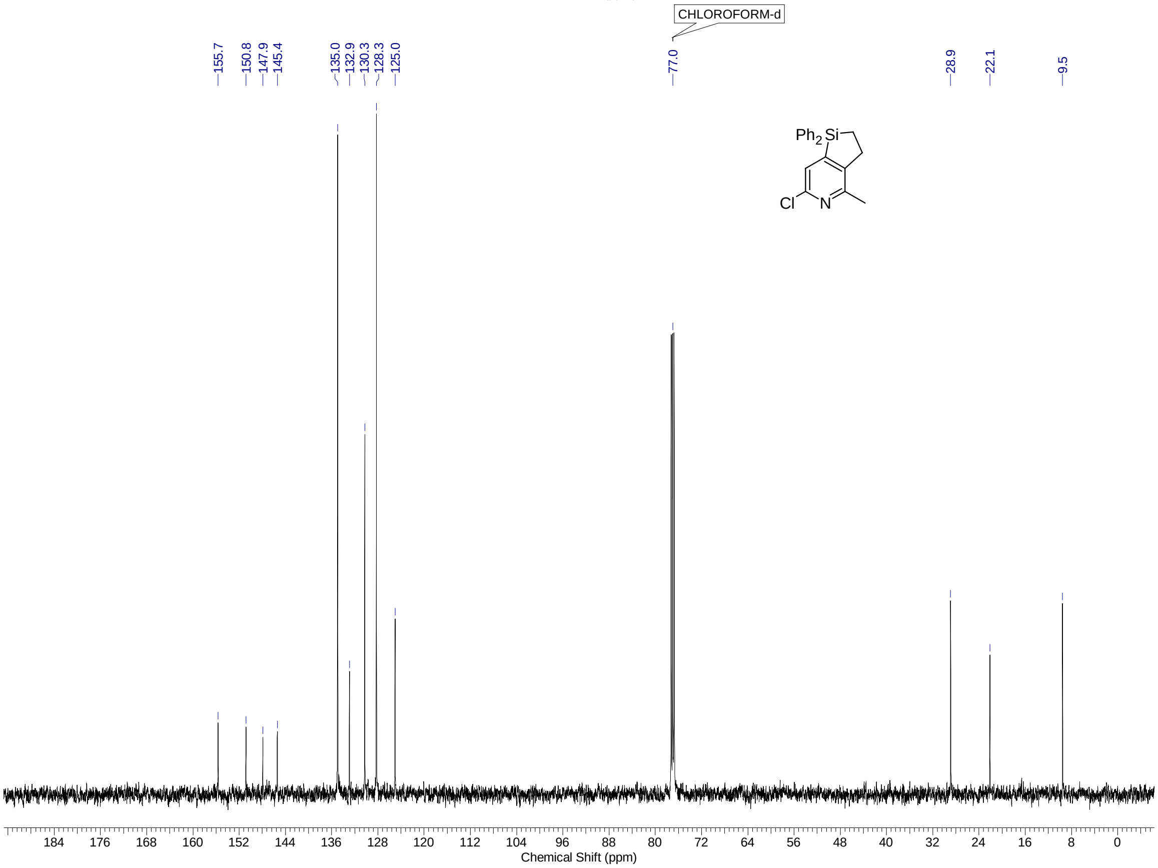
3g:


7.58
7.57
7.45
7.44
7.43
7.41
7.39
7.38
7.29
3.16
3.15
3.14
2.54
2.53
1.57
1.55
1.54
Ph
Ph
Si
H_3C
N
CH_3
4.00
6.07
1.00
2.25
6.32
2.26
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

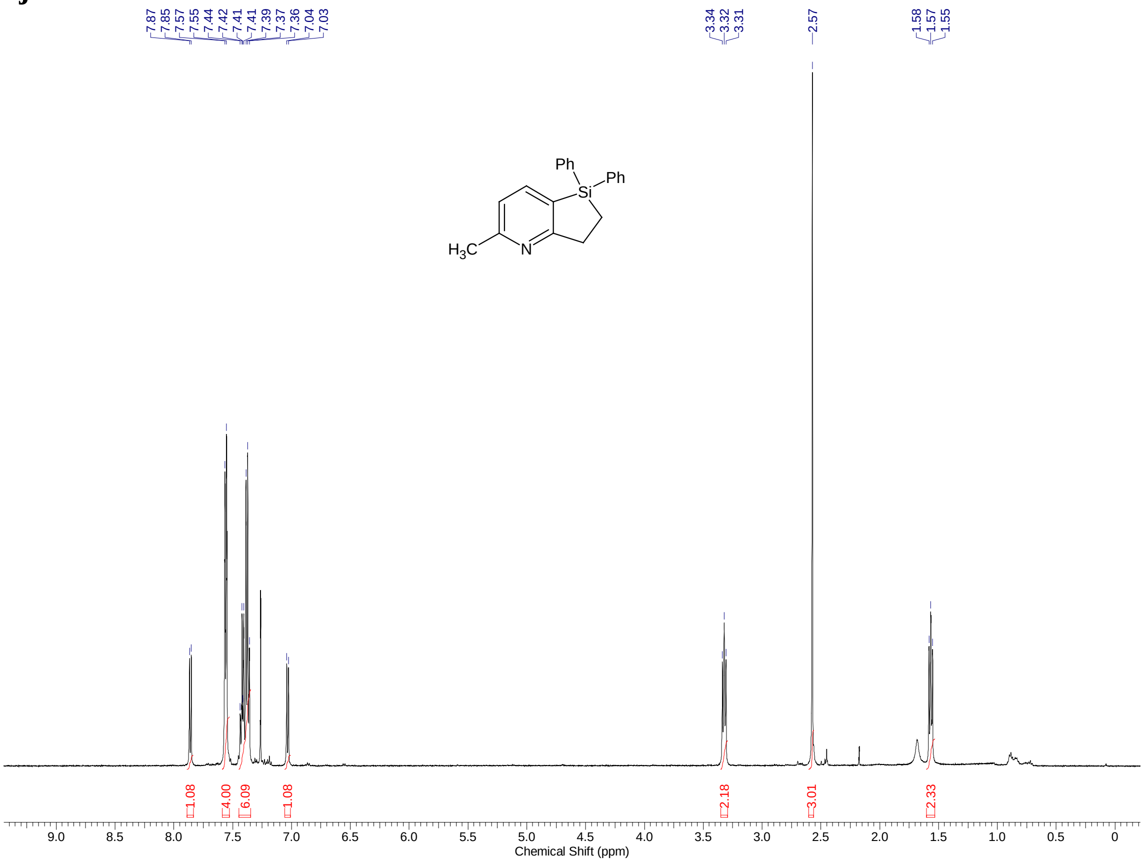

154.1
154.0
143.5
134.9
133.9
129.9
128.0
124.4
29.1
24.0
22.3
9.2
Ph
Ph
Si
H_3C
N
CH_3
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

3h:

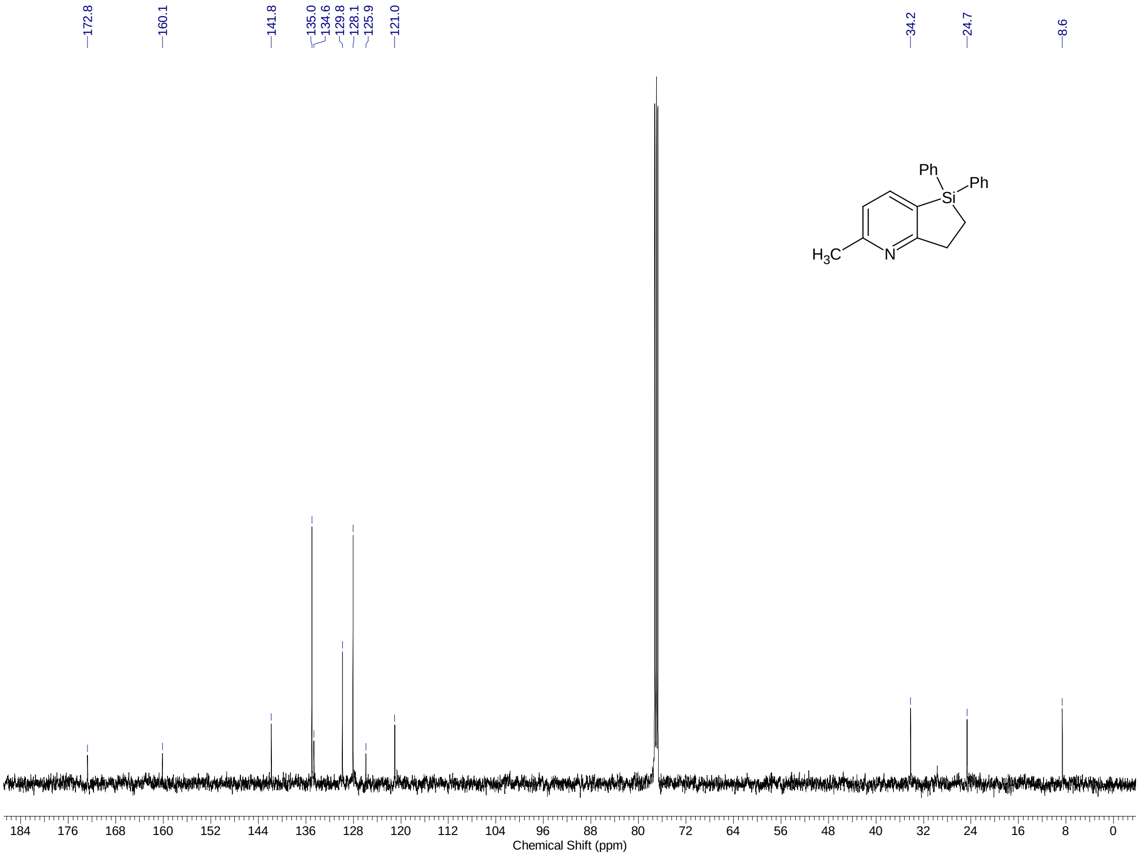

7.56
7.55
7.48
7.46
7.45
7.42
7.42
7.41
7.39
3.15
3.14
3.13
2.52
1.62
1.61
1.59
Ph
Ph
Si
Cl
N
4.24
5.30
2.33
3.27
2.35
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


CHLOROFORM-d
155.7
150.8
147.9
145.4
135.0
132.9
130.3
128.3
125.0
77.0
28.9
22.1
9.5
Ph2Si
Cl
N
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

3j:

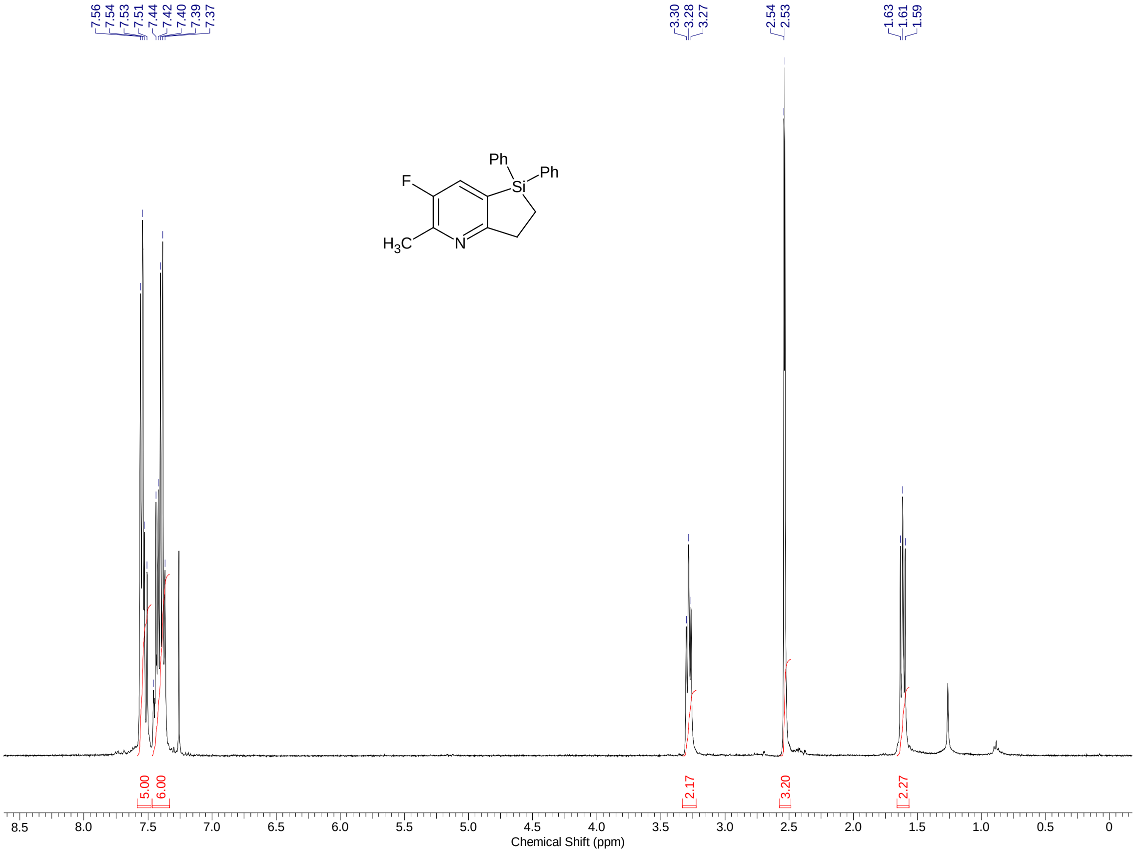


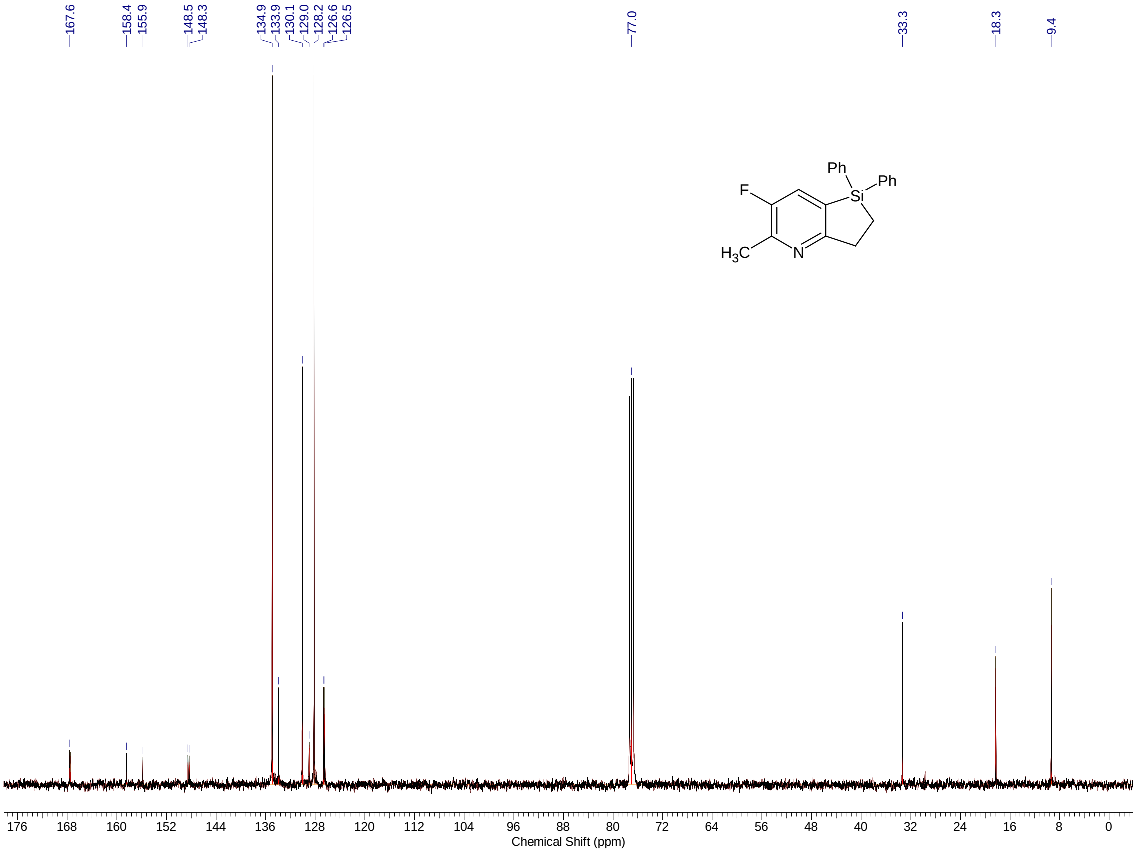
7.87
7.85
7.57
7.55
7.44
7.42
7.41
7.41
7.39
7.37
7.36
7.04
7.03
3.34
3.32
3.31
2.57
1.58
1.57
1.55
Ph
Ph
Si
N
H3C
1.08
4.00
6.09
1.08
2.18
3.01
2.33
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)



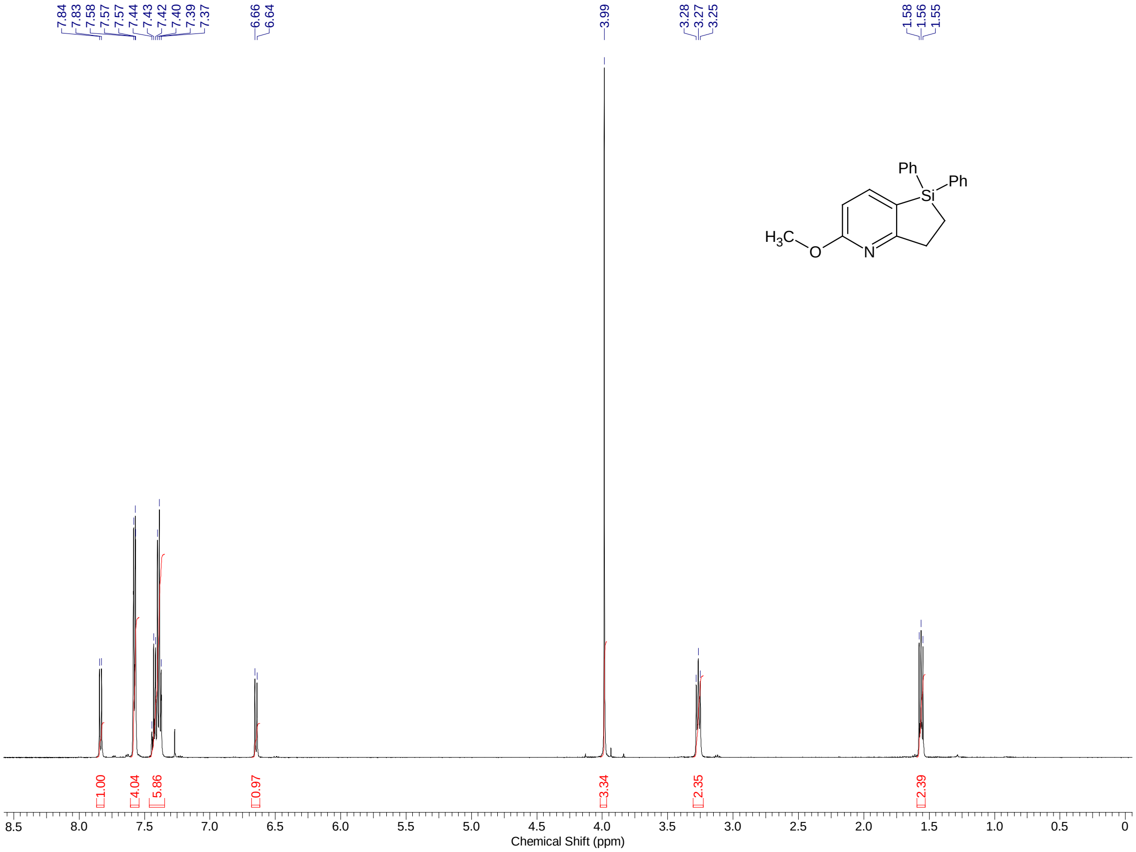
172.8
160.1
141.8
135.0
134.6
129.8
128.1
125.9
121.0
34.2
24.7
8.6
Ph
Ph
Si
N
H3C
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

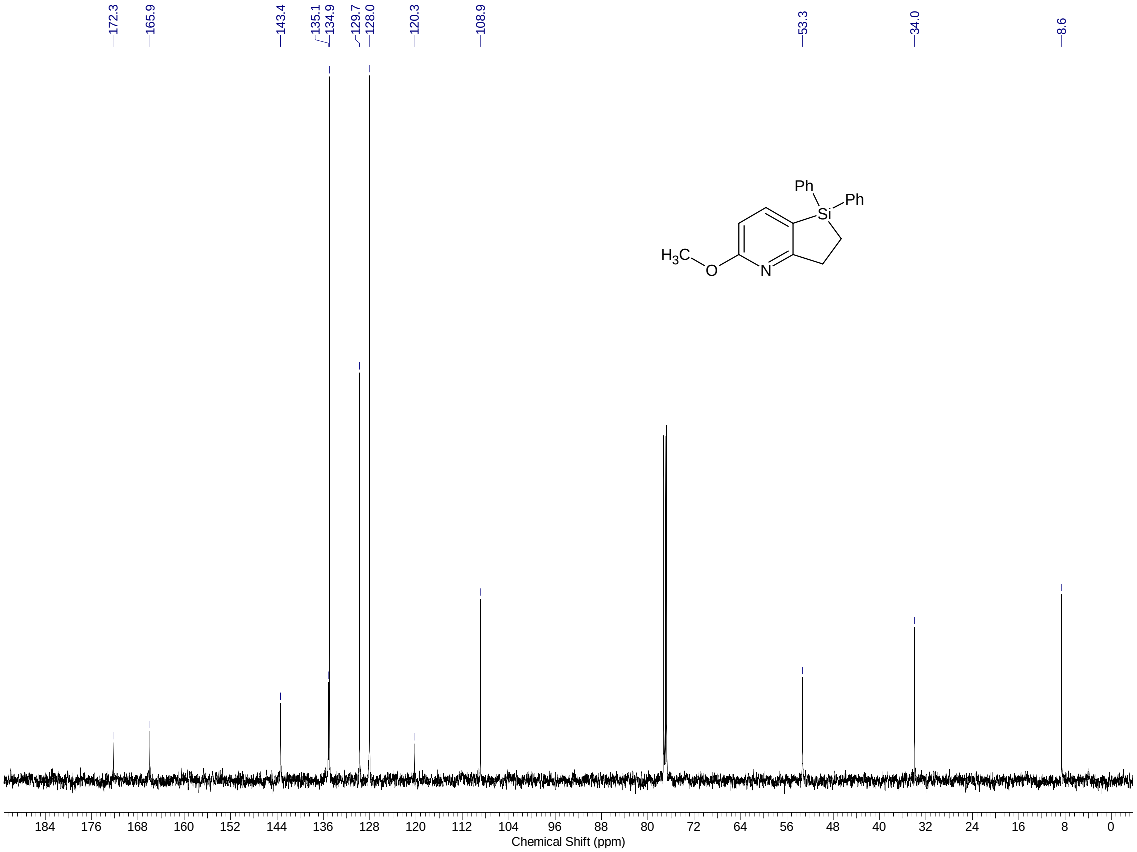
3k:


7.56
7.54
7.53
7.51
7.44
7.42
7.40
7.39
7.37
3.30
3.28
3.27
2.54
2.53
1.63
1.61
1.59
F
Ph
Ph
Si
H_3C
N
5.00
6.00
2.17
3.20
2.27
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

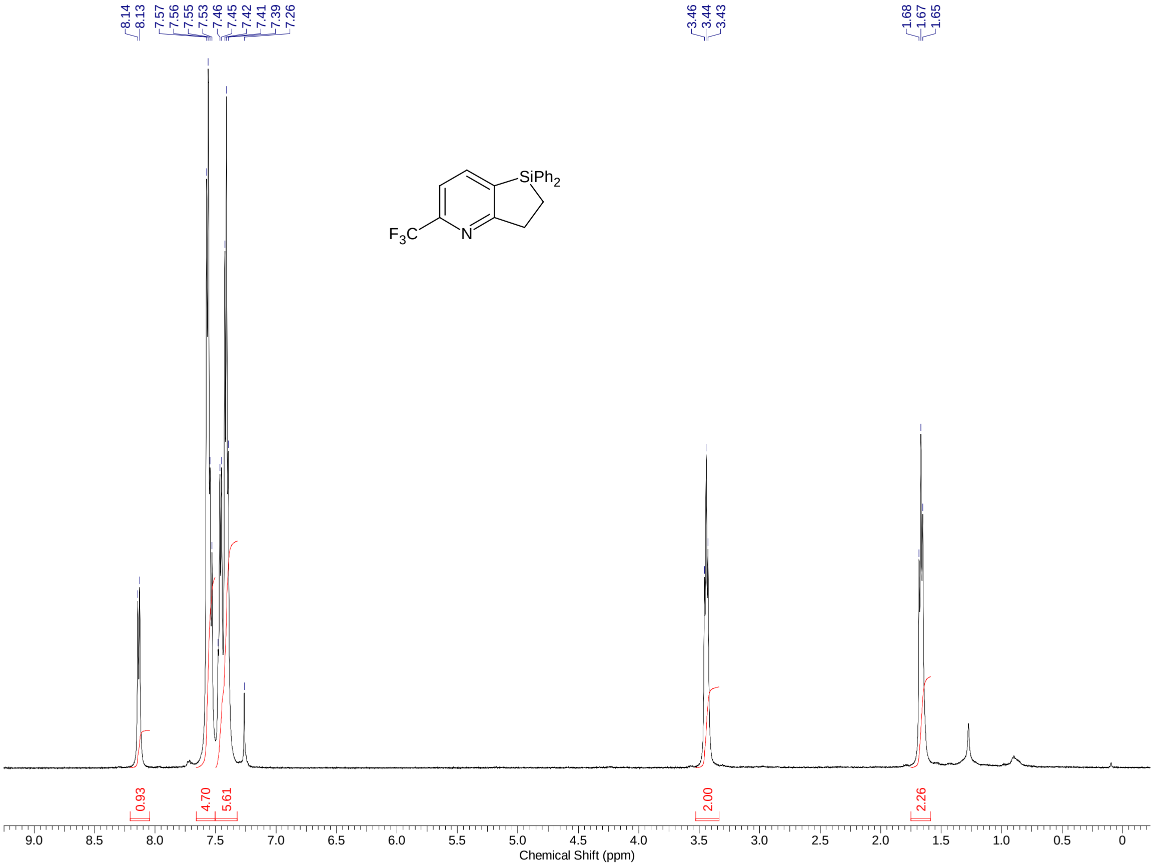

167.6
158.4
155.9
148.5
148.3
134.9
133.9
130.1
129.0
128.2
126.6
126.5
77.0
33.3
18.3
9.4
F
Ph
Ph
Si
H_3C
N
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

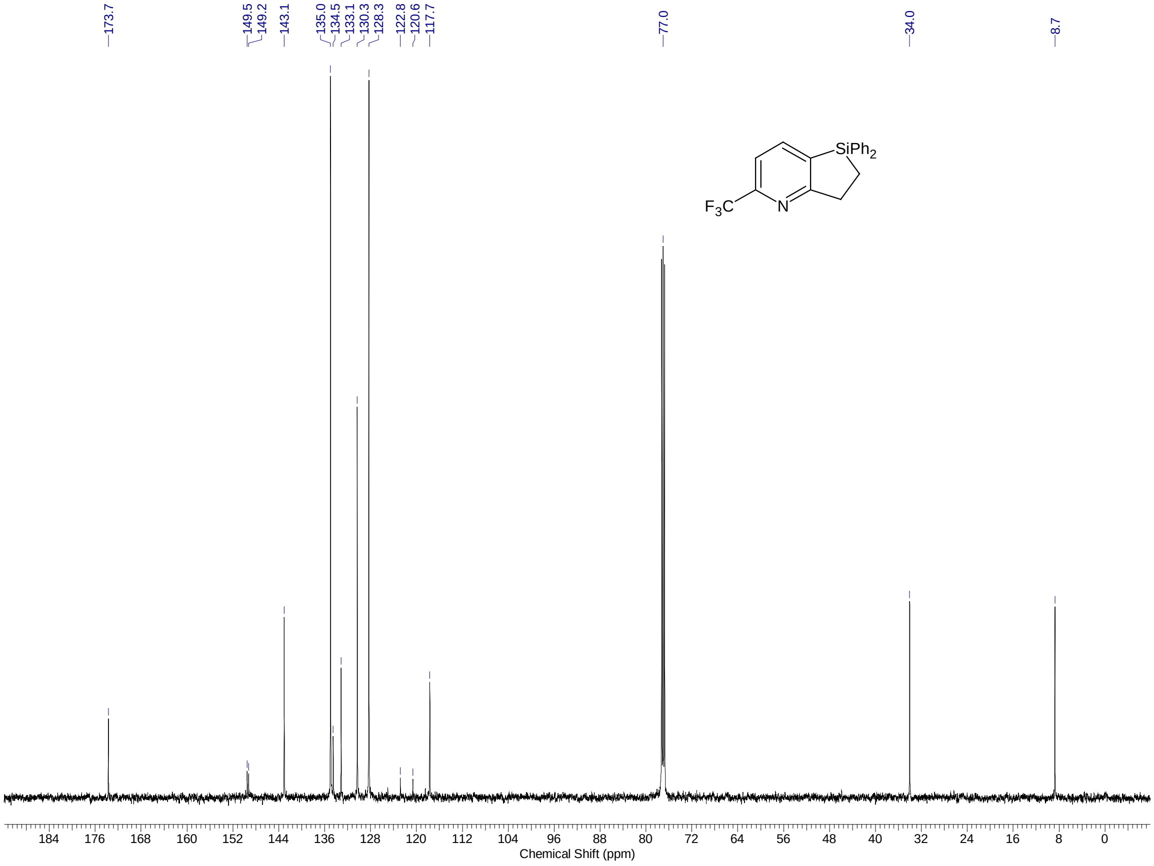
3l:


7.84
7.83
7.58
7.57
7.57
7.44
7.43
7.42
7.40
7.39
7.37
6.66
6.64
3.99
3.28
3.27
3.25
1.58
1.56
1.55
1.00
4.04
5.86
0.97
3.34
2.35
2.39
Ph
Ph
Si
H_3C
O
N
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

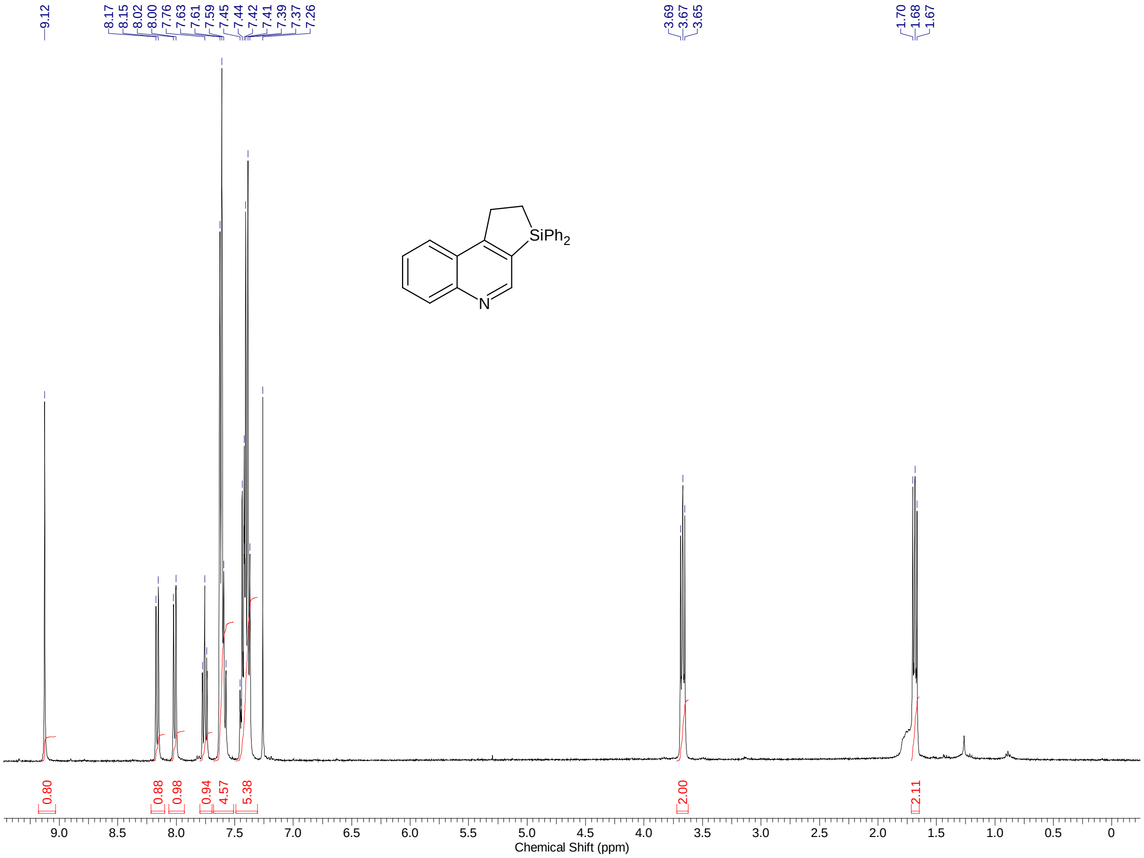

172.3
165.9
143.4
135.1
134.9
129.7
128.0
120.3
108.9
53.3
34.0
8.6
Ph
Ph
Si
H_3C
O
N
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

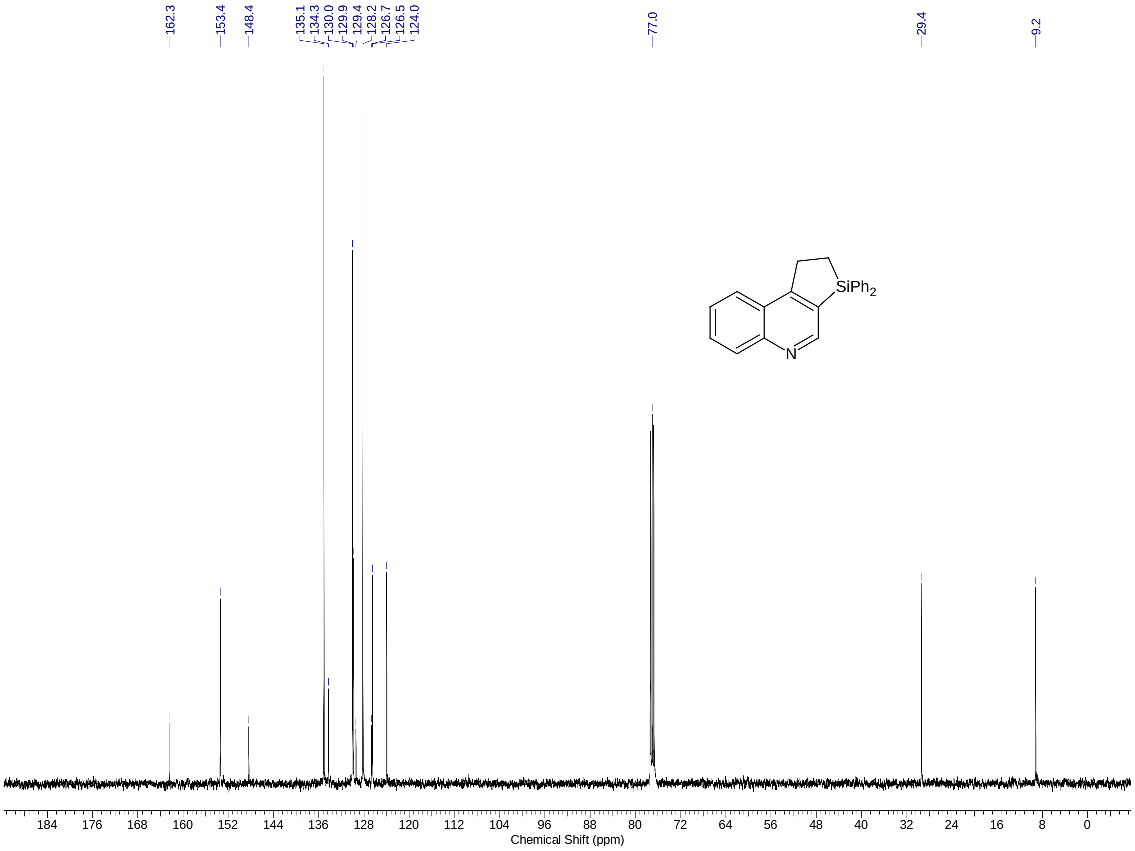
3m:


8.14
8.13
7.57
7.56
7.55
7.53
7.46
7.45
7.42
7.41
7.39
7.26
3.46
3.44
3.43
1.68
1.67
1.65
SiPh$_2$
F$_3$C
N
0.93
4.70
5.61
2.00
2.26
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

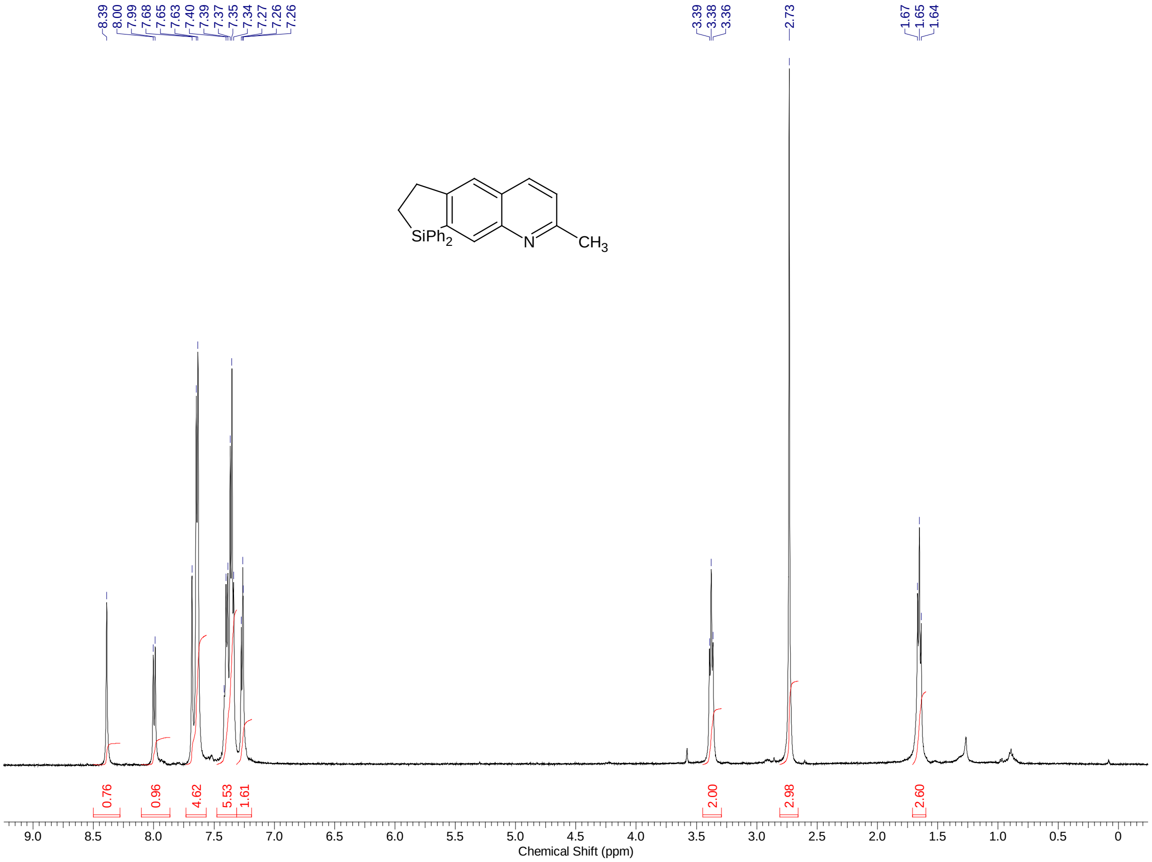

173.7
149.5
149.2
143.1
135.0
134.5
133.1
130.3
128.3
122.8
120.6
117.7
77.0
34.0
8.7
SiPh$_2$
F$_3$C
N
184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

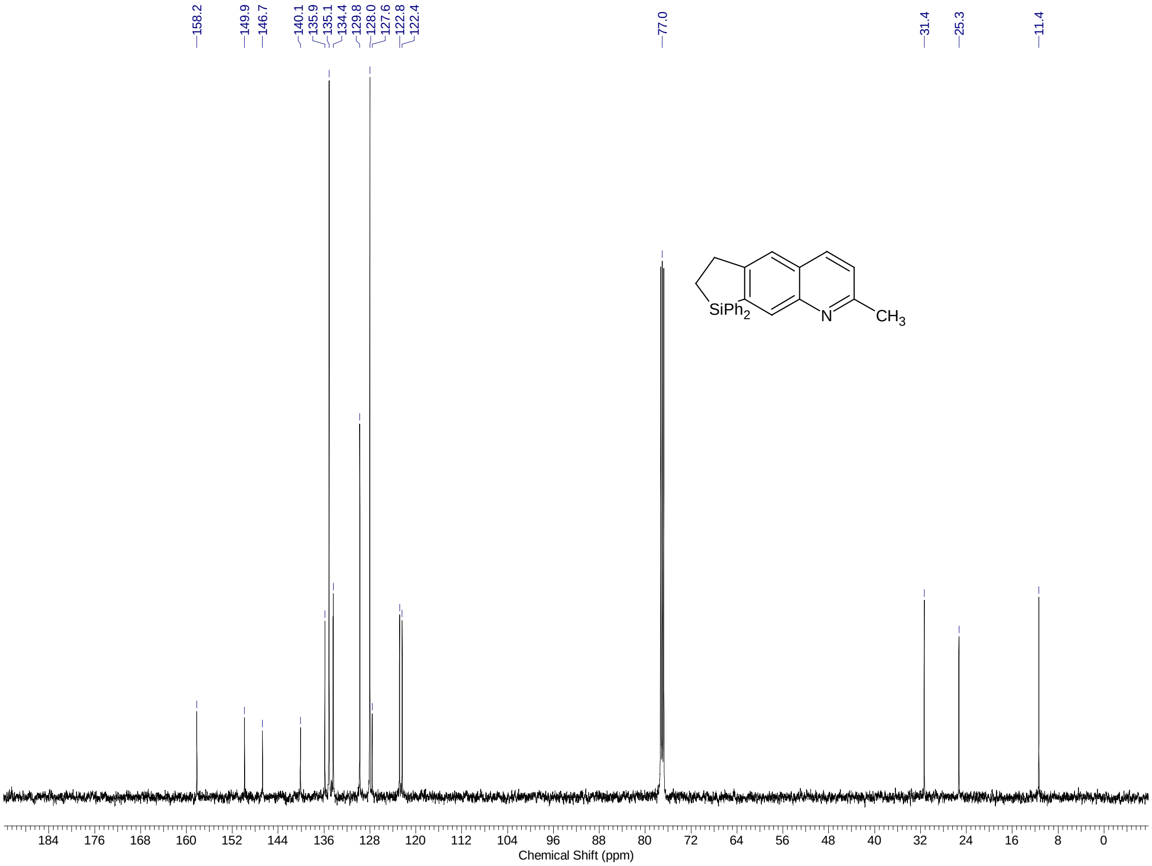
3n:


9.12
8.17
8.15
8.02
8.00
7.76
7.63
7.61
7.59
7.45
7.44
7.42
7.41
7.39
7.37
7.26
3.69
3.67
3.65
1.70
1.68
1.67
SiPh2
N
0.80
0.88
0.98
0.94
4.57
5.38
2.00
2.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

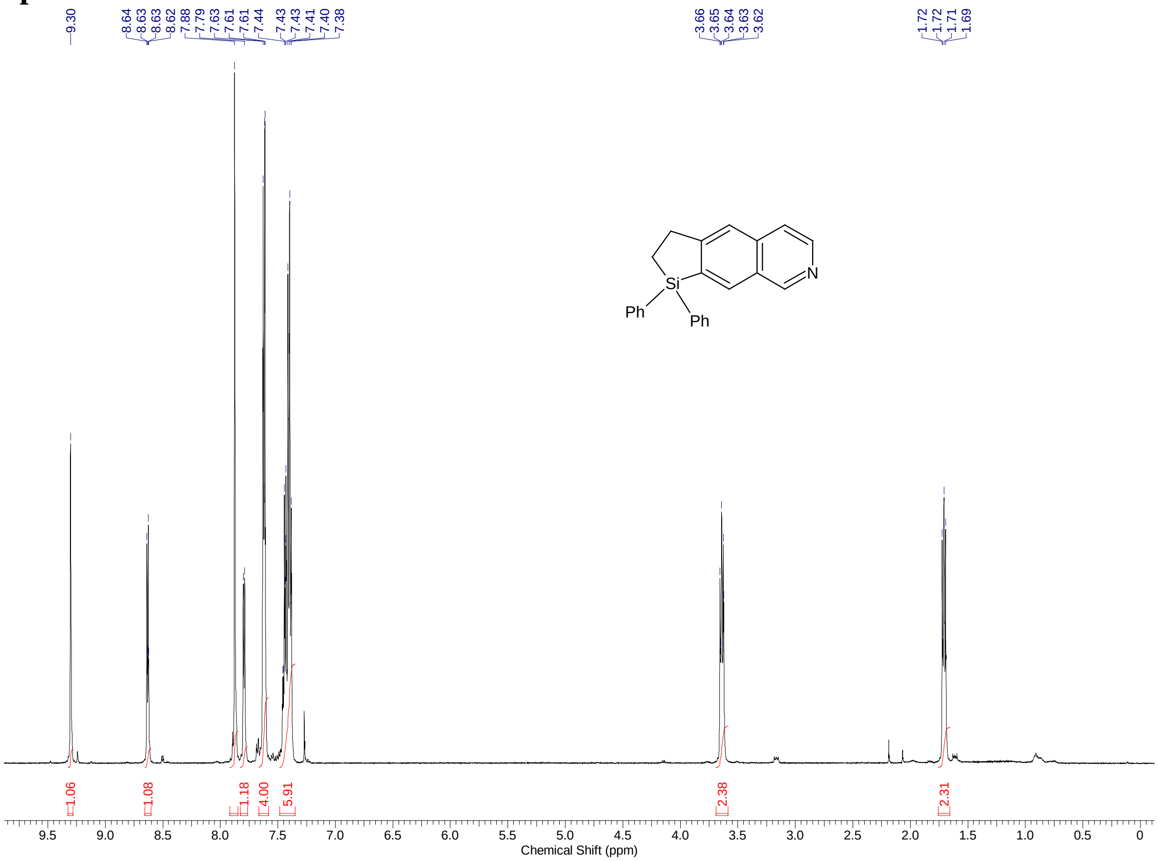

162.3
153.4
148.4
135.1
134.3
130.0
129.9
129.4
128.2
126.7
126.5
124.0
77.0
29.4
9.2
SiPh2
N
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

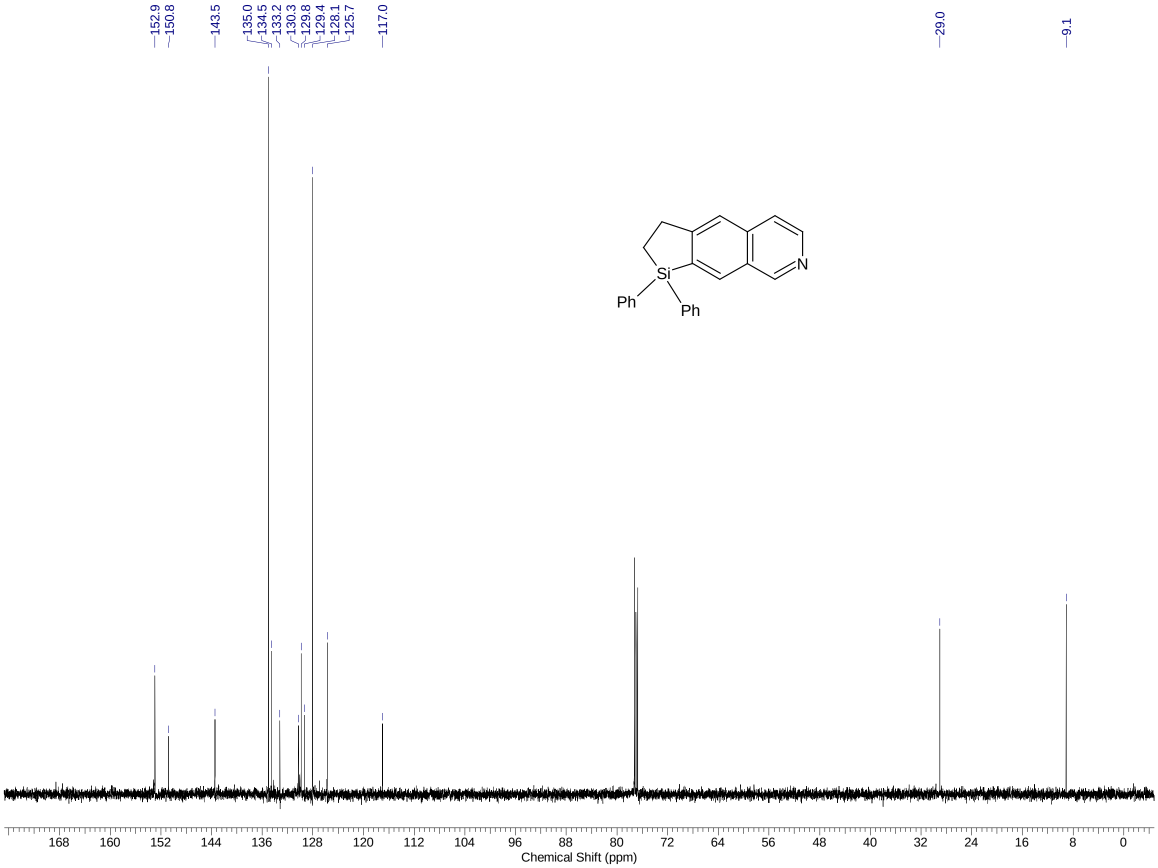
3o:


8.39
8.00
7.99
7.68
7.65
7.63
7.40
7.39
7.37
7.35
7.34
7.27
7.26
7.26
3.39
3.38
3.36
2.73
1.67
1.65
1.64
SiPh2
N
CH3
0.76
0.96
4.62
5.53
1.61
2.00
2.98
2.60
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

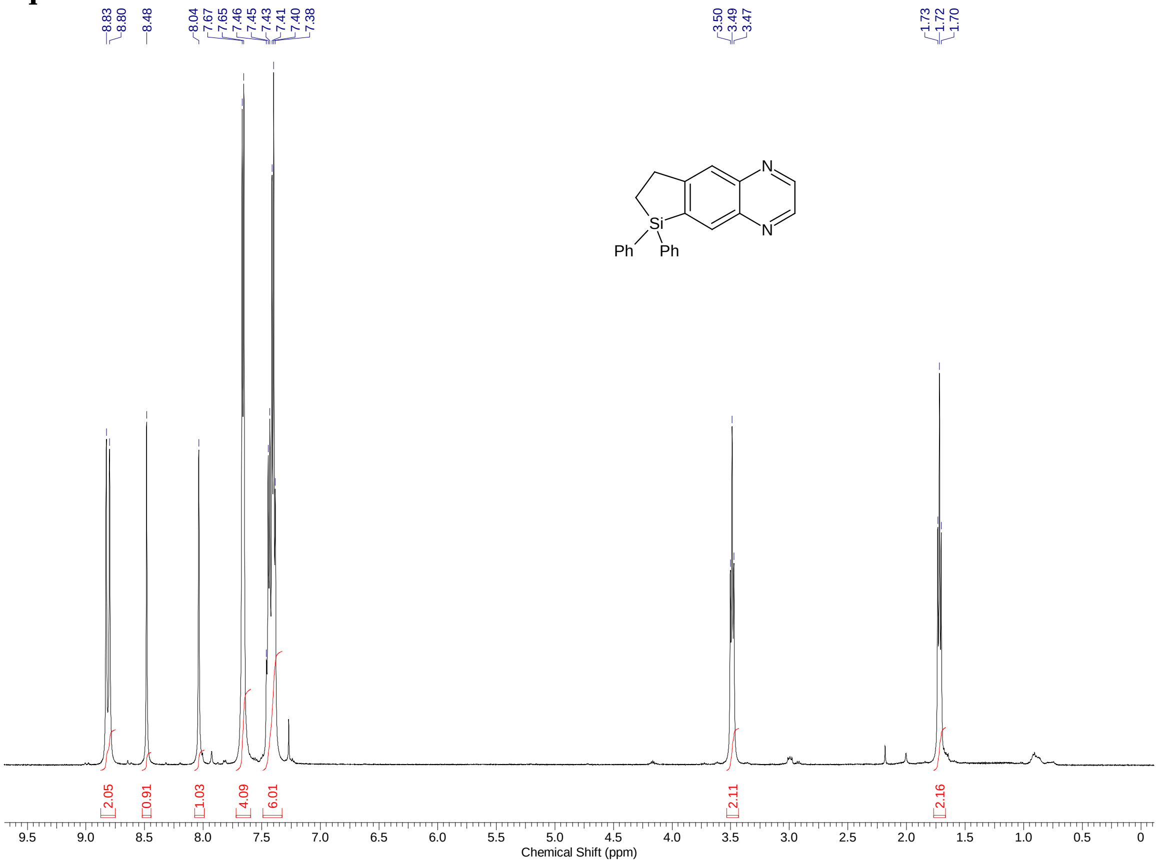

158.2
149.9
146.7
140.1
135.9
135.1
134.4
129.8
128.0
127.6
122.8
122.4
77.0
31.4
25.3
11.4
SiPh2
N
CH3
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

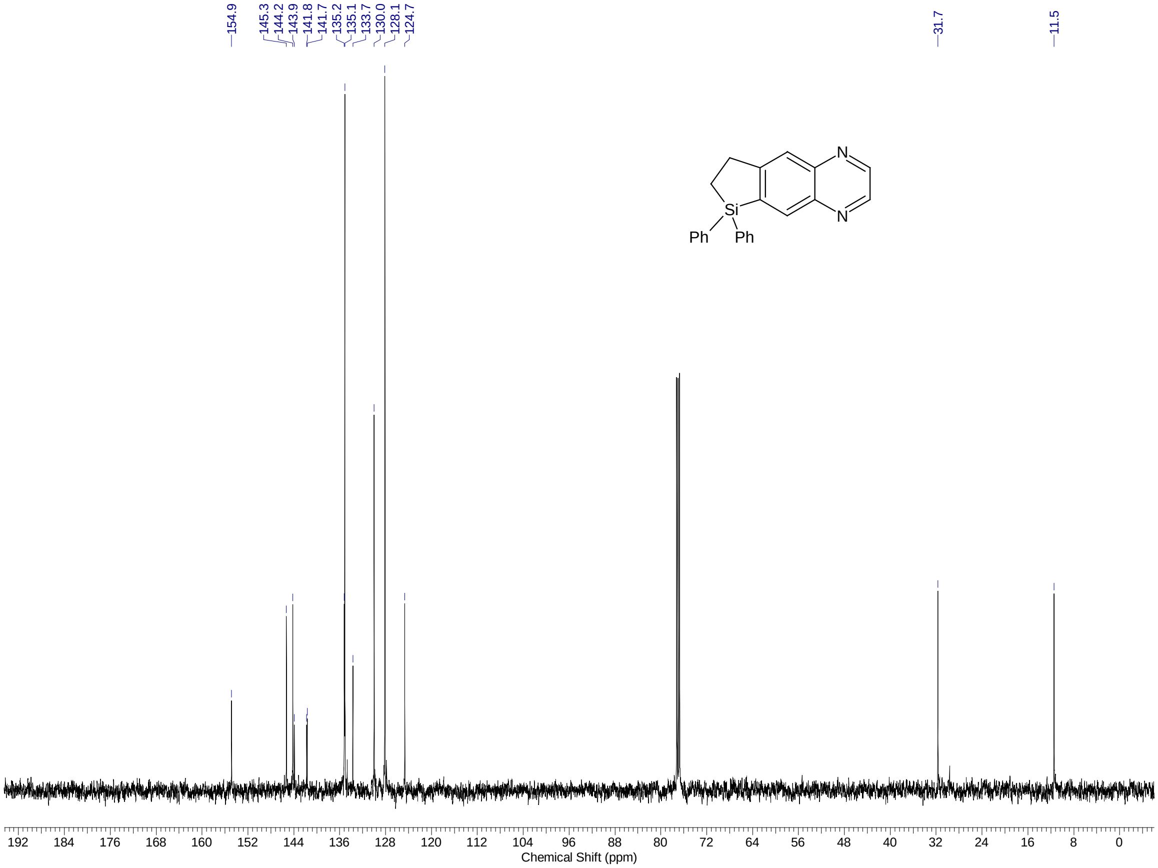
3p:


9.30
8.64
8.63
8.63
8.62
7.88
7.79
7.63
7.61
7.61
7.44
7.43
7.43
7.41
7.40
7.38
3.66
3.65
3.64
3.63
3.62
1.72
1.72
1.71
1.69
Si
Ph
Ph
N
1.06
1.08
1.18
4.00
5.91
2.38
2.31
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

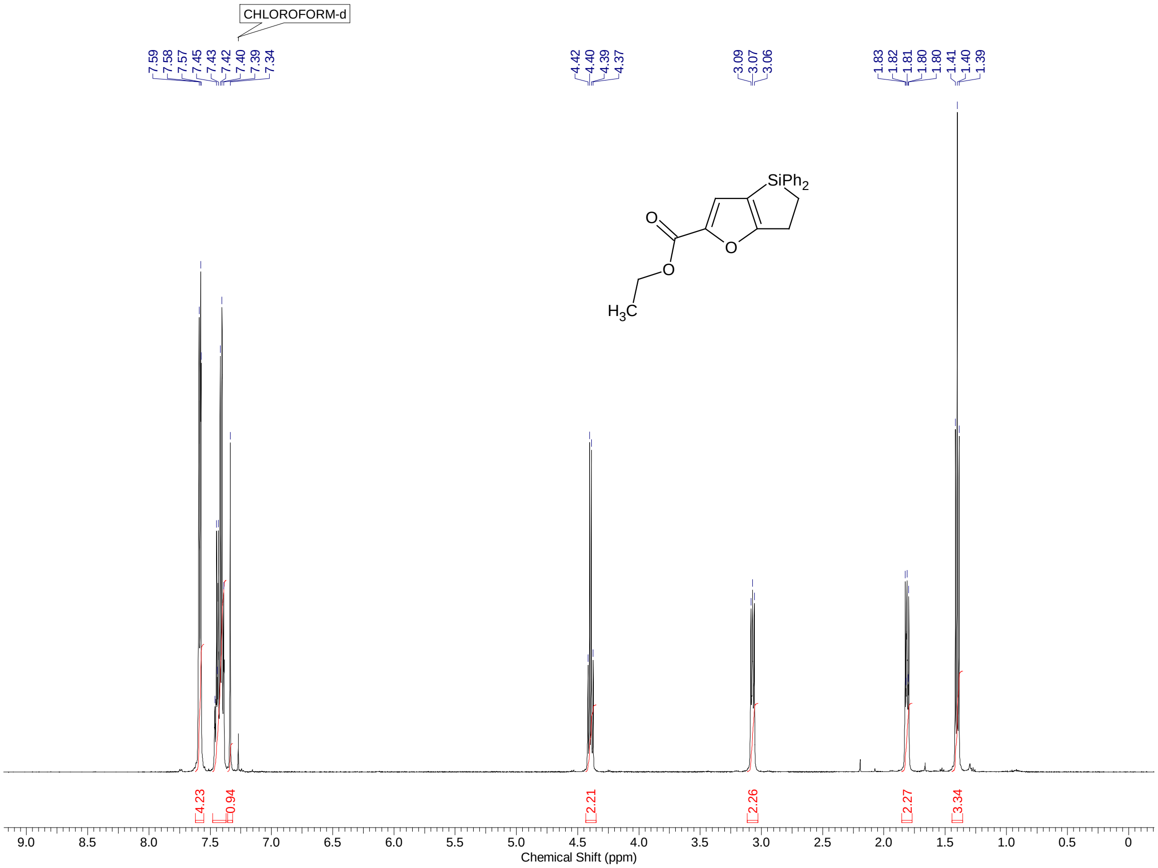

152.9
150.8
143.5
135.0
134.5
133.2
130.3
129.8
129.4
128.1
125.7
117.0
29.0
9.1
Si
Ph
Ph
N
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

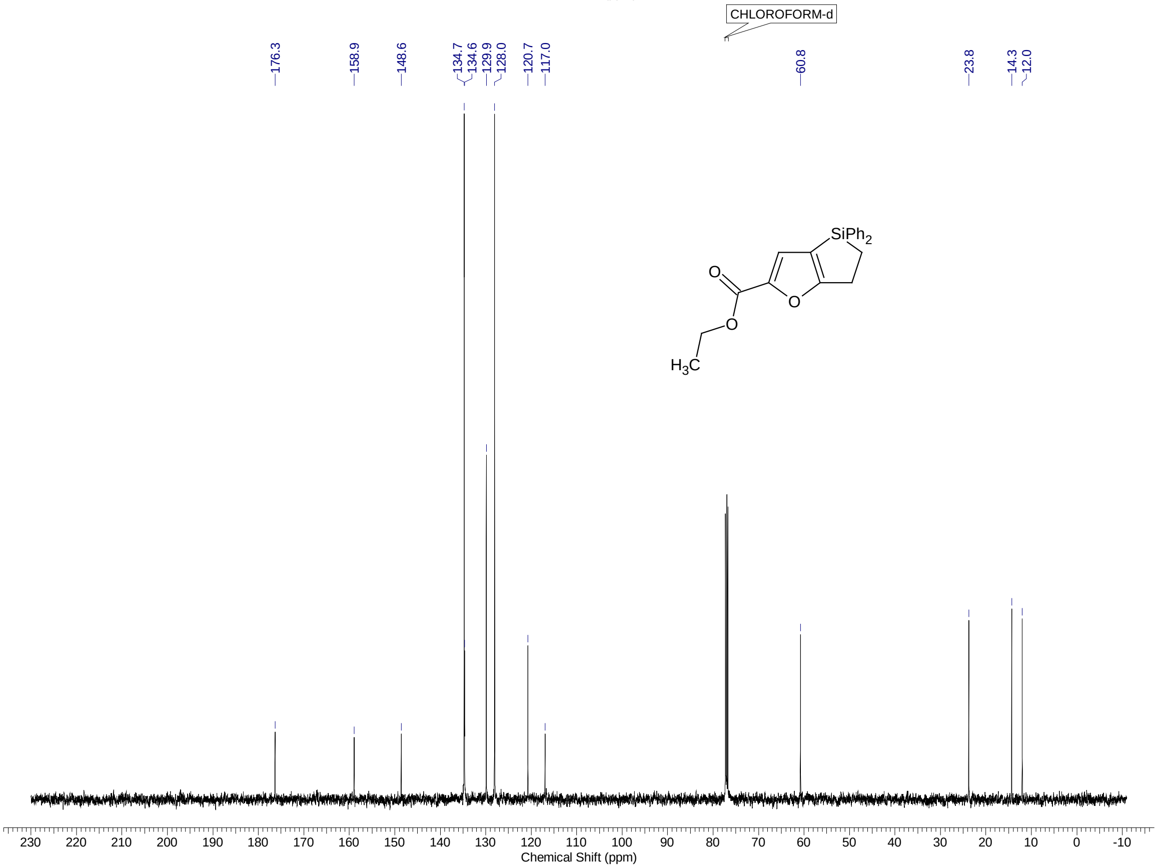
3q:


8.83
8.80
8.48
8.04
7.67
7.65
7.46
7.45
7.43
7.41
7.40
7.38
3.50
3.49
3.47
1.73
1.72
1.70
N
N
Si
Ph
Ph
2.05
0.91
1.03
4.09
6.01
2.11
2.16
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

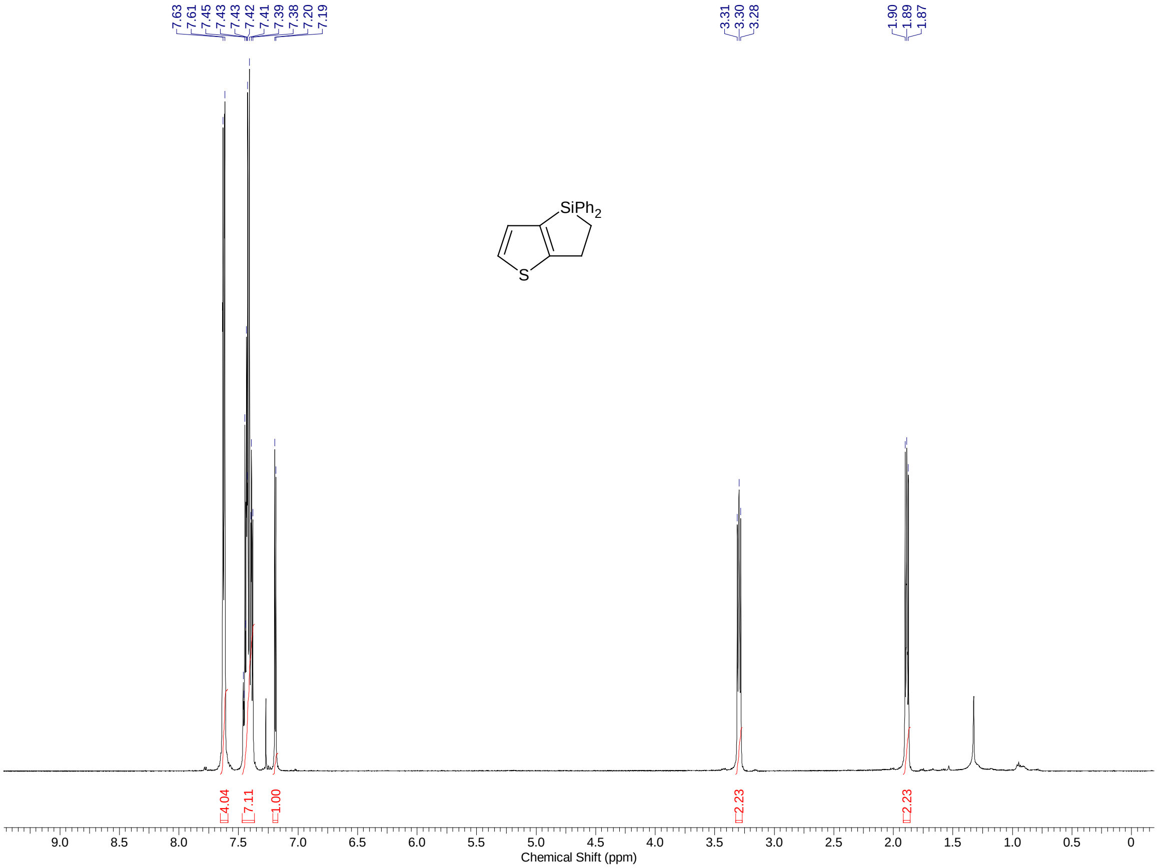

154.9
145.3
144.2
143.9
141.8
141.7
135.2
135.1
133.7
130.0
128.1
124.7
31.7
11.5
N
N
Si
Ph
Ph
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

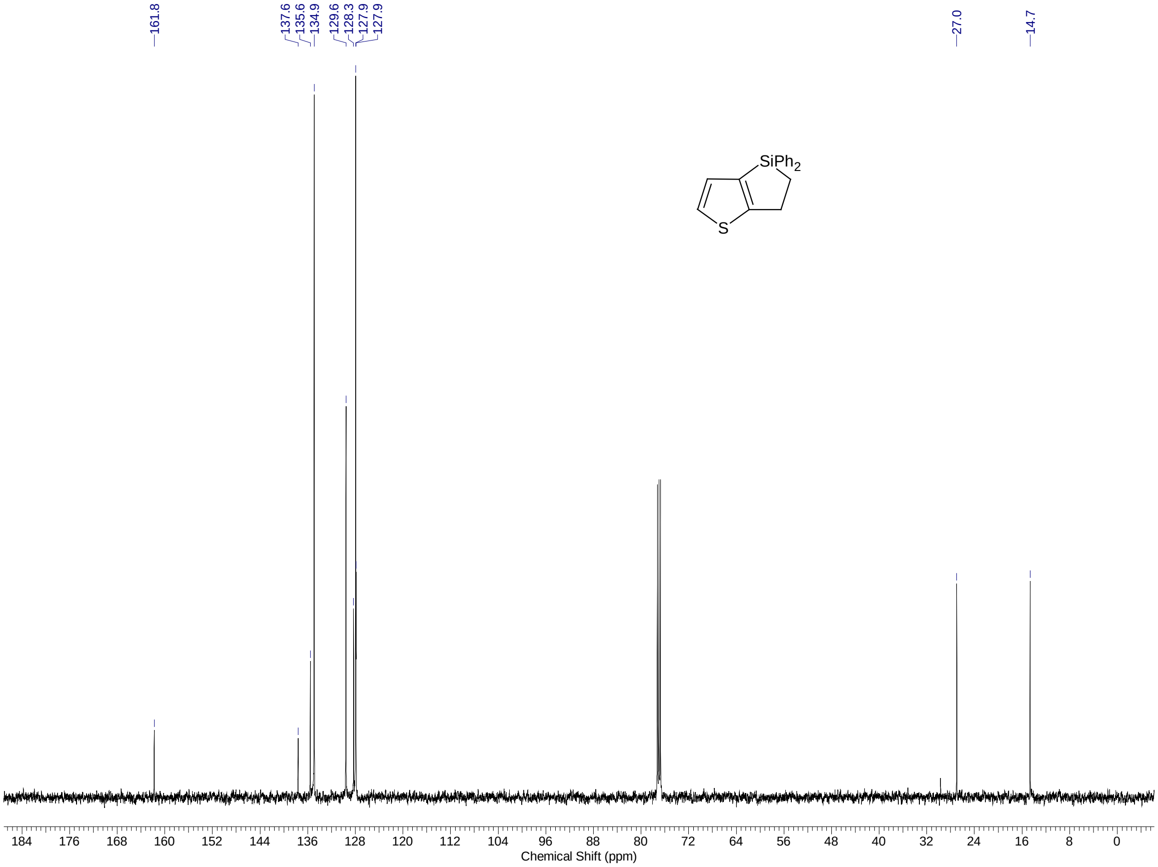
3aa:


CHLOROFORM-d
7.59
7.58
7.57
7.45
7.43
7.42
7.40
7.39
7.34
4.42
4.40
4.39
4.37
3.09
3.07
3.06
1.83
1.82
1.81
1.80
1.80
1.41
1.40
1.39
SiPh2
O
O
O
H3C
4.23
0.94
2.21
2.26
2.27
3.34
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

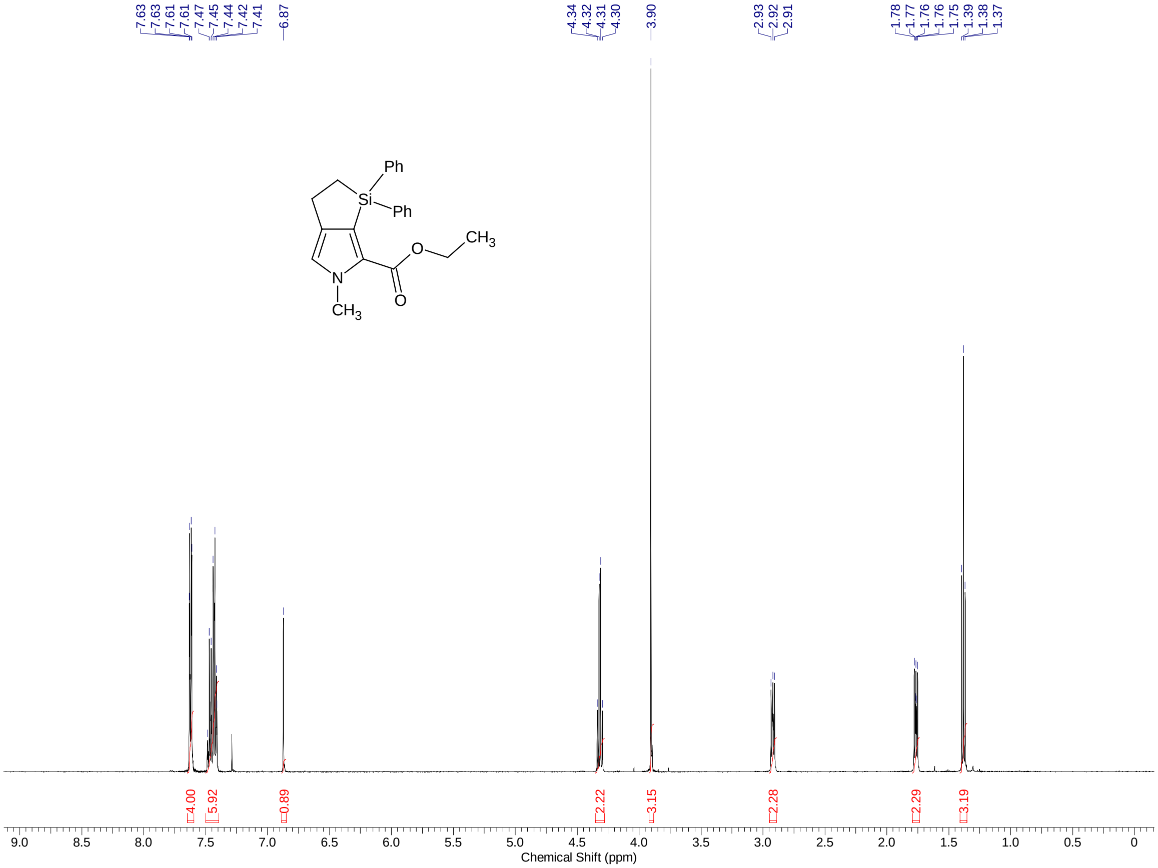

CHLOROFORM-d
176.3
158.9
148.6
134.7
134.6
129.9
128.0
120.7
117.0
60.8
23.8
14.3
12.0
SiPh2
O
O
O
H3C
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
Chemical Shift (ppm)

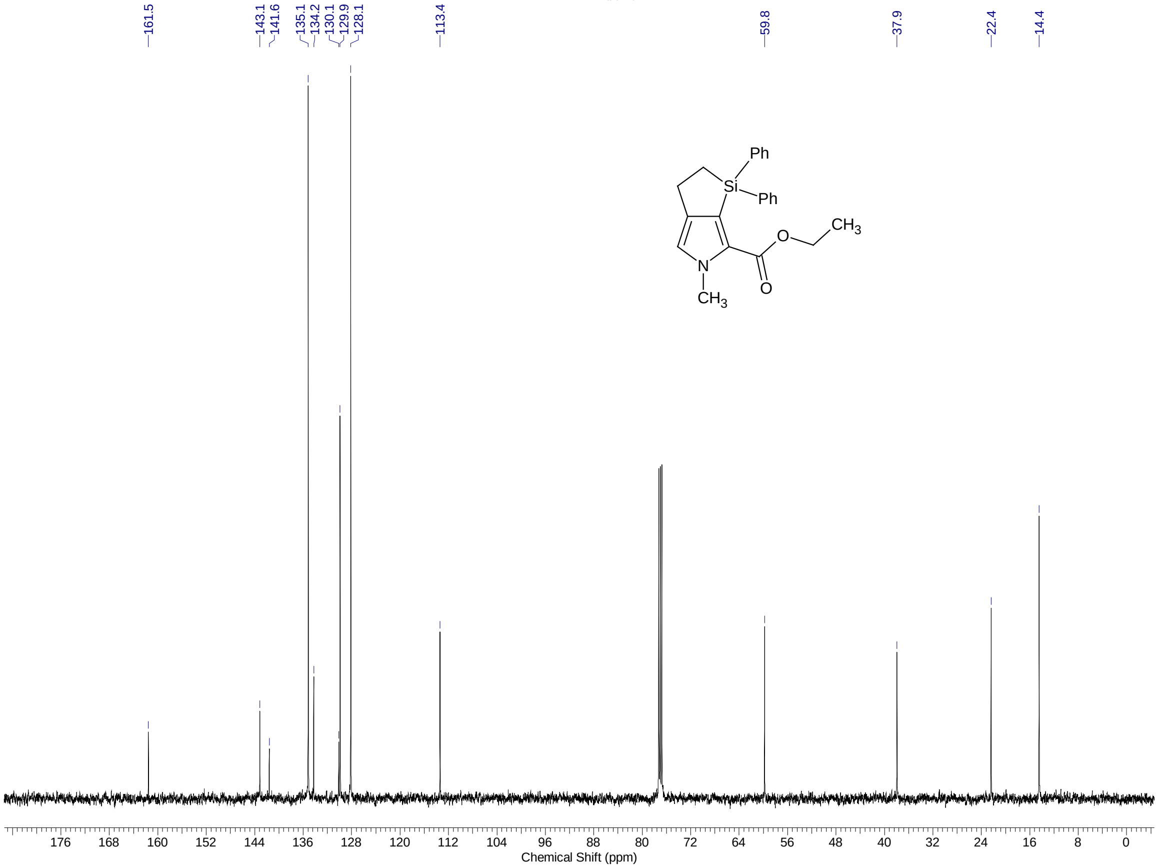
3bb:


7.63
7.61
7.45
7.43
7.43
7.42
7.41
7.39
7.38
7.20
7.19
3.31
3.30
3.28
1.90
1.89
1.87
SiPh$_2$
S
4.04
7.11
1.00
2.23
2.23
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

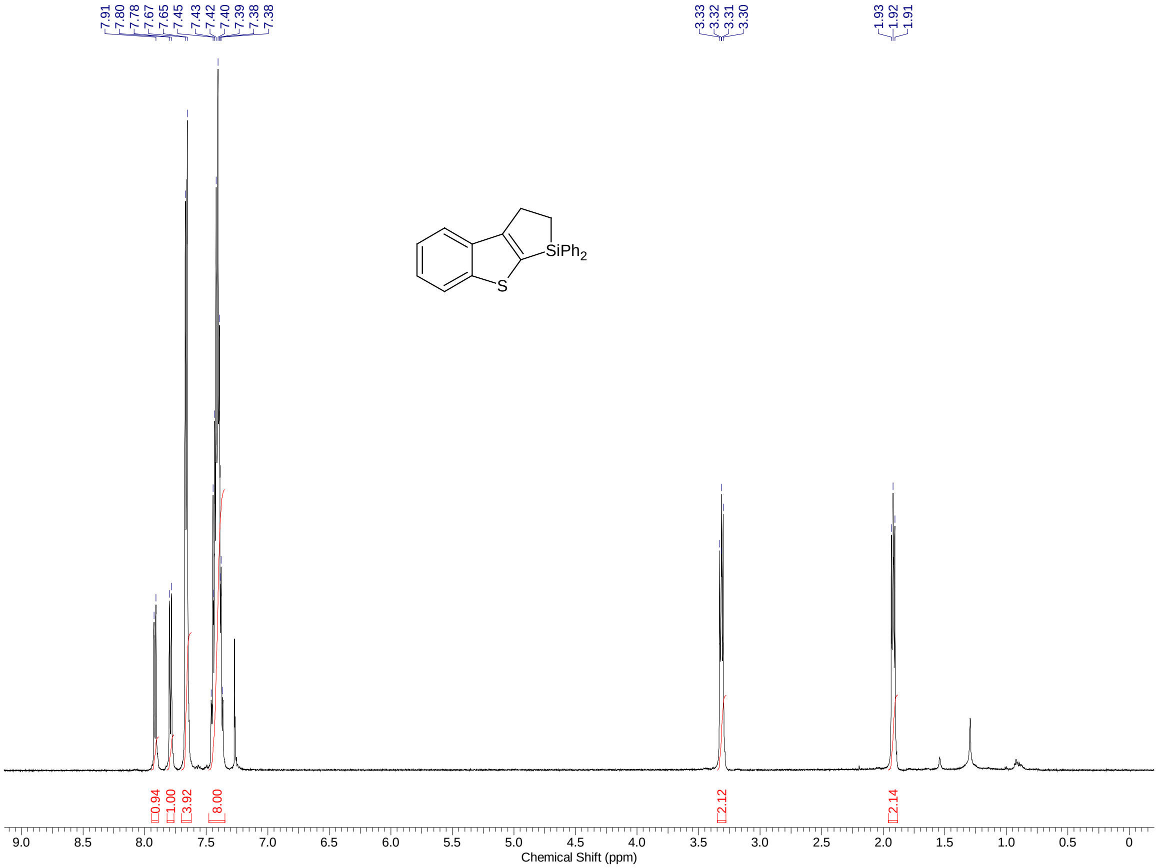

161.8
137.6
135.6
134.9
129.6
128.3
127.9
127.9
27.0
14.7
SiPh$_2$
S
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

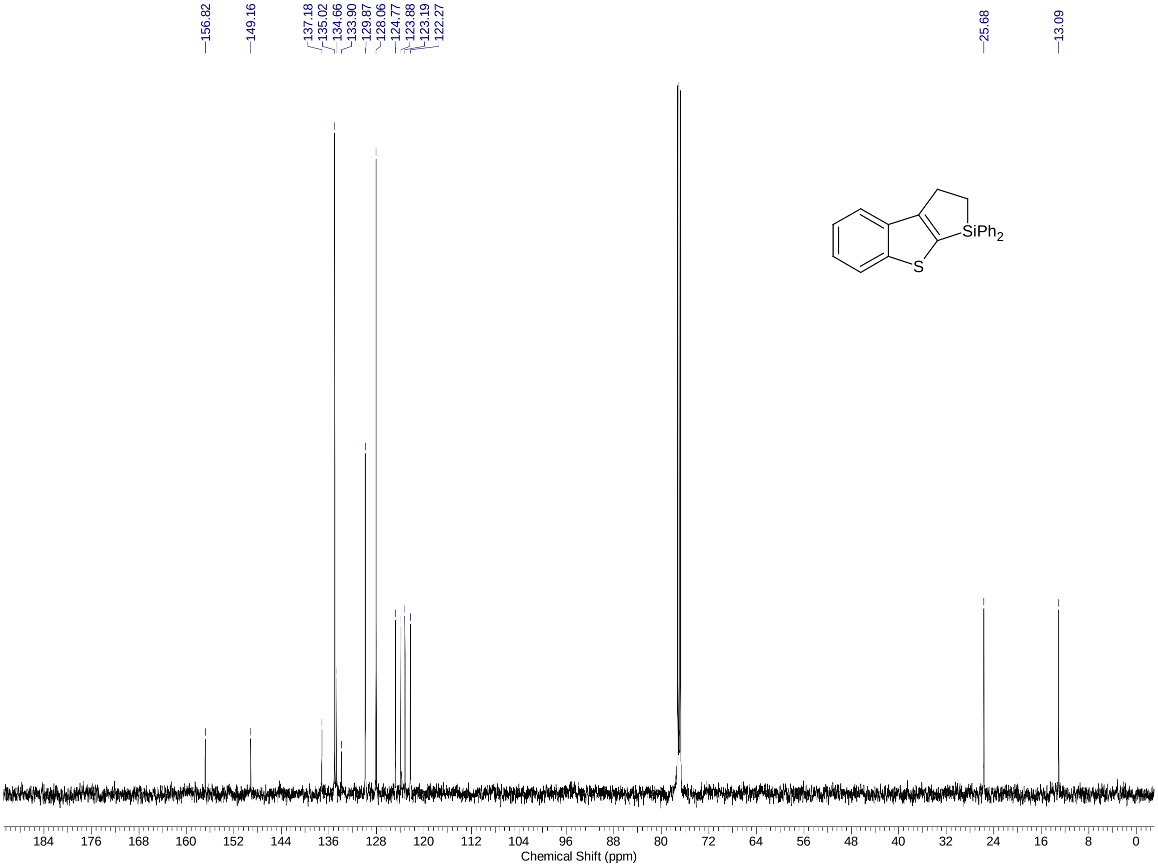
3cc:


7.63
7.63
7.61
7.61
7.47
7.45
7.44
7.42
7.41
6.87
4.34
4.32
4.31
4.30
3.90
2.93
2.92
2.91
1.78
1.77
1.76
1.76
1.75
1.39
1.38
1.37
Ph
Si
Ph
O
CH3
N
CH3
O
4.00
5.92
0.89
2.22
3.15
2.28
2.29
3.19
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

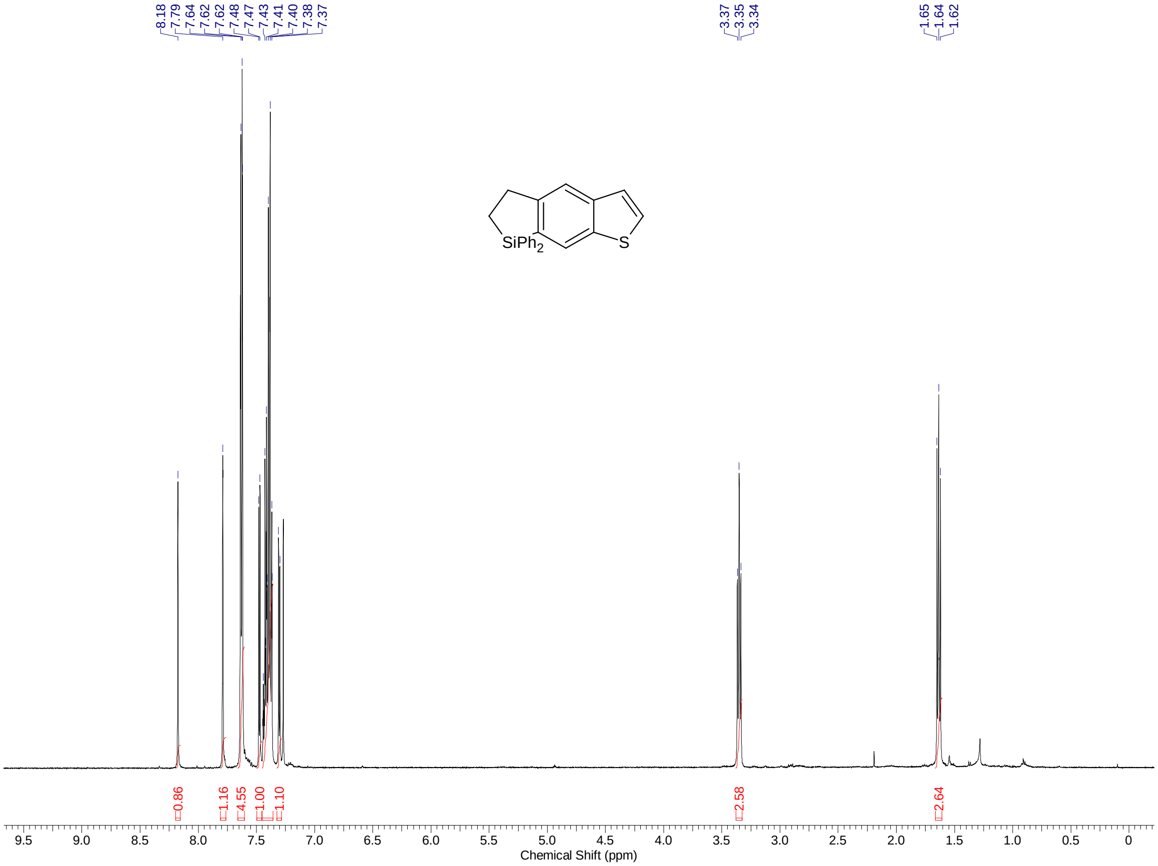

161.5
143.1
141.6
135.1
134.2
130.1
129.9
128.1
113.4
59.8
37.9
22.4
14.4
Ph
Si
Ph
O
CH3
N
CH3
O
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

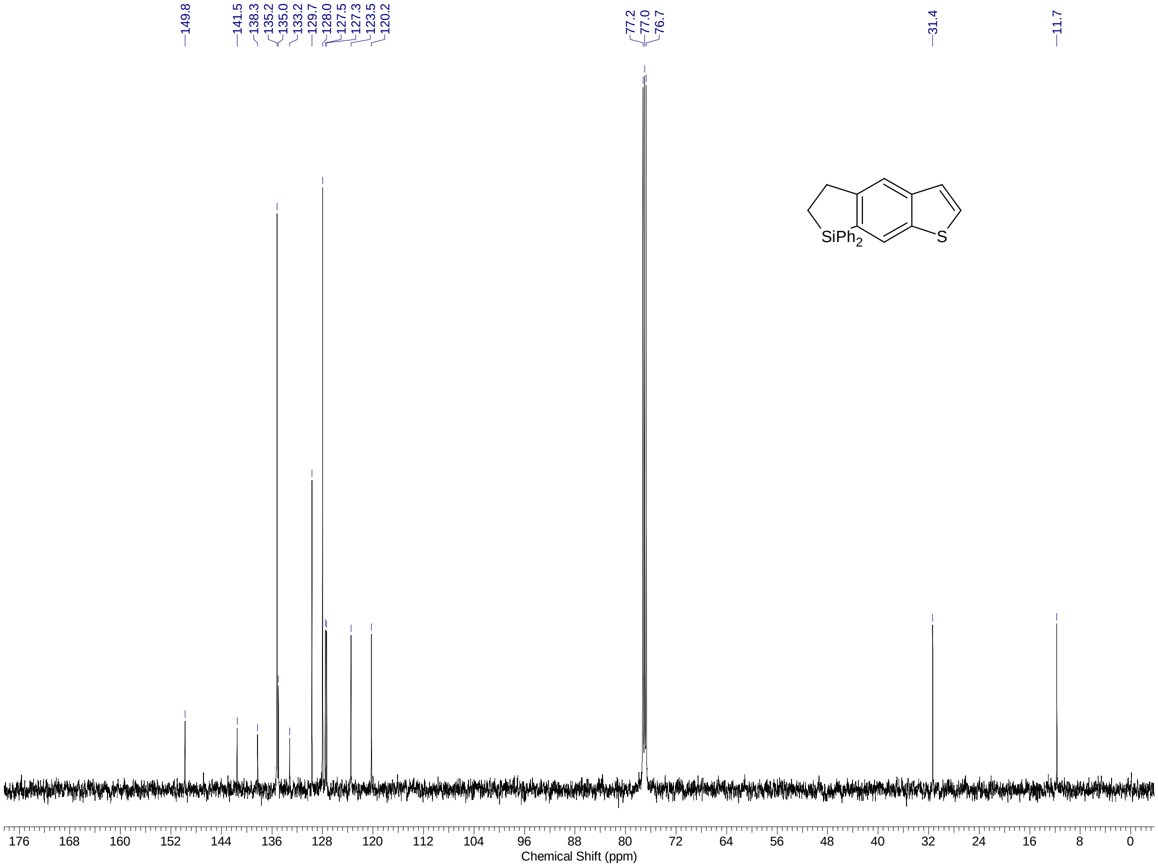
3dd:


7.91
7.80
7.78
7.67
7.65
7.45
7.43
7.42
7.40
7.39
7.38
7.38
3.33
3.32
3.31
3.30
1.93
1.92
1.91
SiPh$_2$
S
0.94
1.00
3.92
8.00
2.12
2.14
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

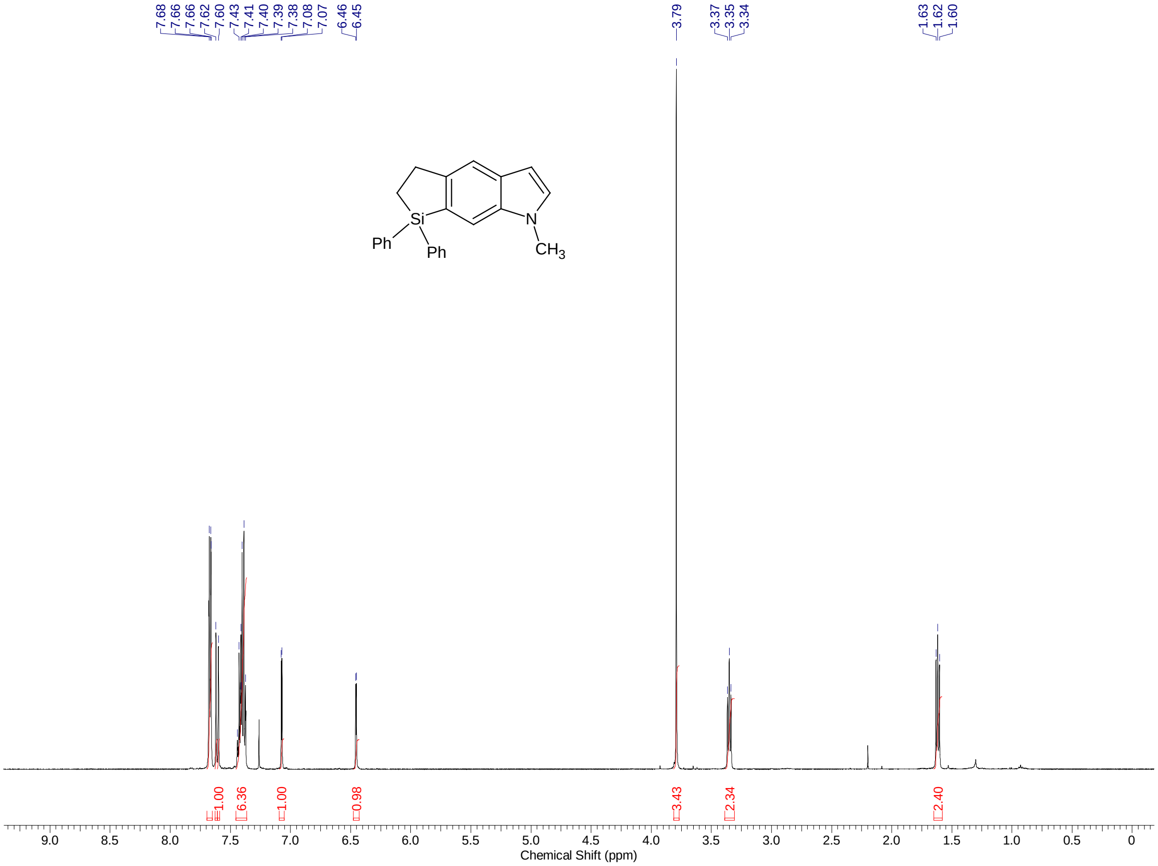

156.82
149.16
137.18
135.02
134.66
133.90
129.87
128.06
124.77
123.88
123.19
122.27
25.68
13.09
SiPh$_2$
S
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

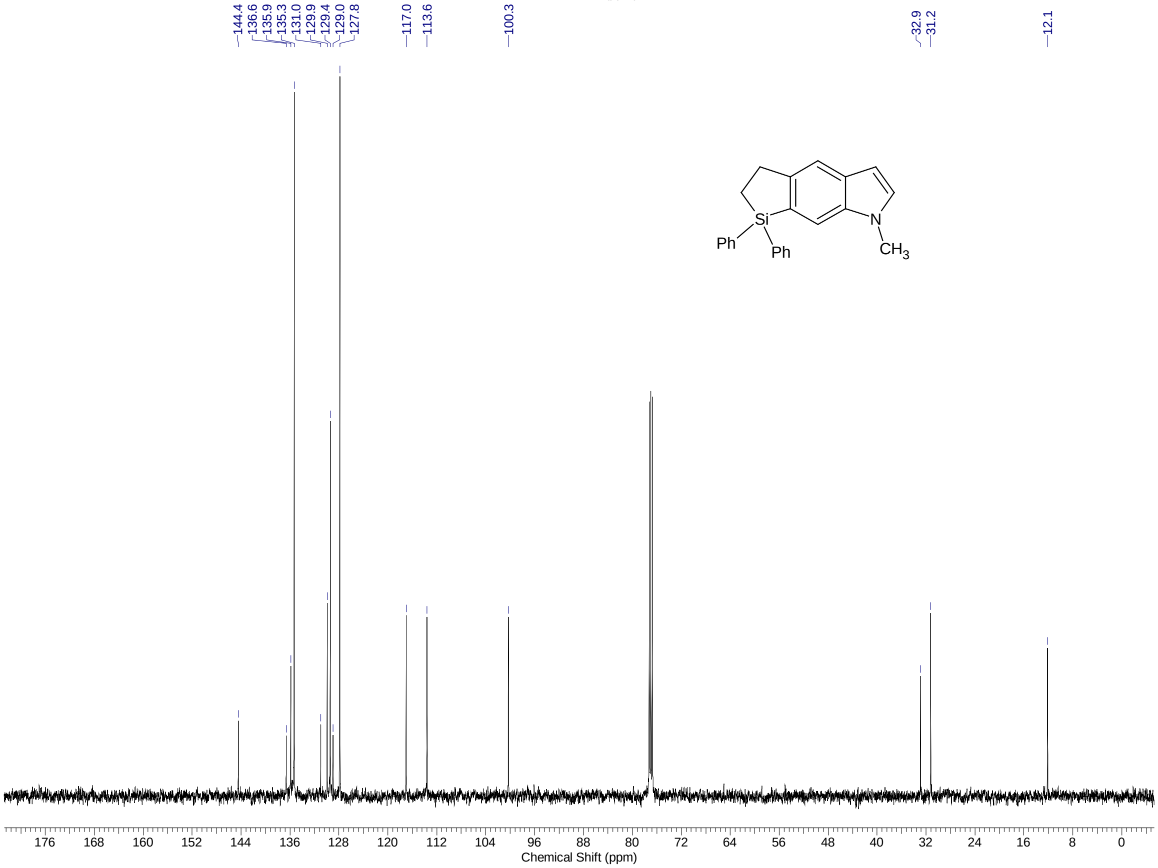
3ee:


8.18
7.79
7.64
7.62
7.62
7.48
7.47
7.43
7.41
7.40
7.38
7.37
3.37
3.35
3.34
1.65
1.64
1.62
SiPh2
S
0.86
1.16
4.55
1.00
1.10
2.58
2.64
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

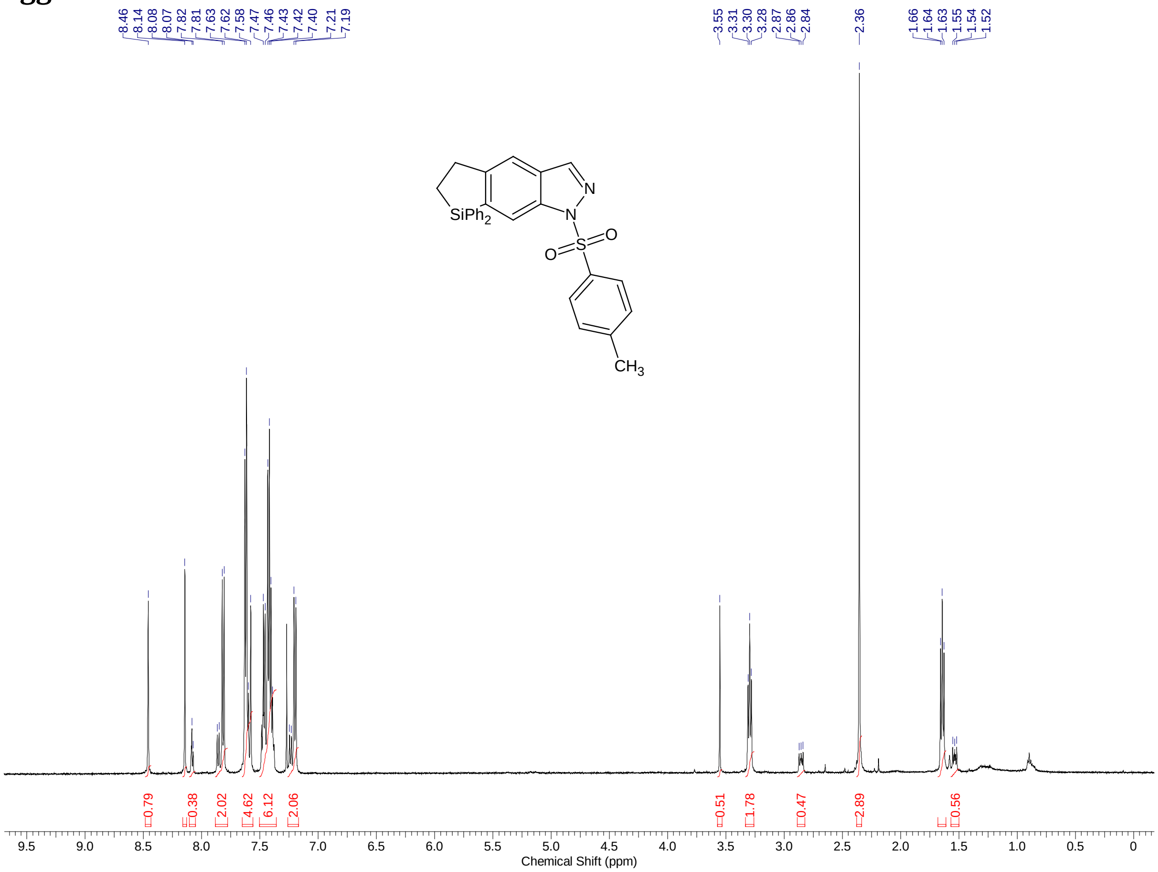

149.8
141.5
138.3
135.2
135.0
133.2
129.7
128.0
127.5
127.3
123.5
120.2
77.2
77.0
76.7
31.4
11.7
SiPh2
S
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

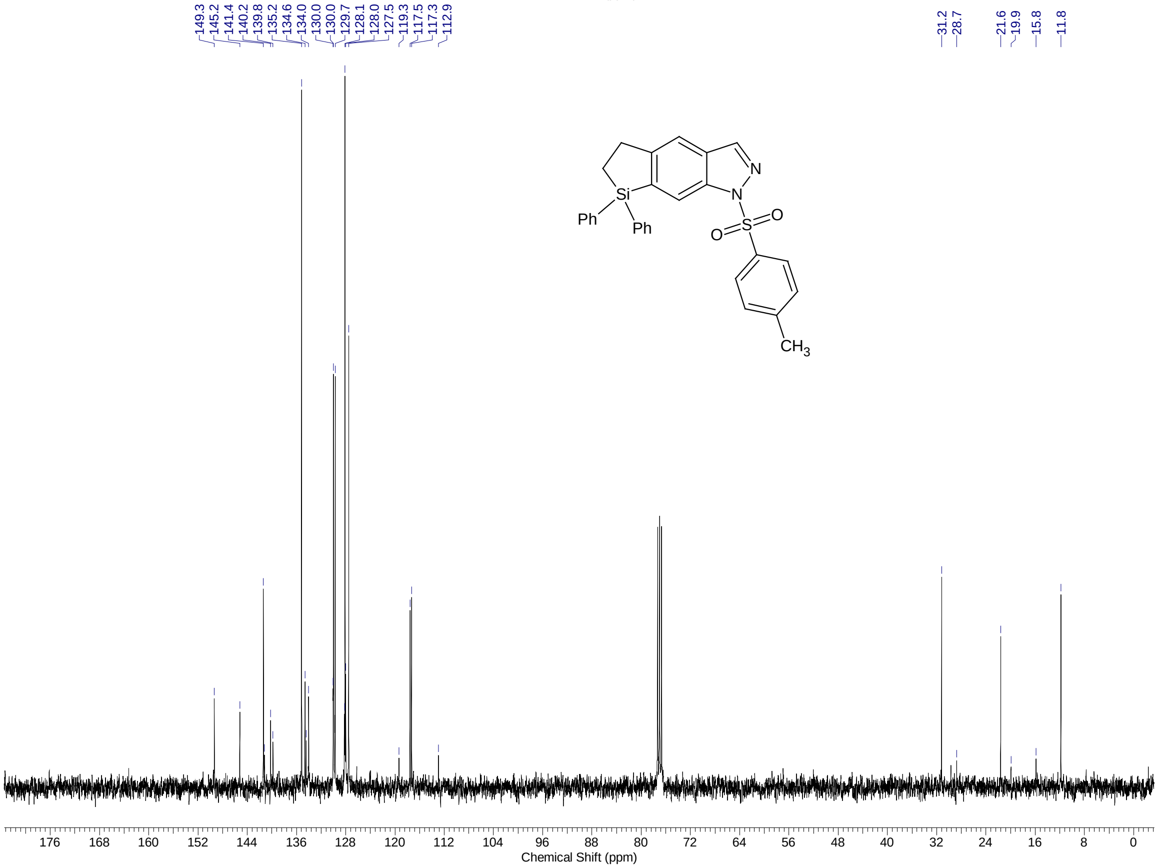
3ff:


7.68
7.66
7.66
7.62
7.60
7.43
7.41
7.40
7.39
7.38
7.08
7.07
6.46
6.45
3.79
3.37
3.35
3.34
1.63
1.62
1.60
Si
Ph
Ph
N
CH3
1.00
6.36
1.00
0.98
3.43
2.34
2.40
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

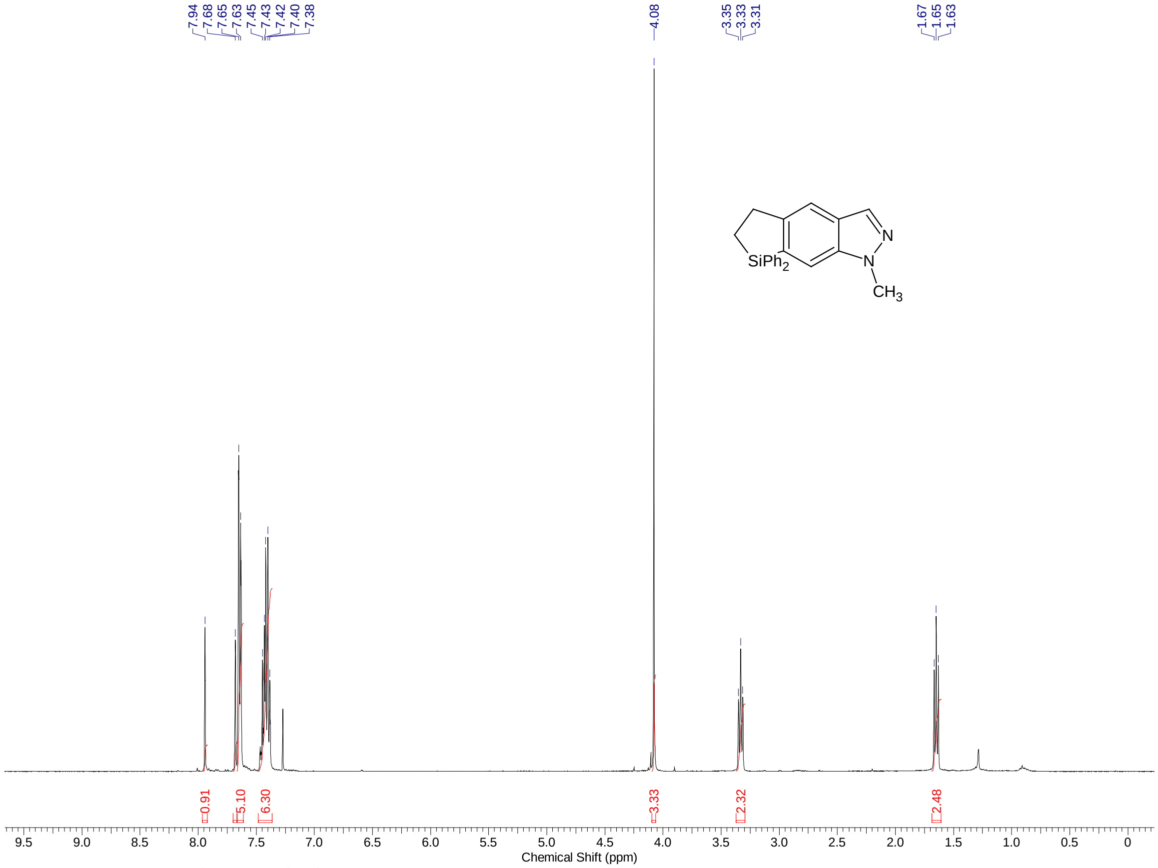

144.4
136.6
135.9
135.3
131.0
129.9
129.4
129.0
127.8
117.0
113.6
100.3
32.9
31.2
12.1
Si
Ph
Ph
N
CH3
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

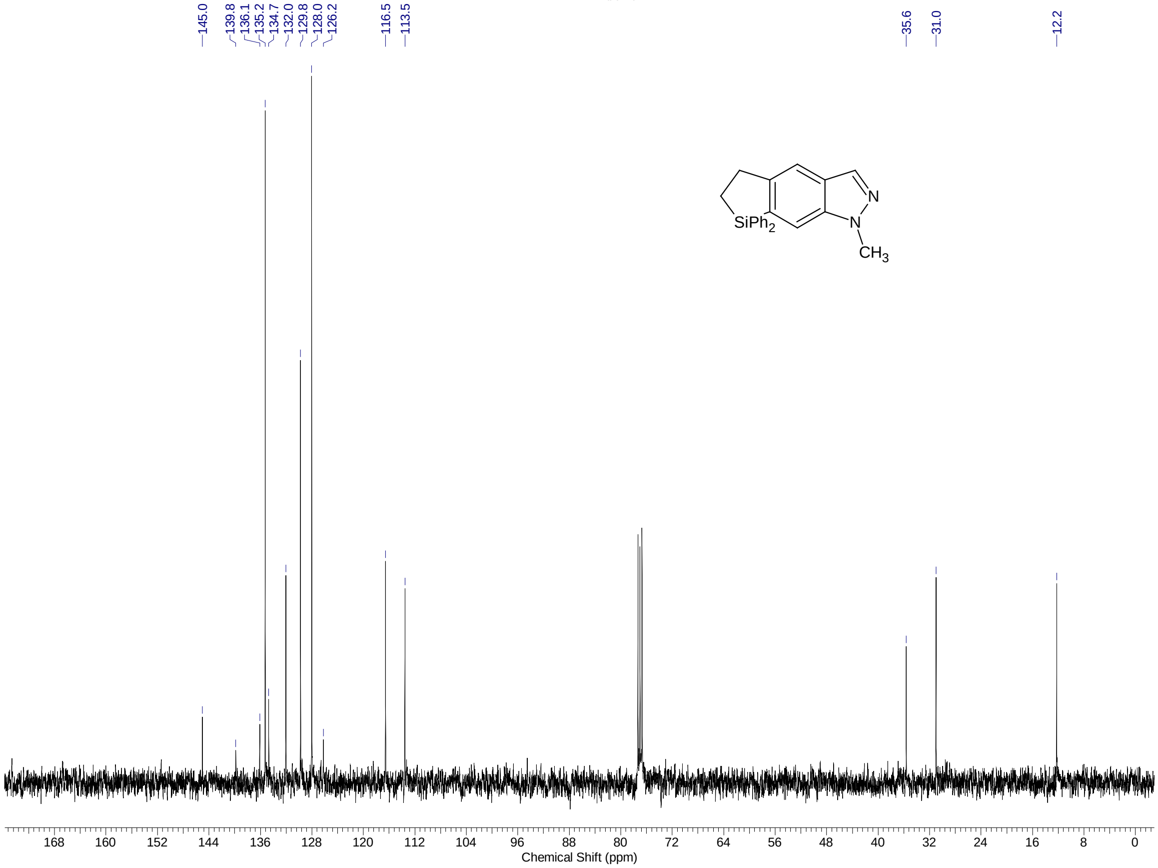
3gg:


8.46
8.14
8.08
8.07
7.82
7.81
7.63
7.62
7.58
7.47
7.46
7.43
7.42
7.40
7.21
7.19
3.55
3.31
3.30
3.28
2.87
2.86
2.84
2.36
1.66
1.64
1.63
1.55
1.54
1.52
SiPh2
N
N
S
O
O
CH3
0.79
0.38
2.02
4.62
6.12
2.06
0.51
1.78
0.47
2.89
0.56
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

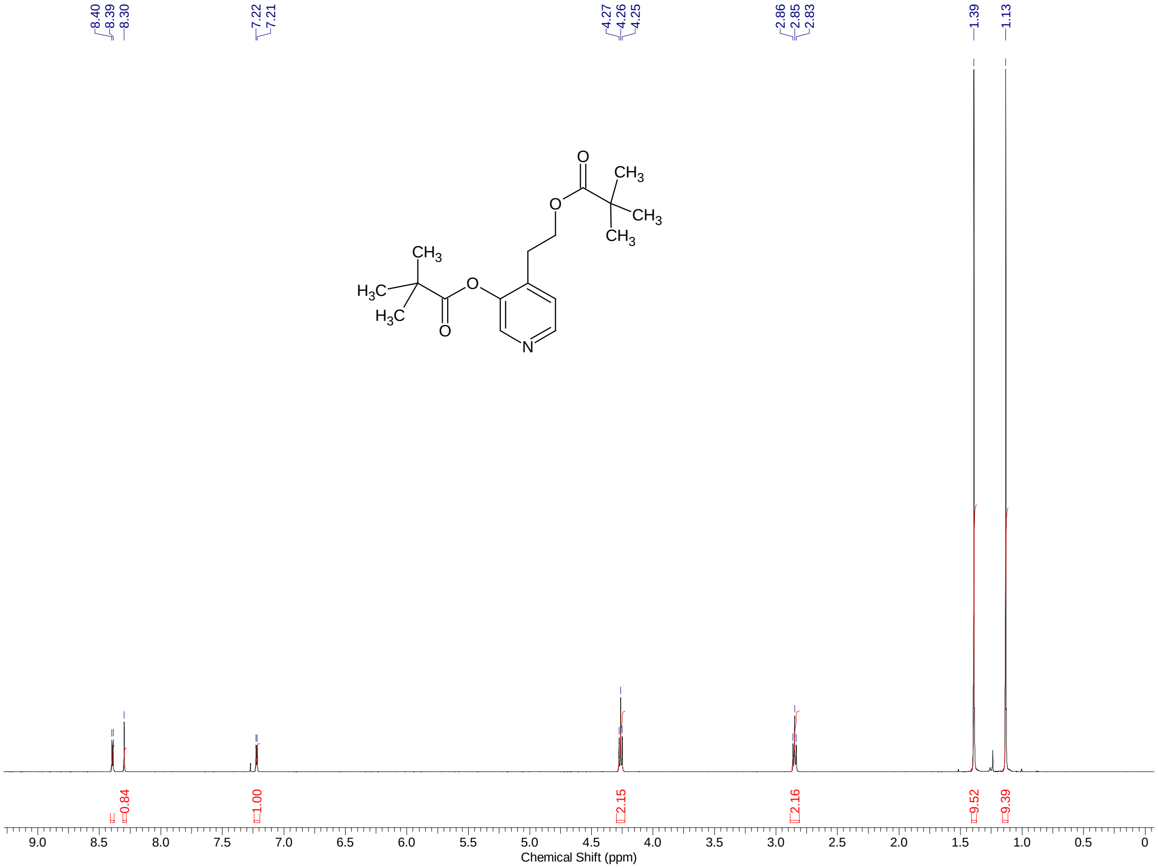

149.3
145.2
141.4
140.2
139.8
135.2
134.6
134.0
130.0
130.0
129.7
128.1
128.0
127.5
119.3
117.5
117.3
112.9
31.2
28.7
21.6
19.9
15.8
11.8
Si
Ph
Ph
N
N
S
O
O
CH3
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

3hh:

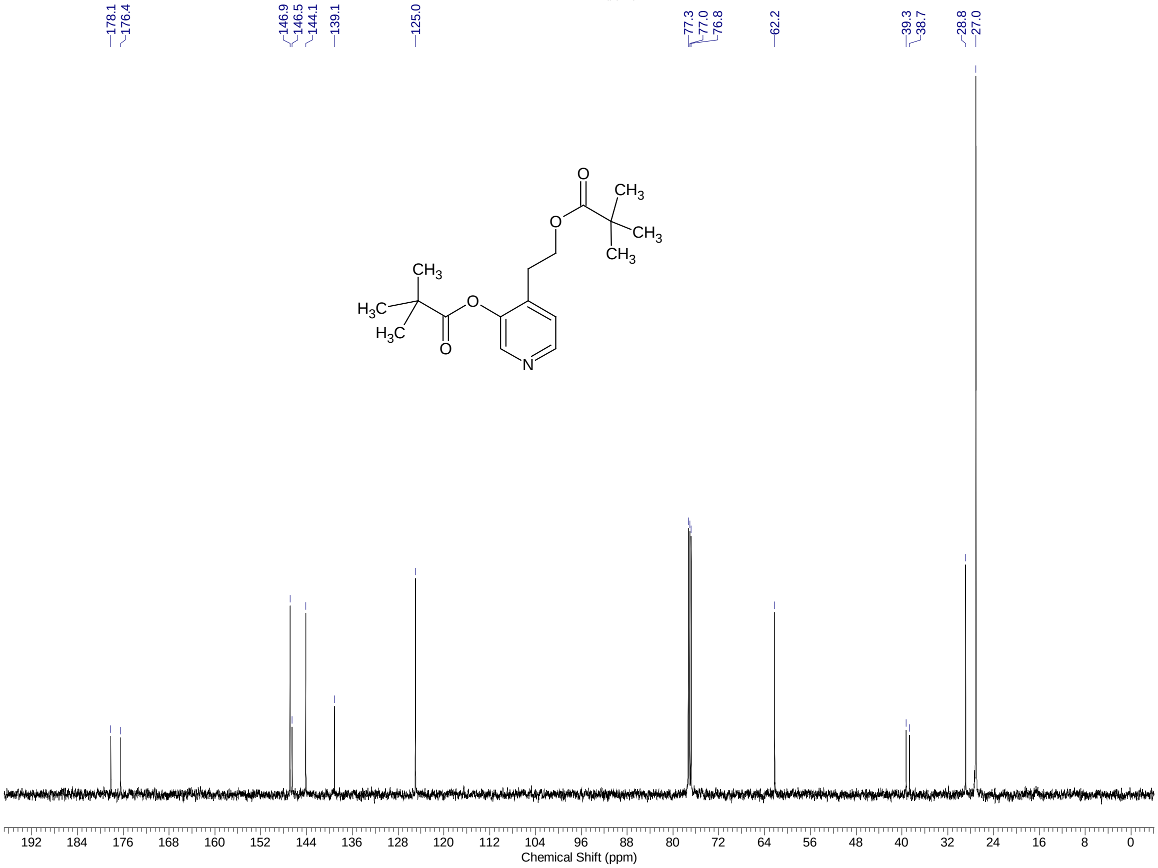

7.94
7.68
7.65
7.63
7.45
7.43
7.42
7.40
7.38
4.08
3.35
3.33
3.31
1.67
1.65
1.63
SiPh2
N
N
CH3
0.91
5.10
6.30
3.33
2.32
2.48
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


145.0
139.8
136.1
135.2
134.7
132.0
129.8
128.0
126.2
116.5
113.5
35.6
31.0
12.2
SiPh2
N
N
CH3
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

4:

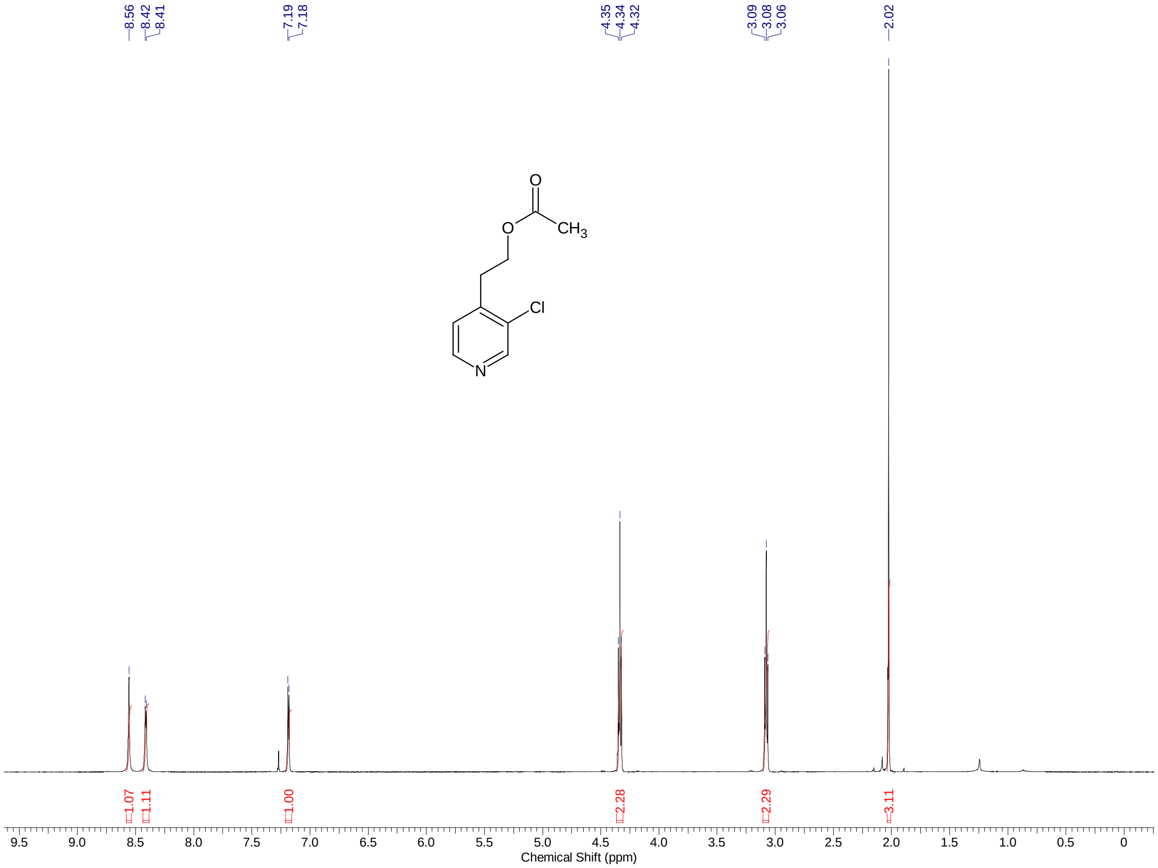


8.40
8.39
8.30
7.22
7.21
4.27
4.26
4.25
2.86
2.85
2.83
1.39
1.13
O
CH$_3$
O
CH$_3$
CH$_3$
CH$_3$
H$_3$C
O
H$_3$C
O
N
0.84
1.00
2.15
2.16
9.52
9.39
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

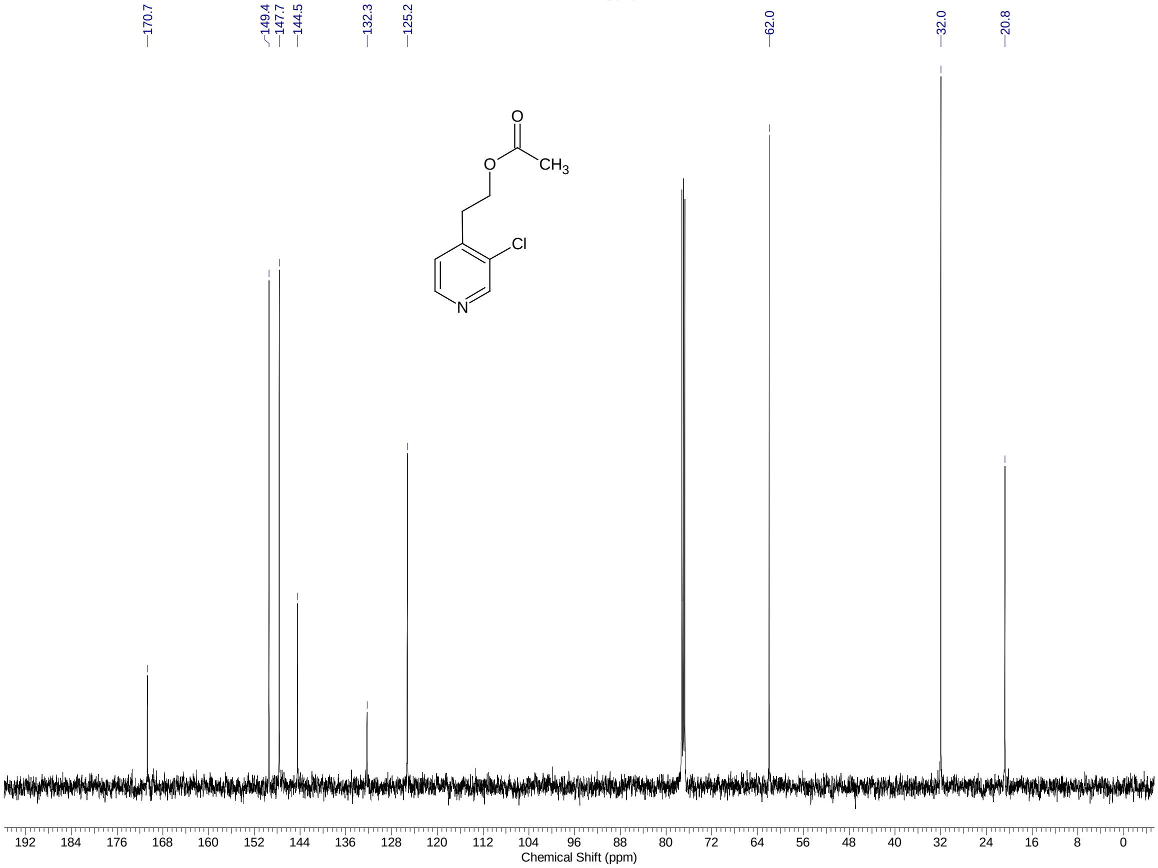


178.1
176.4
146.9
146.5
144.1
139.1
125.0
77.3
77.0
76.8
62.2
39.3
38.7
28.8
27.0
O
CH$_3$
O
CH$_3$
CH$_3$
CH$_3$
H$_3$C
O
H$_3$C
O
N
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

6a:

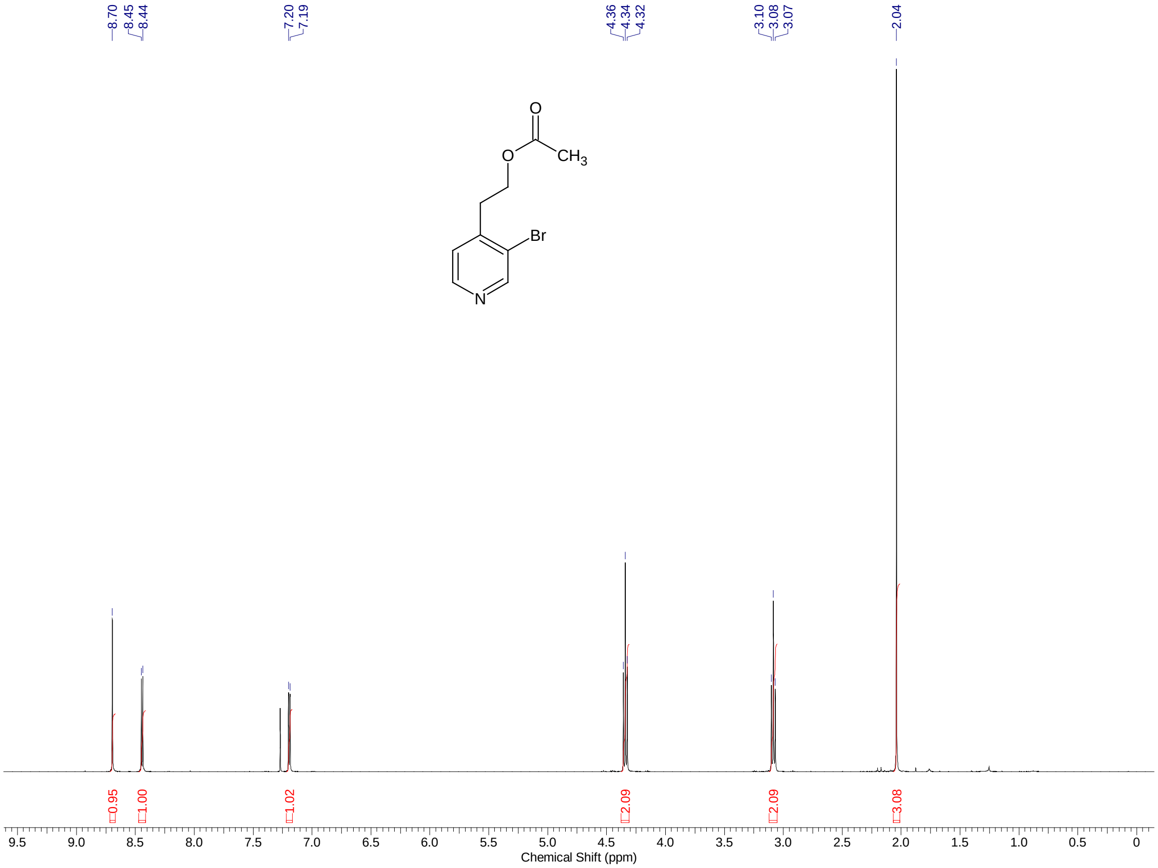


8.56
8.42
8.41
7.19
7.18
4.35
4.34
4.32
3.09
3.08
3.06
2.02
O
O
CH3
Cl
N
1.07
1.11
1.00
2.28
2.29
3.11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

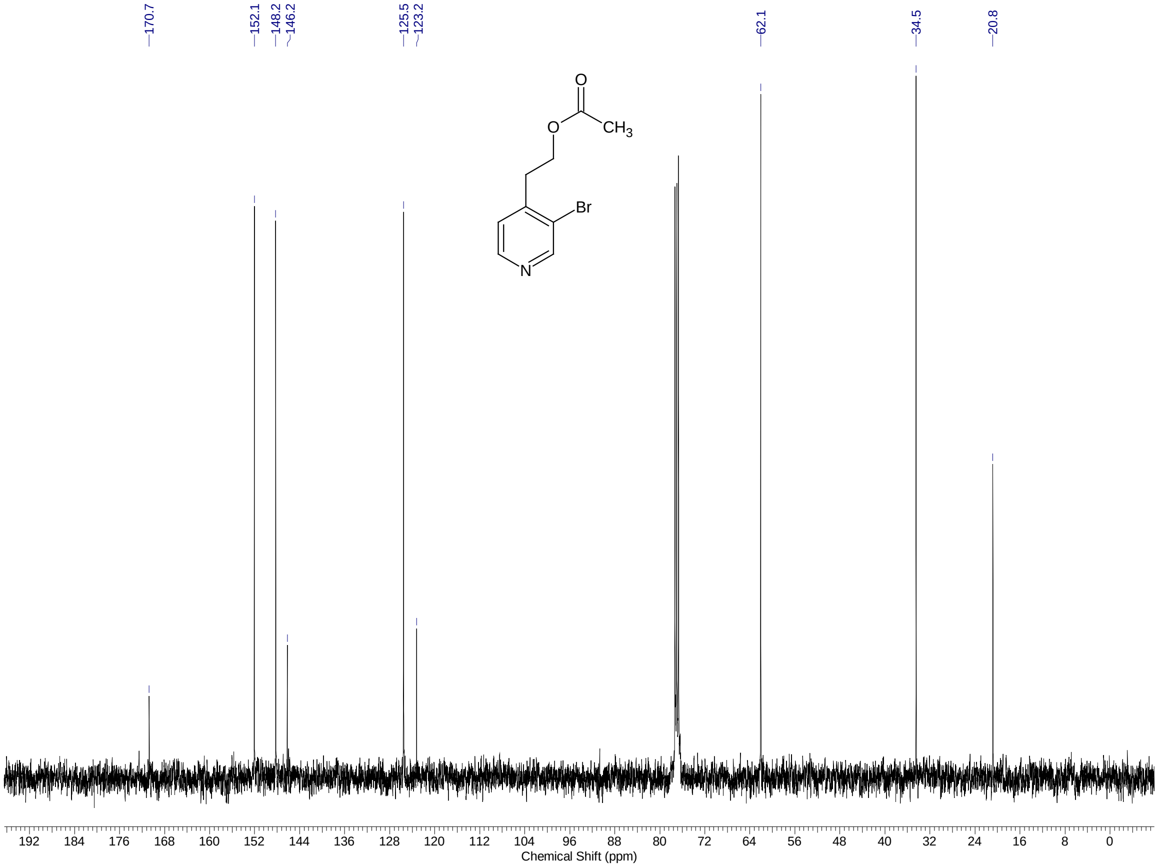


170.7
149.4
147.7
144.5
132.3
125.2
62.0
32.0
20.8
O
O
CH3
Cl
N
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

6b:

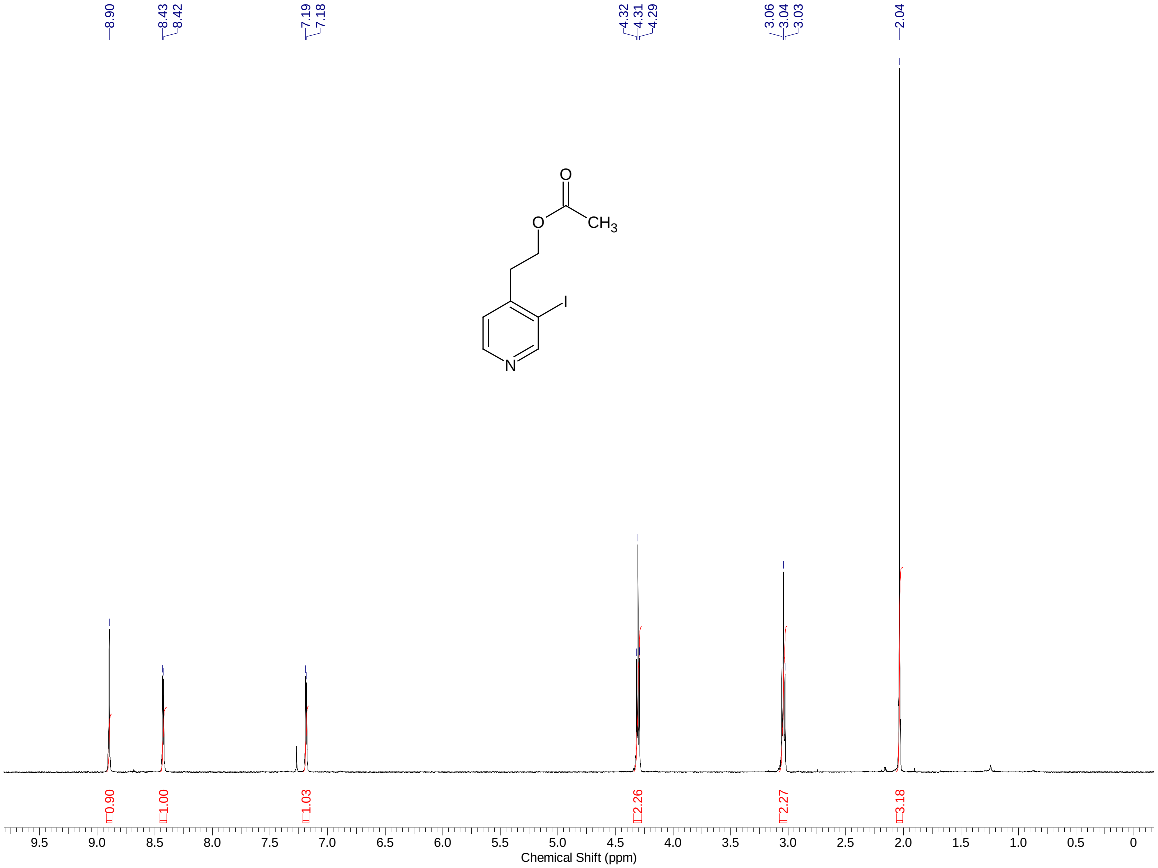


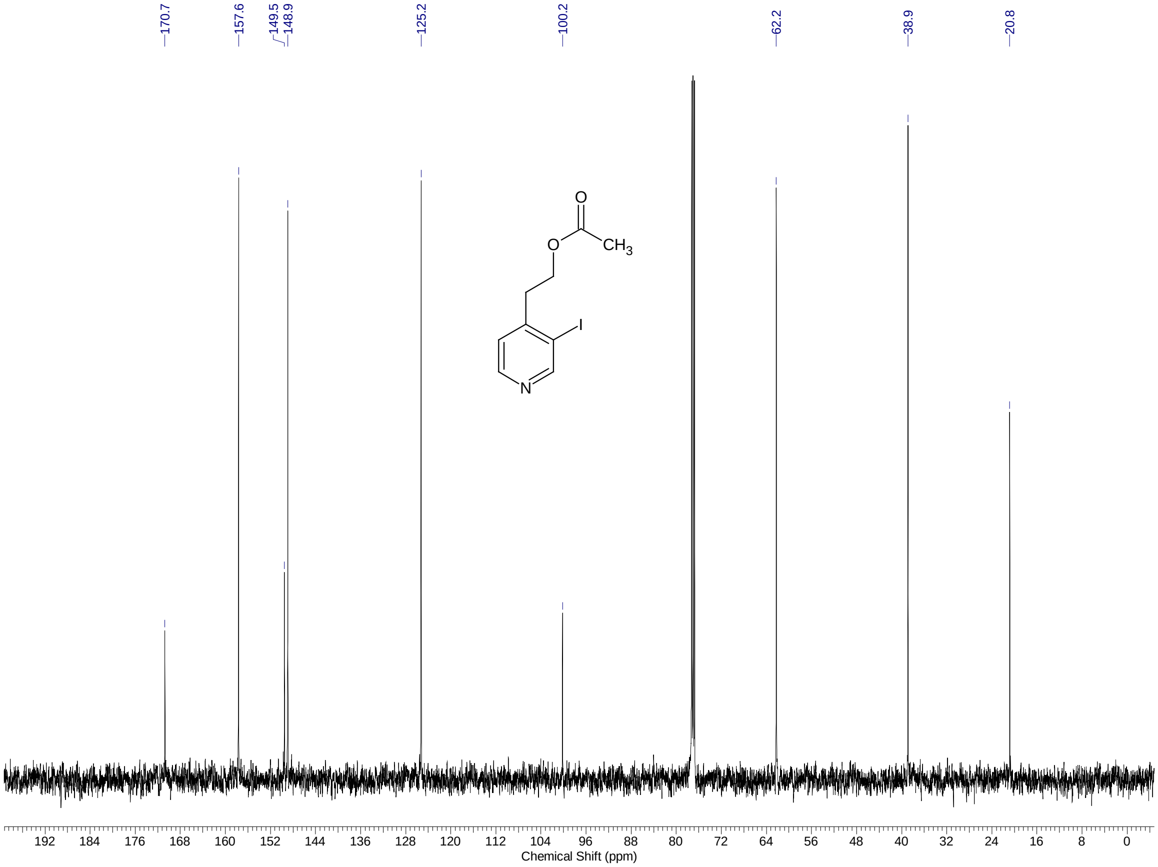
8.70
8.45
8.44
7.20
7.19
4.36
4.34
4.32
3.10
3.08
3.07
2.04
O
O
CH3
Br
N
0.95
1.00
1.02
2.09
2.09
3.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)



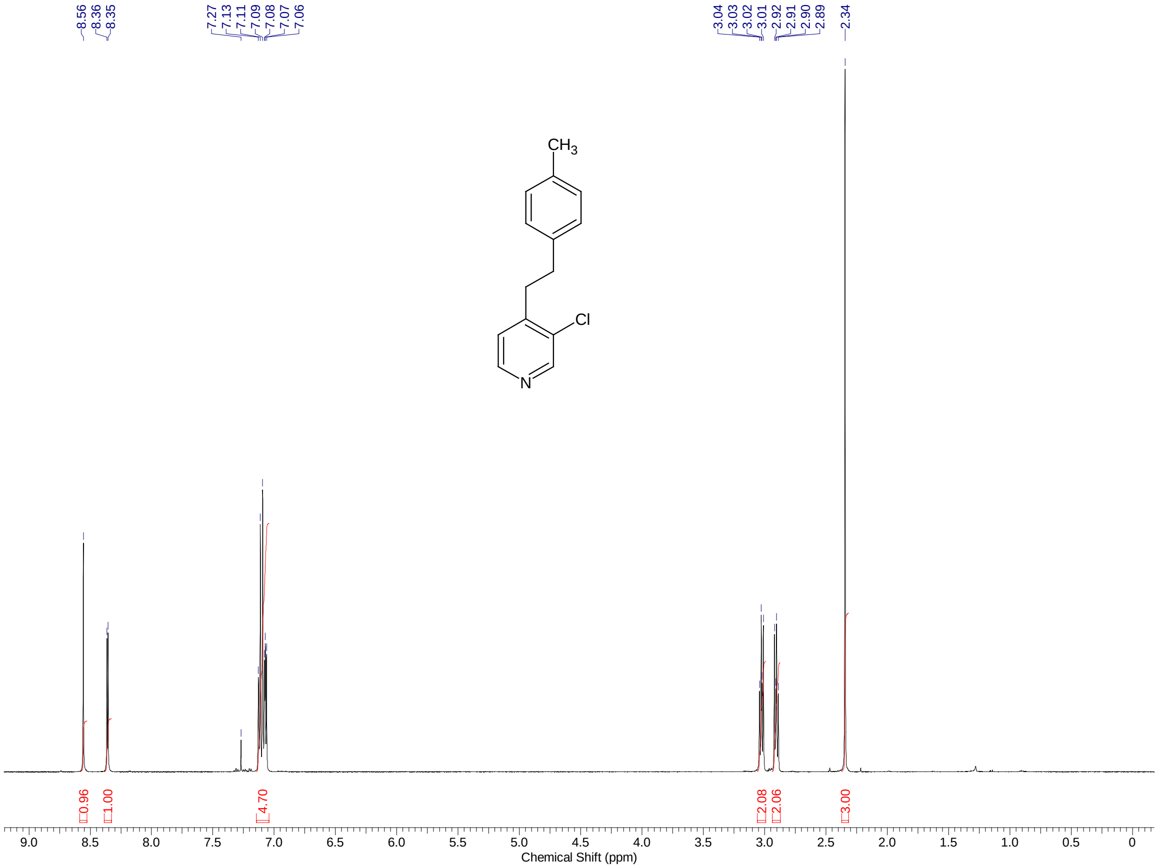
170.7
152.1
148.2
146.2
125.5
123.2
62.1
34.5
20.8
O
O
CH3
Br
N
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

6c:

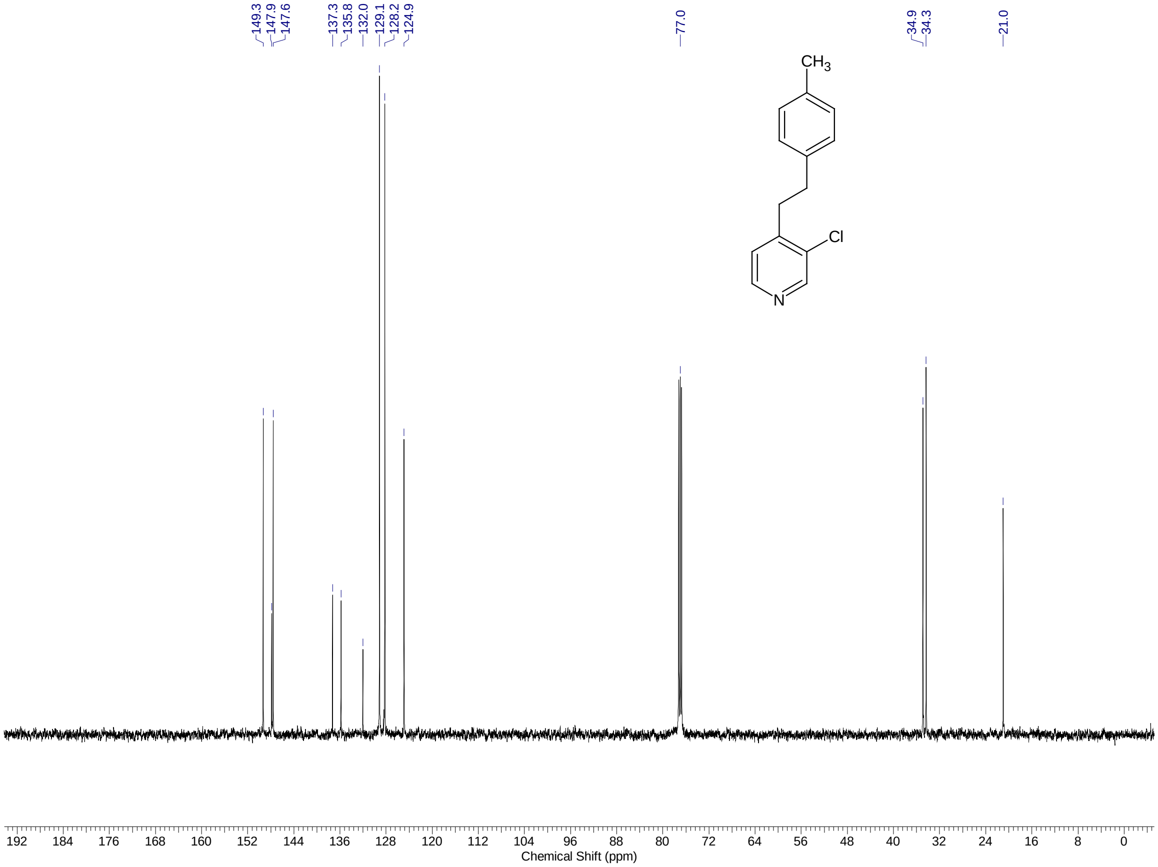

8.90
8.43
8.42
7.19
7.18
4.32
4.31
4.29
3.06
3.04
3.03
2.04
O
O
CH3
I
N
0.90
1.00
1.03
2.26
2.27
3.18
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


170.7
157.6
149.5
148.9
125.2
100.2
62.2
38.9
20.8
O
O
CH3
I
N
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

7a:

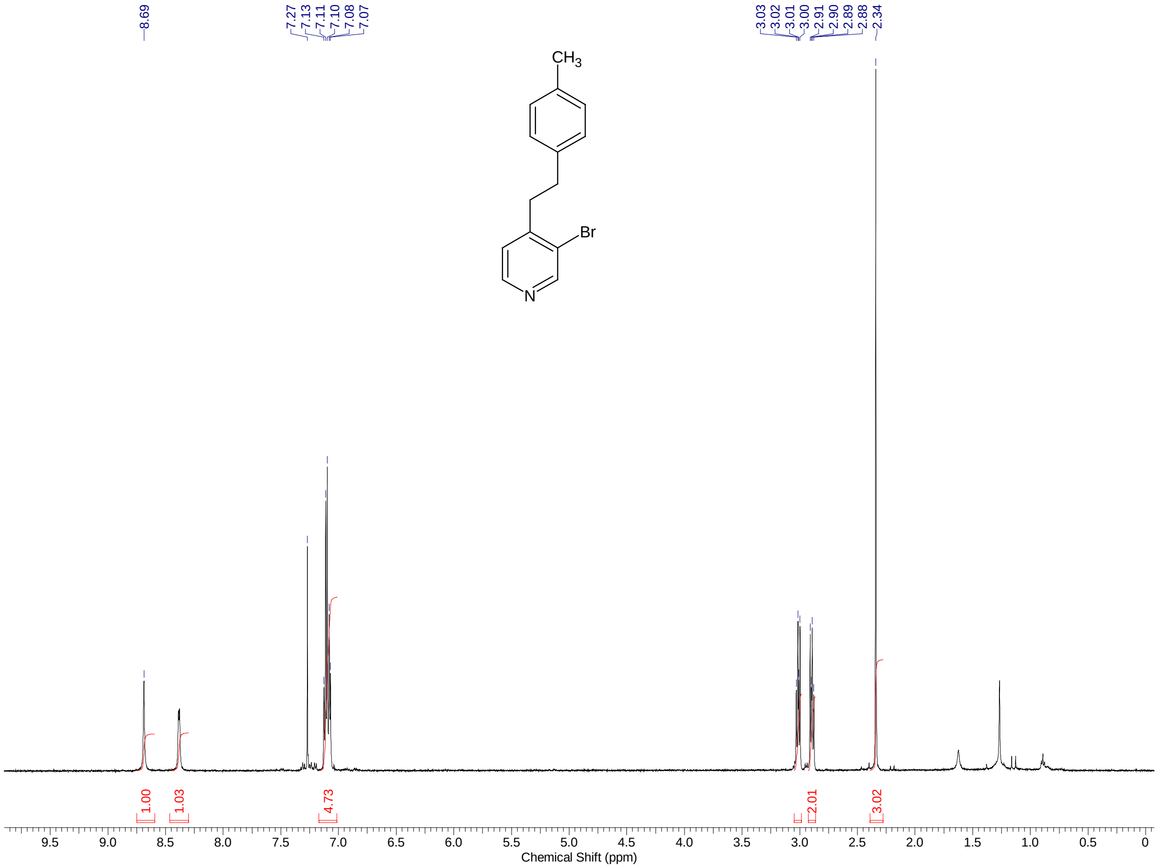


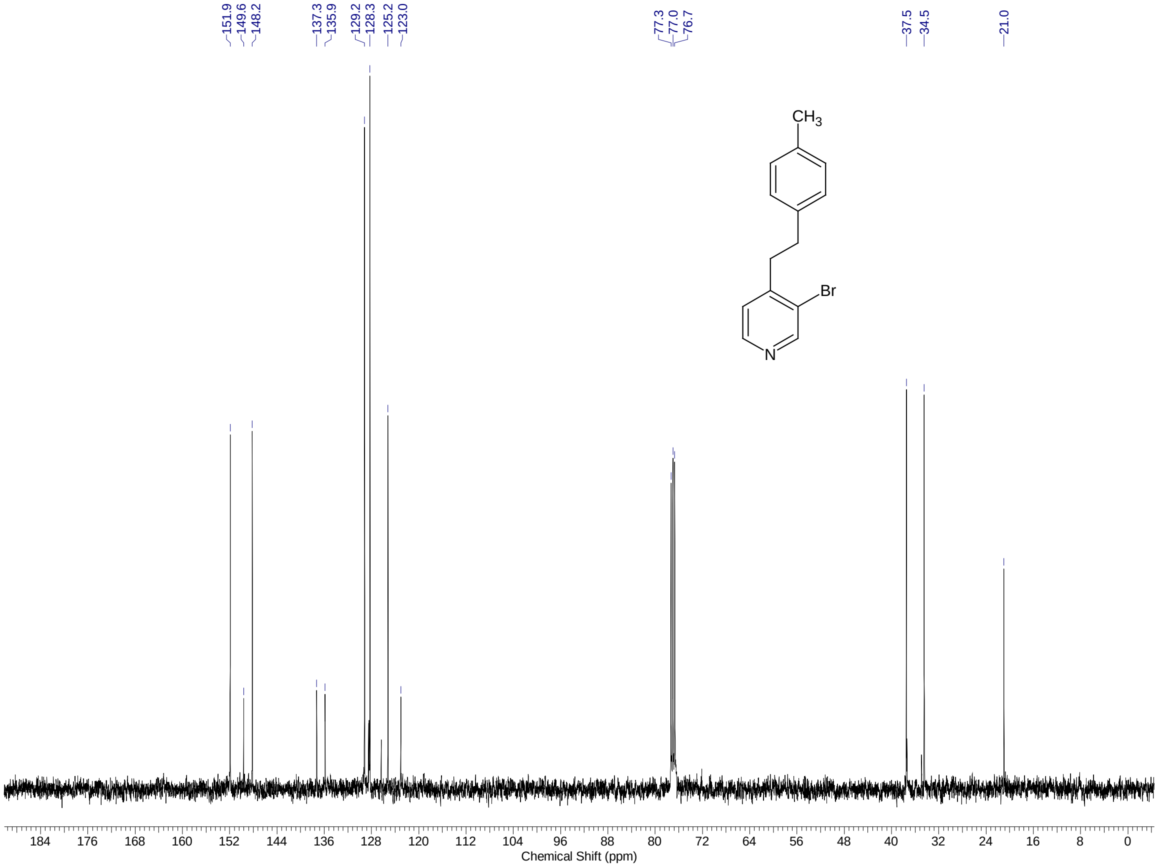
8.56
8.36
8.35
7.27
7.13
7.11
7.09
7.08
7.07
7.06
3.04
3.03
3.02
3.01
2.92
2.91
2.90
2.89
2.34
CH3
Cl
N
0.96
1.00
4.70
2.08
2.06
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)



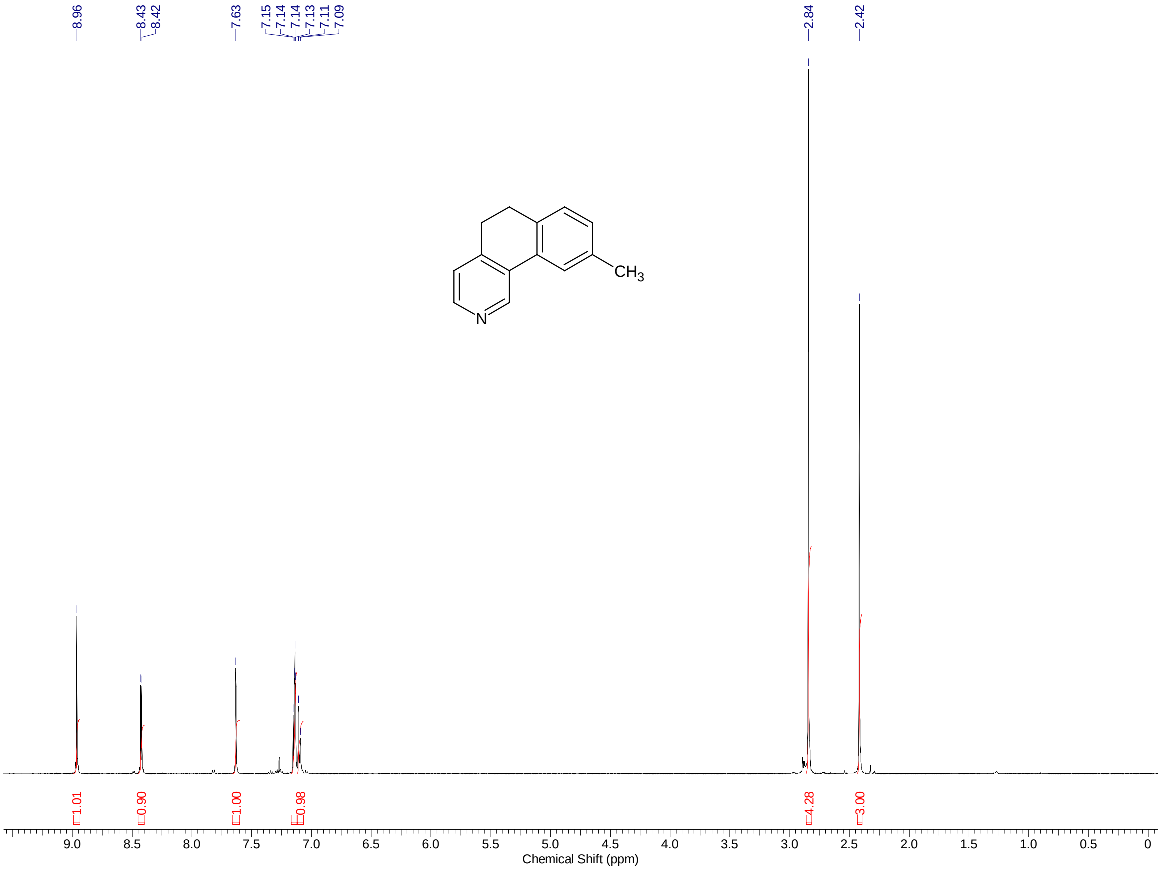
149.3
147.9
147.6
137.3
135.8
132.0
129.1
128.2
124.9
77.0
34.9
34.3
21.0
CH3
Cl
N
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

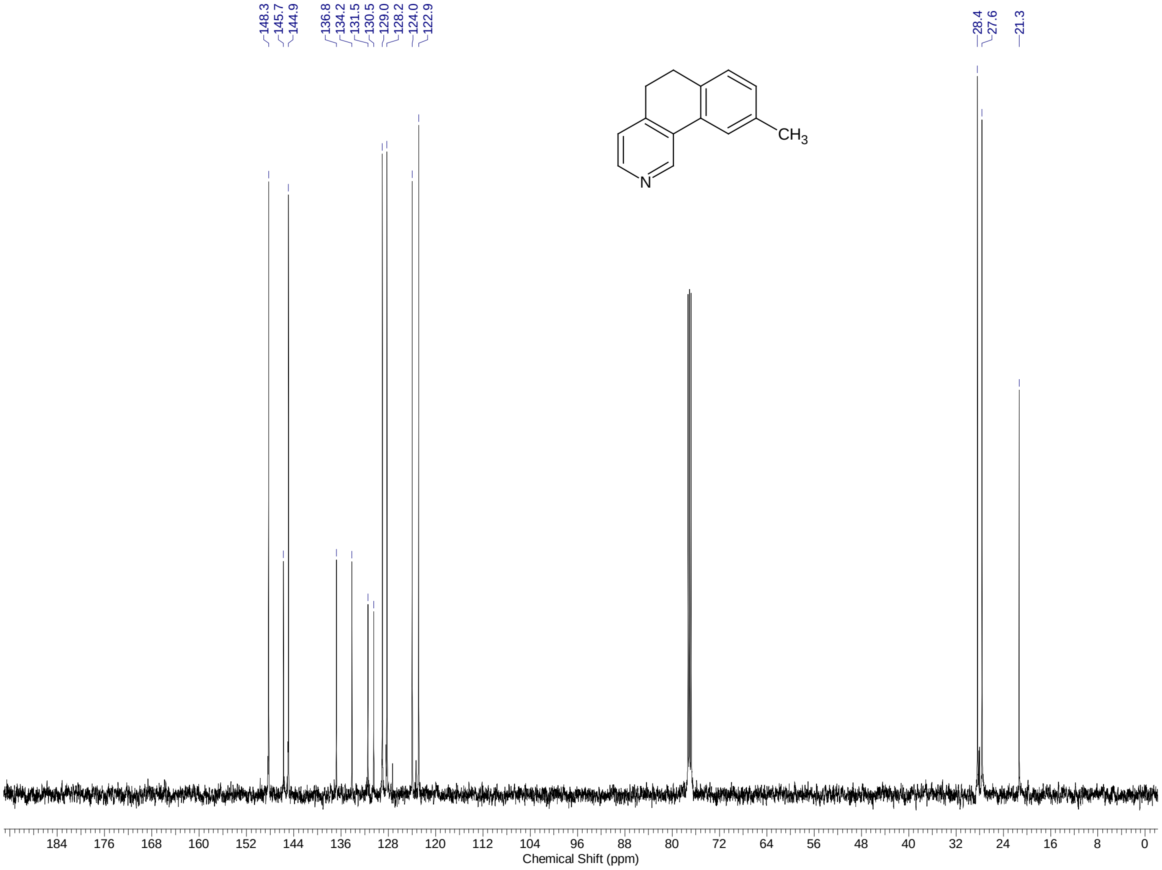
7b:


8.69
7.27
7.13
7.11
7.10
7.08
7.07
3.03
3.02
3.01
3.00
2.91
2.90
2.89
2.88
2.34
CH3
Br
N
1.00
1.03
4.73
2.01
3.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

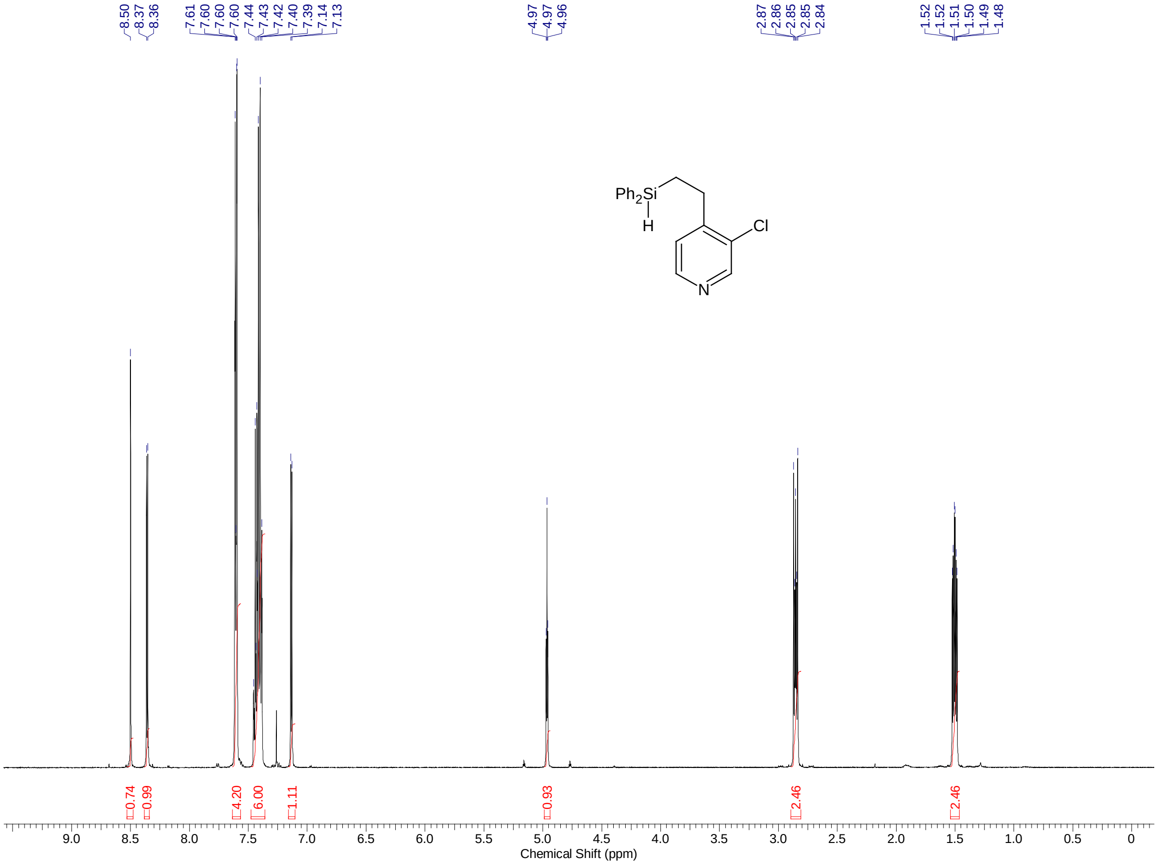

151.9
149.6
148.2
137.3
135.9
129.2
128.3
125.2
123.0
77.3
77.0
76.7
37.5
34.5
21.0
CH3
Br
N
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

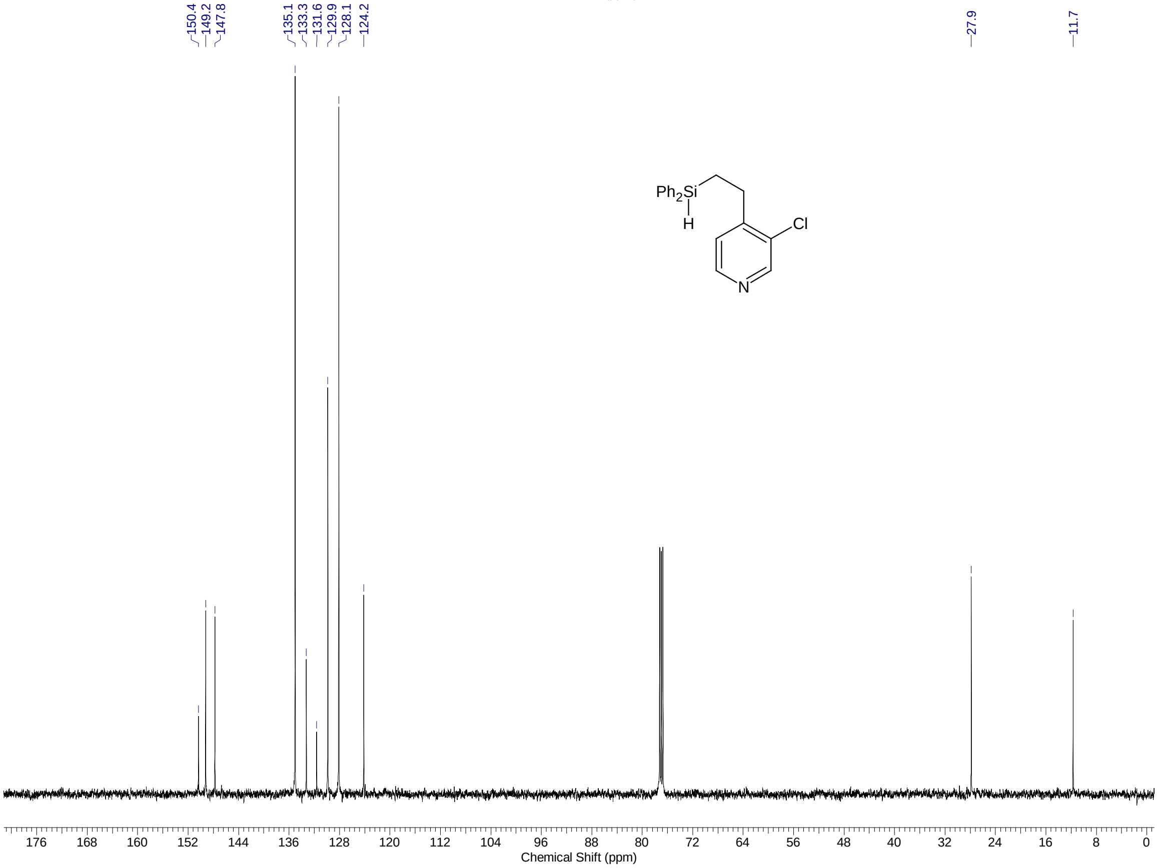
8:


8.96
8.43
8.42
7.63
7.15
7.14
7.14
7.13
7.11
7.09
2.84
2.42
CH3
N
1.01
0.90
1.00
0.98
4.28
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

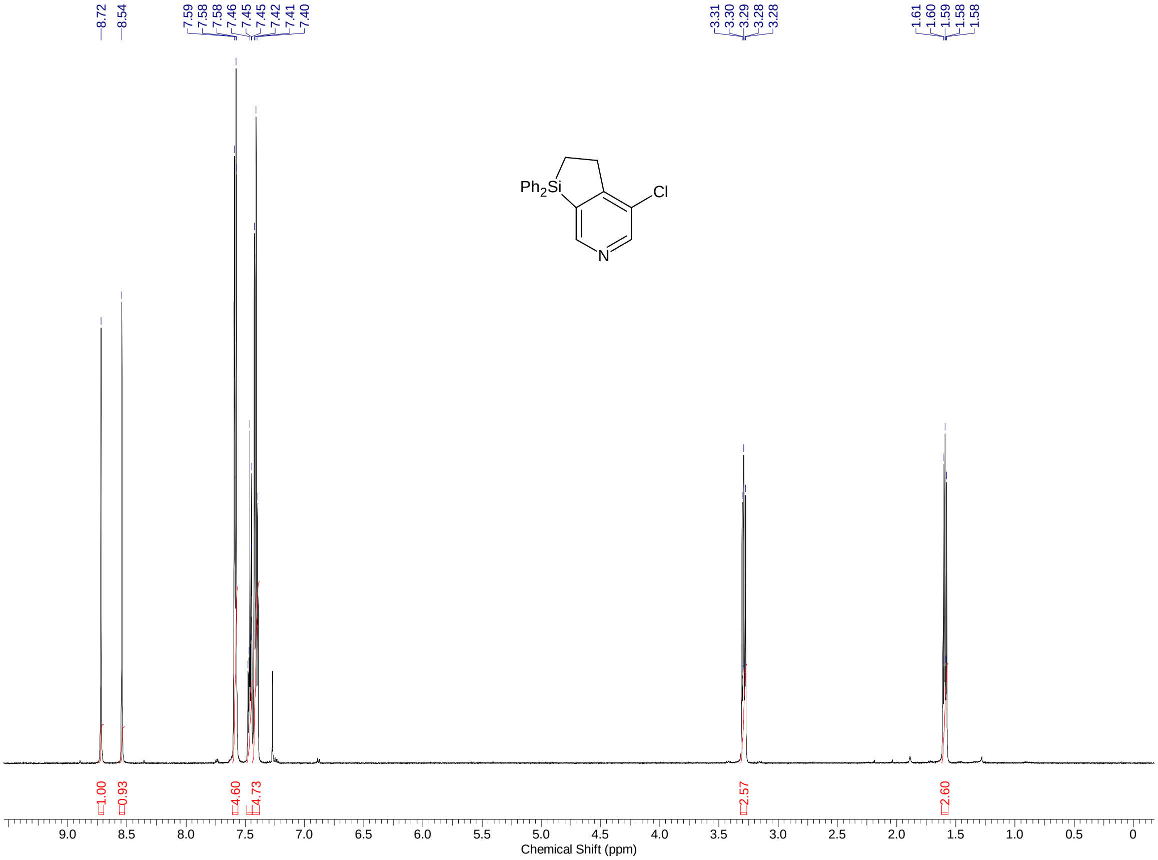

148.3
145.7
144.9
136.8
134.2
131.5
130.5
129.0
128.2
124.0
122.9
28.4
27.6
21.3
CH3
N
184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

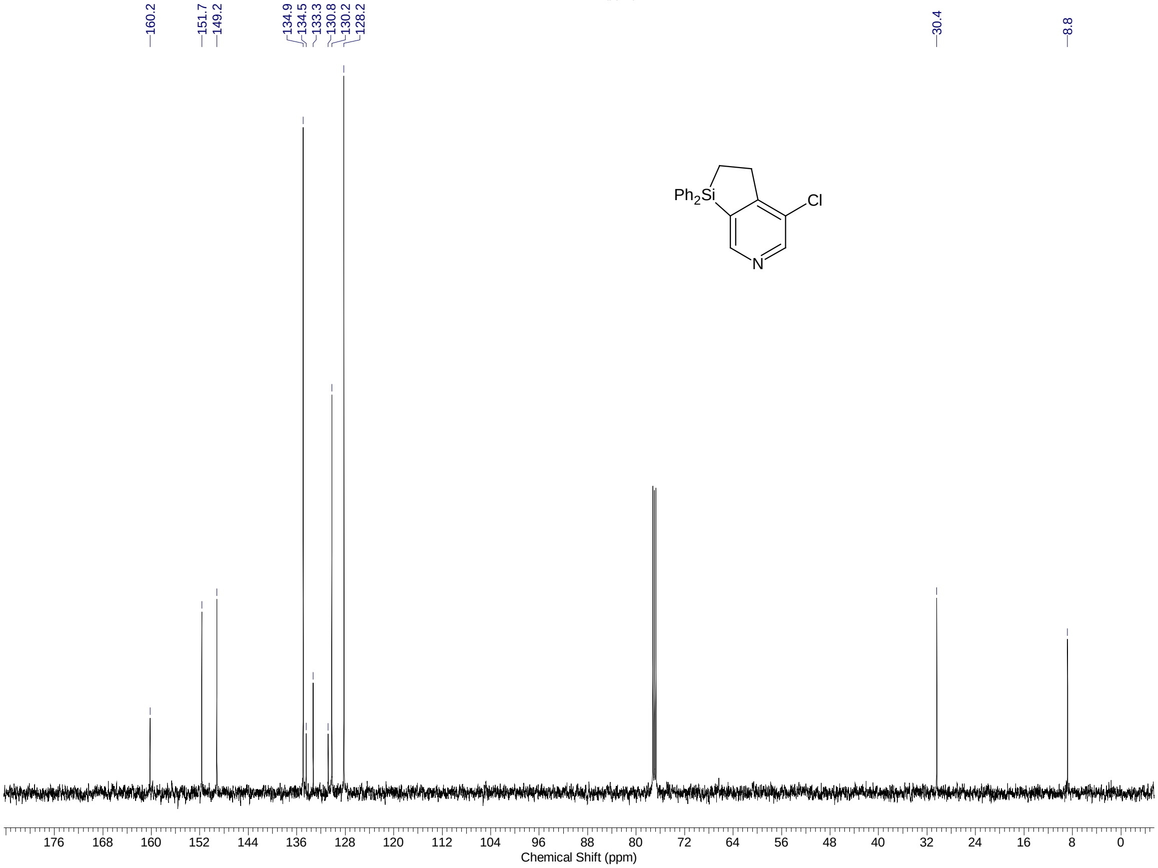
2a’:


8.50
8.37
8.36
7.61
7.60
7.60
7.60
7.44
7.43
7.42
7.40
7.39
7.14
7.13
4.97
4.97
4.96
2.87
2.86
2.85
2.85
2.84
1.52
1.52
1.51
1.50
1.49
1.48
Ph2Si
H
Cl
N
0.74
0.99
4.20
6.00
1.11
0.93
2.46
2.46
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

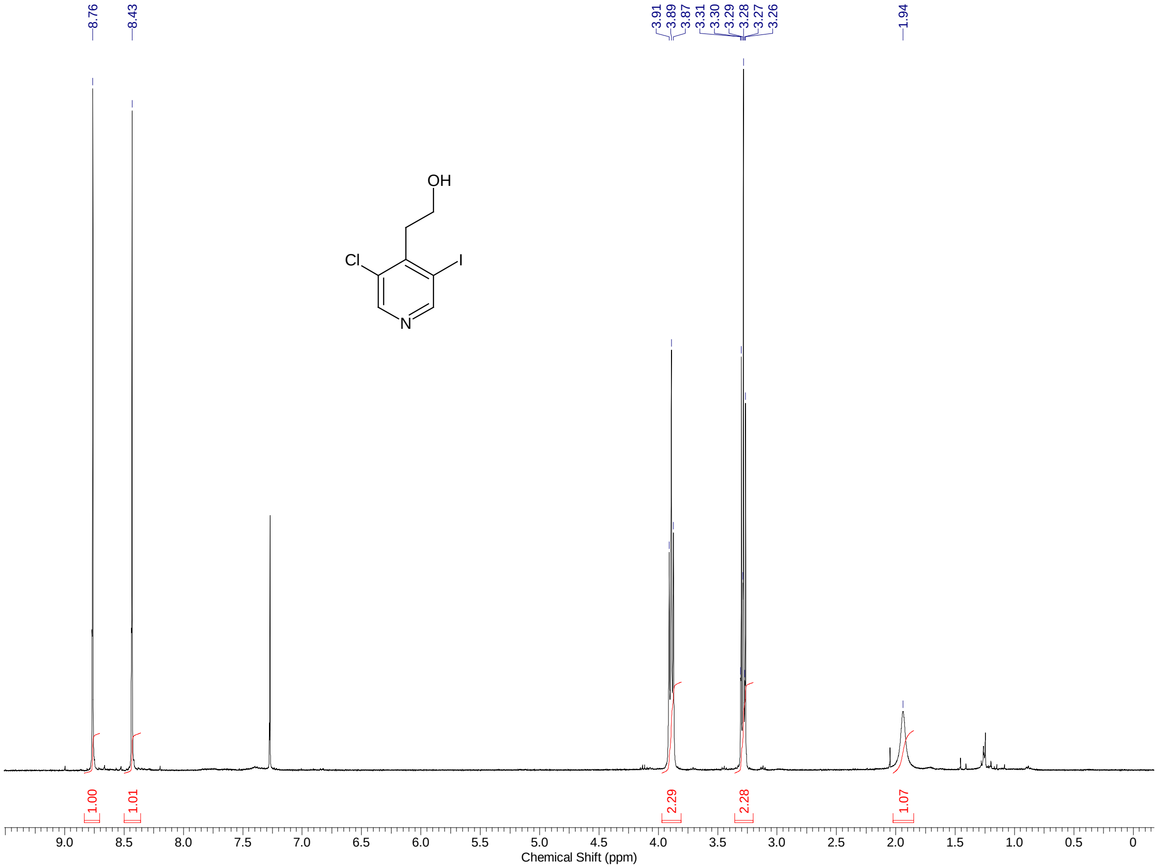

150.4
149.2
147.8
135.1
133.3
131.6
129.9
128.1
124.2
27.9
11.7
Ph2Si
H
Cl
N
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

3a’:

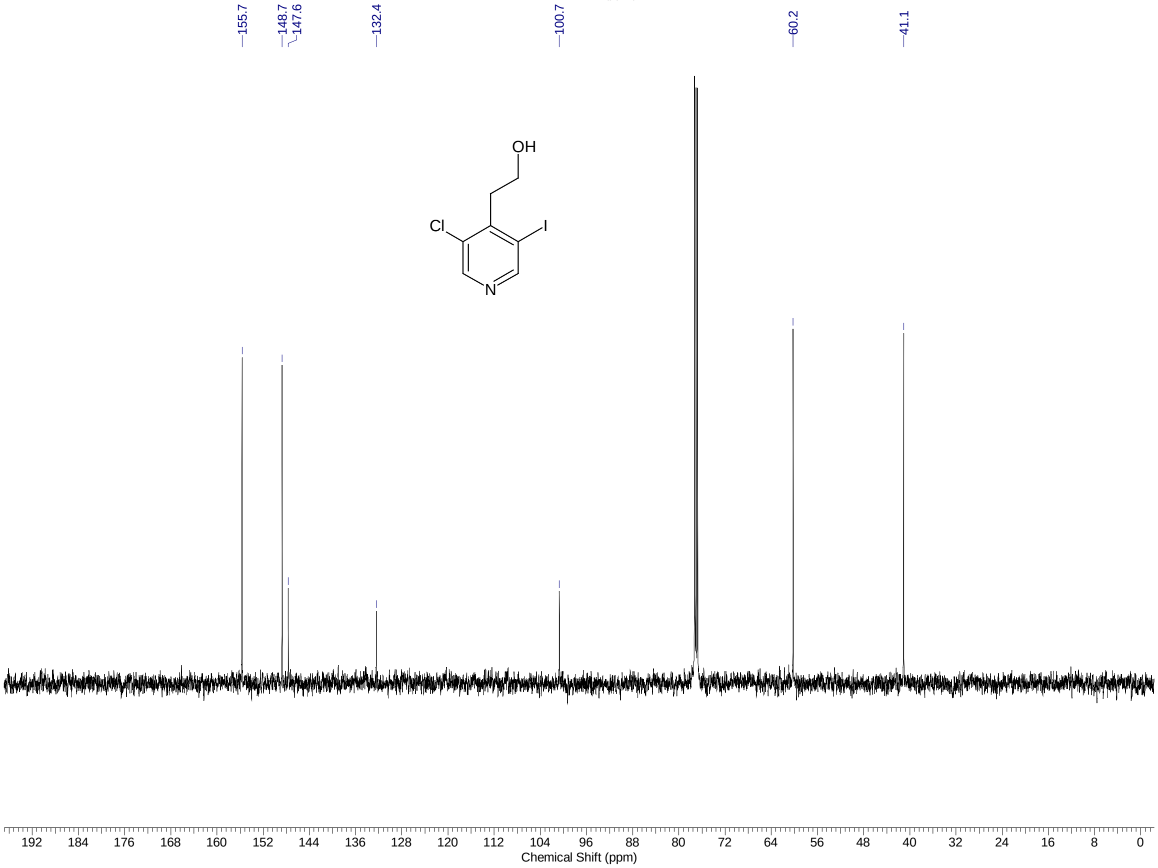

8.72
8.54
7.59
7.58
7.58
7.46
7.45
7.45
7.42
7.41
7.40
3.31
3.30
3.29
3.28
3.28
1.61
1.60
1.59
1.58
1.58
Ph2Si
Cl
N
1.00
0.93
4.60
4.73
2.57
2.60
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


160.2
151.7
149.2
134.9
134.5
133.3
130.8
130.2
128.2
30.4
8.8
Ph2Si
Cl
N
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

9:



8.76
8.43
3.91
3.89
3.87
3.31
3.30
3.29
3.28
3.27
3.26
1.94
OH
Cl
I
N
1.00
1.01
2.29
2.28
1.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)



155.7
148.7
147.6
132.4
100.7
60.2
41.1
OH
Cl
I
N
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)