Supporting Information

Iridium(I) complexes with bidentate NHC ligands as catalysts for dehydrogenative directed C-H silylation

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1. General remarks

Unless indicated otherwise, all reactions requiring an inert atmosphere set up in an argon-filled glove box. All solvents were distilled and degassed prior to use. $[Ir(cod)Cl]_2$ (CAS: 12148-71-9) was purchased from Fluorochem. Every silanes was purchased from Sigma-Aldrich. Several starting materials were synthesized according to modified literature procedures (*vide infra*). Silica gel chromatography was performed with Sigma-Aldrich's silica gel high-purity grade, pore size 60Å, 230-400 mesh particle size, 40-63 μm particle size. Products were visualized using a 254 nm UV lamp on TLC plates unless otherwise noted. NMR spectra were acquired on 400 MHz Bruker instruments at the Laboratoire de Chimie de Coordination, Toulouse. Chemicals shifts were reported relative to residual solvent peaks ($CDCl_3$ = 7.26 ppm for ^1H and 77.2 ppm for ^{13}C; C_6D_6 = 7.16 ppm for ^1H and 128.1 ppm for ^{13}C). Coupling constants are reported in Hertz (Hz). Abbreviations are used as follows: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet, ddd = doublet of doublet of doublet, dt = doublet of triplet, td = triplet of doublet, br = broad. NMR yields were determined by ^1H NMR spectroscopy with mesitylene as an internal standard unless otherwise noted. Mass spectrometric analyses and elemental analyses were performed at Institut de Chimie de Toulouse. Single-crystal X-ray diffraction measurements were recorded on a Bruker Kappa APEX II diffractometer.

2. Synthesis of Ir-NHC complexes

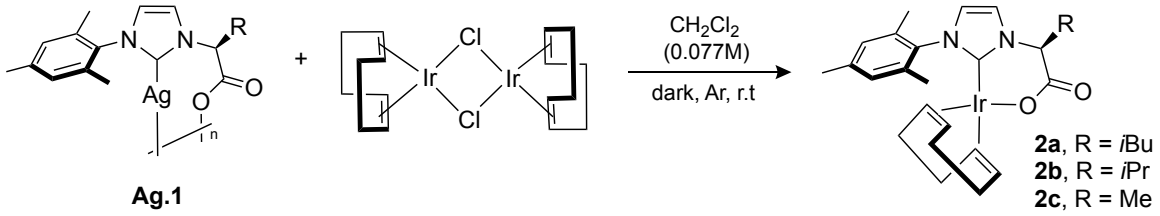
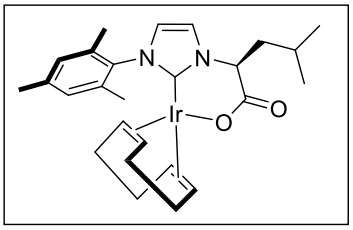
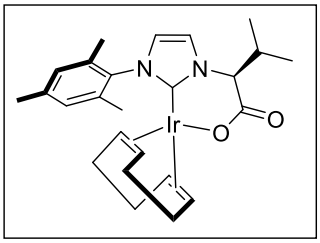


Figure S1. Synthesis of complexes **2a**-**2c.**

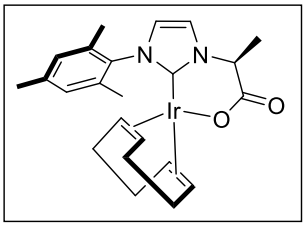
In a dry round-bottomed flask were placed an equivalence of corresponding silver complex[1] (which is considered as a dimer), $[Ir(cod)Cl]_2$ (1 equiv.) and CH_2Cl_2 (0.0077 M). The mixture was stirred for 24 h under Ar atmosphere excluding from the light. Next, CH_2Cl_2 was removed under reduced pressure. Then, acetone was added, and the mixture was filtered through a celite pad using acetone as eluent. Then the filtrate was re-filtered over a microfilter. Then acetone was evaporated, and the complex was washed twice with pentane. The titled complex was obtained after removal of volatiles.



Complex **2a** (orange solid, 87% yield). **^{1}H NMR** (400MHz, C_6D_6) δ 6.71 (s, 1H), 6.70 (d, *J* = 1.9 Hz, 1H), 6.52 (s, 1H), 5.77 (d, *J* = 1.9 Hz, 1H), 5.02 (dd, *J* = 9.6, 6.3 Hz, 1H), 4.92 (td, *J* = 7.6, 2.6 Hz, 1H), 4.56 (td, *J* = 7.8, 5.2 Hz, 1H), 3.36 (td, *J* = 6.9, 2.1 Hz, 1H), 3.07 (ddd, *J* = 13.5, 9.6, 6.1 Hz, 1H), 2.85 (ddd, *J* = 13.6, 9.6, 6.8 Hz, 1H), 2.22 – 2.16 (m, 2H), 2.16 (s, 3H), 2.03 (s, 3H), 1.95 – 1.85 (m, 1H), 1.77 – 1.67 (m, 3H), 1.69 (s, 3H), 1.34 – 1.12 (m, 2H), 1.05 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (101 MHz, C_6D_6) δ 171.8, 171.7, 139.1, 136.9, 136.3, 134.4, 129.2, 128.8, 122.2, 121.2, 85.0, 83.6, 66.7, 51.5, 48.6, 48.0, 36.3, 33.1, 30.2, 28.1, 25.7, 23.3, 22.7, 21.0, 19.1, 17.4. **HRMS** (ESI) calcd for $C_{26}H_{36}N_2O_2Ir$ $[M+H]^+$: *m/z* 601.2406 found 601.2408. **Optical rotation** : $[\alpha]_D^{23}$= -36 (CH_2Cl_2, 1.10^{-3} mol.L^{-1}).



Complex **2b** (orange solid, 79 % yield). **^{1}H NMR** (400MHz, C_6D_6) δ 6.71 (s, 1H), 6.67 (d, *J* = 2.0 Hz, 1H), 6.52 (s, 1H), 5.77 (d, *J* = 1.8 Hz, 1H), 4.92 (td, *J* = 7.6, 2.7 Hz, 1H), 4.54 (td, *J* = 7.8, 5.1 Hz, 1H), 4.36 (d, *J* = 10.5 Hz, 1H), 3.89 (dt, *J* = 10.4, 6.6 Hz, 1H), 3.32 (td, *J* = 6.9, 2.3 Hz, 1H), 2.20 (td, *J* = 6.9, 3.2 Hz, 1H), 2.23 – 2.14 (m, 2H), 2.16 (s, 3H), 2.12 – 2.06 (m, 1H), 2.03 (s, 3H), 1.92 – 1.83 (m, 1H), 1.77 – 1.65 (m, 3H), 1.69 (s, 3H), 1.46 (d, *J* = 6.7 Hz, 3H), 1.34 – 1.25 (m, 1H), 1.22 – 1.14 (m, 1H), 0.88 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, C_6D_6) δ 171.1, 171.0, 139.1, 136.8, 136.3, 134.3, 129.2, 128.9, 122.9, 121.1, 84.9, 83.4, 74.9, 51.2, 48.7, 37.5, 36.2, 33.2, 30.1, 28.2, 21.0, 20.2, 19.4, 19.1, 17.3. HRMS (ESI) calcd for $C_{25}H_{34}N_2O_2Ir$ $[M+H]^+$: *m/z* 587.2250 found 587.2256. **Optical rotation** : $[\alpha]_D^{23}$= -30 (CH_2Cl_2, 1.10^{-3} mol.L^{-1}).



Complex **2c** (orange solid, 79 % yield). **^{1}H NMR** (400MHz, C_6D_6) δ 6.69 (s, 1H), 6.56 (s, 1H), 6.46 (d, *J* = 1.9 Hz, 1H), 5.78 (d, *J* = 1.9 Hz, 1H), 4.92 (q, *J* = 7.1 Hz, 1H), 4.87 (td, *J* = 7.6, 3.3 Hz, 1H), 4.65 (td, *J* = 7.8, 4.8 Hz, 1H), 3.16 (td, *J* = 7.0, 2.5 Hz, 1H), 2.40 (td, *J* = 7.5, 3.7 Hz, 1H), 2.12 (d, *J* = 7.0 Hz, 3H), 2.10 – 2.06 (m, 1H), 2.09 (s, 3H), 2.05 – 1.98 (m, 1H), 2.03 (s, 3H), 1.96 – 1.87 (m, 1H), 1.84 – 1.78 (m, 1H), 1.76 (s, 3H), 1.68 – 1.58 (m, 2H), 1.40 – 1.33 (m, 1H), 1.29 – 1.23 (m, 1H). **^{13}C NMR** (101 MHz, C_6D_6) δ 171.8, 171.5, 139.1, 136.5, 136.4, 134.8, 129.2, 129.0, 121.3, 120.7, 85.4, 84.6, 62.9, 51.2, 49.4, 35.7, 33.7, 29.8, 28.5, 22.7, 21.0, 18.9, 17.8. HRMS (ESI) calcd for $C_{23}H_{30}N_2O_2Ir$ $[M+H]^+$: *m/z* 559.1937 found 559.1942. **Optical rotation** : $[\alpha]_D^{23}$= -18 (CH_2Cl_2, 1.10^{-3} mol.L^{-1}).

3. Substrates synthesis.

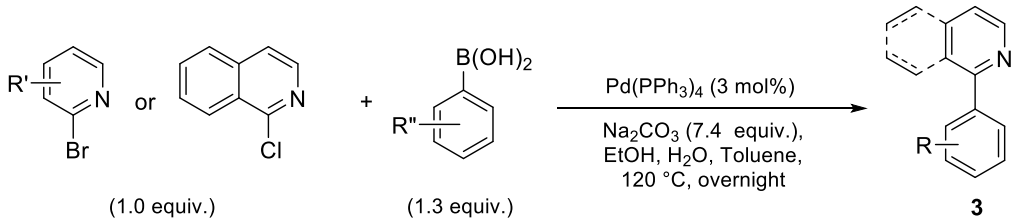


Figure S2. Preparation of compound **3.**

Compounds **3** were prepared according to the reported procedure in the literature.[2] To a solution of corresponding 2-bromopyridines (2 mmol, 1 equiv.) or 1-chloroisoquinoline (2 mmol, 1 equiv.) in toluene (7 mL), ethanol (1.5 mL), and H_2O (7 mL) was added Na_2CO_3 (7.4 equiv.) followed by $Pd(PPh_3)_4$ (3mol%) and corresponding boronic acid (1.3 equiv.) under argon in a 50 mL Schlenk tube. The reaction mixture was refluxed at 120°C for overnight, and then cooled to room temperature. To the reaction mixture was added aqueous NH_4Cl (15 mL), extracted by EtOAc for three times, dried over $MgSO_4$, and evaporated in vacuum to afford the crude product, which was further purified by flash column chromatography on silica gel with *n*-pentane/EtOAc to give the corresponding substrates.

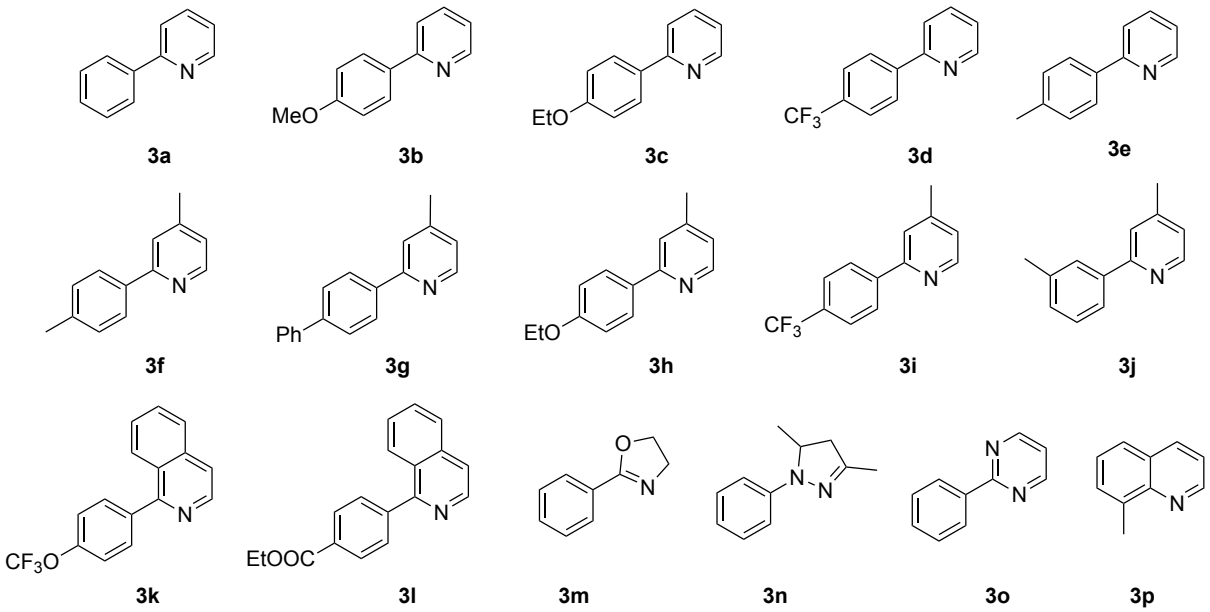


Figure S3. Substrates for silylation.

Compounds (**3a**) (CAS : 1008-89-5), **3b** (CAS: 5957-90-4), **3c** (CAS: 4357-28-2), **3d** (CAS : 203065-88-7), **3e** (CAS : 4467-06-5), **3f** (CAS: 80635-92-3), **3g** (CAS: 1215556-50-5), **3h** (CAS: 446302-06-3), **3i** (CAS: 452342-99-3), **3j** (CAS: 80635-91-2), **3k**, **3l** (CAS: 52947-17-8), **3m** (CAS: 7127-19-7), **3n** (CAS: 24665-41-6), **3o** (CAS: 7431-45-0), **3p** (62882-00-2), were previously reported. Zolimidine[3] (CAS: 1222-57-7) and diazepam[4] (CAS: 439-14-5) were prepared according to reported procedures.

4. Optimization studies

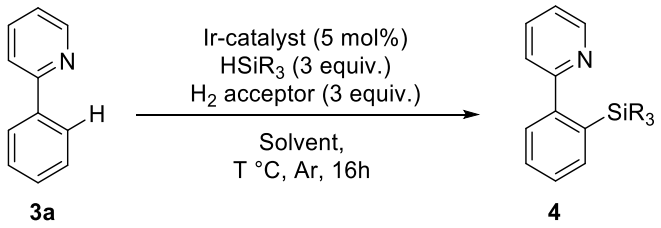


Figure S4. Optimization studies.

In a glove box, in a dry Schlenk tube was placed the Ir-catalyst (5 mol%), hydrogen acceptor (3 equiv.), 2-phenylpyridine (1 equiv.), silane (3 equiv.) and solvent (1mL). The tube was sealed with a screw cap. Outside the glove box, the mixture was stirred at the indicated temperature for 16h. After cooled down, the mixture was concentrated under reduce pressure and dried under vacuum. To the residue was added 1,3,5-trimethylbenzene (as an internal standard) and 0.5 mL of $CDCl_3$. Then the aliquot was analyzed by ^1H NMR to measure the NMR yield.

Table S1. Optimization studies

Entry	Silane (3 equiv.)	H_2-acceptor (3 equiv.)	Solvent	Catalyst (5 mol%)	Temp. (°C)	NMR Yield
1	Et_3SiH	norbornene	Toluene	**2a**	120°C	49%
2	Et_3SiH	norbornene	Toluene	**2a**	90°C	< 5%
3	Et_3SiH	norbornene	THF	**2a**	80°C	14%
4	Et_3SiH	norbornene	Me-THF	**2a**	90°C	8%
5	Et_3SiH	norbornene	neat	**2a**	120°C	36%
6	$(OEt)_3SiH$	norbornene	Toluene	**2a**	120°C	n.r.
7	Et_2MeSiH	norbornene	Toluene	**2a**	120°C	< 5%
8	Me_2PhSiH	norbornene	Toluene	**2a**	120°C	64%
9	$MePh_2SiH$	norbornene	Toluene	**2a**	120°C	82%
10	Ph_3SiH	norbornene	Toluene	**2a**	120°C	74%
11	Et_3SiH	1,5-cod	Toluene	**2a**	120°C	10%
12	Et_3SiH	neohexene	Toluene	**2a**	120°C	40%
13	Et_3SiH	norbornadiene	Toluene	**2a**	120°C	22%
14	$MePh_2SiH$	norbornene	Toluene	**2b**	120°C	72%
15	$MePh_2SiH$	norbornene	Toluene	**2c**	120°C	74%
16	$MePh_2SiH$	norbornene	Toluene	$[Ir(cod)Cl]_2$	120°C	49%
17	$MePh_2SiH$	norbornene	Toluene	(IMes)Ir(cod)Cl[5]	120°C	16%
18	Et_3SiH	norbornene	Toluene	**2a**	30°C	n.r.
19	Et_3SiH	norbornene	Toluene	-	120°C	n.r.
20	Et_3SiH	-	Toluene	**2a**	120°C	n.r.

5. Scope of substrates

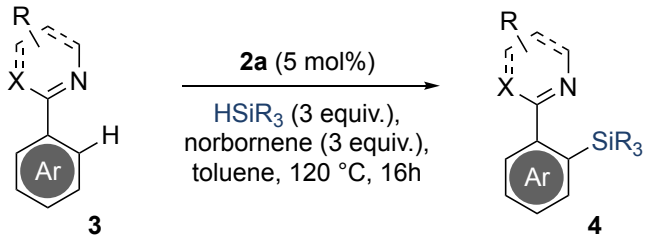
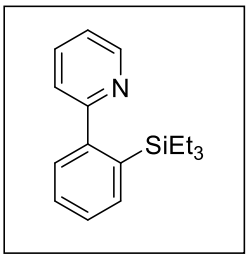


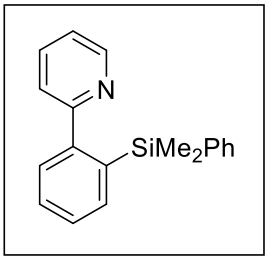
Figure S5. Substrate scope studies.

General procedure: In a glove box, in a dry Schlenk tube was placed **2a** (5 mol%), substrate **3** (0.2 mmol, 1.0 equiv.), norbornene (3 equiv.), silane (3 equiv.) and toluene (1mL) were added respectively. The tube was closed with a screw cap. Outside the glove box, the mixture was stirred at 120°C for 16h. After cooled down, the mixture was concentrated under reduced pressure and dried under vacuum. To the residue was added mesitylene or trimethoxybenzene (as internal standard) and 0.5 mL of $CDCl_3$. Then the aliquot was analyzed by ^1H NMR to measure the NMR yield. The crude mixture was purified by column chromatography on silica gel to isolate the corresponding silylated product **4**.

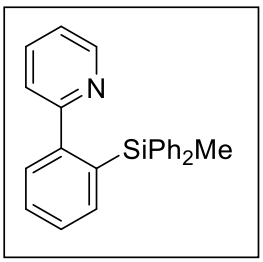
*Characterization of compound **4a–4x***



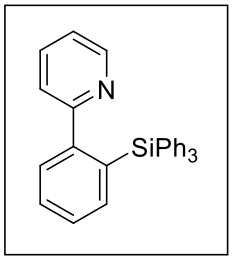
Compound 4a was obtained after column chromatography (hexane/EtOAc = 98/2) as colorless oil (49% NMR yield, 47% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.1 Hz, 1H), 7.73 (td, *J* = 7.7, 1.7 Hz, 1H), 7.65 (d, *J* = 6.9 Hz, 1H), 7.45 – 7.36 (m, 4H), 7.28 – 7.25 (m, 1H), 0.83 (t, *J* = 7.9 Hz, 9H), 0.55 (q, *J* = 7.9 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.0, 148.6, 148.0, 136.5, 136.3, 136.1, 129.2, 128.7, 127.3, 123.4, 122.1, 7.8, 4.6. **^{29}Si NMR** (80 MHz, $CDCl_3$) δ -3.4. The data were consistent with the previous literature.[6]



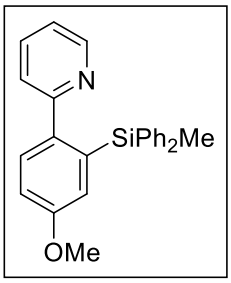
Compound 4b was obtained after column chromatography (hexane/EtOAc = 95/5) as colorless oil (64% NMR yield, 59% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 4.8 Hz, 1H), 7.66 (d, *J* = 7.4 Hz, 1H), 7.57 (td, *J* = 7.7, 1.8 Hz, 1H), 7.53 – 7.40 (m, 5H), 7.38 – 7.33 (m, 2H), 7.27 – 7.23 (m, 3H), 7.13 (ddd, *J* = 7.4, 4.9, 0.9 Hz, 1H), 0.36 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.6, 148.4, 147.2, 141.0, 137.4, 136.9, 136.3, 133.8, 129.3, 128.7, 128.3, 127.6, 127.5, 122.9, 122.0, -0.2. **^{29}Si NMR** (80 MHz, $CDCl_3$) δ -8.8. The data were consistent with the previous literature.[6]



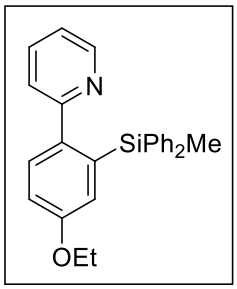
Compound 4c was obtained after column chromatography (hexane/EtOAc = 90/10) as beige solid (82% NMR yield, 71% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 4.9 Hz, 1H), 7.70 (d, *J* = 6.3 Hz, 1H), 7.55 – 7.48 (m, 3H), 7.47 – 7.41 (m, 5H), 7.37 – 7.27 (m, 7H), 7.02 (ddd, *J* = 7.4, 4.8, 1.2 Hz, 1H), 0.63 (s, 3H). **^{13}C NMR** (101MHz, $CDCl_3$) δ 159.2, 148.0, 146.9, 139.7, 138.9, 136.2, 135.5, 134.8, 129.7, 128.4, 128.1, 127.8, 127.6, 122.1, 122.8, -1.2. **^{29}Si NMR** (80 MHz, $CDCl_3$) δ -13.2. The data were consistent with the previous literature.[6]



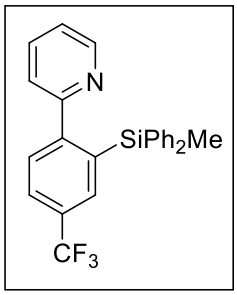
Compound 4d was obtained after column chromatography (hexane/EtOAc = 95/5) as colorless solid (74% NMR yield, 68% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.56 (td, *J* = 7.6, 1.4 Hz, 1H), 7.48 – 7.45 (m, 7H), 7.36 – 7.32 (m, 1H), 7.29 – 7.19 (m, 10H), 6.76 (dd, *J* = 7.0, 5.3 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.1, 147.1, 145.4, 140.6, 139.5, 136.4, 135.7, 133.8, 130.1, 128.5, 128.1, 127.3, 126.7, 122.1, 120.0. **^{29}Si NMR** (80 MHz, $CDCl_3$) δ -21.1. The data were consistent with the previous literature.[6]



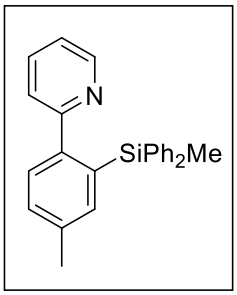
Compound 4e was obtained after column chromatography (hexane/EtOAc = 88/12) as beige solid (94% NMR yield, 87% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 4.8 Hz, 1H), 7.71 – 7.68 (m, 1H), 7.65 – 7.63 (m, 1H), 7.49 – 7.43 (m, 6H), 7.33 – 7.28 (m, 5H), 7.04 – 7.01 (m, 2H), 6.95 (ddd, *J* = 7.2, 5.5, 1.3 Hz, 1H), 3.68 (s, 3H), 0.70 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.2, 158.2, 147.6, 140.1, 139.0, 137.6, 136.3, 134.7, 129.1, 128.3, 127.6, 124.9, 121.4, 121.1, 114.7, 55.1, -1.0. **^{29}Si NMR** (80 MHz, $CDCl_3$) δ -14.1. **HRMS (ESI)** calcd for $[C_{25}H_{24}NOSi]^+$ $[M+H]^+$: *m/z* 382.1627, found 382.1627.



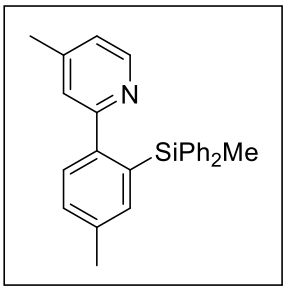
Compound 4f was obtained after column chromatography (hexane/EtOAc = 92/8) as beige solid (99% NMR yield, 90% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (ddd, *J* = 4.9, 1.8, 1.0 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.47 (ddd, *J* = 7.9, 7.2, 1.8 Hz, 1H), 7.44 – 7.38 (m, 5H), 7.30 – 7.22 (m, 6H), 7.00 – 6.96 (m, 2H), 6.92 (ddd, *J* = 7.2, 4.9, 1.3 Hz, 1H), 3.88 (q, *J* = 7.0 Hz, 2H), 1.31 (t, *J* = 7.0 Hz, 3H), 0.65 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.6, 158.3, 147.6, 140.2, 138.9, 137.4, 136.2, 134.7, 129.1, 128.3, 127.5, 125.2, 121.4, 121.1, 115.5, 63.3, 14.9, -0.9. **^{29}Si NMR** (80 MHz, $CDCl_3$) δ -14.1. **HRMS (ESI)** calcd for $[C_{26}H_{26}NOSi]^+$ $[M+H]^+$: *m/z* 396.1785, found 396.1784.



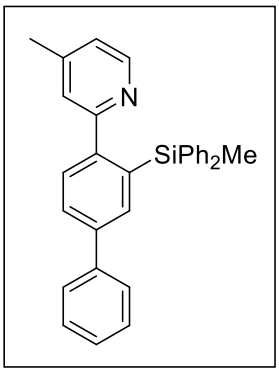
Compound 4g was obtained after column chromatography (hexane/EtOAc = 90/10) as beige solid (92% NMR yield, 76% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (ddd, *J* = 4.9, 1.8, 1.0 Hz, 1H), 7.80 – 7.75 (m, 3H), 7.53 (td, *J* = 7.6, 1.8 Hz 1H), 7.46 – 7.42 (m, 5H), 7.36 – 7.27 (m, 6H), 7.05 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 0.69 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.9, 150.3, 148.3, 138.5, 137.2, 136.5, 135.2 (q, *J* = 3.7 Hz), 134.7, 129.6 (q, *J* = 31.3 Hz), 128.8, 128.3, 127.8, 126.5 (q, *J* = 3.7 Hz), 124.5 (q, *J* = 273.7 Hz), 122.7, 122.3, -1.2. **^{29}Si NMR** (80 MHz, $CDCl_3$) -12.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.7. **HRMS (ESI)** calcd for $[C_{25}H_{21}NF_3Si]^+$ $[M+H]^+$: *m/z* 420.1399, found 420.1395.



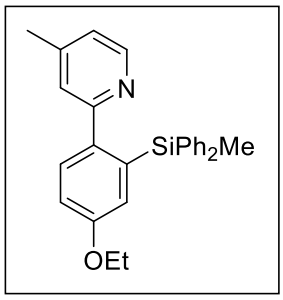
Compound 4h was obtained after column chromatography (hexane/EtOAc = 90/10) as beige solid (99% NMR yield, 81% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (ddd, *J* = 4.9, 1.8, 1.0 Hz, 1H), 7.59 – 7.57 (m, 1H), 7.47 – 7.37 (m, 6H), 7.30 – 7.22 (m, 8H), 6.94 (ddd, *J* = 7.4, 4.9, 1.2 Hz, 1H), 2.28 (s, 3H), 0.61 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.0, 147.9, 144.1, 139.9, 139.7, 137.3, 136.1, 135.2, 134.8, 130.4, 128.3, 128.0, 127.5, 121.8, 121.7, 21.5, -0.9. **^{29}Si NMR** (80 MHz, $CDCl_3$) δ -13.5. **HRMS (ESI)** calcd for $[C_{25}H_{24}NSi]^+$ $[M+H]^+$: *m/z* 366.1670, found 366.1672.



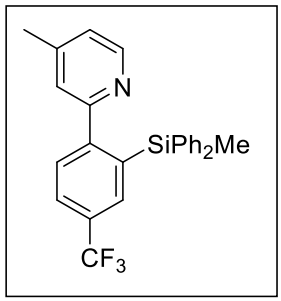
Compound 4i was obtained after column chromatography (hexane/EtOAc = 90/10) as beige solid (96% NMR yield, 90% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 5.6 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.46 – 7.43 (m, 4H), 7.34 – 7.27 (m, 8H), 7.12 (s, 1H), 6.82 (d, *J* = 7.3 Hz, 1H), 2.31 (s, 3H), 2.17 (s, 3H), 0.55 (s, 3H). **^{13}C NMR** (101MHz, $CDCl_3$) δ 159.1, 147.9, 147.0, 144.6, 139.7, 139.4, 137.1, 135.1, 134.8, 130.4, 128.4, 128.1, 127.5, 123.3, 122.8, 21.5, 21.1, -1.2. **^{29}Si NMR** (80 MHz, $CDCl_3$) δ -13.4. **HRMS (ESI)** calcd for $[C_{26}H_{26}NSi]^+$ $[M+H]^+$: *m/z* 380.1835, found 380.1838.



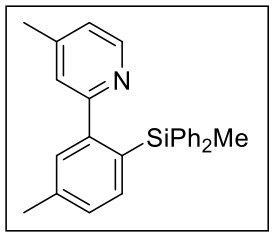
Compound 4j was obtained after column chromatography (hexane/EtOAc = 90/10) as beige solid (92% NMR yield, 81% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 5.6 Hz, 1H), 7.81 – 7.75 (m, 3H), 7.54 – 7.50 (m, 6H), 7.44 – 7.40 (m, 2H), 7.36 – 7.30 (m, 7H), 7.24 (s, 1H), 6.88 (dd, *J* = 5.1, 0.9 Hz, 1H), 2.22 (s, 3H), 0.66 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.6, 147.9, 147.2, 146.1, 140.9, 139.9, 139.6, 137.6, 136.0, 134.8, 134.1, 128.9, 128.5, 128.2, 127.6, 127.4, 127.1, 123.2, 123.1, 21.1, -1.3. **^{29}Si NMR** (80 MHz, $CDCl_3$) δ -13.1. **HRMS (ESI) c**alcd for $[C_{31}H_{28}NSi]^+$ $[M+H]^+$: *m/z* 442.2009, found 442.1991.



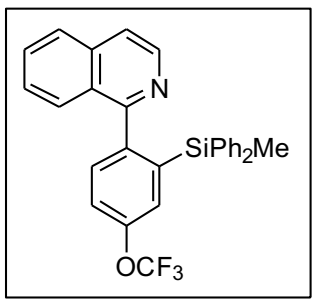
Compound 4k was obtained after column chromatography (hexane/EtOAc = 90/10) as beige solid (95% NMR yield, 90% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 5.0 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.44 – 7.41 (m, 4H), 7.31 – 7.23 (m, 6H), 7.13 (s, 1H), 6.99 – 6.94 (m, 2H), 6.77 (d, *J* = 4.6 Hz, 1H), 3.88 (q, *J* = 7.0 Hz, 2H), 2.16 (s, 3H), 1.31 (t, *J* = 7.0 Hz, 3H), 0.56 (s, 3H). **^{13}C NMR** (101MHz, $CDCl_3$) δ 158.5, 158.4, 147.6, 147.1, 140.0, 139.4, 137.3, 134.8, 129.2, 128.4, 127.6, 125.0, 122.6, 122.6, 115.5, 63.4, 21.2, 14.9, -1.2. **^{29}Si NMR** (80 MHz, $CDCl_3$) δ -14.0. **HRMS (ESI)** calcd for $[C_{27}H_{28}NOSi]^+$ $[M+H]^+$: *m/z* 410.1940, found 410.1947.



Compound 4l was obtained after column chromatography (hexane/EtOAc = 92/8) as beige solid (95% NMR yield, 83% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 5.0 Hz, 1H), 7.72 – 7.70 (m, 3H), 7.41 – 7.39 (m, 4H), 7.34 – 7.28 (m, 6H), 7.09 (s, 1H), 6.88 (dd, *J* = 4.3 Hz, 1H), 2.17 (s, 3H), 0.56 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) 157.9, 150.7, 148.2, 147.5, 138.3, 137.1, 135.0 (q, *J* = 3.7 Hz), 134.7, 129.5 (q, *J* = 32.2 Hz), 128.9, 128.4, 127.8, 126.5 (q, *J* = 3.5 Hz), 124.5 (q, *J* = 273.7 Hz), 123.7, 123.7, 21.1, -1.6. **^{29}Si NMR** (80 MHz, $CDCl_3$) δ -12.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.6. **HRMS (DCI-CH_4)** calcd for $[C_{26}H_{23}NF_3Si]^+$ $[M+H]^+$: *m/z* 434.1552, found 434.1555.

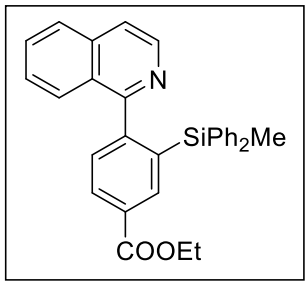


Compound 4m was obtained after column chromatography (hexane/EtOAc = 92/8) as beige solid (98% NMR yield, 92% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 5.0 Hz, 1H), 7.49 – 7.48 (m, 1H), 7.47 – 7.44 (m, 4H), 7.37 – 7.27 (m, 7H), 7.16 (ddd, *J* = 7.6, 1.6, 0.6 Hz, 1H), 7.09 (s, 1H), 6.86 (ddd, *J* = 5.0, 1.5, 0.7 Hz, 1H), 2.43 (s, 3H), 2.15 (s, 3H), 0.51 (s, 3H). **^{13}C NMR** (101MHz, $CDCl_3$) δ 159.4, 148.0, 147.5, 147.1, 139.6, 139.5, 138.7, 134.9, 131.6, 129.3, 128.5, 128.4, 127.6, 123.8, 123.0, 21.5, 21.0, -1.6. **^{29}Si NMR** (80 MHz, $CDCl_3$) δ 13.0. **HRMS (ESI)** calcd for $[C_{26}H_{26}NSi]^+$ $[M+H]^+$: *m/z* 380.1835, found 380.1839.

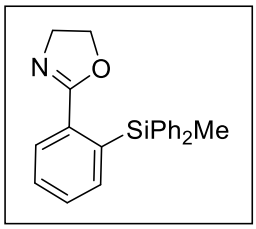


Compound 4n was obtained after column chromatography (hexane/EtOAc = 90/10) as beige solid (93% NMR yield, 80% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 5.7 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.48 (d, *J* = 2.1 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.42 (d, *J* = 6.3 Hz, 1H), 7.37 – 7.31 (m, 2H), 7.29 – 7.27 (m, 4H), 7.19 – 7.14 (m, 2H), 7.11 – 7.07 (m, 4H), 0.42 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) 161.0, 148.7 (q, *J* = 1.9 Hz), 145.0, 141.3, 140.3, 136.2, 135.7, 134.7, 134.1, 131.6, 129.9, 129.0, 128.0, 127.5, 127.4, 126.9, 126.7, 121.1, 120.7, 120.7 (q, *J* = 258.6 Hz), -2.5. **^{19}F NMR** (376

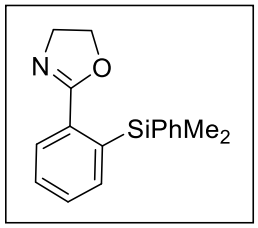
MHz, $CDCl_3$) δ -57.6 **^{29}Si NMR** (80 MHz, $CDCl_3$) δ -11.2. **HRMS (DCI-CH_4)** calcd for $[C_{29}H_{23}NOF_3Si]^+$ $[M+H]^+$: *m/z* 486.1501, found 486.1510.



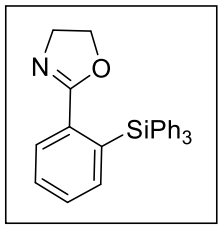
Compound 4o was obtained after column chromatography (hexane/EtOAc = 86/14) as beige solid (85 % NMR yield, 82% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 1.9 Hz, 1H), 8.30 (d, *J* = 5.7 Hz, 1H), 8.18 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.55 – 7.48 (m, 3H), 7.39 (d, *J* = 5.7 Hz, 1H), 7.32 – 7.27 (m, 5H), 7.17 – 7.12 (m, 2H), 7.09 – 7.05 (m, 4H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 0.47 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.7, 161.4, 150.9, 141.3, 138.8, 137.7, 136.2, 136.0, 134.8, 130.2, 130.0, 129.9, 129.4, 128.8, 127.5, 127.4, 127.3, 126.9, 126.7, 120.7, 61.2, 14.4, -2.2. **^{29}Si NMR** (80 MHz, $CDCl_3$) δ -11.3. **HRMS (ESI)** calcd for $[C_{31}H_{28}NO_2Si]^+$ $[M+H]^+$: *m/z* 474.1894, found 474.1889.



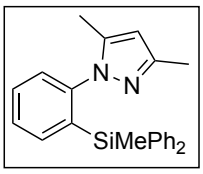
Compound 4p was obtained after column chromatography (hexane/EtOAc = 90/10) as beige solid (99% NMR yield, 93% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 6.2 Hz, 1H), 7.53 – 7.50 (m, 4H), 7.47 – 7.39 (m, 3H), 7.36 – 7.32 (m, 6H), 3.70 (t, *J* = 9.7 Hz, 2H), 3.50 (t, *J* = 9.9 Hz, 2H), 0.95 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.9, 138.1, 137.9, 136.3, 134.9, 134.7, 130.1, 129.5, 129.3, 128.9, 127.8, 67.2, 54.6, -1.7 **^{29}Si NMR** (80 MHz, $CDCl_3$) δ -10.4. **HRMS (ESI)** calcd for $[C_{22}H_{22}NOSi]^+$ $[M+H]^+$: *m/z* 344.1471, found 344.1471.



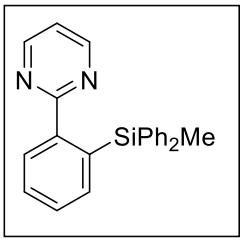
Compound 4q was obtained after column chromatography (hexane/EtOAc = 50/50) as beige oil (81% NMR yield, 69% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.81 (m, 1H), 7.64 (dd, *J* = 6.1, 2.7 Hz, 1H), 7.47 – 7.43 (m, 4H), 7.33 – 7.4332 (m, 3H), 3.93 (t, *J* = 9.5 Hz, 2H), 3.68 (t, *J* = 9.5 Hz, 2H), 0.59 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.0, 139.8, 138.2, 136.4, 134.4, 133.6, 130.0, 129.3, 129.2, 128.5, 127.6, 67.3, 54.7, -0.3. **^{29}Si NMR** (80 MHz, $CDCl_3$) δ -7.1. **HRMS (DCI-CH_4)** calcd for $[C_{17}H_{20}NOSi]^+$ $[M+H]^+$: m/z 282.1314, found 282.1324.



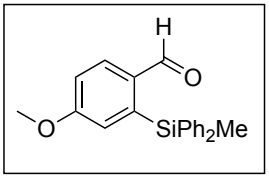
Compound 4r was obtained after column chromatography (hexane/EtOAc = 70/30) as beige solid (91% NMR yield, 82% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.7 Hz, 1H), 7.58 – 7.56 (m, 6H), 7.50 (td, *J* = 7.4, 1.7 Hz, 1H), 7.43 – 7.33 (m, 11H), 7.47 – 7.37 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.6, 139.2, 136.2, 136.0, 135.2, 134.2, 130.3, 129.8, 129.4, 129.0, 127.7, 67.0, 54.4. **^{29}Si NMR** (80 MHz, $CDCl_3$) δ -13.9. **HRMS (ESI)** calcd for $[C_{27}H_{24}NOSi]^+$ $[M+H]^+$: *m/z* 406.1627, found 406.1626.



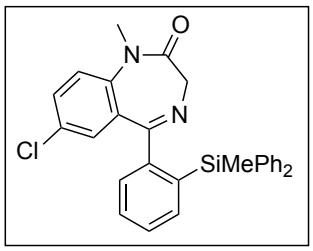
Compound 4s was obtained after column chromatography (hexane/EtOAc = 95/5) as beige solid (39% NMR yield, 27% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 1H), 7.48 (td, *J* = 7.3, 1.6 Hz, 1H), 7.44 – 7.42 (m, 4H), 7.41 – 7.37 (m, 1H), 7.37 – 7.27 (m, 6H), 7.17 (dd, *J* = 7.9, 1.2 Hz, 1H), 5.59 (s, 1H), 2.08 (s, 3H), 1.85 (s, 3H), 0.54 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.9, 145.6, 139.8, 138.5, 136.8, 135.4, 135.1, 130.2, 129.1, 127.7, 127.6, 127.6, 105.9, 13.4, 11.7, -3.5. **^{29}Si NMR** (80 MHz, $CDCl_3$) δ -11.8. **HRMS (ESI)** calcd for $[C_{24}H_{25}N_2Si]^+$ $[M+H]^+$: *m/z* 369.1787, found 369.1783.



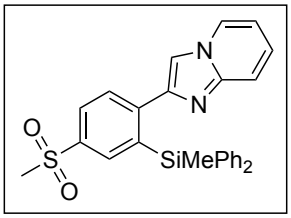
Compound 4t was obtained after column chromatography (hexane/EtOAc = 90/10) as beige solid (98% NMR yield, 85% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 7.8 Hz, 1H), 8.41 (d, *J* = 4.9 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.51 – 7.38 (m, 7H), 7.30 – 7.23 (m, 5H), 6.88 (t, *J* = 4.9 Hz, 1H), 0.92 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.1, 156.1, 144.1, 140.4, 139.2, 136.7, 134.4, 129.9, 129.7, 129.1, 128.2, 127.6, 118.9, -0.5. **^{29}Si NMR** (80 MHz, $CDCl_3$) δ -7.0. **HRMS (DCI-CH_4)** calcd for $[C_{23}H_{21}N_2Si]^+$ $[M+H]^+$: m/z 353.1474 found 353.1472.



Compound 4u was obtained after column chromatography (pentane/Et_2O = 80/20) as beige solid (65% NMR yield, 50% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.96 (d, J = 8.5 Hz, 1H), 7.51 – 7.44 (m, 4H), 7.42 – 7.31 (m, 6H), 7.03 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.93 (d, *J* = 2.6 Hz, 1H), 3.74 (s, 3H), 0.93 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.2, 163.2, 141.9, 136.5, 135.1, 134.9, 134.1, 129.5, 128.1, 124.7, 114.3, 55.4, -2.1. **^{29}Si NMR** (80 MHz, $CDCl_3$) δ -9.6. **HRMS (ESI)** calcd for $[C_{21}H_{21}O_2Si]^+$ $[M+H]^+$: *m/z* 333.1311, found 333.1314.

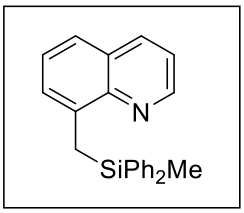


Compound 4v was obtained after column chromatography was obtained after column chromatography (hexane/E_2OAc = 80/20) as white solid (77% NMR yield, 72% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.49 (m, 1H), 7.43 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.34 – 7.19 (m, 7H), 7.19 – 7.12 (m, 2H), 4.27 (d, *J* = 11.1 Hz, 1H), 3.30 (s, 1H), 2.70 (d, J = 11.1 Hz, 1H), 0.97 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.8, 169.4, 145.0, 142.5, 139.43, 139.0, 138.1, 134.8, 134.0, 131.4, 131.1, 130.5, 129.8, 129.4, 129.1, 128.6, 127.7, 122.5, 55.5, 35.0, -1.4. **^{29}Si NMR** (80 MHz, $CDCl_3$) δ -12.7. **HRMS (ESI)** calcd for $[C_{29}H_{26}N_2OClSi]^+$ $[M+H]^+$: *m/z* 481.1499, found 481.1503.



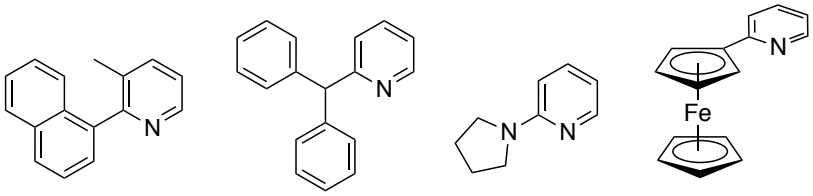
Compound 4w was obtained after column chromatography (pentane/acetone = 70/30) as beige solid (33% NMR yield, 31% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) 8.07 – 7.96 (m, 2H), 7.85 (dd, J = 8.0, 0.6 Hz, 1H), 7.77 (dt, J = 6.8, 1.2 Hz, 1H), 7.46 – 7.35 (m, 5H), 7.33 – 7.22 (m, 6H), 7.16 – 7.06 (m, 2H), 6.69 (td, J = 6.8, 1.2 Hz, 1H), 2.97 (s, 3H),

0.66 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.2, 145.3, 144.6, 138.9, 138.3, 137.0, 136.3, 134.8, 130.4, 129.2, 128.2, 127.8, 125.6, 124.9, 117.8, 112.7, 111.6, 44.5, -2.0. **^{29}Si NMR** (80 MHz, $CDCl_3$) δ -10.1. **HRMS (ESI)** calcd for $[C_{27}H_{25}N_2O_2Si]^+$ $[M+H]^+$: *m/z* 469.1406, found 469.1407.



Compound 4x was obtained after column chromatography (hexane/EtOAc = 95/5) as beige oil (45% NMR yield, 38% isolated yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.77 (dd, *J* = 4.1, 1.8 Hz, 1H), 8.03 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.51 – 7.49 (m, 5H), 7.33 – 7.23 (m, 8H), 7.16 (dd, *J* = 7.1, 1.5 Hz, 1H), 3.39 (s, 2H), 0.29 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.7, 146.8, 139.0, 137.3, 136.1, 134.9, 129.2, 128.6, 128.5, 127.7, 126.2, 124.4, 120.8, 19.2, -4.2. **^{29}Si NMR** (80 MHz, $CDCl_3$) δ -7.0. **HRMS (ESI)** calcd for $[C_{23}H_{22}NSi]^+$ $[M+H]^+$: *m/z* 340.1513, found 340.1517.

Unreactive substrates:



6. Kinetic isotopic effect

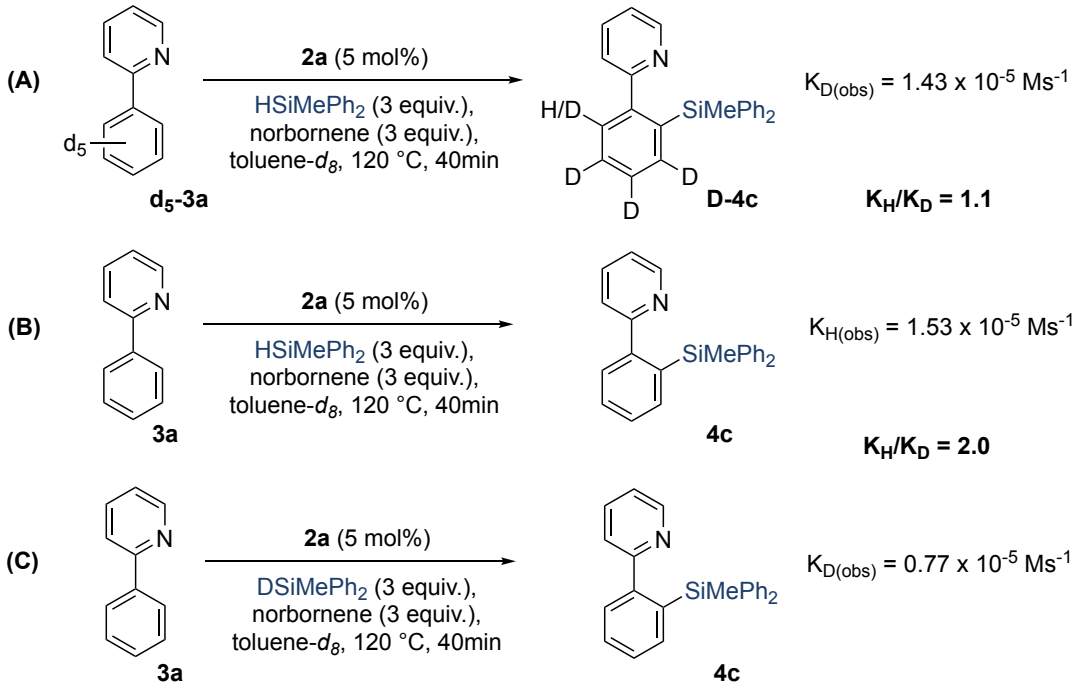


Figure S6. Determination of KIE.

In a glove box, J-Young NMR tube was added **3a** or **d_5-3a** (0.1 mmol, 1 equiv.), iridium catalyst **2a** (5 mol%), norbornene (3 equiv.), $HSiMePh_2$ or $DSiMePh_2$ (3 equiv.) and toluene-d_8 (0.5 mL). Then, the NMR tube was closed with a J-Young valve. Outside the glove box, the mixture was heated at 120 °C. The conversion was monitored by ^{1}H NMR spectroscopy every 10 minutes.

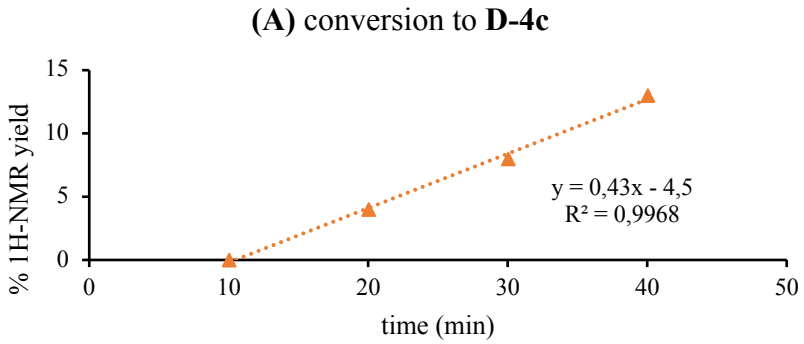


Figure S7. Monitoring of the reaction between 2-phenylpyridine-d_5 (***d_5*-3a**) and $HSiMePh_2$.

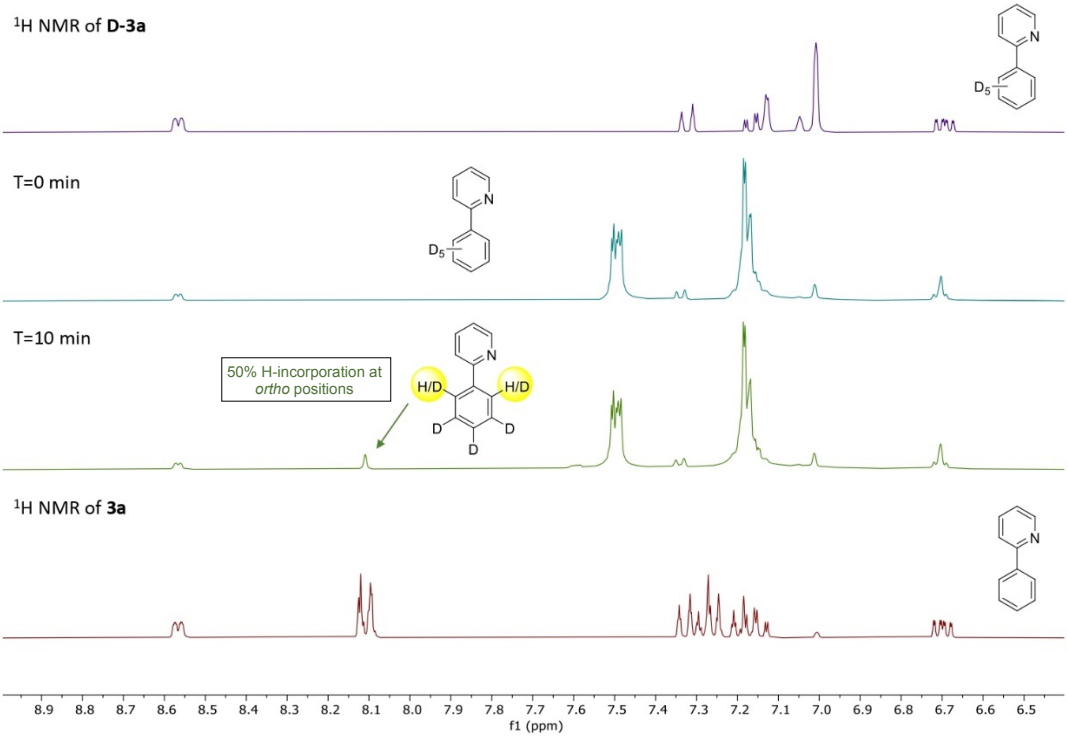


Figure S8. ^{1}H NMR spectroscopy monitoring of the reaction with ***d_5*-3a** and $HSiMePh_2$.

The monitoring of the reaction with ***d_5*-3a** revealed that D-H exchange occurred before C-Si bond formation. After about 50% D/H exchange at *ortho*-positions of ***d_5*-3a** (induction period of 10 minutes), the silylation reaction took place with similar reaction rate than with 2-phenylpyridine (**3a**).

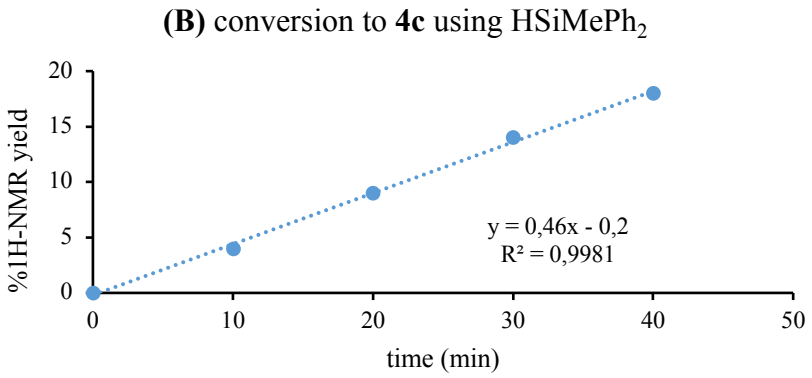


Figure S9. Monitoring of the reaction between 2-phenylpyridine (**3a**) and $HSiMePh_2$.

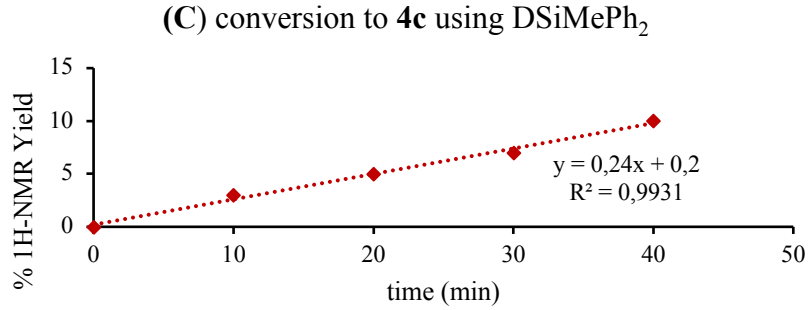
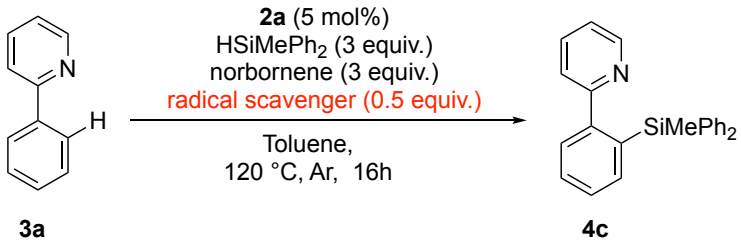


Figure S10. Monitoring of the reaction between 2-phenylpyridine (**3a**) and $DSiMePh_2$.

7. Radical scavenger experiment



Radical scavenger	4c (Yield)
BHT	75%
TEMPO	85%

Figure S11. Radical scavenger experiment.

In a glove box, in a dry Schlenk tube was placed the catalyst **2a** (5 mol%), norbornene (3 equiv.), 2-phenylpyridine (0.2 mmol, 1 equiv.), $HSiMePh_2$ (3 equiv.), radical scavenger (0.5 equiv.) and toluene (1mL). Then, the tube was sealed with a screw cap. Outside the glove box, the mixture was stirred at 120°C for 16h. After cooled down, the mixture was concentrated under reduce pressure and dried under vacuum. To the residue were added 1,3,5-trimethylbenzene (as an internal standard) and 0.5 mL of $CDCl_3$. Then the aliquot was analyzed by ^1H NMR which reveal the NMR yield.

8. Mercury test

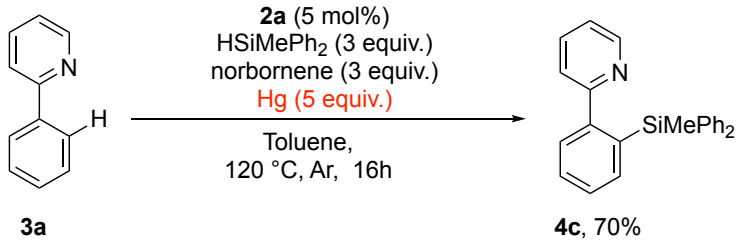
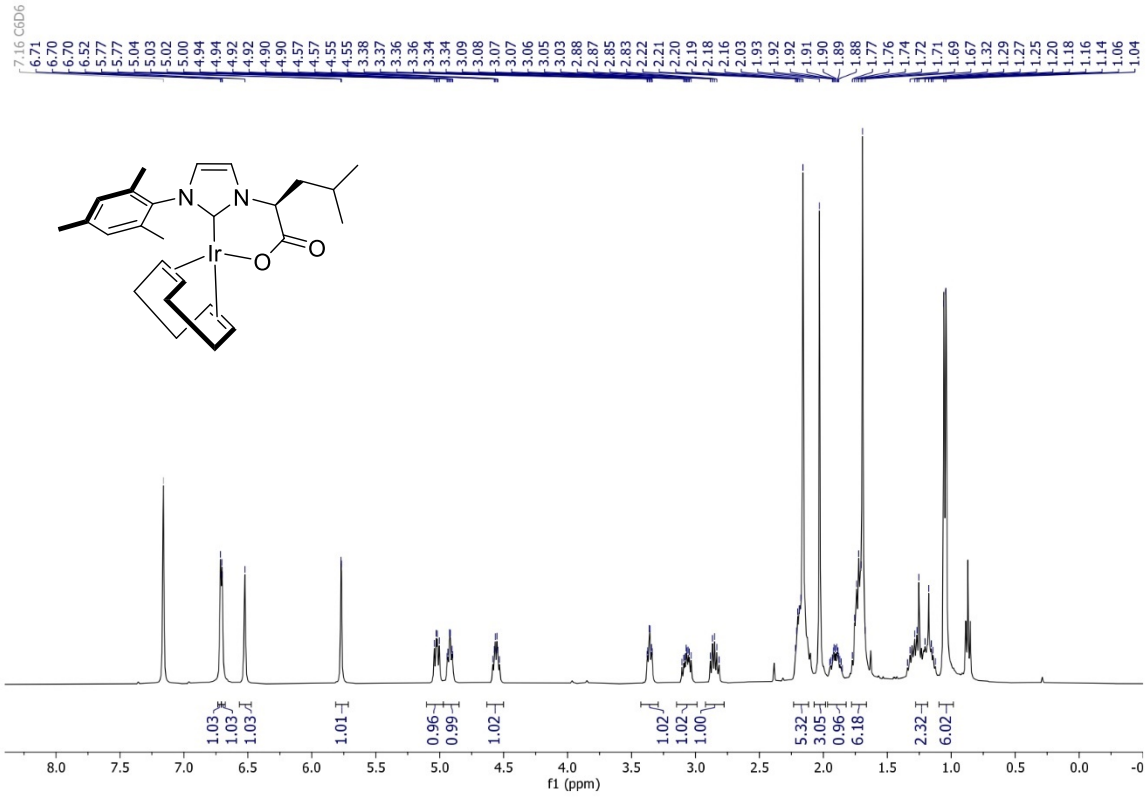


Figure S12. Mercury poisoning test.

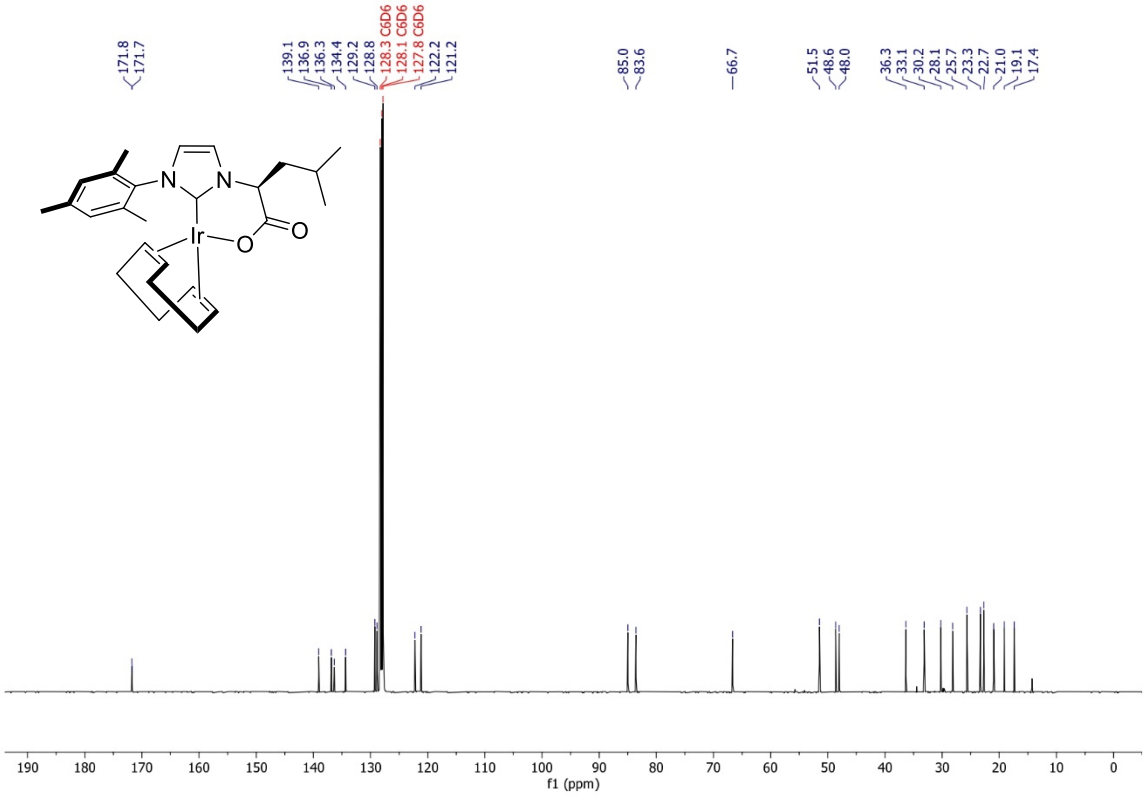
In a glove box, in a dry Schlenk tube was placed the catalyst **2a** (5 mol%), norbornene (3 equiv.), 2-phenylpyridine (0.2 mmol, 1 equiv.), $HSiMePh_2$ (3 equiv.), Hg (5 equiv.) and toluene (1mL). Then, the tube was sealed with a screw cap. Outside the glove box, the mixture was stirred at 120°C for 16h. After cooled down, the mixture was concentrated under reduce pressure and dried under vacuum. To the residue were added 1,3,5-trimethylbenzene (as an internal standard) and 0.5 mL of $CDCl_3$. Then the aliquot was analyzed by ^1H NMR which reveal the NMR yield.

9. NMR spectra

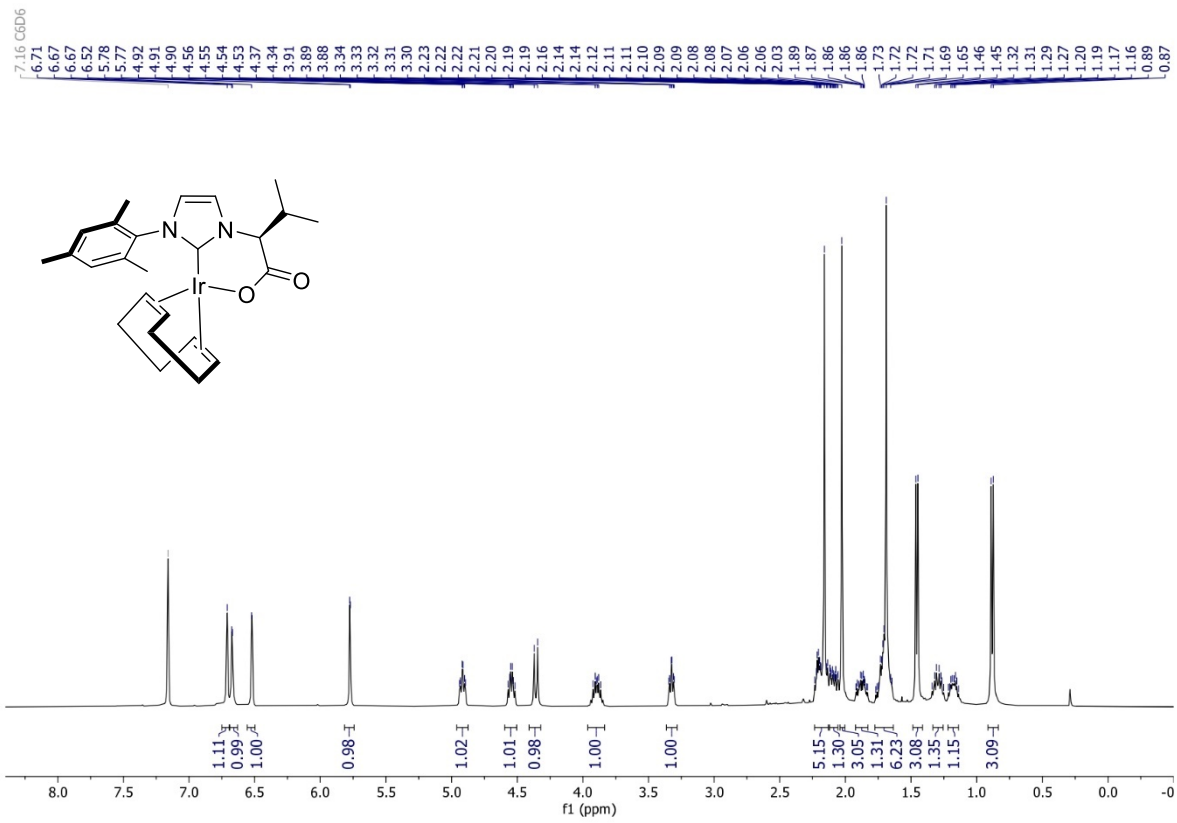
^1H NMR spectrum for **2a**



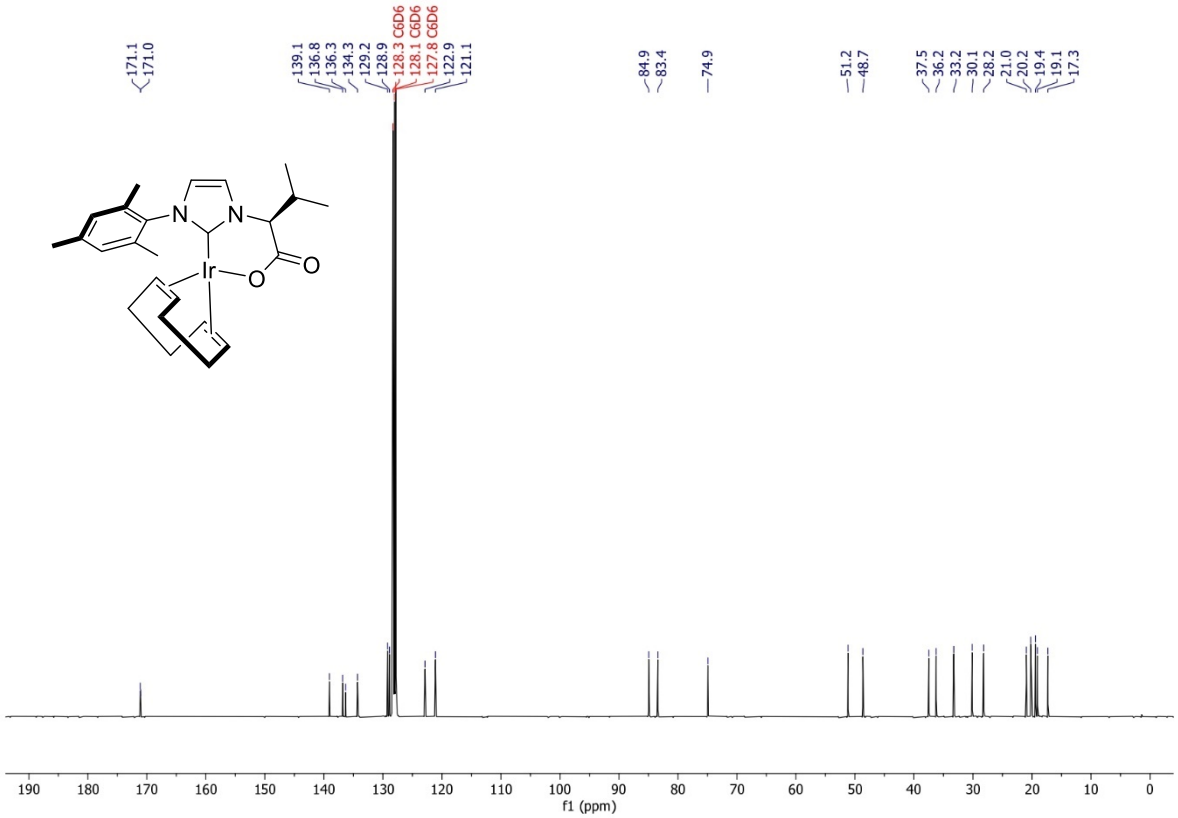
^{13}C NMR spectrum for **2a**



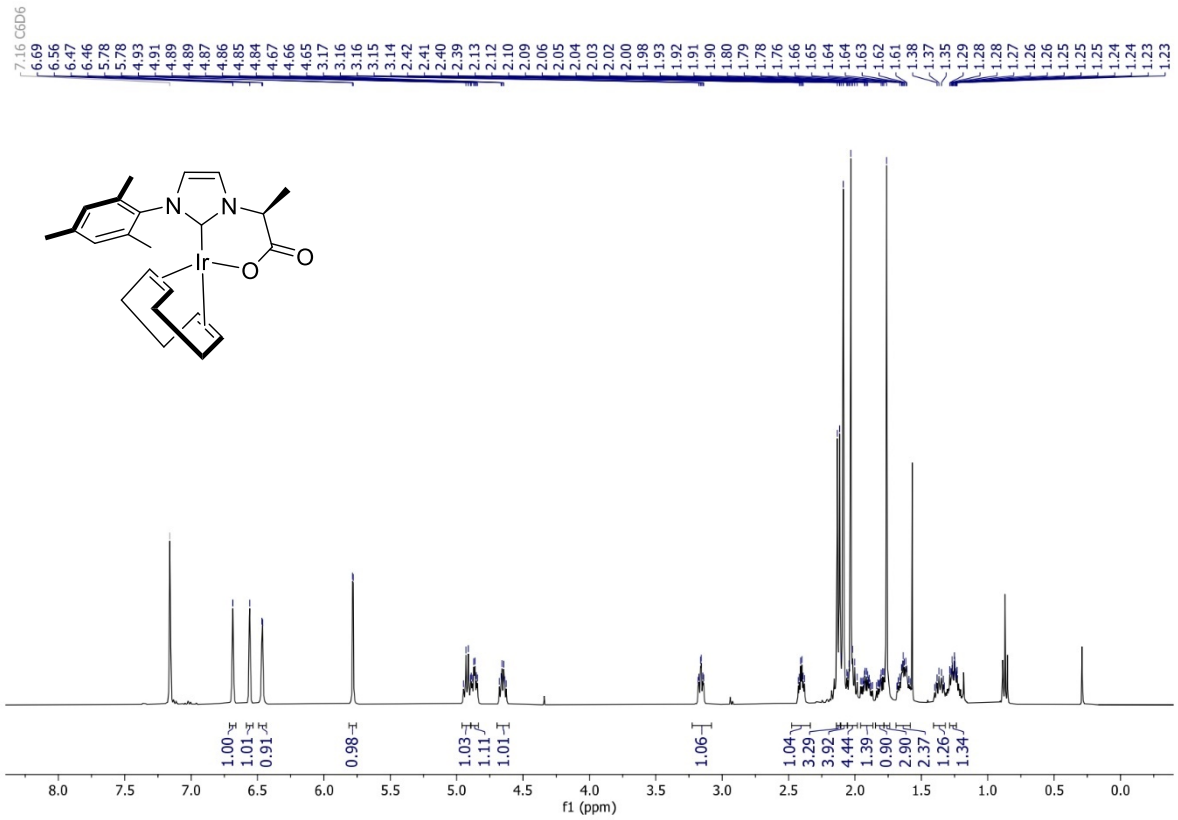
^{1}H NMR spectrum for **2b**



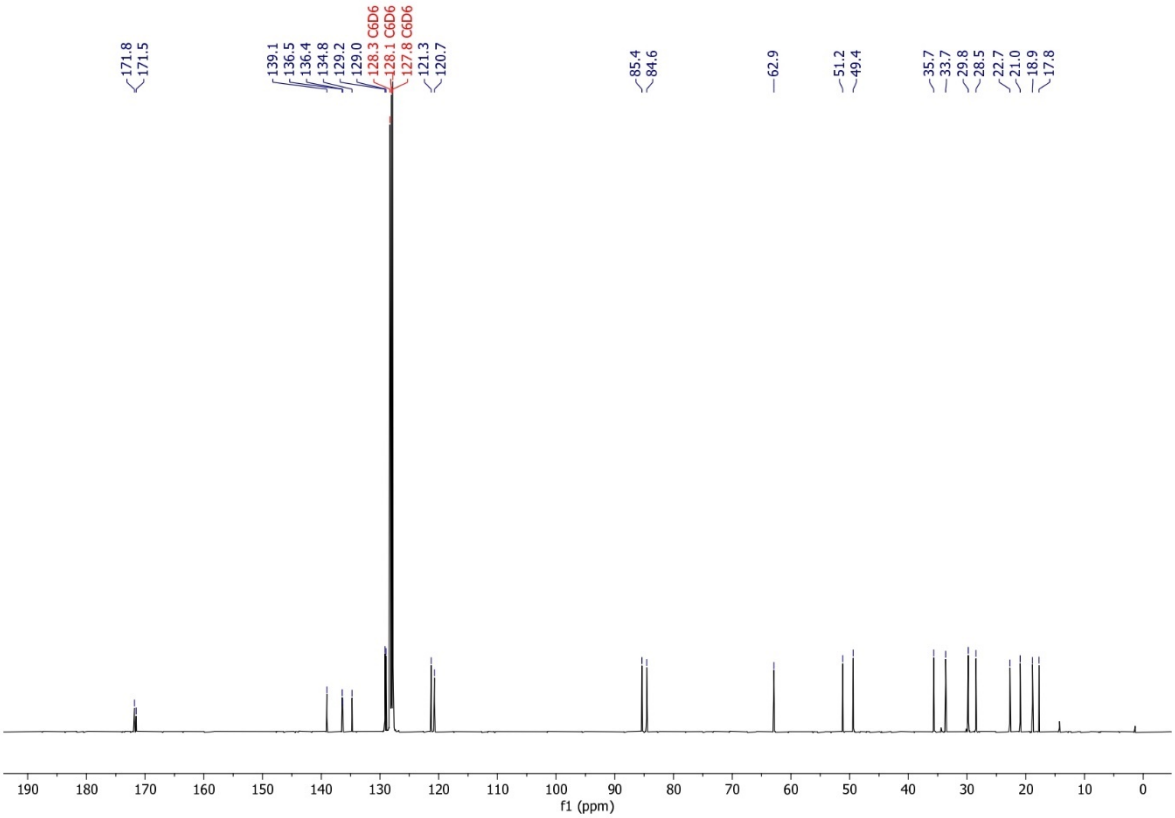
^{13}C NMR spectrum for **2b**



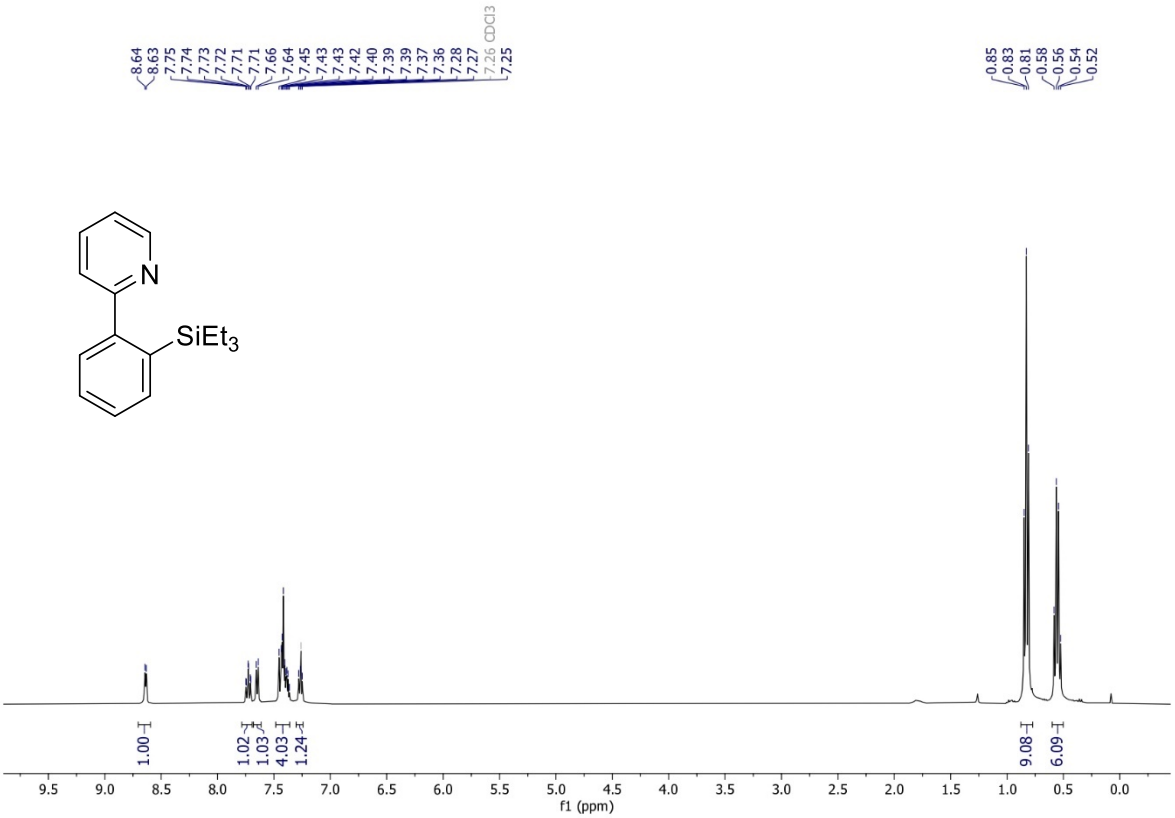
^{1}H NMR spectrum for **2c**



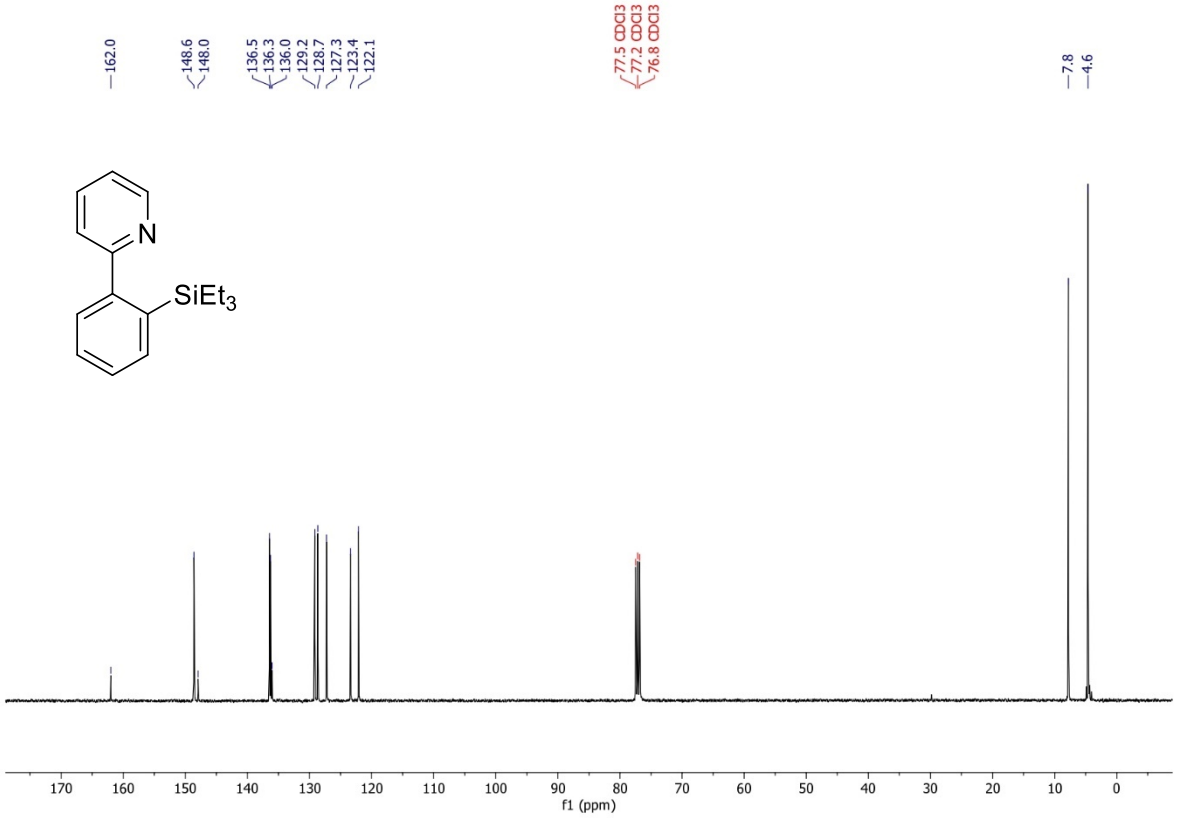
^{13}C NMR spectrum for **2c**



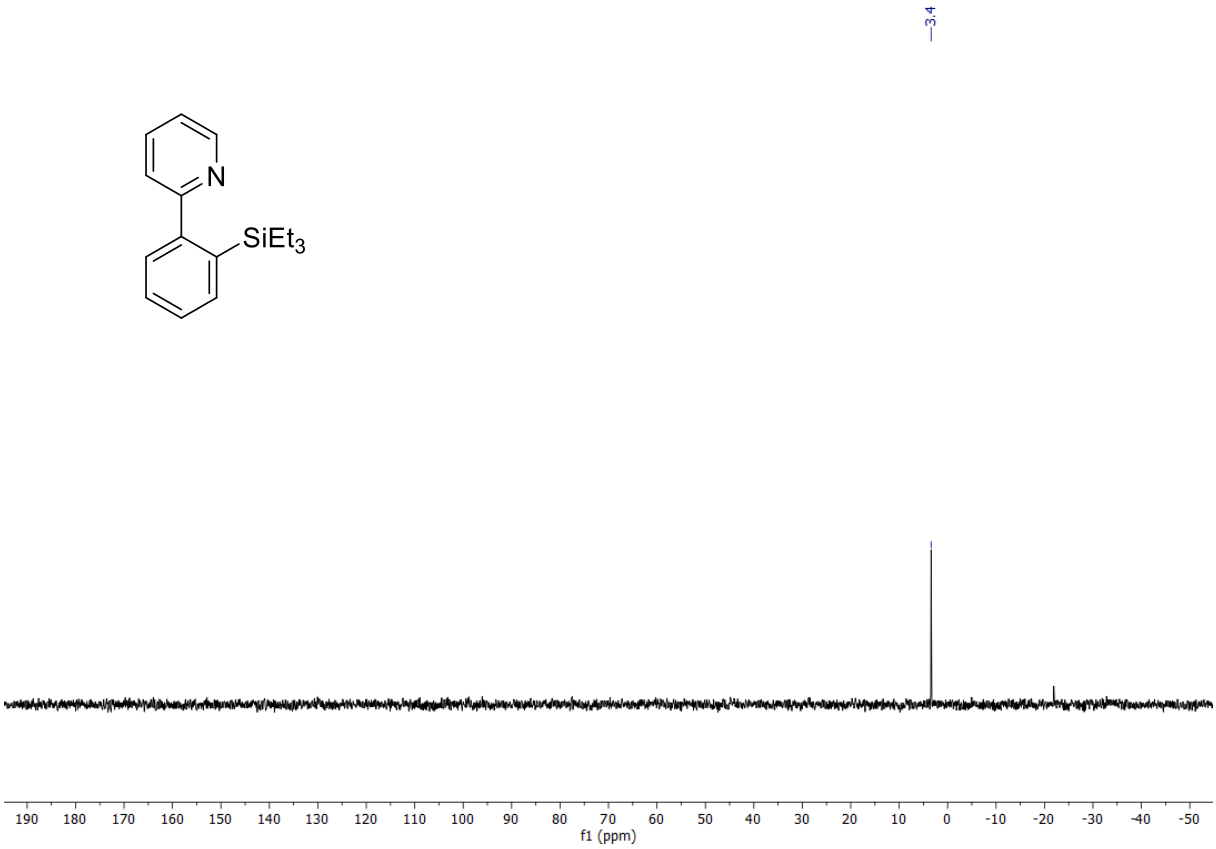
^{1}H NMR spectrum for **4a**



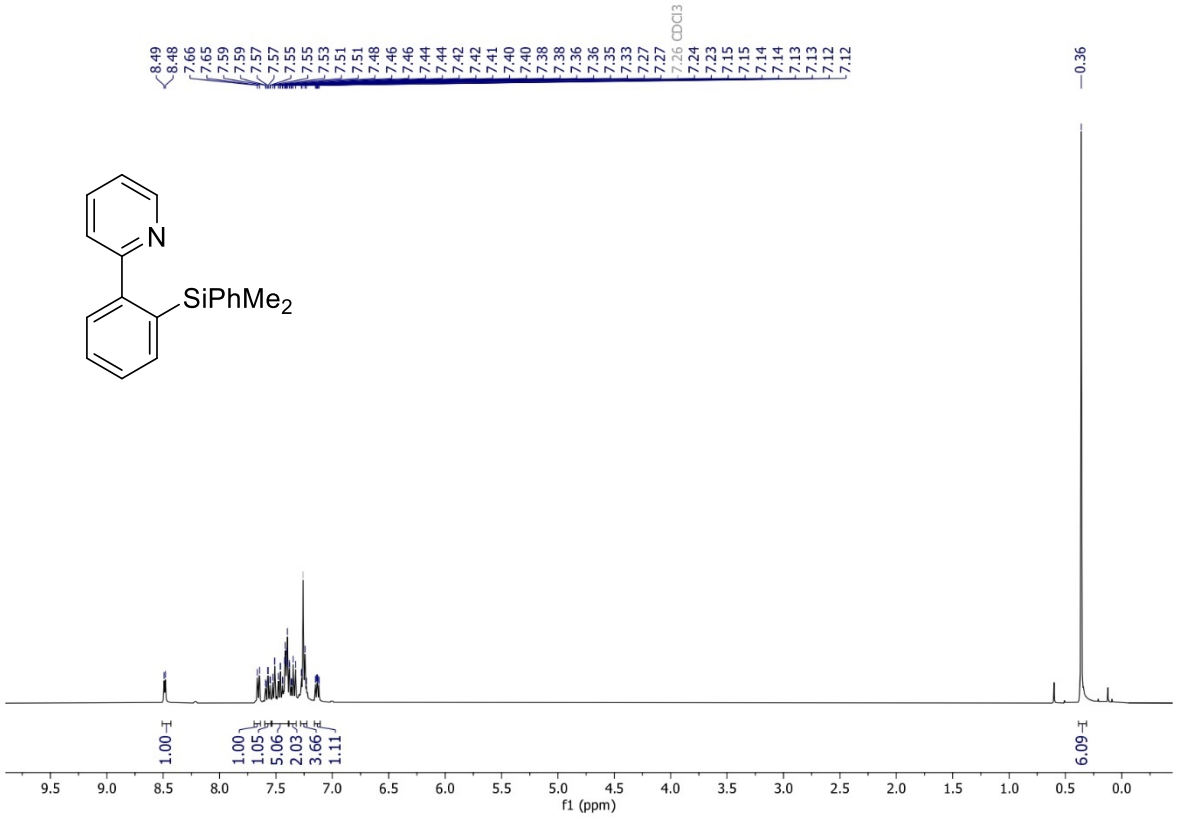
^{13}C NMR spectrum for **4a**



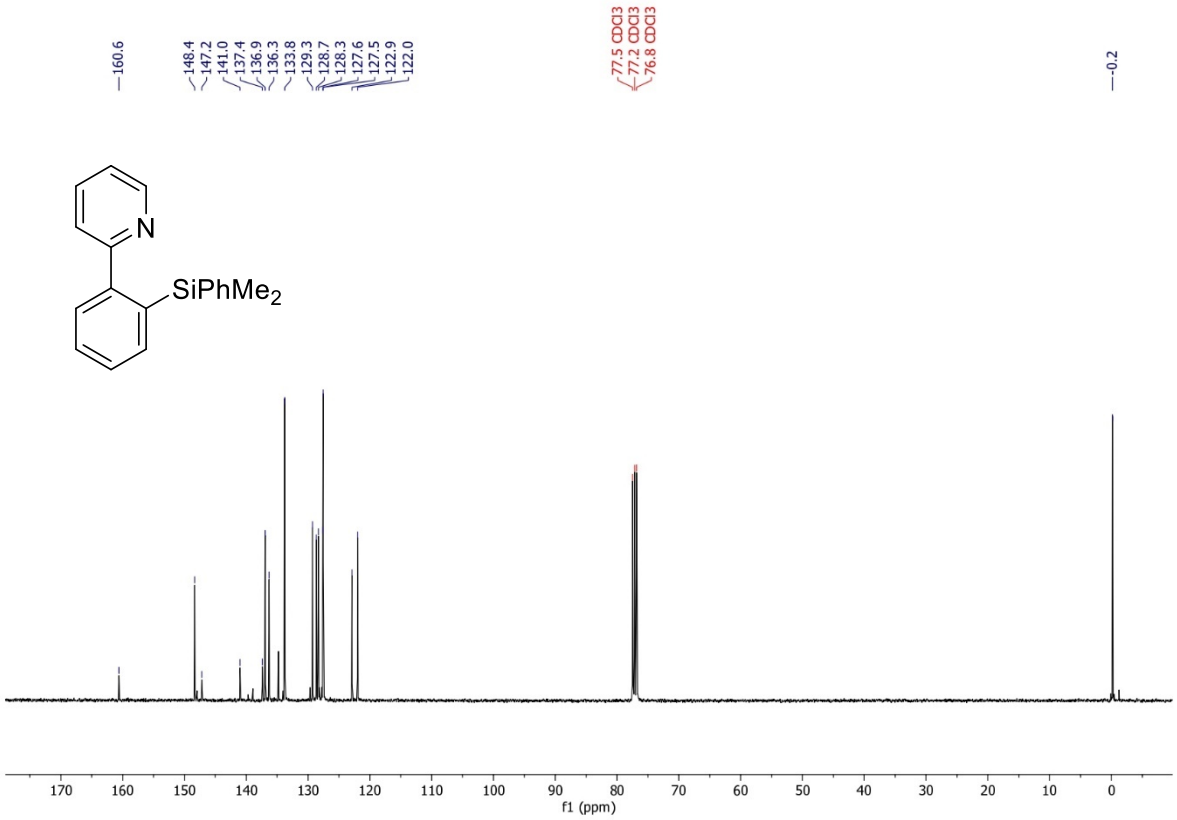
^{29}Si NMR spectrum for **4a**



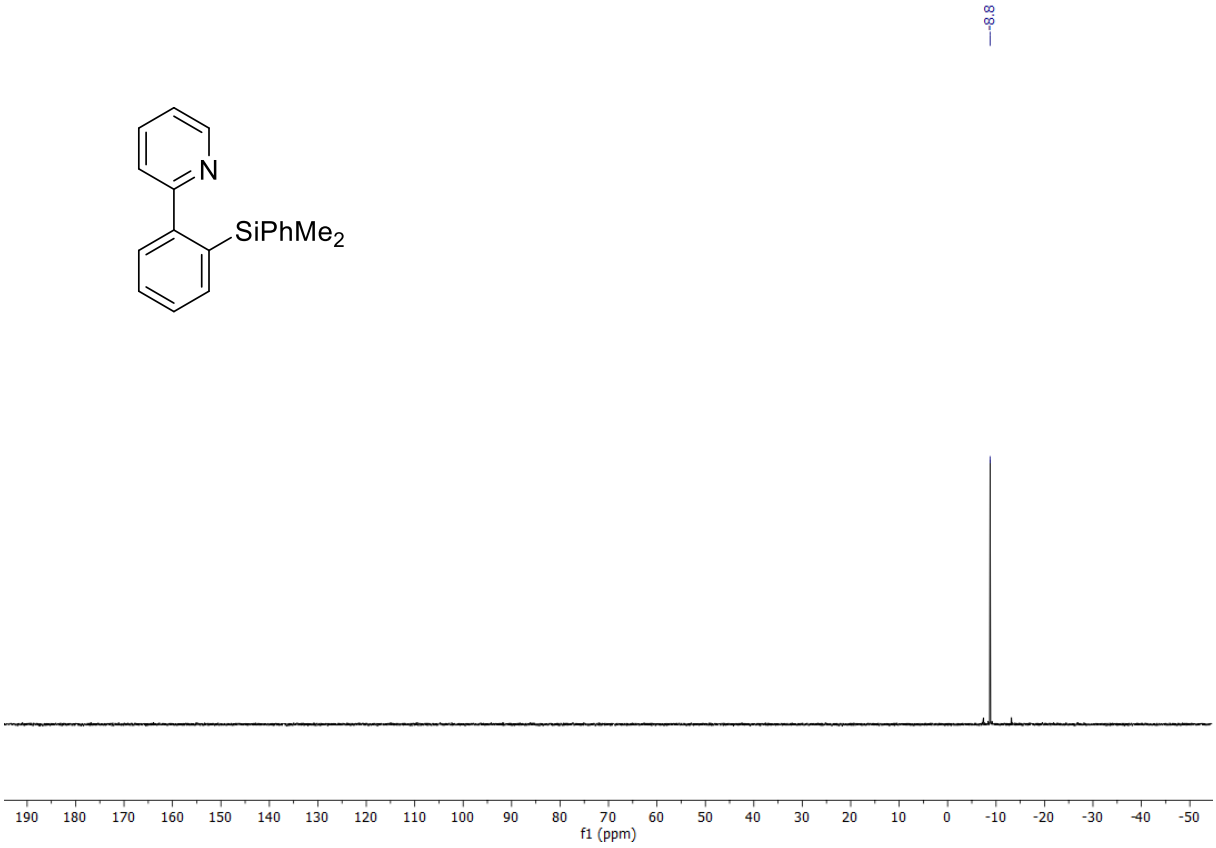
^{1}H NMR spectrum for **4b**



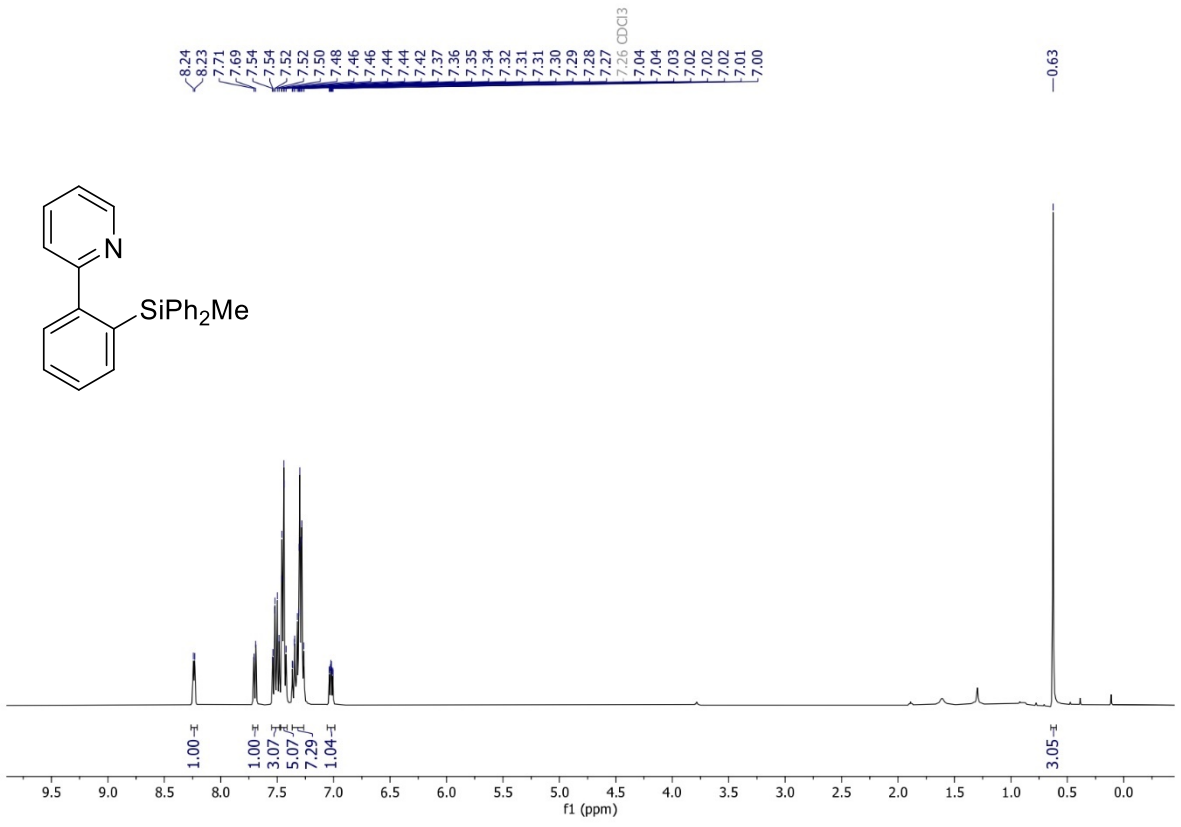
^{13}C NMR spectrum for **4b**



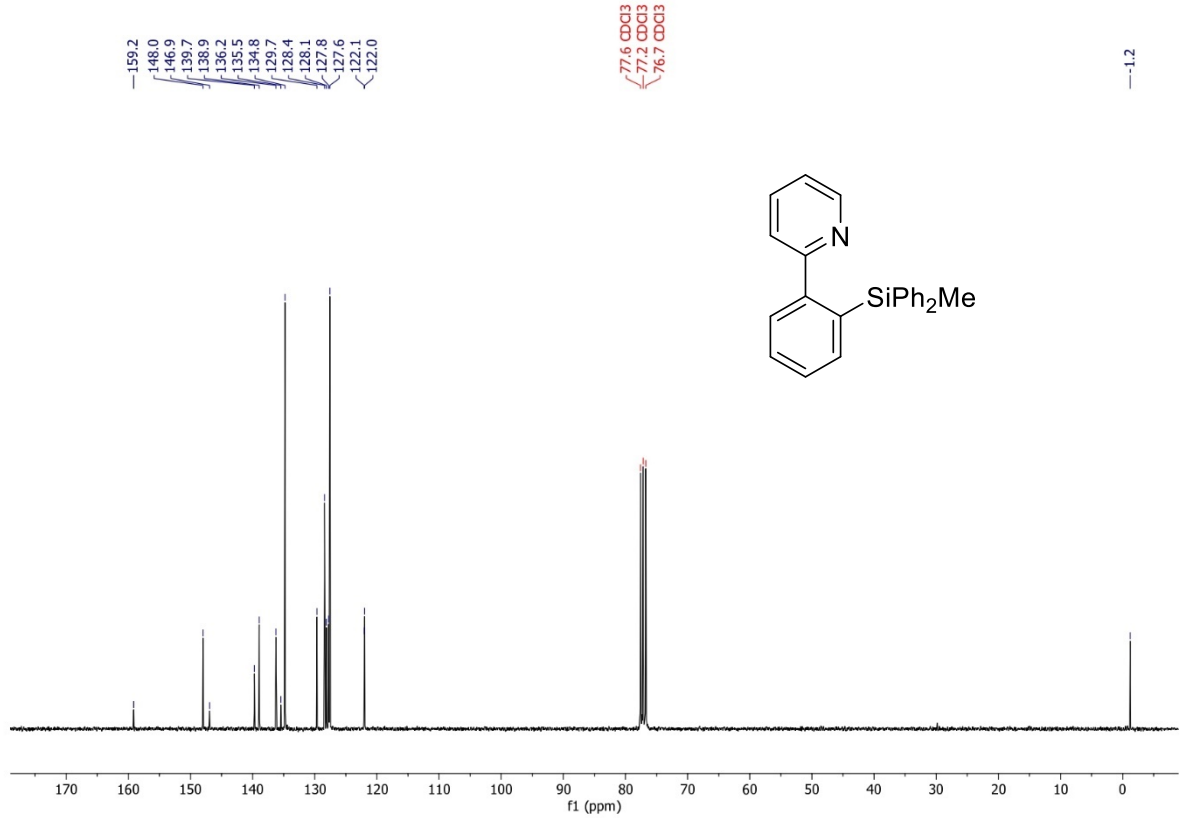
^{29}Si NMR spectrum for **4b**



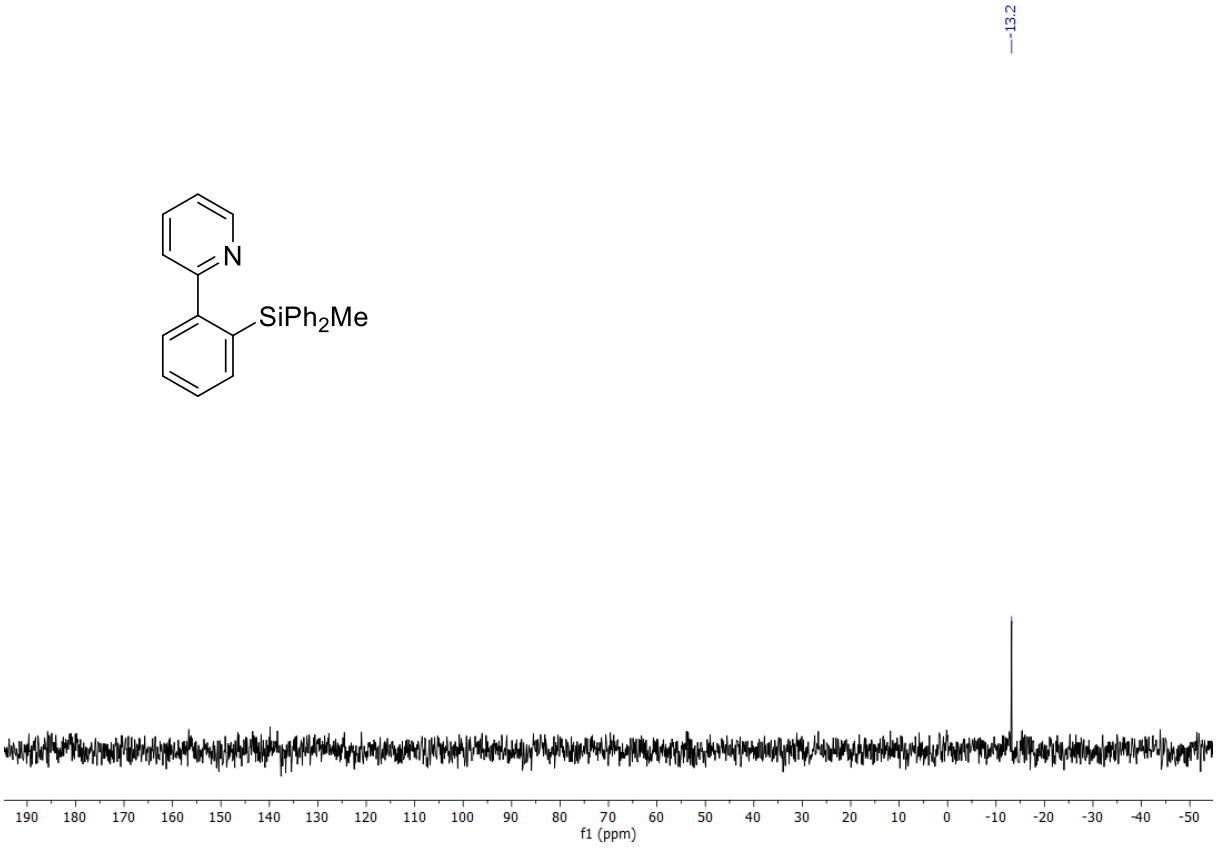
^{1}H NMR spectrum for **4c**



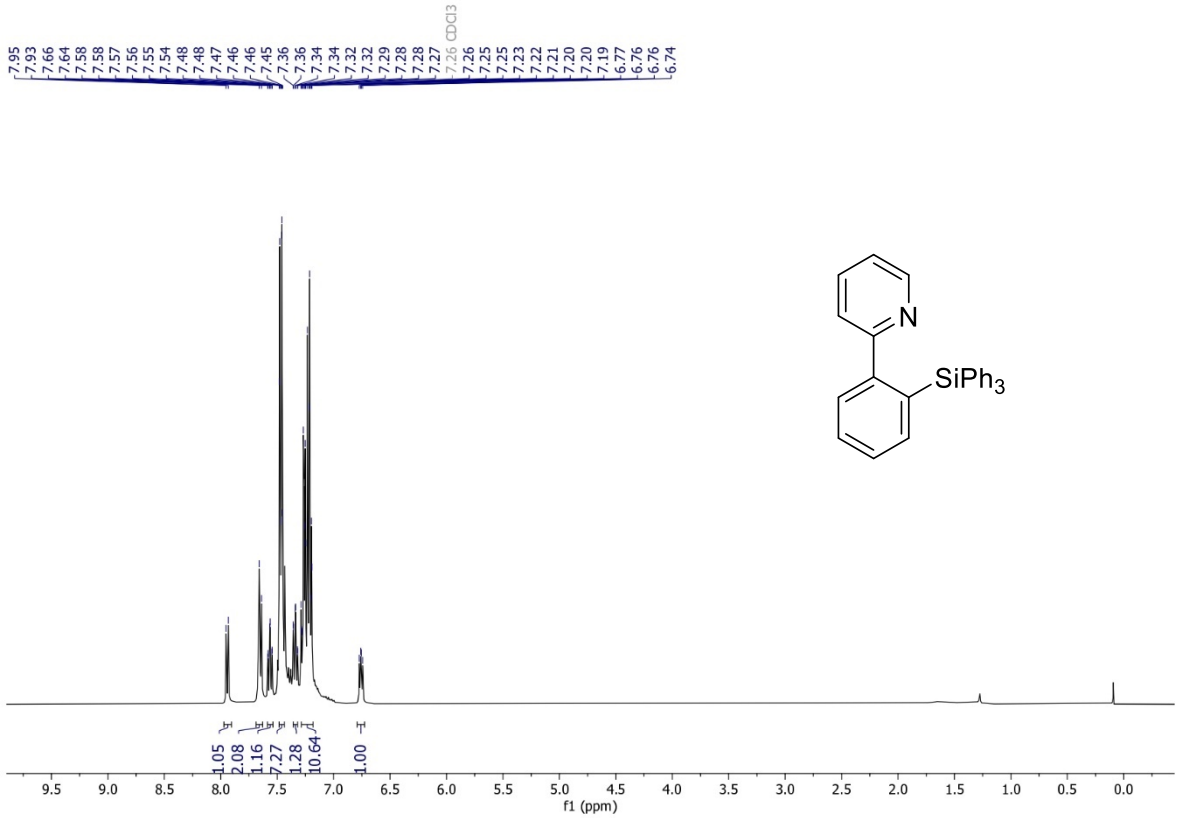
^{13}C NMR spectrum for **4c**



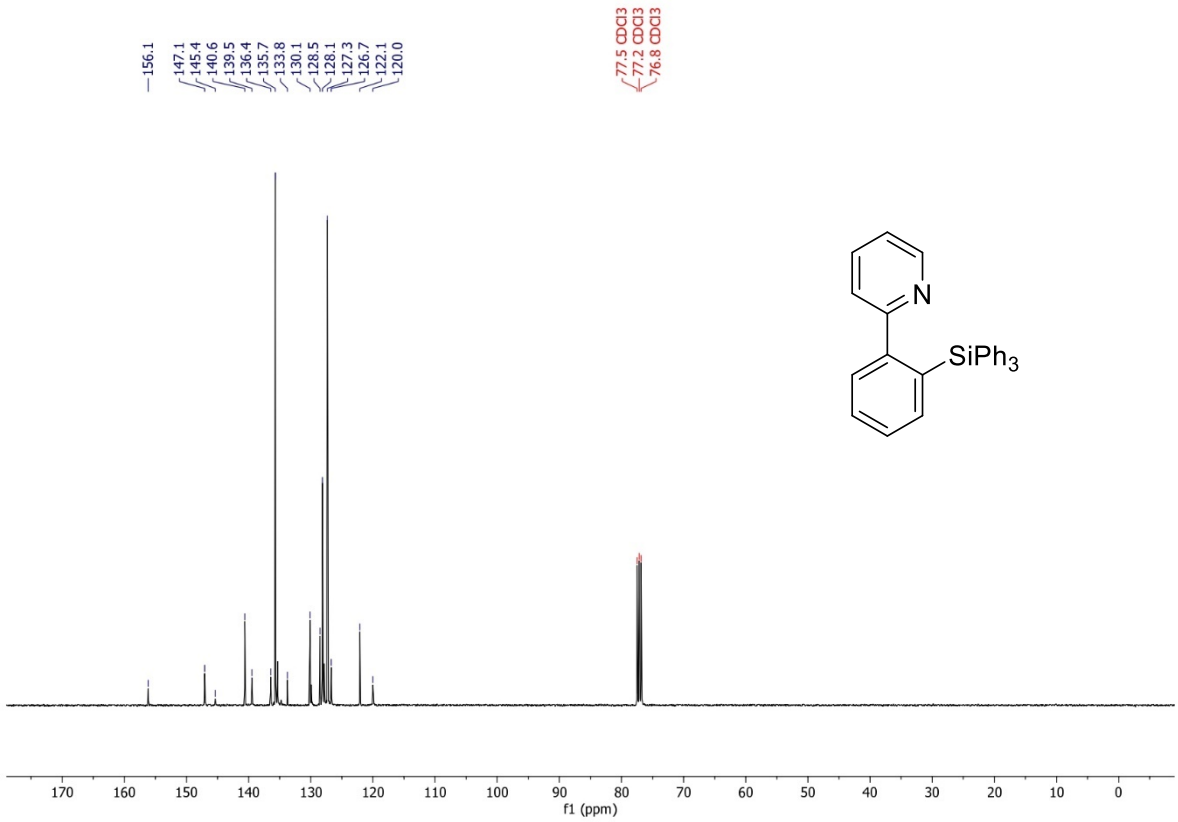
^{29}Si NMR spectrum for **4c**



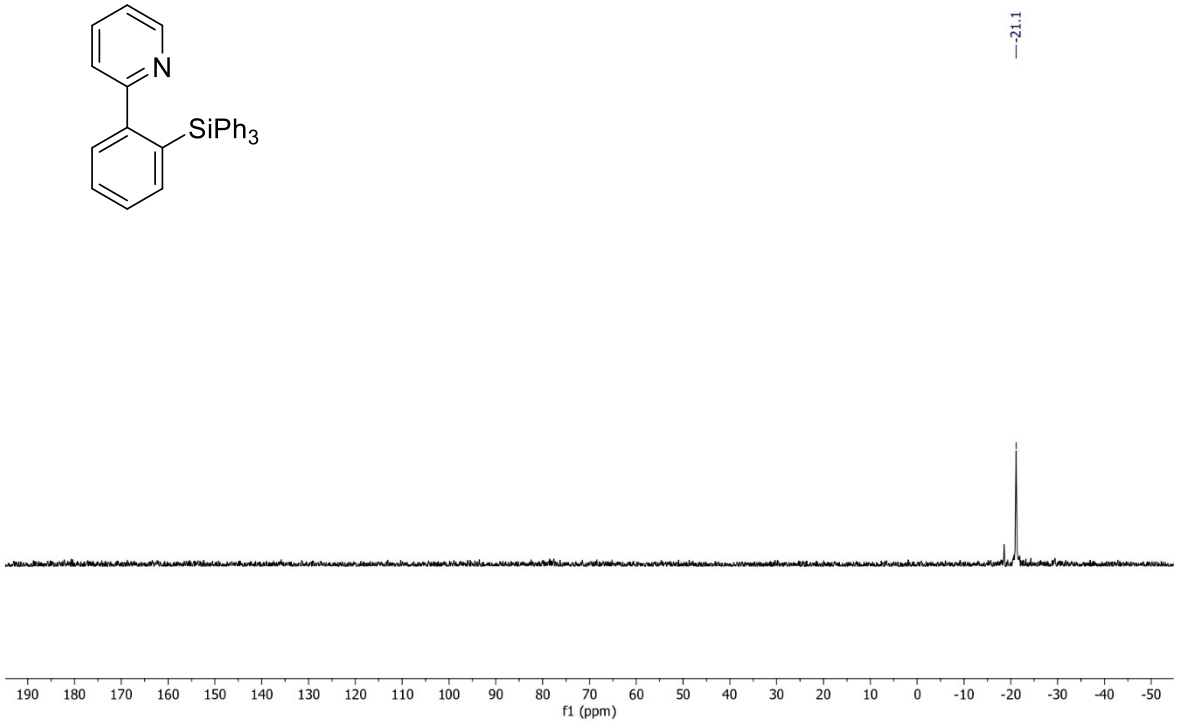
^{1}H NMR spectrum for **4d**



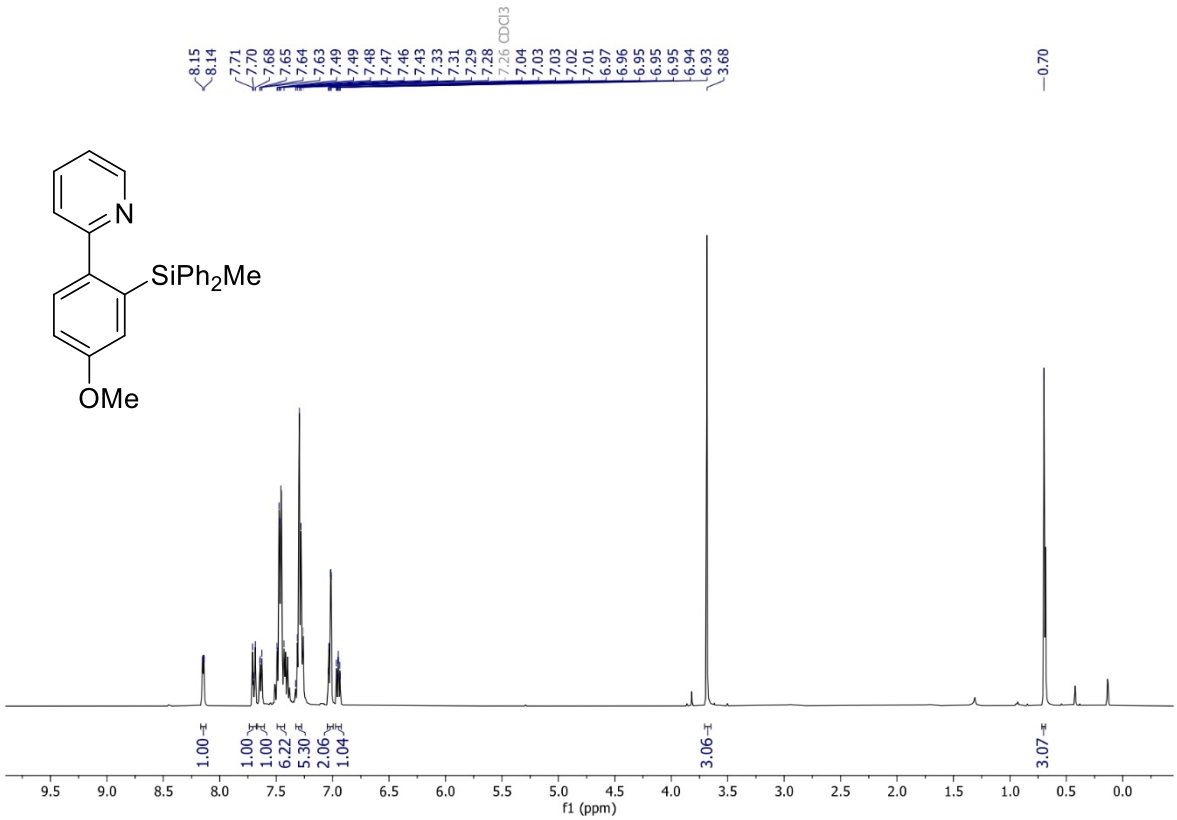
^{13}C NMR spectrum for **4d**



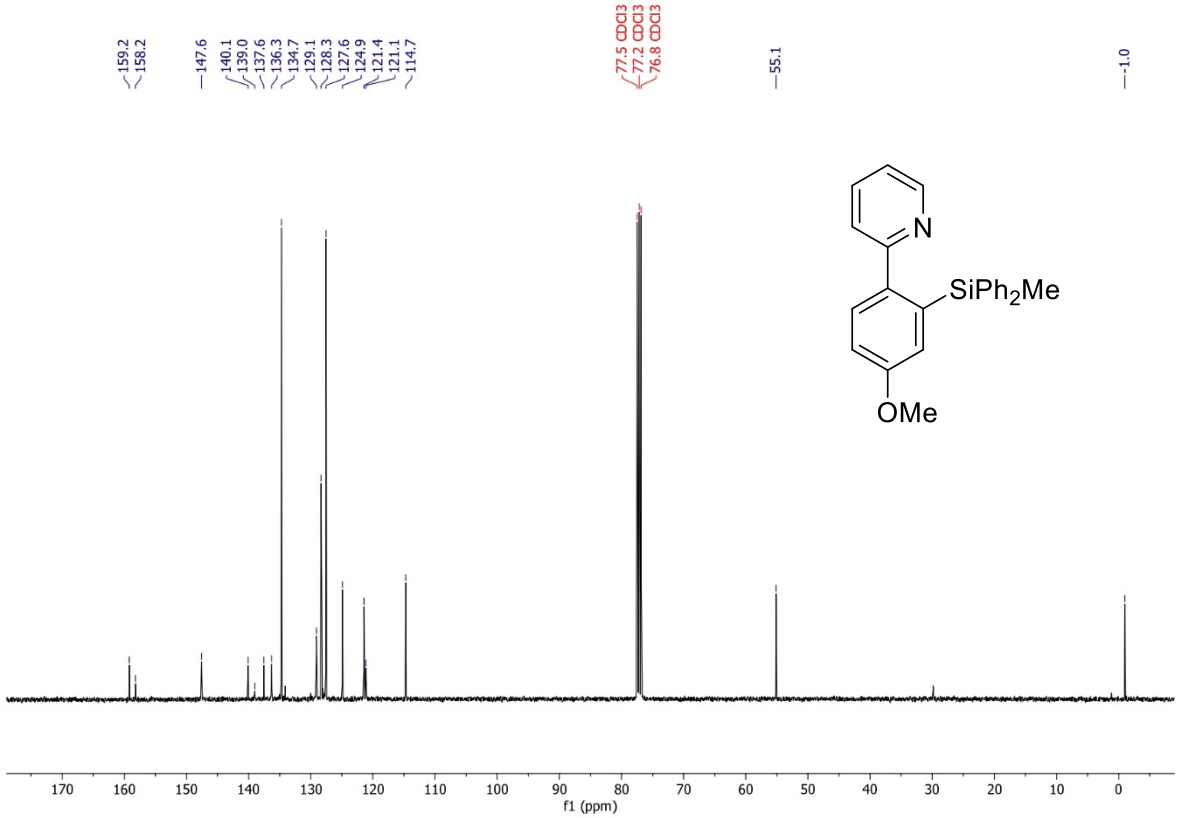
^{29}Si NMR spectrum for **4d**



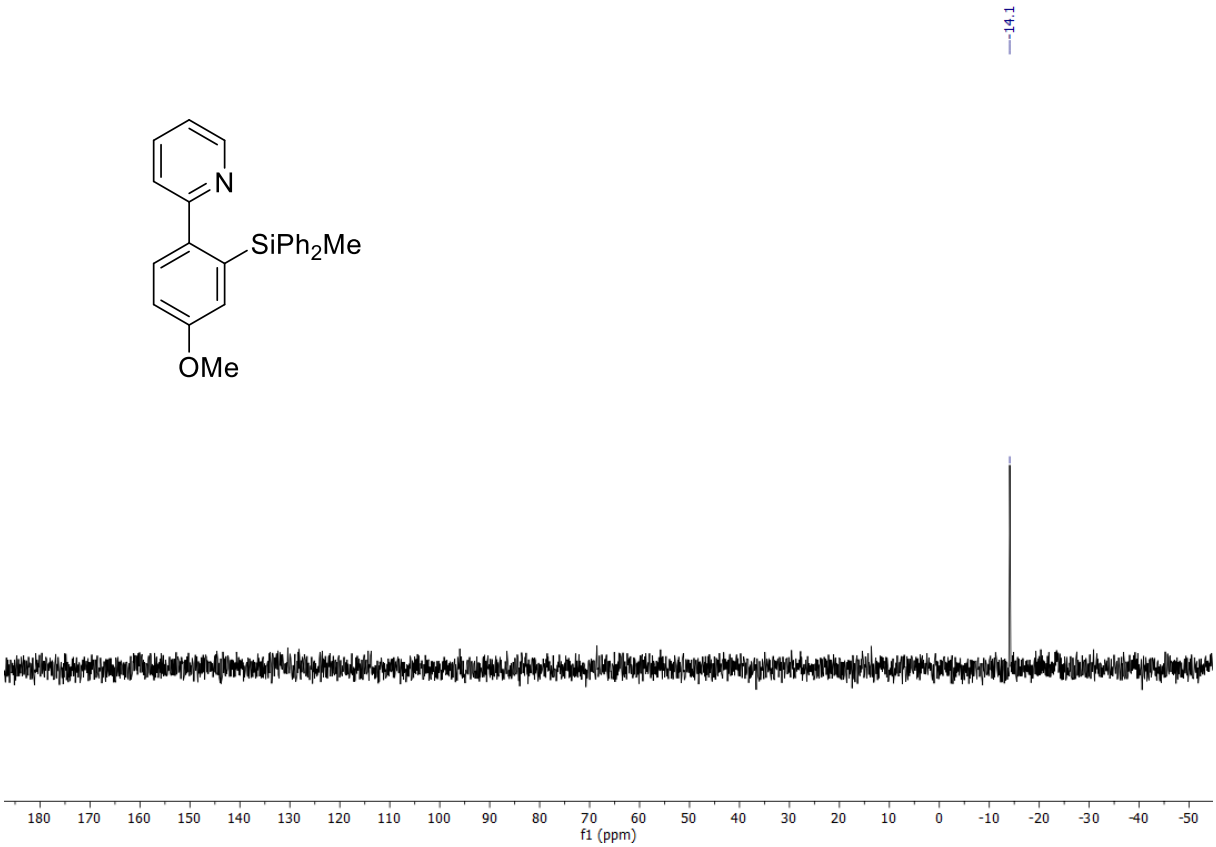
^{1}H NMR spectrum for **4e**



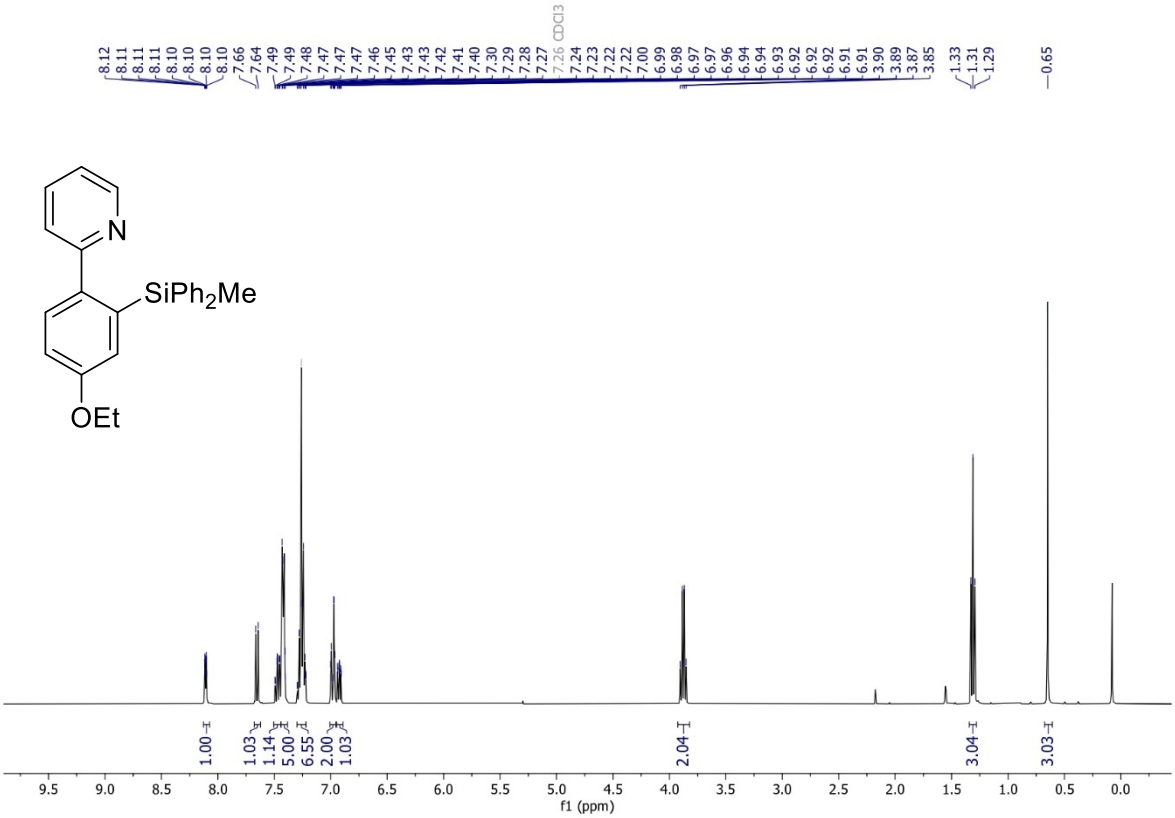
^{13}C NMR spectrum for **4e**



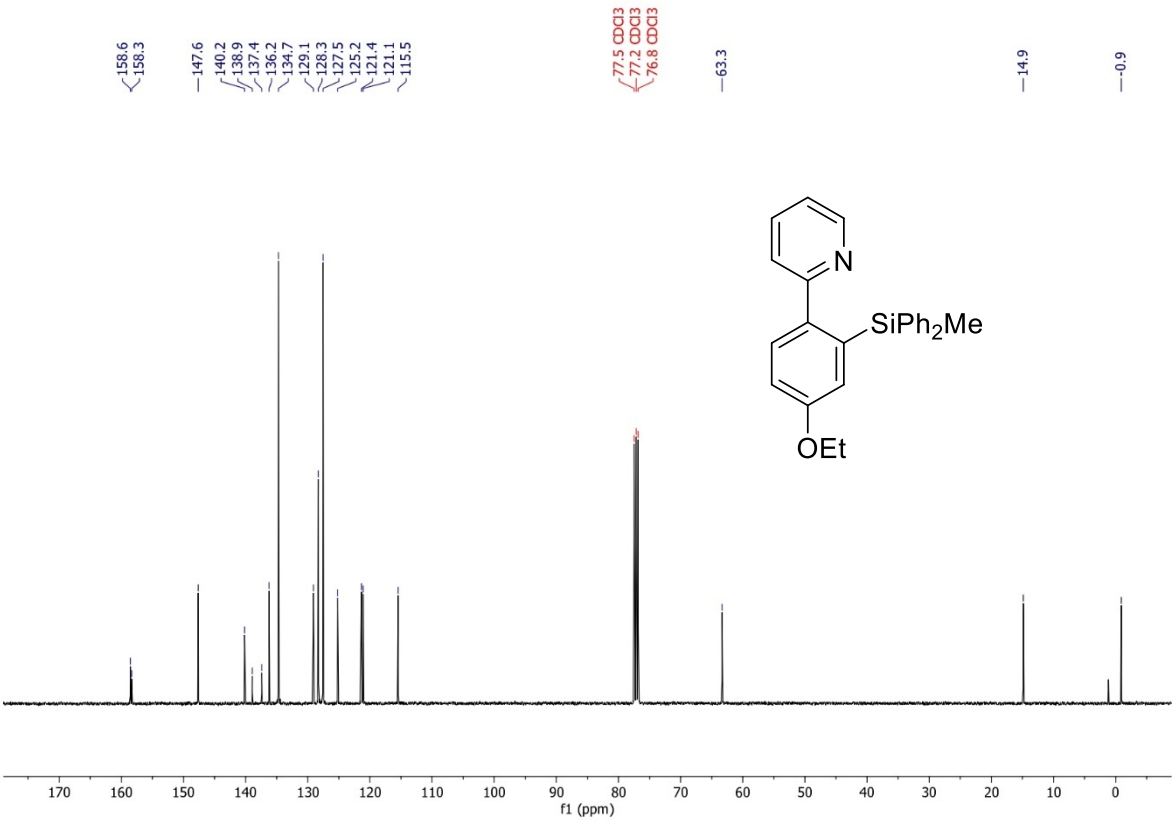
^{29}Si NMR spectrum for **4e**



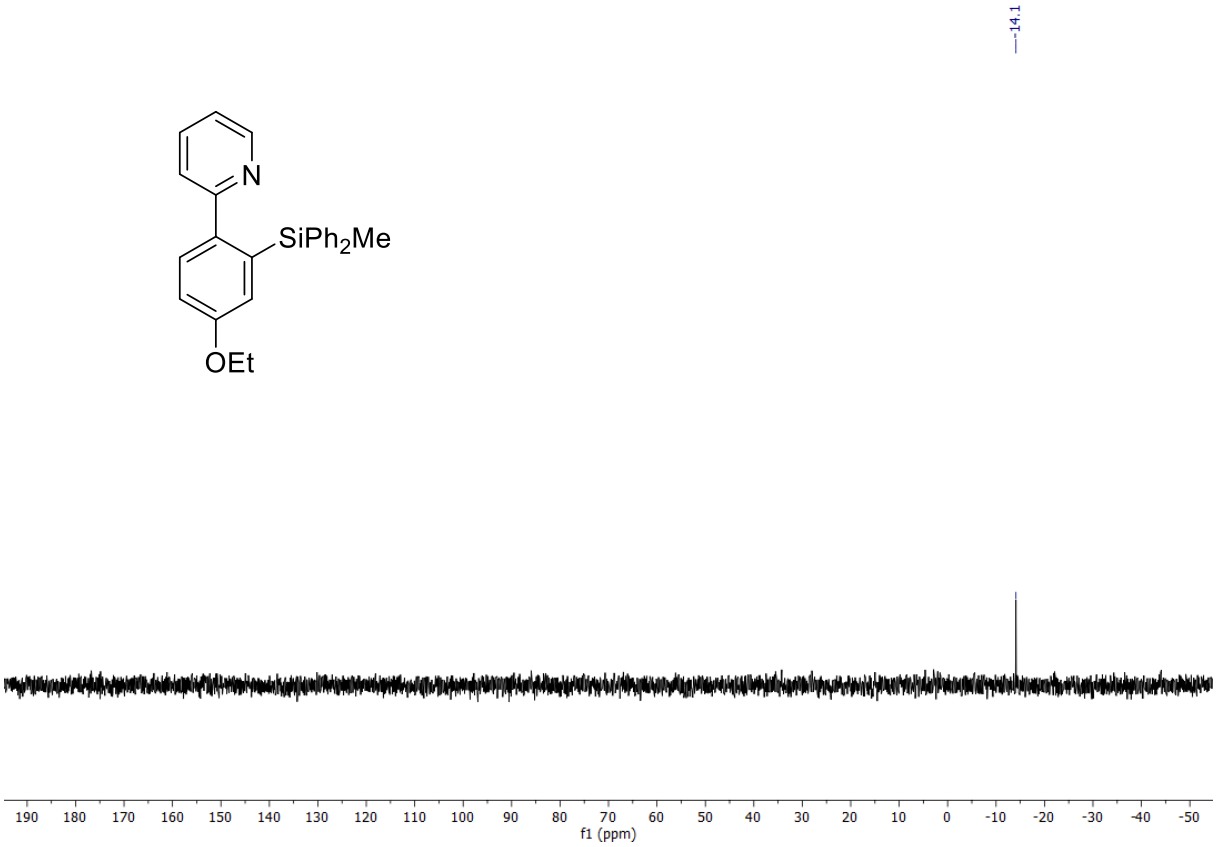
^{1}H NMR spectrum for **4f**



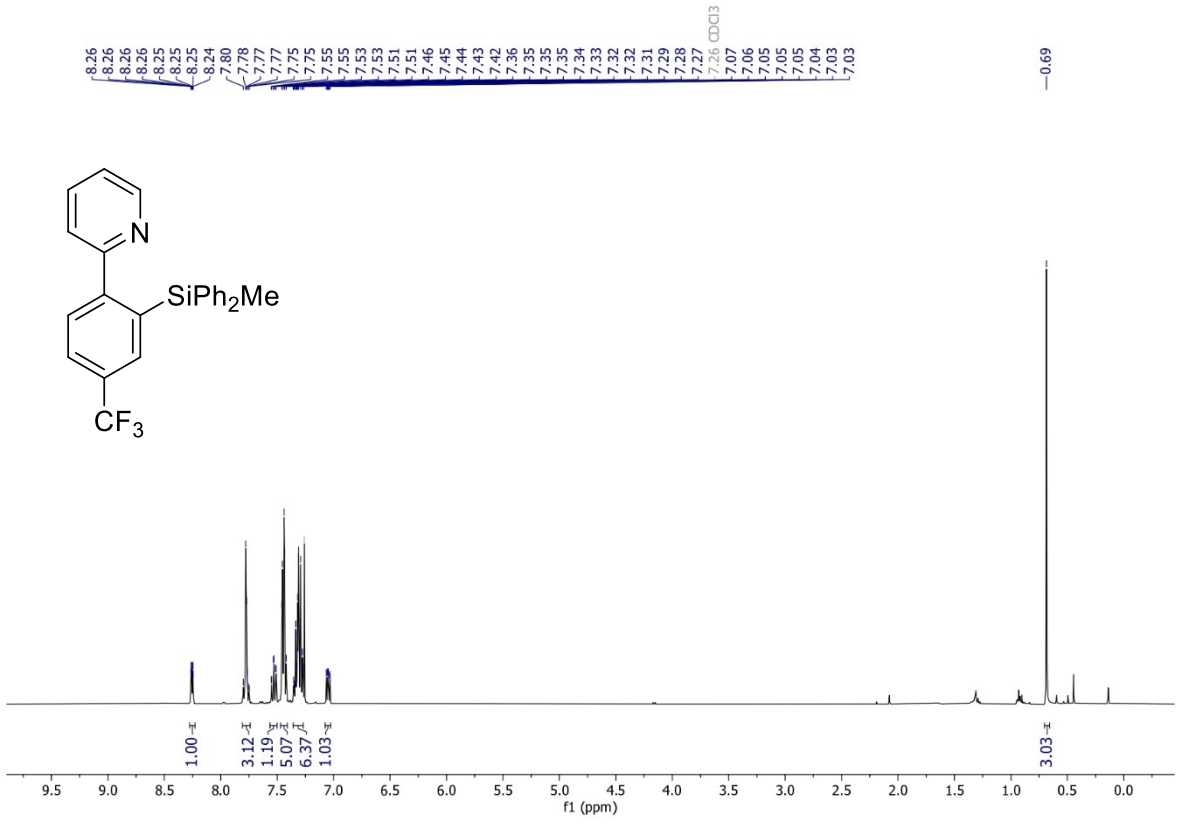
^{13}C NMR spectrum for **4f**



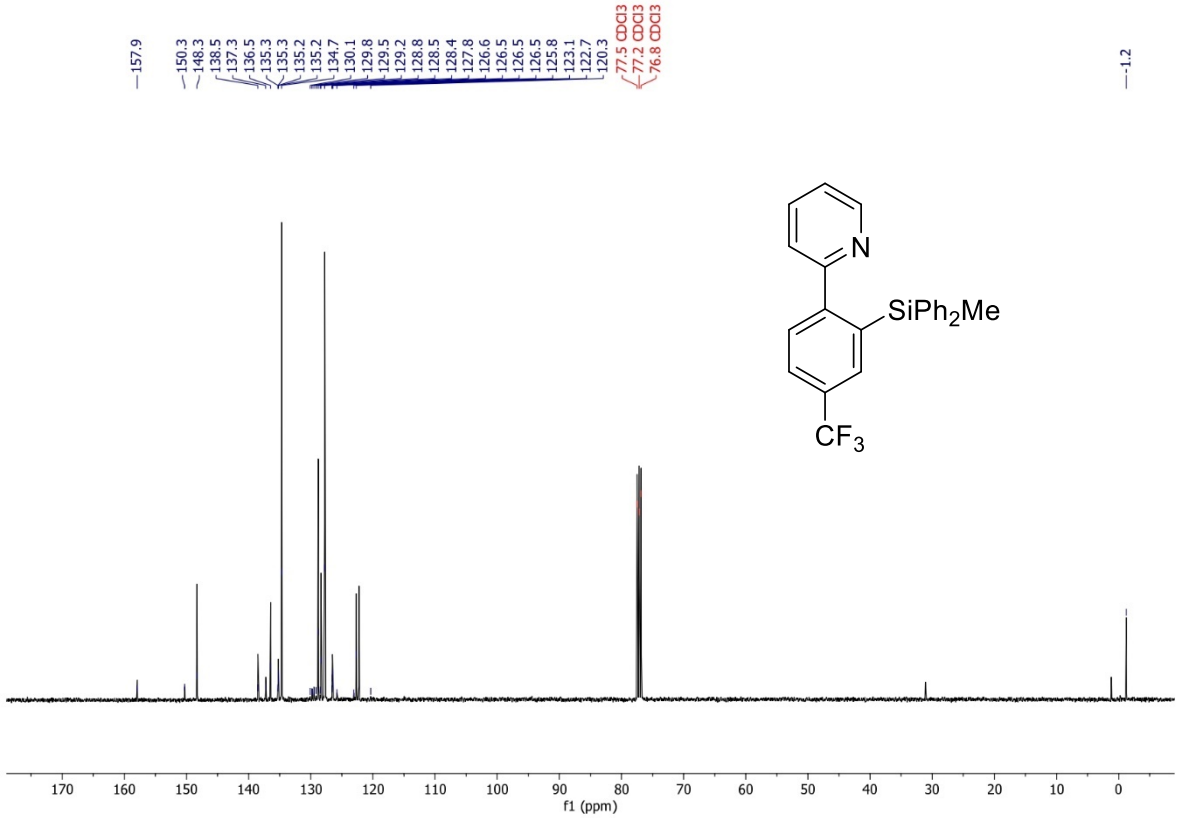
^{29}Si NMR spectrum for **4f**



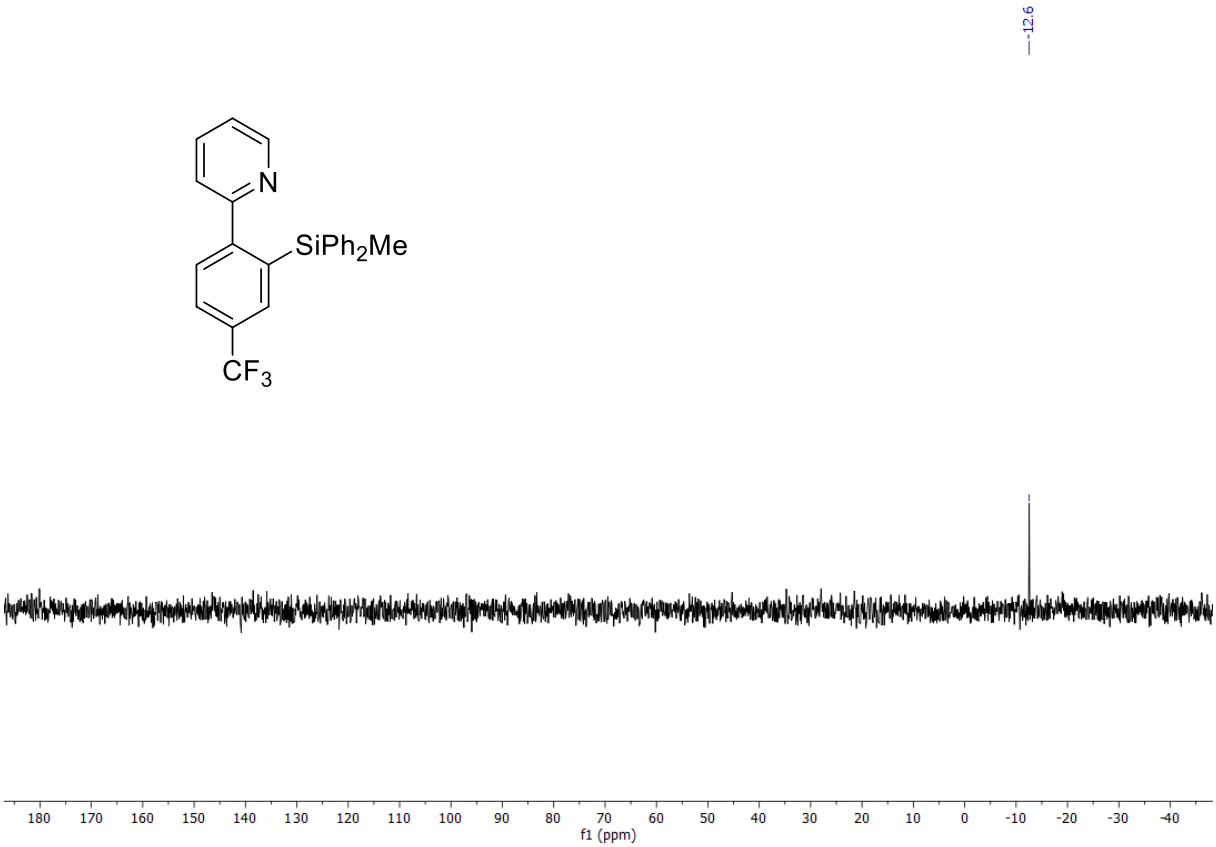
^{1}H NMR spectrum for **4g**



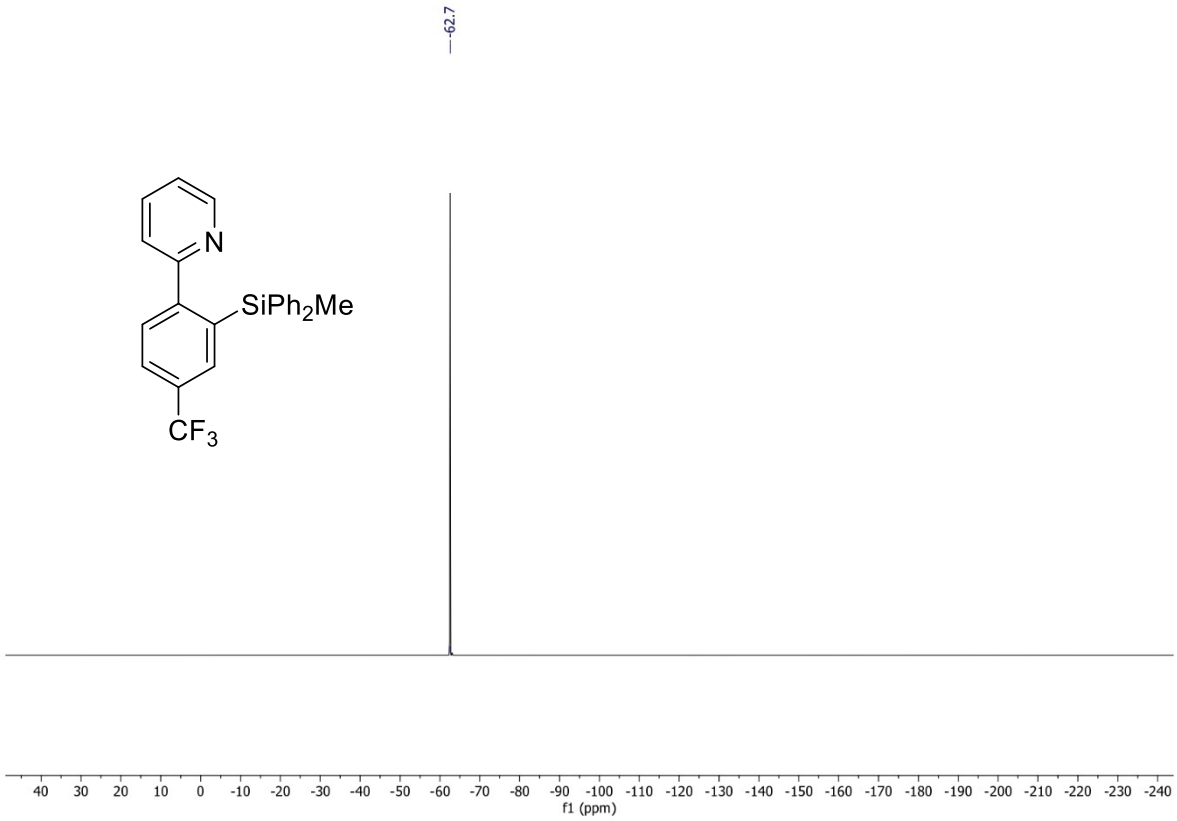
^{13}C NMR spectrum for **4g**



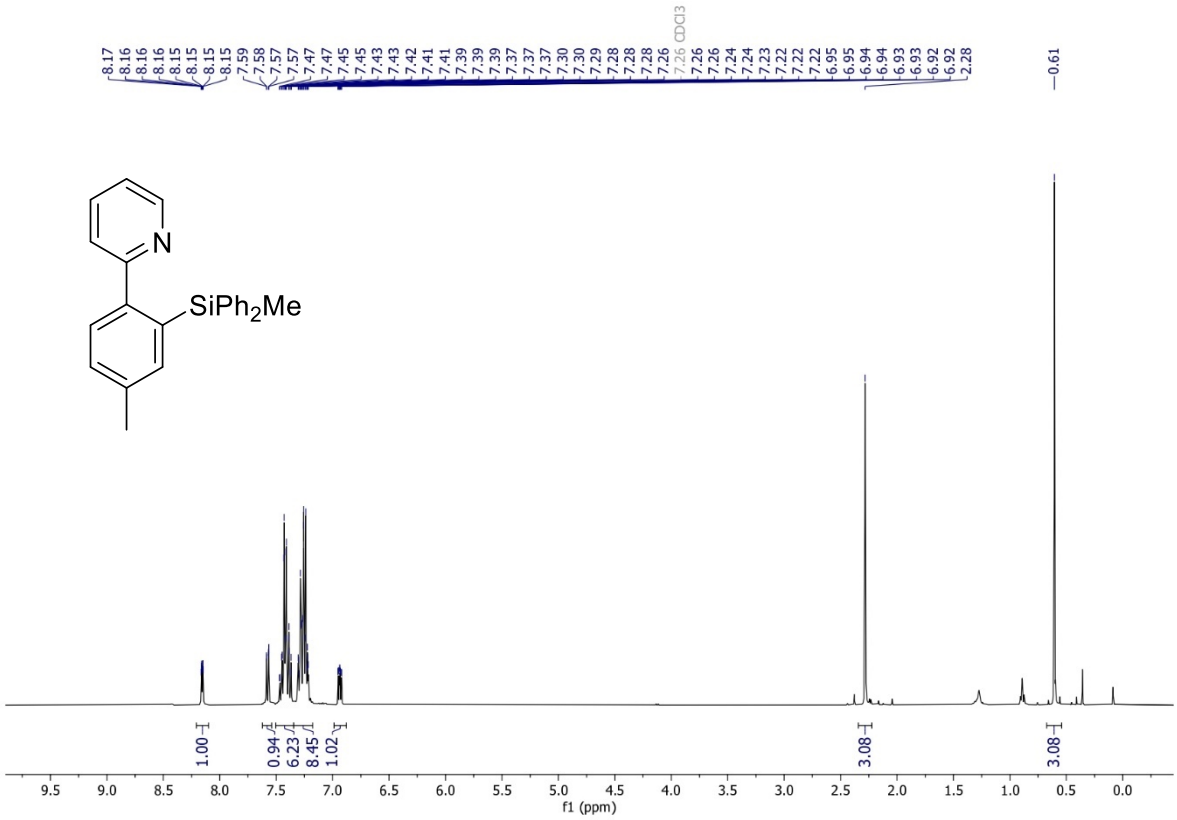
^{29}Si NMR spectrum for **4g**



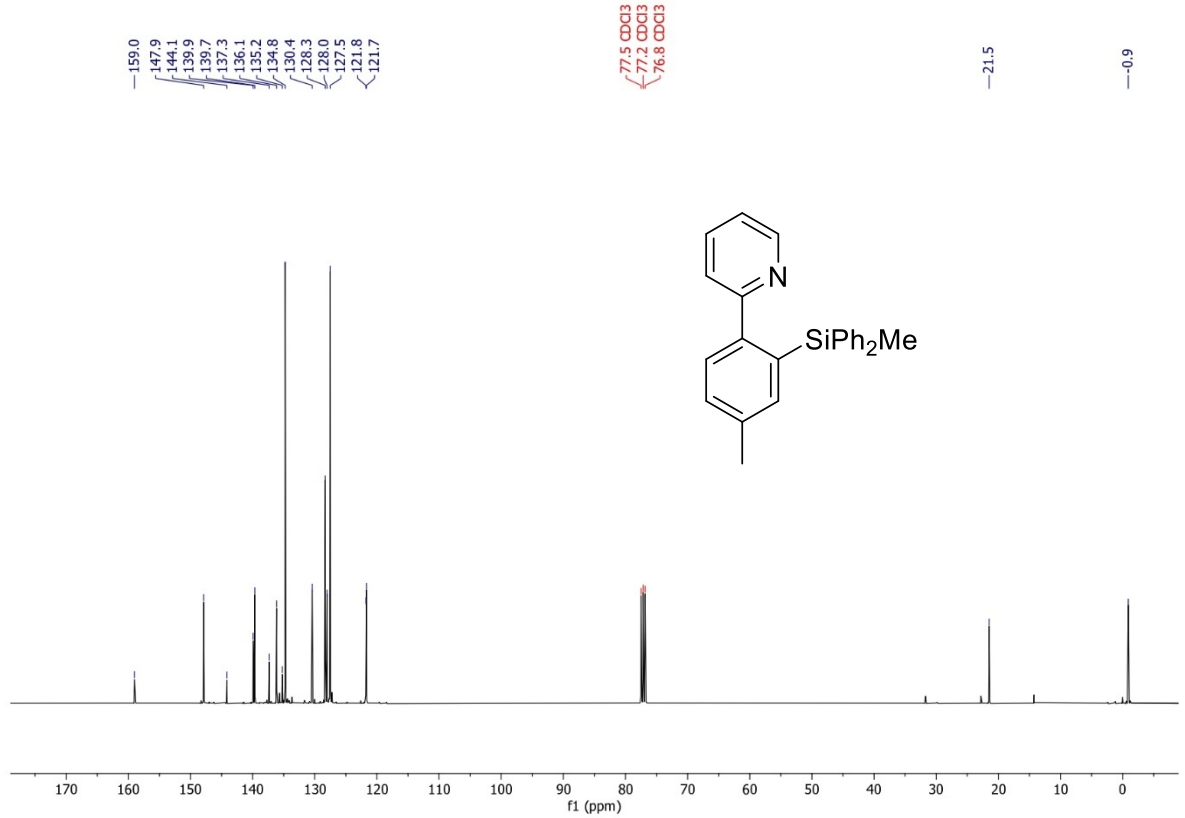
^{19}F NMR spectrum for **4g**



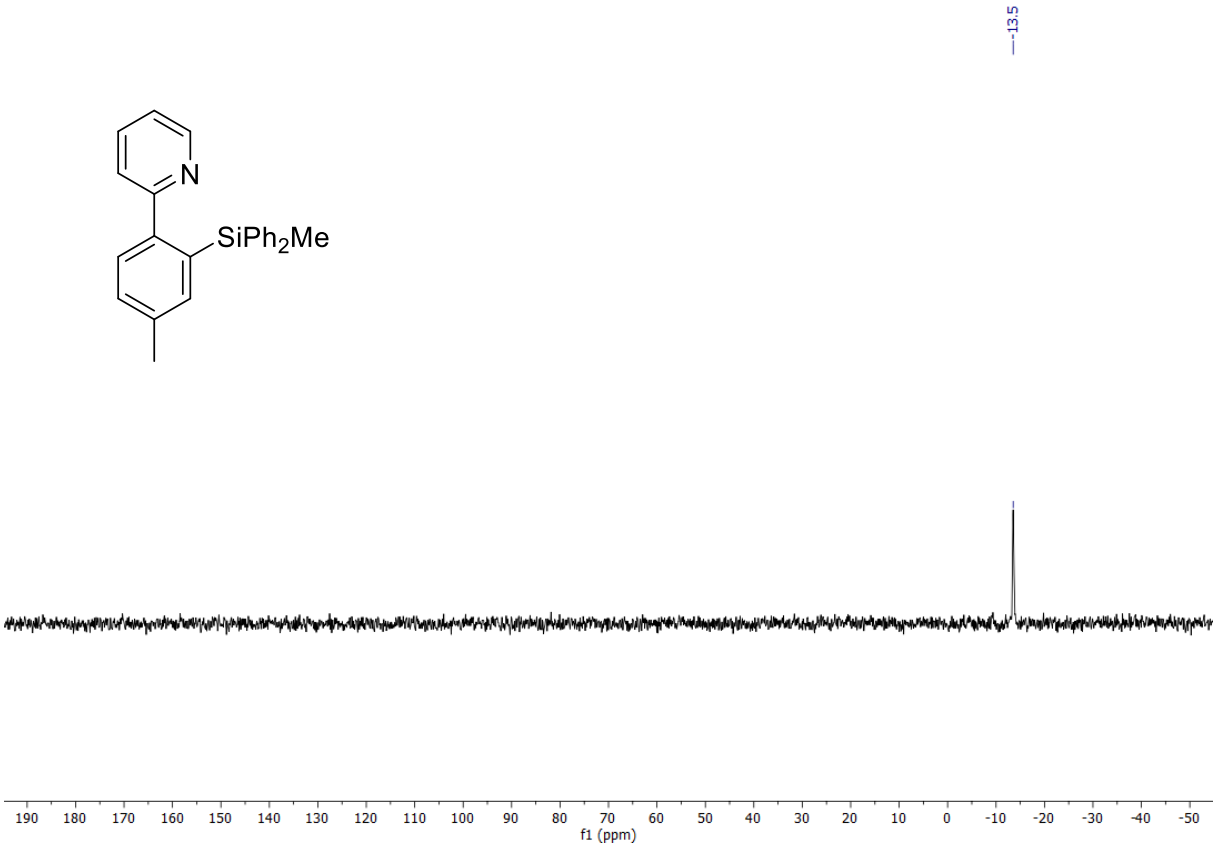
^{1}H NMR spectrum for **4h**



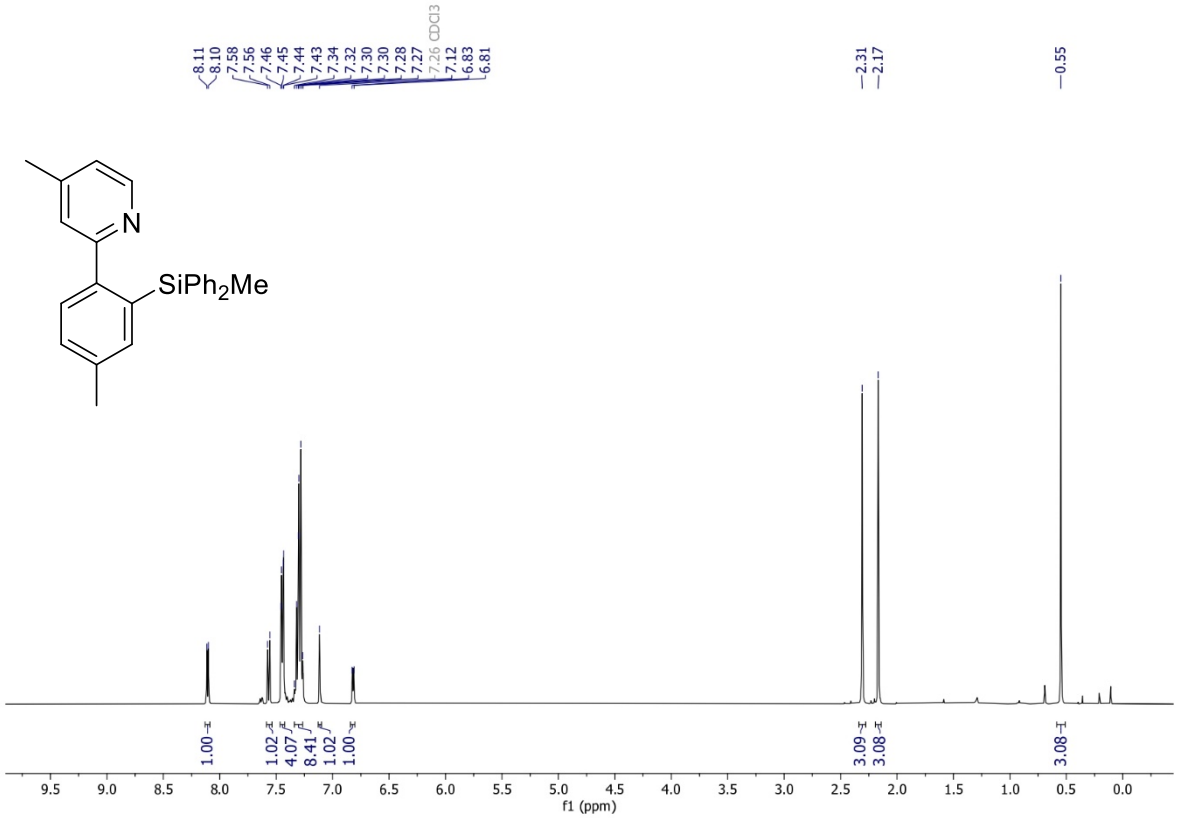
^{13}C NMR spectrum for **4h**



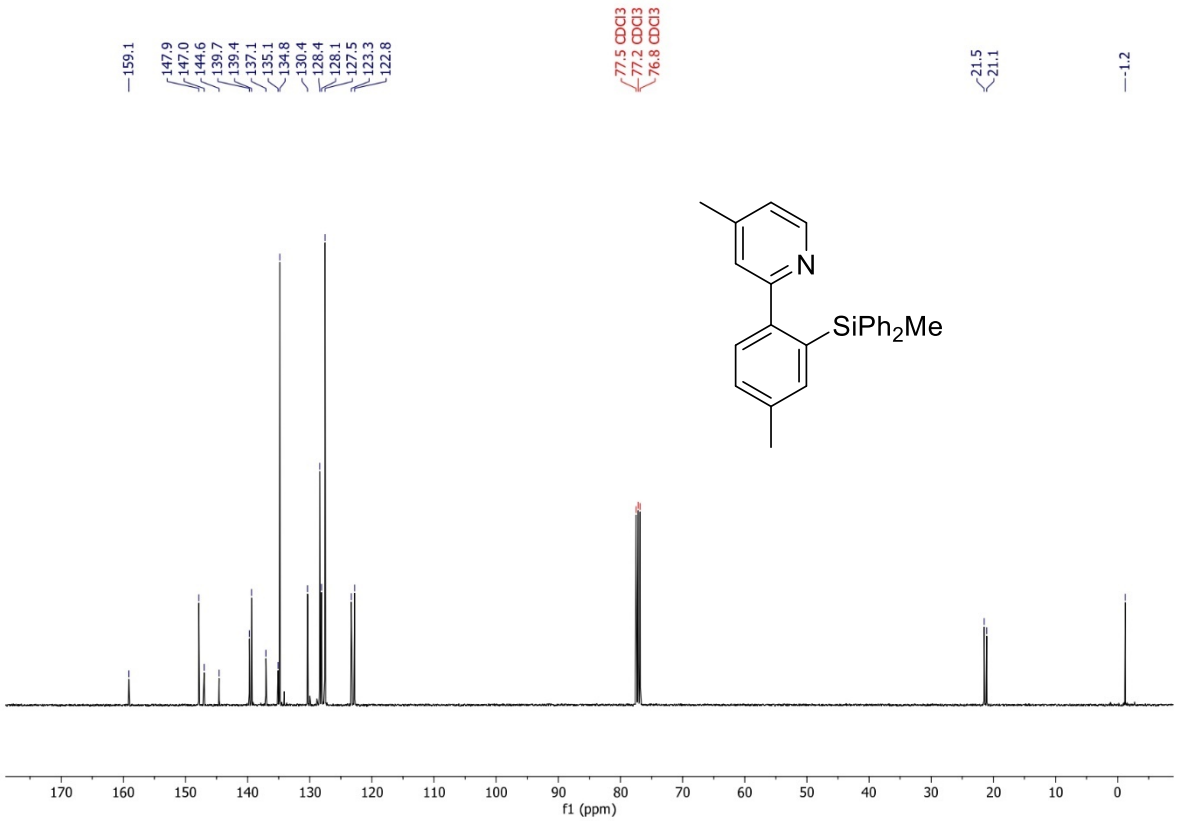
^{29}Si NMR spectrum for **4h**



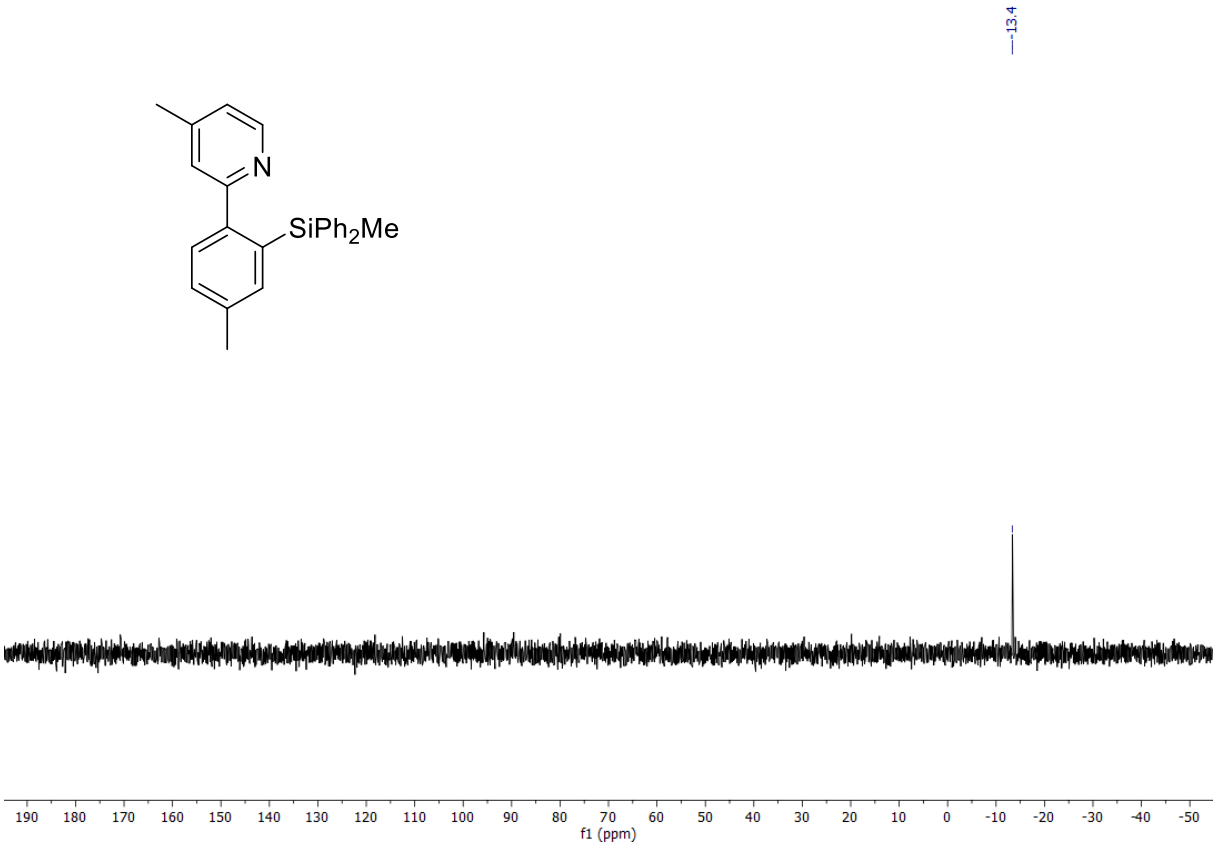
^{1}H NMR spectrum for **4i**



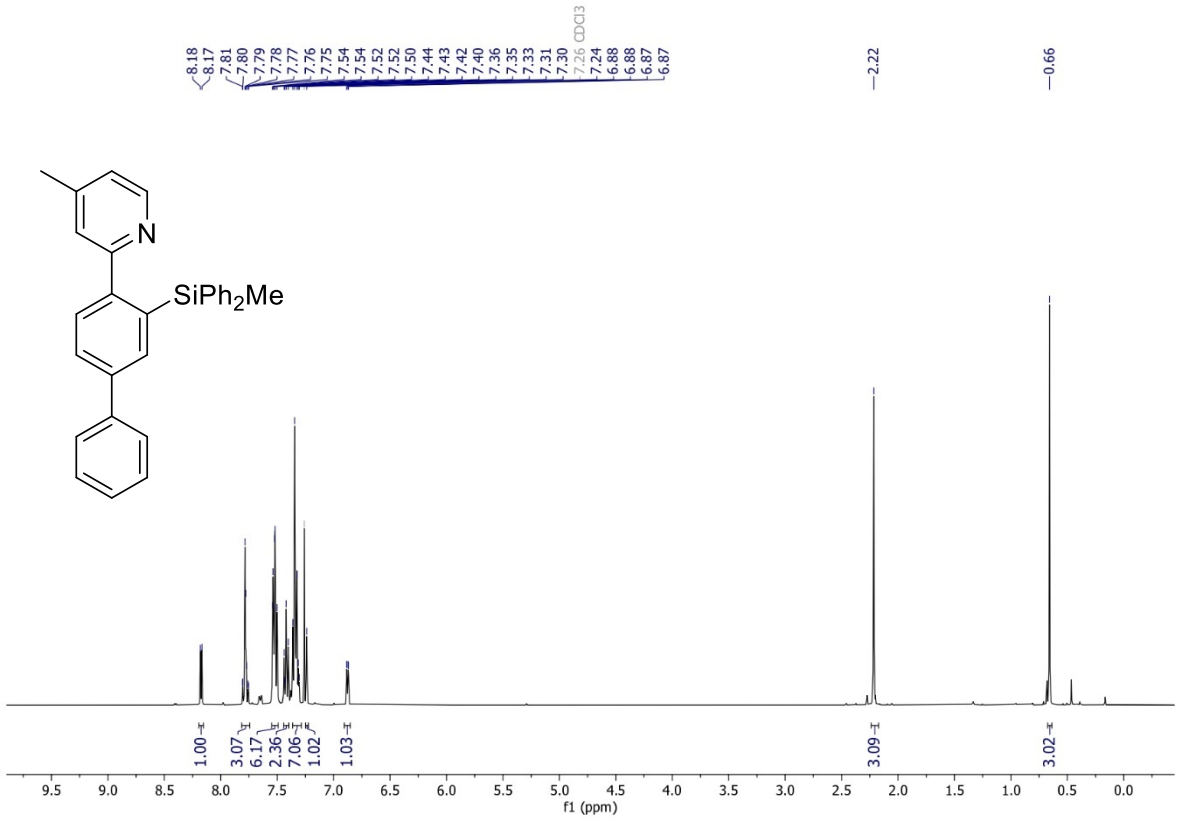
^{13}C NMR spectrum for **4i**



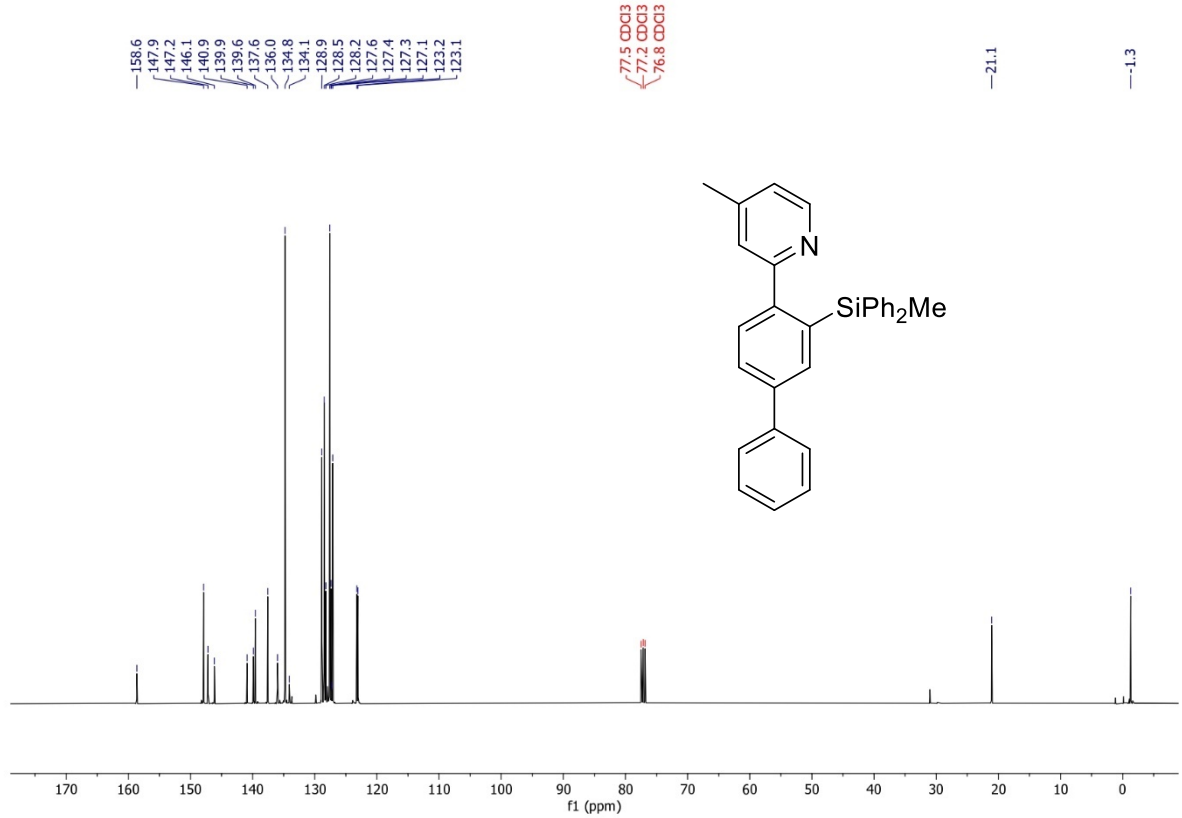
^{29}Si NMR spectrum for **4i**



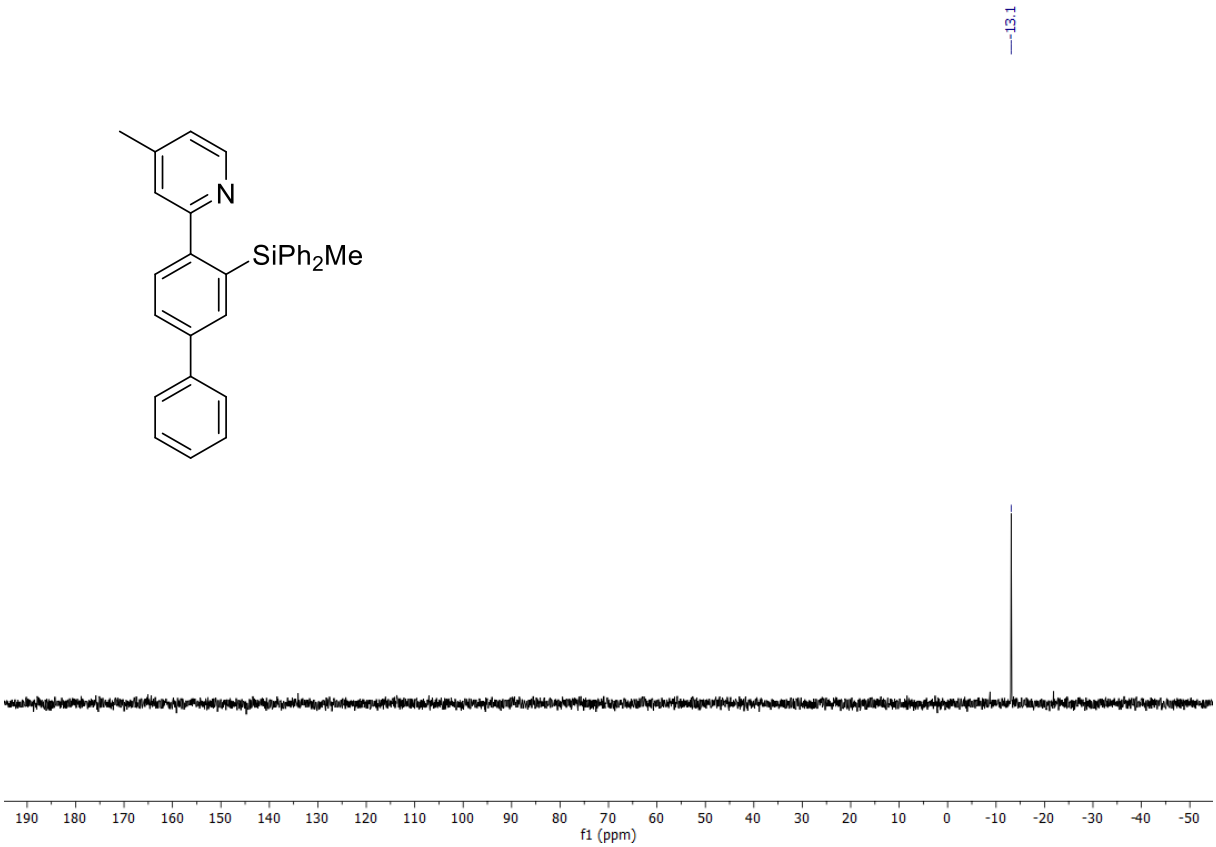
^{1}H NMR spectrum for **4j**



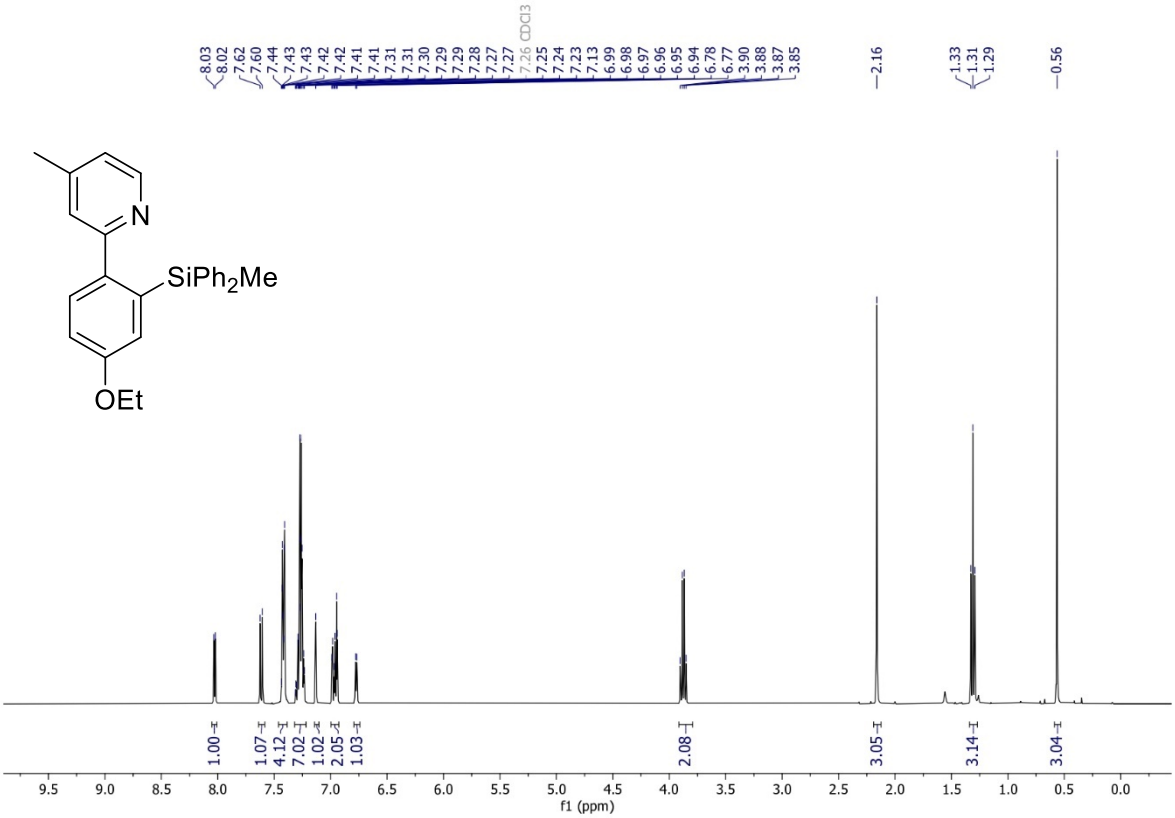
^{13}C NMR spectrum for **4j**



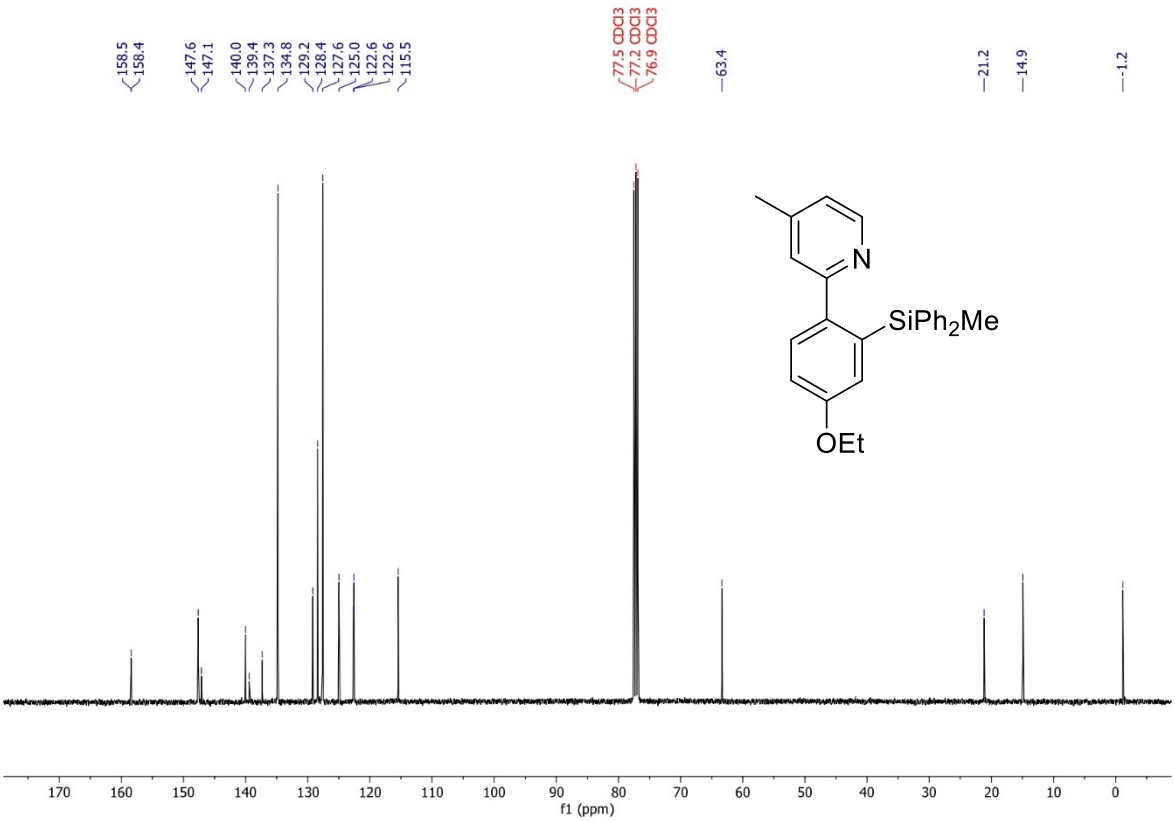
^{29}Si NMR spectrum for **4j**



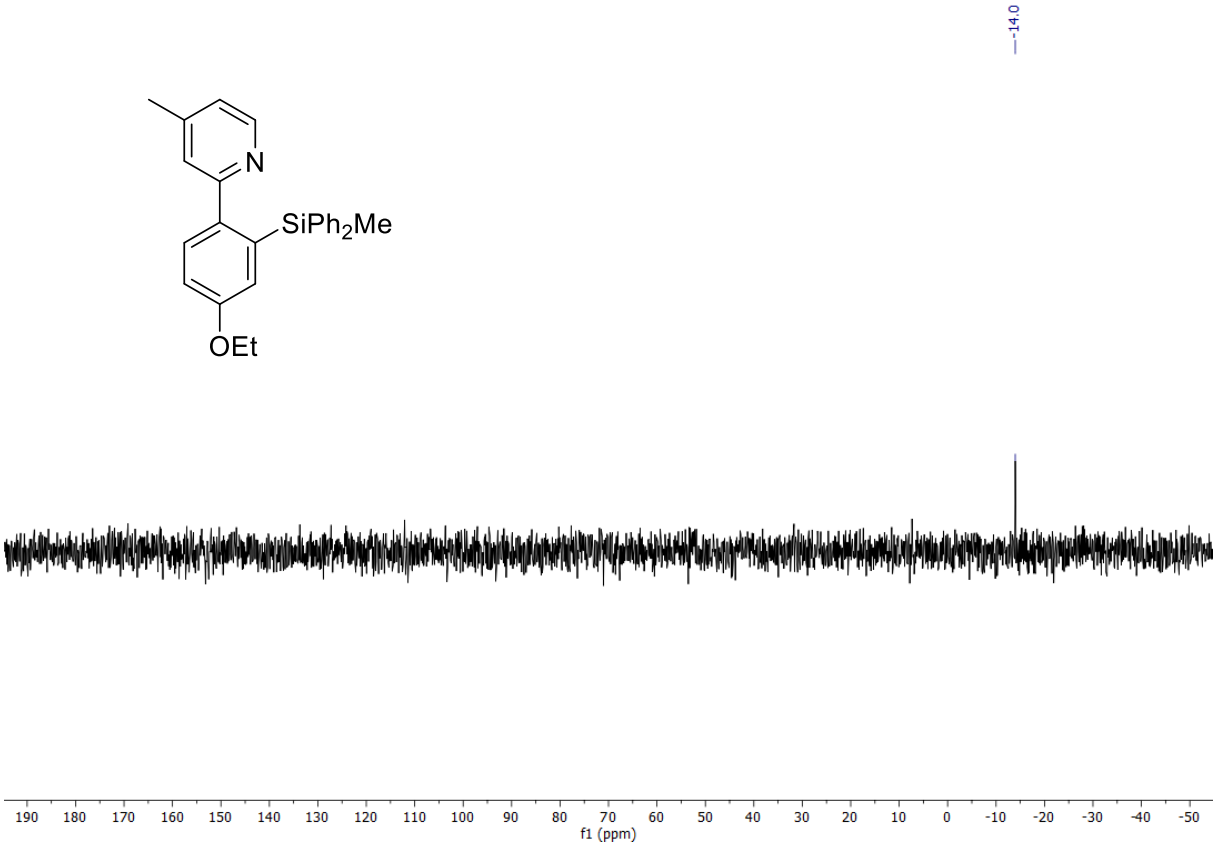
^{1}H NMR spectrum for **4k**



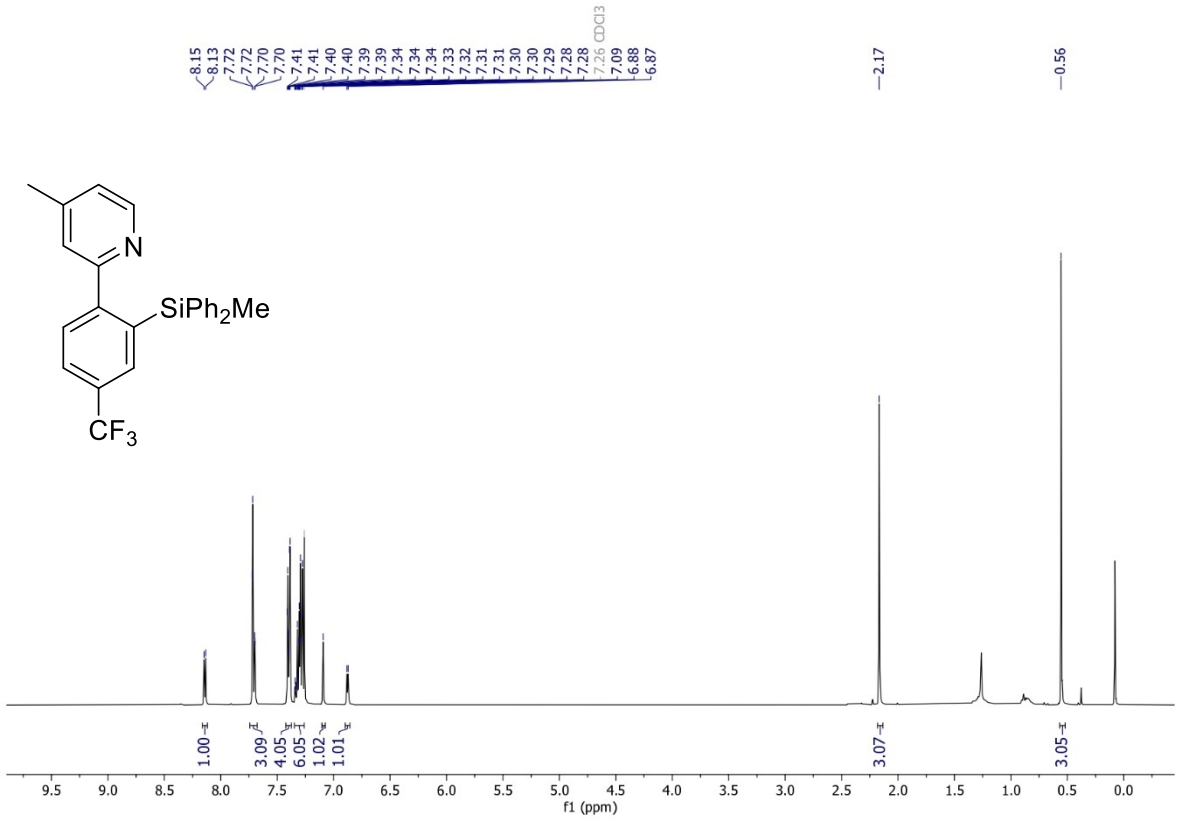
^{13}C NMR spectrum for **4k**



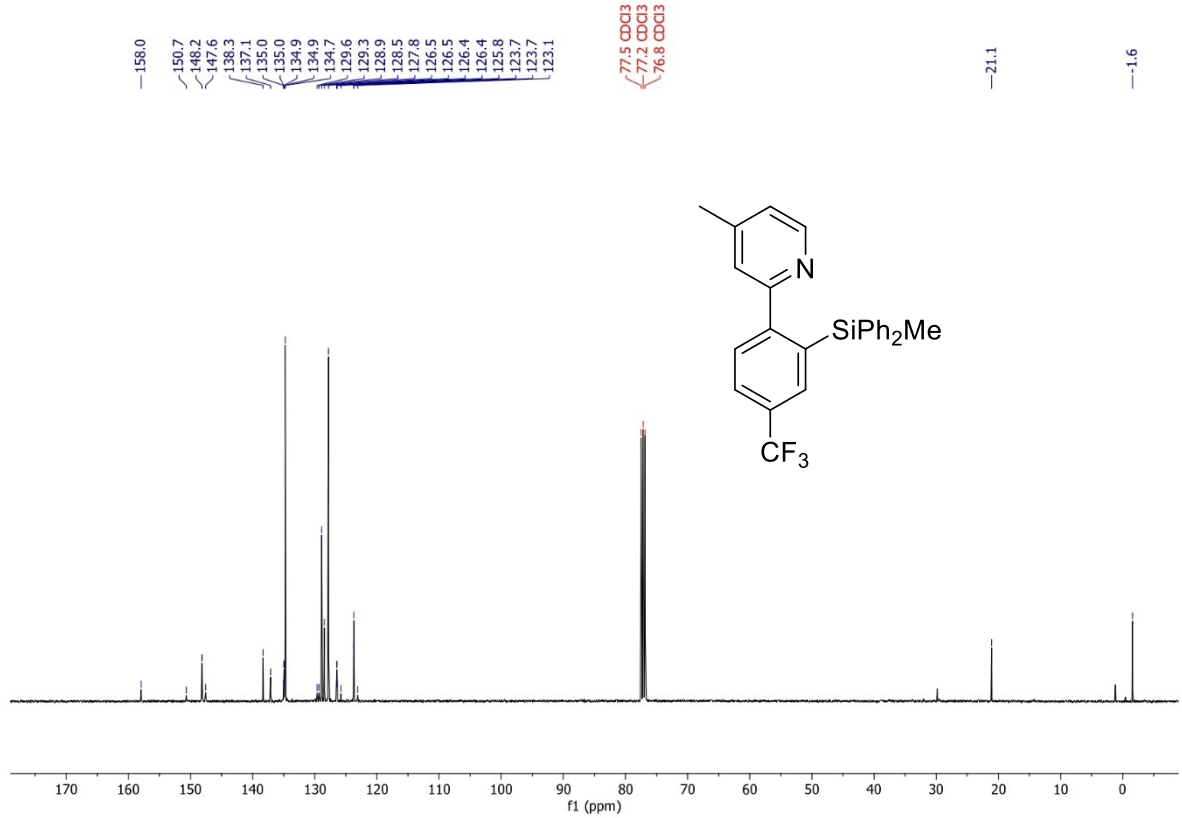
^{29}Si NMR spectrum for **4k**



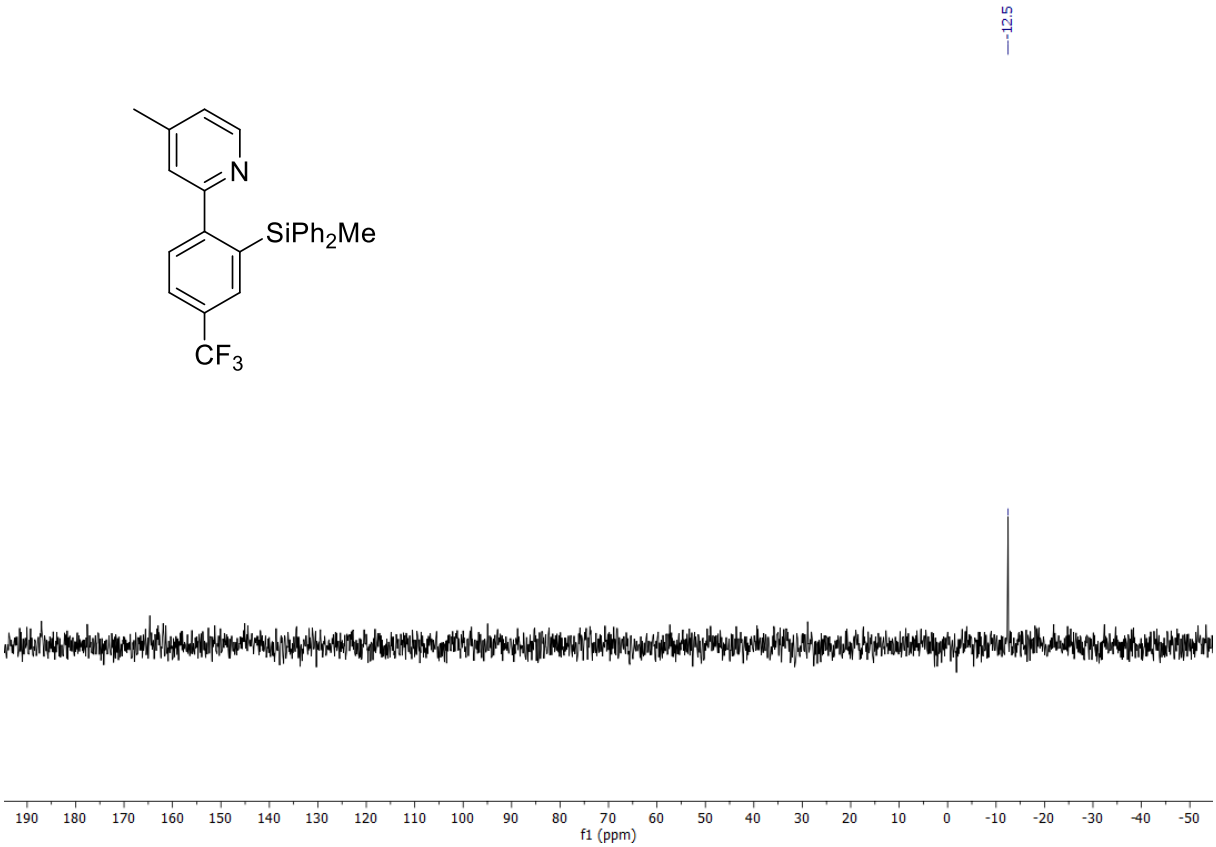
^{1}H NMR spectrum for **4l**



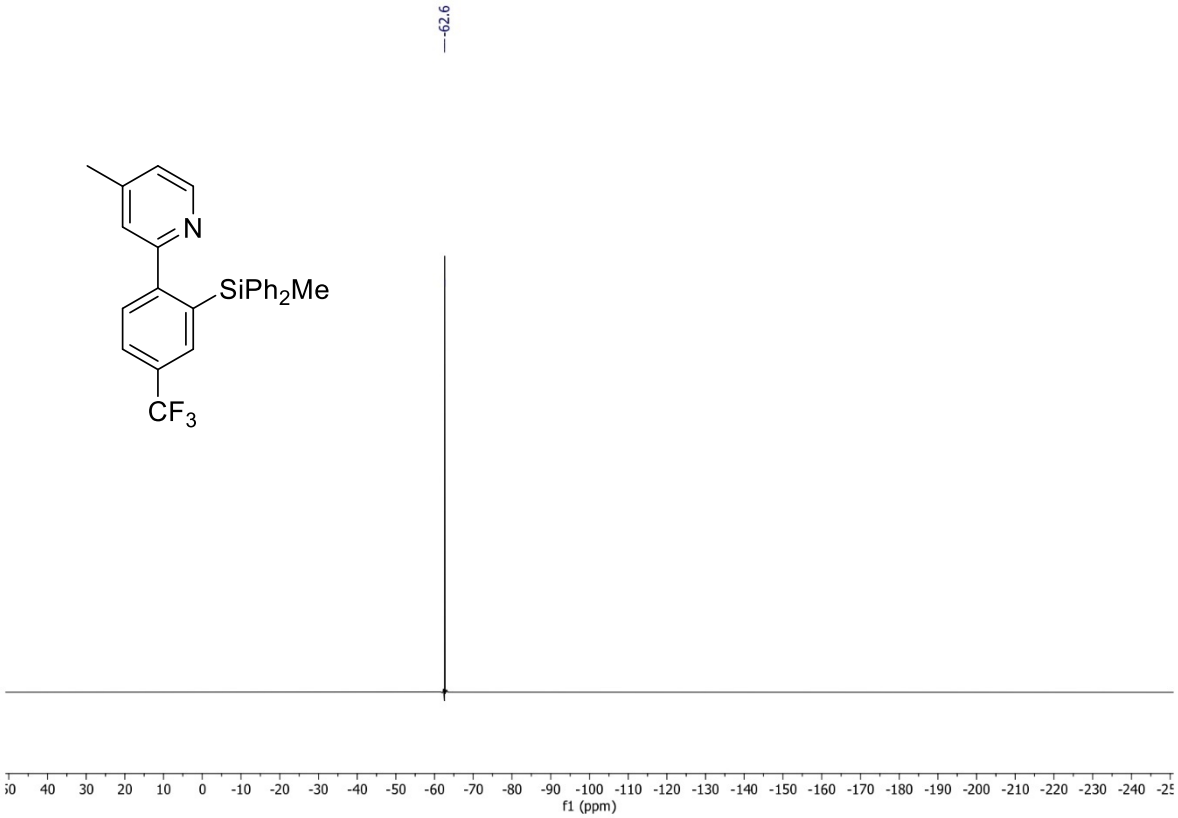
^{13}C NMR spectrum for **4l**



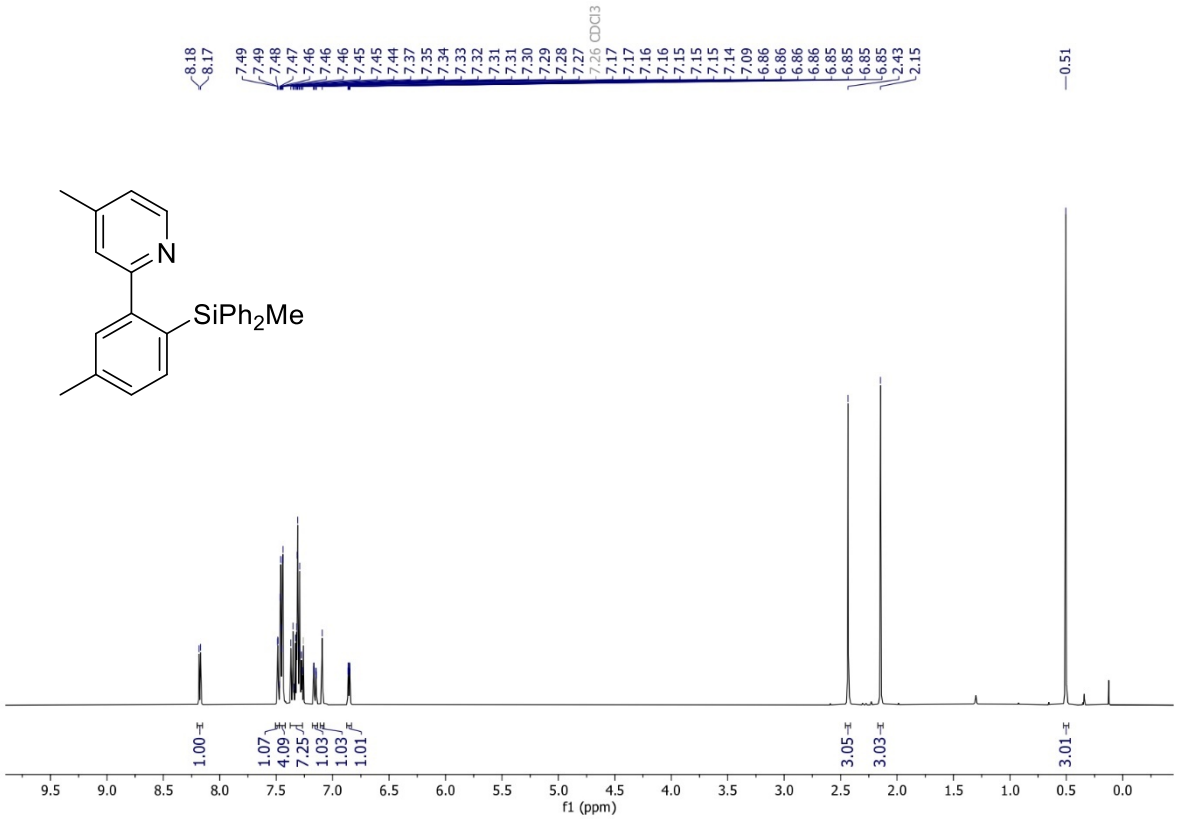
^{29}Si NMR spectrum for **4l**



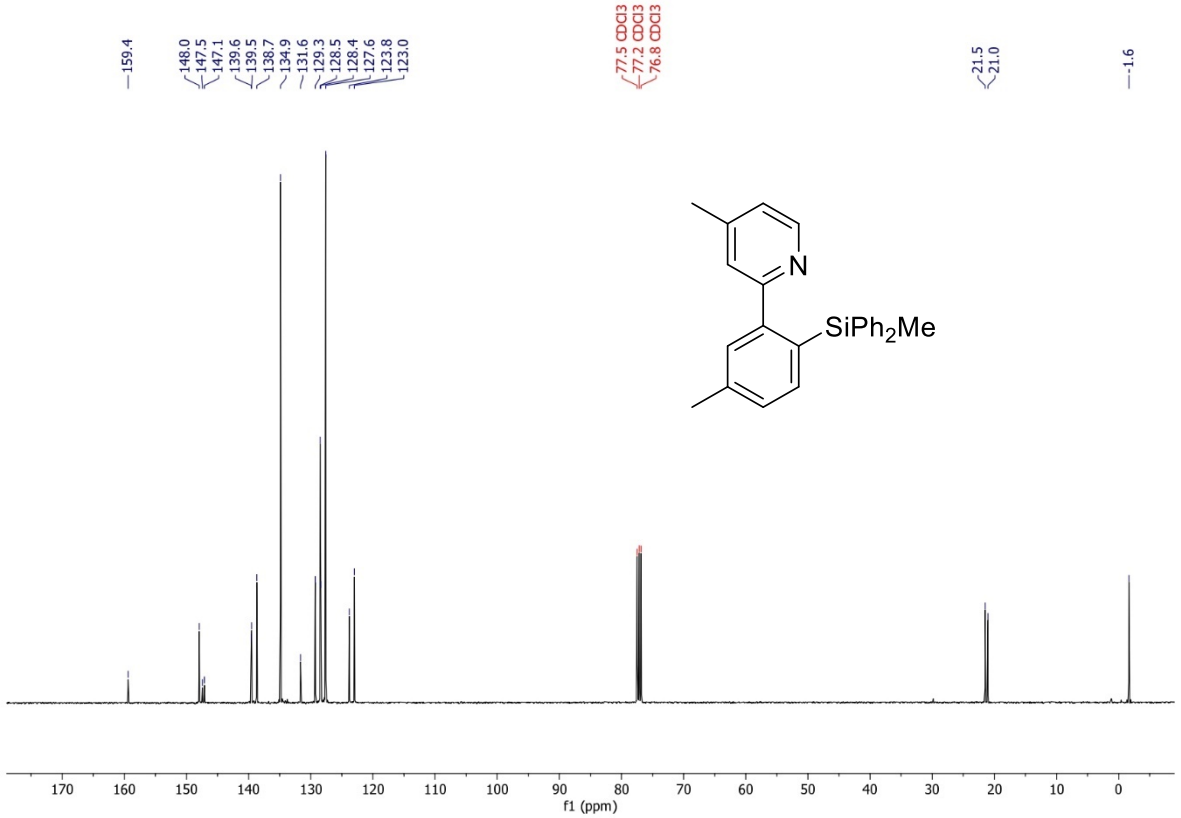
^{19}F NMR spectrum for **4l**



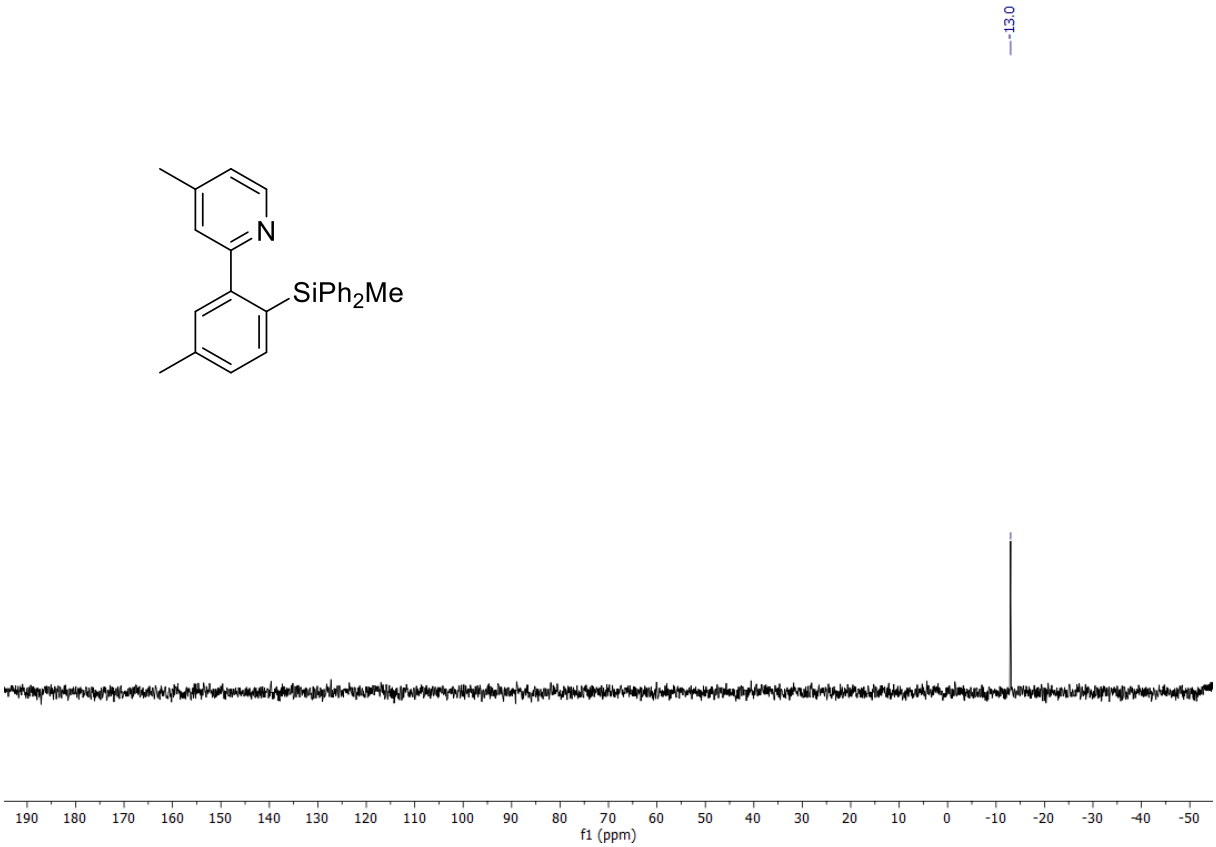
^{1}H NMR spectrum for **4m**



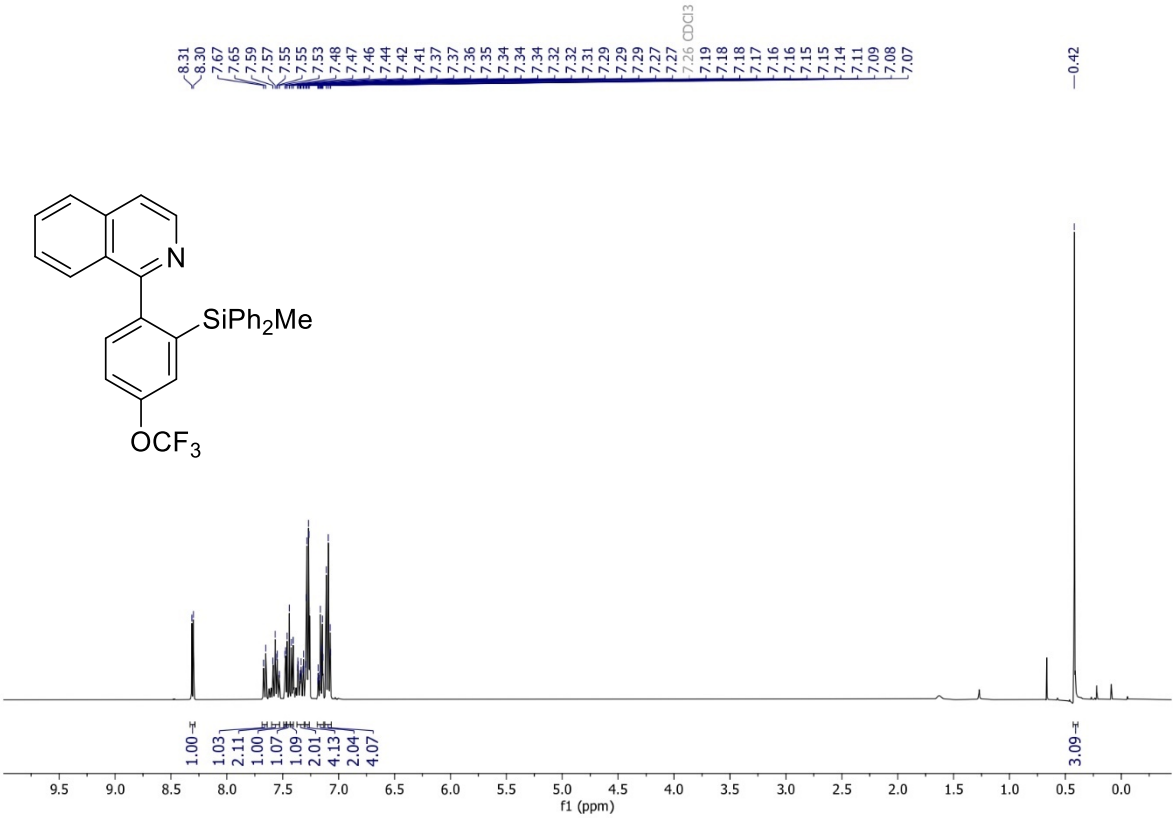
^{13}C NMR spectrum for **4m**



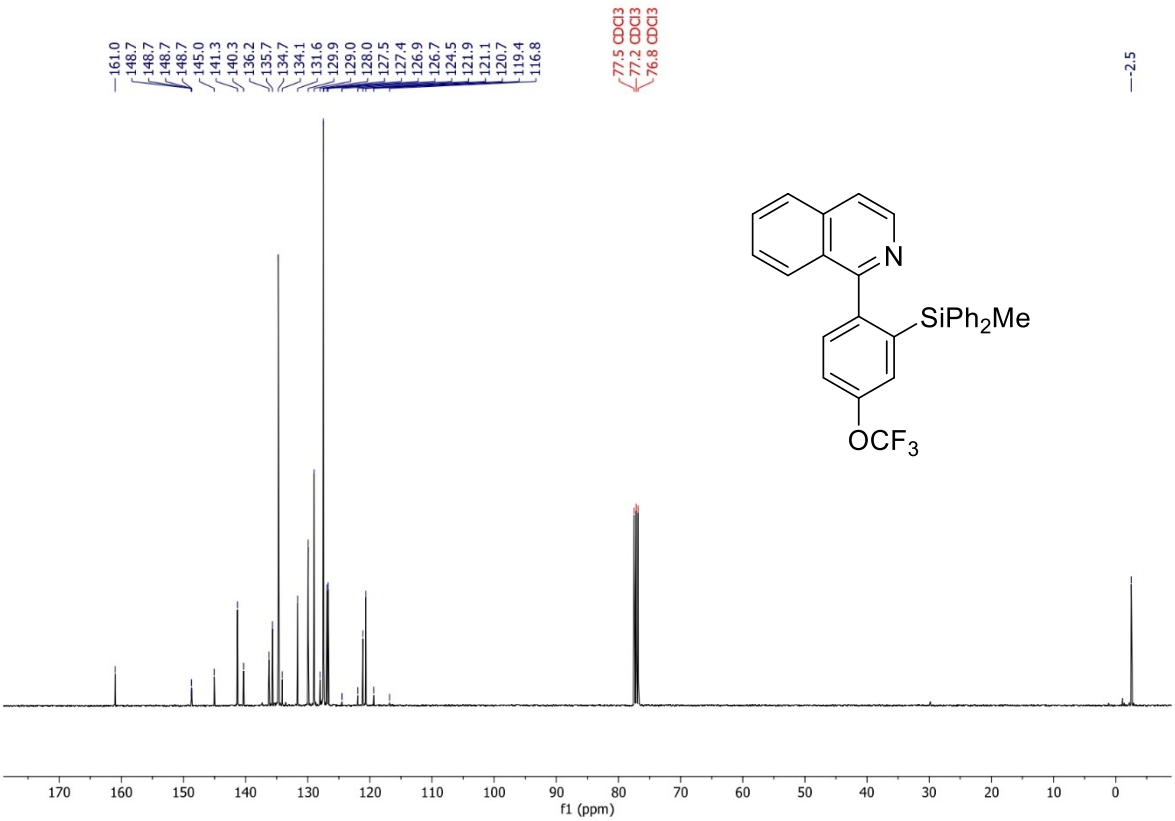
^{29}Si NMR spectrum for **4m**



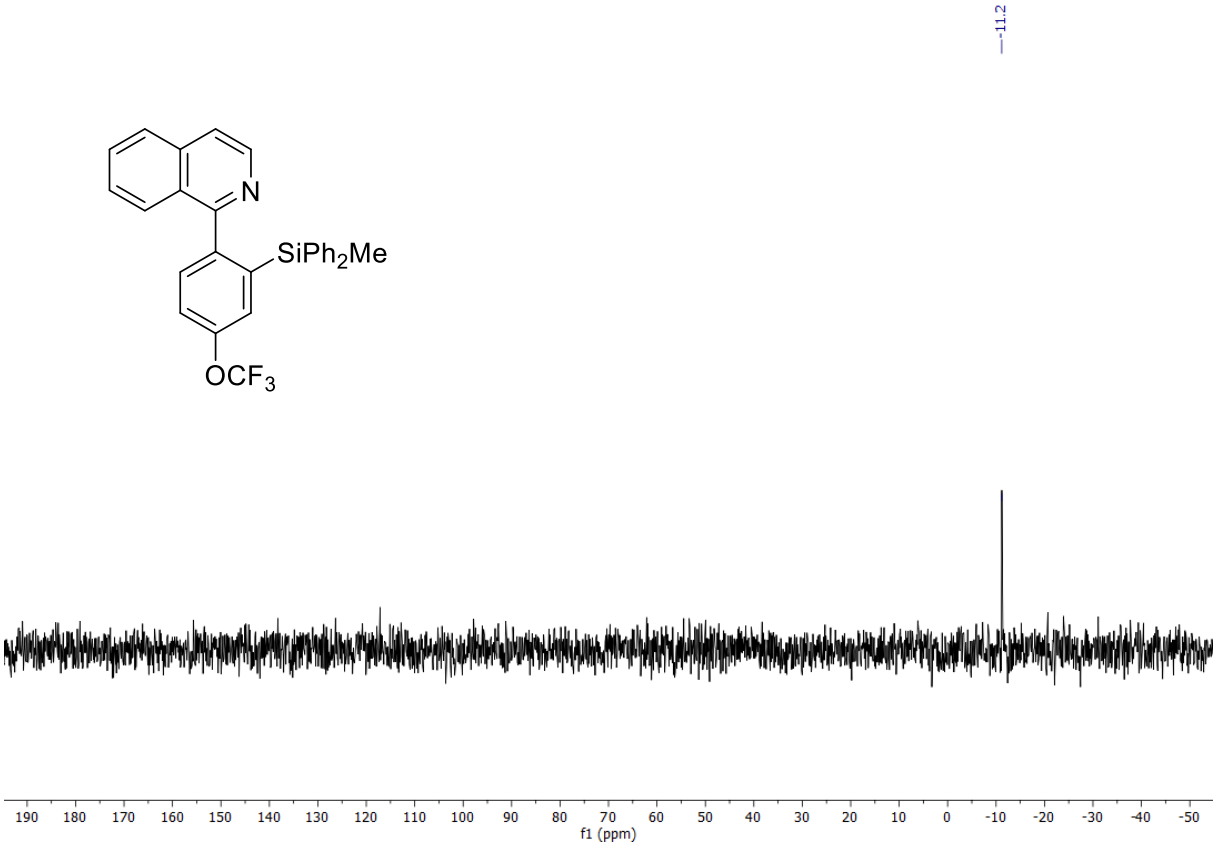
^{1}H NMR spectrum for **4n**



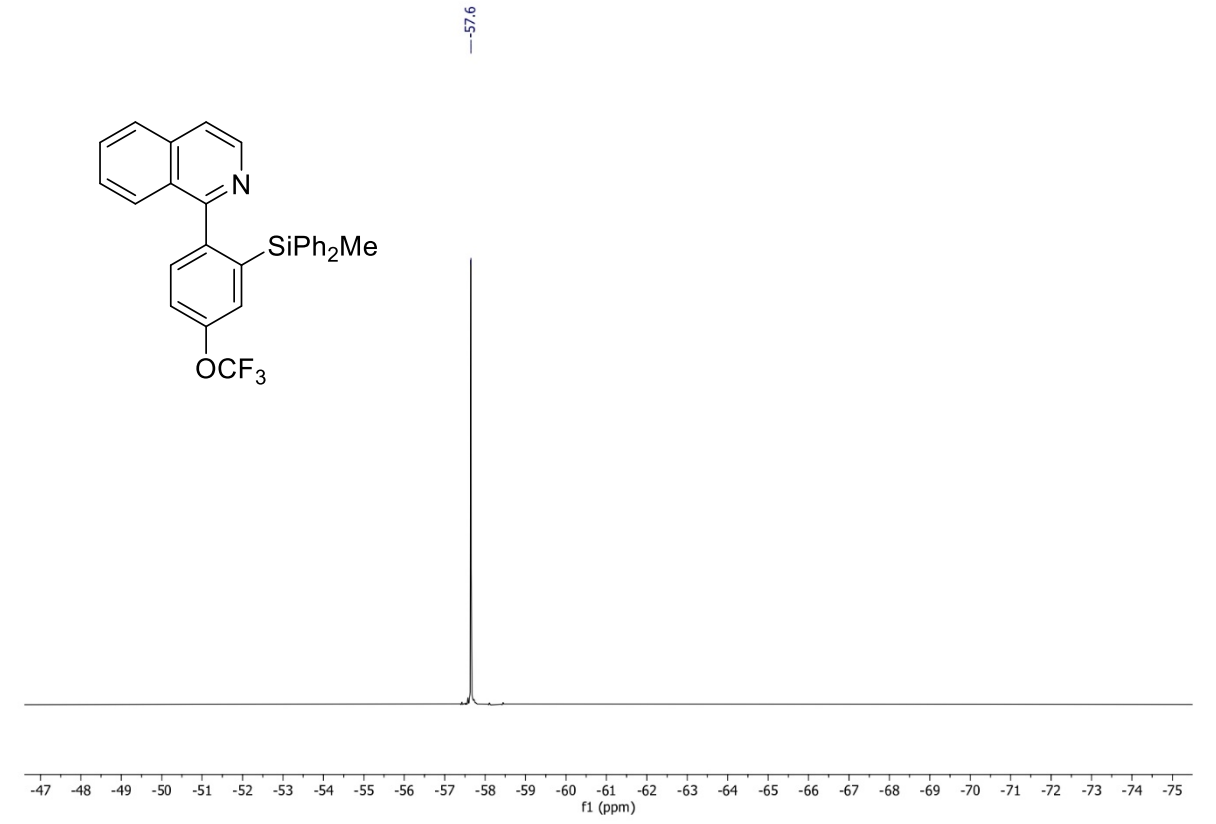
^{13}C NMR spectrum for **4n**



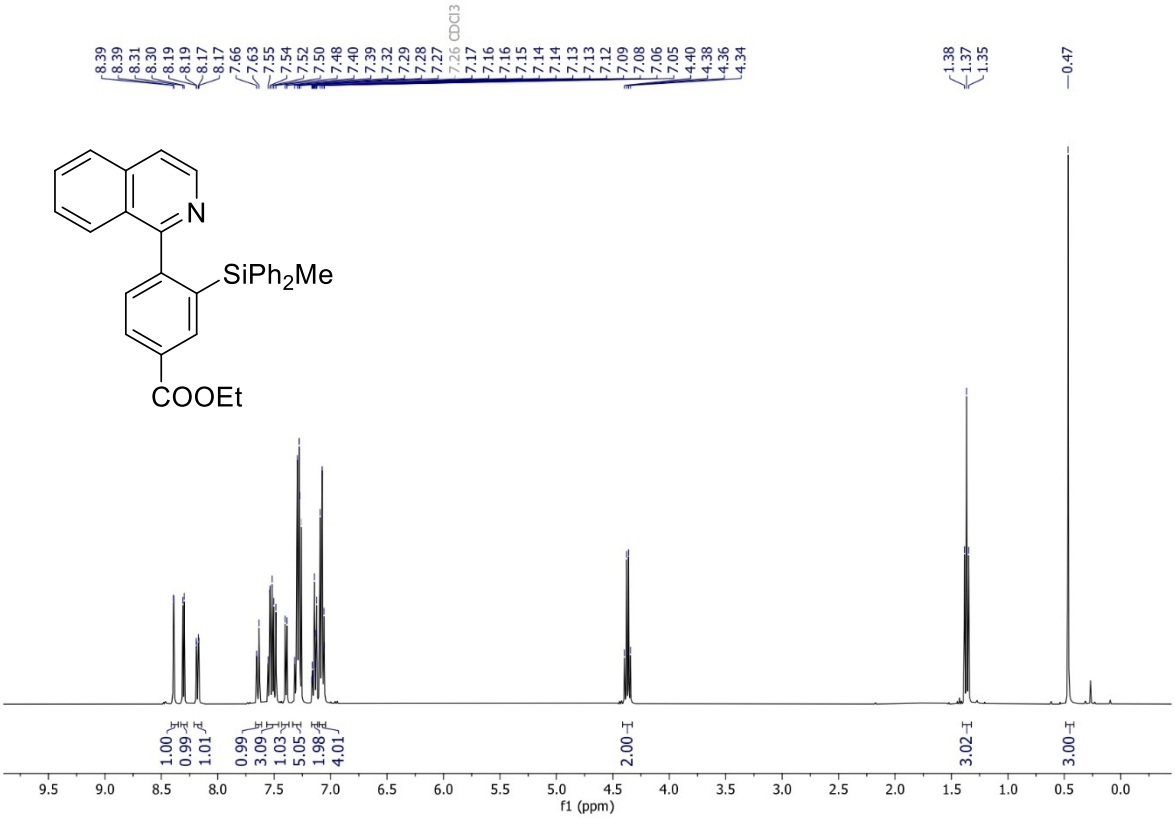
^{29}Si NMR spectrum for **4n**



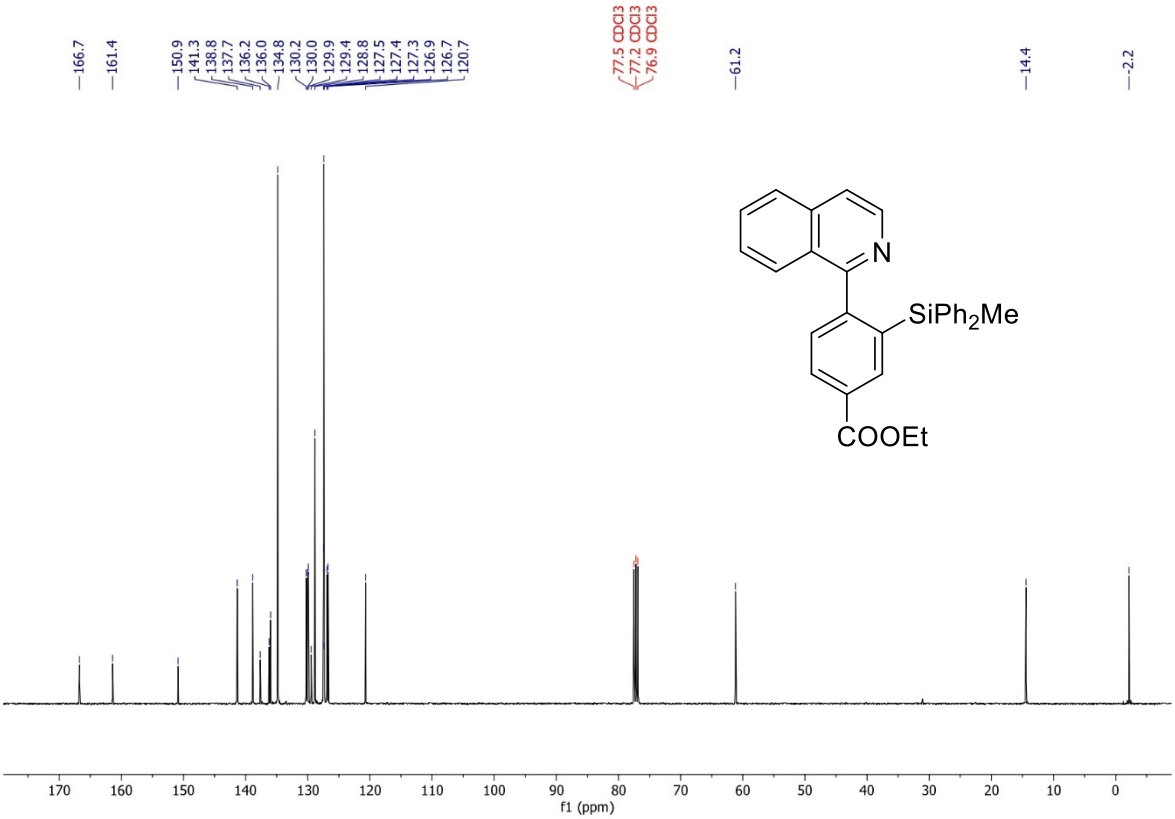
^{19}F NMR spectrum for **4n**



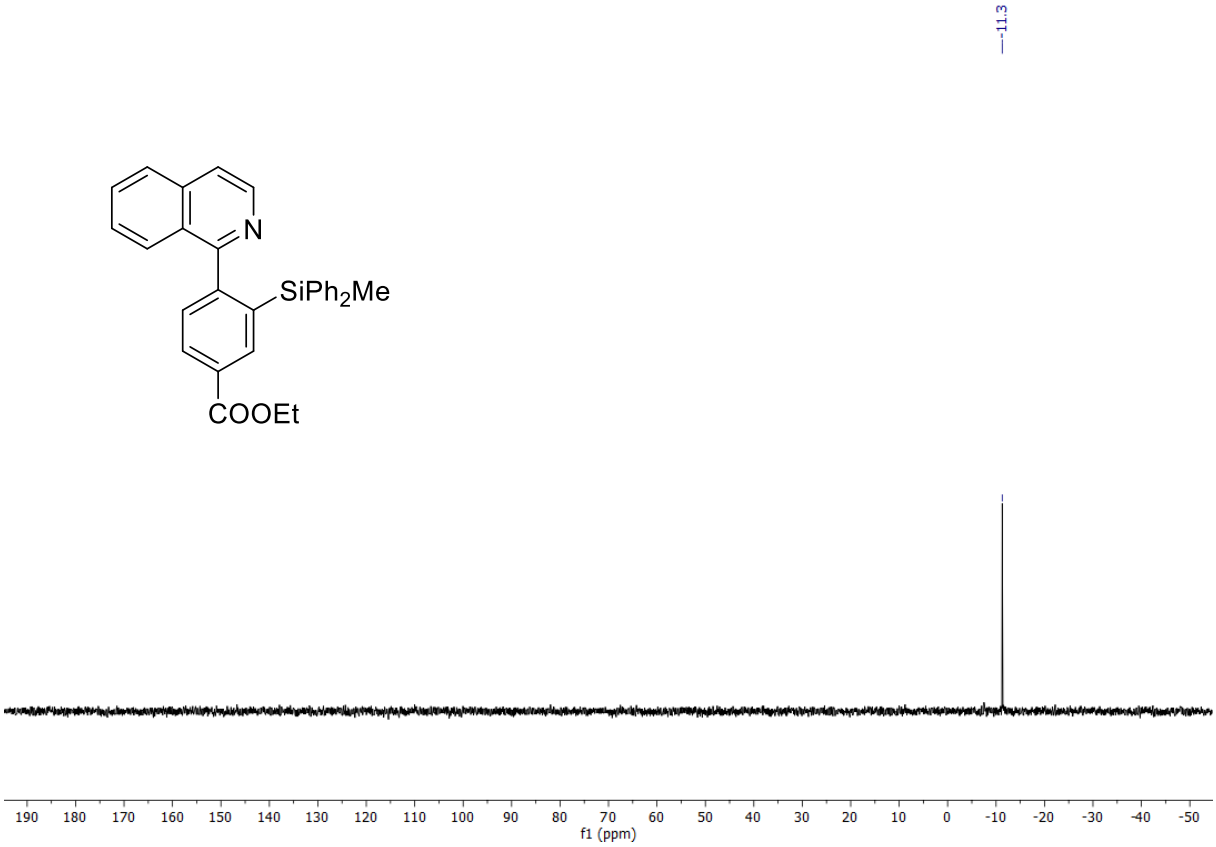
^{1}H NMR spectrum for **4o**



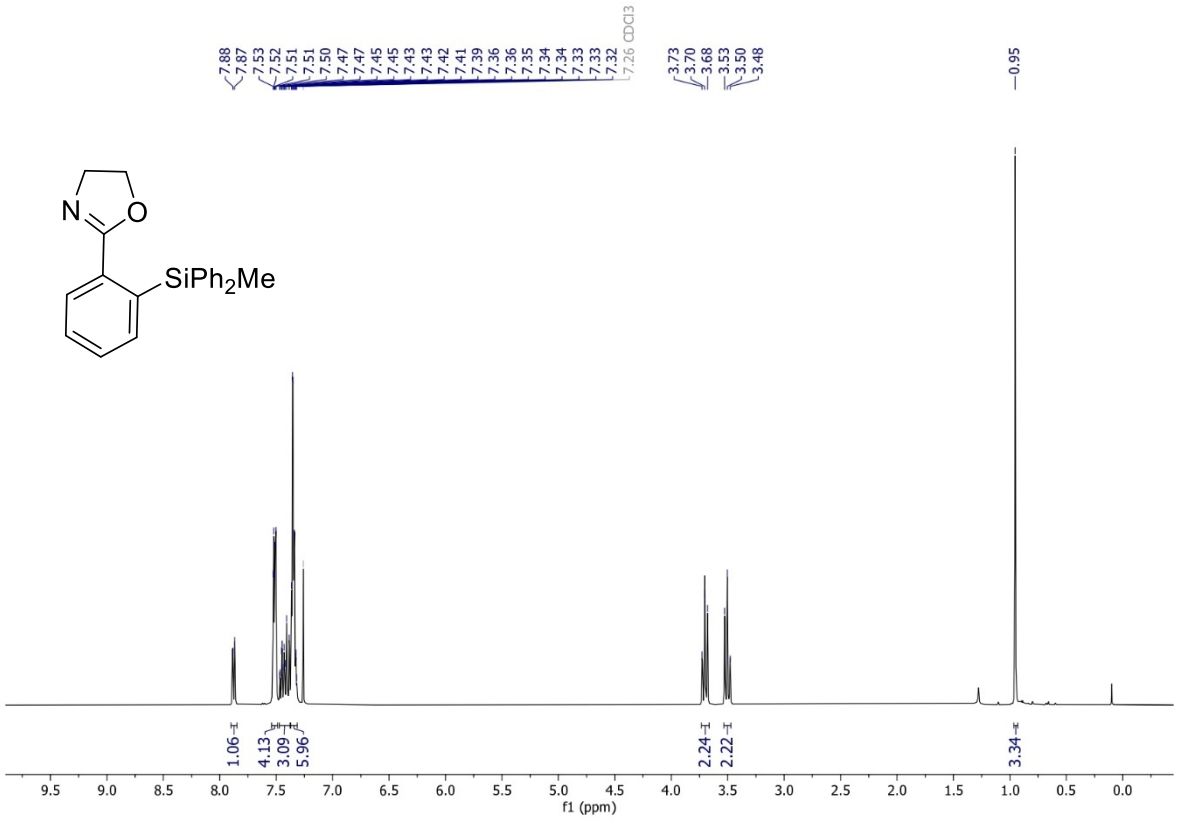
^{13}C NMR spectrum for **4o**



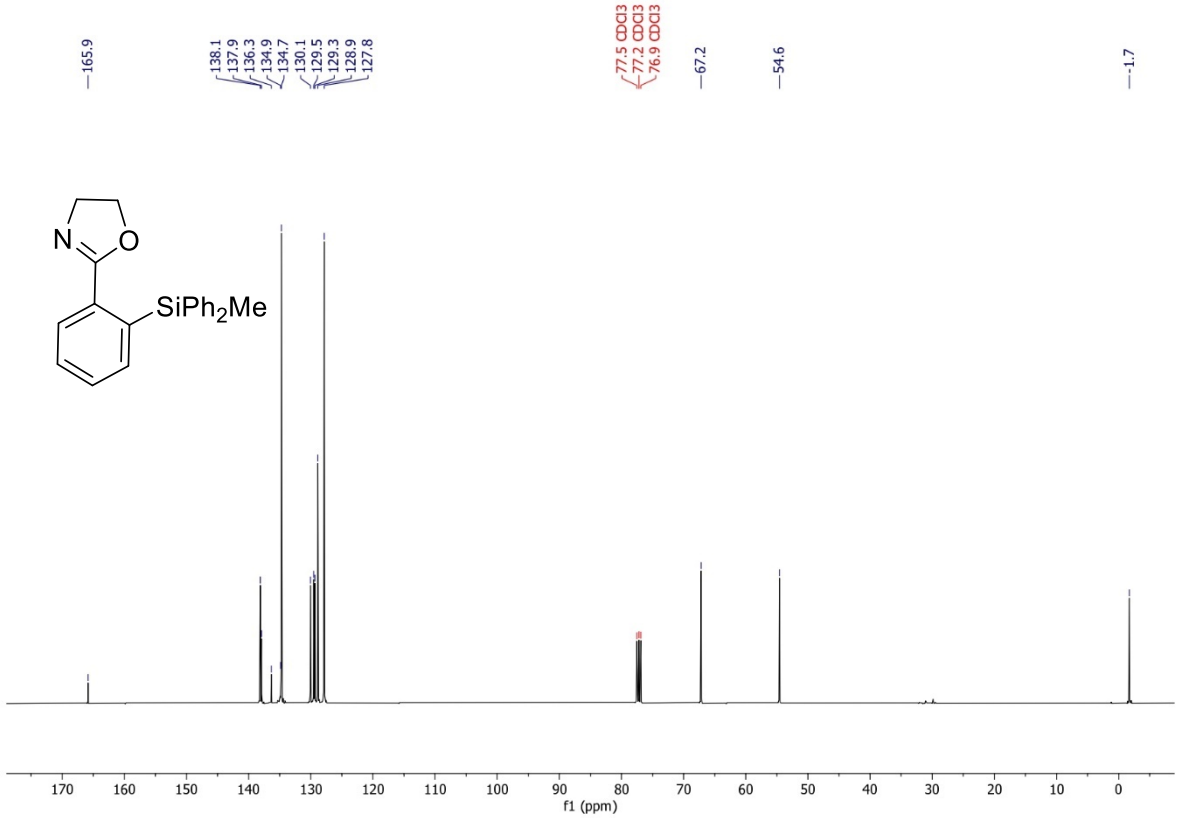
^{29}Si NMR spectrum for **4o**



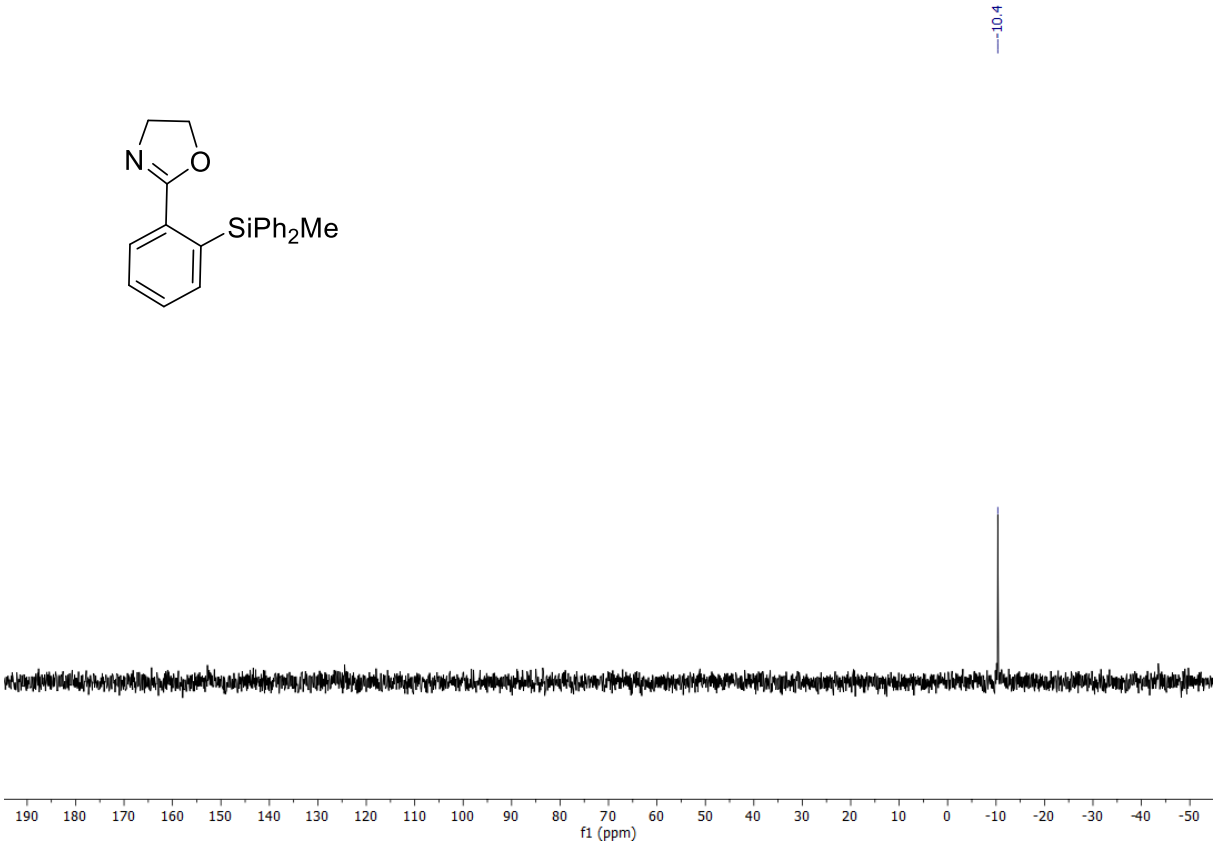
^{1}H NMR spectrum for **4p**



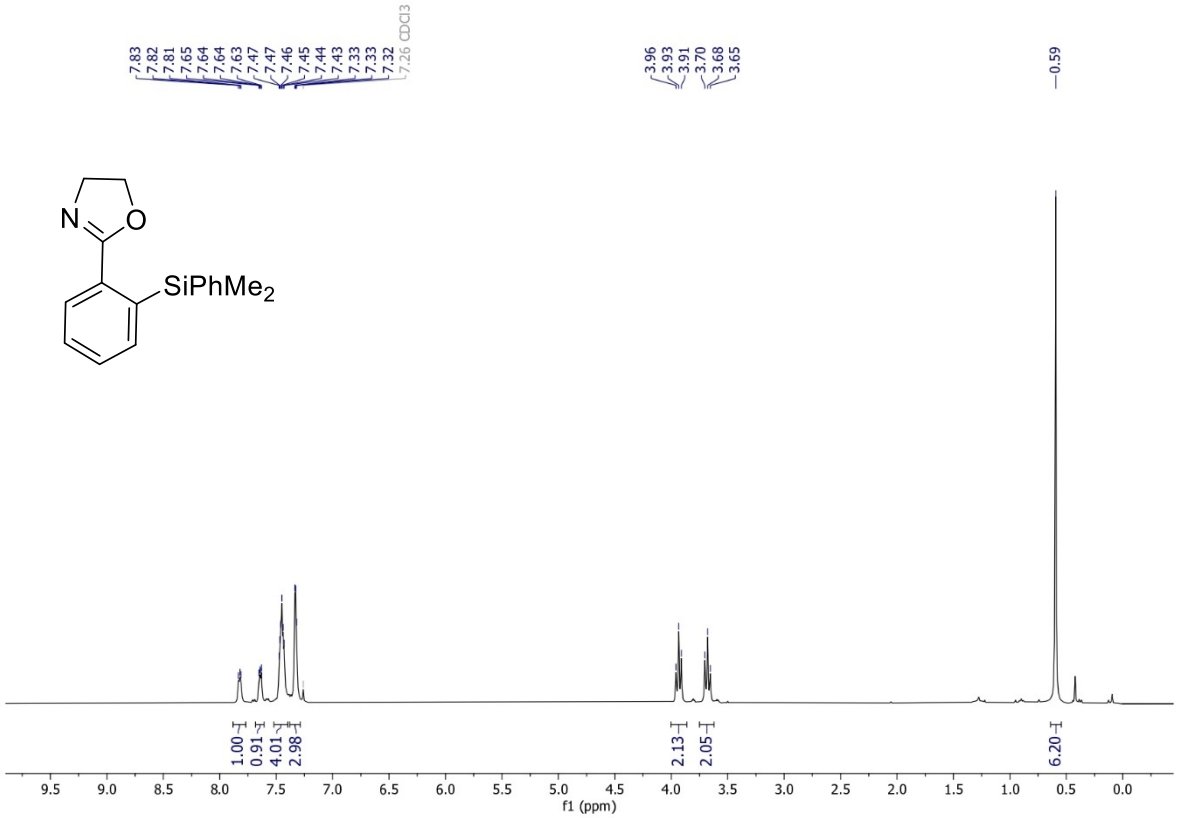
^{13}C NMR spectrum for **4p**



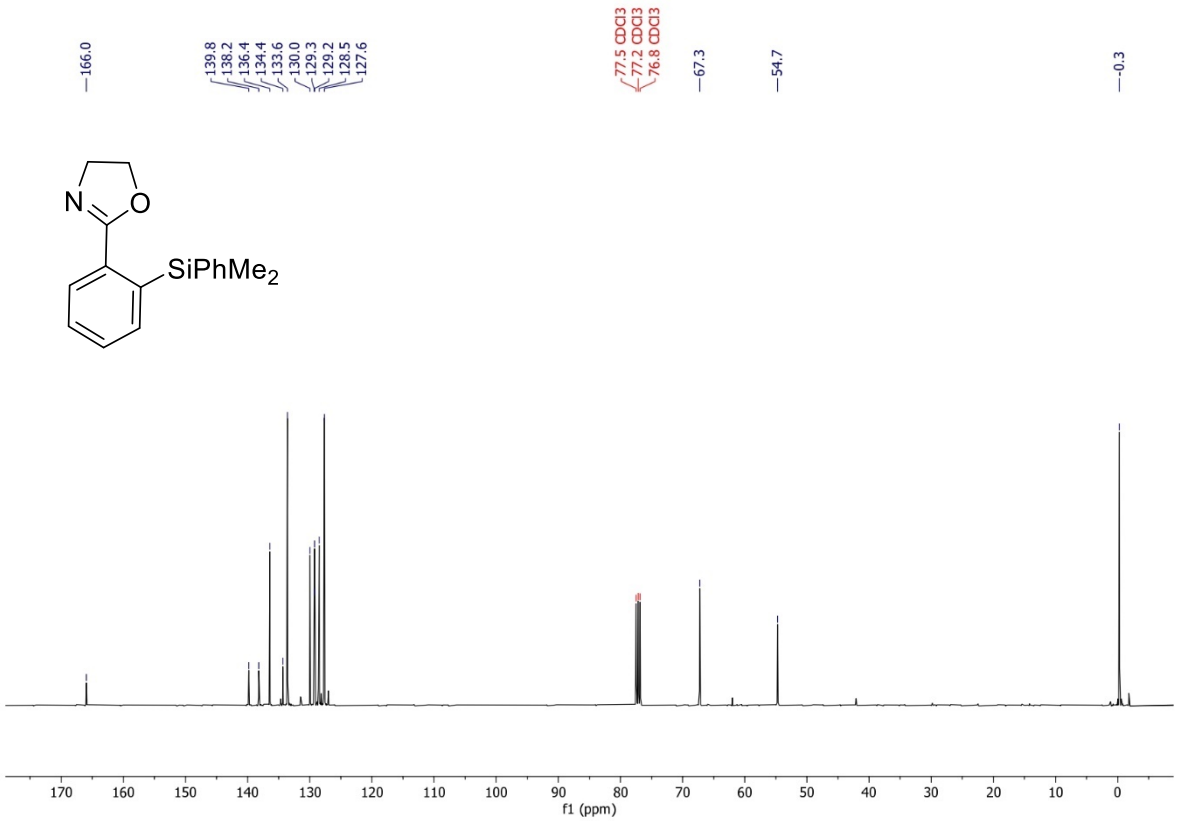
^{29}Si NMR spectrum for **4p**



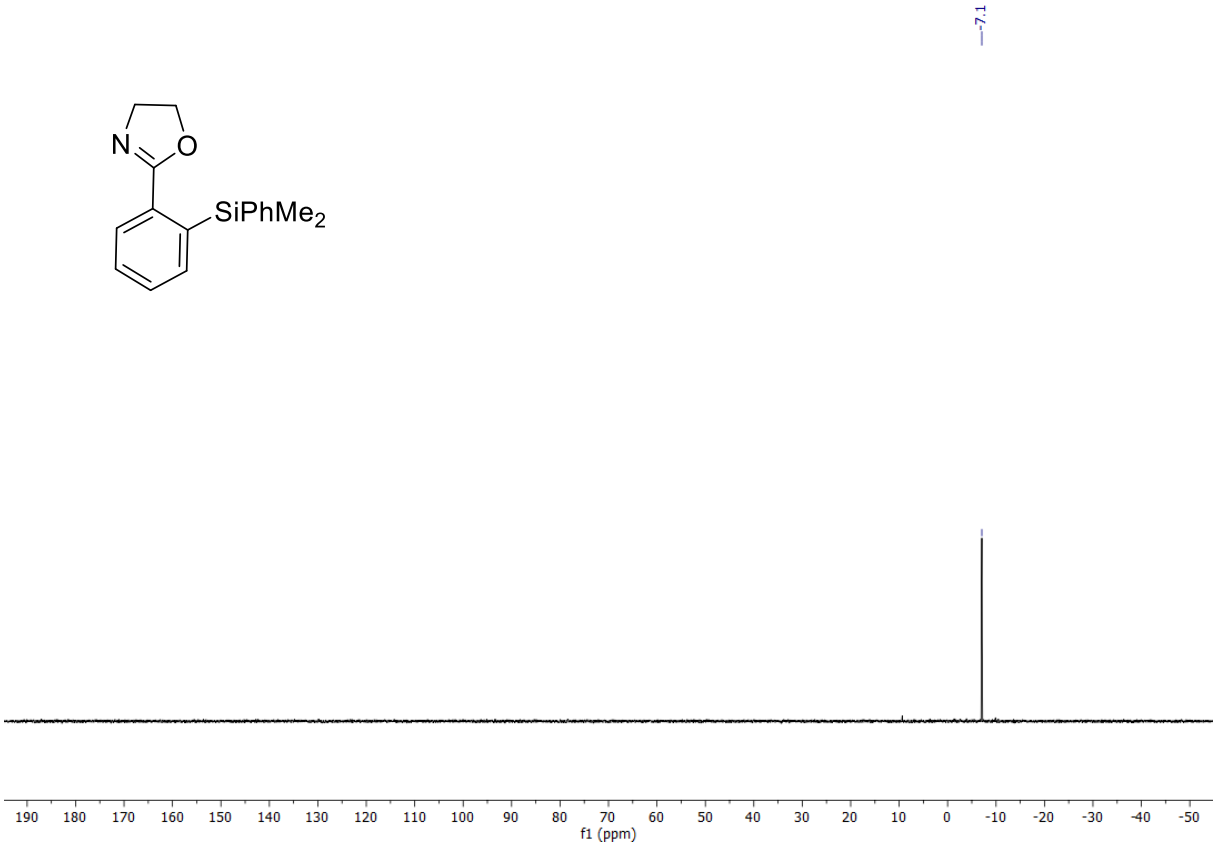
^{1}H NMR spectrum for **4q**



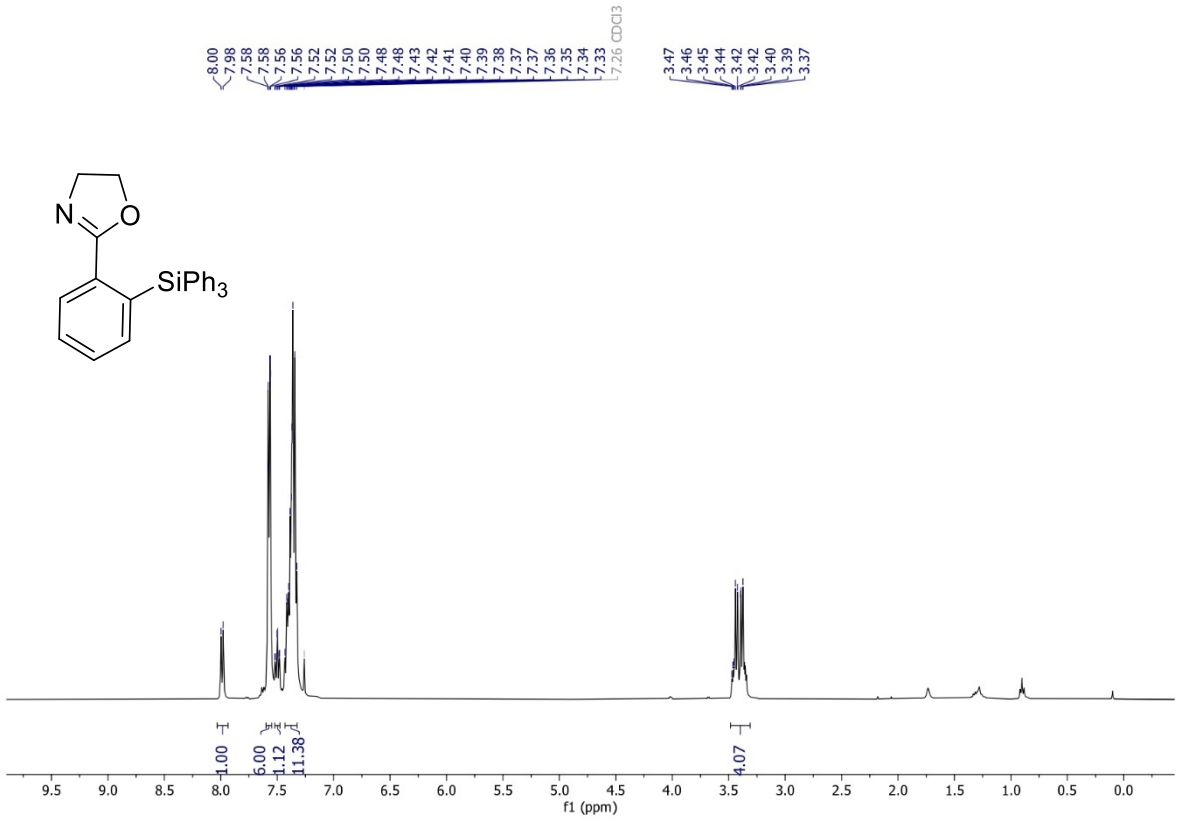
^{13}C NMR spectrum for **4q**



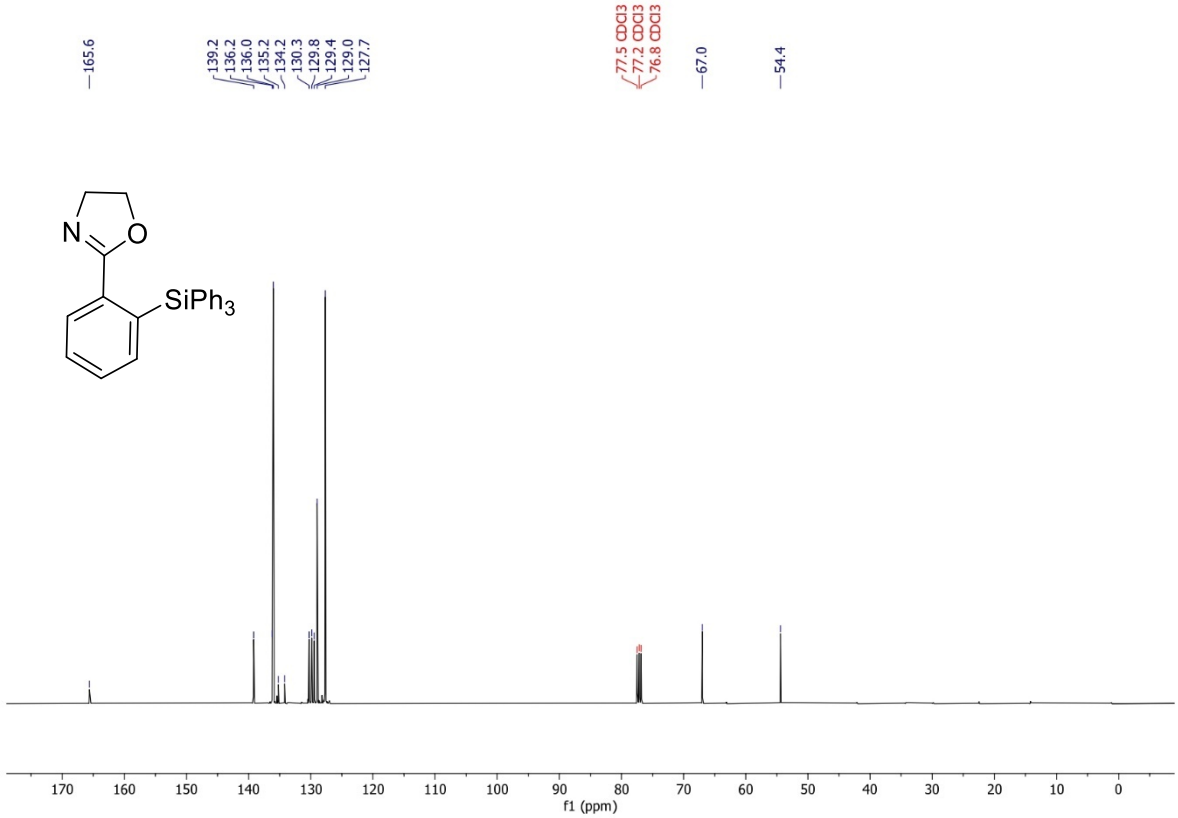
^{29}Si NMR spectrum for **4q**



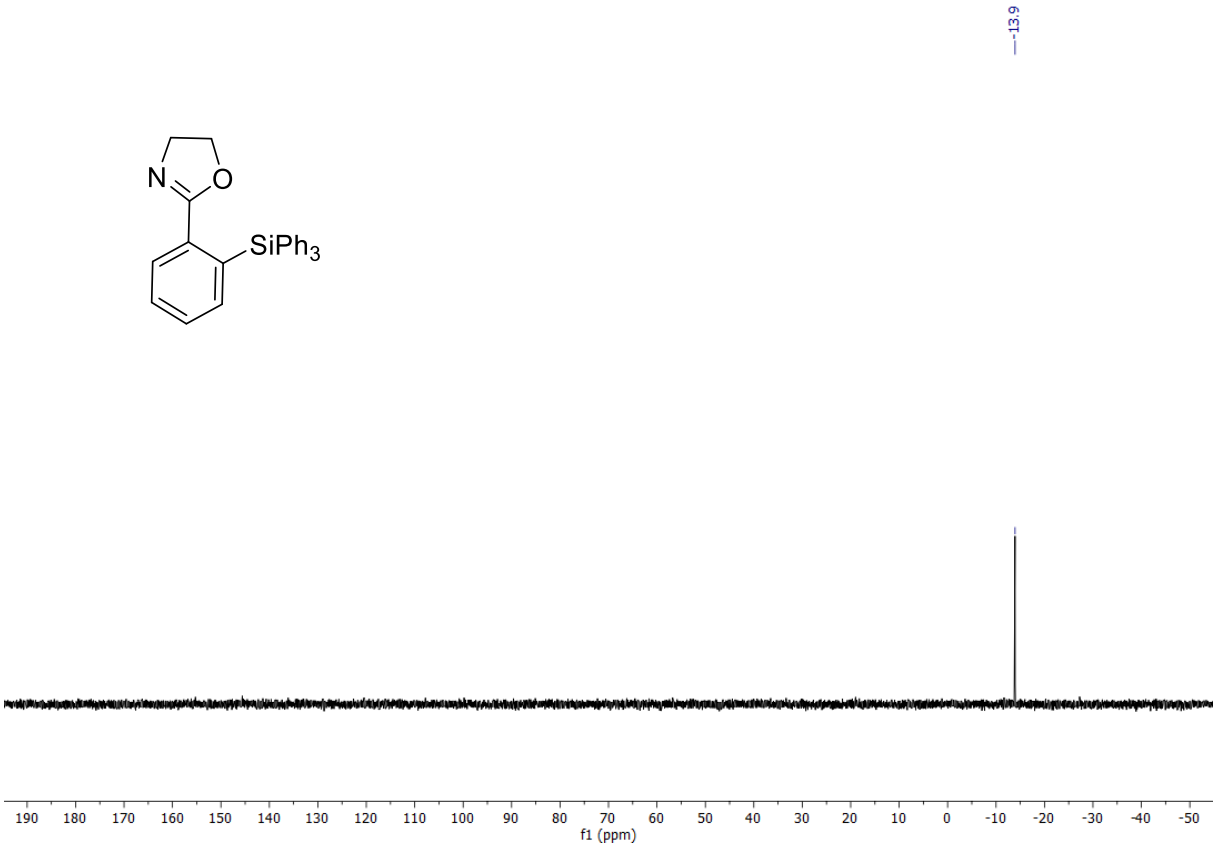
^{1}H NMR spectrum for **4r**



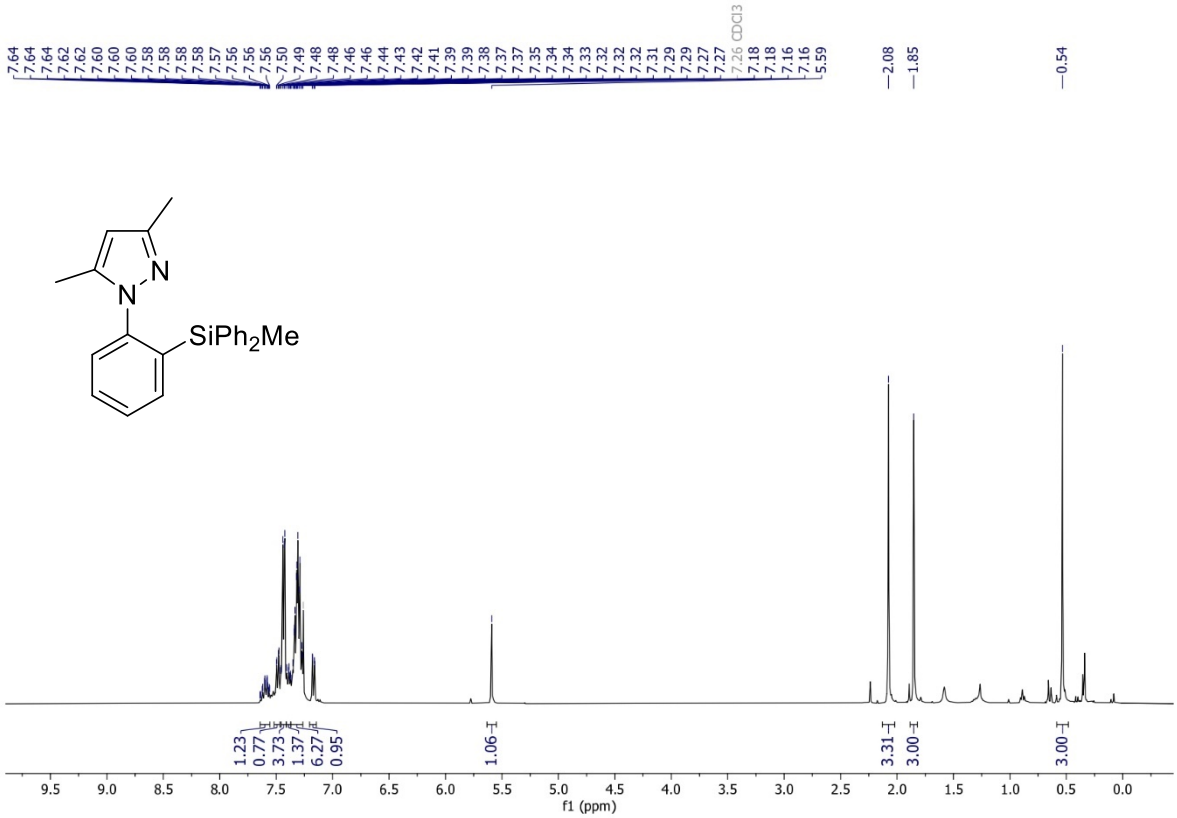
^{13}C NMR spectrum for **4r**



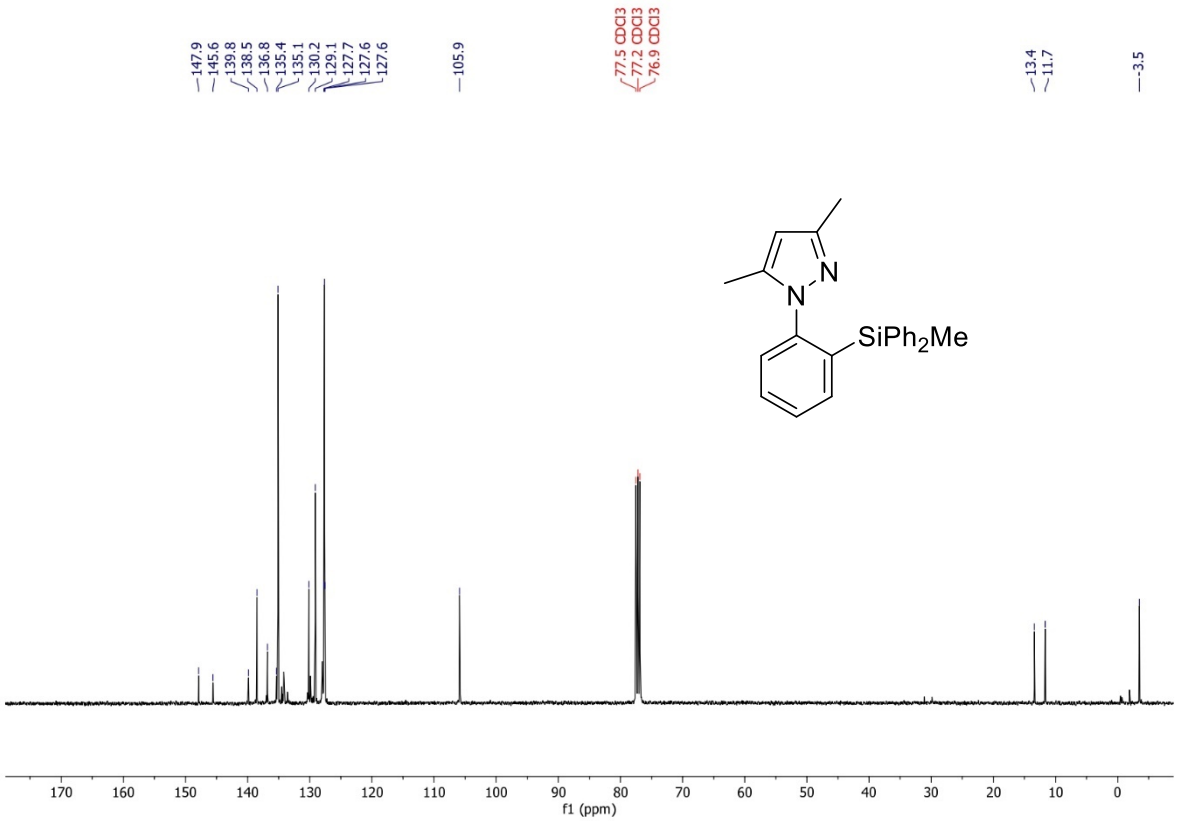
^{29}Si NMR spectrum for **4r**



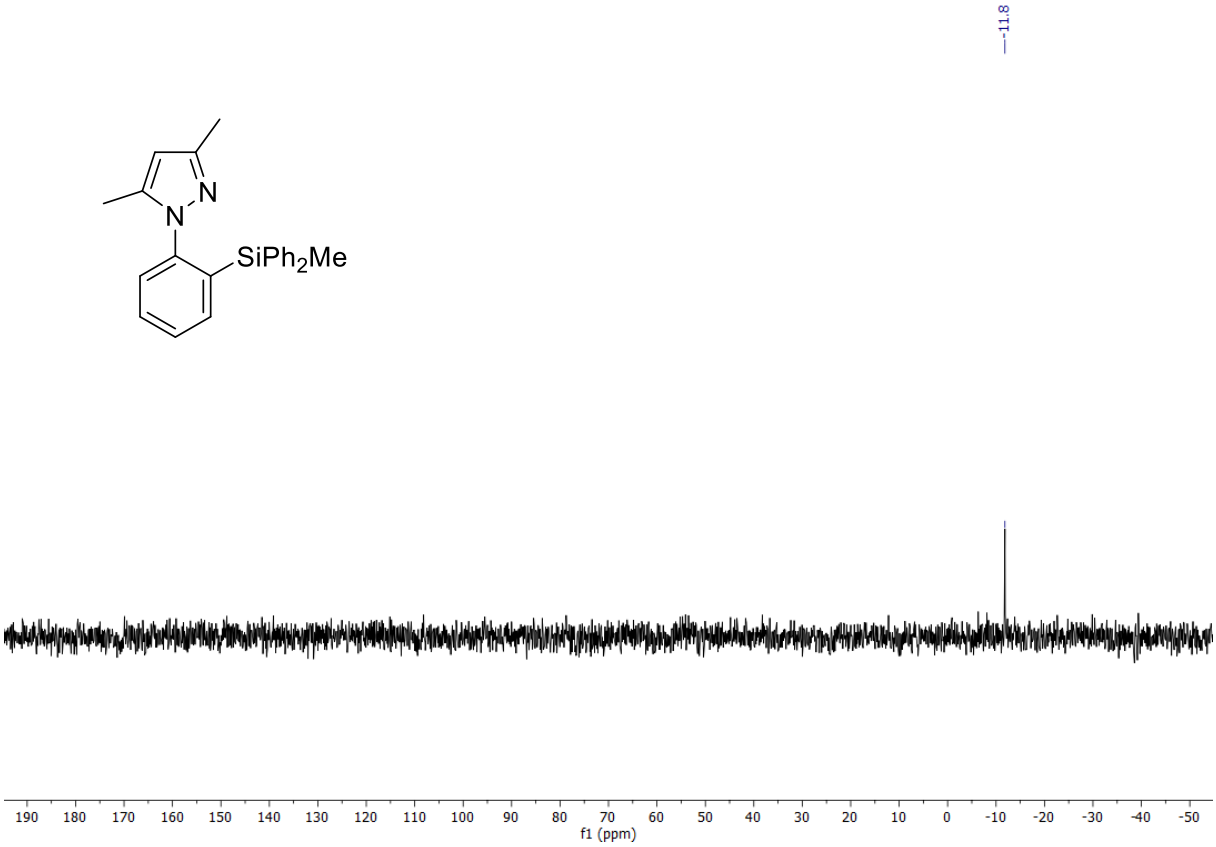
^{1}H NMR spectrum for **4s**



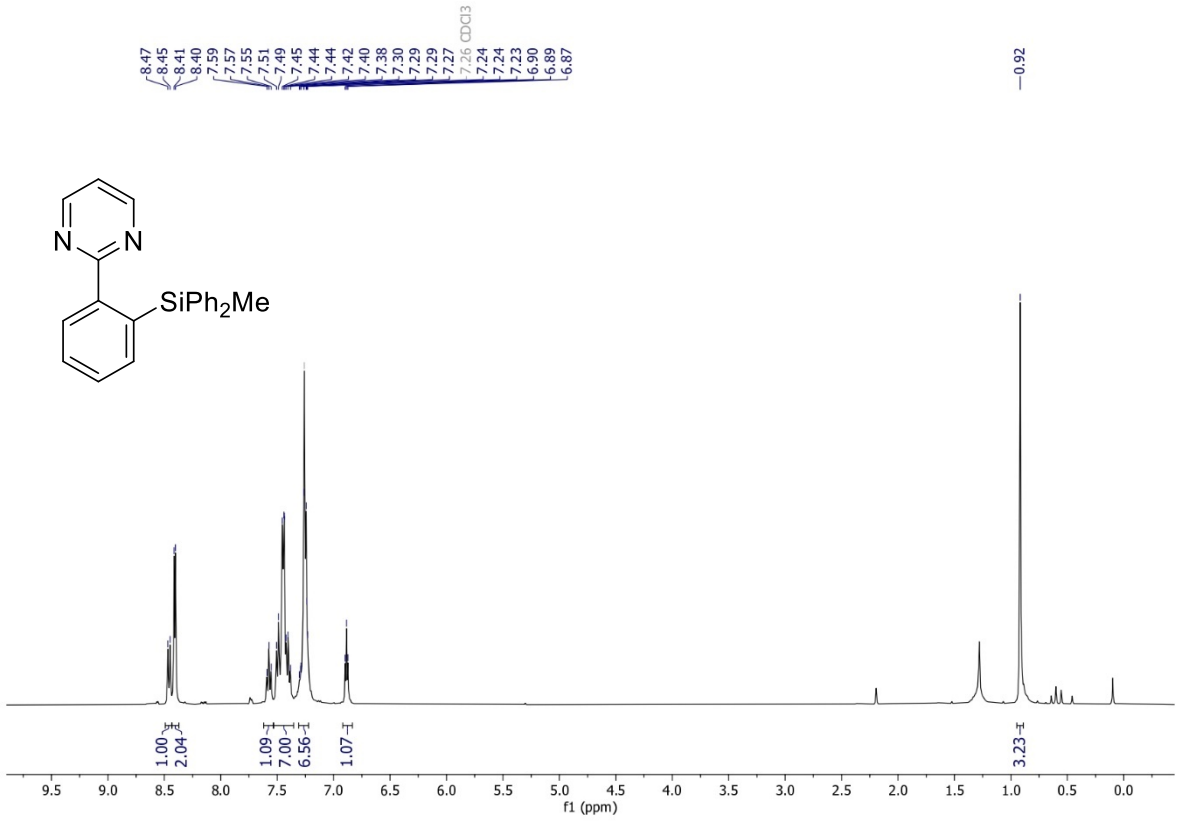
^{13}C NMR spectrum for **4s**



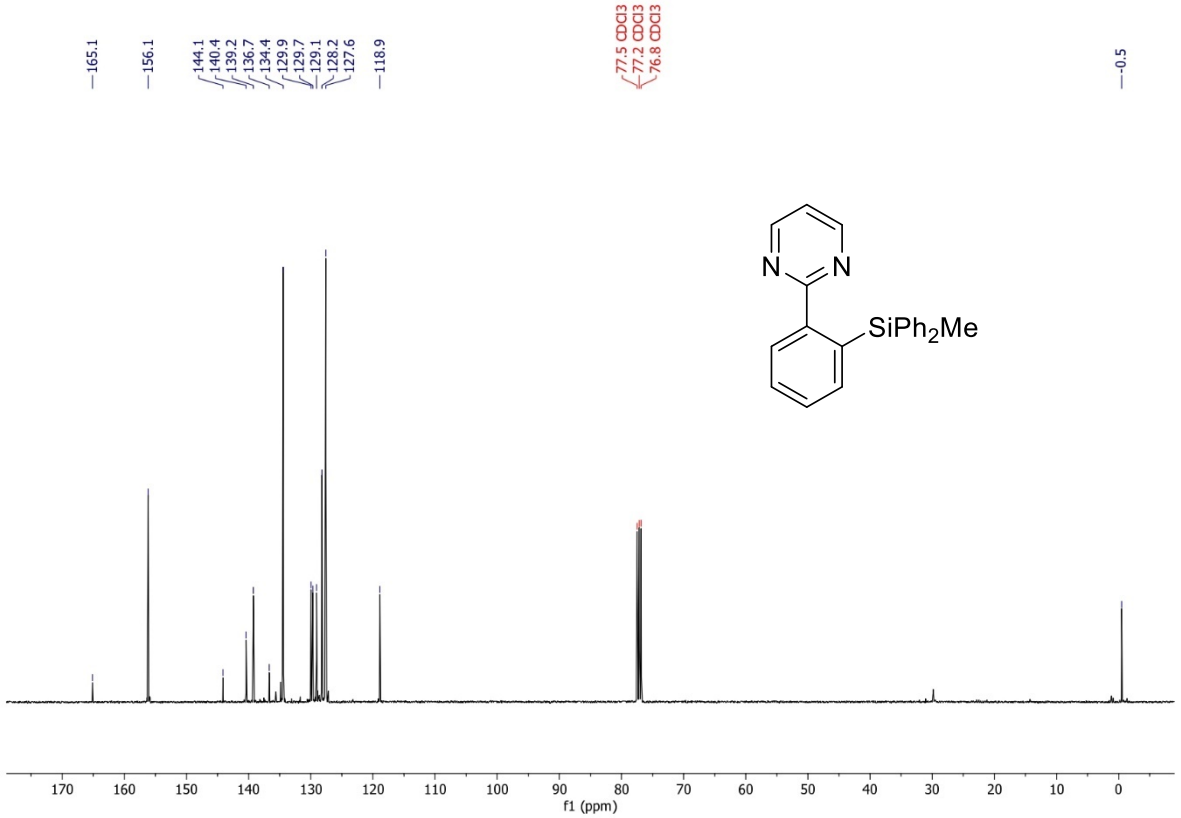
^{29}Si NMR spectrum for **4s**



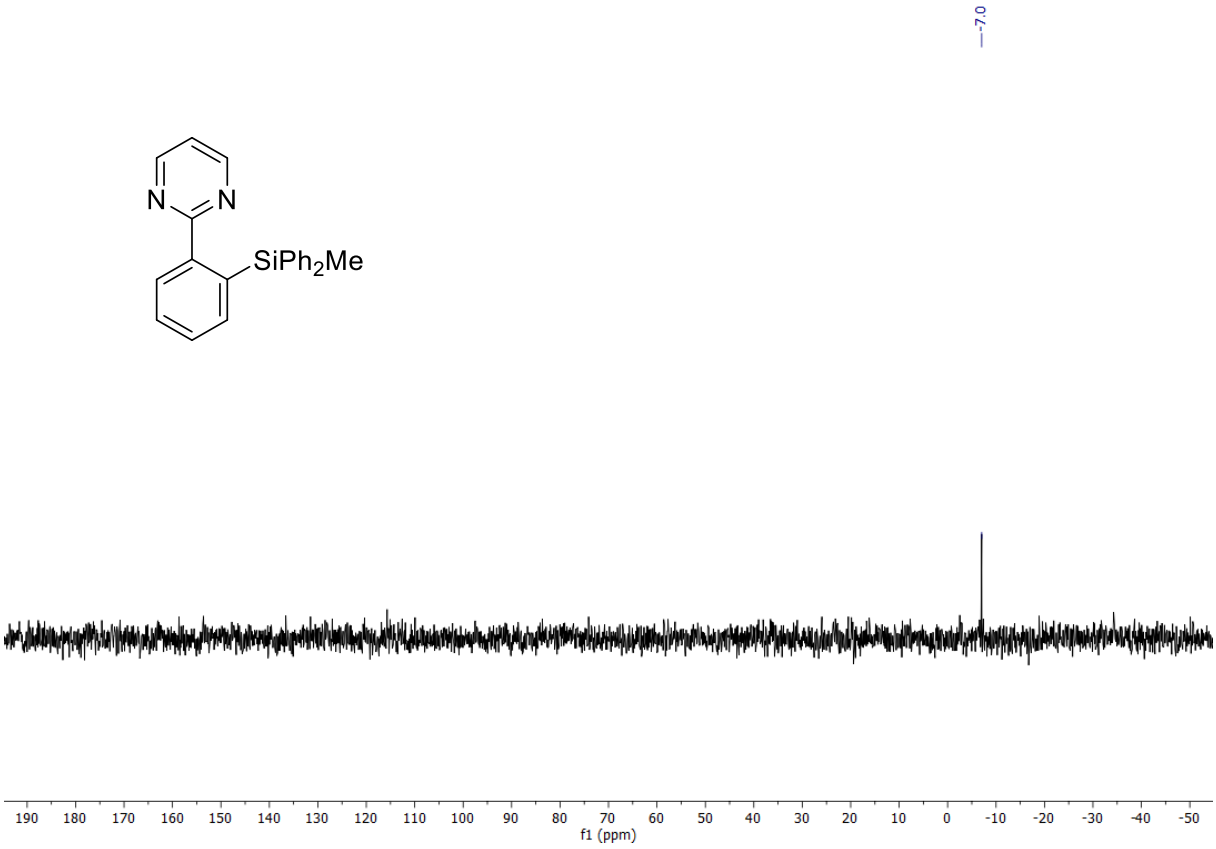
^{1}H NMR spectrum for **4t**



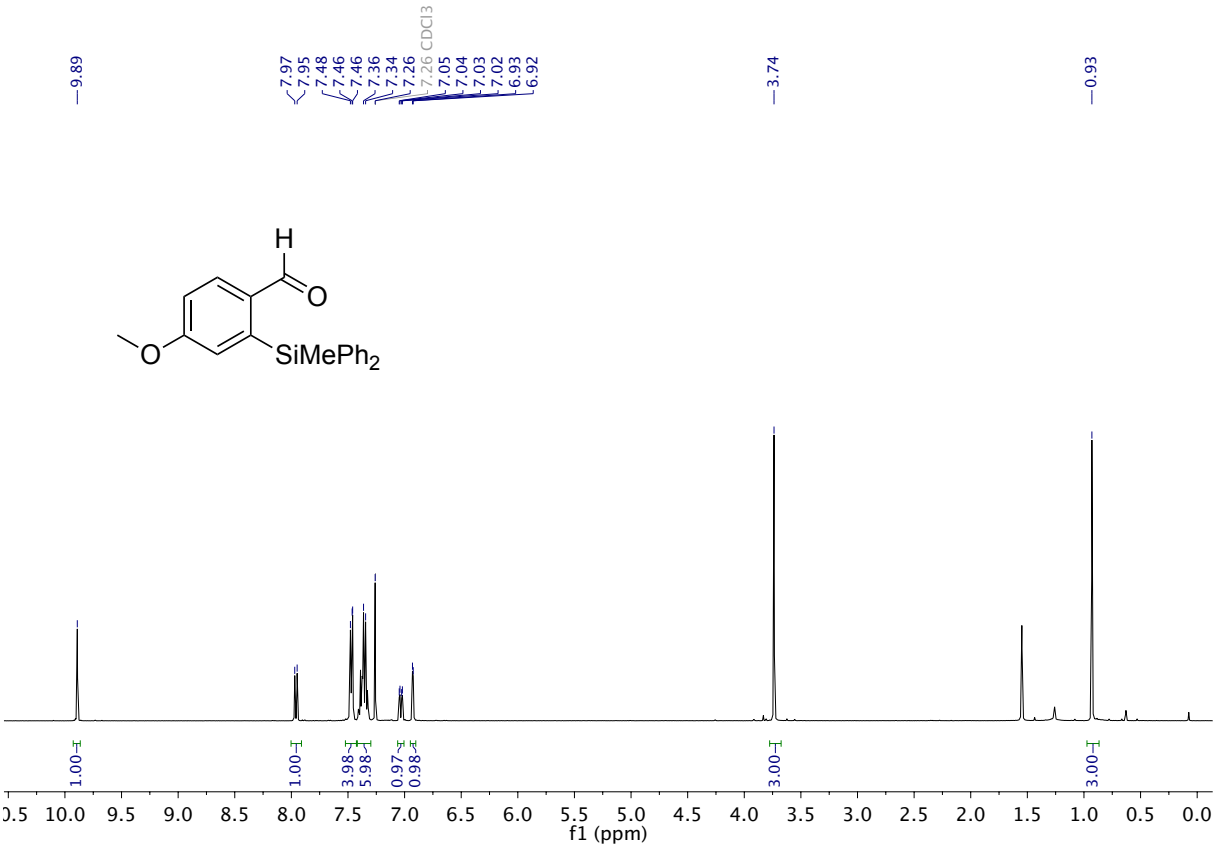
^{13}C NMR spectrum for **4t**



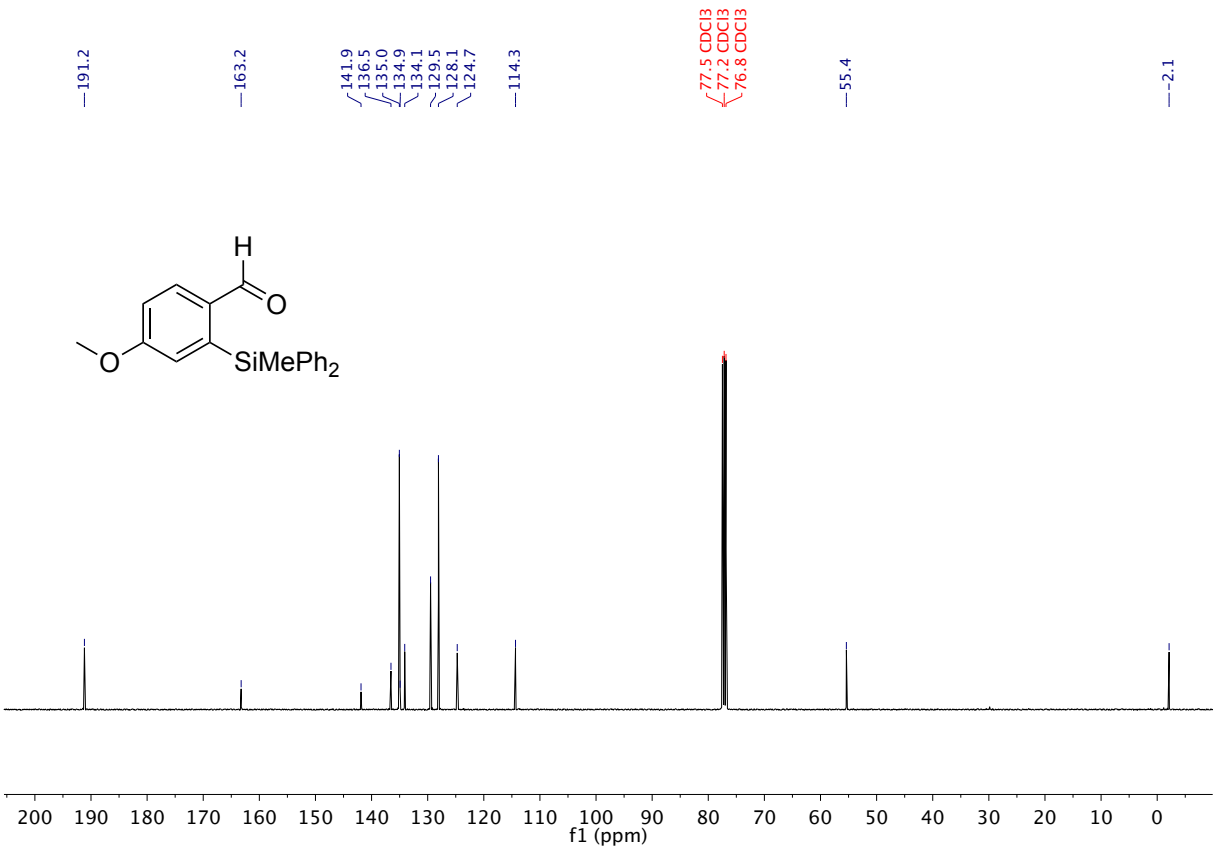
^{29}Si NMR spectrum for **4t**



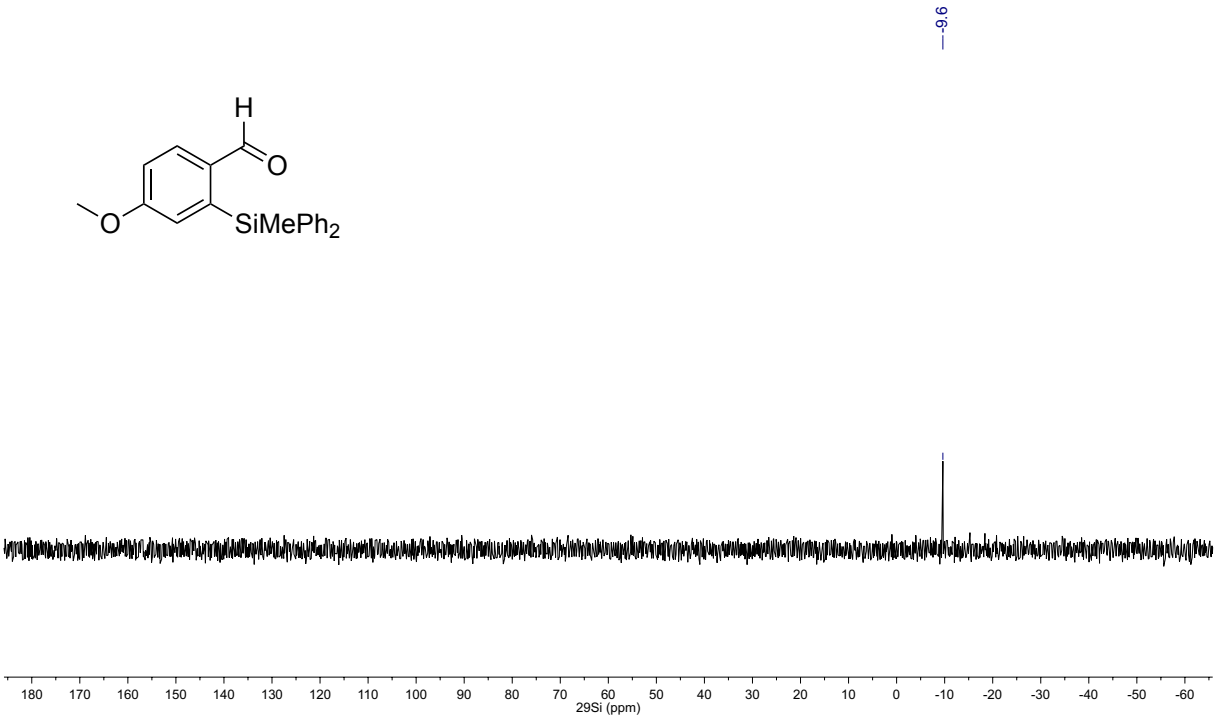
^{1}H NMR spectrum for **4u**



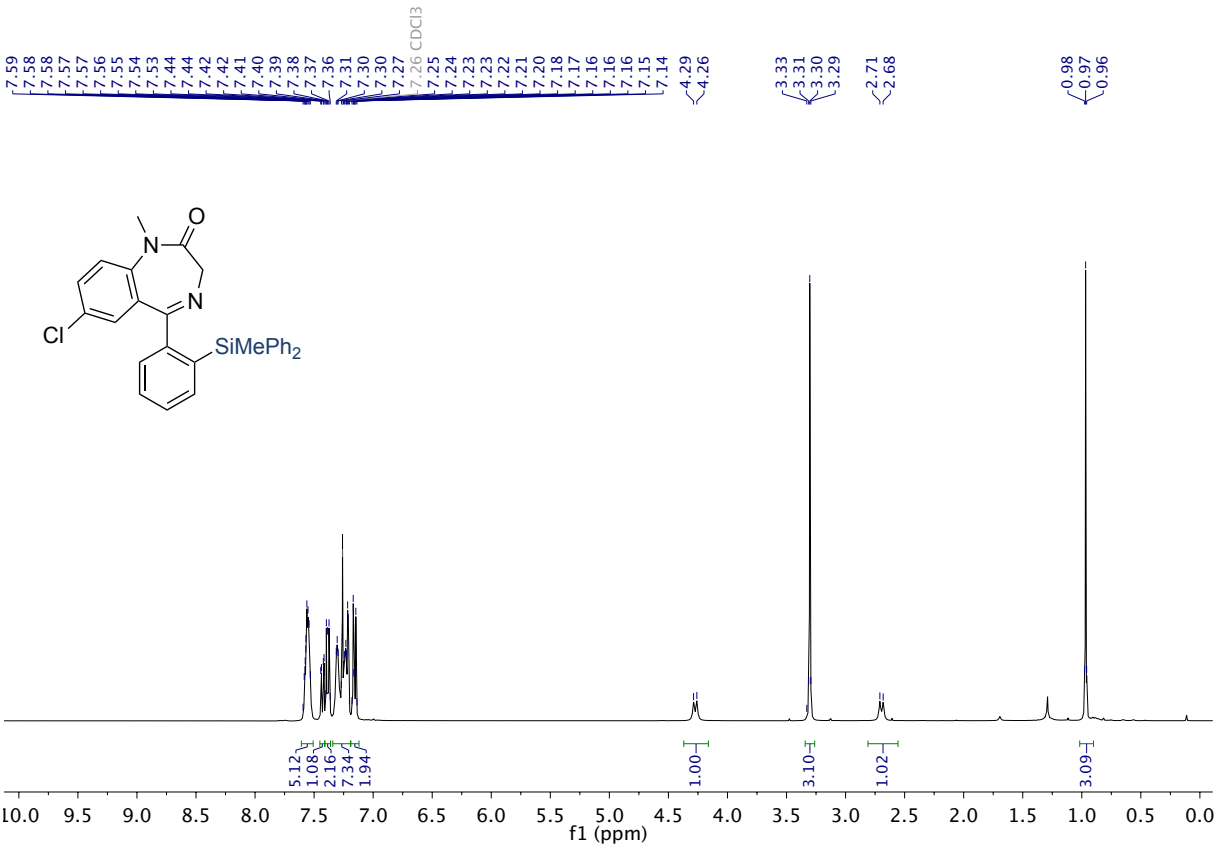
^{13}C NMR spectrum for **4u**



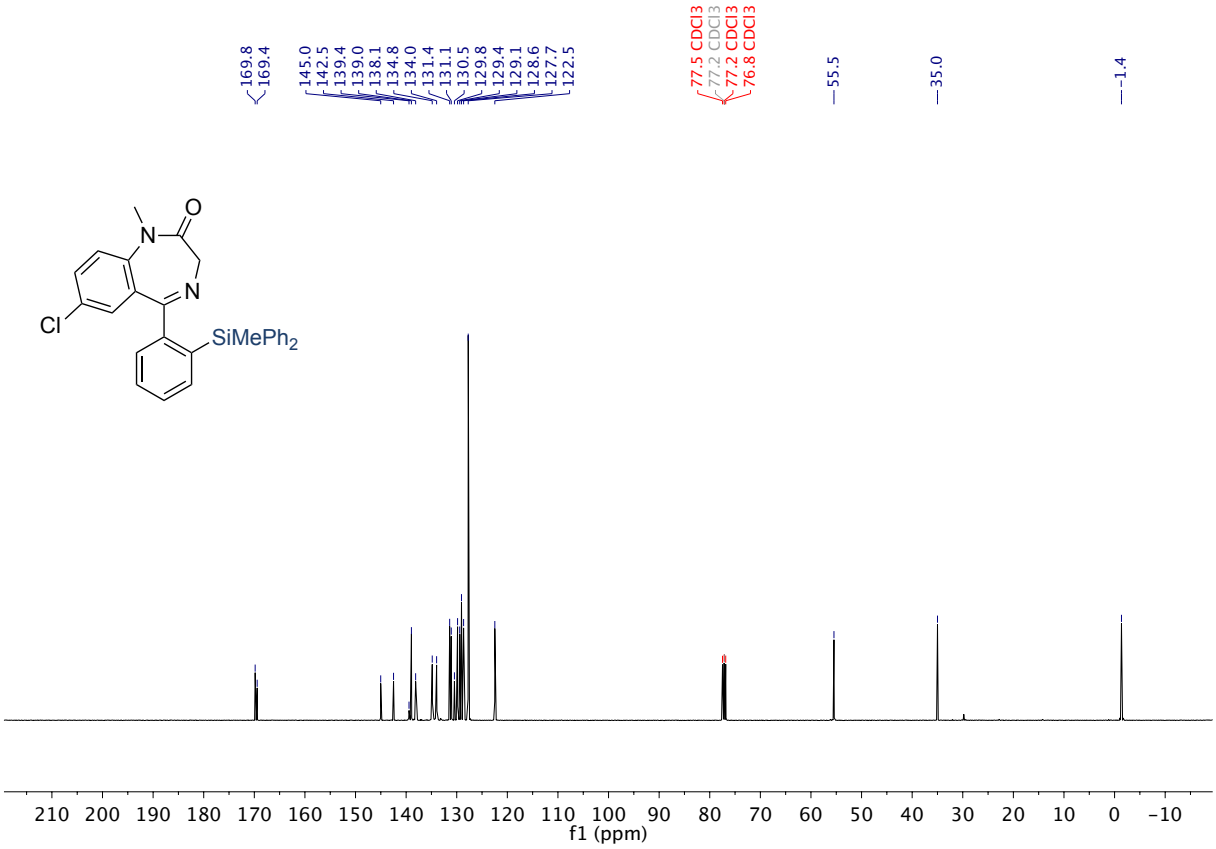
^{29}Si NMR spectrum for **4u**



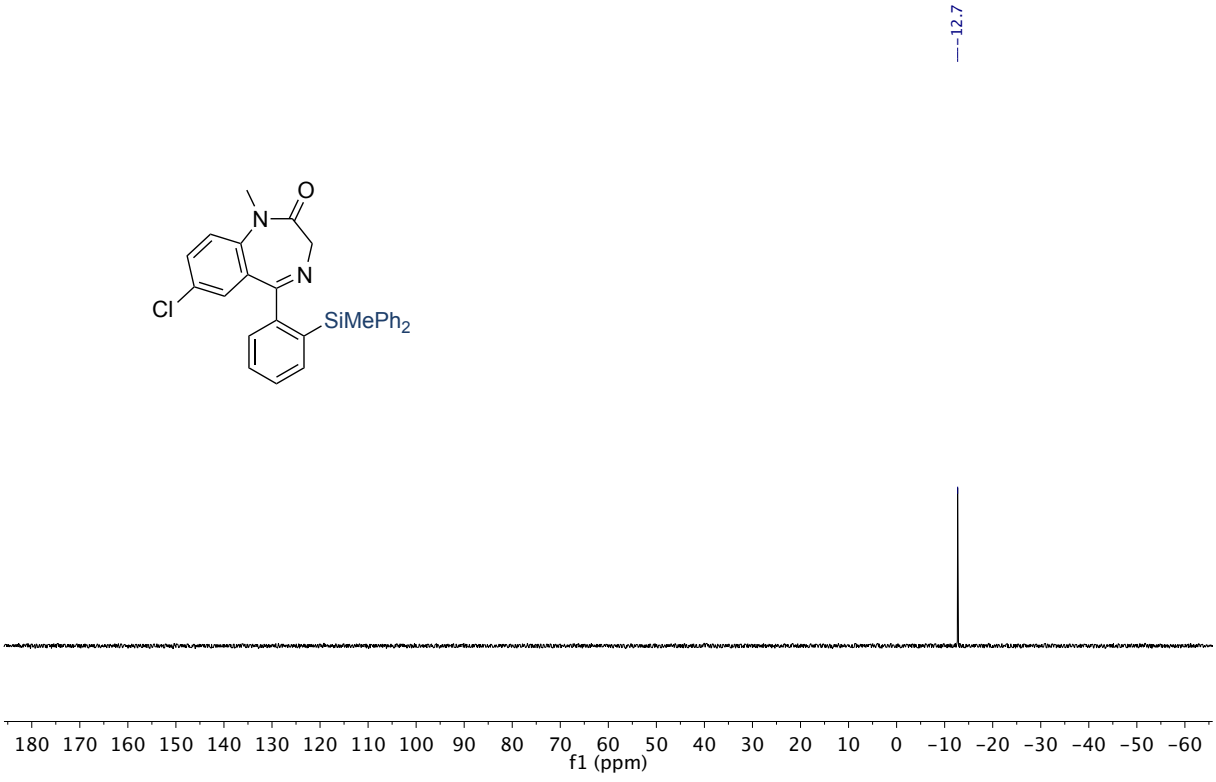
^{1}H NMR spectrum for **4v**



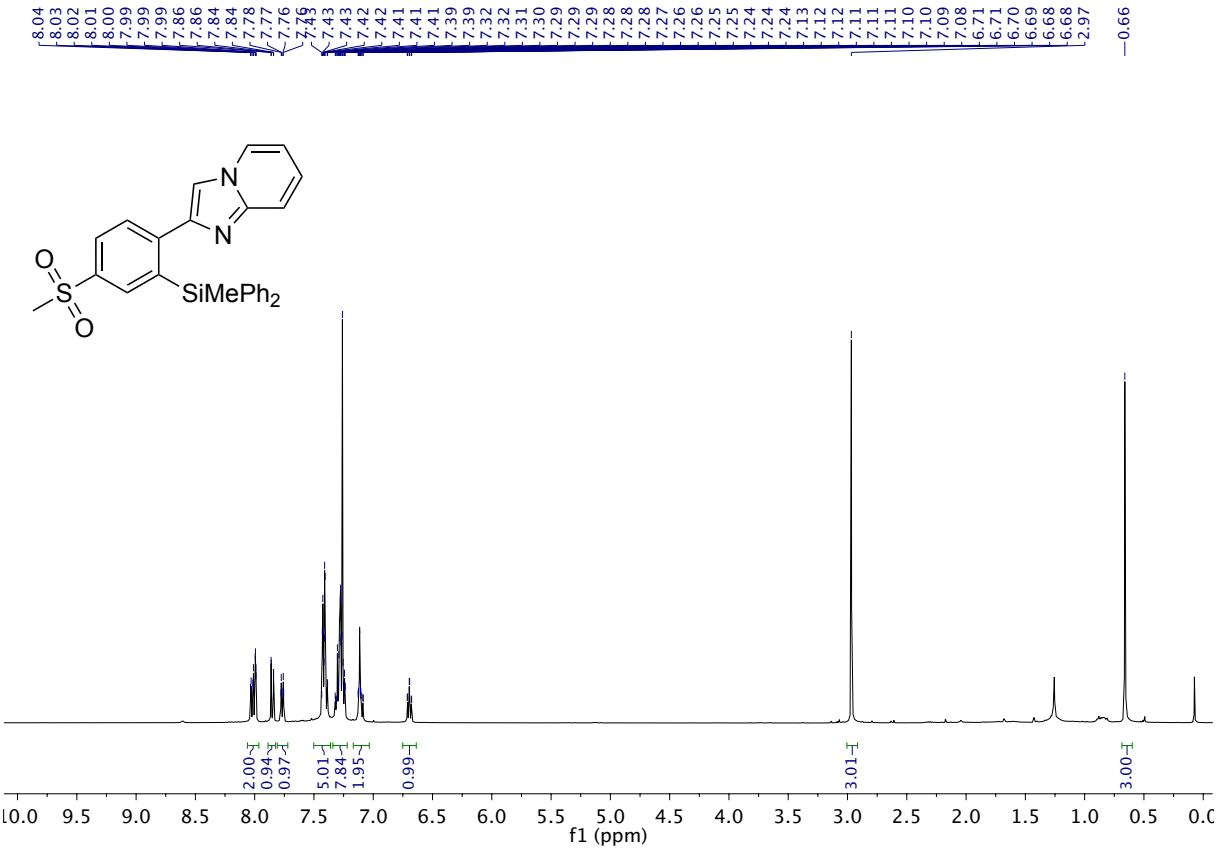
^{13}C NMR spectrum for **4v**



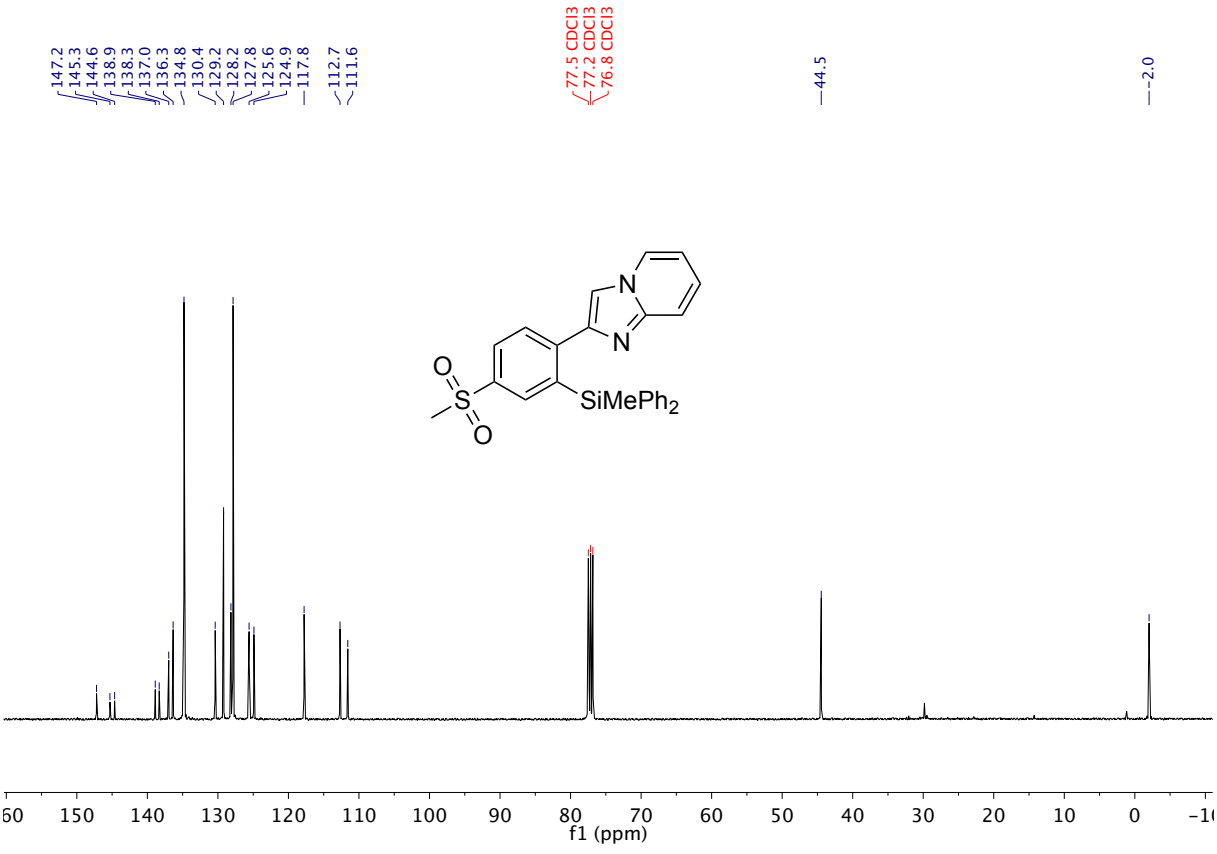
^{29}Si NMR spectrum for **4v**



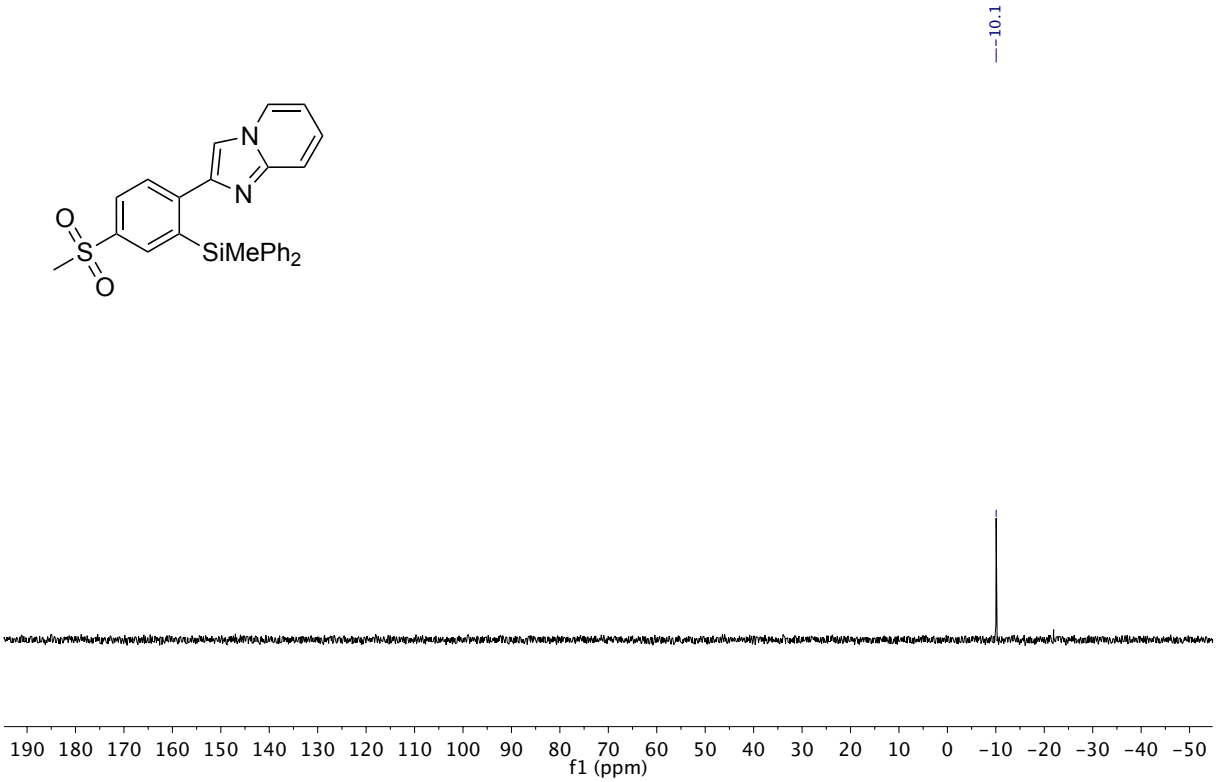
^{1}H NMR spectrum for **4w**



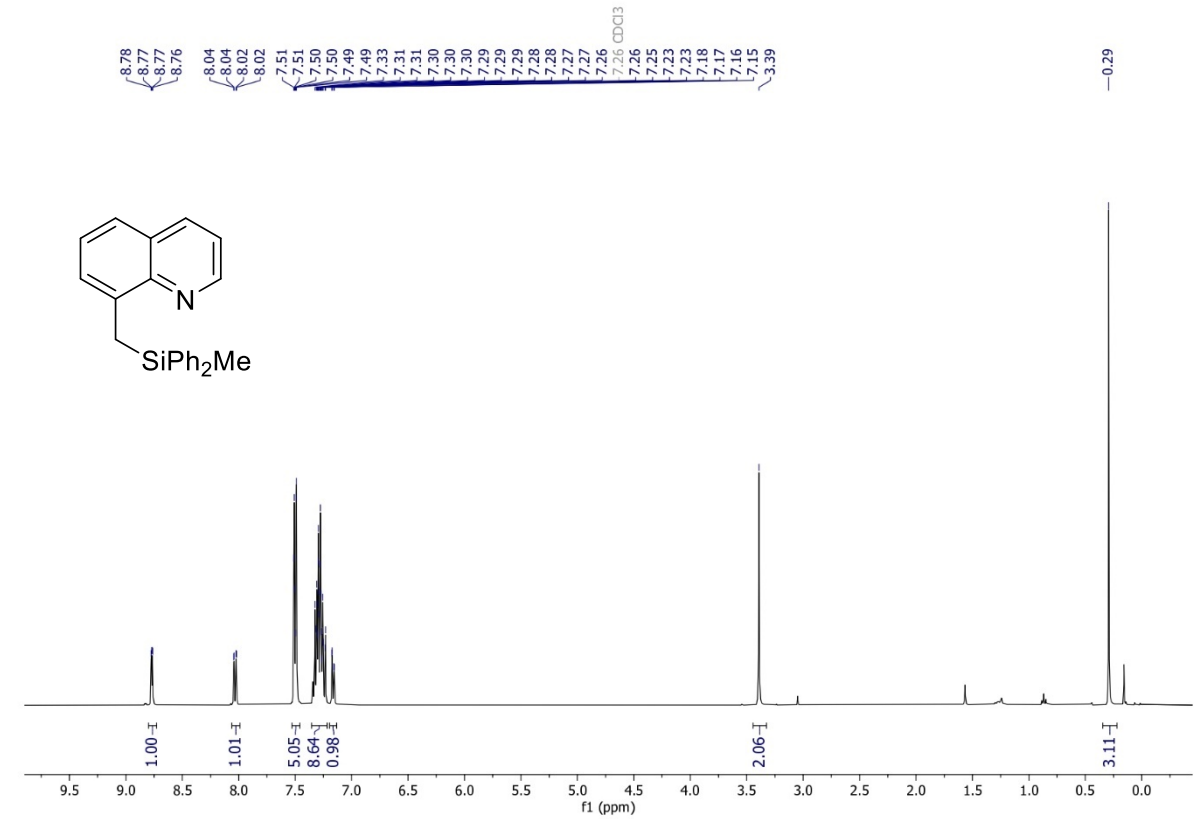
^{13}C NMR spectrum for **4w**



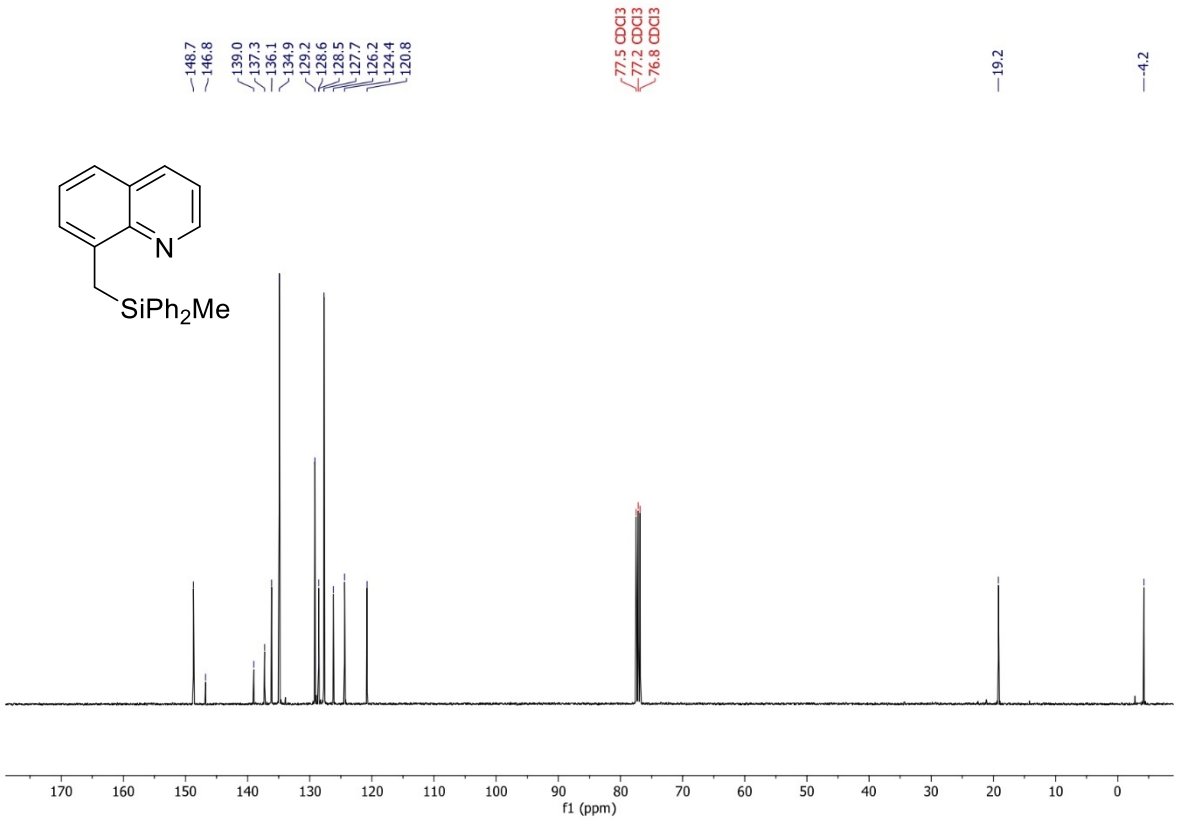
^{29}Si NMR spectrum for **4w**



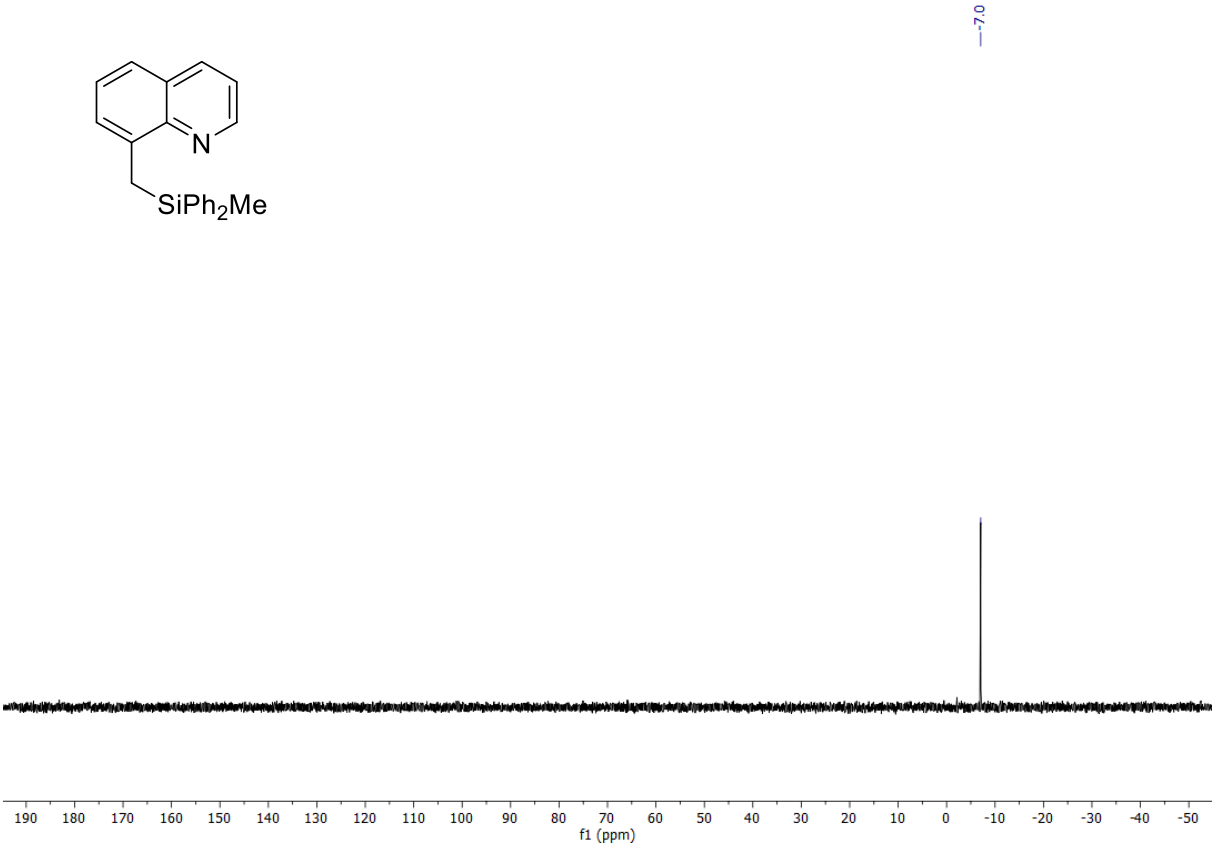
^{1}H NMR spectrum for **4x**



^{13}C NMR spectrum for **4x**



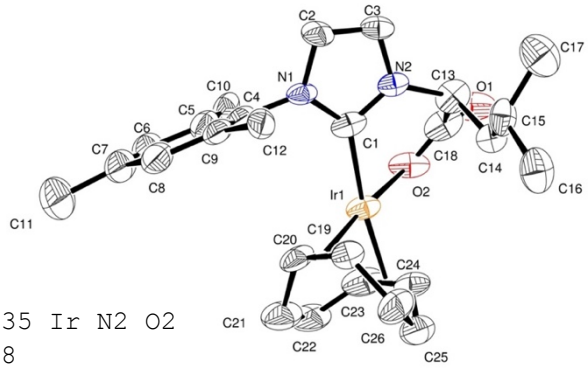
^{29}Si NMR spectrum for **4x**



10. Crystallographic Data

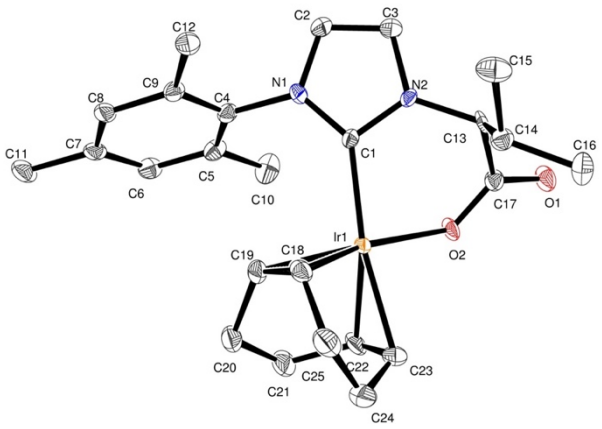
Data were collected on a Bruker Kappa Apex II diffractometer equipped with a 30 W air-cooled microfocus source using MoKα radiation (λ = 0.71073 Å) for **2a**, **2b** and **2c**, and on a Rigaku Oxford Diffraction Gemini diffractometer using CuK_α radiation (λ = 1.54184 Å) for **4o**. Cooling devices were used to collect the data at low temperature (101(2) – 187(2) K). Phi and Omega scans were performed for data collection, an empirical absorption correction was applied and the structures were solved by intrinsic phasing method (ShelXT).[7] All non-hydrogen atoms were refined anisotropically by means of least-squares procedures on F^2 with ShelXL.[8] All the hydrogen atoms were refined isotropically at calculated positions using a riding model. For **2a** and **2c,** the SQUEEZE[9] function of PLATON was used to remove the electron density contribution of the highly disordered solvent molecules from the models.

10.1. Crystal structure of 2a (CCDC No. 2223880)



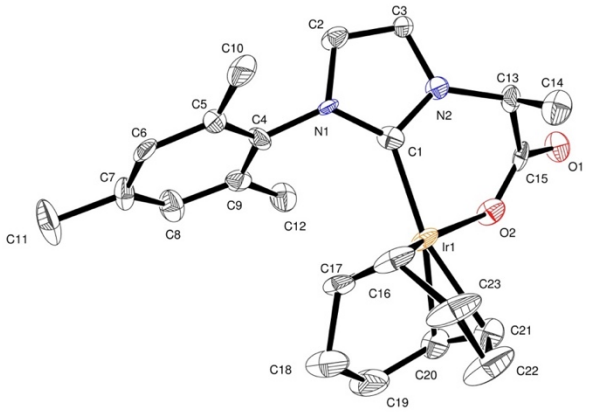
Empirical formula	C26 H35 Ir N2 O2
Formula weight	599.78
Temperature	110(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, C 2 2 21
Unit cell dimensions	a = 14.3819(10) A alpha = 90 deg. b = 27.2526(18) A beta = 90 deg. c = 26.1453(17) A gamma = 90 deg.
Volume	10247.5(12) A^3
Z, Calculated density	16, 1.555 Mg/m^3
Absorption coefficient	5.234 mm^-1
F(000)	4768
Crystal size	0.200 x 0.120 x 0.080 mm
Theta range for data collection	1.494 to 25.101 deg.
Limiting indices	-17<=h<=16, -32<=k<=32, -31<=l<=31
Reflections collected / unique	101612 / 9138 [R(int) = 0.0668]
Completeness to theta = 25.242	99.9 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9138 / 666 / 729
Goodness-of-fit on F^2	1.110
Final R indices [I>2sigma(I)]	R1 = 0.0434, wR2 = 0.1014
R indices (all data)	R1 = 0.0479, wR2 = 0.1144
Absolute structure parameter	0.006(4)
Largest diff. peak and hole	3.402 and -1.466 e.A^-3

10.2. Crystal structure of 2b (CCDC No. 2223881)



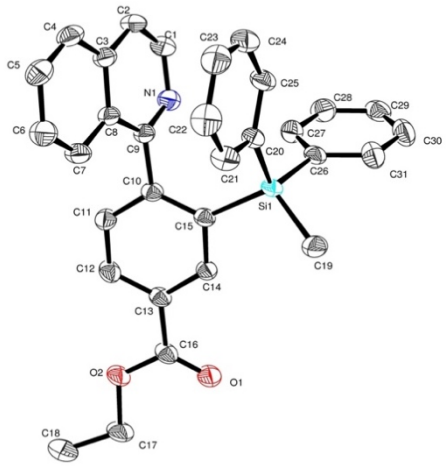
Empirical formula	C25 H33 Ir N2 O2
Formula weight	585.75
Temperature	101(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21
Unit cell dimensions	a = 8.9043(5) A alpha = 90 deg. b = 14.2370(8)A beta = 105.794(3)deg. c = 9.2991(5) A gamma = 90 deg.
Volume	1134.35(11) A^3
Z, Calculated density	2, 1.715 Mg/m^3
Absorption coefficient	5.909 mm^-1
F(000)	580
Crystal size	0.080 x 0.040 x 0.040 mm
Theta range for data collection	2.276 to 32.577 deg.
Limiting indices	-13<=h<=13, -21<=k<=21, -14<=l<=14
Reflections collected / unique	57318 / 8278 [R(int) = 0.0762]
Completeness to theta = 25.242	100.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8278 / 7 / 276
Goodness-of-fit on F^2	1.072
Final R indices [I>2sigma(I)]	R1 = 0.0298, wR2 = 0.0545
R indices (all data)	R1 = 0.0379, wR2 = 0.0571
Absolute structure parameter	-0.019(5)
Largest diff. peak and hole	1.277 and -1.723 e.A^-3

10.3. Crystal structure of 2c (CCDC No. 2223879)



Empirical formula	C23 H29 Ir N2 O2
Formula weight	557.70
Temperature	110(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21
Unit cell dimensions	a = 15.482(3) A alpha = 90 deg. b = 10.1564(17)A beta = 105.727(6)deg. c = 17.192(3) A gamma = 90 deg.
Volume	2602.1(8) A^3
Z, Calculated density	4, 1.424 Mg/m^3
Absorption coefficient	5.148 mm^-1
F(000)	1096
Crystal size	0.080 x 0.060 x 0.040 mm
Theta range for data collection	2.072 to 25.681 deg.
Limiting indices	-18<=h<=18, -11<=k<=12, -20<=l<=20
Reflections collected / unique	47529 / 9712 [R(int) = 0.0887]
Completeness to theta = 25.242	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9712 / 1 / 491
Goodness-of-fit on F^2	0.996
Final R indices [I>2sigma(I)]	R1 = 0.0356, wR2 = 0.0633
R indices (all data)	R1 = 0.0465, wR2 = 0.0670
Absolute structure parameter	-0.022(7)
Largest diff. peak and hole	1.149 and -0.885 e.A^-3

10.4. Crystal structure of 4o (CCDC No. 2226158)



Empirical formula	C31 H27 N O2 Si
Formula weight	473.63
Temperature	187(2) K
Wavelength	1.54184 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 8.3354(2)A alpha = 94.463(2) deg. b = 12.1900(2)A beta = 108.394(2) deg. c = 13.0443(3)A gamma = 96.839(2) deg.
Volume	1239.35(5) A^3
Z, Calculated density	2, 1.269 Mg/m^3
Absorption coefficient	1.058 mm^-1
F(000)	500
Crystal size	0.4 x 0.36 x 0.2 mm
Theta range for data collection	3.598 to 71.376 deg.
Limiting indices	-8<=h<=10, -14<=k<=14, -15<=l<=15
Reflections collected / unique	32341 / 4750 [R(int) = 0.0384]
Completeness to theta = 67.684	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4750 / 0 / 318
Goodness-of-fit on F^2	1.032
Final R indices [I>2sigma(I)]	R1 = 0.0414, wR2 = 0.1083
R indices (all data)	R1 = 0.0432, wR2 = 0.1102
Largest diff. peak and hole	0.442 and -0.348 e.A^-3

11. References

[1] J. Thongpaen, T. E. Schmid, L. Toupet, V. Dorcet, M. Mauduit, O. Baslé, *Chem. Commun.,* 2018, **54**, 8202.

[2] J. Y. Kim, S. H. Park, J. Ryu, S. H. Cho, S. H. Kim, S. Chang, *J. Am. Chem. Soc.* 2012, **134**, 9110.

[3] T. Aneeja, R. M. Philip, G. Anilkumar, *Results in Chemistry*, 2022, **4**, 100474.

[4] N. E. Calcaterra and J. C. Barrow, *ACS Chem. Neurosci.*, 2014, **5**, 253.

[5] L. D. Vazquez-Serrano, B. T. Owens, J. M. Buriak, *Inorganica Chim. Acta,* 2006, **359**, 2786.

[6] L. Rubio-Perez, M. Iglesias, J. Munarriz, V. Polo, V. Passarelli, J. J. Perez-Torrente, L. A. Oro, *Chem. Sci.*, 2017, **8**, 4811.

[7] G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2015, **71**, 3-8.

[8] G. M. Sheldrick, *Acta Crystallogr. Sect. C*, 2015, **71**, 3-8.

[9] A. L., *Acta Crystallogr. Sect. C,* 2015, **71**, 9-18.