Supporting Information

Iridium-Catalyzed Selective 1,2-Hydrosilylation of *N*-Heterocycles

Jinseong Jeong[†,‡] Sehoon Park,*[,‡,†] and Sukbok Chang*[,‡,†]

[†]*Department of Chemistry, Korea Advanced Institute of Science & Technology (KAIST), Daejeon 305-701, South Korea*

[‡]*Center for Catalytic Hydrocarbon Functionalizations, Institute for Basic Science (IBS), Daejeon 305-701, South Korea*

*Email: sehoonp@kaist.ac.kr; sbchang@kaist.ac.kr

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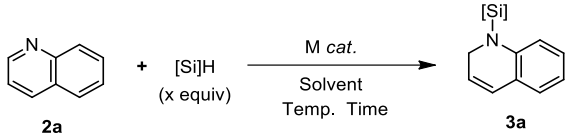
I. General Considerations

Unless otherwise stated, all catalytic reactions were carried out under argon atmosphere. Benzene-d_6 and toluene-d_8 purchased and used without additional purification for the catalytic hydrosilylation and mechanistic studies. All other solvents used in this study were freshly distilled before use. Chlorobis(cyclooctene)iridium(I) dimer $[Ir(coe)_2Cl]_2$ and other iridium complexes were purchased. All other commercial reagents were directly used as received from chemical sources without further purification unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel 60 F254 plates. Visualization on TLC was achieved by the use of UV light (254 nm), exposure to treatment with acidic anisaldehyde, phosphomolybdic acid, ninhydrin or ceric ammonium molydate stain followed by heating. Column chromatography was undertaken on silica gel (400-630 mesh) using proper eluent. ^{1}H NMR was recorded on AVHD 400 (400 MHz) and/or Agilent Technologies DD2 (400 MHz) for mechanistic studies, and Bruker Avance 400 (400 MHz) or Agilent Technologies DD2 600 (600 MHz) for routine characterization of compounds. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak (C_6H_6 in C_6D_6: 7.12 ppm; 1,4-dioxane: 3.32 ppm; mesitylene: 6.73 and 2.22 ppm; DMSO in DMSO-d_6: 2.54 ppm; H_2O in DMSO-d_6: 3.33 ppm). The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, dd = doublet of doublet, td = triplet of doublet, ddd = doublet of doublet of doublet, m = multiplet. Coupling constants, *J*, were reported in hertz unit (Hz). ^{13}C{^{1}H} NMR was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center of a triplet at 127.6 ppm of C_6D_6 or 40.45 ppm of DMSO-d_6. ^{29}Si{^{1}H} NMR was referenced to a peak of external Et_2SiH_2 at -23.0 ppm. Infrared (IR) spectra were acquired on Bruker Alpha ATR FT-IR Spectrometer. Frequencies were given in wave numbers (cm^{-1}) and only selected peaks were reported. High resolution mass spectra were obtained by using EI or FAB method from Korea Basic Science Institute (Daegu) or ESI from KAIST Research Analysis Center (Daejeon).

[*Note that the N-silyl form of hydrosilylation products were highly air- and moisture-sensitive, and thus easily decomposed during the course of conventional purification by silica column chromatography as reported (Ref. 6e and 6g). For this reason, the N-silylated products were directly identified without isolation through 1D and/or 2D NMR experiments, and yields of N-silyl products were in situ determined by ^{1}H NMR based on internal standard materials (1,4-dioxane or mesitylene). However, a range of representative N-silylated products were transformed to the corresponding N-acyl derivatives, which were then successfully isolated by the conventional column chromatography under ambient conditions.*]

II. Optimization of the Iridium-Catalyzed 1,2-Hydrosilylation of Quinoline (2a)



Silane (0.53 ~ 1.05 mmol, 1.5 ~ 3.0 equiv) was added to a solution of an iridium precatalyst (0.00036 ~ 0.015 mmol, 0.1 ~ 4.2 mol %) in deuterated solvent (0.35 mL) or neat in a medium-walled J. Young NMR tube under Ar atmosphere, and the solution was shaken briefly. After 5 min, quinoline (0.35 mmol, 1.0 equiv) was added and the reaction mixture was allowed to react at the indicated temperature and time. Then, it was cooled down to room temperature, into which a suitable internal standard (1,4-dioxane or mesitylene) was added under Ar atmosphere. Finally, the resulting reaction mixture was subject to ^{1}H NMR analysis in order to calculate the crude NMR yields based on the internal standard.

Table S1 **Optimization of 1,2-Hydrosilylation of 2a**[a]

entry	Ir catalyst (mol %)	silane (equiv)	solvent	*T*, (°C)	time (h)	yield (%)[b]
1	$[Ir(coe)_2Cl]_2$ (1.4)	Et_2SiH_2 (1.5)	$CDCl_3$	25	5	62
2	$[Ir(coe)_2Cl]_2$ (1.4)	Et_2SiH_2 (1.5)	THF-d_8	25	15	69
3	$[Ir(coe)_2Cl]_2$ (1.4)	Et_2SiH_2 (1.5)	C_6D_6	25	4	85
4	$[Ir(coe)_2Cl]_2$ (1.4)	Et_2SiH_2 (1.5)	hexane-d_{14}	25	4	99
5	$[Ir(coe)_2Cl]_2$ (1.4)	Et_2SiH_2 (1.5)	*neat*	25	2	99
6	$[Ir(coe)_2Cl]_2$ (1.4)	Et_2SiH_2 (1.5)	C_6D_6	55	1	99
7[c]	$[Ir(coe)_2Cl]_2$ (1.4)	Et_2SiH_2 (1.5)	C_6D_6	55	1	99
8	$[Ir(coe)_2Cl]_2$ (0.1)	Et_2SiH_2 (1.5)	C_6D_6	55	60	99
9	$[Ir(coe)_2Cl]_2$ (0.1)	Et_2SiH_2 (3.0)	*neat*	55	60	99
10	$[Ir(coe)_2Cl]_2$ (4.2)	Et_3SiH (1.5)	C_6D_6	85	15	<1
11	$[Ir(coe)_2Cl]_2$ (4.2)	Me_2PhSiH (1.5)	C_6D_6	55	15	<1
12	$[Ir(coe)_2Cl]_2$ (4.2)	Ph_2SiH_2 (1.5)	C_6D_6	55	15	<1
13	$[Ir(coe)_2Cl]_2$ (4.2)	$^tBu_2SiH_2$ (1.5)	C_6D_6	55	15	<1
14	$[Ir(coe)_2Cl]_2$ (1.4)	$PhMeSiH_2$ (1.5)	C_6D_6	25	4	40
15	$[Ir(coe)_2Cl]_2$ (1.4)	$PhSiH_3$ (1.5)	C_6D_6	25	15	29[d]
16	$[Ir(cod)OMe]_2$ (1.4)	Et_2SiH_2 (1.5)	C_6D_6	25	4	61
17	$[Ir(cod)Cl]_2$ (1.4)	Et_2SiH_2 (1.5)	C_6D_6	25	4	58
18	$[Cp^*IrCl_2]_2$ (1.4)	Et_2SiH_2 (1.5)	$CDCl_3$	25	4	57[e]

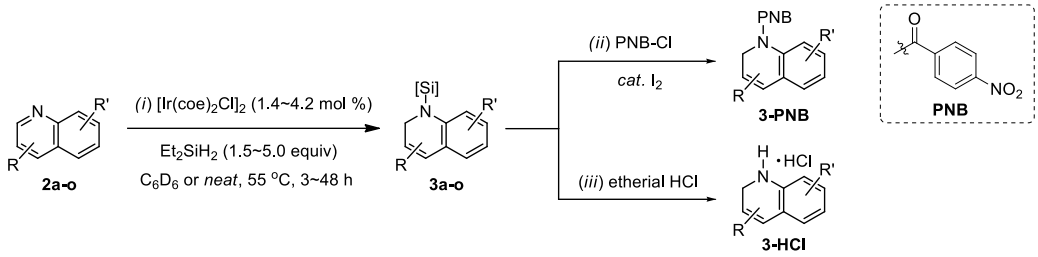
[a]Carried out in J-Young NMR tube in 0.35 mmol scale (**2a**) under argon atmosphere. [b]Yield of **3a** determined by ^{1}H NMR. [c]Performed in a reaction vial. [d]Unidentified side products were also formed. [e]*N*-Silyl-1,4-dihydroquinoline was formed in 43% crude yield.

III. Ir-Catalyzed 1,2-Hydrosilylation of Quinolines

III-A. Preparation of Quinoline Starting Materials

3-Isopropylquinoline (**2d**),[S1] 4-iodoquinoline,[S2] and 6-ethenylquinoline (**2o**)[S3-4] were prepared according to the previous literatures.

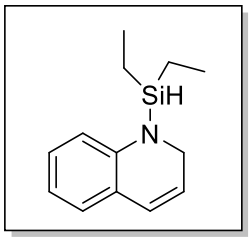
III-B. Typical Procedure for the 1,2-Hydrosilylation of Quinolines (Table 2)



(i) Diethylsilane (0.53 mmol, 1.5 equiv or 1.75 mmol, 5.0 equiv) was added to a solution of $[Ir(coe)_2Cl]_2$ (0.005 to 0.015 mmol, 1.4 to 4.2 mol %) in C_6D_6 (0.35 mL) or *neat* in a medium-walled J-Young NMR tube under Ar atmosphere, and the solution was shaken briefly. After 5 min, quinolines (0.35 mmol, 1.0 equiv) were added into the solution under Ar atmosphere, and it was reacted at the indicated temperature for the indicated period of time. Following an NMR analysis of this crude reaction solution with internal standards (1,4-dioxane = 0.1 mmol; mesitylene = 0.117 mmol), it was diluted with acetonitrile (0.2 mL) and cooled to 0 °C. 4-Nitrobenzoyl chloride (0.53 mmol, 1.5 equiv) with the catalytic amount of I_2 (0.035 mmol, 0.1 equiv, 10 mol %) in acetonitrile (0.3 mL) was slowly added into the above reaction mixture at 0 °C.[S5] Then, the mixture was allowed to react at room temperature for 1 h and quenched by adding $Na_2S_2O_3$ (0.053 mmol, 0.15 equiv). Subsequently, this quenched crude solution was evaporated under reduced pressure, and purified by column chromatography on silica gel (EA/Hx = 1/4) to give the corresponding *N*-benzoylated 1,2-dihydroquinoline products (**3-PNB**).

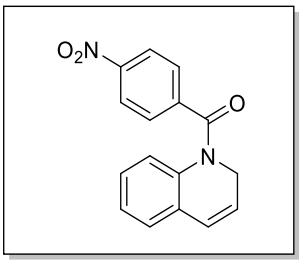
(iii) To the catalytic reaction mixture in a J. Young NMR tube was dropwise added HCl solution in ether (2 M, 1.5 mL) at room temperature and the mixture was vigorously shaken. After 1 h, the precipitated salts were filtered and washed with ether (3 mL x 3) to give the desired products as HCl salt (**3-HCl**). The obtained salts were subject to NMR and/or HRMS analysis.

1-(Diethylsilyl)-1,2-dihydroquinoline (**Table 2**, **3a**) (Crude yield = 99%)



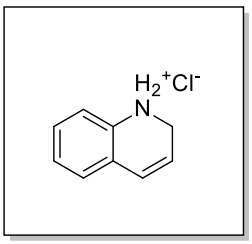
^{1}H NMR (400 MHz, C_6D_6) δ 6.92 (t, J = 7.6 Hz, 1H), 6.83 – 6.74 (m, 2H), 6.68 (t, J = 7.3 Hz, 1H), 6.24 (d, J = 9.5 Hz, 1H), 5.42 (dt, J = 9.0, 4.0 Hz, 1H), 4.50 (quint, J = 3.1 Hz, 1H), 3.66 (dd, J = 4.1, 1.9 Hz, 2H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 146.3, 128.2, 127.5, 127.3, 126.8, 122.8, 119.9, 117.8, 45.6, 7.7 (2C), 5.6 (2C); **^{29}Si NMR (**120 MHz, C_6D_6**)** δ 5.4.

(4-Nitrophenyl)[quinolin-1(2H)-yl]methanone (3a-PNB) (Isolated yield = 82%)



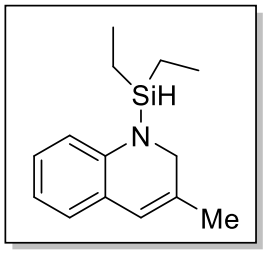
Bright yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.1 Hz, 2H), 7.50 (d, J = 8.2 Hz, 2H), 7.14 (d, J = 7.0 Hz, 1H), 7.06 (t, J = 7.3 Hz, 1H), 6.84 (t, J = 6.8 Hz, 1H), 6.64 (d, J = 9.4 Hz, 1H), 6.47 (s, 1H), 6.17 (dt, J = 9.4, 4.2 Hz, 1H), 4.56 (s, 2H); **^{13}C NMR (**150 MHz, $CDCl_3$**)** δ 167.4, 148.5, 141.6, 136.1, 129.9 (2C), 128.4, 127.0, 126.7 (2C), 126.2, 125.9, 124.6, 123.4 (2C), 43.2; **IR** (cm^{-1}): 2834, 1654, 1600, 1523, 1487, 1342, 1224, 784; **HRMS** (ESI): Calculated for $C_{16}H_{12}N_2O_3$ $[M]^+$: 280.0848, Found: 280.0844.

1,2-Dihydroquinolin-1-ium chloride (3a-HCl) (Isolated yield = 99%)



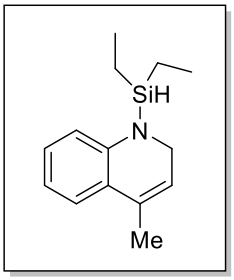
White solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.31 (s, 2H), 7.28 – 7.11 (m, 4H), 6.59 – 6.53 (m, 1H), 6.02 – 5.91 (m, 1H), 3.93 – 3.89 (m, 2H); **^{13}C NMR (**150 MHz, DMSO-d_6**)** δ 132.8, 129.2, 127.6, 127.0, 126.8, 125.7, 123.3, 120.7, 40.9; **IR** (cm^{-1}): 3401, 3372, 2930, 1638, 1595, 1495, 1035, 692; **HRMS** (EI): Calculated for $C_9H_{10}N$ $[M\text{-}Cl]^+$: 132.0808, Found: 132.0810.

1-(Diethylsilyl)-3-methyl-1,2-dihydroquinoline (**3b**) (Crude yield = 99%)



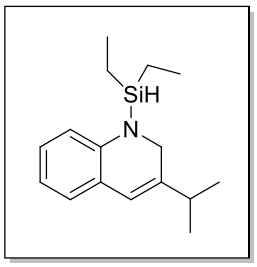
^{1}H NMR (400 MHz, C_6D_6) δ 6.93 (td, J = 7.7, 1.7 Hz, 1H), 6.83 – 6.79 (m, 2H), 6.71 (t, J = 7.4 Hz, 1H), 5.99 (s, 1H), 4.51 (quint, J = 3.4 Hz, 1H), 3.61 (s, 2H), 1.51 (s, 3H), 0.89 (t, J = 8.0 Hz, 6H), 0.72 – 0.64 (m, 2H), 0.62 – 0.54 (m, 2H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 144.1, 131.8, 126.9, 126.8, 126.1, 121.9, 119.4, 116.8, 49.9, 20.2, 7.2 (2C), 5.1 (2C); **HRMS** of HCl salt form (EI): Calculated for $C_{10}H_{12}N$ $[M\text{-}Cl]^+$: 146.0964, Found: 146.0971.

1-(Diethylsilyl)-4-methyl-1,2-dihydroquinoline (**3c**) (Crude yield = 99%)



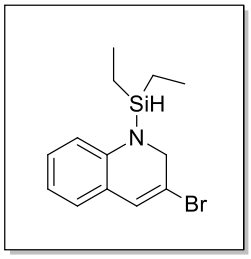
^{1}H NMR (400 MHz, C_6D_6) δ 7.05 (d, J = 7.7 Hz, 1H), 6.98 (t, J = 7.8 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 6.74 (t, J = 7.5 Hz, 1H), 5.30 (s, 1H), 4.53 (s, 1H), 3.66 (s, 2H), 1.82 (s, 3H), 0.90 (t, J = 8.1 Hz, 6H), 0.72 – 0.63 (m, 2H), 0.62 – 0.54 (m, 2H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 146.0, 131.5, 127.9, 127.6, 123.8, 119.4, 119.2, 117.4, 45.0, 18.4, 7.3 (2C), 5.2 (2C); **HRMS** of HCl salt form (EI): Calculated for $C_{10}H_{12}N$ [M-Cl]$^+$: 146.0964, Found: 146.0968.

1-(Diethylsilyl)-3-isopropyl-1,2-dihydroquinoline (**3d**) (Crude yield = 99%)



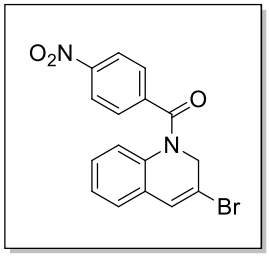
^{1}H NMR (400 MHz, C_6D_6) δ 6.95 (t, J = 7.0 Hz, 1H), 6.90 (d, J = 7.2 Hz, 1H), 6.84 (d, J = 8.1 Hz, 1H), 6.74 (t, J = 6.8 Hz, 1H), 6.08 (s, 1H), 4.54 (s, 1H), 3.69 (s, 2H), 2.14 – 2.06 (m, 1H), 0.95 (d, J = 6.9 Hz, 6H), 0.92 – 0.88 (m, 6H), 0.76 – 0.64 (m, 2H), 0.65 – 0.55 (m, 2H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 144.7, 141.4, 127.2, 126.9, 126.6, 119.6, 118.9, 117.0, 47.3, 32.9, 20.4 (2C), 7.3 (2C), 5.2 (2C); **HRMS** of HCl salt form (EI): Calculated for $C_{12}H_{14}N$ [M-H_2Cl]$^+$: 172.1126, Found: 172.1147.

3-Bromo-1-(diethylsilyl)-1,2-dihydroquinoline (**3e**) (Crude yield = 99%)



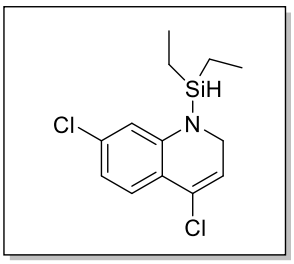
^{1}H NMR (400 MHz, C_6D_6) δ 6.89 (ddd, J = 8.7, 6.2, 2.8 Hz, 1H), 6.72 (d, J = 8.1 Hz, 1H), 6.68 – 6.59 (m, 2H), 6.51 (s, 1H), 4.41 (quint, J = 3.4 Hz, 1H), 3.91 (s, 2H), 0.82 (t, J = 7.9 Hz, 6H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 143.6, 128.1, 128.0, 126.5, 126.3, 120.1, 117.7, 115.2, 52.7, 7.1 (2C), 5.0 (2C).

[3-Bromoquinolin-1(2*H*)-yl](4-nitrophenyl)methanone (3e-PNB) (Isolated yield = 95%)



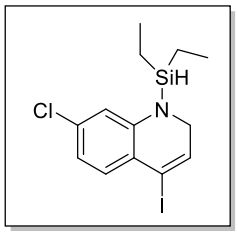
Bright yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.20 – 7.06 (m, 2H), 6.99 (s, 1H), 6.90 (t, J = 7.4 Hz, 1H), 6.47 (s, 1H), 4.80 (s, 2H); **^{13}C NMR (**100 MHz, $CDCl_3$**)** δ 167.3, 148.7, 140.9, 134.5, 130.0 (2C), 128.2, 127.7, 127.4, 126.3 (2C), 124.7, 123.5 (2C), 119.3, 50.0; **IR** (cm^{-1}): 3060, 2882, 1640, 1601, 1521, 1489, 1342, 709, 585; **HRMS** (EI): Calculated for $C_{16}H_{11}BrN_2O_3$ [M]$^+$: 357.9953, Found: 357.9955.

4,7-Dichloro-1-(diethylsilyl)-1,2-dihydroquinoline (**3f**) (Crude yield = 99%)



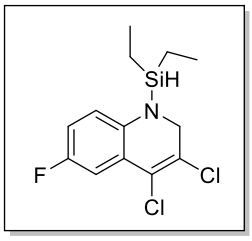
^{1}H NMR (400 MHz, C_6D_6) δ 7.28 (d, J = 8.3 Hz, 1H), 6.82 (s, 1H), 6.64 (d, J = 8.3 Hz, 1H), 5.42 (t, J = 4.6 Hz, 1H), 4.29 (s, 1H), 3.43 (d, J = 4.5 Hz, 2H), 0.76 (t, J = 7.9 Hz, 6H), 0.62 – 0.53 (m, 2H), 0.53 – 0.46 (m, 2H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 147.6, 134.6, 128.9, 126.1, 122.9, 119.7, 119.4, 117.2, 45.6, 7.0 (2C), 4.6 (2C); **HRMS** of HCl salt form (EI): Calculated for $C_9H_6Cl_2N$ [M-$H_2Cl]^+$: 197.9877, Found: 197.9883.

4-Chloro-1-(diethylsilyl)-7-iodo-1,2-dihydroquinoline (**3g**) (Crude yield = 99%)



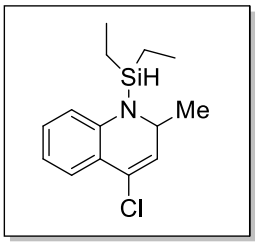
^{1}H NMR (400 MHz, C_6D_6) δ 7.29 (d, J = 8.3 Hz, 1H), 6.86 (s, 1H), 6.72 (dd, J = 8.3, 2.0 Hz, 1H), 6.10 (t, J = 4.7 Hz, 1H), 4.40 (quint, J = 3.3 Hz, 1H), 3.41 (d, J = 4.7 Hz, 2H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 146.8, 134.6, 133.4, 133.0, 125.2, 119.7, 117.4, 94.6, 47.4, 7.2 (2C), 4.8 (2C); **HRMS** of HCl salt form (EI): Calculated for C_9H_6ClIN [M-$H_2Cl]^+$: 289.9233, Found: 289.9242.

3,4-Dichloro-1-(diethylsilyl)-6-fluoro-1,2-dihydroquinoline (**3h**) (Crude yield = 99%)



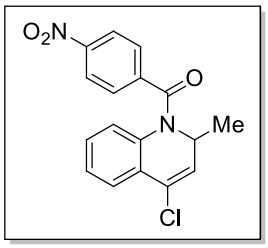
^{1}H NMR (400 MHz, C_6D_6) δ 7.28 (dd, J = 9.4, 2.7 Hz, 1H), 6.71 – 6.60 (m, 2H), 4.40 (quint, J = 3.3 Hz, 1H), 3.85 (s, 2H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 157.3 (d, J = 238.9 Hz), 140.3 (d, J = 2.4 Hz), 126.1 (d, J = 8.4 Hz), 125.1 (d, J = 2.3 Hz), 124.4, 118.9 (d, J = 7.7 Hz), 115.0 (d, J = 22.8 Hz), 111.7 (d, J = 25.5 Hz), 51.8, 6.8 (2C), 4.8 (2C); **HRMS** of HCl salt form (EI): Calculated for $C_{12}H_{14}N$ [M-Cl-$H_2]^+$: 215.9783, Found: 215.9780.

4-Chloro-1-(diethylsilyl)-2-methyl-1,2-dihydroquinoline (**3i**) (Crude yield = 80%)



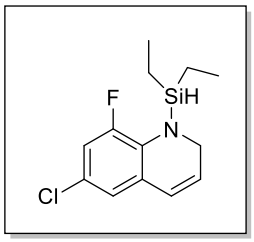
^{1}H NMR (400 MHz, C_6D_6) δ 7.52 – 7.44 (m, 1H, overlapped with **2i**), 6.93 – 6.86 (m, 1H, overlapped with **2i**), 6.71 (d, J = 7.6 Hz, 1H), 6.69 – 6.62 (m, 1H, overlapped with **2i**), 5.66 (d, J = 6.4 Hz, 1H), 4.36 (quint, J = 3.4 Hz, 1H), 3.74 – 3.69 (m, 1H, overlapped with Et_2SiH_2), 1.0 – 0.75 (3H, overlapped with Et_2SiH_2); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 143.7, 129.4, 128.7, 128.5, 124.7, 124.3, 119.2, 118.5, 51.1, 21.0, 7.1 (2C), 4.7 (2C).

[4-Chloro-2-methylquinolin-1(2H)-yl](4-nitrophenyl)methanone (3i-PNB) (Isolated yield = 62%)



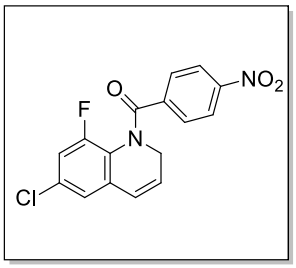
Bright yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.1 Hz, 2H), 7.66 (d, J = 7.7 Hz, 1H), 7.52 (d, J = 8.1 Hz, 2H), 7.18 (t, J = 7.4 Hz, 1H), 6.96 (t, J = 7.6 Hz, 1H), 6.47 (s, 1H), 6.34 (d, J = 5.3 Hz, 1H), 5.42 (s, 1H), 1.26 (d, J = 5.3 Hz, 3H); **^{13}C NMR (**150 MHz, $CDCl_3$**)** δ 167.1, 148.7, 141.3, 134.4, 130.1 (2C), 128.9, 128.5, 127.7, 125.9, 125.6, 125.6, 125.0, 123.5 (2C), 50.0, 17.3; **IR** (cm^{-1}): 3066, 2921, 1657, 1597, 1519, 1485, 1336, 859, 760; **HRMS** (EI): Calculated for $C_{17}H_{13}ClN_2O_3$ $[M]^+$: 328.0615, Found: 328.0613.

6-Chloro-1-(diethylsilyl)-8-fluoro-1,2-dihydroquinoline (**3j**) (Crude yield = 99%)



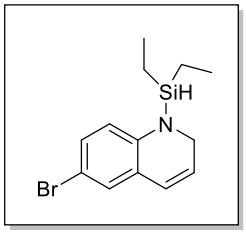
^{1}H NMR (600 MHz, C_6D_6) δ 6.69 (d, J = 11.0 Hz, 1H), 6.51 (s, 1H), 5.97 (d, J = 9.1 Hz, 1H), 5.48 – 5.36 (m, 1H), 4.33 (s, 1H), 3.50 (s, 2H); **^{13}C NMR (**150 MHz, C_6D_6**)** δ 153.0 (d, J = 241.9 Hz), 132.0 (d, J = 12.2 Hz), 130.3 (d, J = 5.0 Hz), 125.9, 125.1 (d, J = 3.9 Hz), 122.1 (d, J = 2.9 Hz), 114.90 (d, J = 24.8 Hz), 45.6, 7.2, 5.4 (d, J = 5.3 Hz).

[6-Chloro-8-fluoroquinolin-1(2*H*)-yl](4-nitrophenyl)methanone (3j-PNB) (Isolated yield = 79%)



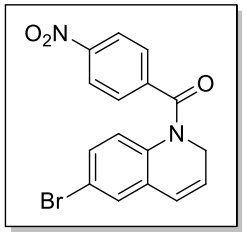
Bright green solid; **^{1}H NMR** (400 MHz, $CDCl_3$) at 328K δ 8.10 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 6.97 (s, 1H), 6.73 (d, J = 9.7 Hz, 1H), 6.60 (d, J = 9.4 Hz, 1H), 6.30 – 6.21 (m, 1H), 4.48 (s, 2H); **^{13}C NMR (**150 MHz, $CDCl_3$**)** δ 167.8, 153.5 (d, J = 251.3 Hz), 148.9, 140.6 (d, J = 4.0 Hz), 132.1 (d, J = 10.3 Hz), 131.4, 130.0, 129.2 (2C), 125.1, 123.2 (2C), 123.0, 122.3, 115.9 (d, J = 24.0 Hz), 43.4; **IR** (cm^{-1}): 3079, 2854, 1655, 1602, 1522, 1478, 1336, 1270, 858, 712; **HRMS** (EI): Calculated for $C_{16}H_{10}ClFN_2O_3$ $[M]^+$: 332.0364, Found: 332.0365.

6-Bromo-1-(diethylsilyl)-1,2-dihydroquinoline (**3k**) (Crude yield = 99%)



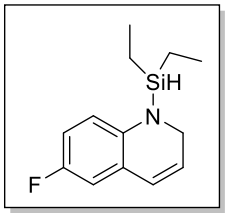
^{1}H NMR (600 MHz, C_6D_6) δ 6.99 (d, J = 8.5 Hz, 1H), 6.89 (s, 1H), 6.49 (d, J = 8.4 Hz, 1H), 5.98 (d, J = 9.2 Hz, 1H), 5.37 – 5.29 (m, 1H), 4.37 (s, 1H), 3.55 (s, 2H), 0.83 (t, J = 7.0 Hz, 6H), 0.63 – 0.53 (m, 4H); **^{13}C NMR (**150 MHz, C_6D_6**)** δ 144.8, 130.2, 129.4, 128.0, 125.6, 123.5, 118.7,111.4, 44.9, 7.2 (2C), 4.9 (2C)

[6-Bromoquinolin-1(2H)-yl](4-nitrophenyl)methanone (3k-PNB) (Isolated yield = 80%)



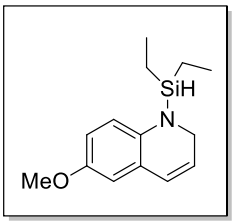
Bright yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H), 7.27 (s, 1H), 6.97 (d, J = 8.5 Hz, 1H), 6.57 (d, J = 9.4 Hz, 1H), 6.39 (s, 1H), 6.25 – 6.14 (m, 1H), 4.53 (s, 2H); **^{13}C NMR (**100 MHz, $CDCl_3$**)** δ 167.4, 148.7, 141.1, 135.1, 130.1, 129.9 (2C), 129.7, 129.4, 128.1, 126.0, 125.3, 123.6 (2C), 118.9, 43.4; **IR** (cm^{-1}): 3062, 2922, 1640, 1600, 1518, 1475, 1363, 808, 692; **HRMS** (EI): Calculated for $C_{16}H_{11}BrN_2O_3$ $[M]^+$: 357.9953, Found: 357.9954.

1-(Diethylsilyl)-6-fluoro-1,2-dihydroquinoline (**3l**) (Crude yield = 99%)



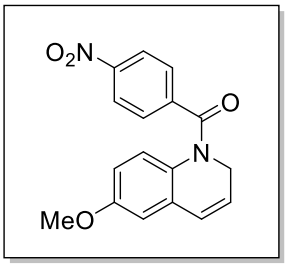
^{1}H NMR (400 MHz, C_6D_6) δ 6.63 – 6.56 (m, 2H), 6.51 (d, J = 8.9 Hz, 1H), 6.04 (d, J = 8.9 Hz, 1H), 5.43 – 5.40 (m, 1H), 4.42 (s, 1H), 3.55 (s, 2H), 0.87 – 0.82 (m, 6H), 0.63 – 0.55 (m, 2H), 0.54 – 0.47 (m, 2H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 157.0 (d, J = 237.0 Hz), 141.6, 129.9, 126.0, 124.2, 118.2 (d, J = 7.5 Hz), 113.7 (d, J = 22.5 Hz), 113.0 (d, J = 22.6 Hz), 44.9, 7.2 (2C), 5.1 (2C); **HRMS** of HCl salt form (EI): Calculated for C_9H_9FN $[M\text{-}Cl]^+$: 150.0714, Found: 150.0729.

1-(Diethylsilyl)-6-methoxy-1,2-dihydroquinoline (**3m**) (Crude yield = 99%)



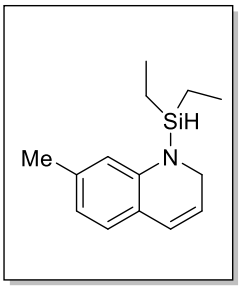
^{1}H NMR (600 MHz, C_6D_6) δ 6.63 (d, J = 8.6 Hz, 1H), 6.47 (dd, J = 8.6, 2.8 Hz, 1H), 6.40 (d, J = 2.8 Hz, 1H), 6.17 (d, J = 9.5 Hz, 1H), 5.50 (dt, J = 8.9, 4.2 Hz, 1H), 4.45 – 4.39 (m, 1H), 3.64 (d, J = 4.2 Hz, 2H), 3.37 (s, 3H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 153.6, 138.9, 127.3, 126.7, 123.5, 118.2, 113.0, 112.1, 54.5, 45.2, 7.2 (2C), 5.3 (2C).

[6-Methoxyquinolin-1(2H)-yl](4-nitrophenyl)methanone (3m-PNB) (Isolated yield = 77%)



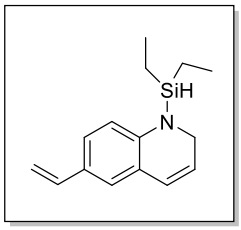
Bright yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 8.2 Hz, 2H), 6.69 (s, 1H), 6.60 (d, J = 9.6 Hz, 1H), 6.45 – 6.11 (m, 3H), 4.55 (s, 2H), 3.75 (s, 3H); **^{13}C NMR (**150 MHz, $CDCl_3$**)** δ 167.1, 157.5, 148.4, 141.8, 129.9, 129.5, 129.1, 127.6, 126.3, 125.6, 123.3 (2C), 112.1, 111.8 (2C), 55.4, 43.0; **IR** (cm^{-1}): 2952, 2926, 1650, 1601, 1519, 1492, 1338, 1272, 817; **HRMS** (EI): Calculated for $C_{17}H_{14}N_2O_4$ $[M]^+$: 310.0954, Found: 310.0952.

1-(Diethylsilyl)-7-methyl-1,2-dihydroquinoline (**3n**) (Crude yield = 99%)



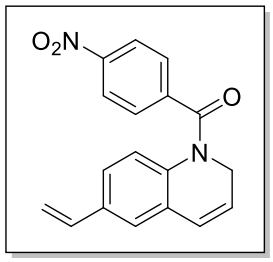
^{1}H NMR (400 MHz, C_6D_6) δ 6.75 (d, J = 7.5 Hz, 1H), 6.70 (s, 1H), 6.52 – 6.50 (m, 1H), 6.27 (d, J = 9.5 Hz, 1H), 5.42 (dt, J = 9.5, 4.2 Hz, 1H), 4.55 (quint, J = 3.8 Hz, 1H), 3.68 (dd, J = 4.3, 1.6 Hz, 2H), 2.10 (s, 3H), 0.91 (t, J = 7.9 Hz, 6H), 0.69 (dqd, J = 15.6, 7.9, 3.8 Hz, 2H), 0.59 (dqd, J = 15.6, 7.9, 3.8 Hz, 2H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 145.8, 137.2, 126.9, 126.7, 123.9, 121.2, 120.3, 118.1, 45.1, 21.3, 7.3 (2C), 5.2 (2C); **HRMS** of HCl salt form (EI): Calculated for $C_{10}H_{10}N$ $[M\text{-}H_2Cl]^+$: 144.0813, Found: 144.0838.

1-(Diethylsilyl)-6-vinyl-1,2-dihydroquinoline (**3o**) (Crude yield = 99%)



^{1}H NMR (600 MHz, C_6D_6) δ 7.00 (d, J = 8.3 Hz, 1H), 6.90 (s, 1H), 6.71 (d, J = 8.3 Hz, 1H), 6.55 (dd, J = 17.6, 10.9 Hz, 1H), 6.21 (d, J = 9.6 Hz, 1H), 5.50 (d, J = 17.6 Hz, 1H), 5.44 – 5.37 (m, 1H), 4.98 (d, J = 10.9 Hz, 1H), 4.48 (s, 1H), 3.66 (s, 2H), 0.88 (t, J = 8.2 Hz, 7H), 0.69 – 0.60 (m, 2H), 0.60 – 0.52 (m, 2H); **^{13}C NMR (**150 MHz, C_6D_6**)** δ 145.7, 136.7, 129.2, 126.7, 126.0, 125.9, 125.0, 122.4, 117.0, 109.9, 45.3, 7.2 (2C), 5.0 (2C).

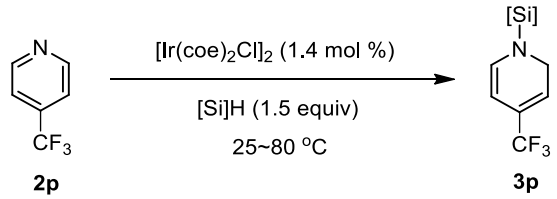
(4-Nitrophenyl)[6-vinylquinolin-1(2H)-yl]methanone (3o-PNB) (Isolated yield = 55%)



Bright yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 8.2 Hz, 2H), 7.15 (s, 1H), 6.86 (d, J = 8.2 Hz, 1H), 6.65 – 6.50 (m, 2H), 6.36 (s, 1H), 6.22 – 6.10 (m, 1H), 5.64 (d, J = 17.6 Hz, 1H), 5.20 (dd, J = 10.7, 3.7 Hz, 1H), 4.53 (s, 2H); **^{13}C NMR (**150 MHz, $CDCl_3$**)** δ 167.4, 148.6, 141.6, 135.6, 135.5, 135.3, 130.0 (2C), 128.4, 126.8, 126.2, 124.7, 124.7, 124.4, 123.5 (2C), 114.4, 43.4; **IR** (cm^{-1}): 3071, 2920, 1641, 1599, 1518, 1340, 1167, 991, 773; **HRMS** (EI): Calculated for $C_{18}H_{14}N_2O_3$ $[M]^+$: 306.1004, Found: 306.1002.

IV. Ir-Catalyzed 1,2-Hydrosilylation of Substituted Pyridines

IV-A. Optimization of the 1,2-Hydrosilylation of 4-(Trifluoromethyl)Pyridine (*Table S2*)



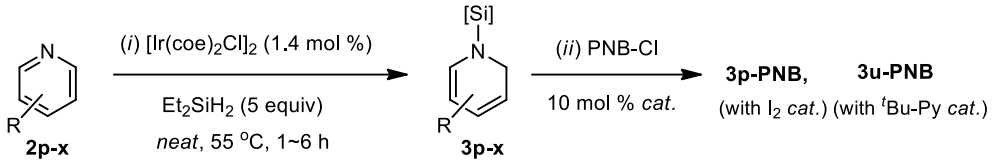
2p **3p**

entry	silane (equiv)	solvent	*T*, (°C)	time (h)	yield (%)[b]
1	Et_2SiH_2 (1.5)	$CDCl_3$	55	1	76
2	Et_2SiH_2 (1.5)	THF-d_8	55	1	76
3	Et_2SiH_2 (1.5)	C_6D_6	55	1	85
4	Et_2SiH_2 (1.5)	*neat*	55	1	89
5	Et_2SiH_2 (1.5)	*neat*	25	3	87
6	Et_2SiH_2 (1.5)	*neat*	55	3	85
7	Et_2SiH_2 (1.5)	*neat*	80	3	83
8	Ph_2SiH_2 (1.5)	*neat*	55	12	47
9	$PhSiH_3$ (1.5)	*neat*	55	12	<1
10	Et_3SiH (1.5)	*neat*	55	12	<1

[a]Carried out in a reaction vial in 0.35 mmol scale under argon atmosphere.

[b]Yield of **3p** determined by ^1H NMR.

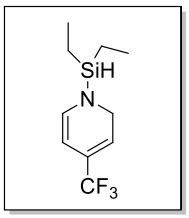
IV-B. Typical Procedure for the 1,2-Hydrosilylation of Substituted Pyridines (Table 3)



(i) Diethylsilane (1.75 mmol, 5.0 equiv) was directly added to $[Ir(coe)_2Cl]_2$ (0.005 mmol, 1.4 mol %) in *neat* in a medium-walled J-Young NMR tube under Ar atmosphere, and the solution was shaken briefly. After 5 min, pyridine substrates (0.35 mmol, 1.0 equiv) were added into the above solution under Ar atmosphere, and it was reacted at 55 °C for the indicated period of time. Following a NMR analysis of this crude reaction solution, it was subject to *N*-benzoylation using 4-nitrobenzoyl chloride.

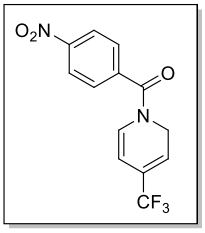
(ii) The catalytic reaction mixture was diluted with toluene (0.2 mL) and cooled down to 0 °C. 4-Nitrobenzoyl chloride (0.53 mmol, 1.5 equiv) was added along with a catalytic amount of I_2 or *tert*-butylpyridine (0.035 mmol, 0.1 equiv, 10 mol %) (Ref. 6d) in toluene (0.3 mL) into the above reaction mixture at 0 °C. The reaction mixture was allowed to react at room temperature for 1 h for **3p-PNB** or 12 h for **3u-PNB**. The solution of **3p-PNB** was additionally quenched by adding $Na_2S_2O_3$ (0.053 mmol, 0.15 equiv). Then, the crude solution was evaporated under reduced pressure, and purified by column chromatography on silica gel (EA/Hx = 1/4) to give the corresponding *N*-benzoylated 1,2-dihydroquinoline products (**3p-PNB** and **3u-PNB**).

1-(Diethylsilyl)-4-(trifluoromethyl)-1,2-dihydropyridine (**Table 3**, **3p**) (Crude yield = 95%)

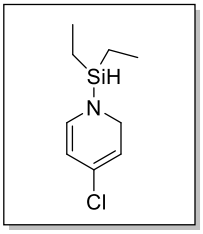


^{1}H NMR (400 MHz, C_6D_6) δ 6.03 (d, J = 7.3 Hz, 1H), 5.10 (s, 1H), 5.01 (dd, J = 7.2, 1.9 Hz, 1H), 4.03 (quint, J = 3.1 Hz, 1H), 3.50 (dd, J = 4.6, 2.3 Hz, 2H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 138.5, 129.0 (q, J = 31.9 Hz), 123.3 (q, J = 271.0 Hz), 108.6 (q, J = 5.8 Hz), 95.5 (q, J = 2.5 Hz), 42.9, 6.4 (2C), 3.6 (2C).

(4-Nitrophenyl)[4-(trifluoromethyl)pyridin-1(2H)-yl]methanone (3p-PNB) (Isolated yield = 57%)

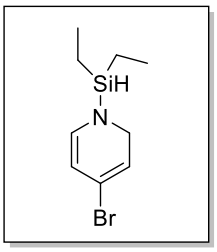


Bright green solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (d, J = 7.6 Hz, 2H), 7.70 (d, J = 7.6 Hz, 2H), 6.46 (s, 1H), 6.22 (s, 1H), 5.30 (s, 1H), 4.69 (s, 2H); **^{13}C NMR (**150 MHz, $CDCl_3$**)** δ 167.2, 149.2, 139..4, 129.5 (2C), 128.6, 126.1, 124 (2C), 122.1 (q, J = 271.4 Hz), 121.4, 101.4, 42.8; **IR** (cm^{-1}): 3092, 2859, 1655, 1588, 1523, 1319, 1300, 715; **HRMS** (EI): Calculated for $C_{13}H_9F_3N_2O_3$ $[M]^+$: 298.0565, Found: 298.0564.



4-Chloro-1-(diethylsilyl)-1,2-dihydropyridine (**3q**) (Crude yield = 94%)

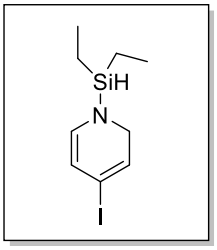
^{1}H NMR (400 MHz, C_6D_6) δ 6.08 (d, J = 7.4 Hz, 1H), 5.01 (dd, J = 7.3, 2.1 Hz, 1H), 4.86 (td, J = 4.6, 2.0 Hz, 1H), 4.18 (quint, J = 3.0 Hz, 1H), 3.70 (d, J = 4.5 Hz, 2H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 138.3, 129.9, 104.1, 102.2, 45.0, 6.6 (2C), 3.7 (2C).



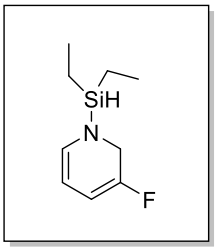
4-Bromo-1-(diethylsilyl)-1,2-dihydropyridine (**3r**) (Crude yield = 83%)

^{1}H NMR (400 MHz, C_6D_6) δ 5.88 (d, J = 7.2 Hz, 1H), 4.97 (dd, J = 7.2, 2.0 Hz, 1H), 4.94 – 4.79 (m, 1H), 4.02 (quint, J = 3.0 Hz, 1H), 3.51 (d, J = 4.6 Hz, 2H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 138.1, 118.0, 107.8, 104.4, 45.7, 6.6 (2C), 3.7 (2C).

1-(Diethylsilyl)-4-iodo-1,2-dihydropyridine (**3s**) (Crude yield = 95%)



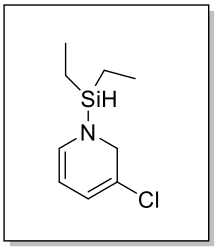
^{1}H NMR (400 MHz, C_6D_6) δ 5.91 (d, J = 7.0 Hz, 1H), 5.33 – 5.27 (m, 2H), 4.15 (quint, J = 2.9 Hz, 1H), 3.57 (d, J = 4.6 Hz, 2H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 137.7, 116.0, 109.2, 89.7, 46.4, 6.8 (2C), 3.9 (2C).



1-(Diethylsilyl)-3-fluoro-1,2-dihydropyridine (**3t**) (Crude yield = 83%)

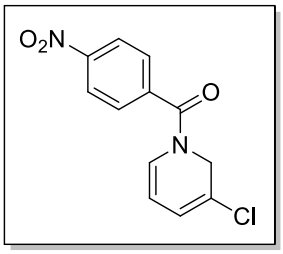
^{1}H NMR (400 MHz, C_6D_6) δ 5.67 (dd, J = 7.0, 2.4 Hz, 1H), 5.21 (dd, J = 11.5, 6.2 Hz, 1H), 4.61 – 4.48 (m, 1H), 4.04 (quint, J = 3.0 Hz, 1H), 3.81 (dd, J = 3.0, 1.2 Hz, 2H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 147.97 (d, J = 267.3 Hz), 130.41 (d, J = 3.3 Hz), 100.20 (d, J = 14.3 Hz), 96.25 (d, J = 4.3 Hz), 44.57 (d, J = 33.3 Hz), 6.6 (2C), 3.5 (2C); **^{29}Si NMR (**120 MHz, C_6D_6**)** δ 7.7.

3-Chloro-1-(diethylsilyl)-1,2-dihydropyridine (**3u**) [Crude yield = 85%; **3u'** (1,6-product) = 3%]



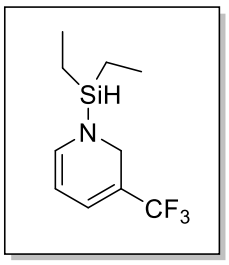
3u(1,2-product):**3u'**(1,6-product) = 28:1; **^{1}H NMR** (400 MHz, C_6D_6) δ 6.13 (s, 1H, 1,6-product), 5.87 (d, J = 6.9 Hz, 1H, 1,2-product), 5.78 (d, J = 5.9 Hz, 1H, 1,2-product), 4.74 - 4.66 (m, 1H, 1,2-product), 4.05 (quint, J = 3.0 Hz, 1H, 1,2-product), 3.83 (s, 2H, 1,2-product); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 133.6, 121.7, 113.6, 99.4, 49.8, 6.5 (2C), 3.6 (2C).

[3-Chloropyridin-1(2H)-yl](4-nitrophenyl)methanone (3u-PNB) (Isolated yield = 47%)

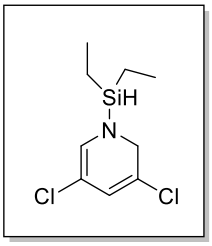


Orange solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 6.25 (d, J = 7.7 Hz, 1H), 6.06 (d, J = 6.2 Hz, 1H), 5.18 (t, J = 7.0 Hz, 1H), 4.64 (s, 2H); **^{13}C NMR (**150 MHz, $CDCl_3$**)** δ 167.0, 149.0, 139.8, 129.5 (2C), 125.1, 124.8, 123.9 (2C), 119.6, 106.0, 48.2; **IR** (cm^{-1}): 3071, 2922, 1631, 1585, 1460, 1349, 731, 704; **HRMS** (EI): Calculated for $C_{12}H_9ClN_2O_3$ $[M]^+$: 264.0302, Found: 264.0300.

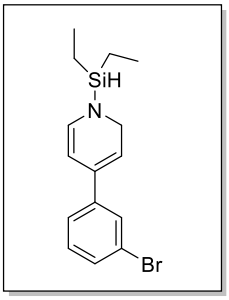
1-(Diethylsilyl)-3-(trifluoromethyl)-1,2-dihydropyridine (**3v**) [Crude yield = 17%; **3v'** (1,6-product) = 82%]



3v(1,2-product):**3v'**(1,6-product) = 1:4.8; **^{1}H NMR** (400 MHz, C_6D_6) δ 6.70 (s, 1H, 1,6-product), 6.39 – 6.35 (m, 1H, 1,2-product), 6.26 (d, J = 6.9 Hz, 1H, 1,2-product), 6.04 (d, J = 9.6 Hz, 1H, 1,6-product), 5.03 (t, J = 6.4 Hz, 1H, 1,2-proudct), 4.87 (dt, J = 9.2, 4.1 Hz, 1H, 1,6-product), 4.70 (quint, J = 3.1 Hz, 1H, 1,2-product), 4.14 (quint, J = 3.1 Hz, 1H, 1,6-product), 3.64 (d, J = 3.8 Hz, 2H, 1,6-product); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 138.3 (q, J = 6.3 Hz), 125.7 (q, J = 266.5 Hz), 120.5 (q, J = 2.4 Hz), 109.2, 103.6 (q, J = 32.4 Hz), 43.3, 6.3 (2C), 3.3 (2C).



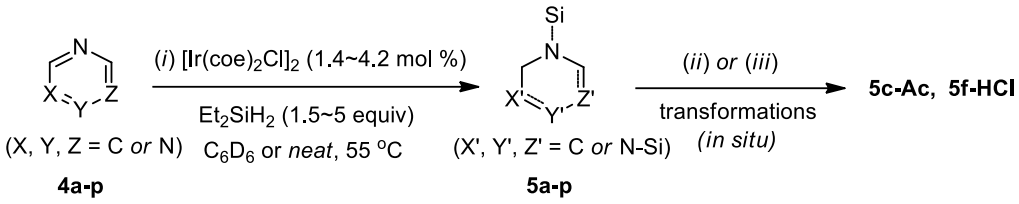
3,5-Dichloro-1-(diethylsilyl)-1,2-dihydropyridine (**3w**) (Crude yield = 93%)
^{1}H NMR (400 MHz, C_6D_6) δ 6.14 (d, J = 0.9 Hz, 1H), 6.00 – 5.94 (m, 1H), 4.12 – 4.08 (m, 1H), 3.81 – 3.75 (m, 2H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 131.0, 123.8, 114.9, 105.9, 49.4, 6.5 (2C), 3.6 (2C).



4-(3-Bromophenyl)-1-(diethylsilyl)-1,2-dihydropyridine (**3x**) (Crude yield = 90%)
^{1}H NMR (400 MHz, C_6D_6) δ 7.59 (s, 1H), 7.26 (d, J = 7.8 Hz, 1H), 7.22 (d, J = 7.8 Hz, 1H), 6.94 (t, J = 7.8 Hz, 1H), 6.31 (d, J = 7.2 Hz, 1H), 5.33 (dd, J = 7.2, 1.7 Hz, 1H), 5.10 – 5.05 (m, 1H), 4.30 (quint, J = 2.9 Hz, 1H), 3.83 (d, J = 4.9 Hz, 2H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 142.2, 136.9, 135.8, 129.6, 129.4, 128.6, 123.9, 122.5, 105.9, 101.1, 44.2, 6.8 (2C), 3.9 (2C).

V. Ir-Catalyzed Dearomative Hydrosilylation of *N*-Heteroaromatics

V-A. Typical Procedure for the Hydrosilylation of *N*-Heteroaromatics (Table 4)

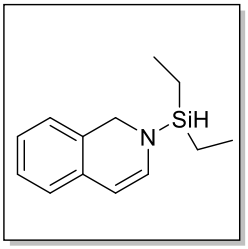


(i) Diethylsilane (0.53 mmol, 1.5 equiv or 1.75 mmol, 5.0 equiv) was added to $[Ir(coe)_2Cl]_2$ (0.005 to 0.015 mmol, 1.4 to 4.2 mol %) in C_6D_6 (0.35 mL) or *neat* in a medium-walled J-Young NMR tube under Ar atmosphere, and the solution was shaken briefly. After 5 min, N-aromatic heterocycle (0.35 mmol, 1.0 equiv) was added into the solution under Ar atmosphere, and it was reacted at 55 °C for the indicated period of time. Following a NMR analysis of this crude reaction solution, the resulting mixture was subject to *N*-acetylation using acetyl chloride or HCl salt formation by adding HCl / ether solution.

(ii) The catalytic reaction mixture was diluted with toluene (0.2 mL) and cooled down to 0 °C. Acetyl chloride (0.53 mmol, 1.5 equiv) with a catalytic amount of *tert*-butylpyridine (0.035 mmol, 0.1 equiv, 10 mol %) in toluene (0.3 mL) was slowly added into the above reaction mixture at 0 °C. The reaction mixture was allowed to react at room temperature for 12 h. The crude mixture was evaporated under reduced pressure, and purified by column chromatography on silica gel (EA/Hx = 1/4) to give the corresponding N-acetylated 1,2-dihydroisoquinoline product (**5c-Ac**) in 83% yield.

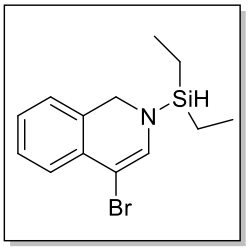
(iii) To the catalytic reaction mixture in a J. Young NMR tube was dropwise added HCl solution in ether (2 M, 1.5 mL) at room temperature and the mixture was vigorously shaken. After 1 h, the precipitated salts were filtered and washed with ether (3 mL x 3) to give the desired product as HCl salt (**5f-HCl**) in 93% yield. The obtained salt was subject to NMR and HRMS analysis.

2-(Diethylsilyl)-1,2-dihydroisoquinoline (**Table 4**, **5a**) (Crude yield = 99%)



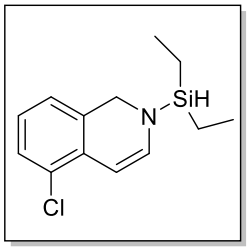
^{1}H NMR (400 MHz, C_6D_6) δ 7.02 (t, J = 7.4 Hz, 1H), 6.93 (t, J = 7.4 Hz, 1H), 6.83 (d, J = 7.4 Hz, 1H), 6.72 (d, J = 7.3 Hz, 1H), 6.20 (d, J = 7.2 Hz, 1H), 5.57 (d, J = 7.2 Hz, 1H), 4.27 (quint, J = 3.0 Hz, 1H), 4.14 (s, 2H), 0.82 (t, J = 7.9 Hz, 6H), 0.64 – 0.53 (m, 2H), 0.54 – 0.43 (m, 2H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 136.2, 134.2, 127.3, 126.7, 125.0, 124.6, 122.4, 103.0, 48.0, 6.9 (2C), 4.0 (2C).

4-Bromo-2-(diethylsilyl)-1,2-dihydroisoquinoline (**5b**) (Crude yield = 99%)



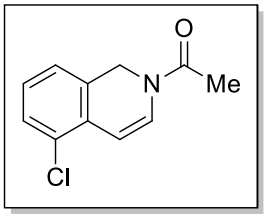
^{1}H NMR (400 MHz, C_6D_6) δ 7.44 – 7.39 (m, 1H), 7.08 – 6.98 (m, 1H), 6.95 – 6.86 (m, 1H), 6.62 – 6.59 (m, 1H), 6.58 (s, 1H), 4.12 (s, 1H), 3.98 (s, 1H), 3.32 (s, 1H), 0.75 – 0.70 (m, 6H), 0.53 – 0.47 (m, 1H), 0.41 – 0.34 (m, 2H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 137.6, 132.9, 127.7, 127.0, 126.4, 124.2, 122.2, 96.9, 48.1, 6.7 (2C), 3.8 (2C).

5-Chloro-2-(diethylsilyl)-1,2-dihydroisoquinoline (**5c**) (Crude yield = 99%)



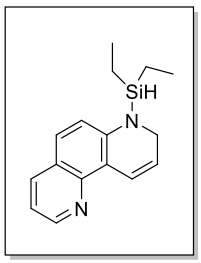
^{1}H NMR (400 MHz, C_6D_6) δ 7.16 (d, J = 8.0 Hz, 1H), 6.83 – 6.65 (m, 1H), 6.58 (d, J = 7.4 Hz, 1H), 6.33 (d, J = 7.4 Hz, 1H), 6.12 (d, J = 7.4 Hz, 1H), 4.31 (quint, J = 3.0 Hz, 1H), 4.12 (s, 2H), 0.90 (t, J = 7.9 Hz, 6H), 0.74 – 0.39 (m, 4H; **^{13}C NMR (**100 MHz, C_6D_6**)** δ 138.2, 132.0, 128.1, 128.0, 127.5, 125.3, 123.1, 98.9, 48.0, 6.9 (2C), 3.9 (2C).

1-[5-Chloroisoquinolin-2(1H)-yl]ethan-1-one (5c-Ac) (Isolated yield = 83%)



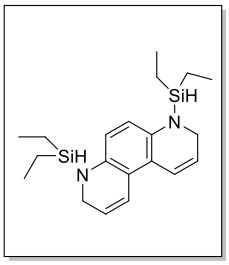
Yellow oil; An isomeric mixture (6:1) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (d, J = 8.0 Hz, 1H, minor), 7.19 – 6.65 (m, 4H, major / 3H, minor), 6.20 (d, J = 8.2 Hz, 1H, minor), 6.13 (d, J = 8.0 Hz, 1H, major), 4.84 (s, 2H, major), 4.74 (s, 2H, minor), 2.20 (s, 3H, minor), 2.16 (s, 3H, major); **^{13}C NMR (**100 MHz, $CDCl_3$**)** δ 168.3 (major), 168.0 (minor), 131.2 (major), 130.2 (minor), 129.9 (minor), 129.7 (major), 129.2 (minor), 128.8 (minor), 128.4 (major), 128.3 (major), 127.8 (major), 127.5 (major), 127.4 (minor), 126.7 (minor), 124.3 (major), 123.8 (minor), 105.7 (minor), 105.8 (major), 47.9 (minor), 44.1 (major), 22.0 (minor), 21.1 (major); **IR** (cm^{-1}): 3071, 2926, 2839, 1667, 1560, 1448, 1215, 758; **HRMS** (EI): Calculated for $C_{11}H_{10}ClNO$ $[M]^+$: 207.0451, Found: 207.0449.

7-(Diethylsilyl)-7,8-dihydro-1,7-phenanthroline (**5d**) (Crude yield = 94%)



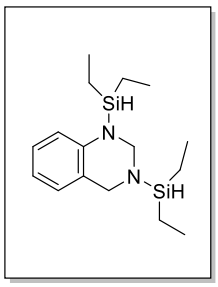
^{1}H NMR (600 MHz, C_6D_6) δ 8.72 – 8.70 (m, 1H), 8.11 (d, J = 9.0 Hz, 1H), 7.49 (d, J = 7.9 Hz, 1H), 7.18 (d, J = 8.6 Hz, 1H), 7.11 (d, J = 8.8 Hz, 1H), 6.78 – 6.64 (m, 1H), 5.66 – 5.43 (m, 1H), 4.70 – 4.44 (m, 1H), 3.77 – 3.65 (m, 2H); **^{13}C NMR (**150 MHz, C_6D_6**)** δ 149.7, 146.7, 145.7, 135.1, 126.5, 123.5, 122.6, 121.3, 119.9, 119.1, 118.1, 44.9, 7.2 (2C), 5.2 (2C).

4,7-Bis(diethylsilyl)-3,4,7,8-tetrahydro-4,7-phenanthroline (**5e)** (Crude yield = 92%)



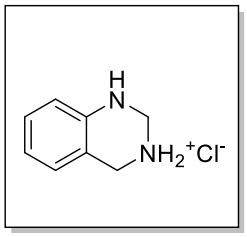
^{1}H NMR (600 MHz, C_6D_6) δ 6.71 (s, 2H), 6.66 (d, J = 9.6 Hz, 2H), 5.71 (dt, J = 9.3, 4.4 Hz, 2H), 4.59 (quint, J = 3.3 Hz, 2H), 3.70 (d, J = 4.6 Hz, 4H); **^{13}C NMR (**150 MHz, C_6D_6**)** δ 138.6 (2C), 123.1 (2C), 122.9 (2C), 122.8 (2C), 117.3 (2C), 44.5 (2C), 7.3 (4C), 5.5 (4C).

1,3-Bis(diethylsilyl)-1,2,3,4-tetrahydroquinazoline (**5f)** (Crude yield = 99%)



^{1}H NMR (400 MHz, C_6D_6) δ 6.86 (t, J = 7.5 Hz, 1H), 6.69 (m, J = 8.0 Hz, 2H), 6.59 (t, J = 7.3 Hz, 1H), 4.45 (quint, J = 3.4 Hz, 1H), 4.31 (quint, J = 2.8 Hz, 1H), 4.27 (s, 2H), 3.99 (s, 2H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 145.0, 126.4, 126.2, 123.3, 118.1, 116.7, 63.1, 48.0, 7.4 (2C), 7.1 (2C), 5.2 (2C), 4.8 (2C).

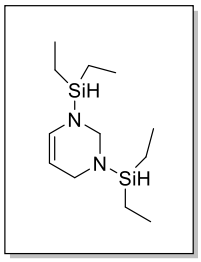
1,2,3,4-Tetrahydroquinazolin-3-ium chloride (5f-HCl) (Isolated yield = 93%)



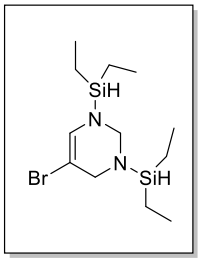
White solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.83 (s, 2H), 7.24 – 6.95 (m, 2H), 6.83 – 6.62 (m, 3H), 4.40 (d, J = 16.3 Hz, 2H), 4.25 (d, J = 16.3 Hz, 2H); **^{13}C NMR (**150 MHz, DMSO-d_6**)** δ 141.6, 128.5, 127.6, 118.6, 115.9, 115.1, 55.0, 43.4; **IR** (cm^{-1}): 3256, 2906, 1611, 1508, 1471, 1120, 1070, 745;

HRMS (EI): Calculated for $C_8H_{11}N_2$ $[M\text{-}Cl]^+$: 135.0917, Found: 135.0916.

1,3-Bis(diethylsilyl)-1,2,3,4-tetrahydropyrimidine (**5g)** (Crude yield = 99%)

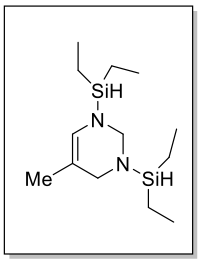


^{1}H NMR (400 MHz, C_6D_6) δ 6.24 (dt, J = 8.0, 1.7 Hz, 1H), 4.57 (dt, J = 8.0, 3.2 Hz, 1H), 4.42 (quint, J = 2.5 Hz, 1H), 4.32 (quint, J = 2.8 Hz, 1H), 4.26 (s, 2H), 3.49 (dd, J = 3.2, 1.7 Hz, 2H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 132.2, 99.3, 60.8, 43.7, 7.2 (2C), 6.9 (2C), 5.0 (2C), 4.4 (2C).



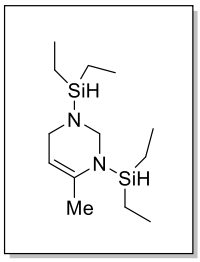
5-Bromo-1,3-bis(diethylsilyl)-1,2,3,4-tetrahydropyrimidine (**5h)** (Crude yield = 99%)

^{1}H NMR (400 MHz, C_6D_6) δ 6.48 (s, 1H), 4.34 (quint, J = 3.0 Hz, 1H), 4.23 (quint, J = 3.1 Hz, 1H), 4.11 (s, 2H), 3.64 (s, 2H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 132.8, 93.0, 60.2, 50.7, 7.0 (2C), 6.8 (2C), 4.9 (2C), 4.2 (2C).



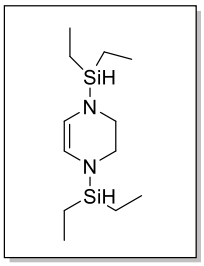
1,3-Bis(diethylsilyl)-5-methyl-1,2,3,4-tetrahydropyrimidine (**5i)** (Crude yield = 99%)

^{1}H NMR (400 MHz, C_6D_6) δ 6.04 (d, J = 1.0 Hz, 1H), 4.42 (quint, J = 2.9 Hz, 1H), 4.34 (quint, J = 2.9 Hz, 1H), 4.19 (s, 2H), 3.39 (s, 2H), 1.58 (s, 3H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 127.7, 107.2, 61.0, 48.9, 18.8, 7.8 (2C), 7.6 (2C), 5.7 (2C), 5.2 (2C).



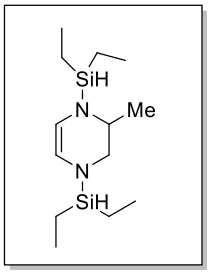
1,3-Bis(diethylsilyl)-4-methyl-1,2,3,4-tetrahydropyrimidine (**5j)** (Crude yield = 99%)

^{1}H NMR (400 MHz, C_6D_6) δ 4.54 – 4.41 (m, 3H), 4.29 (s, 2H), 3.52 – 3.50 (m, 2H) 1.83 (d, J = 1.0 Hz, 3H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 139.6, 98.5, 62.3, 44.4, 20.8, 7.4 (2C), 7.2 (2C), 6.4 (2C), 4.9 (2C); **^{29}Si NMR (**120 MHz, C_6D_6**)** δ 3.1, 0.8.



1,4-Bis(diethylsilyl)-1,2,3,4-tetrahydropyrazine (**5k)** (Crude yield = 99%)

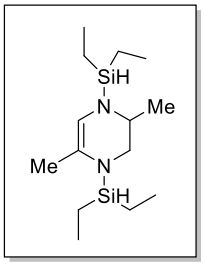
^{1}H NMR (400 MHz, C_6D_6) δ 5.39 (s, 2H), 4.30 (quint, J = 3.3 Hz, 2H), 3.17 (s, 4H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 111.1 (2C), 44.7 (2C), 7.0 (4C), 4.2 (4C).



1,4-Bis(diethylsilyl)-2-methyl-1,2,3,4-tetrahydropyrazine (**5l)** (Crude yield = 99%)

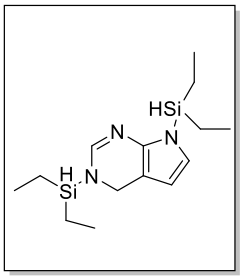
^{1}H NMR (600 MHz, C_6D_6) δ 5.24 (d, J = 5.9 Hz, 1H), 5.19 (d, J = 6.0 Hz, 1H), 4.25 (quint, J = 2.8 Hz, 1H), 4.20 (quint, J = 2.9 Hz, 1H), 3.26 – 3.19 (m, 1H), 2.92 (d, J = 11.2 Hz, 1H), 2.77 (d, J = 11.2 Hz, 1H), 1.01 (d, J = 6.4 Hz, 3H); **^{13}C NMR (**150 MHz, C_6D_6**)** δ 110.0, 109.3, 48.8, 47.9, 18.5, 7.1 (2C), 7.0 (2C), 4.8(2C), 4.3 (2C); **^{29}Si NMR (**120 MHz, C_6D_6**)** δ 4.2, 2.5.

1,4-Bis(diethylsilyl)-2,5-dimethyl-1,2,3,4-tetrahydropyrazine (**5m)** (Crude yield = 94%)

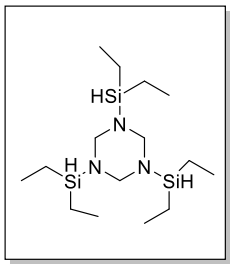


^{1}H NMR (400 MHz, C_6D_6) δ 5.06 (s, 1H), 4.38 (s, 1H), 4.20 (s, 1H), 3.21 – 3.15 (m, 1H), 2.88 (s, 2H), 1.72 (s, 3H), 0.96 (d, J = 6.0 Hz, 3H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 116.0, 107.5, 50.5, 47.5, 19.9, 18.8, 7.5 (2C) 7.3 (2C), 4.7 (2C), 4.3 (2C).

3,7-Bis(diethylsilyl)-4,7-dihydro-3H-pyrrolo[2,3-d]pyrimidine (**5n)** (Crude yield = 99%)



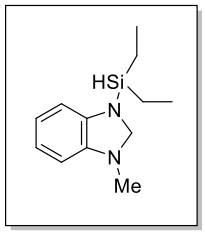
^{1}H NMR (600 MHz, C_6D_6) δ 6.69 (s, 1H), 6.39 (d, J = 3.2 Hz, 1H), 5.80 (d, J = 3.2 Hz, 1H), 4.67 (quint, J = 3.0 Hz, 1H), 4.42 (s, 2H), 4.06 (quint, J = 3.1 Hz, 1H); **^{13}C NMR (**150 MHz, C_6D_6**)** δ 146.3, 139.7 120.0, 106.5, 98.7, 43.6, 6.8 (2C) 6.4 (2C), 4.9 (2C), 2.7 (2C); **^{29}Si NMR (**120 MHz, C_6D_6**)** δ 9.2, 4.3.



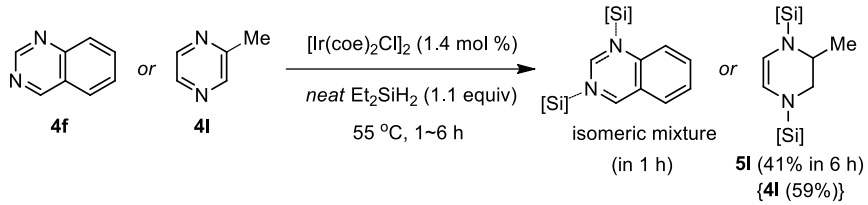
1,3,5-Tris(diethylsilyl)-1,3,5-triazinane (**5o)** (Crude yield = 96%)

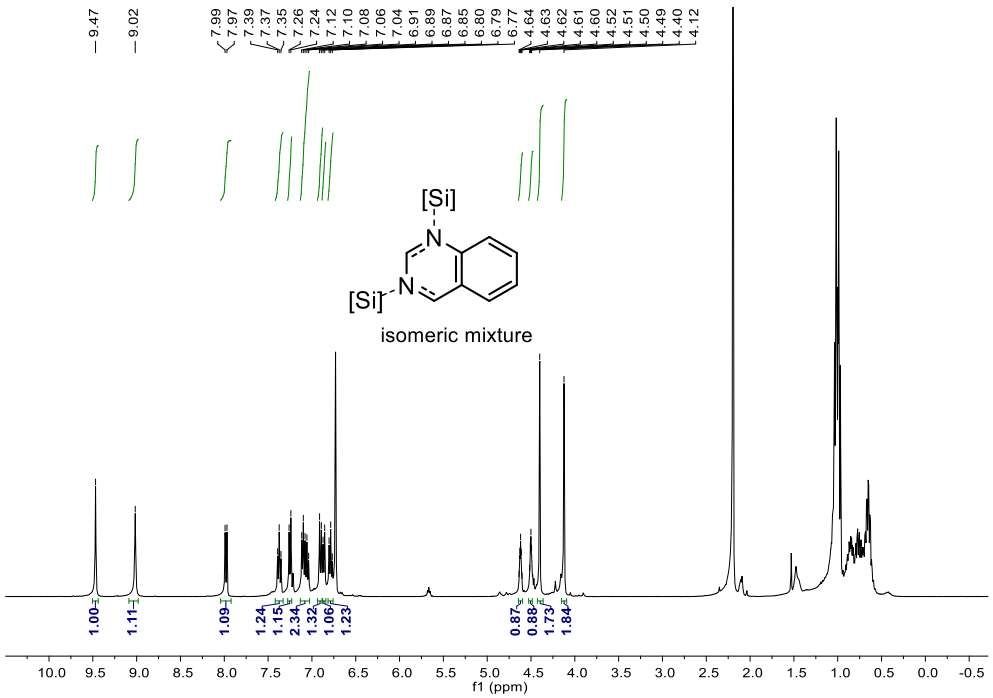
^{1}H NMR (400 MHz, C_6D_6) δ 4.40 (quint, J = 2.7 Hz, 3H), 4.27 (s, 6H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 63.9 (3C), 7.2 (6C), 4.7 (6C).

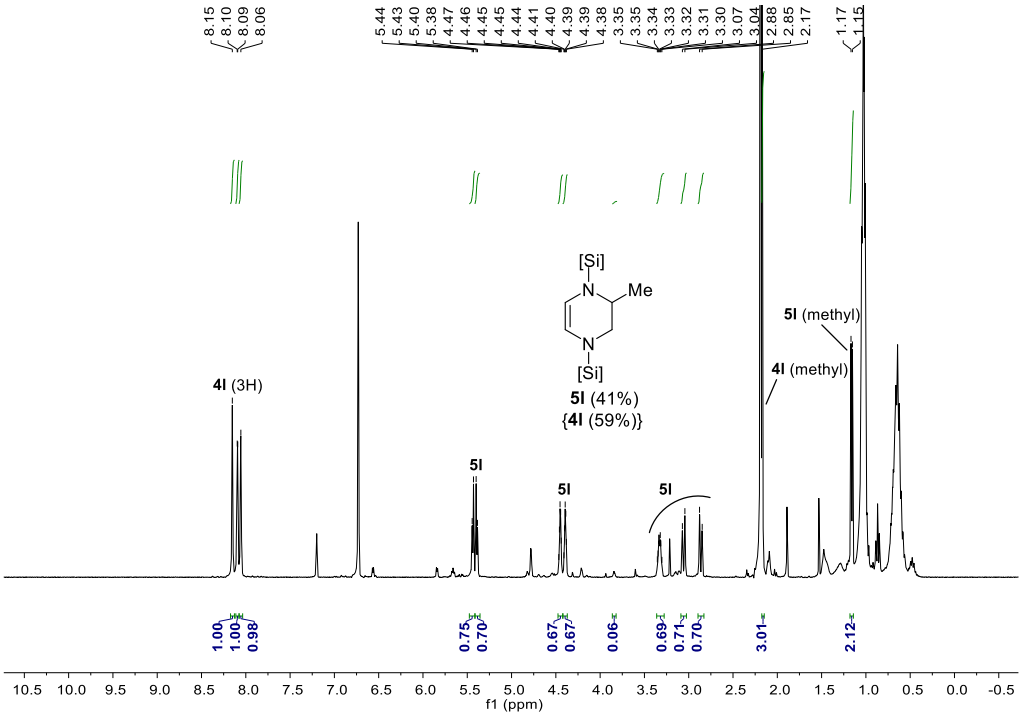
1-(Diethylsilyl)-3-methyl-2,3-dihydro-1H-benzo[d]imidazole (**5p)** (Crude yield = 92%)



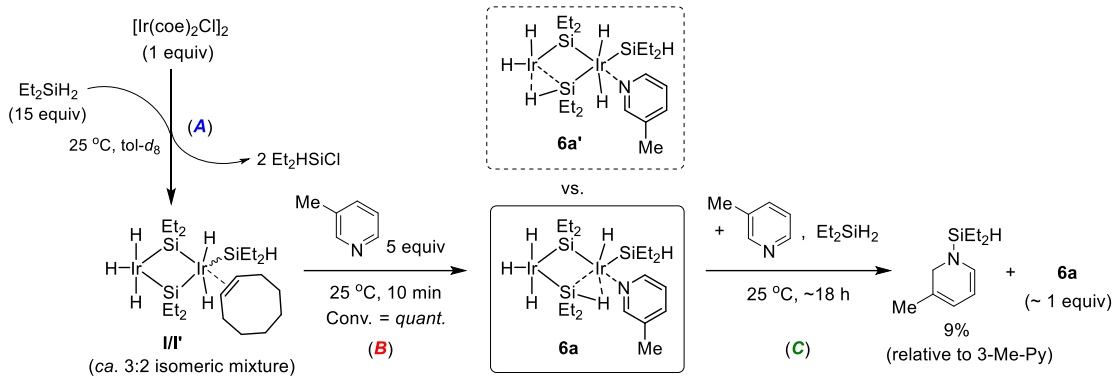
^{1}H NMR (400 MHz, C_6D_6) δ 6.82 – 6.69 (m, 2H), 6.62 (d, J = 6.7 Hz, 1H), 6.35 (d, J = 6.8 Hz, 1H), 4.62 (quint, J = 3.1 Hz, 1H), 4.53 (s, 2H), 2.38 (s, 3H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 144.5, 142.1, 119.0, 118.8, 107.4, 105.8, 75.0, 33.6, 7.2 (2C), 3.9 (2C).


4f
or
4l
[Ir(coe)2Cl]2 (1.4 mol %)
neat Et2SiH2 (1.1 equiv)
55 °C, 1~6 h
[Si]
isomeric mixture
(in 1 h)
or
5l (41% in 6 h)
{4l (59%)}


isomeric mixture
f1 (ppm)


5l (41%)
{4l (59%)}
4l (3H)
5l
5l (methyl)
4l (methyl)
f1 (ppm)

VI. Stoichiometric Reaction of $[Ir(coe)_2Cl]_2$ with Et_2SiH_2 and 3-Methylpyridine (Fig. 1)

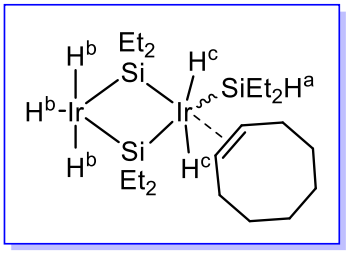


(*A*) $[Ir(coe)_2Cl]_2$ (17.7 mg, 0.02 mmol, 1 equiv) was weighed into a J. Young NMR tube, dried *in vacuo*, and suspended in toluene-d_8 (0.5 mL) under Ar atmosphere, into which Et_2SiH_2 (38.9 μL, 15 equiv) was added, and then the solution was shaken briefly at r.t. (being homogeneous in 10 min) to give rise to an isomeric mixture of **I/I'** with 3:2 ratio. This catalyst solution was subjected to NMR analysis.

(*B*) To a mixture of **I/I'** in toluene-d_8 was subsequently added 3-methylpyridine (9.7 μL, 5 equiv) under argon atmosphere, and it was allowed to react at room temperature to form **6a** (17 mol % relative to initially added 3-methylpyridine) in 10 min. This reaction mixture was analyzed by NMR.

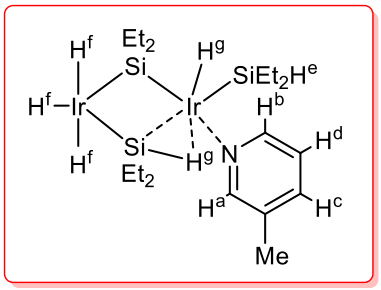
(*C*) Prolonged reaction up to 18 h at the same temperature led to the formation of 3-methyl-1-(diethylsilyl)-1,2-dihydropyridine in 9% NMR yield with the observation of **6a** (17 mol %). This reaction mixture was subjected to NMR analysis.

Cyclooctene Adduct (I/I' = 3:2)



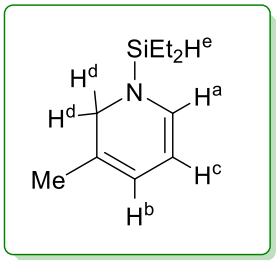
^{1}H NMR (600 MHz, toluene-d_8, selected data) δ 5.63 (2H, olefinic Hs), 4.73 (quint, J = 2.6 Hz, 1H, H^a), -12.48 (3H, H^b, major), -12.52 (3H, H^b, minor), -12.75 (2H, H^c, major), -12.78 (2H, H^c, minor). **^{29}Si NMR (**120 MHz, toluene-d_8**)** δ 130.19 (bridged silylene, minor), 128.68 (bridged silylene, major), 40.70 (terminal silyl, minor), 40.40 (terminal silyl, major), 18.60 (Et_2SiHCl), 1.56 ($Et_2HSiOSiHEt_2$), -0.04 (Me_4Si), -23.0 (Et_2SiH_2).

3-Methylpyridine Adduct (6a)



^{1}H NMR (400 MHz, toluene-d_8, selected data) δ 8.85 (s, 1H, H^{a}), 8.36 (d, J = 5.8 Hz, 1H, H^{b}), 6.79 (1H, H^{c}, overlapped with toluene), 6.59 (dd, J = 8.4, 5.7 Hz, 1H, H^{d}), 4.74 (quint, J = 2.6 Hz, 1H, H^{e}), 1.80 (s, 3H, C3-methyl), -13.01 (3H, H^{f}), -13.20 (2H, H^{g}). **^{29}Si NMR (**120 MHz, toluene-d_8**)** δ 130.4 (bridged silylene), 78.7 [Ir-(Et$_2$)Si-H(η^2)--Ir], 44.5 (terminal silyl), 18.60 (Et$_2$SiHCl), 1.54 (Et$_2$HSiOSiHEt$_2$), -23.0 (Et$_2$SiH$_2$).

1-(Diethylsilyl)-3-methyl-1,2-dihydropyridine



^{1}H NMR (600 MHz, toluene-d_8, selected data) δ 6.12 (d, J = 6.8 Hz, 1H, H^{a}), 5.70 (1H, H^{b}, overlapped with cyclooctene), 5.09 (dd, J = 7.1, 5.5 Hz, 1H, H^{c}), 4.34 (quint, J = 3.1 Hz, 1H, H^{e}), 3.84 – 3.77 (m, 2H, H^{d}), 1.64 (s, 3H, C3-methyl).

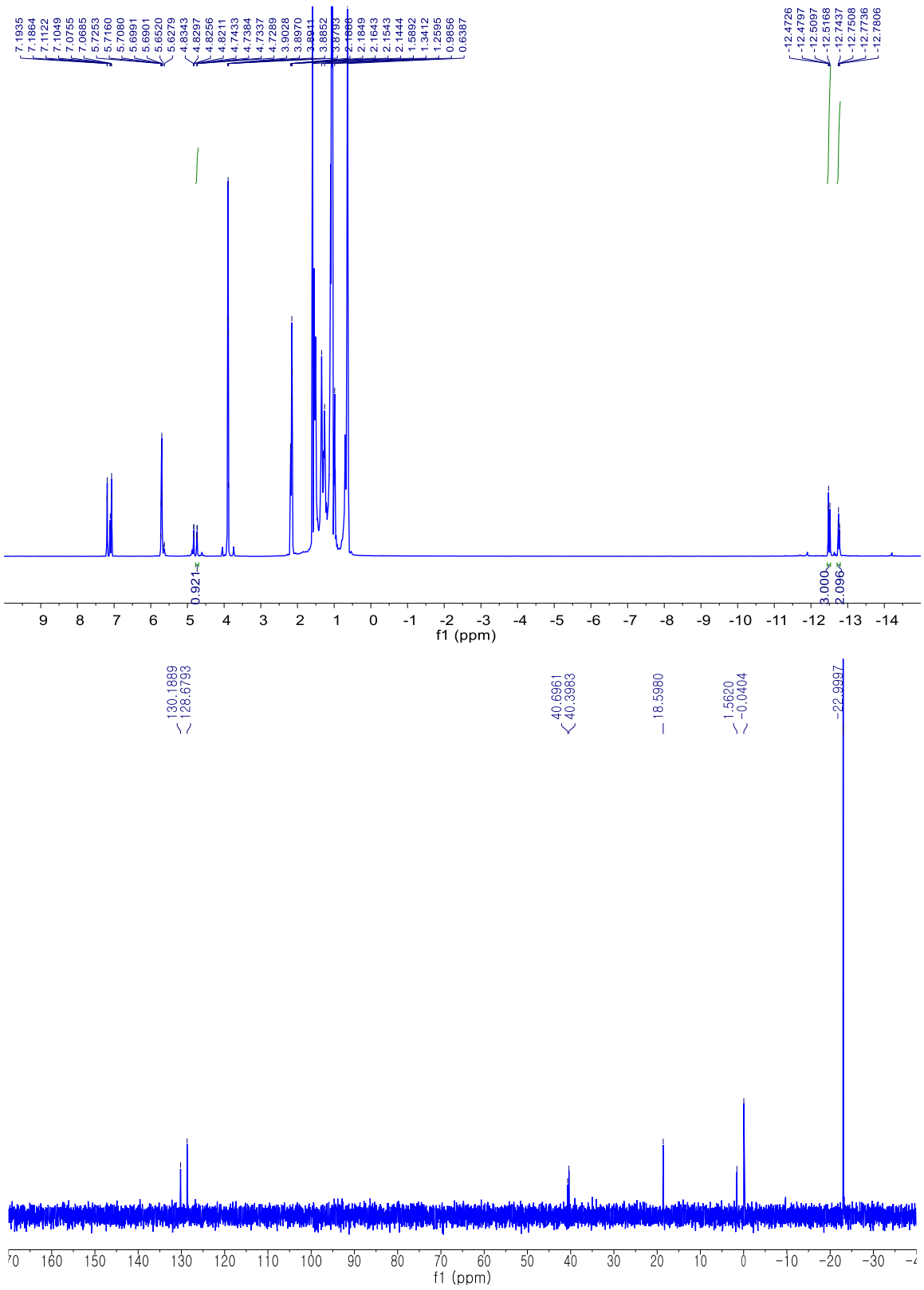


Fig. S1 **Crude ^{1}H and ^{29}Si{^{1}H} NMR Spectra of I/I' in toluene-d_8 at 25 °C (Fig. 1A)**

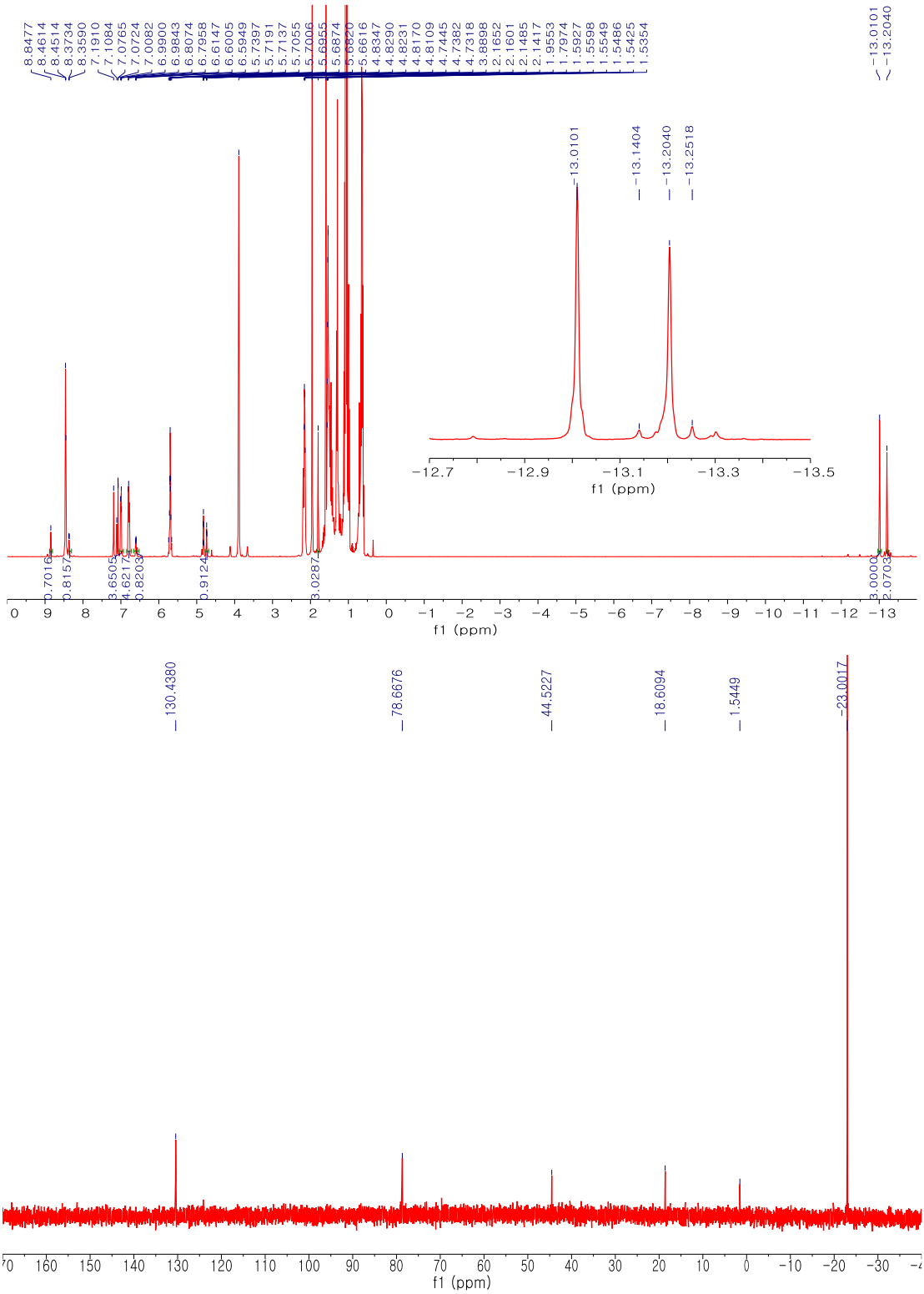


Fig. S2 **^{1}H and ^{29}Si{^{1}H} NMR Spectra in 10 min after the Addition of 3-Methylpyridine at 25 ^{o}C (Fig. 1B)**

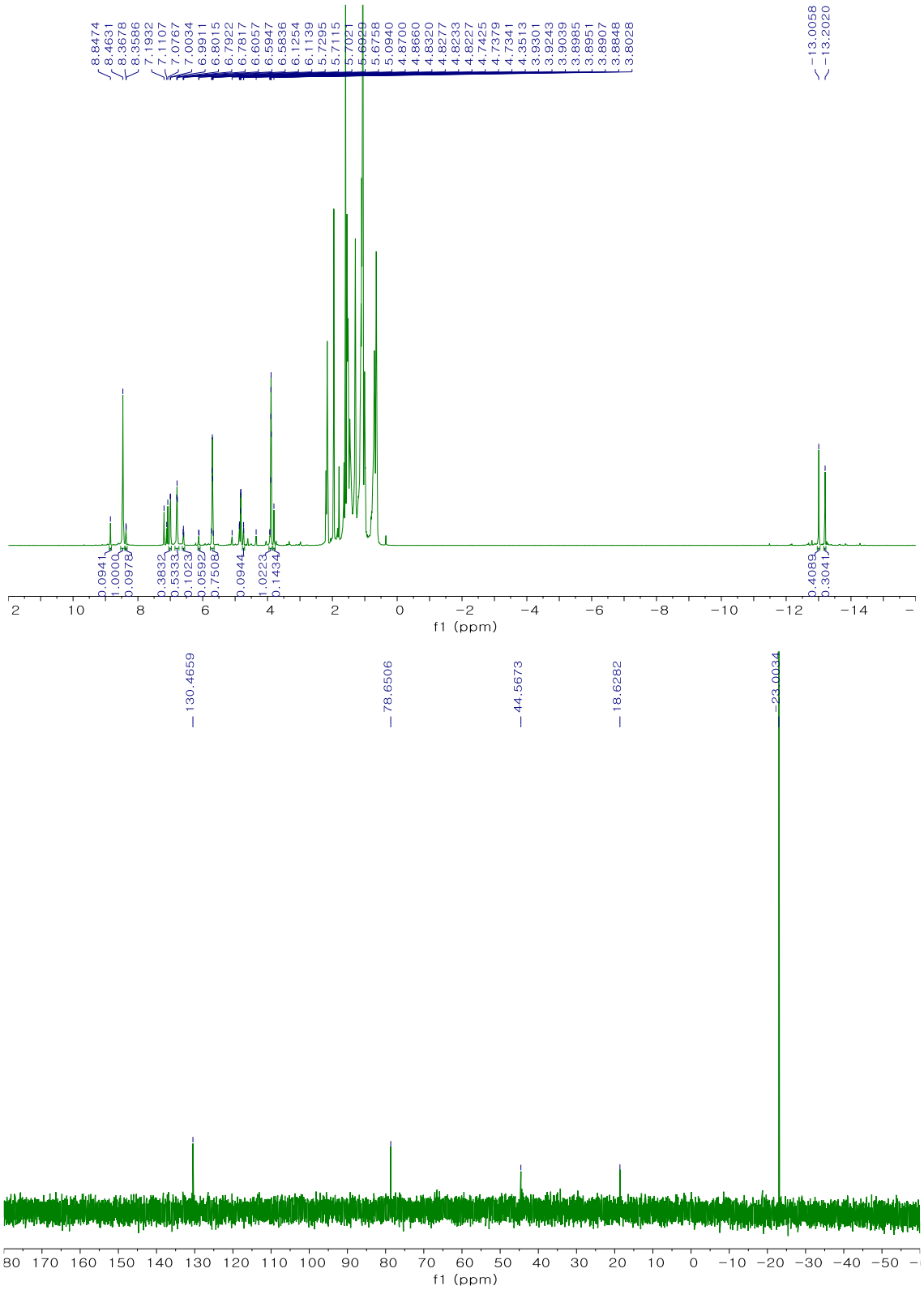


Fig. S3 **^{1}H and ^{29}Si{^{1}H} NMR Spectra in 18 h after the Addition of 3-Methylpyridine at 25 ºC (Fig. 1C)**

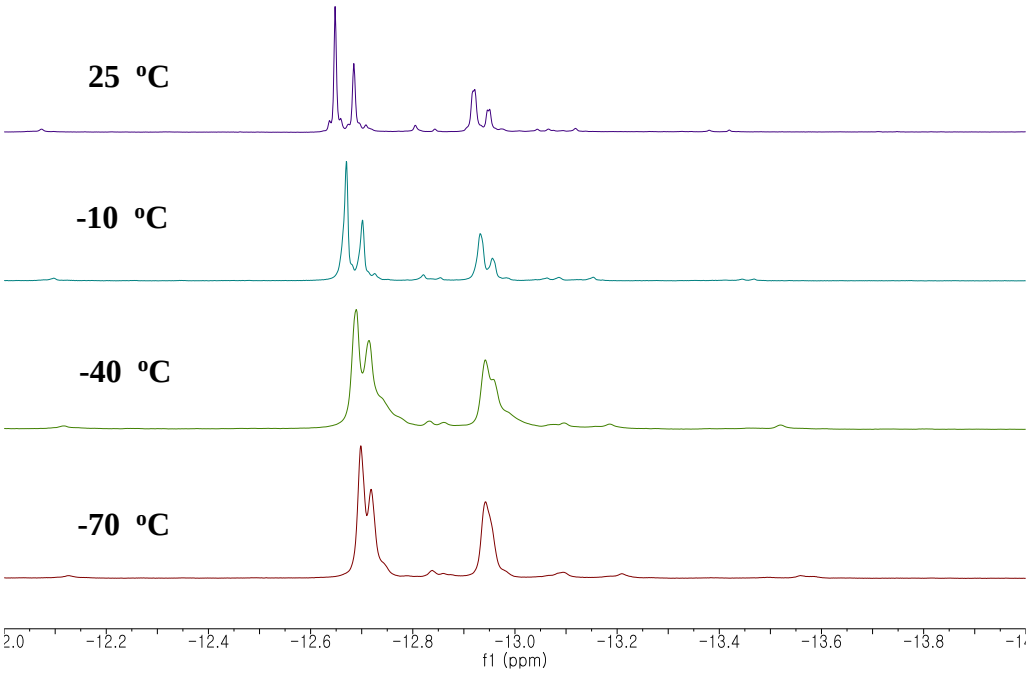


Fig. S4 **Expansion (δ -12.0 ~ -14.0) of the ^{1}H NMR Spectra of I/I' at Variable Temperatures (400 MHz, toluene-d_8)**

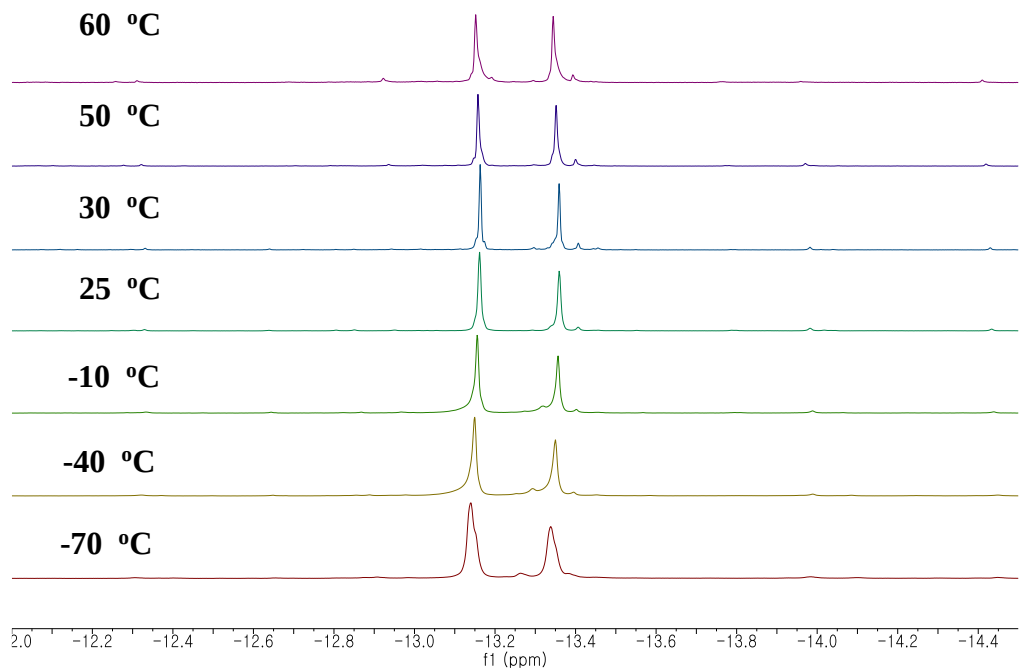


Fig. S5 **Expansion (δ -12.0 ~ -14.5) of the ^{1}H NMR Spectra of 6a at Variable Temperatures (400 MHz, toluene-d_8)**

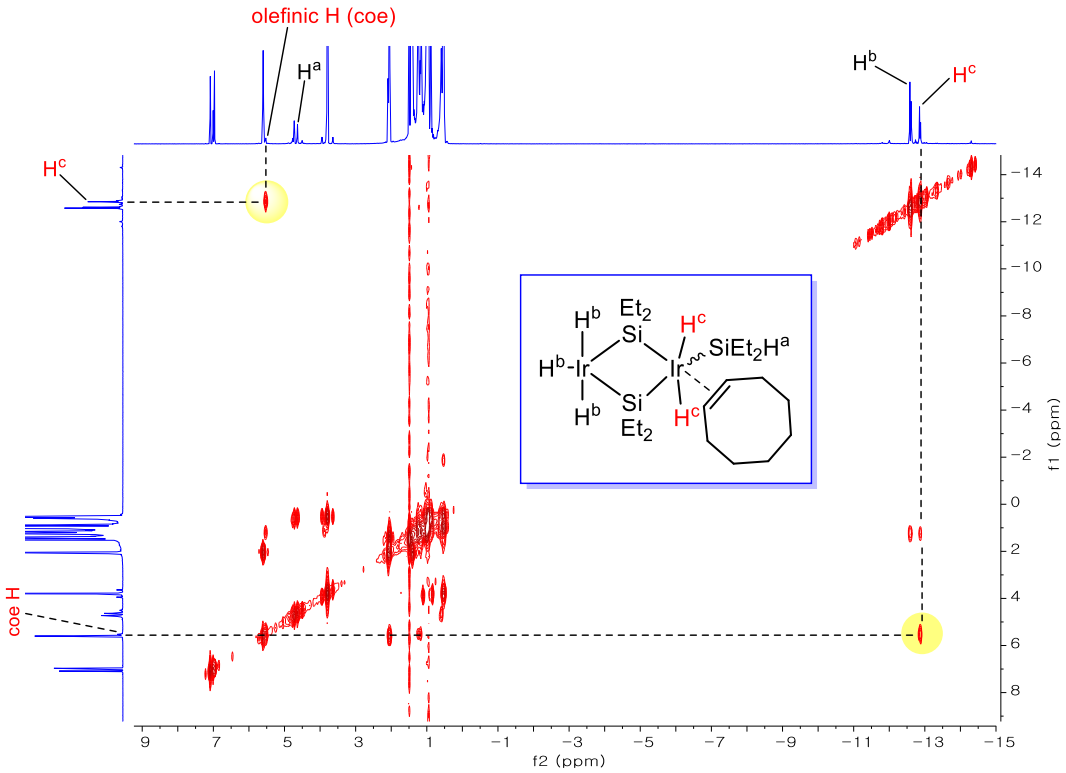


Fig. S6 **^{1}H-^{1}H COSY of I/I' at 25 °C (600 MHz, toluene-d_8)**

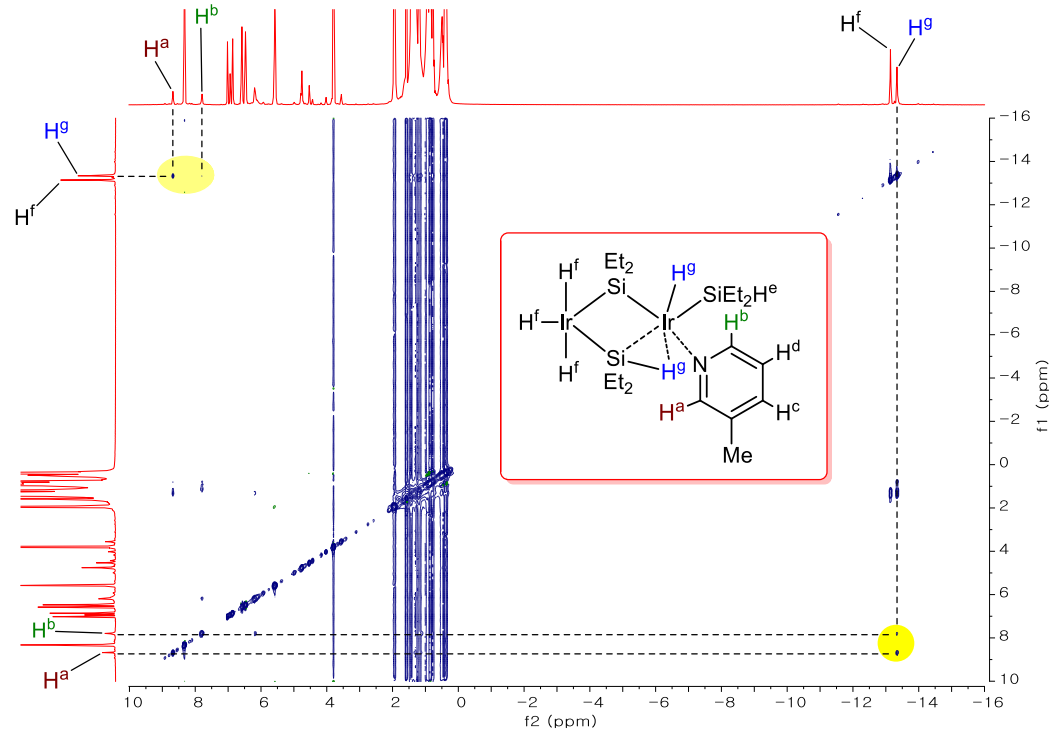


Fig. S7 **^{1}H-^{1}H NOESY of 6a at -70 °C (400 MHz, toluene-d_8)**

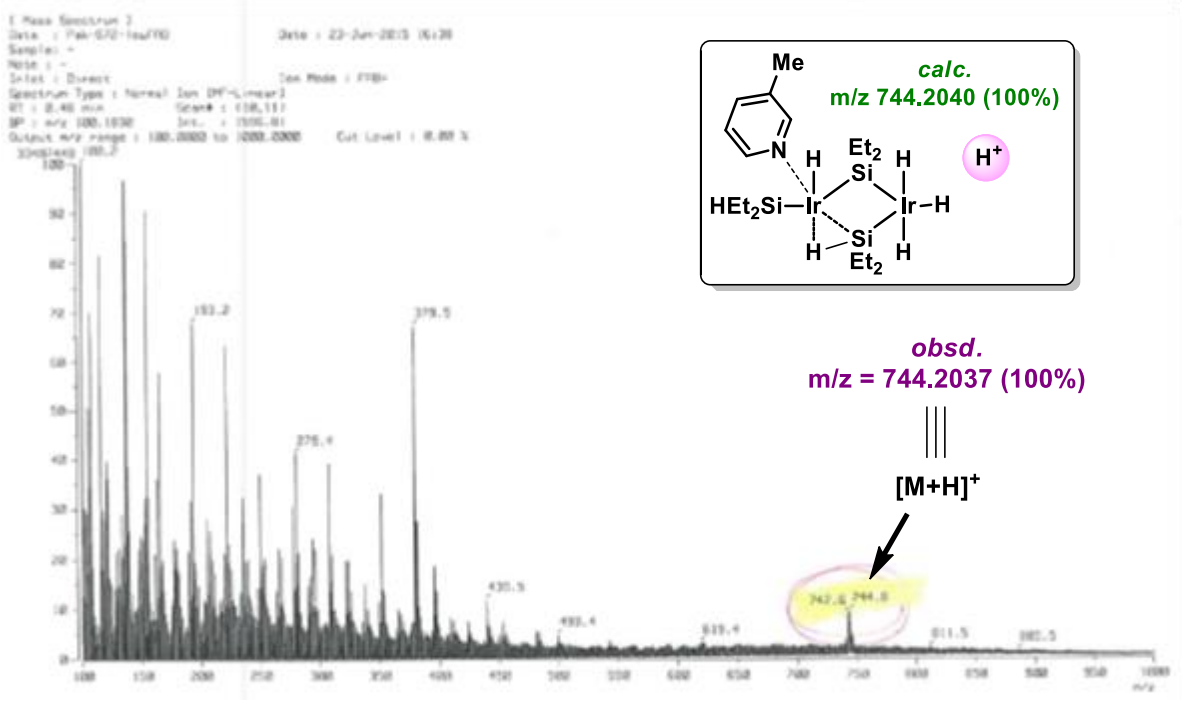


Fig. S8 **Low Resolution Mass Spectrum (FAB-mode) of 6b**

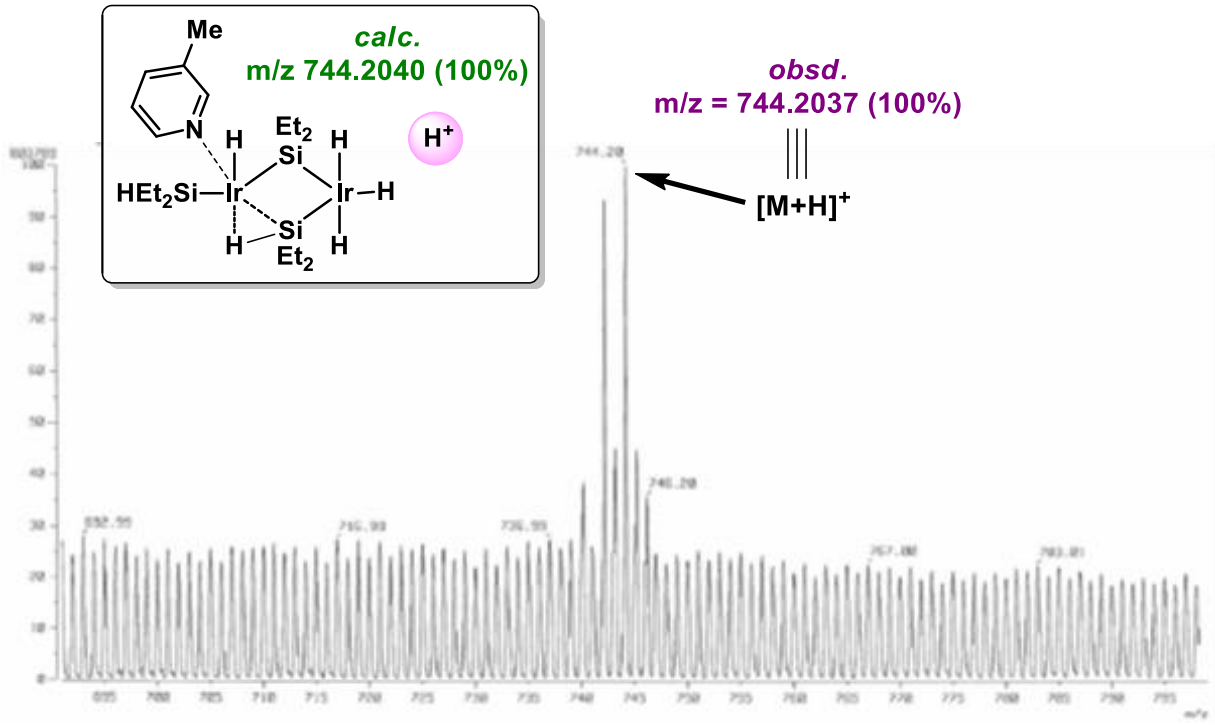
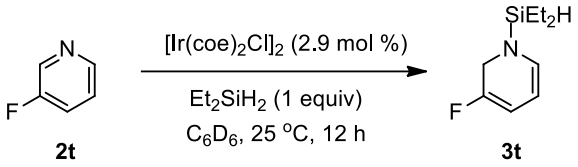


Fig. S9 **High Resolution Mass Spectrum (FAB-mode) of 6a**

VII. Observation of the Catalyst Resting Species in the Hydrosilylation Turnover



Diethylsilane (0.7 mmol, 1 equiv) was added to $[Ir(coe)_2Cl]_2$ (0.02 mmol, 2.9 mol %) in C_6D_6 (0.5 mL) in a medium-walled J-Young NMR tube under Ar atmosphere, and the solution was shaken briefly. After 5 min, 3-fluoropyridine (0.7 mmol, 1 equiv) was added into the solution under Ar atmosphere, and it was allowed to react at 25 °C for 12 h. The crude reaction mixture was then subject to NMR analysis.

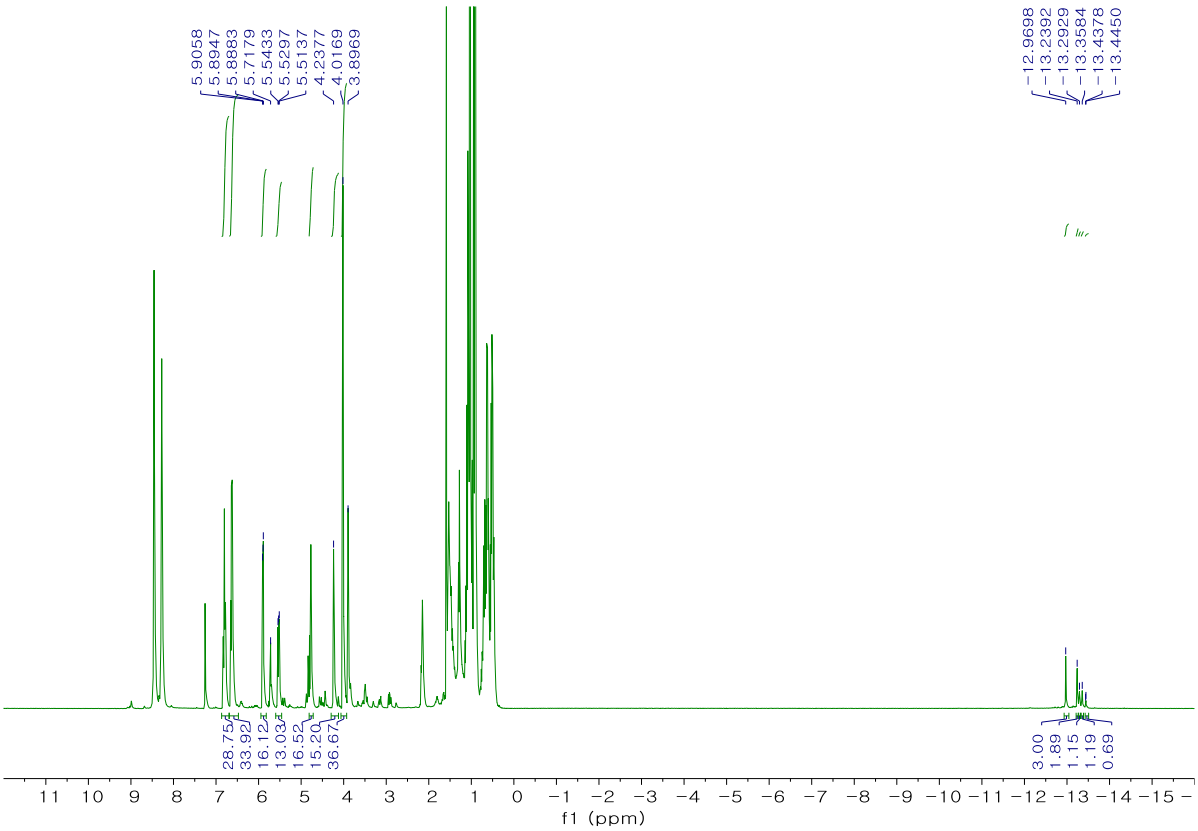


Fig. S10 **^{1}H NMR Spectrum of the 1,2-Hydrosilylation of 3-Fluoropyridine (2t) Using $[Ir(coe)_2Cl]_2$ (2.9 mol %) with Et_2SiH_2 (1 equiv) at 25 °C for 12 h (600 MHz, C_6D_6)**

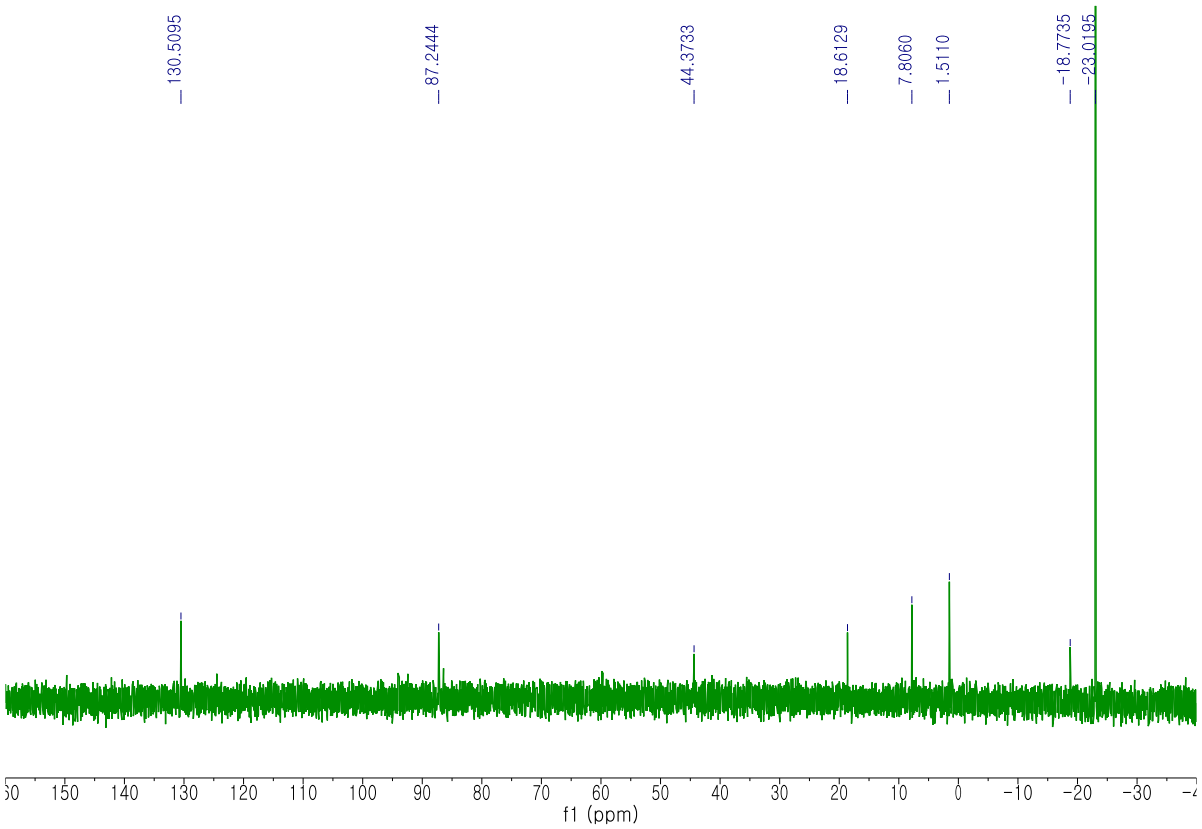


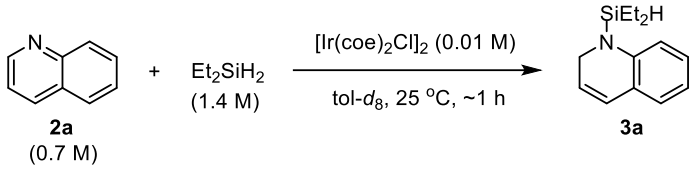
Fig. S11 **$^{29}Si\{^{1}H\}$ NMR Spectrum of the 1,2-Hydrosilylation of 3-Fluoropyridine (2t) Using $[Ir(coe)_2Cl]_2$ (2.9 mol %) with Et_2SiH_2 (1 equiv) at 25 ºC for 12 h (120 MHz, C_6D_6)**

VIII. Initial-Rate Kinetic Measurements (Scheme 4 and 5)

VIII-A. General Considerations for Kinetic Experiments

Reactions used for the kinetic analysis were set up in an Ar-filled J-Young NMR tube. Kinetic analysis of the NMR scale reaction was carried out by collecting multiple (10~20) data points early in the reaction before the substrate concentrations were depleted. Reaction progress was monitored by ^{1}H NMR (400 MHz, toluene-d_8) analysis at 50 sec intervals over 1 h at the specified temperature. The kinetic data were obtained from intensity increase in the dearomatized 1,2-dihydroquinoline-β-H integral over time (up to 20% conversion) on the basis of the internal standard of 1,4-dioxane to determine the initial reaction rate. Data were fit by least-squares analysis ($R^2 > 0.985$).

VIII-B. Representative Procedure for Initial-Rate Kinetics



Iridium species $[Ir(coe)_2Cl]_2$ (4.48 mg, 0.005 mmol, 1.4 mol %) was weighed into a J. Young NMR tube, dried *in vacuo*, and suspended in toluene-d_8 (350 μL) under Ar atmosphere, into which Et_2SiH_2 (90.7 μL, 0.7 mmol, 2 equiv) and 1,4-dioxane as an internal standard (8.5 μL, 0.1 mmol) were added, and then the mixture was briefly shaken for 10 min at r.t. as a homogeneous yellow solution formed. The NMR tube of the resulting solution was put in a pre-cooled bath at -60 °C under argon atmosphere. After 10 min, quinoline (**2a**, 0.35 mmol, 1 equiv) was gently added into the solution containing the Ir precatalyst and excess silane with maintaining the low temperature (< -60 °C), leading to a total reaction volume of approximately 500 μL. The NMR tube was well shaken to mix up all components for approximately 10 seconds, and was quickly put into the NMR probe that was pre-adjusted to the target temperature, 25 °C (298 K). Then, the 1,2-hydrosilylation of **2a** was monitored by ^{1}H NMR at 50 seconds intervals for 1 h to determine an initial rate (v_i) for the appearance of 1-(diethylsilyl)-1,2-dihydroquinoline (**3a**) (up to ~10% conversion) at 25 °C.

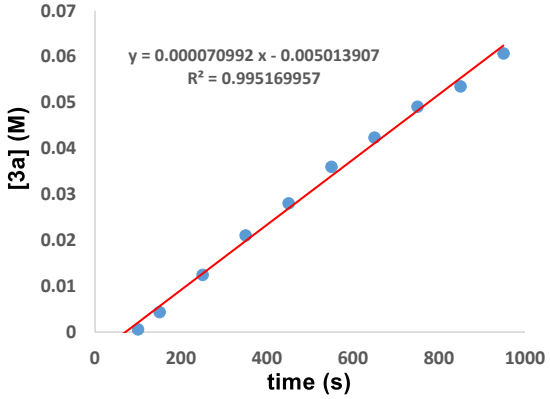
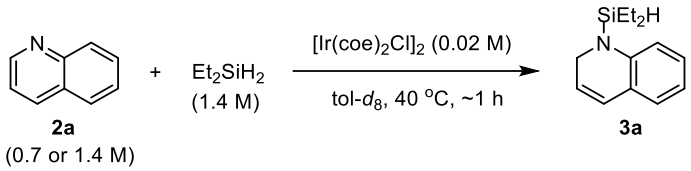


Fig. S12 **Reaction Profile for Initial Rate Calculation in the Reaction of Quinoline at 25 °C**

VIII-C. Reaction Monitoring



$[Ir(coe)_2Cl]_2$ (8.96 mg, 0.01 mmol, 2.9 mol %) was weighed into a J. Young NMR tube, dried *in vacuo*, and suspended in toluene-d_8 (350 μL) under Ar atmosphere, into which Et_2SiH_2 (90.7 μL, 0.7 mmol, 2 equiv) and 1,4-dioxane (internal standard, 8.5 μL, 0.1 mmol) were added, and then the mixture was briefly shaken for 10 min at r.t. as a homogeneous yellow solution formed. After 10 min, quinoline (**2a**, 0.35 mmol, 1 equiv) was added into the solution at < -60 °C, leading to a total reaction volume of approximately 500 μL. The NMR tube was well shaken to mix all components for approximately 10 seconds, and was quickly put into the NMR probe that was pre-adjusted to the target temperature, 40 °C (313 K). The 1,2-hydrosilylation of **2a** was monitored by ^{1}H NMR at 50 second intervals over 1 h to determine an initial rate (v_i) for the appearance of 1-(diethylsilyl)-1,2-dihydroquinoline (**3a**) (up to ~20% conversion) at 40 °C.

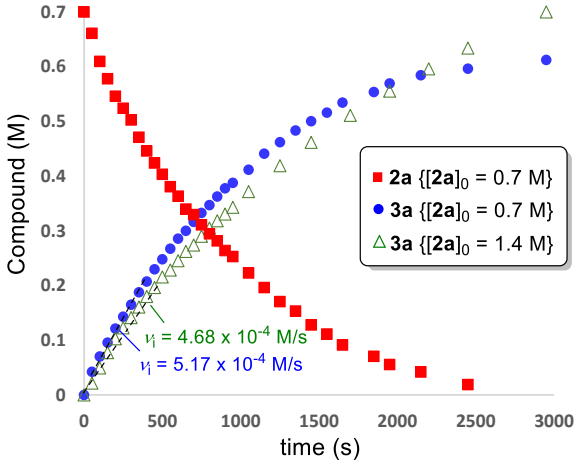
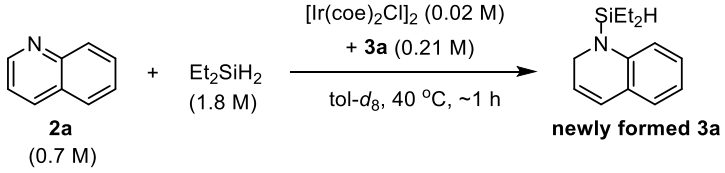


Fig. S13 **Plot of concentrations of 2a ($[2a]_0$ = 0.7 or 1.4 M) and 3a vs time at 40 °C**

VIII-D. Reaction Monitoring in the Presence of 3a



$[Ir(coe)_2Cl]_2$ (8.96 mg, 0.01 mmol, 2.9 mol %) was weighed into a J. Young NMR tube, dried *in vacuo*, and suspended in toluene-d_8 (200 μL) under Ar atmosphere, into which Et_2SiH_2 (90.7 μL, 0.7 mmol, 2 equiv) and 1,4-dioxane (internal standard, 8.5 μL, 0.1 mmol) were added, and then the mixture was briefly shaken for 10 min at r.t. as a homogeneous yellow solution formed. To this solution was added 150 μL of a stock solution containing **3a** (0.105 mmol) and Et_2SiH_2 (0.21 mmol) in toluene, and the NMR tube of the resulting mixture of Ir precatalyst, **3a**, and silane was put in a pre-cooled bath at -60 °C under argon atmosphere.

After 10 min, quinoline (**2a**, 0.35 mmol, 1 equiv) was added into the solution at the same temperature (< -60 °C), leading to a total reaction volume of approximately 500 μL. The NMR tube was well shaken to mix all components for approximately 10 seconds, and was quickly put into the NMR probe that was pre-adjusted to the target temperature, 40 °C (313 K). The 1,2-hydrosilylation of **2a** was monitored by ^{1}H NMR at 50 second intervals over 1 h to determine an initial rate (v_i) for the appearance of newly formed 1-(diethylsilyl)-1,2-dihydroquinoline (**3a**) (up to ~20% conversion) at 40 °C.

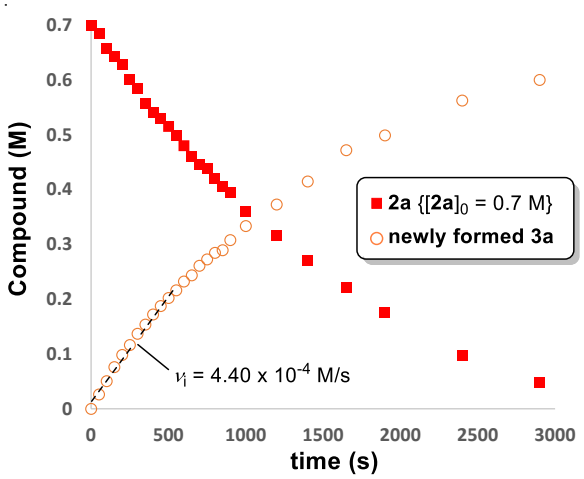
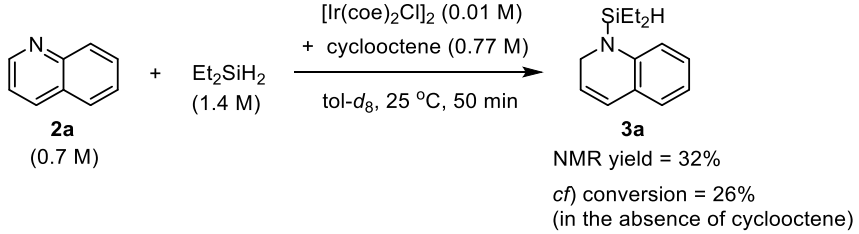


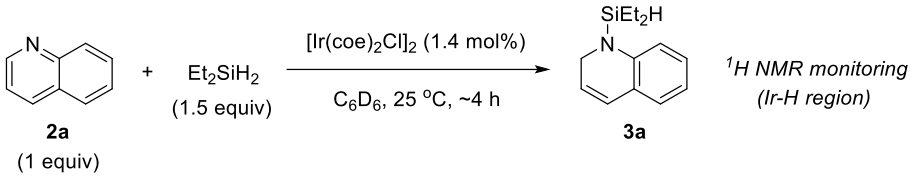
Fig. S14 **Plot of Concentrations of 2a ([2a]$_0$ = 0.7 M) and newly formed 3a vs time in the presence of 3a (0.21 M) at 40 °C**

VIII-E. Hydrosilylation of 2a in the Presence of Cyclooctene



Iridium species $[Ir(coe)_2Cl]_2$ (4.48 mg, 0.005 mmol, 1.4 mol %) was weighed into a J. Young NMR tube, dried *in vacuo*, and suspended in toluene-d_8 (300 μL) under Ar atmosphere, into which Et_2SiH_2 (90.7 μL, 0.7 mmol, 2 equiv), cyclooctene (50 μL, 0.39 mmol, 1.1 equiv), and 1,4-dioxane as an internal standard (8.5 μL, 0.1 mmol) were added, and then the mixture was briefly shaken for 10 min at r.t. as a homogeneous yellow solution formed. After 10 min, quinoline (**2a**, 0.35 mmol, 1 equiv) was gently added into the solution containing the Ir precatalyst, excess silane, and cyclooctene, leading to a total reaction volume of approximately 500 μL. The NMR tube was well shaken to mix up all components for approximately 10 seconds, and was quickly put into the NMR probe that was pre-adjusted to the target temperature, 25 °C (298 K). Then, the 1,2-hydrosilylation of **2a** was monitored by ^{1}H NMR at 25 °C.

VIII-F. ^{1}H NMR Monitoring of the *Ir-H Region* during Hydrosilylation of 2a



$[Ir(coe)_2Cl]_2$ (4.48 mg, 0.005 mmol, 1.4 mol %) was weighed into a J. Young NMR tube, dried *in vacuo*, and suspended in C_6D_6 (350 μL) under Ar atmosphere, into which Et_2SiH_2 (68.0 μL, 0.525 mmol, 1.5 equiv) was added, and then the mixture was briefly shaken for 10 min at r.t. as a homogeneous yellow solution formed. Then, quinoline **2a** (0.35 mmol, 1.0 equiv) was added into the solution containing the Ir precatalyst and excess silane. The 1,2-hydrosilylation of **2a** was monitored over 4 h at 25 °C by ^{1}H NMR especially in order to observe the *Ir-H resting species* during the catalytic turnover.

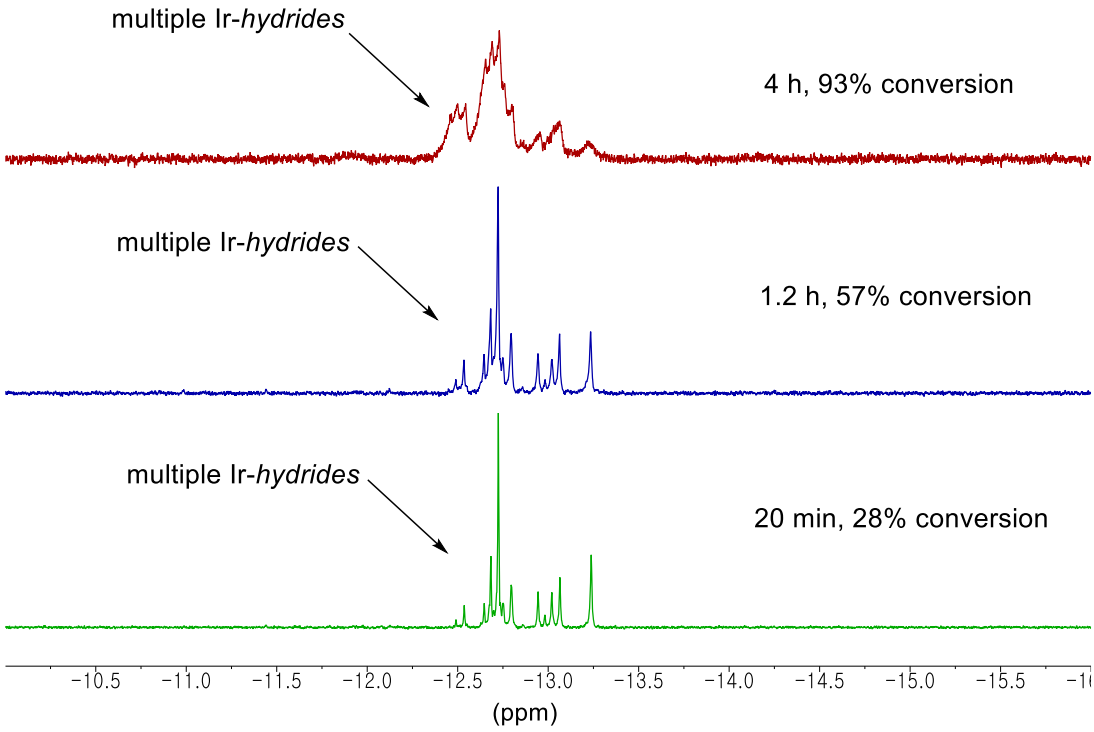
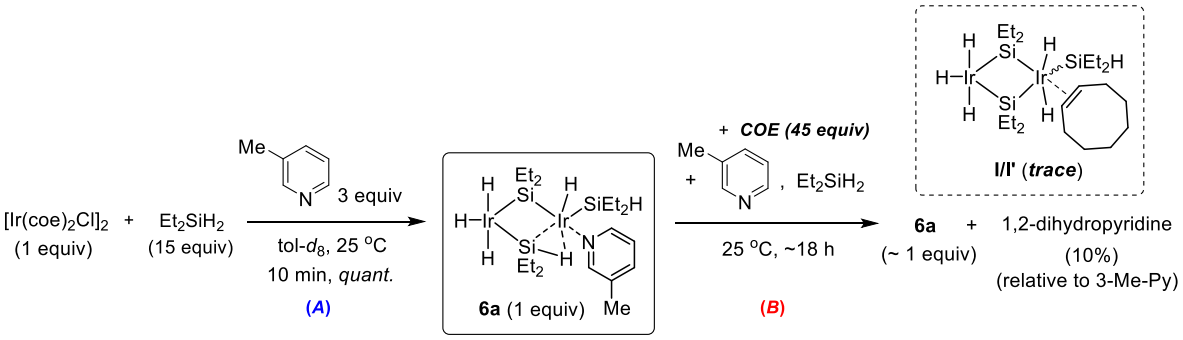


Fig. S15 **Expansion (δ -10.0 ~ -16.0) of the ^{1}H NMR Spectra of the Hydrosilylation of 2a at 25 °C over 4 h (400 MHz, C_6D_6)**

VIII-G. Stoichiometric Reaction of $[Ir(coe)_2Cl]_2$, Et_2SiH_2, 3-Methylpyridine, and *COE* in a ratio of 1:15:3:*45* at 25 °C



(*A*) $[Ir(coe)_2Cl]_2$ (17.7 mg, 0.02 mmol, 1 equiv) was weighed into a J. Young NMR tube, dried *in vacuo*, and suspended in toluene-d_8 (0.5 mL) under Ar atmosphere, into which Et_2SiH_2 (38.9 μL, 15 equiv) was added, and then the solution was shaken briefly at 25 °C (being homogeneous in 10 min). Subsequently, to this mixture in toluene-d_8 was added 3-methylpyridine (5.8 μL, 3 equiv) under argon atmosphere, and it was allowed to react at 25 °C to quantitatively form **6a** in 10 min.

(***B***) Up on confirming the formation of **6a**, ***cyclooctene*** (***COE***, 117.0 μL = 45 equiv) was directly added into the reaction mixture of (***A***). Prolonged reaction up to 18 h at 25 °C led to the formation of 3-methyl-1-(diethylsilyl)-1,2-dihydropyridine in 10% NMR yield with the exclusive observation of **6a**, *but trace **I/I'** detected throughout the reaction*.

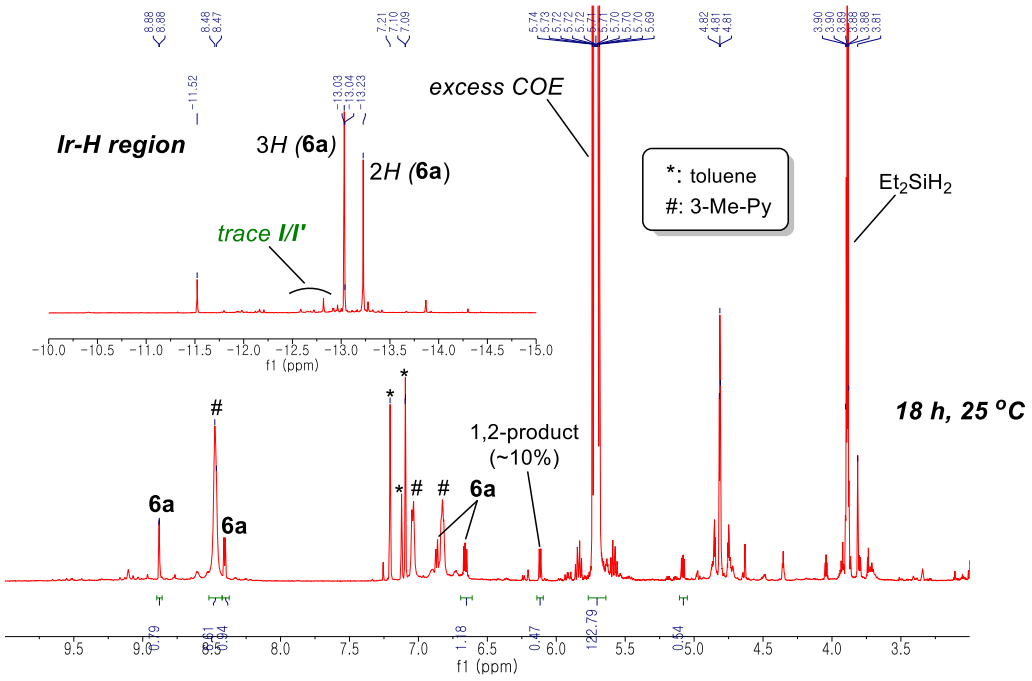
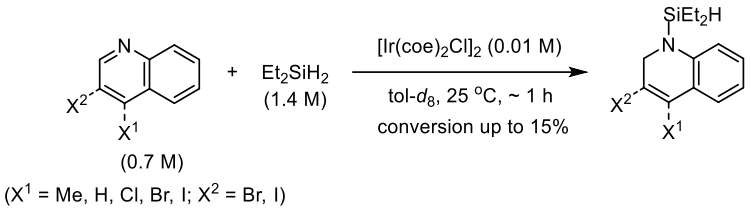


Fig. S16 **^{1}H NMR spectrum of a reaction of $[Ir(coe)_2Cl]_2$, Et_2SiH_2, 3-methylpyridine, and *COE* in a ratio of 1:15:3:*45* in *18 h at 25 °C* (*B*)**

VIII-H. Relative Initial Rates of Substituted Quinolines (Separated Vessel)



$[Ir(coe)_2Cl]_2$ (4.48 mg, 0.005 mmol, 1.4 mol %) was weighed into a J. Young NMR tube, dried *in vacuo*, and suspended in toluene-d_8 (350 μL) under Ar atmosphere, into which Et_2SiH_2 (90.7 μL, 0.7 mmol, 2 equiv) and 1,4-dioxane (internal standard, 8.5 μL, 0.1 mmol) were added, and then the mixture was briefly shaken for 10 min at r.t. as a homogeneous yellow solution formed. The NMR tube of the resulting solution was put in a pre-cooled bath at -60 °C under argon atmosphere. After 10 min, the quinoline substrate (0.35 mmol, 1.0 equiv) was added into the solution containing the Ir precatalyst and excess silane at the same temperature (< -60 °C), leading to a total reaction volume of approximately 500 μL. The NMR tube was then well shaken to mix all components for approximately 10 seconds, and was quickly put into the NMR probe that was pre-adjusted to the target temperature, 25 °C (298 K). The 1,2-hydrosilylation of the quinoline was monitored by ^1H NMR at 50 second interval over 1 h to determine the initial rate (ν_i) for the appearance of dihydroquinoline product (up to ~15% conversion) at 25 °C.

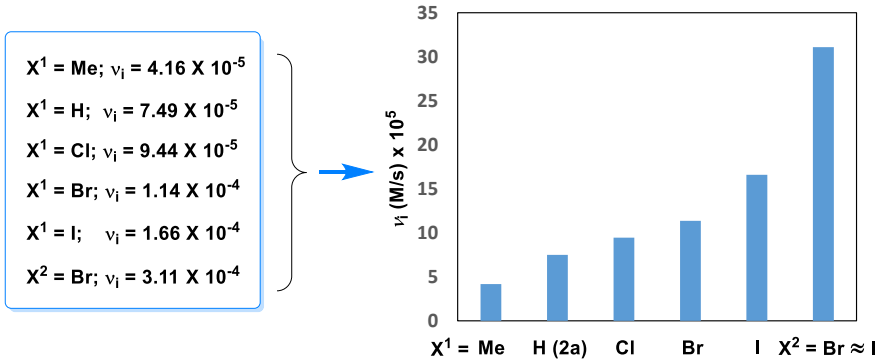
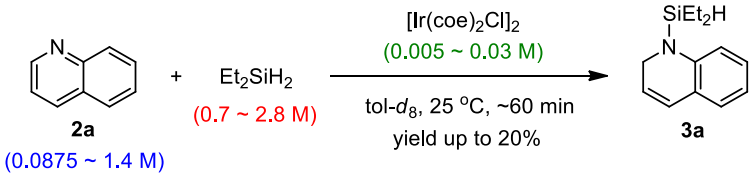


Fig. S17 **Initial Rate as a Function of Quinoline Substituents in the 1,2-Hydrosilylation of Quinolines with Et_2SiH_2 at 25 °C in Separated Flasks**

VIII-I. Rate-Order Assessment Based on Initial-Rate Kinetics



$[Ir(coe)_2Cl]_2$ (2.2~13.4 mg, 0.0025~0.015 mmol) was weighed into a J. Young NMR tube, dried *in vacuo*, and suspended in toluene-d_8 under Ar atmosphere, into which Et_2SiH_2 (45.3~181.2 μL, 0.35~1.4 mmol) and 1,4-dioxane (internal standard, 8.5 μL, 0.1 mmol) were added, and then the mixture was briefly shaken

for 10 min at r.t. as a homogeneous yellow solution formed. The NMR tube of the resulting solution was put in a pre-cooled bath at -60 °C under argon atmosphere. After 10 min, quinoline (**2a**, 0.044~0.7 mmol, 1 equiv) was added into the solution containing the Ir precatalyst and excess silane at the same temperature (< -60 °C), leading to a total reaction volume of approximately 500 μL. The NMR tube was well shaken to mix up all components for approximately 10 seconds, and was quickly put into the NMR probe that was pre-adjusted to the target temperature, 25 °C (298 K). The 1,2-hydrosilylation of **2a** was then monitored by ^{1}H NMR at 50 second intervals over 1 h to determine the initial rate (ν_i) for the appearance of 1-(diethylsilyl)-1,2-dihydroquinoline (**3a**) (up to ~20% conversion) at 25 °C.

(1) Iridium Rate Order

$[(Ir(coe)_2Cl)_2]$ (M)	Rate (M/s)	R^2
0.005	0.00002296	0.9949
0.005	0.00002555	0.9952
0.01	0.00007885	0.9882
0.01	0.00007099	0.9952
0.02	0.0001281	0.9868
0.02	0.0001281	0.9875
0.03	0.0002397	0.9865

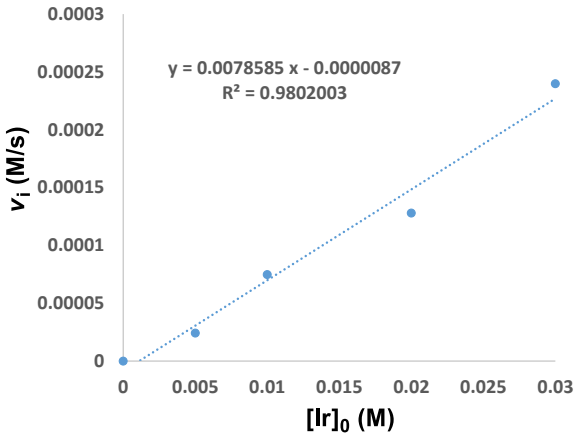


Fig. S18 **Plot of the Initial Rate, v_i of Appearance of 3a vs $[Ir(coe)_2Cl]_2$ Concentration at 25 °C**

(2) Silane Rate Order

Et_2SiH_2 (M)	Rate (M/s)	R^2
0.7	0.00006654	0.9952
0.7	0.00006684	0.9902
1.4	0.00007885	0.9882
1.4	0.00007099	0.9952
2.0	0.00007641	0.9924
2.0	0.00008084	0.9980
2.8	0.00008040	0.9865
2.8	0.00007577	0.9973

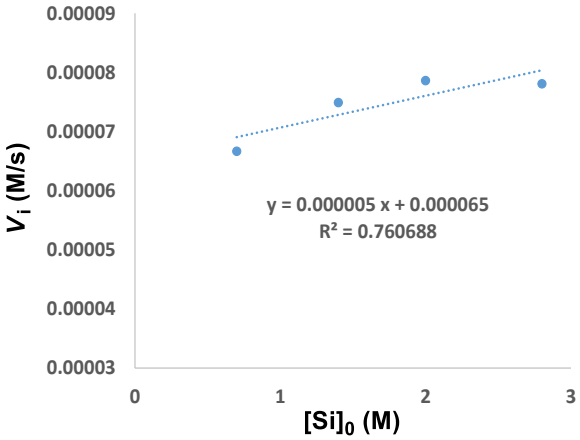


Fig. S19 **Plot of the Initial Rate, v_i of Appearance of 3a vs Et_2SiH_2 Concentration at 25 °C**

(3) Quinoline Rate Order

Quinoline (M)	Rate (M/s)	R^2
0.0875	0.00003463	0.9929
0.175	0.00005324	0.9920
0.175	0.00004921	0.9968
0.35	0.00006230	0.9933
0.7	0.00007885	0.9882
0.7	0.00007099	0.9952
1.0	0.00007429	0.9865
1.0	0.00008378	0.9931
1.4	0.00007047	0.9966
1.4	0.00007739	0.9918

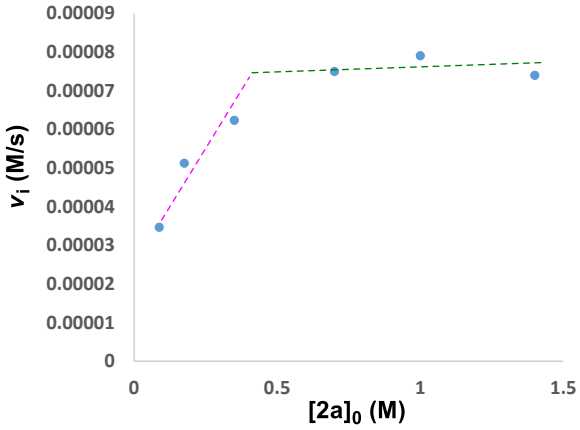
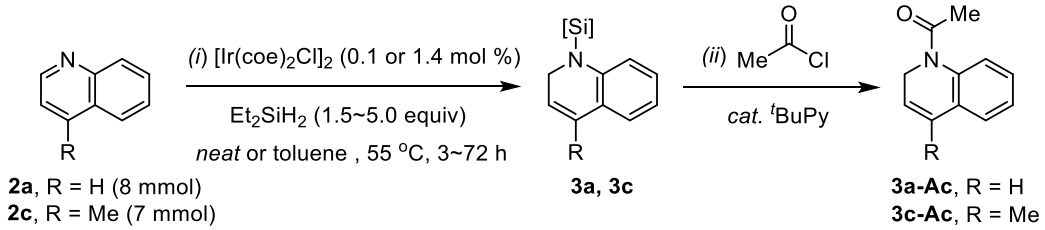


Fig. S20 **Plot of the Initial Rate, v_i of Appearance of 3a vs 2a Concentration at 25 ºC**

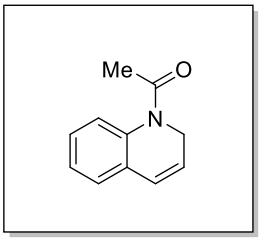
IX. Synthetic Applications (Scheme 7)



(*i*) Diethylsilane (12 mmol for **3a-Ac** or 10.5 mmol for **3c-Ac**, 1.5 equiv) was added to a solution of $[Ir(coe)_2Cl]_2$ (0.008 to 0.098 mmol, 0.1 to 1.4 mol %) in *neat* (for **3a-Ac**) or toluene (7 mL) (for **3c-Ac**) in a flame dried round-bottom flask (25 mL) under Ar atmosphere, and the solution was stirred for 5 min. Quinoline substrate (**2a**, 8 mmol *or* **2c**, 7 mmol, 1.0 equiv, respectively) was added into the solution under Ar atmosphere and stirred at 55 °C for 72 h (for **3a-Ac**) or 3 h (for **3c-Ac**). The resulting mixture was subjected to *N*-acetylation using acetyl chloride.

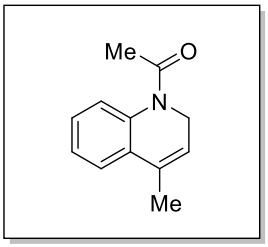
(*ii*) The catalytic reaction mixture was diluted with toluene (1 mL) in case of the neat reaction, and cooled down to 0 °C. Acetyl chloride (6 mmol, 1.2 equiv) with the catalytic amount of *tert*-butylpyridine (0.8 mmol, 0.1 equiv, 10 mol %) in toluene (5 mL) was slowly added into the above reaction mixture at 0 °C. Then, the mixture was allowed to react at room temperature for 12 h, evaporated under reduced pressure, and purified by column chromatography on silica gel (EA/Hx = 1/4) to give the corresponding *N*-acetylated 1,2-dihydroquinoline products (**3a-Ac**, 1.25 g, 90%; **3c-Ac**, 1.03 g, 78% over two steps).

1-[Quinolin-1(2H)-yl]ethan-1-one (3a-Ac) [Isolated yield = 90% (1.25 g)]

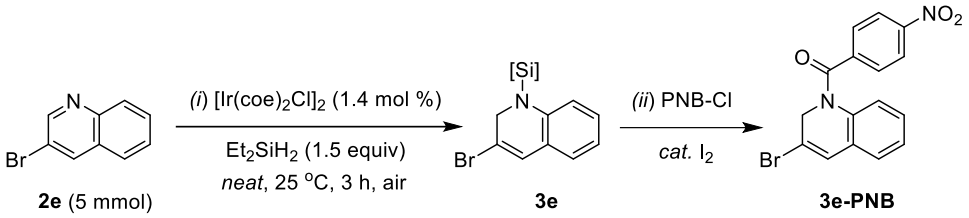


Yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.07 (m, 4H), 6.58 (d, J = 9.5 Hz, 1H), 6.13 (dt, J = 9.0, 4.2 Hz, 1H), 4.46 (s, 2H), 2.20 (s, 3H); **^{13}C NMR (**100 MHz, $CDCl_3$**)** δ 169.5, 137.2, 129.2, 128.1, 127.0, 126.3, 126.2, 125.4, 123.9, 41.4, 22.3; **IR** (cm^{-1}): 3042, 2985, 2841, 1654, 1568, 1458, 1219, 752; **HRMS** (EI): Calculated for $C_{11}H_{11}NO$ $[M]^+$: 173.0841, Found: 173.0838.

1-[4-Methylquinolin-1(2H)-yl]ethan-1-one (3c-Ac) [Isolated yield = 78% (1.03 g)]

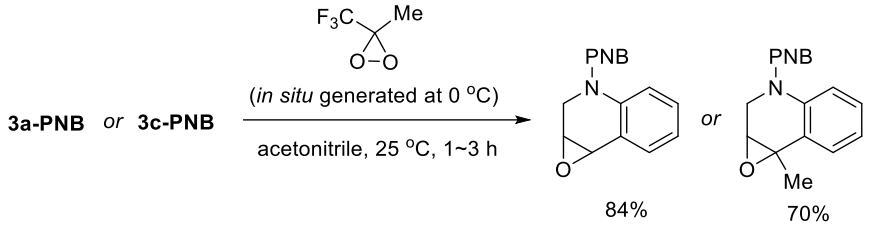


Yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 6.94 (m, 1H), 5.83 (s, 1H), 4.35 (s, 2H), 2.14 (s, 3H), 2.02 (s, 3H); **^{13}C NMR (**100 MHz, $CDCl_3$**)** δ 169.7, 137.1, 131.5, 131.0, 126.9, 125.5, 124.4, 123.8, 123.4, 41.2, 22.3, 18.1; **IR** (cm^{-1}): 3034, 2942, 2849, 1639, 1567, 1452, 1211, 755; **HRMS** (EI): Calculated for $C_{12}H_{13}NO$ $[M]^+$: 187.0997, Found: 187.0995.



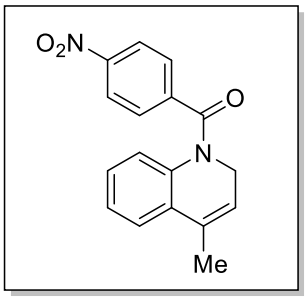
(*i*) Diethylsilane (7.5 mmol, 1.5 equiv) was added to a solution of $[Ir(coe)_2Cl]_2$ (0.07 mmol, 1.4 mol %) in *neat* in a flame dried round-bottom flask (25 mL) under Ar atmosphere, and the solution was stirred for 5 min. Quinoline substrate (**2e**, 5 mmol, 1 equiv) was added into the solution under Ar atmosphere and stirred at 25 °C for 3 h under air. The resulting mixture was subjected to *N*-benzoylation using 4-nitrobenzoyl chloride.

(*ii*) The catalytic reaction mixture was diluted with acetonitrile (1 mL) and cooled down to 0 °C. 4-Nitrobenzoyl chloride (6.0 mmol, 1.2 equiv) with catalytic amount of I_2 (0.5 mmol, 0.1 equiv, 10 mol %) in acetonitrile (3 mL) was slowly added into the above reaction mixture at 0 °C. Then, the mixture was allowed to react at r.t. for 1 h, evaporated under reduced pressure. The desired N-benzoylated 1,2-dihydroquinoline **3e-PNB** was recrystallized out by using acetonitrile and ether, and finally filtered to give **3e-PNB** (1.54 g, 86% over two steps).



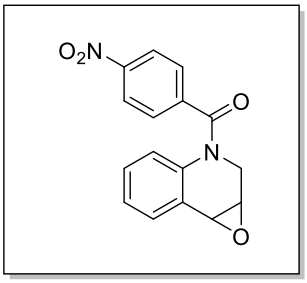
To a flame dried round-bottom flask (25 mL) were added **3a-PNB** or **3c-PNB** (0.5 mmol, 1 equiv), acetonitrile (0.35 mL), and aqueous Na_2EDTA (ethylenediaminetetraacetic acid disodium salt) solution (2.5 mL, 4 x 10^{-4} M). After sealing the flask with a septum, the resulting homogeneous solution was cooled to 0 °C, followed by addition of 1,1,1-trifluoroacetone (1.0~1.5 mL) via a pre-cooled syringe. To this solution was added a mixture of $NaHCO_3$ (0.23 g, 2.75 mmol, 5.5 equiv) and $KHSO_5$ (0.77 g, 2.5 mmol, 5 equiv), and the mixture was stirred for 1~3 h at 25 °C. The reaction mixture was poured into distilled water (30 mL), extracted with CH_2Cl_2 (3 x 20 mL), and dried over anhydrous Na_2SO_4. The solution was filtered, evaporated under reduced pressure, and purified by flash column chromatography on silica gel (ethyl acetate/*n*-hexane, 1:4) to give the corresponding epoxidation products in 84% (from **3a-PNB**) and 70% (from **3c-PNB**) isolated yields over two steps.[S6]

[4-Methylquinolin-1(2H)-yl](4-nitrophenyl)methanone



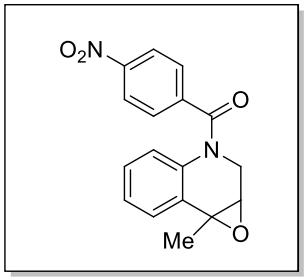
Yellow solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 7.5 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 6.88 (s, 1H), 6.50 (s, 1H), 5.96 (s, 1H), 4.49 (s, 2H), 2.16 (s, 3H); **^{13}C NMR (**100 MHz, $CDCl_3$**)** δ 167.2, 148.5, 141.7, 136.2, 131.6, 130.1, 129.9 (2C), 126.9, 125.7, 124.7, 123.8, 123.4 (2C), 122.9, 43.2, 18.3; **IR** (cm^{-1}): 3051, 2854, 1645, 1598, 1521, 1486, 1454, 768; **HRMS** (EI): Calculated for $C_{17}H_{14}N_2O_3$ $[M]^+$: 294.1004, Found: 294.1002.

[1a,7b-Dihydrooxireno[2,3-c]quinolin-3(2H)-yl](4-nitrophenyl)methanone (Isolated yield = 84%)

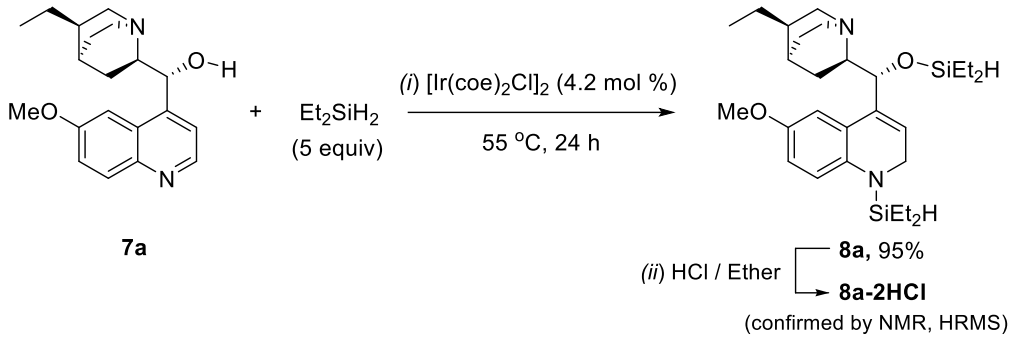


White solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.3 Hz, 2H), 7.58 – 7.42 (m, 3H), 7.11 (t, J = 7.6 Hz, 1H), 6.97 (t, J = 7.8 Hz, 1H), 6.42 (s, 1H), 5.19 (d, J = 14.1 Hz, 1H), 4.04 (s, 2H), 3.18 (d, J = 14.1 Hz, 1H); **^{13}C NMR (**100 MHz, $CDCl_3$**)** δ 168.8, 148.4, 141.9, 137.2, 130.0, 129.8 (2C), 128.7, 126.4, 126.1, 126.0, 123.3 (2C), 58.1, 51.0, 40.4; **IR** (cm^{-1}): 2864, 1641, 1601, 1523, 1493, 1342, 849, 787; **HRMS** (EI): Calculated for $C_{16}H_{12}N_2O_4$ $[M]^+$: 296.0797, Found: 296.0798.

[7b-Methyl-1a,7b-dihydrooxireno[2,3-c]quinolin-3(2H)-yl](4-nitrophenyl)methanone (Isolated yield = 70%)



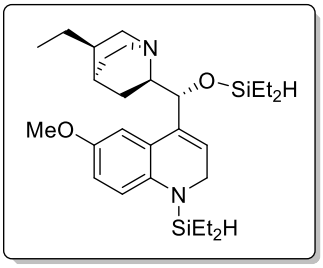
White solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 7.8 Hz, 1H), 7.52 (d, J = 8.3 Hz, 2H), 7.16 (t, J = 7.6 Hz, 1H), 7.04 – 6.92 (m, 1H), 6.43 (s, 1H), 5.20 (d, J = 14.1 Hz, 1H), 3.82 (s, 1H), 3.28 (d, J = 14.0 Hz, 1H), 1.89 (s, 3H); **^{13}C NMR (**150 MHz, $CDCl_3$**)** δ 168.7, 148.4, 142.0, 137.0, 129.9 (2C), 128.9, 128.2, 127.6, 126.2, 126.0, 123.2 (2C), 64.3, 54.4, 40.8, 19.1; **IR** (cm^{-1}): 2921, 1650, 1604, 1522, 1493, 1345, 849, 711; **HRMS** (EI): Calculated for $C_{17}H_{14}N_2O_4$ $[M]^+$: 310.0954, Found: 310.0950.



(*i*) Diethylsilane (1.75 mmol, 5.0 equiv) in *neat* was added to a J-Young NMR tube containing $[Ir(coe)_2Cl]_2$ (0.015 mmol, 4.2 mol %) and hydroquinine (**7a**, 0.35 mmol, 1.0 equiv) under argon atmosphere, and the solution was allowed to react at 55 °C for 24 h.

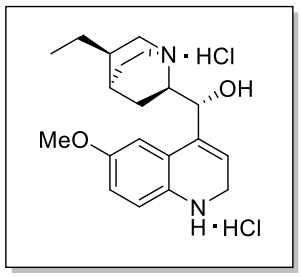
(*ii*) To the resulting crude mixture in a J-Young NMR tube was subsequently dropwise added 2 M HCl solution in ether (1.5 mL) at -78 °C and the mixture was vigorously stirred. After 1 h, the precipitated salts were filtered and washed with ether (3 mL x 3) at 25 °C to give the desired product (**8a-2HCl**). The structure of **8a-2HCl** was confirmed by 1D/2D-NMR experiments (DMSO-d_6), HRMS, and IR. However, **8a-2HCl** in DMSO was found to readily undergo rearomatization (*e.g.* 25% rearomatization in 30 min at 25 °C).

(1*S*,2*R*,4*S*,5*R*)-2-[(*R*)-(1-(diethylsilyl)-6-methoxy-1,2-dihydroquinolin-4-yl]-[(diethylsilyl)oxymethyl]-5-ethylquinuclidine (8a) (Crude yield = 95%)



^{1}H NMR (400 MHz, C_6D_6, selected data) δ 7.24 – 7.11 (m, 1H), 6.78 (d, J = 8.7 Hz, 1H), 6.54 (dd, J = 8.7, 2.9 Hz, 1H), 5.76 (s, 1H), 4.81 – 4.65 (m, 1H), 4.62 (quint, J = 2.4 Hz, 1H), 4.49 (quint, J = 3.3 Hz, 1H), 3.68 (d, J = 4.5 Hz, 2H), 3.47 (s, 3H), 3.19 – 3.03 (m, 1H), 3.01 – 2.91 (m, 1H), 2.81 (dd, J = 13.5, 8.7 Hz, 1H), 2.49 – 2.37 (m, 1H); **^{13}C NMR (**100 MHz, C_6D_6**)** δ 153.5, 139.3, 137.0, 129.8, 120.9, 119.1, 112.5, 109.9, 59.1, 58.6, 54.6, 45.0, 42.7, 42.4, 37.9, 27.6, 11.9, 7.9, 7.1, 6.6, 6.5, 5.6, 5.2, 2.4.

(1*S*,2*R*,4*S*,5*R*)-5-Ethyl-2-[(*R*)-hydroxy(6-methoxy-1,2-dihydroquinolin-1-ium-4-yl)methyl]-quinuclidin-1-ium chloride (8a-2HCl)



White solid; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 11.65 (s, 2H), 11.08 (s, 1H), 7.46 (d, J = 8.7 Hz, 1H), 7.39 (d, J = 2.7 Hz, 1H), 6.95 (dd, J = 8.8, 2.6 Hz, 1H), 6.31 (t, J = 4.1 Hz, 1H), 5.46 (s, 1H), 3.91 (dd, J = 16.4, 5.1 Hz, 1H), 3.83 (s, 3H), 3.82 – 3.72 (m, 2H), 3.37 – 3.29 (m, 1H), 3.18 (t, J = 7.0 Hz, 1H), 3.01 (td, J = 11.7, 5.6 Hz, 1H), 2.69 (dd, J = 13.1, 5.5 Hz, 1H), 1.93 – 1.89 (m, 1H), 1.89 – 1.82 (m, 2H), 1.82 – 1.73 (m, 2H), 1.66 (t, J = 10.0 Hz, 1H), 1.34 – 1.20 (m, 2H), 0.76 (t, J = 7.3 Hz, 3H); **^{13}C NMR (**150 MHz, $CDCl_3$**)** δ 160.0, 135.8, 128.4, 123.7, 123.4, 121.9, 114.5, 110.7, 66.9, 65.3 (ether), 58.6, 56.7, 55.4, 42.7, 40.9, 35.1, 26.2, 24.7, 24.5, 15.6 (ether), 11.9, 7.3; **IR** (cm^{-1}): 3246 (OH stretch), 2932, 1590, 1503, 1457, 1260, 1033, 827; **HRMS** (EI): Calculated for $C_{20}H_{29}N_2O_2$ $[M\text{-}Cl\text{-}HCl]^+$: 329.2229, Found: 329.2228.

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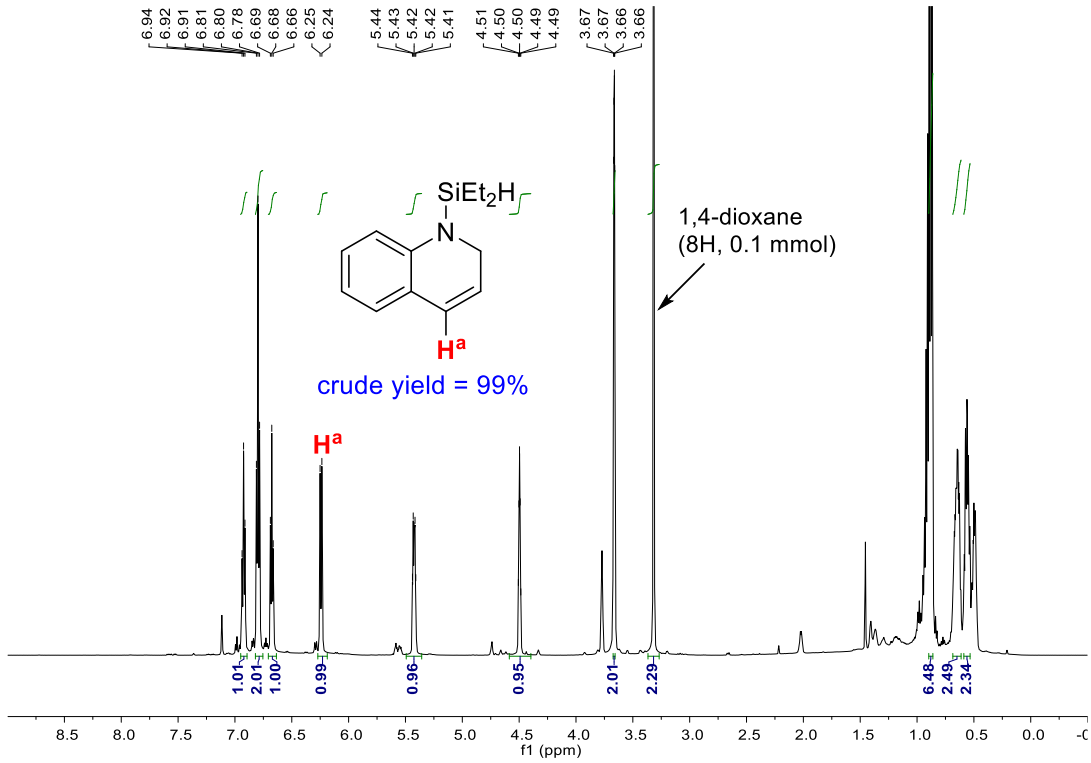
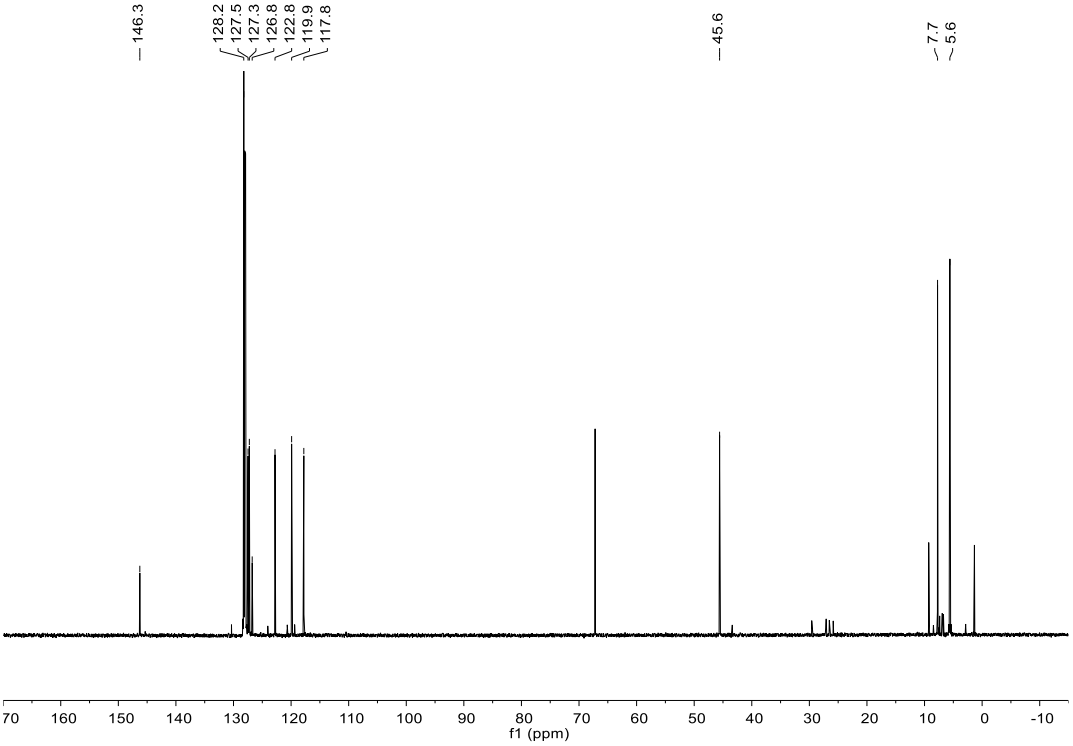
Appendix I

Spectral Copies of ^{1}H and ^{13}C NMR of Compounds Obtained in This Study

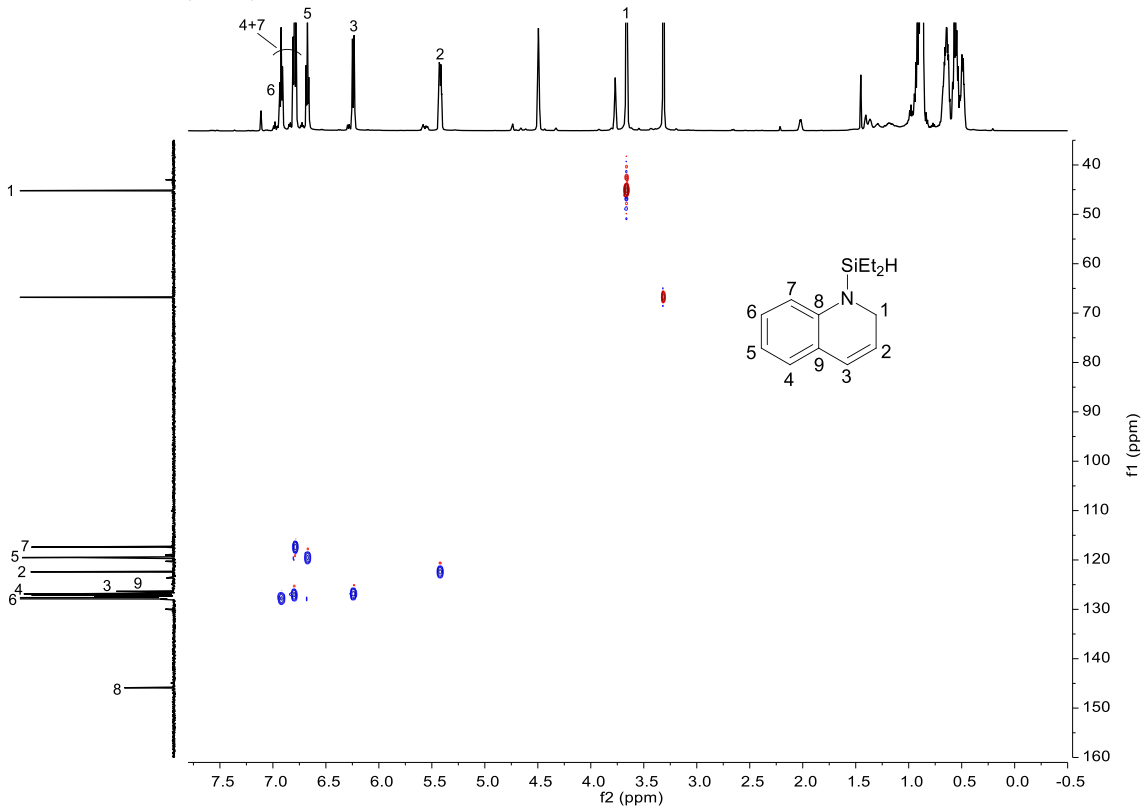
1-(Diethylsilyl)-1,2-dihydroquinoline (Table 2, 3a)

^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); 1,4-dioxane (internal standard)

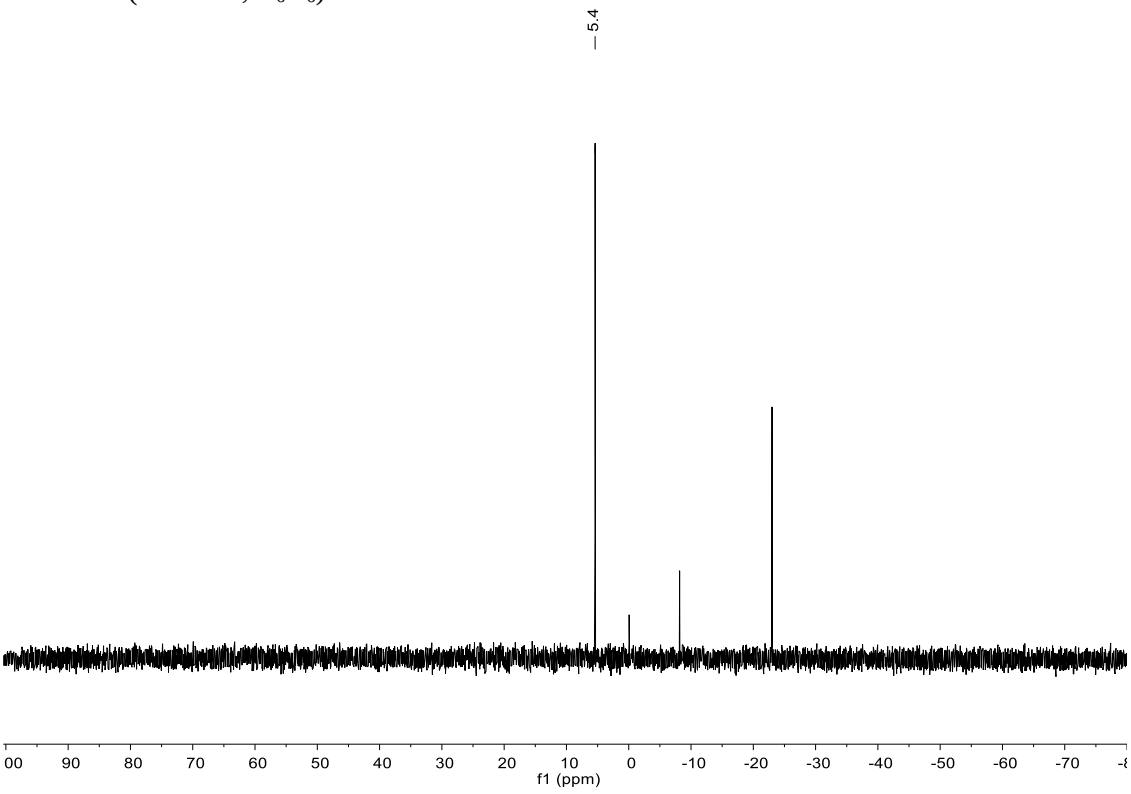




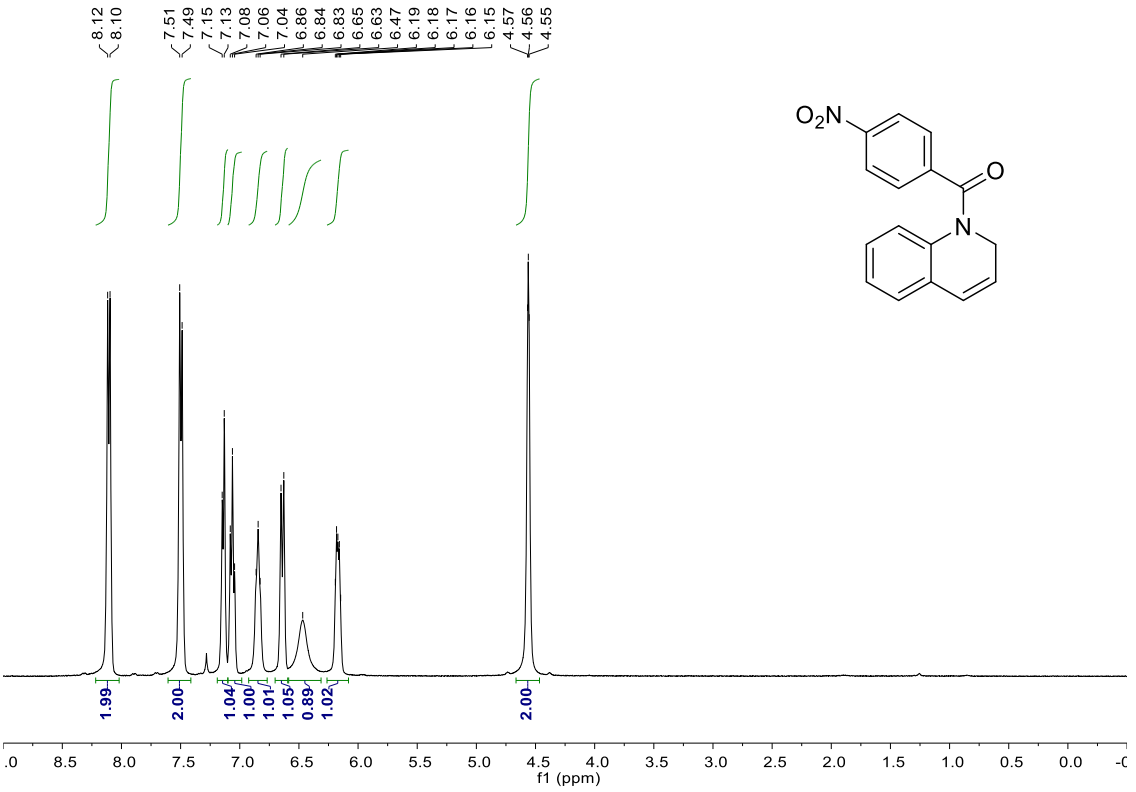
^{1}H -^{13}C HSQC (C_6D_6)

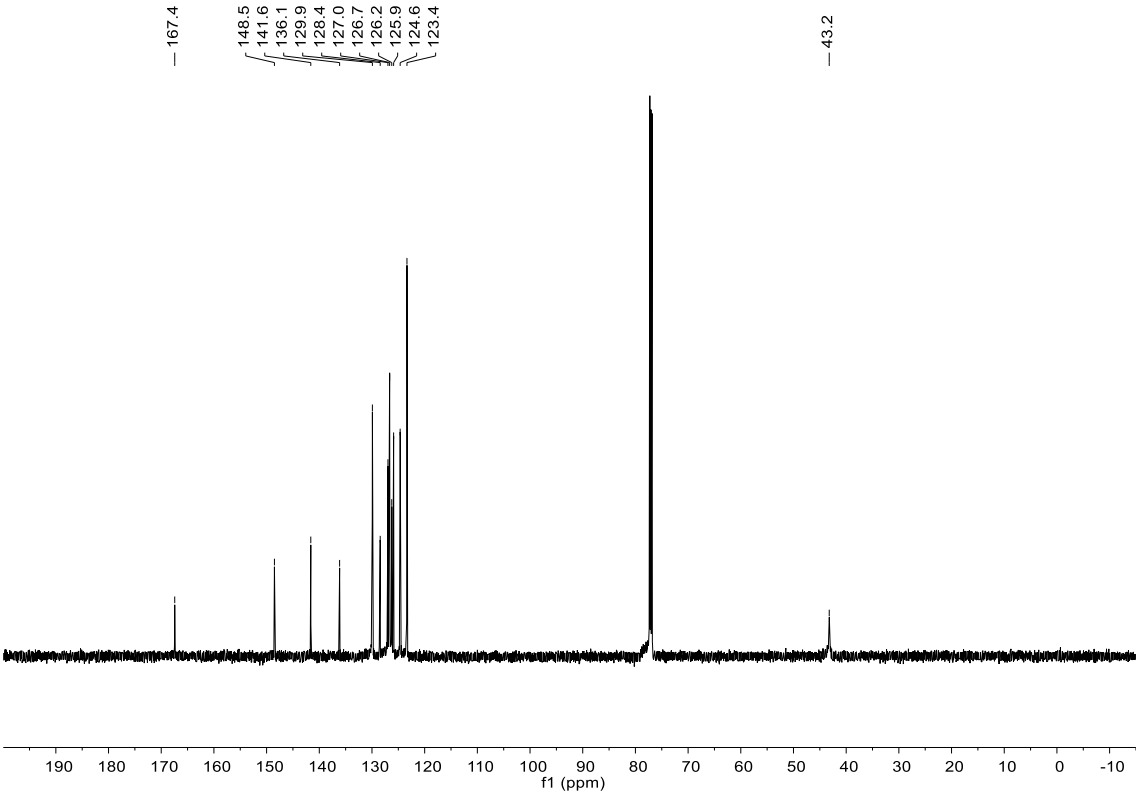


^{29}Si NMR (120MHz, C_6D_6)

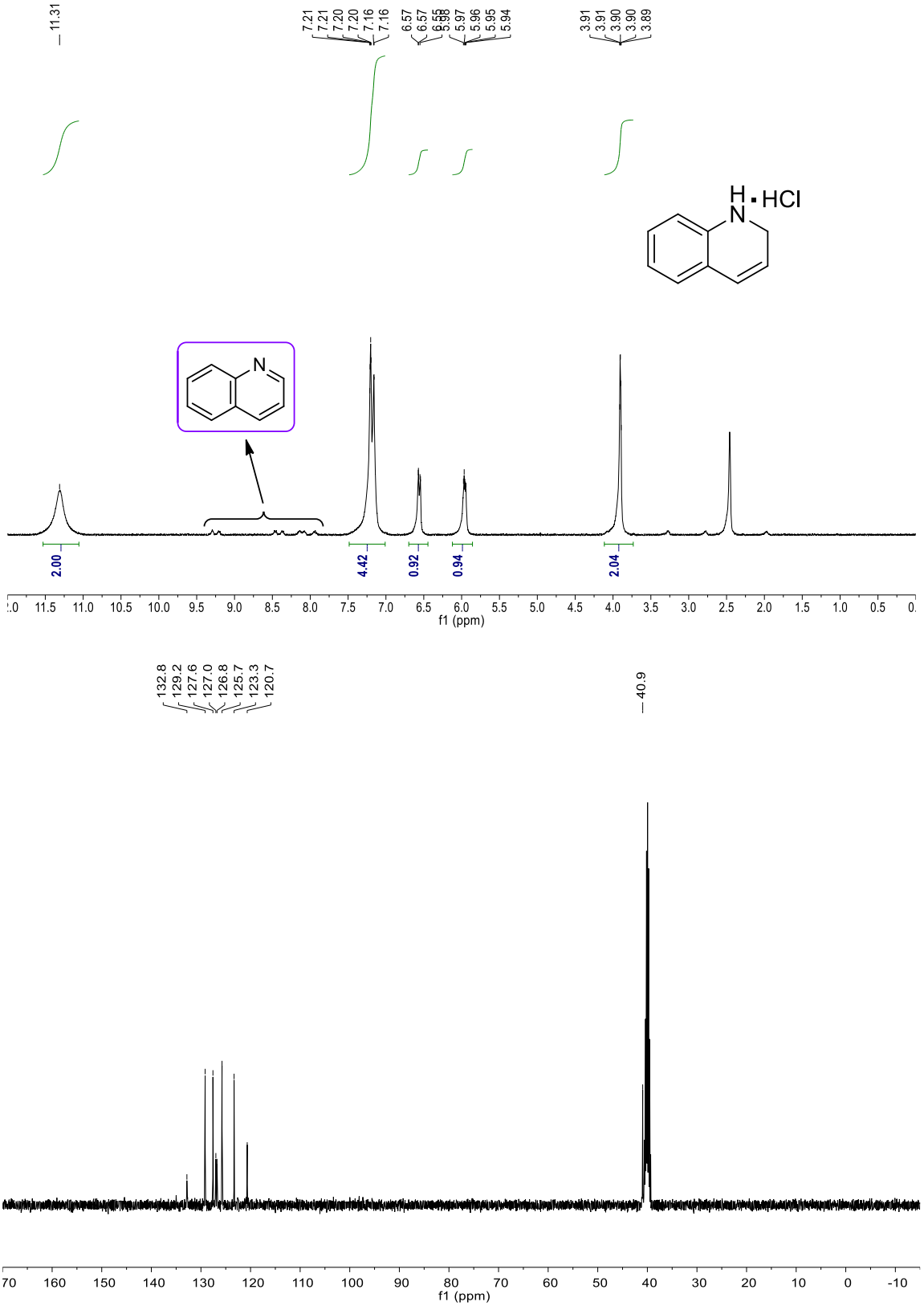


4-Nitrophenyl-[quinolin-1(2*H*)-yl]methanone (3a-PNB)



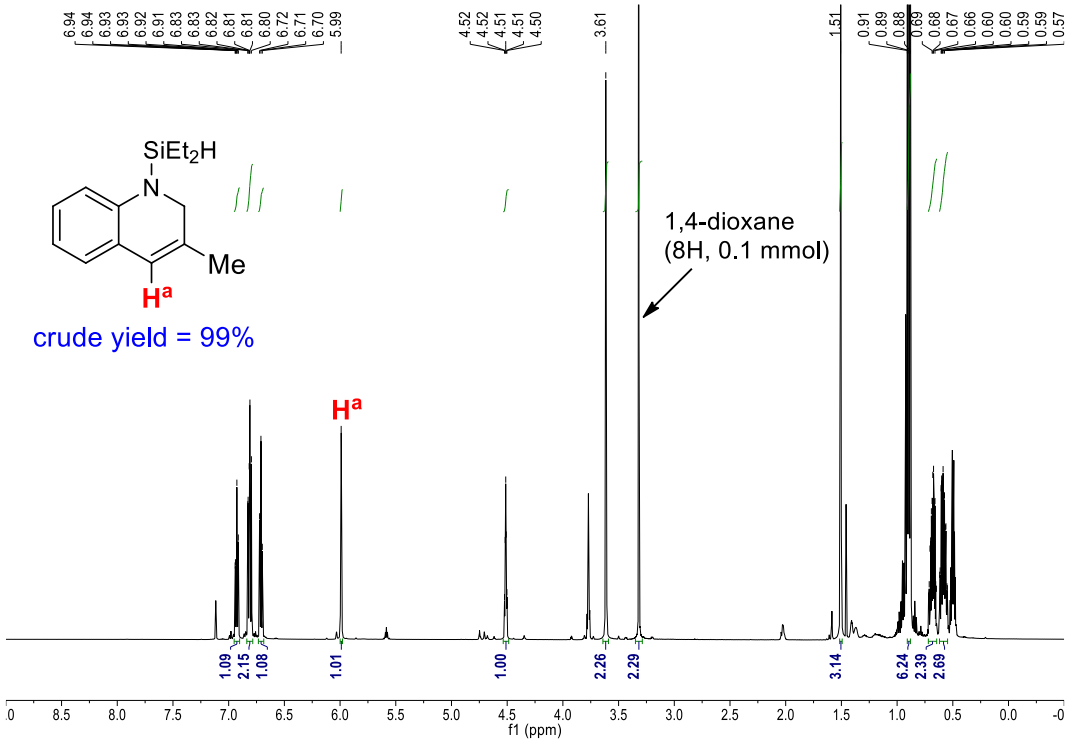


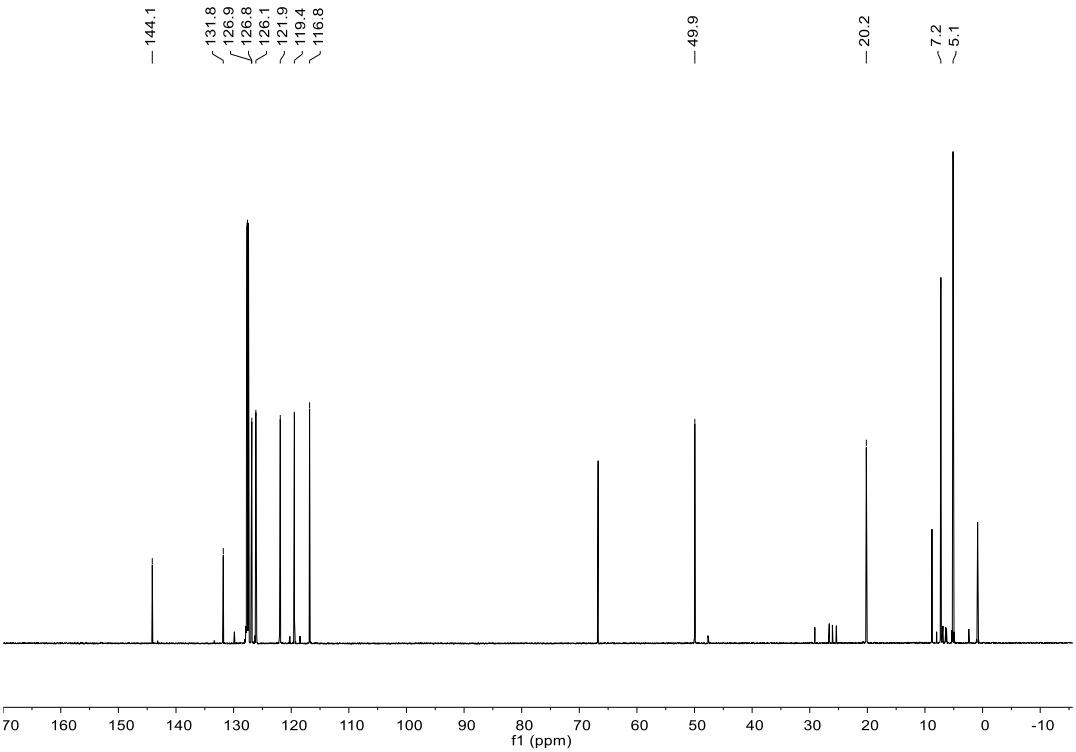
1,2-Dihydroquinolin-1-ium chloride (3a-HCl in DMSO-d_6)



1-(Diethylsilyl)-3-methyl-1,2-dihydroquinoline (3b)

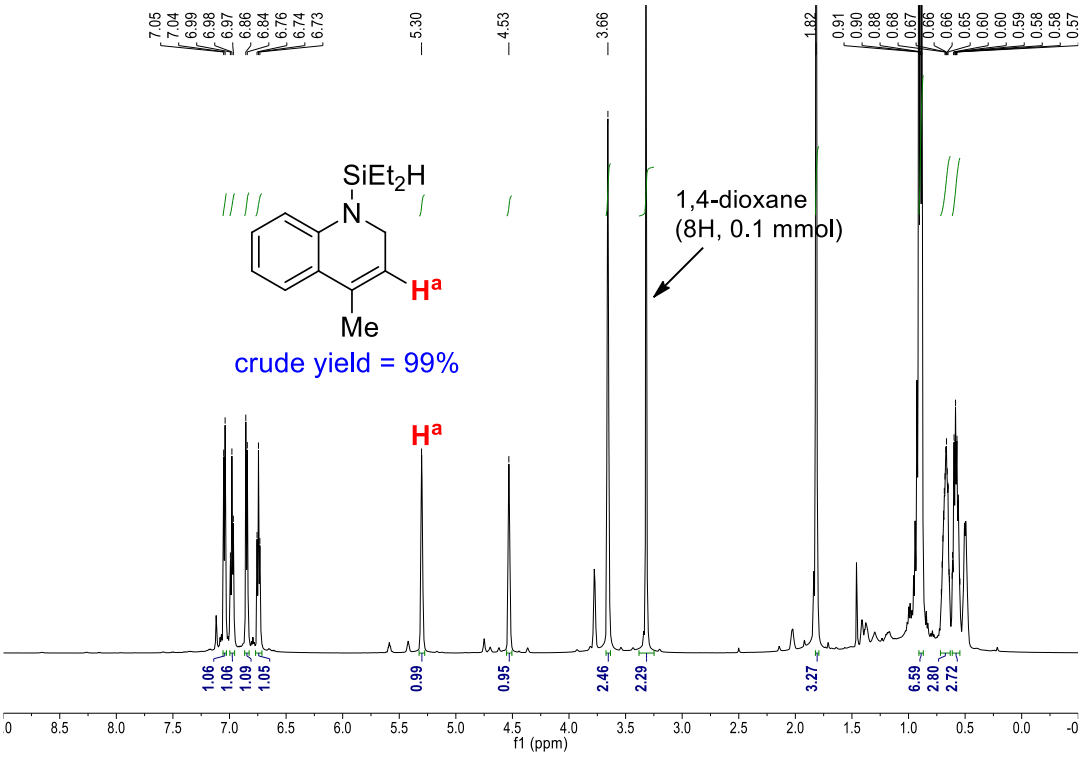
^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); 1,4-dioxane, internal standard

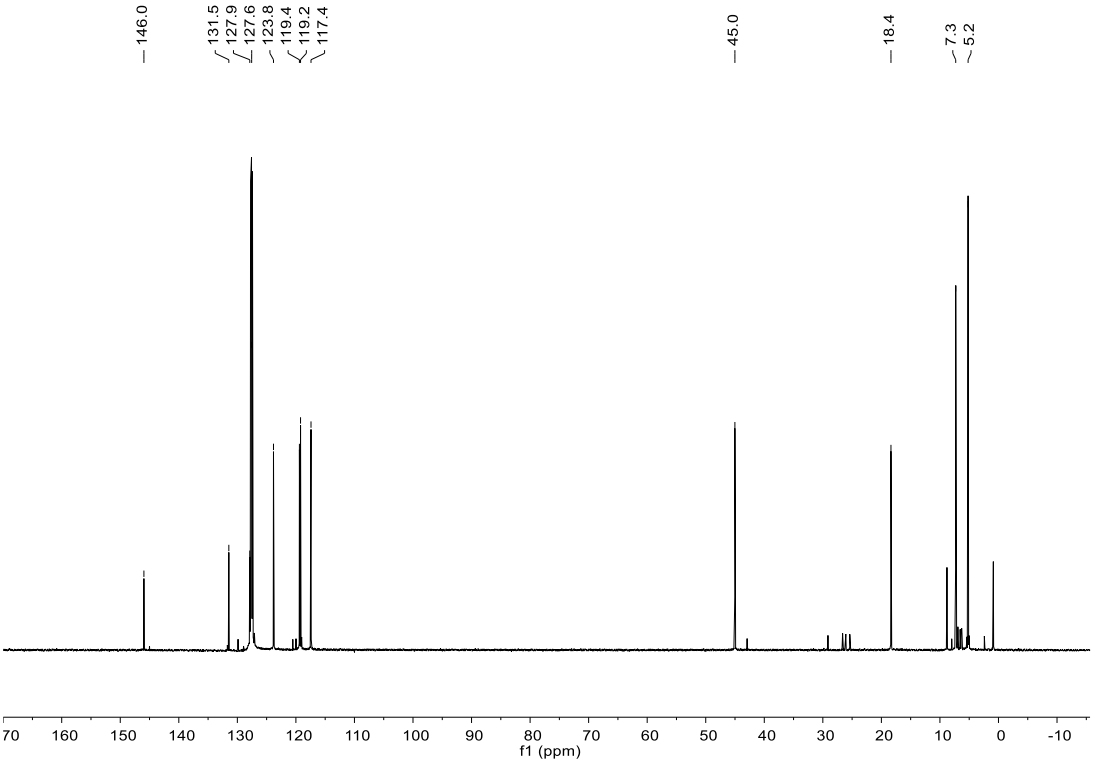




1-(Diethylsilyl)-4-methyl-1,2-dihydroquinoline (3c)

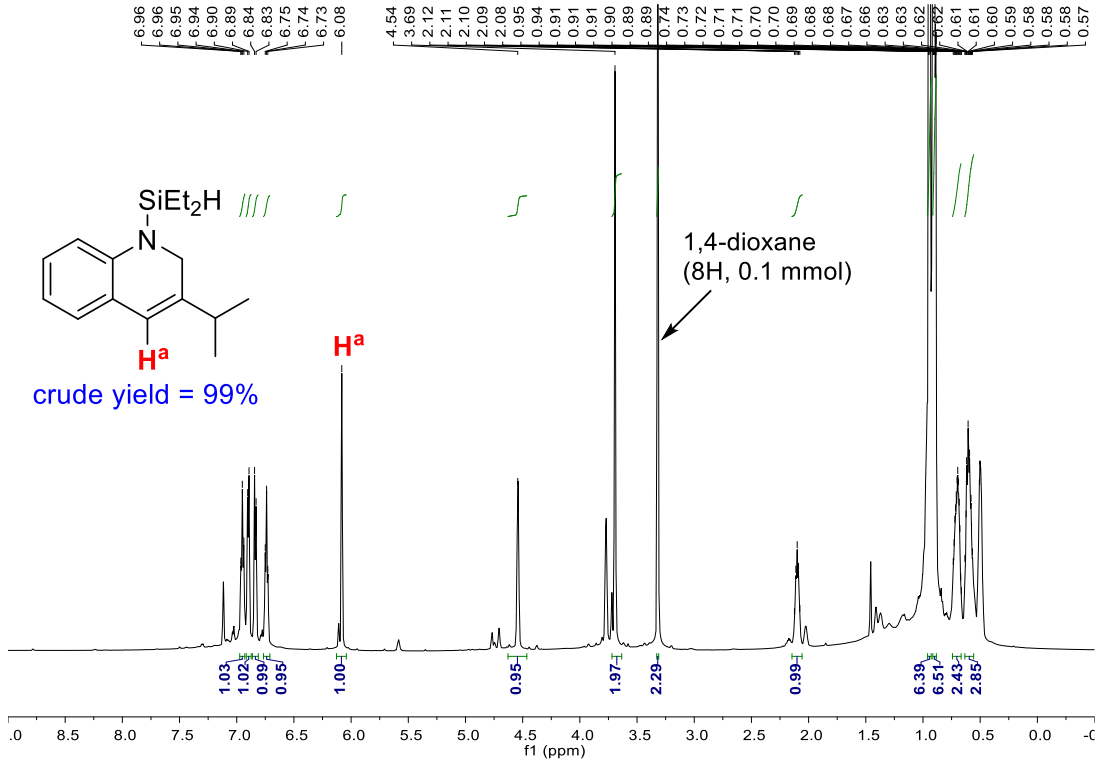
^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); 1,4-dioxane, internal standard

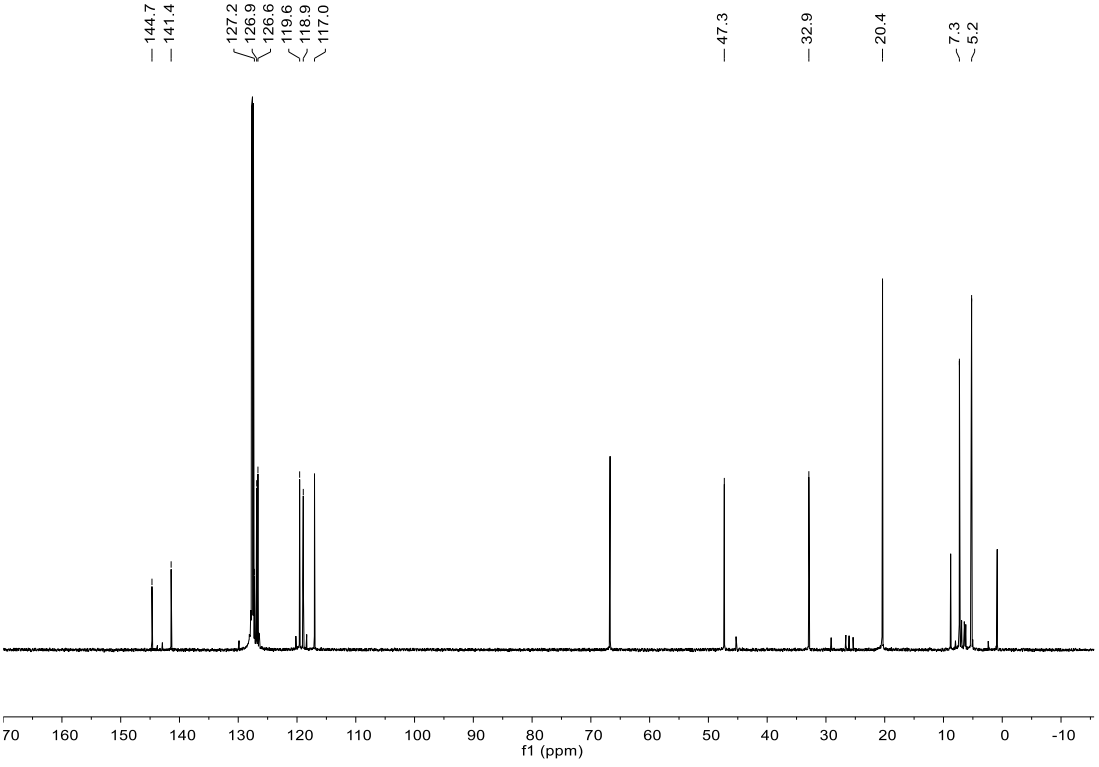




1-(Diethylsilyl)-3-isopropyl-1,2-dihydroquinoline (3d)

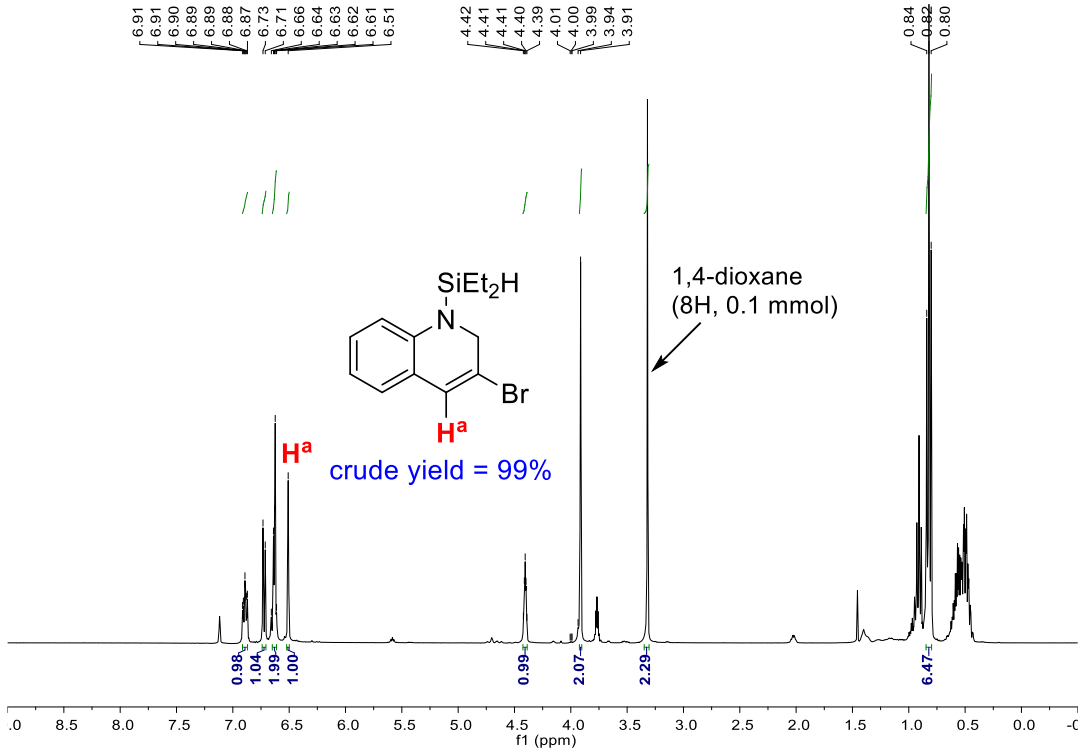
^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); 1,4-dioxane, internal standard

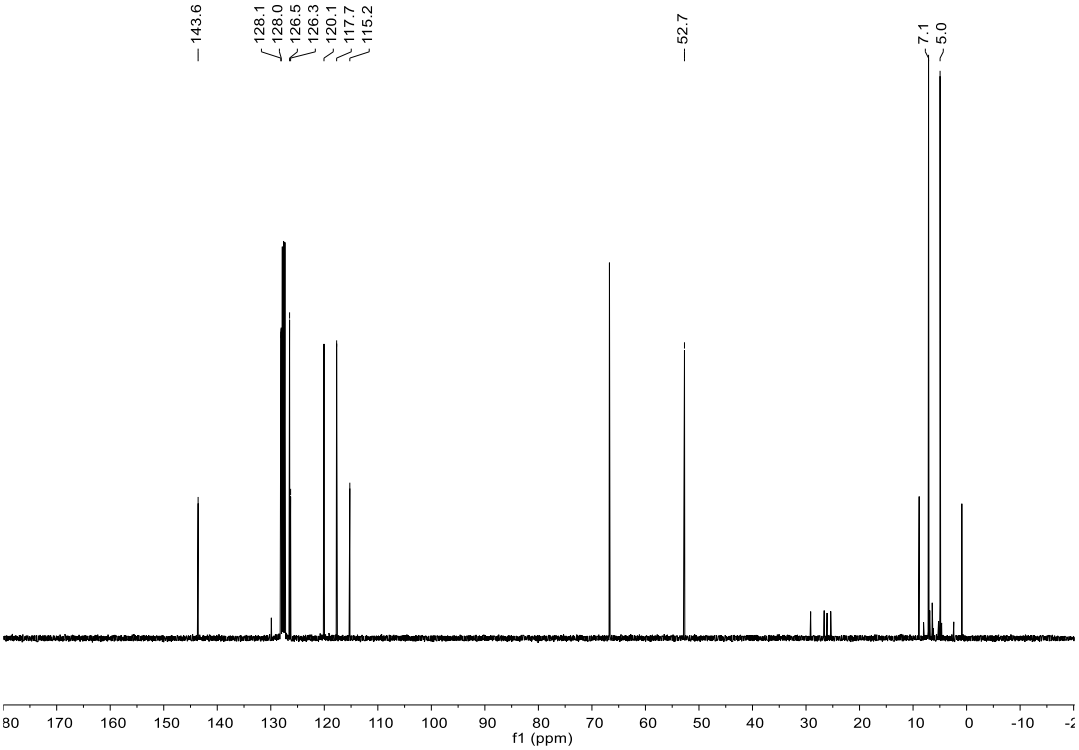




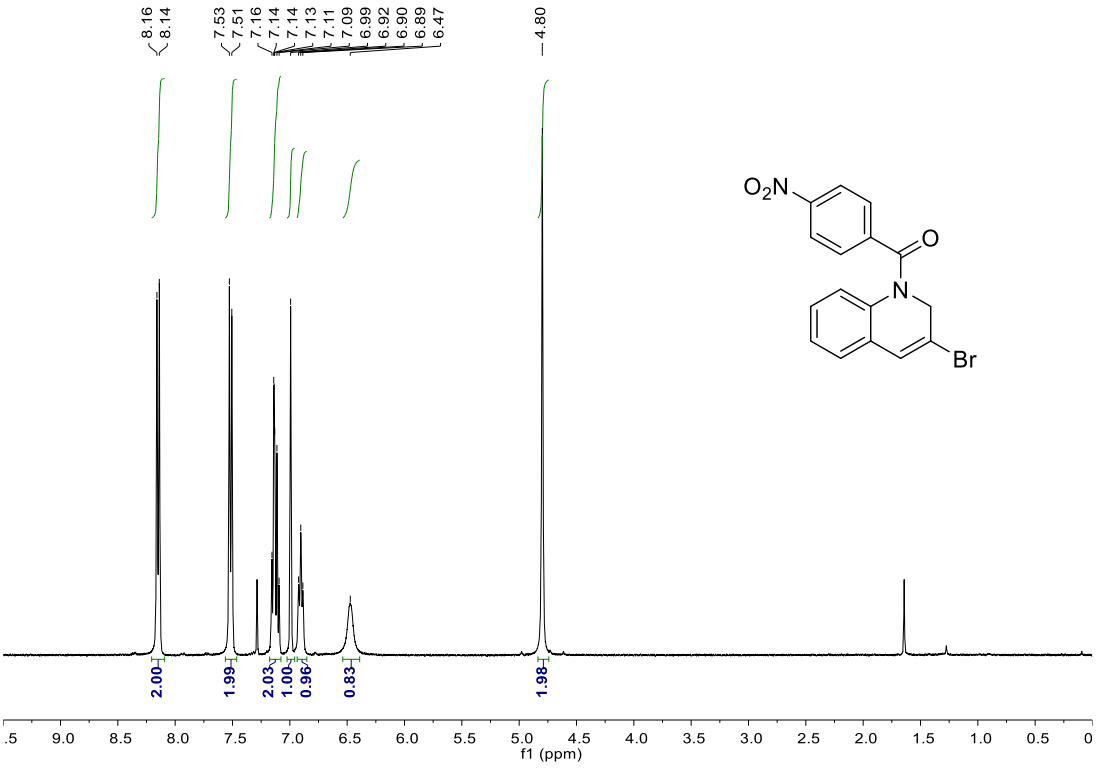
3-Bromo-1-(diethylsilyl)-1,2-dihydroquinoline (**3e**)

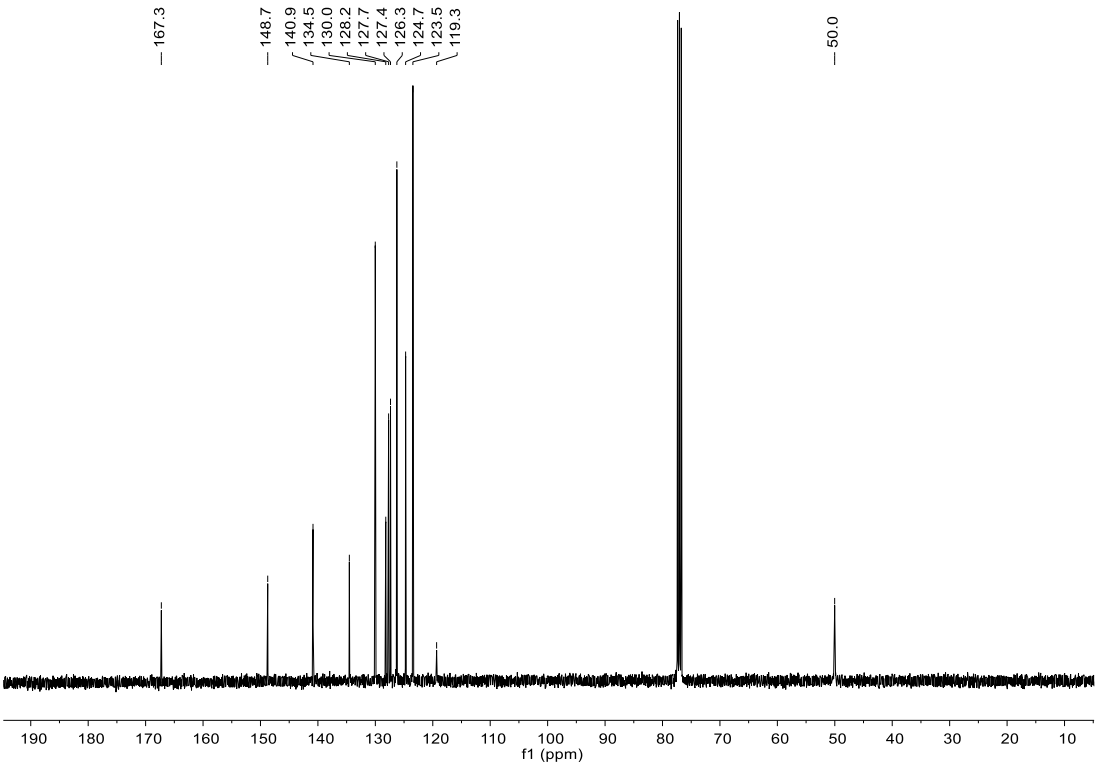
^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); 1,4-dioxane, internal standard





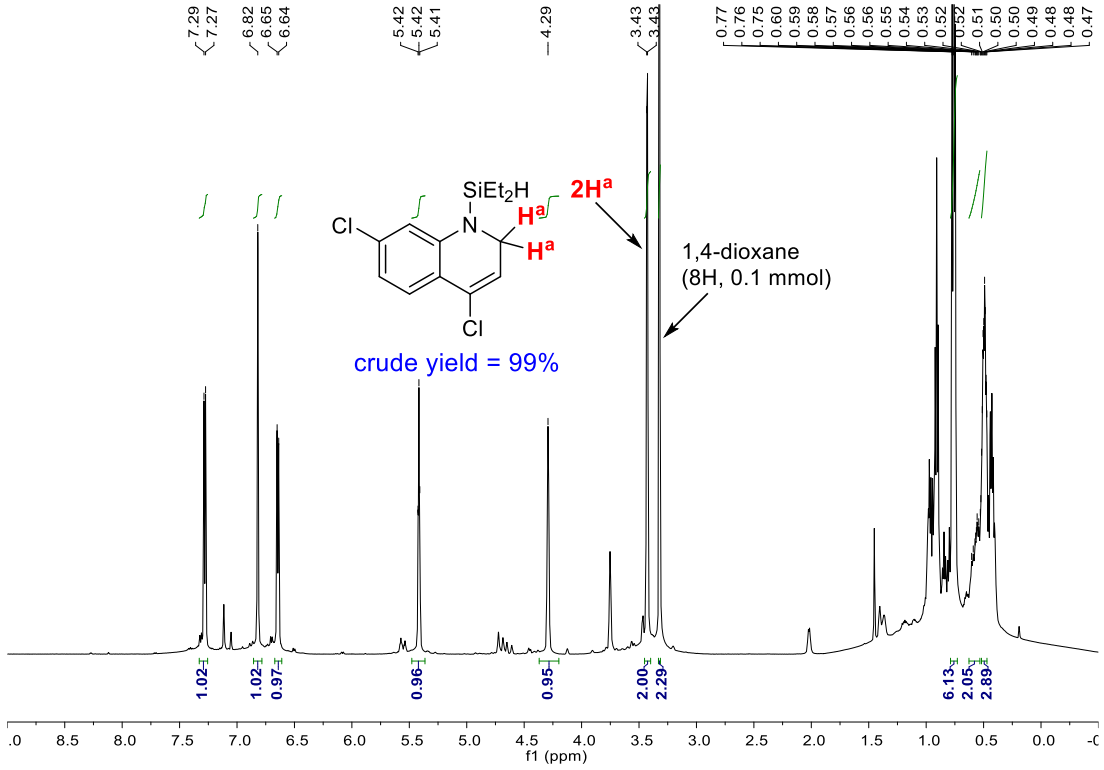
[3-Bromoquinolin-1(2H)-yl](4-nitrophenyl)methanone (3e-PNB)

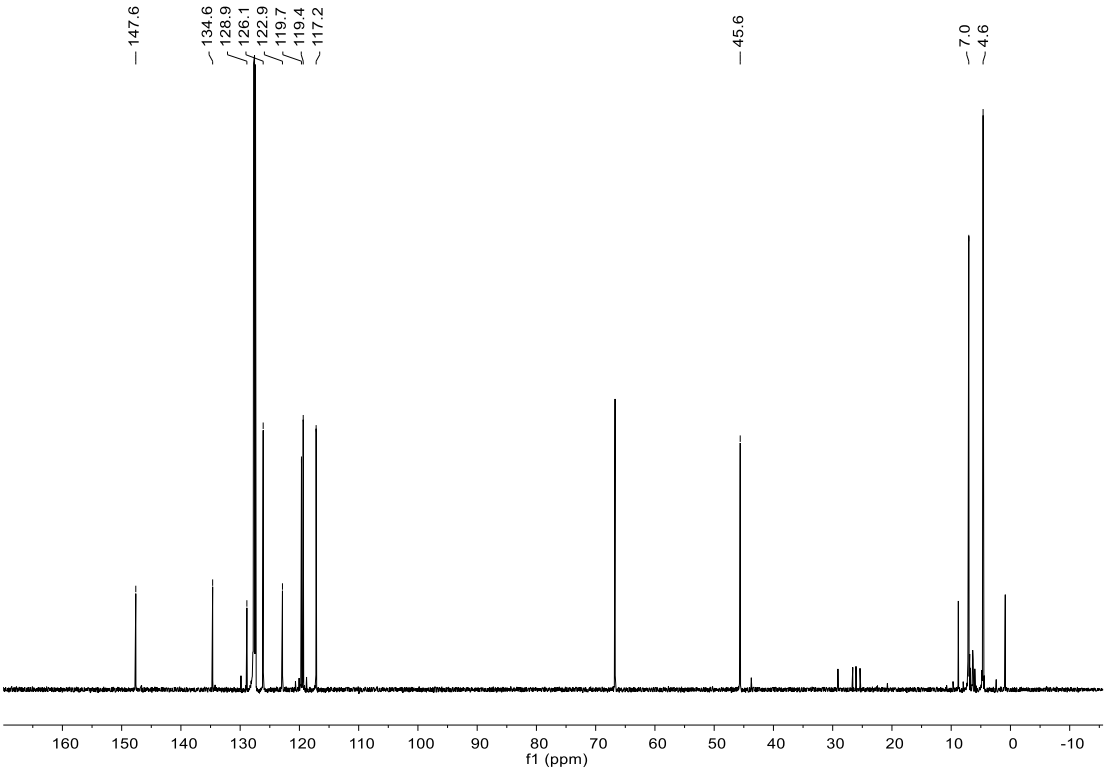




4,7-Dichloro-1-(diethylsilyl)-1,2-dihydroquinoline (**3f**)

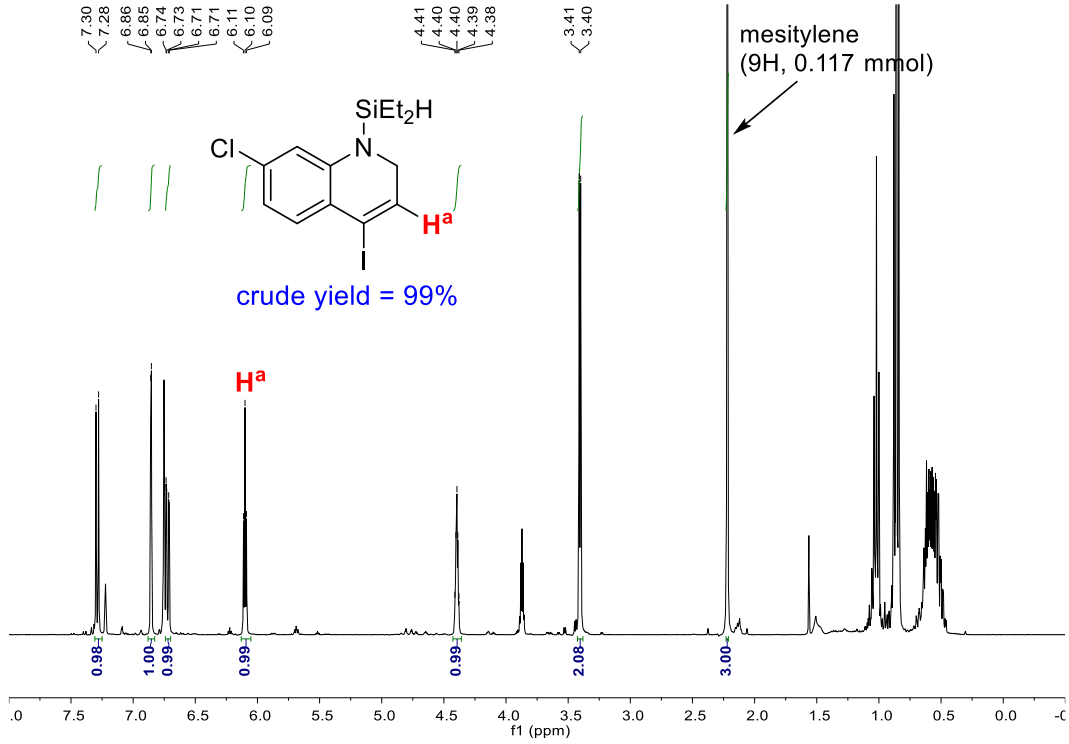
^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); 1,4-dioxane, internal standard

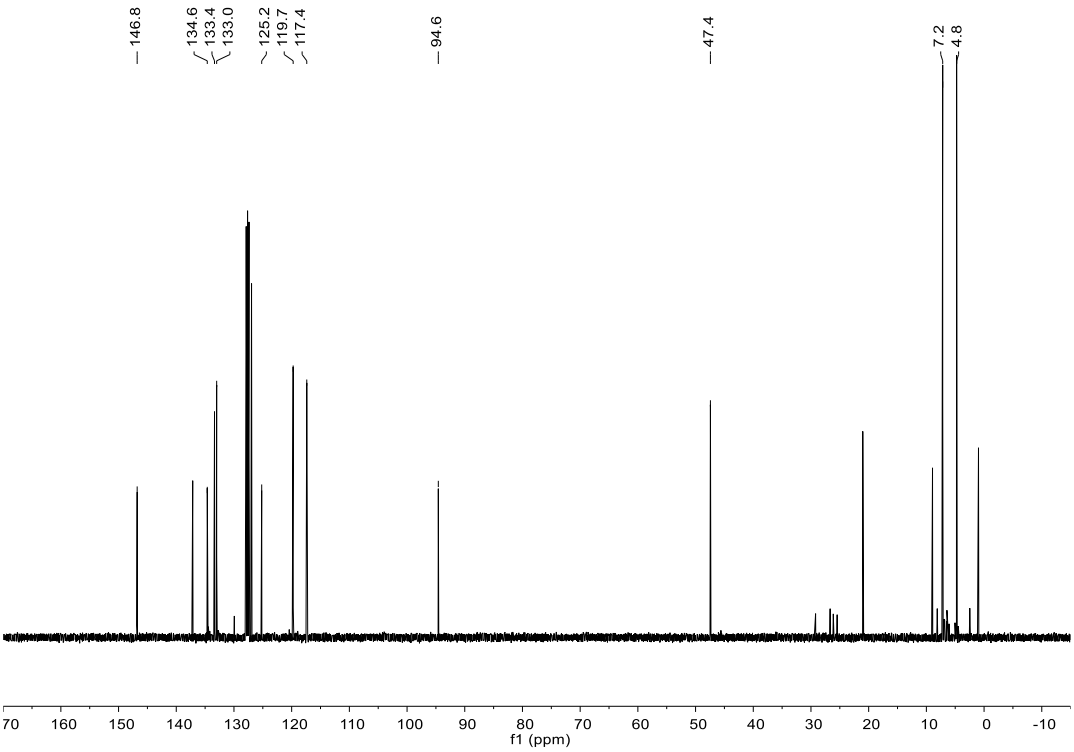




4-Chloro-1-(diethylsilyl)-7-iodo-1,2-dihydroquinoline (3g)

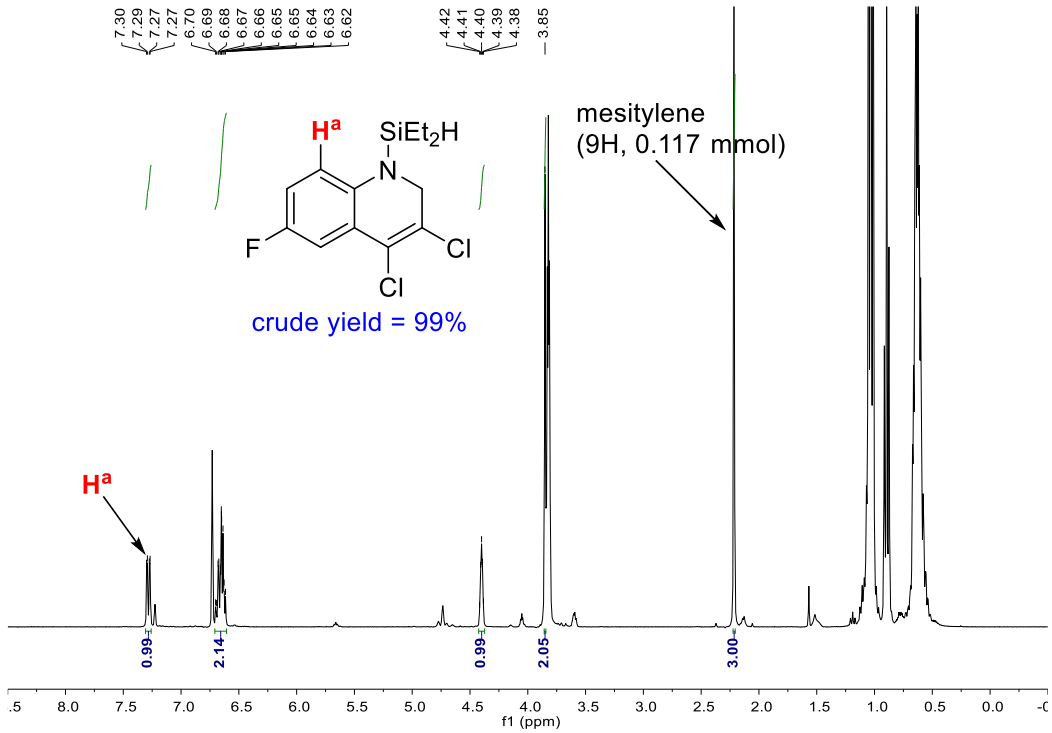
^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (150 MHz, C_6D_6); mesitylene, internal standard

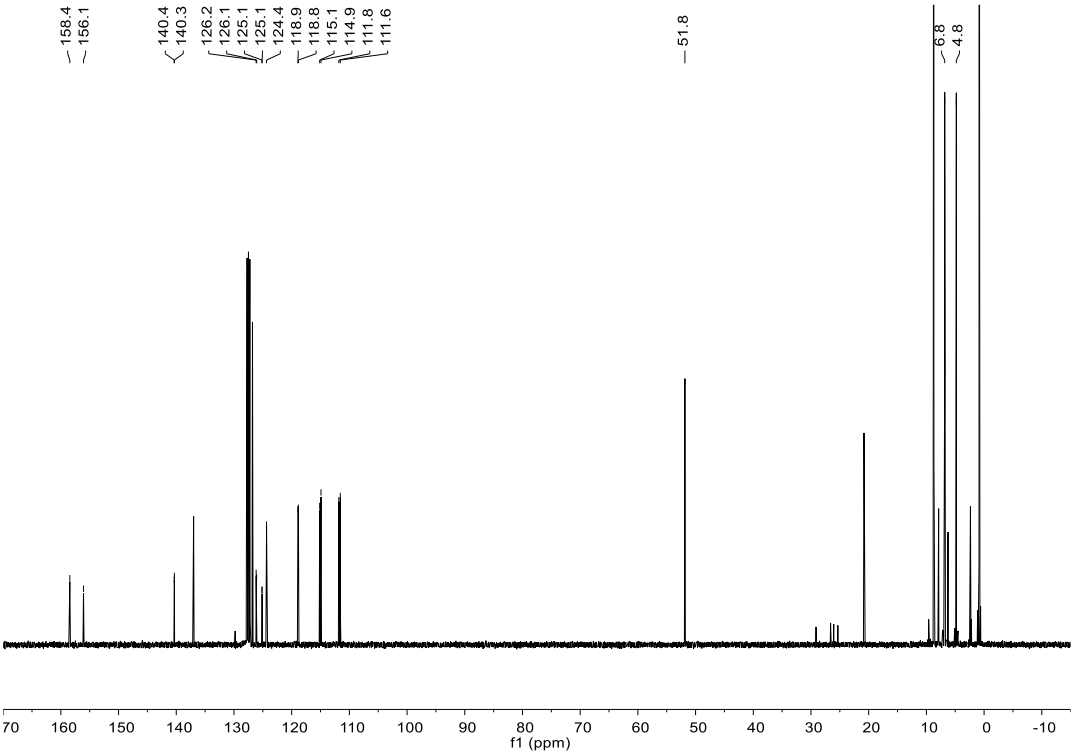




3,4-Dichloro-1-(diethylsilyl)-6-fluoro-1,2-dihydroquinoline (**3h**)

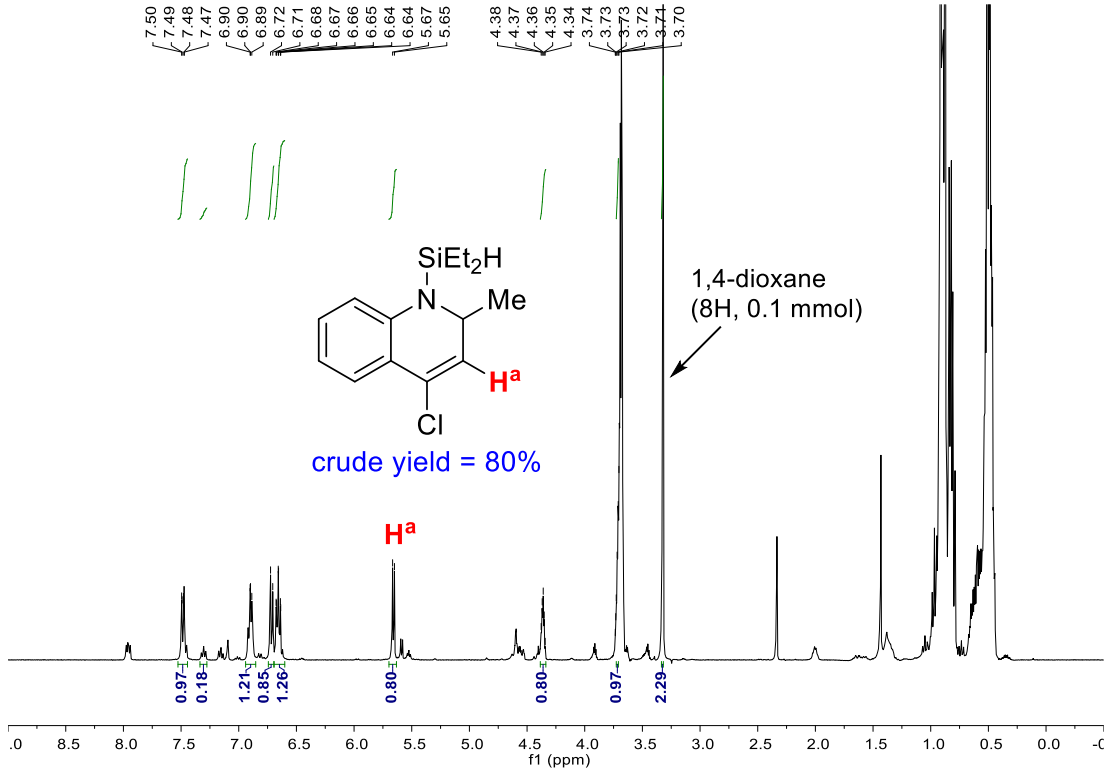
^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); mesitylene, internal standard

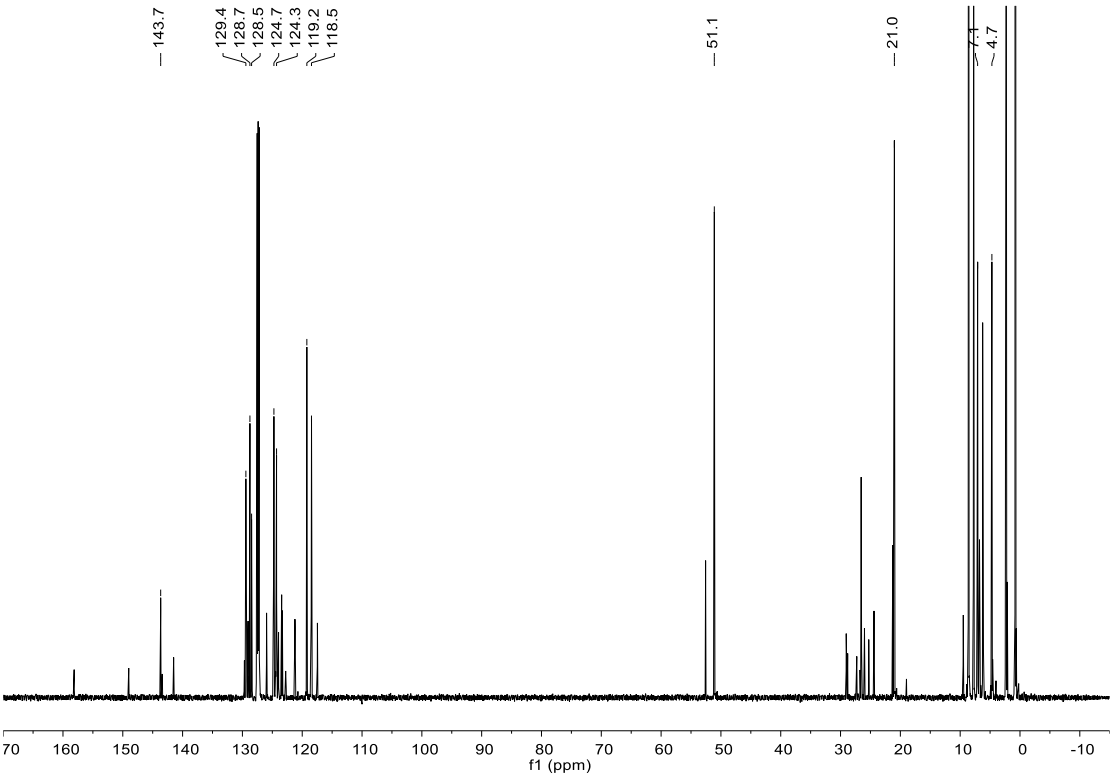




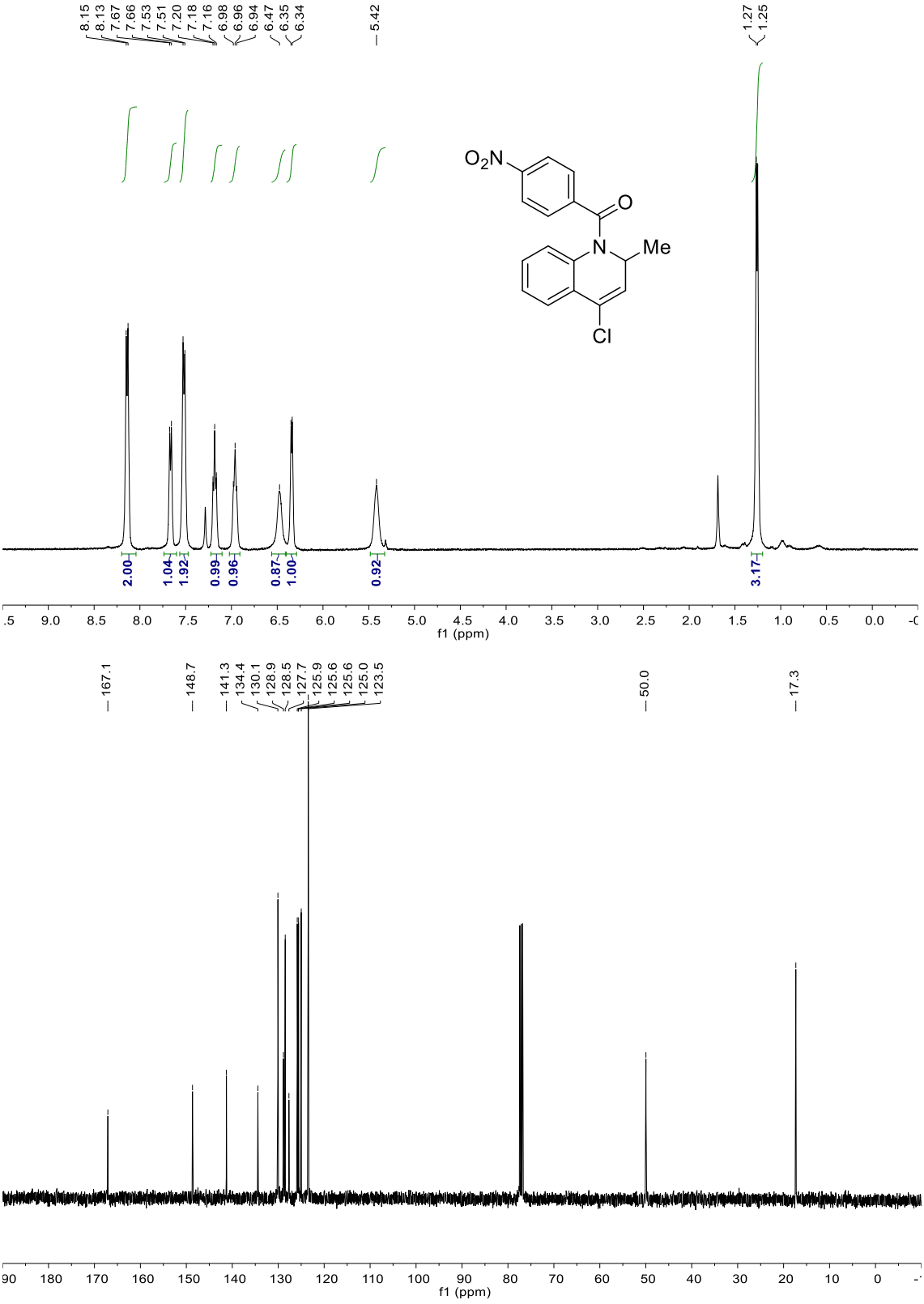
4-Chloro-1-(diethylsilyl)-2-methyl-1,2-dihydroquinoline (3i)

^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); 1,4-dioxane, internal standard



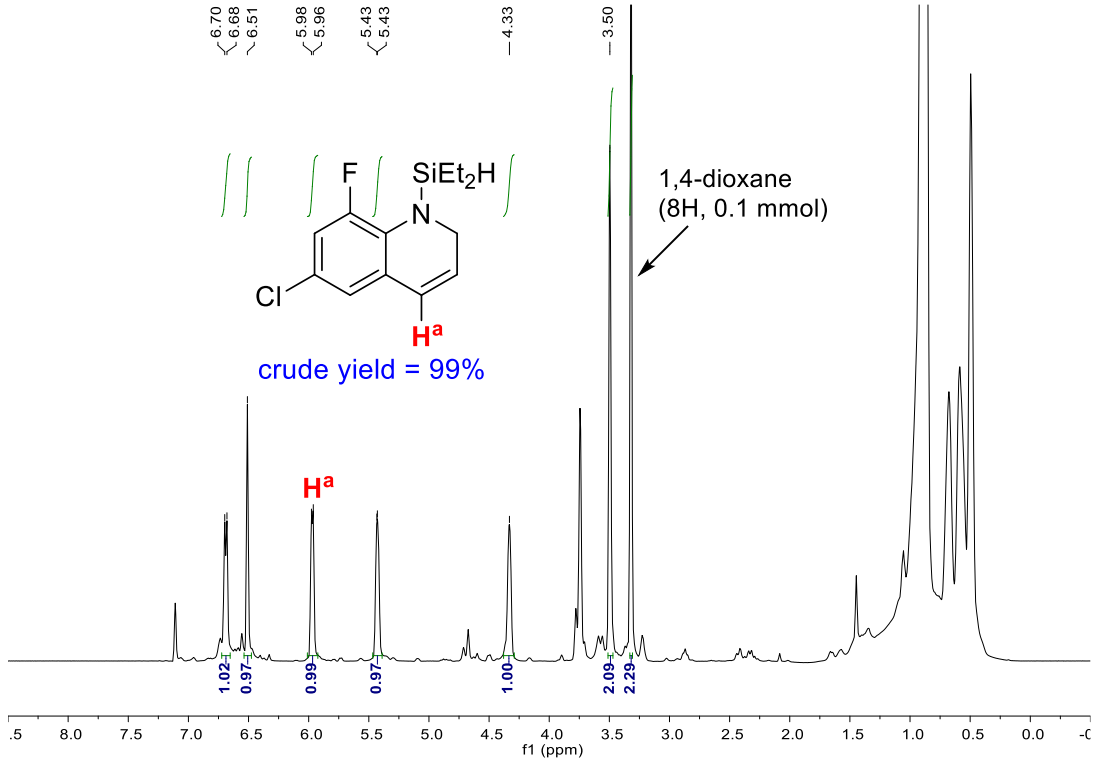


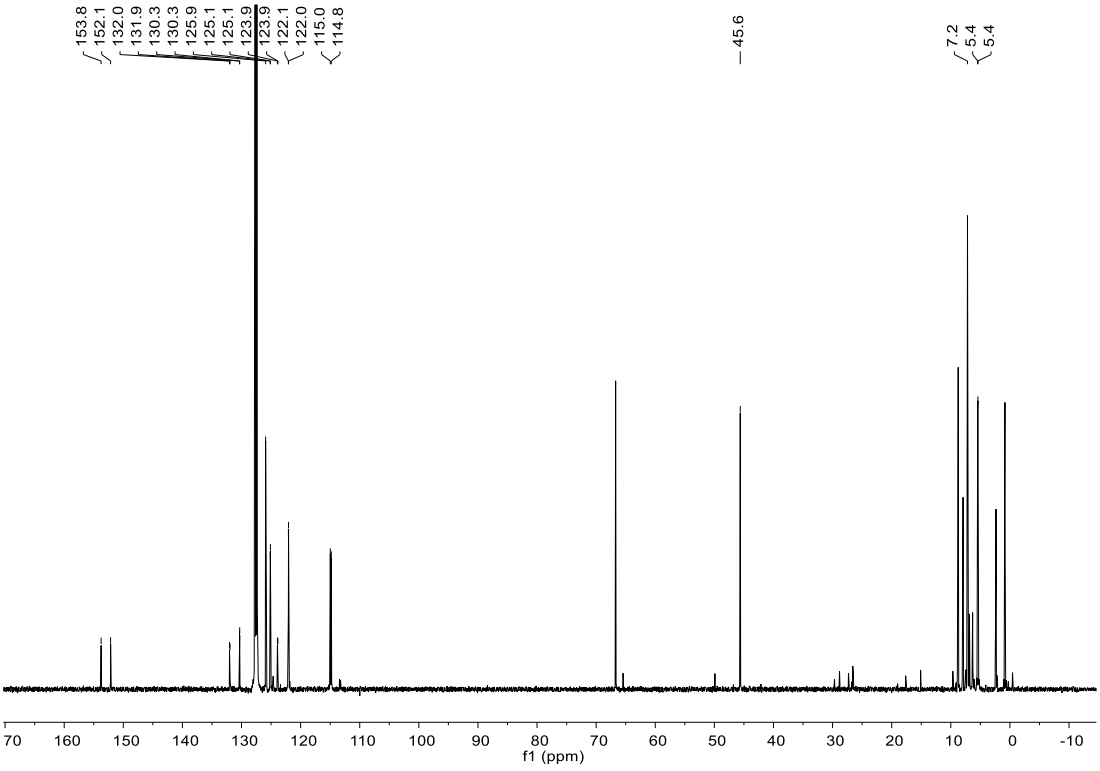
[4-Chloro-2-methylquinolin-1(2H)-yl](4-nitrophenyl)methanone (3i-PNB)



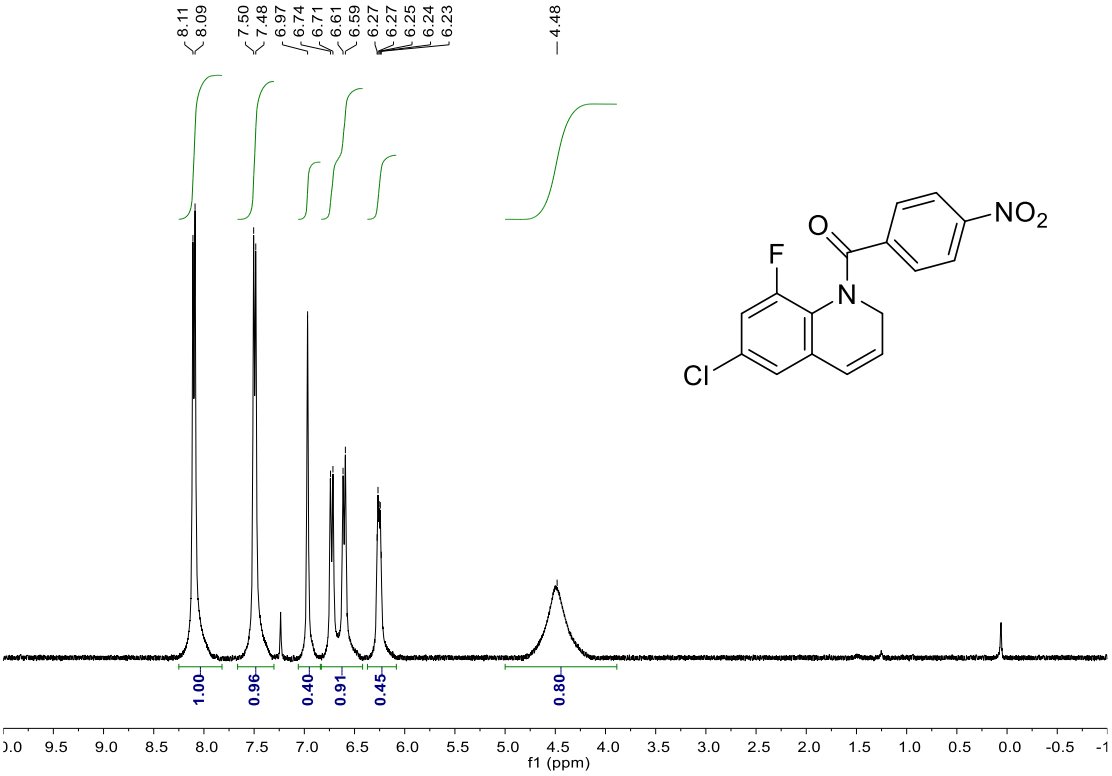
5-Chloro-1-(diethylsilyl)-8-fluoro-1,2-dihydroquinoline (3j)

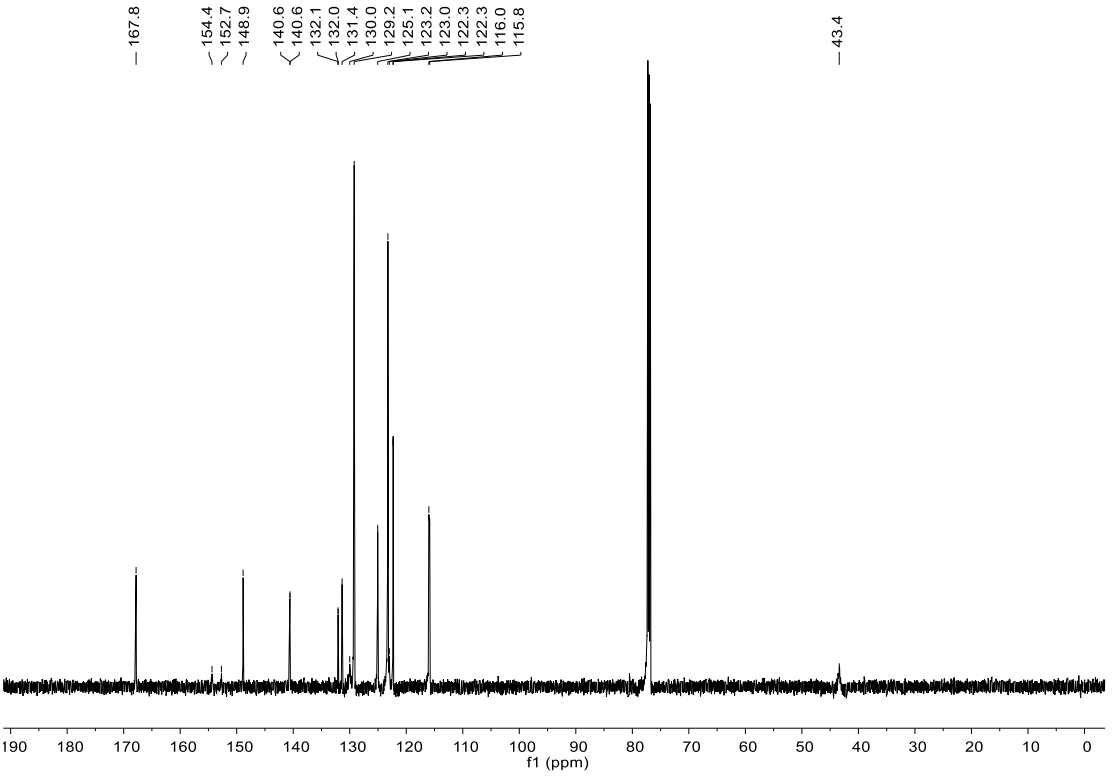
^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); 1,4-dioxane, internal standard





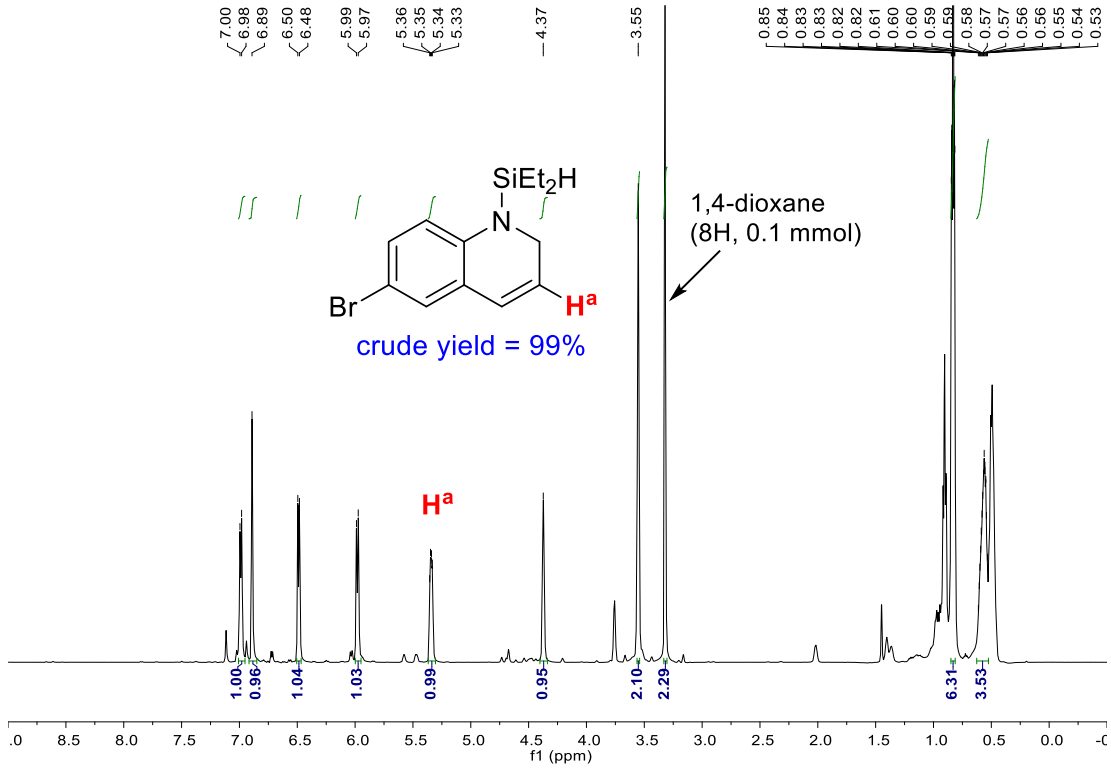
[6-Chloro-8-fluoroquinolin-1(2H)-yl](4-nitrophenyl)methanone (3j-PNB)

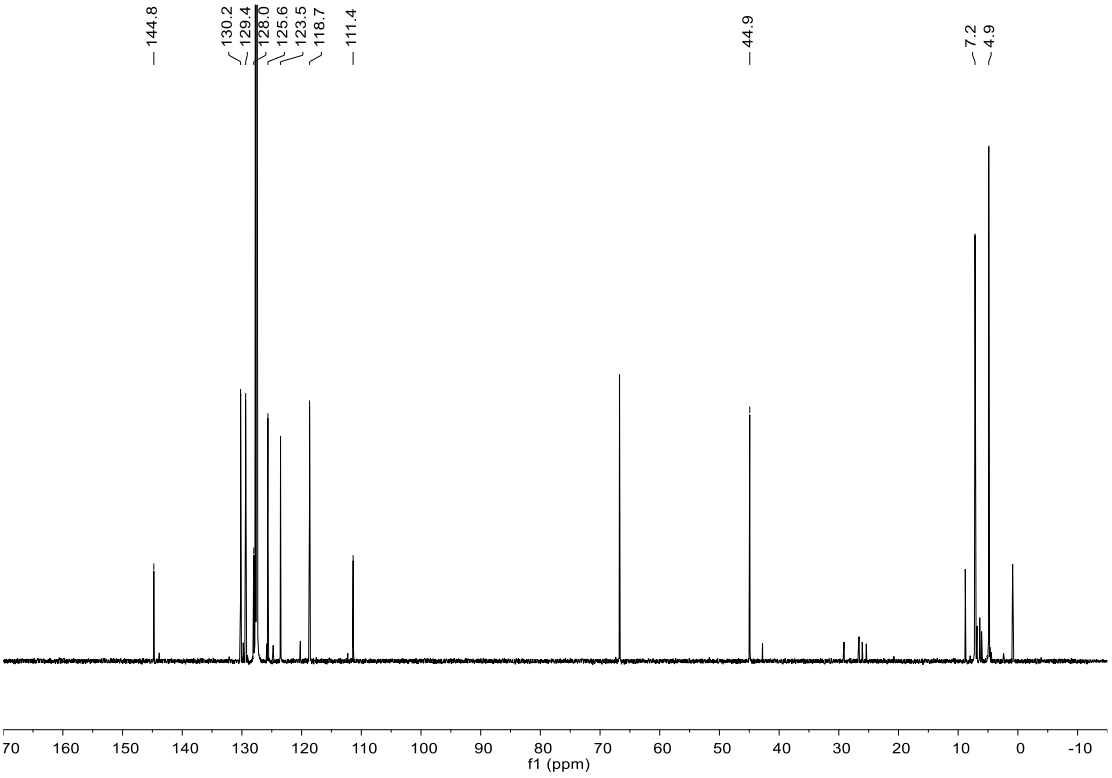




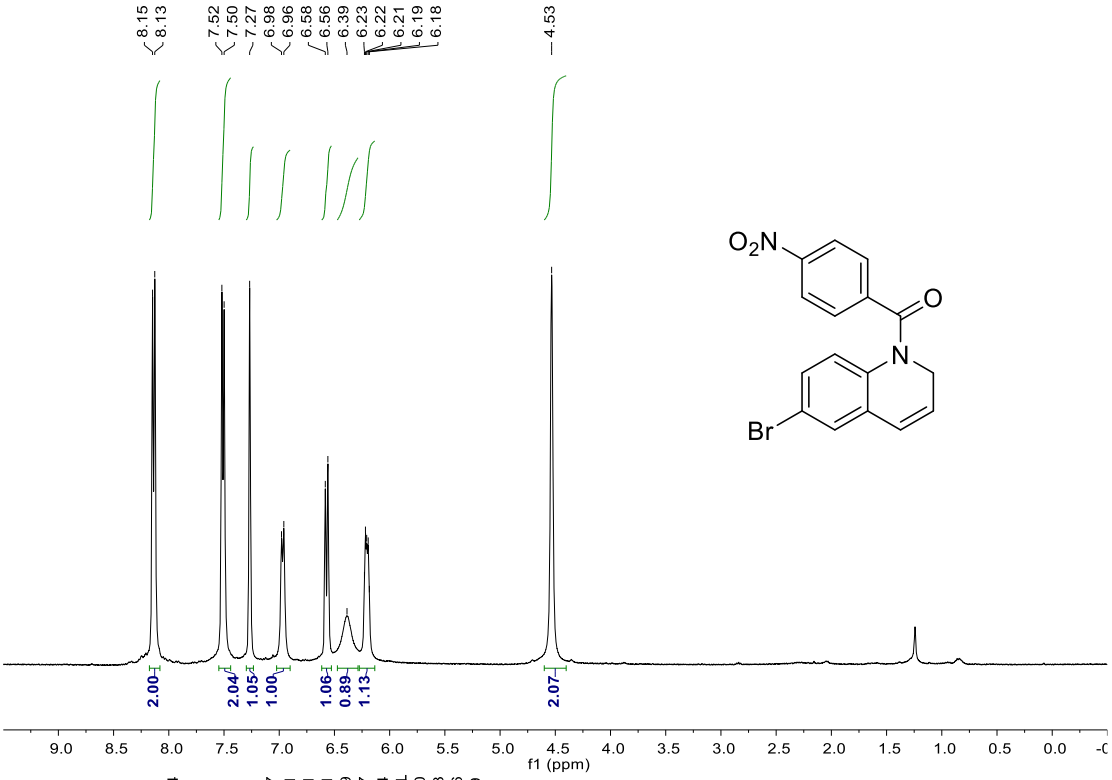
6-Bromo-1-(diethylsilyl)-1,2-dihydroquinoline (3k)

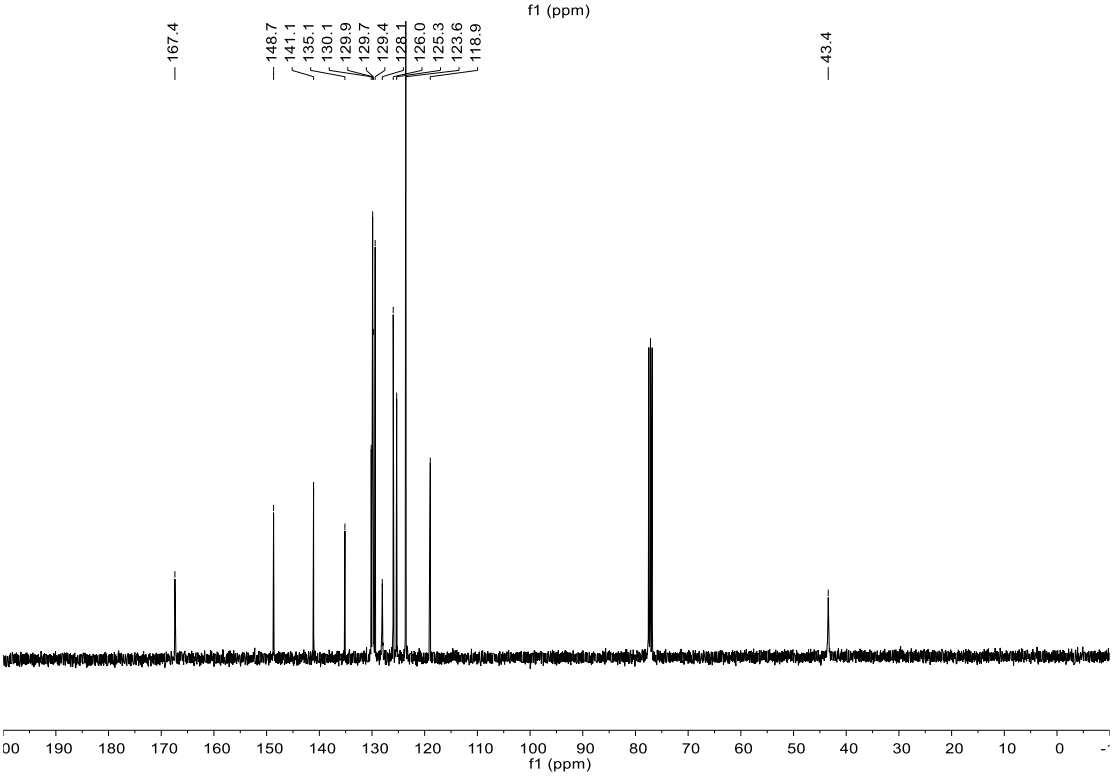
^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); 1,4-dioxane, internal standard





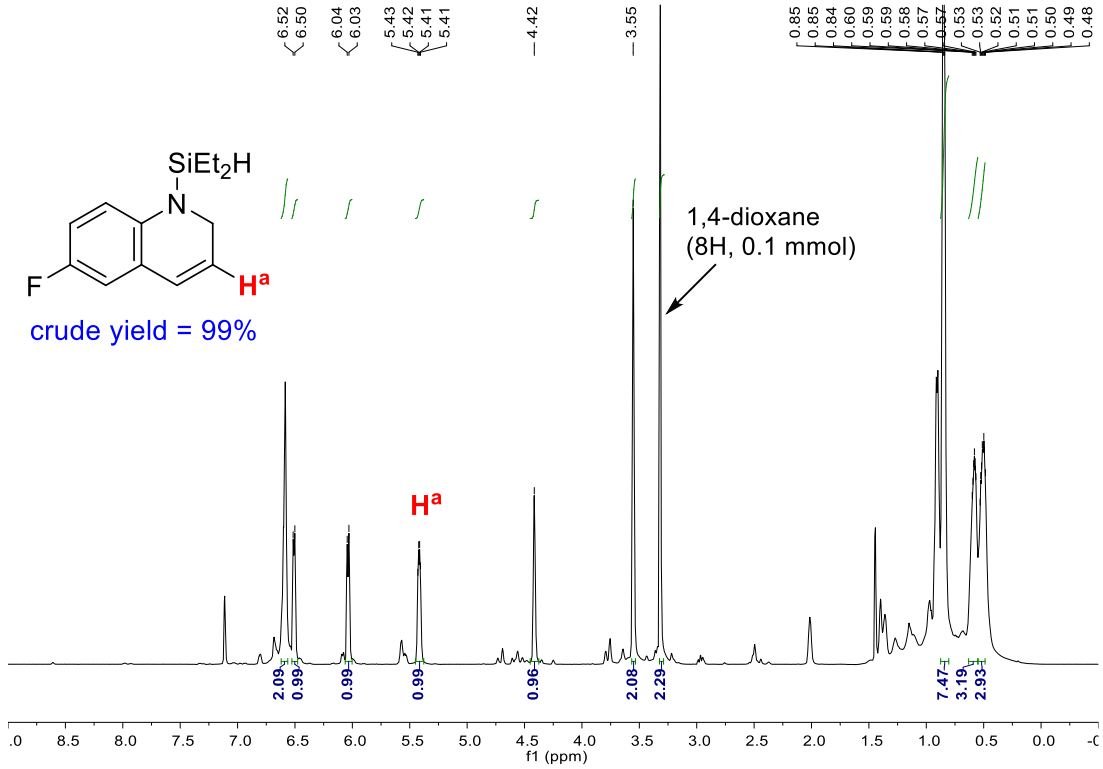
[6-Bromoquinolin-1(2H)-yl](4-nitrophenyl)methanone (3k-PNB)

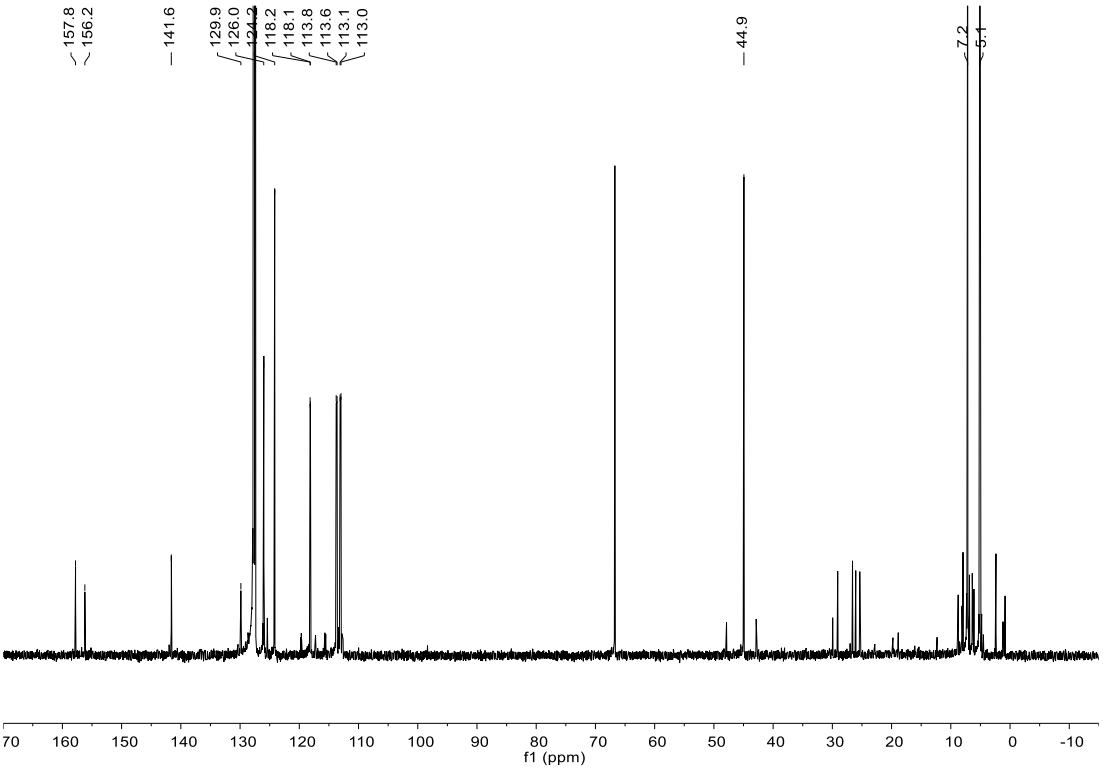




6-Fluoro-1-(diethylsilyl)-1,2-dihydroquinoline (3l)

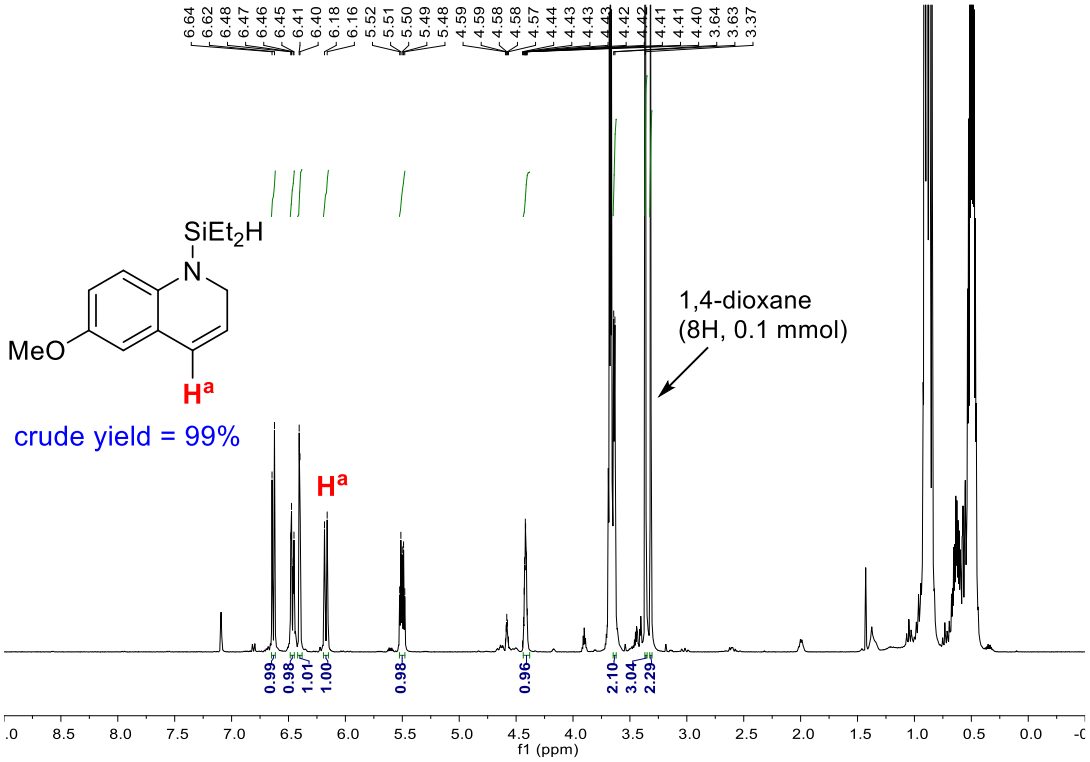
^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); 1,4-dioxane, internal standard

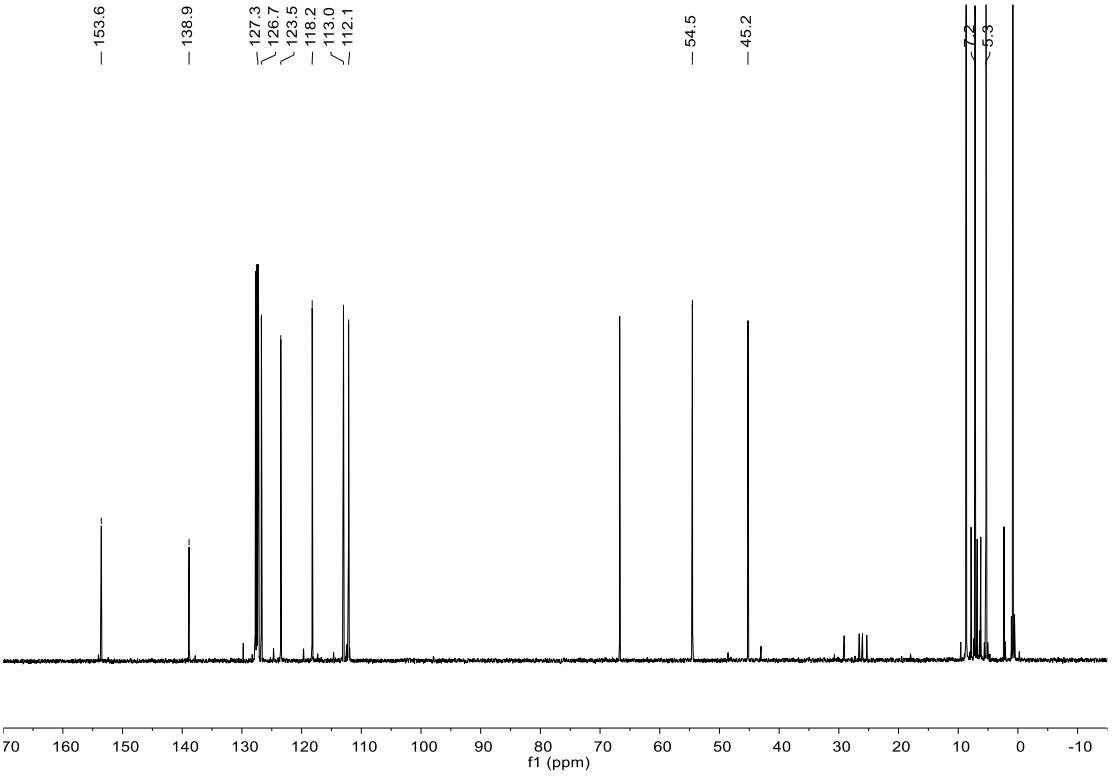




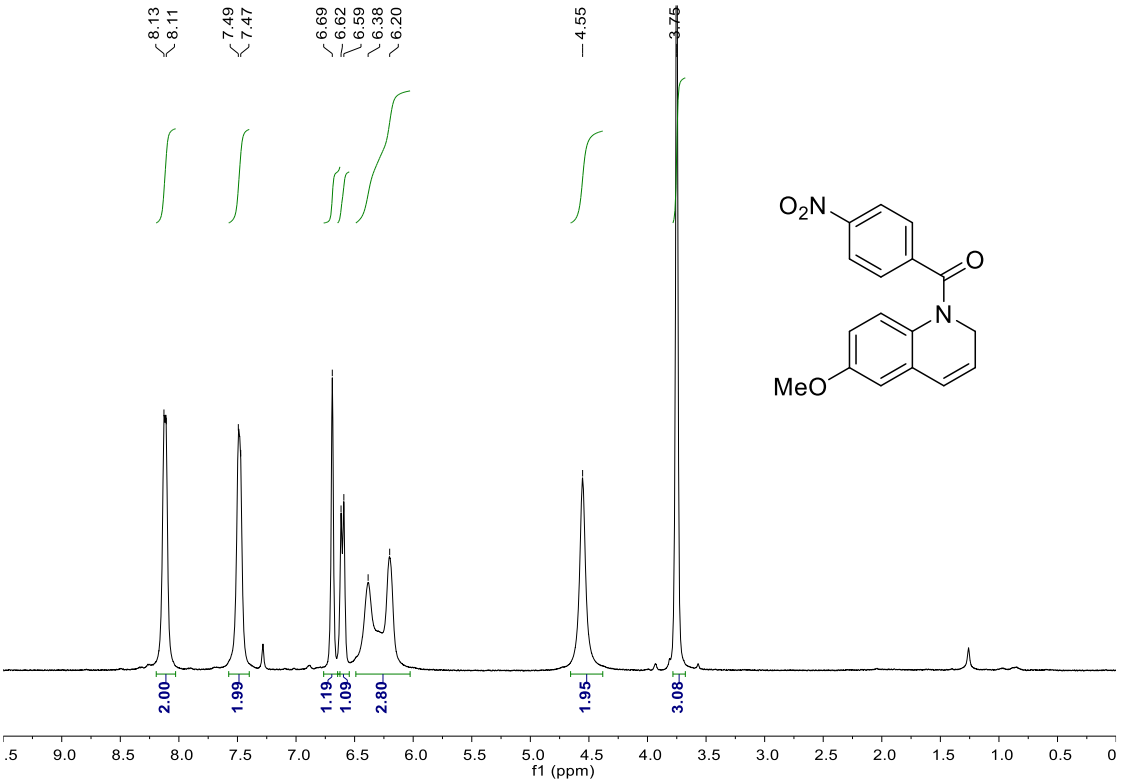
1-(Diethylsilyl)-6-methoxy-1,2-dihydroquinoline (3m)

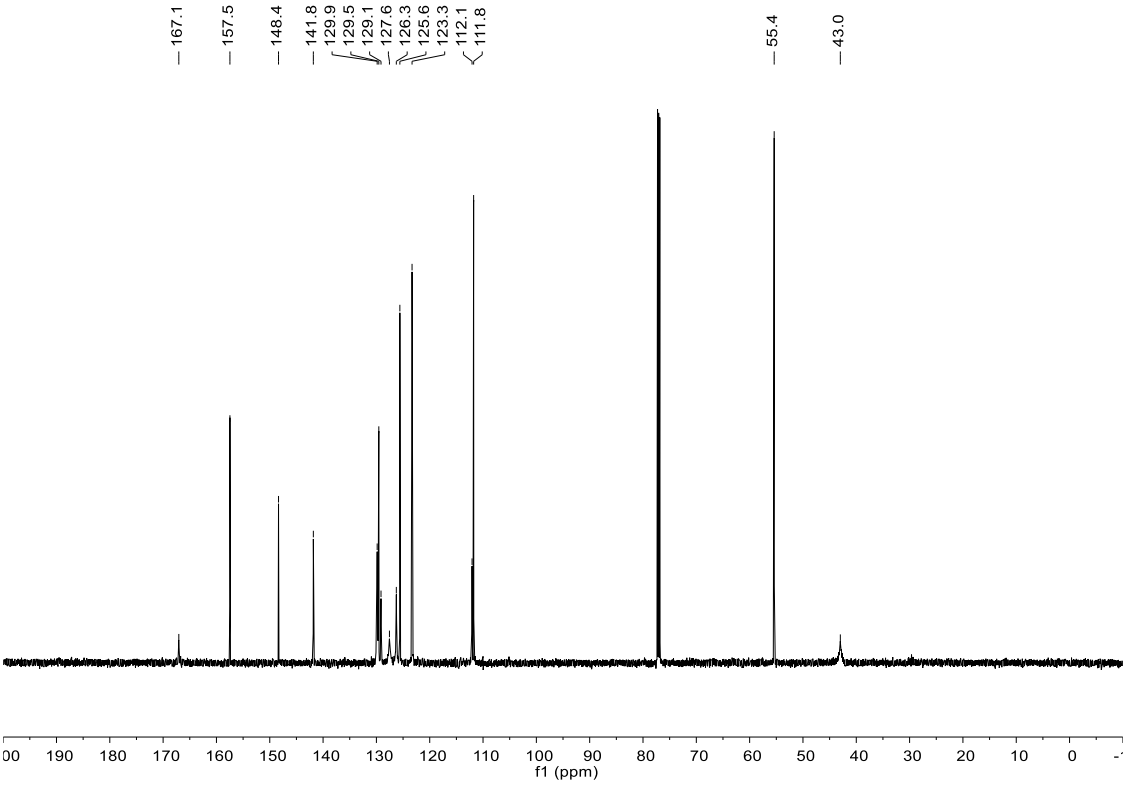
^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); 1,4-dioxane, internal standard





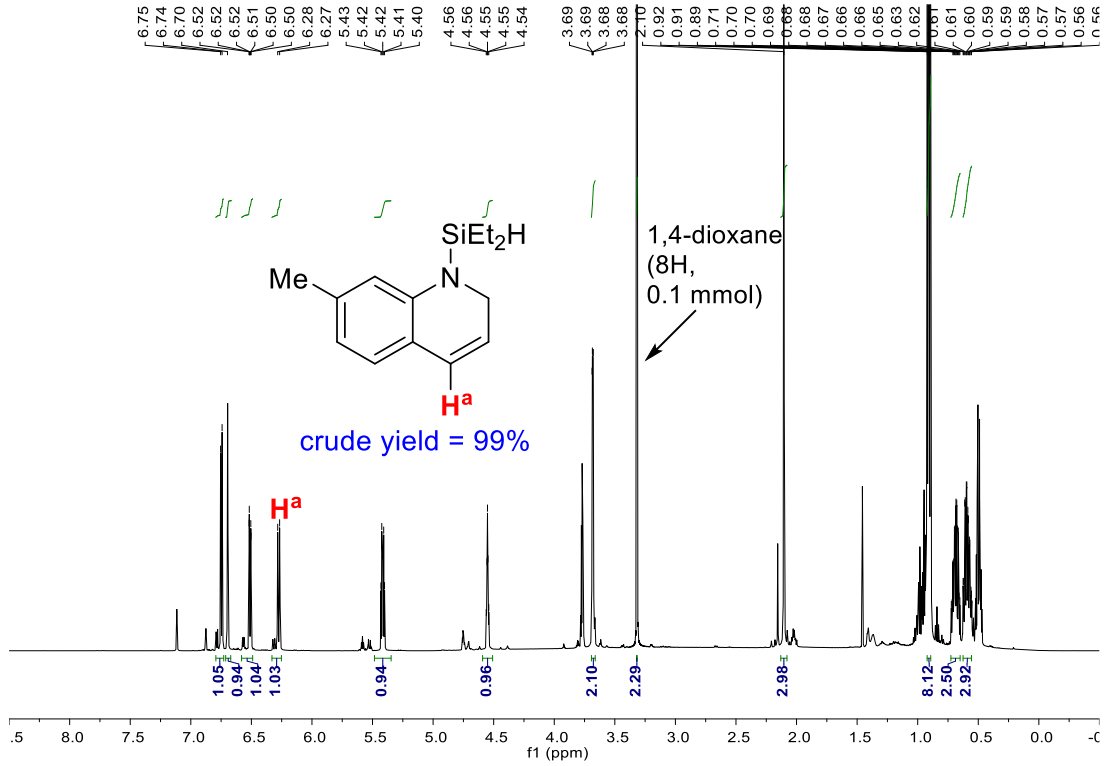
[6-Methoxyquinolin-1(2H)-yl](4-nitrophenyl)methanone (3m-PNB)

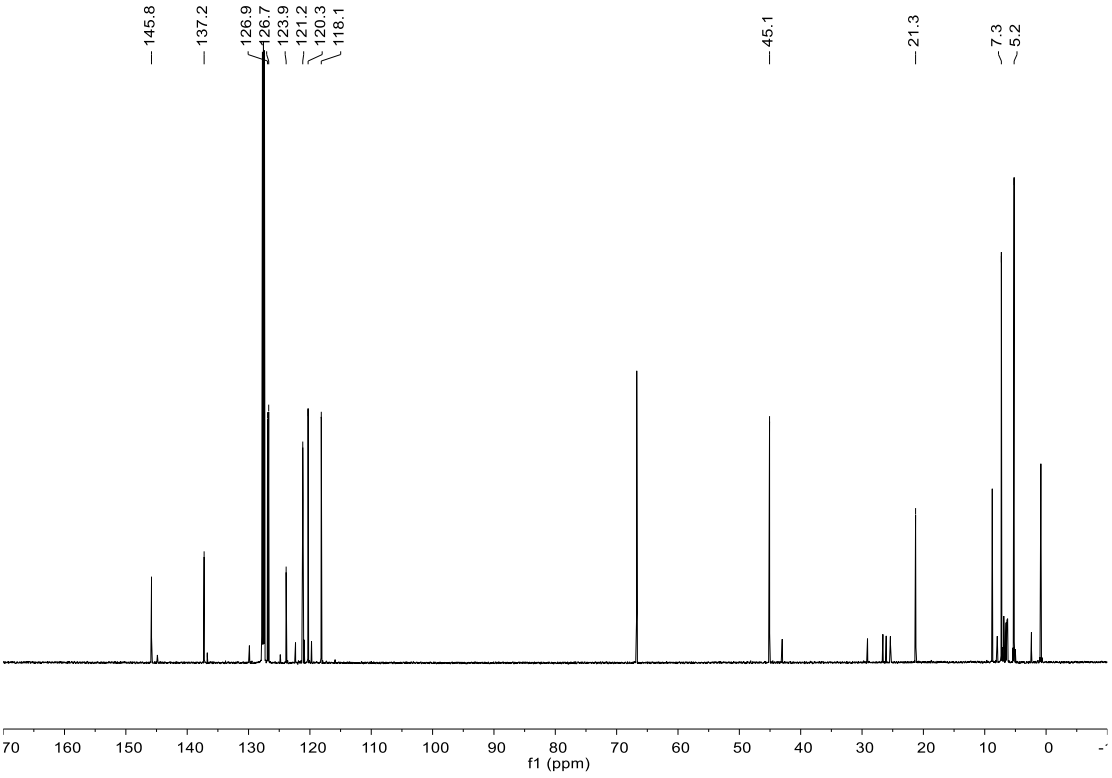




1-(Diethylsilyl)-7-methyl-1,2-dihydroquinoline (3n)

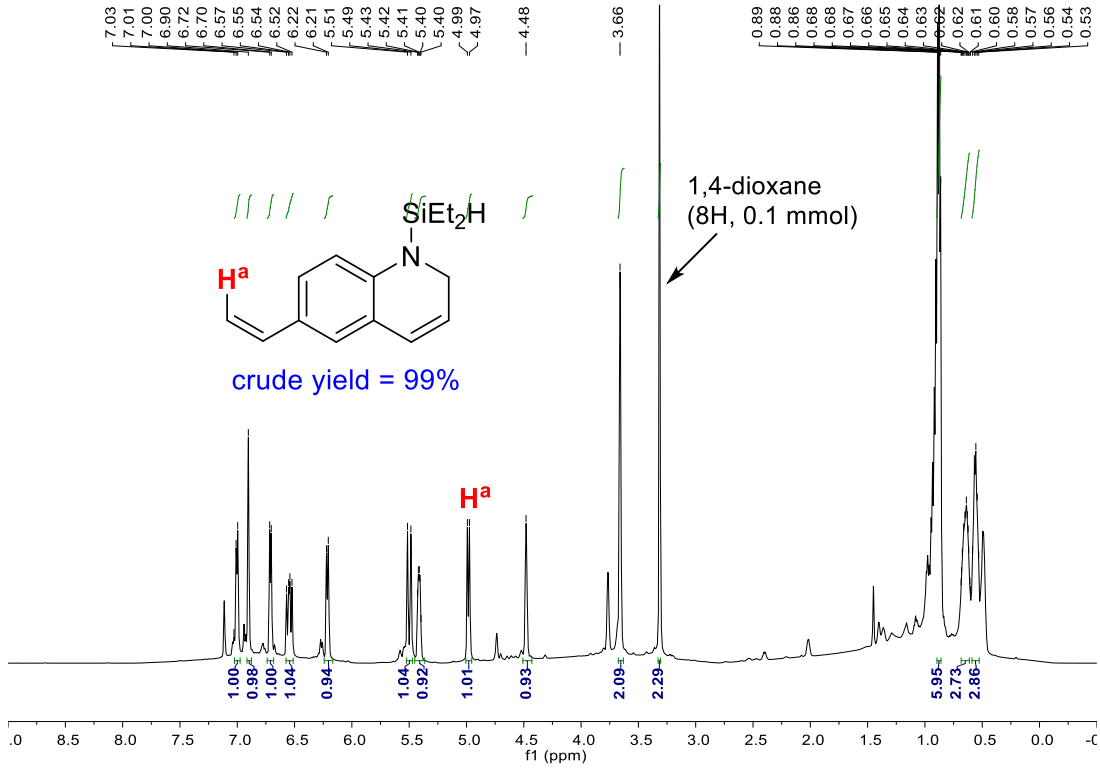
^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); 1,4-dioxane, internal standard

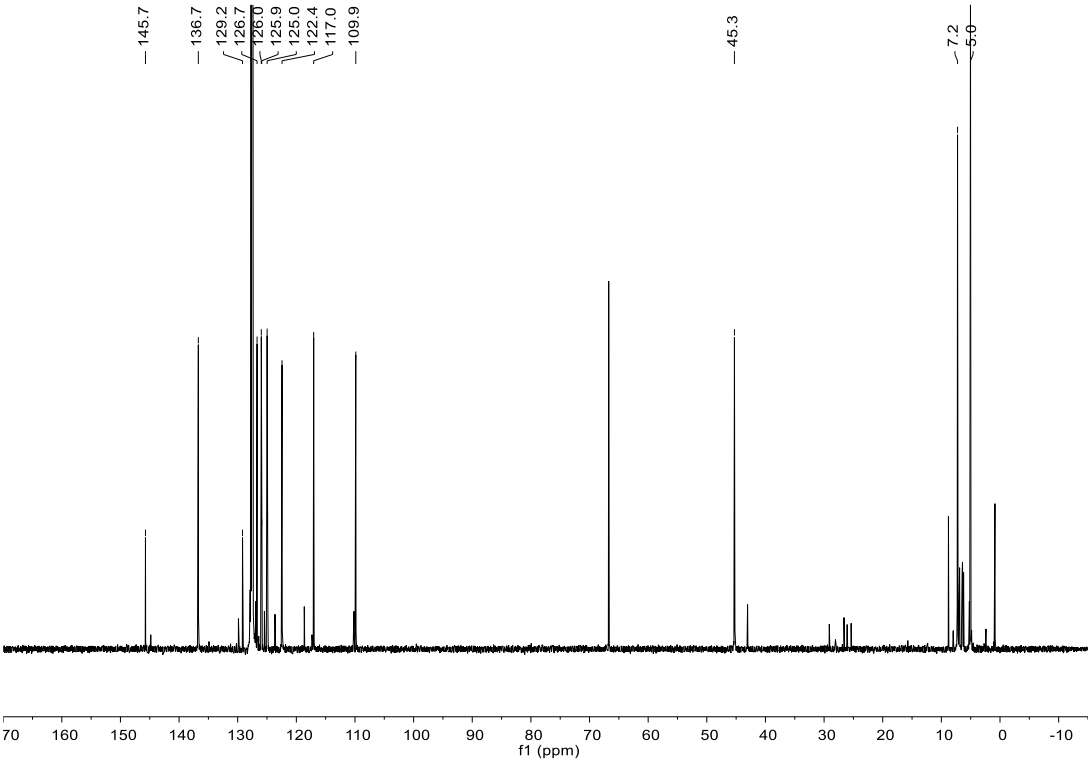




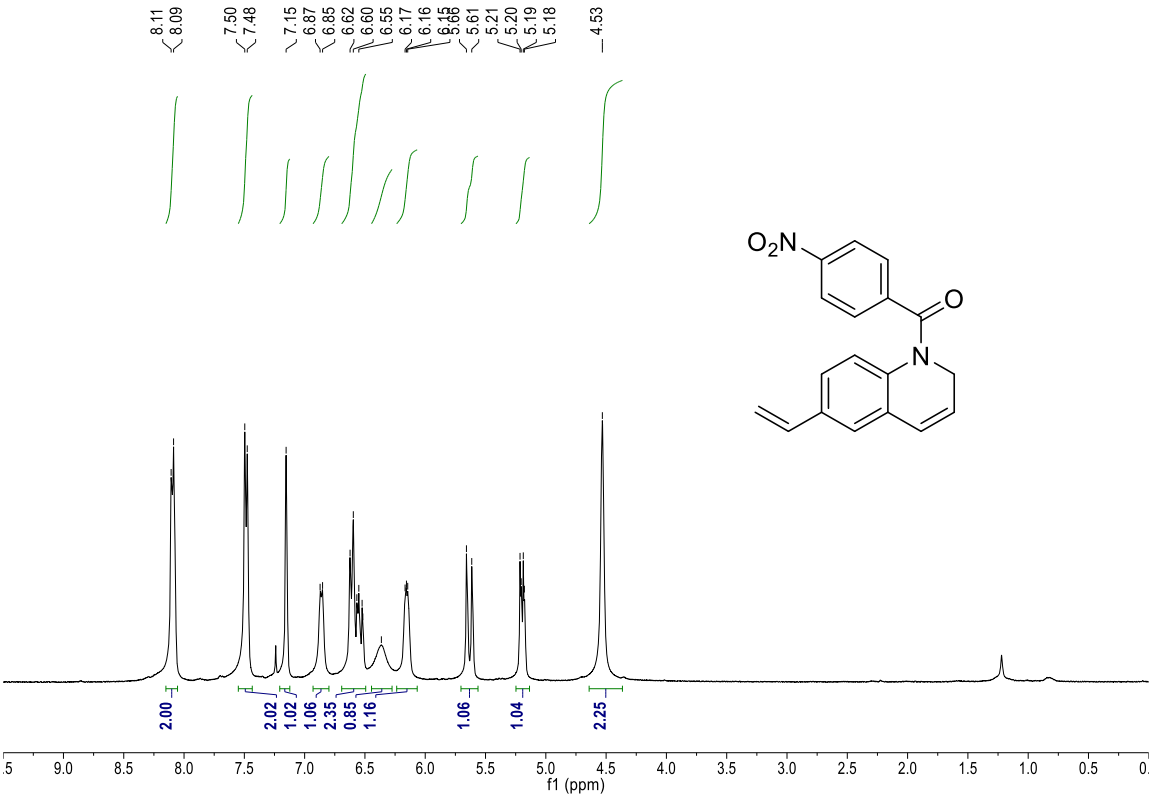
1-(Diethylsilyl)-6-vinyl-1,2-dihydroquinoline (3o)

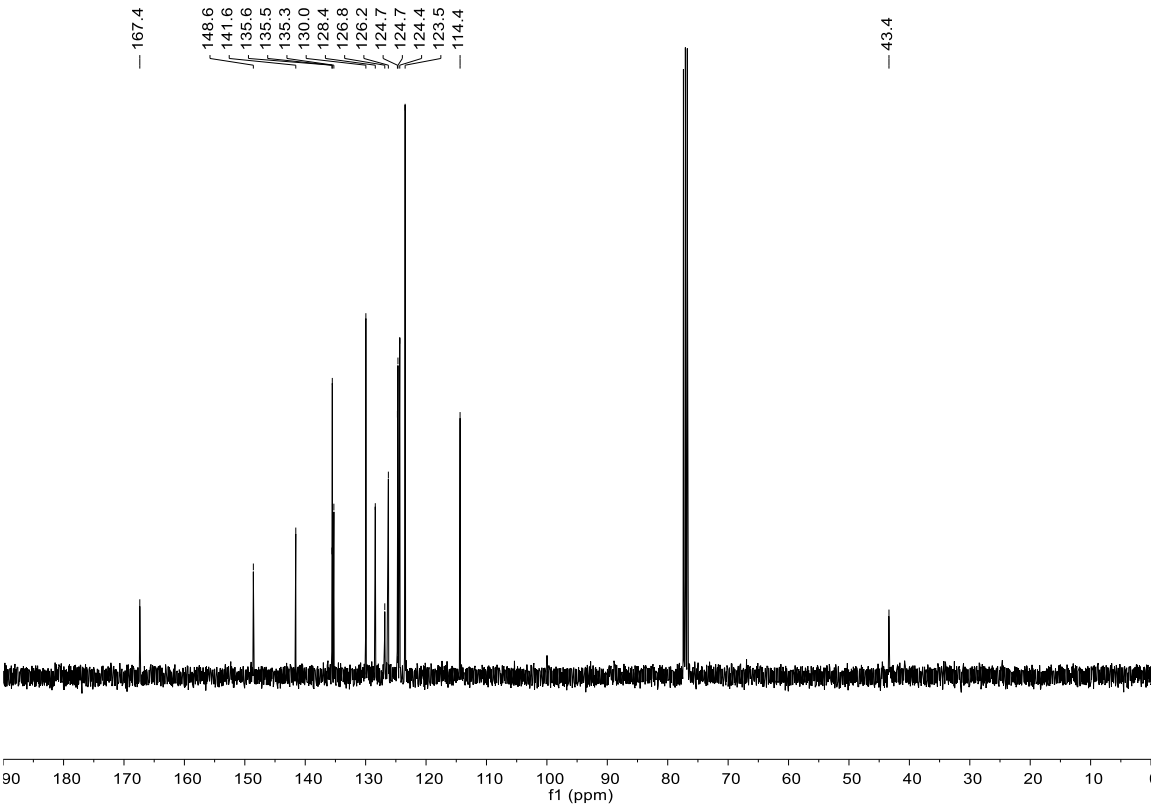
^{1}H NMR (600 MHz, C_6D_6) & ^{13}C NMR (150 MHz, C_6D_6); 1,4-dioxane, internal standard





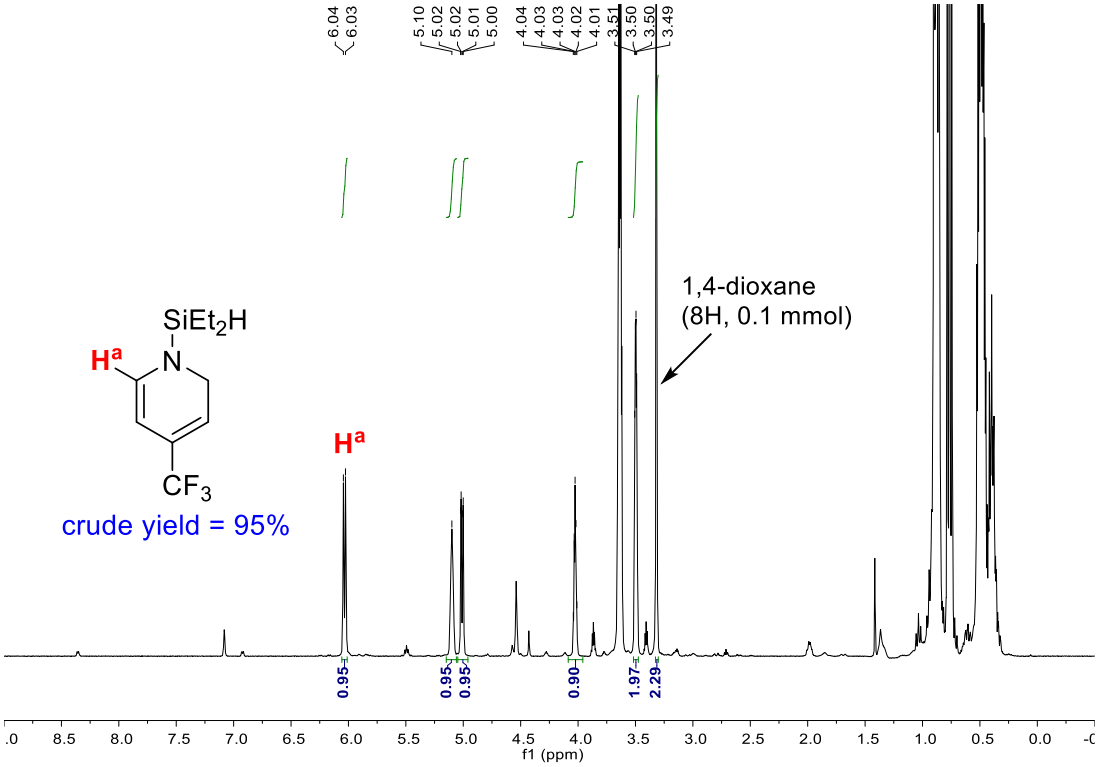
(4-Nitrophenyl)[6-vinylquinolin-1(2H)-yl]methanone (3o-PNB)

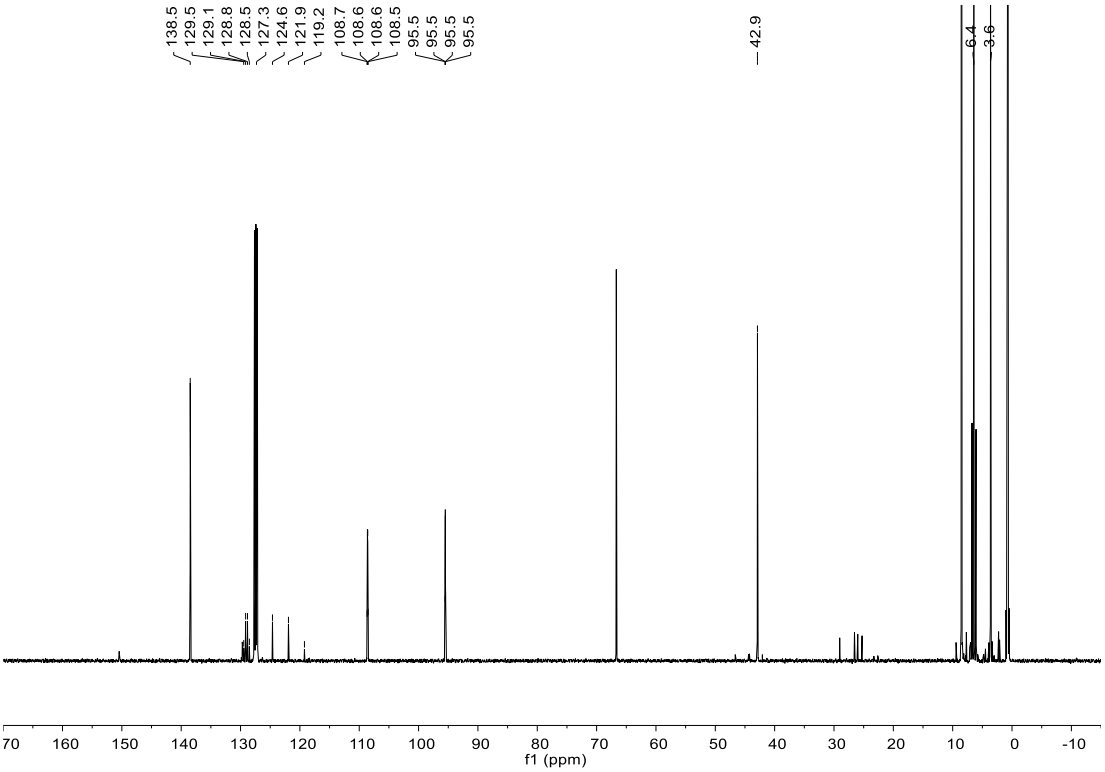




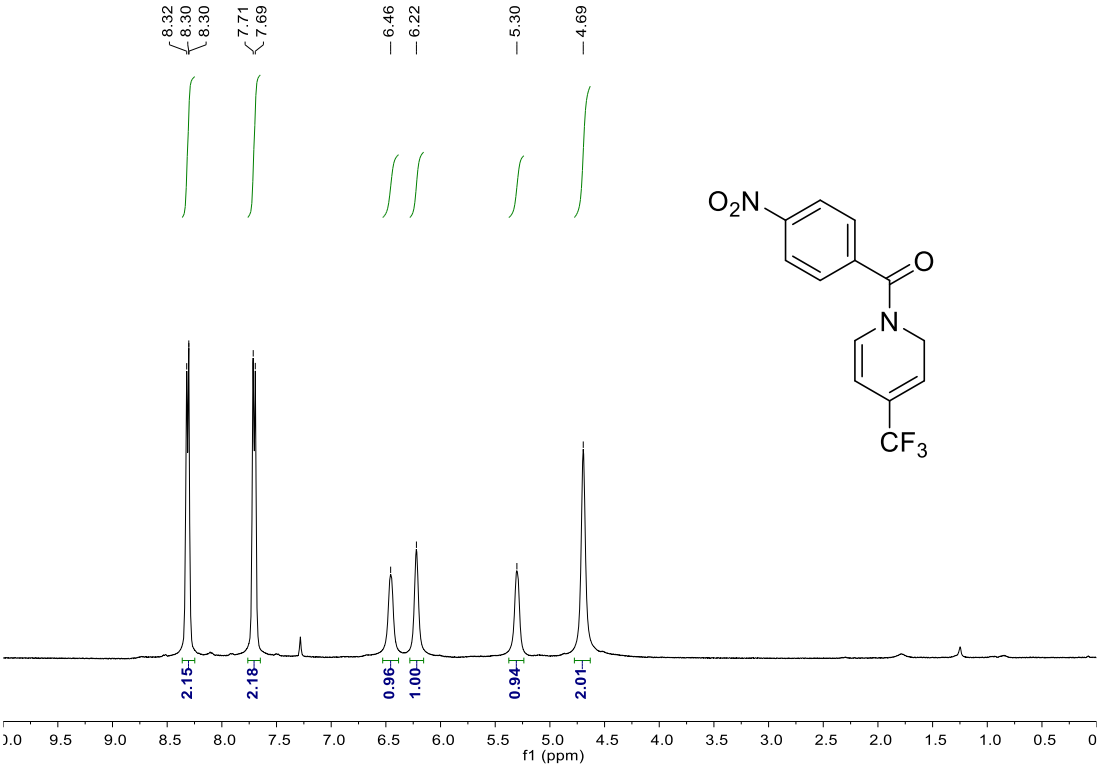
1-(Diethylsilyl)-4-(trifluoromethyl)-1,2-dihydropyridine (Table 3, 3p)

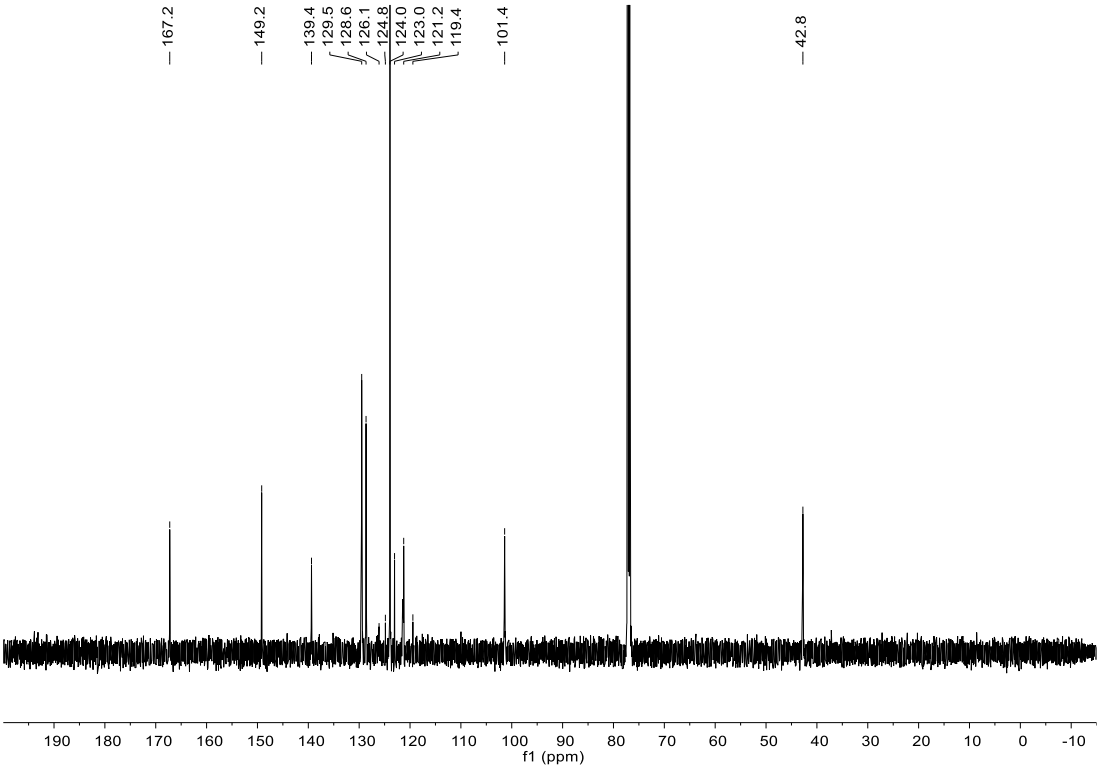
^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); 1,4-dioxane, internal standard





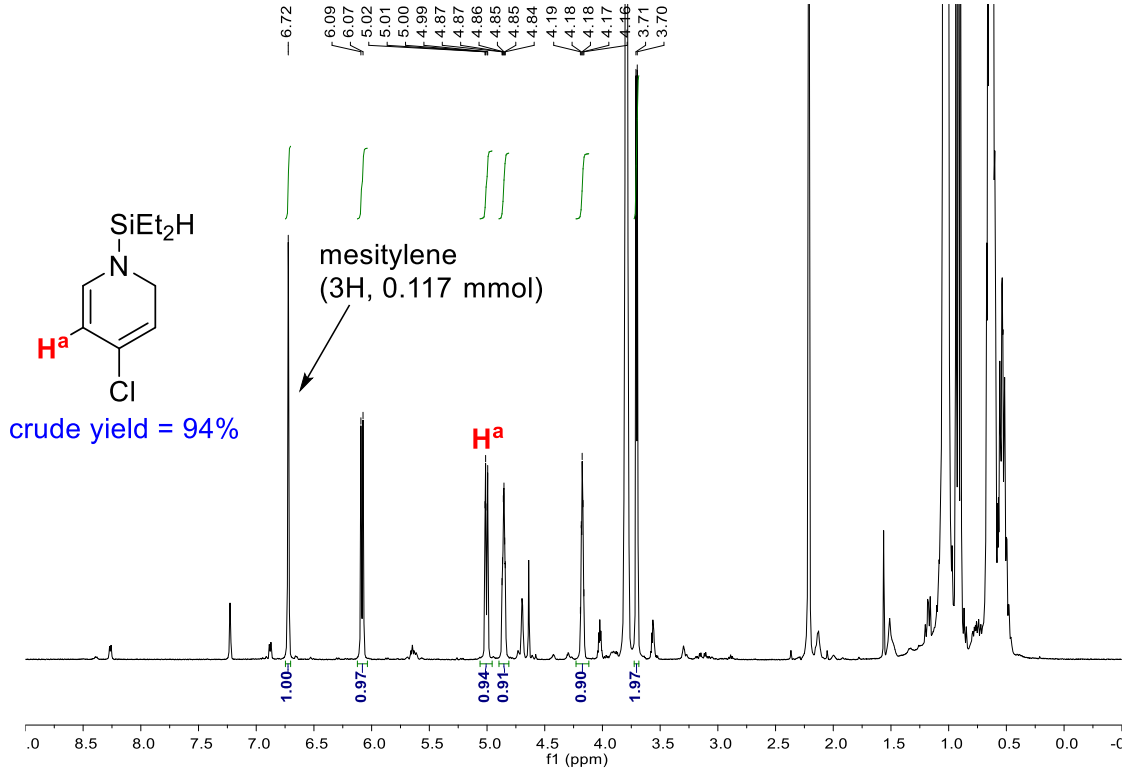
(4-Nitrophenyl)[4-(trifluoromethyl)pyridin-1(2H)-yl]methanone (3p-PNB)

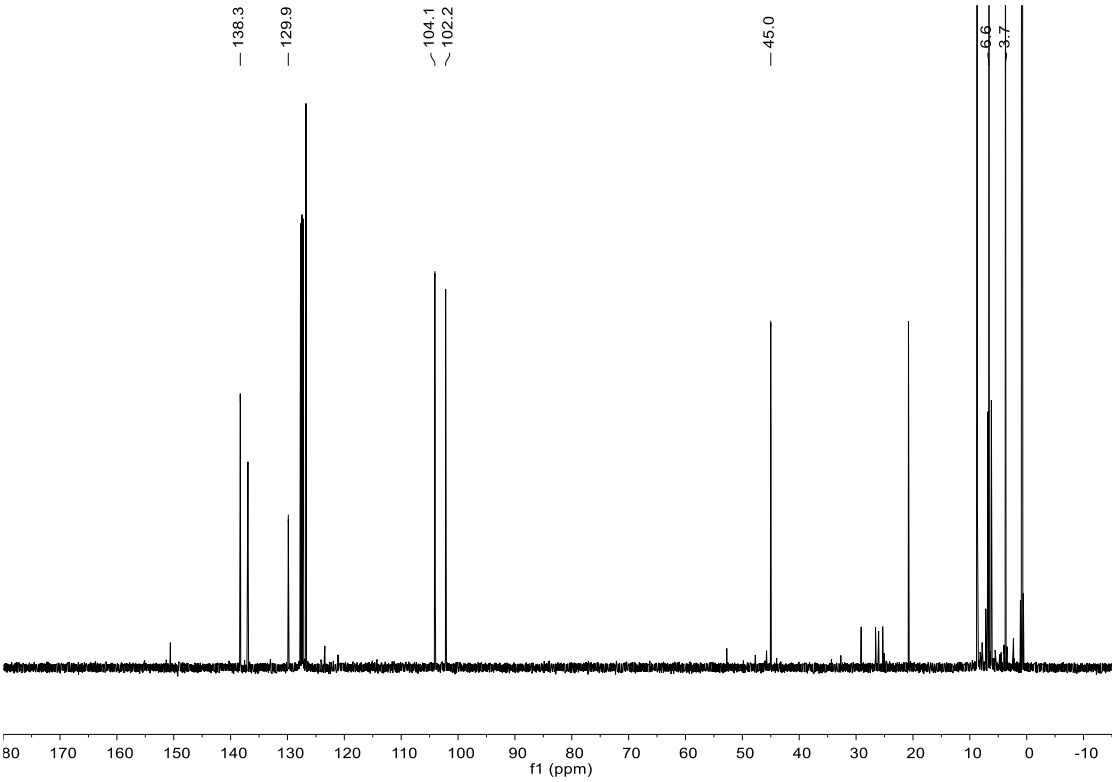




4-Chloro-1-(diethylsilyl)-1,2-dihydropyridine (3q)

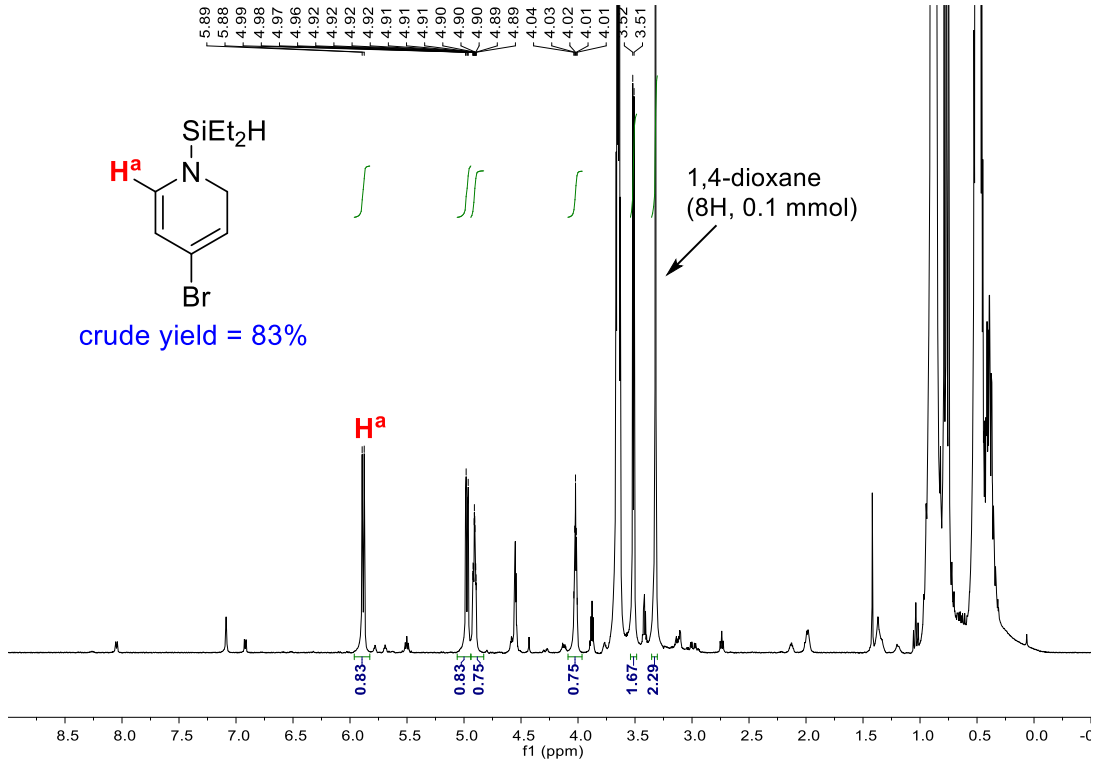
^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); mesitylene, internal standard

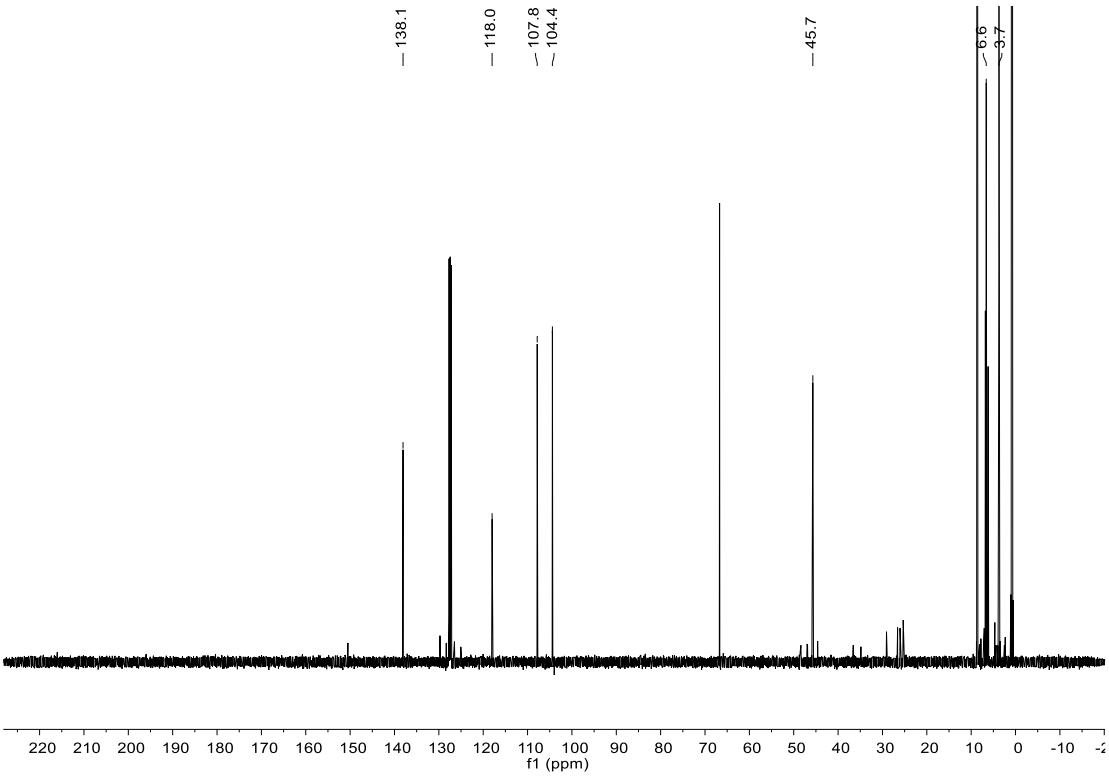




4-Bromo-1-(diethylsilyl)-1,2-dihydropyridine (**3r**)

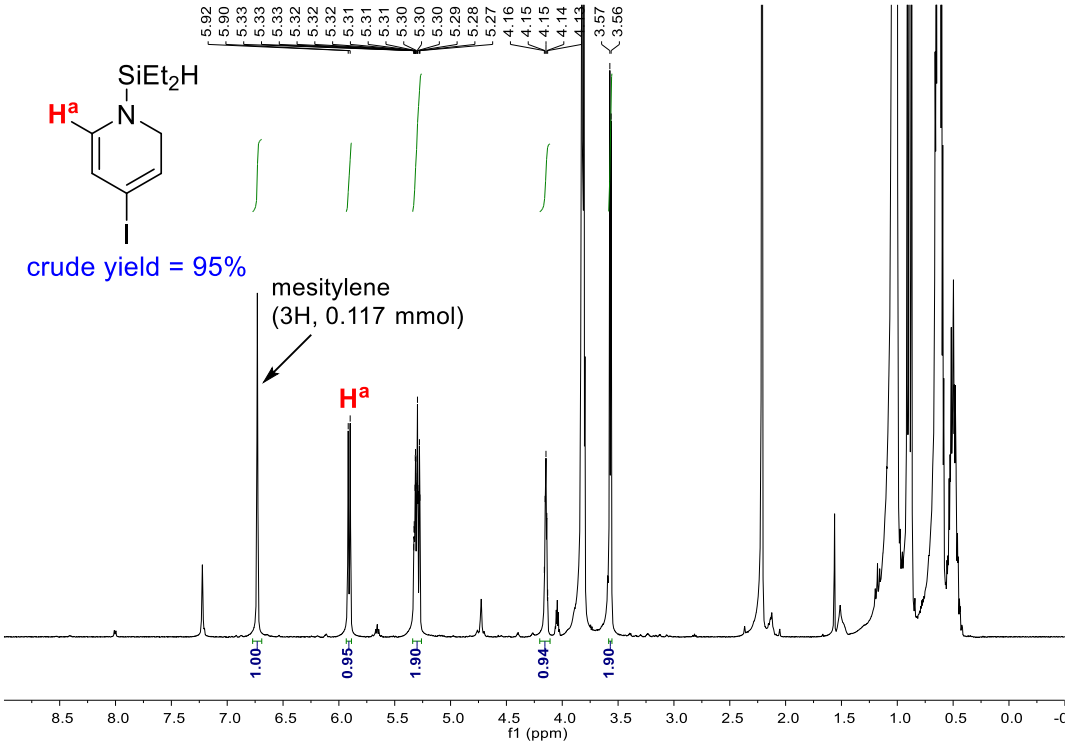
^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); 1,4-dioxane, internal standard

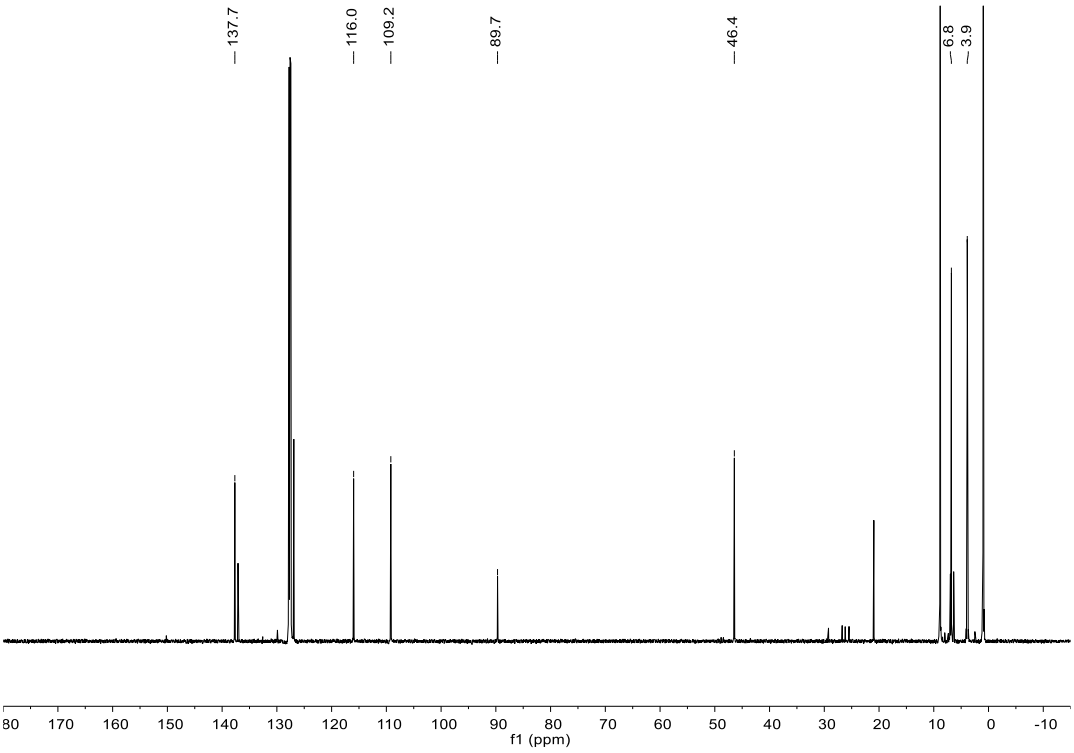




1-(Diethylsilyl)-4-iodo-1,2-dihydropyridine (**3s**)

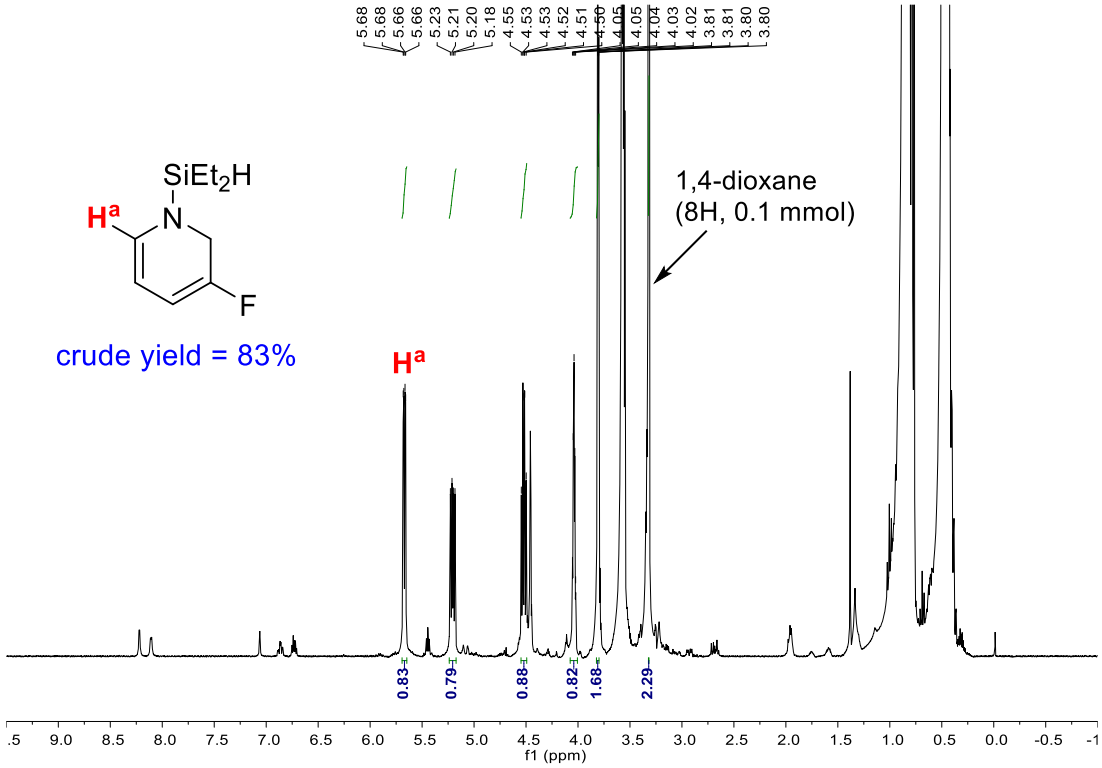
^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); mesitylene, internal standard

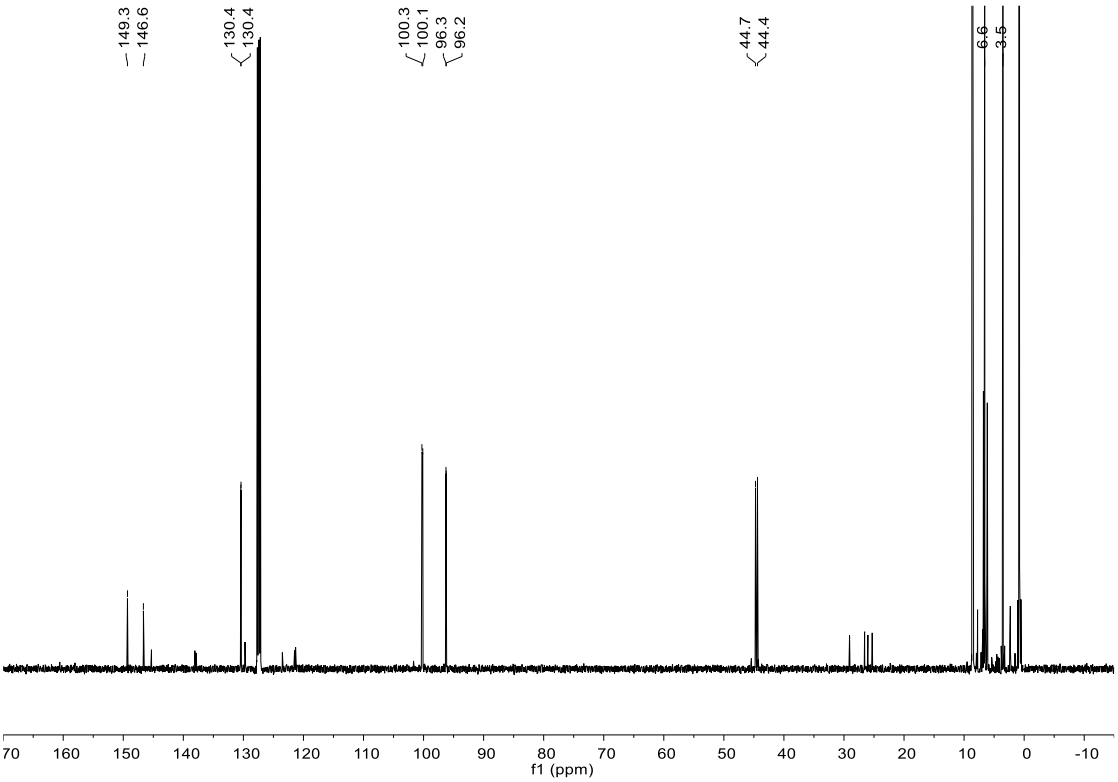




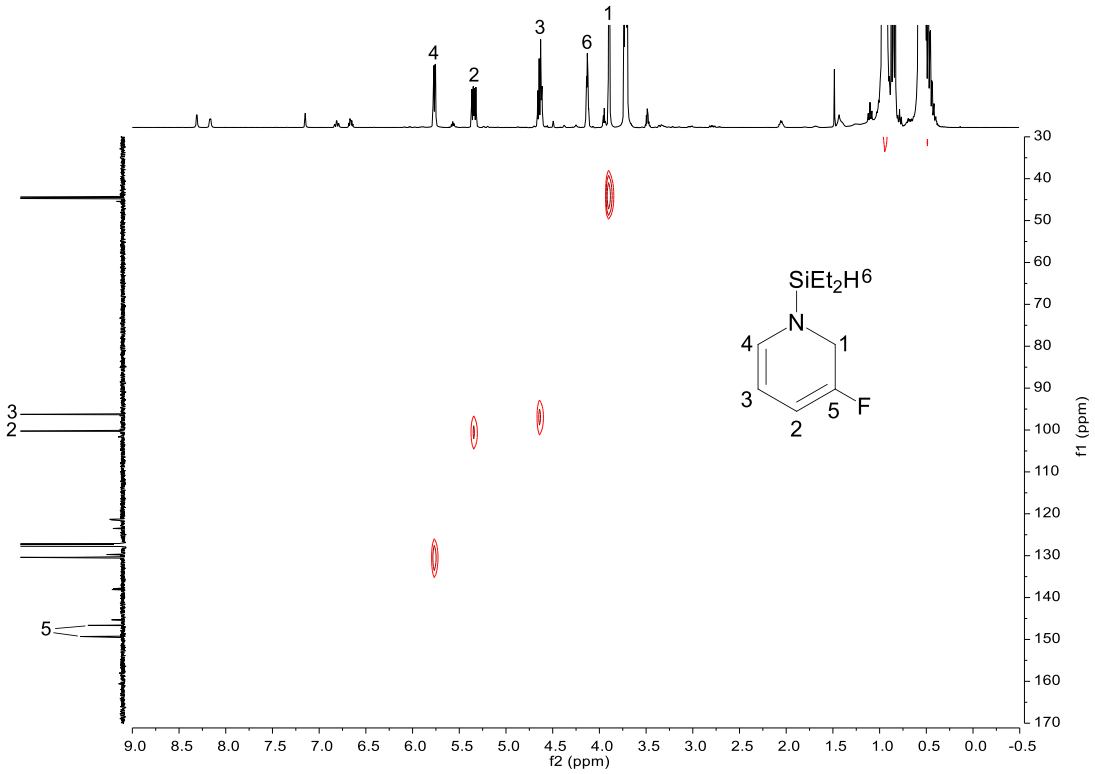
1-(Diethylsilyl)-3-fluoro-1,2-dihydropyridine (3t)

^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); 1,4-dioxane, internal standard

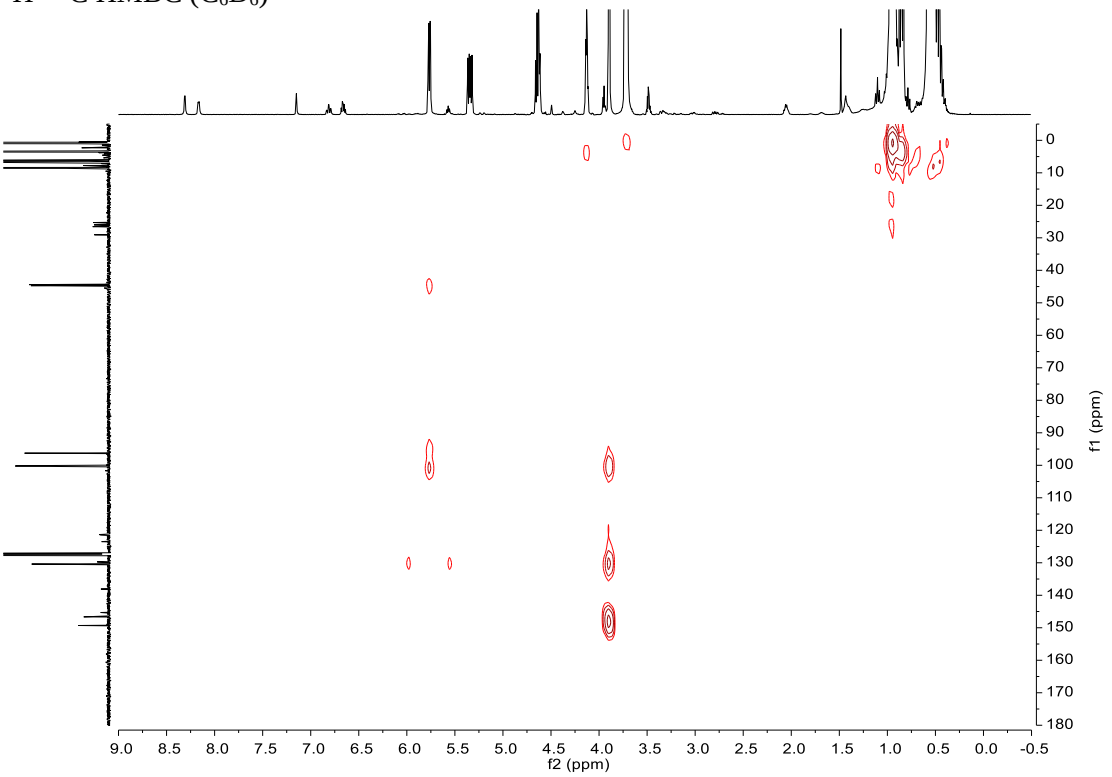




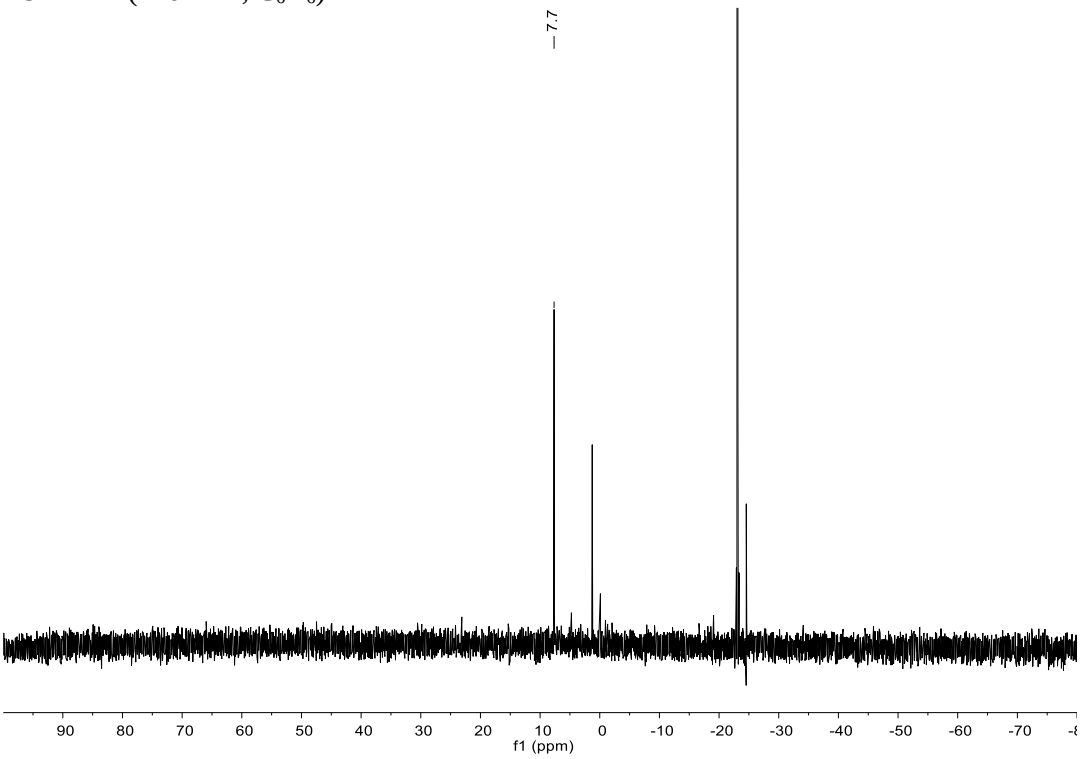
^{1}H -^{13}C HSQC (C_6D_6)



^{1}H -^{13}C HMBC (C_6D_6)

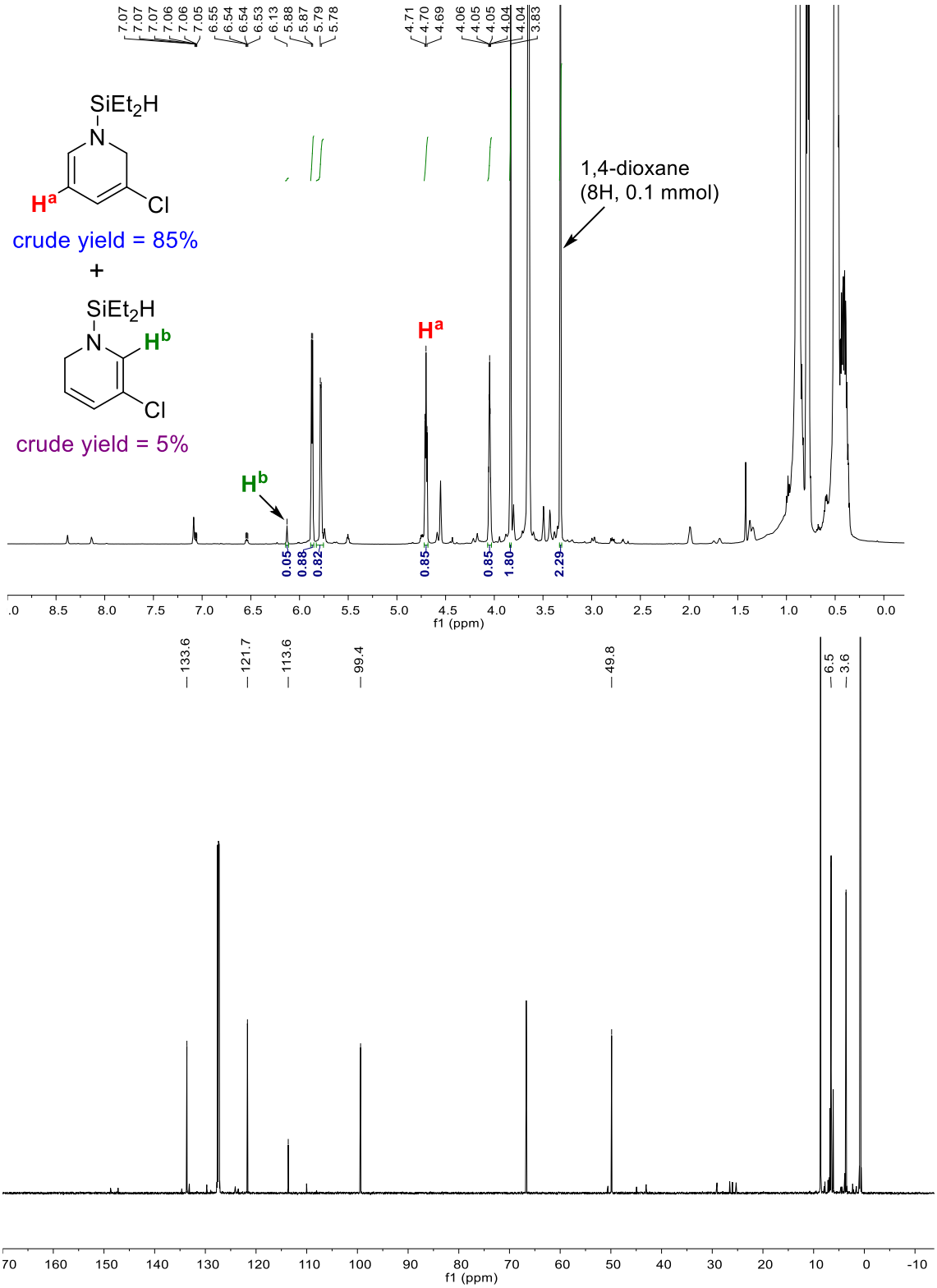


^{29}Si NMR (120MHz, C_6D_6)

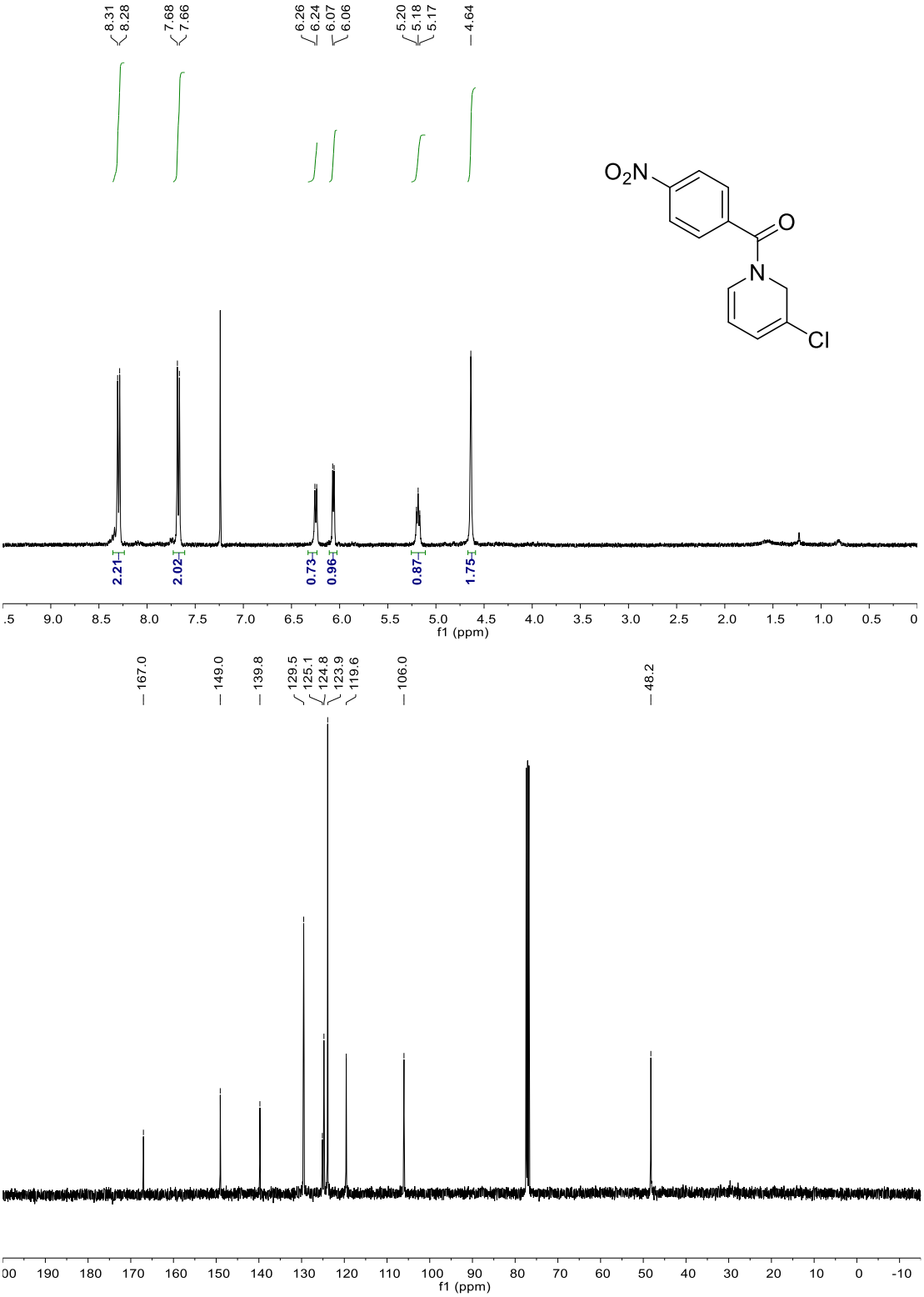


3-Chloro-1-(diethylsilyl)-1,2-dihydropyridine (3u)

^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR(100 MHz, C_6D_6); 1,4-dioxane, internal standard

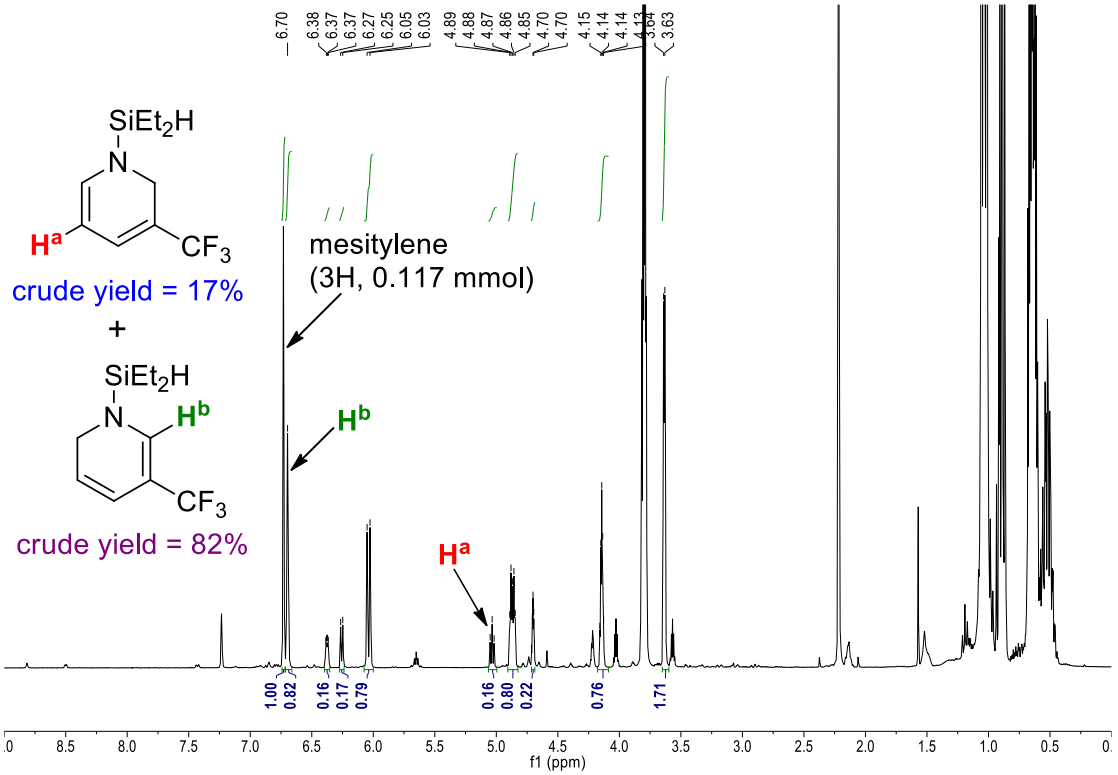


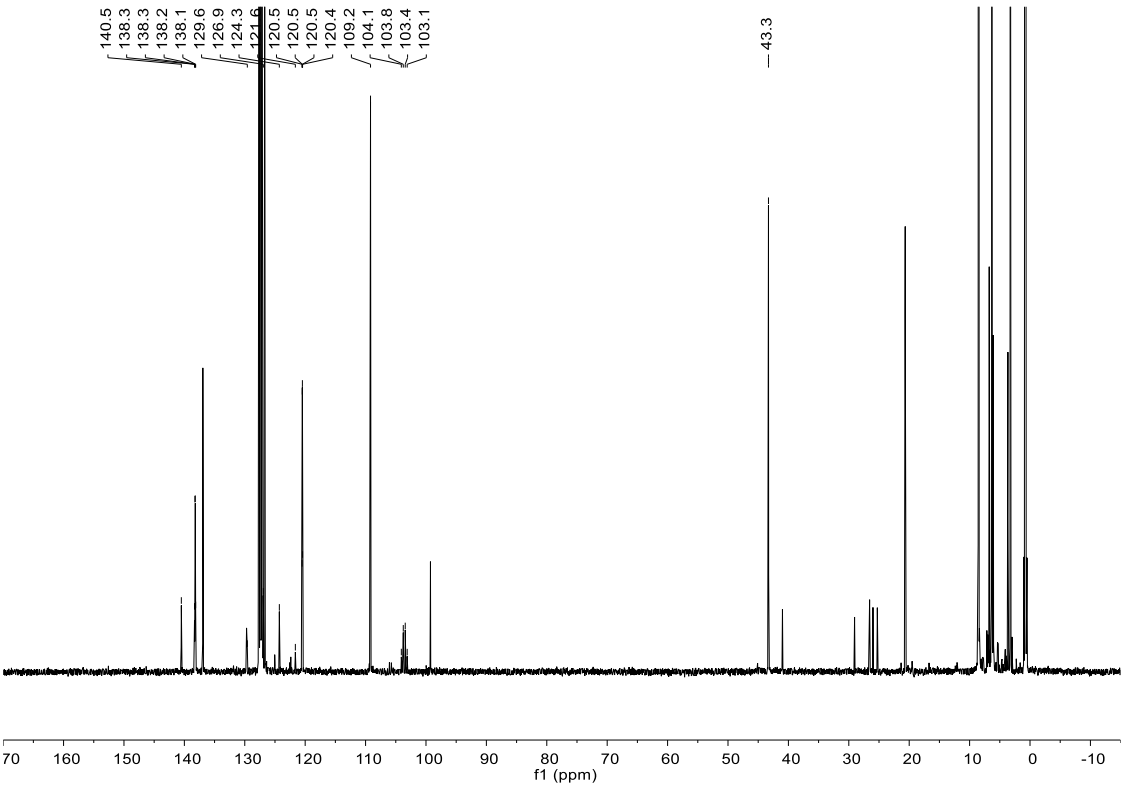
[3-Chloropyridin-1(2H)-yl](4-nitrophenyl)methanone (3u-PNB)



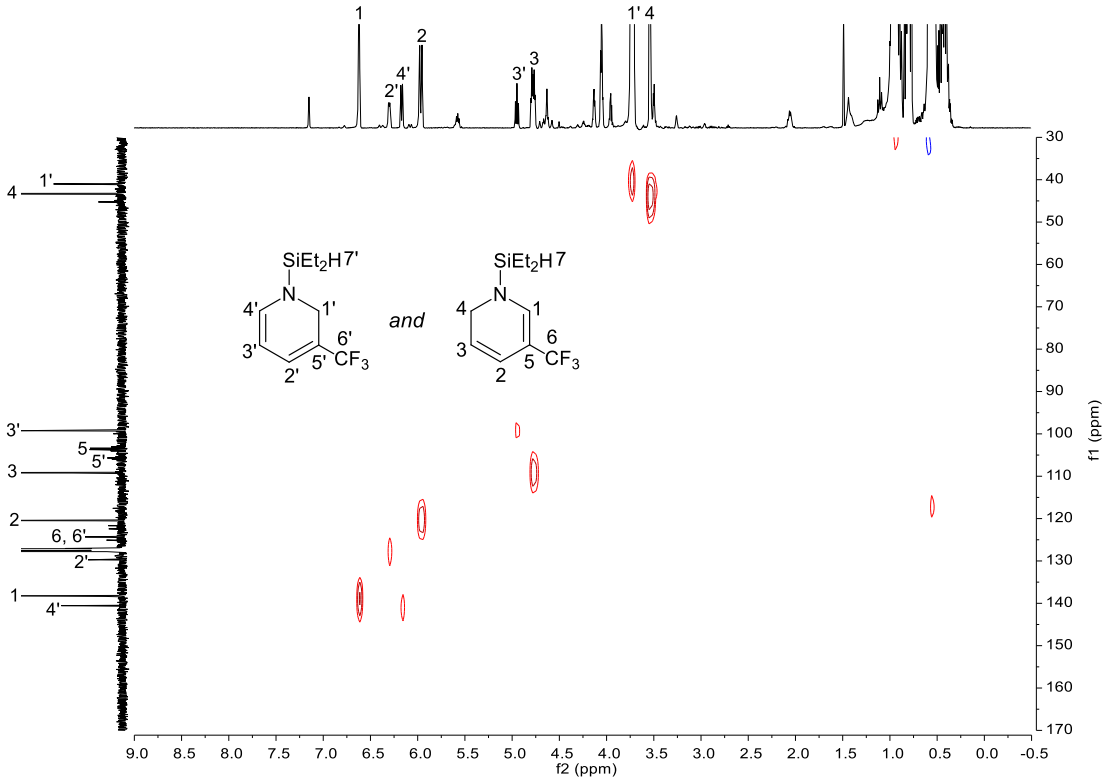
1-(Diethylsilyl)-3-(trifluoromethyl)-1,2-dihydropyridine (3v)

^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); mesitylene, internal standard

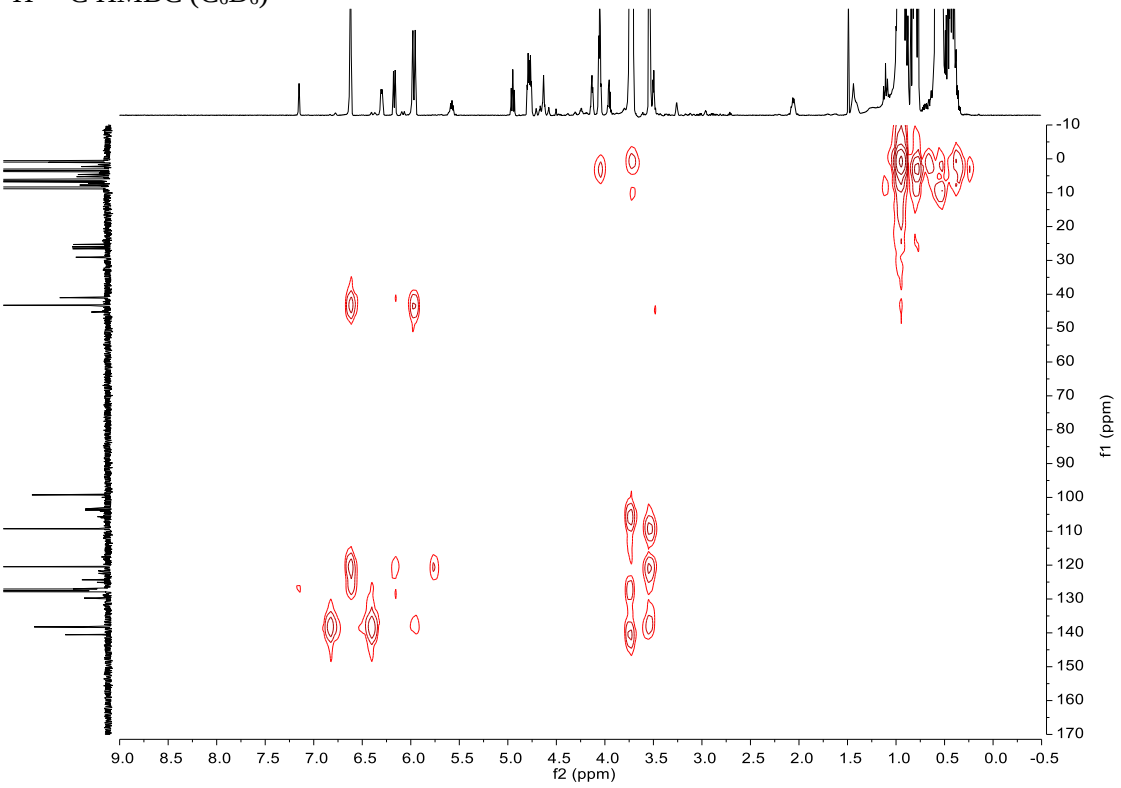




^{1}H -^{13}C HSQC (C_6D_6)

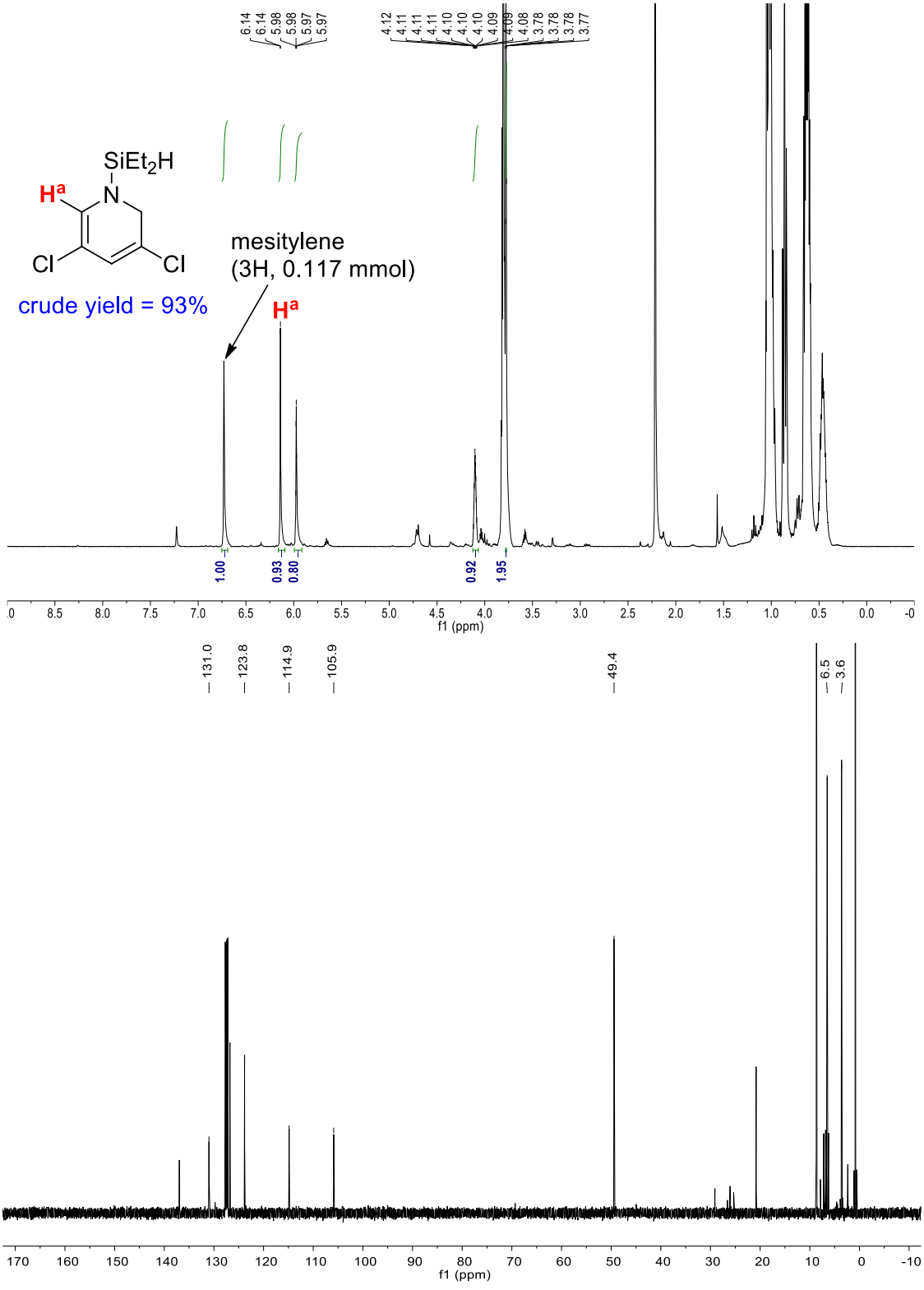


^{1}H -^{13}C HMBC (C_6D_6)



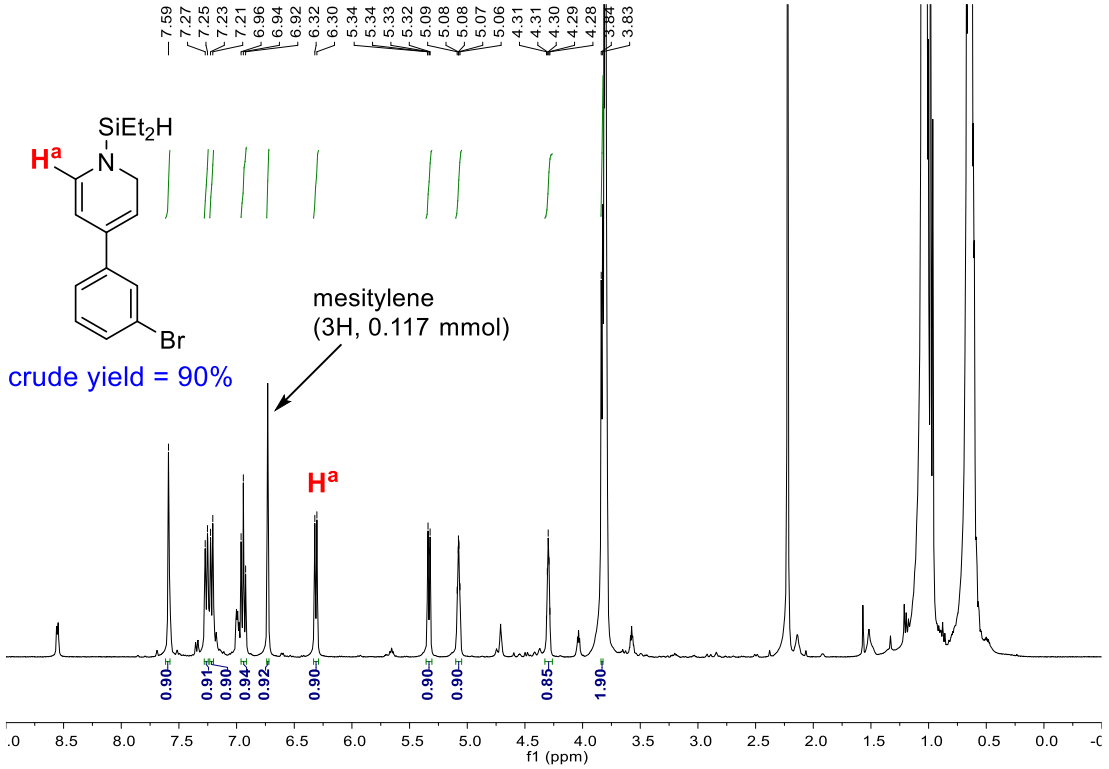
3,5-Dichloro-1-(diethylsilyl)-1,2-dihydropyridine (3w)

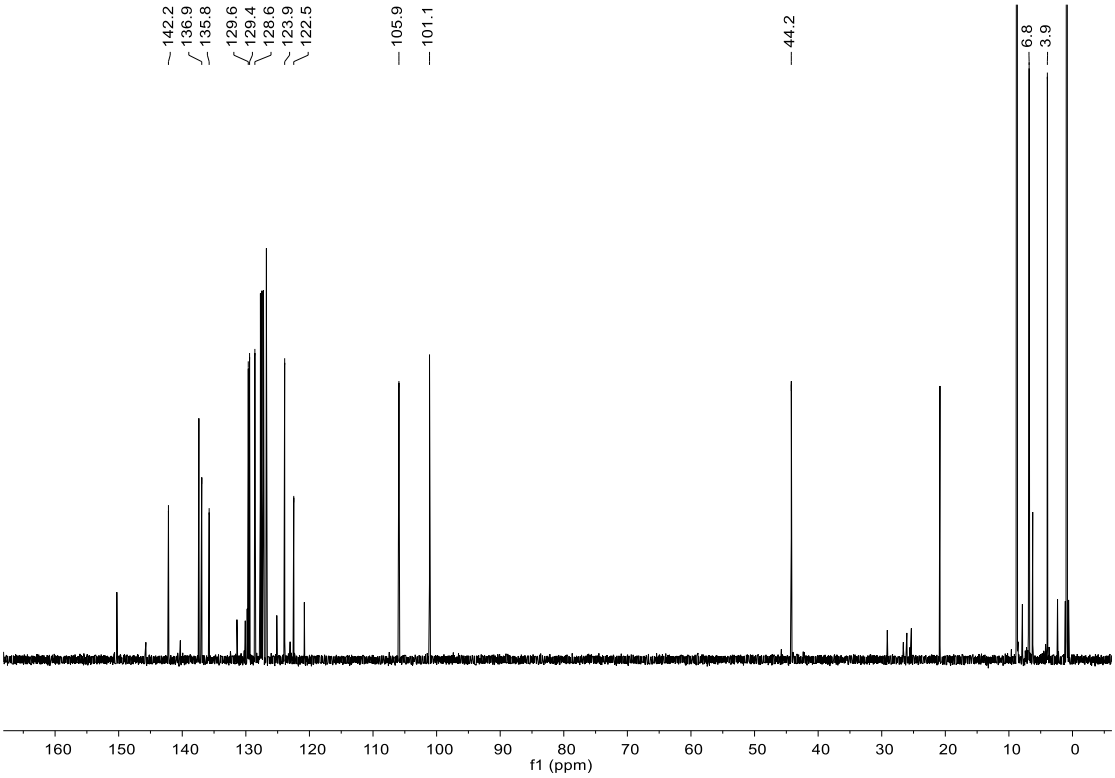
^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); mesitylene, internal standard



4-(3-Bromophenyl)-1-(diethylsilyl)-1,2-dihydropyridine (3x)

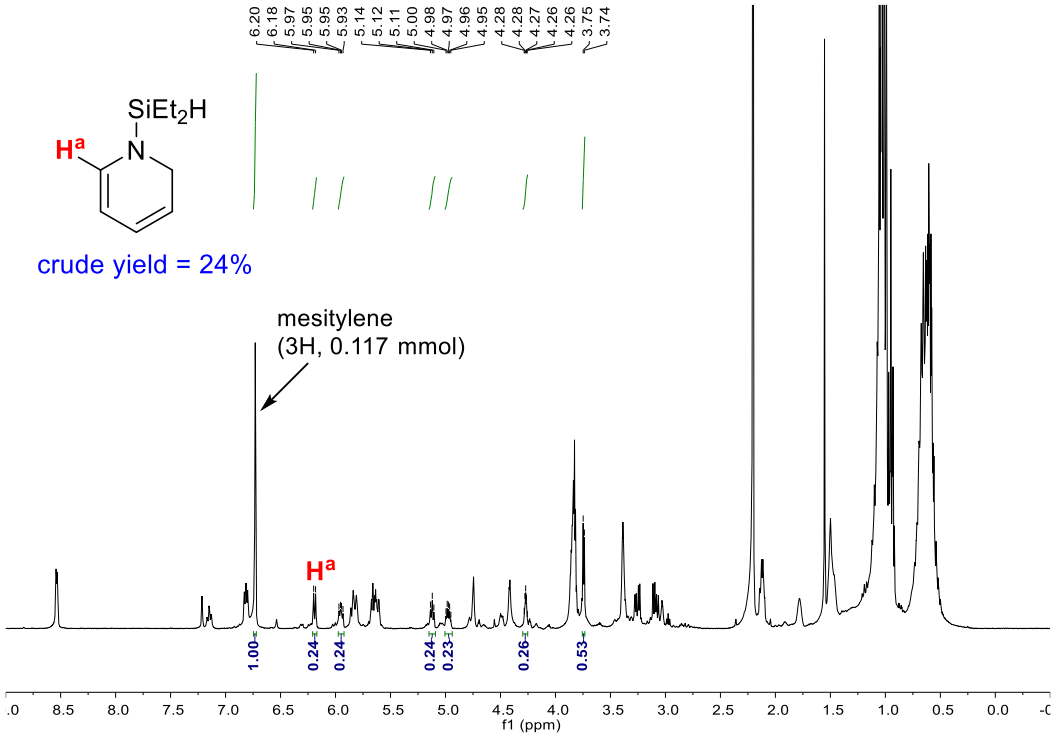
^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); mesitylene, internal standard





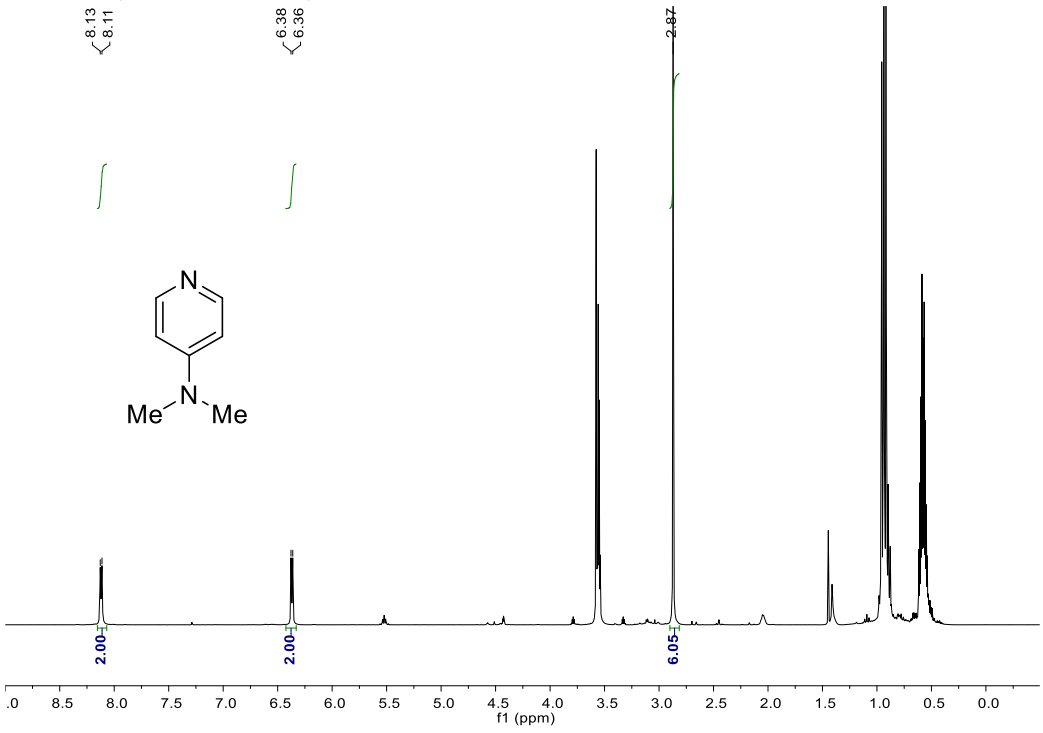
1-(Diethylsilyl)-1,2-dihydropyridine (A dotted box in Table 3)

^{1}H NMR (400 MHz, C_6D_6); mesitylene, internal standard



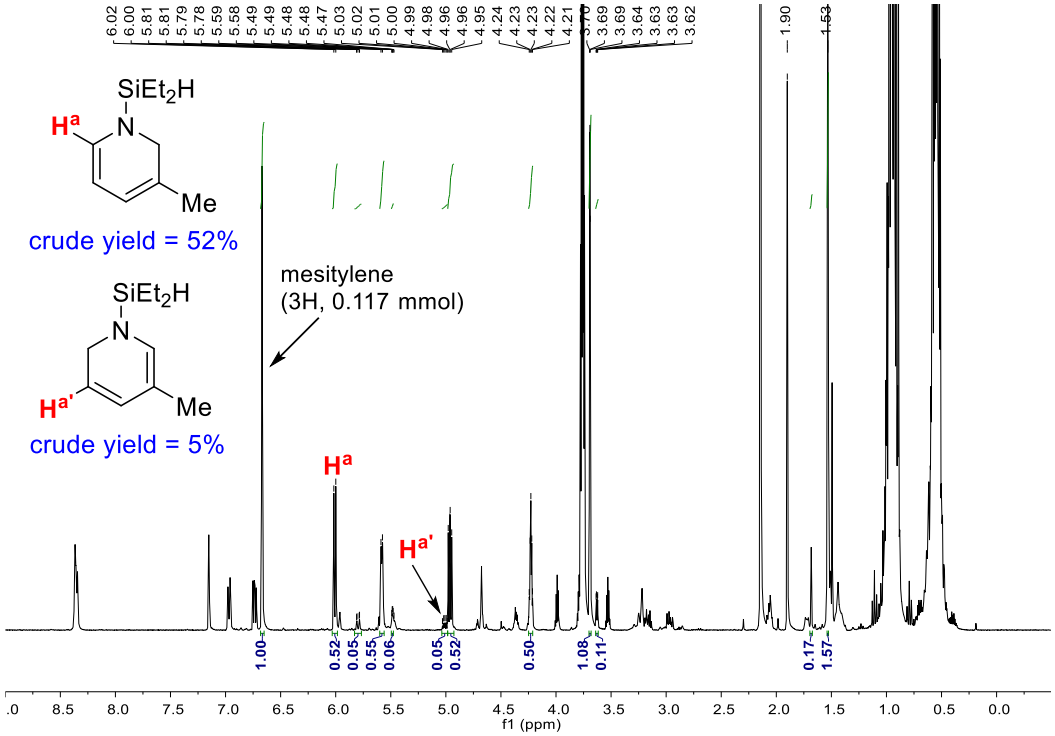
4-Dimethylaminopyridine (A dotted box in Table 3)

^{1}H NMR (400 MHz, C_6D_6); No reaction



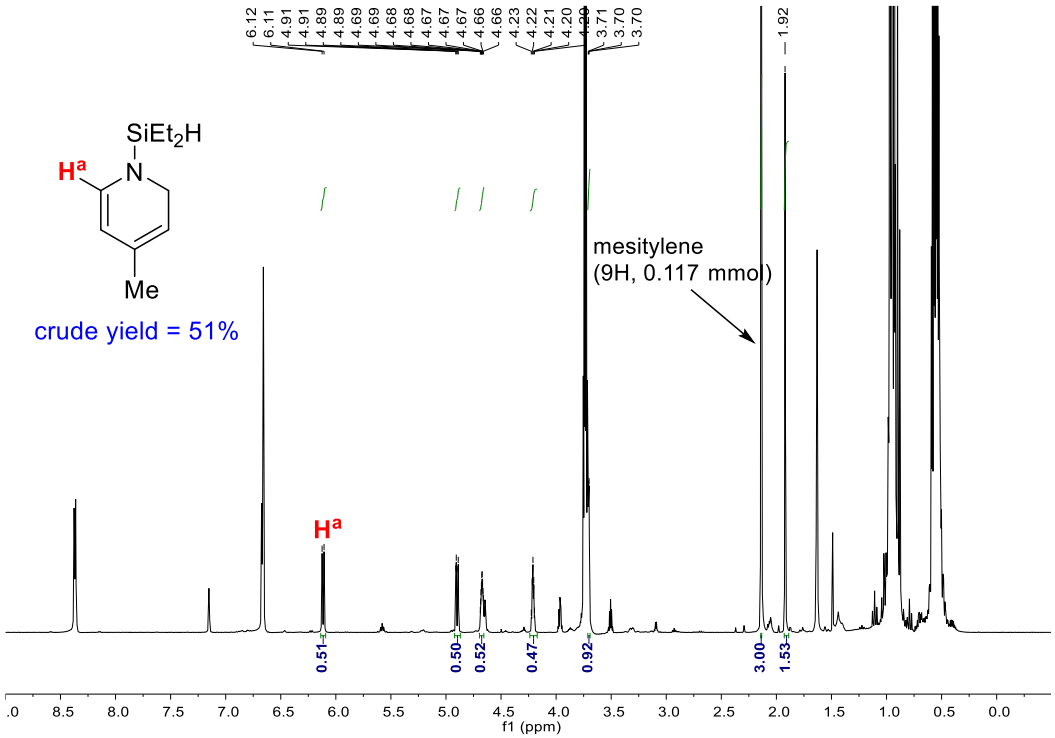
1-(Diethylsilyl)-3-methyl-1,2-dihydropyridine (A dotted box in Table 3)

^{1}H NMR (400 MHz, C_6D_6); mesitylene, internal standard



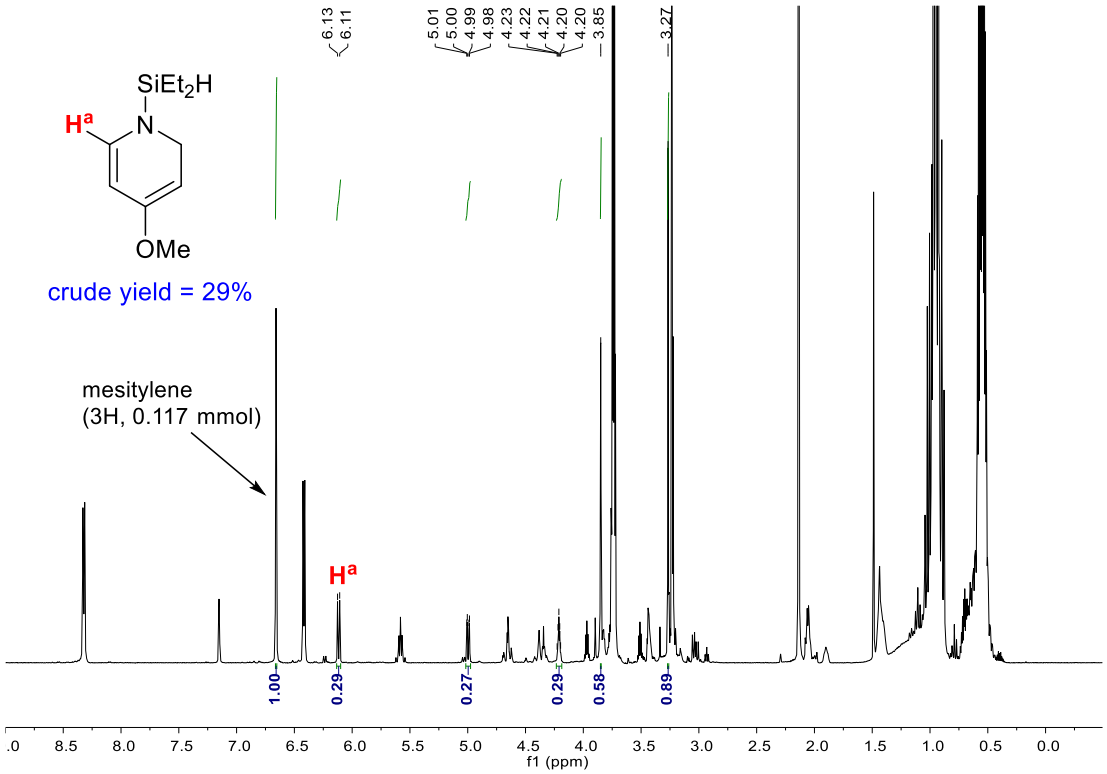
1-(Diethylsilyl)-4-methyl-1,2-dihydropyridine (A dotted box in Table 3)

^{1}H NMR (400 MHz, C_6D_6); mesitylene, internal standard



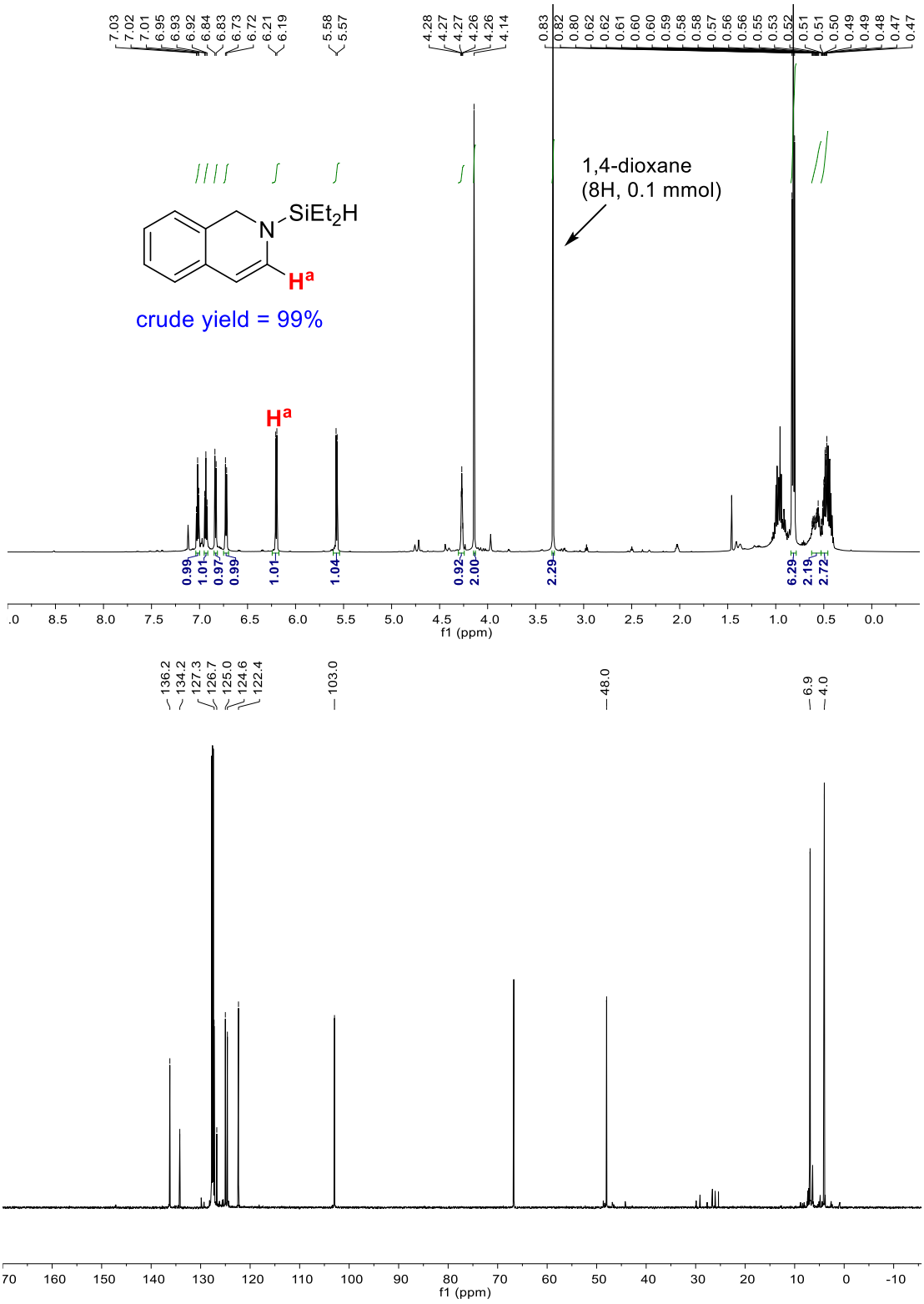
1-(Diethylsilyl)-4-methoxy-1,2-dihydropyridine (A dotted box in Table 3)

^{1}H NMR (400 MHz, C_6D_6); mesitylene, internal standard



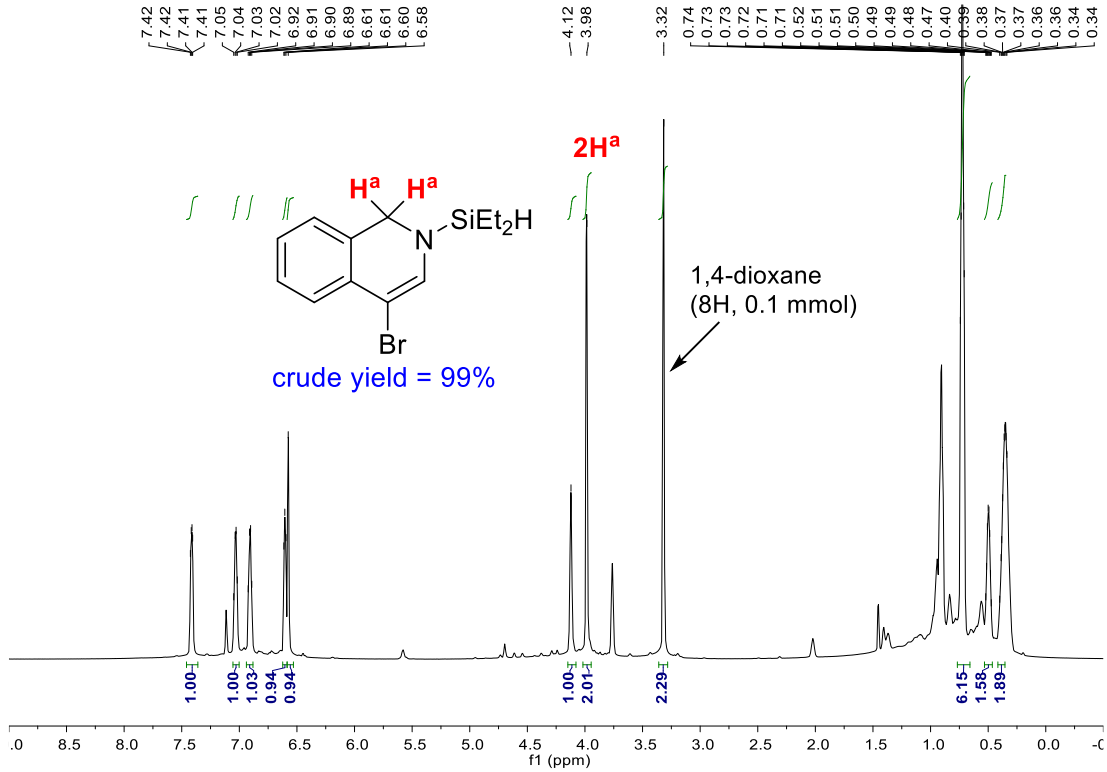
2-(Diethylsilyl)-1,2-dihydroisoquinoline (**Table 4, 5a**)

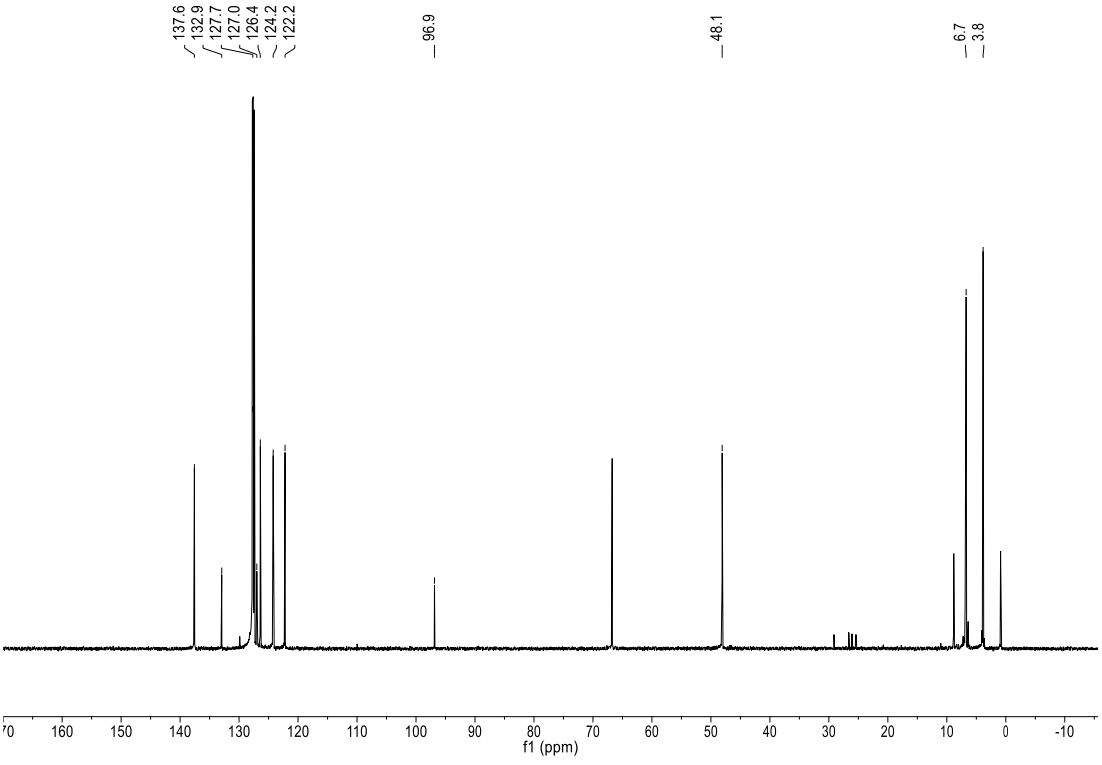
^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); 1,4-dioxane, internal standard



4-Bromo-2-(diethylsilyl)-1,2-dihydroisoquinoline (5b)

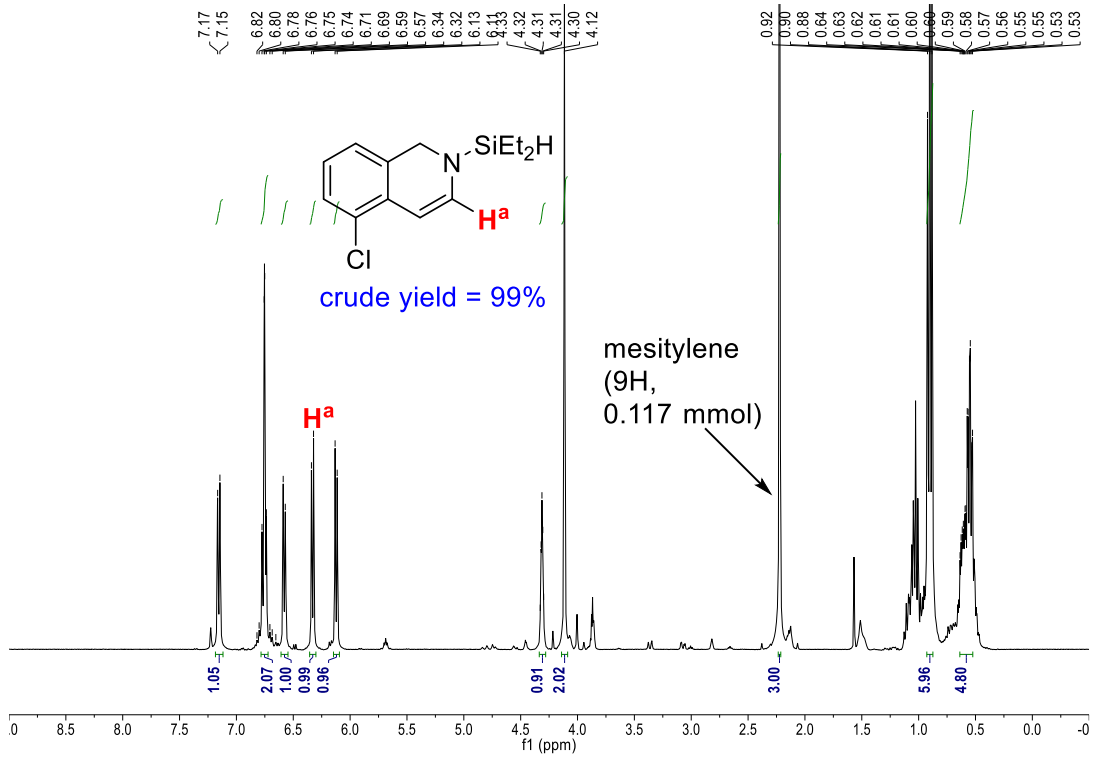
^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); 1,4-dioxane, internal standard

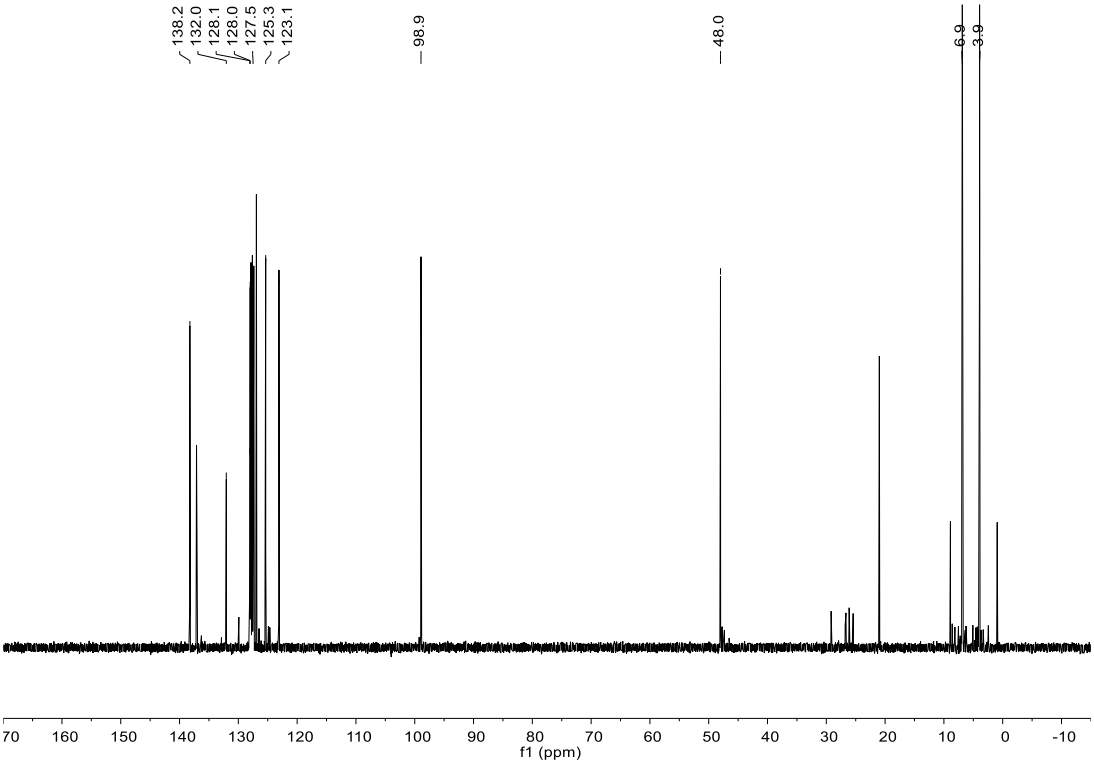




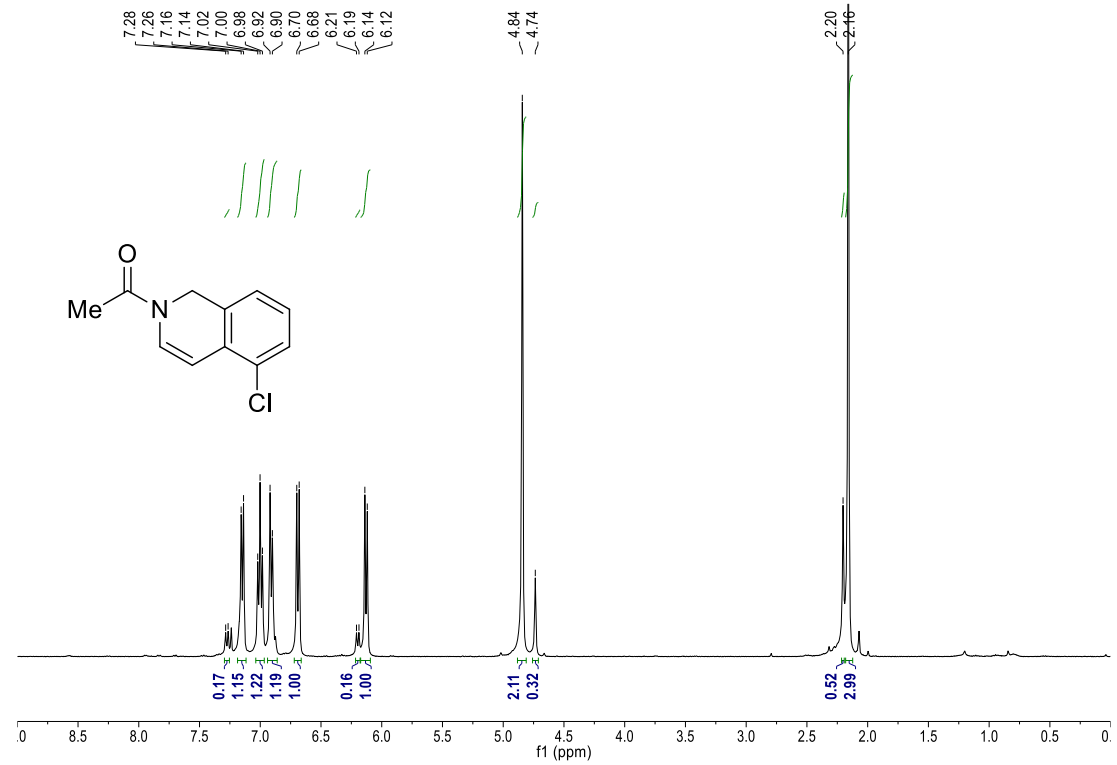
5-Chloro-2-(diethylsilyl)-1,2-dihydroisoquinoline (5c)

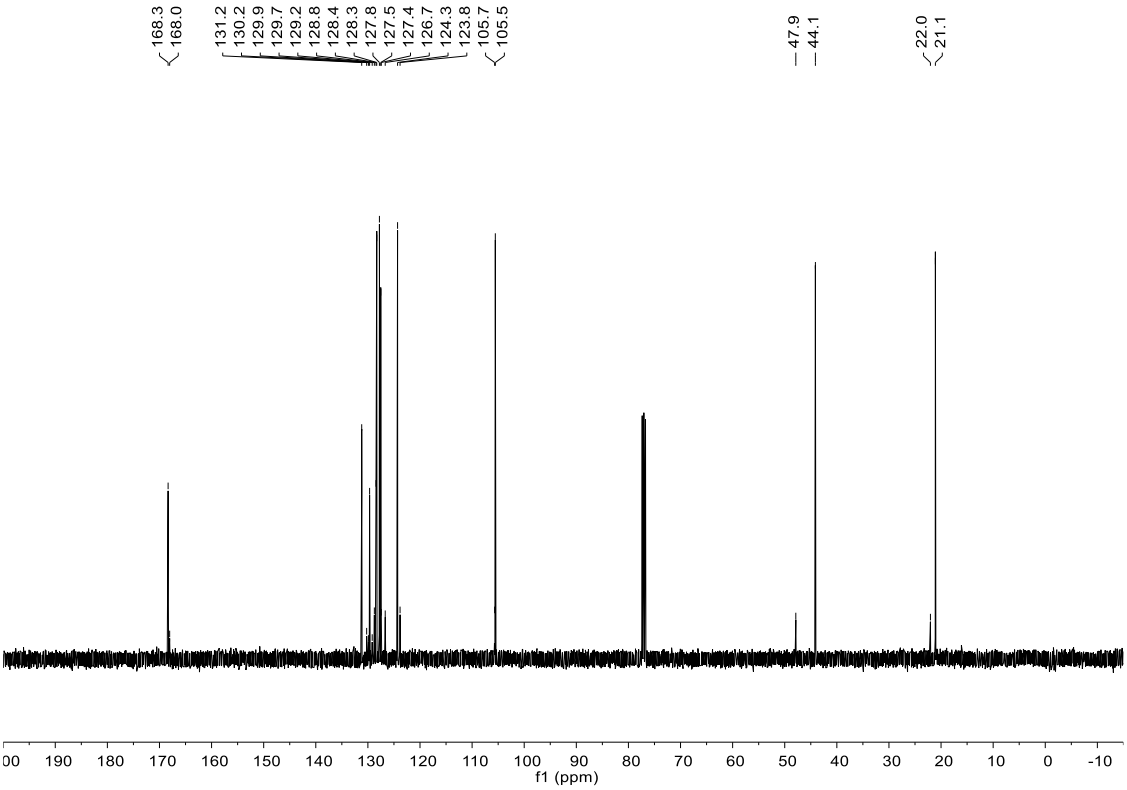
^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); mesitylene, internal standard





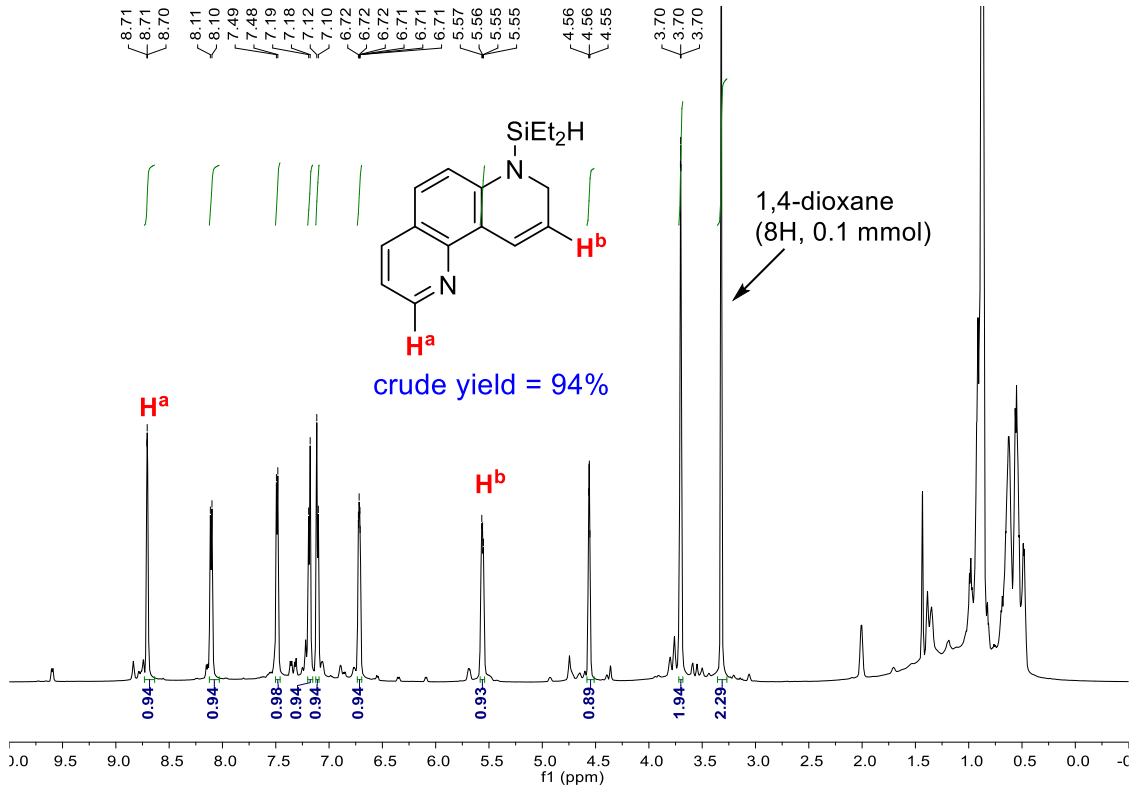
1-[5-Chloroisoquinolin-2(1H)-yl]ethan-1-one (5c-Ac)

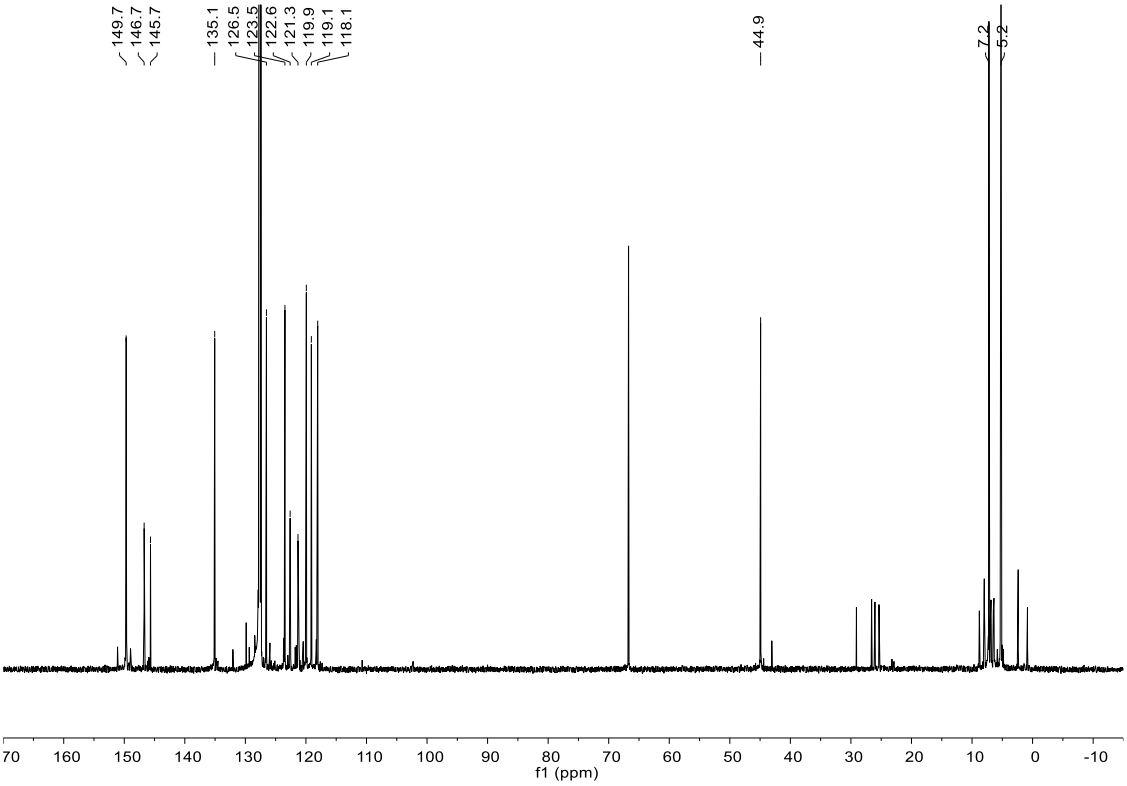




7-(Diethylsilyl)-7,8-dihydro-1,7-phenanthroline (5d)

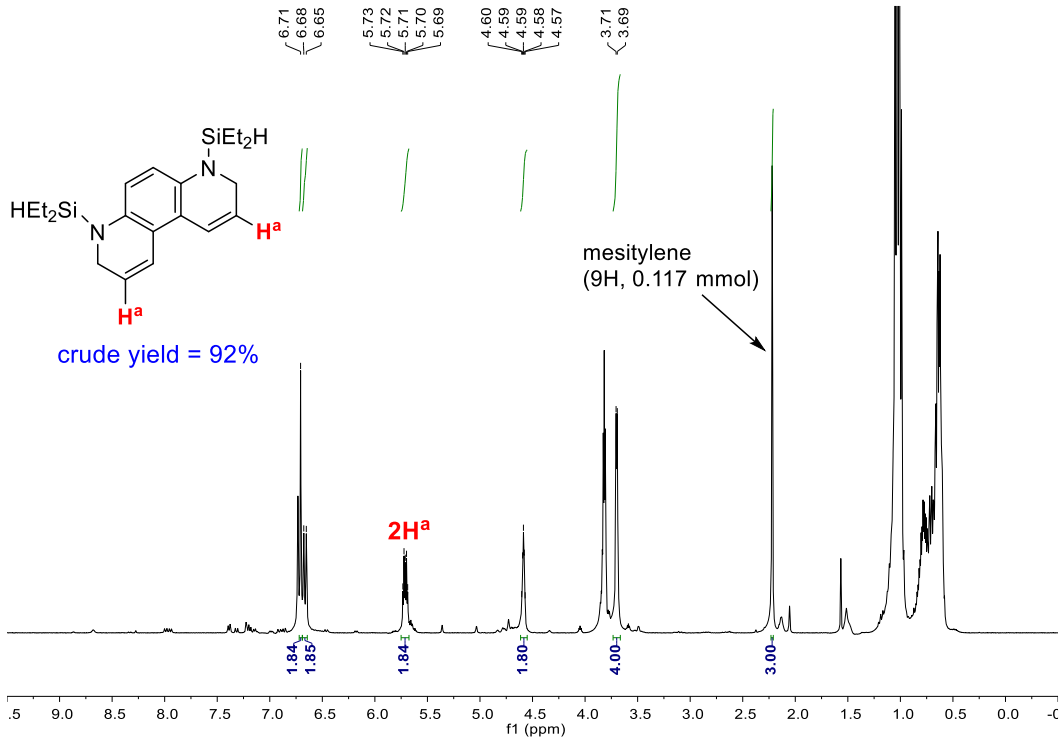
^{1}H NMR (600 MHz, C_6D_6) & ^{13}C NMR (150 MHz, C_6D_6); 1,4-dioxane, internal standard

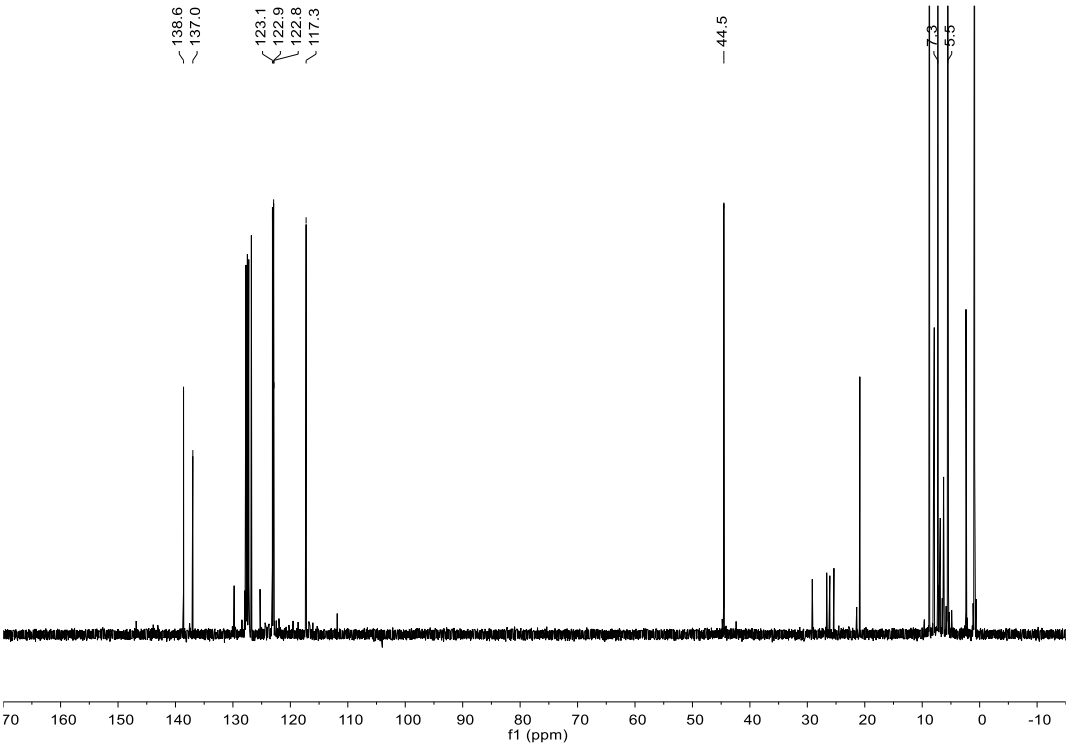




4,7-Bis(diethylsilyl)-3,4,7,8-tetrahydro-4,7-phenanthroline (5e)

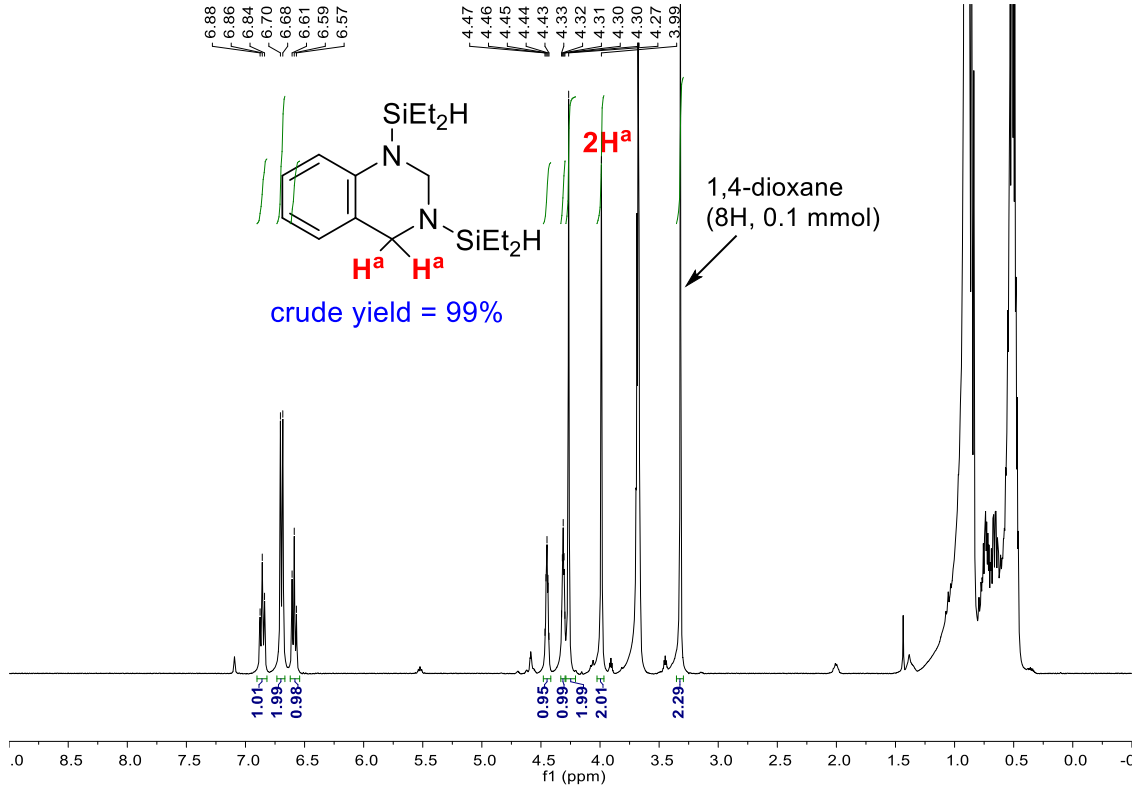
^{1}H NMR (600 MHz, C_6D_6) & ^{13}C NMR (150 MHz, C_6D_6); mesitylene, internal standard

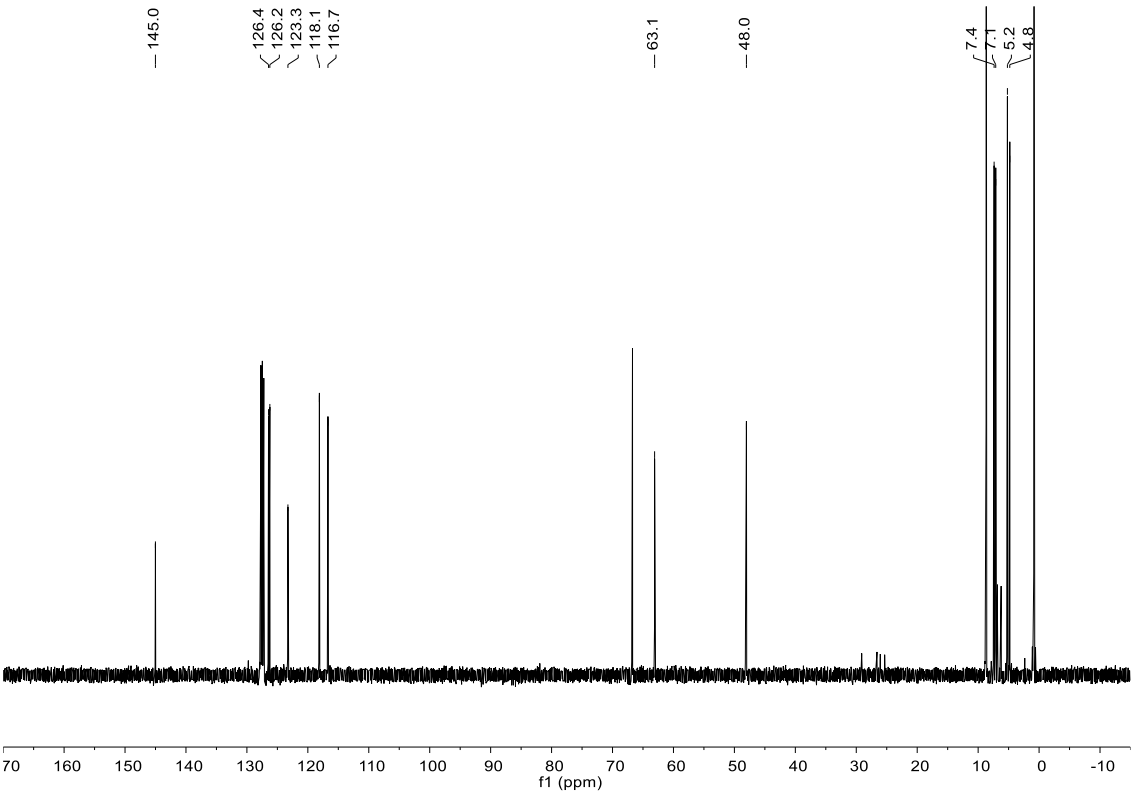




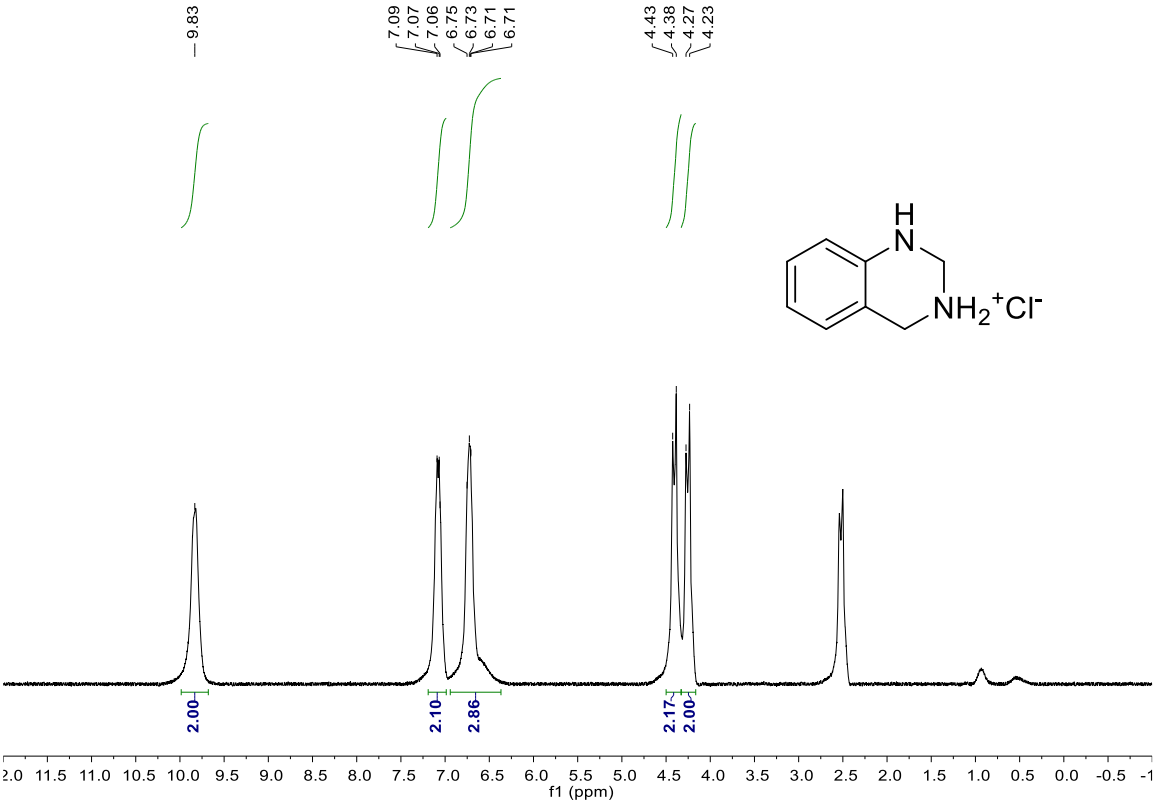
1,3-Bis(diethylsilyl)-1,2,3,4-tetrahydroquinazoline (5f)

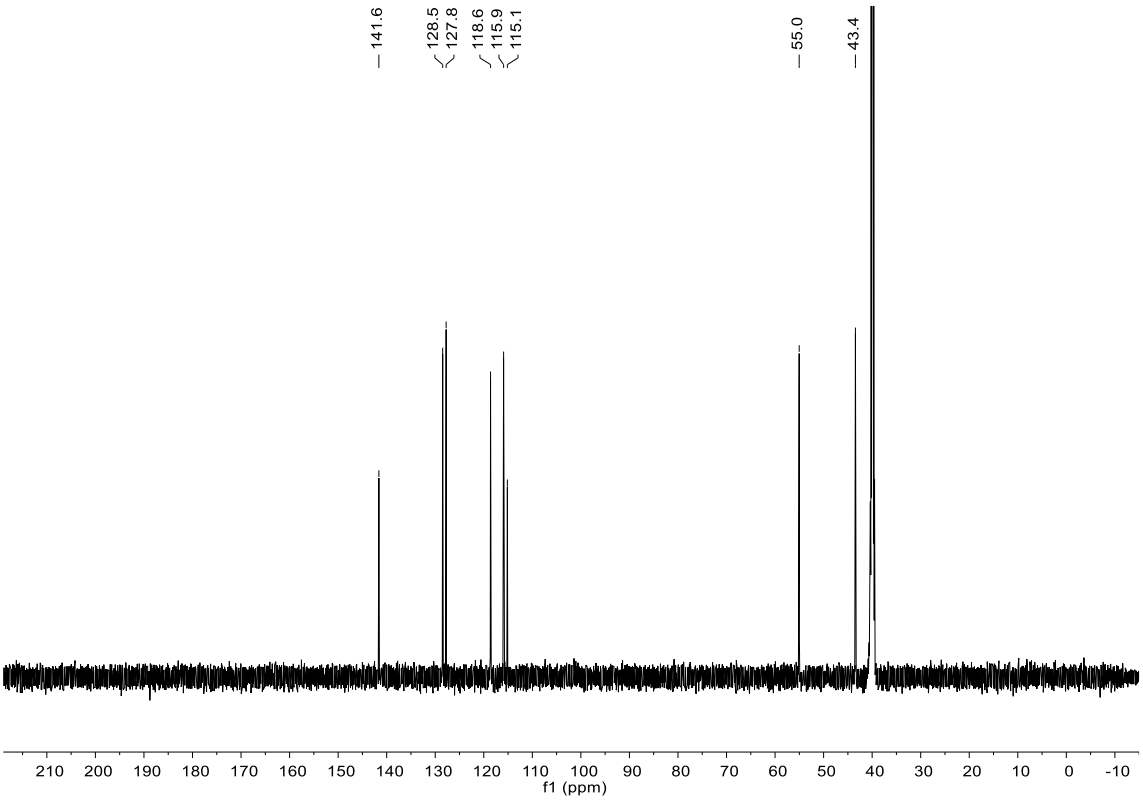
^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (150 MHz, C_6D_6); 1,4-dioxane, internal standard





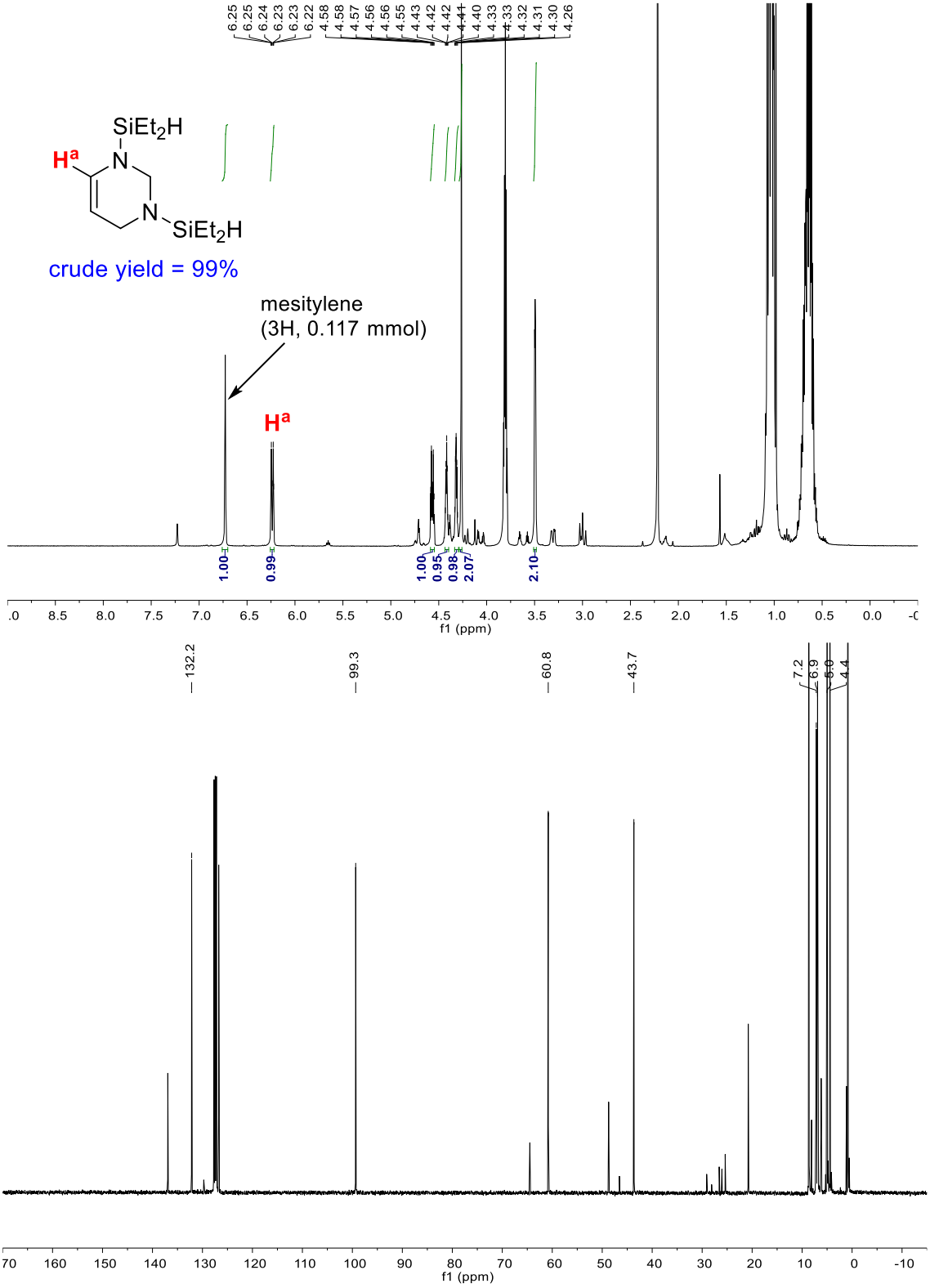
1,2,3,4-Tetrahydroquinazolin-3-ium chloride (5f-HCl)





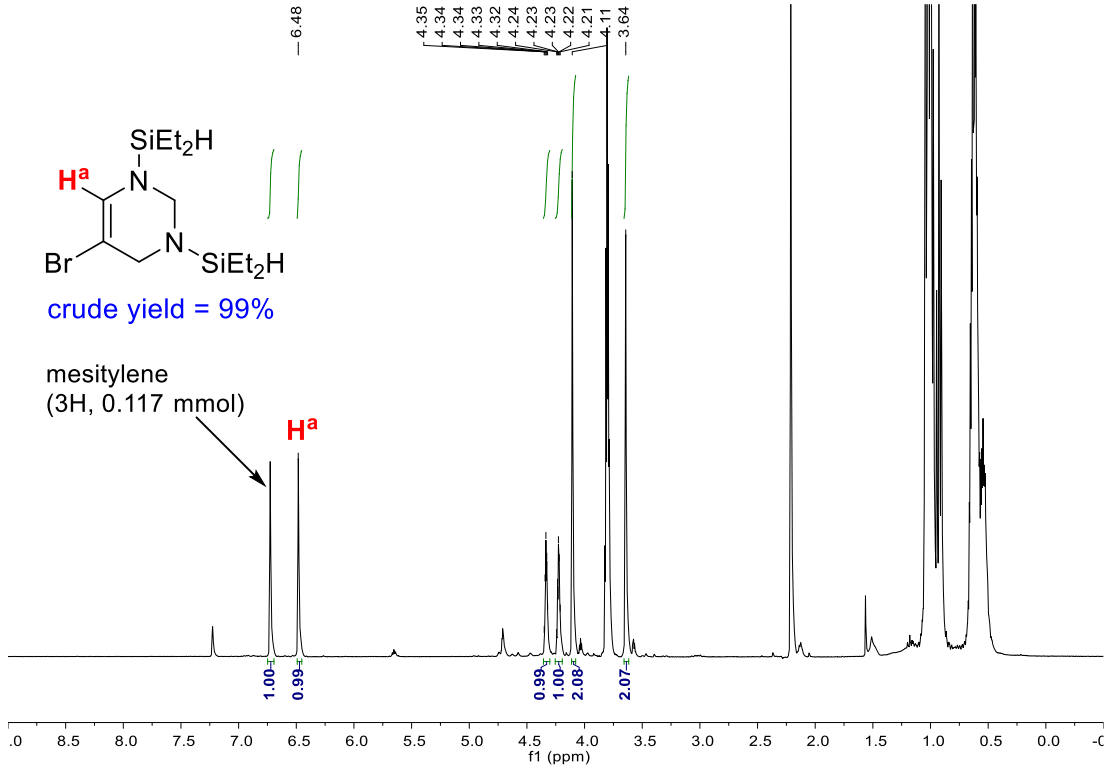
1,3-Bis(diethylsilyl)-1,2,3,4-tetrahydropyrimidine (5g)

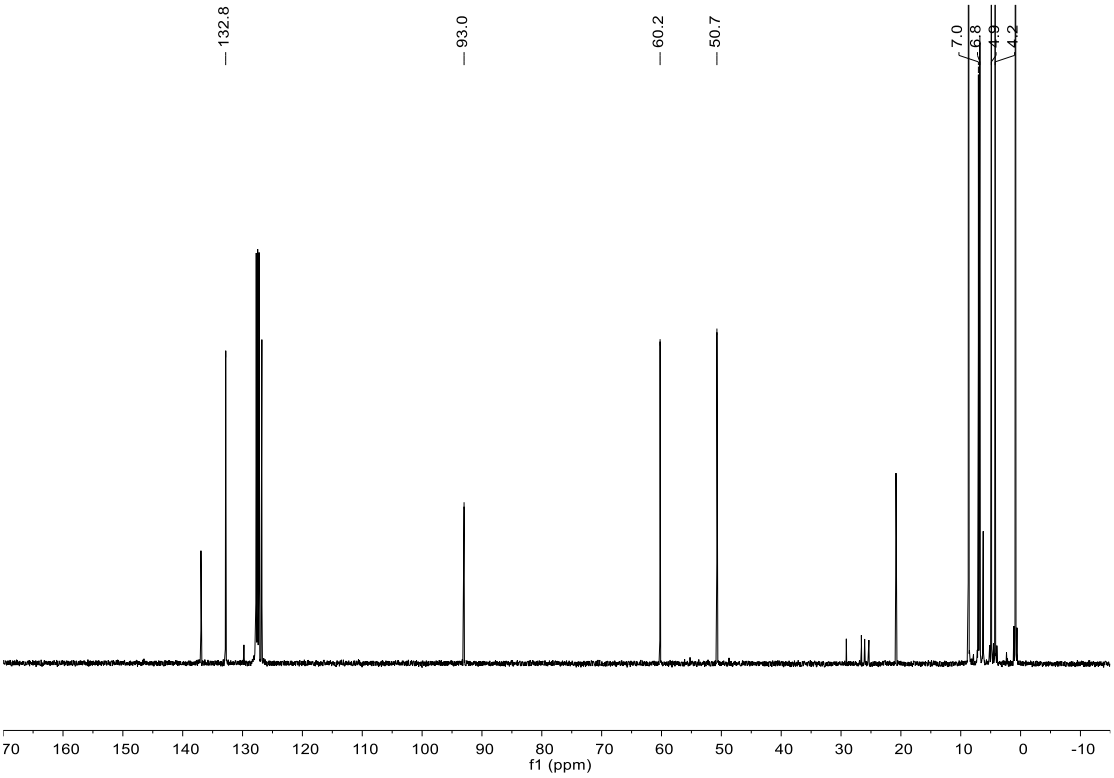
^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (150 MHz, C_6D_6); mesitylene, internal standard



5-Bromo-1,3-bis(diethylsilyl)-1,2,3,4-tetrahydropyrimidine (5h)

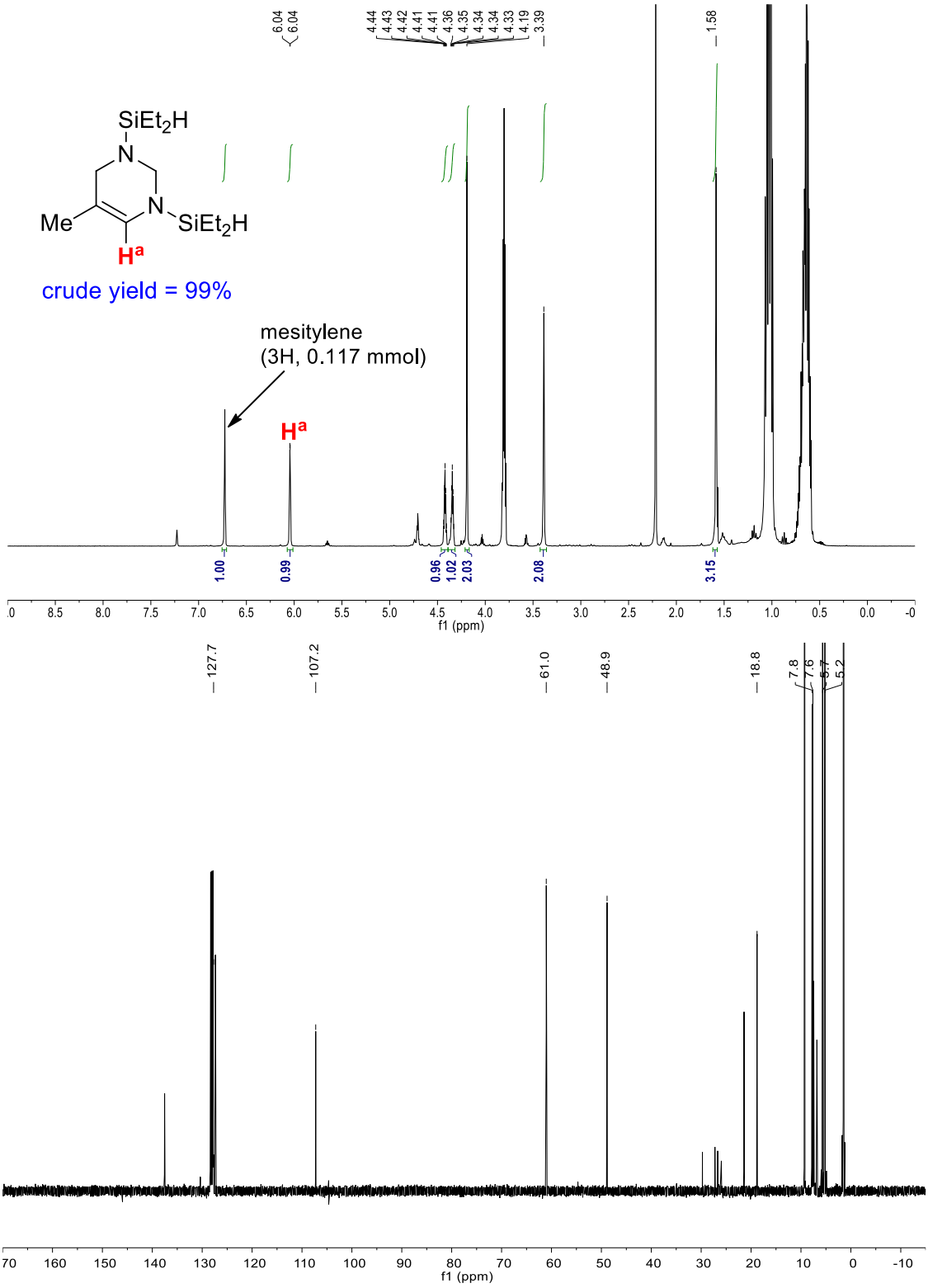
^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); mesitylene, internal standard





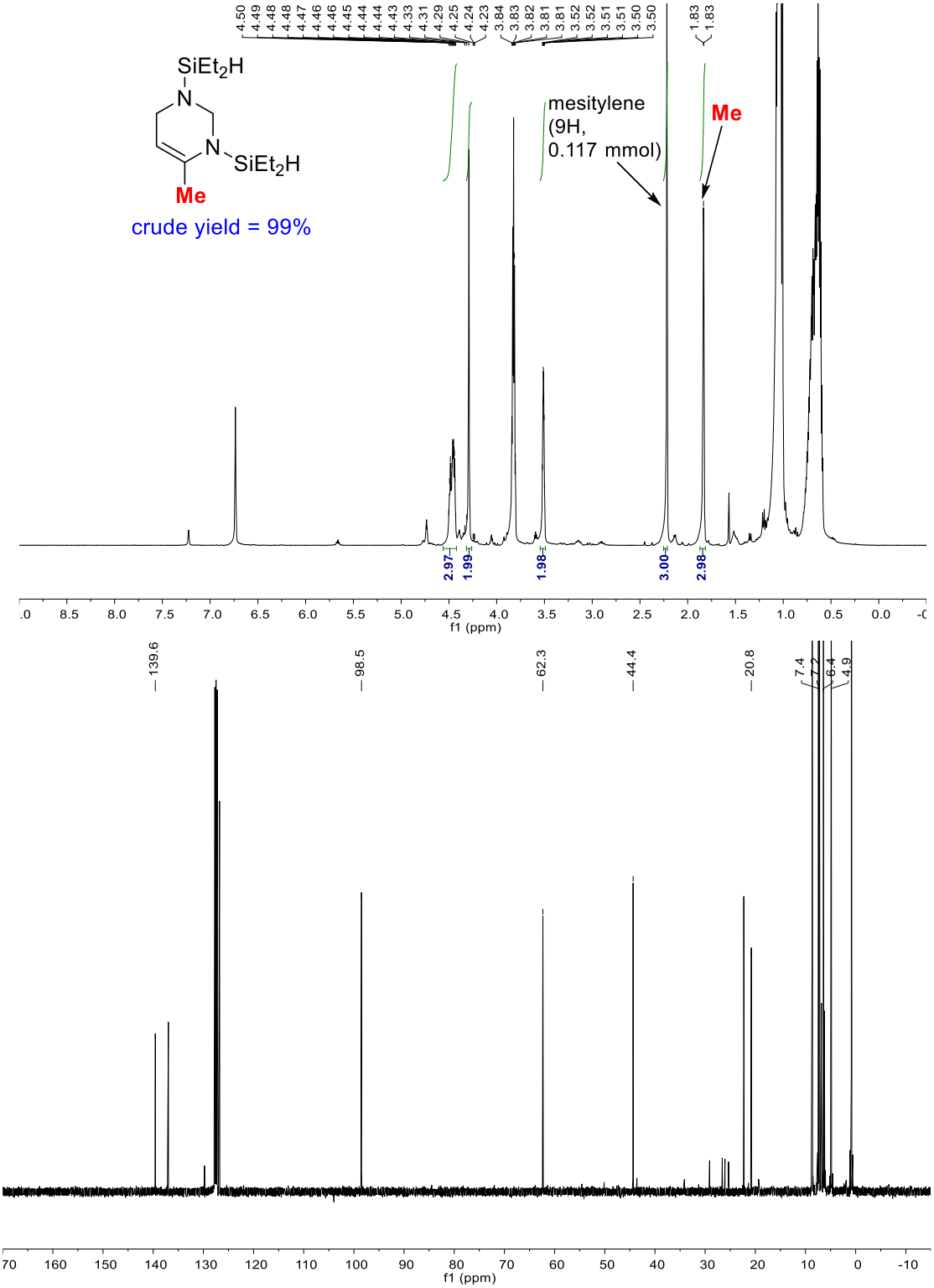
1,3-Bis(diethylsilyl)-5-methyl-1,2,3,4-tetrahydropyrimidine (5i)

^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); mesitylene, internal standard

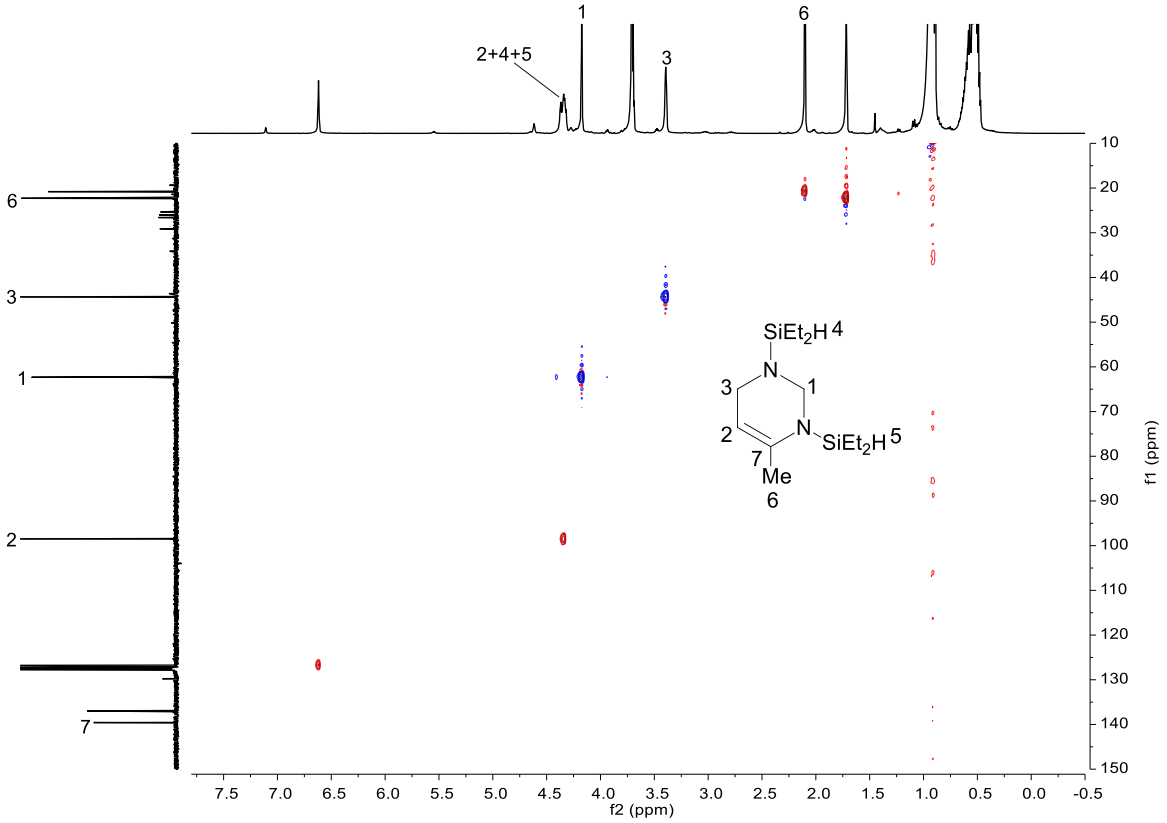


1,3-Bis(diethylsilyl)-4-methyl-1,2,3,4-tetrahydropyrimidine (5j)

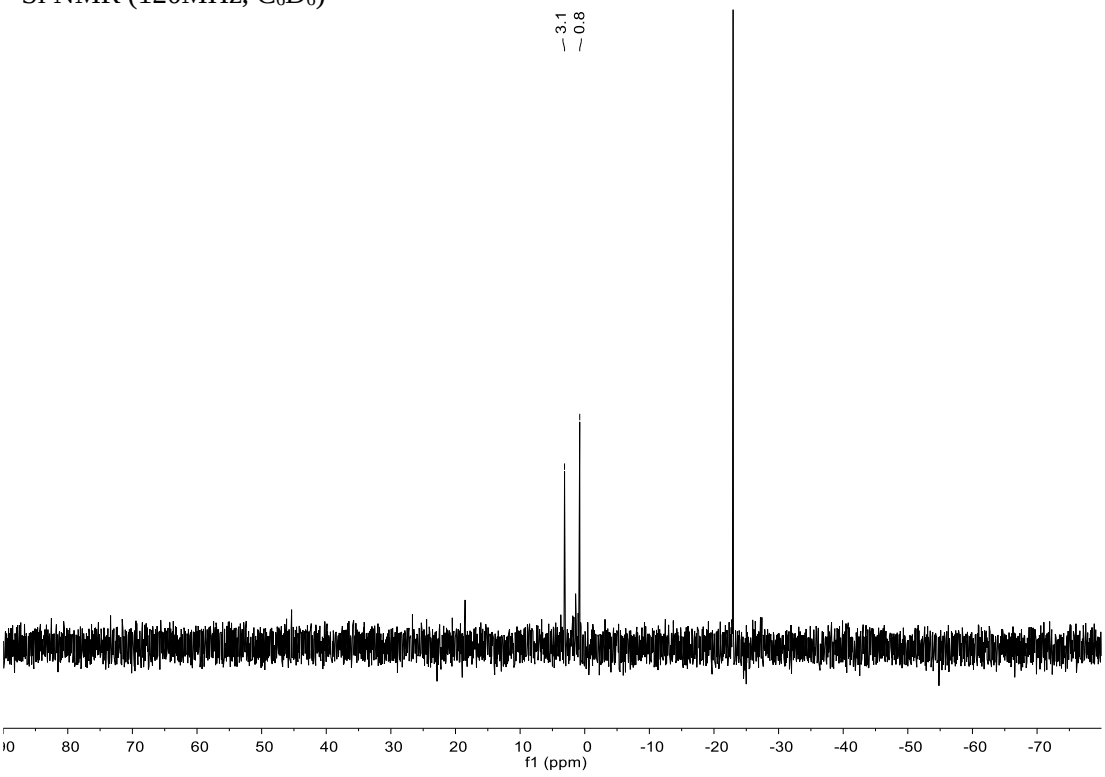
^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); mesitylene, internal standard



^{1}H -^{13}C HSQC (C_6D_6)

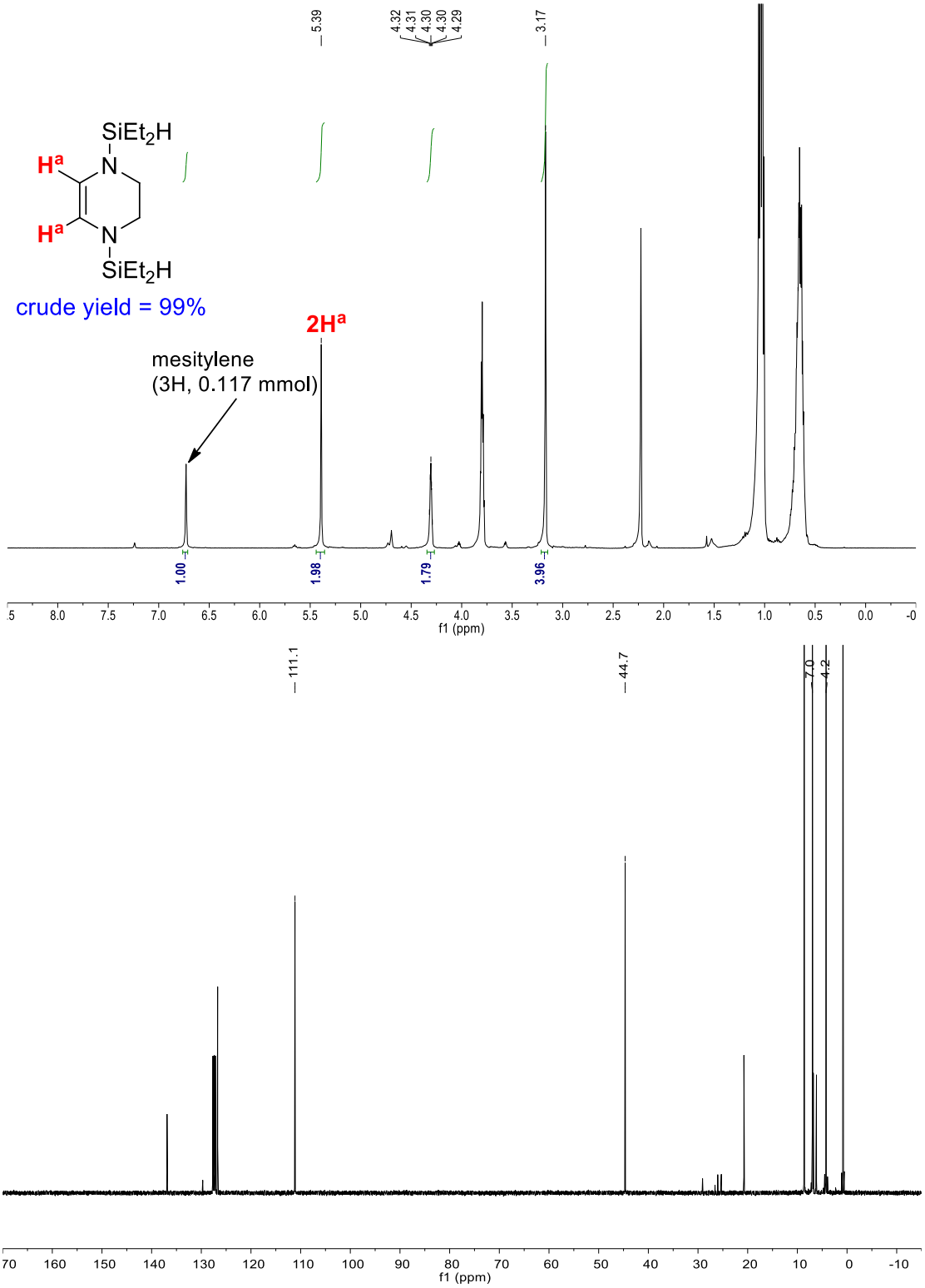


^{29}Si NMR (120MHz, C_6D_6)



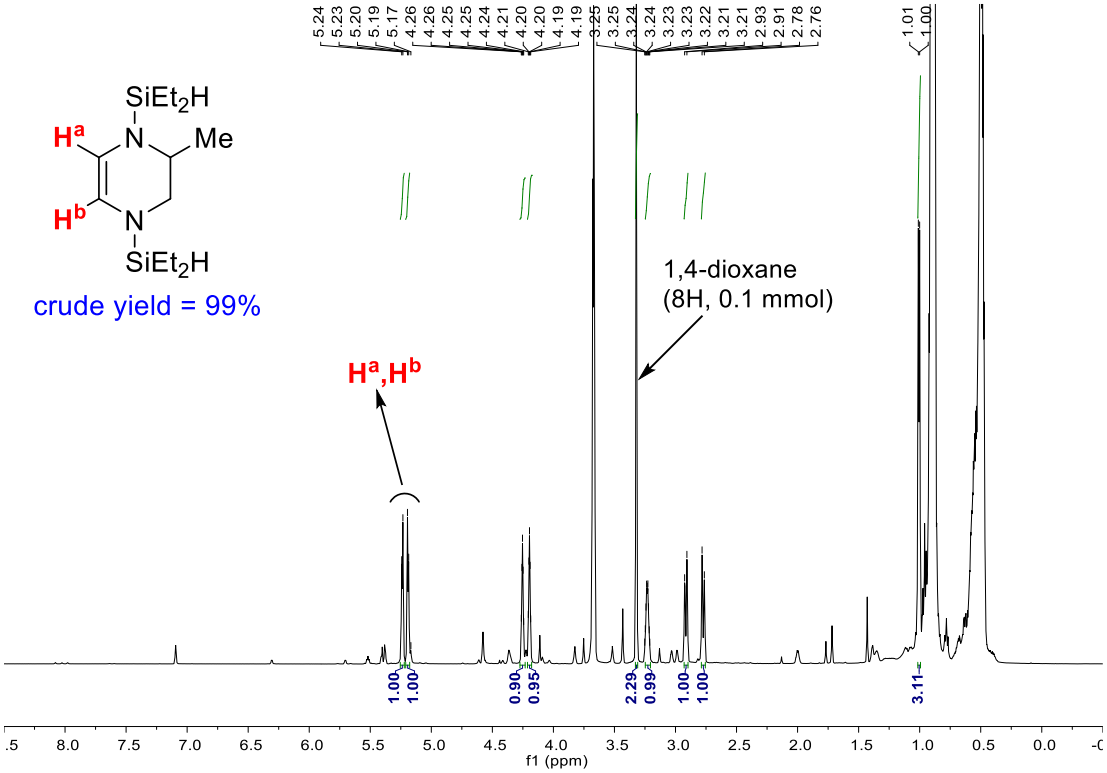
1,4-Bis(diethylsilyl)-1,2,3,4-tetrahydropyrazine (5k)

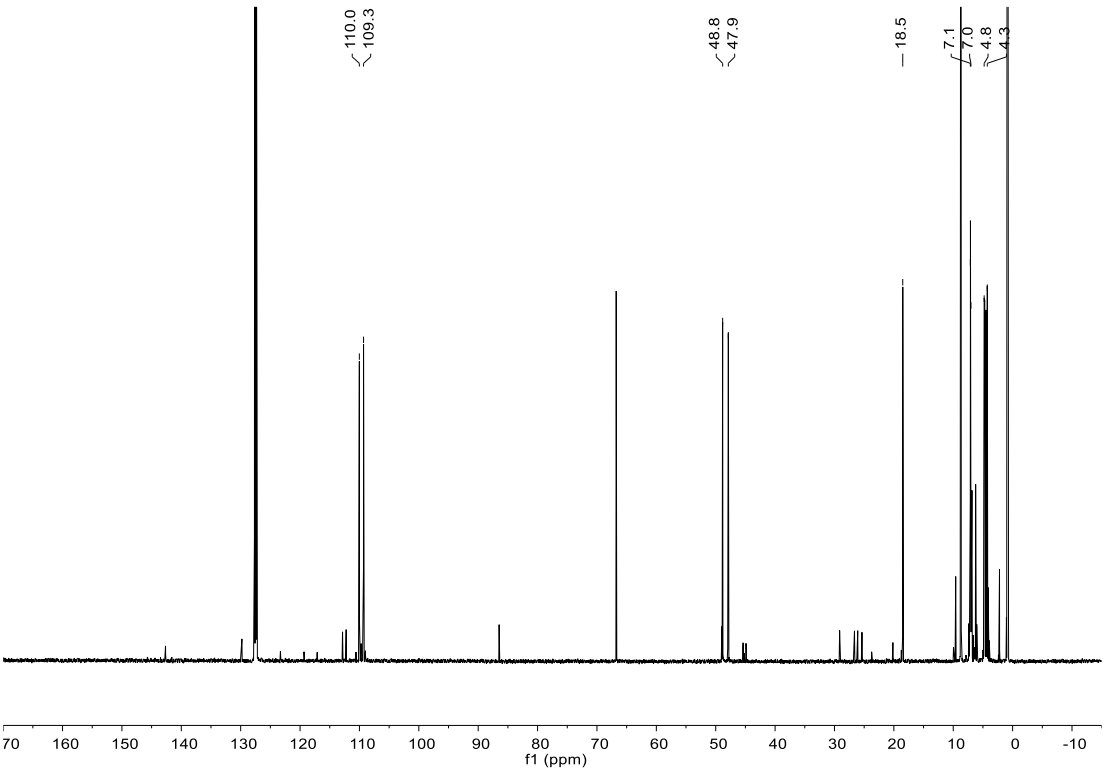
^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); mesitylene, internal standard



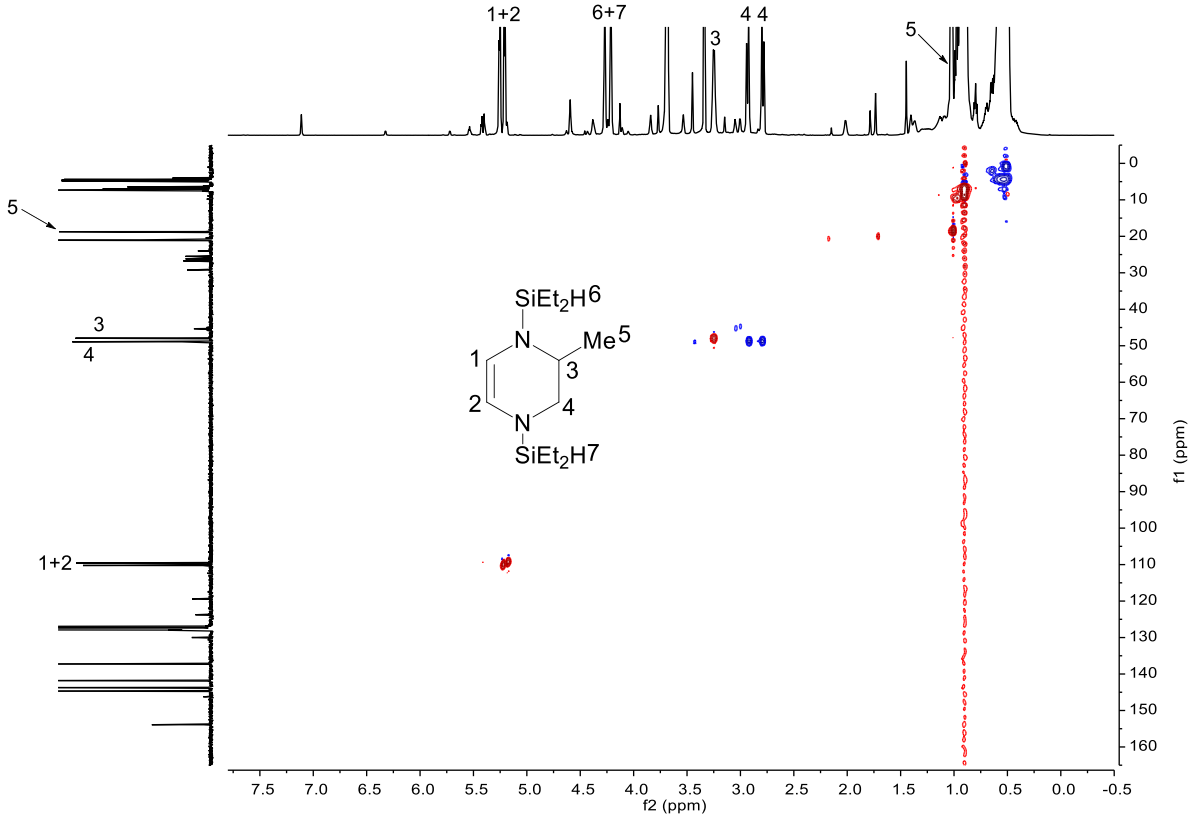
1,4-Bis(diethylsilyl)-2-methyl-1,2,3,4-tetrahydropyrazine (5l)

^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); 1,4-dioxane, internal standard

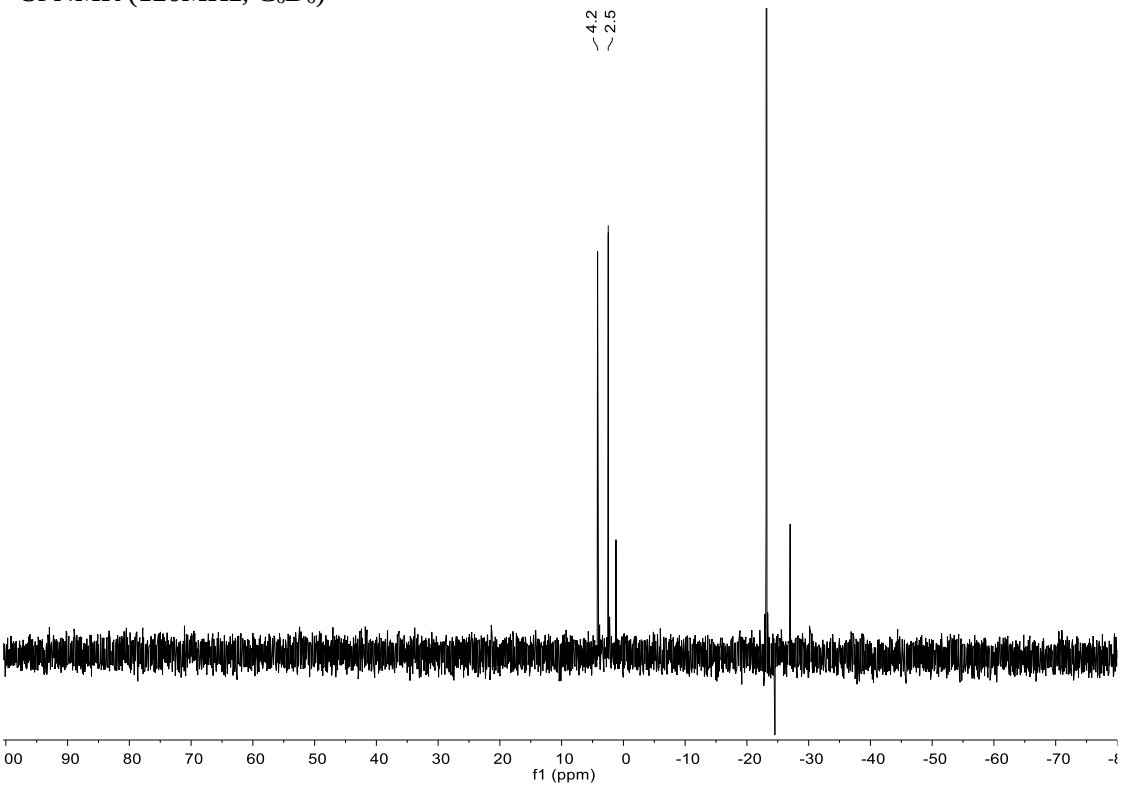




^{1}H -^{13}C HSQC (C_6D_6)

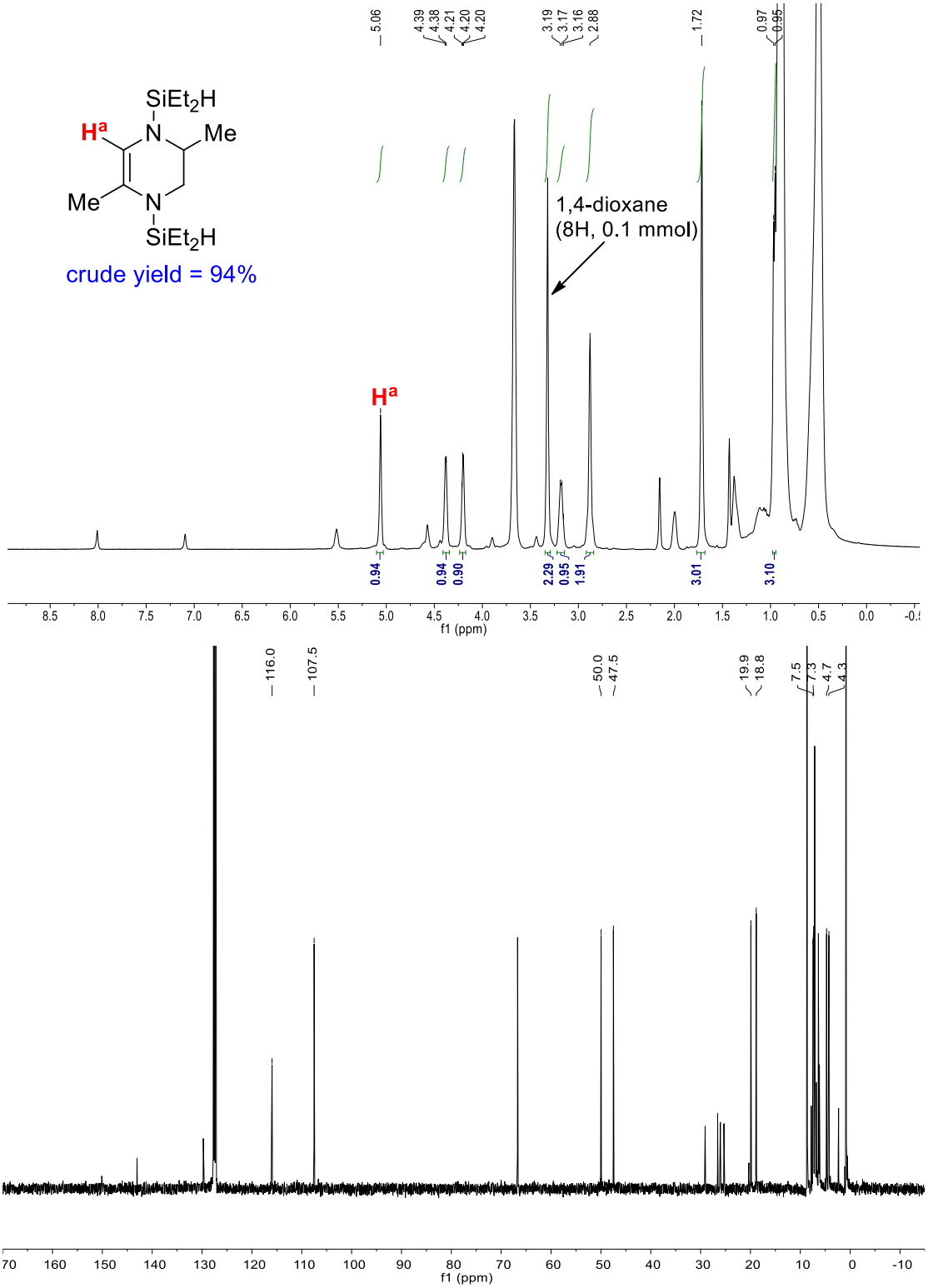


^{29}Si NMR (120MHz, C_6D_6)



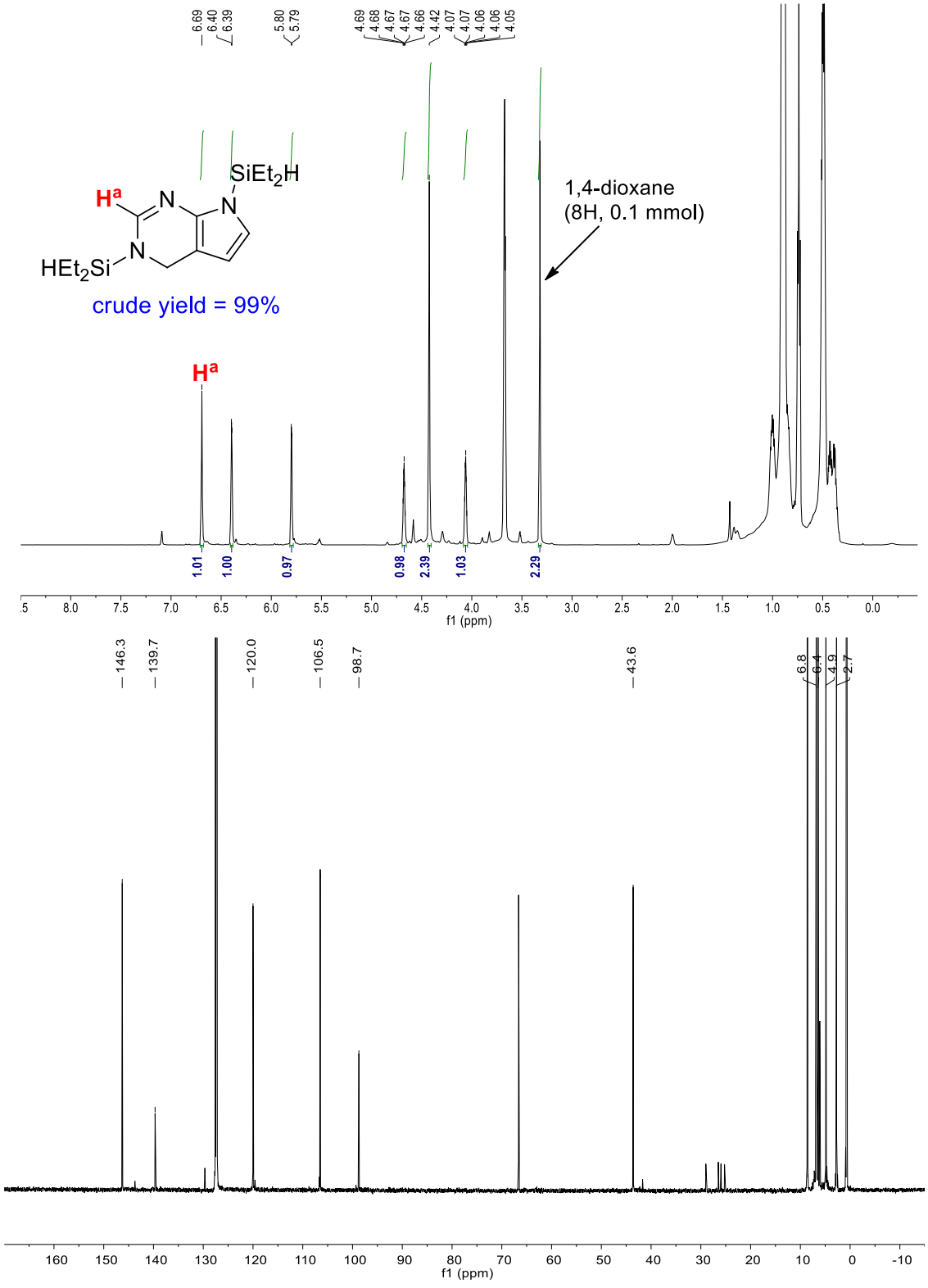
1,4-Bis(diethylsilyl)-2,5-dimethyl-1,2,3,4-tetrahydropyrazine (5m)

^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); 1,4-dioxane, internal standard

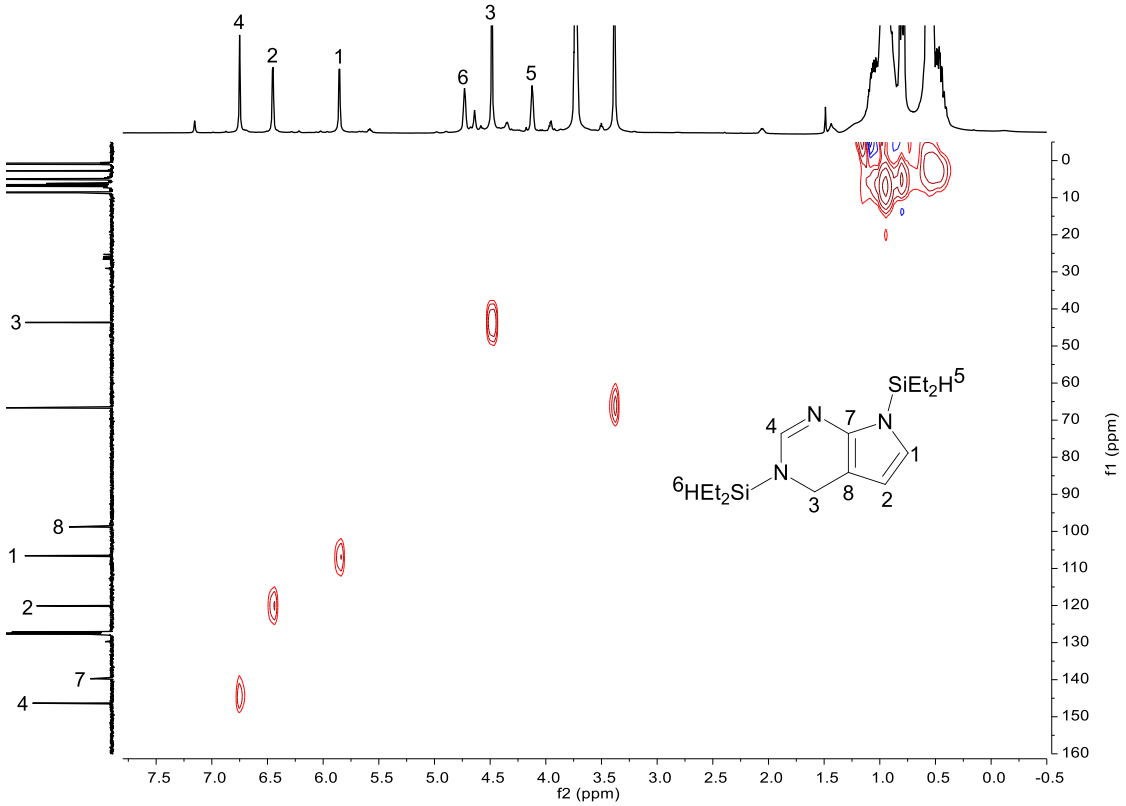


3,7-Bis(diethylsilyl)-4,7-dihydro-3H-pyrrolo[2,3-d]pyrimidine (5n)

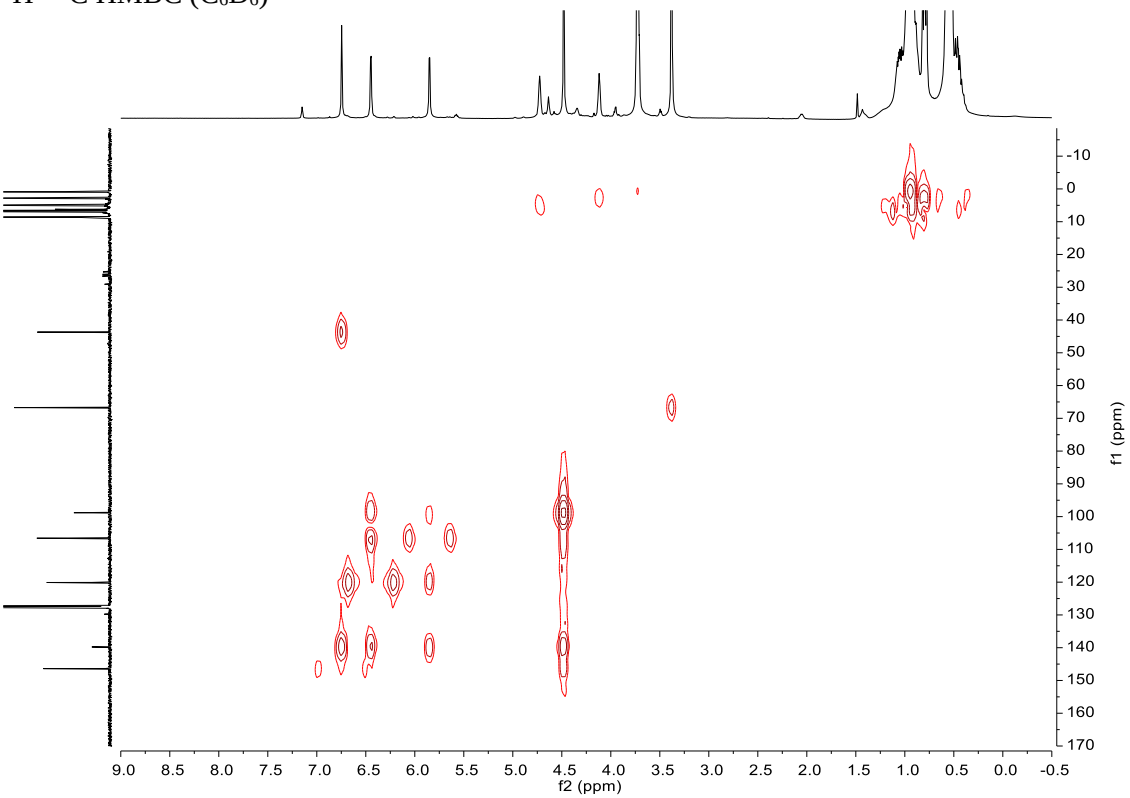
^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR(100 MHz, C_6D_6); 1,4-dioxane, internal standard



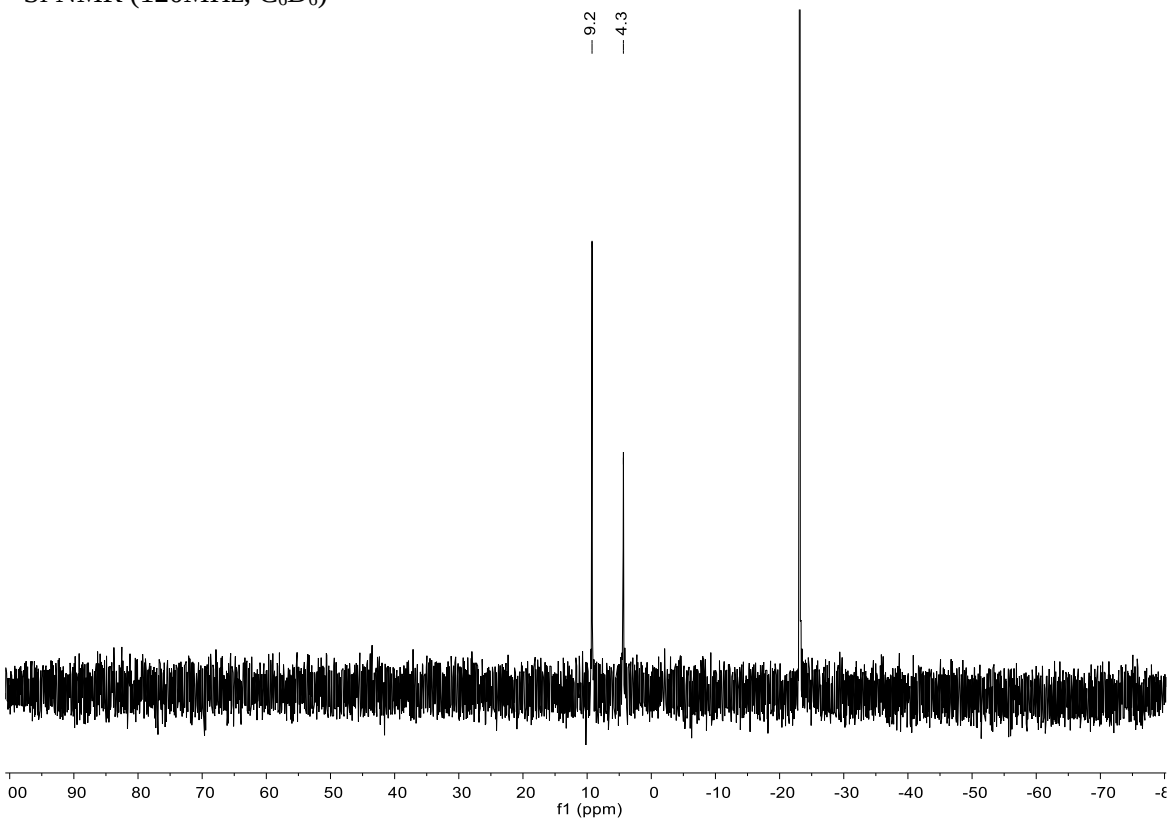
^{1}H -^{13}C HSQC (C_6D_6)



^{1}H -^{13}C HMBC (C_6D_6)

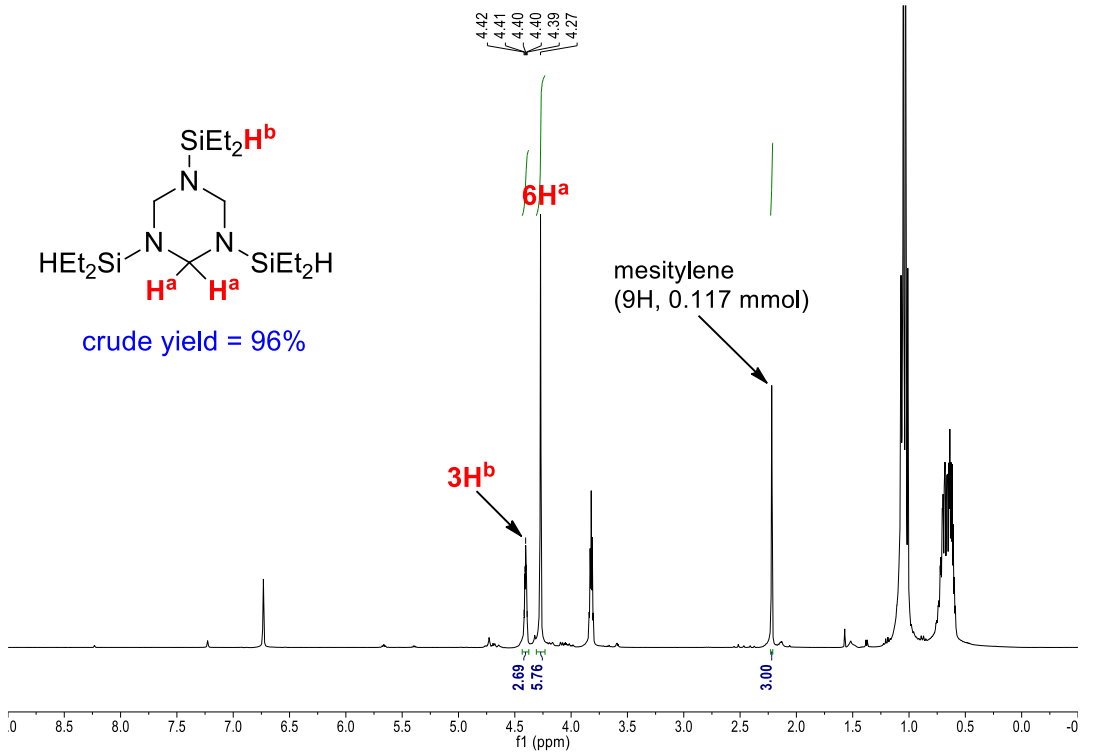


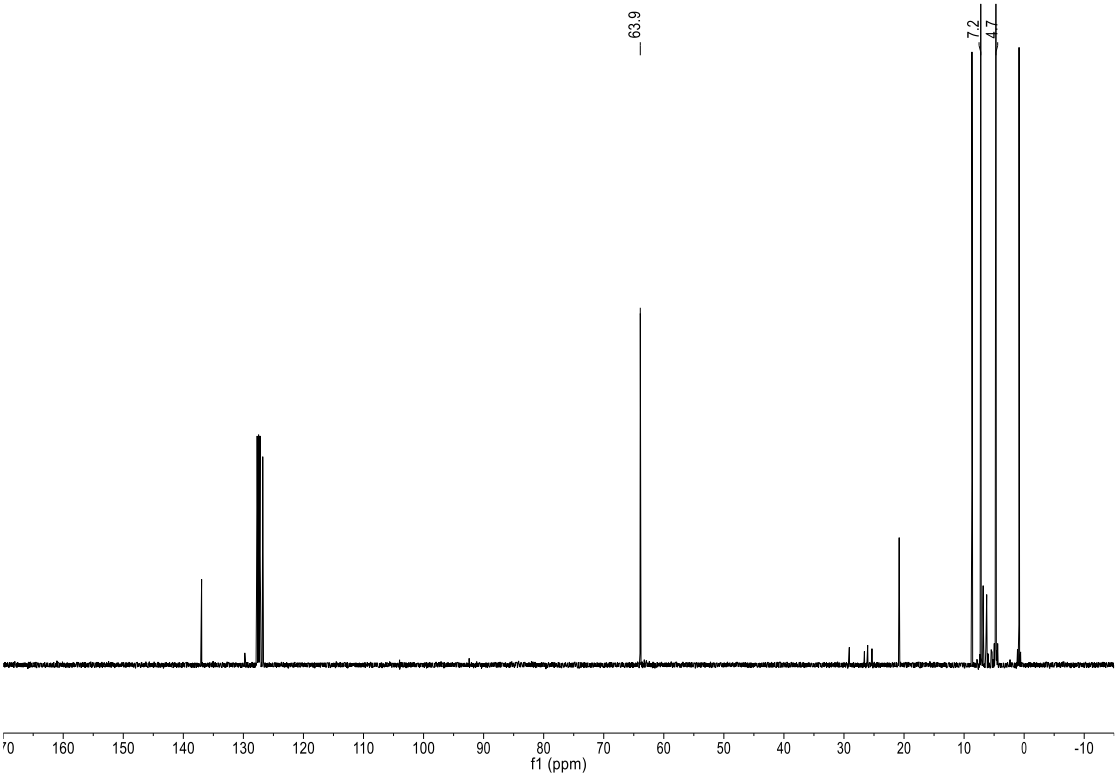
^{29}Si NMR (120MHz, C_6D_6)



1,3,5-Tris(diethylsilyl)-1,3,5-triazinane (5o)

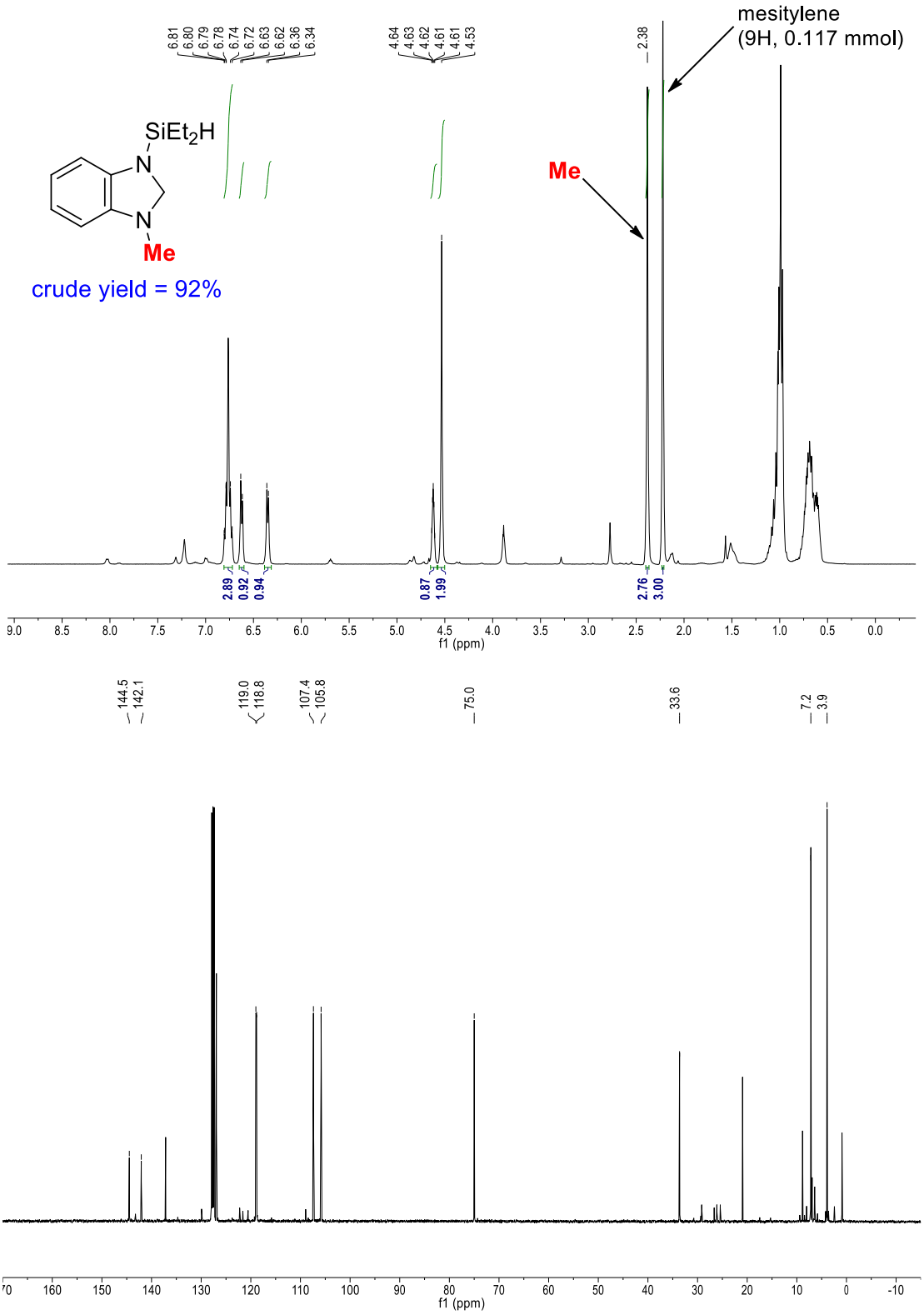
^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); mesitylene, internal standard



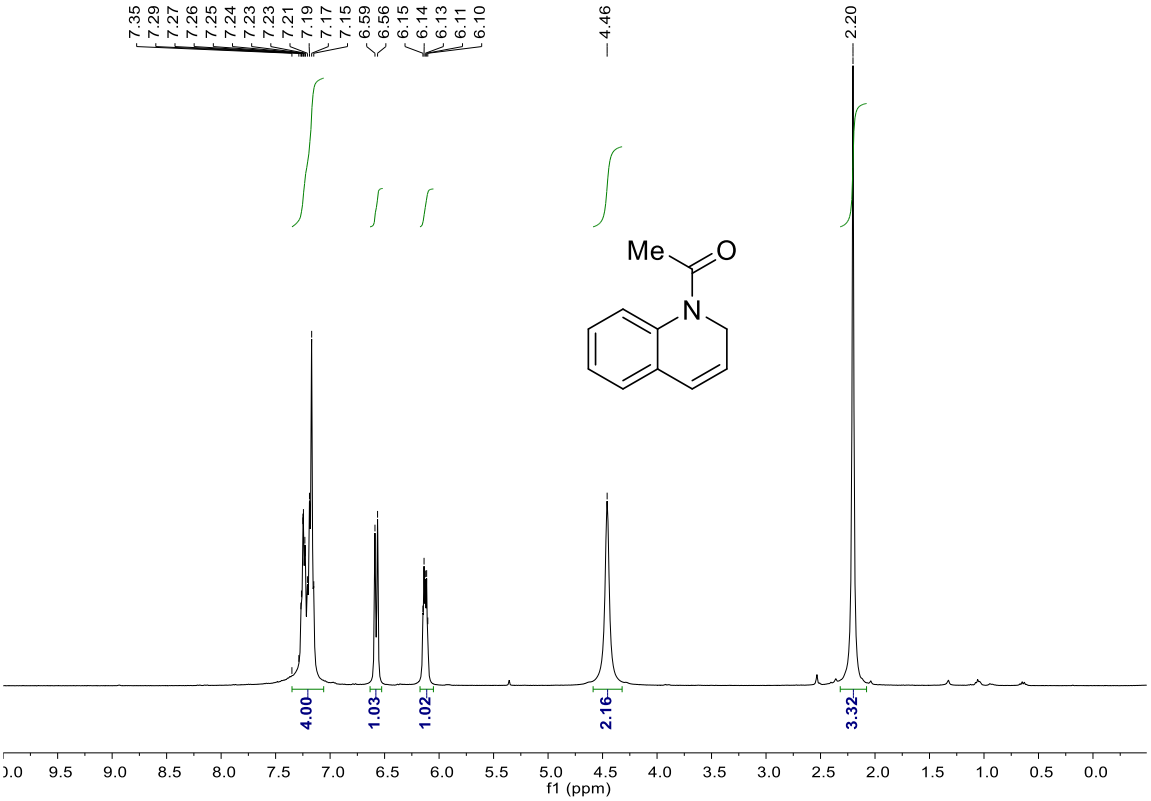


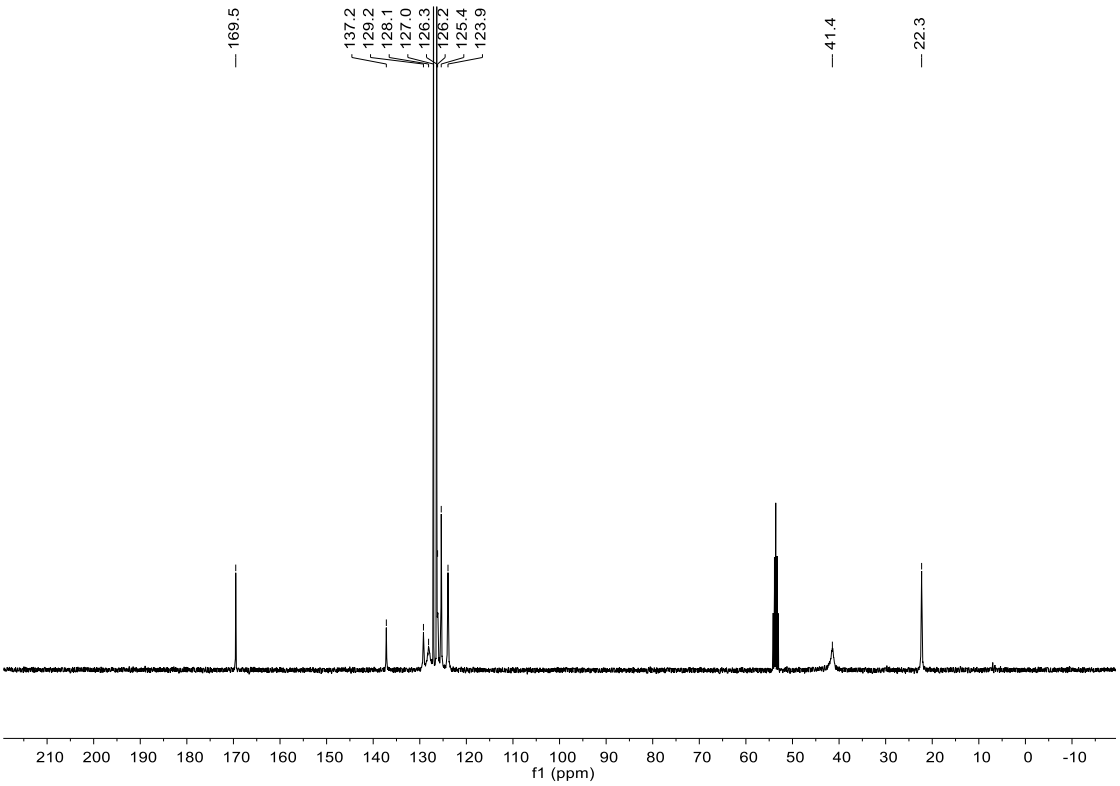
1-(Diethylsilyl)-3-methyl-2,3-dihydro-1H-benzo[d]imidazole (5p)

^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); mesitylene, internal standard

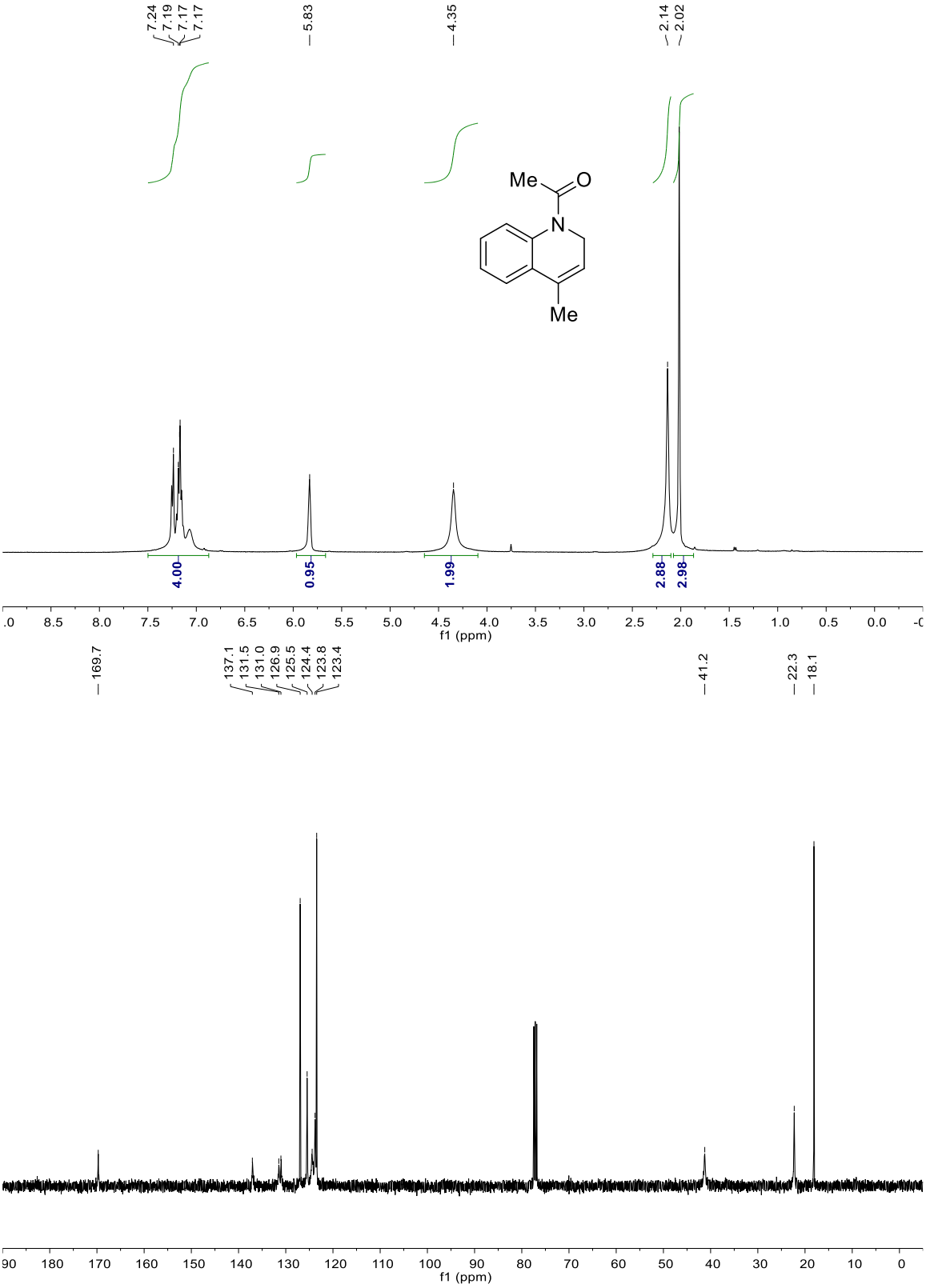


1-[Quinolin-1(2H)-yl]ethan-1-one (3a-Ac)

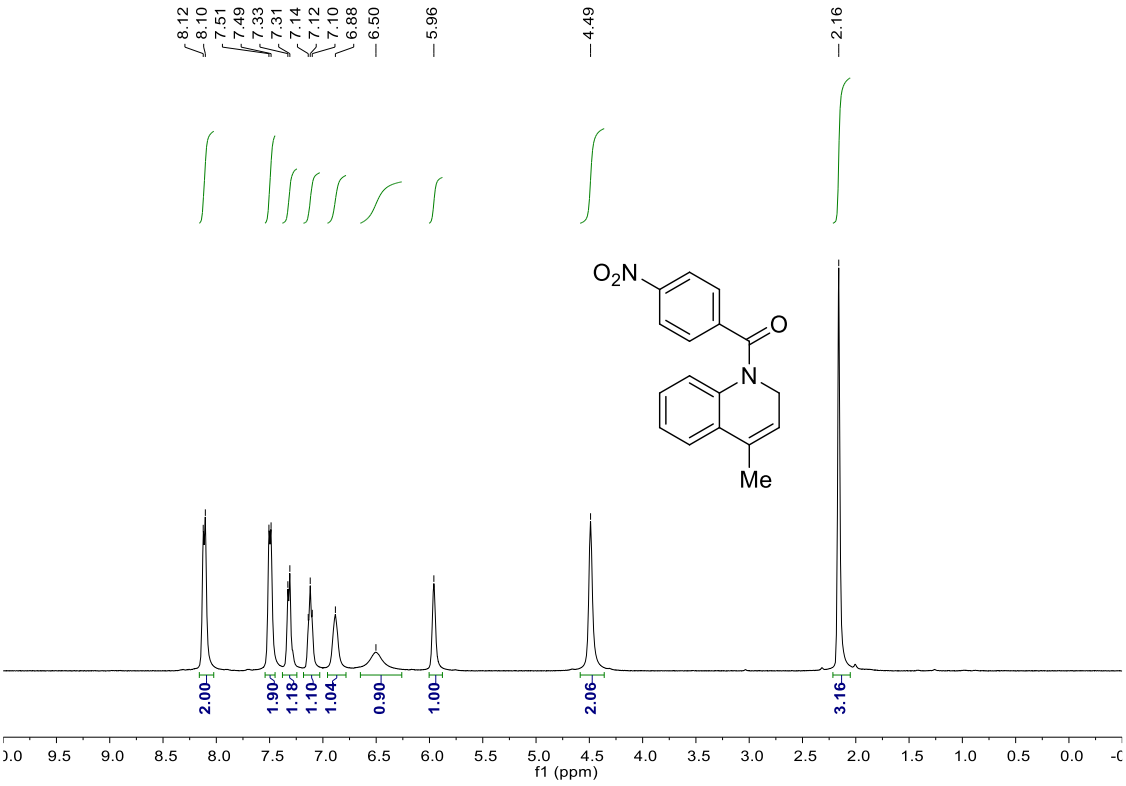


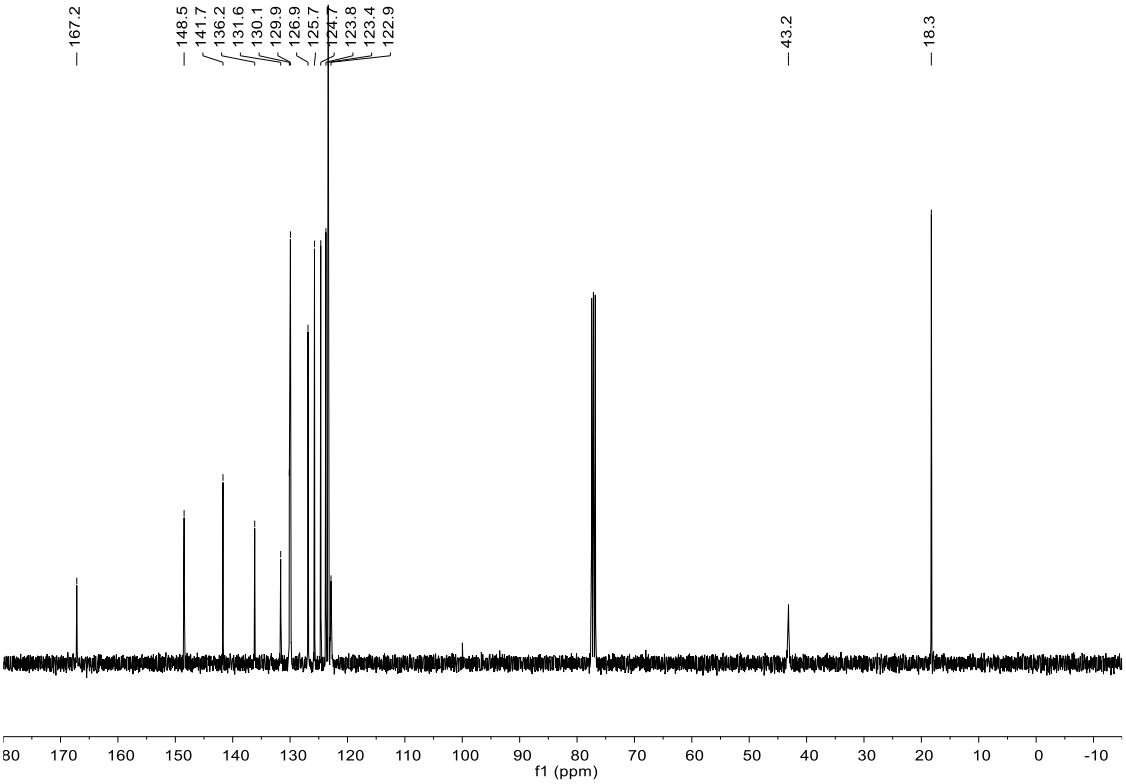


1-[4-Methylquinolin-1(2H)-yl]ethan-1-ono (3c-Ac)

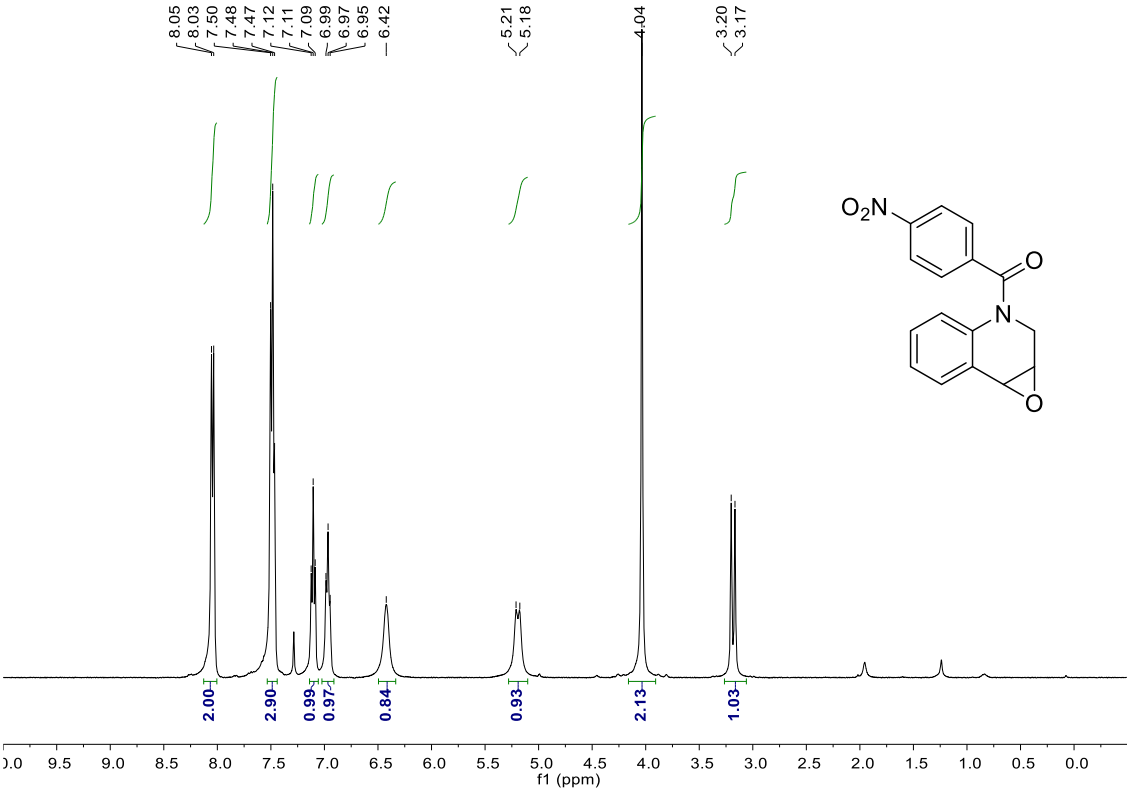


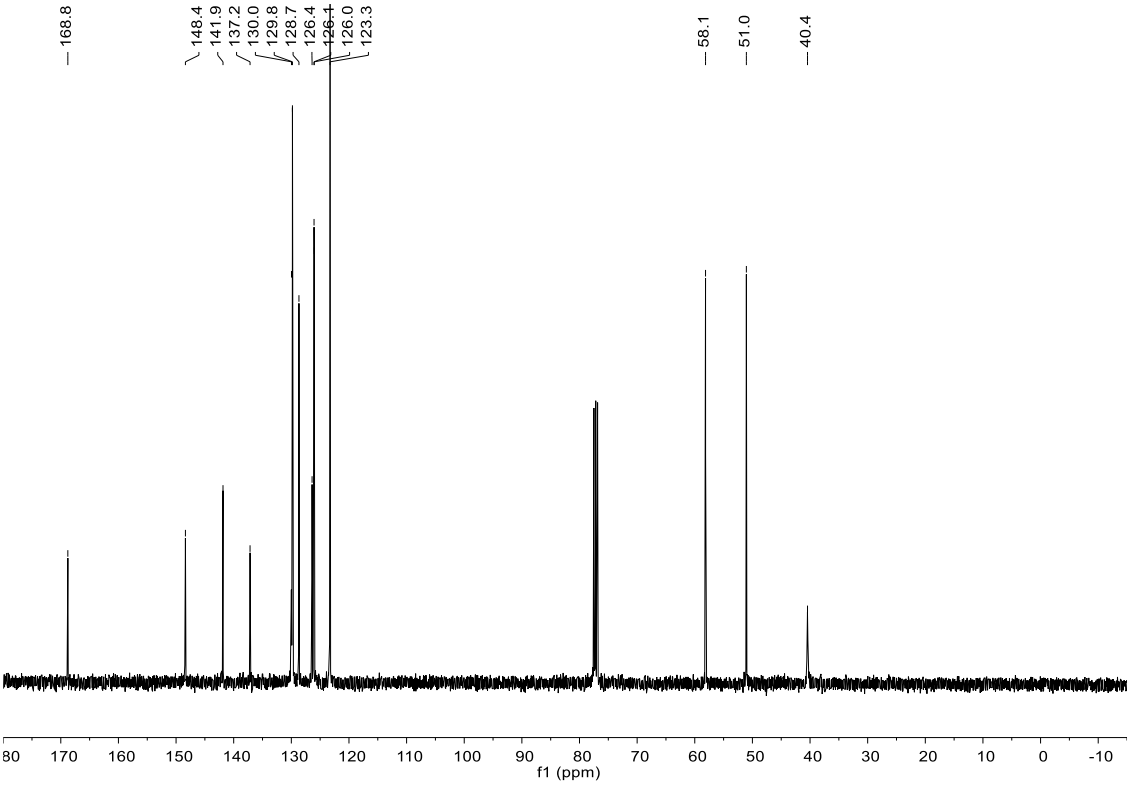
[4-Methylquinolin-1(2H)-yl](4-nitrophenyl)methanone (3c-PNB)



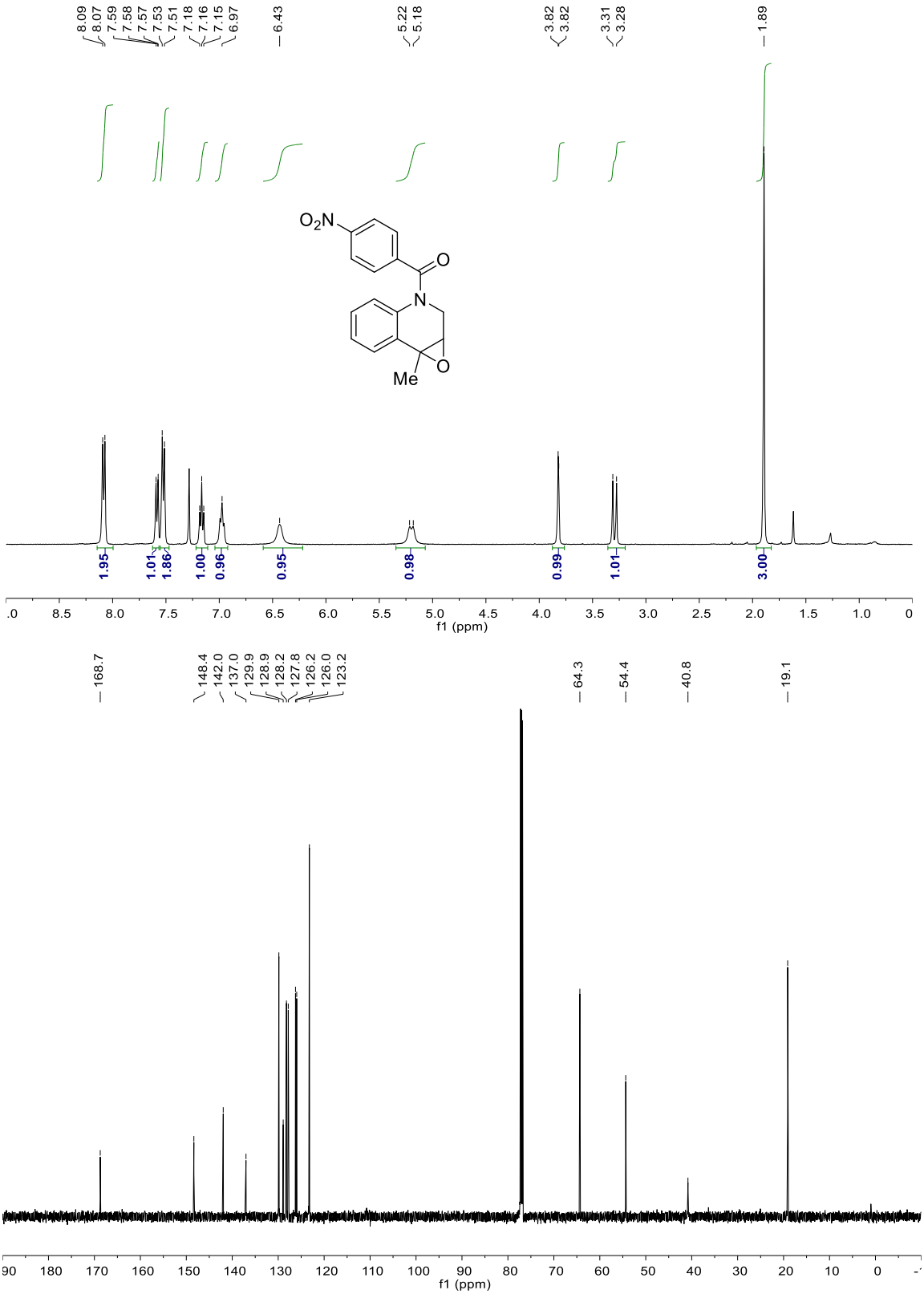


[1a,7b-Dihydrooxireno[2,3-c]quinolin-3(2H)-yl](4-nitrophenyl)methanone



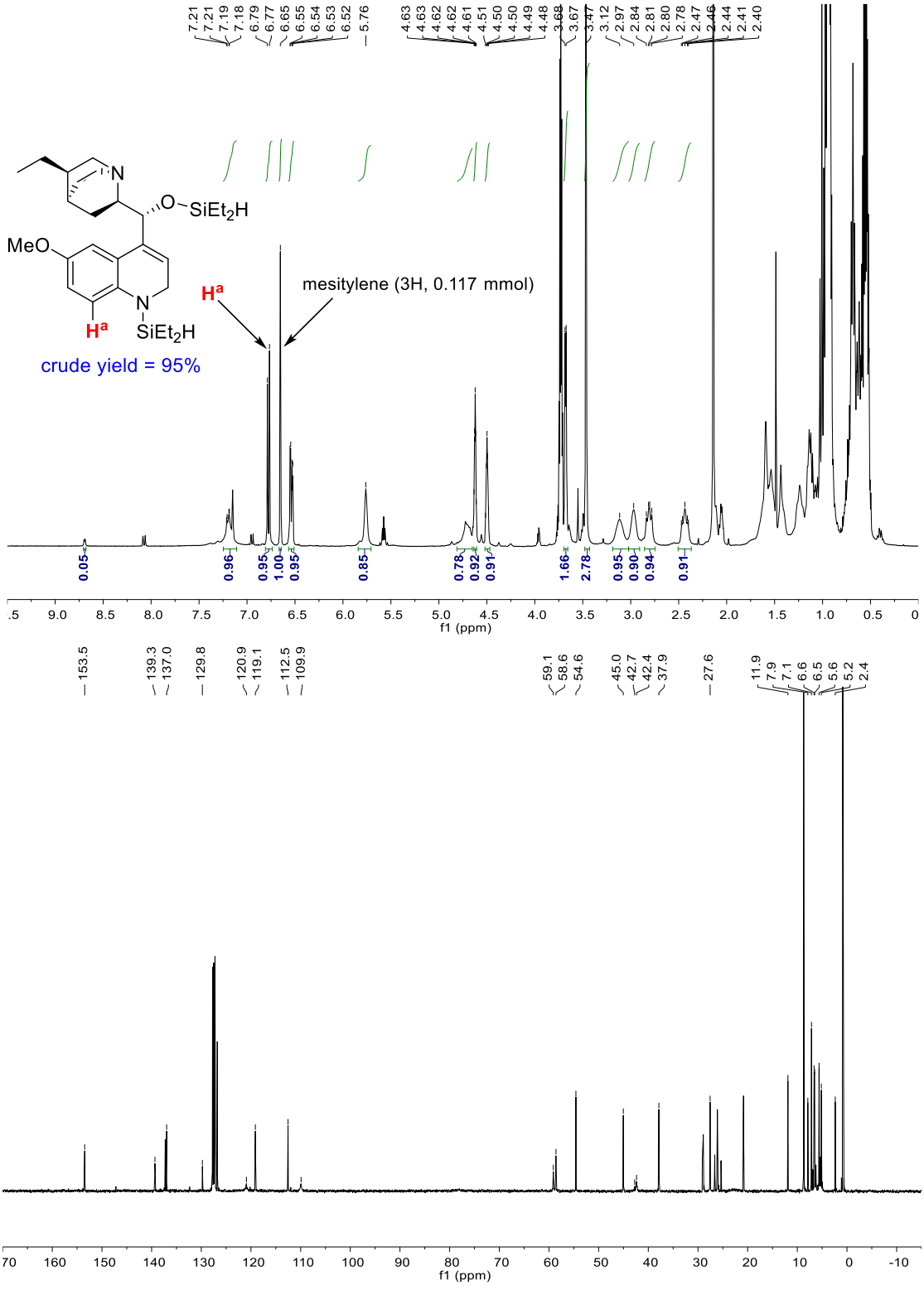


[7b-Methyl-1a,7b-dihydrooxireno[2,3-c]quinolin-3(2H)-yl](4-nitrophenyl)methanone

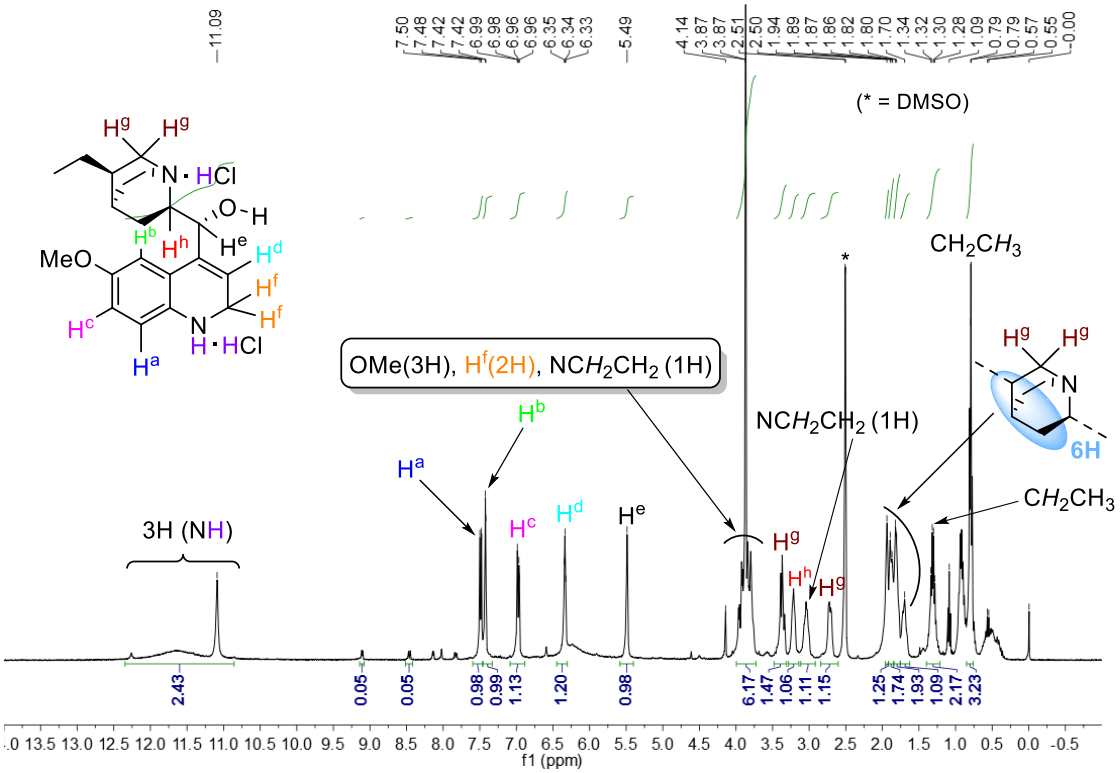


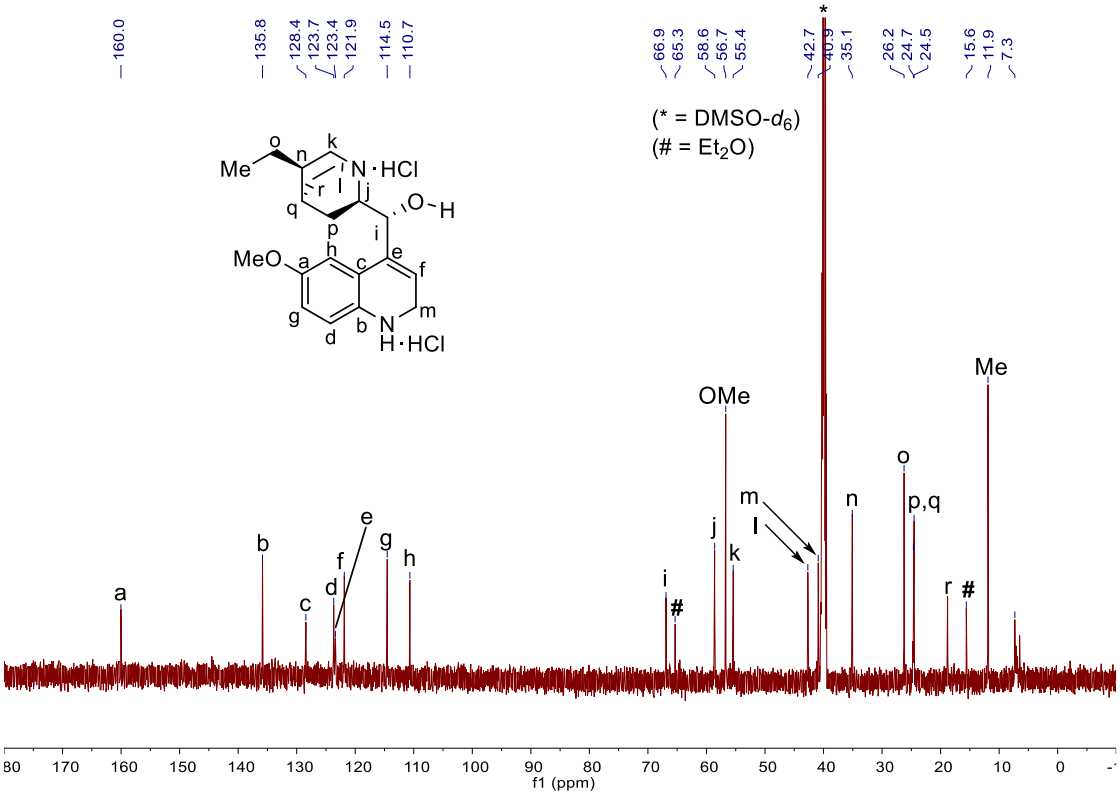
(1*S*,2*R*,4*S*,5*R*)-2-[(*R*)-(1-(diethylsilyl)-6-methoxy-1,2-dihydroquinolin-4-yl]-[(diethylsilyl)oxymethyl]-5-ethylquinuclidine (8a)

^{1}H NMR (400 MHz, C_6D_6) & ^{13}C NMR (100 MHz, C_6D_6); mesitylene, internal standard

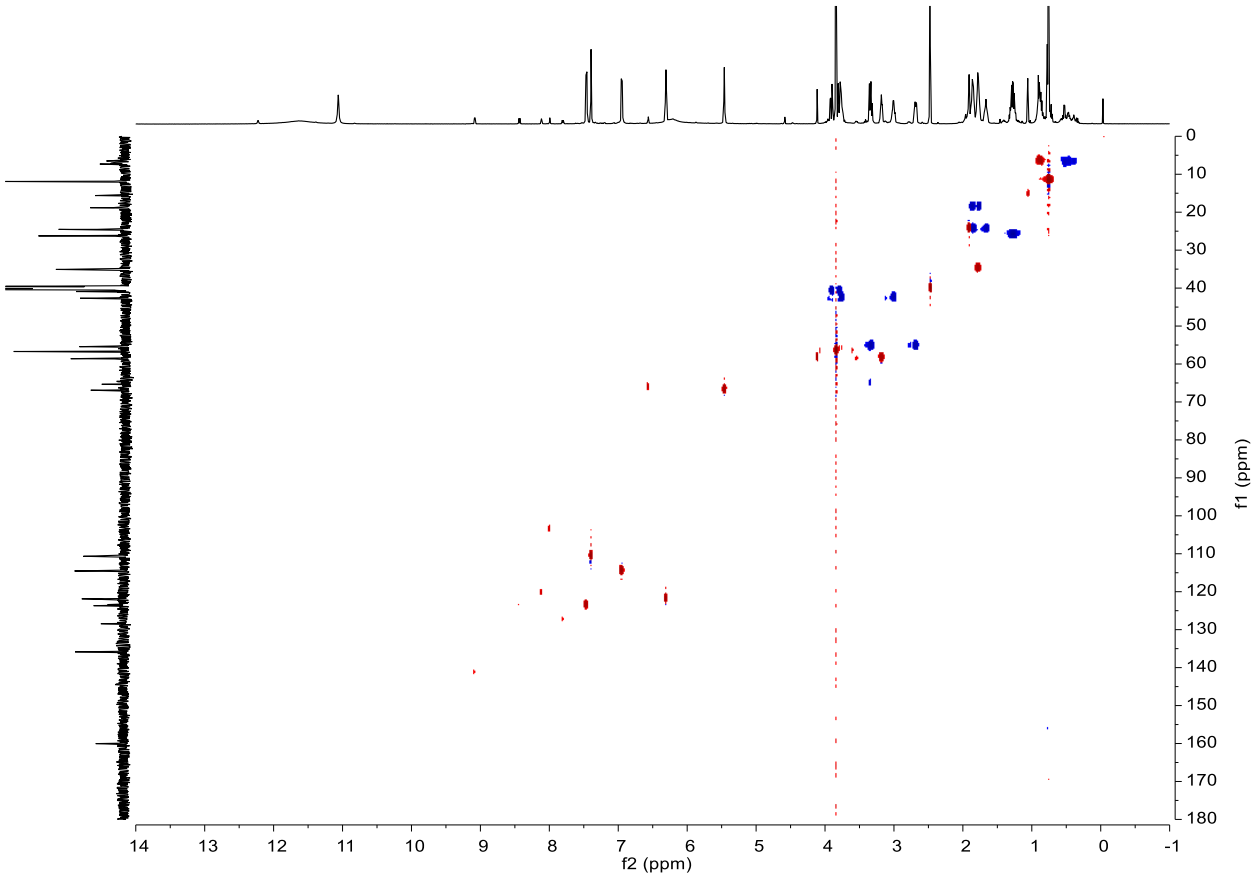


(1*S*,2*R*,4*S*,5*R*)-5-Ethyl-2-[(*R*)-hydroxy(6-methoxy-1,2-dihydroquinolin-1-ium-4-yl)methyl]quinuclidin-1-ium chloride (8a-2HCl) (DMSO-d_6)





^{1}H-^{13}C HSQC (DMSO-d_6)



Appendix II

Crystallographic Data for 3k-PNB

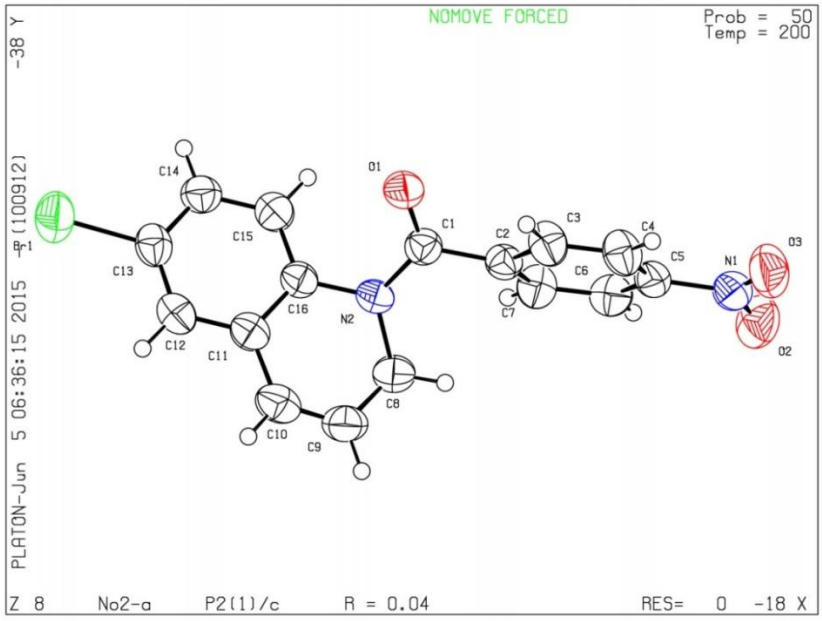


Table S3 Crystal data and structure refinement of **3k-PNB**.

Identification code	**3k-PNB**
Empirical formula	C_{16} H_{11} Br N_2 O_3
Formula weight	359.18
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 7.593(3) Å α= 90°. b = 11.744(4) Å β= 99.277(7)°. c = 16.592(5) Å γ = 90°.
Volume	1460.3(8) $Å^3$
Z	4
Density (calculated)	1.634 Mg/m^3
Absorption coefficient	2.829 mm^{-1}
F(000)	720
Crystal size	0.28 x 0.25 x 0.14 mm^3
Theta range for data collection	2.13 to 26.04°.
Index ranges	-9<=h<=9, -14<=k<=12, -20<=l<=18
Reflections collected	8870
Independent reflections	2875 [R(int) = 0.0461]
Completeness to theta = 26.04°	99.4%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6928 and 0.5047
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2875 / 0 / 199
Goodness-of-fit on F^2	1.021
Final R indices [I>2sigma(I)]	R1 = 0.0416, wR2 = 0.0813
R indices (all data)	R1 = 0.0885, wR2 = 0.1074
Largest diff. peak and hole	0.257 and -0.375 $e.Å^{-3}$

Table S4 Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å ^{2}x 103) for **3k-PNB**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	9500(5)	5709(3)	3047(2)	48(1)
O(1)	8505(3)	6531(2)	2923(2)	63(1)
C(2)	11326(5)	5868(3)	3544(2)	47(1)
C(3)	11465(5)	6570(3)	4224(2)	59(1)
C(4)	13096(5)	6798(3)	4687(2)	61(1)
C(5)	14600(5)	6337(3)	4459(2)	50(1)
C(6)	14516(5)	5674(3)	3774(2)	58(1)
N(1)	16350(4)	6562(3)	4972(2)	62(1)
O(2)	17645(4)	6045(3)	4812(2)	83(1)
O(3)	16401(4)	7224(3)	5546(2)	88(1)
N(2)	9030(4)	4652(2)	2735(2)	51(1)
C(7)	12885(5)	5442(3)	3316(2)	56(1)
C(8)	9914(5)	3589(3)	3068(2)	63(1)
C(9)	8605(6)	2782(3)	3325(2)	67(1)
C(10)	6898(6)	2806(3)	2993(2)	63(1)
C(11)	6244(5)	3621(3)	2348(2)	50(1)
C(12)	4562(5)	3533(3)	1876(2)	56(1)
C(13)	4037(5)	4325(3)	1277(2)	54(1)
Br(1)	1657(1)	4292(1)	690(1)	86(1)
C(14)	5174(5)	5178(3)	1100(2)	56(1)
C(15)	6848(5)	5272(3)	1568(2)	57(1)
C(16)	7376(5)	4512(3)	2201(2)	49(1)

Table S5 Bond lengths [Å] and angles [°] for **3k-PNB**.

C(1)-O(1)	1.223(4)
C(1)-N(2)	1.370(4)
C(1)-C(2)	1.506(5)
C(2)-C(3)	1.387(5)
C(2)-C(7)	1.393(5)
C(3)-C(4)	1.374(5)
C(3)-H(3)	0.9500
C(4)-C(5)	1.371(5)
C(4)-H(4)	0.9500
C(5)-C(6)	1.370(5)
C(5)-N(1)	1.482(5)
C(6)-C(7)	1.372(5)
C(6)-H(6)	0.9500
N(1)-O(2)	1.221(4)
N(1)-O(3)	1.226(4)
N(2)-C(16)	1.425(4)
N(2)-C(8)	1.482(4)
C(7)-H(7)	0.9500
C(8)-C(9)	1.484(5)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.324(5)
C(9)-H(9)	0.9500
C(10)-C(11)	1.462(5)
C(10)-H(10)	0.9500
C(11)-C(12)	1.390(5)
C(11)-C(16)	1.400(5)
C(12)-C(13)	1.373(5)
C(12)-H(12)	0.9500
C(13)-C(14)	1.384(5)
C(13)-Br(1)	1.910(4)
C(14)-C(15)	1.383(5)
C(14)-H(14)	0.9500
C(15)-C(16)	1.387(5)
C(15)-H(15)	0.9500
O(1)-C(1)-N(2)	122.4(3)
O(1)-C(1)-C(2)	118.9(3)
N(2)-C(1)-C(2)	118.7(3)
C(3)-C(2)-C(7)	118.5(3)
C(3)-C(2)-C(1)	117.5(3)
C(7)-C(2)-C(1)	123.7(3)
C(4)-C(3)-C(2)	120.9(3)
C(4)-C(3)-H(3)	119.5
C(2)-C(3)-H(3)	119.5
C(5)-C(4)-C(3)	119.0(3)
C(5)-C(4)-H(4)	120.5
C(3)-C(4)-H(4)	120.5
C(6)-C(5)-C(4)	121.6(3)
C(6)-C(5)-N(1)	119.7(3)

C(4)-C(5)-N(1)	118.8(3)
C(5)-C(6)-C(7)	119.3(3)
C(5)-C(6)-H(6)	120.4
C(7)-C(6)-H(6)	120.4
O(2)-N(1)-O(3)	124.0(3)
O(2)-N(1)-C(5)	117.8(4)
O(3)-N(1)-C(5)	118.2(3)
C(1)-N(2)-C(16)	119.3(3)
C(1)-N(2)-C(8)	123.2(3)
C(16)-N(2)-C(8)	115.8(3)
C(6)-C(7)-C(2)	120.6(3)
C(6)-C(7)-H(7)	119.7
C(2)-C(7)-H(7)	119.7
N(2)-C(8)-C(9)	111.2(3)
N(2)-C(8)-H(8A)	109.4
C(9)-C(8)-H(8A)	109.4
N(2)-C(8)-H(8B)	109.4
C(9)-C(8)-H(8B)	109.4
H(8A)-C(8)-H(8B)	108.0
C(10)-C(9)-C(8)	121.5(4)
C(10)-C(9)-H(9)	119.2
C(8)-C(9)-H(9)	119.2
C(9)-C(10)-C(11)	120.8(4)
C(9)-C(10)-H(10)	119.6
C(11)-C(10)-H(10)	119.6
C(12)-C(11)-C(16)	119.4(3)
C(12)-C(11)-C(10)	122.4(3)
C(16)-C(11)-C(10)	118.1(3)
C(13)-C(12)-C(11)	119.4(3)
C(13)-C(12)-H(12)	120.3
C(11)-C(12)-H(12)	120.3
C(12)-C(13)-C(14)	121.7(3)
C(12)-C(13)-Br(1)	119.7(3)
C(14)-C(13)-Br(1)	118.5(3)
C(15)-C(14)-C(13)	119.1(3)
C(15)-C(14)-H(14)	120.4
C(13)-C(14)-H(14)	120.4
C(14)-C(15)-C(16)	120.1(4)
C(14)-C(15)-H(15)	120.0
C(16)-C(15)-H(15)	120.0
C(15)-C(16)-C(11)	120.2(3)
C(15)-C(16)-N(2)	121.0(3)
C(11)-C(16)-N(2)	118.8(3)

Symmetry transformations used to generate equivalent atoms:

Table S6 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3k-PNB**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
C(1)	48(2)	49(2)	49(2)	2(2)	9(2)	0(2)
O(1)	56(2)	43(2)	85(2)	-3(1)	2(1)	7(1)
C(2)	47(2)	42(2)	52(2)	-2(2)	10(2)	2(2)
C(3)	46(2)	59(3)	73(3)	-16(2)	16(2)	0(2)
C(4)	57(2)	62(3)	64(2)	-18(2)	14(2)	-4(2)
C(5)	44(2)	47(2)	59(2)	4(2)	8(2)	-3(2)
C(6)	51(2)	61(3)	64(3)	0(2)	21(2)	6(2)
N(1)	53(2)	59(2)	72(2)	12(2)	6(2)	-7(2)
O(2)	47(2)	104(2)	97(2)	5(2)	12(2)	1(2)
O(3)	76(2)	81(2)	100(2)	-28(2)	-9(2)	-9(2)
N(2)	55(2)	35(2)	59(2)	-2(1)	5(2)	1(1)
C(7)	56(2)	63(3)	50(2)	-12(2)	12(2)	4(2)
C(8)	65(3)	45(2)	77(3)	-3(2)	3(2)	9(2)
C(9)	84(3)	47(2)	66(3)	5(2)	5(2)	4(2)
C(10)	80(3)	52(2)	58(2)	2(2)	19(2)	-8(2)
C(11)	58(2)	45(2)	49(2)	-8(2)	14(2)	0(2)
C(12)	56(2)	50(2)	63(3)	-8(2)	15(2)	-7(2)
C(13)	52(2)	55(2)	55(2)	-16(2)	8(2)	-1(2)
Br(1)	60(1)	86(1)	103(1)	-8(1)	-10(1)	-4(1)
C(14)	65(3)	50(2)	51(2)	2(2)	7(2)	0(2)
C(15)	59(2)	53(2)	57(2)	0(2)	7(2)	-5(2)
C(16)	52(2)	42(2)	52(2)	-5(2)	7(2)	0(2)

Table S7 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å ^{2}x 10^3) for **3k-PNB**.

	x	y	z	U(eq)
H(3)	10419	6899	4371	70
H(4)	13180	7268	5158	73
H(6)	15576	5378	3619	69
H(7)	12819	4986	2839	67
H(8A)	10836	3773	3543	76
H(8B)	10512	3225	2647	76
H(9)	9001	2236	3737	80
H(10)	6088	2287	3177	75
H(12)	3782	2931	1968	67
H(14)	4808	5692	663	67
H(15)	7637	5858	1456	68

Table S8 Torsion angles [°] for **3k-PNB**.

O(1)-C(1)-C(2)-C(3)	40.3(5)
N(2)-C(1)-C(2)-C(3)	-141.1(3)
O(1)-C(1)-C(2)-C(7)	-133.2(4)
N(2)-C(1)-C(2)-C(7)	45.4(5)
C(7)-C(2)-C(3)-C(4)	-3.2(6)
C(1)-C(2)-C(3)-C(4)	-177.0(3)
C(2)-C(3)-C(4)-C(5)	1.3(6)
C(3)-C(4)-C(5)-C(6)	1.2(6)
C(3)-C(4)-C(5)-N(1)	-178.5(3)
C(4)-C(5)-C(6)-C(7)	-1.6(6)
N(1)-C(5)-C(6)-C(7)	178.0(3)
C(6)-C(5)-N(1)-O(2)	-7.6(5)
C(4)-C(5)-N(1)-O(2)	172.1(3)
C(6)-C(5)-N(1)-O(3)	174.8(3)
C(4)-C(5)-N(1)-O(3)	-5.5(5)
O(1)-C(1)-N(2)-C(16)	4.4(5)
C(2)-C(1)-N(2)-C(16)	-174.2(3)
O(1)-C(1)-N(2)-C(8)	-160.3(3)
C(2)-C(1)-N(2)-C(8)	21.1(5)
C(5)-C(6)-C(7)-C(2)	-0.4(6)
C(3)-C(2)-C(7)-C(6)	2.7(5)
C(1)-C(2)-C(7)-C(6)	176.2(3)
C(1)-N(2)-C(8)-C(9)	122.4(4)
C(16)-N(2)-C(8)-C(9)	-42.8(4)
N(2)-C(8)-C(9)-C(10)	25.8(5)
C(8)-C(9)-C(10)-C(11)	1.1(6)
C(9)-C(10)-C(11)-C(12)	167.1(4)
C(9)-C(10)-C(11)-C(16)	-12.2(5)
C(16)-C(11)-C(12)-C(13)	-0.3(5)
C(10)-C(11)-C(12)-C(13)	-179.6(3)
C(11)-C(12)-C(13)-C(14)	3.3(5)
C(11)-C(12)-C(13)-Br(1)	-174.5(2)
C(12)-C(13)-C(14)-C(15)	-3.4(5)
Br(1)-C(13)-C(14)-C(15)	174.4(3)
C(13)-C(14)-C(15)-C(16)	0.5(5)
C(14)-C(15)-C(16)-C(11)	2.5(5)
C(14)-C(15)-C(16)-N(2)	-174.5(3)
C(12)-C(11)-C(16)-C(15)	-2.6(5)
C(10)-C(11)-C(16)-C(15)	176.8(3)
C(12)-C(11)-C(16)-N(2)	174.4(3)
C(10)-C(11)-C(16)-N(2)	-6.2(5)
C(1)-N(2)-C(16)-C(15)	45.6(5)
C(8)-N(2)-C(16)-C(15)	-148.6(3)
C(1)-N(2)-C(16)-C(11)	-131.4(3)
C(8)-N(2)-C(16)-C(11)	34.4(4)

Symmetry transformations used to generate equivalent atoms: