Supporting Information

Gold-Catalyzed 1,2-Migration of Silicon, Tin, and Germanium *en route* to C-2 Substituted Fused Pyrrole-Containing Heterocycles

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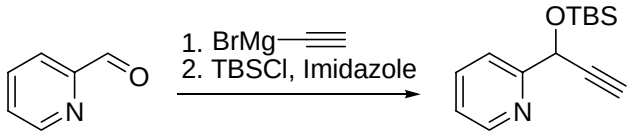
General Information

NMR spectra were recorded on Bruker Avance DRX-500 (500 MHz) and DPX-400 (400 MHz) instruments. GC/MS analyses were performed on a Hewlett Packard Model 6890 GC interfaced to a Hewlett Packard Model 5973 mass selective detector (15 m × 0.25 mm capillary column, HP-5MS). Column chromatography was carried out employing Silicycle silica gel (43-60 μm). HRMS (EI) analysis was performed on a JEOL GCmate II instrument. All manipulations with transition metal catalysts were conducted under inert atmosphere using a combination of glovebox and standard Schlenk techniques. Anhydrous toluene, tetrahydrofuran, and dichloromethane, purchased from Aldrich, were additionally purified on PureSolv PS-400-4 by Innovative Technology, Inc. purification system. All other chemicals and solvents were purchased from Aldrich, Acros Organics, TCI, and Alfa Aesar and used without additional purification.

Preparation of Starting Materials

***2-(1-(t-butyldimethyl)silanyloxy)prop-2-ynyl)pyridine* (1):**



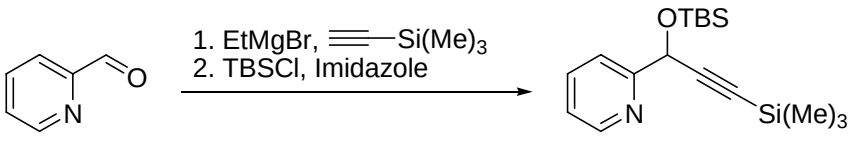
1

1. To a 100 mL flash-dried round-bottomed two-necked flask equipped with a stir bar, rubber septum, and T-shaped stopcock with an argon filled balloon was added 22 mL of 0.5M solution of ethynylmagnesium bromide in THF (11 mmol). The solution was cooled to -78ºC while stirring in

a dry ice/acetone bath and a solution of 0.95 mL (10 mmol) of 2-picolyl aldehyde in 3 mL of THF was added slowly dropwise. The solution was stirred at –78ºC for 1 hour, then allowed to warm up to room temperature and stirred for another hour. The reaction was then poured into 50 mL of saturated ammonium chloride solution and thoroughly extracted with ethyl acetate. The organic phase was then washed once each with 50 mL saturated ammonium chloride solution and 50 mL brine, dried over magnesium sulfate, and concentrated. The residue was purified over 100 mL silica gel using 1:1 ethyl acetate : hexanes as eluent to afford a 1.14 g (86%) of 2-((hydroxy)prop-2-ynyl)pyridine as a light yellow oil. ^{1}H NMR (500.13 MHz, acetone-d_6) δ 8.52 (1H, d, *J*=5.01 Hz), 7.86 (1H, dd, *J*=8.61, 7.74 Hz), 7.64 (1H, d, *J*=7.91 Hz), 7.33 (1H, dd, *J*=9.25, 6.77 Hz), 5.46 (1H, bs), 5.28 (1H, s), 3.01 (1H, s); ^{13}C NMR (125.76 MHz, acetone-d_6) δ 161.28, 149.60, 137.45, 124.23, 120.67, 84.85, 74.89, 69.25.

2. A solution of 2-((hydroxy)prop-2-ynyl)pyridine (1.14 g, 8.6 mmol) in DCM (2 mL) was added to a stirred solution of TBSCl (1.36 g, 9.0 mmol) and imidazole (0.65 g, 9.5 mmol) in DCM (10 ml). The mixture was stirred at room temperature for 1 hour. The solvent was removed under reduced pressure and the residue was purified over 100 mL silica gel using 1:9 ethyl acetate : hexanes as eluent to afford a 2.04 g (97%) of 2-(1-(*t*-butyldimethyl)silanyloxy)prop-2-ynyl)pyridine **1** as a light yellow oil. ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.51 (1H, d, *J*=4.77 Hz), 7.84 (1H, dd, *J*=9.72, 7.89 Hz), 7.65 (1H, d, *J*=7.89 Hz), 7.30 (1H, dd, *J*=8.25, 4.77 Hz), 5.54 (1H, s), 3.06 (1H, s), 0.94 (9H, s), 0.22 (3H, s), 0.13 (3H, s). ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 161.26, 149.52, 137.77, 123.71, 120.76, 84.86, 75.27, 67.35, 26.15, 18.74, -4.55, -4.91.

2-(1-(t-butyldimethyl)silanyloxy)-3-(trimethylsilyl)prop-2-ynyl)pyridine **(3a):**



3a

1. To a 100 mL flash-dried round-bottomed two-necked flask equipped with a stir bar, rubber septum, and T-shaped stopcock with an argon filled balloon were sequentially added 20 mL of anhydrous THF and 1.7 mL (12.0 mmol) of TMS-acetylene. The solution was cooled to 0ºC while stirring and a solution of ethylmagnesium bromide (3.67 mL,11.0 mmol, 3.0 M in diethyl ether) was added slowly dropwise. The solution was stirred at room temperature for 1 hour and then cooled down to –78ºC. A solution of 0.95 mL (10.0 mmol) 2-picolyl aldehyde in THF (3 mL) was

added dropwise. The reaction was stirred at –78ºC for 1 hour and then allowed to warm up to room temperature and poured into 50 mL of saturated ammonium chloride solution and thoroughly extracted with ethyl acetate. The organic phase was then washed once each with 50 mL saturated ammonium chloride solution and 50 mL brine, dried over magnesium sulfate, and concentrated. Flash chromatography with 1:20 ethyl acetate : hexane as eluent afforded 1.87 g (91%) of 2-hydroxy-3-(trimethylsilyl)prop-2-ynyl)pyridine as a yellow oil.

2. *t*-Butyldimetylsilyl protection of the alcohol 2-hydroxy-3-(trimethylsilyl)prop-2-ynyl)pyridine with was done analoguosly to the procedure described for **1** resulting in 1.05 g (91%) 2-(1-(*t*-butyldimethyl)silanyloxy)-3-(trimethylsilyl)prop-2-ynyl)pyridine **3a** as a light yellow oil. ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.53 (1H, d, *J*=4.73 Hz), 7.69 (1H, dd, *J*=9.54, 7.71 Hz), 7.61 (1H, d, *J*=7.95 Hz), 7.18 (1H, dd, *J*=8.05, 4.49 Hz), 5.51 (1H, s), 0.94 (9H, s), 0.22 (3H, s), 0.13 (3H, s), 0.09 (9H, s). ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 160.45, 148.74, 136.92, 122.58, 120.06, 90.22, 73.21, 63.95, 25.78, 18.31, -0.24, -4.53, -4.95.

***2-((1-(t-butyldimethyl)silanyloxy)prop-2-ynyl)quinoxaline* (3f):**

Prepared analogously to compound **1** from 2-quinoxalinecarboxaldehyde.[1]

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 9.20 (1H, s), 8.09 (1H, dd, *J*=6.43, 3.22 Hz), 8.05 (1H, dd, *J*=6.87, 2.78 Hz), 7.74 (1H, d, *J*=2.92 Hz), 7.72 (1H, d, *J*=4.38 Hz), 5.70 (1H, s), 2.64 (1H, s), 0.91 (9H, s), 0.22 (3H, s), 0.12 (3H, s). ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 154.50, 143.76, 142.09, 141.01, 130.13, 130.08, 129.86, 129.18, 82.71, 75.50, 65.94, 25.61, 18.15, -4.65, -5.07.

***2-((1-(t-butyldimethyl)silanyloxy)prop-2-ynyl)pyrazine* (3h):**

Prepared analogously to compound **1** from 2-pyrazinecarboxaldehyde.[2]

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.87 (1H, s), 8.49 (1H, d, *J*=3.80 Hz), 8.47 (1H, d, *J*=3.80 Hz), 5.55 (1H, s), 2.57 (1H, s), 0.90 (9H, s), 0.18 (3H, s), 0.12 (3H, s). ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 155.58, 144.12, 143.49, 142.95, 142.92, 83.01, 74.80, 65.21, 25.84, 18.40, -4.44, -4.95

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(1) Quinoxalinecarboxaldehyde was prepared via published procedure (Goto, Y. et al. *Heterocycles* **2003**, *60*, 953)

(2) Pyrazinecarboxaldehyde was prepared via the conventional reduction protocol from commercialy available methylpyrazinecarboxylate (DIBAL-H, 1.05 equiv in THF at -78ºC)

***2-((1-(t-butyldimethyl)silanyloxy)-3-(trimethylsilyl)prop-2-ynyl)quinoxaline* (3g):**

Prepared analogously to compound **3a** from 2-quinoxalinecarboxaldehyde.

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 9.19 (1H, s), 8.11 (1H, dd, *J*=6.38, 3.27 Hz), 8.07 (1H, dd, *J*=6.81, 2.79 Hz), 7.78 (1H, d, *J*=2.68 Hz), 7.76 (1H, d, *J*=2.59 Hz), 5.68 (1H, s), 0.93 (9H, s), 0.24 (3H, s), 0.16 (3H, s), 0.14 (9H, s). ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 155.09, 144.50, 142.36, 141.38, 130.35, 130.06, 129.55, 109.82, 104.35, 93.06, 72.35, 25.97, 18.54, -0.10, -4.75, -4.94.

***2-((1-(t-butyldimethyl)silanyloxy)-3-(trimethylsilyl)prop-2-ynyl)pyrazine* (3i):**

Prepared analogously to compound **3a** from 2-pyrazinecarboxaldehyde.

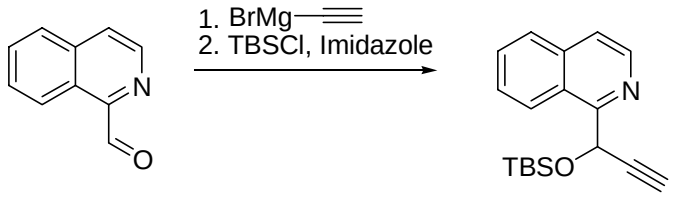
^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.88 (1H, s), 8.48 (1H, d, *J*=3.61 Hz), 8.47 (1H, d, *J*=3.62 Hz), 5.54 (1H, s), 0.92 (9H, s), 0.20 (3H, s), 0.15 (3H, s), 0.13 (9H, s). ^{13}C NMR (125.76 MHz, $CDCl_3$), δ 155.61, 143.73, 143.26, 142.90, 104.17, 91.66, 65.66, 25.69, 18.24, -0.38, -4.54, -5.02.

***2-((1-(t-butyldimethyl)silanyloxy)-3-(trimethylsilyl)prop-2-ynyl)thiazole* (3j):**

Prepared analogously to compound **3a** from 2-thiazolecarboxaldehyde.[3]

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.73 (1H, d, *J*=3.12 Hz), 7.28 (1H, d, *J*=3.12 Hz), 5.73 (1H, s), 0.94 (9H, s), 0.21 (3H, s), 0.18 (3H, s), 0.16 (9H, s). ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 171.97, 142.71, 119.36, 103.30, 91.16, 63.65, 25.61, 18.20, -0.41, -4.56, -5.11.

***2-((1- (t-butyldimethyl)silanyloxy)prop-2-ynyl)isoquinoline* (3e):**



3e

1. To a 10 mL flash-dried round-bottomed two-necked flask equipped with a stir bar, rubber septum, and T-shaped stopcock with an argon filled balloon was added 3.2 mL of 0.5M solution of ethynylmagnesium bromide in THF (1.6 mmol). The solution was cooled to -78ºC while stirring in a dry ice/acetone bath and a solution of 0.21 g (1.3 mmol) of 1-isoquinolinecarboxaldehyde in 3 mL of THF was added slowly dropwise.[4] The solution was stirred at –78ºC for 1 hour, then allowed to warm up to room temperature and stirred for another hour. The reaction was then

(3) Thiazolecarboxaldehyde was prepared via published procedure (Dondoni, A. et al. *J. Org. Chem*. **1995**, *60*, 4749)
(4) Isoquinolinecarboxaldehyde was prepared via published procedure (Giordano C. *J .Am. Chem. Soc*. **1986**, *51*, 536)

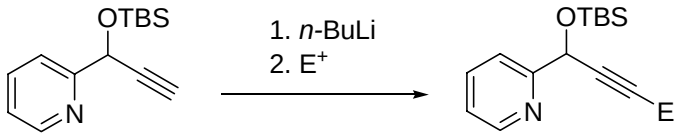
poured into 50 mL of saturated ammonium chloride solution and thoroughly extracted with ethyl acetate. The organic phase was then washed once each with 50 mL saturated ammonium chloride solution and 50 mL brine, dried over magnesium sulfate, and concentrated. The residue was used in the next step without further purification.

2. *t*-Butyldimethylsilyl protection was performed analogously to the procedure described for **1**, resulting in 2-(1-(*t*-butyldimethyl)silanyloxy)-3-(trimethylsilyl)prop-2-ynyl)isoquinoline **3e** as a yellow oil (96% for 2 steps). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.83 (1H, d, *J*=8.07 Hz), 8.38 (1H, d, *J*=5.69 Hz), 7.80 (1H, d, *J*=8.25 Hz), 7.66 (1H, dd, *J*=15.04, 8.07 Hz), 7.60 (1H, dd, *J*=6.97, 1.28 Hz), 7.59 (1H, d, *J*=6.42 Hz), 5.98 (1H, s), 2.63 (1H, s), 0.85 (9H, s), 0.20 (3H, s), -0.02 (3H, s); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 158.51, 140.99, 137.17, 130.00, 127.19, 126.99, 126.69, 125.75, 121.46, 83.65, 75.53, 69.05, 25.60, 18.10, -4.86, -5.06.

6-bromo-2-((1-(t-butyldimethyl)silanyloxy)prop-2-ynyl)pyridine **(3d):**

3d was prepared from commercially available 6-bromo-2-pyridinecarboxaldehyde analogously to **1**, resulting in a colorless oil at ambient temperature (78% for 2 steps). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.58 (1H, d, *J*=0.81 Hz), 7.57 (1H, d, *J*=3.85 Hz), 7.38 (1H, dd, *J*=6.05, 2.38 Hz), 5.47 (1H, s), 2.50 (1H, s), 0.91 (9H, s), 0.18 (3H, s), 0.12 (3H, s); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 161.46, 140.65, 139.06, 126.90, 118.52, 82.99, 73.79, 65.39, 25.42, 17.94, -4.97, -5.36.

General procedure for derivatization of alkyne



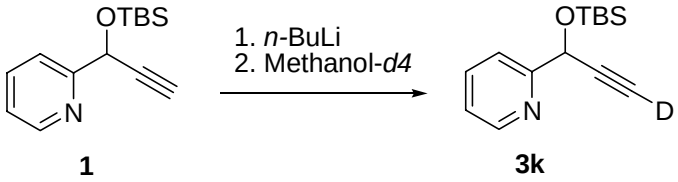
1 **3b-c**

To a flash-dried round-bottomed two-necked flask equipped with a stir bar, rubber septum, and T-shaped stopcock with an argon filled balloon were successively added anhydrous THF and **1** (0.2 M). The solution was cooled to -78ºC in a dry ice/acetone bath while stirring and a solution of *n*-BuLi (1.05 equiv., 2.5 M in hexane) was added slowly dropwise. A solution of the electrophile[5] (1.10 equiv.) in a small amount of anhydrous THF was added and the reaction was stirred for 1-1.5 hours until completion (monitored by TLC). After warming to room temperature, the solvent was removed under reduced pressure and the residue filtered through a short silica gel column (hexane

[5] Electrophiles used: Me_3GeBr (E = Me_3Ge), Bu_3SnCl (E = Bu_3Sn).

as eluent). The products were used in the cycloisomerization step without further purification due to stability issues.

2-((1-(t-butyldimethyl)silanyloxy)prop-2-ynyl)pyridine-d_1 (**3k**):



1 **3k**

To a 25 mL flash-dried round-bottomed two-necked flask equipped with a stir bar, rubber septum, and T-shaped stopcock with an argon filled balloon were added anhydrous hexane (10 mL) and **1** (0.49 g, 2.0 mmol). The solution was cooled to -78ºC in a dry ice/acetone bath while stirring and 0.80 mL of *n*-BuLi solution (1.00 equiv., 2.5 M in hexane) was added slowly dropwise. After 10 minutes 0.20 mL of methanol-d_4 (2.5 equiv., 99.5% D) were added and the reaction was stirred for 20 minutes at -78ºC. After warming to room temperature, the solvent was removed under reduced pressure and the residue filtered through a short silica gel column (hexane : ethyl acetate 9:1 as eluent) affording 0.44g of **3k** as a yellow oil (89% yield, 99.5% D). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.52 (1H, d, *J*=4.76 Hz), 7.85 (1H, dd, *J*=9.71, 7.88 Hz), 7.66 (1H, d, *J*=7.88 Hz), 7.31 (1H, dd, *J*=8.23, 4.74 Hz), 5.52 (1H, s), 0.95 (9H, s), 0.24 (3H, s), 0.15 (3H, s). ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 161.23, 149.49, 137.74, 123.68, 120.73, 84.83, 75.24, 67.32, 26.12, 18.71, -4.58, -4.94.

Catalyst optimization

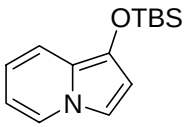
AuCl, AuBr and $AuBr_3$ were nearly equally effective in this reaction. CuCl and CuI gave traces of products. Employment of $PtCl_2$, $AgBF_4$, $AgPF_6$, $AgSbF_6$, $Al(OTf)_3$, $AlCl_3$, Au(TPP)Cl and $Pd(TPP)_2Cl_2$ gave no cycloizomerization at all.

General procedure for cycloisomerization

In a glovebox under nitrogen atmosphere, to a 3.0 mL Wheaton microreactor equipped with a spin vane and screw cap with a PTFE faced silicone septum under nitrogen atmosphere was added 2 mol% of $AuBr_3$. The microreactor was removed from the glovebox, alkyne **1** or **3a-k** and anhydrous toluene (0.5M) were successively added and the mixture was stirred until completion (as monitored by TLC and/or GC/MS). The solvent was removed under reduced pressure and the

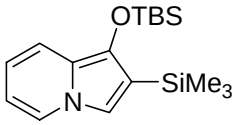
residue was purified using flash-column chromatography using hexane as eluent to afford pure fused pyrroloheterocycles **2**, **4a-k**.

***1-((t-butyldimethyl)silanyloxy)indolizine*, 2**



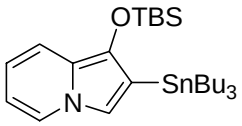
2: (62%, 1.4 mmol) ^{1}H NMR (500.13 MHz, acetone-d_6) δ 7.87 (1H, d, *J*=6.97 Hz), 7.24 (1H, d, *J*=9.17 Hz), 7.17 (1H, d, *J*=1.83 Hz), 6.42 (1H, dd, *J*=8.99, 6.42 Hz), 6.36 (1H, d, *J*=2.57 Hz), 6.29 (1H, dd, *J*=6.69, 6.68 Hz), 1.04 (9H, s), 0.20 (6H, s). ^{13}C NMR (125.76 MHz, acetone-d_6) δ 133.18, 126.36, 122.72, 117.90, 115.11, 111.07, 109.68, 106.15, 26.90, 19.45, -3.70. HRMS (EI) calcd. for $C_{14}H_{21}NOSi$ [M^+]: 247.13924. Found: 247.13920.

***1-(t-butyldimethyl)silanyloxy-2-(trimethylsilyl)indolizine*, 4a**



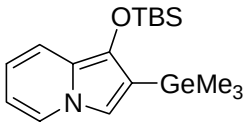
4a: (63% for 2 steps, 1 mmol) ^{1}H NMR (500.13 MHz, acetone-d_6) δ 7.84 (1H, d, *J*=7.15 Hz), 7.23 (1H, d, *J*=9.90 Hz), 7.17 (1H, s), 6.39 (1H, dd, *J*=10.18, 6.33 Hz), 6.25 (1H, dd, *J*=7.34, 6.24 Hz), 1.09 (9H, s), 0.32 (9H, s), 0.22 (6H, s); ^{13}C NMR (125.76 MHz, acetone-d_6) δ 137.17, 125.47, 122.29, 117.78, 115.15, 114.46, 110.23, 26.49, 18.83, 0.48, -3.18. HRMS (EI) calcd. for $C_{17}H_{29}NOSi_2$ [M^+]: 319.17877. Found: 319.17820.

***1-(t-butyldimethyl)silanyloxy-2-(tributylstannyl)indolizine*, 4b**



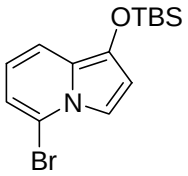
4b: (64% for 2 steps (NMR), 0.8 mmol) ^{1}H NMR (500.13 MHz, benzene-d_6) δ 7.36 (1H, d, *J*=8.99 Hz), 7.08 (1H, d, *J*=6.97 Hz), 6.80 (1H, s), 6.22 (1H, dd, *J*=9.54, 6.79 Hz), 5.90 (1H, dd, *J*=7.52, 6.42 Hz), 1.67 - 1.79 (6H, m), 1.42 - 1.51 (6H, m), 1.25 - 1.32 (6H, m), 1.14 (9H, s), 0.93 - 1.01 (9H, m), 0.21 (6H, s); ^{13}C NMR (125.76 MHz, benzene-d_6) δ 124.20, 117.27, 115.51, 114.49, 113.57, 109.26, 29.70, 27.87, 26.25, 18.43, 13.94, 10.55, 2.18, -3.71. MS *m/z* (relative intensity) 537 (M^+, 84), 480 (M^+ - *t*Bu, 80), 368 (M^+ - 3*n*Bu, 210); $C_{26}H_{47}NOSiSn$.

***1-(t-butyldimethyl)silanyloxy-2-(trimethylgermyl)indolizine,* 4c**



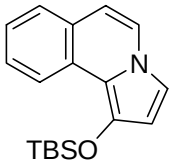
4c: (92%, 0.75 mmol) ^{1}H NMR (500.13 MHz, acetone-d_6) δ 7.85 (1H, d, *J*=7.02 Hz), 7.22 (1H, d, *J*=9.06 Hz), 7.12 (1H, s), 6.40 (1H, dd, *J*=9.14, 6.36 Hz), 6.25 (1H, dd, *J*=7.16, 6.43 Hz), 1.08 (9H, s), 0.44 (9H, s), 0.20 (6H, s); ^{13}C NMR (125.76 MHz, acetone-d_6) δ 129.86, 125.55, 122.52, 117.70, 114.59, 114.05, 110.19, 105.60, 26.63, 0.14, -3.20. HRMS (EI) calcd. for $C_{17}H_{29}GeNOSi$ [M^+]: 365.12302. Found: 365.12440.

***1-(t-butyldimethyl)silanyloxy-5-(bromo)indolizine,* 4d**



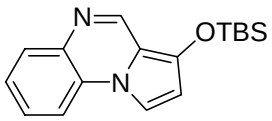
4d: (62%, 0.5 mmol) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.31 (1H, d, *J*=9.90 Hz), 7.28 (1H, d, *J*=2.93 Hz), 6.64 (1H, d, *J*=6.79 Hz), 6.46 (1H, d, *J*=2.93 Hz), 6.34 (1H, dd, *J*=8.90, 6.88 Hz), 1.03 (9H, s), 0.20 (6H, s); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 133.60, 123.72, 115.77, 114.21, 113.76, 113.45, 108.80, 105.43, 25.76, 18.18, -4.60. HRMS (EI) calcd. for $C_{14}H_{20}BrNOSi$ [M^+]: 325.04975. Found: 325.05010.

***1-((t-butyldimethyl)silanyloxy)pyrrolo[2,1-a]isoquinoline,* 4e**



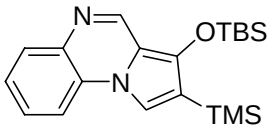
4e: (81%, 0.084 mmol) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.45 (1H, d, *J*=8.07 Hz), 7.46 (1H, d, *J*=7.34 Hz), 7.44 (1H, dd, *J*=10.71, 8.02 Hz), 7.42 (1H, dd, *J*=11.00, 8.25 Hz), 7.23 (1H, d, 5.03 Hz), 6.95 (1H, d, *J*=2.93 Hz), 6.50 (1H, d, *J*=7.34 Hz), 6.31 (1H, d, *J*=2.93 Hz), 1.10 (9H, s), 0.30 (6H, s); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 136.85, 127.54, 127.14, 126.64, 126.30, 124.85, 124.48, 122.47, 115.92, 110.60, 110.53, 103.96, 26.24, 18.53, -3.97. HRMS (EI) calcd. for $C_{18}H_{23}NOSi$ [M^+]: 297.15489. Found: 297.15360.

***3-((t-butyldimethyl)silanyloxy)pyrrolo[1,2]quinoxaline,* 4f**



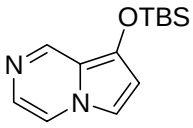
4f: (94%, 1.6 mmol) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.68 (1H, s), 7.83 (1H, d, *J*=7.89 Hz), 7.66 (5H, d, *J*=8.04 Hz), 7.58 (5H, d, *J*=2.92 Hz), 7.38 (1H, dd, *J*=8.04, 1.61 Hz), 7.34 (1H, dd, *J*=7.89, 1.46 Hz), 6.32 (1H, d, *J*=2.92 Hz), 1.02 (9H, s), 0.22 (6H, s). ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 143.63, 139.74, 136.15, 129.76, 127.63, 127.24, 124.82, 116.02, 112.81, 110.89, 109.47, 104.68, 25.60, 18.20, -4.71. HRMS (EI) calcd. for $C_{17}H_{22}N_2OSi$ [M^+]: 298.15014. Found: 298.15030.

***2-(trimethylsilyl)-3-((t-butyldimethyl)silanyloxy)pyrrolo[1,2]quinoxaline,* 4g**



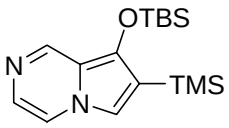
4g: (78%, 0.4 mmol) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.69 (1H, s), 7.82 (1H, d, *J*=7.71 Hz), 7.75 (1H, d, *J*=8.25 Hz), 7.60 (1H, s), 7.44 (1H, d, *J*=8.05 Hz), 7.36 (1H, d, *J*=7.98 Hz), 7.26 (1H, s), 1.09 (9H, s), 0.35 (9H, s), 0.27 (6H, s). ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 144.73, 144.49, 136.19, 129.88, 127.88, 127.65, 125.21, 117.08, 116.86, 115.21, 113.19, 26.22, 25.95, 0.23, -3.36. HRMS (EI) calcd. for $C_{20}H_{30}N_2OSi_2$ [M^+]: 370.18967. Found: 370.18930.

***8-((t-butyldimethyl)silanyloxy)pyrrolo[1,2]pyrazine,* 4h**



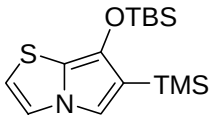
4h: (72%, 0.7 mmol) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.64 (1H, s), 7.47 (1H, d, *J*=4.95 Hz), 7.23 (1H, d, *J*=4.95 Hz), 7.07 (1H, d, *J*=2.75 Hz), 6.30 (1H, d, *J*=2.57 Hz), 0.99 (9H, s), 0.18 (6H, s). ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 143.68, 136.53, 126.71, 118.53, 117.47, 111.13, 105.12, 25.97, 18.38, -4.52. HRMS (EI) calcd. for $C_{13}H_{20}N_2OSi$ [M^+]: 248.13449. Found: 248.13470.

***7-(trimethylsilyl)-8-((t-butyldimethyl)silanyloxy)pyrrolo[1,2]pyrazine*, 4i**



4i: (87%, 0.15 mmol) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.63 (1H, s), 7.46 (1H, d, *J*=4.95 Hz), 7.18 (3H, d, *J*=4.95 Hz), 7.06 (1H, s), 1.05 (9H, s), 0.30 (9H, s), 0.23 (6H, s). ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 144.04, 140.88, 126.20, 118.76, 117.07, 116.68, 115.23, 25.96, 18.33, -0.11, -3.62. HRMS (EI) calcd. for $C_{16}H_{28}N_2OSi_2$ [M^+]: 320.17402. Found: 320.17410.

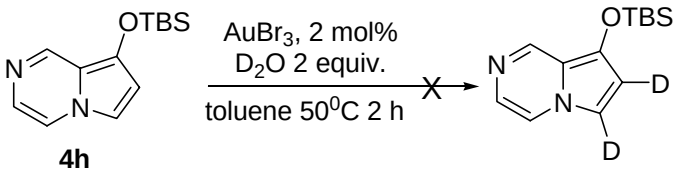
***6-(trimethylsilyl)-7-((t-butyldimethyl)silanyloxy)pyrrolo[1,2]thiazole*, 4j**



4j: (56%, 0.3 mmol) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.11 (1H, d, *J*=4.22 Hz), 6.86 (1H, s), 6.44 (1H, d, *J*=4.22 Hz), 1.02 (9H, s), 0.27 (6H, s), 0.26 (9H, s). ^{13}C NMR (125.76 MHz, $CDCl_3$), δ 137.26, 119.57, 117.12, 113.47, 112.34, 110.61, 25.94, 25.76, 18.07, -0.27, -3.43. HRMS (EI) calcd. for $C_{15}H_{27}NOSSi_2$ [M^+]: 325.13519. Found: 325.13470.

Mechanistic studies

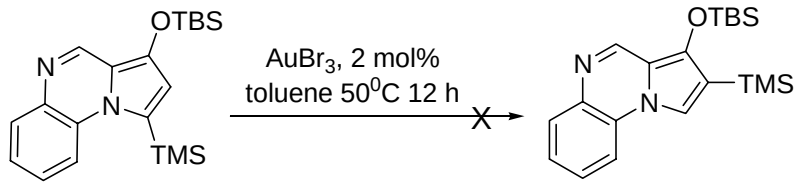
Studies on possible deuterium scrambling in pyrrole ring



4h

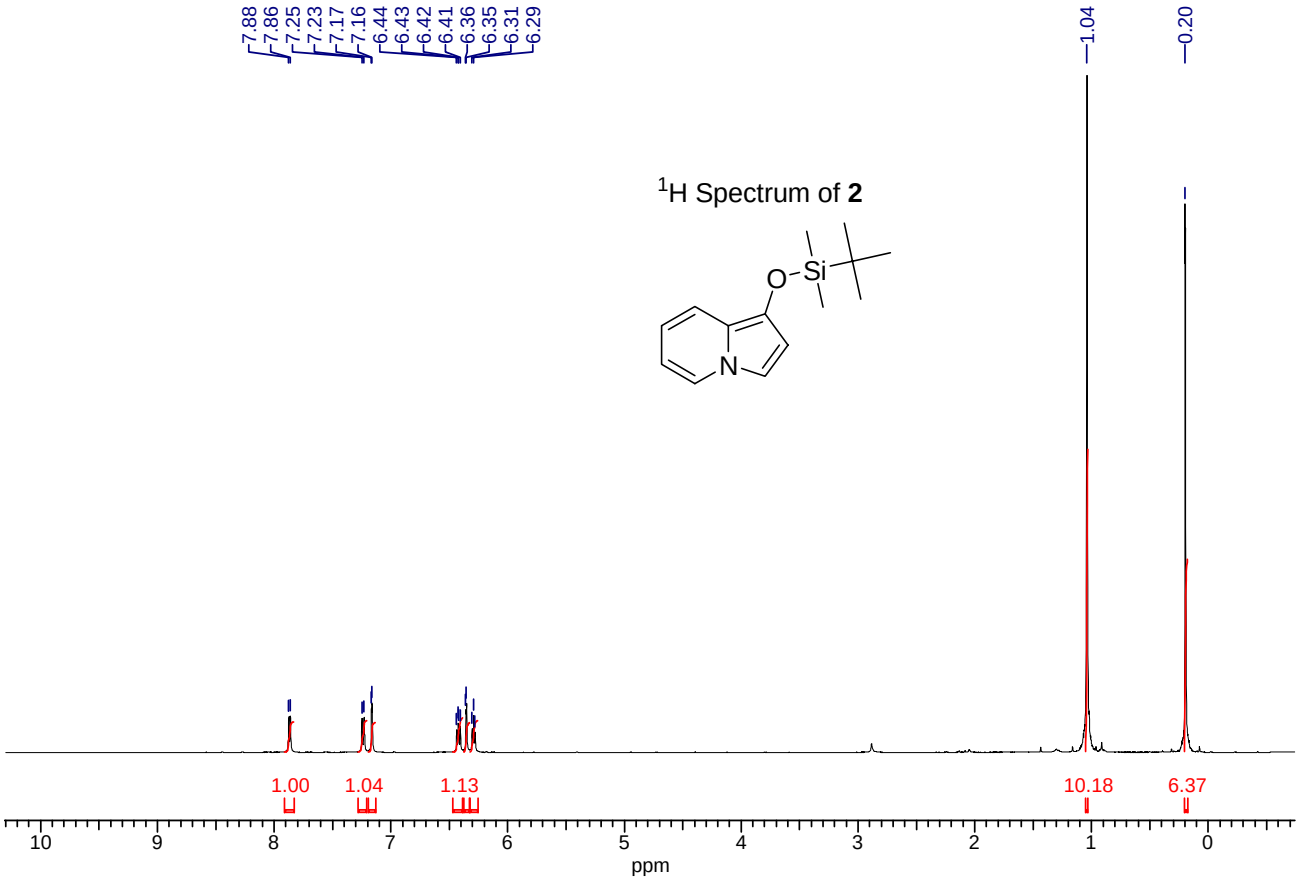
In a glovebox under nitrogen atmosphere, to a 1.0 mL Wheaton microreactor equipped with a spin vane and screw cap with a PTFE faced silicone septum was added 2 mol% of $AuBr_3$. The microreactor was removed from the glovebox, pyrrolopyrazine **4h** (0.05 g, 0.2 mmol), anhydrous toluene (0.4 mL, 0.5M) and deuterium oxide (2 eq., 0.004 mL) were successively added and the mixture was stirred at 50ºC for 2 hours. The solvent was removed under reduced pressure and the residue was filtered through a short flash-column using 1:1 hexanes and ethylacetate mixture. Neither ^{1}H and ^{2}H NMR experiments nor GC/MS analysis indicated the incorporation of deuterium into pyrrolopyrazine **4h**.

Studies on possible Au-catalyzed C3-C2 shift of TMS-group

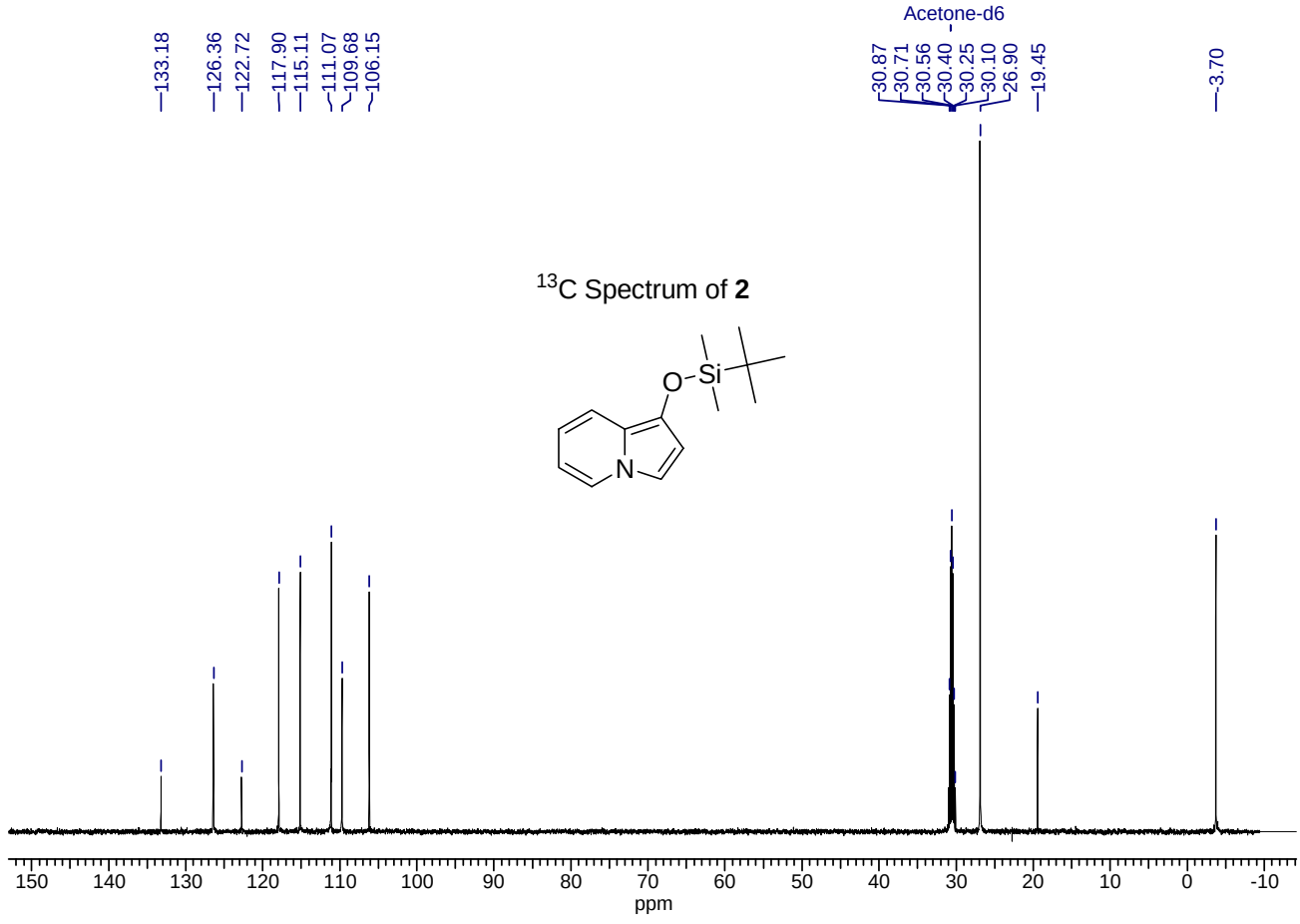


8 **4g**

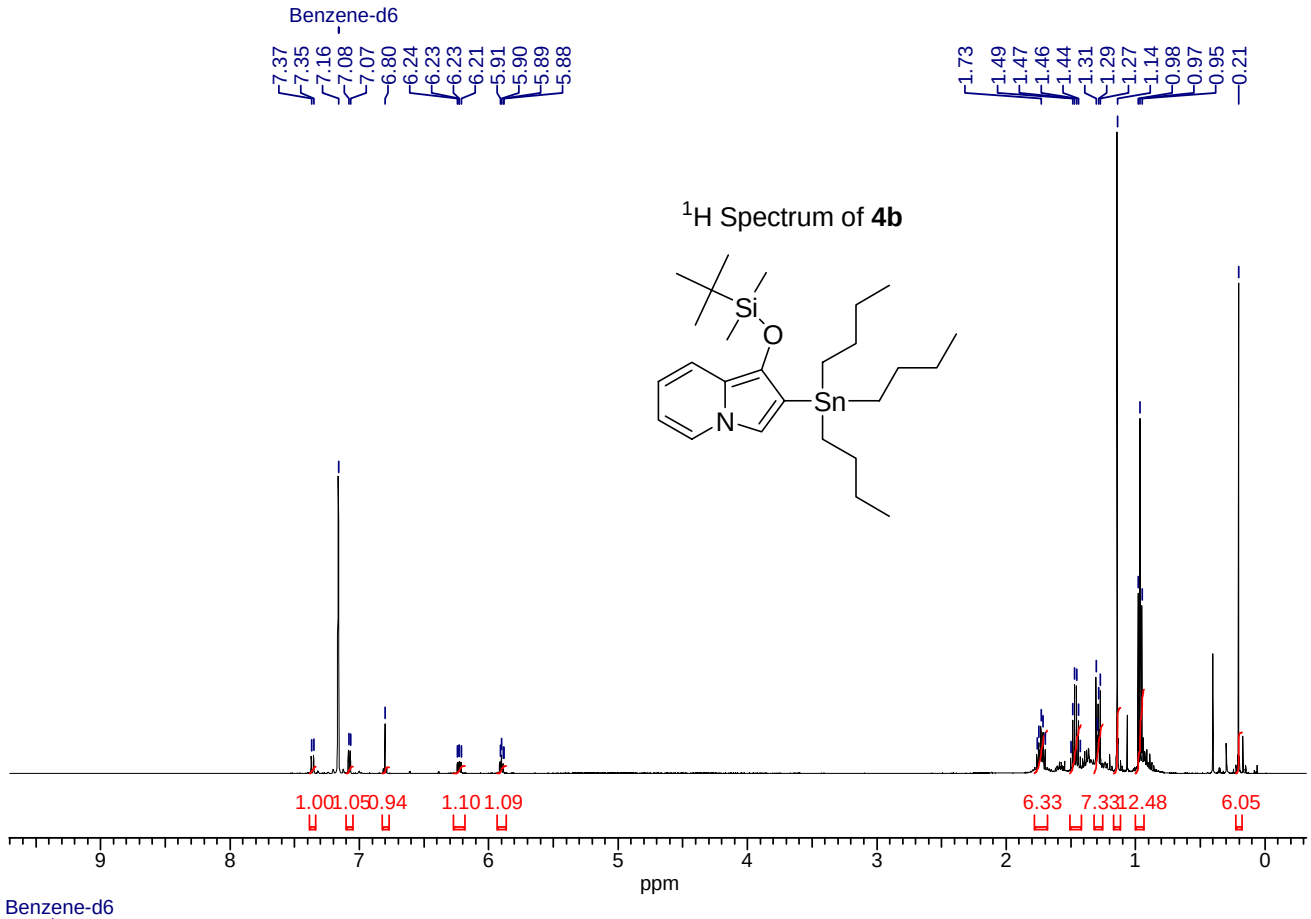
In a glovebox under nitrogen atmosphere, to a 1.0 mL Wheaton microreactor equipped with a spin vane and screw cap with a PTFE faced silicone septum was added 2 mol% of $AuBr_3$. The microreactor was removed from the glovebox, pyrroloquinoxaline **8** (0.025 g, 0.380 mmol) and anhydrous toluene (0.2 mL, 0.3M) were successively added and the mixture was stirred at 50ºC for 12 hours. GC/MS and TLC analyses indicated no traces of isomeric **4g** formed under these conditions.

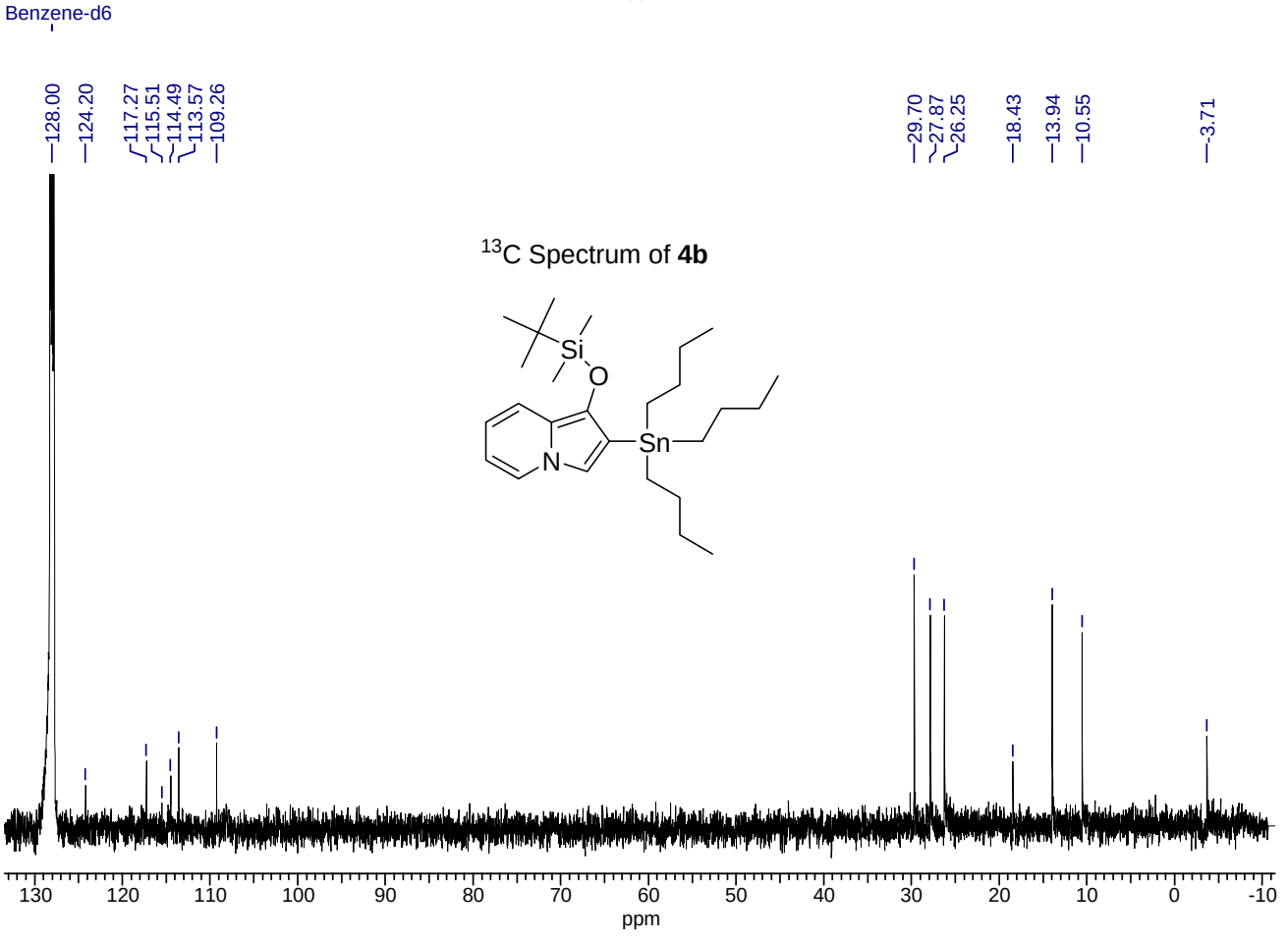


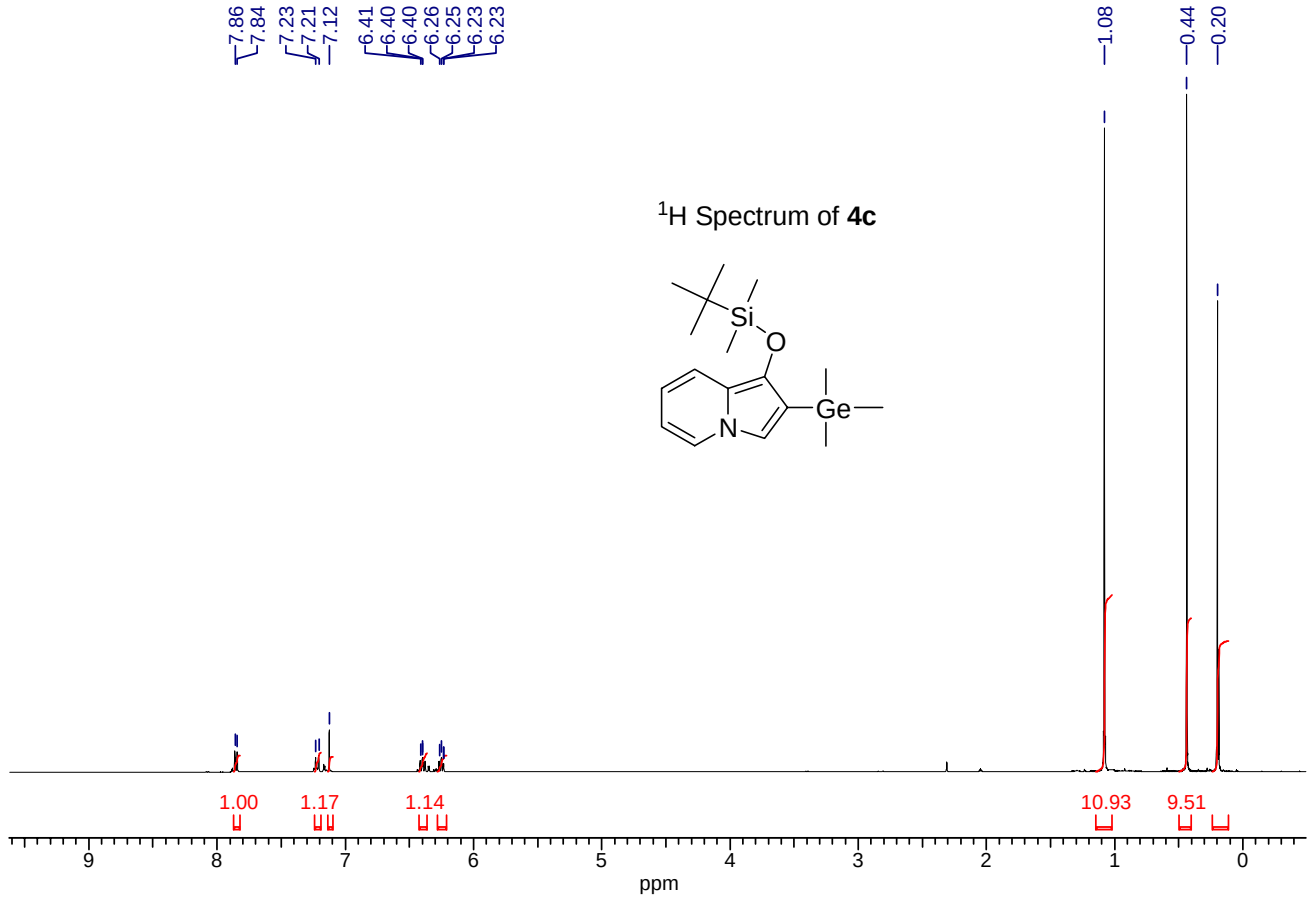
^{1}H Spectrum of **2**

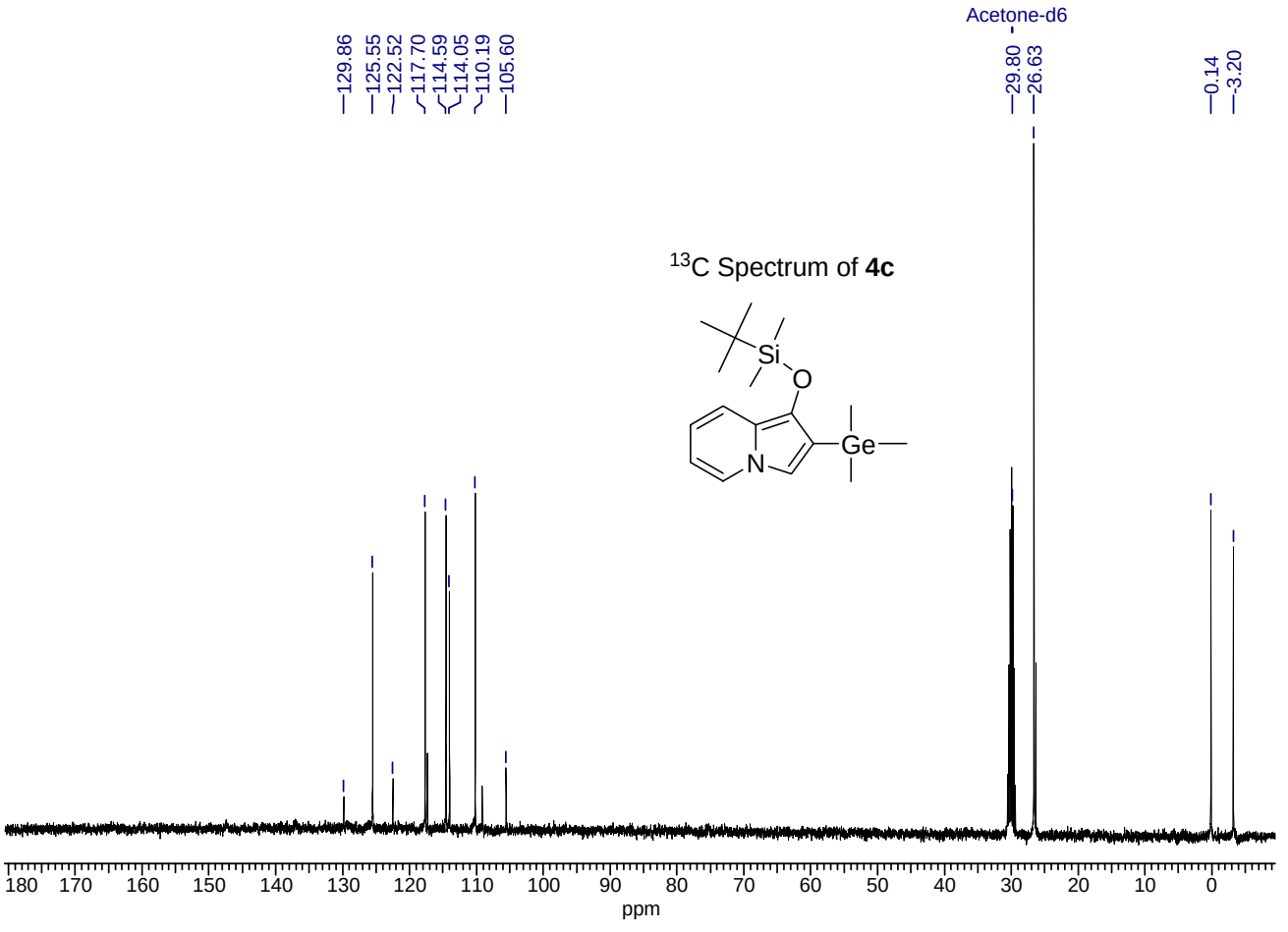


^{13}C Spectrum of **2**

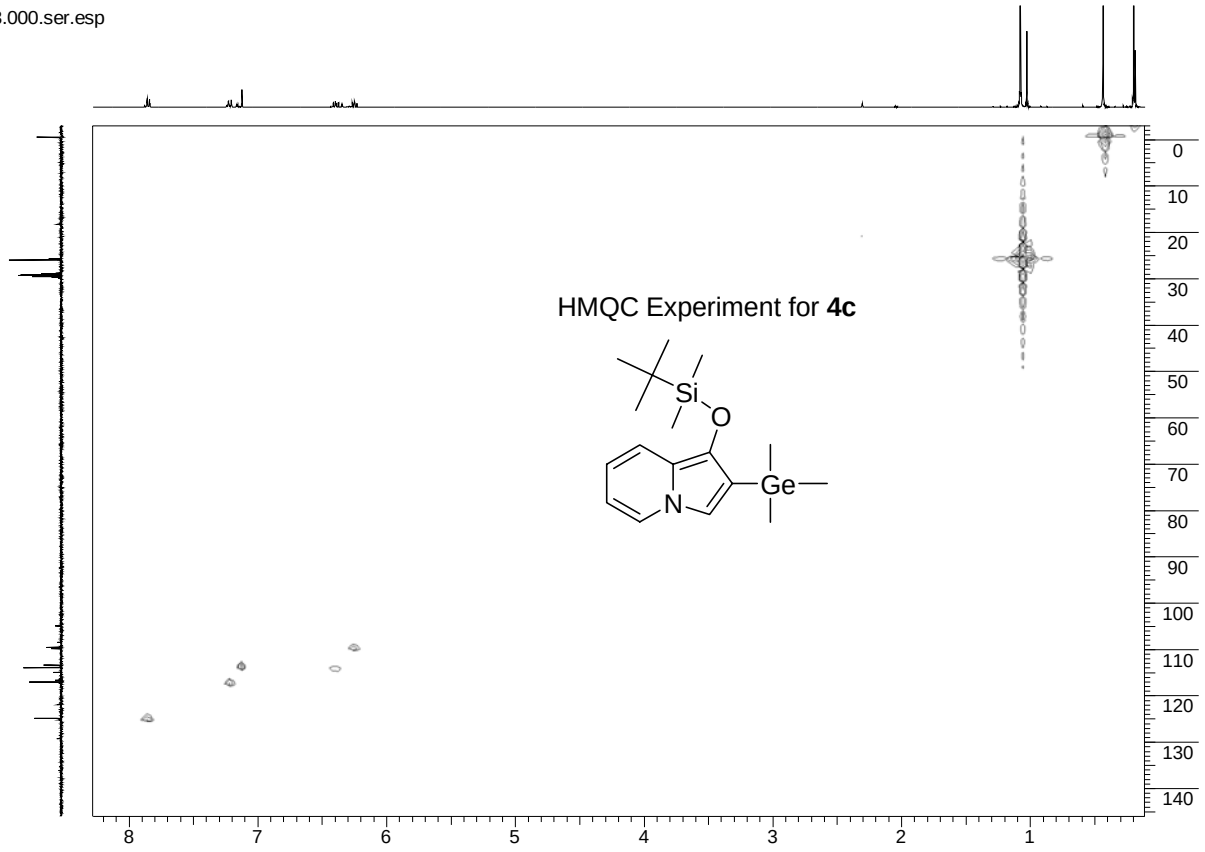

Benzene-d6
7.37
7.35
7.16
7.08
7.07
6.80
6.24
6.23
6.23
6.21
5.91
5.90
5.89
5.88
1.73
1.49
1.47
1.46
1.44
1.31
1.29
1.27
1.14
0.98
0.97
0.95
0.21
1H Spectrum of 4b
Si
O
N
Sn
1.00
1.05
0.94
1.10
1.09
6.33
7.33
12.48
6.05
9
8
7
6
5
4
3
2
1
0
ppm


Benzene-d6
128.00
124.20
117.27
115.51
114.49
113.57
109.26
29.70
27.87
26.25
18.43
13.94
10.55
-3.71
13C Spectrum of 4b
Si
O
N
Sn
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

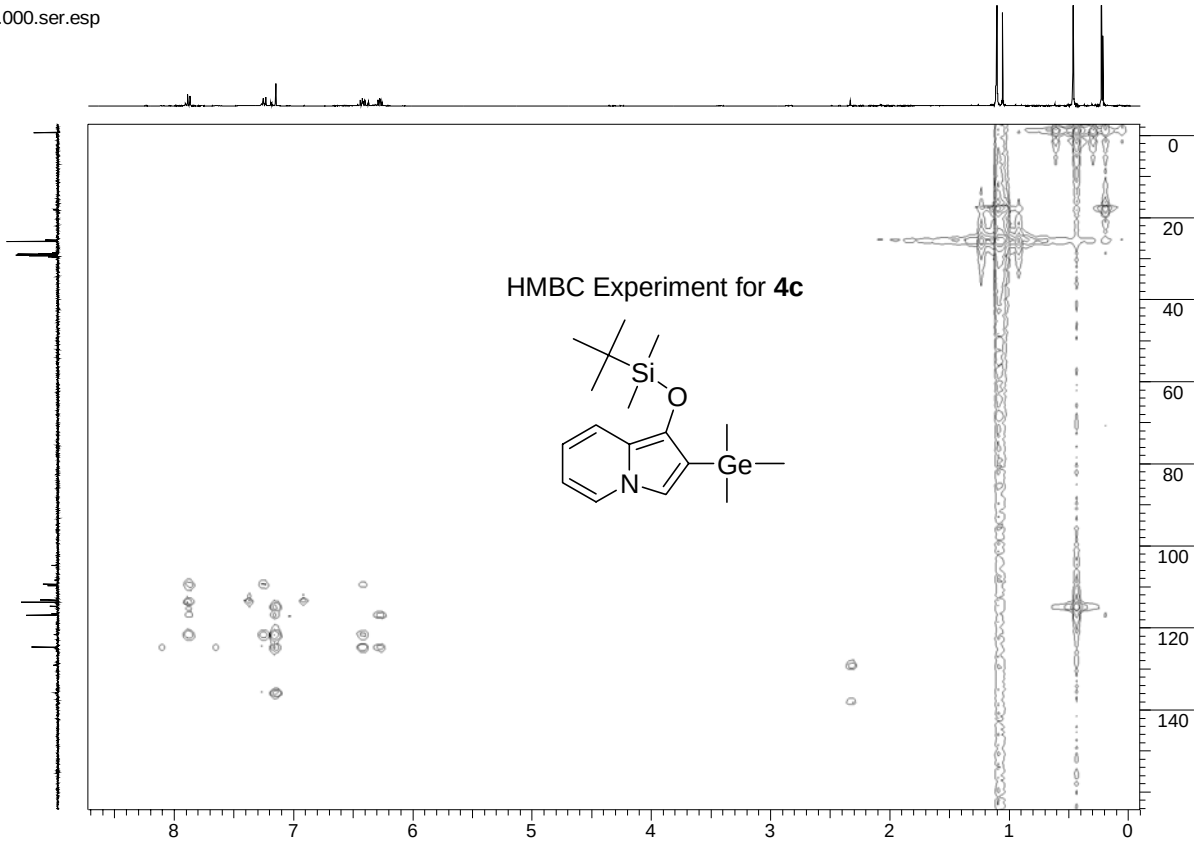

7.86
7.84
7.23
7.21
7.12
6.41
6.40
6.40
6.26
6.25
6.23
6.23
1.08
0.44
0.20
1H Spectrum of 4c
Si
O
Ge
N
1.00
1.17
1.14
10.93
9.51
ppm

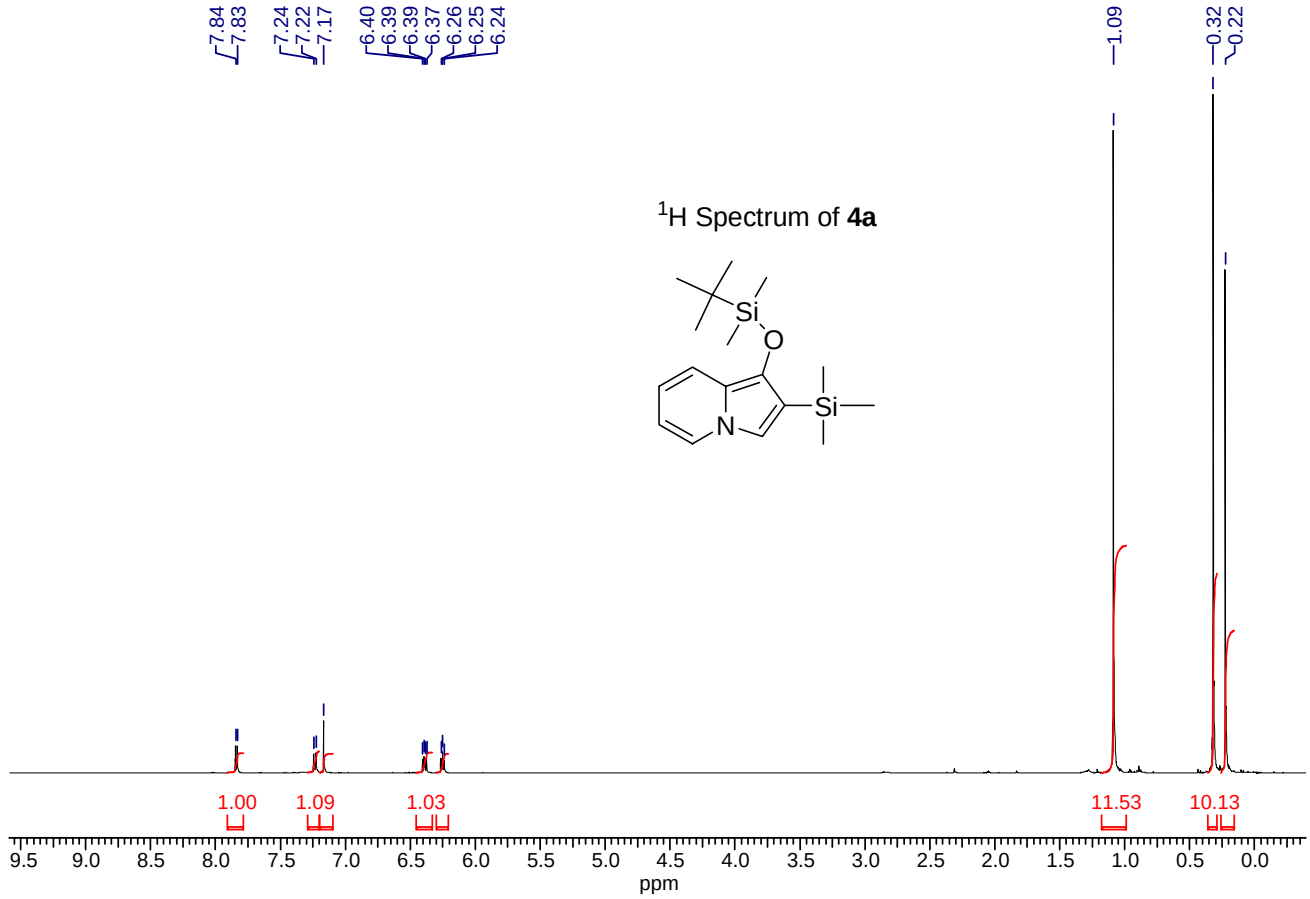

129.86
125.55
122.52
117.70
114.59
114.05
110.19
105.60
Acetone-d6
29.80
26.63
0.14
-3.20
13C Spectrum of 4c
Si
O
Ge
N
ppm

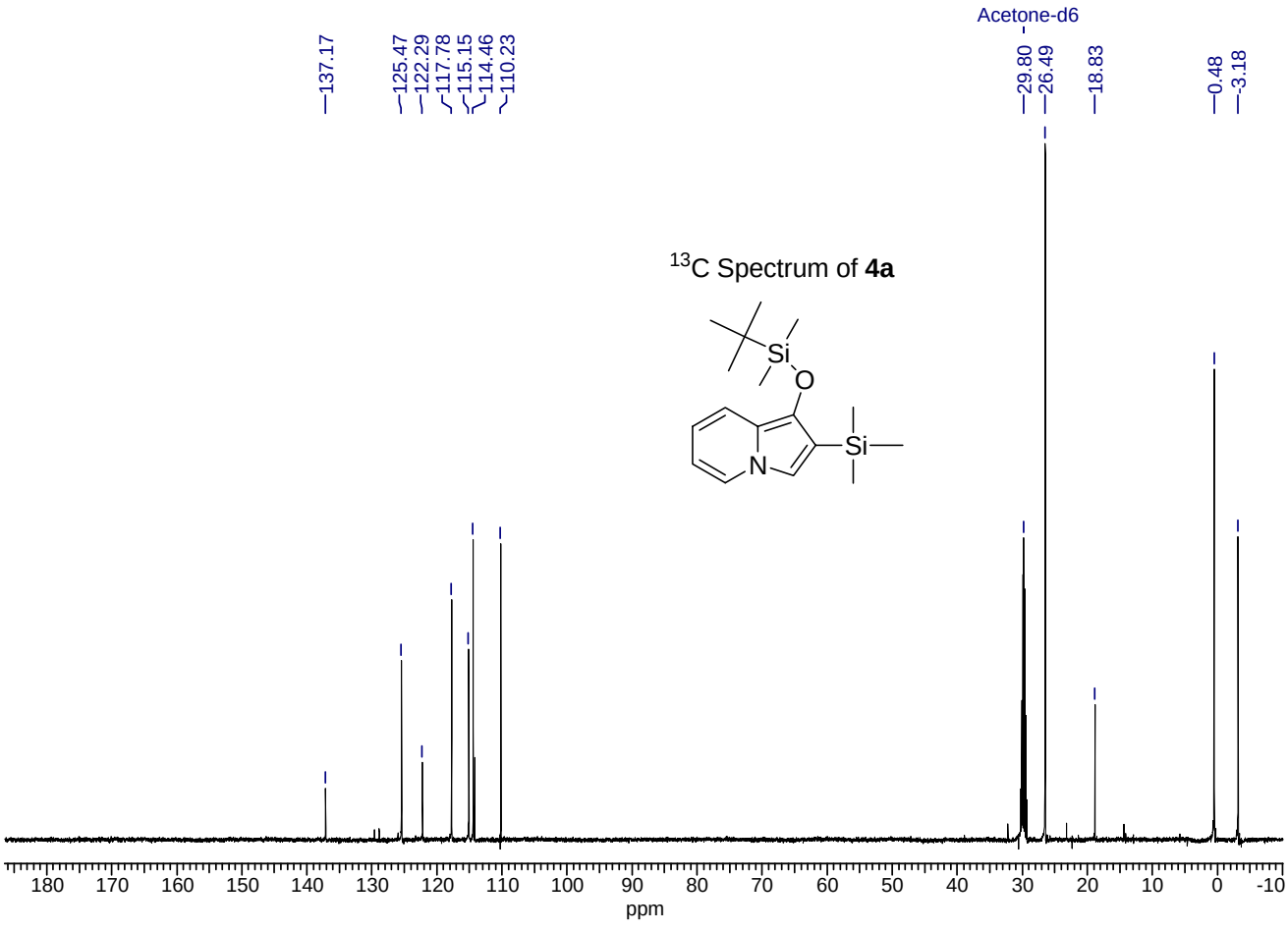
is276a.003.000.ser.esp

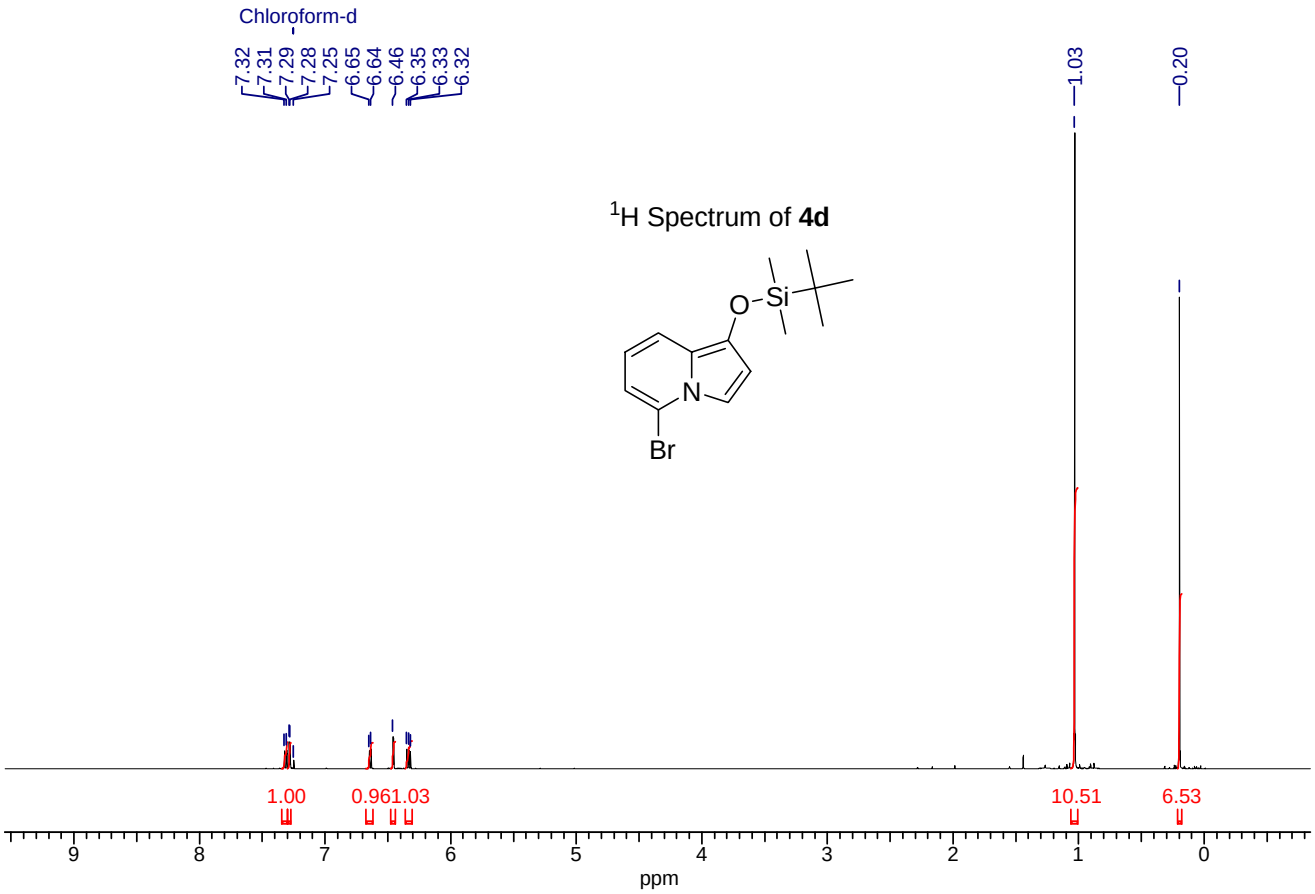


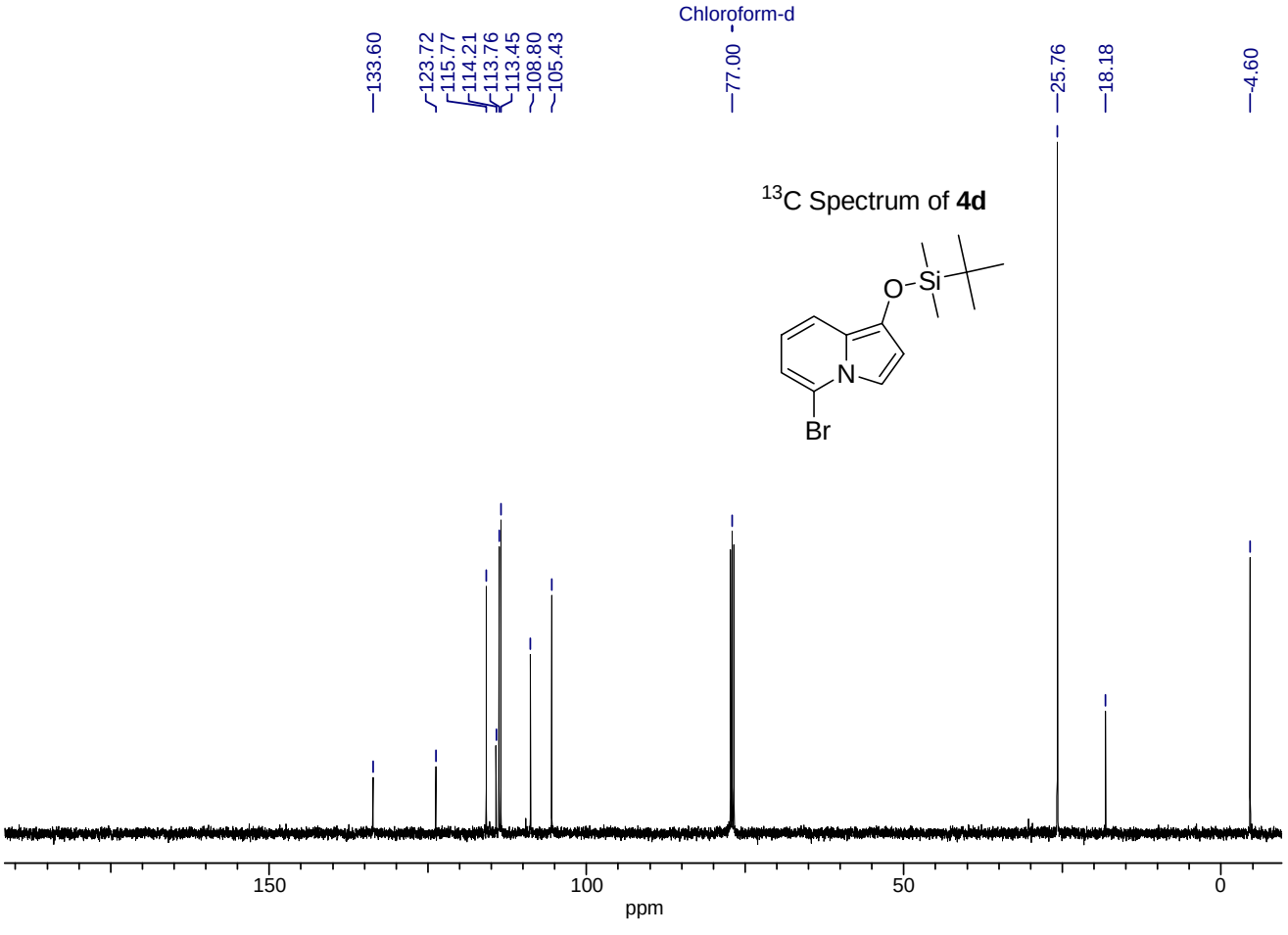
is276a.004.000.ser.esp

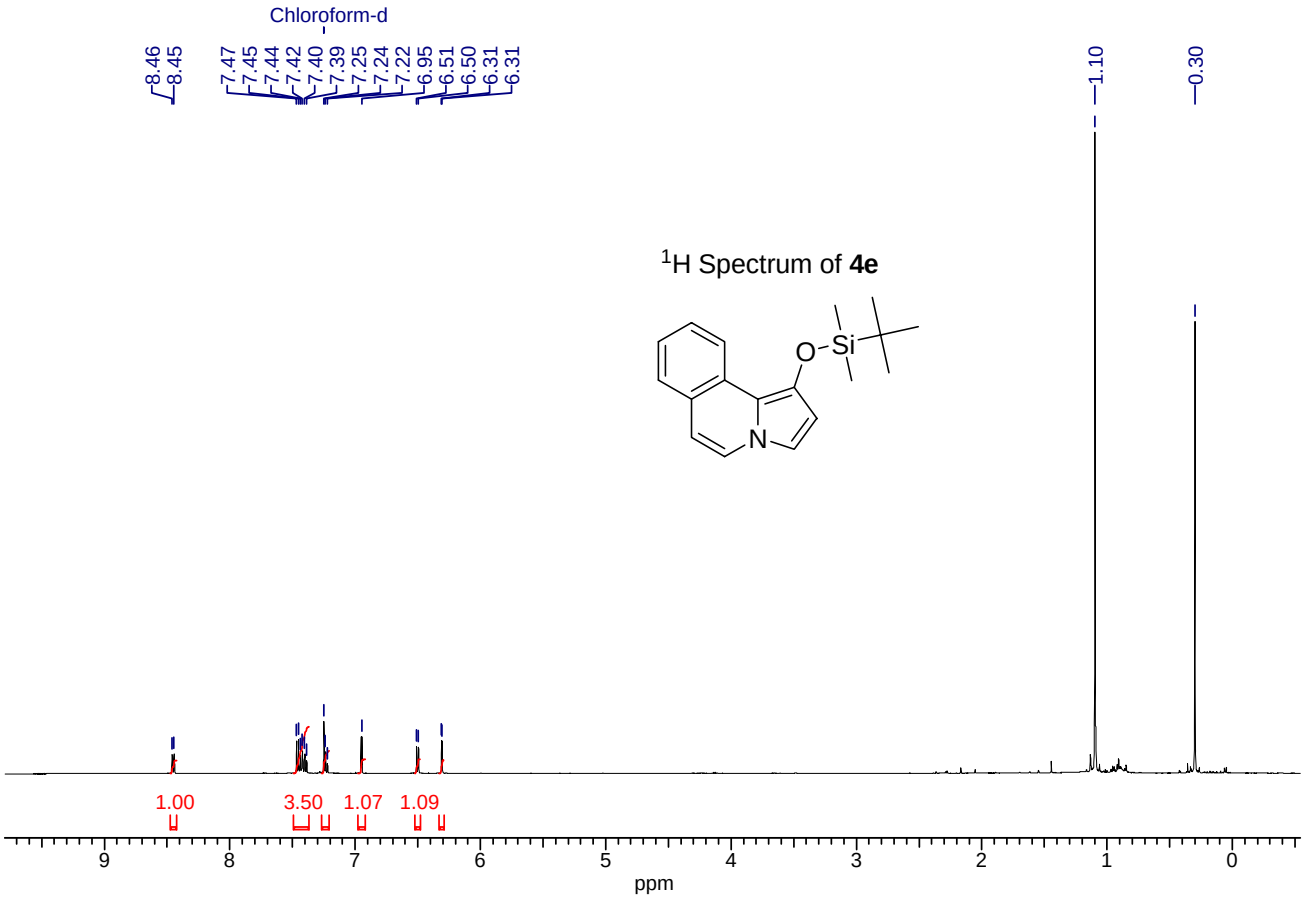


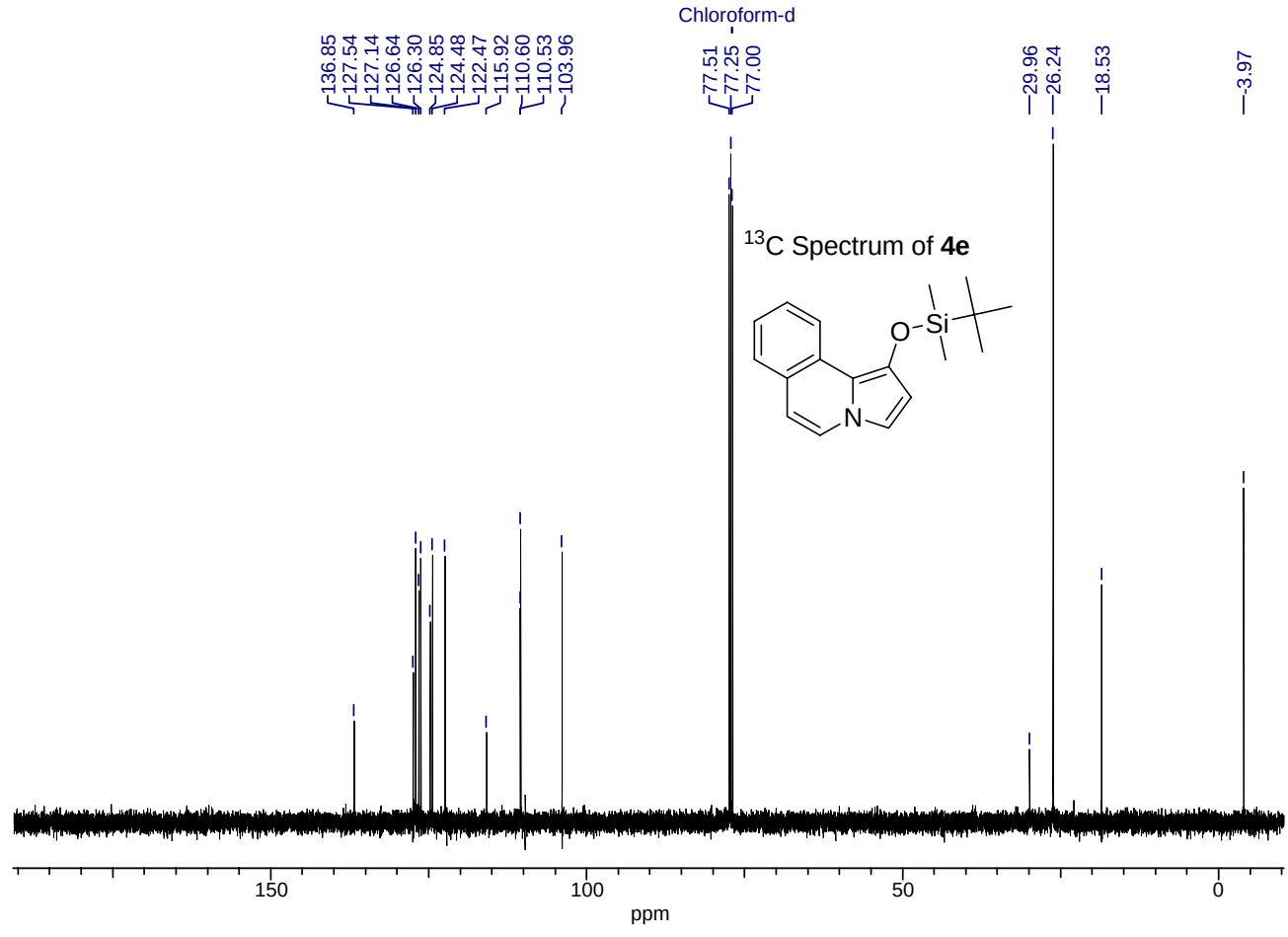

7.84
7.83
7.24
7.22
7.17
6.40
6.39
6.39
6.37
6.26
6.25
6.24
1.09
0.32
0.22
^{1}H Spectrum of **4a**
Si
O
N
Si
1.00
1.09
1.03
11.53
10.13
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

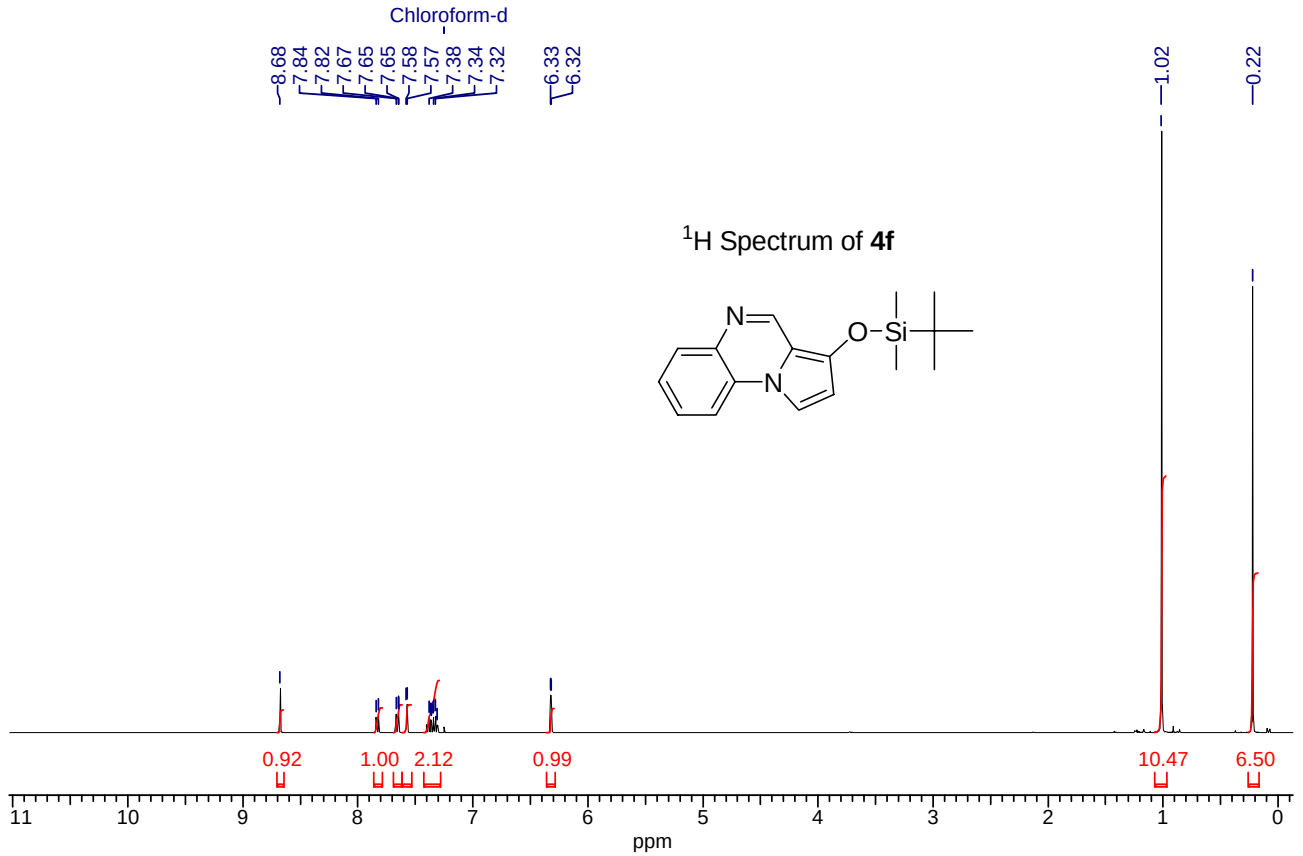

Acetone-d6
137.17
125.47
122.29
117.78
115.15
114.46
110.23
29.80
26.49
18.83
0.48
-3.18
^{13}C Spectrum of **4a**
Si
O
N
Si
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm


Chloroform-d
7.32
7.31
7.29
7.28
7.25
6.65
6.64
6.46
6.35
6.33
6.32
1.03
0.20
^{1}H Spectrum of **4d**
O
Si
N
Br
1.00
0.96
1.03
10.51
6.53
9
8
7
6
5
4
3
2
1
0
ppm

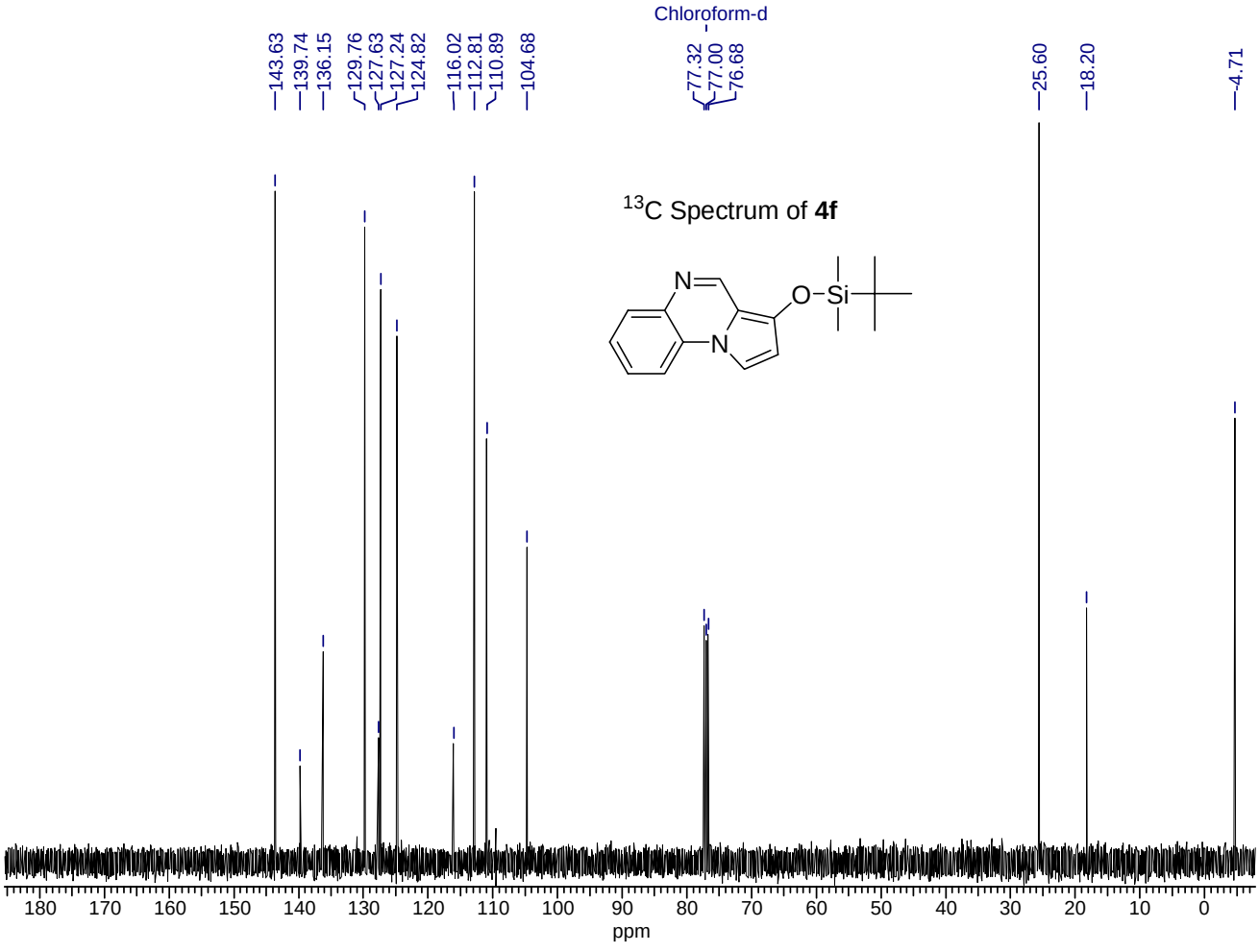

Chloroform-d
133.60
123.72
115.77
114.21
113.76
113.45
108.80
105.43
77.00
25.76
18.18
4.60
^{13}C Spectrum of **4d**
O
Si
N
Br
150
100
50
0
ppm


Chloroform-d
8.46
8.45
7.47
7.45
7.44
7.42
7.40
7.39
7.25
7.24
7.22
6.95
6.51
6.50
6.31
6.31
1.10
0.30
1H Spectrum of 4e
O
Si
N
1.00
3.50
1.07
1.09
9
8
7
6
5
4
3
2
1
0
ppm

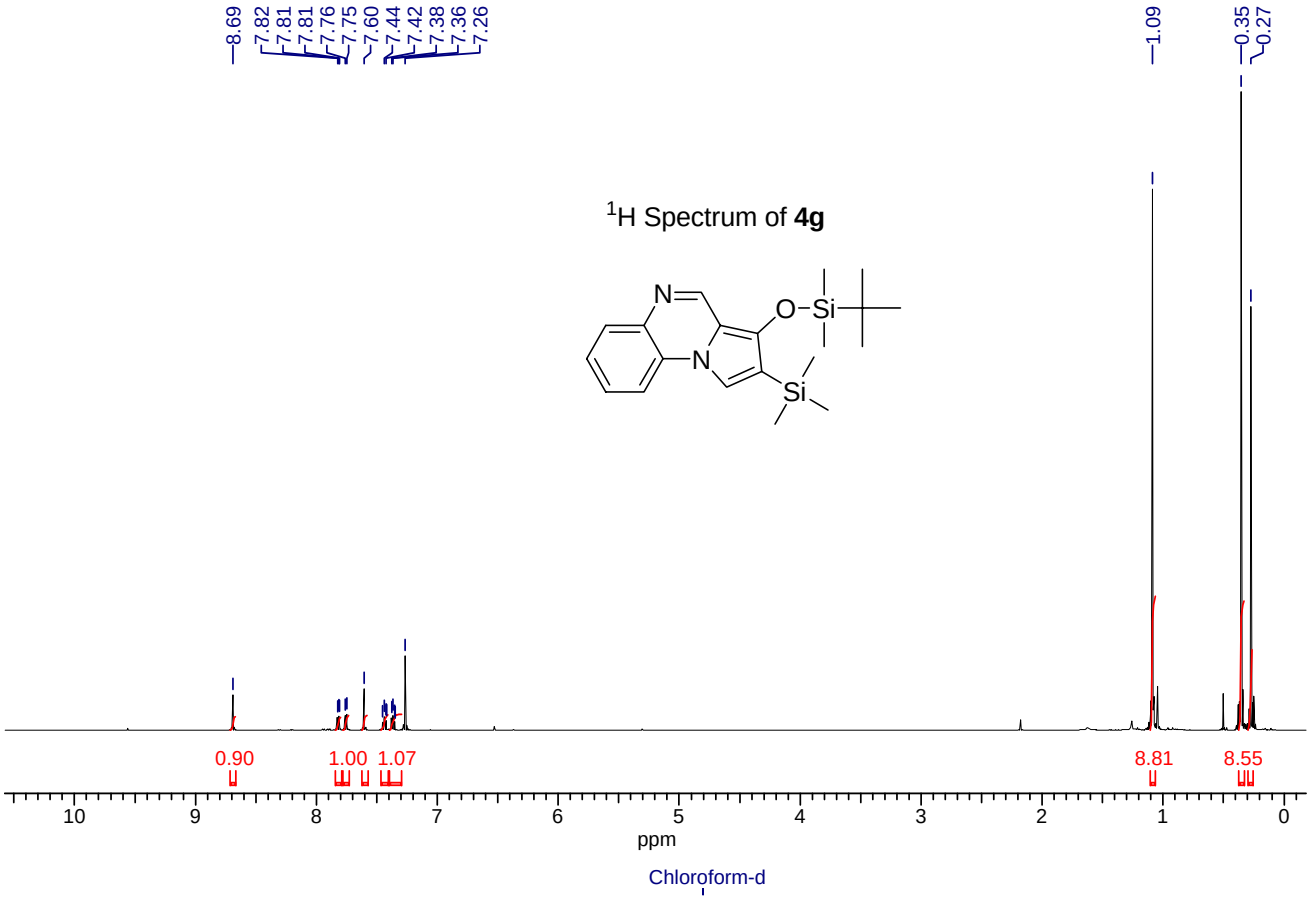

Chloroform-d
136.85
127.54
127.14
126.64
126.30
124.85
124.48
122.47
115.92
110.60
110.53
103.96
77.51
77.25
77.00
29.96
26.24
18.53
-3.97
13C Spectrum of 4e
O
Si
N
150
100
50
0
ppm



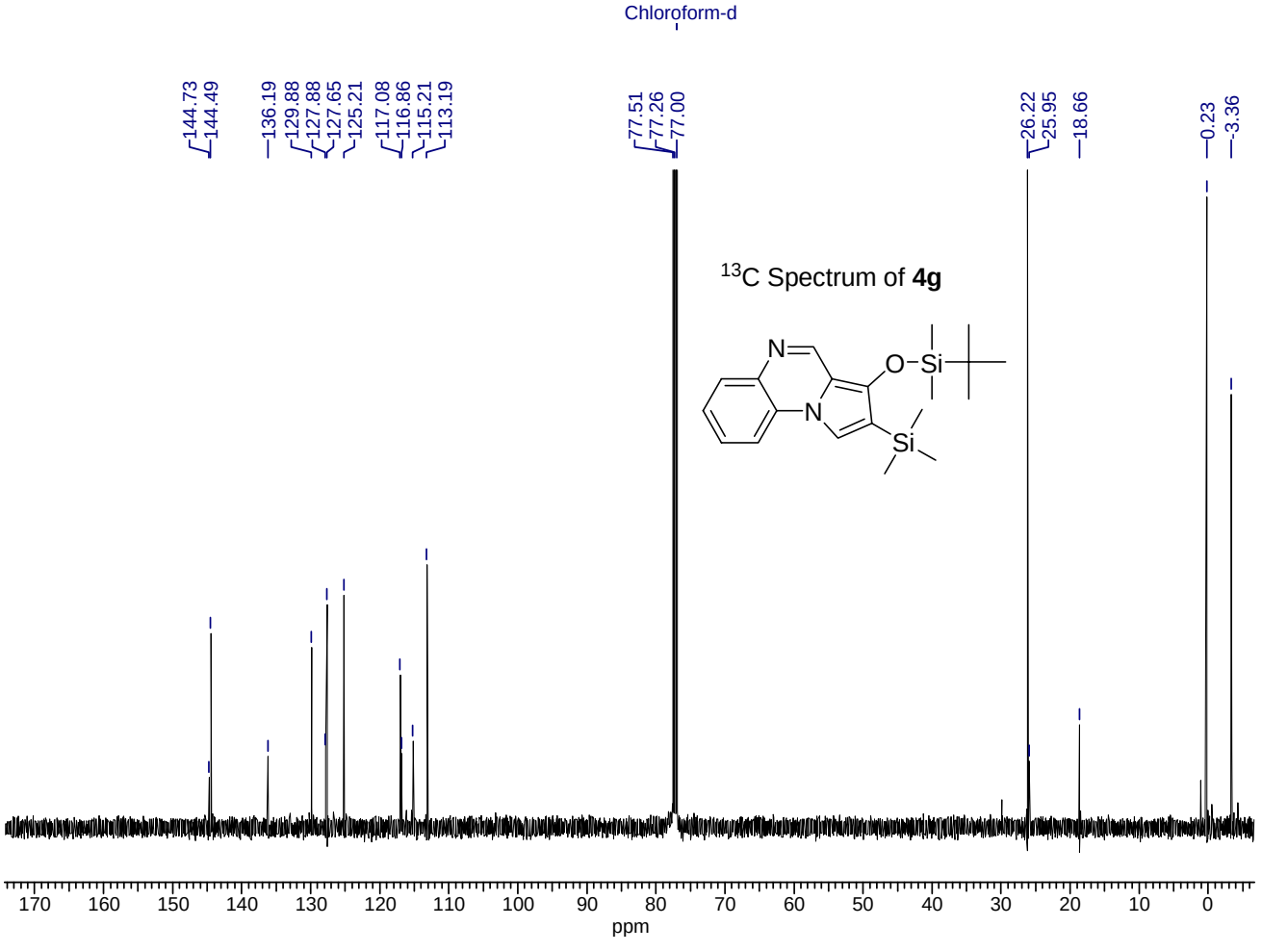
^{1}H Spectrum of **4f**



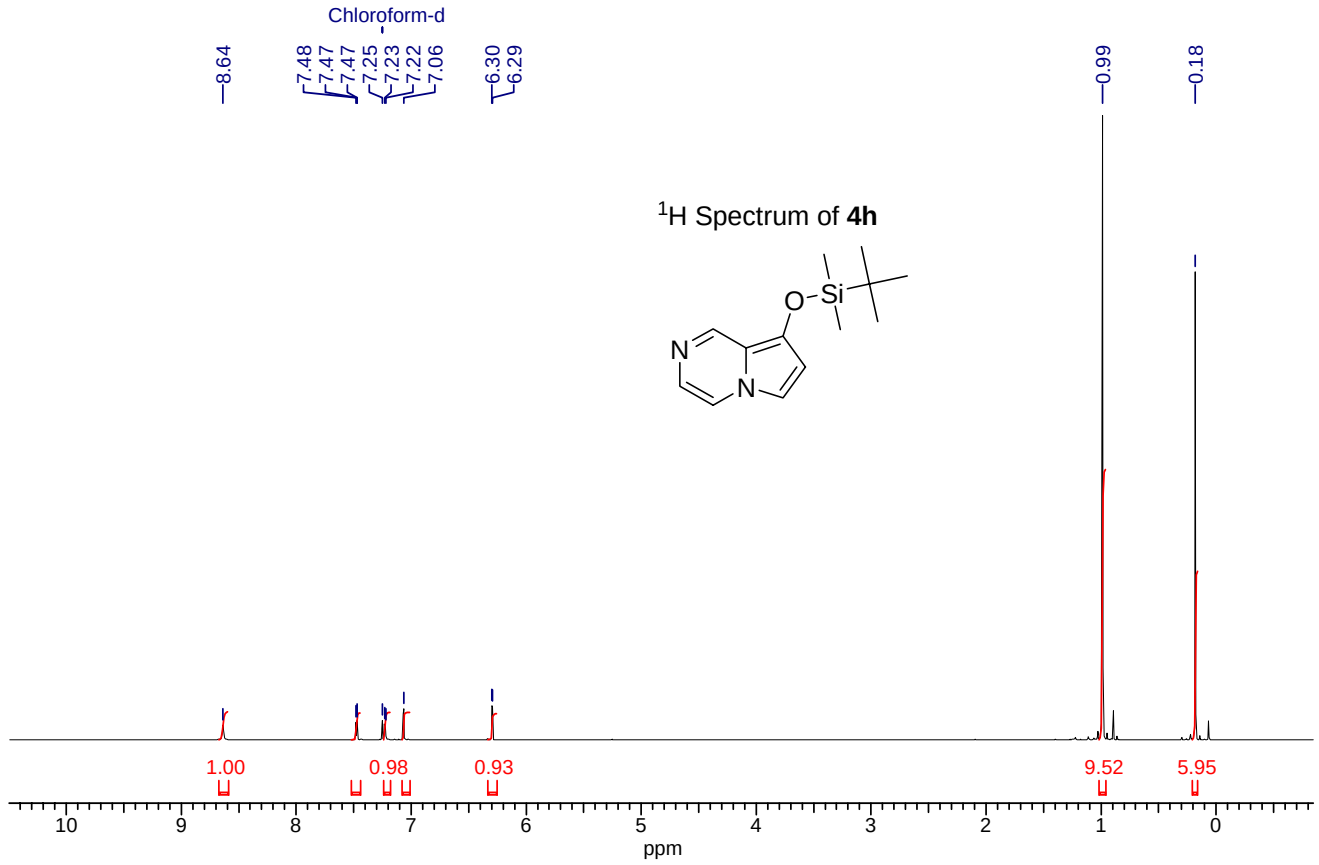
^{13}C Spectrum of **4f**

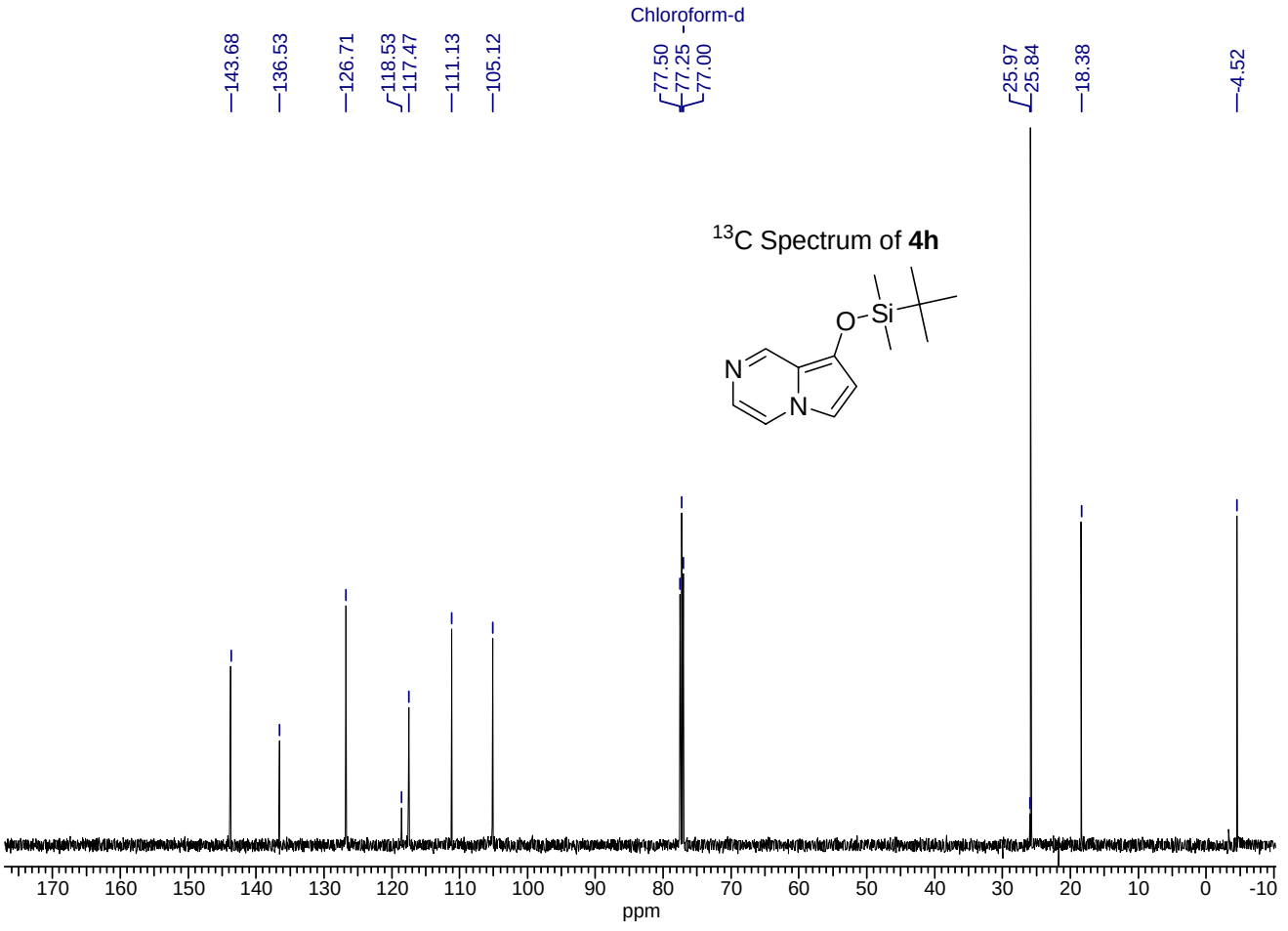


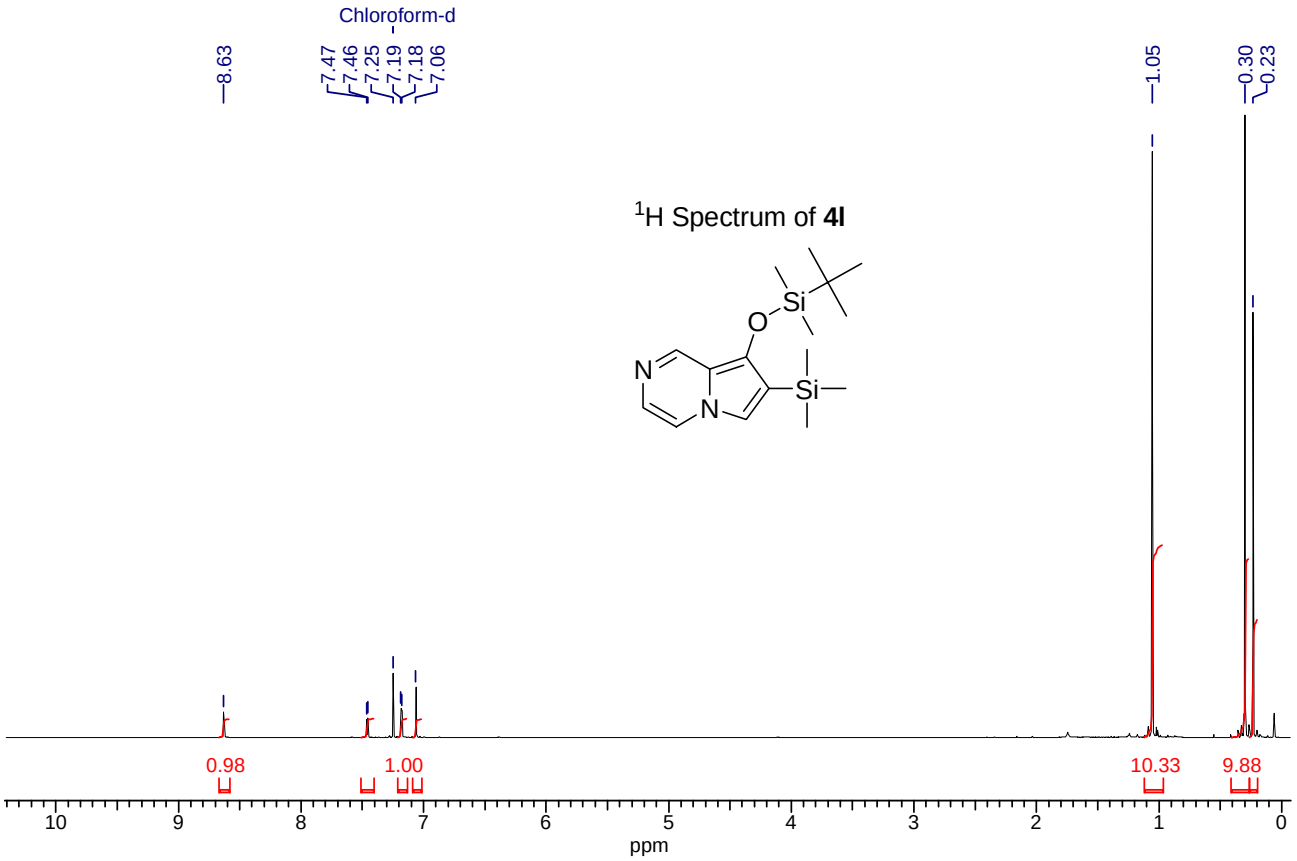
^{1}H Spectrum of **4g**

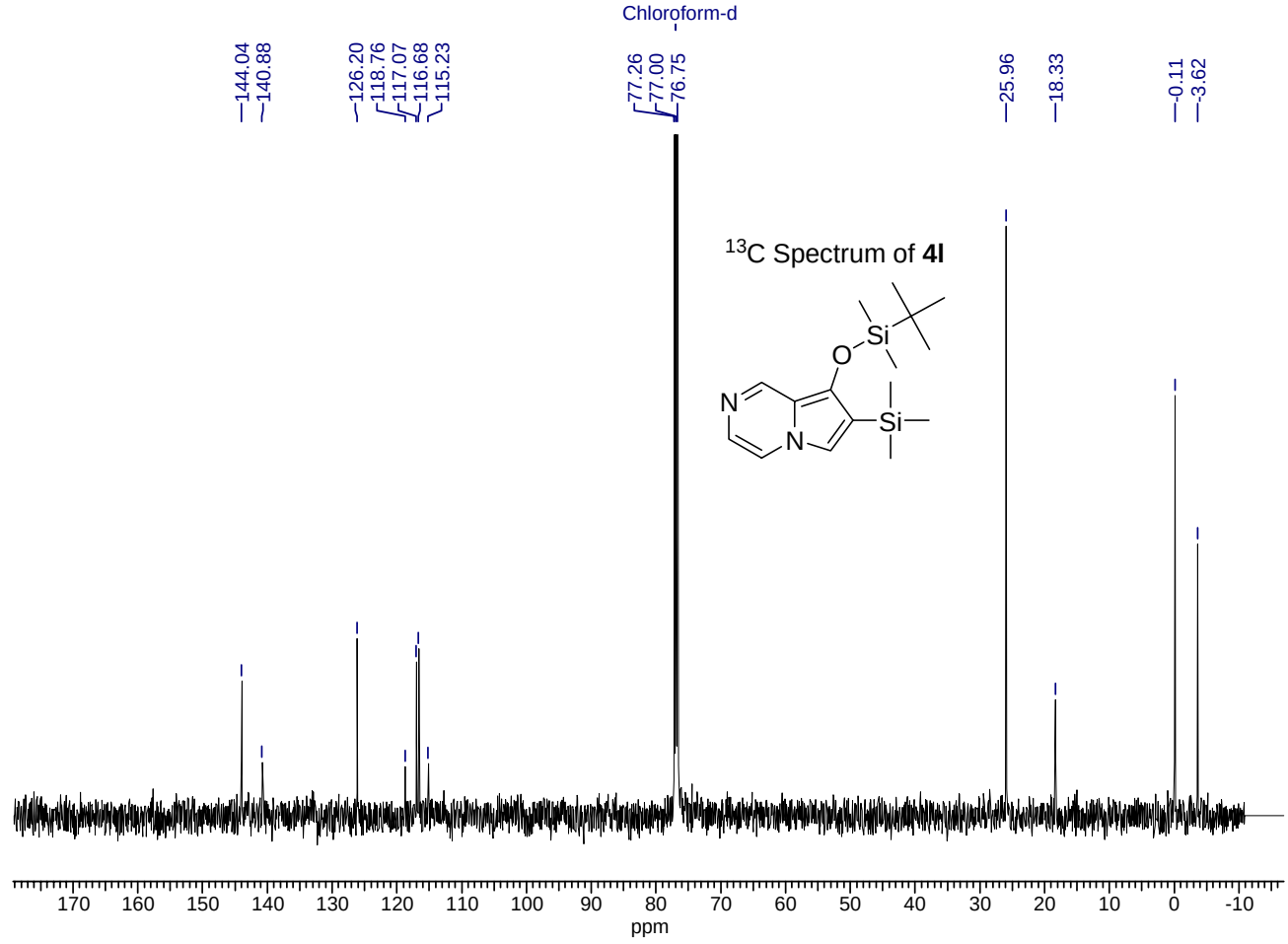


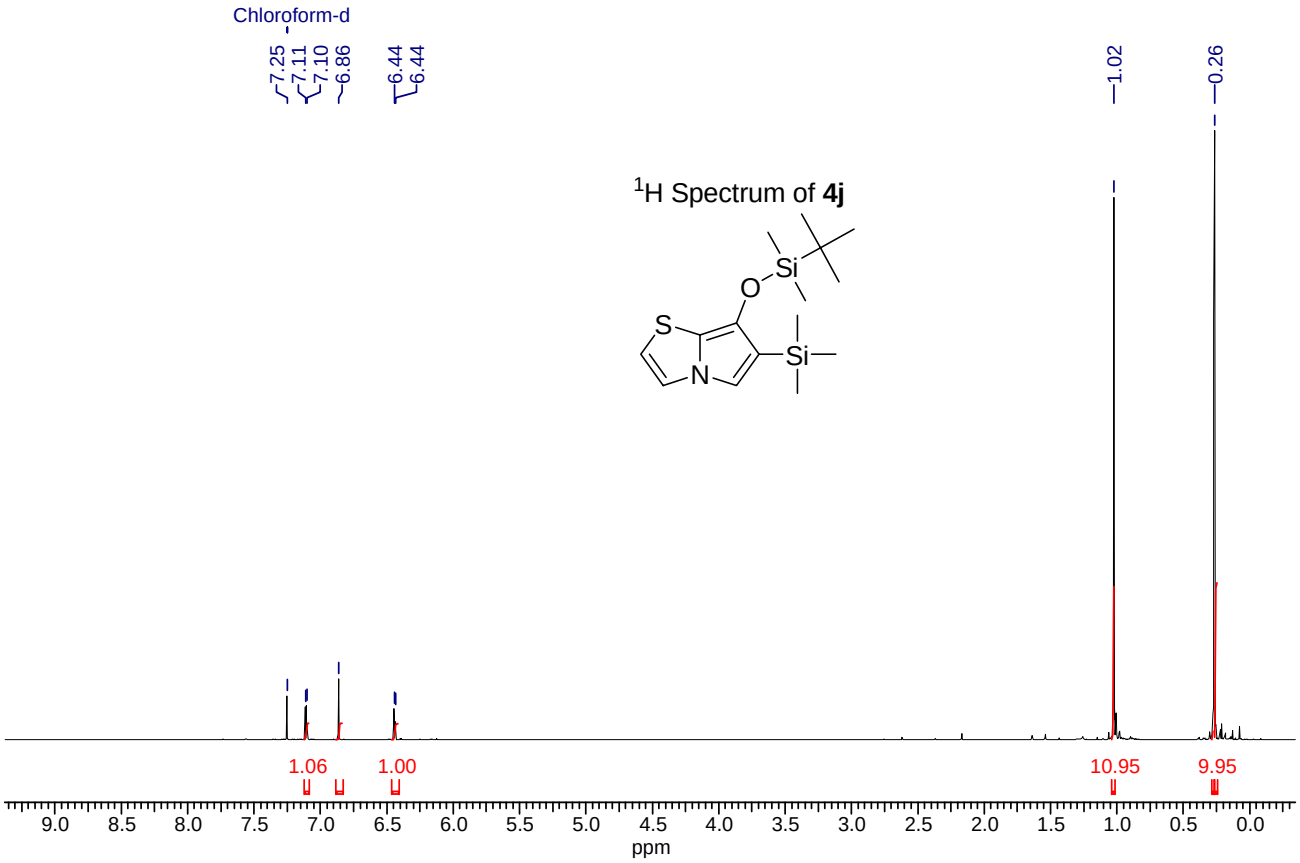
^{13}C Spectrum of **4g**

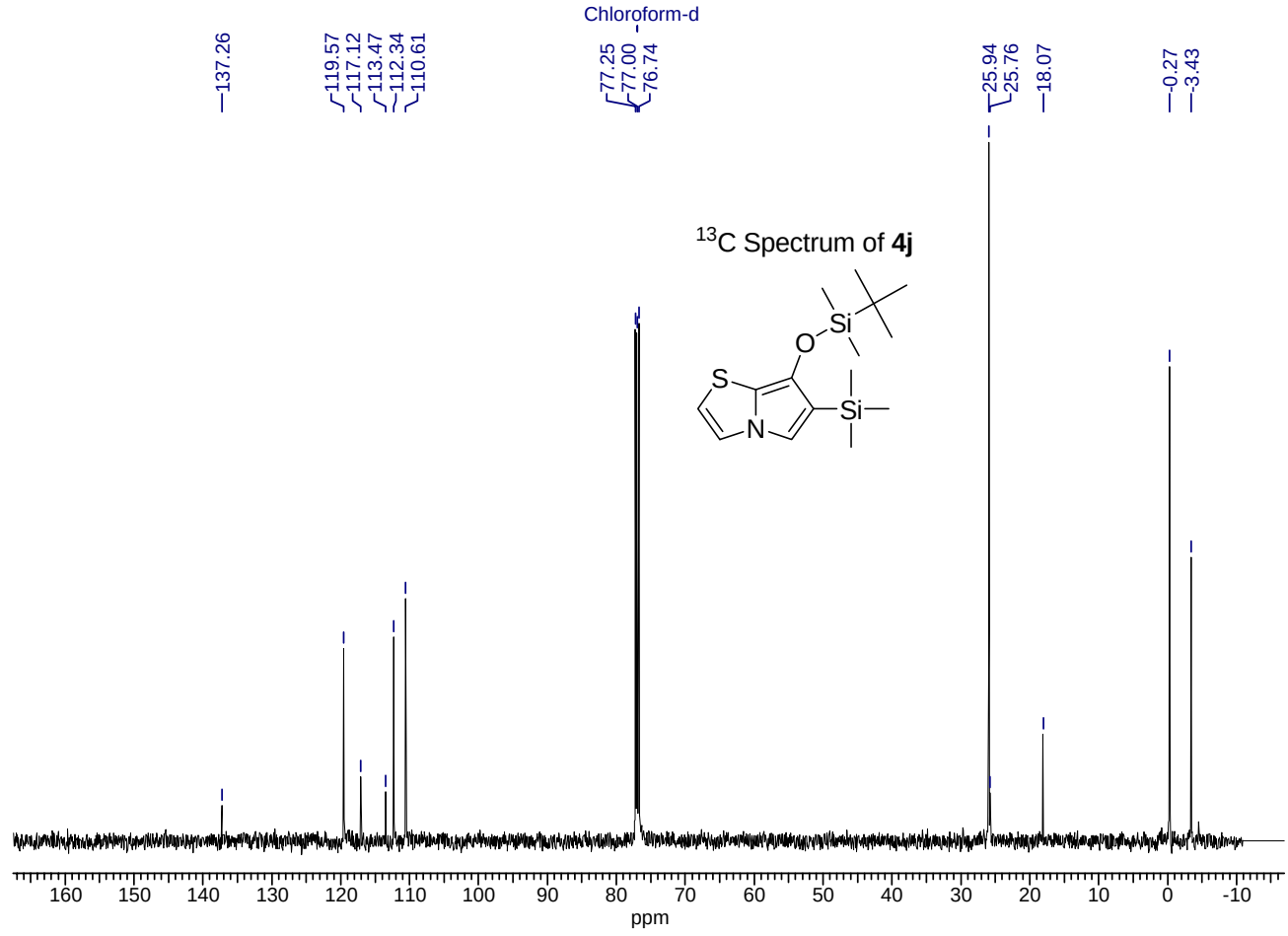

Chloroform-d
8.64
7.48
7.47
7.47
7.25
7.23
7.22
7.06
6.30
6.29
0.99
0.18
1H Spectrum of 4h
O
Si
N
N
1.00
0.98
0.93
9.52
5.95
10
9
8
7
6
5
4
3
2
1
0
ppm

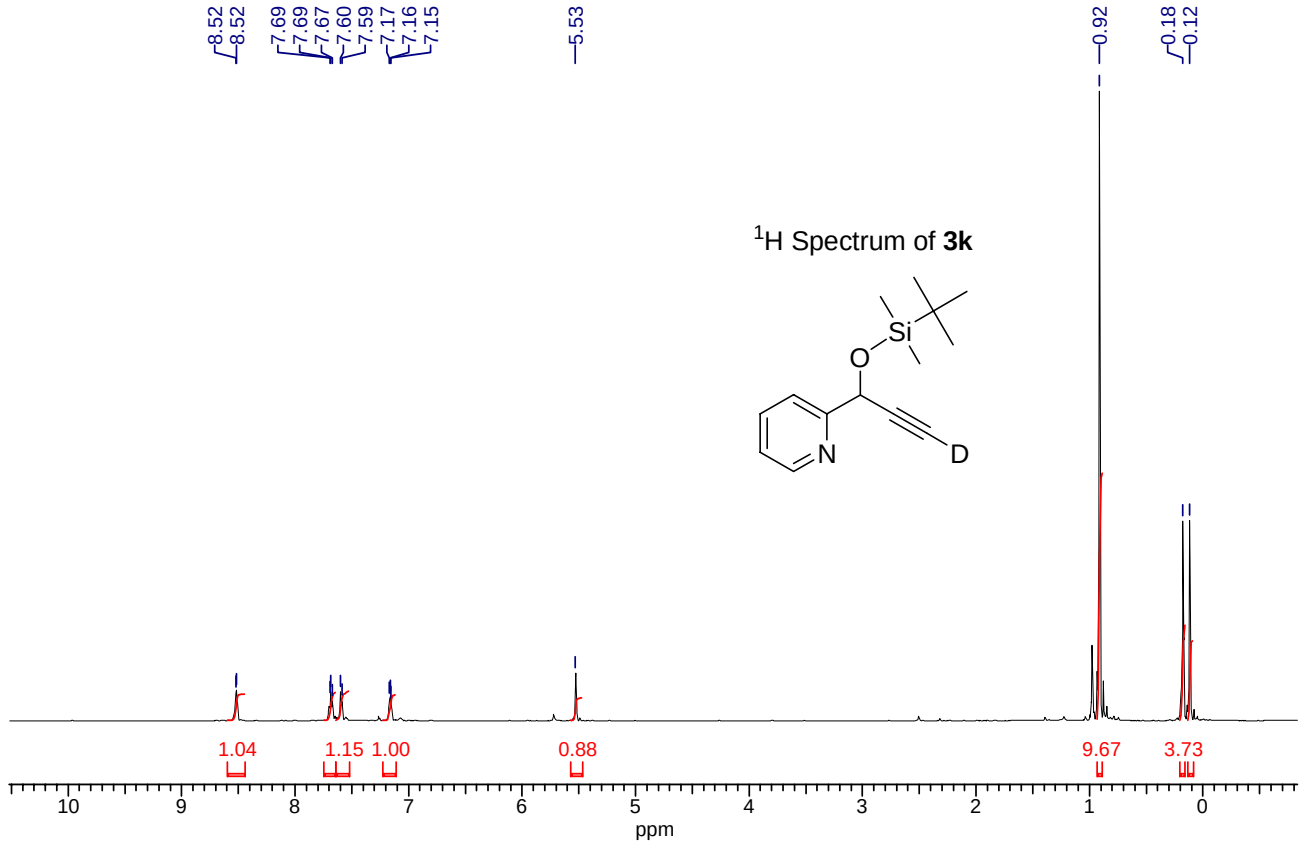

Chloroform-d
143.68
136.53
126.71
118.53
117.47
111.13
105.12
77.50
77.25
77.00
25.97
25.84
18.38
-4.52
13C Spectrum of 4h
O
Si
N
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

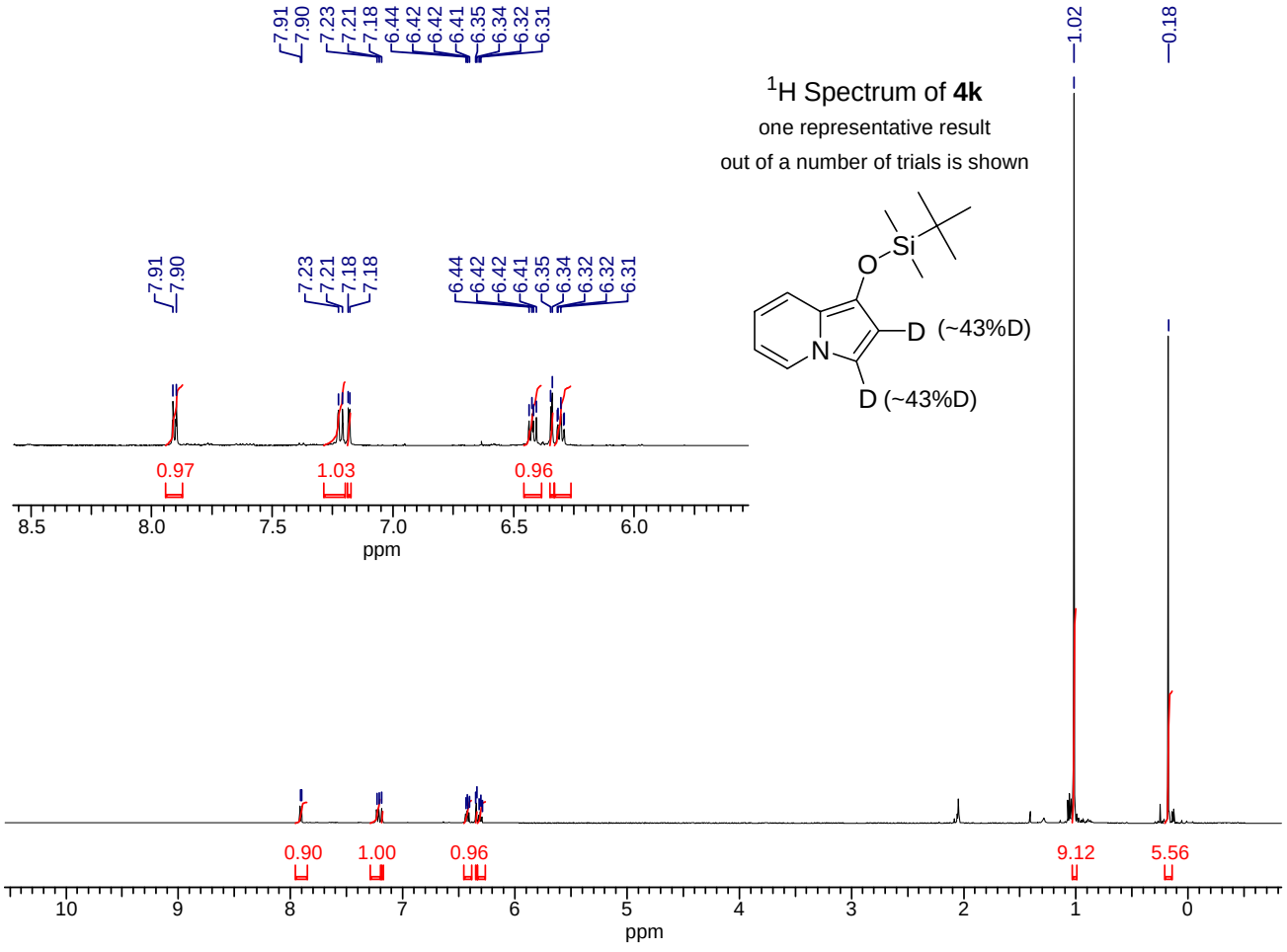

Chloroform-d
8.63
7.47
7.46
7.25
7.19
7.18
7.06
1.05
0.30
0.23
^{1}H Spectrum of **4l**
Si
O
N
N
Si
0.98
1.00
10.33
9.88
10
9
8
7
6
5
4
3
2
1
0
ppm

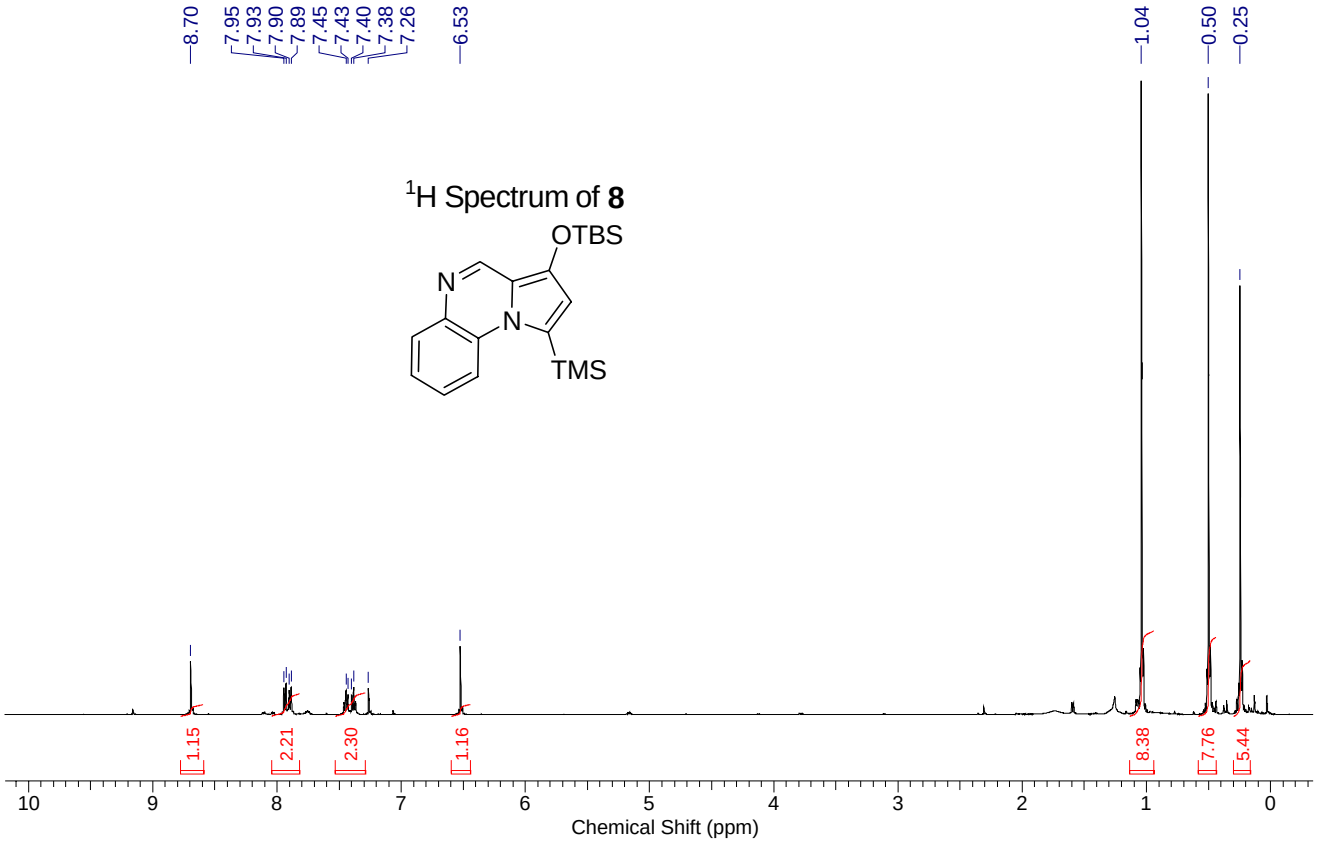

Chloroform-d
144.04
140.88
126.20
118.76
117.07
116.68
115.23
77.26
77.00
76.75
25.96
18.33
-0.11
-3.62
^{13}C Spectrum of **4l**
Si
O
N
N
Si
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

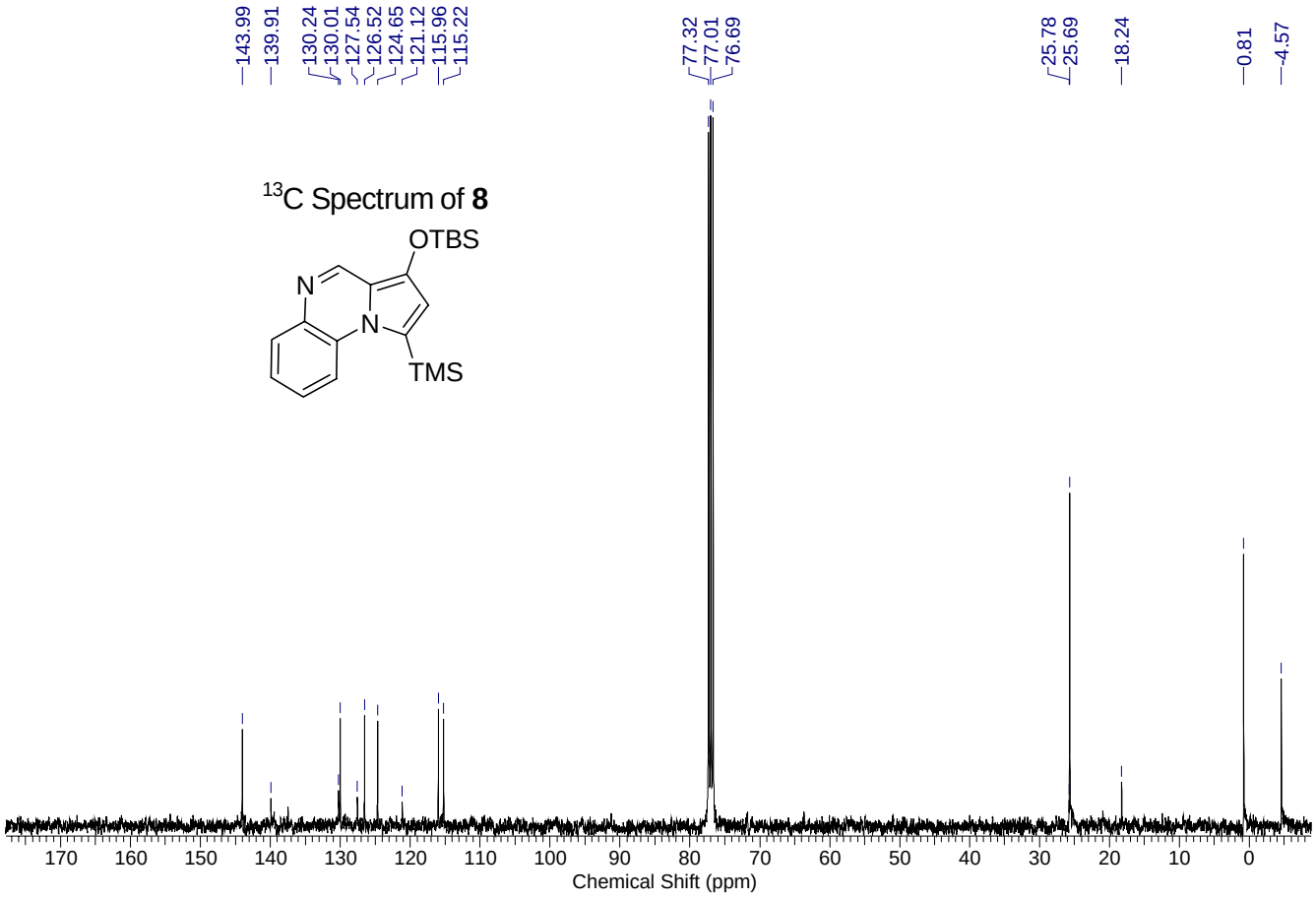

Chloroform-d
7.25
7.11
7.10
6.86
6.44
6.44
1.02
0.26
^{1}H Spectrum of **4j**
Si
O
S
N
Si
1.06
1.00
10.95
9.95
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


137.26
119.57
117.12
113.47
112.34
110.61
Chloroform-d
77.25
77.00
76.74
25.94
25.76
18.07
-0.27
-3.43
^{13}C Spectrum of **4j**
Si
O
S
N
Si
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm


8.52
8.52
7.69
7.69
7.67
7.60
7.59
7.17
7.16
7.15
5.53
0.92
0.18
0.12
1H Spectrum of 3k
Si
O
N
D
1.04
1.15
1.00
0.88
9.67
3.73
10
9
8
7
6
5
4
3
2
1
0
ppm


7.91
7.90
7.23
7.21
7.18
6.44
6.42
6.42
6.41
6.35
6.34
6.32
6.31
1.02
0.18
1H Spectrum of 4k
one representative result
out of a number of trials is shown
Si
O
N
D (~43%D)
D (~43%D)
0.97
1.03
0.96
8.5
8.0
7.5
7.0
6.5
6.0
ppm
0.90
1.00
0.96
9.12
5.56
10
9
8
7
6
5
4
3
2
1
0
ppm


8.70
7.95
7.93
7.90
7.89
7.45
7.43
7.40
7.38
7.26
6.53
1.04
0.50
0.25
1H Spectrum of 8
OTBS
N
N
TMS
1.15
2.21
2.30
1.16
8.38
7.76
5.44
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


143.99
139.91
130.24
130.01
127.54
126.52
124.65
121.12
115.96
115.22
77.32
77.01
76.69
25.78
25.69
18.24
0.81
-4.57
13C Spectrum of 8
OTBS
N
N
TMS
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)