Supporting Information

Borenium-Catalyzed Reduction of Pyridines Through the Combined Action of Hydrogen and Hydrosilane

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1. General remarks

Synthesis and techniques

All preparative scale reactions were conducted in oven dried (160°C) glassware with magnetic stirring using Schlenk-line techniques or in a glove box under an atmosphere of dry dinitrogen if not mentioned otherwise. Experiments on NMR tube scale were carried out in Teflon cap sealed NMR tubes (ø 5mm). Solvents were purified by passage over an activated aluminum oxide column, followed by distillation from Na-benzophenone ketal where necessary (toluene, benzene, THF, hexanes, pentane) and degassed prior to use. Dichloromethane, CD_2Cl_2, and α,α,α-trifluorotoluene were distilled from CaH_2 (followed by 3 freeze-pump-thaw cycles and stored over a mixture of 4Å molecular sieves). Toluene-d_8 and benzene-d_6 were degassed by 3 freeze-pump-thaw cycles and stored over activated 4Å molecular sieves. DMF was of DrySolv-quality and used as received. Solvents for chromatography and other syntheses were used as received from commercial sources and were at least of ACS reagent grade. Solvents for routine NMR spectroscopy experiments were used as received. Silica gel 60 (particle size 0.040 -0.063mm, 230 -400 mesh) was purchased from Silicycle. TLCs were carried out on silica gel coated aluminum plates with UV indicator (F254) obtained by EMD Chemicals, Inc. and analyzed by UV/VIS and stained using a cerium ammonium molybdate solution.

Reagents and materials

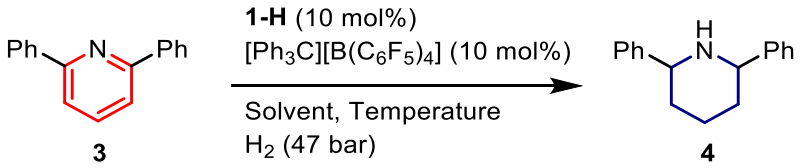
Reagents for piperidine synthesis were used as received without further purification unless noted otherwise. 9-Borabicyclo[3.3.1]nonane dimer, and sodium bis(trimethylsilyl)amide (NaHMDS) were purchased from Aldrich, stored in a glove box, and used as received. 2-Bromopyridine, 2,6-lutidine, and 2-phenylpyridine were purchased from Aldrich, distilled from CaH_2 (followed by 3 freeze-pump-thaw cycles and stored over a mixture of 4Å molecular sieves) and stored in a glove box. $Ph_3C^+B(C_6F_5)_4^-$, was purchased from Strem stored in a glove box, and used as received. 2-Bromo-6-methylpyridine was purchased from Oakwood Chemicals and used as received. Aryl boronic acids were purchased from Aldrich, Frontier Scientific or Acros Chemicals and used as received. Pyridine **7h** was synthesized using a published procedure.[1] All silanes in this study were purchased from Aldrich, distilled from CaH_2 (followed by 3 freeze-pump-thaw cycles and stored over a mixture of 4Å molecular sieves) and stored in a glove box before use. Palladium (II) acetate, benzoic acid and *cis*-2,6-dimethylpiperidine were purchased from Aldrich and used as received. Potassium tribasic phosphate was purchased from Fischer Scientific and used as received. Diphenyliodonium tetrafluoroborate [2] and **1-H** [3] were synthesized via known procedures.

Characterization

NMR spectra were recorded on Bruker Avance 300 (^{1}H: 300.13 ^{13}C: 75.47; TXI probe), Bruker Avance 400 (^{1}H: 400.13, ^{11}B: 128.38, ^{13}C: 100.62, ^{19}F: 376.50, ^{31}P: 161.98; BBI, BBFO and QNP probes), Bruker Avance 500 (^{1}H: 500.19, ^{2}H: 426.80, ^{11}B: 160.27, ^{13}C: 125.62; BBFO probe), Bruker NEO 500 (^{1}H: 500.19, ^{2}H: 426.80, ^{11}B: 160.27, ^{13}C: 125.62; BBFO probe), Bruker Avance 600 (^{1}H: 600.17, ^{11}B: 192.56, ^{13}C: 150.93; ^{31}P: 242.94,TBI probe) or Bruker NEO 700 (^{1}H: 700.13, ^{11}B: 224.63, ^{13}C: 176.05, ^{31}P: 283.42; BBFO probe) instruments operating at the denoted spectrometer frequency given in mega Hertz (MHz) for the specified nucleus. The samples were measured as solutions in the stated solvent at ambient temperature in non-spinning mode if not mentioned otherwise. To specify the signal multiplicity, the following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, qu = quintet, sept = septet, oct = octet, and m = multiplet; br. indicates a broad resonance. Shifts δ are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as an external standard for ^{1}H and ^{13}C NMR spectra and calibrated against the solvent residual peak or in case of proteo-solvents against known solvent resonances. ^{11}B signals are calibrated against external $BF_3{\cdot}OEt_2$ and ^{19}F against $CFCl_3$. Coupling constants J are given in Hertz (Hz). GC-MS measurements were performed on an Agilent Technologies GC 6850N/ MS 5975N VL MSD equipped with an Agilent Technologies HP-5MS column (length: 30m, 0.25 mm inner diameter, 0.25 μm coating thickness) coupled to a quadrupole mass filter. Helium was used as the carrier gas with a constant flow of 1.2mL/min. Separation of the injected species was achieved using the denoted temperature program and retention times t_R are given in minutes (min). High resolution mass-spectra (HRMS) were measured by the Queen's Mass Spectrometry and Proteomics Unit (MSPU) at Queen's University, Kingston, Ontario, Canada. Mass spectra were measured on Applied Biosystems/MDS Sciex QStar XL QqTOF or Waters ZQ Single Quad. Fragment signals are given in mass per charge number (m/z).

2. Optimization of Reaction Conditions

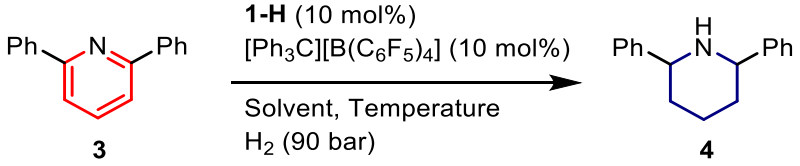
Table S1. Solvent optimization of 1^+-catalyzed hydrogenation of 2,6-diphenylpyridine



Entry	Solvent	Temperature (°C)	Yield[a] (Conversion)
1	Dioxane	110	No reaction
2	1,2-dichloroethane	90	20 (21)
3	$C_6H_5CF_3$	110	No reaction
4	Toluene	120	31 (38)

All reactions were carried out on 0.125 mmol scale of **3**. [a]Based on crude ^{1}H NMR analysis compared to 1,3,5-trimethoxybenzene as internal standard.

Table S2. Temperature optimization of 1^+-catalyzed hydrogenation of 2,6-diphenylpyridine

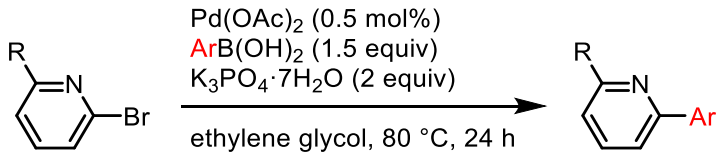


Entry	Solvent	Temperature (°C)	Yield[b] (Conversion)
1	Toluene	60	36 (33)
2	Toluene	90	40 (49)
3	Toluene	120	40 (41)
4	DCE	60	48 (43)
5	DCE	90	40 (41)
6[a]	DCE	60	48 (63)

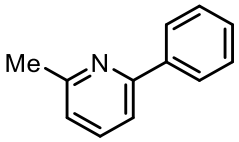
All reactions were carried out on 0.125 mmol scale of **3** [a]20 mol% of **1-H** and $[Ph_3C][B(C_6F_5)_4]$ [b]Based on crude ^{1}H NMR analysis compared to 1,3,5-trimethoxybenzene as internal standard.

3. Substrate Spectroscopic Data

7a-7f, **7i**, and **9b-9d** were synthesized using reported methods [*Eur. J. Org. Chem.* **2010**, *29*, 5548].



2-Methyl-6-phenylpyridine (7a)

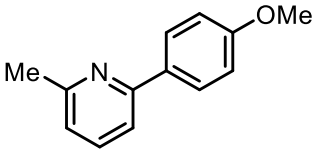


Spectra match literature: Paterson, A. J., Heron, C. J., McMullen, C. L., Mahon, M. F., Press, N. J., and Frost, C. G., *Org. Biomol. Chem*. **2017**, *15*, 5993-6000

Physical description: white solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, 2H, *J* = 8.4 Hz), 7.63 (t, 1H, *J* = 8.0 Hz), 7.54-7.35 (m, 4H), 7.09 (d, 1H), 2.63 (s, 3H)

2-(4-Methoxyphenyl)-6-methyl-pyridine (7b)

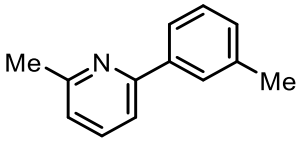


Spectra match literature: Deng, D., Hu, B., Yang, M., and Chen, D., *Organometallics* **2018**, *37*, 2386-2394

Physical description: white solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.97 (2H, m), 7.59 (1H, t, *J* = 7.8 Hz), 7.45 (1H, d, *J* = 7.8 Hz), 7.03 (1H, d, *J* = 7.5 Hz), 6.97-7.01 (2H, m), 3.86 (3H, s), 2.61 (3H, s).

2-Methyl-6-(*m*-tolyl)pyridine (7c)



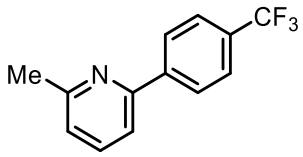
Spectra match literature: Yao, X.; Qi, L.; Li, R.; Zhen, Q.; Liu, J.; Zhao, Z.; Shao, Y.; Hu, M.; Chen, J., *ACS Comb. Sci.* **2020,** *22*, 114-119.

Physical description: white solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (1H, s), 7.78 (1H, d, *J* = 7.8 Hz), 7.61 (1H, t, *J* = 7.7 Hz), 7.51 (1H, d, *J* = 7.8 Hz), 7.37 (1H, t, *J* = 7.6 Hz), 7.23 (1H, d, *J* = 7.6 Hz), 7.08 (1H, d, *J* = 7.6 Hz), 2.65 (3H, s), 2.46 (3H, s).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.3, 157.2, 139.8, 138.3, 136.8, 129.5, 128.6, 127.8, 124.2, 121.5, 117.7, 24.8, 21.6.

2-Methyl-6-(4-(trifluoromethyl)phenyl)pyridine (7d)



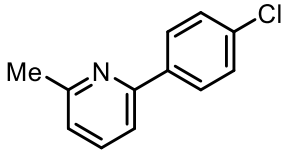
Spectra match literature: Ackermann, L., Potukuchi, H. K., and Kapdi, A. R., Schulze, C., *Chem. Eur. J.* **2010**, *16*, 3300-3303

Physical description: white solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (2H, d, *J* = 8.1 Hz), 7.71 (2H, d, *J* = 8.2 Hz), 7.68 (1H, t, *J* = 7.7 Hz), 7.55 (1H, d, *J* = 7.8 Hz), 7.16 (1H, d, *J* = 7.6 Hz), 2.64 (3H, s).

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.0

2-(4-Chlorophenyl)-6-methylpyridine (7e)

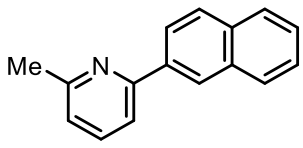


Spectra match literature: Ackermann, L., Potukuchi, H. K., Kapdi, A. R., and Schulze, C., *Chem. Eur. J.* **2010**, *16*, 3300-3303

Physical description: white solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (2H, d, *J* = 8.5 Hz), 7.63 (1H, t, *J* = 7.7 Hz), 7.48 (1H, d, *J* = 7.8 Hz), 7.43 (2H, d, *J* = 8.6 Hz), 7.10 (1H, d, *J* = 7.6 Hz), 2.62 (3H, s)

2-Methyl-6-(naphthalen-2-yl)pyridine (7f)

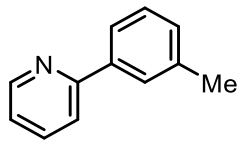


Spectra match literature: Addla, D. and Kantevari, S., *Journal of Heterocyclic Chemistry*, **2014**, *51*, E384-E388

Physical description: white solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (1H, s), 8.14 (1H, dd, *J* = 8.6 Hz, *J* = 1.8 Hz), 7.91-7.97 (2H, m), 7.84-7.89 (1H, m), 7.65-7.71 (2H, m), 7.47-7.53 (2H, m), 7.11-7.15 (1H, m), 2.68 (3H, s)

2-(*m*-Tolyl)pyridine (9b)

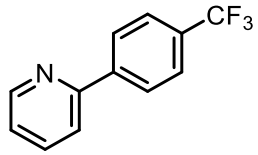


Spectra match literature: Rao, X., Liu, C., Qiu, J., and Jin, Z., *Org. Biomol. Chem.*, **2012**, *10*, 7875-7883

Physical description: white solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (1H, d, *J* = 4.8 Hz), 7.84 (1H, s), 7.71-7.76 (3H, m), 7.36 (1H, t, *J* = 7.6 Hz), 7.21-7.26 (2H, m), 2.44 (3H, s)

2-(4-(Trifluoromethyl)phenyl)pyridine (9c)

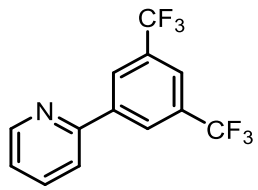


Spectra match literature: Zhang, E., Tang, J., Li, S., Wu, P., Moses, J. E., and Sharpless, K. B., *Chem. Eur. J.* **2016**, *22*, 5692-5697

Physical description: white solid

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.73 (1H, d, *J* = 3.5 Hz), 8.12 (2H, d, *J* = 8.2 Hz), 7.66-7.86 (4H, m), 7.27-7.33 (1H, m).

2-(3,5-Bis(trifluoromethyl)phenyl)pyridine (9d)



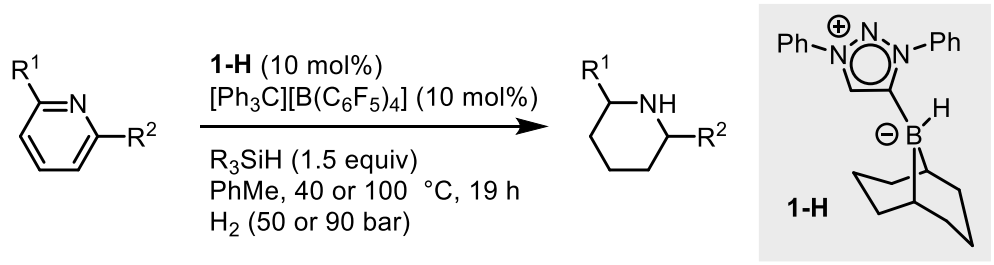
Spectra match literature: Xu, M., Zhou, R., Yang, G., Xiao, Q., and Du, W., *Inorganica Chimica Acta* **2008**, *361*, 2407-2412

Physical description: white solid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (1H, d, *J* = 4.7 Hz), 8.49 (2H, s), 7.92 (1H, s), 7.81-7.87 (2H, m), 7.36 (1H, ddd, *J* = 6.7, 4.9, 1.7 Hz) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.8 ppm.

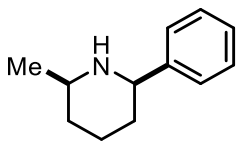
4. Reduction of Pyridines



General procedure for the synthesis of pyridine substrates:

In a glovebox, a 0.5 dram vial was charged with $[Ph_3C][B(C_6F_5)_4$ (0.1 eq.) and **1-H** (0.1 eq.) then toluene (0.5 M) was added. The mixture was swirled until the colour changed from red to pale yellow. A second 0.5 dram vial was charged with the pyridine (1.0 eq.) substrate and a magnetic stir bar. The liquid solution in the first vial was directly transferred to the second vial and swirled until dissolved. The hydrosilane (1.5 eq.) was added via an Eppendorf pipette to the vial. The reaction mixture was placed in a 50 mL stainless steel Parr pressure vessel and sealed with the gas regulator outside the glovebox. The pressure vessel was pressurized and depressurized five times with hydrogen gas (28 bar) then brought up to the required pressure before heating (45 bar for 40 °C, 76 bar for 100 °C). The vessel was then submerged in an oil bath of the proper temperature and heated for 19 h. Afterwards, the vessel was slowly depressurized. Internal standard (ferrocene) was added to the reaction mixture to enable analysis of the crude by NMR spectroscopy. Then the crude reaction mixture was added to 10 mL of distilled H_2O and the aqueous layer was extracted three times with ethyl acetate. The organic fractions were dried over Na_2SO_4, filtered and evaporated. After drying, the resulting oil was subjected to silica gel column chromatography to give the desired product as either an oil or solid.

2-Methyl-6-phenylpiperidine (8a)



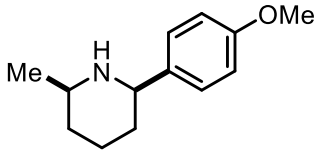
Prepared from pyridine **7a** (21.2 mg, 0.125 mmol), phenylsilane (23.1 mL, 0.19 mmol), $[Ph_3C][B(C_6F_5)_4]$ (11.5 mg, 0.013 mmol) and **1-H** (4.4 mg, 0.013 mmol.) in toluene (0.25 mL) according to General Procedure. The crude residue was purified by column chromatography to give **8a** (colourless oil, 19 mg, 87%).

Spectra match literature: Liu, Y., Du, H. *J. Am. Chem. Soc.* **2013**, *135*, 12968-12971.

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.37 (2H, d, *J* = 7.3 Hz), 7.31 (2H, t, *J* = 7.5 Hz), 7.23 (1H, t, *J* = 7.4 Hz), 3.66 (1H, dd, *J* = 11.1, 2.5 Hz), 2.81 (1H, m), 1.88 (1H, dt, *J* = 12.9, 3.1 Hz), 1.76 (1H, m), 1.65 (1H, m), 1.51 (1H, qt, *J* = 13.0, 3.8 Hz), 1.45 (1H, qd, *J* = 12.9, 3.6 Hz), 1.09-1.20 (5H, m) ppm.

^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$) δ 145.7, 128.5, 127.1, 126.9, 62.6, 53.4, 34.4, 34.0, 25.5, 23.2 ppm.

2-(4-Methoxyphenyl)-6-methylpiperidine (8b)



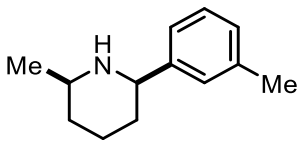
Prepared from pyridine **7b** (49.8 mg, 0.25 mmol), phenylsilane (46.2 mL, 0.38 mmol), $[Ph_3C][B(C_6F_5)_4]$ (23.1 mg, 0.025 mmol) and **1-H** (10.3 mg, 0.03 mmol) in toluene (0.5 mL) according to General Procedure. The crude residue was purified by column chromatography to give **8b** (colourless oil, 26.5 mg, 52%).

Spectra match literature: Liu, Y., Du, H. *J. Am. Chem. Soc.* **2013**, *135*, 12968-12971.

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.29 (2H, d, *J* = 8.5 Hz), 6.85 (2H, d, *J* = 8.7 Hz), 3.79 (3H, s), 3.60 (1H, dd, *J* = 10.9, 2.7 Hz), 2.76-2.83 (1H, m), 1.81-1.90 (1H, m), 1.61-1.75 (3H, m), 1.38-1.6 (2H, m), 1.09-1.18 (4H, m) ppm.

^{13}C NMR (176 MHz, $CDCl_3$) δ 158.7, 138.0, 127.9, 113.8, 62.0, 55.4, 53.4, 34.4, 34.0, 25.5, 23.2 ppm.

2-Methyl-6-(*m*-tolyl)piperidine (8c)



Prepared from pyridine **7c** (22.9 mg, 0.125 mmol), phenylsilane (23.1 mL, 0.19 mmol), $[Ph_3C][B(C_6F_5)_4]$ (11.5 mg, 0.013 mmol) and **1-H** (5.1 mg, 0.015 mmol.) in toluene (0.25 mL) according to General Procedure. The crude residue was purified by column chromatography to give **8c** (colourless oil, 18 mg, 76%).

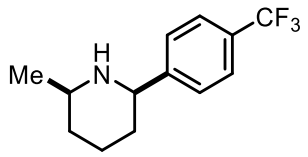
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.22 (1H, s), 7.20 (1H, t, *J* = 7.5 Hz), 7.16 (1H, d, *J* = 7.6 Hz), 7.05 (1H, d, *J* = 7.4 Hz), 3.63 (1H, dd, *J* = 10.9, 2.1 Hz), 2.81 (1H, m), 2.35 (3H, s), 1.88 (1H, m), 1.76 (1H, d, *J* =

12.0 Hz), 1.65 (1H, dd, *J* = 10.8, 1.7 Hz), 1.58 (1H, br. s), 1.43-1.54 (2H, m), 1.16 (1H, qd, *J* = 12.7, 3.7 Hz), 1.12 (3H, d, *J* = 6.2 Hz) ppm.

$^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$) δ 145.6, 138.1, 128.4, 127.8, 127.4, 124.0, 62.7, 53.4, 34.4, 34.0, 25.6, 23.2, 21.6 ppm.

HRMS (EI): calcd. for $C_{13}H_{19}N$ 189.1517, found 189.1508

2-Methyl-6-(4-(trifluoromethyl)phenyl)piperidine (8d)



Prepared from pyridine **7d** (29.6 mg, 0.125 mmol), phenylsilane (23.1 mL, 0.19 mmol), $[Ph_3C][B(C_6F_5)_4]$ (11.5 mg, 0.013 mmol) and **1-H** (5.1 mg, 0.015 mmol.) in toluene (0.25 mL) at 90 °C according to General Procedure. The crude residue was purified by column chromatography to give **8d** (colourless oil, 19.4 mg, 64%).

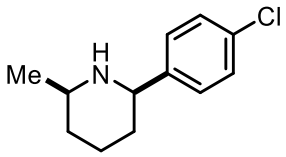
Spectra match literature: Liu, Y., Du, H. *J. Am. Chem. Soc.* **2013**, *135*, 12968-12971.

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.56 (2H, d, *J* = 8.1 Hz), 7.49 (2H, d, *J* = 8.1 Hz), 3.72 (1H, dd, *J* = 11.2, 2.7 Hz), 2.79-2.84 (1H, m), 1.86-1.90 (1H, m), 1.75 (1H, dd, *J* = 12.3, 2.6 Hz), 1.66 (1H, dd, *J* = 15.4, 2.5 Hz), 1.59 (1H, br. s), 1.51 (1H, qt, *J* = 13.1, 3.9 Hz), 1.37-1.43 (1H, m), 1.13-1.18 (1H, m), 1.12 (3H, d, *J* = 6.2 Hz) ppm.

^{13}C NMR (176 MHz, $CDCl_3$) δ 149.8, 129.3 (q, *J* = 32 Hz), 127.2, 125.4 (q, *J* = 4 Hz), 124.4 (q, *J* = 272 Hz), 62.2, 53.2, 34.6, 33.8, 25.4, 23.2 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.8 ppm.

2-(4-Chlorophenyl)-6-methylpiperidine (8e)

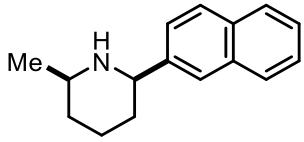


Prepared from pyridine **7e** (50.9 mg, 0.25 mmol), phenylsilane (46.2 mL, 0.38 mmol), $[Ph_3C][B(C_6F_5)_4]$ (23.1 mg, 0.025 mmol) and **1-H** (10.3 mg, 0.03 mmol.) in toluene (0.5 mL) at 90 °C according to General Procedure. The crude residue was purified by column chromatography to give **8e** (colourless oil, 32.5 mg, 62%).

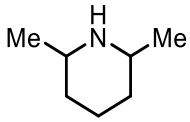
Spectra match literature: Liu, Y., Du, H. *J. Am. Chem. Soc.* **2013**, *135*, 12968-12971.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (2H, d, *J* = 8.6 Hz), 7.26 (2H, d, *J* = 8.6 Hz), 3.63 (1H, dd, *J* = 11.1, 2.7 Hz), 2.75-2.83 (1H, m), 1.83-1.90 (1H, m), 1.72 (1H, dd, *J* = 12.1, 2.0 Hz), 1.64 (1H, dd, *J* = 12.5, 2.2 Hz), 1.32-1.56 (3H, m), 1.08-1.22 (4H, m) ppm.
^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) δ 144.3, 132.6, 128.6, 128.2, 61.9, 53.2, 34.6, 33.9, 25.4, 23.2 ppm.

2-Methyl-6-(naphthalen-2-yl)piperidine (8f)

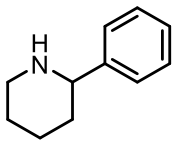


Prepared from pyridine **7f** (27.4 mg, 0.125 mmol), phenylsilane (23.1 mL, 0.19 mmol), $[Ph_3C][B(C_6F_5)_4]$ (11.5 mg, 0.013 mmol) and **1-H** (5.1 mg, 0.015 mmol.) in toluene (0.25 mL) at 90 °C according to General Procedure. The crude residue was purified by column chromatography to give **8f** (colourless oil, 22.3 mg, 79%).
Spectra match literature: Liu, Y., Du, H. *J. Am. Chem. Soc.* **2013**, *135*, 12968-12971.
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.79-7.85 (4H, m), 7.52 (1H, d, *J* = 8.5 Hz), 7.42-7.47 (2H, m), 3.83 (1H, dd, *J* = 10.8, 2.7 Hz), 2.85-2.90 (1H, m),1.91-1.95 (1H, m), 1.86 (1H, d, *J* = 11.6), 1.74 (1H, br. s), 1.70 (1H, dd, *J* = 12.1, 2.4 Hz), 1.50-1.61 (2H, m), 1.19-1.27 (1H, m), 1.17 (3H, dd, *J* = 6.3, 1.3 Hz) ppm.
^{13}C NMR (176 MHz, $CDCl_3$) δ 143.2, 133.7, 132.9, 128.0, 128.0, 127.7, 126.0, 125.7, 125.6, 124.9, 62.7, 53.4, 34.5, 34.0, 25.6, 23.2 ppm.



Prepared from pyridine **7g** (28.3 mg, 0.25 mmol), phenylsilane (46.2 mL, 0.38 mmol), $[Ph_3C][B(C_6F_5)_4]$ (23.1 mg, 0.025 mmol) and **1-H** (10.3 mg, 0.03 mmol.) in toluene (2 mL) at 40 °C according to General Procedure. 1,3,5-Trimethoxy benzene (9.2 mg, 0.055 mmol) was added to the resulting reaction mixture as an internal standard, and the crude residue was analyzed by ^{1}H NMR, which shows 47% of **8g** was obtained with 50% of unreacted **7g**.

2-Phenylpiperidine (10a)



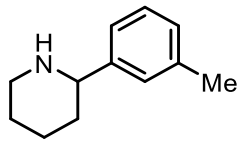
Prepared from pyridine **9a** (0.14 mL, 1 mmol), phenyldimethylsilane (0.23 mL, 1.5 mmol), $[Ph_3C][B(C_6F_5)_4]$ (92 mg, 0.1 mmol) and **1-H** (35 mg, 0.1 mmol.) in toluene (2 mL) according to General Procedure. The crude residue was purified by preparative thin layer chromatography to give **10a** (colourless oil, 143 mg, 89%).

Spectra match literature: Yamaguchi, R., Kawagoe, S., Asai, C., and Fujita, K., *Org. Lett.* **2008**, *10*, 181-184.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (2H, d, *J* = 7.1 Hz), 7.31 (2H, t, *J* = 7.2 Hz), 7.22 (1H, t, *J* = 7.2 Hz), 3.60 (1H, dd, *J* = 10.0, 2.2 Hz), 3.18 (1H, d, *J* = 11.2 Hz), 2.80 (1H, td, *J* = 11.4, 2.7 Hz), 1.85-1.92 (1H, m), 1.73-1.84 (2H, m), 1.62-1.71 (1H, m), 1.42-1.61 (3H, m) ppm.

^{13}C NMR (176 MHz, $CDCl_3$) δ 145.0, 128.5, 127.3, 126.8, 62.4, 47.7, 34.7, 25.7, 25.4 ppm.

2-(*m*-Tolyl)piperidine (10b)



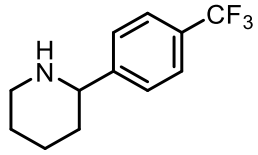
Prepared from pyridine **9b** (42.3 mg, 0.25 mmol), phenyldimethylsilane (57.6 μL, 0.38 mmol), $[Ph_3C][B(C_6F_5)_4]$ (23.1 mg, 0.025 mmol) and **1-H** (10.3 mg, 0.03 mmol.) in toluene (0.5 mL) according to General Procedure. The crude residue was purified by column chromatography to give **10b** (colourless oil, 35.2 mg, 81%).

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.19-7.21 (2H, m), 7.14 (1H, d, *J* = 4.5 Hz), 7.05 (1H, d, *J* = 4.0 Hz), 3.56 (1H, dd, *J* = 6.0, 1.5 Hz), 3.18-3.21 (1H, m), 2.79 (1H, td, *J* = 6.7, 1.5 Hz), 2.34 (3H, s), 1.94 (1H, br. s), 1.87-1.90 (1H, m), 1.78 (1H, m), 1.66 (1H, m), 1.45-1.58 (3H, m) ppm.

^{13}C NMR (176 MHz, $CDCl_3$) δ 145.6, 138.1, 128.4, 127.9, 127.4, 123.8, 62.5, 48.0, 35.1, 26.0, 25.6, 21.5 ppm.

HRMS (EI): calcd. for $C_{12}H_{17}N$ 175.1361, found 175.1369

2-(4-(Trifluoromethyl)phenyl)piperidine (10c)



Prepared from pyridine **9c** (55.8 mg, 0.25 mmol), phenyldimethylsilane (57.6 μL, 0.38 mmol), $[Ph_3C][B(C_6F_5)_4]$ (23.1 mg, 0.025 mmol) and **1-H** (10.3 mg, 0.03 mmol.) in toluene (0.5 mL) according to

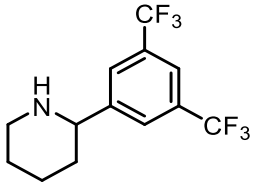
General Procedure. The crude residue was purified by column chromatography to give **10c** (colourless oil, 31.5 mg, 57%).

Spectra match literature: Martins, J. E. D., Redondo, M. A. C., and Wills, M., *Tetrahedron: Asymmetry* **2010**, *21*, 2258.

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.56 (2H, d, *J* = 8.1 Hz), 7.48 (2H, d, *J* = 8.0 Hz), 3.66 (1H, d, *J* = 10.6 Hz), 3.21 (1H, d, *J* = 11.7 Hz), 2.80 (1H, td, *J* = 11.5, 2.2 Hz), 1.90 (1H, d, *J* = 10.2 Hz), 1.78 (1H, d, *J* = 11.3 Hz), 1.67 (1H, d, *J* = 12.4 Hz), 1.44-1.57 (3H, m) ppm.

^{13}C NMR (176 MHz, $CDCl_3$) δ 149.8, 129.4 (q, *J* = 32.4 Hz), 127.1, 125.4 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 271.8 Hz), 62.1, 47.8, 35.3, 25.9, 25.4 ppm.

2-(3,5-Bis(trifluoromethyl)phenyl)pyridine (10d)



Prepared from pyridine **9d** (36.4 mg, 0.125 mmol), phenyldimethylsilane (28.8 μL, 0.19 mmol), $[Ph_3C][B(C_6F_5)_4]$ (11.5 mg, 0.013 mmol) and **1-H** (5.1 mg, 0.015 mmol.) in toluene (0.25 mL) according to General Procedure. The crude residue was purified by column chromatography to give **10d** (colourless oil, 18 mg, 48%).

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.85 (2H, s), 7.75 (1H, s), 3.74 (1H, dd, *J* = 10.9, 2.8 Hz), 3.21-3.24 (1H, m), 2.81 (1H, td, *J* = 11.6, 2.6 Hz), 1.90-1.93 (1H, m), 1.84 (1H, br. s), 1.80-1.83 (1H, m), 1.67-1.70 (1H, m), 1.44-1.58 (3H, m) ppm.

^{13}C NMR (176 MHz, $CDCl_3$) δ 148.3, 131.7 (q, *J* = 33 Hz), 127.1 (q, *J* = 3 Hz), 123.6 (q, *J* = 272 Hz), 121.2 (sept, *J* = 5 Hz), 61.6, 47.6, 35.4, 25.7, 25.3 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.7 ppm.

HRMS (EI): calcd. for $C_{13}H_{13}F_6N$ 297.0952, found 297.0959

Large Scale Reduction of 1-Phenyl Pyridine 9a with 2.5 mol% of Borenium Catalyst

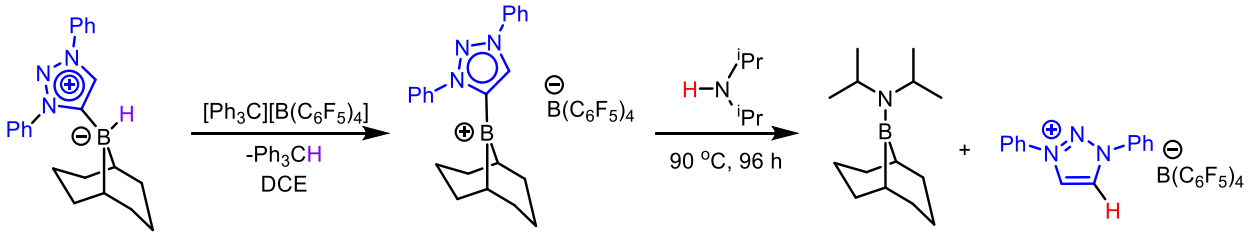
In a glovebox, a 1 dram vial was charged with $[Ph_3C][B(C_6F_5)_4]$ (73.8 mg, 0.08 mmol) and **1-H** (30.0 mg, 0.09 mmol) then toluene (1.6 mL) was added. The mixture was swirled until the colour changed from red to pale yellow. A second 1 dram vial was charged with 2-phenyl pyridine (0.5 g, 3.2 mmol) and dimethylphenylsilane (0.74 mmL, 4.8 mmol) in toluene (1.6 mL). These solutions were transferred to a 50 mL glass tube equipped with a magnetic stir bar. The reaction mixture was placed in a 50 mL stainless steel

Parr pressure vessel and sealed with the gas regulator outside the glovebox. The pressure vessel was pressurized and depressurized five times with hydrogen gas (28 bar) then brought up to the required pressure before heating (76 bar). The vessel was then submerged in an oil bath at 100 °C and heated for 60 h. Afterwards the vessel was slowly depressurized. Internal standard (1,3,5-trimethoxybenzene) was added to the reaction mixture. Then the crude reaction mixture was diluted with 3 mL of ethyl acetate and added to 10 mL of distilled H_2O. The aqueous layer was extracted three times with 3 mL of ethyl acetate. The organic fractions were dried over Na_2SO_4, filtered and evaporated. After drying, the resulting oil was subjected to silica gel column chromatography (ethyl acetate:hexane:triethylamine = 1:15:1) to give the desired product as a colorless oil along with siloxane by-product. The obtained product was dissolved in 5 mL of ethyl ether and extracted with 2M HCl aq. three times. Then the combined water phase was neutralized with 2M NaOH aq. and extracted with ethyl ether three times. The combined organic phase was dried over Na_2SO_4, filtered and evaporated to give the desired product (447 mg, 2.76 mmol, 86%) as a colorless solid.

5. Control Experiments

Catalyst Decomposition

In a glovebox, a 0.5 dram vial was charged with $[Ph_3C][B(C_6F_5)_4]$ (23.1 mg, 0.025 mmol) and 1-H (8.6 mg, 0.025 mmol) then 0.5 mL of 1,2-dichloroethane was added. The mixture was swirled until the colour changed from red to pale yellow. Diisopropylamine (35 μL, 0.25 mmol) was added to the mixture and the solution was transferred to a J-Young tube. The solution was heated at 90 °C for 96 h after which the reaction was monitored by NMR spectroscopy.



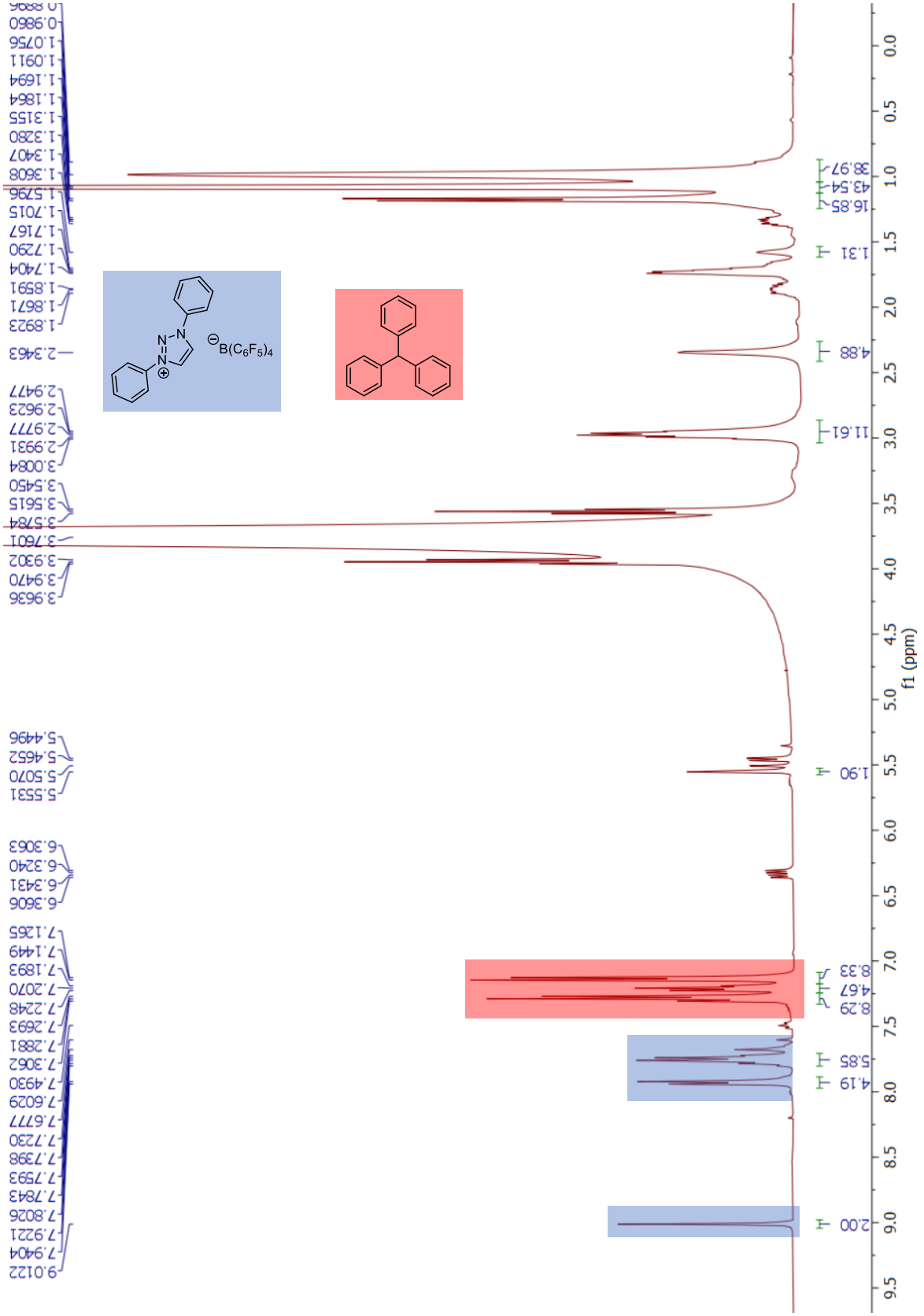


Figure S1. Crude catalyst decomposition reaction, 1H NMR (700 MHz) in 1,2-dichloroethane

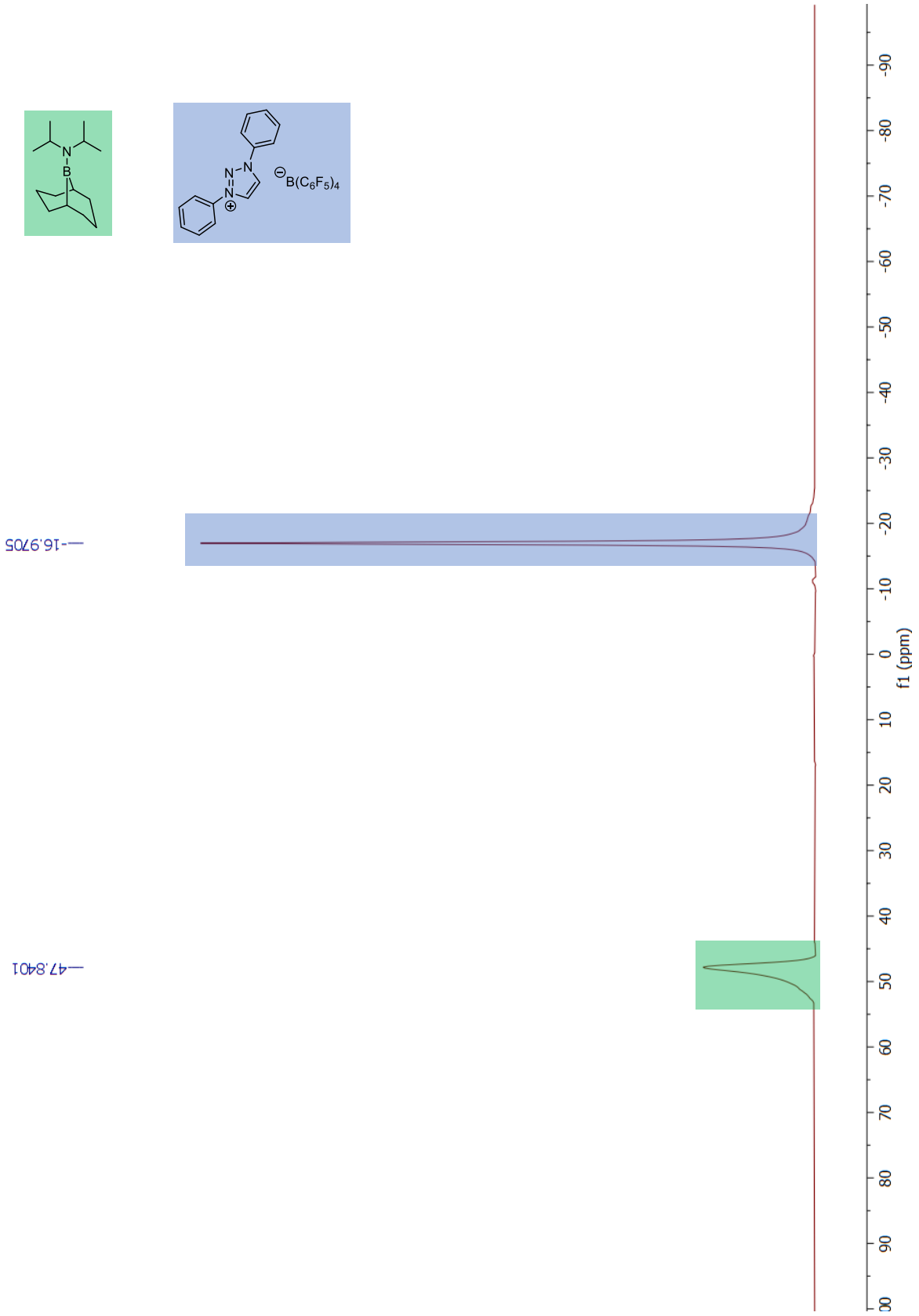
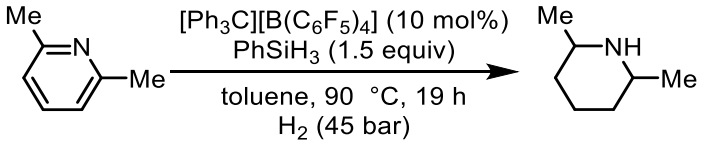


Figure S2. Crude catalyst decomposition reaction, ^{11}B NMR (128 MHz) in 1,2-dichloroethane

6. Mechanistic Studies

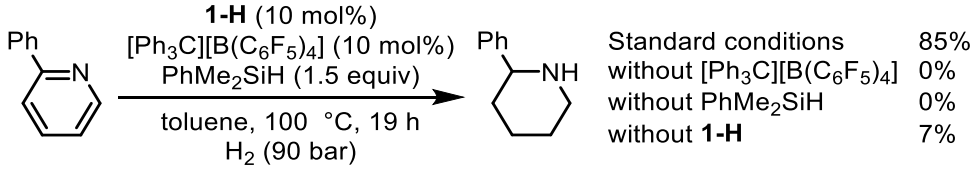
6.1 Control Experiments

Reduction of 2,6-lutidine without borenium precursor 1-H



In a glovebox, a 0.5 dram vial was charged with $[Ph_3C][B(C_6F_5)_4]$ (11.5 mg, 0.0125 mmol) and phenylsilane (23.1 mL, 0.19 mmol) then 0.5 mL of toluene was added. The mixture was swirled until the colour changed from red to pale yellow. 2,6-lutidine (13 mg, 0.125 mmol) was added to the solution. The reaction mixture was placed in a 50 mL stainless steel Parr pressure vessel and sealed with the gas regulator outside the glovebox. The pressure vessel was pressurized and depressurized five times with hydrogen gas (28 bar) then brought up to the required pressure before heating (45 bar). The vessel was then submerged in an oil bath of 90 °C and heated for 19 h. After cooling the reaction to room temperature, the crude mixture was analyzed by ^{1}H NMR and ^{13}C NMR spectroscopy showing no reduced product formation.

Reduction of 2-phenyl pyridine with various changes to reaction conditions



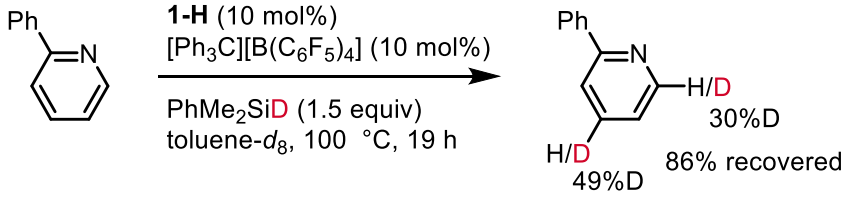
Without $[Ph_3C][B(C_6F_5)_4]$: In a glovebox, a 0.5 dram vial was charged with **1-H** (6.9 mg, 0.02 mmol) then 0.4 mL of toluene was added. 2-Phenylpyridine (31 mg, 0.2 mmol) was added to the solution followed by phenyldimethylsilane (41 mg, 0.3 mmol) added directly to the vial. The reaction mixture was placed in a 50 mL stainless steel Parr pressure vessel and sealed with the gas regulator outside the glovebox. The pressure vessel was pressurized and depressurized five times with hydrogen gas (28 bar) then brought up to the required pressure before heating (76 bar). The vessel was then submerged in an oil bath of 100 °C and heated for 19 h. After cooling the reaction to room temperature, the crude mixture was analyzed by ^{1}H NMR spectroscopy showing no reduced product formation.

Without Silane: In a glovebox, a 0.5 dram vial was charged with $[Ph_3C][B(C_6F_5)_4]$ (18 mg, 0.02 mmol) and **1-H** (6.9 mg, 0.02 mmol) then 0.4 mL of toluene was added. 2-phenylpyridine (31 mg, 0.2 mmol) was added to the solution directly to the vial. The reaction mixture was placed in a 50 mL stainless steel Parr

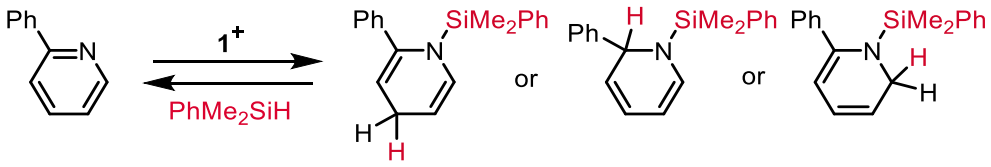
pressure vessel and sealed with the gas regulator outside the glovebox. The pressure vessel was pressurized and depressurized five times with hydrogen gas (28 bar) then brought up to the required pressure before heating (76 bar). The vessel was then submerged in an oil bath of 100 °C and heated for 19 h. After cooling the reaction to room temperature, the crude mixture was analyzed by ^{1}H NMR spectroscopy showing no reduced product formation.

Without Borenium precursor 1-H: In a glovebox, a 0.5 dram vial was charged with $[Ph_3C][B(C_6F_5)_4]$ (23 mg, 0.025 mmol), 2-phenylpyridine (39 mg, 0.25 mmol), and 0.25 mL of toluene was added. Then, phenyldimethylsilane (51 mg, 0.38 mmol) in 0.25 mL of toluene was added to the solution directly to the vial. The reaction mixture was placed in a 50 mL stainless steel Parr pressure vessel and sealed with the gas regulator outside the glovebox. The pressure vessel was pressurized and depressurized five times with hydrogen gas (28 bar) then brought up to the required pressure before heating (76 bar). The vessel was then submerged in an oil bath of 100 °C and heated for 19 h. After cooling the reaction to room temperature, 1,3,5-trimethoxybenzene was added to the reaction mixture. The crude mixture was analyzed by ^{1}H NMR spectroscopy showing 7% of reduced product formation with 93% of unreacted starting pyridine.

6.1 Deuterium Labelling Experiment in the Absence of Hydrogen Gas



In a glovebox, a 0.5 dram vial was charged with $[Ph_3C][B(C_6F_5)_4]$ (11.5 mg, 0.0125 mmol) and **1-H** (4.3 mg, 0.0125 mmol) then 0.5 mL of toluene-d_8 was added. The mixture was swirled until the colour changed from red to pale yellow. 2-Phenylpyridine (19 mg, 0.125 mmol) was added to the solution followed by phenyldimethylsilane-*d* (26 mg, 0.1875 mmol) added directly to the vial. The solution was heated at 100 °C for 19 h. After cooling the reaction to room temperature, 1,3,5-trimethoxybenzene (13.5 mg) was added to the reaction mixture. Then the crude mixture was analyzed by ^{1}H NMR spectroscopy without water work-up showing no reduced product formation with 93% of 2-phenyl pyridine. The crude mixture was purified by column chromatography to afford deuterated 2-phenyl pyridine, with deuterium incorporation at four and six positions (86% yield). This result indicates that the boreniuum cation $\mathbf{1}^+$ catalyzes the hydrosilylation of 2-phenyl pyridine and that this process is reversible.



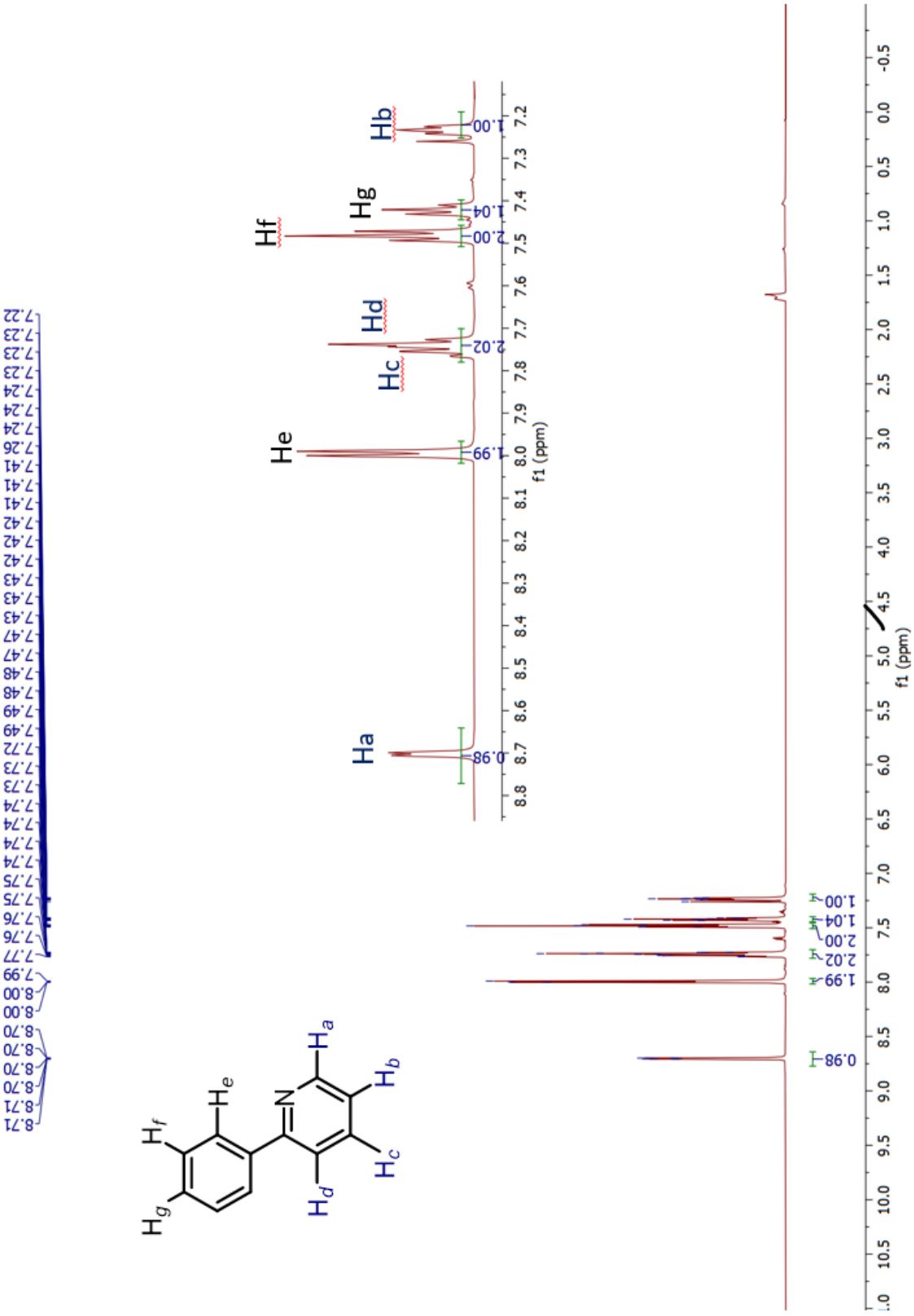


Figure S3. ^{1}H NMR (700 MHz) of 2-phenyl pyridine in $CDCl_3$

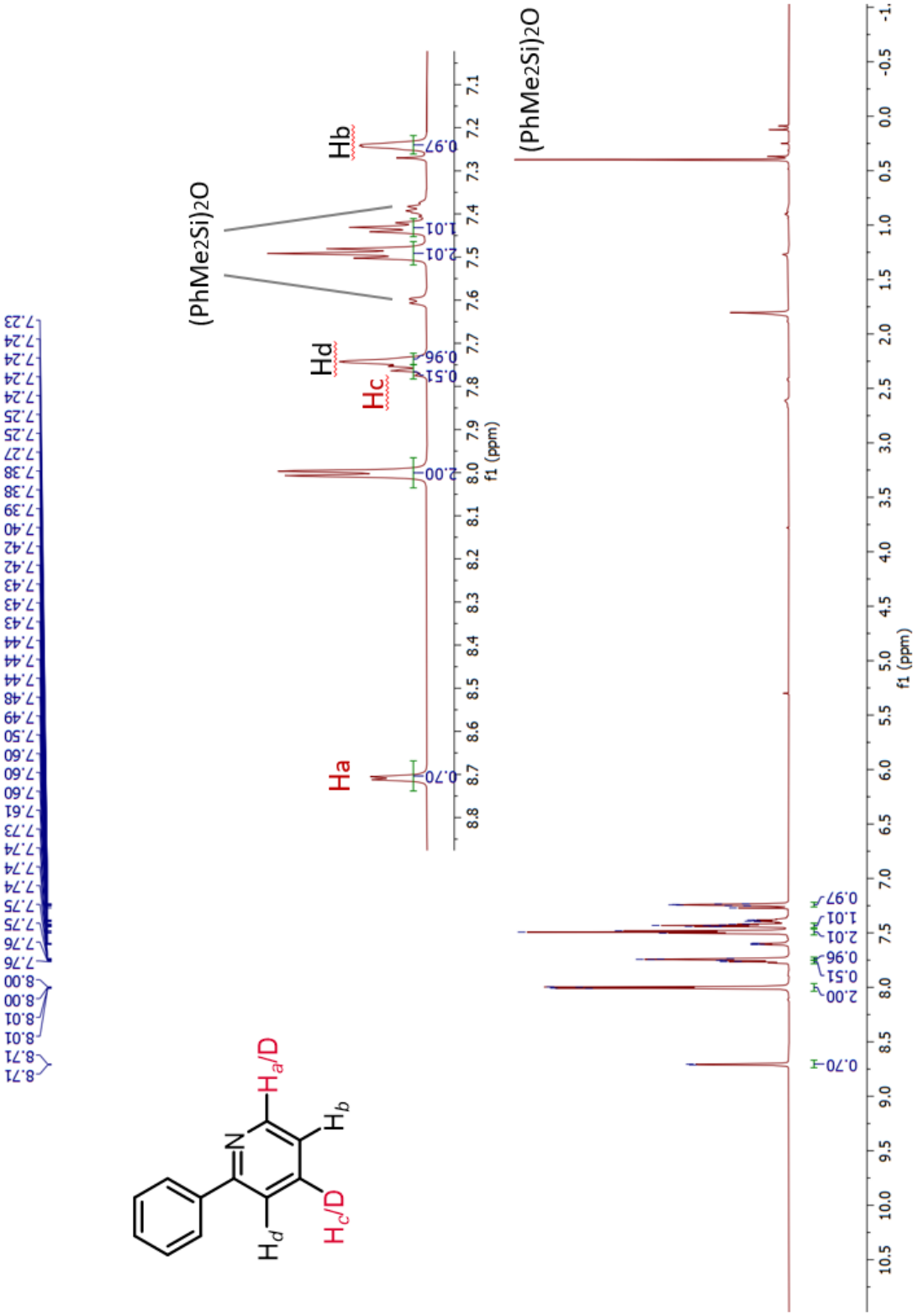


Figure S4. ^{1}H NMR (700 MHz) of deuterated 2-phenyl pyridine in $CDCl_3$

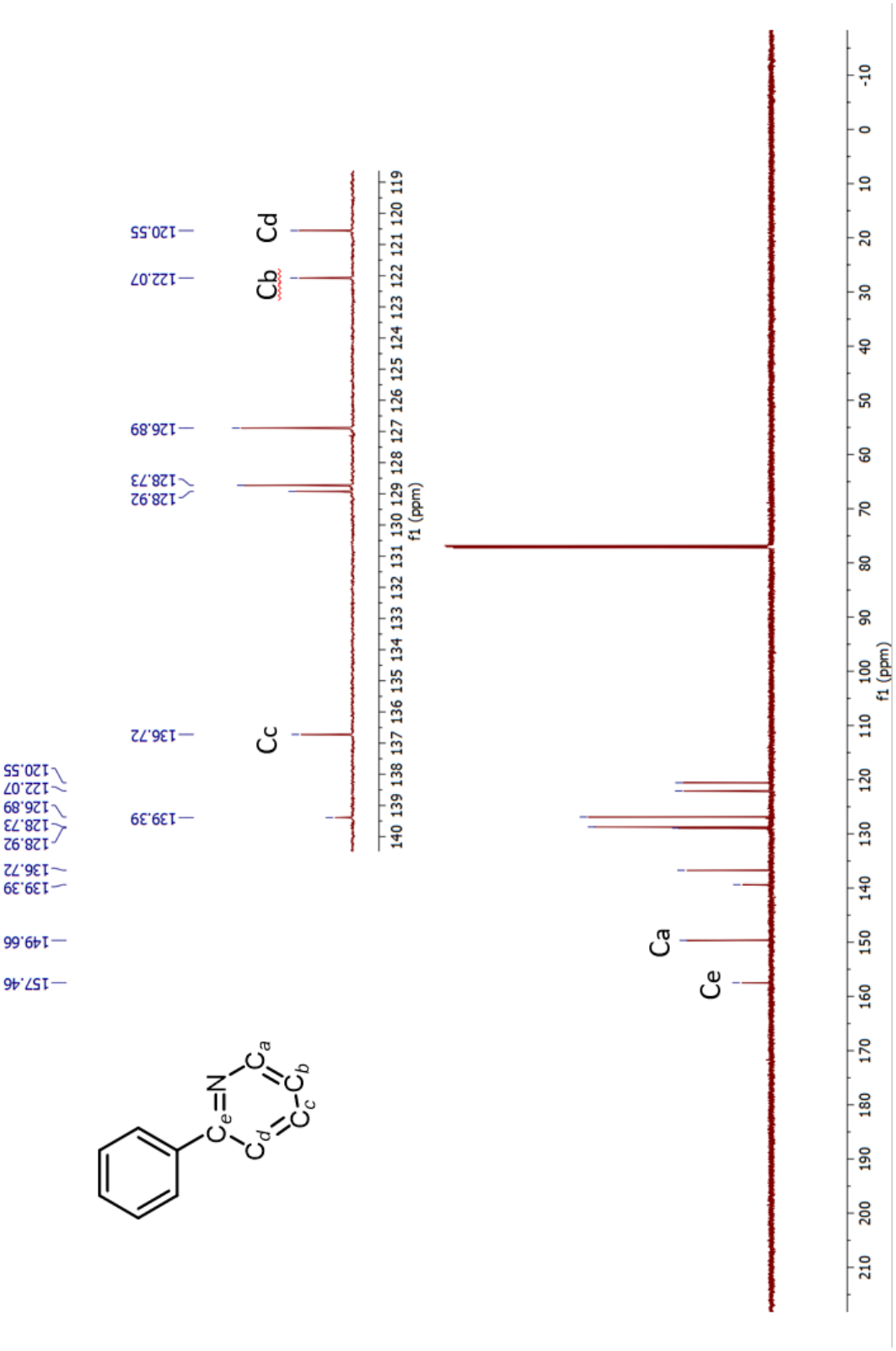


Figure S5. ^{13}C NMR (176 MHz) of 2-phenyl pyridine in $CDCl_3$

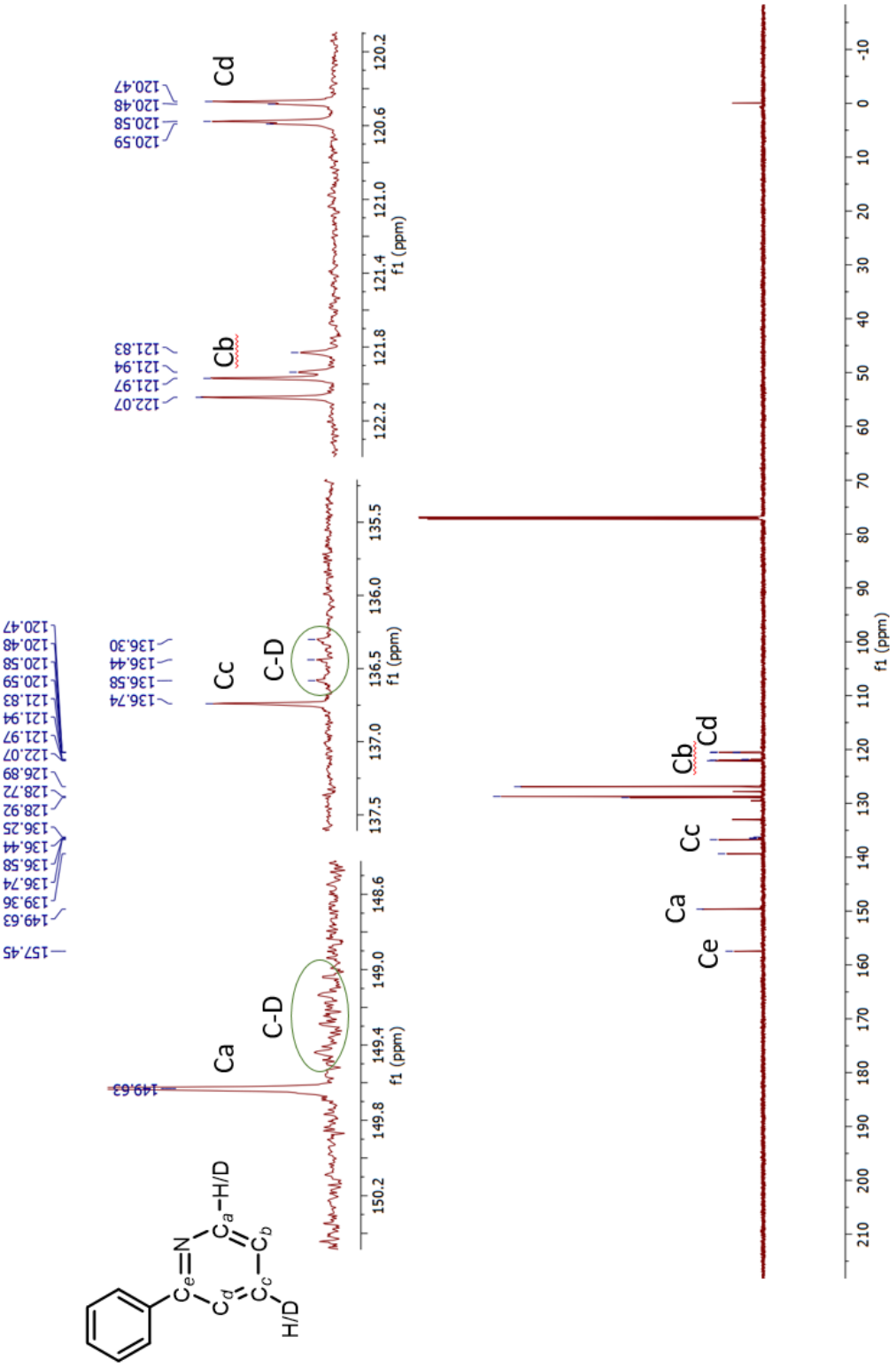


Figure S6. ^{13}C NMR (176 MHz) of deuterated 2-phenyl pyridine in $CDCl_3$

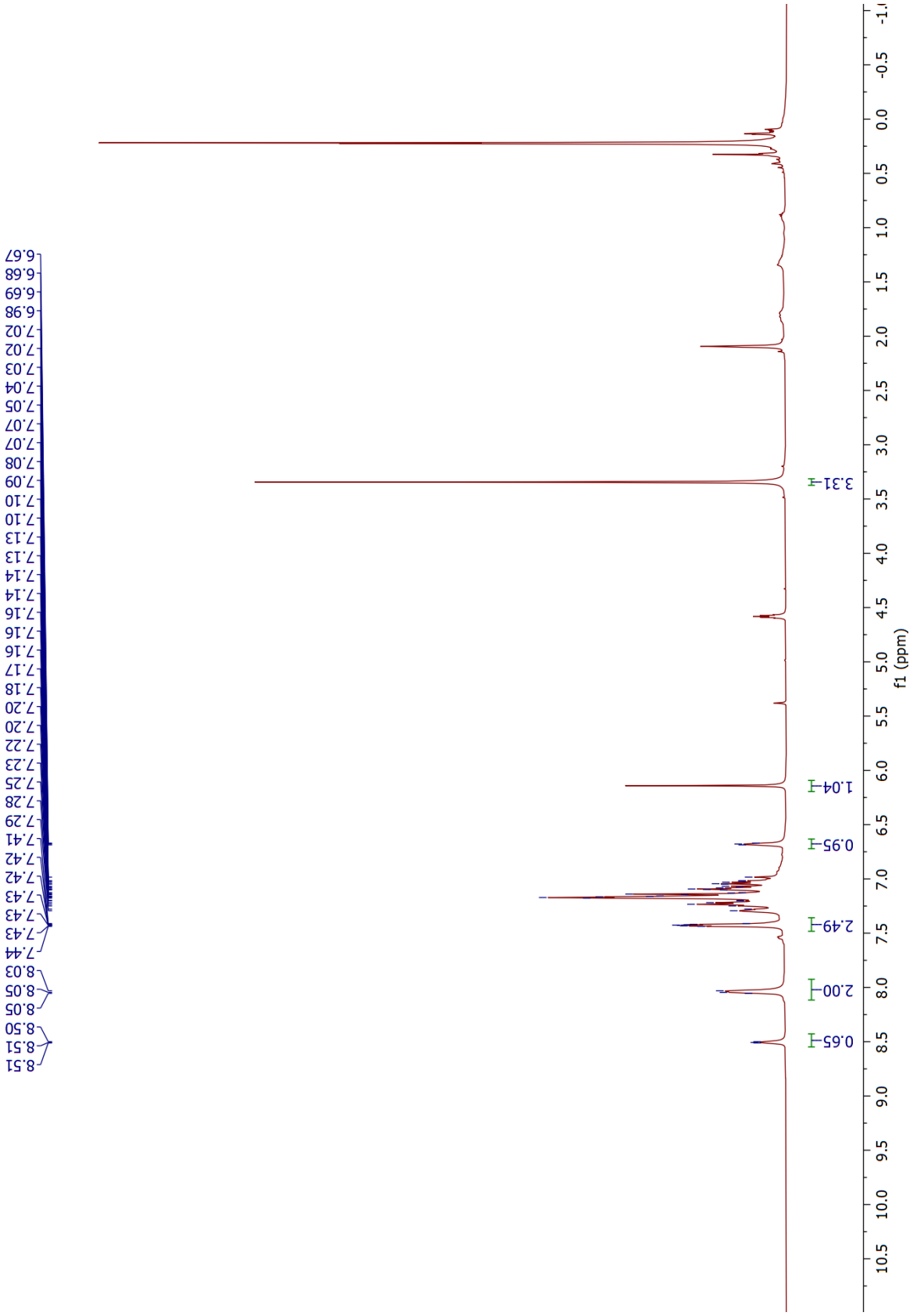
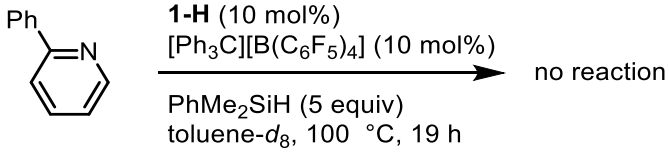


Figure S7. ^{1}H NMR (700 MHz) of a crude reaction mixture in toluene-d_8 before reaction work-up

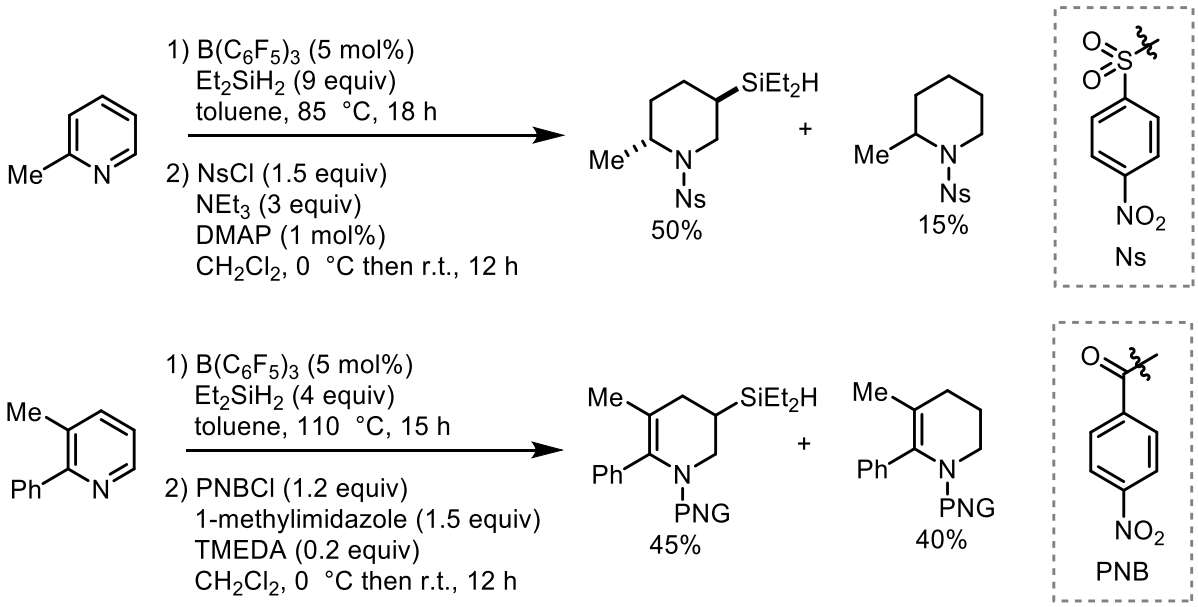
6.1 Control experiment with excess silane in the absence of hydrogen gas



In a glovebox, a 0.5 dram vial was charged with $[Ph_3C][B(C_6F_5)_4]$ (11.5 mg, 0.02 mmol) and **1-H** (4.3 mg, 0.02 mmol) then 0.5 mL of toluene-d_8 was added. The mixture was swirled until the colour changed from red to pale yellow. 2-phenylpyridine (19 mg, 0.2 mmol) was added to the solution followed by phenyldimethylsilane (26 mg, 1 mmol) added directly to the vial. The solution was heated at 100 °C for 19 h. After cooling the reaction to room temperature, 1,3,5-trimethoxybenzene was added to the reaction mixture. Then the crude mixture was analyzed by ^{1}H NMR spectroscopy without water work-up showing no product formation.

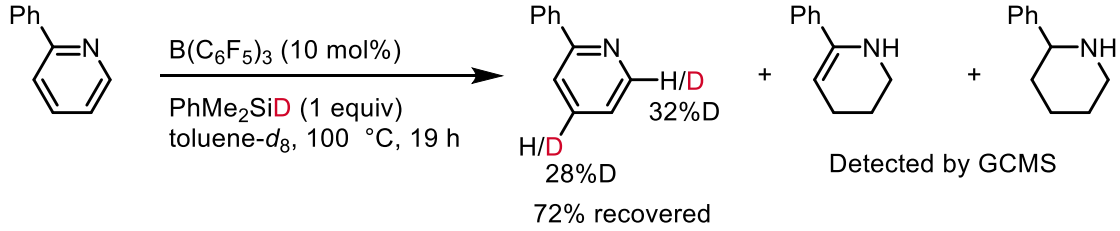
6.2 Deuterium labelling experiment with $B(C_6F_5)_3$ as a catalyst in the absence of hydrogen gas

The reaction with BCF ($B(C_6F_5)_3$) was conducted to see if any reduced product can be formed as shown in Chang's[4] report (Scheme 1) or deuterium exchange of 2-phenylpyridine occurs in the presence of BCF.



Scheme 1. BCF-Catalyzed reduction of pyridine reported by a Chang group

In a glovebox, a 0.5 dram vial was charged with $B(C_6F_5)_3$ (11.5 mg, 0.02 mmol) and 0.5 mL of toluene-d_8 was added. Then, 2-phenylpyridine (19 mg, 0.2 mmol) was added to the solution followed by phenyldimethylsilane-*d* (26 mg, 0.2 mmol) added directly to the vial. The solution was heated at 100 °C for 19 h. After cooling the reaction to room temperature, 1,3,5-trimethoxybenzene was added to the reaction mixture. Then the crude mixture was analyzed by ^{1}H NMR spectroscopy without water work-up showing 76% of 2-phenyl pyridine. Then the crude reaction mixture was added to 10 mL of distilled H_2O and the aqueous layer was extracted three times with ethyl acetate. The organic fractions were dried over Na_2SO_4, filtered, evaporated, and analyzed by GC-MS and ^{1}H NMR. The resulting oil was subjected to preparative thin layer chromatography to give the deuterated starting pyridine (22 mg, 72%).



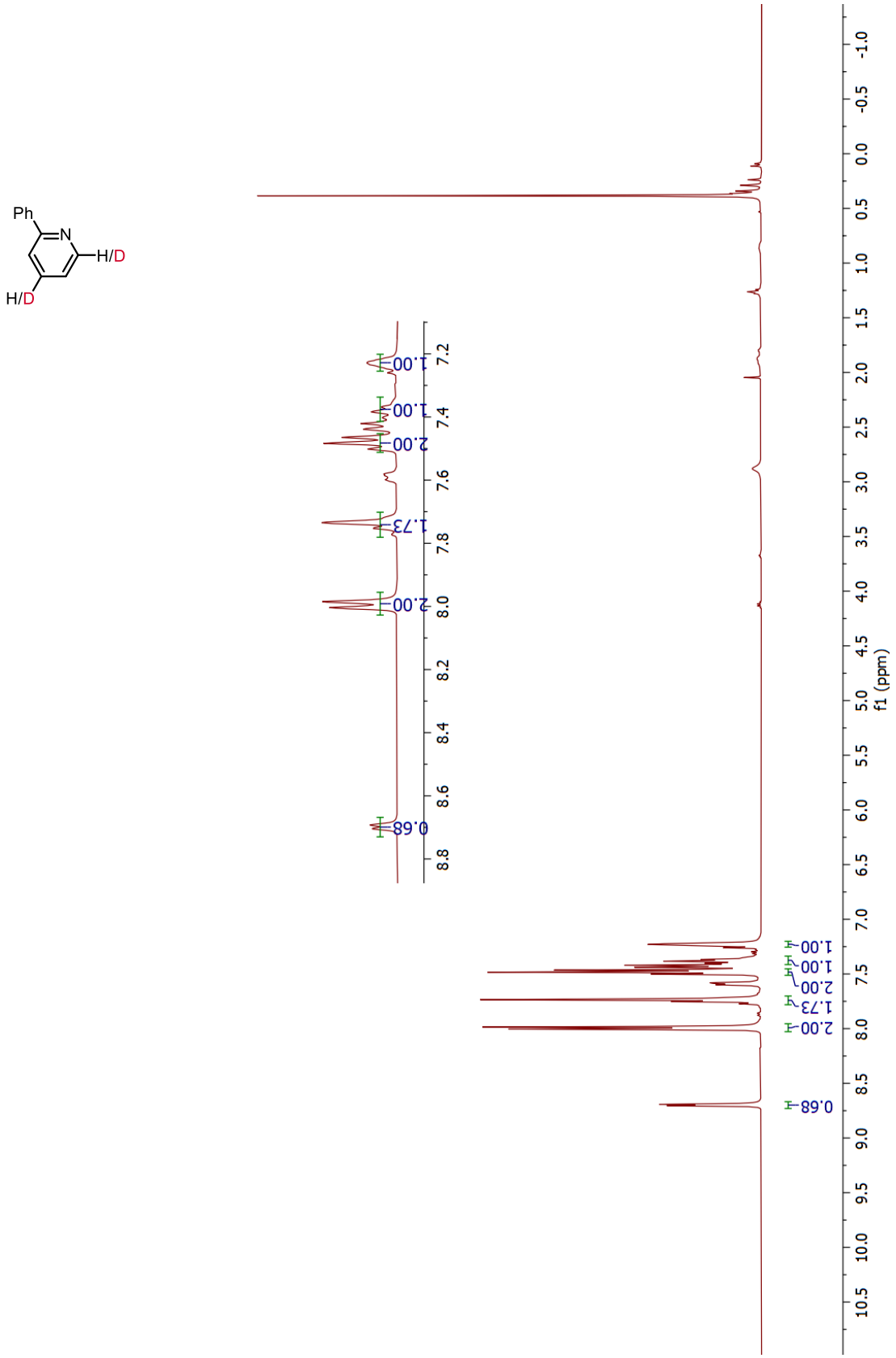


Figure S8. ^{1}H NMR (400 MHz) of purified deuterated 2-phenyl pyridine in $CDCl_3$

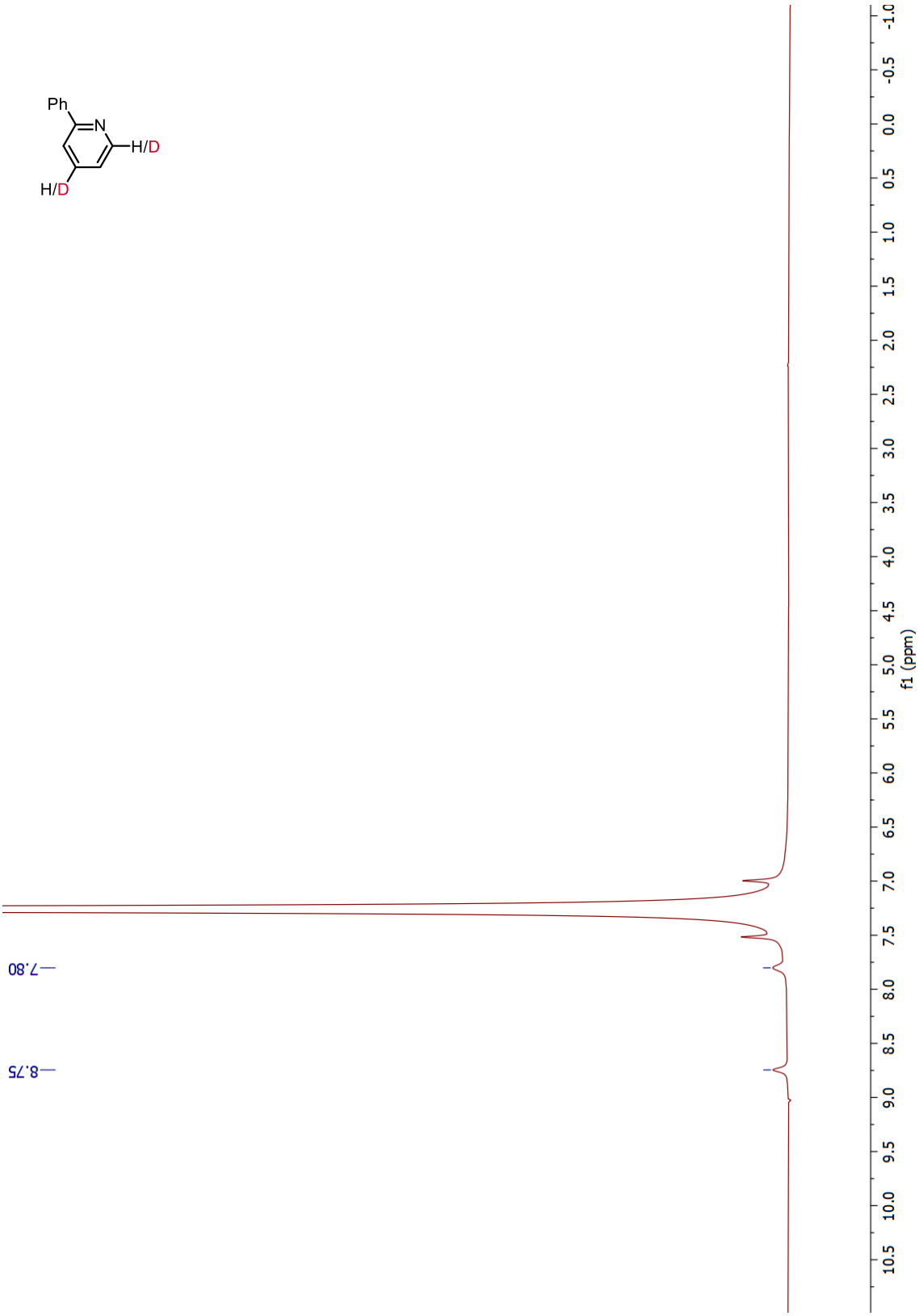


Figure S9. ^{2}H NMR (400 MHz) of purified deuterated 2-phenyl pyridine in $CDCl_3$

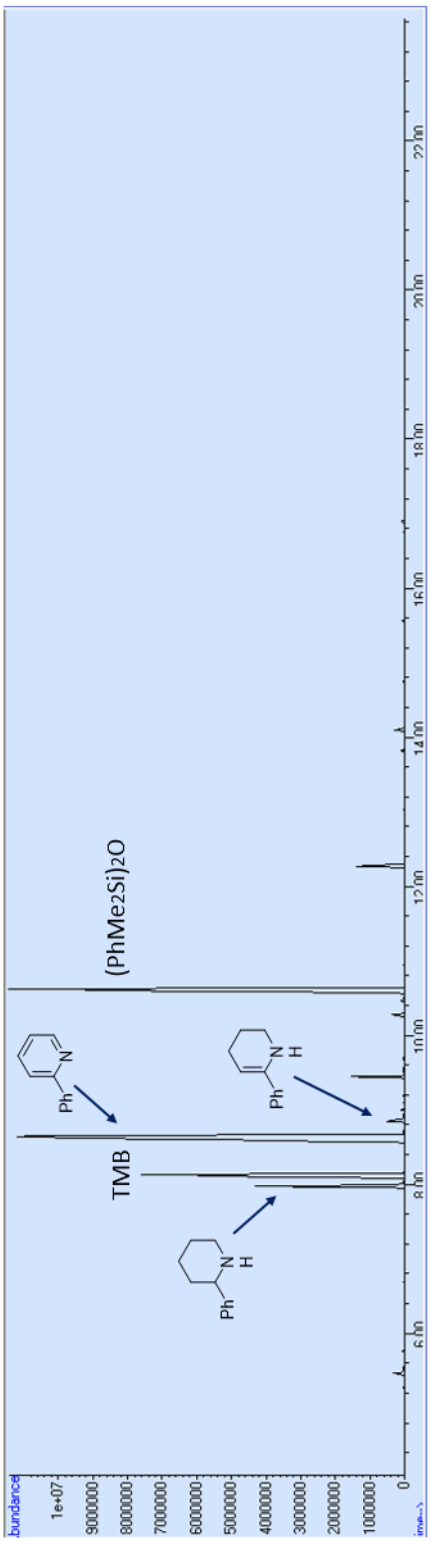
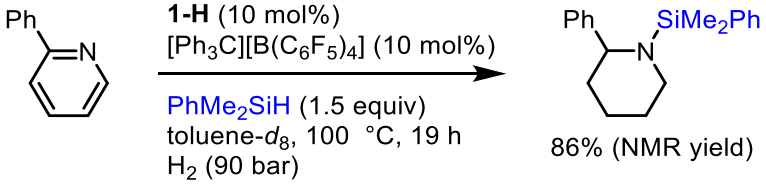


Figure S10. GC-MS analysis of crude mixture after workup with water

6.3. Observation of the *N*-silyl protected product without reaction work-up



In a glovebox, a 0.5 dram vial was charged with $[Ph_3C][B(C_6F_5)_4]$ (11.5 mg, 0.0125 mmol) and **1-H** (4.3 mg, 0.0125 mmol) then 0.5 mL of toluene-d_8 was added. The mixture was swirled until the colour changed from red to pale yellow. 2-Phenylpyridine (19 mg, 0.125 mmol) was added to the solution followed by phenyldimethylesilane (26 mg, 0.1875 mmol) added directly to the vial. The reaction mixture was placed in a 50 mL stainless steel Parr pressure vessel and sealed with the gas regulator outside the glovebox. The pressure vessel was pressurized and depressurized five times with hydrogen gas (26 bar) then brought up to the required pressure before heating (76 bar for 100 °C). The vessel was then submerged in an oil bath of the proper temperature and heated for 19 h. Afterwards the vessel was slowly depressurized. After cooling the reaction to room temperature, 1,3,5-trimethoxybenzene (7.7 mg) was added to the reaction mixture. The crude mixture was transferred into an NMR tube and analyzed by ^{1}H and ^{13}C NMR spectroscopy without further purification due to the instability of the *N*-silylated product on silica gel and in moisture, which indicated that *N*-silylated product was obtained as a colourless oil in 86% yield.

^{1}H NMR (500 MHz, Toluene-d_8): δ 7.60 (d, J = 6.1 Hz, 2H), 7.36 (d, J = 7.8 Hz, 2H), 7.24-7.19 (m, 4H), 7.11-7.04 (m, 2H), 4.26 (t, J = 3.8 Hz, 1H), 2.82 (dd, J = 6.9, 3.0 Hz, 2H), 2.18-1.99 (m, 1H), 1.71-1.59 (m, 1H), 1.46-1.39 (m, 1H), 1.37-1.26 (m, 1H), 1.24-1.18 (m, 1H), 0.35 (s, 3H), 0.31 (s, 3H).

^{13}C{^{1}H} NMR (176 MHz, Toluene-d_8): δ 144.4, 139.9, 134.1, 129.3, 128.5, 128.0, 127.7,126.1, 54.2, 41.3, 30.3, 27.8, 20.8, -1.3, -1.4.

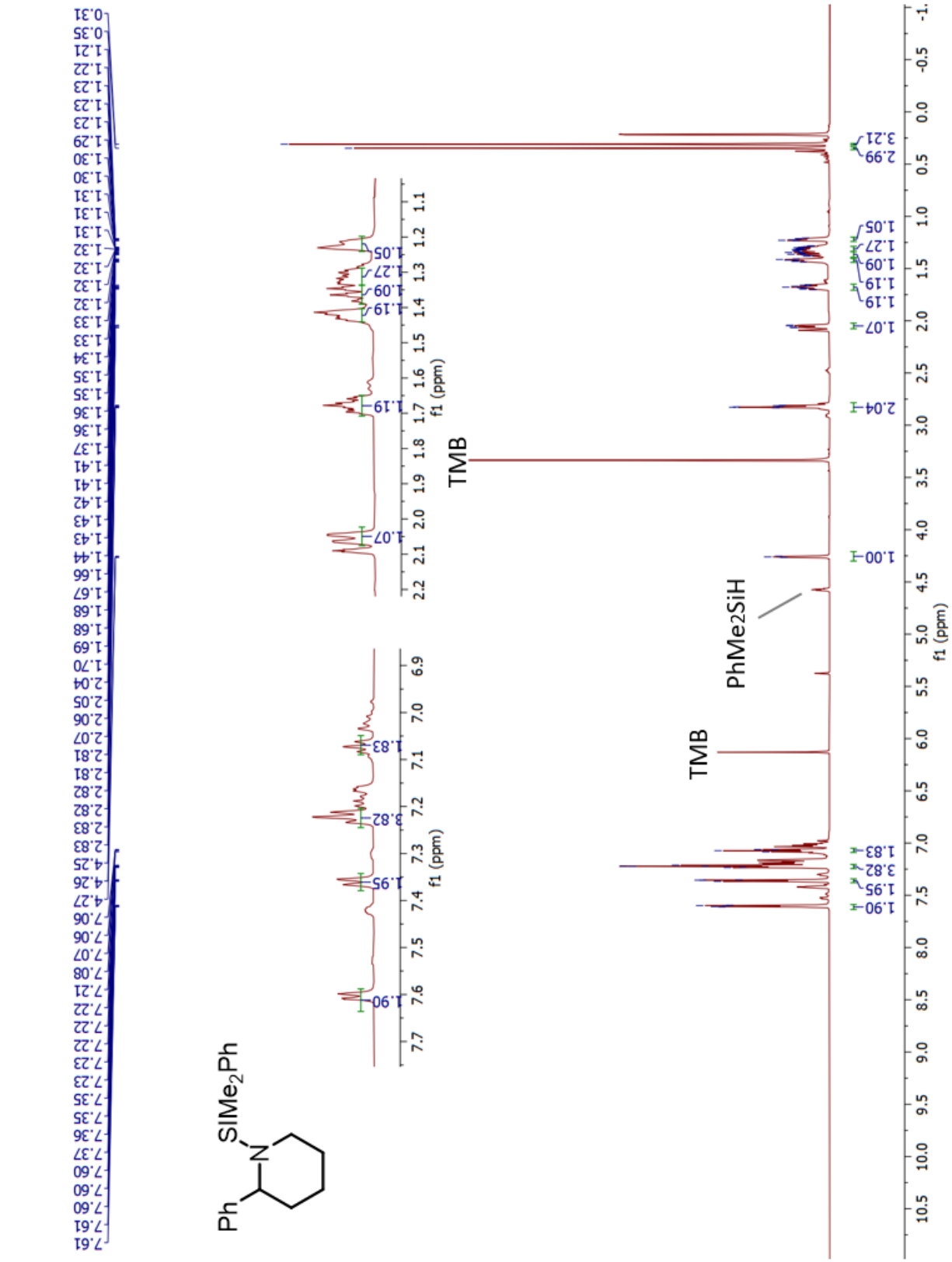


Figure S11. ^{1}H NMR (500 MHz) of *N*-silylated product in toluene-d_8

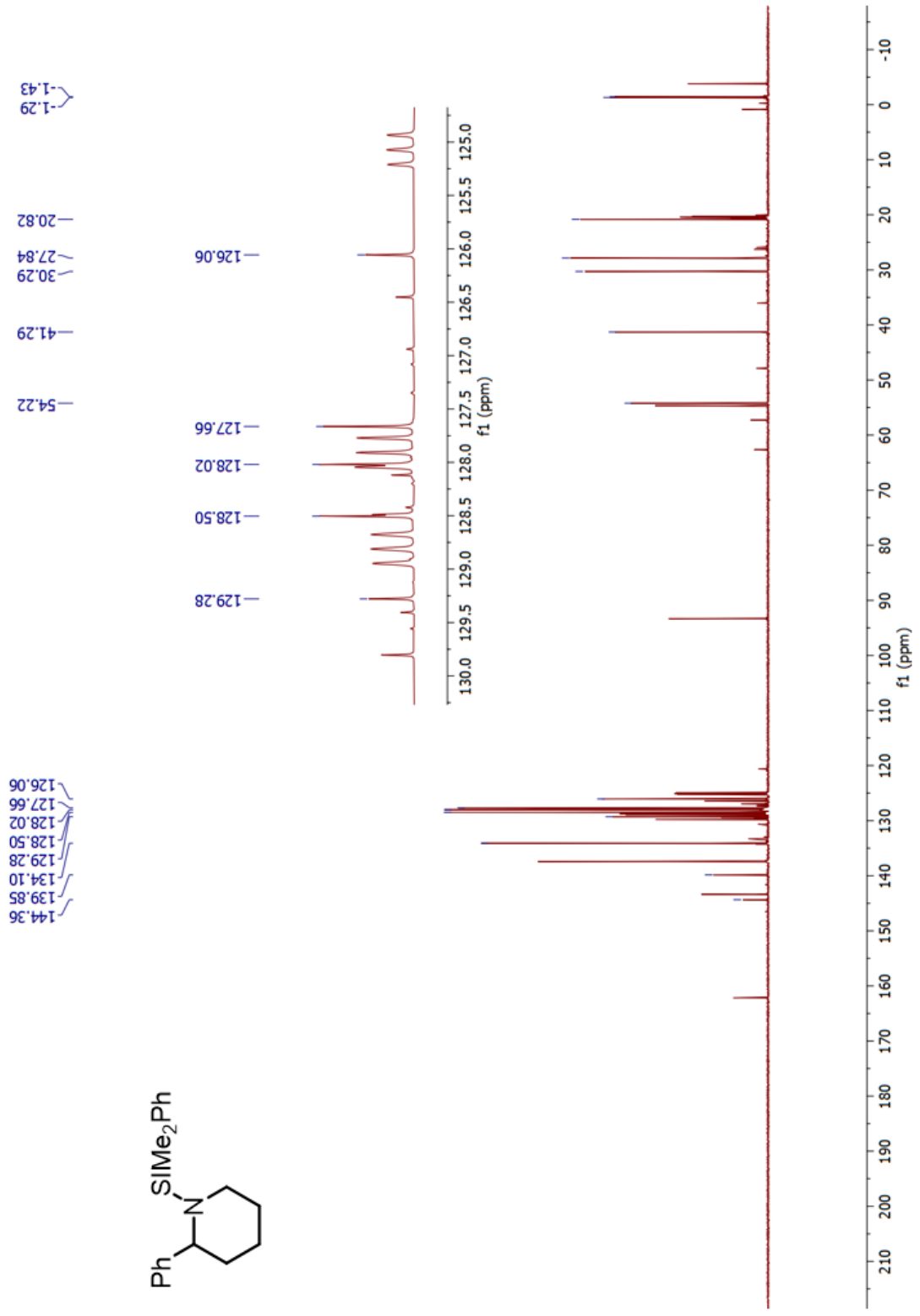


Figure S12. ^{13}C NMR (176 MHz) of *N*-silylated product in toluene-d_8

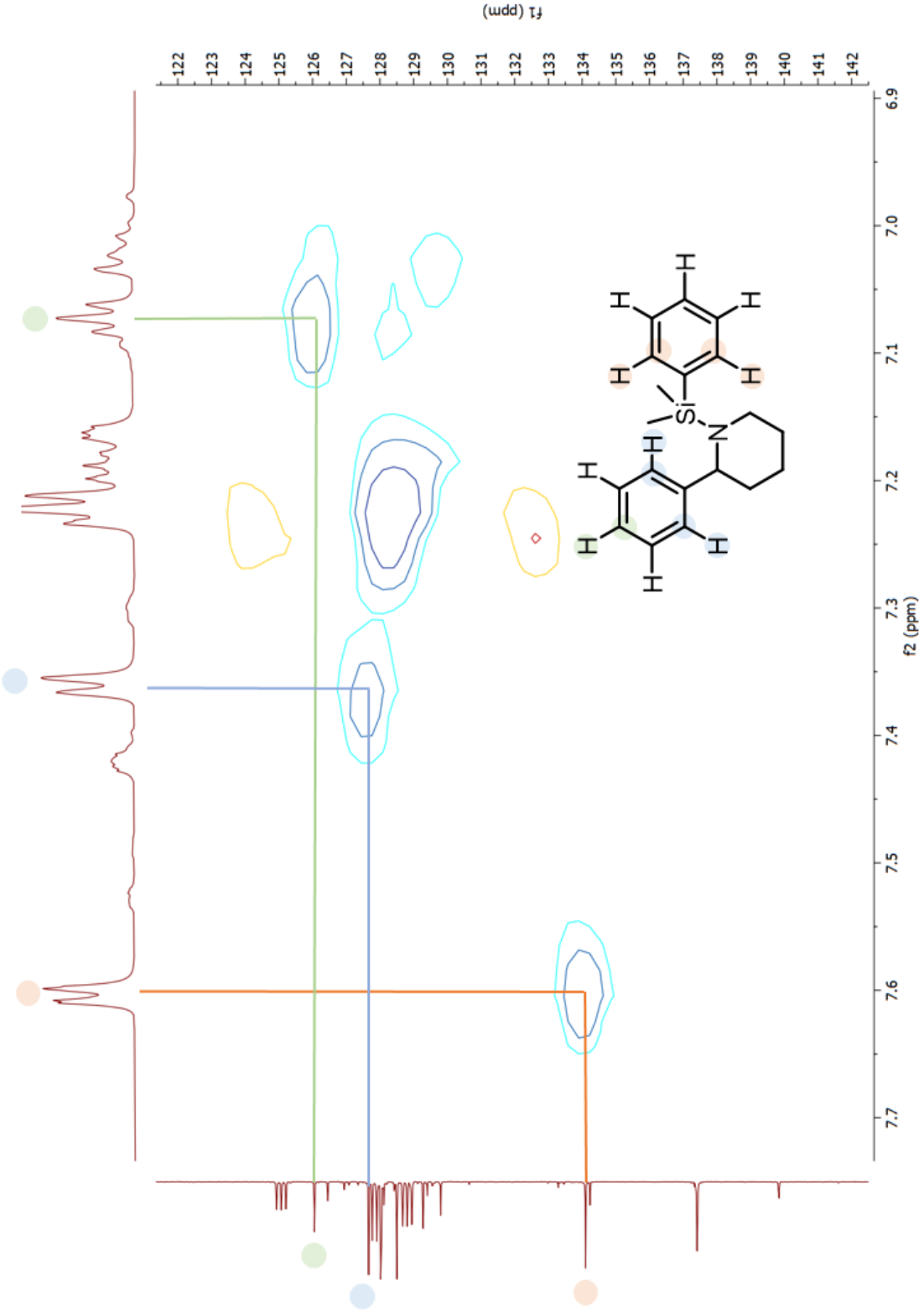


Figure S13. HSQC of *N*-silylated product in toluene-d_8

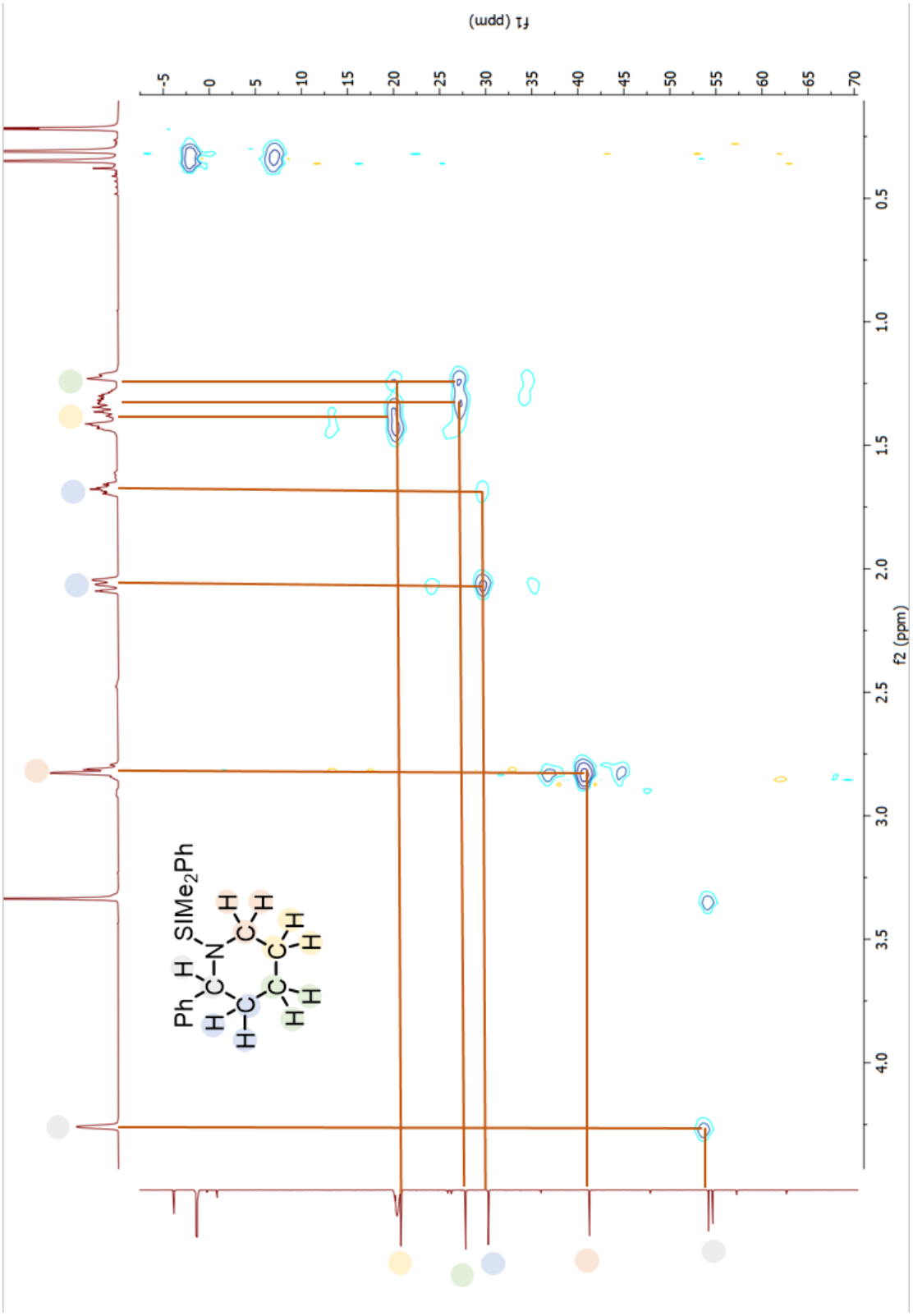


Figure S14. HSQC of *N*-silylated product in toluene-d_8

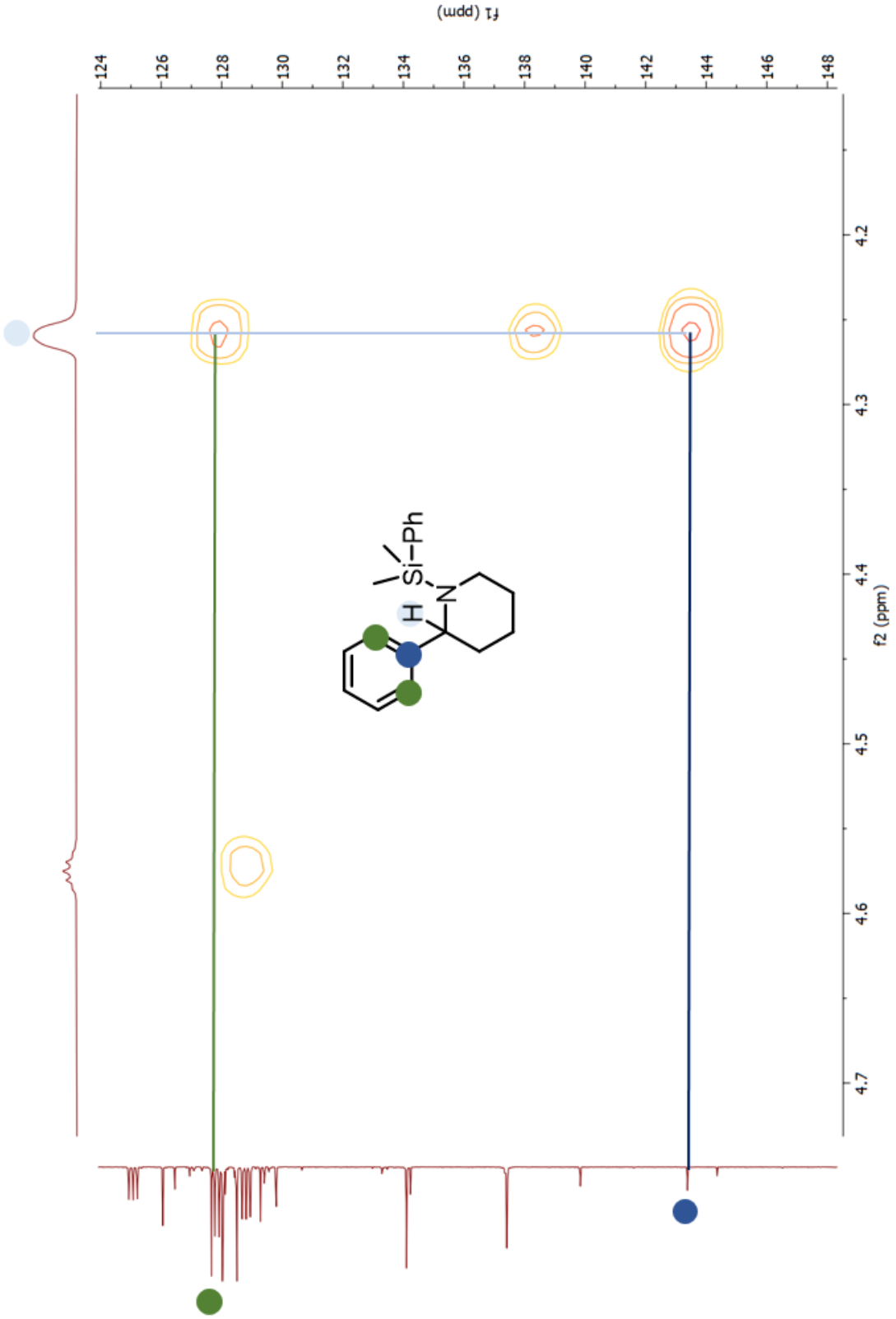


Figure S15. HMBC of *N*-silylated product in toluene-d_8

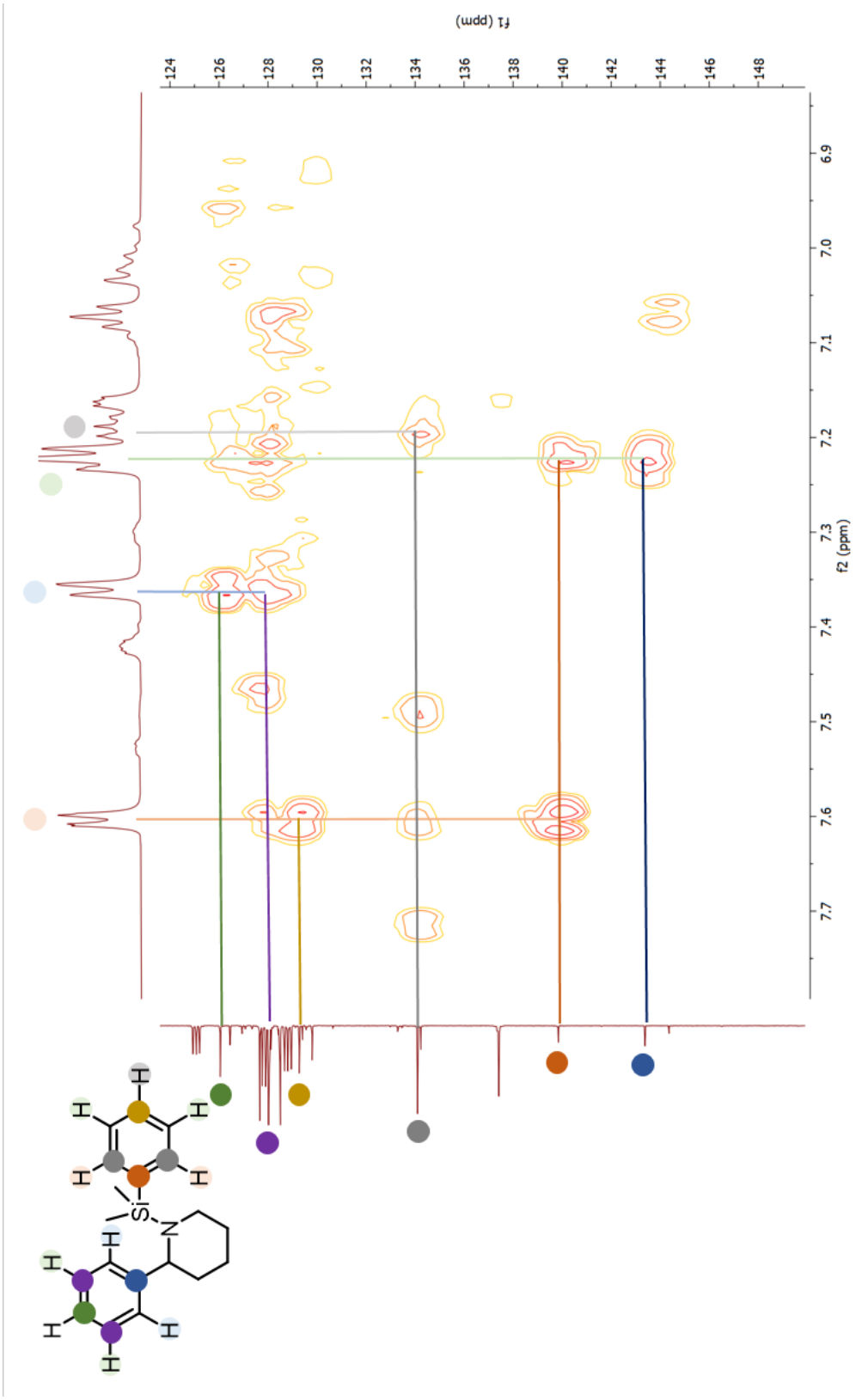
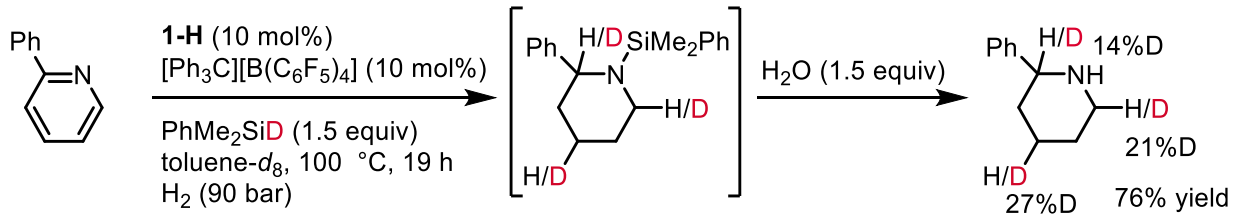


Figure S16. HMBC of *N*-silylated product in toluene-d_8

6.4 Deuterium labelling experiments



In a glovebox, a 0.5 dram vial was charged with $[Ph_3C][B(C_6F_5)_4]$ (11.5 mg, 0.0125 mmol) and **1-H** (4.3 mg, 0.0125 mmol) then 0.5 mL of toluene-d_8 was added. The mixture was swirled until the colour changed from red to pale yellow. 2-phenylpyridine (19 mg, 0.125 mmol) was added to the solution followed by phenyldimethylesilane-*d* (26 mg, 0.1875 mmol) added directly to the vial. The reaction mixture was placed in a 50 mL stainless steel Parr pressure vessel and sealed with the gas regulator outside the glovebox. The pressure vessel was pressurized and depressurized five times with hydrogen gas (26 bar) then brought up to the required pressure before heating (76 bar for 100 °C). The vessel was then submerged in an oil bath of the proper temperature and heated for 19 h. Afterwards the vessel was slowly depressurized. After cooling the reaction to room temperature, 1,3,5-trimethoxybenzene was added to the reaction mixture. The crude mixture was transferred into an NMR tube and analyzed by ^{1}H and ^{13}C NMR spectroscopy, which indicated that *N*-silylated product was obtained. The crude mixture was treated with water (3 μL, 0.18 mmol) and purified by column chromatography on silica gel to give the deuterated piperidine in 76% yield, which is then analyzed by ^{1}H and ^{2}H NMR spectroscopy. To remove the overlapped N-H signal, the product was further analyzed by ^{1}H and ^{13}C NMR analysis in $CDCl_3/D_2O$ (0.5 mL:0.05mL).

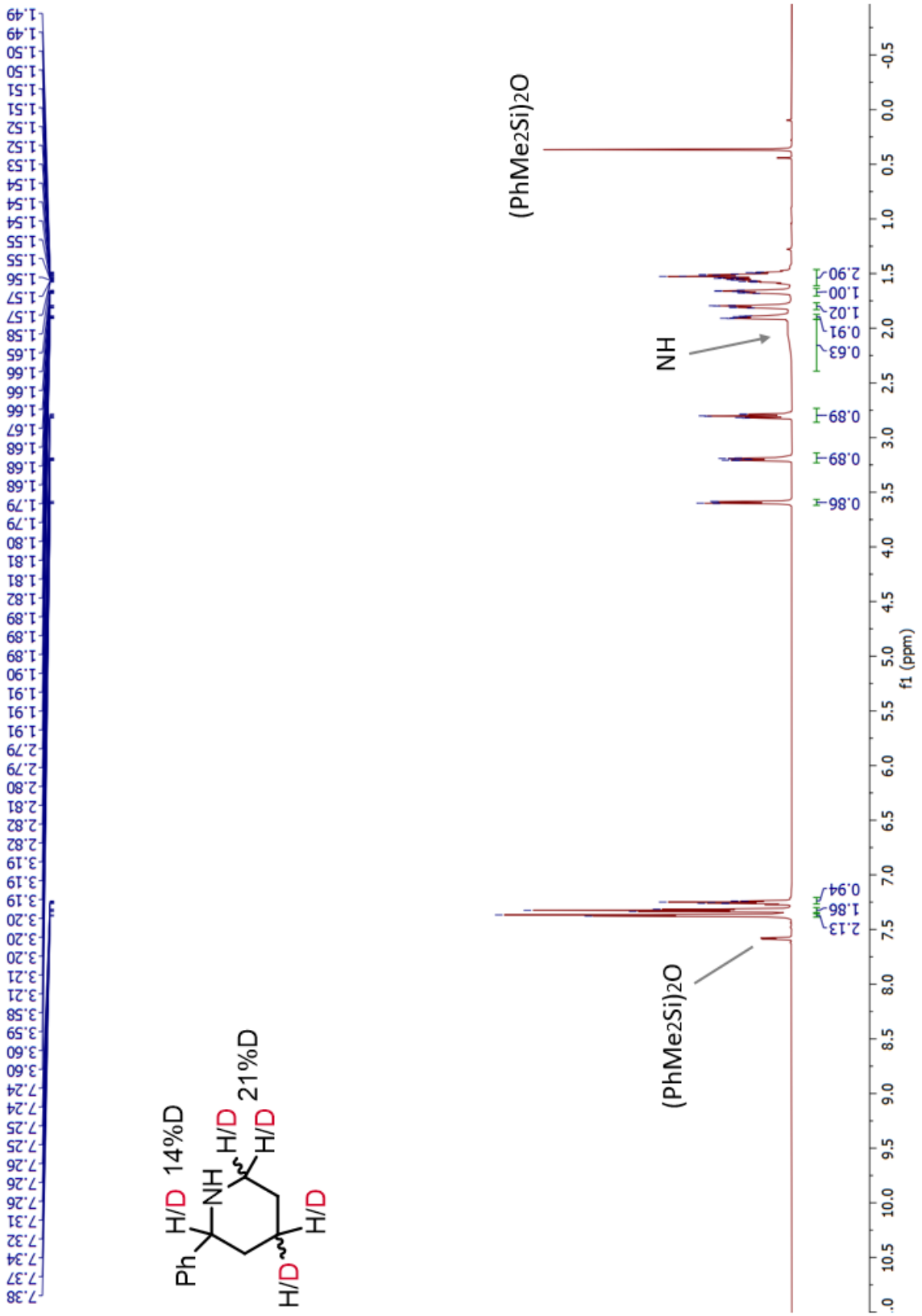


Figure S17. ^{1}H NMR (700 MHz) of deuterated product in $CDCl_3$

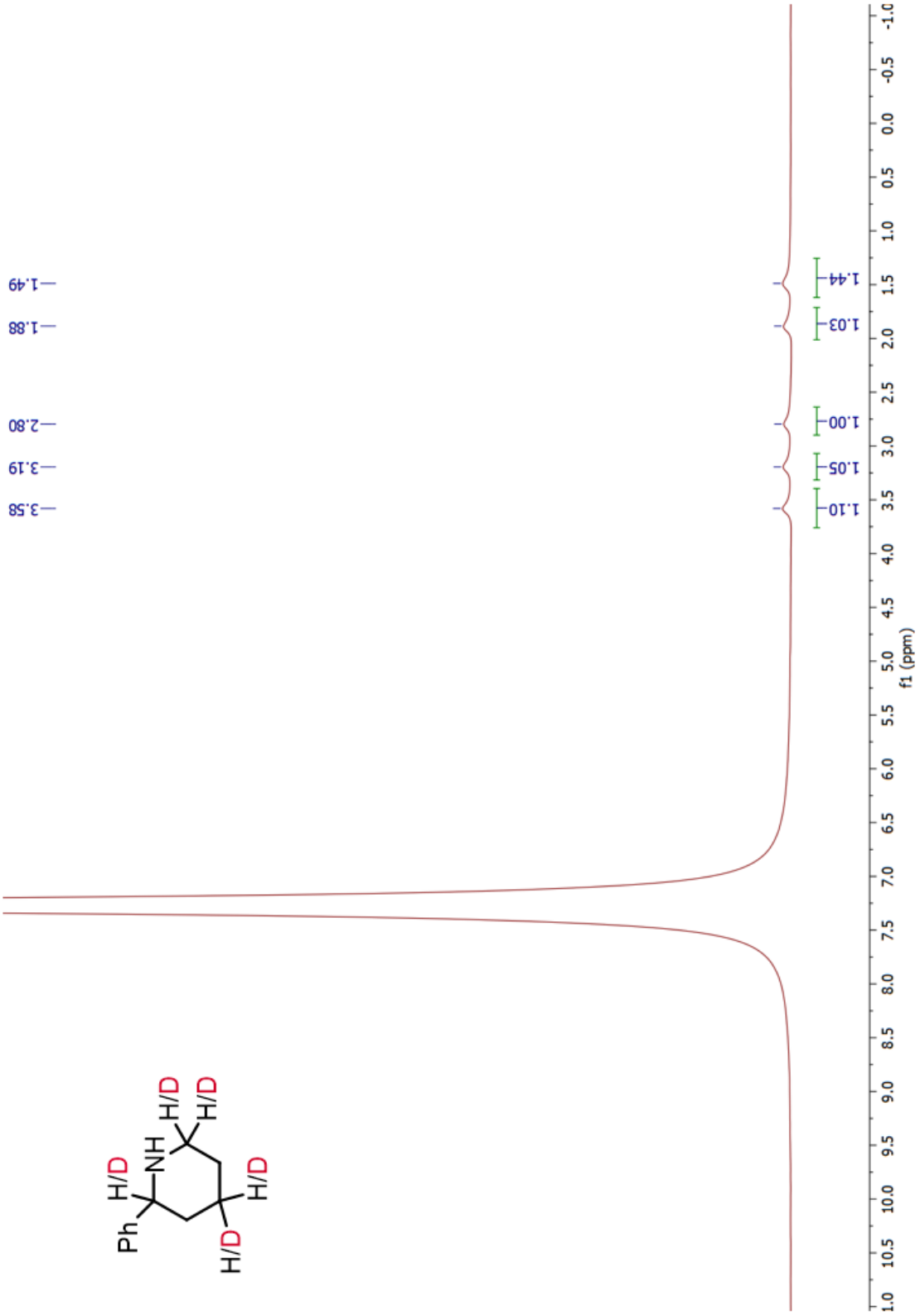


Figure S18. ^{2}H NMR (400 MHz) of deuterated product in $CDCl_3$

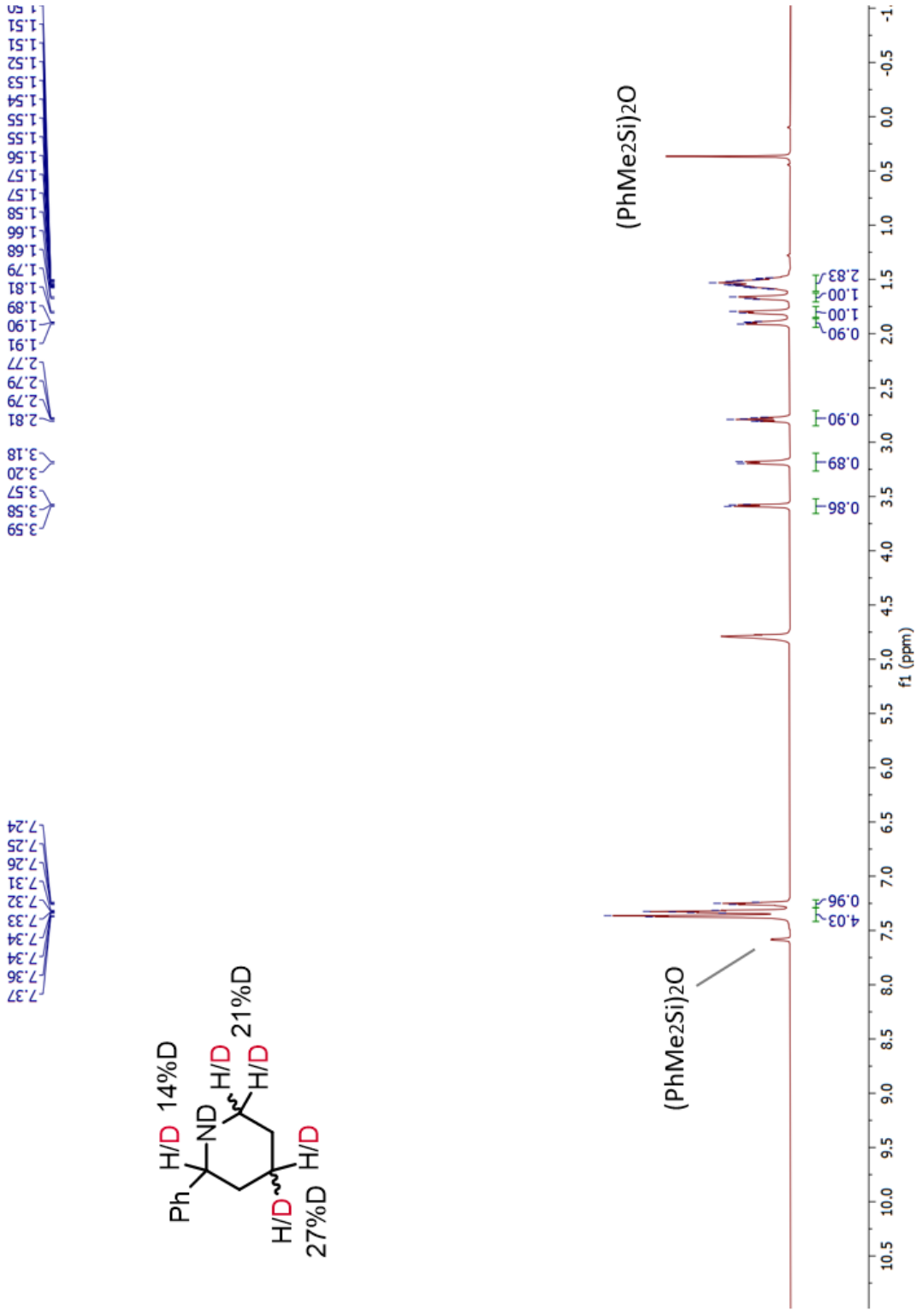


Figure S19. ^{1}H NMR (700 MHz) of deuterated product in $CDCl_3/D_2O$

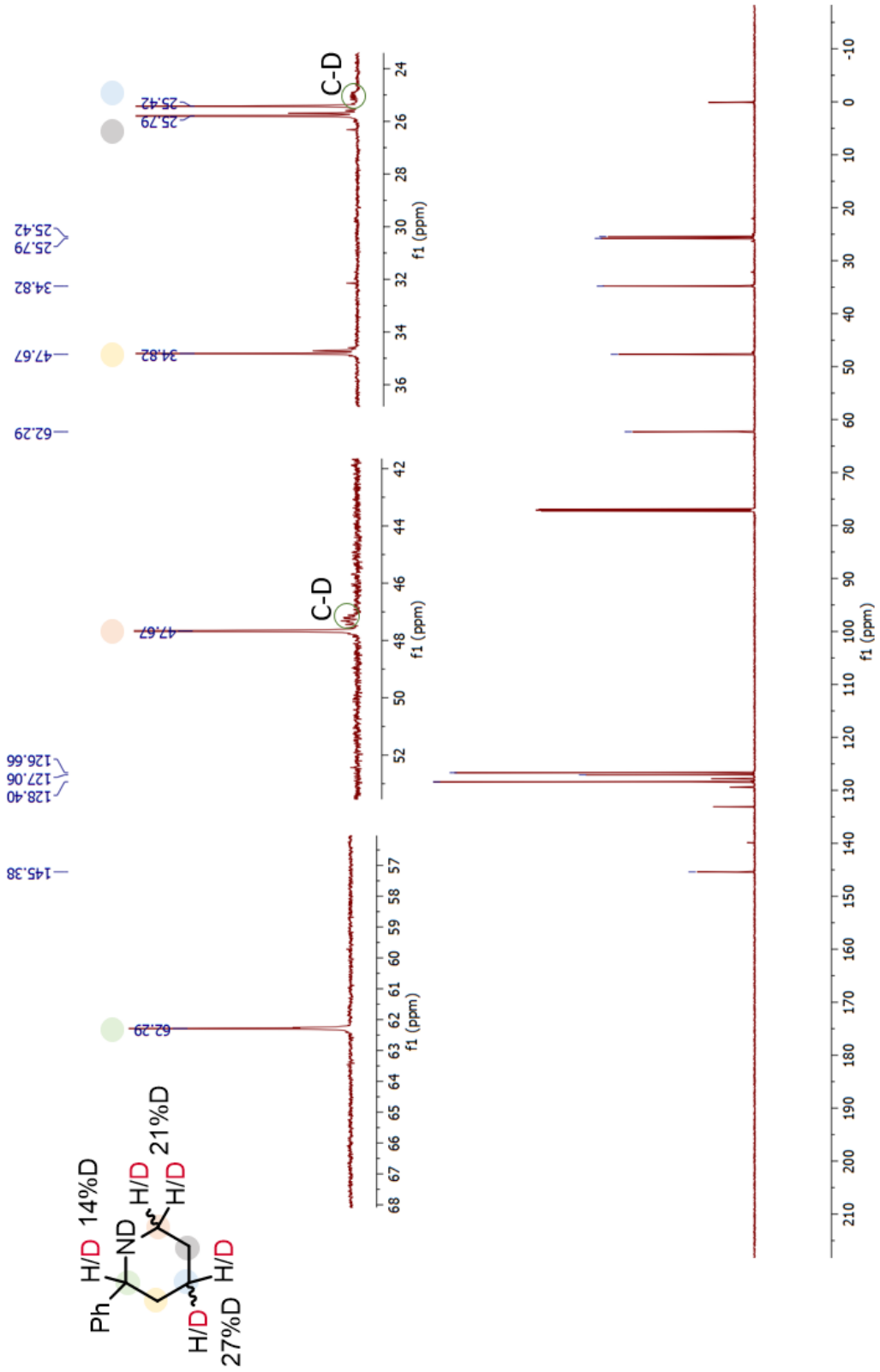


Figure S20. ^{13}C NMR (176 MHz) of deuterated product in $CDCl_3/D_2O$

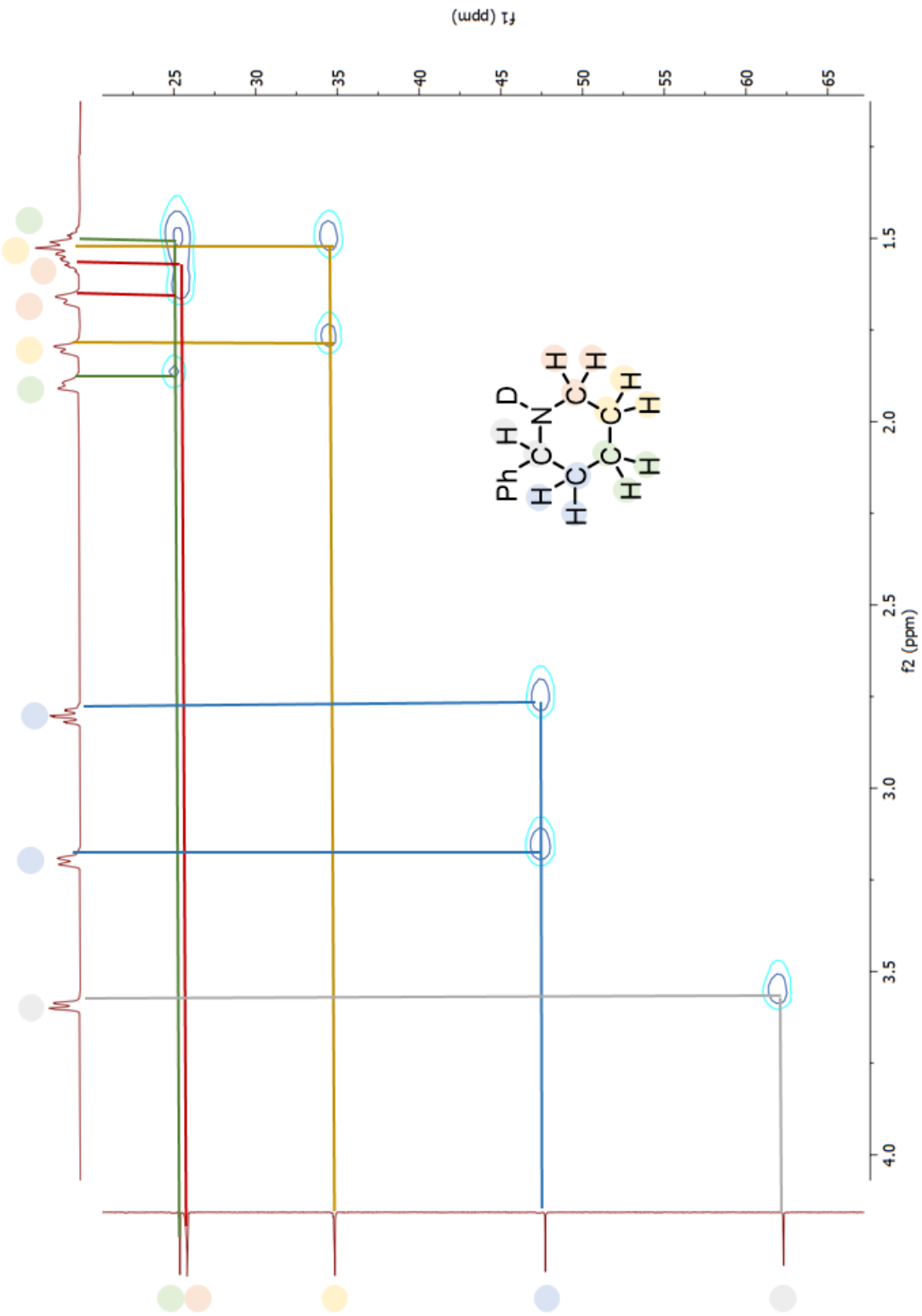


Figure S21. HMBC of deuterated product in $CDCl_3/D_2O$

7. References

[1] Labonne, A.; Kribber, T.; Hintermann, L., Highly Active in Situ Catalysts for Anti-Markovnikov Hydration of Terminal Alkynes. *Org. Lett.* 2006, *8*, 5853-5856.

[2] Bielawski, M., Aili, D., and Olofsson, B., Regiospecific One-Pot Synthesis of Diaryliodonium Tetrafluoroborates from Arylboronic Acids and Aryl Iodides, *J. Org. Chem*. 2008, *73*, 12, 4602-4607.

[3] Eisenberger, P., Bestvater, B. P., Keske, E. C., and Crudden, C. M., Hydrogenations at room temperature and atmospheric pressure with mesoionic carbene-stabilized borenium catalysts, *Angew. Chem. Int. Ed.* 2015, *54*, 2467-2471.

[4] N. Gandhamsetty, S. Park and S. Chang, Selective Silylative Reduction of Pyridines Leading to Structurally Diverse Azacyclic Compounds with the Formation of sp^3 C–Si Bonds, *J. Am. Chem. Soc.* 2015, **137**, 15176-15184.

8. ^{1}H and ^{13}C NMR Spectra of Products

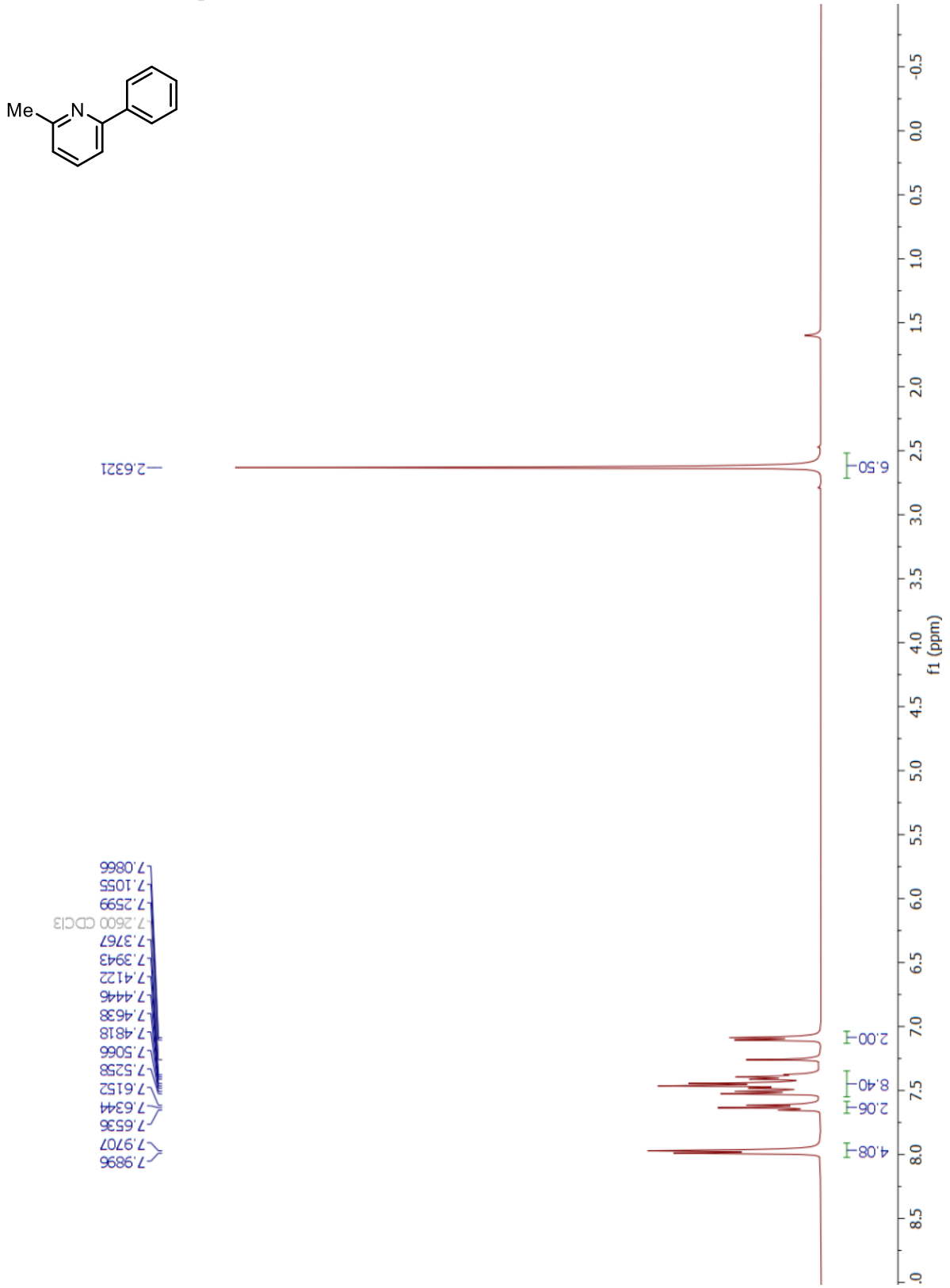


Figure S22. ^{1}H NMR (400 MHz) in $CDCl_3$ 7a

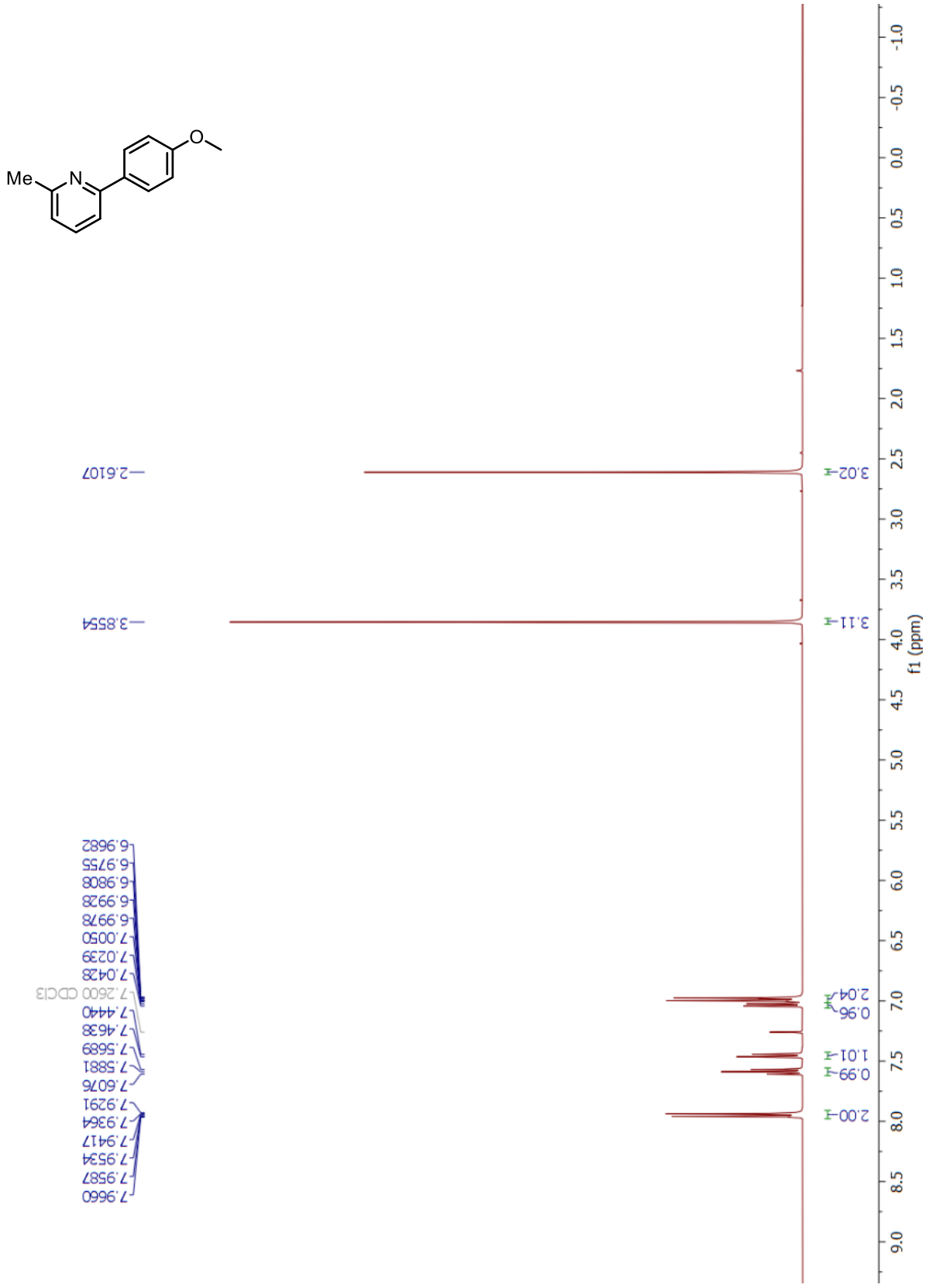


Figure S23. ^{1}H NMR (400 MHz) in $CDCl_3$ 7b

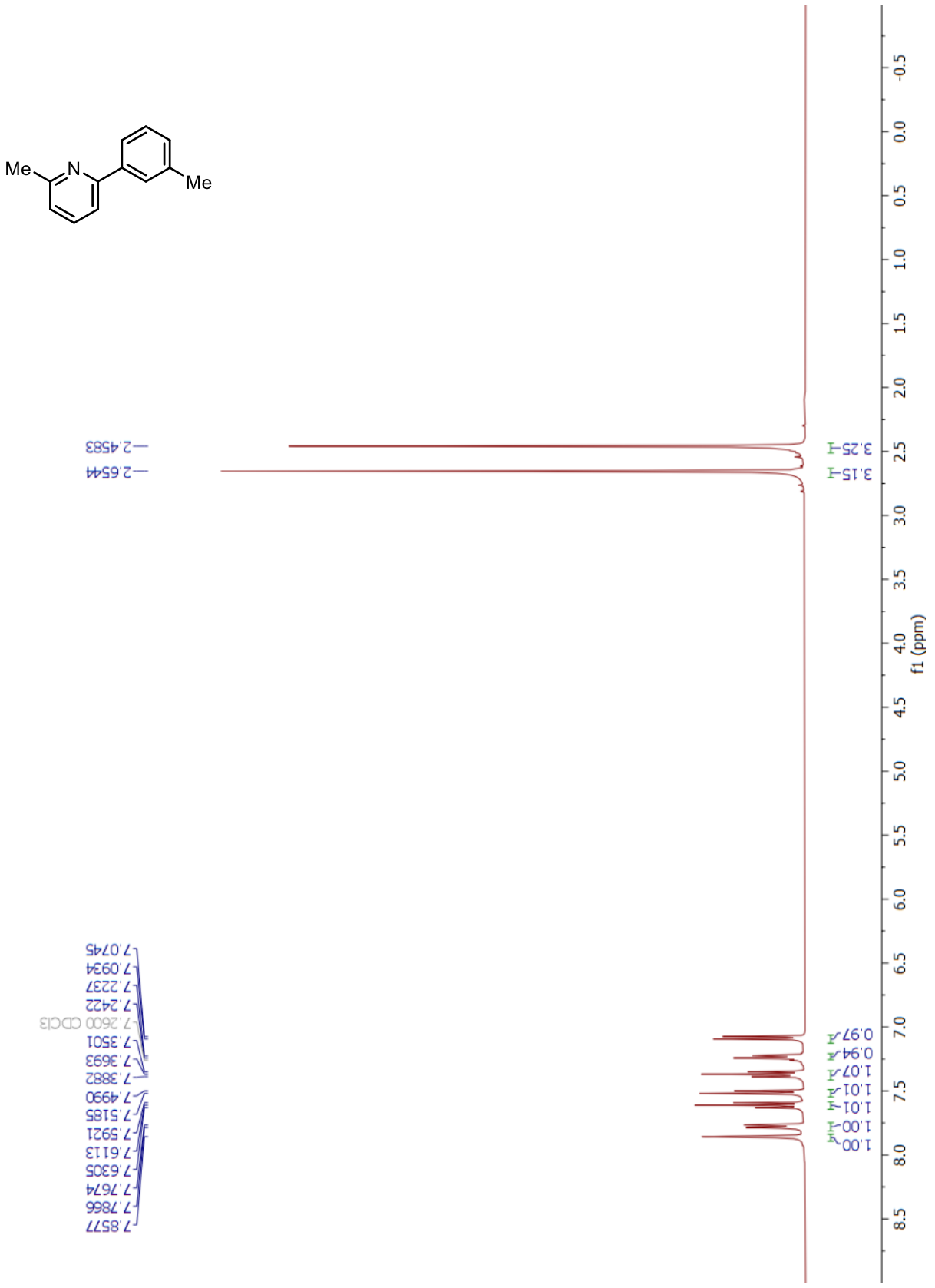


Figure S24. ^{1}H NMR (400 MHz) in $CDCl_3$ 7c

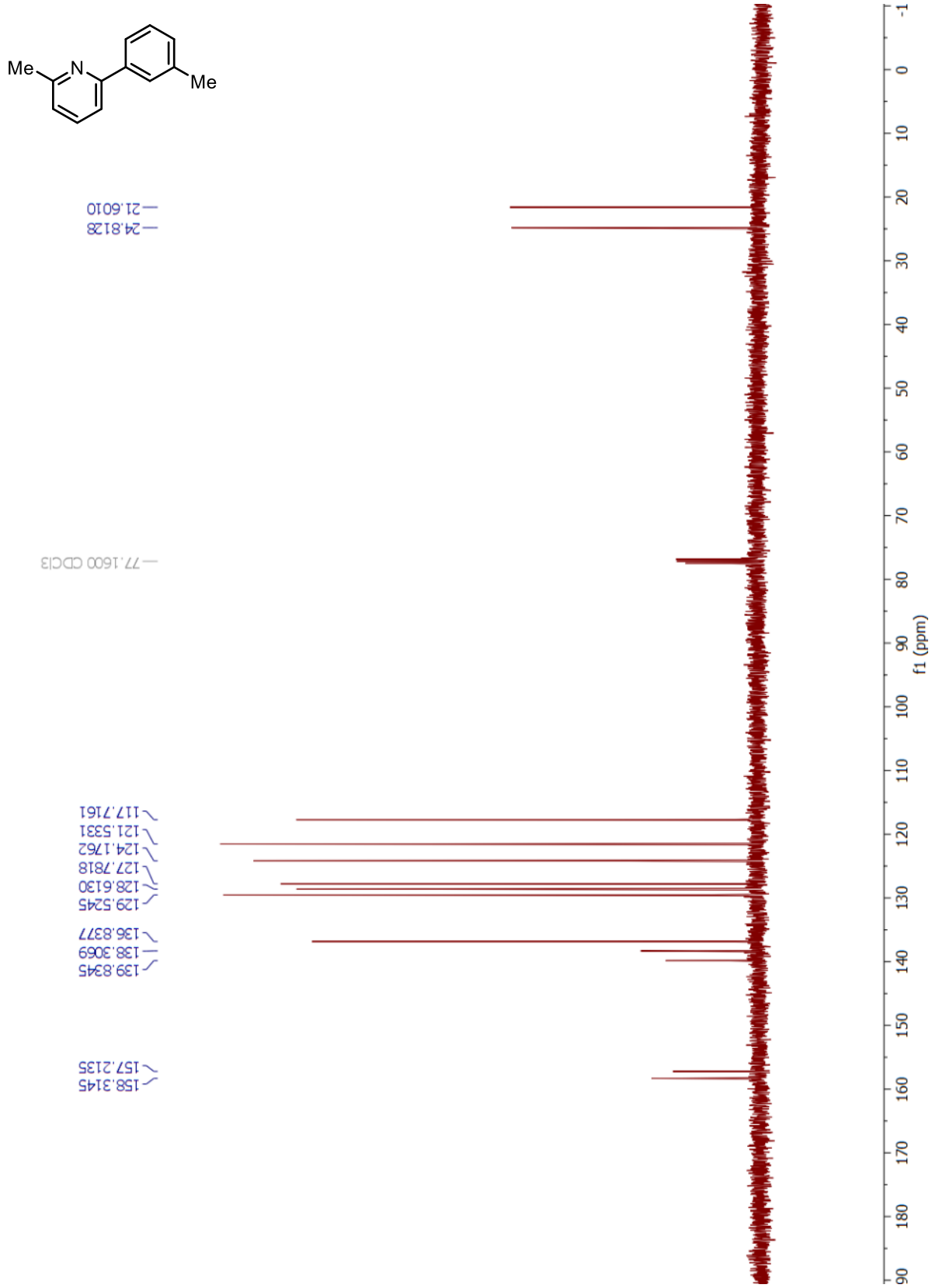


Figure S25. $^{13}C\{^{1}H\}$ NMR (101 MHz) in $CDCl_3$ 7c

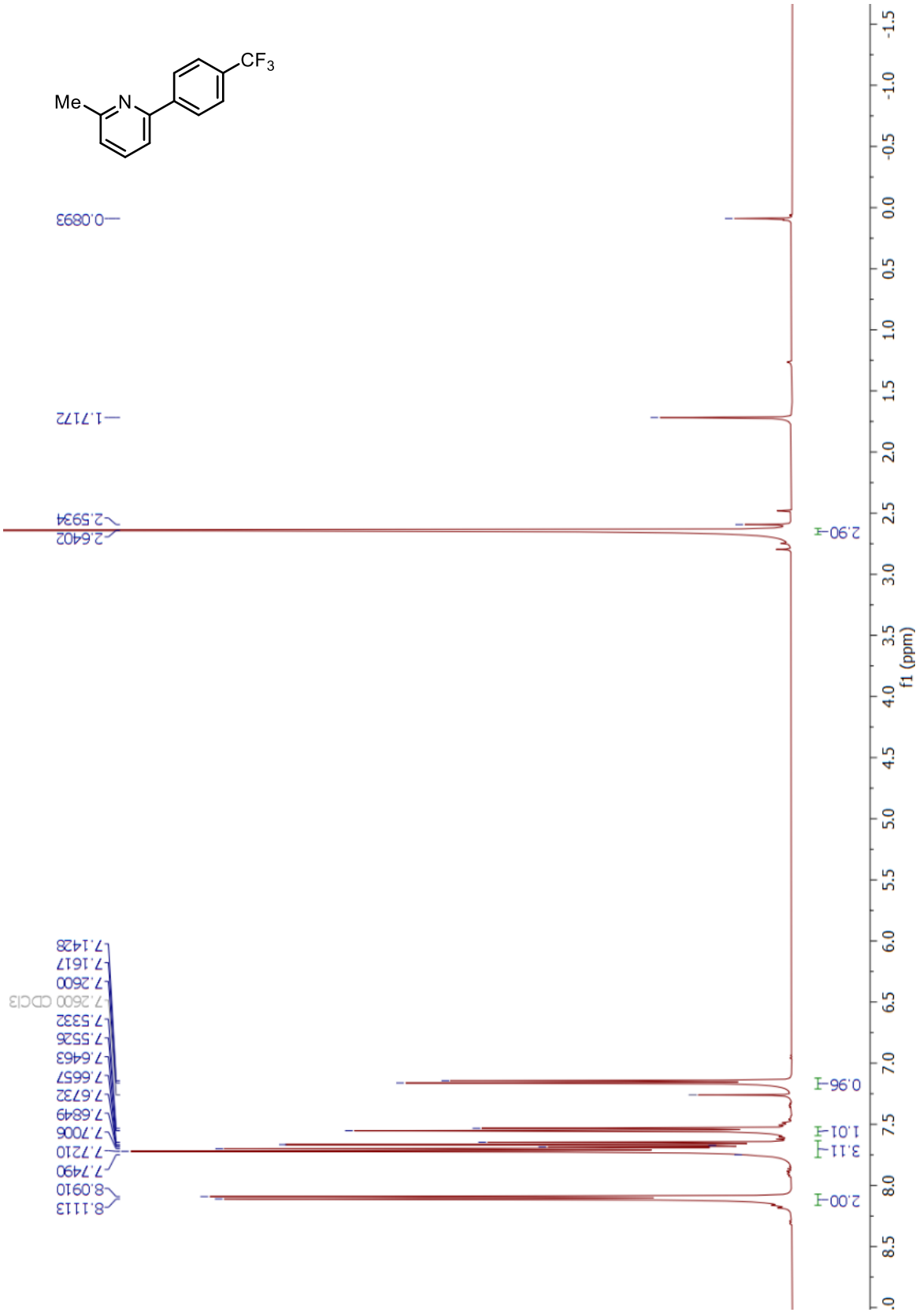


Figure S26. ^{1}H NMR (400 MHz) in $CDCl_3$ 7d

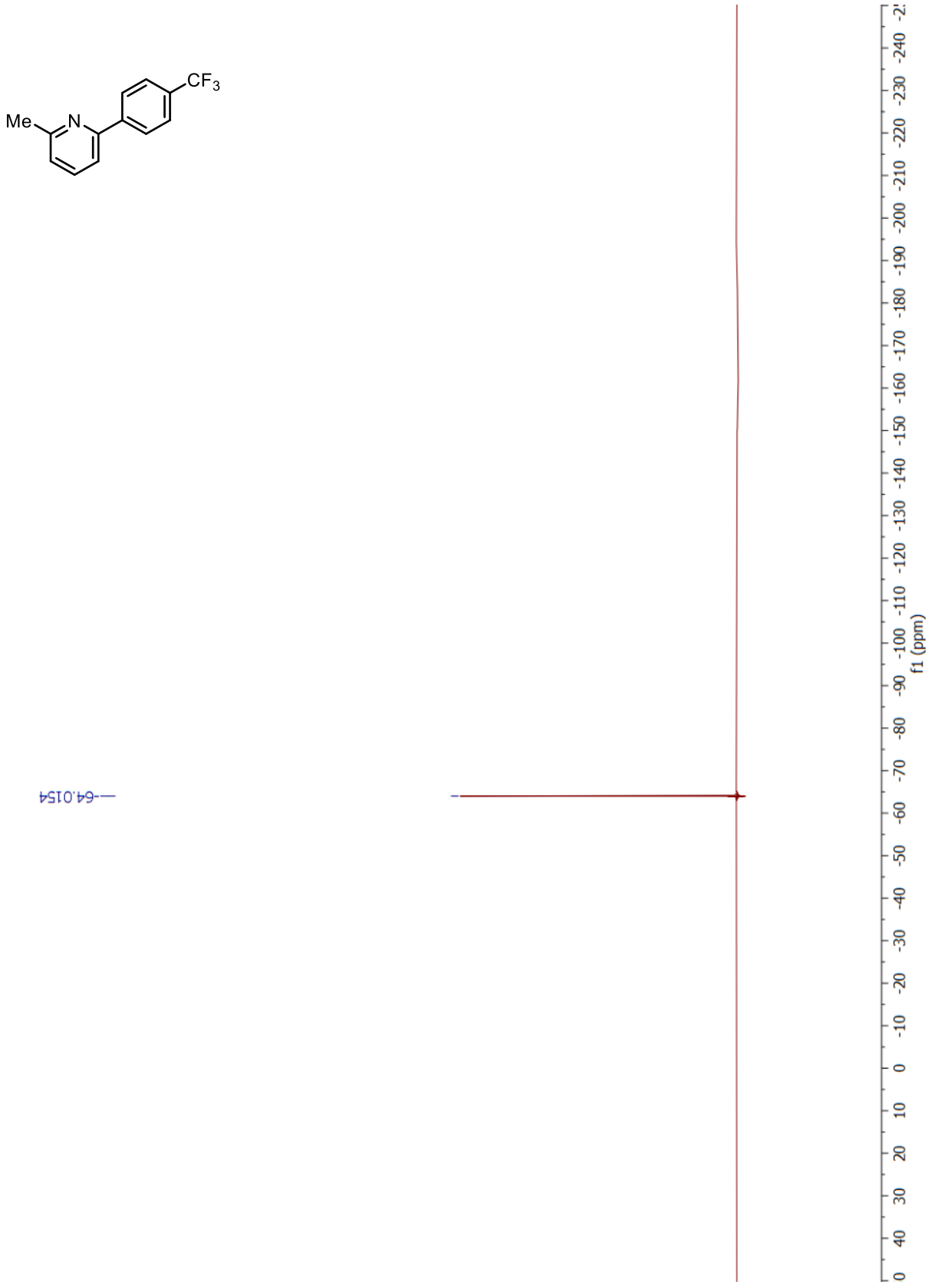


Figure S27. ^{19}F NMR (376 MHz) in $CDCl_3$ 7d

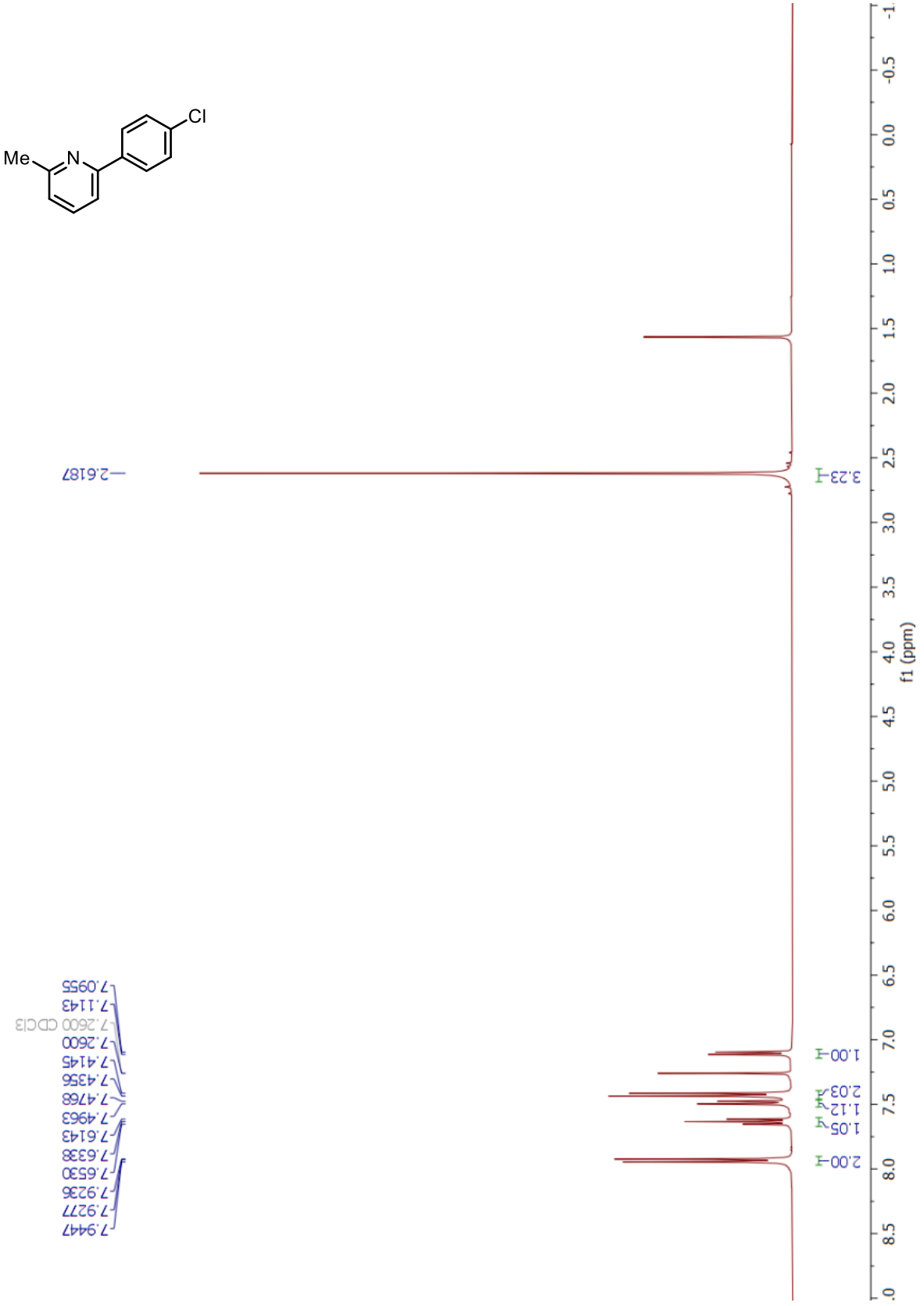


Figure S28. ^{1}H NMR (400 MHz) in $CDCl_3$ 7e

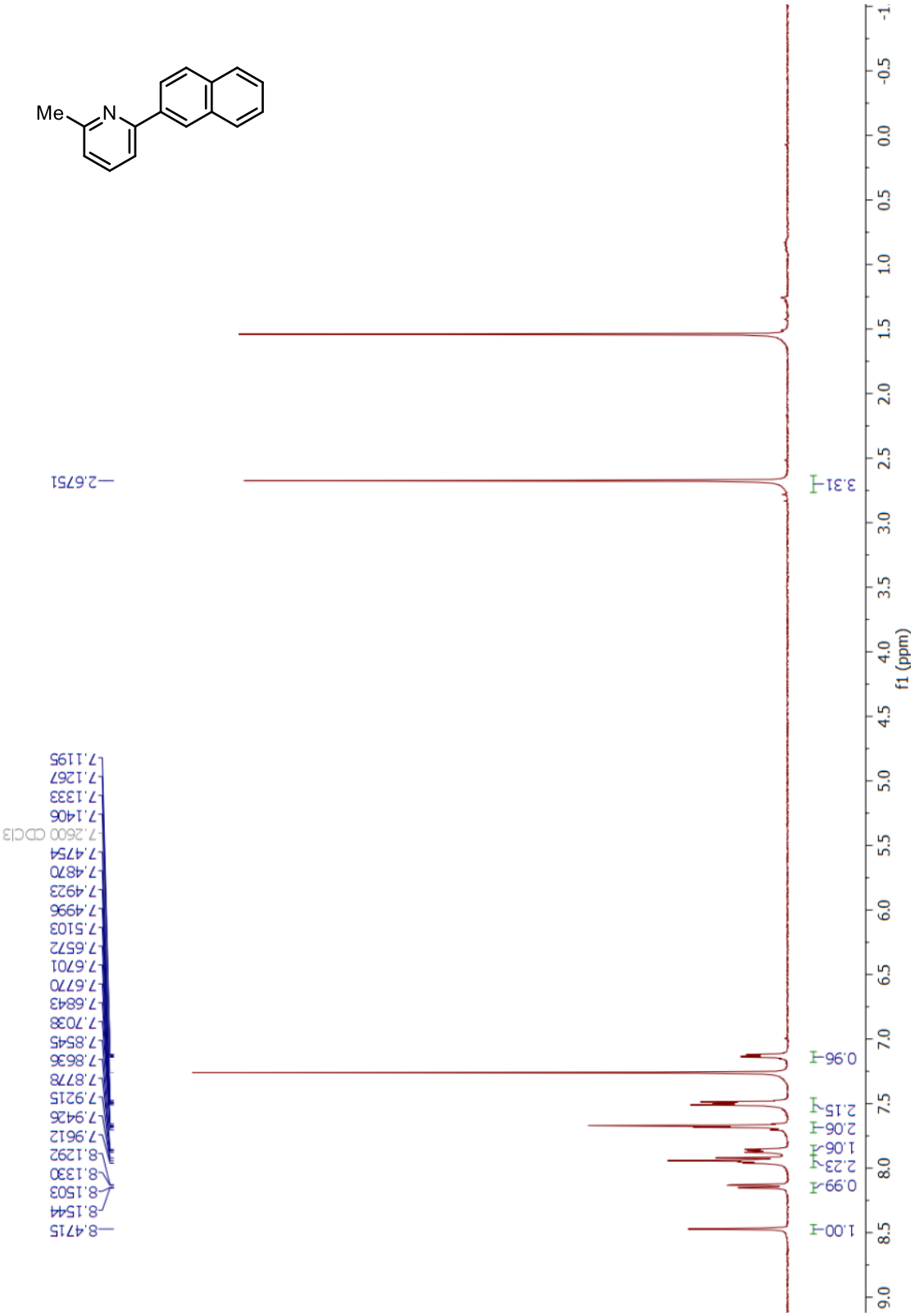


Figure S29. ^{1}H NMR (400 MHz) in $CDCl_3$ 7f

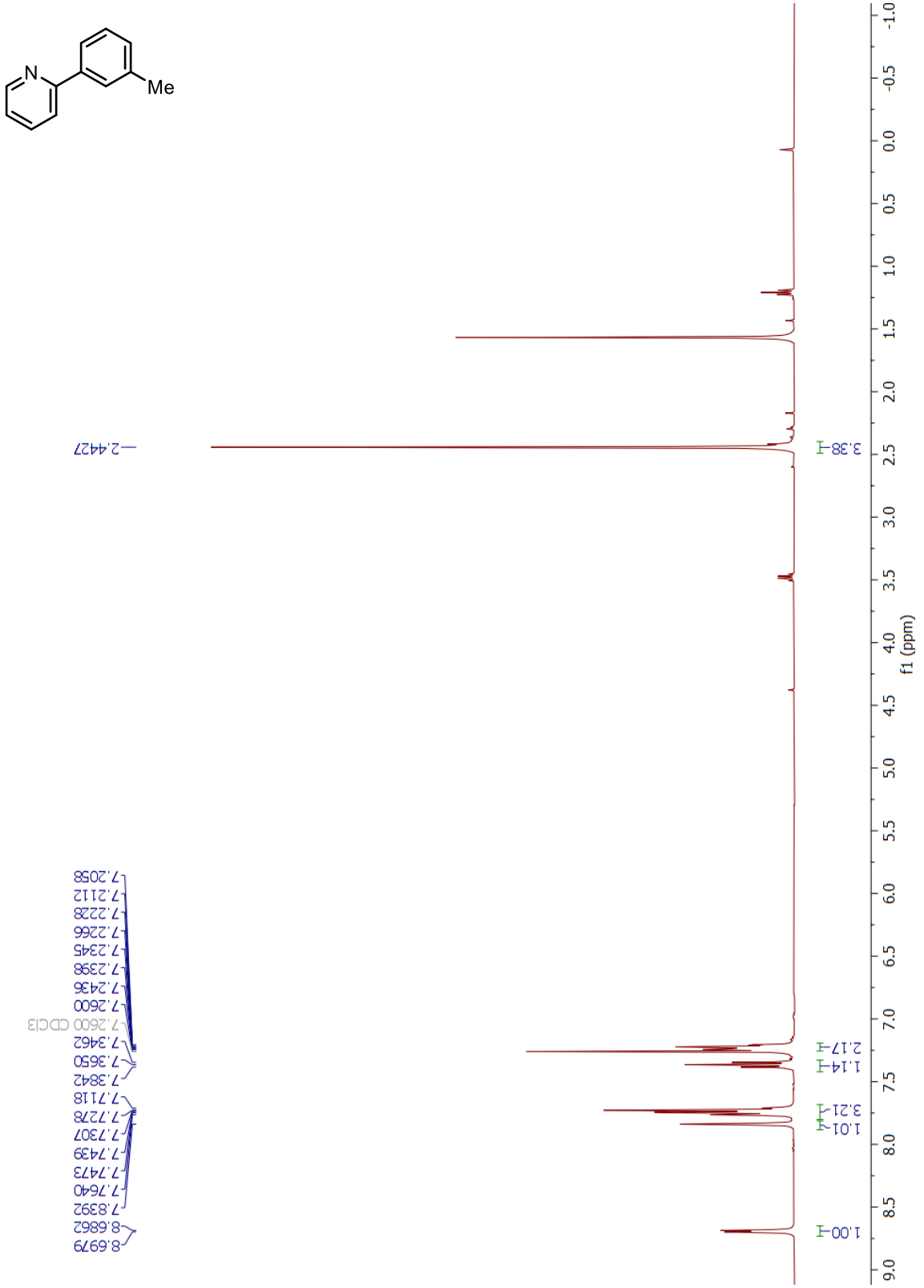


Figure S30. ^{1}H NMR (400 MHz) in $CDCl_3$ 9b

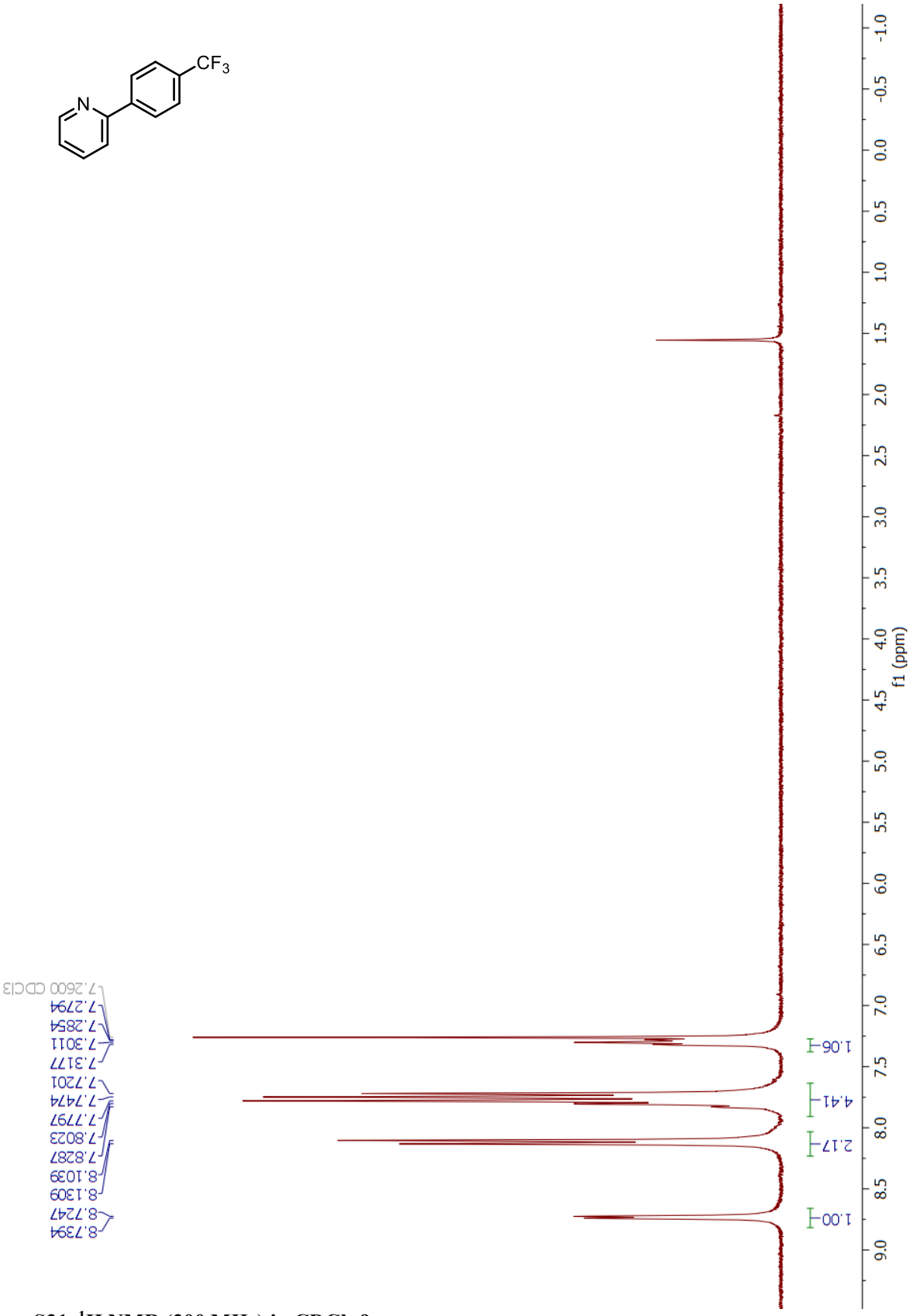


Figure S31. ^{1}H NMR (300 MHz) in $CDCl_3$ 9c

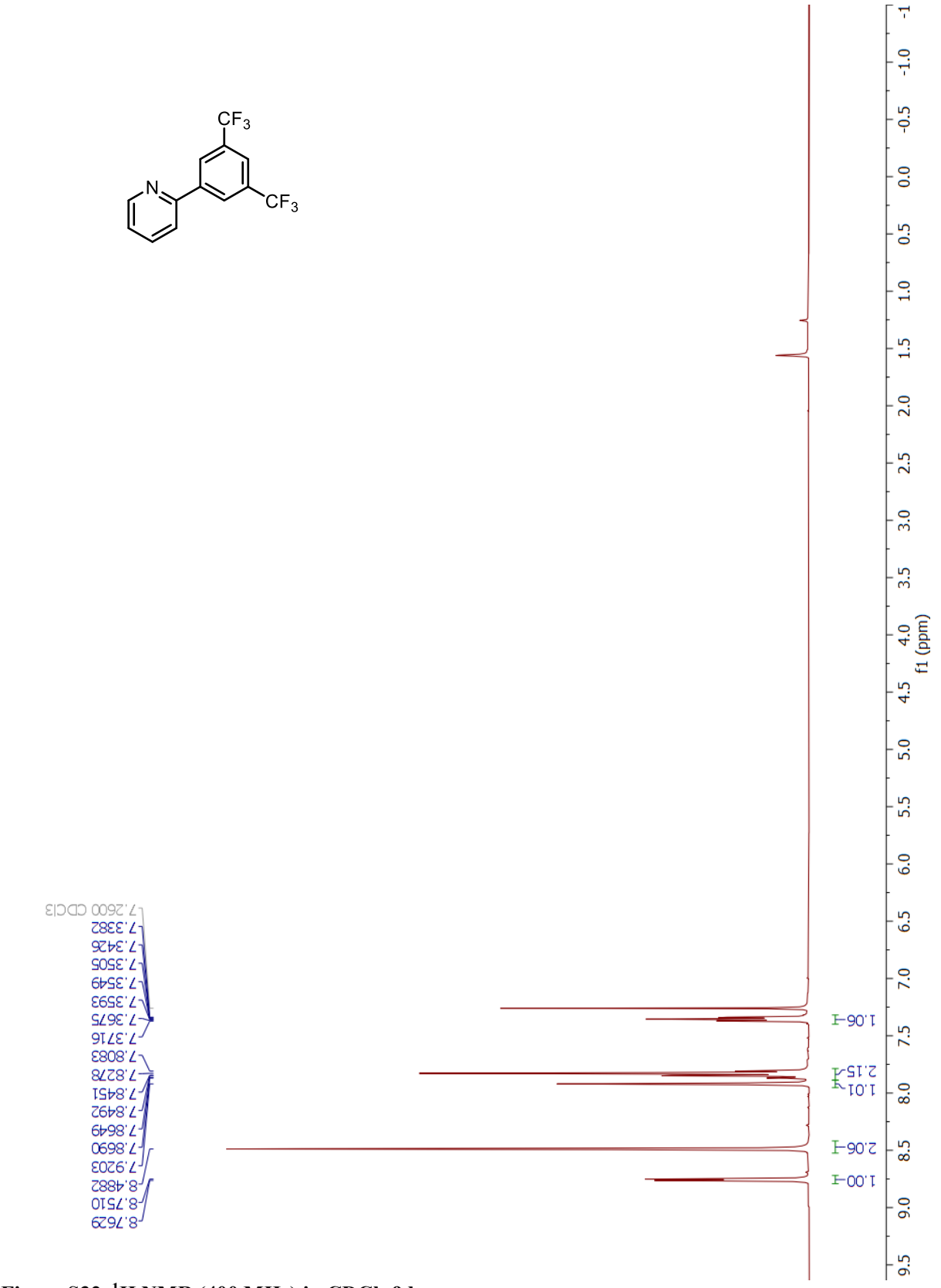


Figure S32. ^{1}H NMR (400 MHz) in $CDCl_3$ 9d

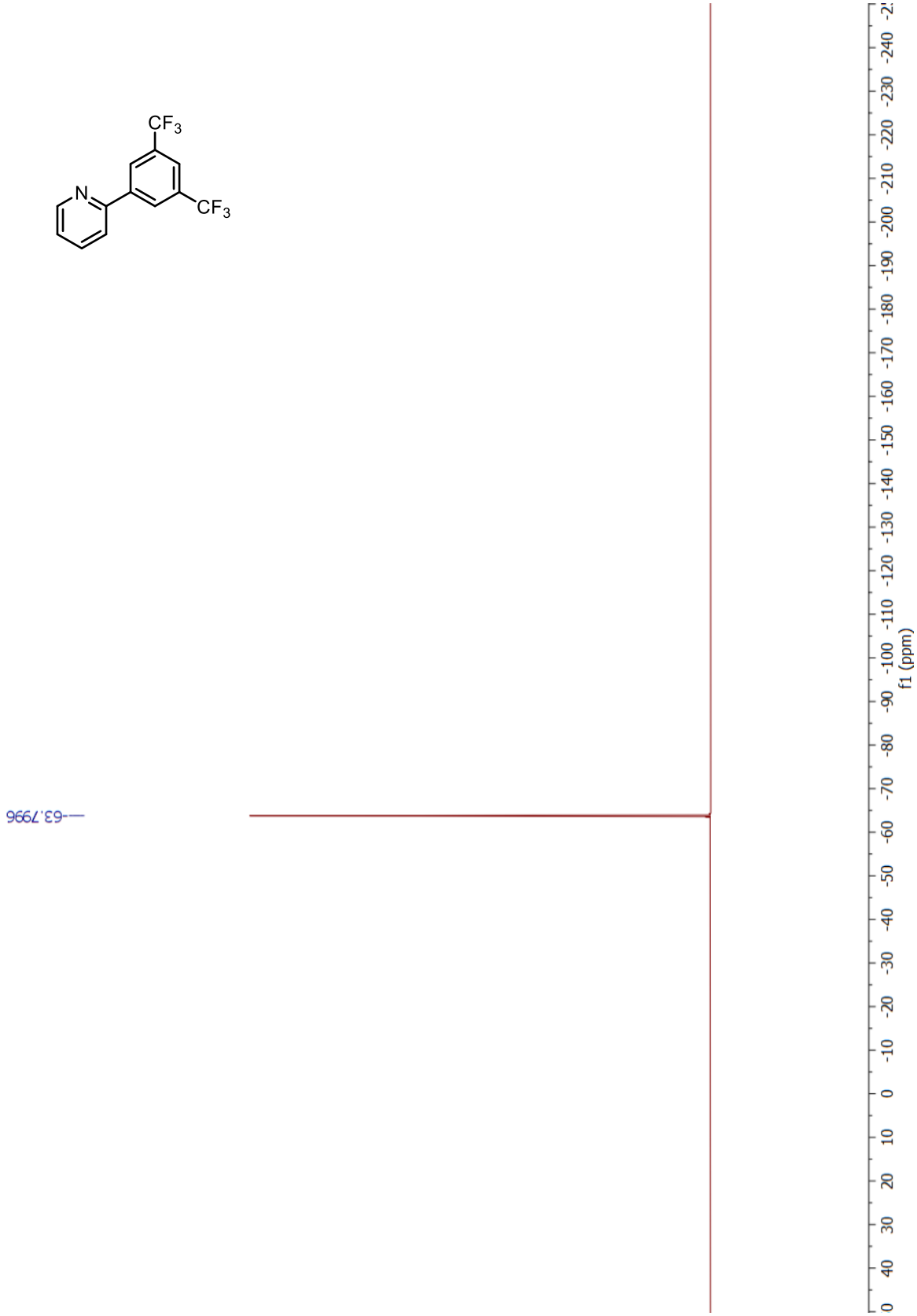


Figure S33. ^{19}F NMR (376 MHz) in $CDCl_3$ 9d

Spectra of Piperidine Products

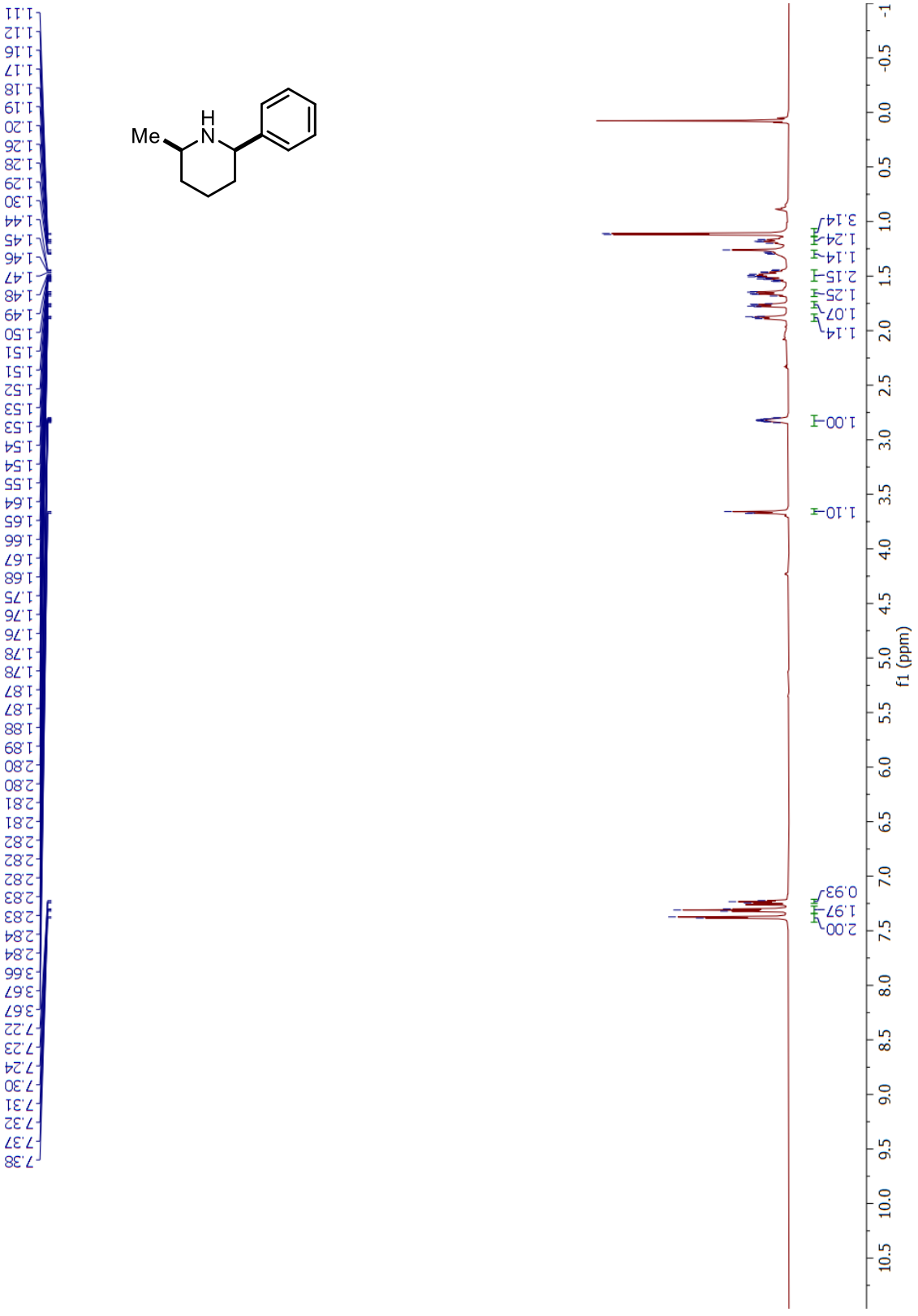


Figure S34. ^{1}H NMR (700 MHz) in $CDCl_3$ 8a

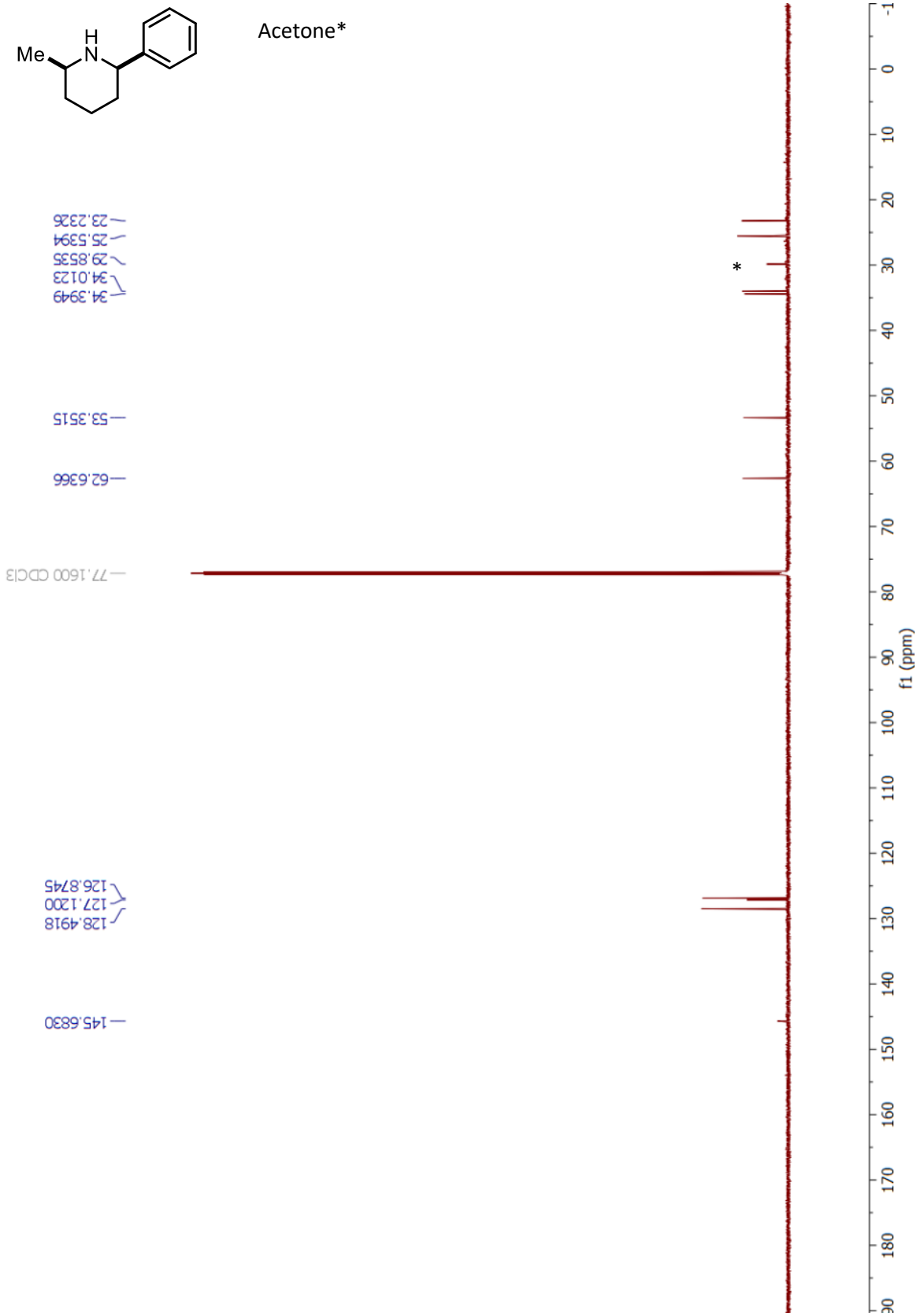


Figure S35. $^{13}C\{^{1}H\}$ NMR (176 MHz) in $CDCl_3$ 8a

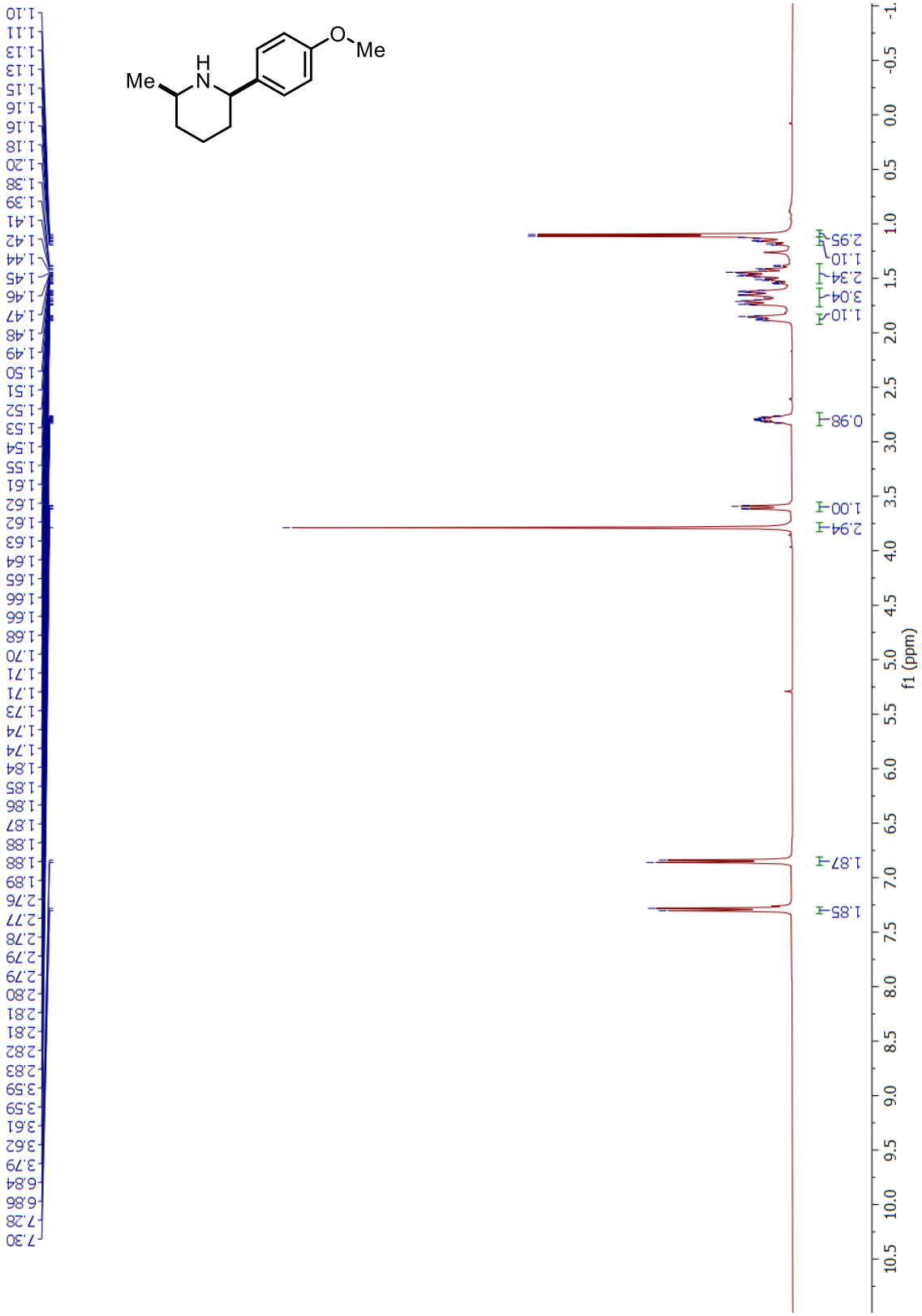


Figure S36. ^{1}H NMR (400 MHz) in $CDCl_3$ 8b

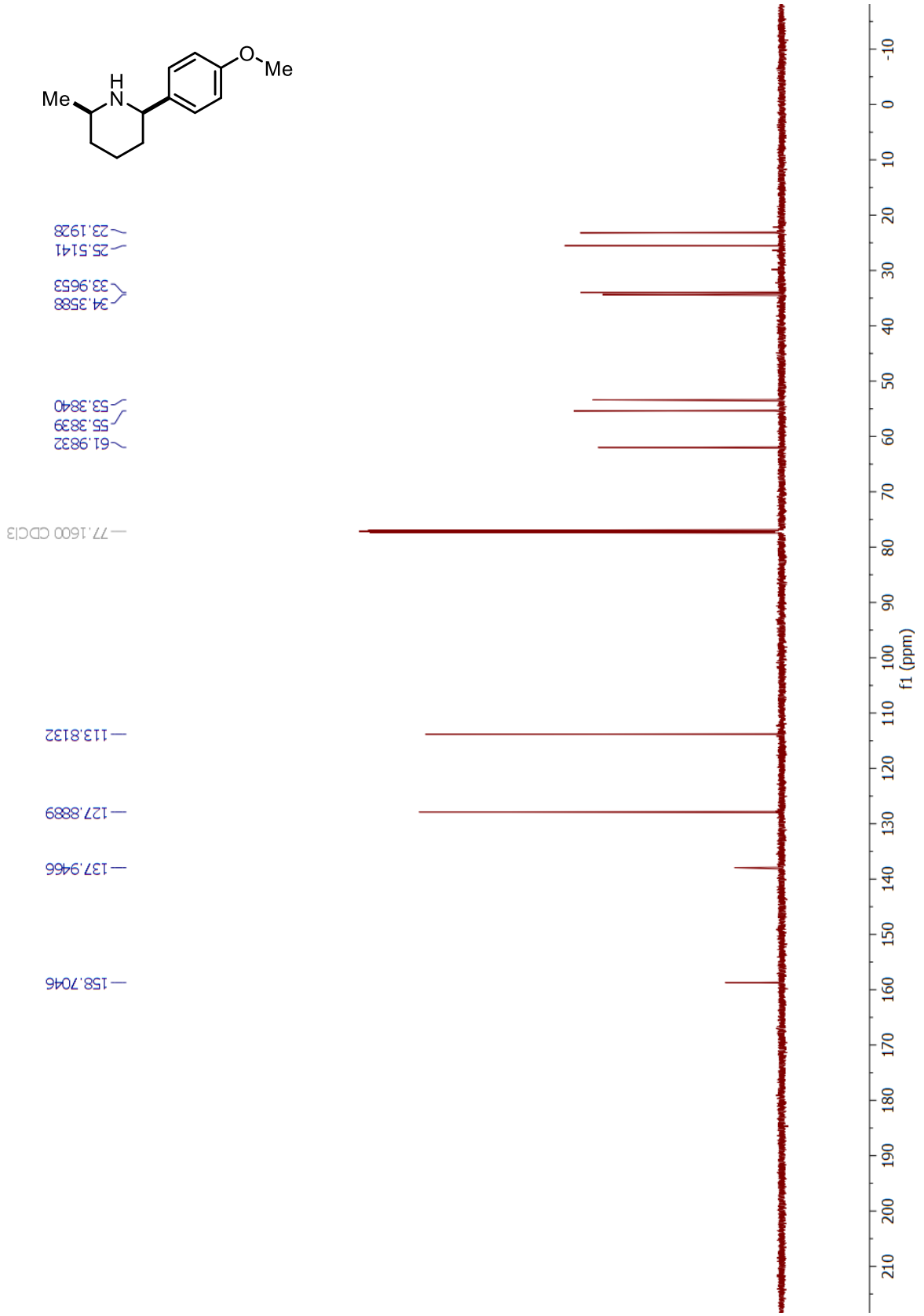


Figure S37. $^{13}C\{^{1}H\}$ NMR (176 MHz) in $CDCl_3$ 8b

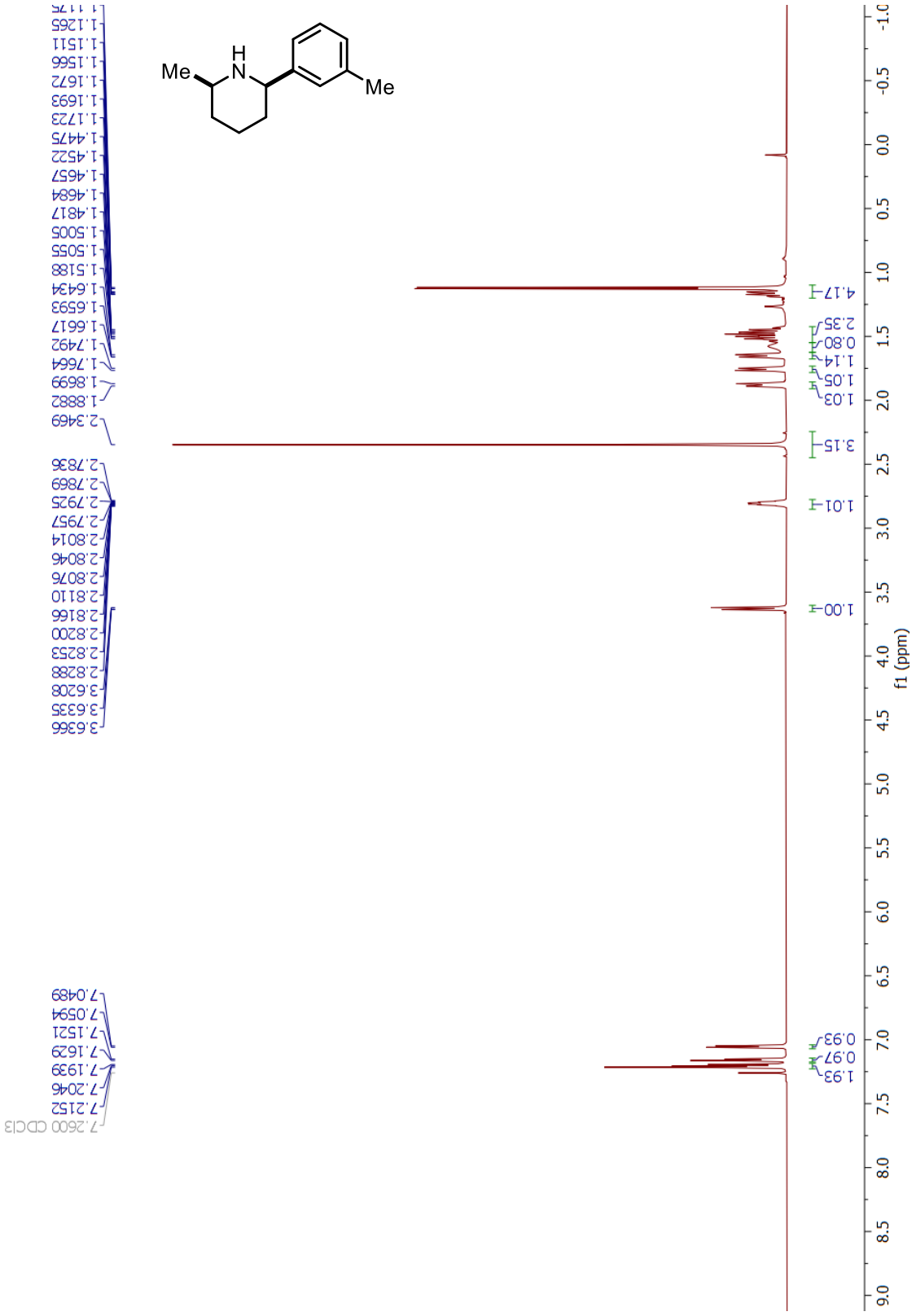


Figure S38. ^{1}H NMR (700MHz) in $CDCl_3$ 8c

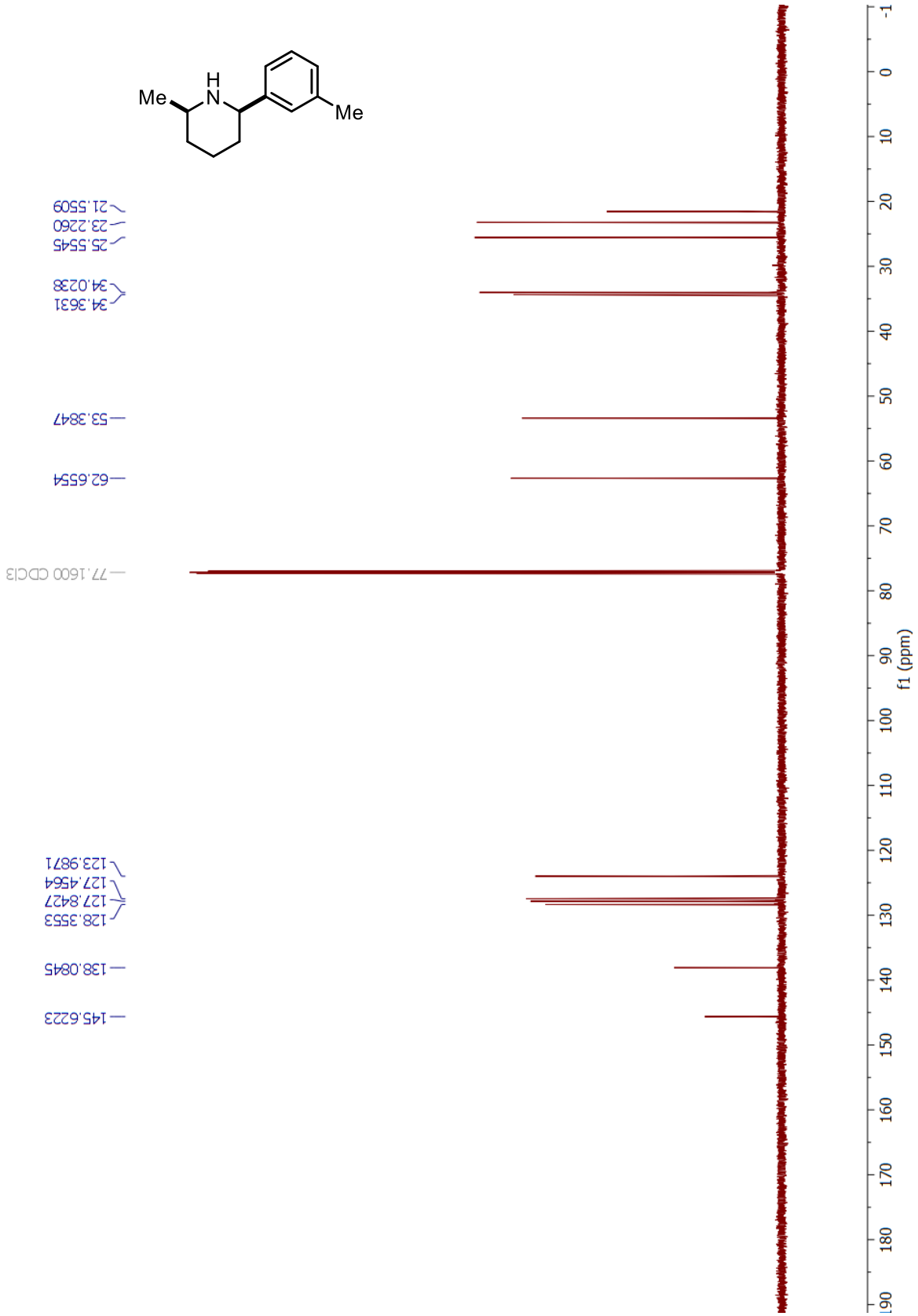


Figure S39. $^{13}C\{^{1}H\}$ NMR (176 MHz) in $CDCl_3$ 8c

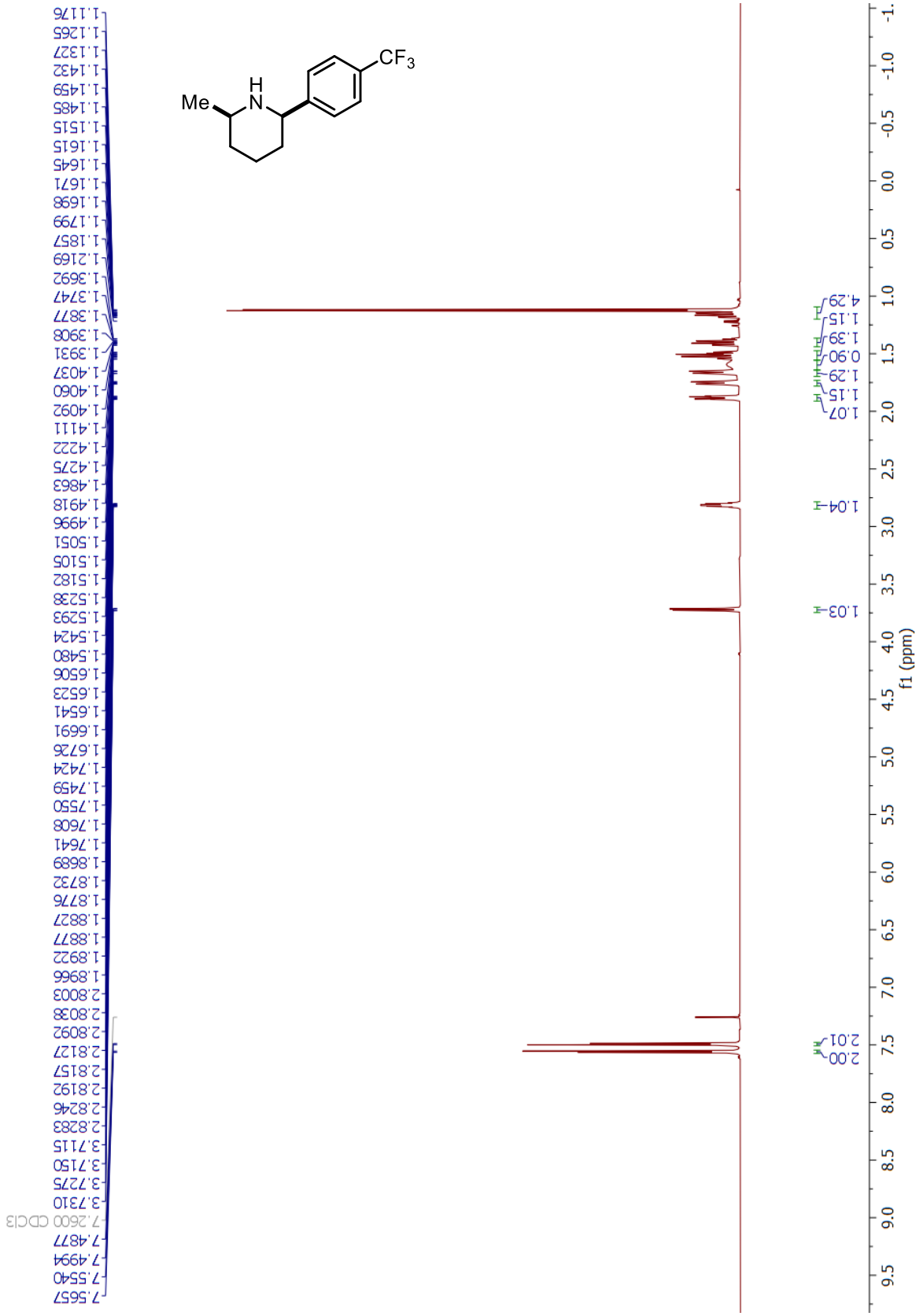


Figure S40. ^{1}H NMR (700MHz) in $CDCl_3$ 8d

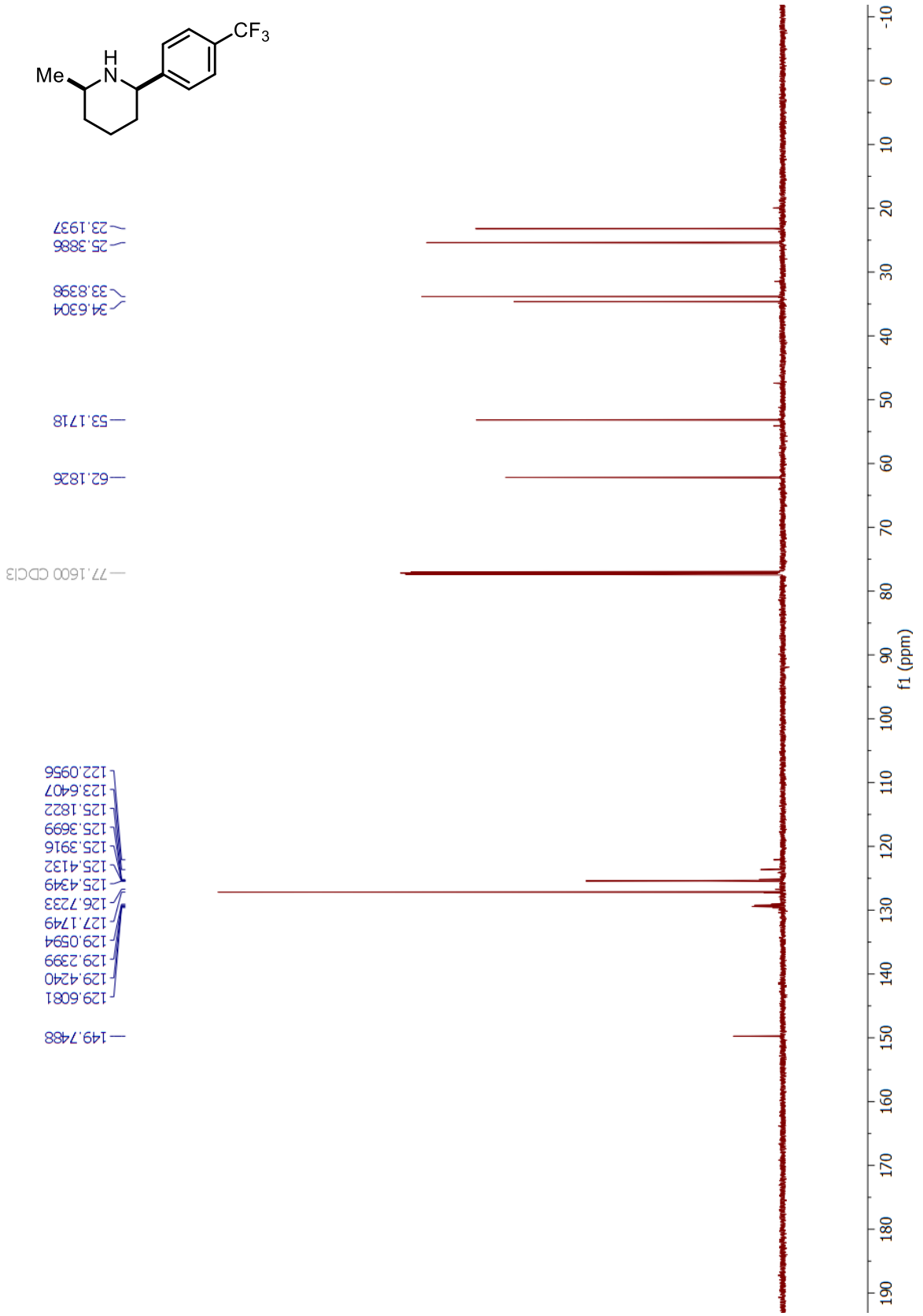


Figure S41. $^{13}C\{^{1}H\}$ NMR (176 MHz) in $CDCl_3$ 8d

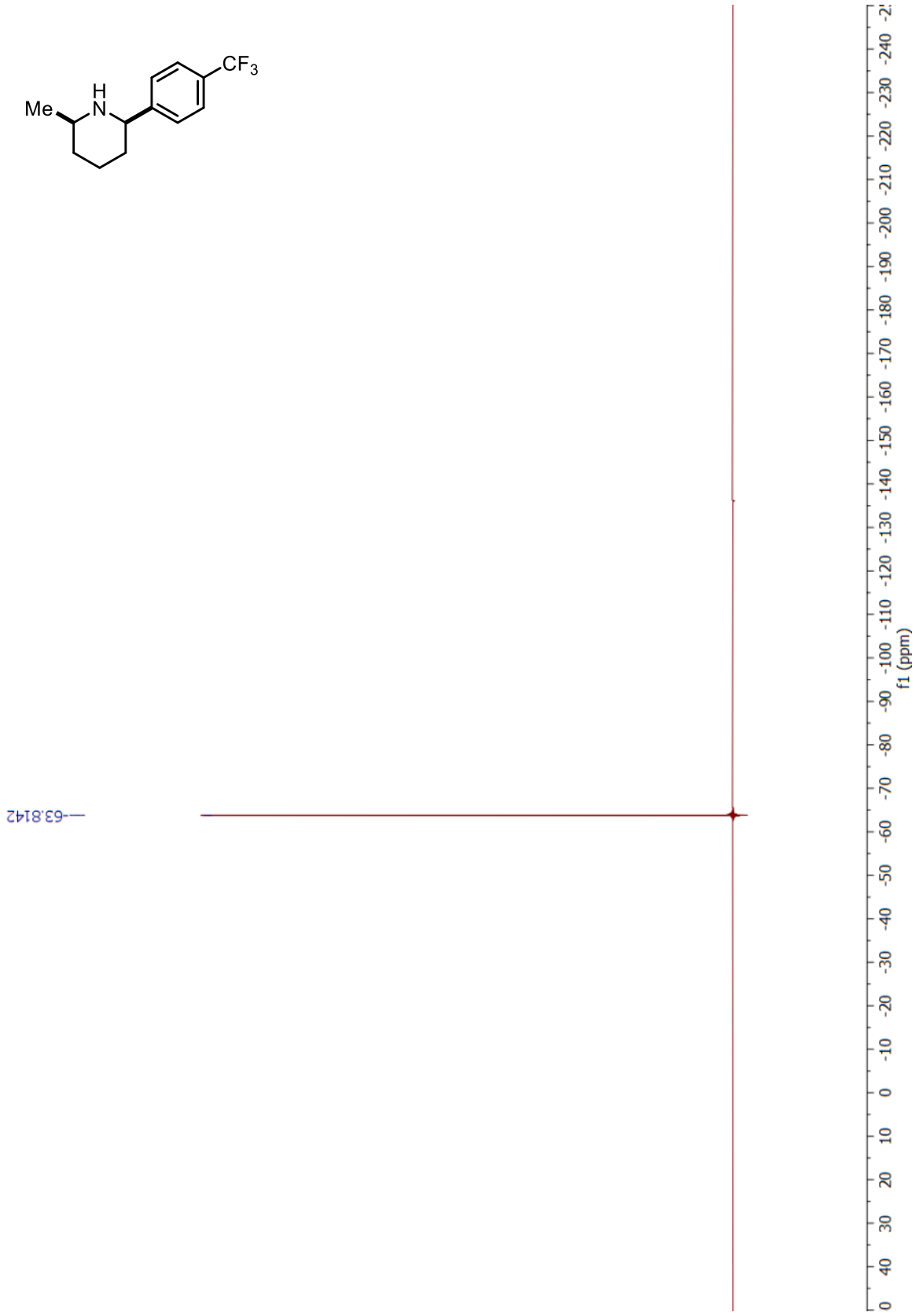


Figure S42. ^{19}F NMR (376 MHz) in $CDCl_3$ 8d

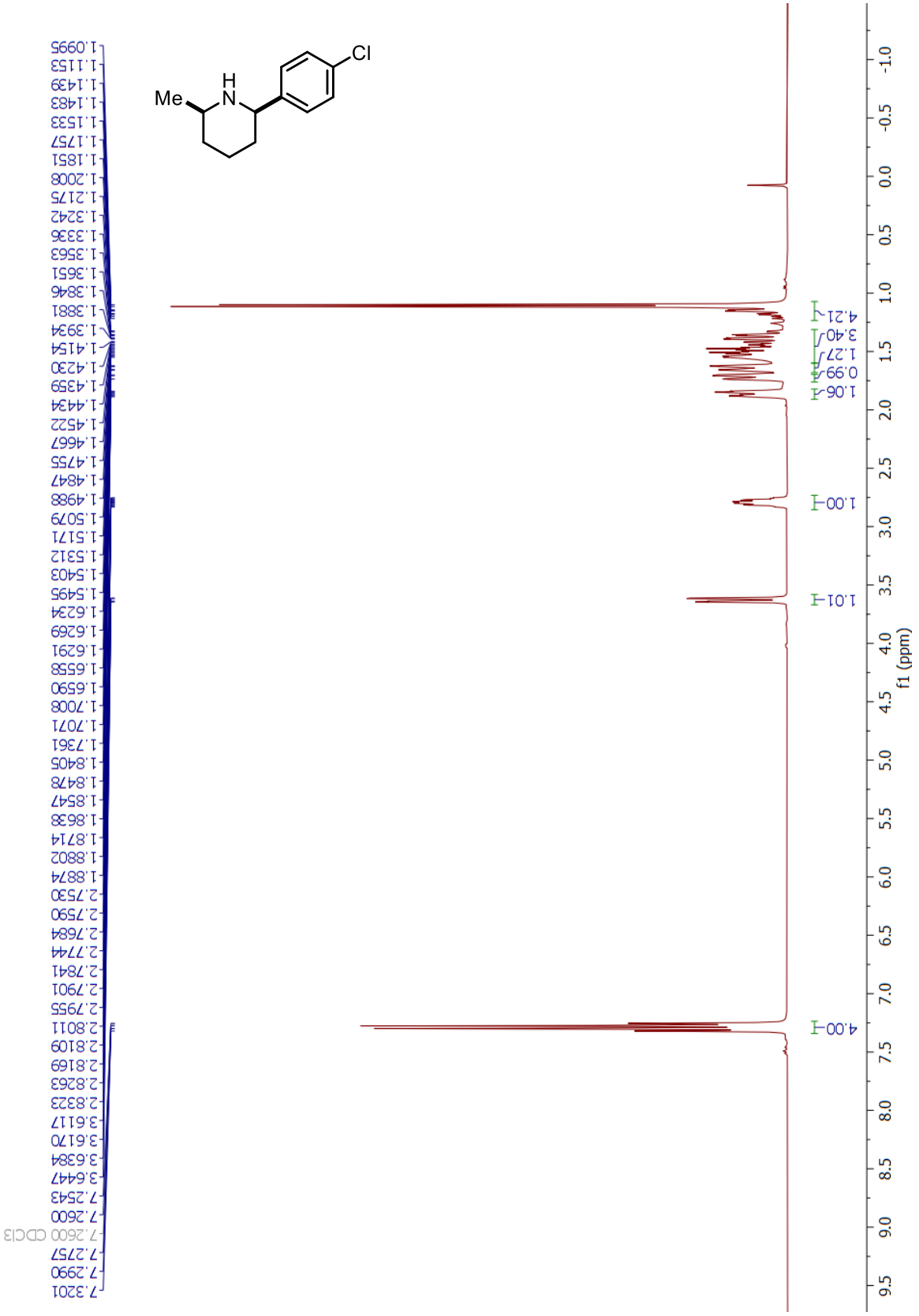


Figure S43. ^{1}H NMR (400 MHz) in $CDCl_3$ 8e

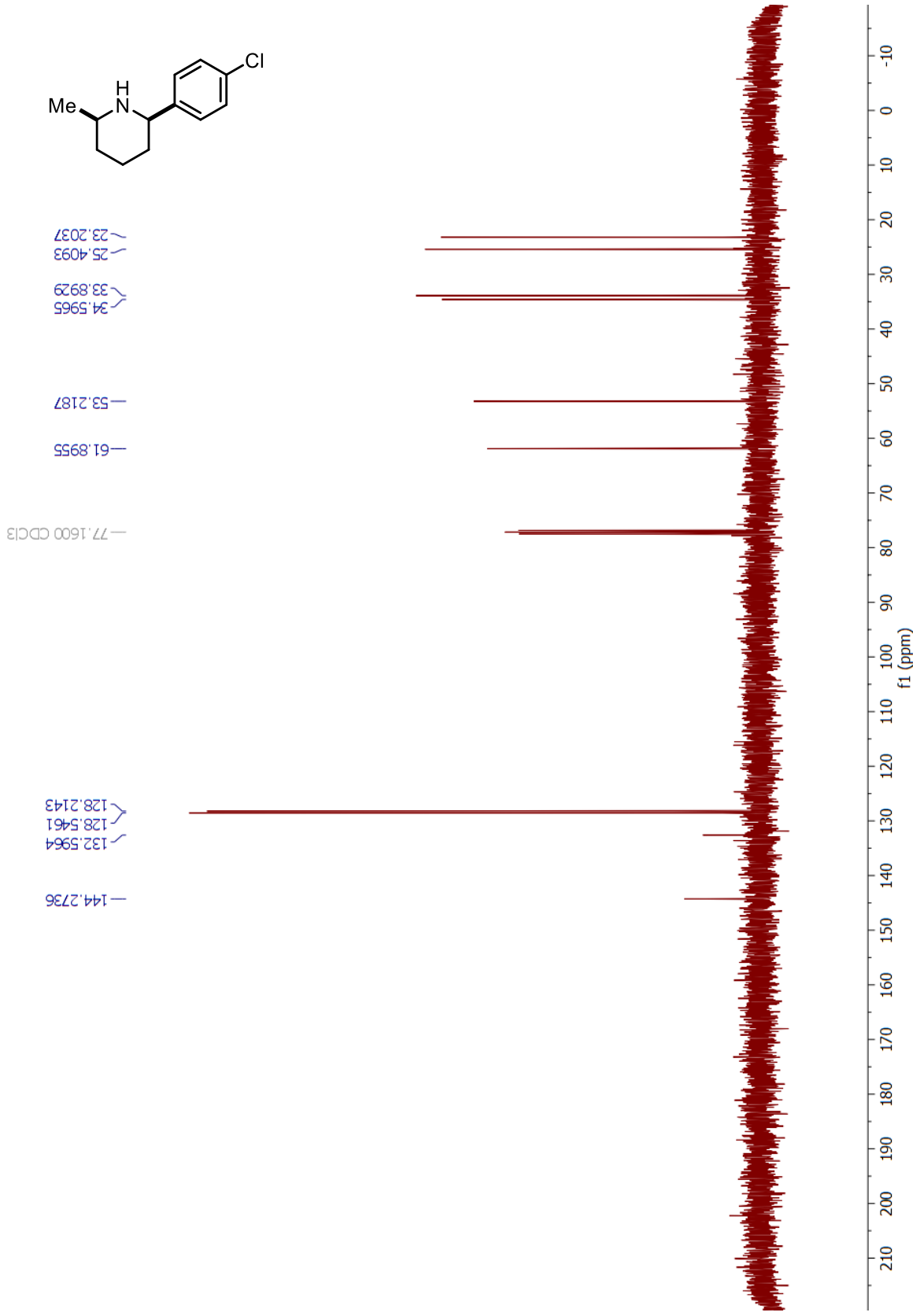


Figure S44. $^{13}C\{^{1}H\}$ NMR (101 MHz) in $CDCl_3$ 8e

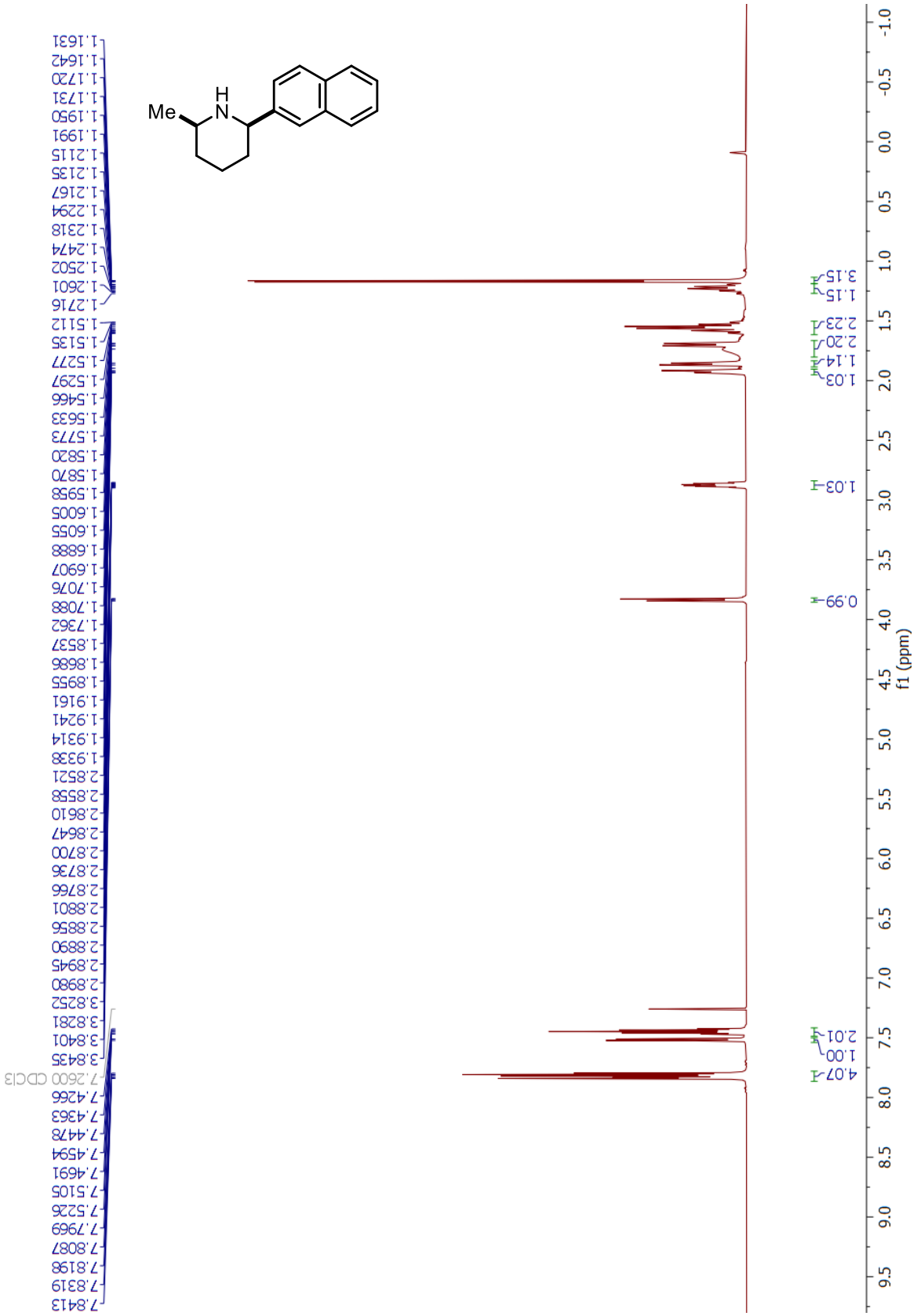


Figure S45. ^{1}H NMR (700MHz) in $CDCl_3$ 8f

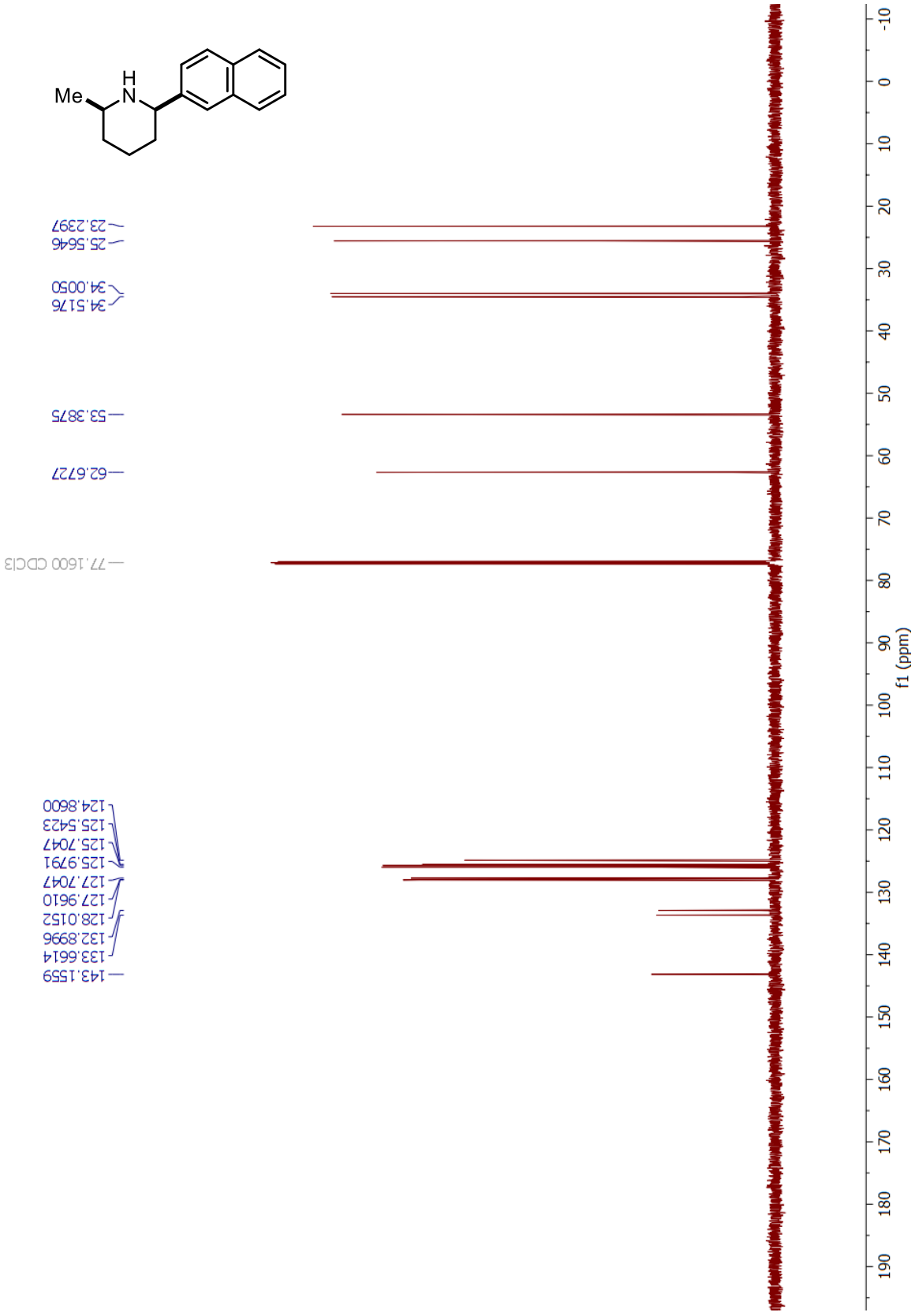
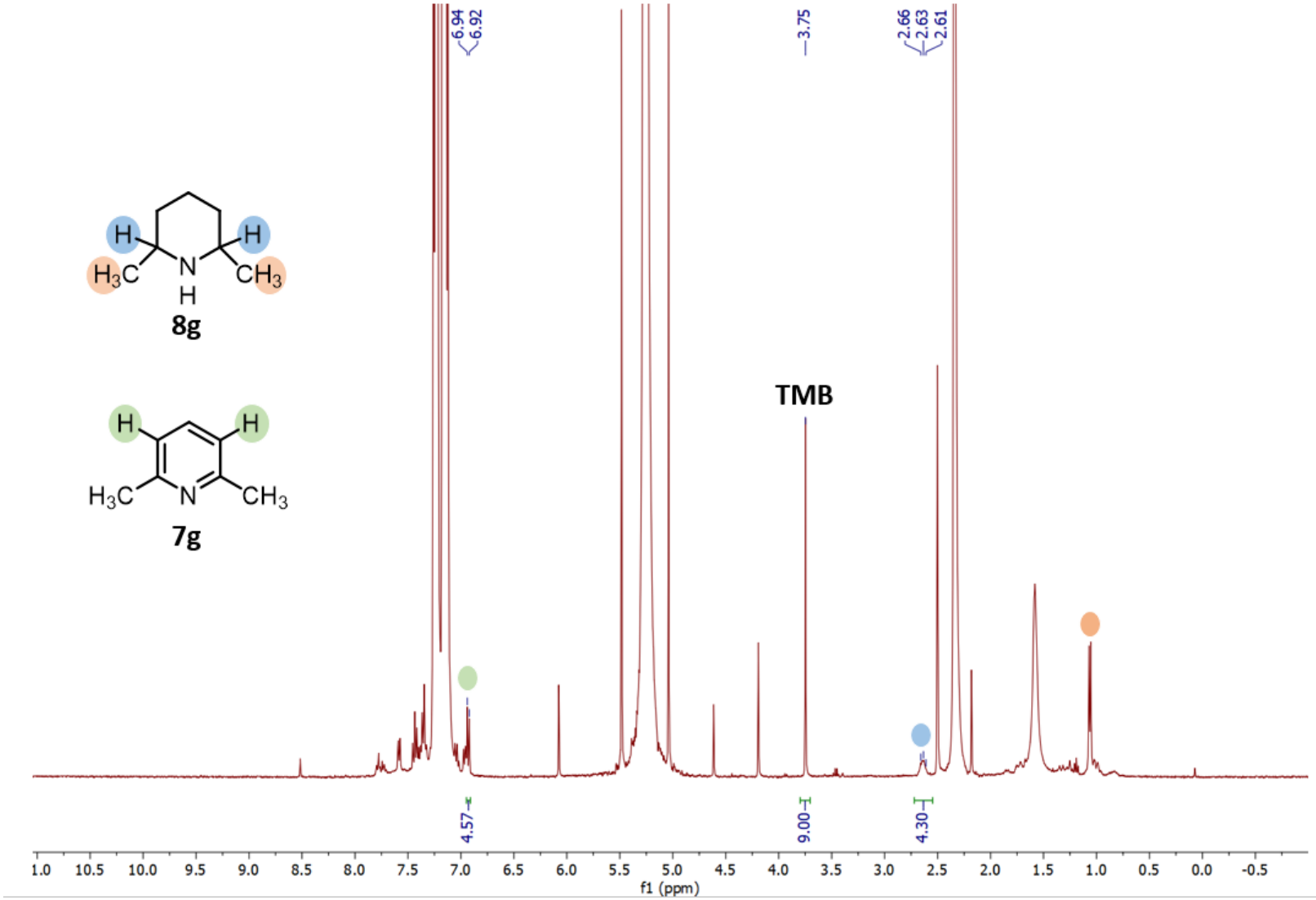


Figure S46. $^{13}C\{^{1}H\}$ NMR (176 MHz) in $CDCl_3$ 8f



8g

7g

Figure S47. ^{1}H NMR (400MHz) in $CDCl_3$ 8g (TMB = 1,3,5-trimethoxy benzene)

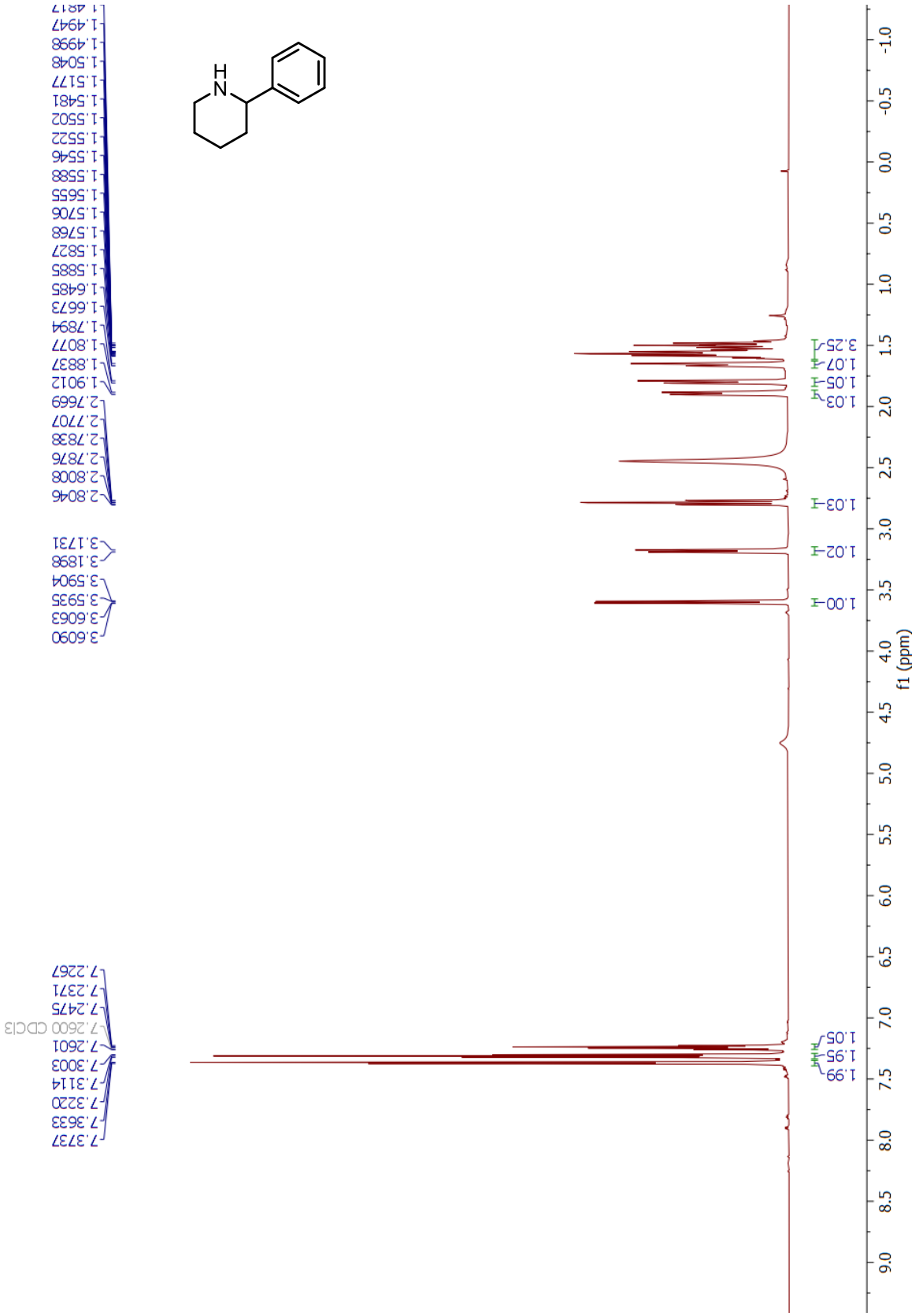


Figure S48. ^{1}H NMR (700 MHz) in $CDCl_3$ 10a

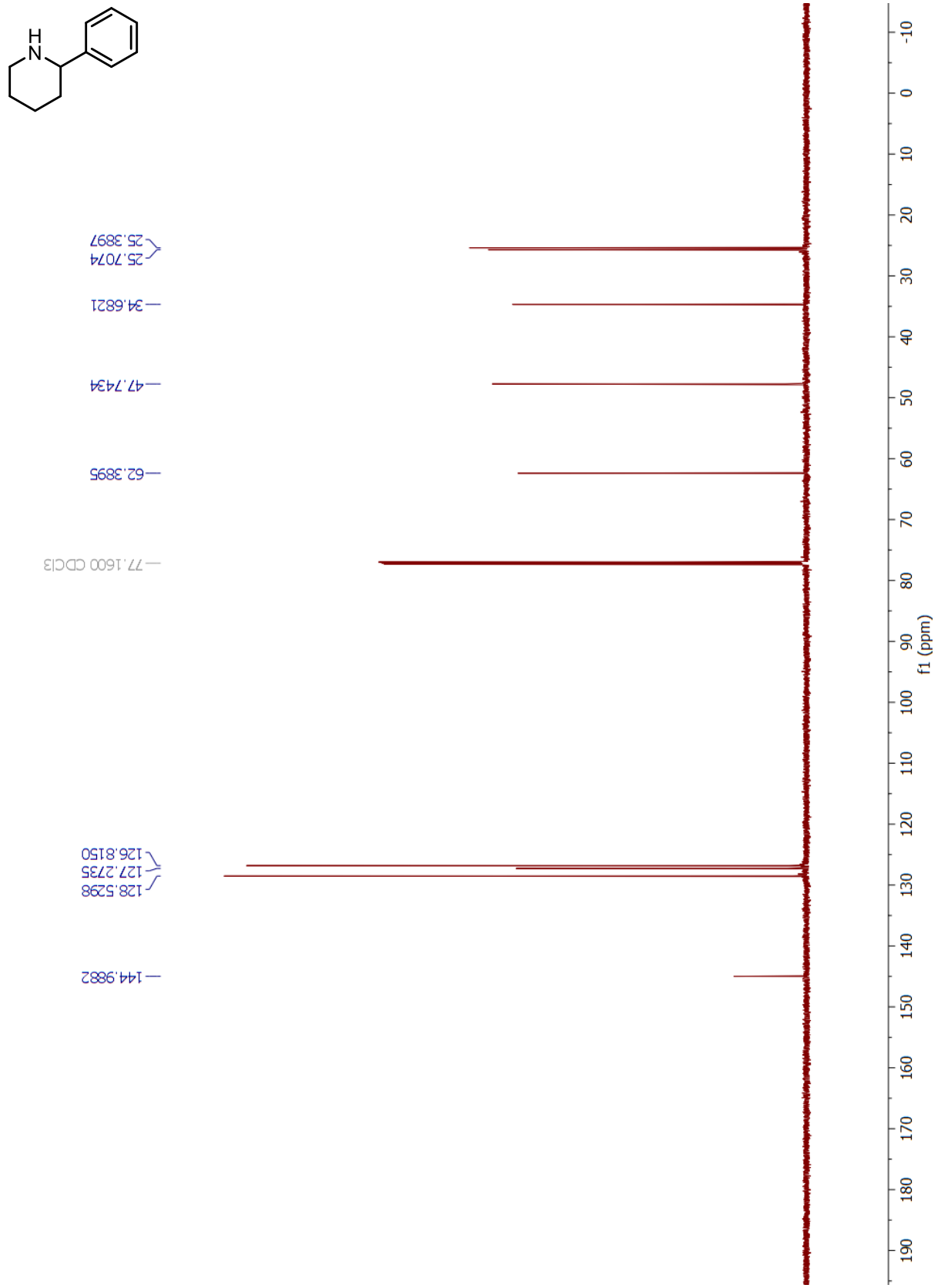


Figure S49. $^{13}C\{^{1}H\}$ NMR (176 MHz) in $CDCl_3$ 10a

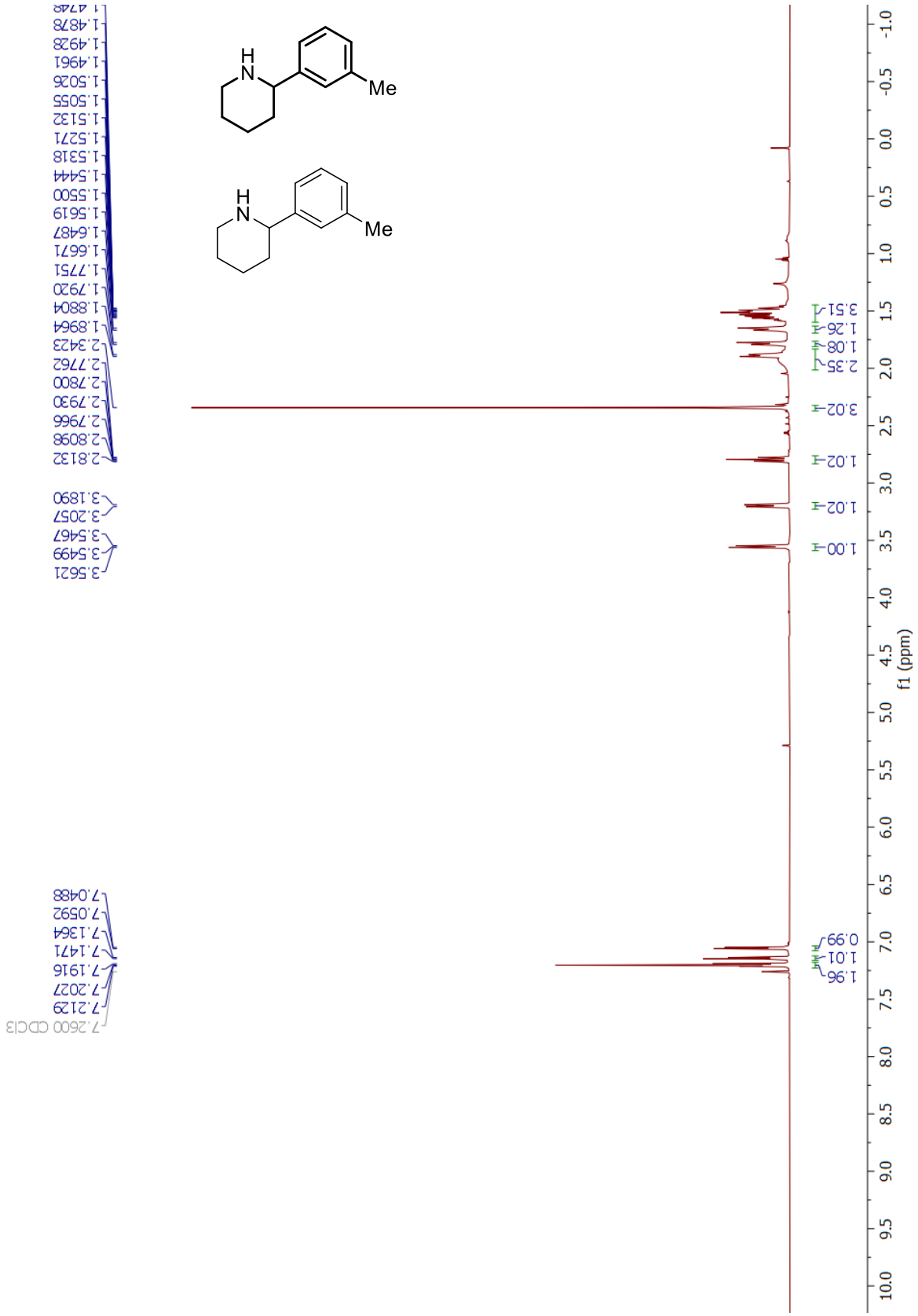


Figure S50. ^{1}H NMR (700 MHz) in $CDCl_3$ 10b

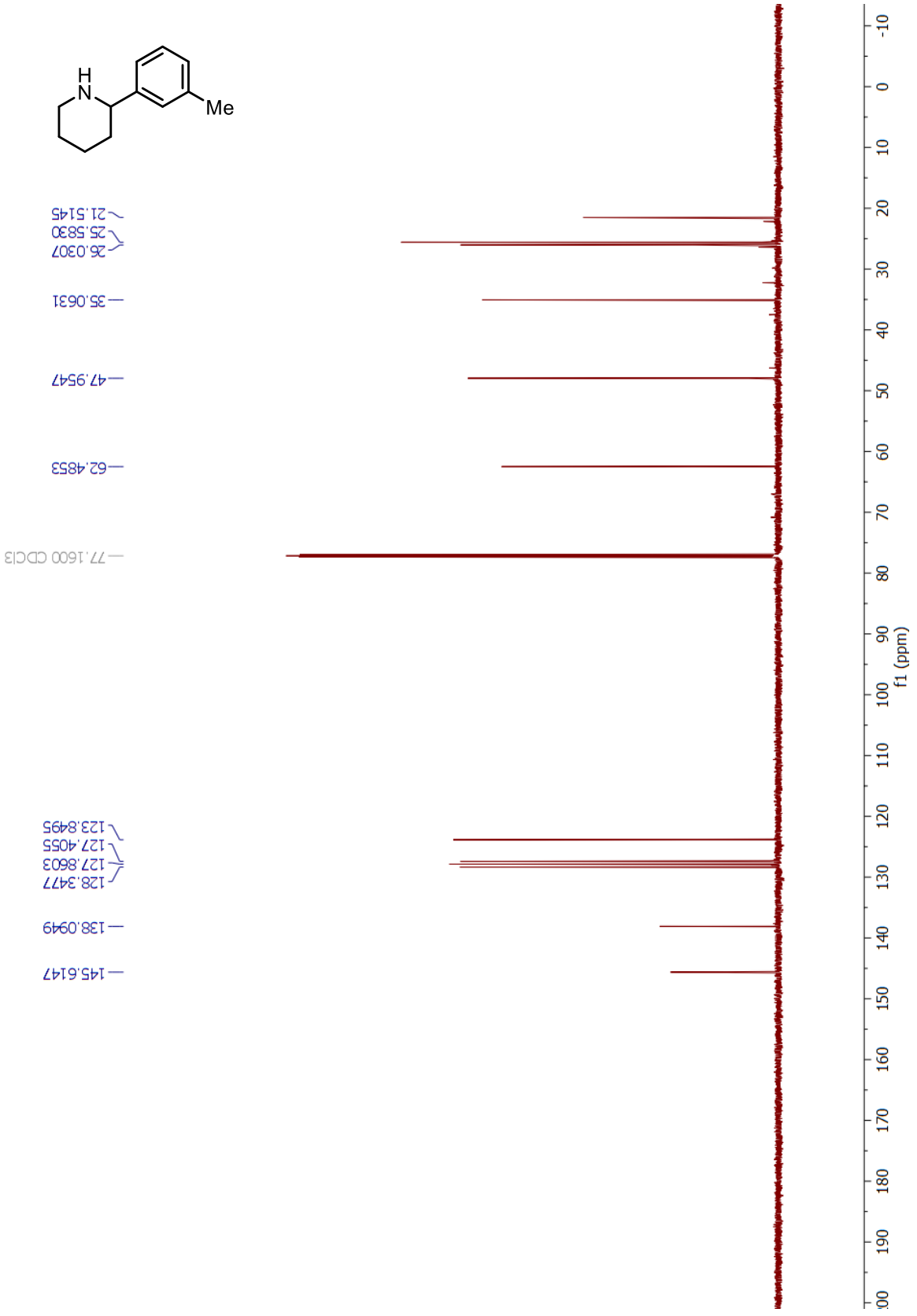


Figure S51. $^{13}C\{^{1}H\}$ NMR (176 MHz) in $CDCl_3$ 10b

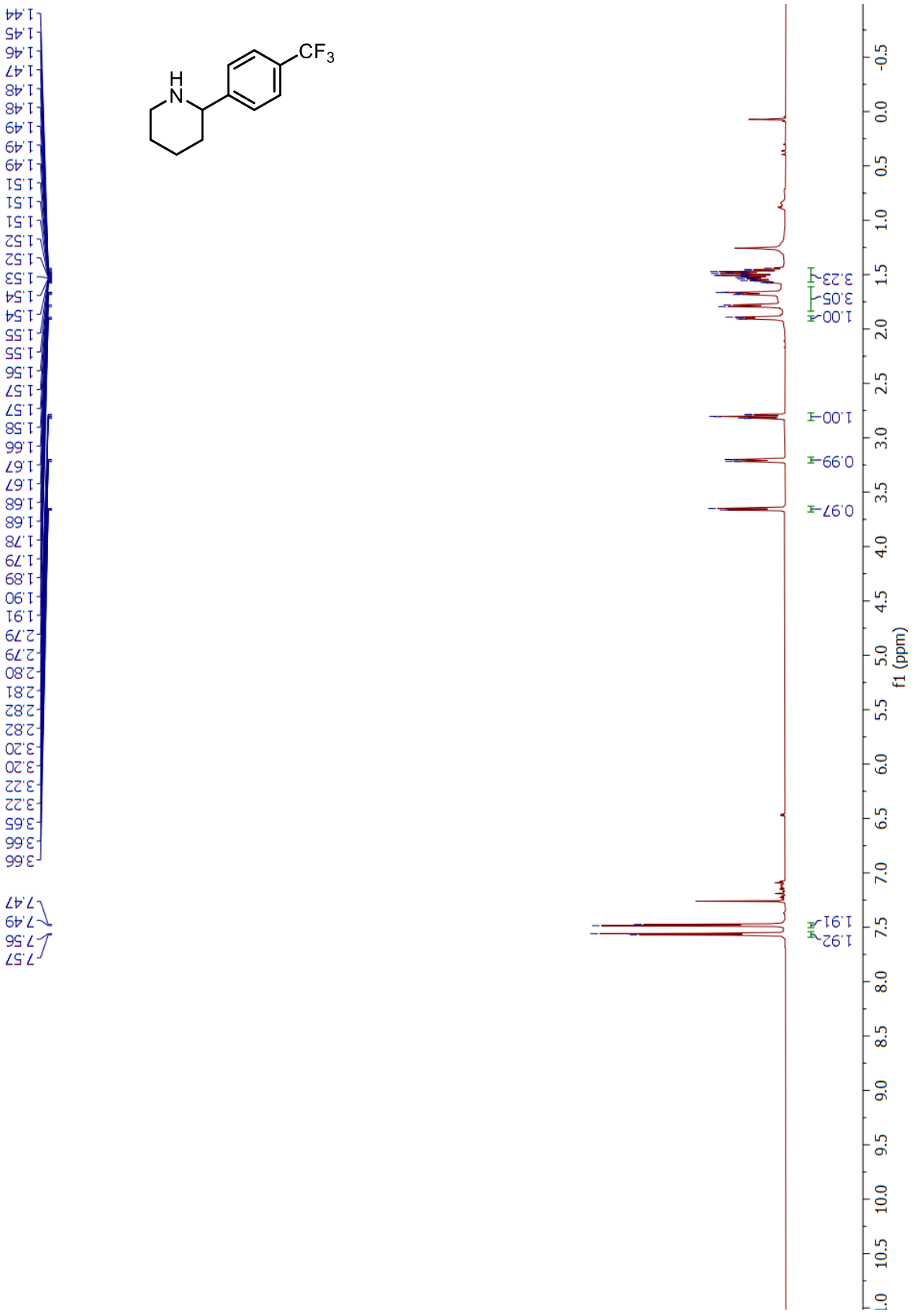


Figure S52. ^{1}H NMR (700 MHz) in $CDCl_3$ 10c

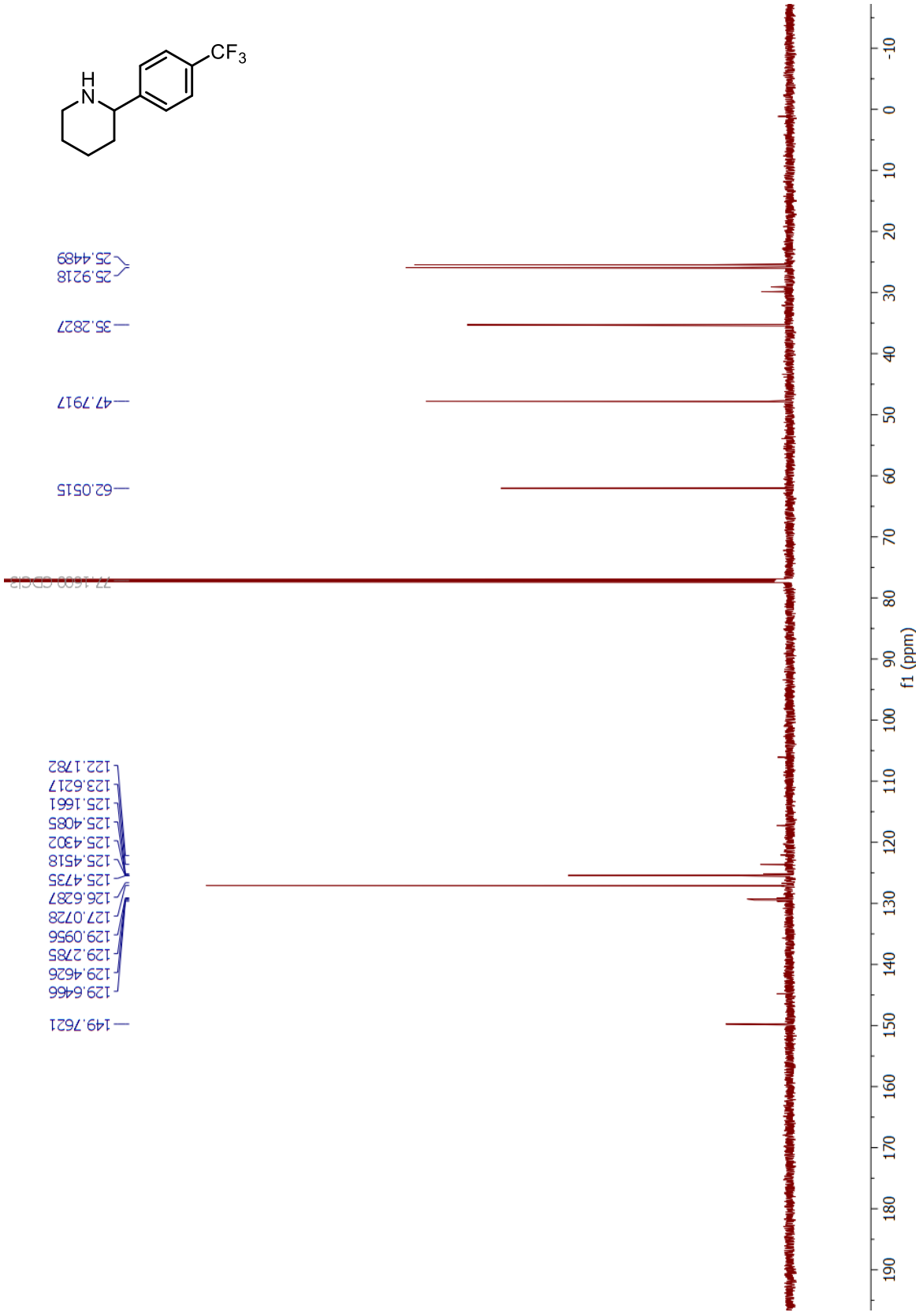


Figure S53. $^{13}C\{^{1}H\}$ NMR (176 MHz) in $CDCl_3$ 10c

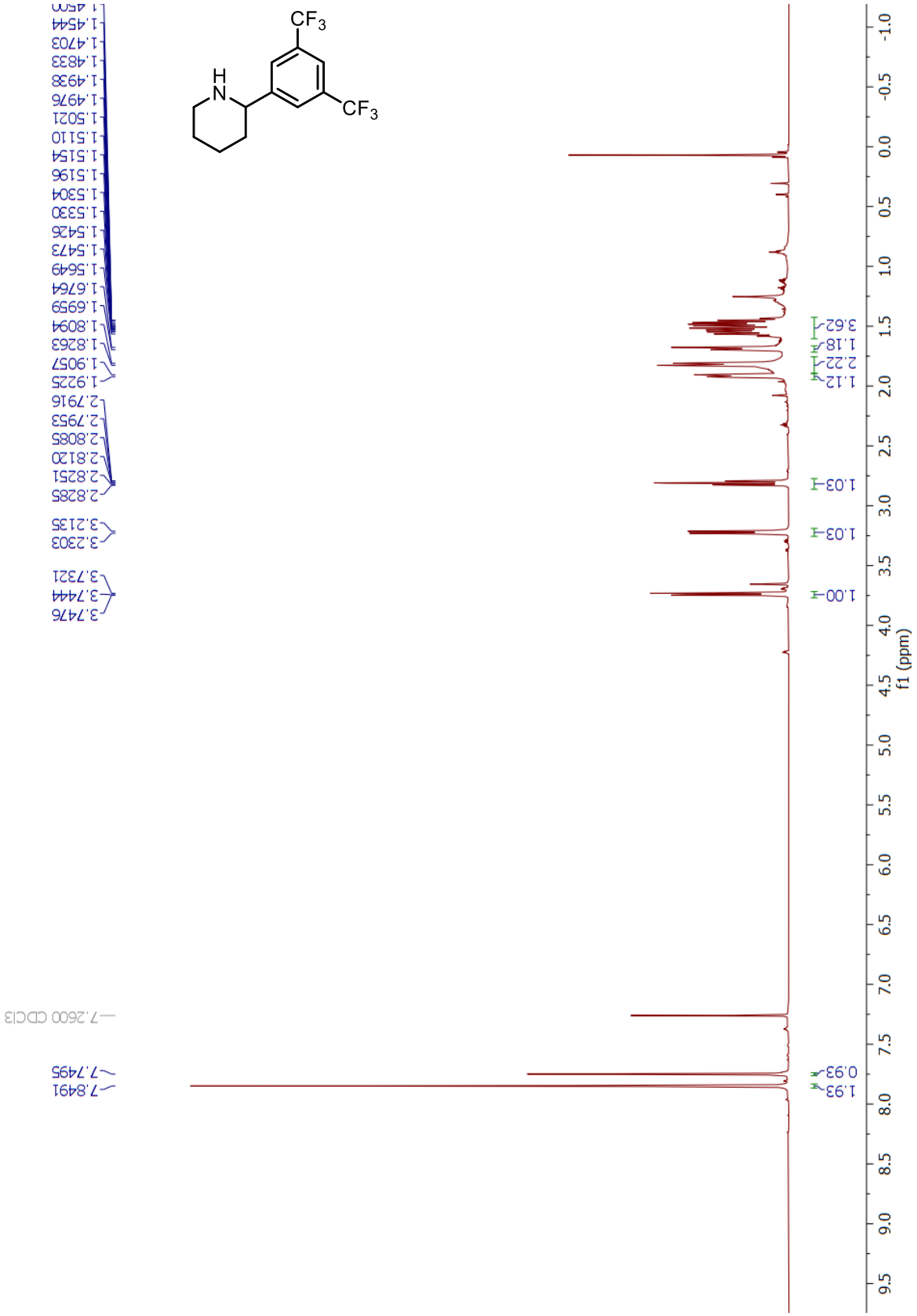


Figure S54. ^{1}H NMR (700 MHz) in $CDCl_3$ 10d

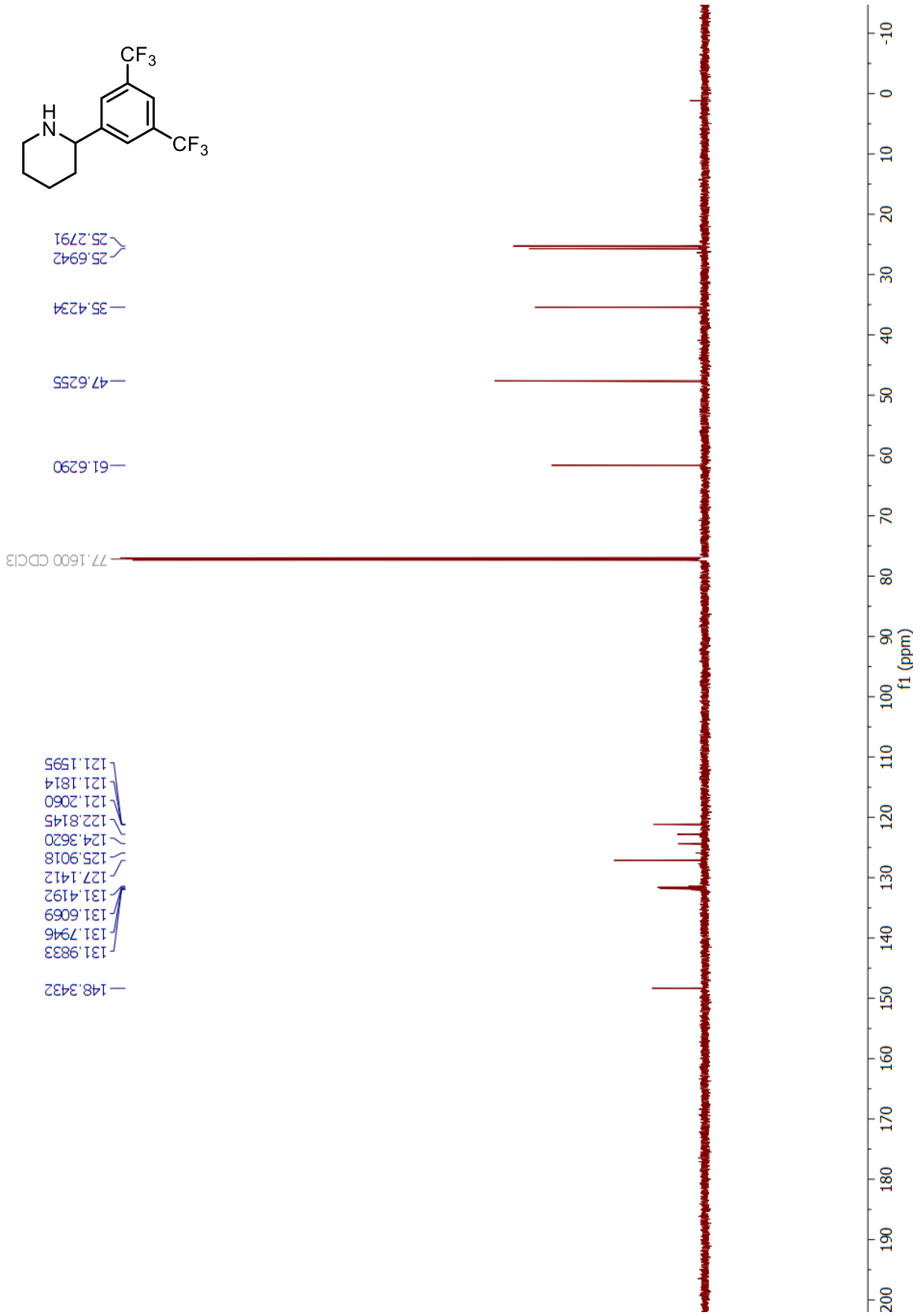


Figure S55. $^{13}C\{^{1}H\}$ NMR (176 MHz) in $CDCl_3$ 10d

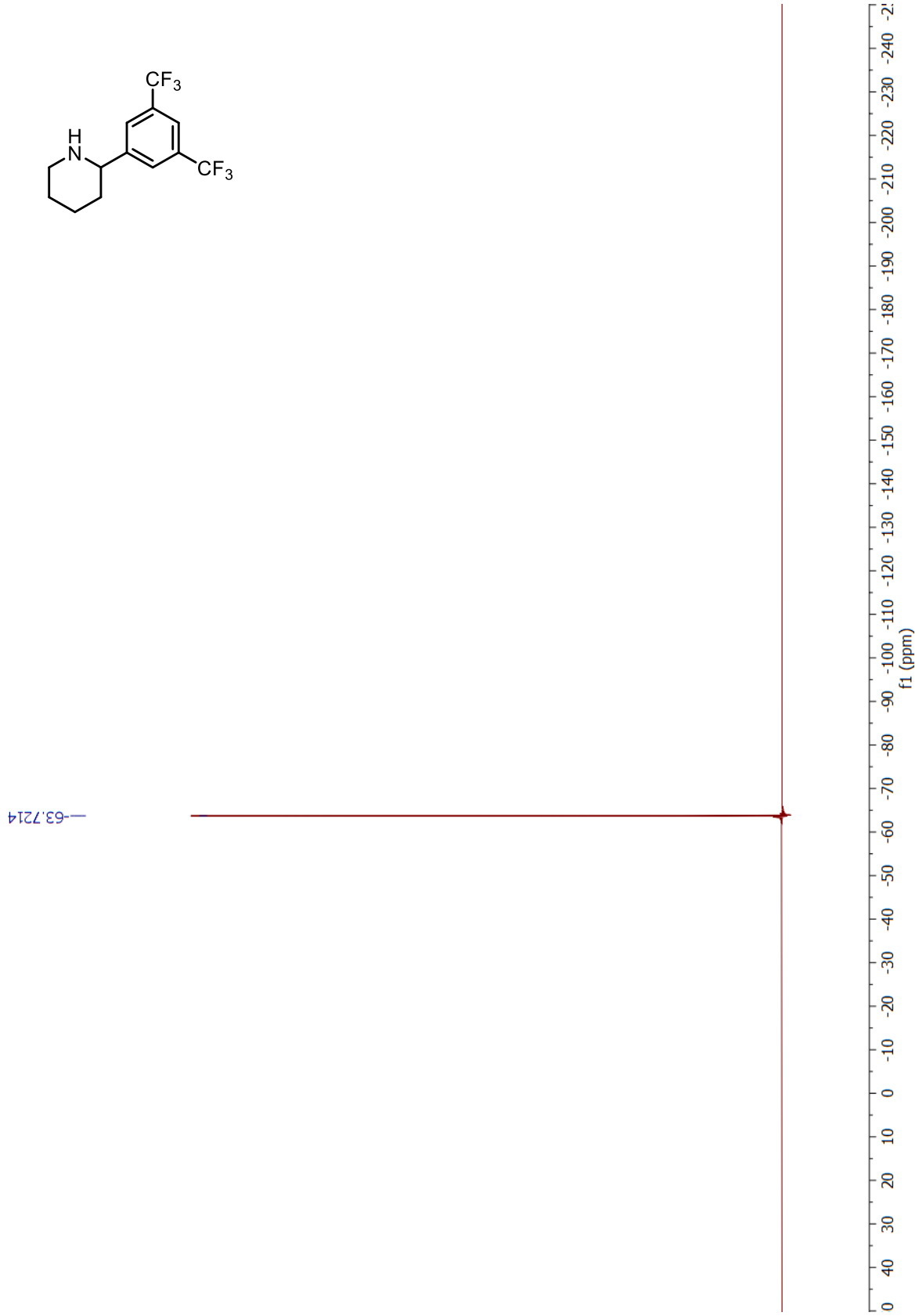


Figure S56. ^{19}F NMR (376 MHz) in $CDCl_3$ 10d