Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information:

Cobalt-Catalyzed Acceptorless Dehydrogenative Coupling of Aminoalcohols with alcohols: Direct Access to Pyrrole, Pyridine and Pyrazine Derivatives

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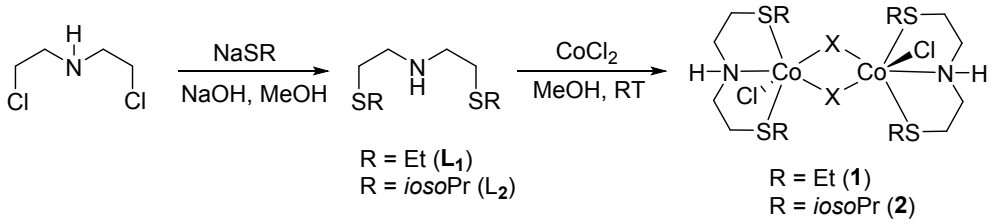
1. General Information

All catalytic experiments were carried out using standard Schlenk techniques. All solvents were reagent grade or better. Deuterated solvents were used as received. *m*-Xylene was refluxed over sodium/benzophenone ketyl and distilled under argon atmosphere and stored over sodium. Cobalt salt precursors were used without additional purification. Most of the chemicals used in the catalytic reactions were purified according to standard procedure.[S1] Thin layer chromatography (TLC) was performed using silica gel precoated glass plates, which were visualized with visualized with UV light at 254 nm or under iodine. Column chromatography was performed with SiO_2 (Silicycle Siliaflash F60 (230-400 mesh). ^1H NMR (200, 400 or 500 MHz), ^{13}C NMR (100 or 126 MHz) spectra were recorded on the NMR spectrometer. Deuterated chloroform was used as the solvent, and chemical shift values (δ) are reported in parts per million relative to the residual signals of this solvent [δ 7.27 for ^1H (chloroform-d), δ 77.0 for ^{13}C (chloroform-d). Abbreviations used in the NMR follow-up experiments: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. GC analysis was carried out using a HP-5 column (30 m, 0.25 mm, 0.25μ). Mass spectra were obtained on a GCMS-QP 5000 instruments with ionization voltages of 70 eV. High resolution mass spectra (HRMS) were obtained on a High-resolution mass spectra (HRMS) were obtained by fast atom bombardment (FAB) using a double focusing magnetic sector mass spectrometer and electron impact (EI) ionization technique (magnetic sector-electric sector double focusing mass analyzer). Elemental analyses were performed on a Vario-EL cube elemental analyzer. MALDI-TOF mass spectra were performed by Applied Biosystem MALDI-TOF/TOF spectrometer. Fourier transform infrared (FT-IR) FTIR analysis was carried out on a Perkin-Elmer Spectrometer. Optical absorption measurements were carried out by Shimadazu UV-vis-IR-3600 Plus spectrophotometer. Electron paramagnetic resonance spectra were recorded with a Bruker EMX-plus X-band spectrometer. The crystals were mounted on a Super Nova Dual source X-ray Diffractometer system (Agilent Technologies) equipped with a CCD area detector and operated at 250 W power (50 kV, 0.8 mA) to generate Mo Kα radiation (λ= 0.71073 Å) and Cu Kα radiation (λ= 1.54178 Å) at 298(2) K.

2. Experimental Section

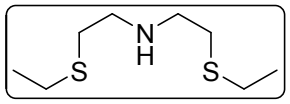
2.1 Synthesis of ligands and Cobalt-complexes



Scheme 1. Synthesis of cobalt complexes (**1-2**)

2.1.1 Synthesis of Ligands

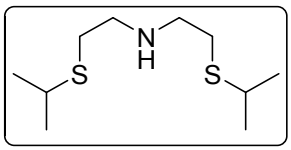
a) Bis(2-(ethylthio)ethyl)amine (^{Et}SNS; L1)



Gusev and co-workers reported the synthesis of Ligand **L1**.[S2] The procedure was modified as mentioned below to yield pure **L1**.

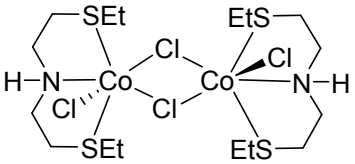
To a solution of bis(2-chloroethyl)amine hydrochloride (2.39 g, 13.4 mmol) in methanol (20 mL), 0.627 g of NaOH (15.7 mmol) and 2.5 g of sodium ethanethiolate (29.5 mmol) was added step wise. The resulting reaction mixture was allowed to stir for 12 h at room temperature, then the solvent was removed under reduced pressure, subsequently the reaction mixture was extracted with dichloromethane. The organic layer was collected and dried over anhyd.Na_2SO_4, then evaporated in vacuum under the reduced and the product (**L1**) was purified through neutral alumina column chromatography. Yield (0.862 g, 50%). **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ = 2.83 (t, *J* = 6.5 Hz, 4H), 2.69 (t, *J* = 6.9 Hz, 4H), 2.55 (q, *J* = 7.2 Hz, 4H), 1.98 (s, br, 1H), 1.26 (t, *J* = 7.25 Hz, 6H). **HRMS (EI)**: *m/z* Calcd for $C_8H_{19}NS_2$ $[M+H]^+$: 194.0959; Found: 194.1043.

b) Bis(2-(isopropylthio)ethyl)amine (^{iso}PrSNS; L2)



To a solution of bis(2-chloroethyl)amine hydrochloride (2.39 g, 13.4 mmol) in methanol (20 mL), 0.627 g of NaOH (15.7 mmol) and 2.9 g of sodium 2-propanethiolate (29.5 mmol) was added step wise. The resulting reaction mixture was allowed to stir for 12 h at room temperature, then the solvent was removed under reduced pressure, subsequently the reaction mixture was extracted with dichloromethane. The organic layer was collected and dried over anhyd.Na_2SO_4, then evaporated in vacuum under the reduced and the product (**L2**) was purified through neutral alumina column chromatography. Yield (1.42 g, 48%). **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ = 2.94 (2H), 2.83 (t, *J* = 6.9 Hz, 4H), 2.71 (t, *J* = 6.5 Hz, 4H), 2.05 (s, br, 1H), 1.28 (d, *J* = 6.5 Hz, 12H). **^{13}C NMR** (126 MHz, CHLOROFORM-d) δ = 48.64, 34.81, 30.74, 23.49. **HRMS (EI)**: *m/z* Calcd for $C_{10}H_{24}NS_2$ $[M+H]^+$: 222.1345; Found: 222.1356.

2.1.2 Synthesis of Cobalt-complexes



1

Anhydrous $CoCl_2$ (130 mg, 1 mmol) in methanol (2 mL) was added drop-wise to solution of **^{Et}SNS** (**L1**) (193 mg, 1 mmol) in MeOH (2 mL) with stirring. The resulting reaction mixture was allowed to stir for 3 h at room temperature. The resulting solution was passed through syringe filter and dried in vacuo giving a blue crystalline powder. The crystal suitable for a single-crystal X-ray diffraction was obtained from MeOH : diethyl ether (by diffusion method) at room temperature after one day.

Yield (249 mg, 77%)

IR (KBr): 3213, 2936, 2868, 2792, 1625, 1462, 1412, 1377, 1306, 1268, 1093, 957, 731 cm^{-1}.

The UV-Visible spectra of **1** recorded in acetonitrile show absorption centred at 589 and 680 nm.

Elemental analysis calcd (%) for $C_{16}H_{38}Cl_4Co_2N_2S_4$: C 29.73; H 5.93; N 4.33; S 19.84; found: C 29.98; H 6.08; N 4.40; S 19.89.

The formation of dimer is evidenced by MALDI-TOF mass spectrum (m/z = 643.62).

EPR study of **1** shows the paramagnetic nature of cobalt(II) complex and the g value is 2.58.

Magnetic moment: 2.23 μB

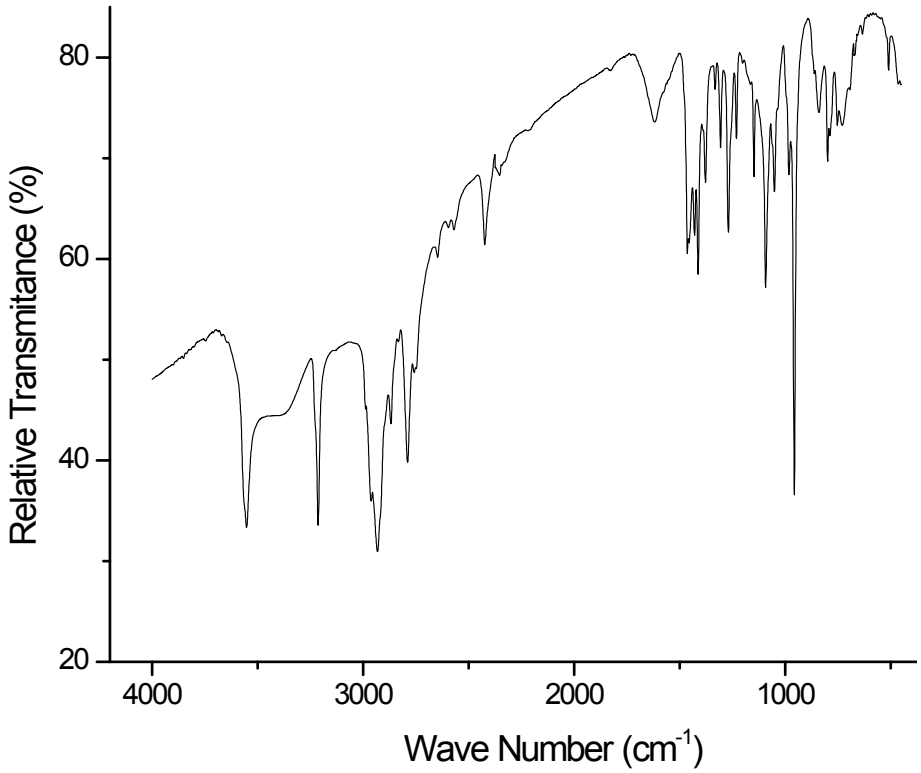


Figure S1. IR spectrum of **1**

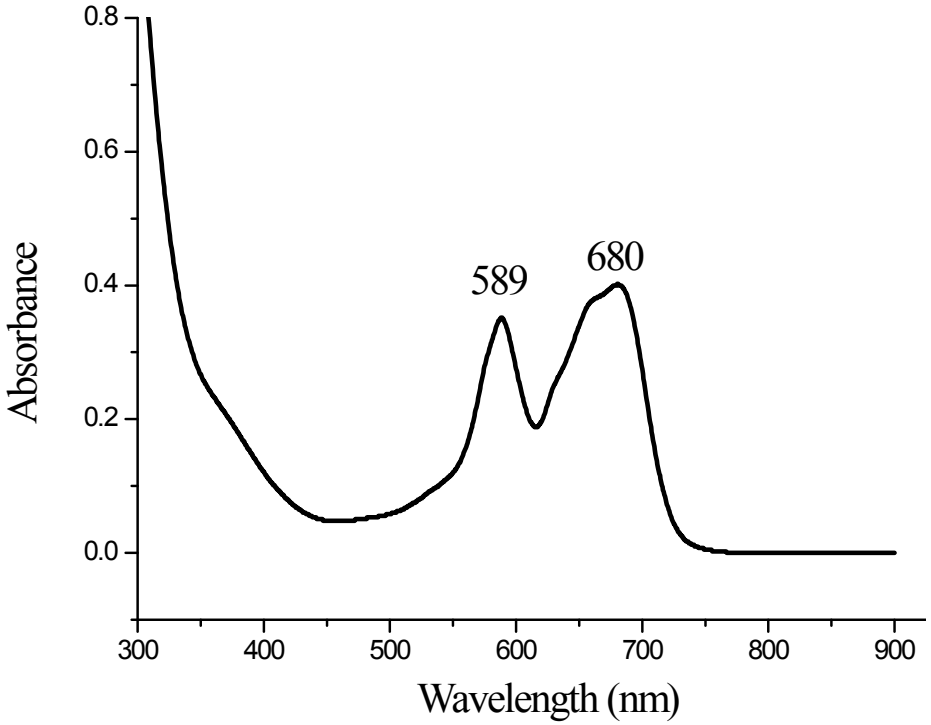


Figure S2. UV spectrum of **1**.

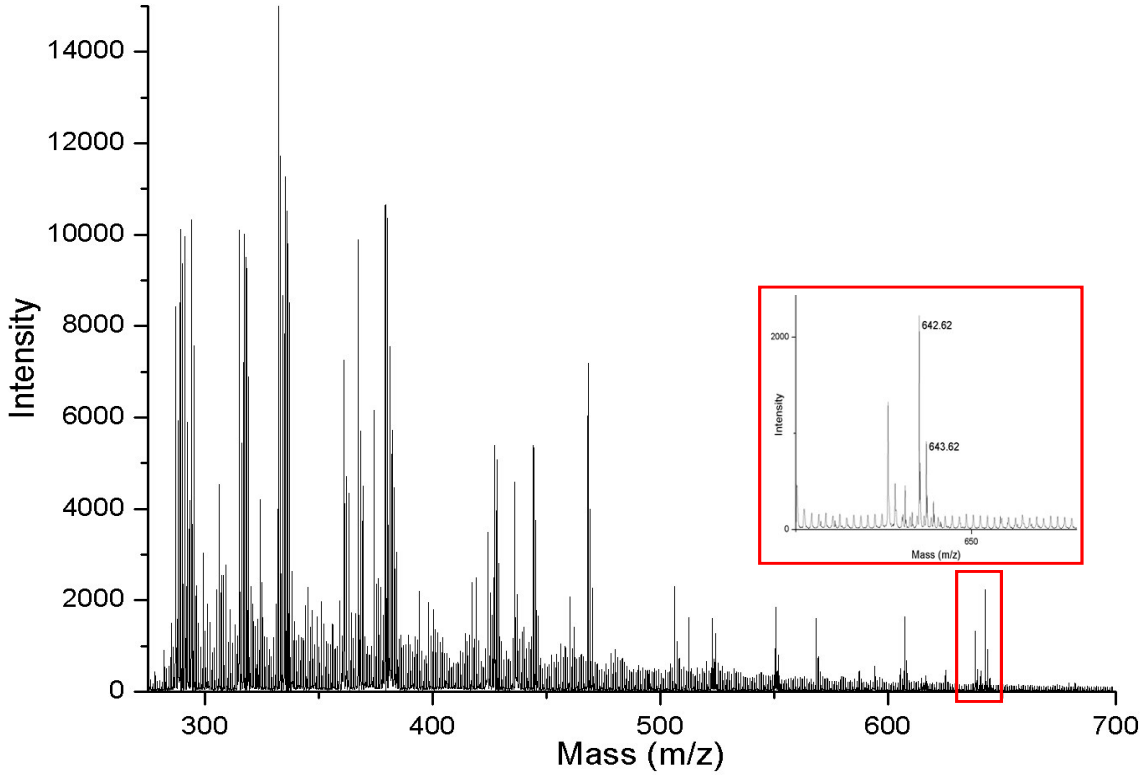
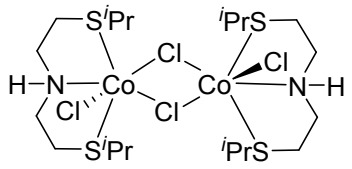


Figure S3. MALDI-TOF Mass spectrum of **1**.



2

Anhydrous $CoCl_2$ (130 mg, 1 mmol) in methanol (2 mL) was added drop-wise to solution of **L2** (221 mg, 1 mmol) in MeOH (2 mL) with stirring. The resulting reaction mixture was allowed to stir for 3 h at room temperature. The resulting solution was passed through syringe filter and then kept for crystallization (diffusion method using diethyl ether). After 1 day, blue crystalline solid was obtained.

Yield (252 mg, 72%).

IR (KBr): 3236, 2959, 2867, 2808, 2751, 1626, 1524, 1449, 1368, 1248, 1155, 997, 955, 725 cm^{-1}.

The UV-Visible spectra of **2** recorded in acetonitrile show absorption centred at 588 and 680 nm.

EPR study of **2** shows the paramagnetic nature of cobalt(II) complexes and having the g_x and g_y values 2.33 and 2.13, respectively

Elemental analysis calcd (%) for $C_{20}H_{46}Cl_4Co_2N_2S_4$: C 34.19; H 6.60; N 3.99; S 18.25; found: C 34.30; H 6.78; N 4.10; S 18.36.

The formation of dimer is evidenced by MALDI-TOF mass spectrum (m/z = 701.42).

Magnetic moment: 2.29 μB

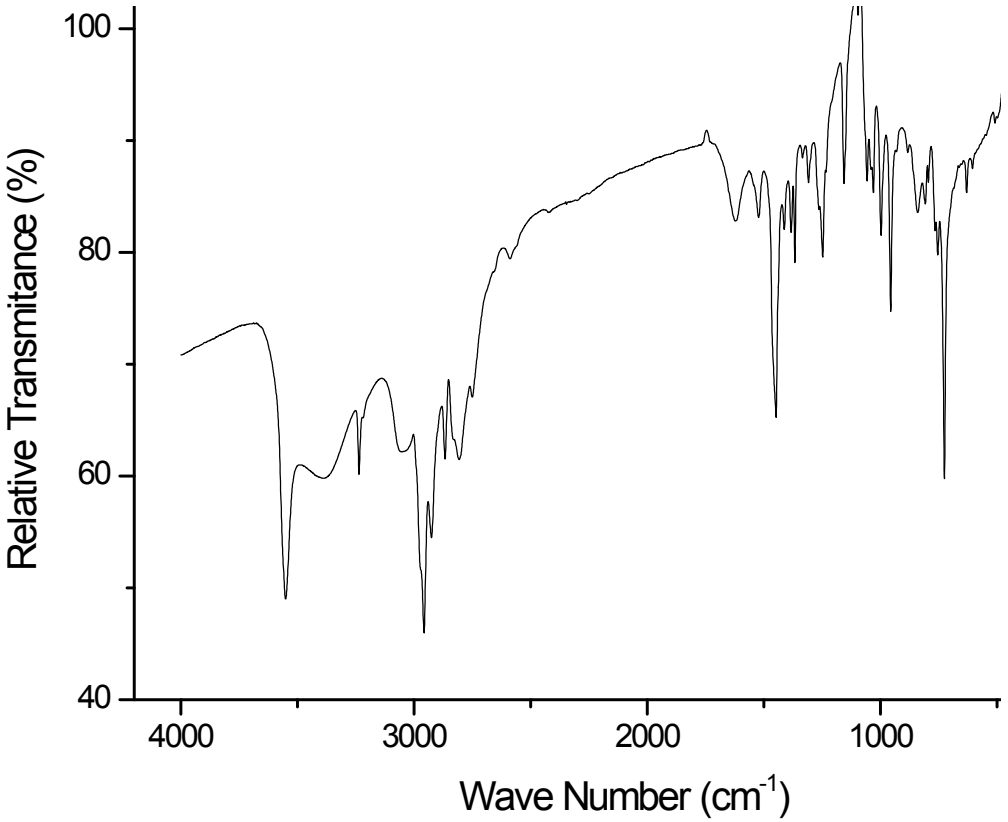


Figure S4. IR spectrum of **2**.

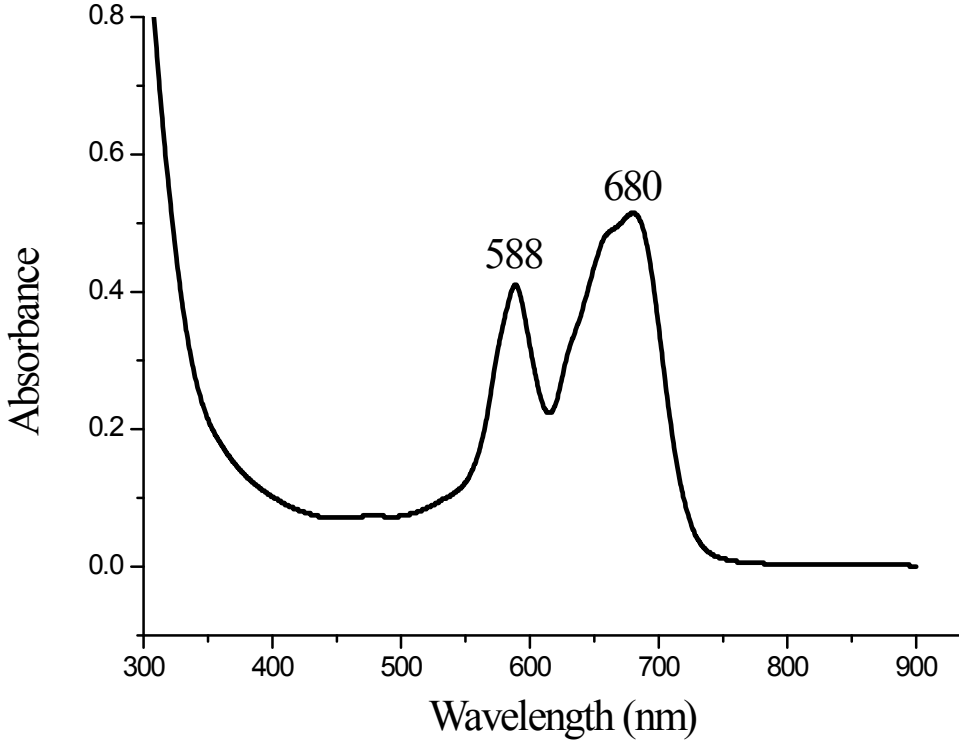


Figure S5. UV spectrum of **2**.

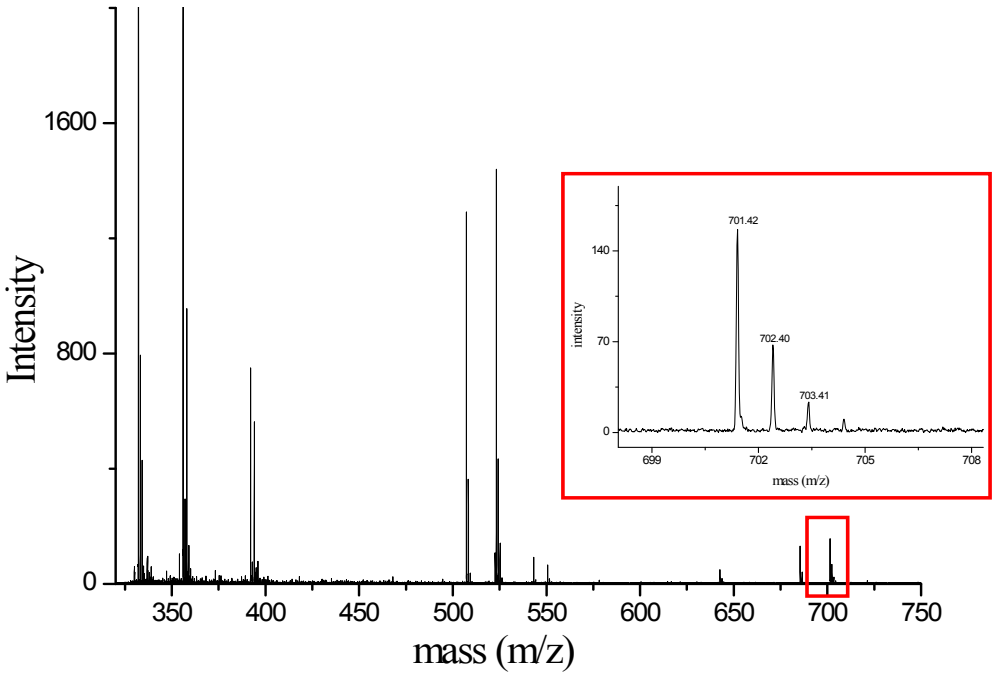


Figure S6. MALDI-TOF Mass spectrum **1**.

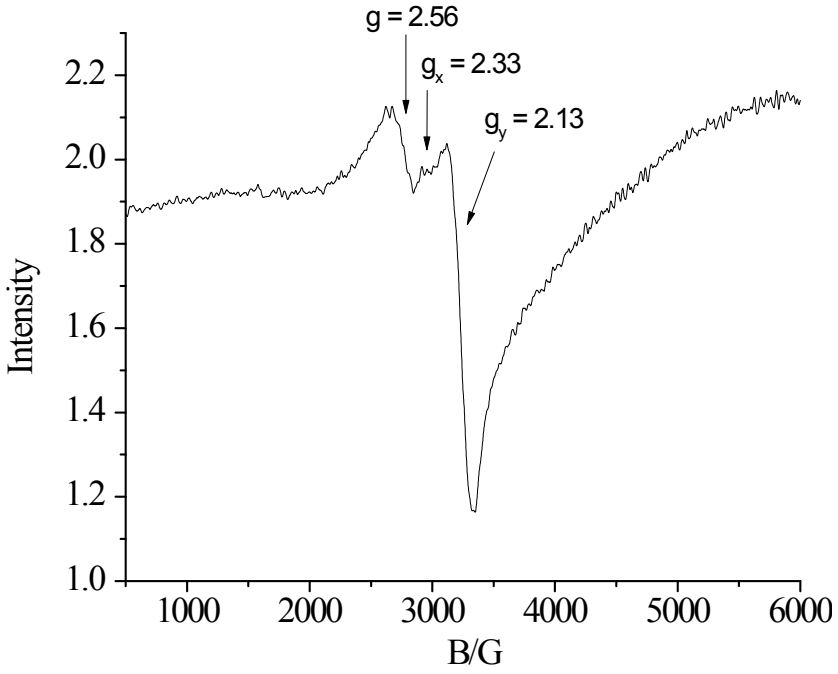


Figure S7. EPR spectrum of **2**.

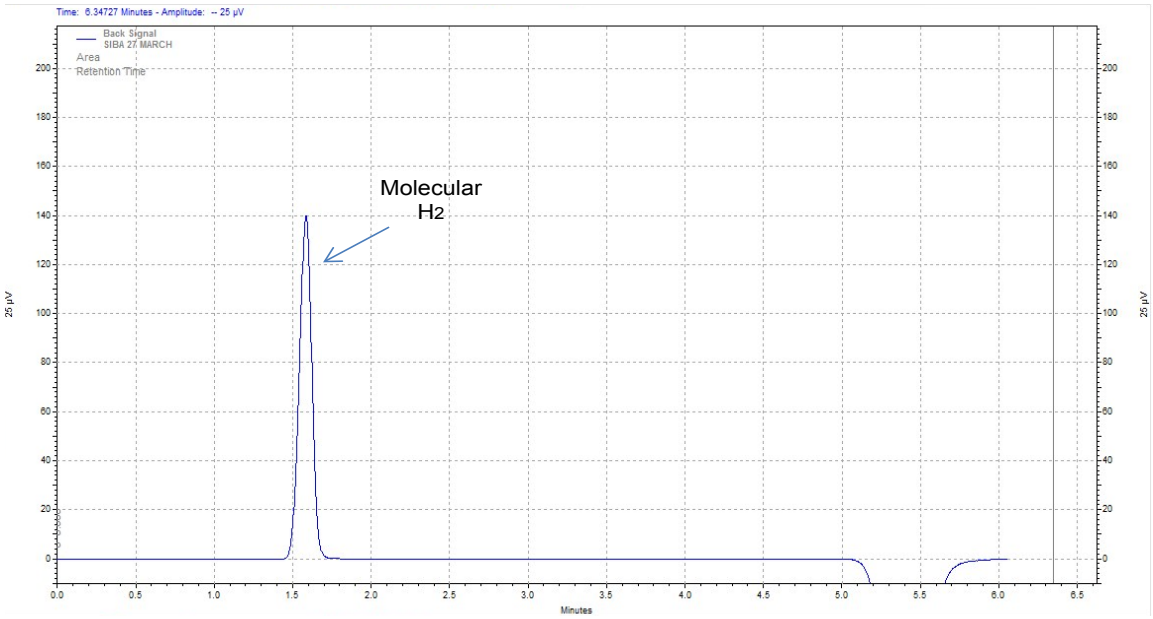
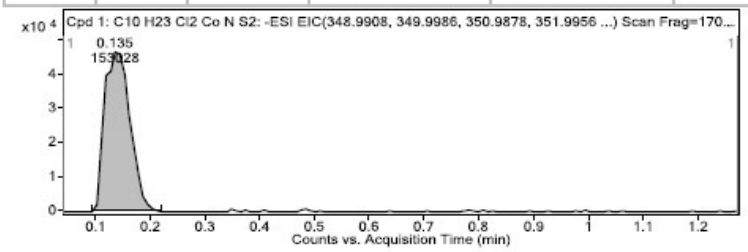


Figure S8. Gas gromatography (detection of dihydrogen).

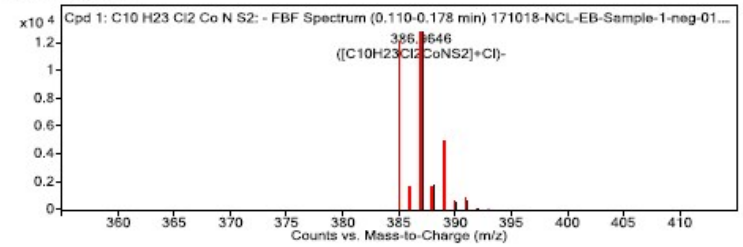
Compound Table

Label	Tgt Score	Mass Error (ppm)	MFG Formula	Tgt Formula	Obs. RT	Ref. Mass	Obs. Mass
Cpd 1: C10 H23 Cl2 Co N S2	99.04	0.99	C10 H23 Cl2 Co N S2	C10 H23 Cl2 Co N S2	0.135	349.9981	349.9984

Obs. m/z	Obs. RT	Obs. Mass	DB Formula	Tgt Formula	Tgt Mass	Tgt Mass Error	Find Cpds Algorith
386.9646	0.135	349.9984	C10 H23 Cl2 Co N S2	C10 H23 Cl2 Co N S2	349.9981	0.99	Find By Formula



MS Zoomed Spectrum



MS Spectrum Peak List

Obs. m/z	Charge	Abund	Formula	Ion/Isotope
384.9681	1	11629.73	C10H23Cl2CoNS2	(M+Cl)-
385.9707	1	1532.18	C10H23Cl2CoNS2	(M+Cl)-
386.9646	1	12798.54	C10H23Cl2CoNS2	(M+Cl)-
387.9677	1	1802	C10H23Cl2CoNS2	(M+Cl)-
388.9616	1	4826.2	C10H23Cl2CoNS2	(M+Cl)-
389.9658	1	513.36	C10H23Cl2CoNS2	(M+Cl)-
390.9588	1	701.26	C10H23Cl2CoNS2	(M+Cl)-
391.9659	1	140.94	C10H23Cl2CoNS2	(M+Cl)-

--- End Of Report ---

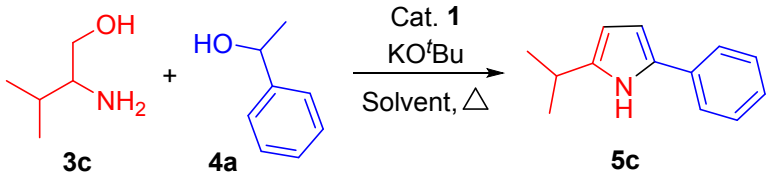
Figure S9. HRMS data of the reaction mixture (using complex **2**) before reaction.

2.1.3 Synthesis of $RuCl_2(PPh_3)[HN(C_2H_4SEt)_2]$ catalyst

According to the reported procedure (by Gusev and co-workers)[S2] the Ru(II) complex $RuCl_2(PPh_3)[HN(C_2H_4SEt)_2]$ was prepared and used directly for the catalysis.

2.2 Reaction Optimization

Table S1: Screening of solvent[a]

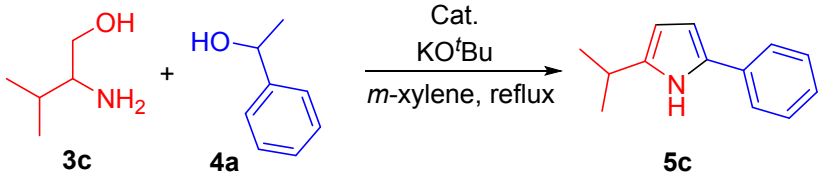


3c **4a** **5c**

Entry	Solvent	Yield (%)[b]
1	Toluene	47
2	*m*-xylene	77
3	Mesitylene	57
4	n-octane	52
5	THF	32

[a] Reactions performed using amino alcohol **3c** (0.125 mmol), 1-Phenyl ethanol **4a** (0.15 mmol), catalyst **1** (2.5 mol%), KO^{t}Bu (1.1 equiv.) at 180 ^{o}C of bath temp. [b] Yield determined by GC using 1,4-dibromo butane as an internal standard.

Table S2: Screening of catalyst[a]

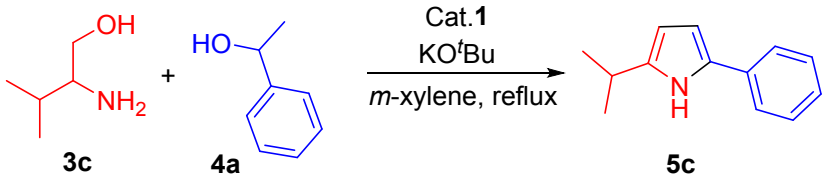


3c **4a** **5c**

Entry	Catalyst	Yield (%)[b]
1	Cat. **1**	77
2	Cat. **2**	34
3	$CoCl_2$	trace
4	---	NR
5	$RuCl_2(PPh_3)[HN(C_2H_4SEt)_2]$	45

[a] Reactions performed using amino alcohol **3c** (0.125 mmol), 1-Phenyl ethanol **4a** (0.15 mmol), catalyst (2.5 mol%), KO^{t}Bu (1.1 equiv.) at reflux. [b] Yield determined by GC using 1,4-dibromo butane as an internal standard. NR = No reaction.

Table S3: Screening of base[a]

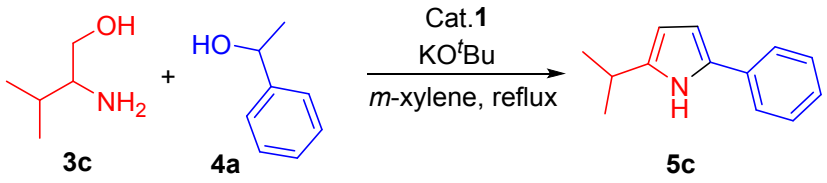


3c 4a 5c

Entry	Base	Yield (%)[b]
1	NaO^{t}Bu	63
2	NaO^{i}Pr	17
3	KOH	62
4	KO^{t}Bu	77
5	KHMDS	67
6	KH	71
7	K_2CO_3	NR
8	KOAc	NR
9	-	NR

[a] Reactions performed using amino alcohol **3c** (0.125 mmol), 1-Phenyl ethanol **4a** (0.15 mmol), catalyst **1** (2.5 mol%), base (1.1 equiv.) at reflux. [b] Yield determined by GC using 1,4-dibromo butane as an internal standard. NR = No reaction.

Table S4: Screening of base amount[a]

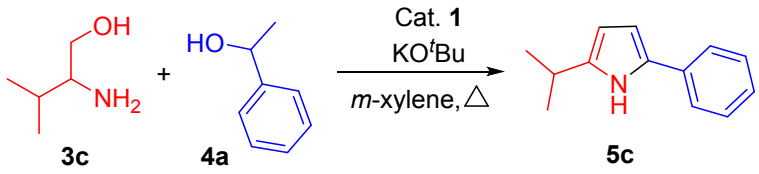


3c 4a 5c

Entry	Base (x equiv)	Yield (%)[b]
1	0.5 eq	20
2	1.1 eq	77
3	1.5 eq	55
4	2 eq	39
5	2.5 eq	35

[a] Reactions performed using amino alcohol **3c** (0.125 mmol), 1-Phenyl ethanol **4a** (0.15 mmol), catalyst (2.5 mol%), KO^{t}Bu (equiv.) at reflux. [b] Yield determined by GC using 1,4-dibromo butane as an internal standard.

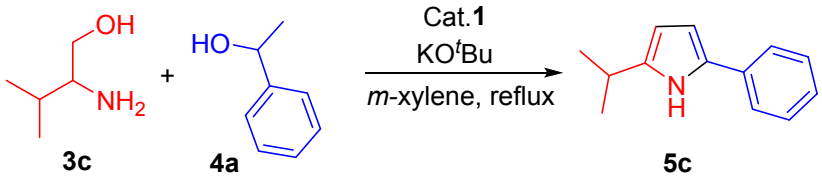
Table S5: Screening of temperature[a]



Entry	Temperature	Yield (%)[b]
1	50 °C	NR
2	80 °C	trace
3	120 °C	23
4	150 °C	48
5	180 °C (reflux)	77

[a] Reactions performed using amino alcohol **3c** (0.125 mmol), 1-Phenyl ethanol **4a** (0.15 mmol), catalyst (2.5 mol%), KO^{t}Bu (equiv.) at different (bath) temperature. [b] Yield determined by GC using 1,4-dibromo butane as an internal standard. NR = No reaction.

Table S6: Screening of alcohol and amino alcohol ratio[a]

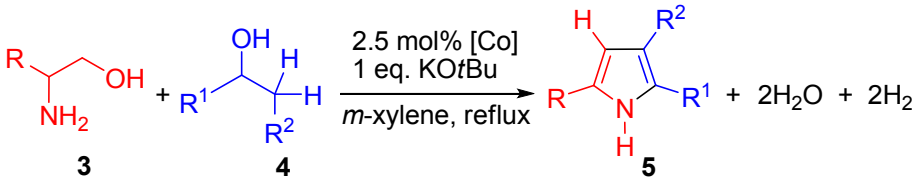


Entry	Alcohol/amino alcohol ratio	Yield (%)[b]
1	1/1	69
2	1/1 (cat **2**)	67
3	1.5/1	71
4	2/1	77
5	3/1	65

[a] Reactions performed using amino alcohol **3c** (0.125 mmol), 1-Phenyl ethanol **4a** (0.15 mmol), catalyst (2.5 mol%), KO^{t}Bu (equiv.) at reflux. [b] Yield determined by GC using 1,4-dibromo butane as an internal standard. NR = No reaction.

2.3 Synthesis and characterization of products

2.3.1 (a) Synthesis of *1H*-pyrroles



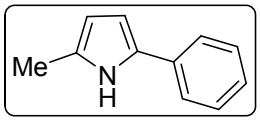
Scheme 2. Synthesis of *1H*-pyrrole derivatives (**5a-o**)

General procedure:

To an oven-dried 15 mL ace pressure tube, 1,2 amino alcohol **3** (0.25 mmol), secondary alcohol **4** (0.5 mmol), Co-complex **1** (2.5 mol%) and *m*-xylene (2 mL) were added under a gentle stream of argon. The mixture was of heated at reflux for 24 h followed by cooling to room temperature. The reaction mixture was diluted with water (4 mL) and extracted with dichloromethane (3 x 5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.

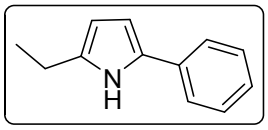
2.3.2 Characterization *1H*-pyrroles

2-methyl-5-phenyl-1*H*-pyrrole (5a)



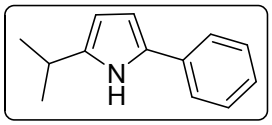
Colorless oil. Yield: 77%. **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ = 8.13 (s, br, 1H), 7.45 (d, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.41 (s, 1H), 5.98 (s, 1H), 2.35 (s, 3H). **^{13}C NMR** (126 MHz, CHLOROFORM-d) δ = 132.94, 129.02, 128.80, 125.64, 123.33, 107.93, 106.18, 13.19. **HRMS (EI)**: *m/z* Calcd for $C_{11}H_{12}N$ $[M+H]^+$: 158.0964; Found: 158.0965.

2-ethyl-5-phenyl-1*H*-pyrrole (5b)



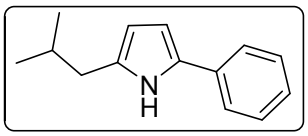
Colorless oil. Yield: 81%. **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ = 8.15 (s, br, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.44 (s, 1H), 6.01 (s, 1H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (126 MHz, CHLOROFORM-d) δ = 135.60, 132.99, 130.58, 128.79, 125.65, 123.38, 106.23, 105.98, 21.00, 13.59. **HRMS (EI)**: *m/z* Calcd for $C_{12}H_{12}N$ $[M-H]^+$: 170.0964; Found: 170.0964.

2-isopropyl-5-phenyl-1*H*-pyrrole (5c)



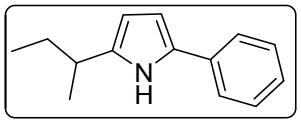
Colorless oil. Yield: 73%. **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ = 8.14 (s, br, 1H), 7.45 (d, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.42 (s, 1H), 6.00 (s, 1H), 3.1-2.98 (m, 1H), 1.32 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (126 MHz, CHLOROFORM-d) δ = 140.30, 133.03, 130.46, 128.79, 125.67, 123.43, 105.81, 104.97, 27.21, 22.66. **HRMS (EI)**: *m/z* Calcd for $C_{13}H_{16}N$ $[M+H]^+$: 186.1277; Found: 186.1279.

2-isobutyl-5-phenyl-1*H*-pyrrole (5d)



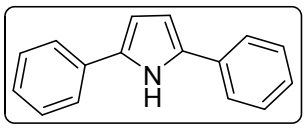
Colorless oil. Yield: 86%. **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ = 8.10 (s, br, 1H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.44 (s, 1H), 5.98 (s, 1H), 2.52 (d, *J* = 7.2 Hz, 2H), 1.94-1.88 (m, 1H), 0.98 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (126 MHz, CHLOROFORM-d) δ = 133.21, 133.00, 130.42, 128.79, 125.57, 123.30, 107.99, 106.04, 37.38, 29.27, 22.45. **HRMS (EI)**: *m/z* Calcd for $C_{14}H_{16}N$ $[M-H]^+$: 198.1277; Found: 198.1277.

2-*sec*-butyl-5-phenyl-1*H*-pyrrole (5e)



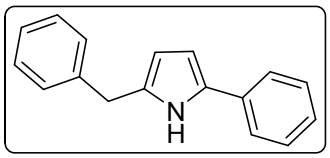
Colorless oil. Yield: 78%. **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ = 8.13 (s, br, 1H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.46 (s, 1H), 6.01 (s, 1H), 2.77-2.73 (m, 1H), 1.74-1.68 (m, 1H), 1.64-1.61 (m, 1H), 1.32 (d, *J* = 6.9 Hz, 3H), 0.96 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (126 MHz, CHLOROFORM-d) δ = 139.17, 133.05, 130.24, 128.77, 125.58, 123.34, 105.83, 105.64, 34.41, 30.23, 20.06, 11.82. **HRMS (EI)**: *m/z* Calcd for $C_{14}H_{18}N$ $[M+H]^+$: 200.1434; Found: 200.1432.

2,5-diphenyl-1*H*-pyrrole (5f)



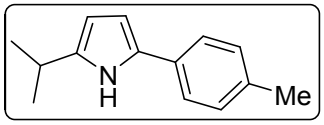
Brown liquid. Yield: 58%. **^{1}H NMR** (200 MHz, CHLOROFORM-d) δ = 8.60(s, br, 1H), 7.55(d, *J* = 7.7 Hz, 4H), 7.40 (t, *J* = 7.3 Hz, 4H), 7.27 (t, *J* = 7.3 Hz, 2H), 6.60 (d, *J* = 2.5 Hz, 2H). **HRMS (EI)**: *m/z* Calcd for $C_{16}H_{13}N$ $[M+H]^+$: 219.1043; Found: 219.1043. (Known compound: Michlik, S.; Kempe, R. *Nat. Chem.* **2013**, *5*, 140).

2-benzyl-5-phenyl-1*H*-pyrrole (5g)



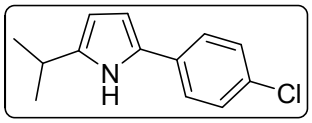
Light brown oil. Yield: 70%. **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ = 8.05 (s, br, 1H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.35-7.31 (m, 5H), 7.26 (d, *J* = 7.2 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 6.44 (s, 1H), 6.06 (s, 1H), 4.04 (s, 2H). **HRMS (EI)**: *m/z* Calcd for $C_{17}H_{14}N$ $[M-H]^+$: 232.1121; Found: 232.1121. (Known compound: Michlik, S.; Kempe, R. *Nat. Chem.* **2013**, *5*, 140).

2-isopropyl-5-*p*-tolyl-1*H*-pyrrole (5h)



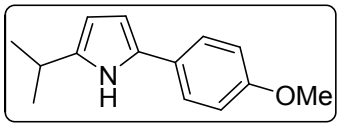
Colorless oil. Yield: 85%. **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ = 8.10 (s, br, 1H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.38 (s, 1H), 5.99 (s, 1H), 3.00-2.98 (m, 1H), 2.36 (s, 3H), 1.32 (d, *J* = 7.3 Hz, 6H). **^{13}C NMR** (126 MHz, CHLOROFORM-d) δ = 139.84, 135.33, 130.60, 130.31, 129.45, 123.44, 105.18, 104.76, 27.19, 22.66, 21.06. **HRMS (EI)**: *m/z* Calcd for $C_{14}H_{18}N$ $[M+H]^+$: 200.1434; Found: 200.1431.

2-(4-chlorophenyl)-5-isopropyl-1*H*-pyrrole (5i)



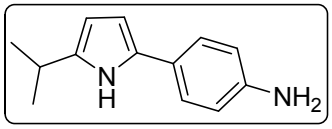
Colorless oil. Yield: 70%. **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ = 8.10 (s, br, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 6.41 (s, 1H), 6.00 (s, 1H), 3.01-2.95 (m, 1H), 1.32 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (126 MHz, CHLOROFORM-d) δ = 140.78, 131.52, 131.11, 128.92, 124.56, 123.43, 106.36, 105.23, 27.23, 22.64. **HRMS (EI)**: *m/z* Calcd for $C_{13}H_{15}ClN$ $[M+H]^+$: 220.0888; Found: 220.0886.

2-isopropyl-5-(4-methoxyphenyl)-1*H*-pyrrole (5j)



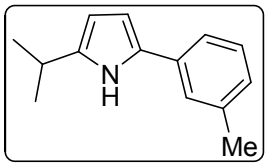
White solid. Yield: 89%. **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ = 8.03 (s, br, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.30 (s, 1H), 5.97 (s, 1H), 3.83 (s, 3H), 3.00-2.95 (m, 1H), 1.32 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (126 MHz, CHLOROFORM-d) δ = 157.91, 139.58, 130.48, 126.22, 124.89, 114.26, 104.66, 55.30, 27.18, 22.68. **HRMS (EI)**: *m/z* Calcd for $C_{14}H_{18}ON$ $[M+H]^+$: 216.1383; Found: 216.1381.

4-(5-isopropyl-1*H*-pyrrol-2-yl)aniline (5k)



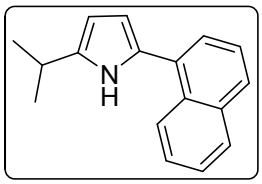
Light brown liquid. Yield: 67%. **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ = 7.99 (s, br, 1H), 7.26 (d, *J* = 6.7 Hz, 2H), 6.69 (d, *J* = 7.9 Hz, 2H), 6.24 (s, 1H), 5.95 (s, 1H), 3.65 (s, br, 3H), 2.99-2.94 (m, 1H), 1.31 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (126 MHz, CHLOROFORM-d) δ = 144.48, 139.08, 131.03, 124.93, 124.31, 115.53, 104.45, 103.88, 27.16, 22.69. **HRMS (EI)**: *m/z* Calcd for $C_{13}H_{17}N_2$ $[M+H]^+$: 201.1386; Found: 201.1385.

2-isopropyl-5-*m*-tolyl-1*H*-pyrrole (5l)



Colorless oil. Yield: 70%. **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ = 8.15 (s, br, 1H), 7.76 (s, 1H), 7.28-7.26 (m, 2H), 7.03-7.01 (m, 1H), 6.42 (s, 1H), 6.01 (s, 1H), 3.03-2.97 (m, 1H), 2.40 (s, 3H), 1.34 (d, *J* = 7.3 Hz, 6H). **^{13}C NMR** (126 MHz, CHLOROFORM-d) δ = 140.12, 138.32, 133.69, 128.68, 128.40, 126.50, 124.18, 120.62, 105.67, 104.87, 27.21, 22.66, 21.52. **HRMS (EI)**: *m/z* Calcd for $C_{14}H_{18}N$ $[M+H]^+$: 200.1434; Found: 200.1432.

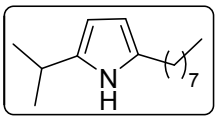
2-isopropyl-5-(naphthalen-1-yl)-1*H*-pyrrole (5m)



Light yellow sticky liquid. Yield: 61%. **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ = 8.39-8.38 (m, 1H), 8.16 (s, br, 1H), 7.90-7.89 (m, 1H), 7.80-7.79 (m, 1H), 7.51 (m, 4H), 6.44 (s, 1H), 6.12 (s, 1H), 3.11-3.03 (m, 1H), 3.37 (d, *J* = 6.5 Hz, 6H). **^{13}C NMR** (126 MHz, CHLOROFORM-d) δ = 139.82, 134.10, 131.84, 131.28, 128.89, 128.39, 127.05, 126.19, 125.85, 125.62, 125.45,

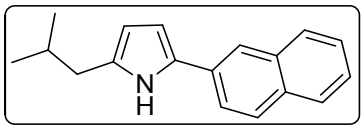
109.34, 104.34, 27.17, 22.67. **HRMS (EI)**: *m/z* Calcd for $C_{17}H_{18}N$ $[M+H]^+$: 236.1434; Found: 236.1425.

2-isopropyl-5-octyl-1*H*-pyrrole (5n)



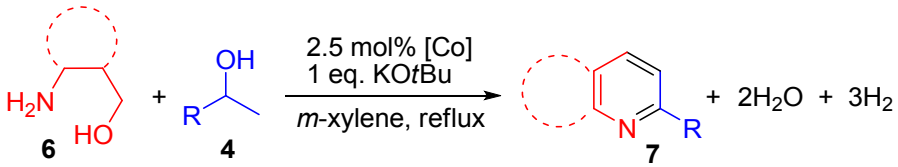
Ration of alcohol/amino alcohol = 1.5/1 has taken under the identical reaction condition. Colorless oil. Yield: 45%. **^{1}H NMR** (200 MHz, CHLOROFORM-d) δ = 5.79 (d, *J* = 2.3 Hz, 2H), 2.96-2.82 (m, 1H), 2.56 (t, *J* = 7.3 Hz, 2H), 1.62 (m, 2H), 1.27 (m, 16H), 0.89 (t, *J* = 5.0 Hz, 3H). **HRMS (EI)**: *m/z* Calcd for $C_{15}H_{28}N$ $[M+H]^+$: 222.2216; Found: 222.2213. The product contains dehydrogenated product derived from secondary alcohol (Product: other dehydrogenated products = 1:1.5).

2-isobutyl-5-(naphthalen-2-yl)-1*H*-pyrrole (5o)



Light yellow sticky liquid. Yield: 74%. **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ = 8.26 (s, br, 1H), 7.83-7.79 (m, 4H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 1H), 6.58 (s, 1H), 6.04 (s, 1H), 2.56 (d, *J*= 6.9 Hz, 2H), 1.98-1.93 (m, 1H), 1.01 (d, *J* = 6.5 Hz, 6H). **^{13}C NMR** (126 MHz, CHLOROFORM-d) δ = 133.85, 131.81, 130.43, 128.45, 127.70, 127.51, 126.36, 125.06, 123.06, 120.02, 108.23, 106.84, 37.44, 29.29, 22.51. **HRMS (EI)**: *m/z* Calcd for $C1_8H_{20}N$ $[M+H]^+$: 250.1590; Found: 250.1583.

2.3.3 Synthesis of pyridine derivatives



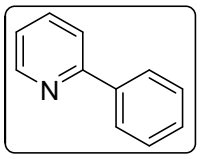
Scheme 3. Synthesis of pyridine derivatives (**7a-k**)

General procedure:

To an oven-dried 15 mL ace pressure tube, 1,2 amino alcohol **6** (0.25 mmol), secondary alcohol **4** (0.5 mmol), Co-complex **1** (2.5 mol%) and *m*-xylene (1 mL) were added under a gentle stream of argon. The mixture was heated at reflux for 24 h followed by cooling to room temperature. The reaction mixture was diluted with water (4 mL) and extracted with dichloromethane (3 x 5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.

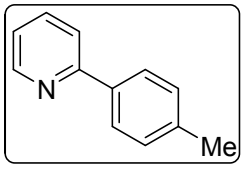
2.3.4 Characterization of pyridine derivatives

2-pheny lpyridine (7a)



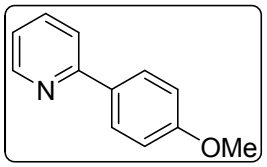
Colorless oil. Yield: 68%. **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ = 8.71 (d, *J* = 4.9 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 2H), 7.73 (m, 2H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.23-7.21 (m, 1H). **^{13}C NMR** (126 MHz, CHLOROFORM-d) δ = 157.35, 149.57, 139.31, 136.64, 128.86, 128.65, 126.81, 121.99, 120.45. **HRMS (EI)**: *m/z* Calcd for $C_{11}H_{10}N$ $[M+H]^+$: 156.0808; Found: 156.0807.

2-*p*-tolyl pyridine (7b)



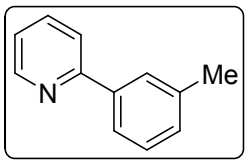
Colorless oil. Yield: 79%. **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ = 8.69 (d, *J* = 4.6 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.76-7.71 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 5.3 Hz, 1H), 2.42 (s, 3H). **^{13}C NMR** (126 MHz, CHLOROFORM-d) δ = 157.49, 149.58, 138.93, 136.67, 129.46, 126.76, 121.78, 120.26, 21.25. **HRMS (EI)**: *m/z* Calcd for $C_{12}H_{12}N$ $[M+H]^+$: 170.0964; Found: 170.0964.

2-(4-methoxyphenyl) pyridine (7c)



Colorless oil. Yield: 83%. **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ = 8.66 (d, *J* = 4.2 Hz, 1H), 7.96 (d, *J* = 9.2 Hz, 2H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 8.8 Hz, 1H), 3.88 (s, 3H). **^{13}C NMR** (126 MHz, CHLOROFORM-d) δ = 160.46, 157.13, 149.54, 136.64, 132.04, 128.15, 121.39, 119.80, 114.11, 55.35. **HRMS (EI)**: *m/z* Calcd for $C_{12}H_{12}ON$ $[M+H]^+$: 186.0913; Found: 186.0912.

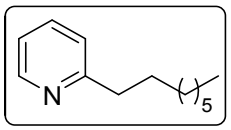
2-*m*-tolylpyridine (7d)



Colorless oil. Yield: 69%. **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ = 8.70 (d, *J* = 4.6 Hz, 1H), 7.85 (s, 1H), 7.77-7.72 (m, 3H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.24 (t, *J* = 7.2 Hz, 2H), 2.45 (s, 3H). **^{13}C NMR** (126 MHz, CHLOROFORM-d) δ = 157.65, 149.60, 139.35, 138.43, 136.70,

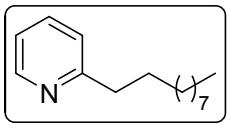
129.71, 128.63, 127.65, 123.99, 122.01, 120.64, 21.51. **HRMS (EI)**: *m/z* Calcd for $C_{12}H_{12}N$ $[M+H]^+$: 170.0964; Found: 194.1043.

2-octyl pyridine (7e)



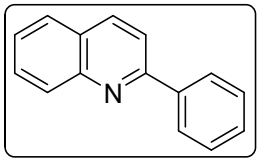
Ration of alcohol/amino alcohol = 1.5/1 has taken under the identical reaction condition. Colorless oil. Yield: 60%. **^{1}H NMR** (200 MHz, CHLOROFORM-d) δ = 8.53 (d, *J* = 4.8 Hz, 1H), 7.59 (t, *J* = 9.3 Hz, 1H), 7.16-7.07 (m, 2H), 2.79 (t, *J* = 8.1 Hz, 2H), 1.73 (m, 2H), 1.28 (m, 10H), 0.89 (t, *J* = 6.7 Hz, 3H). **HRMS (EI)**: *m/z* Calcd for $C_{13}H_{22}N$ $[M+H]^+$: 192.1747; Found: 192.1744. The product contains dehydrogenated product derived from secondary alcohol (Product: other dehydrogenated products = 1:1.8). (Known compound: Nakamura, Y.; Yoshikai, N.; Ilies, L.; Nakamura, E. *Org. Lett.* **2012**, *14*, 12).

2-decyl pyridine (7f)



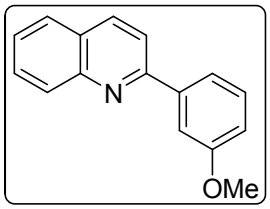
Ration of alcohol/amino alcohol = 1.5/1 has taken under the identical reaction condition. Colorless oil. Yield: 63%. **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ = 8.53 (d, *J* = 4.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 5.7 Hz, 1H), 2.78 (t, *J* = 7.6 Hz, 2H), 1.76-1.68 (m, 2H), 1.26 (m, 14H), 0.88 (t, *J* = 6.9 Hz, 3H). **HRMS (EI)**: *m/z* Calcd for $C_{15}H_{26}N$ $[M+H]^+$: 220.2060; Found: 220.2057. Unable to isolate complete pure product, product identified from its unreacted secondary alcohol. Product : unreacted secondary alcohol = 1:1.6. (Known compound: Vandromme, L.; Reißig, H. -U.; Gröper, S.; Rabe, J. P. *Eur. J. Org. Chem.* **2008**, 2049-2055).

2-phenyl quinoline (7g)



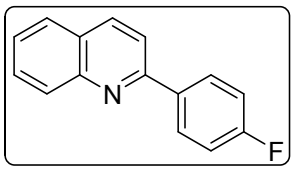
White solid. Yield: 81%. **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ = 8.21 (t, J = 9.2 Hz, 4H), 7.88 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.75 (t, J = 8.0 Hz, 1H), 7.57-7.53 (m, 3H), 7.49 (t, J = 7.2 Hz, 1H). **^{13}C NMR** (126 MHz, CHLOROFORM-d) δ = 157.29, 148.24, 139.64, 136.70, 129.70, 129.59, 129.26, 128.79, 127.52, 127.41, 127.13, 126.22, 118.94. (Known compound: Rao, M. L. N.; Dhanorkar, R. J. *Eur. J. Org. Chem.* **2014**, 5214-5228).

2-(3-methoxyphenyl) quinoline (7h)



Colorless oil. Yield: 75%. **^{1}H NMR** (200 MHz, CHLOROFORM-d) δ = 8.22-8.19 (m, 2H), 7.87-7.80 (m, 3H), 7.74 (t, *J* = 8.5 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.9 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 1H), 3.94 (s, 3H). **^{13}C NMR** (126 MHz, CHLOROFORM-d) δ = 160.08, 157.04, 148.15, 141.09, 136.68, 129.74, 129.68, 129.58, 127.39, 126.25, 119.95, 119.02, 115.30, 112.66, 55.34. **HRMS (EI)**: *m/z* Calcd for $C_{16}H_{14}ON$ $[M+H]^+$: 236.1070; Found: 236.1068.

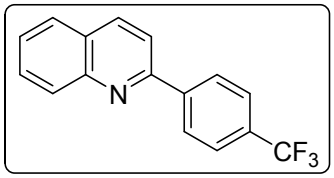
2-(4-fluorophenyl)quinoline (7i)



White solid. Yield: 72%. **^{1}H NMR** (400 MHz, CHLOROFORM-d) δ = 8.21-8.15 (m, 4H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.74 (t, *J* = 6.7 Hz, 1H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.22 (t, *J* = 8.5 Hz, 2H).

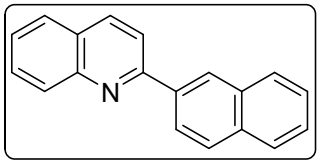
^{13}C NMR (126 MHz, CHLOROFORM-d) δ = 164.76, 162.77, 156.77, 148.19, 136.85, 136.85, 135.78, 129.74, 129.39, 129.33, 127.43, 127.04, 126.30, 118.58, 115.80, 115.63. **HRMS (EI)**: *m/z* Calcd for $C_{15}H_{11}NF$ $[M+H]^+$: 224.0870; Found: 224.0869.

2-(4-(trifluoromethyl)phenyl)quinoline (7j)



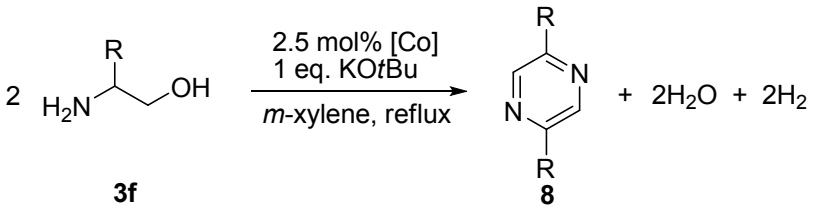
White solid. Yield: 67%. **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ = 8.29 (d, *J* = 8.4 Hz, 2H), 8.25 (d, *J* = 8.4 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.80-7.75 (m, 3H), 7.58 (t, *J* = 8.0 Hz, 1H). **^{13}C NMR** (126 MHz, CHLOROFORM-d) δ = 155.62, 148.25, 142.92, 137.08, 129.96, 129.83, 127.80, 127.50, 126.82, 125.72, 125.69, 118.73. **HRMS (EI)**: *m/z* Calcd for $C_{16}H_{11}NF_3$ $[M+H]^+$: 274.0838; Found: 274.0838.

2-(naphthalen-2-yl)quinoline (7k)



White solid. Yield: 87%. **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ = 8.64 (s, 1H), 8.40 (d, *J* = 8.8 Hz, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 8.05-8.01 (m, 3H), 7.93-7.91 (m, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.77 (t, *J* = 6.9 Hz, 1H), 7.57-7.54 (m, 3H). **^{13}C NMR** (126 MHz, CHLOROFORM-d) δ = 157.12, 148.35, 136.94, 136.76, 133.84, 133.48, 129.72, 129.68, 128.79, 128.54, 127.70, 127.46, 127.19, 127.11, 126.67, 126.30, 125.03, 119.11. **HRMS (EI)**: *m/z* Calcd for $C_{19}H_{14}N$ $[M+H]^+$: 256.1121; Found: 256.1120.

2.3.5 Synthesis of pyrazine derivative



Scheme 4. Synthesis of pyridine derivative (**8**)

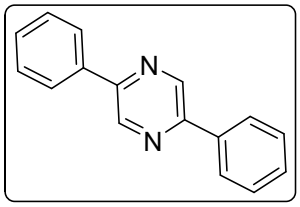
General procedure:

To an oven-dried 15 mL ace pressure tube, 1,2 amino alcohol **3f** (0.25 mmol), Co-complex **1** (2.5 mol%) and *m*-xylene (1 mL) were added under a gentle stream of argon. The mixture was heated at 135°C (bath temperature). After 24 h, the reaction mixture was diluted with water (4 mL) and extracted with dichloromethane (3 x 5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.

Gram-scale synthesis: The present cobalt-catalyzed direct pyrazine synthesis was tested for the gram-scale synthesis, and it worked excellently and gave **8** in 61% (1.02 g) isolated yield.

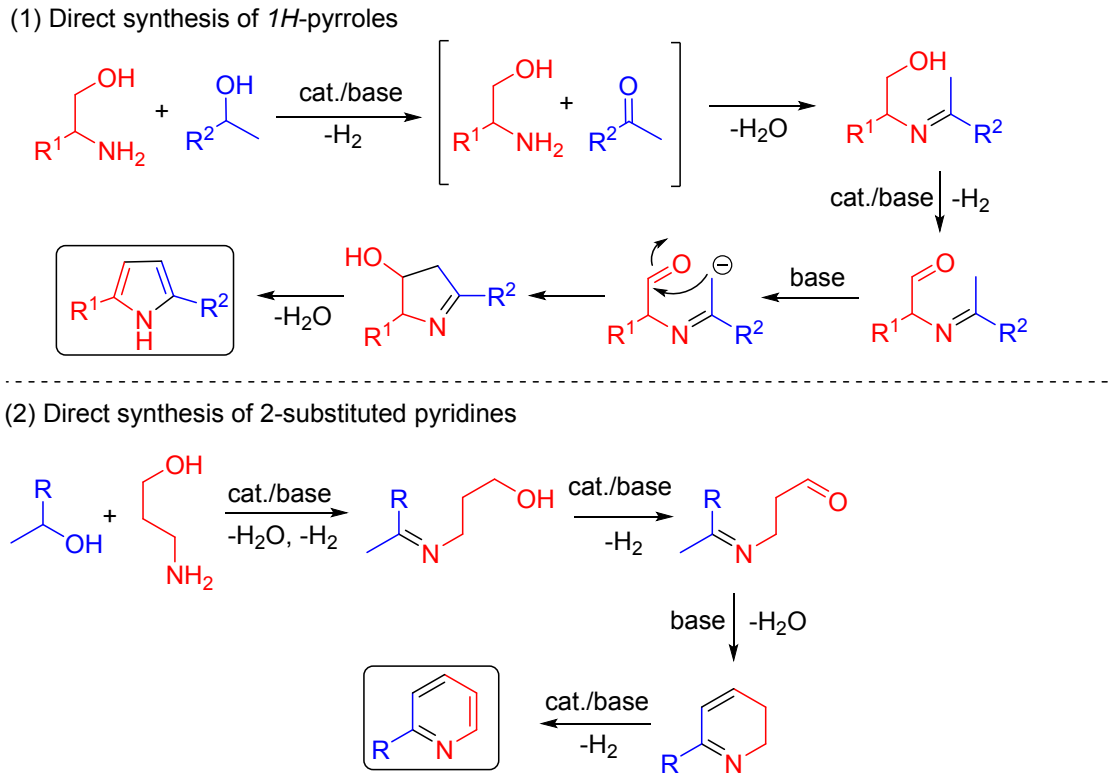
2.3.6 Characterization of pyrazine

2,5-diphenyl pyrazine (8)



White solid. Yield: 68%. **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ = 9.10 (s, 2H), 8.08 (d, *J* = 7.2 Hz, 4H), 7.55 (t, *J* = 7.2 Hz, 4H), 7.50 (q, *J* = 7.2 Hz, 2H). **^{13}C NMR** (126 MHz, CHLOROFORM-d) δ = 150.68, 141.25, 136.27, 129.77, 129.07, 126.79. (Known compound: Gnanaprakasam, B.; Balaraman, E.; Ben-David, Y.; Milstein, D. *Angew. Chem. Int. Ed.* **2011**, *50*, 12240).

2.3.7 A plausible mechanism



2.3.8 Homogenous test

To an oven-dried 15 mL ace pressure tube, 1,2 amino alcohol **3** (0.25 mmol), secondary alcohol **4** (0.5 mmol), Co-complex **1** (2.5 mol%), 10 equiv. of mercury, and *m*-xylene (2 mL) were added under a gentle stream of argon. The mixture was of heated at reflux for 24 h followed by cooling to room temperature. Then, the reaction mixture was diluted with water (4 mL) and extracted with dichloromethane (3 x 5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system

3. **Crystallographic data** (CCDC 1555768)

Compound	**1**
Empirical formula	$C_{48}H_{104}Cl_{12}Co_6N_6S_{12}$
Formula weight	1929.07
Temperature/K	149.97(15)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	29.8732(14)
b/Å	7.1198(4)
c/Å	20.6123(11)
α/°	90.00
β/°	108.276(5)
γ/°	90.00
Volume/Å^3	4162.9(4)
Z	2
ρ_{calc}g/cm^3	1.539
μ/mm^{-1}	1.889
F(000)	1984.0
Crystal size/mm^3	0.4 × 0.3 × 0.2
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.9 to 58.68
Index ranges	$-38 \le h \le 39$, $-9 \le k \le 9$, $-27 \le l \le 24$
Reflections collected	25358
Independent reflections	9858 [R_{int} = 0.0423, R_{sigma} = 0.0497]
Data/restraints/parameters	9858/0/401
Goodness-of-fit on F^2	1.123
Final R indexes [I>=2σ (I)]	R_1 = 0.1044, wR_2 = 0.2496
Final R indexes [all data]	R_1 = 0.1246, wR_2 = 0.2632
Largest diff. peak/hole / e Å^{-3}	4.00/-1.13

*To avoid the disorder in the structure, chemical occupancy of C16A and C16B has been assigned as 0.5.

Datablock:

Bond precision: C-C = 0.0139 A Wavelength=0.71073

Cell: a=29.8732(14) b=7.1198(4) c=20.6123(11)
alpha=90 beta=108.276(5) gamma=90

Temperature: 150 K

	Calculated	Reported
Volume	4162.9(4)	4162.9(4)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C16 H33 Cl4 Co2 N2 S4, 2(C16 H35.50 Cl4 Co2 N2 S4)	C16 H33 Cl4 Co2 N2 S4, 2(C16 H35.50 Cl4 Co2 N2 S4)
Sum formula	C48 H104 Cl12 Co6 N6 S12	C48 H104 Cl12 Co6 N6 S12
Mr	1929.07	1929.07
Dx,g cm-3	1.539	1.539
Z	2	2
Mu (mm-1)	1.889	1.889
F000	1984.0	1984.0
F000'	1994.95	
h,k,lmax	41,9,28	39,9,27
Nref	11426	9858
Tmin,Tmax	0.512,0.685	0.593,1.000
Tmin'	0.465	

Correction method= # Reported T Limits: Tmin=0.593 Tmax=1.000
AbsCorr = MULTI-SCAN
Data completeness= 0.863 Theta(max)= 29.340
R(reflections)= 0.1044(7627) wR2(reflections)= 0.2632(9858)

S = 1.123 Npar= 401

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT097_ALERT_2_B Large Reported Max. (Positive) Residual Density 4.00 eA-3
PLAT234_ALERT_4_B Large Hirshfeld Difference C15 -- C16A .. 0.30 Ang.

Alert level C

DIFMX02_ALERT_1_C The maximum difference density is > 0.1*ZMAX*0.75
The relevant atom site should be identified.
PLAT018_ALERT_1_C _diffrn_measured_fraction_theta_max .NE. *_full ! Check
PLAT084_ALERT_3_C High wR2 Value (i.e. > 0.25) ..... 0.26 Report
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density .... 3.53 Report
PLAT213_ALERT_2_C Atom Cl6 has ADP max/min Ratio ..... 3.4 prolat
PLAT220_ALERT_2_C Non-Solvent Resd 2 C Ueq(max)/Ueq(min) Range 3.2 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference C23 -- C24B .. 0.22 Ang.
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C14 Check
PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C15 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of S4 Check
PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0139 Ang.
PLAT601_ALERT_2_C Structure Contains Solvent Accessible VOIDS of . 31 Ang3

Alert level G

PLAT005_ALERT_5_G No Embedded Refinement Details found in the CIF Please Do !
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 3 Report
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large 78.61 Why ?
PLAT093_ALERT_1_G No s.u.'s on H-positions, Refinement Reported as mixed Check
PLAT300_ALERT_4_G Atom Site Occupancy of C24A is Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of C24B is Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H7A is Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H14A is Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H14B is Constrained at 0.5 Check
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PLAT300_ALERT_4_G Atom Site Occupancy of C16B is Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H2A is Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H2B is Constrained at 0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of H4 is Constrained at 0.5 Check
PLAT301_ALERT_3_G Main Residue Disorder .....(Resd 1).. 7 % Note
PLAT301_ALERT_3_G Main Residue Disorder .....(Resd 2).. 4 % Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms (63.50) in Resd. # 2 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact C16B .. C24A .. 3.04 Ang.
PLAT793_ALERT_4_G The Model has Chirality at N2 (Centro SPGR) R Verify
PLAT793_ALERT_4_G The Model has Chirality at N3 (Centro SPGR) R Verify
PLAT950_ALERT_5_G Calculated (ThMax) and CIF-Reported Hmax Differ 2 Units

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
2 **ALERT level B** = A potentially serious problem, consider carefully
12 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
21 **ALERT level G** = General information/check it is not something unexpected

3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
10 ALERT type 2 Indicator that the structure model may be wrong or deficient
4 ALERT type 3 Indicator that the structure quality may be low
15 ALERT type 4 Improvement, methodology, query or suggestion
3 ALERT type 5 Informative message, check

Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

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# start Validation Reply Form
_vrf_DIFMX02_sibada1
;
PROBLEM: The maximum difference density is > 0.1*ZMAX*0.75
RESPONSE: ...
;
_vrf_PLAT018_sibada1
;
PROBLEM: _diffrn_measured_fraction_theta_max .NE. *_full           ! Check
RESPONSE: ...
;
_vrf_PLAT084_sibada1
;
PROBLEM: High wR2 Value (i.e. > 0.25) ...................       0.26 Report
RESPONSE: ...
;
_vrf_PLAT094_sibada1
;
PROBLEM: Ratio of Maximum / Minimum Residual Density ....       3.53 Report
RESPONSE: ...
;
_vrf_PLAT213_sibada1
;
PROBLEM: Atom Cl6             has ADP max/min Ratio .....        3.4 prolat
RESPONSE: ...
;
_vrf_PLAT220_sibada1
;
PROBLEM: Non-Solvent Resd 2   C   Ueq(max)/Ueq(min) Range        3.2 Ratio
RESPONSE: ...
;
_vrf_PLAT234_sibada1
;
PROBLEM: Large Hirshfeld Difference C23    --  C24B    ..       0.22 Ang.
RESPONSE: ...
;
_vrf_PLAT241_sibada1
;
PROBLEM: High   'MainMol' Ueq as Compared to Neighbors of        C14 Check
RESPONSE: ...
;
_vrf_PLAT242_sibada1
;
PROBLEM: Low    'MainMol' Ueq as Compared to Neighbors of         S4 Check
RESPONSE: ...
;
_vrf_PLAT341_sibada1
;
PROBLEM: Low Bond Precision on  C-C Bonds ...............     0.0139 Ang.
RESPONSE: ...
;
_vrf_PLAT601_sibada1
;
PROBLEM: Structure Contains Solvent Accessible VOIDS of .         31 Ang3
RESPONSE: ...
;
# end Validation Reply Form
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It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more
serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

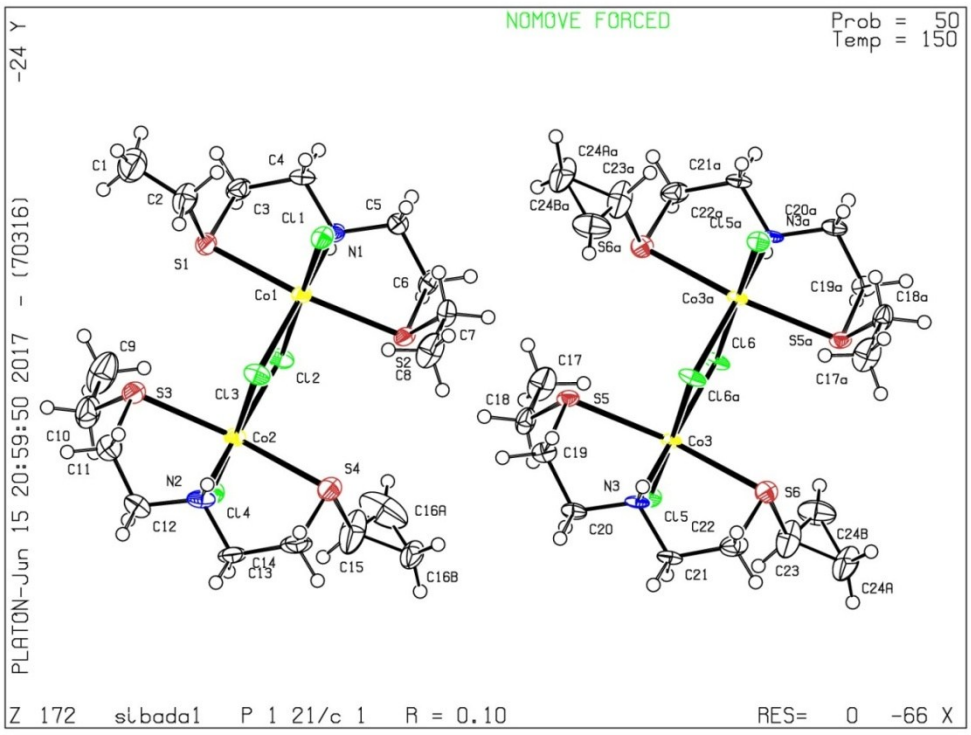
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 27/03/2017; check.def file version of 24/03/2017

Datablock - ellipsoid plot



4. References:

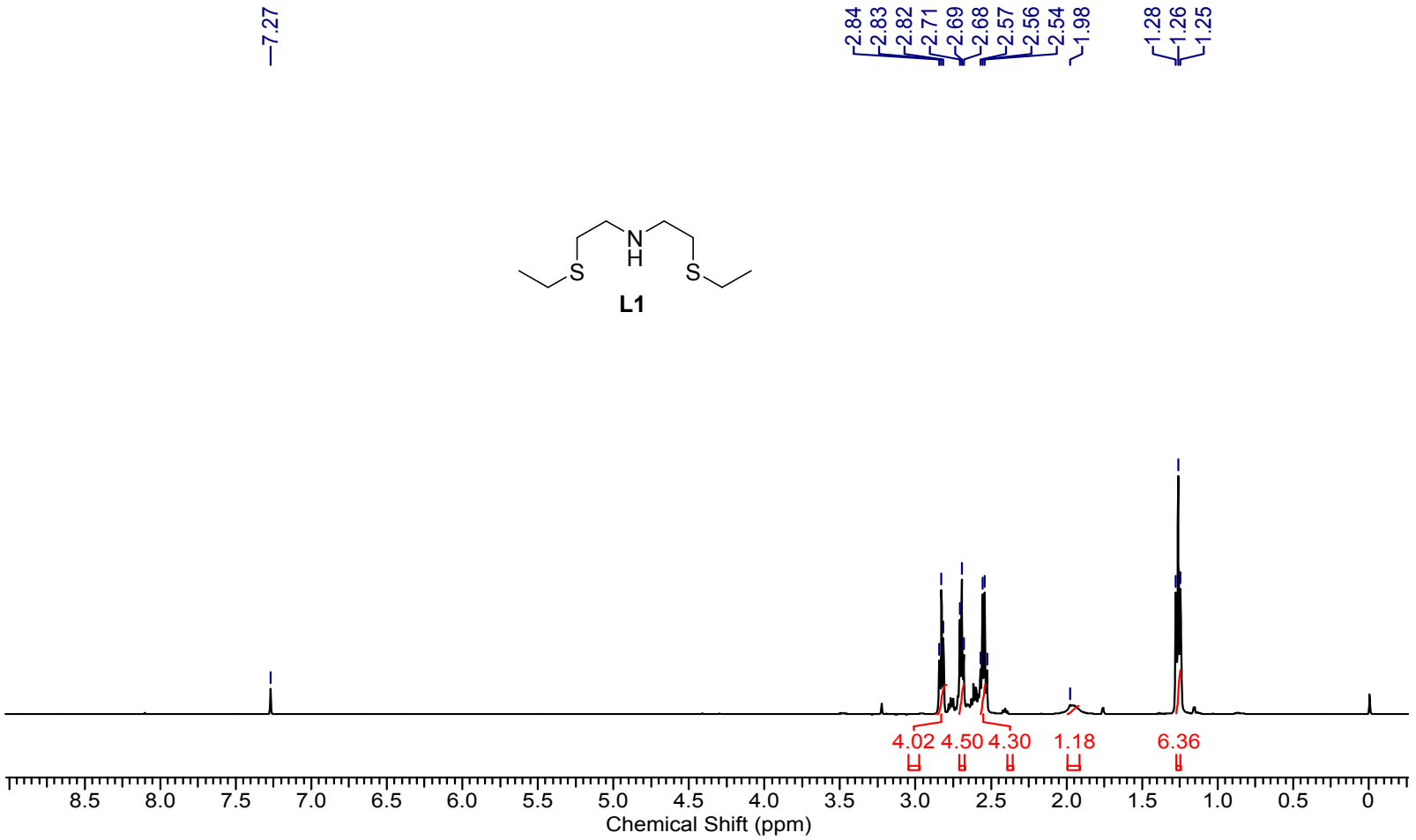
S1. W. L. F. Armarego and Perrin, D. D. *Purification of Laboratory Chemicals* (Pergamon Press, Oxford, 1988) ed 3.

S2. Spasyuk, D.; Smith, S.; Gusev, D. G. *Angew. Chem. Int. Ed.* **2013**, *52*, 2538.

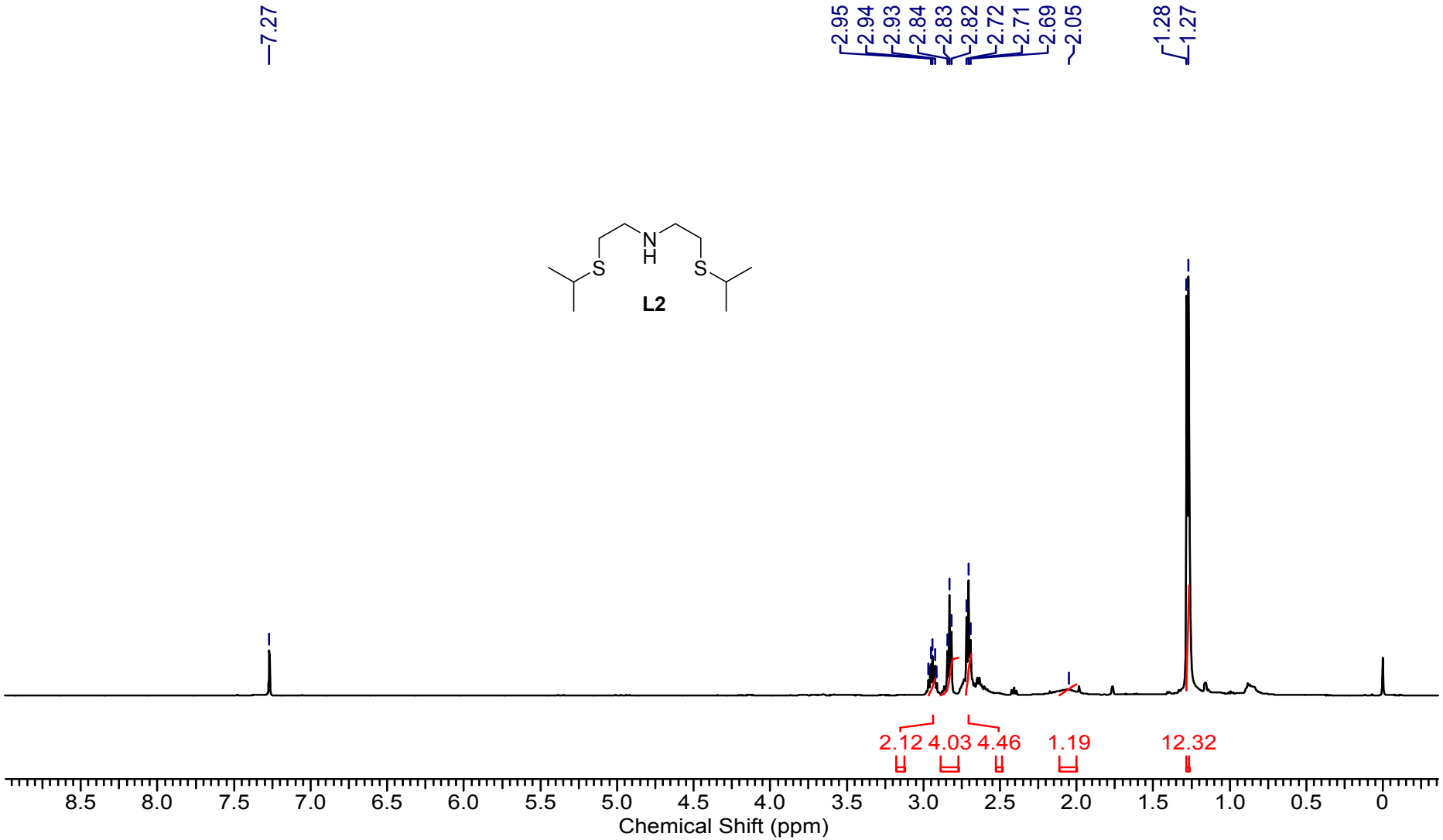
S3. APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA, 2006.

S4. Sheldrick, G. M. *Acta Crystallogr*. **2008**, *A64*, 112.

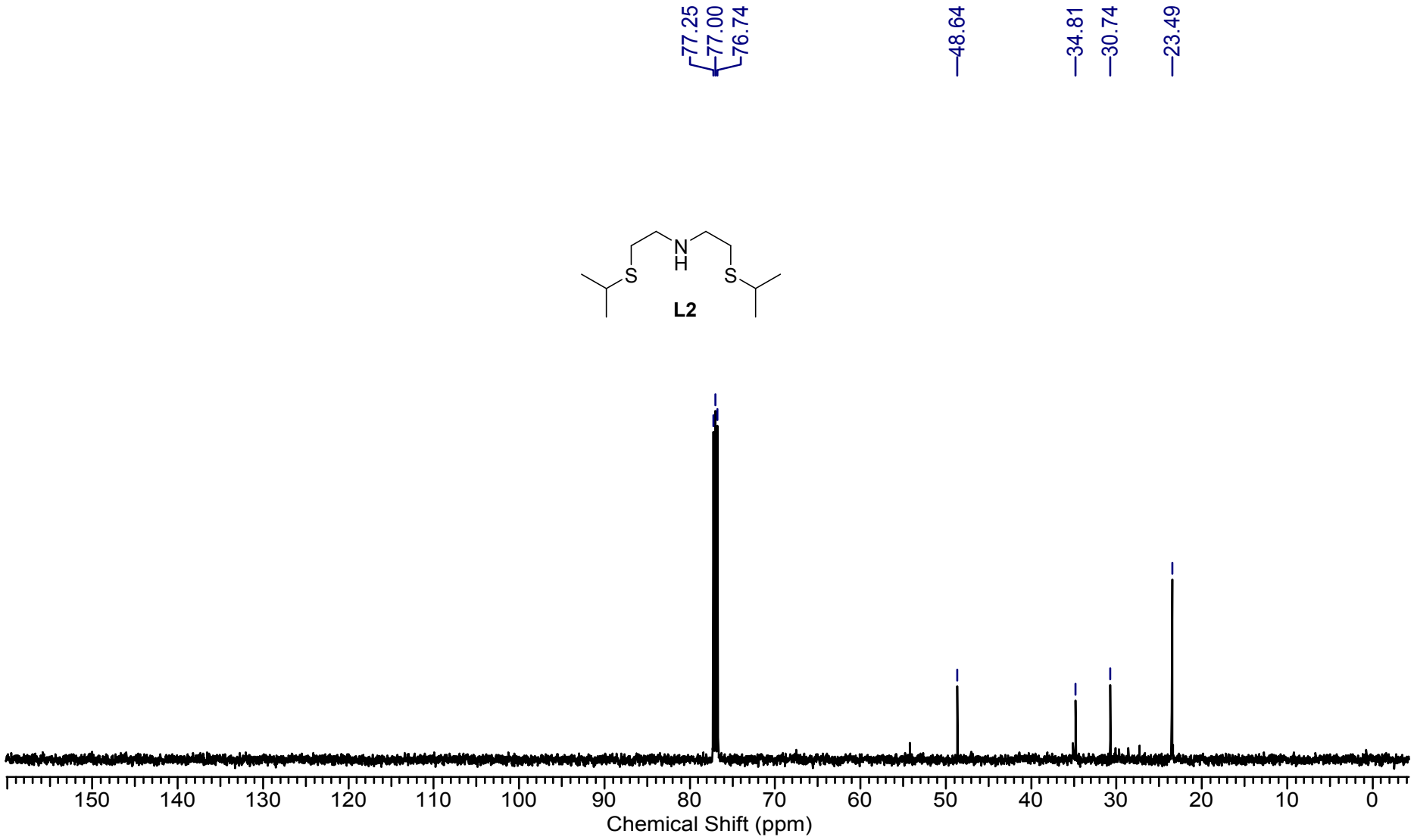
5. Copy of Spectra



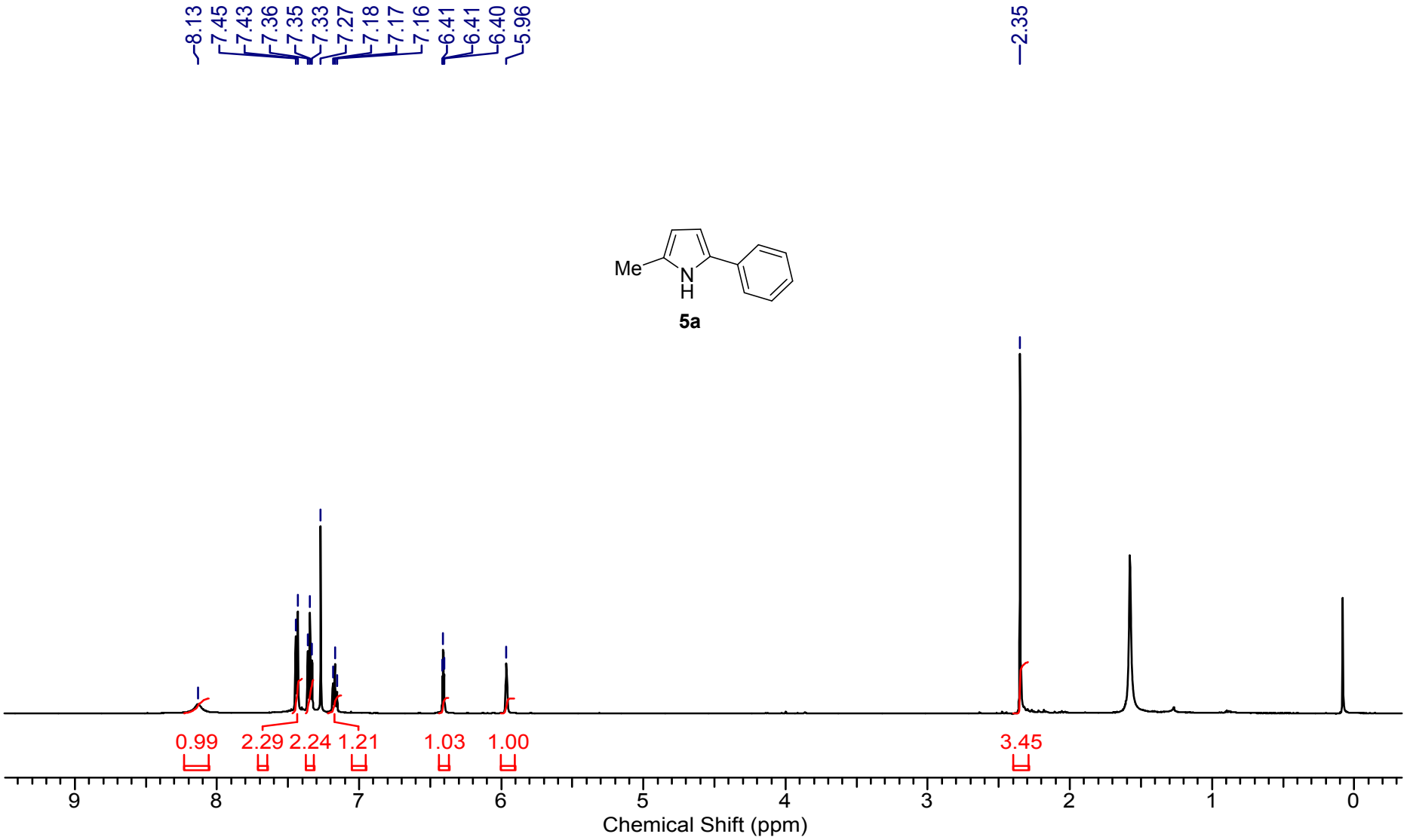
^{1}H NMR of ^{Et}**SNS-L1**



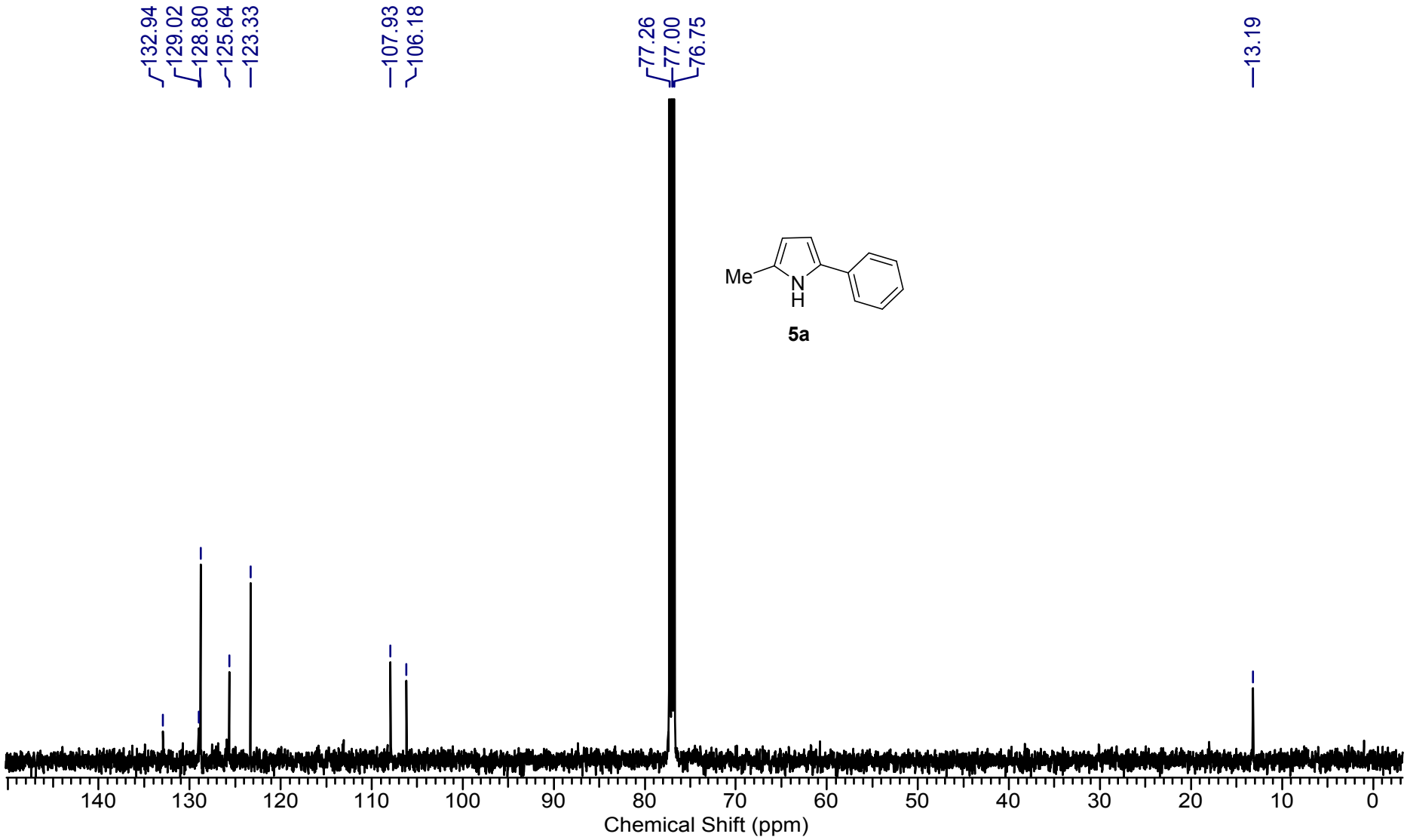
^{1}H NMR of $^{iso\text{Pr}}$**SNS-L2**



^{13}C NMR of $^{iso\text{Pr}}$**SNS-L2**


8.13
7.45
7.43
7.36
7.35
7.33
7.27
7.18
7.17
7.16
6.41
6.41
6.40
5.96
2.35
Me
N
H
5a
0.99
2.29
2.24
1.21
1.03
1.00
3.45
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

^{1}H NMR of **5a**


132.94
129.02
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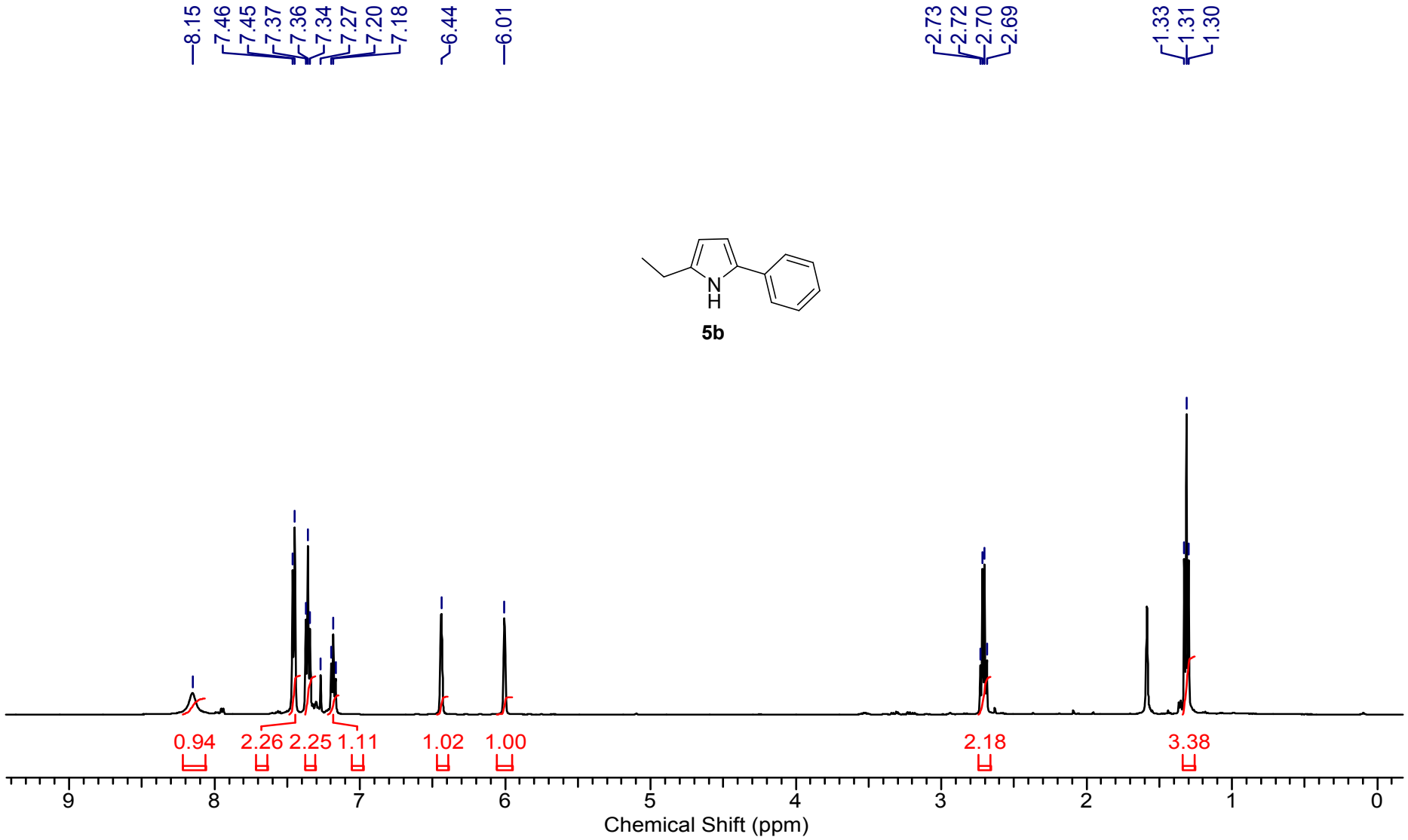
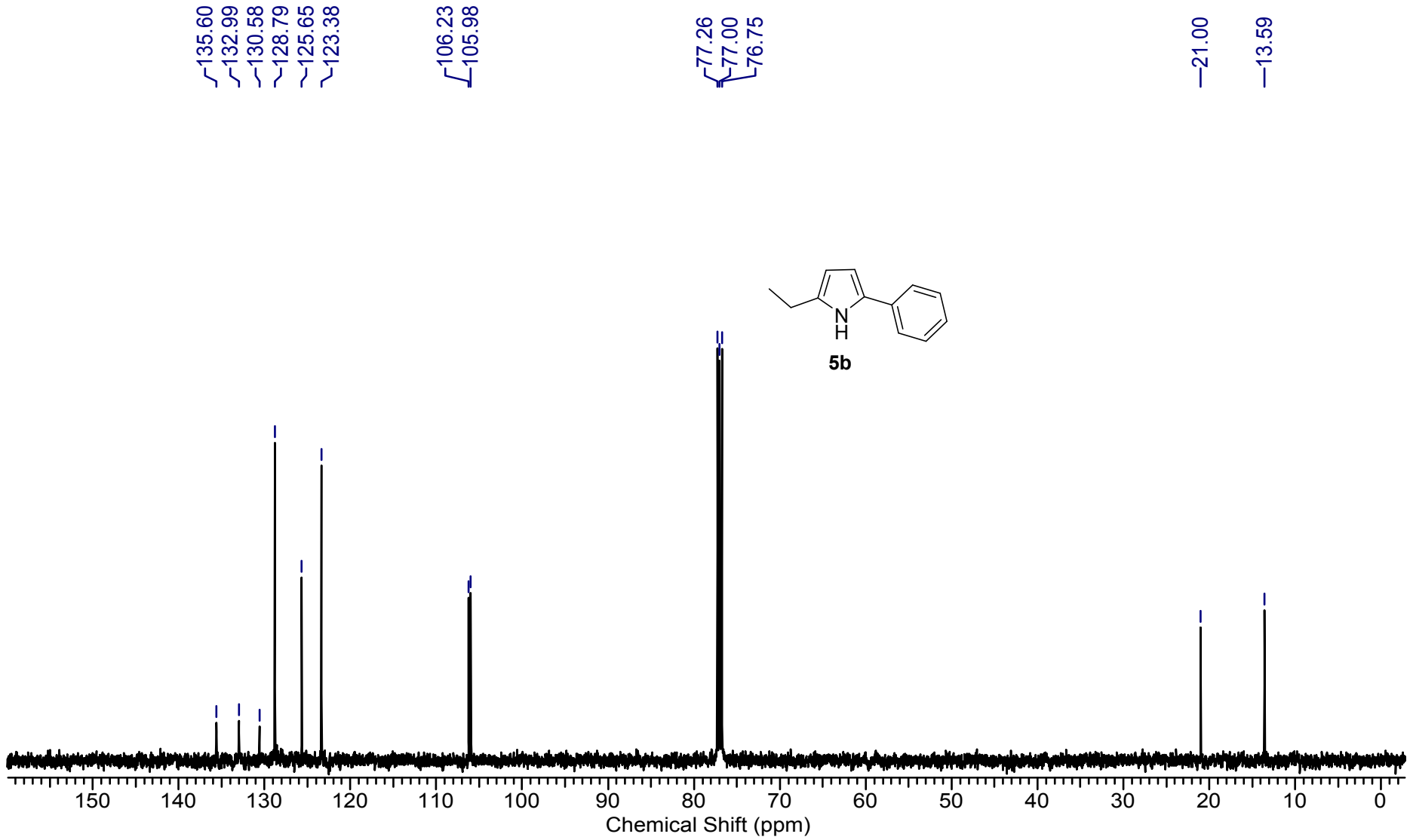
125.64
123.33
107.93
106.18
77.26
77.00
76.75
13.19
Me
N
H
5a
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

^{13}C NMR of **5a**

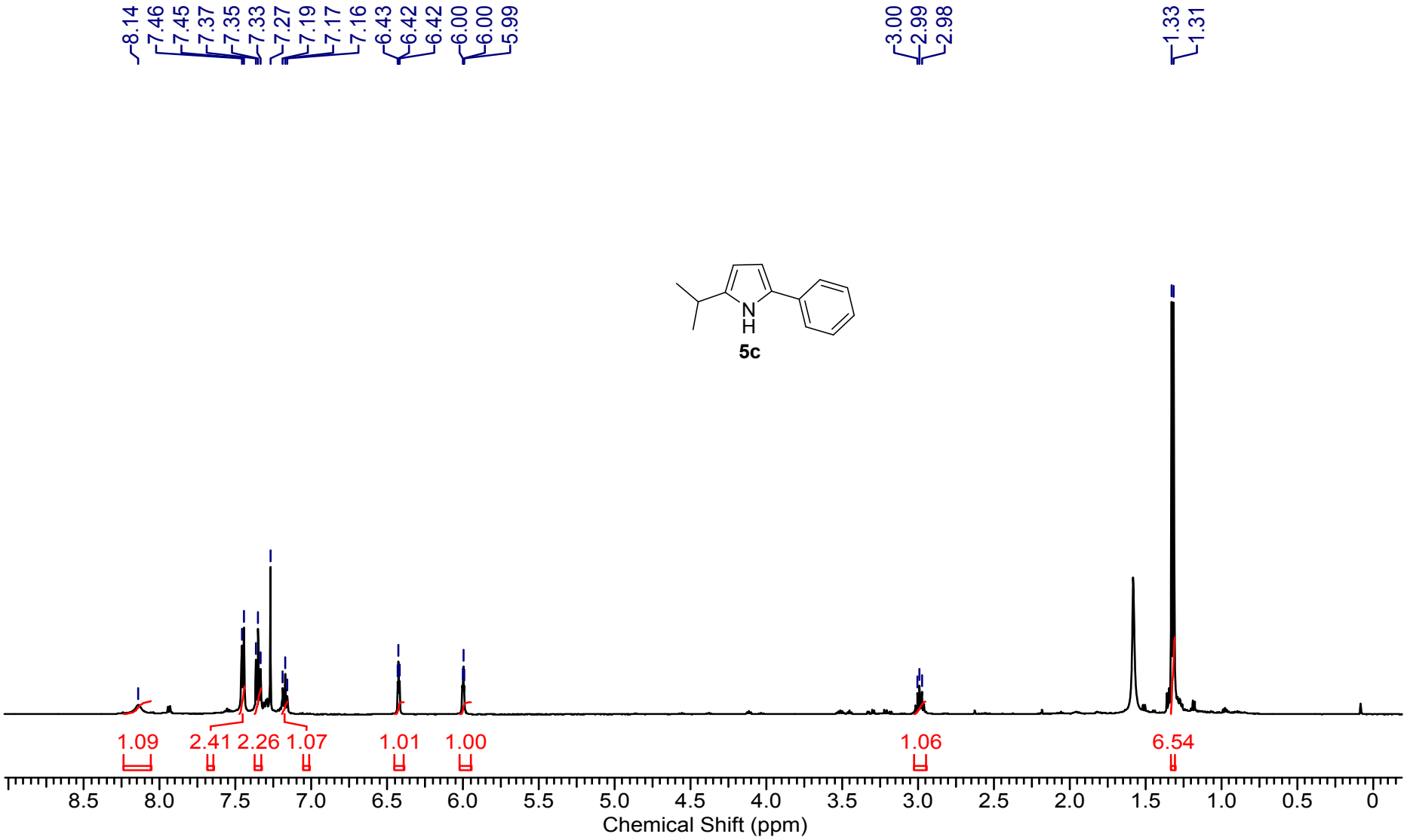


5b

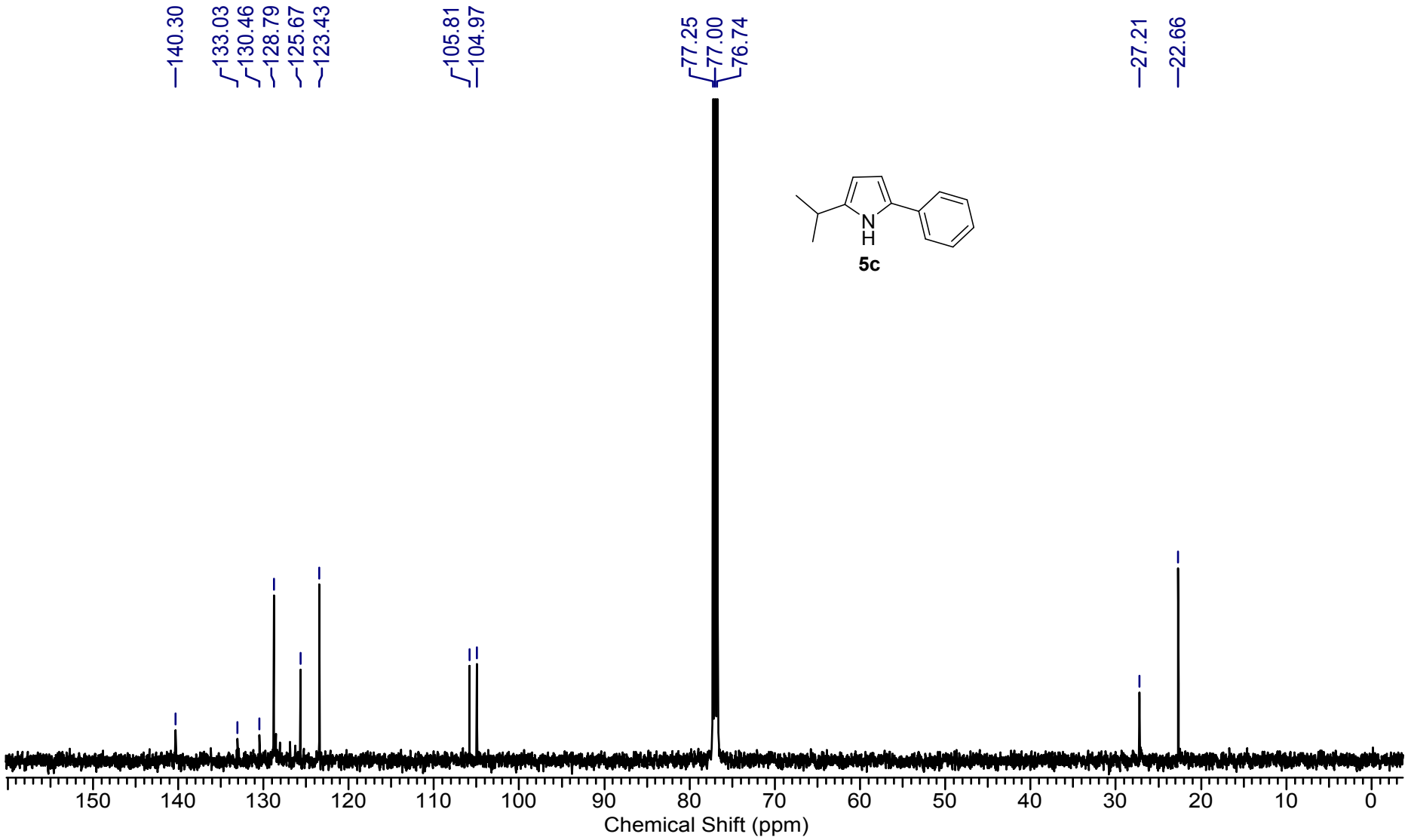
^{1}H NMR of **5b**


135.60
132.99
130.58
128.79
125.65
123.38
106.23
105.98
77.26
77.00
76.75
21.00
13.59
N
H
5b
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

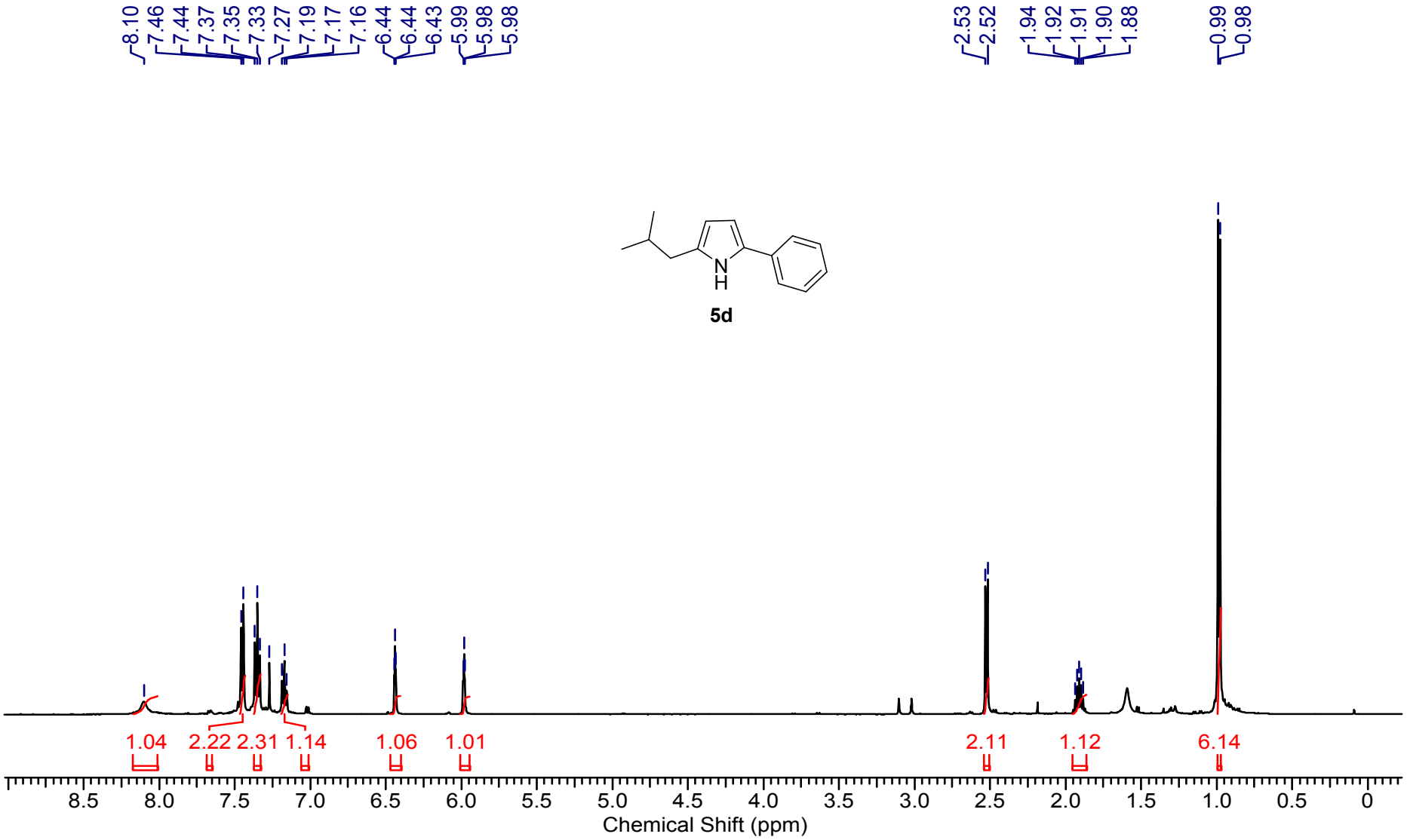
^{13}C NMR of **5b**


8.14
7.46
7.45
7.37
7.35
7.33
7.27
7.19
7.17
7.16
6.43
6.42
6.42
6.00
6.00
5.99
3.00
2.99
2.98
1.33
1.31
N
H
5c
1.09
2.41
2.26
1.07
1.01
1.00
1.06
6.54
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

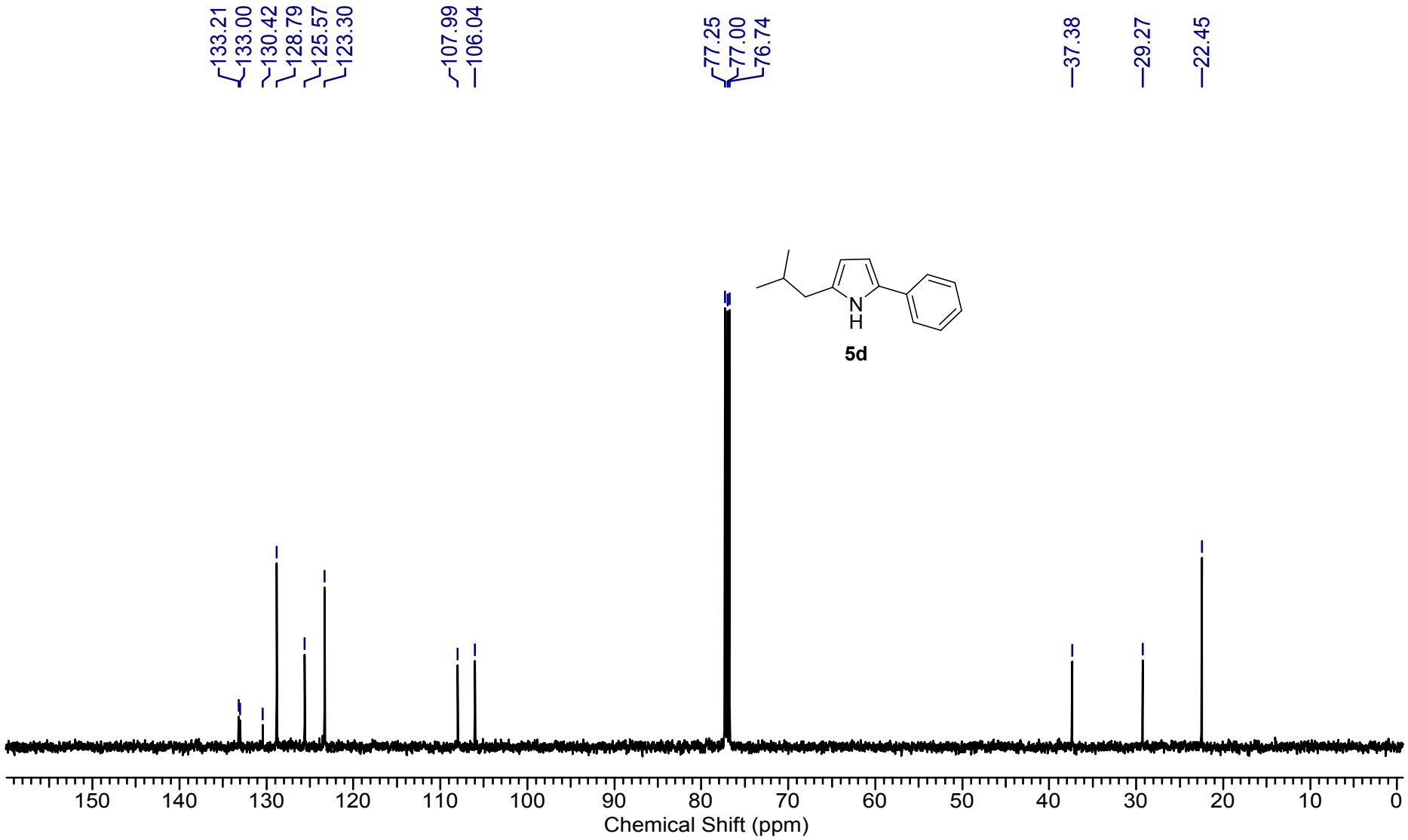
^{1}H NMR of **5c**


140.30
133.03
130.46
128.79
125.67
123.43
105.81
104.97
77.25
77.00
76.74
27.21
22.66
N
H
5c
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

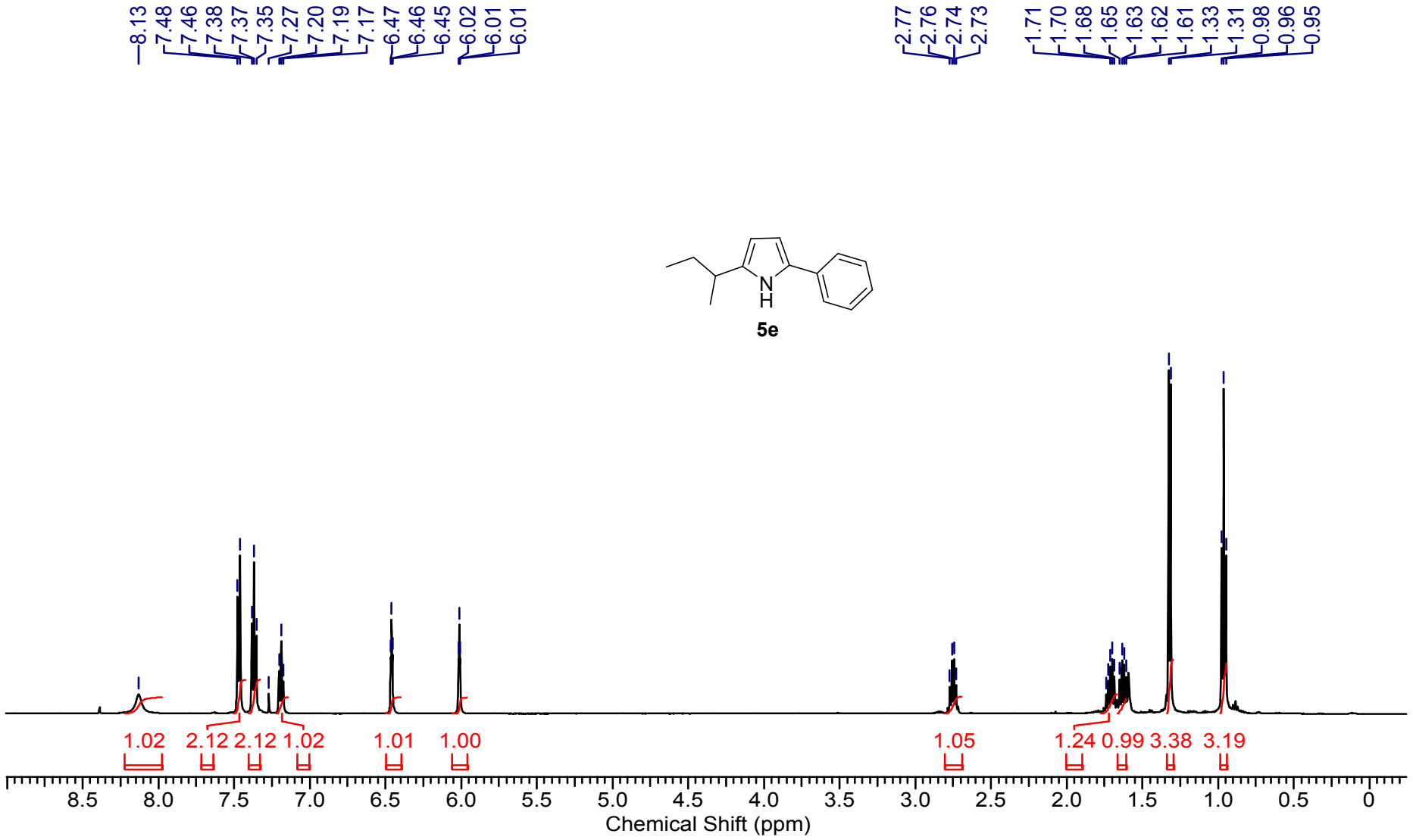
^{13}C NMR of **5c**


8.10
7.46
7.44
7.37
7.35
7.33
7.27
7.19
7.17
7.16
6.44
6.44
6.43
5.99
5.98
5.98
2.53
2.52
1.94
1.92
1.91
1.90
1.88
0.99
0.98
N
H
5d
1.04
2.22
2.31
1.14
1.06
1.01
2.11
1.12
6.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

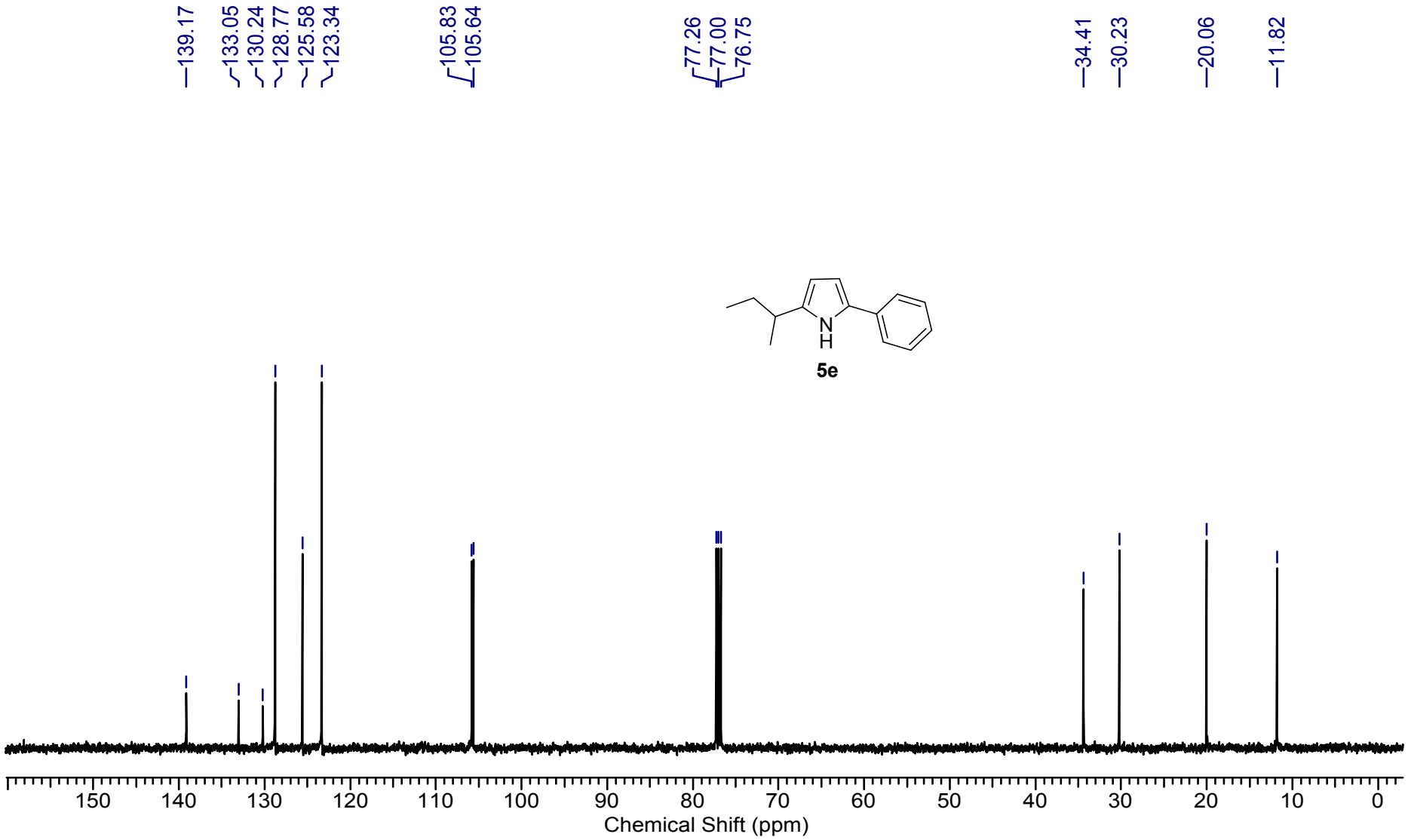
^{1}H NMR of **5d**


133.21
133.00
130.42
128.79
125.57
123.30
107.99
106.04
77.25
77.00
76.74
37.38
29.27
22.45
N
H
5d
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

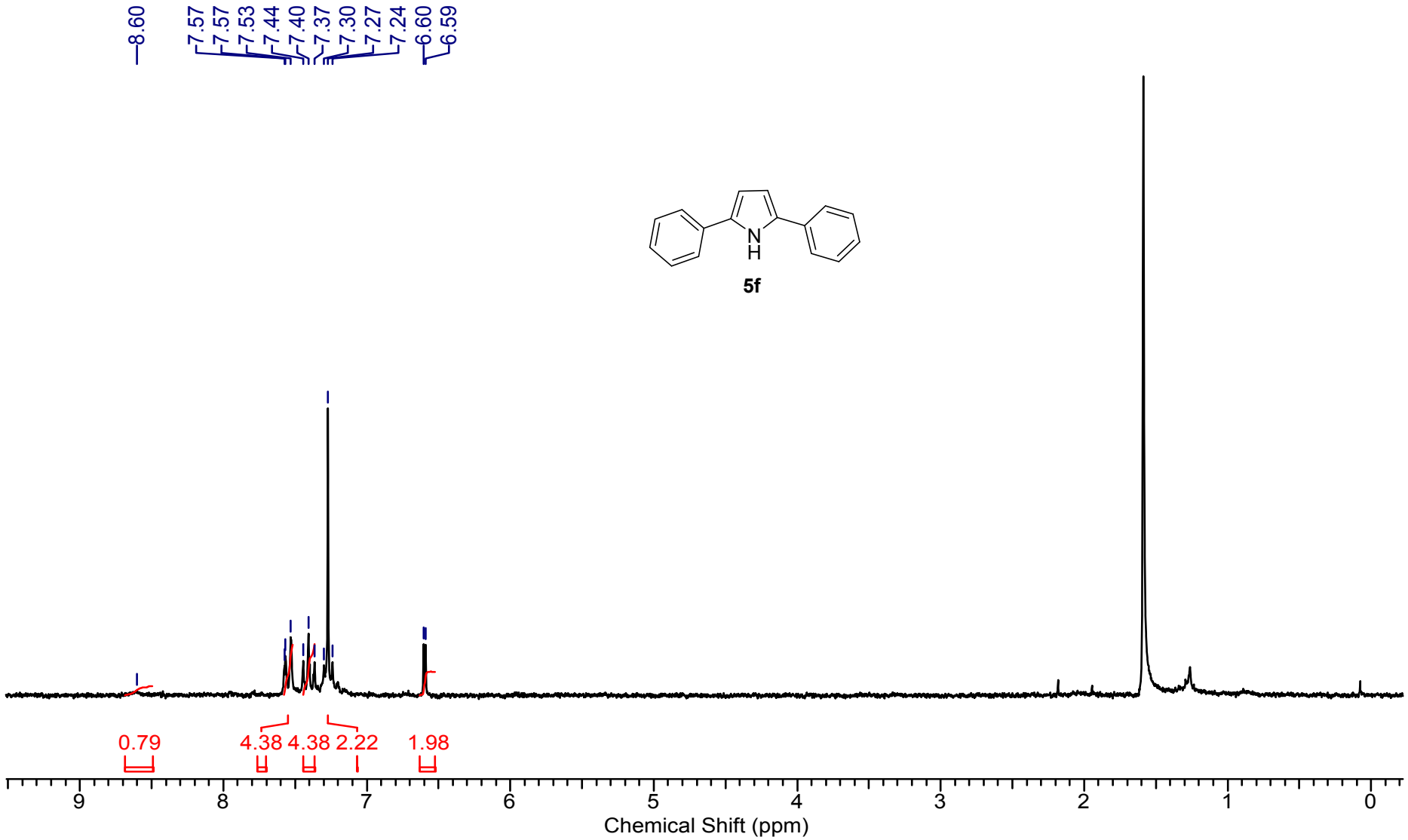
^{13}C NMR of **5d**


8.13
7.48
7.46
7.38
7.37
7.35
7.27
7.20
7.19
7.17
6.47
6.46
6.45
6.02
6.01
6.01
2.77
2.76
2.74
2.73
1.71
1.70
1.68
1.65
1.63
1.62
1.61
1.33
1.31
0.98
0.96
0.95
N
H
5e
1.02
2.12
2.12
1.02
1.01
1.00
1.05
1.24
0.99
3.38
3.19
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

^{1}H NMR of **5e**

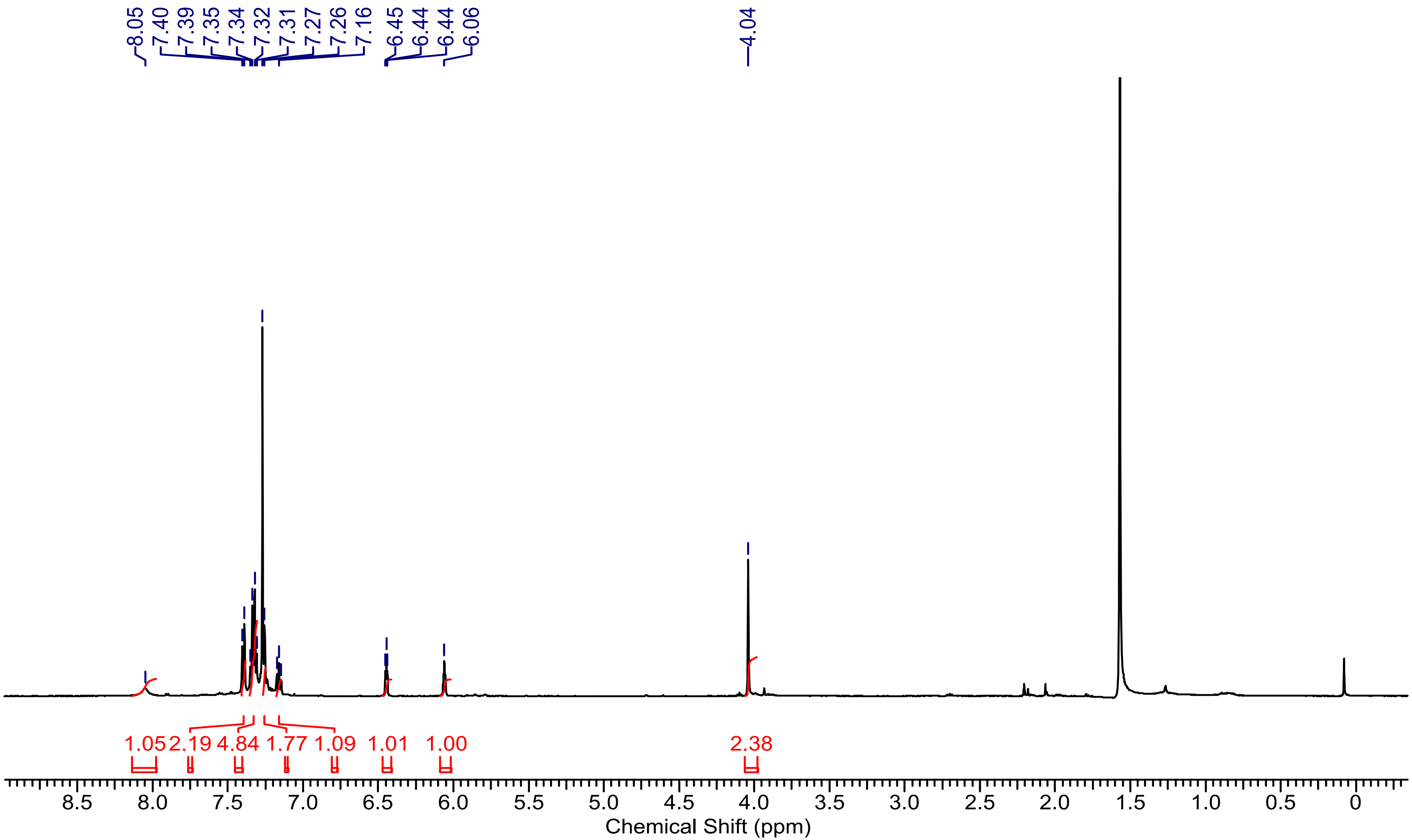

139.17
133.05
130.24
128.77
125.58
123.34
105.83
105.64
77.26
77.00
76.75
34.41
30.23
20.06
11.82
N
H
5e
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

^{13}C NMR of **5e**

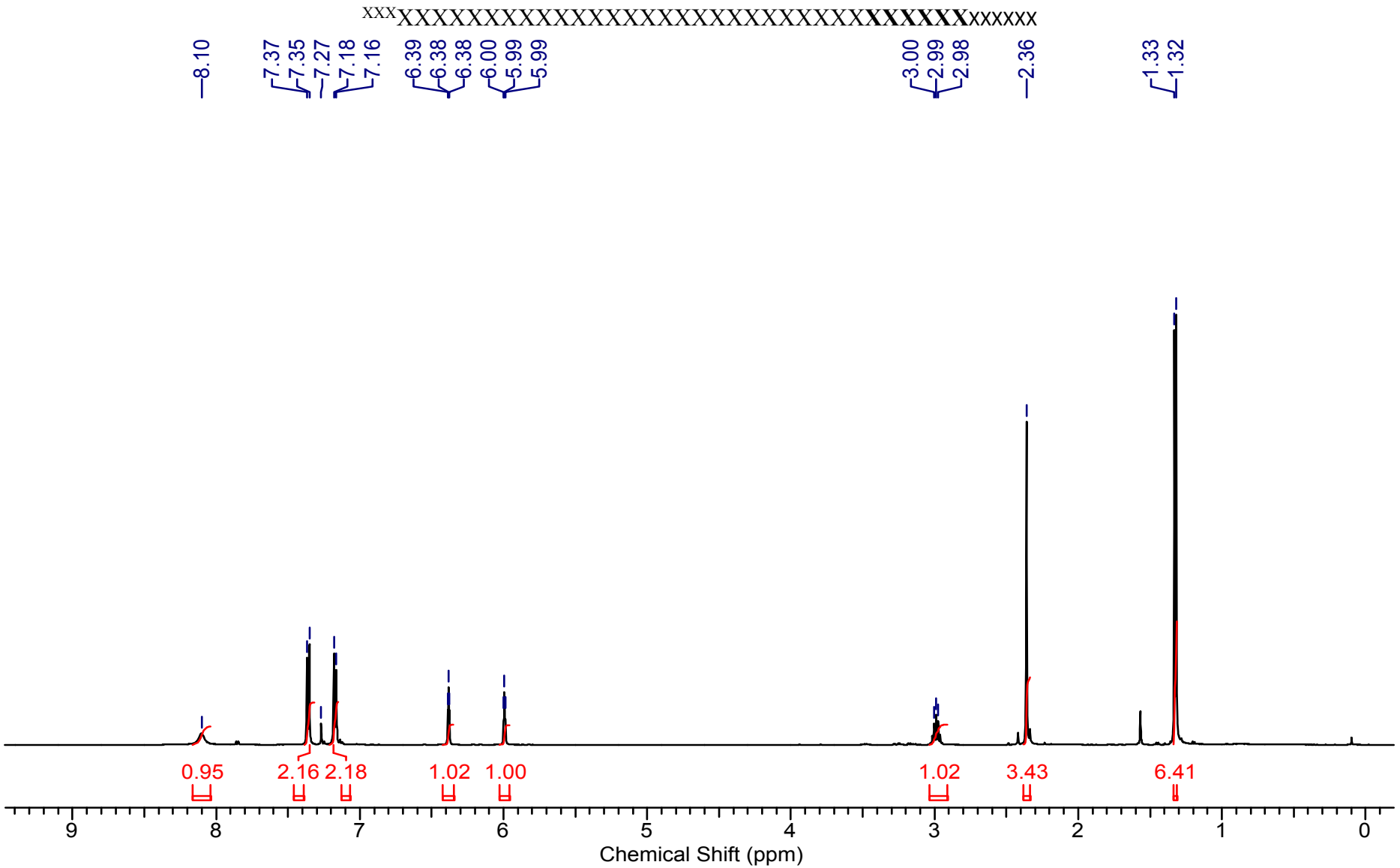

8.60
7.57
7.57
7.53
7.44
7.40
7.37
7.30
7.27
7.24
6.60
6.59
N
H
5f
0.79
4.38
4.38
2.22
1.98
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

^{1}H NMR of **5f**

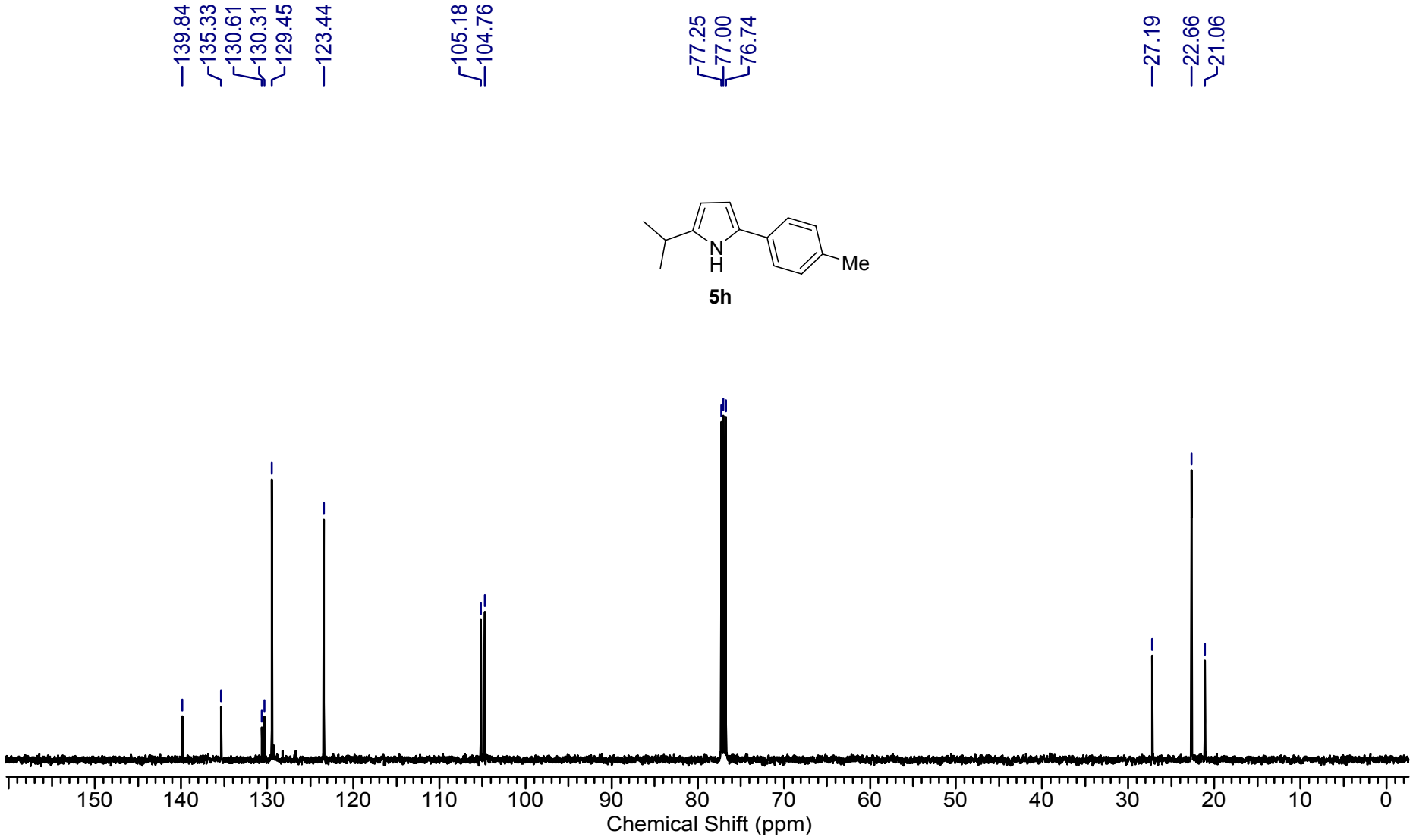
XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX



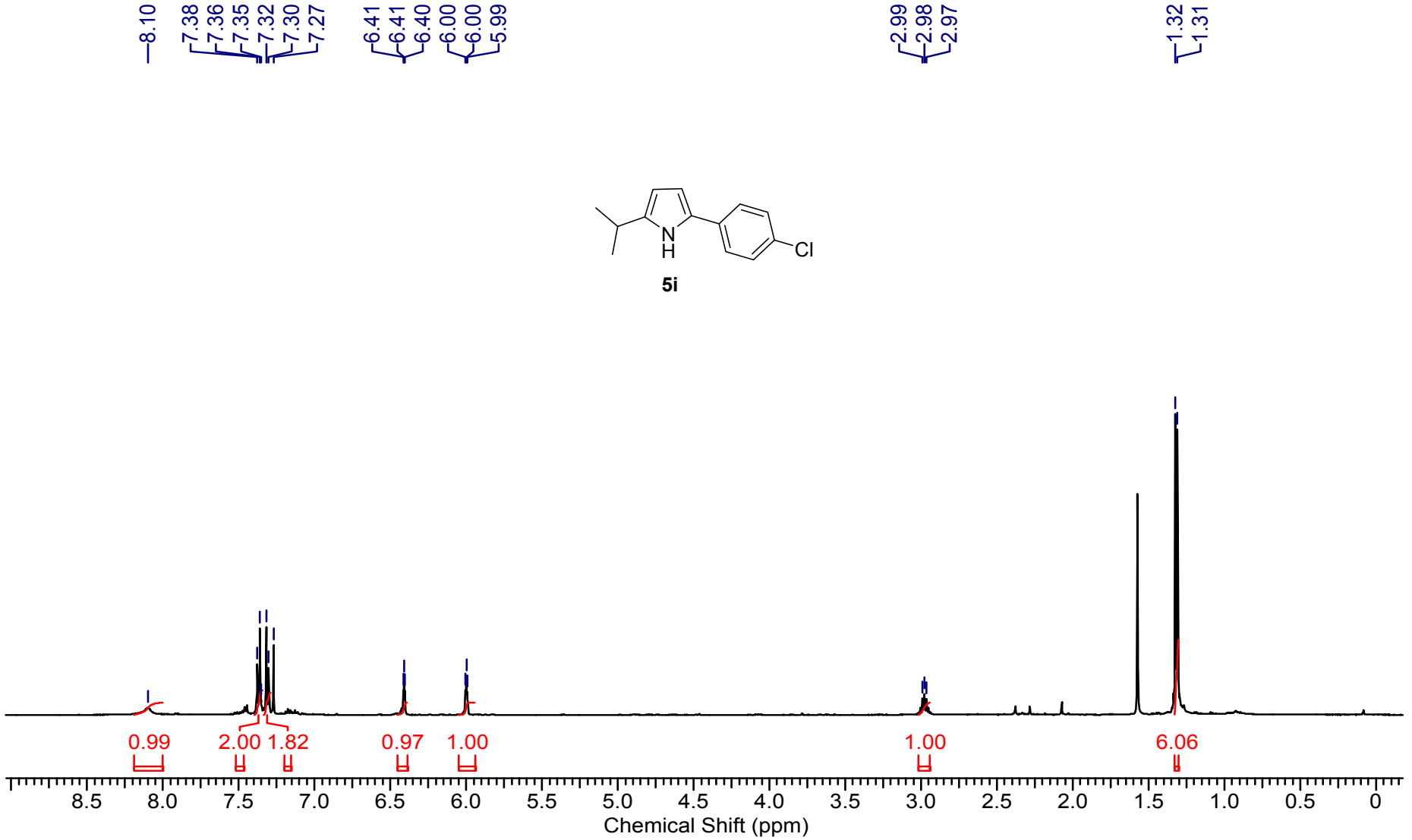
XXX



xxx^{1}H NMR of **5h**

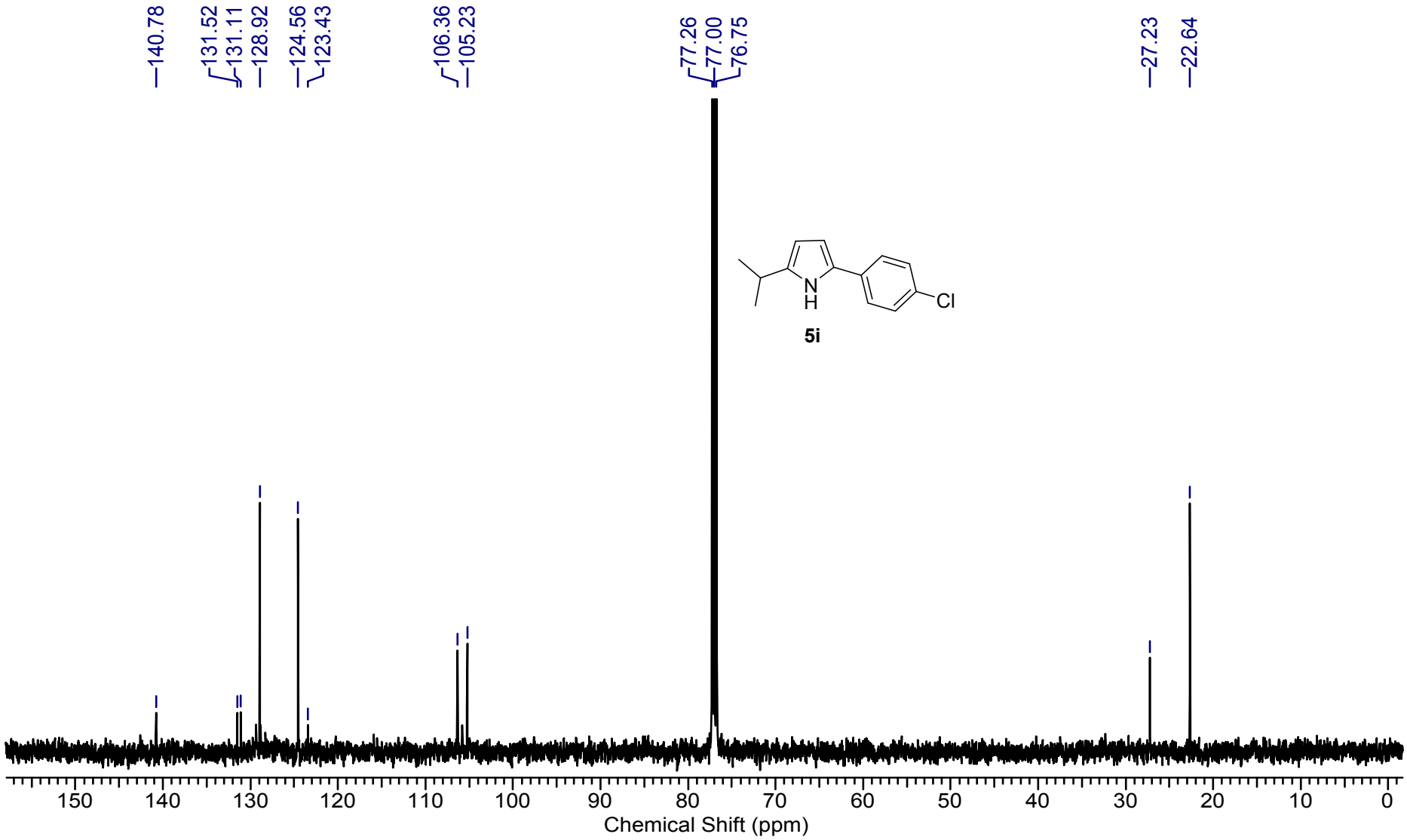

139.84
135.33
130.61
130.31
129.45
123.44
105.18
104.76
77.25
77.00
76.74
27.19
22.66
21.06
N
H
Me
5h
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

^{13}C NMR of **5h**

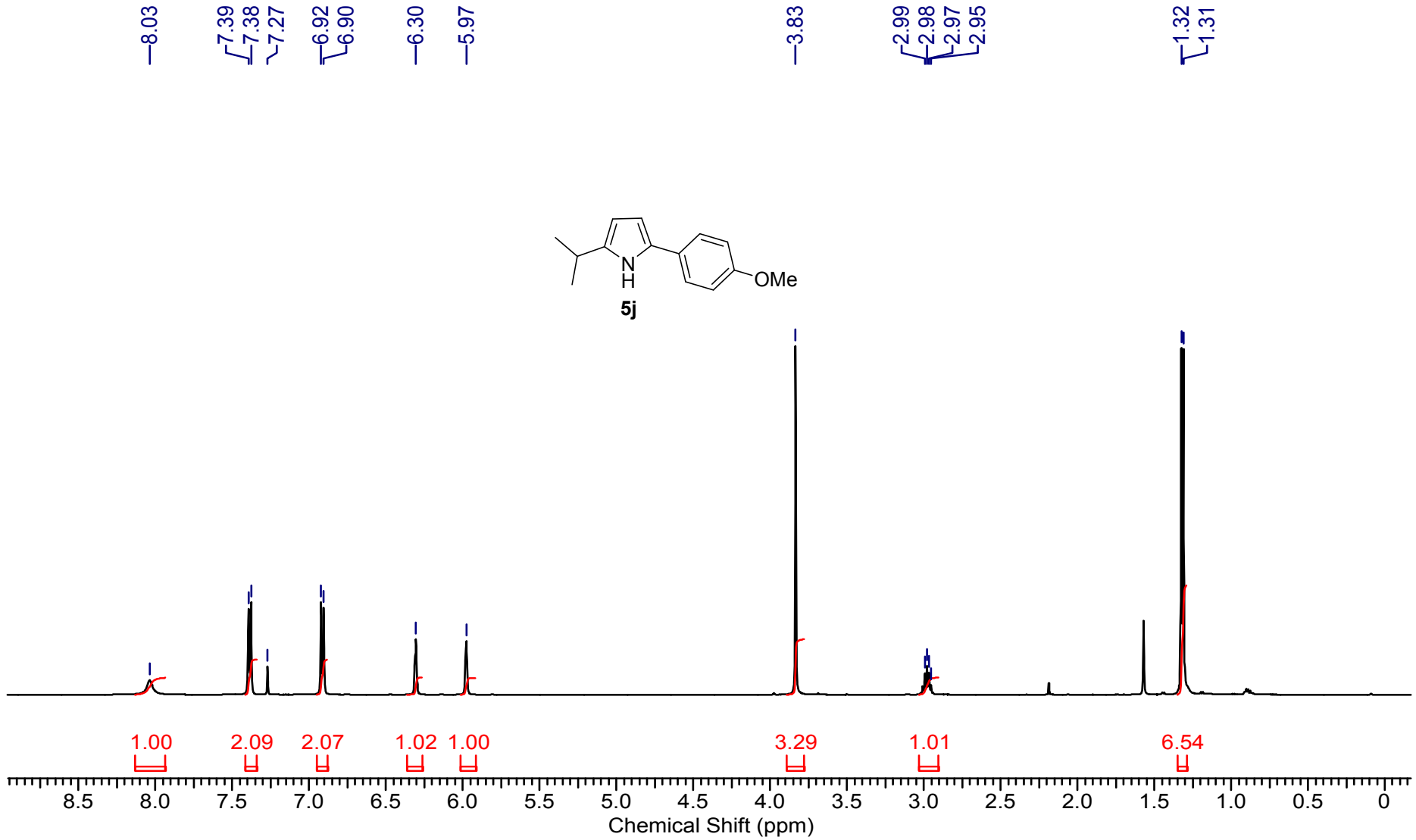


5i

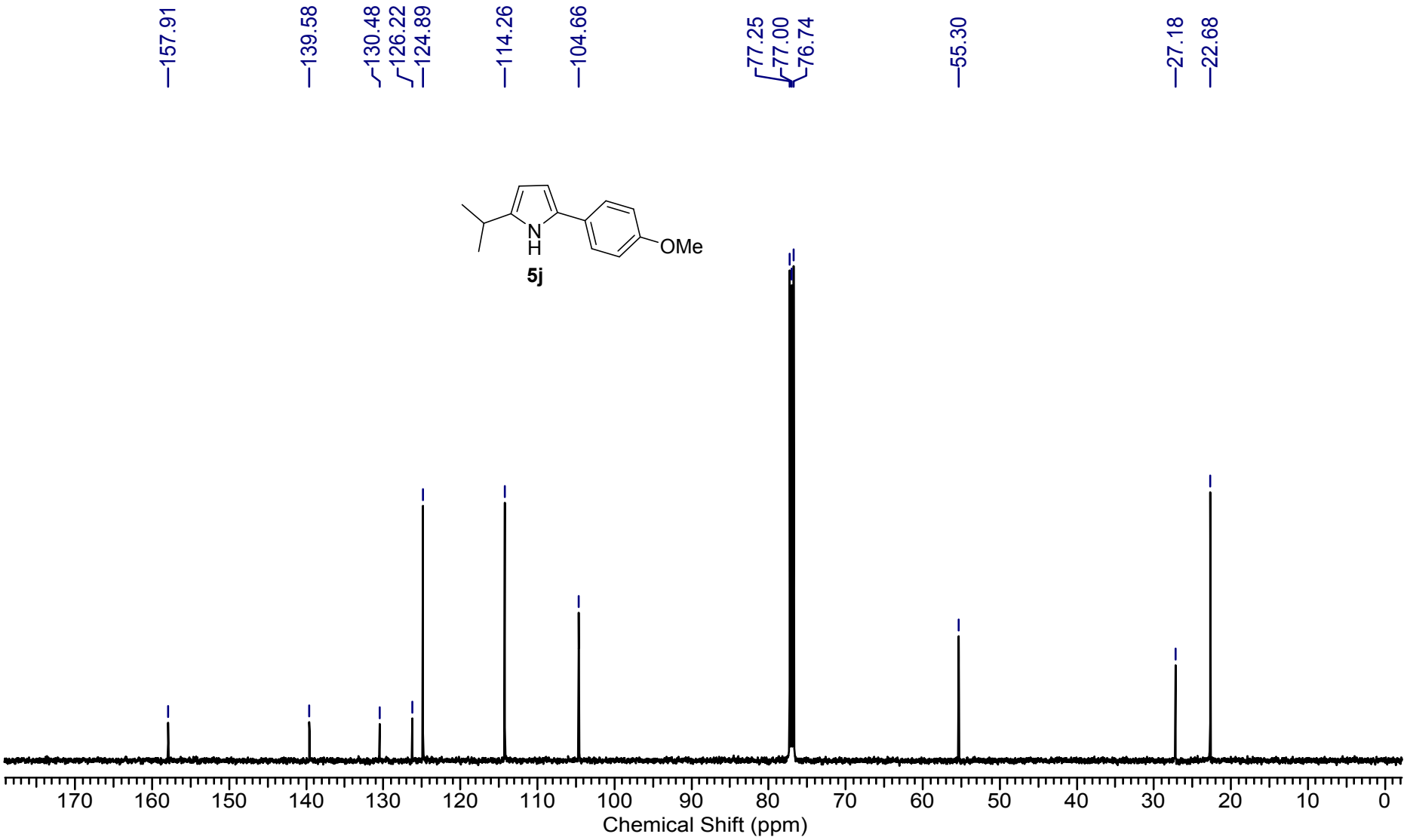
^{1}H NMR of **5i**


140.78
131.52
131.11
128.92
124.56
123.43
106.36
105.23
77.26
77.00
76.75
27.23
22.64
N
H
Cl
5i
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

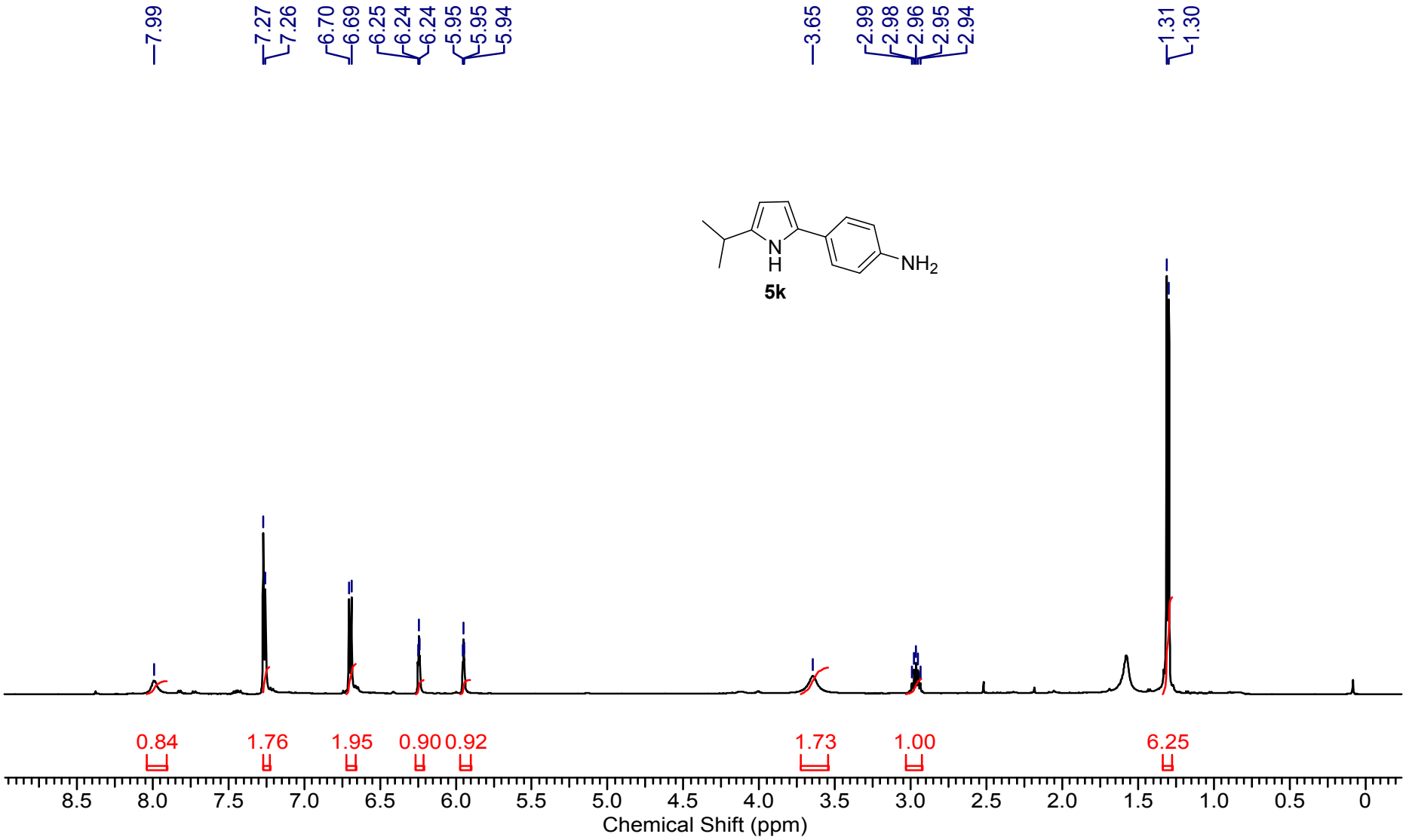
^{13}C NMR of **5i**


8.03
7.39
7.38
7.27
6.92
6.90
6.30
5.97
3.83
2.99
2.98
2.97
2.95
1.32
1.31
N
H
OMe
5j
1.00
2.09
2.07
1.02
1.00
3.29
1.01
6.54
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

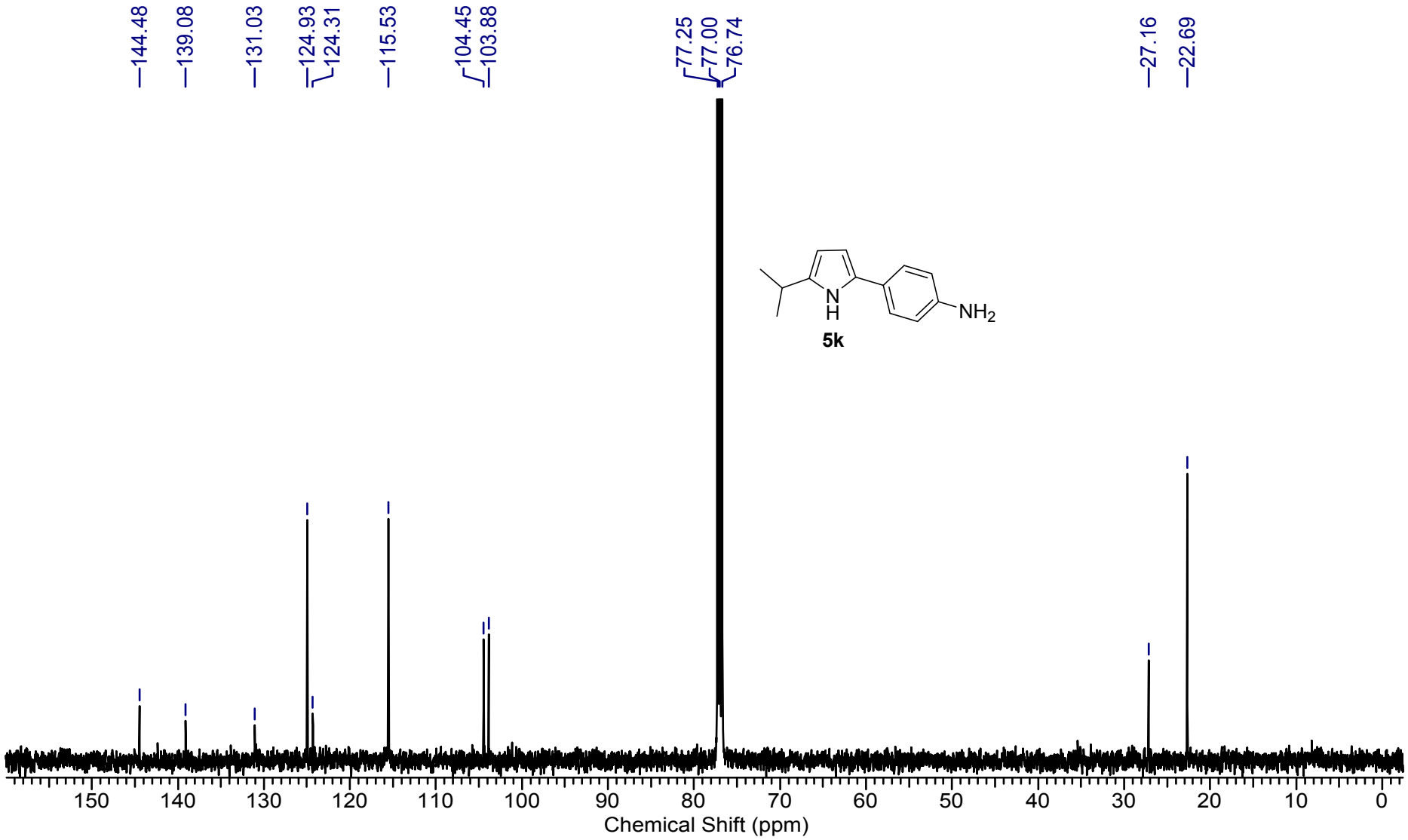
^{1}H NMR of **5j**


157.91
139.58
130.48
126.22
124.89
114.26
104.66
77.25
77.00
76.74
55.30
27.18
22.68
N
H
OMe
5j
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

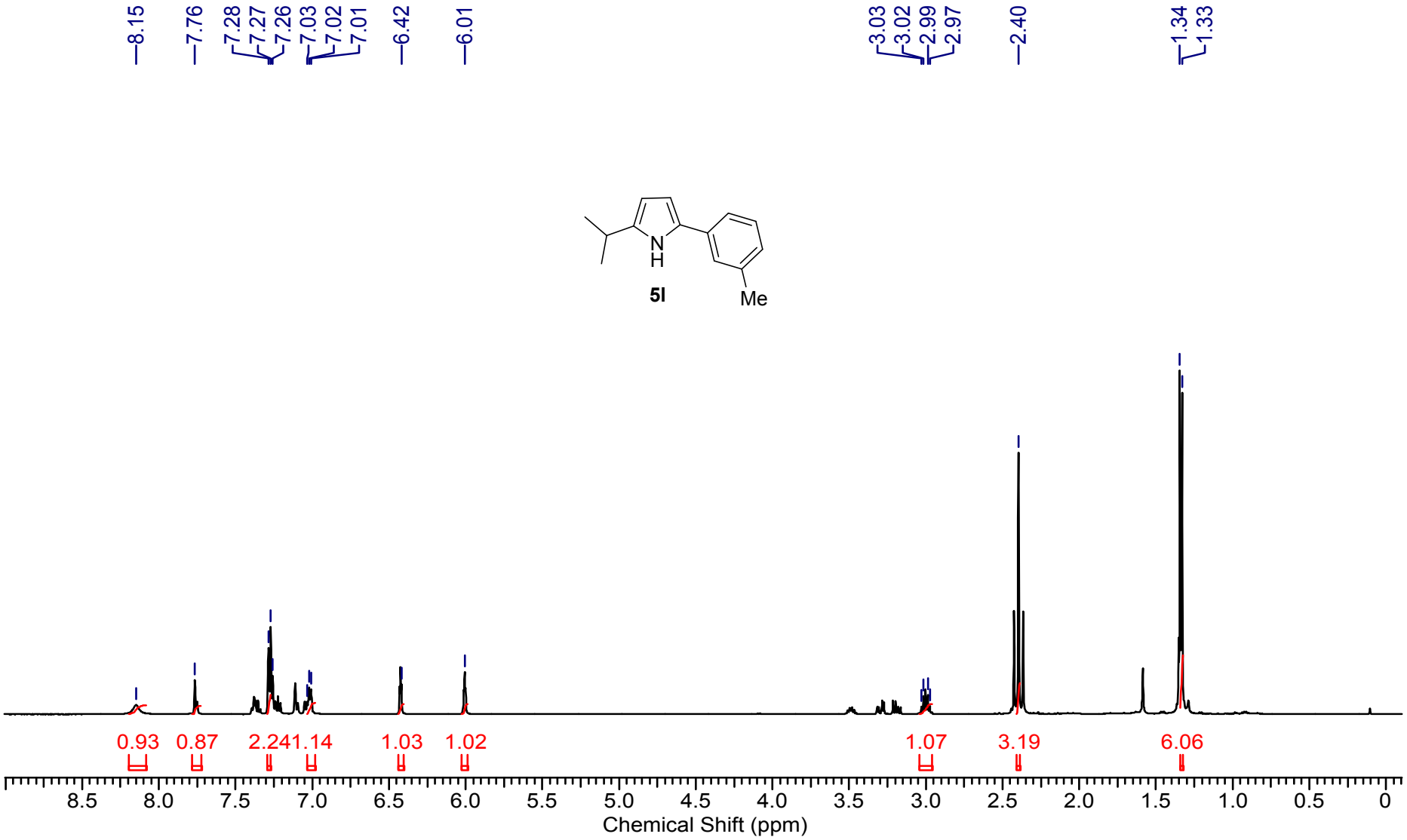
^{13}C NMR of **5j**


7.99
7.27
7.26
6.70
6.69
6.25
6.24
6.24
5.95
5.95
5.94
3.65
2.99
2.98
2.96
2.95
2.94
1.31
1.30
N
H
NH2
5k
0.84
1.76
1.95
0.90
0.92
1.73
1.00
6.25
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

^{1}H NMR of **5k**

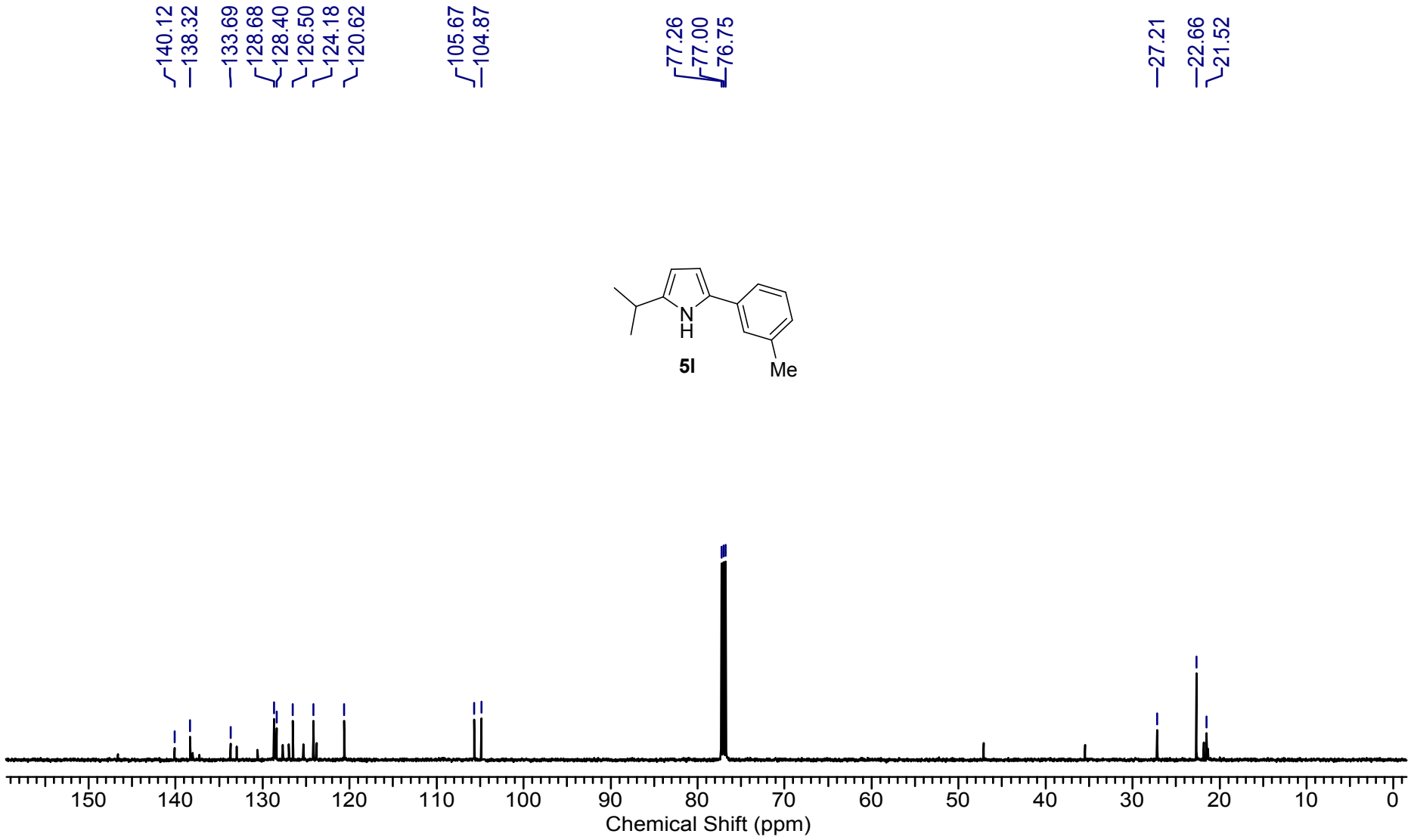

144.48
139.08
131.03
124.93
124.31
115.53
104.45
103.88
77.25
77.00
76.74
27.16
22.69
N
H
NH2
5k
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

^{13}C NMR of **5k**



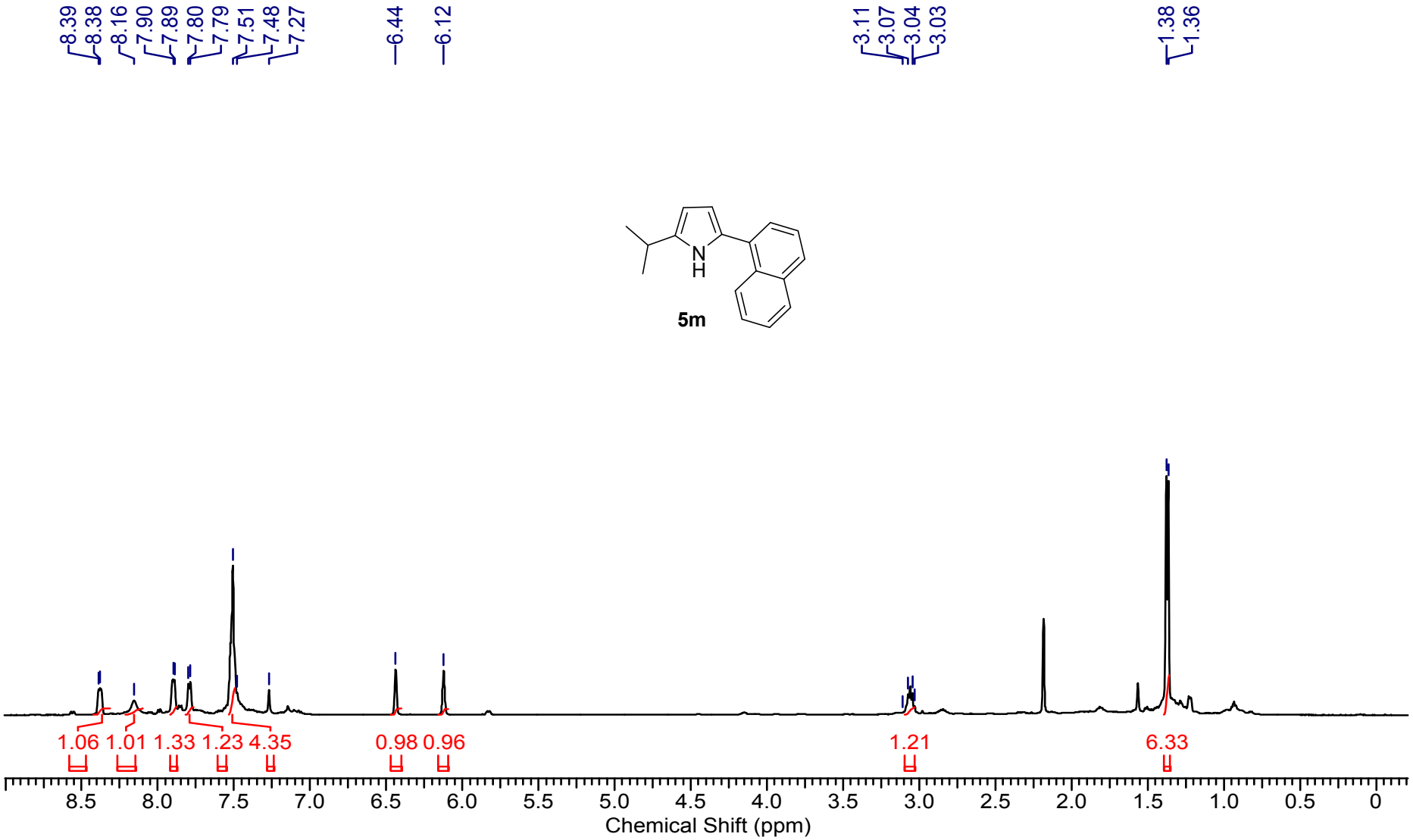
5l

^{1}H NMR of **5l**

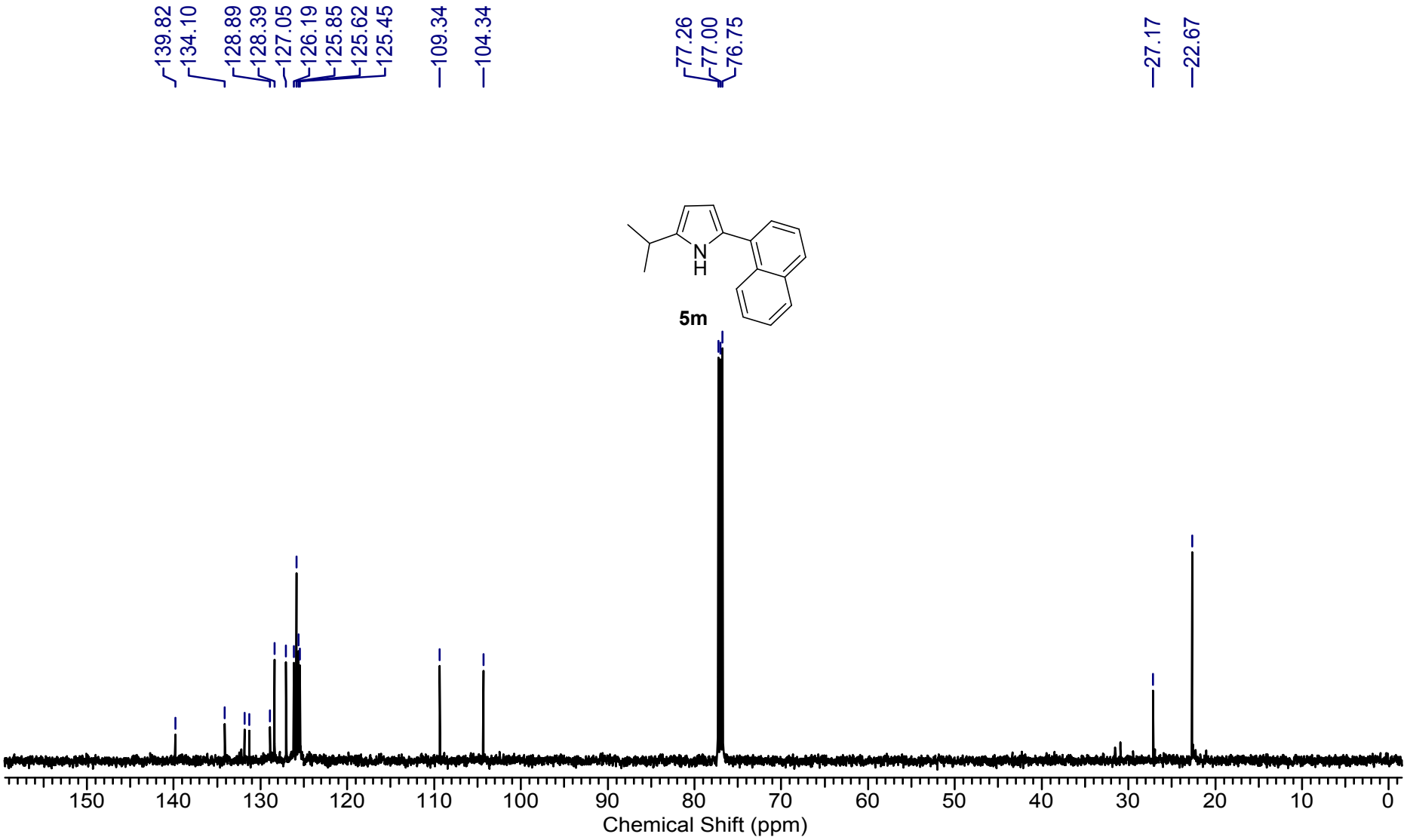


5l

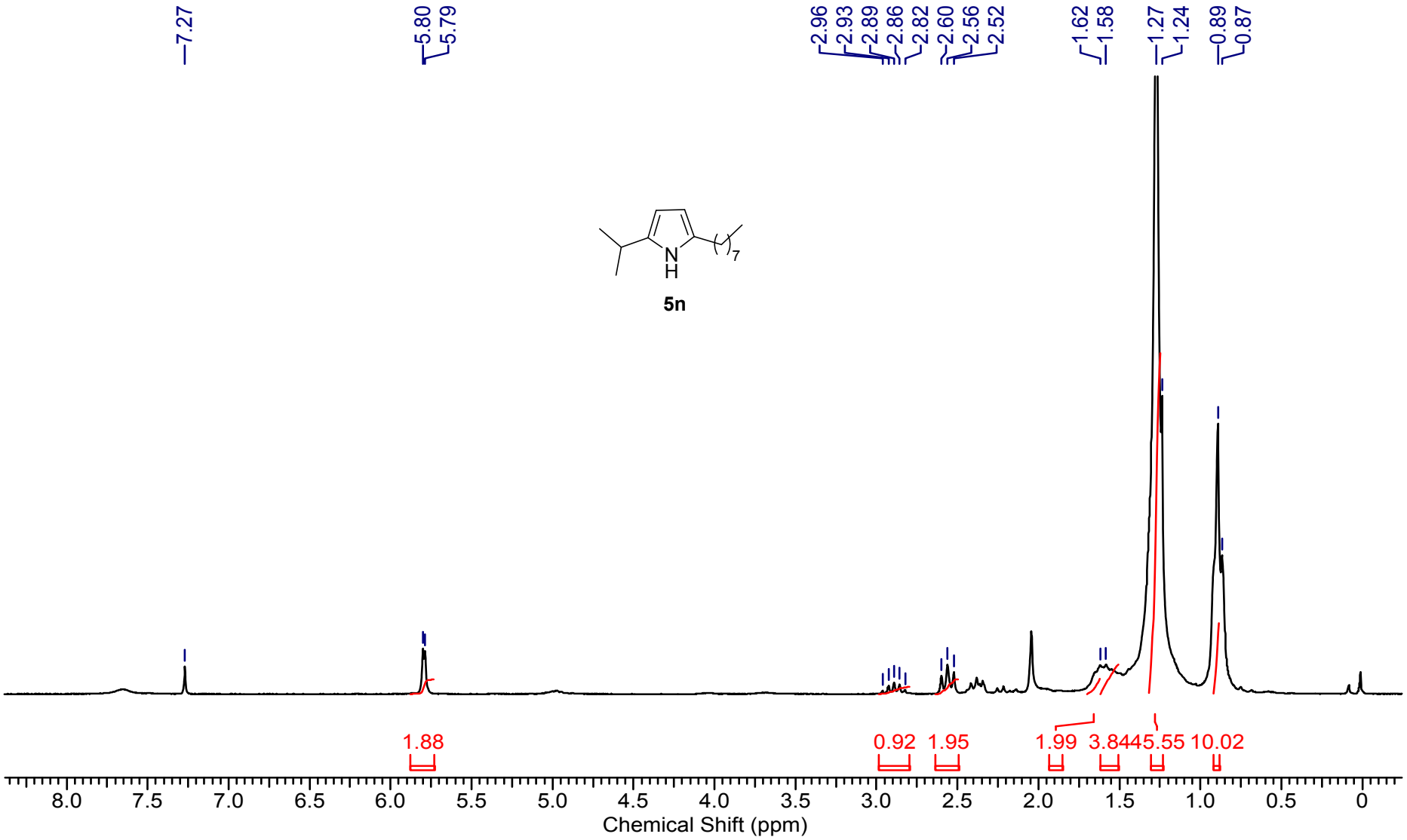
^{13}C NMR of **5l**


8.39
8.38
8.16
7.90
7.89
7.80
7.79
7.51
7.48
7.27
6.44
6.12
3.11
3.07
3.04
3.03
1.38
1.36
N
H
5m
1.06 1.01 1.33 1.23 4.35
0.98 0.96
1.21
6.33
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

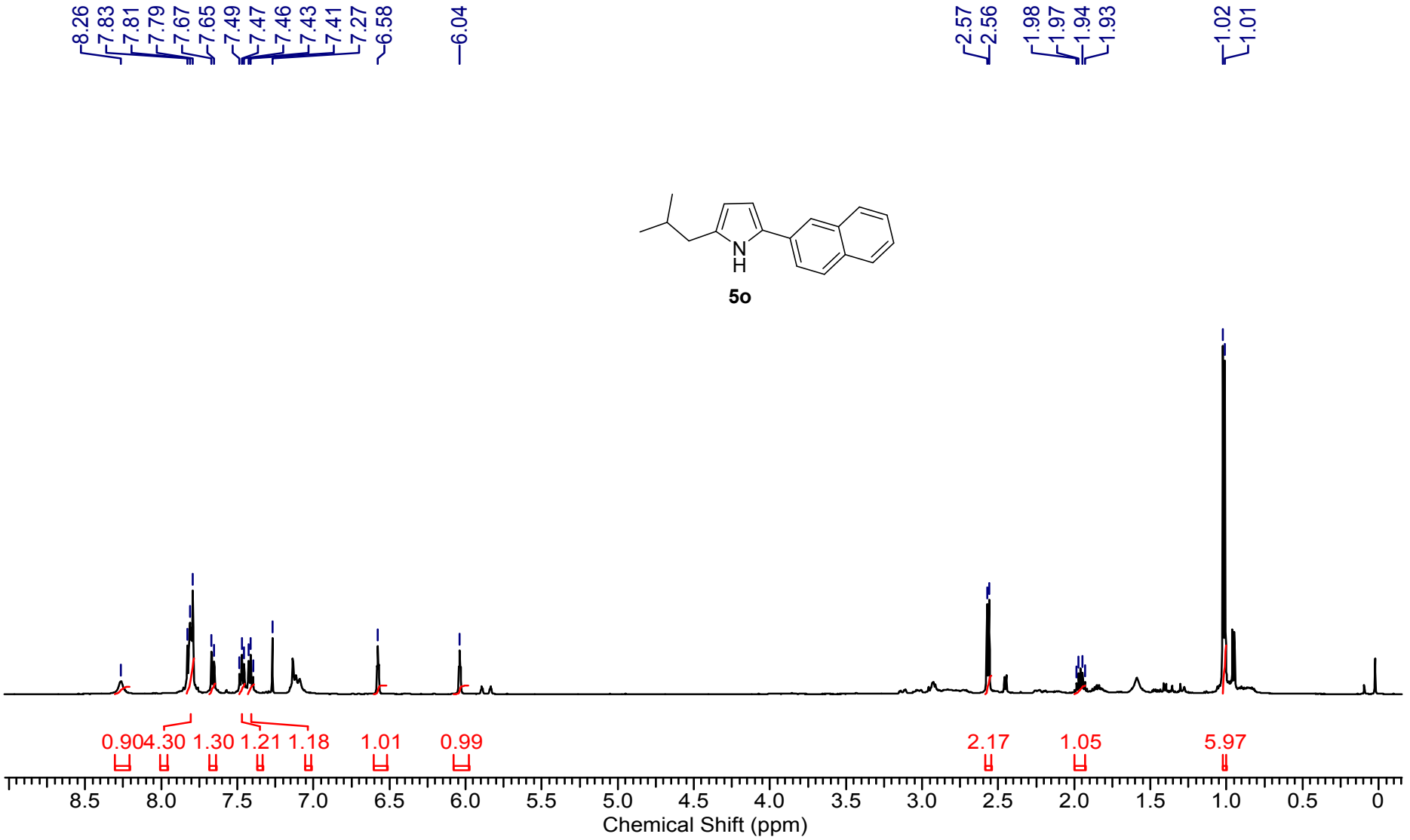
^{1}H NMR of **5m**


139.82
134.10
128.89
128.39
127.05
126.19
125.85
125.62
125.45
109.34
104.34
77.26
77.00
76.75
27.17
22.67
N
H
5m
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

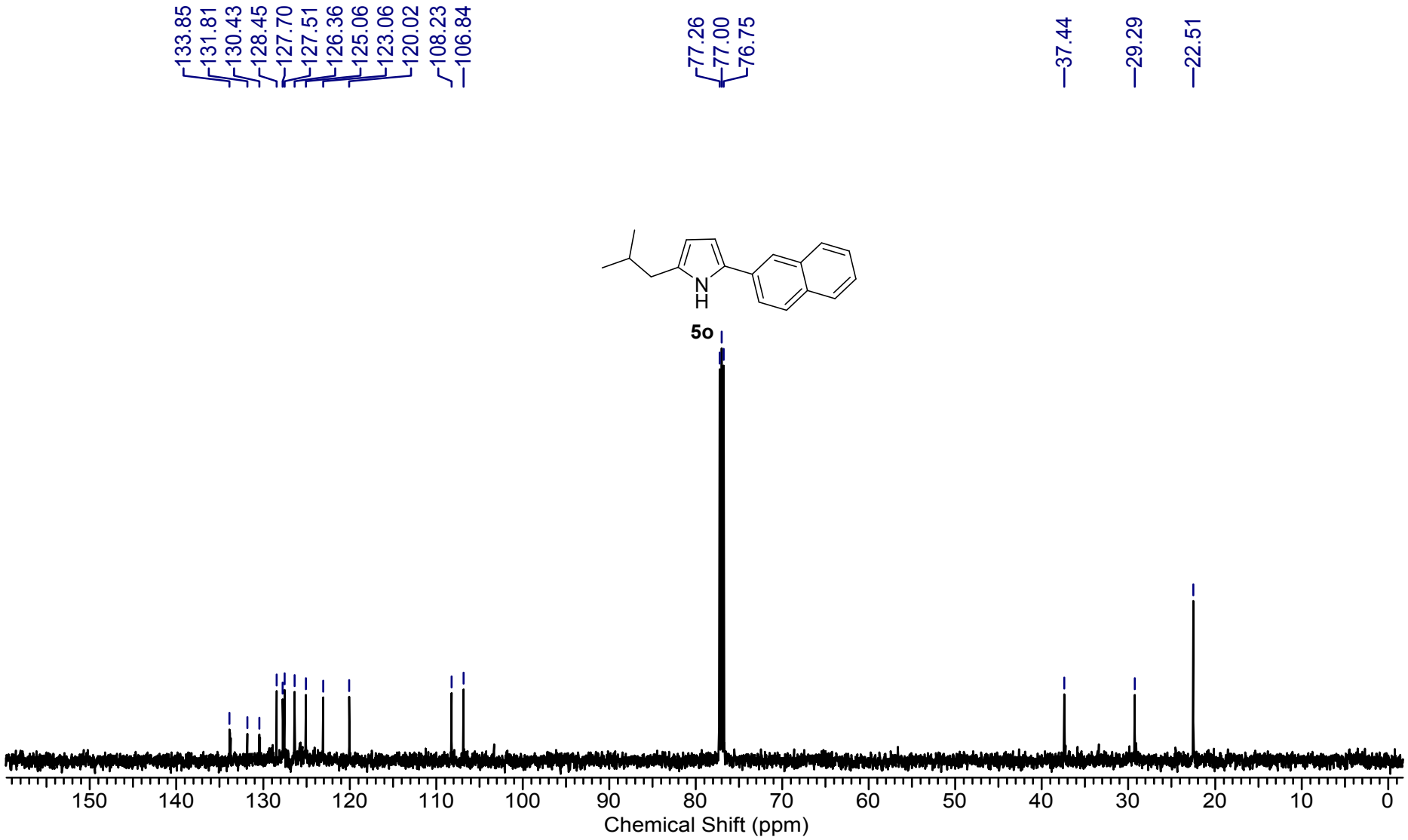
^{13}C NMR of **5m**



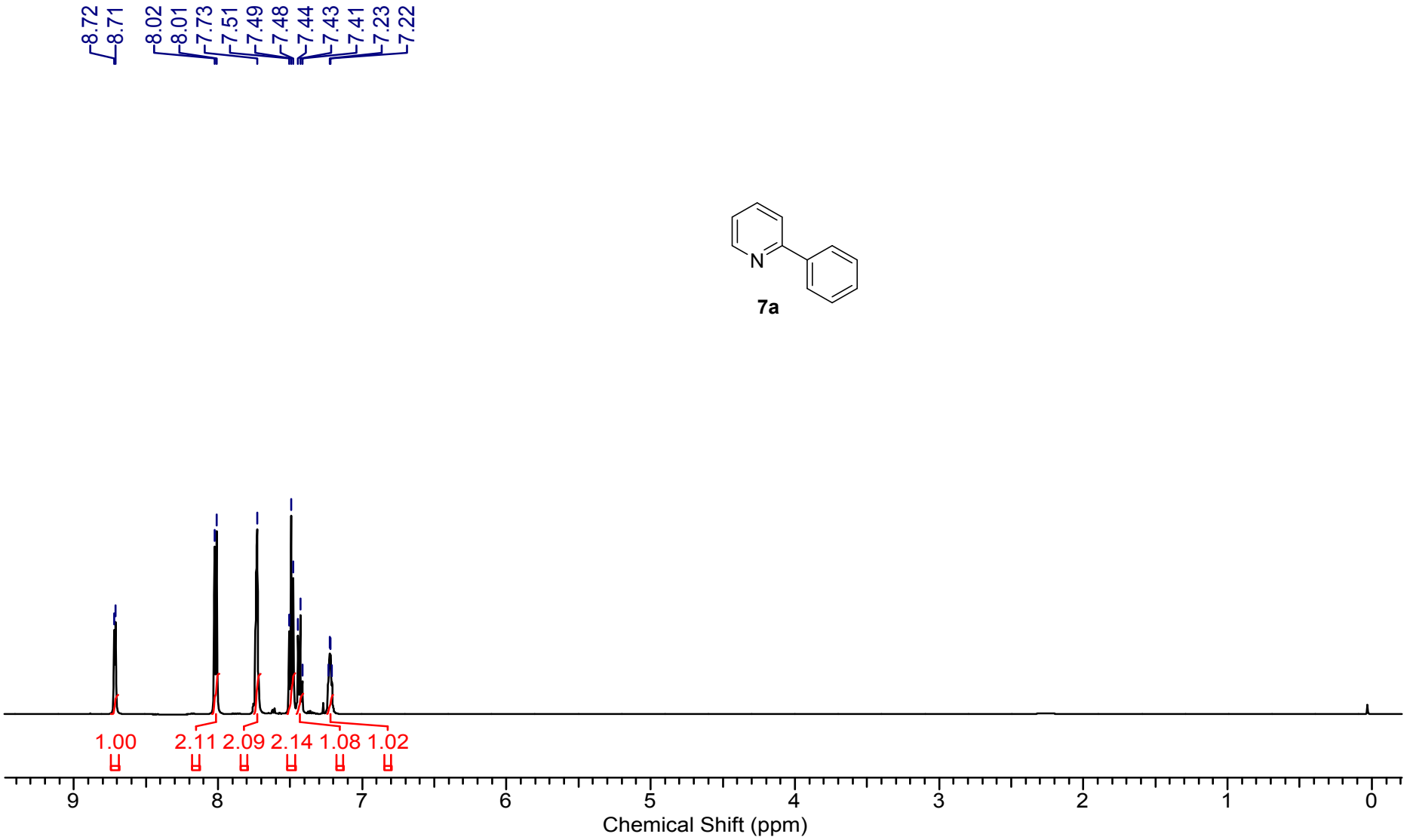
^{1}H NMR of **5n** (product : unreacted secondary alcohol = 1:2)


8.26
7.83
7.81
7.79
7.67
7.65
7.49
7.47
7.46
7.43
7.41
7.27
6.58
6.04
2.57
2.56
1.98
1.97
1.94
1.93
1.02
1.01
N
H
5o
0.90
4.30
1.30
1.21
1.18
1.01
0.99
2.17
1.05
5.97
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

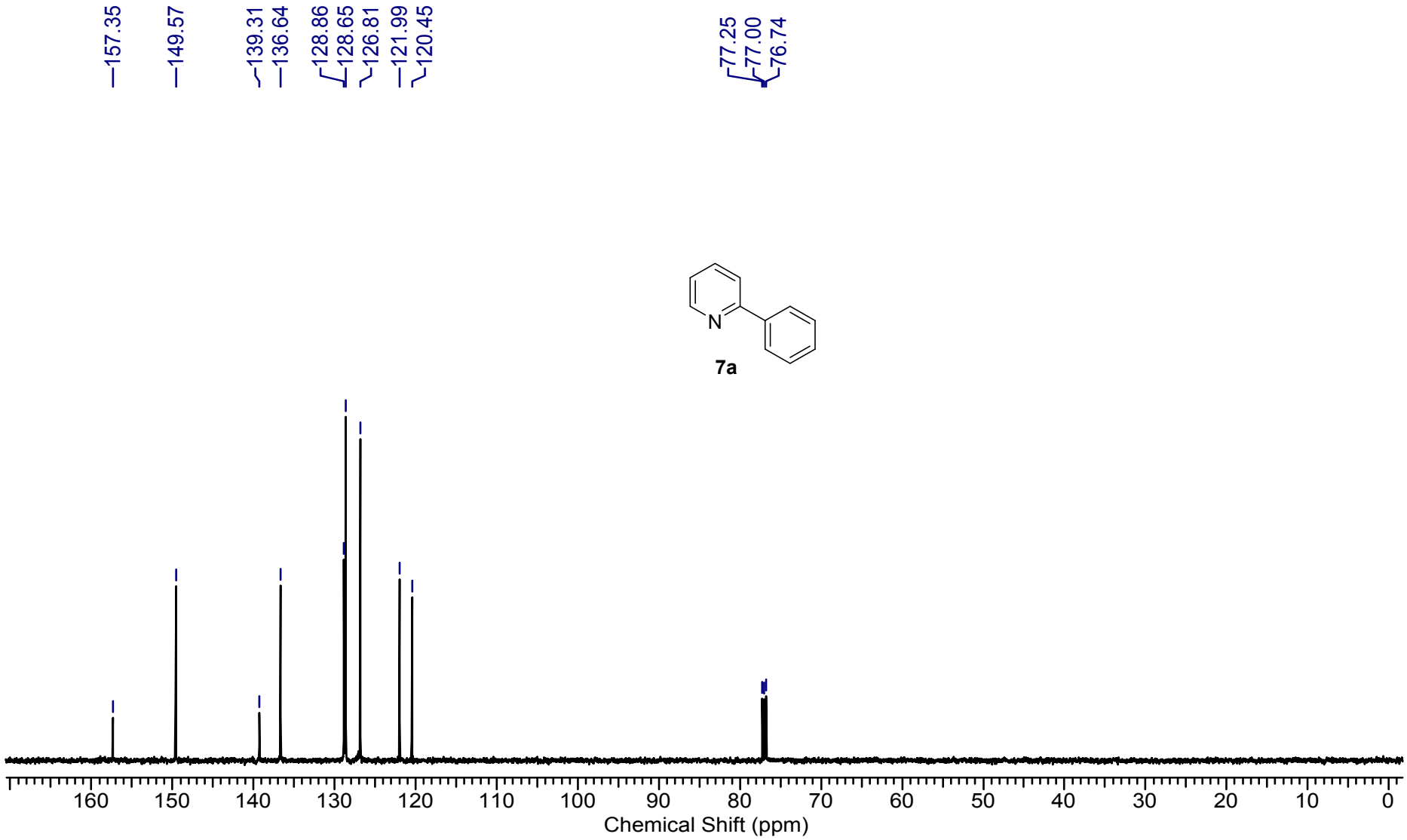
^{1}H NMR of **5o**


133.85
131.81
130.43
128.45
127.70
127.51
126.36
125.06
123.06
120.02
108.23
106.84
77.26
77.00
76.75
37.44
29.29
22.51
N
H
5o
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

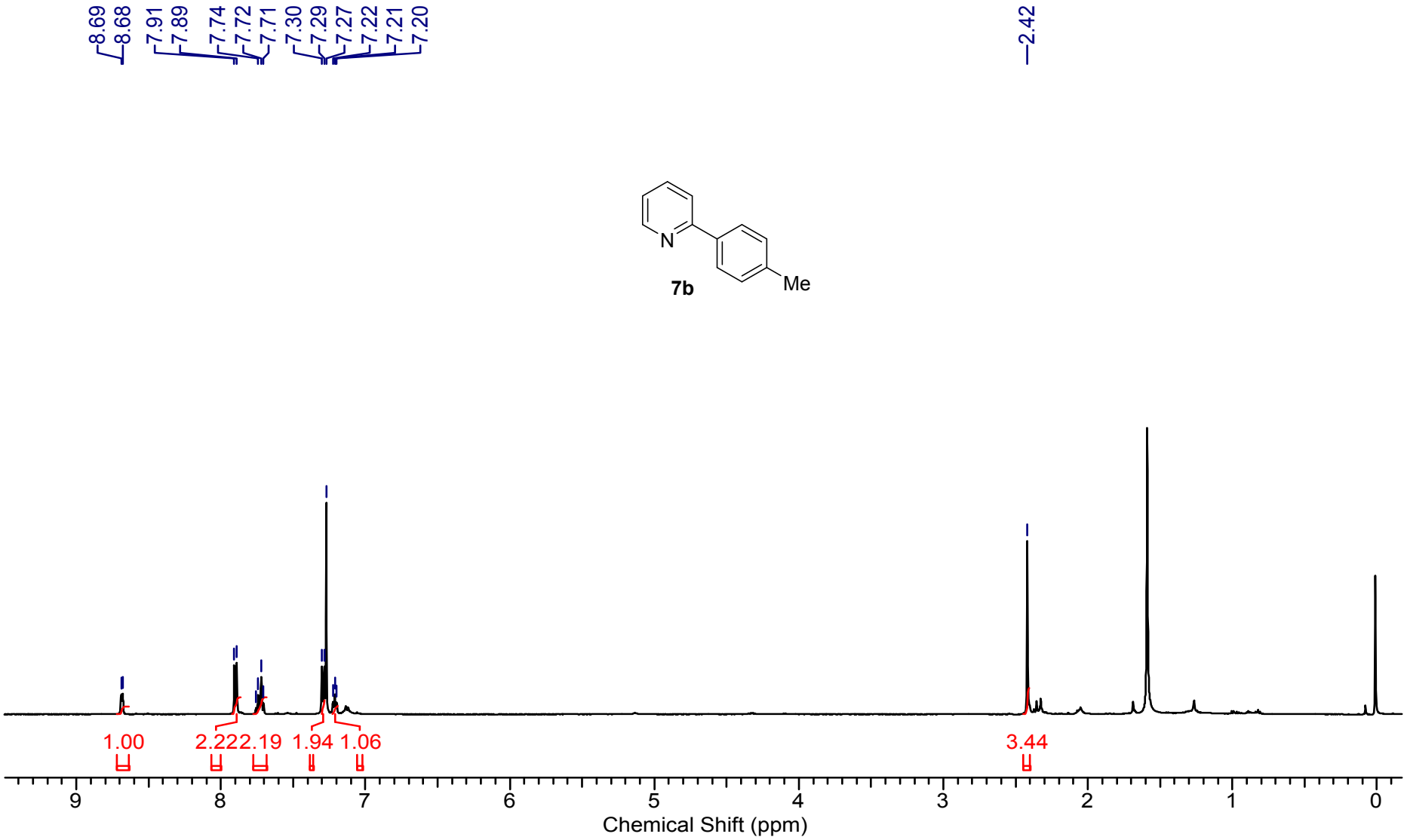
^{13}C NMR of **5o**


8.72
8.71
8.02
8.01
7.73
7.51
7.49
7.48
7.44
7.43
7.41
7.23
7.22
N
7a
1.00
2.11
2.09
2.14
1.08
1.02
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

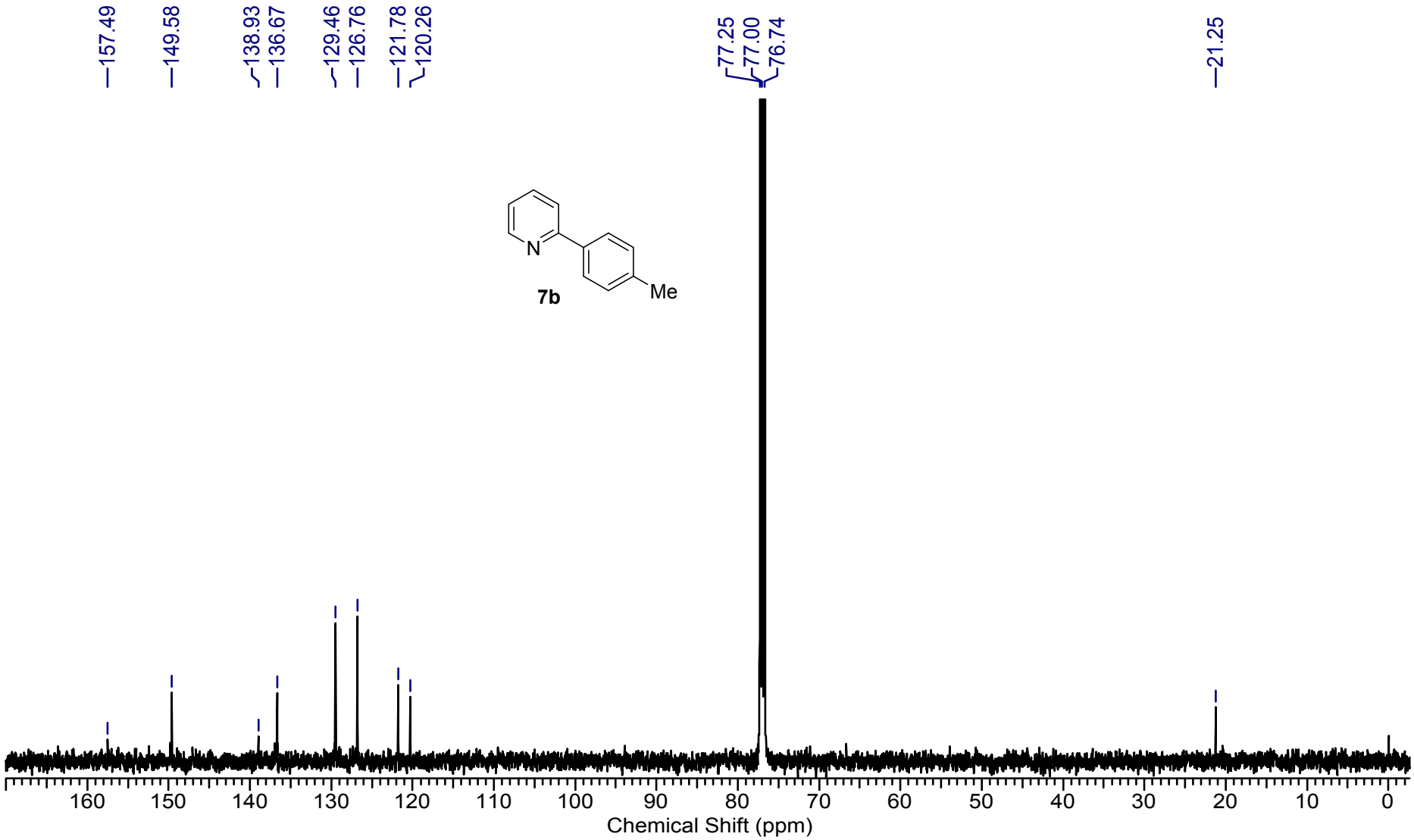
^{1}H NMR of **7a**


157.35
149.57
139.31
136.64
128.86
128.65
126.81
121.99
120.45
77.25
77.00
76.74
N
7a
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

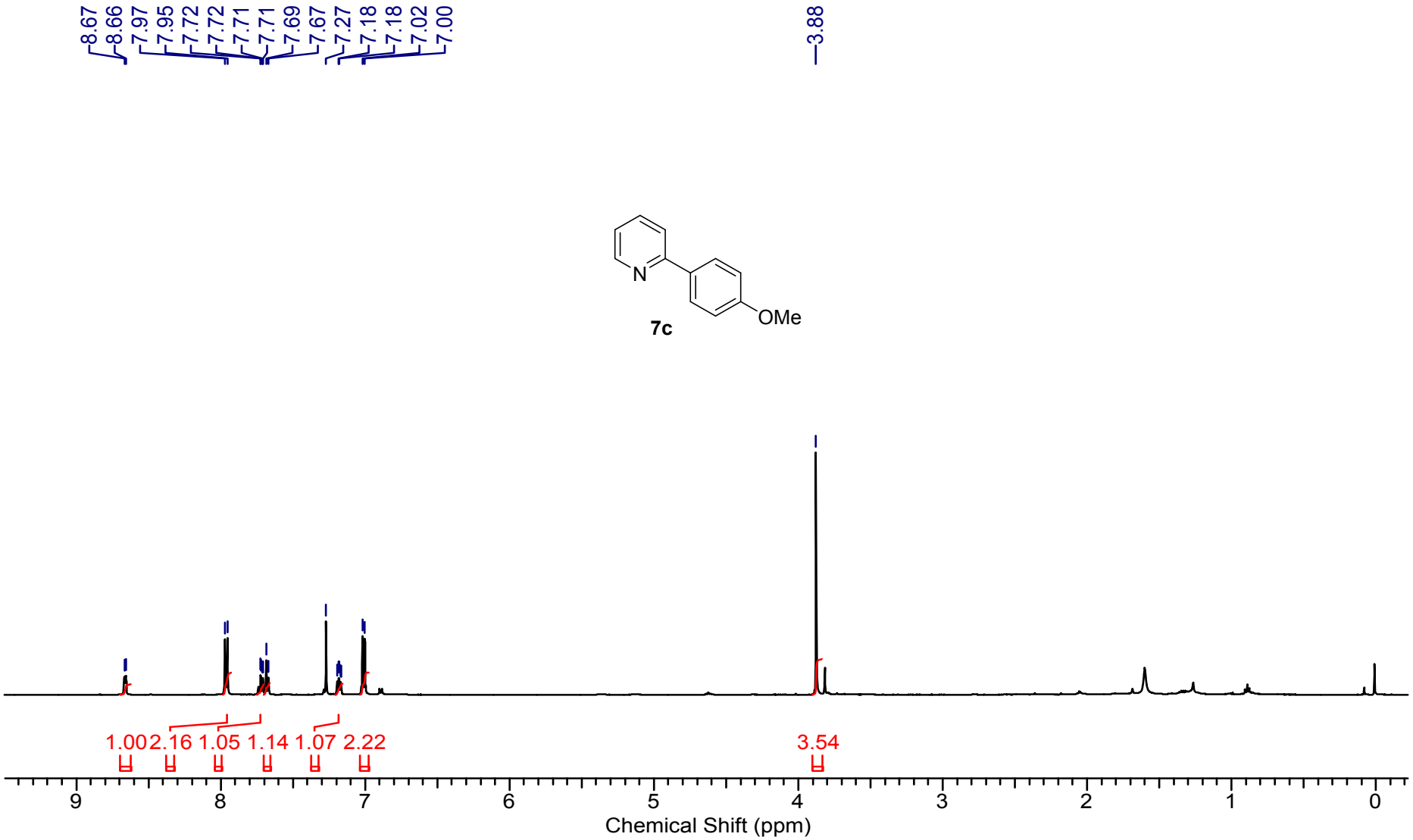
^{13}C NMR of **7a**


8.69
8.68
7.91
7.89
7.74
7.72
7.71
7.30
7.29
7.27
7.22
7.21
7.20
2.42
N
Me
7b
1.00
2.22
2.19
1.94
1.06
3.44
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

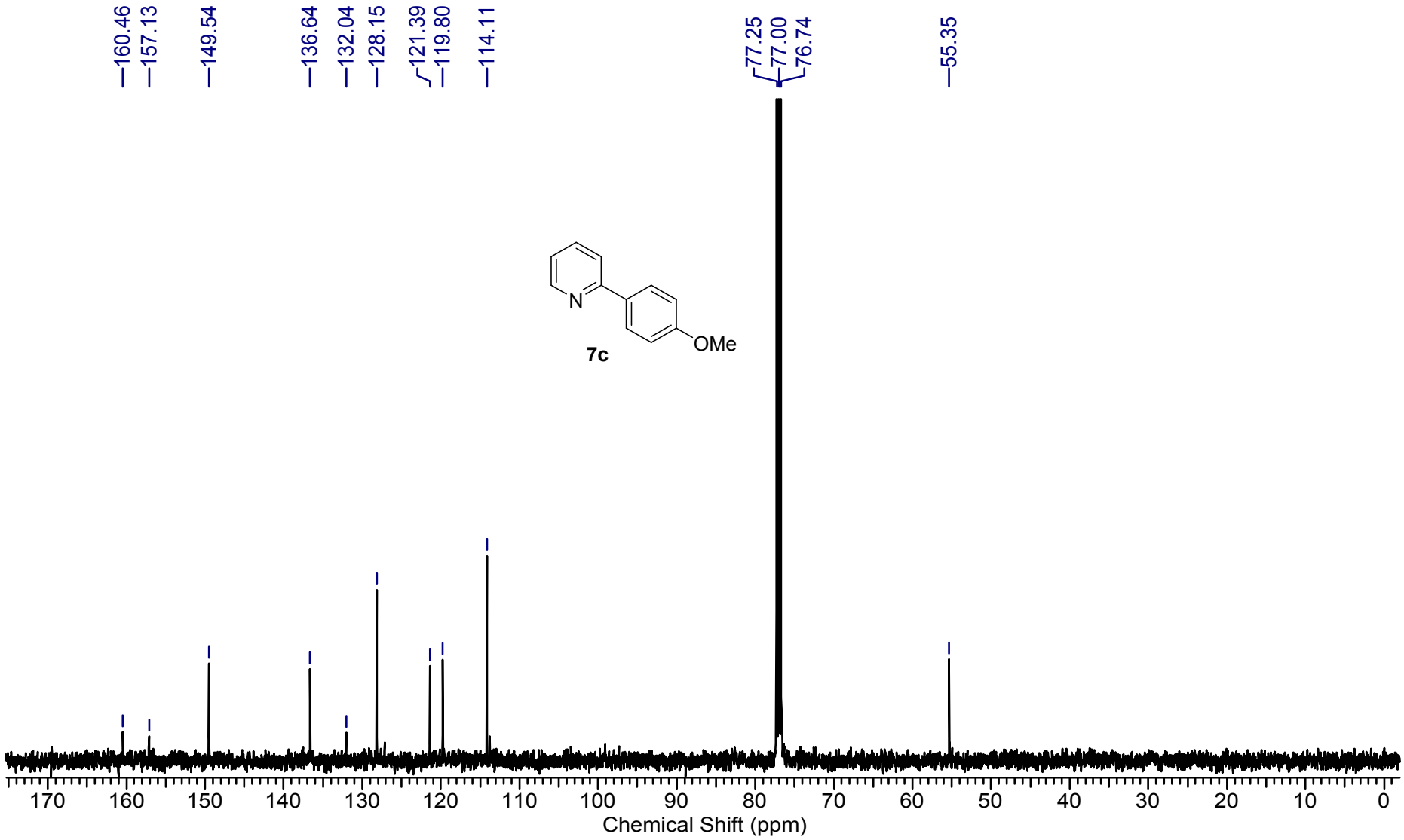
^{1}H NMR of **7b**


157.49
149.58
138.93
136.67
129.46
126.76
121.78
120.26
77.25
77.00
76.74
21.25
N
Me
7b
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

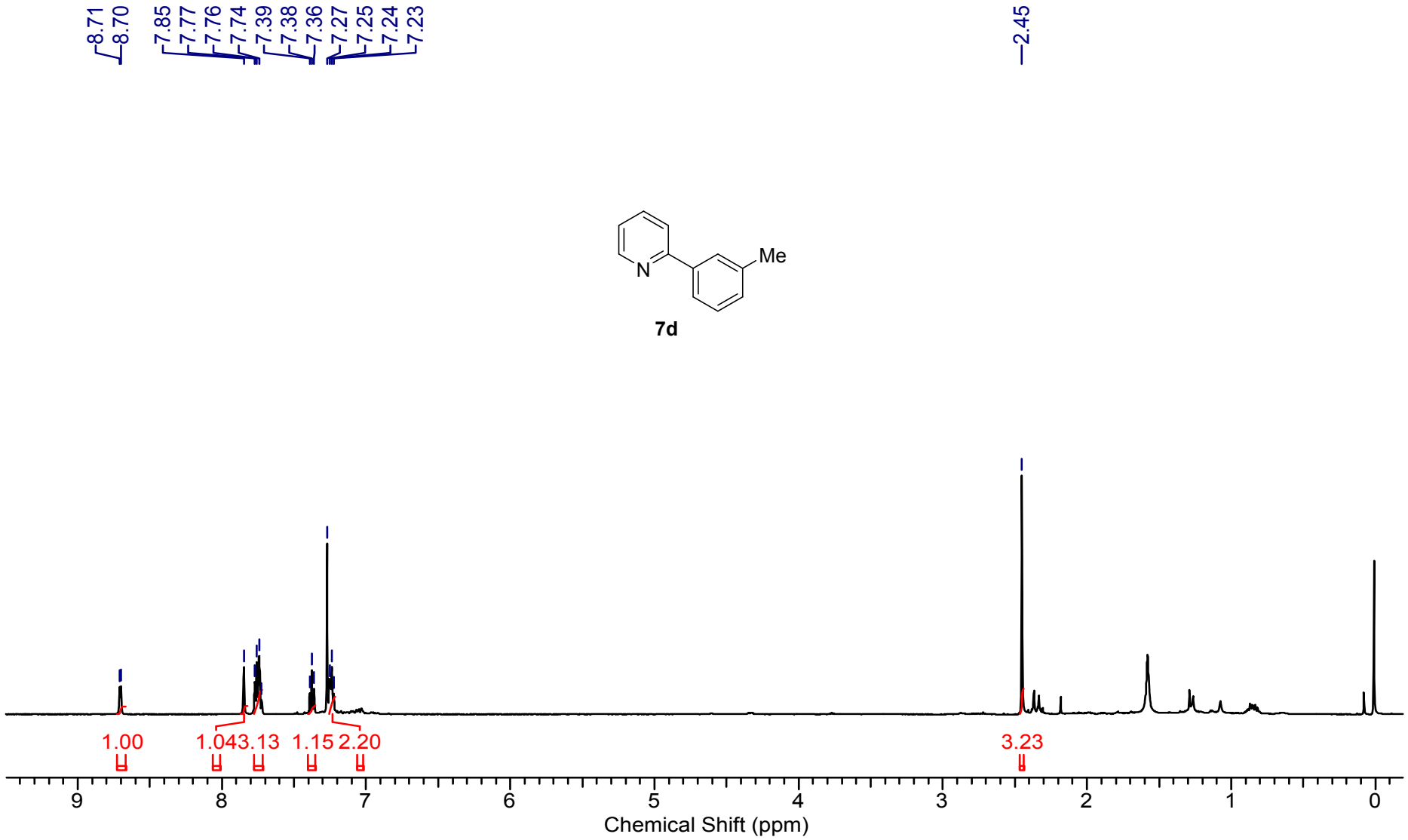
^{13}C NMR of **7b**


8.67
8.66
7.97
7.95
7.72
7.72
7.71
7.71
7.69
7.67
7.27
7.18
7.18
7.02
7.00
3.88
N
OMe
7c
1.00 2.16 1.05 1.14 1.07 2.22
3.54
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

^{1}H NMR of **7c**

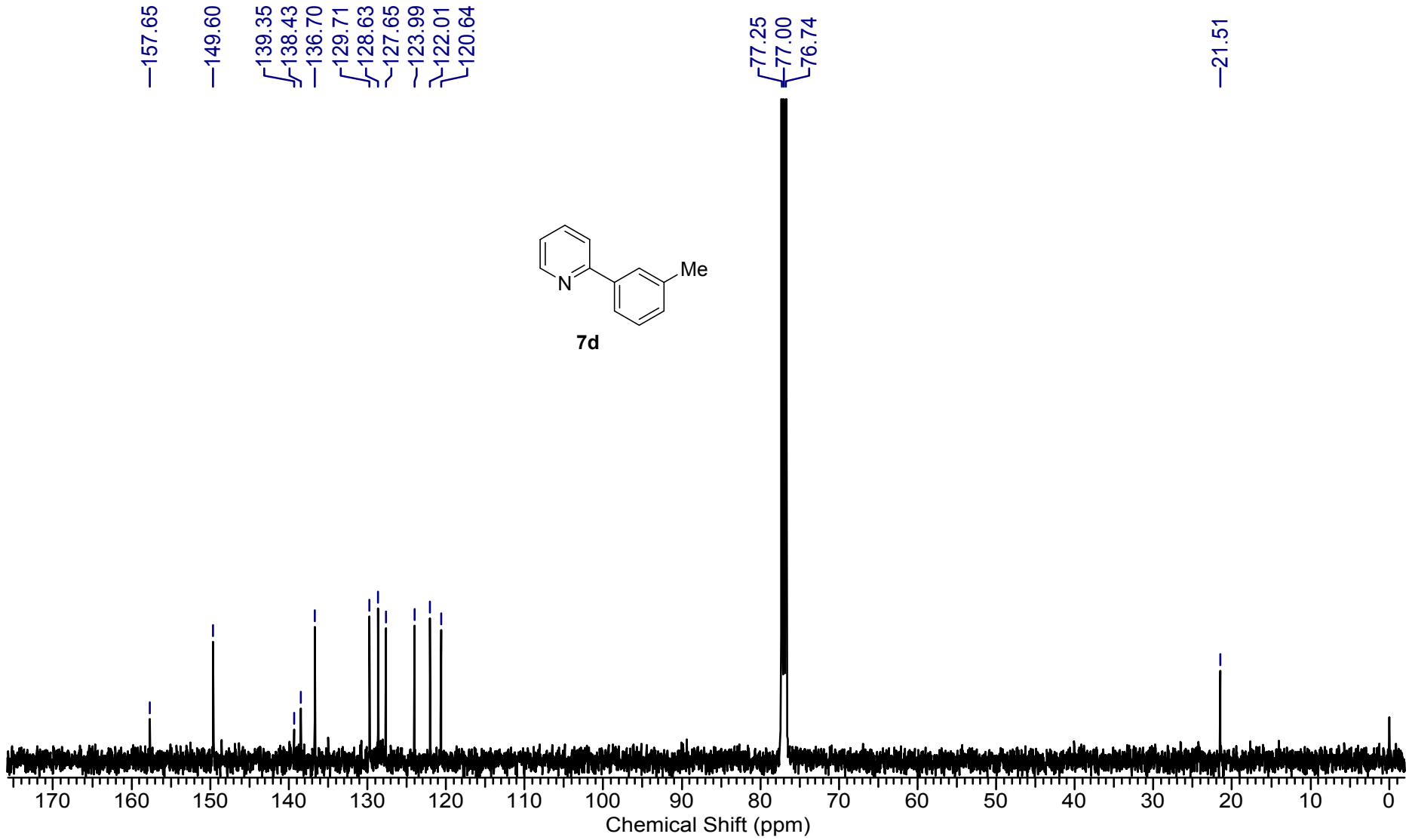

160.46
157.13
149.54
136.64
132.04
128.15
121.39
119.80
114.11
77.25
77.00
76.74
55.35
N
OMe
7c
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

^{13}C NMR of **7c**

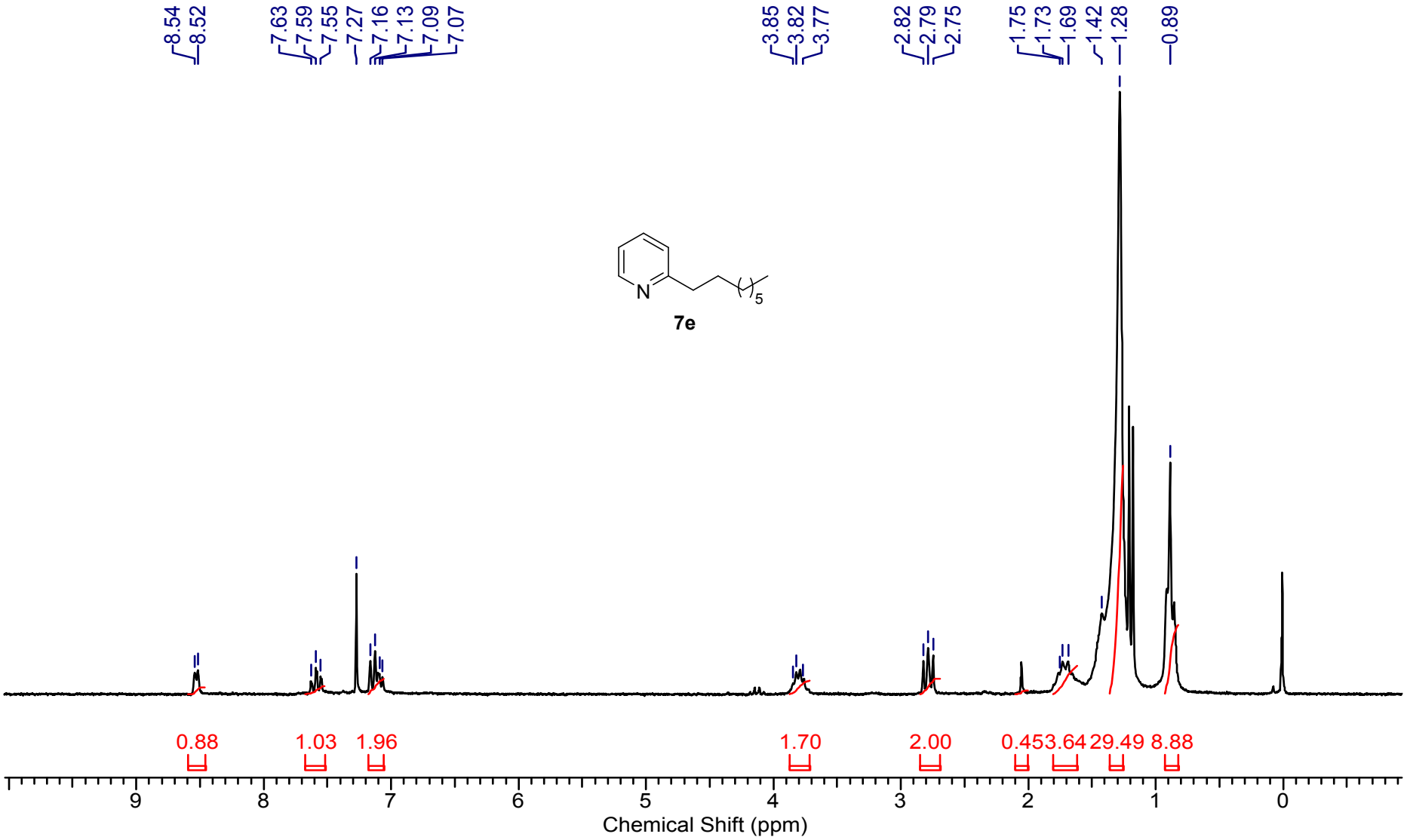


7d

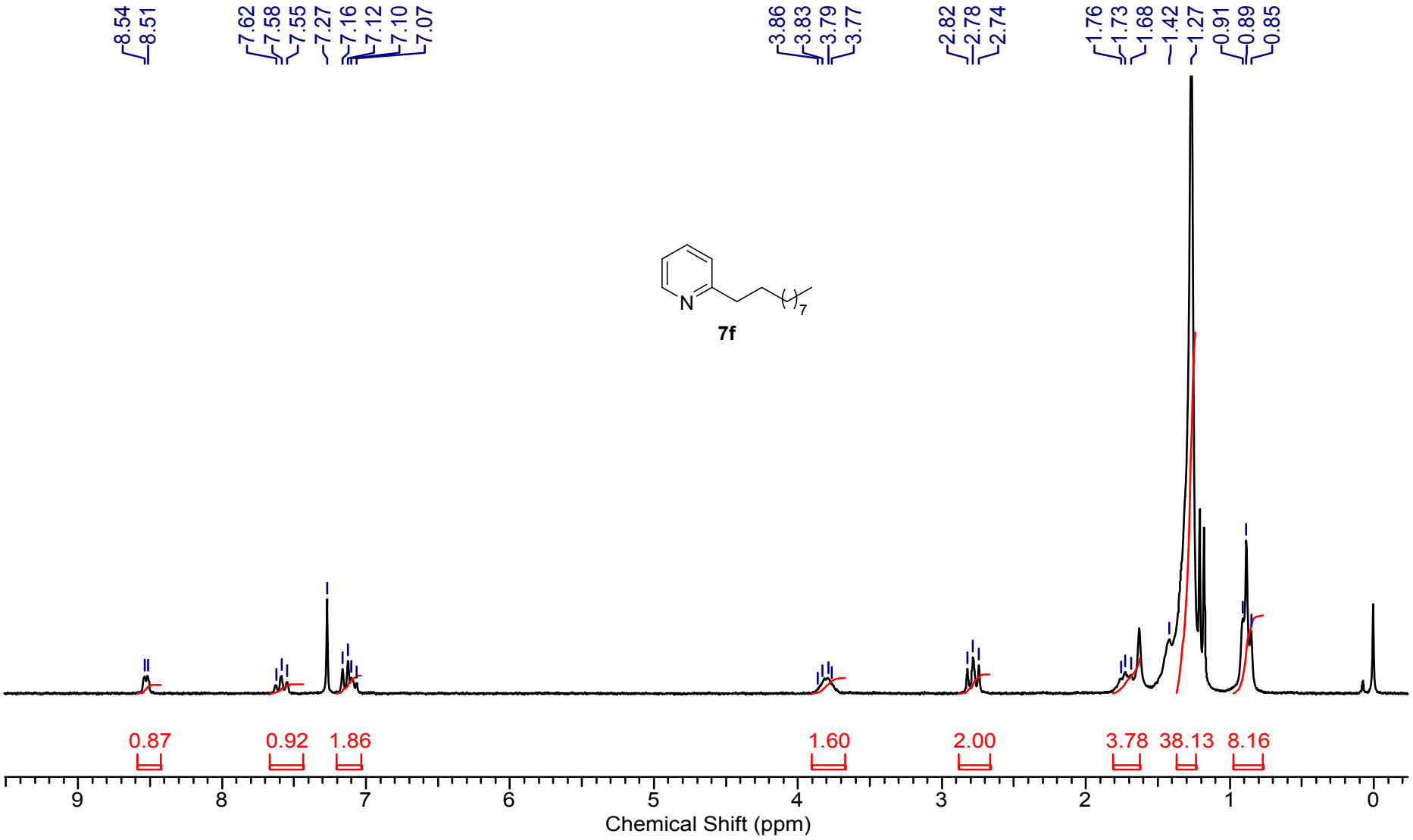
^{1}H NMR of **7d**


157.65
149.60
139.35
138.43
136.70
129.71
128.63
127.65
123.99
122.01
120.64
77.25
77.00
76.74
21.51
N
Me
7d
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

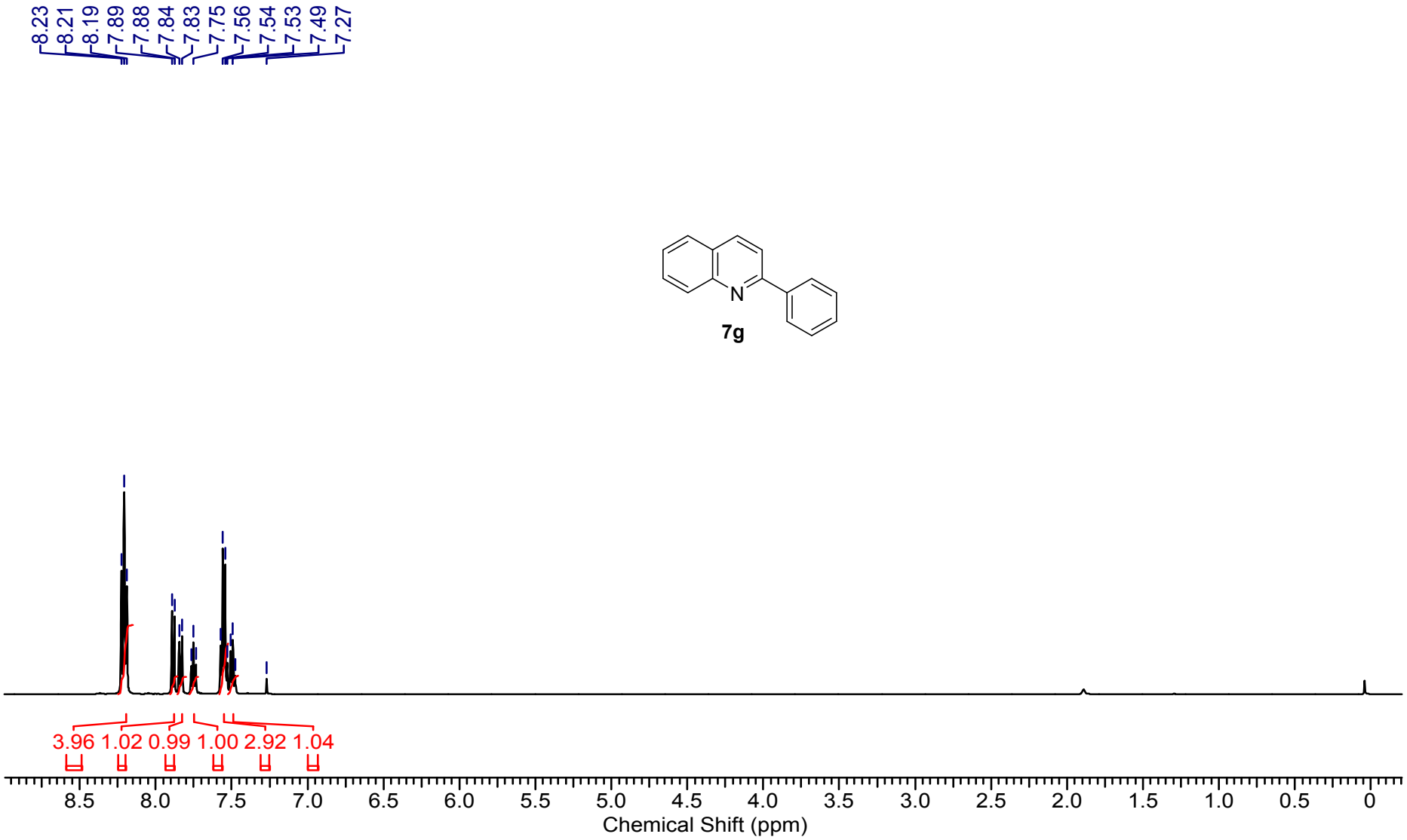
^{13}C NMR of **7d**



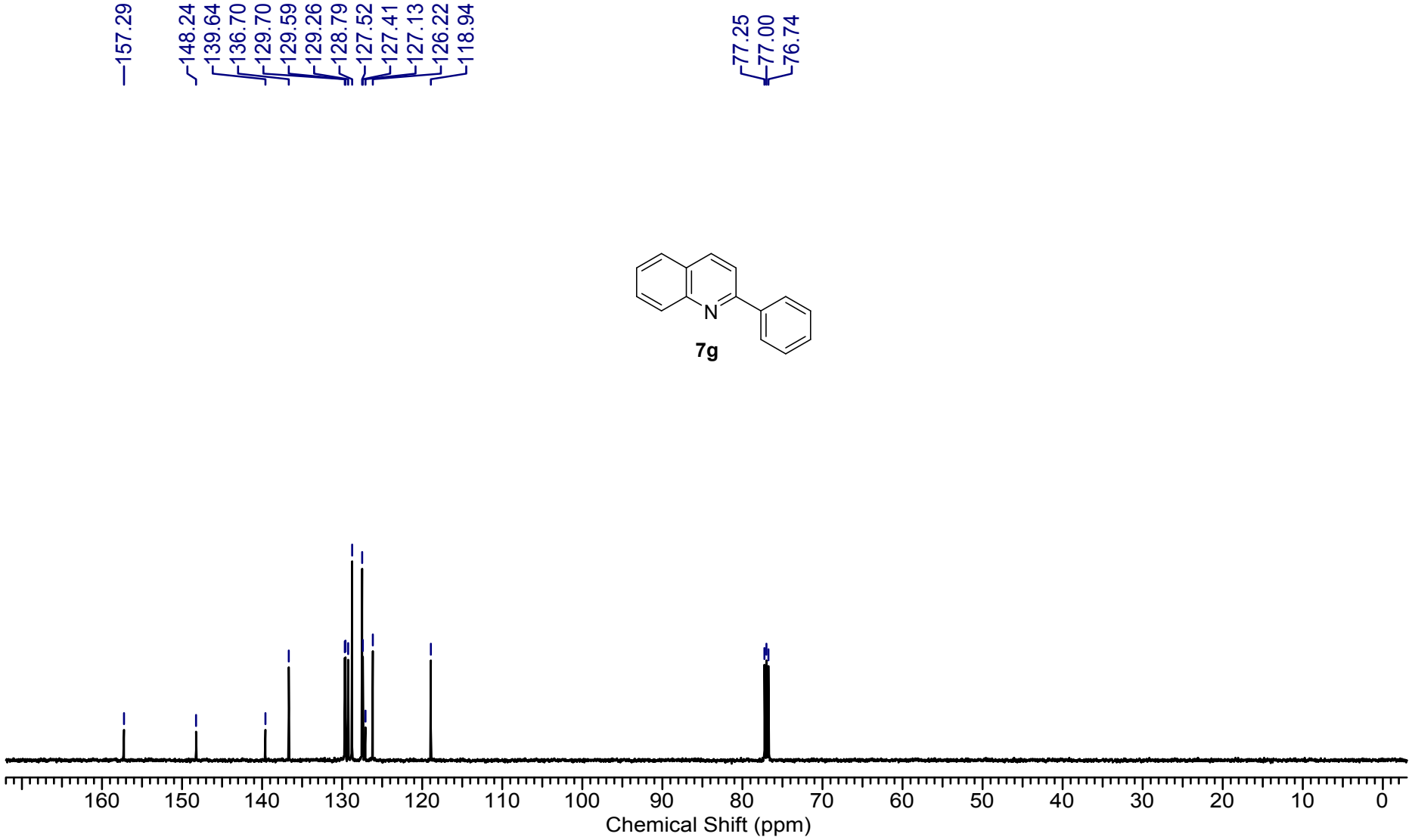
^{1}H NMR of **7e** (product : unreacted secondary alcohol = 1:1.7)



^{1}H NMR of **7f** (product : unreacted secondary alcohol = 1 : 1.6)

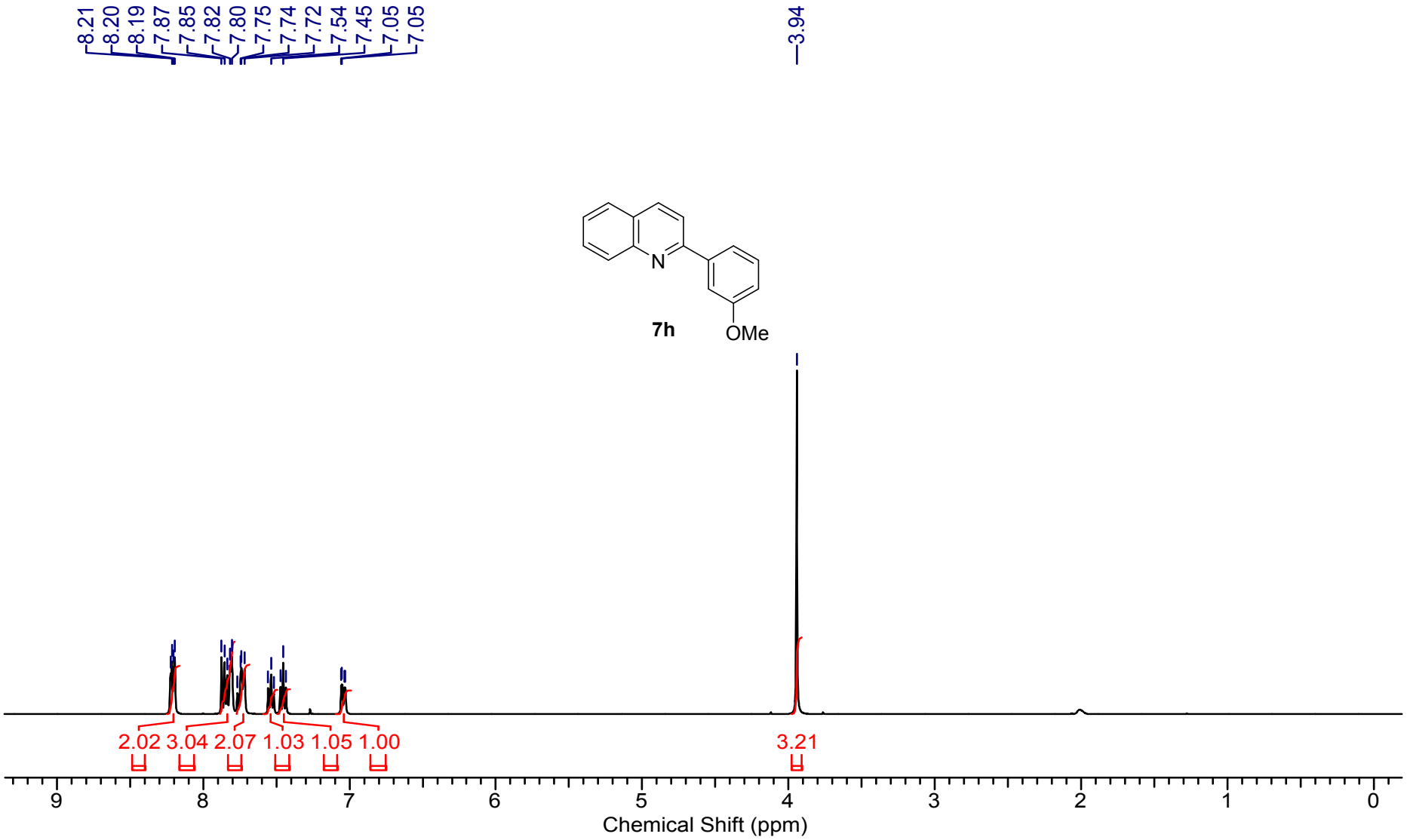

8.23
8.21
8.19
7.89
7.88
7.84
7.83
7.75
7.56
7.54
7.53
7.49
7.27
N
7g
3.96 1.02 0.99 1.00 2.92 1.04
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

^{1}H NMR of **7g**

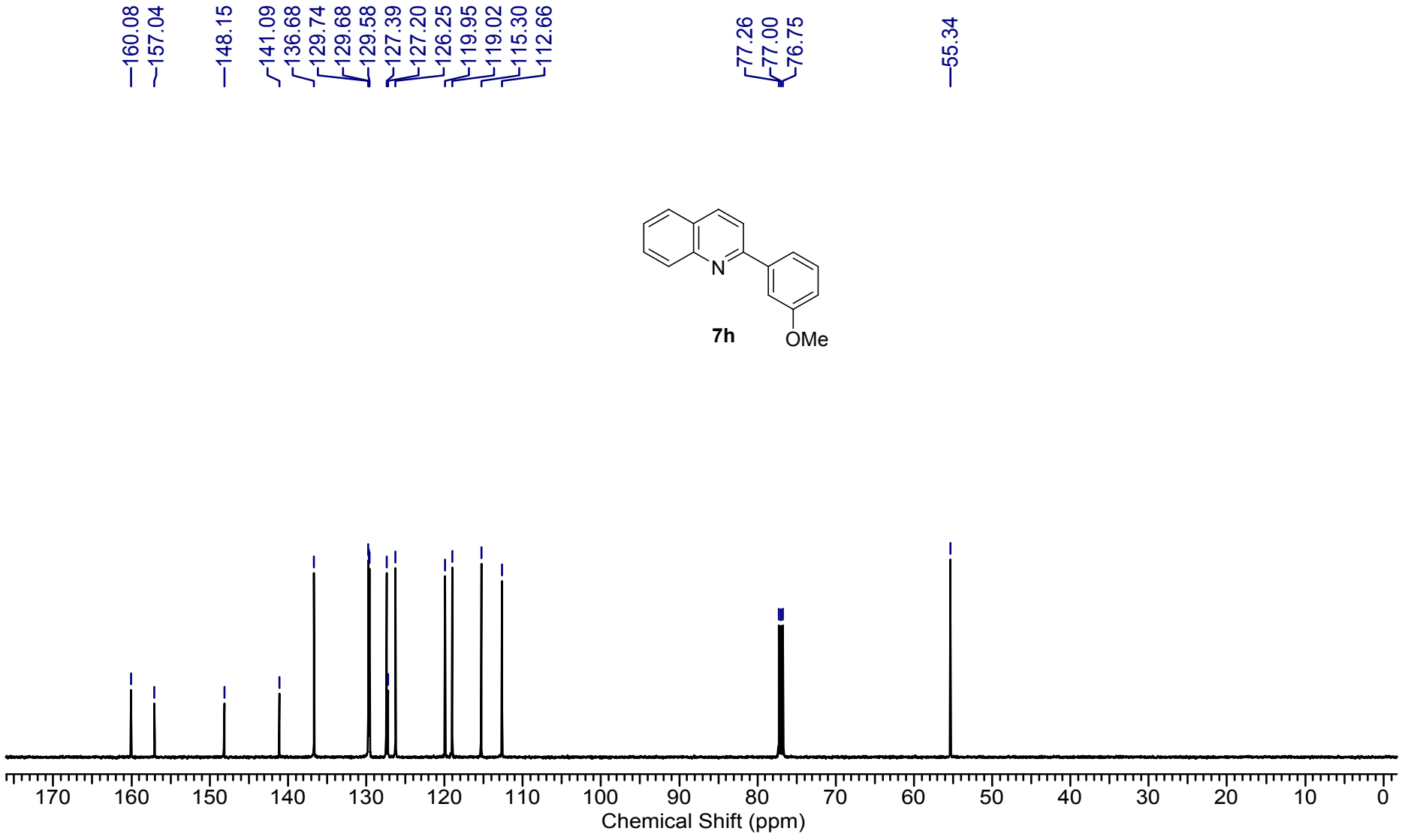


7g

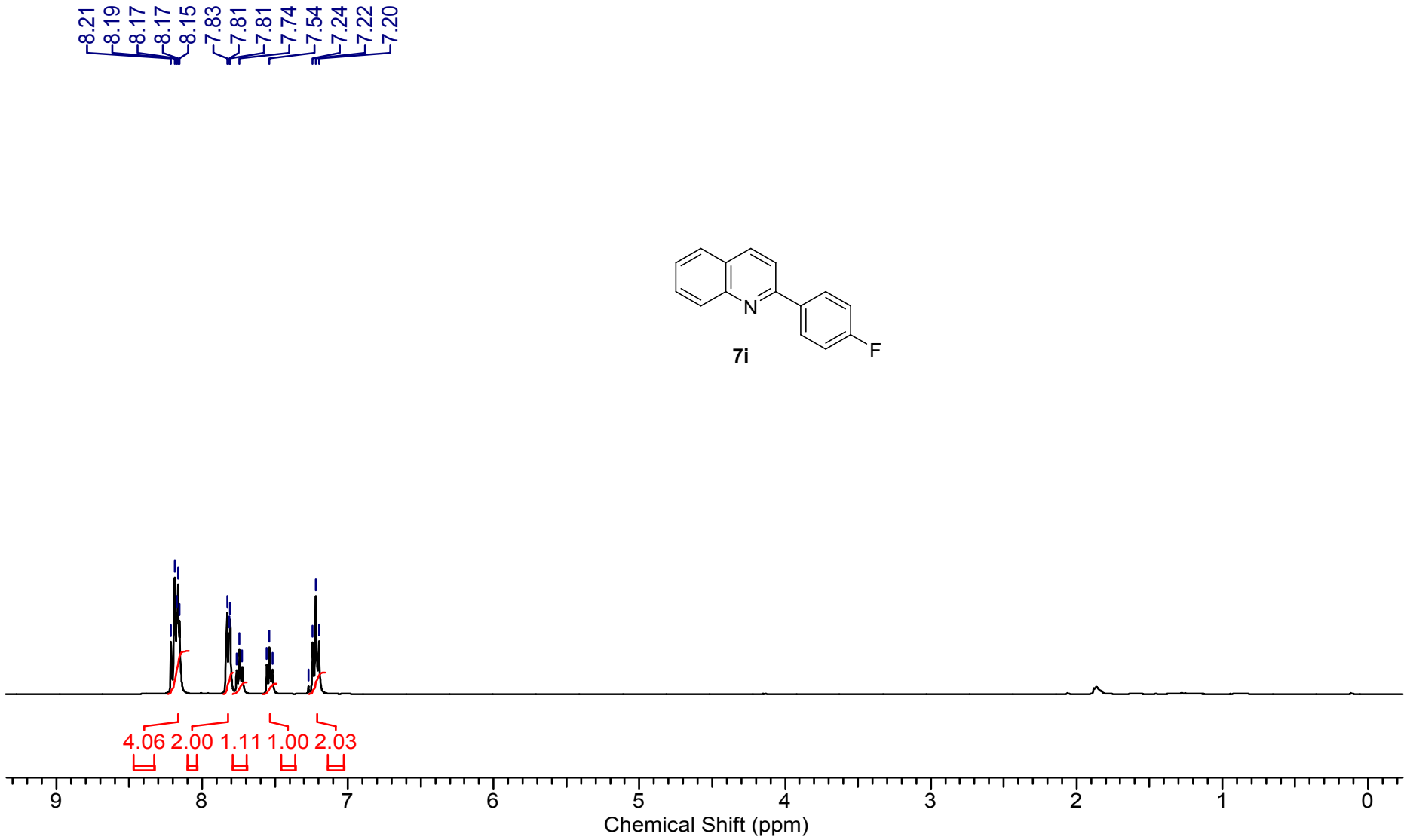
^{13}C NMR of **7g**


8.21
8.20
8.19
7.87
7.85
7.82
7.80
7.75
7.74
7.72
7.54
7.45
7.05
7.05
3.94
N
OMe
7h
2.02 3.04 2.07 1.03 1.05 1.00
3.21
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

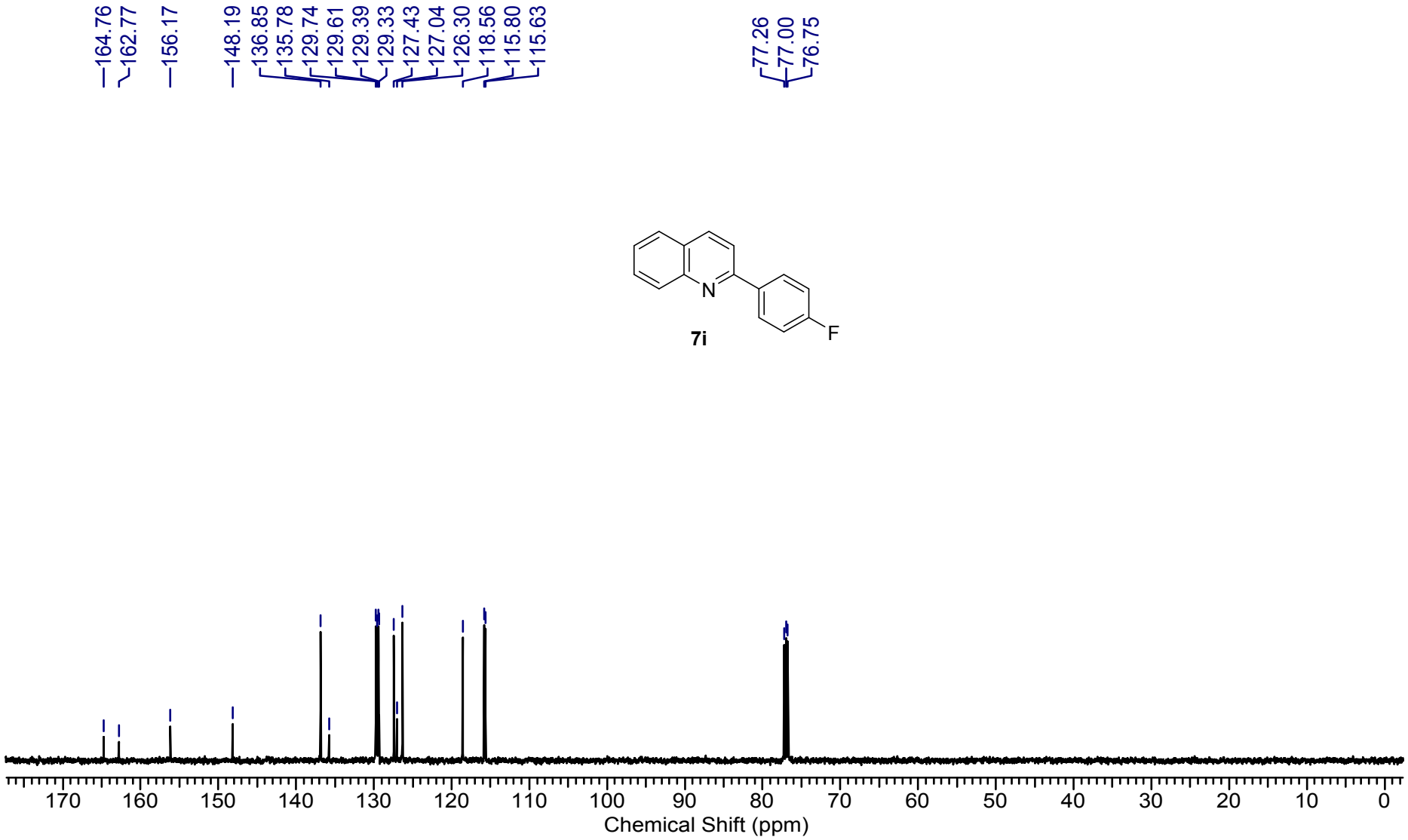
^{1}H NMR of **7h**


160.08
157.04
148.15
141.09
136.68
129.74
129.68
129.58
127.39
127.20
126.25
119.95
119.02
115.30
112.66
77.26
77.00
76.75
55.34
N
OMe
7h
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

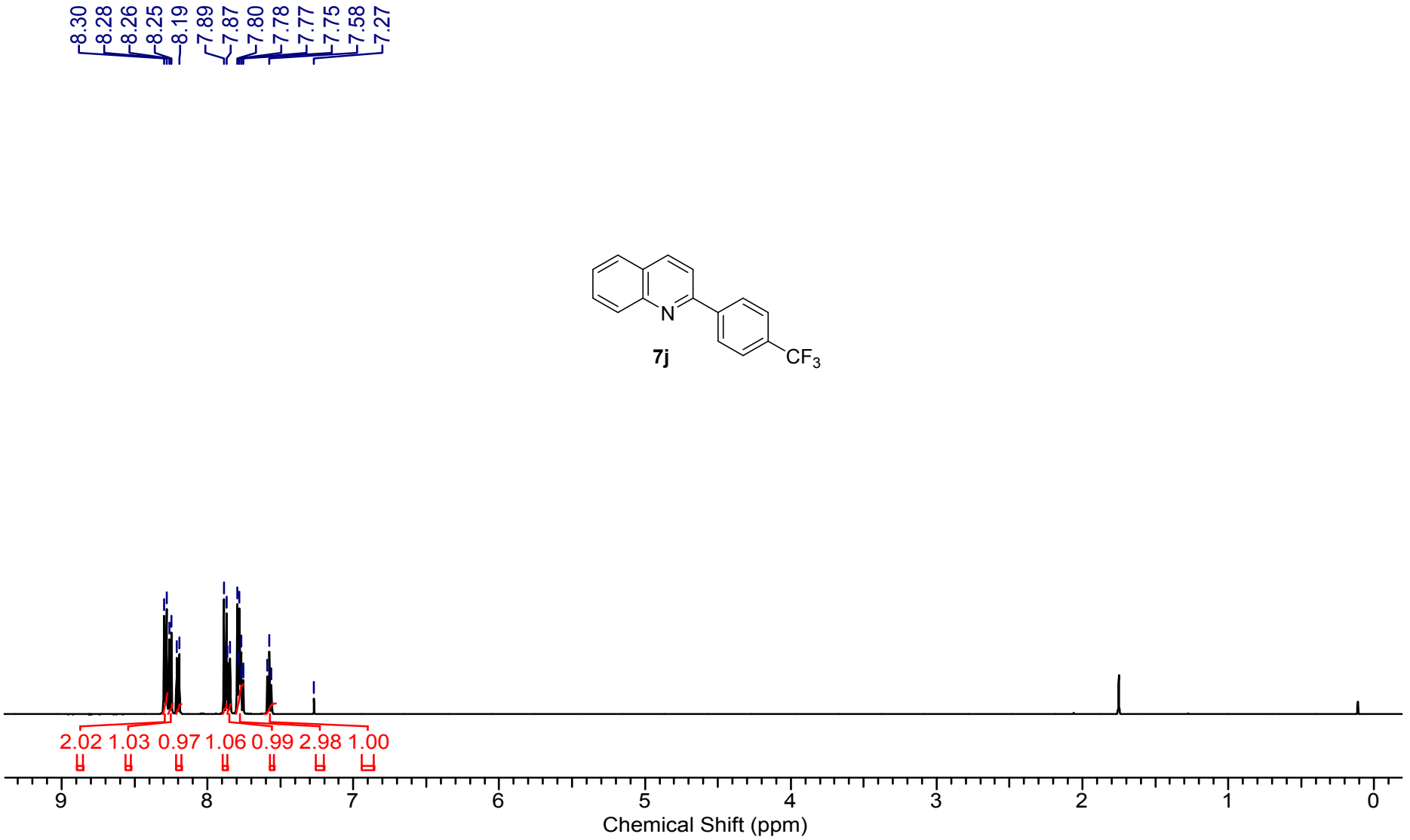
^{13}C NMR of **7h**


8.21
8.19
8.17
8.17
8.15
7.83
7.81
7.81
7.74
7.54
7.24
7.22
7.20
N
F
7i
4.06 2.00 1.11 1.00 2.03
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

^{1}H NMR of **7i**

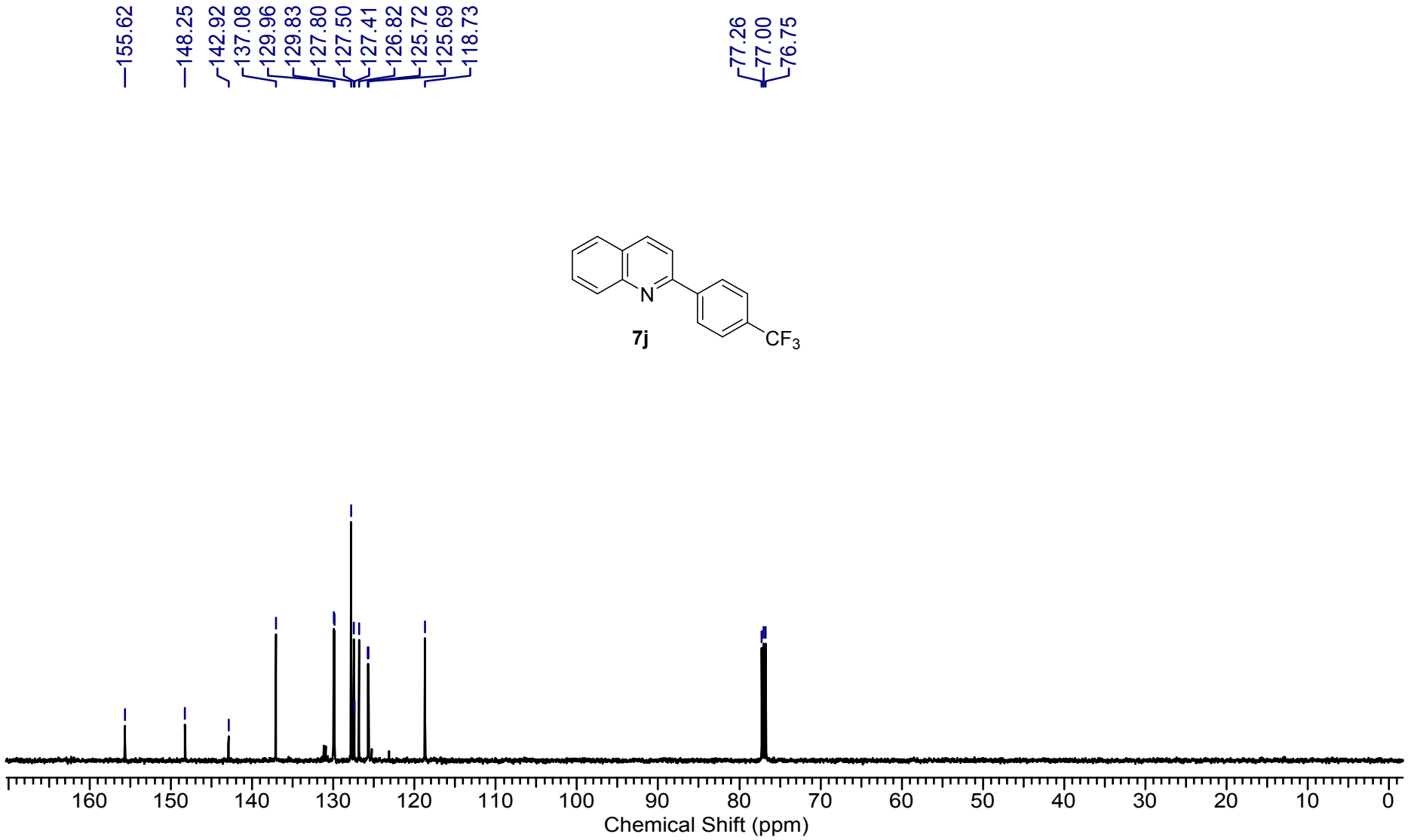

164.76
162.77
156.17
148.19
136.85
135.78
129.74
129.61
129.39
129.33
127.43
127.04
126.30
118.56
115.80
115.63
77.26
77.00
76.75
N
F
7i
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

^{13}C NMR of **7i**

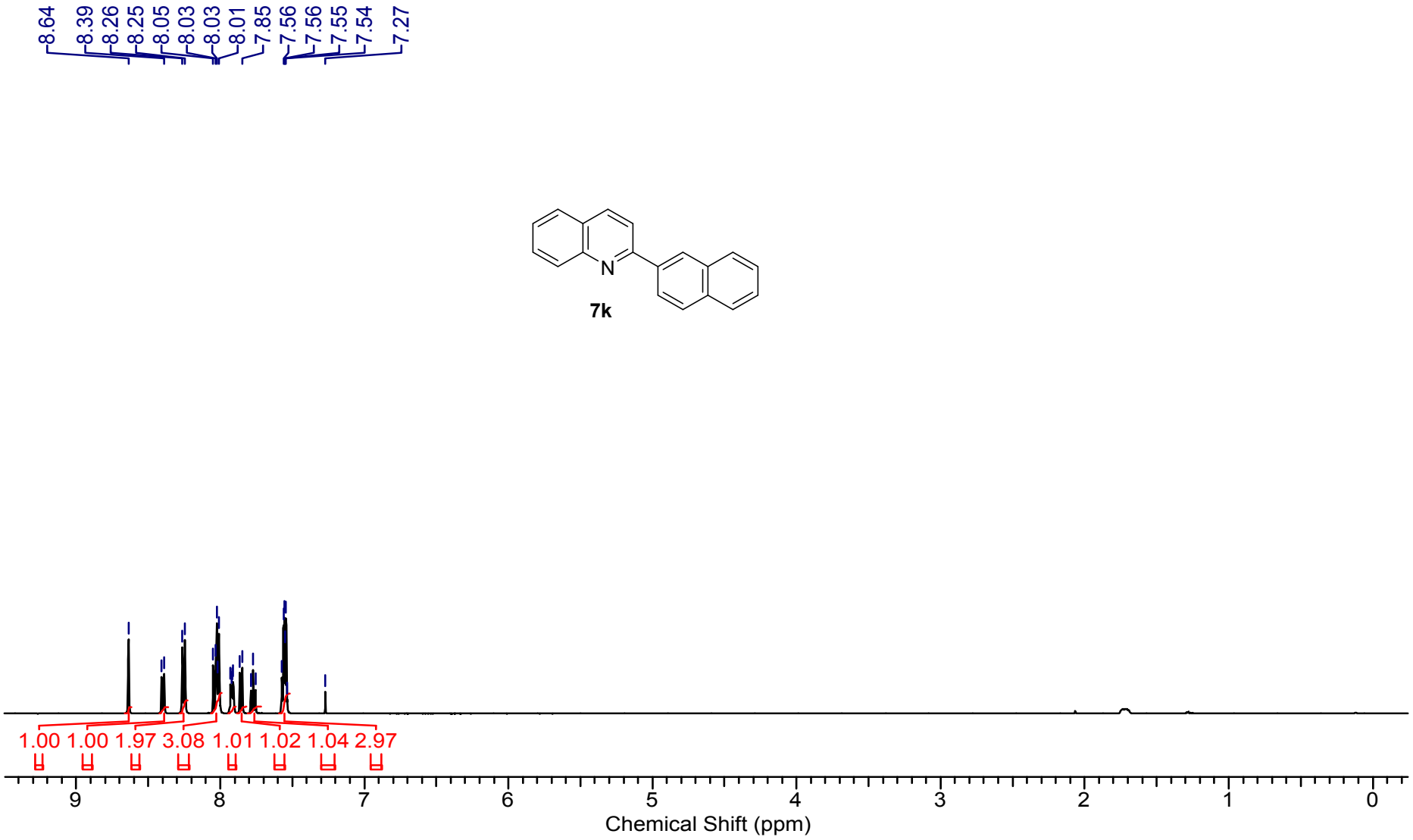


7j

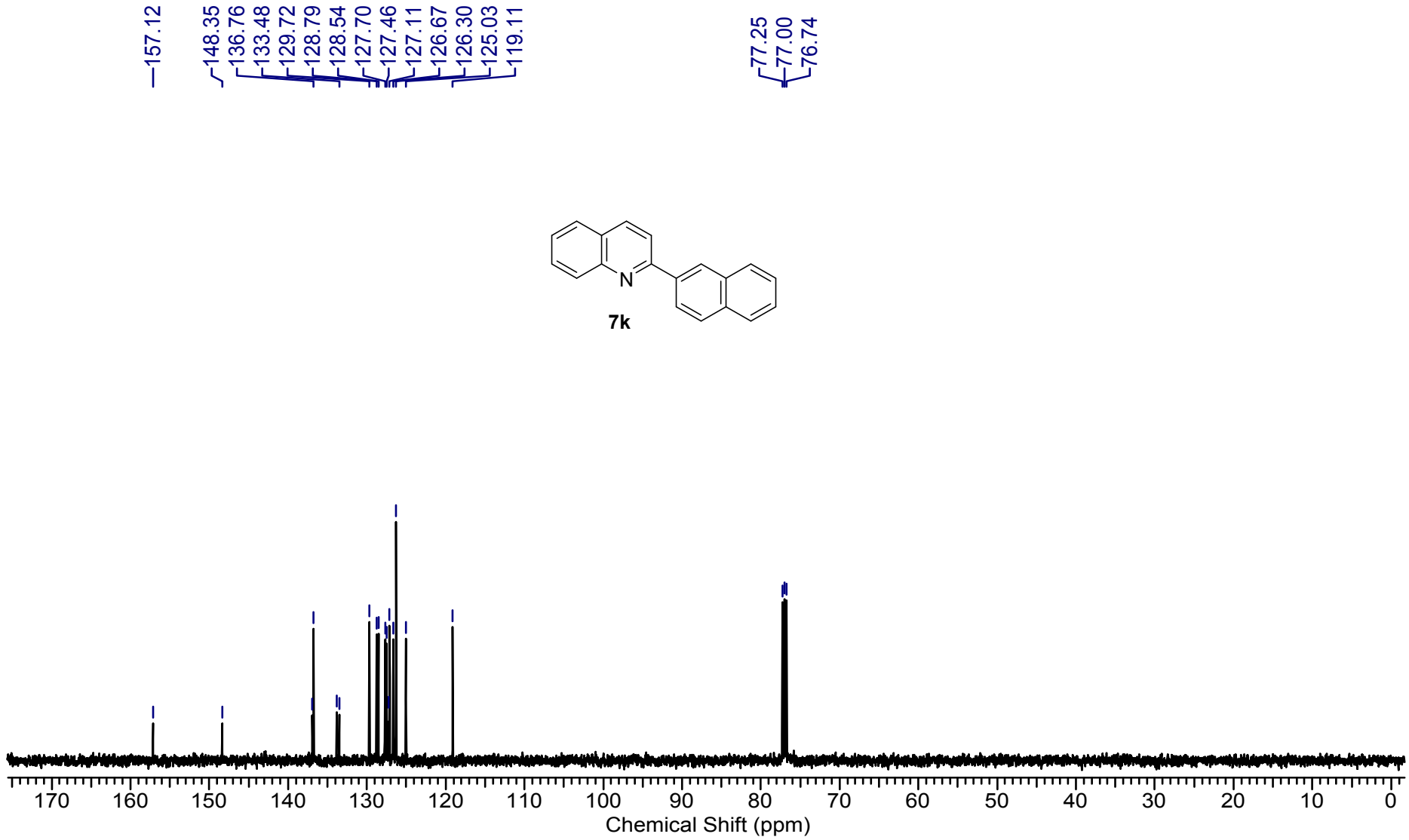
^{1}H NMR of **7j**


155.62
148.25
142.92
137.08
129.96
129.83
127.80
127.50
127.41
126.82
125.72
125.69
118.73
77.26
77.00
76.75
N
CF3
7j
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

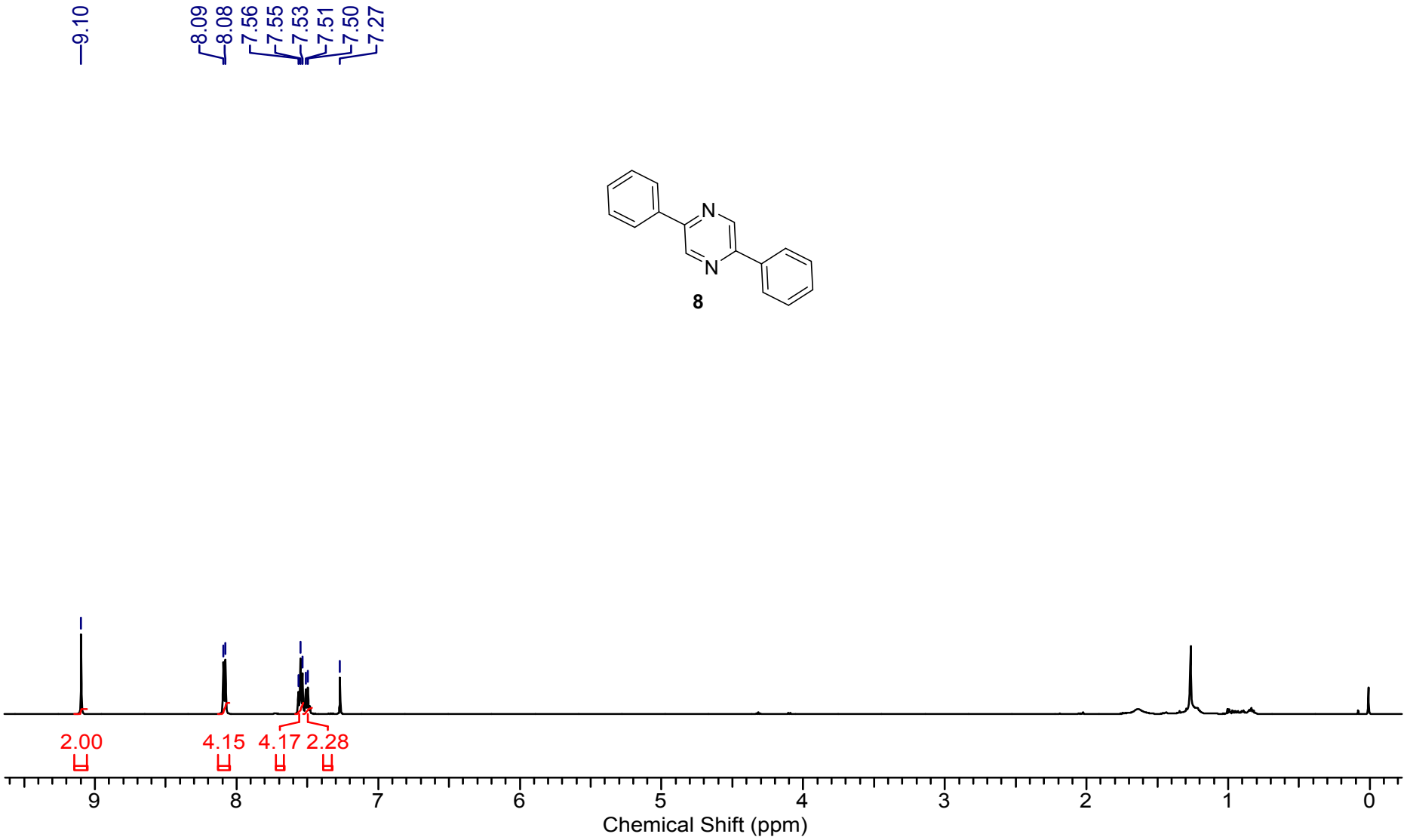
^{13}C NMR of **7j**


8.64
8.39
8.26
8.25
8.05
8.03
8.03
8.01
7.85
7.56
7.56
7.55
7.54
7.27
N
7k
1.00 1.00 1.97 3.08 1.01 1.02 1.04 2.97
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

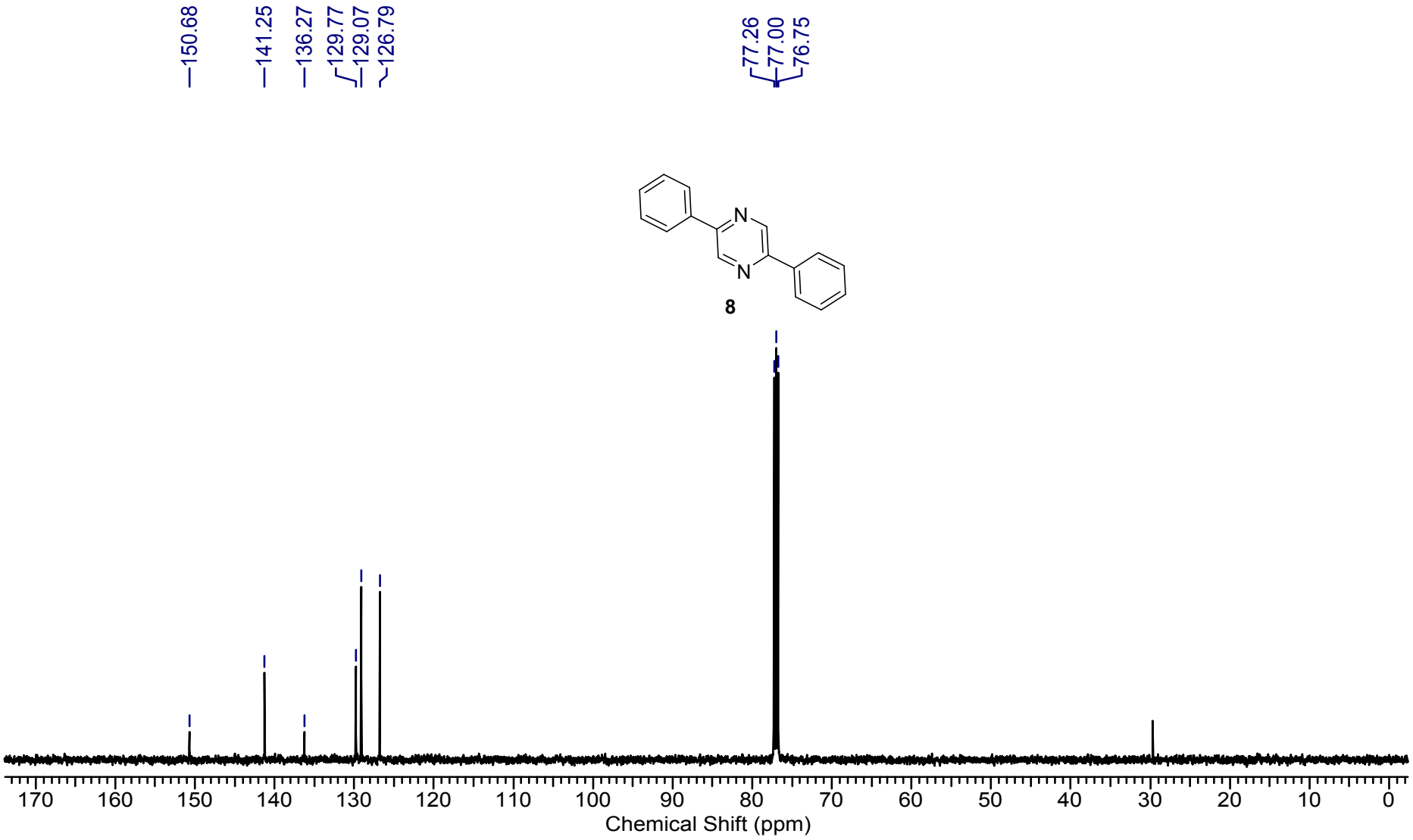
^{1}H NMR of **7k**


157.12
148.35
136.76
133.48
129.72
128.79
128.54
127.70
127.46
127.11
126.67
126.30
125.03
119.11
77.25
77.00
76.74
N
7k
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

^{13}C NMR of **7k**


9.10
8.09
8.08
7.56
7.55
7.53
7.51
7.50
7.27
N
N
8
2.00
4.15
4.17
2.28
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

^{1}H NMR of **8**


150.68
141.25
136.27
129.77
129.07
126.79
77.26
77.00
76.75
N
N
8
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

^{13}C NMR of **8**