Supporting Information

Synthesis of Polyfluoroalkyl Aza-Polycyclic Aromatic Hydrocarbons Enabled by Addition of Perfluoroalkyl Radicals onto Vinyl Azides

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1. General

^{1}H NMR (400 MHz) spectra were recorded on a Bruker Avance 400 spectrometers in $CDCl_3$ [using $CDCl_3$ (for ^{1}H, $\delta = 7.26$) as the internal standard unless otherwise stated]. ^{13}C NMR (100 MHz) spectra on a Bruker Avance 400 spectrometer in $CDCl_3$ [using $CDCl_3$ (for ^{13}C, $\delta = 77.00$) as internal standard]. ^{19}F NMR (376 MHz) spectra were recorded on a Bruker Avance 400 spectrometer. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ddd = doublet of doublet of doublet, tt = triplet of triplet, m = multiplet, br = broad. IR spectra were recorded on a Shimazu IR Prestige-21 FT-IR Spectrometer. High-resolution mass spectra were obtained with a Q-Tof Premier LC HR mass spectrometer (Waters). Melting points were uncorrected and were recorded on a Buchi B-54 melting point apparatu. Absorbance spectra were measured on Beckman Coulter DU 800 UV-Vis spectrophotometer. Flash column chromatography was performed using Merck silica gel 60 with distilled solvents. $PhI(OAc)_2$, KF and Me_3SiCF_3 were purchased from Sigma-Aldrich Co., Inc. $Me_3SiC_2F_5$ and $Me_3SiC_3F_7$ were purchased from Alfa Aesar.

2. The safety issues for handling of azido compounds[1,2]

2.1. Sodium azide (NaN_3)

Sodium azide is toxic (LD_{50} oral = 27 mg/kg for rats) and can be absorbed through skin. Appropriate gloves are necessary when using it. It decomposes explosively upon heating to above 275 °C. Sodium azide is relatively safe especially in aqueous solution, *unless acidified to form HN_3*, which is volatile and highly toxic.

2.2. Organic azides

Organic azides are potentially explosive substances that can decompose with the slight input of energy from external sources (heat, light, pressure, etc). When designing the organic azides used for the project, we keep in mind the following equation. It is noted that this equation takes into account all nitrogen atoms in the organic azide, not just those in the azido group.

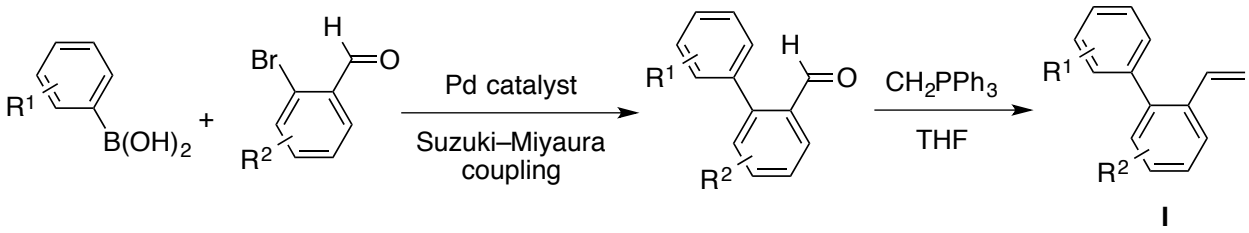
$$\frac{N_C + N_O}{N_N} \geq 3 \quad \text{(N: number of the atom)}$$

All organic azides prepared in this work are satisfied with the equation above and they are enough stable to be stored under –20 ºC at leatst for 6 months except for **1s**. We have never experienced a safety problem with these materials.

3. Synthesis of biaryl vinyl azides 1

3.1 Synthesis of biaryl alkenes I

Biaryl alkenes **I**, which are the basic starting materials for biaryl vinyl azides **1**, were prepared by a two-step sequences including Suzuki-Miyaura coupling and Wittig reaction.



I

A general procedure for synthesis of biaryl alkene **Ia** ($R^1 = R^2 = H$):

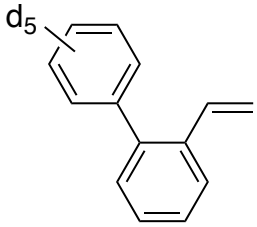
To a solution of 2-bromobenzaldehyde (9.41g, 50.9 mmol) and phenylboronic acid (7.45 g, 61.1 mmol) in ethanol (60 mL) and cyclopentyl methyl ether (CPME) (80 mL) was added an aqueous solution of Na_2CO_3 2M (100 mL, 200 mmol), followed by $Pd(PPh_3)_4$ (4.62 g, 4.0 mmol). The reaction was stirred at 90°C under nitrogen atmosphere for 6 h. After completion, the reaction mixture was filter through a short pad of celite and washed with Et_2O. The aqueous phase was extracted with Et_2O three times. The organic fractions were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane : EtOAc = 95 : 5) to afford the intermediate aldehyde (8.81 g, 48.3 mmol).

To a suspension of $MePPh_3Br$ (27.29 g, 76.4 mmol) in THF (120 mL), *t*-BuOK (8.57 g, 76.4 mmol) was added portionwise. The reaction was allowed to stir at room temperature for 30 min. It was then cooled to -78°C and a solution of the intermediate aldehyde (8.81g, 48.3 mmol) in THF (50 mL) was added dropwise. The mixture was stirred at -78°C for 1 h and then warmed to room temperature for 1 h. The reaction was quenched with water. The aqueous phase was extracted with Et_2O three times. The organic fractions were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column

chromatography (hexane : EtOAc = 97 : 3) to afford **Ia** (8.69g, 48.3 mmol) in 95% yield from 2-bromobenzaldehyde.

All biaryl alkenes **I** were prepared through the same synthetic route as that of **Ia**. The characterization data of new biaryl alkenes were shown below.

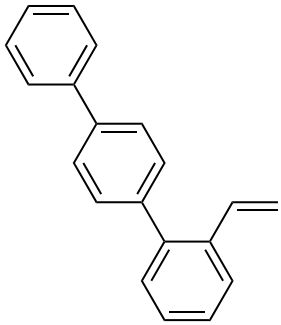
2',3',4',5'6'-Pentadeutero-2-vinyl-1,1'-biphenyl (Ia-d_5):



Biaryl alkene **Ia-d_5** was prepared in 74% yield by following the same procedure as **Ia** from 2-bromobenzaldehyde and phenyl-d_5-boronic acid.

Colorless oil; IR (KBr) 3065, 2276, 1628, 1556, 1481, 1382, 1280 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.27 (1H, d, *J* = 10.8 Hz), 5.79 (1H, d, *J* = 17.2 Hz), 6.82 (1H, dd, *J* = 10.8, 17.2 Hz), 7.37-7.44 (3H, m), 7.74 (1H, d, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 114.59, 125.67, 126.45 (t, *J* = 24.5 Hz), 127.43, 127.47 (t, *J* = 24.1 Hz), 127.62, 129.34 (t, *J* = 24.3 Hz), 130.07, 135.71, 135.90, 140.64, 140.80; ESIHRMS: Found: *m/z* 186.1328. Calcd for $C_{14}{}^1H_8{}^2H_5$: $(M+H)^+$ 186.1331.

2-Vinyl-1,1':4',1''-terphenyl (Ib):

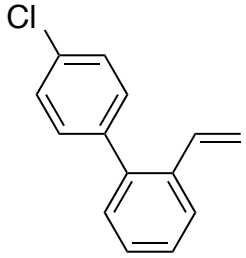


Biaryl alkene **Ib** was prepared in 67% yield by following the same procedure as **Ia** from 2-bromobenzaldehyde and 4-biphenylboronic acid.

White solid, mp 100-102 °C; IR (KBr) 3024, 1620, 1597, 1474, 1250 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.25 (1H, d, *J* = 11.2 Hz), 5.76 (1H, d, *J* = 17.6 Hz), 5.83 (1H, dd, *J* = 11.2, 17.6 Hz),

7.37-7.41 (4H, m), 7.45-7.51 (4H, m), 7.67-7.69 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 114.73, 125.80, 126.73, 127.07, 127.31, 127.52, 127.69, 128.79, 130.06, 130.22, 135.81, 135.95, 139.80, 139.83, 140.39, 140.75; ESIHRMS: Found: *m/z* 257.1333. Calcd for $C_{20}H_{17}$: $(M+H)^+$ 257.1330.

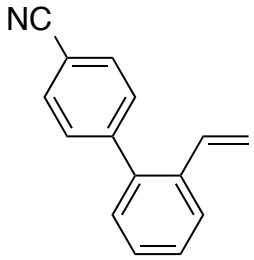
4'-Chloro-2-vinyl-1,1'-biphenyl (If):



Biaryl alkene **If** was prepared in 81% yield by following the same procedure as **Ia** from 2-bromobenzaldehyde and 4-chlorophenylboronic acid.

Colorless oil; IR (KBr) 3063, 1628, 1597, 1473, 1265 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.23 (1H, d, *J* = 10.8 Hz), 5.72 (1H, d, *J* = 17.2 Hz), 6.69 (1H, dd, *J* = 10.8, 17.2 Hz), 7.27 (1H, dd, *J* = 1.6, 7.2 Hz), 7.30 (2H, d, *J* = 8.4 Hz), 7.34 (1H, ddd, *J* = 1.6, 7.2, 7.6 Hz), 7.36 (1H, ddd, *J* = 1.6, 7.2, 7.6 Hz), 7.41 (2H, d, *J* = 8.4 Hz), 7.66 (1H, dd, *J* = 1.6, 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.15, 125.89, 127.74, 127.78, 128.21, 129.89, 131.07, 133.13, 135.58, 135.77, 139.24, 139.50; ESIHRMS: Found: *m/z* 215.0638. Calcd for $C_{15}H_{12}Cl$: $(M+H)^+$ 215.0628.

2'-Vinyl-[1,1'-biphenyl]-4-carbonitrile (Ig):

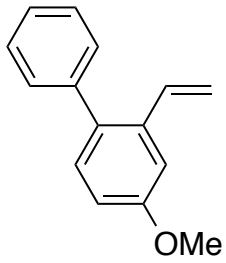


Biaryl alkene **Ig** was prepared in 88% yield by following the same procedure as **Ia** from 2-bromobenzaldehyde and 4-cyanophenylboronic acid.

White solid, mp 56-58 °C; IR (KBr) 3055, 2230, 1605, 1504, 1474, 1265 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.26 (1H, d, *J* = 10.8 Hz), 5.73 (1H, d, *J* = 17.6 Hz), 6.61 (1H, dd, *J* = 10.8, 17.6 Hz), 7.26 (1H, d, *J* = 7.6 Hz), 7.37 (1H, dd, *J* = 7.6, 7.6 Hz), 7.41 (1H, dd, *J* = 7.6, 7.6 Hz), 7.47 (2H, d, *J* = 8.0 Hz), 7.66 (1H, d, *J* = 7.6 Hz), 7.71 (2H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 110.84, 115.95, 118.80, 126.15, 127.88, 128.49, 129.64, 130.45, 131.80, 135.02, 135.69, 138.67, 145.61; ESIHRMS: Found: *m/z* 206.0965. Calcd for $C_{15}H_{12}N$: $(M+H)^+$ 206.0970.

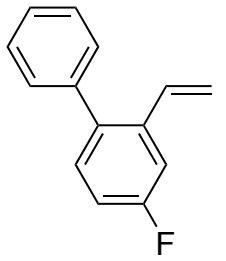
4-Methoxy-2-vinyl-1,1'-biphenyl (Ih):



Biaryl alkene **Ih** was prepared in 66% yield by following the same procedure as **Ia** from 2-bromo-5-methoxybenzaldehyde and phenylboronic acid.

White solid, mp 53-55 °C; IR (KBr) 3024, 2908, 1597, 1481, 1303, 1226 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.91 (3H, s), 5.25 (1H, d, *J* = 11.2 Hz), 5.75 (1H, d, *J* = 17.6 Hz), 6.77 (1H, dd, *J* = 11.2, 17.6 Hz), 7.95 (1H, dd, *J* = 2.4, 8.4 Hz), 7.23 (1H, d, *J* = 2.4 Hz), 7.28 (1H, d, *J* = 8.4 Hz), 7.37-7.39 (3H, m), 7.43-7.46 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.29, 110.57, 113.56, 114.73, 126.64, 127.94, 129.90, 131.18, 133.78, 135.95, 136.79, 140.53, 158.95; ESIHRMS: Found: *m/z* 211.1131. Calcd for $C_{15}H_{15}O$: $(M+H)^+$ 211.1123.

4-Fluoro-2-vinyl-1,1'-biphenyl (Ii):

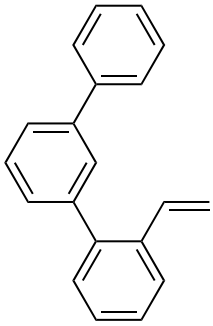


Biaryl alkene **Ii** was prepared in 83% yield by following the same procedure as **Ia** from 2-bromo-5-fluorobenzaldehyde and phenylboronic acid.

Colorless oil; IR (KBr) 3063, 1605, 1573, 1473, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.21 (1H, dd, *J* = 0.8, 11.2 Hz), 5.68 (1H, dd, *J* = 0.8, 17.6 Hz), 6.65 (1H, ddd, *J* = 1.6, 11.2, 17.6 Hz), 6.99 (1H, ddd, *J* = 2.8, 8.0, 8.4 Hz), 7.22 (1H, dd, *J* = 6.0, 8.4 Hz), 7.27-7.29 (2H, m), 7.30-7.35 (2H, m), 7.37-7.40 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 111. 94 (d, *J* = 21.8 Hz), 114.54 (d, *J* = 21.3 Hz), 115.65, 127.11, 128.08, 129.81, 131.65 (d, *J* = 8.2 Hz), 135.03 (d, *J* = 2.2 Hz),

136.91 (d, J = 2.9 Hz), 137.64 (d, J = 7.6 Hz), 139.89, 162.30 (d, J = 253.9 Hz); ESIHRMS: Found: *m/z* 199.0928. Calcd for $C_{14}H_{12}F$: $(M+H)^+$ 199.0923.

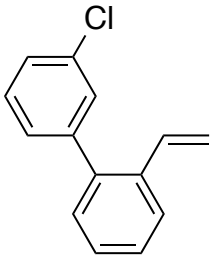
2-Vinyl-1,1':3',1''-terphenyl (Ij):



Biaryl alkene **Ij** was prepared in 85% yield by following the same procedure as **Ia** from 2-bromobenzaldehyde and 3-biphenylboronic acid.

Colorless oil; IR (KBr) 3063, 1620, 1597, 1473, 1404, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.25 (1H, d, J = 11.2 Hz), 5.77 (1H, d, J = 17.2 Hz), 6.82 (1H, dd, J = 11.2, 17.2 Hz), 7.36-7.41 (5H, m), 7.46-7.54 (3H, m), 7.62-7.72 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 114.78, 125.72, 125.76, 127.17, 127.34, 127.57, 127.67, 128.45, 128.61, 128.70, 128.77, 130.08, 135.79, 135.84, 140.72, 140.90, 140.95, 141.31; ESIHRMS: Found: *m/z* 257.1335. Calcd for $C_{20}H_{17}$: $(M+H)^+$ 257.1330.

3'-Chloro-2-vinyl-1,1'-biphenyl (Il)

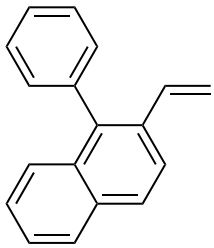


Biaryl alkene **Il** was prepared in 87% yield by following the same procedure as **Ia** from 2-bromobenzaldehyde and 3-chlorophenylboronic acid.

Colorless oil; IR (KBr) 3062, 1628, 1566, 1465, 1249 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.22 (1H, dd, J = 1.2, 10.8 Hz), 5.70 (1H, dd, J = 1.2, 17.6 Hz), 6.67 (1H, dd, J = 10.8, 17.6 Hz), 7.21-7.25 (2H, m), 7.30-7.38 (5H, m), 7.64 (1H, dd, J = 1.6, 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.25, 125.81, 127.10, 127.70, 127.92, 128.00, 129.20, 129.73, 129.86, 133.91,

135.37, 135.69, 139.27, 142.64; ESIHRMS: Found: *m/z*215.0634. Calcd for $C_{14}H_{12}Cl$: $(M+H)^+$ 215.0628.

1-Phenyl-2-vinylnaphthalene (Im):



The Suzuki-Miyaura coupling reaction of 1-bromo-2-naphthaldehyde and phenylboronic acid was performed following the literature reported procedure.[3] The subsequent Wittig reaction (the same procedure as that of **Ia**) gave biaryl alkene **Im** in 90% yield

Colorless oil; IR (KBr) 3055, 1620, 1498, 1435, 1381 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.24 (1H, d, *J* = 11.2 Hz), 5.83 (1H, d, *J* = 17.6 Hz), 6.68 (1H, dd, *J* = 11.2, 17.6 Hz), 7.35-7.41 (3H, m), 7.46-7.57 (5H, m), 7.85-7.90 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 114.53, 122.56, 125.67, 126.09, 126.91, 127.23, 127.68, 127.76, 128.20, 130.74, 132.65, 132.96, 133.01, 135.63, 138.03, 138.59; ESIHRMS: ESIHRMS: Found: *m/z* 231.1169. Calcd for $C_{18}H_{15}$: $(M+H)^+$ 231.1174.

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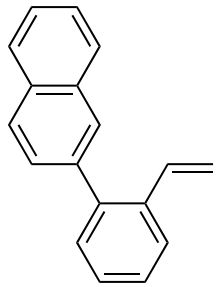
2-(2-Vinylphenyl)naphthalene (In):

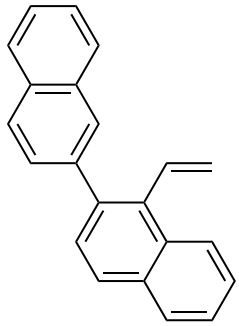


Biaryl alkene **In** was prepared in 95% yield by following the same procedure as **Ia** from 2-bromobenzaldehyde and 2-naphthylboronic acid.

White solid, mp 52-54 °C; IR (KBr) 3055, 1620, 1597, 1481, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.20 (1H, dd, *J* = 1.2, 10.8 Hz), 5.75 (1H, dd, *J* = 1.2, 17.6 Hz), 6.76 (1H, dd, *J* = 10.8, 17.6 Hz), 7.38-7.41 (3H, m), 7.49-7.53 (3H, m), 7.70 (1H, dd, *J* = 2.0, 7.6 Hz), 7.82 (1H, s), 7.87-7.91 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 114.77, 125.73, 125.97, 126.21, 127.46,

127.56, 127.64, 127.67, 128.03, 128.17, 128.50, 130.30, 132.33, 133.14, 135.87, 135.91, 138.36, 140.74; ESIHRMS: Found: *m/z* 231.1183. Calcd for $C_{18}H_{15}$: $(M+H)^+$ 231.1174.

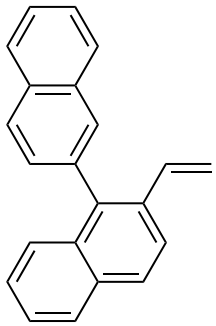
1-Vinyl-2,2'-binaphthalene (Io):



Biaryl alkene **Io** was prepared in 78% yield by following the same procedure as **In** from 2-bromo-1-naphthaldehyde[4] and 2-naphthylboronic acid.

White solid, mp 74-75 °C; IR (KBr) 3048, 1620, 1589, 1497, 1420, 1250 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.43 (1H, dd, *J* = 1.6, 18.0 Hz), 5.61 (1H, dd, *J* = 1.6, 11.6 Hz), 7.02 (1H, dd, *J* = 11.6, 18.0 Hz), 7.53-7.61 (6H, m), 7.87-7.95 (6H, m), 8.38 (1H, dd, *J* = 1.6, 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.13, 125.72, 125.88, 125.91, 126.11, 126.30, 127.24, 127.27, 127.66, 128.01, 128.22, 128.38, 128.73, 128.88, 131.57, 132.21, 133.03, 133.20, 134.17, 134.26, 137.76, 139.70; ESIHRMS: Found: *m/z* 281.1324. Calcd for $C_{22}H_{17}$: $(M+H)^+$ 281.1330.

2-Vinyl-1,2'-binaphthalene (Ip):

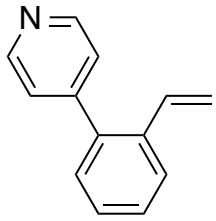


Biaryl alkene **Ip** was prepared in 81% yield by following the same procedure as **In** from 1-bromo-2-naphthaldehyde and 2-naphthylboronic acid.

White solid, mp 70-71 °C; IR (KBr) 3055, 1620, 1504, 1427, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.18 (1H, dd, *J* = 0.8, 10.8 Hz), 5.82 (1H, dd, *J* = 0.8, 17.6 Hz), 6.67 (1H, dd, *J* = 10.8, 17.6 Hz), 7.33 (1H, ddd, *J* = 1.2, 7.2, 8.0 Hz), 7.44-7.50 (3H, m), 7.57-7.60 (2H, m), 7.81 (1H, s),

7.89-7.92 (4H, m), 7.98 (1H, d, J = 7.2 Hz), 8.00 (1H, d, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 114.66, 122.59, 125.72, 126.10, 126.17, 126.31, 126.99, 127.78, 127.80, 127.82 (overlapped), 128.02, 128.99, 129.64, 132.58, 132.92, 133.04, 133.06, 133.25, 135.66, 136.13, 137.87; ESIHRMS: Found: *m/z* 281.1339. Calcd for $C_{22}H_{17}$: $(M+H)^+$ 281.1330.

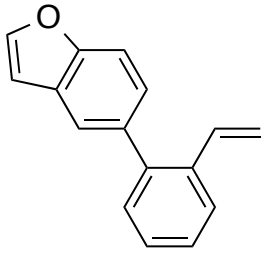
4-(2-Vinylphenyl)pyridine (Iq):



The Suzuki-Miyaura coupling reaction of 2-bromobenzaldehyde and 4-pyridinylboronic acid was performed following the literature reported procedure.[5] The subsequent Wittig reaction (the same procedure as that of **Ia**) gave biaryl alkene **Im** in 98% yield.

White solid, mp 54-56 °C; IR (KBr) 3063, 1597, 1543, 1404, 1265 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.26 (1H, dd, J = 1.2, 10.8 Hz), 5.73 (1H, dd, J = 1.2, 17.6 Hz), 6.65 (1H, dd, J = 10.8, 17.6 Hz), 7.26-7.30 (3H, m), 7.36 (1H, ddd, J = 1.2, 7.2, 7.6 Hz), 7.41 (1H, ddd, J = 1.2, 7.2, 7.6 Hz), 7.66 (1H, dd, J = 1.2, 7.6 Hz), 7.65 (2H, d, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.93, 124.61, 126.10, 127.88, 128.59, 129.48, 134.98, 135.63, 137.82, 148.59, 149.51; ESIHRMS: Found: *m/z* 182.0973. Calcd for $C_{13}H_{12}N$: $(M+H)^+$ 182.0970.

5-(2-Vinylphenyl)benzofuran (Ir):

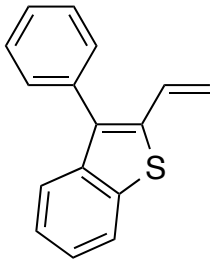


Biaryl alkene **Ir** was prepared in 77% yield by following the same procedure as **Ia** from 2-bromobenzaldehyde and benzofuran-5-boronic acid.

Colorless oil; IR (KBr) 3063, 1628, 1535, 1458, 1265 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.17 (1H, d, J = 11.2 Hz), 5.71 (1H, d, J = 17.6 Hz), 6.72 (1H, dd, J = 11.2, 17.6 Hz), 6.80 (1H, dd, J = 0.8, 2.0 Hz), 7.27 (1H, dd, J = 1.6, 8.4 Hz), 7.32-7.37 (3H, m), 7.53 (1H, d, J = 8.4 Hz), 7.55

(1H, d, J = 1.6 Hz), 7.65-7.70 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 106.66, 110.75, 114.49, 122.25, 125.61, 126.35, 127.27 (overlapped), 127.55, 130.44, 135.64, 135.92, 136.00, 141.05, 145.44, 154.16; ESIHRMS: Found: *m/z* 221.0961. Calcd for $C_{16}H_{13}O$: $(M+H)^+$ 221.0966.

3-Phenyl-2-vinylbenzo[b]thiophene (Is):

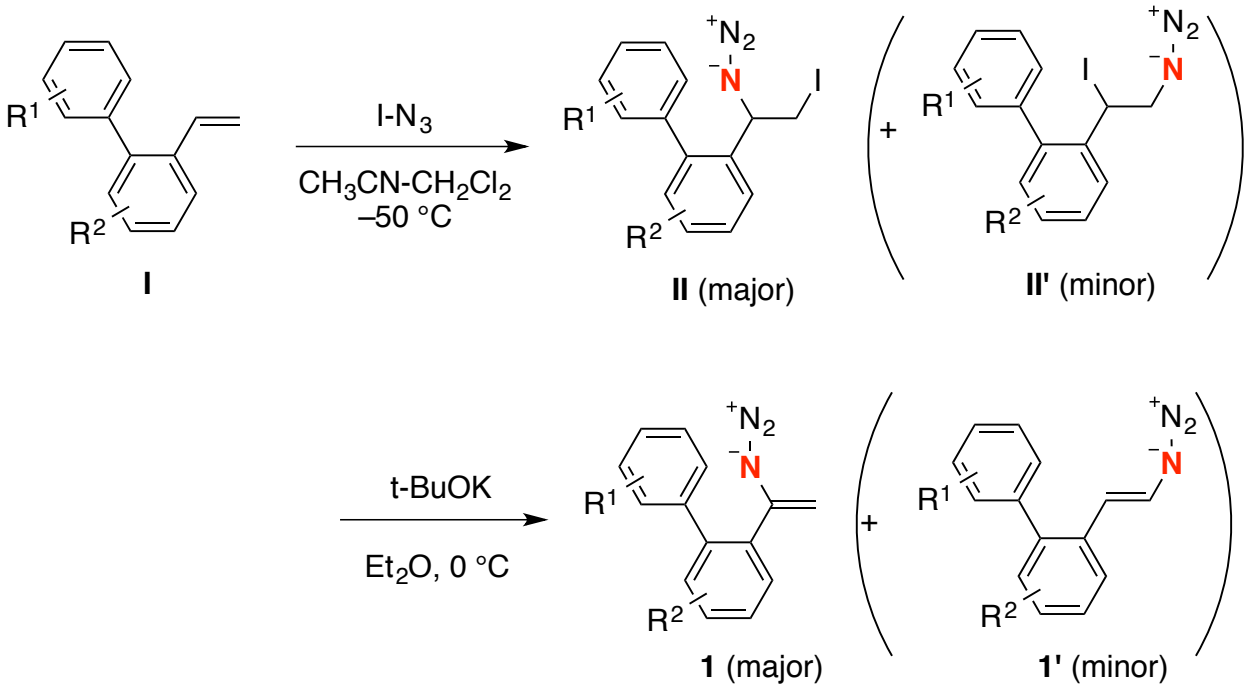


Biaryl alkene **Is** was prepared in 71% yield by following the same procedure as **Ia** from 3-bromothiophene-2-carboxaldehyde and phenylboronic acid.

Colorless oil; IR (KBr) 3055, 1612, 1489, 1435, 1265 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.29 (1H, d, J = 10.8 Hz), 5.74 (1H, d, J = 17.2 Hz), 6.89 (1H, dd, J = 10.8, 17.2 Hz), 7.31 (1H, dd, J = 7.2, 7.6 Hz), 7.36 (1H, dd, J = 7.2, 7.6 Hz), 7.44-7.47 (3H, m), 7.51-7.59 (3H, m), 7.83 (1H, d, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 116.14, 122.18, 123.18, 124.37, 125.14, 127.67, 128.49, 129.64, 130.33, 134.66, 135.68, 137.94, 138.62, 140.34; ESIHRMS: Found: *m/z* 237.0744. Calcd for $C_{16}H_{13}S$: $(M+H)^+$ 237.0738.

3.2 Synthesis of biaryl vinyl azides 1 by method A (Hassner's method)[6]

This method involves iodoazidation of **I** with IN_3 generated *in situ* from NaN_3 and ICl, leading to two possible regioisomers **II** and **II'**. In most cases, only the desired one (**II**) was formed as single isomers and the subsequent treatment with *t*-BuOK afforded biaryl vinyl azides **1**. However, in several case, the undesired one (**II'**) was formed as a minor product, and the separation of **II** and **II'** proved challenging. The following deprotonation step afforded a mixture of **1** and **1'**. For most substrates, the resulted two products could be separated partially by silica gel column chromatography. In case that these two products were unable to be separated, method B (see below) could be applied.



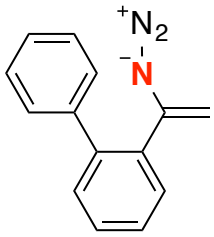
A general procedure of method A (R^1 = R^2 = H): this procedure was slightly modified from Hassner's method.[6]

To a suspension of NaN_3 (2.119 g, 32.4 mmol) in acetonitrile (8.0 mL) was added dropwise a solution of iodine monochloride (3.175 g, 19. 6 mmol) in CH_2Cl_2 (30 mL) at 0 °C. The mixture was stirred at the same temperature for 30 min and then cooled to –50 °C. A solution of 2-vinyl-1,1'-biphenyl (2.350 g, 13.0 mmol) in CH_2Cl_2 (15 mL) was added slowly over 30 min. After that, the mixture was further kept at the same temperature for 15 min, and then was quenched with saturated aqueous $Na_2S_2O_3$. The aqueous layer was extracted two times with EtOAc. The combined extracts were washed with brine and dried over $MgSO_4$. After evaporation of solvents, the resulting crude materials were used immediately for the next step without any furthur purification. This step only led to a single regioisomer **IIa**.

To a solution of the obtained compounds above in Et_2O (30 mL) was added *t*-BuOK (1.602 g, 14.3 mmol) at 0 °C, and the mixture was stirred for 2 h at the same temperature. The reaction was quenched with water, and the organic materials were extracted with Et_2O. The Et_2O solution was washed with brine, and dried over $MgSO_4$. The solvent was removed in vacuo, and the resulting crude materials were purified by flash column chromatography (silica gel; hexane :

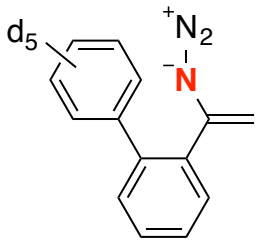
EtOAc = 99 : 1) to give vinyl azide **1a** (2.470 g, 11.2 mmol, 86% yield from 2-vinyl-1,1'-biphenyl) as a pale yellow solid.

2-(1-Azidovinyl)-1,1'-biphenyl (1a):



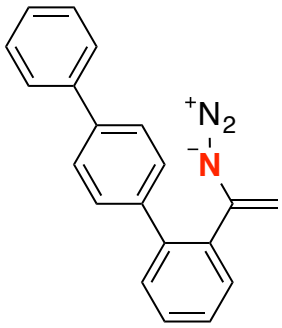
mp 32-34°C; IR (KBr) 3053, 2097, 1628, 1597, 1474, 1435, 1265 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.80 (1H, s), 4.95 (1H, s), 7.36-7.48 (9H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 103.66, 127.39, 128.15, 128.75, 129.35, 129.96, 130.45, 133.76, 140.52, 140.53, 145.66; ESIHRMS: Found: m/z 216.0786. Calcd for $C_{14}H_{11}NNa$: $(M-N_2+Na)^+$ 216.0789.

2',3',4',5'6'-Pentadeutero-2-(1-azidovinyl)-1,1'-biphenyl (1a-d_5)



The iodoazidation step led to a single regioisomer. Vinyl azide **1a-d_5** was isolated by column chromatography (silica gel; hexane : EtOAc = 99 : 1) in 91% yield from biaryl alkene **Ia-d_5**.
Pale yellow oil; IR (KBr) 3055, 2276, 2099, 1620, 1481, 1442, 1296 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.79 (1H, s), 4.94 (1H, s), 7.36-7.39 (2H, m), 7.43-7.46 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 103.61, 126.83 (d, J = 23.5 Hz), 127.36, 127.62 (d, J = 24.2 Hz), 128.91 (d, J = 24.7 Hz), 129.33, 129.95, 130.42, 133.73, 140.31, 140.48, 145.66; ESIHRMS: Found: m/z 227.1346. Calcd for $C_{14}{}^{1}H_7{}^{2}H_5N_3$: $(M+H)^+$ 227.1345.

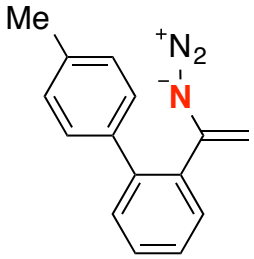
2-(1-Azidovinyl)-1,1':4',1''-terphenyl (1b):



The iodoazidation step led to a regioisomeric mixture of **II:II'** (ratio = 84:16), which could not be separated by column chromatography. Treatment of the regioisomeric mixture with *t*-BuOK gave two vinyl azides **2b** and **2b'** in 66% combined yield from **Ib** after column chromatography (silica gel; hexane : EtOAc = 99 : 1). The pure vinyl azide **2b** could be obtained by recrystallization of the mixture from hexane/CH_2Cl_2 in -20 °C freezer.

Pale yellow solid, mp 105 °C decomposed; IR (KBr) 3055, 2099, 1628, 1481, 1442, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.86 (1H, s), 4.99 (1H, s), 7.38-7.50 (7H, m), 7.56 (2H, d, J = 8.0 Hz), 7.67 (2H, d, J = 8.0 Hz), 7.68 (2H, d, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 103.70, 126.86, 127.05, 127.34, 127.46, 128.77, 129.16, 129.42, 130.08, 130.43, 133.77, 139.48, 140.07, 140.12, 140.64, 145.73; ESIHRMS: Found: m/z 270.1276. Calcd for $C_{20}H_{16}N$: $(M-N_2+H)^+$ 270.1283.

2-(1-Azidovinyl)-4'-methyl-1,1'-biphenyl (1c):

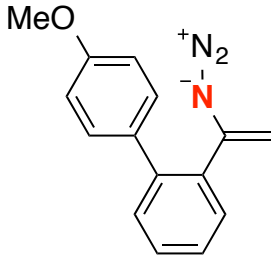


The iodoazidation step led to a single regioisomer. Vinyl azide **1c** was isolated by column chromatography (silica gel; hexane : EtOAc = 99 : 1) in 79% yield from biaryl alkene **Ic**.

Pale yellow oil; IR (KBr) 3024, 2924, 2091, 1620, 1512, 1442, 1296 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.38 (3H, s), 4.76 (1H, s), 4.92 (1H, s), 7.20 (2H, d, J = 8.0 Hz), 7.30-7.36 (4H, m),

7.39-7.42 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.18, 103.52, 127.15, 128.59, 128.88, 129.33, 129.99, 130.40, 133.66, 137.09, 137.52, 140.45, 145.78; ESIHRMS: Found: m/z 208.1130. Calcd for $C_{15}H_{14}N$: $(M-N_2+H)^+$ 208.1126.

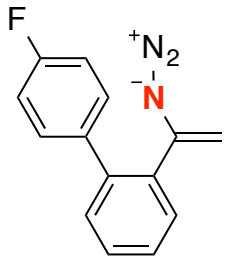
2-(1-Azidovinyl)-4'-methoxy-1,1'-biphenyl (1d):



The iodoazidation step led to a regioisomeric mixture of **II:II'** (ratio = 91:9), which could not be separated by column chromatography. Treatment of the regioisomeric mixture with *t*-BuOK gave two vinyl azides **1c** and **1c'** in 82% combined yield from biaryl alkene **Id** after column chromatography (silica gel; hexane : EtOAc = 99 : 1). The pure vinyl azide **1d** could be partially obtained.

Pale yellow oil; IR (KBr) 3059, 2957, 2095, 1614, 1514, 1441, 1244 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (3H, s), 4.79 (1H, d, J = 0.8 Hz), 4.94 (1H, d, J = 0.8 Hz), 6.95 (2H, d, J = 8.8 Hz), 7.32-7.36 (2H, m), 7.40-7.42 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.23, 103.48, 113.62, 127.02, 129.38, 129.86, 130.10, 130.36, 132.80, 133.63, 140.09, 145.91, 159.05; ESIHRMS: Found: m/z 224.1066. Calcd for $C_{15}H_{14}NO$: $(M-N_2+H)^+$ 224.1075.

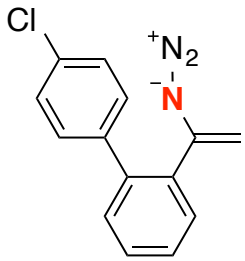
2-(1-Azidovinyl)-4'-fluoro-1,1'-biphenyl (1e):



The iodoazidation step led to a regioisomeric mixture of **II:II'** (ratio = 93:7), which could not be separated by column chromatography. Treatment of the regioisomeric mixture with *t*-BuOK gave two vinyl azides **1e** and **1e'** in 70% combined yield from biaryl alkene **Ie** after column chromatography (silica gel; hexane : EtOAc = 99 : 1). The pure vinyl azide **1e** could be partially obtained.

Pale yellow oil; IR (KBr) 3061, 2097, 1626, 1514, 1477, 1445, 1290 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.80 (1H, s), 4.95 (1H, s), 7.10 (2H, dd, *J* = 8.4, 8.8 Hz), 7.34 (1H, d, *J* = 7.6 Hz), 7.37-7.46 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 103.74, 115.14 (d, *J* = 21.3 Hz), 127.56, 129.44, 130.08, 130.36 (d, *J* = 7.9 Hz), 130.37, 133.80, 136.46 (d, *J* = 3.4 Hz), 139.44, 145.59, 162.36 (d, *J* = 245.2 Hz); ESIHRMS: Found: m/z 212.0883. Calcd for $C_{14}H_{11}FN$: $(M\text{-}N_2+H)^+$ 212.0876.

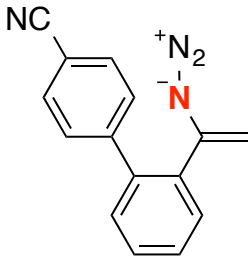
2-(1-Azidovinyl)-4'-chloro-1,1'-biphenyl (1f):



The iodoazidation step led to a regioisomeric mixture of **II:II'** (ratio = 91:9), which could not be separated by column chromatography. Treatment of the regioisomeric mixture with t-BuOK gave two vinyl azides **1f** and **1f'** in 77% combined yield from biaryl alkene **If** after column chromatography (silica gel; hexane : EtOAc = 99 : 1). The pure vinyl azide **1f** could be partially obtained.

Pale yellow oil; IR (KBr) 3061, 2095, 1620, 1599, 1497, 1443, 1288 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.81 (1H, s), 4.96 (1H, s), 7.33-7.47 (8H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 103.80, 127.74, 128.39, 129.46, 130.04, 130.08, 130.25, 133.50, 133.73, 138.94, 139.19, 145.43; ESIHRMS: Found: m/z 228.0577. Calcd for $C_{14}H_{11}ClN$: $(M\text{-}N_2+H)^+$ 228.0580.

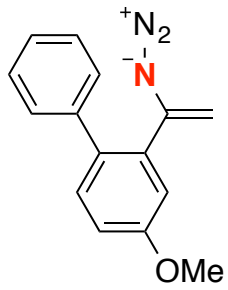
2'-(1-Azidovinyl)-[1,1'-biphenyl]-4-carbonitrile (1g):



The iodoazidation step led to a regioisomeric mixture of **II:II'** (ratio = 89:11), which could not be separated by column chromatography. Treatment of the regioisomeric mixture with *t*-BuOK gave two vinyl azides **1g** and **1g'** in 75% combined yield from biaryl alkene **Ig** after column chromatography (silica gel; hexane : EtOAc = 99 : 1). The pure vinyl azide **1g** could be partially obtained.

Pale yellow solid, mp 61-63 °C; IR (KBr) 3055, 2230, 2099, 1620, 1481, 1419, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.84 (1H, s), 4.97 (1H, s), 7.33 (1H, d, *J* = 7.6 Hz), 7.42-7.49 (3H, m), 7.56 (2H, d, *J* = 8.0 Hz), 7.70 (2H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 104.08, 111.22, 118.79, 128.53, 129.45, 129.62, 130.12, 130.17, 132.00, 133.82, 138.48, 145.11, 145.40; ESIHRMS: Found: m/z 219.0926. Calcd for $C_{15}H_{12}N_2$: $(M-N_2+H)^+$ 219.0922.

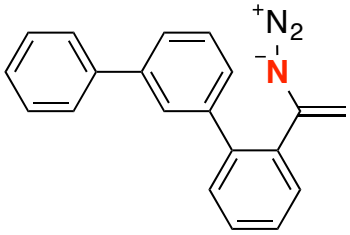
2-(1-Azidovinyl)-4-methoxy-1,1'-biphenyl (1h):



The iodoazidation step led to a regioisomeric mixture of **II:II'** (ratio = 97:3), which could not be separated by column chromatography. Treatment of the regioisomeric mixture with *t*-BuOK gave two vinyl azides **1h** and **1h'**. The pure vinyl azide **1h** was isolated by column chromatography (hexane : EtOAc = 99 : 1) in 80% yield from biaryl alkene **Ih**.

Pale yellow solid, mp 43-45 °C; IR (KBr) 3055, 2986, 2106, 1605, 1481, 1420, 1265 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (3H, s), 4.78 (1H, s), 4.93 (1H, s), 6.97-7.00 (2H, m), 7.28-7.43 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.42, 103.63, 114.83, 115.30, 126.99, 128.11, 128.83, 131.63, 133.03, 134.73, 140.23, 145.56, 158.70; ESIHRMS: Found: m/z 224.1067. Calcd for $C_{15}H_{14}NO$: $(M-N_2+H)^+$ 244.1075.

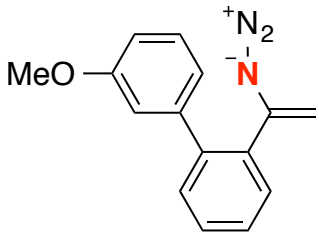
2-(1-Azidovinyl)-1,1':3',1''-terphenyl (1j):



The iodoazidation step led to a regioisomeric mixture of **II:II'** (ratio = 95:5), which could not be separated by column chromatography. Treatment of the regioisomeric mixture with t-BuOK gave two vinyl azides **1j** and **1j'** in 81% combined yield from biaryl alkene **Ij** after column chromatography (silica gel; hexane : EtOAc = 99 : 1). The pure vinyl azide **1j** could be partially obtained.

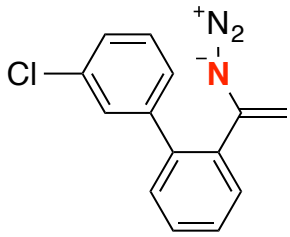
Pale yellow oil; IR (KBr) 3053, 2097, 1626, 1597, 1472, 1422, 1265 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.84 (1H, d, J = 0.8 Hz), 4.98 (1H, d, J = 0.8 Hz), 7.34-7.49 (9H, m), 7.59-7.64 (3H, m), 7.70 (1H, dd, J = 1.6, 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 103.75, 126.19, 127.18, 127.34, 127.54, 127.68 (overlapped), 128.60, 128.77, 129.43, 130.04, 130.43, 133.84, 140.45, 140.95, 141.00, 141,06, 145.72; ESIHRMS: Found: m/z 270.1288. Calcd for $C_{20}H_{16}N$: $(M-N_2+H)^+$ 270.1283.

2-(1-Azidovinyl)-3'-methoxy-1,1'-biphenyl (1k):



The iodoazidation led to a single regioisomer. Vinyl azide **1k** was isolated by column chromatography (silica gel, hexane : EtOAc = 94 : 6) in 82% yield from biaryl alkene **Ik**.
Pale yellow oil; IR (KBr) 3055, 2955, 2099, 1605, 1473, 1427, 1265 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (3H, s), 4.81 (1H, s), 4.95 (1H, s), 6.92 (1H, dd, *J* = 2.4, 8.0 Hz), 7.03 (1H, d, *J* = 2.4 Hz), 7.05 (1H, d, *J* = 8.0 Hz), 7.33 (1H, dd, *J* = 8.0, 8.0 Hz), 7.36-7.39 (2H, m), 7.43-7.47 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.23, 103.56, 113.01, 114.38, 121.28, 127.46, 129.14, 129.31, 129.95, 130.32, 133.76, 140.41, 141.91, 145.70, 159.30; ESIHRMS: Found: m/z 224.1076. Calcd for $C_{15}H_{14}NO$: $(M-N_2+H)^+$ 244.1075.

2-(1-Azidovinyl)-3'-chloro-1,1'-biphenyl (1l):

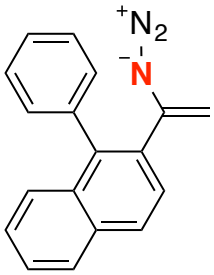


The iodoazidation step led to a regioisomeric mixture of **II:II'** (ratio = 94:6), which could not be separated by column chromatography. Treatment of the regioisomeric mixture with *t*-BuOK gave two vinyl azides **1l** and **1l'** in 56% combined yield from biaryl alkene **Il** after column chromatography (silica gel; hexane : EtOAc = 99 : 1). The pure vinyl azide **1l** could be partially obtained.

Pale yellow oil; IR (KBr) 3053, 2097, 1626, 1595, 1443, 1265 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.84 (1H, s), 4.98 (1H, s), 7.34-7.47 (8H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 103.89, 126.98,

127.45, 127.90, 128.76, 129.37, 129.42, 129.99, 130.27, 133.78, 133.99, 139.00, 142.37, 145.29; ESIHRMS: Found: m/z 228.0584. Calcd for $C_{14}H_{11}ClN$: $(M\text{-}N_2+H)^+$ 228.0580.

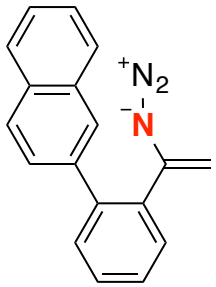
2-(1-Azidovinyl)-1-phenylnaphthalene (1m):



The iodoazidation led to a single regioisomer. Vinyl azide **1m** was isolated by column chromatography (silica gel; hexane : EtOAc = 99 : 1) in 89% yield from biaryl alkene **Im**.

Pale yellow oil; IR (KBr) 3055, 2106, 1628, 1497, 1442, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.65 (1H, s), 4.91 (1H, s), 7.35-7.38 (2H, m), 7.41 (1H, ddd, *J* = 1.2, 8.0, 8.4 Hz), 7.44-7.54 (5H, m), 7.60 (1H, d, *J* = 8.4 Hz), 7.89 (2H, d, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 104.33, 126.43, 126.48, 127.05, 127.53, 127.82, 127.89, 128.05, 130.33, 131.55, 132.41, 133.57, 138.00, 138.64, 145.10; ESIHRMS: Found: m/z 244.1123. Calcd for $C_{18}H_{14}N$: $(M\text{-}N_2+H)^+$ 244.1126.

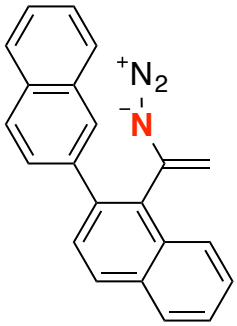
2-(2-(1-Azidovinyl)phenyl)naphthalene (1n):



The iodoazidation led to a single regioisomer. Vinyl azide **1n** was isolated by column chromatography (silica gel; hexane : EtOAc = 99 : 1) in 84% yield from biaryl alkene **In**.

Pale yellow oil; IR (KBr) 3055, 2099, 1628, 1498, 1396, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.86 (1H, s), 4.97 (1H, s), 7.42-7.45 (1H, m), 4.50-7.55 (5H, m), 7.62 (1H, dd, J = 1.6, 8.8 Hz), 7.88-7.96 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 103.79, 126.06, 126.16, 127.11, 127.50, 127.55, 127.61, 127.66, 128.14, 129.39, 129.98, 130.80, 132.56, 133.30, 133.94, 138.14, 140.41, 145.61; ESIHRMS: Found: m/z 244.1125. Calcd for $C_{18}H_{14}N$: $(M-N_2+H)^+$ 244.1126.

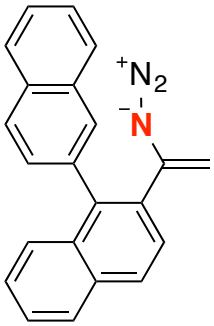
1-(1-Azidovinyl)-2,2'-binaphthalene (1o):



The iodoazidation led to a single regioisomer. Vinyl azide **1o** was isolated by column chromatography (silica gel; hexane : EtOAc = 99 : 1) in 78% yield from biaryl alkene **Io**.

Pale yellow solid, mp 95 °C decomposed; IR (KBr) 3055, 2091, 1628, 1504, 1419, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.71 (1H, s), 5.20 (1H, s), 7.54-7.66 (6H, m), 7.91-8.00 (6H, m), 8.22 (1H, d, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 106.51, 125.48, 126.13, 126.25, 126.28, 127.28, 127.52, 127.58, 127.70, 128.08, 128.16, 128.20, 128.23, 129.31, 130.49, 131.57, 132.51, 132.62, 133.16, 138.47, 139.15, 141.66; ESIHRMS: Found: m/z 294.1284. Calcd for $C_{22}H_{16}N$: $(M-N_2+H)^+$ 294.1283.

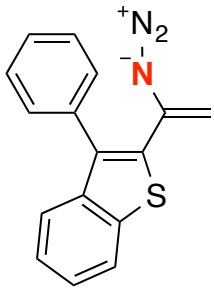
2-(1-Azidovinyl)-1,2'-binaphthalene (1p):



The iodoazidation led to a single regioisomer. Vinyl azide **1p** was isolated by column chromatography (silica gel; hexane : EtOAc = 99 : 1) in 79% yield from biaryl alkene **Ip**.

Pale yellow oil; IR (KBr) 3053, 2101, 1632, 1599, 1503, 1422, 1263 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.71 (1H, d, *J* = 1.2 Hz), 4.89 (1H, d, *J* = 1.2 Hz), 7.40 (1H, dd, *J* = 7.2, 8.4 Hz), 7.50-7.64 (6H, m), 7.86-7.98 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 104.47, 126.17, 126.25, 126.45, 126.47, 126.56, 127.12, 127.57, 127.80, 127.95, 128.11, 128.62, 129.24, 131.84, 132.58, 132.69, 133.15, 133.59, 135.60, 138.47, 144.98; ESIHRMS: Found: m/z 294.1290. Calcd for $C_{22}H_{16}N$: $(M-N_2+H)^+$ 294.1283.

2-(1-Azidovinyl)-3-phenylbenzo[*b*]thiophene (1q):

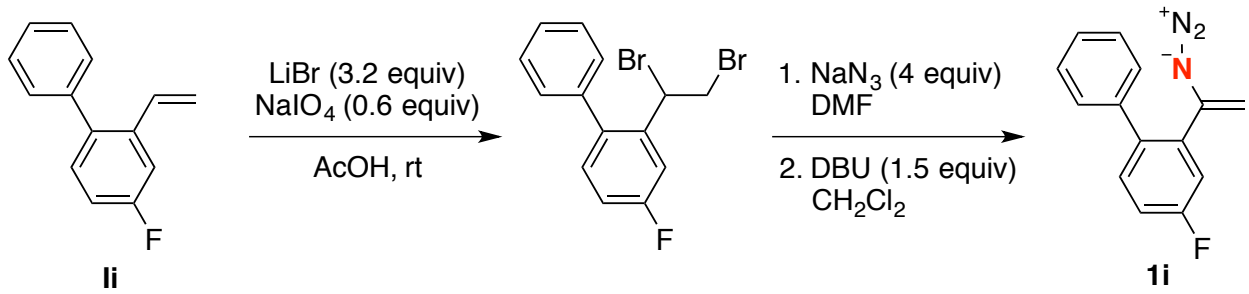


The iodoazidation led to a single regioisomer. Vinyl azide **1q** was isolated by column chromatography (silica gel; hexane : EtOAc = 99 : 1) in 66% yield from biaryl alkene **Iq**. This compound is not stable even at -20 °C and it should be used immediately after purification.

Pale yellow oil; IR (KBr) 3055, 2099, 1628, 1535, 1458, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.00 (1H, d, *J* = 2.0 Hz), 5.01 (1H, d, *J* = 2.0 Hz), 7.36 (1H, ddd, *J* = 1.2, 7.2, 7.6 Hz), 7.42 (1H, ddd, *J* = 1.2, 7.2, 7.6 Hz), 7.45-7.54 (5H, m), 7.56 (1H, d, *J* = 8.0 Hz), 7.88 (1H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 103.80, 122.11, 123.70, 124.63, 125.37, 127.96, 128.71, 129.70, 132.57, 134.92, 135.72, 138.54, 139.15, 140.25; ESIHRMS: Found: *m/z* 250.0683. Calcd for $C_{16}H_{12}NS$: $(M-N_2+H)^+$ 250.0690.

3.3 Synthesis of biaryl vinyl azides 1 by method B

A general procedure:



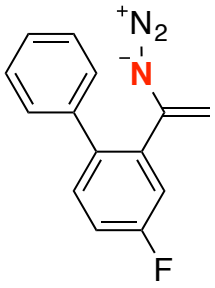
Ii **1i**

To solution of **Ii** (0.338 g, 1.71 mmol) in AcOH (4.0 mL) was added LiBr (0.326 g, 3.75 mmol) and $NaIO_4$ (0.109 mg, 0.512 mmol). The mixture was stirred at room temperature. After 2 h, a new batch of LiBr (0.150 g, 1.73 mmol) and $NaIO_4$ (0.109 mg, 0.512 mmol) were added and the mixture was stirred for additional 2 h at room temperature. The reaction was diluted with water. The aqueous phase was extracted with CH_2Cl_2 three times. The organic fractions were successively washed with saturated aqueous $Na_2S_2O_3$, saturated aqueous $NaHCO_3$ (two times) and brine. It was then dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane) to afford dibromide (0.449 g, 1.19 mmol).

To a solution of dibromide (0.449 g, 1.19 mmol) in DMF (4.0 mL) was added NaN_3 (0.307 g, 4.72 mmol) at 0 °C. The reaction was stirred from 0°C to room temperature for 18 h. Water was added and the aqueous phase was extracted with Et_2O three times. The organic fractions were washed with brine three times, dried over $MgSO_4$ and concentrated under reduced pressure. The resulting crude diazide was used for the next step without further purification.

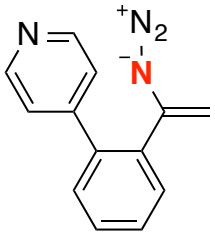
DBU (88.0 μL, 0.588 mmol) was added into a solution of the obtained crude diazide in CH_2Cl_2 (3.0 mL) at 0°C. After 1 h, water was added and the aqueous phase was extracted with CH_2Cl_2 three times. The organic fractions were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel; hexane : EtOAc = 98:2) to afford **1i** (0.264 g, 1.11 mmol) in 65% yield from biaryl alkene **Ii** as a pale yellow oil.

2-(1-Azidovinyl)-4-fluoro-1,1'-biphenyl (1i):



IR (KBr) 3063, 2104, 1607, 1584, 1476, 1260 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.82 (1H, d, *J* = 1.6 Hz), 4.96 (1H, d, *J* = 1.6 Hz), 7.14 (1H, ddd, *J* = 2.8, 7.6, 8.4 Hz), 7.17 (1H, dd, *J* = 2.8, 8.8 Hz), 7.33 (1H, dd, *J* = 5.6, 8.4 Hz), 7.35-7.42 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 104.17, 116.13 (d, *J* = 20.9 Hz), 116.68 (d, *J* = 22.3 Hz), 127.47, 128.24, 128.76, 132.16 (d, *J* = 8.0 Hz), 135.47 (d, *J* = 7.8 Hz), 136.66 (d, *J* = 3.3 Hz), 139.64, 144.62 (d, *J* = 1.8 Hz), 161.70 (d, *J* = 246.0 Hz); ESIHRMS: Found: m/z 212.0883. Calcd for $C_{14}H_{11}FN$: $(M-N_2+H)^+$ 212.0876.

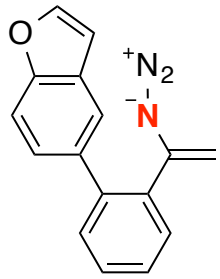
4-(2-(1-Azidovinyl)phenyl)pyridine (1q):



Vinyl azide **1q** was prepared in 60% yield by following the same procedure as **1i** from biaryl alkene **Iq**.

Pale yellow oil; IR (KBr) 3055, 2099, 1628, 1587, 1543, 1473, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.84 (1H, d, *J* = 1.6 Hz), 4.96 (1H, d, *J* = 1.6 Hz), 7.33-7.38 (3H, m), 7.40-7.49 (3H, m), 8.64 (2H, d, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 104.03, 123.54, 128.63, 129.58, 129.97, 130.11, 133.78, 137.64, 144.97, 148.46, 149.68; ESIHRMS: Found: *m/z* 223.0989. Calcd for $C_{13}H_{11}N_4$: $(M+H)^+$ 223.0984.

5-(2-(1-Azidovinyl)phenyl)benzofuran (1r):

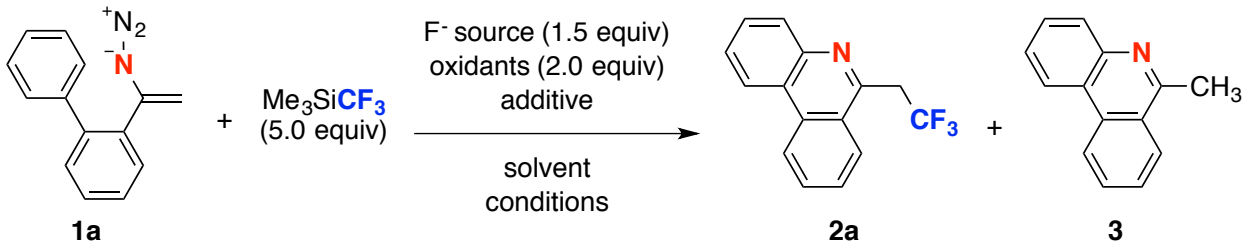


Vinyl azide **1r** was prepared in 62% yield by following the same procedure as **Ii** from biaryl alkene **Ir**.

Pale yellow oil; IR (KBr) 3055, 2099, 1628, 1535, 1458, 1265 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.79 (1H, d, J = 0.8 Hz), 4.93 (1H, d, J = 0.8 Hz), 6.80 (1H, dd, J = 0.8, 2.0 Hz), 7.35-7.46 (5H, m), 7.53 (1H, d, J = 8.8 Hz), 7.66-7.67 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 103.67, 106.78, 110.97, 121.31, 125.43, 127.21, 127.41, 129.32, 130.00, 130.85, 133.95, 135.39, 140.77, 145.42, 145.79, 154.42; ESIHRMS: Found: *m/z* 262.0981. Calcd for $C_{16}H_{13}N_3O$: $(M+H)^+$ 262.0980.

4. Optimization of the reaction conditions

Table S-1. Screening of other bases, oxidants, and solvents

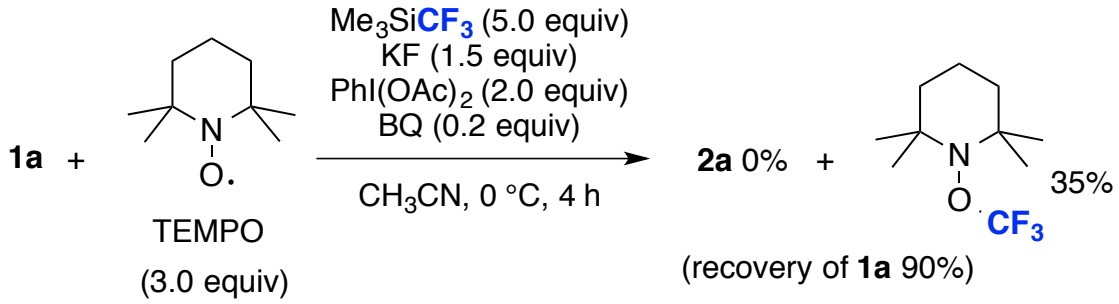


1a **2a** **3**

entry	F^- source	oxidants	additive [equiv]	solvents	conditions	yield of **2a** [%][a]	yield of **3** [%][a]
1	CsF	$PhI(OAc)_2$	--	CH_3CN	0 °C, 1 h	60	6
2	KF	$PhI(OAc)_2$	--	CH_3CN	0 °C, 2 h	50	11
3	CsF	$PhI(OAc)_2$	--	DMF	0 °C, 5 min	54	0
4	KF	$PhI(OAc)_2$	--	DMF	0 °C, 5 min	56	0
5	CsF	$PhI(OAc)_2$	--	DMSO	0 °C, 5 min	50	4
6	CsF	$PhI(OAc)_2$	--	NMP	0 °C, 3 h	48	0
7	NaOAc	$PhI(OAc)_2$	--	NMP	0 °C-rt, 45 min	45	12
8	K_3PO_4	$PhI(OAc)_2$	--	DMF	0 °C, 5 min	58	0
9	KF	$PhI(OAc)_2$	--	EtOAc	0 °C-rt, 5 h	65	17
10	KF	$PhI(OCOCF_3)_2$	--	EtOAc	0 °C-rt, 6 h	12	0
11	KF	$PhI(OCO^tBu)_2$	--	EtOAc	0 °C-rt, 3.5 h	25	0
12	KF	$PhI(OAc)_2$	--	^{t}BuCN	rt, 2 h	45	13
13	KF	$PhI(OAc)_2$	BQ (0.2)	EtOAc	0 °C-rt, 10 h	85 (78)[b]	0
14	KF	$PhI(OAc)_2$	BQ (0.2)	DMF	0 °C, 5 min	69	0
15	KF	$PhI(OAc)_2$	BQ (0.5)	DMF	0 °C, 5 min	73	0
16	KF	$PhI(OAc)_2$	BQ (0.2)	CH_3CN	0 °C, 2 h	91 (86)	0

[a] Yield was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. [b] Isolated yield by flash column chromatography.

5. Mechanistic experiment using TEMPO

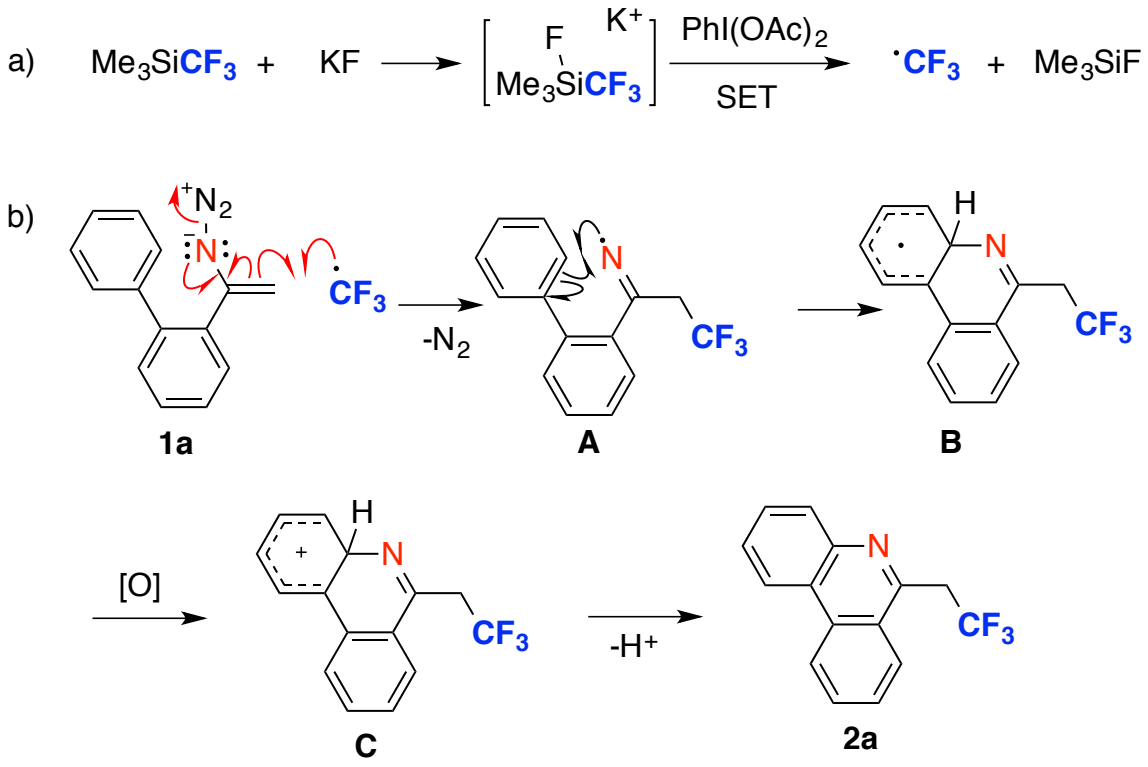


To a suspension of biaryl vinyl azide **1a** (127.2 mg, 0.575 mmol), TEMPO (269.5 mg, 1.725 mmol), KF (50.1 mg, 0.863 mmol), BQ (12.4 mg, 0.115 mmol) and $PhI(OAc)_2$ (370.4 mg, 1.15 mmol) in acetonitrile (5.8 mL) was added dropwise Me_3SiCF_3 (425 μL, 2.875 mmol) at 0 °C. The reaction mixture was stirred at the same temperature for 4 h. The reaction was quenched with water, the aqueous layer was extracted with EtOAc. The organic extracts were washed with brine and dried over $MgSO_4$, and evaporation. Analysis of the crude mixture by ^{19}F NMR using α,α,α-trifluorotoluene (20 μL, 0.163 mmol) as an internal standard showed that **2a** was not formed, while TEMPO-CF_3 was obtained in 35% yield based on TEMPO. At the same time, **1a** was recovered in 90% yield based on ^1H NMR analysis of the crude mixture using 1,1,2,2-tetrachloroethane as an internal standard.

This experiment suggested that the CF_3 radical is most likely involved in the reaction course.

6. A proposed mechanism for the formation of 2a

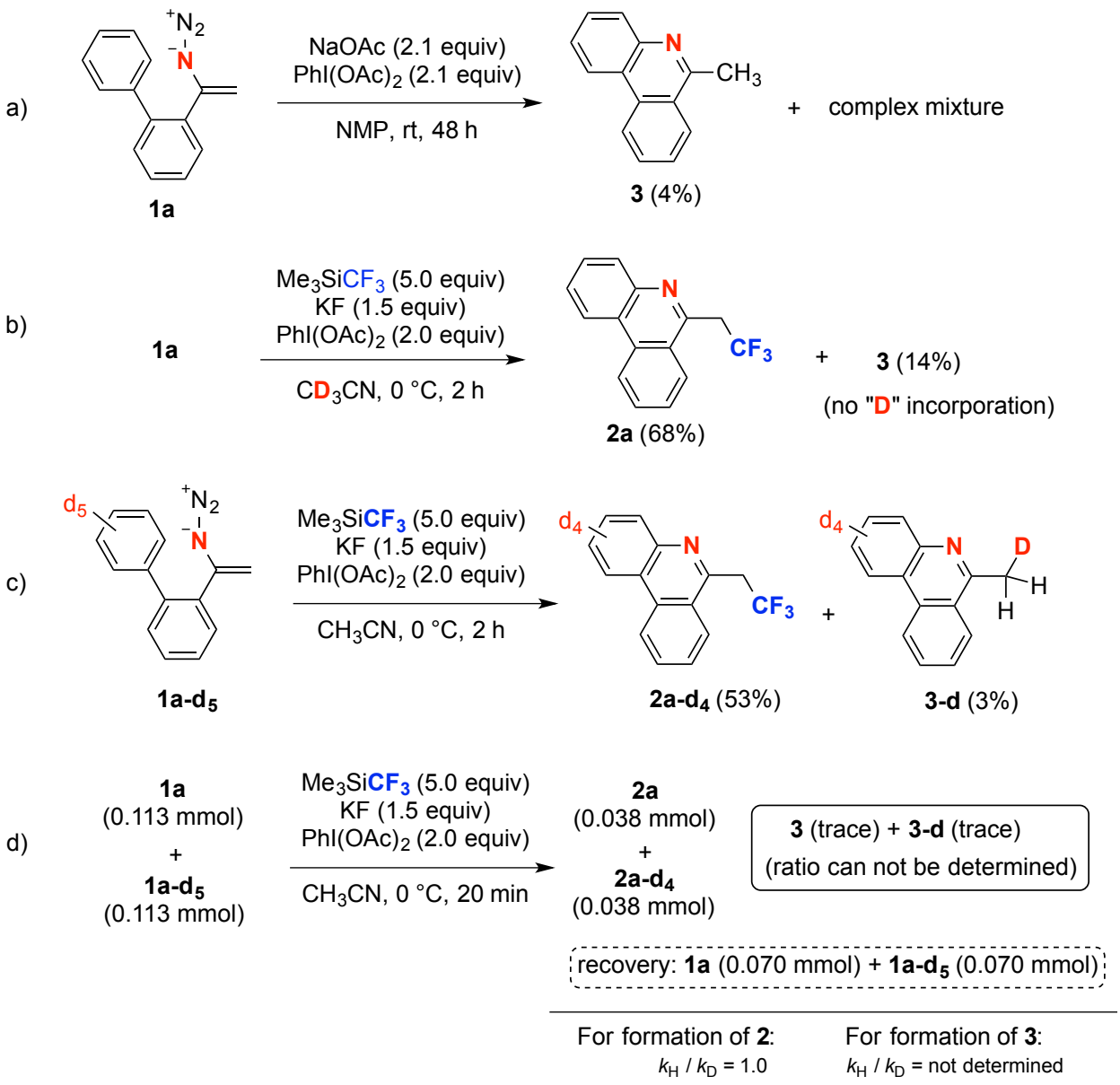
Based on the above mechanistic observation and our previous findings, a proposed reaction pathway for the formation of **2a** is outlined in the Scheme S-1. Initially, a silicate was formed through the interaction of Me_3SiCF_3 and KF.[7] Oxidation of this silicate by $PhI(OAc)_2$ through single-electron transfer (SET) generates the CF_3 radical (Eq. a).[8] Addition of the resulting CF_3 radical to the C=C bond of vinyl azide **1a** forms iminyl radical **A**, which undergoes intramolecular cyclization to the arene, giving cyclohexadienyl radical **B**. Single electron oxidation of **B**, followed by deprotonation yields the product **2a** (Eq. b).[9] Although the role of BQ in this reaction is not clear at this moment, especially how it works to depress the formation of side product **3**, we supposed that it may at least play an important role to accelerate the oxidation of cyclohexadienyl radical **B** to give **C**, thereby decreasing the degradation of **B**.



Scheme S-1. A proposed mechanism for 2a

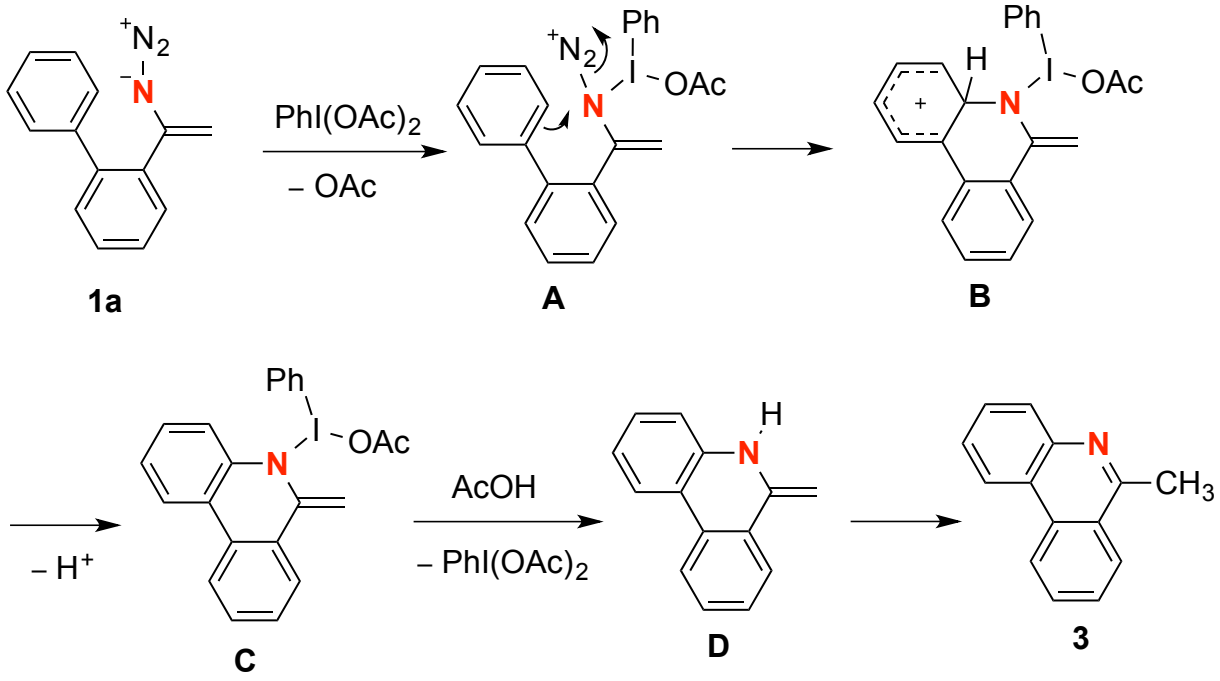
7. Mechanistic studies for the formation of phenanthridine 3

In order to gain more insight into the mechanism of the formation of 6-methylphenanthridine (**3**), a series of mechanistic studies have been carried out as demonstrated in Scheme S-2. As shown in Scheme S-2-a, compound **3** was also formed by treating vinyl azide **1a** with $PhI(OAc)_2$ in the absence of Me_3SiCF_3, albeit in only 4% yield. This indicates that the formation of **3** is independent from the radical trifluoromethylation process. Moreover, when CD_3CN was utilized as the solvent, no deuterium incorporation was observed (Scheme S-2-b). Notably, the reaction of deuterated vinyl azide **1a-d$_5$** led to the formation of **3-d** in 3% yield (Scheme S-2-c; the yield of **3-d** was determined by analysis of ^{1}H NMR spectra of crude reaction mixture using 1,1,2,2-tetrachloroethane as an internal standard. The structure of this compound was further confirmed by ^{1}H NMR and ESIHRMS.). This result demonstrates that an ionic deuterium transfer process may occur in this reaction system. Eventually, an examination of intermolecular kinetic isotopic effect was attempted (Scheme S-2-d). A mixture of **1a** and **1a-d$_5$** (1:1) was subjected into the standard reaction conditions and the reaction was quenched in 20 min. However, only a trace amount of products **3** and **3-d** were detected, which is not viable for the determination of KIE. On the other hand, the KIE for the formation of **2** is 1.0. Further studies to clarify the mechanism for the formation of **3** are in progress.



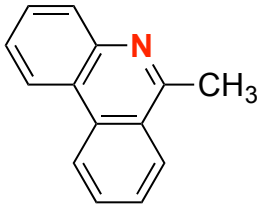
Scheme S-2. Mechanistic studies for the formation of 3

Based on these observations, a possible mechanism to rationalize the formation of **3** is depicted in Scheme S-3. Initially, vinyl azide **1a** reacts with $PhI(OAc)_2$ to generate intermediate **A**. The subsequent intramolecular electrophilic aromatic substitution occurs to form the key intermediate **C** with the release of dinitrogen and a proton. Protonation of intermediate **C** would give enamine type intermediate **D**, which tautomerizes to product **3**.

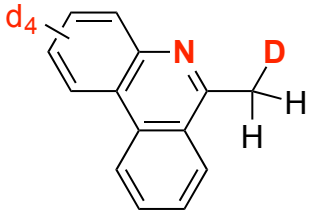


Scheme S-3 A proposed mechanism the formation of 3

6-Methylphenanthridine (3):[10]

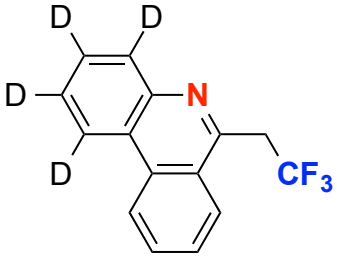


^{1}H NMR (400 MHz, $CDCl_3$) δ 3.06 (3H, s), 7.63 (1H, ddd, *J* = 1.2, 7.2, 8.0 Hz), 7.69-7.74 (2H, m), 7.85 (1H, ddd, *J* = 0.8, 7.2, 8.0 Hz), 8.11 (1H, d, *J* = 8.0 Hz), 8.23 (1H, dd, *J* = 8.0 Hz), 8.55 (1H, d, *J* = 8.0 Hz), 8.64 (1H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.38, 121.94, 122.32, 123.78, 125.92, 126.32, 126.55, 127.30, 128.63, 129.35, 130.49, 132.58, 143.68, 158.87.



^{1}H NMR (400 MHz, $CDCl_3$) δ 3.04-3.06 (2H, m), 7.71 (1H, dd, *J* = 7.2, 8.0 Hz), 7.86 (1H, dd, *J* = 7.2, 8.0 Hz), 8.23 (1H, d, *J* = 8.0 Hz), 8.55 (1H, d, *J* = 8.0 Hz), 8.64 (1H, d, *J* = 8.0 Hz); ESIHRMS: Found: m/z 199.1288. Calcd for $C_{14}{}^1H_7{}^2H_5N$: $(M+H)^+$ 199.1284.

1,2,3,4-Tetradeutero-6-(2,2,2-Trifluoroethyl)phenanthridine (2a-d_4):

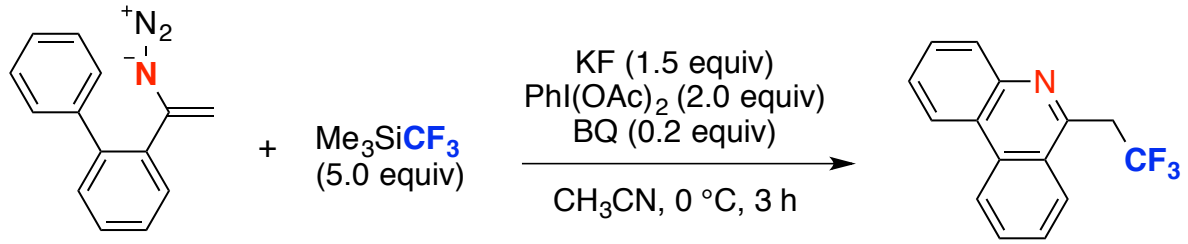


White solid; mp 50-52 °C; IR (KBr) 3078, 2954, 2268, 1612, 1566, 1512, 1435, 1373, 1249 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (2H, q, *J* = 10.4 Hz), 7.74 (1H, ddd, *J* = 0.8, 7.2, 8.0 Hz), 7.88 (1H, ddd, *J* = 1.2, 7.2, 8.0 Hz), 8.21 (1H, d, *J* = 8.0 Hz), 8.68 (1H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.54 (q, *J* = 29.0 Hz), 121.58 (t, *J* = 24.1 Hz), 122.56, 124.00, 125.54, 125.63 (q, *J* = 276.4 Hz), 126.23, 127.01 (t, *J* = 24.0 Hz), 127.60, 128.40 (t, *J* = 24.0 Hz), 129.77 (t, *J* = 24.8 Hz), 130.78, 133.23, 143.42, 151.12 (q, *J* = 3.4 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -

62.5 (t, J = 10.4 Hz); ESIHRMS: Found: m/z 266.1089. Calcd for $C_{15}{}^{1}H_{7}{}^{2}H_{4}F_{3}N$: $(M+H)^{+}$ 266.1095.

8. Synthesis of polyfluoroalkyl aza-polycyclic aromatic hydrocarbons

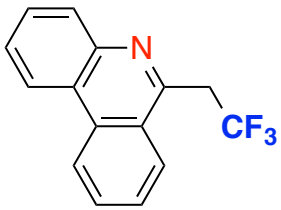
Typical procedure:



1a **2a**

To a suspension of vinyl azide **1a** (73.6 mg, 0.333 mmol), KF (29.0 mg, 0.499 mmol), *p*-benzoquinone (7.2 mg, 0.067 mmol), and $PhI(OAc)_2$ (0.214 g, 0.665 mmol) in CH_3CN (3.3 mL) was added dropwise Me_3SiCF_3 (246 μL, 1.663 mmol) at 0 °C. The reaction mixture was stirred for 3 h at the same temperature, which was then quenched by adding saturated aqueous $Na_2S_2O_3$. The aqueous layer was extracted with EtOAc. The organic extracts were washed with brine and dried over $MgSO_4$. After removal of solvents under reduced pressure, the crude product was purified by flash column chromatography (silica gel, hexane : EtOAc = 94 : 6) to afford **2a** (74.9 mg, 0.287 mmol) in 86% yield as a white solid.

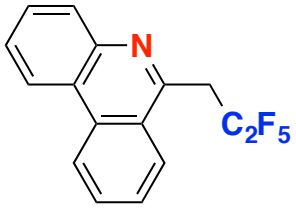
6-(2,2,2-Trifluoroethyl)phenanthridine (2a):



White solid, mp 96-98 °C; IR (KBr) 3071, 2988, 1614, 1574, 1528, 1489, 1369, 1263 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.21 (2H, q, J = 10.4 Hz), 7.69-7.79 (3H, m), 7.87 (1H, ddd, J = 1.2, 7.2, 8.0 Hz), 8.18-8.21 (2H, m), 8.60 (1H, dd, J = 1.2, 8.4 Hz), 8.69 (1H, d, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.51 (q, J = 29.0 Hz), 121.95, 122.51, 124.03, 125.50, 125.61 (q, J = 276.4 Hz), 126.20, 127.50, 127.59, 128.88, 130.16, 130.76, 133.19, 143.43, 151.12 (q, J = 3.4

Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -62.5 (t, J = 10.3 Hz); ESIHRMS: Found: m/z 262.0838. Calcd for $C_{15}H_{11}F_3N$: $(M+H)^+$ 262.0844.

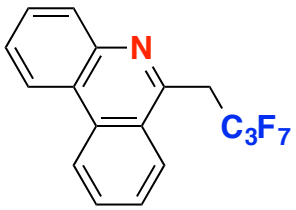
6-Pentafluoroethylmethylenephenanthridine (4):



This product was prepared in 72% yield by following the same procedure as **2a** from vinyl azide **1a** and $Me_3SiC_2F_5$.

Yield: 72%; white solid, mp 105-106 °C; IR (KBr) 3075, 2953, 1614, 1582, 1528, 1487, 1358, 1207 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.16 (2H, t, J = 17.6 Hz), 7.69-7.79 (3H, m), 7.89 (1H, ddd, J = 1.2, 7.6, 8.0 Hz), 8.16-8.21 (2H, m), 8.59 (1H, dd, J = 1.2, 8.0 Hz), 8.69 (1H, d, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) $\underline{C}F_2\underline{C}F_3$-signals are not assigned, δ 37.18 (t, J = 21.4 Hz), 121.99, 122.49, 124.06, 126.01, 126.35 (t, J = 2.0 Hz), 127.56, 127.62, 128.91, 130.19, 130.79, 133.19, 143.47, 150.77; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -114.4 (2F, t, J = 17.7 Hz), -85.0 (3F, s); LC-MS: Found: m/z 312.0811. Calcd for $C_{16}H_{11}F_5N$: $(M+H)^+$ 312.0812.

6-Heptafluoropropylmethylenephenanthridine (5):

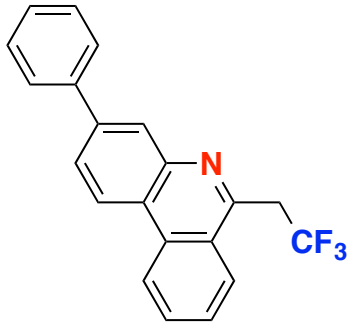


This product was prepared in 80% yield by following the same procedure as **2a** from vinyl azide **1a** and $Me_3SiC_3F_7$.

White solid, mp 84-85 °C; IR (KBr) 3067, 2965, 1613, 1576, 1528, 1487, 1350, 1215 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.20 (2H, t, J = 18.4 Hz), 7.69-7.79 (3H, m), 7.90 (1H, ddd, J = 0.8, 7.2, 8.0 Hz), 8.16 (1H, d, J = 8.0 Hz), 8.20 (1H, dd, J = 0.8, 8.0 Hz), 8.61 (1H, d, J = 8.0 Hz), 8.70 (1H, d, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) $\underline{C}F_2\underline{C}F_2\underline{C}F_3$ signals are not assigned, δ

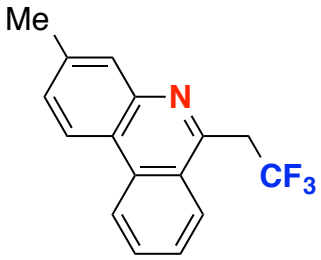
36.95 (t, J = 21.3 Hz), 121.99, 122.50, 124.08, 126.17, 126.35 (t, J = 2.5 Hz), 127.57, 127.63, 128.92, 130.22, 130.78, 133.23, 143.53, 150.70; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -127.07 (2F, brm), -111.67 (2F, brm), -80.18 (3F, t, J = 10.2 Hz); ESIHRMS: Found: m/z 362.0781. Calcd for $C_{17}H_{11}F_7N$: $(M+H)^+$ 362.0780.

3-Phenyl-6-(2,2,2-trifluoroethyl)phenanthridine (2b):



Yield: 63%; white solid, mp 165-166 °C; IR (KBr) 3063, 2955, 1612, 1566, 1481, 1366, 1250 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (2H, q, J = 10.4 Hz), 7.42 (1H, t, J = 7.2 Hz), 7.52 (2H, dd, J = 7.2, 8.0 Hz), 7.72 (1H, dd, J = 7.2, 8.0 Hz), 7.81 (2H, d, J = 8.0 Hz), 7.86 (1H, dd, J = 7.2, 8.0 Hz), 7.94 (1H, dd, J = 2.0, 8.4 Hz), 8.20 (1H, d, J = 8.4 Hz), 8.44 (1H, d, J = 2.0 Hz), 8.58 (1H, d, J = 8.4 Hz), 8.63 (1H, d, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.52 (q, J = 29.0 Hz), 122.48, 122.52, 123.02, 125.45, 125.62 (q, J = 276.4 Hz), 126.23, 126.59, 127.31, 127.54, 127.80, 127.93, 128.96, 130.85, 133.04, 139.99, 141.60, 143.77, 151.58 (q, J = 3.3 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -62.4 (t, J = 10.5 Hz); ESIHRMS: Found: m/z 338.1159. Calcd for $C_{21}H_{15}F_3N$: $(M+H)^+$ 338.1157.

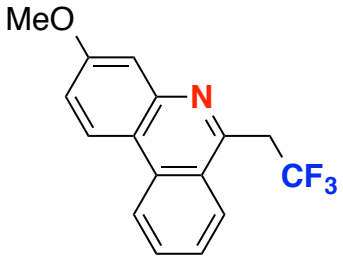
3-Methyl-6-(2,2,2-trifluoroethyl)phenanthridine (2c):



Yield: 82%; white solid, mp 126-127 °C; IR (KBr) 3070, 2962, 1620, 1574, 1489, 1350, 1242 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.60 (3H, s), 4.20 (2H, q, J = 10.4 Hz), 7.53 (1H, dd, J = 1.6,

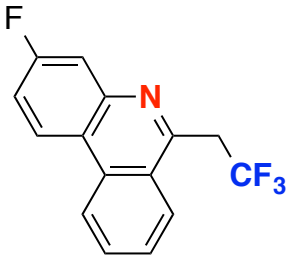
8.0 Hz), 7.71 (1H, ddd, J = 0.8, 7.2, 8.0 Hz), 7.86 (1H, ddd, J = 0.8, 7.2, 8.0 Hz), 7.99 (1H, s), 8.19 (1H, d, J = 8.4 Hz), 8.47 (1H, d, J = 8.4 Hz), 8.64 (1H, d, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.50, 40.50 (q, J = 29.0 Hz), 121.72, 121.76, 122.35, 125.22, 125.63 (q, J = 276.4 Hz), 126.20, 127.12, 129.28, 129.68, 130.71, 133.28, 139.15, 143.58, 151.09 (q, J = 3.3 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -62.5 (t, J = 10.4 Hz); ESIHRMS: Found: *m/z* 276.1004. Calcd for $C_{16}H_{14}F_3N$: $(M+H)^+$ 276.1000.

3-Methoxy-6-(2,2,2-trifluoroethyl)phenanthridine (2d):



Yield: 84%; white solid, mp 139-140 °C; IR (KBr) 3013, 2943, 1616, 1570, 1487, 1371, 1263 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.98 (3H, s), 4.17 (2H, q, J = 10.4 Hz), 7.29 (1H, dd, J = 2.8, 8.8 Hz), 7.56 (1H, d, J = 2.8 Hz), 7.63 (1H, ddd, J = 1.2, 7.2, 8.0 Hz), 7.80 (1H, ddd, J = 1.2, 7.2, 8.4 Hz), 8.14 (1H, d, J = 8.4 Hz), 8.40 (1H, d, J = 8.8 Hz), 8.51 (1H, d, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.45 (q, J = 28.9 Hz), 55.57, 109.64, 118.07, 118.77, 121.97, 123.12, 124.55, 125.60 (q, J = 276.4 Hz), 126.15, 126.45, 130.77, 133.37, 145.02, 151.49 (q, J = 3.2 Hz), 160.24; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -62.5 (t, J = 10.3 Hz); ESIHRMS: Found: m/z 292.0945. Calcd for $C_{16}H_{13}F_3NO$: $(M+H)^+$ 292.0949.

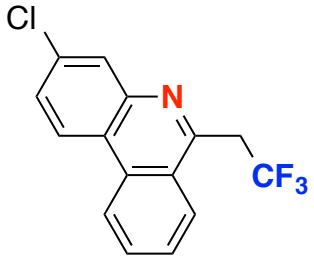
3-Fluoro-6-(2,2,2-trifluoroethyl)phenanthridine (2e):



Yield: 79%; pale yellow solid, mp 120-122 °C; IR (KBr) 3053, 2961, 1616, 1584, 1489, 1373, 1261 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.19 (2H, q, J = 10.4 Hz), 7.42 (1H, ddd, J = 2.8, 8.4, 8.4 Hz), 7.72 (1H, dd, J = 7.2, 8.0 Hz), 7.81 (1H, dd, J = 2.8, 9.2 Hz), 7.86 (1H, dd, J = 7.2, 8.0

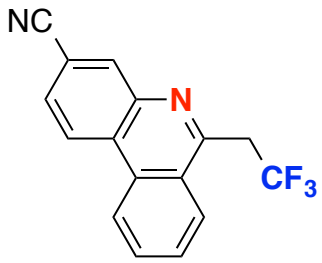
Hz), 8.18 (1H, d, J = 8.4 Hz), 8.50 (1H, dd, J = 6.0, 9.2 Hz), 8.55 (1H, d, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.43 (q, J = 29.1 Hz), 114.62 (d, J = 20.4 Hz), 116.60 (d, J = 23.7 Hz), 120.69 (d, J = 2.0 Hz), 122.28, 123.90 (d, J = 9.4 Hz), 125.03, 125.49 (q, J = 276.5 Hz), 126.29, 127.44, 131.14, 132.94, 144.61 (d, J = 11.8 Hz), 152.52 (q, J = 3.4 Hz), 162.66 (d, J = 247.1 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -111.64 (1F, m), -62.4 (3F, t, J = 10.2 Hz); ESIHRMS: Found: m/z 280.0751. Calcd for $C_{15}H_{10}F_4N$: $(M+H)^+$ 280.0749.

3-Chloro-6-(2,2,2-trifluoroethyl)phenanthridine (2f):



Yield: 71%; white solid, mp 123-124 °C; IR (KBr) 3076, 2963, 1603, 1582, 1570, 1479, 1371, 1271 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.17 (2H, q, J = 10.4 Hz), 7.58 (1H, dd, J = 1.6, 8.4 Hz), 7.73 (1H, dd, J = 7.6, 7.6 Hz), 7.85 (1H, dd, J = 7.6, 7.6 Hz), 8.14 (1H, d, J = 1.6 Hz), 8.17 (1H, d, J = 8.4 Hz), 8.40 (1H, d, J = 8.4 Hz), 8.53 (1H, d, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.40 (q, J = 29.1 Hz), 122.38, 122.41, 123.26, 125.33, 125.46 (q, J = 276.4 Hz), 126.26, 127.87, 127.98, 129.33, 131.15, 132.68, 134.51, 143.95, 152.42 (q, J = 3.2 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -62.4 (t, J = 10.3 Hz); ESIHRMS: Found: m/z 296.0453. Calcd for $C_{15}H_{10}ClF_3N$: $(M+H)^+$ 296.0454.

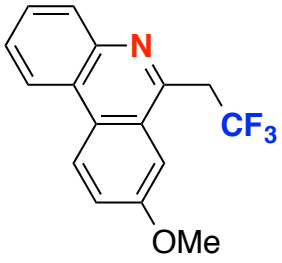
6-(2,2,2-Trifluoroethyl)phenanthridine-3-carbonitrile (2g):



Yield: 70%; white solid, mp 204-205 °C; IR (KBr) 3062, 2939, 2222, 1612, 1589, 1528, 1489, 1396, 1258 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23 (2H, q, J = 10.4 Hz), 7.84-7.89 (2H, m), 7.98 (1H, ddd, J = 1.2, 7.2, 8.4 Hz), 8.26 (1H, d, J = 8.4 Hz), 8.50 (1H, d, J = 1.2 Hz), 8.64 (1H,

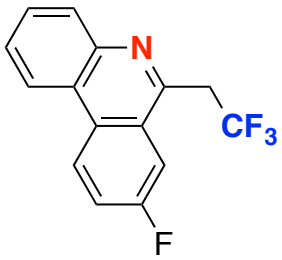
d, J = 8.4 Hz), 8.68 (1H, d, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.45 (q, J = 29.3 Hz), 112.25, 118.42, 123.07, 123.37, 125.31 (q, J = 276.4 Hz), 126.25, 126.52, 127.18, 128.92, 129.41, 131.65, 132.08, 135.26, 142.64, 153.42 (q, J = 3.4 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -62.4 (t, J = 10.1 Hz); ESIHRMS: Found: *m/z* 287.0800. Calcd for $C_{16}H_{10}F_3N_2$: $(M+H)^+$ 287.0796.

8-Methoxy-6-(2,2,2-trifluoroethyl)phenanthridine (2h):



Yield: 80%; white solid, mp 142-143 °C; IR (KBr) 3063, 2954, 1620, 1573, 1528, 1465, 1351, 1258 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.99 (3H, s), 4.17 (2H, q, J = 10.4 Hz), 7.47-7.50 (2H, m), 7.65 (1H, ddd, J = 0.8, 7.6, 8.0 Hz), 7.69 (H, ddd, J = 0.8, 7.6, 8.0 Hz), 8.16 (1H, dd, J = 0.8, 8.4 Hz), 8.46 (1H, d, J = 7.6 Hz), 8.55 (1H, d, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.76 (q, J = 29.0 Hz), 55.53, 106.45, 121.25, 121.45, 124.12, 124.15, 125.70 (q, J = 276.6 Hz), 126.80, 127.55 (overlapped), 127.88, 130.07, 142.60, 150.19 (q, J = 3.4 Hz), 158.79; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -62.3 (t, J = 10.4 Hz); ESIHRMS: Found: *m/z* 292.0943. Calcd for $C_{16}H_{13}F_3NO$: $(M+H)^+$ 292.0949.

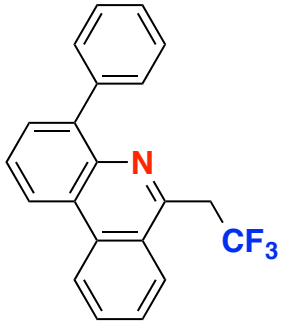
8-Fluoro-6-(2,2,2-trifluoroethyl)phenanthridine (2i):



Yield: 76%; white solid, mp 130-131 °C; IR (KBr) 3069, 3034, 1626, 1574, 1537, 1483, 1354, 1269 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.13 (2H, q, J = 10.4 Hz), 7.58 (1H, ddd, J = 2.4, 8.0, 10.4 Hz), 7.67 (1H, ddd, J = 1.2, 7.2, 8.4 Hz), 7.73 (1H, ddd, J = 1.2, 7.2, 8.4 Hz), 8.17 (1H, dd, J = 1.2, 8.0 Hz), 8.17 (1H, dd, J = 1.2, 8.0 Hz), 8.45 (1H, dd, J = 1.2, 8.0 Hz), 8.59 (1H, dd, J = 5.2, 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.58 (q, J = 29.1 Hz), 110.79 (d, J = 21.8 Hz),

119.99 (d, J = 23.7 Hz), 121.66, 123.50, 125.07 (d, J = 8.5 Hz), 125.45 (q, J = 276.4 Hz), 126.66 (d, J = 7.7 Hz), 127.91, 128.76, 129.83 (d, J = 1.8 Hz), 130.27, 143.06, 150.18 (qd, J = 3.5, 3.6 Hz), 161.42 (d, J = 247.4 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -111.20 (1F, brm), -62.5 (3F, t, J = 10.2 Hz); ESIHRMS: Found: m/z 280.0752. Calcd for $C_{15}H_{10}F_4N$: $(M+H)^+$ 280.0749.

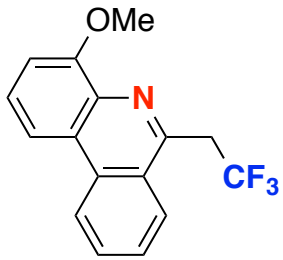
4-Phenyl-6-(2,2,2-trifluoroethyl)phenanthridine (2j):



A mixture of two unseparable regioisomers was isolated in 64% combined yield (ratio = 3.0:1) by column chromatography (silica gel, hexane : EtOAc = 94 : 6). NMR data stated below are for major regioisomer **2j**, obtained by recrystallization from CH_2Cl_2/hexane.

White solid, mp 164-165 °C; IR (KBr) 3069, 2967, 1611, 1578, 1526, 1466, 1371, 1258 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.13 (2H, q, J = 10.4 Hz), 7.45 (1H, tt, J = 2.0, 7.2 Hz), 7.53 (2H, dd, J = 7.2, 8.0 Hz), 7.73-7.82 (4H, m), 7.84 (1H, dd, J = 1.6, 7.2 Hz), 7.89 (1H, ddd, J = 1.2, 7.2, 8.0 Hz), 8.19 (1H, d, J = 8.4 Hz), 8.61 (1H, dd, J = 1.2, 8.0 Hz), 8.73 (1H, d, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.10 (q, J = 28.8 Hz), 121.37, 122.84, 124.36, 125.22, 125.83 (q, J = 276.4 Hz), 125.84, 127.11, 127.20, 127.60, 127.64, 130.06, 130.60, 131.18, 133.38, 139.51, 140.61, 141.41, 150.29 (q, J = 3.2 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -62.5 (t, J = 10.3 Hz); ESIHRMS: Found: m/z 338.1159. Calcd for $C_{21}H_{15}F_3N$: $(M+H)^+$ 338.1157.

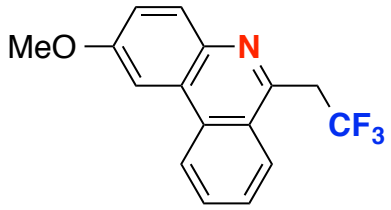
4-Methoxy-6-(2,2,2-trifluoroethyl)phenanthridine (2k):



Two regioisomers (**2k** : **2k'** = 5.7 : 1, combined yield: 83%) could be separated by column chromatography (hexane : EtOAc = 95 : 5).

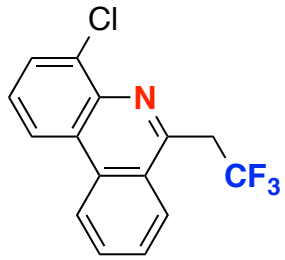
2k: Yield: 71%; white solid, mp 182-183 °C; IR (KBr) 3070, 2940, 1605, 1574, 1528, 1474, 1366, 1258 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.13 (3H, s), 4.31 (2H, q, *J* = 10.4 Hz), 7.18 (1H, d, *J* = 8.0 Hz), 7.62 (1H, dd, *J* = 8.0, 8.4 Hz), 7.74 (1H, ddd, *J* = 1.2, 7.2, 8.0 Hz), 7.87 (1H, ddd, *J* = 1.2, 7.2, 8.0 Hz), 8.16 (1H, d, *J* = 8.4 Hz), 8.23 (1H, d, *J* = 8.4 Hz), 8.66 (1H, d, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.71 (q, *J* = 29.0 Hz), 56.51, 108.90, 113.89, 123.04, 125.42, 125.65 (q, *J* = 276.6 Hz), 125.68, 126.29, 127.70, 127.79, 130.68, 133.18, 134.67, 149.80 (q, *J* = 3.5 Hz), 156.12; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -62.3 (t, *J* = 10.4 Hz); ESIHRMS: Found: *m/z* 292.0954. Calcd for $C_{16}H_{13}F_3NO$: $(M+H)^+$ 292.0949.

2-Methoxy-6-(2,2,2-trifluoroethyl)phenanthridine (2k'):



Yield: 12%; white solid, mp 128-129 °C; IR (KBr) 3062, 2939, 1605, 1574, 1528, 1474, 1366, 1258 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.03 (3H, s), 4.18 (2H, q, *J* = 10.4 Hz), 7.39 (1H, dd, *J* = 2.8, 8.8 Hz), 7.74 (1H, dd, *J* = 7.6, 7.6 Hz), 7.86 (1H, dd, *J* = 7.6, 7.6 Hz), 7.91 (1H, d, *J* = 2.8 Hz), 8.11 (1H, d, *J* = 8.8 Hz), 8.19 (1H, d, *J* = 8.0 Hz), 8.61 (1H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.35 (q, *J* = 29.0 Hz), 55.69, 102.81, 118.86, 122.55, 125.22, 125.66, 125.70 (q, *J* = 276.4 Hz), 126.23, 127.67, 130.33, 131.60, 132.72, 138.82, 148.40 (q, *J* = 3.4 Hz), 158.87; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -62.7 (t, *J* = 10.4 Hz); ESIHRMS: Found: *m/z* 292.0941. Calcd for $C_{16}H_{13}F_3NO$: $(M+H)^+$ 292.0949.

4-Chloro-6-(2,2,2-trifluoroethyl)phenanthridine (2l):

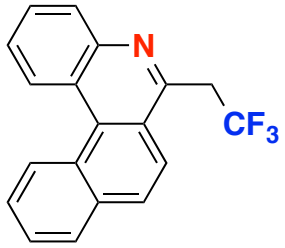


A mixture of two unseparable regioisomers was isolated in 75% combined yield (ratio = 3.3:1) by column chromatography. NMR data stated below are for major regioisomer **2l**, obtained by recrystallization from CH_2Cl_2/hexane.

White solid, mp 132-133 °C; IR (KBr) 3078, 2960, 1611, 1584, 1524, 1460, 1371, 1267 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.26 (2H, q, *J* = 10.4 Hz), 7.57 (1H, dd, *J* = 8.0, 8.0 Hz), 7.76 (1H, ddd, *J* = 1.2, 7.2, 8.0 Hz), 7.84 (1H, dd, *J* = 1.2, 8.0 Hz), 7.88 (1H, ddd, *J* = 1.2, 7.2, 8.0 Hz), 8.22 (1H, d, *J* = 8.4 Hz), 8.45 (1H, dd, *J* = 1.2, 8.4 Hz), 8.62 (1H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.49 (q, *J* = 29.0 Hz), 120.79, 122.81, 125.49 (q, *J* = 276.4 Hz), 125.51, 125.67, 126.23, 127.31, 128.20, 129.27, 131.10, 132.97, 134.68, 139.73, 151.80 (q, *J* = 3.3 Hz); ^{19}F

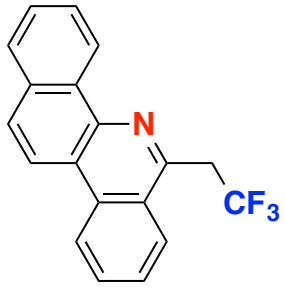
NMR ($CDCl_3$, 376 MHz) δ -62.4 (t, J = 10.2 Hz); ESIHRMS: Found: m/z 296.0460. Calcd for $C_{15}H_{10}ClF_3N$: $(M+H)^+$ 296.0454.

6-(2,2,2-Trifluoroethyl)benzo[k]phenanthridine (2m):



Yield: 68%; white solid, mp 171-172 °C; IR (KBr) 3055, 2962, 1605, 1566, 1481, 1366, 1249 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.28 (2H, q, J = 10.4 Hz), 7.69-7.76 (3H, m), 7.80 (1H, ddd, J = 1.2, 7.2, 8.0 Hz), 7.99 (1H, d, J = 8.8 Hz), 8.03-8.07 (2H, m), 8.31 (1H, dd, J = 1.2, 8.4 Hz), 8.97 (1H, d, J = 8.4 Hz), 9.07-9.10 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.74 (q, J = 29.0 Hz), 122.18, 124.22, 125.72 (q, J = 276.5 Hz), 126.99, 127.02, 127.07, 128.08, 128.50, 128.53, 128.58, 128.61, 128.97, 130.01, 132.52, 134.57, 145.42, 150.08 (q, J = 3.3 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -62.5 (t, J = 10.2 Hz); ESIHRMS: Found: m/z 312.1004. Calcd for $C_{19}H_{13}F_3N$: $(M+H)^+$ 312.1000.

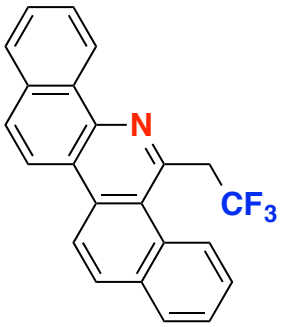
6-(2,2,2-Trifluoroethyl)benzo[c]phenanthridine (2n):



Yield: 67%; white solid, mp 171-172 °C; IR (KBr) 3063, 2924, 1612, 1566, 1512, 1435, 1373, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.32 (2H, q, J = 10.4 Hz), 7.70 (1H, dd, J = 7.6, 8.4 Hz), 7.74 (1H, dd, J = 7.6, 8.4 Hz), 7.78 (1H, dd, J = 7.6, 7.6 Hz), 7.89 (1H, dd, J = 7.6, 7.6 Hz), 7.97 (1H, d, J = 8.0 Hz), 8.02 (1H, d, J = 9.2 Hz), 8.25 (1H, d, J = 8.4 Hz), 8.51 (1H, d, J = 9.2 Hz), 8.71 (1H, d, J = 8.4 Hz), 9.45 (1H, d, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.33 (q, J = 28.8 Hz), 119.55, 120.91, 122.92, 124.96, 125.82 (q, J = 276.5 Hz), 125.84 (overlapped),

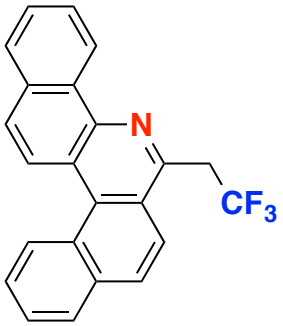
127.09, 127.27, 127.51 (overlapped), 128.23, 130.47, 131.89, 133.24, 133.40, 140.30, 149.52 (q, J = 3.3 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -62.5 (t, J = 10.2 Hz); ESIHRMS: Found: *m/z* 312.0998. Calcd for $C_{19}H_{13}F_3N$: $(M+H)^+$ 312.1000.

14-(2,2,2-trifluoroethyl)dibenzo[c,i]phenanthridine (2o):



Yield: 61%; white solid, mp 170-171 °C; IR (KBr) 3048, 2962, 1612, 1566, 1512, 1443, 1350, 1242 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.63 (2H, q, J = 10.0 Hz), 7.67-7.82 (4H, m), 7.95 (1H, d, J = 7.2 Hz), 7.96 (1H, d, J = 8.8 Hz), 8.00 (1H, dd, J = 0.8, 7.6 Hz), 8.06 (1H, d, J = 8.8 Hz), 8.44 (1H, d, J = 8.8 Hz), 8.54 (1H, d, J = 8.8 Hz), 8.57 (1H, d, J = 8.0 Hz), 9.45 (1H, d, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.25 (q, J = 27.3 Hz), 119.85, 120.36, 120.56, 123.13, 125.17, 126.04 (q, J = 276.1 Hz), 126.36, 126.83, 127.24, 127.28, 127.43, 127.90, 128.13, 129.20, 129.37, 131.52, 131.82, 133.05, 133.27, 134.33, 140.93, 147.74 (q, J = 2.9 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -60.7 (t, J = 9.7 Hz); ESIHRMS: Found: m/z 362.1161. Calcd for $C_{23}H_{15}F_3N$: $(M+H)^+$ 362.1157.

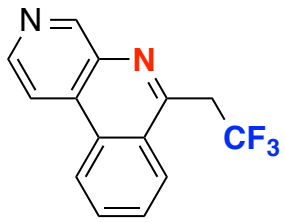
6-(2,2,2-Trifluoroethyl)dibenzo[c,k]phenanthridine (2p):



Yield: 76%; white solid, mp 150-152 °C; IR (KBr) 3061, 3001, 1618, 1566, 1475, 1356, 1261 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.36 (2H, q, J = 10.4 Hz), 7.72-7.76 (3H, m), 7.80 (1H, ddd,

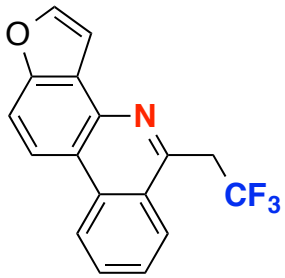
J = 1.2, 7.2, 8.0 Hz), 7.95-7.99 (3H, m), 8.02-8.07 (2H, m), 8.85 (1H, d, J = 9.2 Hz), 9.05-9.07 (1H, m), 9.53 (1H, d, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.53 (q, J = 28.8 Hz), 121.41, 121.97, 124.39, 124.55, 125.37, 125.92 (q, J = 276.3 Hz), 126.72, 127.05, 127.18, 127.37, 127.88, 128.07, 128.49, 128.55, 129.05 (overlapped), 131.78, 132.80, 132.94, 134.51, 142.80, 148.23 (q, J = 3.2 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -62.6 (t, J = 10.2 Hz); ESIHRMS: Found: m/z 362.1153. Calcd for $C_{23}H_{15}F_3N$: $(M+H)^+$ 362.1157.

6-(2,2,2-Trifluoroethyl)benzo[*c*][1,7]naphthyridine (2q):



Yield: 81%; white solid, mp 148-150 °C; IR (KBr) 3040, 2940, 1589, 1528, 1481, 1396, 1258 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (2H, q, J = 10.4 Hz), 7.87 (1H, ddd, J = 1.2, 7.2, 8.4 Hz), 7.95 (1H, ddd, J = 1.2, 7.2, 8.4 Hz), 8.25 (1H, d, J = 8.4 Hz), 8.28 (1H, ddd, J = 5.6, 7.2, 8.0 Hz), 8.64 (1H, d, J = 8.4 Hz), 8.78 (1H, d, J = 5.6 Hz), 9.50 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.45 (q, J = 29.4 Hz), 115.01, 123.12, 125.34 (q, J = 276.5 Hz), 126.40, 126.97, 128.88, 129.89, 131.22, 131.44, 138.46, 145.96, 153.01 (q, J = 3.3 Hz), 153.48; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -62.4 (t, J = 10.4 Hz); ESIHRMS: Found: *m/z* 263.0793. Calcd for $C_{14}H_{10}N_2F_3$: $(M+H)^+$ 263.0796.

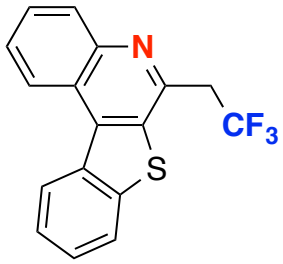
5-(2,2,2-Trifluoroethyl)furo[2,3-c]phenanthridine (2r):



Yield: 61%; white solid, mp 157-158 °C; IR (KBr) 3071, 2963, 1612, 1574, 1535, 1489, 1365, 1265 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.27 (2H, q, J = 10.4 Hz), 7.59 (1H, dd, J = 0.8, 2.0

Hz), 7.70 (1H, ddd, J = 1.2, 7.2, 8.0 Hz), 7.82 (1H, d, J = 2.0 Hz), 7.83 (1H, dd, J = 0.8, 8.8 Hz), 7.85 (1H, ddd, J = 1.2, 7.2, 8.4 Hz), 8.21 (1H, d, J = 8.0 Hz), 8.44 (1H, d, J = 8.8 Hz), 8.65 (1H, d, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.43 (q, J = 29.0 Hz), 106.37, 112.60, 118.27, 119.60, 122.60, 124.97, 125.70 (q, J = 276.4 Hz), 125.81, 126.17, 126.73, 130.69, 133.76, 138.21, 145.11, 150.81 (q, J = 3.3 Hz), 154.81; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -62.4 (t, J = 10.2 Hz); ESIHRMS: Found: *m/z* 302.0789. Calcd for $C_{17}H_{11}F_3NO$: $(M+H)^+$ 302.0793.

6-(2,2,2-Trifluoroethyl)benzo[4,5]thieno[2,3-*c*]quinoline (2s):



Yield: 65%; pale yellow solid, mp 178-180 °C; IR (KBr) 3071, 2970, 1589, 1543, 1497, 1358, 1249 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.07 (2H, q, J = 10.4 Hz), 7.64-7.70 (2H, m), 7.79-7.81 (2H, m), 7.08 (1H, d, J = 7.6 Hz), 8.32-8.35 (1H, m), 8.90-8.95 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.53 (q, J = 29.0 Hz), 122.61, 123.47, 124.70, 125.41 (q, J = 276.6 Hz), 125.50, 125.92, 127.72 (overlapped), 128.01, 130.76, 133.80, 135.38, 136.54, 140.49, 145.61, 145.75 (q, J = 3.4 Hz); ^{19}F NMR ($CDCl_3$, 376 MHz) δ -62.6 (t, J = 10.4 Hz); ESIHRMS: Found: *m/z* 318.0566. Calcd for $C_{17}H_{11}F_3NS$: $(M+H)^+$ 319.0564.

9. Solubility testing of aza-PAHs 2m-p

The solubility properties of new aza-PAHs **2m-p** in commonly used organic solvents such as ethyl acetate, THF, chloroform, and toluene are summarized in Table SI-2. These polyfluoroalkyl aza-PAHs exhibited quite good solubility, thereby demonstrating the unique effect arising from the polyfluoroalkyl group

Table S-2. The solubility of **2m-p** in ethyl acetate, THF, chloroform, and toluene[a]

Entry	Compound	EtOAc	THF	$CHCl_3$	$PhCH_3$
1	**2m**	29.7	118.7	71.2	39.6
2	**2n**	62.0	206.7	77.5	68.9
3	**2o**	21.6	129.3	48.5	32.3
4	**2p**	39.0	156.0	78.0	52.0

[a] The unit is mg solute per 1 mL solvent at 22 °C.

10. References

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(4) Paul, S.; Samanta, S.; Ray, J. K. *Tetrahedron Lett*. **2010**, *51*, 5604.
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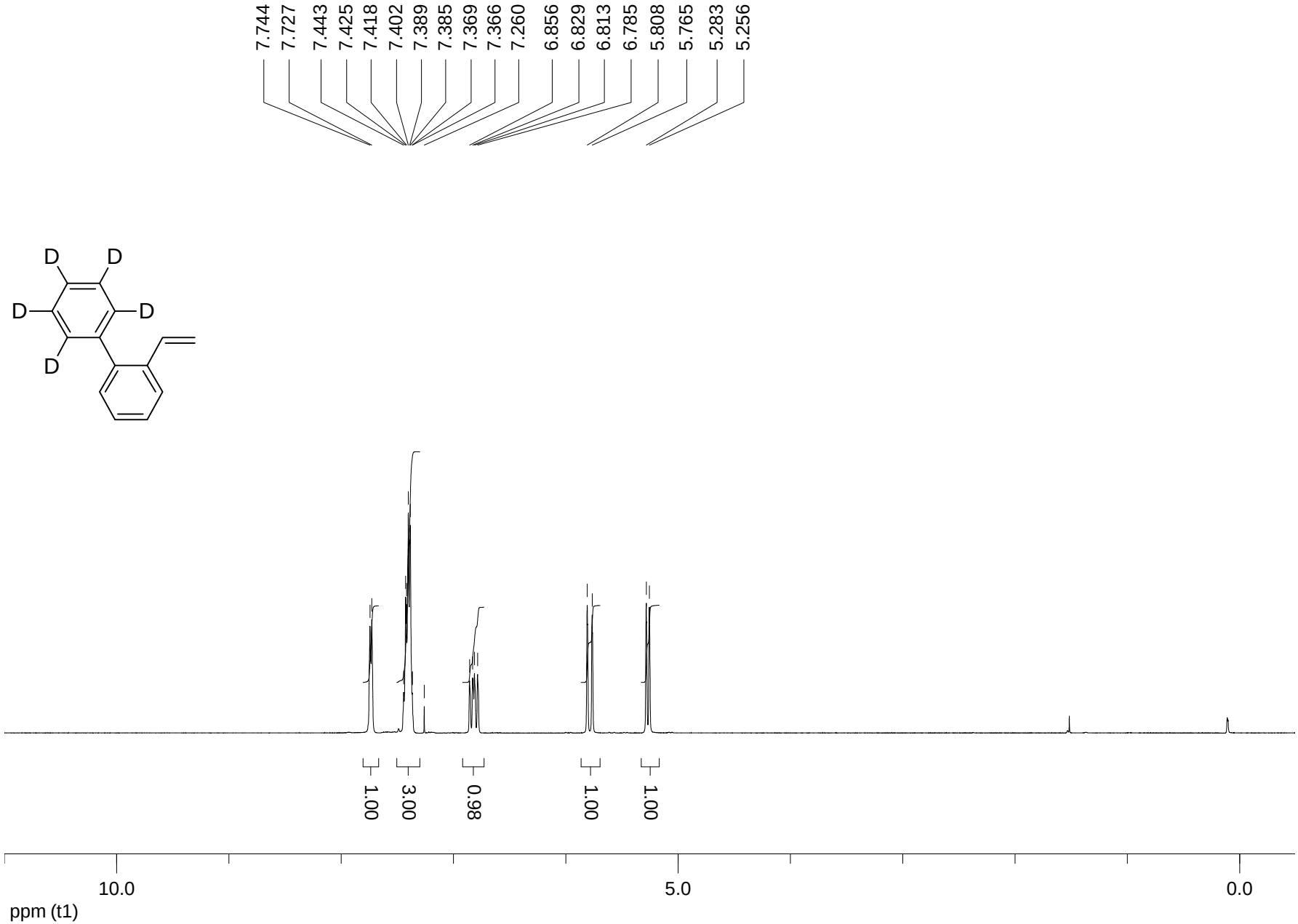
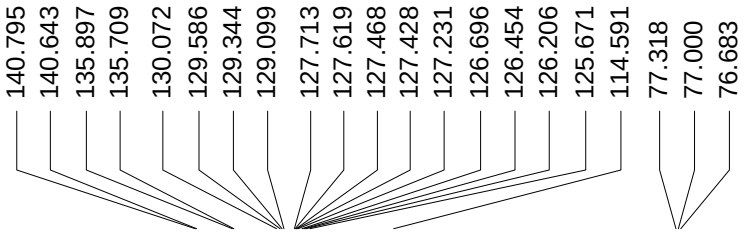
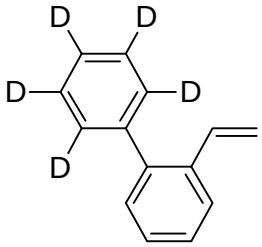
(8) Zhou suggested that a phenyltrifluoromethyliodonium acetate [$PhI(OAc)CF_3$] intermediate generated from interaction of $PhI(OAc)_2$ and Me_3SiCF_3 is propably responsible for the generation of the CF_3 radical, see: Wang, Q.; Dong, X.; Xiao, T.; Zhou, L. *Org. Lett*. **2013**, *15*, 4846.
(9) Alternatively, deprotonation of **B**, followed by single-electron oxidation to produce **2a** is also operative, see: (a) Studer, A.; Curran, D. P. *Angew. Chem. Int. Ed.* **2011**, *50*, 5018. (b) Zhang, B.; Mück-Lichtenfeld, C.; Daniliuc, C. G.; Studer, A. *Angew. Chem. Int. Ed.* **2013**, *52*, 10792.
(10) Gerfaud, T.; Neuville, L.; Zhu, J. *Angew. Chem. Int. Ed.* **2009**, *48*, 572.

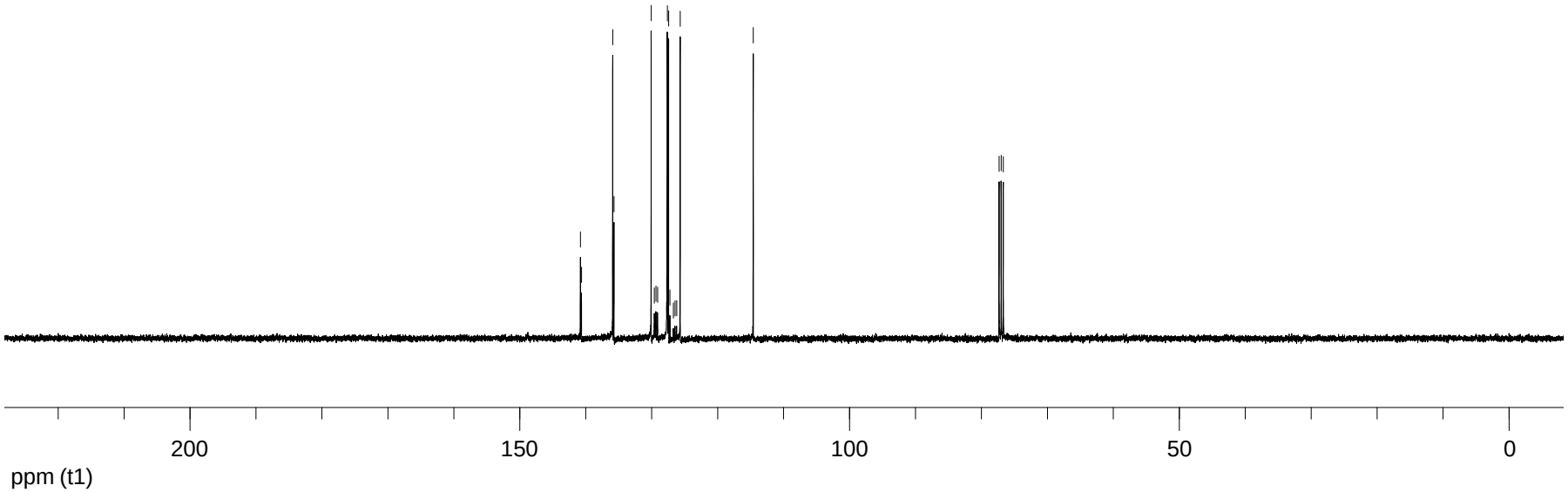
^{1}H NMR Spectrum of **Ia-d$_5$** (400 MHz, $CDCl_3$)



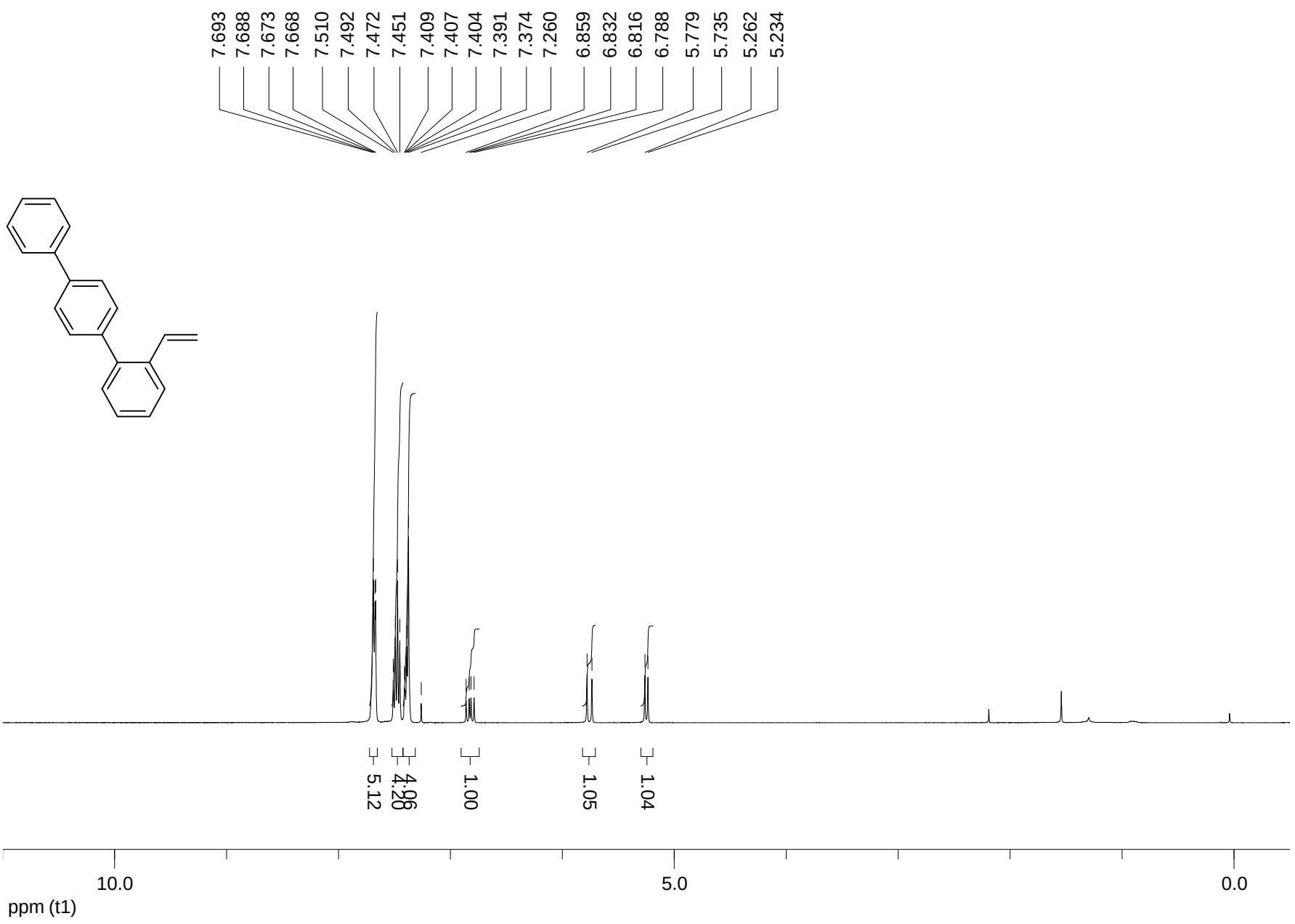
^{13}C NMR Spectrum of **Ia-d$_5$** (100 MHz, $CDCl_3$)



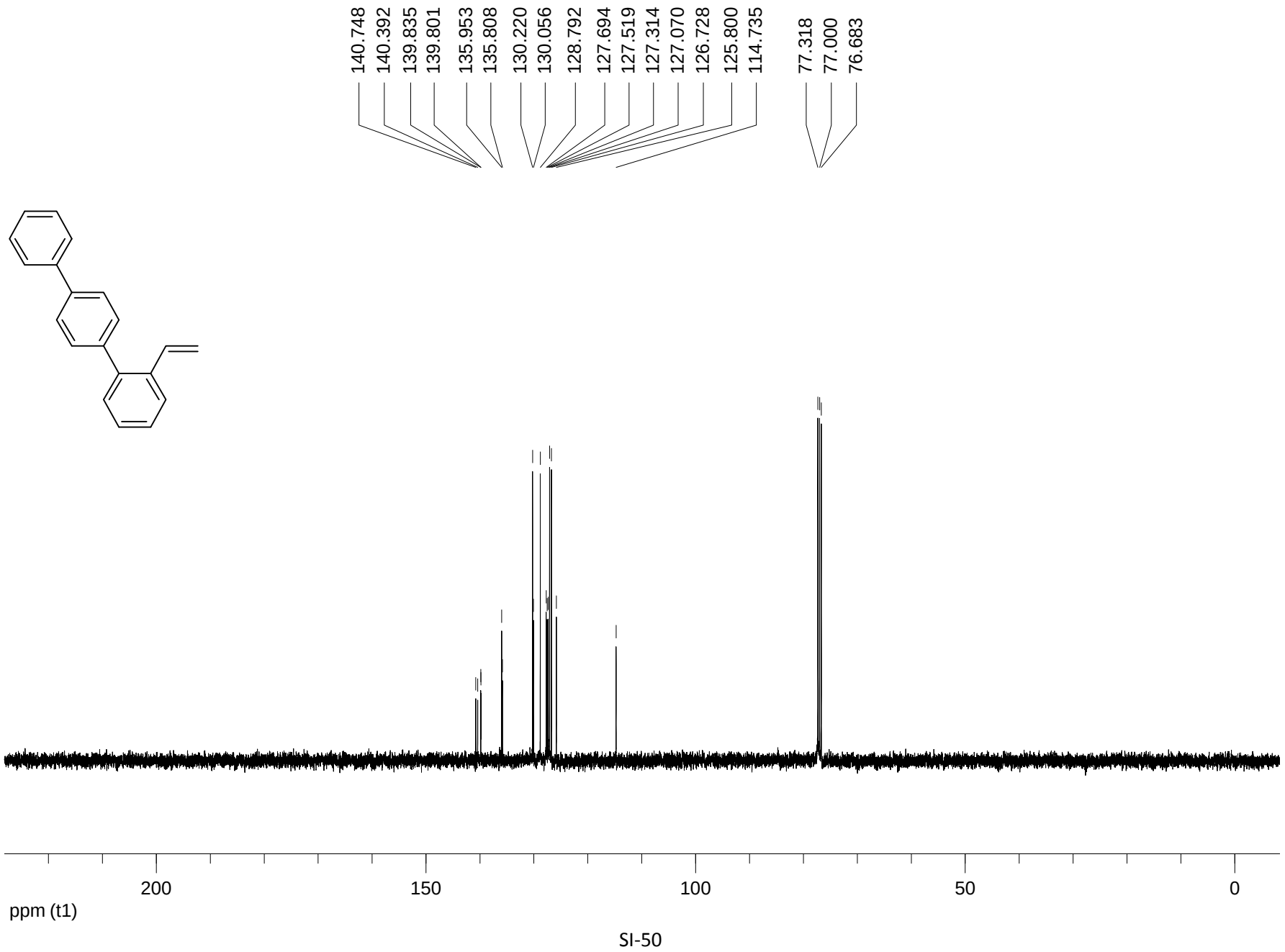




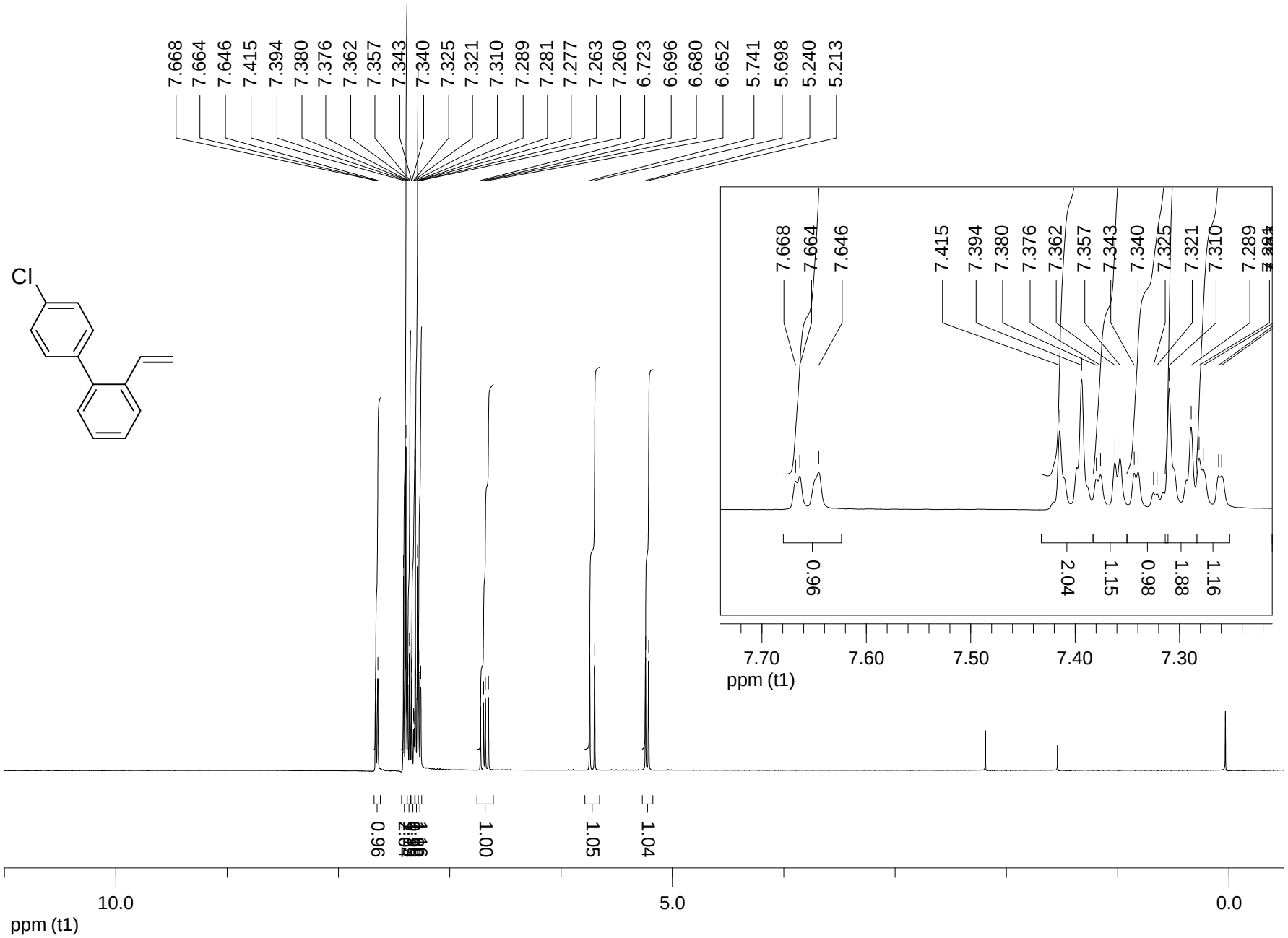
^{1}H NMR Spectrum of **Ib** (400 MHz, $CDCl_3$)



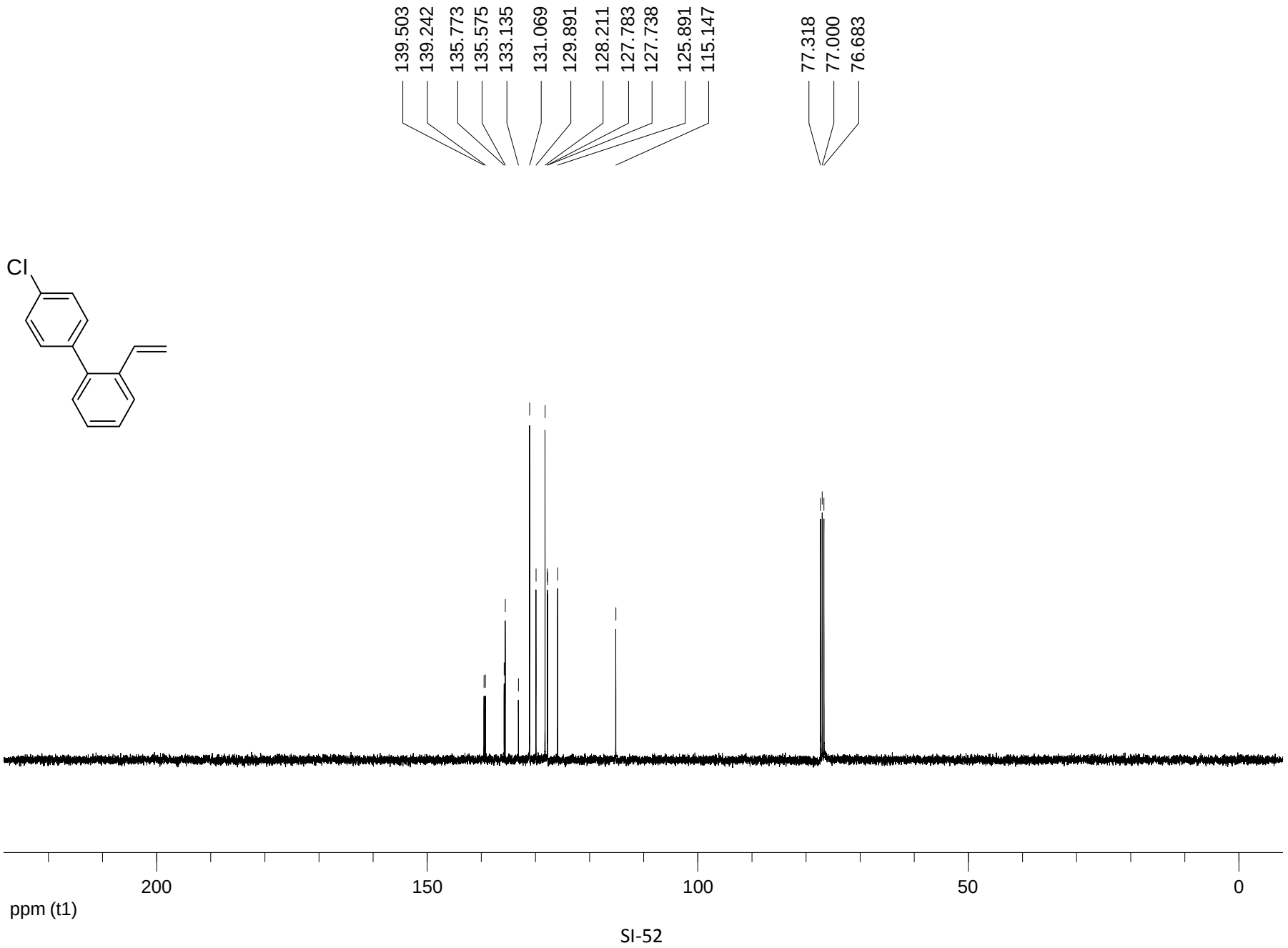
^{13}C NMR Spectrum of **Ib** (100 MHz, $CDCl_3$)



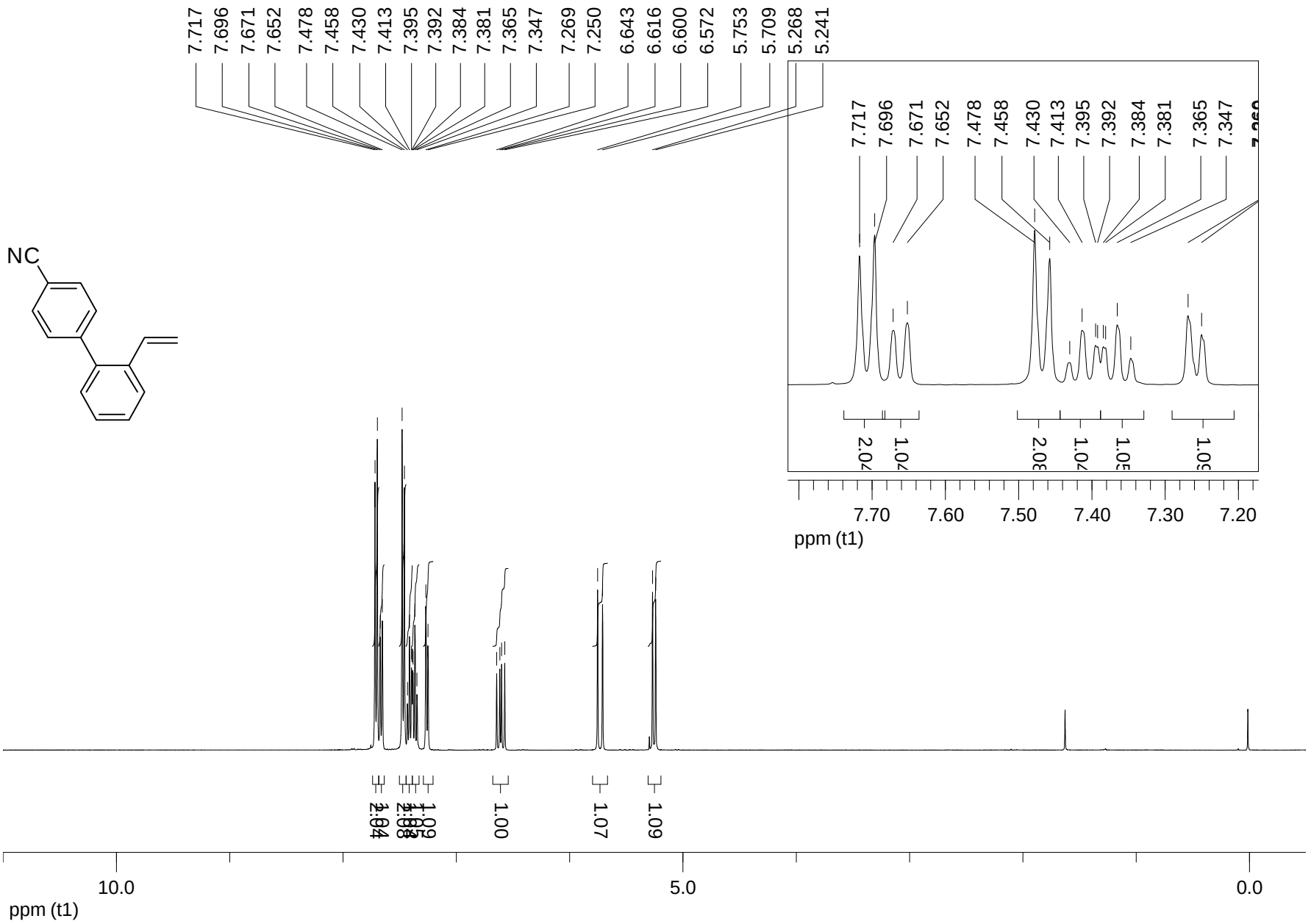
^{1}H NMR Spectrum of **If** (400 MHz, $CDCl_3$)



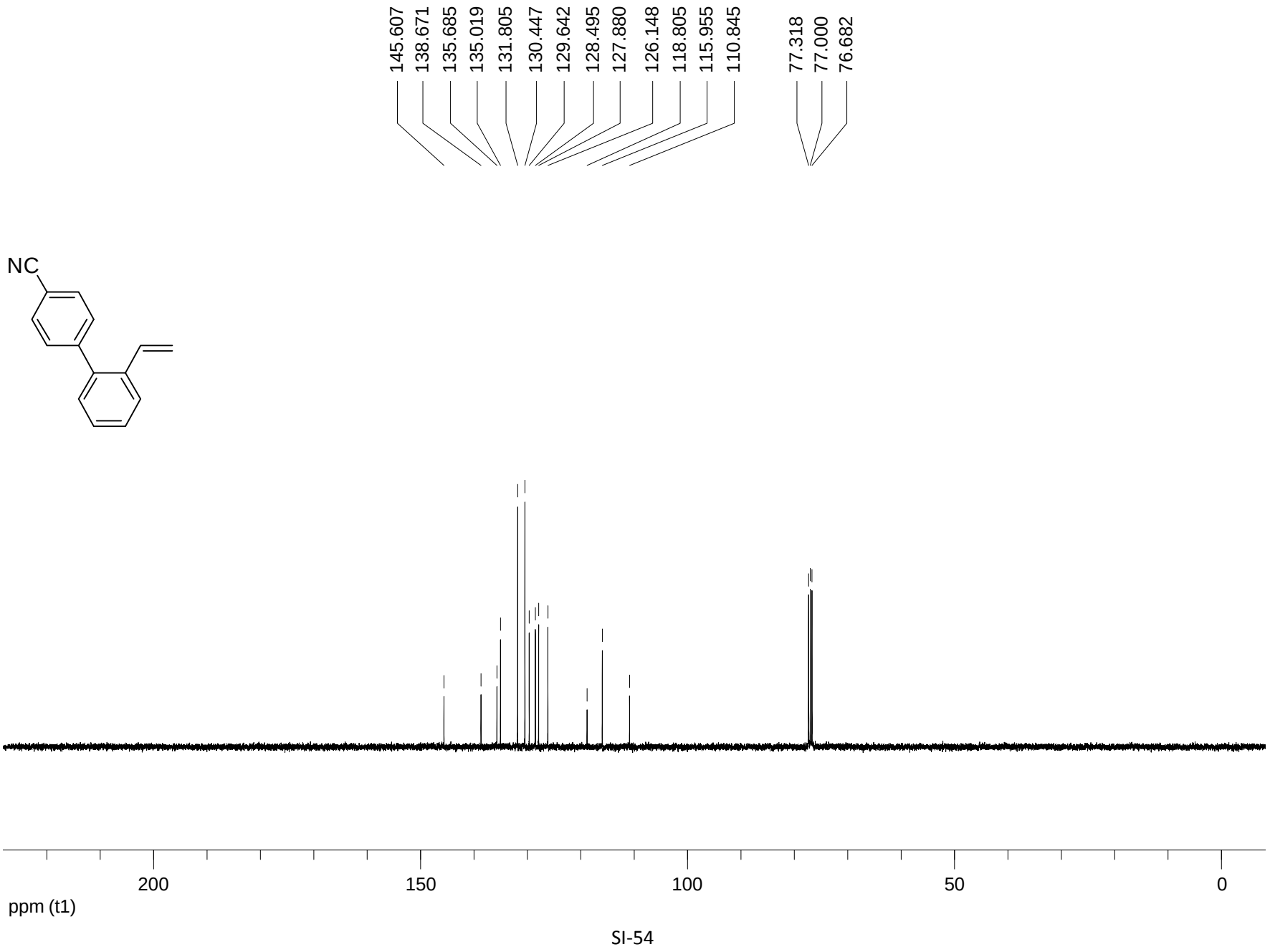
^{13}C NMR Spectrum of **If** (100 MHz, $CDCl_3$)



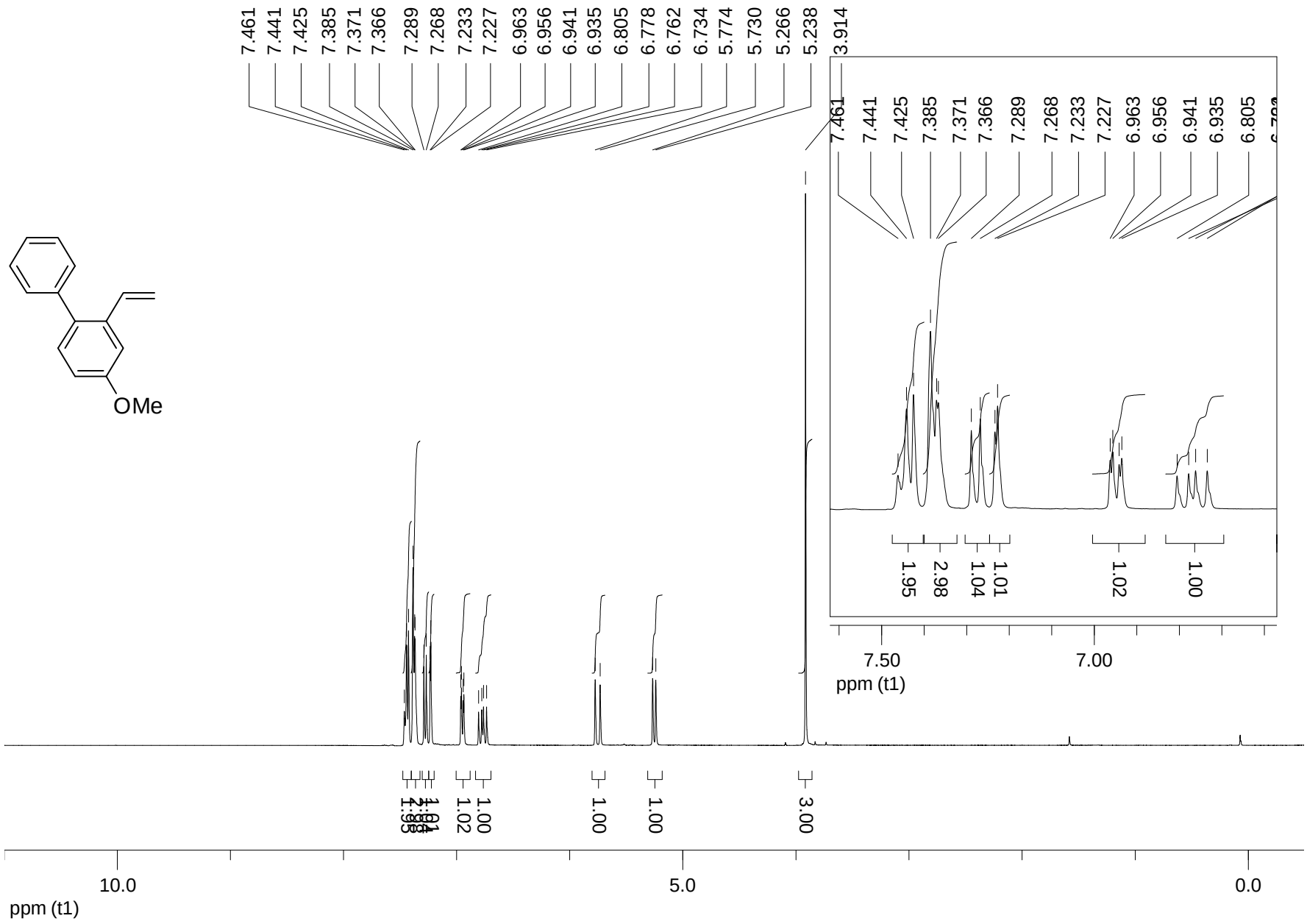
^{1}H NMR Spectrum of **Ig** (400 MHz, $CDCl_3$)



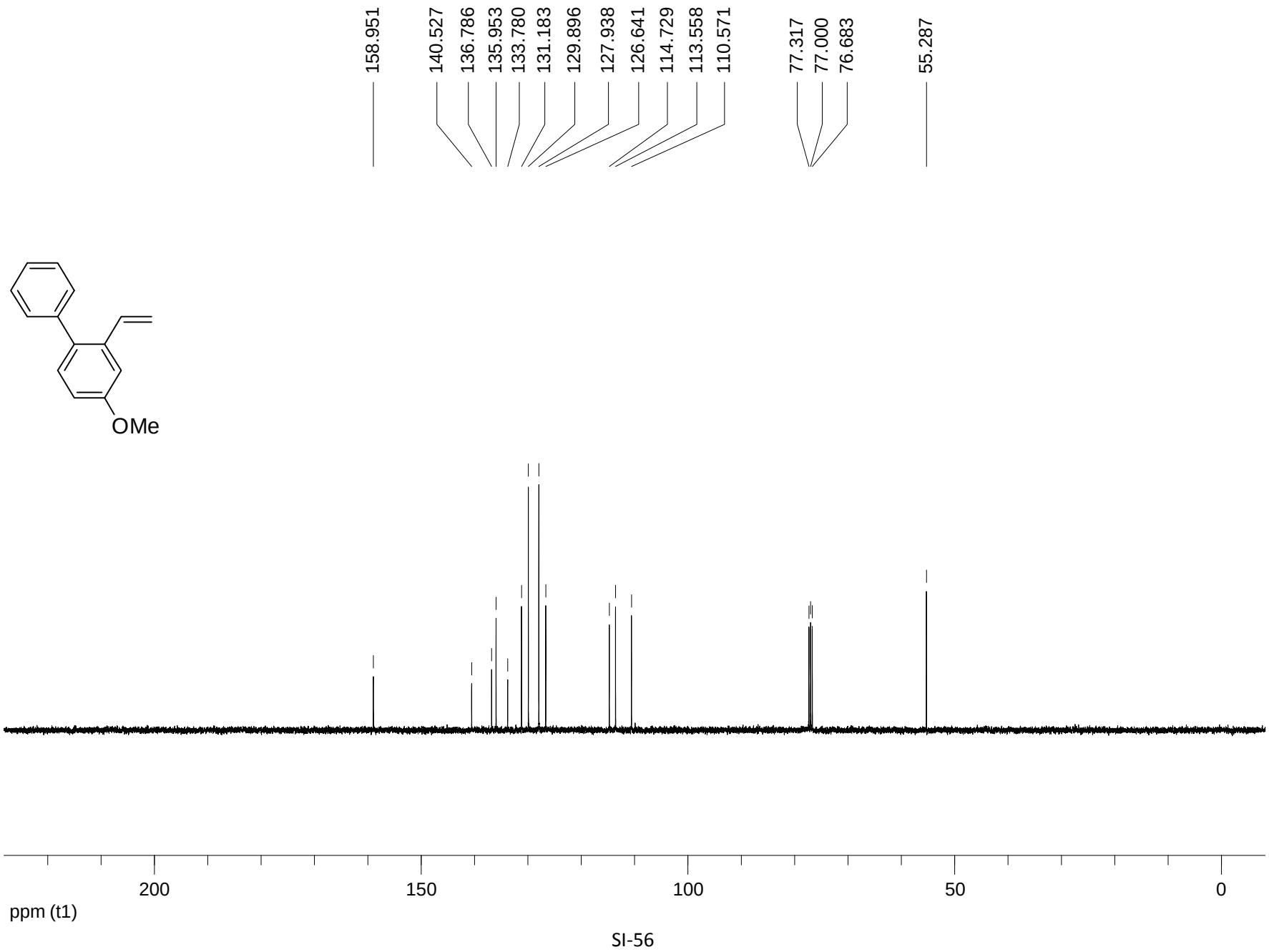
^{13}C NMR Spectrum of **Ig** (100 MHz, $CDCl_3$)



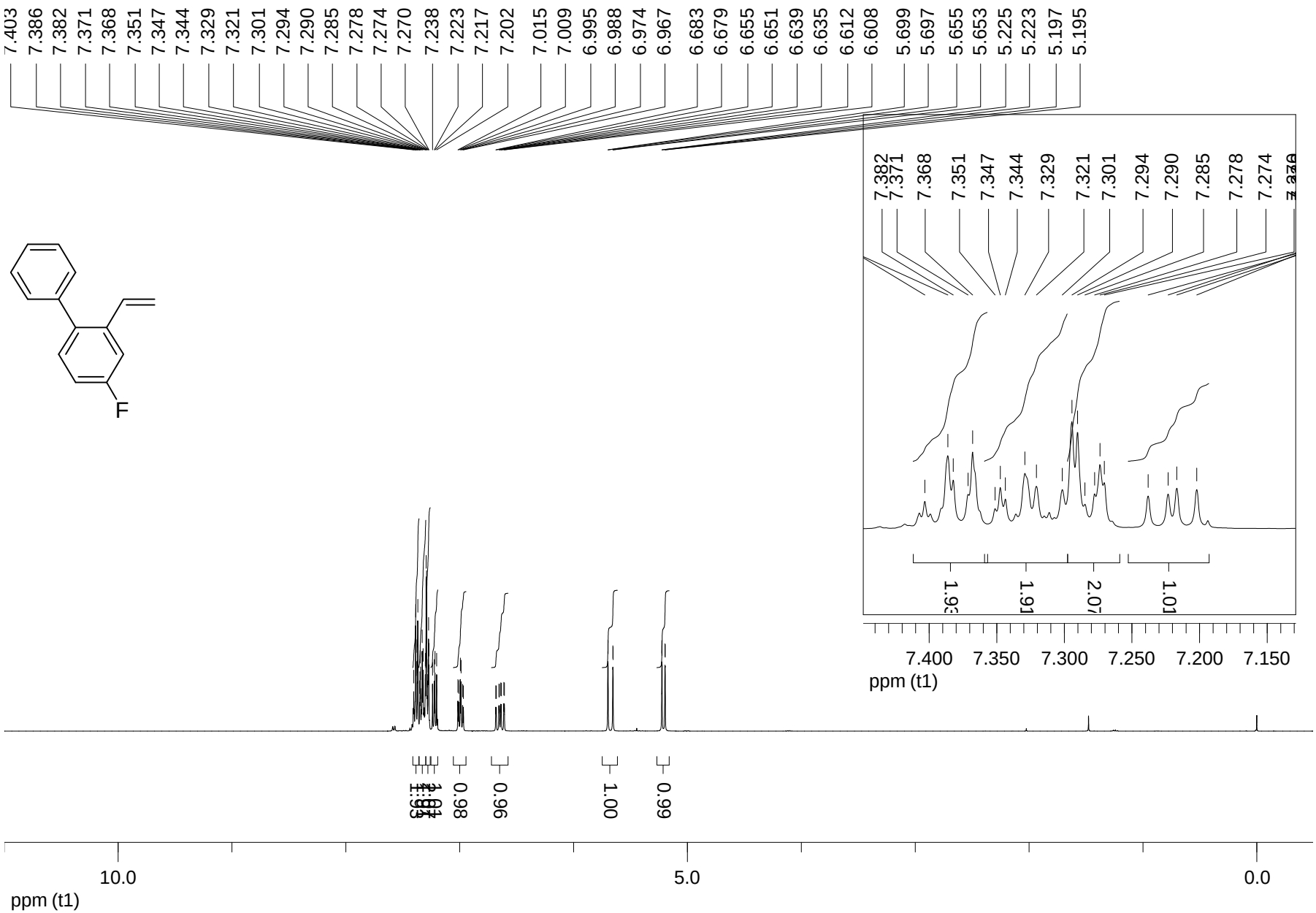
^{1}H NMR Spectrum of **Ih** (400 MHz, $CDCl_3$)



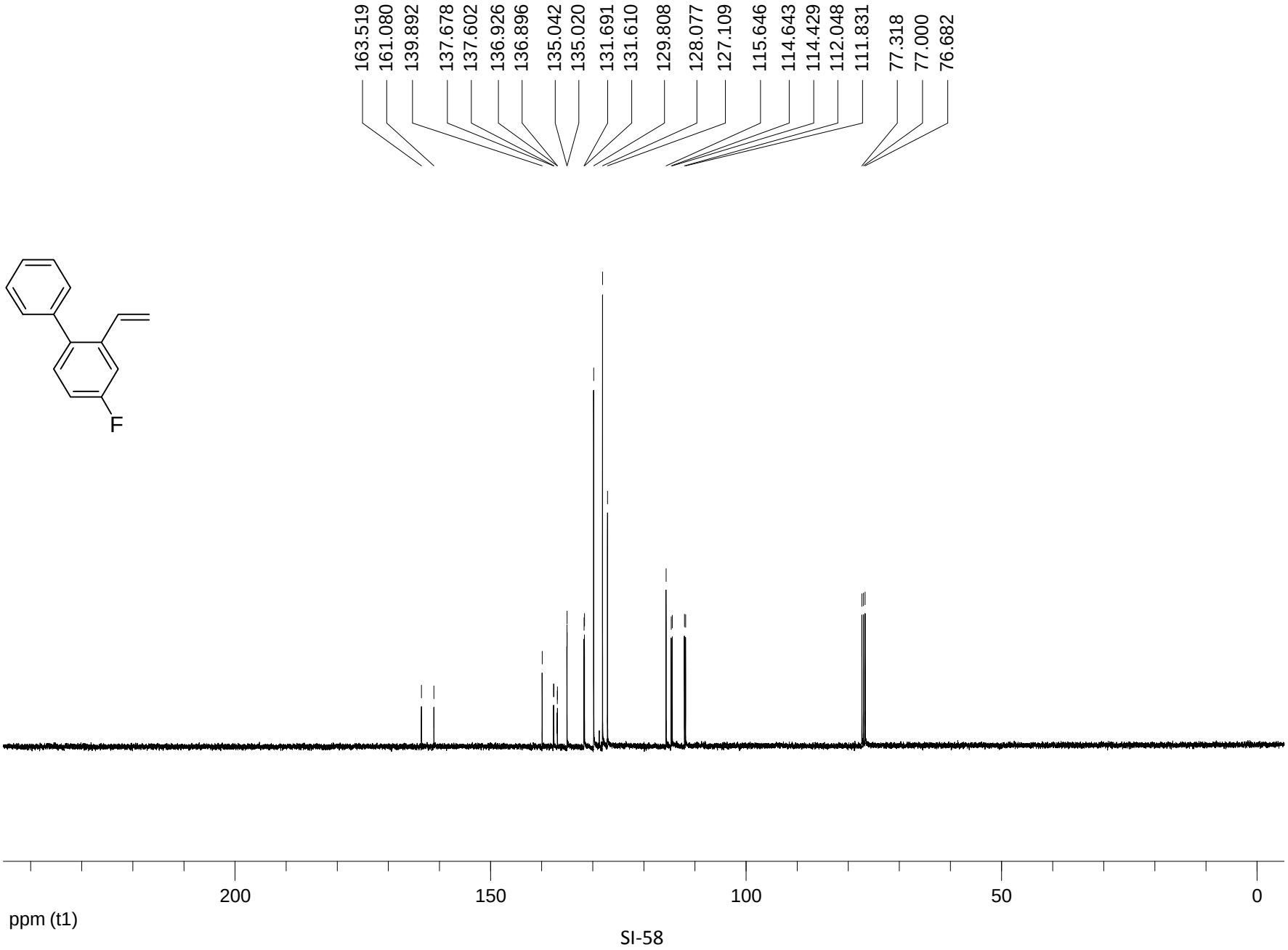
^{13}C NMR Spectrum of **Ih** (100 MHz, $CDCl_3$)



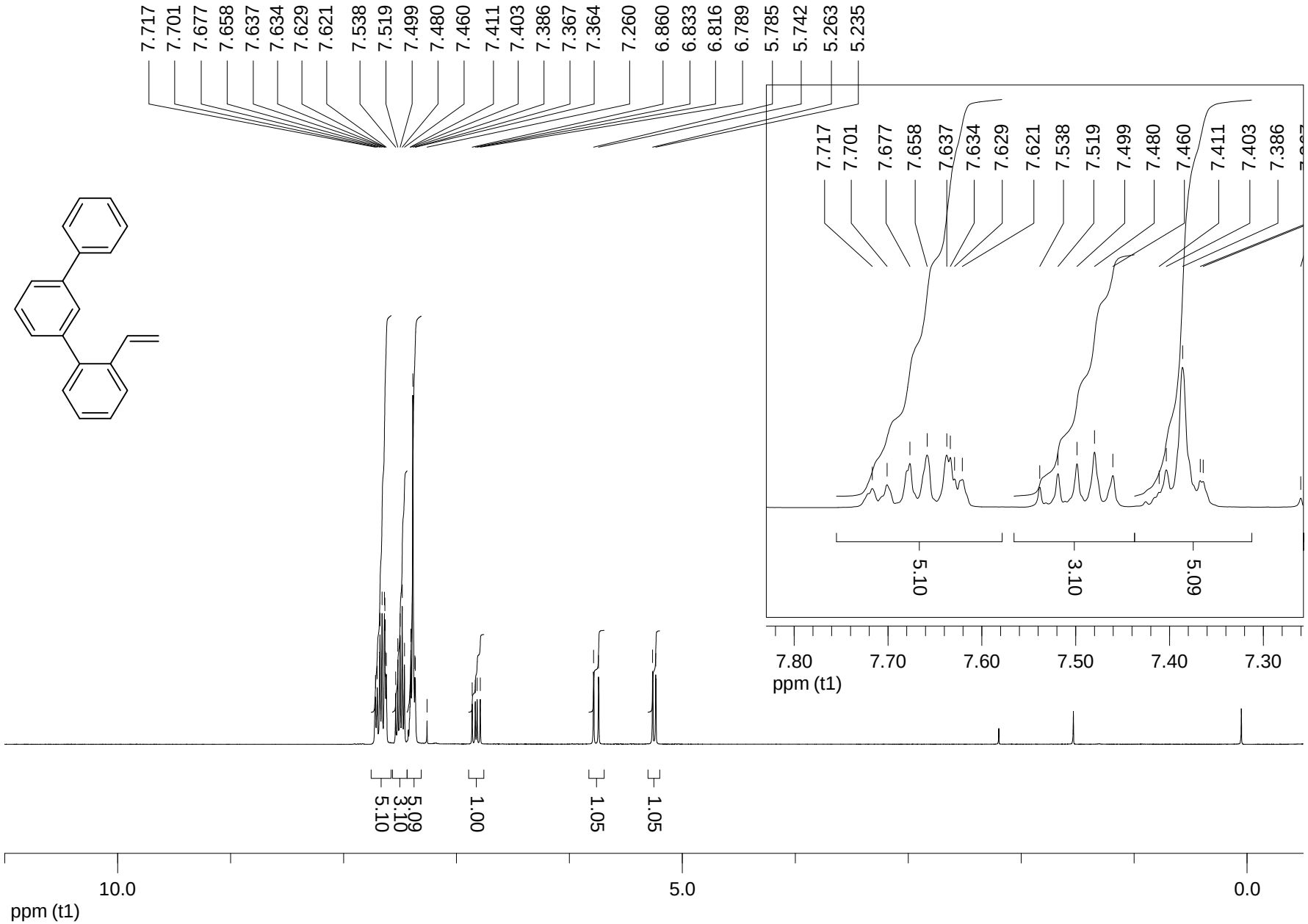
^{1}H NMR Spectrum of **Ii** (400 MHz, $CDCl_3$)



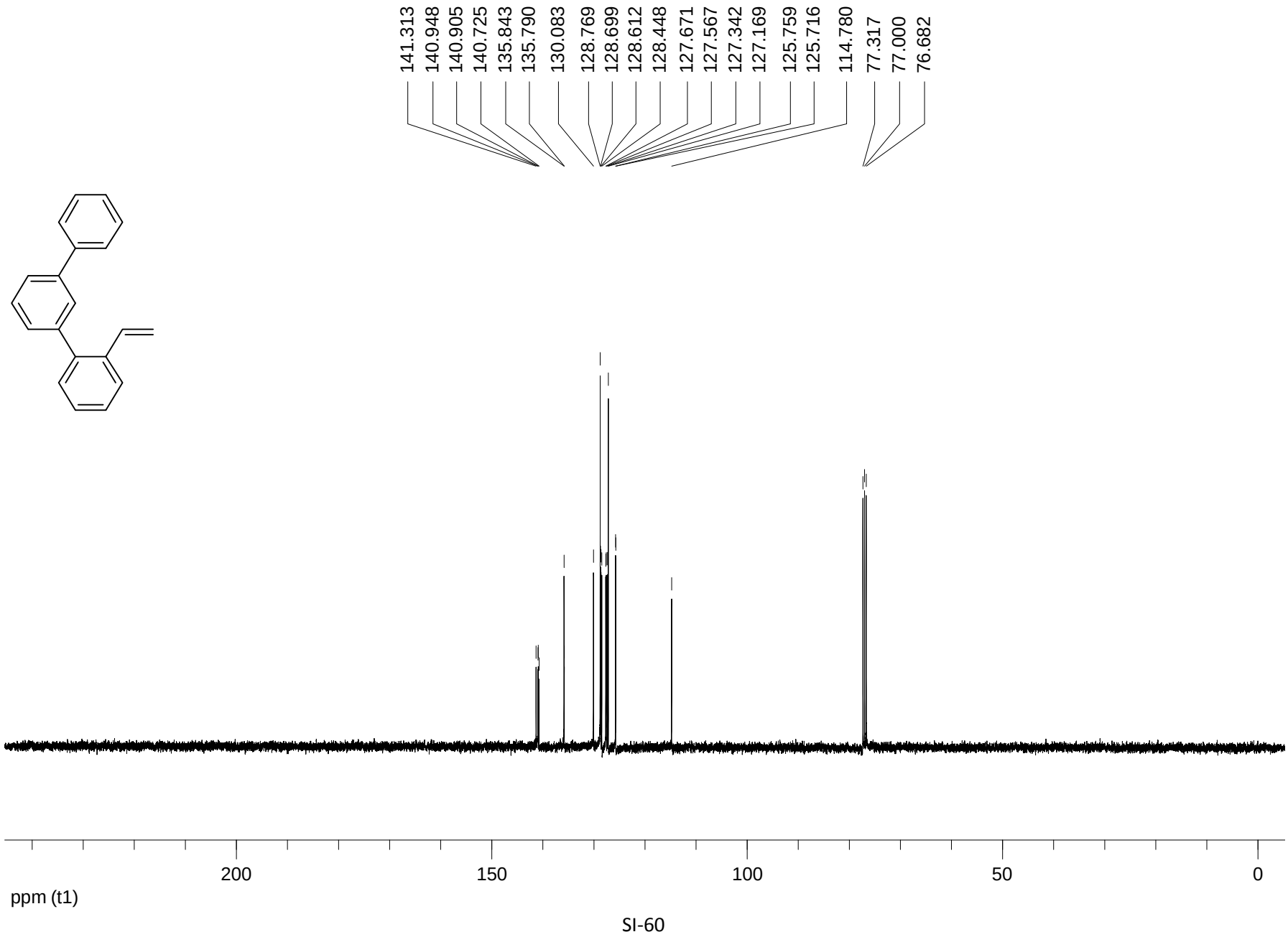
^{13}C NMR Spectrum of **Ii** (100 MHz, $CDCl_3$)



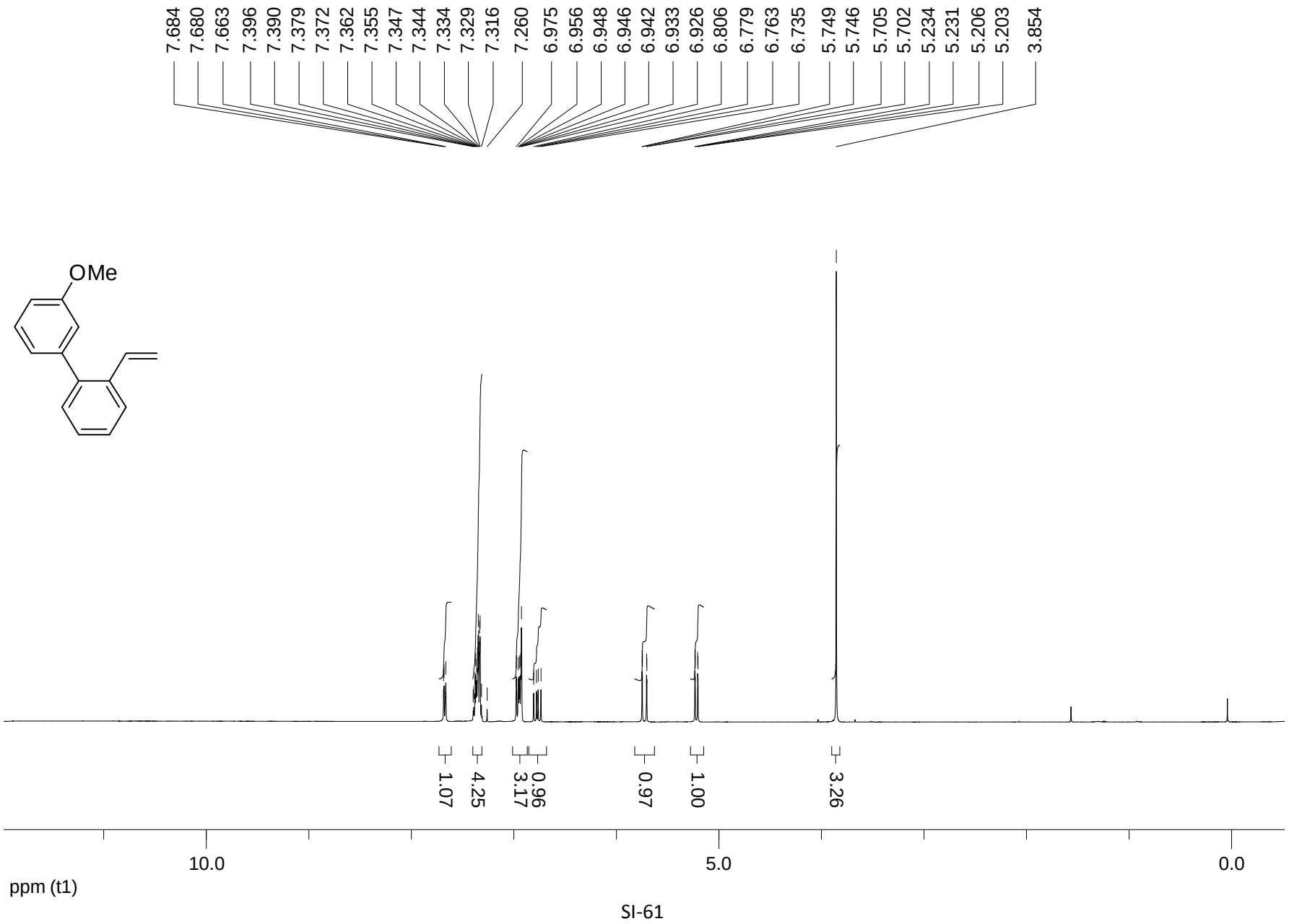
^{1}H NMR Spectrum of **Ij** (400 MHz, $CDCl_3$)



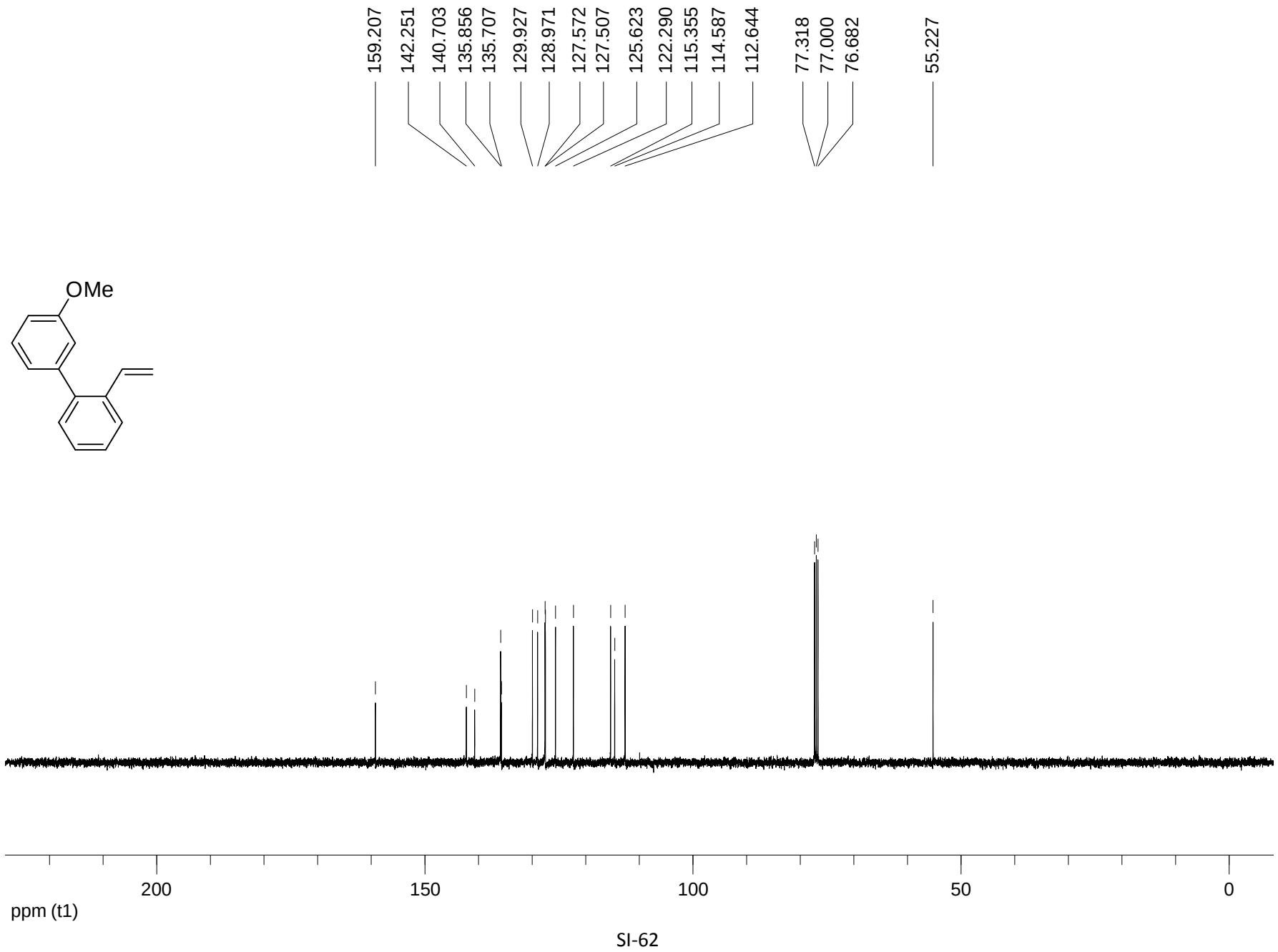
^{13}C NMR Spectrum of **Ij** (100 MHz, $CDCl_3$)



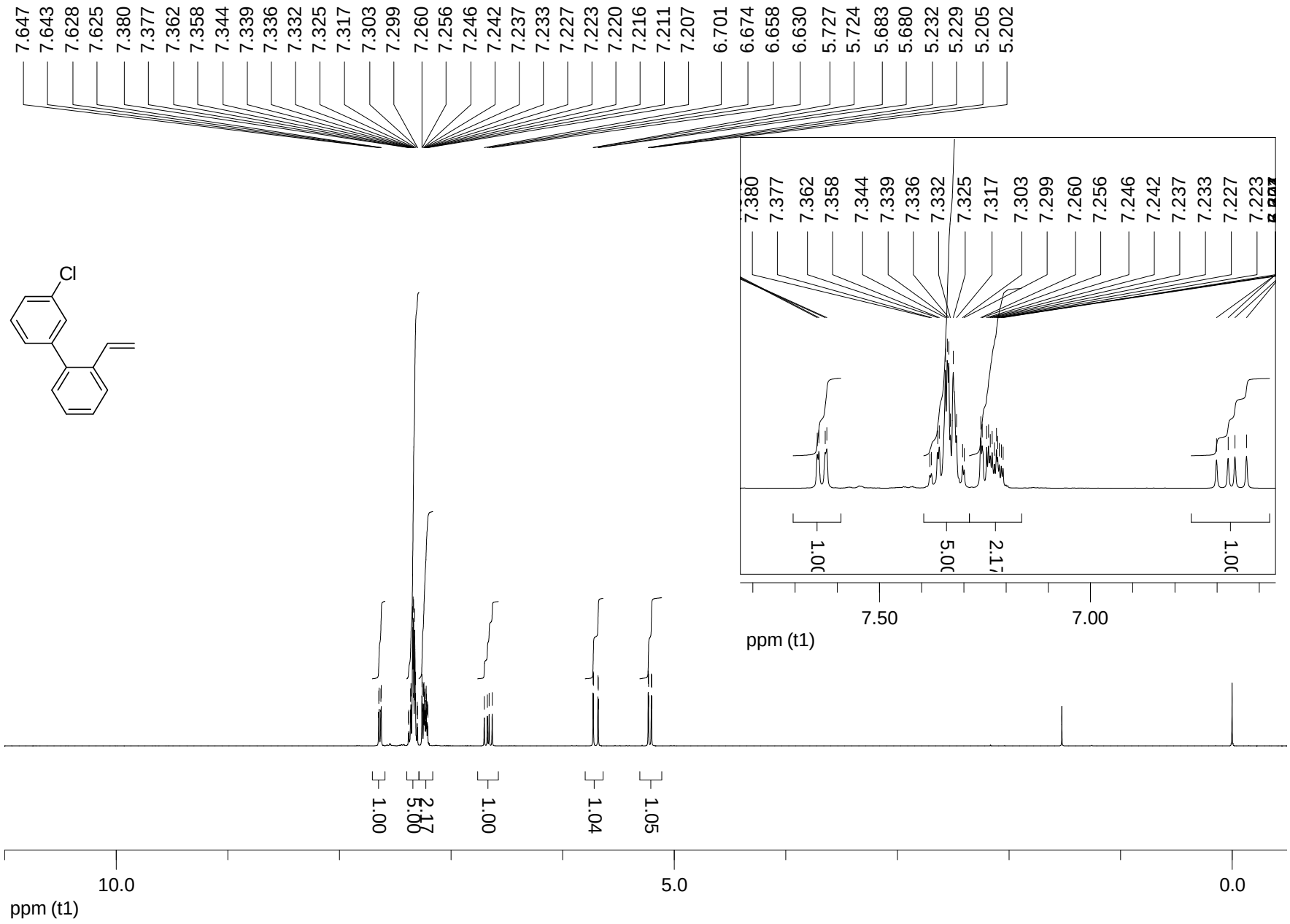
^{1}H NMR Spectrum of **Ik** (400 MHz, $CDCl_3$)



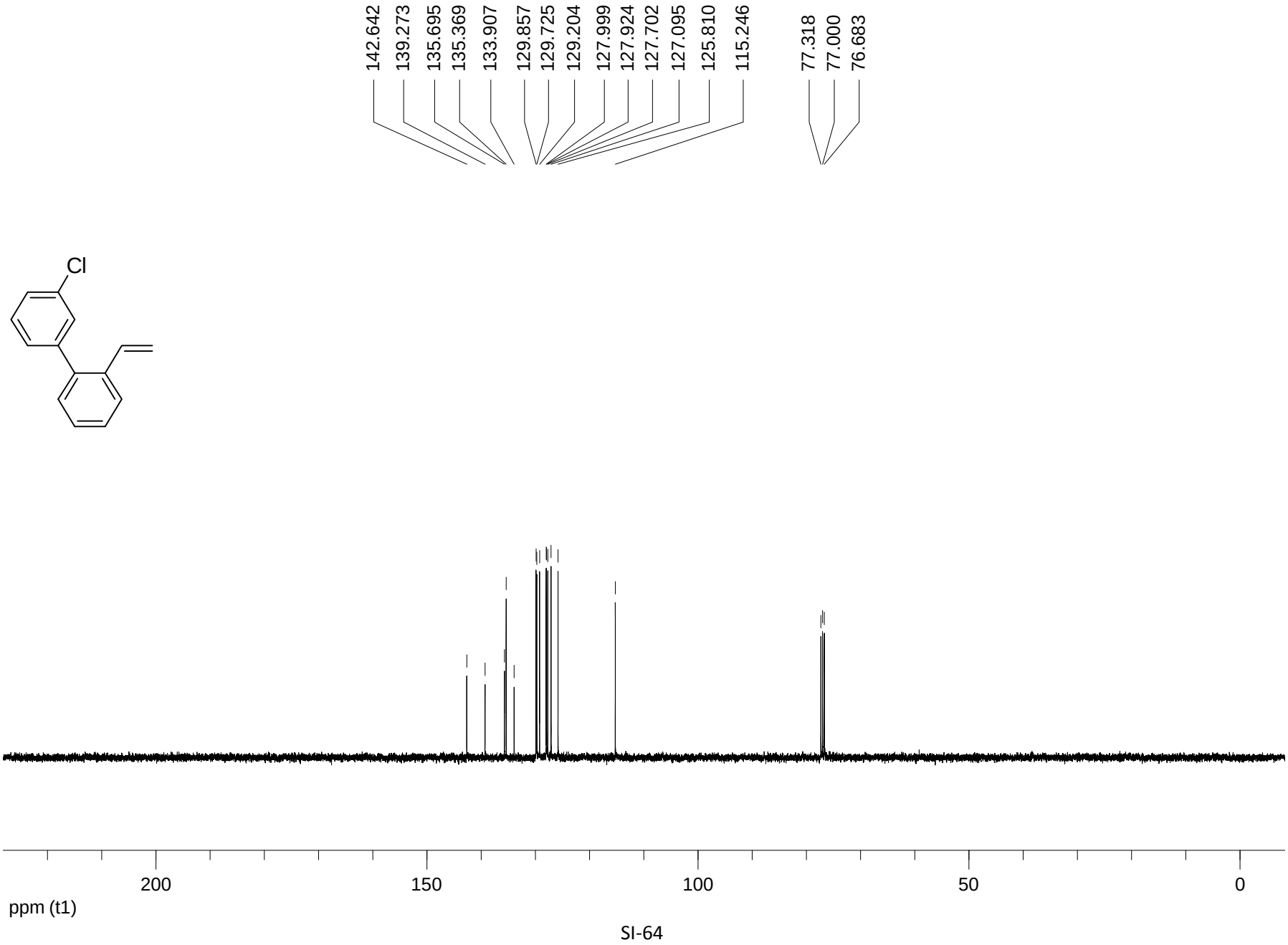
^{13}C NMR Spectrum of **Ik** (100 MHz, $CDCl_3$)



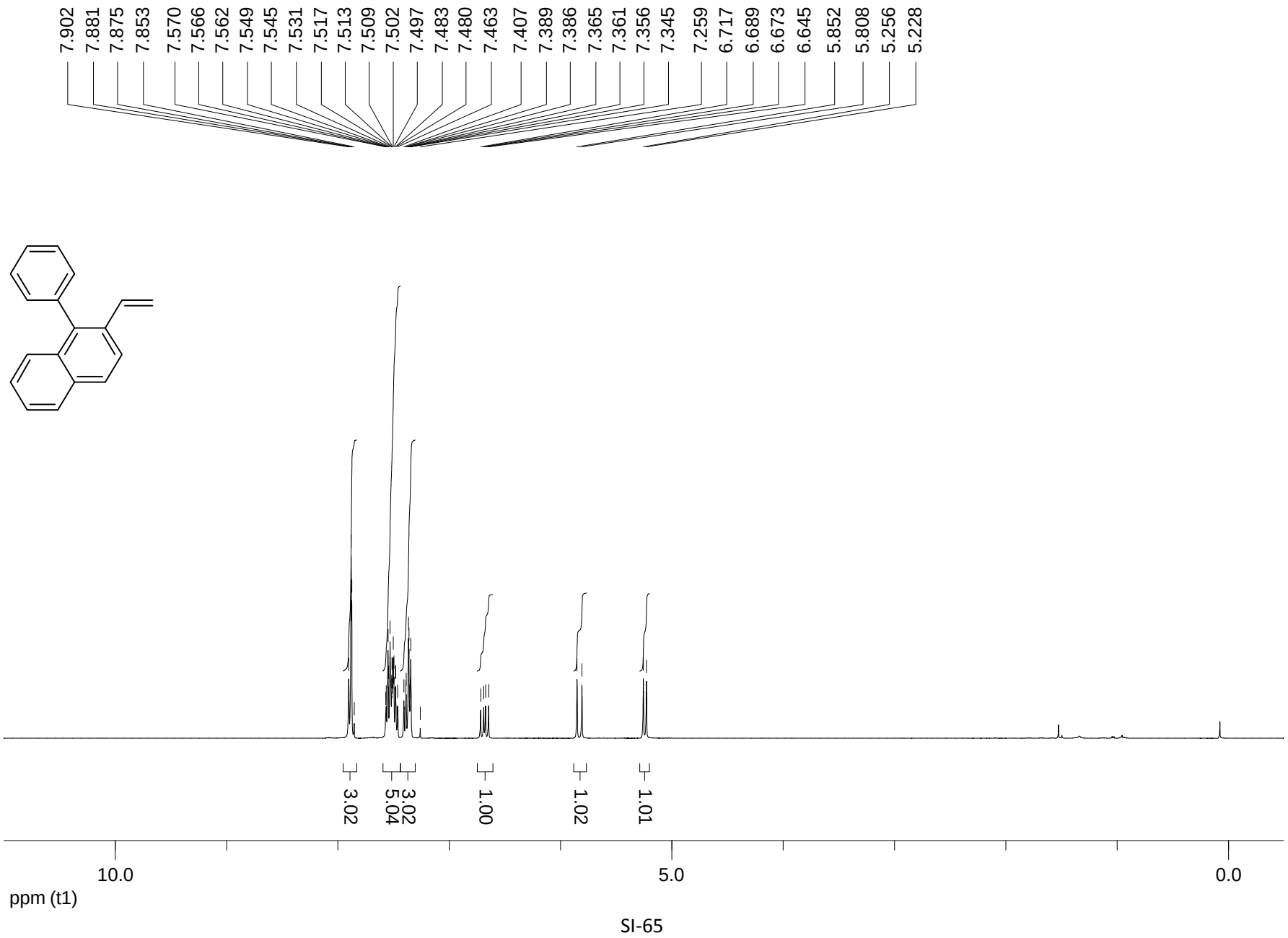
^{1}H NMR Spectrum of **II** (400 MHz, $CDCl_3$)



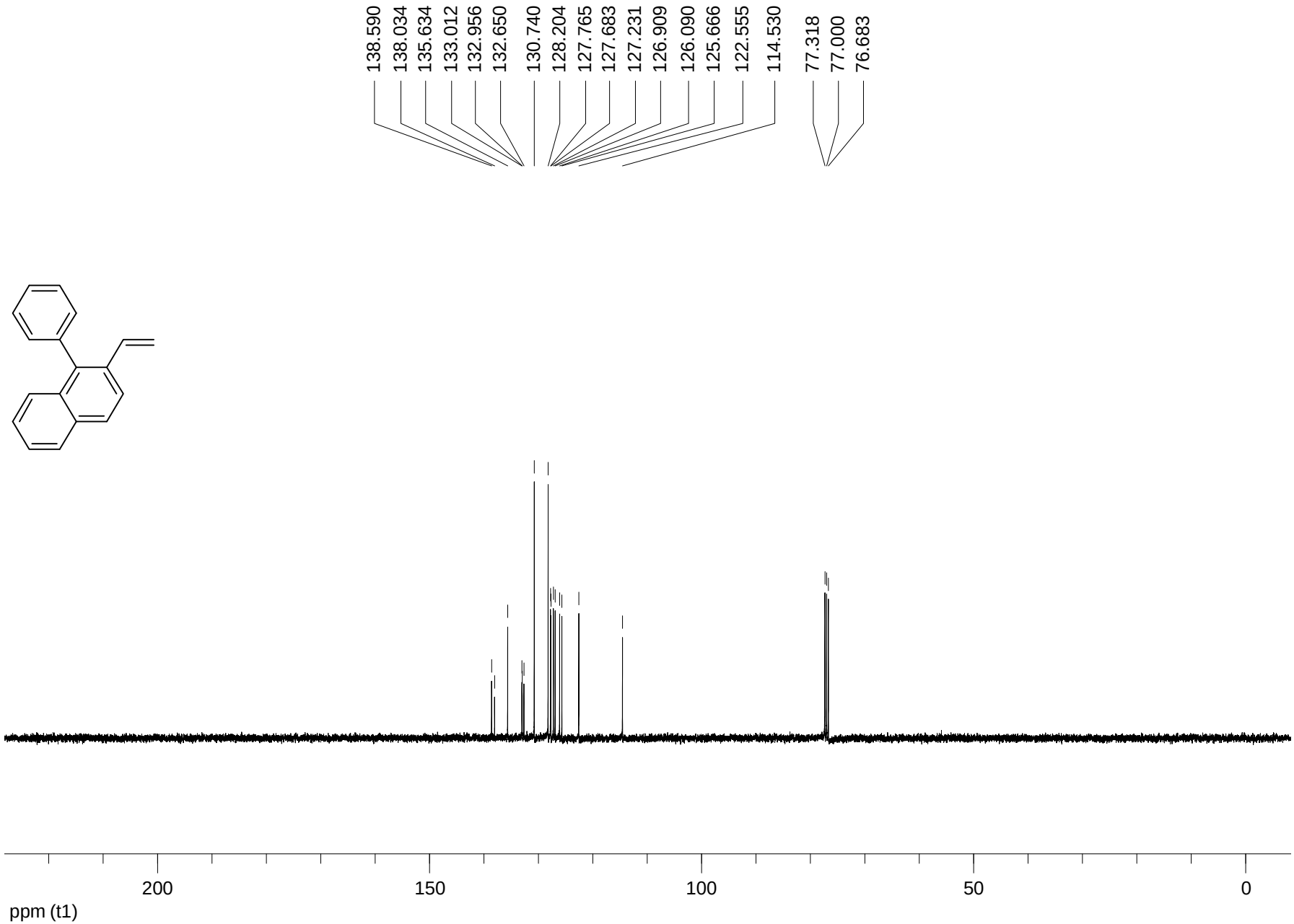
^{13}C NMR Spectrum of **II** (100 MHz, $CDCl_3$)



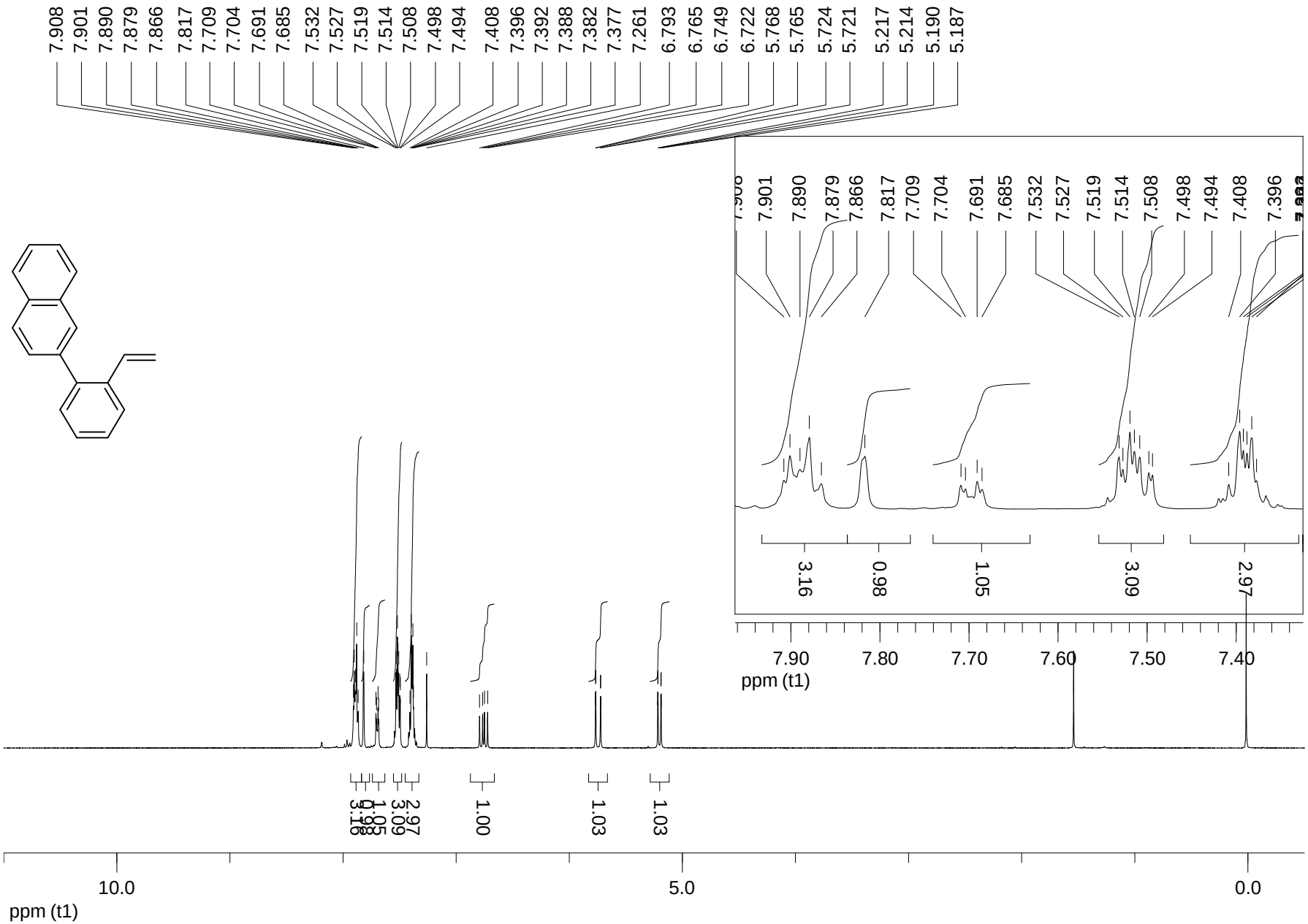
^{1}H NMR Spectrum of **Im** (400 MHz, $CDCl_3$)



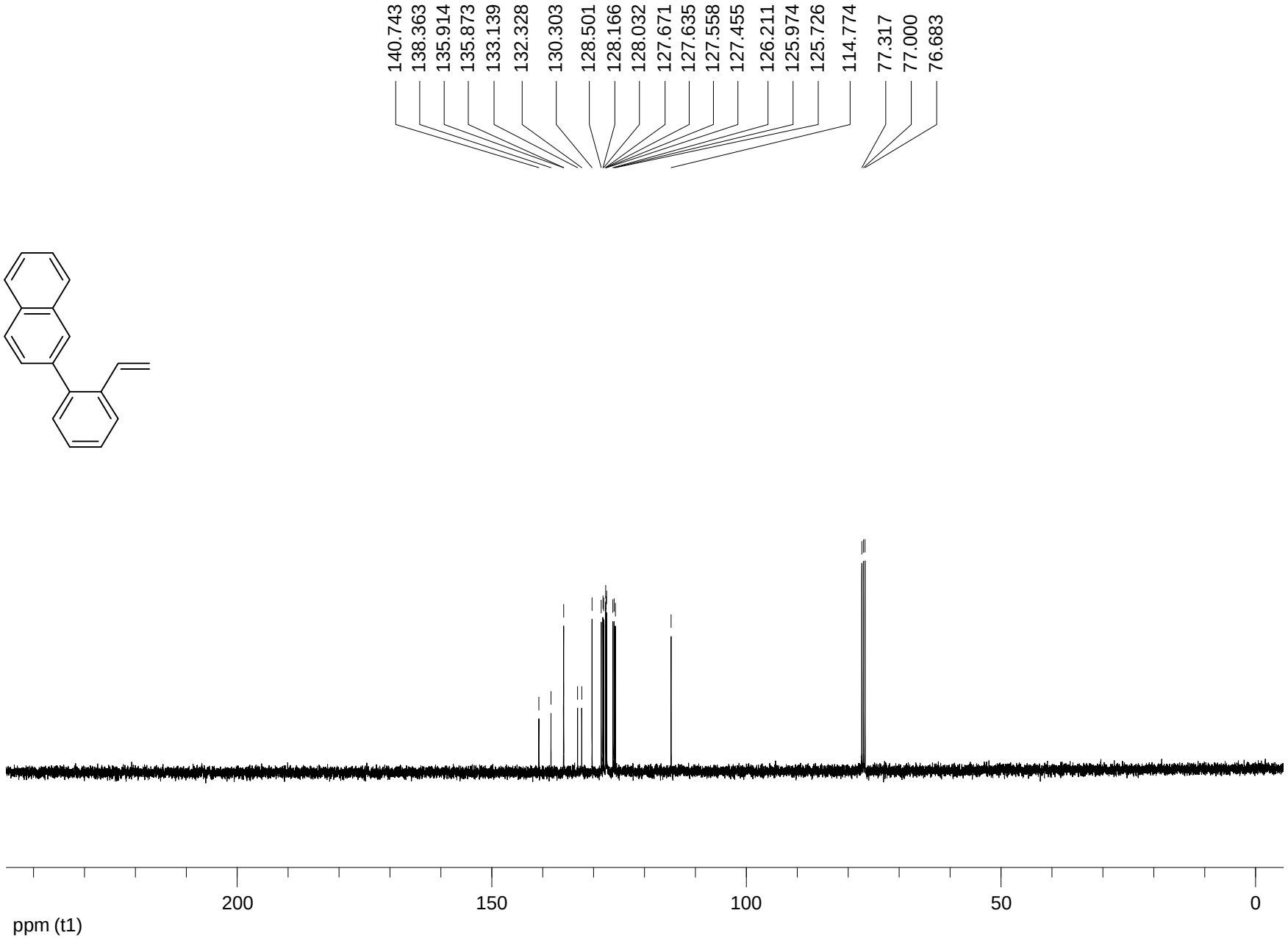
^{13}C NMR Spectrum of **Im** (100 MHz, $CDCl_3$)



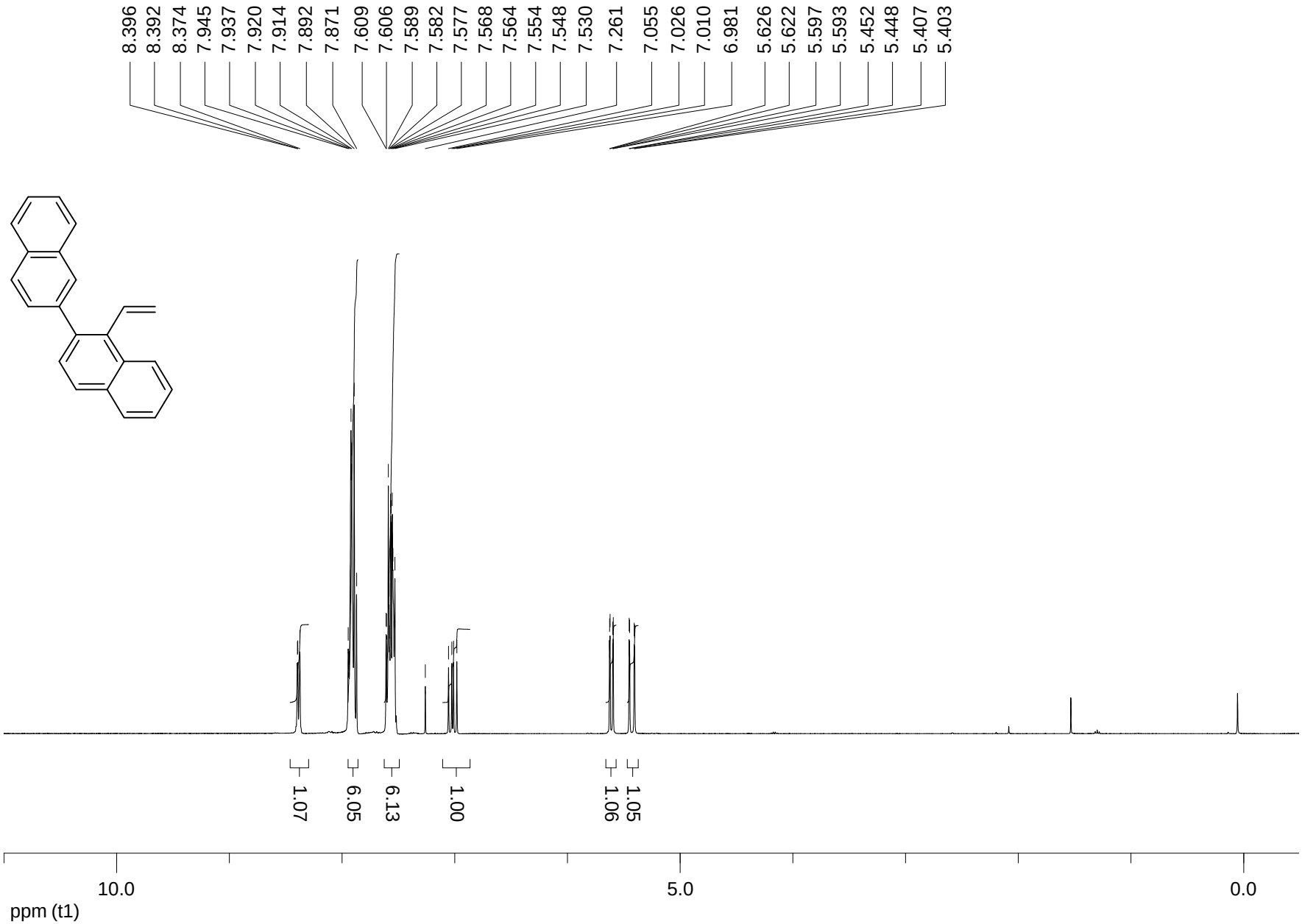
^{1}H NMR Spectrum of **In** (400 MHz, $CDCl_3$)



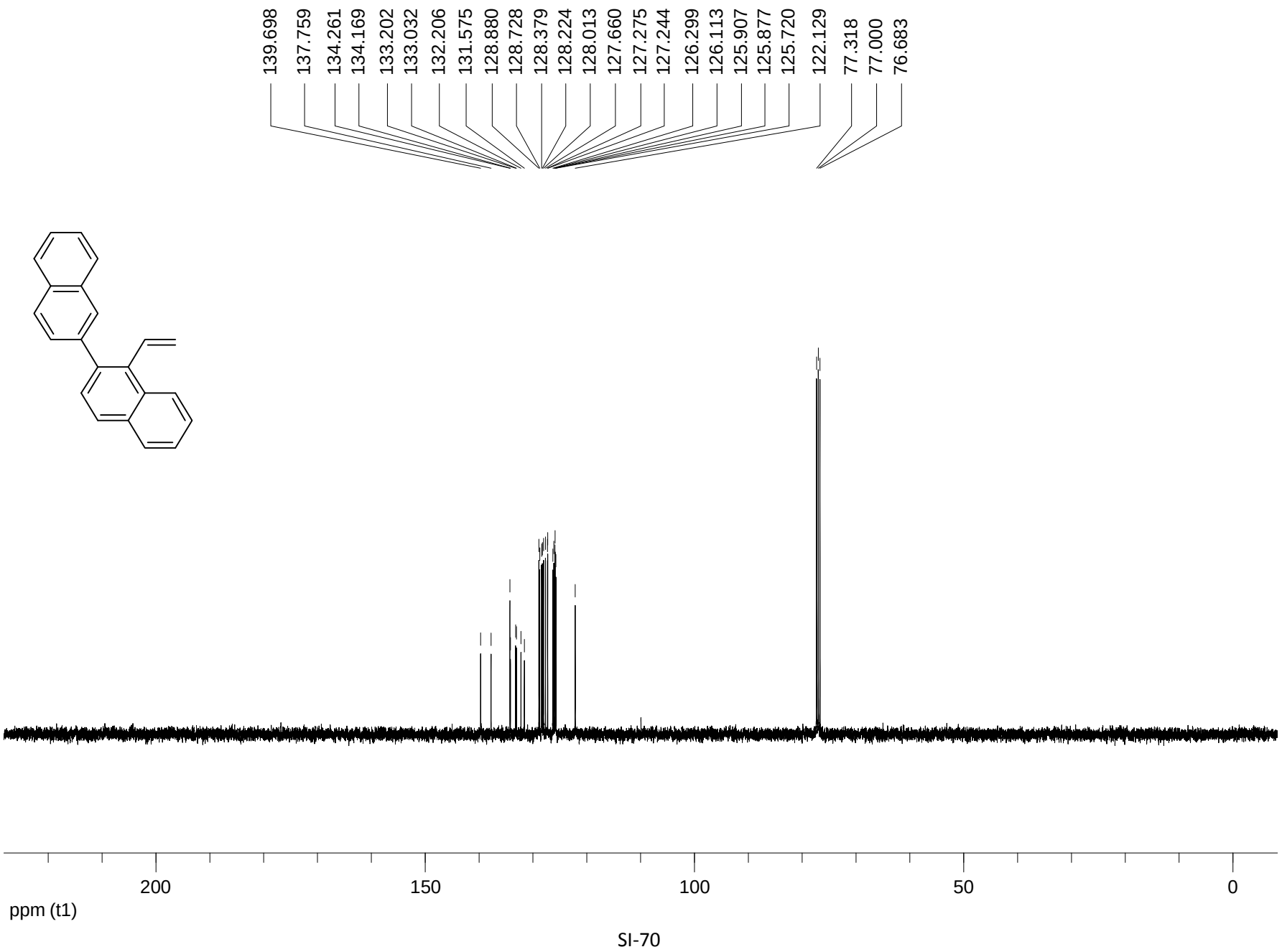
^{13}C NMR Spectrum of **In** (100 MHz, $CDCl_3$)



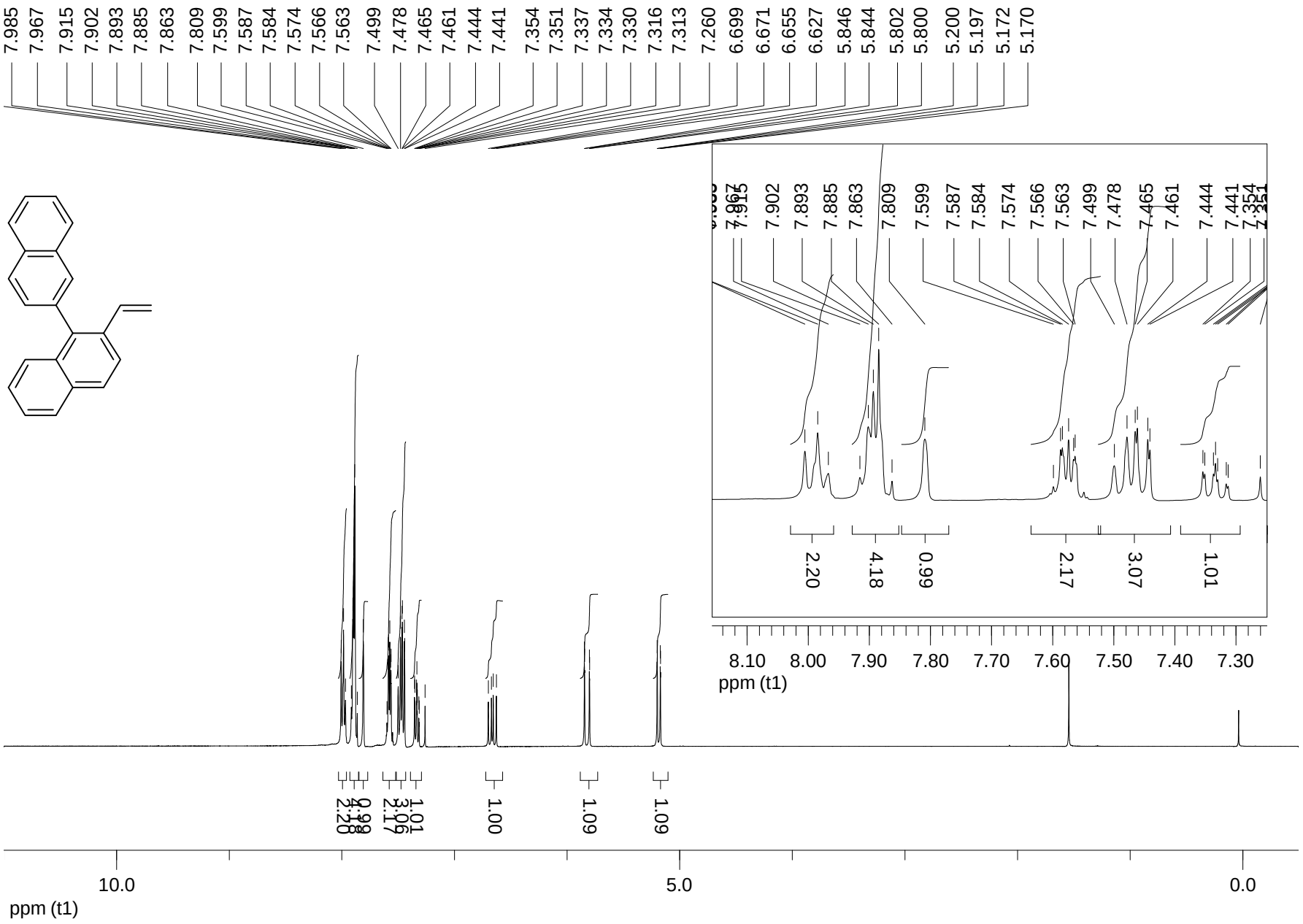
^{1}H NMR Spectrum of **Io** (400 MHz, $CDCl_3$)



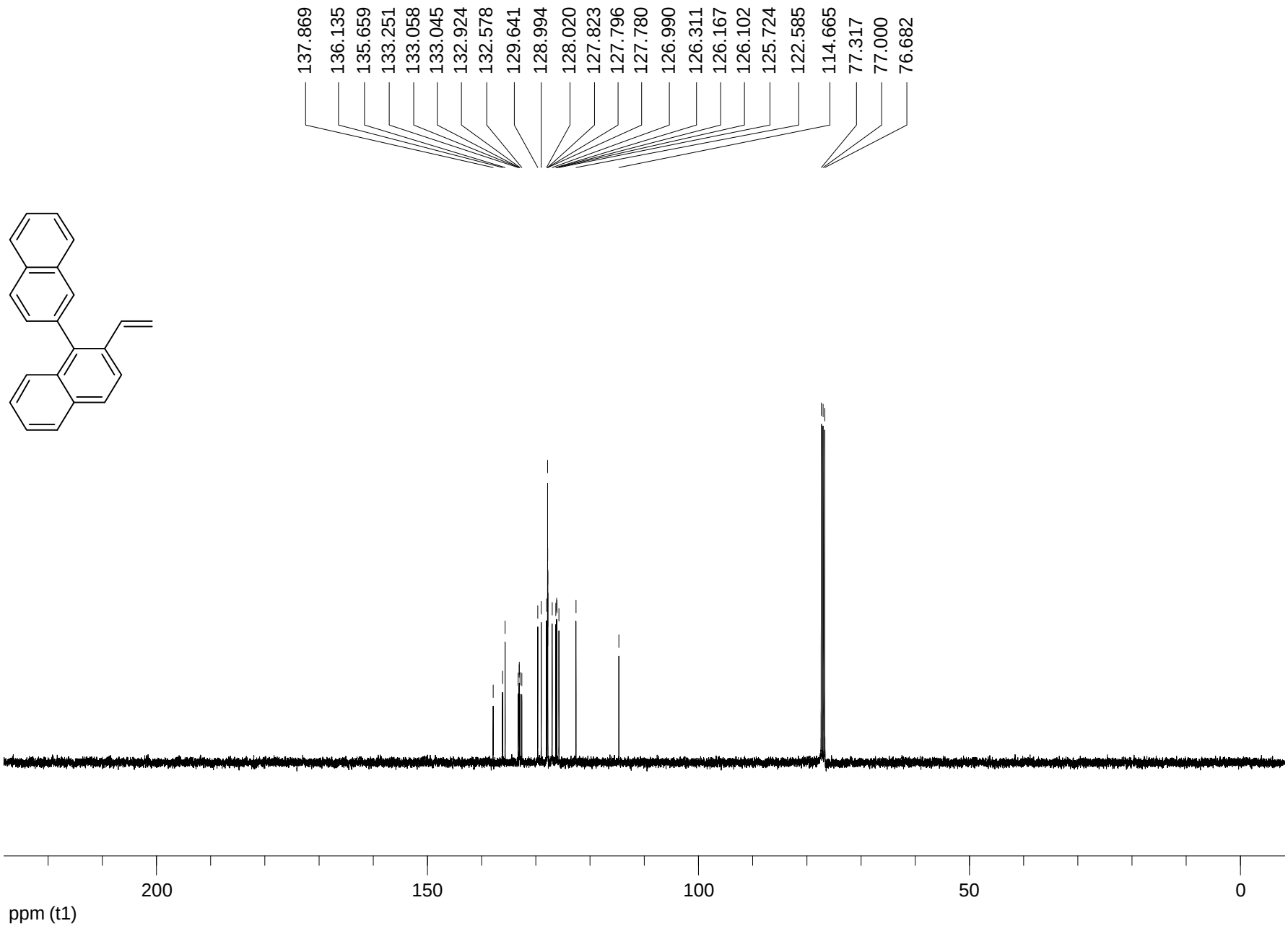
^{13}C NMR Spectrum of **Io** (100 MHz, $CDCl_3$)



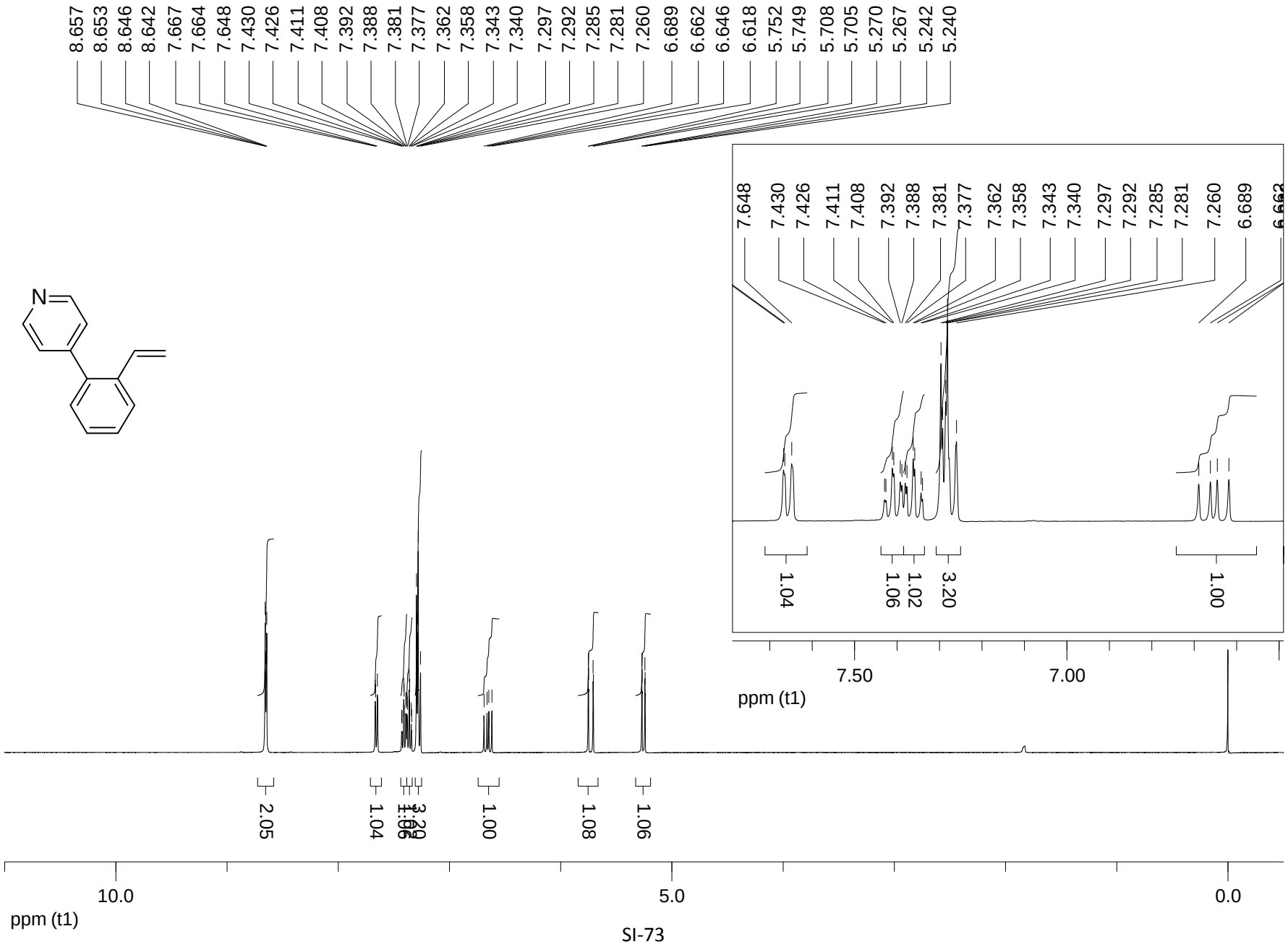
^{1}H NMR Spectrum of **Ip** (400 MHz, $CDCl_3$)



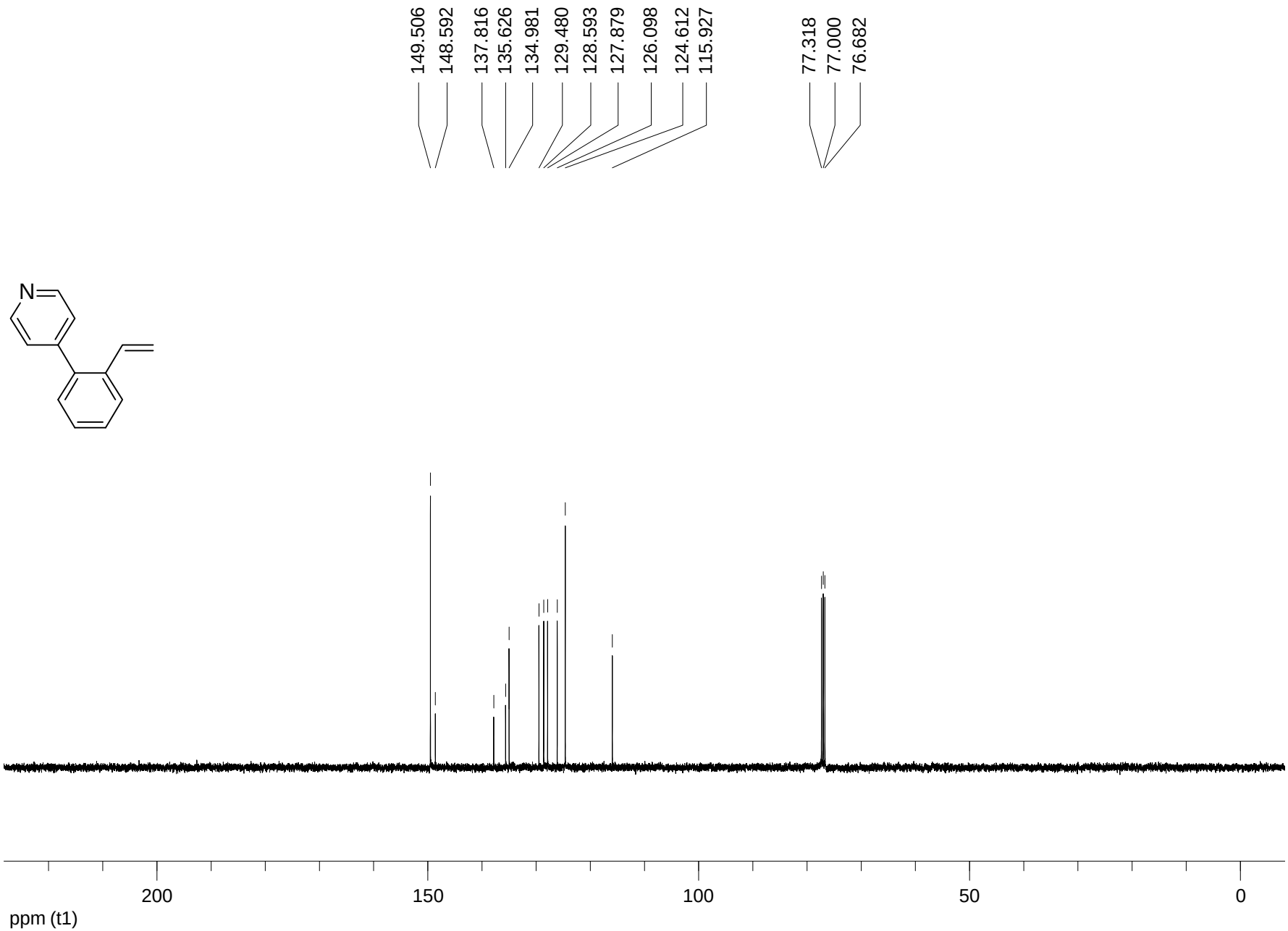
^{13}C NMR Spectrum of **Ip** (100 MHz, $CDCl_3$)



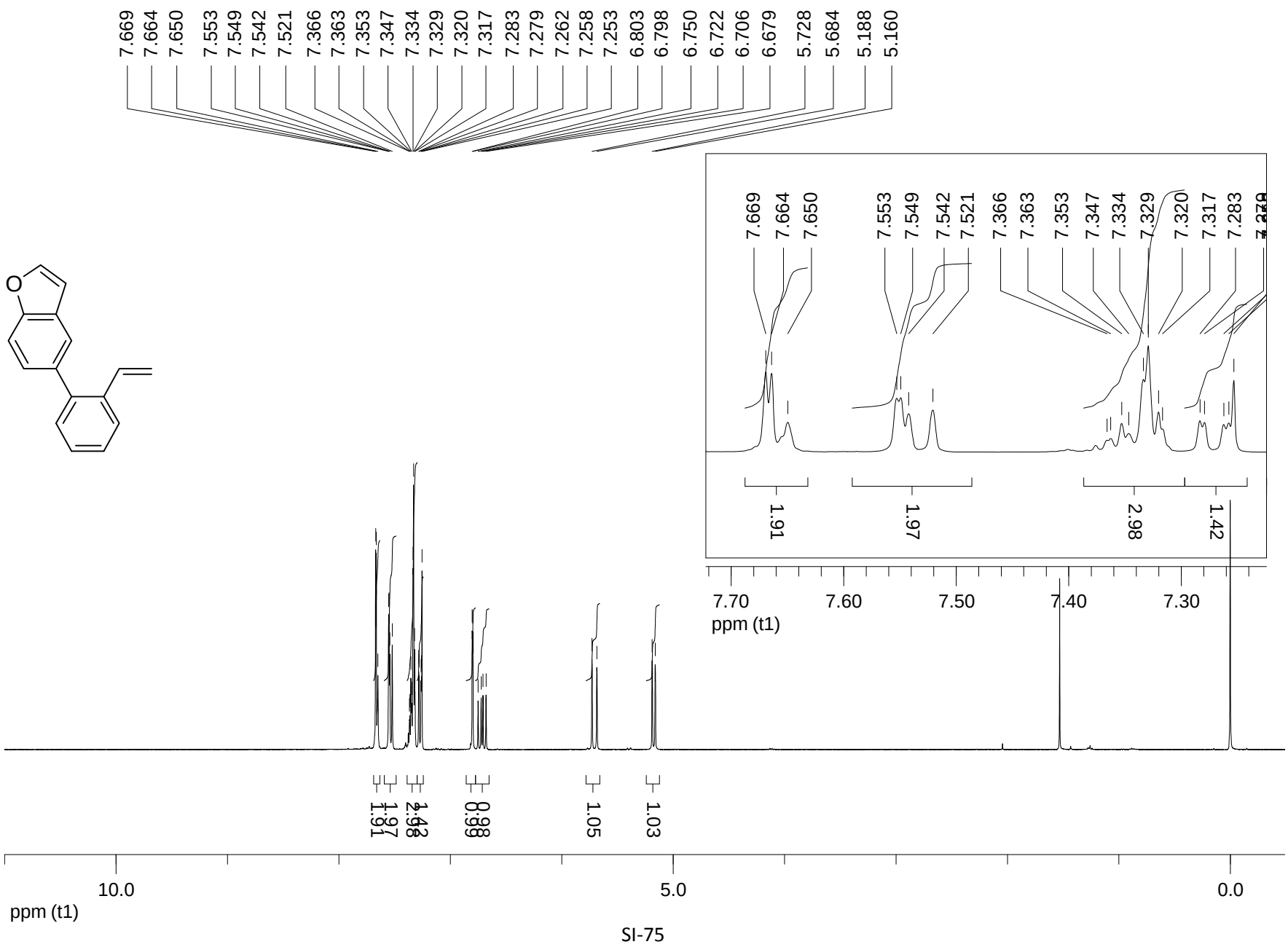
^{1}H NMR Spectrum of **Iq** (400 MHz, $CDCl_3$)



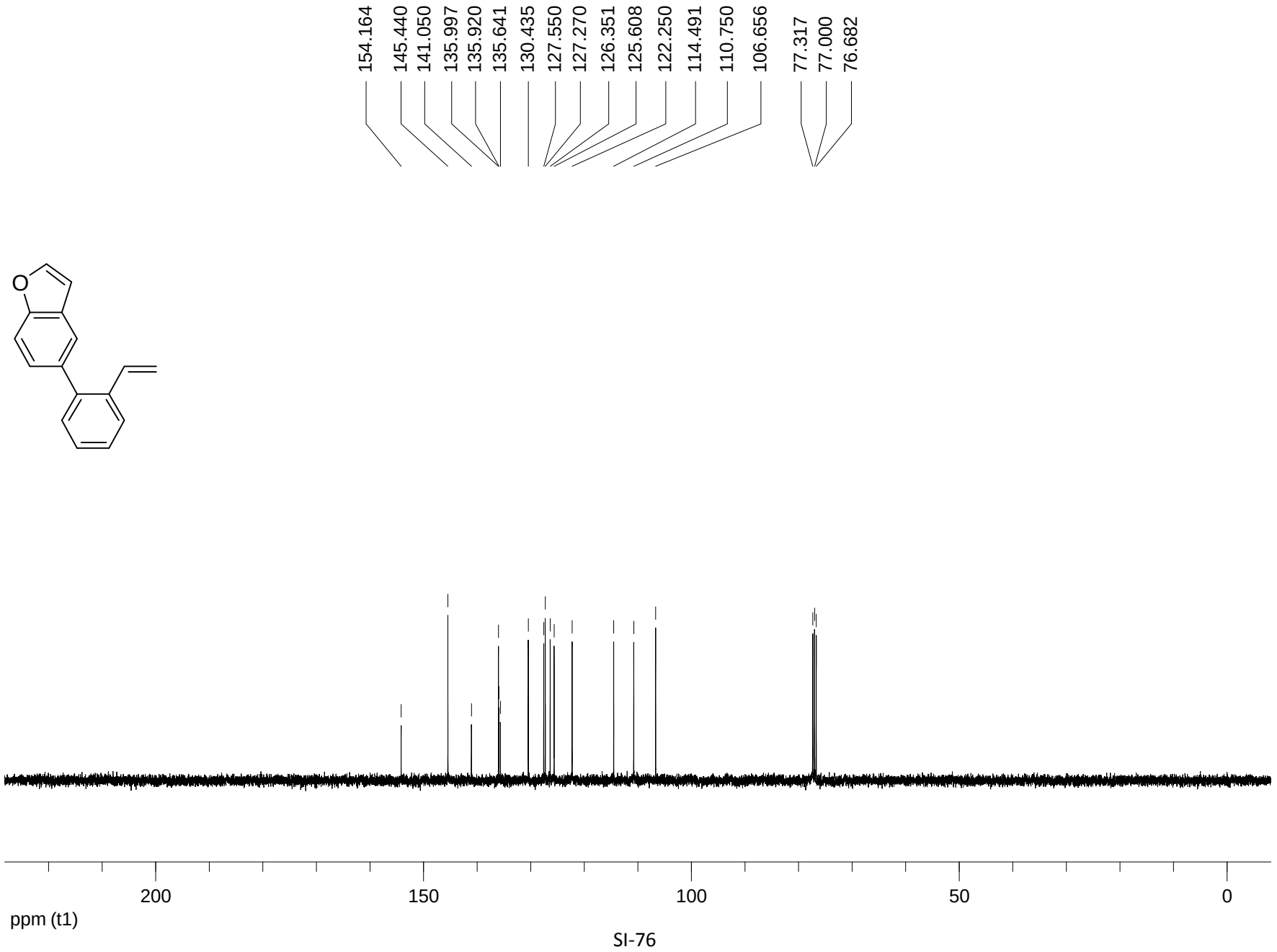
^{13}C NMR Spectrum of **Iq** (100 MHz, $CDCl_3$)



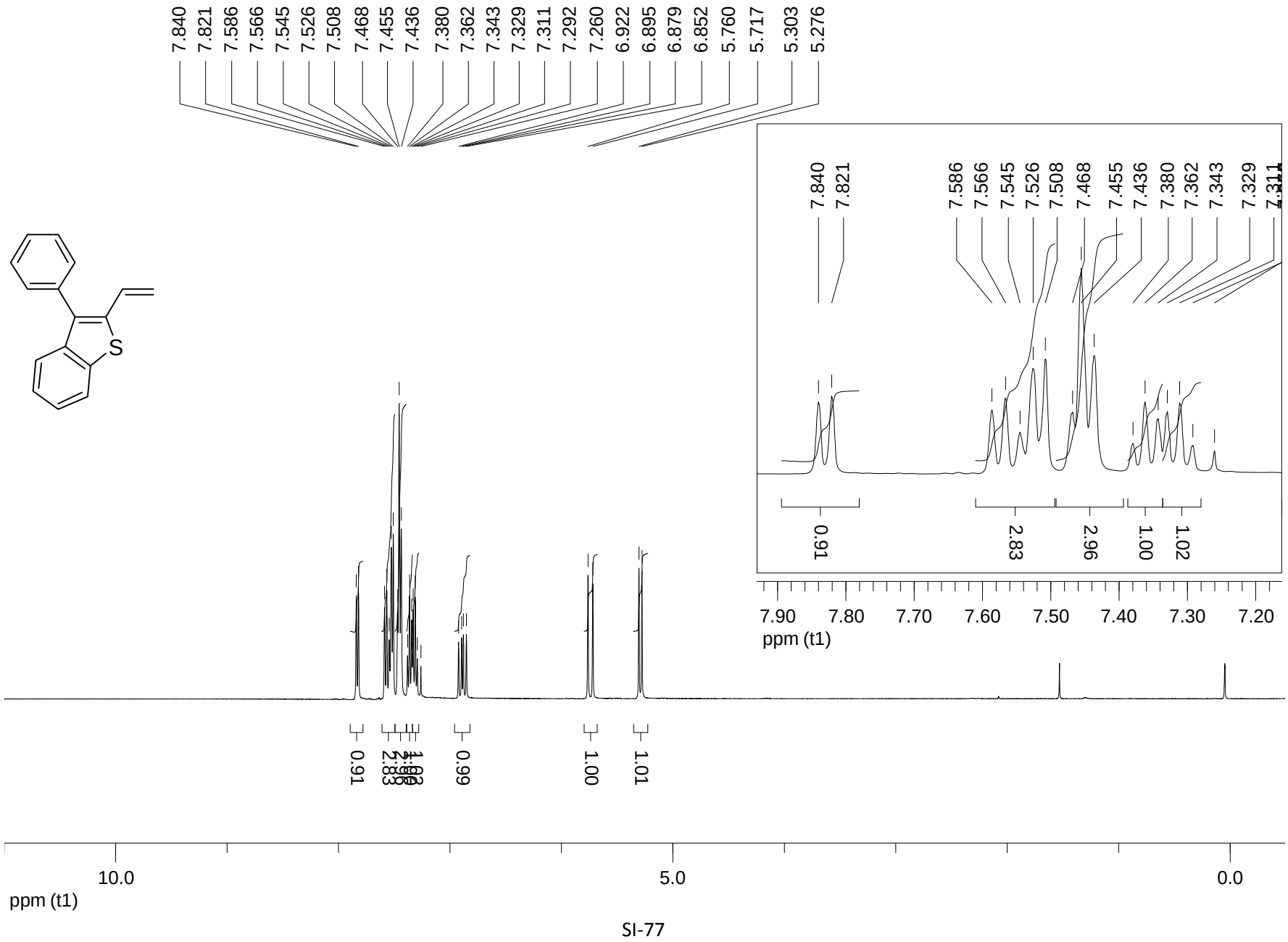
^{1}H NMR Spectrum of **Ir** (400 MHz, $CDCl_3$)



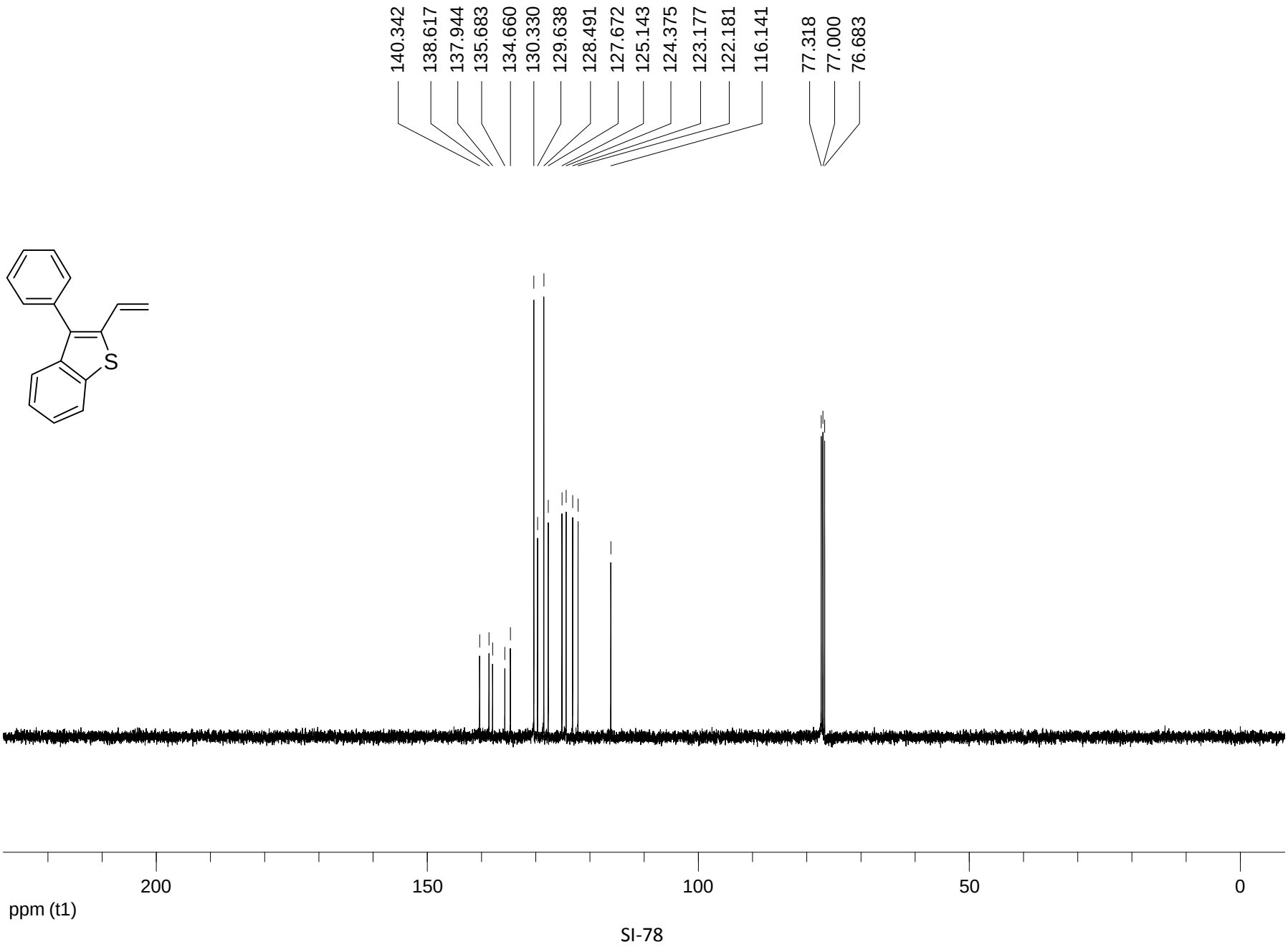
^{13}C NMR Spectrum of **Ir** (100 MHz, $CDCl_3$)



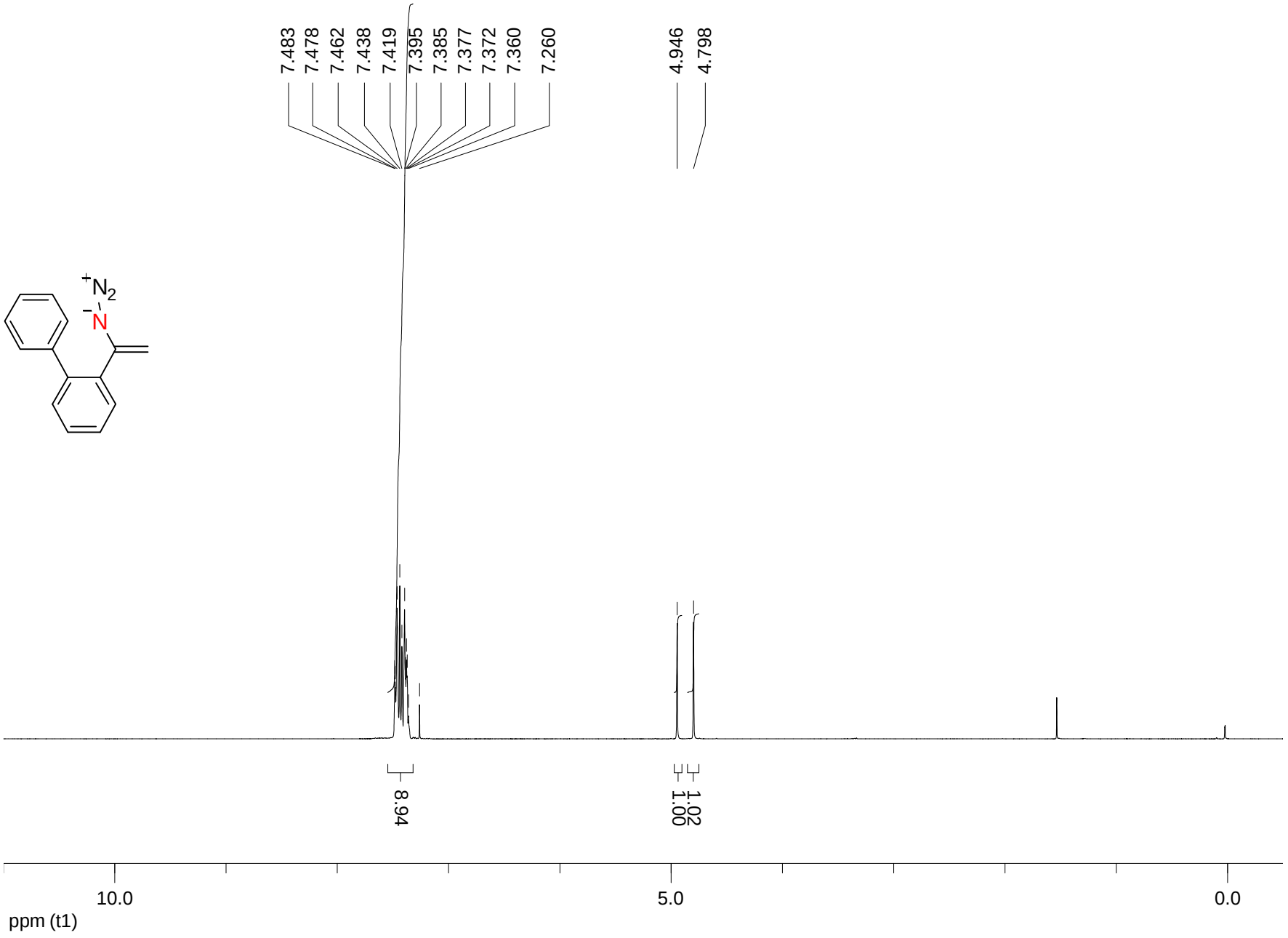
^{1}H NMR Spectrum of **Is** (400 MHz, $CDCl_3$)



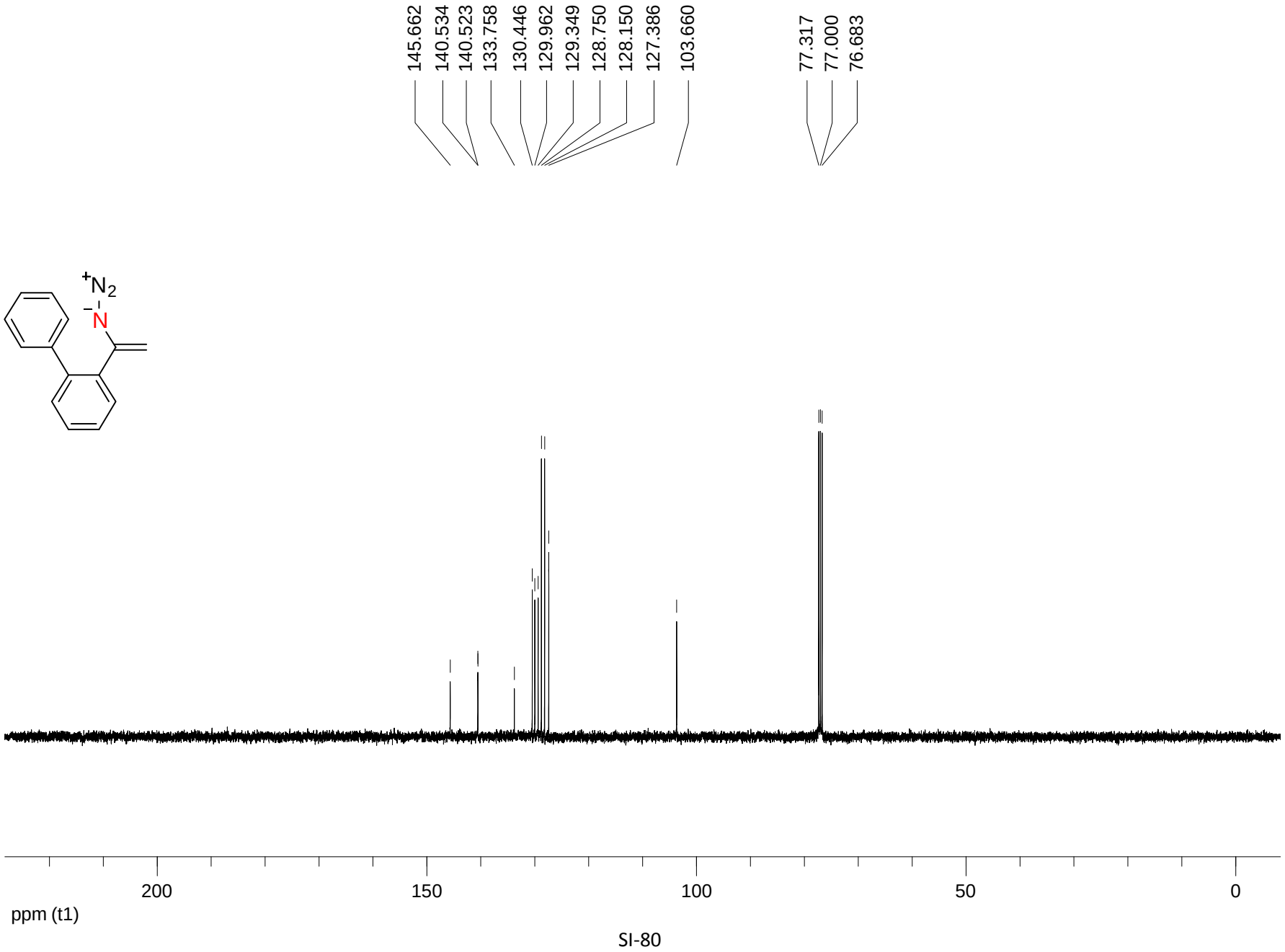
^{13}C NMR Spectrum of **Is** (100 MHz, $CDCl_3$)



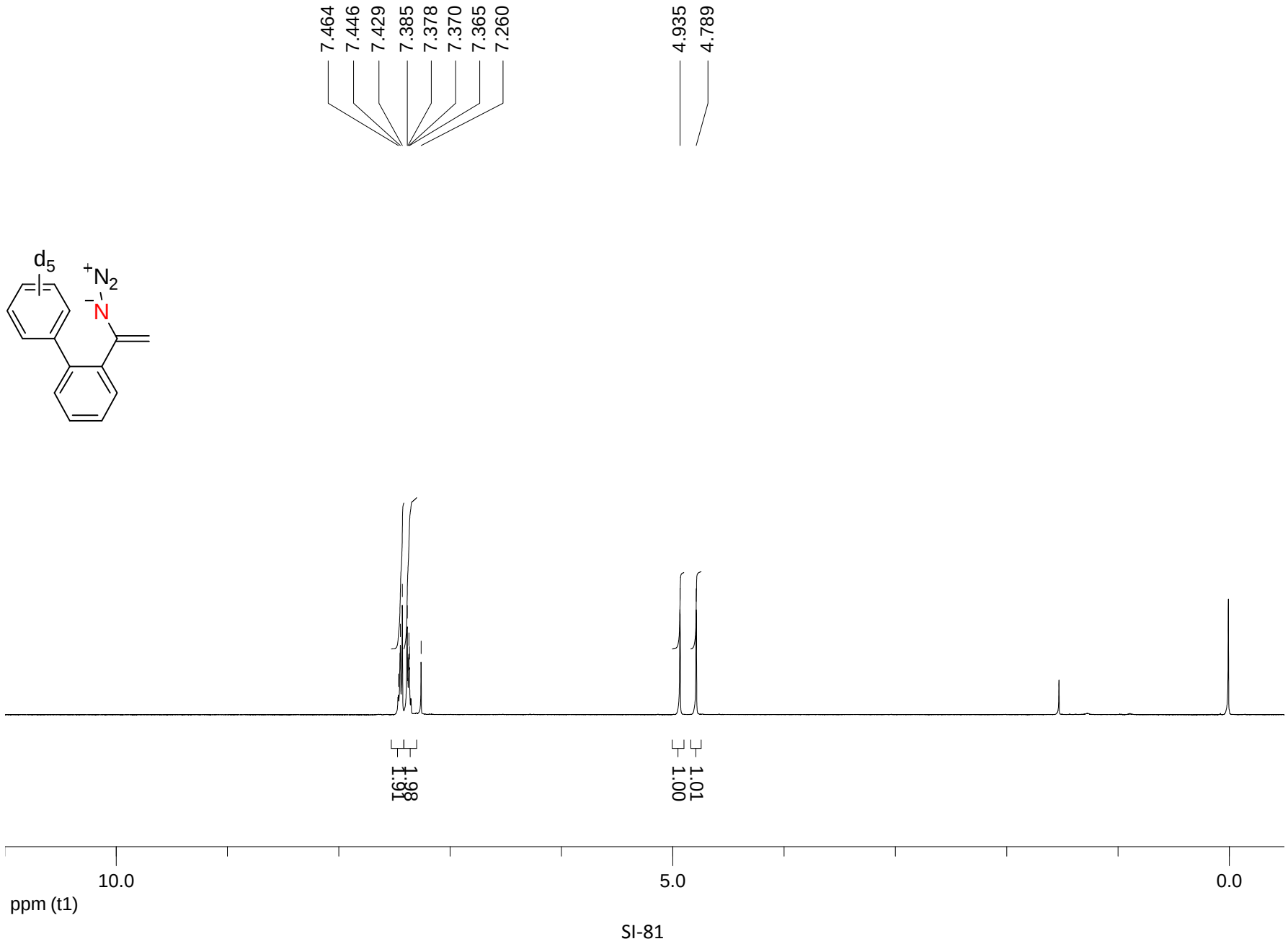
^{1}H NMR Spectrum of **1a** (400 MHz, $CDCl_3$)



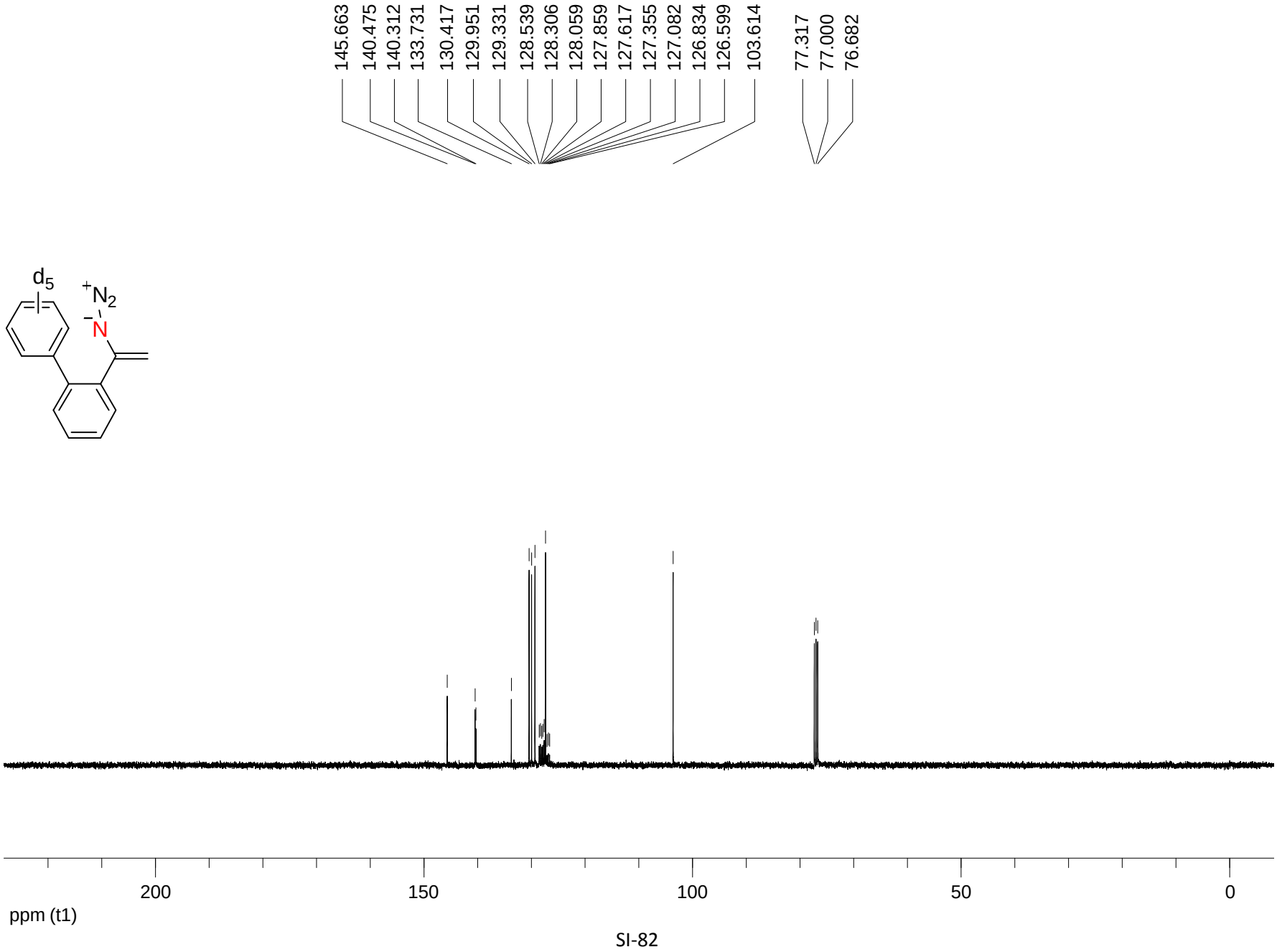
^{13}C NMR Spectrum of **1a** (100 MHz, $CDCl_3$)



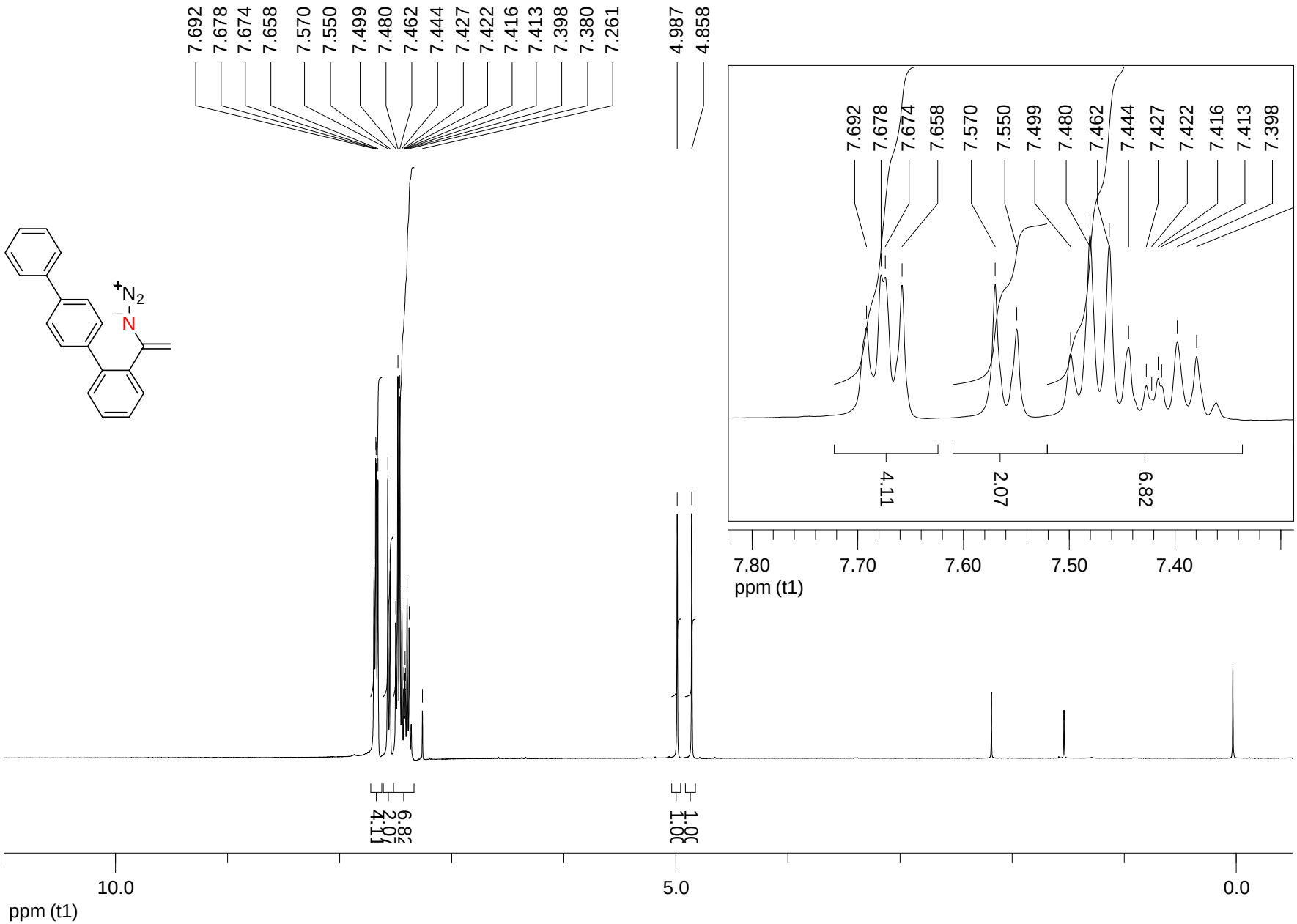
^{1}H NMR Spectrum of **1a-d$_5$** (400 MHz, $CDCl_3$)



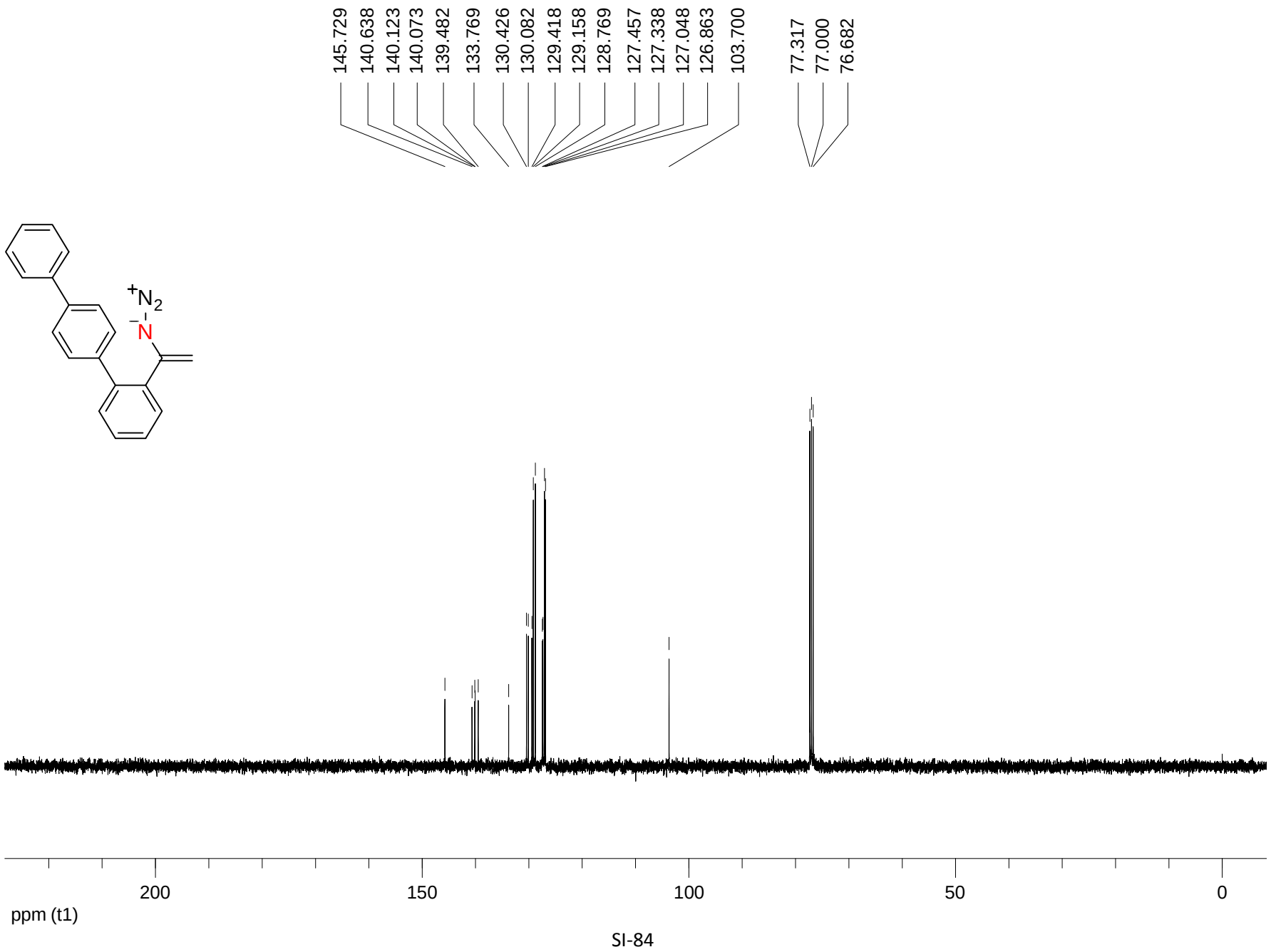
^{13}C NMR Spectrum of **1a-d$_5$** (100 MHz, $CDCl_3$)



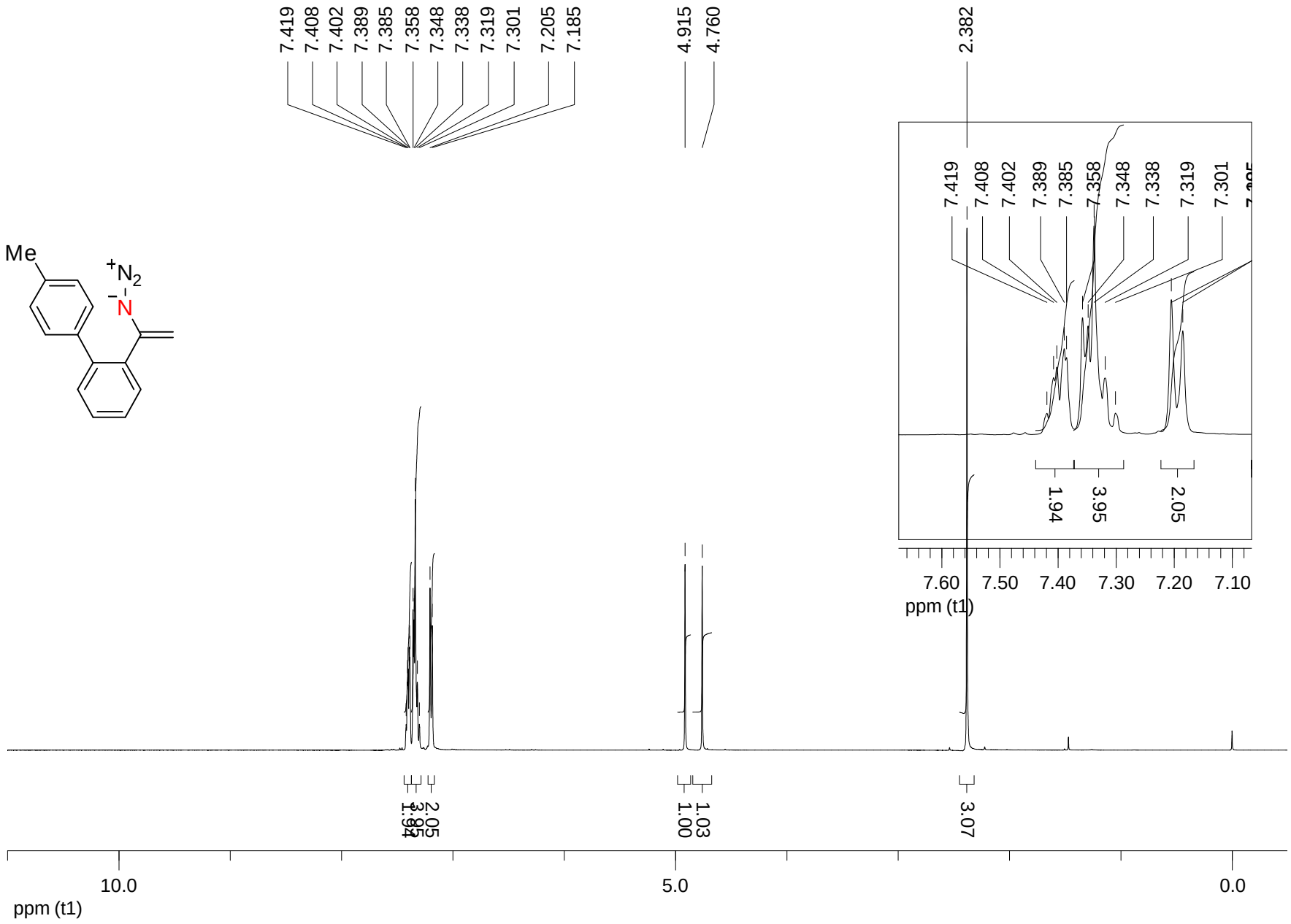
^{1}H NMR Spectrum of **1b** (400 MHz, $CDCl_3$)



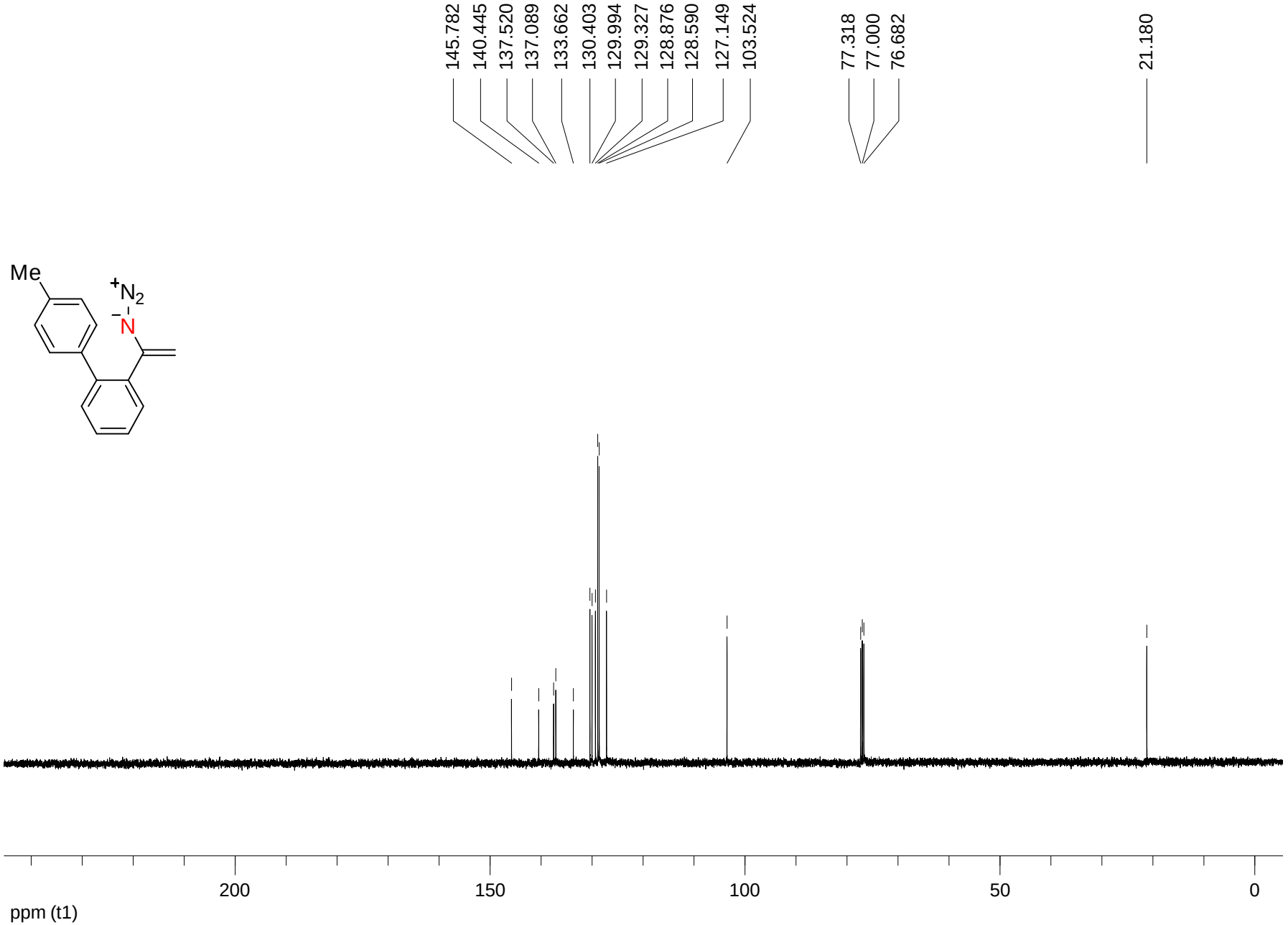
^{13}C NMR Spectrum of **1b** (100 MHz, $CDCl_3$)



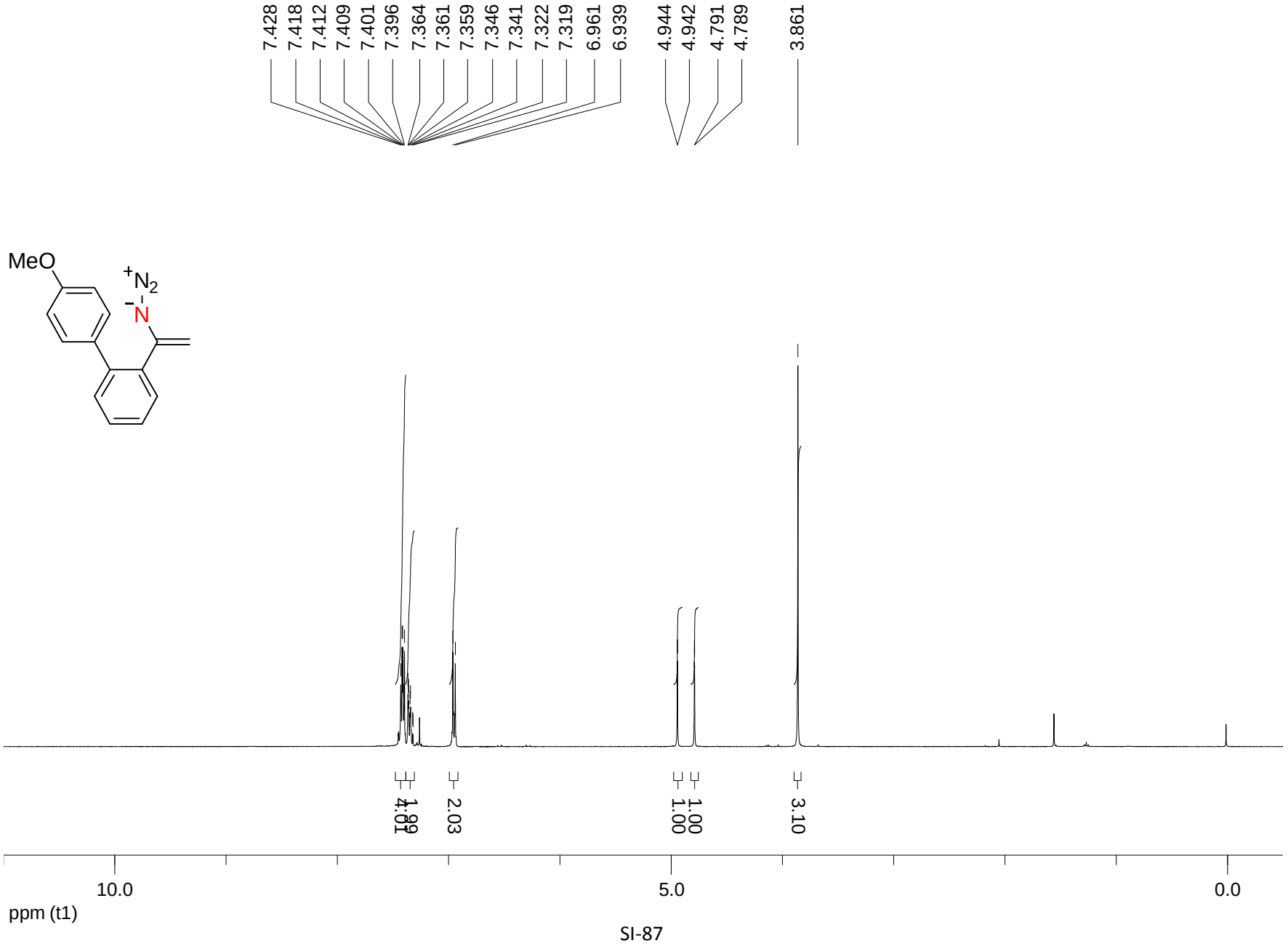
^{1}H NMR Spectrum of **1c** (400 MHz, $CDCl_3$)



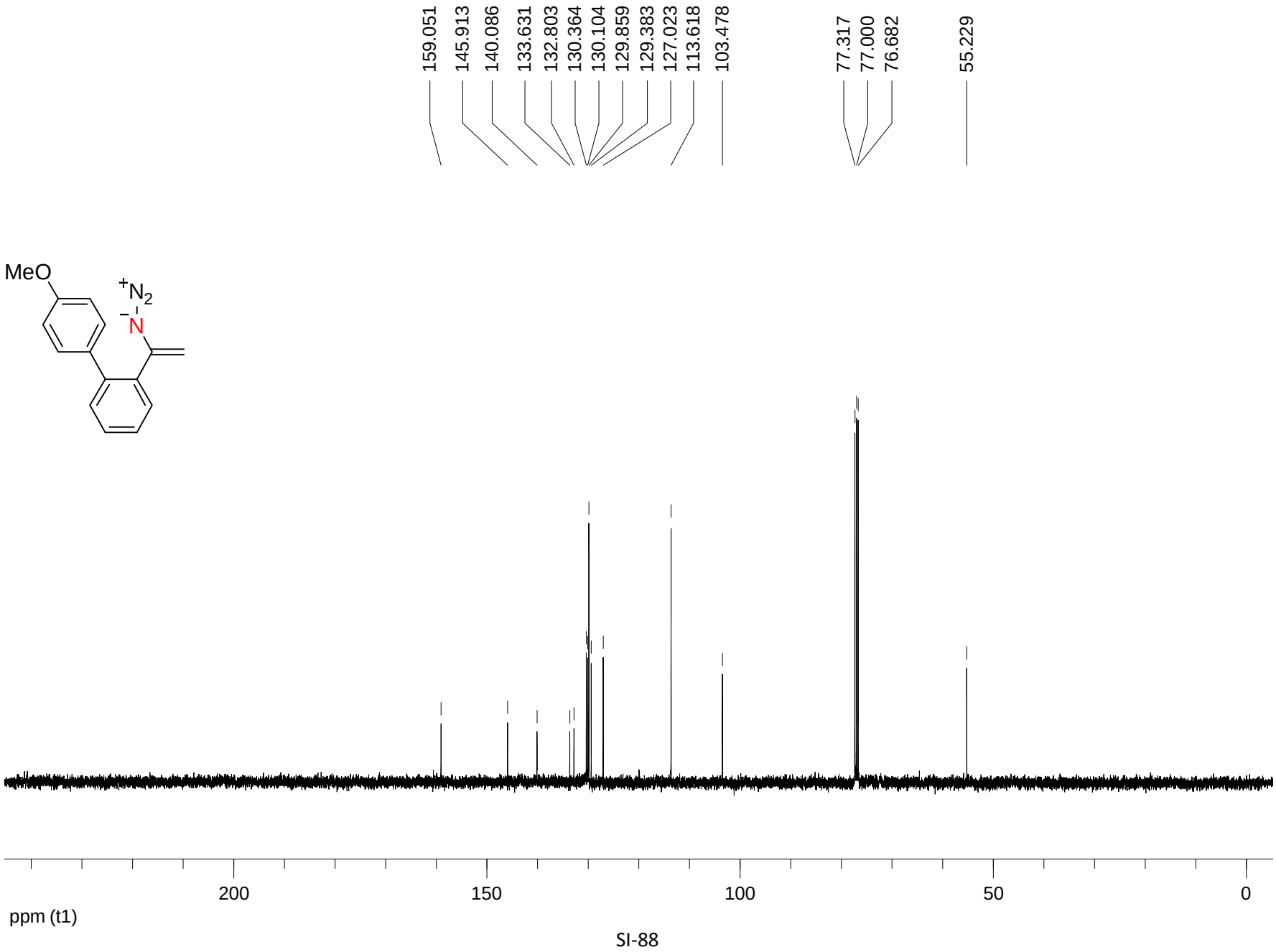
^{13}C NMR Spectrum of **1c** (100 MHz, $CDCl_3$)



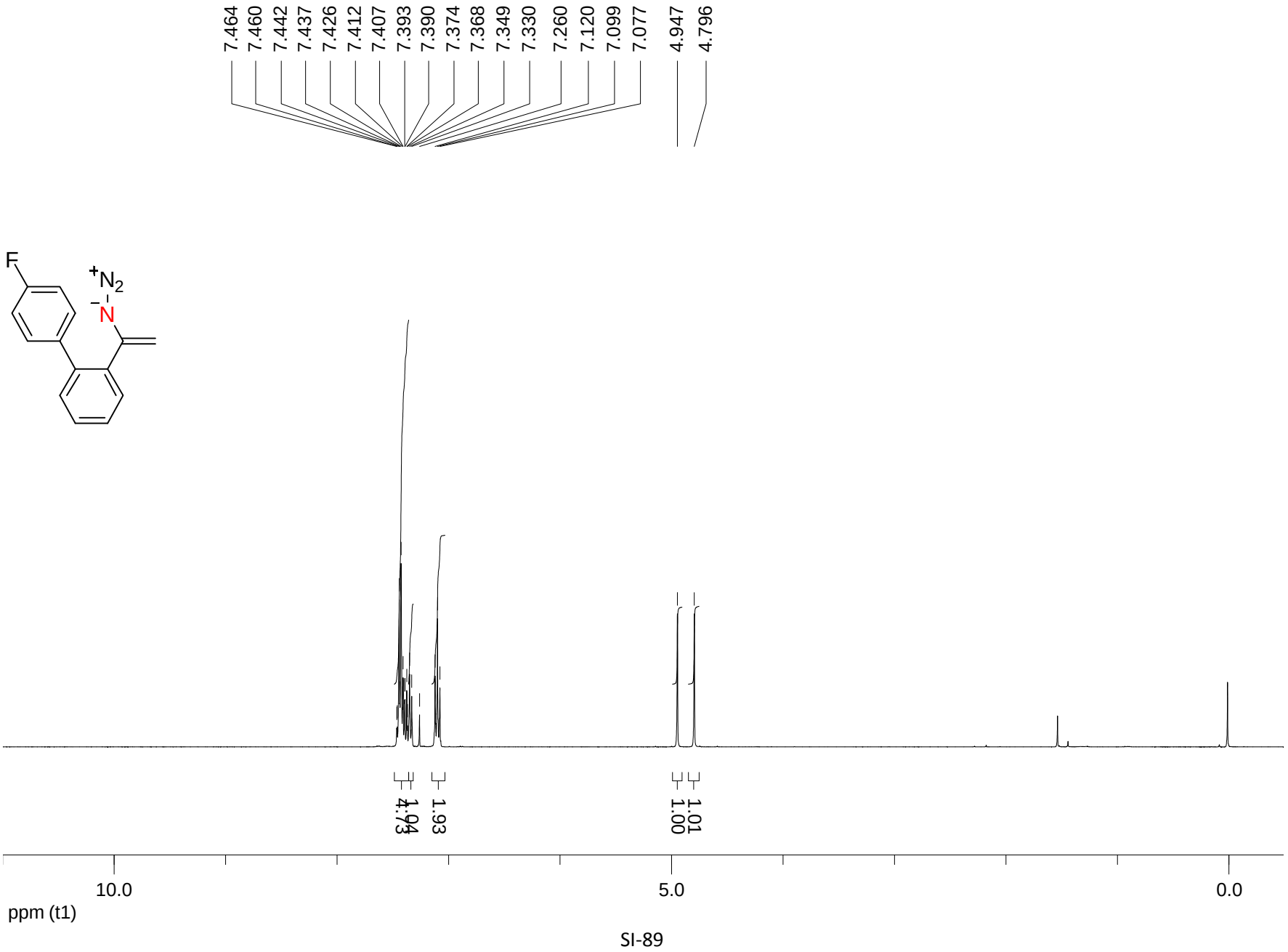
^{1}H NMR Spectrum of **1d** (400 MHz, $CDCl_3$)



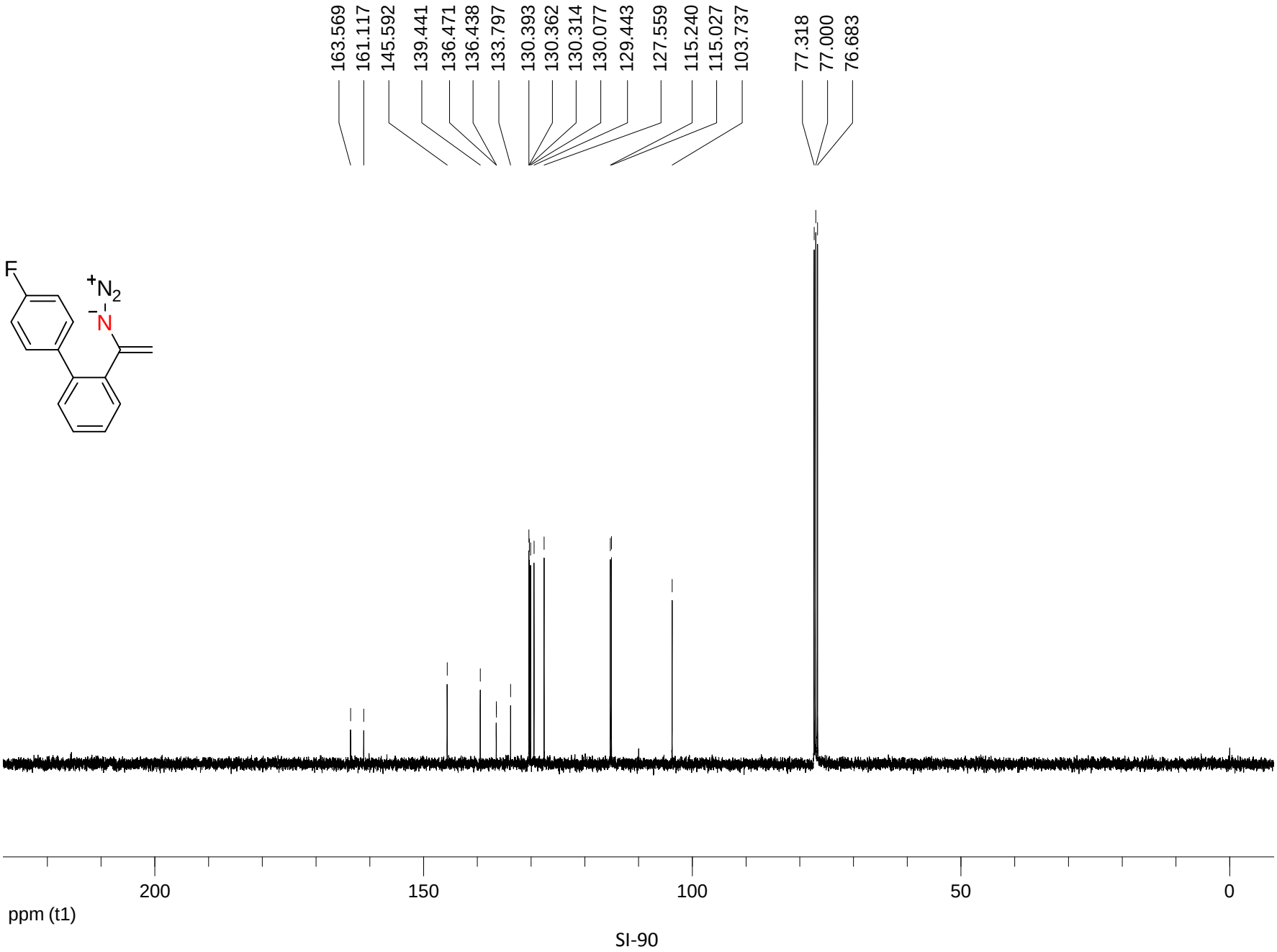
^{13}C NMR Spectrum of **1d** (100 MHz, $CDCl_3$)



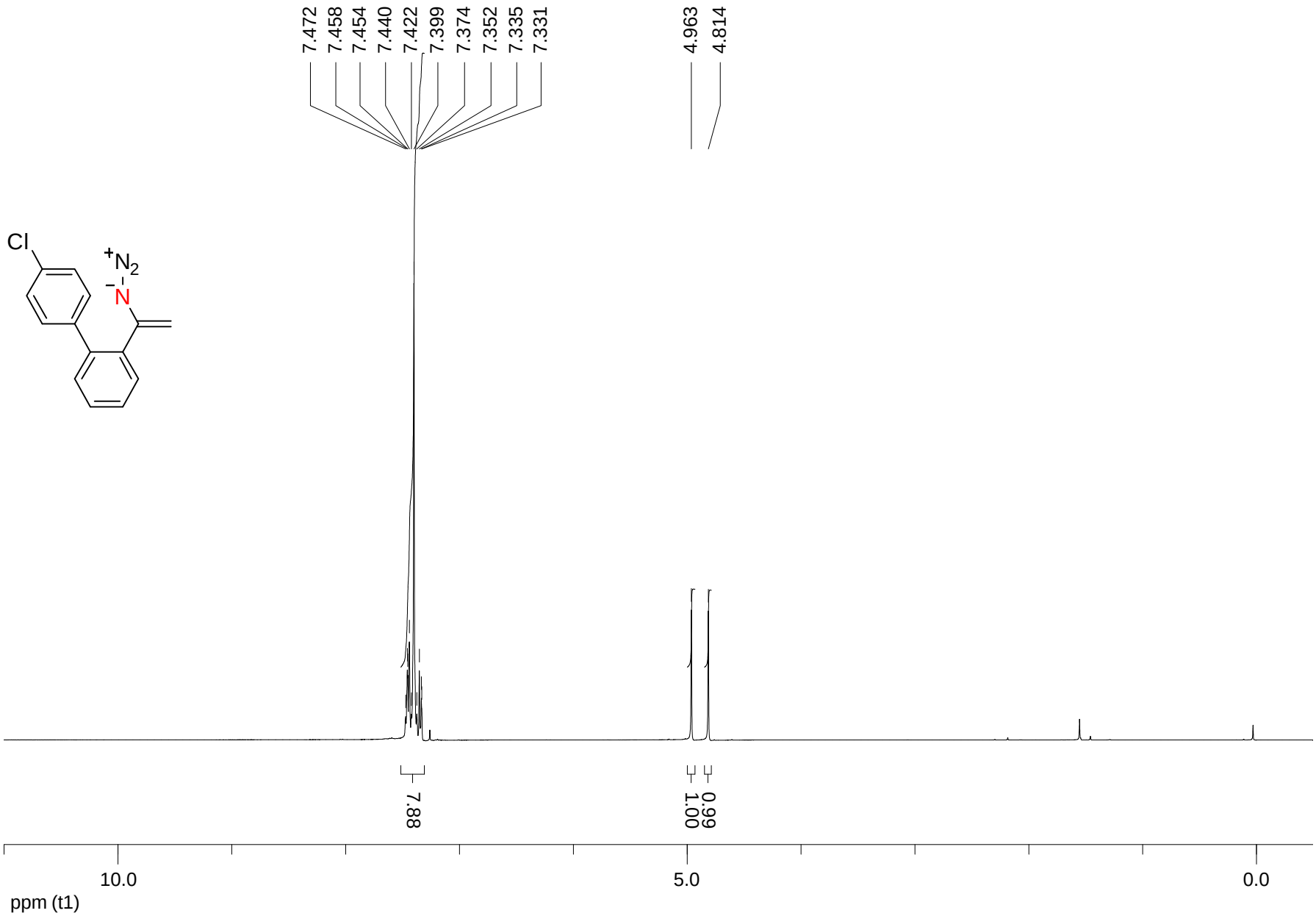
^{1}H NMR Spectrum of **1e** (400 MHz, $CDCl_3$)



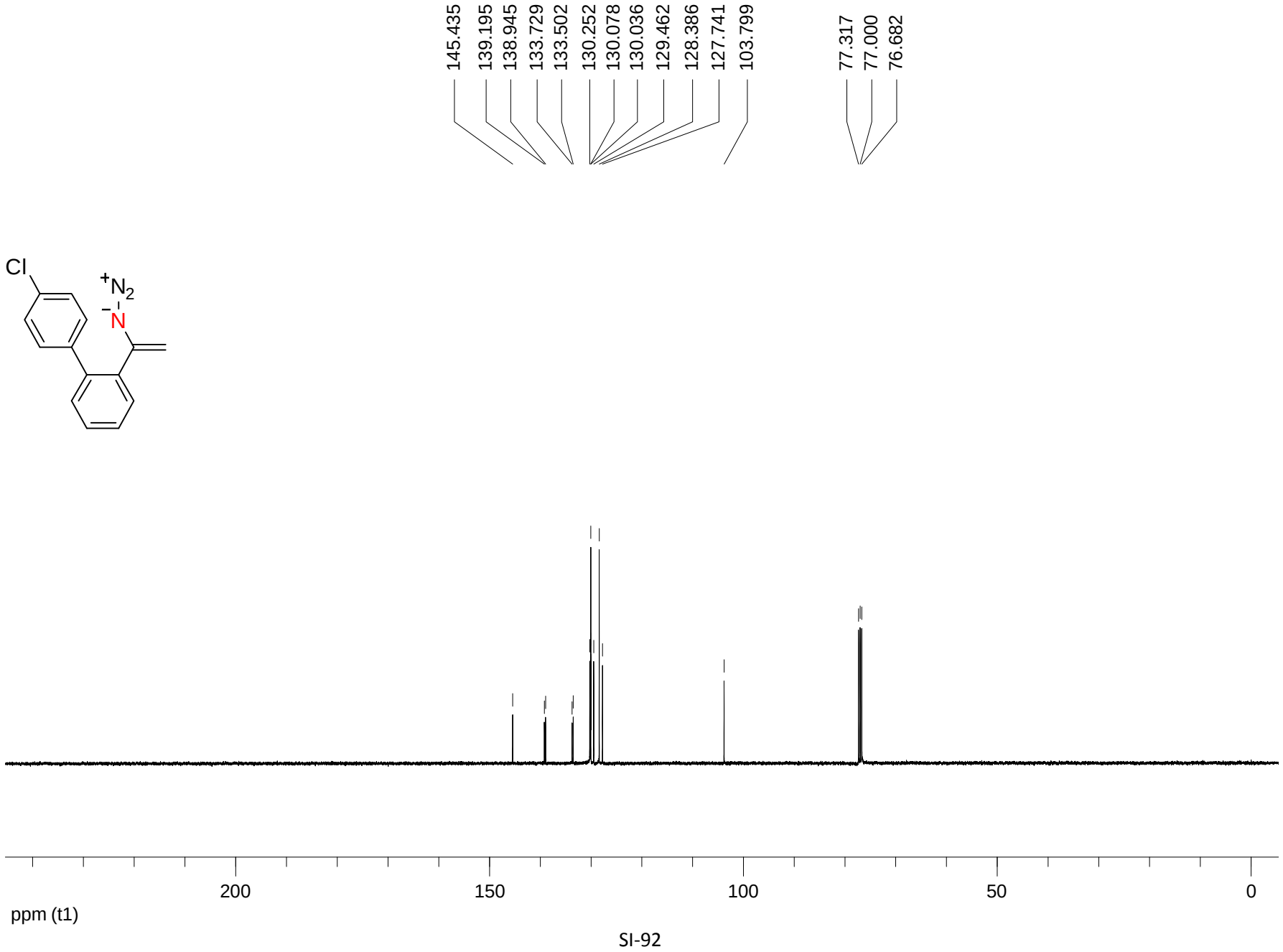
^{13}C NMR Spectrum of **1e** (100 MHz, $CDCl_3$)



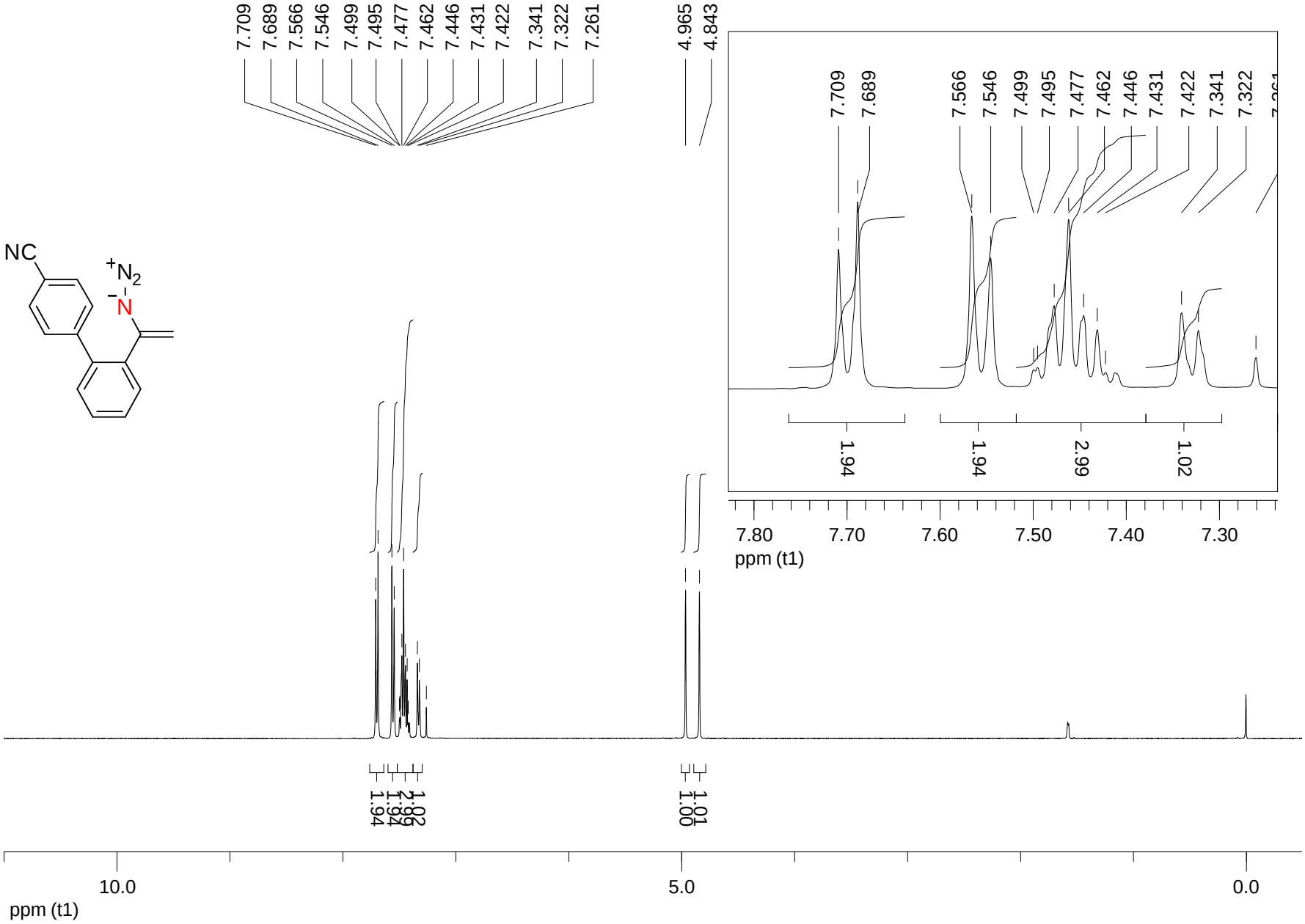
^{1}H NMR Spectrum of **1f** (400 MHz, $CDCl_3$)



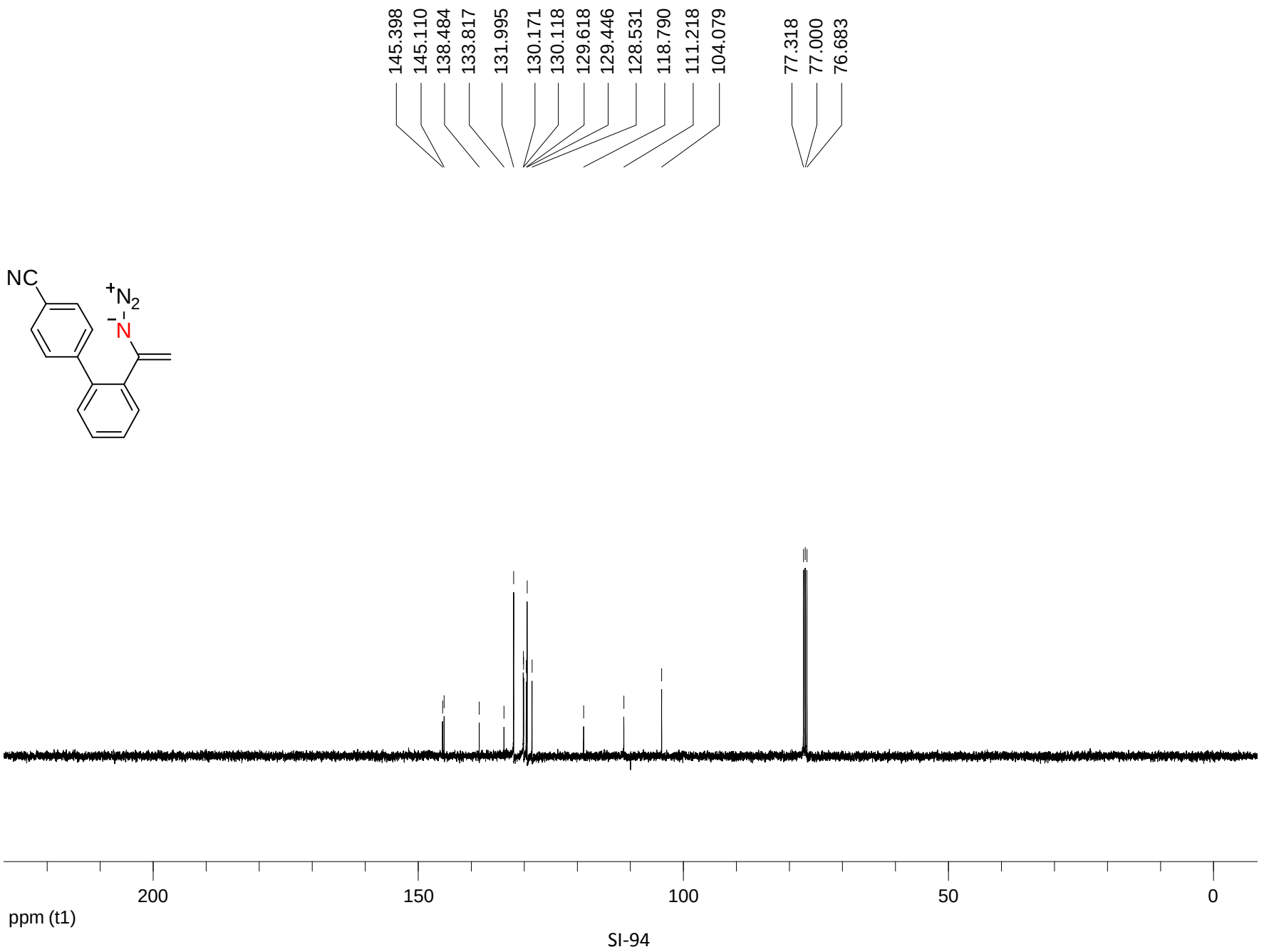
^{13}C NMR Spectrum of **1f** (100 MHz, $CDCl_3$)



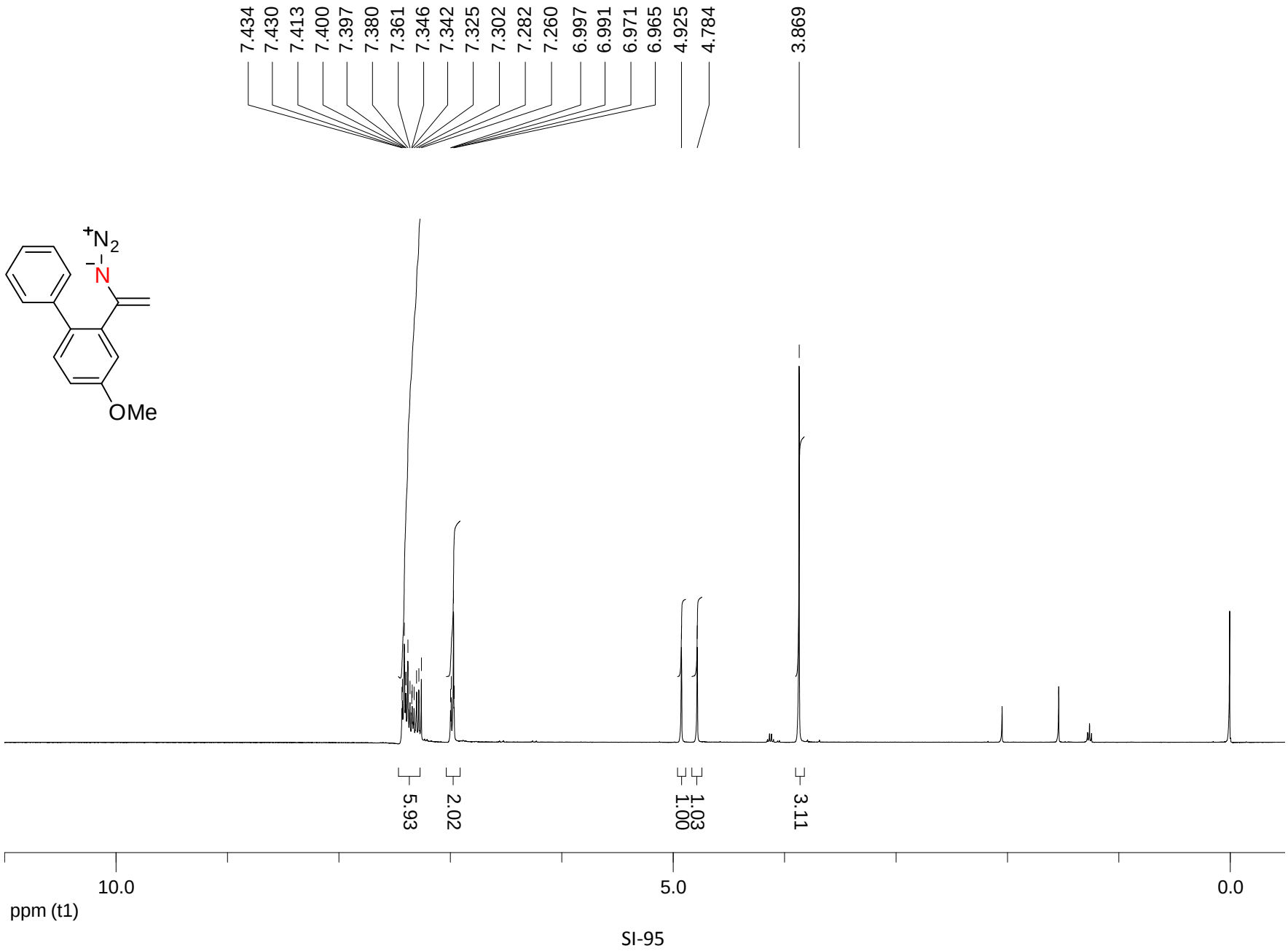
^{1}H NMR Spectrum of **1g** (400 MHz, $CDCl_3$)



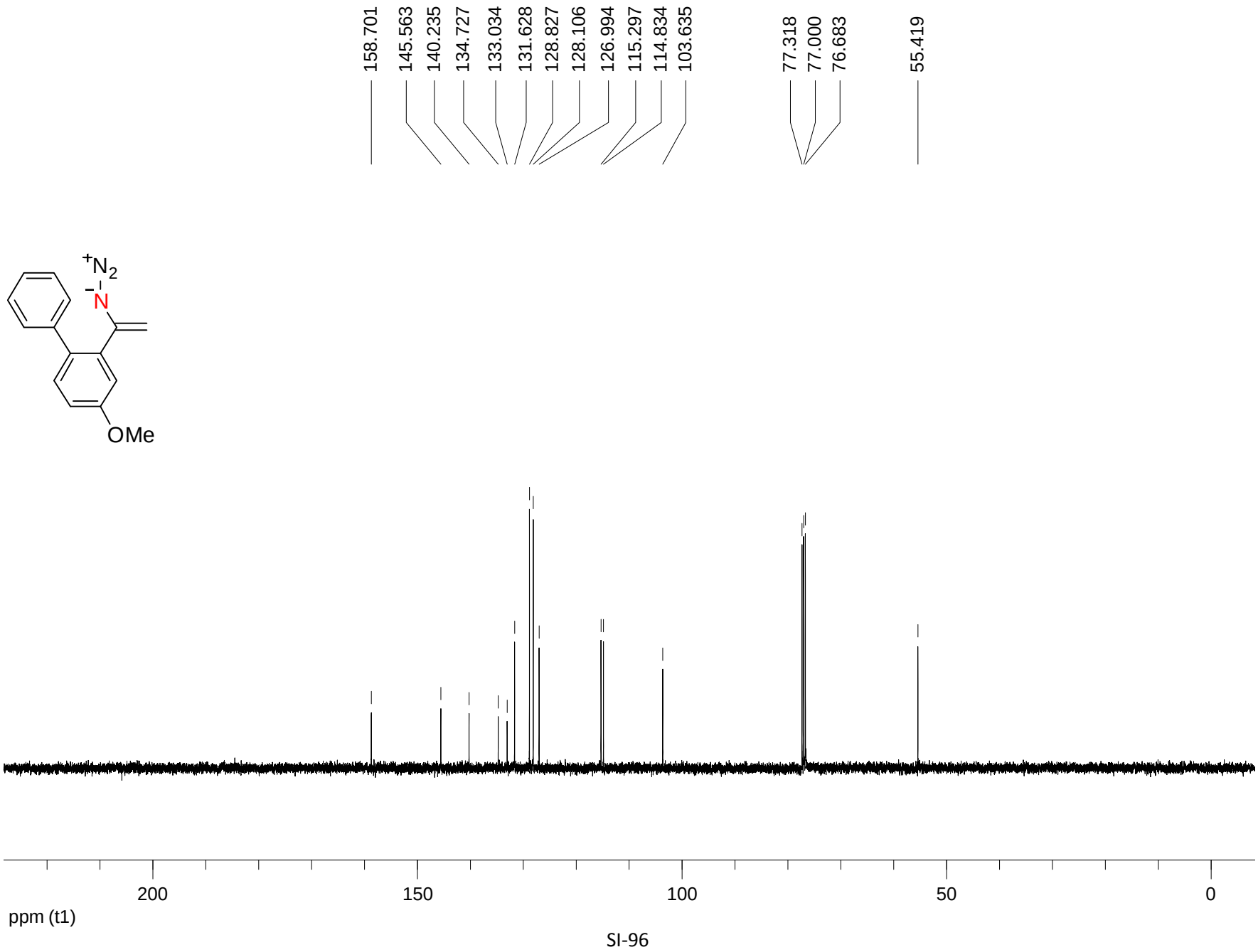
^{13}C NMR Spectrum of **1g** (100 MHz, $CDCl_3$)



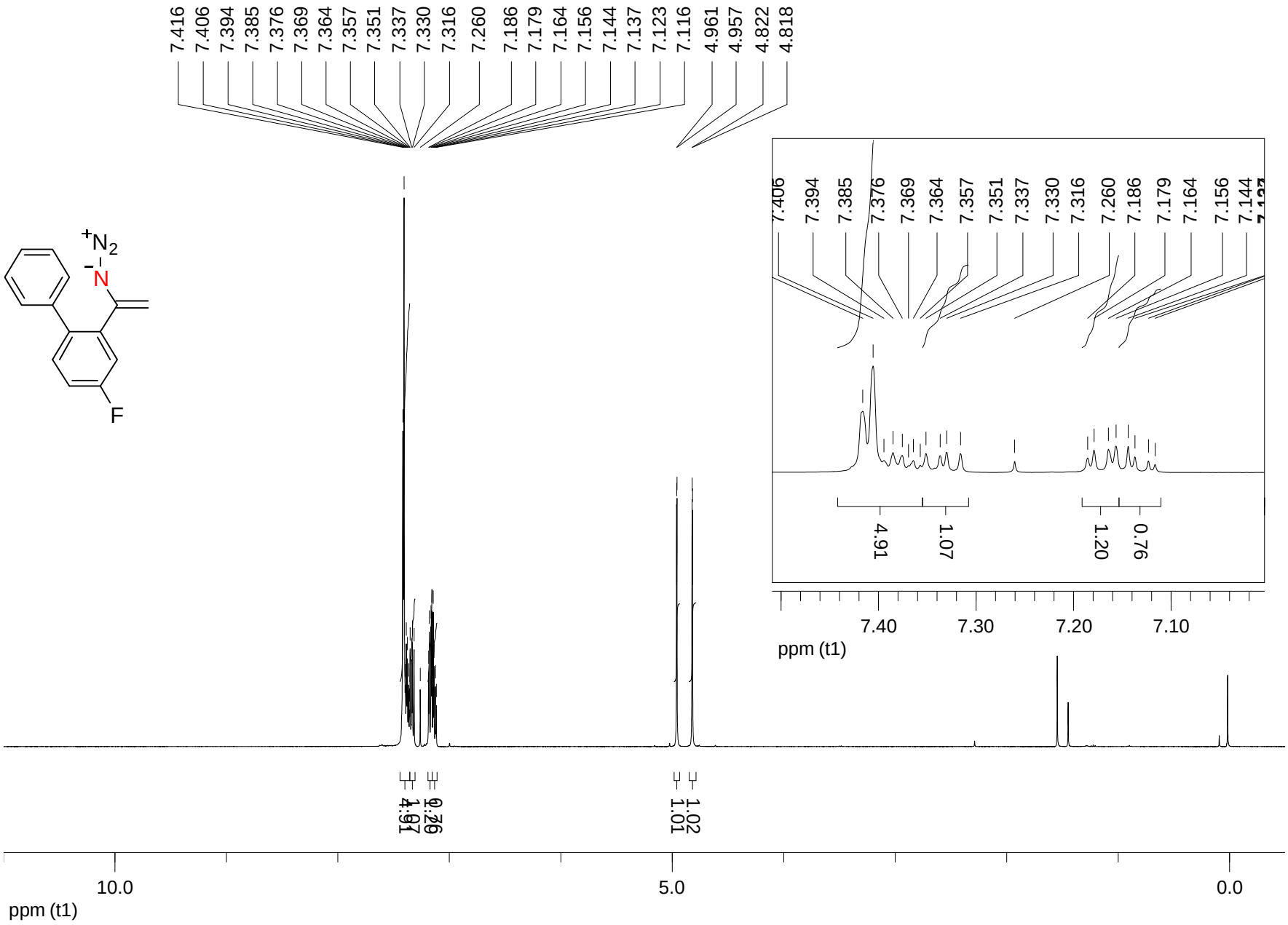
^{1}H NMR Spectrum of **1h** (400 MHz, $CDCl_3$)



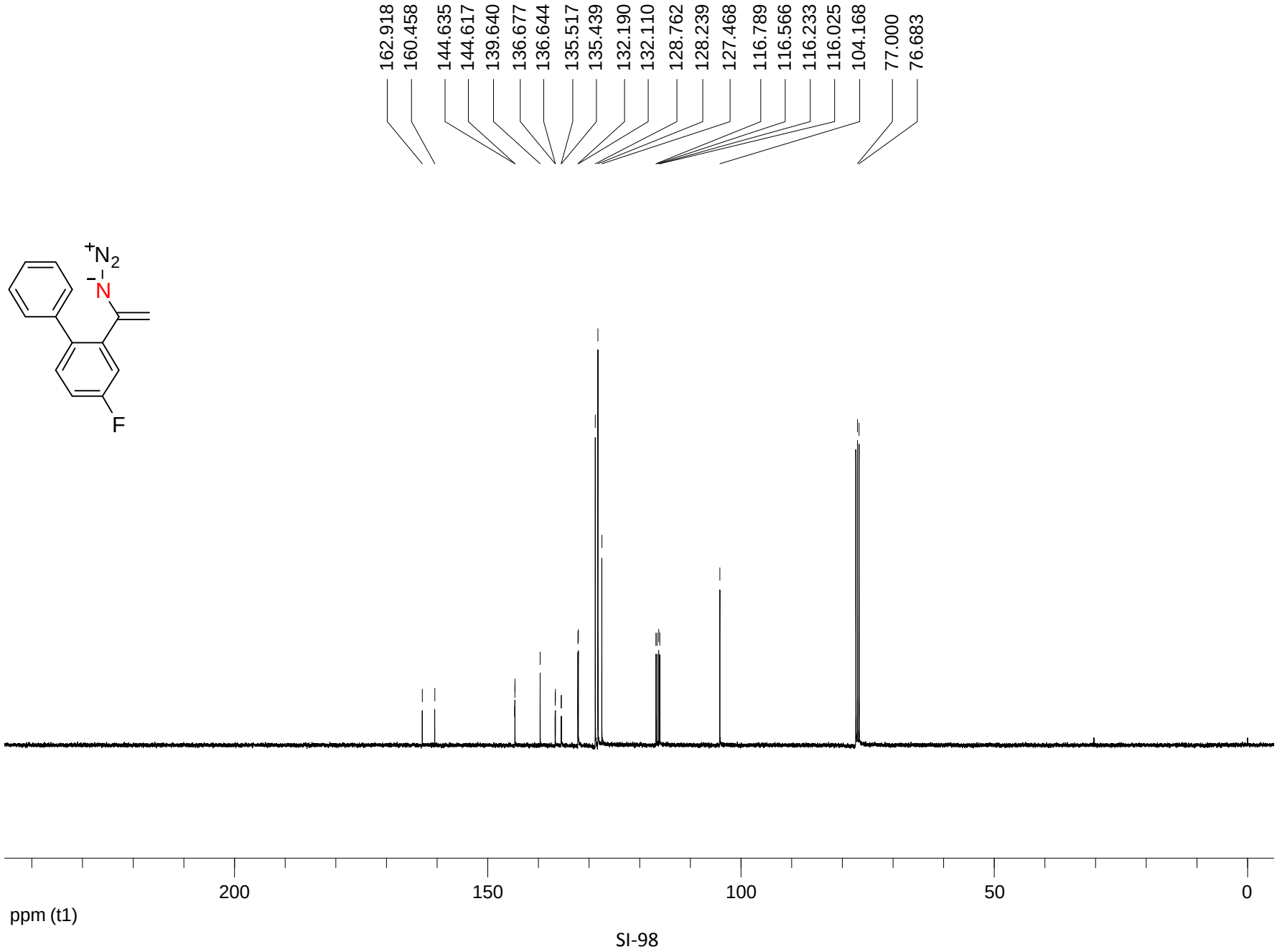
^{13}C NMR Spectrum of **1h** (100 MHz, $CDCl_3$)



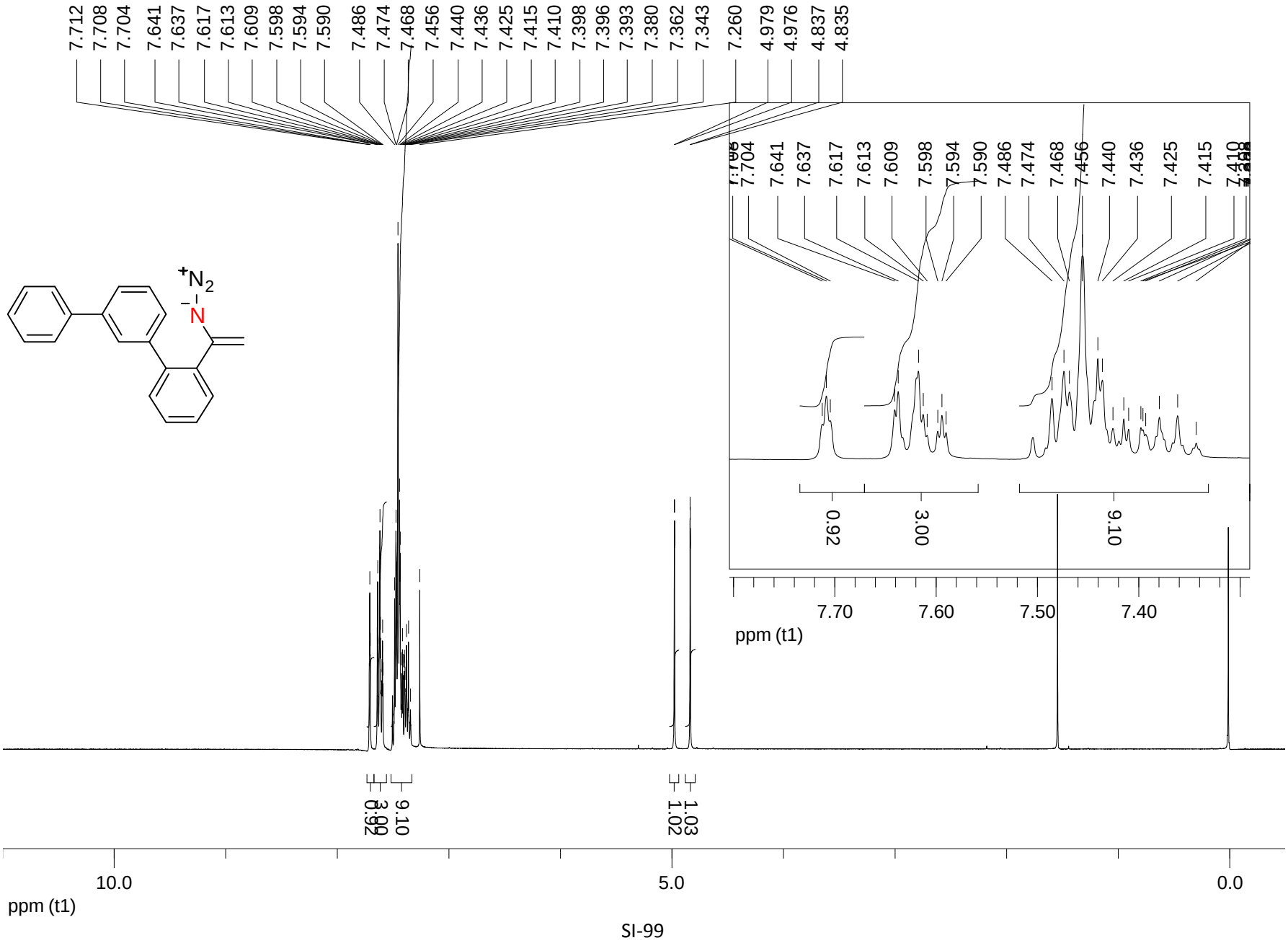
^{1}H NMR Spectrum of **1i** (400 MHz, $CDCl_3$)



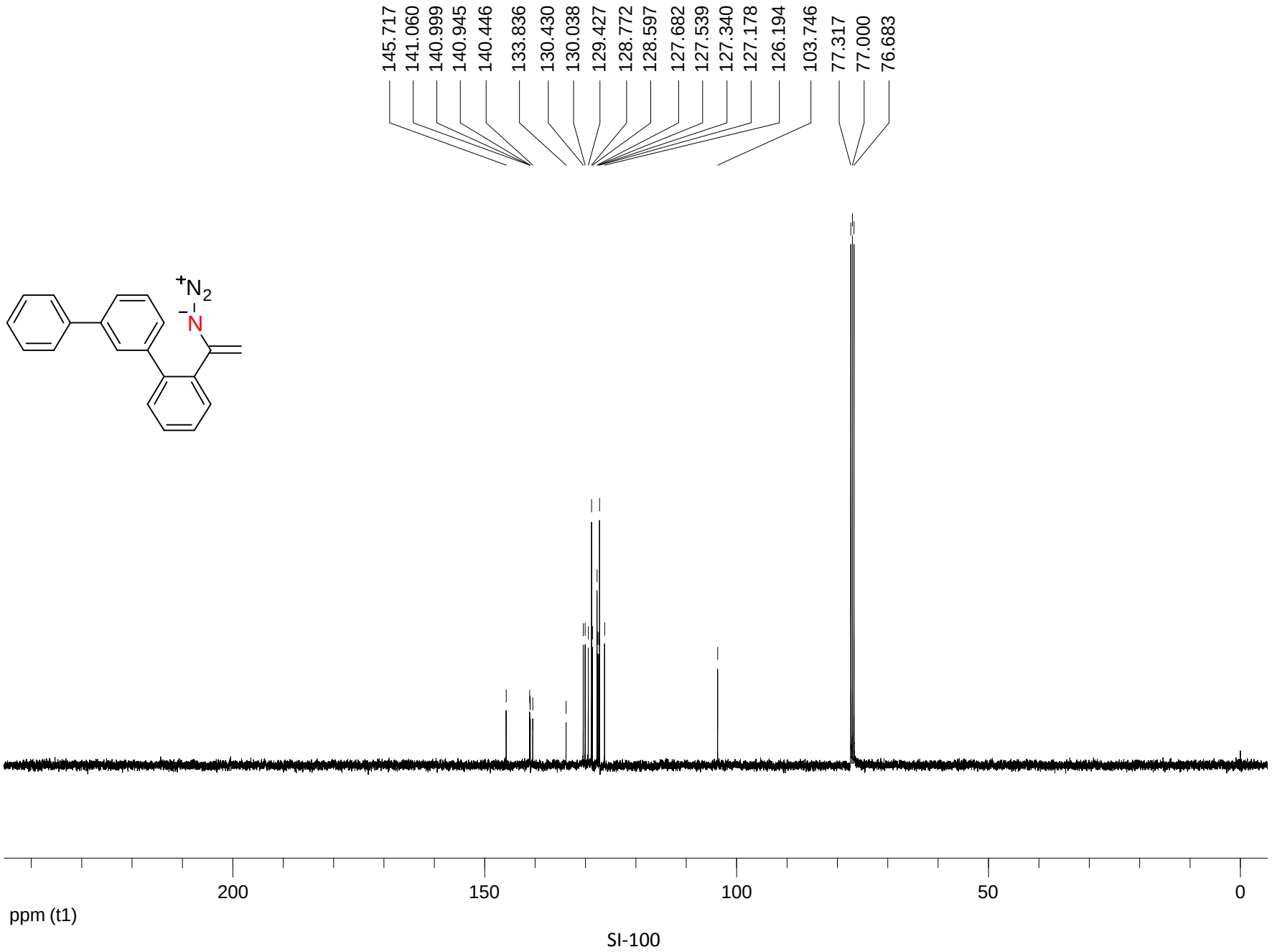
^{13}C NMR Spectrum of **1i** (100 MHz, $CDCl_3$)



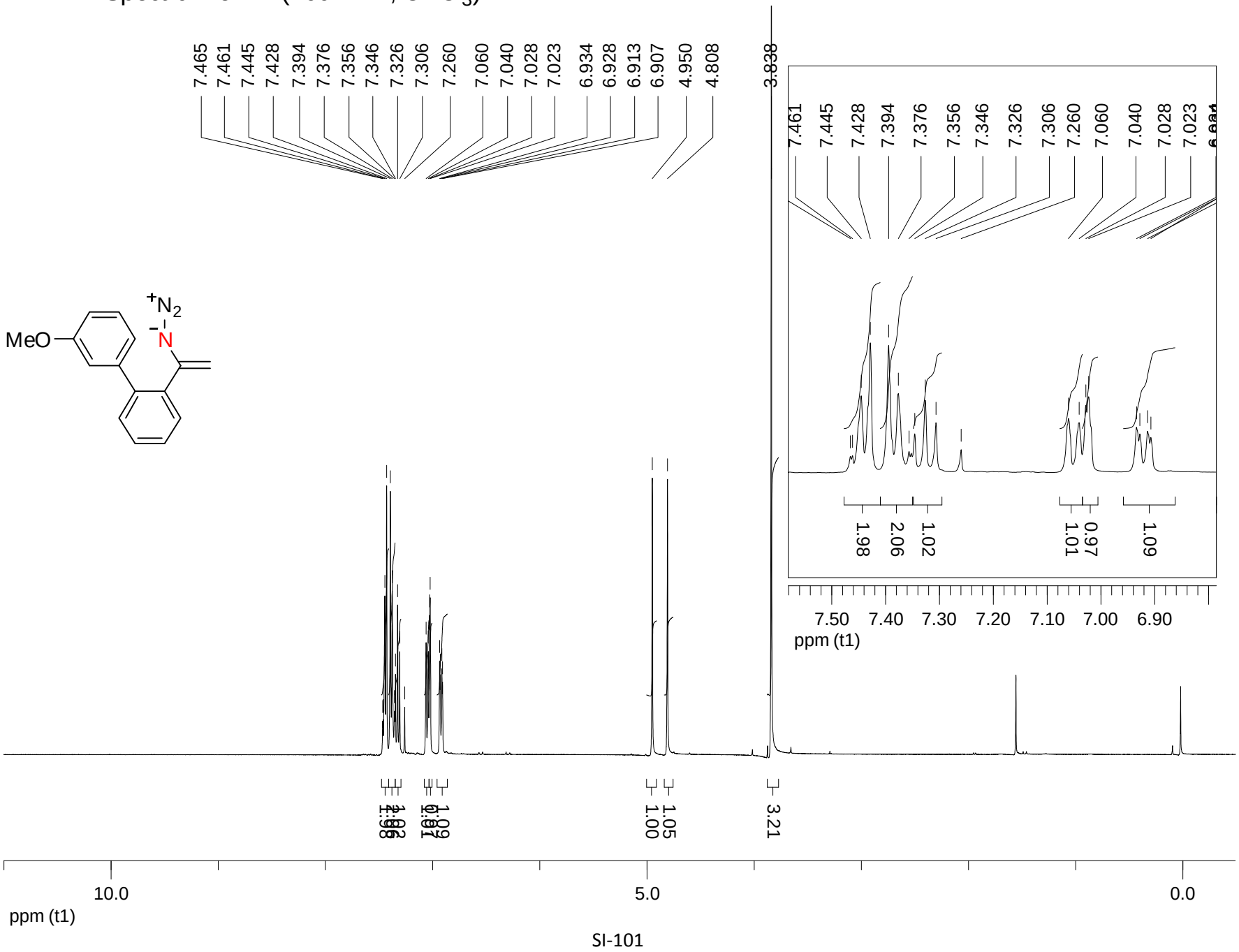
^{1}H NMR Spectrum of **1j** (400 MHz, $CDCl_3$)



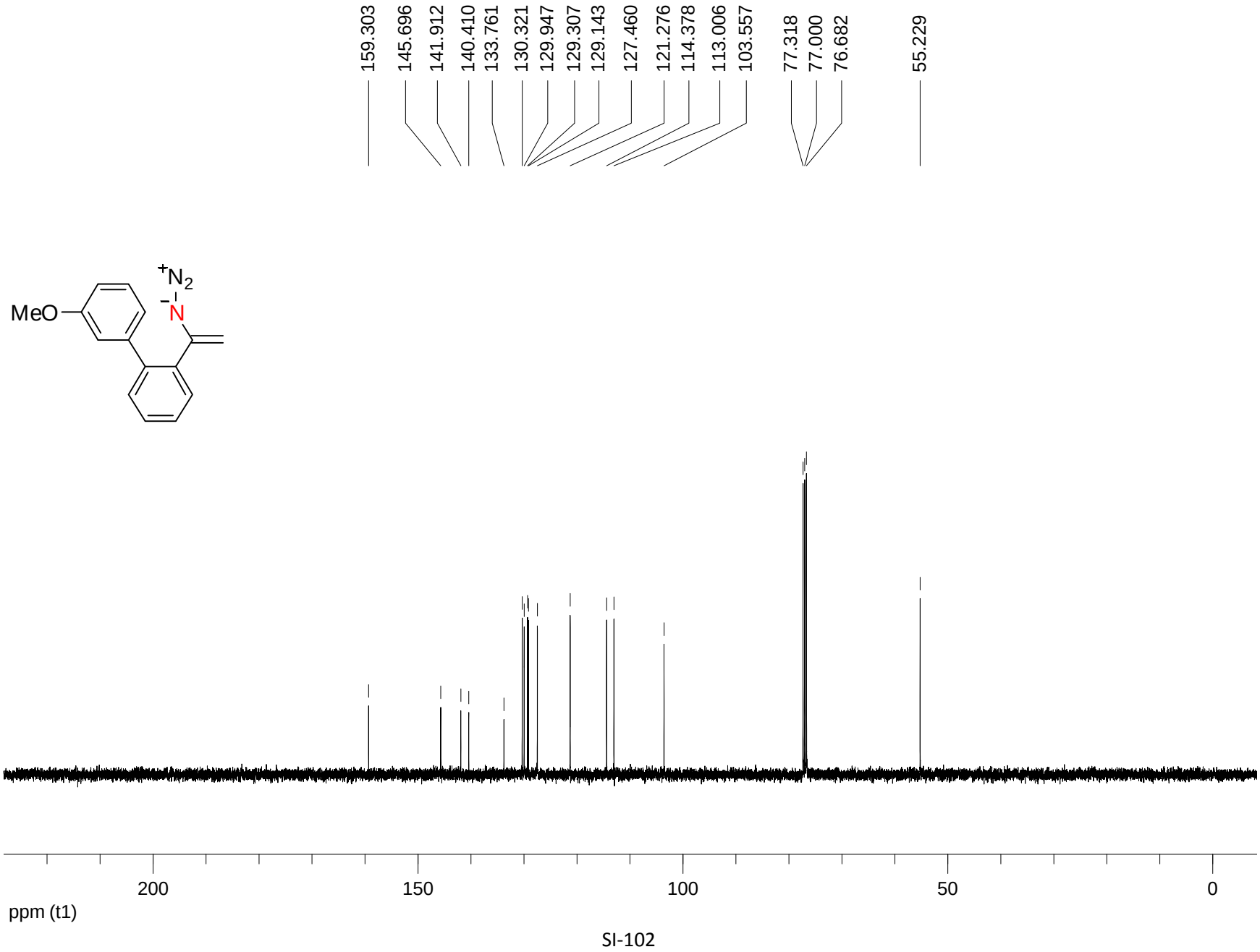
^{13}C NMR Spectrum of **1j** (100 MHz, $CDCl_3$)



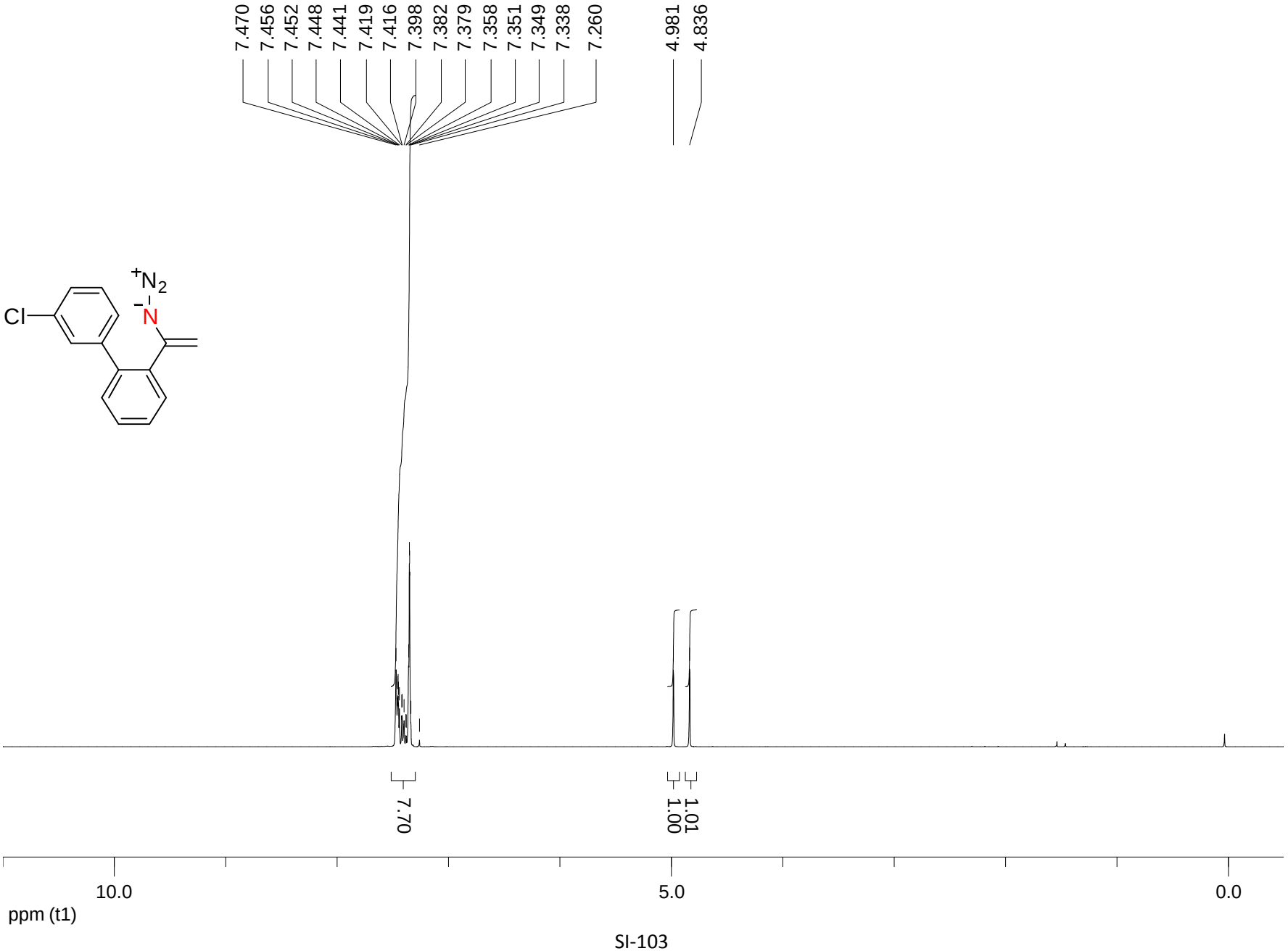
^{1}H NMR Spectrum of **1k** (400 MHz, $CDCl_3$)



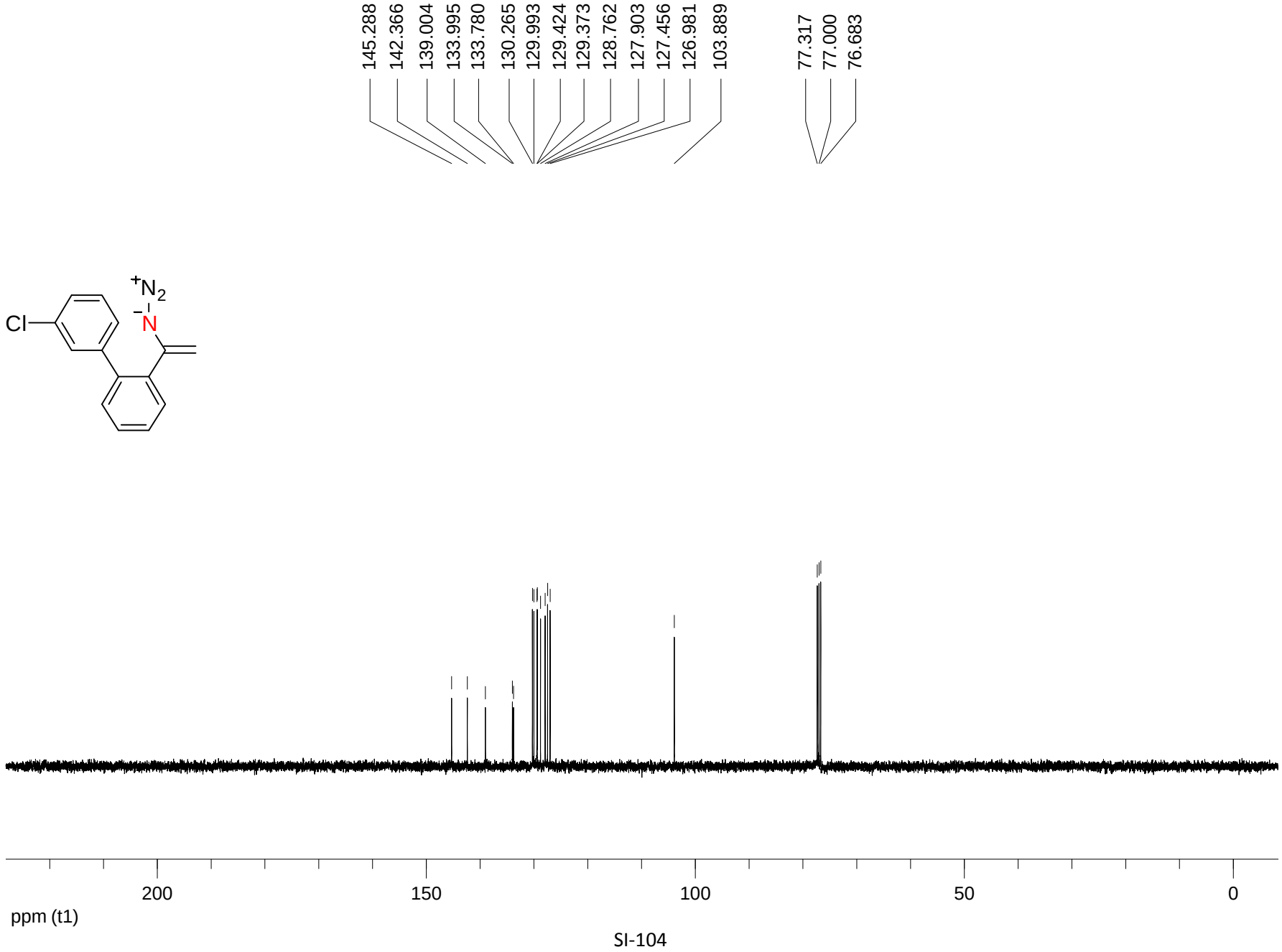
^{13}C NMR Spectrum of **1k** (100 MHz, $CDCl_3$)



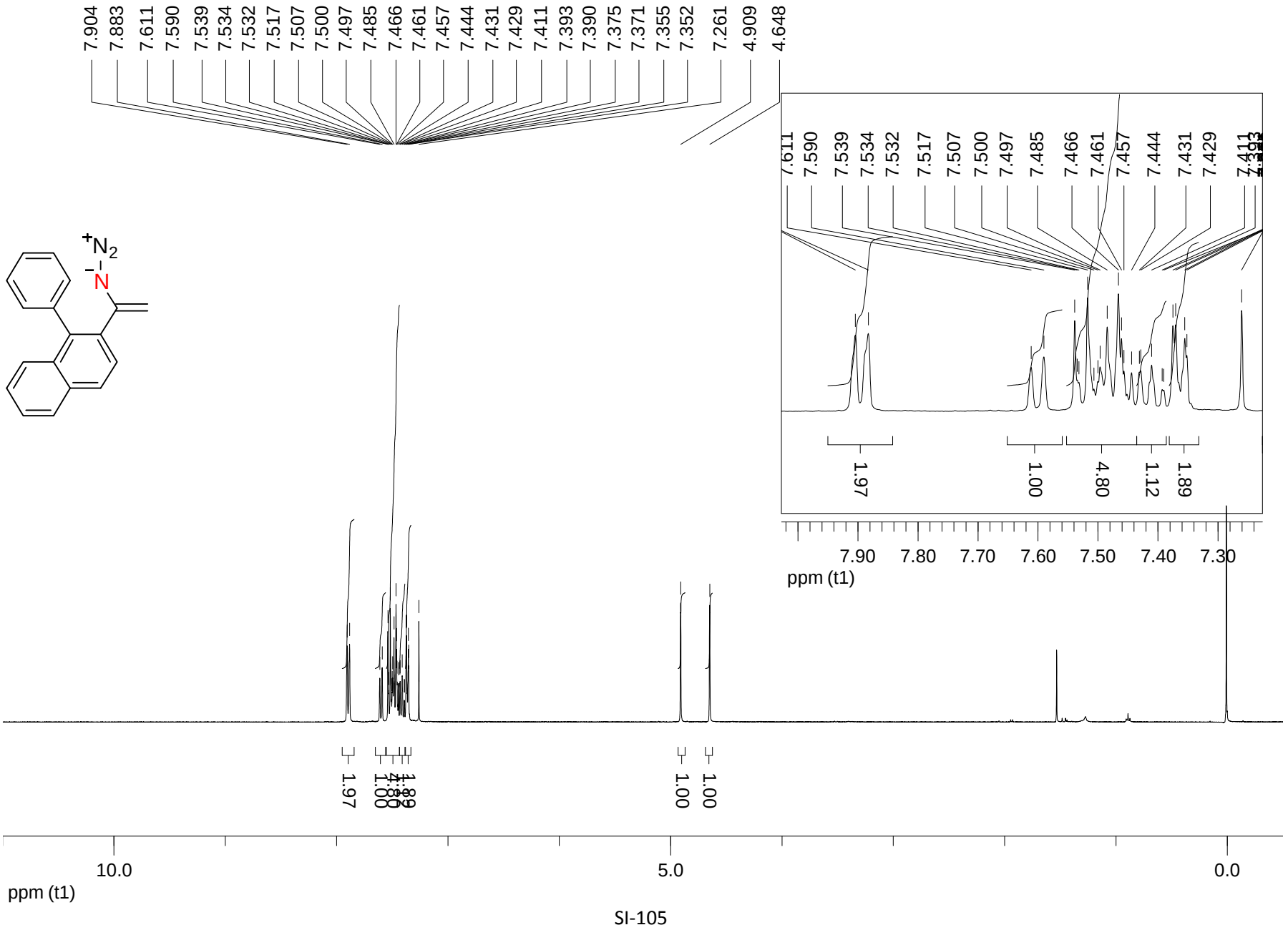
^{1}H NMR Spectrum of **1l** (400 MHz, $CDCl_3$)



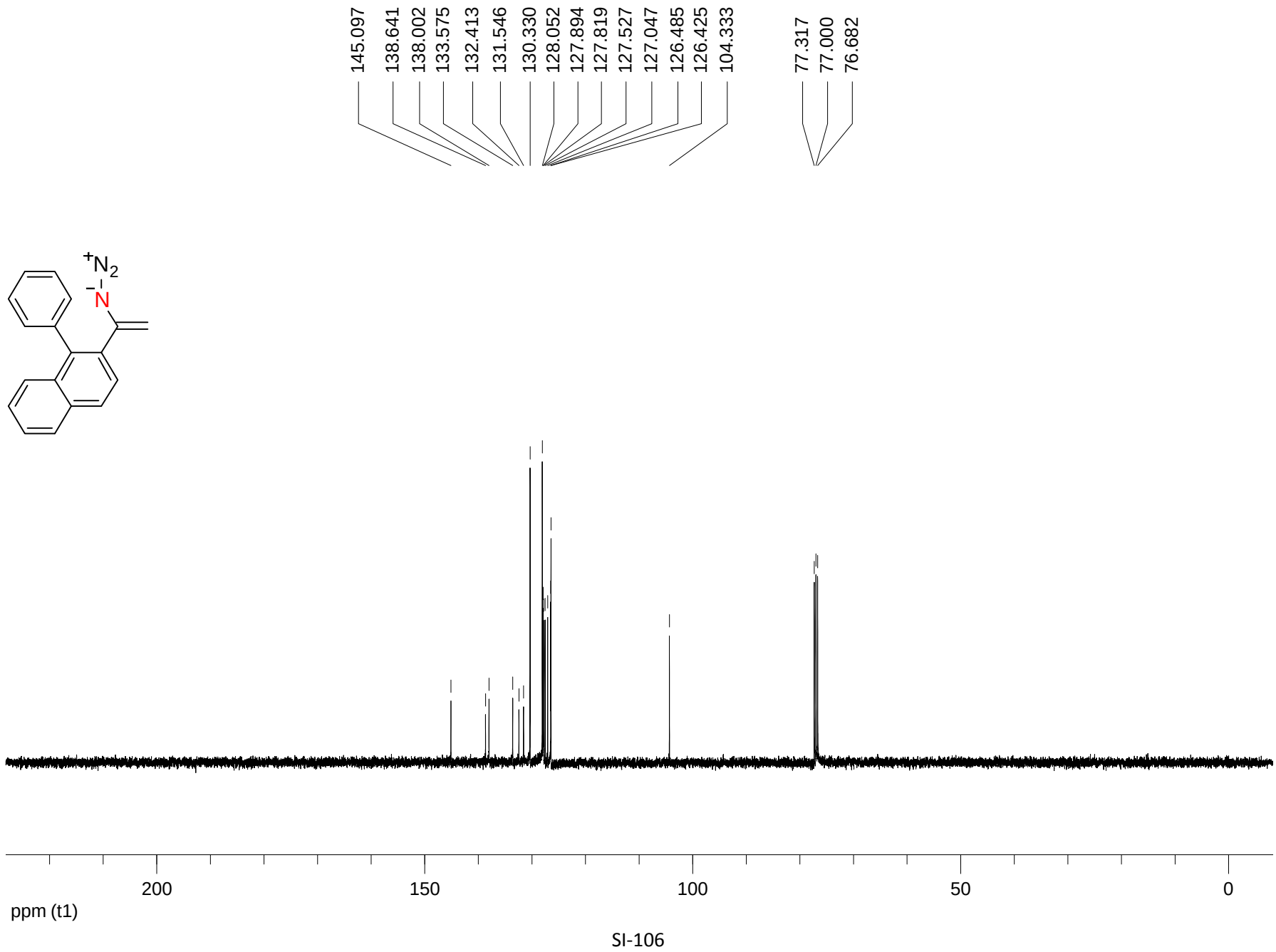
^{13}C NMR Spectrum of **1l** (100 MHz, $CDCl_3$)



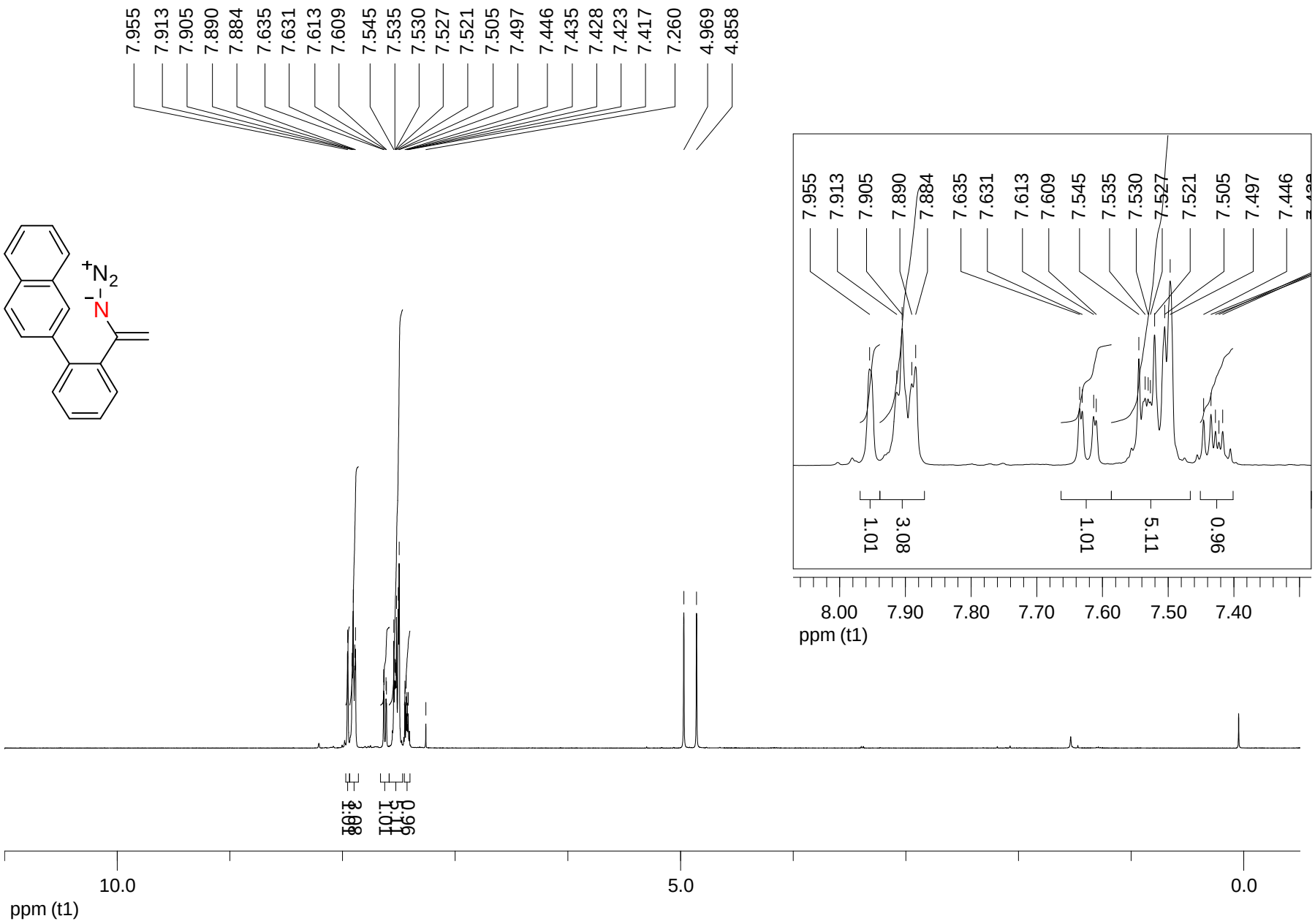
^{1}H NMR Spectrum of **1m** (400 MHz, $CDCl_3$)



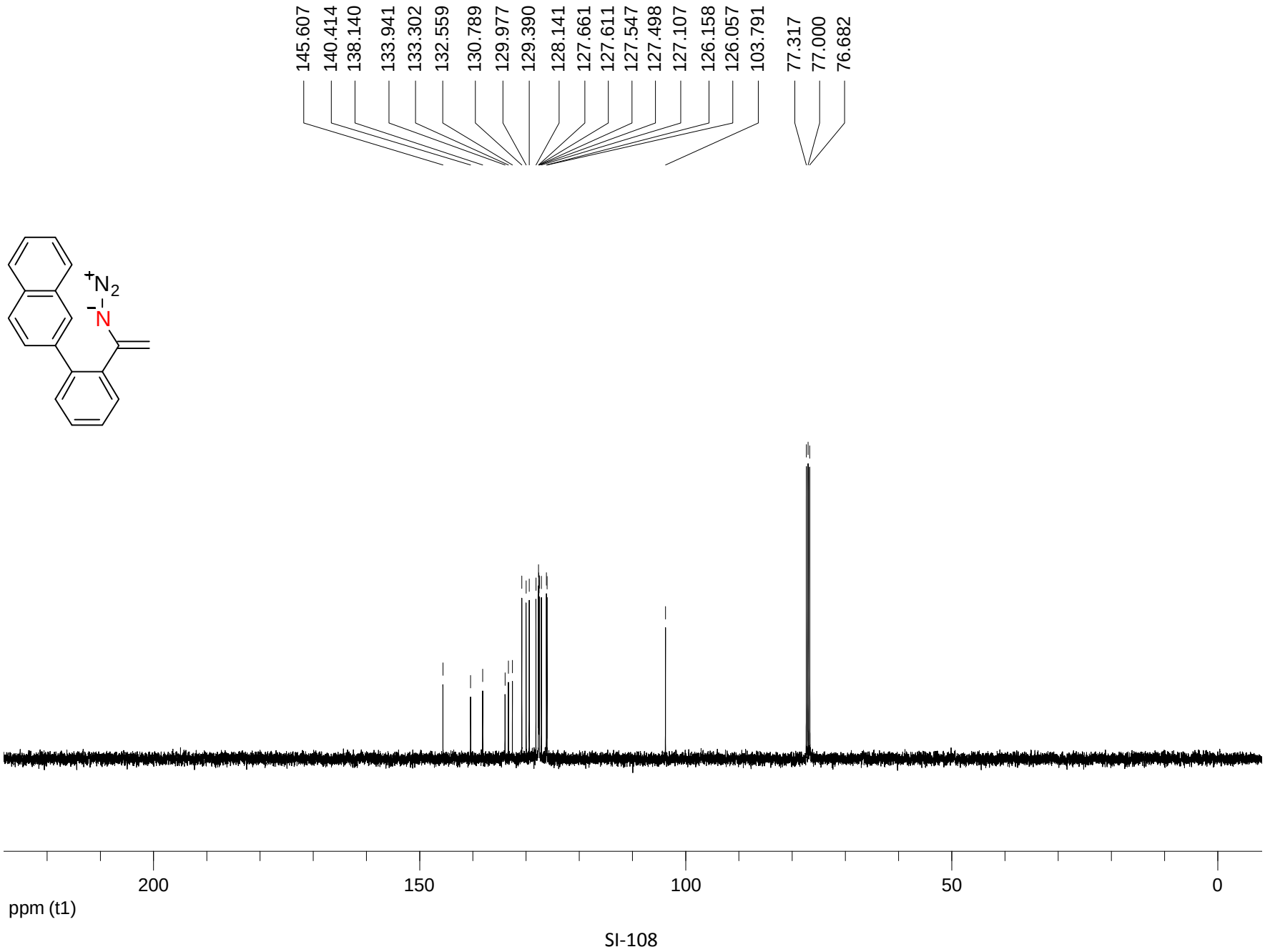
^{13}C NMR Spectrum of **1m** (100 MHz, $CDCl_3$)



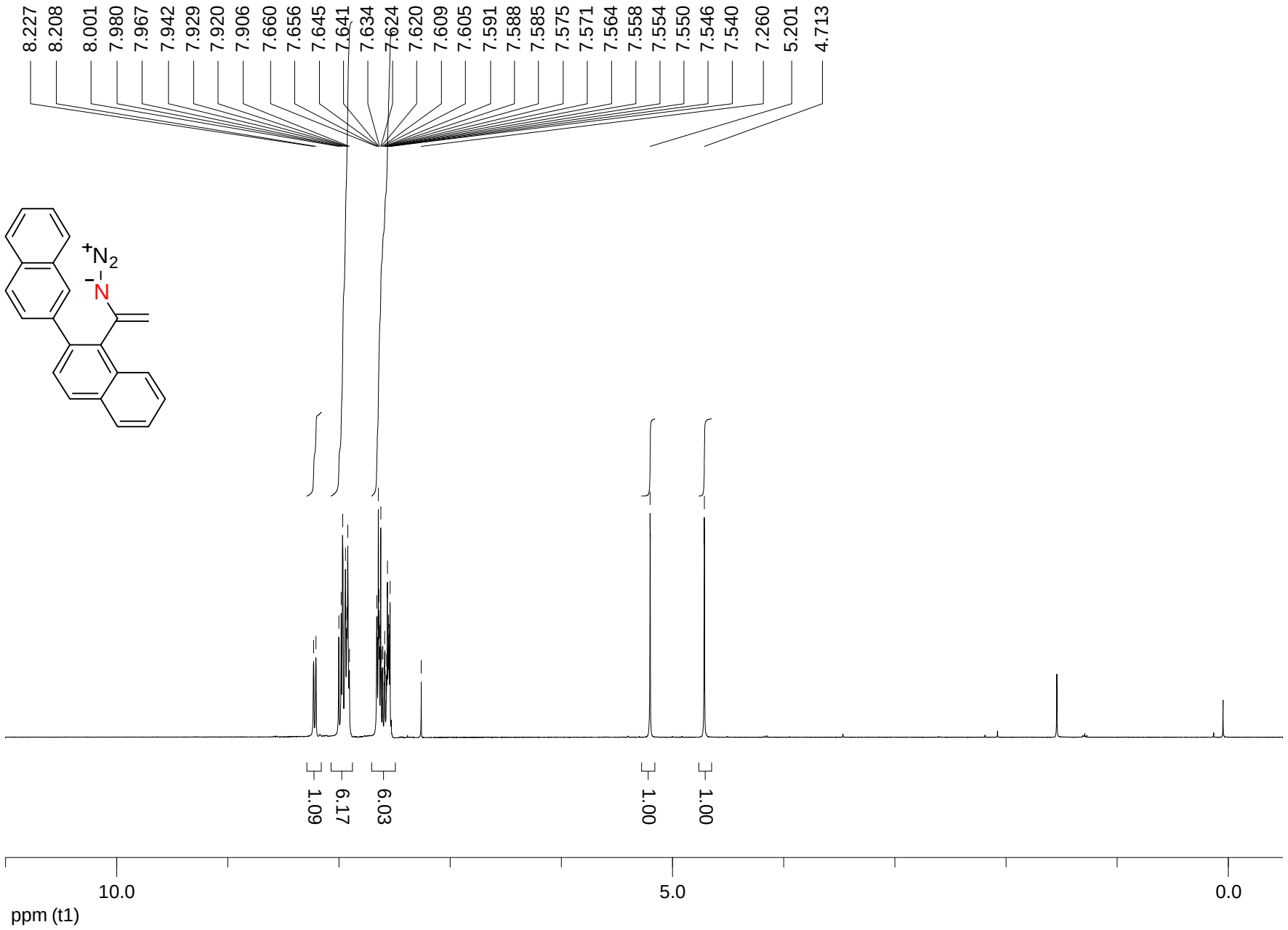
^{1}H NMR Spectrum of **1n** (400 MHz, $CDCl_3$)



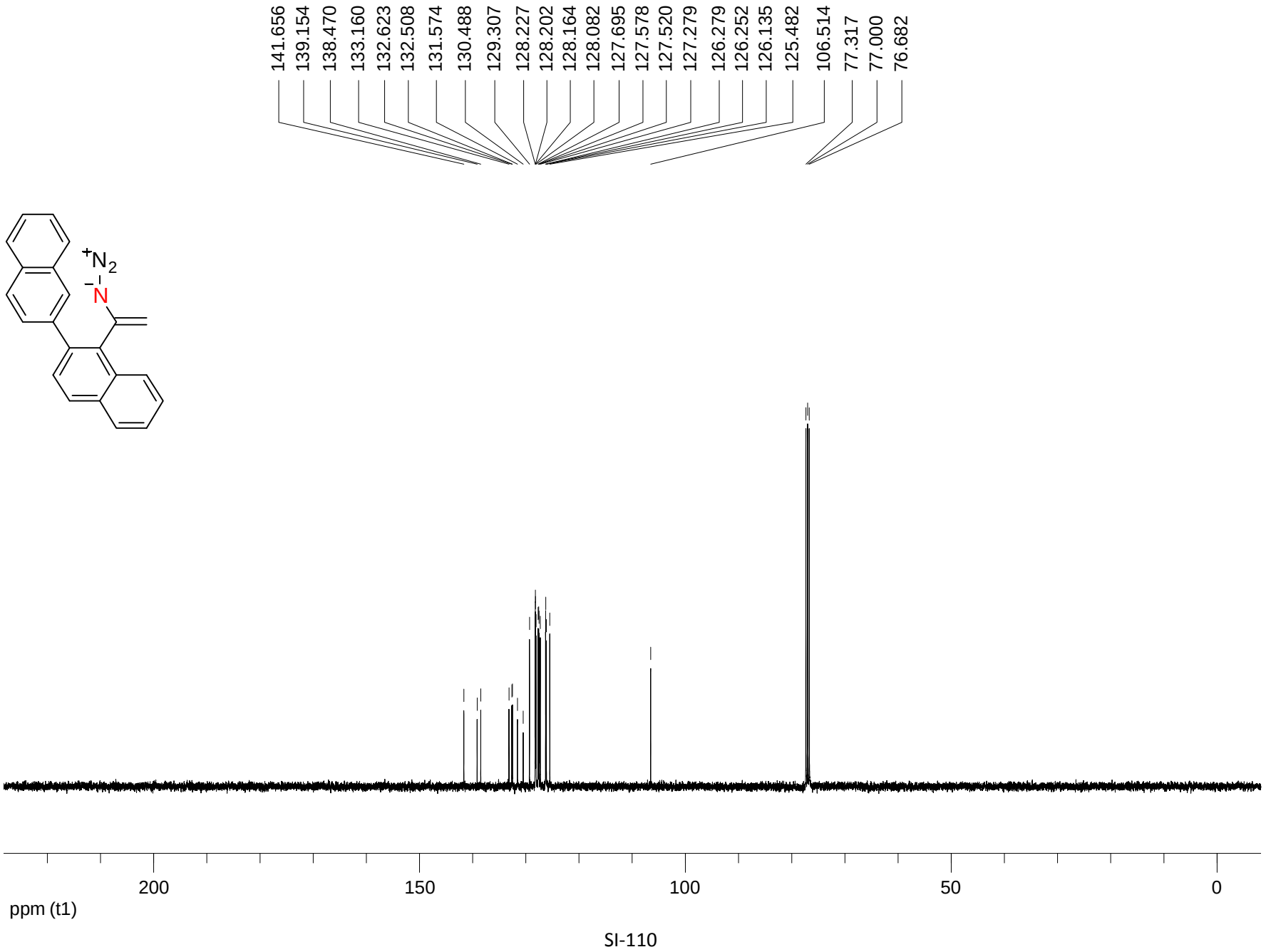
^{13}C NMR Spectrum of **1n** (100 MHz, $CDCl_3$)



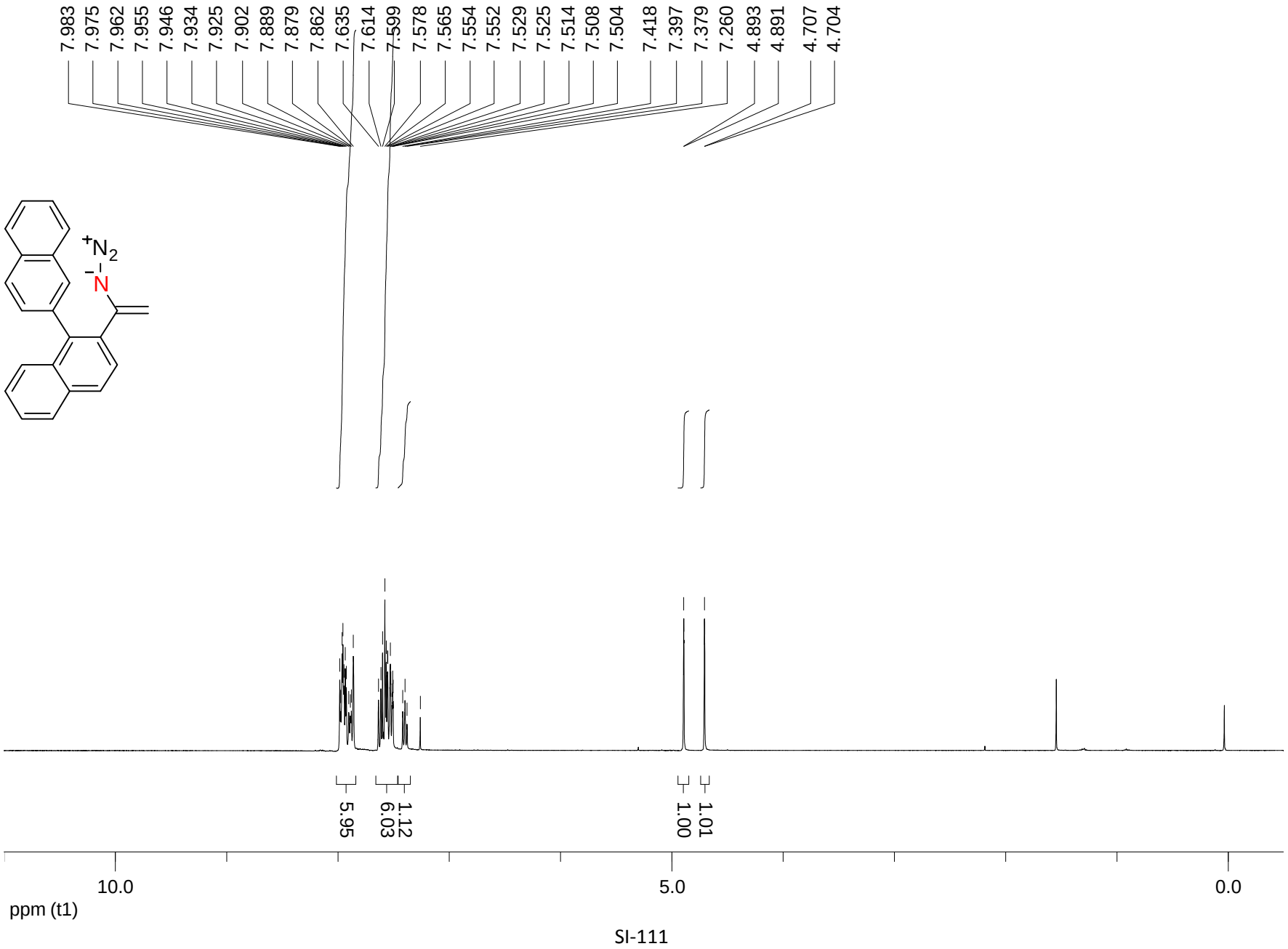
^{1}H NMR Spectrum of **1o** (400 MHz, $CDCl_3$)



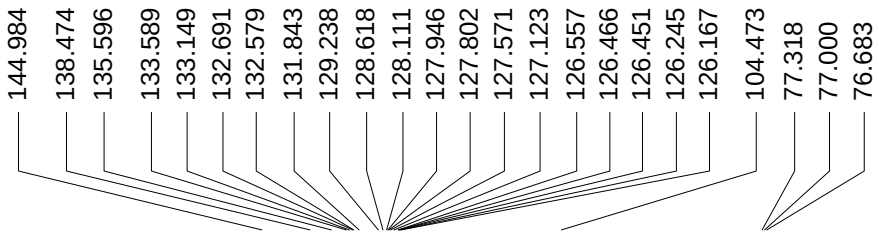
^{13}C NMR Spectrum of **1o** (100 MHz, $CDCl_3$)

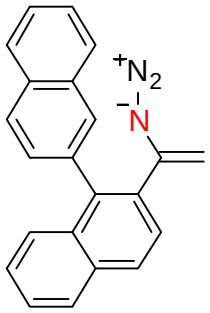


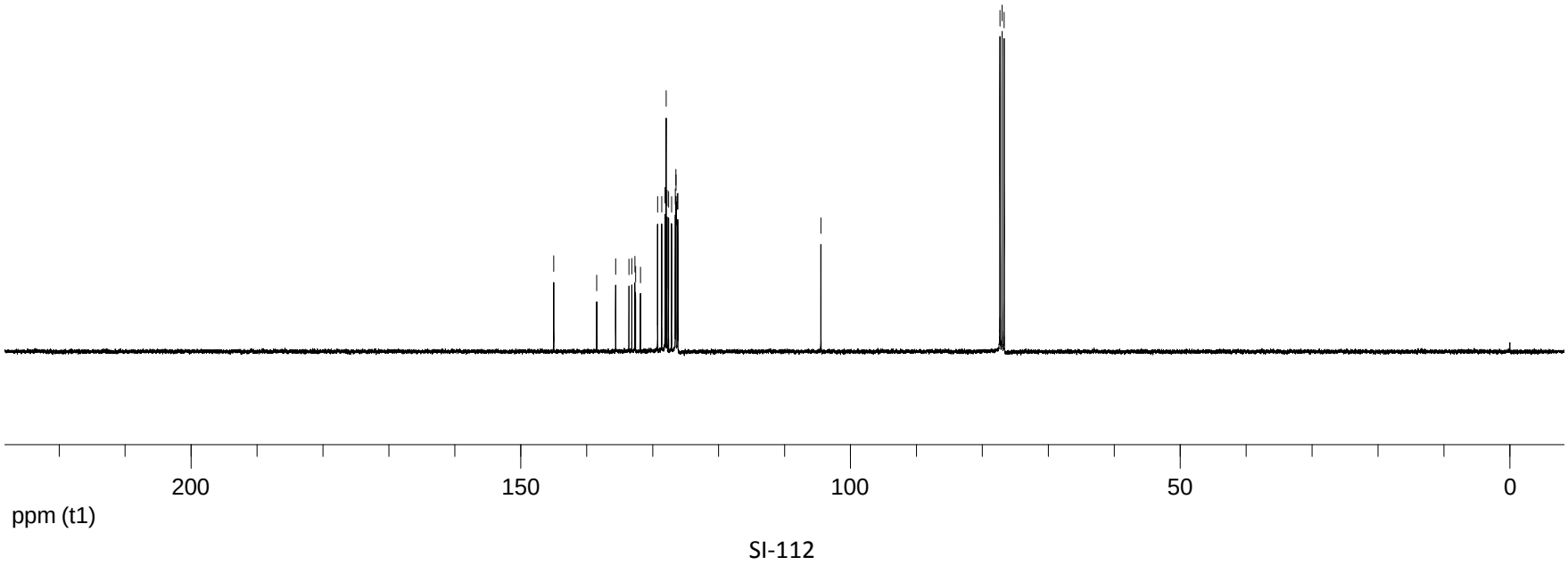
^{1}H NMR Spectrum of **1p** (400 MHz, $CDCl_3$)



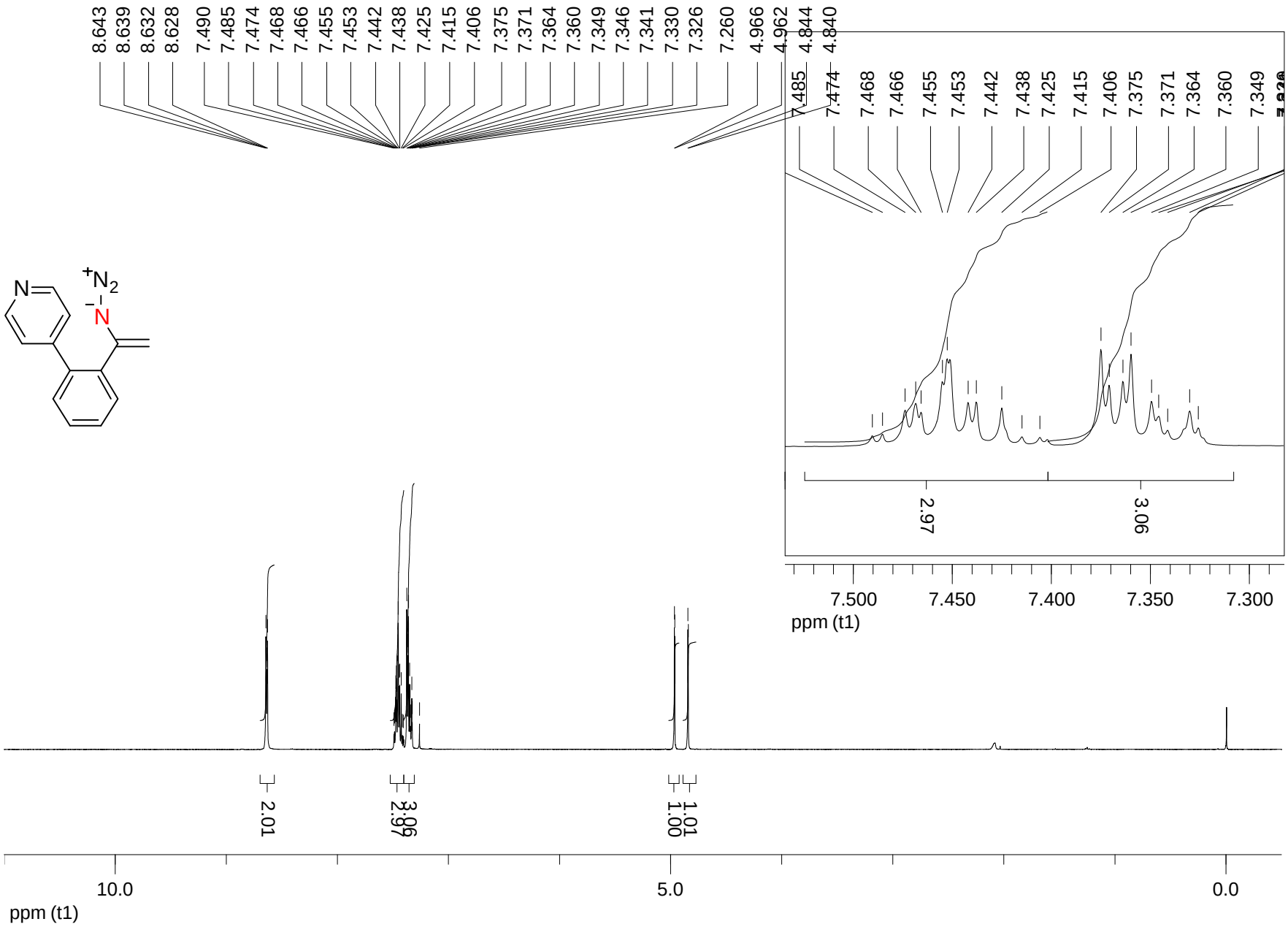
^{13}C NMR Spectrum of **1p** (100 MHz, $CDCl_3$)



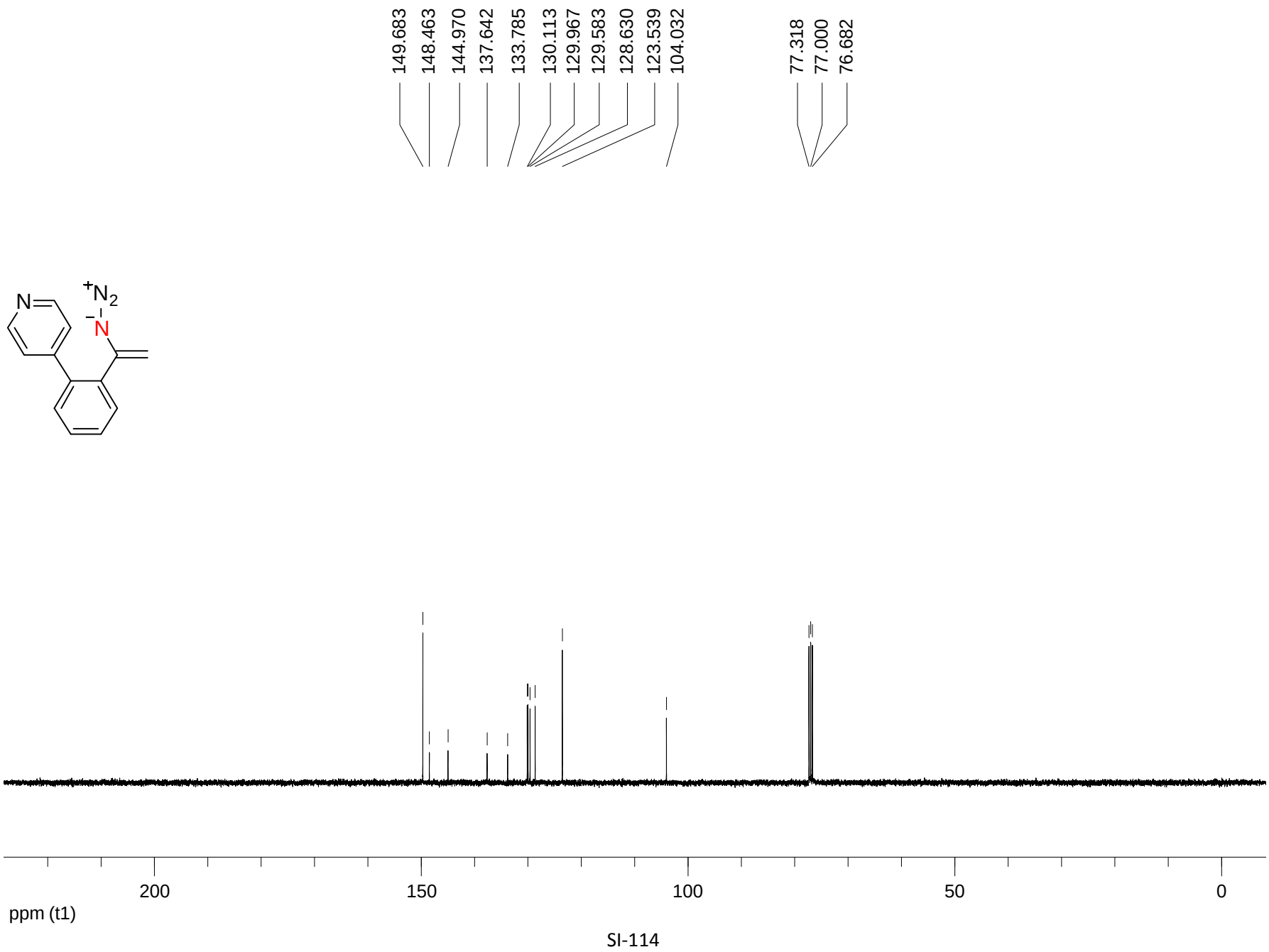




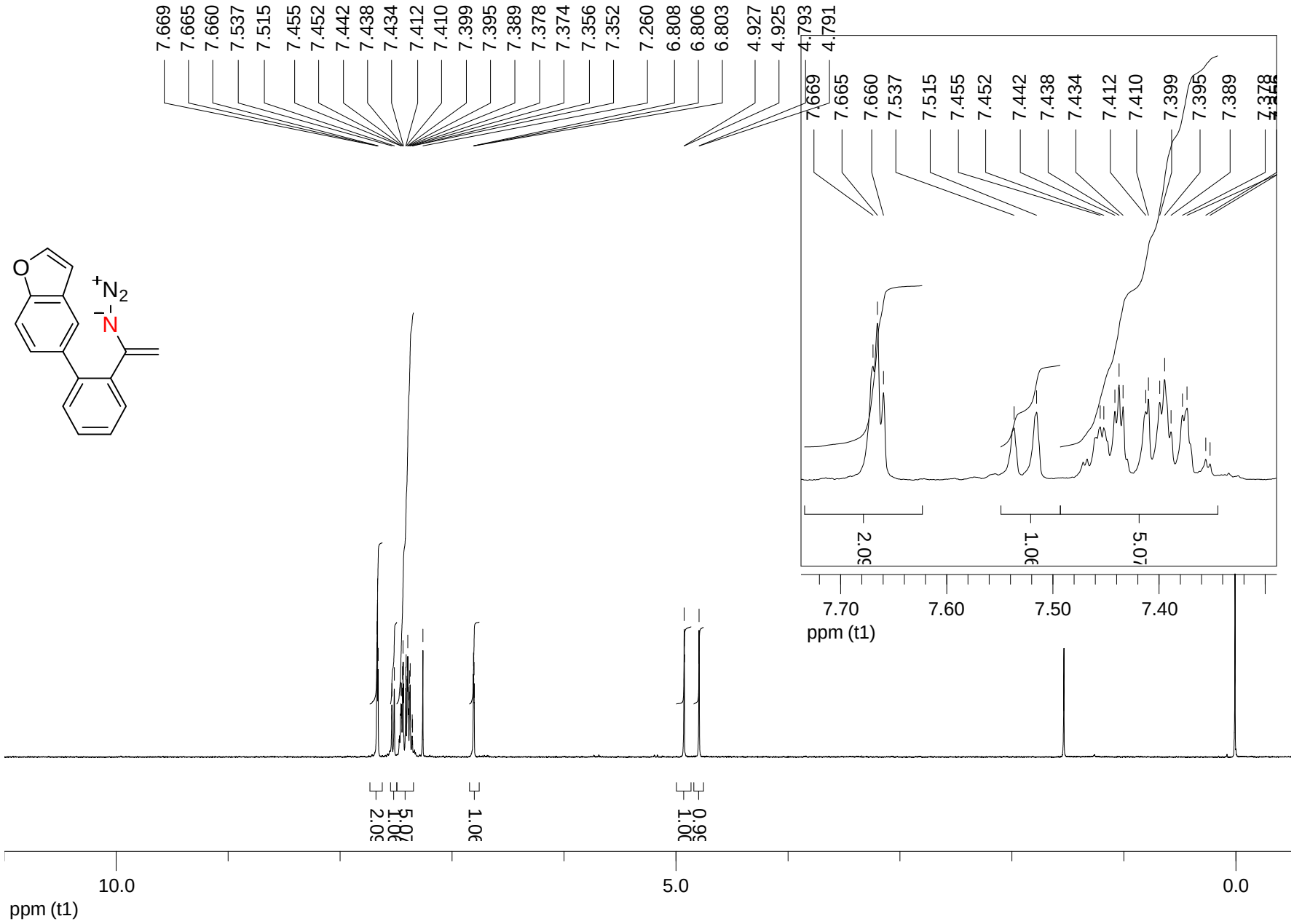
^{1}H NMR Spectrum of **1q** (400 MHz, $CDCl_3$)



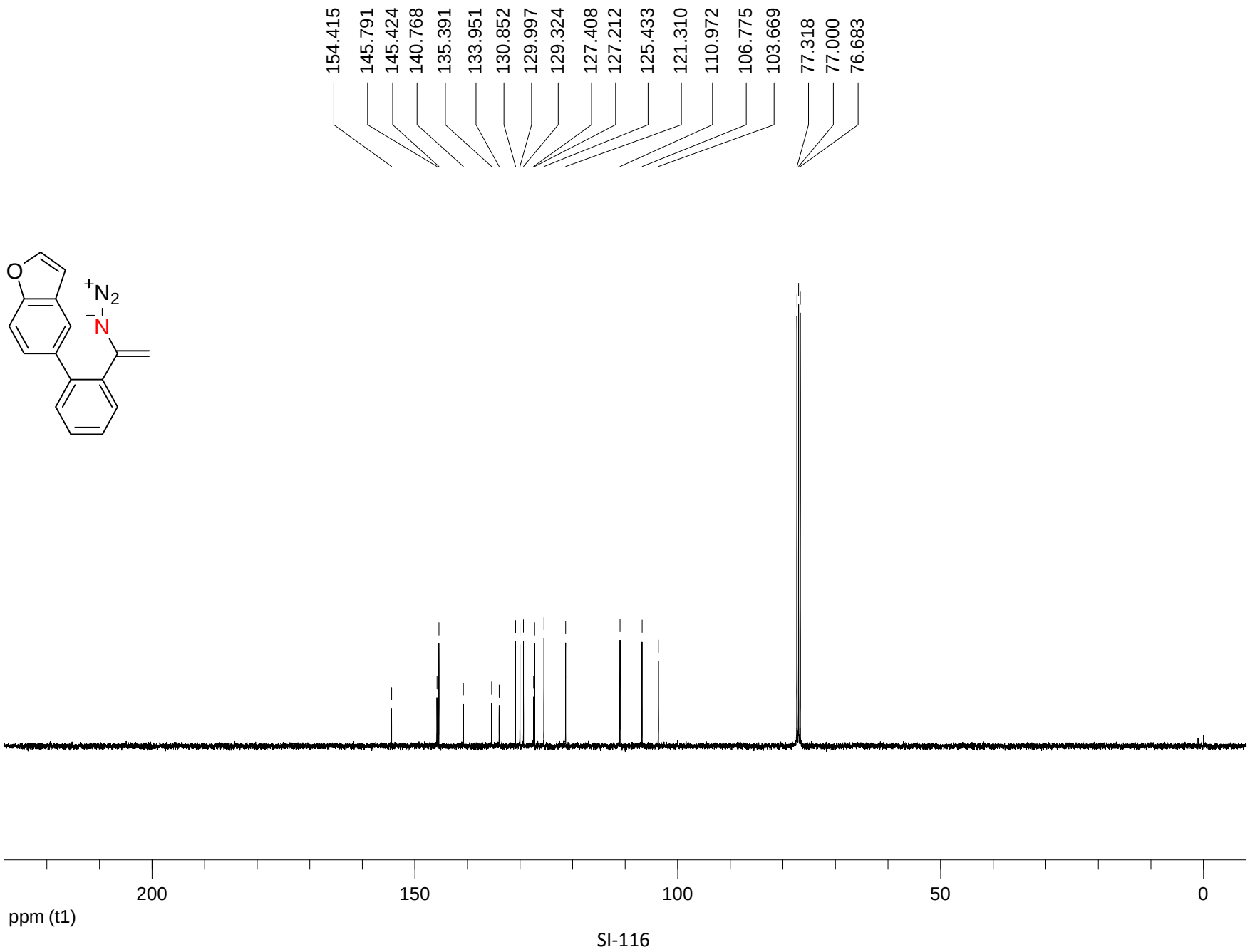
^{13}C NMR Spectrum of **1q** (100 MHz, $CDCl_3$)



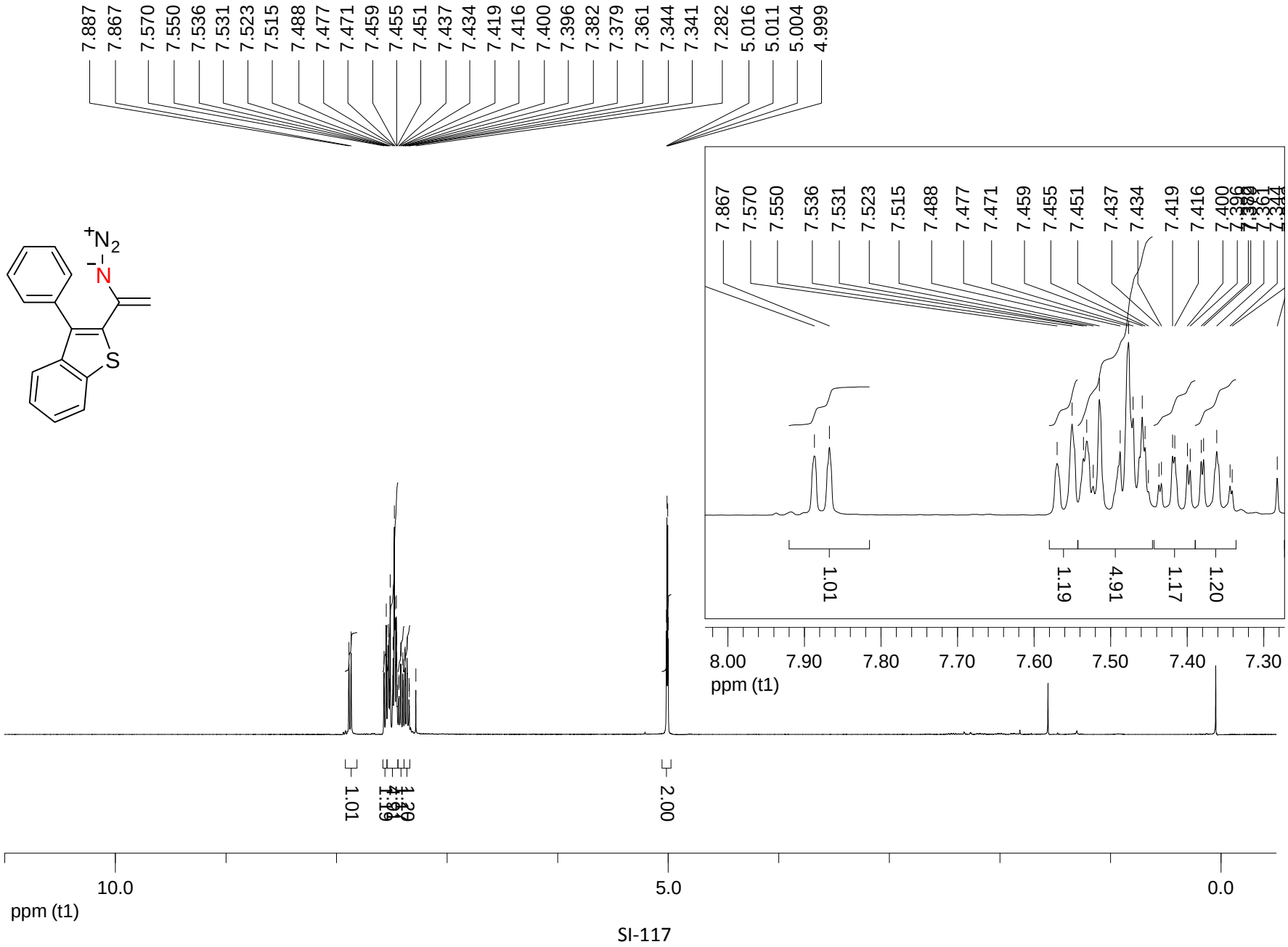
^{1}H NMR Spectrum of **1r** (400 MHz, $CDCl_3$)



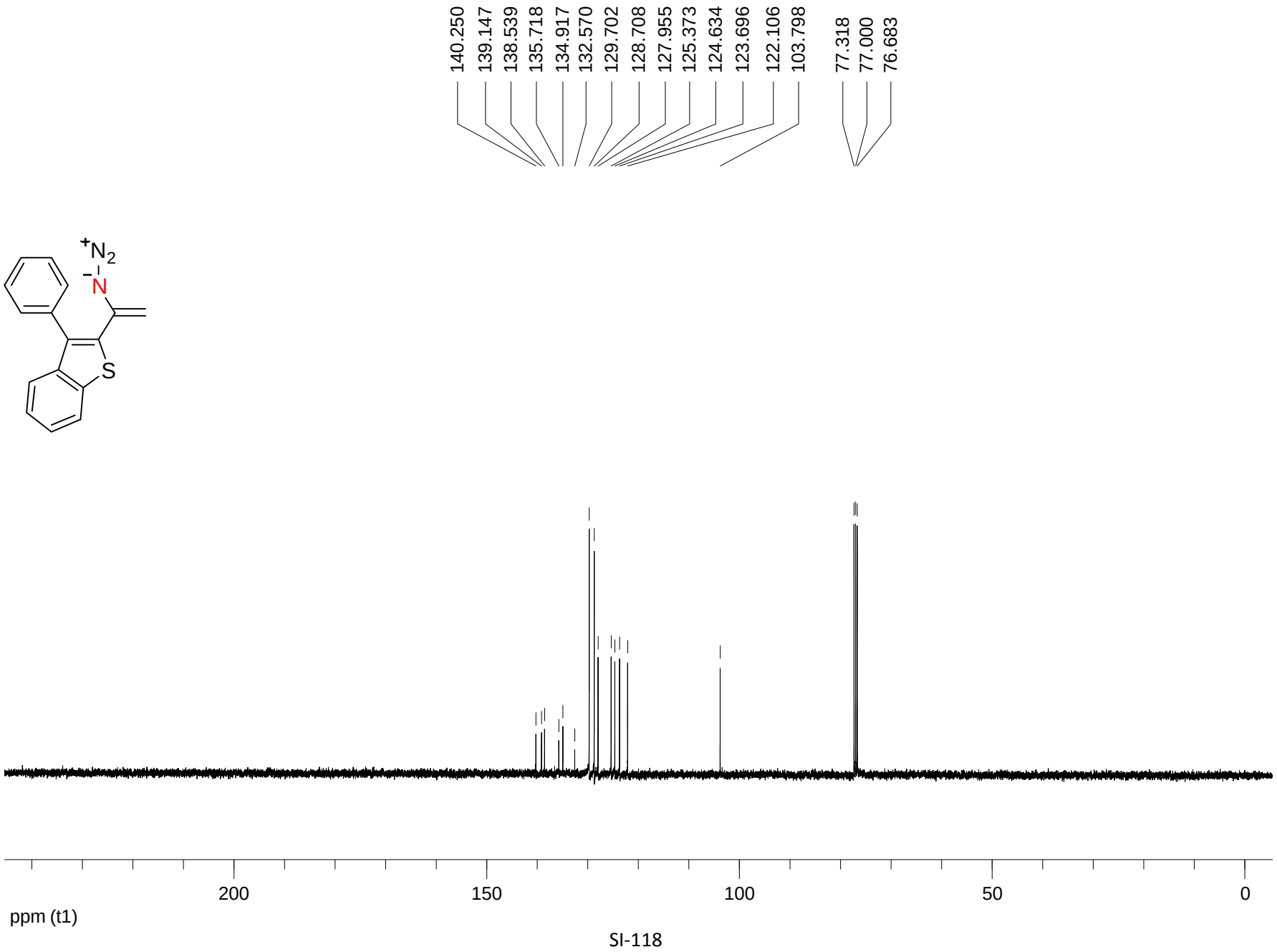
^{13}C NMR Spectrum of **1r** (100 MHz, $CDCl_3$)



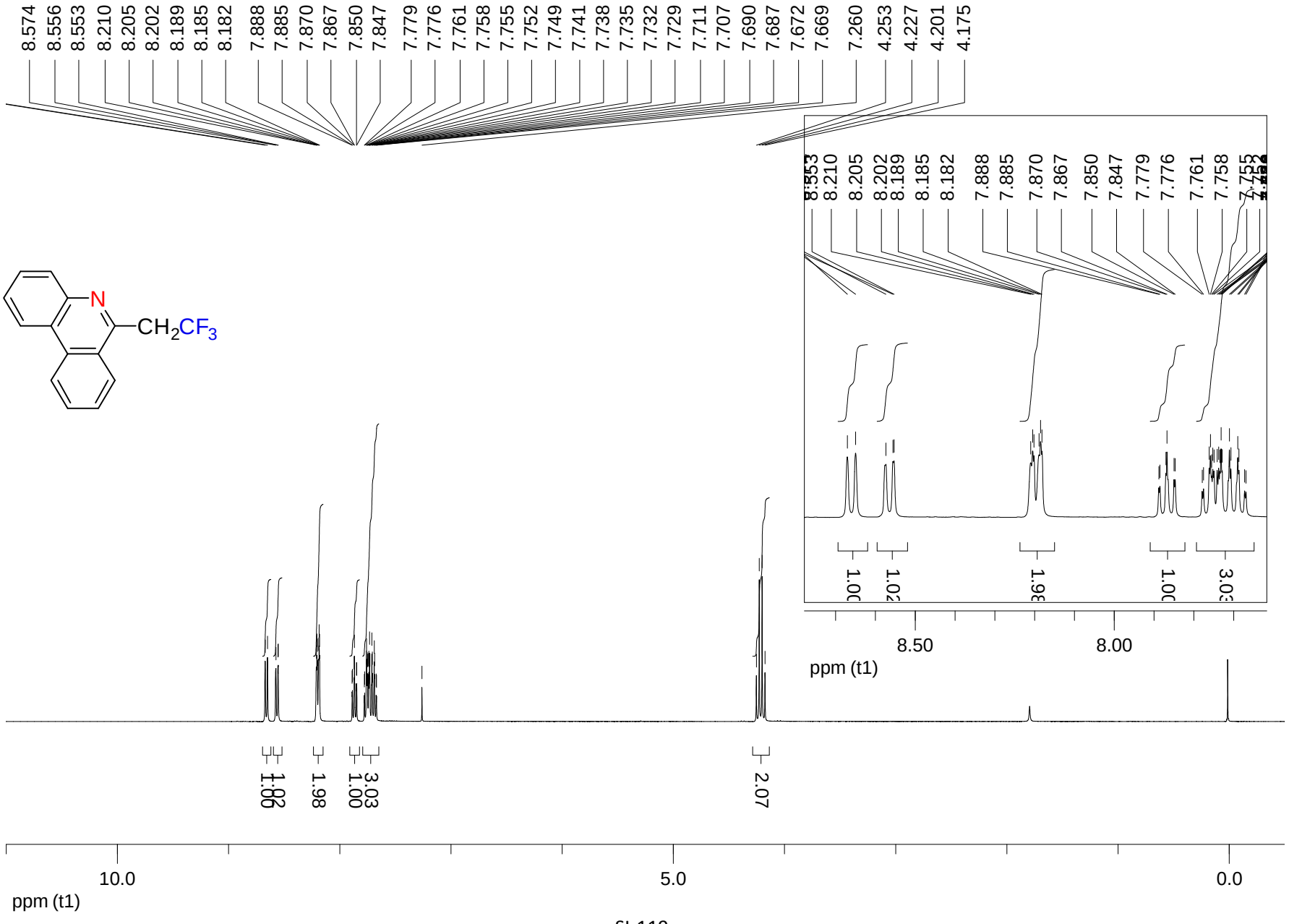
^{1}H NMR Spectrum of **1s** (400 MHz, $CDCl_3$)



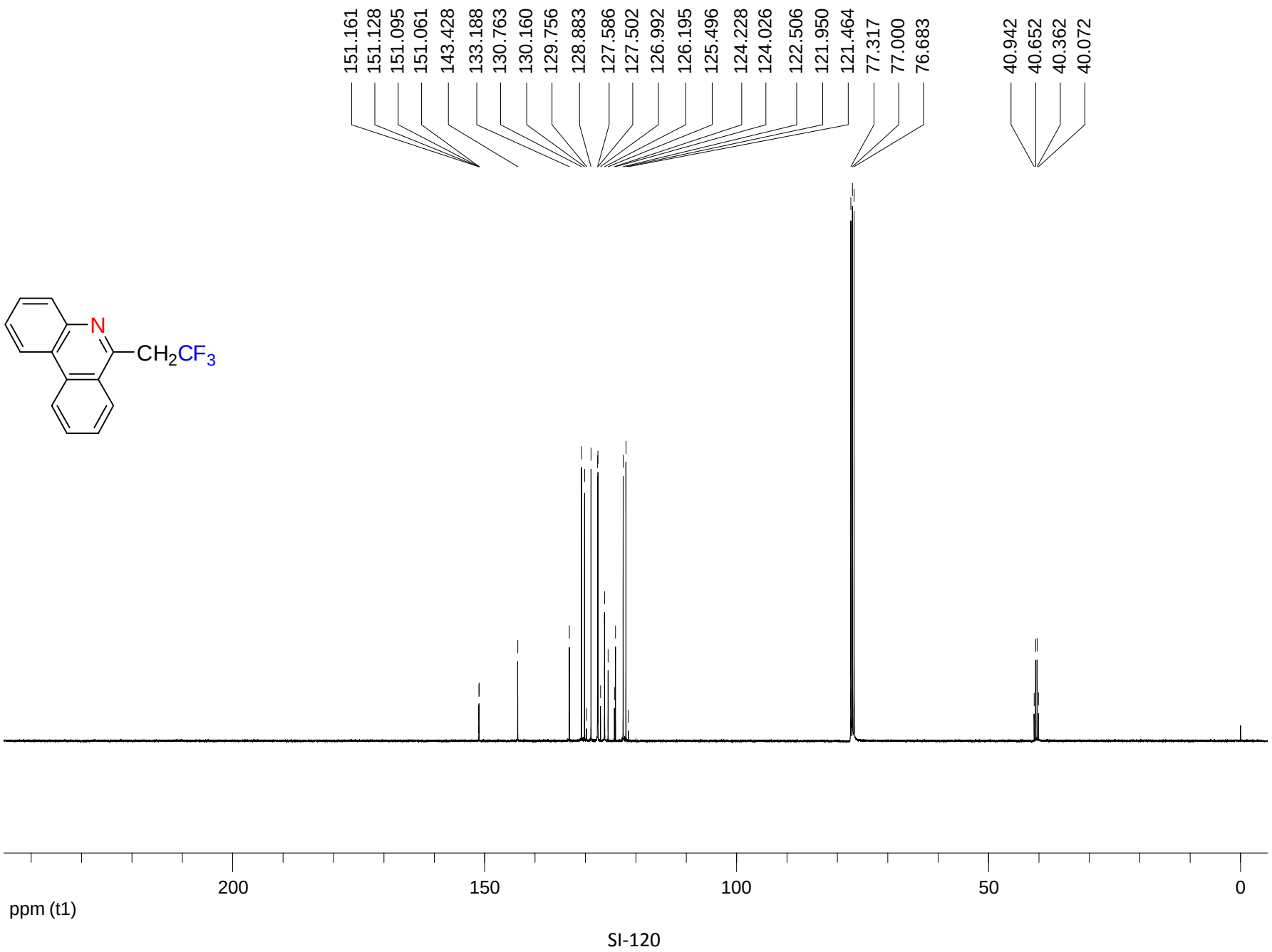
^{13}C NMR Spectrum of **1s** (100 MHz, $CDCl_3$)



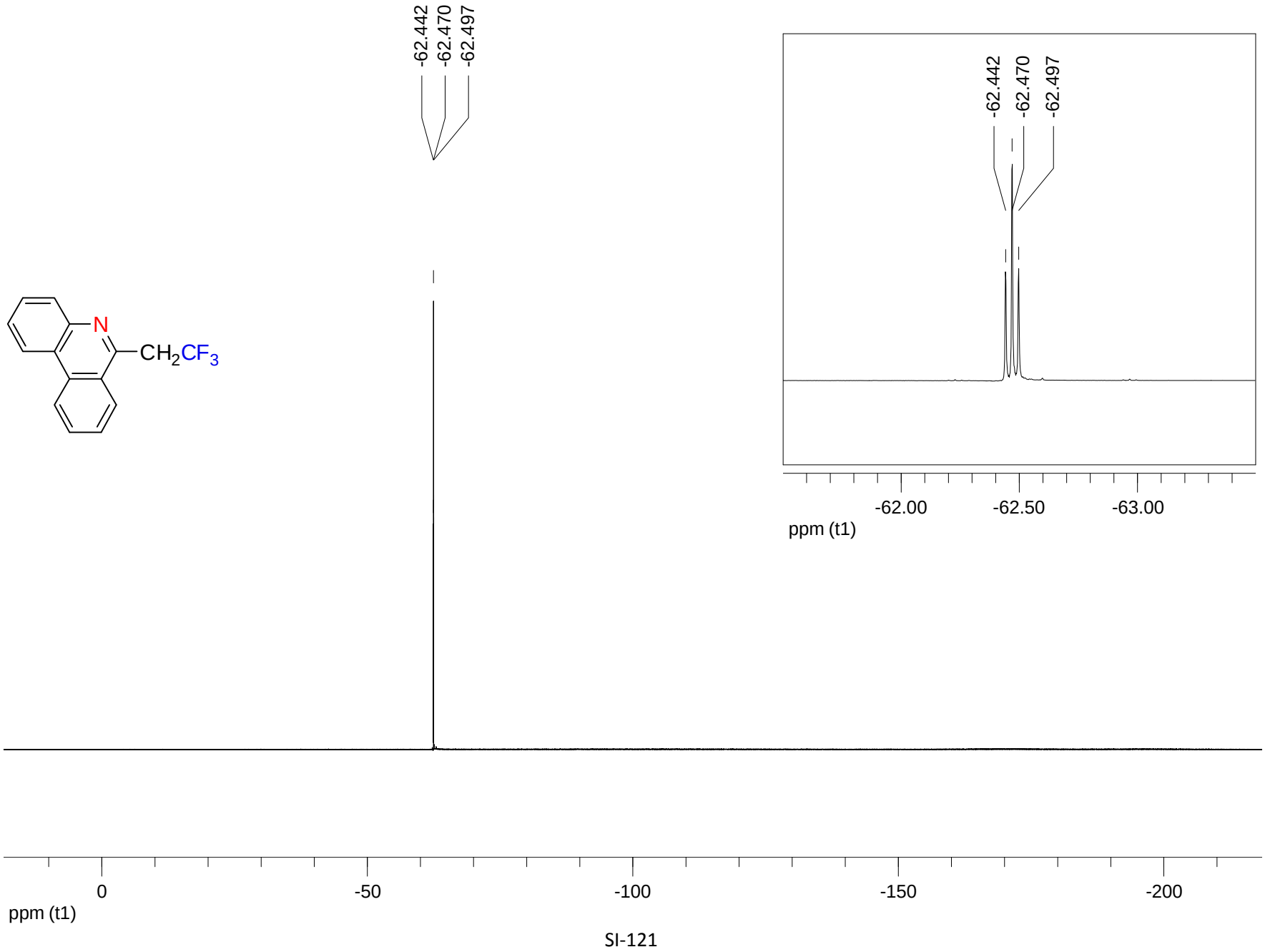
^{1}H NMR Spectrum of **2a** (400 MHz, $CDCl_3$)



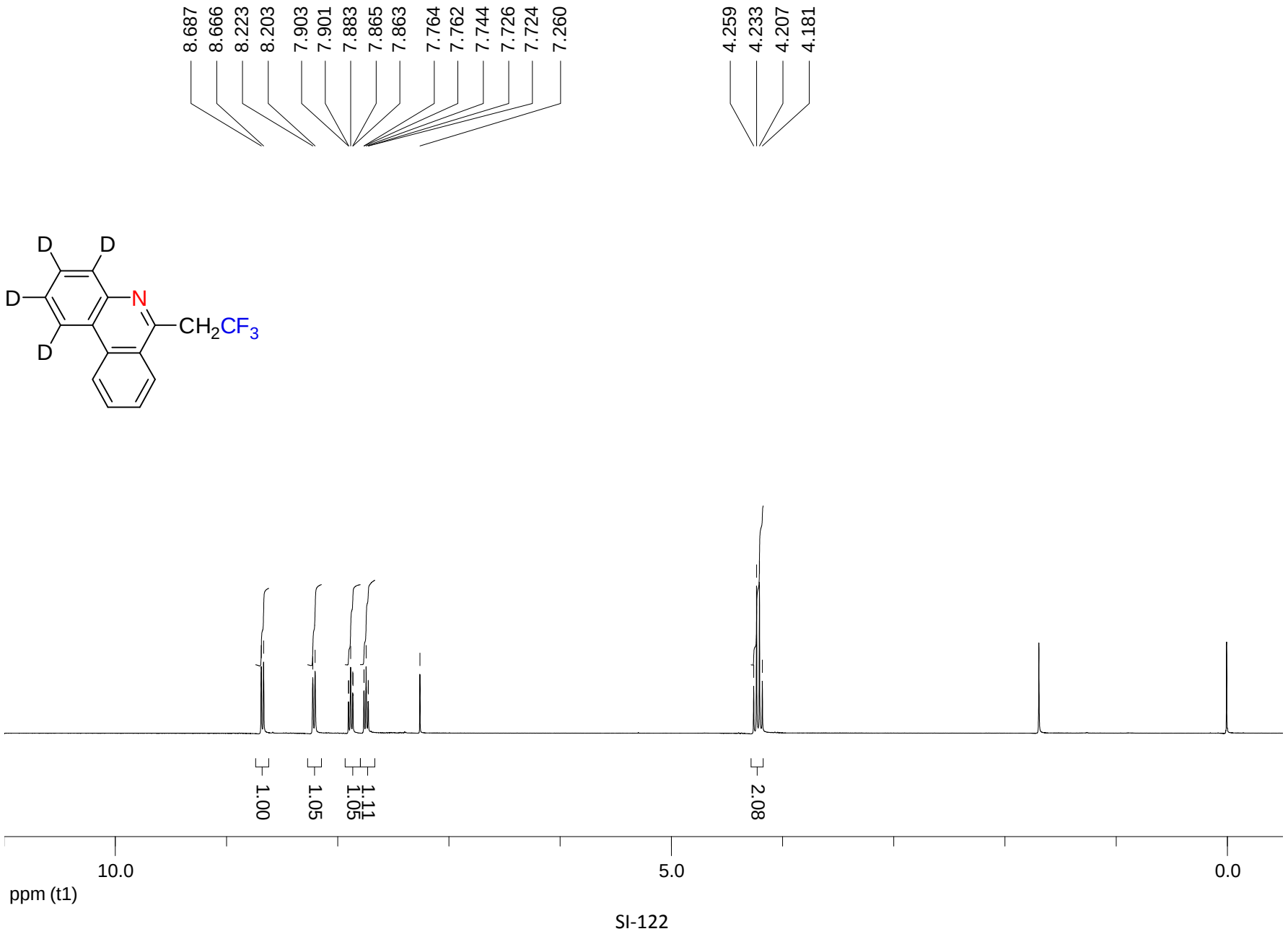
^{13}C NMR Spectrum of **2a** (100 MHz, $CDCl_3$)



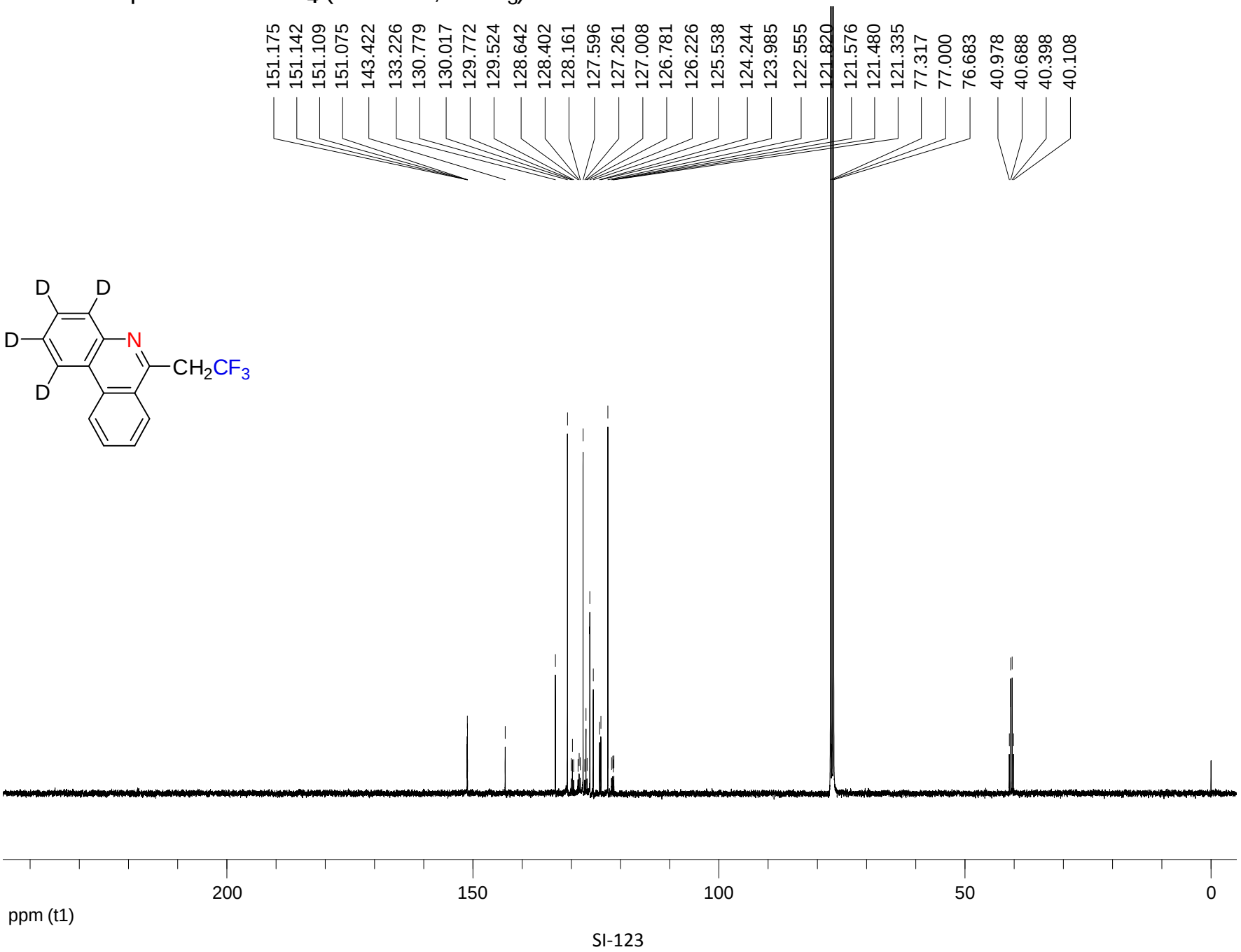
^{19}F NMR Spectrum of **2a** (376 MHz, $CDCl_3$)



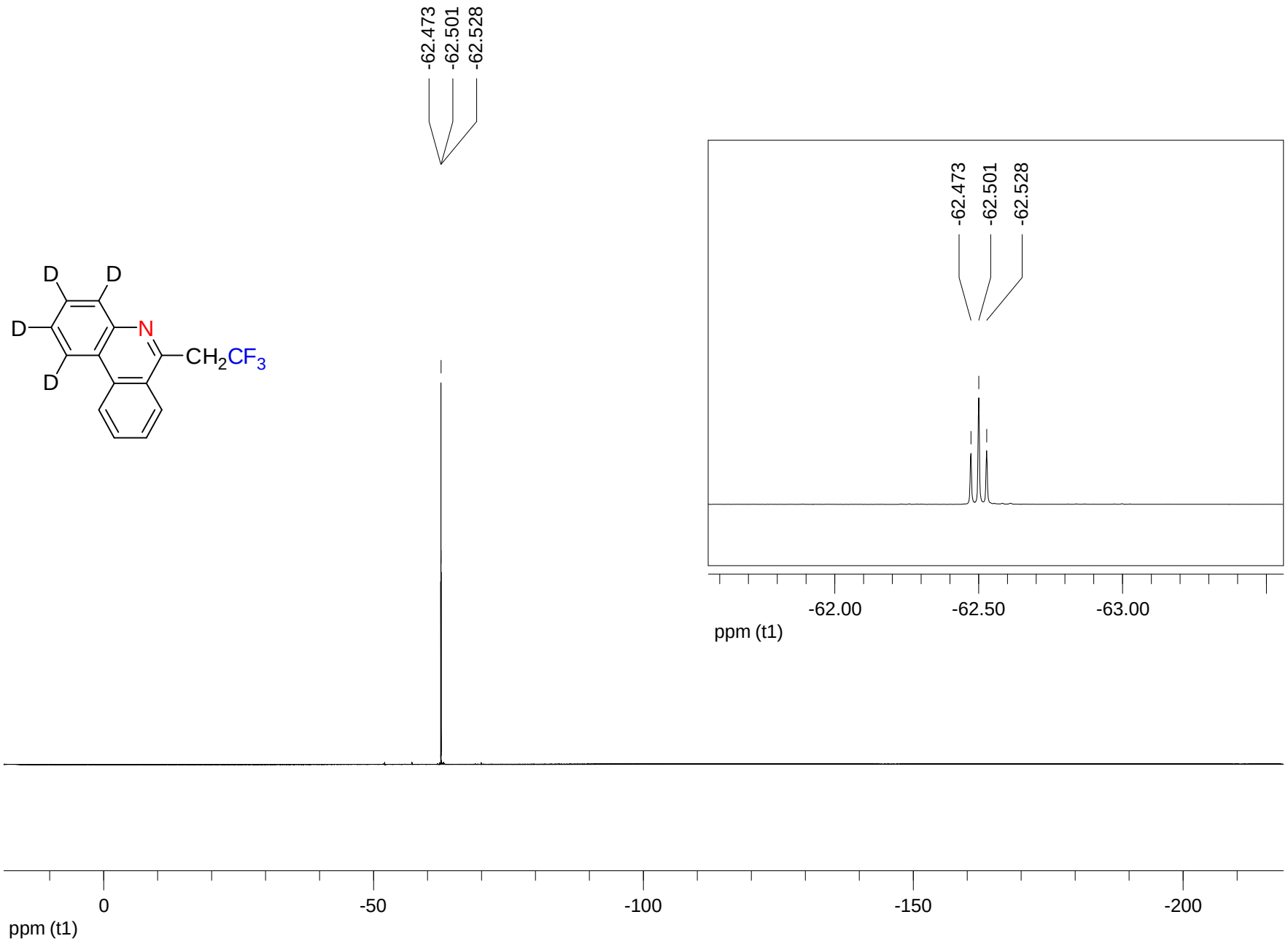
^{1}H NMR Spectrum of **2a-d$_4$** (400 MHz, $CDCl_3$)



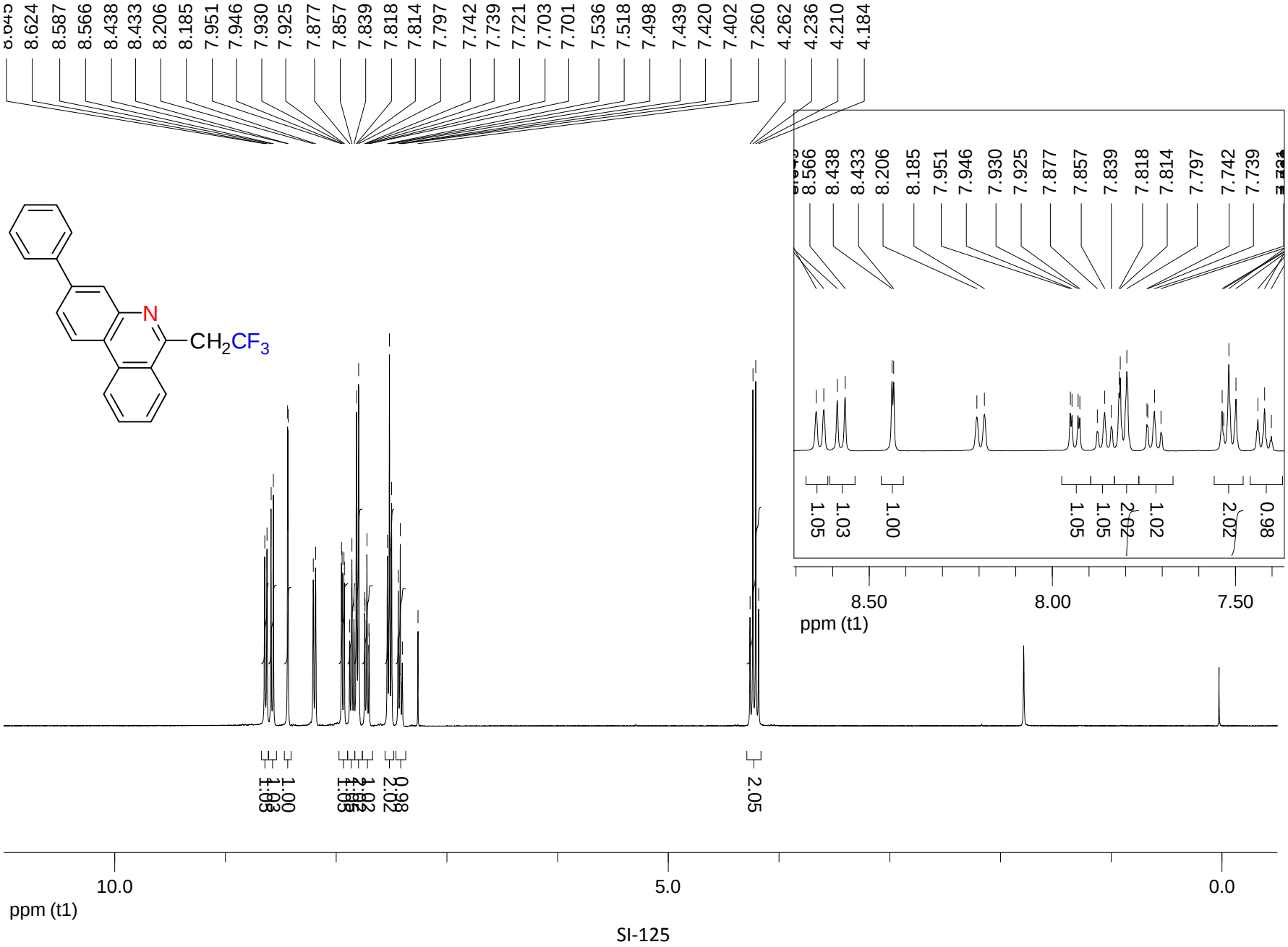
^{13}C NMR Spectrum of **2a-d$_4$** (100 MHz, $CDCl_3$)



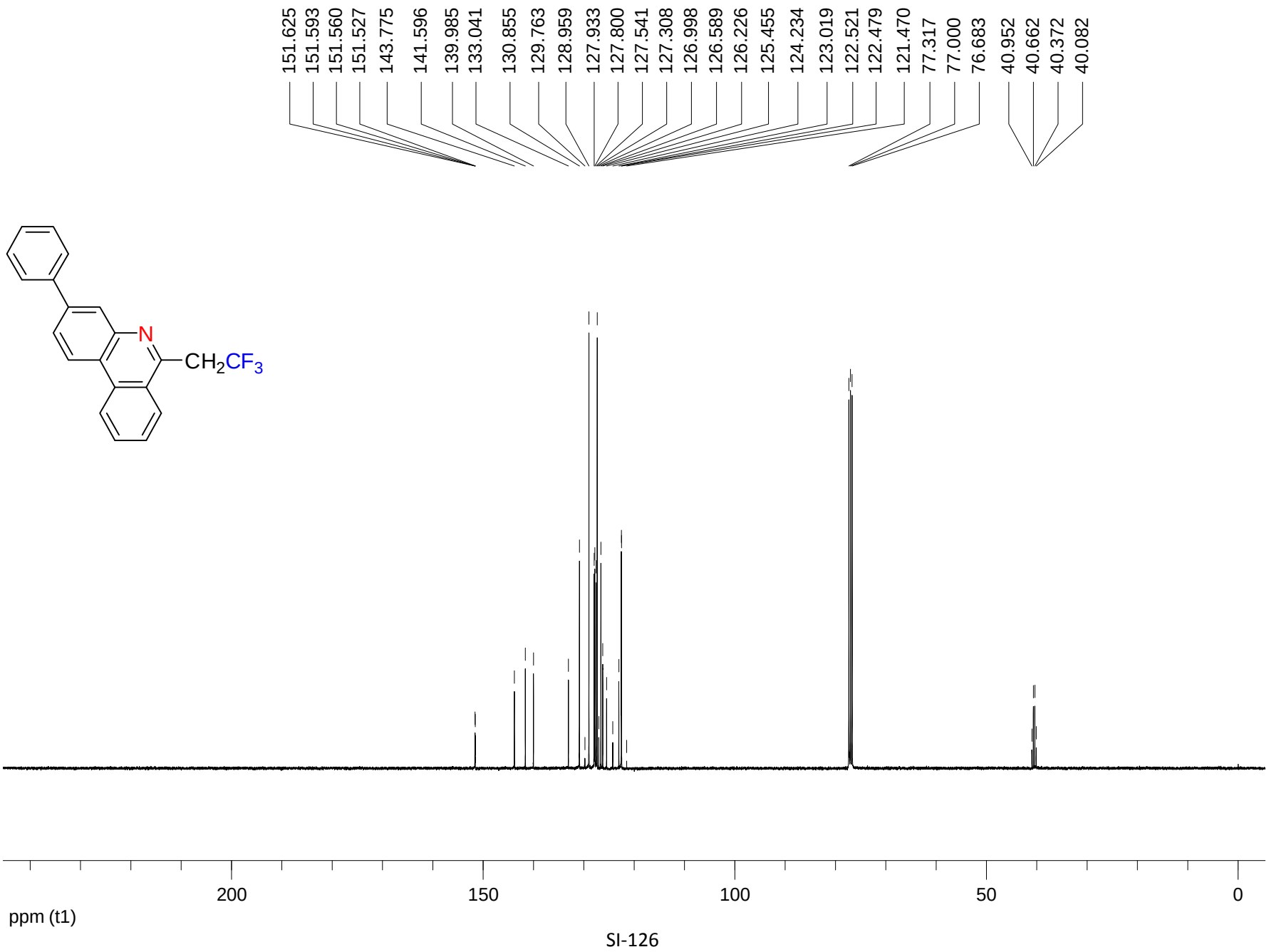
^{19}F NMR Spectrum of **2a-d$_4$** (376 MHz, $CDCl_3$)



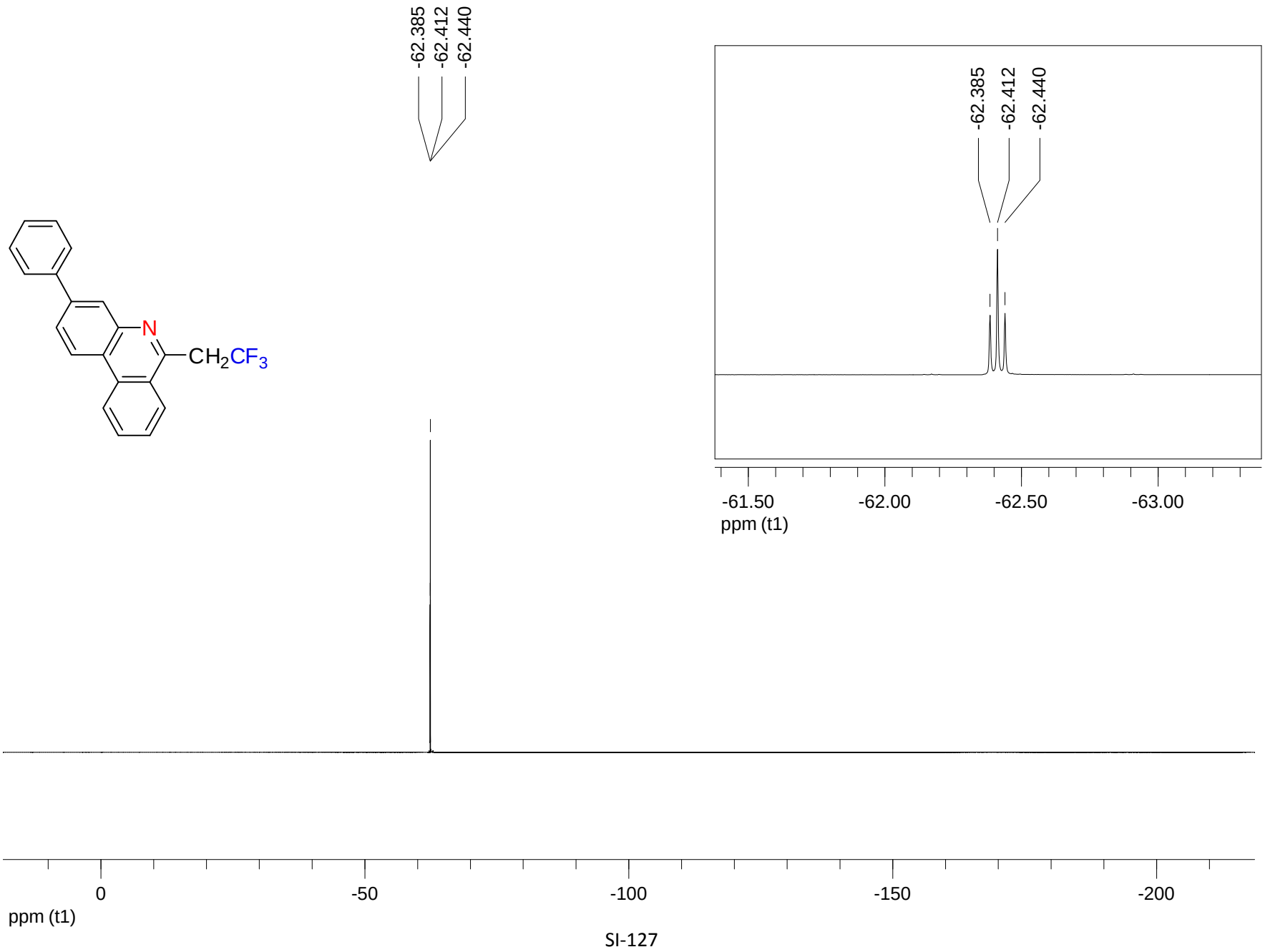
^{1}H NMR Spectrum of **2b** (400 MHz, $CDCl_3$)



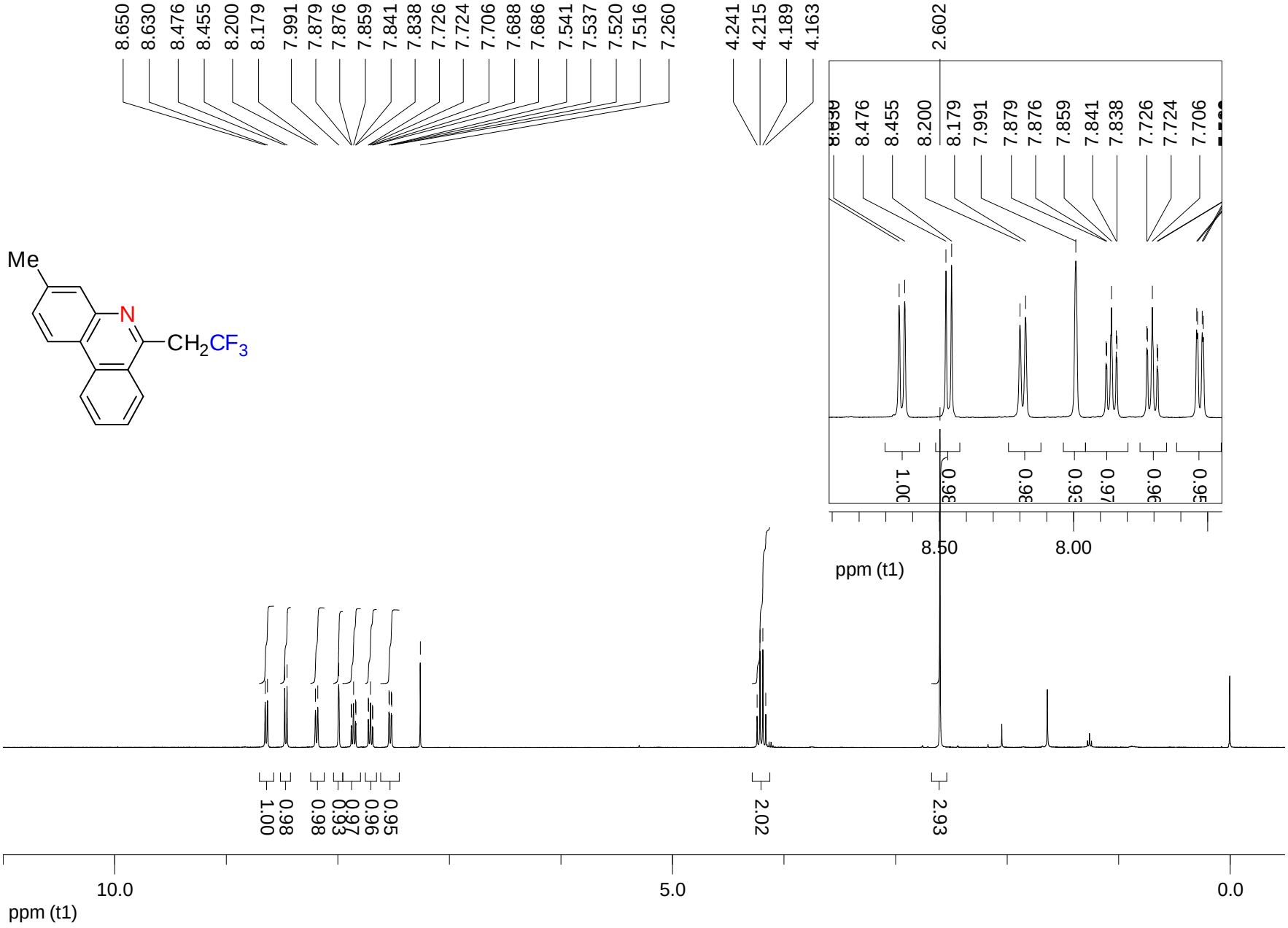
^{13}C NMR Spectrum of **2b** (100 MHz, $CDCl_3$)



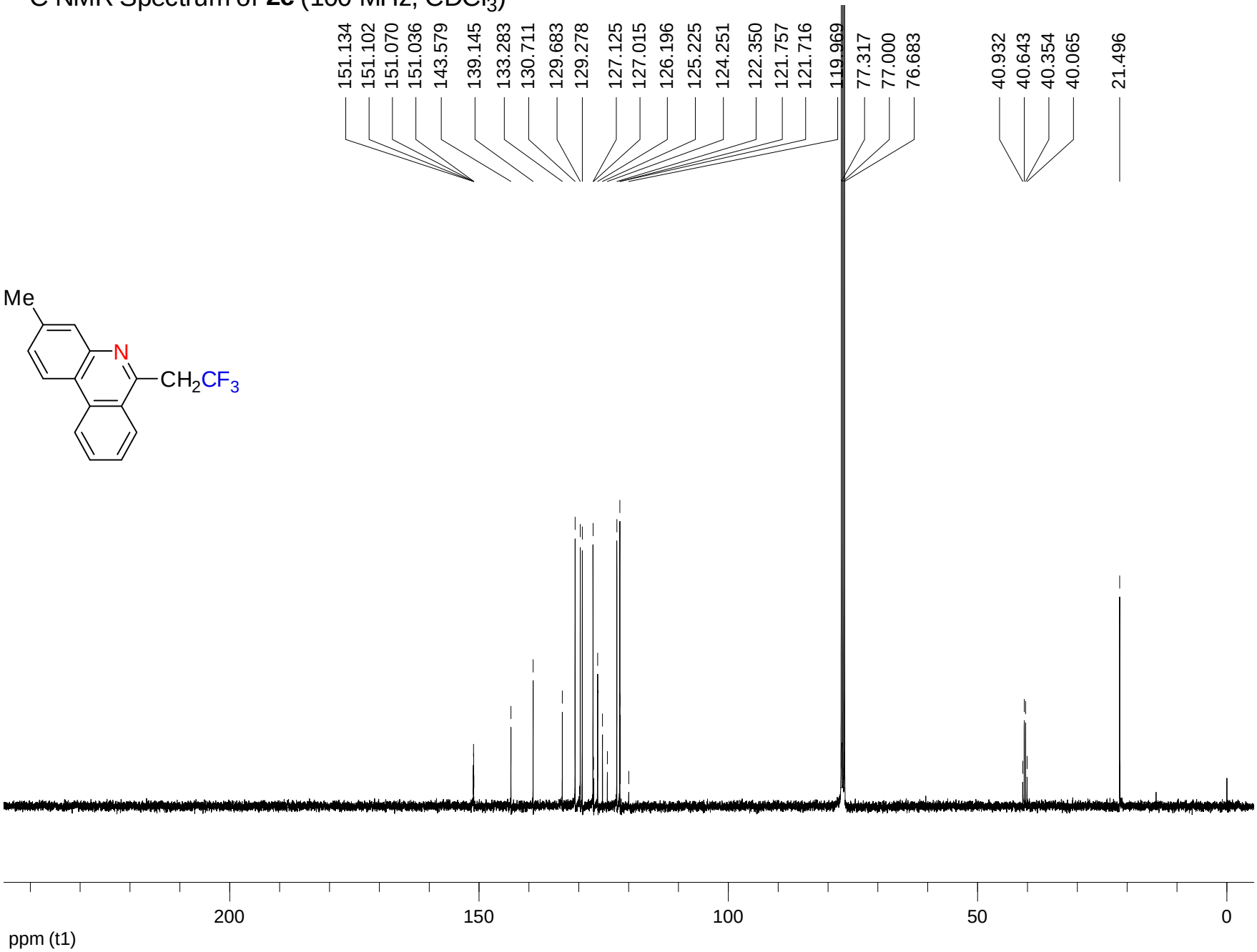
^{19}F NMR Spectrum of **2b** (376 MHz, $CDCl_3$)



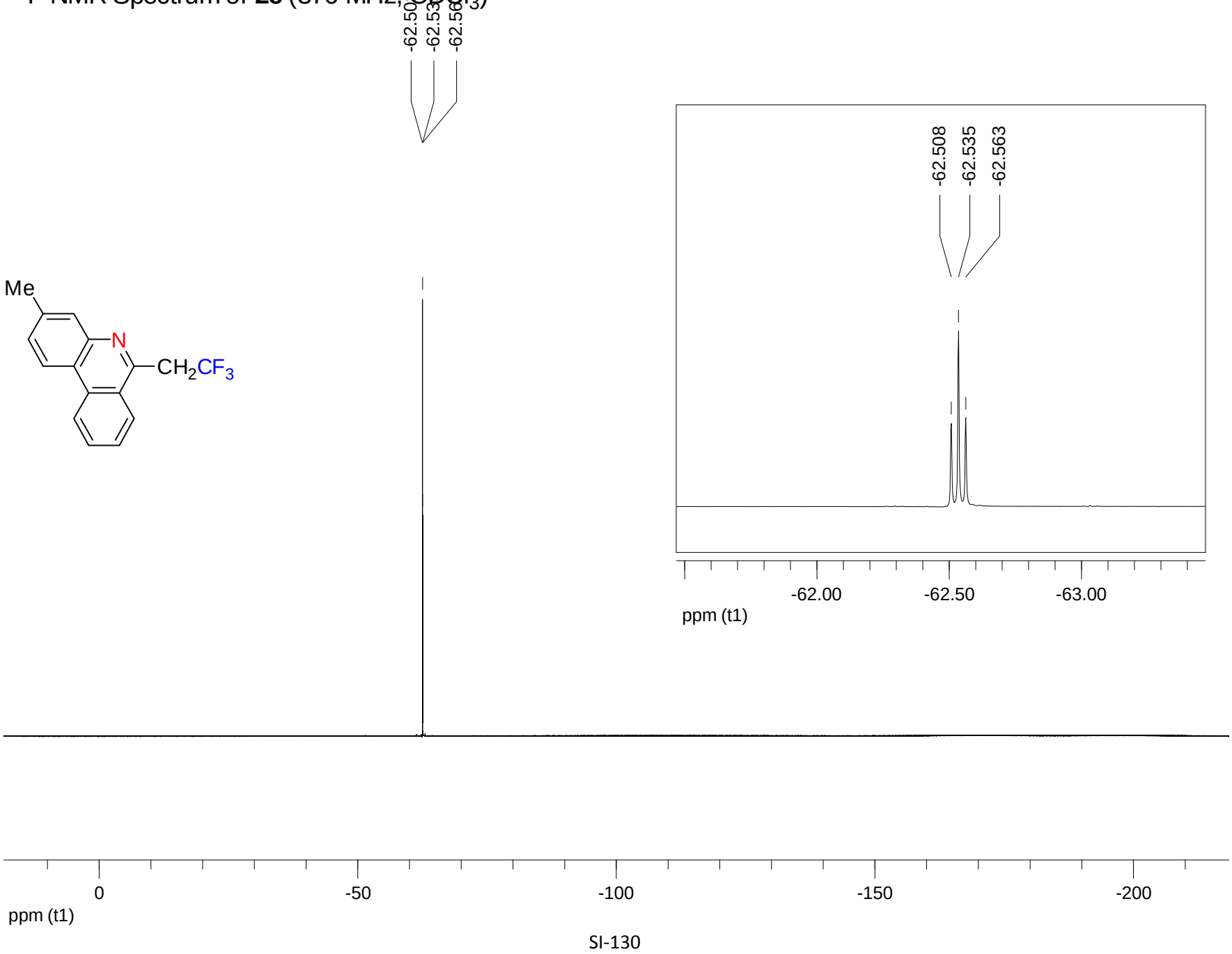
^{1}H NMR Spectrum of **2c** (400 MHz, $CDCl_3$)



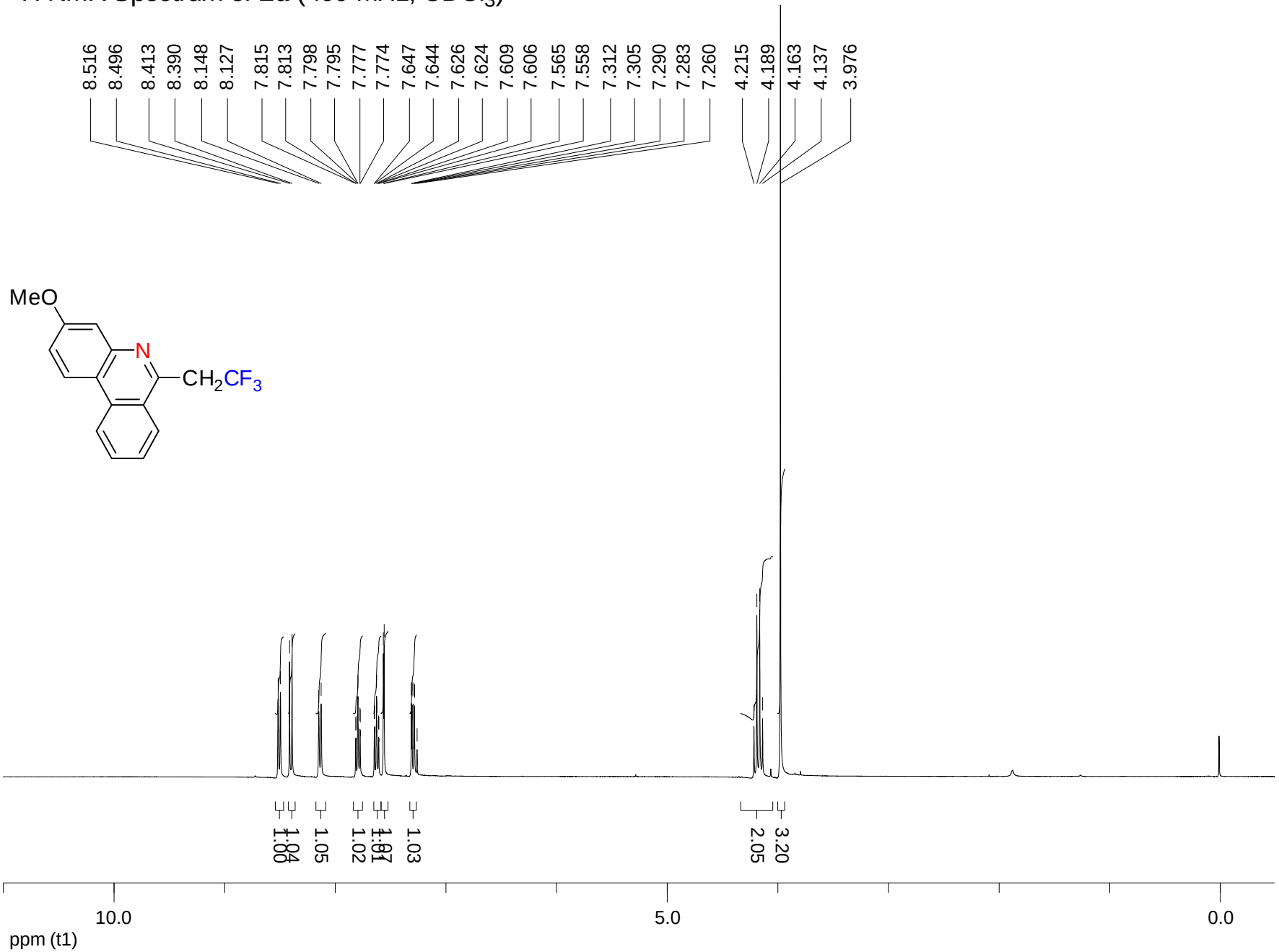
^{13}C NMR Spectrum of **2c** (100 MHz, $CDCl_3$)



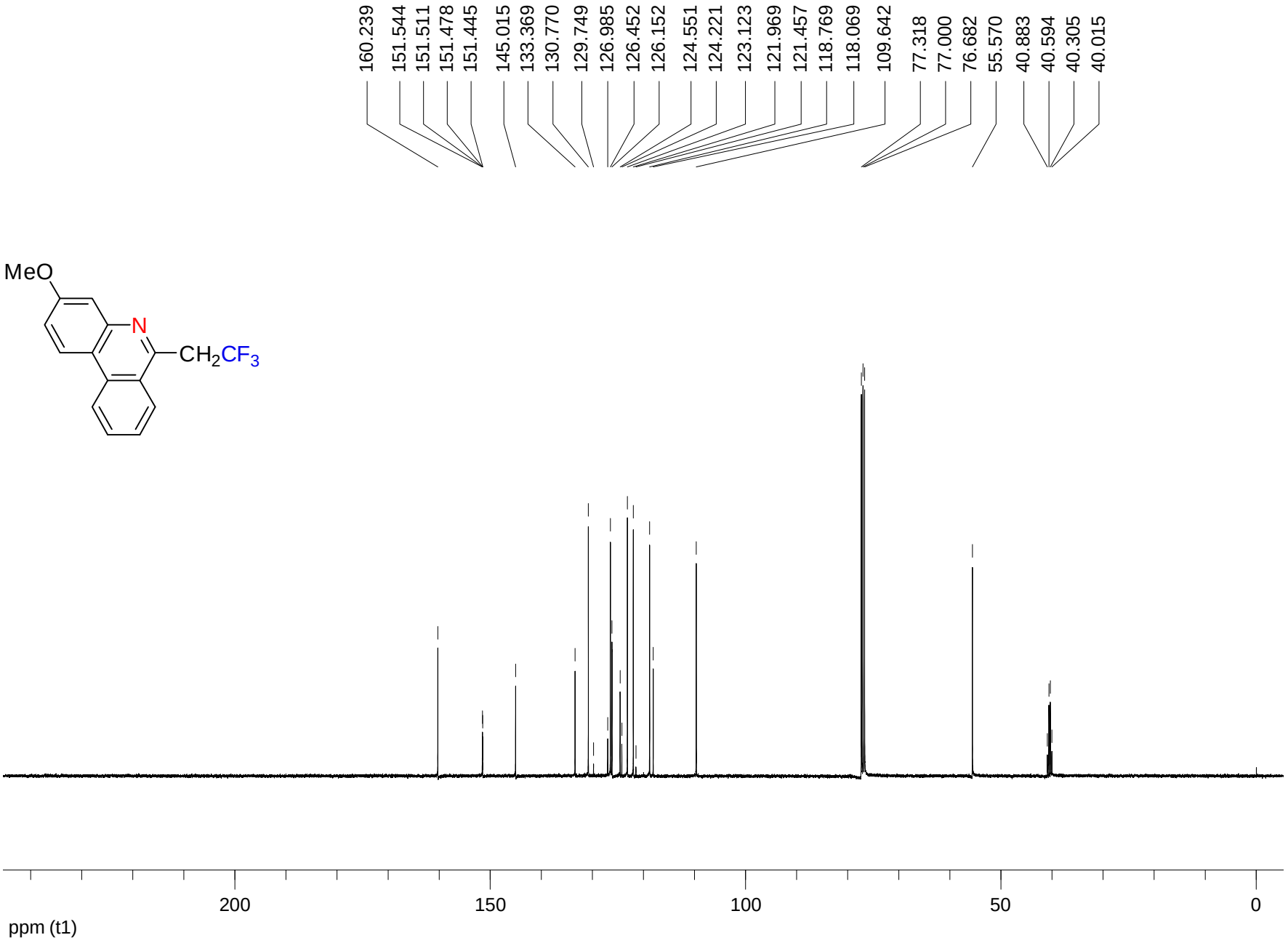
^{19}F NMR Spectrum of **2c** (376 MHz, $CDCl_3$)



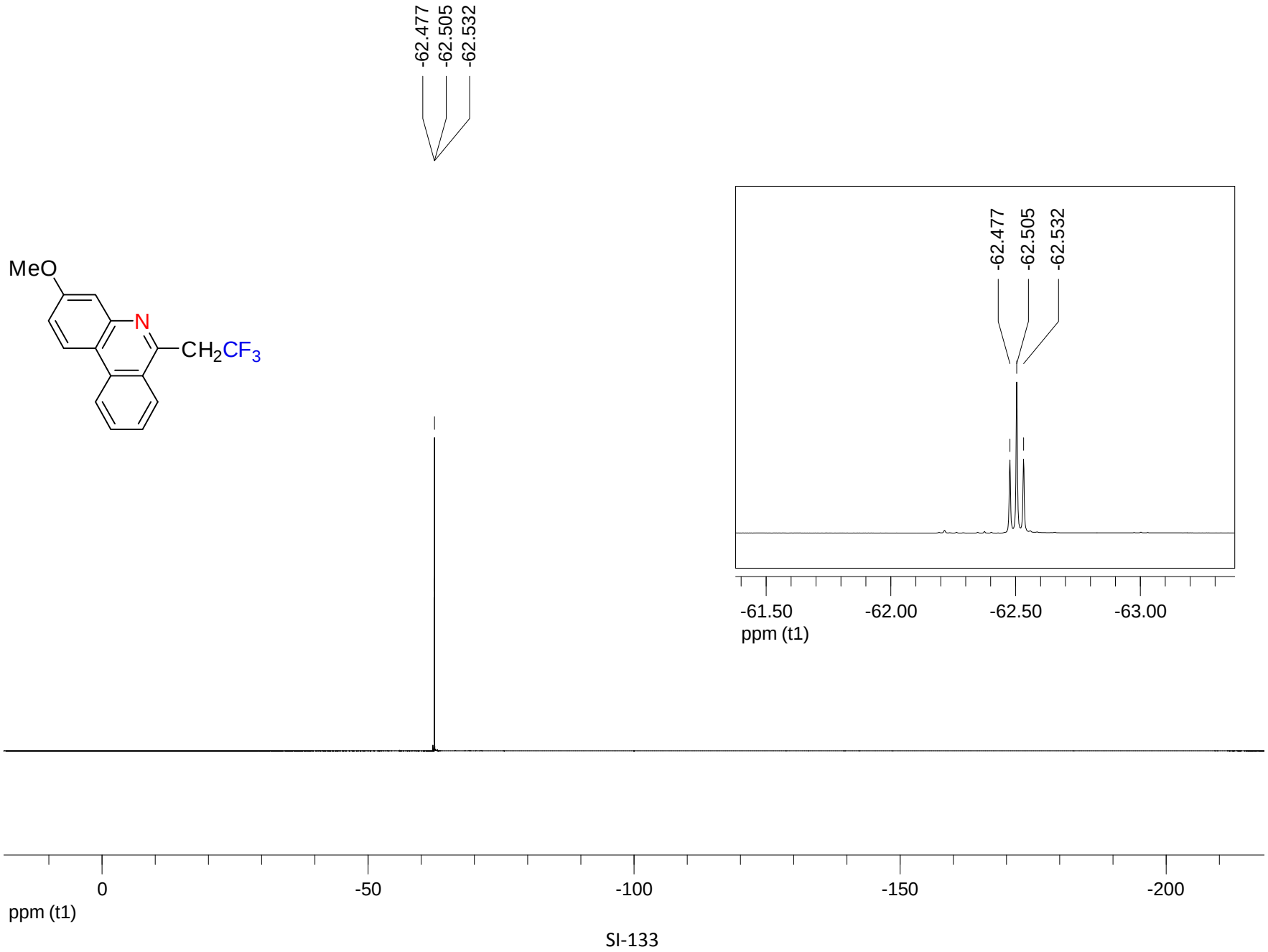
^{1}H NMR Spectrum of **2d** (400 MHz, $CDCl_3$)



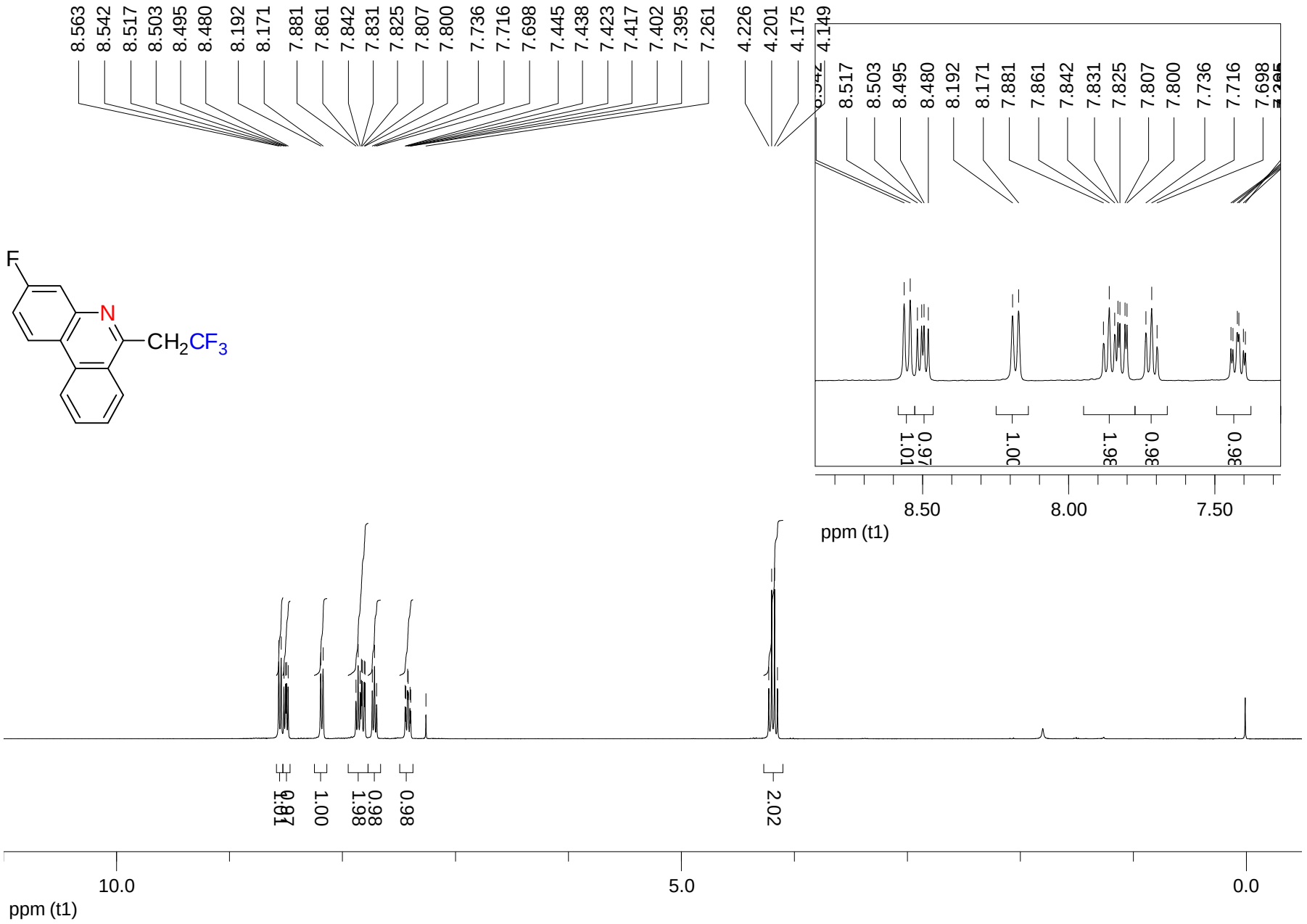
^{13}C NMR Spectrum of **2d** (100 MHz, $CDCl_3$)



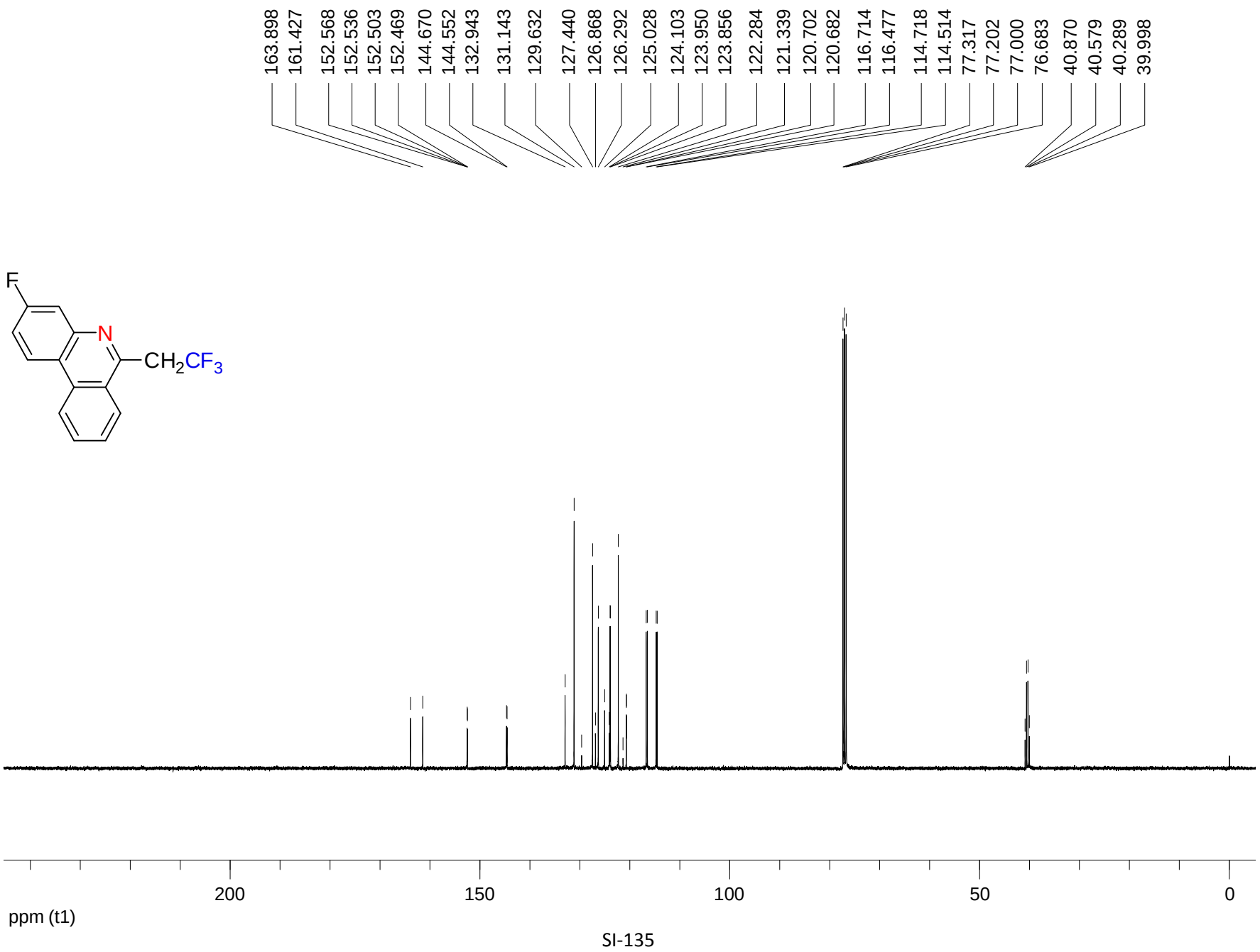
^{19}F NMR Spectrum of **2d** (376 MHz, $CDCl_3$)



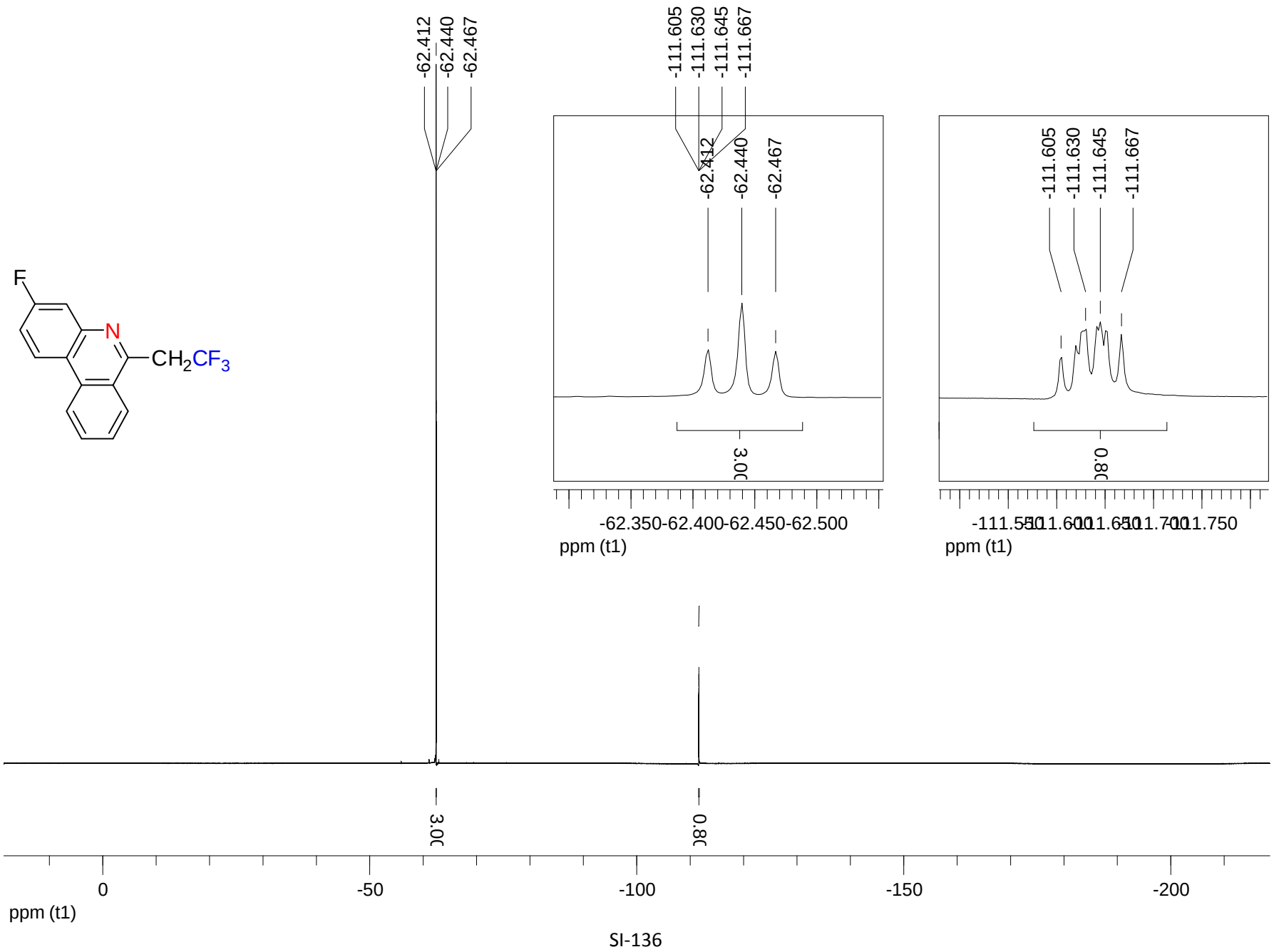
^{1}H NMR Spectrum of **2e** (400 MHz, $CDCl_3$)



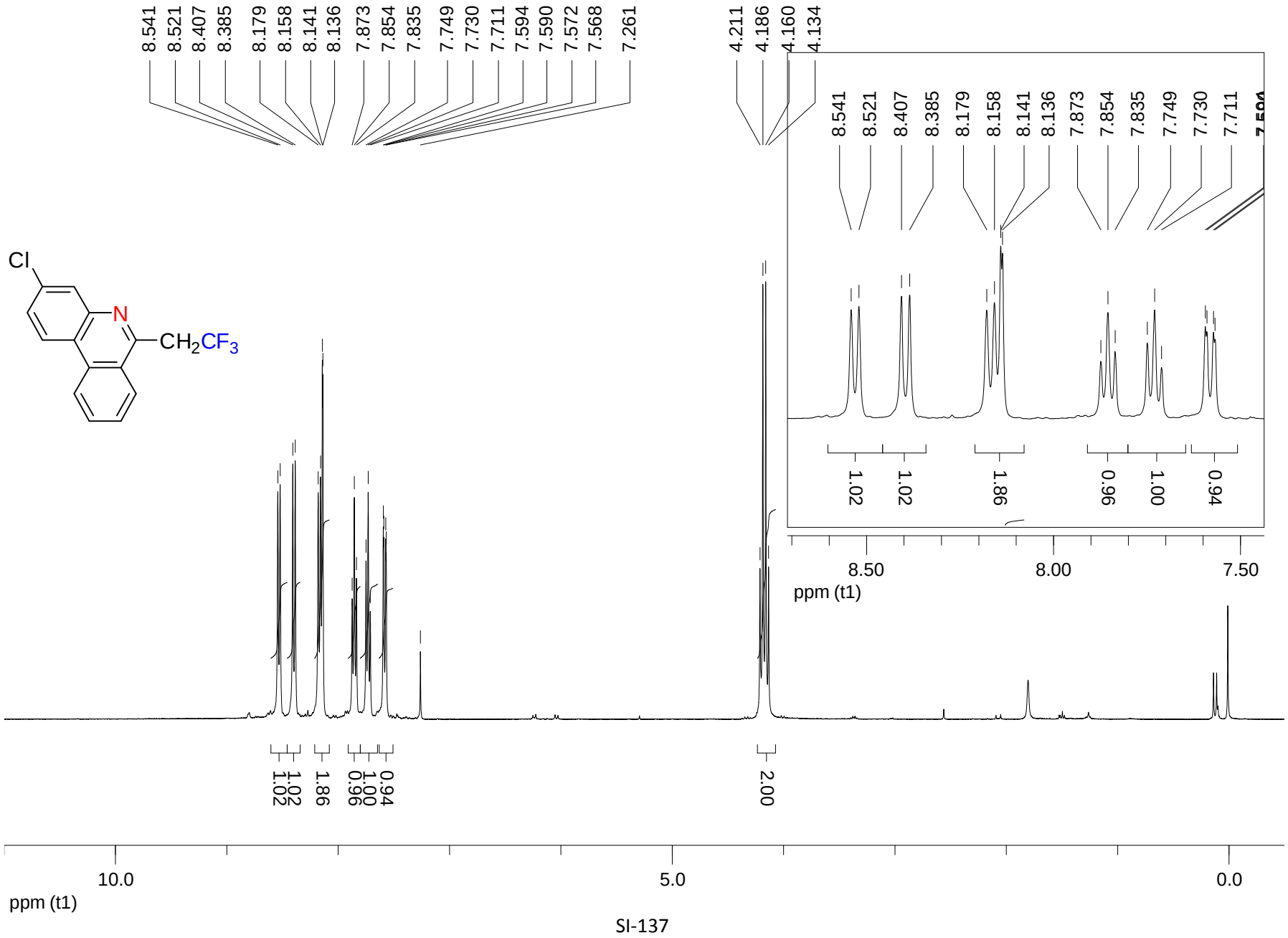
^{13}C NMR Spectrum of **2e** (100 MHz, $CDCl_3$)



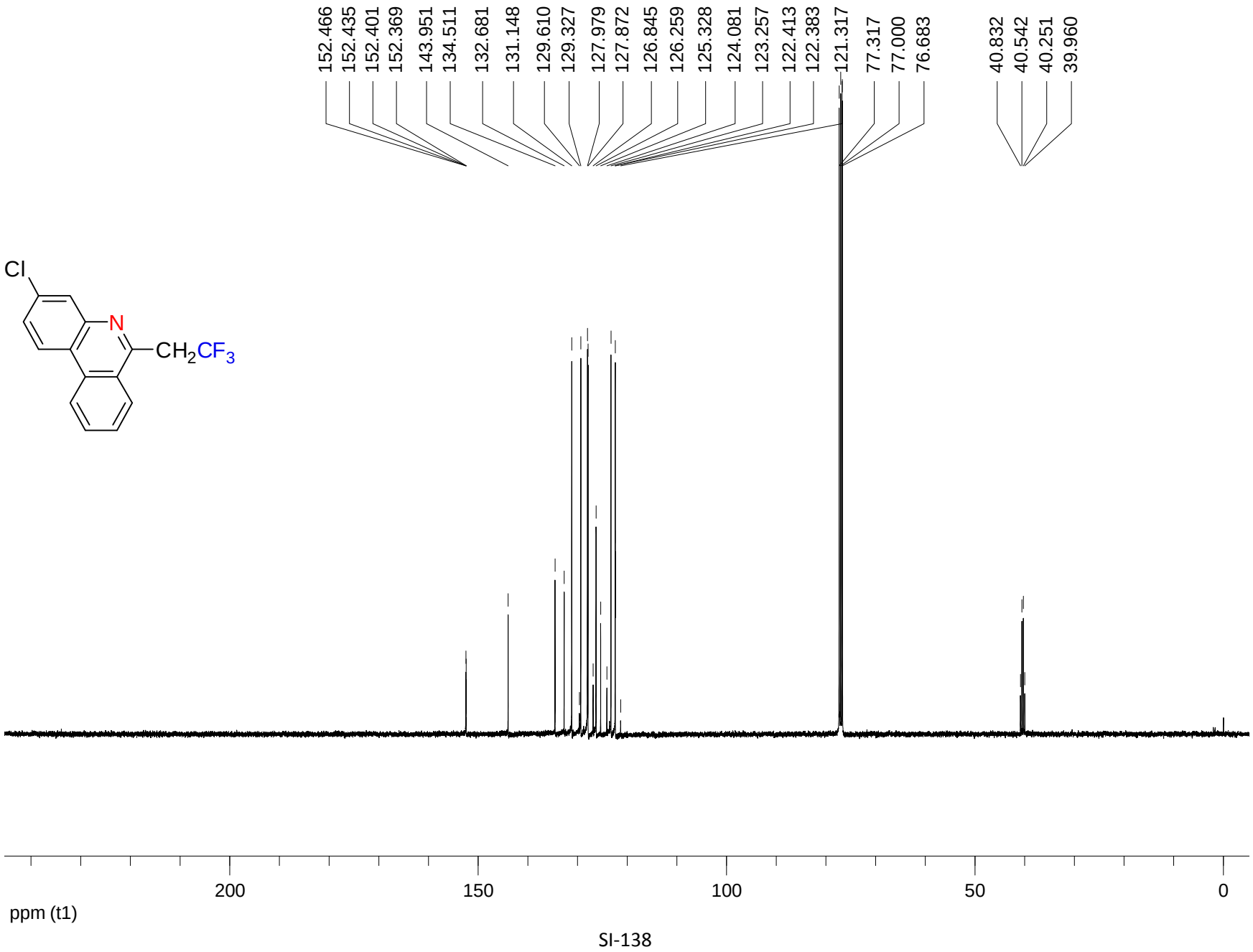
^{19}F NMR Spectrum of **2e** (376 MHz, $CDCl_3$)



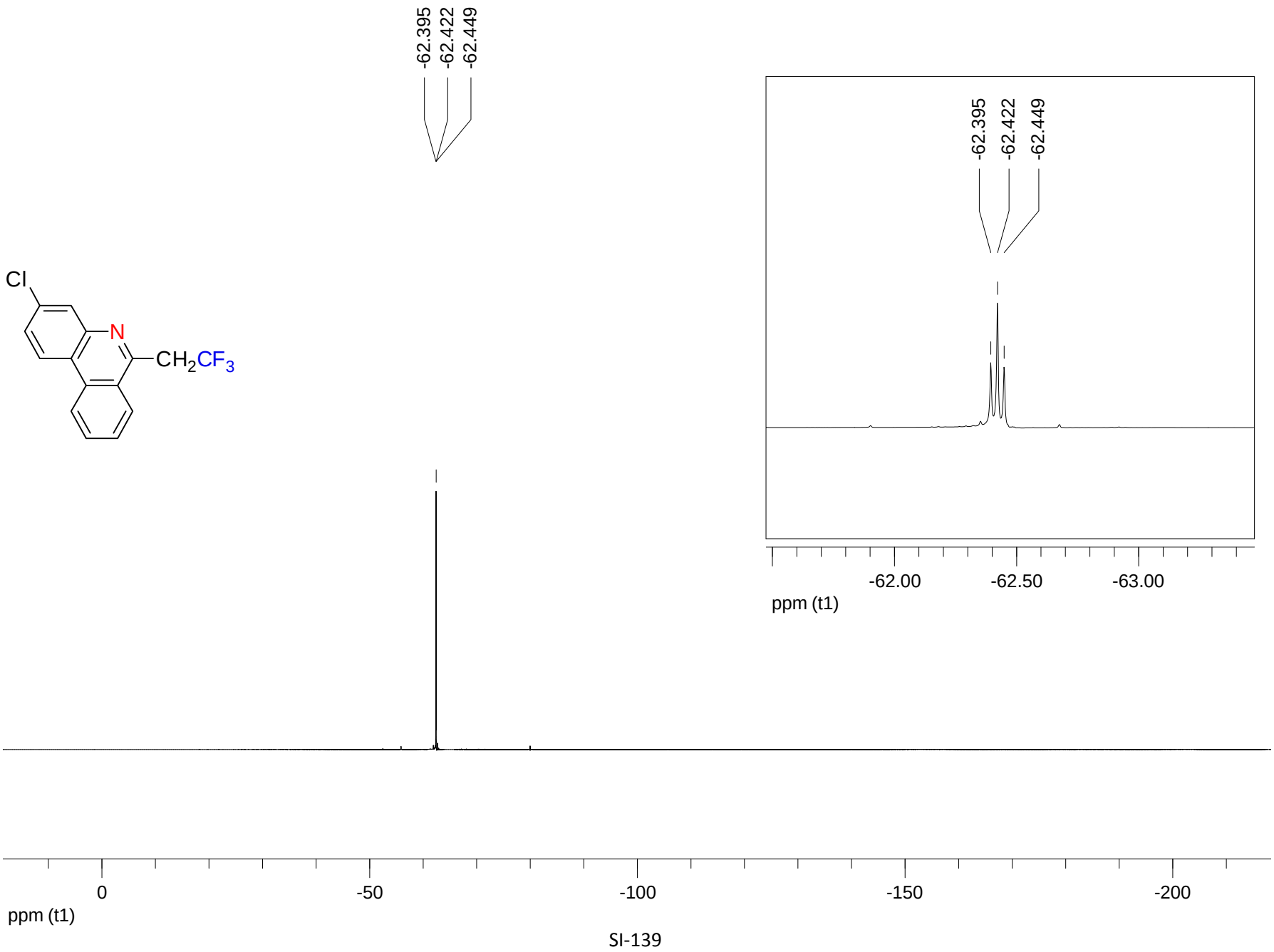
^{1}H NMR Spectrum of **2f** (400 MHz, $CDCl_3$)



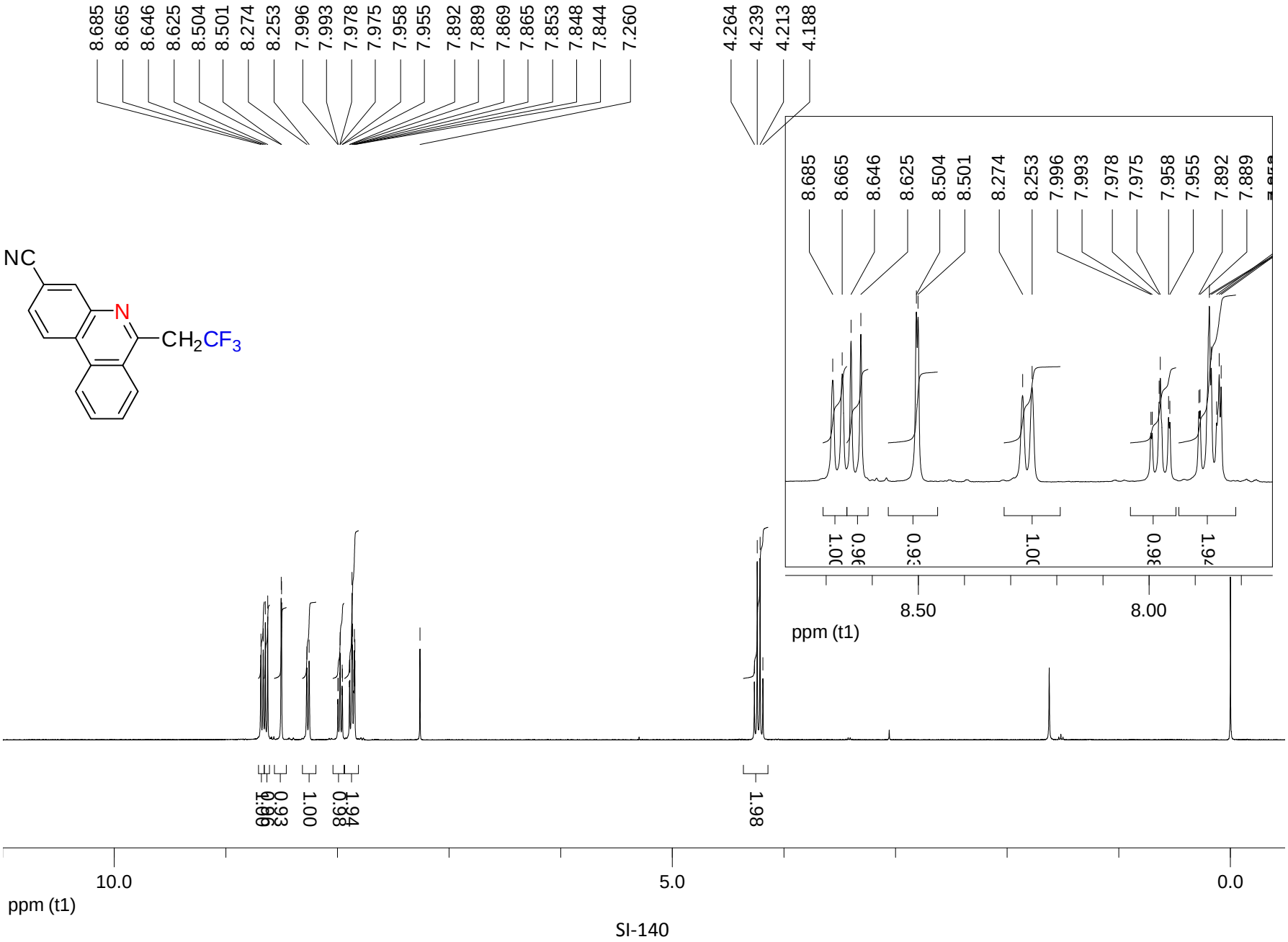
^{13}C NMR Spectrum of **2f** (100 MHz, $CDCl_3$)



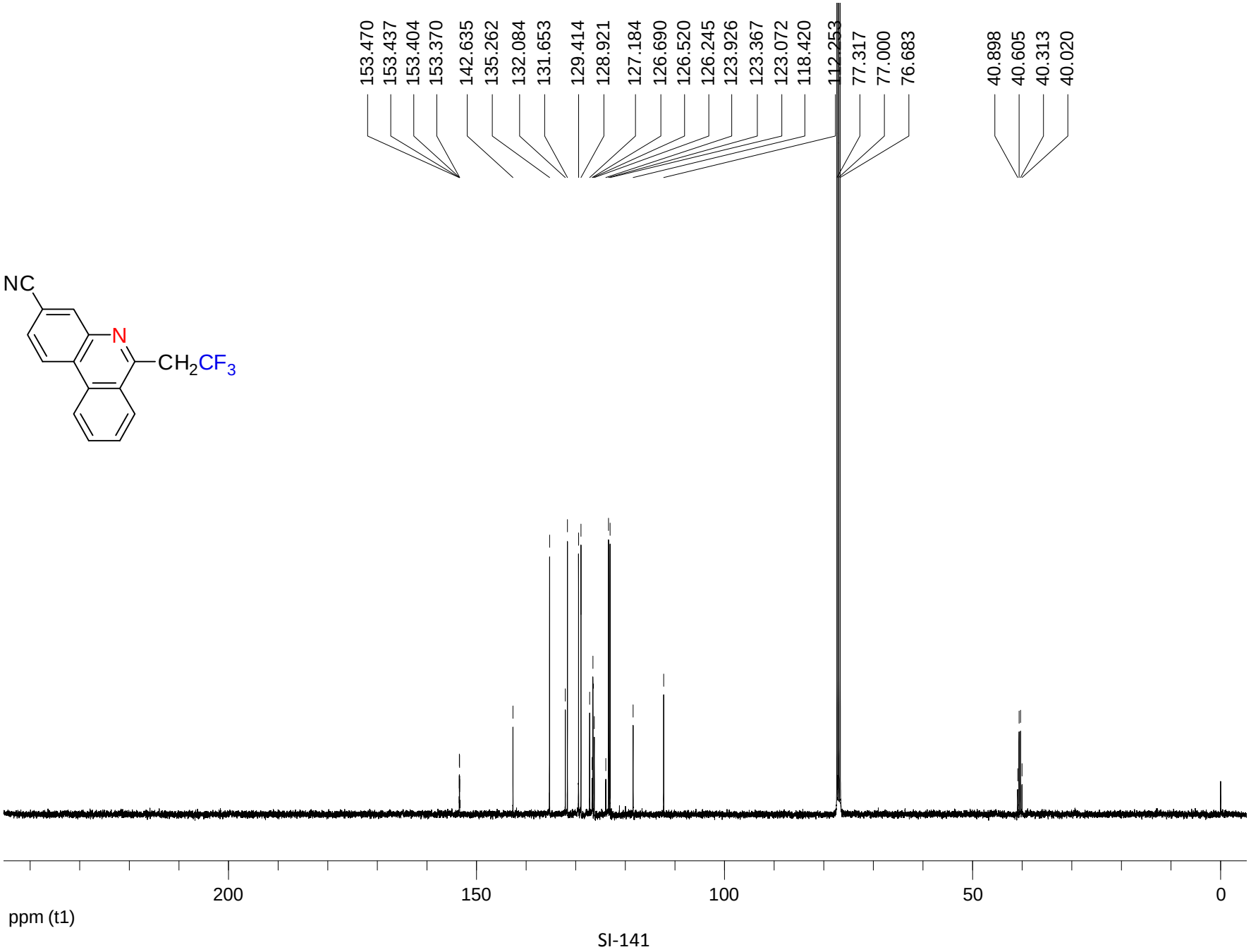
^{19}F NMR Spectrum of **2f** (376 MHz, $CDCl_3$)



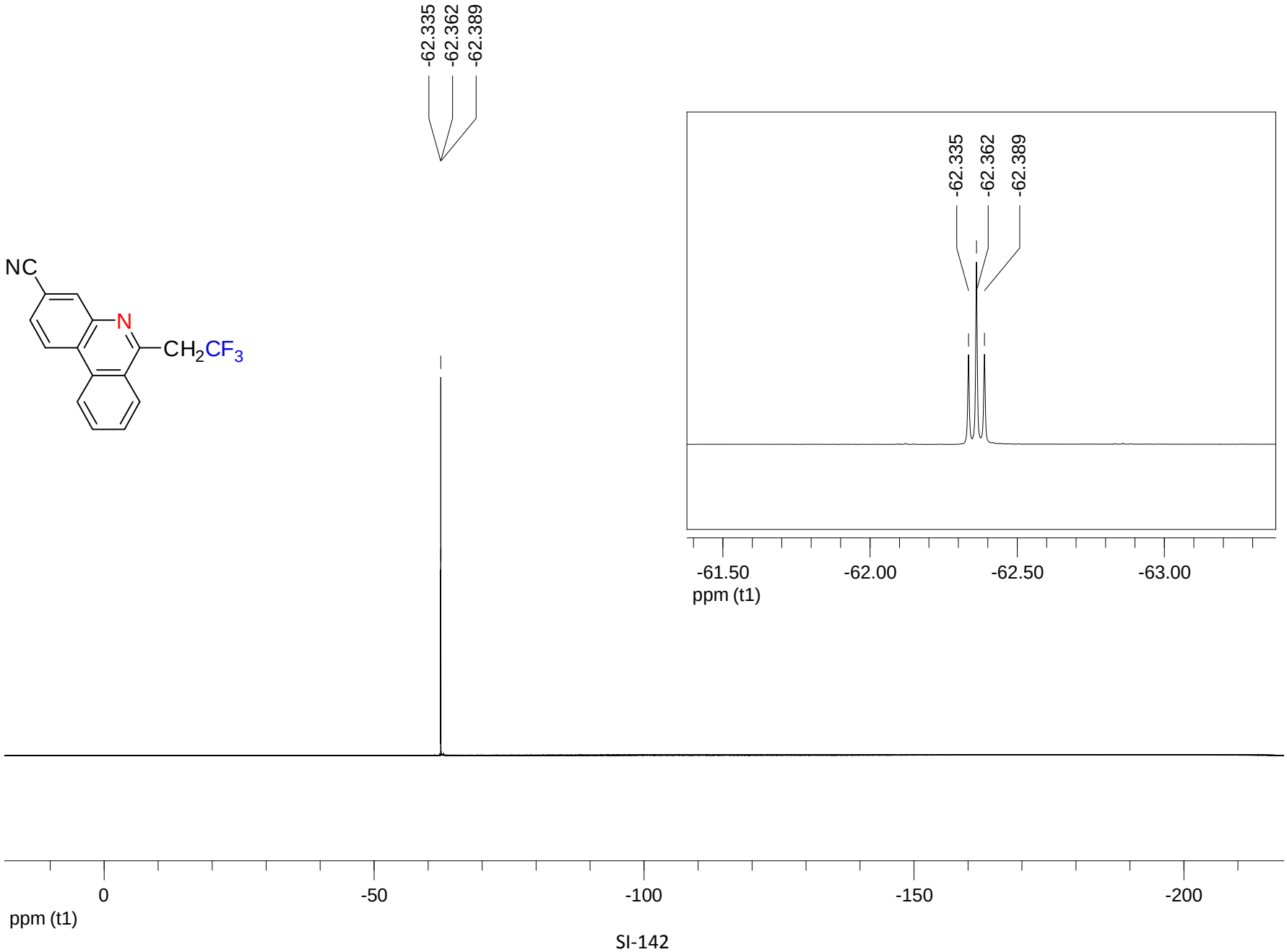
^{1}H NMR Spectrum of **2g** (400 MHz, $CDCl_3$)



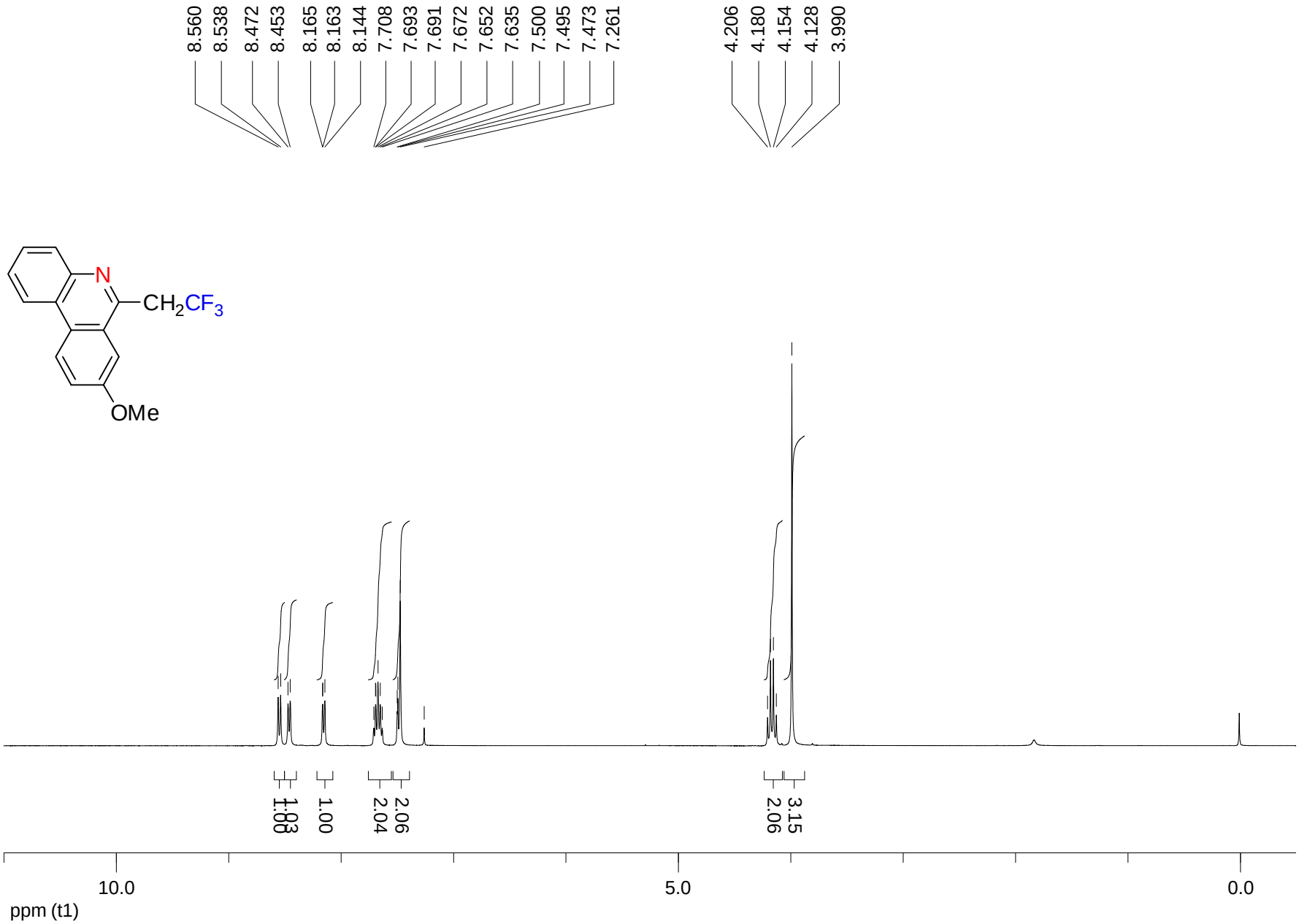
^{13}C NMR Spectrum of **2g** (100 MHz, $CDCl_3$)



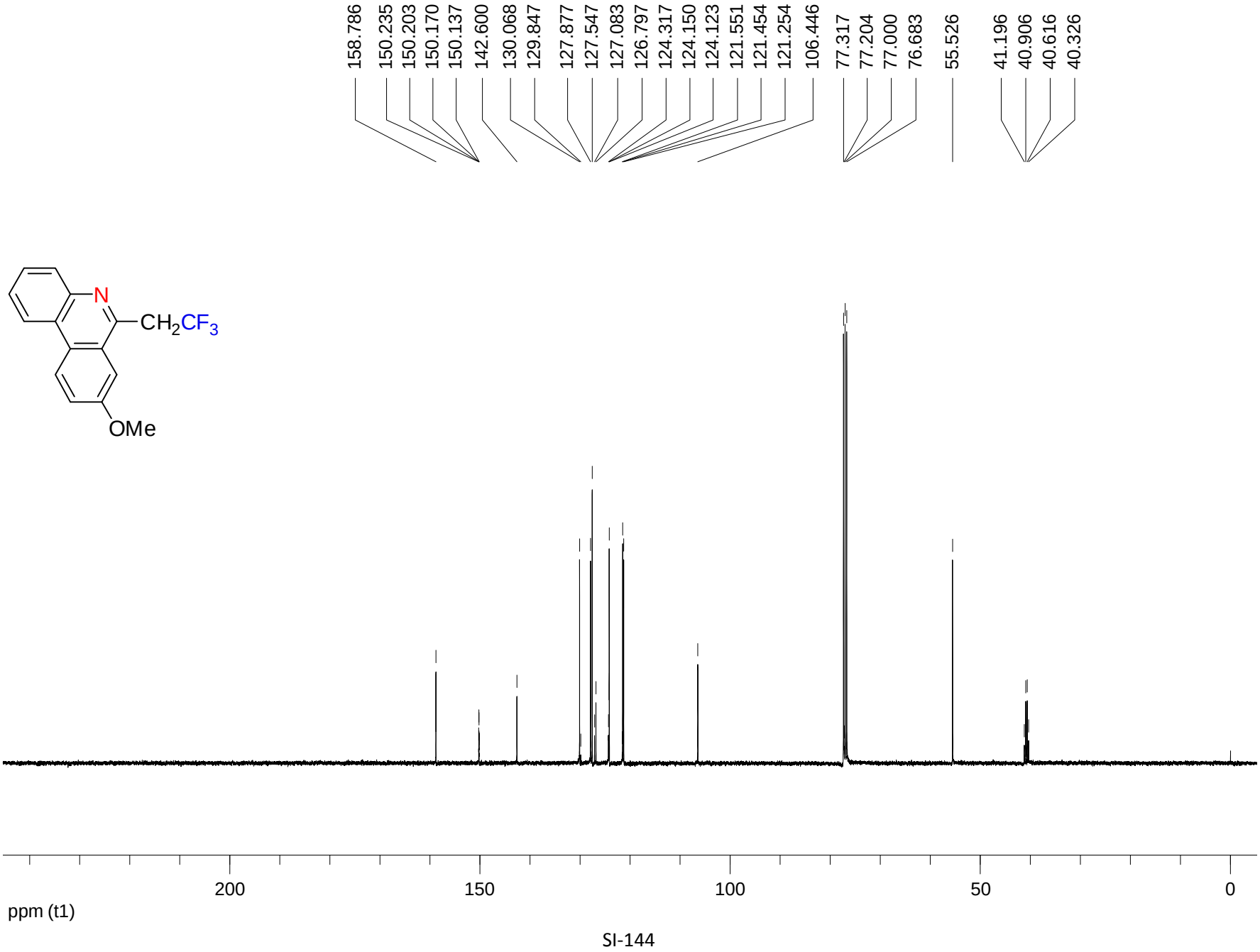
^{19}F NMR Spectrum of **2g** (376 MHz, $CDCl_3$)



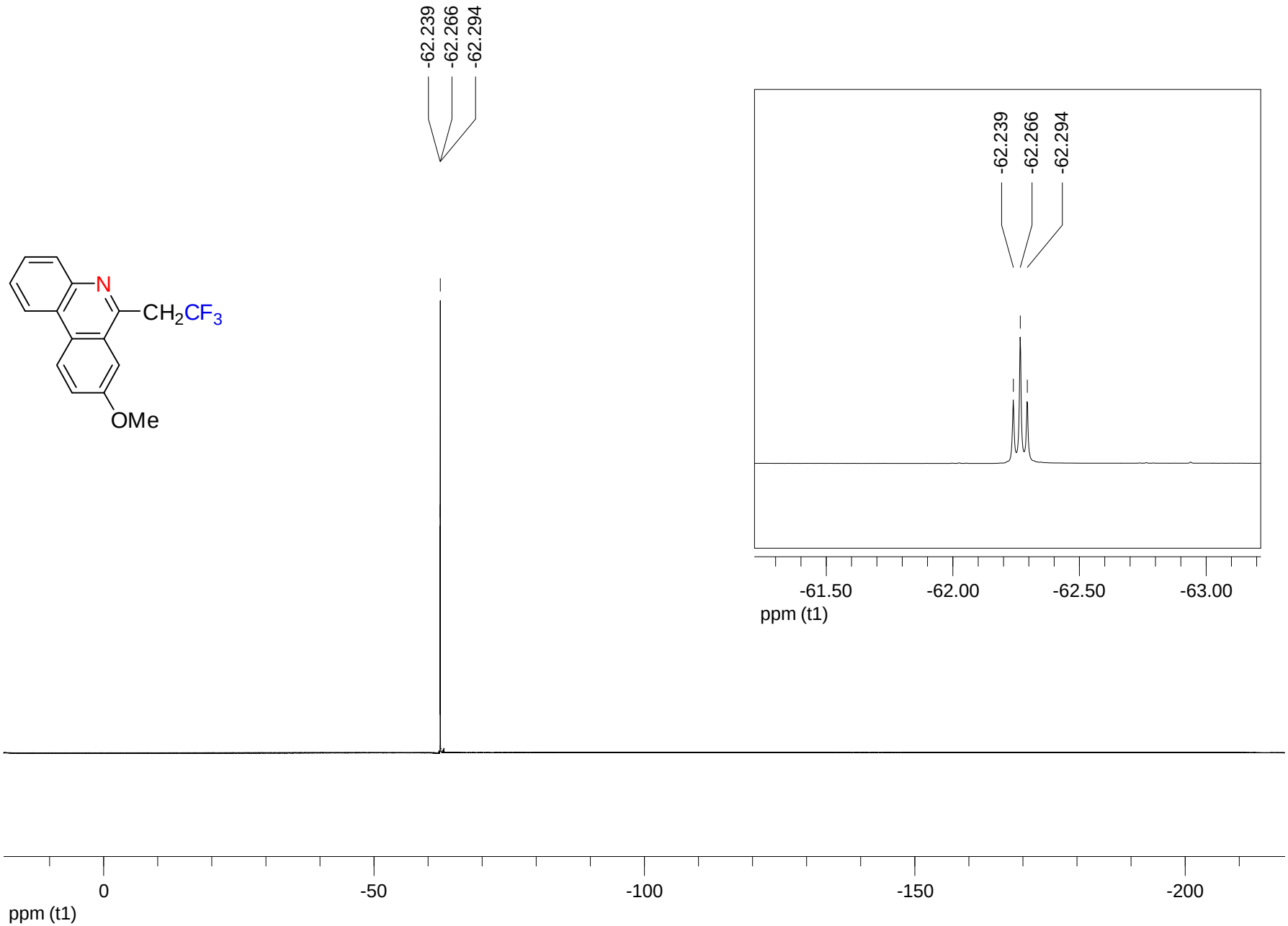
^{1}H NMR Spectrum of **2h** (400 MHz, $CDCl_3$)



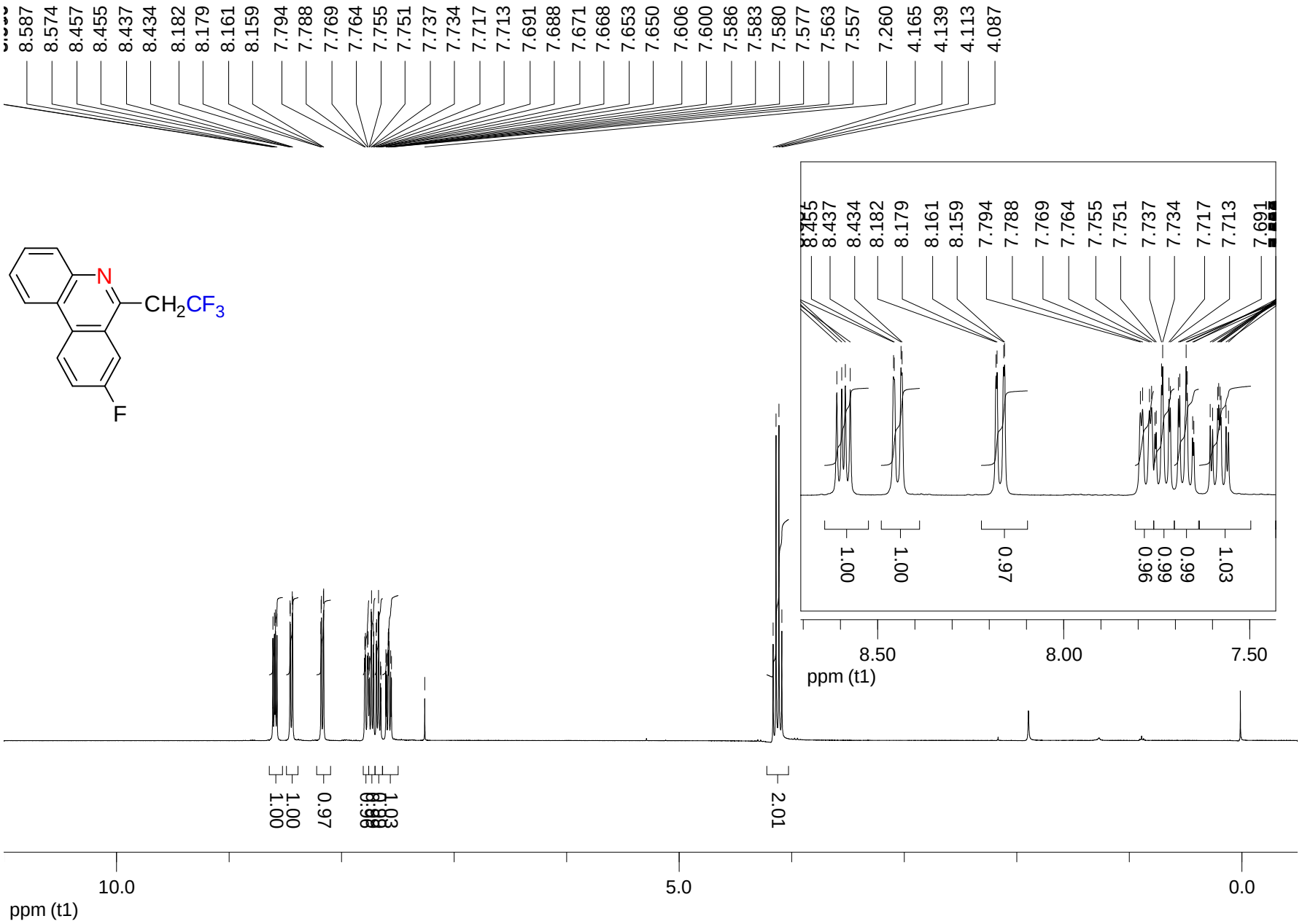
^{13}C NMR Spectrum of **2h** (100 MHz, $CDCl_3$)



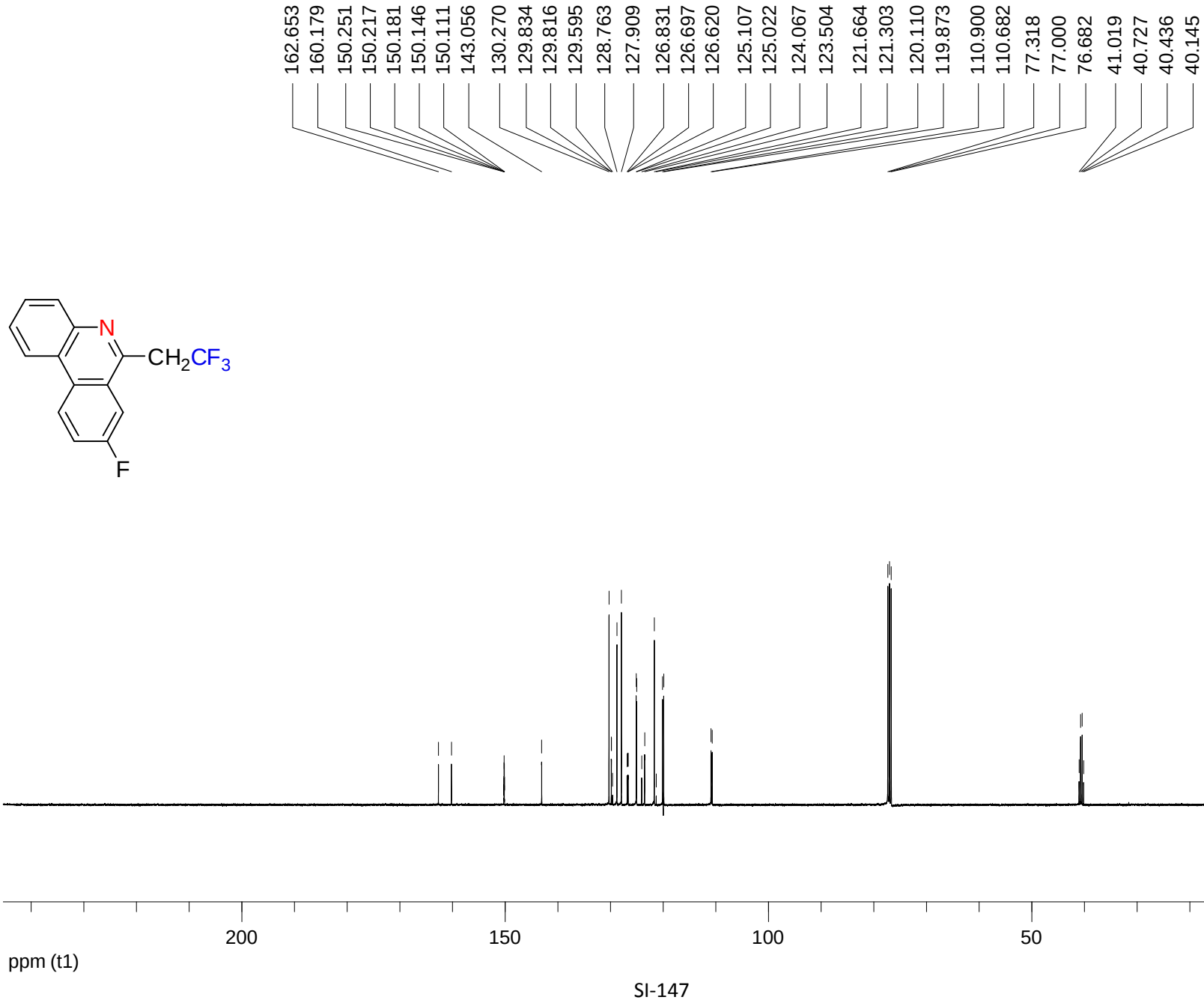
^{19}F NMR Spectrum of **2h** (376 MHz, $CDCl_3$)



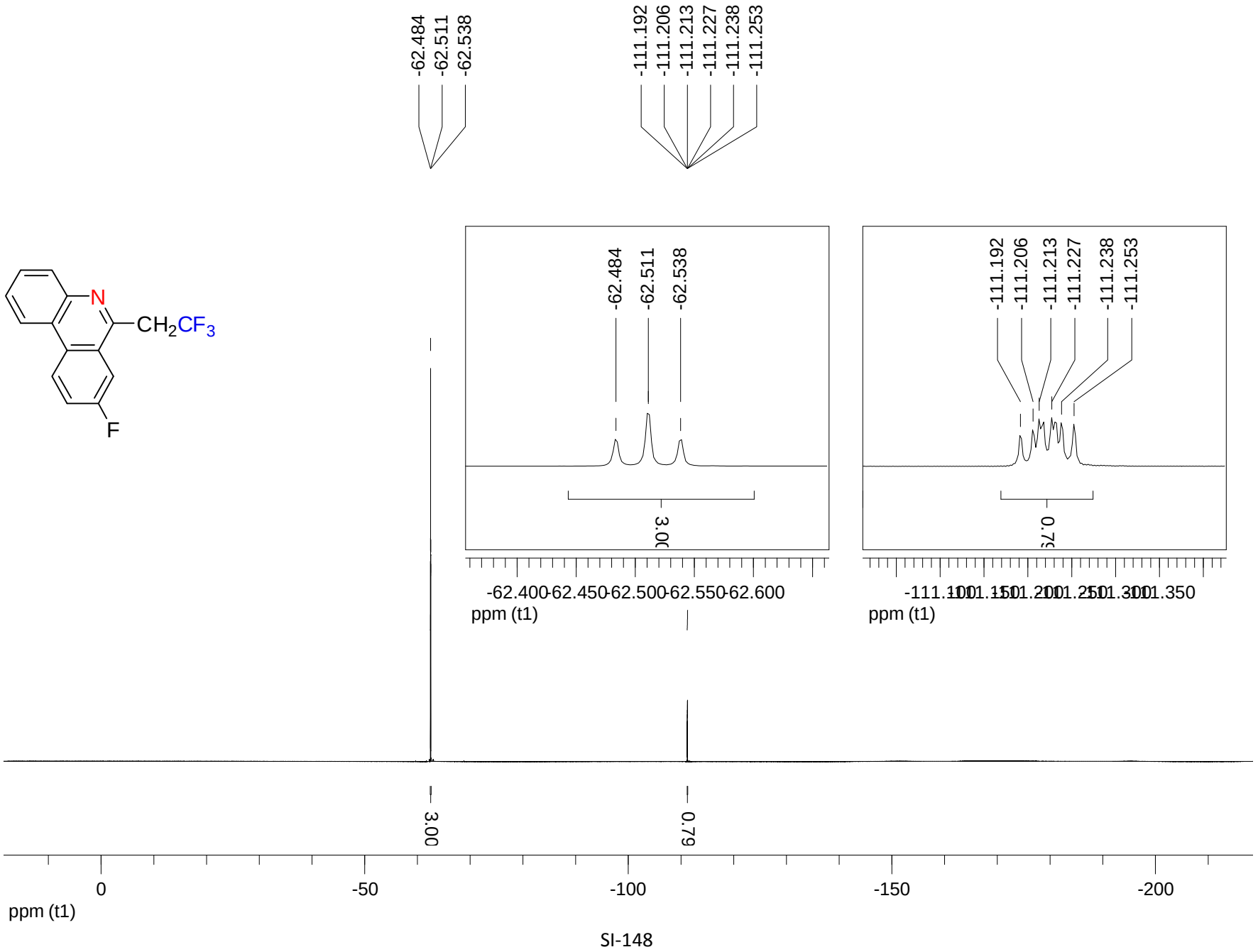
^{1}H NMR Spectrum of **2i** (400 MHz, $CDCl_3$)



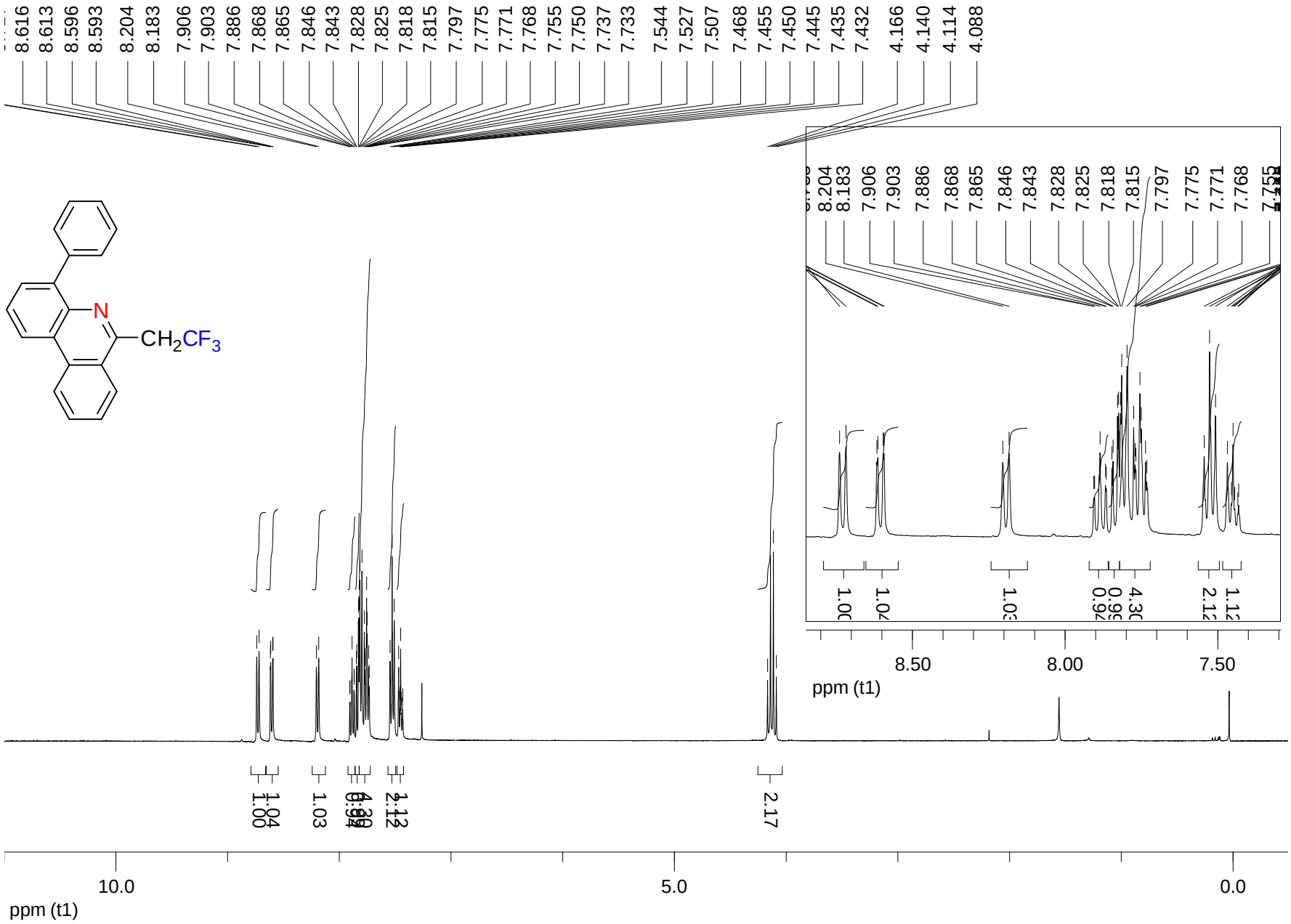
^{13}C NMR Spectrum of **2i** (100 MHz, $CDCl_3$)



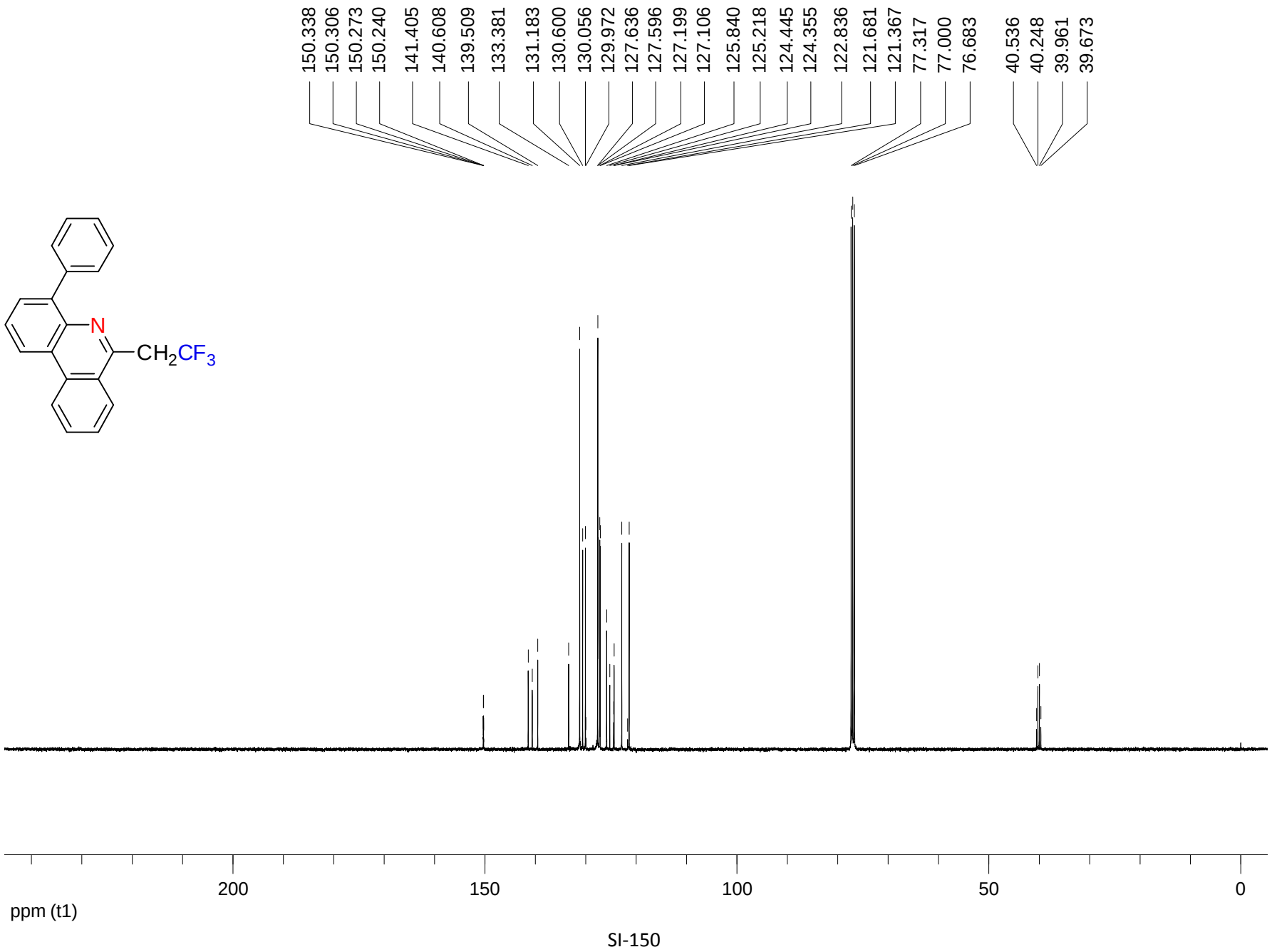
^{19}F NMR Spectrum of **2i** (376 MHz, $CDCl_3$)



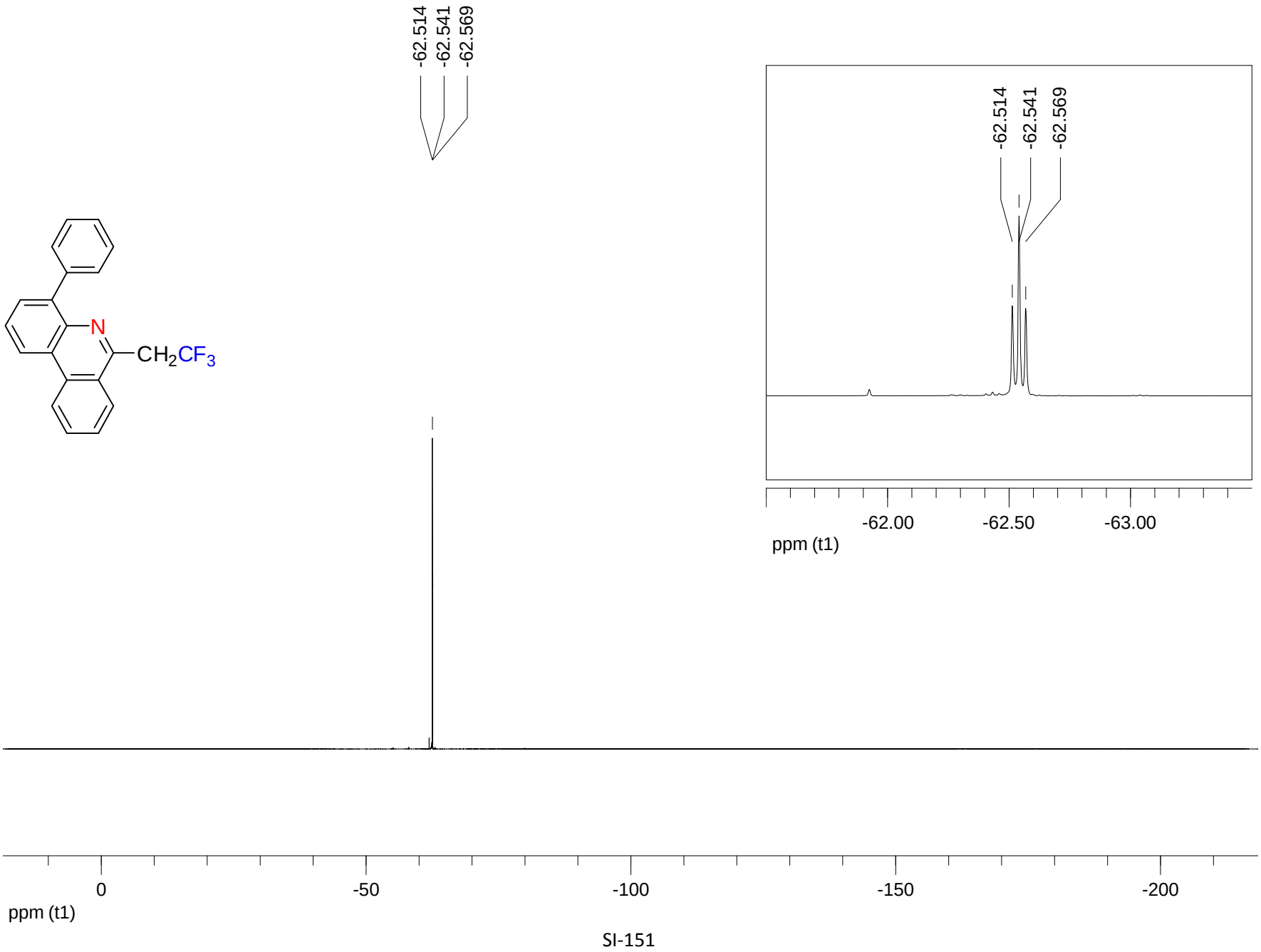
^{1}H NMR Spectrum of **2j** (400 MHz, $CDCl_3$)



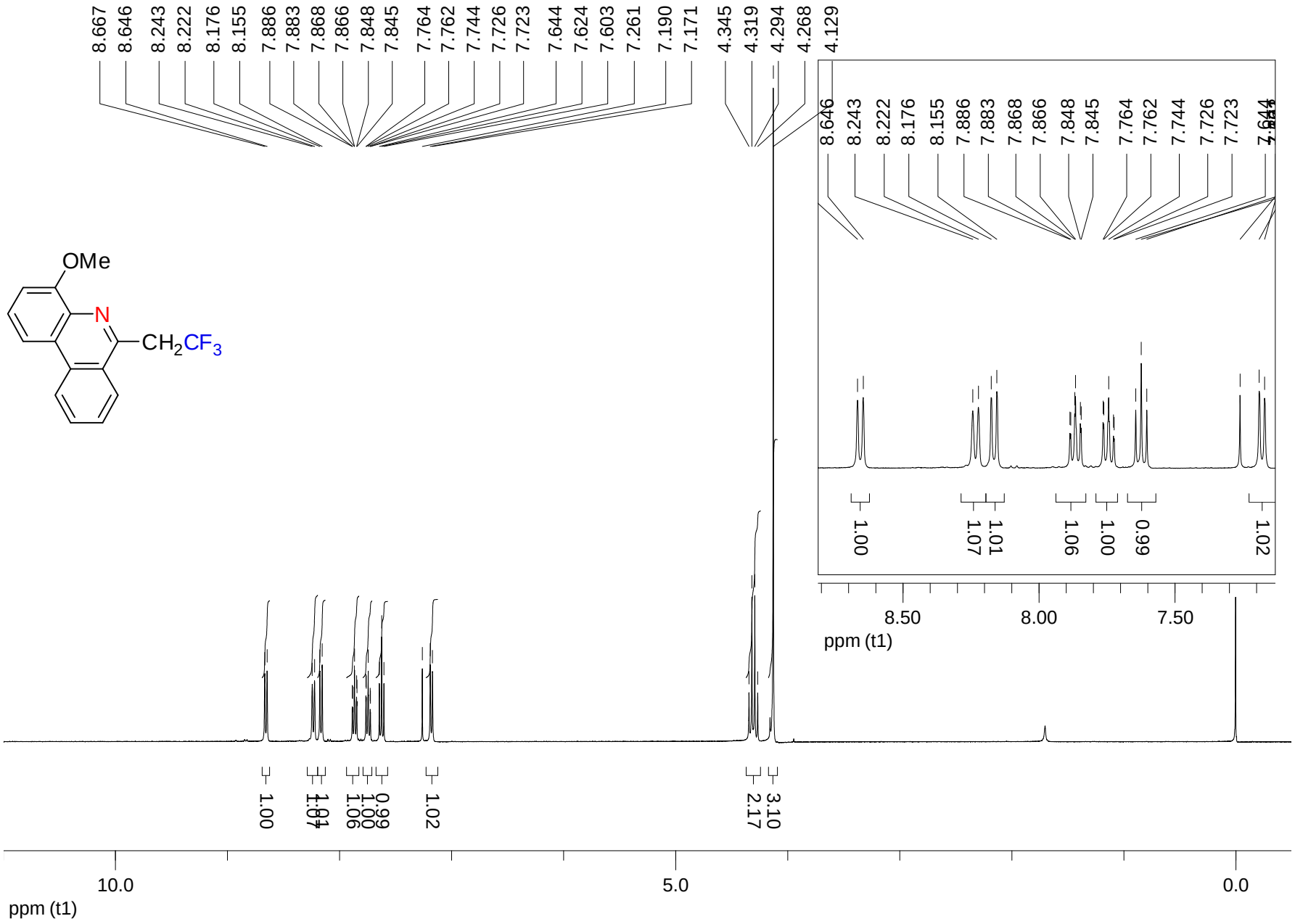
^{13}C NMR Spectrum of **2j** (100 MHz, $CDCl_3$)



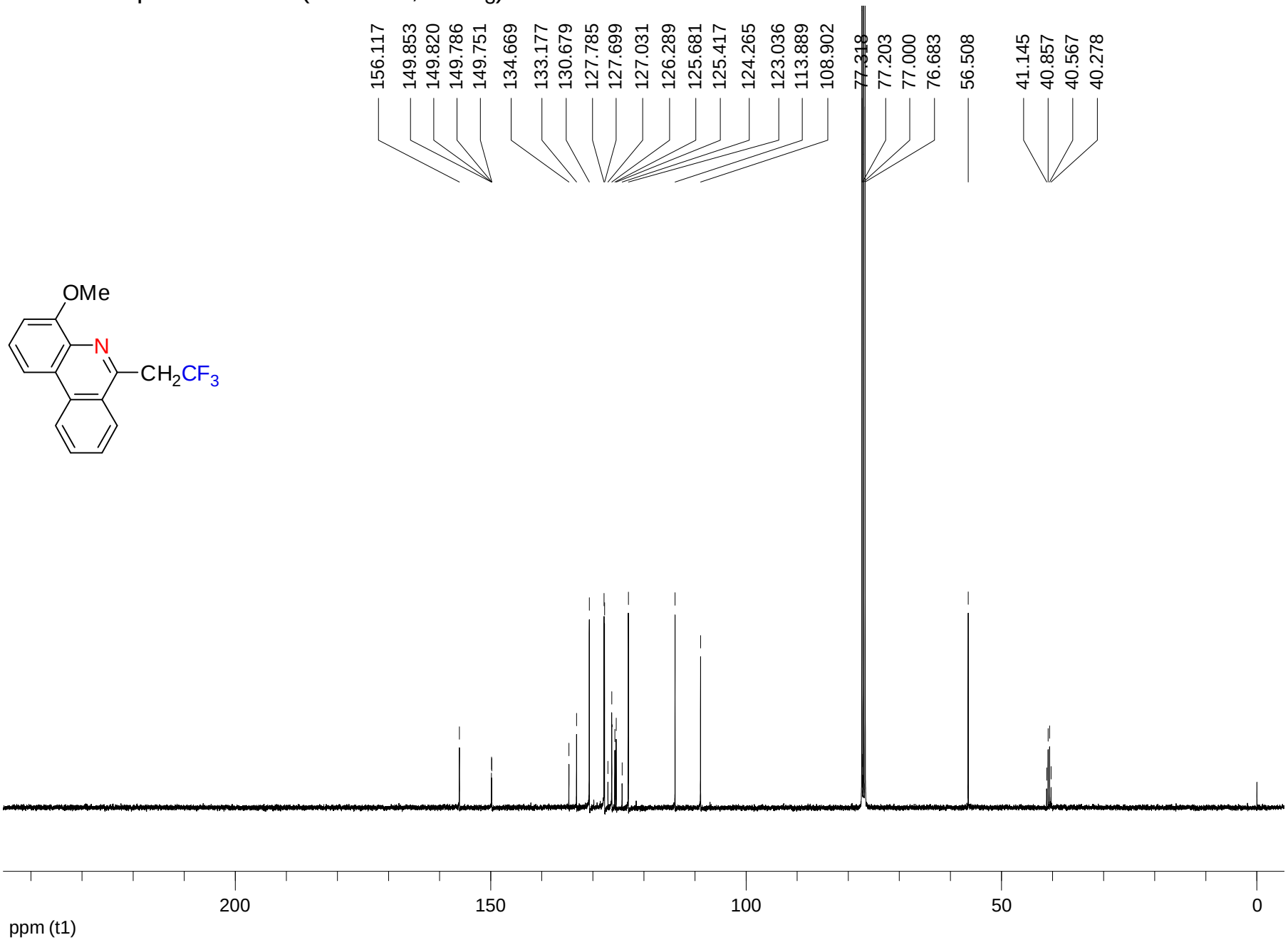
^{19}F NMR Spectrum of **2j** (376 MHz, $CDCl_3$)



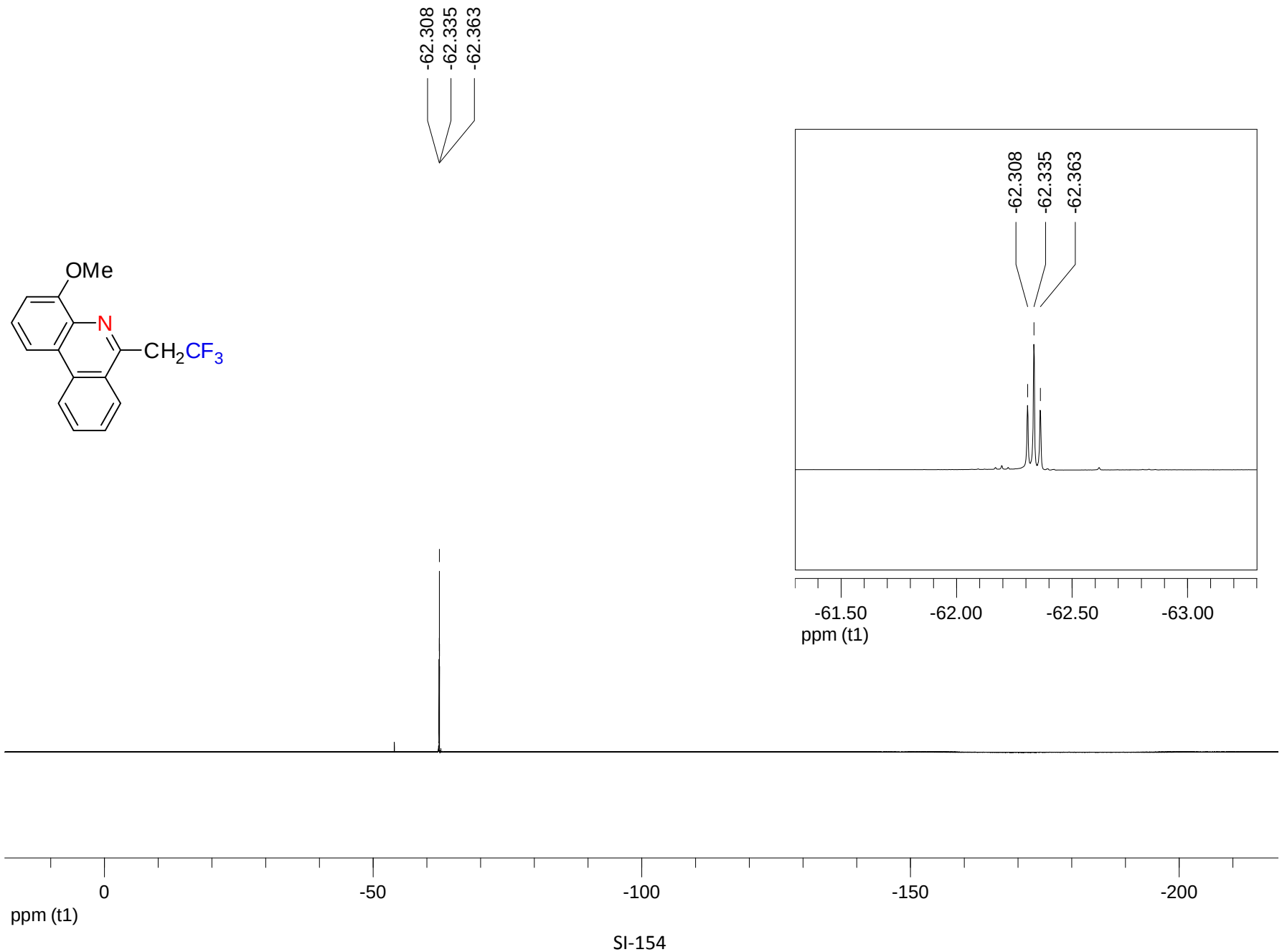
^{1}H NMR Spectrum of **2k** (400 MHz, $CDCl_3$)



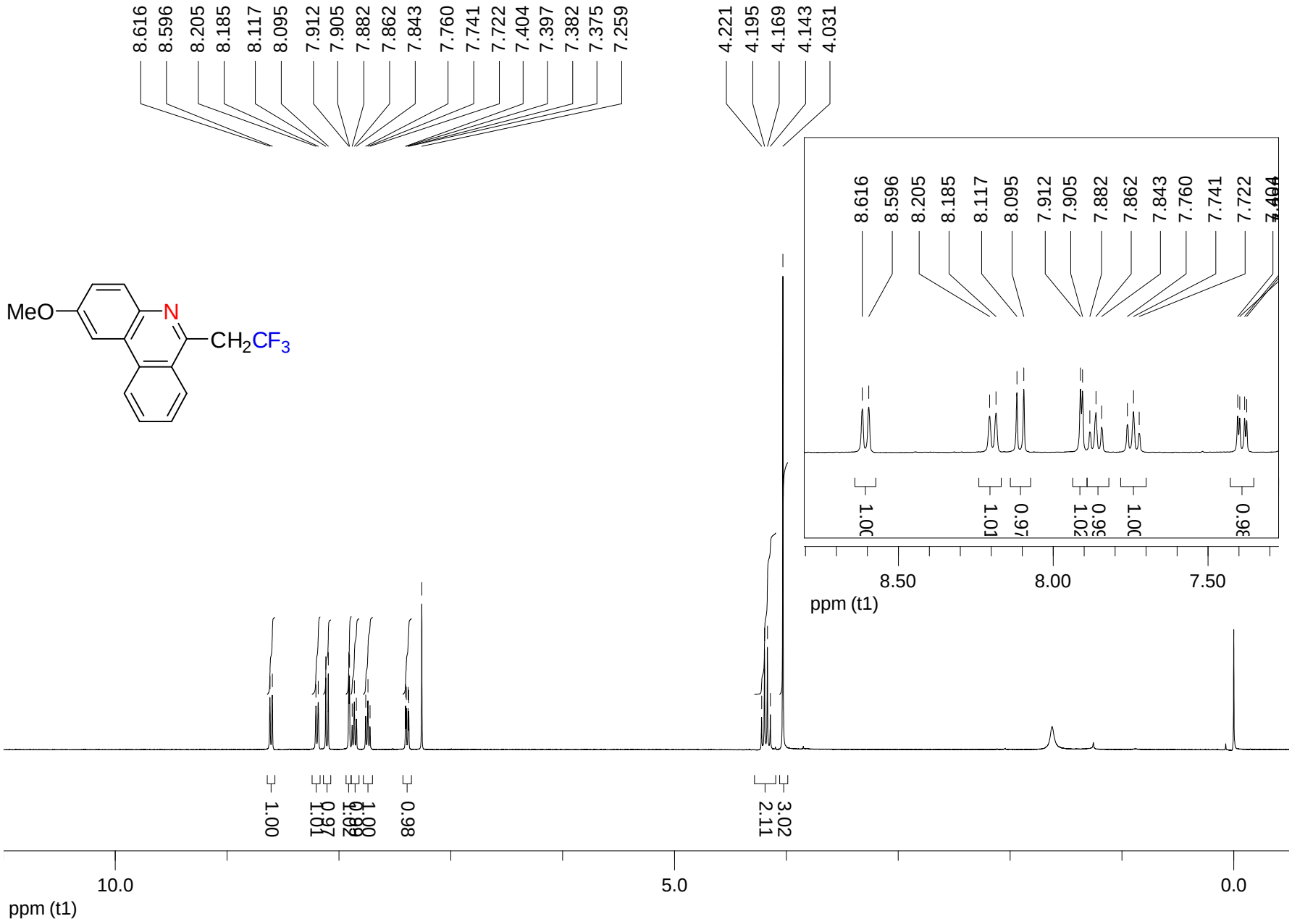
^{13}C NMR Spectrum of **2k** (100 MHz, $CDCl_3$)



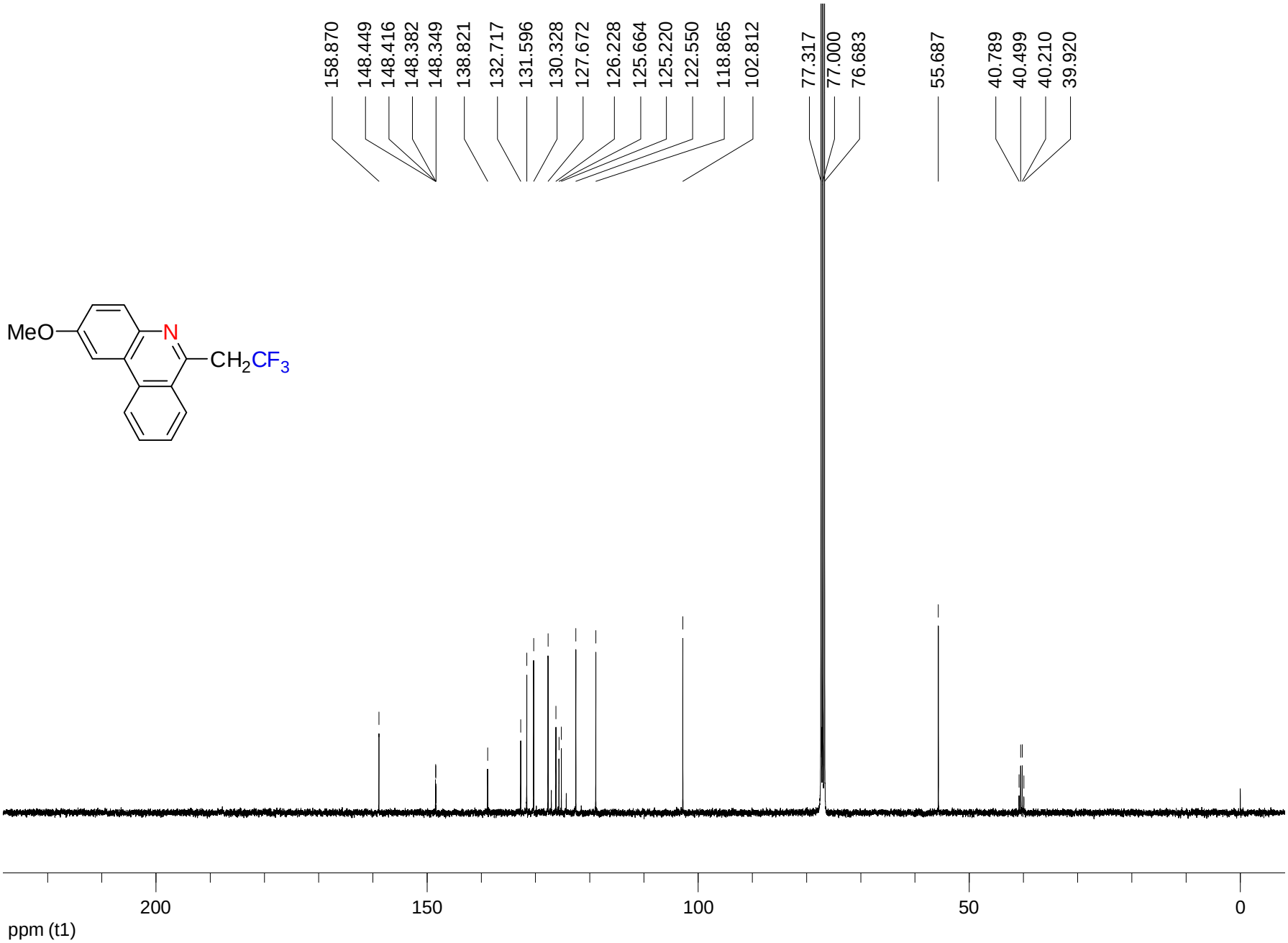
^{19}F NMR Spectrum of **2k** (376 MHz, $CDCl_3$)



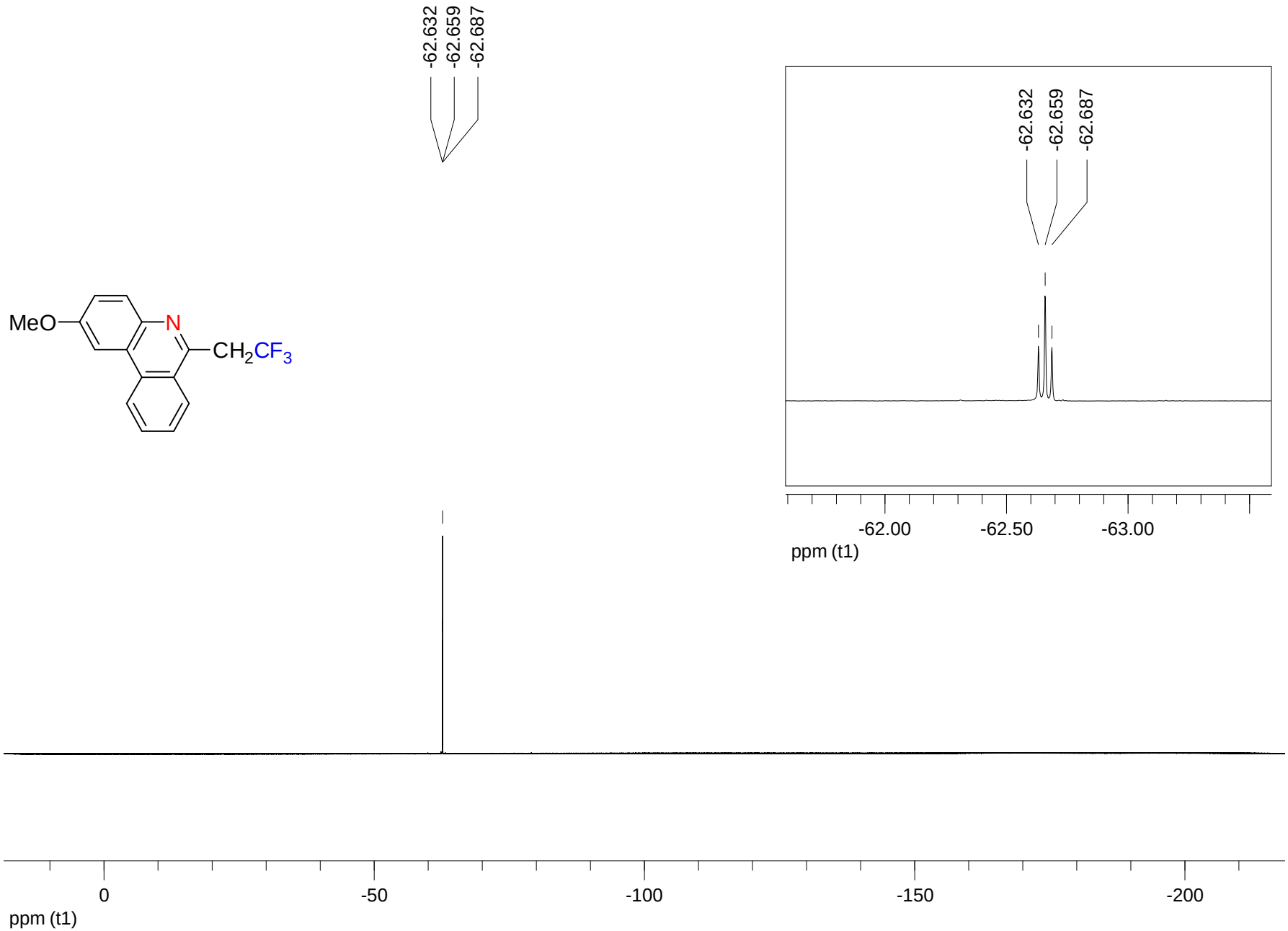
^{1}H NMR Spectrum of **2k'** (400 MHz, $CDCl_3$)



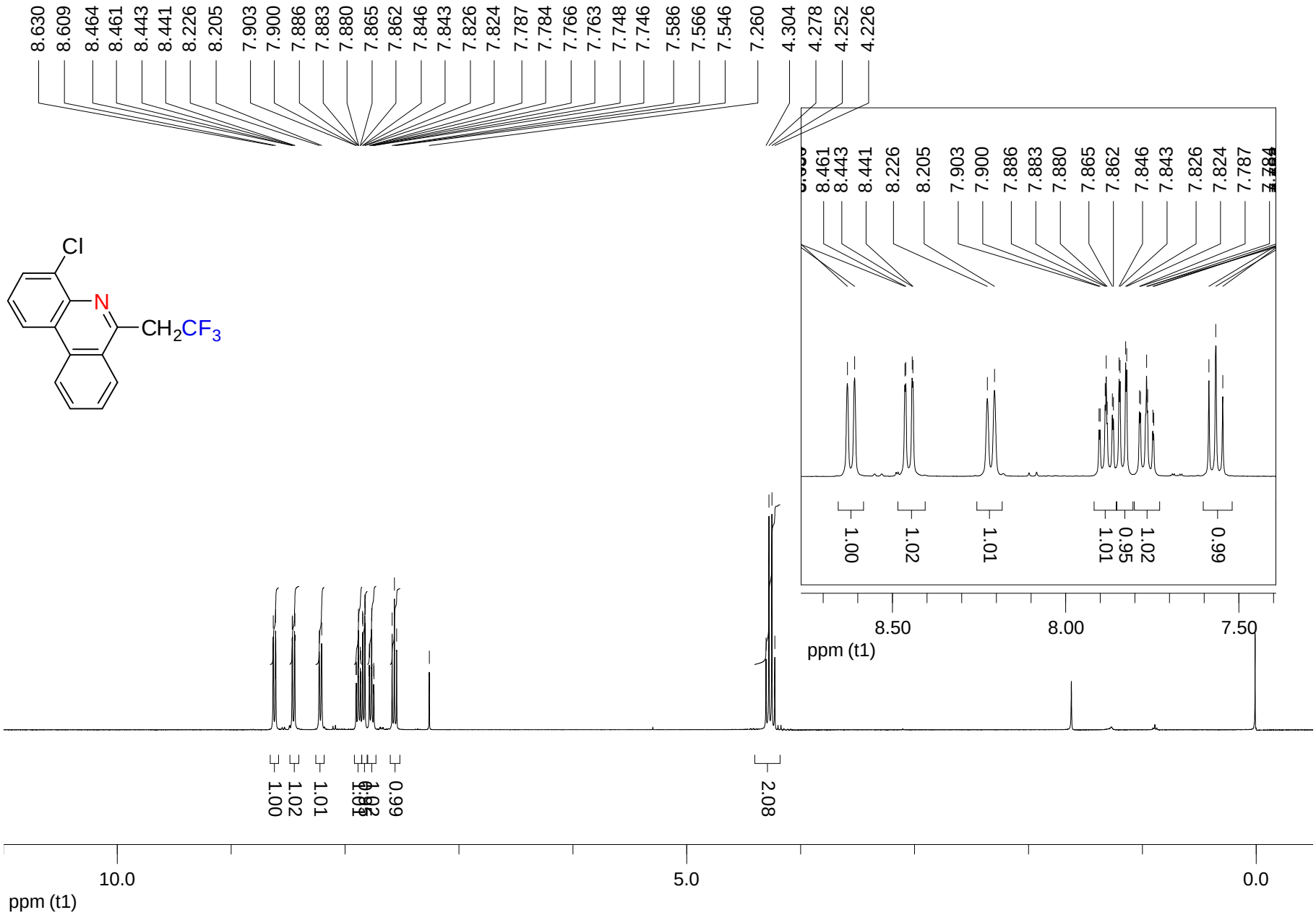
^{13}C NMR Spectrum of **2k'** (100 MHz, $CDCl_3$)



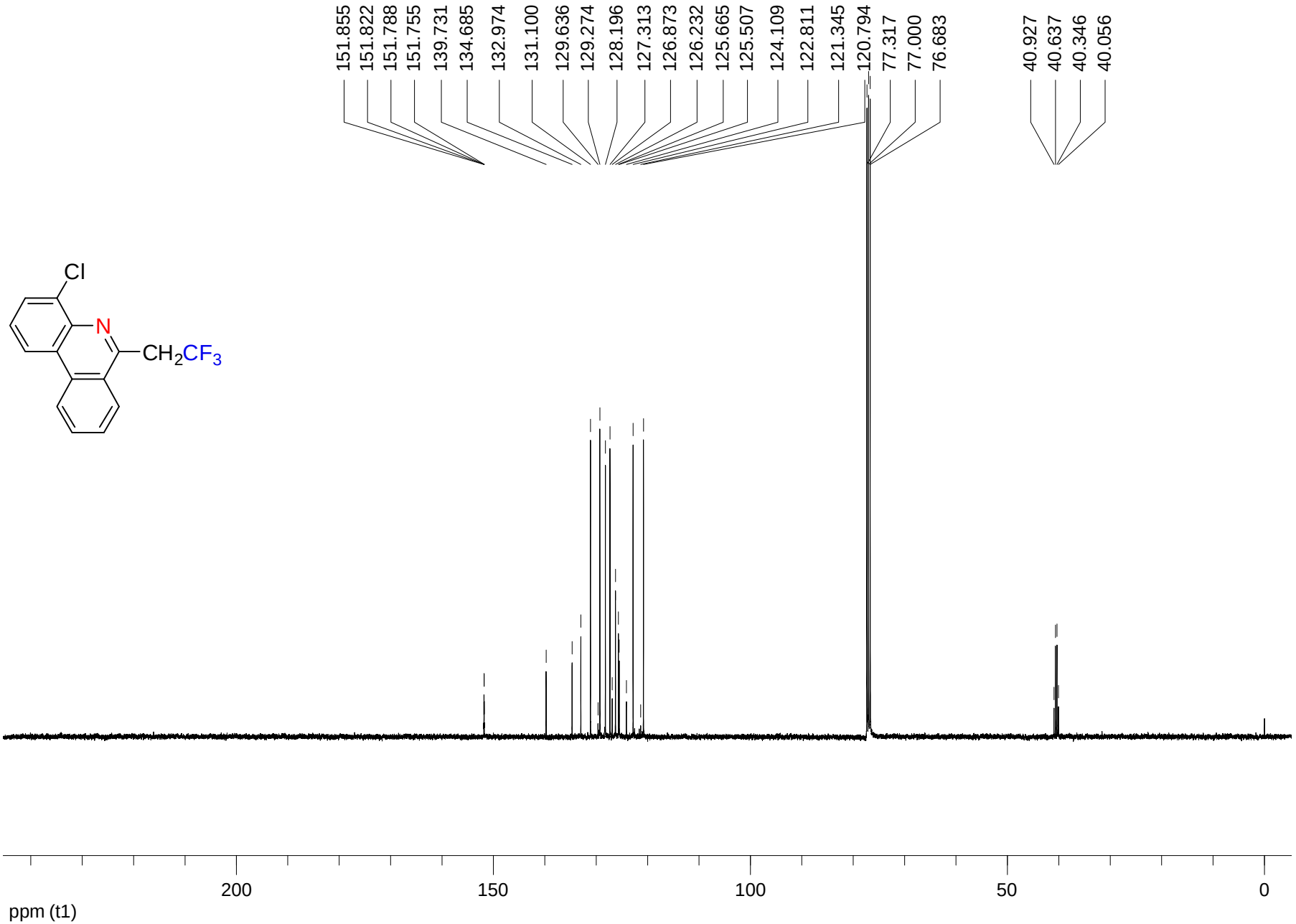
^{19}F NMR Spectrum of **2k'** (376 MHz, $CDCl_3$)



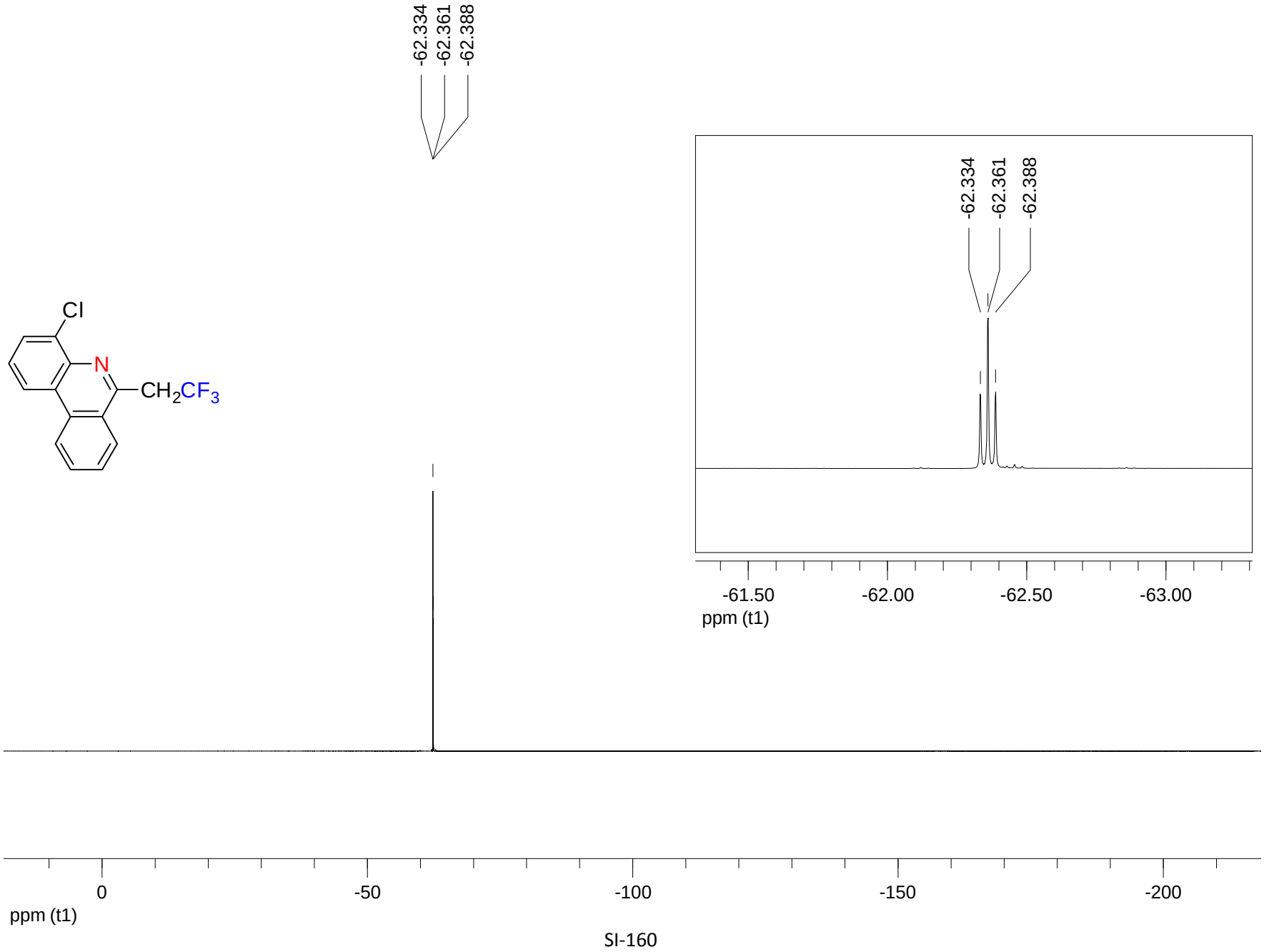
^{1}H NMR Spectrum of **2l** (400 MHz, $CDCl_3$)



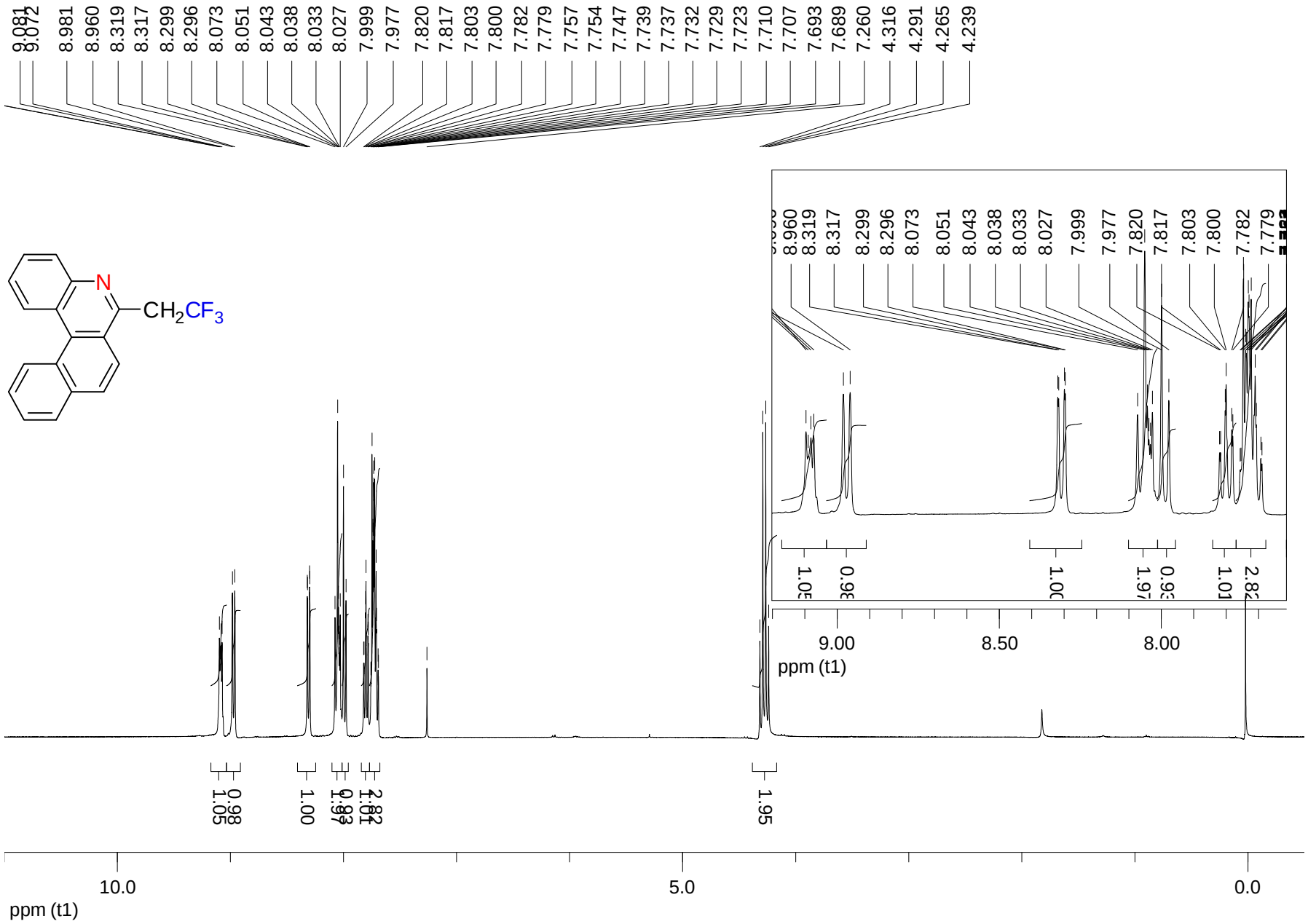
^{13}C NMR Spectrum of **2l** (100 MHz, $CDCl_3$)



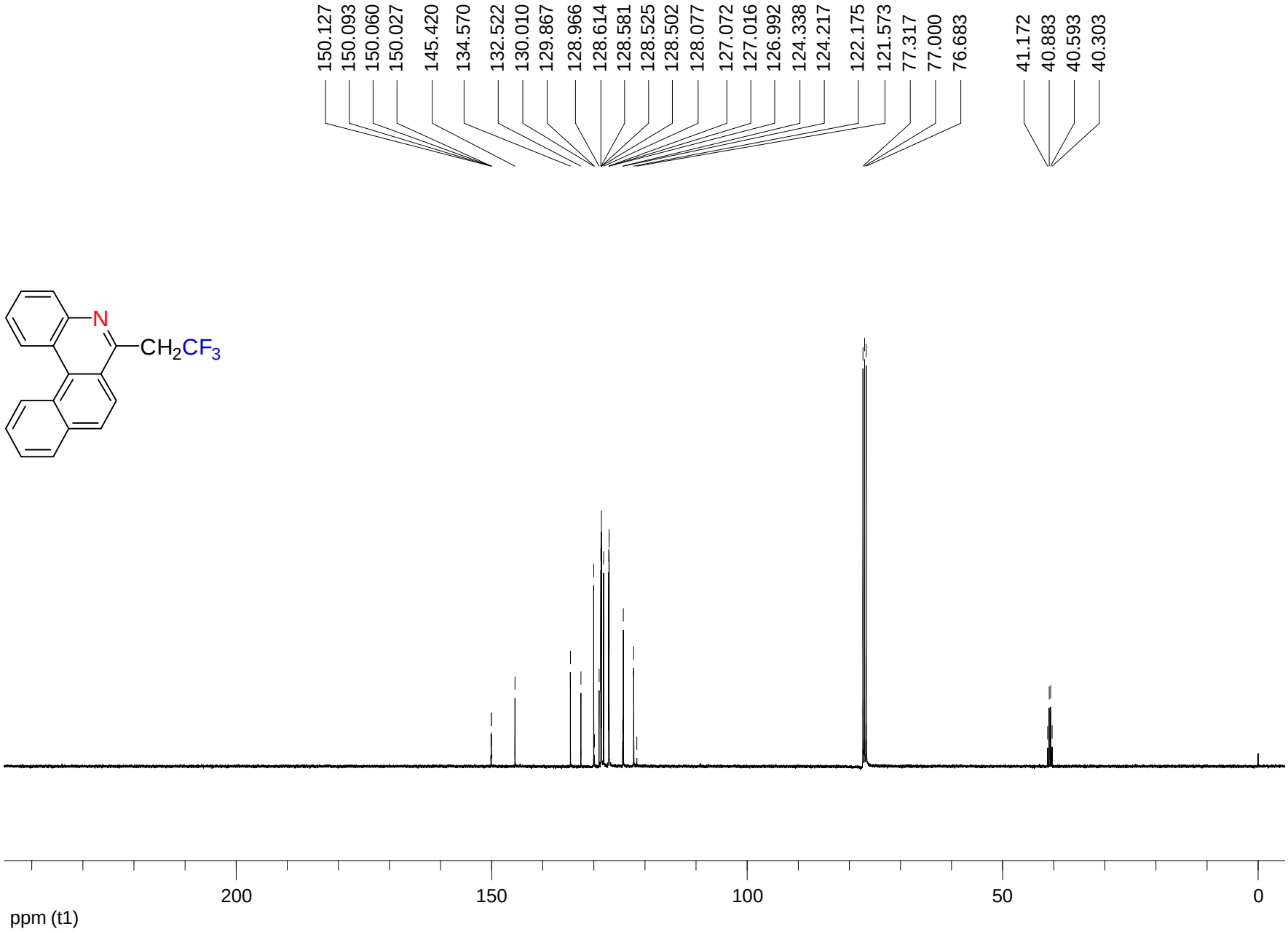
^{19}F NMR Spectrum of **2l** (376 MHz, $CDCl_3$)



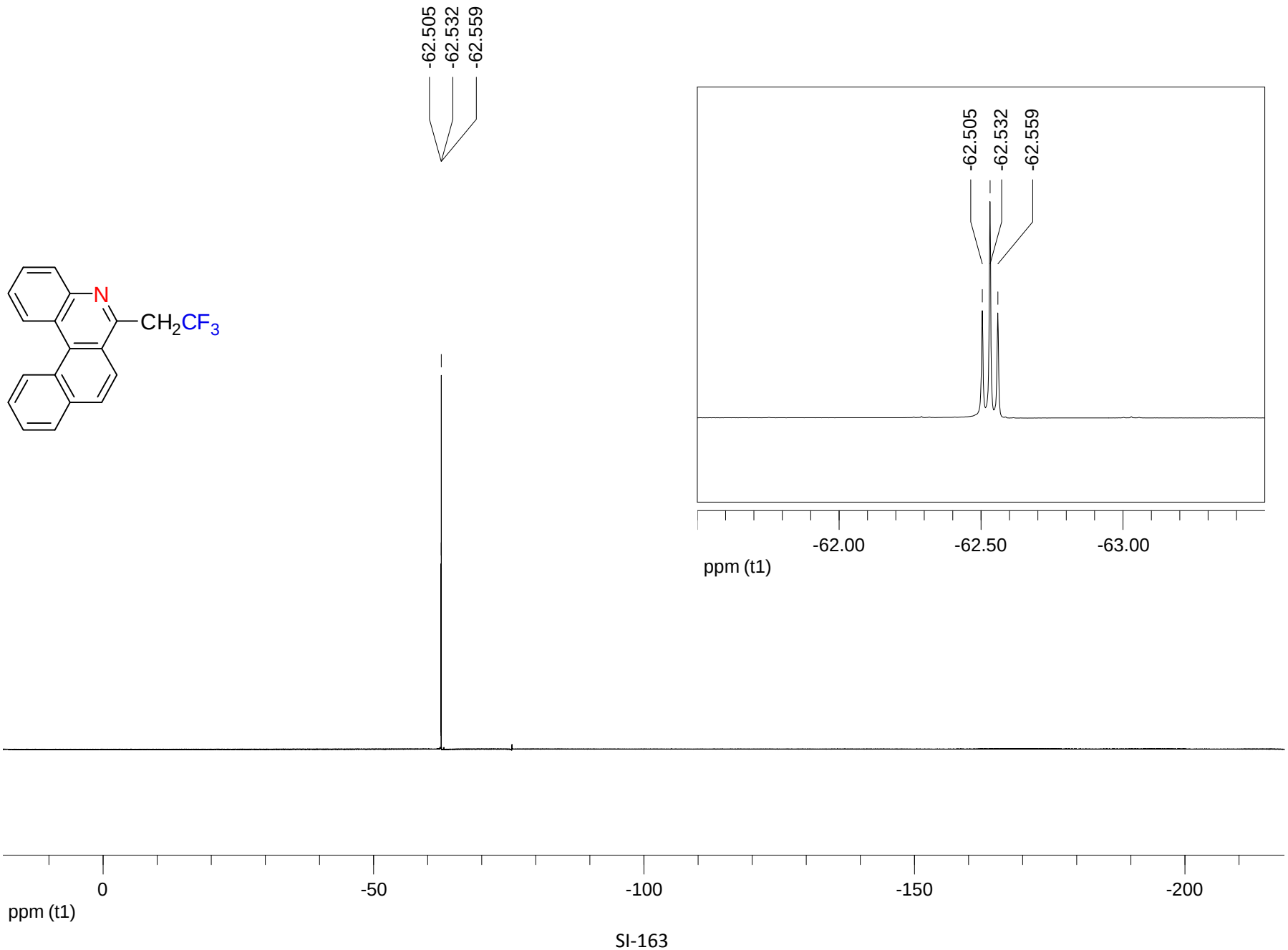
^{1}H NMR Spectrum of **2m** (400 MHz, $CDCl_3$)



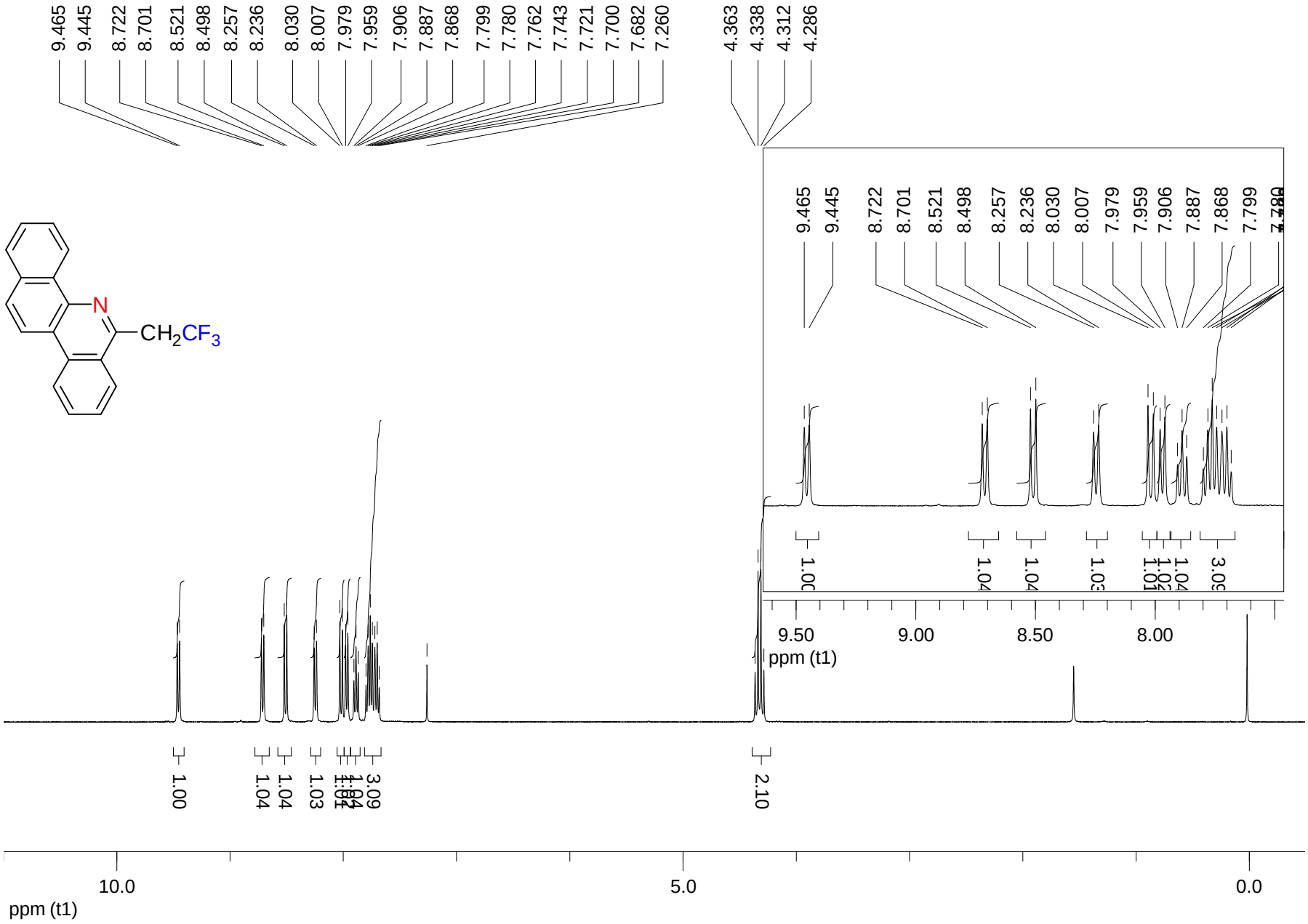
^{13}C NMR Spectrum of **2m** (100 MHz, $CDCl_3$)



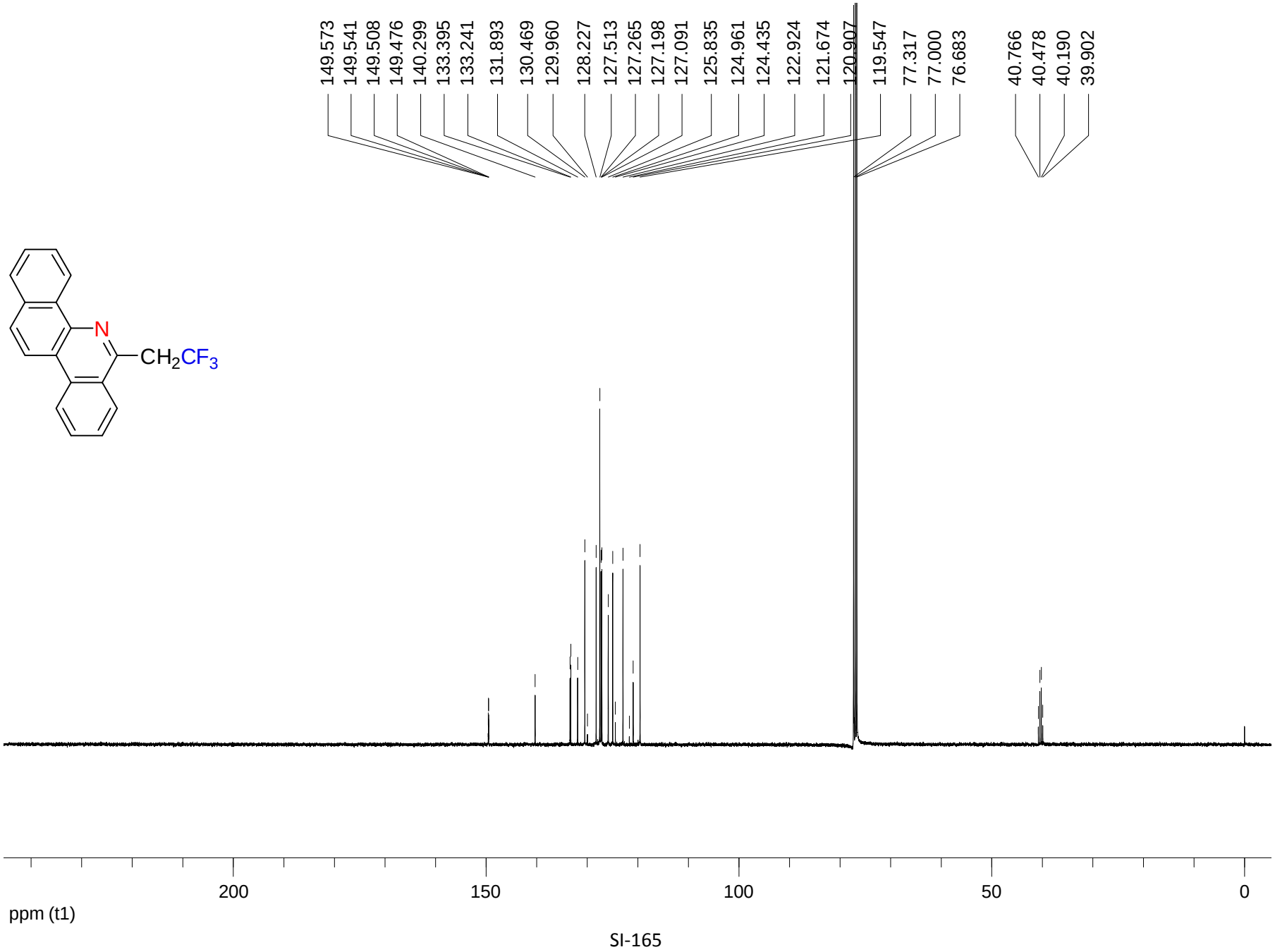
^{19}F NMR Spectrum of **2m** (376 MHz, $CDCl_3$)



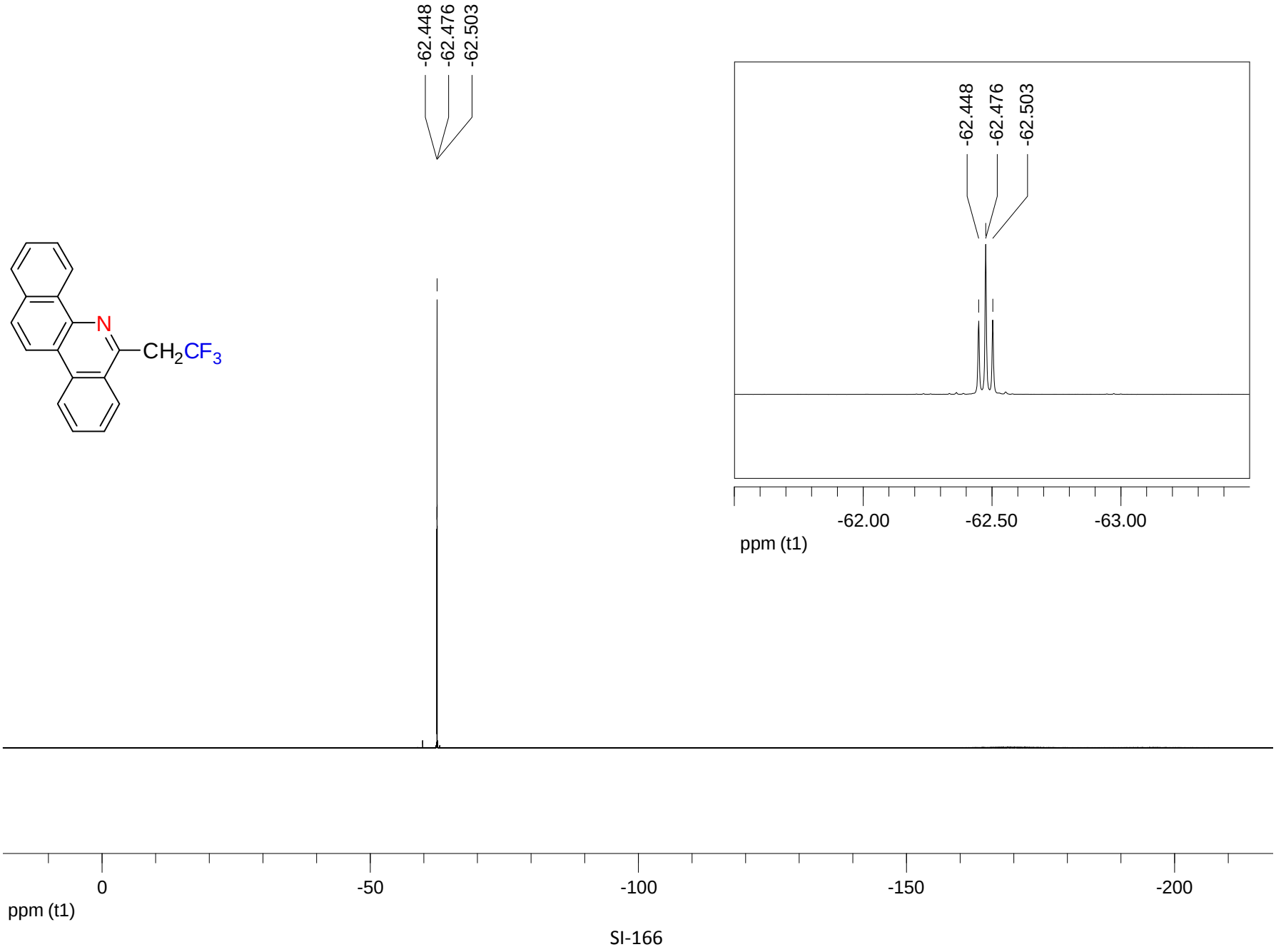
^{1}H NMR Spectrum of **2n** (400 MHz, $CDCl_3$)



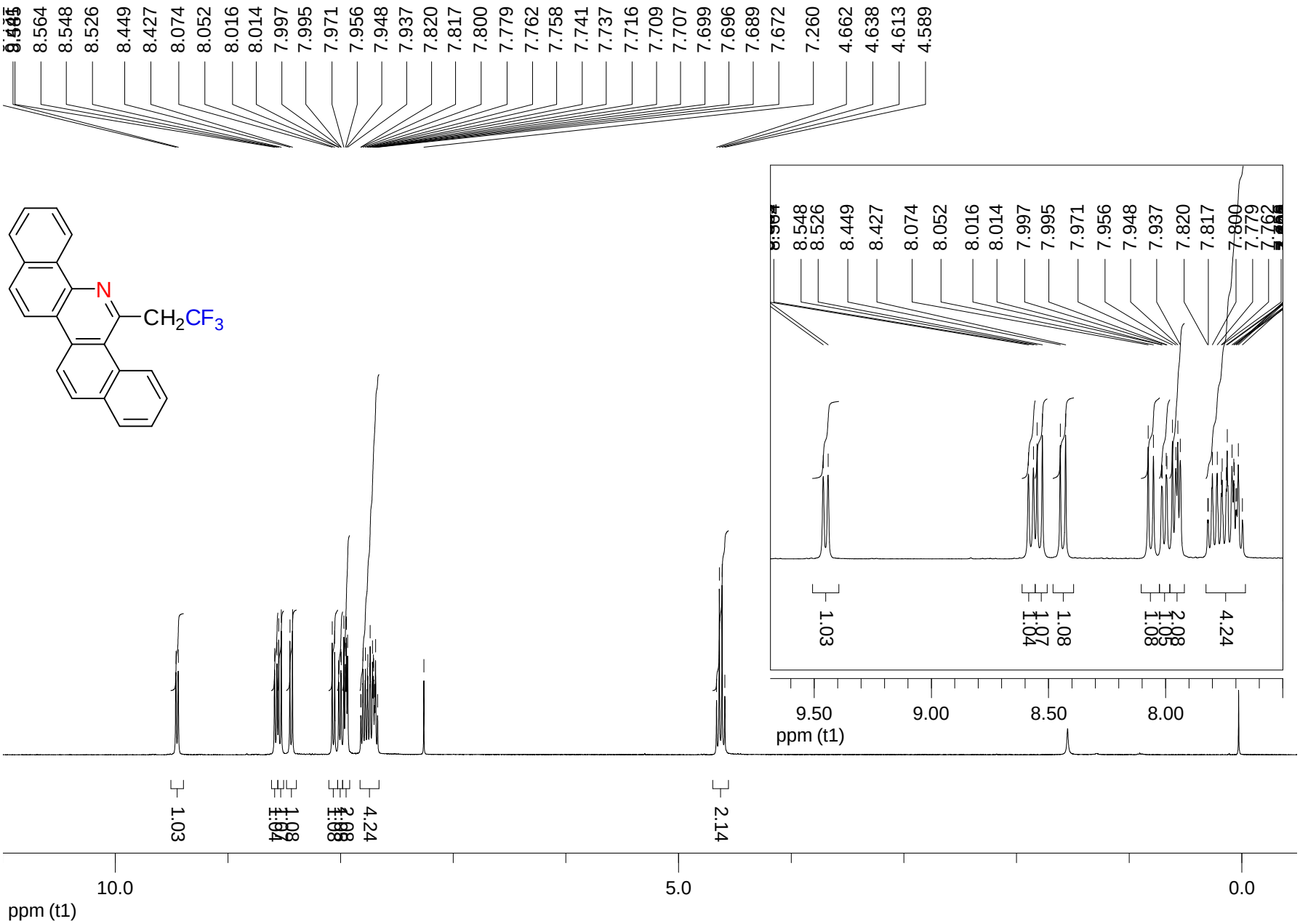
^{13}C NMR Spectrum of **2n** (100 MHz, $CDCl_3$)



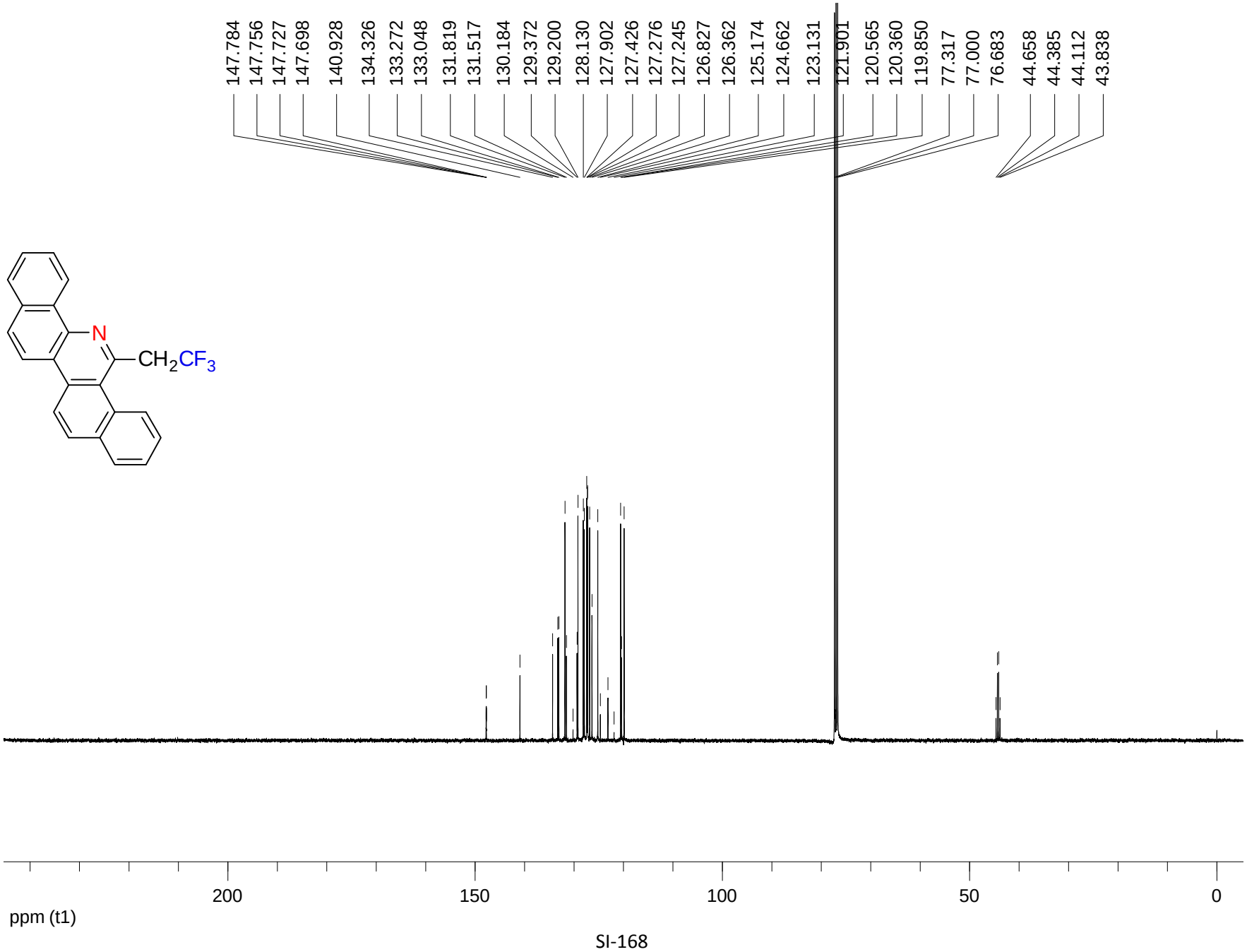
^{19}F NMR Spectrum of **2n** (376 MHz, $CDCl_3$)



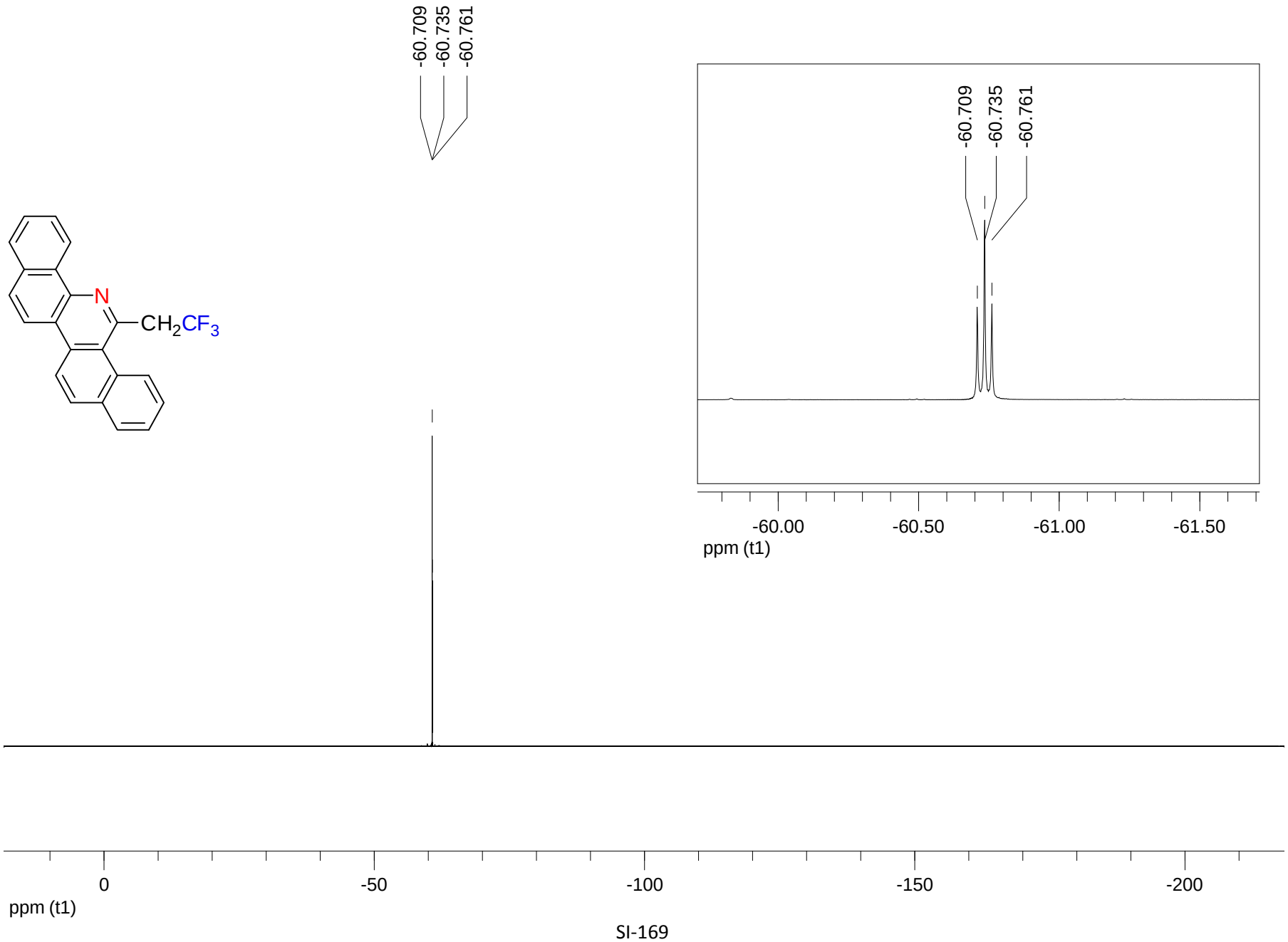
^{1}H NMR Spectrum of **2o** (400 MHz, $CDCl_3$)



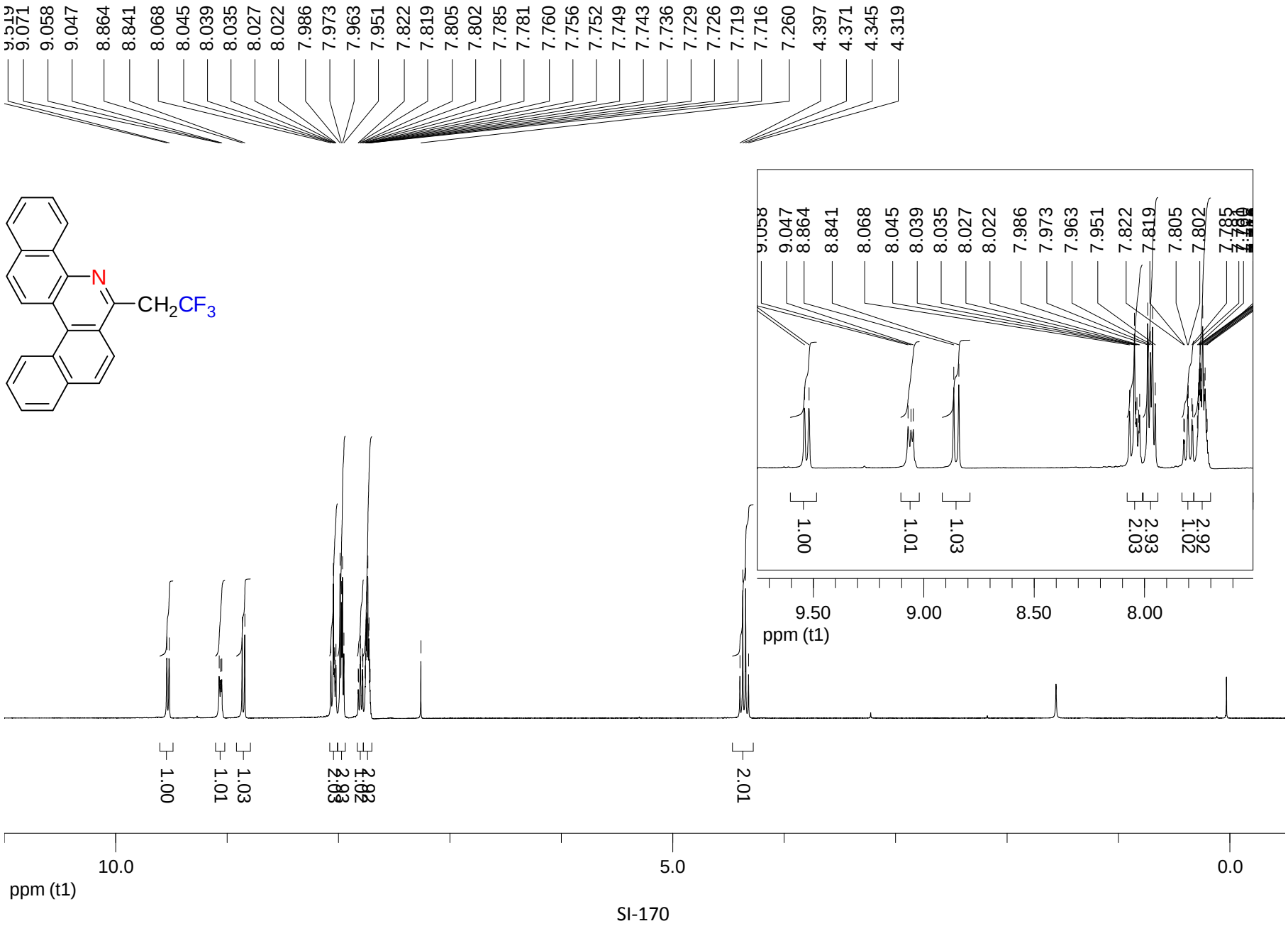
^{13}C NMR Spectrum of **2o** (100 MHz, $CDCl_3$)



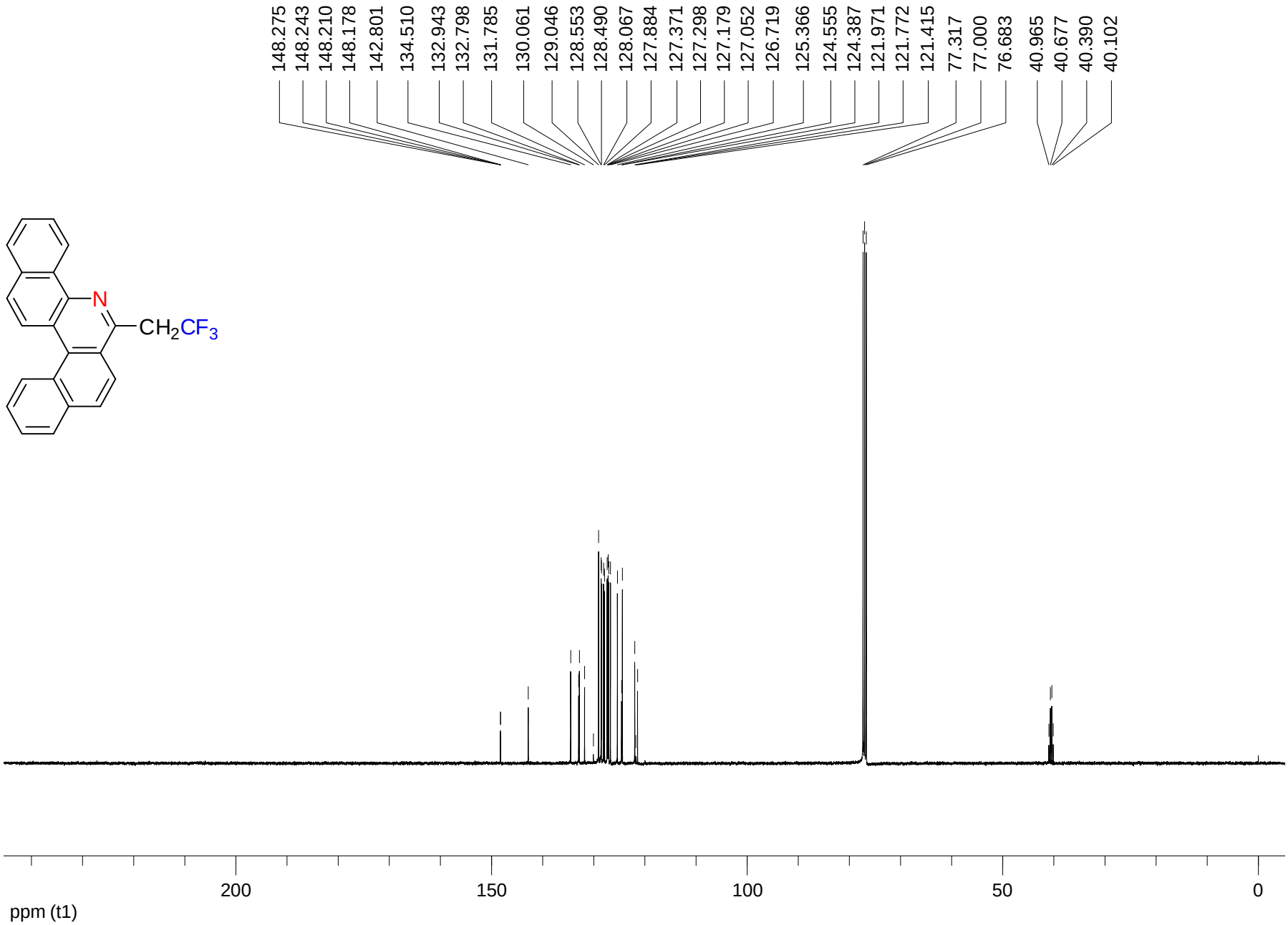
^{19}F NMR Spectrum of **2o** (376 MHz, $CDCl_3$)



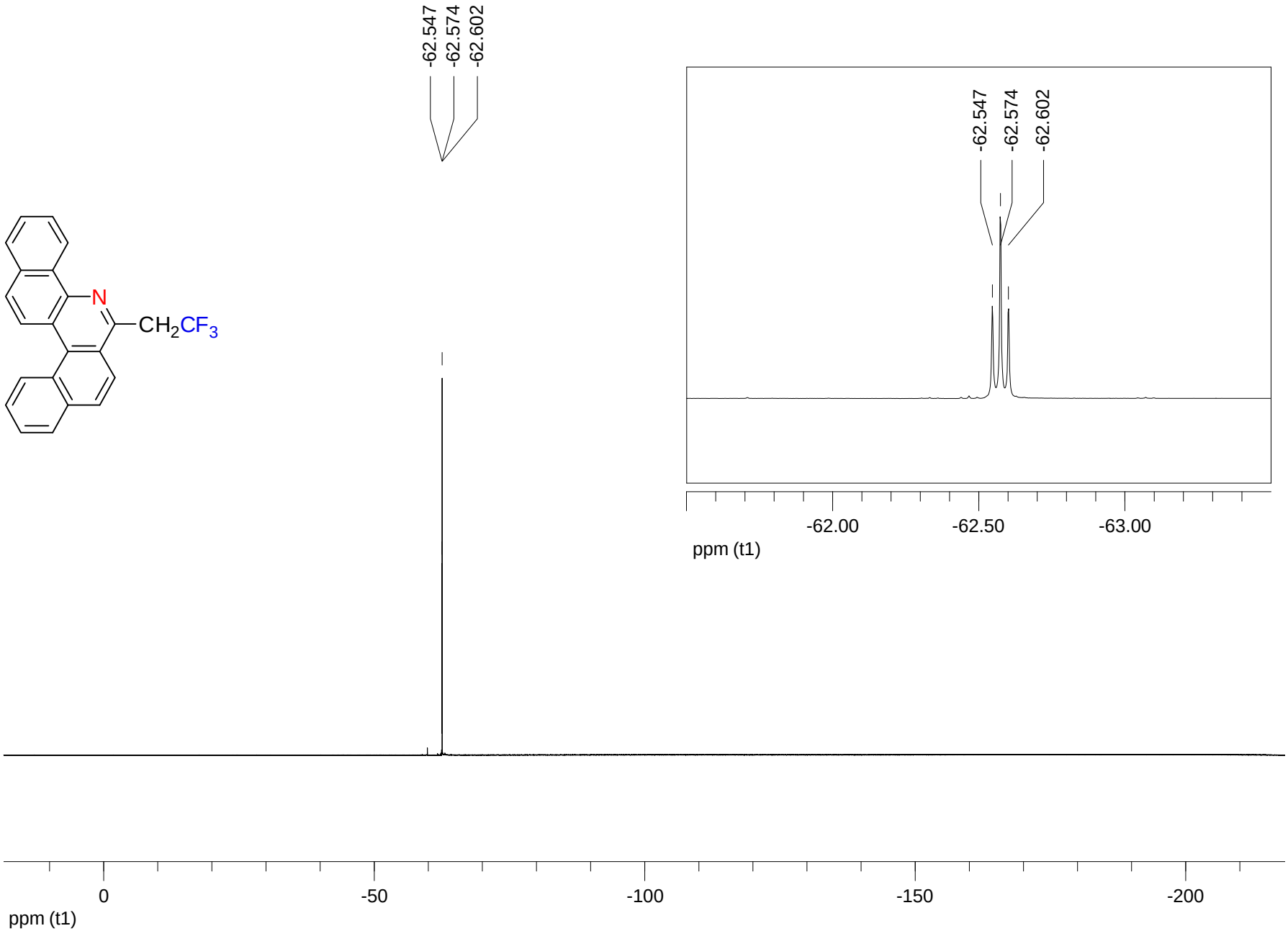
^{1}H NMR Spectrum of **2p** (400 MHz, $CDCl_3$)



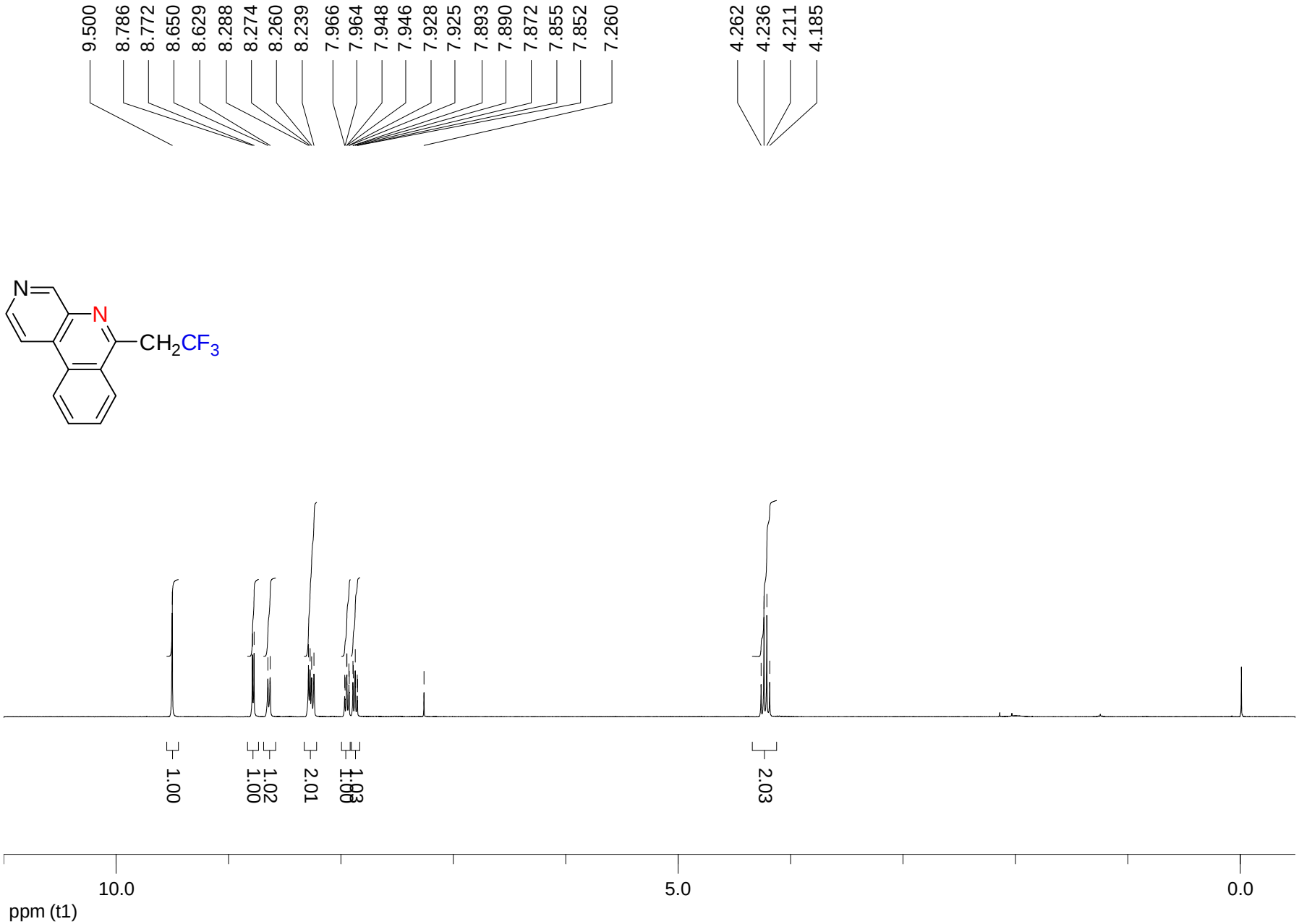
^{13}C NMR Spectrum of **2p** (100 MHz, $CDCl_3$)



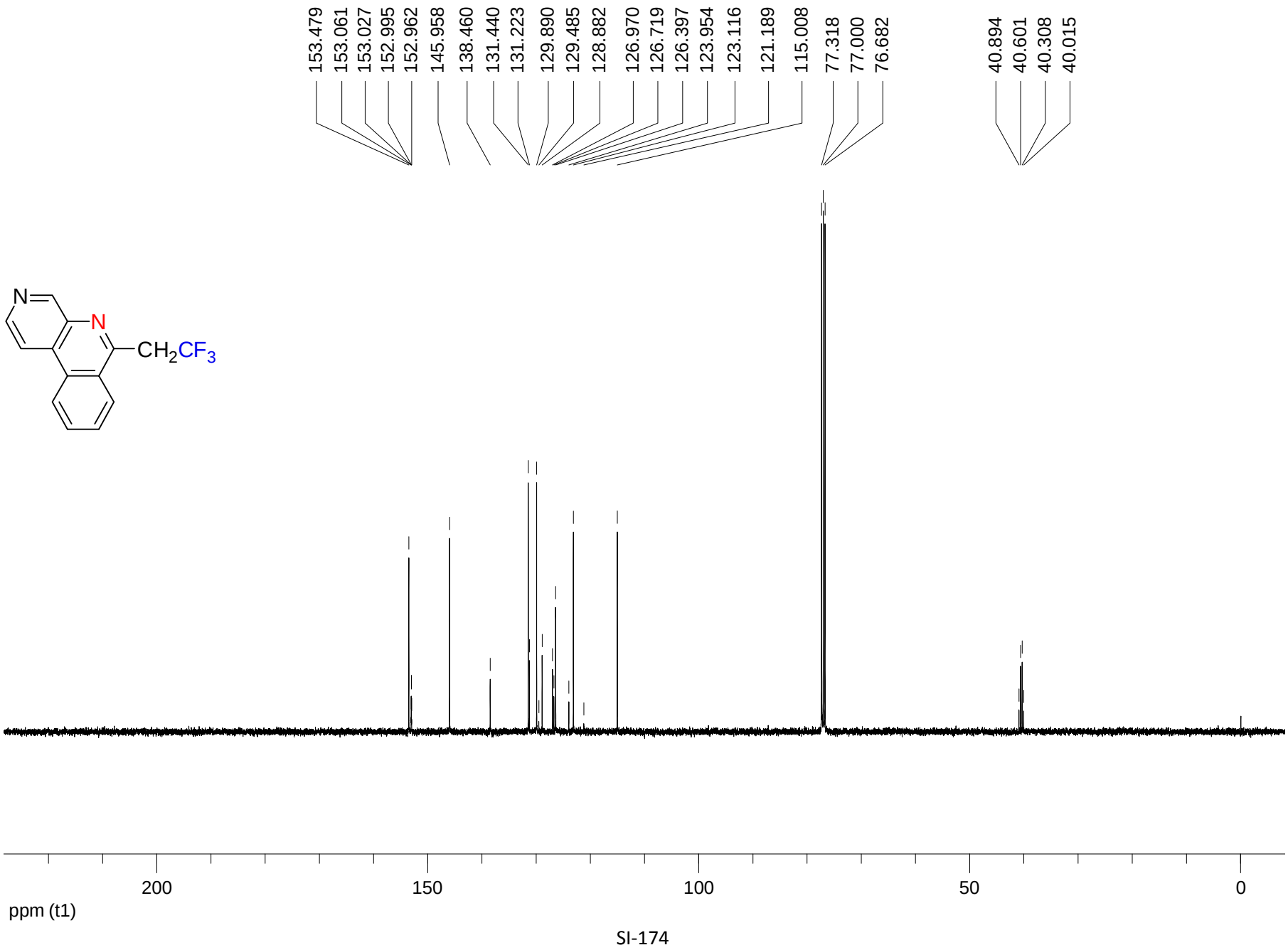
^{19}F NMR Spectrum of **2p** (376 MHz, $CDCl_3$)



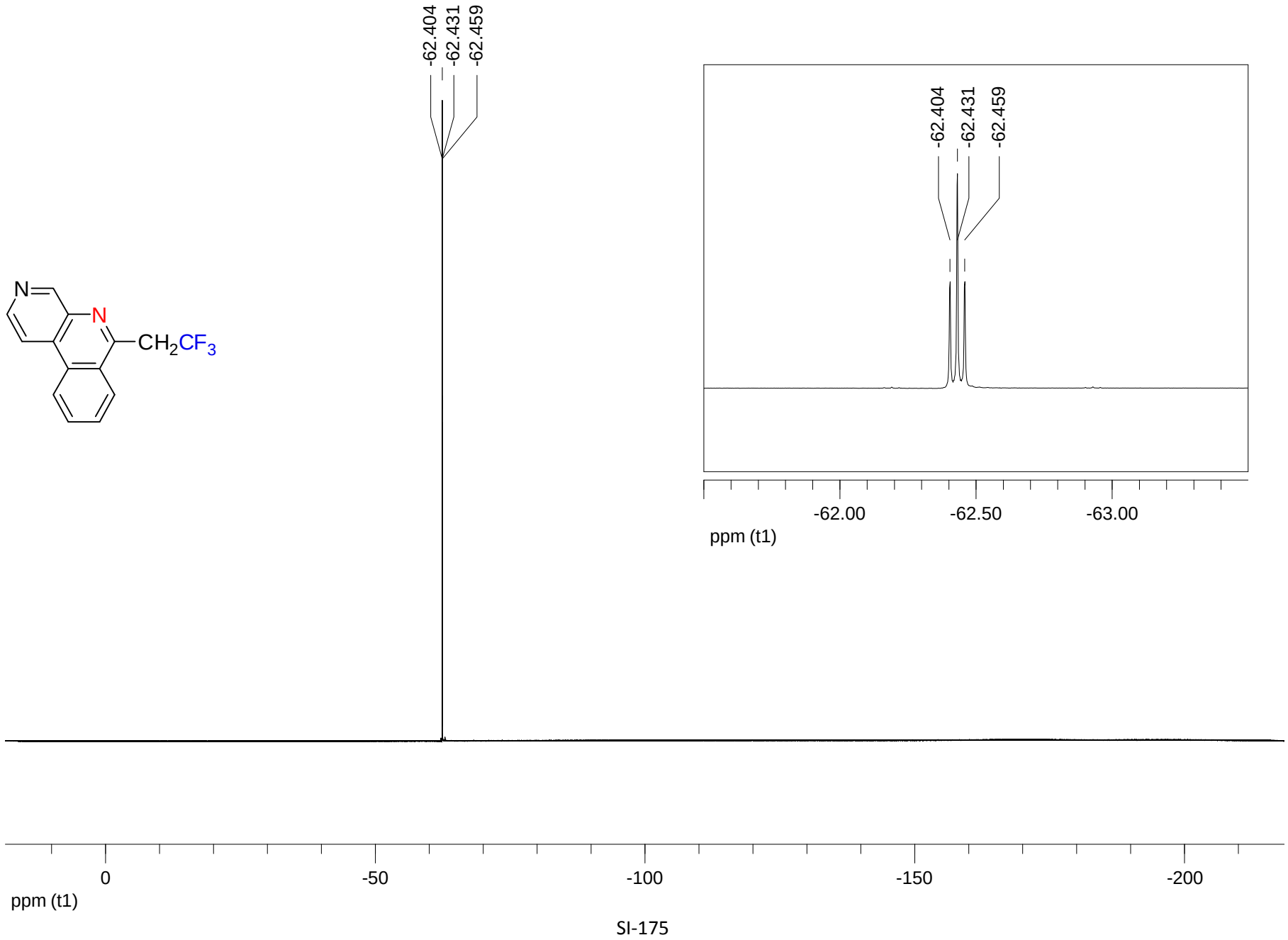
^{1}H NMR Spectrum of **2q** (400 MHz, $CDCl_3$)



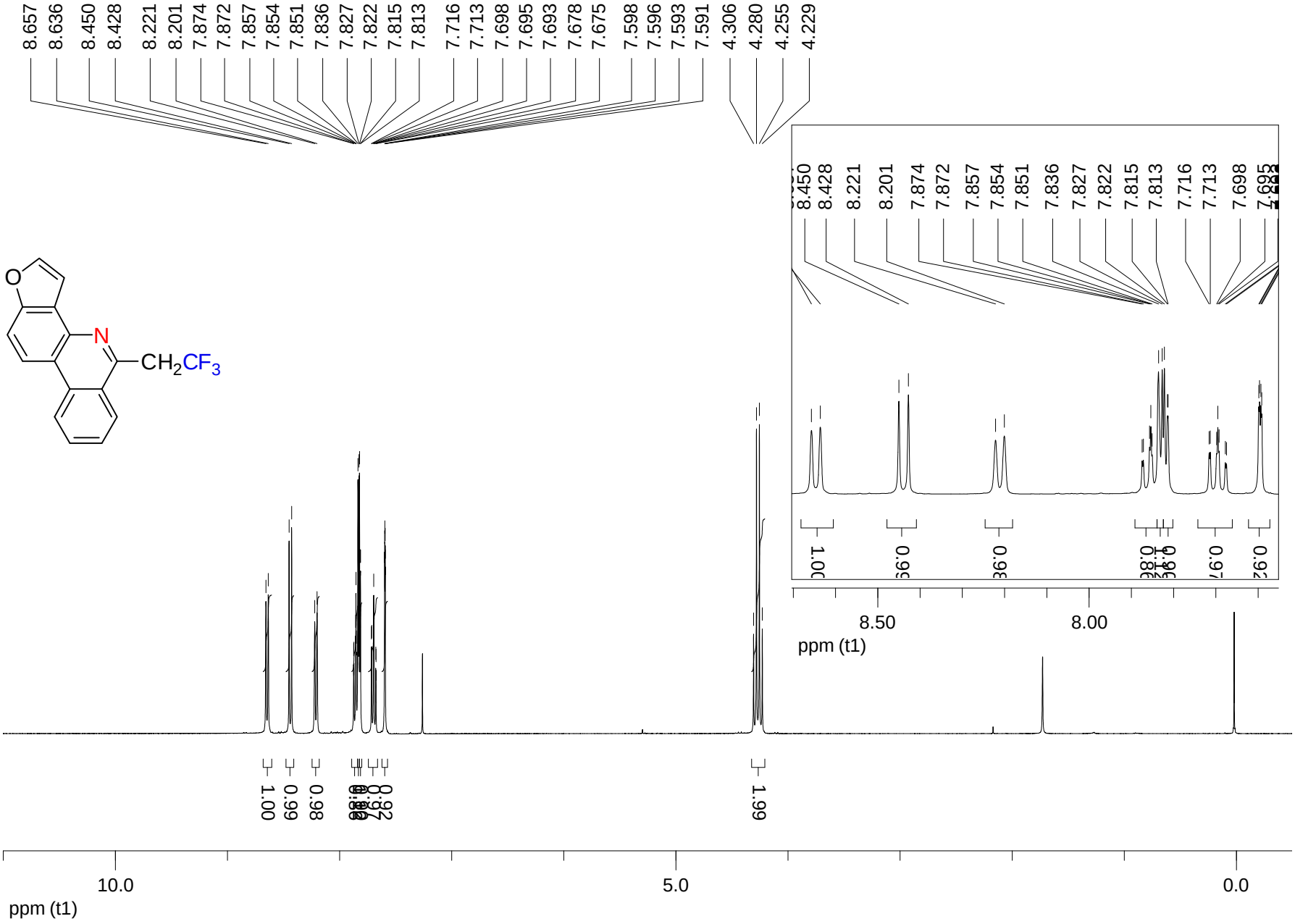
^{13}C NMR Spectrum of **2q** (100 MHz, $CDCl_3$)



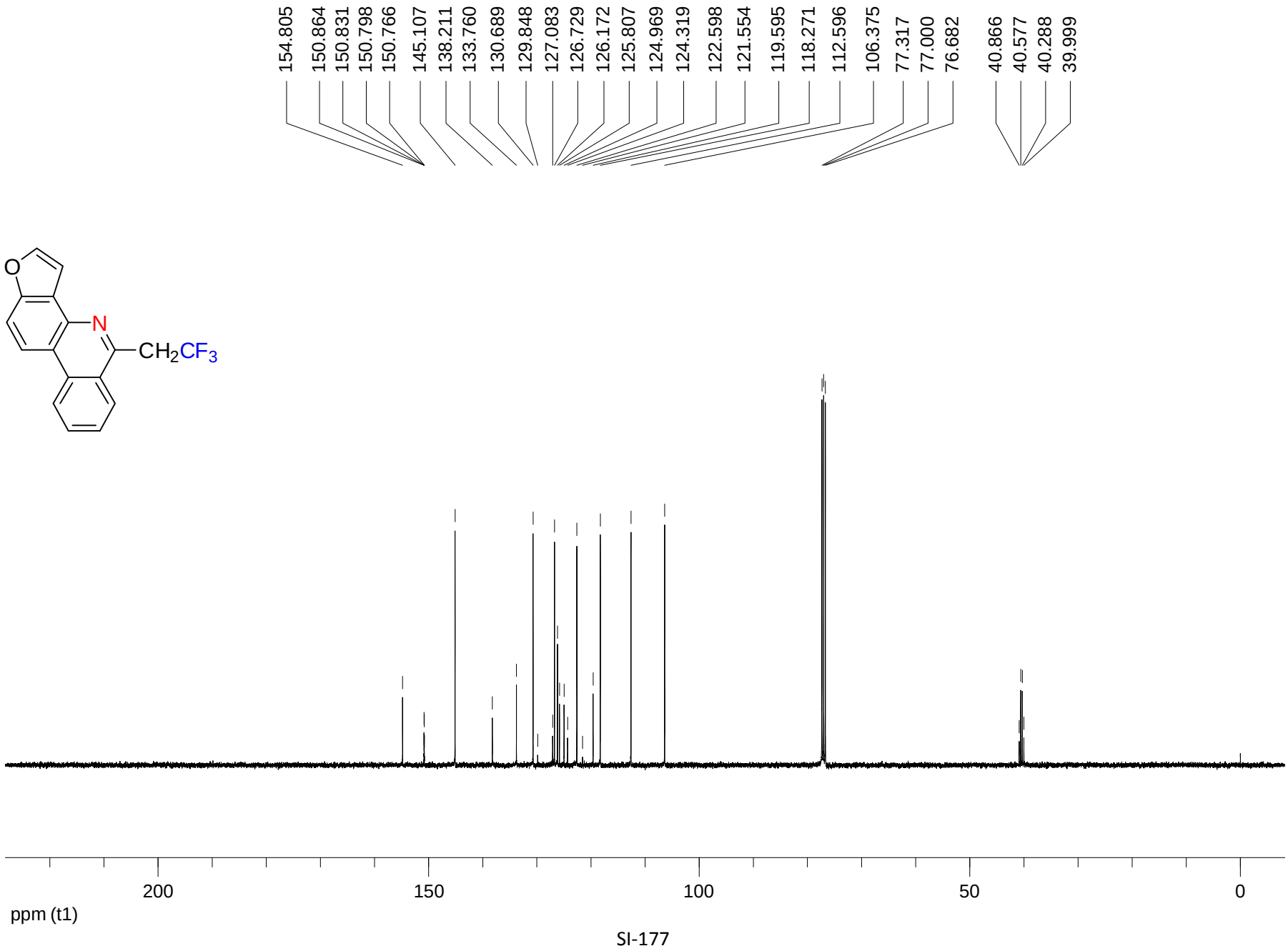
^{19}F NMR Spectrum of **2q** (376 MHz, $CDCl_3$)



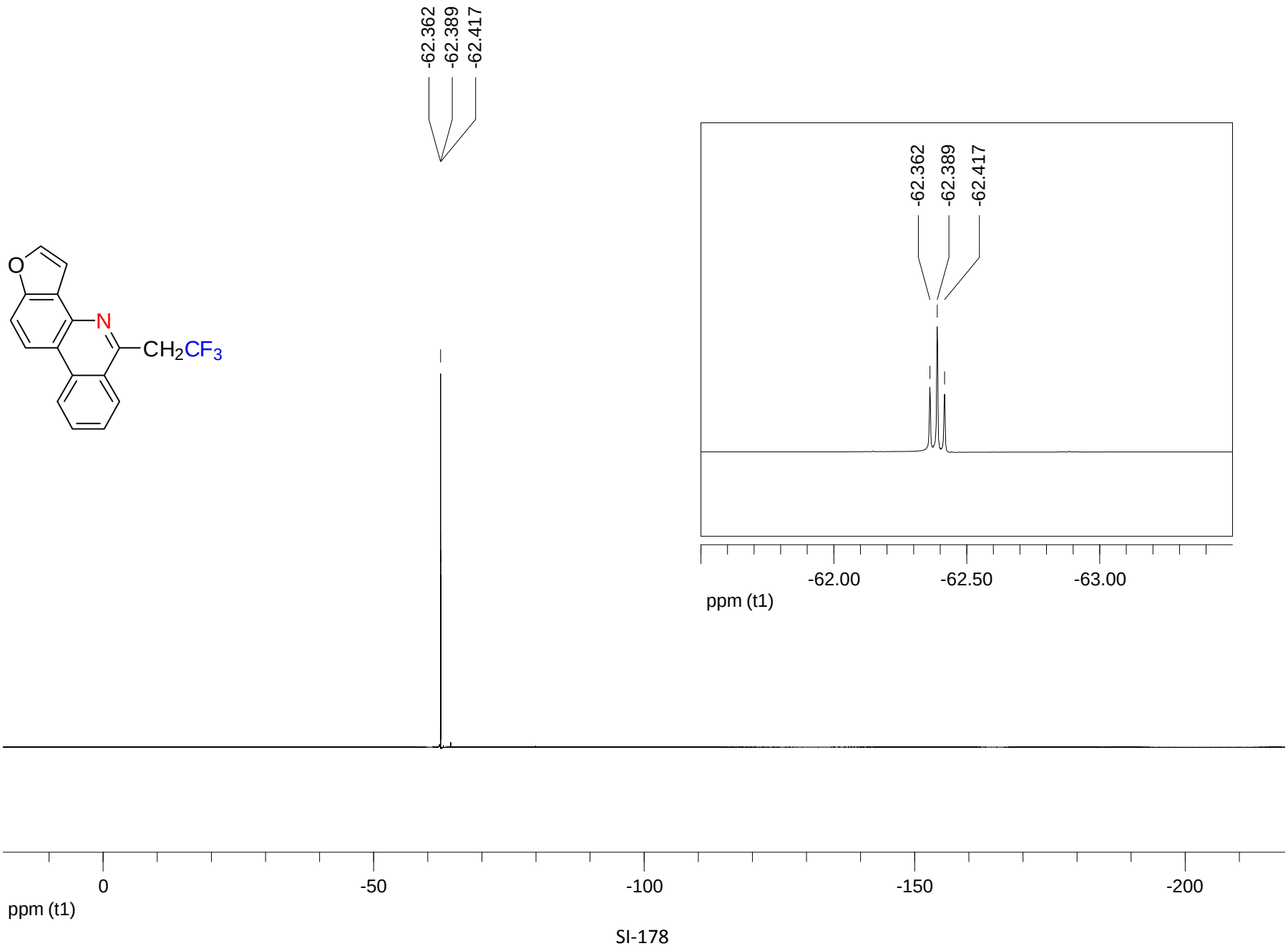
^{1}H NMR Spectrum of **2r** (400 MHz, $CDCl_3$)



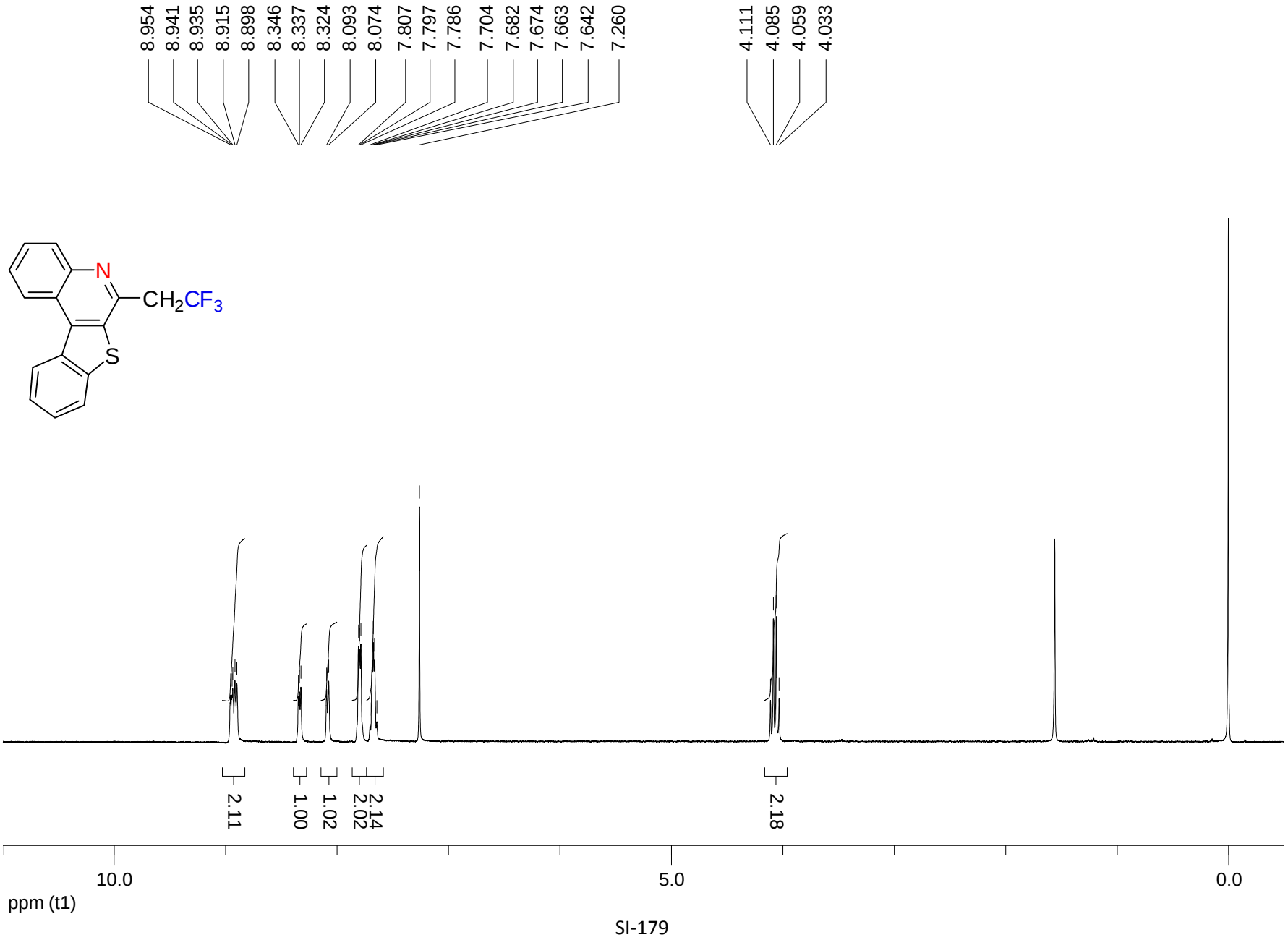
^{13}C NMR Spectrum of **2r** (100 MHz, $CDCl_3$)



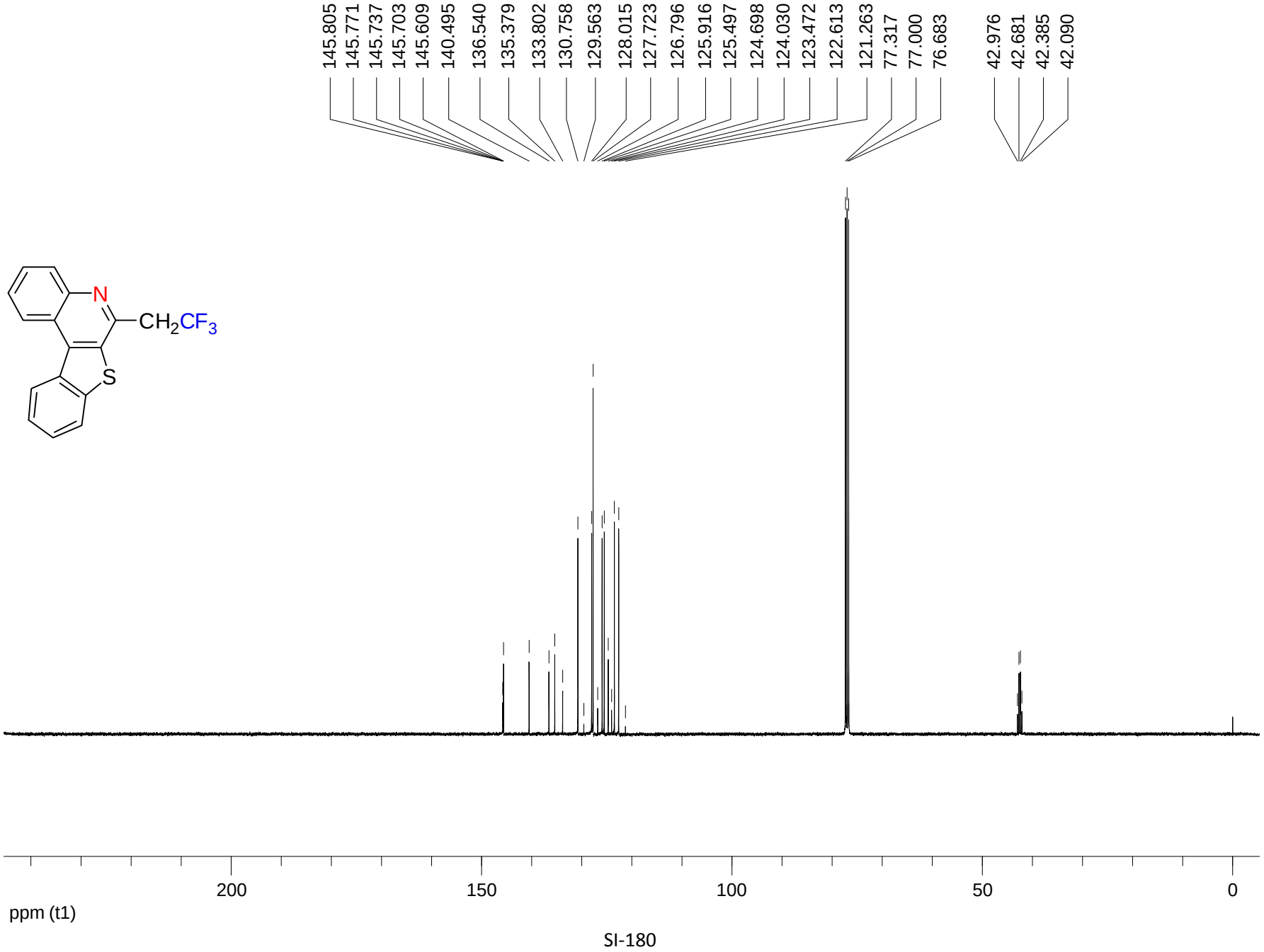
^{19}F NMR Spectrum of **2r** (376 MHz, $CDCl_3$)



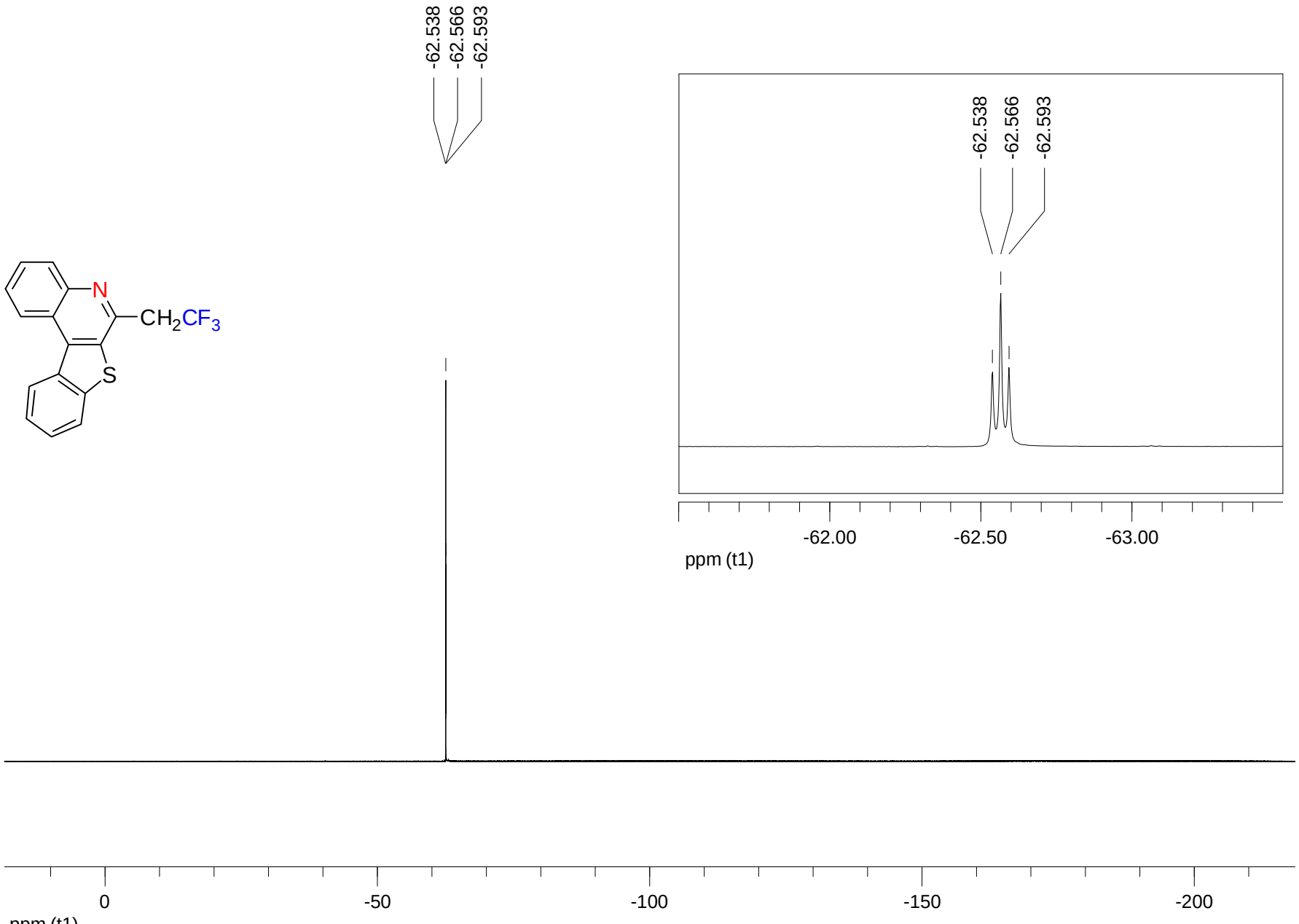
^{1}H NMR Spectrum of **2s** (400 MHz, $CDCl_3$)



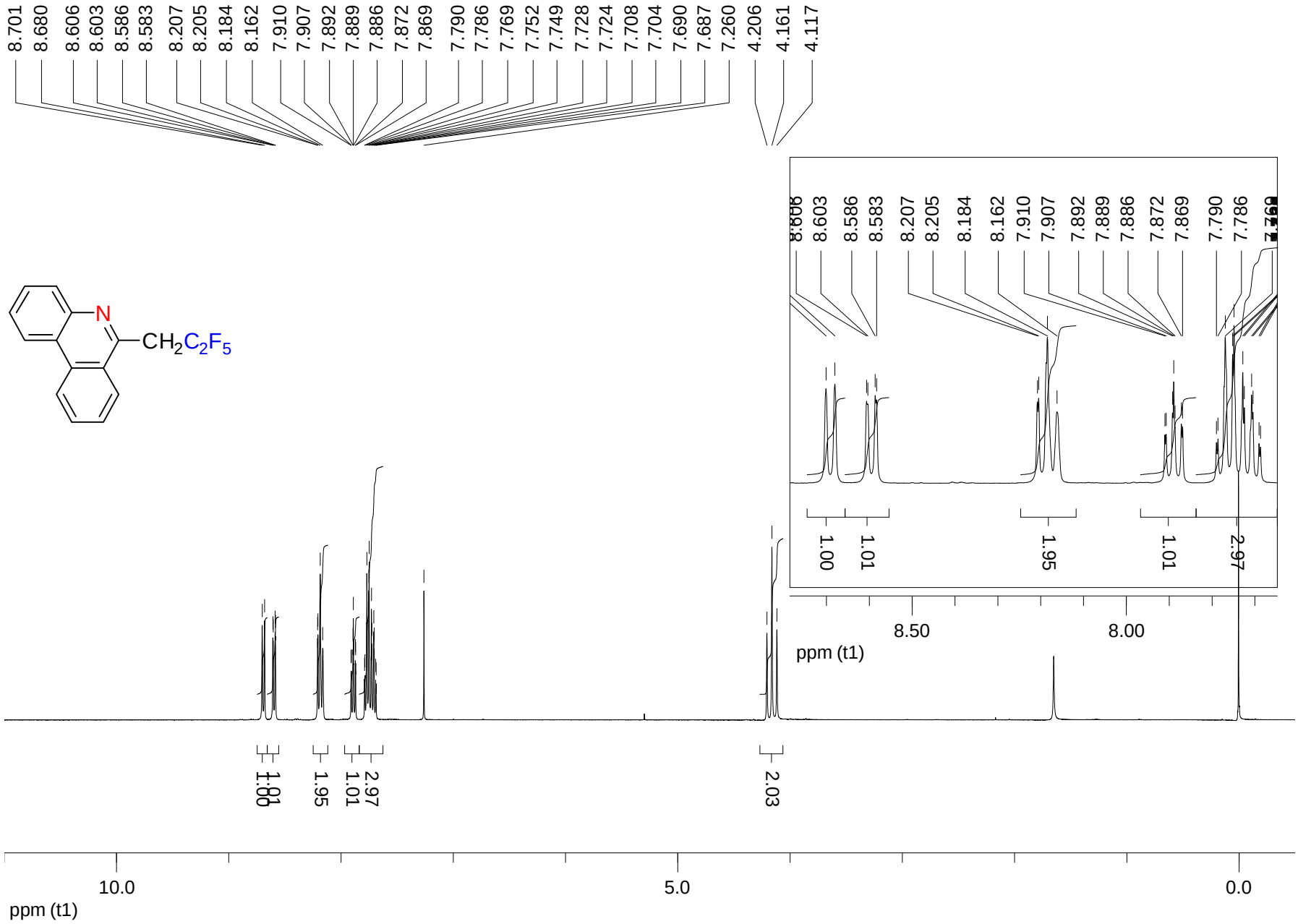
^{13}C NMR Spectrum of **2s** (100 MHz, $CDCl_3$)



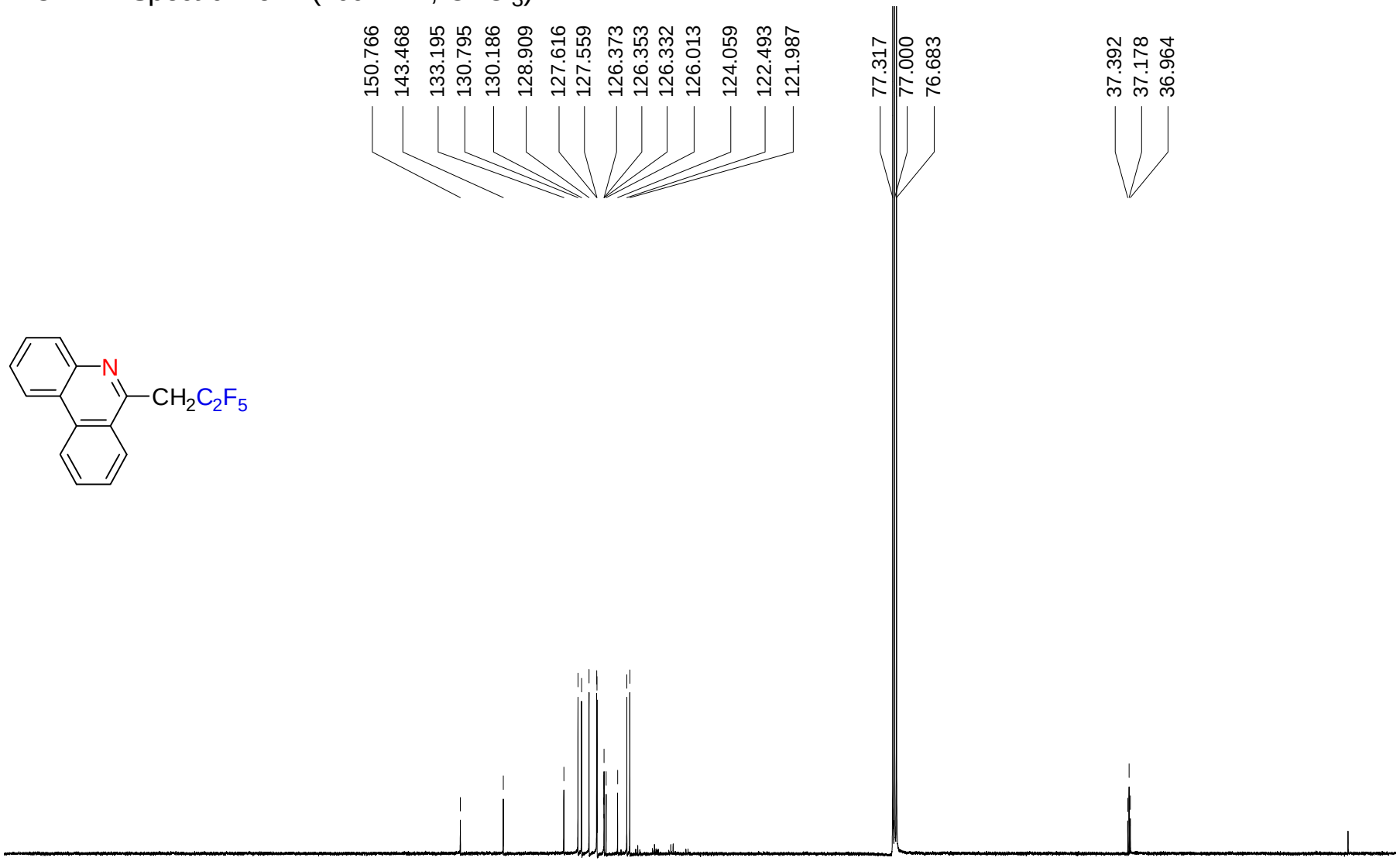
^{19}F NMR Spectrum of **2s** (376 MHz, $CDCl_3$)



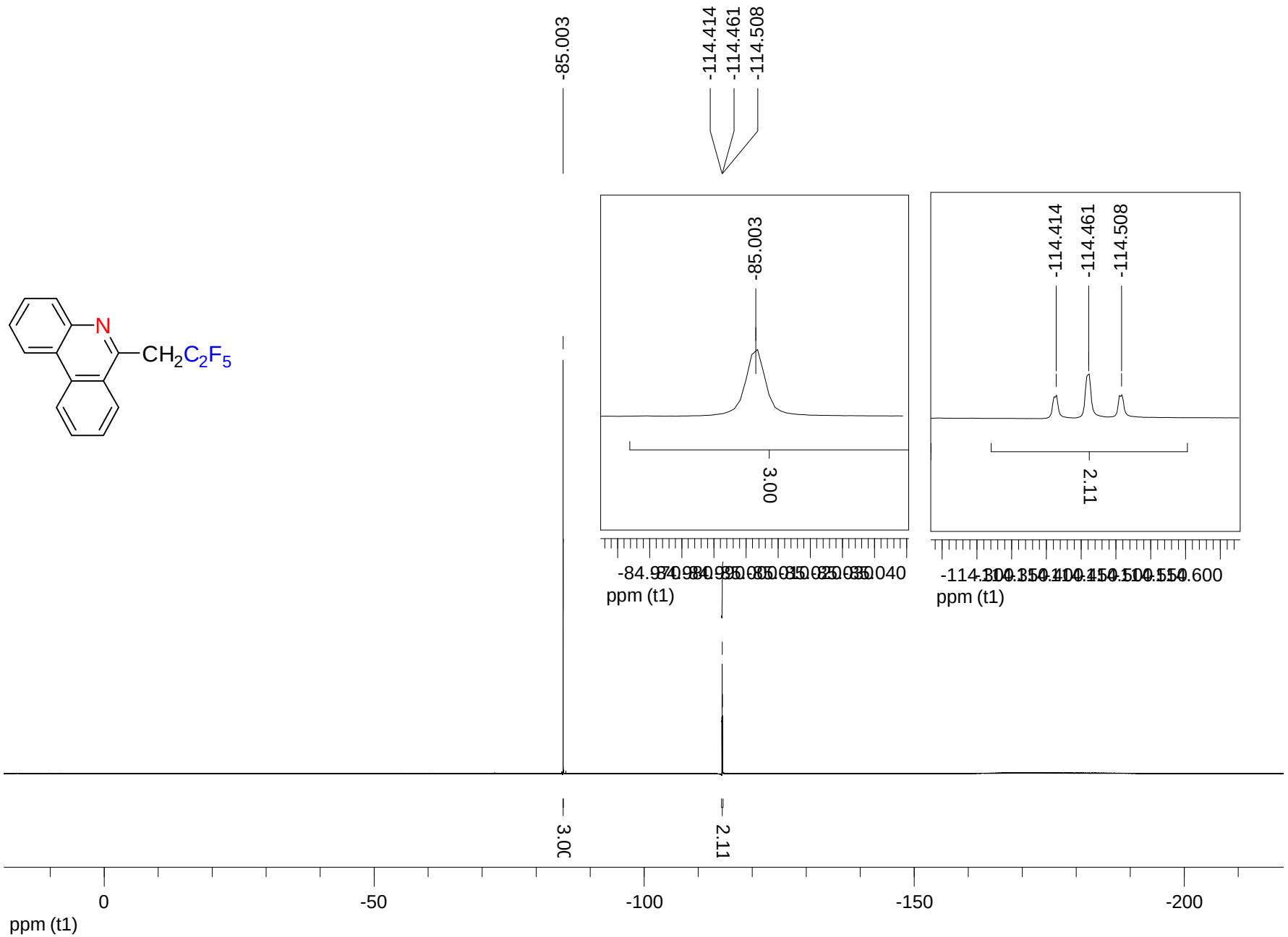
^{1}H NMR Spectrum of **4** (400 MHz, $CDCl_3$)



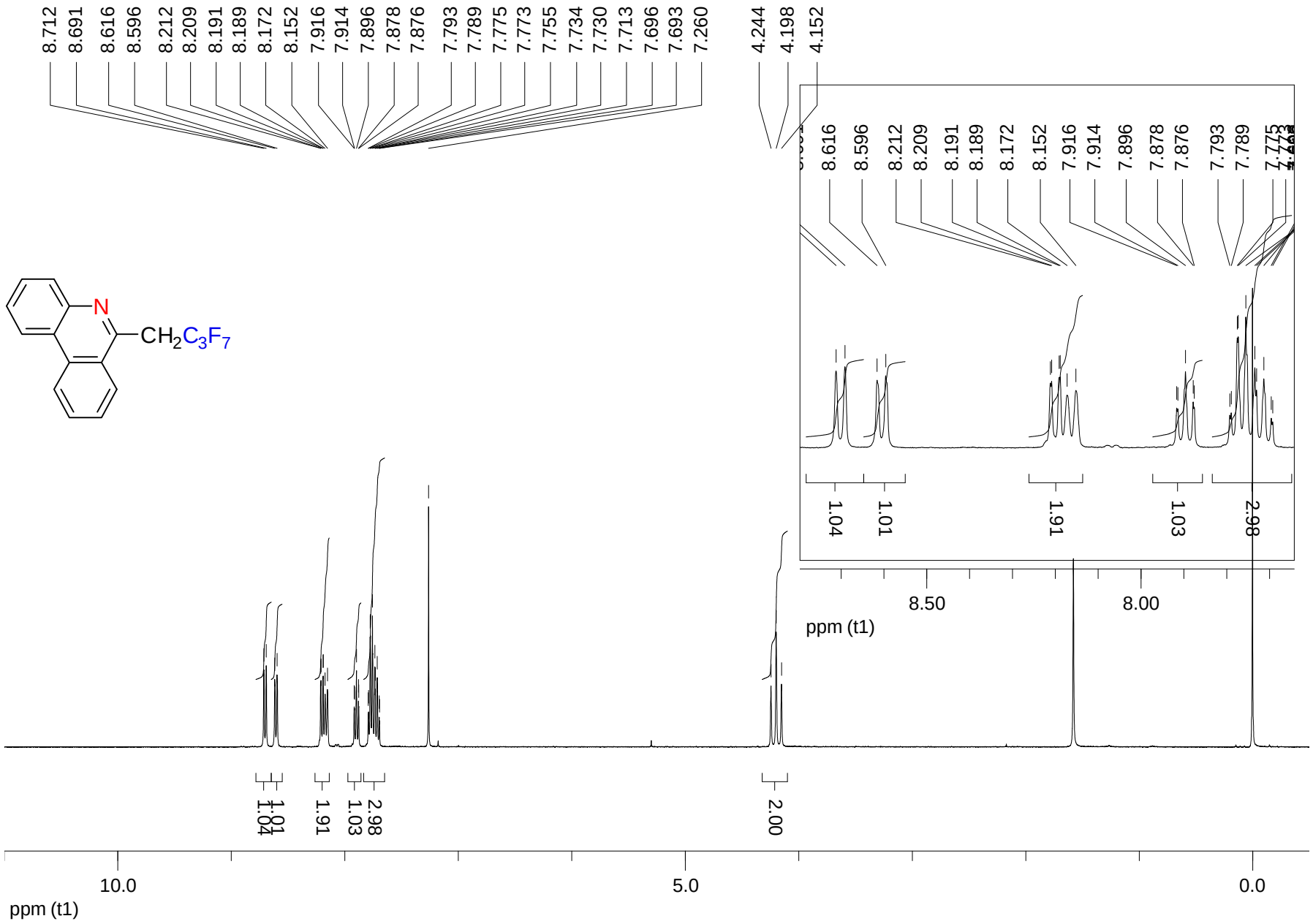
^{13}C NMR Spectrum of **4** (100 MHz, $CDCl_3$)



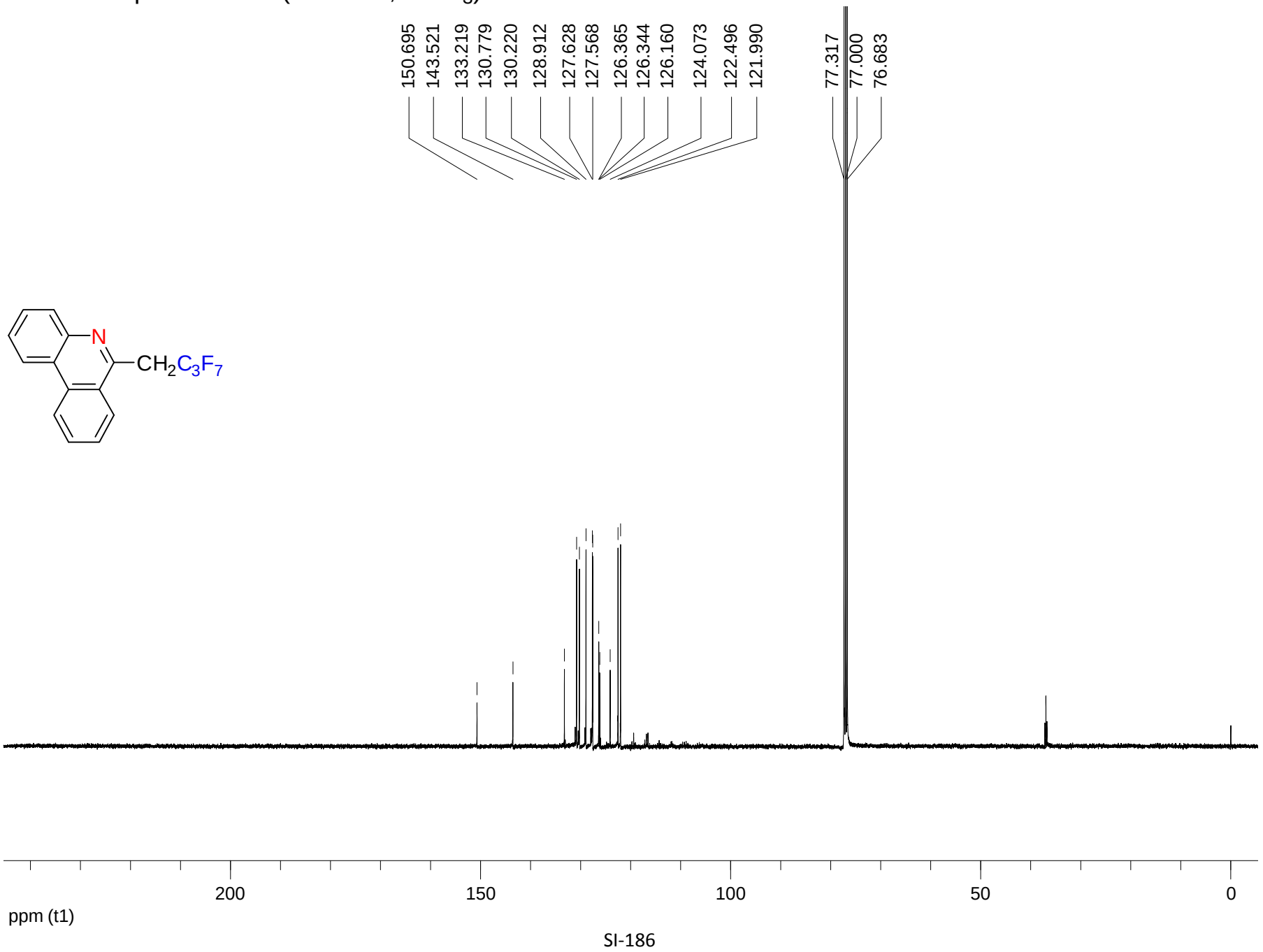
^{19}F NMR Spectrum of **4** (376 MHz, $CDCl_3$)



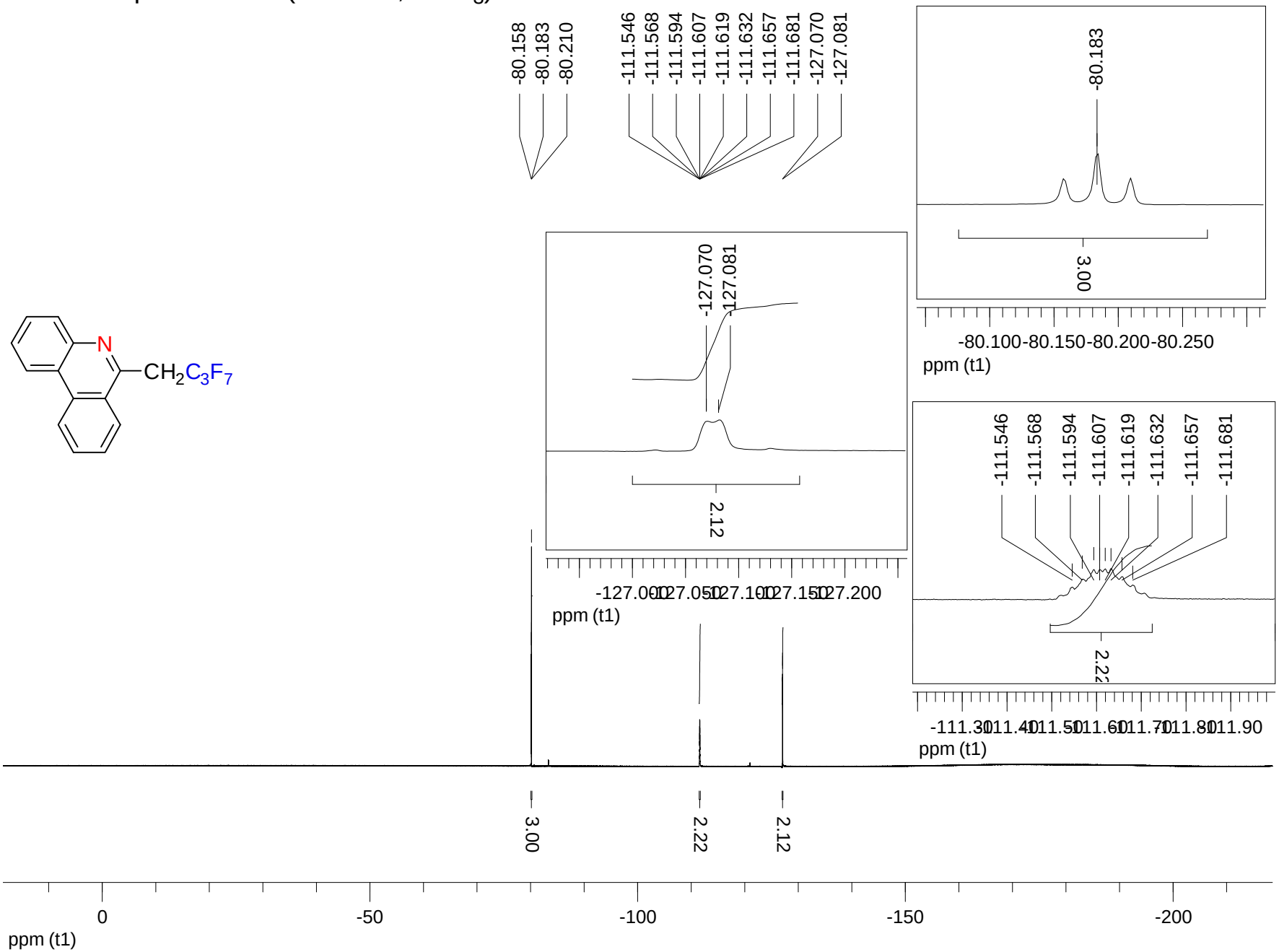
^{1}H NMR Spectrum of **5** (400 MHz, $CDCl_3$)



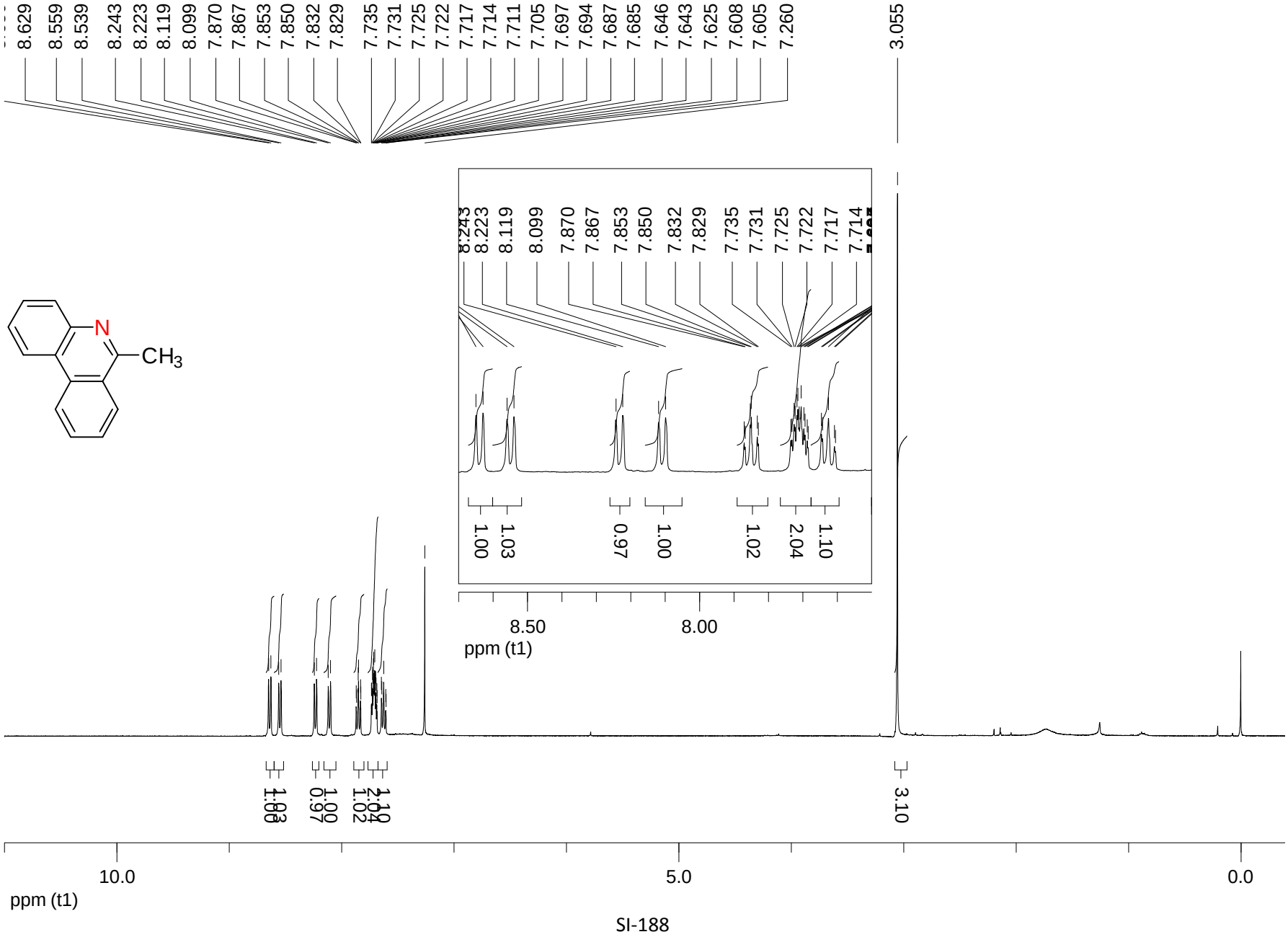
^{13}C NMR Spectrum of **5** (100 MHz, $CDCl_3$)



^{19}F NMR Spectrum of **5** (376 MHz, $CDCl_3$)



^{1}H NMR Spectrum of **3** (400 MHz, $CDCl_3$)



^{1}H NMR Spectrum of **3-D** (400 MHz, $CDCl_3$)