Supporting Information

for

"Copper-Catalyzed Synthesis of Aminoquinolines from *β*-(2-aminophenyl)-*α*,*β*-ynones using DMF as Dual Synthon"

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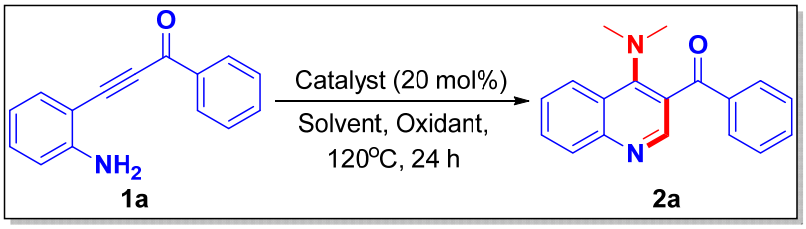
1. General Information:

All chemicals were purchased from commercial providers (Sigma Aldrich, Alfa Aesar, TCI, and matrix scientific) and used directly without further purification, unless otherwise noted. Well cleaned and oven dried glassware were used for the experiments. Reaction was monitored by Thin Layer Chromatography (TLC), purchased as pre-coated with silica gel 60 F254 from Merck. Column chromatography was carried out using the silica gel 230-400 mesh (purchased from Merck) with mixture of ethyl acetate/hexane or hexane as the eluent. ^{1}H NMR spectra were recorded on 400 MHz, Varian mercury spectrometer using $CDCl_3$ or DMSO-d_6 as solvent. ^{13}C-NMR spectra were recorded on 100 MHz, Varian mercury spectrometer using $CDCl_3$ or DMSO-d_6 as solvent. The spectra were recorded and presented in chemical shifts (ppm) with tetramethylsilane (TMS) used as internal standard. Multiplicities were provided in s (singlet), d (doublet), t (triplet), q (quartet), br (broad single), and m (multiplet). Coupling constants (J) were reported in Hz. All the compounds were characterized by ESI mass on ThermoFinnigan (TRACEGC- POLARISQ) and HRMS (FAB+ mode) on JMS-700 spectrometer. Melting points were determined using fargo intruments.

2. Screening the reaction parameters

Table S1. Optimization table



Scheme S1. Synthesis of 4-aminoquinoline

Entry	Catalyst	Mol % of catalyst	Oxidant	Solvent	Temp. (°C)	Isolated Yield (%)
1	-		-	DMF	120	N.R
2	$AgNO_3$	20%	-	DMF	120	20
3	AgO	20%	-	DMF	120	40
4	$Pd(OAc)_2$	20%	-	DMF	120	NR
5	$NiCl_2$	20%	-	DMF	120	54
6	$CoCl_2.6H_2O$	20%	-	DMF	120	34
7	Cu (0)	20%	-	DMF	120	36
8	$Cu(TFA)_{2.}\,xH_2O$	20%	-	DMF	120	28
9	$Cu(OAc)_{2.}\,H_2O$	20%	-	DMF	120	37
10	CuO	20%	-	DMF	120	33
11	$CuCl_2$	20%	-	DMF	120	56
12	$CuBr_2$	20%	-	DMF	120	50
13	CuCN	20%	-	DMF	120	62
14	CuBr	20%	-	DMF	120	47
15	CuCl	20%	-	DMF	120	71
16	CuCl	20%	-	DMF	100	25
17	CuCl	20%	-	DMF	140	55
18[a]	CuCl	20%	-	DMF	120	62
19[b]	CuCl	20%	-	DMF	120	30
20	CuCl	10%	-	DMF	120	64
21	CuCl	5%	-	DMF	120	51
21	CuCl	20%	-	DMA	120	31
22	CuCl	20%	-	DEF	120	NR
23	CuCl	20%	-	DMSO	120	NR
24	CuCl	20%	-	Toluene	120	NR
25	CuCl	20%	-	PhCl	120	NR
26	CuCl	20%	-	Dioxane	120	NR

27	CuCl	20%	DMSO	DMF	120	82
28	CuCl	20%	H_2O_2	DMF	120	Trace
29	CuCl	20%	TBHP	DMF	120	Trace
30	CuCl	20%	DTBP	DMF	120	Trace
31	CuCl	20%	$K_2S_2O_8$	DMF	120	Trace
32	CuCl	20%	DMSO	DMF	120	58
33	CuCl	20%	DMSO	DMF	120	70

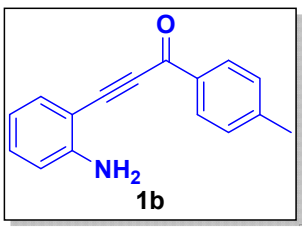
Reaction Conditions: The reactions were performed with **1a** (0.2 mmol), catalyst and oxidant (1 equiv.) in solvent 3 mL, stirred for 24 h indicated time unless otherwise noted. [a] Reaction was carried out under open air. [b] Reaction was carried out under N_2. Abbreviations: DTBP = di-*tert*-butyl peroxide and TBHP = *tert*-butyl hydroperoxide.

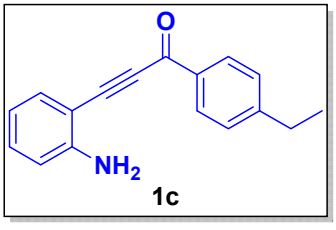
3. Synthesis of starting materials (1a-t) & (1a-Boc)

All the starting materials **(1a-t)** were synthesized on 5 mmol scale, according to literature procedure [1] and obtained in 30% - 70% yield, unless otherwise noted. The ^{1}H-NMR spectra of starting materials **1a, 1e, 1g,** and **1h** were matched with previous literature. [2] The rest of the new starting materials (**1b-d, 1f, 1i-t, 1a-Boc**) were characterized and the data were presented as followed.

4. Characterization data of starting materials (1a-t, 1a-Ph and 1a-Boc)

3-(2-aminophenyl)-1-(*p*-tolyl)prop-2-yn-1-one (1b): Yellow solid; m.p. 148 °C - 150 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.0 Hz, 2H), 7.47 - 7.45 (m, 1H), 7.31 - 7.22 (m, 4H), 6.74 - 6.70 (m, 2H), 4.46 (s, 2H), 2.43 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.4, 150.2, 145.0, 134.7, 133.7, 132.4, 129.6, 129.3, 117.3, 114.6, 104.0, 93.3, 90.5, 21.8; HRMS (m/z, FAB+) calcd $[C_{16}H_{14}NO]^+$ $[M+H]^+$ 236.1075, observed 236.1075.

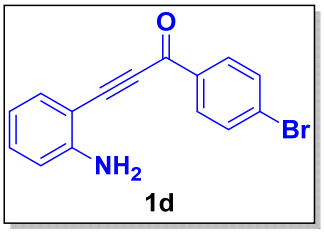




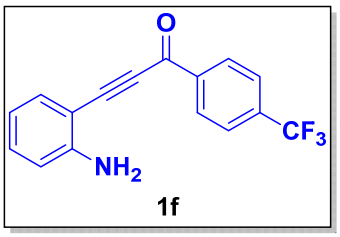
3-(2-aminophenyl)-1-(4-ethylphenyl)prop-2-yn-1-one (1c): Brown solid; m.p. 114 °C - 116 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.0 Hz, 2H), 7.46 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.26

- 7.21 (m, 1H), 6.73 - 6.70 (m, 2H), 2.72 (q, J = 15.2, 7.2 Hz, 2H), 1.26 (t, J = 7.2 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.5, 151.2, 150.2, 134.8, 133.7, 132.4, 129.6, 128.1, 117.9, 114.6, 103.9, 93.3, 90.6, 29.0, 15.1; HRMS (m/z, FAB+) calcd $[C_{17}H_{16}NO]^+$ $[M+H]^+$ 250.1232, observed 250.1233.

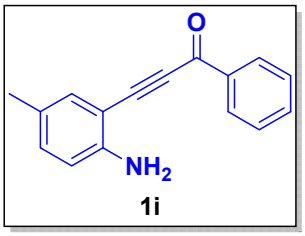
3-(2-aminophenyl)-1-(4-bromophenyl)prop-2-yn-1-one (1d): Yellow solid; m.p. 178 °C - 180 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.5 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.8 Hz, 2H), 7.47 - 7.44 (m, 1H), 7.25 - 7.24 (m, 1H), 6.75 - 6.71 (m, 2H), 4.47 (br, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 176.5, 150.4, 135.7, 133.7, 132.8, 131.9, 130.7, 130.4, 128.9, 117.9, 114.7, 103.4, 93.4, 91.8; HRMS (m/z, FAB+) calcd $[C_{15}H_{11}BrNO]^+$ $[M+H]^+$ 300.0024, observed 300.0026.

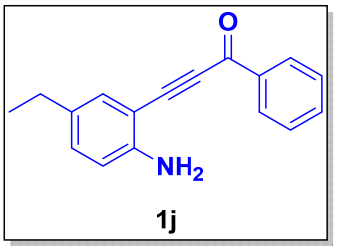


3-(2-aminophenyl)-1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-one (1f): Brown solid; m.p. 157 °C - 159 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 7.47 - 7.45 (m, 1H), 7.28 - 7.24 (m, 1H), 6.75 - 6.70 (m, 3H), 4.49 (br, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 176.4, 150.6, 133.8, 133.0, 132.6, 129.6, 127.5, 125.6, 119.6, 118.0, 114.7, 103.2, 93.1, 92.7; HRMS (m/z, FAB+) calcd $[C_{16}H_{11}F_3NO]^+$ $[M+H]^+$ 290.0793, observed 290.0793.



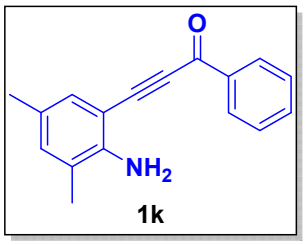
3-(2-amino-5-methylphenyl)-1-phenylprop-2-yn-1-one (1i): Yellow solid; m.p. 139 °C - 141 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.4 Hz, 2H), 7.63 - 7.46 (m, 3H), 7.27 - 7.24 (m, 1H), 7.07 - 7.05 (m,1H), 6.65 (d, J = 8.4 Hz), 2.23 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.8, 148.1, 137.0, 133.9, 133.7, 133.5, 130.1, 129.4, 128.6, 127.34, 114.9, 103.8, 93.1, 91.5, 20.1; HRMS (m/z, FAB+) calcd $[C_{16}H_{13}NO]^+$ $[M]^+$ 235.0997, observed 290.0995.





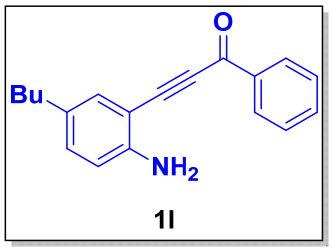
3-(2-amino-5-ethylphenyl)-1-phenylprop-2-yn-1-one (1j): Brown solid; m.p. 261 °C - 263 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.2 Hz, 2H), 7.64 - 7.61 (m, 1H), 7.54 - 7.45 (m, 2H), 7.31 - 7.30 (m, 1H), 7.12 - 7. 10 (m, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 2.55 (q, *J* = 14.8, 7.2 Hz, 2H), 1.20 (t, *J* = 8.0 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.8, 148.4, 137.0, 133.9, 132.7, 132.4, 130.1, 129.4, 128.6, 128.2, 114.9, 103.7, 93.1, 91.6, 27.6 15.6; HRMS (m/z, FAB+) calcd $[C_{17}H_{16}NO]^+$ $[M+H]^+$ 250.1232, observed 250.1225.

3-(2-amino-3,5-dimethylphenyl)-1-phenylprop-2-yn-1-one (1k): Yellow fluffy; m.p. 192 °C - 194 °C;

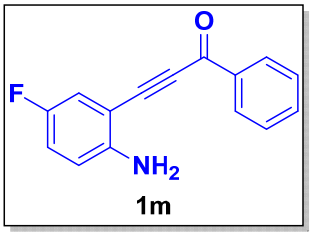


^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.22 - 8.20 (d, 2H), 7.64 - 7.60 (m, 1H), 7.54 - 7.50 (m, 2H), 7.19 (s, 1H), 6.99 (s, 1H), 4.37 (s, 2H), 2.23 (s, 3H), 2.16 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.8, 146.6, 137.0, 134.8, 133.8, 131.2, 129.4, 128.6, 126.9, 122.1, 103.4, 93.1, 92.1, 20.1, 17.4; HRMS (m/z, FAB+) calcd $[C_{17}H_{15}NO]^+$ $[M]^+$ 249.1154, observed 249.1147.

3-(2-amino-5-butylphenyl)-1-phenylprop-2-yn-1-one (1l): Brown solid; m.p. 102 °C - 104 °C; ^{1}H-



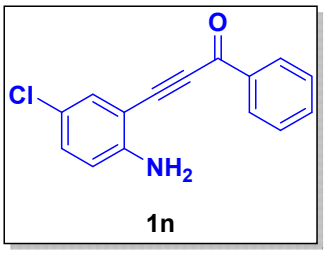
NMR (400 MHz, $CDCl_3$) δ 8.26 - 8.19 (m, 1H), 7.61 - 7.48 (m, 4H), 7.31 - 7.24 (m, 1H), 7.10 - 7.06 (m, 1H), 6.71 - 6.64 (m, 1H), 4.37 (br, 2H), 2.53 - 2.47 (m, 2H), 1.71 - 1.19 (m, 4H), 0.95 - 0.91 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.7, 148.4, 137.0, 133.8, 133.1, 132.9, 132.5, 129.4, 128.6, 114.8, 103.7, 93.1, 91.6, 34.3, 33.6, 22.1, 13.9: HRMS (m/z, FAB+) calcd $[C_{19}H_{20}NO]^+$ $[M+H]^+$ 278.1545, observed 278.1544.



3-(2-amino-5-fluorophenyl)-1-phenylprop-2-yn-1-one (1m): Yellow fluffy; m.p. 176 °C - 178 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.19 - 8.14 (m, 2H), 7.61 - 7.60 (m, 1H), 7.51 - 7.49 (m, 1H), 7.16 - 7.12 (m, 1H), 7.00 - 6.97 (m, 1H), 6.68 - 6.65 (m, 1H), 4.36 (br, 2H); ^{13}C-NMR (100 MHz,

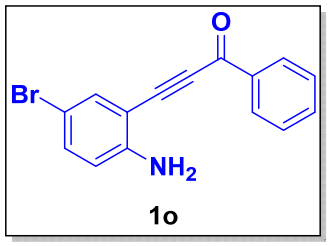
$CDCl_3$) δ 177.5, 155.9, 153.6, 146.9, 136.7, 134.1, 129.4, 128.6, 120.18, 118.8, 115.9, 104.2, 93.1, 89.4; HRMS (m/z, FAB+) calcd $[C_{15}H_{11}FNO]^+$ $[M]^+$ 239.0746, observed 239.0749.

3-(2-amino-5-chlorophenyl)-1-phenylprop-2-yn-1-one (1n): Yellow solid; m.p. 128 °C - 130 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 6.4 Hz, 2H), 7.76 (d, J = 8.0 Hz, 1H), 7.64 - 7.62 (m, 1H), 7.54 - 7.51 (m, 2H), 7.38 - 7.37 (m, 2H), 6.69 - 6.66 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.5, 148.9, 136.7, 134.1, 132.6. 132.5, 129.4, 128.7, 126.2, 122.1, 121.0, 115.9, 104.9, 93.4, 89.1; HRMS (m/z, FAB+) calcd $[C_{15}H_{11}ClNO]^+$ $[M+H]^+$ 256.0529, observed 256.0524.



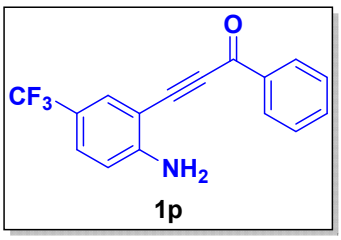
1n

3-(2-amino-5-bromophenyl)-1-phenylprop-2-yn-1-one (1o): Yellow solid; m.p. 146 °C - 148 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 7.2 Hz, 2H), 7.62 - 7.49 (m, 4H), 7.30 - 7.28 (m, 1H), 6.60 (d, J = 8.8 Hz, 1H), 4.5 (br, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.5, 149.3, 136.6, 135.3, 134.1, 129.4, 128.6, 126.1, 116.2, 108.6, 105.4, 93.6, 89.1; HRMS (m/z, FAB+) calcd $[C_{15}H_{11}BrNO]^+$ $[M+H]^+$ 300.0024, observed 300.0015.



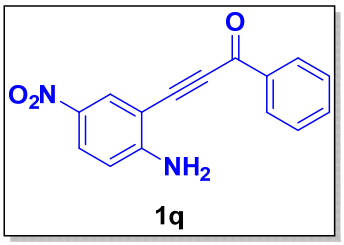
1o

3-(2-amino-5-(trifluoromethyl)phenyl)-1-phenylprop-2-yn-1-one (1p): Brown solid; m.p. 200 °C - 202 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.4 Hz, 2H), 7.68 (s, 1H), 7.66 - 7.60 (m, 1H), 7.54 - 7.49 (m, 2H), 7.43- 7.32 (m, 2H), 6.77 (d, J = 8.8 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$ + 4 drops DMSO-d_6) δ 177.4, 152.7, 136.5, 134.2, 130.9, 129.7, 129.4, 129.0, 128.6, 128.3, 128.3, 126.1, 114.3, 102.9, 93.3, 88.9; HRMS (m/z, FAB+) calcd $[C_{16}H_{11}F_3NO]^+$ $[M+H]^+$ 290.0793, observed 290.0796.

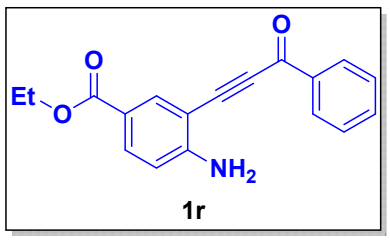


1p

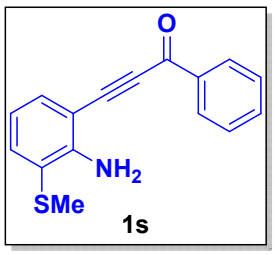
3-(2-amino-5-nitrophenyl)-1-phenylprop-2-yn-1-one (1q): Yellow solid; m.p. 188 °C - 190 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 2.8 Hz, 1H), 8.17 - 8.14 (m, 2H), 8.08 - 8.05 (m, 1H), 7.65 - 7.61 (m, 1H), 7.53 - 7.49 (m, 2H), 6.75 (d, *J* = 8.8 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$ + 4 drops DMSO-d_6) δ 177.3, 155.3, 137.7, 136.3, 134.3, 130.3, 129.4, 128.7, 128.1, 113.7, 102.4, 93.1, 87.6; HRMS (m/z, FAB+) calcd $[C_{15}H_{11}N_2O_3]^+$ $[M+H]^+$ 267.0770, observed 267.0767.



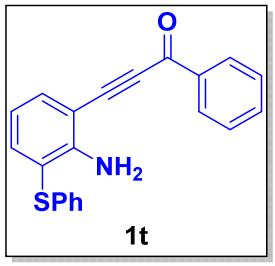
ethyl 4-amino-3-(3-oxo-3-phenylprop-1-yn-1-yl)benzoate (1r): Yellow solid; m.p. 164 °C - 166 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.8 Hz, 2H), 7.92 - 7.89 (m, 1H), 7.66 - 7.59 (m, 1H), 7.55 - 7.51 (m, 2H), 7.37 (s, 1H), 6.73 6.70 (m, 1H), 4.99 (br, 2H), 4.34 (q, *J* = 8.8, 4.0 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.6, 166.1, 153.6, 136.1, 134.1, 133.8, 129.5, 128.6, 126.2, 119.4, 113.8, 103.0, 93.1, 89.5, 60.7, 14.3; HRMS (m/z, FAB+) calcd $[C_{18}H_{16}NO_3]^+$ $[M+H]^+$ 294.1130, observed 294.1135.



3-(2-amino-3-(methylthio)phenyl)-1-phenylprop-2-yn-1-one (1s): Yellow solid; m.p. 112 °C - 114 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.6 Hz, 2H), 7.71 (s, 1H), 7.70 - 7.59 (m, 1H), 7.50 - 7.49 (m, 2H), 7.43 - 7.41 (m, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 4.75 (br, 2H), 2.38 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.9, 149.6, 138.8, 137.1, 134.4, 133.7, 129.3, 128.4, 120.2, 114.3, 108.8, 95.4, 87.1, 17.7; HRMS (m/z, FAB+) calcd $[C_{16}H_{14}NOS]^+$ $[M+H]^+$ 268.0796, observed 268.0795.

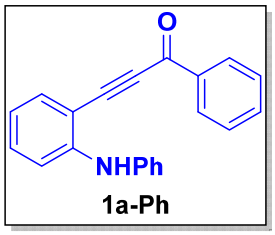


3-(2-amino-3-(phenylthio)phenyl)-1-phenylprop-2-yn-1-one (1t): Yellow solid; m.p. 138 °C - 140 °C;^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.20 - 8.16 (m, 2H), 7.84 - 7.83 (m, 1H), 7.60 - 7.45 (m, 4H), 7.25 - 7.08 (m, 5H), 6.78 - 6.74 (m, 1H), 4.75 (br, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.9, 151.0, 142.9, 137.0, 136.3, 135.3,



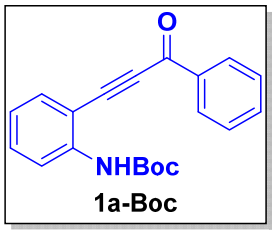
133.7, 129.4, 129.2, 128.5, 126.8, 126.0, 114.9, 114.6, 94.8, 87.2; HRMS (m/z, FAB+) calcd $[C_{21}H_{16}NOS]^+$ $[M+H]^+$ 330.0953, observed 330.0949.

1-phenyl-3-(2-(phenylamino)phenyl)prop-2-yn-1-one (1a-Ph): The title compound was prepared



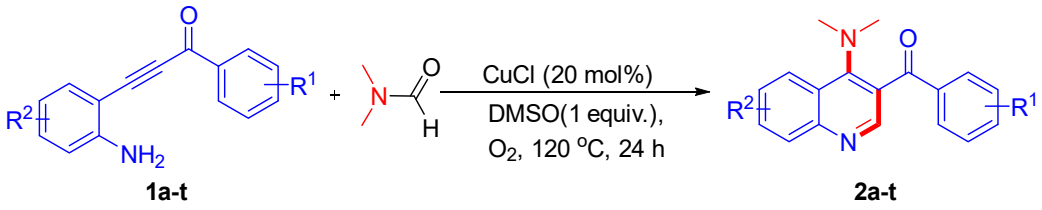
accordingly the reported literature by wang et al.[3] The starting substrate of 3-(2-aminophenyl)-1-phenyl-2-propyn-1-one **1a** (0.5 mmol) was taken in toluene (0.25 M) and followed by addition of 1.5 equiv. of phenylboronic acid, 2,6-lutidine (1.1 equiv.), nonanoic acid (0.2 equiv.), and $Cu(OAc)_2$ (0.1 equiv.). Then the reaction mixture was allowed to stir (22~ 30 h) in room temperature and the reaction condition was monitored by TLC. The reaction mixture was quenched with 10 mL of water and extracted with ethyl acetate (3X10 mL). Finally, the combined organic layer was washed with brine (2X10 mL), dried over $MgSO_4$, filtered through funnel and removed the solvent under reduced pressure. The obtained crude was purified by column chromatography using 5-10% ethyl acetate in hexane as eluent to afford the desired product (**1a-Ph**) in 68% yield in form of brown liquid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.6 Hz, 1H), 7.61 - 7.58 (m, 2H), 7.51 - 7.48 (m, 2H), 7.37 - 7.30 (m, 2H), 7.28 - 7.21 (m, 4H), 7.10 - 7.08 (m, 1H), 6.83 - 6.81 (m, 1H), 6.31 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.6, 147.6, 140.6, 136.9, 134.3, 134.0, 132.4, 129.5, 129.4, 128.6, 123.5, 121.1, 119.2, 113.7, 106.1, 93.1, 90.7; HRMS (m/z, FAB+) calcd $[C_{21}H_{15}NO]^+$ $[M]^+$ 297.1154, observed 297.1162.

***tert*-butyl (2-(3-oxo-3-phenylprop-1-yn-1-yl)phenyl)carbamate (1a-Boc):** The initial stage of starting



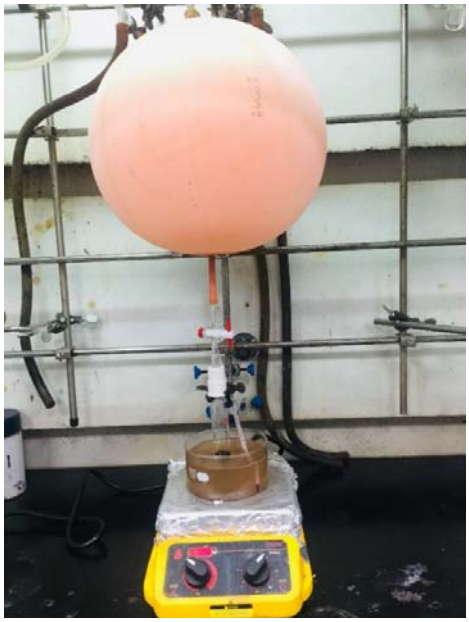
material (Boc protected alkyne) was prepared according to literature. [4] The title compound was prepared according the general procedure 3 on 5 mmol scale based literature. White solid, m.p. 159 °C - 161 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.24 - 8.19 (m, 3H), 7.67 - 7.60 (m, 2H), 7.55 - 7.52 (m, 2H), 7.48 - 7.44 (m, 1H), 7.36 - 7. 34 (m, 1H), 7.07 - 7.03 (m, 1H), 1.55 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177. 4, 152.1, 141.6, 136.7, 134.3, 133.5, 132.4, 129.4, 128.7, 122.4, 118.2, 107.9, 93.5, 88.5, 81.3, 28.2; HRMS (m/z, FAB+) calcd $[C_{20}H_{20}NO_3]^+$ $[M+H]^+$ 322.1443, observed 322.1445.

5. General procedure for synthesis of 4-aminoquinoline



Scheme S2. General synthetic scheme for 4-aminoquinoline synthesis

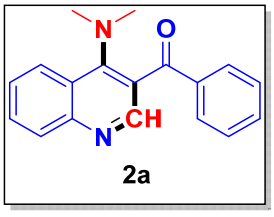
Well cleaned and an oven dried sealed tube was equipped with a magnetic stir bar was added



sequentially starting material **1a-t** (0.2 mmol), 20 mol % of CuCl, DMSO as oxidant (1 equiv.), and 3 mL of DMF. The reaction was allowed to stir at 120 °C for 24 h under oxygen atmosphere (Reaction setup as shown). The reaction was cooled to room temperature and followed by 10 ml of water was added for quenching. The reaction mixture was extracted with ethyl acetate (3X10 mL) and collected organic layer washed with brine (2X10 mL). The organic layer was dried over $MgSO_4$ and filtered through funnel, the solvent was evaporated under vacuum to get the crude. The obtained crude was purified by column chromatography using 15-20 % of ethyl acetate in hexane. Further, the obtained desired products were characterized by NMR, and HRMS, the data were shown given below.

5.1. Characterization data of 4-aminoquinoline

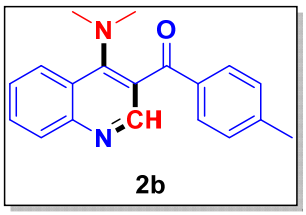
(4-(dimethylamino)quinolin-3-yl)(phenyl)methanone (2a): Title compound was synthesized



according to the general procedure and obtain as yellow liquid (45mg, 82%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.16 (d, J = 8.8 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.87 - 7.85 (m, 2H), 7.73 - 7.70 (m, 1H), 7.63 - 7.59 (m, 1H),

7.55 - 7.47 (m, 3H), 2.95 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 196.3, 157.2, 150.6, 150.2, 137.7, 133.5, 130.3, 130.0, 129.8, 128.6, 125.6, 125.5, 124.4, 122.4, 44.8; HRMS (m/z, FAB+) calcd $[C_{18}H_{17}N_2O]^+$ $[M+H]^+$ 277.1341, observed 277.1333.

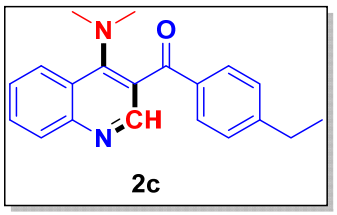
(4-(dimethylamino)quinolin-3-yl)(*p*-tolyl)methanone (2b): Title compound was synthesized



2b

according to the general procedure and obtain as yellow liquid (40 mg, 70%); ^{1}H-NMR (400 MHz, $CDCl_3$ + 4 drops of DMSO-d_6) δ 8.54 (d, J = 4.8 Hz, 1H), 8.09 (d, J = 7.6Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.70 - 7.63 (m, 3H), 7.51 - 7.45 (m, 1H), 7.24 - 7.21 (m, 2H), 2.88 (s, 6H), 2.37 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$ + 4 drops of DMSO-d_6) δ 195.9, 156.8, 150.4, 144.4, 135.0, 130.0, 129.6, 129.2, 128.9, 128.5, 125.5, 124.2, 122.5, 44.6, 29.5; HRMS (m/z, FAB+) calcd $[C_{19}H_{19}N_2O]^+$ $[M+H]^+$ 291.1497, observed 291.1492.

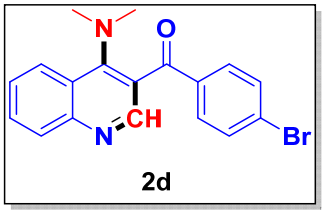
(4-(dimethylamino)quinolin-3-yl)(4-ethylphenyl)methanone (2c): Title compound was synthesized



2c

according to the general procedure and obtain as brown liquid (39 mg, 64%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.16 (d, J = 8.8 Hz, 1H), 8.08 (d, J = 8.8 Hz, 1H), 7.79 (d, J = 8.0 Hz, 2H), 7.73 - 7.69 (m, 1H), 7.54 - 7.50 (m, 1H), 7.30 (d, J = 8.0 Hz, 2H), 2.96 (s, 6H), 2.76 - 2.70 (m, 2H), 1.27 (t, J = 7.2 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 196.0, 157.1, 150.7, 150.4, 150.0, 135.2, 130.3, 130.2, 129.7, 128.1, 125.6, 125.4, 124.4, 122.6, 44.8, 28.9, 15.1; HRMS (m/z, FAB+) calcd $[C_{20}H_{21}N_2O]^+$ $[M+H]^+$ 305.1654, observed 305.1645.

(4-bromophenyl)(4-(dimethylamino)quinolin-3-yl)methanone (2d): Title compound was

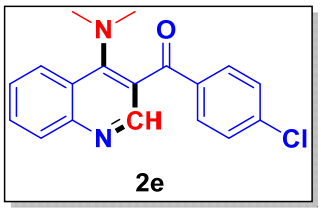


2d

synthesized according to the general procedure and obtain as yellow semi solid (41 mg, 58%);^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.16 - 8.07 (m, 2H), 7.75 - 7.71 (m, 3H), 7.64 - 7.62 (m, 2H), 7.56 - 7.52 (m, 1H), 2.96 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 195.1, 157.3, 150.2, 136.4, 132.0, 131.4, 130.5, 129.8, 129.0,

128.8, 125.7, 125.5, 124.2, 121.6, 44.9; HRMS (m/z, FAB+) calcd $[C_{18}H_{16}BrN_2O]^+$ $[M+H]^+$ 355.0446, observed 355.0456.

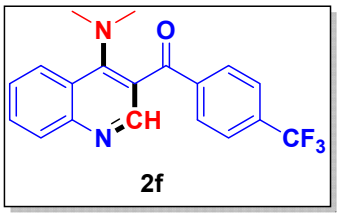
(4-chlorophenyl)(4-(dimethylamino)quinolin-3-yl)methanone (2e): Title compound was synthesized



2e

according to the general procedure and obtain as yellow liquid (38 mg, 62%); ^{1}H-NMR (400 MHz, $CDCl_3$ + 4 drops of DMSO-d_6) δ 8.60 (s, 1H), 8.16 (d, J = 8.8 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.81 - 7.79 (m, 1H), 7.75 - 7.73 (m, 1H), 7.48 - 7.46 (m, 3H), 7.33 - 7. 32 (m, 1H), 2.96 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$ + 4 drops of DMSO-d_6) δ 194.9, 157.0, 150.3, 135.9, 131.2, 130.5, 130.3, 129.8, 128.8, 128.4, 125.6, 125.3, 124.1, 44.7; HRMS (m/z, FAB+) calcd $[C_{18}H_{16}ClN_2O]^+$ $[M+H]^+$ 311.0951, observed 311.0955.

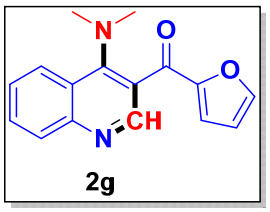
(4-(dimethylamino)quinolin-3-yl)(4-(trifluoromethyl)phenyl)methanone (2f): Title compound was



2f

synthesized according to the general procedure and obtain as yellow semi solid (32 mg, 46%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.17 - 8.08 (m, 2H), 7.96 (d, J = 8.4 Hz, 2H), 7.76 - 7.72 (m, 3H), 7.56 - 7.52 (m, 1H), 2.96 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 194.9, 157.6, 150.4, 140.5, 134.4, 130.6, 130.2, 129.9, 125.8, 125.7, 125.6, 125.0, 124.2, 122.1, 121.4, 44.9; HRMS (m/z, FAB+) calcd $[C_{19}H_{16}F_3N_2O]^+$ $[M+H]^+$ 345.1215, observed 345.1210.

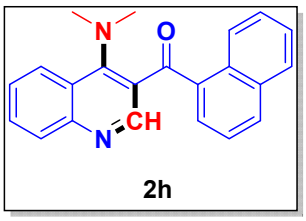
(4-(dimethylamino)quinolin-3-yl)(furan-2-yl)methanone (2g): Title compound was synthesized



2g

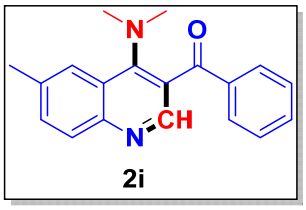
according to the general procedure and obtain as brown semi solid (28 mg, 52%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.17 - 8.06 (m, 1H), 7.69 (s, 2H), 7.52 - 7.46 (m, 1H), 7.10 - 7.09 (m, 1H), 6.97 - 6.96 (m, 1H), 6.59 - 6.58 (m, 1H), 6.45 - 6.44 (m, 1H), 3.01 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 182.9, 160.3, 157.2, 152.8, 148.7, 147.7, 143.7, 130.3, 125.6, 120.7, 116.0, 112.5, 111.1, 44.8; HRMS (m/z, FAB+) calcd $[C_{16}H_{15}N_2O_2]^+$ $[M+H]^+$ 267.1134, observed 267.1133.

(4-(dimethylamino)quinolin-3-yl)(naphthalen-1-yl)methanone (2h): Title compound was

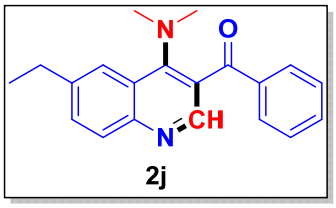


synthesized according to the general procedure and obtain as yellow liquid (32mg, 48%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.87 (d, J = 8.8 Hz, 1H), 8.29 - 8.16 (m, 2H), 8.07 - 7.91 (m, 2H), 7.87 - 7.72 (m, 1H), 7.69 - 7.64 (m, 1H), 7.62 - 7.41 (m, 4H), 7.35 - 7.28 (m, 1H), 3.05 (s, 6H); ^{13}C-NMR (100 MHz, DMSO-d_6) δ 197.2, 174.7, 157.1, 151.6, 150.6, 145.1, 139.7, 139.0, 134.1, 133.7, 133.1, 132.6, 131.1, 130.7, 130.0, 129.3, 128.8, 127.3, 126.9, 126.4, 126.0, 125.5, 120.0, 119.5, 45.0; HRMS (m/z, FAB+) calcd $[C_{22}H_{19}N_2O]^+$ $[M+H]^+$ 327.1497, observed 327.1493.

(4-(dimethylamino)-6-methylquinolin-3-yl)(phenyl)methanone (2i): Title compound was

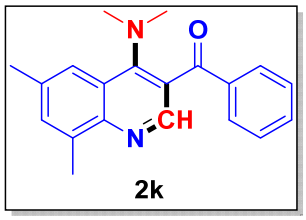


synthesized according to the general procedure and obtain as yellow semi solid (43 mg, 74%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.00 - 7.84 (m, 4H), 7.61 - 7.46 (4H), 2.94 (s, 6H), 2.56 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 196.4, 156.9, 149.5, 148.5, 137.6, 135.6, 133.4, 132.4, 130.0, 129.4, 128.6, 128.1, 124.3, 122.6, 44.7, 22.0; HRMS (m/z, FAB+) calcd $[C_{19}H_{19}N_2O]^+$ $[M+H]^+$ 291.1497, observed 291.1489.



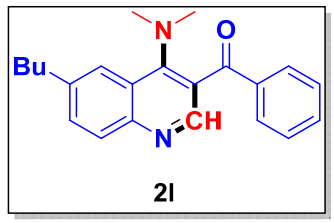
(4-(dimethylamino)-6-ethylquinolin-3-yl)(phenyl)methanone (2j): Title compound was synthesized according to the general procedure and obtain as yellow liquid (48 mg, 78%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.00 (d, J = 8.8, 1H), 7.91 (s, 1H), 7.85 - 7.82 (m, 2H), 7.61 - 7.56 (m, 2H), 7.46 (t, J = 8.0 Hz, 2H), 2.93 (s, 6H), 2.87 - 2.81 (m, 2H), 1.33 (t, J = 7.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 196.4, 156.9, 149.6, 148. 8, 141.9, 137.7,133.4, 131.4, 130.0, 129.5, 128.6, 124.3, 123.1, 122.6, 44.7, 29.2, 15.5; HRMS (m/z, FAB+) calcd $[C_{20}H_{21}N_2O]^+$ $[M+H]^+$ 305.1654, observed 305.1646.

(4-(dimethylamino)-6,8-dimethylquinolin-3-yl)(phenyl)methanone (2k): Title compound was synthesized according to the general procedure and obtain as yellow liquid (34 mg,55%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8. 60 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.75 (s, 1H), 7.61 - 7.57 (m, 1H), 7.48 - 7.41 (m, 3H), 2.91 (s, 6H), 2.75 (s, 3H), 2.51 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 196.7, 157.0, 148.5, 147.8, 137.7, 137.1, 135.1, 133.3, 132.7, 130.0, 128.5, 124.5, 122.9, 122.2, 44.7, 21.9, 18.5; HRMS (m/z, FAB+) calcd $[C_{20}H_{21}N_2O]^+$ $[M+H]^+$ 305.1654, observed 305.1654.



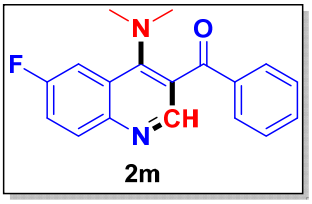
2k

(6-butyl-4-(dimethylamino)quinolin-3-yl)(phenyl)methanone (2l): Title compound was synthesized according to the general procedure and obtain as yellow liquid (25 mg, 37%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.87 - 7.85 (m, 3H), 7.63 - 7.47 (m, 5H), 2.95 (s, 6H), 2.88 - 2.81 (m, 2H), 1.75 - 1.67 (m, 2H), 1.47 - 1.37 (m, 2H), 0.98 - 0.94 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 196.5, 156.8, 153.9, 149.3, 140.6, 137.7, 133.4, 131.8, 130.1, 129.8, 129.1, 128.9, 128.6, 123.9, 121.1, 44.8, 35.9, 33.5, 22.3, 13.9; HRMS (m/z, FAB+) calcd $[C_{22}H_{25}N_2O]^+$ $[M+H]^+$ 333.1967, observed 333.1966.



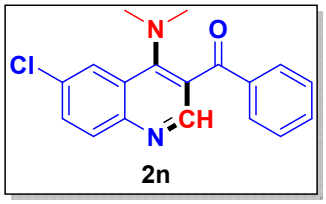
2l

(4-(dimethylamino)-6-fluoroquinolin-3-yl)(phenyl)methanone (2m): Title compound was synthesized according to the general procedure and obtain as brown liquid (28 mg, 46%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.5 (s, 1H), 8.12 - 8.09 (m, 1H), 7.86 - 7.84 (m, 2H), 7.78 - 7.75 (m, 1H), 7.64 -7.60 (m, 1H), 7.51 - 7.46 (m, 3H), 2.93 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 196.0, 161.2, 158.8, 156.9, 149.7, 146.9, 137.4, 133.7, 132.1, 130.0, 128.7, 123.0, 120.4, 109.3, 44.6; HRMS (m/z, FAB+) calcd $[C_{18}H_{16}FN_2O]^+$ $[M+H]^+$ 295.1247, observed 295.1241.



2m

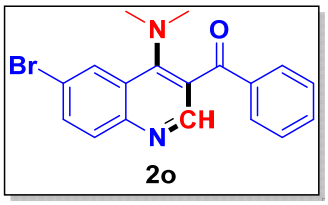
(6-chloro-4-(dimethylamino)quinolin-3-yl)(phenyl)methanone (2n): Title compound was



2n

synthesized according to the general procedure and obtain as brown liquid (32 mg, 52%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.12 (d, J = 2.0 Hz, 1H), 8.02 (d, J = 8.8 Hz, 1H), 7.86 - 7.84 (m, 2H), 7.66 - 7.61 (m, 2H), 7.51 - 7.48 (m, 2H), 2.94 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 195.9, 156.5, 150.6, 148.5, 137.3, 133.7, 131.6, 131.3, 131.0, 130.0, 128.7, 125.3, 124.4, 123.1, 44.7; HRMS (m/z, FAB+) calcd $[C_{18}H_{16}ClN_2O]^+$ $[M+H]^+$ 311.0951, observed 311.0949.

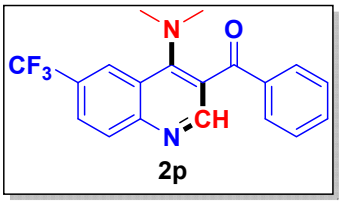
(6-bromo-4-(dimethylamino)quinolin-3-yl)(phenyl)methanone (2o): Title compound was



2o

synthesized according to the general procedure and obtain as yellow liquid (38 mg, 54%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.30 (s, 1H), 7.96 - 7.93 (m, 1H), 7.86 - 7.84 (m, 2H), 7.78 - 7.76 (m, 1H), 7.65 - 7.61 (m, 1H), 7.52 - 7.48 (m, 2H), 2.94 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 195.9, 156.3, 150.8, 148.9, 137.4, 133.7, 133.6, 131.6, 130.0, 128.7, 127.8,125.8, 123.1, 119.7, 44.8; HRMS (m/z, FAB+) calcd $[C_{18}H_{16}BrN_2O]^+$ $[M+H]^+$ 355.0446, observed 355.0445.

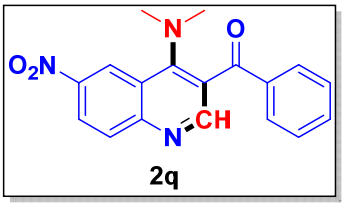
(4-(dimethylamino)-6-(trifluoromethyl)quinolin-3-yl)(phenyl)methanone (2p): Title compound



2p

was synthesized according to the general procedure and obtain as yellow liquid (36 mg, 53%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.46 (s, 1H), 8.20 (d, J = 9.2 Hz, 1H), 7.89 - 7.85 (m, 3H), 7.64 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 2.99 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 195.6, 157.7, 152.4, 151.4, 137.2, 133.8, 131.0, 128.8, 127.4, 127.1, 125.9, 125. 4, 123.6, 122.9, 45.0; HRMS (m/z, FAB+) calcd $[C_{19}H_{16}F_3N_2O]^+$ $[M+H]^+$ 345.1215, observed 345.1220.

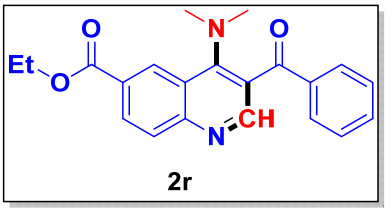
(4-(dimethylamino)-6-nitroquinolin-3-yl)(phenyl)methanone (2q): Title compound was synthesized



2q

according to the general procedure and obtain as brown semi solid (32 mg, 50%); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.70 (s, 1H), 8.46 - 8.43 (m, 1H), 8.15 (d, *J* = 9.2 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 3.05 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 195.2, 158.3, 153.8, 152.8, 144.38, 137.0, 133.9, 131.6, 130.0, 128.8, 123.6, 123.3, 122.9, 122.7, 45.2; HRMS (m/z, FAB+) calcd $[C_{18}H_{16}N_3O_3]^+$ $[M+H]^+$ 322.1192, observed 322.1190.

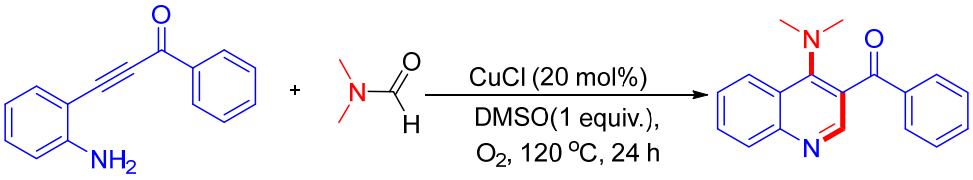
ethyl 3-benzoyl-4-(dimethylamino)quinoline-6-carboxylate (2r): Title compound was synthesized



2r

according to the general procedure and obtain as yellow liquid (trace); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.66 (s, 1H), 8.30 - 8.28 (m, 1H), 8.10 - 8.08 (m, 1H), 7.88 - 7.85 (m, 1H), 7.65 - 7.62 (m, 1H), 7.52 - 7.49 (m, 2H), 4.46 (q, *J* = 14, 7.2 Hz, 2H), 3.02 (s, 6H), 1.45 (t, *J* = 6.4 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 195.8, 166.2, 158.0, 152.6, 144.2, 137.4, 133.7, 130.0, 129.8, 129.0, 128.8, 128.7, 127.1, 123.5, 122.2, 61.4, 45.1, 14.3; HRMS (m/z, FAB+) calcd $[C_{21}H_{21}N_2O_3]^+$ $[M+H]^+$ 349.1552, observed 349.1551.

5.2. Gram scale synthesis



1a (4.5 mmol) 1.0 g

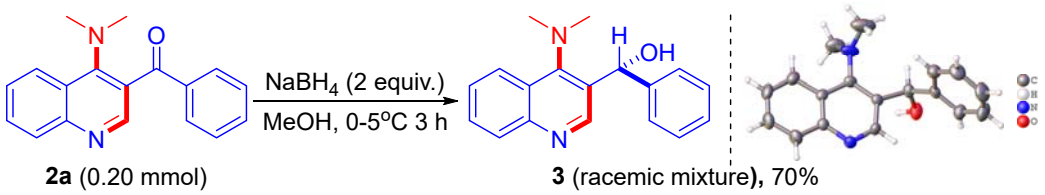
2a, 0.95 g, 80%

Scheme S3. Gram scale synthesis

Using this new synthetic method, we able to demonstrate the gram synthesis of **2a**. The starting material **1a** (1.0 g, 4.5 mmol) was taken in an oven dried glassware, and followed by 20 mol% of CuCl, DMSO (1 equiv.), 65 ml of DMF were added. The reaction mixture was allowed to stir at 120 °C under

O_2 atmosphere for 24 h. Then the reaction was quenched with 20 mL of water, and 20 mL of ethyl acetate was added, organic layer was separated by extraction. The organic layer washed with ethyl acetate (3X20 mL), and brine wash (2X20 mL), collected organic layer dried over $MgSO_4$. Then filtered through funnel and the solvent removed under reduced pressure to get crude. The obtained crude was purified by column chromatography using 20 % ethyl acetate in hexane as eluent afford the desired product in 0.95 g (80%).

5.3. Further chemical transformation of 2a: Reduction with $NaBH_4$

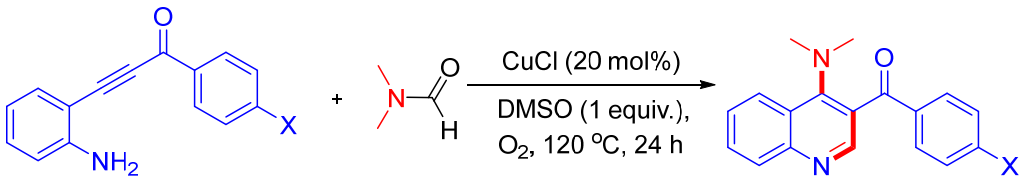


2a (0.20 mmol) **3** (racemic mixture), 70%

Scheme S4. Reduction with $NaBH_4$

(4-(dimethylamino)quinolin-3-yl)(phenyl)methanol (3): An oven dried glassware was taken with magnetic stir bar, and 0.2 mmol of **2a** in methanol. Followed by a portion wise addition of 2 equiv. of $NaBH_4$ under ice cold condition and the reaction mixture was allowed to stir for 3 h. The reaction was quenched with 10% NaOH solution (10 mL), and extracted with ethyl acetate (3X10 mL), and brine wash (2X10 mL). The collected organic layer was dried with help of $MgSO_4$, filtered and removed the solvent under vacuum. The obtained crude was purified by column chromatography using the 15-25 % of ethyl acetate in hexane. Racemic mixture of 3 was obtained as yellow solid (38 mg, 70%); m.p: 205 °C - 207 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 7.97 - 7.84 (m, 2H), 7.52 - 7.08 (m, 7H), 6. 07 (s, 1H), 2.81 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 153.8, 151.7, 143.9, 132.9, 130.4, 128.8, 128.4, 127.3, 126.9, 126.7, 126.4, 125.9, 124.0, 72.7, 44.2; HRMS (m/z, FAB+) calcd $[C_{18}H_{19}N_2O]^+$ $[M+H]^+$ 279.1497, observed 279.1504.

5.4. Competition experiments (electron donating Vs electron withdrawing)



1b, X= *p*-Me, (0.25 mmol)
1d, X= *p*-Br, (0.25 mmol)

2b,X= *p*-Me, 55%
2d,X= *p*-Br, 44%
by GC-MS

Scheme S5. Competition experiment (effect of substituents)

We carried out a competition experiment between starting substrates (**1b** with **1d**) with DMF, to determine the effect of substituents. Each substrate (1b and 1d) were taken in 0.25 mmol, and performed the reaction under standard conditions. The reaction was monitored by TLC, and characterized the reaction mixture using GC/MS. The data revealed that the electron rich substrate (*p*-Me, **1b)** produced the corresponding product **2b** in more favour, when compared with electron poor substrate (*p*-Br, **1d**). The GC/MS data shown below in Figure S1.

ThermoFinnigan (*TRACE***GC -** *POLARIS***Q)**
He Gas Carrier Flow 1.0 ml/min.
Column: **GsBP-5MS 30m*0.25mm*0.50µm**
GC Inlet Temp. 250 °C
Oven Ramp:

Rate	Temp.	min.
-	120 °C	2
15 °C/min.	300 °C	21

EI-MS 70 eV
(Ion Source Temp. 230 °C)

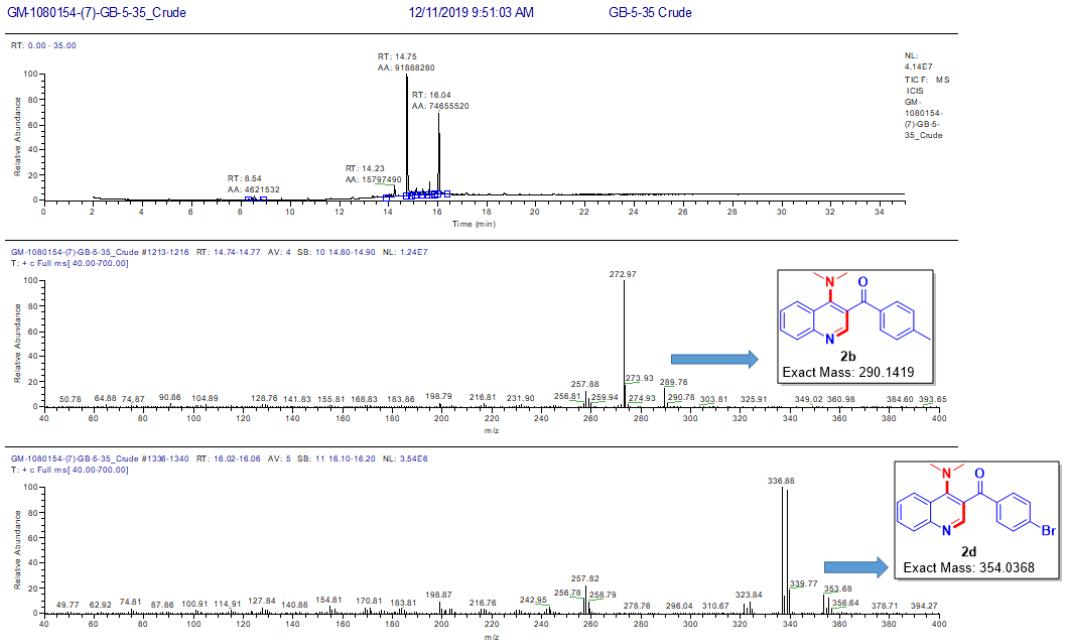
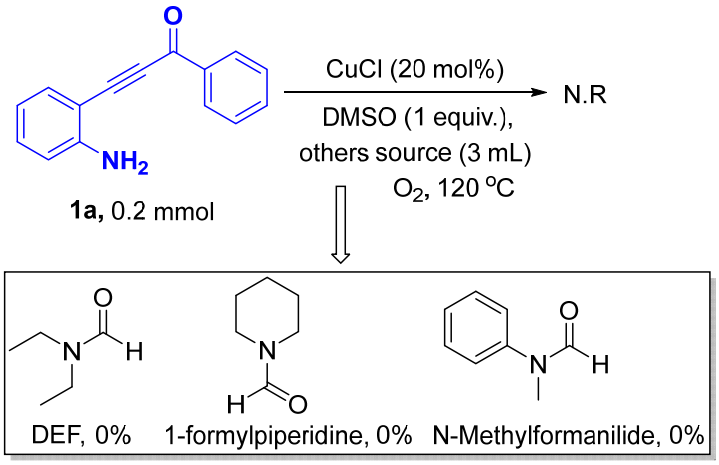


Figure S1. GC/MS spectra of crude mixture of competition experiment 4.4

5.5. Control reaction with other solvents

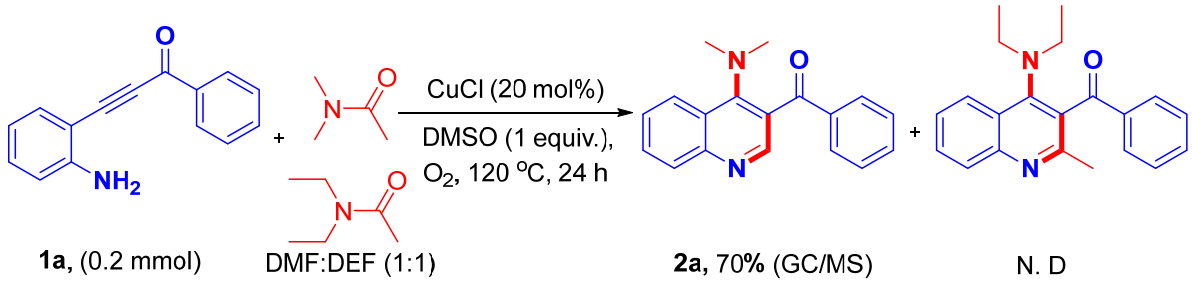


Scheme S6. Control reaction with other solvents

Using optimized conditions, the ynone **1a** (0.2 mmol), 20 mol% of CuCl, 1 equiv. of DMSO were taken with other solvent sources such as *N, N*-Diethylformamide (DEF)/1-formylpiperidine/*N*-methylformanilide. These reactions were failed to deliver its corresponding products. This results suggest that the *N*- should attached with methyl group, in the form of ethyl, cyclic or unsymmetrical.

The methyl group can easily to form, an iminium species, when compared with other solvent sources that may influence the formation of the desired product.

5.6. Competition experiment (DMF Vs DEF)



Scheme S7. Competition experiment (Solvent effect)

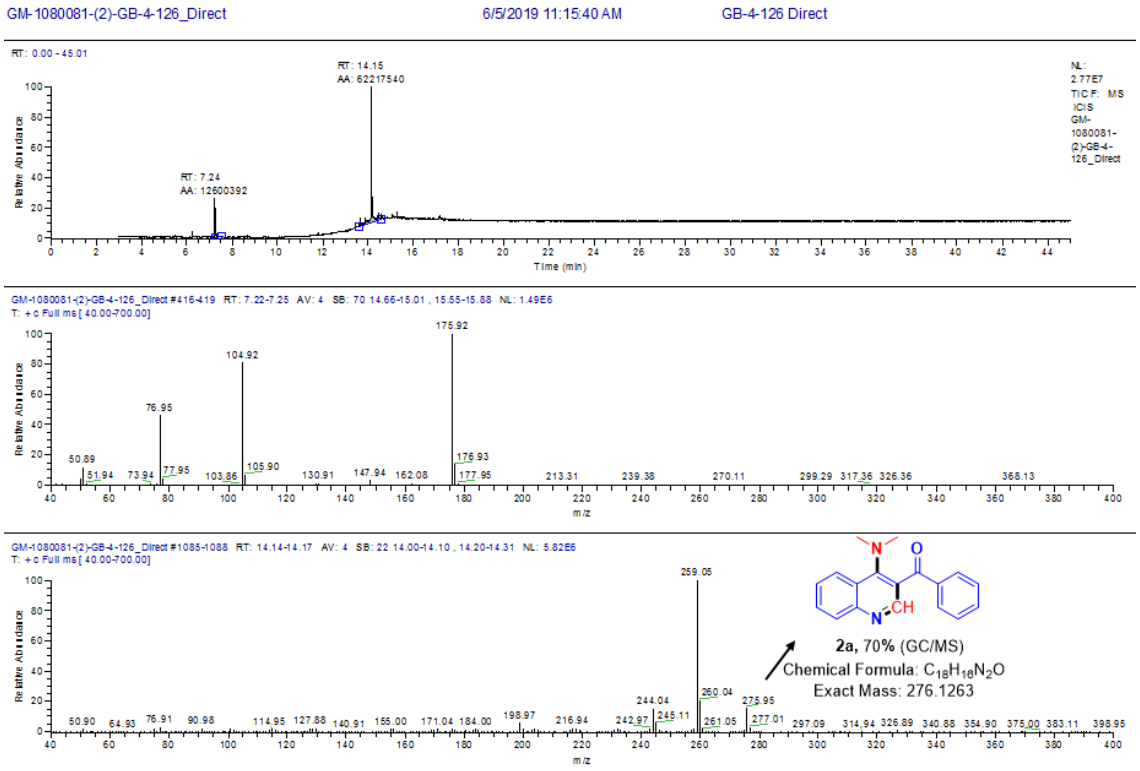
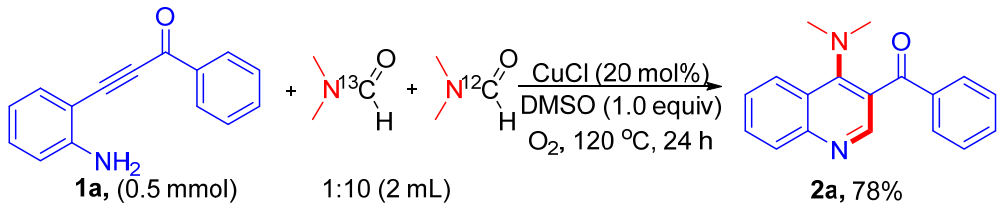


Figure S2. GC/MS spectra of solvent competition experiment

The solvent competition experiment was performed between DMF Vs DEF, with the starting material **1a** (0.2 mmol). The substrate **1a** with 3 mL of DMF:DEF (1:1) taken allowed under optimized conditions of others. After 24 h, the reaction was checked by TLC and confirmed by GC/MS, which resulted in the formation of 2a only in 70%, not obtained other expected product.

6. Labelling Experiments

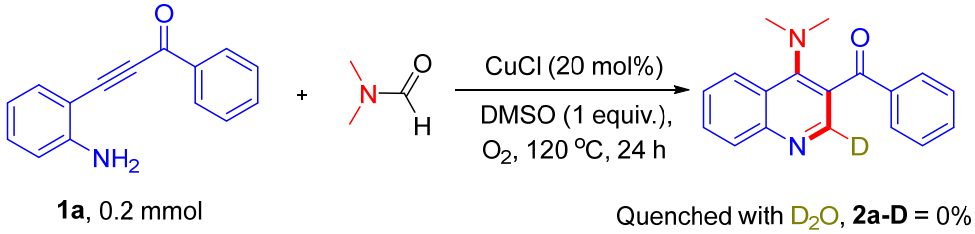
6.1. ^{13}C-labelled DMF experiment



Scheme S8. ^{13}C labelled DMF experiment

In order to find the source of methine at C2 position of quinoline motif **2a**, we performed a ^{13}C-labelling experiment. 0.5 mmol of **1a** the starting material was taken in reaction tube with *N,N*-dimethylformamide (2 mL, ^{13}C:^{12}C 1:10) (based on literature). [5] The CuCl (20 mol%), and dry DMSO (1.0 equiv.) were added to the reaction mixture, and allowed to stir at 120 ℃ under O_2 atmosphere for 24 h. Then the reaction was quenched with 10 mL of water, and 10 mL of ethyl acetate was added, organic layer was separated by extraction. The organic layer washed with ethyl acetate (3X10 mL), and brine wash (2X10 mL), collected organic layer dried over $MgSO_4$. Then filtered through funnel and the solvent removed under reduced pressure to get crude. The crude was purified by column to afford the desired product of **2a** 78% in yield, was confirmed by LC/MS, and ^{13}C-NMR, the data revealed that methine source is not coming from the carbonyl part of DMF. ^{13}C-NMR (100 MHz, $CDCl_3$) δ 196.1, 157.4, 150.3, 149.8, 137.6, 133.5, 130.4, 130.1, 129.5, 128.6, 125.7, 125.5, 124.3, 122.1, 44.9., the data was matched the compound **2a.**

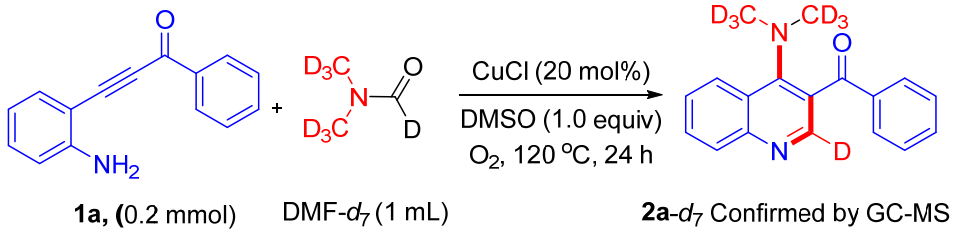
6.2. D_2O labelling experiment



Scheme S9. D_2O labelling experiment

We performed a D_2O experiment, in order to find C2-position proton source. The 0.2 mmol of **1a**, was taken and carry out the reaction under standard conditions, then the reaction was quenched with 30 equiv. of D_2O. The reaction mixture was characterized by GC/MS and ^{1}H-NMR; the obtained data resembled with standard compound of **2a**. From this experiment results, we concluded that C2 position proton is not from water.

6.3. DMF-d_7 labelling experiment



Scheme S10. DMF-d_7 labelling experiment

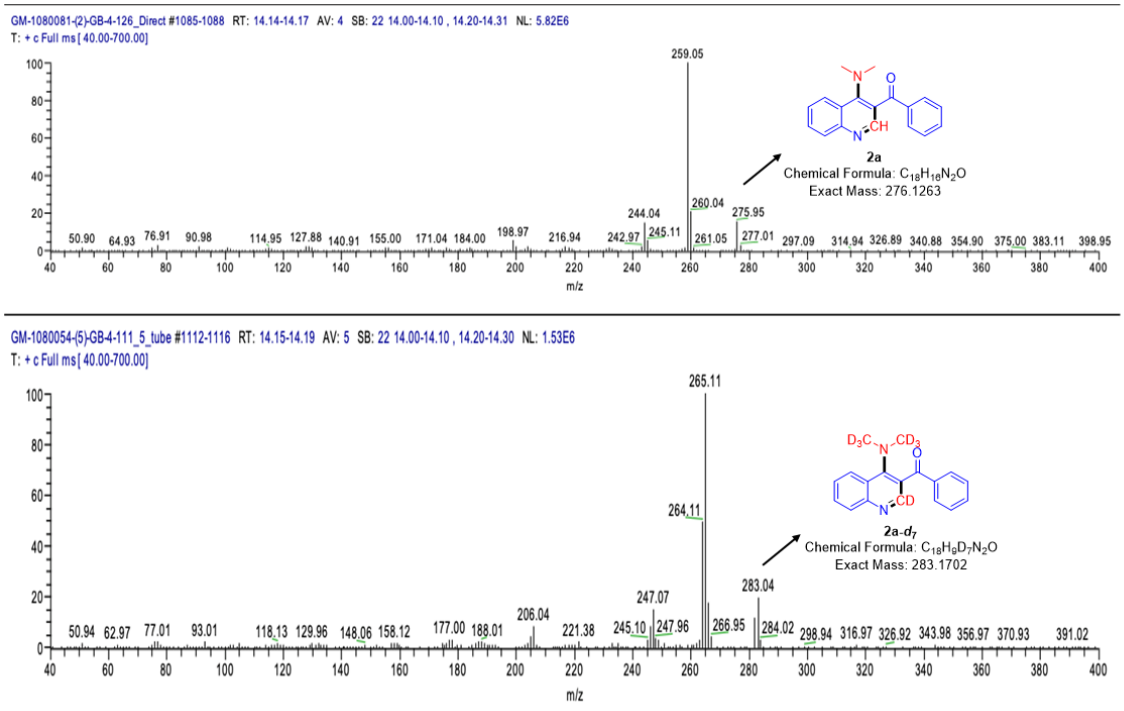
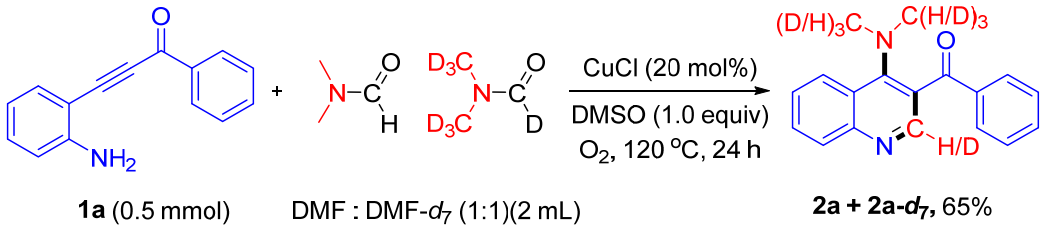


Figure S3. GC/MS spectra of compound 2a and 2a-d_7

We performed an experiment with DMF-d_7 labelling experiment. An oven dried sealed was equipped with stir bar and followed by **1a** (0.2 mmol), CuCl (20 mol %), dry DMSO (1.0 equiv.), and 1 mL of DMF-d_7 were added. The reaction was allowed to stir under standard conditions, then the reaction quenched with water (5 mL), extracted with ethyl acetate (5 mL) the collected organic layer washed with ethyl acetate (2X5mL) and brine (2X5mL). Organic layer dried over $MgSO_4$, and the solvent removed under vacuum to get crude. The crude was characterized by GCMS, which found that m/z 283. The m/z value is matched with expected product of **2a-*d*$_7$** and which revealed that all the C2 position methine source, C4 position dimethyl were come from DMF.

6.4. DMF-d_7 labelling experiment with DMF



1a (0.5 mmol) DMF : DMF-d_7 (1:1)(2 mL) **2a + 2a-*d*$_7$,** 65%

Scheme S11. DMF-d_7 labelling experiment with DMF

0.5 mmol of **1a** the starting material was taken in reaction tube with *N,N*-dimethylformamide (2 mL, DMF:DMF-d_7 (1:1)). The catalyst CuCl (20 mol%), and dry DMSO (1.0 equiv.) were added to the reaction mixture, and allowed to stir at 120 °C under O_2 atmosphere for 24 h. Then the reaction was quenched with 10 mL of water, and 10 mL of ethyl acetate was added, organic layer was separated by extraction. The organic layer washed with ethyl acetate (3X10 mL), and brine wash (2X10 mL), collected organic layer dried over $MgSO_4$. Then filtered through funnel and the solvent removed under reduced pressure to get crude. The crude was purified by column to afford the desired product ((4-(bis(methyl-d3)amino)quinolin-3-yl-2-d)(phenyl)methanone)in brown liquid, **2a**+**2a-*d*$_7$** together in 65% (90 mg) yield, NMR. The spectra of ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 0.47 H), 8.14 - 8.07 (m, 2H),

7.87 - 7.84 (m, 2H), 7.80 - 7.47 (m, 5H), 2.96 (s, 2.5 H). This data found that 60% incorporated, which revealed that DMF can act dual synthon of methine and dimethyl.

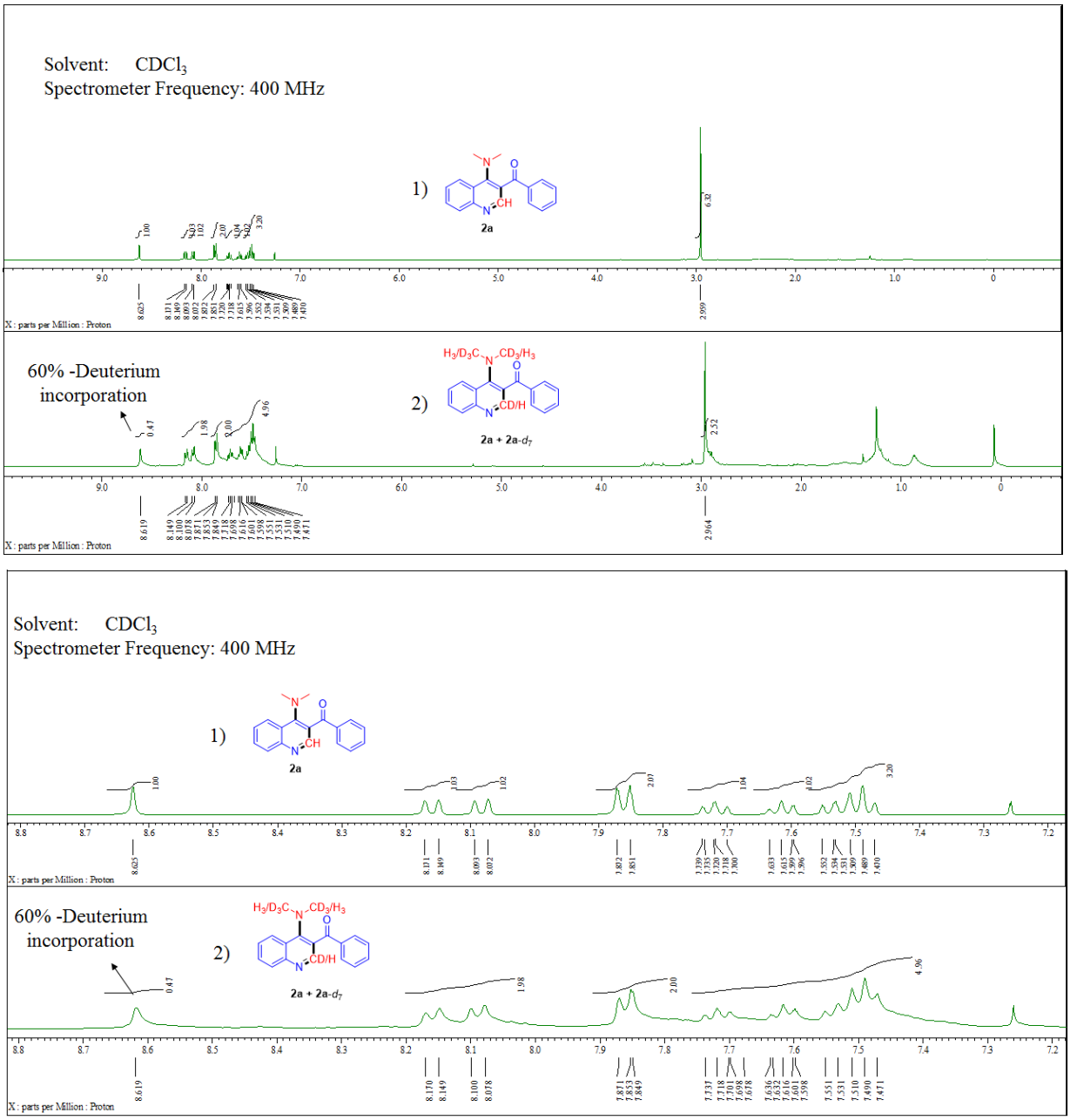


Figure S4. ^{1}H-NMR spectra of 1) 2a and 2) 2a + 2a-d_7

7. The CO detection test

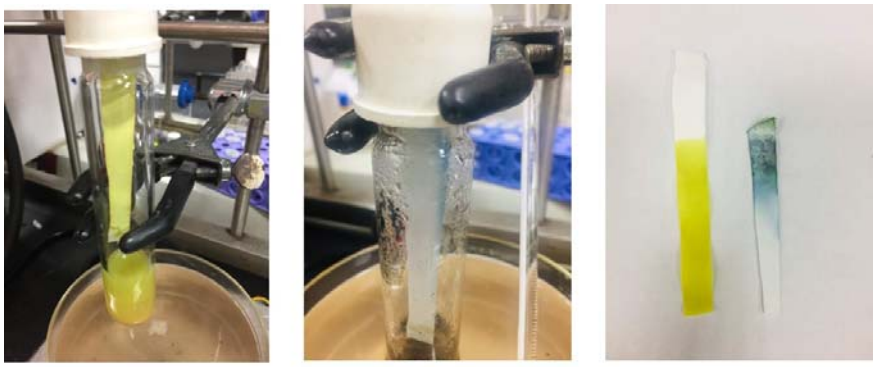


Figure S5a. The CO detection test using PMA-$PdCl_2$ strip

The detection of CO was tested using PMA-$PdCl_2$ strip.[13] The strip was prepared and tipped in the stain (1:2 ratio of PMA: $PdCl_2$), and dried for 1 h at room temperature. Then the strip was inserted in the flask and the reaction was performed under the standard condition. After 24 hr reaction, the strip colour changed from yellow to blue, which was confirmed the evolution of CO gas from DMF in the reaction.

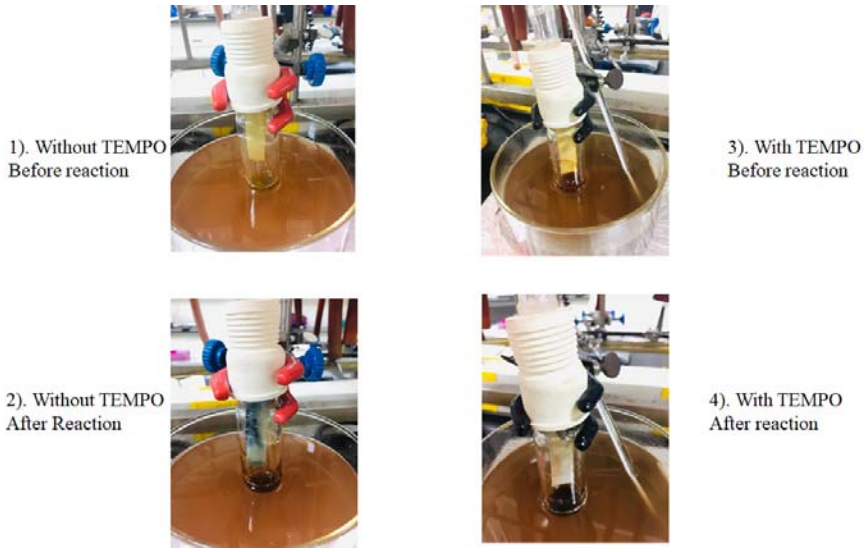
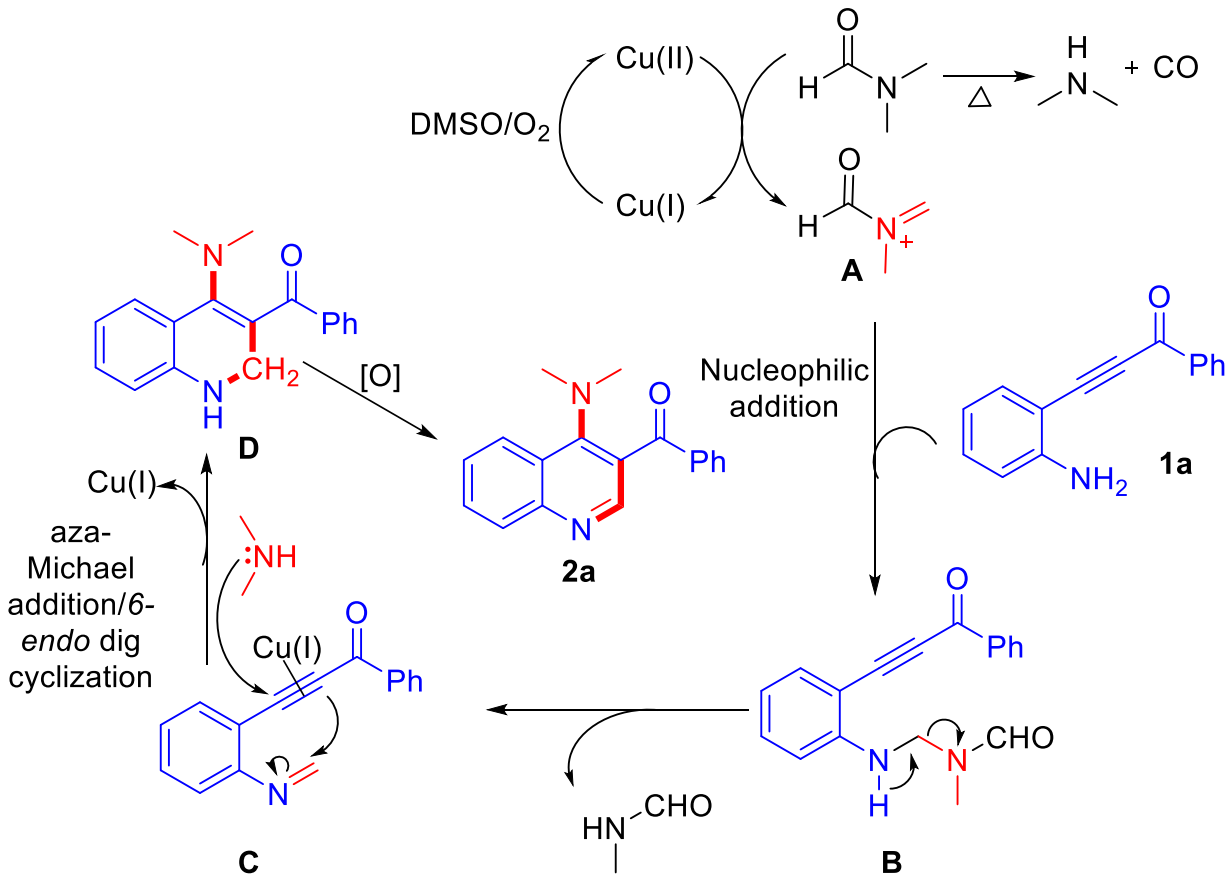


Figure S5b. The CO detection test using PMA-$PdCl_2$ strip with and without TEMPO

In continuation the CO detection test, we have performed the reaction with and without 0.5 equiv. of TEMPO to the reaction. (Figure S5b) The PMA-$PdCl_2$ strip was inserted in the reaction tube, allowed

to stir under standard condition. After 24 h, we found the colour of the strip did not changed which suggested that the reaction inhibited by TEMPO.

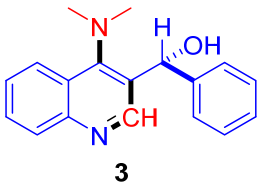
8. An alternative way of plausible mechanism



Scheme S12. Plausible mechanism

The combination of DMSO and O_2, the Cu (I) get oxidized into Cu(II), which was initiate the DMF to get oxidized the iminium ion A, and it turn into Cu(II) to Cu (I). [6] [7] The nucleophilic addition between **1a** and iminium ion **A**, which leads to produce the intermediate **B**. [8] Upon the imine hydrolysis process, which helps to the removal of *N*-methyl formamide from intermediate **B**, which leads to formation of intermediate **C**. [9] Subsequently, aza-Michael addition of dimethylamine to the α,β-unsaturated bond assisted by Cu(I), and leads to generation of **D**, through 6-*endo*-dig cyclization. [10] [11] [12] Finally, it gets oxidized and generates the desired product of **2a**. [8]

9. X-Ray crystal data of 3



3

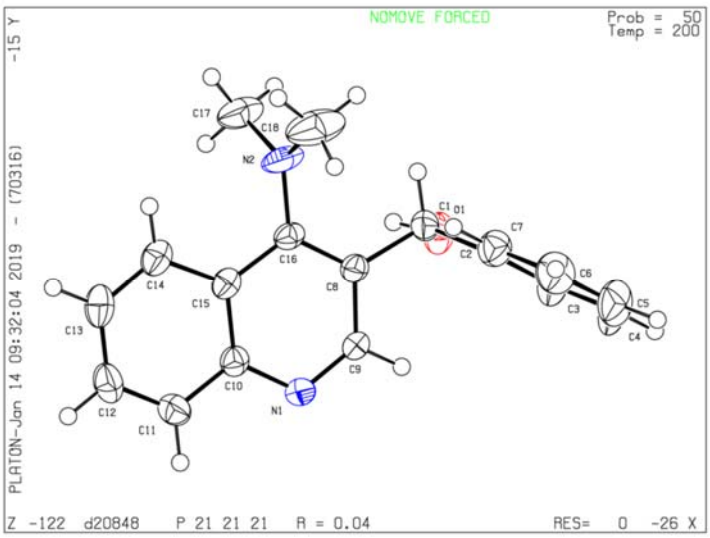


Figure S6. The thermal ellipsoid was drawn at 50% probability level

Table S2. Crystal data and structure refinement for **3**.

Identification code	**3**	
Empirical formula	C18 H18 N2 O	
Formula weight	278.34	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 7.5891(3) Å	a= 90°.
	b = 10.7774(5) Å	b= 90°.
	c = 17.9836(6) Å	g = 90°.

Volume	1470.89(10) $Å^3$
Z	4
Density (calculated)	1.257 Mg/m^3
Absorption coefficient	0.079 mm^{-1}
F(000)	592
Crystal size	0.29 x 0.20 x 0.11 mm^3
Theta range for data collection	2.26 to 25.04°.
Index ranges	-9<=h<=8, -12<=k<=12, -21<=l<=21
Reflections collected	9256
Independent reflections	2560 [R(int) = 0.0357]
Completeness to theta = 25.04°	98.7 %
Absorption correction	multi-scan
Max. and min. transmission	0.9914 and 0.9775
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2560 / 0 / 192
Goodness-of-fit on F^2	1.068
Final R indices [I>2sigma(I)]	R1 = 0.0420, wR2 = 0.0986
R indices (all data)	R1 = 0.0510, wR2 = 0.1048
Absolute structure parameter	0(2)
Largest diff. peak and hole	0.149 and -0.168 $e.Å^{-3}$

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) d20848

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: d20848

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Bond precision:  C-C = 0.0032 A          Wavelength=0.71073

Cell:            a=7.5891(3)     b=10.7774(5)     c=17.9836(6)
                 alpha=90        beta=90          gamma=90
Temperature:     200 K
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	Calculated	Reported
Volume	1470.89(10)	1470.89(10)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	?
Moiety formula	C18 H18 N2 O	C18 H18 N2 O
Sum formula	C18 H18 N2 O	C18 H18 N2 O
Mr	278.34	278.34
Dx,g cm-3	1.257	1.257
Z	4	4
Mu (mm-1)	0.079	0.079
F000	592.0	592.0
F000'	592.22	
h,k,lmax	9,12,21	9,12,21
Nref	2592[1513]	2560
Tmin,Tmax	0.981,0.991	0.978,0.991
Tmin'	0.977	

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Correction method= # Reported T Limits: Tmin=0.978 Tmax=0.991
AbsCorr = MULTI-SCAN

Data completeness= 1.69/0.99       Theta(max)= 25.040

R(reflections)= 0.0420( 2268)      wR2(reflections)= 0.1048( 2560)

S = 1.068                  Npar= 192
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The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

10. References

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11· ^{1}H, and ^{13}C Spectra

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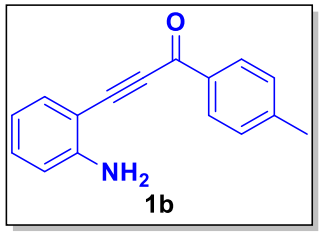
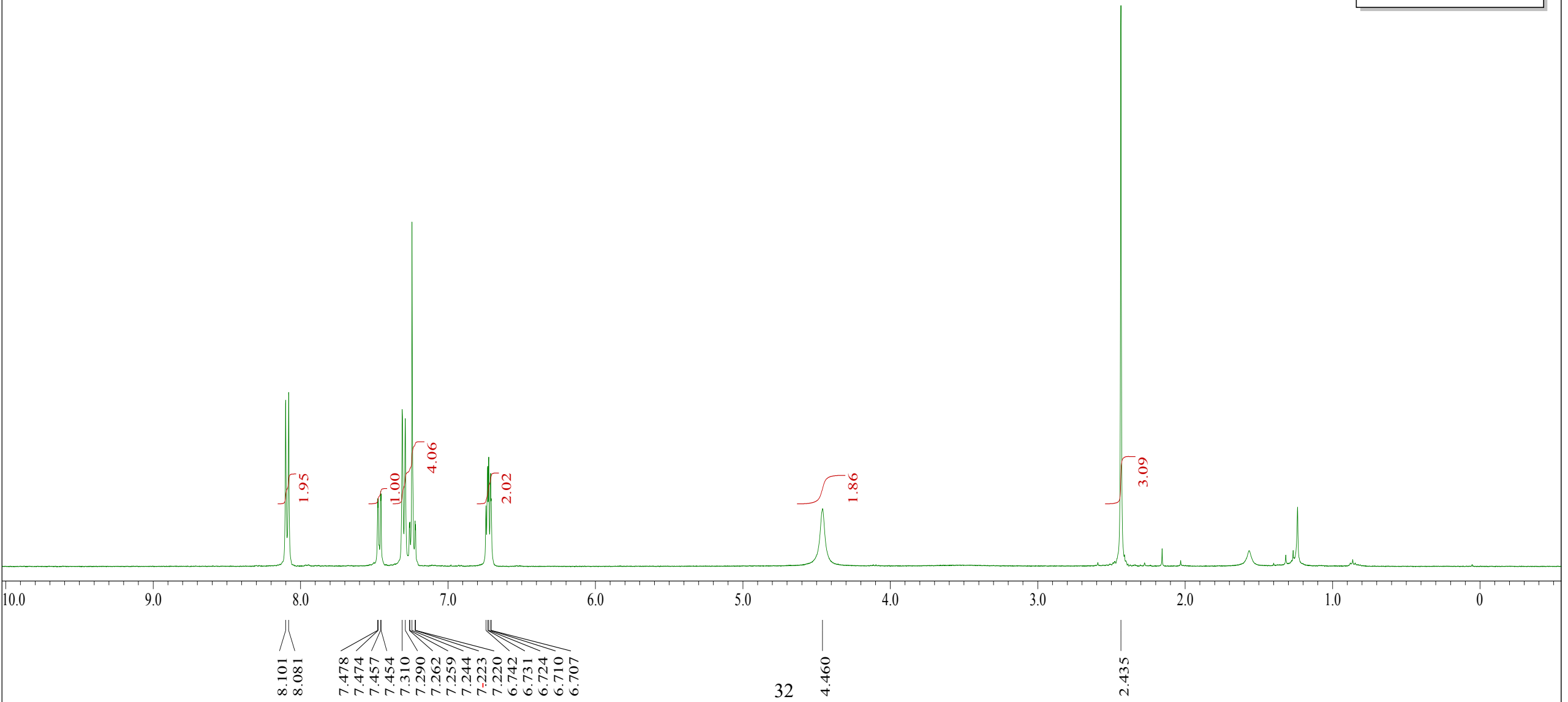
Spectrometer Frequency: 400 MHz

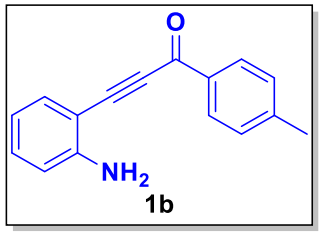


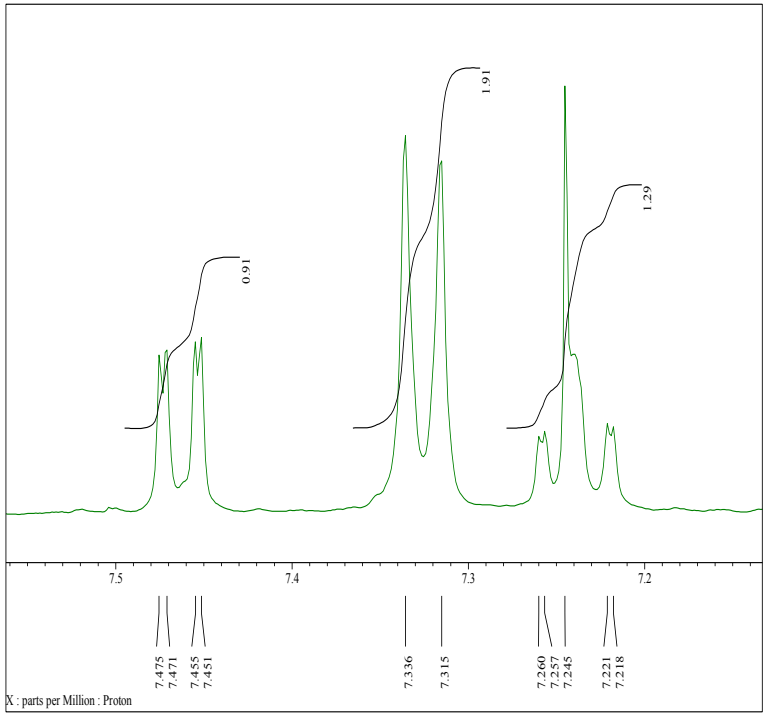


X : parts per Million : Proton

Solvent: $CDCl_3$

Spectrometer Frequency: 100 MHz





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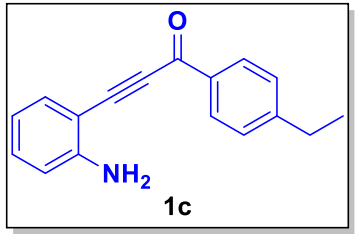

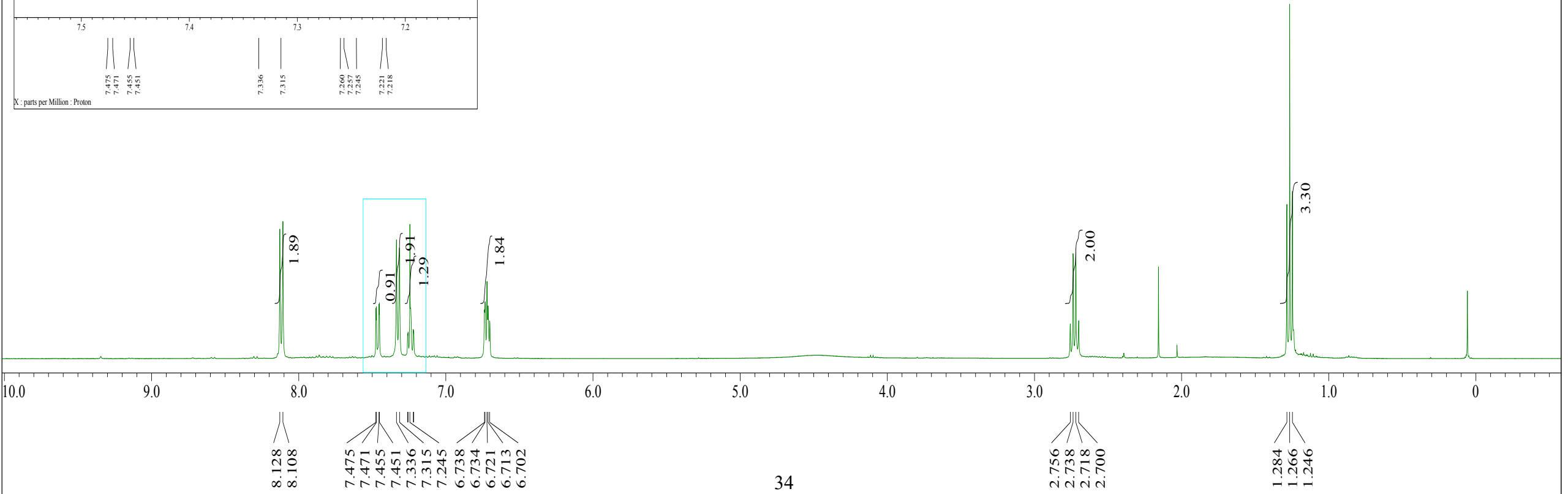

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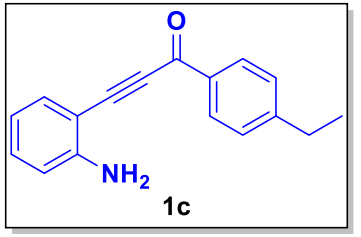
Solvent: $CDCl_3$

Spectrometer Frequency: 100 MHz



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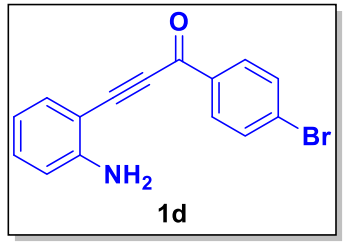
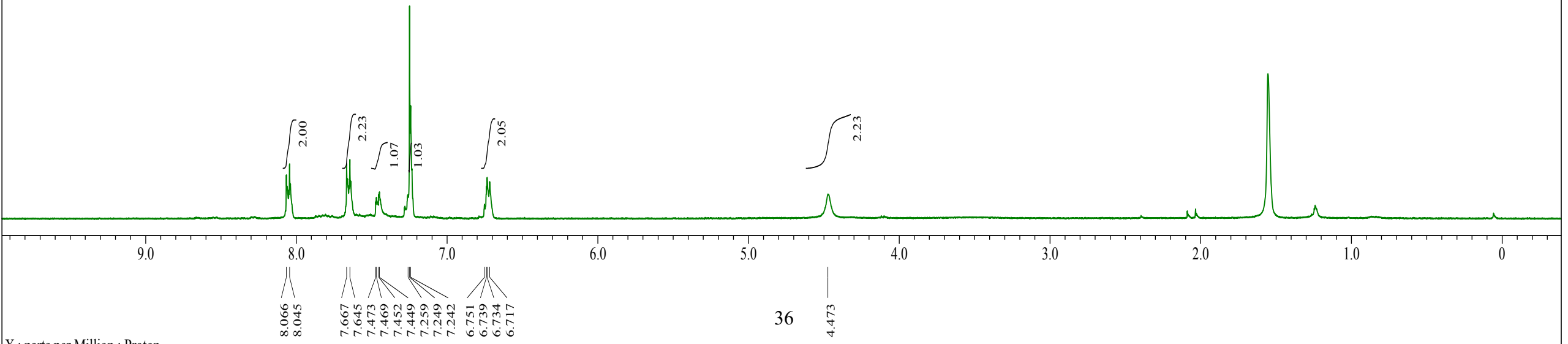
Solvent: $CDCl_3$

Spectrometer Frequency: 400 MHz

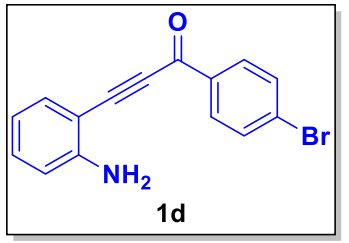


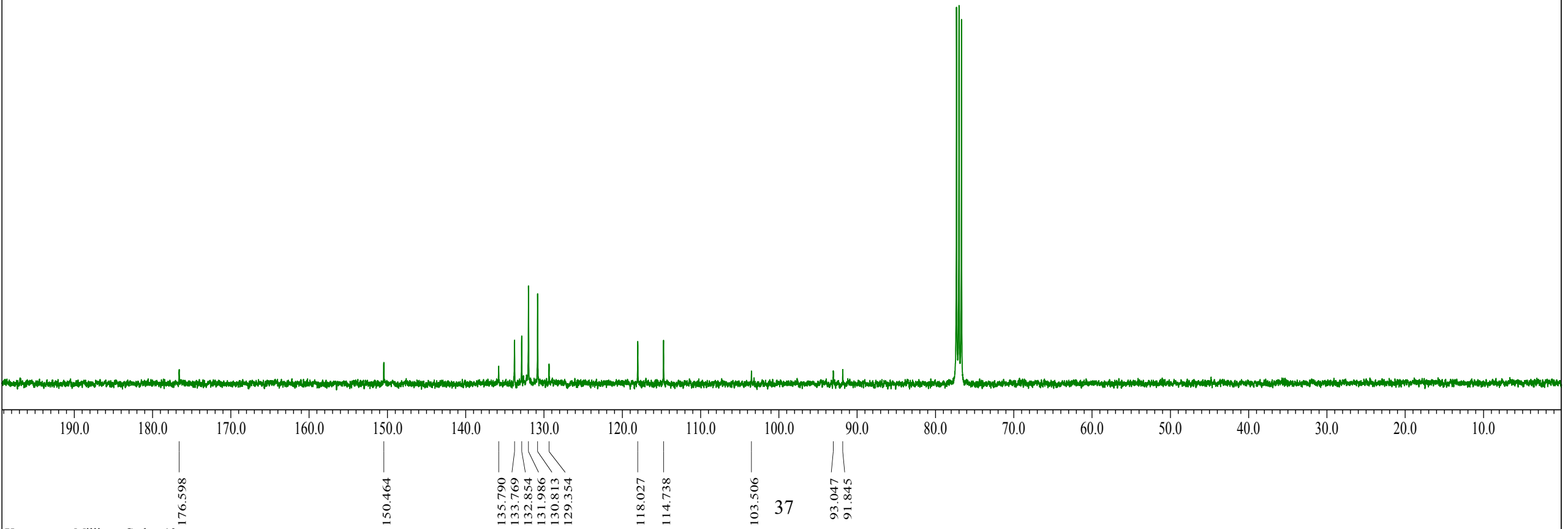


X : parts per Million : Proton

Solvent: $CDCl_3$

Spectrometer Frequency: 100 MHz





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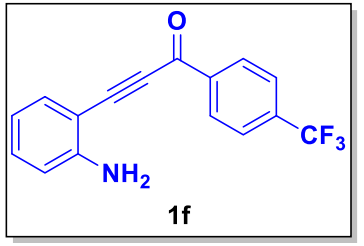
Spectrometer Frequency: 400 MHz



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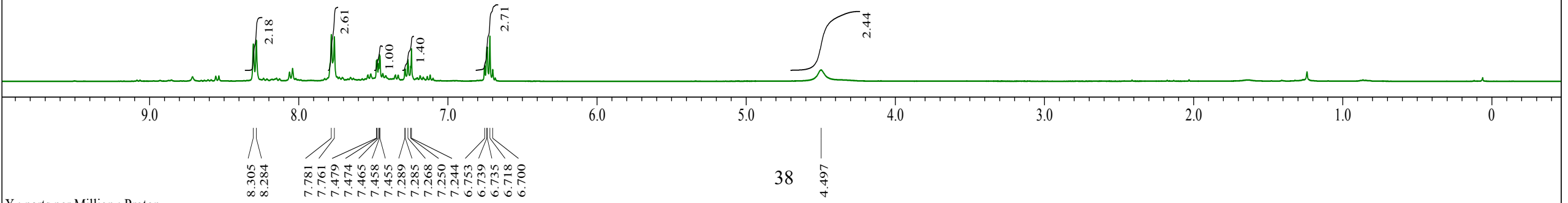
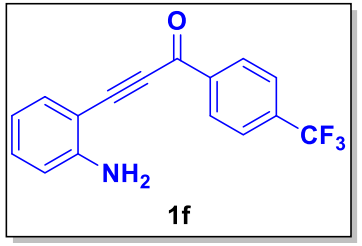


X : parts per Million : Proton

Solvent: $CDCl_3$

Spectrometer Frequency: 100 MHz



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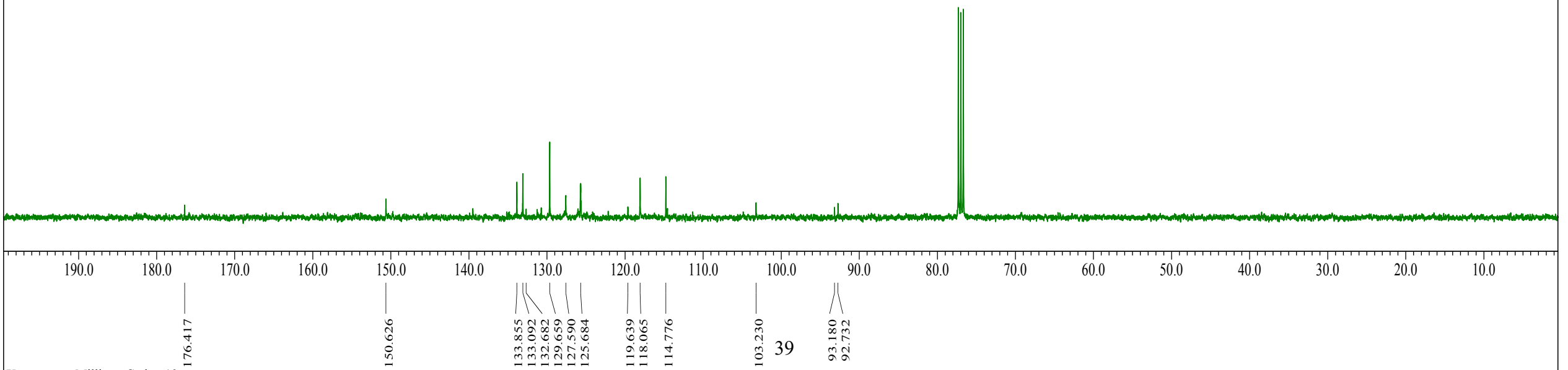

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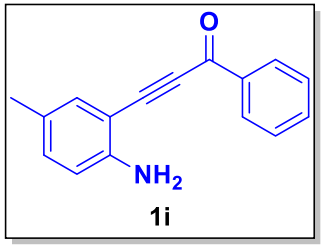
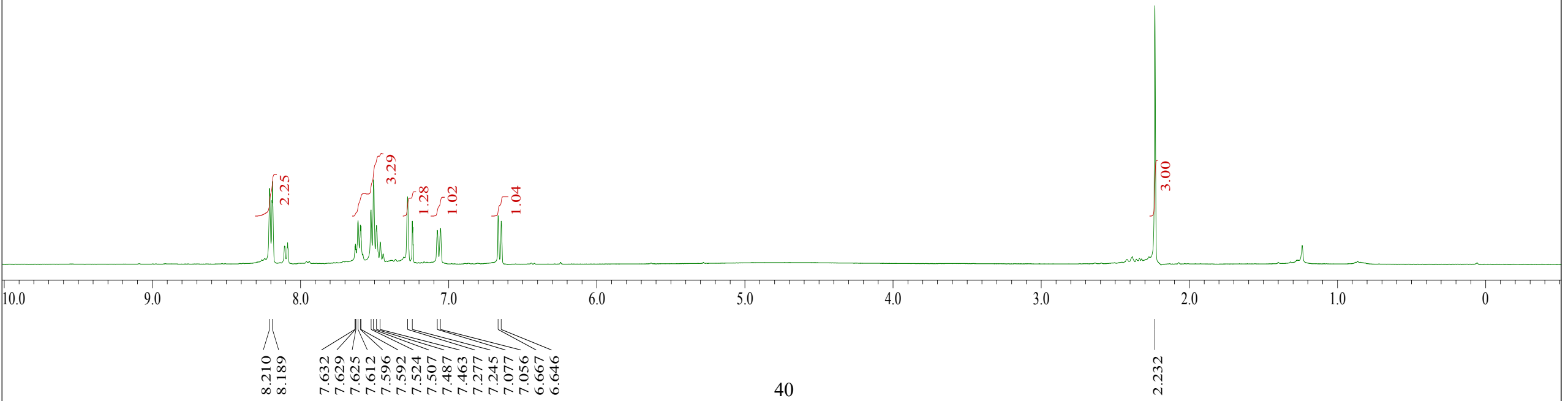
Spectrometer Frequency: 400 MHz





X : parts per Million : Proton

Solvent: $CDCl_3$

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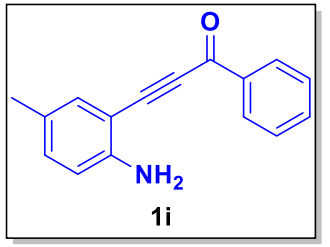

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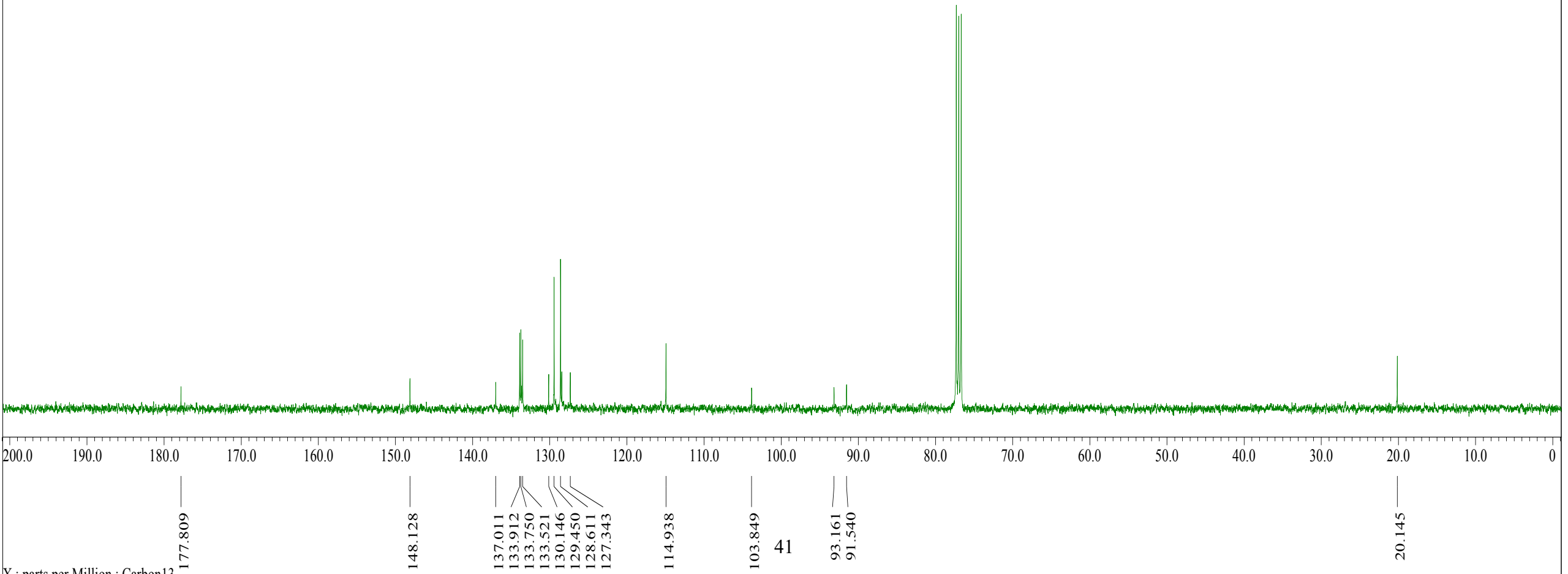

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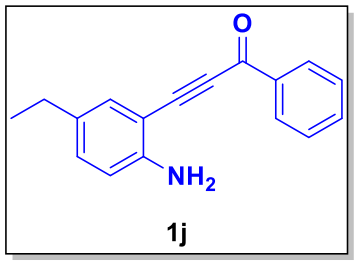

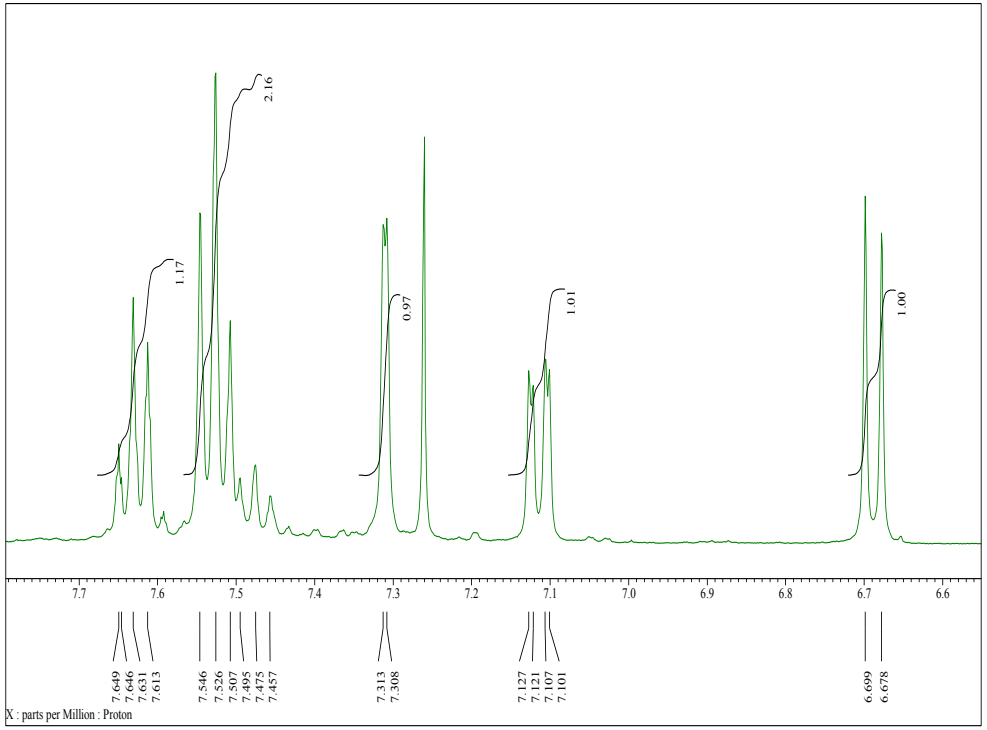

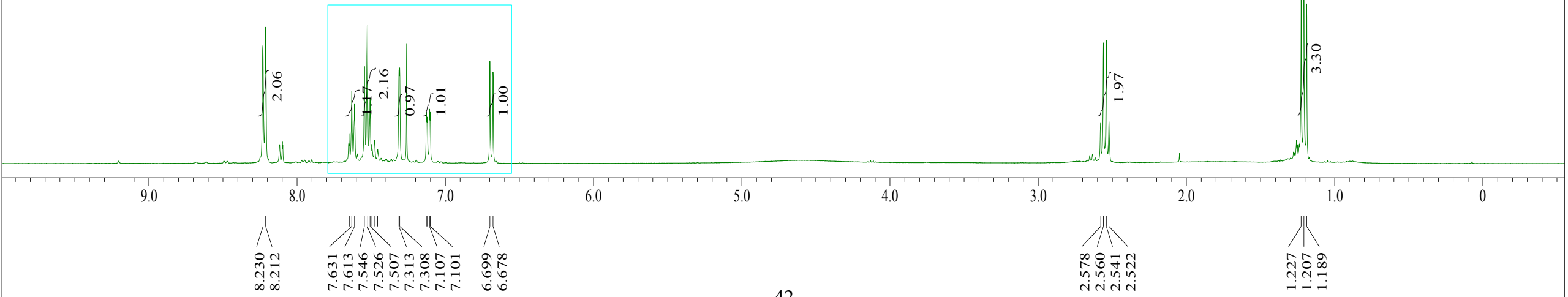

X : parts per Million : Proton

Solvent: $CDCl_3$

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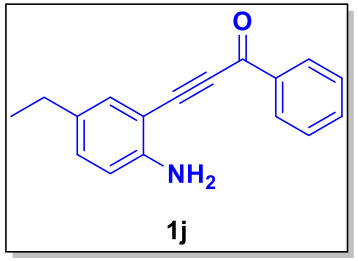

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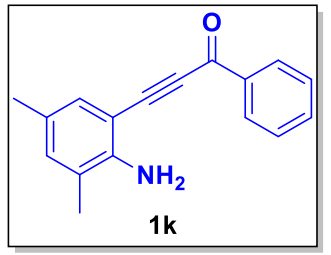
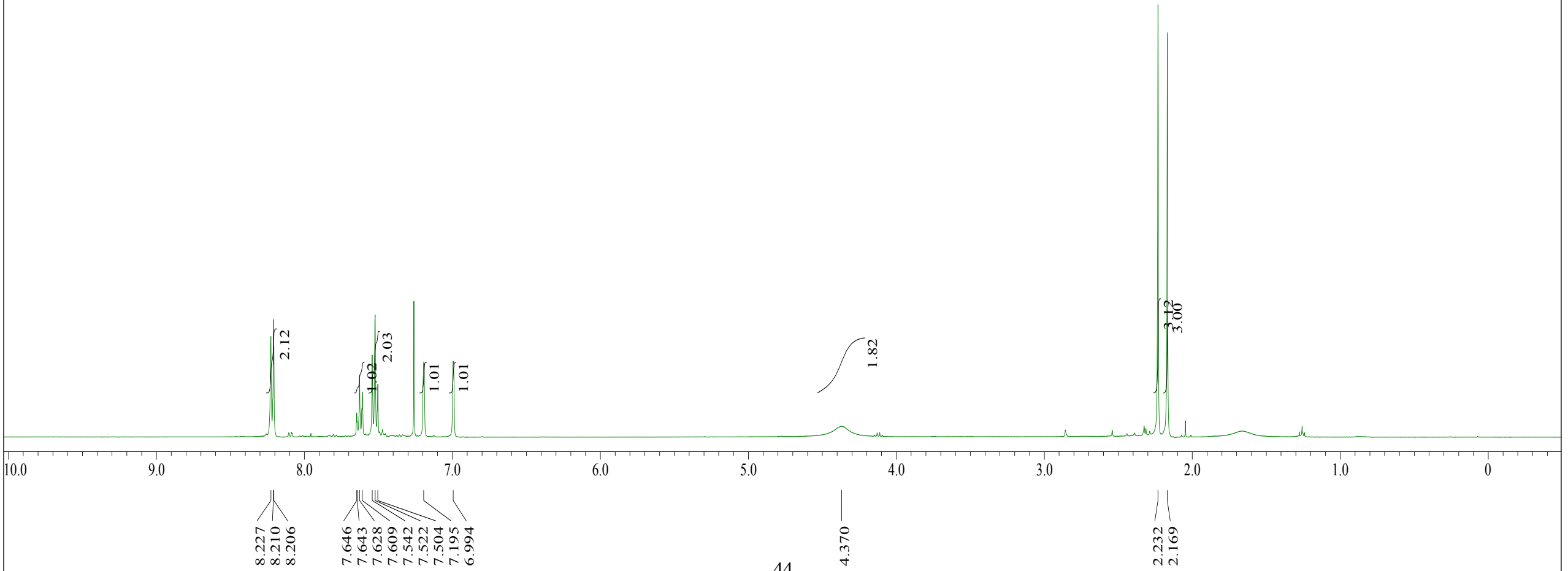
Solvent: $CDCl_3$

Spectrometer Frequency: 400 MHz





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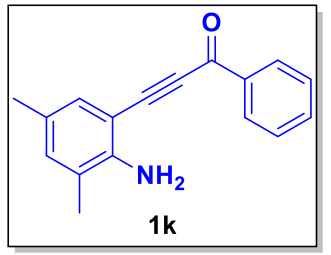

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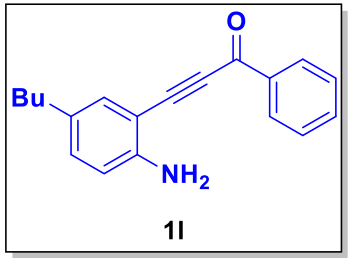

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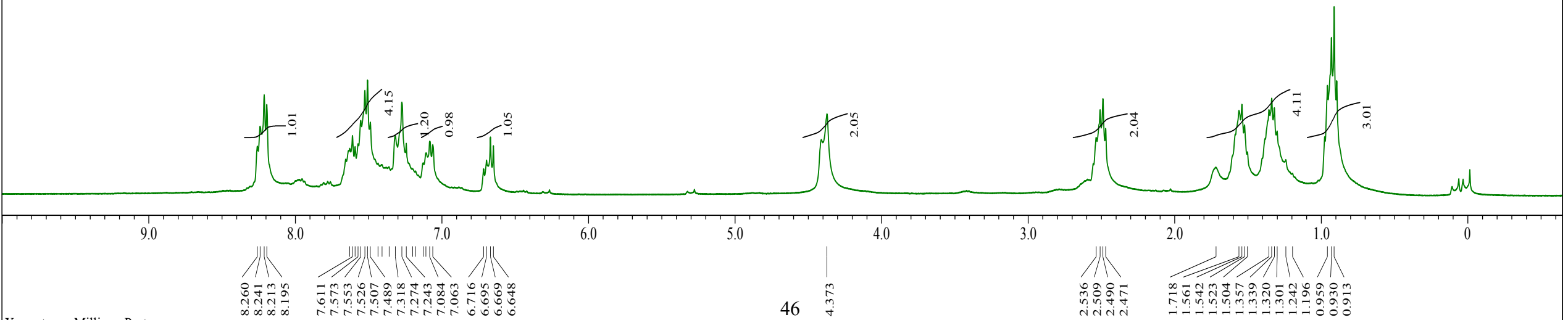

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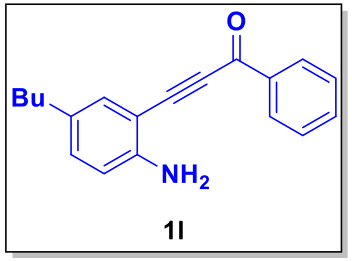

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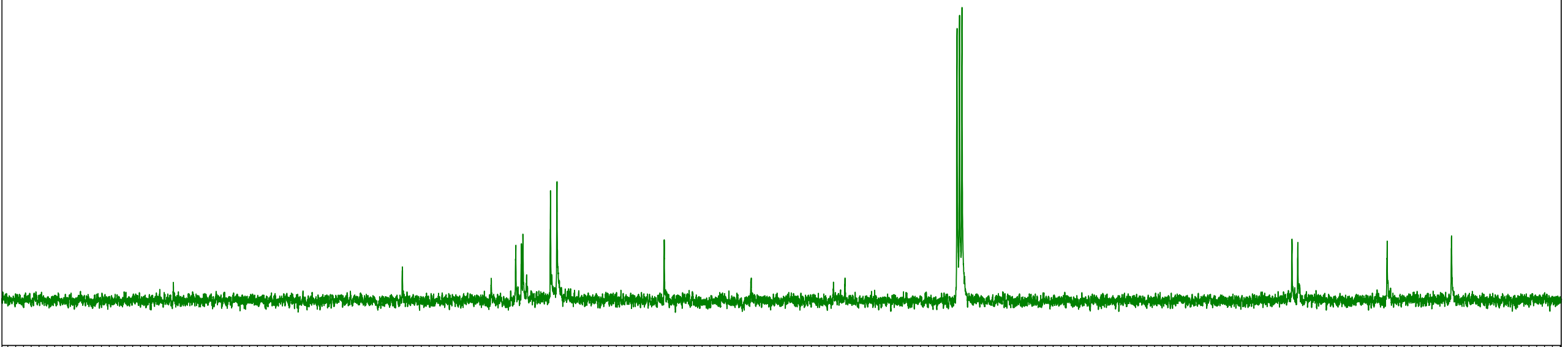

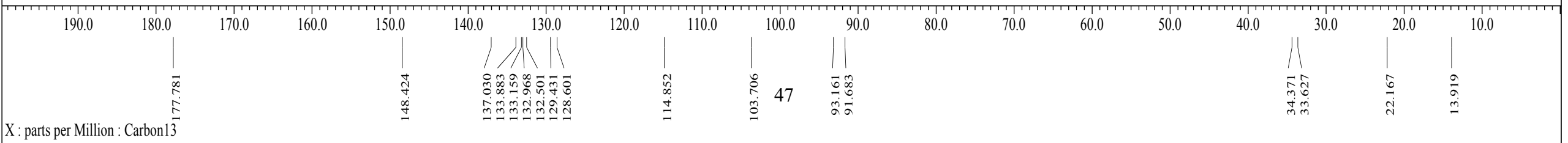

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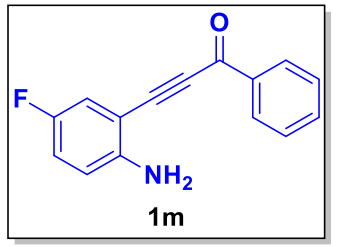

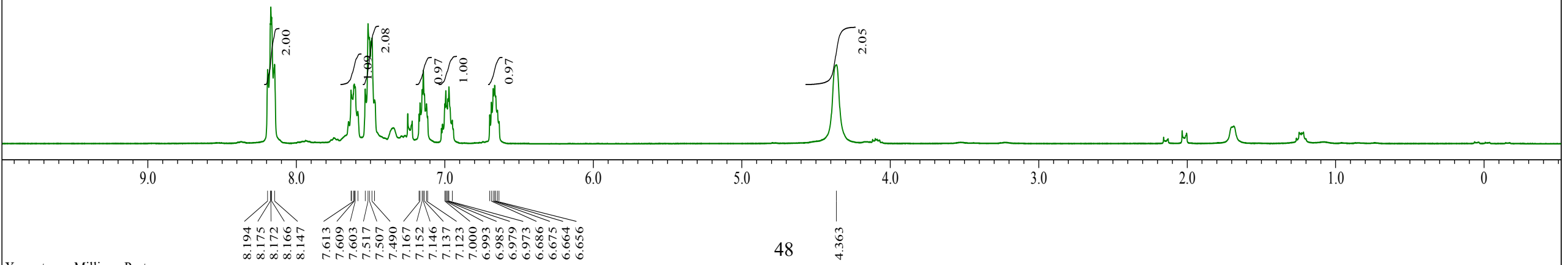

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Solvent: $CDCl_3$

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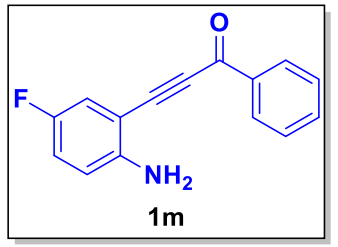

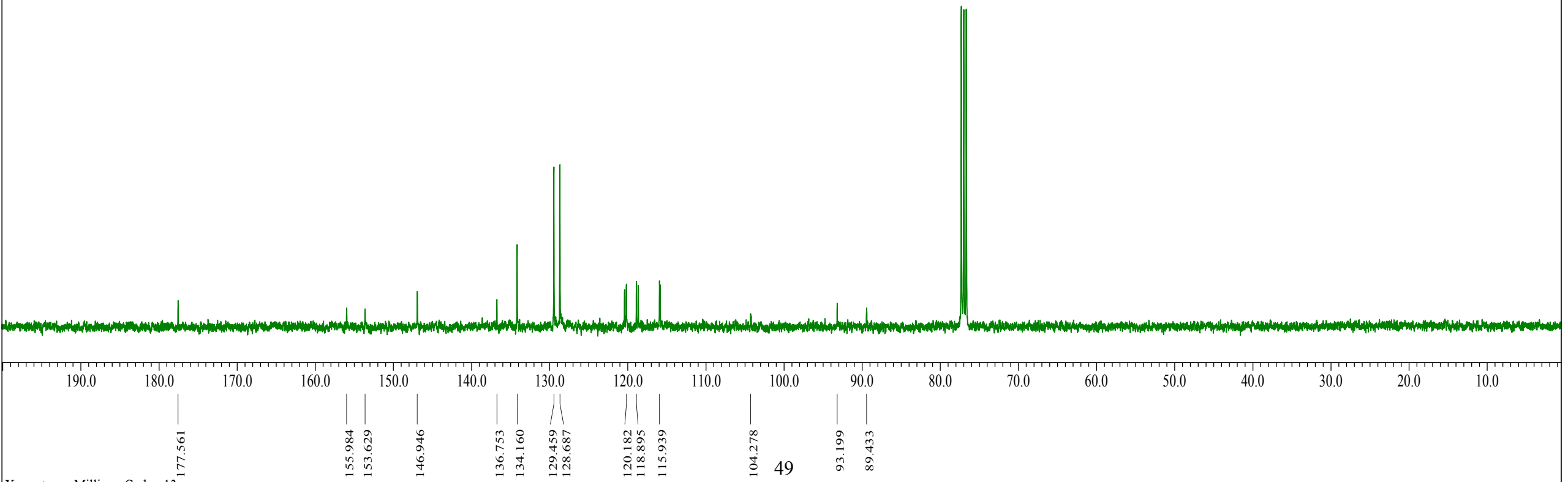

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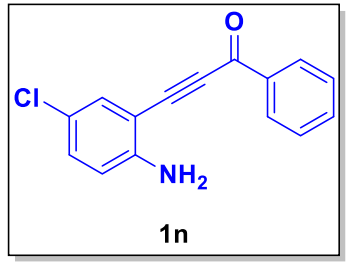

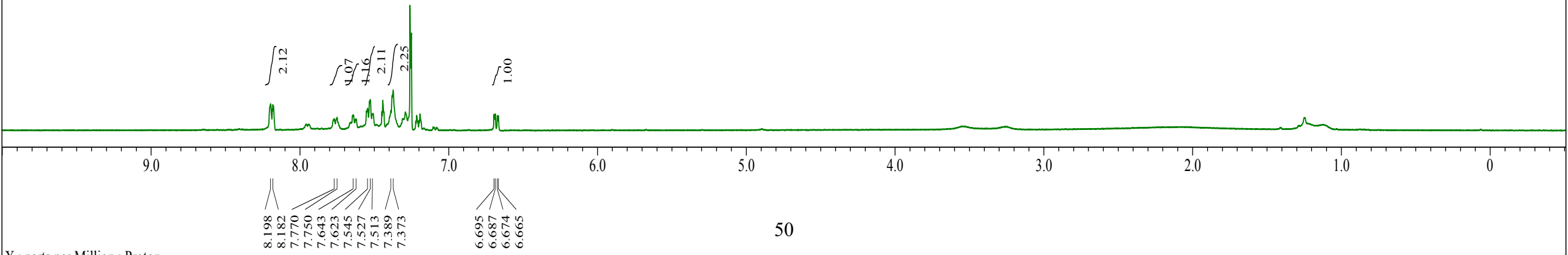

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Solvent: $CDCl_3$

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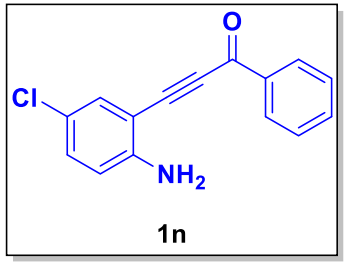

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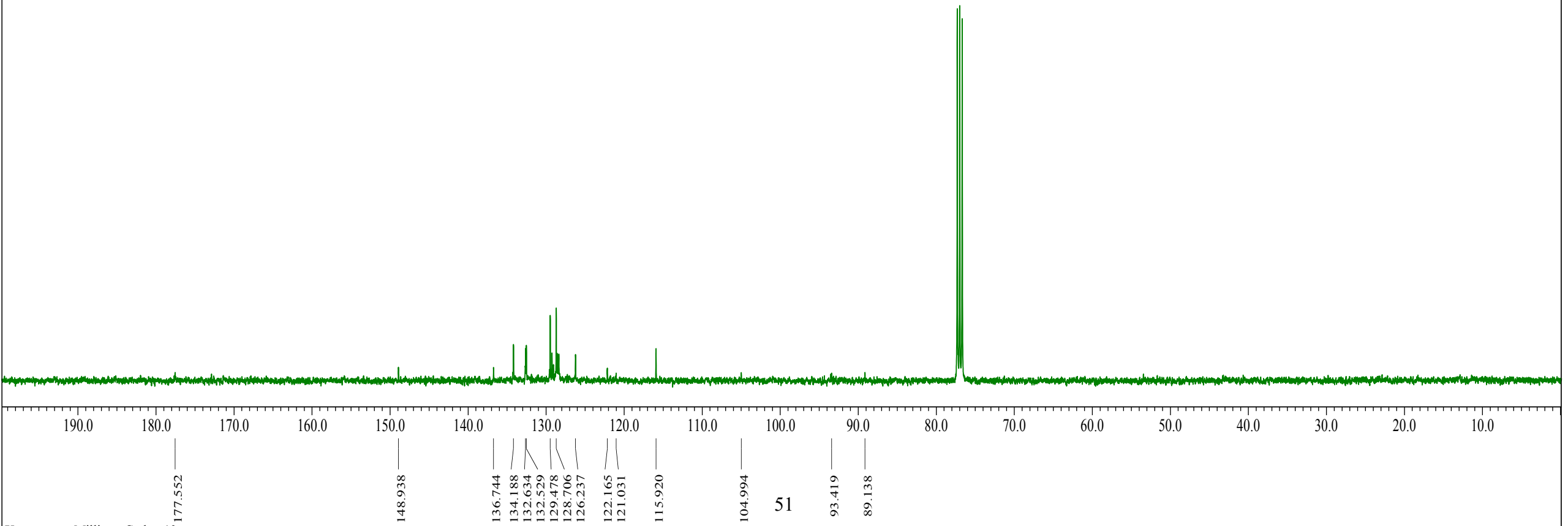

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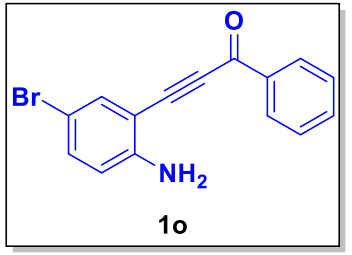

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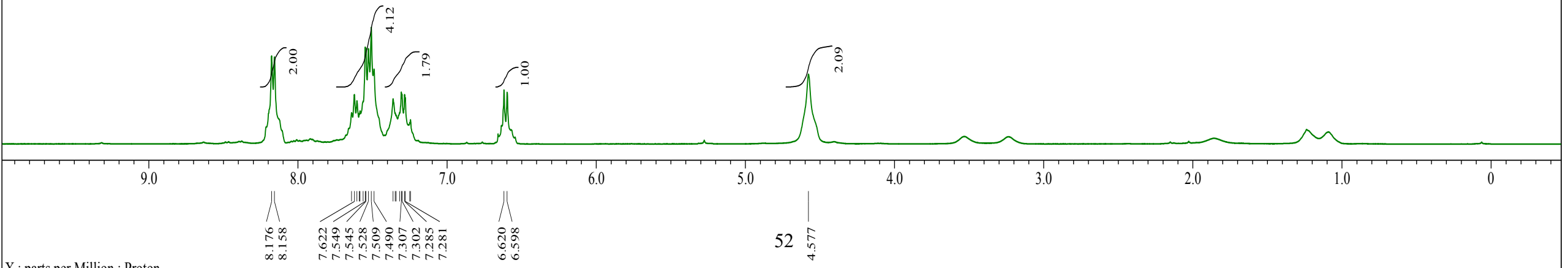

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Solvent: $CDCl_3$

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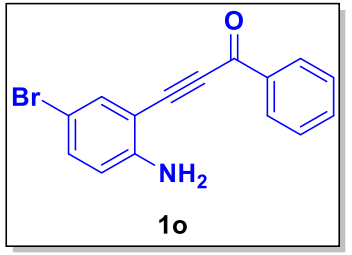

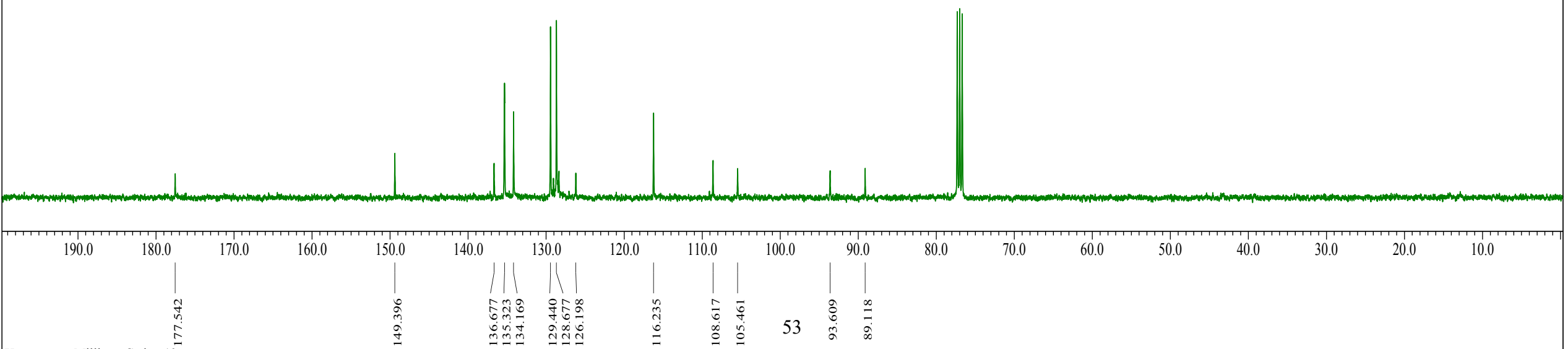

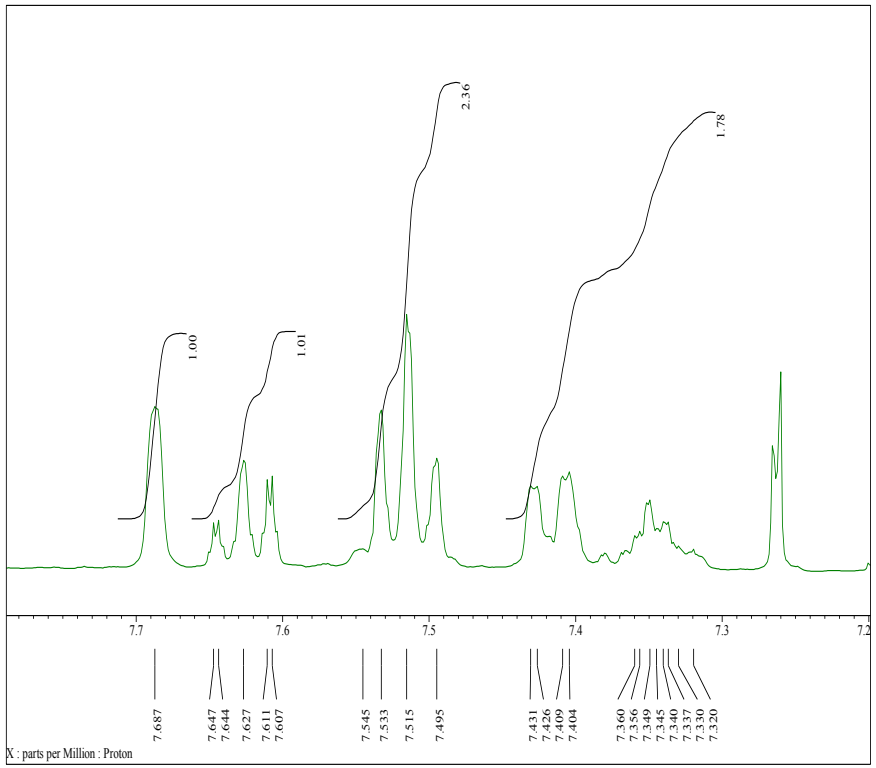

Solvent: $CDCl_3$

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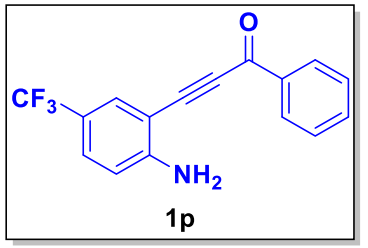
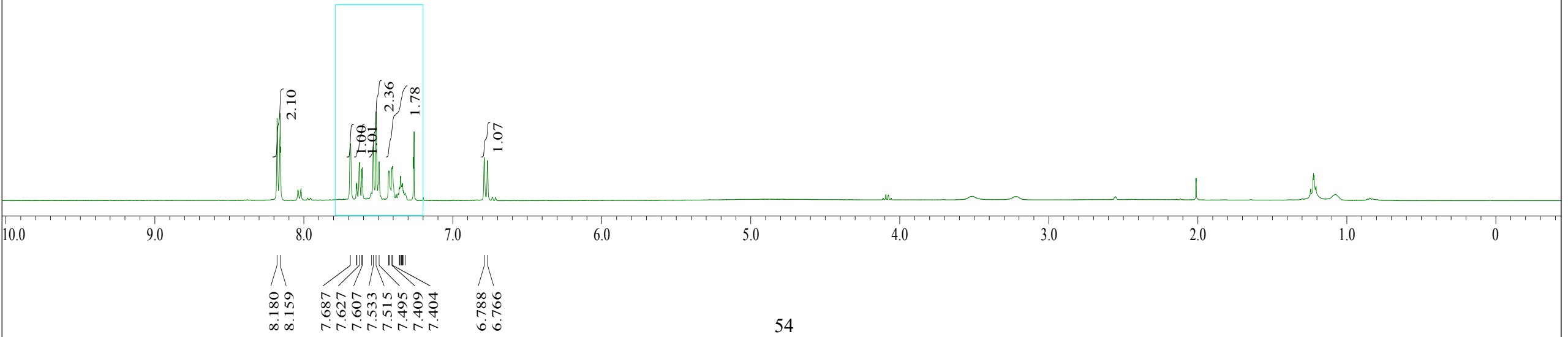
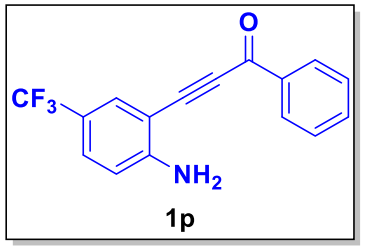




X : parts per Million : Proton

Solvent: $CDCl_3$ + 4 drops of DMSO-d_6
Spectrometer Frequency: 100 MHz



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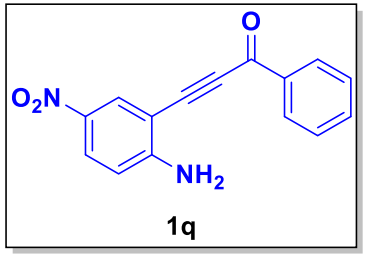
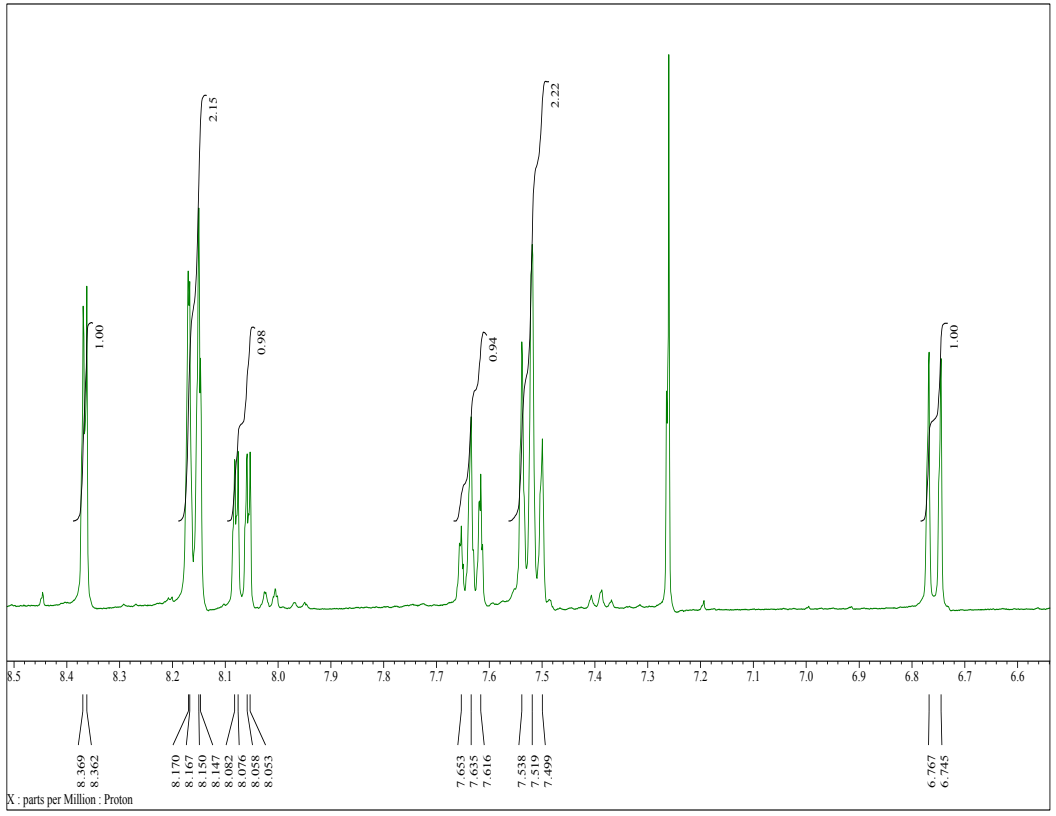
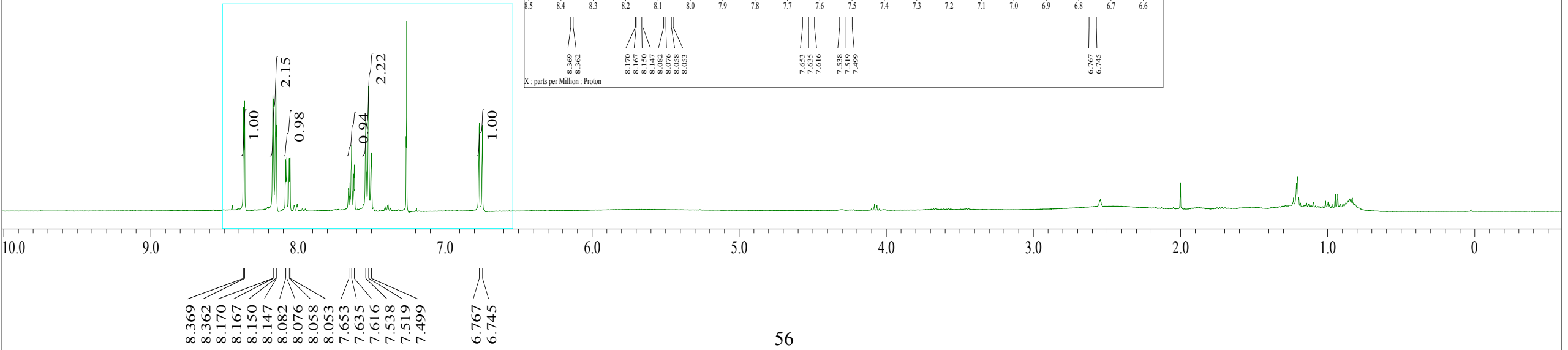
Solvent: $CDCl_3$

Spectrometer Frequency: 400 MHz

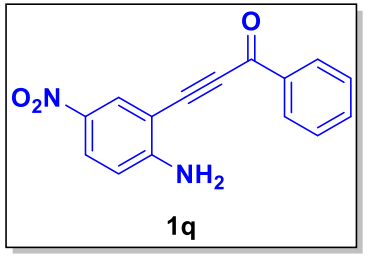






X : parts per Million : Proton

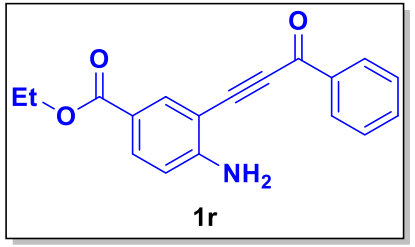
Solvent: $CDCl_3$ + 4 drops of DMSO-d_6
Spectrometer Frequency: 100 MHz



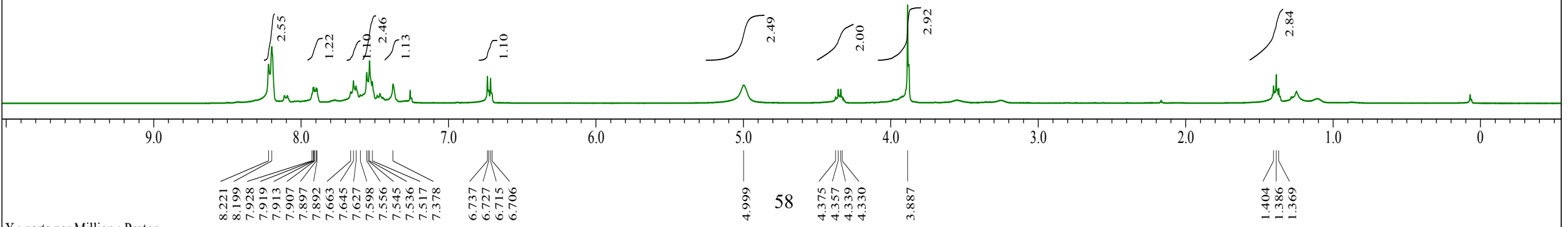
1q

Solvent: $CDCl_3$

Spectrometer Frequency: 400 MHz



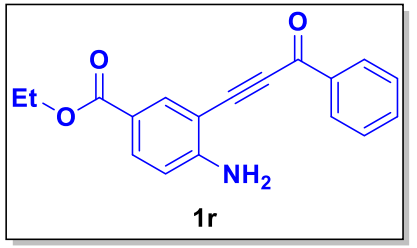
1r



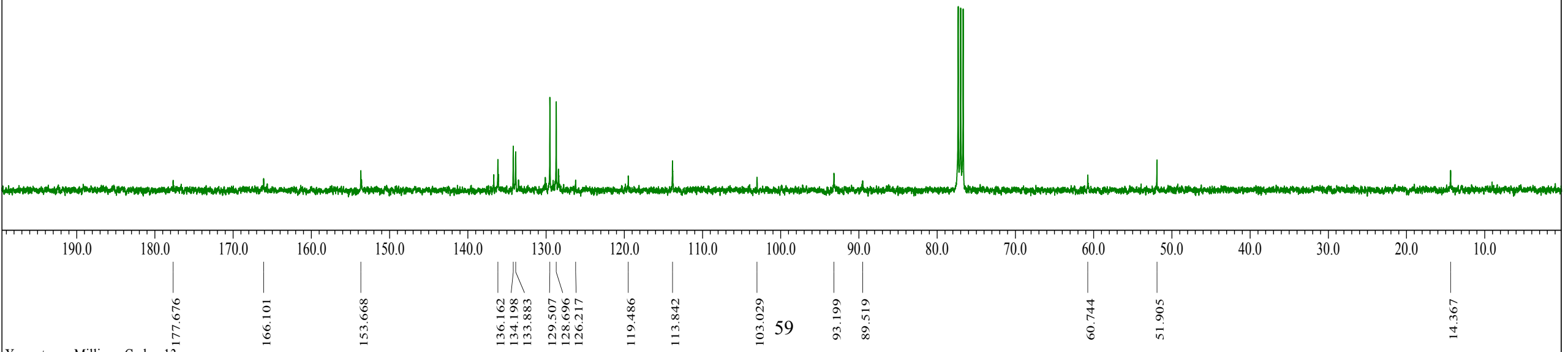
X : parts per Million : Proton

Solvent: $CDCl_3$

Spectrometer Frequency: 100 MHz

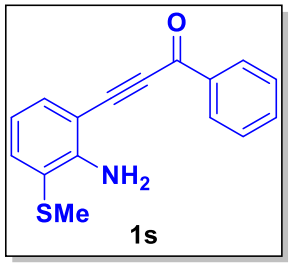


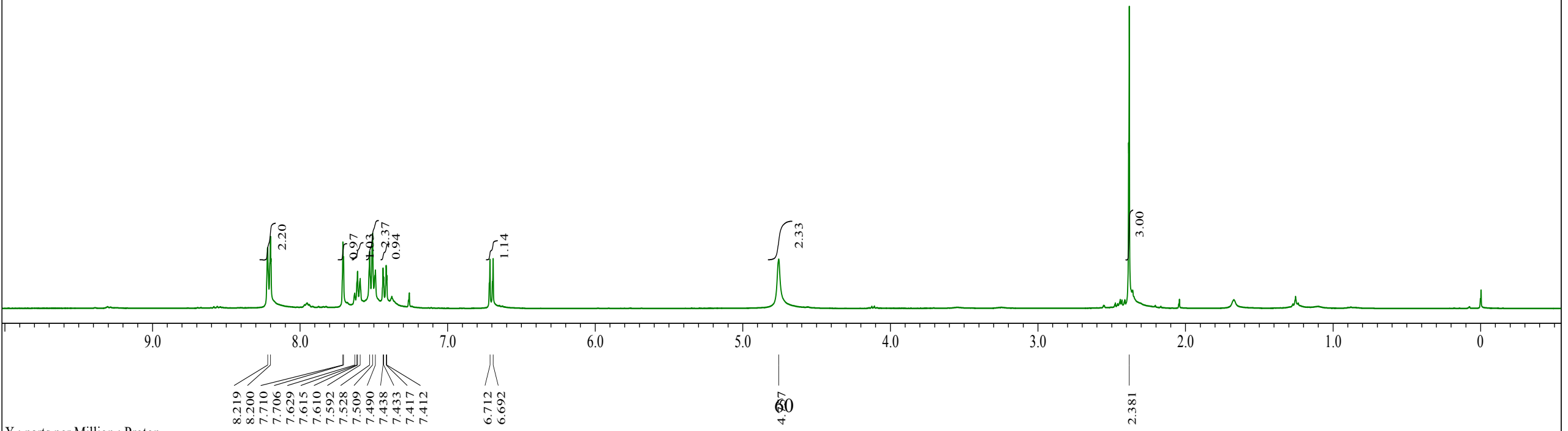
1r



Solvent: $CDCl_3$

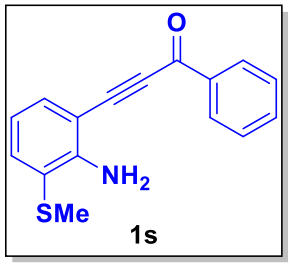
Spectrometer Frequency: 400 MHz

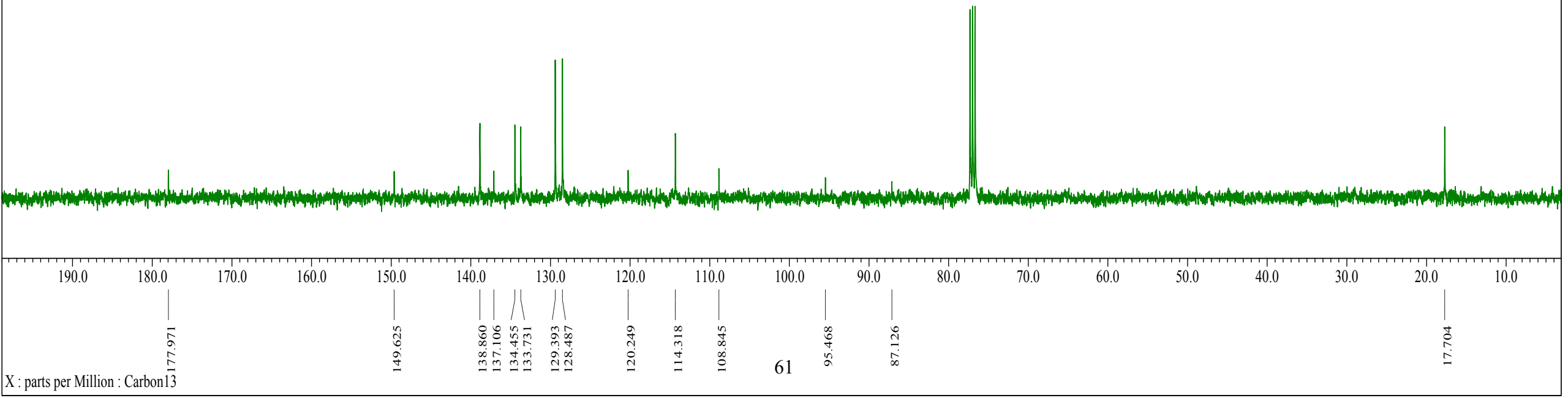




Solvent: $CDCl_3$

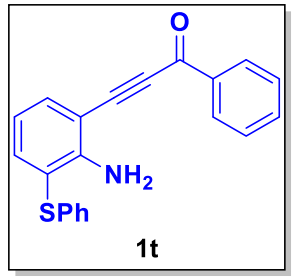
Spectrometer Frequency: 100 MHz

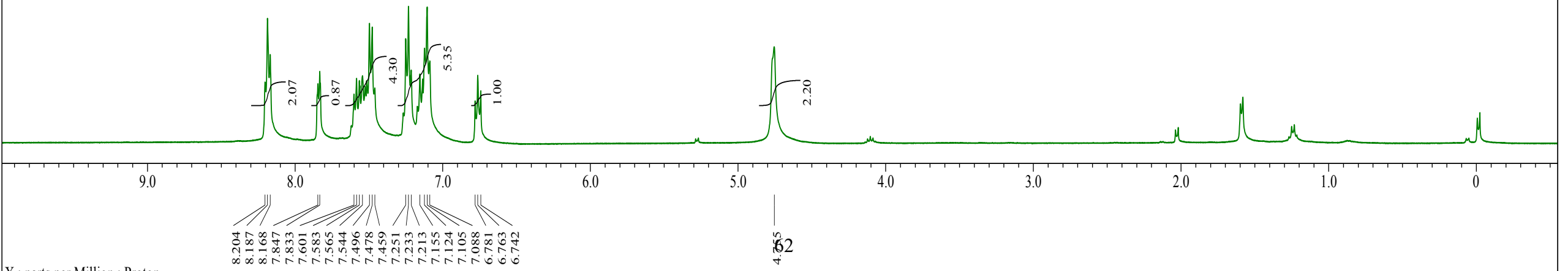




Solvent: $CDCl_3$

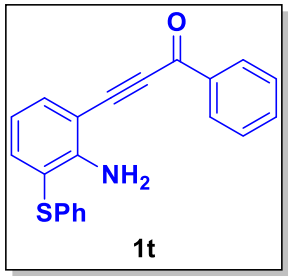
Spectrometer Frequency: 400 MHz

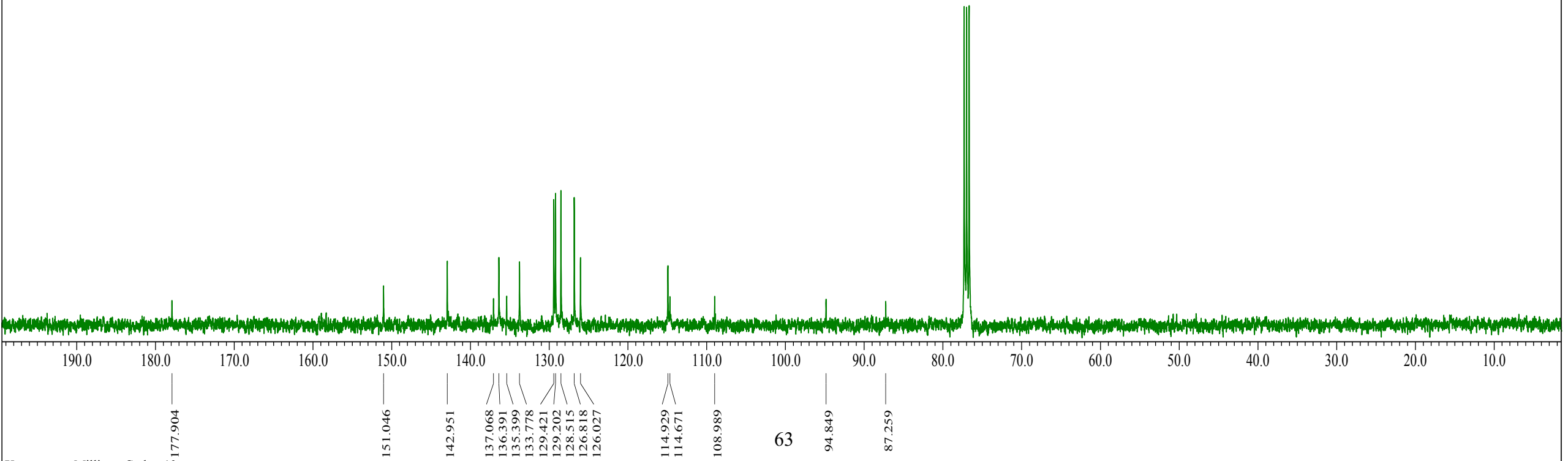




Solvent: $CDCl_3$

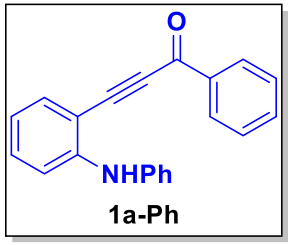
Spectrometer Frequency: 100 MHz

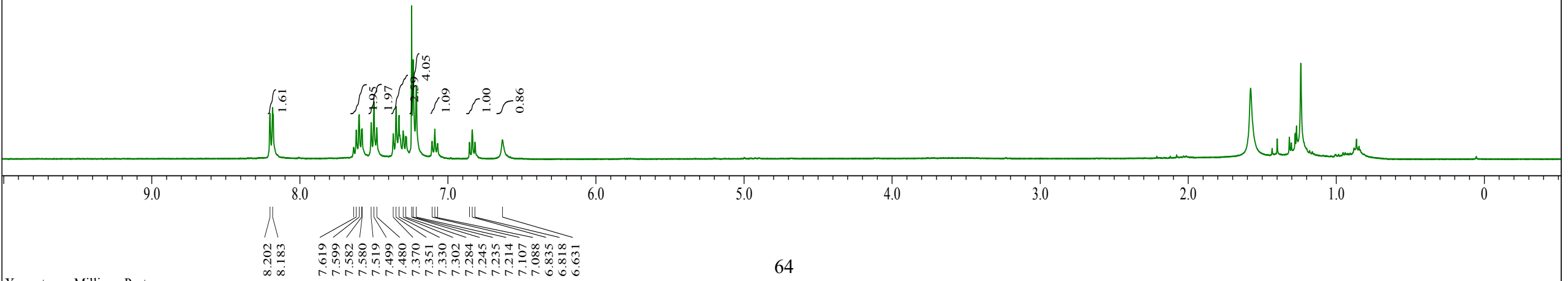




Solvent: $CDCl_3$

Spectrometer Frequency: 400 MHz

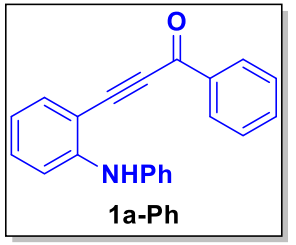


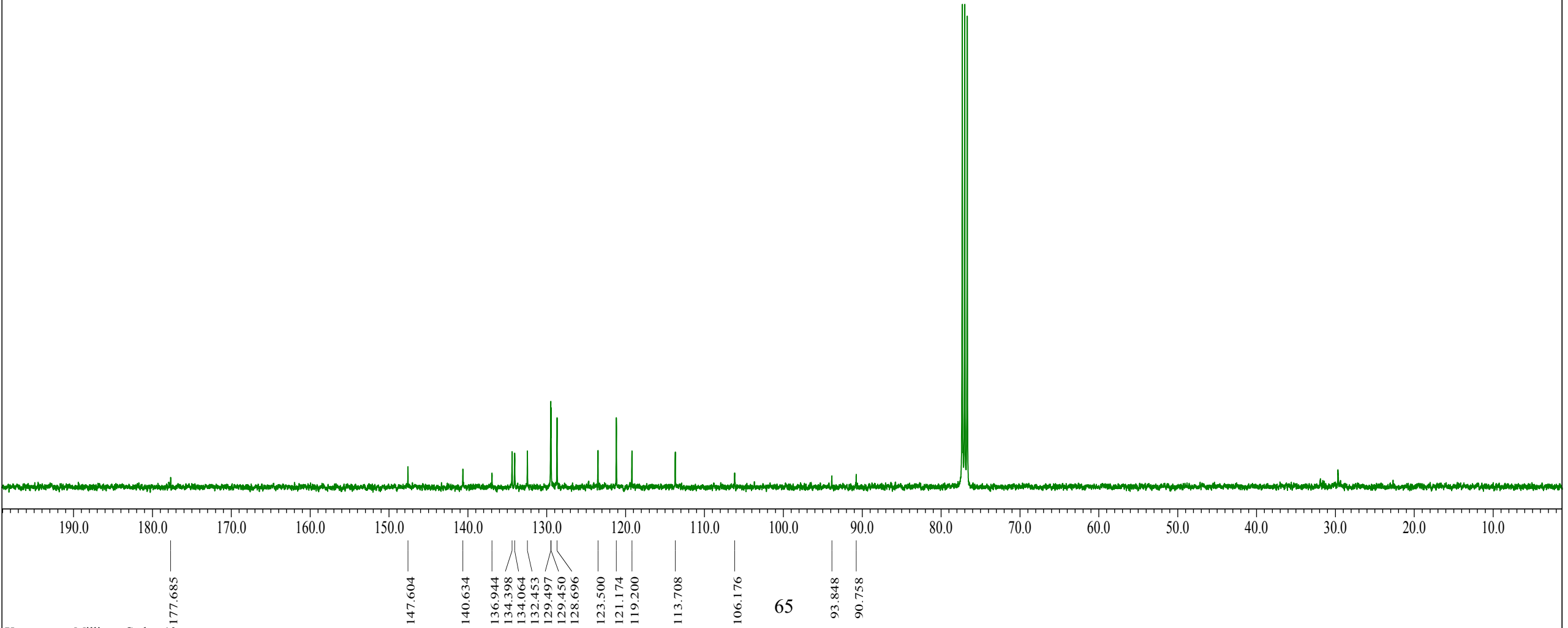


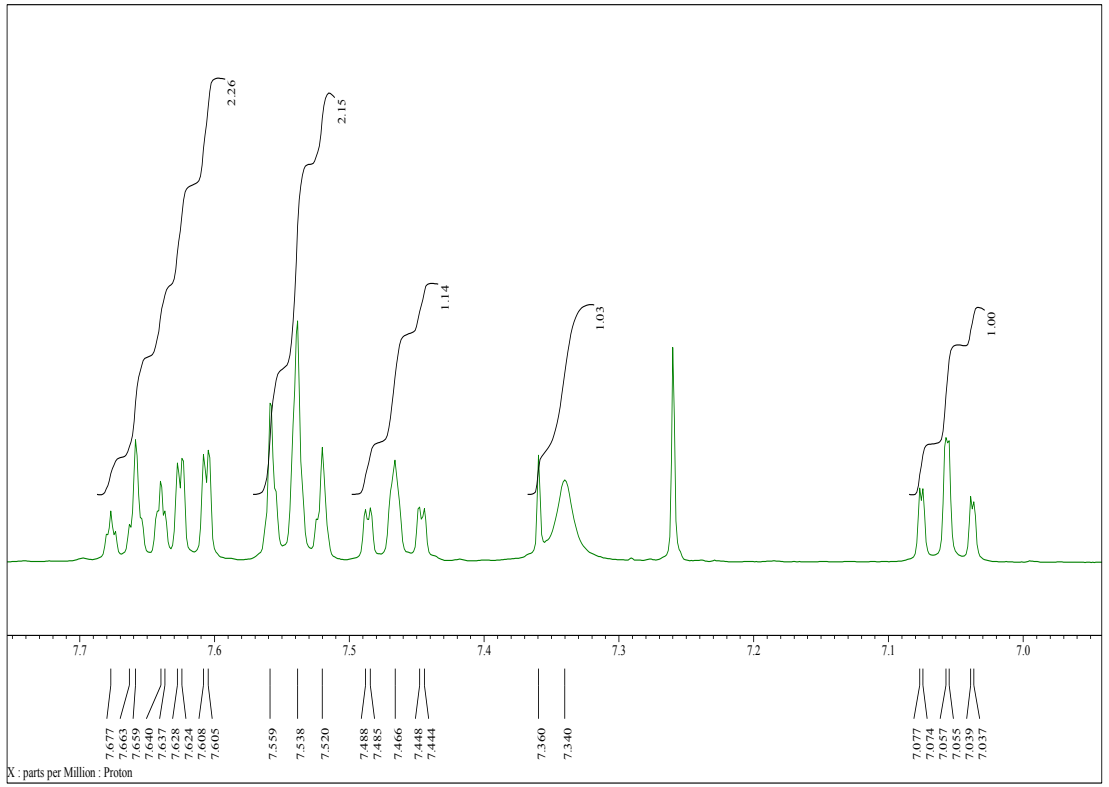
X : parts per Million : Proton

Solvent: $CDCl_3$

Spectrometer Frequency: 100 MHz

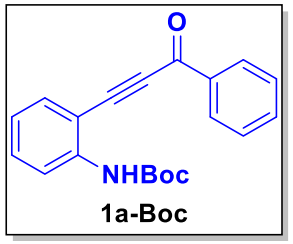






Solvent: $CDCl_3$

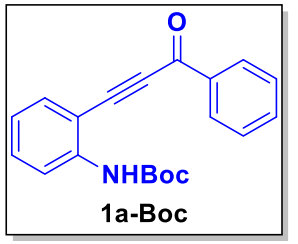
Spectrometer Frequency: 400 MHz



X : parts per Million : Proton

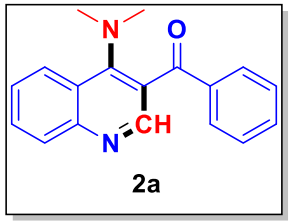
Solvent: $CDCl_3$

Spectrometer Frequency: 100 MHz

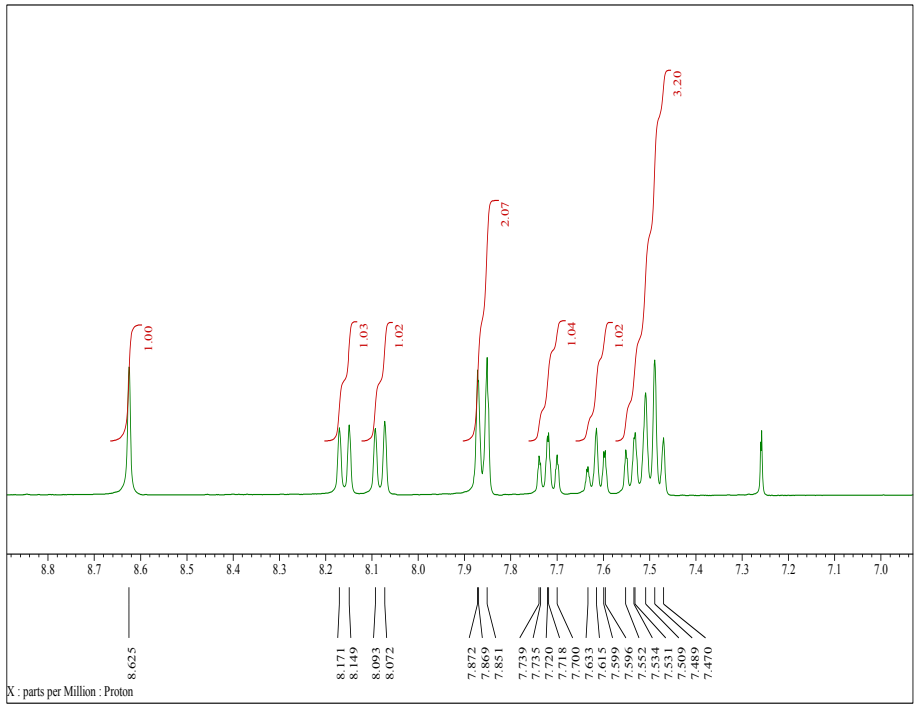


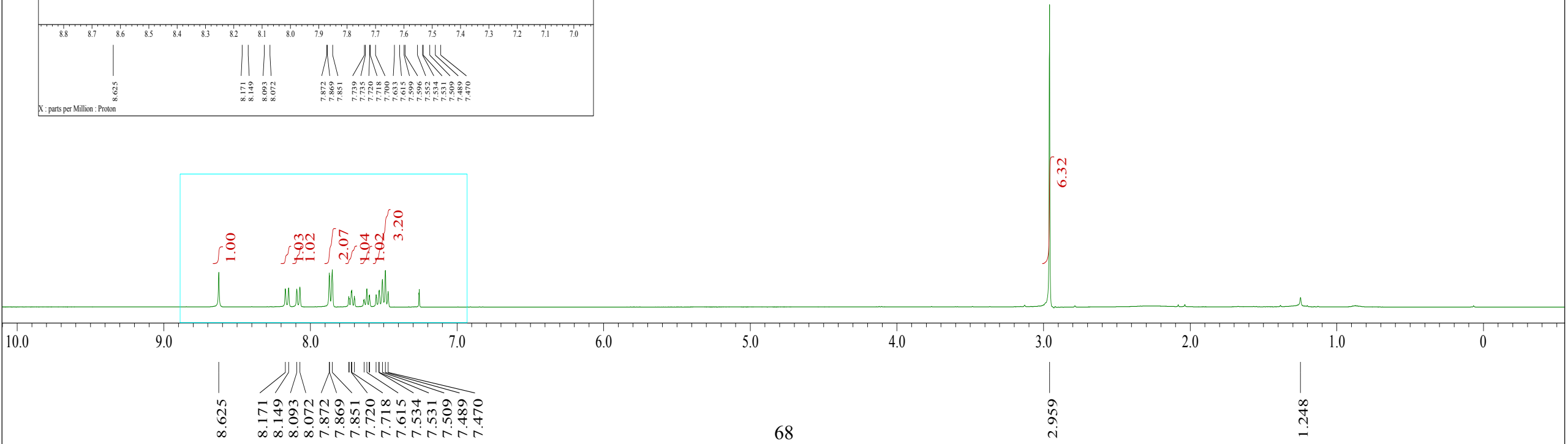
Solvent: $CDCl_3$

Spectrometer Frequency: 400 MHz



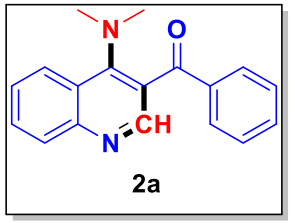
2a



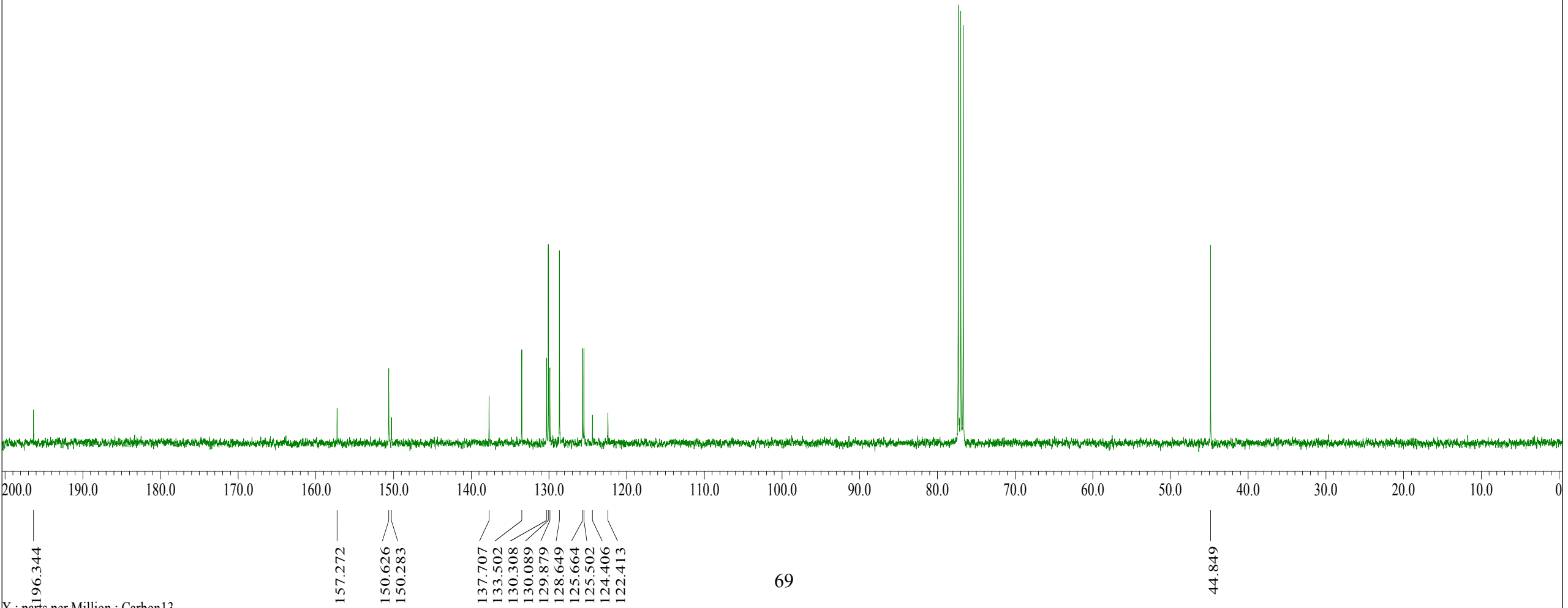


Solvent: $CDCl_3$

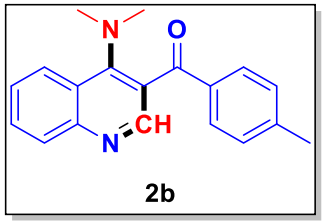
Spectrometer Frequency: 100 MHz



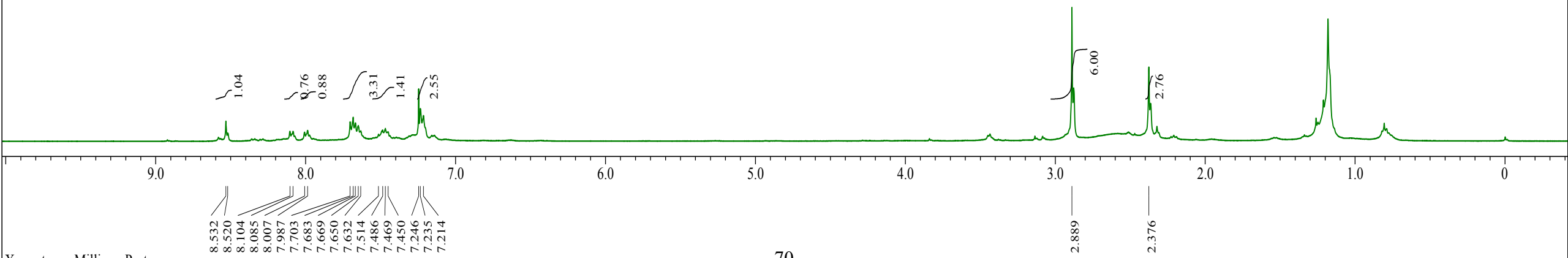
2a



Solvent: $CDCl_3$ + 4 drops of DMSO-d_6
Spectrometer Frequency: 400 MHz

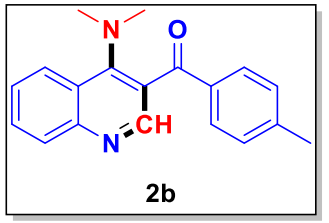


2b

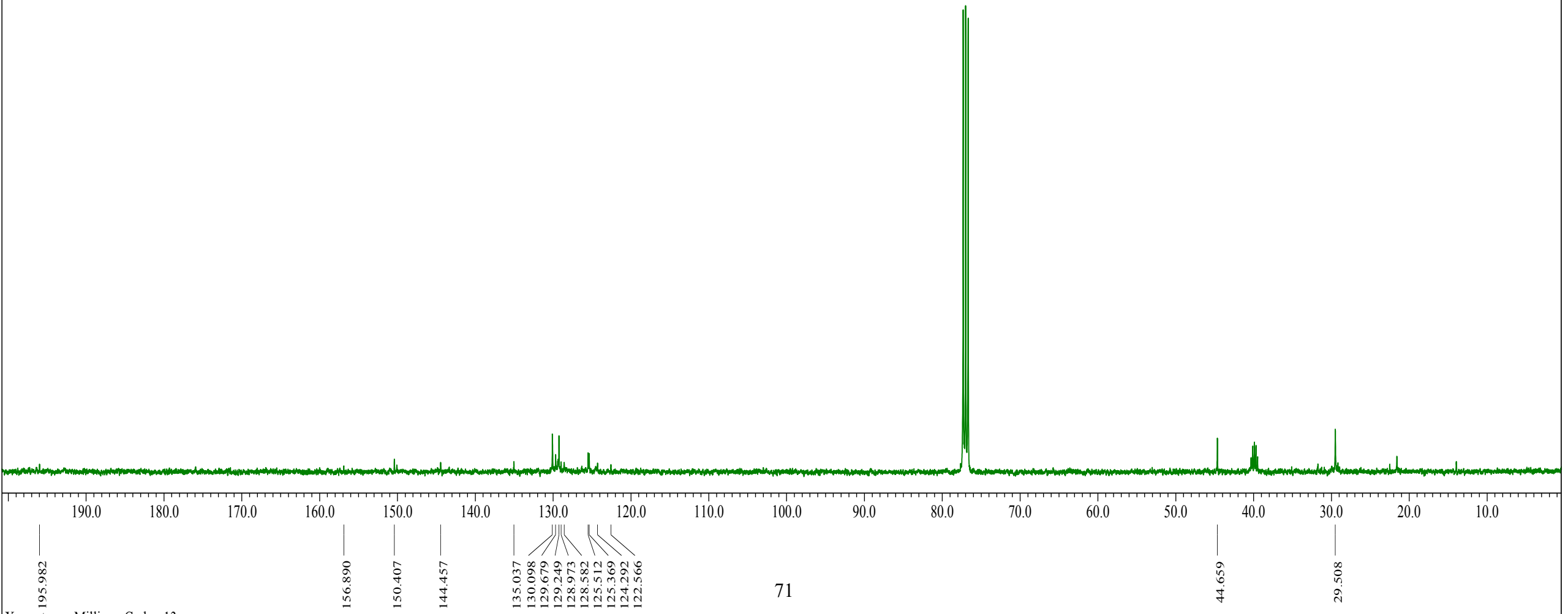


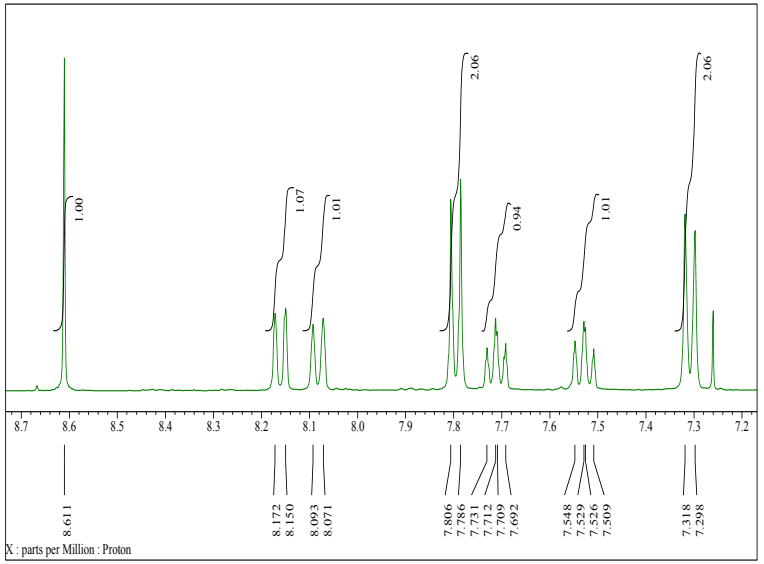
X : parts per Million : Proton

Solvent: $CDCl_3$ + 4 drops of DMSO-d_6
Spectrometer Frequency: 100 MHz



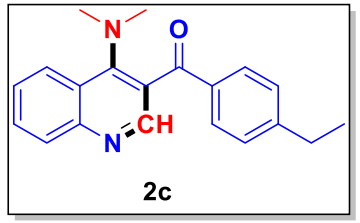
2b

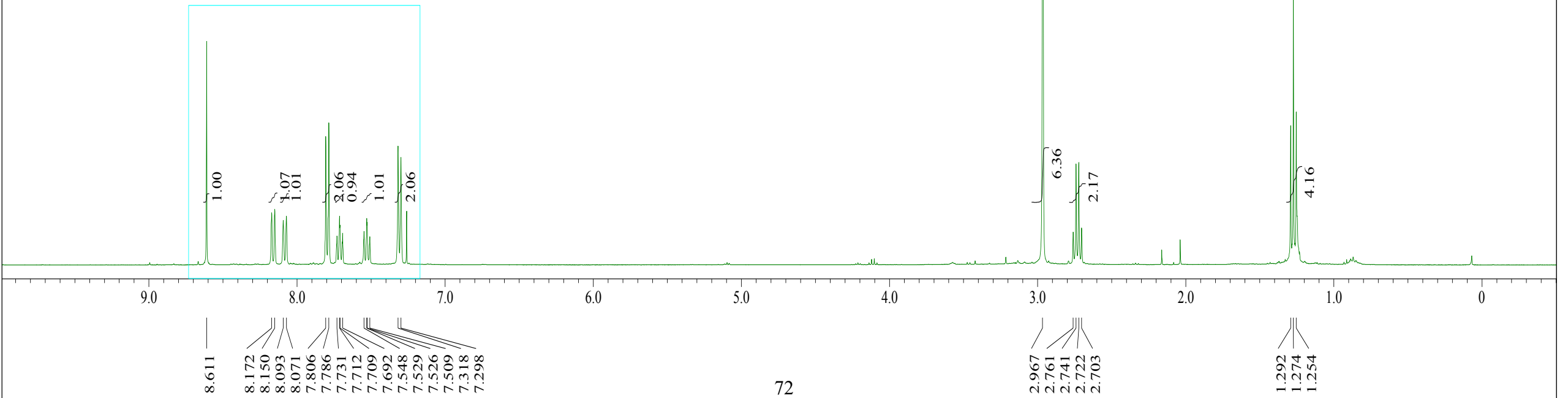




Solvent: $CDCl_3$

Spectrometer Frequency: 400 MHz

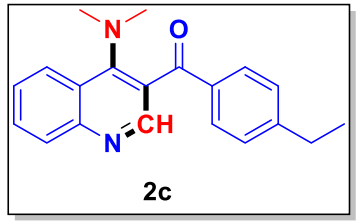




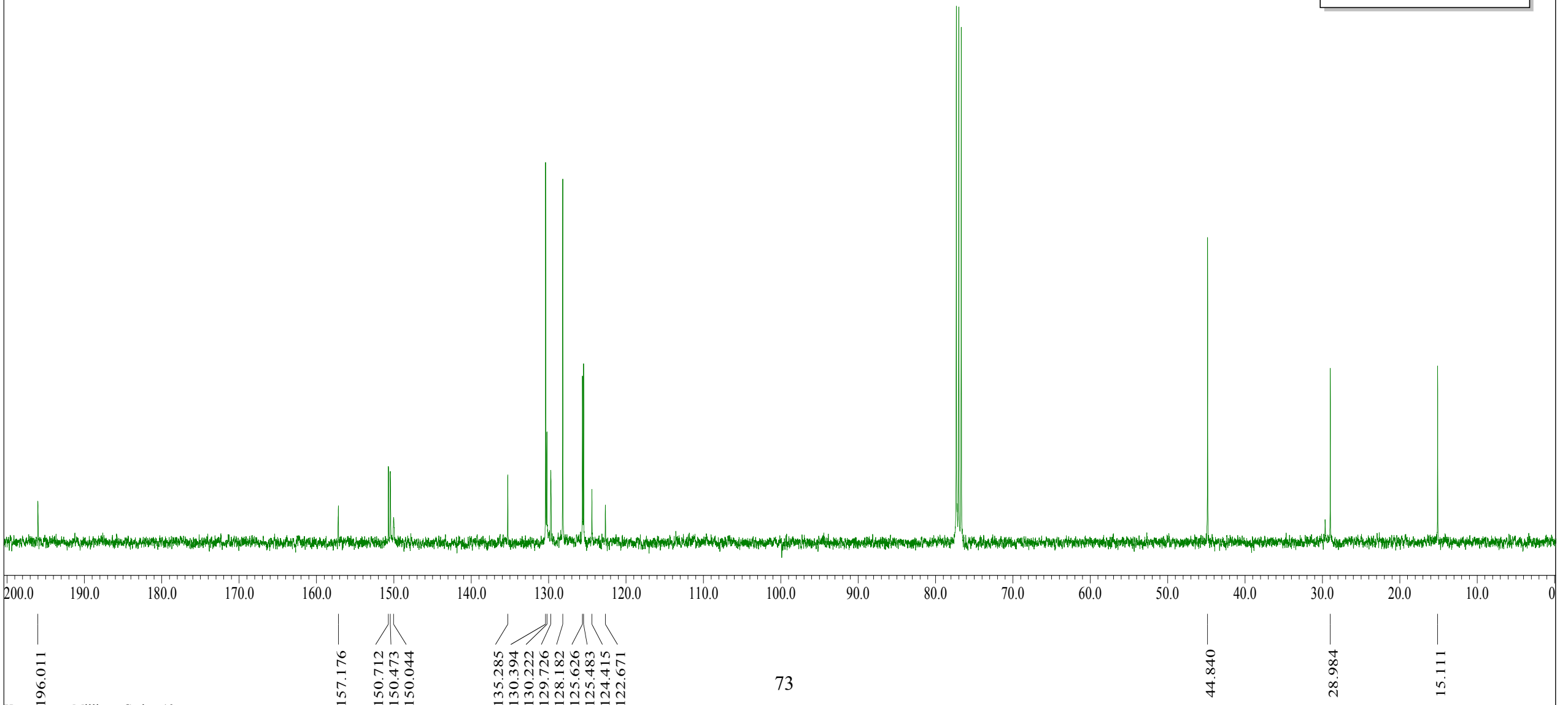
X : parts per Million : Proton

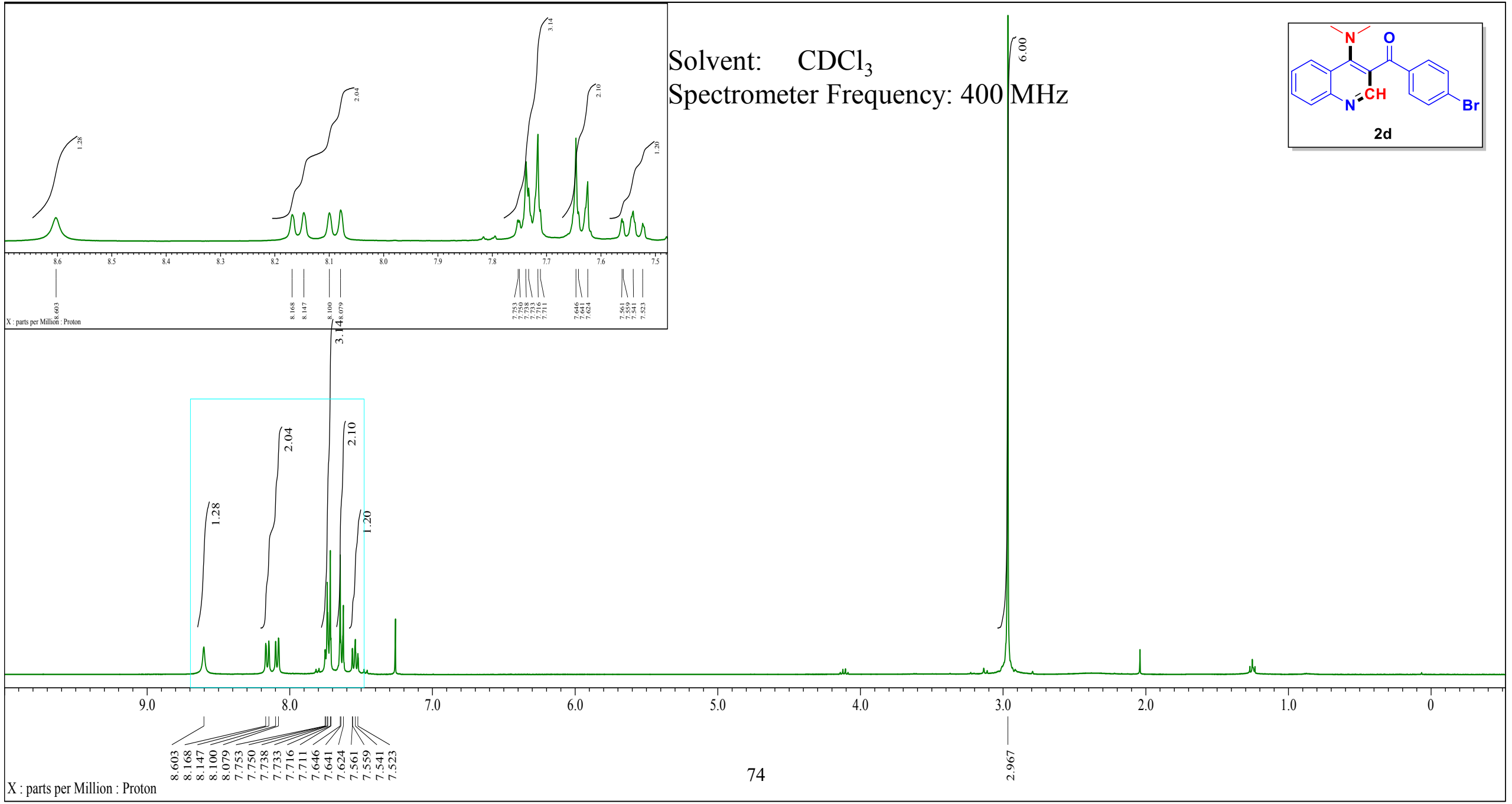
Solvent: $CDCl_3$

Spectrometer Frequency: 100 MHz

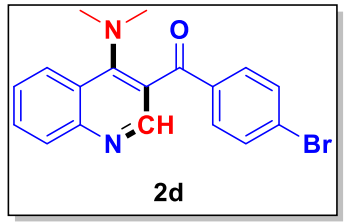


2c

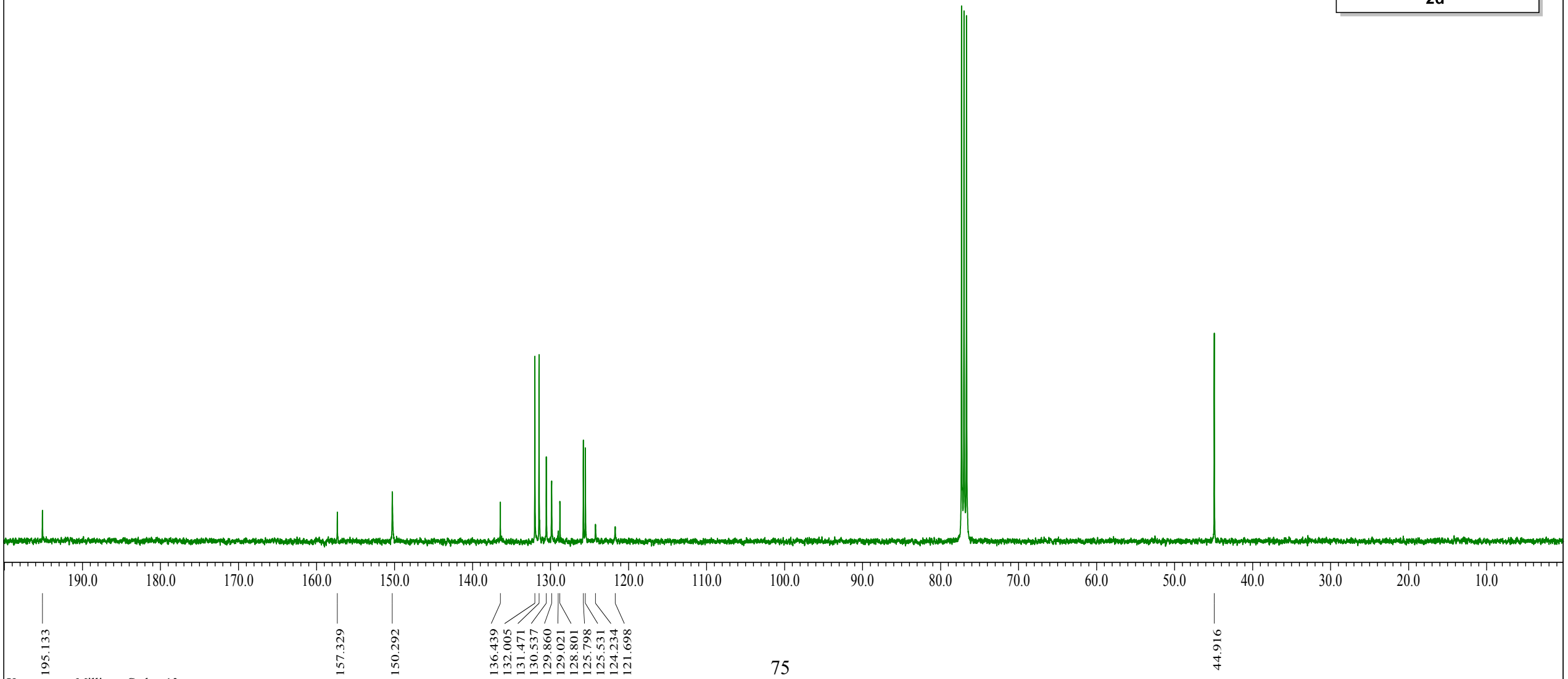



Solvent: $CDCl_3$
Spectrometer Frequency: 400 MHz
2d
X : parts per Million : Proton

Solvent: $CDCl_3$
Spectrometer Frequency: 100 MHz

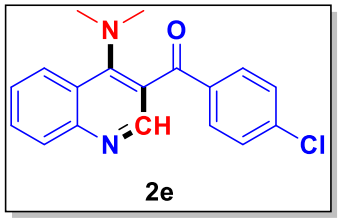


2d

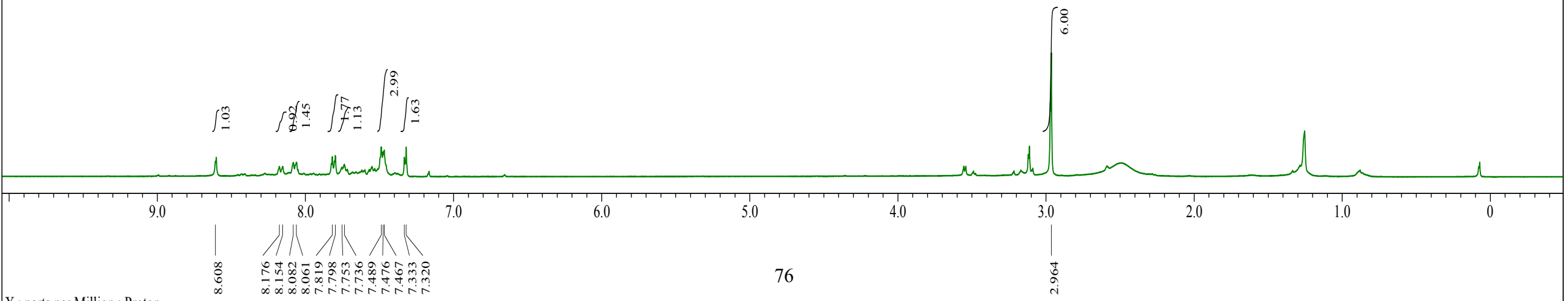


X : parts per Million : Carbon13

Solvent: $CDCl_3$ + 4 drops of DMSO-d_6
Spectrometer Frequency: 400 MHz

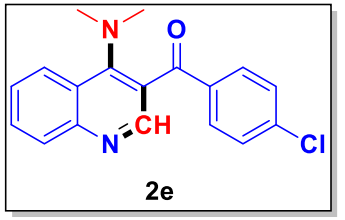


2e

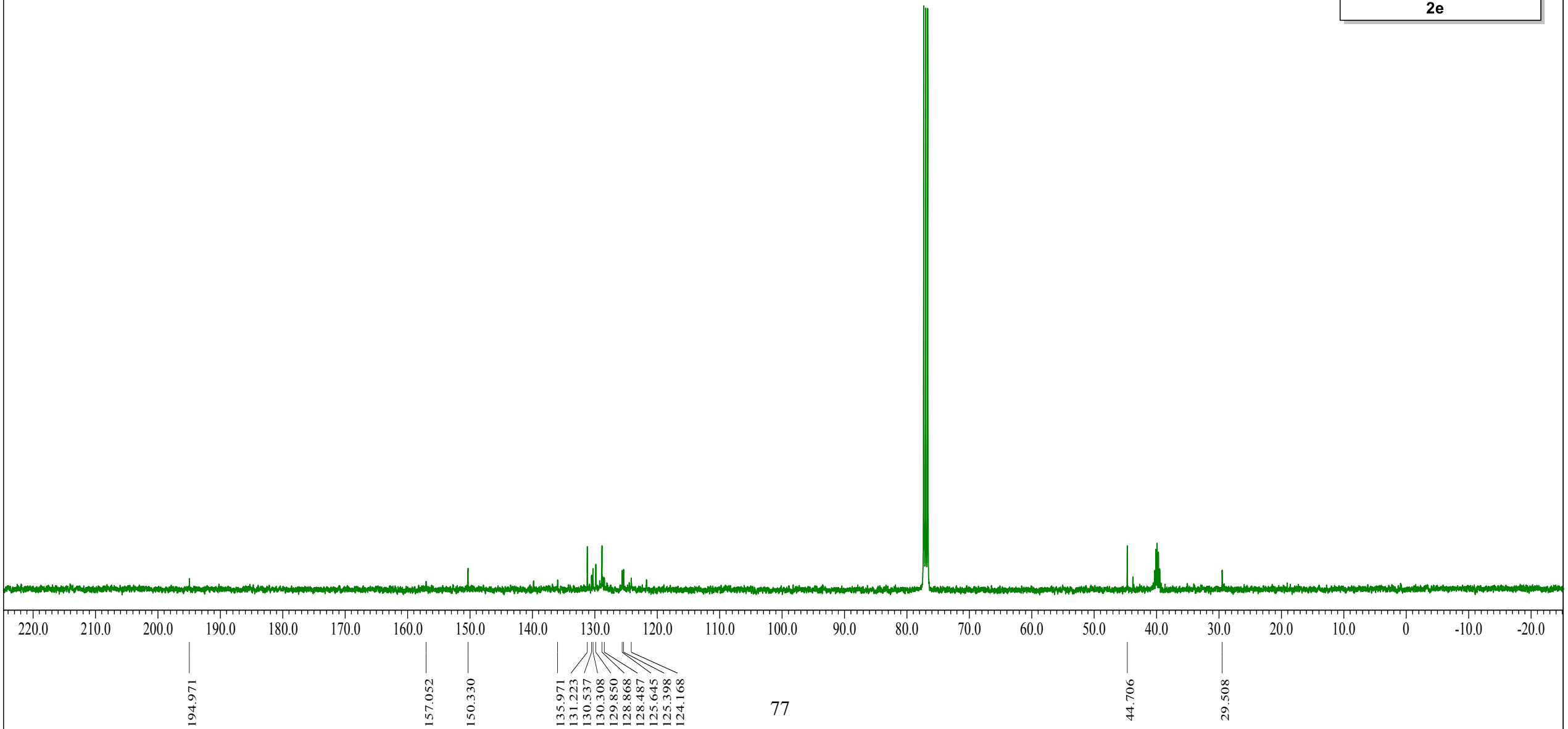


X : parts per Million : Proton

Solvent: $CDCl_3$ + 4 drops of DMSO-d_6
Spectrometer Frequency: 100 MHz

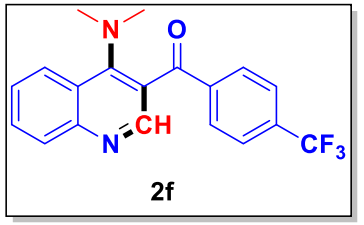


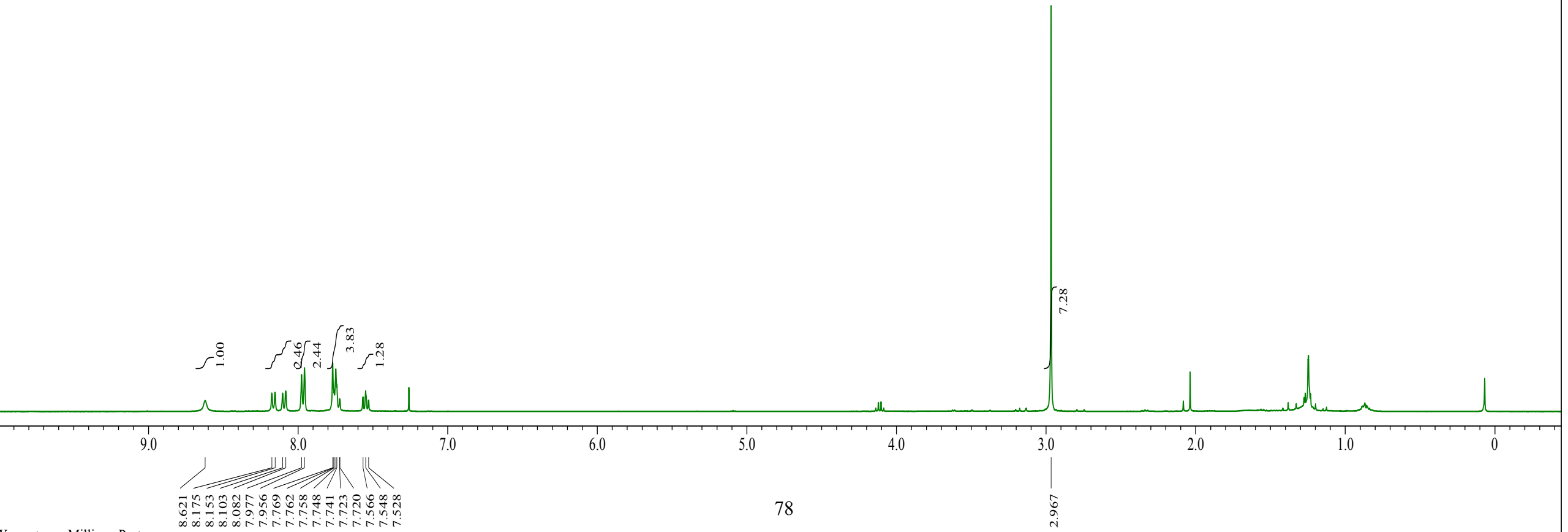
2e



Solvent: $CDCl_3$

Spectrometer Frequency: 400 MHz

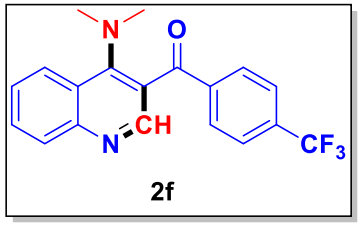




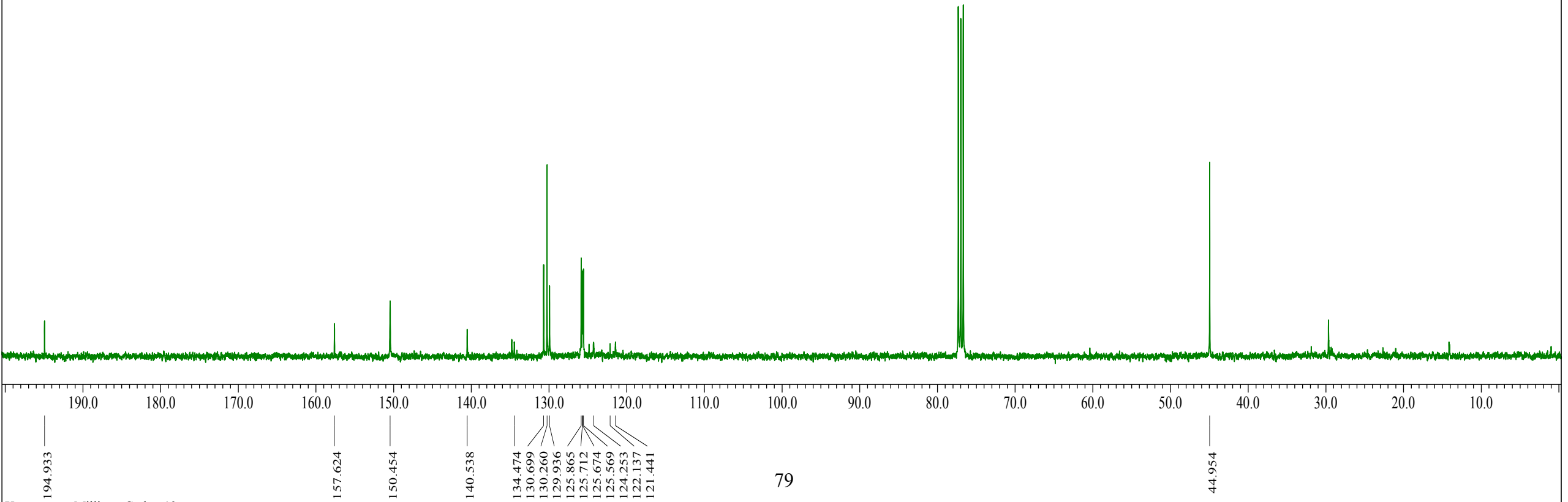
X : parts per Million : Proton

Solvent: $CDCl_3$

Spectrometer Frequency: 100 MHz

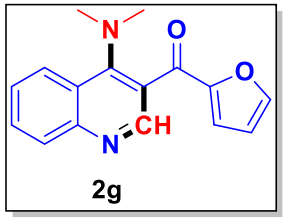


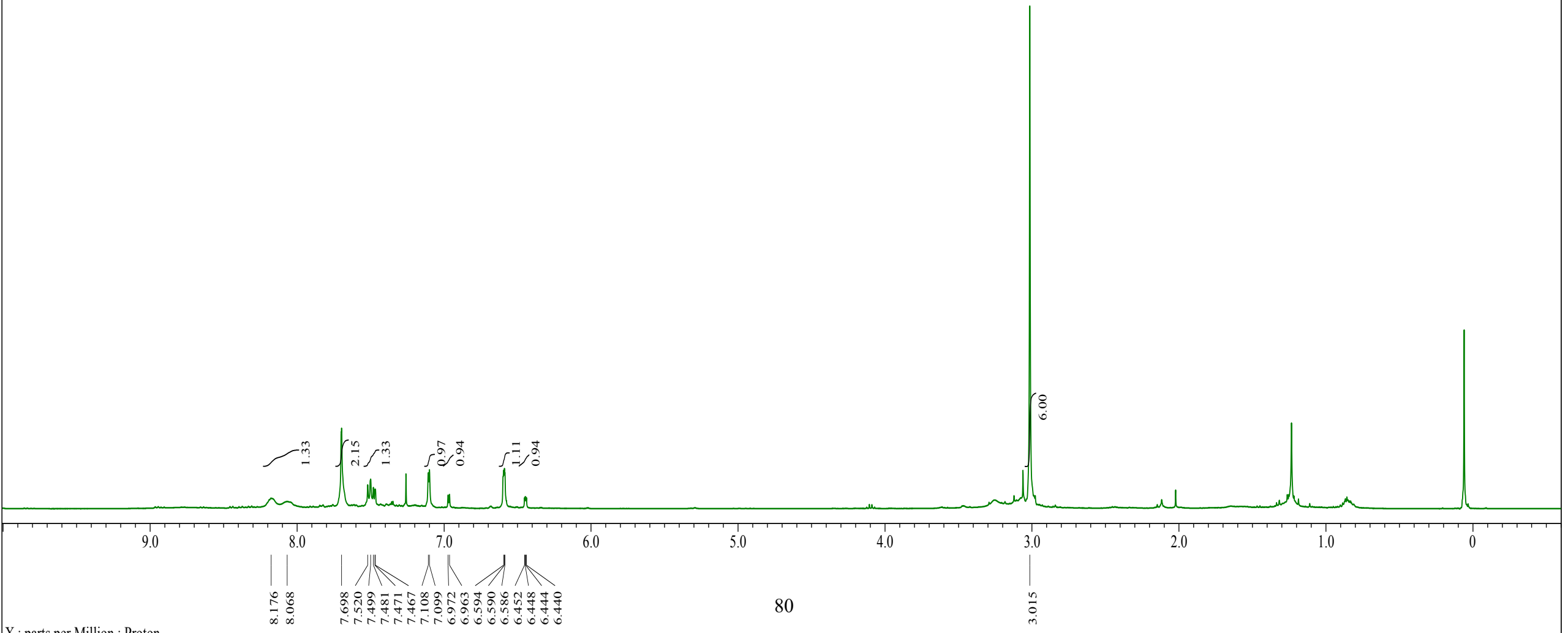
2f



X : parts per Million : Carbon13

Solvent: $CDCl_3$
Spectrometer Frequency: 400 MHz

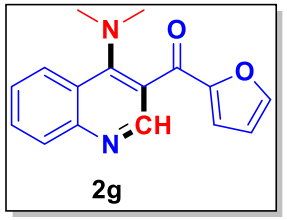




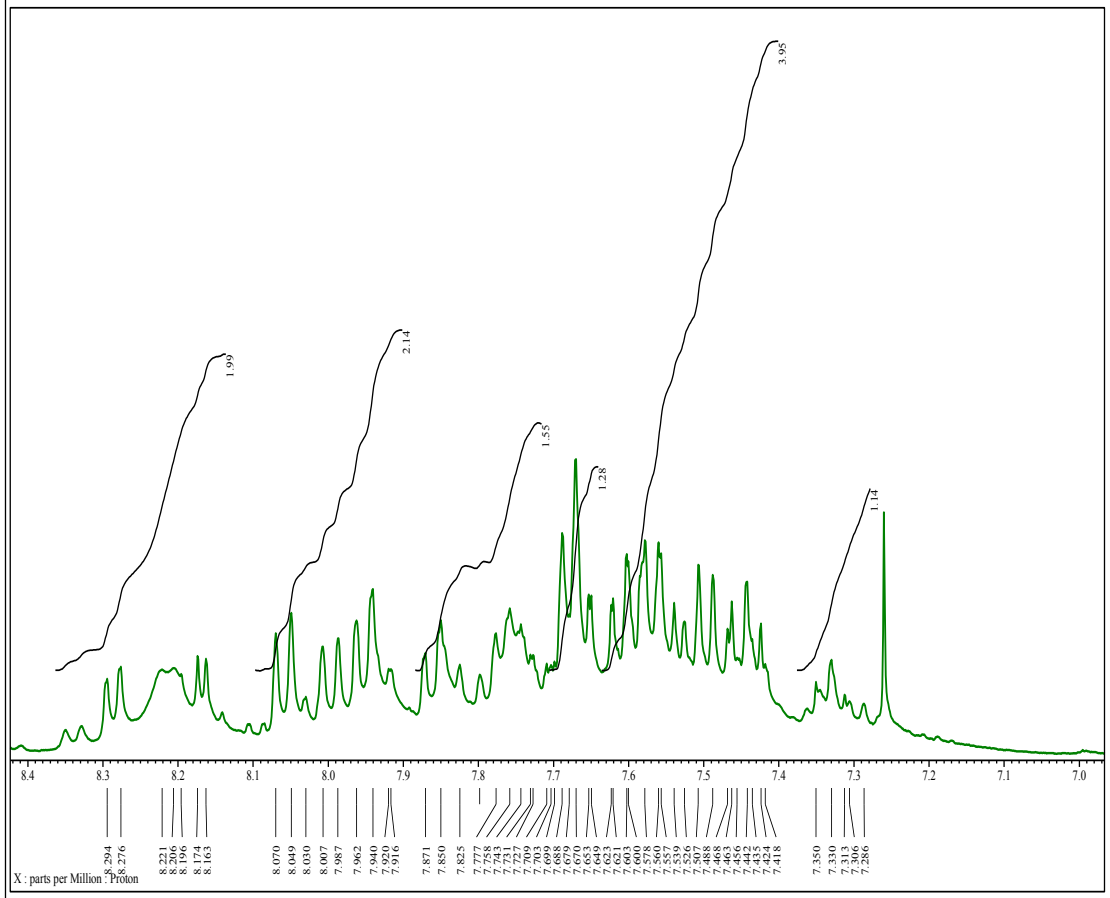
X : parts per Million : Proton

Solvent: $CDCl_3$

Spectrometer Frequency: 100 MHz

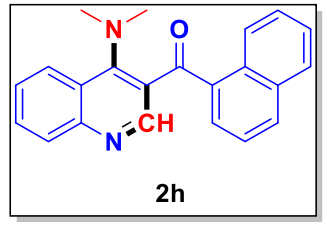


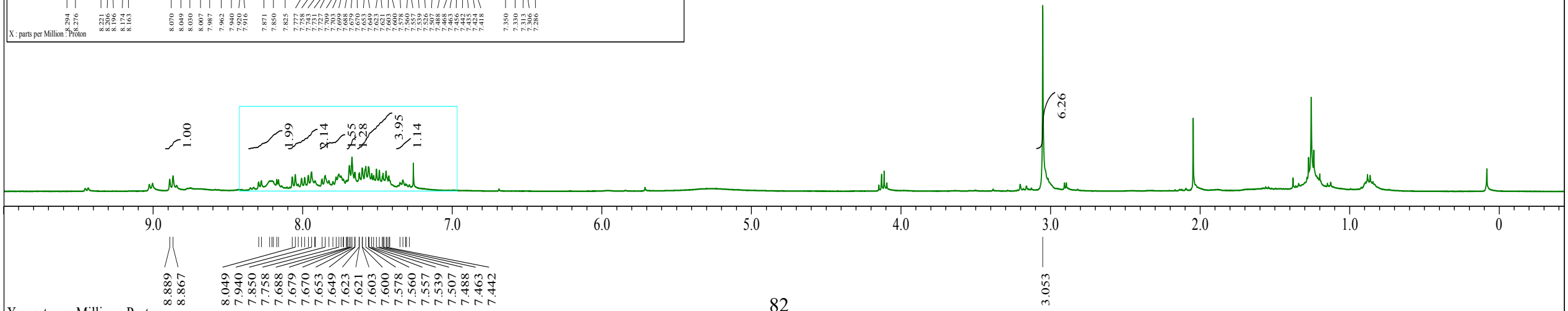
2g



Solvent: $CDCl_3$

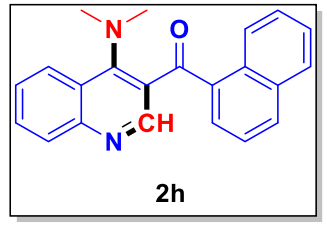
Spectrometer Frequency: 400 MHz





Solvent: DMSO-d_6

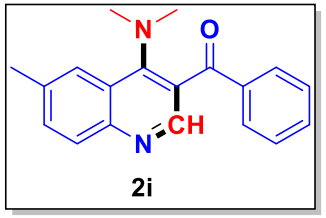
Spectrometer Frequency: 100 MHz



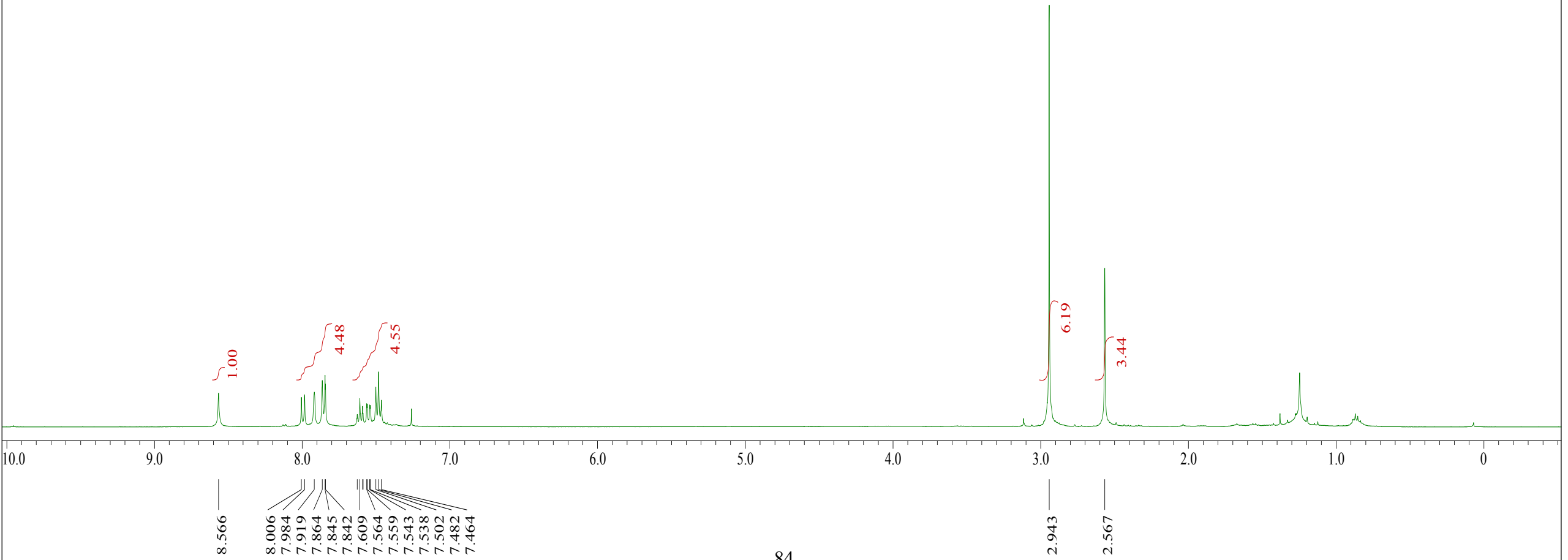
2h

Solvent: $CDCl_3$

Spectrometer Frequency: 400 MHz



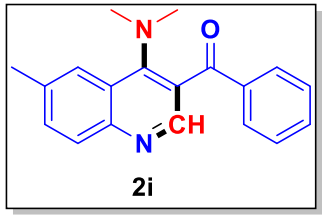
2i



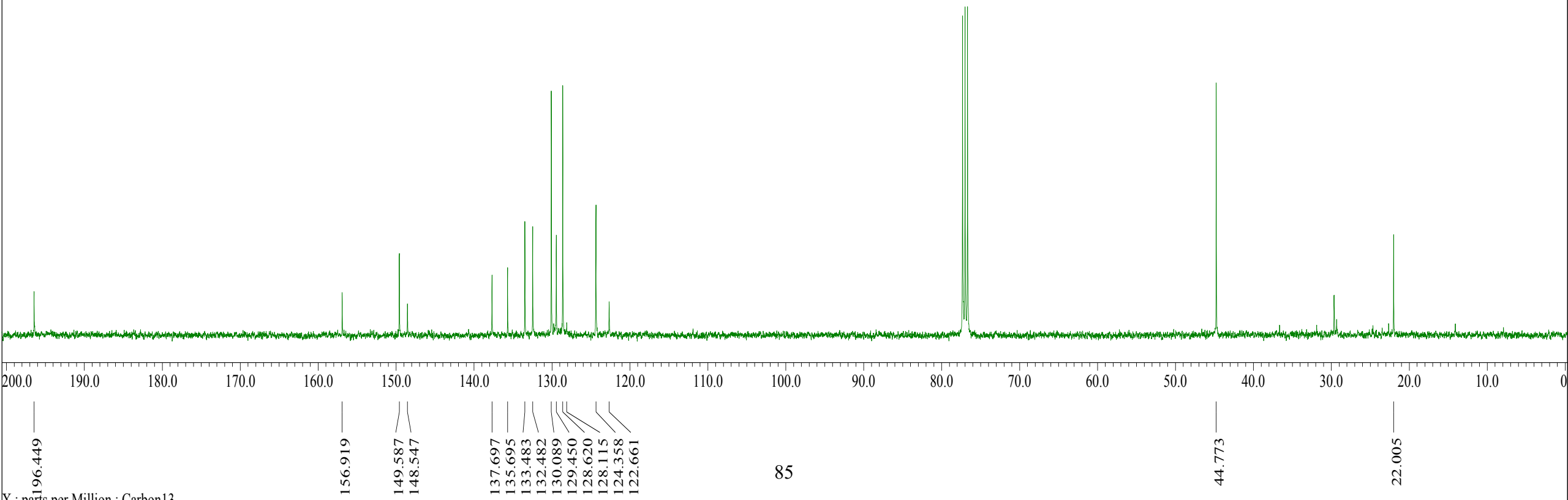
X : parts per Million : Proton

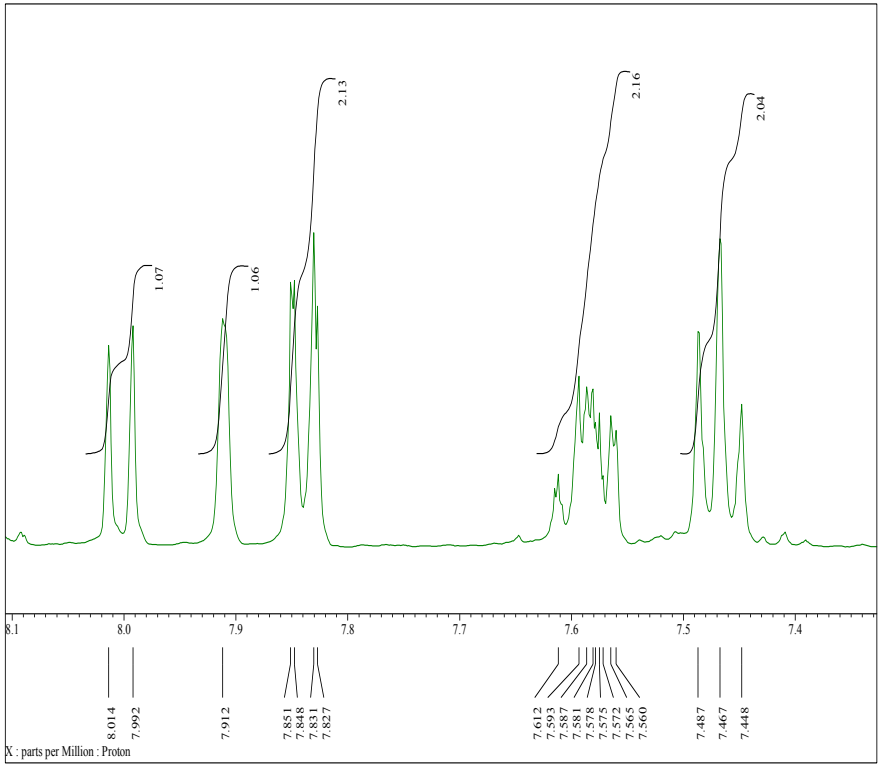
Solvent: $CDCl_3$

Spectrometer Frequency: 100 MHz



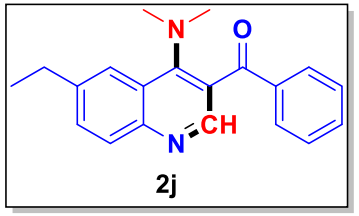
2i





Solvent: $CDCl_3$

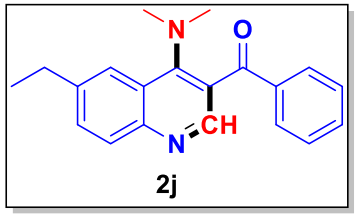
Spectrometer Frequency: 400 MHz



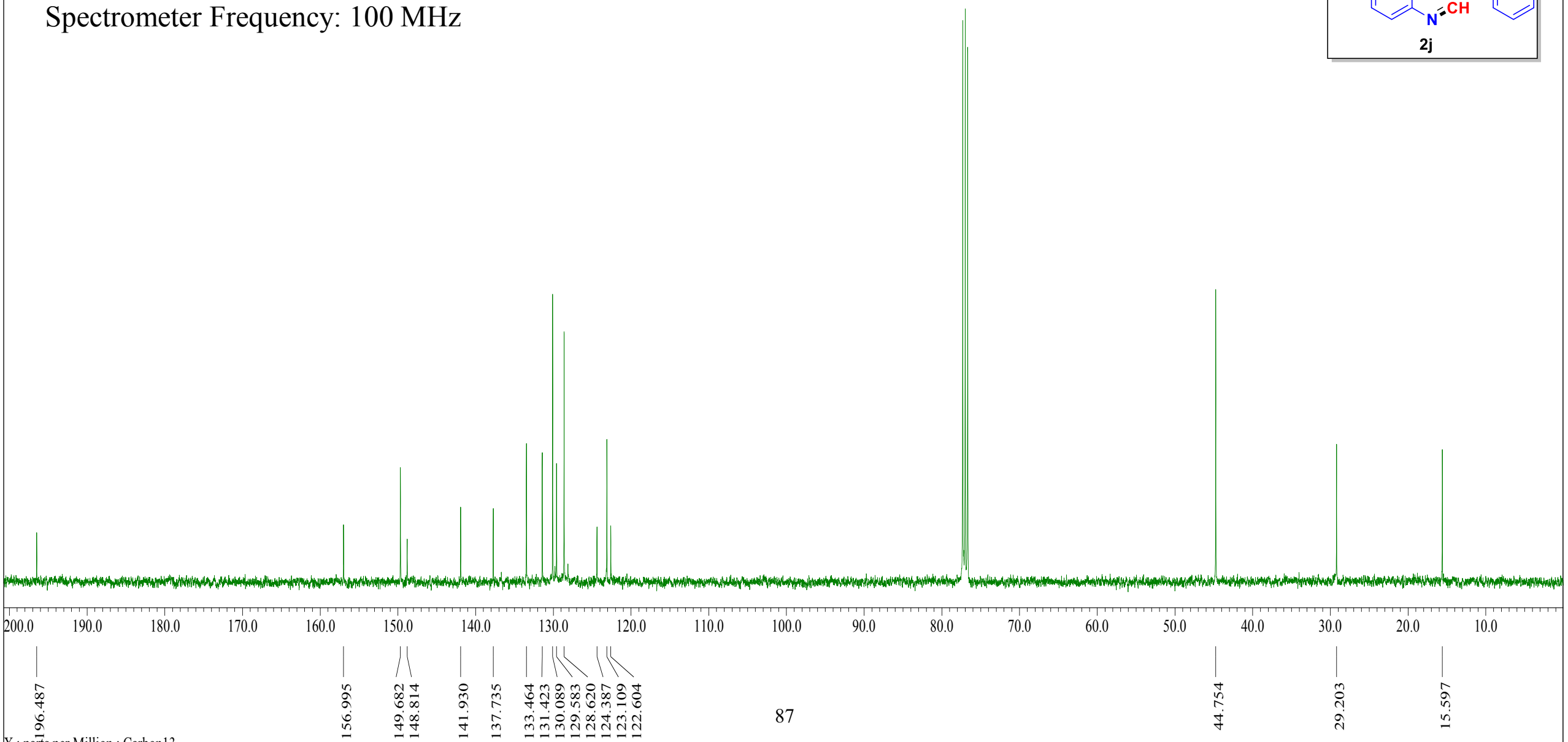
X : parts per Million : Proton

Solvent: $CDCl_3$

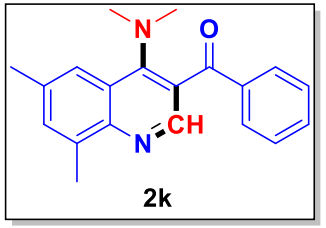
Spectrometer Frequency: 100 MHz

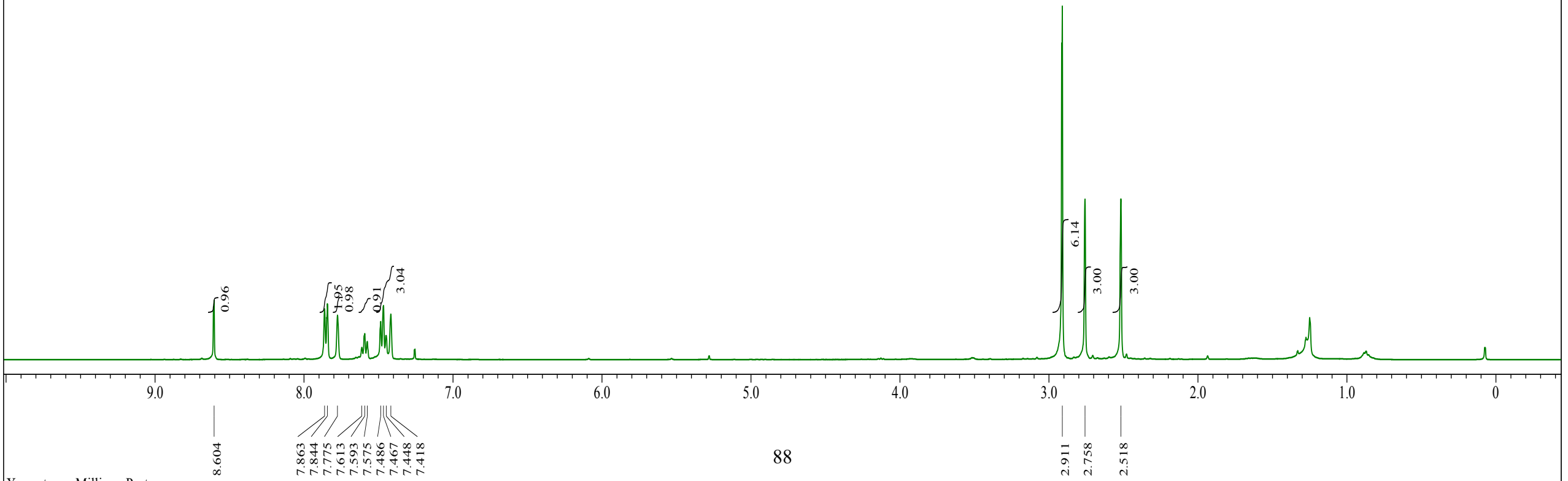


2j



Solvent: $CDCl_3$
Spectrometer Frequency: 400 MHz

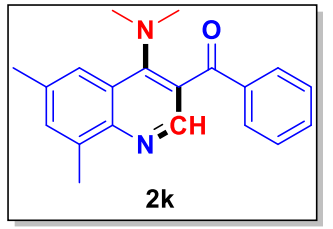




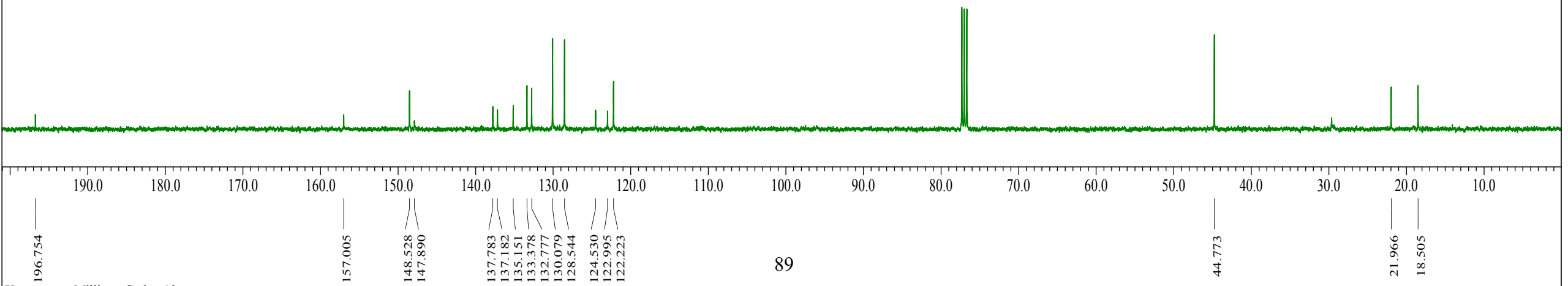
X : parts per Million : Proton

Solvent: $CDCl_3$

Spectrometer Frequency: 100 MHz



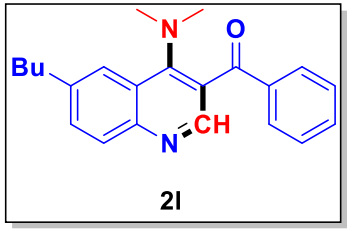
2k



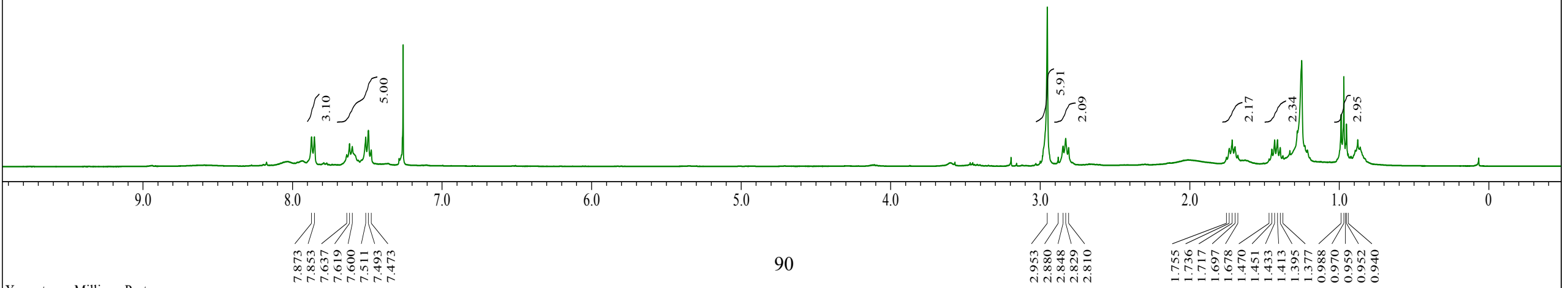
X : parts per Million : Carbon13

Solvent: $CDCl_3$

Spectrometer Frequency: 400 MHz



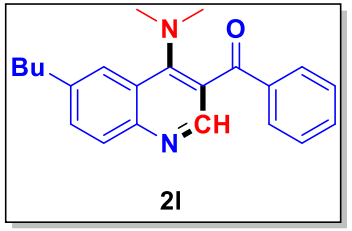
2l



X : parts per Million : Proton

Solvent: $CDCl_3$

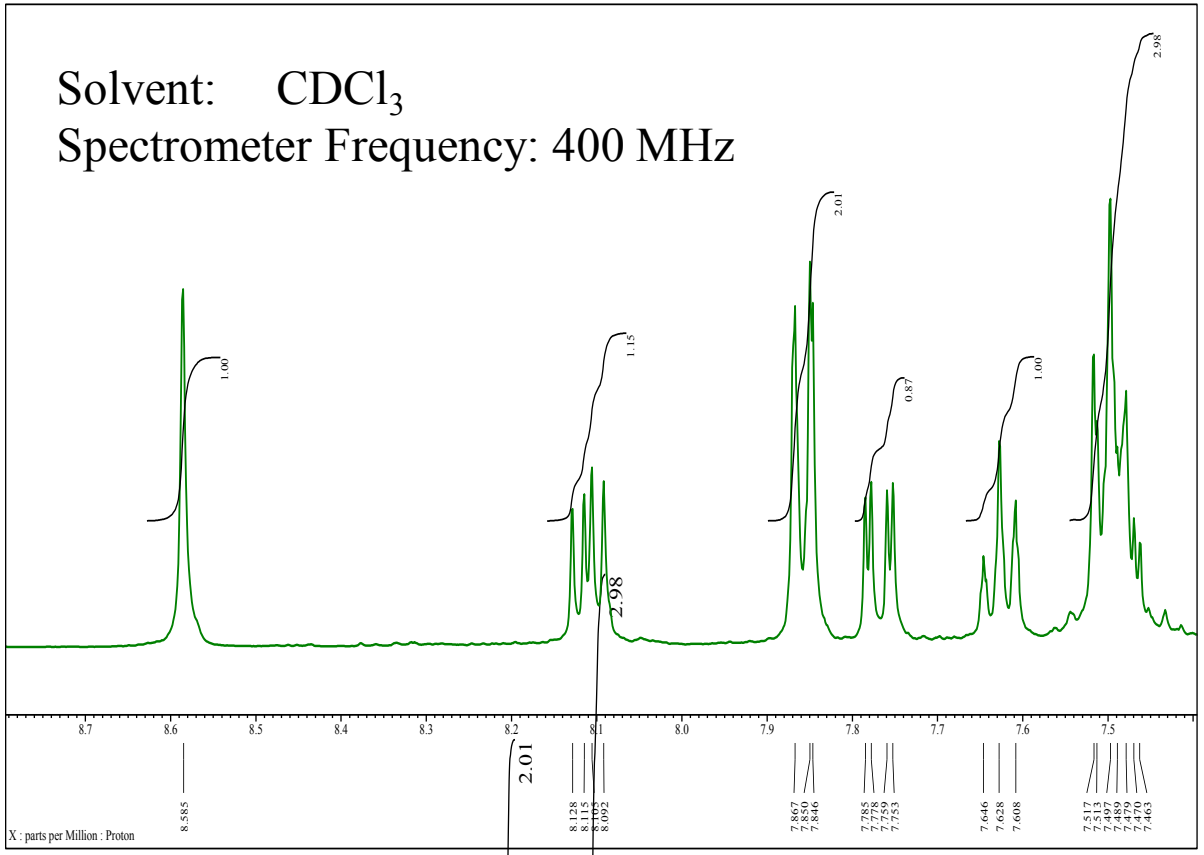
Spectrometer Frequency: 100 MHz

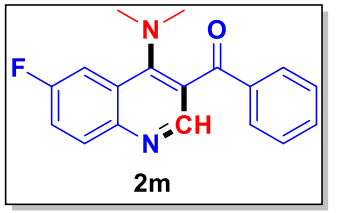


2l

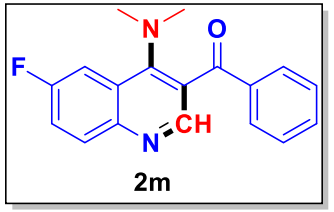
Solvent: $CDCl_3$

Spectrometer Frequency: 400 MHz

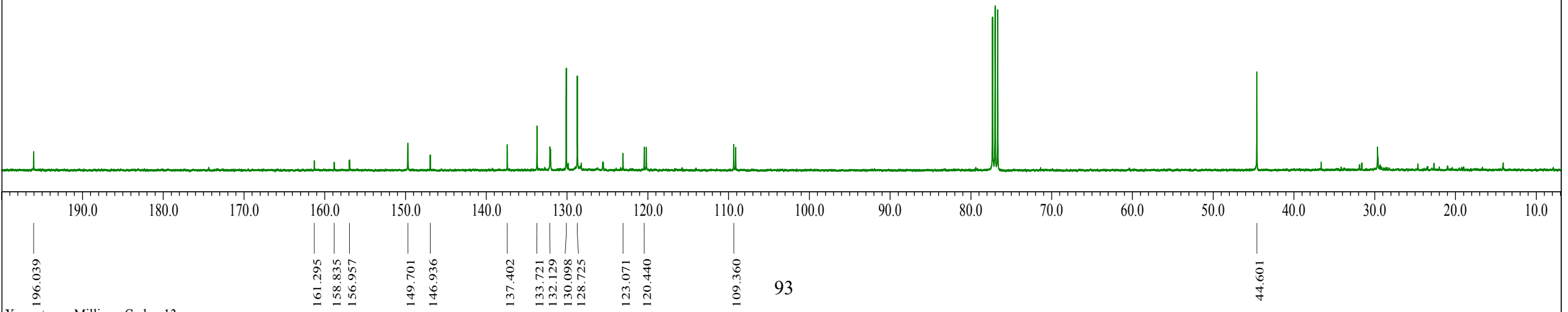




Solvent: $CDCl_3$
Spectrometer Frequency: 100 MHz

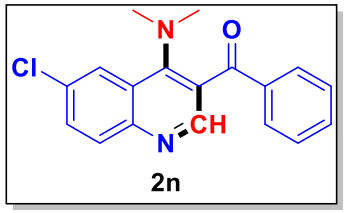


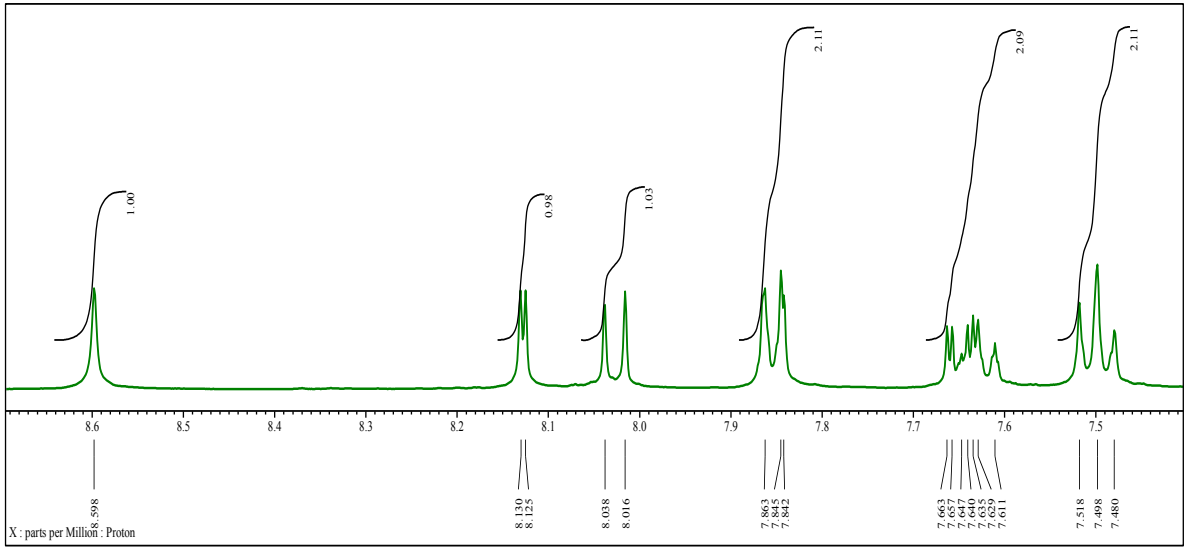
2m



Solvent: $CDCl_3$

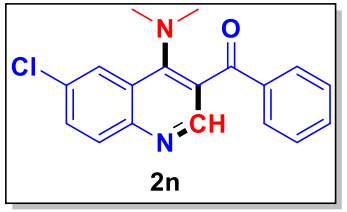
Spectrometer Frequency: 400 MHz



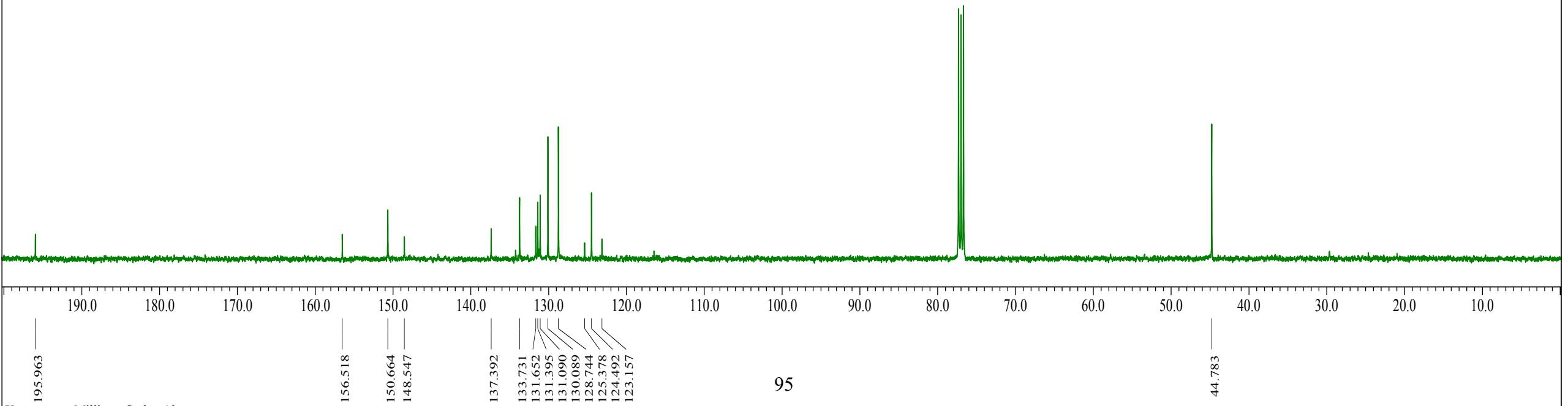


Solvent: $CDCl_3$

Spectrometer Frequency: 100 MHz



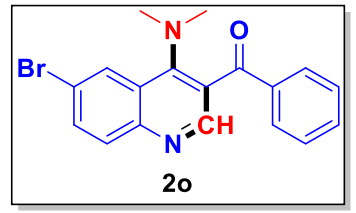
2n



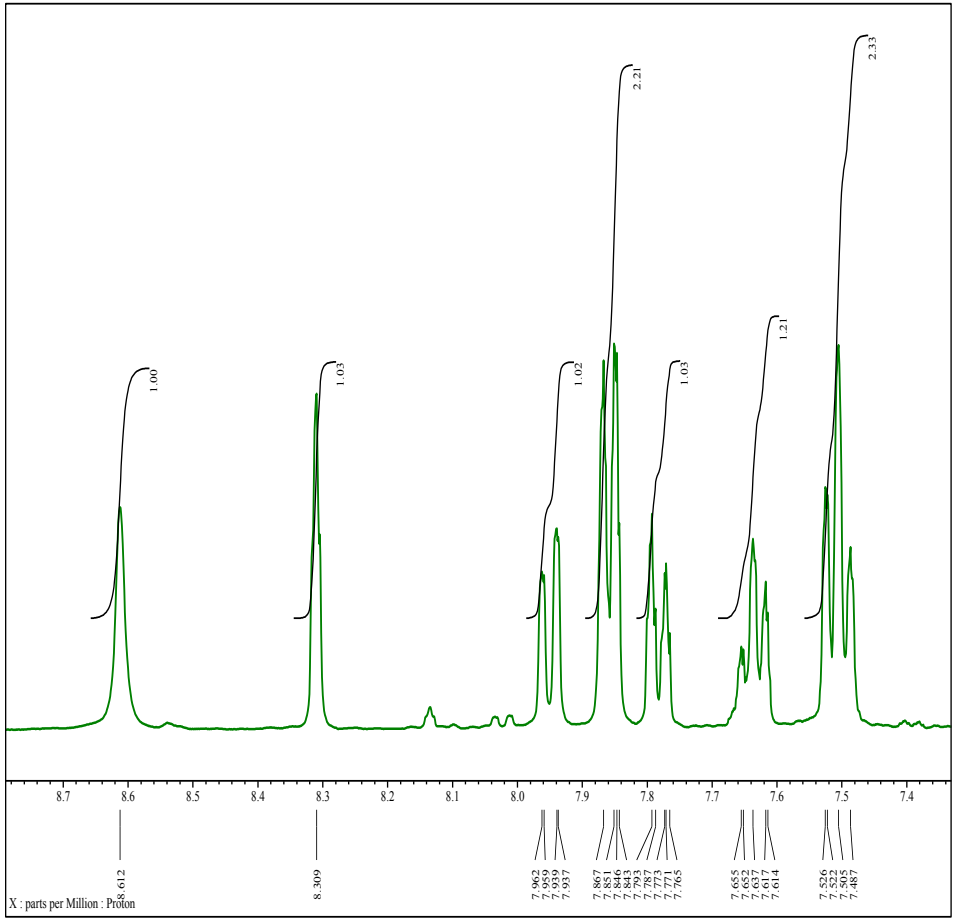
X : parts per Million : Carbon13

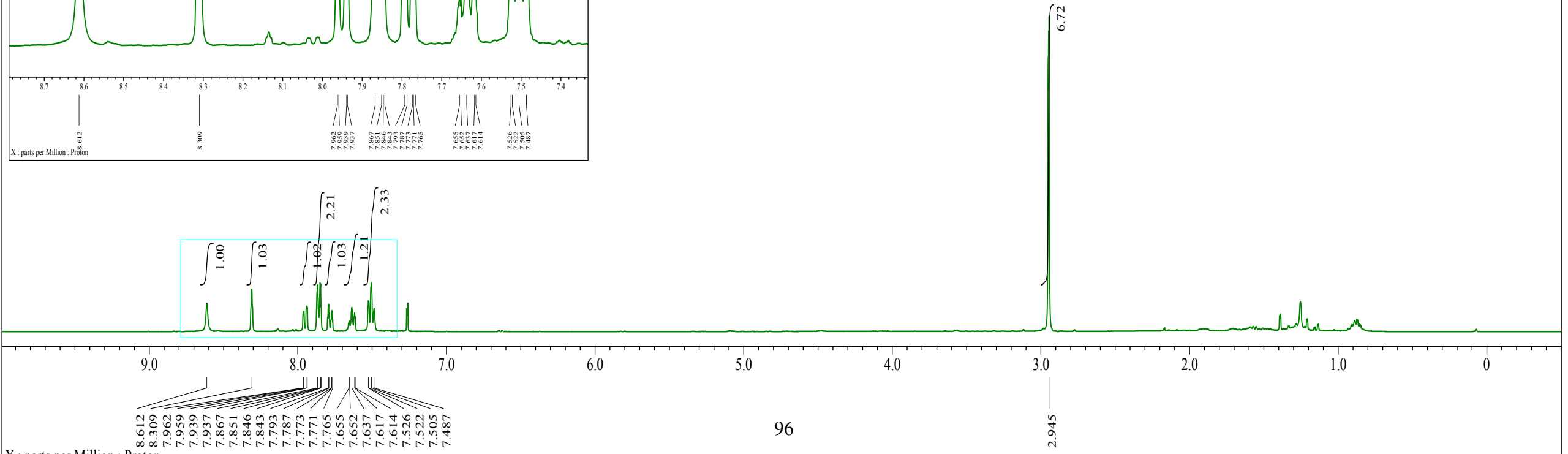
Solvent: $CDCl_3$

Spectrometer Frequency: 400 MHz



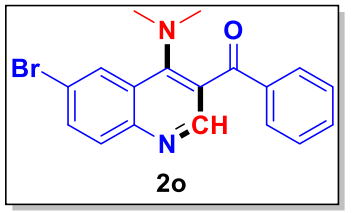
2o



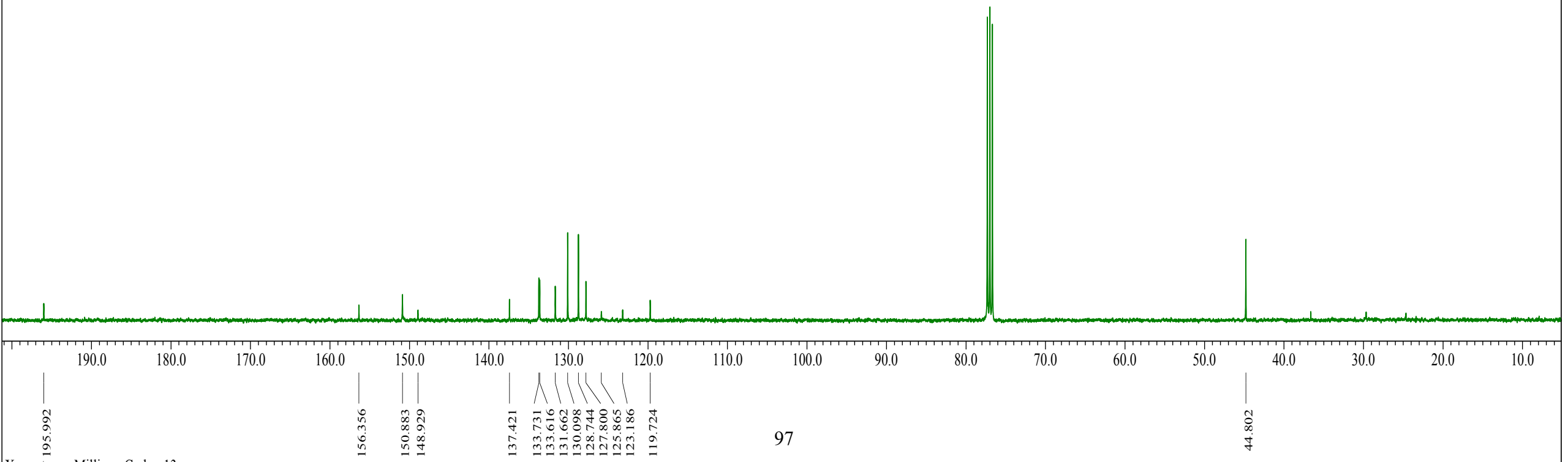


Solvent: $CDCl_3$

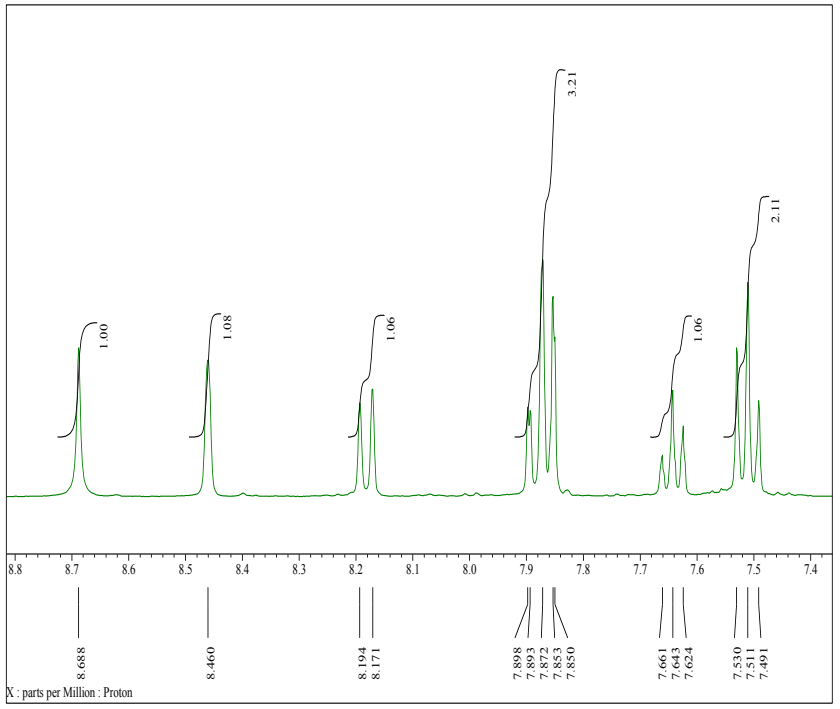
Spectrometer Frequency: 100 MHz



2o

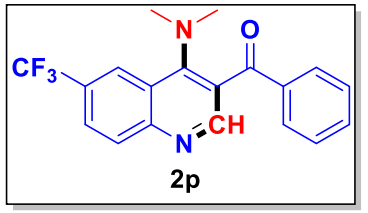


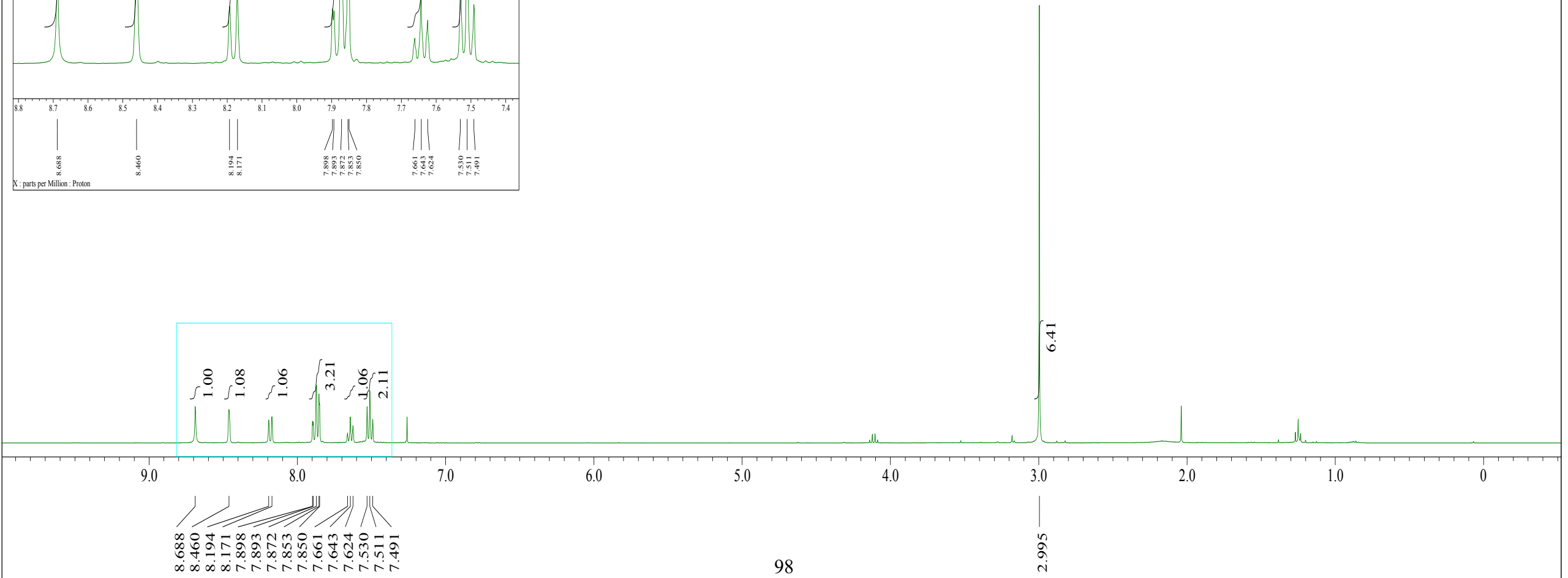
X : parts per Million : Carbon13



Solvent: $CDCl_3$

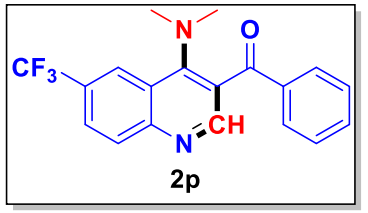
Spectrometer Frequency: 400 MHz



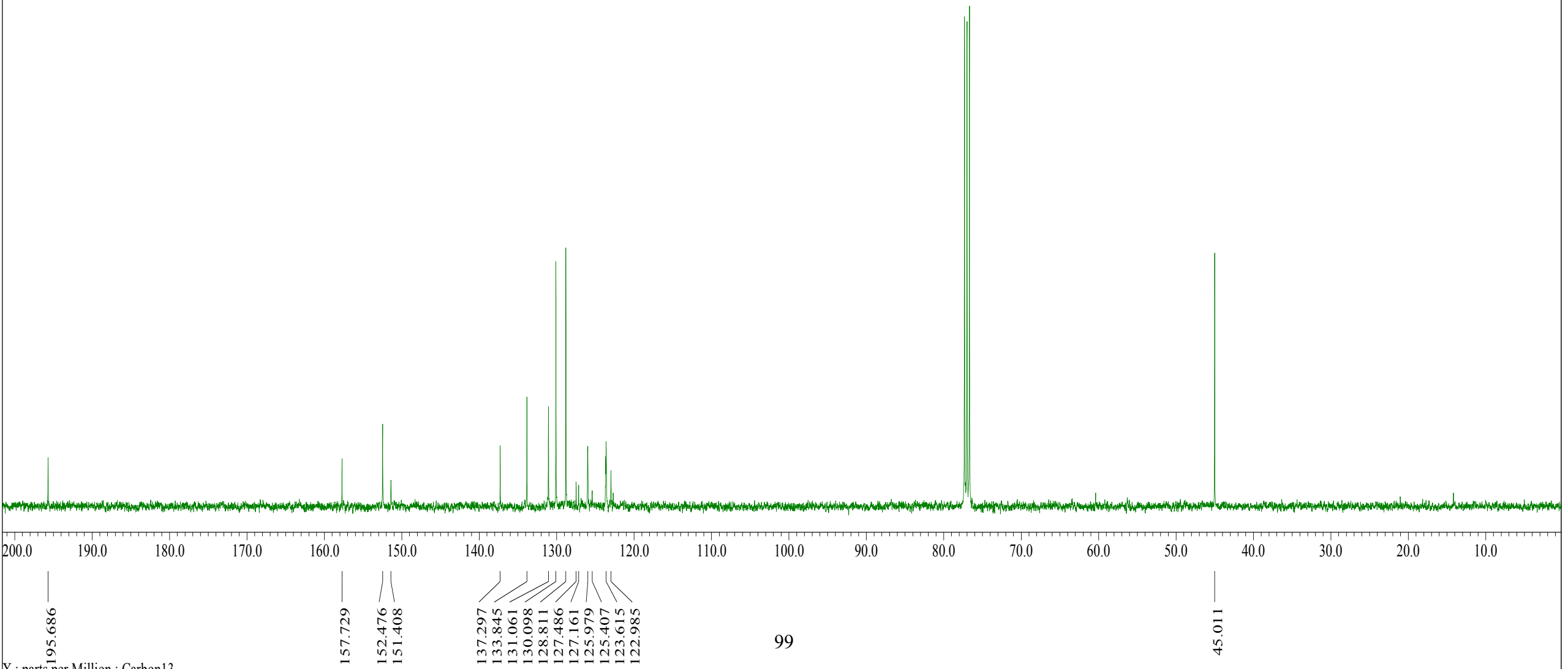


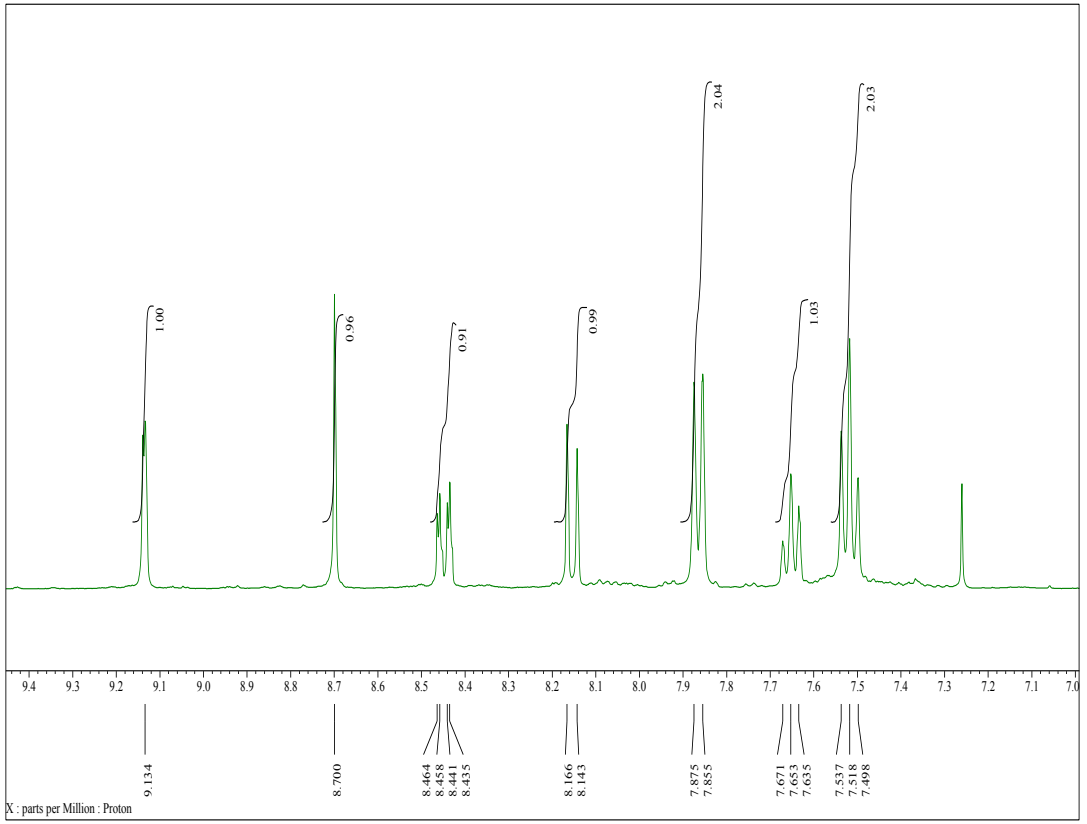
X : parts per Million : Proton

Solvent: $CDCl_3$
Spectrometer Frequency: 100 MHz



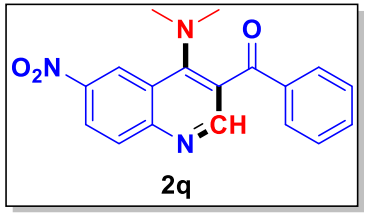
2p





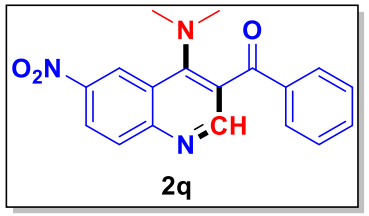
Solvent: $CDCl_3$

Spectrometer Frequency: 400 MHz

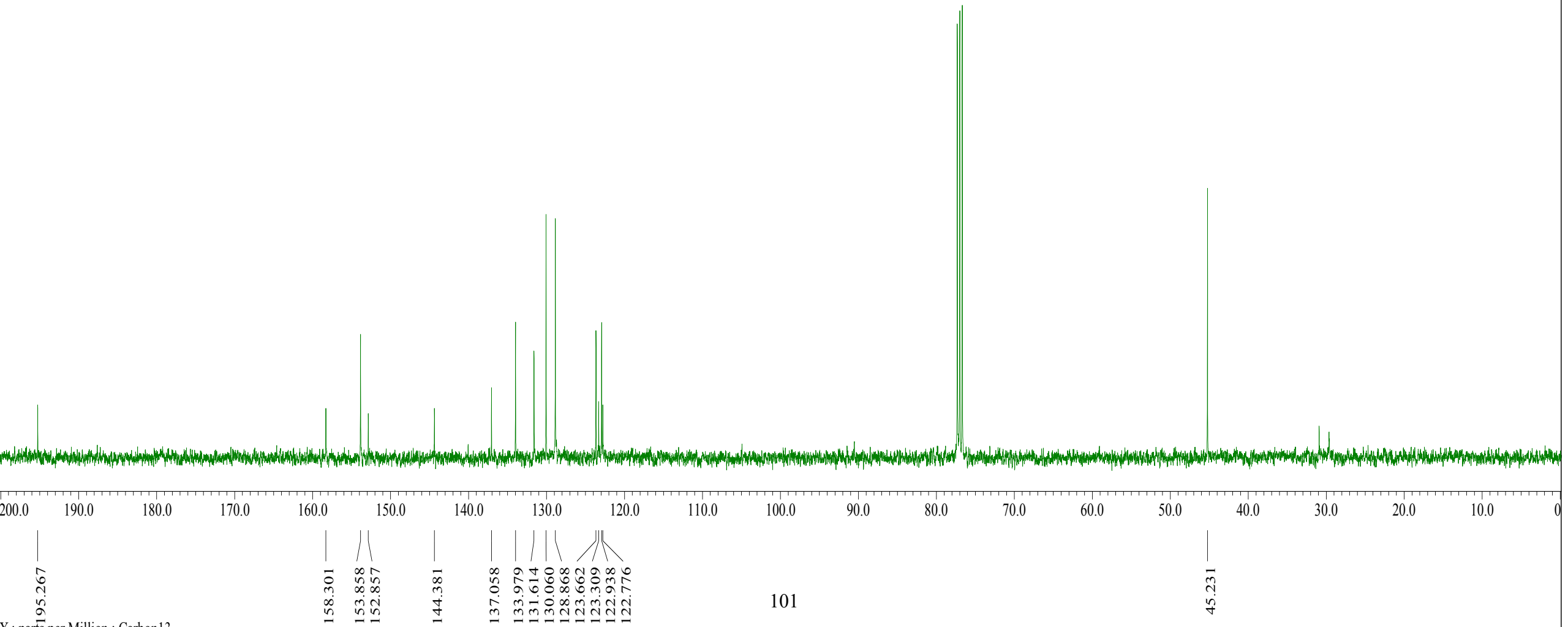


Solvent: $CDCl_3$

Spectrometer Frequency: 100 MHz

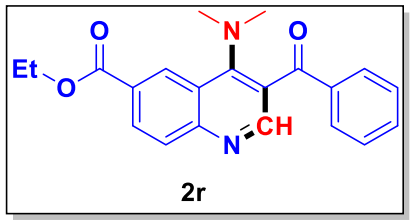


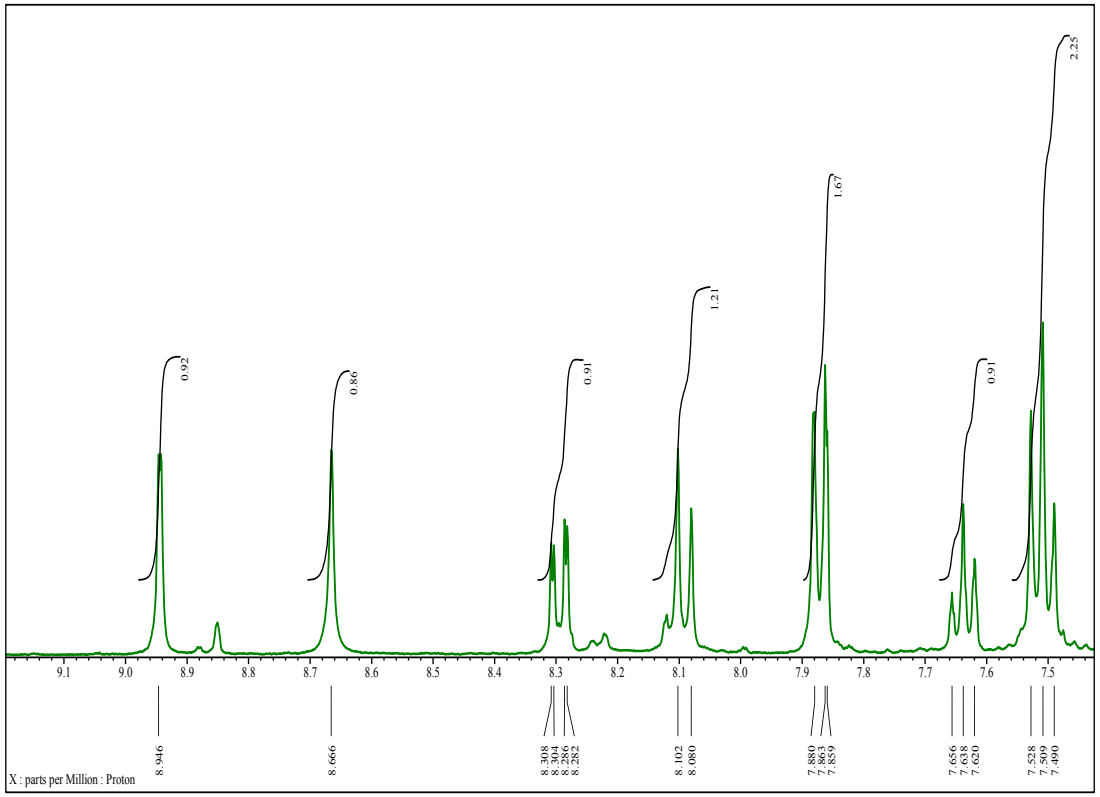
2q

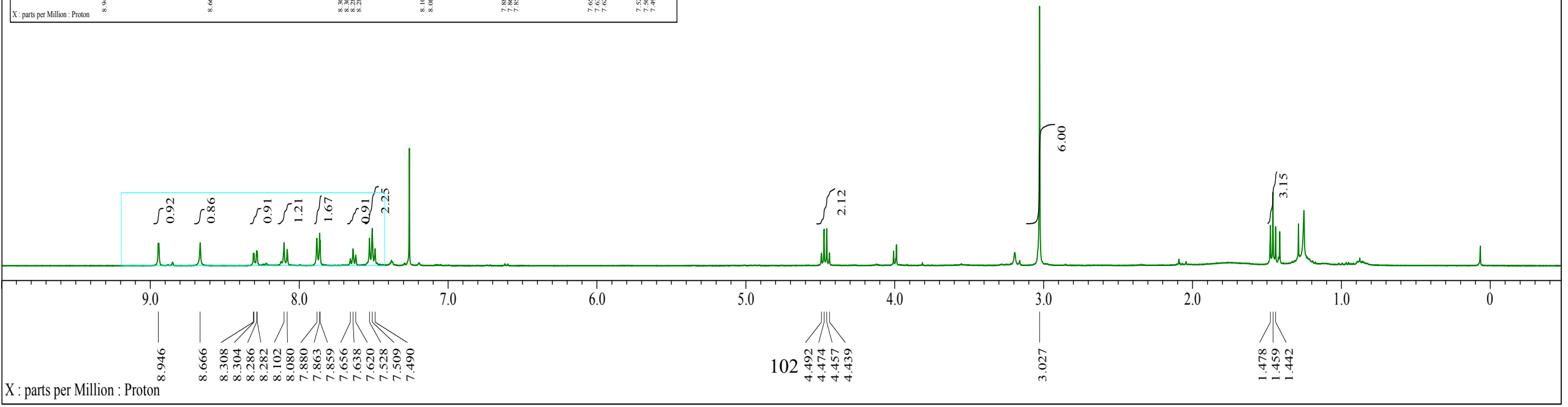


Solvent: $CDCl_3$

Spectrometer Frequency: 400 MHz

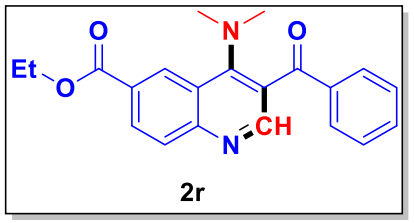




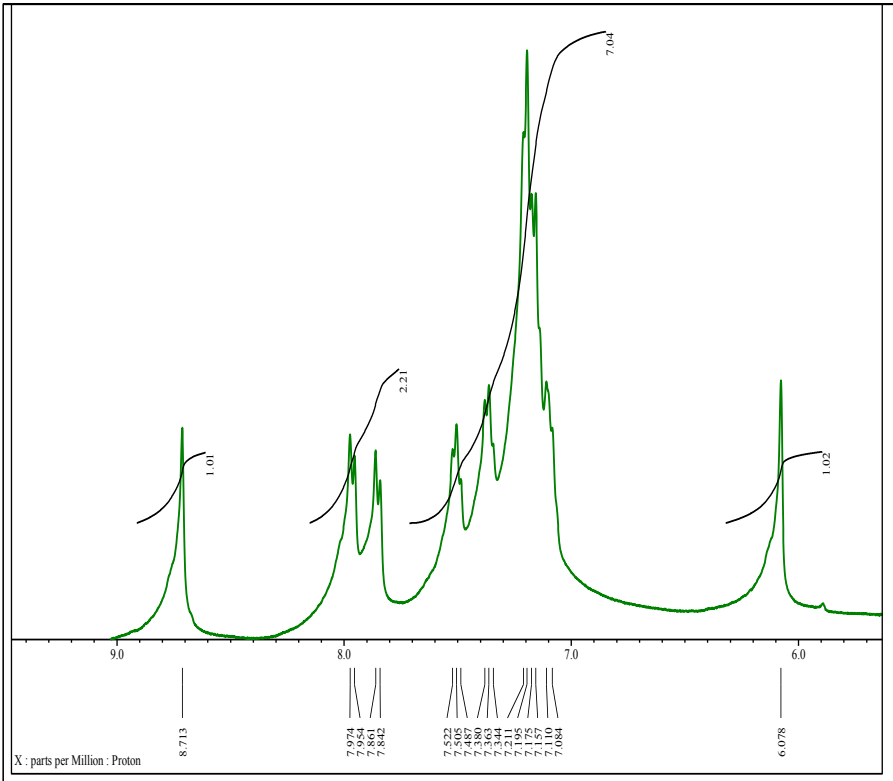


Solvent: $CDCl_3$

Spectrometer Frequency: 100 MHz

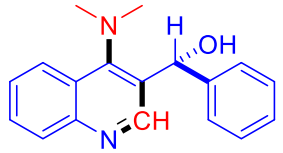


2r

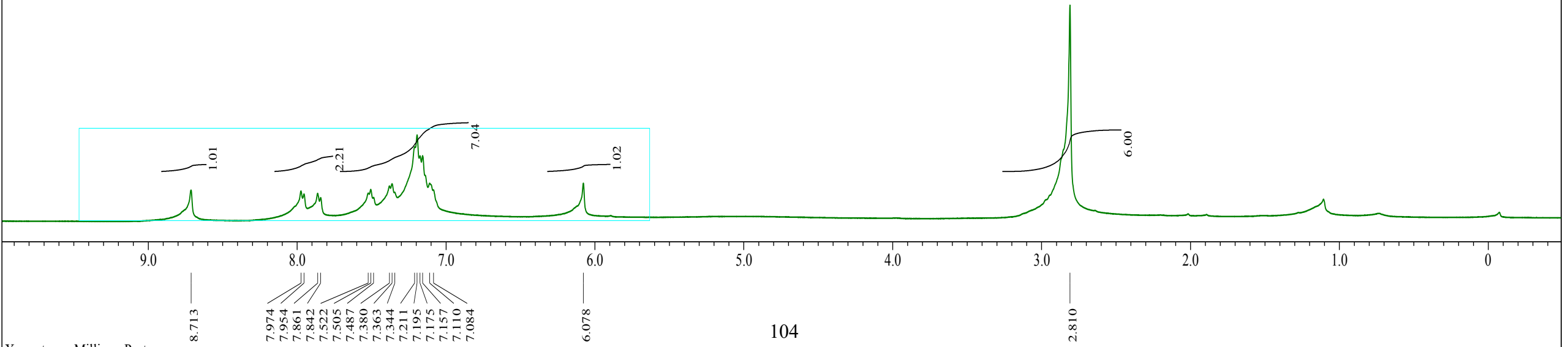


Solvent: $CDCl_3$

Spectrometer Frequency: 400 MHz

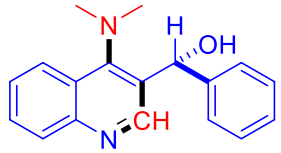


3 (racemic mixture)

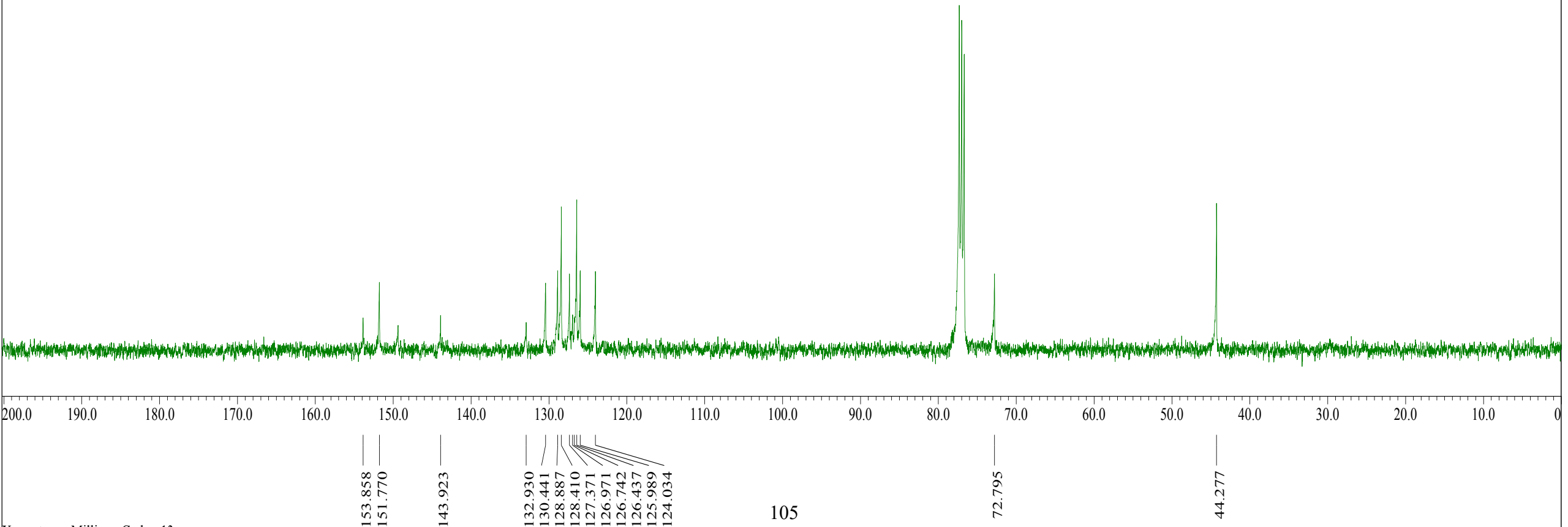


Solvent: $CDCl_3$

Spectrometer Frequency: 100 MHz



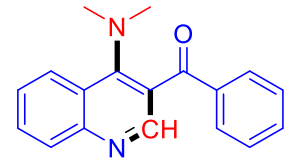
3 (racemic mixture)



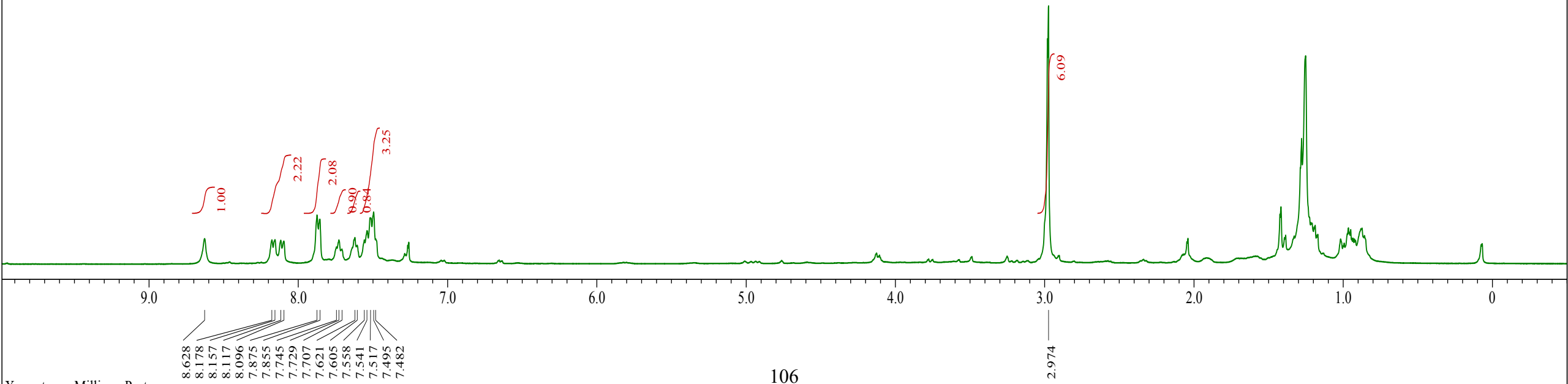
X : parts per Million : Carbon13

Solvent: $CDCl_3$

Spectrometer Frequency: 400 MHz



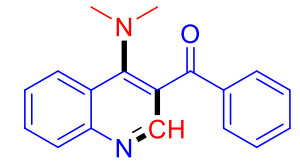
^{13}C labeled DMF experiment



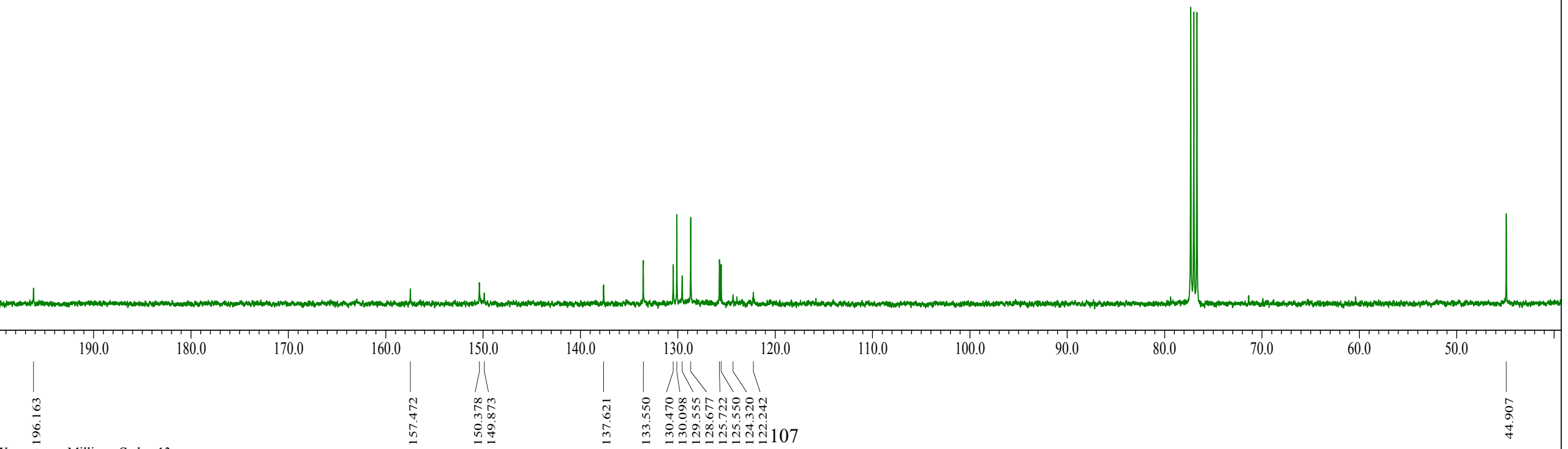
X : parts per Million : Proton

Solvent: $CDCl_3$

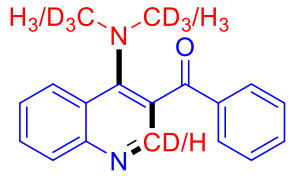
Spectrometer Frequency: 100 MHz



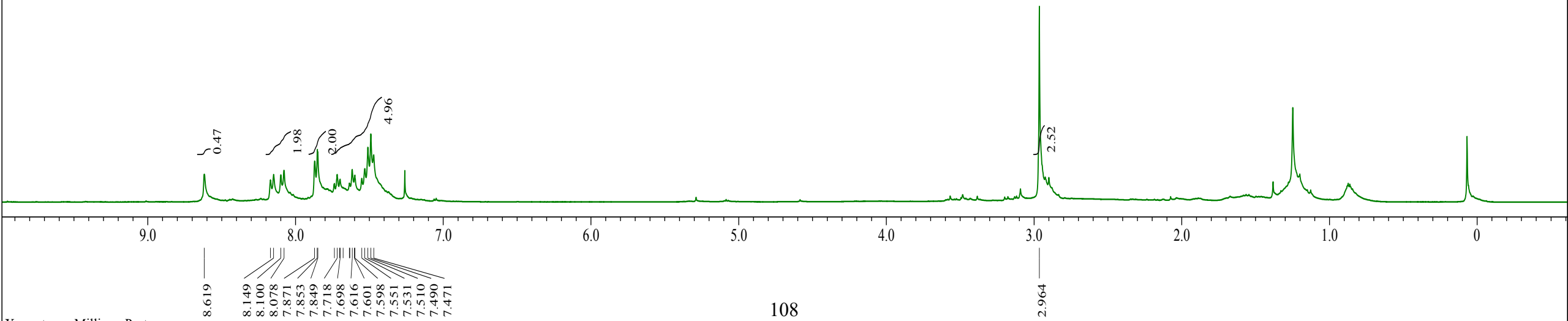
^{13}C labeled DMF experiment



Solvent: $CDCl_3$
Spectrometer Frequency: 400 MHz



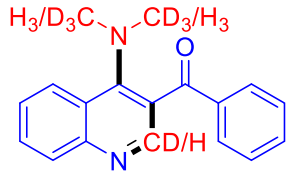
2a + 2a-d_7



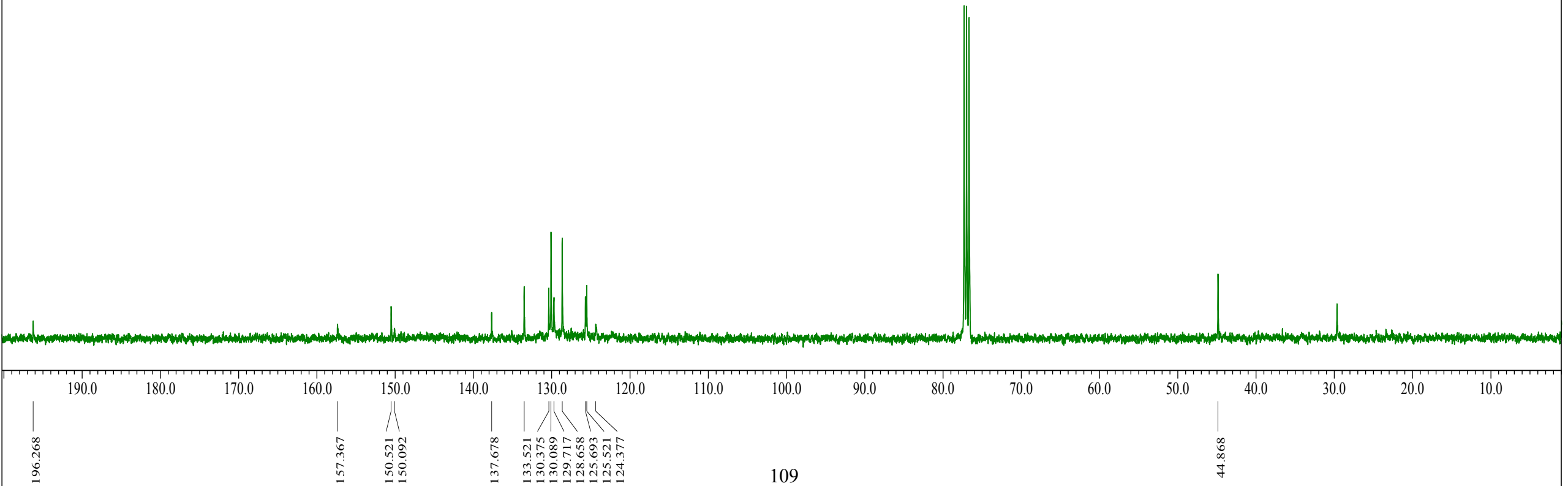
X : parts per Million : Proton

Solvent: $CDCl_3$

Spectrometer Frequency: 100 MHz



2a + 2a-d_7



X : parts per Million : Carbon13