Supporting Information

Palladium-Catalyzed Synthesis of Benzofurans via C-H Activation/Oxidation Tandem Reaction and Its Application to the Synthesis of Decursivine and Serotobenine

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General information

All reagents were obtained from commercial suppliers unless otherwise stated. Tetrahydrofuran (THF) and diethyl ether was distilled from potassium sodium alloys; Dichloromethane and acetonitrile was distilled from calcium hydride; Methanol was distilled from Magnesium and Iodine; Acetone was distilled from Potassium Permanganate. *N, N*-Dimethylacetamide (DMA) and *N, N*-dimethylformamide (DMF) was distilled from magnesium sulfate under vacuum. Flasks were flame-dried under vacuum and cooled under a stream of argon.

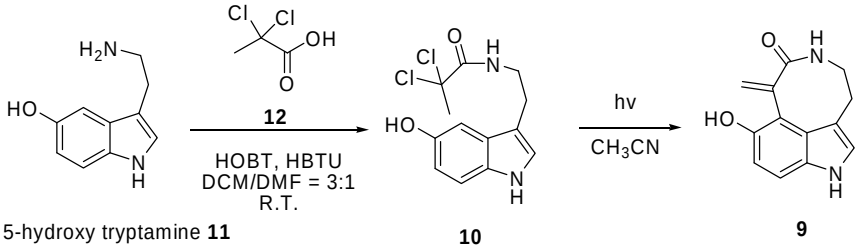
Flash chromatography was performed using silica gel (200-300 mesh) with solvents distilled prior to use. Visualization was achieved under a UV lamp (254 nm and 365 nm), and by developing the plates with phosphomolybdic acid or p-methoxybezaldehyde in ethanol.

Nuclear magnetic resonance [^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz)] spectra were determined on Bruker AVIII-400 spectrometers. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, quint: quintet, m: multiplet, br s: broad singlet for proton spectra and carbon spectra. Coupling constants (*J*) are reported in Hertz (Hz). Infrared spectra were recorded with a thin layer of the product on a KBr disk.

The following abbreviations are used: **EtOAc**: ethyl acetate; **THF**: Tetrahydrofuran; **DMA**: *N, N*-Dimethylacetamide; **PE**: petroleum ether; **CH_3CN**: acetonitrile; **TBAC**: tetrabutyl ammonium chloride; **DIPEA**: diisopropylethylamine; **HOBt**: 1-Hydroxybenzotriazole; **HBTU**: *O*-Benzotriazole- *N,N,N′,N′*-tetramethyluronium hexafluorophosphate; **PivOH**: Pivalic acid; **FCC**: flash column chromatography.

The total synthesis of decursivine、serotobenine and analogues

Synthesis of compound **9**



To a solution of compound **11** (2.13 g, 10.0 mmol**)** and acid **12** (1.25 mL, 12.0 mmol) in dry CH_2Cl_2/DMF (3:1, 120 mL) was added HBTU (4.93g, 13.0 mmol), HOBt (1.76 g, 13.0 mmol) and DIPEA (2.69 mL, 15.0 mmol) at 0 °C. The resulting mixture was allowed to warm to room temperature and stirred for 24 h. The solvent was removed at reduced pressure, and the residue was taken up with H_2O and extracted with EtOAc. The combined organic layers were washed with 5% HCl solution, saturated sodium bicarbonate solution, water and brine, dried over anhydrous Na_2SO_4, and concentrated at reduced pressure. Purification with FCC (PE: EtOAc = 2:1) afforded compound **10** (2.67 g, 89%) as foam like white solid.

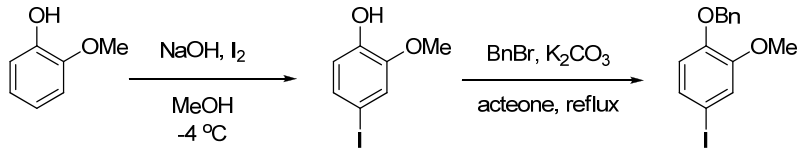
^{1}H NMR (400 MHz, Acteone-d_6) δ 9.75 (br s,1 H), 7.97 (br s, 1 H), 7.65 (br s, 1 H), 7.20 (d, J = 8.4 Hz, 1 H), 7.11 (d, J = 2.0 Hz, 1 H), 7.02 (d, J = 2.4 Hz, 1 H), 6.71(dd, J = 8.4, 2.0 Hz, 1 H), 3.54 (m, 2 H), 2.94 (t, J = 7.6 Hz, 2 H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, Acteone-d_6) δ 167.5 152.3, 133.3, 130.0, 124.9, 113.3, 113.2, 112.7, 104.2, 84.6, 42.6, 35.5, 26.5; IR (KBr) ν_{max}3392, 1678, 1526 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{13}H_{15}Cl_2N_2O_2$ $(M + H)^+$ 301.0505, found 301.0500.

A solution of compound **10** (300 mg, 1.0 mmol) in dry CH_3CN (220 mL) in a quartz flask was purged with dry argon for 30 min. This solution was irradiated on a 300 W high-pressure mercury lamp at room temperature for 5 h. The solvent was removed at reduced pressure. Purification with FCC (CH_2Cl_2: CH_3OH = 50:1) afforded compound **9** (100 mg, 45%) as faint yellow solid. Mp: 127 ^{o}C.

^{1}H NMR (400 MHz, 10% D_2O/DMSO-d_6) δ 10.78 (s, 1 H), 7.11 (d, J = 8.0 Hz, 1 H), 7.06 (s, 1 H), 6.70 (d, J = 8.0 Hz, 1 H), 5.44 (d, J = 1.2 Hz, 1 H), 5.39 (d, J = 1.2 Hz, 1 H), 3.92 (m, 1 H), 3.37 (m, 1 H), 3.02 (t, J = 5.6 Hz, 2 H); ^{13}C NMR (100 MHz, 10% D_2O/DMSO-d_6) δ 174.2, 147.7, 141.0, 131.4, 125.8, 124.9, 117.2, 114.0, 112.2, 111.3, 41.6, 29.6; IR (KBr) 3305, 1721, 1665, 1459, 1377, 1255, 1102 cm^{-1}; HRMS

(ESI) *m/z* calcd for $C_{13}H_{13}N_2O_2$ $(M + H)^+$ 229.0972, found 229.0970;

Synthesis of Iodobenzene **8c**

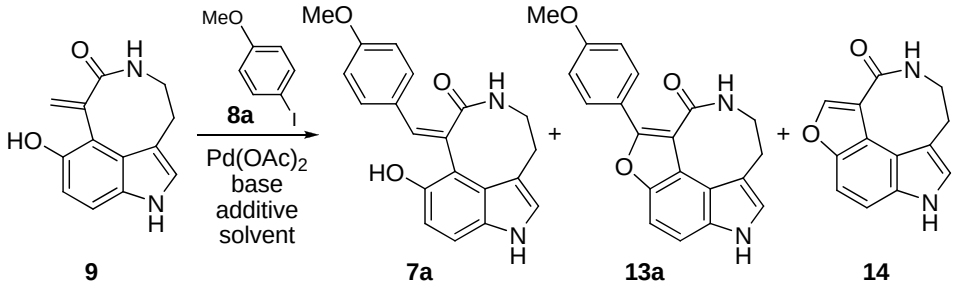


Guaiacol **8c**

To a solution of Guaiacol (1.03 g, 8.3 mmol) and NaOH (0.61 g, 15.3 mmol) in MeOH (20 mL) was added I_2 (2.15 g, 8.47 mmol) at -4 °C. The mixture was stirred at -4 °C for 1 h and poured into H_2O. The product was extracted with EtOAc twice, and the combined organic layers were washed with aq. $Na_2S_2O_3$ and brine, dried over Na_2SO_4, and concentrated to afford colorless oil. Then the residual oil was dissolved in acetone (20 mL), K_2CO_3 (2.29 g, 16.6 mmol) and BnBr (1.01 mL, 8.5 mmol) were successively added. The mixture was refluxed overnight. The solvent was removed at reduced pressure, and the residue was taken up with H_2O and extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, concentrated at reduced pressure. Purification with FCC (PE: EtOAc = 20:1) afforded compound **8c** (1.89 g, 67%) as white solid; Mp: 173 ^oC.

^1H NMR (400 MHz, $CDCl_3$) δ 7.43-7.30 (m, 5 H), 7.17-7.14 (m, 2 H), 6.62 (d, J = 8.8 Hz, 1 H), 5.12 (s, 2 H), 3.86 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 148.3, 136.7, 129.7, 128.6, 128.0, 127.2, 120.9, 116.0, 83.1, 71.1, 56.2; IR (KBr) ν_{max} 3062, 3031, 2935, 2905, 1581, 1501, 1454, 1249 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{14}H_{12}IO_2(M - H)^-$ 338.9882, found 338.9884.

Optimization of the tandem reaction conditions [a]

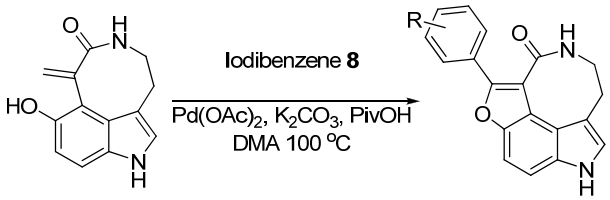


9 **7a** **13a** **14**

Entry	Ligand	Additive	Temperature(^{o}C)	Solvent	13a Yield (%)[b]
1[c]	---	TBAC	R.T.	CH_3CN	17
2	PPh_3	---	R.T.	DMA	28
3	$PCy_3 \cdot HBF_4$	---	100	DMA	23
4	$PCy_3 \cdot HBF_4$	PivOH	100	DMA	40
5	---	PivOH	100	DMA	61
6	---	---	100	DMA	25
7	$P(t\text{-}Bu)_3 \cdot HBF_4$	---	100	DMA	32
8	---	PivOH	100	DMF	33
9	---	PivOH	100	DMSO	6
10	---	PivOH	60	DMA	30

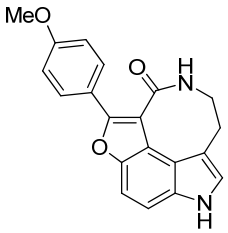
[a] Reaction conditions: 9 (0.1 mmol), 8a (0.3 mmol), $Pd(OAc)_2$ (0.01 mmol), additive (0.3 mmol), Ligand 0.03 mmol, K_2CO_3 (0.15 mmol) in solvent (2.0 mL). [b] Isolated yields. [c] $NaHCO_3$ (0.3 mmol) as base, 0.03 mmol TBAC was used.

General procedure for synthesis of compound **13**

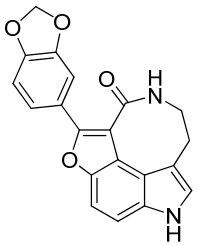


9 **13**

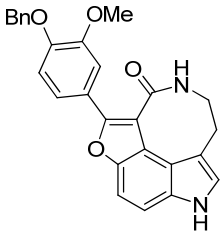
A solution of compound **9** (0.3 mmol), iodibenzene **8** (0.9 mmol), PivOH (91.8 mg, 0.9 mmol), K_2CO_3 (62.1 mg, 0.45 mmol) in dry DMA (6 mL) was degassed with dry argon for 20 min. $Pd(OAc)_2$ (6.7 mg, 0.03 mmol) was added to the reaction and the resulting reaction mixture was stirred at 100 °C for 6 hours. The residue was taken up with H_2O and extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated at reduced pressure. Purification with FCC (CH_2Cl_2: MeOH = 80:1) afforded compound **13**.



Compound 13a. Faint yellow solid (59.6 mg, 60%); Mp: 290 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.24 (s, 1 H), 8.14 (t, J = 7.6 Hz, 1 H), 7.81 (d, J = 8.8 Hz, 2 H), 7.37 (s, 2 H), 7.23 (s, 1 H), 7.02 (d, J = 8.8 Hz, 2 H), 3.82 (s, 4 H), 3.60 (br s, 1 H), 3.20 (br s, 1 H), 2.99 (br s, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.9, 159.8, 157.4, 147.3, 133.1, 129.6, 123.1, 122.9, 118.4, 117.8, 113.7, 113.6, 111.0, 109.5, 105.0, 55.2, 40.7, 30.4; IR (KBr) ν_{max} 3281, 2925, 1626, 1581, 1562, 1503, 1469, 1252 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{15}N_2O_3(M - H)^-$ 331.1083, found 331.1082.

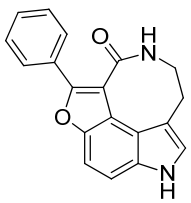


Compound 13b. Faint yellow solid (64.2 mg, 62%); Mp: 263 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.25 (s, 1 H), 8.17 (t, J = 7.6 Hz, 1 H), 7.40 (dd, J = 8.2, 1.8 Hz, 1 H), 7.39-7.34 (m, 3 H), 7.23 (d, J = 2.4 Hz, 1 H), 7.02 (d, J = 8.2 Hz, 1 H), 6.10 (s, 2 H), 3.80 (br s, 1 H), 3.60 (br s, 1 H), 3.20 (br s, 1 H), 2.96 (br s, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.3, 157.4, 148.4, 147.7, 147.5, 133.5, 124.7, 123.7, 122.9, 118.8, 118.2, 114.2, 112.0, 110.2, 108.8, 108.6, 105.5, 101.9, 41.2, 30.8; IR (KBr) ν_{max} 3426, 2937, 2852, 1736, 1696, 1587, 1531, 1455, 1254 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{13}N_2O_4(M - H)^-$ 345.0875, found 345.0868.

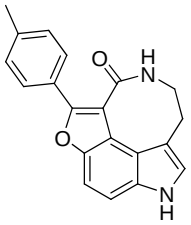


Compound 13c. Faint yellow solid (56.6 mg, 43%); Mp: 287 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.25 (s, 1 H), 8.19 (t, J = 7.6 Hz, 1 H), 7.52- 7.48 (m, 3 H), 7.45- 7.34 (m, 6 H), 7.24 (s, 1 H), 7.14 (d, J = 8.6 Hz, 1 H), 5.17 (s, 2 H), 3.84 (s, 4 H), 3.60 (br s, 1 H), 3.21 (br s, 1 H), 2.99 (br s, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.9, 157.1, 148.7, 148.4, 147.3, 136.9, 133.1, 128.4,

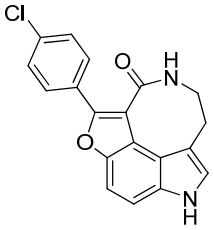
127.9, 127.8, 123.2, 123.1, 121.3, 118.5, 117.8, 113.8, 112.9, 111.9, 111.3, 109.6, 105.0, 79.1, 55.6, 40.7, 30.4; IR (KBr) ν_{max} 3359, 2955, 2923, 1629, 1502, 1451, 1250 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{27}H_{23}N_2O_4(M + H)^+$ 439.1658, found 439.1655.



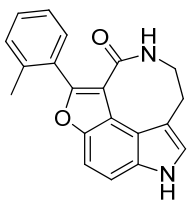
Compound 13d. Faint yellow solid (61.8 mg, 68%); Mp: 249 ^oC; ^1H NMR (400 MHz, DMSO-d_6) δ 11.29 (s, 1 H),8.20 (t, J = 7.6 Hz, 1 H), 7.85 (d, J = 6.8 Hz, 2 H), 7.48-7.40 (m, 5 H), 7.25 (d, J = 2.4 Hz, 1 H) 3.83 (br s, 1 H), 3.61 (br s, 1 H), 3.21 (br s, 1 H), 3.00 (br s, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.7, 157.1, 147.7, 133.0, 130.3, 128.9, 128.1, 128.0, 123.2, 118.3, 117.8, 113.8, 112.5, 110.1, 105.1, 40.7, 30.4; IR (KBr) ν_{max} 3417, 2256, 2128, 1649, 1048 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{19}H_{15}N_2O_2$ $(M + H)^+$ 303.1134, found 303.1134.



Compound 13e. Faint yellow solid (52.3 mg, 55%); Mp: 256 ^oC; ^1H NMR (400 MHz, DMSO-d_6) δ 11.25 (s, 1 H), 8.17 (t, J = 7.6 Hz, 1 H), 7.74 (d, J = 8.2 Hz, 2 H), 7.38 (s, 2 H), 7.28 (d, J = 8.2 Hz, 2 H), 7.24 (d, J = 2.0 Hz, 1 H), 3.82 (br s, 1 H), 3.60 (br s, 1 H), 3.23 (br s, 1 H), 2.97 (br s, 1 H), 2.37 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.8, 157.4, 147.5, 138.6, 133.0, 128.7, 128.0, 127.6, 123.2, 118.4, 117.8, 113.8, 111.9, 109.8, 105.0, 40.7, 30.4, 20.9; IR (KBr) ν_{max} 3422, 1657, 1026, 1049 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{17}N_2O_2(M + H)^+$ 317.1290, found 317.1286.



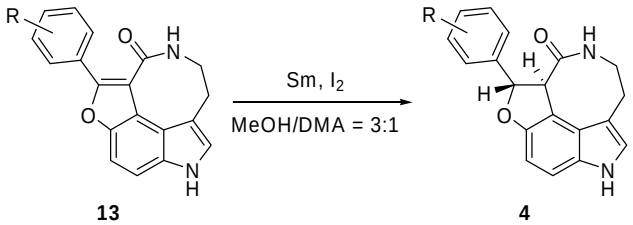
Compound 13f. Yellow solid (26.1 mg, 26%); Mp: 244 ^oC; ^1H NMR (400 MHz, DMSO-d_6) δ 11.31 (s, 1 H), 8.26 (t, J = 7.6 Hz, 1 H), 7.88 (d, J = 8.6 Hz, 2 H), 7.53 (d, J = 8.6 Hz, 2 H), 7.43 (d, J = 8.8 Hz, 1 H), 7.39 (d, J = 8.8 Hz, 1 H), 7.26 (s, 1 H), 3.82 (br s, 1 H), 3.62 (br s, 1 H), 3.22 (br s, 1 H), 2.99 (br s, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.5, 155.7, 147.8, 133.5, 133.1, 129.7, 129.1, 128.2, 123.3, 118.2, 117.8, 113.8, 113.1, 110.4, 105.0, 40.7, 30.3; IR (KBr) ν_{max} 3226, 2924, 1734, 1601, 1506, 1449, 1025 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{19}H_{12}N_2O_2Cl(M - H)^-$ 335.0587, found 335.0588.



Compound 13g. Faint yellow solid (29.5 mg, 31%); Mp: 251 ^oC; ^1H NMR (400 MHz, DMSO-d_6) δ 11.24 (s, 1 H), 8.08 (t, J = 7.6 Hz, 1 H), 7.51 (d, J = 7.5 Hz, 1 H), 7.41-7.25 (m, 6 H), 3.81 (br s, 1 H), 3.59 (br s, 1 H), 3.24 (br s, 1 H), 2.93 (br s, 1 H), 2.31 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.3, 158.1, 148.0, 137.0, 133.0, 131.1, 130.1, 130.0, 128.9, 125.3, 123.0, 117.9, 117.3, 114.4, 113.9, 109.6, 105.1, 40.6, 30.5, 19.8; IR (KBr) ν_{max} 3422, 2254, 2127, 1654, 1050, 1026

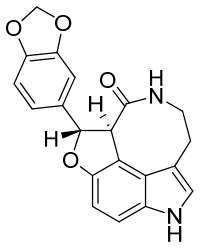
cm^{-1}HRMS (ESI) *m/z* calcd. for $C_{20}H_{17}N_2O_2(M + H)^+$ 317.1288, found 317.1290.

General procedure for synthesis of decursivine **(1)** and compound **4**

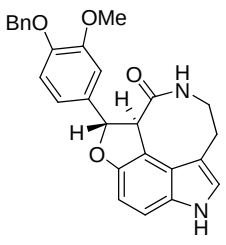


13 **4**

A solution of **13** (0.1 mmol) in MeOH/DMA (3:1, 4 mL) was degassed with dry argon for 20 min. Metallic samarium (300 mg, 2.0 mmol) and iodine (169 mg, 0.67 mmol) was added under an argon atmosphere. The reaction mixture was stirred at room temperature under an argon atmosphere for 2 h. The reaction mixture was evaporated to 1.0 mL and 0.1 N hydrochloric acid was added. The mixture was stirred vigorously to make clear solution. The product was extracted from acidic solution with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated at reduced pressure. Purification with FCC (CH_2Cl_2: MeOH = 100: 1) afforded decursivine **(1)** or compound **4**.

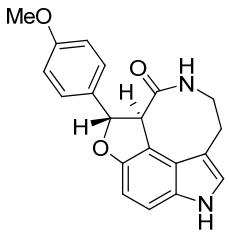


Decursivine (1). Faint yellow solid (27.1 mg, 78%); Mp: 251 ^{o}C; ^{1}H NMR (400 MHz, pyridine-d_5) δ 12.03 (br s, 1 H), 8.82 (dd, J = 10.0, 4.4 Hz, 1 H), 7.46 (d, J = 8.4 Hz, 1 H), 7.36 (d, J = 0.9 Hz, 1 H), 7.28 (dd, J = 9.6, 1.2 Hz, 1 H), 7.27 (s, 1 H), 7.06 (d, J = 8.4 Hz, 1 H), 7.04 (d, J = 8.8 Hz, 1 H), 6.91 (d, J = 8.0 Hz, 1 H), 5.95 (m, 2 H), 5.03 (d, J = 9.6 Hz, 1 H), 4.15 (m, 1 H), 3.57 (m, 1 H), 3.16 (m, 2 H); ^{13}C NMR (100 MHz, pyridine-d_5) δ 171.6, 153.5, 148.5, 147.7, 137.0, 134.1, 125.8, 123.9, 120.2, 114.8, 112.2, 111.9, 108.6, 107.4, 105.3, 101.6, 85.1, 55.7, 41.3, 30.6; IR (KBr) 3407, 2921, 1649, 1501, 1487, 1443, 1250, 1038 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{20}H_{16}N_2NaO_4$ $(M + Na)^+$ 371.1002; found 371.0999.

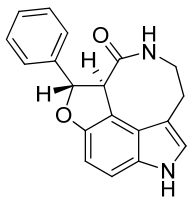


Compound 4c. Faint yellow, foam like solid (33.4 mg, 76%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.92 (br s, 1 H), 7.86 (dd, J = 10.0, 4.4 Hz, 1 H), 7.30-7.42 (m, 4 H), 7.20 (d, J = 8.8 Hz, 2 H), 7.14 (s, 1 H),7.01 (d, J = 8.0 Hz, 1 H), 7.01 (d, J = 2.8 Hz, 1 H), 6.90 (d, J = 8.0 Hz, 1 H), 6.56 (d, J = 8.8 Hz, 1 H), 6.11 (d, J = 9.6 Hz, 1 H),

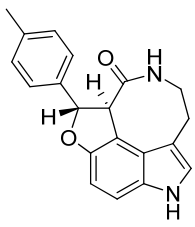
5.05 (s, 2 H), 4.74 (d, J = 9.6 Hz, 1 H), 3.98-4.04 (m, 1 H), 3.73(s, 3 H), 3.34-3.37 (m, 1 H), 2.86-3.07 (m, 2 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 171.0, 152.1, 149.6, 147.9, 137.4, 134.3, 132.8, 128.8, 128.2, 128.1, 125.4, 122.8, 119.2, 114.1, 113.9, 111.8, 111.0, 110.7, 104.5, 84.3, 70.3, 56.0, 53.6, 40.4, 29.6; IR (KBr) 3413, 2923, 1649, 1512, 1447, 1265 cm-1; HRMS (ESI) *m/z* calcd for $C_{27}H_{24}N_2NaO_4$ $(M + Na)^+$ 463.1628; found 463.1624.



Compound 4a. Faint yellow, foam like solid (26.3 mg, 79%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.95 (s, 1 H), 7.88 (dd, J = 9.6, 4.0 Hz, 1 H), 7.36 (d, J = 8.4 Hz, 2 H), 7.20 (d, J = 8.4 Hz, 1 H), 7.16 (s, 1 H), 6.95 (d, J = 8.4 Hz, 2 H), 6.67 (d, J = 8.4 Hz, 1 H), 6.18 (d, J = 9.6 Hz, 1 H), 4.72 (d, J = 9.6 Hz, 1 H), 4.03 (m, 1 H), 3.76 (s, 3 H), 3.38 (m, 1 H), 3.06 (m, 1 H), 2.92 (m, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 170.4, 159.0, 151.8, 133.3, 132.5, 127.7, 125.2, 122.5, 113.9, 113.8, 111.4, 110.7, 104.1, 83.7, 55.1, 53.4, 40.1, 29.4; IR (KBr) 3418, 2966, 2901, 1737, 1661, 1515, 1490, 1444, 1368, 1251, 1037 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{20}H_{19}N_2O_3$ $(M + H)^+$ 335.1390, found 335.1387.

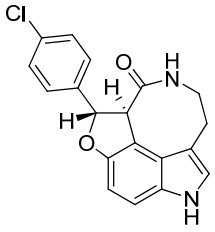


Compound 4d. Faint yellow, foam like solid (23.7 mg, 78%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.97 (br s, 1 H), 7.92 (dd, J = 9.6, 4.0 Hz, 1 H), 7.31-7.43 (m, 4 H), 7.20 (d, J = 8.4 Hz, 2 H), 7.16 (s, 1 H), 6.69 (d, J = 8.4 Hz, 1 H), 6.24 (d, J = 9.6 Hz, 1 H), 4.73 (d, J = 9.6 Hz, 1 H), 4.04 (m, 1 H), 3.37 (m, 1 H), 3.05 (dd, J = 16.4, 3.2 Hz, 1 H), 2.91 (m, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 170.4, 151.8, 141.5, 132.6, 128.5, 127.8, 126.1, 125.2, 122.5, 113.7, 111.5, 110.7, 104.1, 83.8, 53.6, 40.1, 29.4; IR (KBr) 3358, 2921, 1656 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{16}N_2NaO_2$ $(M + Na)^+$ 327.1104, found 327.1102.



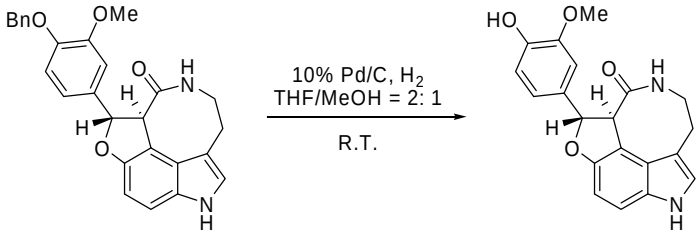
Compound 4e. Faint yellow, foam like solid (25.8 mg, 81%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.96 (s, 1 H), 7.89 (m, 1 H), 7.32 (d, J = 8.0 Hz, 2 H), 7.20 (d, J = 8.0 Hz, 2 H), 7.19 (d, J = 8.4 Hz, 1 H), 7.16 (d, J = 2.0 Hz, 1 H), 6.68 (d, J = 8.4 Hz, 1 H), 6.22 (d, J = 9.6

Hz, 1 H), 4.70 (d, J = 9.6 Hz, 1 H), 4.04 (m, 1 H), 3.36 (m, 1 H), 3.06 (m, 1 H), 2.91 (m, 1 H), 2.31 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 170.4, 151.8, 138.6, 137.0, 132.5, 129.0, 126.0, 125.1, 122.4, 113.7, 111.4, 110.6, 104.0, 83.7, 53.5, 40.1, 29.4, 20.7; IR (KBr) 3433, 3364, 2923, 1658, 1484, 1251 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{40}H_{36}N_4O_4Na$ $(2M + Na)^+$ 659.2629; found 659.2636.



Compound 4f. Faint yellow, foam like solid (24.2 mg, 75%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.97 (br s, 1 H), 7.93 (m, 1 H), 7.54-7.39 (m, 4 H), 7.22 (d, J = 8.8 Hz, 1 H), 7.17 (d, J = 2.0 Hz, 1 H), 6.70 (d, J = 8.8 Hz, 1 H), 6.25 (d, J = 9.6 Hz, 1 H), 4.75 (d, J = 9.6 Hz, 1 H), 4.04 (m, 1 H), 3.36 (m, 1 H), 3.06 (m, 1 H), 2.92 (m, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 170.2, 151.6, 140.4, 132.6, 132.3, 128.5, 127.9, 125.2, 122.4, 113.6, 111.4, 110.6, 104.0, 83.0, 53.5, 40.0, 29.3; IR (KBr) 3354, 2921, 1658, 1490, 1432, 1250, 1091 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{38}H_{30}Cl_2N_4O_4Na$ $(2M + Na)^+$ 699.1536; found 699.1525.

Synthesis of **Serotobenine (2)**



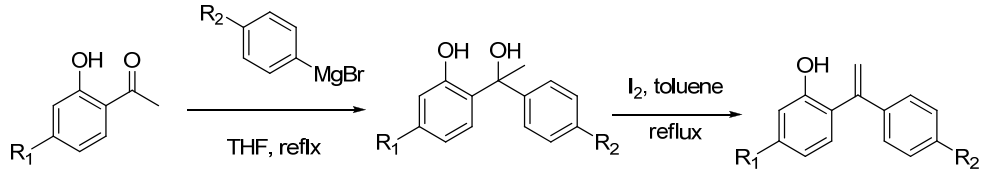
4c serotobenine (**2**)

To a solution of **4c** (30 mg, 0.068 mmol) in THF/MeOH (2:1, 12 mL) was added 10% Pd/C (15 mg) at room temperature, and then the reaction mixture was stirred under H_2 atomosphere for 3 h. The reaction mixture was filtered through a pad of celite, the filtrate was concentrated under reduced pressure to afforded Serotobenine **(2)** (24 mg, 99%) as faint yellow, foam like solid.

^{1}H NMR (400 MHz, pyridine-d_5) δ 12.03 (br s, 1 H), 11.1 (br s, 1 H), 8.79 (dd, J = 10.0, 3.6 Hz, 1 H), 7.51 (d, J = 1.0 Hz, 1 H), 7.46 (d, J = 8.8, 1 H), 7.43 (dd, J = 8.4, 1.6 Hz, 1 H), 7.29 (d, J = 8.0 Hz, 1 H), 7.26 (s, 1 H), 7.14 (d, J = 9.6 Hz, 1 H), 7.09 (d, J = 8.4 Hz, 1 H), 5.14 (d, J = 9.6 Hz, 1 H), 4.15 (m, 1 H), 3.66 (s, 3 H), 3.55 (m, 1 H), 3.15 (m, 2 H); ^{13}C NMR (100 MHz, pyridine-d_5) δ 171.9, 153.7, 148.9, 148.2, 134.1, 134.0, 125.8, 124.0, 120.1, 116.7, 115.0, 112.2, 111.9, 111.2, 105.3, 85.6, 55.9, 55.7, 41.3, 30.6; IR (KBr) 3419, 2925, 1650, 1519, 1435, 1280 cm^{-1}; HRMS (ESI) *m/z*

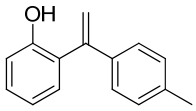
calcd for $C_{20}H_{18}N_2NaO_4$ $(M + Na)^+$ 373.1159; found 373.1155.

General procedure for synthesis of 2-hydroxystyrene 15a-15e

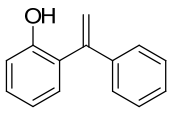


15a-15e

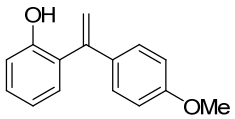
To a solution of *o*-hyrdoxyacetophenone (14.7 mmol) in dry THF (20 mL) was added arylmagnesium bromide solution (32.3 mmol 2.2 equiv) at 0 °C. The solution was warmed to reflux temperature and stirred for 8 h. The reaction mixture was cooled to 0 °C and then 15% AcOH aq. was added. The aqueous layer was extracted with EtOAc three times and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The obtained residue was dissolved in toluene (10 mL), and then 10.0 mg I_2 was added. The mixture was stirred at reflux temperature overnight. The reaction mixture was cooled to room temperature, washed with aq. $Na_2S_2O_3$ and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. Purification with FCC (PE: EtOAc = 10:1) afforded compound **15**.



Compound 15a. Faint yellow liquid (2.47 g, 11.8 mmol, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.26 (m, 3 H), 7.19-7.17 (m, 3 H), 7.00-6.95 (m, 2 H), 5.85 (d, J = 1.2 Hz, 1 H), 5.39 (d, J = 1.2 Hz, 1 H), 5.32 (s, 1 H), 2.39 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 145.1, 138.5, 136.5, 130.4, 129.4, 129.3, 127.7, 126.9, 120.3, 115.8, 21.1; IR (KBr) ν_{max} 3519, 3084, 1607, 1579, 1510, 1486, 1451 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{15}H_{13}O(M - H)^-$ 209.0966, found 209.0967.

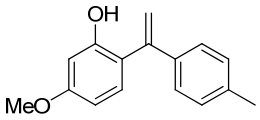


Compound 15b. Faint yellow liquid (2.42 g, 12.3 mmol, 84%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.36 (m, 4 H), 7.30 (td, J = 7.8, 1.7 Hz, 1 H), 7.19 (dd, J = 7.6, 1.7 Hz, 1 H), 7.01-6.96 (m, 2 H), 5.91 (d, J = 1.2 Hz, 1 H), 5.46 (d, J = 1.2 Hz, 1 H), 5.24 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 138.2, 132.4, 123.4, 122.4, 121.6, 121.5, 120.5, 120.0, 113.4, 109.7, 108.8; IR (KBr) ν_{max} 3514, 3057, 1604, 1578, 1487, 1449, 1238 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{14}H_{11}O(M - H)^-$ 195.0810, found 195.0812.

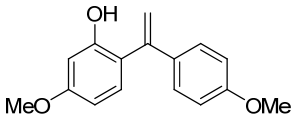


Compound 15c. Faint yellow solid (2.76 g, 12.2 mmol, 83%); Mp: 72 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.9 Hz, 2 H), 7.26 (td, J = 7.8, 1.7 Hz, 1 H), 7.15 (dd, J = 7.6, 1.7 Hz, 1 H), 6.96-6.91 (m, 2 H), 6.87 (d, J = 8.9 Hz, 2 H), 5.78 (d, J = 1.2 Hz, 1 H), 5.31 (d, J =

1.2 Hz, 1 H), 5.21 (s, 1 H), 3.82 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 153.1, 144.5, 131.7, 130.4, 129.4, 128.3, 127.7, 120.4, 115.7, 114.9, 114.1, 55.3; IR (KBr) ν_{max} 3442, 3090, 3033, 2980, 2938 , 1895, 1821, 1604, 1578, 1510, 1484, 1446, 1251 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{15}H_{13}O_2(M - H)^-$ 225.0916, found 225.0924.

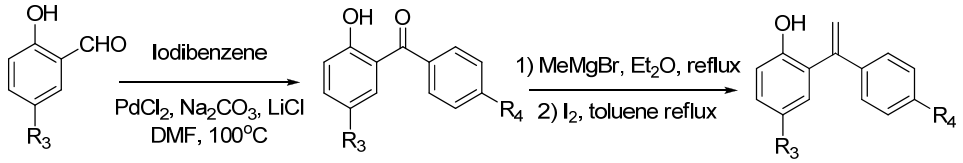


Compound 15d. Faint yellow liquid (2.70 g, 11.3 mmol, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 8.0 Hz, 2 H), 7.15 (d, J = 8.0 Hz, 2 H), 7.04 (d, J = 8.2 Hz, 1 H), 6.52 (m, 2 H), 5.75 (d, J = 1.2 Hz, 1 H), 5.32 (d, J = 1.2 Hz, 1 H), 5.28 (s, 1 H), 3.81 (s, 3 H), 2.36 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 154.2, 144.9, 138.2, 136.9, 131.0, 129.2, 126.9, 120.2, 114.9, 106.5, 101.0, 55.1, 21.0; IR (KBr) ν_{max} 3511, 2919, 2836, 1620, 1574, 1505, 1445, 1250, 1147 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{16}H_{15}O_2(M - H)^-$ 239.1072, found 239.1075.



Compound 15e. Faint yellow solid (3.01 g, 11.7 mmol, 78%); Mp: 79 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.8 Hz, 2 H), 7.04 (d, J = 8.2 Hz, 1 H), 6.87 (d, J = 8.8 Hz, 2 H), 6.53-6.49 (m, 2 H), 5.70 (d, J = 1.2 Hz, 1 H), 5.34 (d, J = 1.2 Hz, 1 H), 5.27 (s, 1 H), 3.82 (s, 3 H), 3.81 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 160.0, 154.3, 144.4, 132.2, 131.0, 128.5, 120.2, 114.2, 114.0, 106.6, 101.0, 55.3; IR (KBr) ν_{max} 3437, 3091, 3040, 2998, 2970, 2936, 2837, 1891, 1811, 1619, 1575, 1507, 1446, 1245 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{16}H_{15}O_3(M - H)^-$ 255.1021, found 255.1020.

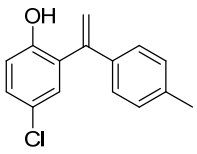
General procedure for synthesis of 2-hydroxystyrene 15f-15h



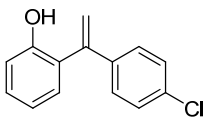
A solution of salicylaldehyde (7.98 mmol), iodibenzene (15.9 mmol), Na_2CO_3 (0.68 g, 16.0 mmol), LiCl (0.21 g, 1.4 mmol) in dry DMF (30 mL) was degassed with dry argon for 20 min. $PdCl_2$ (71.6 mg, 0.4 mmol) was added to the reaction and the resulting reaction mixture was stirred at 100 °C for 6 hours. The mixture was taken up with H_2O and extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated at reduced pressure. Purification with FCC (PE:CH_2Cl_2 = 2:1) afforded yellow solid compound. Within an over dried flask, the yellow solid was dissolved in aqueous diethyl ether

(10 mL), then a solution of MeMgBr (12.6 mmol) was added under an ice bath. The mixture was stirred under reflux for 16 h, and 15% AcOH aq. was added. The aqueous layer was extracted with EtOAc three times and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated.

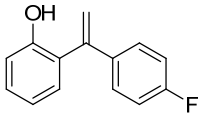
The obtained residue was dissolved in toluene (10 mL), and then 10.0 mg I_2 was added. The mixture was stirred at reflux temperature overnight. The reaction mixture was cooled to room temperature, washed with $Na_2S_2O_3$ aq. and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. Purification with FCC (PE: EtOAc = 10:1) afforded Compound **15f-15h**.



Compound 15f. Deep yellow liquid (1.17 g, 4.79 mmol, 60%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.26 (m, 2 H), 7.23 (dd, J = 8.6, 2.6 Hz, 1 H), 7.18 (d, J = 8.0 Hz, 2 H), 7.16 (d, J = 2.6 Hz, 1 H), 6.90 (d, J = 8.7 Hz, 1 H), 5.85 (d, J = 0.9 Hz, 1 H), 5.38 (d, J = 0.9 Hz, 1 H), 5.15 (s, 1 H), 2.38 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 144.1, 139.0, 135.7, 129.8, 129.6, 129.2, 129.1, 126.9, 125.2, 117.2, 116.6, 21.2; IR (KBr) ν_{max} 3516, 3026, 2921, 1605, 1570, 1510, 1478 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{15}H_{12}OCl(M - H)^-$ 243.0577, found 243.0580.

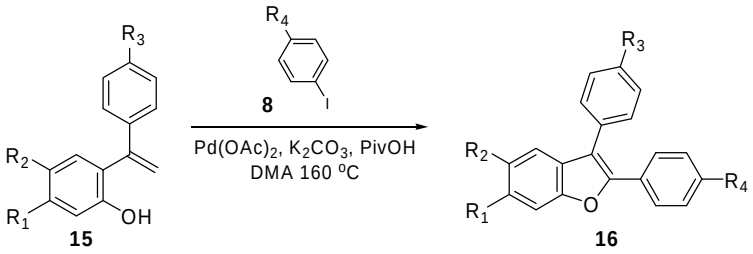


Compound 15g. Deep yellow liquid (1.25 g, 5.43 mmol, 68%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.28 (m, 4 H), 7.26-7.25 (m, 1 H), 7.10 (dd, J = 7.6, 1.6 Hz, 1 H), 6.96-6.91 (m, 2 H), 5.87 (d, J = 0.9 Hz, 1 H), 5.43 (d, J = 0.9 Hz, 1 H), 5.12 (brs, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 144.2, 138.0, 134.5, 130.4, 129.7, 128.8, 128.3, 127.1, 120.6, 117.0, 115.9; IR (KBr) ν_{max} 3510, 3417, 3061, 2976, 2931, 1603, 1579, 1488, 1450 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{14}H_{10}OCl(M - H)^-$ 229.0420, found 229.0419.

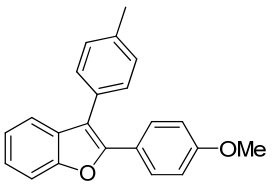


Compound 15h. Deep yellow liquid (0.97 g, 4.55 mmol, 57%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.33 (m, 2 H), 7.29-7.25(m, 1 H), 7.13 (dd, J = 7.6, 1.6 Hz, 1 H), 7.05-7.01 (m, 2 H), 6.98-6.92 (m, 2 H), 5.83 (d, J = 0.8 Hz, 1 H), 5.41 (d, J = 0.8 Hz, 1 H), 5.30 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0 (d, J_{F-C} = 246.7 Hz), 153.0, 144.2, 135.6 (d, J_{F-C} = 3.4 Hz), 130.4, 129.6, 128.8 (d, J_{F-C} = 8.0 Hz), 127.4, 120.6, 116.4 (d, J_{F-C} = 1.1 Hz), 115.9, 115.6, 115.4; IR (KBr) ν_{max} 3518, 3045, 1898, 1602, 1507, 1486, 1450, 1230 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{14}H_{10}OF(M - H)^-$ 213.0716, found 213.0721.

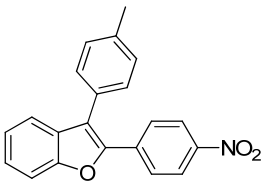
General procedure for the synthesis of benzofuran compounds 16



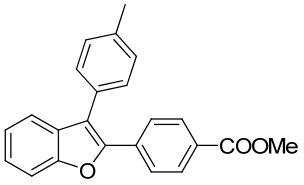
A solution of compound **15** (0.3 mmol), iodibenzene **8** (0.9 mmol), PivOH (91.8 mg, 0.9 mmol), K_2CO_3 (62.1 mg, 0.45 mmol) in dry DMA (6 mL) was degassed with dry argon for 20 min. $Pd(OAc)_2$ (6.7 mg, 0.03mmol) was added to the reaction and the resulting reaction mixture was stirred at 160 °C for 12 hours. The residue was taken up with H_2O and extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated at reduced pressure. Purification with FCC (PE: EtOAc = 100:1) afforded compound **16**.



Compound 16a. White solid (73.5 mg, 78%); Mp: 103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.1 Hz, 2 H), 7.56 (d, J = 8.1 Hz, 1 H), 7.52 (d, J = 7.6 Hz, 1 H), 7.43 (d, J = 6.7 Hz, 2 H), 7.34-7.29 (m, 3 H), 7.25(t, J = 7.2 Hz, 1 H), 6.88(d, J = 7.9 Hz, 2 H), 3.83 (s, 3 H), 2.47 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 153.8, 150.6, 137.1, 130.5, 130.0, 129.7, 129.6, 128.4, 124.1, 123.5, 122.7, 119.8, 116.0, 113.9, 111.9, 55.2, 21.3; IR (KBr) ν_{max} 3433, 3058, 2920, 1607, 1515, 1500, 1451, 1250 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{19}O_2$ $(M + H)^+$ 315.1380, found 315.1387.

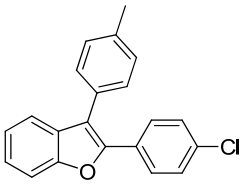


Compound 16b. Yellow needles (39.5 mg, 40%); Mp: 186 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 9.0 Hz, 2 H), 7.83 (d, J = 9.0 Hz, 2 H), 7.58 (d, J = 8.2 Hz, 1 H), 7.50 (d, J =7.8 Hz, 1H), 7.42-7.37 (m, 3 H), 7.35 (d, J = 8.0 Hz, 2 H), 7.27 (t, J = 7.5 Hz, 1 H), 2.47 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 147.7, 146.8, 138.3, 136.9, 130.1, 129.4, 128.8, 127.0, 126.0, 123.8, 123.4, 121.3, 120.7, 111.3, 21.4; IR (KBr) ν_{max} 3466, 2921, 2855, 1592, 1510, 1448, 1335 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{21}H_{16}NO_3$ $(M + H)^+$ 330.1125, found 330.1126.

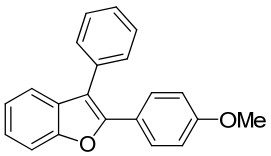


Compound 16c. Yellow solid (61.6 mg, 60%); Mp: 128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.5 Hz, 2 H), 7.75, (d, J = 8.5 Hz, 2 H), 7.57 (d, J = 8.2 Hz, 1 H), 7.51 (d, J = 7.7 Hz, 1 H), 7.40-7.35 (m, 3 H), 7.31 (d, J = 7.9 Hz, 2

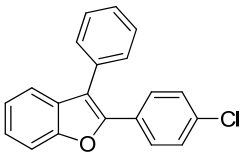
H), 7.26 (t, *J* = 7.5 Hz, 1 H), 3.91 (s, 3 H), 2.46 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 154.2, 149.1, 137.8, 137.7, 135.0, 130.2, 129.9, 129.7, 129.5, 129.3, 126.5, 125.4, 123.1, 120.5, 119.6, 111.2, 52.1, 21.4; IR (KBr) ν_{max} 3419, 2921, 1725, 1607, 1561, 1517, 1450, 1433, 1284 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{23}H_{19}O_3$ $(M + H)^+$ 343.1329, found 343.1328.



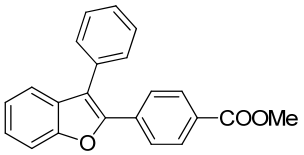
Compound 16d. White solid (69.6 mg, 73%); Mp: 114 ^{o}C; ^{1}NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.7 Hz, 2 H), 7.55 (d, *J* = 8.2 Hz, 1 H), 7.50 (d, *J* = 7.6 Hz, 1 H), 7.39 (d, *J* = 8.0 Hz, 2 H), 7.34 (dd, *J* = 8.2, 1.0 Hz, 1 H), 7.31-7.28 (m, 4 H), 7.25 (t, *J* = 7.4 Hz, 1 H), 2.46 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 149.2, 137.6, 134.1, 130.3, 129.8, 129.5, 129.4, 129.3, 128.7, 128.2, 124.9, 123.0, 120.2, 118.0, 111.1, 21.4; IR (KBr) ν_{max} 3449, 3054, 3030, 2920, 2854, 1651, 1585, 1513, 1485, 1450, 1401, 1375, 1253, 1201 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{21}H_{15}ClO$ $(M)^+$ 318.0806, found 318.0798.



Compound 16e. White solid (63.0 mg, 70%); Mp: 105 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.7 Hz, 2 H), 7.54-7.47 (m, 6 H), 7.42 (t, *J* = 7.6 Hz, 1 H), 7.32 (t, *J* = 7.6 Hz, 1 H), 7.26-7.24 (m, 1 H), 6.87 (d, *J* = 8.7 Hz, 2 H), 3.83 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 153.9, 150.8, 133.1, 130.4, 129.8, 129.0, 128.5, 127.5, 124.3, 123.3, 122.9, 119.8, 116.0, 114.0, 111.0, 55.3; IR (KBr) ν_{max} 3448, 3060, 2958, 2925, 2836, 1609, 1512, 1491, 1452, 1250, cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{21}H_{17}O_2(M + H)^+$ 301.1223, found 301.1228;

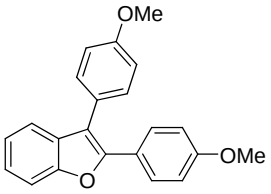


Compound 16f. White solid (62.0 mg, 68%); Mp: 106 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.6 Hz, 2 H), 7.57 (d, *J* = 8.2 Hz, 1 H), 7.53-7.44 (m, 6 H), 7.37 (t, *J* = 7.8 Hz, 1 H), 7.30 (d, *J* = 8.6 Hz, 2 H), 7.27 (t, *J* = 7.3 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 149.3, 134.2, 132.5, 130.1, 129.7, 129.1, 129.0, 128.7, 128.1, 127.8, 124.9, 123.1, 120.1, 118.0, 111.1; IR (KBr) ν_{max} 3517, 3466, 3058, 3033, 2926, 2855, 1619, 1484, 1446, 1087, 1066 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{20}H_{13}ClO(M)^+$ 304.0649, found 304.0651;

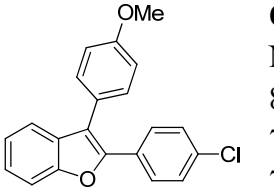


Compound 16g. Yellow solid (45.3 mg, 46%); Mp: 123 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.6 Hz, 2 H), 7.73 (d, *J* = 8.6 Hz, 2 H), 7.51-7.43(m, 7 H), 7.37 (t, *J* = 7.2 Hz, 1 H), 7.26 (t, *J* = 7.2 Hz, 1 H), 3.91 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 154.2, 149.2, 134.9, 132.4, 130.1, 129.7, 129.4, 129.1, 128.0, 126.6, 125.4, 123.2, 120.4, 119.6, 111.2, 52.1; IR (KBr) ν_{max} 3416, 3064, 3032,

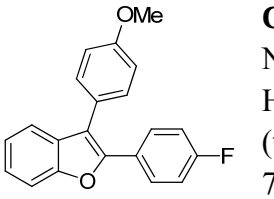
2955, 2921, 2852, 1725, 1605, 1557, 1507, 1448, 1431,1407, 1280, 1108 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{17}O_3(M + H)^+$ 329.1172, found 329.1171.



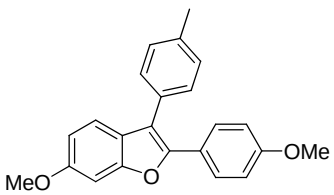
Compound 16h. White solid (87.1 mg, 88%); Mp: 137 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 9.0 Hz, 2 H), 7.53 (d, J = 7.9 Hz, 1 H), 7.48 (d, J = 7.9 Hz, 1 H), 7.43 (d, J = 8.8 Hz, 2 H), 7.30 (t, J = 8.0 Hz, 1 H), 7.22 (t, J = 8.0 Hz, 1 H), 7.01 (d, J = 8.8 Hz, 2 H), 6.86 (d, J = 9.0 Hz, 2 H), 3.89 (s, 3 H), 3.82 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 159.0, 153.8, 150.5, 130.9, 130.6, 128.4, 125.2, 124.2, 123.5, 122.8, 119.7, 115.6, 114.4, 113.9, 110.9, 55.3, 55.2; IR (KBr) ν_{max} 3008, 2918, 2839, 1508, 1452, 1415, 1243 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{19}O_3(M + H)^+$ 331.1329, found 331.1333.



Compound 16i. White solid (63.1mg, 63%); Mp: 142 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.6 Hz, 2 H), 7.44 (d, J = 8.2 Hz, 1 H), 7.39 (d, J = 7.7 Hz, 1 H), 7.31 (d, J = 8.6 Hz, 2 H), 7.24 (t, J = 7.2 Hz, 1 H), 7.19 (d, J = 8.6 Hz, 2 H), 7.15 (t, J = 7.8 Hz, 1 H), 6.92 (d, J = 8.6 Hz, 2 H), 3.79 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 154.0, 149.2, 134.1, 130.9, 130.4, 129.4, 128.7, 128.1, 124.9, 124.6, 123.0, 120.2, 117.7, 114.6, 111.1, 55.3; IR (KBr) ν_{max} 3446, 3051, 3006, 2957, 2920, 2842, 1605, 1585, 1513, 1487, 1446, 1248, 1088, 1065 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{21}H_{15}ClO_2$ $(M)^+$ 334.0755, found 334.0756.

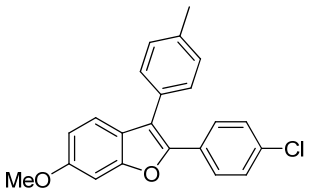


Compound 16j. White solid (44.8mg, 47%); Mp: 76 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.67-7.64 (m, 2 H), 7.54 (d, J = 8.1 Hz, 1 H), 7.49 (d, J = 7.2 Hz, 1 H), 7.41 (d, J = 8.8 Hz, 2 H), 7.33 (td, J = 7.2, 1.2 Hz, 1 H), 7.25 (td, J = 7.6, 1.2 Hz, 1 H), 7.05-7.00 (m, 4 H), 3.89 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (d, J_{F-C} = 247.4 Hz), 159.2, 153.9, 149.4, 130.8, 130.4, 128.8 (d, J_{F-C} = 8.0 Hz) 127.0 (d, J_{F-C} = 3.2 Hz), 124.7, 124.6, 122.9, 120.0, 116.9, 115.5 (d, J_{F-C} = 21.8 Hz), 114.5, 111.0, 55.3; IR (KBr) ν_{max} 3448, 3056, 3005, 2935, 2838, 1598, 1515, 1499, 1452, 1247, 1175, 1028 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{21}H_{15}O_2F(M)^+$ 318.1057, found 318.1062.

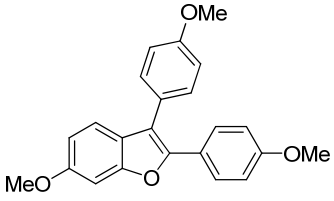


Compound 16k. White solid (83.6mg, 81%); Mp: 98 ^oC; ^1HNMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.8 Hz, 2 H), 7.41 (d, J = 7.9 Hz, 2 H), 7.37 (d, J = 8.6 Hz, 1 H), 7.28 (d, J = 7.9 Hz, 2 H), 7.10 (d, J = 2.0 Hz, 1 H), 6.89 (d, J = 2.0 Hz, 1 H), 6.86 (d, J = 8.6 Hz, 2 H), 3.89 (s, 3 H), 3.82 (s, 3 H), 2.45 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 158.0, 154.7, 149.6, 137.0, 130.0, 129.6, 129.5, 128.0, 123.9, 123.7, 119.9, 115.8, 113.8, 111.5, 95.7, 55.7, 55.2,

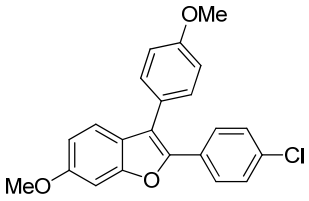
21.3; IR (KBr) ν_{max} 2999, 2925, 2835, 1616, 1594, 1519, 1491, 1461, 1251, 1151 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{23}H_{21}O_3$ $(M + H)^+$ 345.1485, found 345.1478.



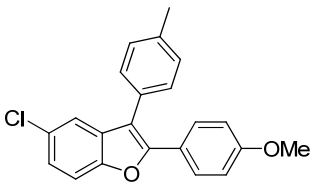
Compound 16l. White solid (79.3 mg, 76%); Mp: 133 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.8 Hz, 2 H), 7.35 (t, J = 7.3 Hz, 3 H), 7.29-7.26 (m, 4 H), 7.08 (d, J = 2.2 Hz, 1 H), 6.87 (dd, J = 8.6, 2.2 Hz, 1 H), 3.89 (s, 3 H), 2.44 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 155.0, 148.3, 137.6, 133.5, 129.8, 129.6, 129.5, 129.4, 128.6, 127.7, 123.7, 120.4, 118.0, 112.0, 95.7, 55.8, 21.3; IR (KBr) ν_{max} 3443, 3012, 2956, 2924, 2834, 1621, 1586, 1513, 1488, 1466, 1277, 1151, 1088, 1059 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{18}ClO_2$ $(M + H)^+$ 349.0990, found 349.0998.



Compound 16m. Faint yellow solid (92.9 mg, 86%); Mp: 263 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 9.0 Hz, 2 H), 7.43 (d, J = 8.8 Hz, 2 H), 7.35 (d, J = 8.6 Hz, 1 H), 7.09 (d, J = 2.2 Hz, 1 H), 7.04 (d, J = 8.8 Hz, 2 H), 6.89-6.84 (m, 3 H), 3.89 (s, 3 H), 3.88 (s, 3 H), 3.82 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 158.9, 158.0, 154.7, 149.5, 130.8, 127.9, 125.2, 124.0, 123.7, 119.8, 115.5, 114.4, 113.8, 111.5, 95.7, 55.7, 55.2, 55.1; IR (KBr) ν_{max} 3421, 3062, 3002, 2931, 2834, 1611, 1591, 1516, 1501, 1490, 1249 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{23}H_{20}O_4$ $(M)^+$ 360.1356, found 360.1352.

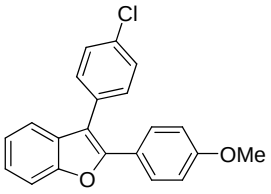


Compound 16n. Faint yellow solid (95.0 mg, 87%); Mp: 117 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.7 Hz, 2 H), 7.42 (d, J = 8.8 Hz, 2 H), 7.37 (d, J = 8.6 Hz, 1 H), 7.29 (d, J = 8.7 Hz, 2 H), 7.10 (d, J = 2.2 Hz, 1 H), 7.04 (d, J = 8.8 Hz, 2 H), 6.89 (dd, J = 8.6, 2.2 Hz, 1 H), 3.91 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 158.5, 154.9, 148.2, 133.4, 130.7, 129.5, 128.6, 127.5, 124.6, 123.8, 120.3, 117.6, 114.5, 112.0, 95.6, 55.7, 55.2; IR (KBr) ν_{max} 3515, 3449, 3003, 2928, 2837, 1622, 1587, 1513, 1485, 1462, 1280, 1249, 1152 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{17}O_3Cl$ $(M)^+$ 364.0861, found 364.0863.

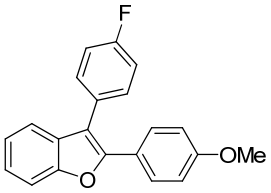


Compound 16o. Colorless liquid (66.8 mg, 64%); Mp: 103 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 9.0 Hz, 2 H), 7.44-7.42 (m, 2 H), 7.36 (d, J = 8.0 Hz, 2 H), 7.28 (d, J = 8.0 Hz, 2 H), 7.24 (dd, J = 8.7, 2.0 Hz, 1 H), 6.86 (d, J = 9.0 Hz, 2 H), 3.82 (s, 3 H), 2.44 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 152.2, 151.9, 137.5, 132.0, 129.8, 129.5, 129.2, 128.5, 128.4, 124.2, 122.9, 119.4, 115.5, 113.9, 111.9, 55.3, 21.3; IR (KBr) ν_{max} 3413, 3002, 2925,

2837, 1713, 1609, 1519, 1501, 1446, 1253 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{17}O_2Cl$ $(M)^+$ 348.0912, found 348.0907.

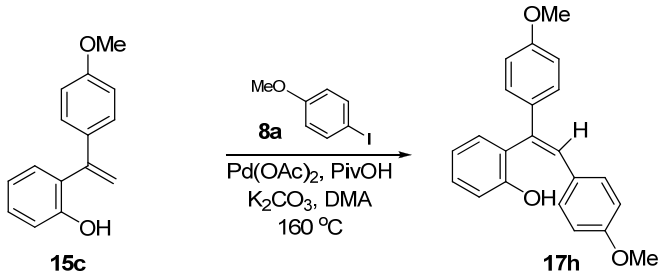


Compound 16p. White solid (52.1 mg, 52%); Mp: 84 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 9.0 Hz, 2 H), 7.54 (d, J = 8.2 Hz, 1 H), 7.46-7.44 (m, 5 H), 7.32 (td, J = 7.2, 1.2 Hz, 1 H), 7.24 (t, J = 7.2 Hz, 1 H), 6.87 (d, J = 9.0 Hz, 2 H), 3.83 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 153.8, 151.0, 133.3, 131.6, 131.1, 130.0, 129.2, 128.6, 124.4, 123.0, 119.4, 114.8, 114.0, 111.1, 55.3; IR (KBr) ν_{max} 3421, 3082, 3018, 2920, 2839, 1605, 1582, 1509, 1487, 1451, 1250 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{21}H_{15}O_2Cl(M)^+$ 334.0761, found 334.0763.



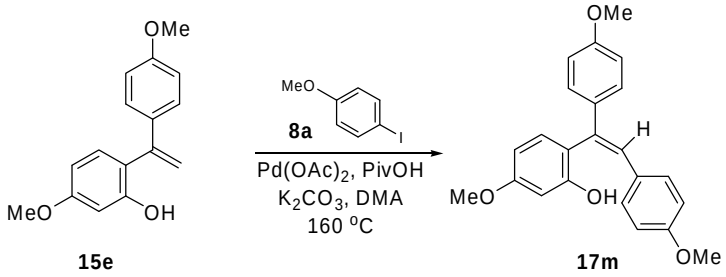
Compound 16q. White solid (39.1 mg, 41%); Mp: 77 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 9.0 Hz, 2 H), 7.54 (d, J = 8.1 Hz, 1 H), 7.48-7.44 (m, 3 H), 7.31 (td, J = 7.7, 1.2 Hz, 1 H), 7.24 (t, J = 7.2 Hz, 1 H), 7.16 (t, J = 8.7 Hz, 2 H), 6.87 (d, J = 9.0 Hz, 2 H), 3.83 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, $J_{F\text{-}C}$ = 254.4 Hz), 159.8, 153.8, 150.6, 131.4 (d, $J_{F\text{-}C}$ = 7.9 Hz), 130.3, 129.0 (d, $J_{F\text{-}C}$ = 3.2 Hz), 128.5, 124.3, 123.1, 122.9, 119.5, 116.0 (d, $J_{F\text{-}C}$ = 21.3 Hz) , 115.0, 114.0, 111.0, 55.3; IR (KBr) ν_{max} 3444, 3060, 2928, 2838, 1608, 1591, 1515, 1501, 1453, 1251 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{21}H_{15}O_2F(M)^+$ 318.1057, found 318.1055.

Mechanistic insights for the tandem reaction



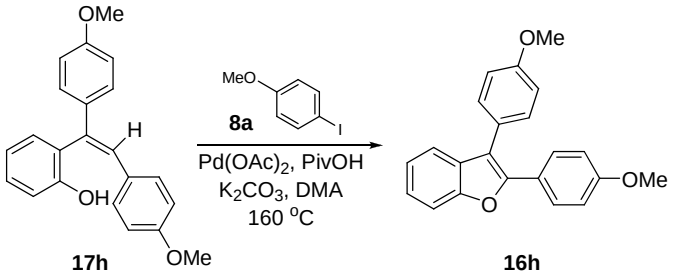
A solution of compound **15c** (67.8 mg, 0.3 mmol), iodibenzene **8a** (210.6 mg, 0.9 mmol), PivOH (91.8 mg, 0.9 mmol), K_2CO_3 (62.1 mg, 0.45 mmol) in dry DMA (6 mL) was degassed with dry argon for 20 min. $Pd(OAc)_2$ (6.7 mg, 0.03mmol) was added to the reaction and the resulting reaction mixture was stirred at 160 °C for 1 hours. The residue was taken up with H_2O and extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated at reduced pressure. Purification with FCC (PE: EtOAc = 100:1) afforded compound **17h** (85.7 mg, 86%) as faint yellow liquid. The configuration of Z isomer was evidenced by NOESY.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.28 (m, 3 H), 7.10 (dd, J = 7.8, 1.8 Hz, 1 H), 7.07 (s, 1 H), 7.03 (d, J = 8.8 Hz, 2 H), 6.99- 6.95 (m, 2 H), 6.86 (d, J = 8.9 Hz, 2 H), 6.71 (d, J = 8.9 Hz, 2 H), 5.21 (br s, 1 H), 3.81 (s, 3 H), 3.75 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 159.0, 152.9, 134.4, 133.5, 131.0, 130.2, 129.5, 129.1, 128.2, 128.1, 126.3, 121.1, 115.8, 113.9, 113.8, 55.3, 55.1; IR (KBr) ν_{max} 3453, 3122, 1598, 1532, 1487 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{22}H_{19}O_3$(M - H)$^-$ 331.1334, found 331.1338.

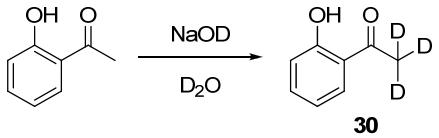


A solution of compound **15e** (76.8 mg, 0.3 mmol), iodibenzene **8a** (210.6 mg, 0.9 mmol), PivOH (91.8 mg, 0.9 mmol), K_2CO_3 (62.1 mg, 0.45 mmol) in dry DMA (6 mL) was degassed with dry argon for 20 min. $Pd(OAc)_2$ (6.7 mg, 0.03mmol) was added to the reaction and the resulting reaction mixture was stirred at 160 °C for 1 hours. The residue was taken up with H_2O and extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated at reduced pressure. Purification with FCC (PE: EtOAc = 100:1) afforded compound **17m** (93.4 mg, 86%) as faint yellow liquid. The configuration of Z isomer was evidenced by NOESY.

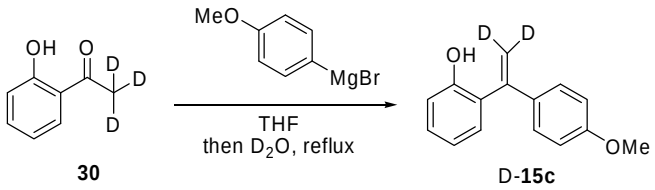
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.15 (s, 1 H), 7.21 (d, J = 8.9 Hz, 2 H), 7.00 (d, J = 8.8 Hz, 2 H), 6.92 (s, 1 H), 6.85 (d, J = 8.9 Hz, 2 H), 6.78 (d, J = 8.4 Hz, 1 H), 6.71 (d, J = 8.8 Hz, 2 H), 6.48 (d, J = 2.2 Hz, 1 H), 6.42 (dd, J = 8.2, 2.6 Hz, 1 H), 3.74 (s, 3 H), 3.73 (s, 3 H), 3.68 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.7, 158.3, 157.8, 156.1, 135.8, 135.2, 131.4, 130.3, 129.9, 127.1, 125.7, 119.4, 113.5, 113.4, 105.1, 101.7, 55.1, 54.9, 54.8; IR (KBr) ν_{max} 3428, 3088, 2920, 1605, 1570, 1438 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{23}H_{21}O_4$(M - H)$^-$ 361.1447, found 361.1454.



A solution of compound **17h** (33.2 mg, 0.1 mmol), iodibenzene **8a** (46.8 mg, 0.2 mmol), PivOH (30.6 mg, 0.3 mmol), K_2CO_3 (20.7 mg, 0.45 mmol) in dry DMA (2 mL) was degassed with dry argon for 20 min. $Pd(OAc)_2$ (2.2 mg, 0.01mmol) was added to the reaction and the resulting reaction mixture was stirred at 160 °C for 8 hours. The residue was taken up with H_2O and extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated at reduced pressure. Purification with FCC (PE: EtOAc = 100:1) afforded compound **16h** (27.1 mg, 82%) as white solid.



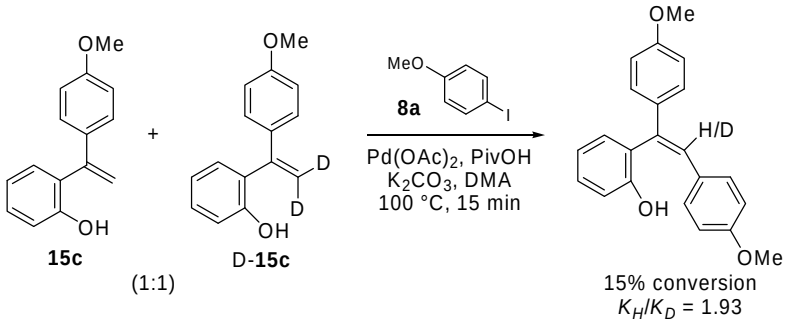
O-hyrdoxyacetophenone (24.5 mg, 0.18 mmol) was dissolved in NaOD (5 mg) and D_2O (5 mL) and stirred overnight at room temperature. The reaction mixture was extracted with Et_2O for three times, the combined organic layers was dried over Na_2SO_4 and concentrated at reduced pressure afford the desired product **30** (24.1mg, 0.17 mmol) in 96% yield as faint yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, J = 8.0, 2.0 Hz, 2 H), 7.13 (m, 1 H), 6.55 (dd, J = 1.0, 8.5 Hz, 1 H), 6.35 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.0, 170.6, 135.3, 130.4, 127.2, 123.5, 113.1.



30 D-**15c**

To a solution of compound **30** (24.5 mg, 0.17 mmol) in dry THF (2 mL) was added (4-methoxyphenyl) magnesium bromide solution (0.37 mmol 2.2 equiv) at 0 °C. The solution was warmed to reflux temperature and stirred for 8 h. The reaction mixture was cooled to 0 °C and then 1 mL D_2O was added, and then the mixture was warmed to reflux temperature and stirred for an additional 6 h. The aqueous layer was extracted with Et_2O three times and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. Purification with FCC (PE: EtOAc = 10:1) afforded Compound D-**15c** (35.3 mg, 0.12 mmol, 72%) as a yellow oil.

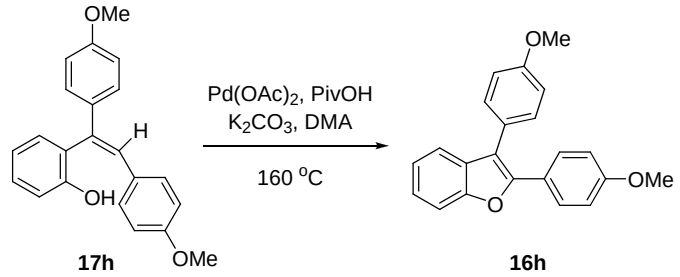
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.9 Hz, 2 H), 7.27 (m, 1 H), 7.16 (dd, J = 7.6, 1.6 Hz, 1 H), 6.97- 6.92 (m, 2 H), 6.87 (d, J = 8.9 Hz, 2 H), 5.25 (s, 1 H), 3.82 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 153.2, 114.4, 131.7, 130.4, 129.4, 128.4, 127.7, 120.4, 115.8, 114.1, 55.3.



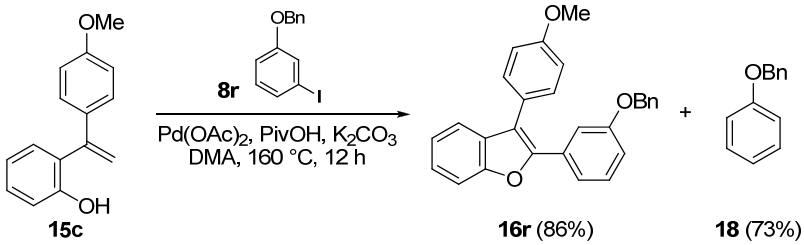
15c (1:1) D-**15c**

15% conversion
K_H/K_D = 1.93

A solution of compound **15c** (67.8 mg, 0.3 mmol), compound D-**15c** (68.4 mg, 0.3 mmol), iodibenzene **8a** (134.4 mg, 0.6 mmol), PivOH (183.6 mg, 1.8 mmol), K_2CO_3 (124.2 mg, 0.9 mmol) in dry DMA (12 mL) was degassed with dry argon for 20 min. $Pd(OAc)_2$ (13.4 mg, 0.06mmol) was added to the reaction and the resulting reaction mixture was stirred at 100 °C for 15 min. The residue was taken up with H_2O and extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated at reduced pressure. Purification with FCC (PE: EtOAc = 15:1) afforded a mixture of product, and the ratio was determined by ^{1}H-NMR.



A solution of compound **17h** (33.2 mg, 0.1 mmol), PivOH (30.6 mg, 0.3 mmol), K_2CO_3 (20.7 mg, 0.15 mmol) in dry DMA (2 mL) was degassed with dry argon for 20 min. $Pd(OAc)_2$ (2.2 mg, 0.01mmol) was added to the reaction and the resulting reaction mixture was stirred at 160 °C for 8 hours. The residue was taken up with H_2O and extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated at reduced pressure. Purification with FCC (PE: EtOAc = 100:1) afforded compound **16h** (3.0 mg, 9%) as white solid.

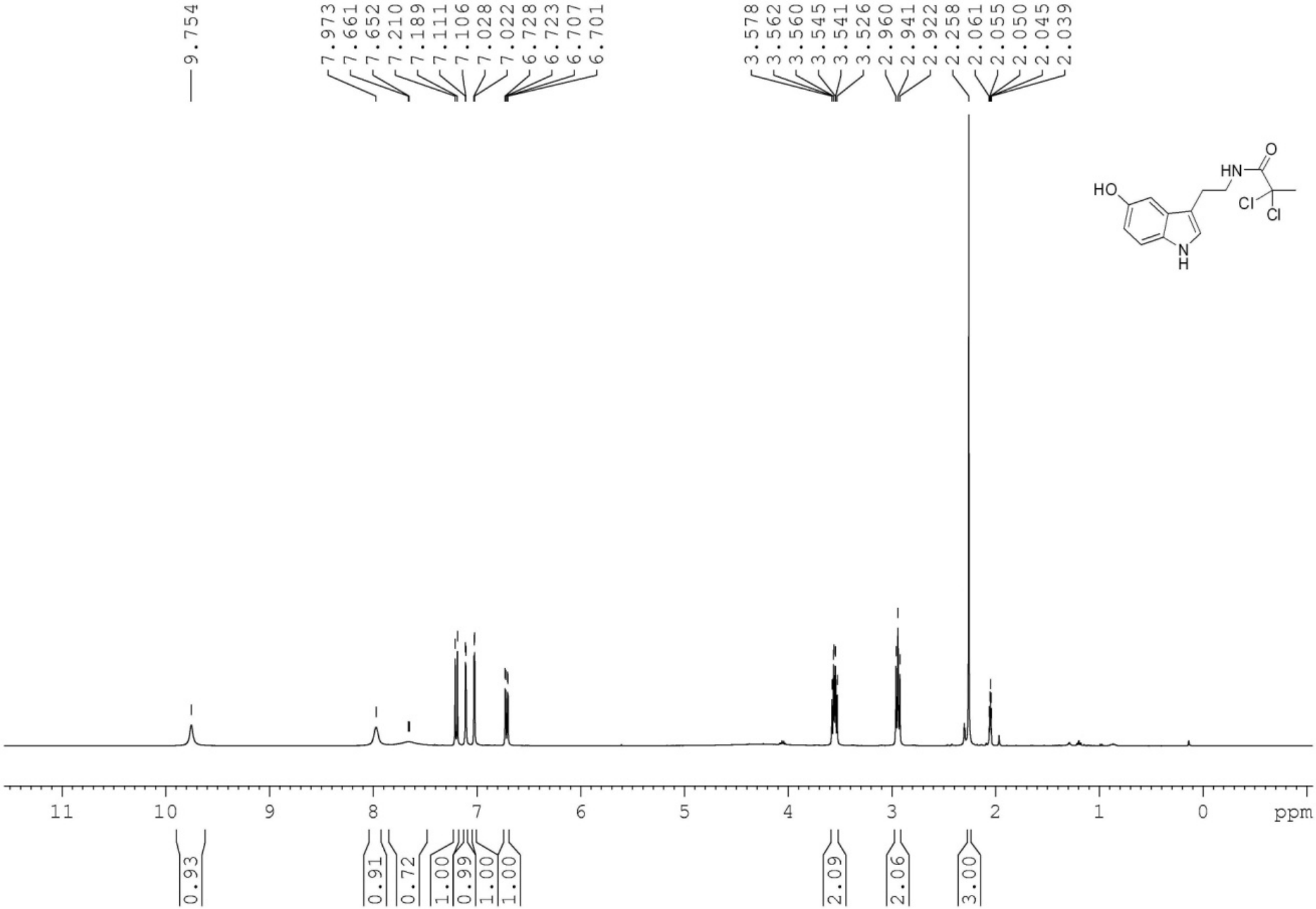


A solution of compound **15c** (67.8 mg, 0.3 mmol), iodobenzene (279.0 mg, 0.9 mmol), PivOH (91.8 mg, 0.9 mmol), K_2CO_3 (62.1 mg, 0.45 mmol) in dry DMA (6 mL) was degassed with dry argon for 20 min. $Pd(OAc)_2$ (6.7 mg, 0.03mmol) was added to the reaction and the resulting reaction mixture was stirred at 160 °C for 12 hours. The residue was taken up with H_2O and extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated at reduced pressure. Purification with FCC afforded compound **16r** (white solid, 104.7 mg, 86%) and **18** (white solid, 40.3 mg, 73%).

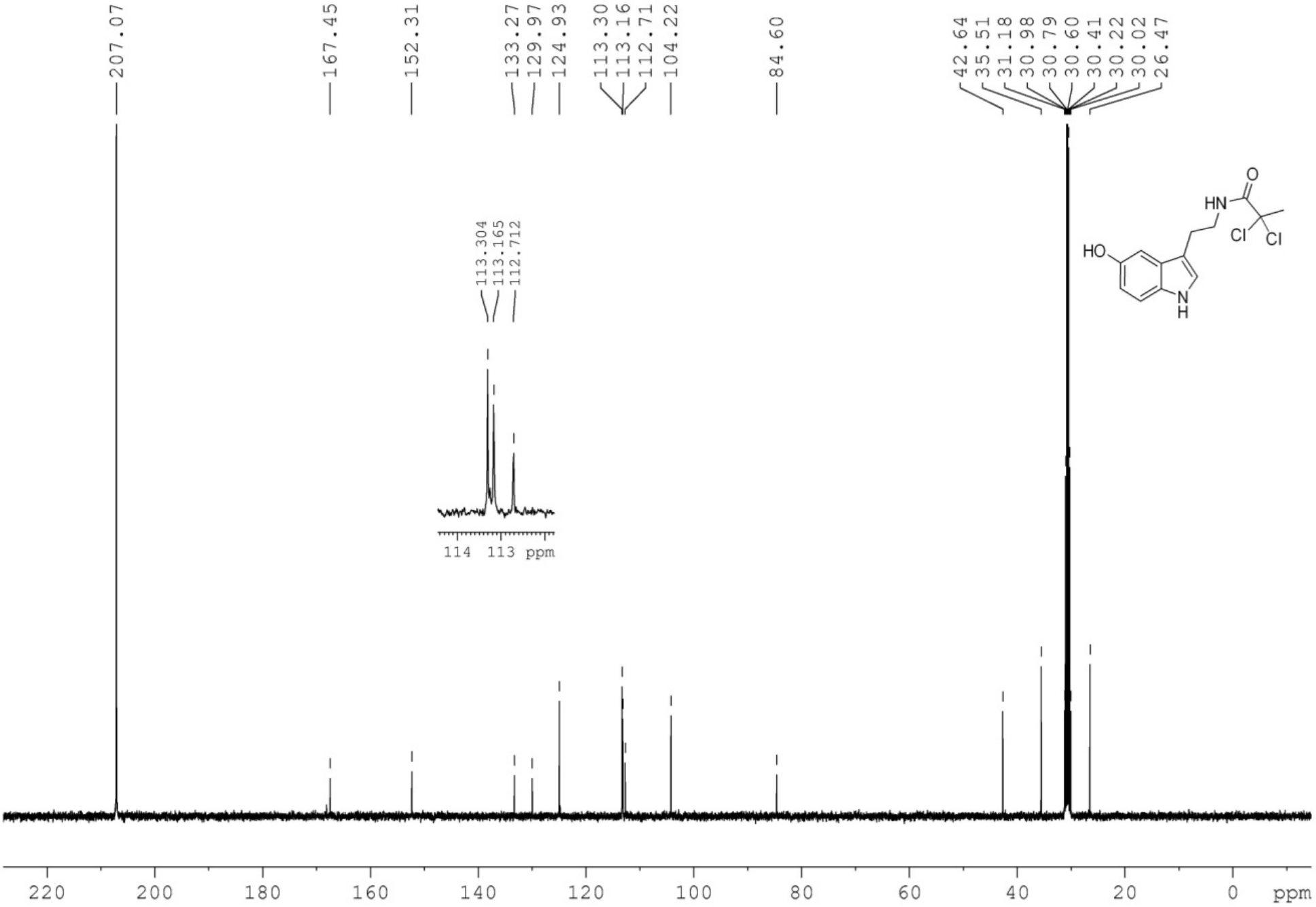
Compound 16r. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.2 Hz, 1 H), 7.48 (d, J = 7.8 Hz, 1 H), 7.44 (d, J = 8.7 Hz, 2 H), 7.39-7.31 (m, 7 H), 7.28-7.20 (m, 3 H), 7.02 (d, J = 8.7 Hz, 2 H), 6.91 (d, J = 8.0 Hz, 1 H), 4.97 (s, 2 H), 3.89 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 158.7, 153.9, 150.0, 136.9, 132.1, 131.0, 130.5, 129.5, 128.6, 128.0, 127.5, 124.9, 124.7, 122.9, 120.1, 119.7, 117.5, 115.5, 114.5, 112.7, 111.1, 69.9, 55.3; IR (KBr) ν_{max} 3400, 3033, 1623, 1596, 1511 cm^{-1}; HRMS (ESI) *m/z* calcd. for $C_{28}H_{21}O_3$ $(M - H)^-$ 405.1496, found 405.1490. Mp: 62 °C.

Compound 18. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.38 (m, 4 H), 7.35-7.29 (m, 3 H), 7.01-6.96 (m, 3 H), 5.08 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 137.1, 129.5, 128.6, 128.0, 127.5, 121.0, 114.9, 69.9; Mp: 142 °C.

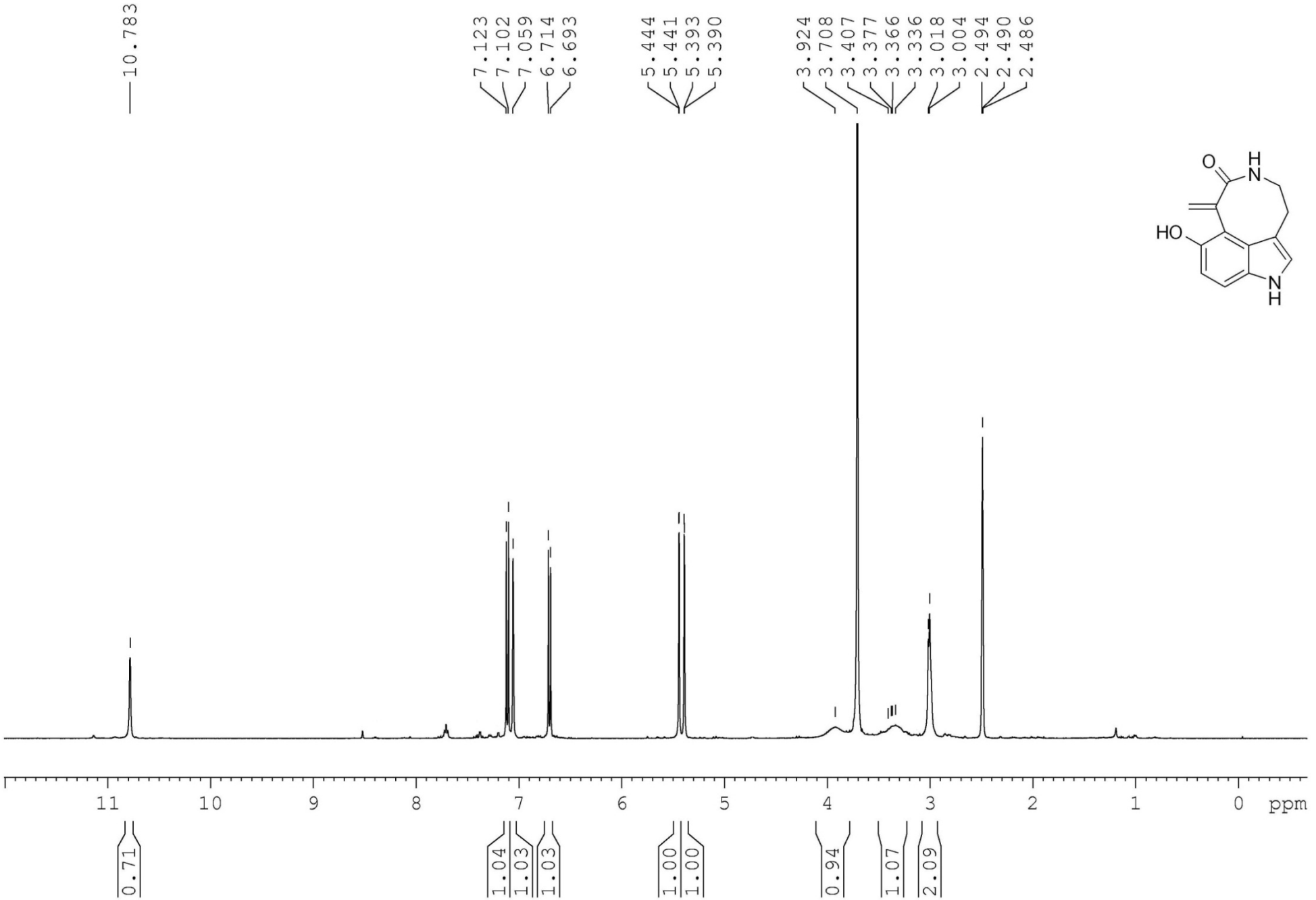
^{1}H NMR of compound 10 (Acteone-d_6; 400 MHz)



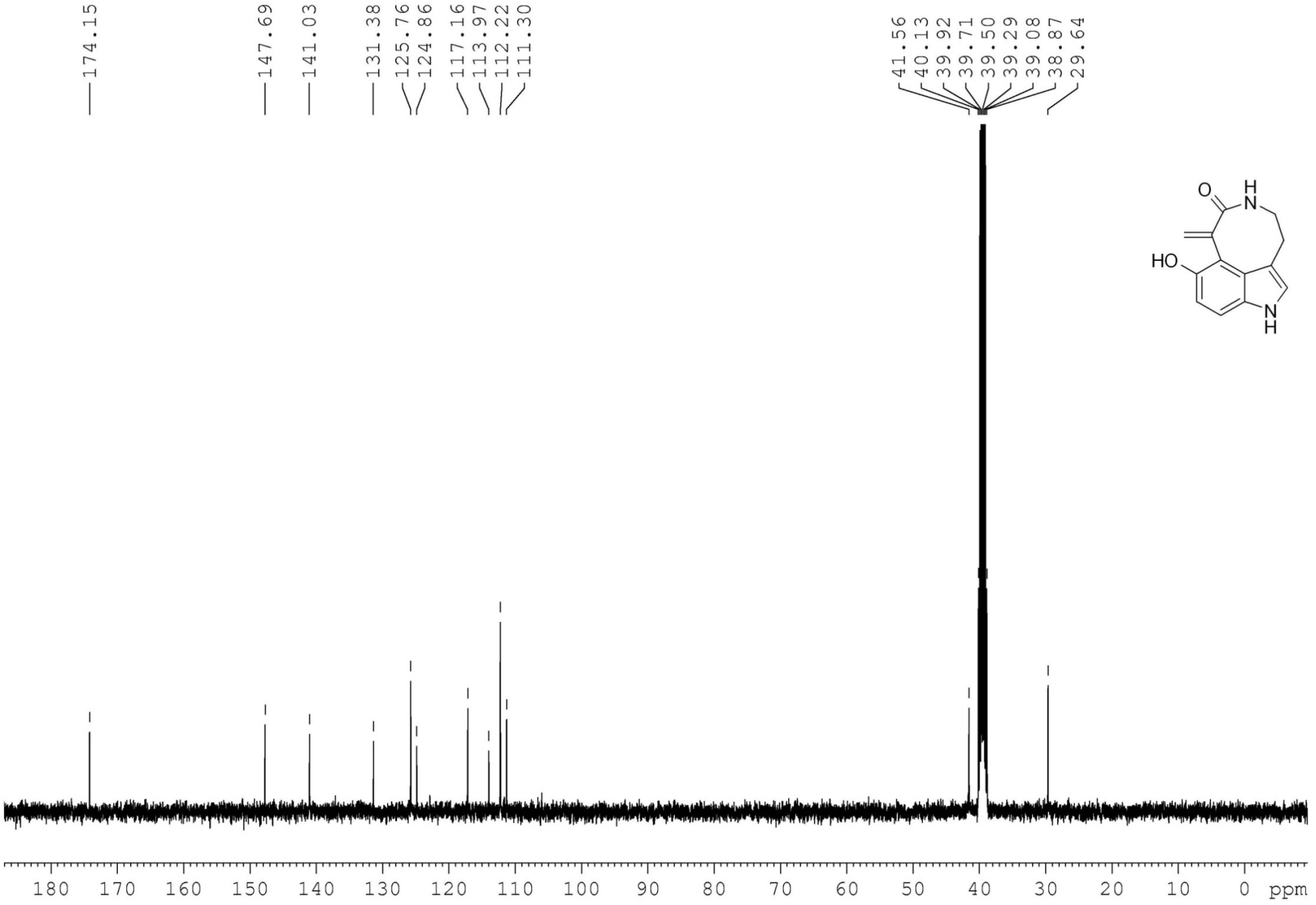
^{13}C NMR of compound 10 (Acteone-d_6; 100 MHz)



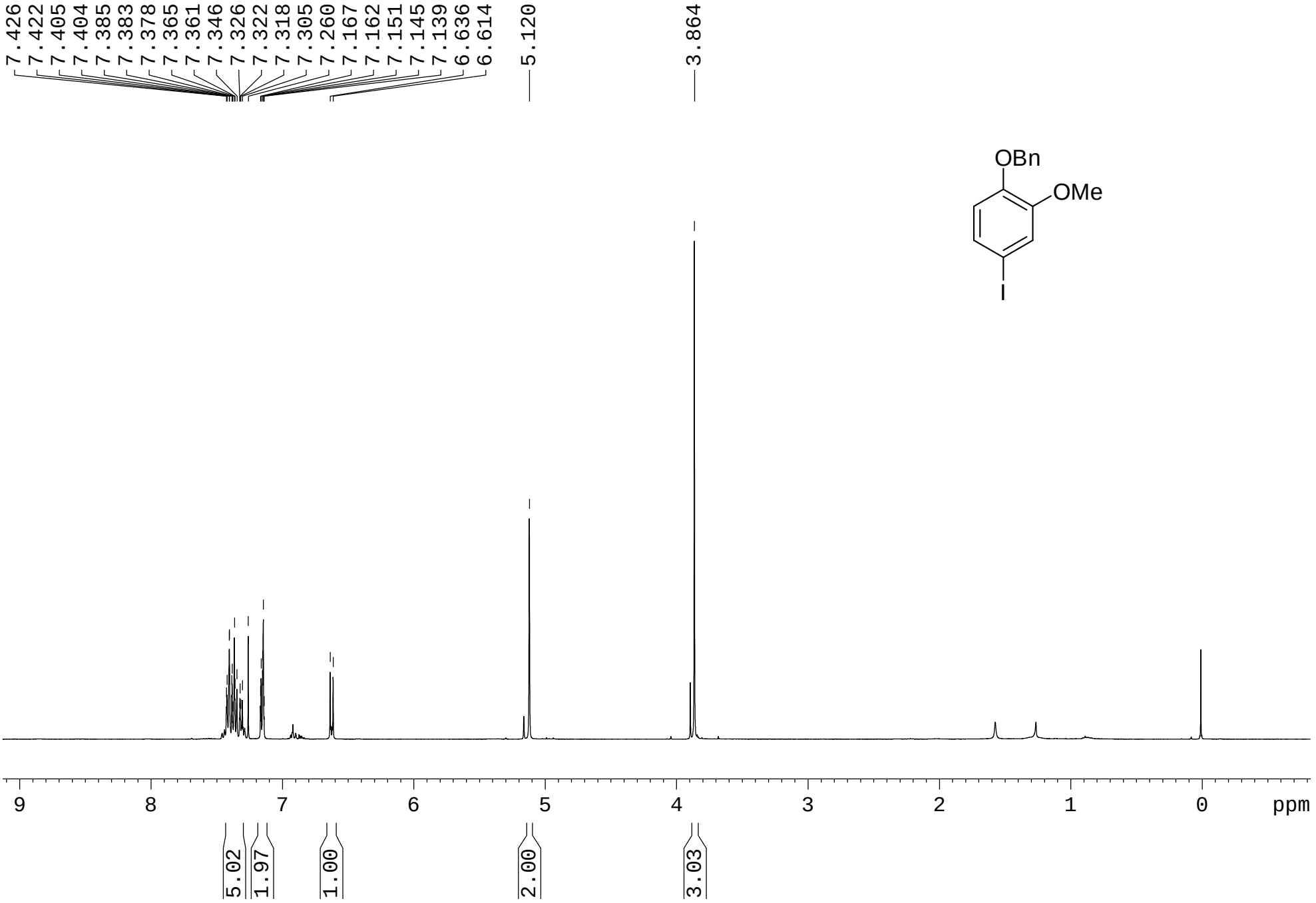
^{1}H NMR of compound 9（10% D_2O/DMSO-d_6; 400 MHz）



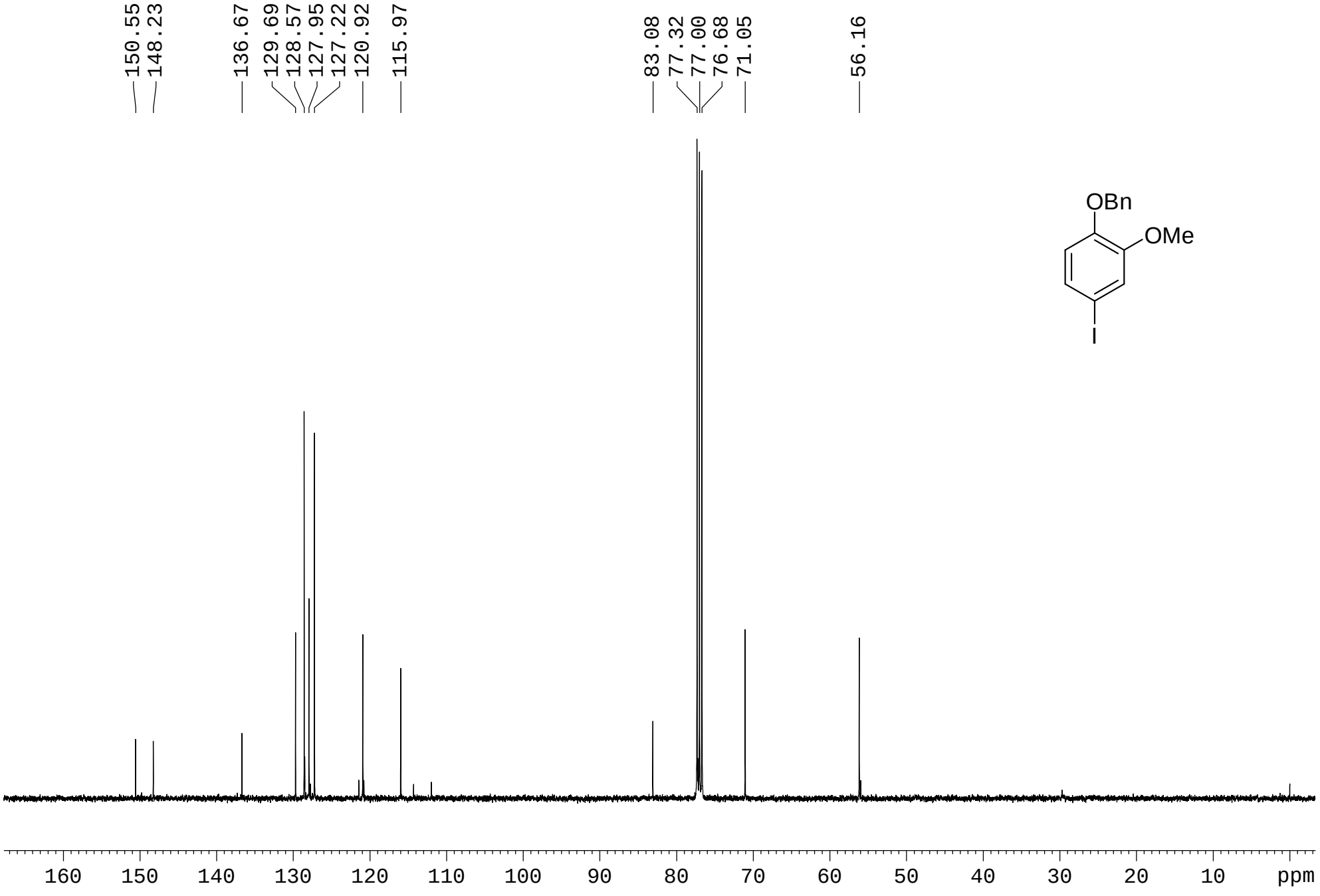
^{13}C NMR of compound 10 (10% D_2O/DMSO-d_6; 100 MHz)



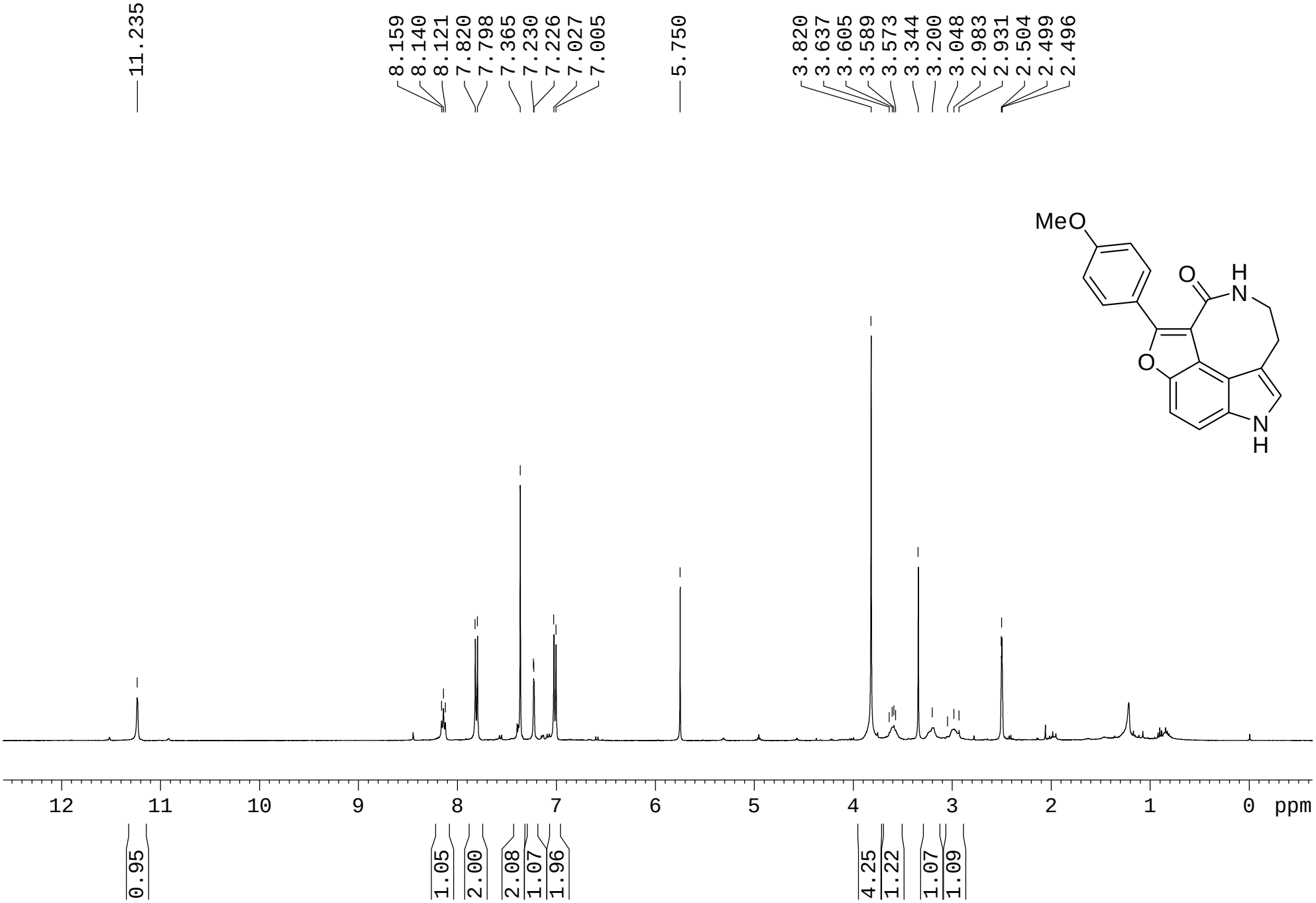
^{1}H NMR of compound 8c ($CDCl_3$; 400 MHz)



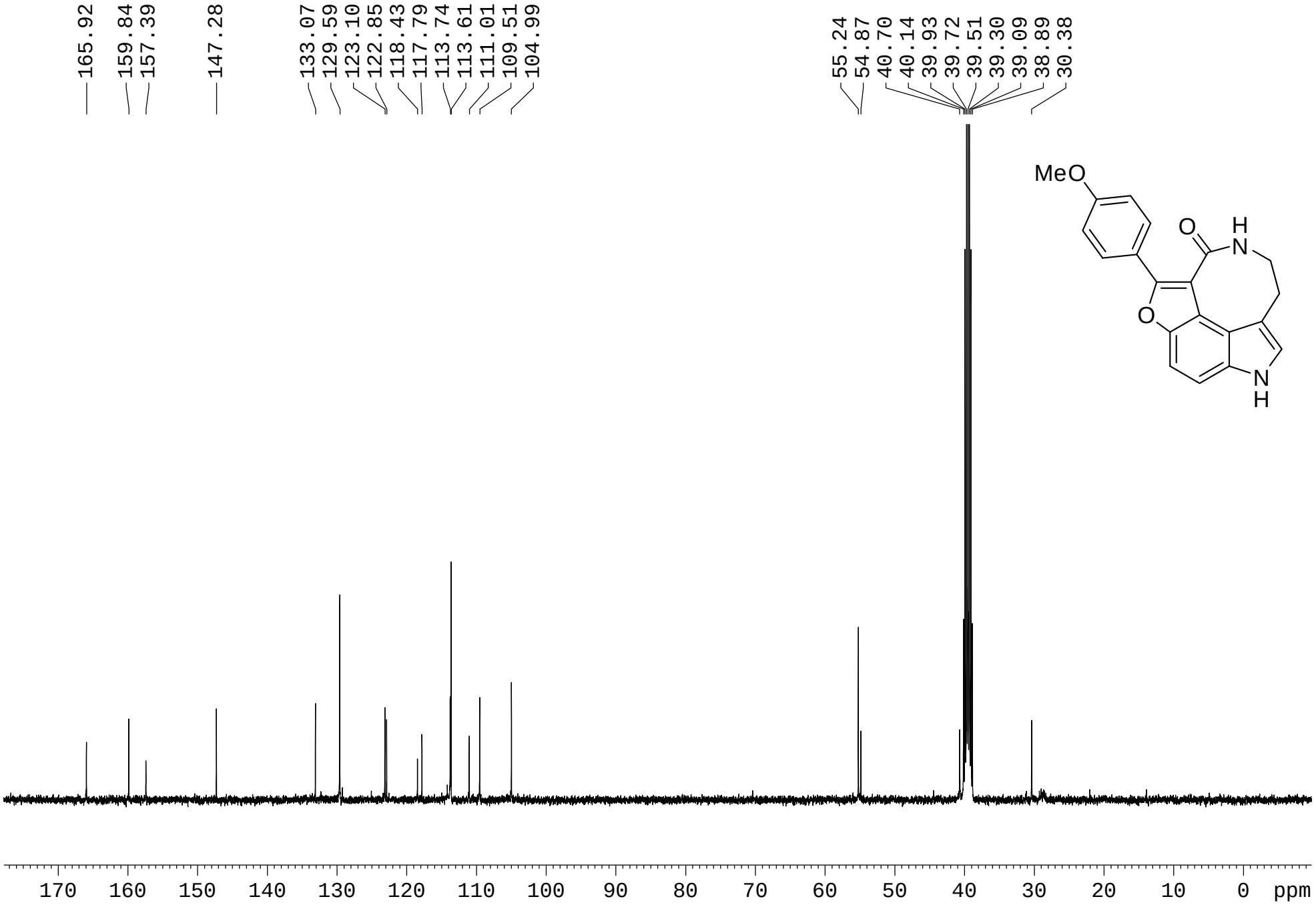
^{13}C NMR of compound 8c ($CDCl_3$; 100 MHz)



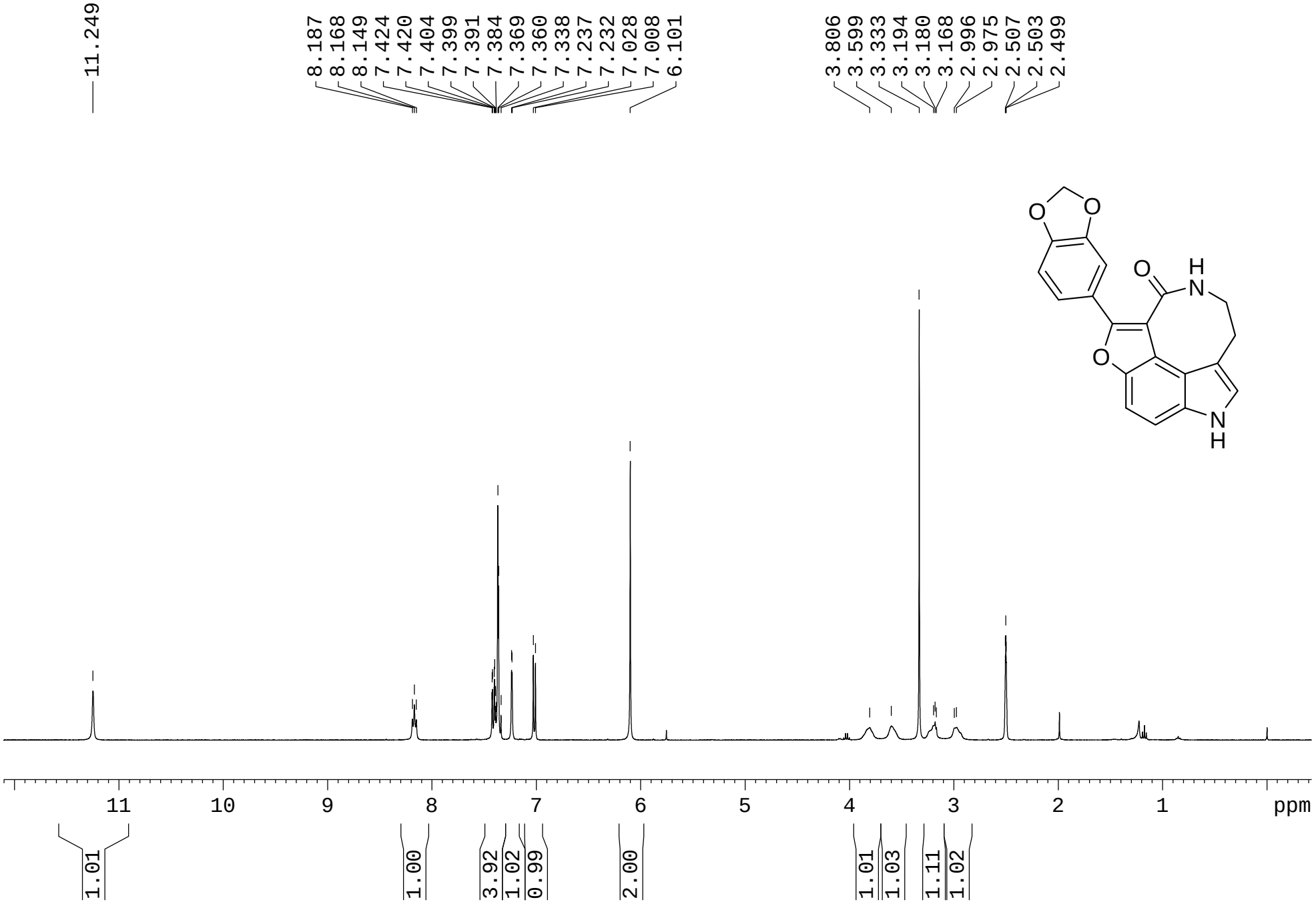
^{1}H NMR of compound 13a (DMSO-d_6; 400 MHz)



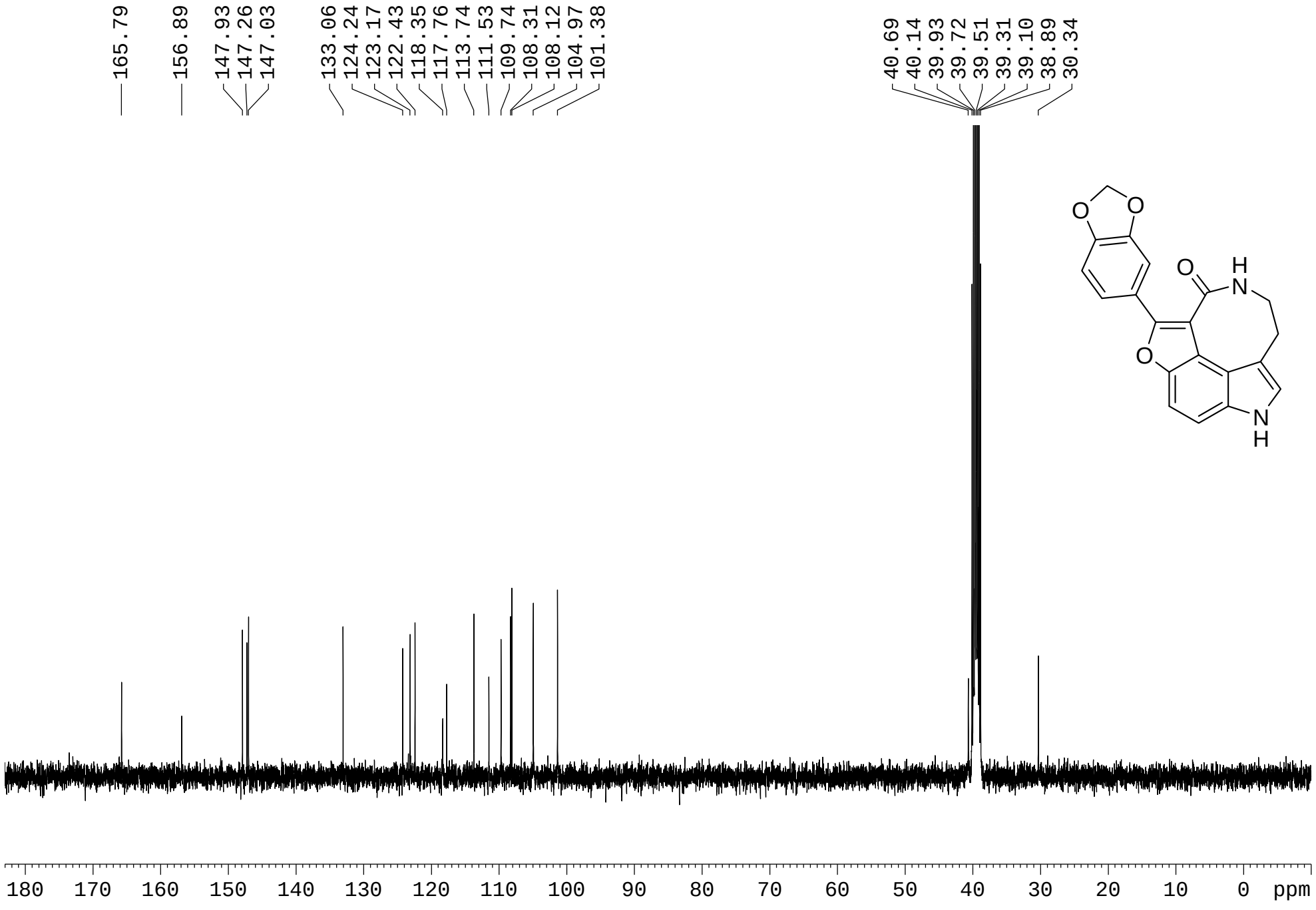
^{13}C NMR of compound 13a (DMSO-d_6; 100 MHz)



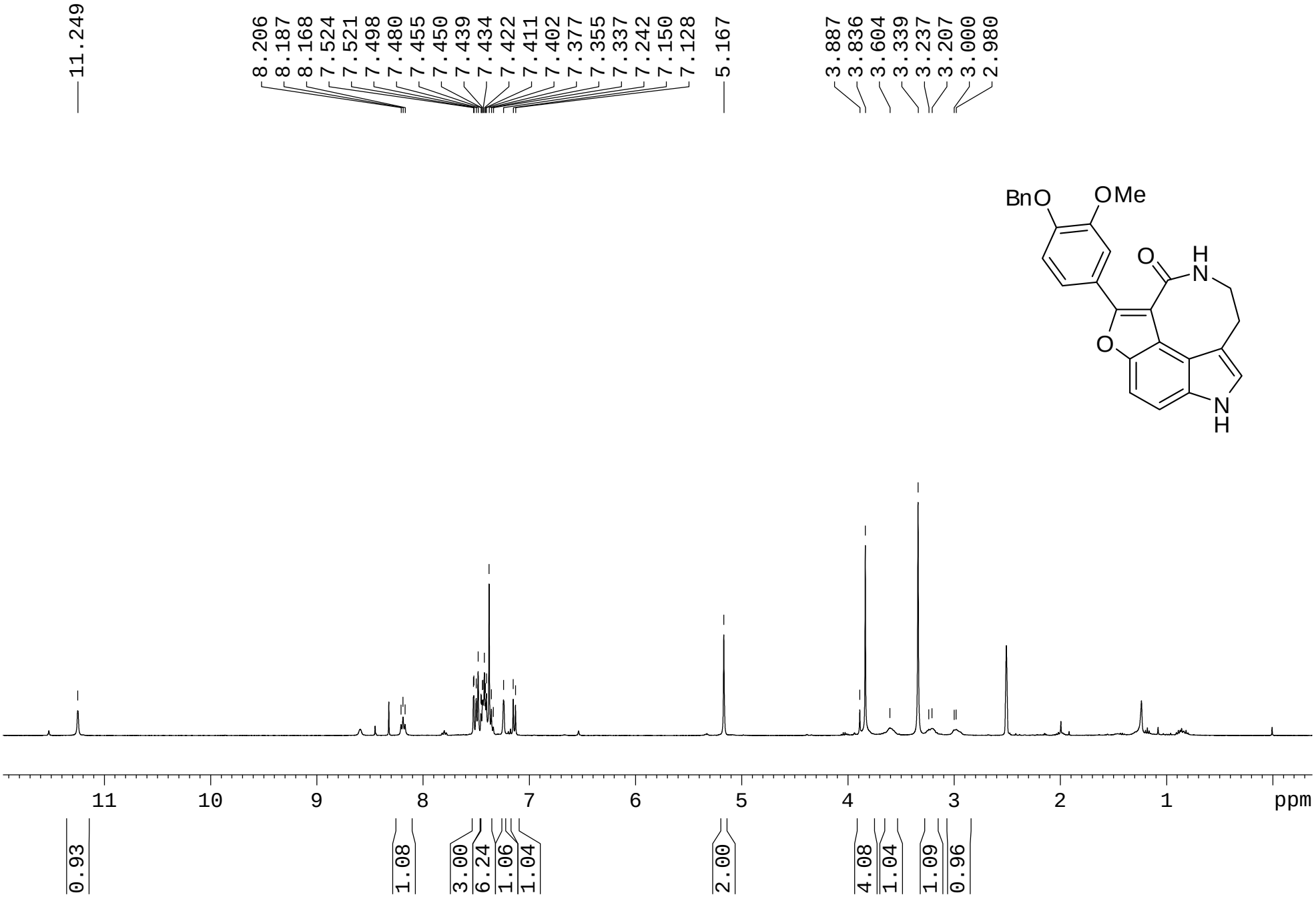
^{1}H NMR of compound 13b (DMSO-d_6; 400 MHz)



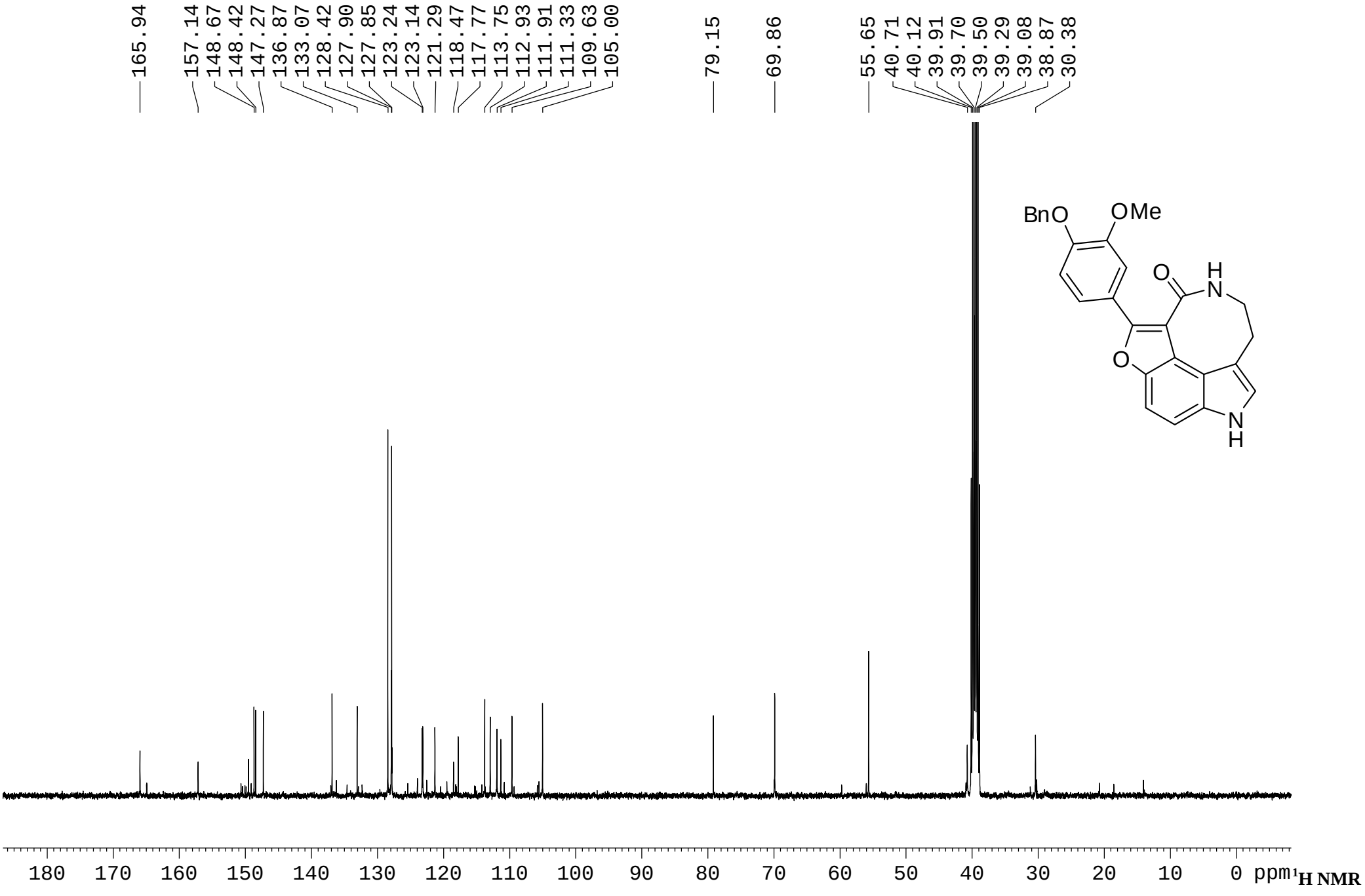
^{13}C NMR of compound 13b (DMSO-d_6; 100 MHz)



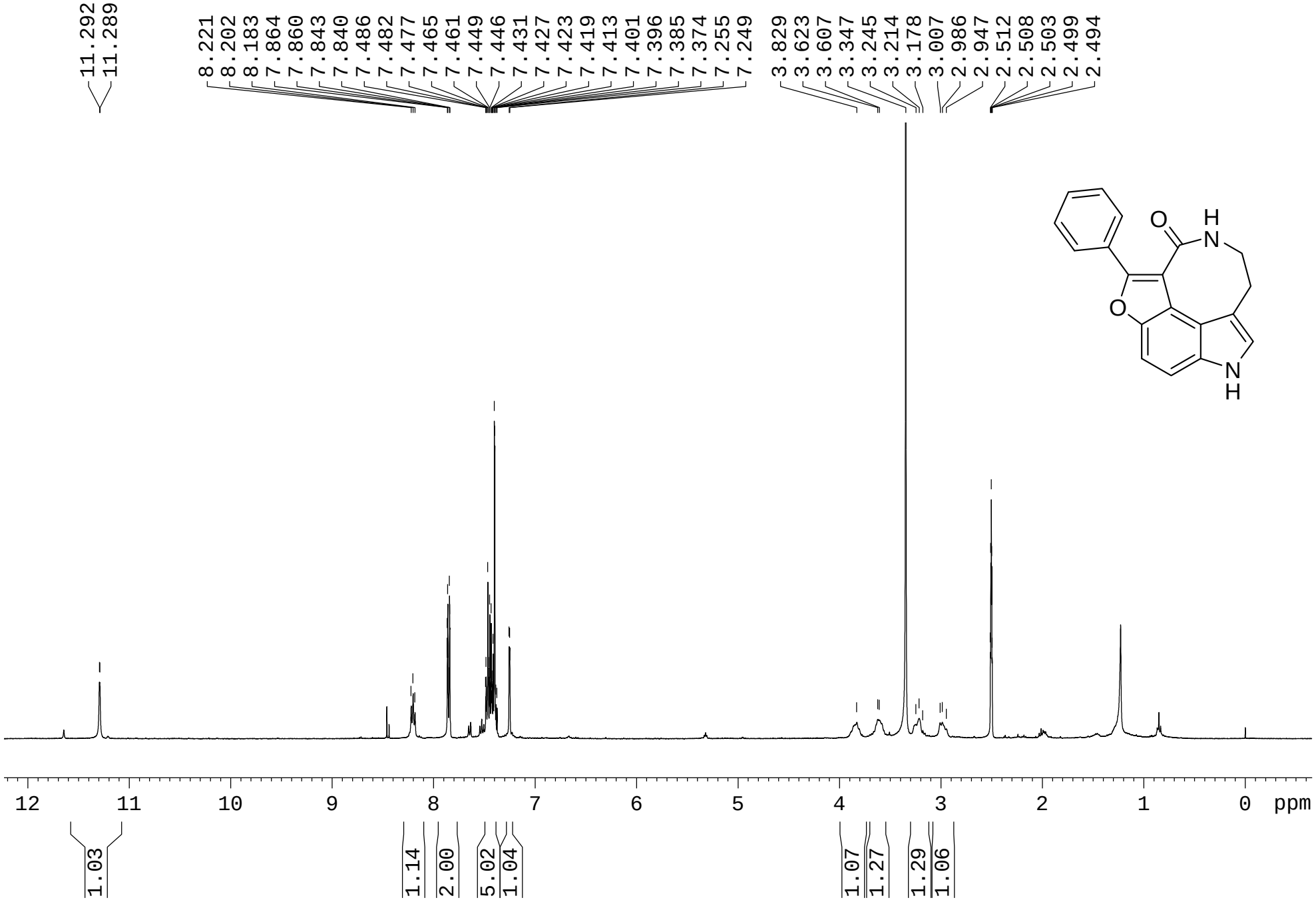
^{1}H NMR of compound 13c (DMSO-d_6; 400 MHz)



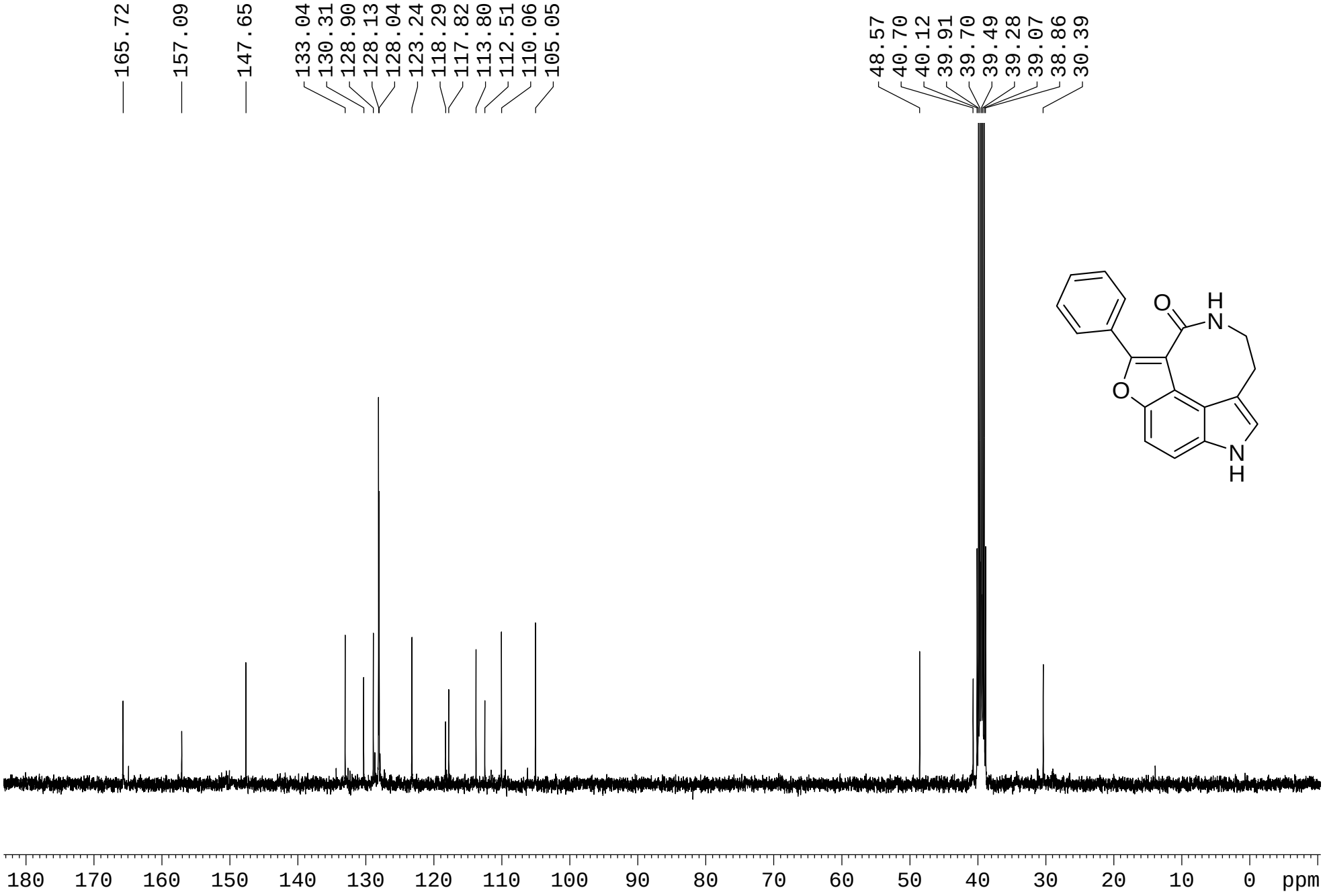
^{13}C NMR of compound 13c (DMSO-d_6; 100 MHz)



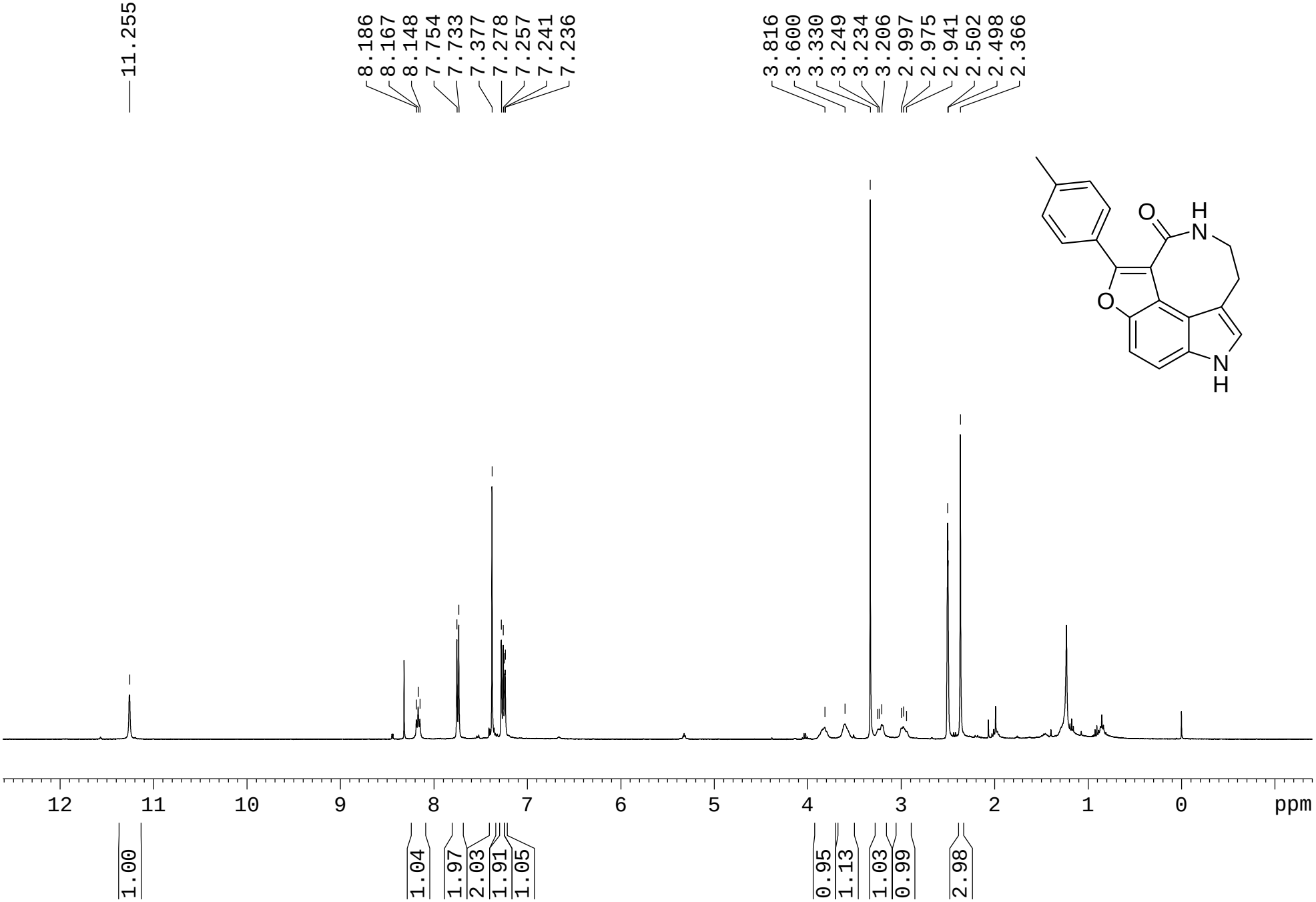
^{1}H NMR of compound 13d (DMSO-d_6; 400 MHz)



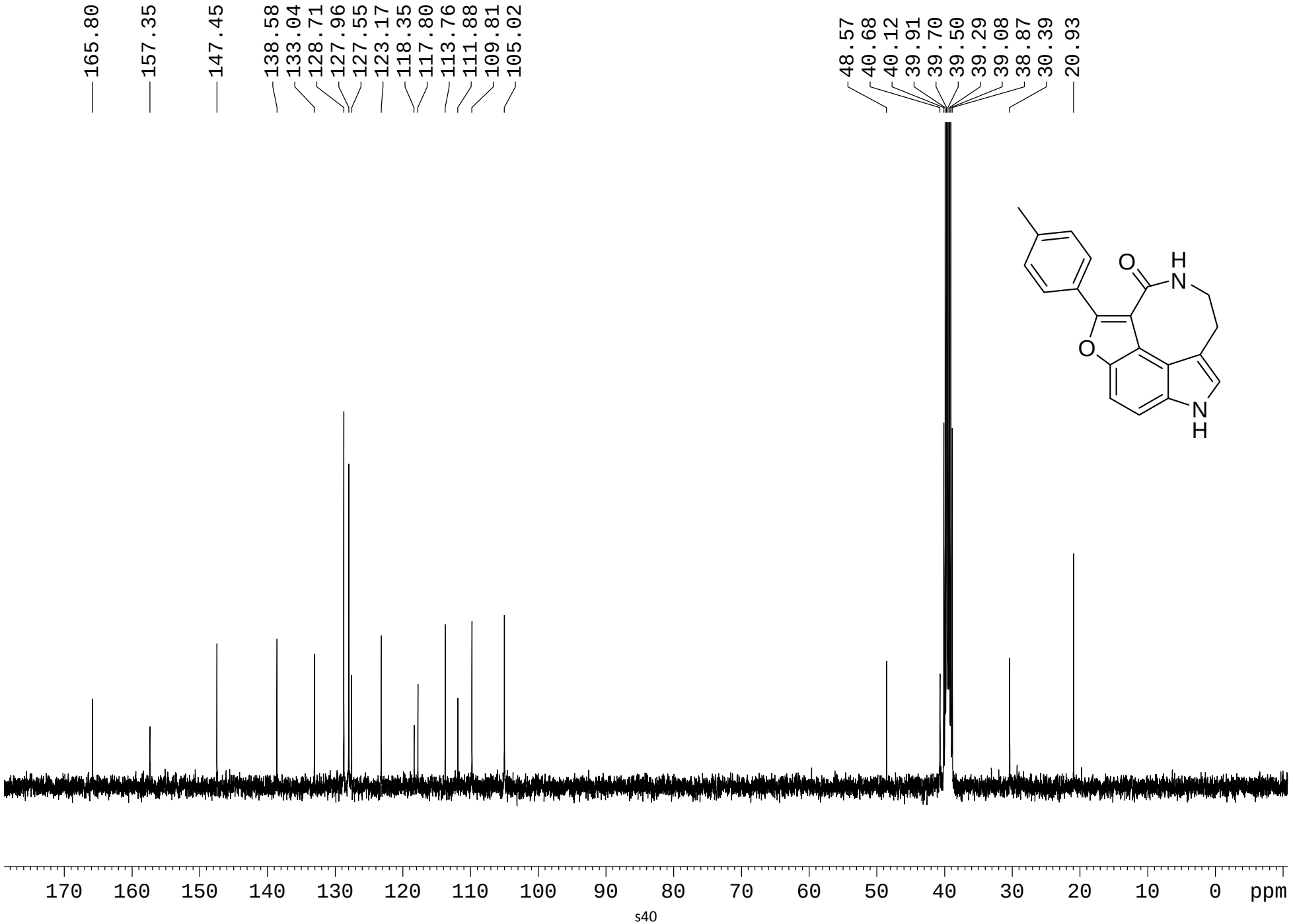
^{13}C NMR of compound 13d (DMSO-d_6; 100 MHz)



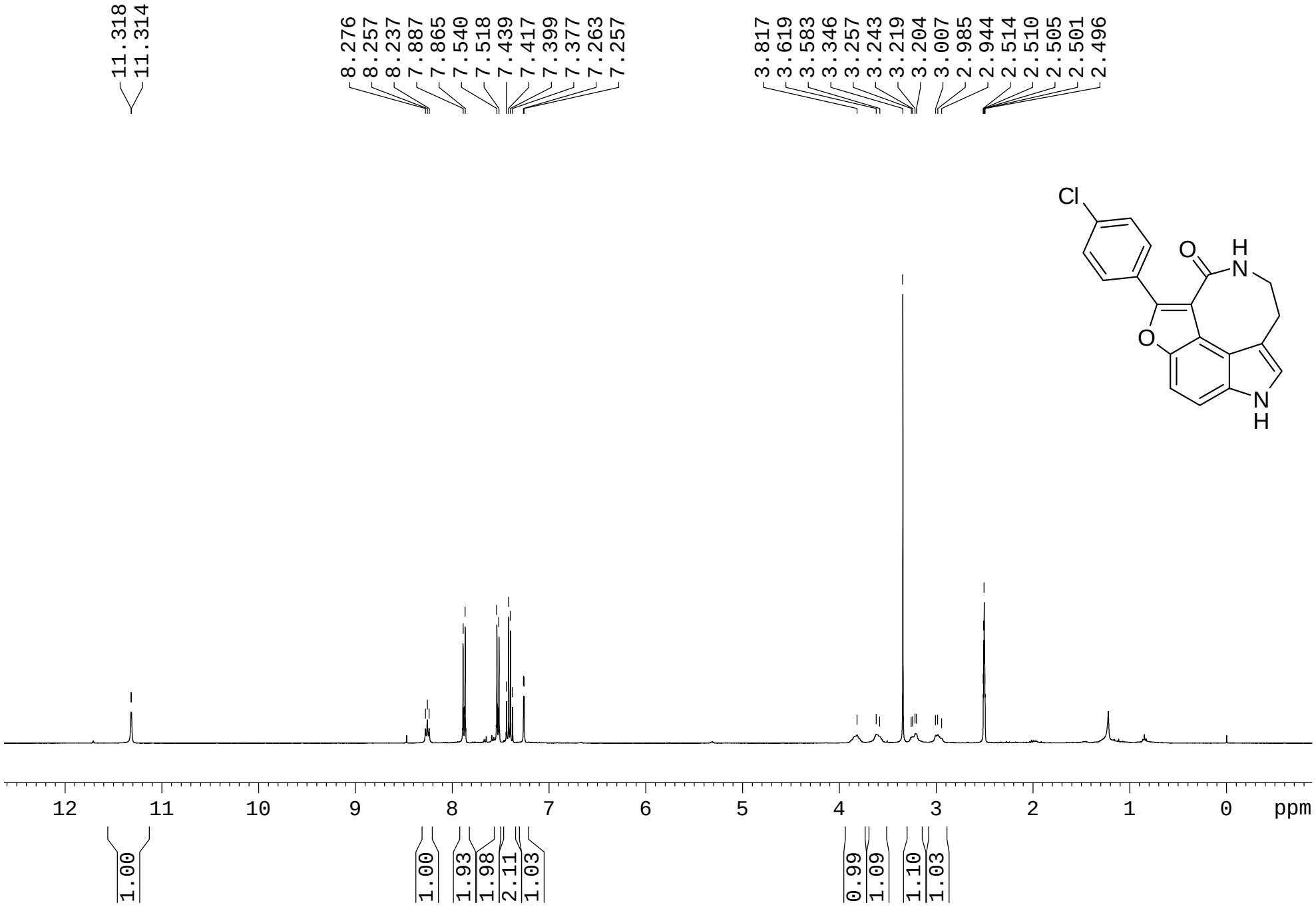
^{1}H NMR of compound 13e (DMSO-d_6; 400 MHz)



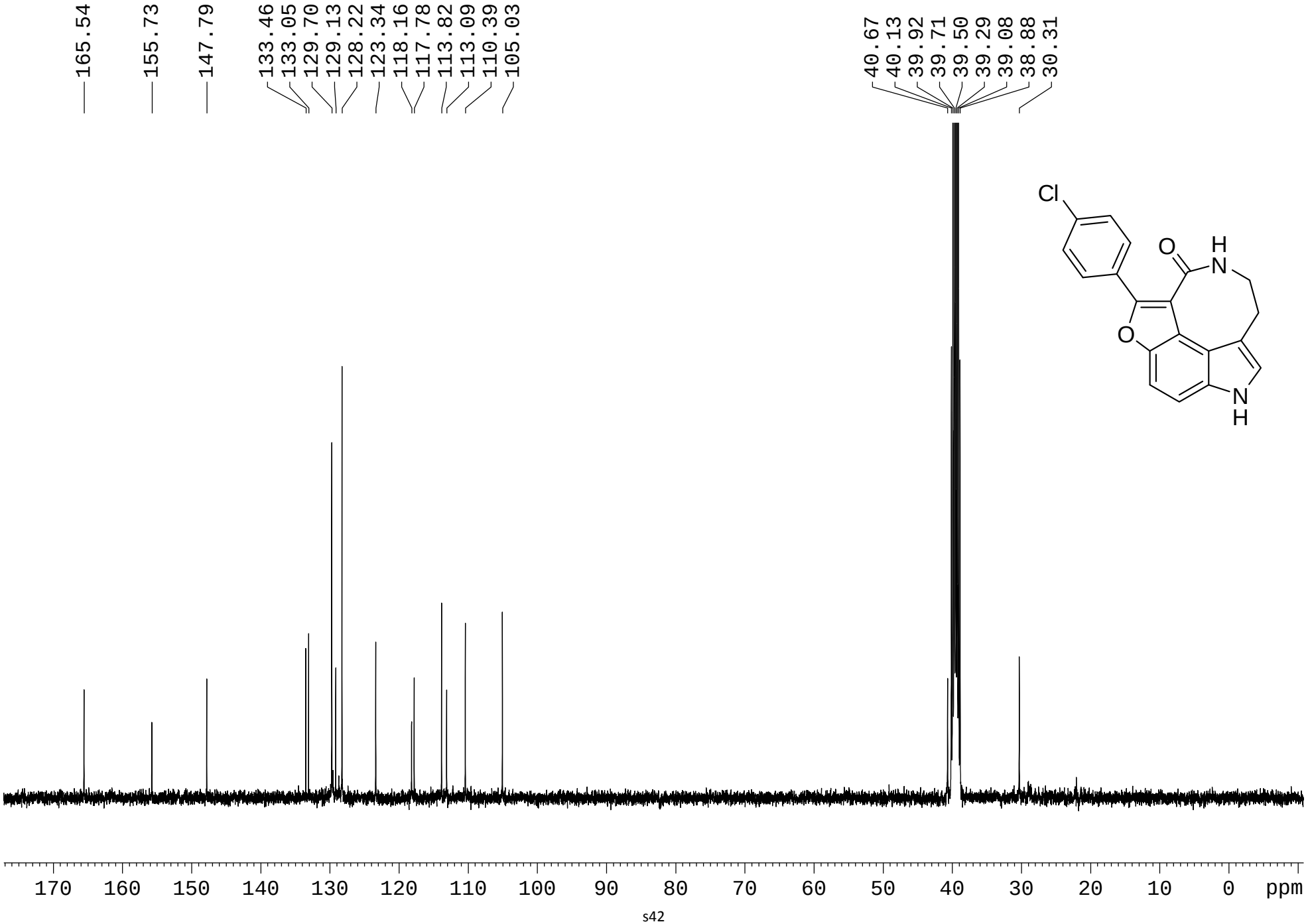
^{13}C NMR of compound 13e (DMSO-d_6; 100 MHz)



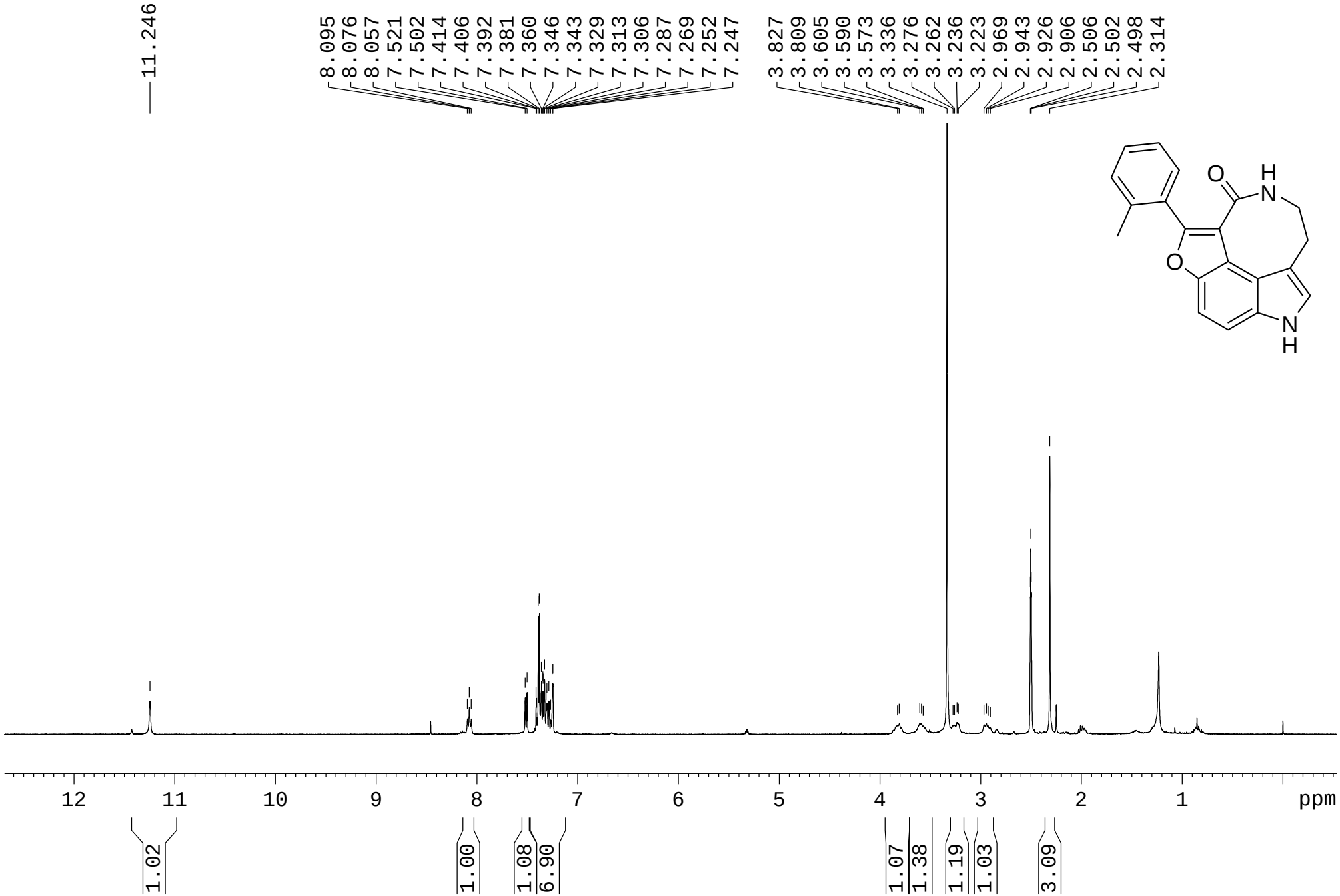
^{1}H NMR of compound 13f (DMSO-d_6; 400 MHz)



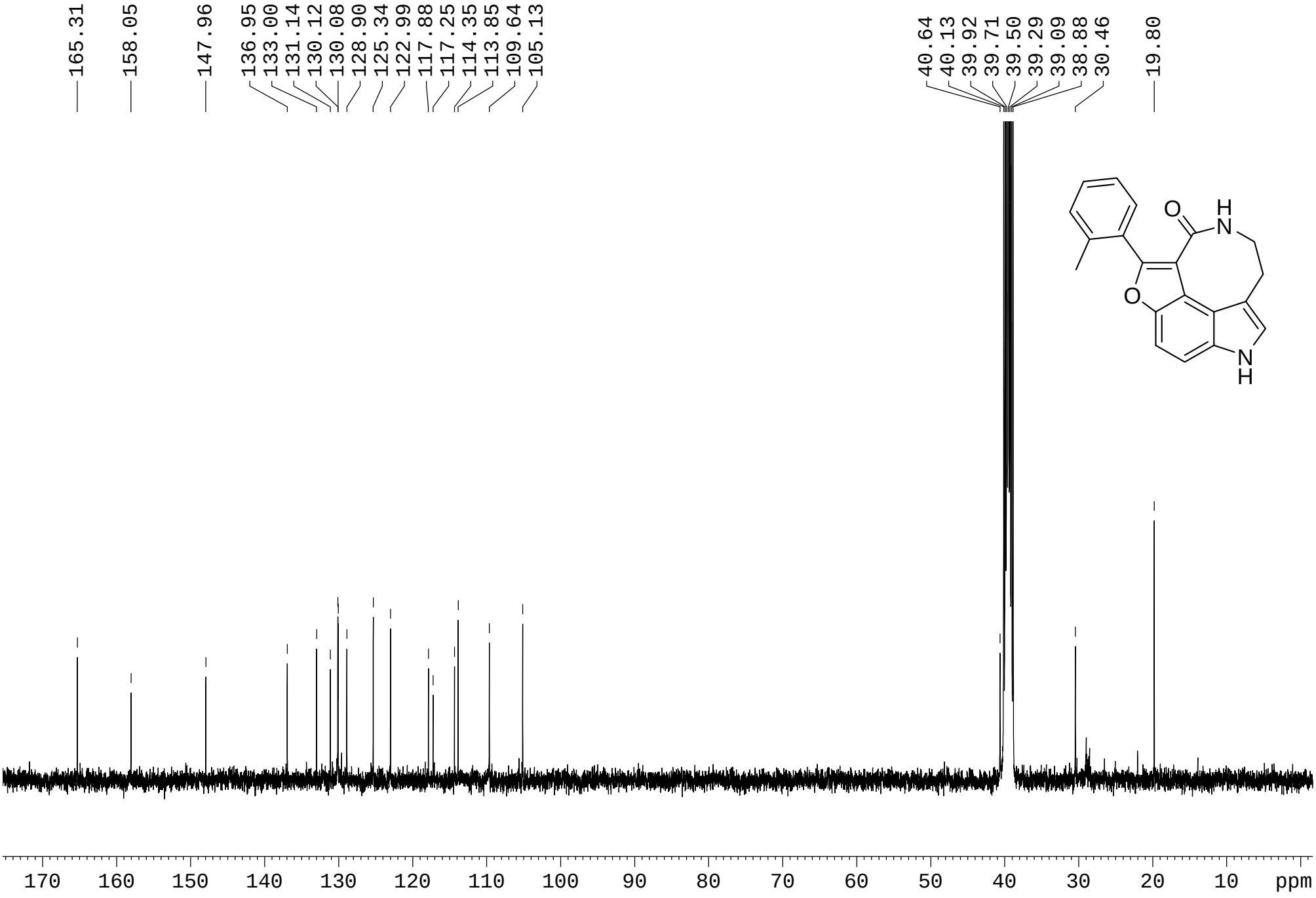
^{13}C NMR of compound 13f (DMSO-d_6; 100 MHz)



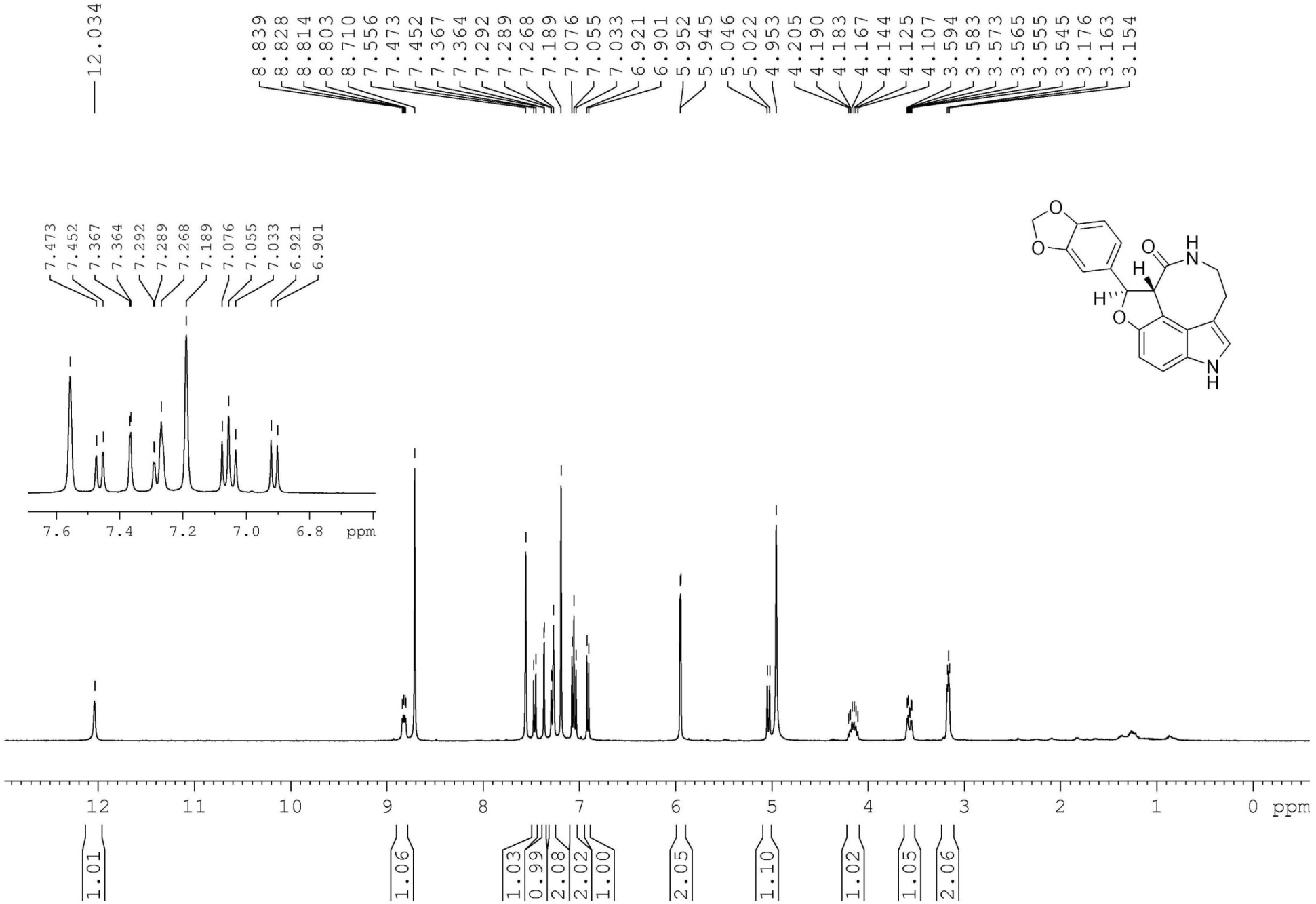
^{1}H NMR of compound 13g (DMSO-d_6; 400 MHz)



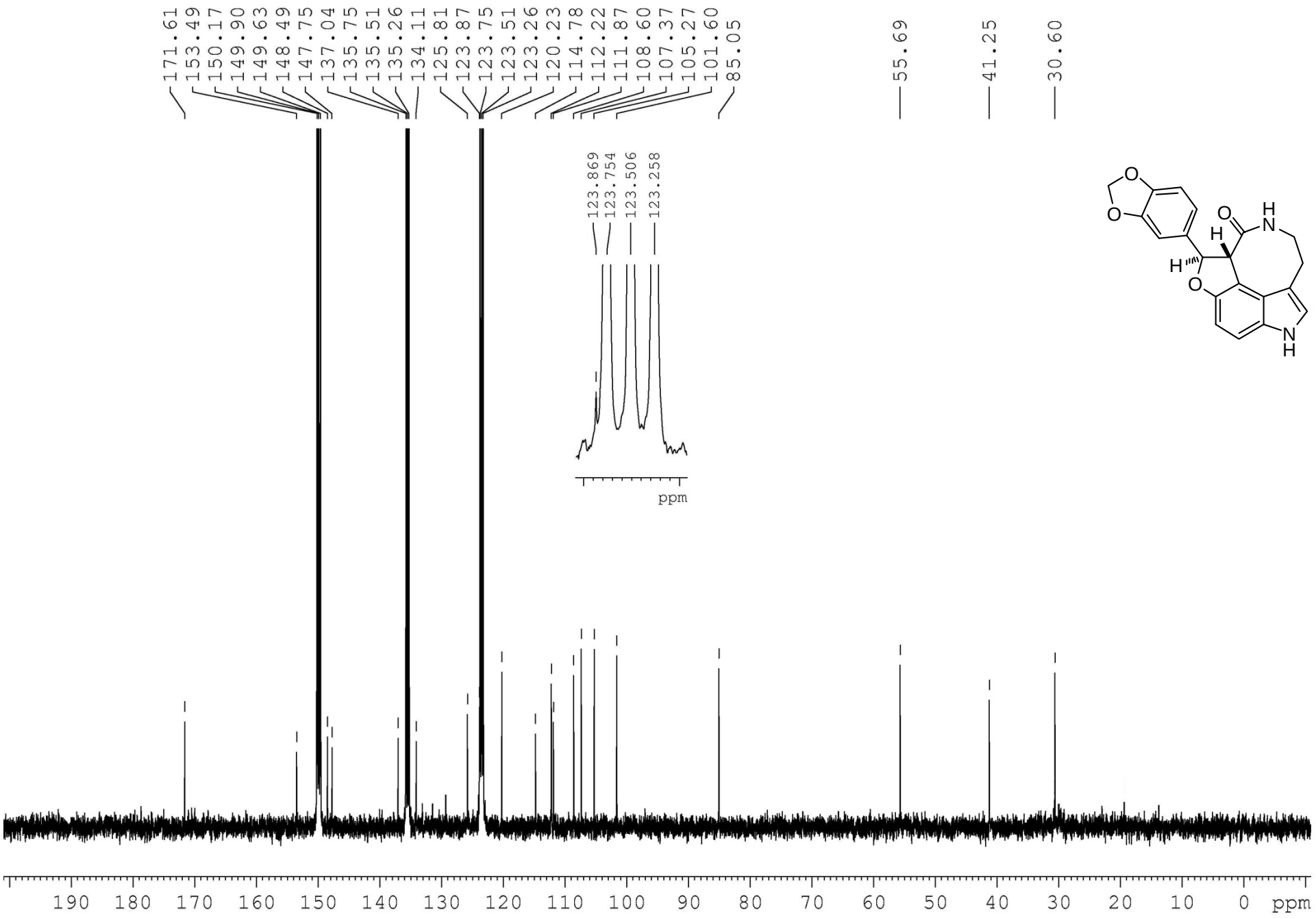
^{13}C NMR of compound 13g (DMSO-d_6; 100 MHz)



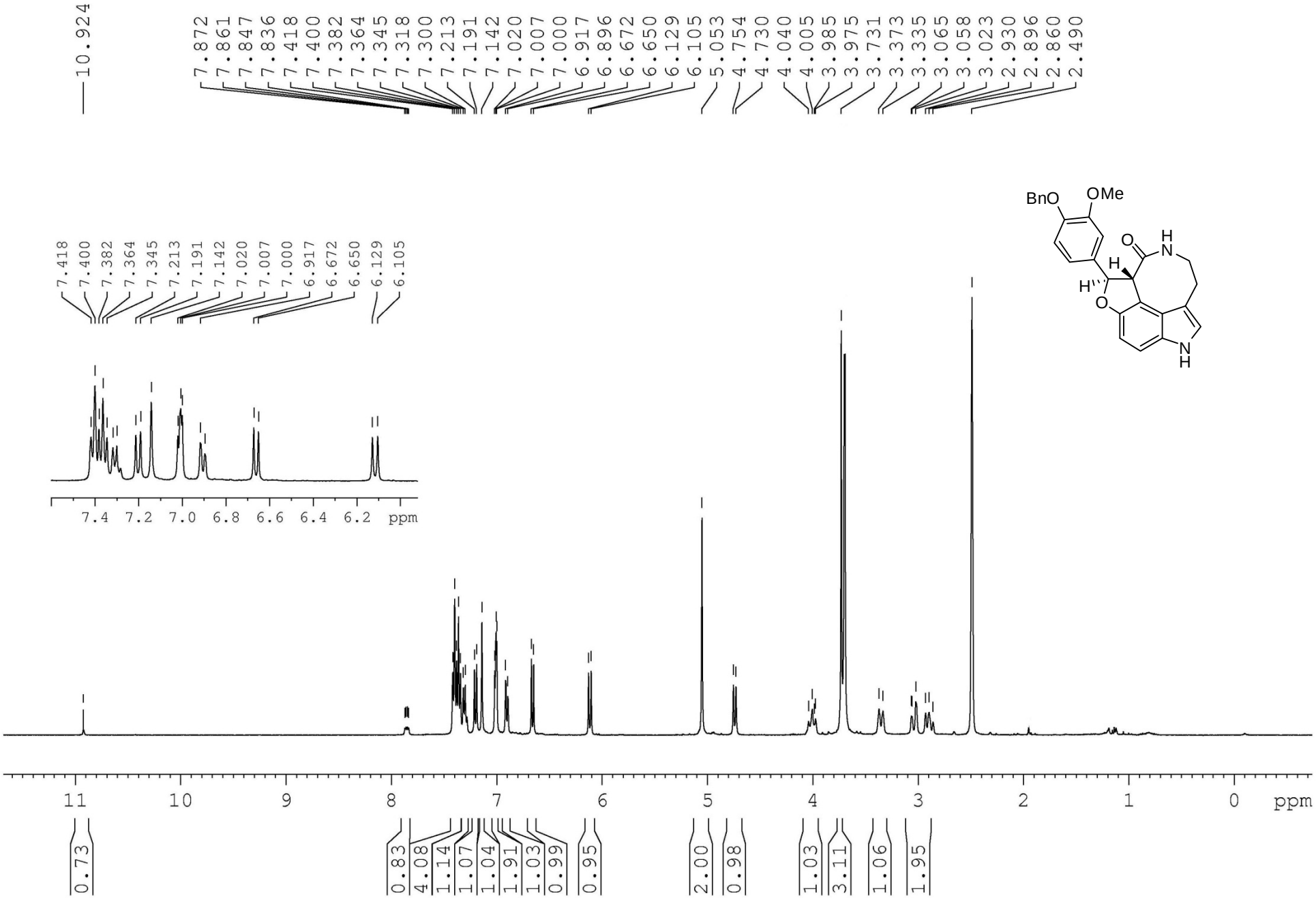
^{1}H NMR of (±)-Decursivine (Pyridine-d_5, 400 MHz)



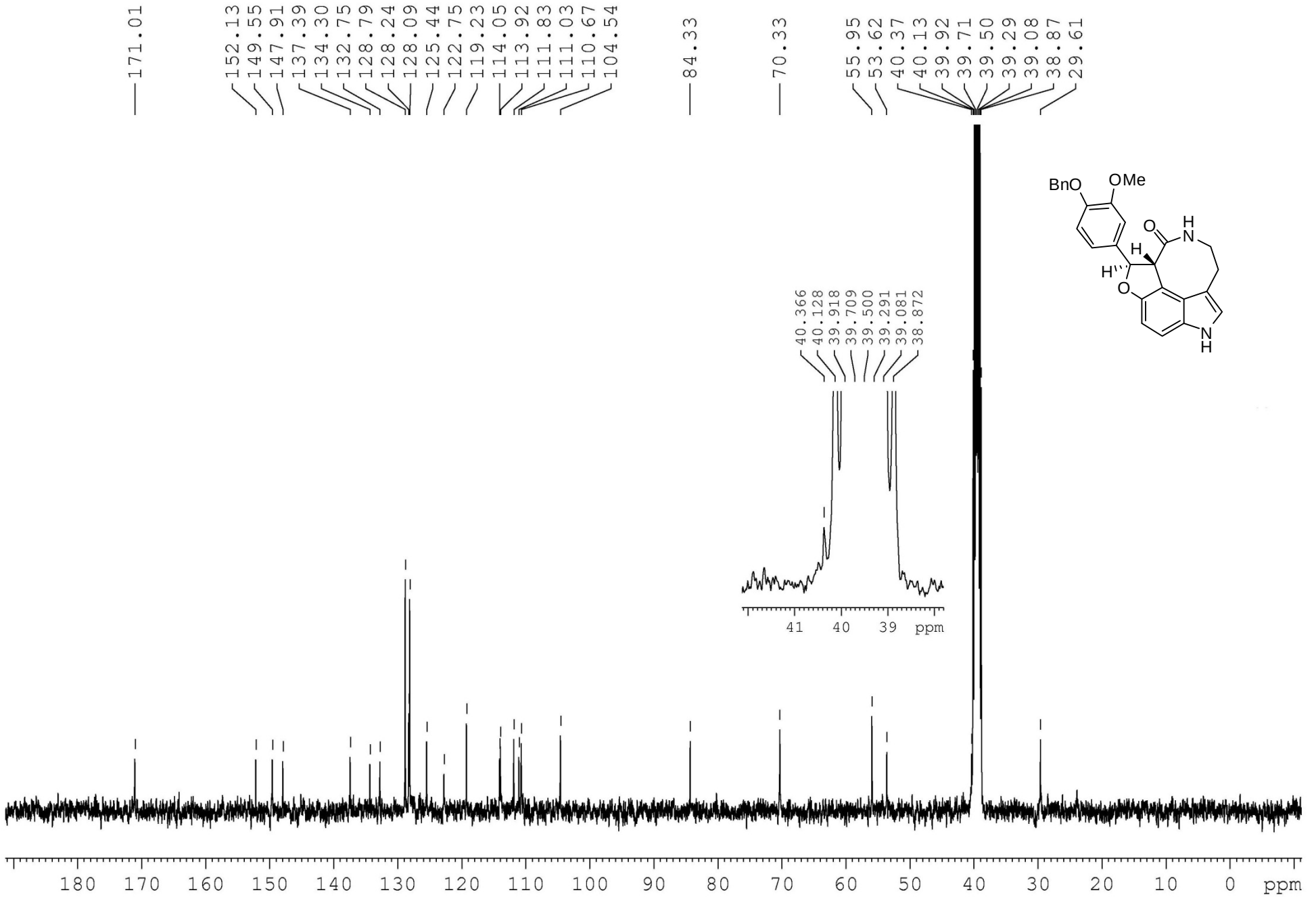
^{13}C NMR of (±)-Decursivine (Pyridine-d_5, 100 MHz)



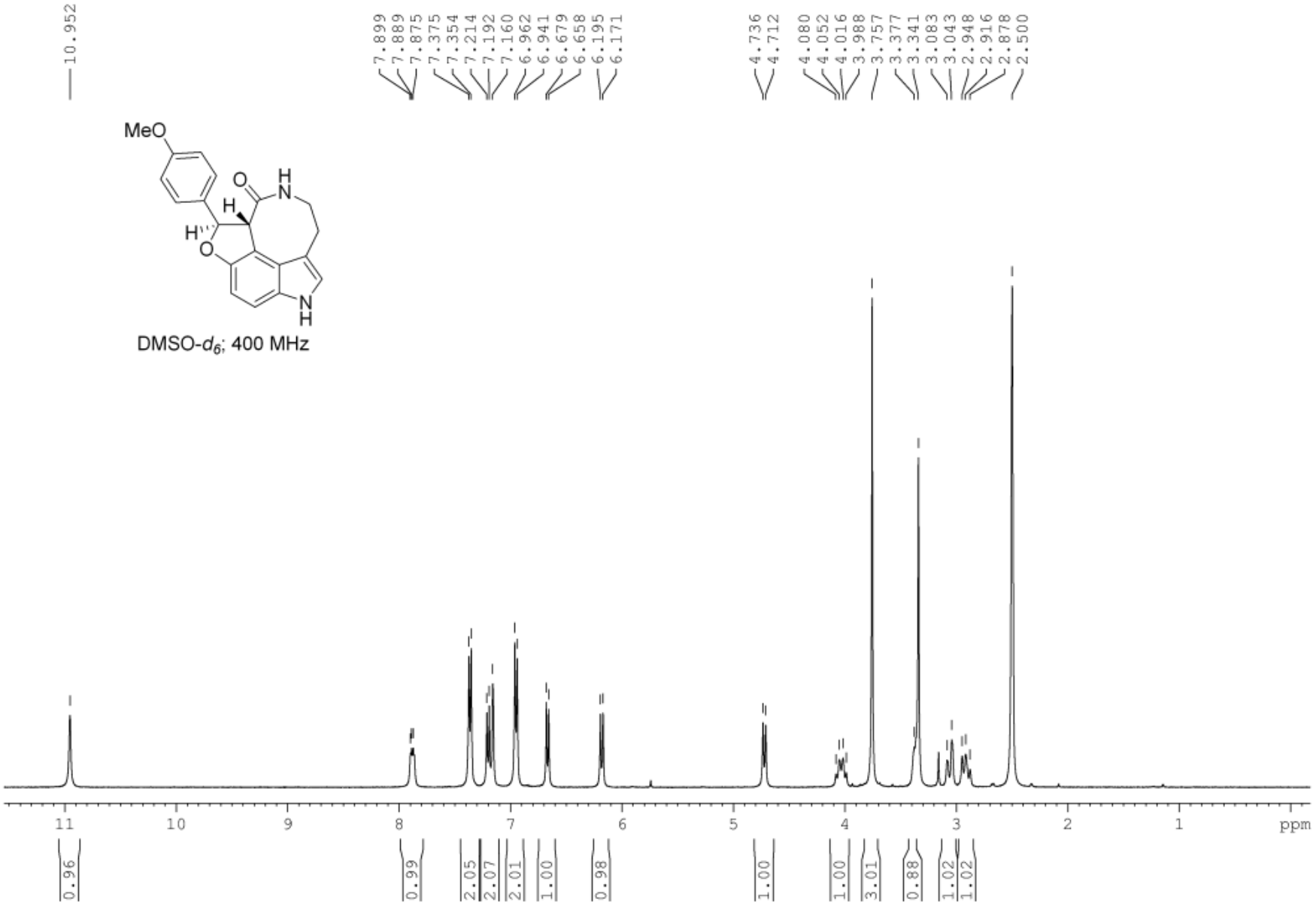
^{1}H NMR of compound 4c (DMSO-d_6, 400 MHz)



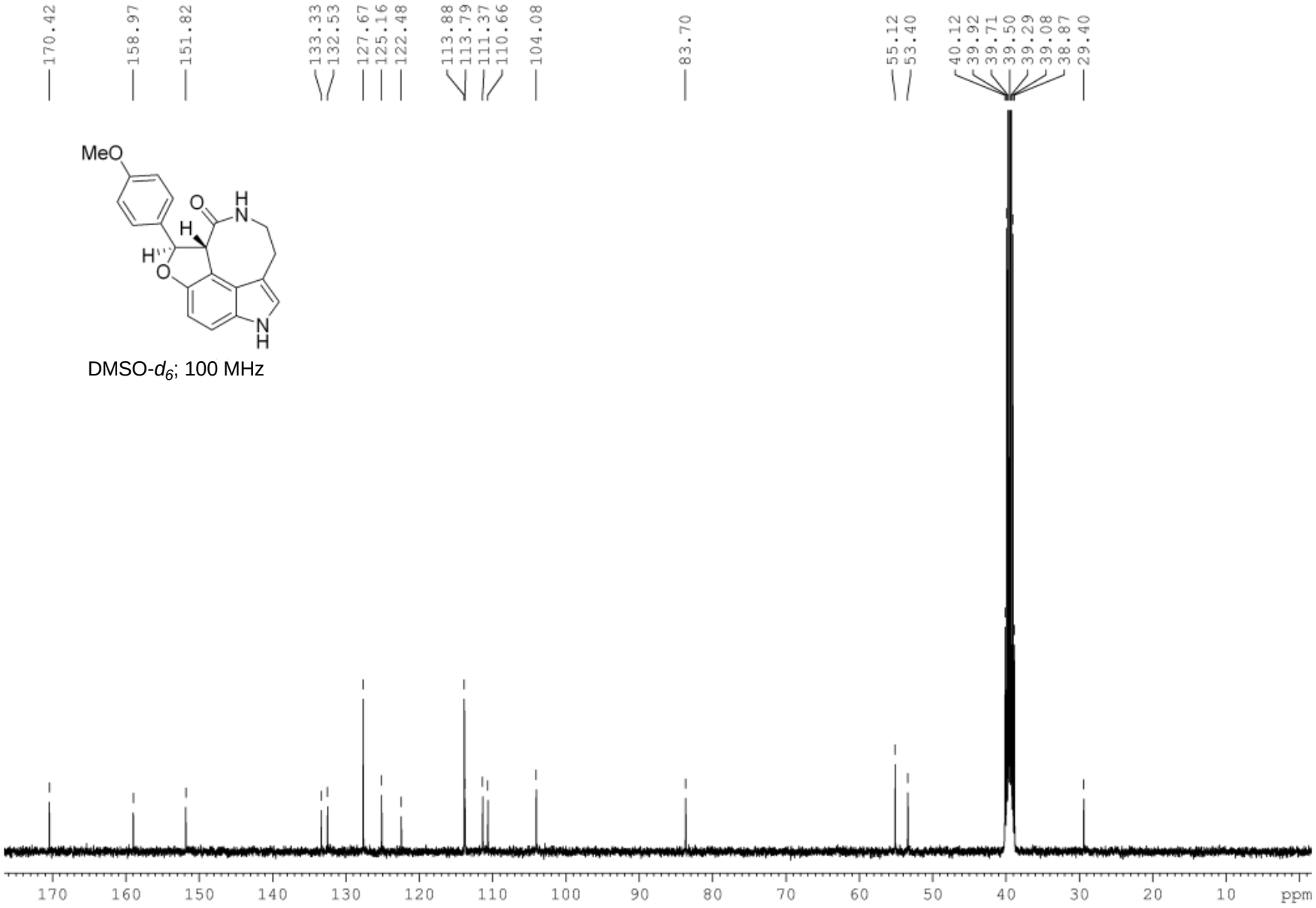
^{13}C NMR of compound 4c (DMSO-d_6, 100 MHz)



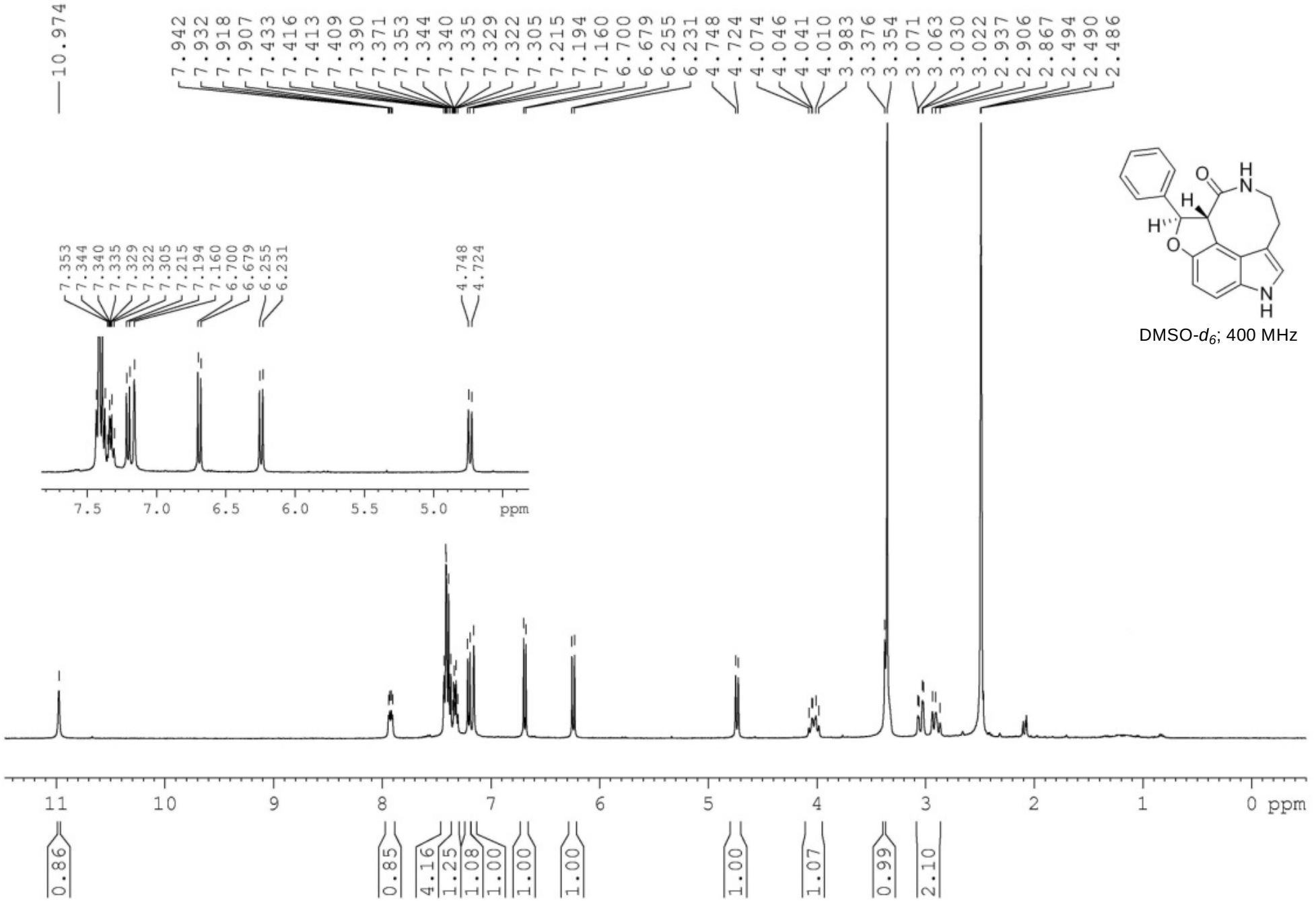
^{1}H NMR of compound 4a (DMSO-d_6, 400 MHz)



^{13}C NMR of compound 4a (DMSO-d_6, 100 MHz)

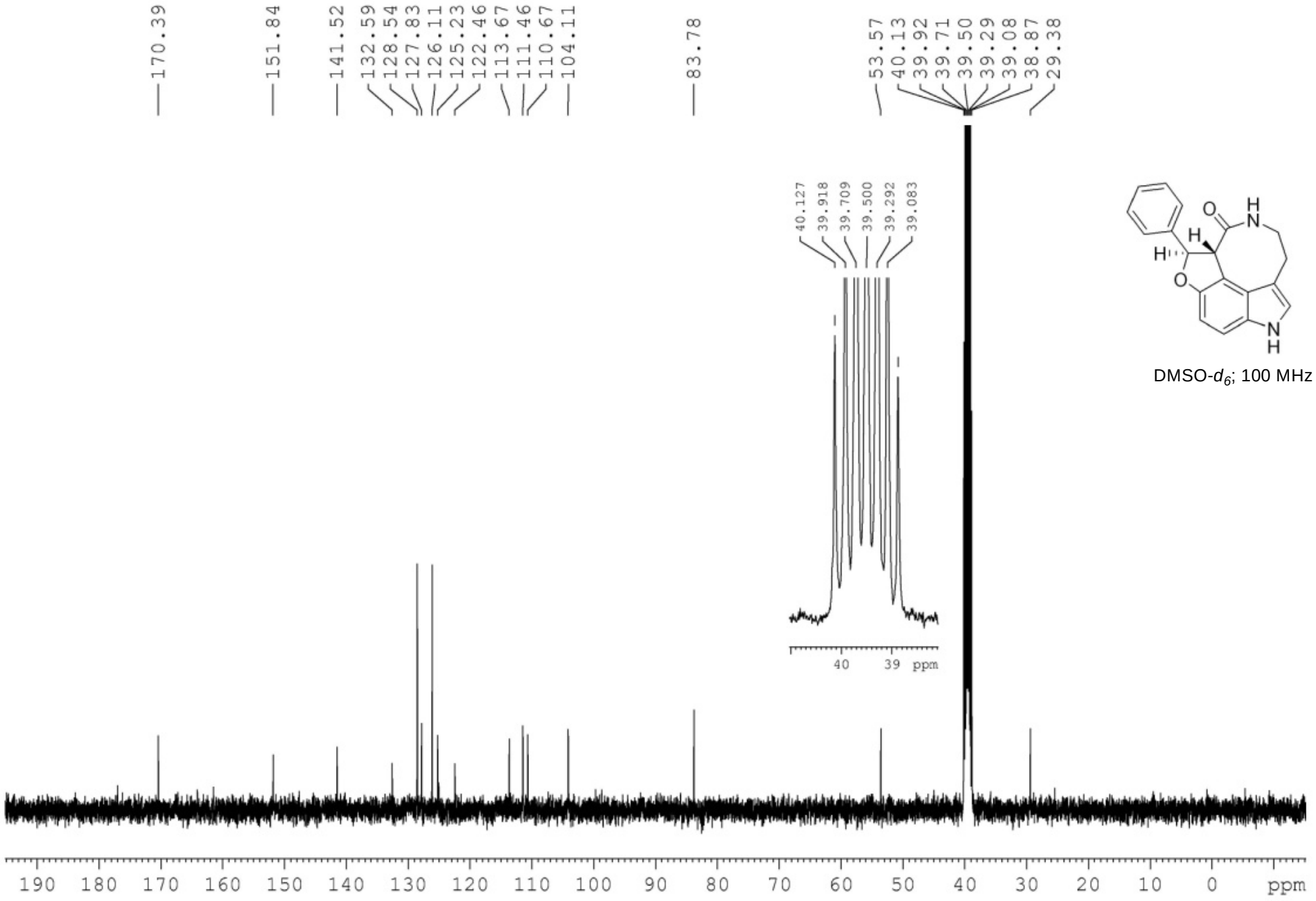


^{1}H NMR of compound 4d (DMSO-d_6, 400 MHz)

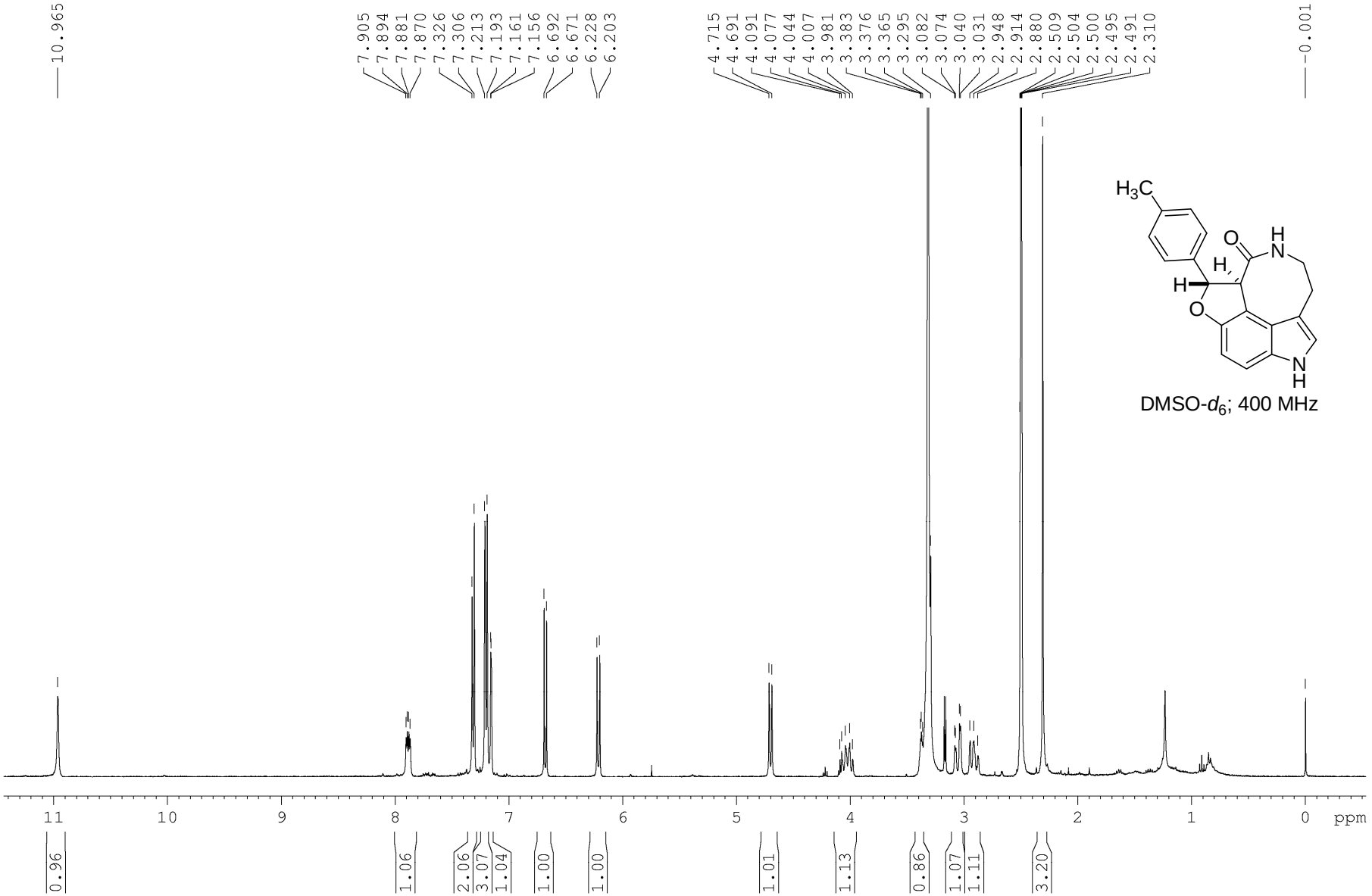


DMSO-d_6; 400 MHz

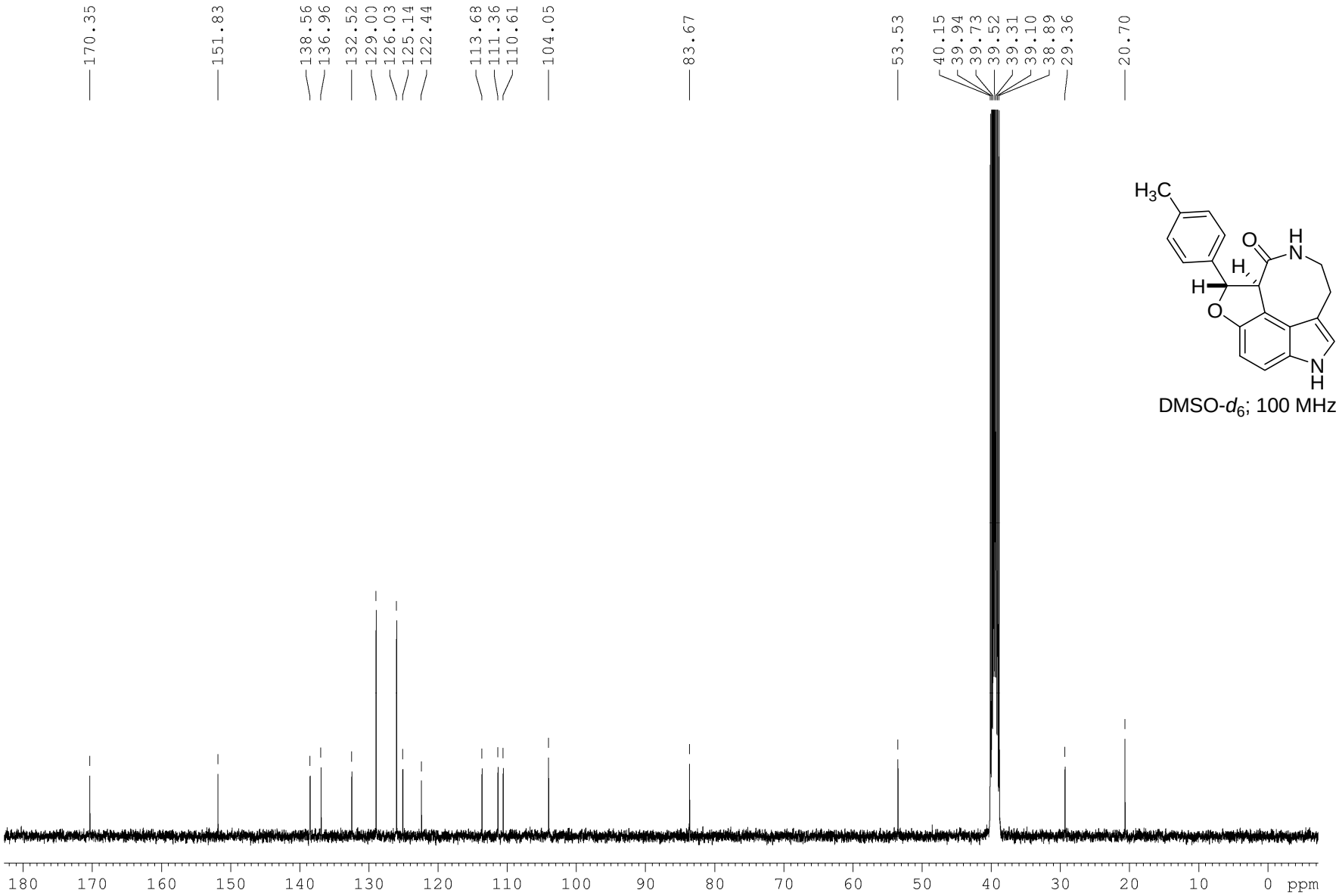
^{13}C NMR of compound 4d (DMSO-d_6, 100 MHz)



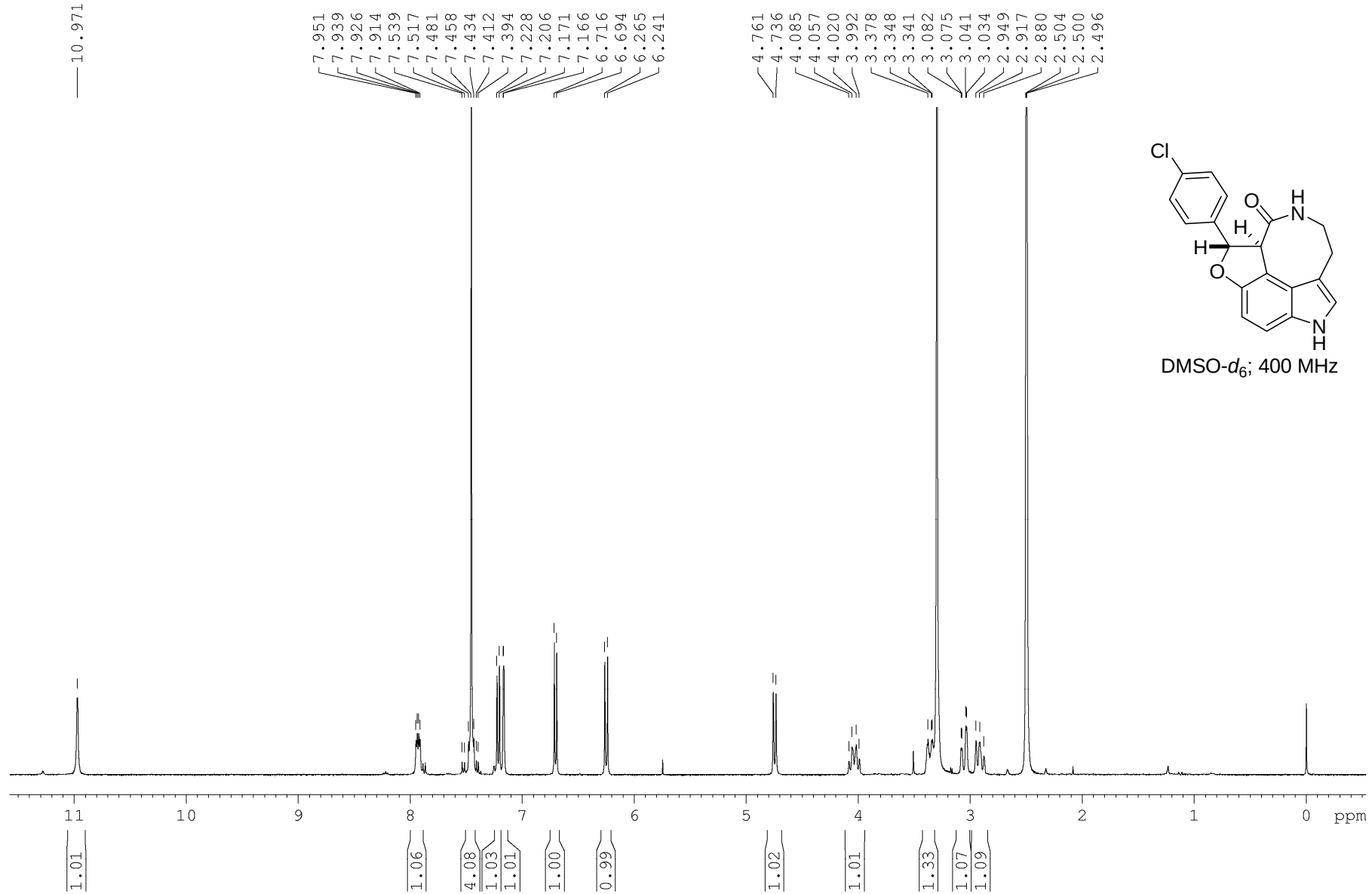
^{1}H NMR of compound 4e (DMSO-d_6, 400 MHz)



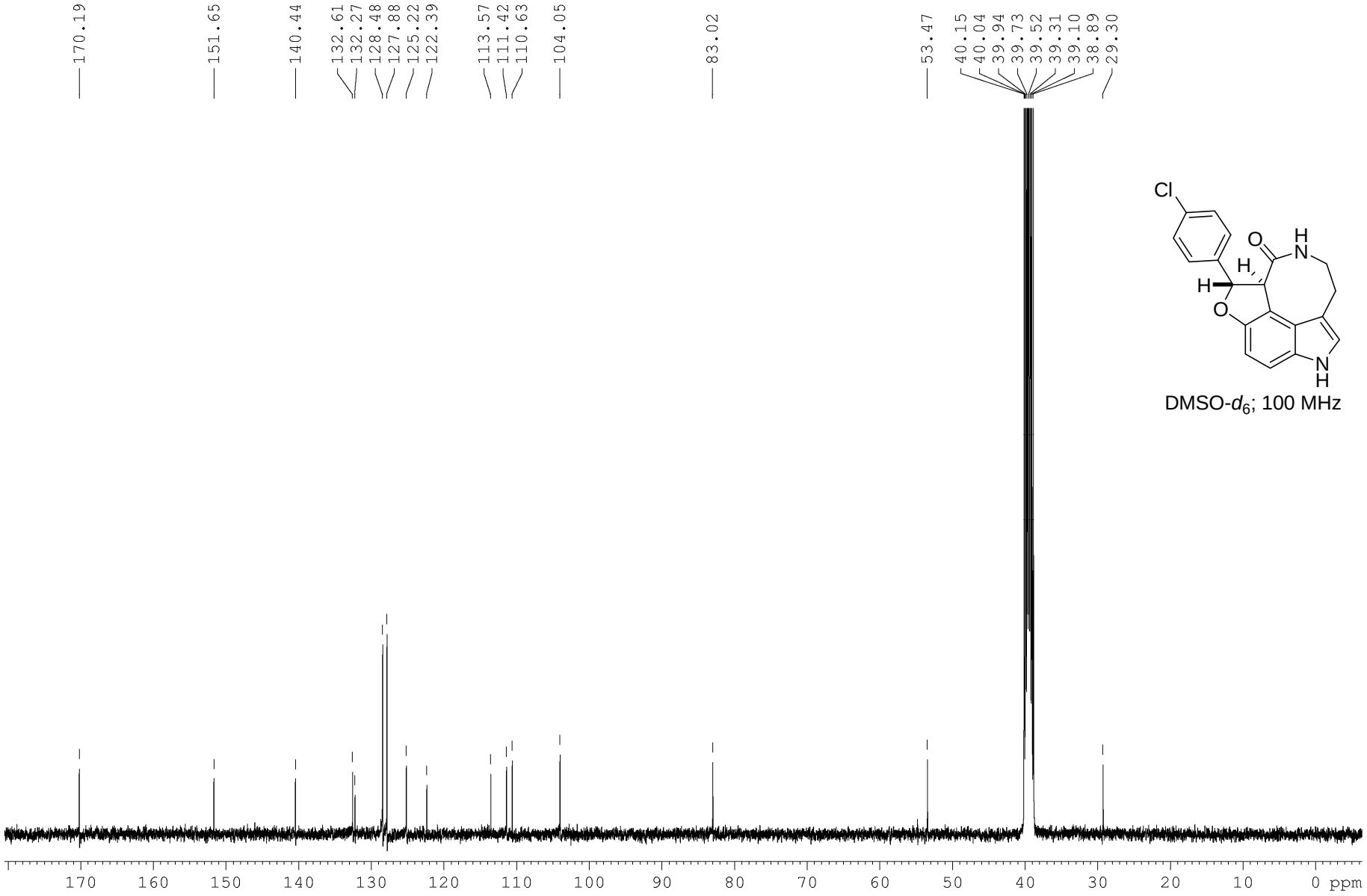
^{13}C NMR of compound 4e (DMSO-d_6, 100 MHz)



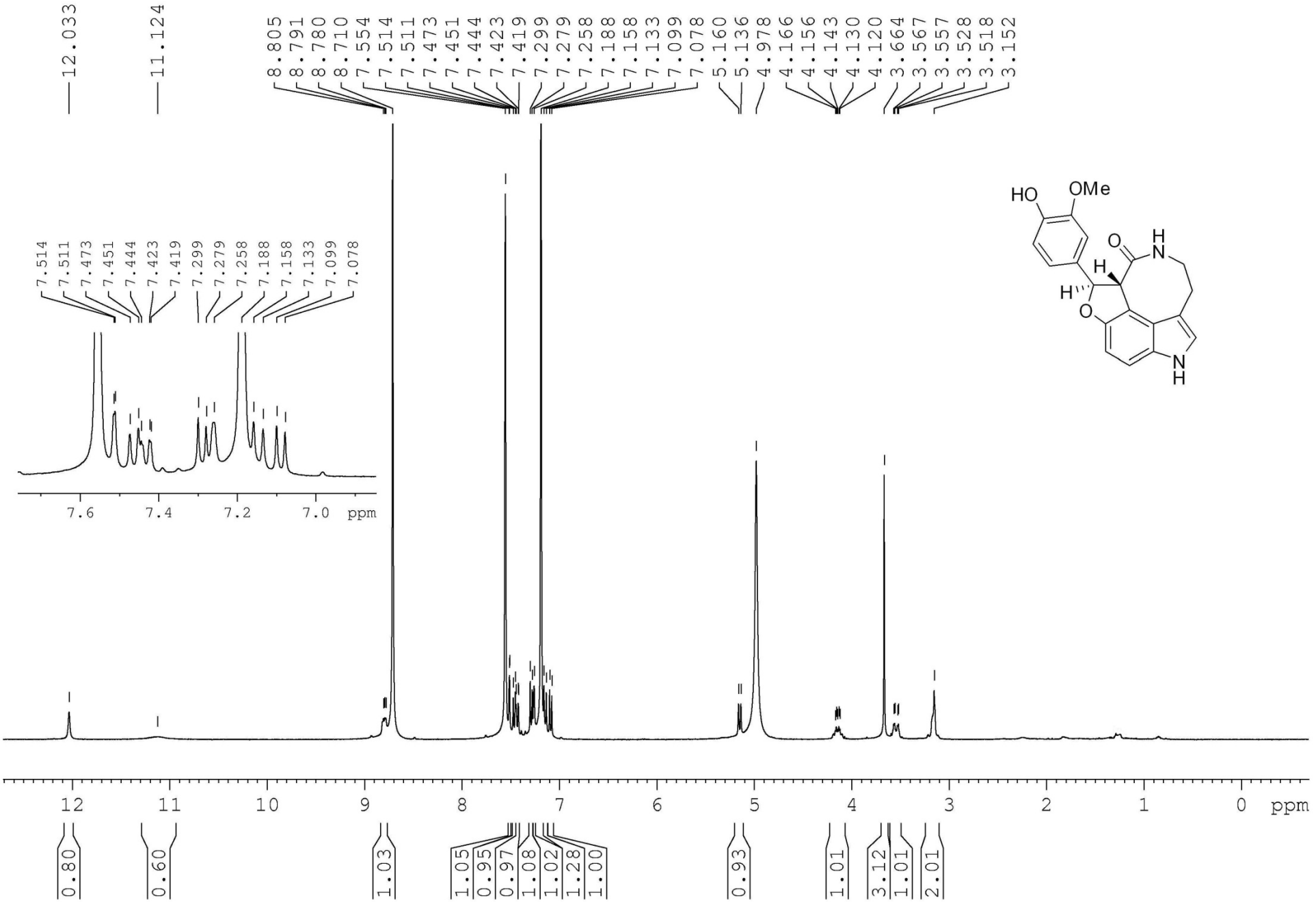
^{1}H NMR of compound 4f (DMSO-d_6, 400 MHz)



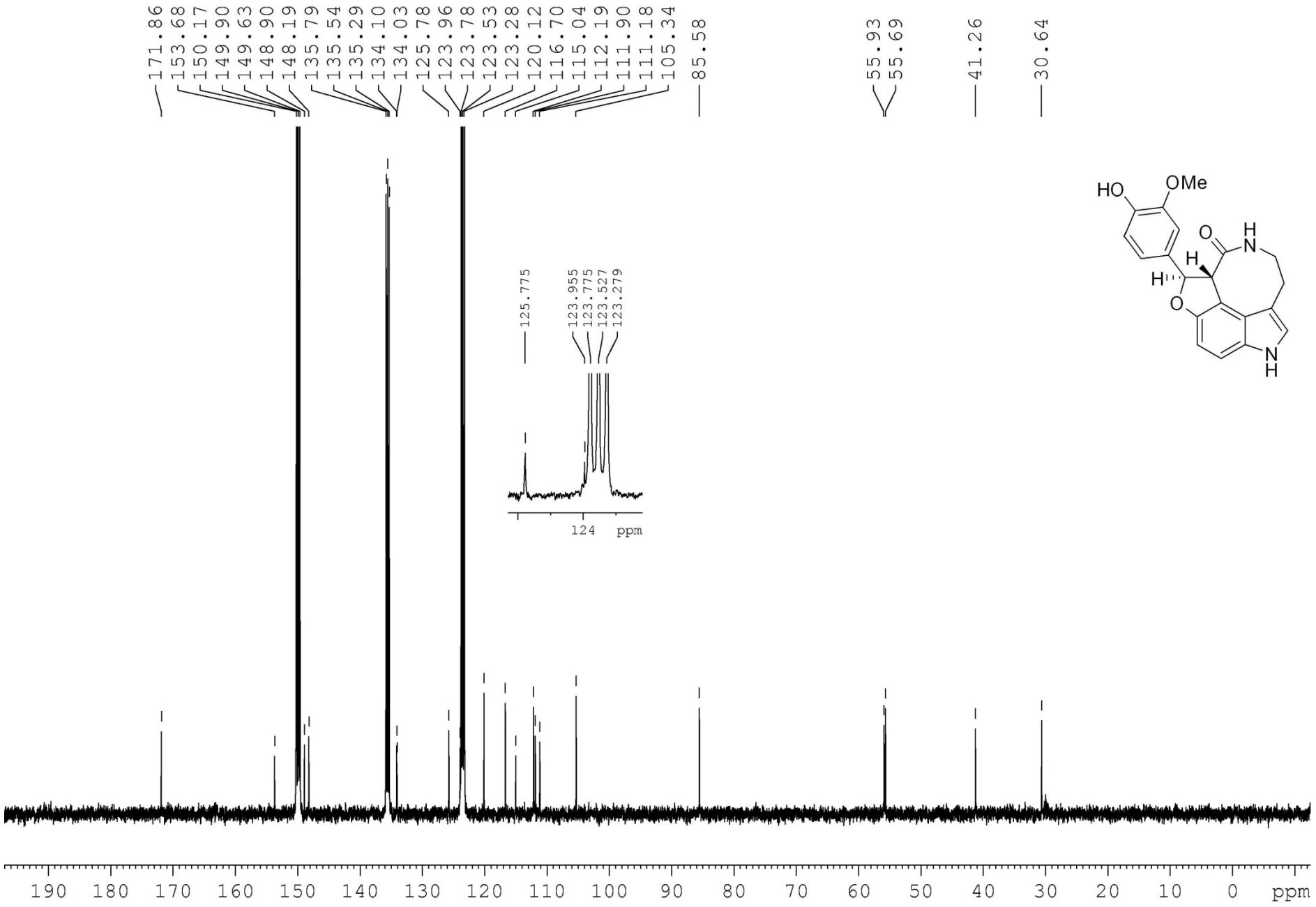
^{13}C NMR of compound 4f (DMSO-d_6, 100 MHz)



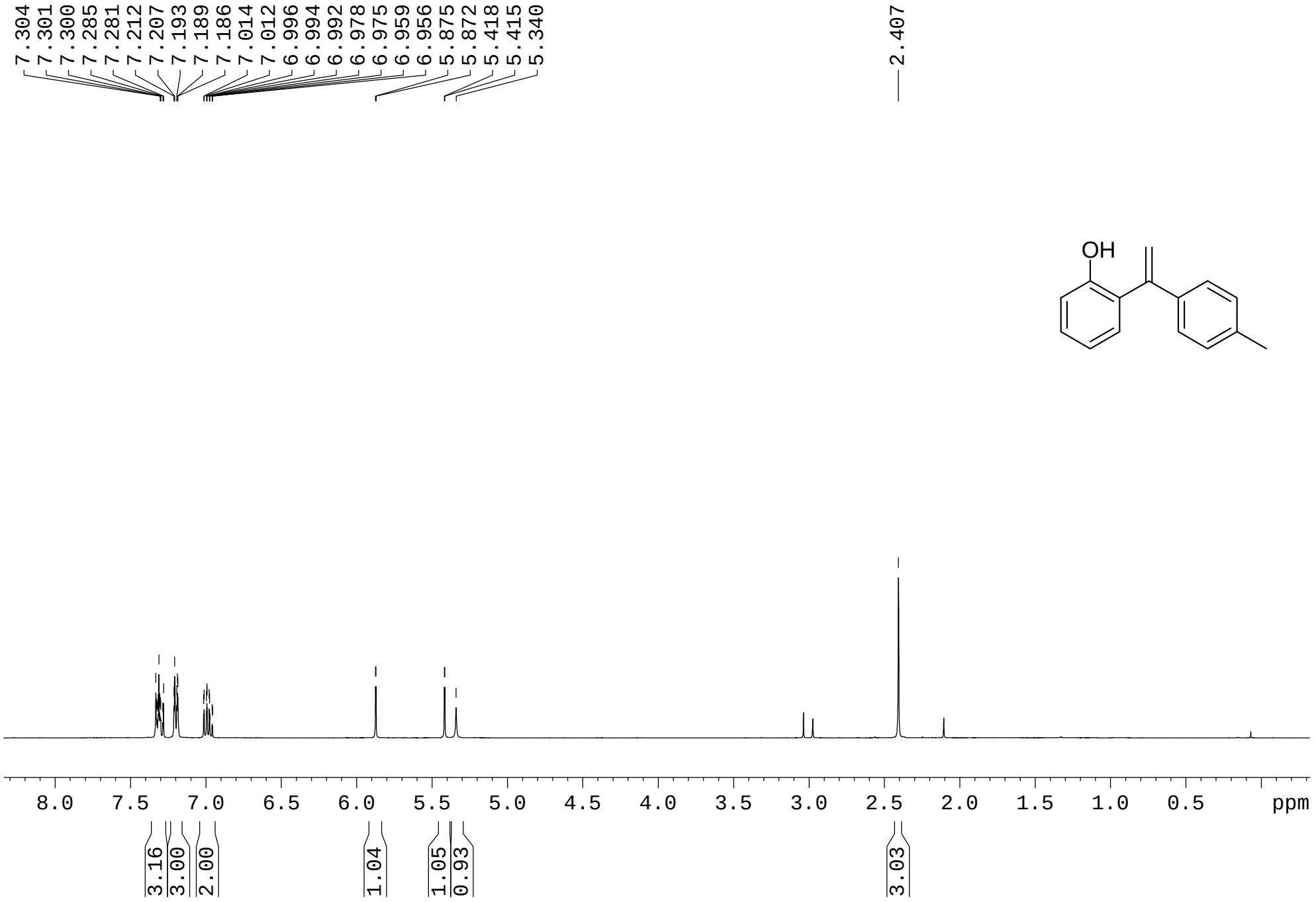
^{1}H NMR of (±)-Serotobenine (Pyridine-d_5, 400 MHz)



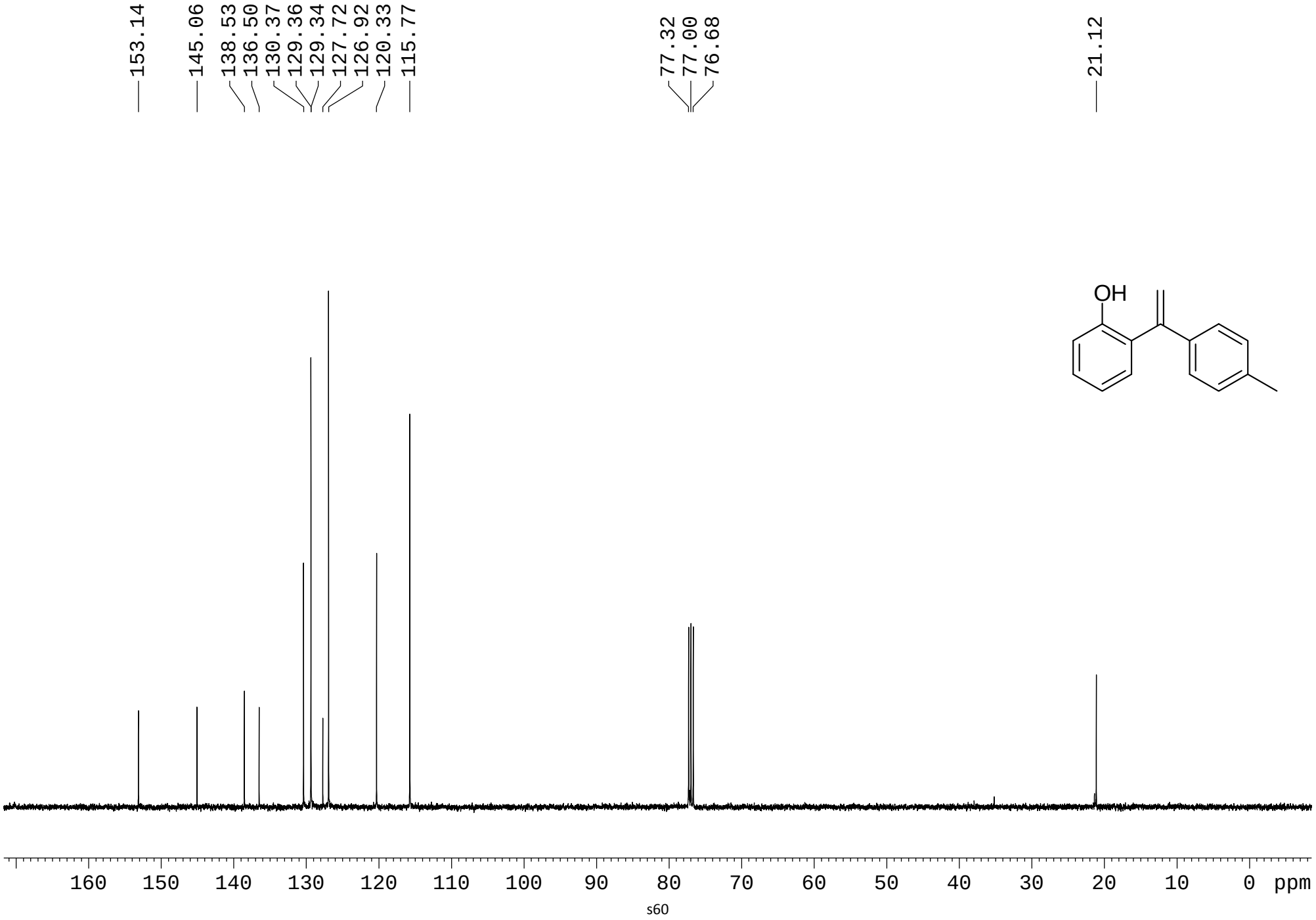
^{13}C NMR of (±)-Serotobenine (Pyridine-d_5, 100 MHz)



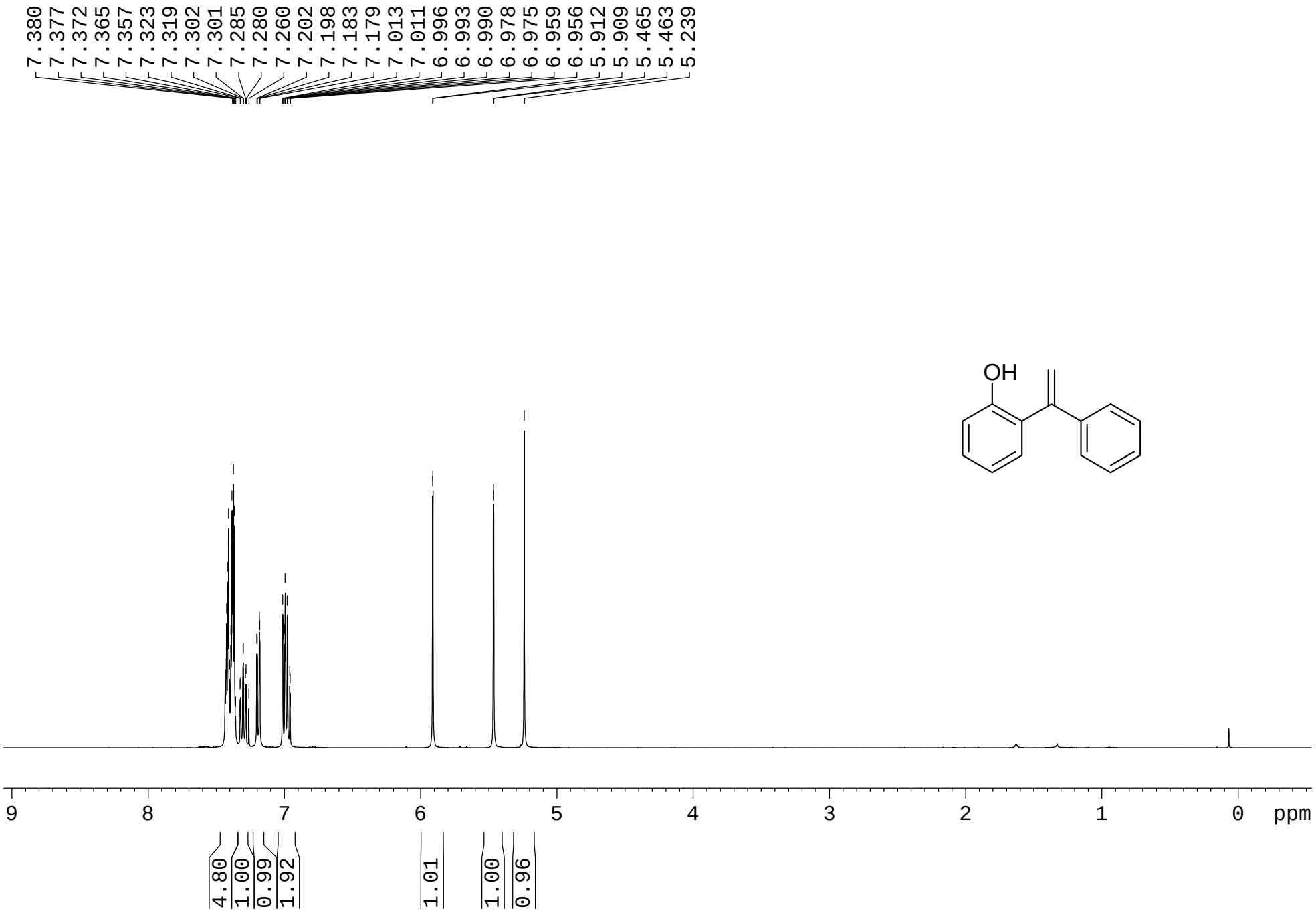
^{1}H NMR of compound 15a ($CDCl_3$, 400 MHz)



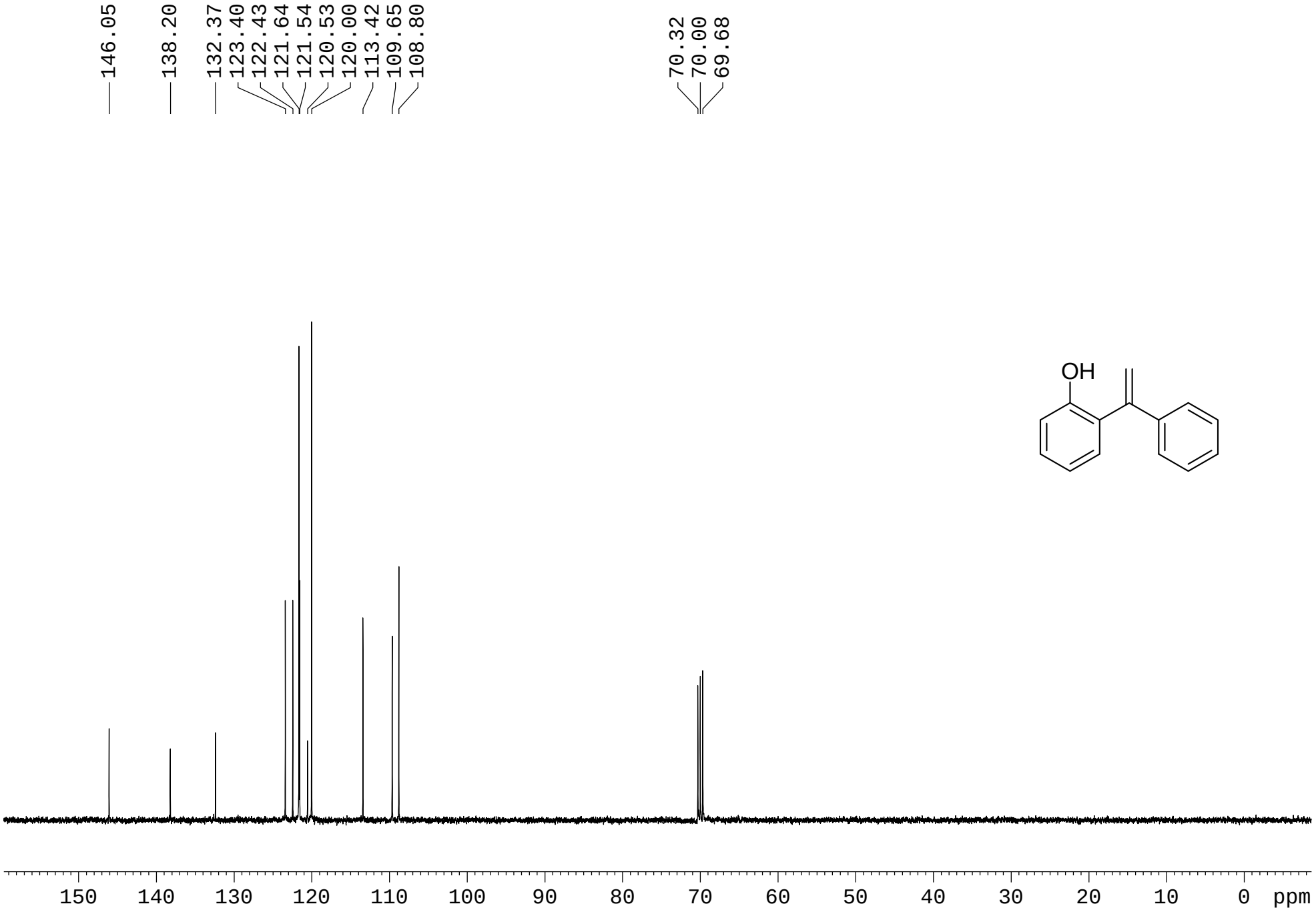
^{13}C NMR of compound 15a ($CDCl_3$, 100 MHz)



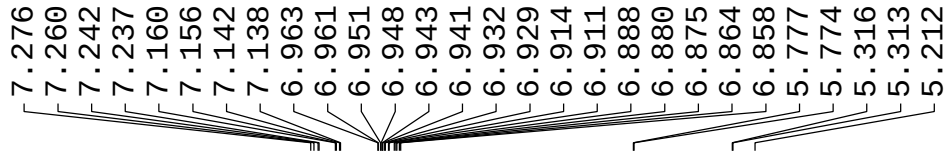
^{1}H NMR of compound 15b ($CDCl_3$, 400 MHz)

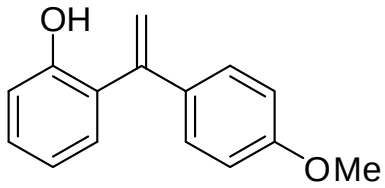


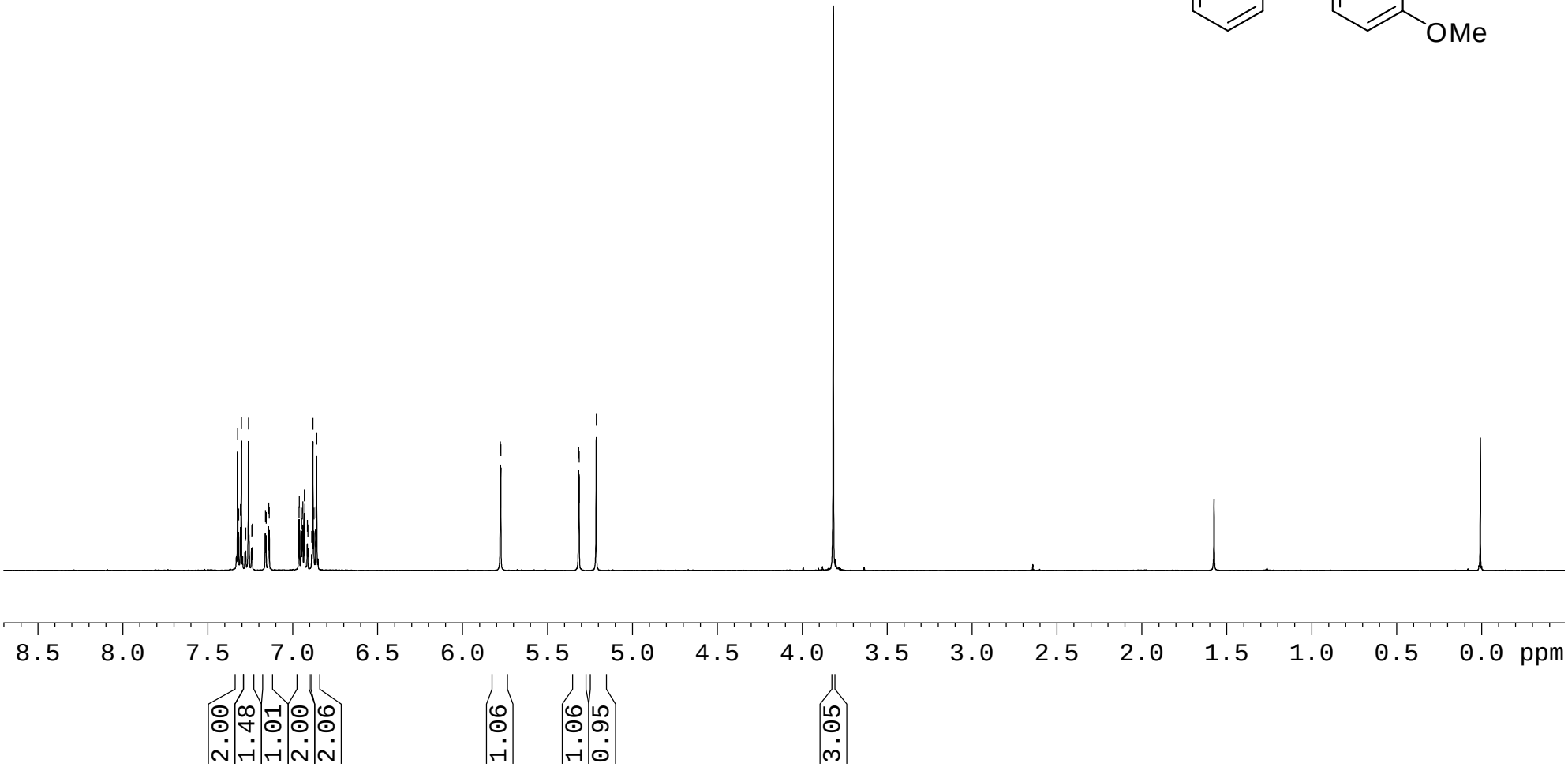
^{13}C NMR of compound 15b ($CDCl_3$, 100 MHz)



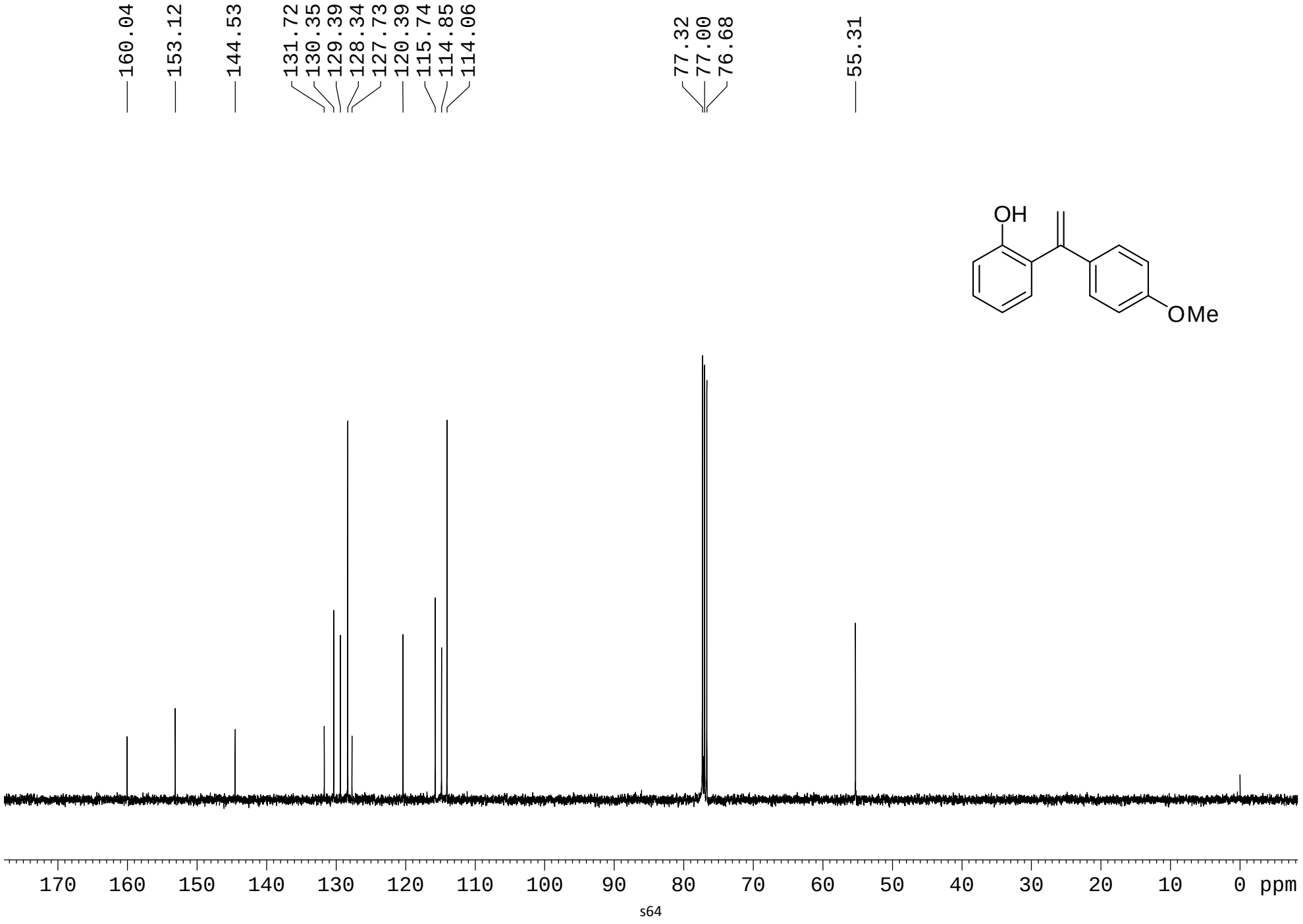
^{1}H NMR of compound 15c ($CDCl_3$, 400 MHz)



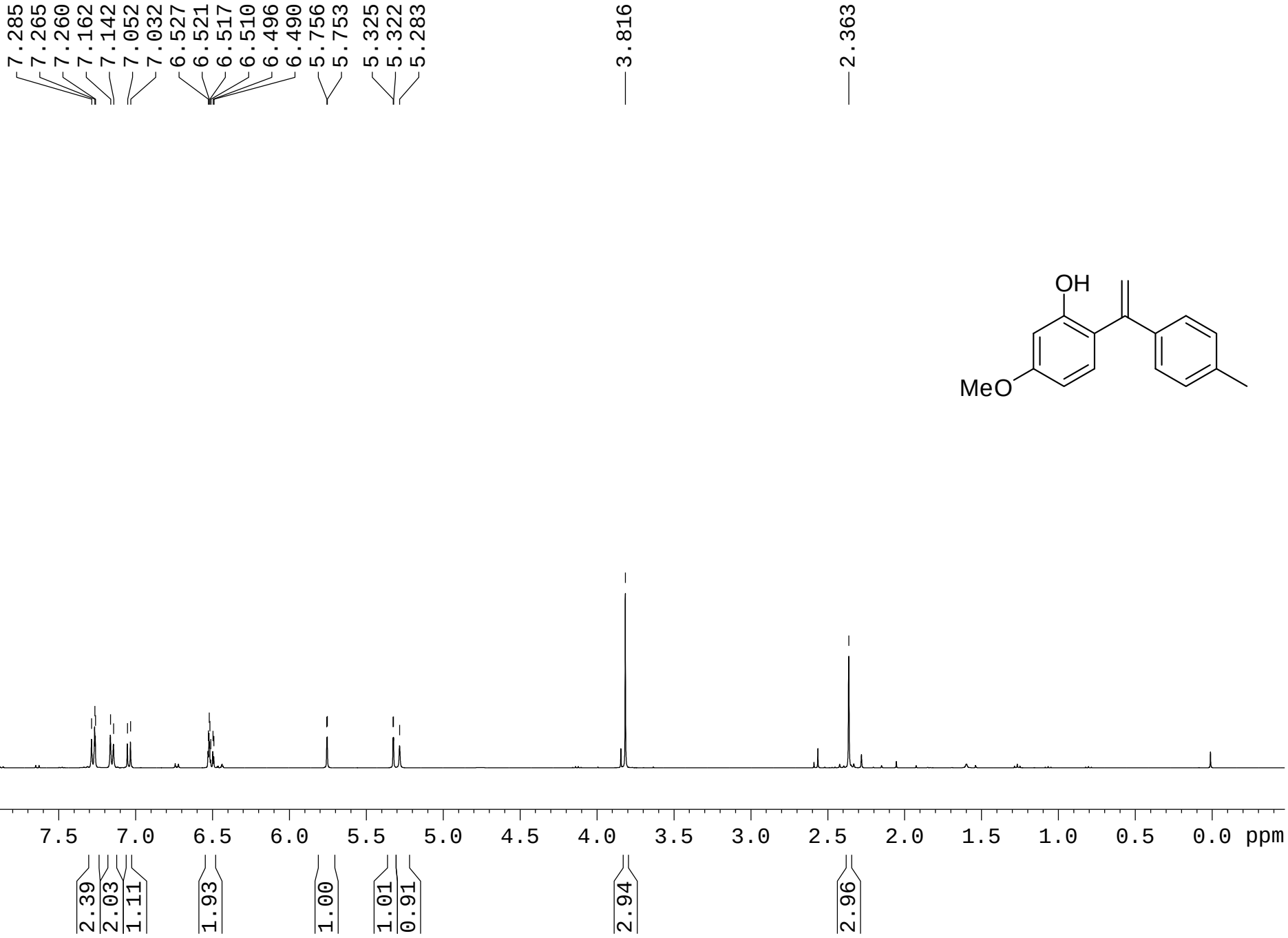




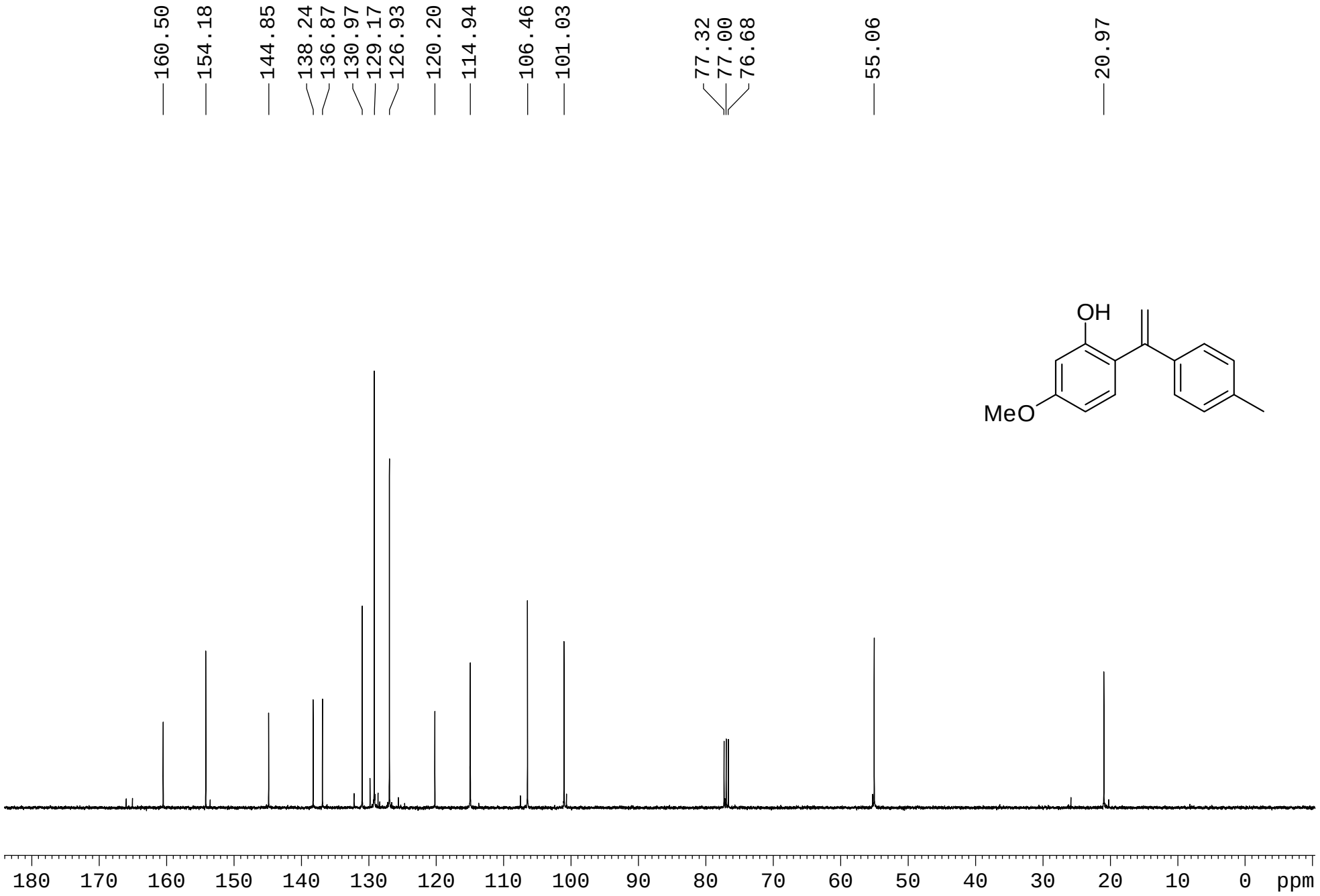
^{13}C NMR of compound 15c ($CDCl_3$, 100 MHz)



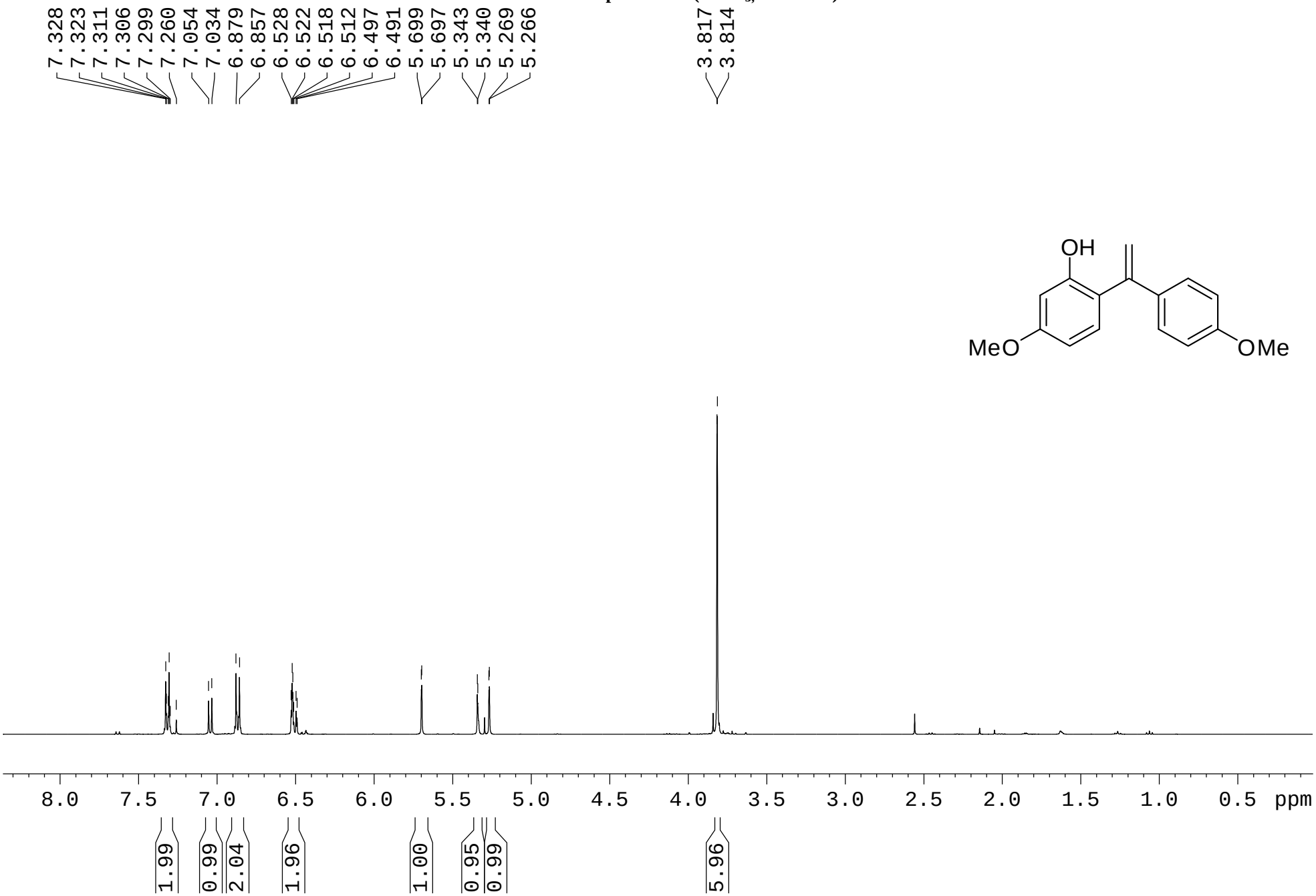
^{1}H NMR of compound 15d ($CDCl_3$, 400 MHz)



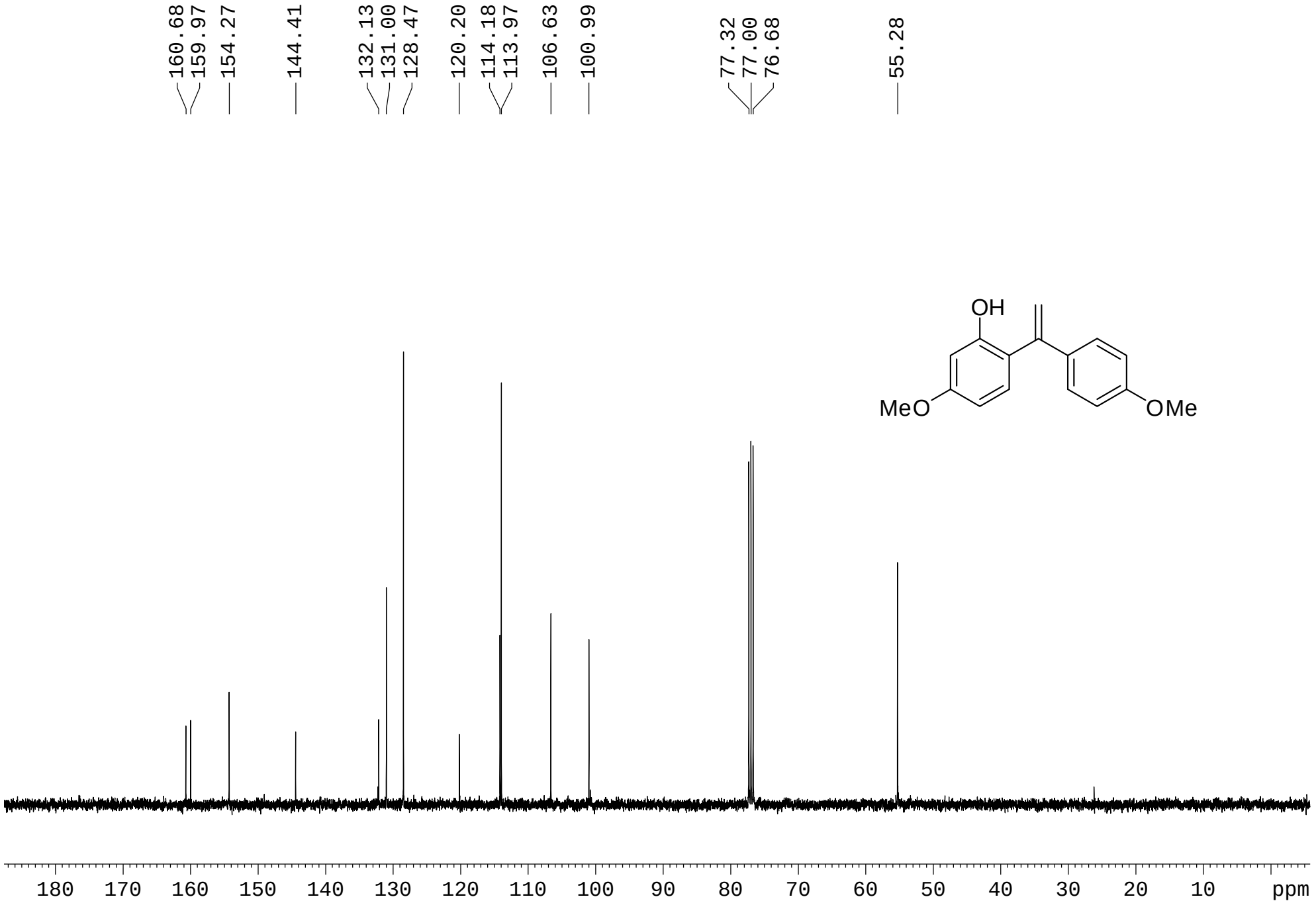
^{13}C NMR of compound 15d ($CDCl_3$, 100 MHz)



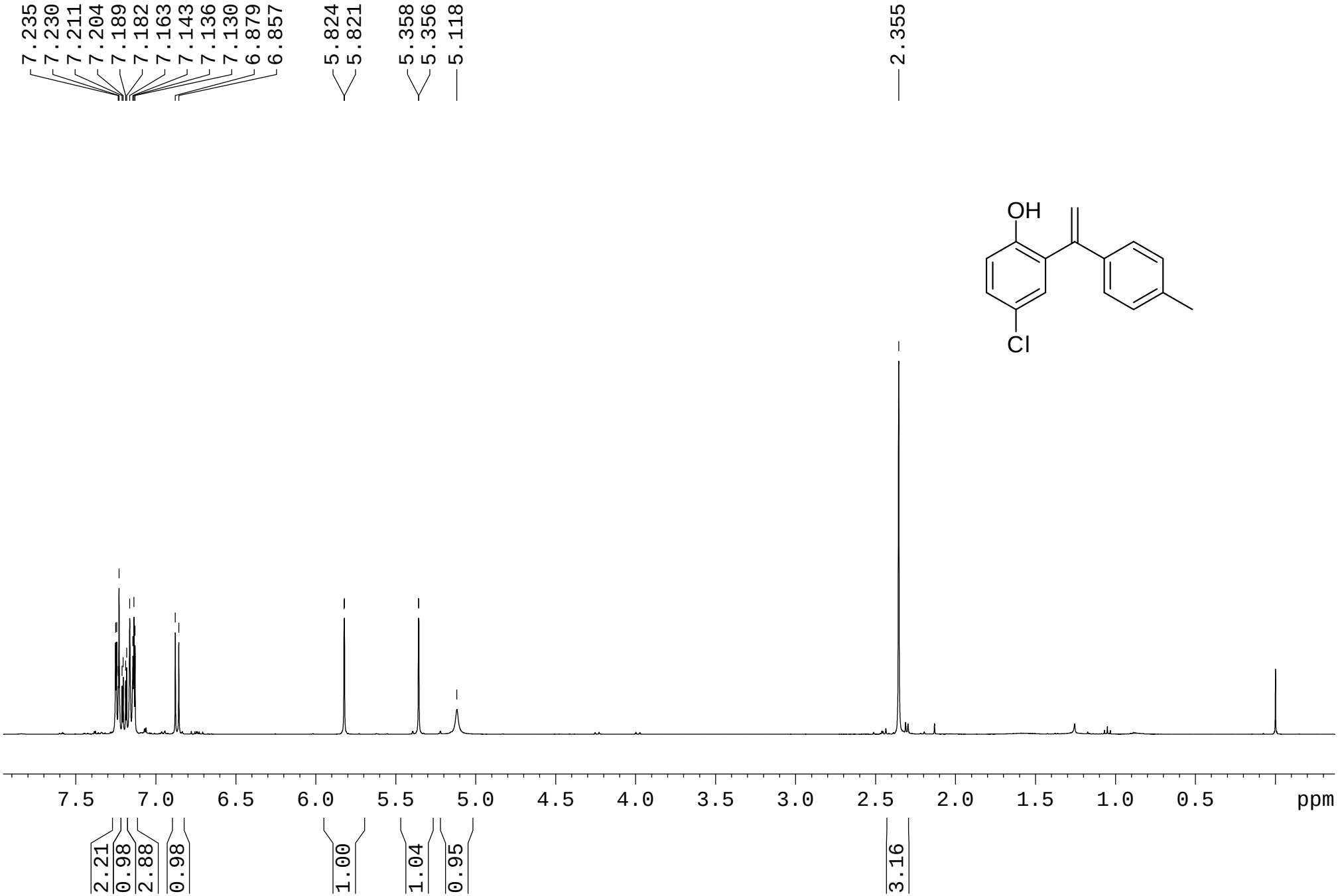
^{1}H NMR of compound 15e ($CDCl_3$, 400 MHz)



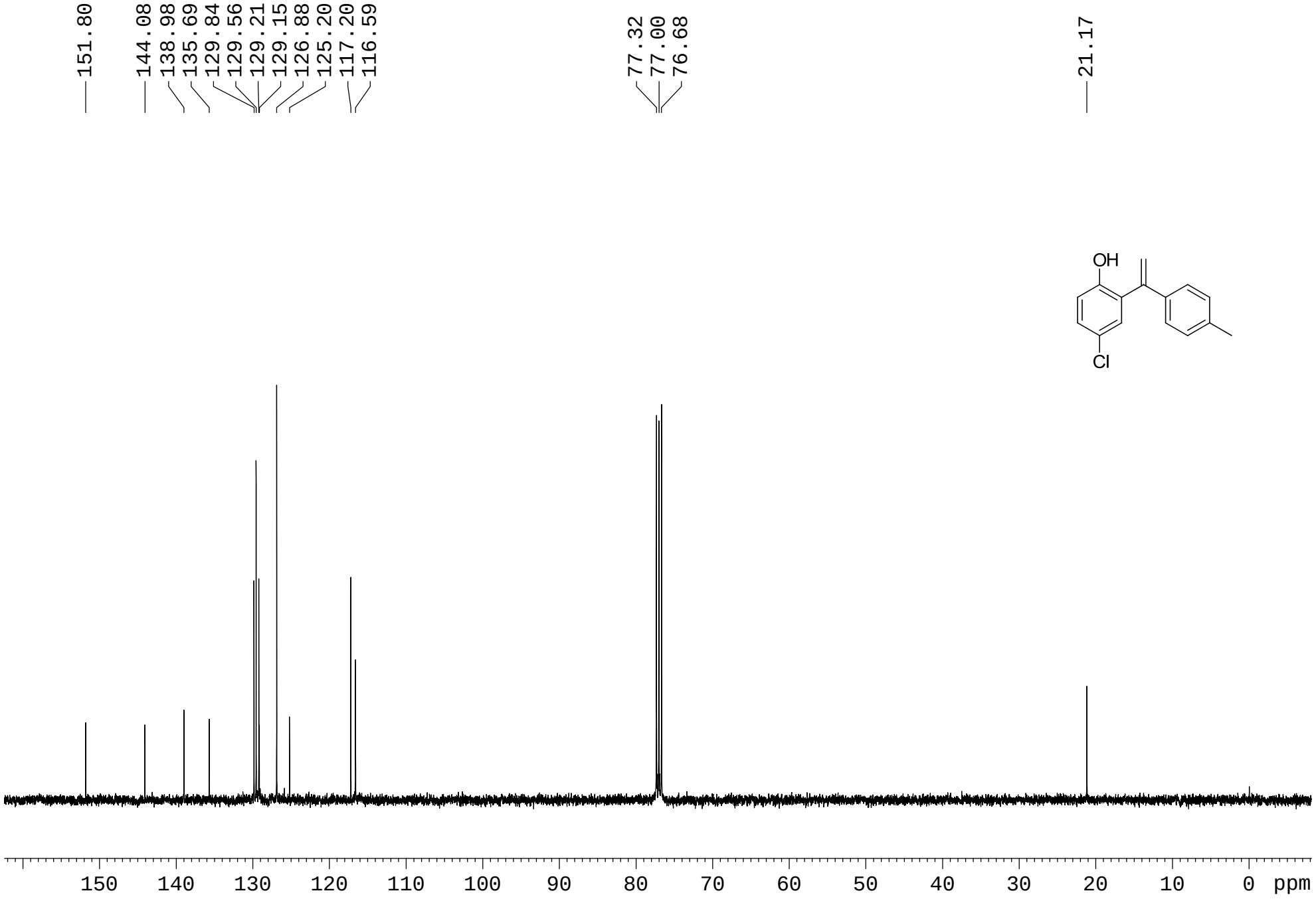
^{13}C NMR of compound 15e ($CDCl_3$, 100 MHz)



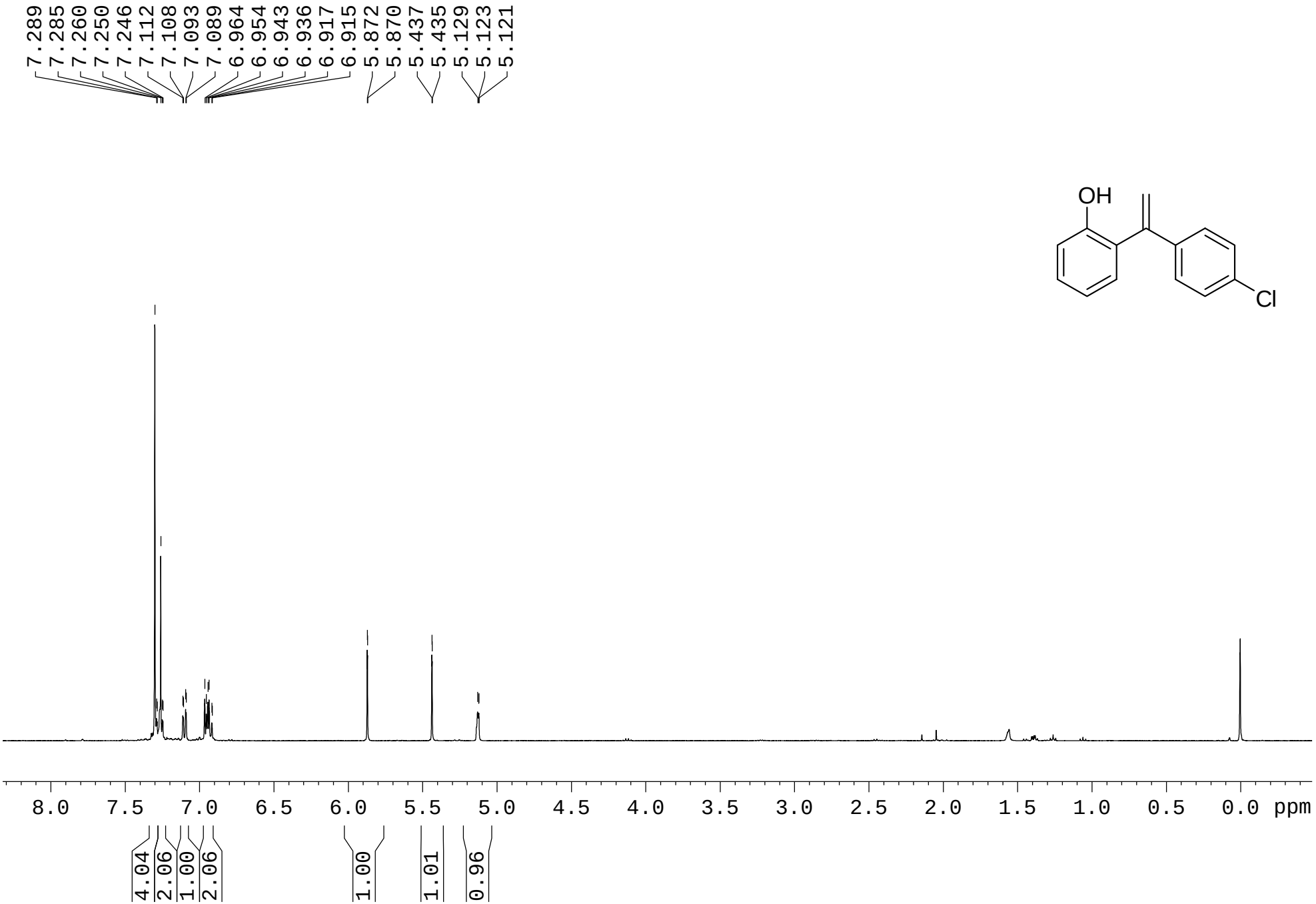
^{1}H NMR of compound 15f ($CDCl_3$, 400 MHz)



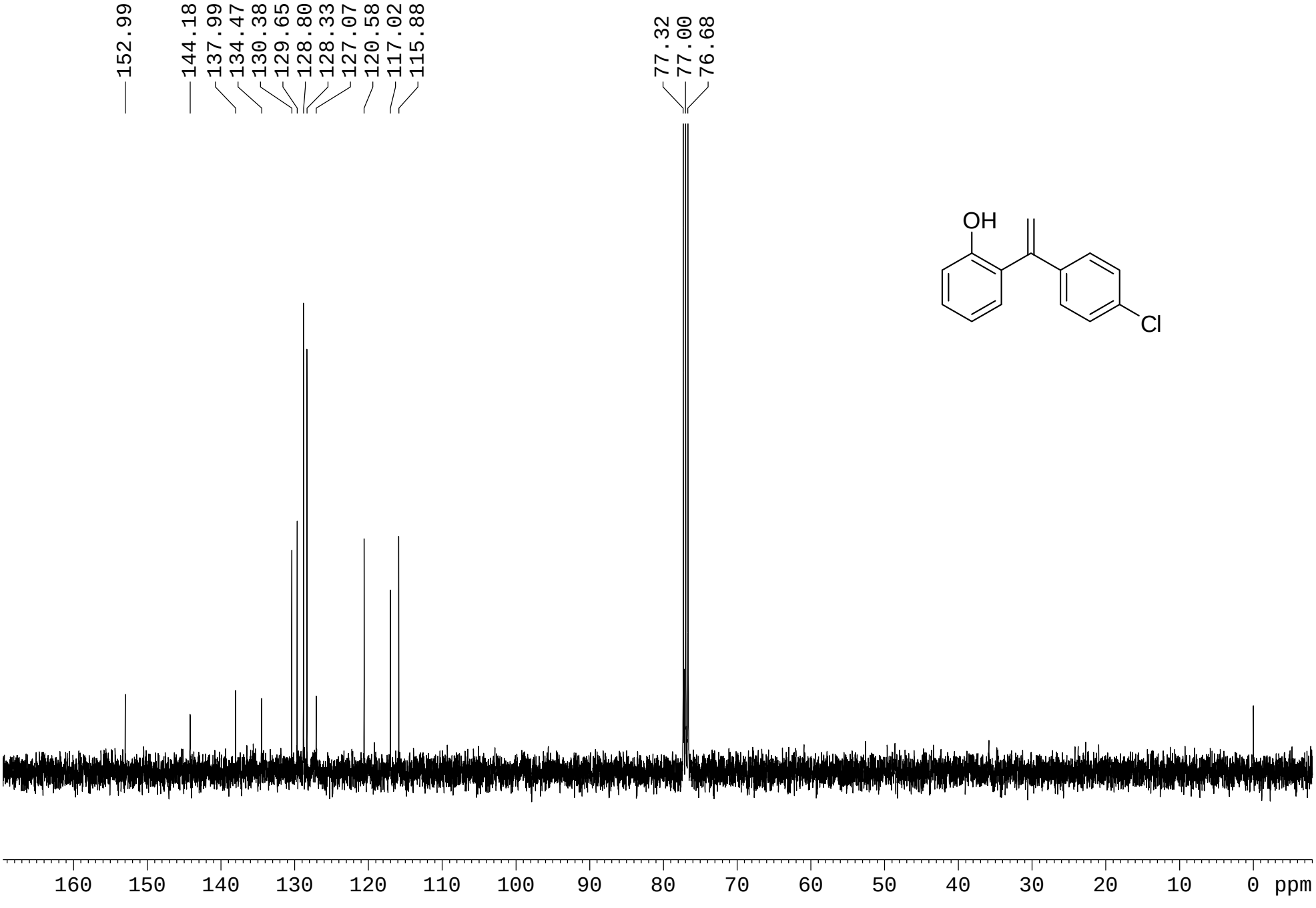
^{13}C NMR of compound 15f ($CDCl_3$, 100 MHz)



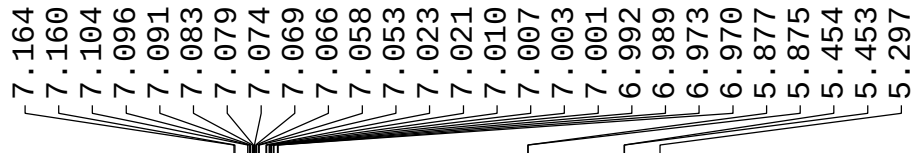
^{1}H NMR of compound 15g ($CDCl_3$, 400 MHz)

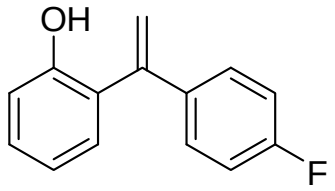


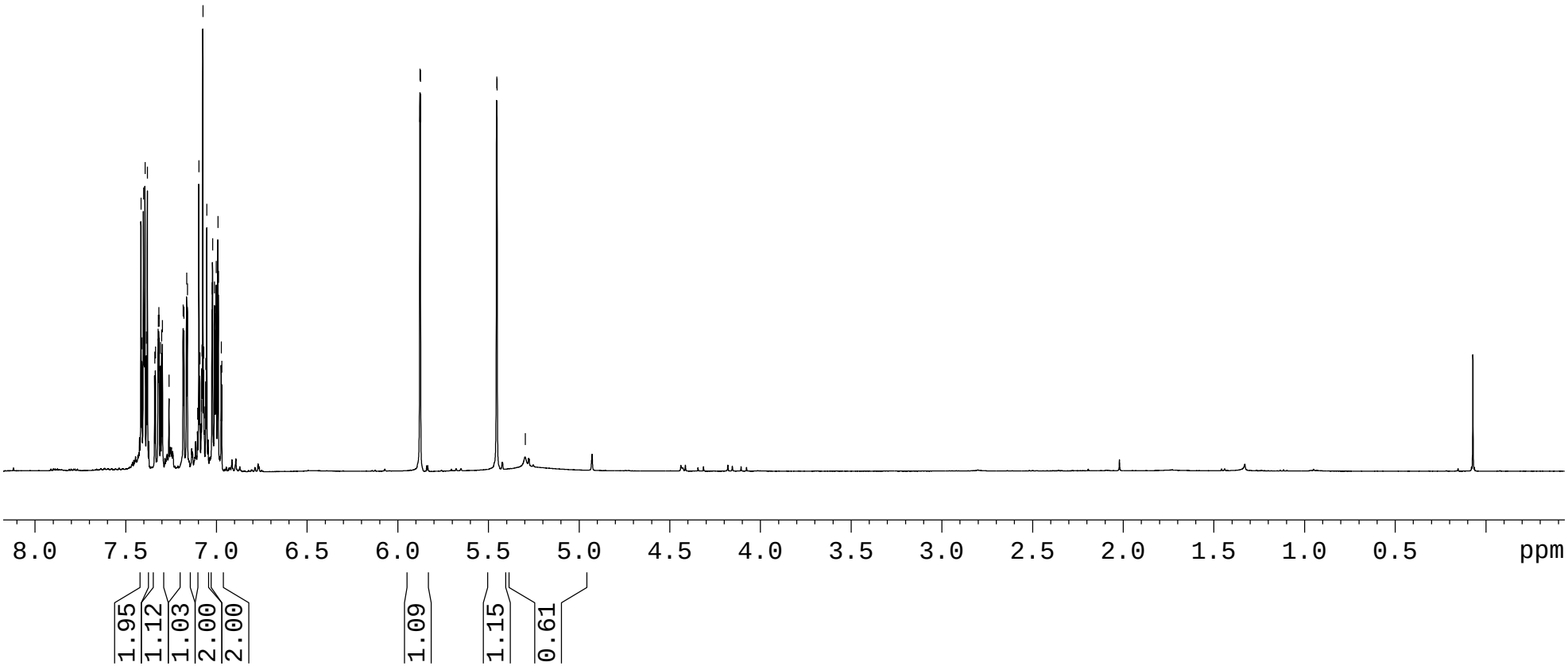
^{13}C NMR of compound 15g ($CDCl_3$, 100 MHz)



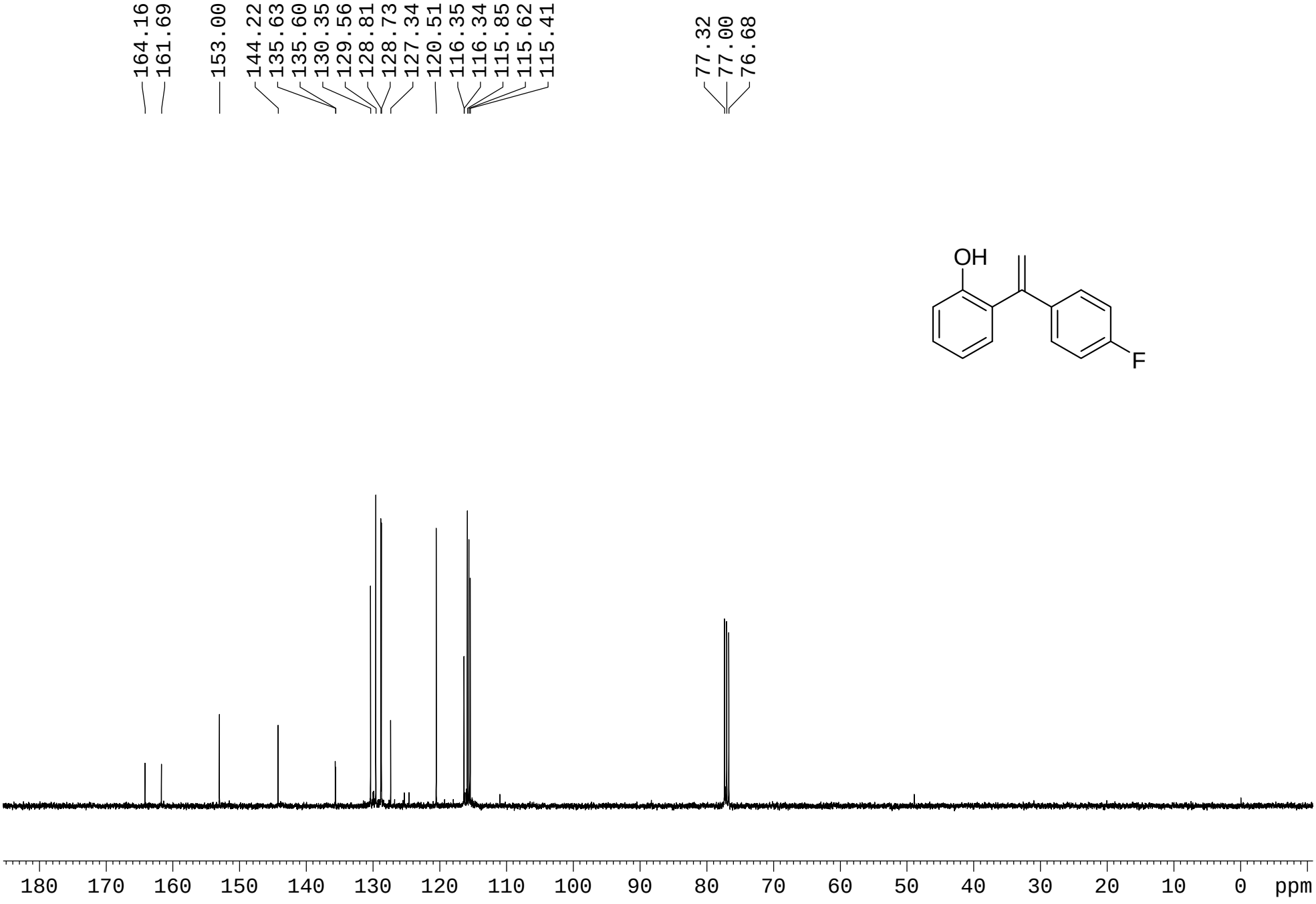
^{1}H NMR of compound 15h ($CDCl_3$, 400 MHz)



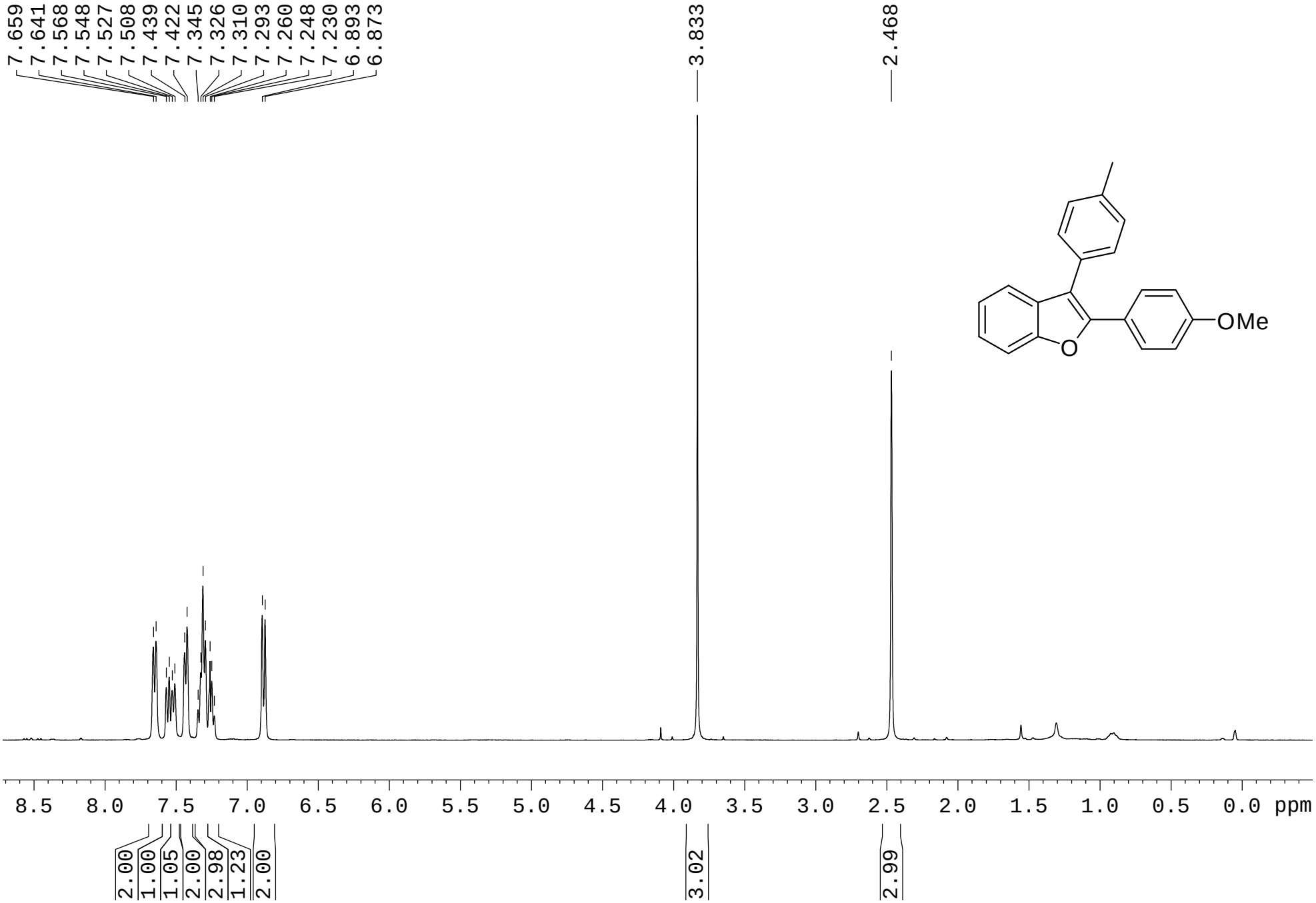




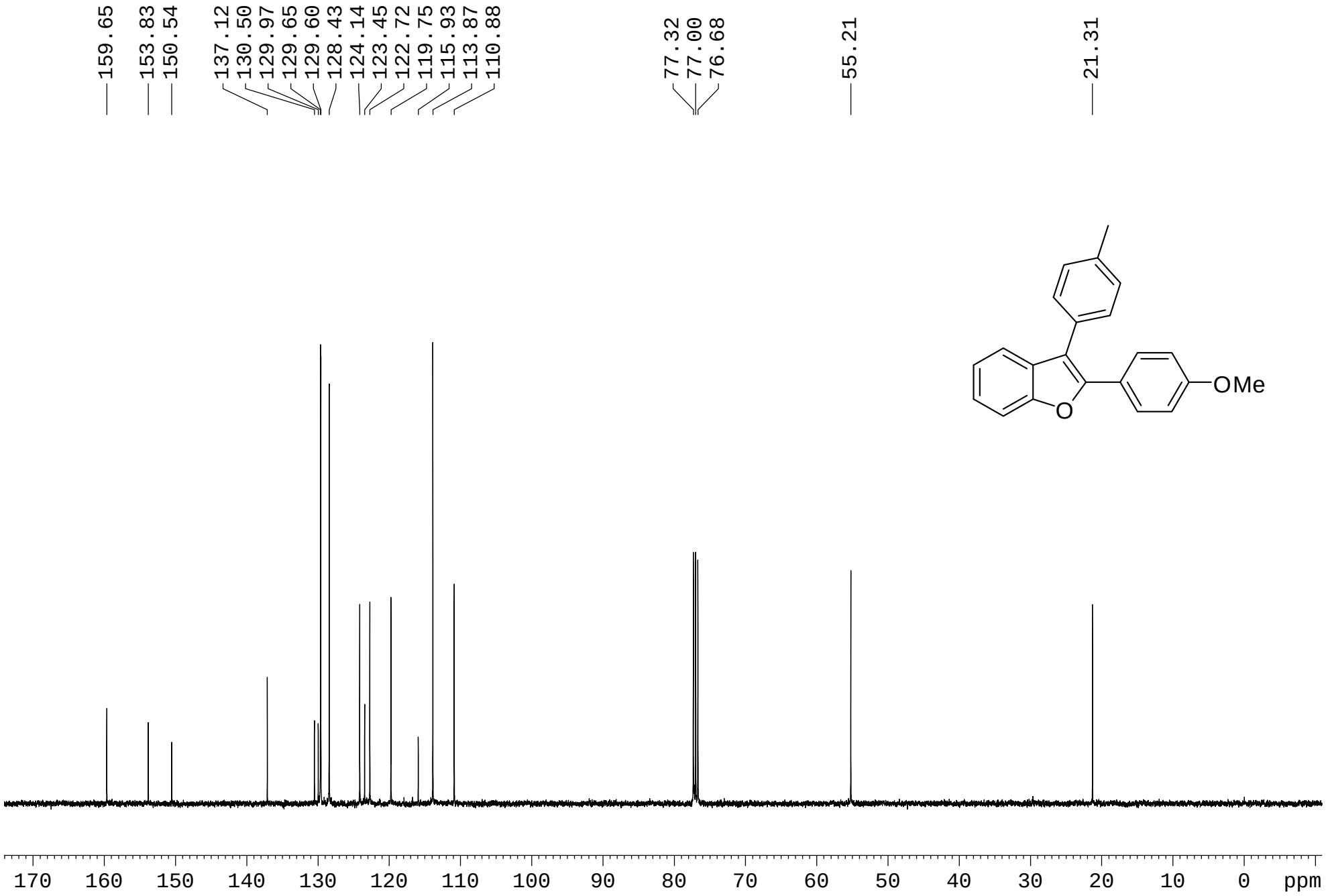
^{13}C NMR of compound 15h ($CDCl_3$, 100 MHz)



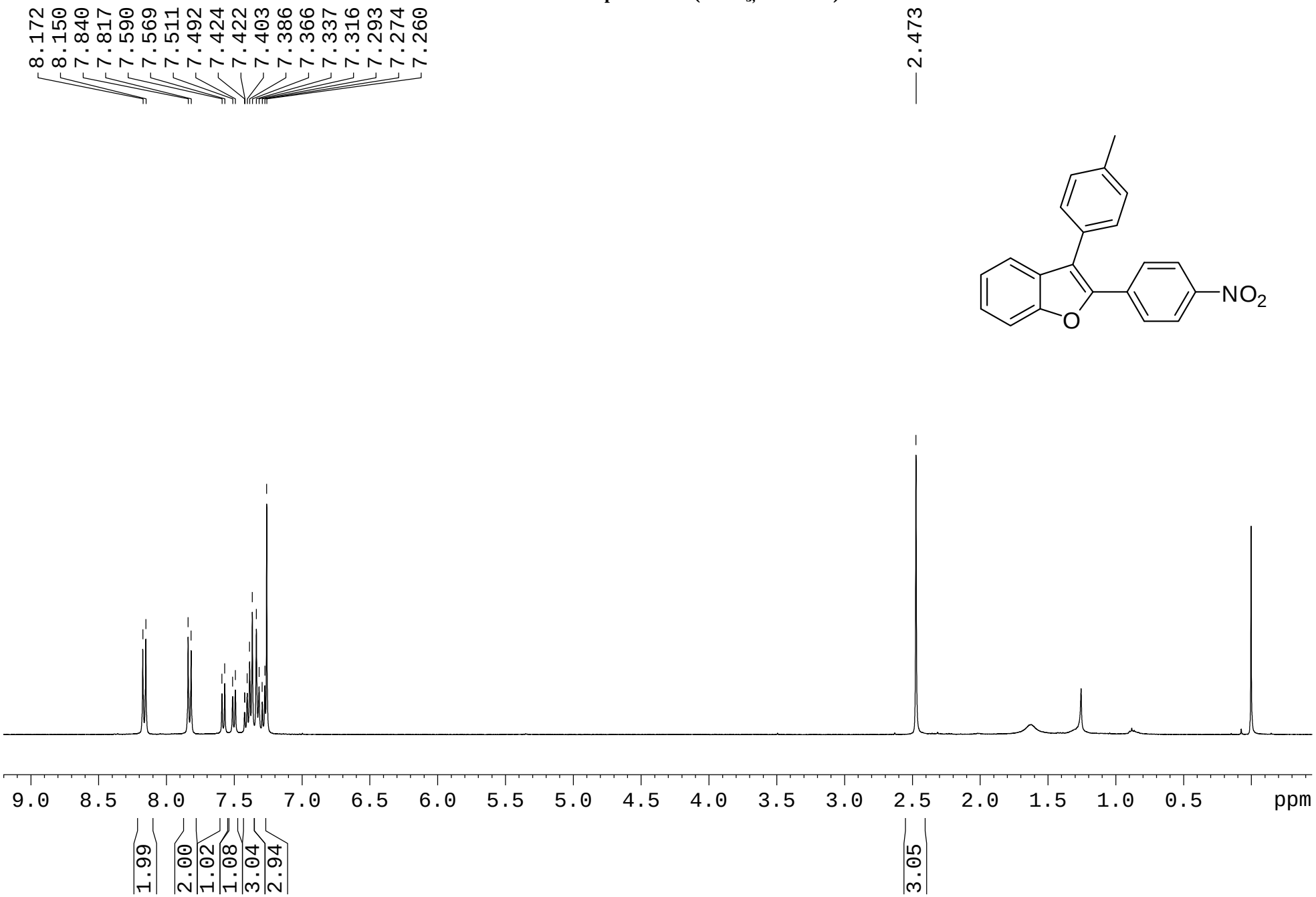
^{1}H NMR of compound 16a ($CDCl_3$, 400 MHz)



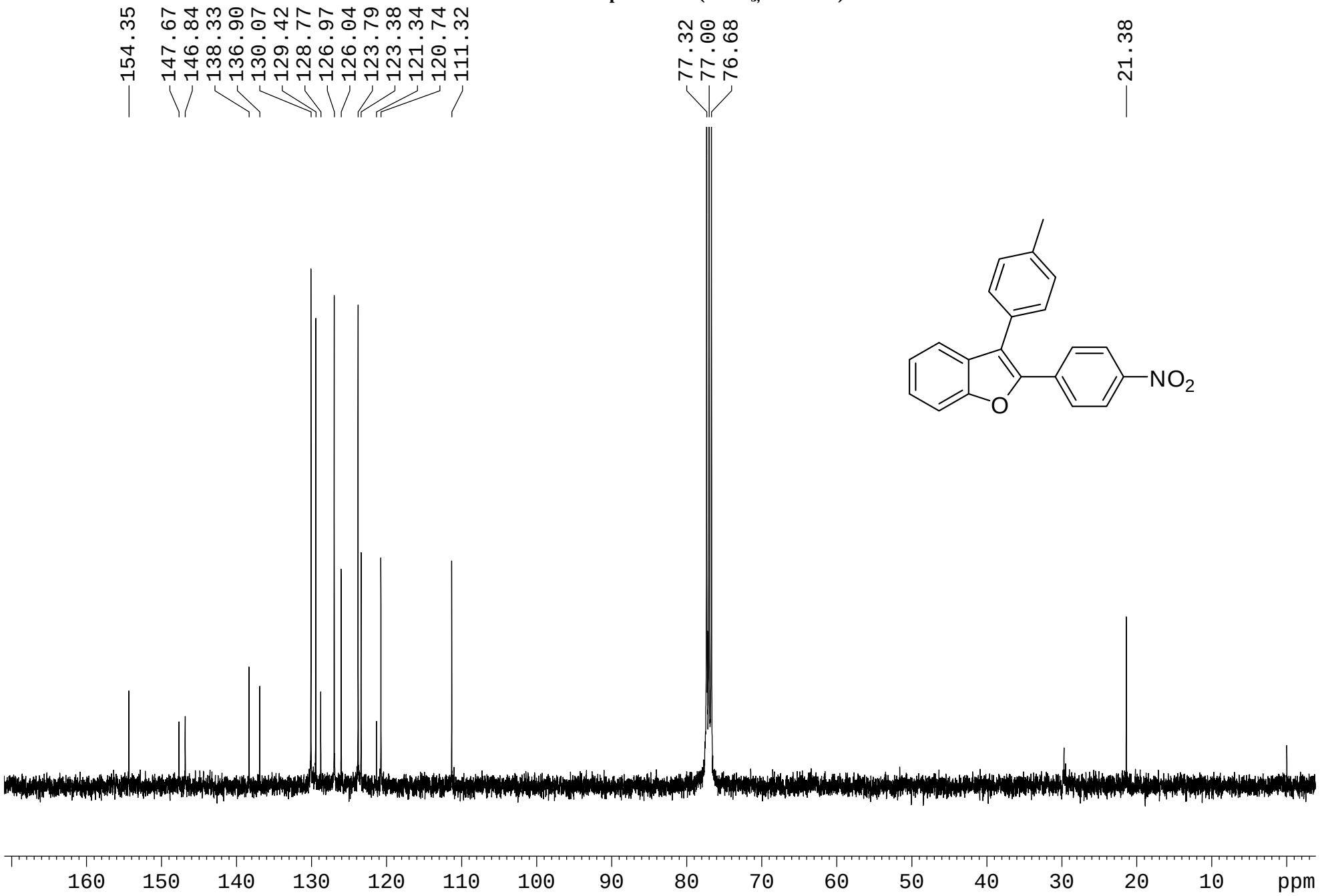
^{13}C NMR of compound 16a ($CDCl_3$, 100 MHz)



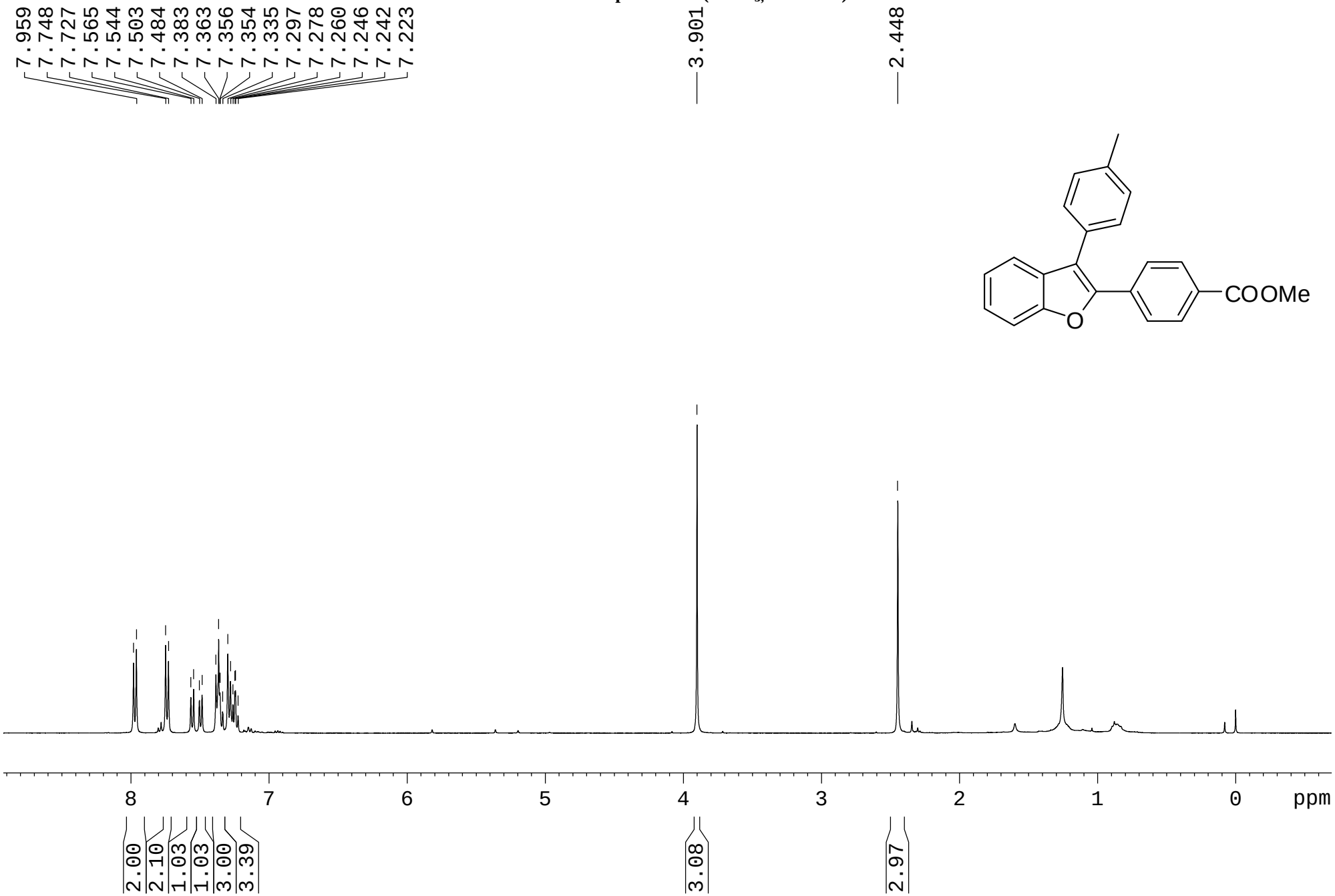
^{1}H NMR of compound 16b ($CDCl_3$, 400 MHz)



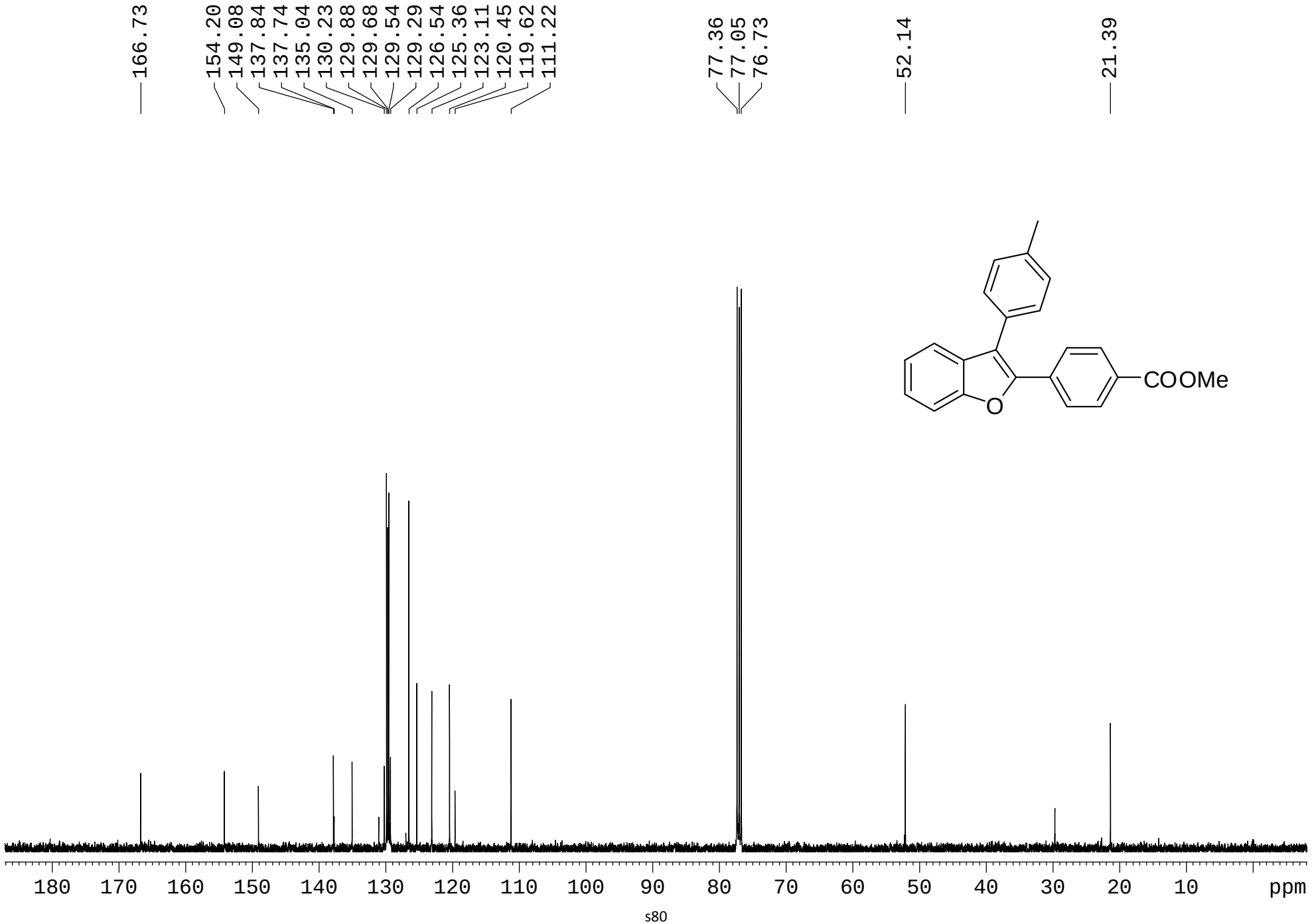
^{13}C NMR of compound 16b ($CDCl_3$, 100 MHz)



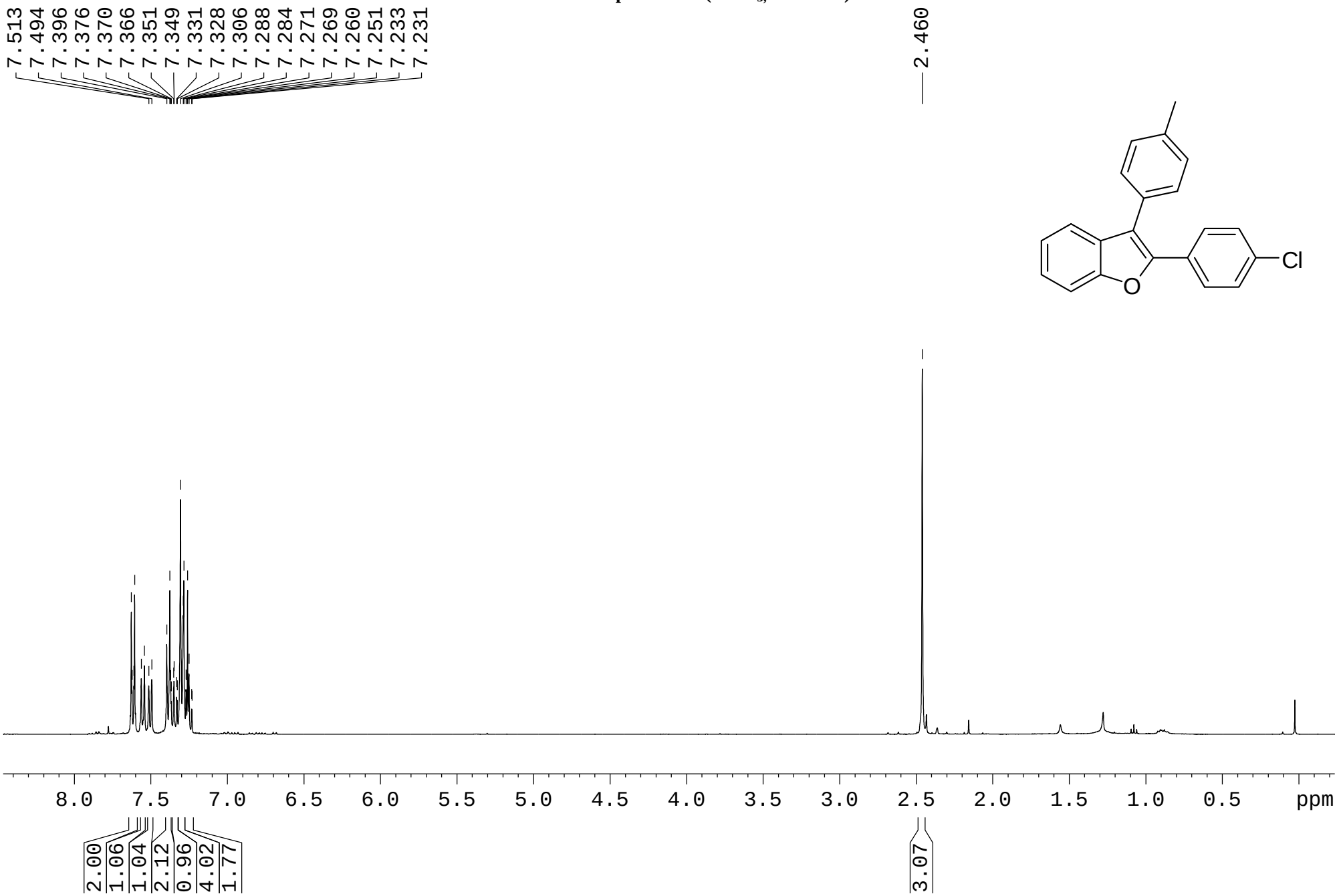
^{1}H NMR of compound 16c ($CDCl_3$, 400 MHz)



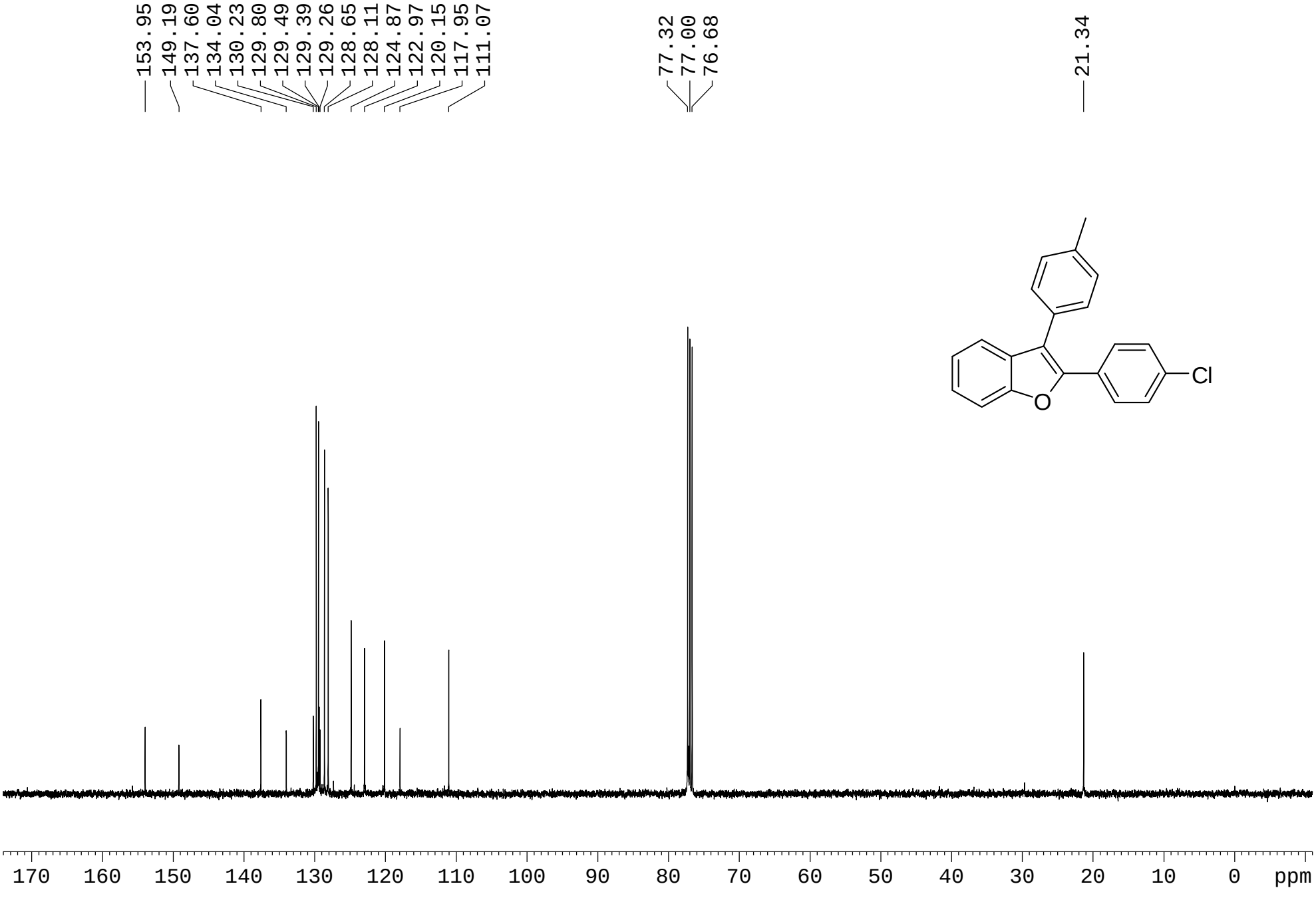
^{13}C NMR of compound 16c ($CDCl_3$, 100 MHz)



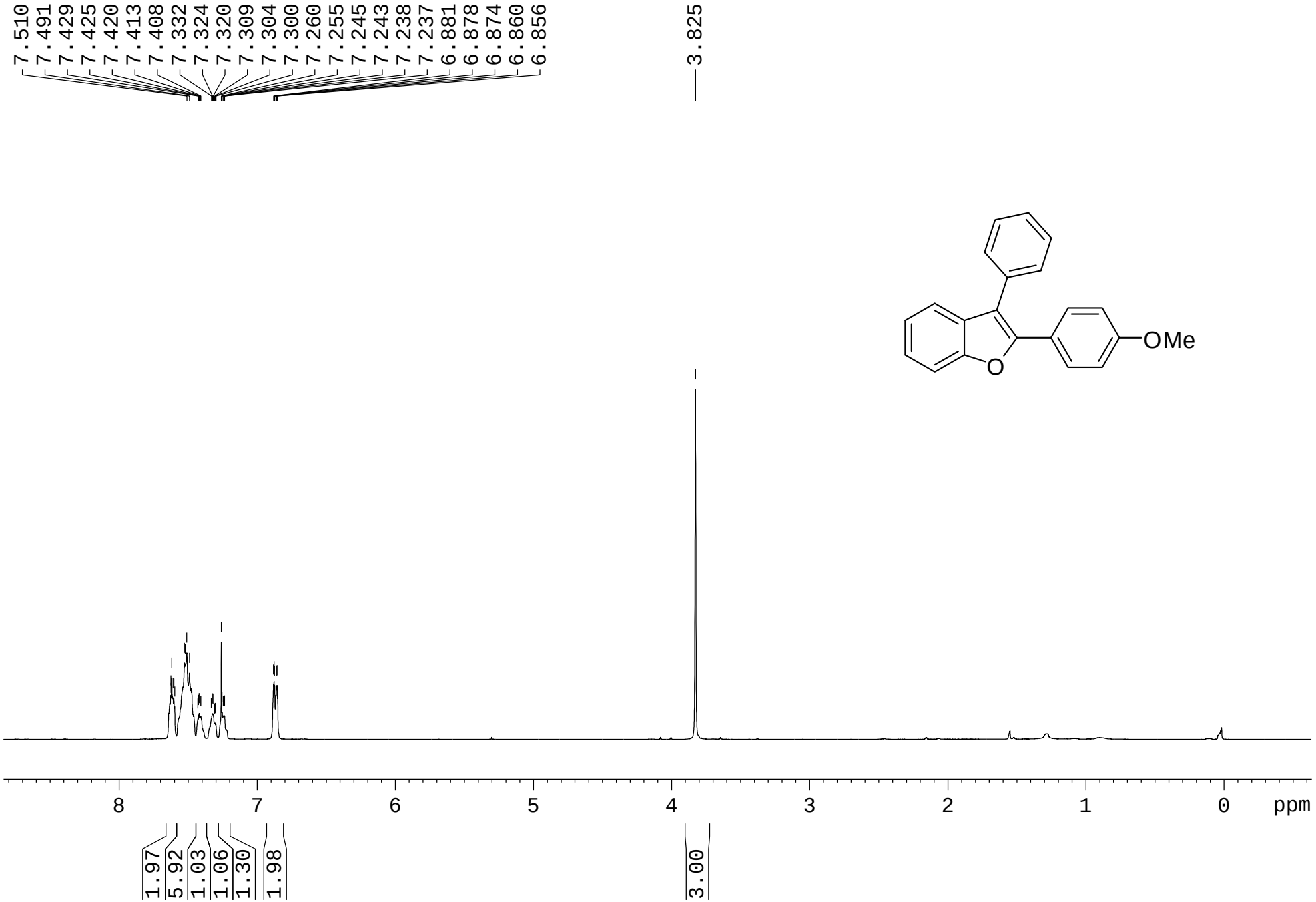
^{1}H NMR of compound 16d ($CDCl_3$, 400 MHz)



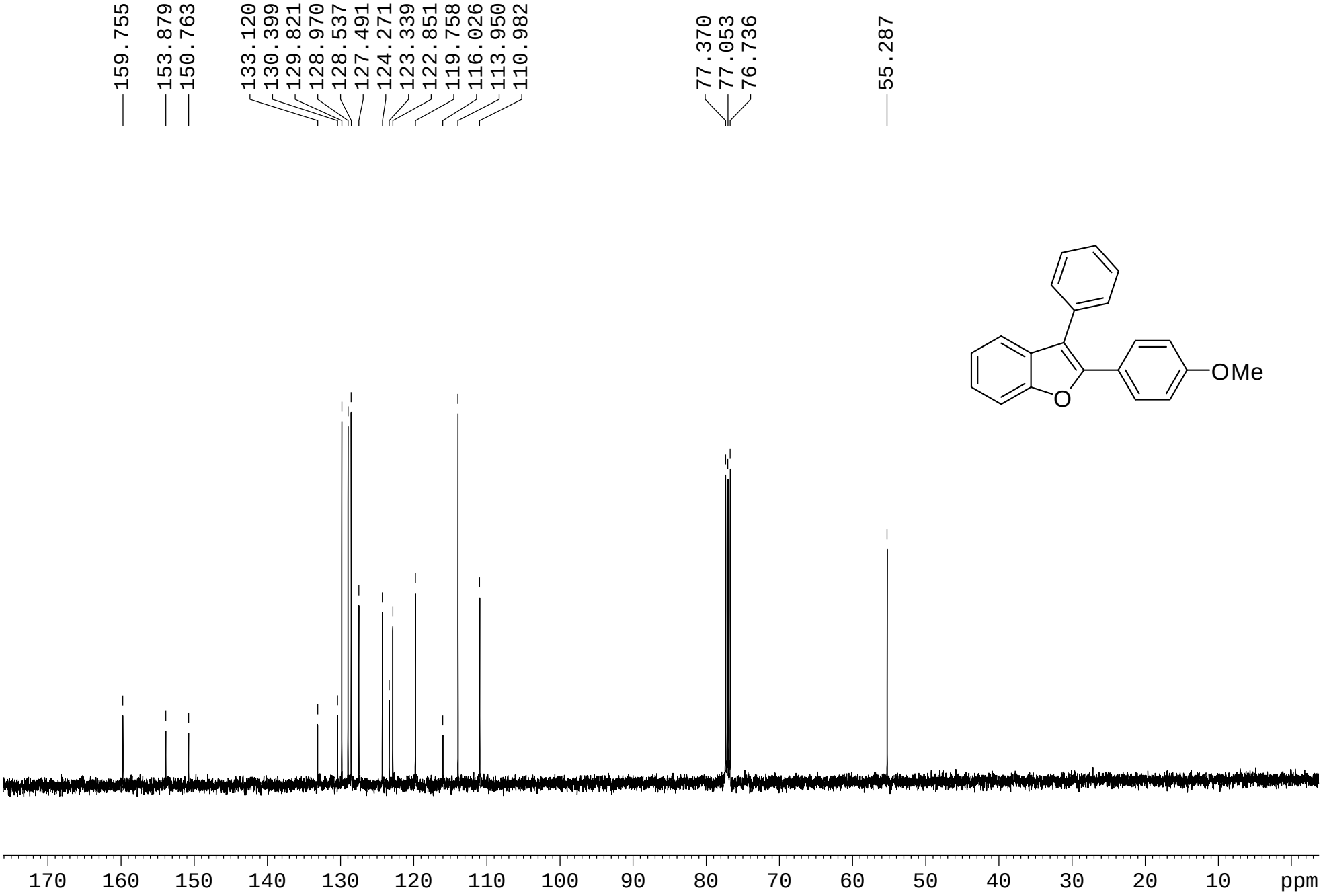
^{13}C NMR of compound 16d ($CDCl_3$, 100 MHz)



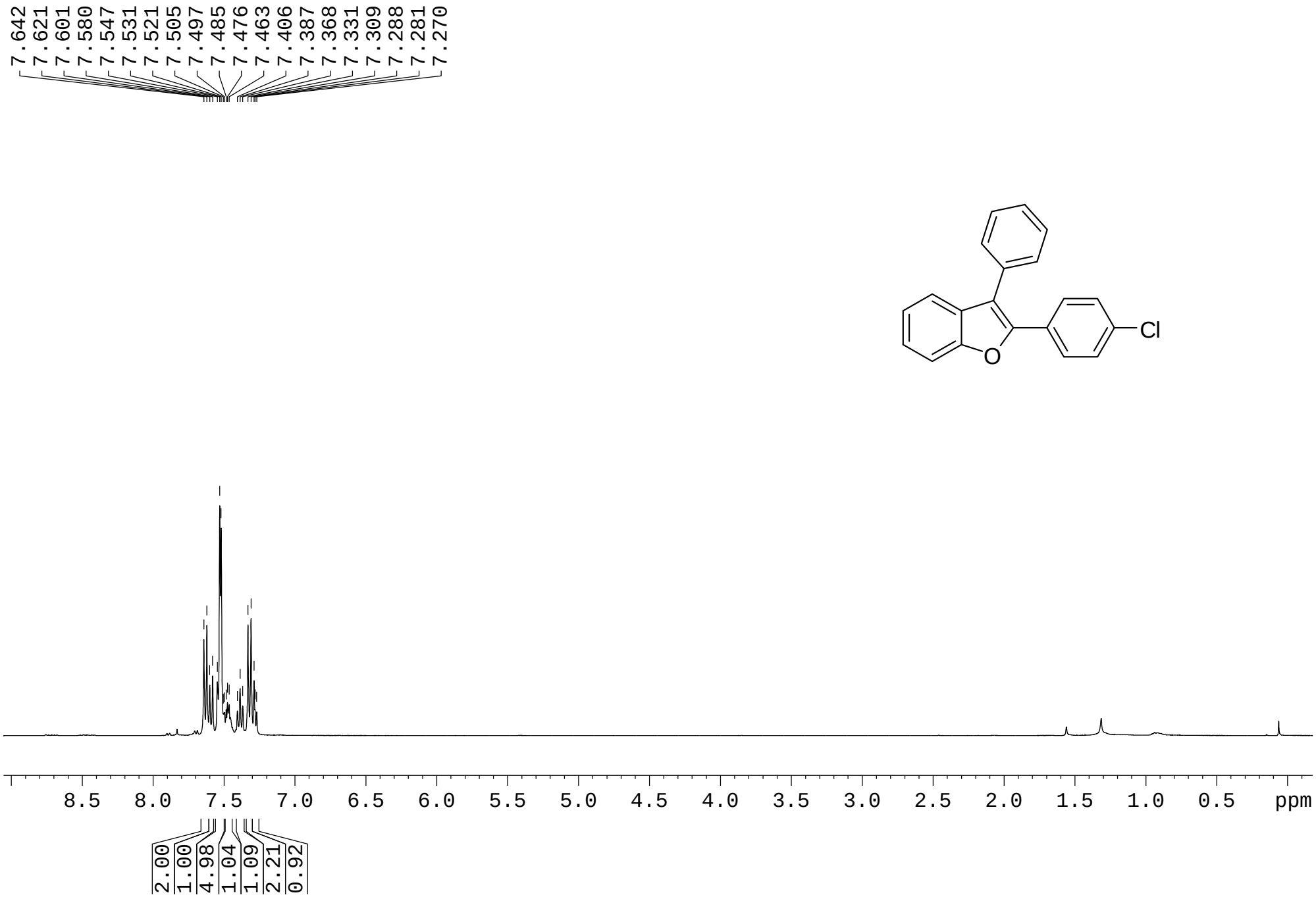
^{1}H NMR of compound 16e ($CDCl_3$, 400 MHz)



^{13}C NMR of compound 16e ($CDCl_3$, 100 MHz)



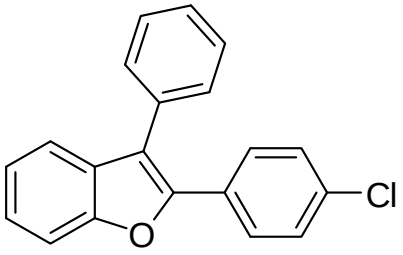
^{1}H NMR of compound 16f ($CDCl_3$, 400 MHz)

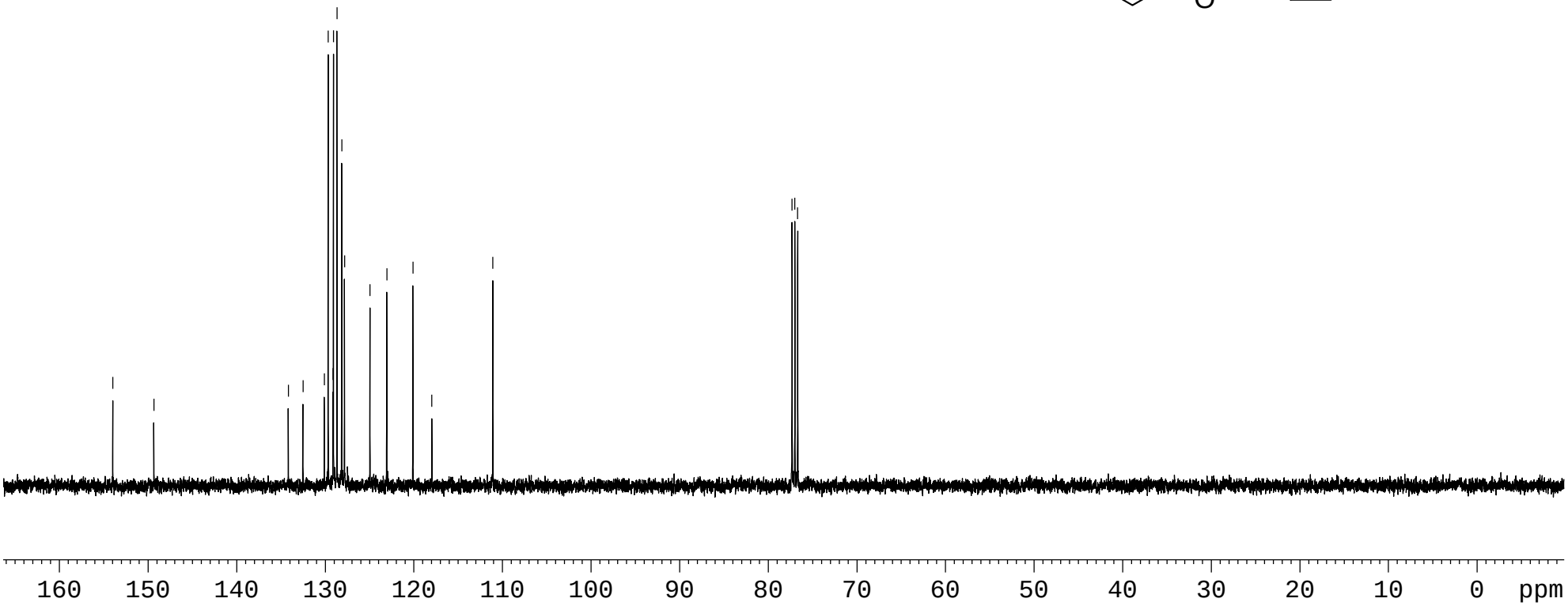


^{13}C NMR of compound 16f ($CDCl_3$, 100 MHz)

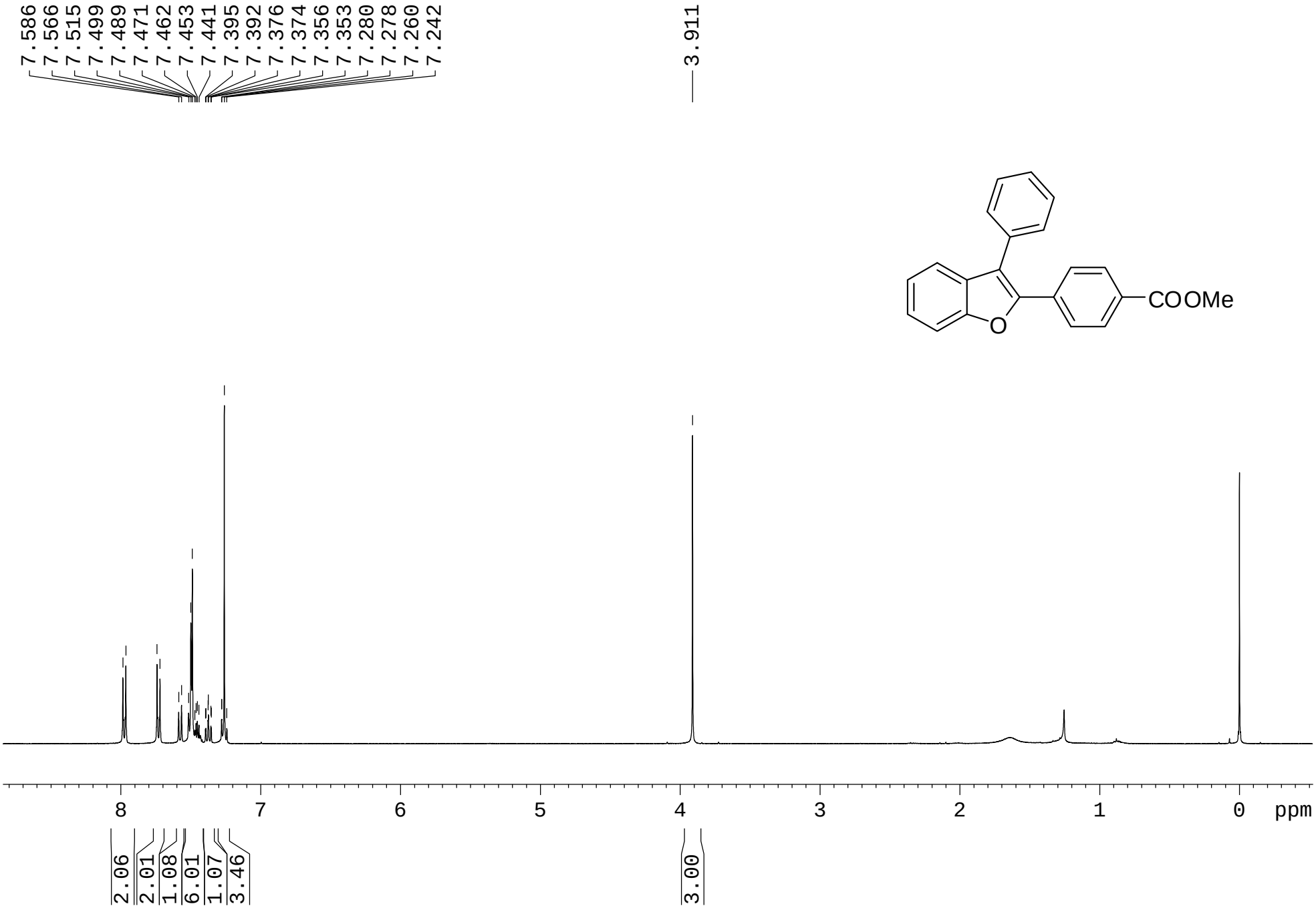
153.96
149.34
134.16
132.51
130.09
129.66
129.11
129.06
128.66
128.13
127.82
124.94
123.05
120.09
117.98
111.10

77.32
77.00
76.68

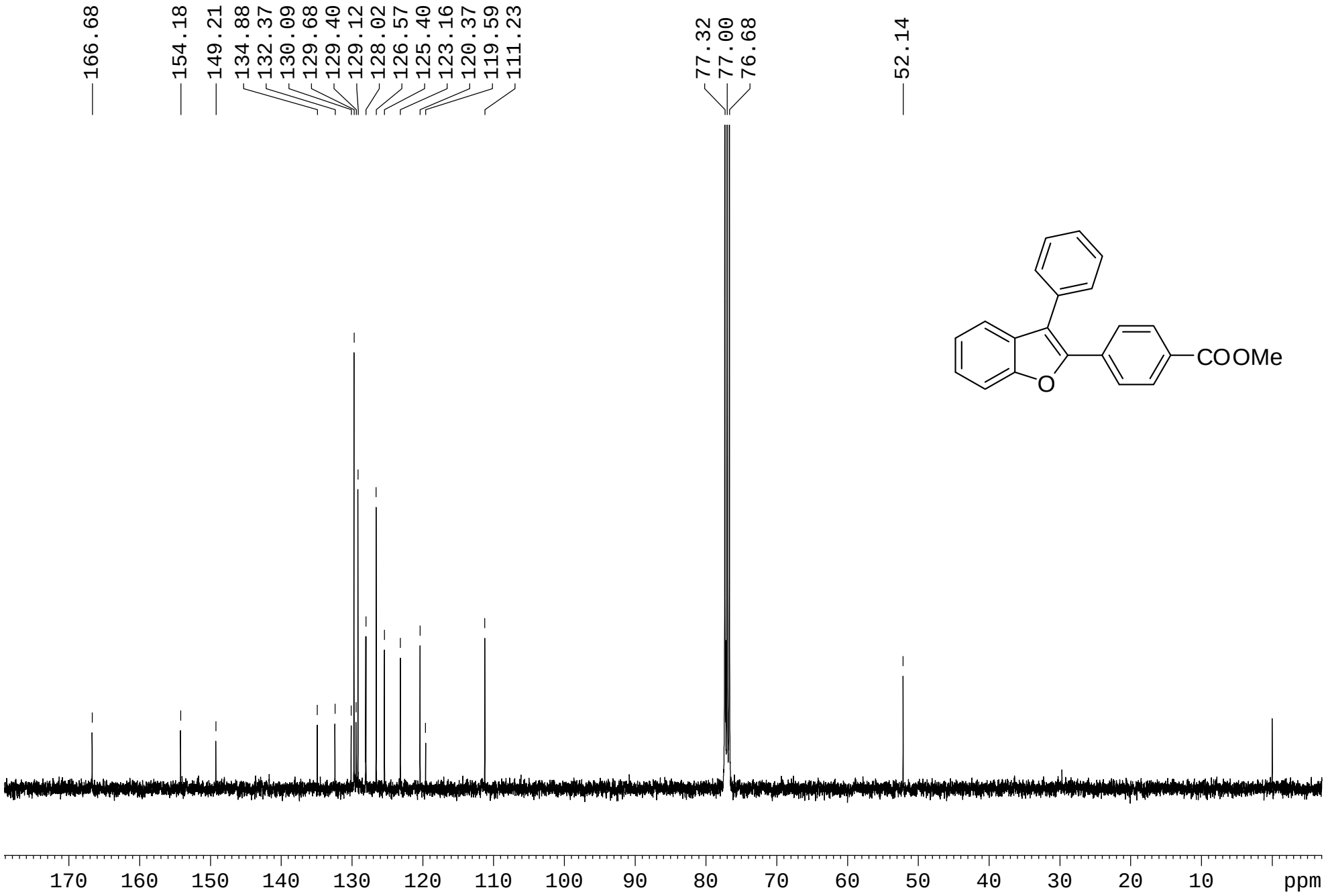




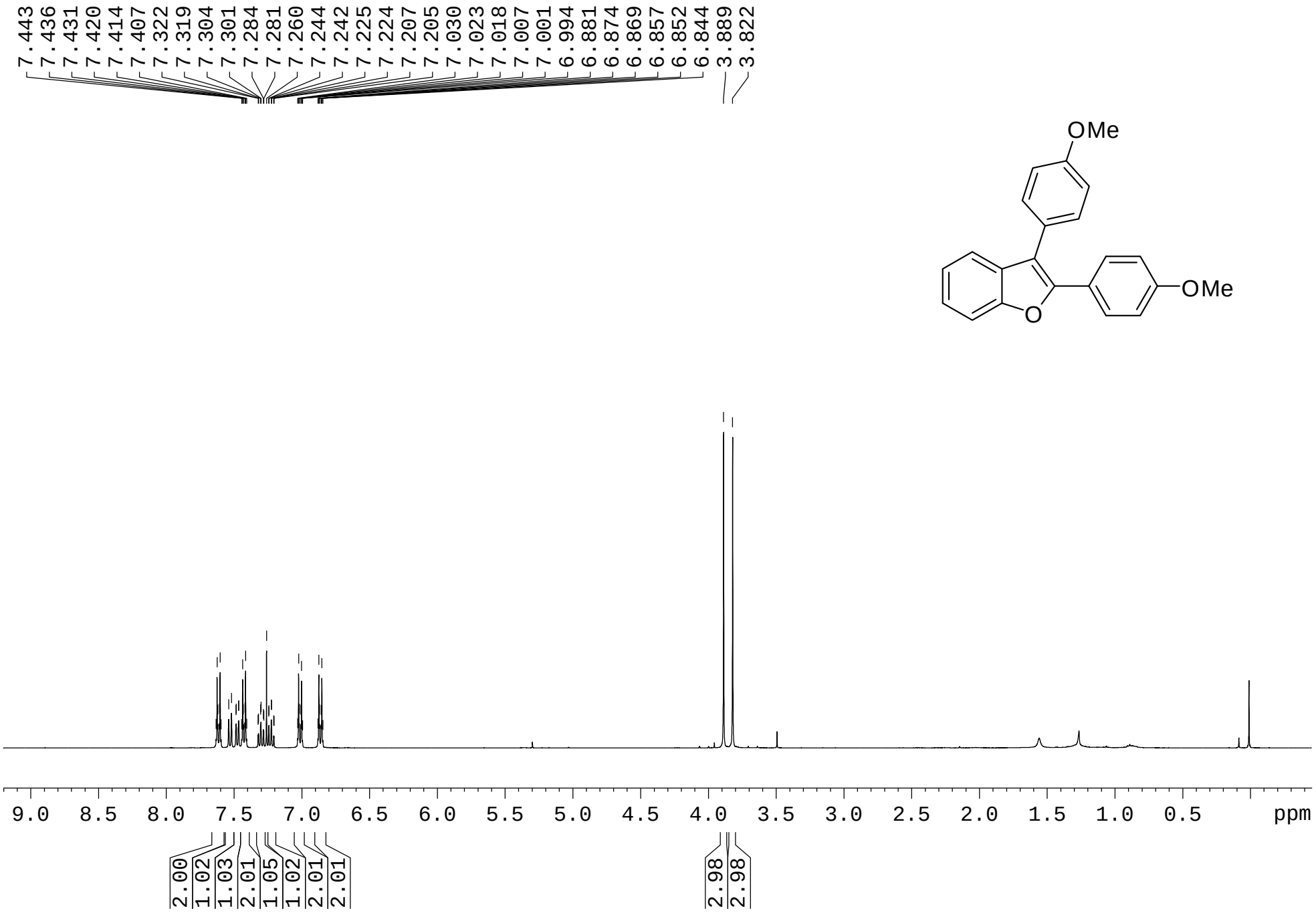
^{1}H NMR of compound 16g ($CDCl_3$, 400 MHz)



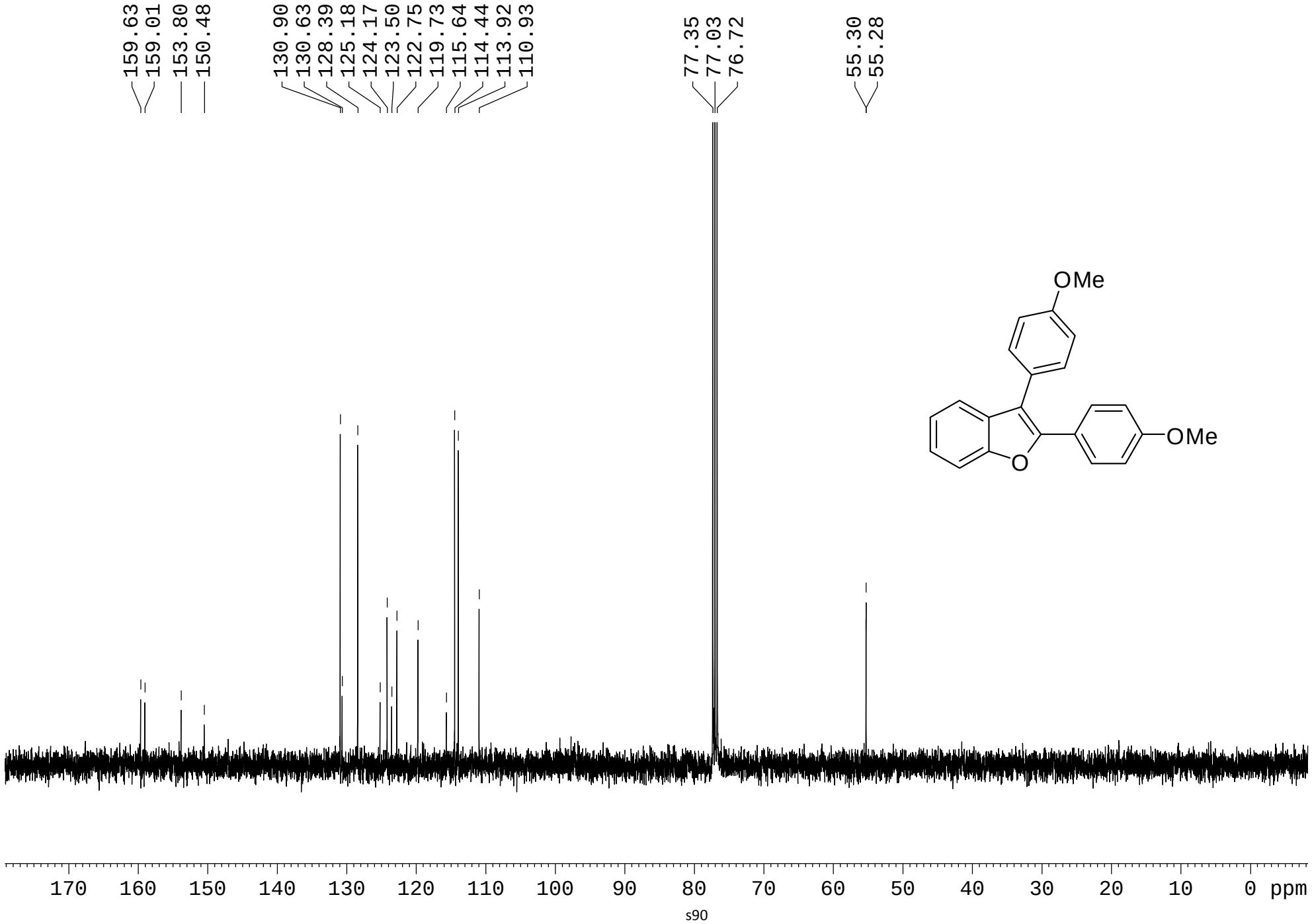
^{13}C NMR of compound 16g ($CDCl_3$, 100 MHz)



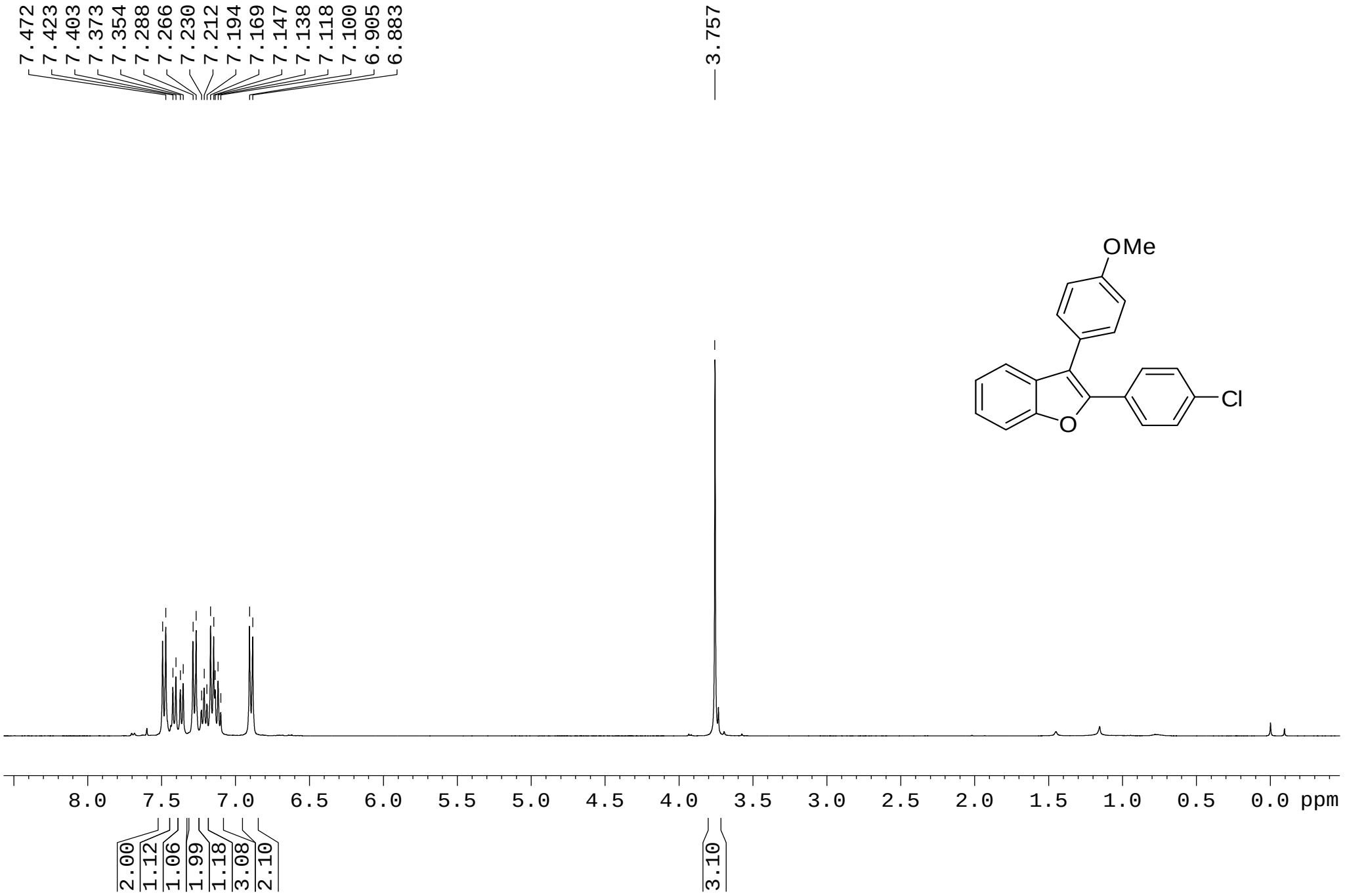
^{1}H NMR of compound 16h ($CDCl_3$, 400 MHz)



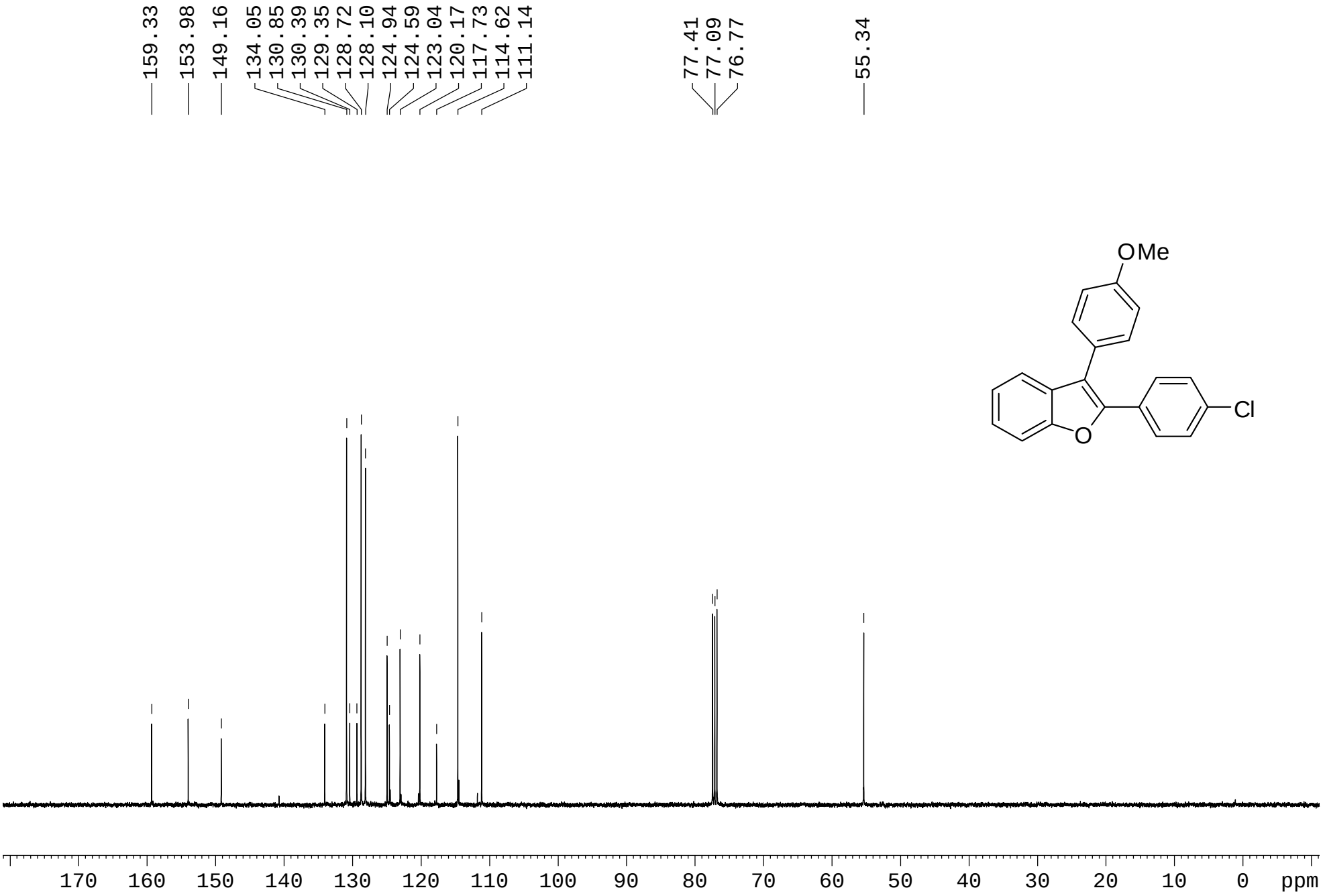
^{13}C NMR of compound 16h ($CDCl_3$, 100 MHz)



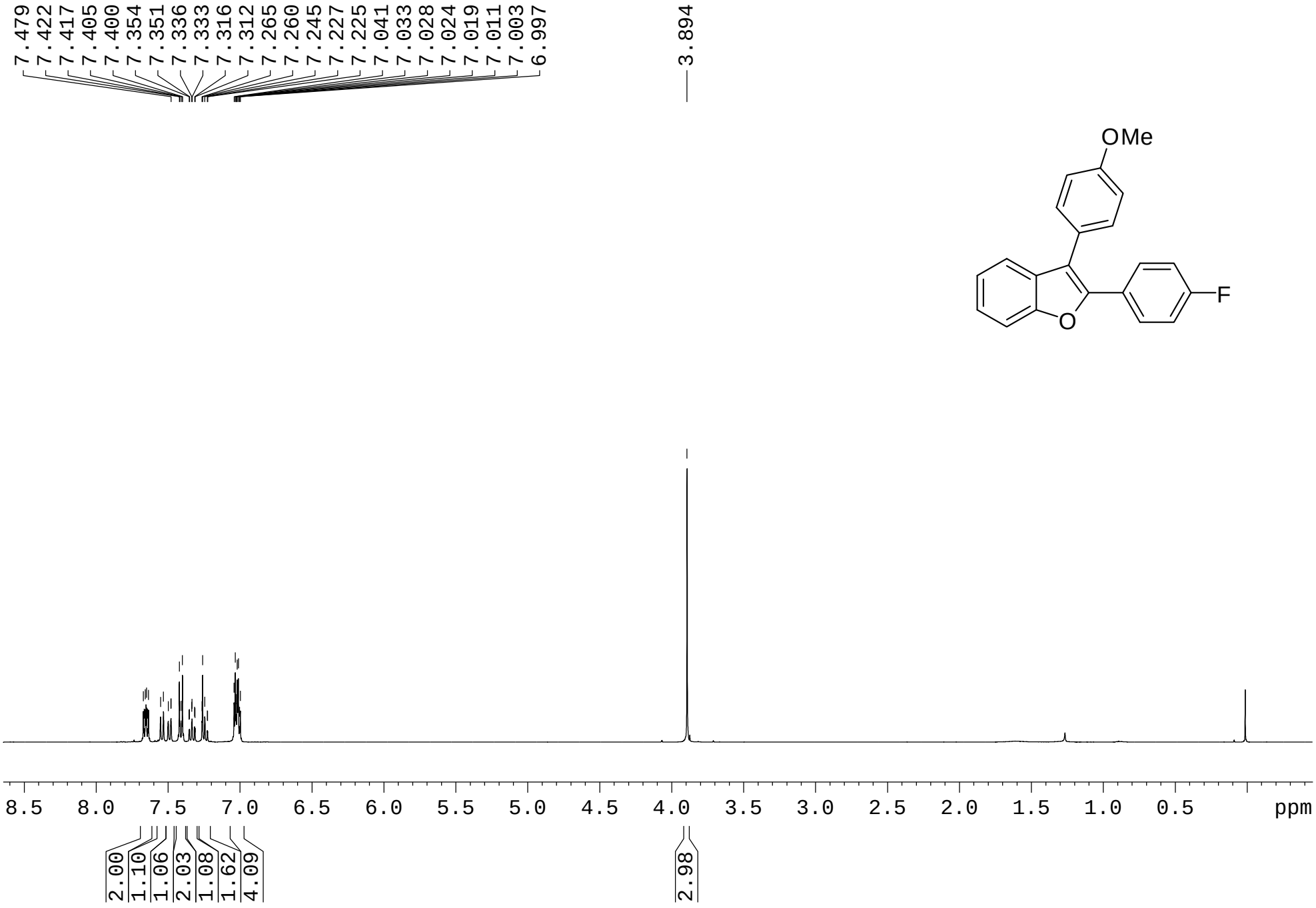
^{1}H NMR of compound 16i ($CDCl_3$, 400 MHz)



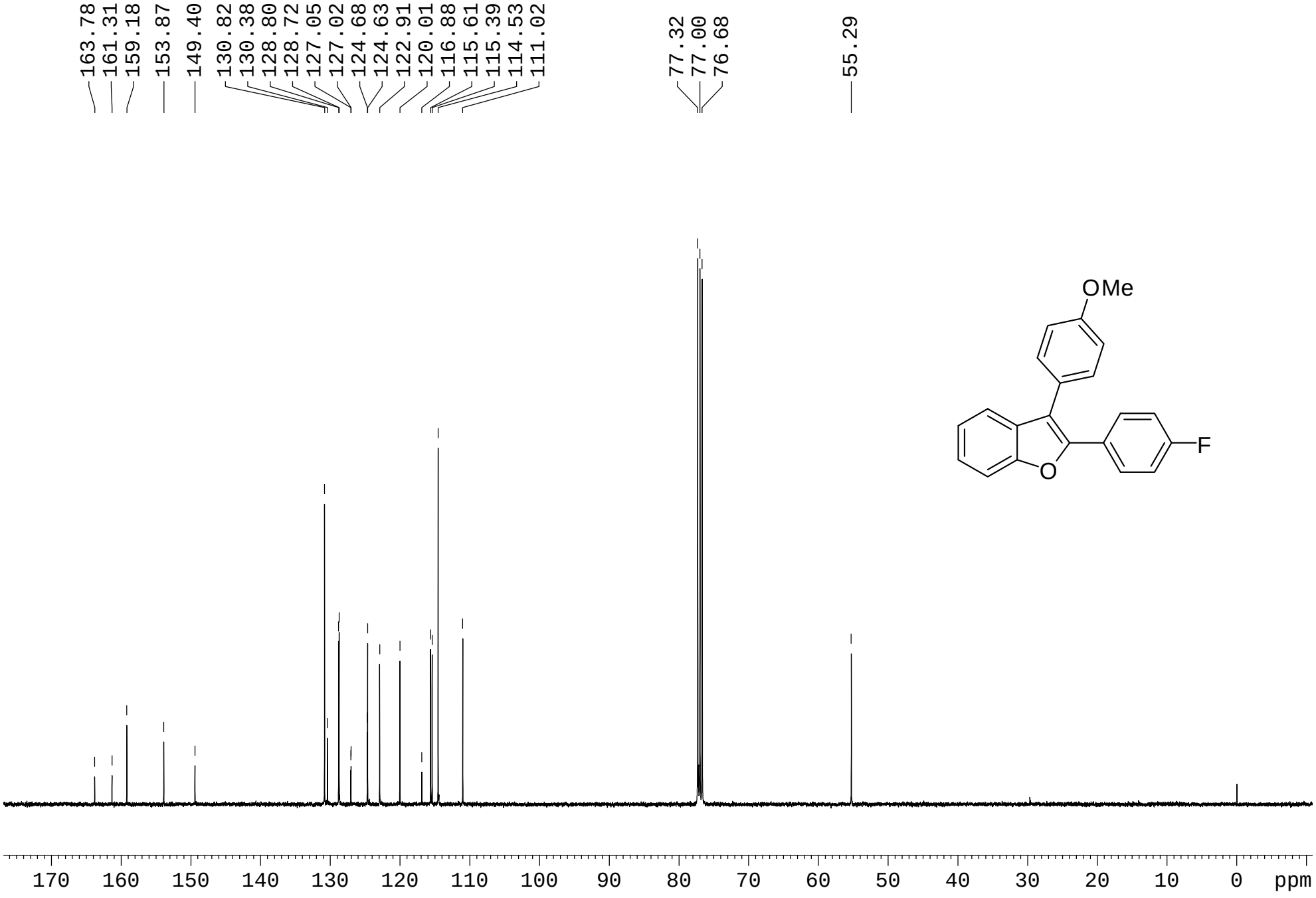
^{13}C NMR of compound 16i ($CDCl_3$, 100 MHz)



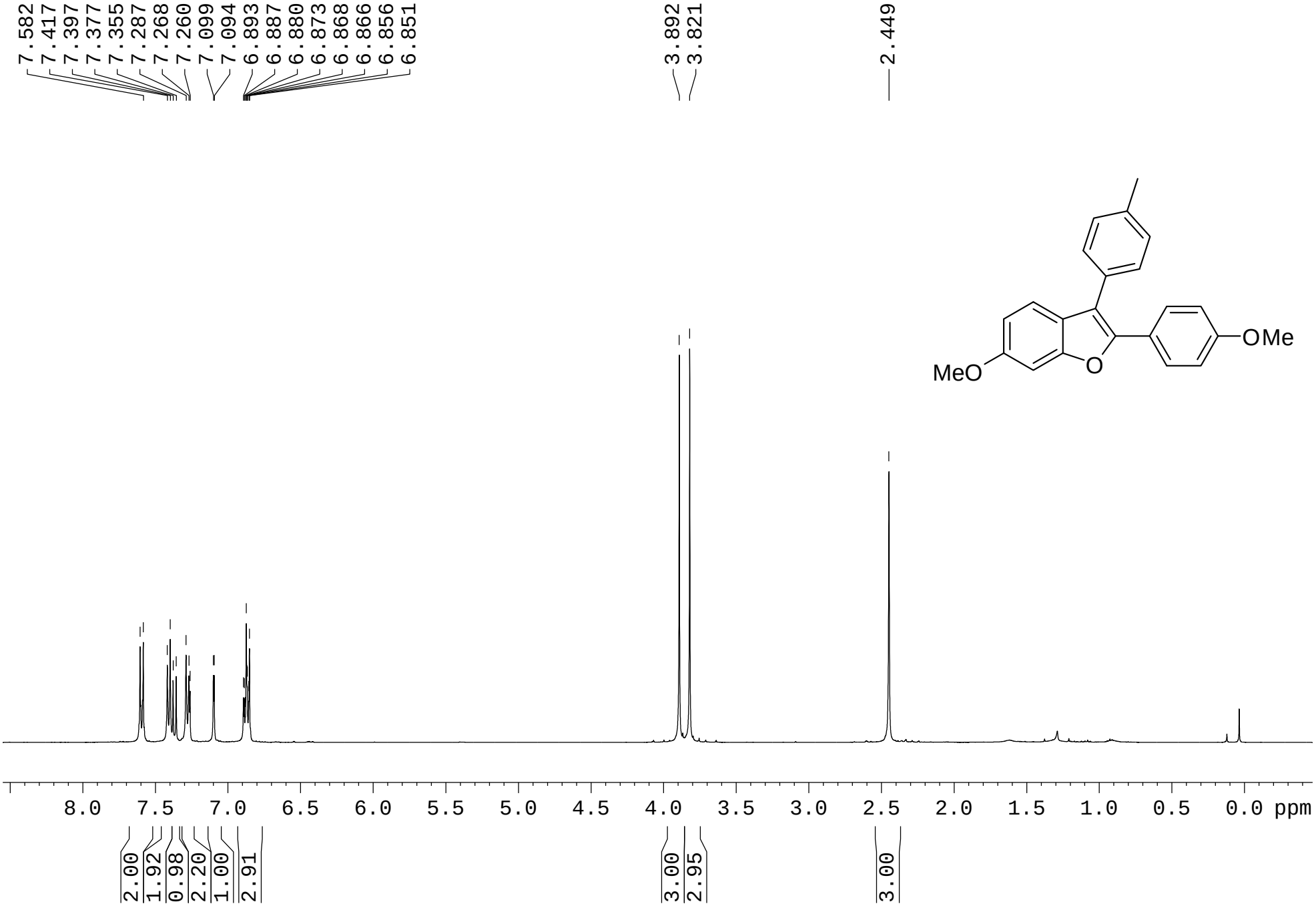
^{1}H NMR of compound 16j ($CDCl_3$, 400 MHz)



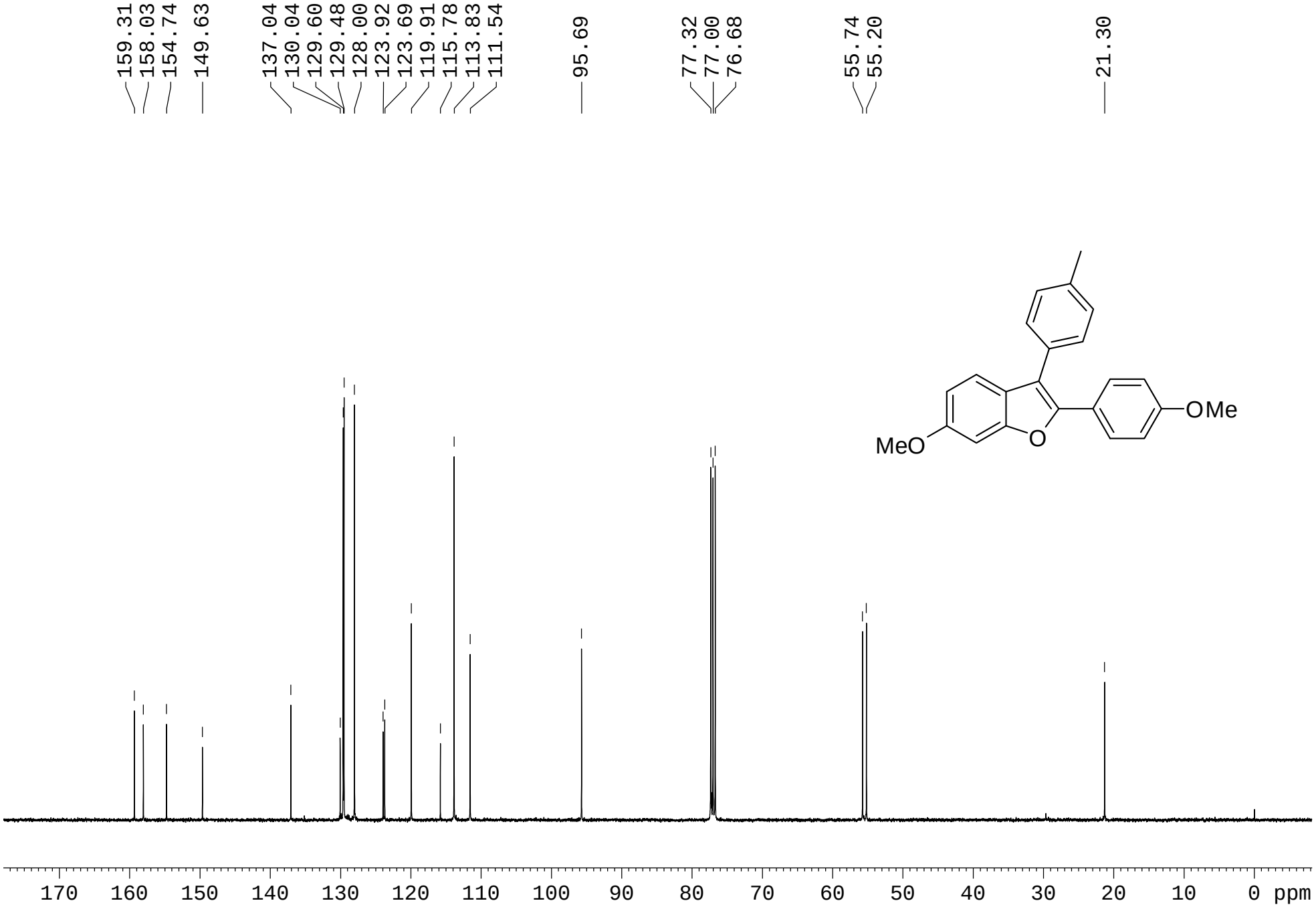
^{13}C NMR of compound 16j ($CDCl_3$, 100 MHz)



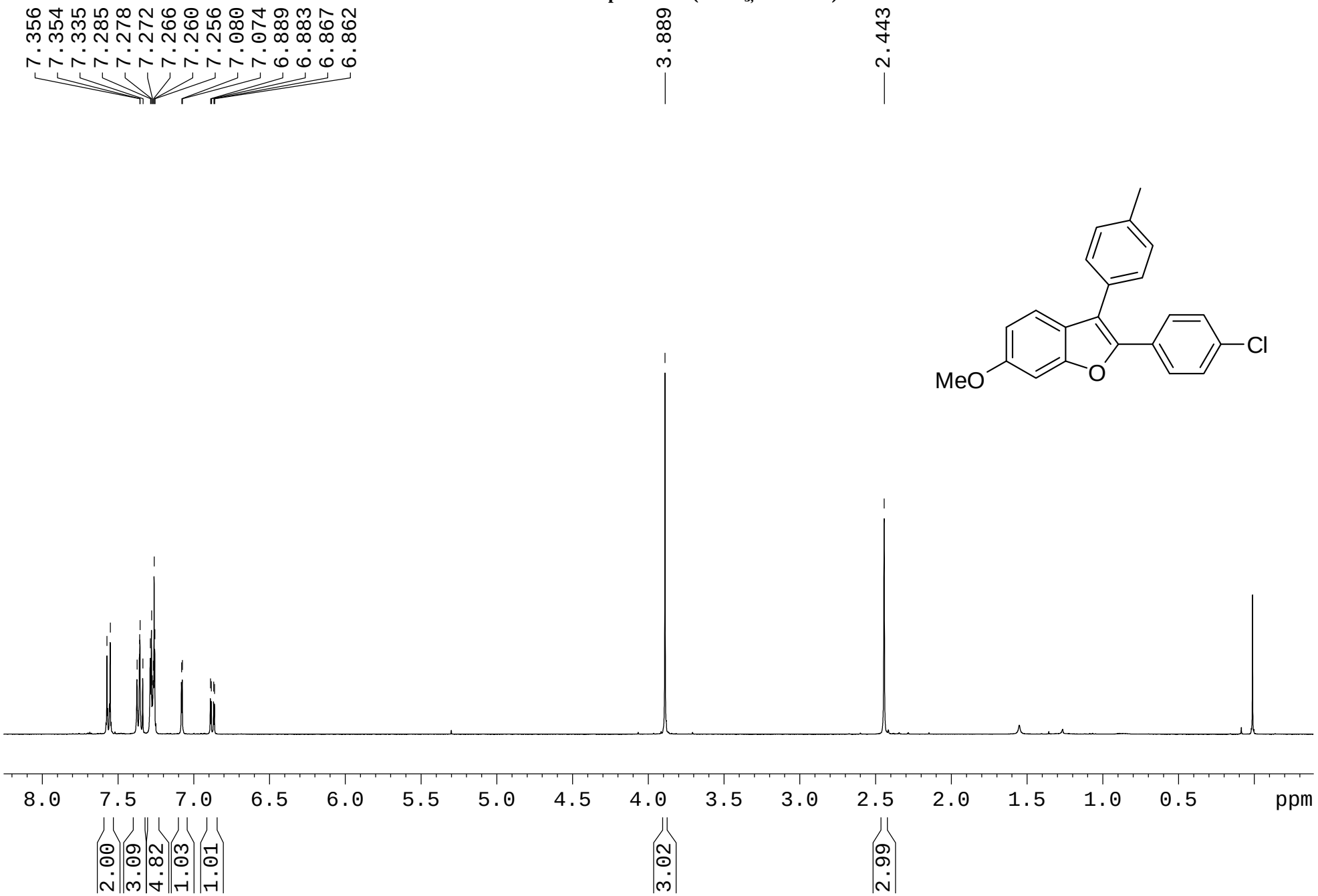
^{1}H NMR of compound 16k ($CDCl_3$, 400 MHz)



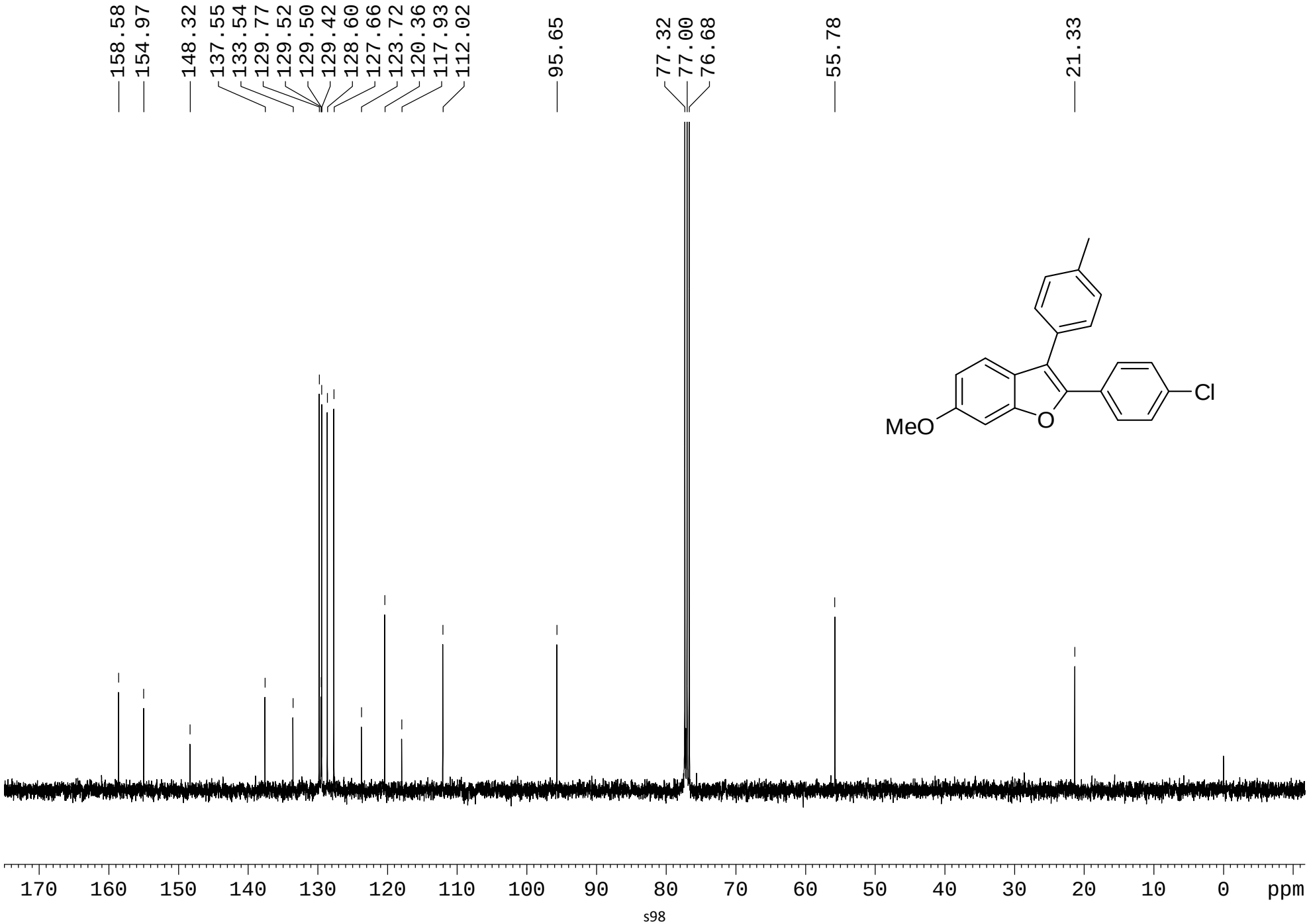
^{13}C NMR of compound 16k ($CDCl_3$, 100 MHz)



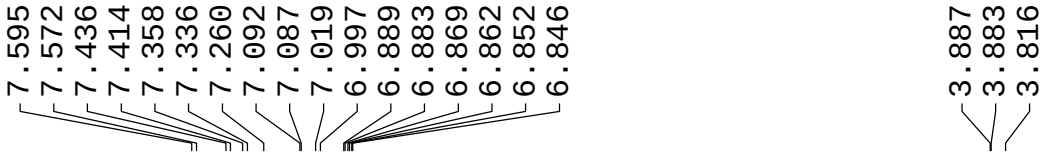
^{1}H NMR of compound 16l ($CDCl_3$, 400 MHz)

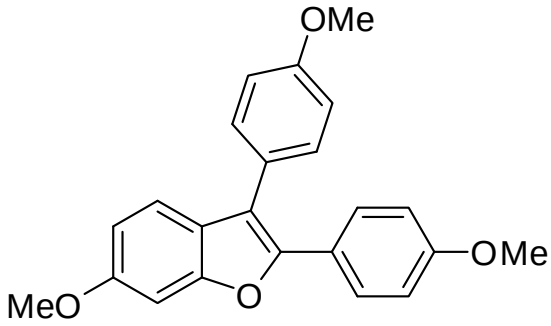


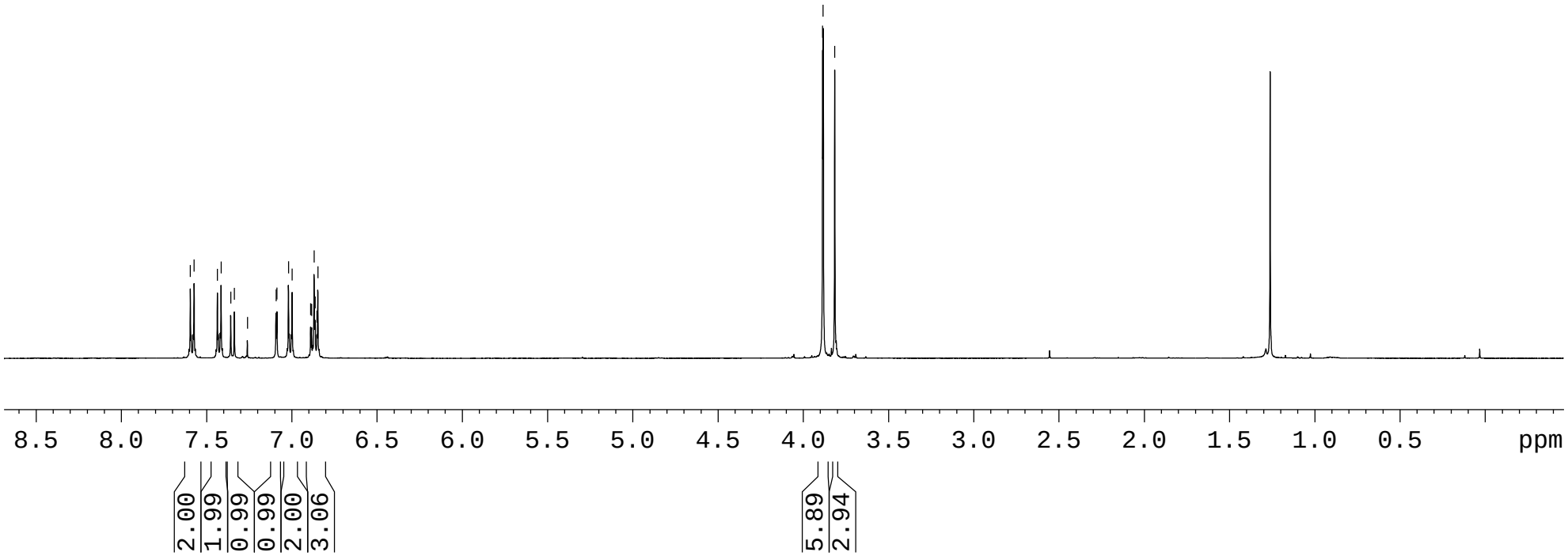
^{13}C NMR of compound 16l ($CDCl_3$, 100 MHz)



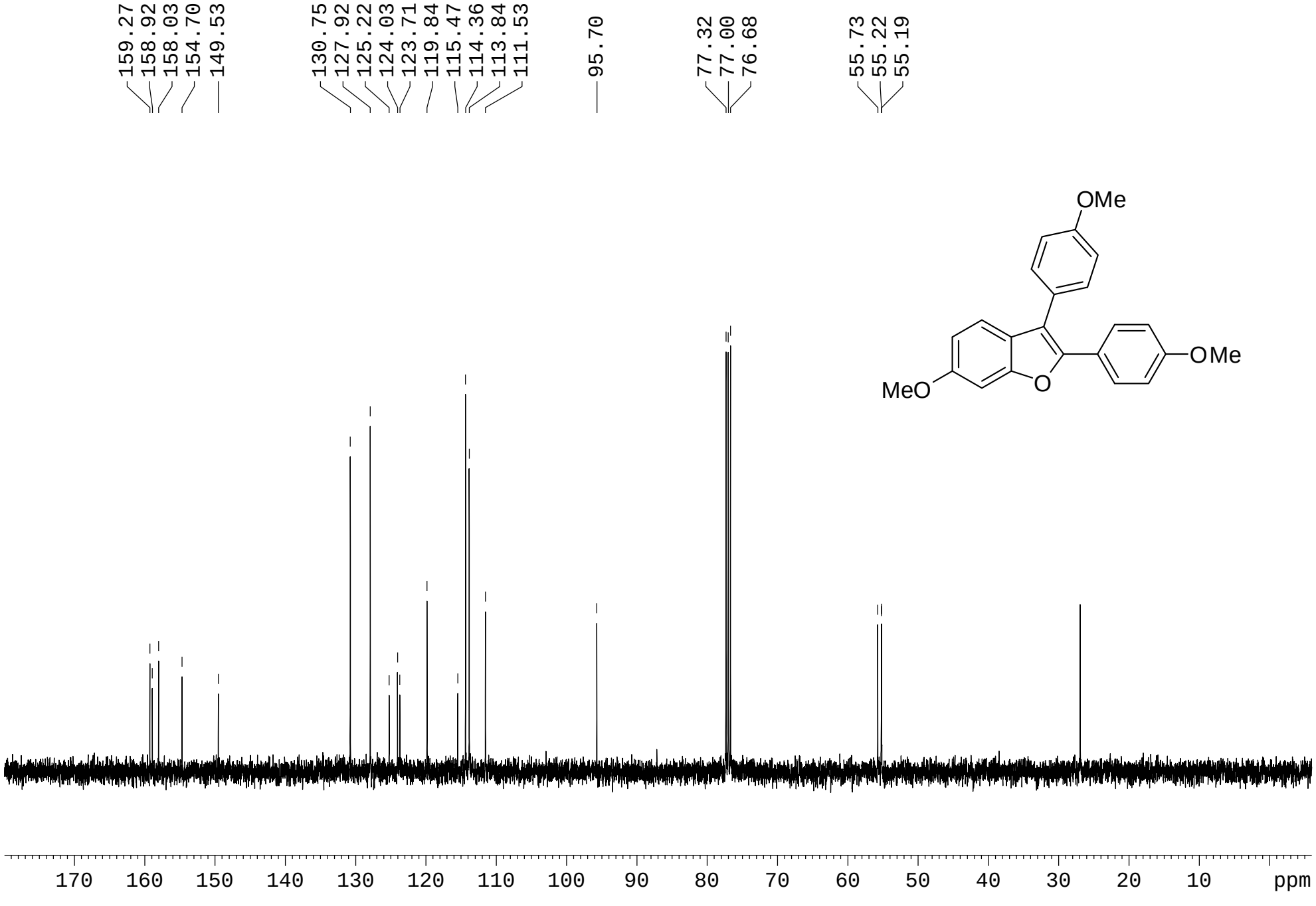
^{1}H NMR of compound 16m ($CDCl_3$, 400 MHz)



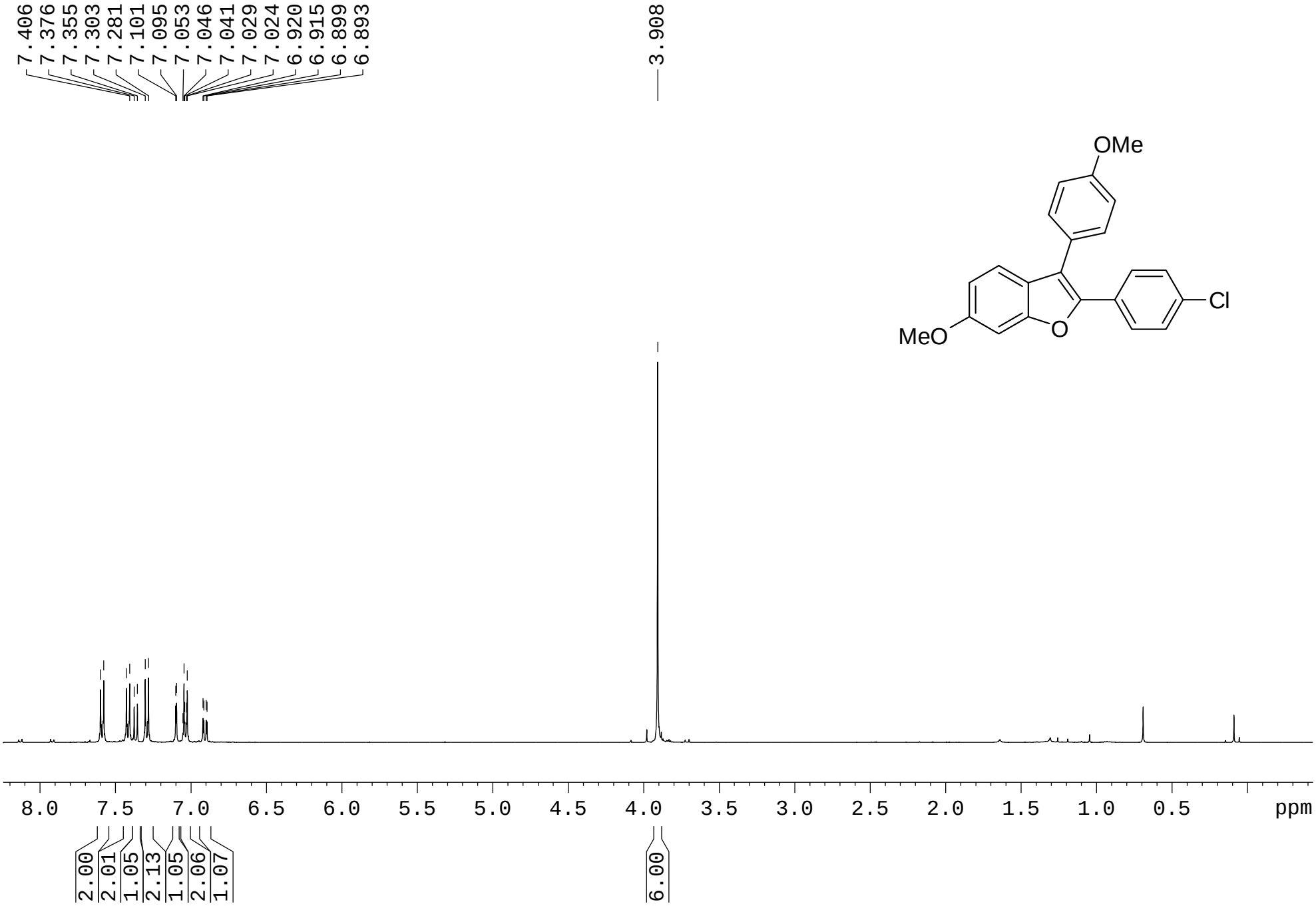




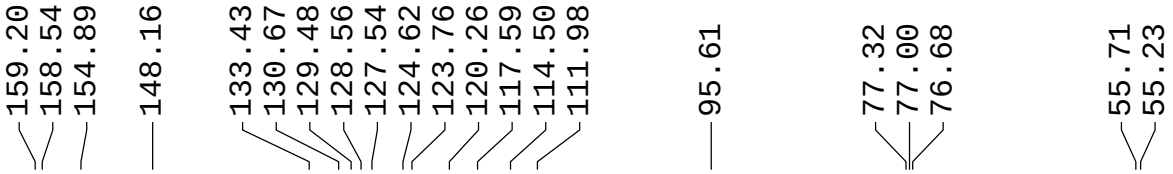
^{13}C NMR of compound 16m ($CDCl_3$, 100 MHz)

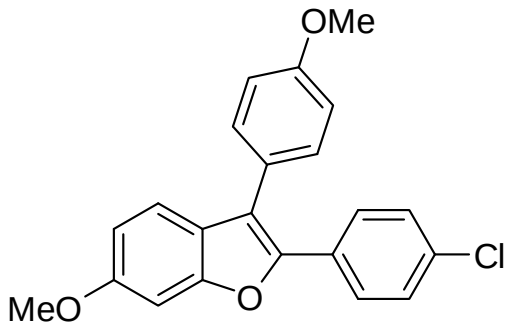


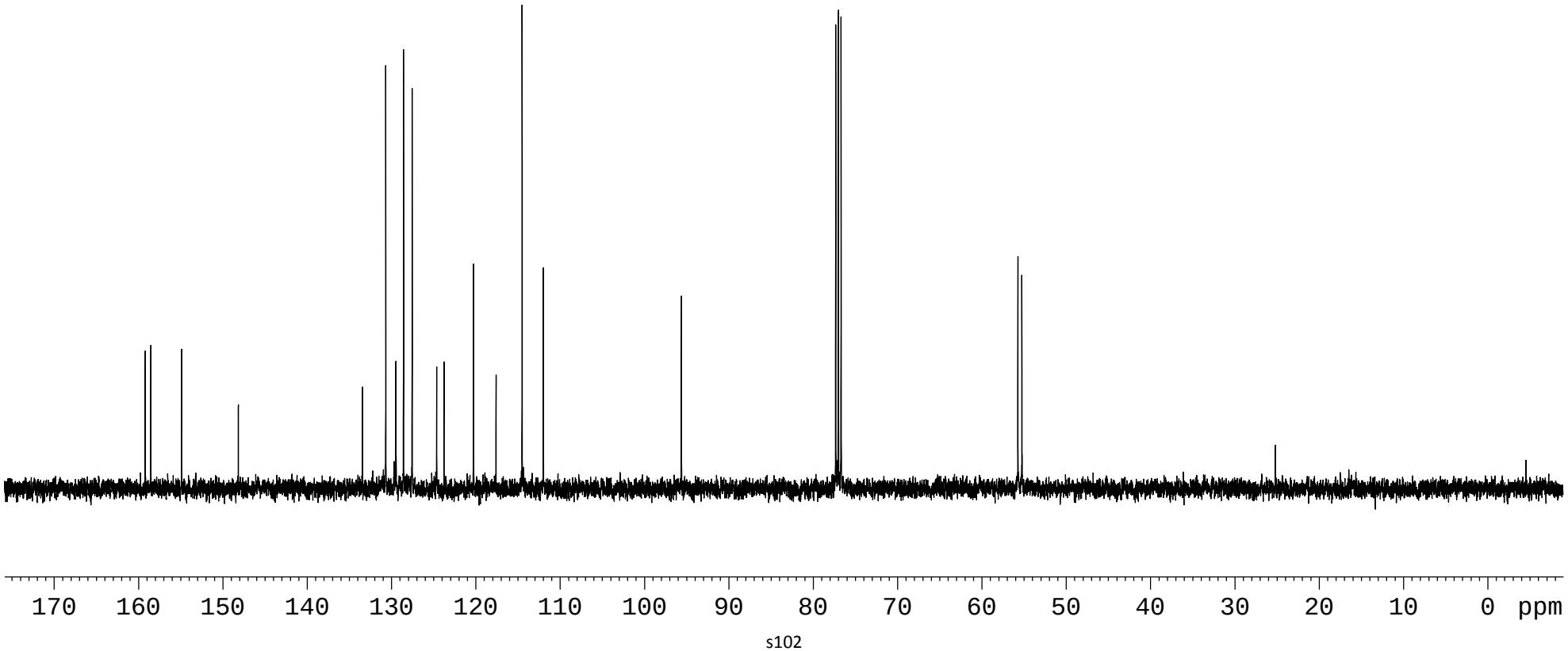
^{1}H NMR of compound 16n ($CDCl_3$, 400 MHz)



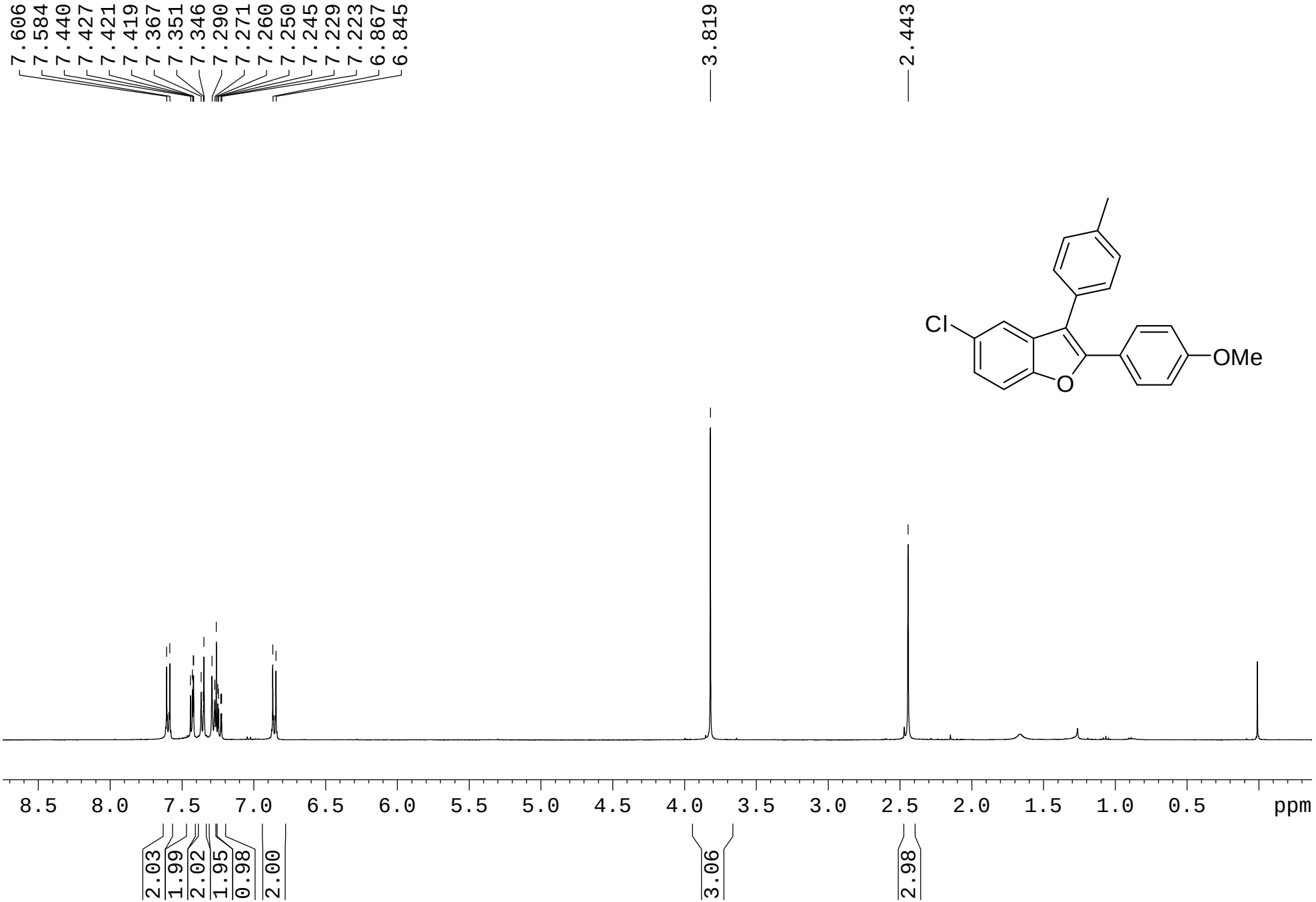
^{13}C NMR of compound 16n ($CDCl_3$, 100 MHz)



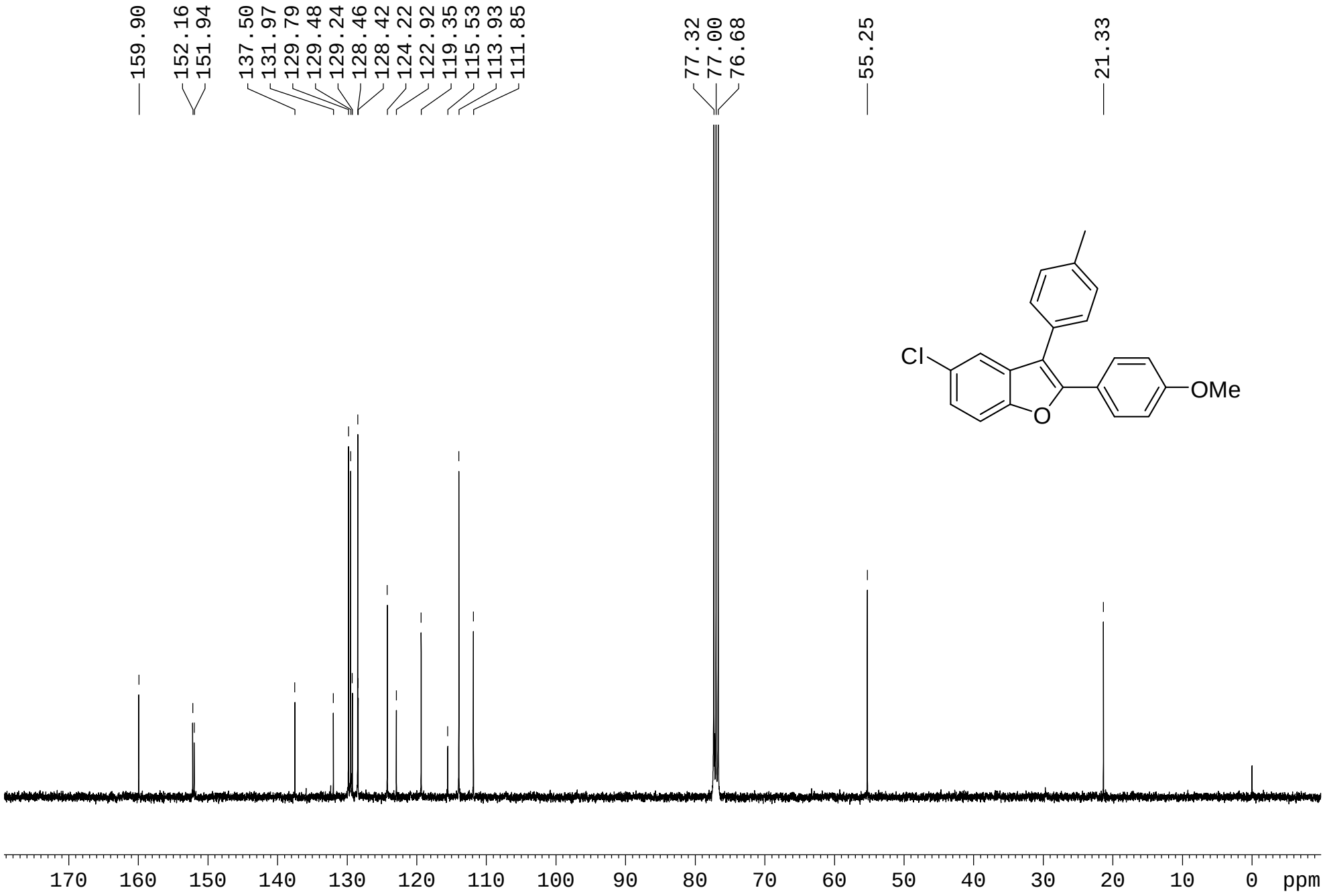




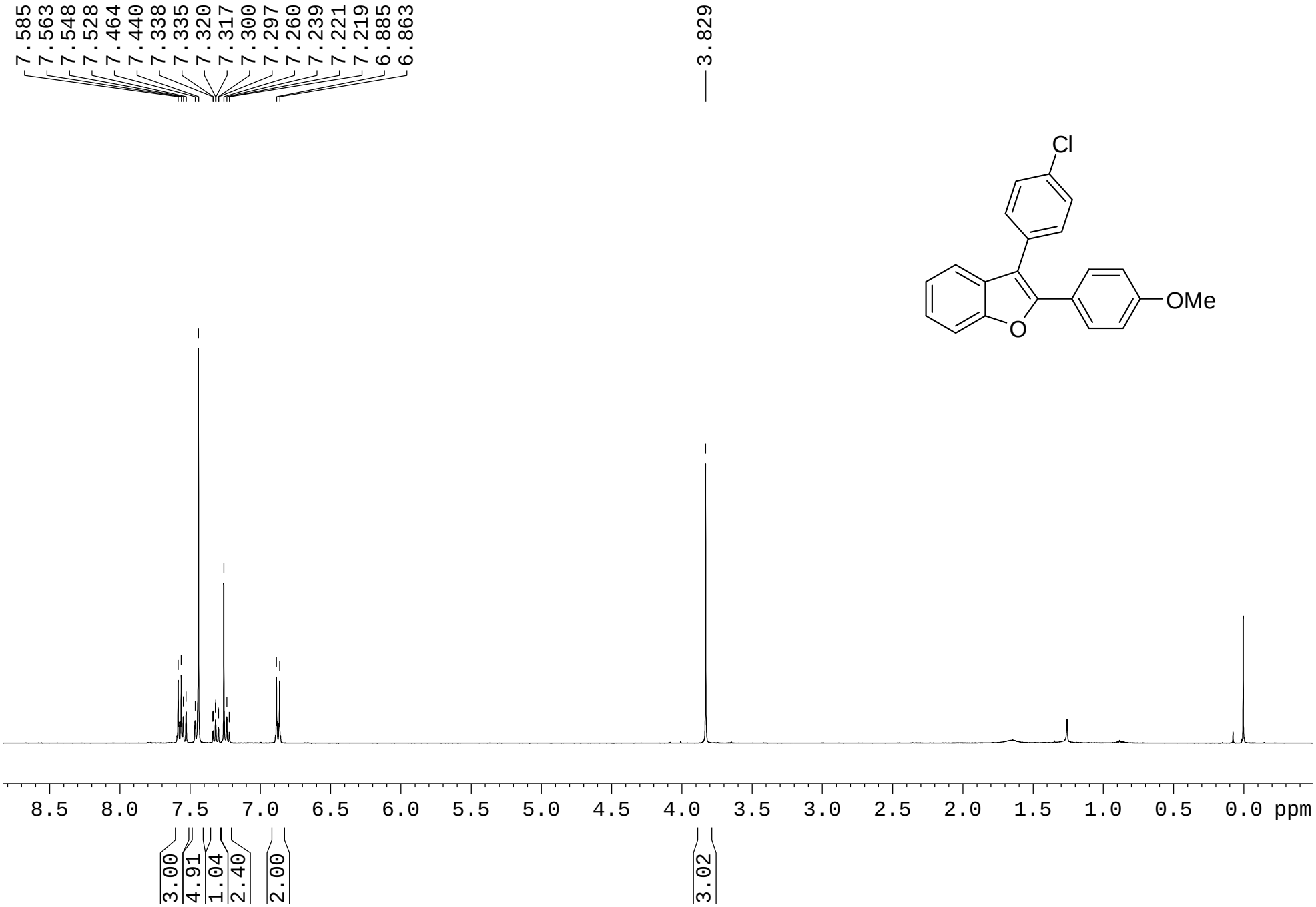
^{1}H NMR of compound 16o ($CDCl_3$, 400 MHz)



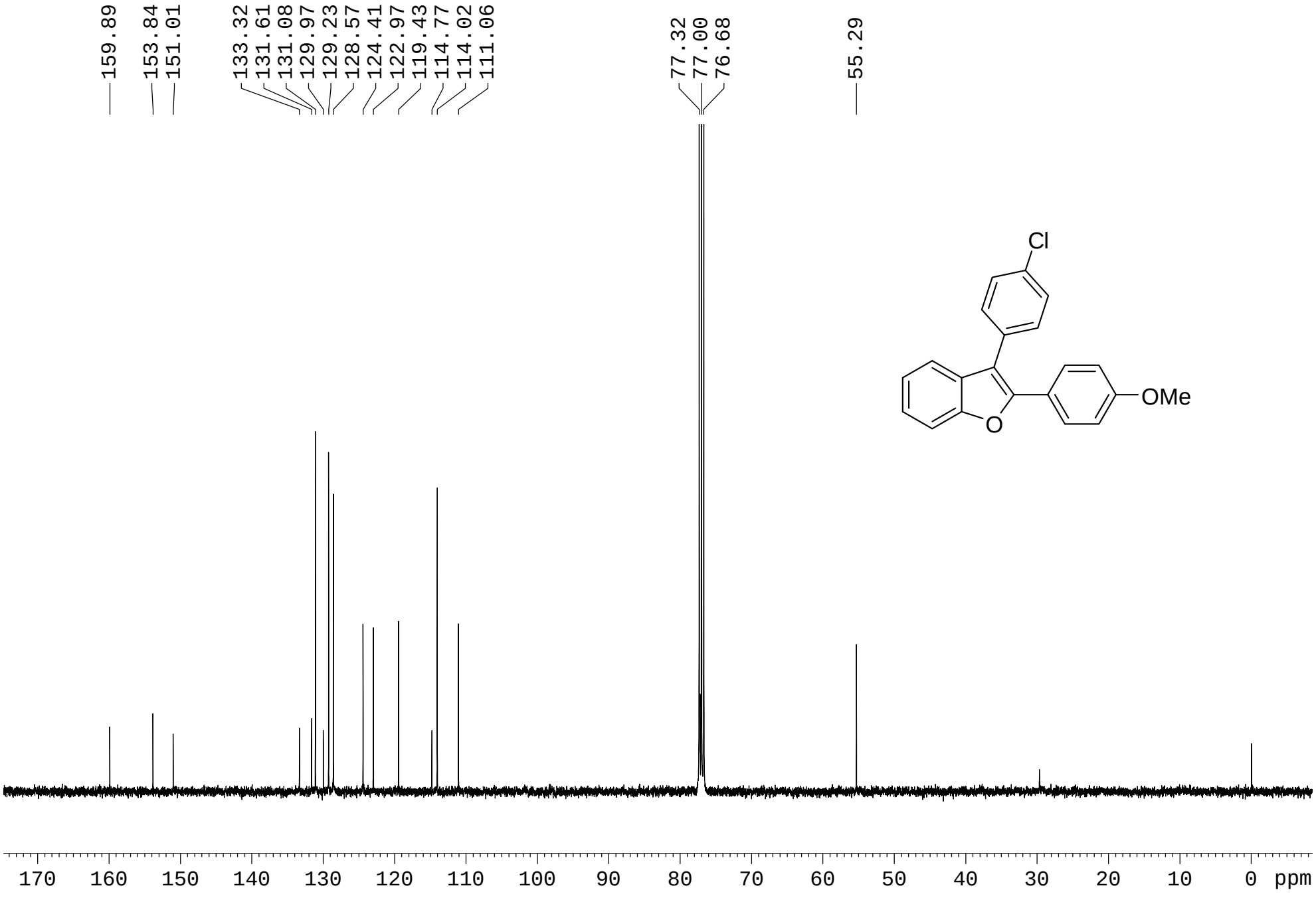
^{13}C NMR of compound 16o ($CDCl_3$, 100 MHz)



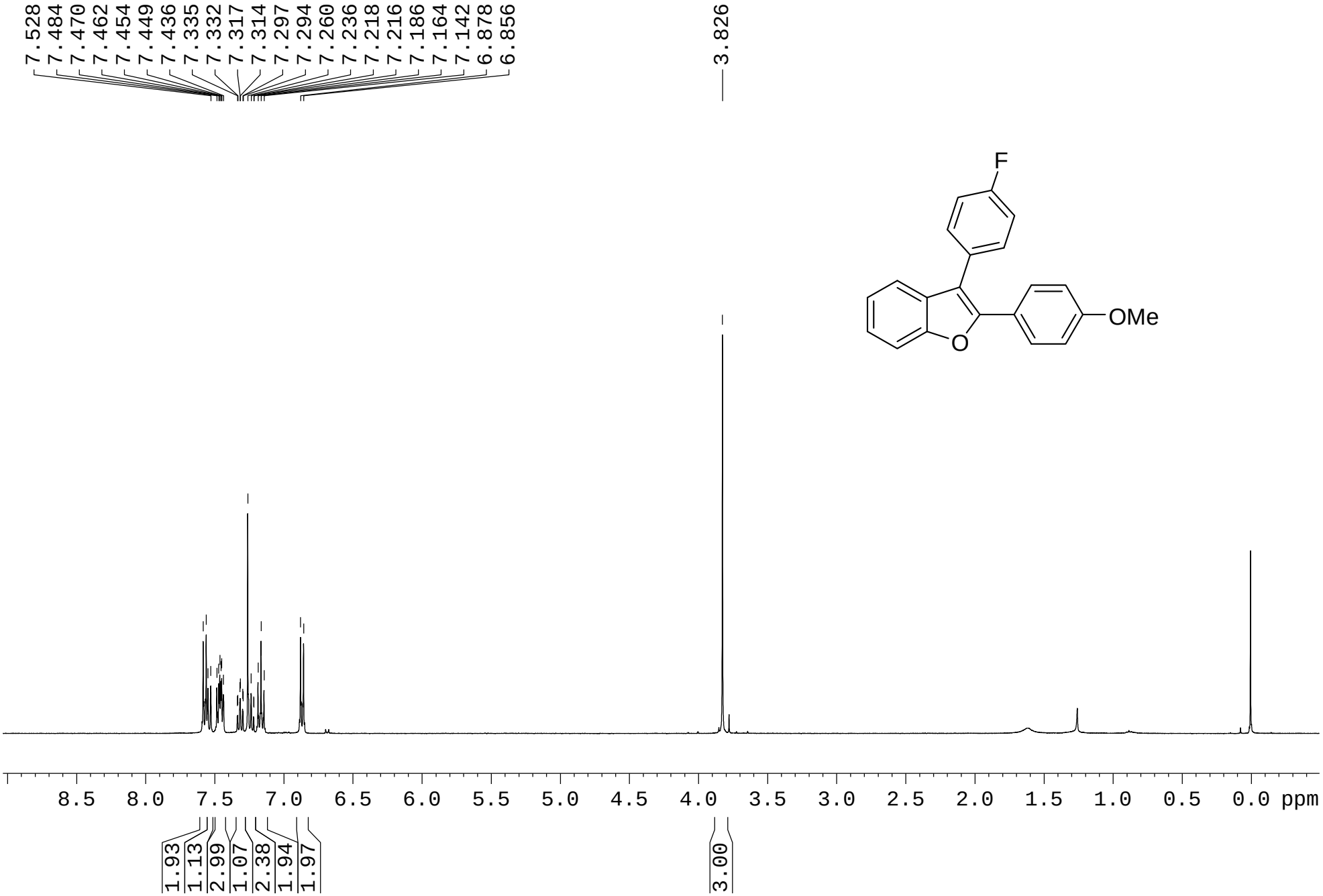
^{1}H NMR of compound 16p ($CDCl_3$, 400 MHz)



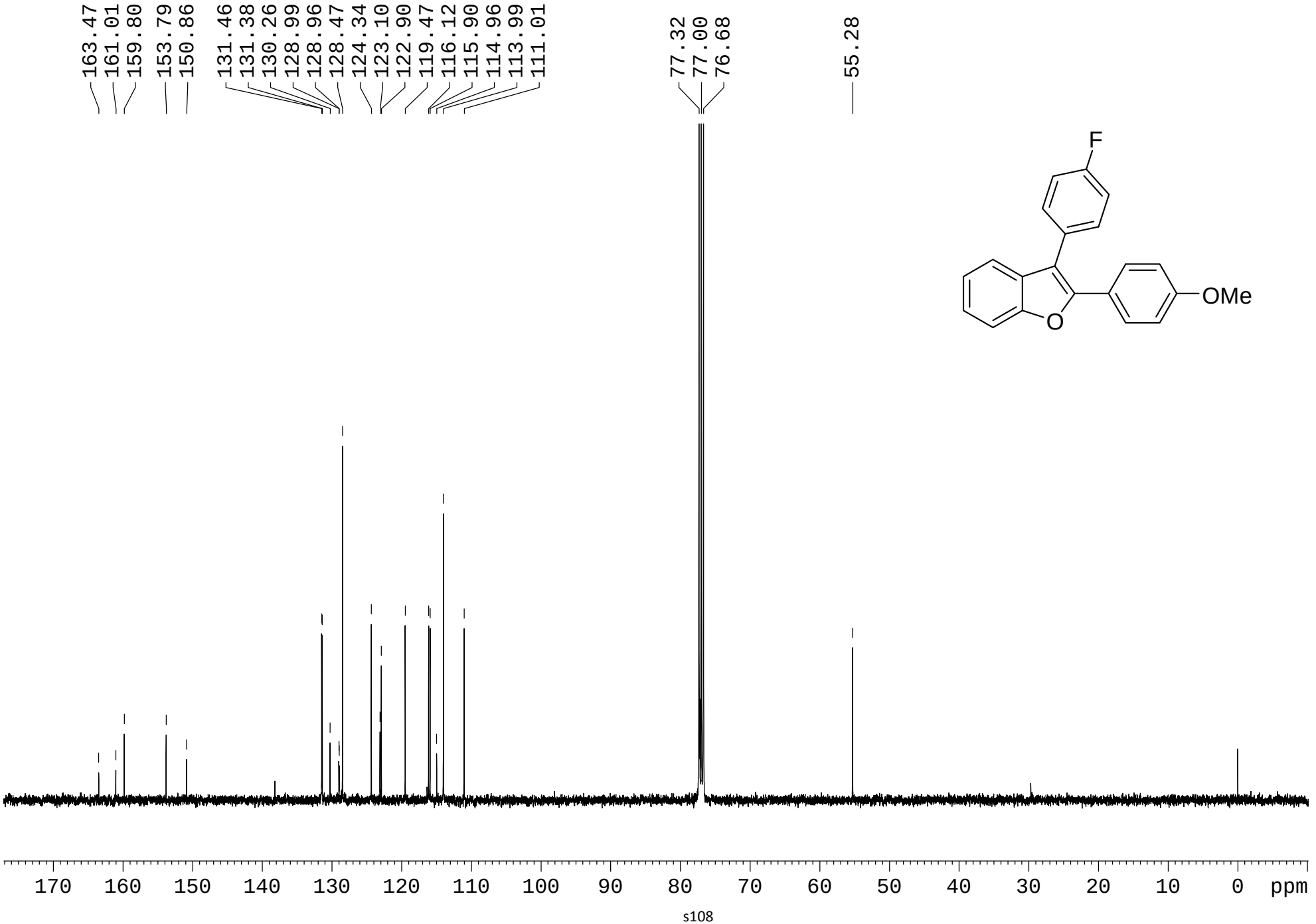
^{13}C NMR of compound 16p ($CDCl_3$, 100 MHz)



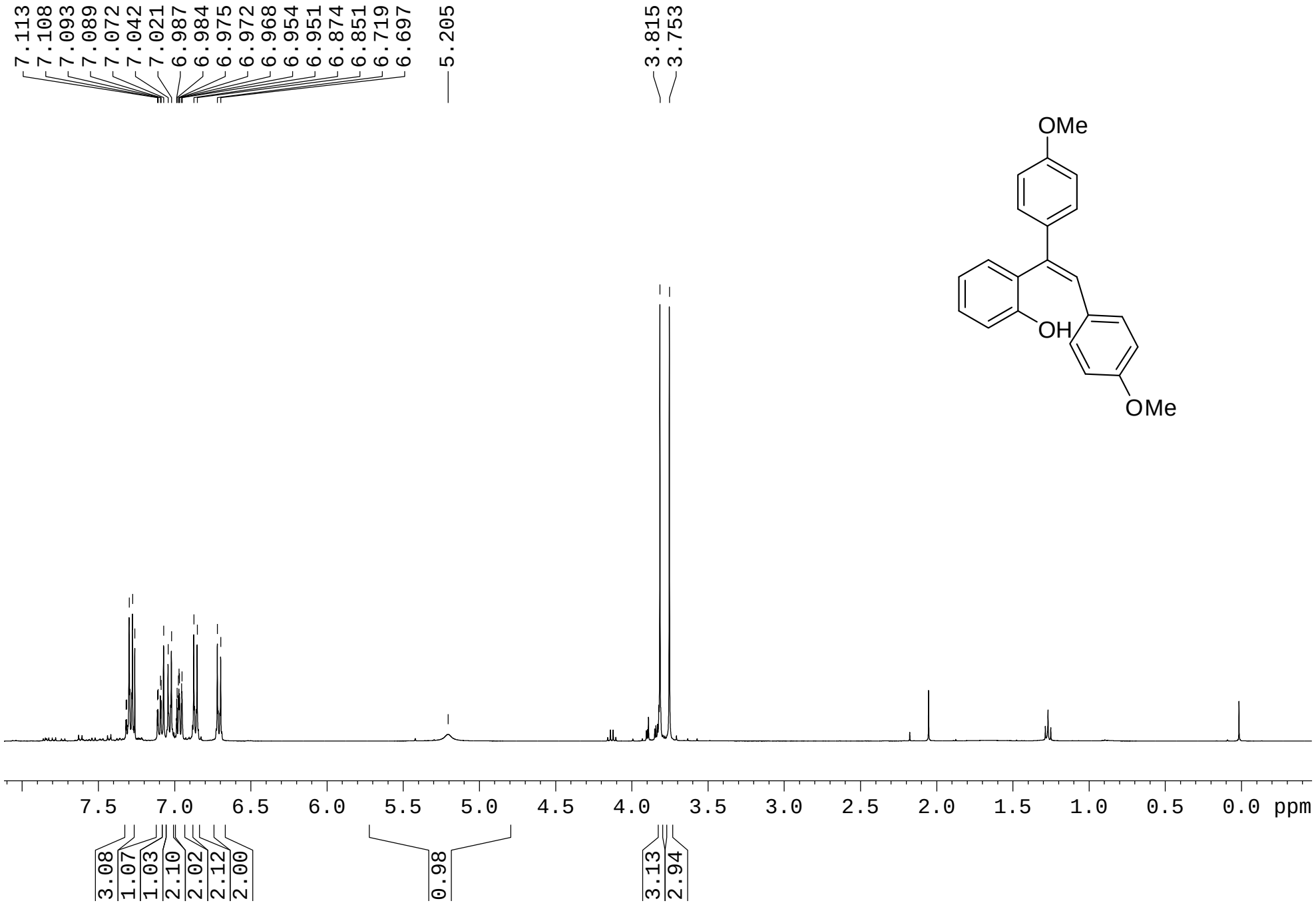
^{1}H NMR of compound 16q ($CDCl_3$, 400 MHz)



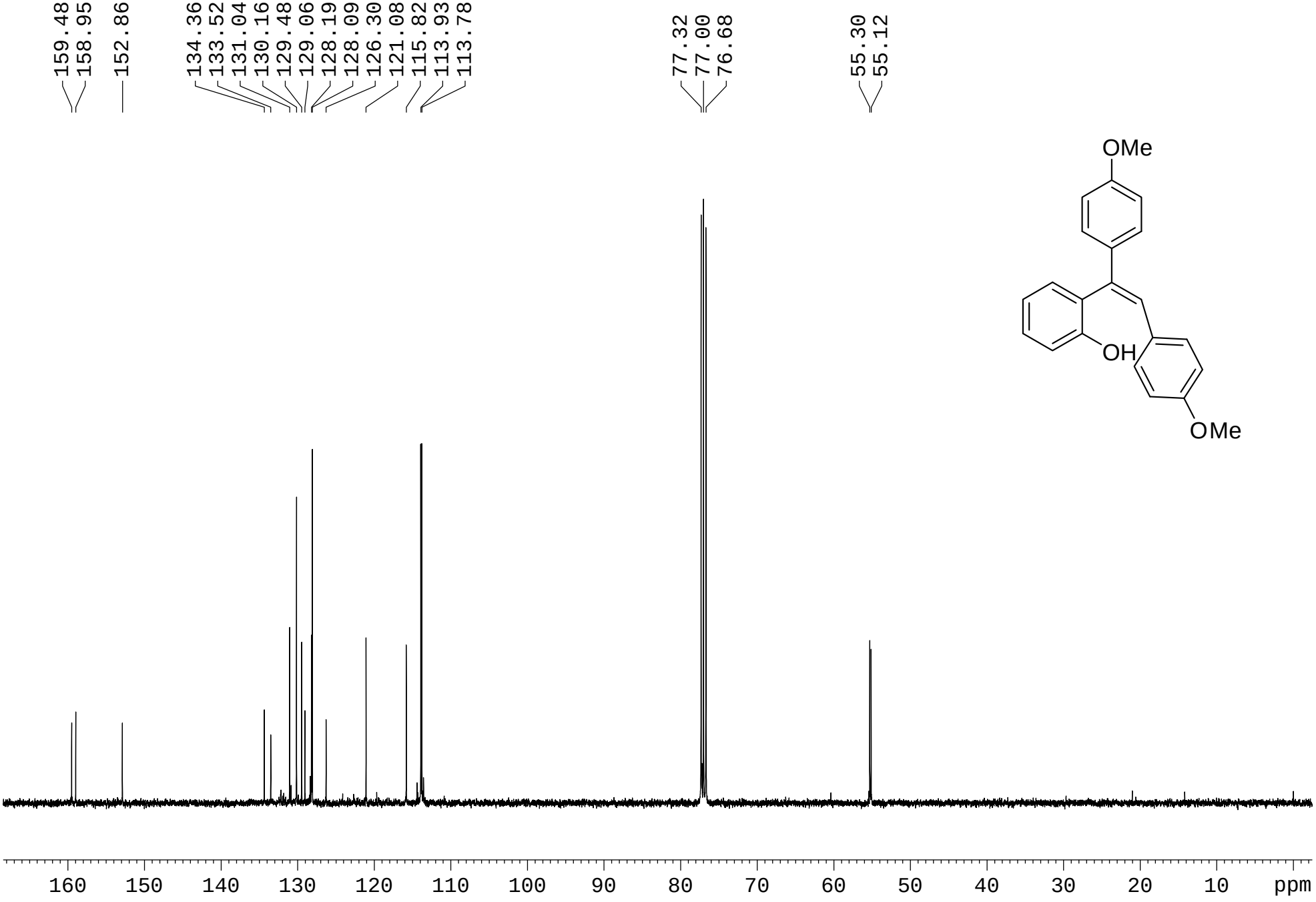
^{13}C NMR of compound 16q ($CDCl_3$, 100 MHz)



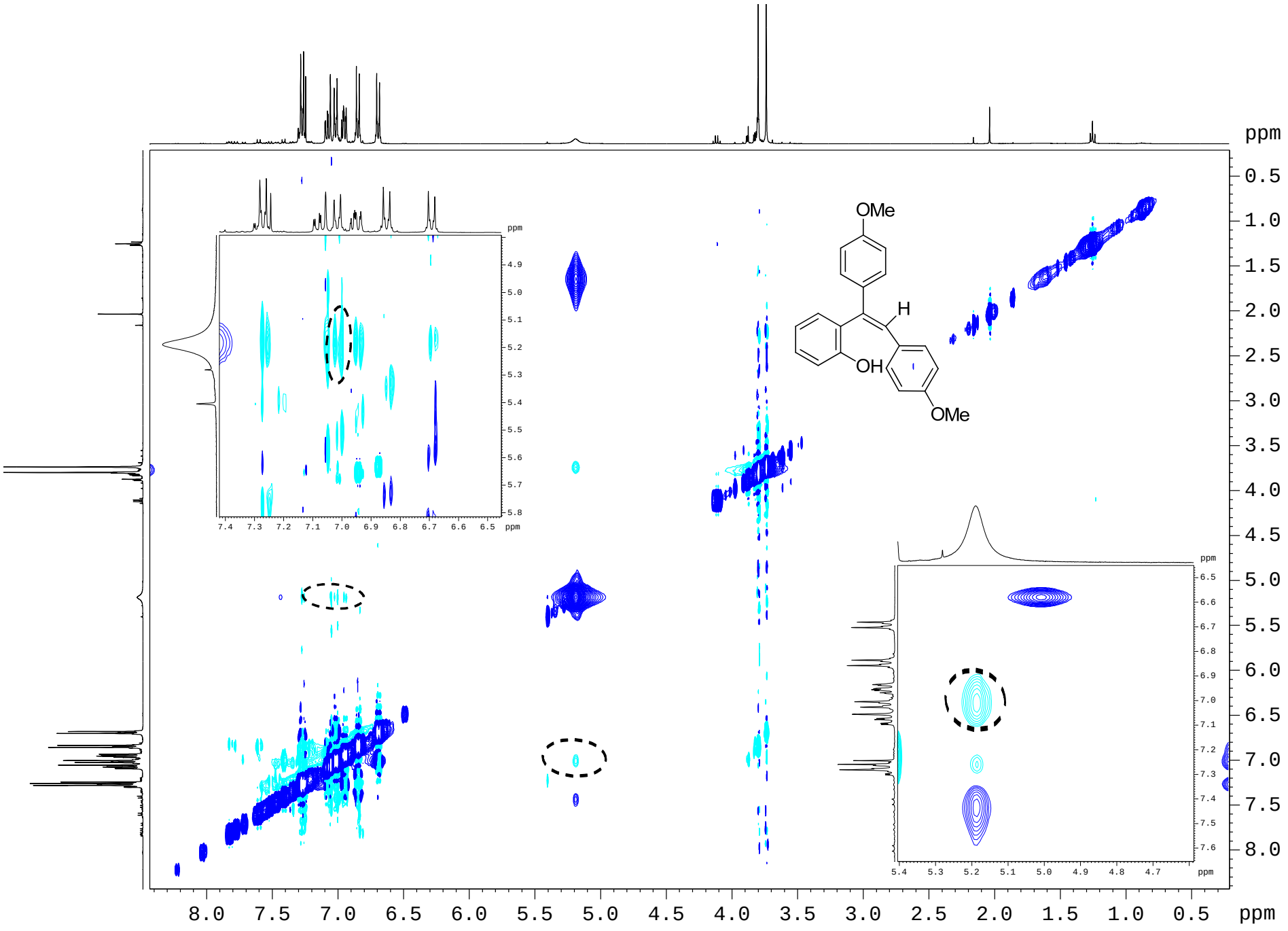
^{1}H NMR of compound 17h ($CDCl_3$, 400 MHz)



^{13}C NMR of compound 17h ($CDCl_3$, 100 MHz)

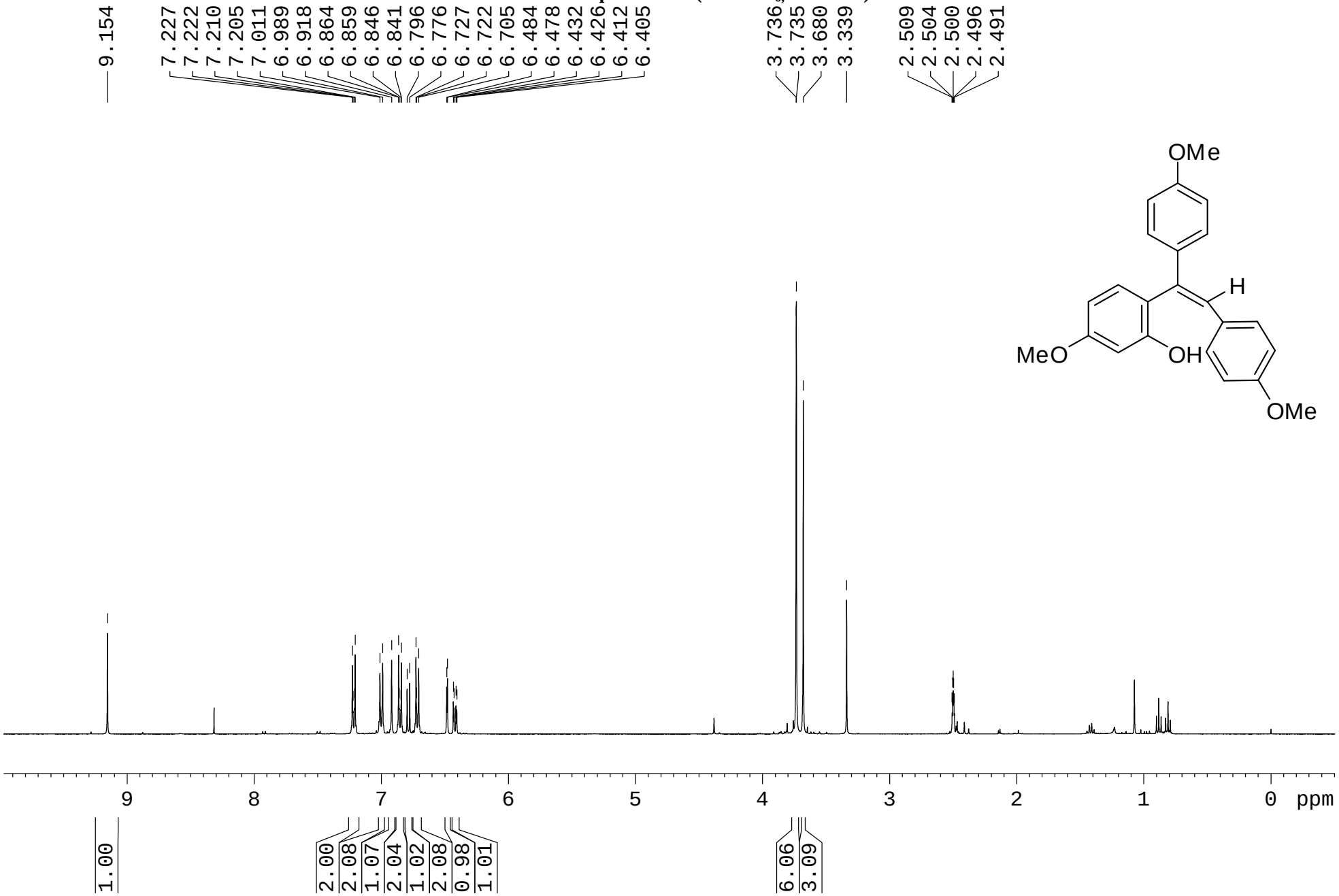


NOE spectrum of compound 17h ($CDCl_3$, 400 MHz)

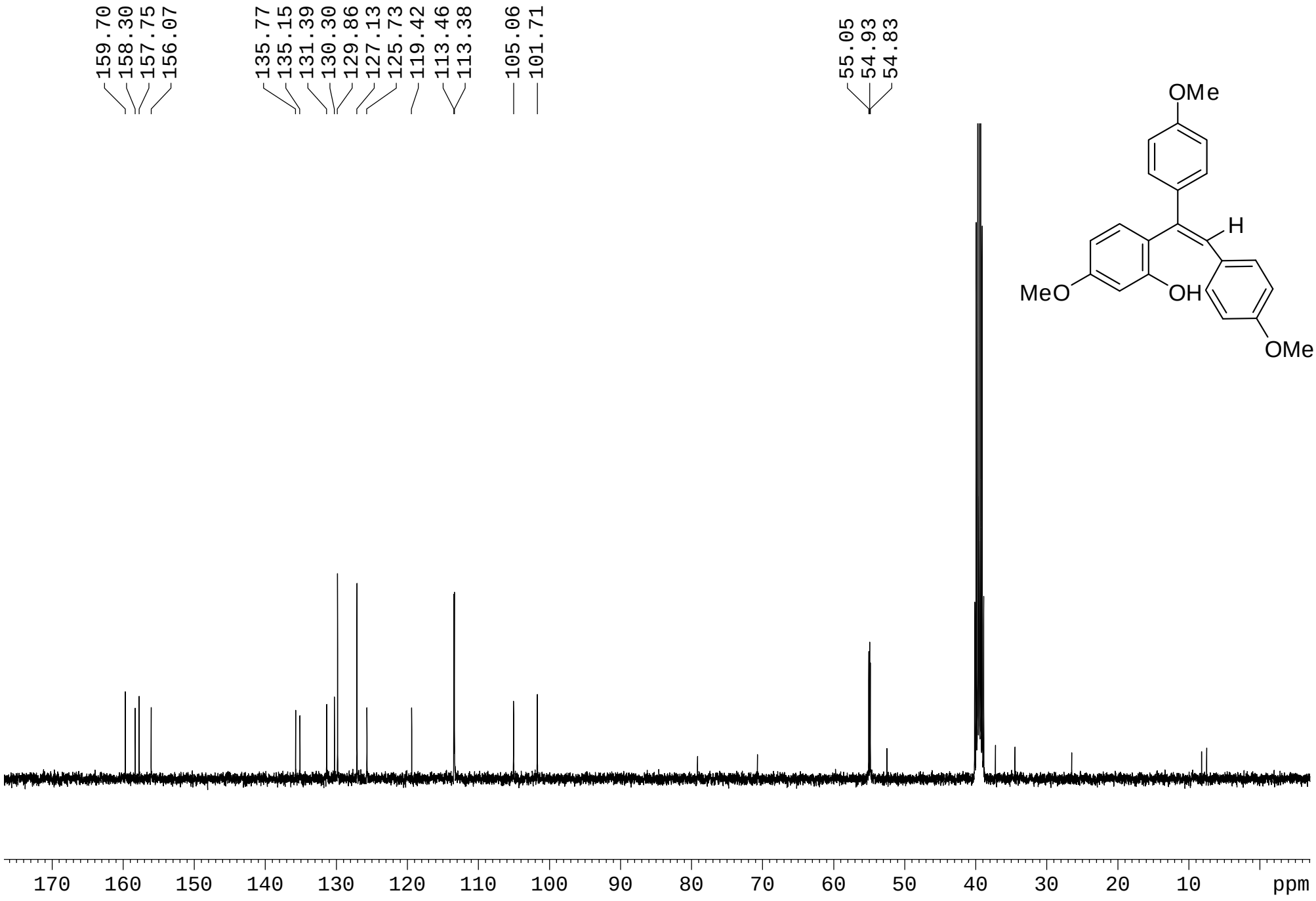


s111

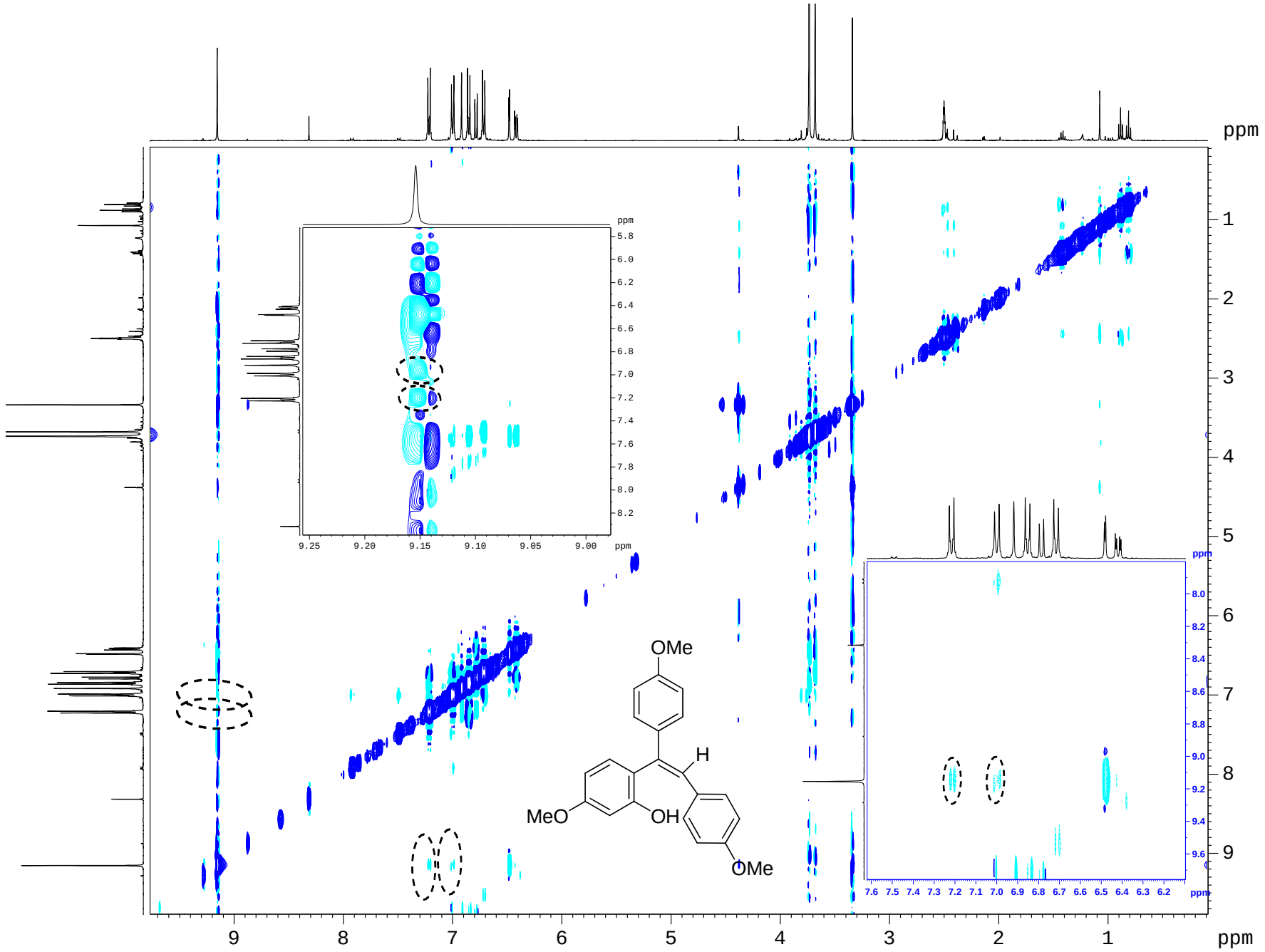
^{1}H NMR of compound 17m (DMSO-d_6, 400 MHz)



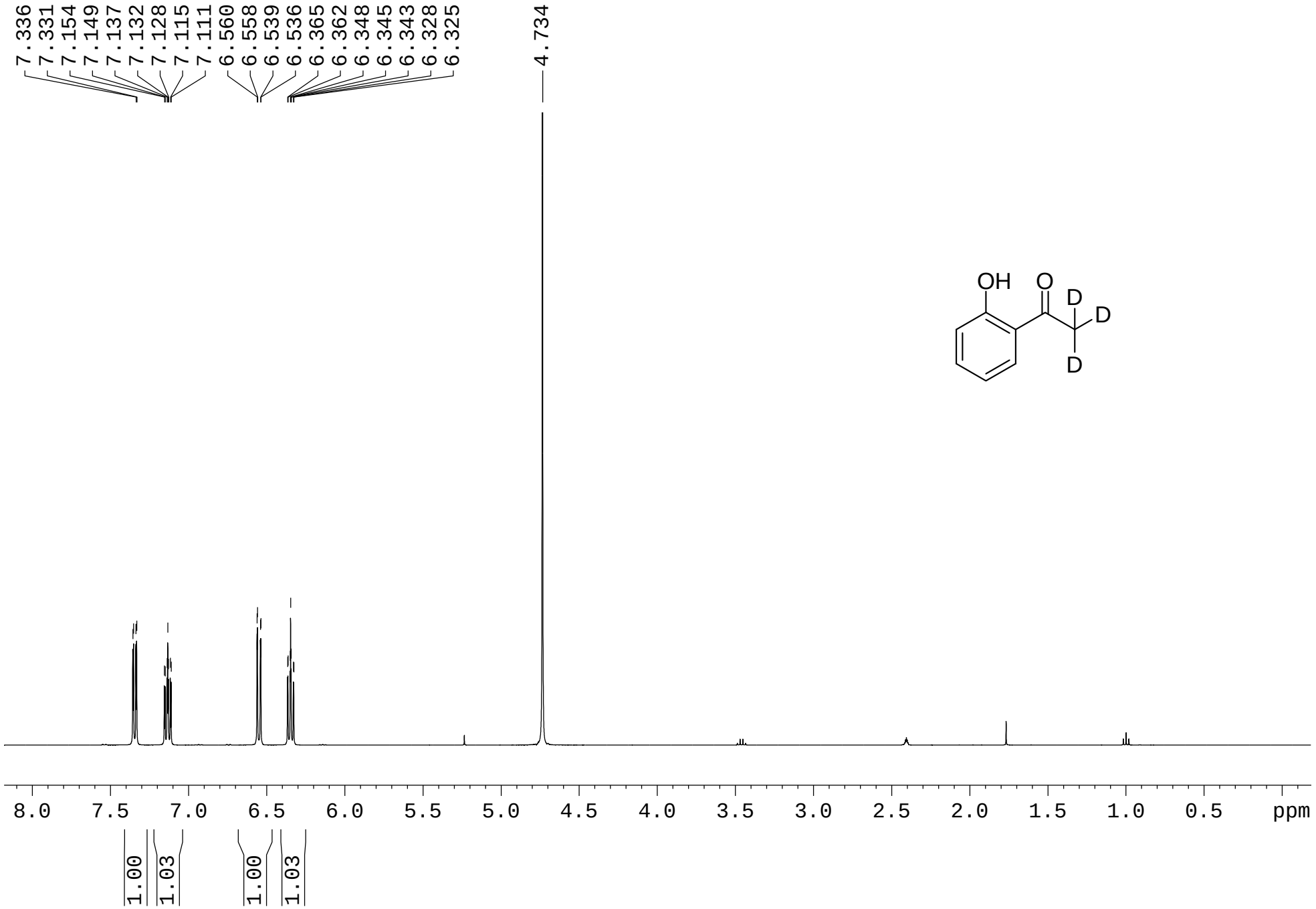
^{13}C NMR of compound 17m (DMSO-d_6, 100 MHz)



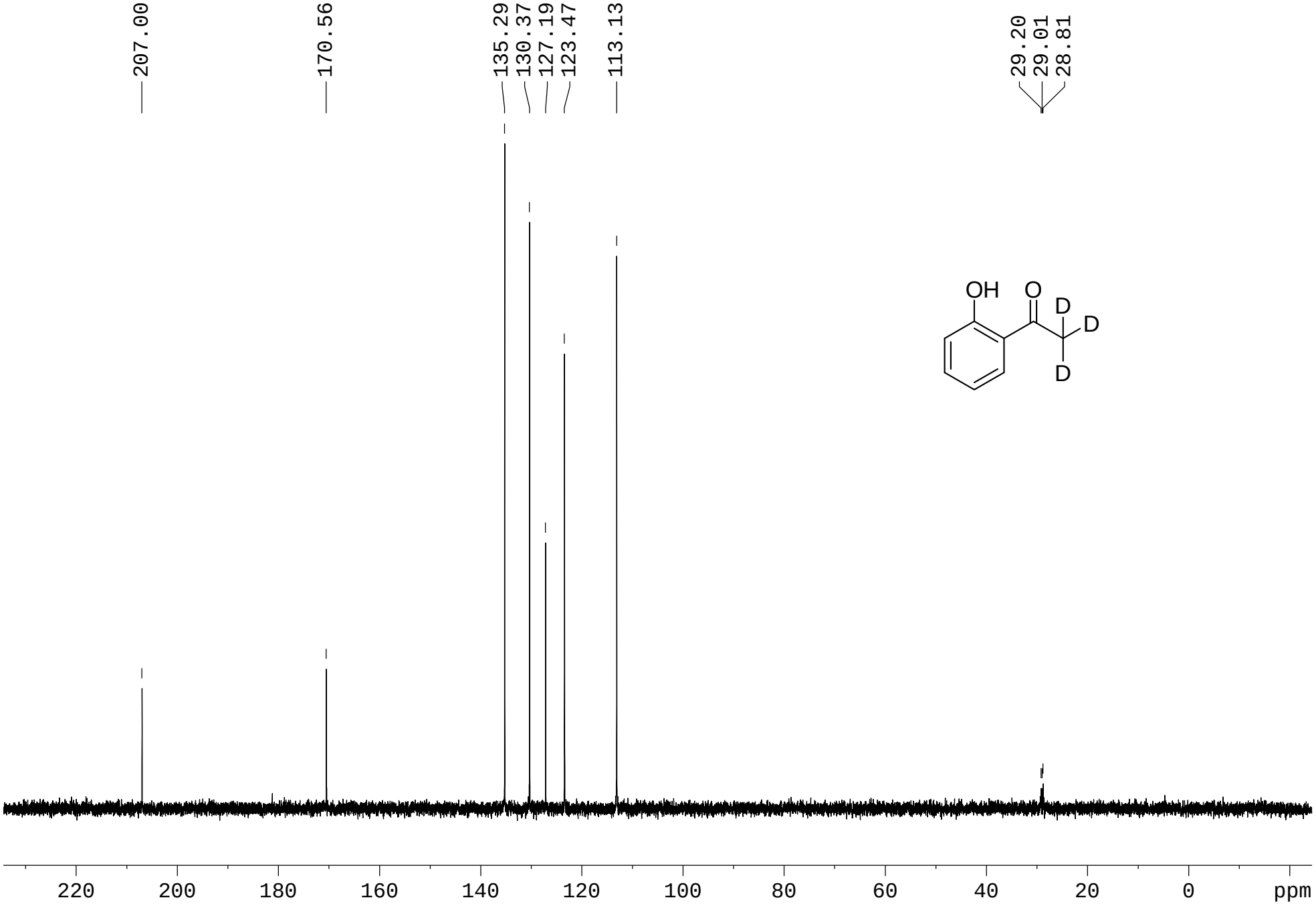
NOE spectrum of compound 17m (DMSO-d_6, 400 MHz)



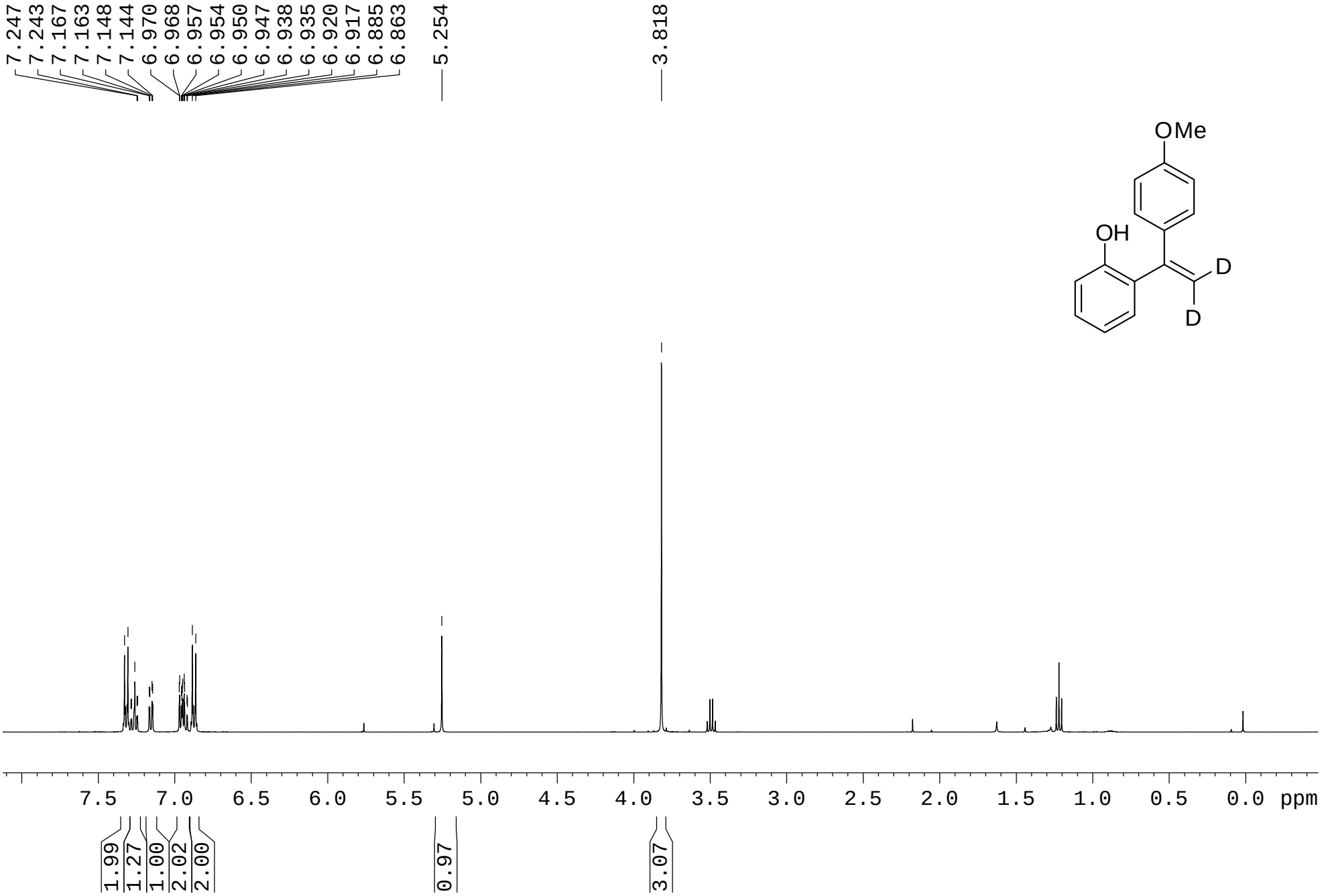
^{1}H NMR of compound 30 (D_2O, 400 MHz)



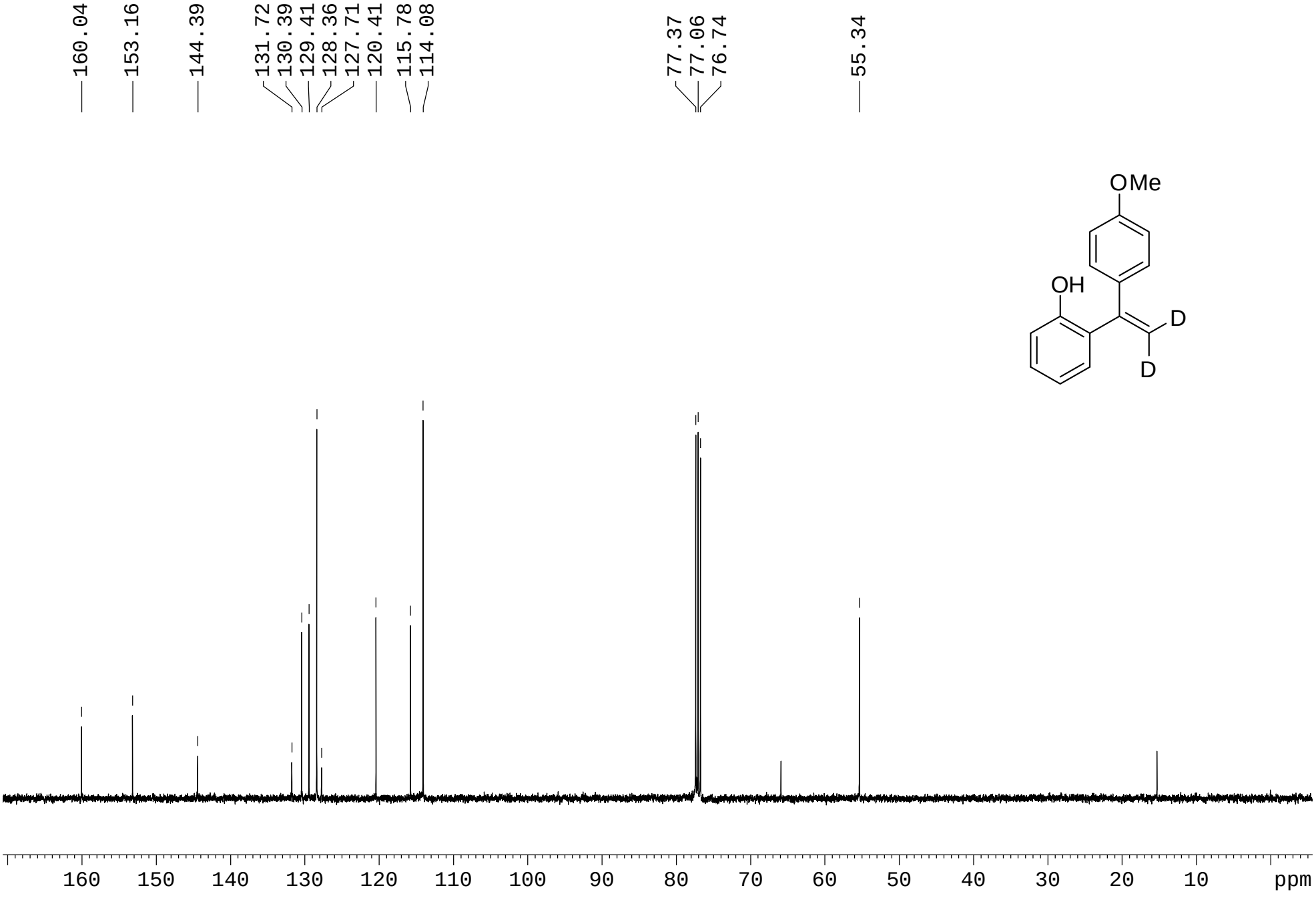
^{13}C NMR of compound 30 (D_2O, 100 MHz)



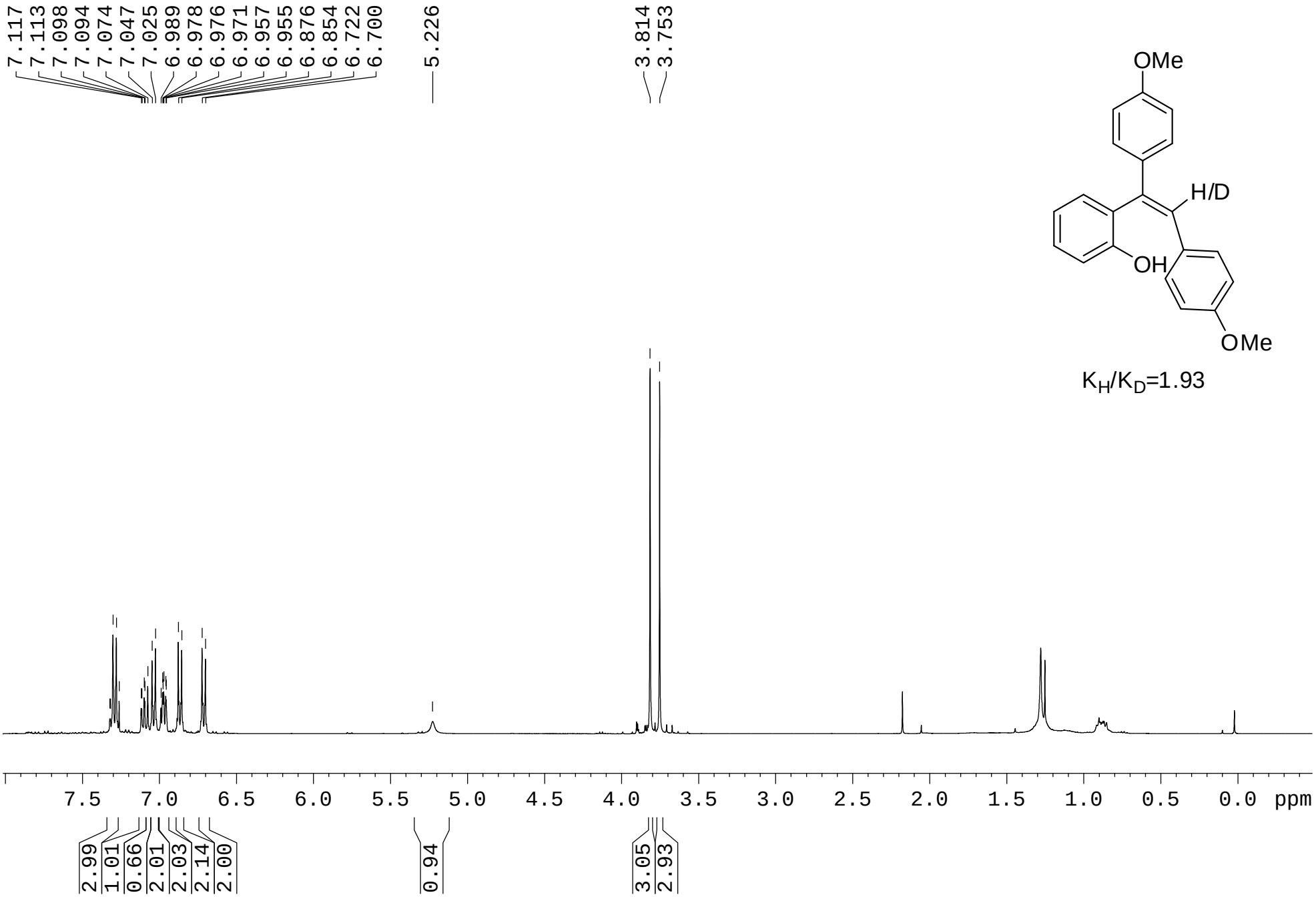
^{1}H NMR of compound 31 ($CDCl_3$, 400 MHz)



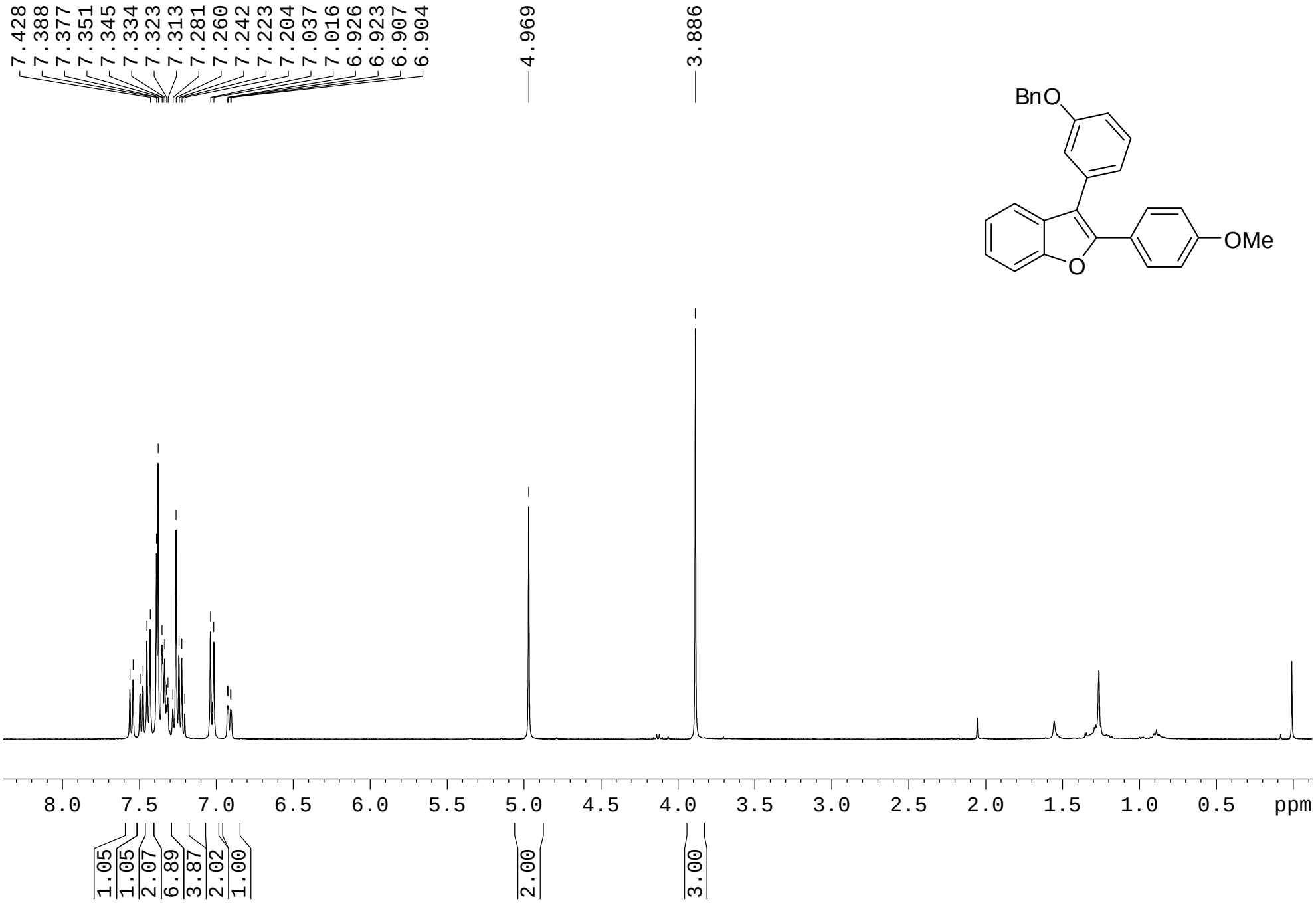
^{13}C NMR of compound 31 ($CDCl_3$, 100 MHz)



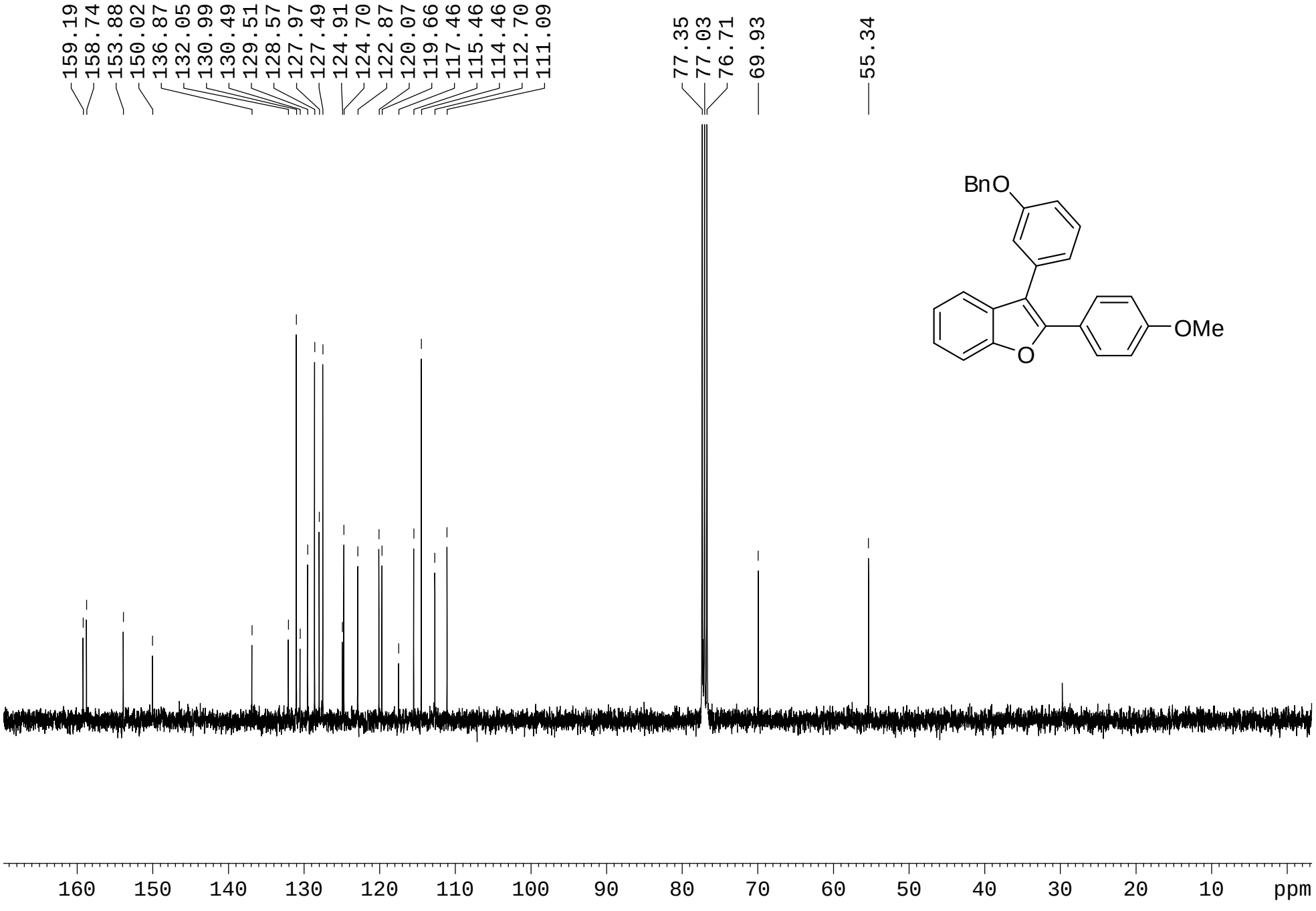
^{1}H NMR of Kinetic isotope effect experiment ($CDCl_3$, 400 MHz)



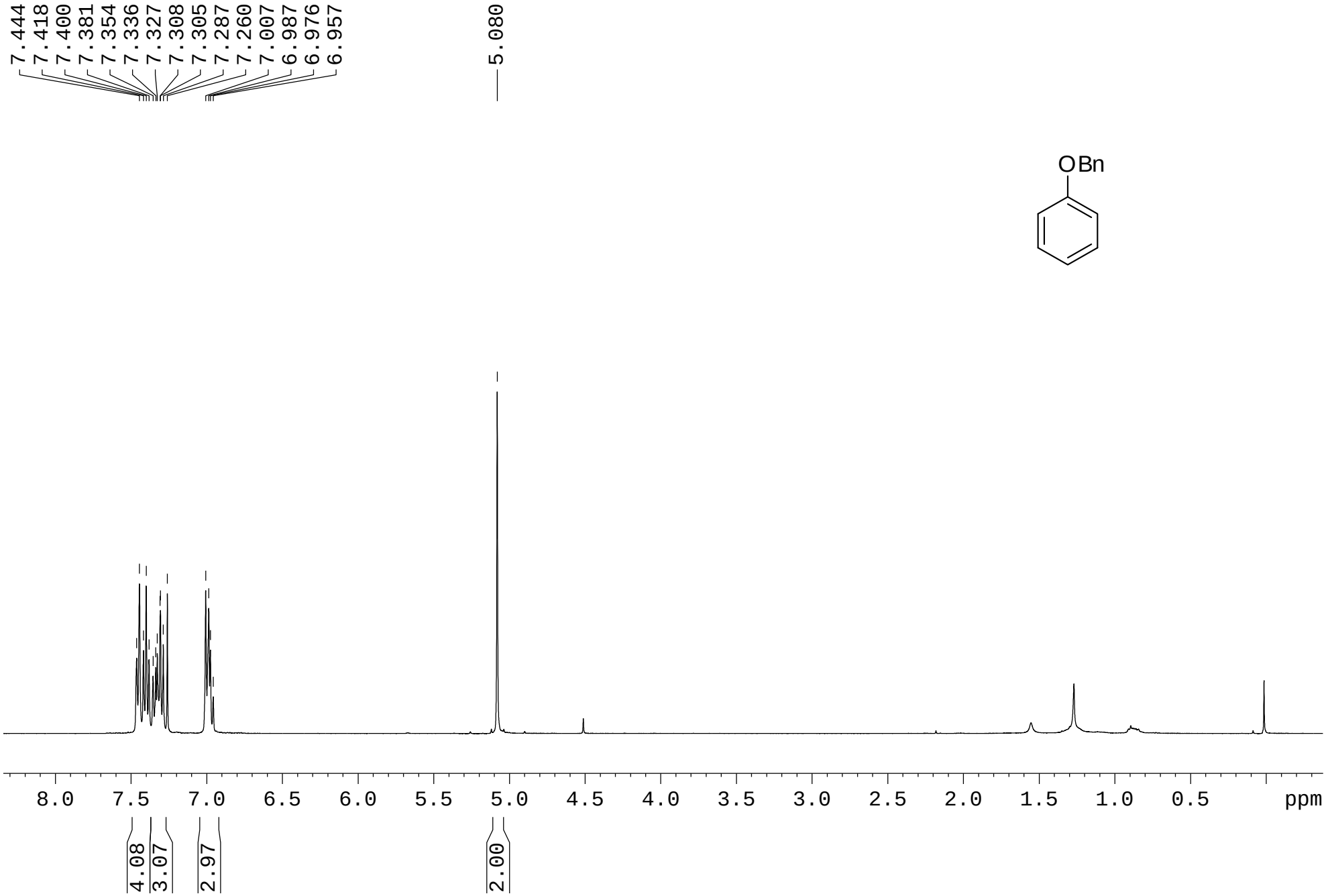
^{1}H NMR of compound 16r ($CDCl_3$, 400 MHz)



^{13}C NMR of compound 16r ($CDCl_3$, 100 MHz)



^{1}H NMR of compound 18 ($CDCl_3$, 400 MHz)



^{13}C NMR of compound 18 ($CDCl_3$, 100 MHz)