Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Rhodium-catalyzed intramolecular annulation via C-H activation leading to fused tricyclic indole scaffolds

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S2. General information

S2-S9. Synthetic procedures and analytical data of compound **2** and **4**.

S10-S53. ^{1}H NMR, ^{13}C NMR spectrum of compounds

I. General information

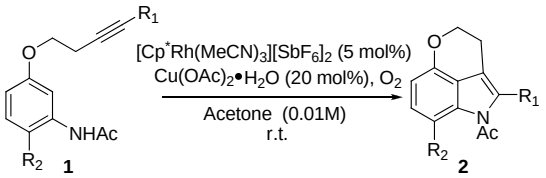
All reagents were obtained from commercial suppliers unless otherwise stated. Visualization was achieved under a UV lamp (254 nm and 365 nm), and by developing the plates with phosphomolybdic acid or p-methoxybezaldehyde in ethanol. Flash column chromatography was performed using silica gel (200-300 mesh) with solvents distilled prior to use.

^{1}H NMR were recorded 400 MHz NMR spectrometer, ^{13}C NMR at 100 MHz NMR spectrometer unless otherwise stated. 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.

High resolution mass spectral (HRMS) data were obtained with an ionization mode of ESI.

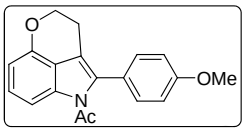
The substrates **1** were prepared according to the previous literature[1, 2].

II. Synthetic procedures and analytical data of compound 2 and 4.



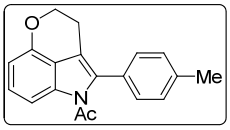
To a stirred solution of the acetanilide **1** (0.1 mmol, 1 eq) in acetone (10 mL, 0.01M) was added $[Cp^{*}Rh(MeCN)_3][SbF_6]_2$ (4.2 mg, 0.005 mmol, 5 mol%), $Cu(OAc)_2 \cdot H_2O$ (4.0 mg, 0.02 mmol, 20 mol%) successfully. Molecular oxygen was briefly purged through the solution (~ 1.5 min) via a 16 cm needle and a balloon of oxygen. The reaction was then placed at room temperature for 12-72 h and left under a positive pressure of oxygen. After the substrate **1** was completely consumed by TLC analysis, the reaction was filtered over celite and washed with dicholoromethane. The solvent was removed and the residue purified by flash column chromatography on silica gel with PE/EtOAc as the solvent.

Analytical data of compound 2

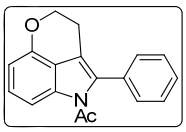


Compound **2a** (19 mg, 63%): white solid. m.p. 144-145 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.74 (d, *J* = 8.0 Hz, 1H), 4.36 (t, *J* = 5.6 Hz, 2H), 3.87 (s, 3H), 2.90 (t, *J* = 5.6 Hz, 2H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 159.6, 150.4, 136.5, 130.7, 130.6, 126.7, 125.1, 118.5, 114.4, 114.2, 109.4, 107.8, 67.7,

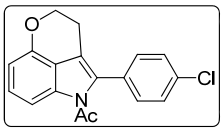
55.3, 27.2, 23.0; IR(KBr): 3435, 2931, 1509, 1450, 1062, 835, 757 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{17}NO_3$ $(M + H)^+$ 308.1281; found 308.1282.



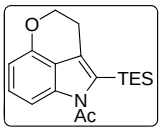
Compound **2b**. (17 mg, 60%). white solid. m.p. 141-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.4 Hz, 1H), 7.28 (br s, 4H), 7.23 (t, J = 8.0 Hz, 1H), 6.74 (d, J = 7.6 Hz, 1H), 4.35 (t, J = 5.6 Hz, 2H), 2.91 (t, J = 5.6 Hz, 2H), 2.43 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 150.5, 138.2, 136.6, 130.9, 130.0, 129.5, 129.2, 126.8, 118.5, 114.6, 109.4, 107.8, 67.7, 27.3, 23.1, 21.3; IR(KBr): 3433, 2920, 1508, 1452, 1062, 832, 747 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{17}NO_2$ $(M + H)^+$ 292.1332; found 292.1336.



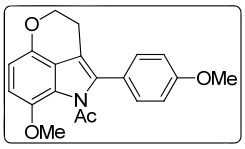
Compound **2c**. (15 mg, 55%). white solid. m.p. 135-136 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.4 Hz, 1H), 7.50-7.39 (m, 5H), 7.25 (t, J = 8.0 Hz, 1H), 6.75 (d, J = 7.6 Hz, 1H), 4.36 (t, J = 5.6 Hz, 2H), 2.93 (t, J = 5.6 Hz, 2H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 150.6, 136.7, 133.0, 130.8, 129.3, 128.7, 128.2, 127.0, 118.5, 115.0, 109.3, 107.8, 67.7, 27.3, 23.0; IR(KBr): 3433, 2927, 1490, 1451, 1063, 811, 749 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{15}NO_2$ $(M + H)^+$ 278.1181; found 278.1176.



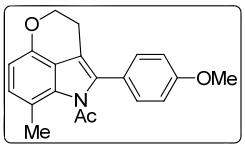
Compound **2d** (15 mg, 48%): yellow solid. m.p. 148-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.0 Hz, 1H), 7.45 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.25 (t, J = 8.0 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 4.36 (t, J = 5.6 Hz, 2H), 2.91 (t, J = 5.6 Hz, 2H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 150.7, 136.6, 134.2, 131.5, 130.4, 129.7, 129.0, 127.2, 118.5, 115.6, 109.1, 107.9, 67.6, 27.4, 23.0; IR(KBr): 3435, 2925, 1510, 1450, 1061, 841, 747 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{14}NO_2Cl$ $(M + H)^+$ 312.0786; found 312.0784.



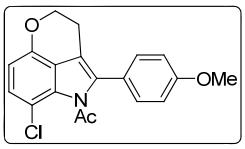
Compound **2e**. (17 mg, 55%). white solid. m.p. 79-81 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, J = 8.0 Hz, 1H), 7.12 (d, J = 8.4 Hz, 1H), 6.68 (d, J = 8.0 Hz, 1H), 4.36 (t, J = 5.6 Hz, 2H), 3.15 (t, J = 5.6 Hz, 2H), 2.78 (s, 3H), 0.97-0.92 (m, 9H), 0.90-0.86 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 151.3, 137.1, 130.9, 126.8, 126.5, 121.5, 106.9, 106.8, 67.8, 26.0, 25.6, 8.04, 5.14; IR(KBr): 3371, 2929, 1489, 1456, 1071, 781, 737 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{25}NO_2Si$ $(M + H)^+$ 316.1727; found 316.1726.



Compound **2f.** (33 mg, 99%). yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 6.69 (d, J = 8.4 Hz, 1H), 6.63 (d, J = 8.4 Hz, 1H), 4.31 (t, J = 5.6 Hz, 2H), 3.91 (s, 3H), 3.85 (s, 3H), 2.92 (t, J = 5.6 Hz, 2H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 159.2, 144.9, 141.8, 132.7, 130.6, 124.5, 124.4, 121.0, 113.7, 111.9, 108.0, 106.4, 67.7, 56.5, 55.2, 28.2, 23.1; IR(KBr): 3429, 2933, 1513, 1454, 1051, 796, 742 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{20}H_{19}NO_4$ $(M + H)^+$ 338.1387; found 338.1383.

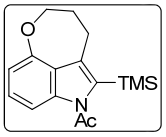


Compound **2g**. (30 mg, 92%). white solid. m.p. 131-132 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.8 Hz, 2H), 7.02-6.97 (m, 3H), 6.64 (d, J = 8.0 Hz, 1H), 4.32 (t, J = 5.6 Hz, 2H), 3.88 (s, 3H), 2.91 (t, J = 5.6 Hz, 2H), 2.45 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 159.5, 148.7, 135.1, 130.8, 130.4, 128.7, 125.0, 119.2, 117.9, 114.3, 112.8, 107.1, 67.5, 55.3, 28.4, 23.1, 20.9; IR(KBr): 3412, 2925, 1506, 1464, 1065, 778, 739 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{20}H_{19}NO_3$ $(M + H)^+$ 322.1443; found 322.1447.

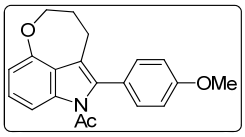


Compound **2h**. (10 mg, 29%). white solid. m.p. 141-142 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.4 Hz, 1H), 7.00 (d, J = 8.4 Hz, 2H), 6.64 (d, J = 8.4 Hz, 1H), 4.35 (t, J = 5.6 Hz, 2H), 3.87 (s, 3H), 2.93 (t, J = 5.6 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 159.8, 149.5,

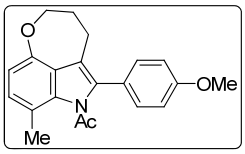
132.0, 131.9, 130.8, 126.9, 123.7, 121.1, 114.2, 111.2, 110.9, 107.8, 67.9, 55.4, 28.8, 22.9; IR(KBr): 3435, 2925, 1510, 1461, 1061, 812, 732 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{16}NO_3Cl$ $(M + H)^+$ 342.0897; found 342.0889.



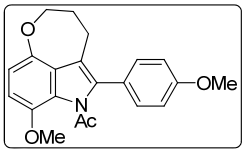
Compound **2i**. (18 mg, 63%). yellow solid. m.p. 88-90 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 8.0 Hz, 1H), 7.19 (t, J = 8.0 Hz, 1H), 6.77 (d, J = 7.6 Hz, 1H), 4.35-4.33 (m, 2H), 3.08 (t, J = 6.0 Hz, 2H), 2.78 (s, 3H), 2.19-2.14 (m, 2H), 0.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 153.3, 139.5, 135.3, 132.2, 125.5, 121.5, 111.3, 106.3, 72.8, 29.4, 29.1, 26.7, 2.91; IR(KBr): 3359, 2925, 1522, 1483, 1082, 771, 732 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{16}H_{21}NO_2Si$ $(M + H)^+$ 288.1420; found 288.1418.



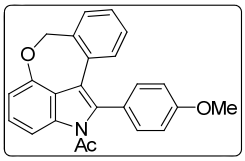
Compound **2j.** (23 mg, 72%). white solid. m.p. 151-153 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.4 Hz, 1H), 7.29 (d, J = 8.8 Hz, 2H), 7.23 (t, J = 7.6 Hz, 1H), 7.01 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.0 Hz, 1H), 4.35-4.33 (m, 2H), 3.87 (s, 3H), 2.71 (t, J = 6.0 Hz, 2H), 2.14-2.09 (m, 2H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 159.8, 152.4, 138.8, 132.6, 131.4, 125.9, 125.9, 120.1, 118.2, 114.3, 111.7, 108.9, 72.6, 55.3, 29.5, 27.8, 27.3; IR(KBr): 3434, 2922, 1510, 1484, 1098, 788, 742 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{20}H_{19}NO_3$ $(M + H)^+$ 322.1438; found 322.1441.



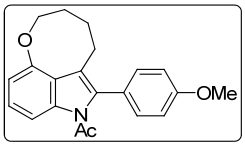
Compound **2k.** (33 mg, 98%). yellow solid. m.p. 184-185 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.8 Hz, 2H), 7.02-6.99 (m, 3H), 6.75 (d, J = 8.0 Hz, 1H), 4.33-4.31 (m, 2H), 3.88 (s, 3H), 2.71 (t, J = 6.0 Hz, 2H), 2.27 (s, 3H), 2.13-2.09 (m, 2H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 159.8, 151.0, 137.2, 132.9, 131.5, 127.8, 125.1, 119.3, 117.8, 116.9, 114.2, 110.9, 72.6, 55.3, 29.7, 28.2, 26.9, 20.8; IR(KBr): 3399, 2921, 1511, 1466, 1088, 788, 736 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{21}H_{21}NO_3$ $(M + H)^+$ 336.1600; found 336.1592.



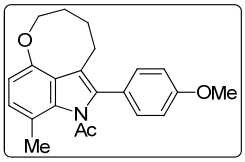
Compound **2l**. (35 mg, 99%). white solid. m.p. 119-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 6.70 (br s, 2H), 4.32-4.29 (m, 2H), 3.89 (s, 3H), 3.86 (s, 3H), 2.74 (t, J = 6.4 Hz, 2H), 2.33 (s, 3H), 2.14-2.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 159.5, 147.1, 141.4, 134.2, 131.7, 126.6, 124.2, 120.4, 116.3, 113.6, 109.2, 106.4, 72.6, 56.3, 55.2, 30.0, 28.5, 26.9; IR(KBr): 3434, 2915, 1509, 1463, 1092, 792, 740 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{21}H_{21}NO_4$ $(M + H)^+$ 352.1549; found 352.1547.



Compound **2m**. (14 mg, 38%). white solid. m.p. 219-220 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 1H), 7.41 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 7.2 Hz, 1H), 7.23 (t, J = 8.0 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 7.03 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 7.6 Hz, 1H), 6.88-6.83 (m, 2H), 5.22 (br s, 2H), 3.91 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 160.5, 155.4, 138.5, 136.8, 134.5, 133.3, 132.1, 129.9, 128.4, 128.2, 126.6, 125.8, 125.4, 119.1, 117.6, 115.0, 111.3, 109.4, 75.6, 55.4, 28.0; IR(KBr): 3445, 2933, 1509, 1458, 1076, 792, 754 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{19}NO_3$ $(M + H)^+$ 370.1443; found 370.1436.

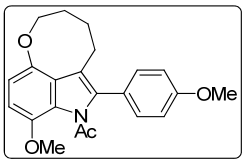


Compound **2n**. (6 mg, 18%). white solid. m.p. 110-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.4 Hz, 1H), 7.30-7.28 (m, 3H), 7.02 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.0 Hz, 1H), 4.24 (t, J = 4.8 Hz, 2H), 3.90 (s, 3H), 2.84 (t, J = 6.4 Hz, 2H), 1.98 (s, 3H), 1.83-1.78 (m, 2H), 1.73-1.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 159.8, 151.0, 137.6, 133.8, 131.6, 126.0, 125.3, 121.1, 116.4, 114.1, 112.6, 75.5, 55.3, 29.7, 27.63, 27.60, 23.2 (One signal is missing due to overlap); IR(KBr): 3433, 2925, 1511, 1484, 1086, 798, 735 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{21}H_{21}NO_3$ $(M + H)^+$ 336.1594; found 336.1598.



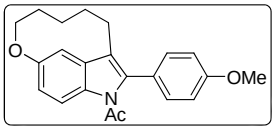
Compound **2o.** (22mg, 62%). yellow solid. m.p. 125-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.4

Hz, 2H), 7.03-6.99 (m, 3H), 6.84 (d, *J* = 8.0 Hz, 1H), 4.22-4.20 (m, 2H), 3.88 (s, 3H), 2.84 (t, *J* = 6.0 Hz, 2H), 2.34 (s, 3H), 2.02 (s, 3H), 1.78-1.76 (m, 2H), 1.69-1.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 159.9, 149.4, 136.1, 134.0, 131.7, 127.9, 127.1, 124.7, 120.9, 119.1, 115.7, 114.0, 75.6, 55.3, 28.2, 27.8, 25.5, 23.0, 21.1; IR(KBr): 3437, 2928, 1503, 1460, 1084, 808, 726 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{22}H_{23}NO_3$ $(M + H)^+$ 350.1756; found 350.1758.

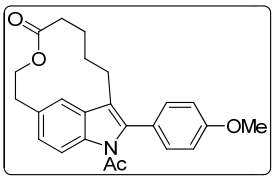


Compound **2p**. (23 mg, 64%). white solid. m.p. 132-133 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 4.19 (t, *J* = 4.8 Hz, 2H), 3.92 (s, 3H), 3.86 (s, 3H), 2.85 (t, *J* = 6.4 Hz, 2H), 2.34 (s, 3H), 1.82-1.76 (m, 2H), 1.71-1.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 159.5, 145.4, 143.9, 135.4, 131.7, 128.2, 125.5, 124.0, 117.5, 114.6, 113.6, 105.9, 75.8, 56.0, 55.2, 28.5, 27.9, 25.7, 22.9; IR(KBr): 3438, 2923, 1508, 1449, 1084, 810, 720 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{22}H_{23}NO_4$ $(M + H)^+$ 366.1705; found 366.1706.

Analytical data of compound 4

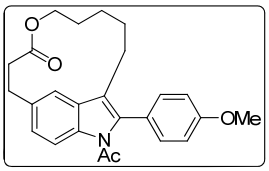


Compound **4a.** (13 mg, 36%). yellow solid. m.p. 260-261 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.8 Hz, 1H), 7.28 (d, *J* = 8.8 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.95-6.92 (m, 2H), 4.05 (t, *J* = 7.2 Hz, 2H), 3.89 (s, 3H), 2.51 (t, *J* = 8.0 Hz, 2H), 1.92 (s, 3H), 1.92-1.89 (m, 2H), 1.72-1.65 (m, 2H), 1.58-1.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 159.9, 155.6, 135.2, 131.6, 131.5, 130.3, 125.6, 122.3, 117.7, 114.5, 114.2, 101.3, 67.4, 55.3, 28.9, 28.0, 27.4, 25.6, 24.6; IR(KBr): 3434, 2939, 1509, 1465, 1089, 826, 731 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{44}H_{46}N_2O_6$ $(2M + H)^+$ 699.3434; found 699.3420.

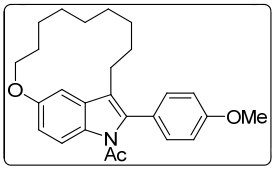


Compound **4b**. (20 mg, 50%). white solid. m.p. 163-164 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.0 Hz, 1H), 7.54 (s, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 4.36-4.33 (m, 2H), 3.87 (s, 3H), 3.02-3.00 (m, 2H), 2.70-2.66 (m, 2H), 2.39 (t, *J* = 6.0 Hz, 2H), 1.95 (s, 3H),

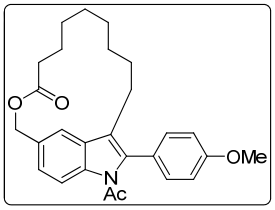
1.60-1.54 (m, 2H), 1.40-1.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 170.8, 159.8, 136.0, 135.4, 132.5, 131.4, 129.9, 125.6, 125.1, 121.4, 120.7, 117.0, 114.2, 64.6, 55.3, 34.8, 33.3, 27.3, 27.1, 22.0, 21.5; IR(KBr): 3436, 2934, 1509, 1444, 1076, 818, 734 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{25}NO_4$ $(M + H)^+$ 392.1862; found 392.1855.



Compound **4c**. (21 mg, 51%). white amorphous. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 1.2 Hz, 1H), 7.29 (d, *J* = 8.8 Hz, 2H), 7.13 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 4.24 (t, *J* = 4.8 Hz, 2H), 3.88 (s, 3H), 3.14-3.11 (m, 2H), 2.55-2.52 (m, 2H), 1.93 (s, 3H), 1.89-1.83 (m, 2H), 1.50-1.44 (m, 2H), 1.34-1.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 170.9, 159.8, 135.8, 135.3, 135.1, 131.5, 131.2, 125.6, 122.7, 118.3, 116.4, 114.2, 64.9, 55.3, 37.4, 32.1, 29.9, 27.9, 27.4, 23.4, 20.3 (One signal is missing due to overlap); IR(KBr): 3736, 2919, 1508, 1461, 1078, 811, 738 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{25}H_{27}NO_4$ $(M + H)^+$ 406.2013; found 406.2018.

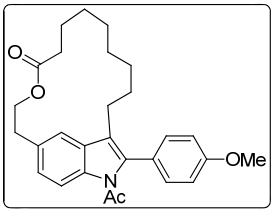


Compound **4d**. (22 mg, 54%). white solid. m.p. 154-155 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.8 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.94-6.91 (m, 2H), 4.22 (t, *J* = 8.0 Hz, 2H), 3.88 (s, 3H), 2.45 (t, *J* = 8.0 Hz, 2H), 1.94 (s, 3H), 1.84-1.82 (m, 2H), 1.55-1.52 (m, 8H), 1.42-1.41 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 159.8, 154.2, 134.9, 131.4, 131.2, 130.3, 125.7, 123.0, 118.2, 115.8, 114.1, 100.9, 67.0, 55.3, 27.3, 27.0, 26.9, 26.0, 25.7, 24.6, 23.3, 22.8, 21.9; IR(KBr): 3435, 2933, 1509, 1468, 1072, 810, 734 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{26}H_{31}NO_3$ $(M + H)^+$ 406.2382; found 406.2379.



Compound **3e**. (19 mg, 44%). yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.8 Hz, 1H), 7.55 (d, *J* = 0.8 Hz, 1H), 7.29-7.27 (m, 3H), 7.00 (d, *J* = 8.8 Hz, 2H), 5.32 (s, 2H), 3.88 (s, 3H), 2.51 (t, *J* = 7.2 Hz,

2H), 2.45-2.42 (m, 2H), 1.94 (s, 3H), 1.70-1.65 (m, 2H), 1.61-1.54 (m, 2H), 1.40-1.38 (m, 2H), 1.32-1.31 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 171.1, 159.9, 136.6, 135.3, 132.0, 131.5, 130.3, 125.4, 125.0, 122.6, 118.2, 116.1, 114.2, 65.9, 55.3, 33.8, 27.7, 27.5, 27.24, 27.17, 27.1, 27.0, 25.3, 23.6; IR(KBr): 3714, 2925, 1508, 1448, 1028, 821, 736 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{27}H_{31}NO_4$ $(M + K)^+$ 472.1885; found 472.1890.



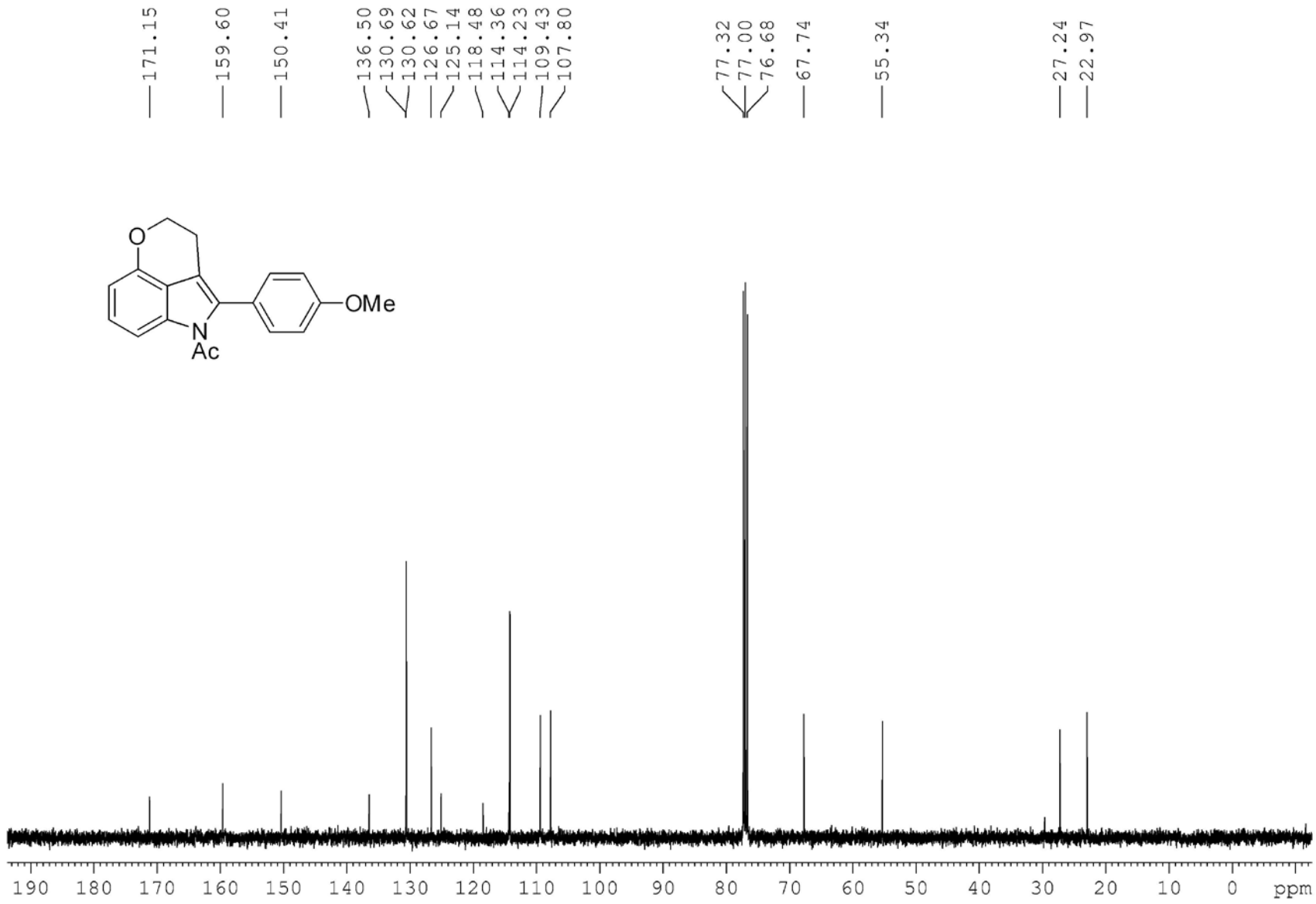
Compound **4f.** (22mg, 50%). white solid. m.p. 94-95 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.4 Hz, 1H), 7.34 (s, 1H), 7.28 (d, *J* = 8.8 Hz, 2H), 7.22 (dd, J = 8.4, 1.6 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 4.48 (t, *J* = 5.2 Hz, 2H), 3.88 (s, 3H), 3.10 (t, *J* = 5.2 Hz, 2H), 2.50 (t, *J* = 7.2 Hz, 2H), 2.29 (t, *J* = 6.4 Hz, 2H), 1.94 (s, 3H), 1.65-1.62 (m, 2H), 1.56-1.48 (m, 2H), 1.37-1.27 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 171.0, 159.8, 135.4, 134.9, 133.7, 131.5, 129.9, 125.7, 125.5, 122.6, 118.6, 116.7, 114.1, 64.9, 55.3, 34.9, 33.4, 28.7, 27.7, 27.5, 27.5, 27.3, 26.8, 24.7, 23.7; IR(KBr): 3436, 2928, 1509, 1469, 1031, 835, 736 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{28}H_{33}NO_4$ $(M + H)^+$ 448.2488; found 448.2485.

Reference:

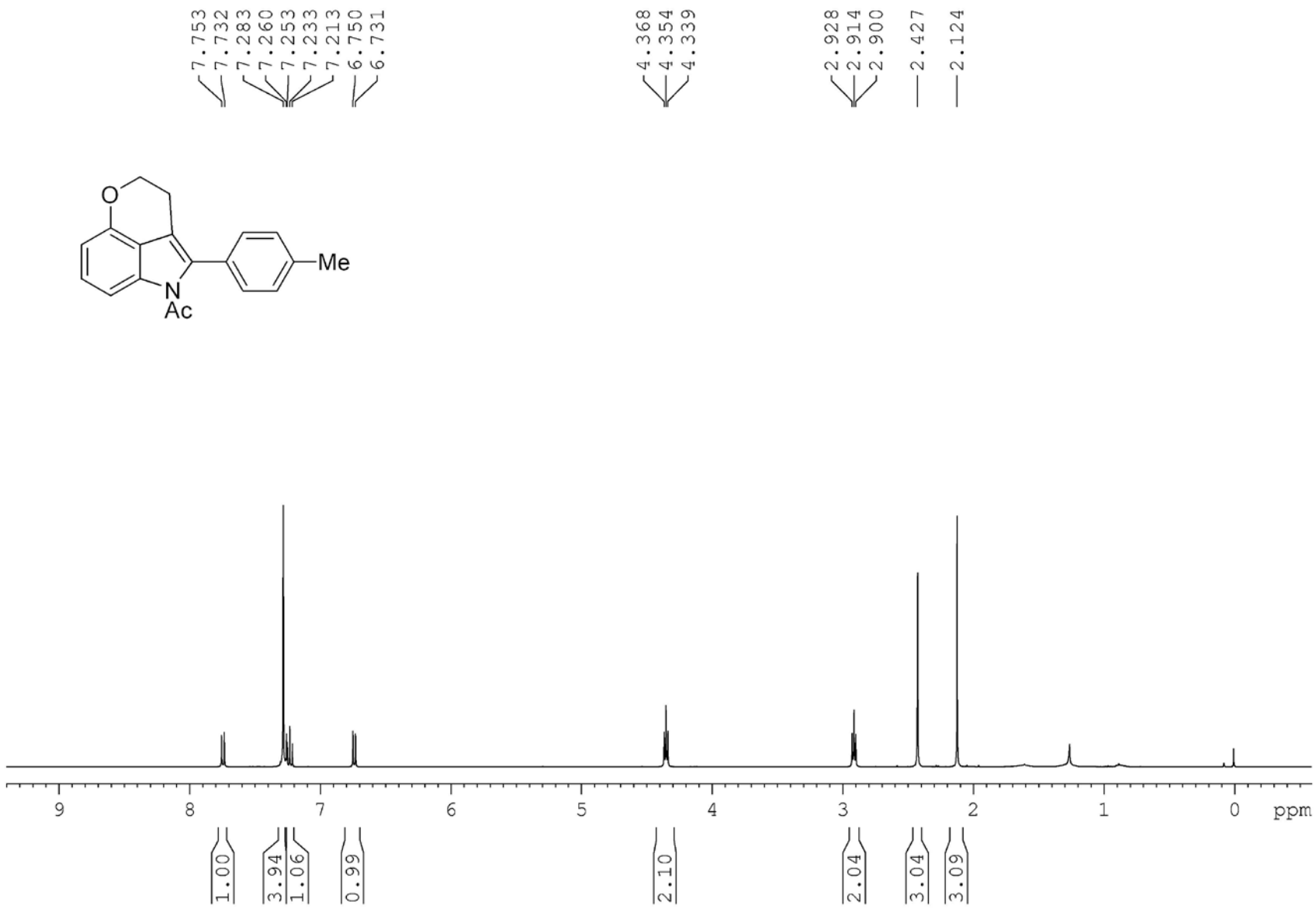
1. D. Shan, Y. Gao, Y. Jia, *Angew. Chem. Int. Ed.*, 2013, **52**, 4902.
2. S. P. Breazzano, Y. B. Poudel, D. L. Boger, *J. Am. Chem. Soc*., 2013, **135**, 1600.

^{1}H NMR of compound 2a ($CDCl_3$; 400MHz)

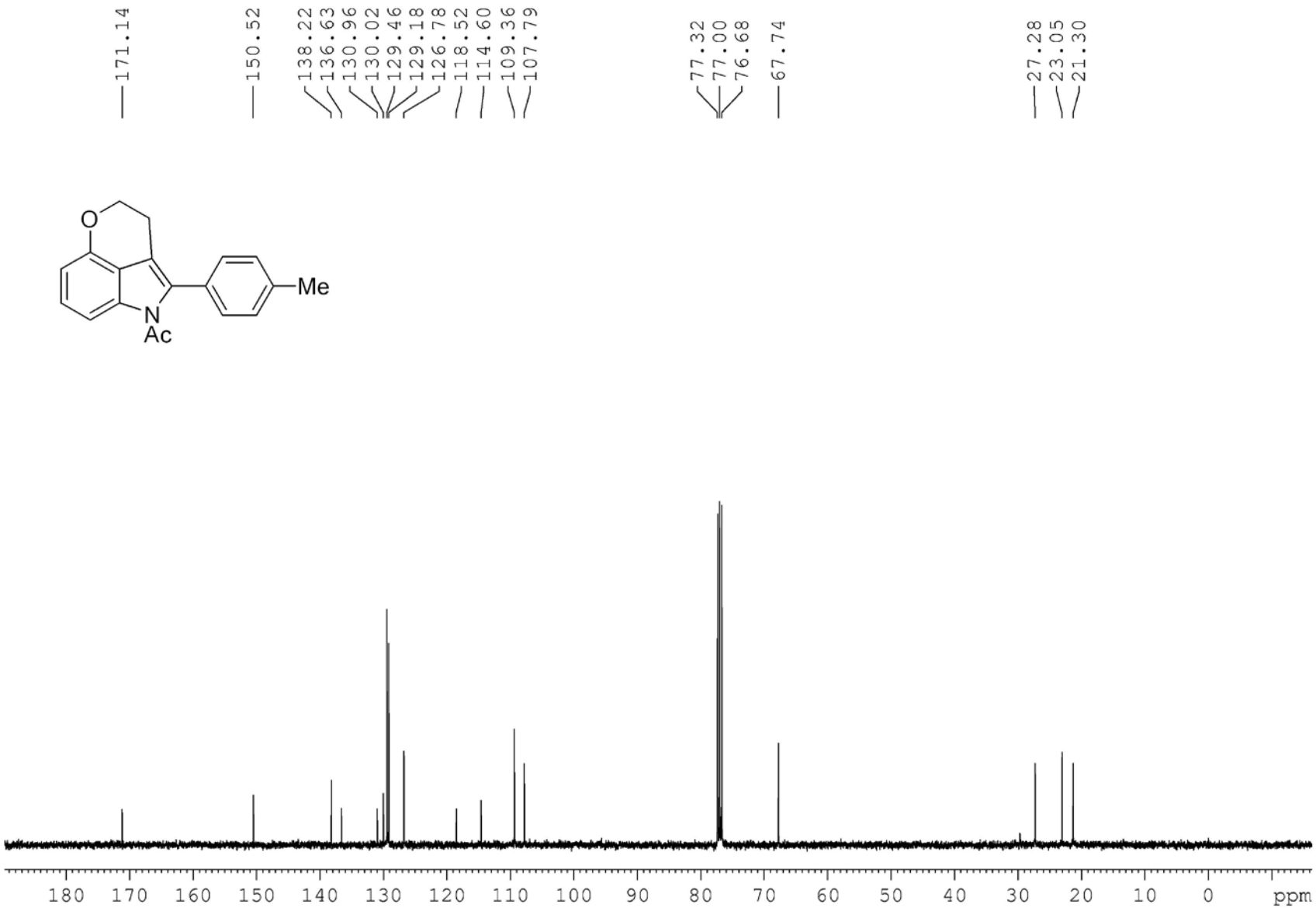
^{13}C NMR of compound 2a ($CDCl_3$; 100MHz)



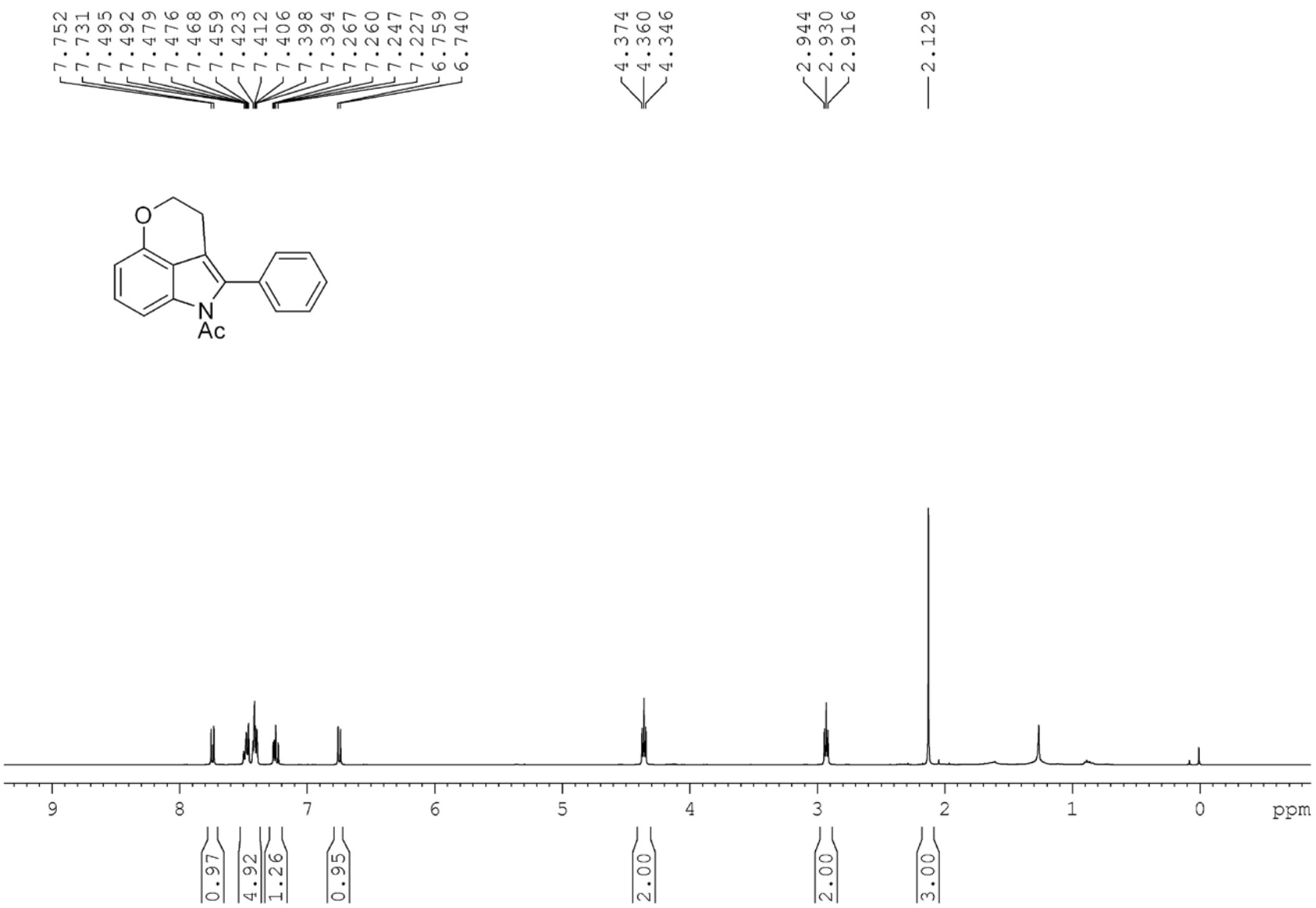
^{1}H NMR of compound 2b ($CDCl_3$; 400MHz)



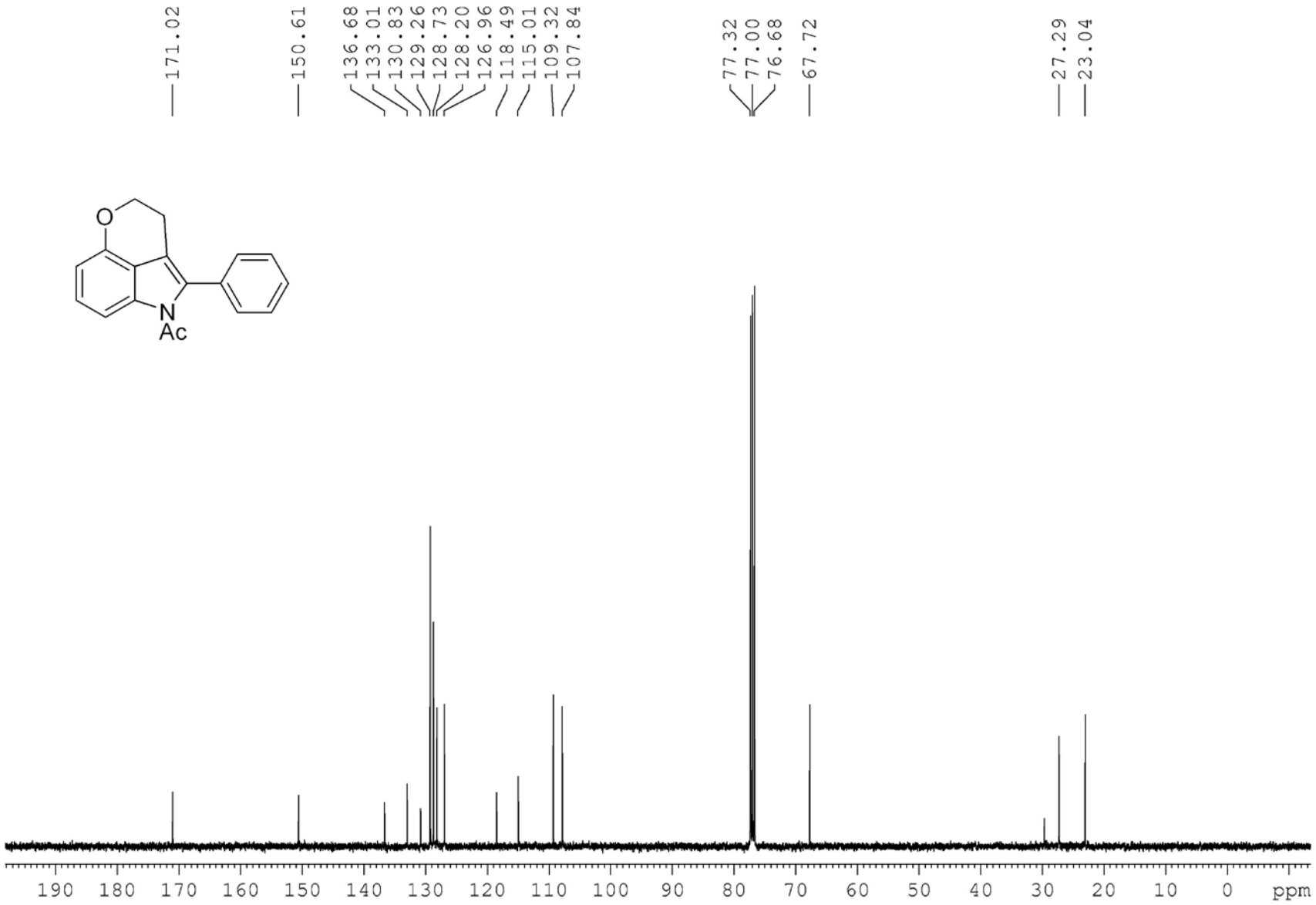
^{13}C NMR of compound 2b ($CDCl_3$; 100MHz)



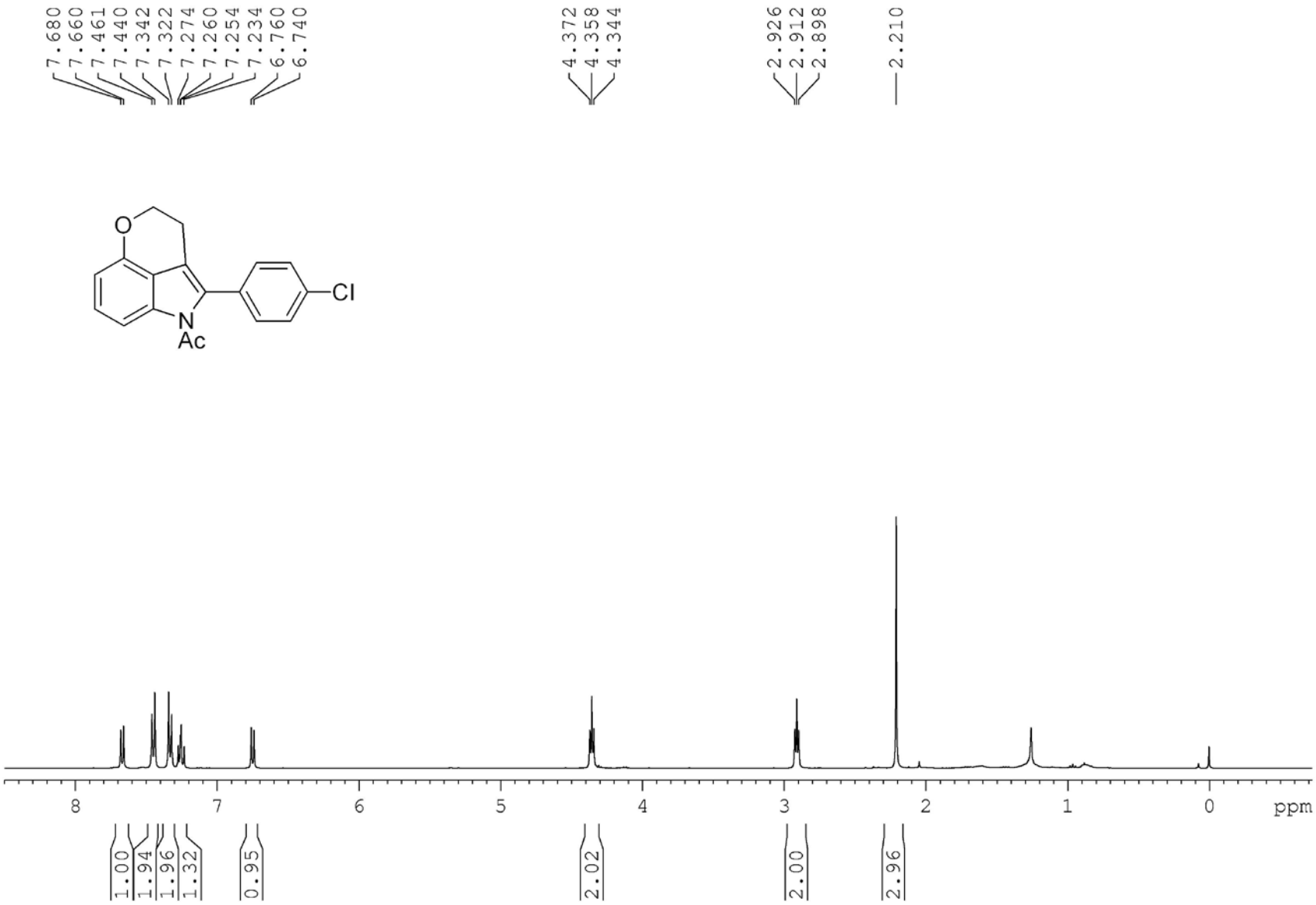
^{1}H NMR of compound 2c ($CDCl_3$; 400MHz)



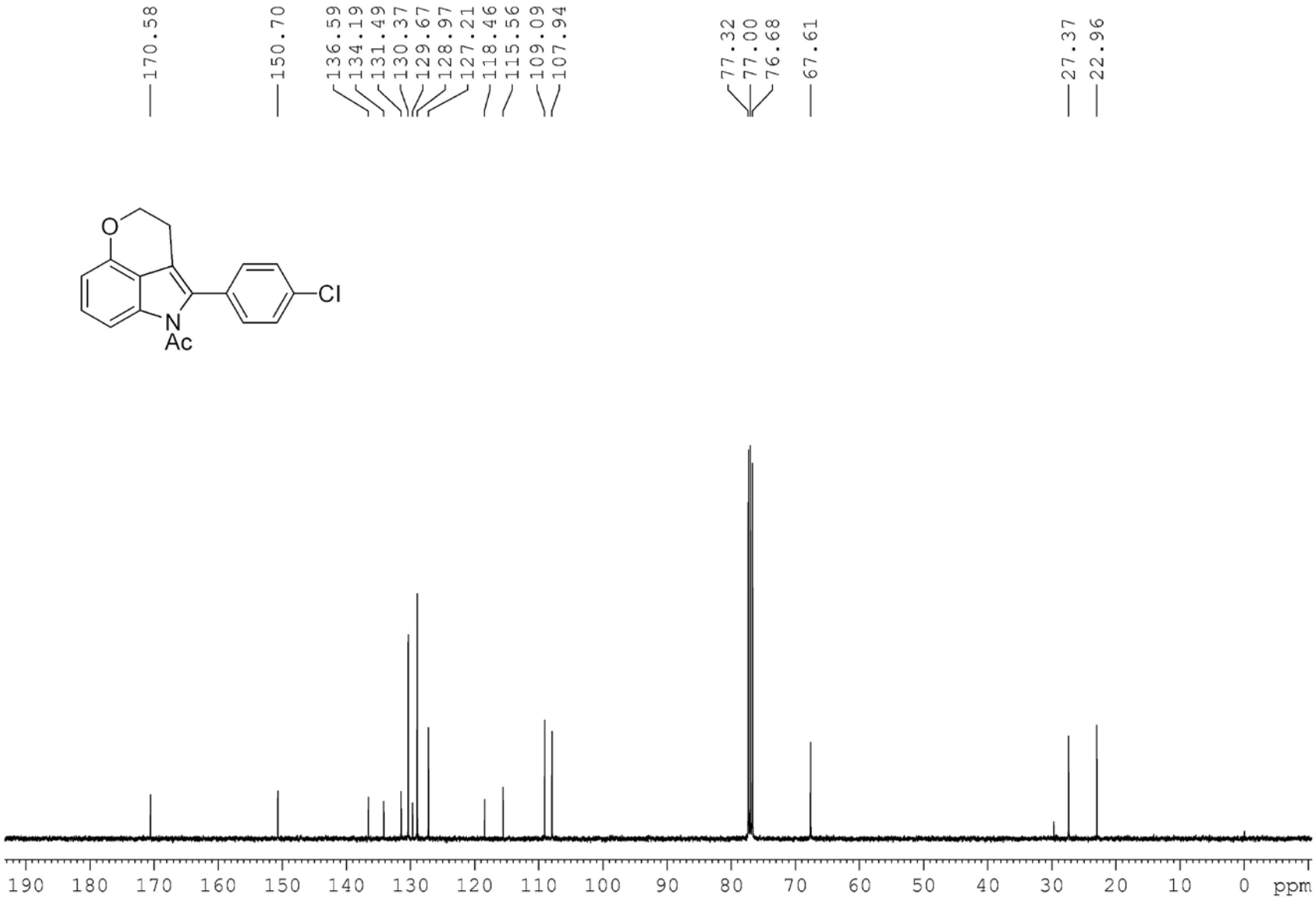
^{13}C NMR of compound 2c ($CDCl_3$; 100MHz)



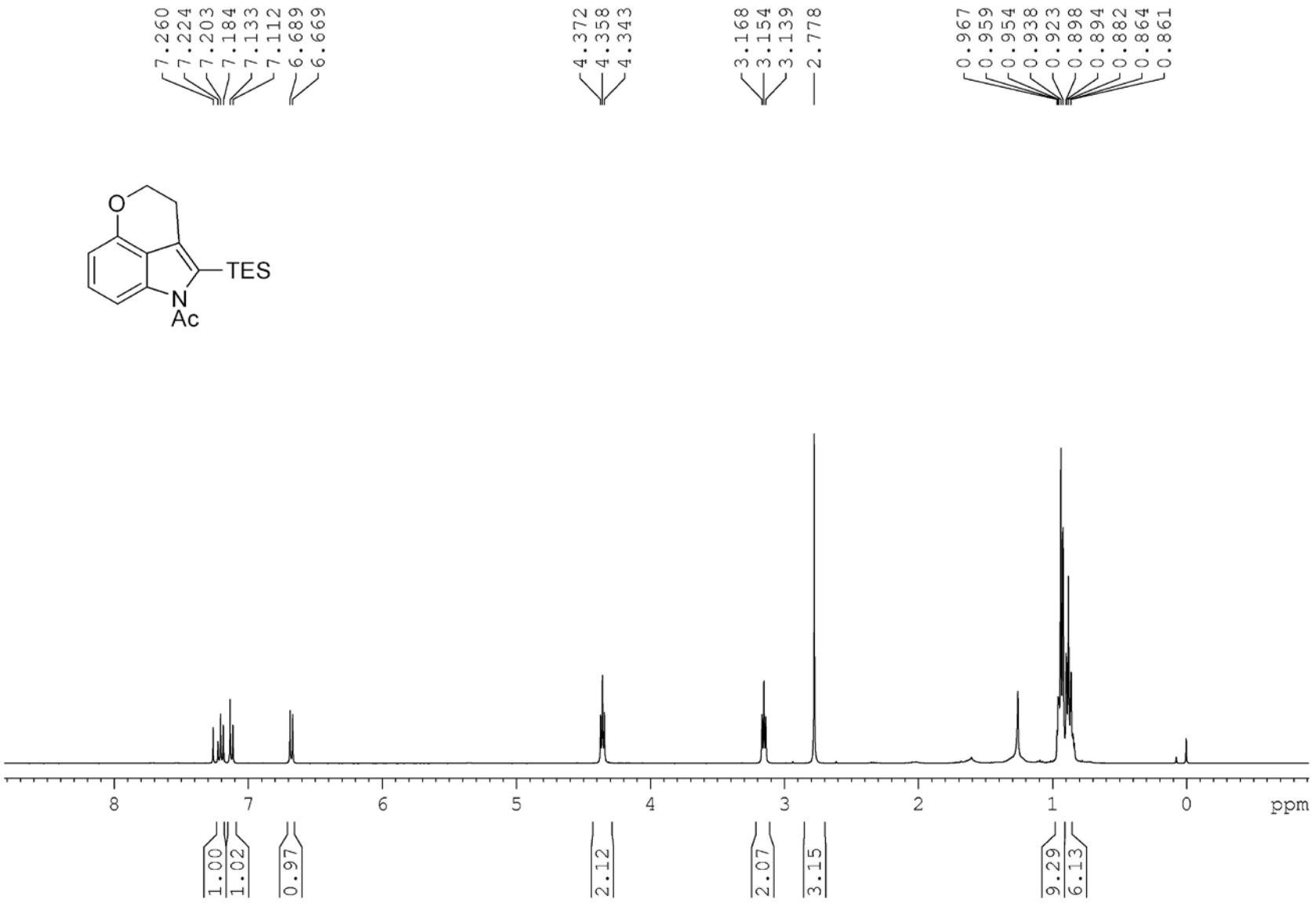
^{1}H NMR of compound 2d ($CDCl_3$; 400MHz)



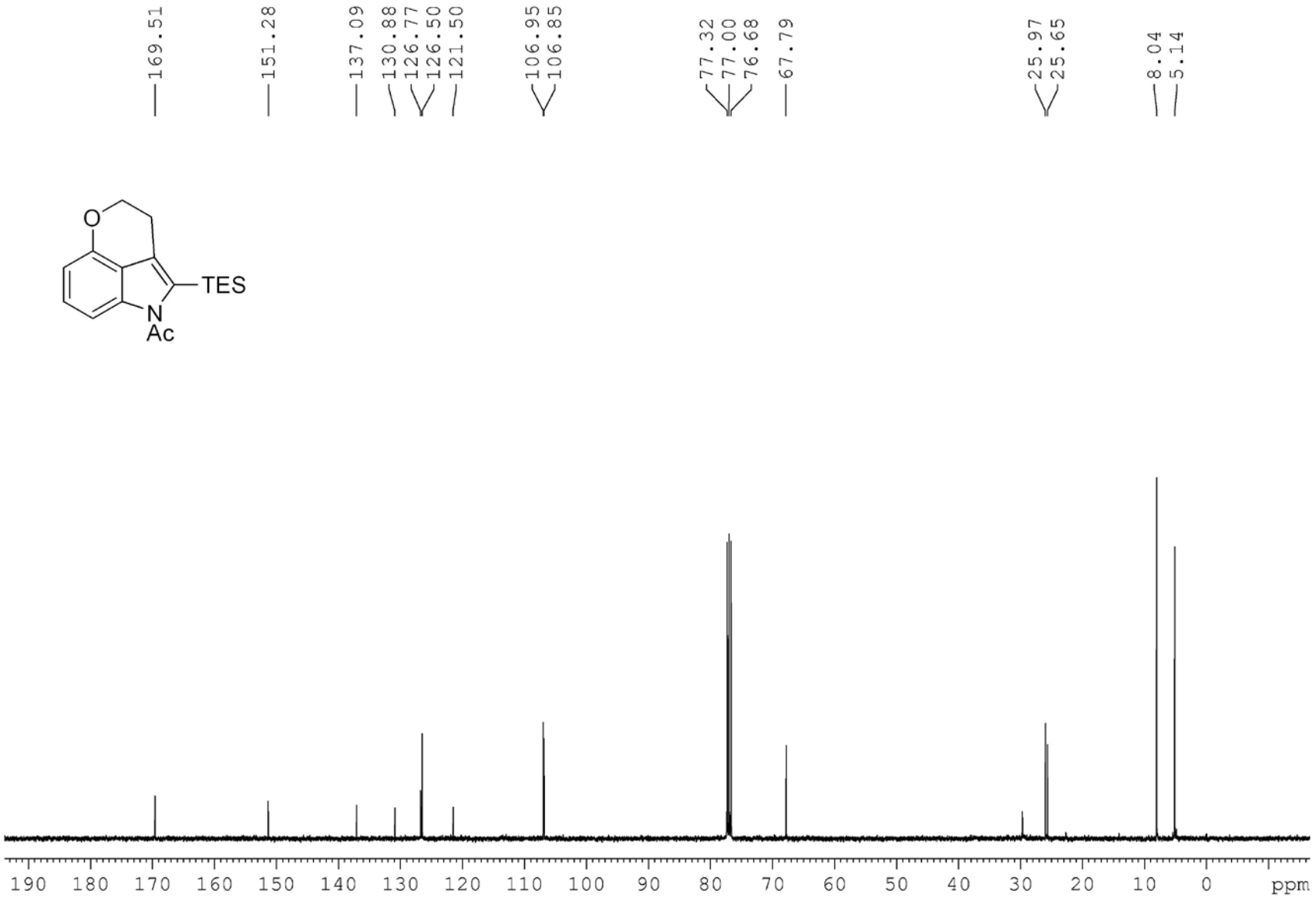
^{13}C NMR of compound 2d ($CDCl_3$; 100MHz)



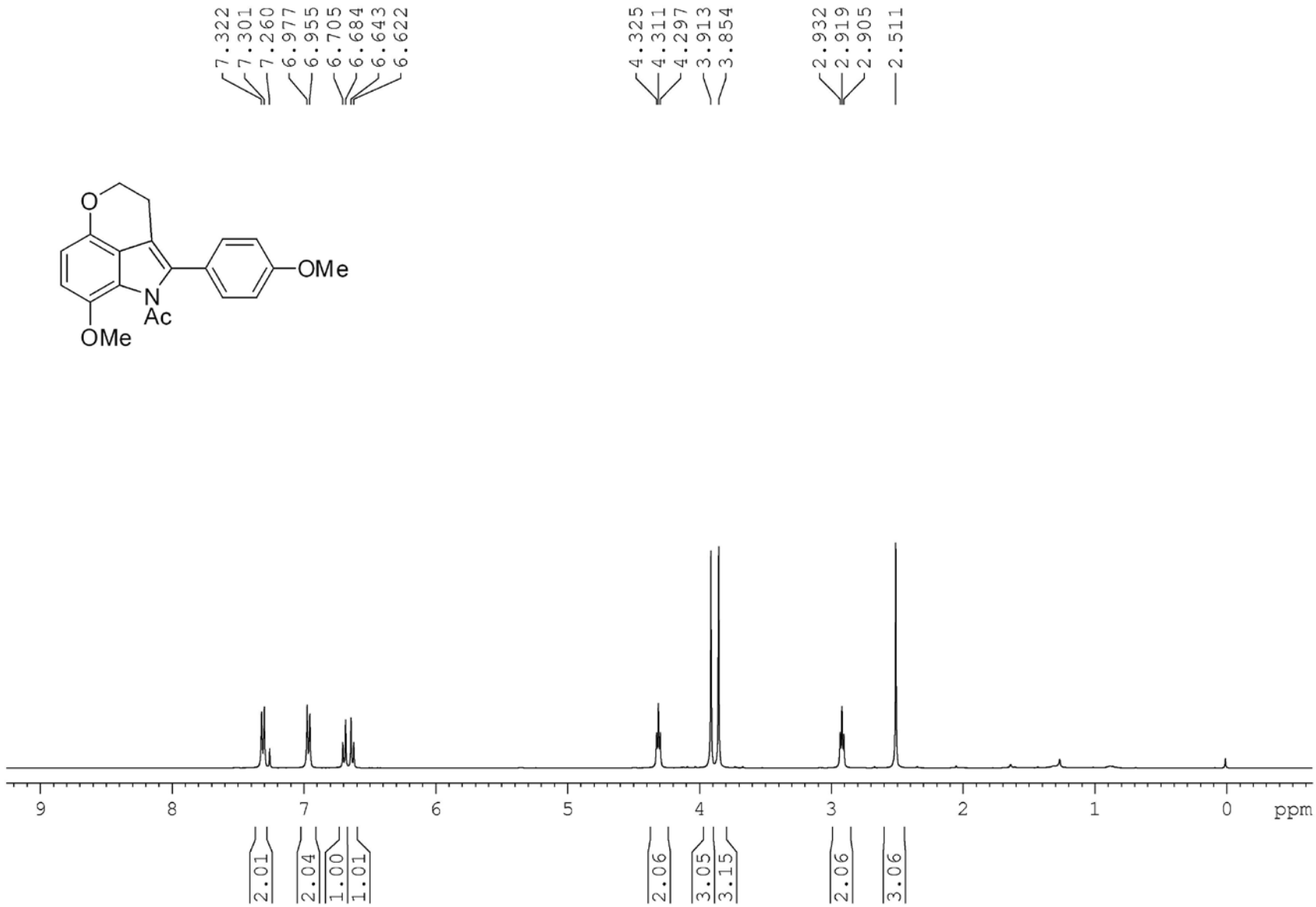
^{1}H NMR of compound 2e ($CDCl_3$; 400MHz)



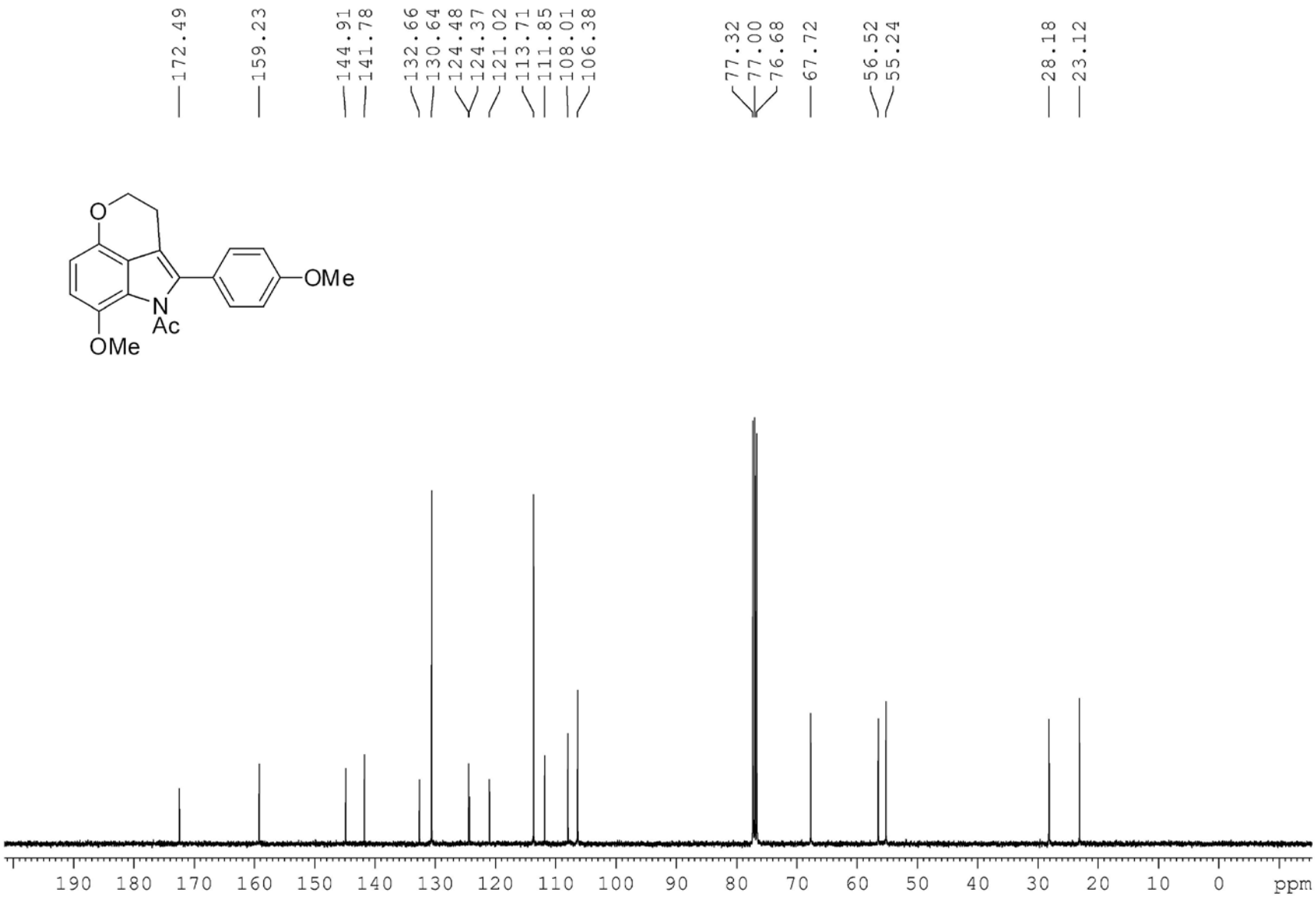
^{13}C NMR of compound 2e ($CDCl_2$; 100MHz)



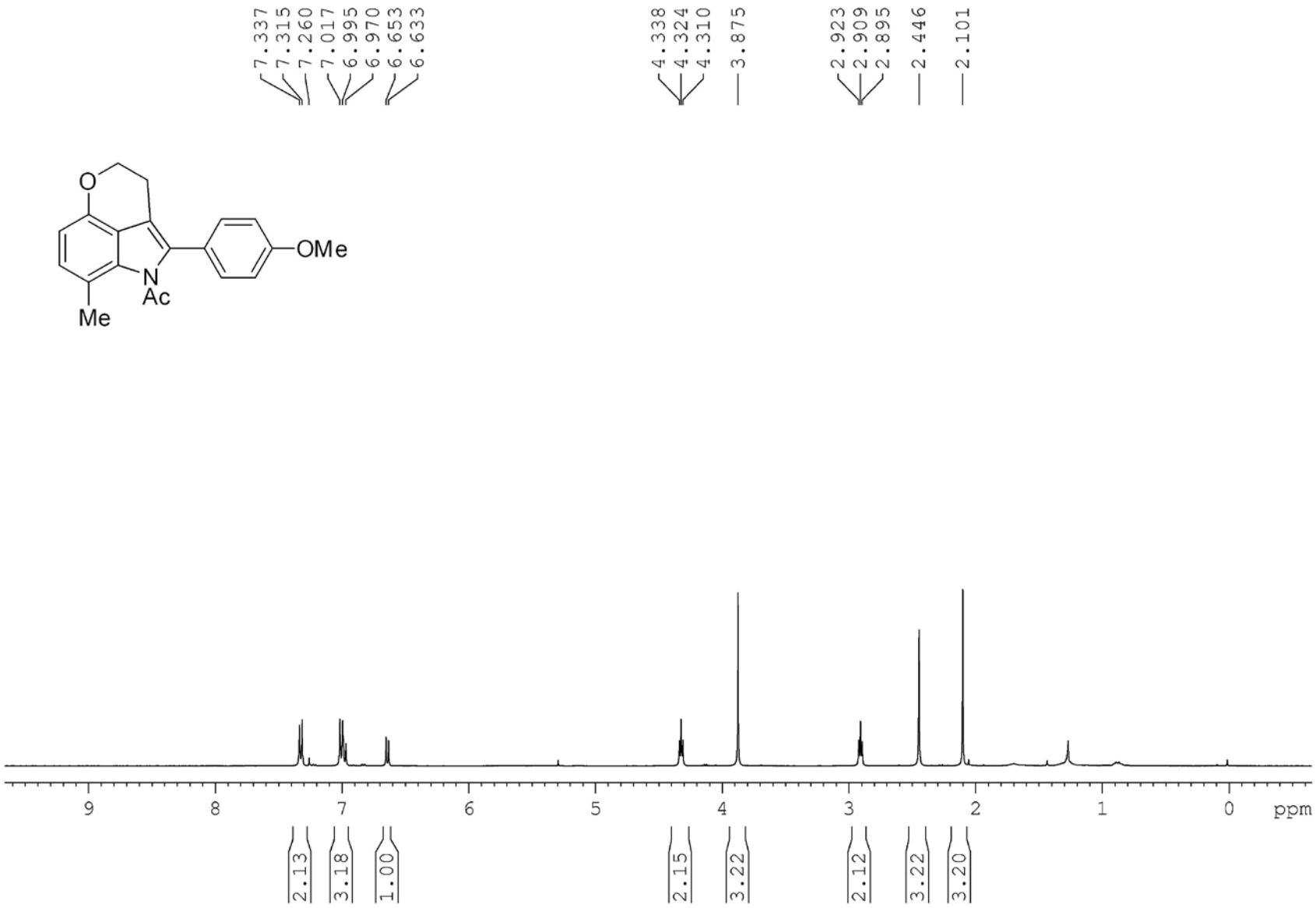
^{1}H NMR of compound 2f ($CDCl_3$; 400MHz)



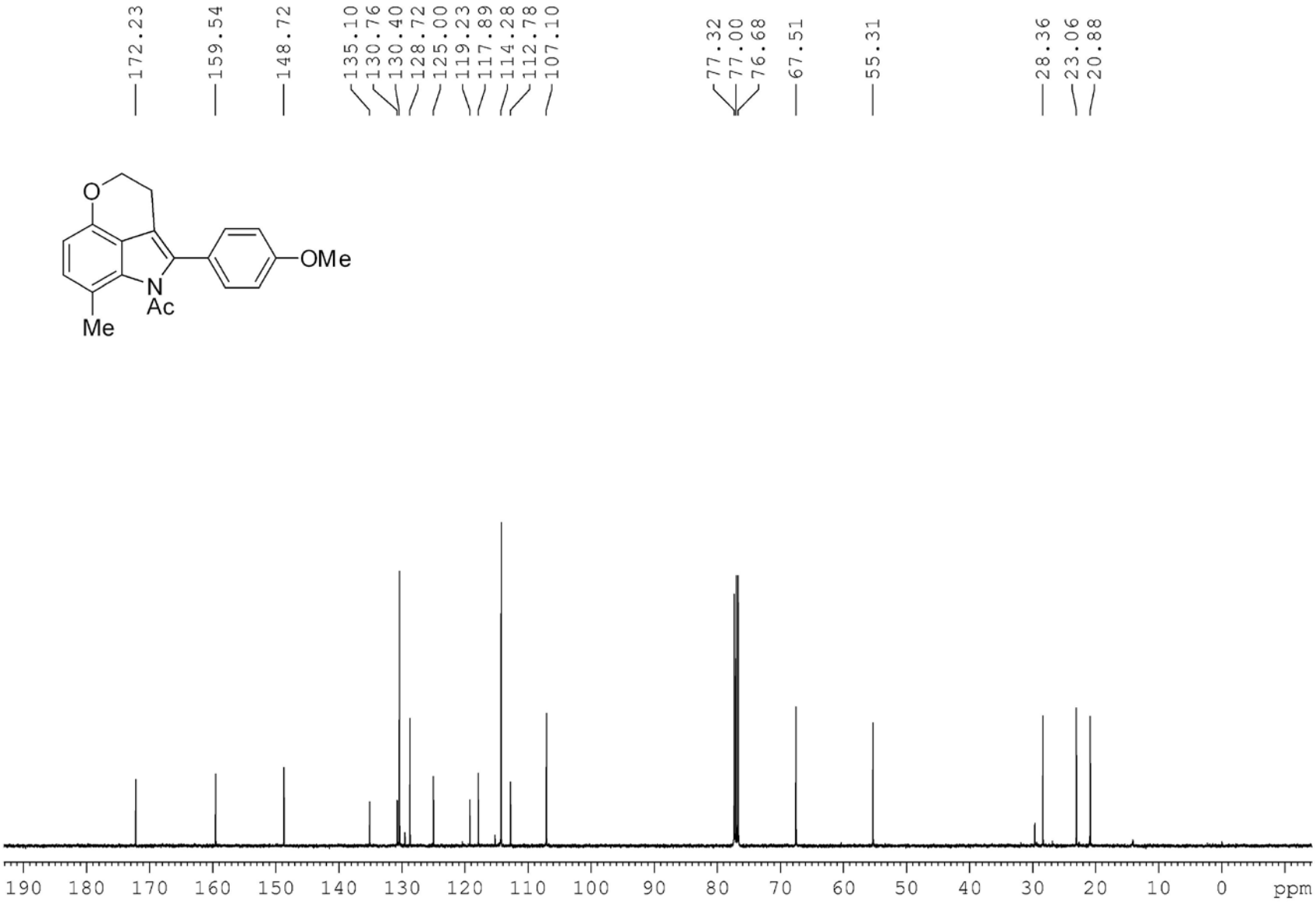
^{13}C NMR of compound 2f ($CDCl_3$; 100MHz)



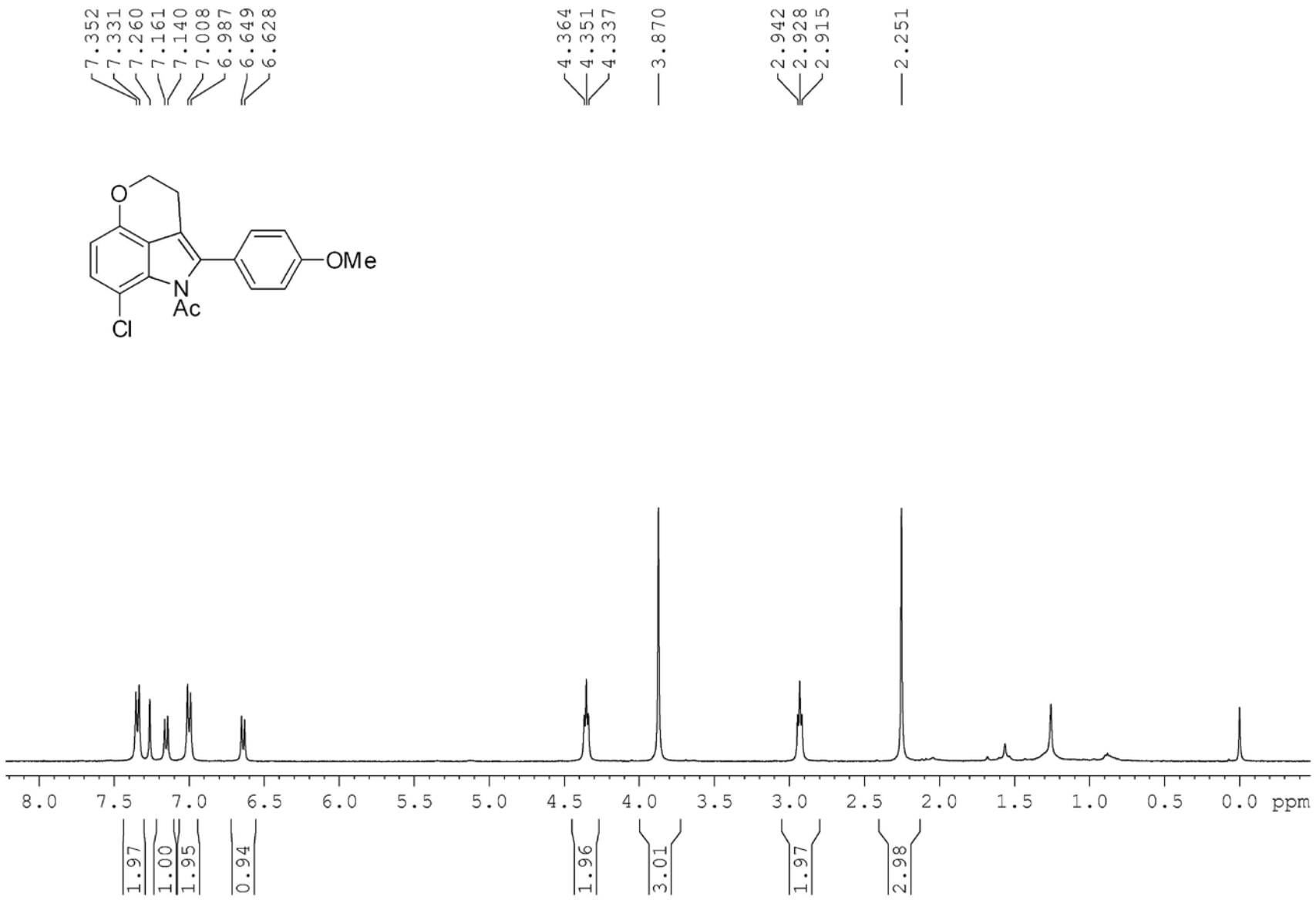
^{1}H NMR of compound 2g ($CDCl_3$; 400MHz)



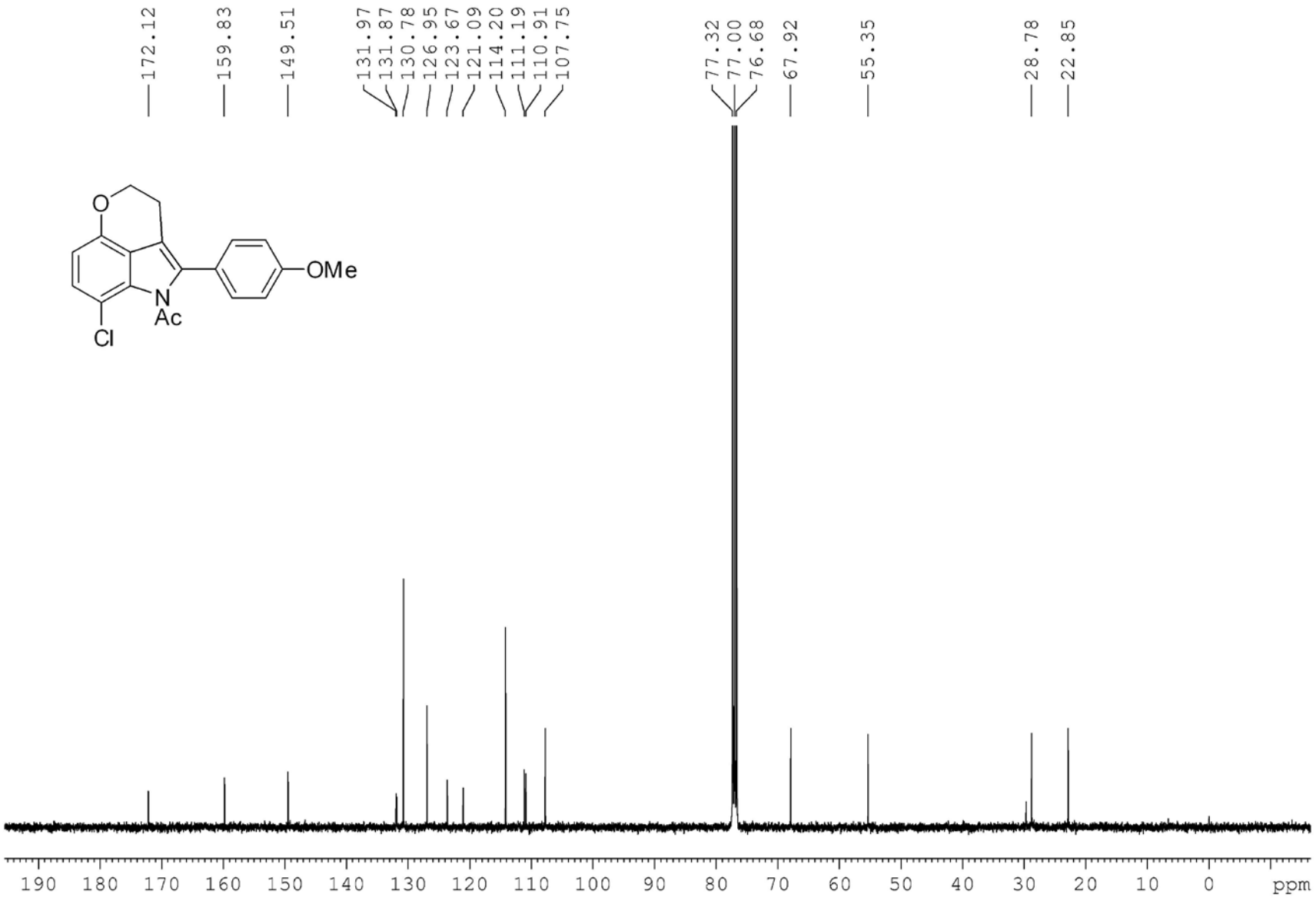
^{13}C NMR of compound 2g ($CDCl_3$; 100MHz)



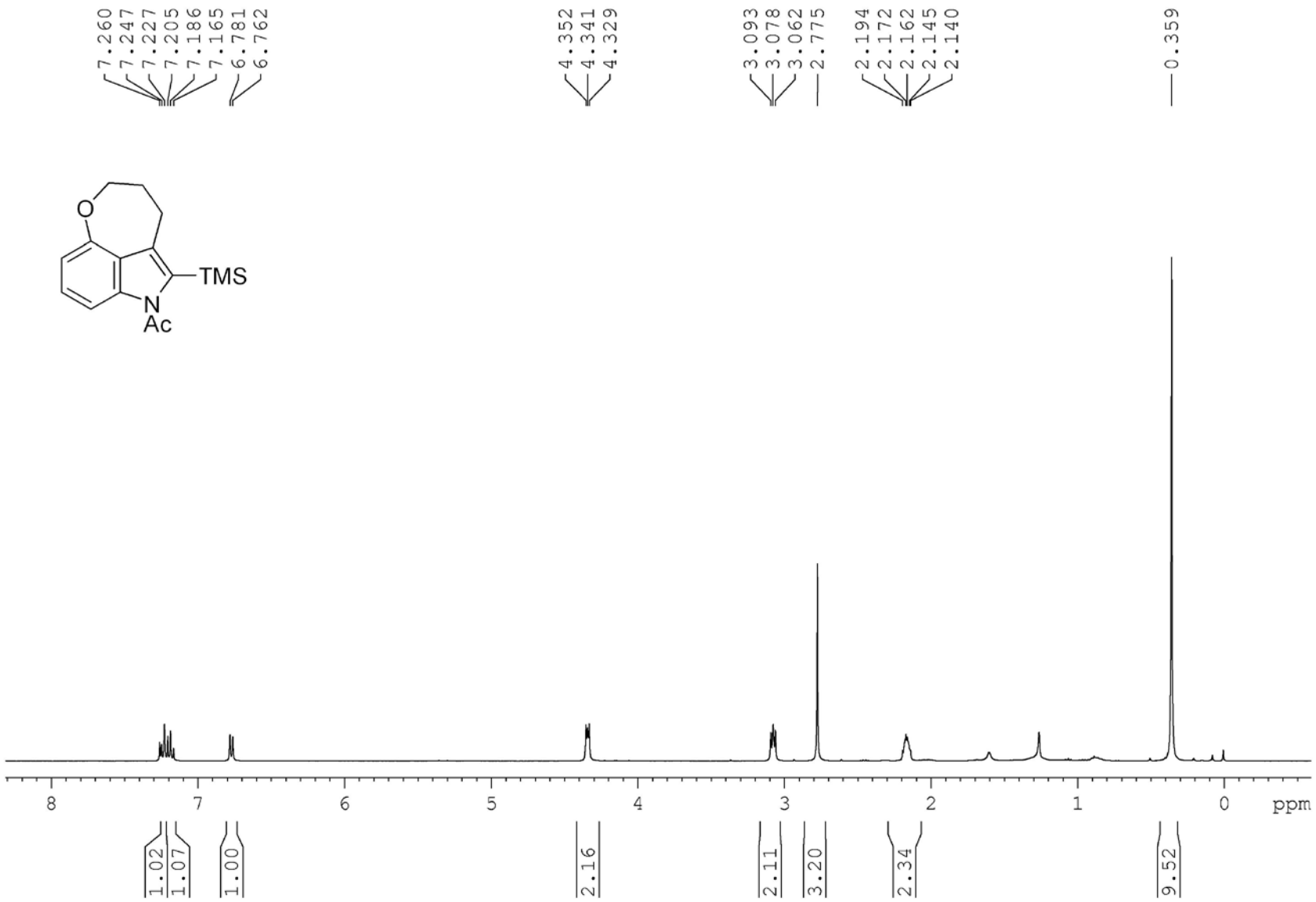
^{1}H NMR of compound 2h ($CDCl_3$; 400MHz)



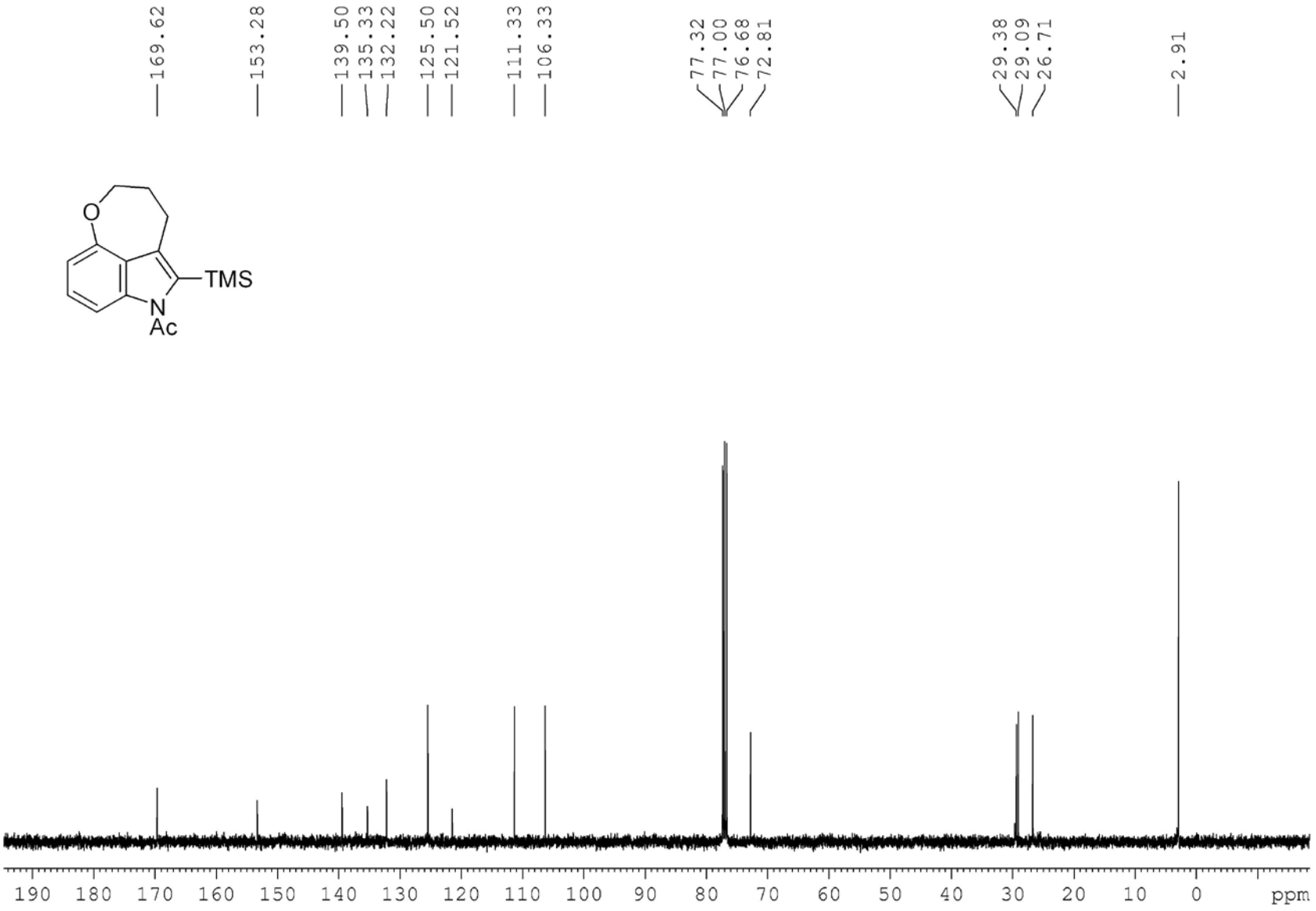
^{13}C NMR of compound 2h ($CDCl_3$; 100MHz)



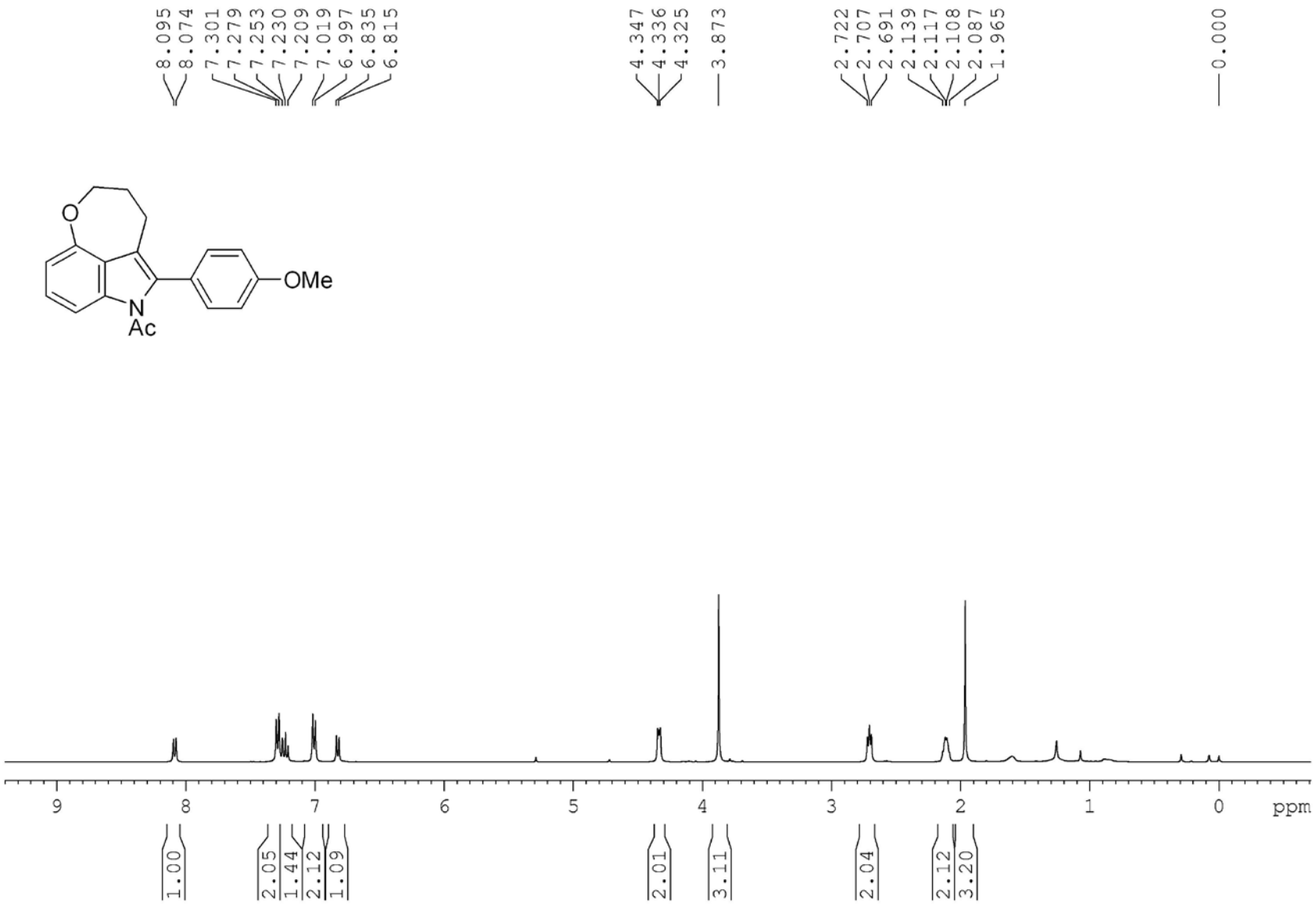
^{1}H NMR of compound 2i ($CDCl_3$; 400MHz)



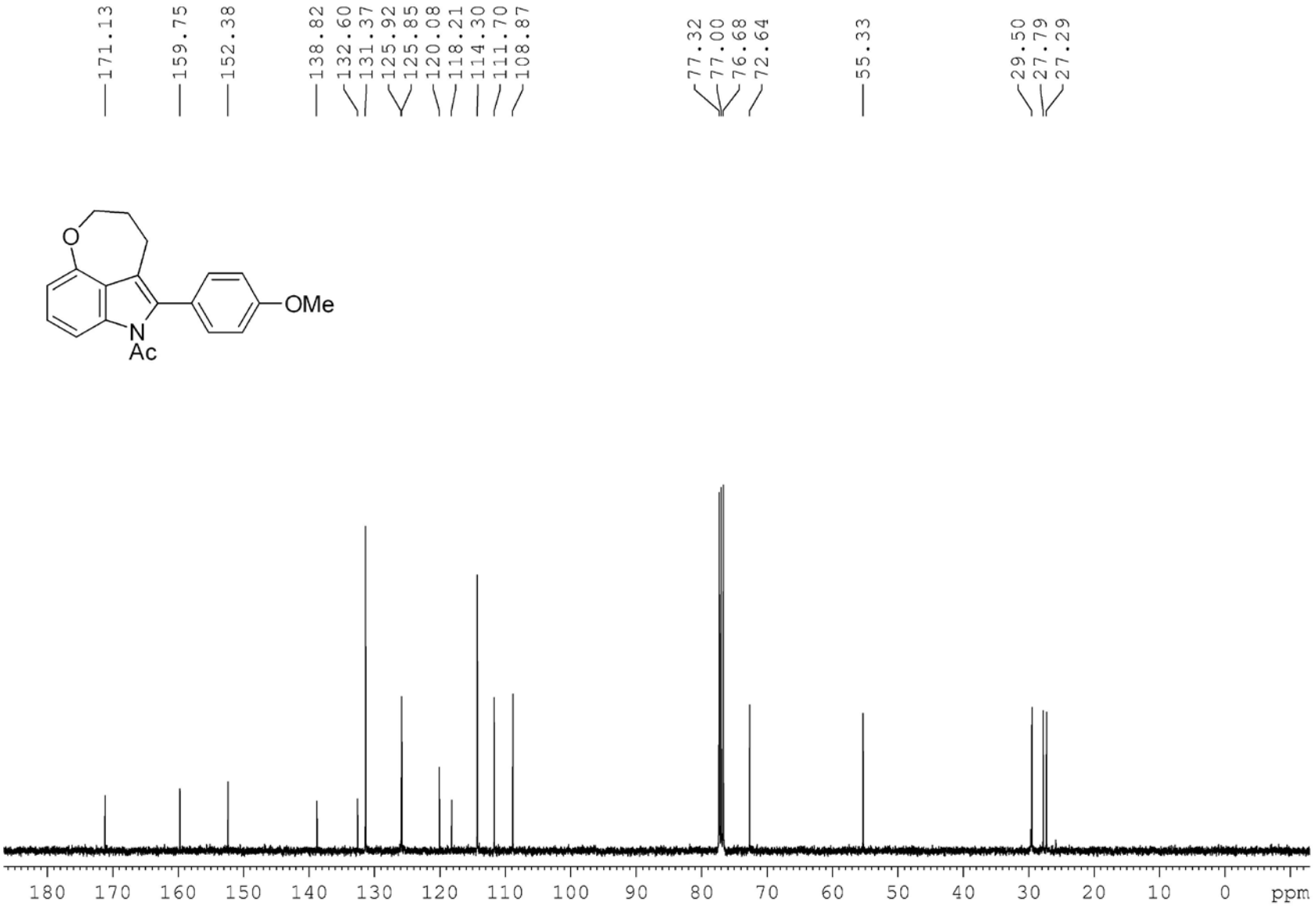
^{13}C NMR of compound 2i ($CDCl_3$; 100MHz)



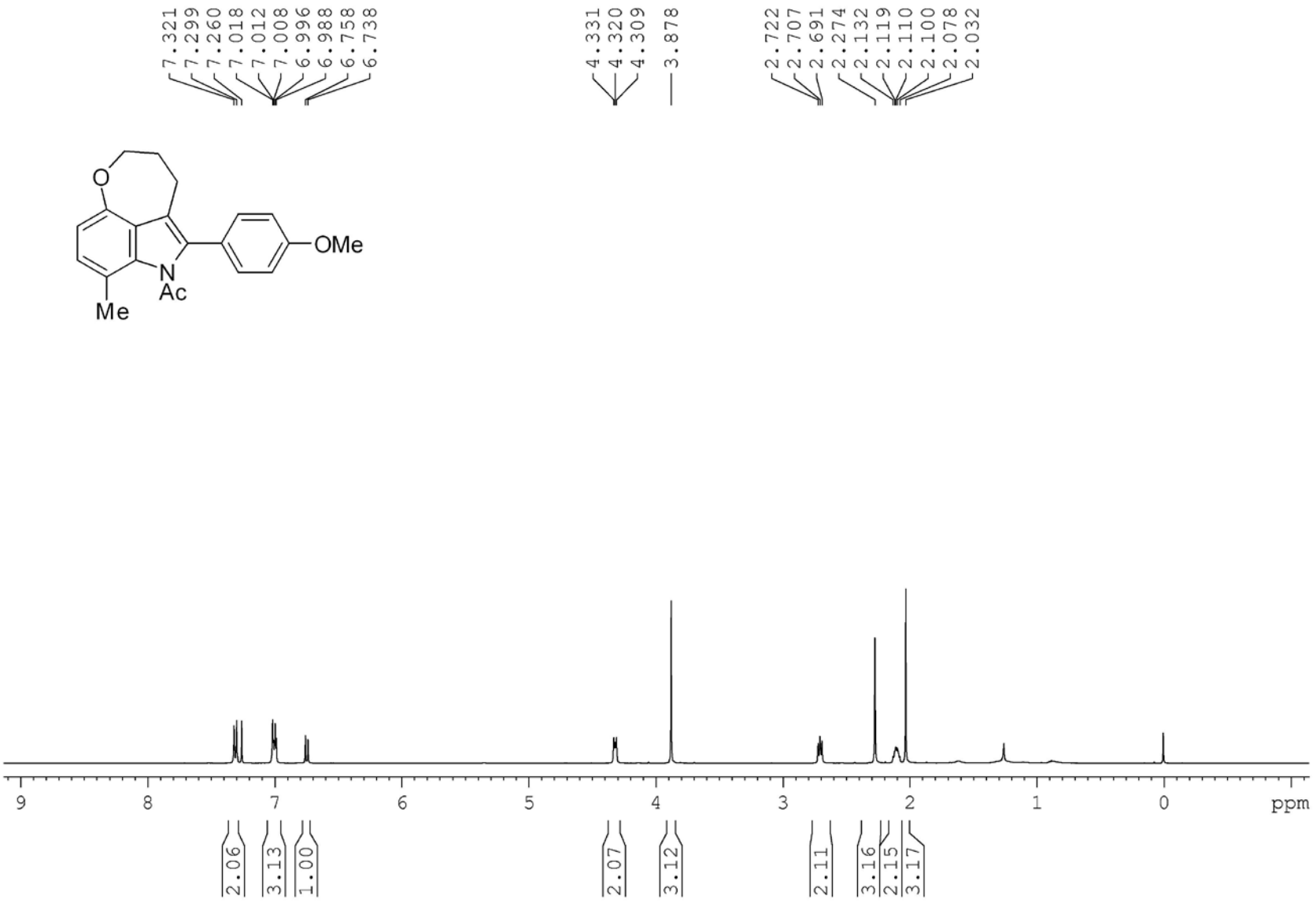
^{1}H NMR of compound 2j ($CDCl_3$; 400MHz)



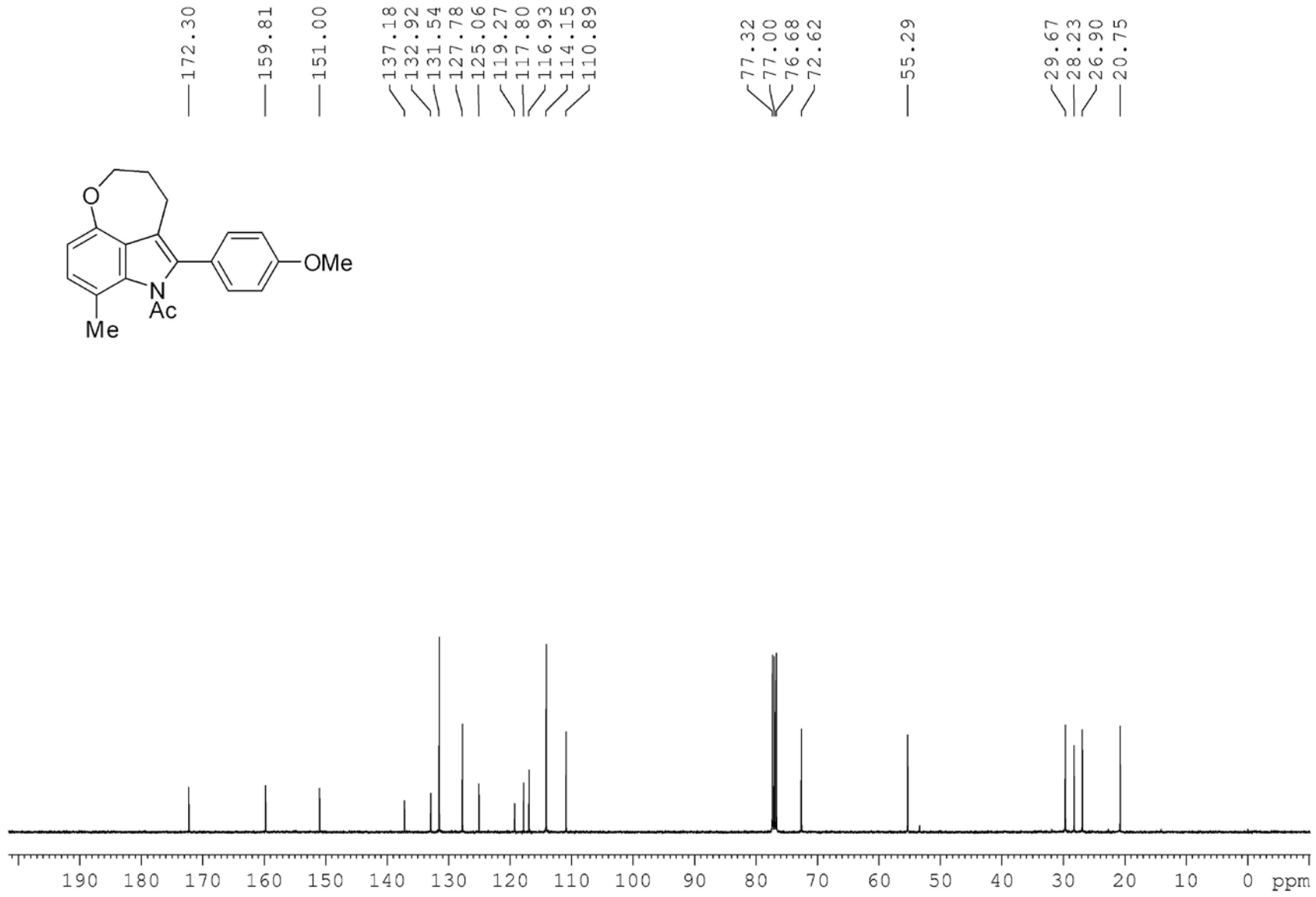
^{13}C NMR of compound 2j ($CDCl_3$; 100MHz)



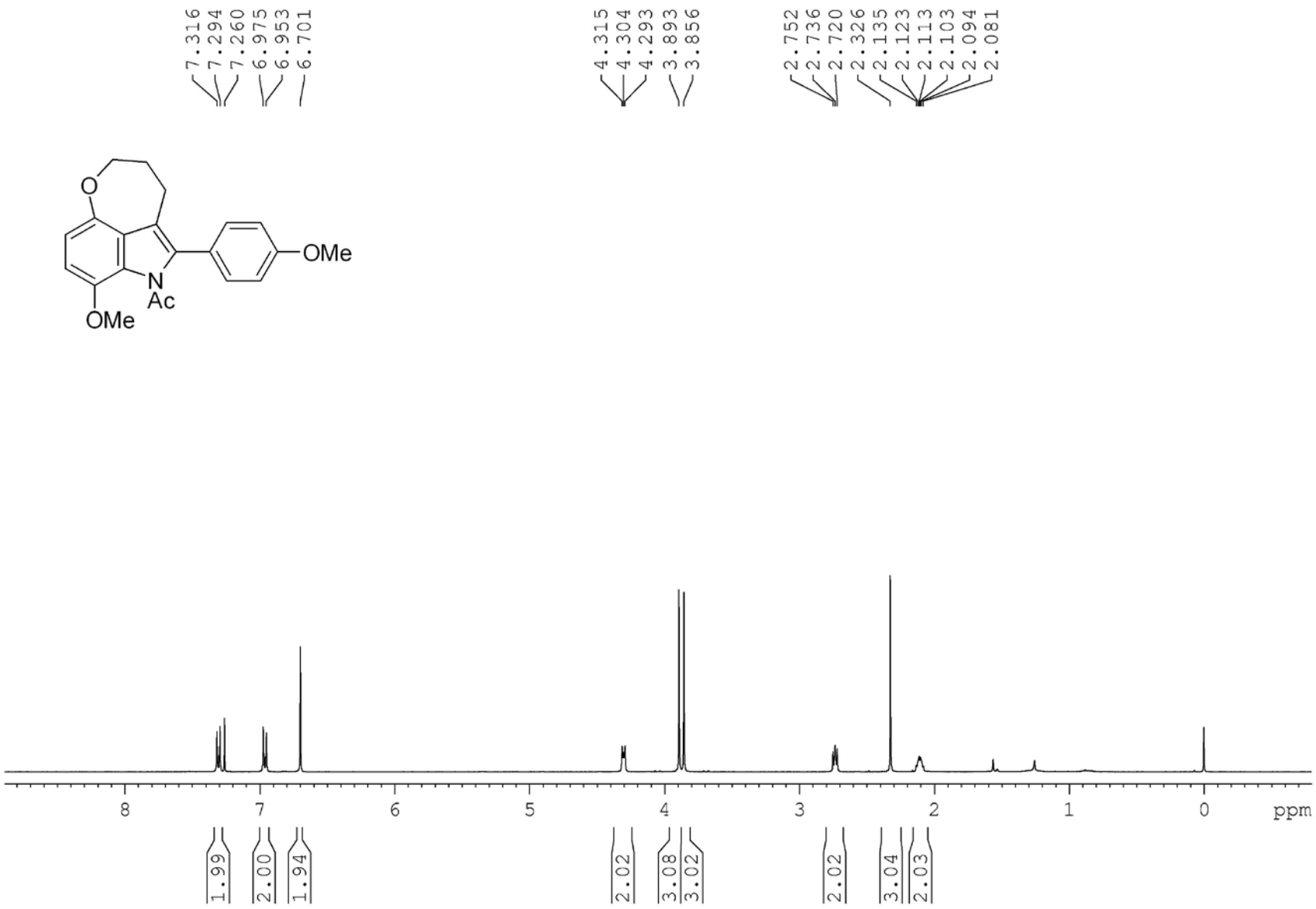
^{1}H NMR of compound 2k ($CDCl_3$; 400MHz)



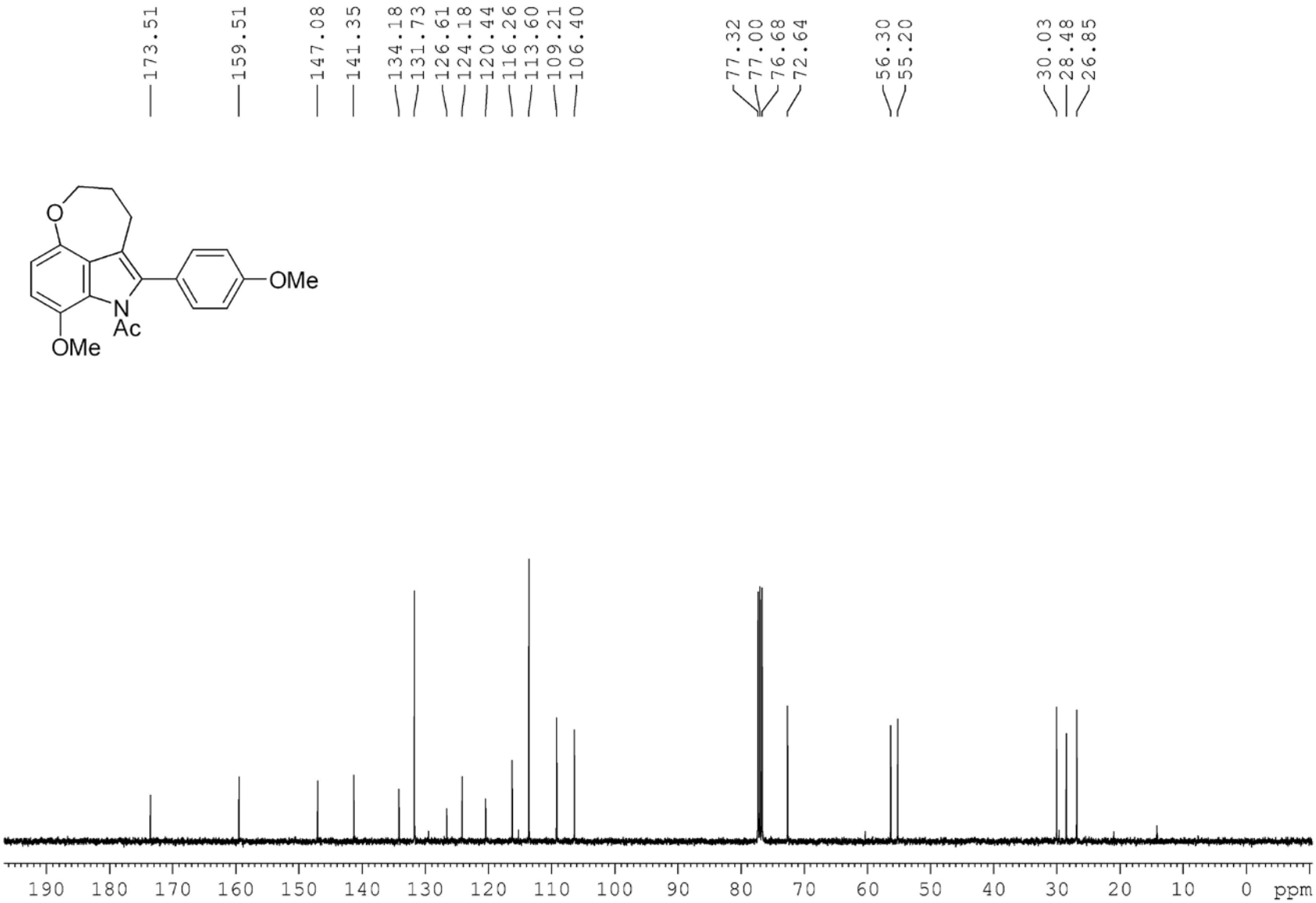
^{13}C NMR of compound 2k ($CDCl_3$; 100MHz)



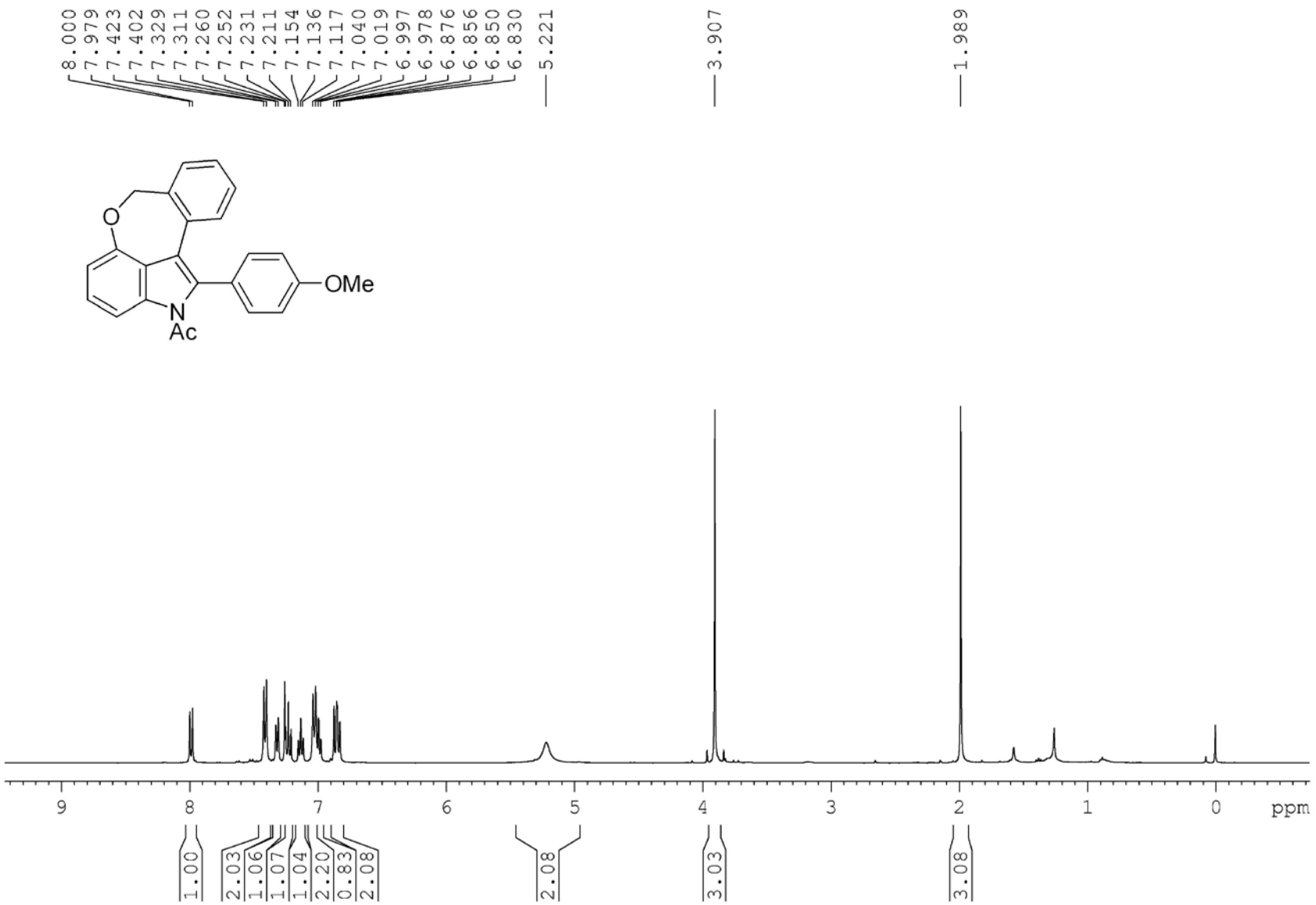
^{1}H NMR of compound 2l ($CDCl_3$; 400MHz)



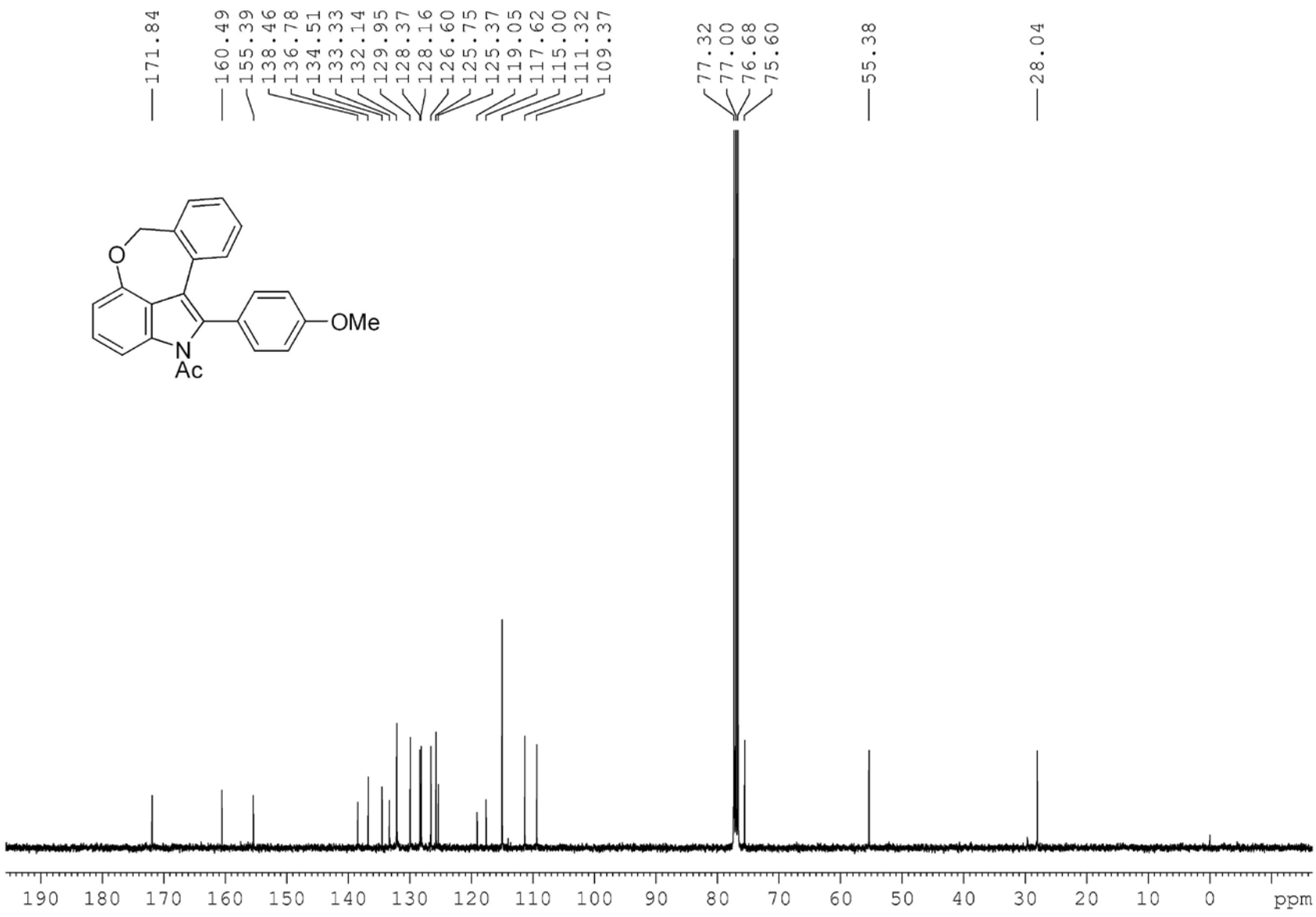
^{13}C NMR of compound 2l ($CDCl_3$; 100MHz)



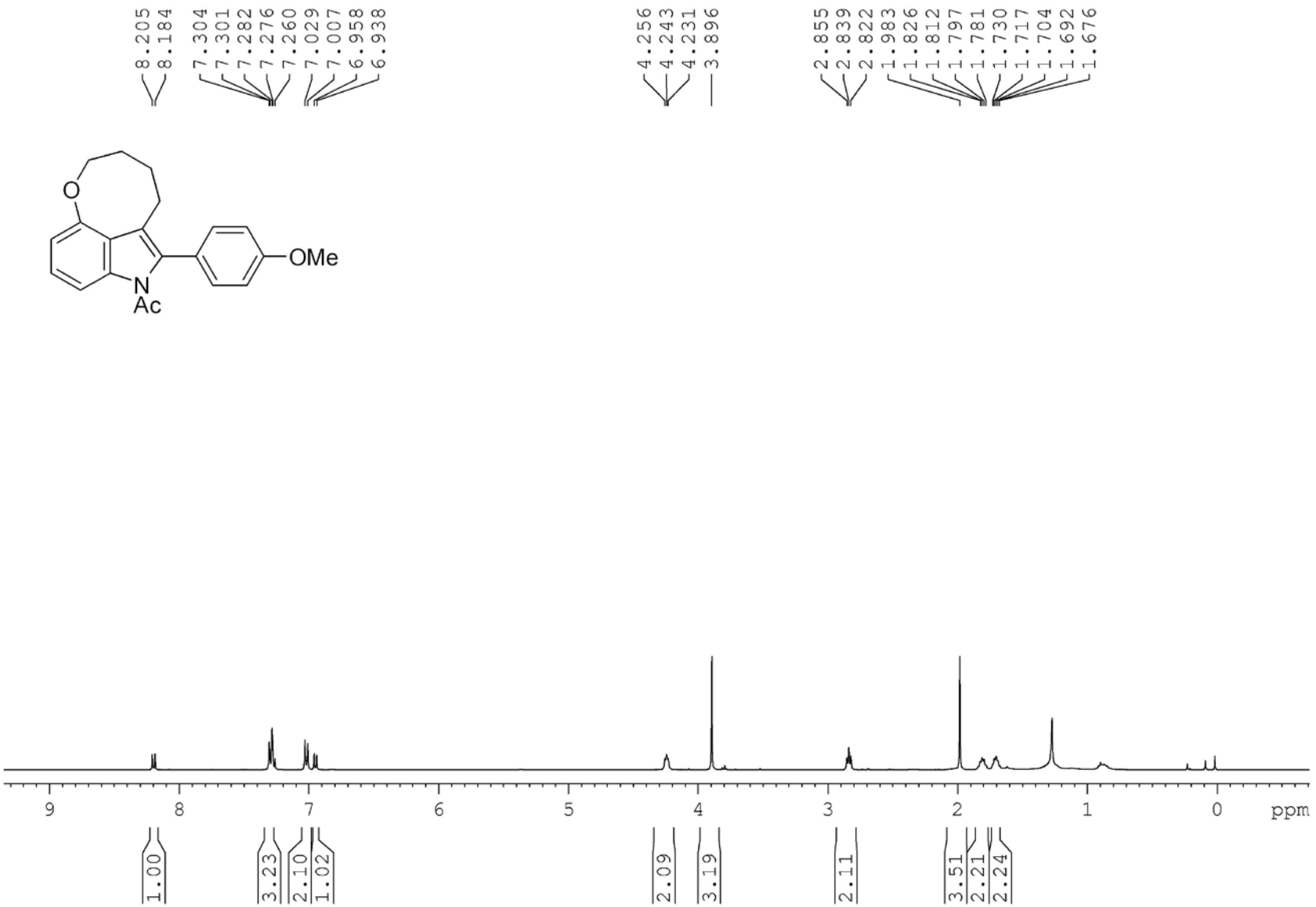
^{1}H NMR of compound 2m ($CDCl_3$; 400MHz)



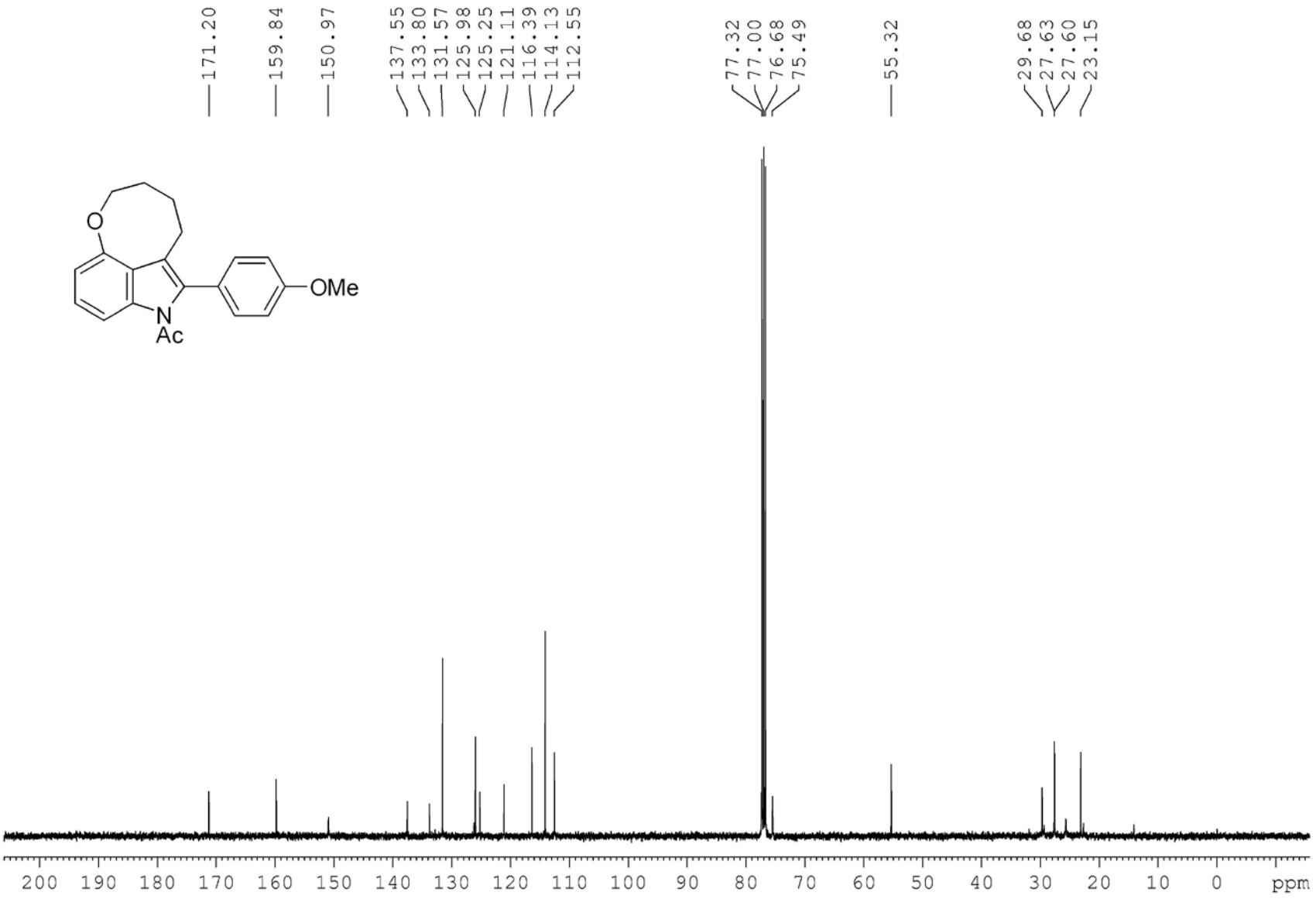
^{13}C NMR of compound 2m ($CDCl_3$; 100MHz)



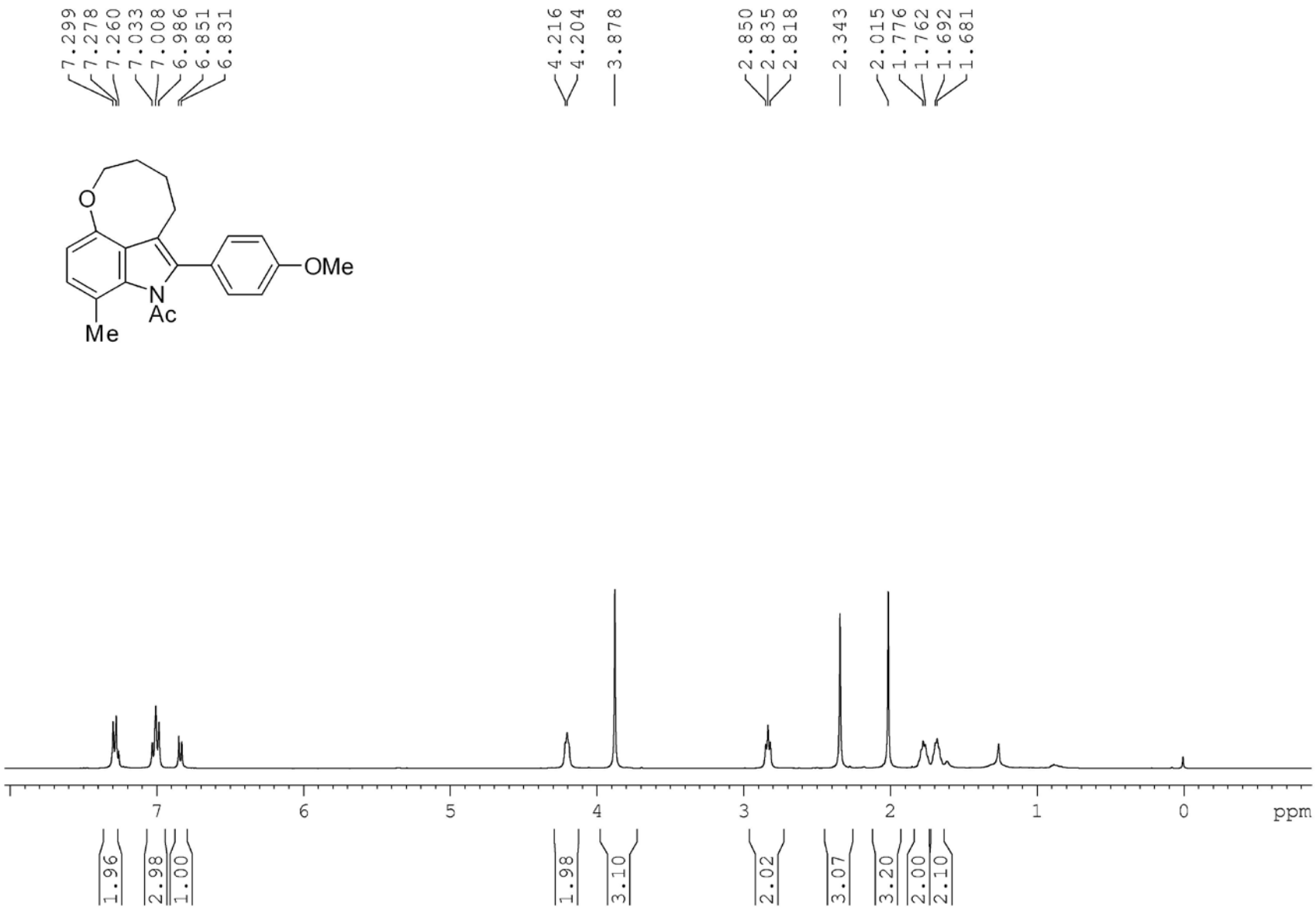
^{1}H NMR of compound 2n ($CDCl_3$; 400MHz)



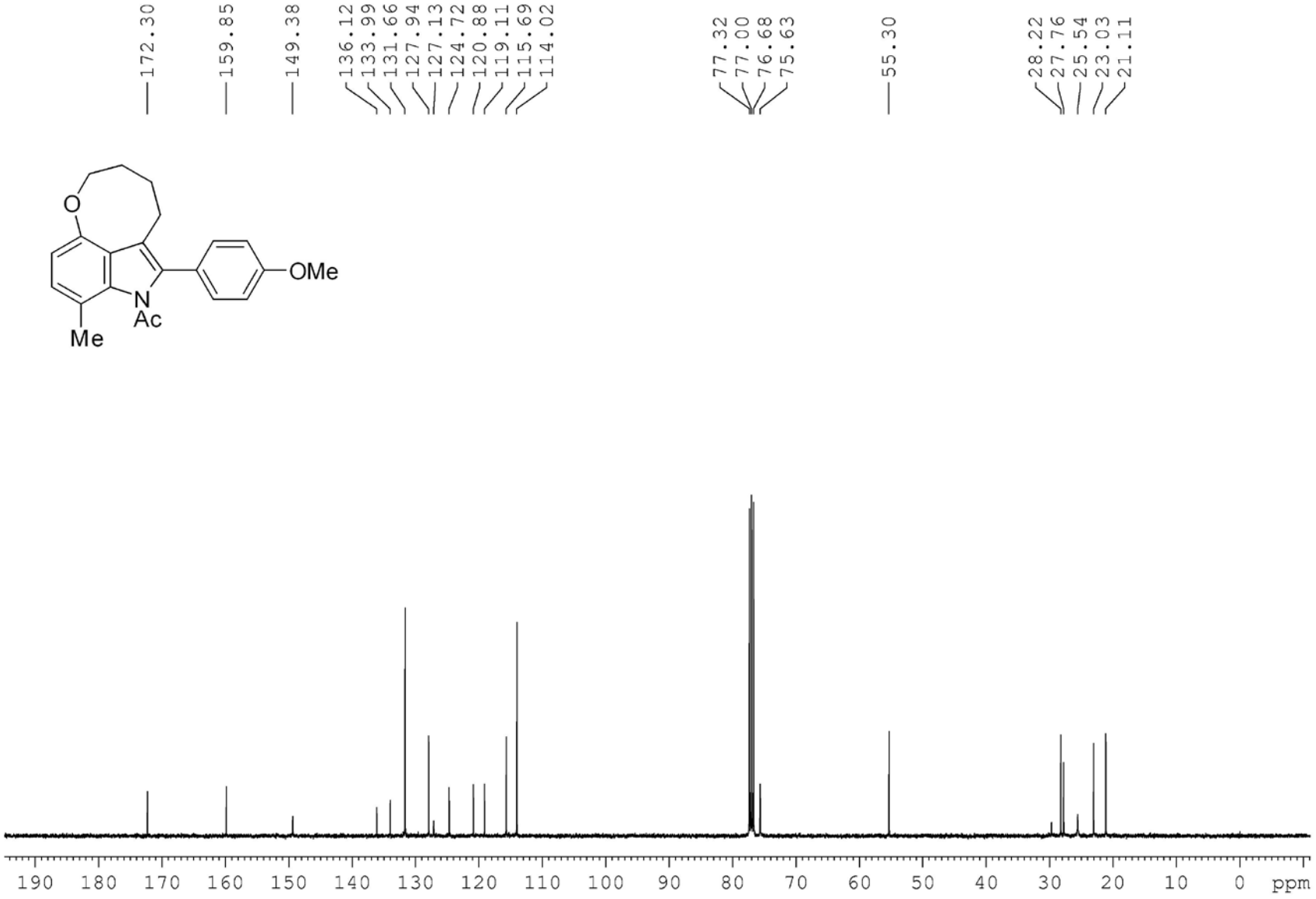
^{13}C NMR of compound 2n ($CDCl_3$; 100MHz)



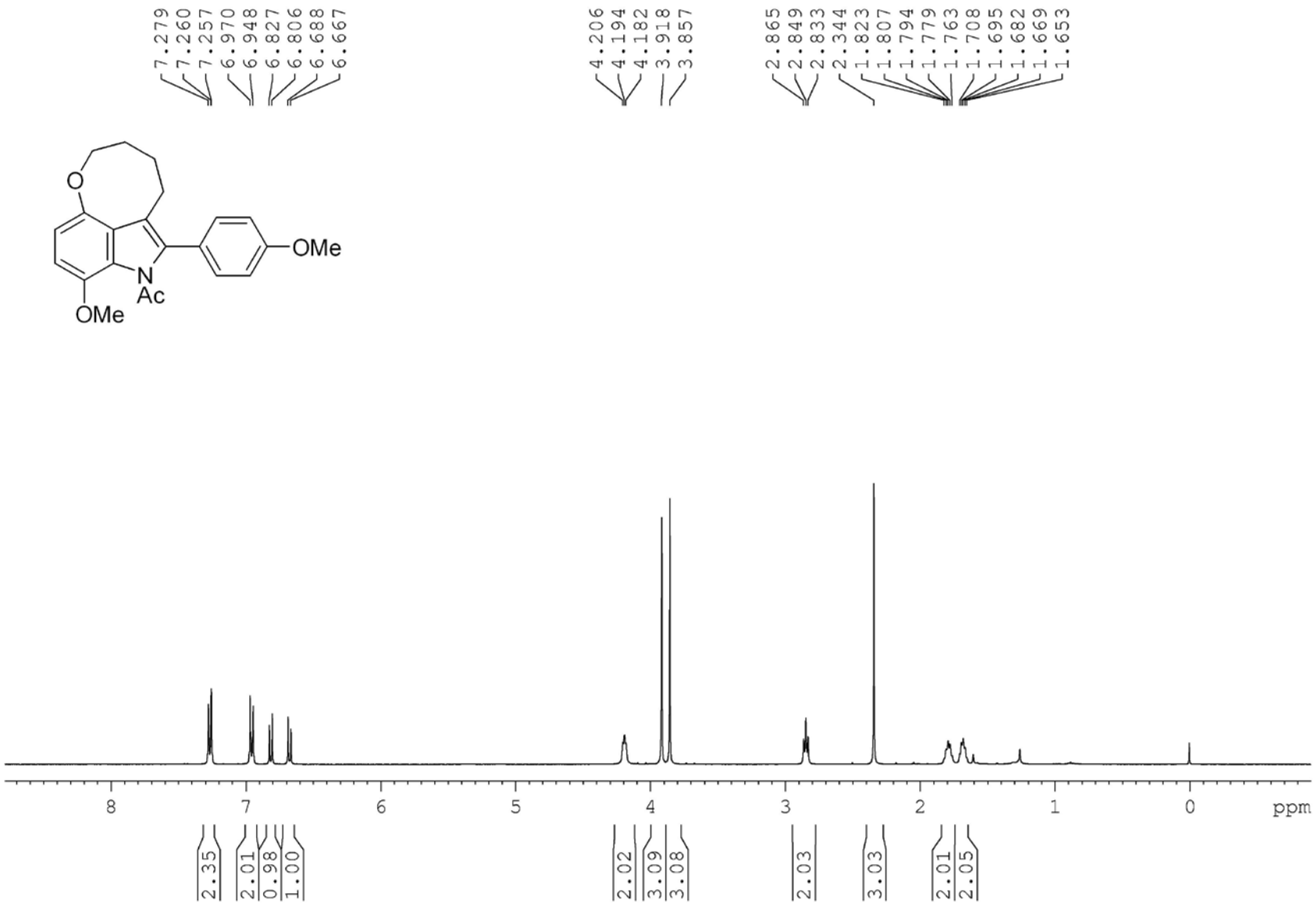
^{1}H NMR of compound 2o ($CDCl_3$; 400MHz)



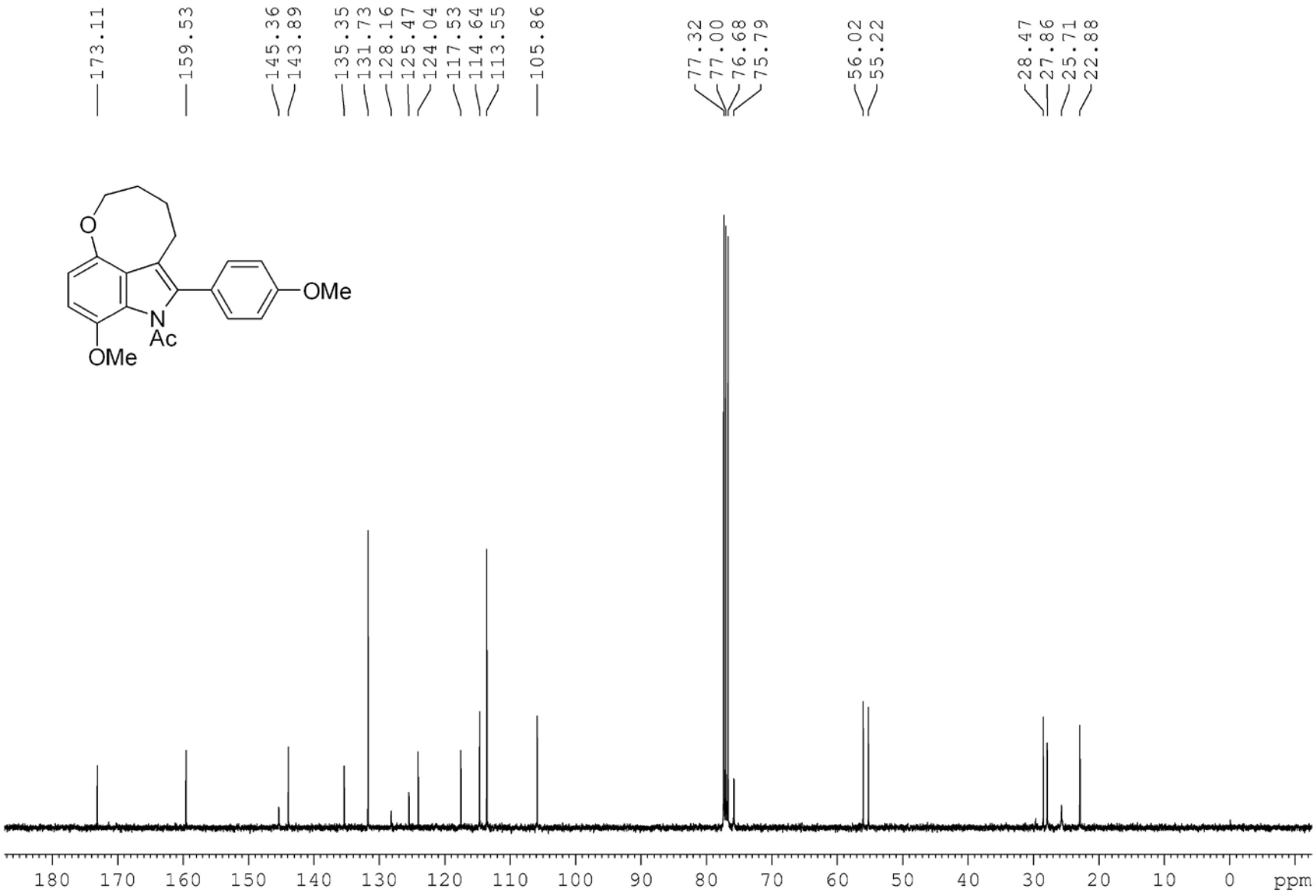
^{13}C NMR of compound 2o ($CDCl_3$; 100MHz)



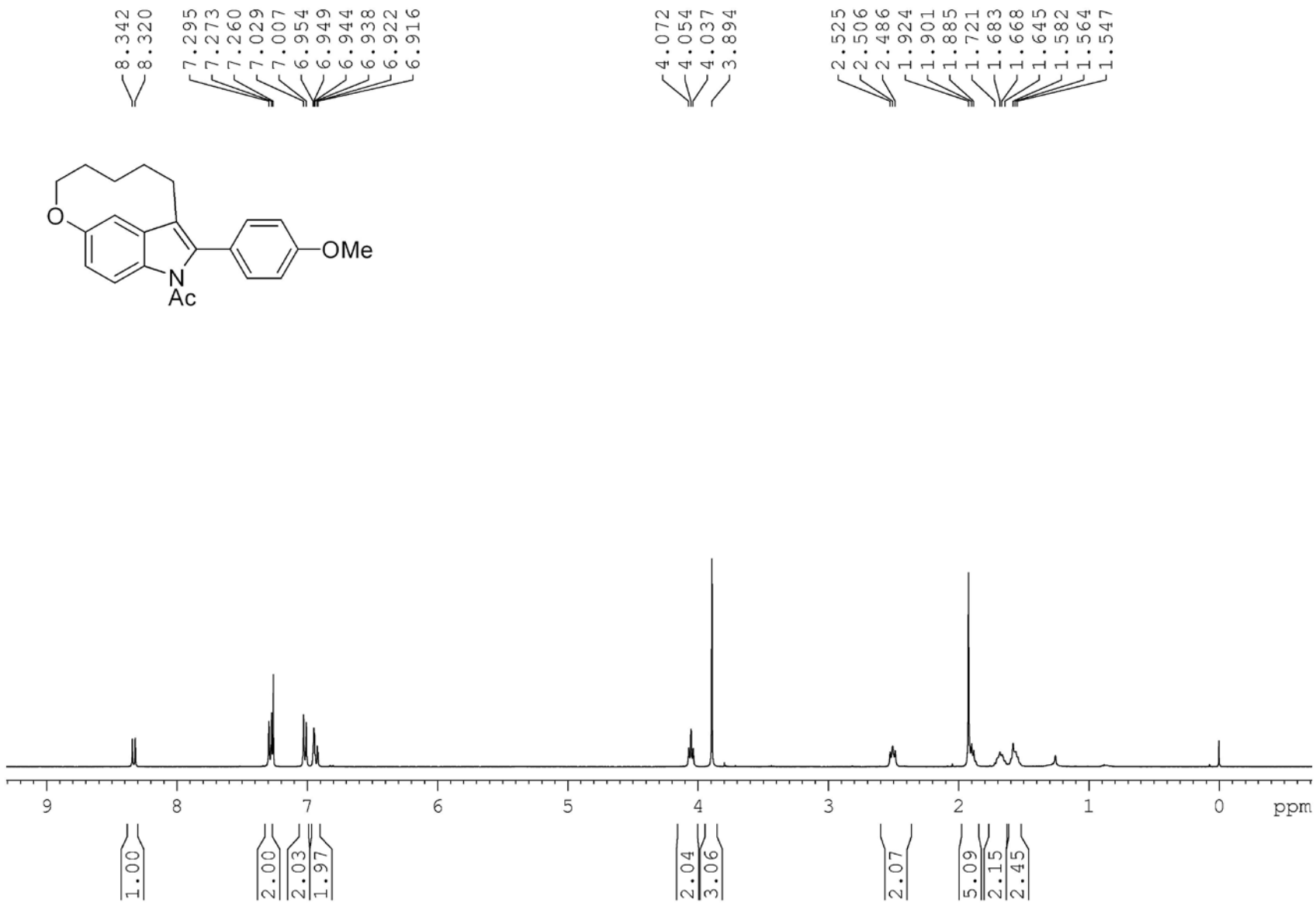
^{1}H NMR of compound 2p ($CDCl_3$; 400MHz)



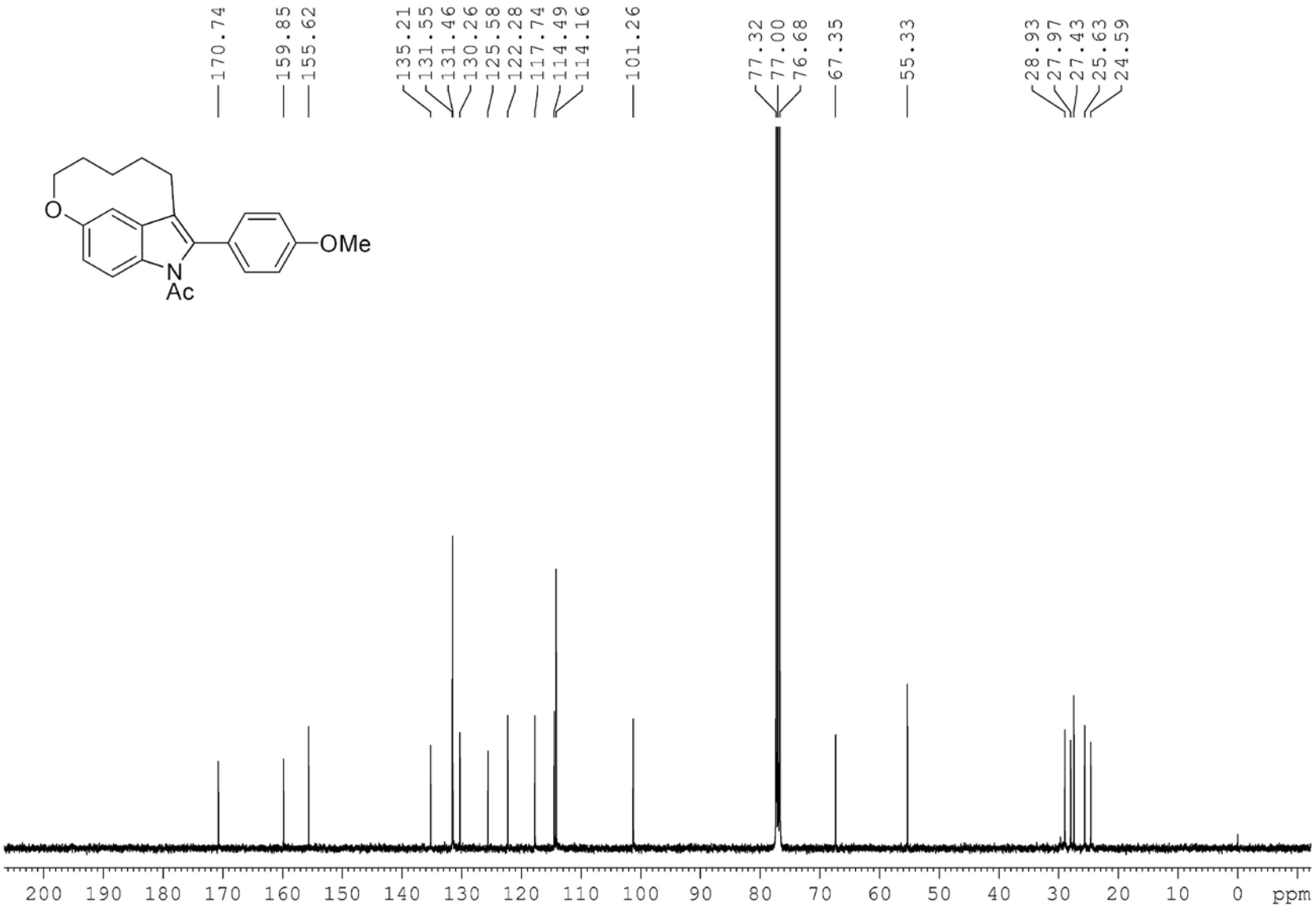
^{13}C NMR of compound 2p ($CDCl_3$; 100MHz)



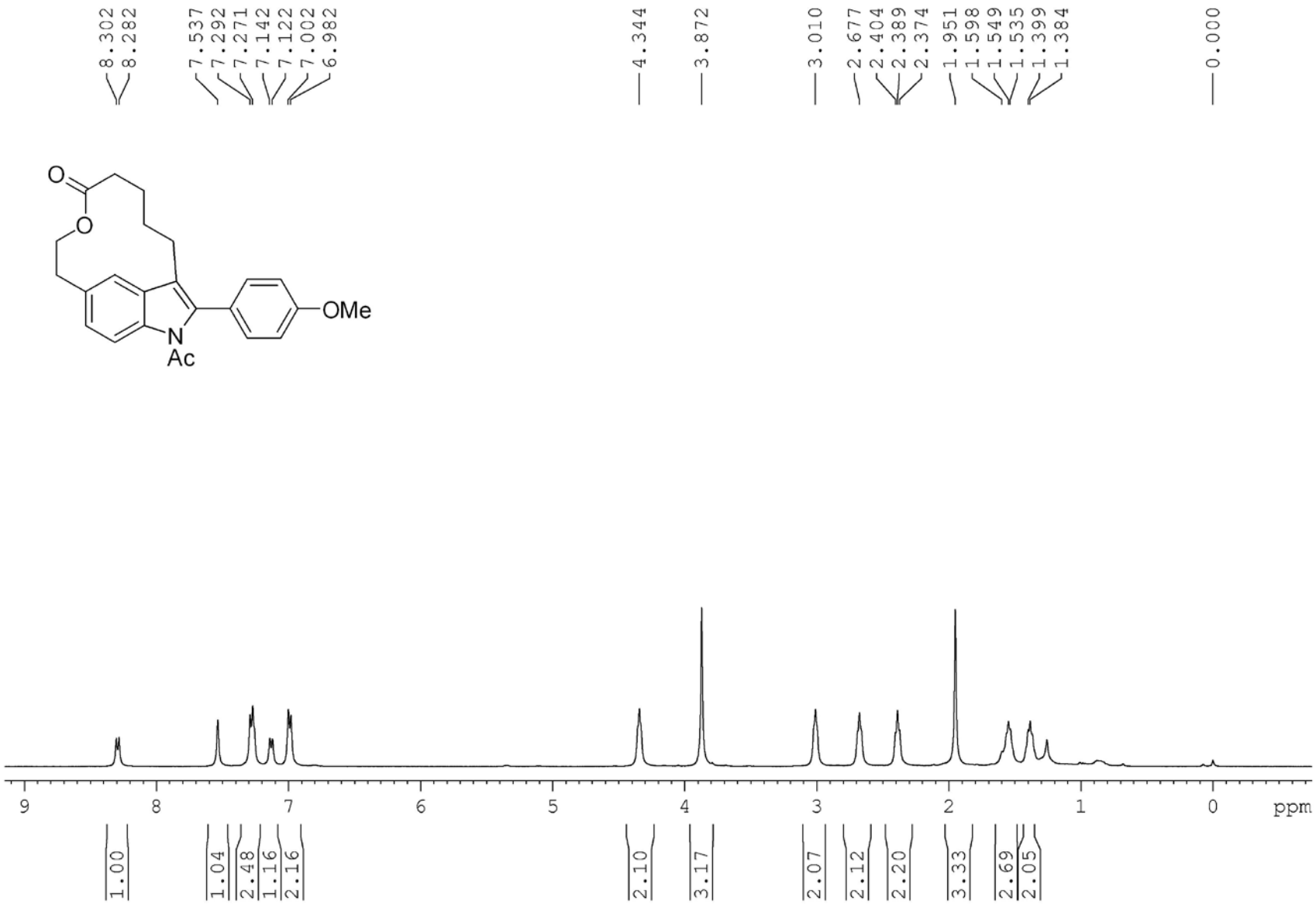
^{1}H NMR of compound 4a ($CDCl_3$; 400MHz)



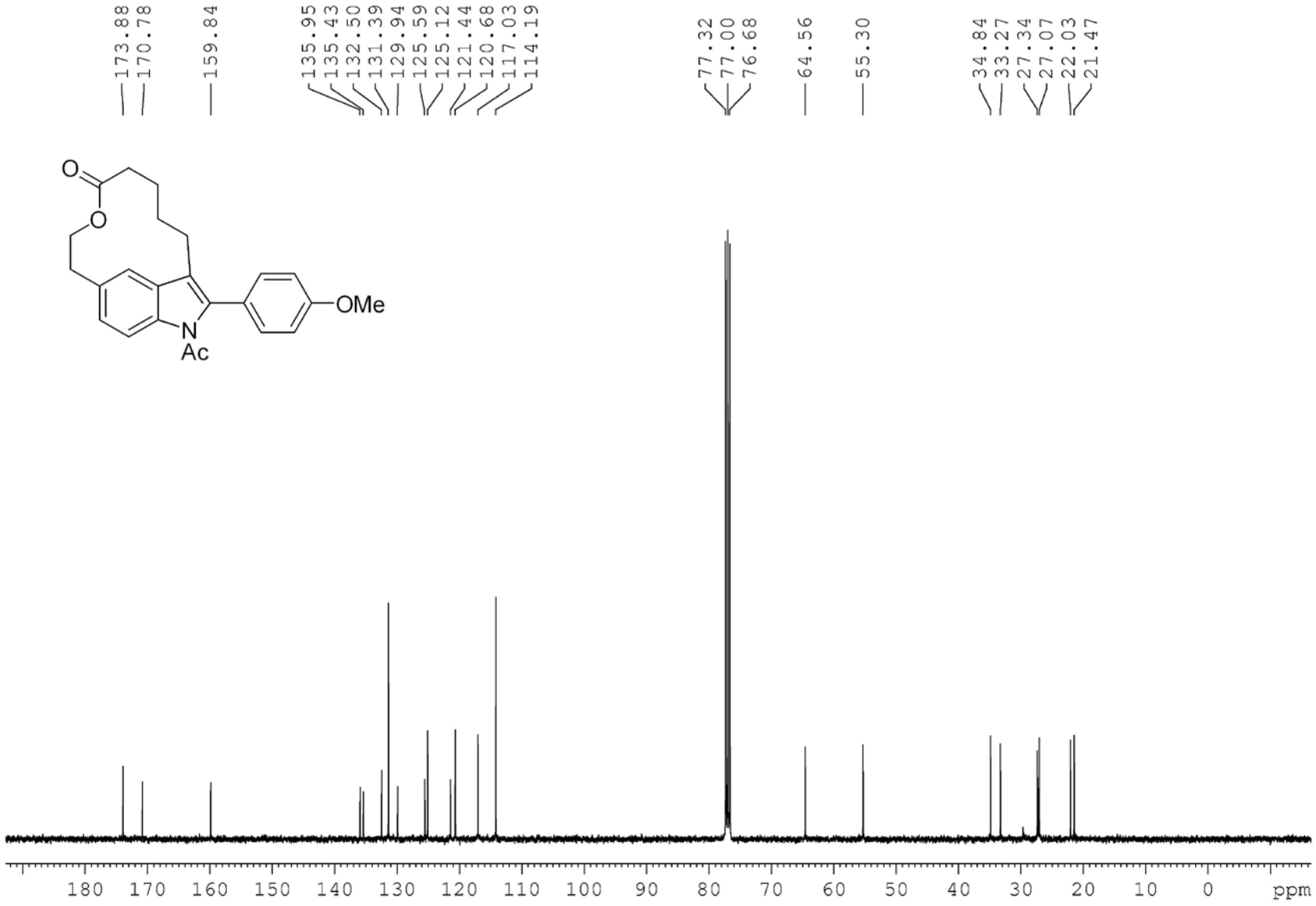
^{13}C NMR of compound 4a ($CDCl_3$; 100MHz)



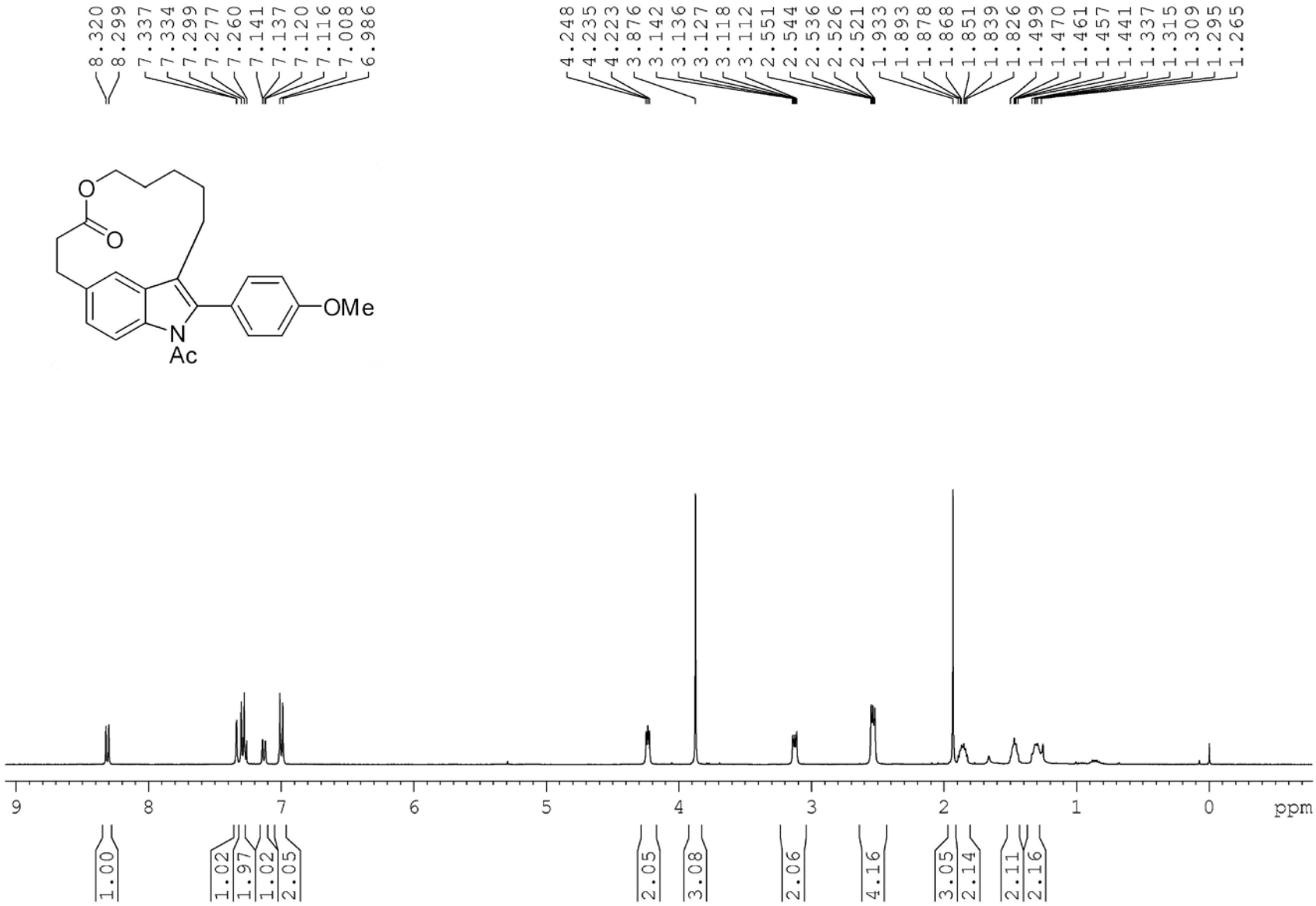
^{1}H NMR of compound 4b ($CDCl_3$; 400MHz)



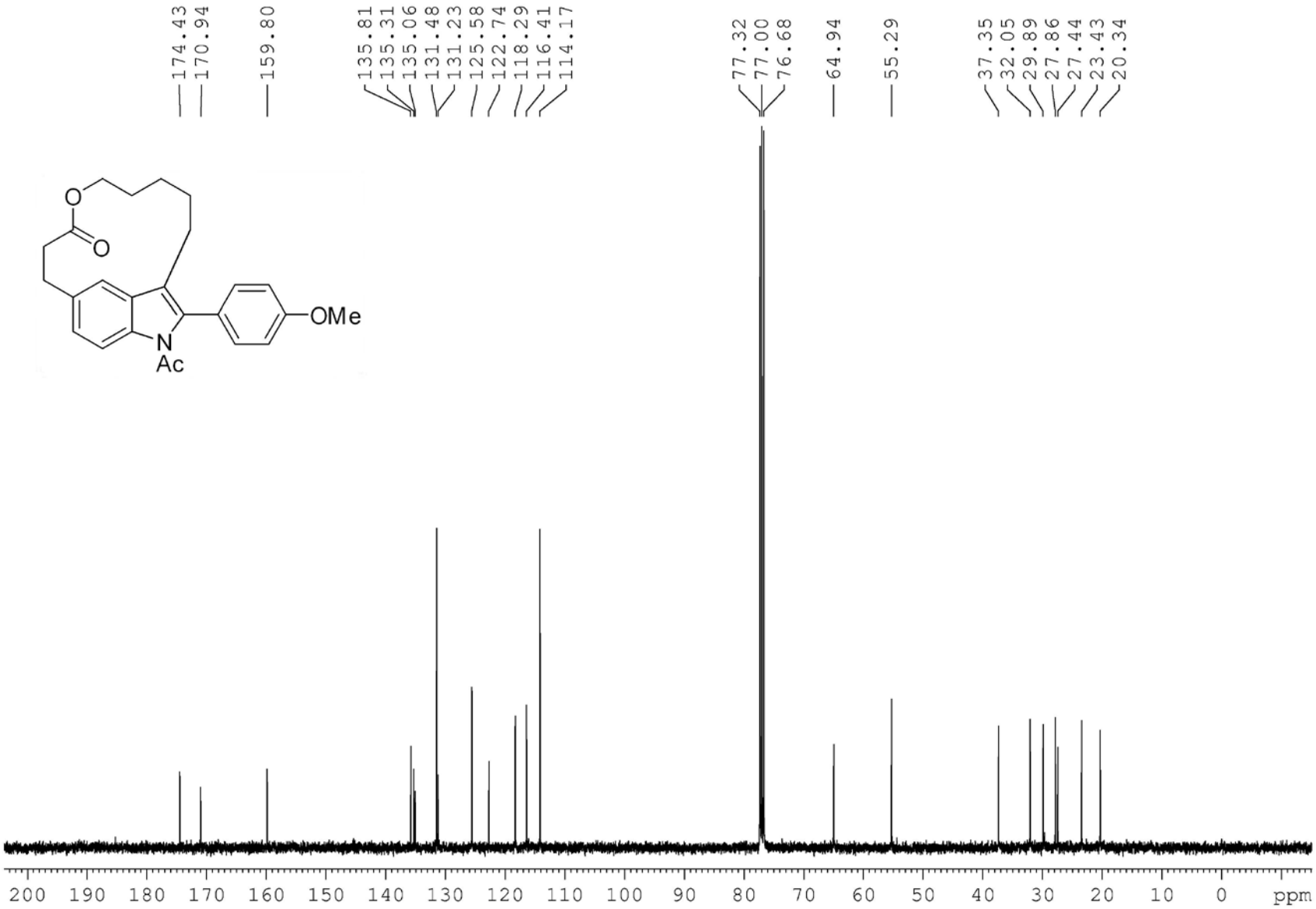
^{13}C NMR of compound 4b ($CDCl_3$; 100MHz)



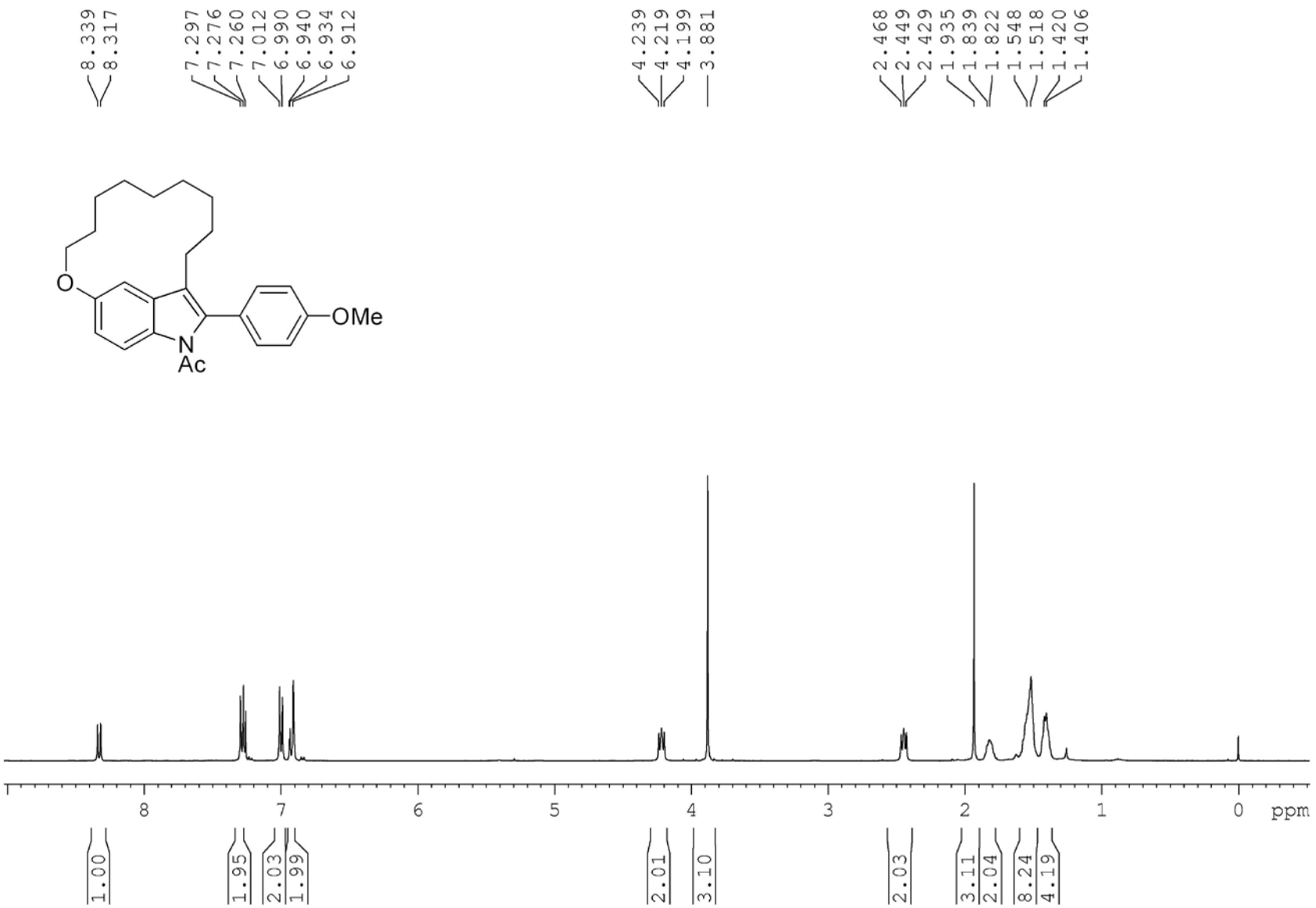
^{1}H NMR of compound 4c ($CDCl_3$; 400MHz)



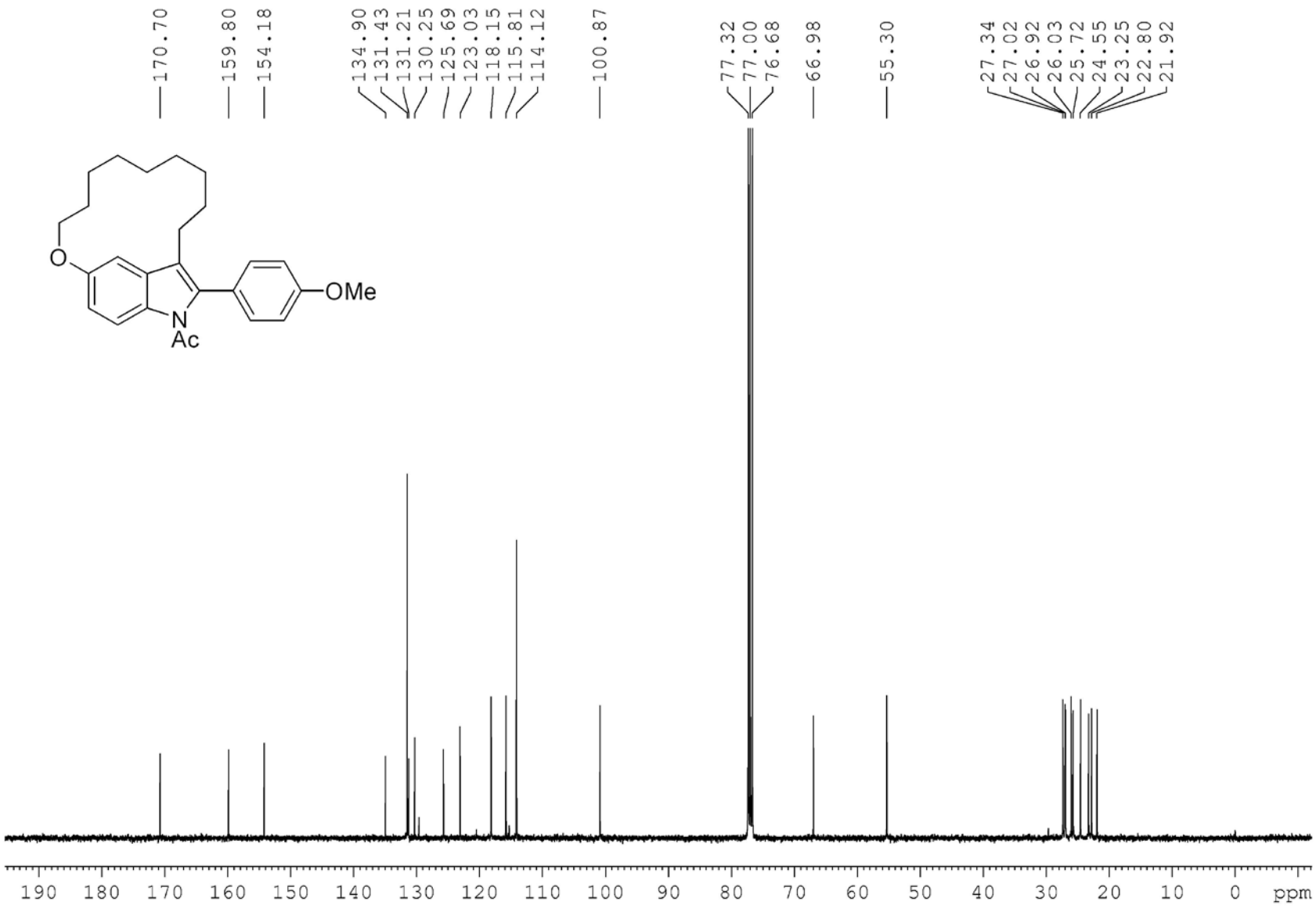
^{13}C NMR of compound 4c ($CDCl_3$; 100MHz)



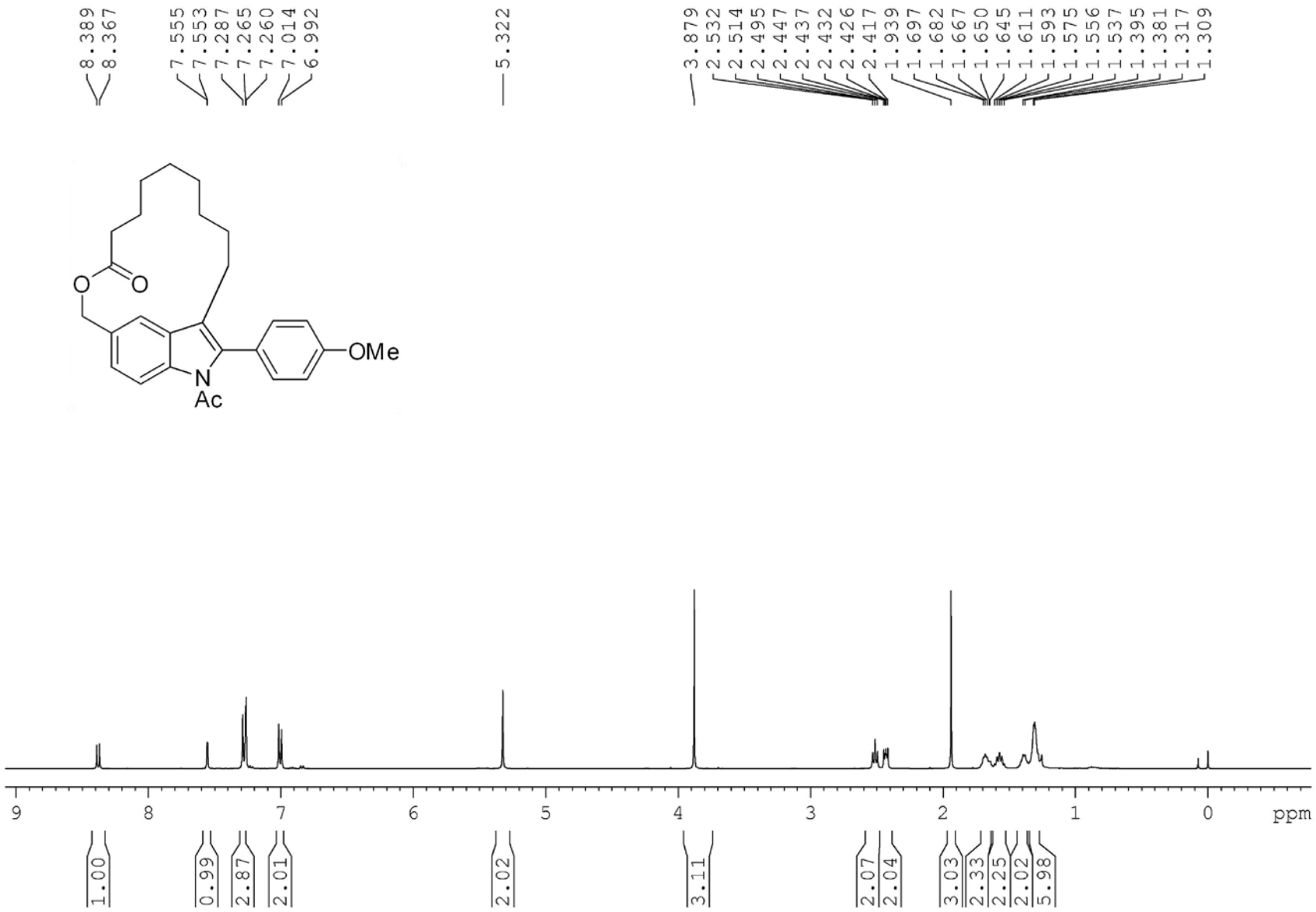
^{1}H NMR of compound 4d ($CDCl_3$; 400MHz)



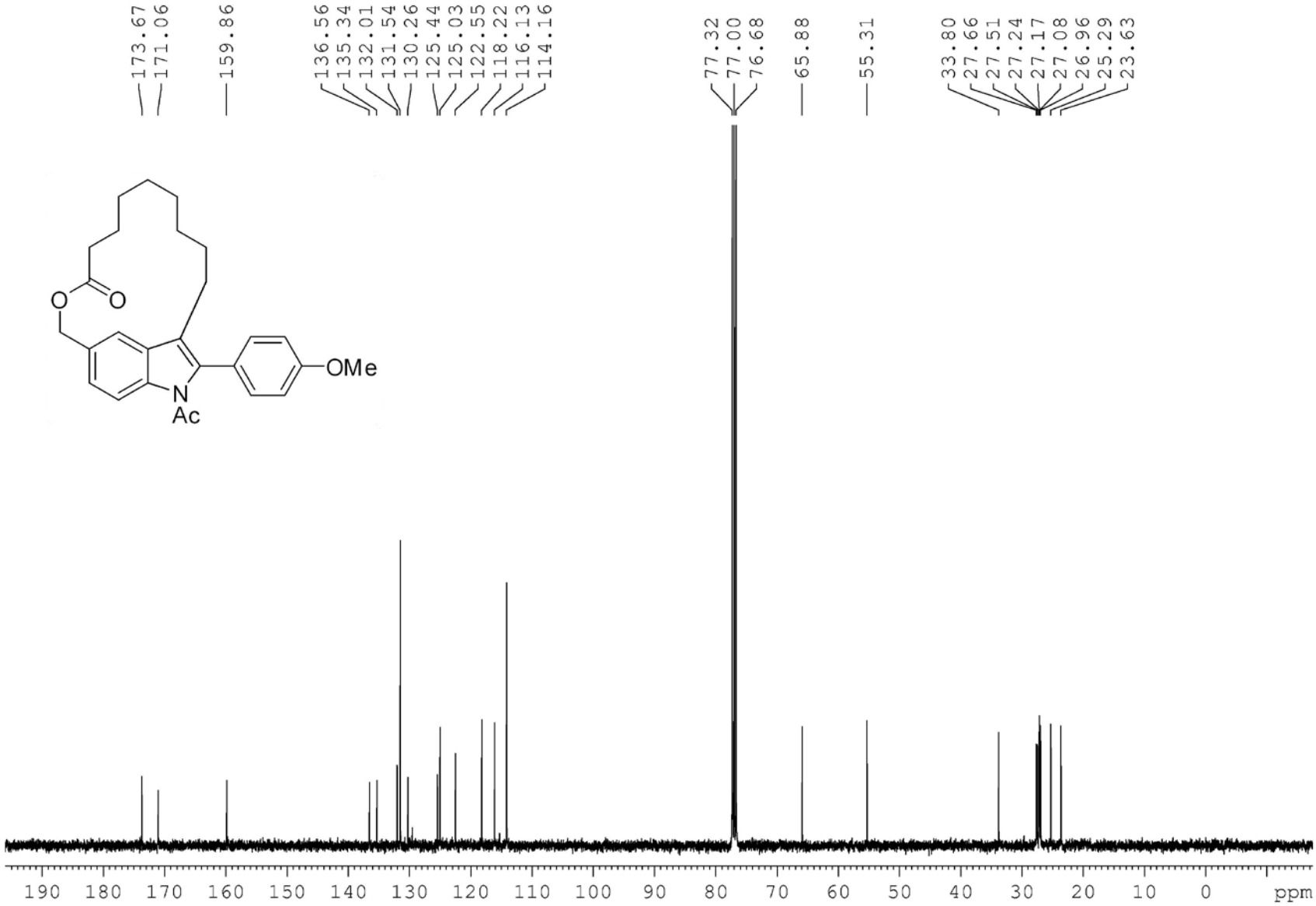
^{13}C NMR of compound 4d ($CDCl_3$; 100MHz)



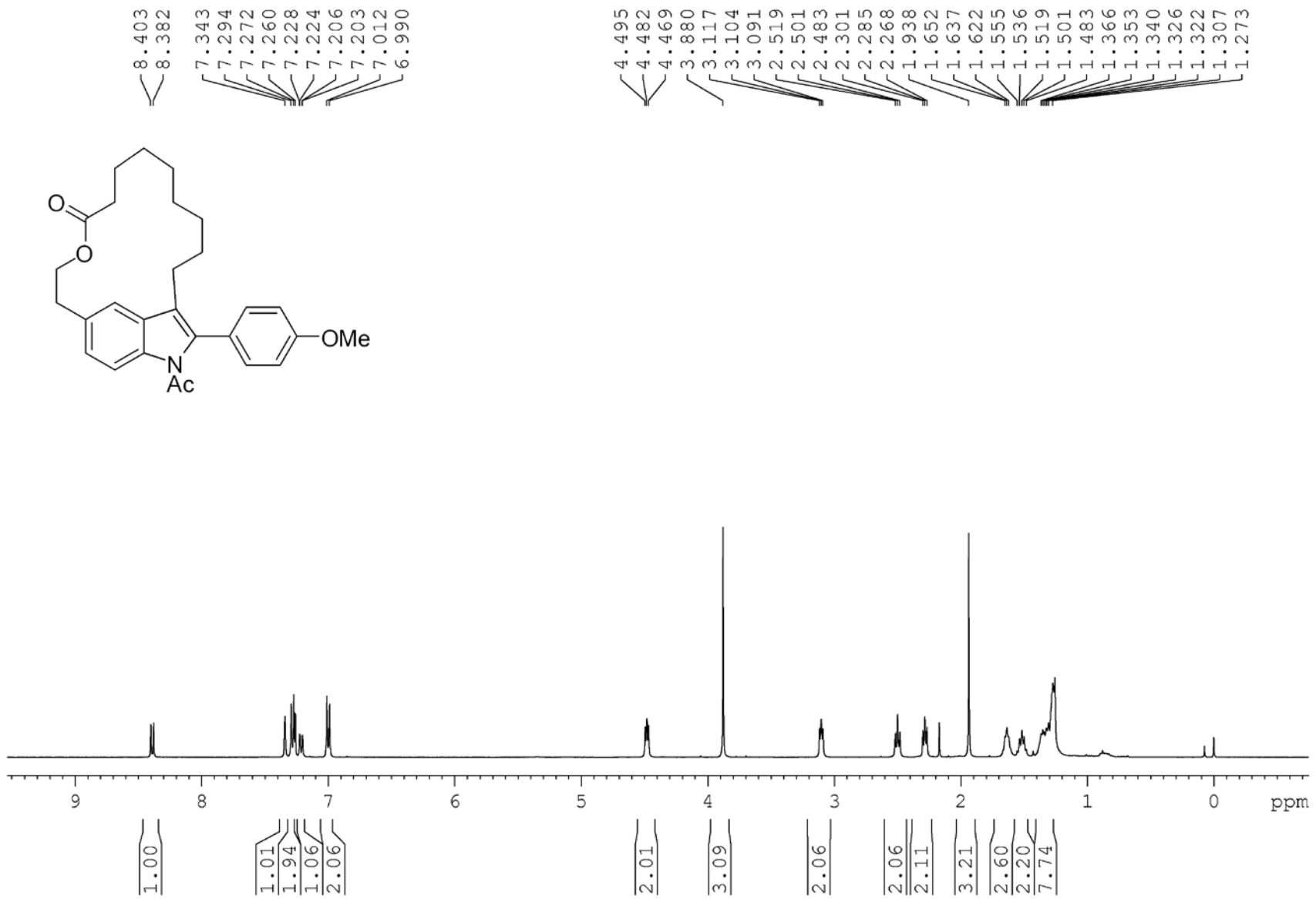
^{1}H NMR of compound 4e ($CDCl_3$; 400MHz)



^{13}C NMR of compound 4e ($CDCl_3$; 100MHz)



^{1}H NMR of compound 4f ($CDCl_3$; 400MHz)



^{13}C NMR of compound 4f ($CDCl_3$; 100MHz)