Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Iodine Catalyzed Oxidative C-C Bond Cleavage for Benzoic Acids and Benzamides From Alkyl Aryl Ketones

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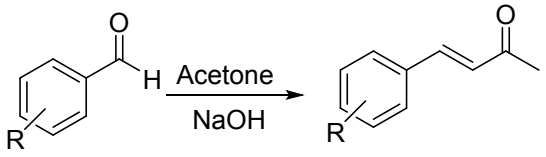
1 General Information:

All reactions were carried out in oven-dried glassware. IR spectra were recorded on FT-IR spectrometer (KBr) and reported in reciprocal centimetres (cm^{-1}). ^{1}H NMR spectra were recorded at 300 MHz and ^{13}C NMR at 75 MHz. For ^{1}H NMR, tetramethylsilane (TMS) was used as internal standard (δ = 0) and the values are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t= triplet, q = quartet, m = multiplet, brs = broadsinglet, dt = doublet of triplet), and the coupling constants in Hz. For ^{13}C NMR, DMSO (δ = 39.51), $CDCl_3$ (δ = 77.23) were used as internal standards and spectra were obtained with complete proton decoupling. Melting points were measured on micro melting point apparatus. The precursors, (E)-4-arylbut-3-en-2-ones prepared according to reported procedures. Commercially available acetophenones, phenylacetylenes, hydroxylamine hydrochloride, sodium azide, iodine and DMSO were used without further purification.

2 Synthesis of starting materials:

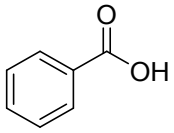
2.1 synthesis of (E)-4-arylbut-3-en-2-ones was done following the procedure (A):[1]

Aryl-benzaldehyde (33mmol) was suspended in a mixture of acetone/water (10 mL/1mL). A 1% aqueous solution of sodium hydroxide (1 mL) was rapidly added to the reaction mixture. The reaction mixture was heated to 65°C and stirred for 3h. The reaction mixture was cooled to ambient temperature then neutralized by the addition of 1M HCl. The product was then extracted with DCM (2x30 mL), washed with brine (30 mL) and dried over Na_2SO_4. The solution was filtered and the solvent removed in vacuo to give the required product.

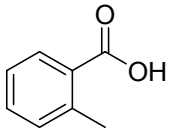


3 General procedure for the synthesis of Benzoic acids (B): A mixture of acetophenones/(E)-4-arylbut-3-en-2-ones/phenylacetylenes (1 mmol, 1 eq.), Hydroxylamine hydrochloride (4 mmol, 4 eq.) and Iodine(10 mol%) in dimethyl sulfoxide (10 mL) was stirred at

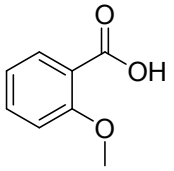
100 °C under open air for the appropriate time (Table 1). After completion of the reaction, as indicated by TLC, the mixture was diluted with water and extracted with EtOAc (4×15 mL). The extract was washed with brine, drying over Na_2SO_4 and evaporation, the crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc) to afford the product.



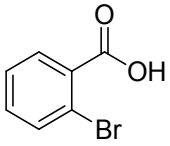
Benzoic acid (3a):[2] According to general procedure B, **1a** (120 mg, 1 mmol) gave **3a** (95% mg, 78%) as a white solid. R_f = 0.4 (EtOAc/hexanes, 3:7); m.p. 121-123 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.96 (d, *J* = 8.17, 2H), 7.64-7.61 (m, 1H), 7.47 (t, *J* = 7.08 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 172.3, 134.0, 130.4, 129.4, 128.7; IR (KBr) ν: 3020.6, 1687.9, 934.8, 708.9 cm^{-1}. MS (EI) *m/z* 121 $[M-1]^+$.



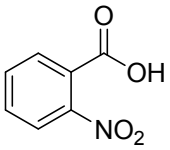
2-methylbenzoic acid (3b):[3] According to general procedure B, **1b** (134 mg, 1 mmol) gave **3b** (109 mg, 80%) as a white solid. R_f = 0.5 (EtOAc/hexanes, 3:7); m.p. 104-106 ºC; ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d) δ: 7.83-7.81 (m, 1H), 7.28-7.24 (m, 1H), 7.12-7.10 (m, 1H) 2.49 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d) δ: 170.0, 140.1, 131.7, 131.5, 130.8, 130.0, 125.5, 21.7; IR (KBr) ν: 3019.5, 1692.6, 1215.5, 757.8, 669.1 cm^{-1}. MS (EI) *m/z* 135 $[M-1]^+$.



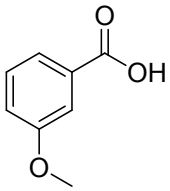
2-methoxybenzoic acid (3c):[2] According to general procedure B, **1c** (150 mg, 1 mmol) gave **3c** (140 mg, 86%) as a white solid. R_f = 0.4 (EtOAc/hexanes, 3:7); m.p. 101-103 ºC; ^{1}H NMR (300 MHz, DMSO) δ: 7.52 (d, *J* = 7.51 Hz ,1H,), 7.43-7.38 (m, 2H), 7.20 - 7.16 (m, 1H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ: 167.3, 158.0, 133.0, 130.6, 121.3, 120.0, 112.4, 55.6; IR (KBr) ν: 3020.6, 1692.9, 1287.9, 1216.5, 759.7, 670.0 cm^{-1}. MS (EI) *m/z* 151 $[M-1]^+$.



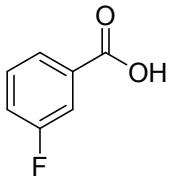
2-bromobenzoic acid (3d):[4] According to general procedure B, **1d** (197 mg, 1 mmol) gave **3d** (115 mg, 58%) as a white solid. R_f = 0.5 (EtOAc/hexanes, 3:7); m.p. 146-148 ºC; ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d) δ: 13.37 (bs, 1H), 7.74-7.70 (m, 2H), 7.48-7.42 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d) δ: 167.3, 133.5, 132.6, 131.7, 130.7, 126.6, 120.6; IR (KBr) ν: 3019.5, 1702.3, 1406.1, 1300.6, 1215.4, 1030.6, 757.3, 669.0 cm^{-1}. MS (EI) *m/z* 198 [M-1]$^+$.



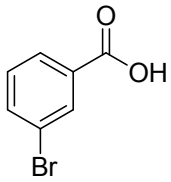
2-nitrobenzoic acid (3e):[5] According to general procedure B, **1e** (165 mg, 1 mmol) gave **3e** (102 mg, 61%) as a white solid. R_f = 0.45 (EtOAc/hexanes, 3:7); m.p. 146-147 ºC; ^{1}H NMR (300 MHz, DMSO-d) δ: 13.84 (bs, 1H), 7.98-7.96 (m, 1H), 7.86-7.84 (m, 1H), 7.79-7.75 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d) δ: 165.9, 148.4, 133.1, 132.4, 129.8, 127.2, 123.7; IR (KBr) ν: 3021.2, 1676.4, 1382.1, 1216.1, 765.5 cm^{-1}. MS (EI) *m/z* 166 [M-1]$^+$.



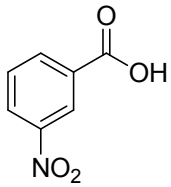
3-methoxybenzoic acid (3f):[2] According to general procedure B, **1f** (150 mg, 1 mmol) gave **3f** (137 mg, 90%) as a white solid. R_f = 0.4 (EtOAc/hexanes, 3:7); m.p. 103-105 ºC; ^{1}H NMR (300 MHz, DMSO) δ: 7.63 (dd, *J* = 7.60, 1.68 Hz, 1H), 7.52-7.46 (m, 1H), 7.11 (d, *J* = 8.33 Hz, 1H), 6.98 (t, *J* = 7.57 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d) δ: 167.1, 159.2, 132.1, 129.6, 121.5, 118.8, 113.8, 55.2; IR (KBr) ν: 3394.3, 3020.9, 1693.2, 1411.7, 1216.1, 760.0, 670.0 cm^{-1}. MS (EI) *m/z* 151 [M-1]$^+$.



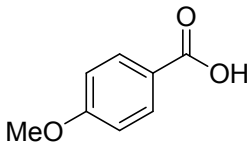
3-fluorobenzoic acid (3g):[6] According to general procedure B, **1g** (138 mg, 1 mmol) gave **3g** (90mg, 64%) as a white solid. R_f = 0.5 (EtOAc/hexanes, 3:7); m.p. 120-122 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 10.42 (bs, 1H), 7.94-7.91 (m, 1H), 7.82-7.78 (m, 1H), 7.49-7.44 (m, 1H), 7.35-7.30 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.4, 164.0, 161.5, 131.7, 131.6, 130.48, 130.41, 126.24, 126.22, 121.3, 121.1, 117.4, 117.2; IR (KBr) ν: 3397.2, 3021.3, 1694.1, 1413.7, 1216.0, 759.7 cm^{-1}. MS (EI) *m/z* 139 $[M-1]^+$.



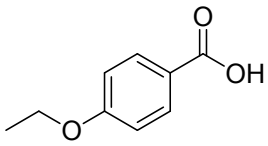
3-bromobenzoic acid (3h):[7] According to general procedure B, **1h** (197 mg, 1 mmol) gave **3h** (139 mg, 70%) as a white solid. R_f = 0.5 (EtOAc/hexanes, 3:7); m.p. 155-157 ºC; ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d) δ: 7.86-7.85 (m, 1H), 7.68-7.66 (m, 1H), 7.38-7.36 (m, 1H) 7.06-7.02 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d) δ: 166.3, 134.9, 132.6, 132.1, 129.5, 127.8, 121.6; IR (KBr) ν: 3400.7, 3019.7, 1692.5, 1308.8, 1216.5, 760.3, 669.4 cm^{-1}. MS (EI) *m/z* 198 $[M-1]^+$.



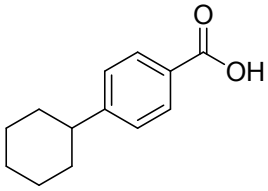
3-nitrobenzoic acid (3i):[3] According to general procedure B, **1i** (165 mg, 1 mmol) gave **3i** (103 mg, 62%) as a white solid. R_f = 0.45 (EtOAc/hexanes, 3:7); m.p. 138-140 ºC; ^{1}H NMR (300 MHz, DMSO-d) δ: 8.59 (s, 1H), 8.45-8.43 (m, 1H), 8.33-8.31 (m, 1H) 7.79 (t, *J* = 7.97 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d) δ: 165.5, 147.8, 135.3, 132.4, 130.5, 127.3, 123.6; IR (KBr) ν: 3021.7, 1705.9, 1352.1, 1288.4, 1215.7, 759.9, 669.5 cm^{-1}. MS (EI) *m/z* 166 $[M-1]^+$.



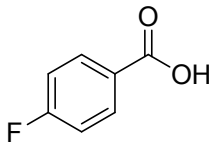
4-methoxybenzoic acid (3j):[2] According to general procedure B, **1j** (150 mg, 1 mmol) gave **3j** (141 mg, 93%) as a white solid. R_f = 0.4 (EtOAc/hexanes, 3:7); m.p. 180-182 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.08-8.05 (m, 2H), 6.96 - 6.93 (m, 2H), 3.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d) δ: 167.5, 162.6, 131.1, 122.7, 112.9, 54.9; IR (KBr) ν: 30.9.4, 1685.8, 1215.4, 757.7, 669.1 cm^{-1}. MS (EI) *m/z* 151 [M-1]$^+$.



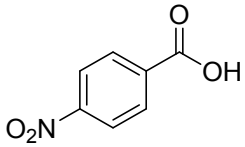
4-ethoxybenzoic acid (3k):[8] According to general procedure B, **1k** (164 mg, 1 mmol) gave **3k** (146 mg, 88%) as a white solid. R_f = 0.4 (EtOAc/hexanes, 3:7); m.p. 196-198 ºC; ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d) δ: 7.72-7.70 (m, 2H), 6.64-6.62 (m, 2H), 3.82 (q, *J* = 13.96, 7.00 Hz, 2H) 1.17 (t, *J* = 6.97 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d) δ: 167.1, 161.7, 130.8, 122.3, 113.1, 62.8, 13.9; IR (KBr) ν: 3402.7, 3021.0, 1603.9, 1300.0, 1216.0, 1169.6, 761.5, 669.8 cm^{-1}. MS (EI) *m/z* 165 [M-1]$^+$.



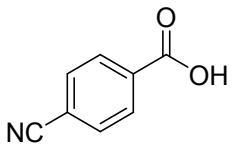
4-cyclohexylbenzoic acid (3l):[9] According to general procedure B, **1l** (202 mg, 1 mmol) gave **3l** (132 mg, 65%) as a white solid. R_f = 0.5 (EtOAc/hexanes, 3:7); m.p. 136-138 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.02 (d, *J* = 8.21 Hz, 2H), 7.30 (d, *J* = 8.15 Hz, 2H), 2.59-2.52 (m, 1H) 1.87-1.74 (m, 5H), 1.46-1.25 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.9, 154.6, 130.5, 127.2, 127.0, 45.0, 34.3, 26.9, 26.2; IR (KBr) ν: 3407.1, 3019.2, 1654.1, 1215.9, 768.8, 668.5 cm^{-1}.



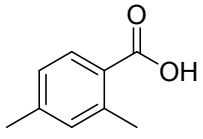
4-fluorobenzoic acid (3m):[6] According to general procedure B, **1m** (138 mg, 1 mmol) gave **3m** (87 mg, 62%) as a white solid. R_f = 0.5 (EtOAc/hexanes, 3:7); m.p. 182-184 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.15-8.13 (m, 2H), 7.17-7.14 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.3, 168.2, 164.9, 133.1, 133.0, 125.7, 116.1, 115.8; IR (KBr) ν: 3408.3, 3019.5, 2400.1, 1601.6, 1420.2, 1215.4, 1069.0, 758.0, 669.0 cm^{-1}. MS (EI) *m/z* 139 [M-1]$^+$.



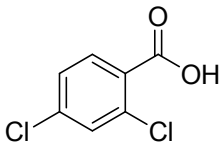
4-nitrobenzoic acid (3n):[6] According to general procedure B, **1n** (165 mg, 1 mmol) gave **3n** (120 mg, 72%) as a white solid. R_f = 0.45 (EtOAc/hexanes, 3:7); m.p. 233-235 ºC; ^{1}H NMR (300 MHz, DMSO-d) δ: 8.29 (d, *J* = 8.80 Hz, 2H), 8.14 (d, *J* = 8.79 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d) δ: 165.8, 150.0, 136.3, 130.6, 123.7; IR (KBr) ν: 3019.6, 1654.5, 1384.6, 1215.5, 1069.8, 757.3, 669.1 cm^{-1}. MS (EI) *m/z* 166 [M-1]$^+$.



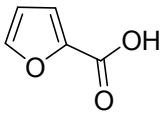
4-Cynobenzoic acid (3o):[10] According to general procedure B, **1o** (145 mg, 1 mmol) gave **3o** (89 mg, 61%) as a white solid. R_f = 0.45 (EtOAc/hexanes, 3:7); m.p. 233-235 ºC; ^{1}H NMR (300 MHz, DMSO-d) δ: 8.09-8.06 (m, 2H), 7.99-7.96 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d) δ:166.0, 134.8, 133.2, 132.6, 129.9, 118.1, 115.0; IR (KBr) ν: 3100, 2240, 1710, 1557, 988, 773, 639cm^{-1}. MS (EI) *m/z* 146 [M-1]$^+$.



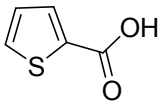
2, 4-dimethylbenzoic acid (3p):[11] According to general procedure B, **1p** (148 mg, 1 mmol) gave **3p** (130.5 mg, 87%) as a white solid. R_f = 0.5 (EtOAc/hexanes, 3:7); m.p. 120-122 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.98-7.97 (m, 1H), 7.09-7.08 (m, 2H), 2.63 (s, 3H) 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 173.2, 143.8, 141.7, 132.9, 132.0, 126.8, 125.6, 22.3, 21.6; IR (KBr) ν: 3020.5, 1692.6, 1216.5, 757.5s, 669.1 cm^{-1}. MS (EI) *m/z* 149 [M-1]$^+$.



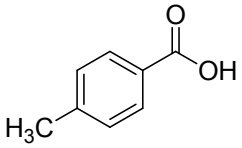
2, 4-dichlorobenzoic acid (3q):[12] According to general procedure B, **1q** (188 mg, 1 mmol) gave **3q** (99 mg, 52%) as a white solid. R_f = 0.5 (EtOAc/hexanes, 3:7); m.p. 154-156 ºC; ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d) δ: 9.00 (bs, 1H), 7.76-7.73 (m, 1H), 7.339-7.331 (m, 1H), 7.18-7.15 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d) δ: 166.1, 137.3, 134.3, 132.3, 130.3, 128.8, 126.5; IR (KBr) ν: 3399.4, 1698.7, 1588.1, 1384.2, 1216.3, 1051.9, 771.0, 668.5 cm^{-1}. MS (EI) *m/z* 189 [M-1]$^+$.



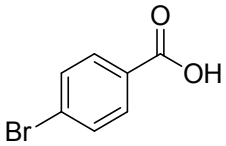
Furan-2-carboxylic acid (3r):[13] According to general procedure B, **1r** (110 mg, 1 mmol) gave **3r** (89 mg, 80%) as a white solid. R_f = 0.5 (EtOAc/hexanes, 3:7); m.p. 228-230 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.42 (bs, 1H), 7.62 (s, 1H), 7.31 (d, *J* = 3.27 Hz, 1H), 6.54-6.53 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 163.9, 147.6, 144.0, 120.3, 112.4; IR (KBr) ν: 3381.8, 2914.2, 1680.6, 1581.3, 1420.8, 1301.9, 1183.4, 921.6, 758.1, 593.8 cm^{-1}. MS (EI) *m/z* 113 [M+1]$^+$.



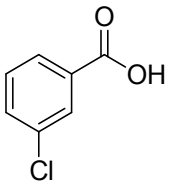
Thiophene-2-carboxylic acid (3s):[2] According to general procedure B, **1s** (126 mg, 1 mmol) gave **3s** (114 mg, 89%) as a white solid. R_f = 0.5 (EtOAc/hexanes, 3:7); m.p. 122-124 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.89 (dd, *J* = 3.75, 1.25 Hz, 1H), 7.65 (dd, *J* = 4.95, 1.17 Hz, 1H), 7.15-7.14 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 167.7, 135.2, 134.2, 133.0, 128.2; IR (KBr) ν: 3019.6, 1654.5, 1384.6, 1215.5, 1069.8, 757.3, 669.1 cm^{-1}. MS (EI) *m/z* 128 [M+1]$^+$.



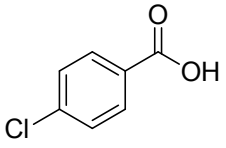
4-methylbenzoic acid (3t):[6] According to general procedure B, **5f** (160 mg, 1 mmol) gave **3t** (122 mg, 90%) as a white solid. R_f = 0.5 (EtOAc/hexanes, 3:7); m.p. 181-183 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.01 (d, *J* = 8.23 Hz, 2H), 7.27 (d, *J* = 7.91 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 172.3, 144.8, 130.4, 129.4, 126.7, 21.9; IR (KBr) ν: 170.4, 140.1, 131.7, 131.5, 130.8, 130.0, 125.5, 21.7 cm^{-1}. MS (EI) *m/z* 135 [M-1]$^+$.



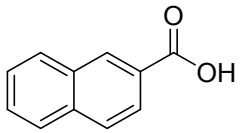
4-bromobenzoic acid (3u):[2] According to general procedure B, **5h** (224 mg, 1 mmol) gave **3u** (155 mg, 78%) as a white solid. R_f = 0.5 (EtOAc/hexanes, 3:7); m.p. 248-250 ºC; ^{1}H NMR (300 MHz, DMSO-d) δ: 13.17 (bs, 1H), 7.87-7.85 (m, 2H), 7.71-7.69 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d) δ: 166.5, 131.6, 131.2, 130.0, 126.8; IR (KBr) ν: 3395.8, 3021.1, 1676.2, 1425.1, 1296.8, 1215.6, 761.7 cm^{-1}. MS (EI) *m/z* 198 [M-1]$^+$.



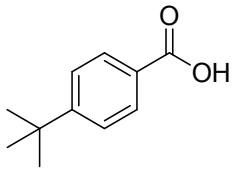
3-chlorobenzoic acid (3v):[14] According to general procedure B, **5d** (180 mg, 1 mmol) gave **3v** (100 mg, 64%) as a white solid. R_f = 0.5 (EtOAc/hexanes, 3:7); m.p. 154-156 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.10 (t, *J* = 1.83 Hz, 1H), 8.01 - 7.99 (dt, *J* = 7.83, 1.27 Hz, 1H), 7.61-7.58 (m, 1H) 7.43 (t, *J* = 7.87 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.1, 134.9, 134.1, 131.1, 130.4, 130.0, 128.5; IR (KBr) ν: 3019.7, 1302.7, 1261.5, 1215.5, 757.7, 669.0 cm^{-1}. MS (EI) *m/z* 155 [M-1]$^+$.



4-chlorobenzoic acid (3w):[2] According to general procedure B, **5g** (180 mg, 1 mmol) gave **3w** (106 mg, 68%) as a white solid. R_f = 0.5 (EtOAc/hexanes, 3:7); m.p. 236-238 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.76-7.74 (m, 2H), 7.44-7.42 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.4, 138.5, 131.9, 129.1, 129.0; IR (KBr) ν: 3400.5, 3019.5, 1647.0, 1215.4, 757.9, 669.1 cm^{-1}. MS (EI) *m/z* 155 [M-1]$^+$.

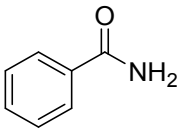


2-naphthoic acid (3x):[3] According to general procedure B, **5k** (196 mg, 1 mmol) gave **3x** (100 mg, 58%) as a white solid. R_f = 0.3 (EtOAc/hexanes, 3:7); m.p. 182-184 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.72 (s, 1H), 8.12 (dd, *J* = 8.59, 1.57 Hz, 1H), 8.00 (d, *J* = 8.06 Hz, 1H), 7.9- 7.90 (m, 2H), 7.64 - 7.56 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 171.5, 136.1, 132.6, 132.3, 129.7, 128.8, 128.5, 128.0, 127.0, 125.6; IR (KBr) ν: 3066.3, 1686.2, 1216.4, 769.6, 669.6 cm^{-1}. MS (EI) *m/z* 171 [M-1]$^+$.

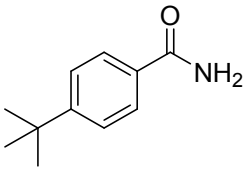


4-(tert-butyl) benzoic acid (3y):[4] According to general procedure B, **6e** (158 mg, 1 mmol) gave **3y** (108 mg, 61%) as a white solid. R_f = 0.5 (EtOAc/hexanes, 3:7); m.p. 166-168 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.05 (d, *J* = 8.80 Hz, 2H), 7.50 (d, *J* = 8.80 Hz, 2H), 1.36 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 172.7, 157.8, 130.3, 126.8, 125.7, 35.4, 31.3; IR (KBr) ν: 3020.8, 2965.0, 1687.6, 1286.5, 1215.9, 760.1, 669.6 cm^{-1}. MS (EI) *m/z* 177 [M-1]$^+$.

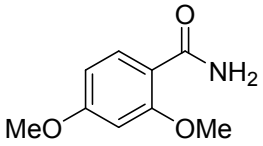
4 General procedure for the synthesis of Benzamides (C): A mixture of acetophenones (1 mmol, 1 eq.), sodiumazied (6 mmol, 6 eq.) and Iodine(30 mol%) in dimethyl sulfoxide/water (1:1) and acetic acid (4eq) was stirred at 100 °C under open air for the appropriate time (Table 7). After completion of the reaction, as indicated by TLC, the mixture was diluted with water and extracted with EtOAc (4×20 mL). The extract was washed with brine, drying over Na_2SO_4 and evaporation, the crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc) to afford the product.



Benzamide (7a):[15]According to general procedure c, **1a** (120 mg, 1 mmol) gave **7a** (78.6 mg, 65%) as a white solid. R_f = 0.3 (EtOAc/hexanes, 3:7); m.p.126-128 ºC; ^{1}H NMR (300 MHz, DMSO) δ: 7.97(bs, 1H), 7.88-7.85 (m, 2H), 7.51-7.41(m, 3H); ^{13}C NMR (75 MHz, DMSO) δ: 167.9, 134.2, 131.2, 128.2, 127.4; IR (KBr) ν: 3358.3, 3160.5, 2980.6, 1650.3, 1620.5, 1570.2, 1440.5, 1179.5, 1070.6.6, 1024.5, 917.8, 768.9cm^{-1}. MS (EI) *m/z* 122 [M+1]$^+$.

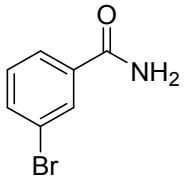


4-(tert-butyl)benzamide (7b):[16]According to general procedure c, **1t** (176 mg, 1 mmol) gave **7b** (154 mg, 87%) as a white solid. R_f = 0.3 (EtOAc/hexanes, 7:3); m.p. 183-185 ºC; ^{1}H NMR (300 MHz, DMSO-d) δ: 7.89 (bs, 1H), 7.79 (d, *J* = 8.35 Hz, 2H), 7.74 (d, *J* = 8.34 Hz, 2H), 7.27 (bs, 1H), 1.28(s, 9H); ^{13}C NMR (75 MHz, DMSO-d) δ: 167.7, 153.9, 131.5, 127.2, 124.9, 117.9, 34.5, 31.2, 30.9; IR (KBr) ν: 3351.3, 3145.3, 3062.5, 1560.2, 1145.0, 1062.5, 860.6, 774.6cm^{-1}. MS (EI) *m/z* 178 [M+1]$^+$.

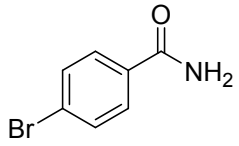


2, 4- dimethoxybenzamide (7c):[17]According to general procedure c, **1u** (180 mg, 1 mmol) gave **7c** (130 mg, 72%) as a white solid. R_f = 0.3 (EtOAc/hexanes, 7:3); m.p. 132-134ºC; ^{1}H NMR

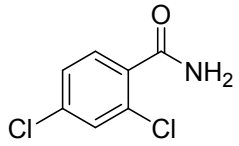
(300 MHz, DMSO-d) δ: 7.83 (d, *J* = 8.43 Hz, 1H), 7.49 (bs, 1H), 7.37 (bs, 1H), 6.62-6.59(m, 2H), 3.89 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d) δ:165.6, 162.9, 158.8, 132.6, 114.6, 105.5, 98.3, 55.9, 55.4; IR (KBr) ν: 3365.2, 3120.5, 1650.2, 1440.8, 1220.6, 1203.0, 1150.9, 760.5cm^{-1}. MS (EI) *m/z* 182 [M+1]$^{+}$.



3-bromobenzamide (7d):[18]According to general procedure c, **1h** (197 mg, 1 mmol) gave **7d** (115 mg, 58%) as a white solid. R_f = 0.3 (EtOAc/hexanes, 7:3); m.p. 152-153 ºC; ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d) δ: 8.00 (s, 1H), 7.77 (d, *J* = 7.83 Hz, 2H), 7.70 (bs, 1H), 7.54 (s, 1H), 7.24 (t, *J* = 7.95 Hz, 1H), 6.57 (bs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d) δ: 167.1, 135.7, 133.6, 129.4, 125.9, 121.6; IR (KBr) ν: 3340.2, 3150.8, 3065.2, 1650, 1562.9, 1426.0, 1147.6, 1125.0, 1064.5cm^{-1}. MS (EI) *m/z* 200 [M+2]$^{+}$.

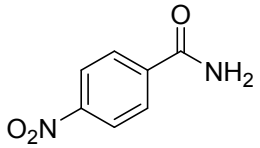


4-bromobenzamide (7e):[15] According to general procedure c, **1v** (197 mg, 1 mmol) gave **7e** (123 mg, 62%) as a white solid. R_f = 0.3 (EtOAc/hexanes, 7:3); m.p. 186-188 ºC; ^{1}H NMR (300 MHz, DMSO-d) δ: 8.05 (s, 1H), 7.80 (d, *J* = 8.41 Hz, 2H), 7.65 (d, *J* = 8.36 Hz, 2H), 7.47 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d) δ: 166.8, 133.3, 131.1, 129.5, 124.9; IR (KBr) ν: 3350.2, 3170.6, 1652.6, 1614.2, 1520.8, 14.3.6, 1380.5, 1145.3, 1065, 775.5cm^{-1}. MS (EI) *m/z* 200 [M+2]$^{+}$.

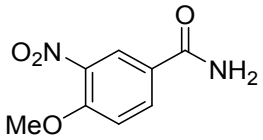


2,4-dichlorobenzamide (7f):[19]According to general procedure c, **1q** (189 mg, 1 mmol) gave **7f** (114 mg, 60%) as a white solid. R_f = 0.3 (EtOAc/hexanes, 7:3); m.p. 187-189 ºC; ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d) δ: 7.40 (bs, 1H), 7.42 (s, 1H), 7.35 (d, *J* = 1.92 Hz, 1H), 7.23 (dd, *J* = 8.25, 1.94 Hz, 1H), 7.13 (bs, 1H); ^{13}C NMR (75 MHz, DMSO-d) δ: 167.2, 135.0, 134.3, 131.0,

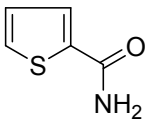
129.8, 129.0, 126.4; IR (KBr) ν: 3377.2, 3182.2, 1620, 1570.3, 1360.2, 1141cm^{-1}. MS (EI) *m/z* 190 [M+2]$^{+}$.



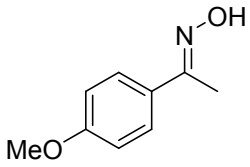
4-nitrobenzamide (7g):[20]According to general procedure c, **1n** (165 mg, 1 mmol) gave **7g** (88 mg, 53%) as a white solid. R_f = 0.2 (EtOAc/hexanes, 7:3); m.p. 196-198 ºC; ^{1}H NMR (300 MHz, DMSO-d) δ: 8.30 (d, *J* = 8.66 Hz, 2H), 8.09 (d, *J* = 8.73 Hz, 2H), 7.73 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d) δ: 166.1, 149.0, 139.9, 128.8, 123.4; IR (KBr) ν: 3410.5, 3300.2, 3182.3, 1650.8, 1613.8, 1580.5, 1502.6, 1338.6, 1117.8, 865, 761.5cm^{-1}. MS (EI) *m/z* 167 [M+1]$^{+}$.



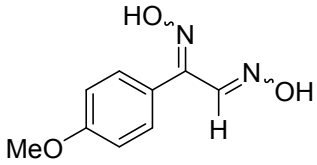
4-methoxy-3-nitrobenzamide (7h): According to general procedure c, **1w** (195 mg, 1 mmol) gave **7h** (110 mg, 56%) as a white solid. R_f = 0.2 (EtOAc/hexanes, 7:3); m.p. 205-207 ºC; ^{1}H NMR (300 MHz, DMSO-d) δ: 8.38 (d, *J* = 2.13 Hz, 1H), 8.19-8.16 (m, 2H), 7.52 (bs, 1H), 7.45 (d, *J* = 8.85, 1H), 3.98 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d) δ: 165.4, 154.0, 138.6, 133.5, 126.2, 124.3, 114.1, 57.0; IR (KBr) ν: 3380.4, 3290.5, 3008.2, 1620.5, 1601.7, 1332.5, 1200.5, 1102.3, 820.5, 752.3cm^{-1}. HRMS (ESI) calcd for $C_8H_8N_2O_4$ [M+H]$^{+}$: 197.0562; found: 197.0566



Thiophene-2-carboxamide (7i):[21]According to general procedure c, **1s** (126 mg, 1 mmol) gave **7** (95 mg, 75%) as a white solid. R_f = 0.3 (EtOAc/hexanes, 7:3); m.p. 175-177 ºC; ^{1}H NMR (300 MHz, DMSO-d) δ: 7.96 (bs, 1H), 7.73 (d, *J* = 4.36 Hz, 2H), 7.38 (bs, 1H), 7.12 (t, *J* = 4.31 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d) δ:162.8, 140.2, 130.9, 128.6, 127.8; IR (KBr) ν: 3350, 3160.2, 1650.8, 1532.5,1430.8, 1140.3, 1105, 825.3, 770.8cm^{-1}. MS (EI) *m/z* 128 [M+1]$^{+}$.

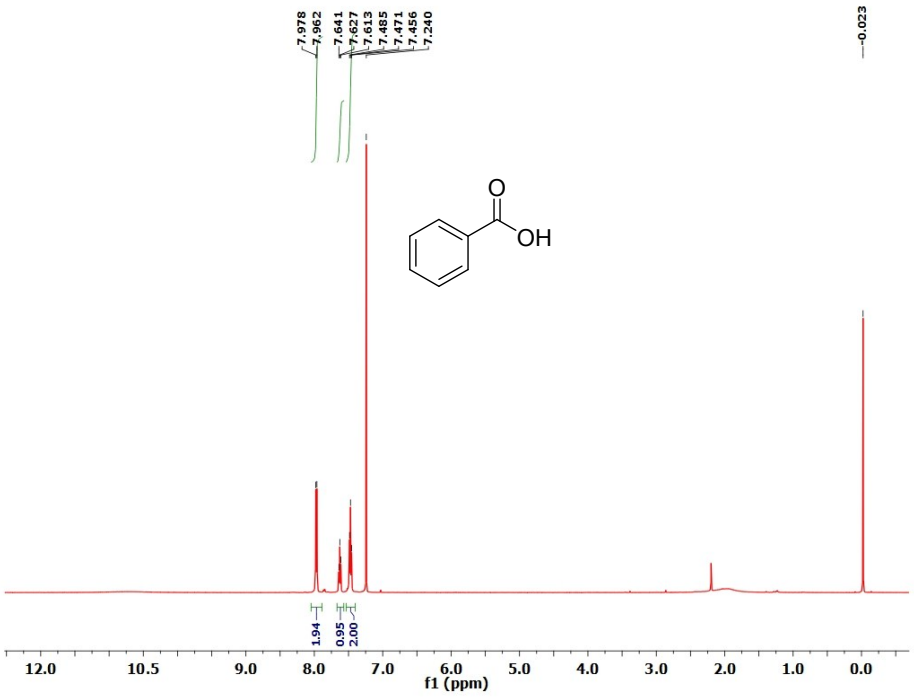


5. (E)-1-(4-methoxyphenyl)ethan-1-one oxime (2j):[22] A mixture of acetophenone (1j, 1 mmol, 1 eq.), Hydroxylamine hydrochloride (2 mmol, 2 eq.) and I_2 (10 mol%) in dimethyl sulfoxide (5 mL) was stirred at 50 °C for 2 h . After completion of the reaction, as indicated by TLC, the mixture was diluted with water and extracted with EtOAc (3×20 mL). The extract was washed with brine, drying over Na_2SO_4 and evaporation, the crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc) to afford the product 2j (158 mg, 95%) as a white solid. R_f = 0.4 (EtOAc/hexanes, 3:7); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.69 (bs, 1H), 7.57 (d, *J* = 8.85 Hz, 2H), 6.90 (d, *J* = 8.85 Hz, 2H), 3.83 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 160.6, 155.7, 129.2, 127.5, 114.0, 55.5,12.3; IR (KBr) ν: 3205.1, 3071.5, 2986.8, 1620.6, 1288.0, 1026.4, 910.0, 756.2 cm^{-1}. MS (EI) *m/z* 166 $[M]^+$.

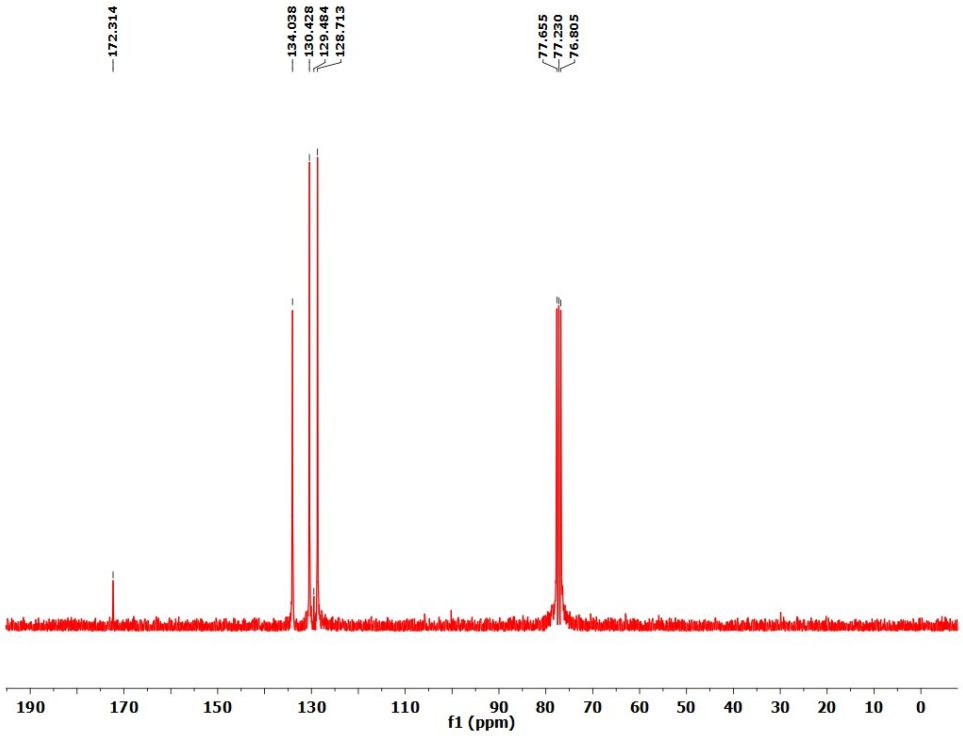


6. 2-(hydroxyimino)-2-(4-methoxyphenyl)acetaldehyde oxime (9): A mixture of 2-(4-methoxyphenyl)-2-oxoacetaldehyde (1 mmol, 1 eq.), Hydroxylamine hydrochloride (4 mmol, 4 eq.) and pyridine(1 mmol, 1 eq) in methnol (25 mL) was stirred at 60 °C for 4 h . After completion of the reaction, as indicated by TLC, the mixture was concentrated, diluted with water and extracted with EtOAc (3×20 mL). The extract was washed with brine, drying over Na_2SO_4 and evaporation, the crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc) to afford the product (116 mg, 60%) as a white solid. R_f = 0.3 (EtOAc/hexanes, 7:3); ^{1}H NMR (300 MHz, DMSO) δ: 11.83 (s, 1H), 11.72 (s, 1H), 11.65 (s, 0.3H), 11.30 (s, 0.3H), 8.44 (s, 1H), 7.84 (s, 0.3H), 7.54 (d, *J* = 8.30 Hz, 2H), 7.31 (d, *J* = 8.40 Hz, 0.7 H), 6.93 (d, *J* = 9.20 Hz, 2H), 3.77 (s, 4H); ^{13}C NMR (75 MHz, DMSO) δ: 159.7, 159.1, 152.3, 150.3, 148.1, 140.8, 130.6, 129.7, 126.3, 122.6, 113.3, 112.9, 55.14, 55.10; MS (EI) *m/z* 195 $[M+1]^+$.

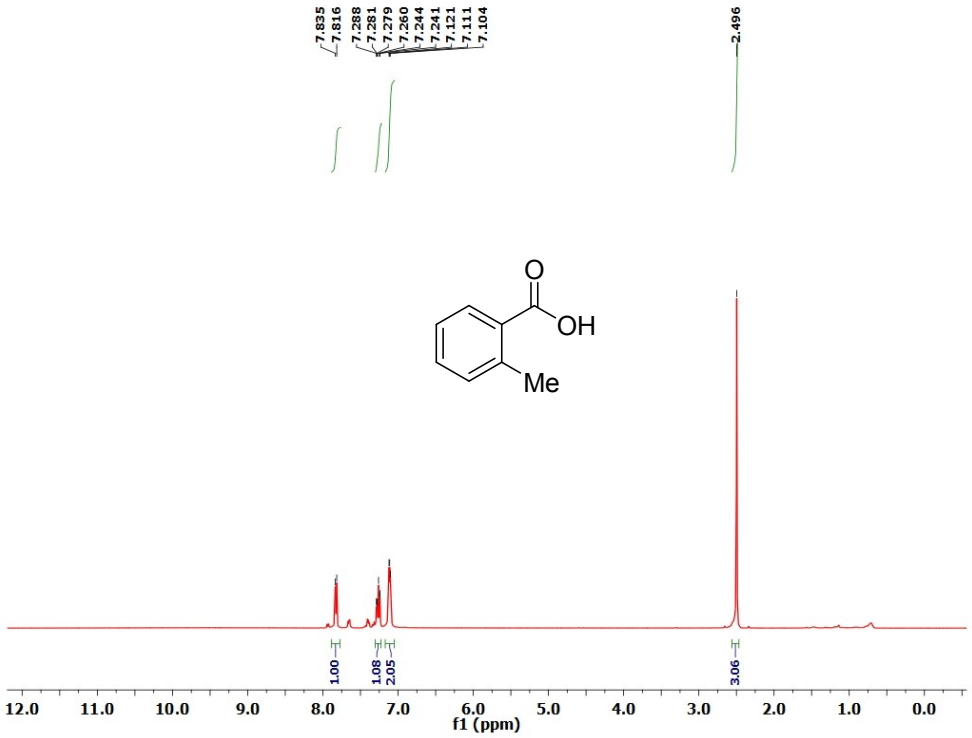
7. ^{1}H and ^{13}C NMR spectra



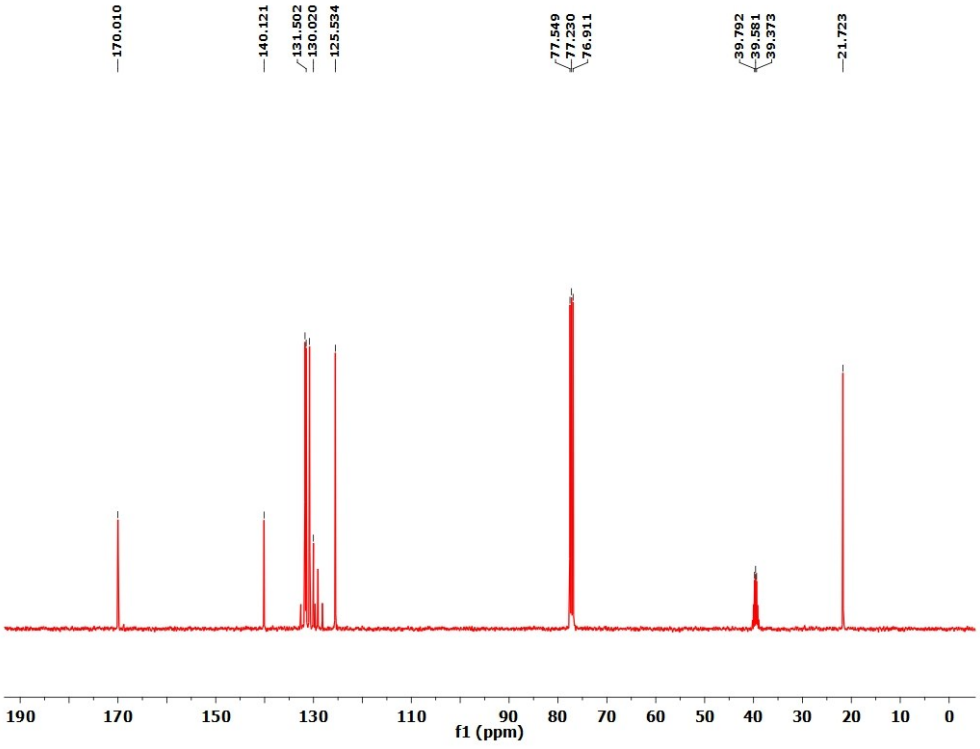
^{1}H-NMR spectrum of **3a** (75 MHz, $CDCl_3$)



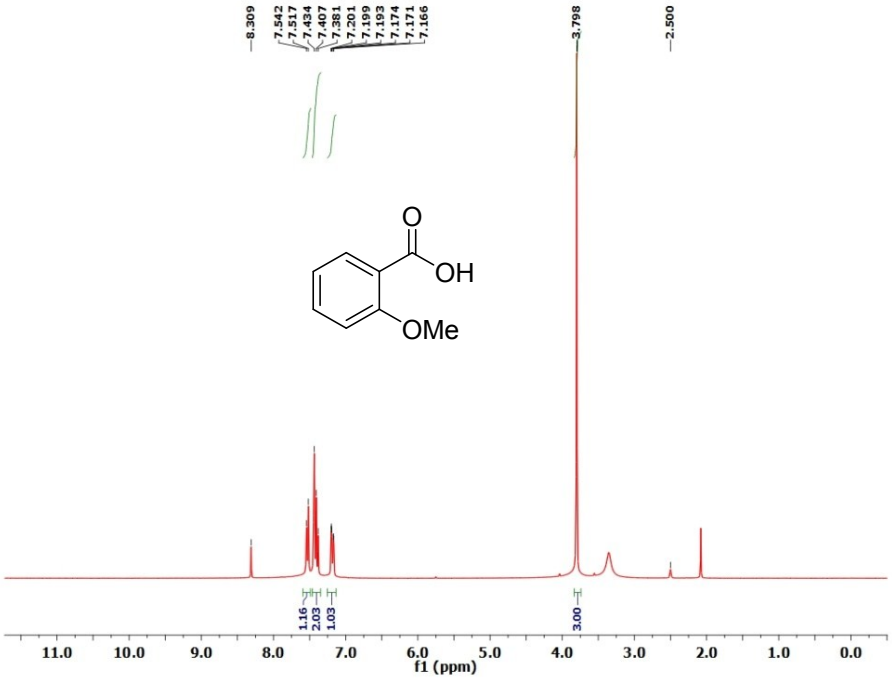
^{13}C-NMR spectrum of **3a** (75 MHz, $CDCl_3$)



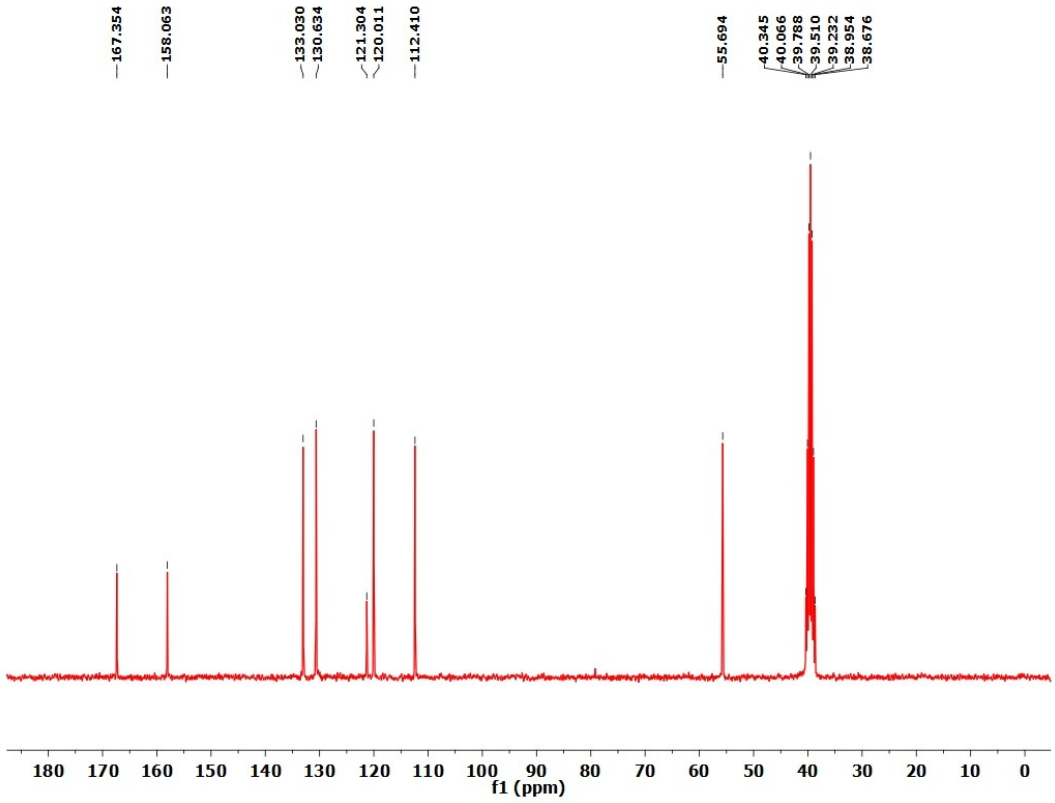
^{1}H-NMR spectrum of **3b** (75 MHz, $CDCl_3$ + DMSO)



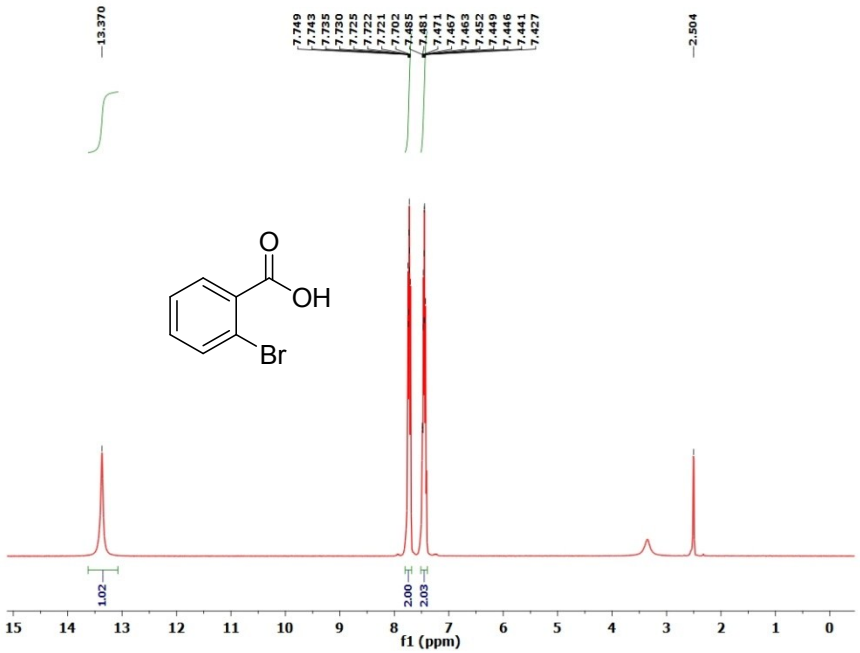
^{13}C-NMR spectrum of **3b** (75 MHz, $CDCl_3$ + DMSO)



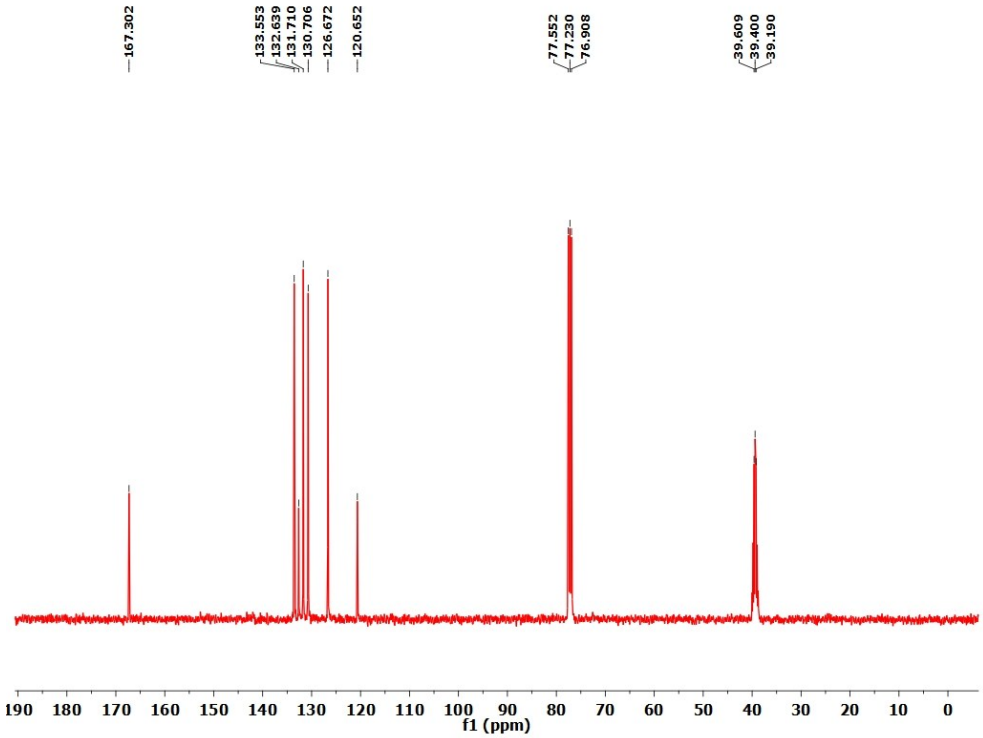
^{1}H-NMR spectrum of **3c** (75 MHz, DMSO)



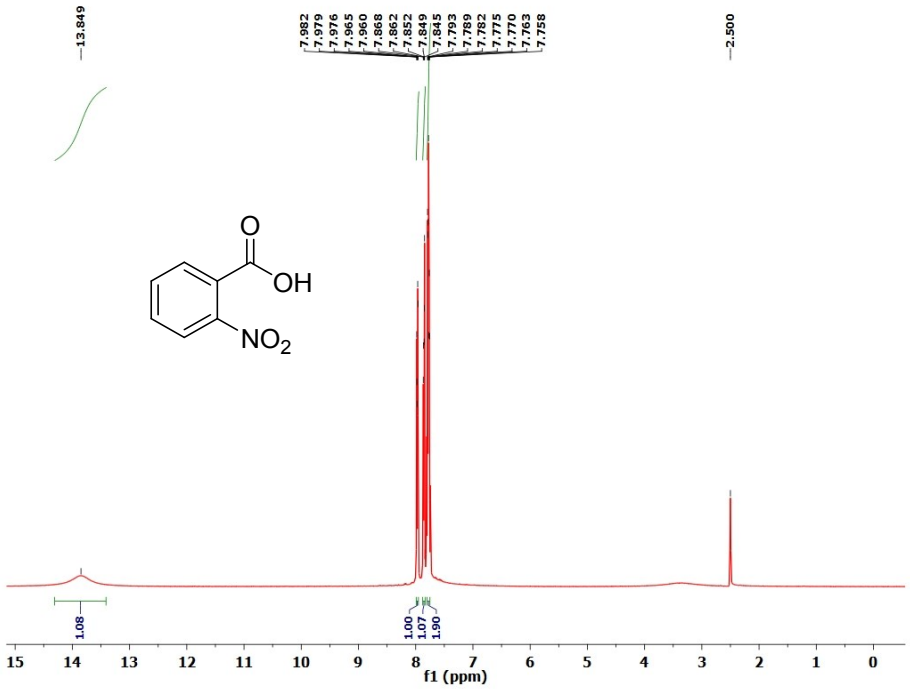
^{13}C-NMR spectrum of **3c** (75 MHz, DMSO)



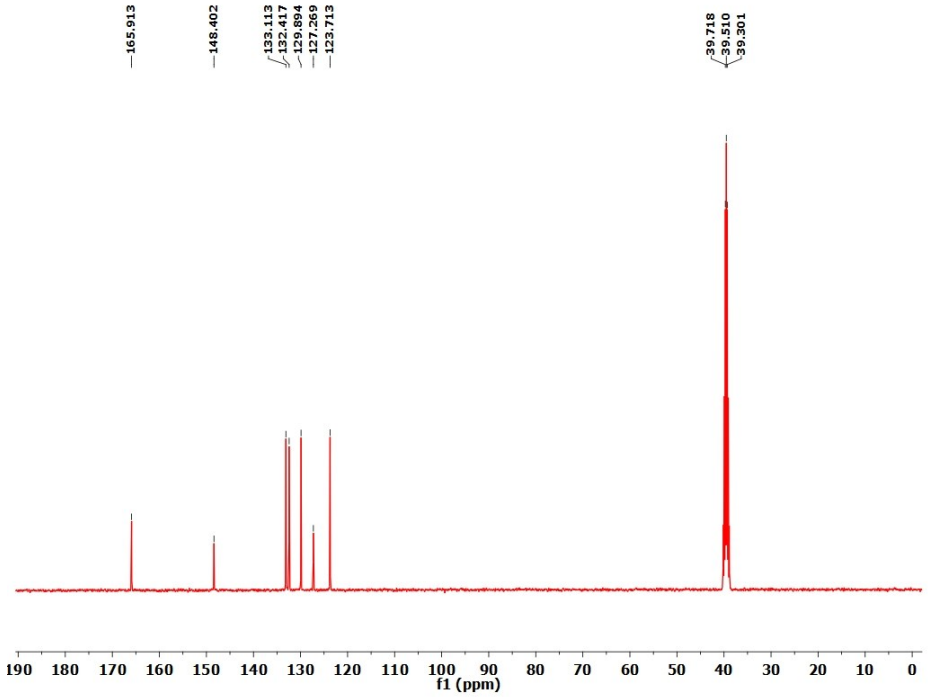
^{1}H-NMR spectrum of **3d** (75 MHz, $CDCl_3$ + DMSO)



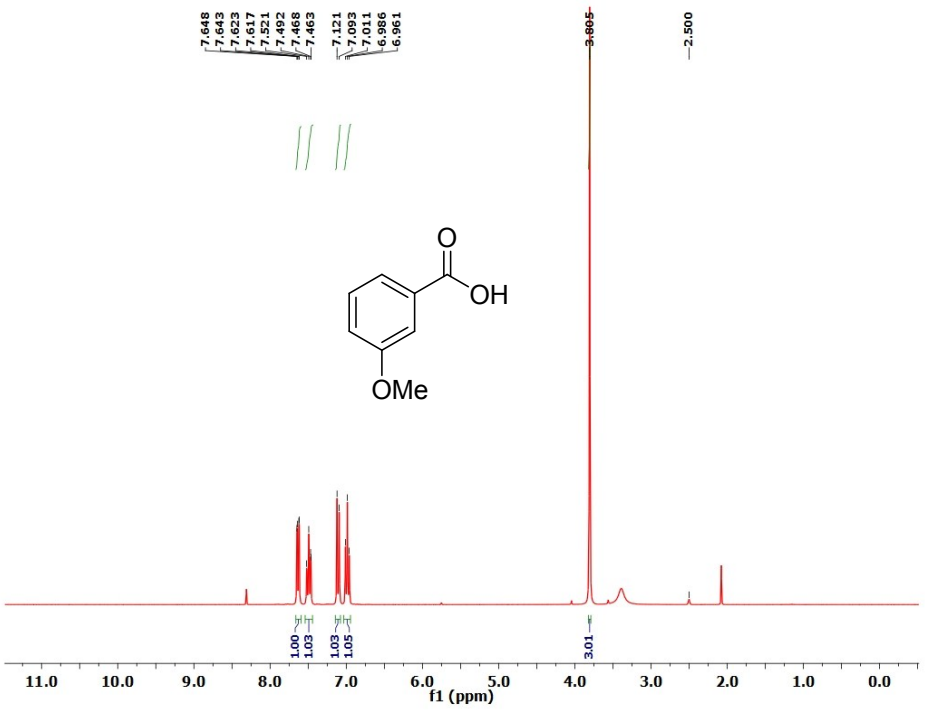
^{13}C-NMR spectrum of **3d** (75 MHz, $CDCl_3$ + DMSO)



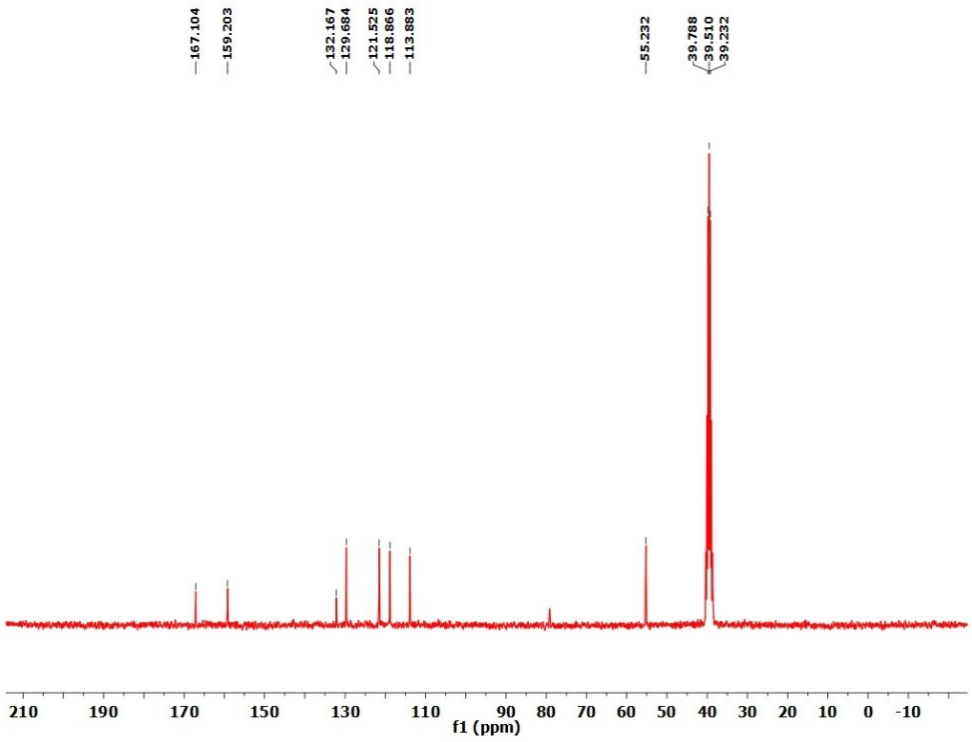
^{1}H-NMR spectrum of **3e** (75 MHz, DMSO)



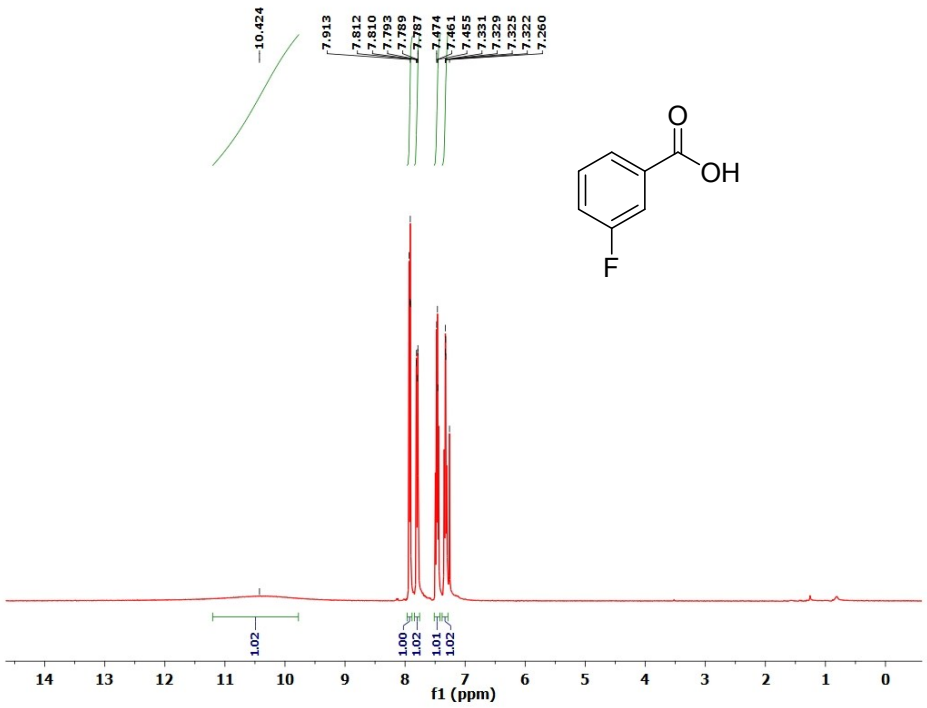
^{13}C-NMR spectrum of **3e** (75 MHz, DMSO)



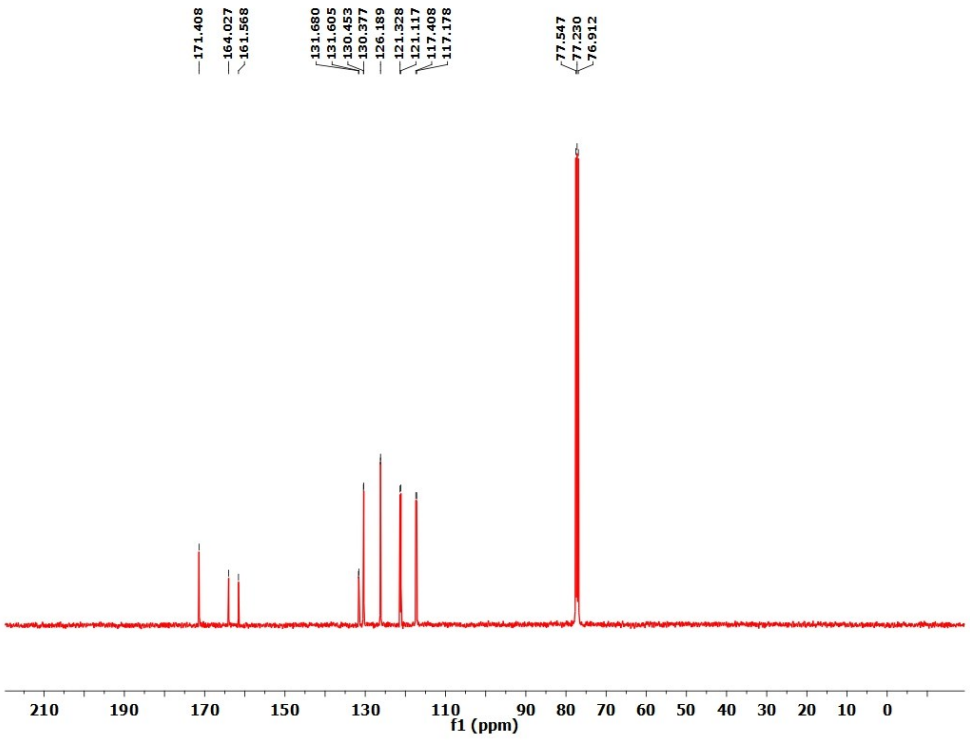
^{1}H-NMR spectrum of **3f** (75 MHz, DMSO)



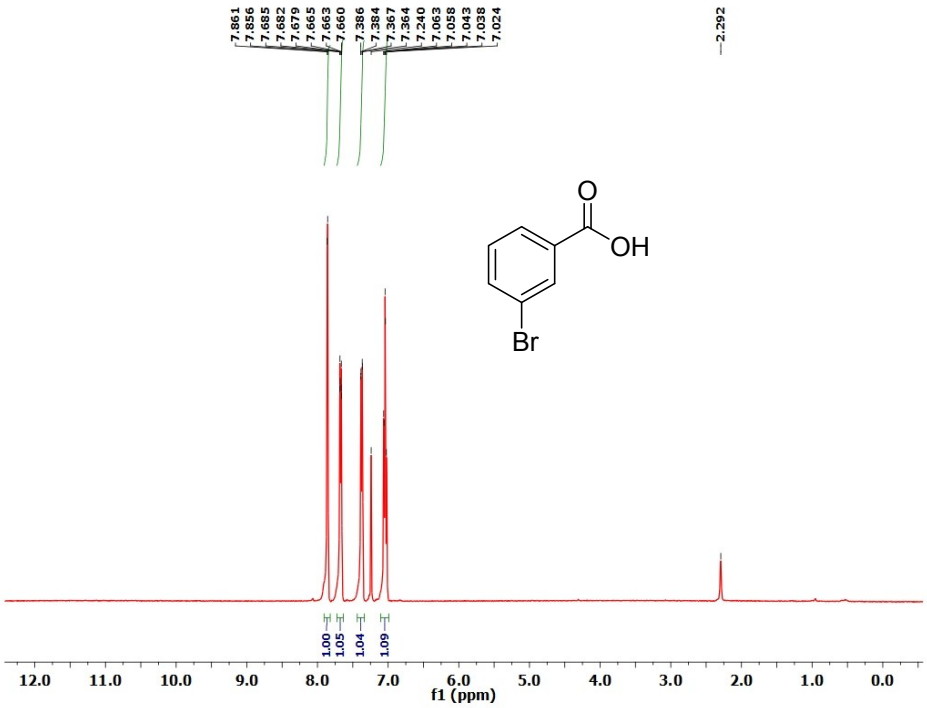
^{13}C-NMR spectrum of **3f** (75 MHz, DMSO)



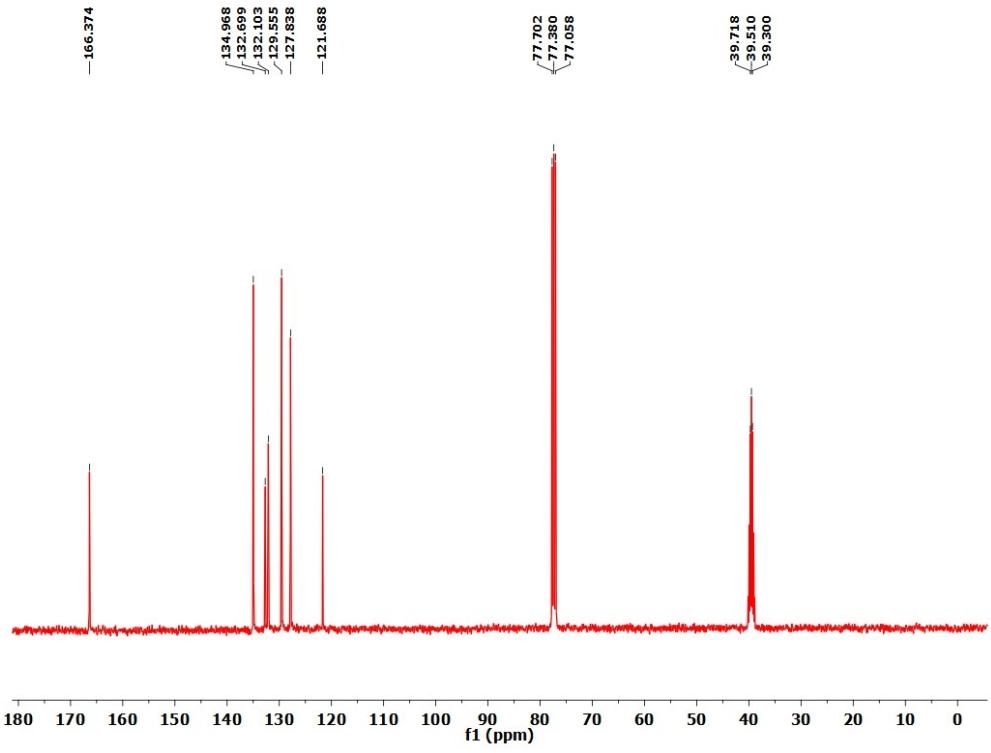
^{1}H-NMR spectrum of **3g** (75 MHz, $CDCl_3$)



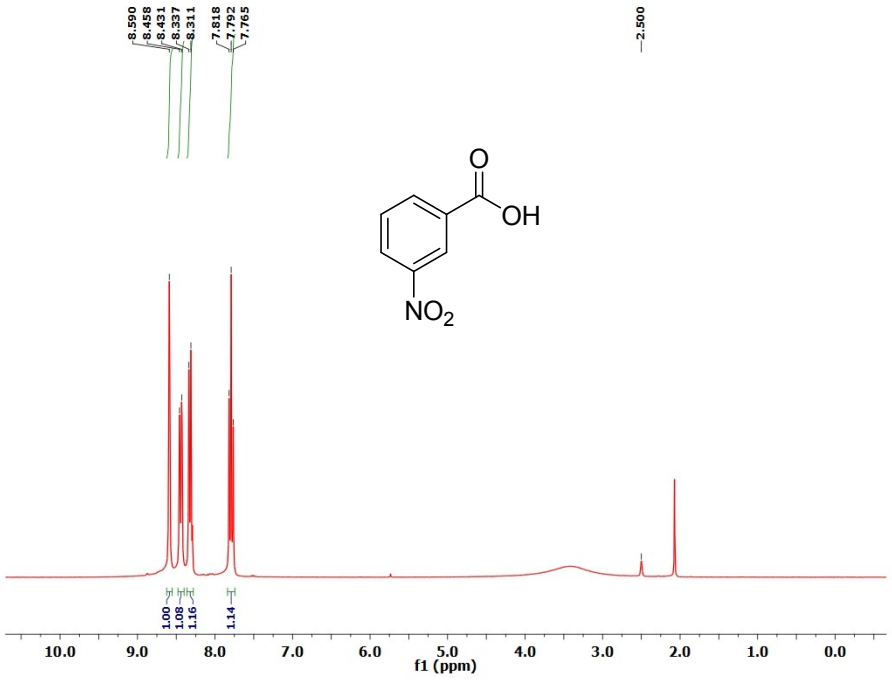
^{13}C-NMR spectrum of **3g** (75 MHz, $CDCl_3$)



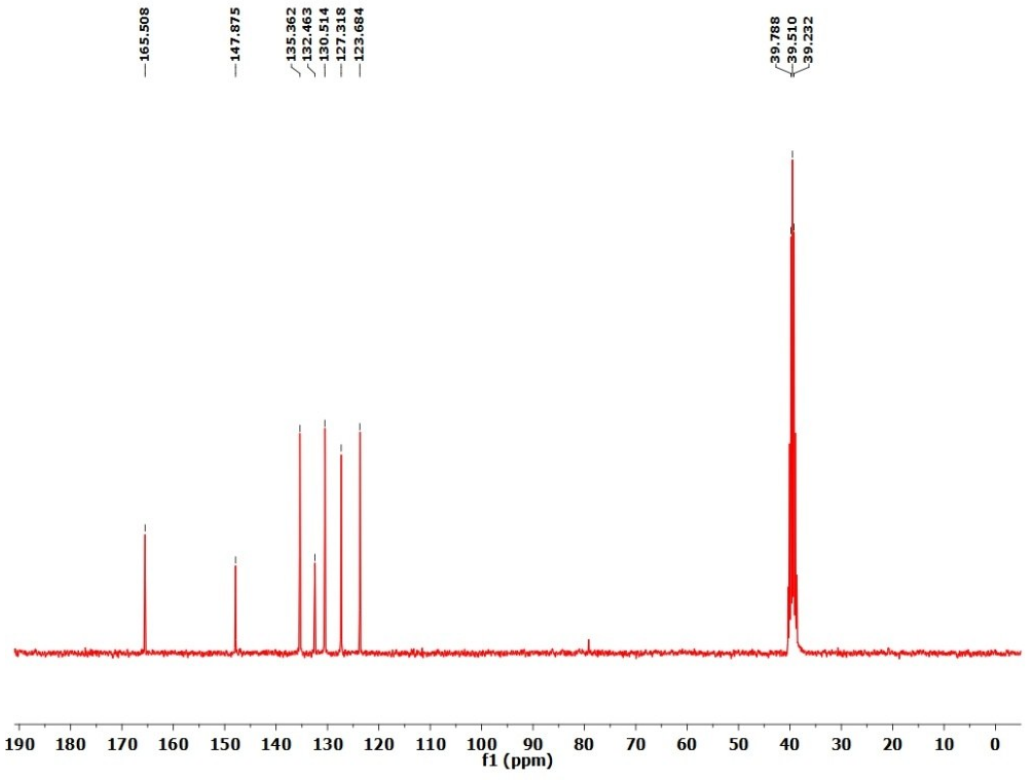
^{1}H-NMR spectrum of **3h** (75 MHz, $CDCl_3$ + DMSO)



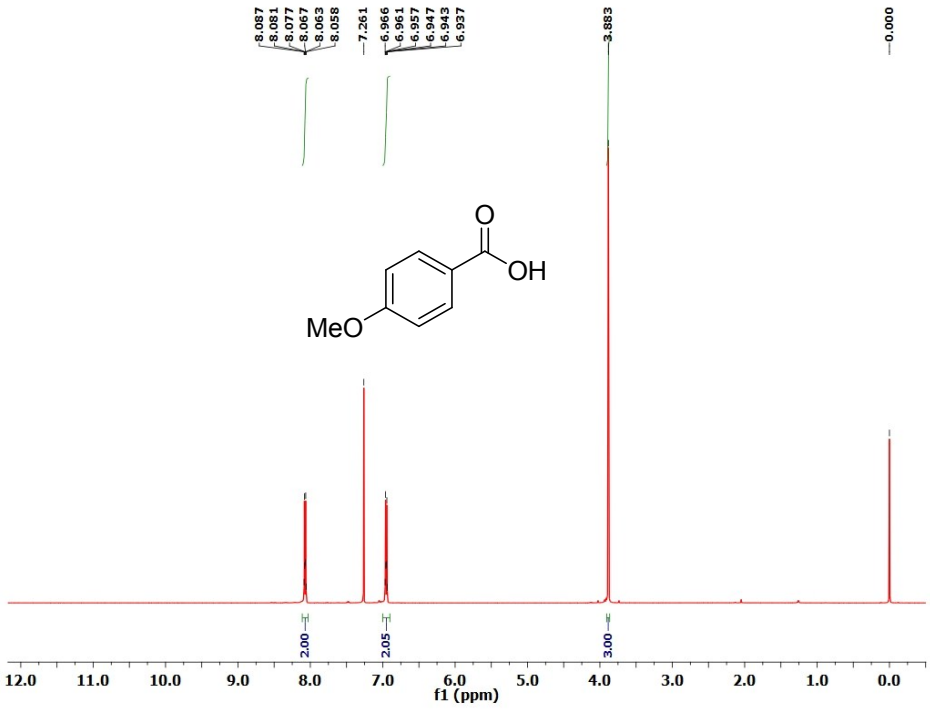
^{13}C-NMR spectrum of **3h** (75 MHz, $CDCl_3$ + DMSO)



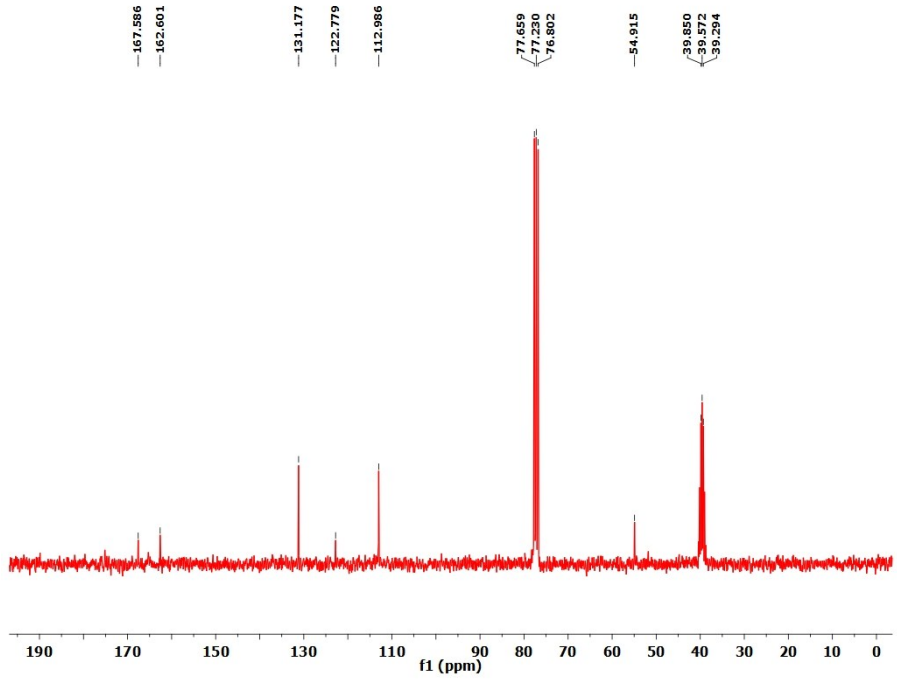
^{1}H-NMR spectrum of **3i** (75 MHz, DMSO)



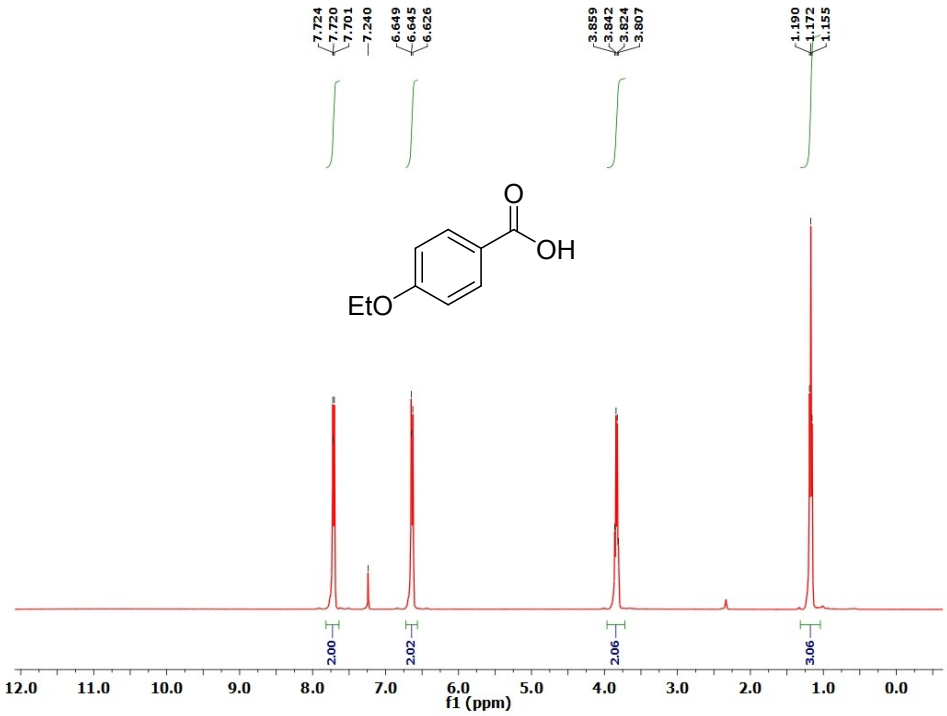
^{13}C-NMR spectrum of **3i** (75 MHz, DMSO)



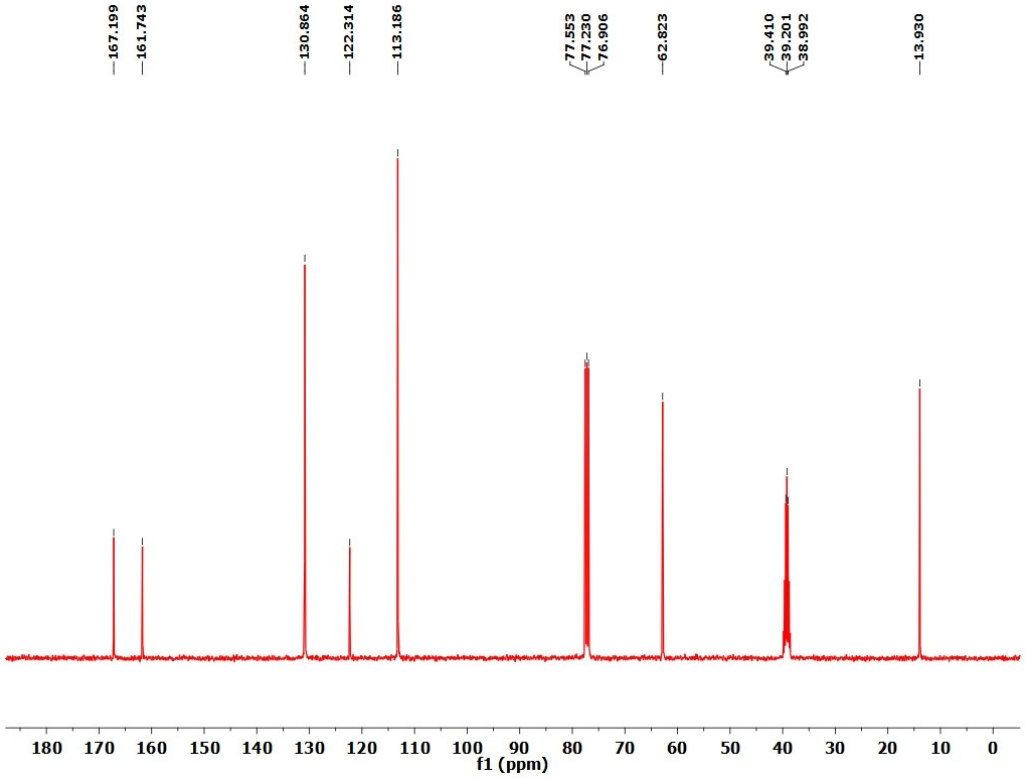
^{1}H-NMR spectrum of **3j** (75 MHz, $CDCl_3$)



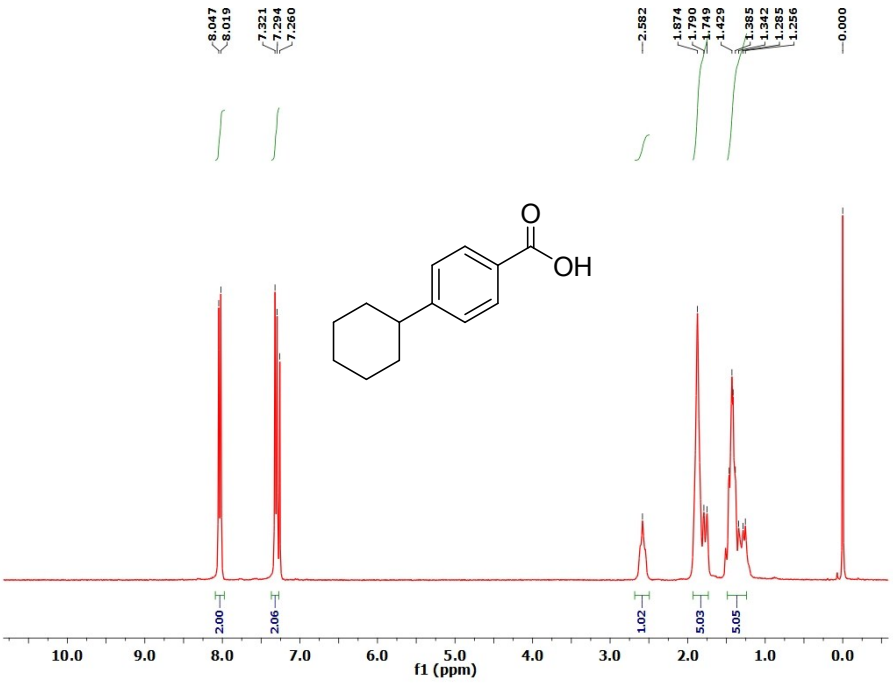
^{13}C-NMR spectrum of **3j** (75 MHz, $CDCl_3$+ DMSO)



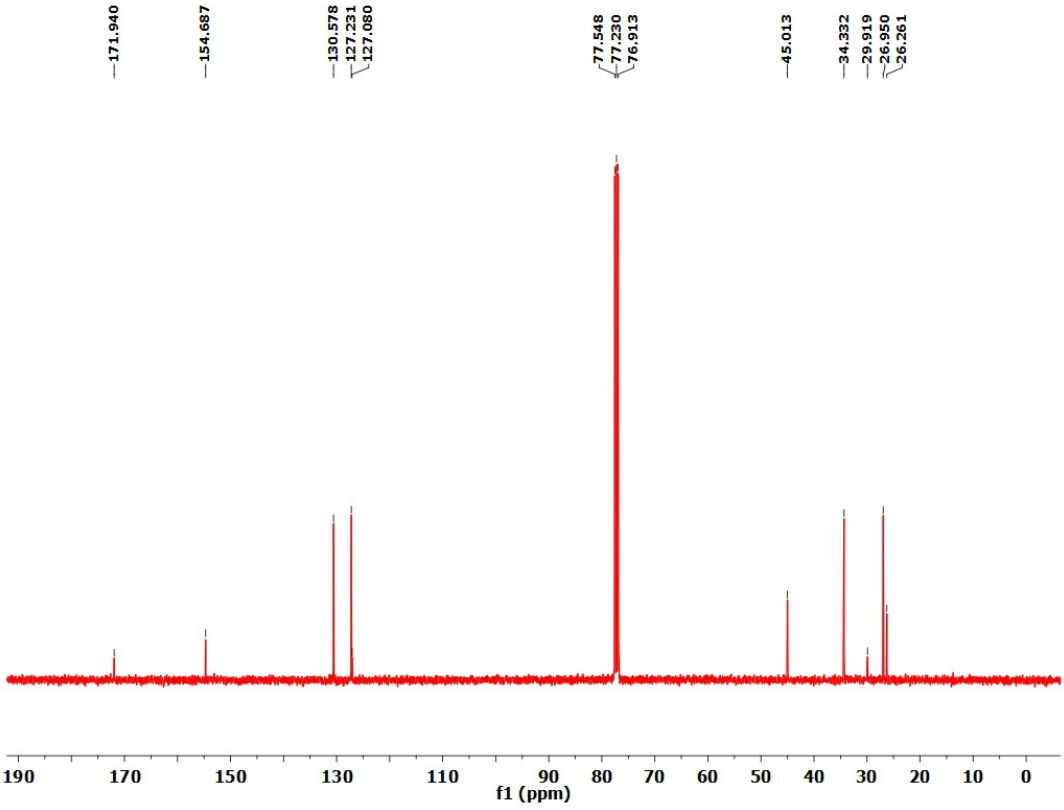
^{1}H-NMR spectrum of **3k** (75 MHz, $CDCl_3$+ DMSO)



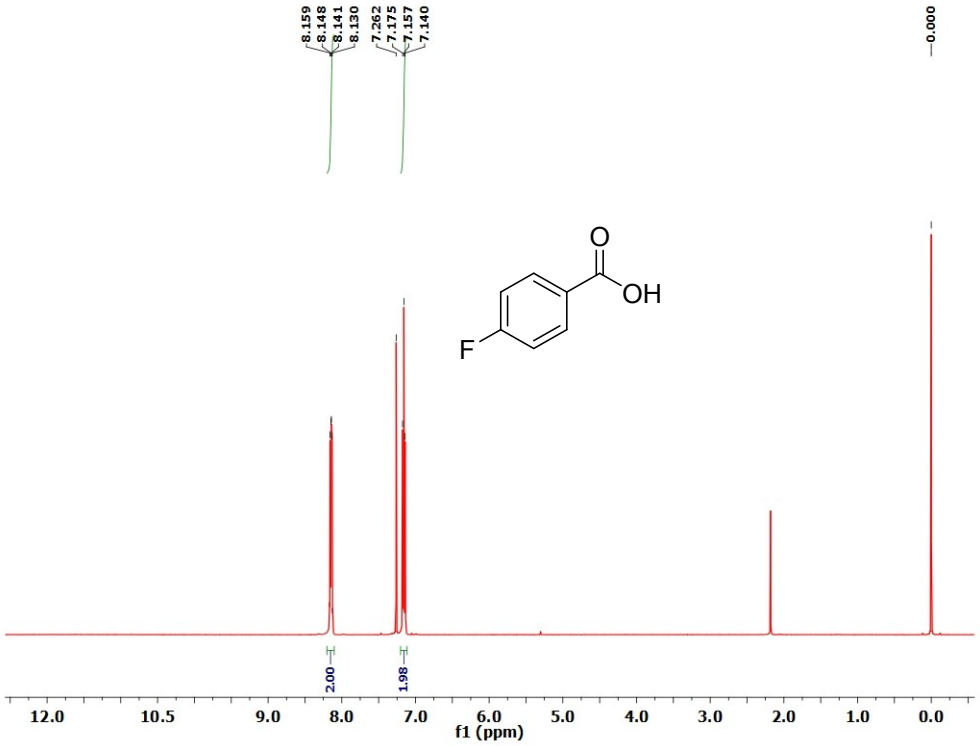
^{13}C-NMR spectrum of **3k** (75 MHz, $CDCl_3$+ DMSO)



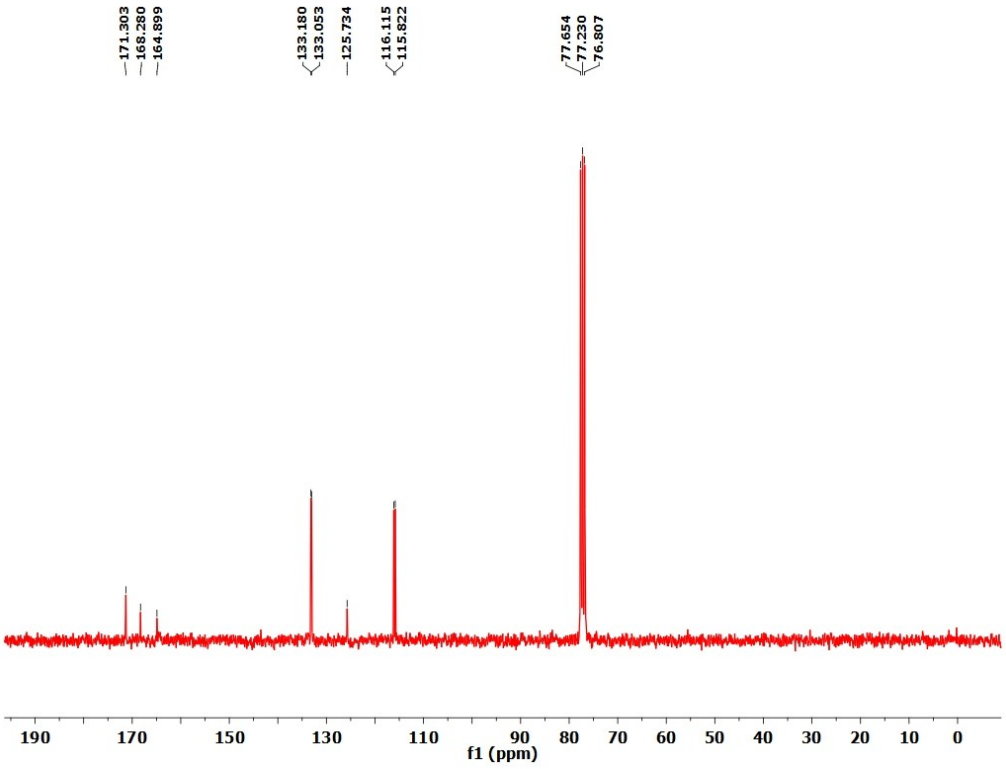
^{1}H-NMR spectrum of **3l** (75 MHz, $CDCl_3$)



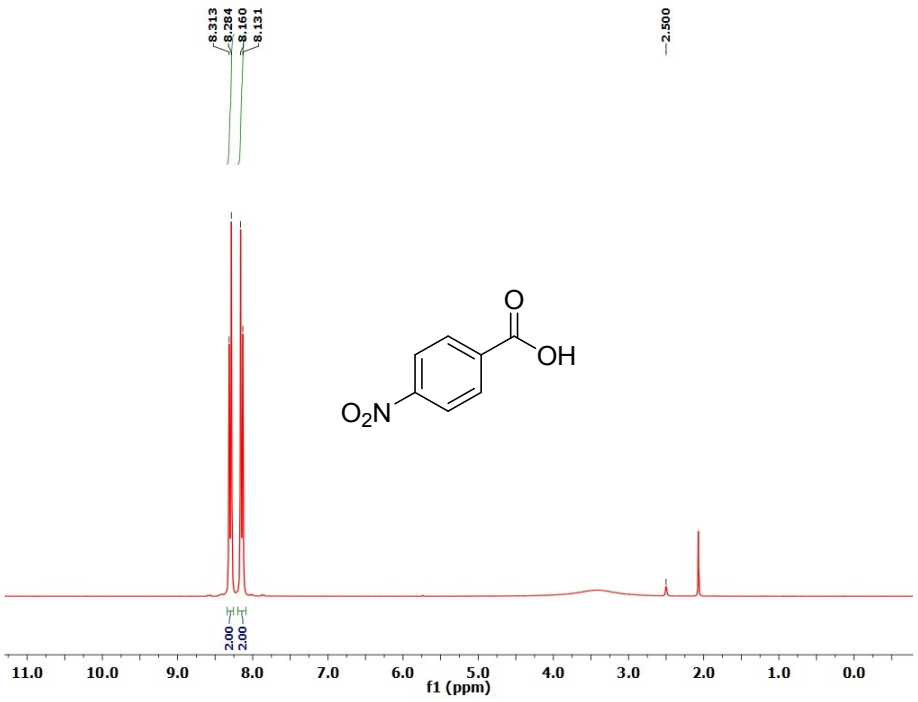
^{13}C-NMR spectrum of **3l** (75 MHz, $CDCl_3$)



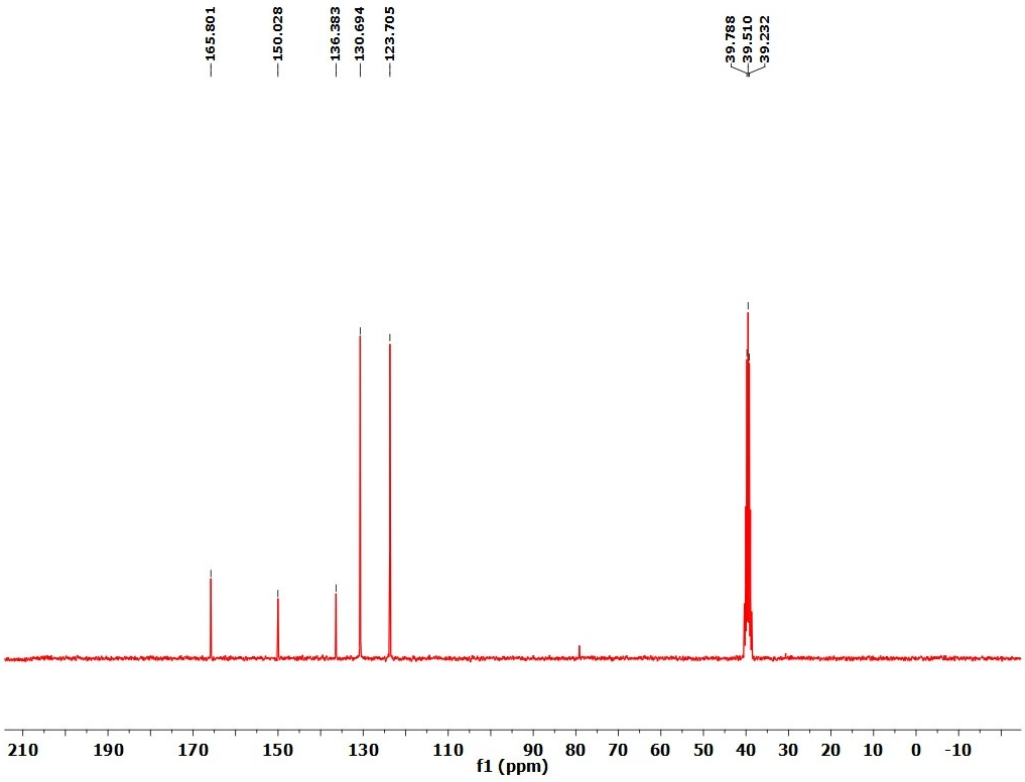
^{1}H-NMR spectrum of **3m** (75 MHz, $CDCl_3$)



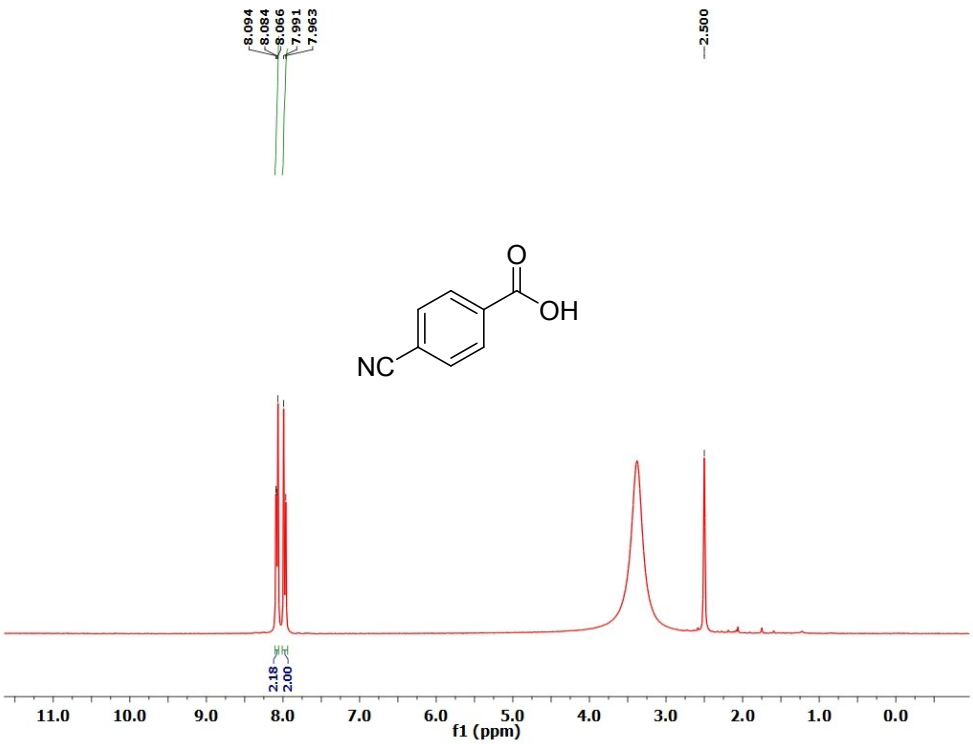
^{13}C-NMR spectrum of **3m** (75 MHz, $CDCl_3$)



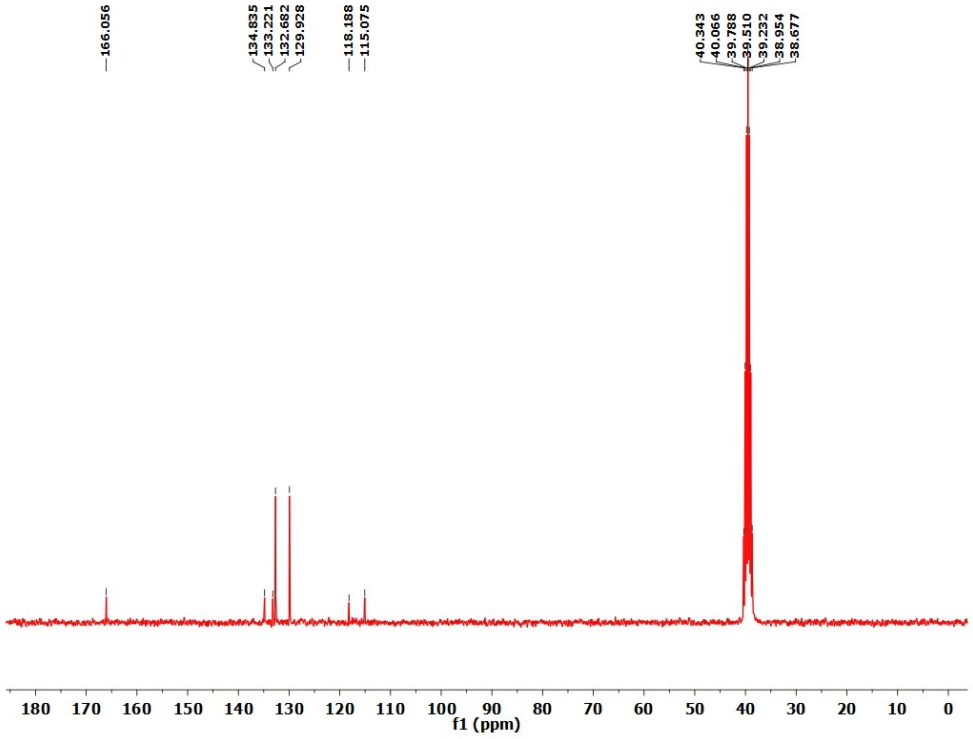
^{1}H-NMR spectrum of **3n** (75 MHz, DMSO)



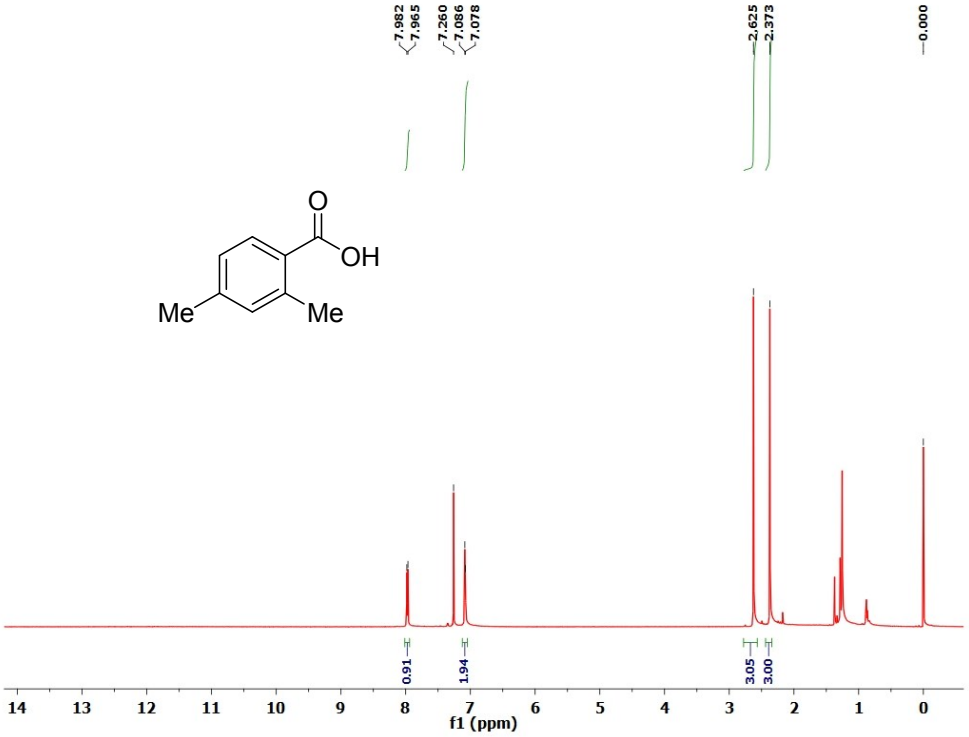
^{13}C-NMR spectrum of **3n** (75 MHz, DMSO)



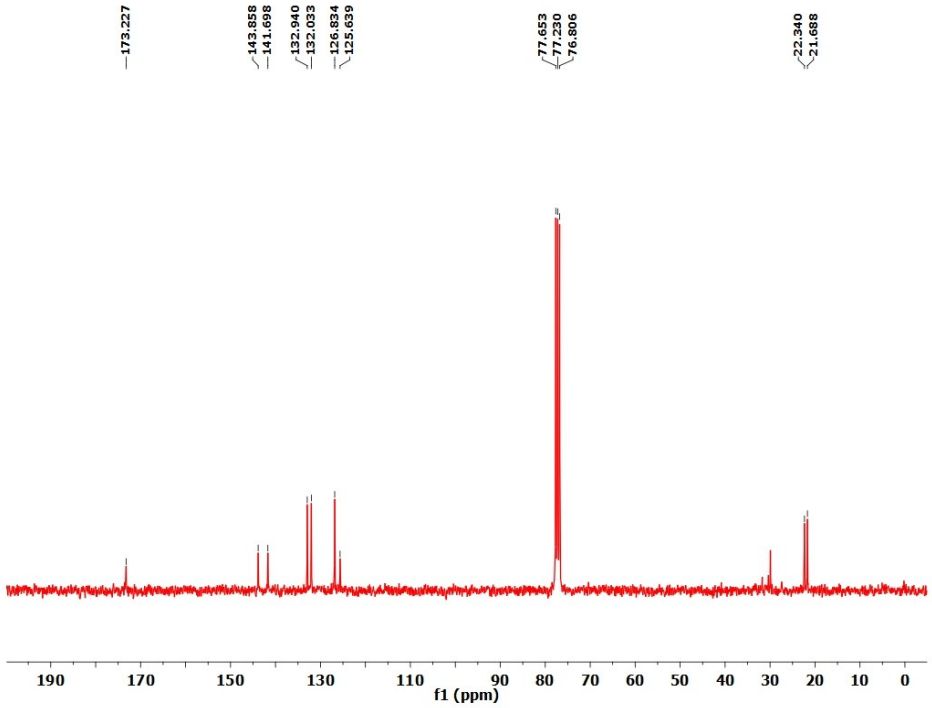
^{1}H-NMR spectrum of **3o** (75 MHz, DMSO)



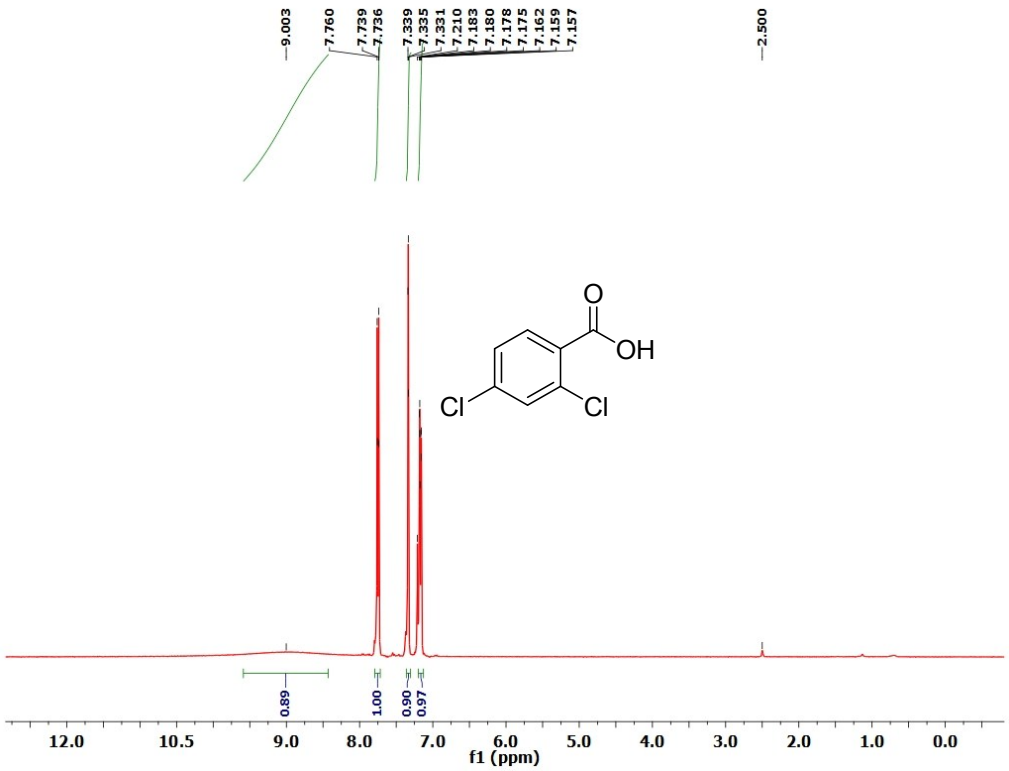
^{13}C-NMR spectrum of **3o** (75 MHz, DMSO)



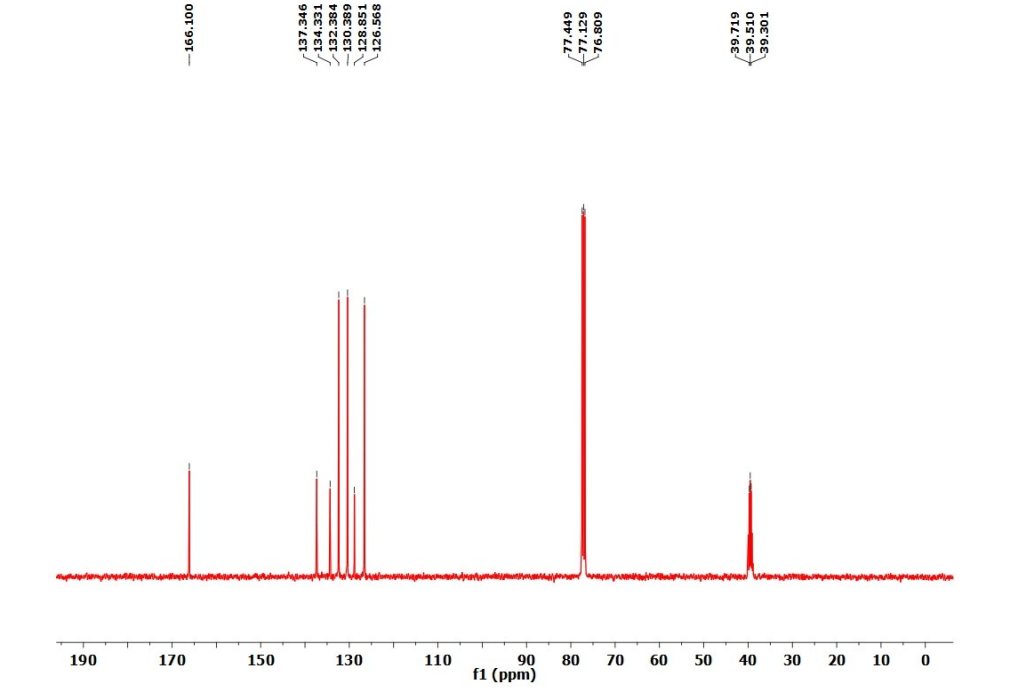
^{1}H-NMR spectrum of **3p** (75 MHz, $CDCl_3$)



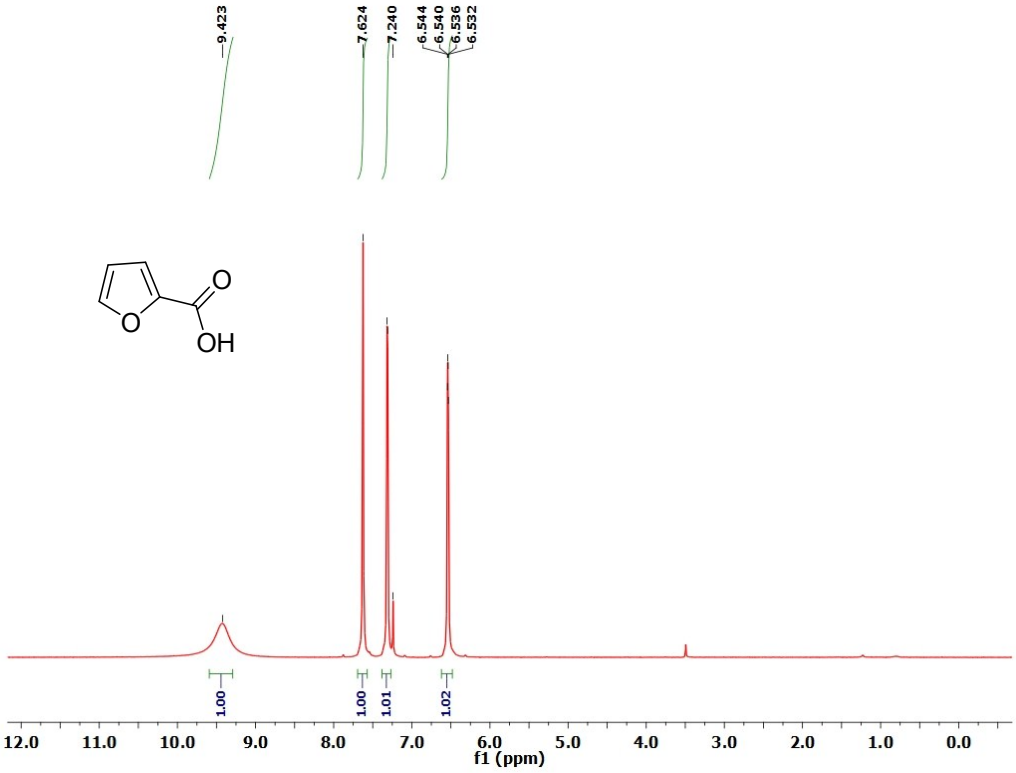
^{13}C-NMR spectrum of **3p** (75 MHz, $CDCl_3$)



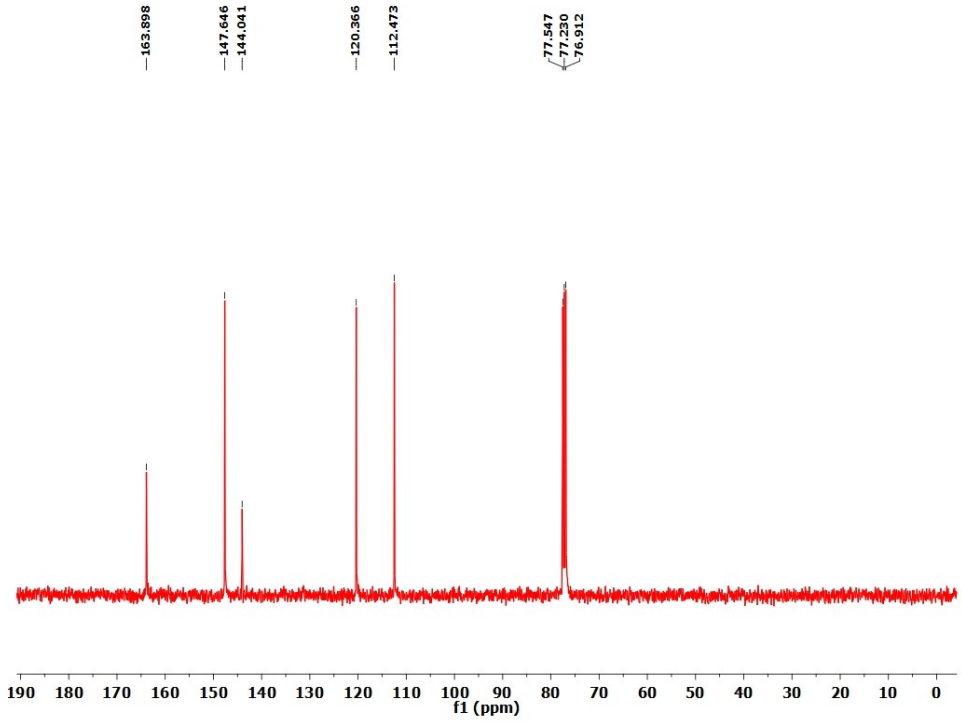
^{1}H-NMR spectrum of **3q** (75 MHz, $CDCl_3$ + DMSO)



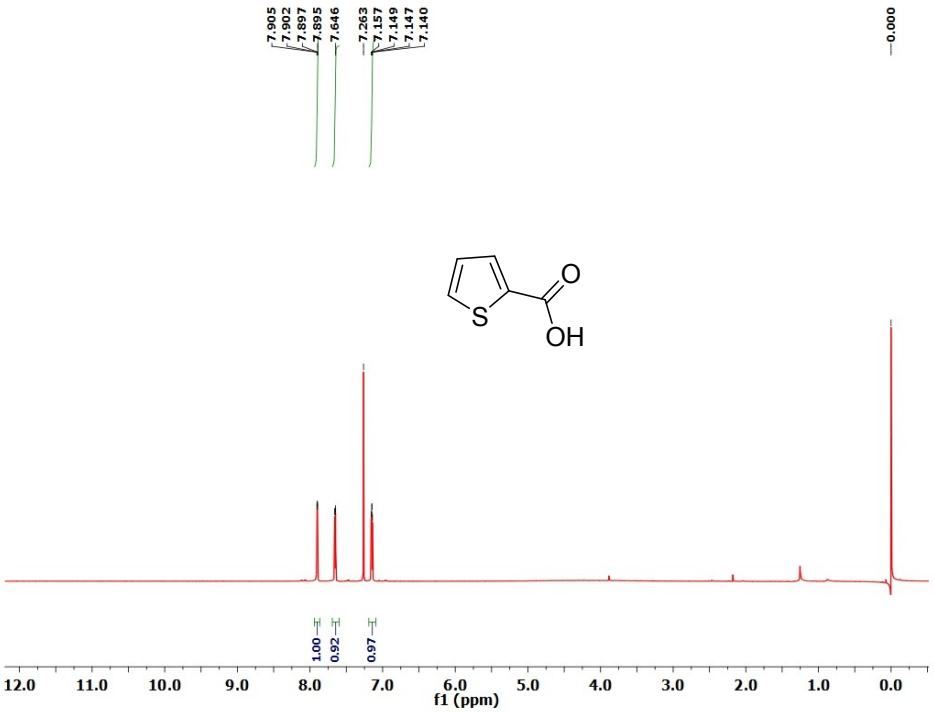
^{13}C-NMR spectrum of **3q** (75 MHz, $CDCl_3$ + DMSO)



^{1}H-NMR spectrum of **3r** (75 MHz, $CDCl_3$)

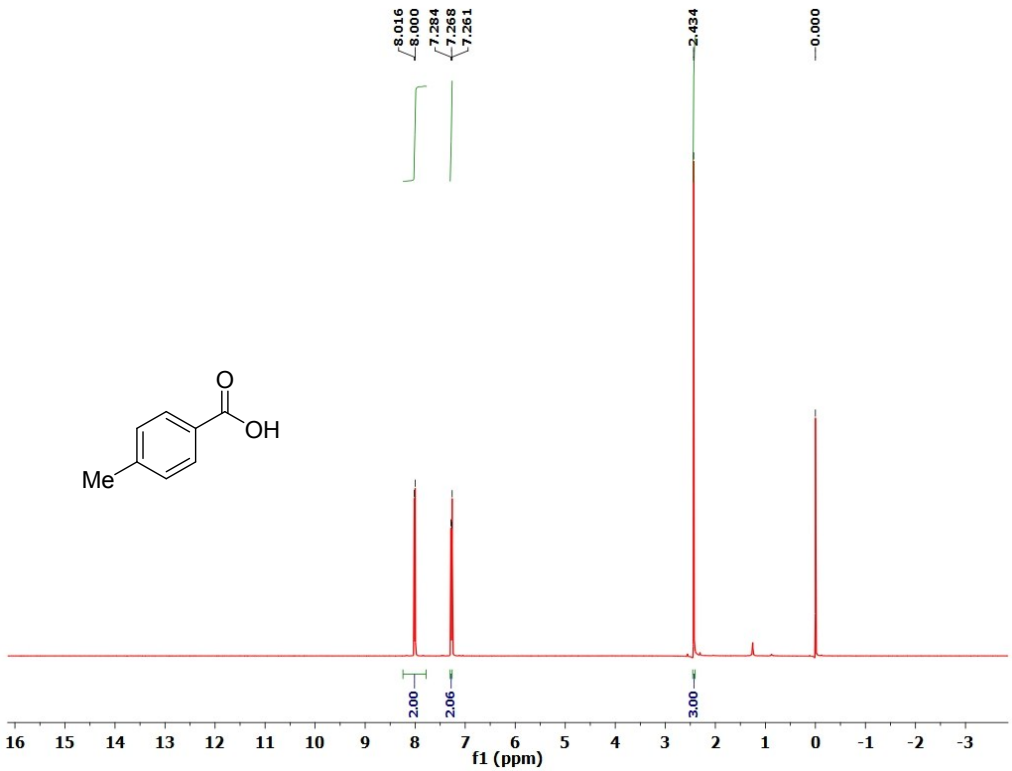


^{13}C-NMR spectrum of **3r** (75 MHz, $CDCl_3$)

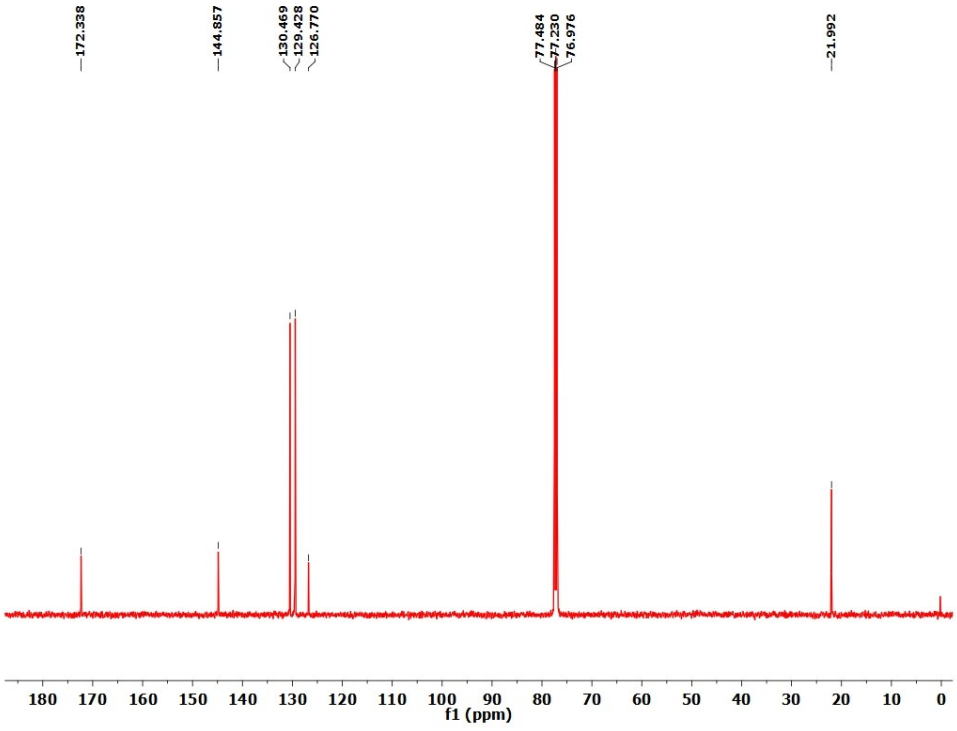


^{1}H-NMR spectrum of **3s** (75 MHz, $CDCl_3$)

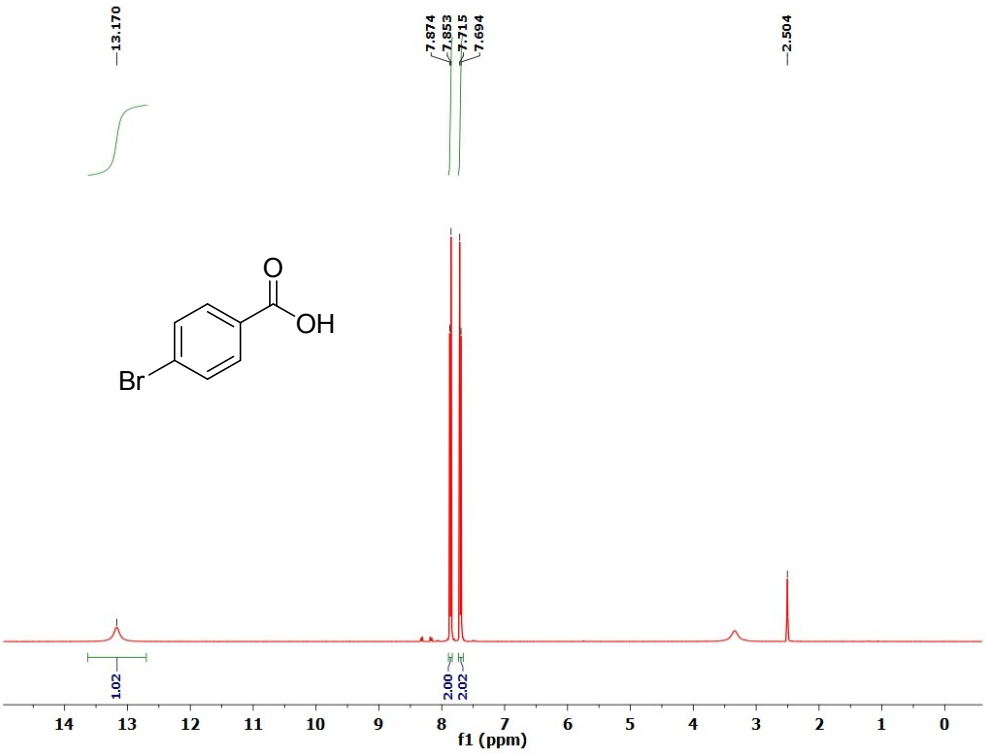
^{13}C-NMR spectrum of **3s** (75 MHz, $CDCl_3$)



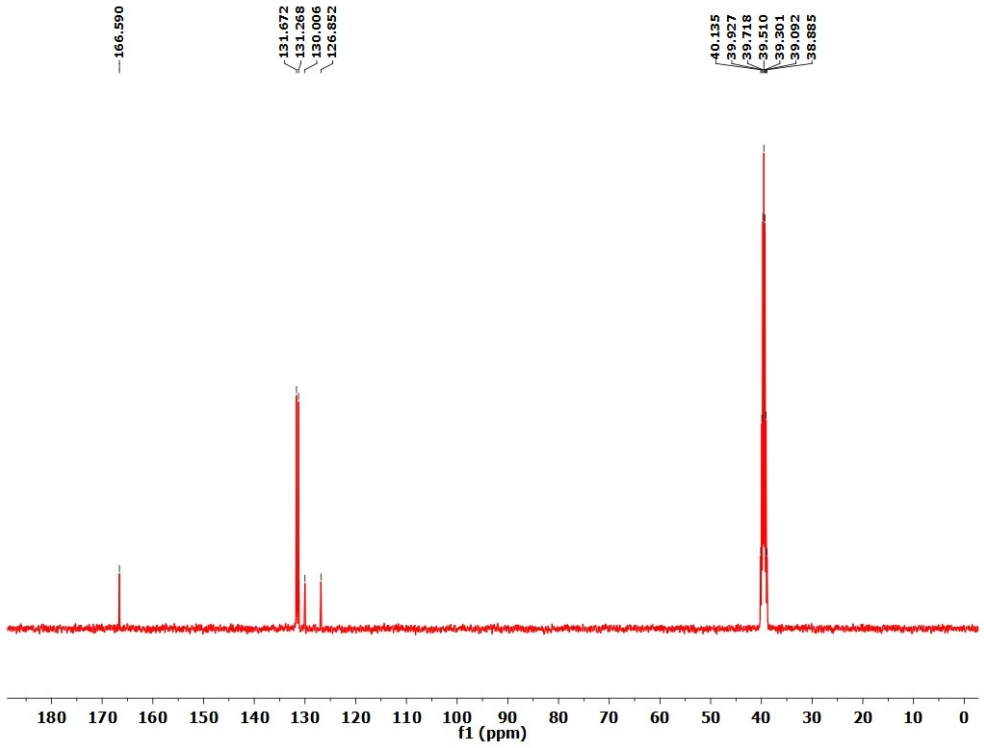
^{1}H-NMR spectrum of **3t** (75 MHz, $CDCl_3$)



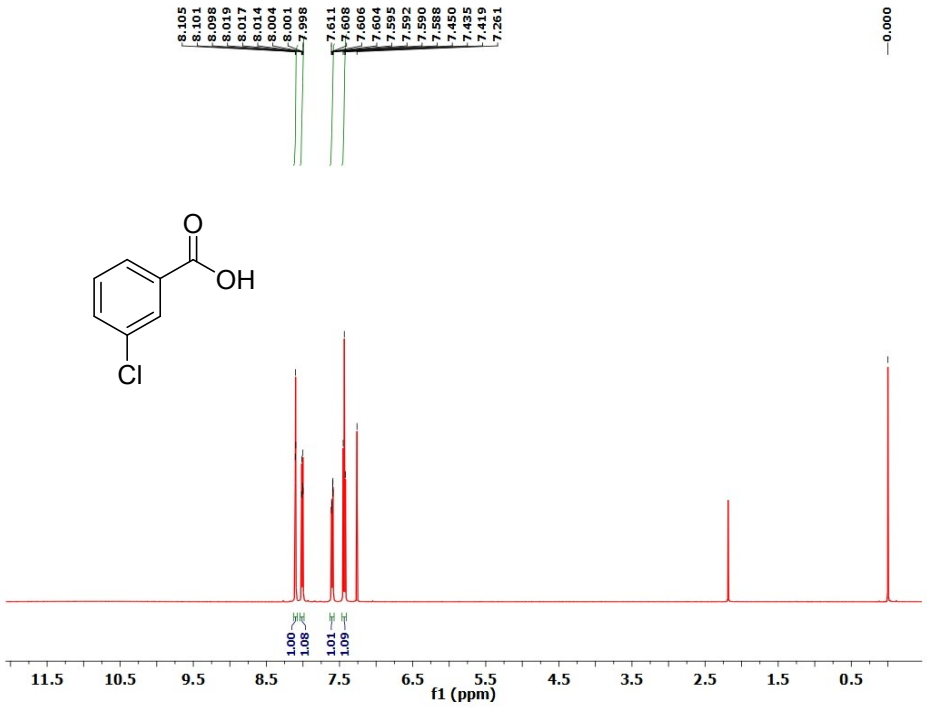
^{13}C-NMR spectrum of **3t** (75 MHz, $CDCl_3$)



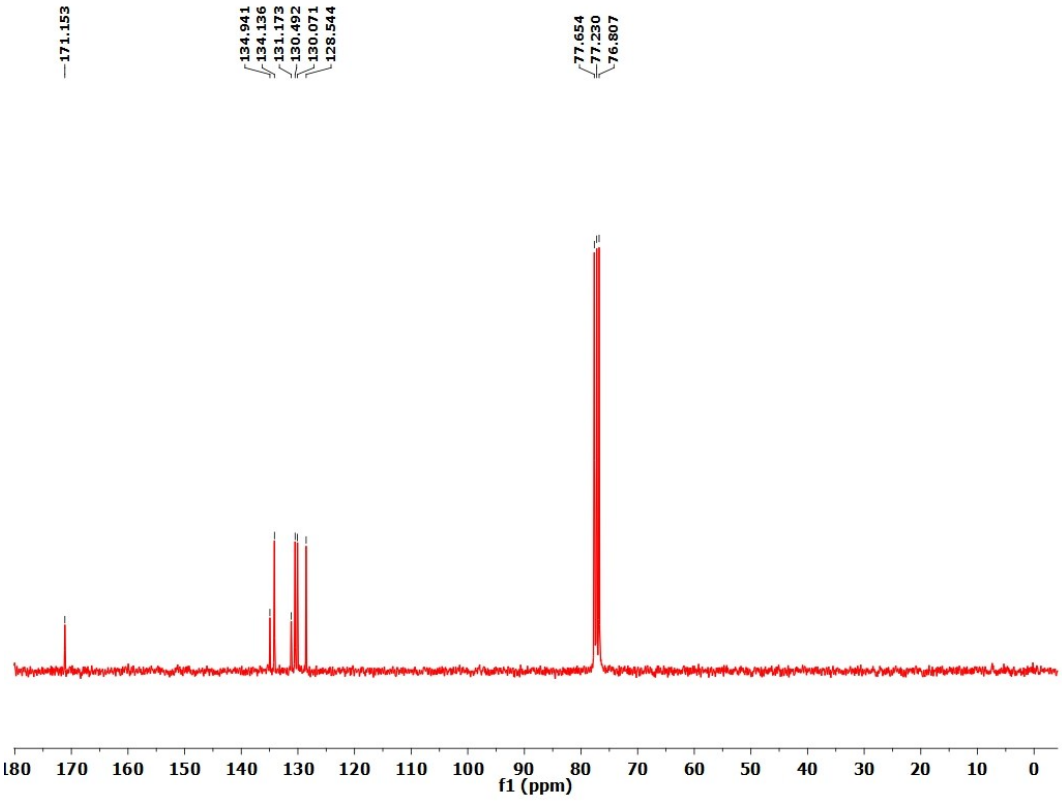
^{1}H-NMR spectrum of **3u** (75 MHz, DMSO)



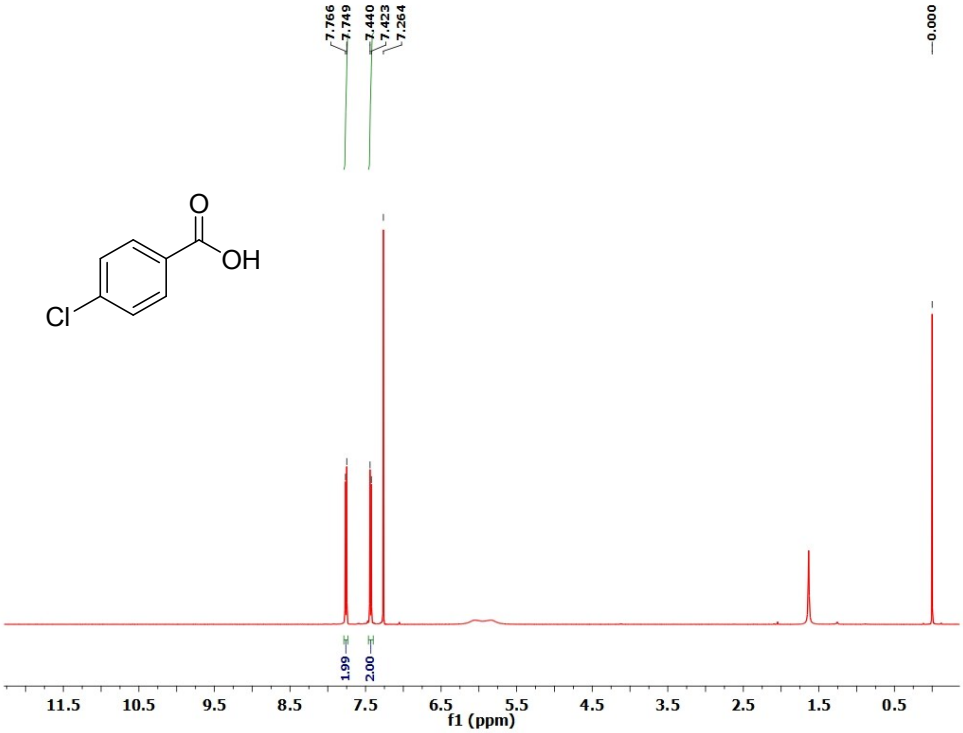
^{13}C-NMR spectrum of **3u** (75 MHz, DMSO)



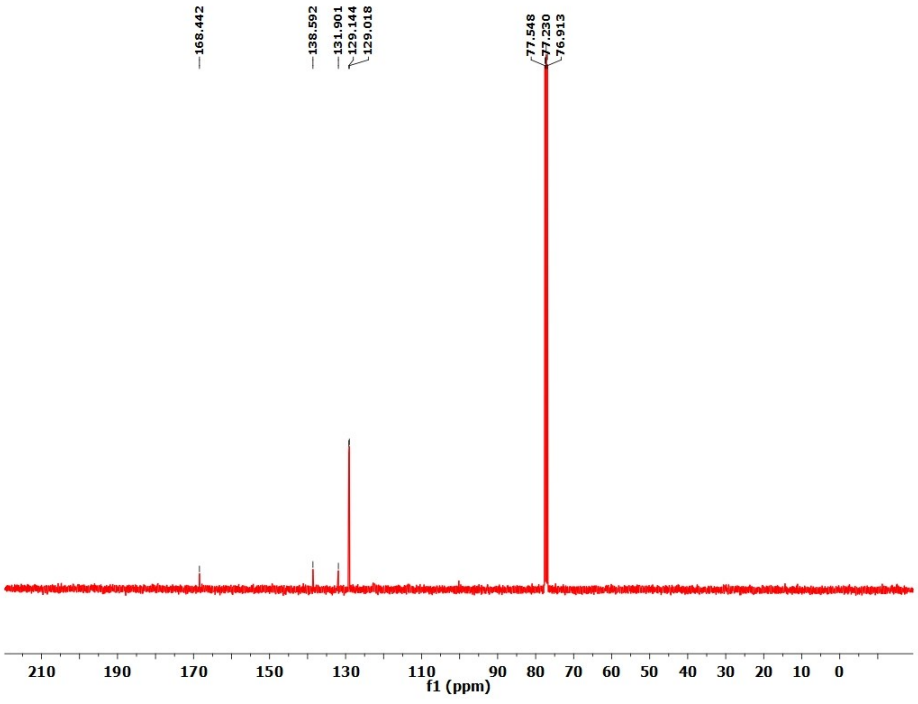
^{1}H-NMR spectrum of **3v** (75 MHz, $CDCl_3$)



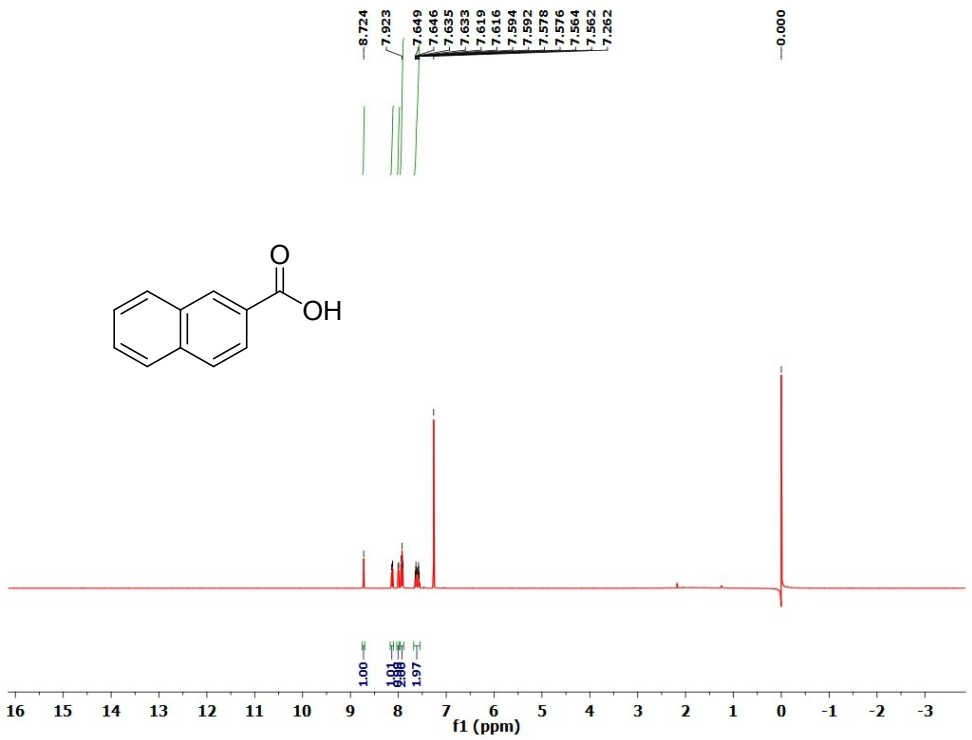
^{13}C-NMR spectrum of **3v** (75 MHz, $CDCl_3$)



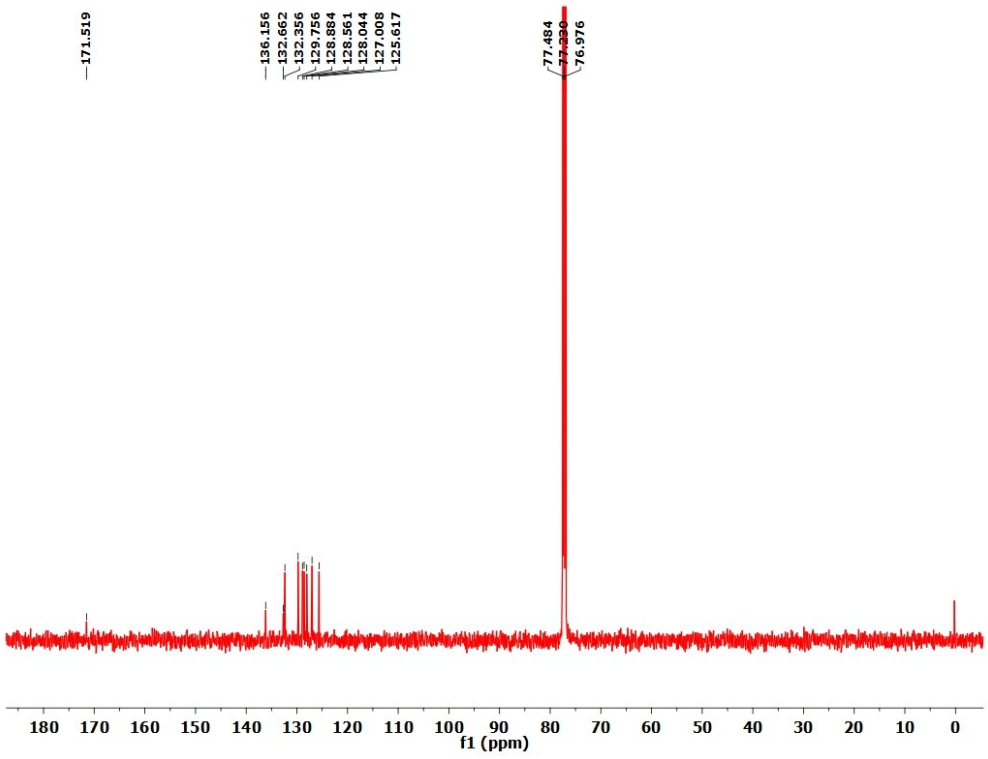
^{1}H-NMR spectrum of **3w** (75 MHz, $CDCl_3$)



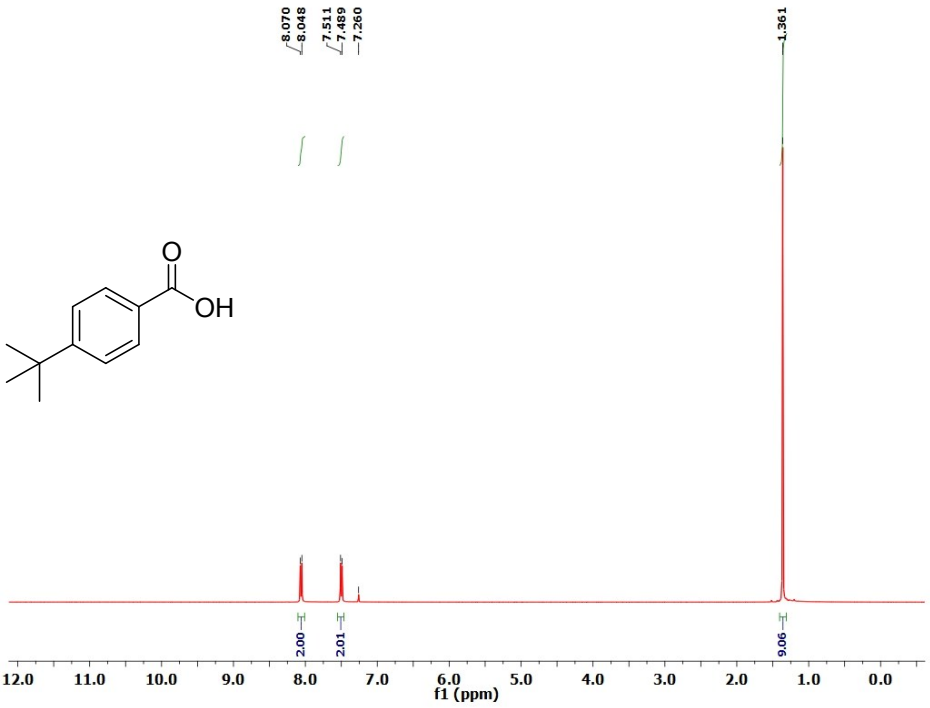
^{13}C-NMR spectrum of **3w** (75 MHz, $CDCl_3$)



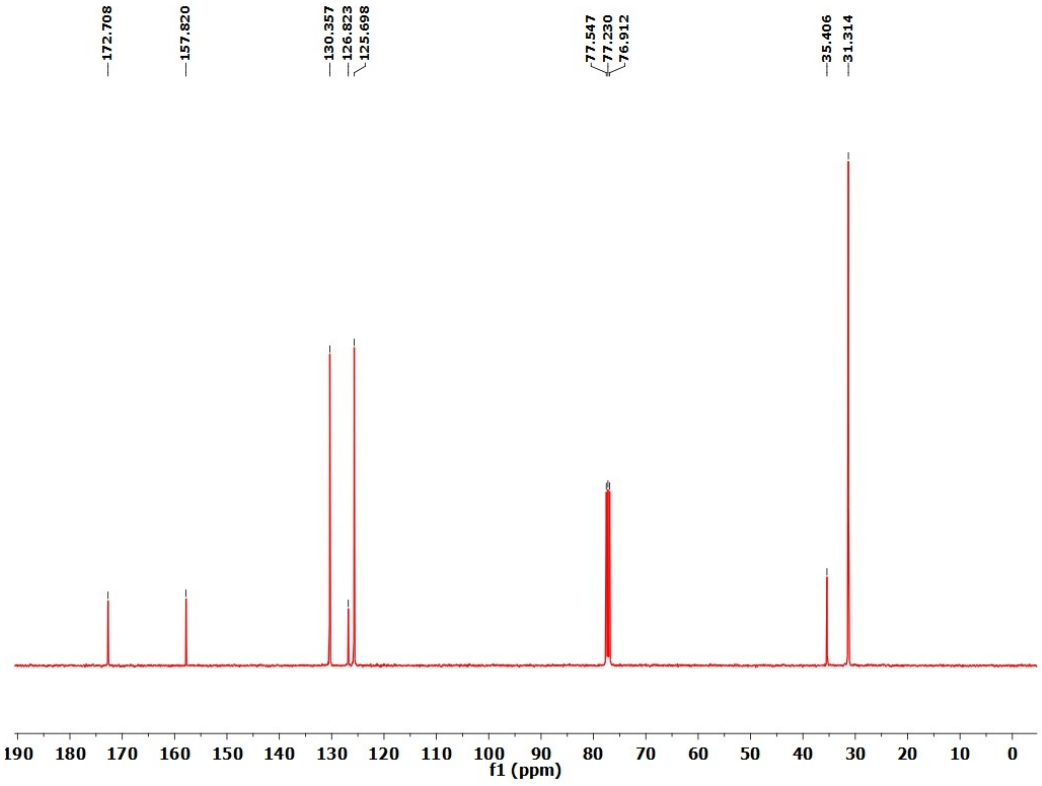
^{1}H-NMR spectrum of **3x** (75 MHz, $CDCl_3$)



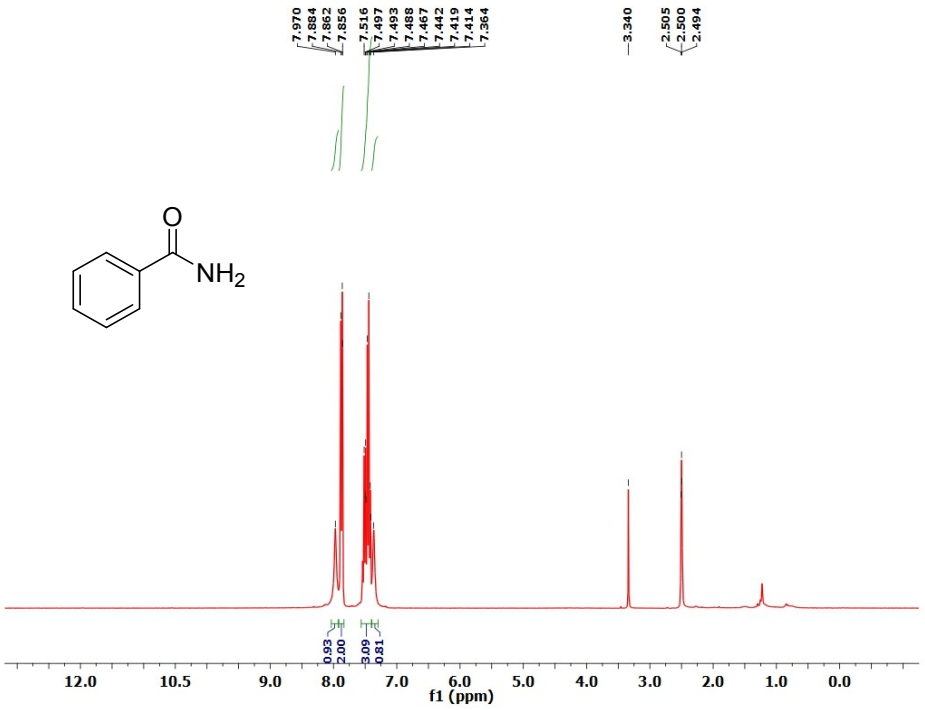
^{13}C-NMR spectrum of **3x** (75 MHz, $CDCl_3$)



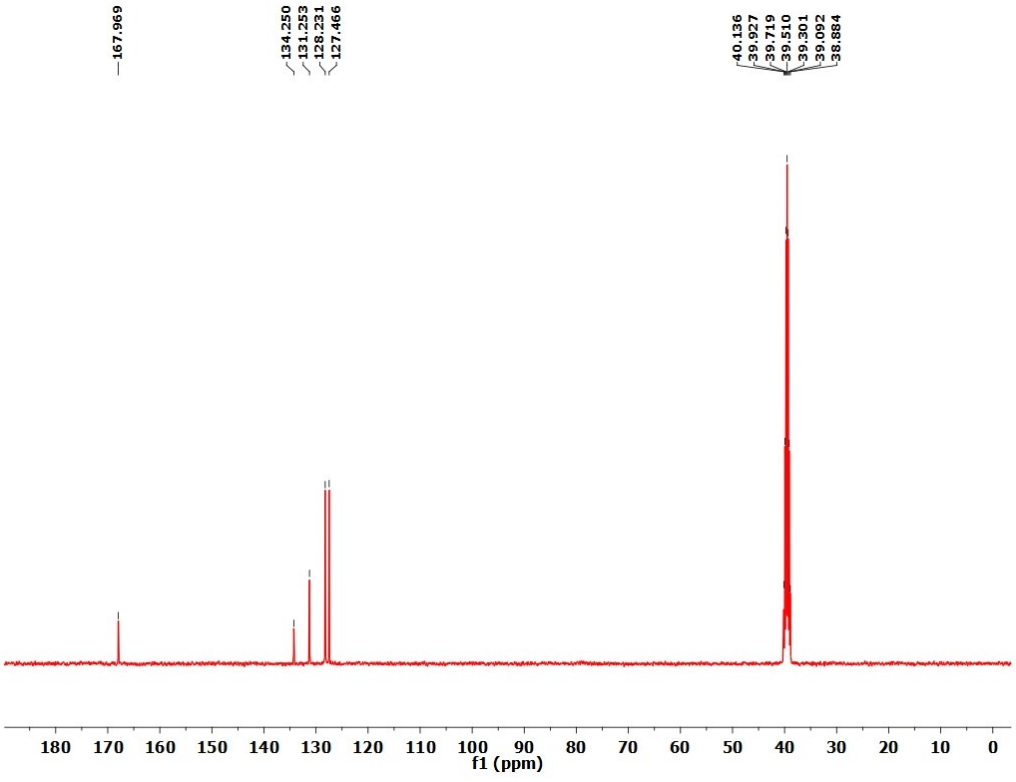
^{1}H-NMR spectrum of **3y** (75 MHz, $CDCl_3$)



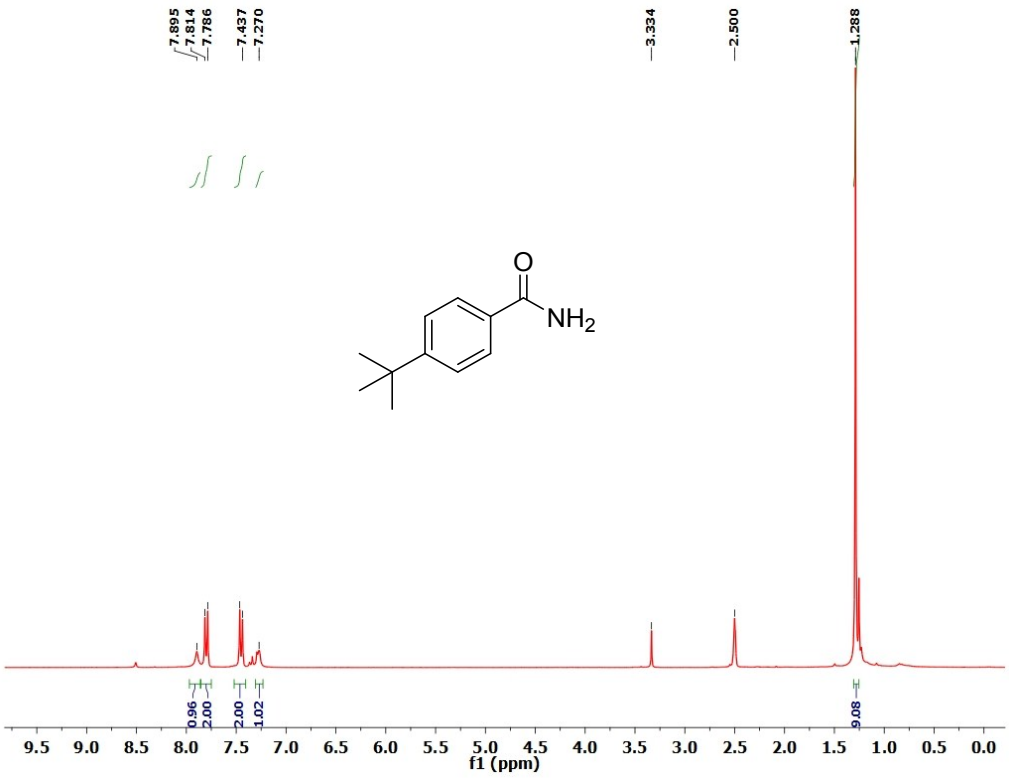
^{13}C-NMR spectrum of **3y** (75 MHz, $CDCl_3$)



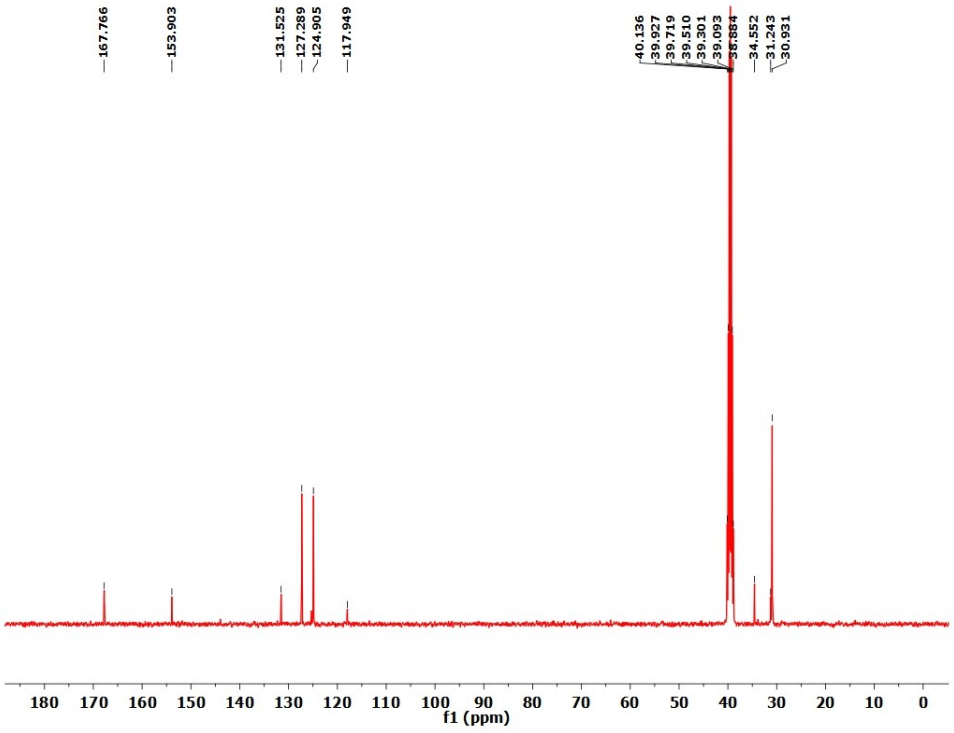
^{1}H-NMR spectrum of **7a** (75 MHz, DMSO)



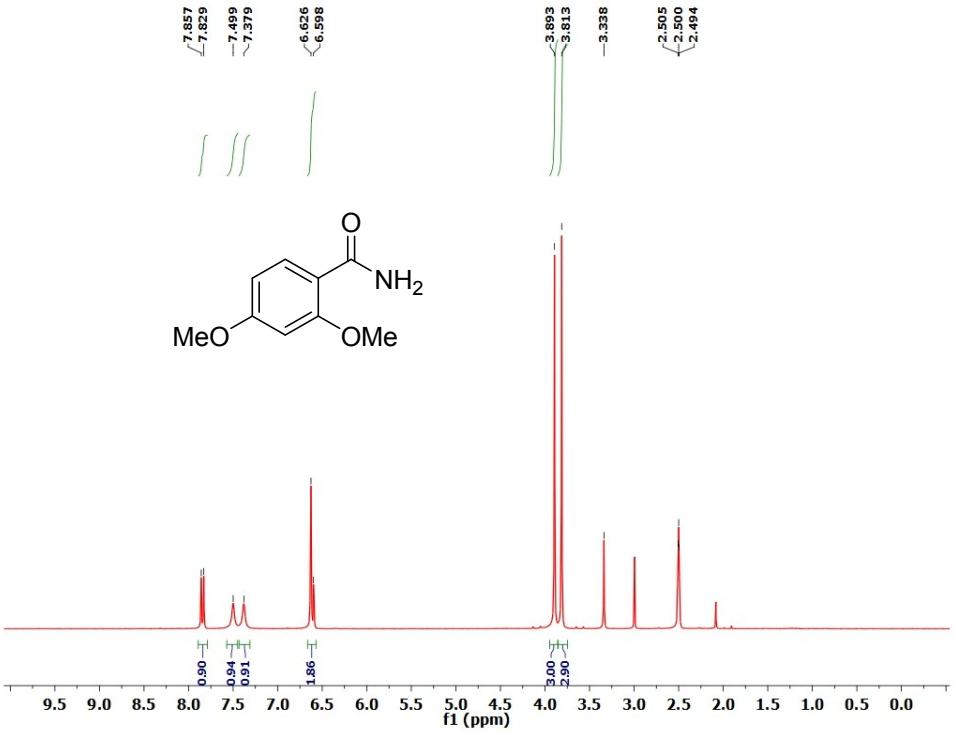
^{13}C -NMR spectrum of **7a** (75 MHz, DMSO)



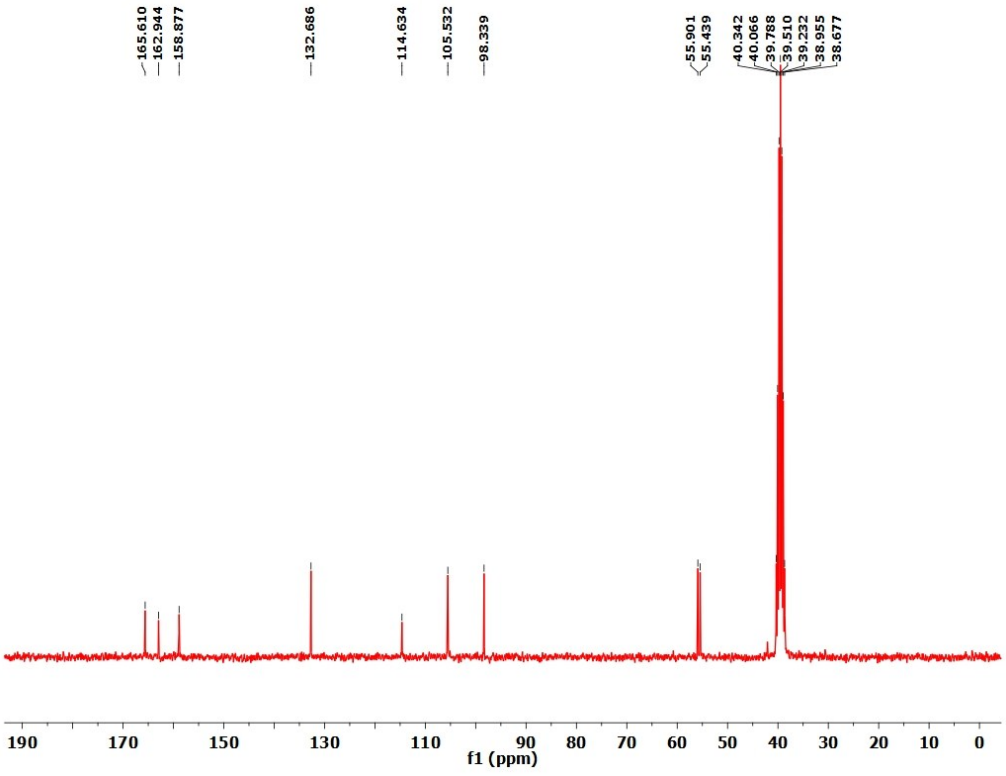
^{1}H-NMR spectrum of **7b** (75 MHz, DMSO)



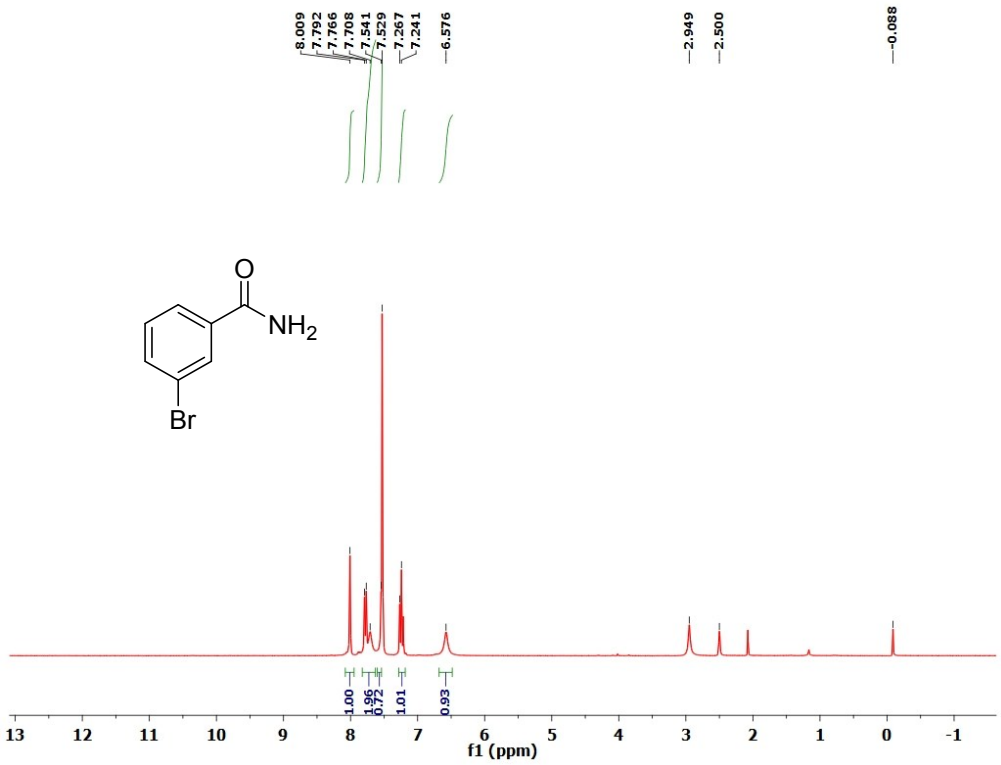
^{13}C-NMR spectrum of **7b** (75 MHz, DMSO)



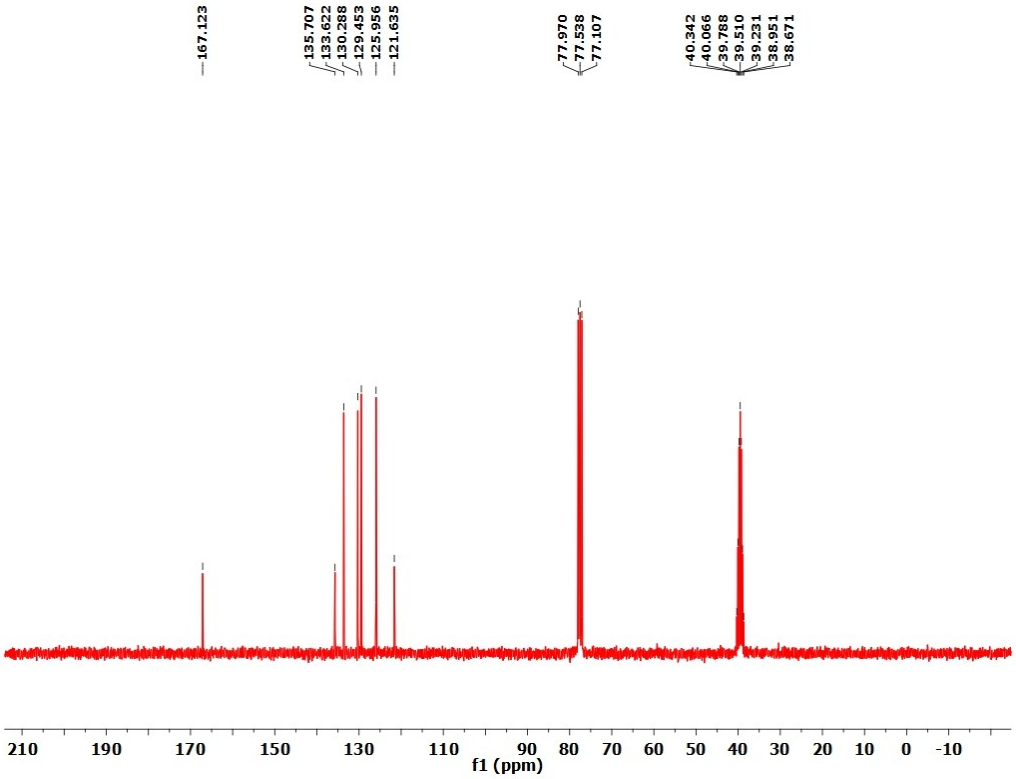
^{1}H-NMR spectrum of **7c** (75 MHz, DMSO)



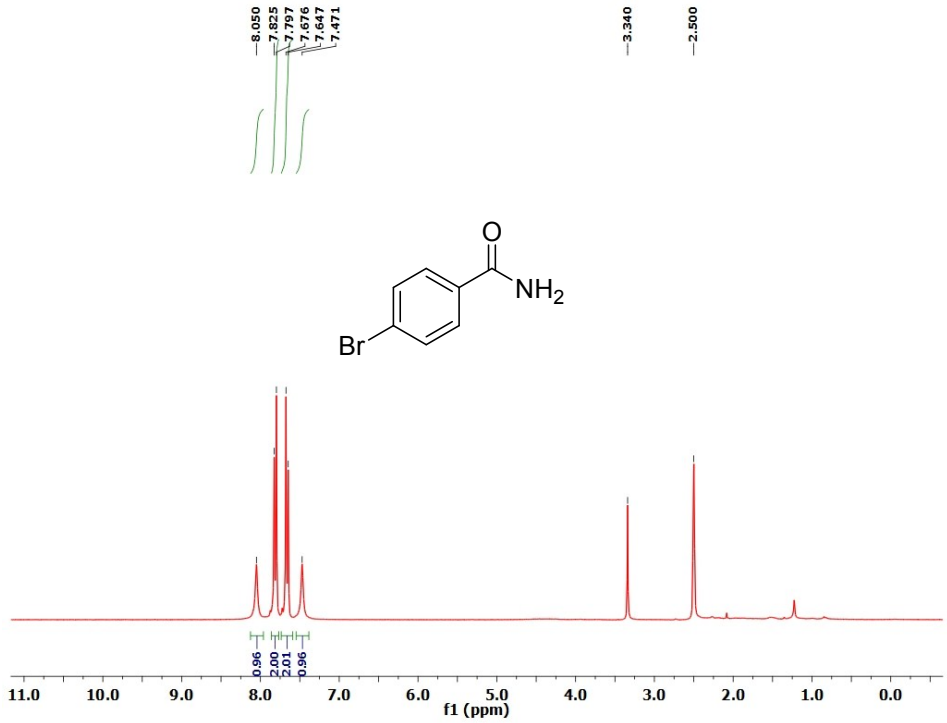
^{13}C-NMR spectrum of **7c** (75 MHz, DMSO)



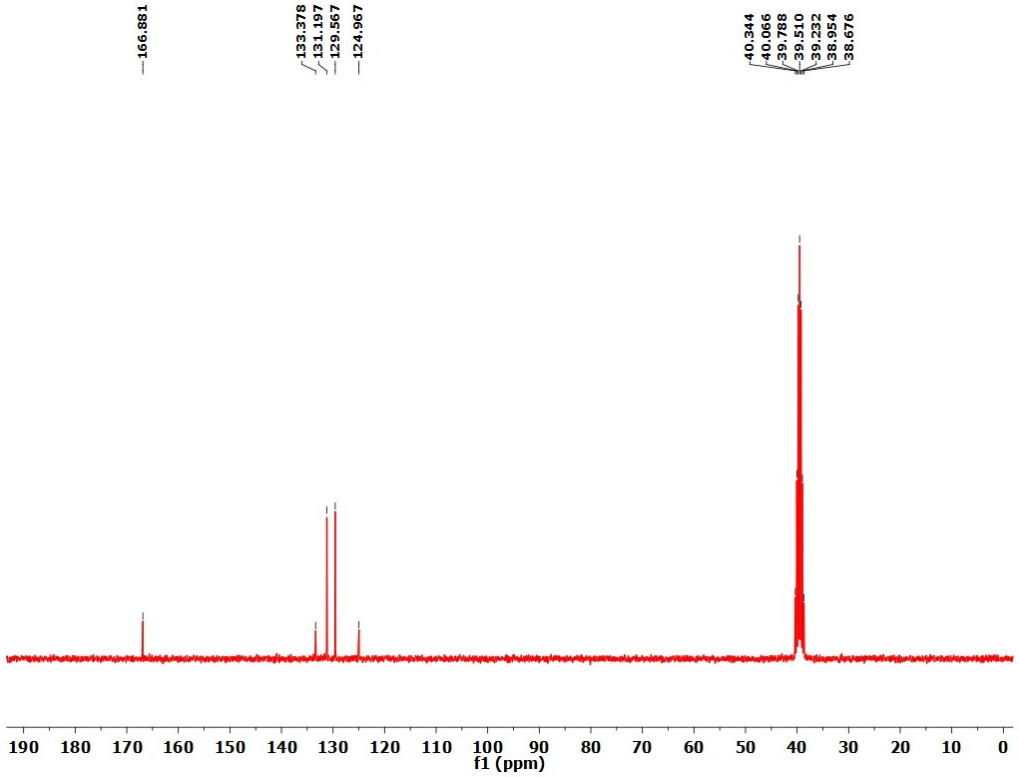
^{1}H-NMR spectrum of **7d** (75 MHz, CDCl3 + DMSO)



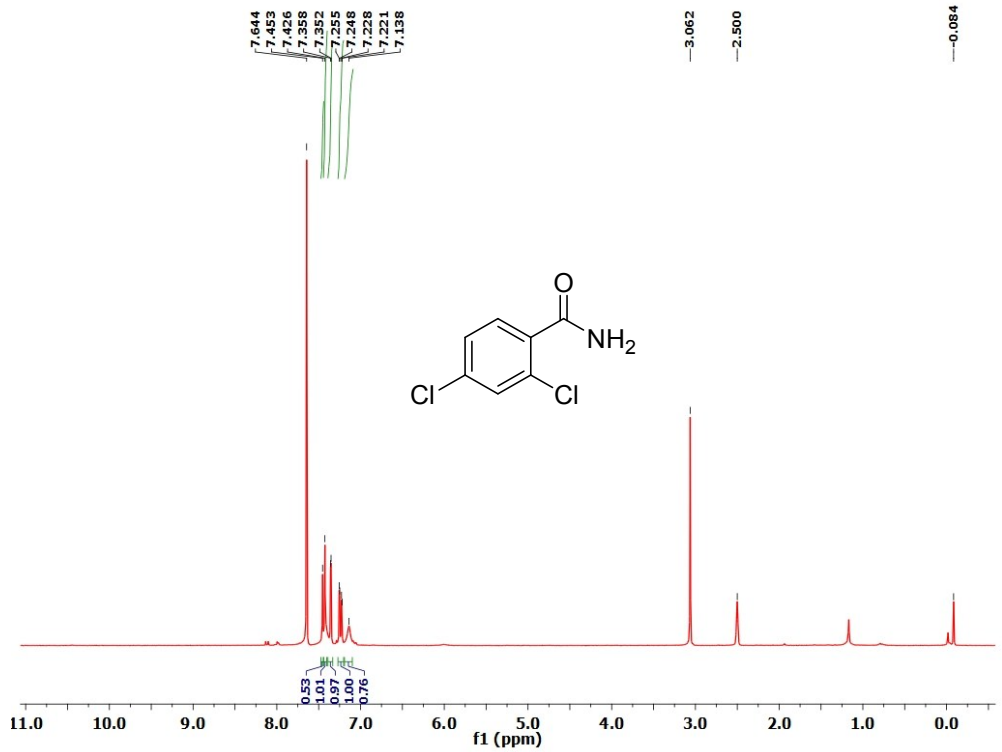
^{13}C-NMR spectrum of **7d** (75 MHz, CDCl3 + DMSO)



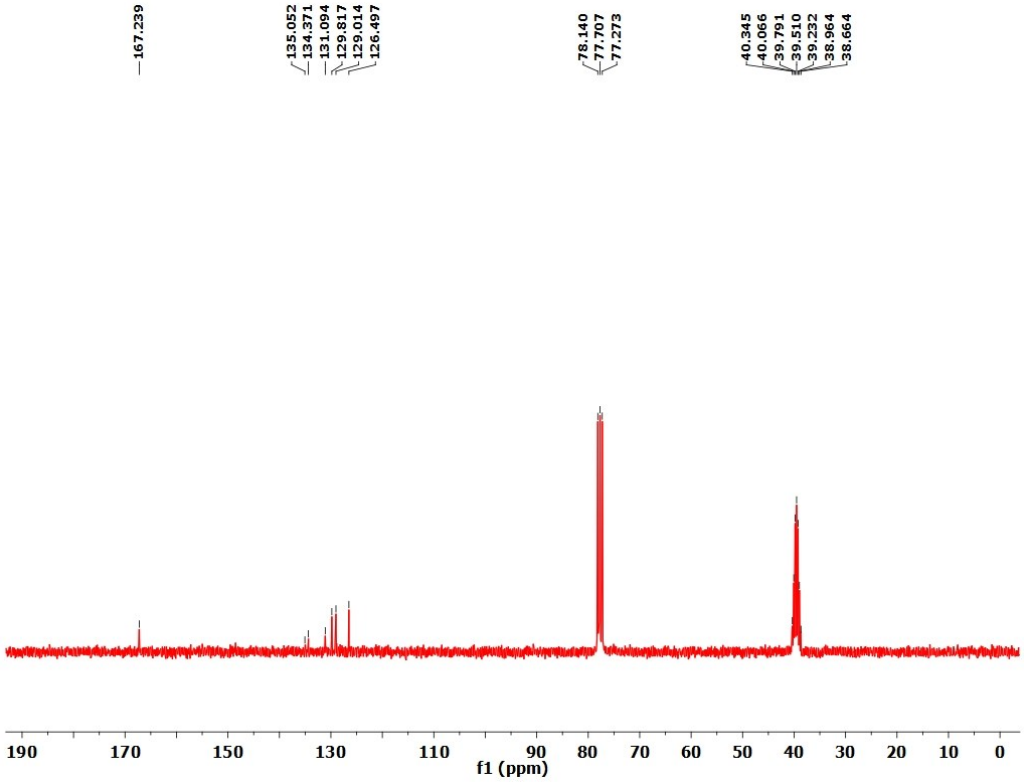
^{1}H-NMR spectrum of **7e** (75 MHz, DMSO)



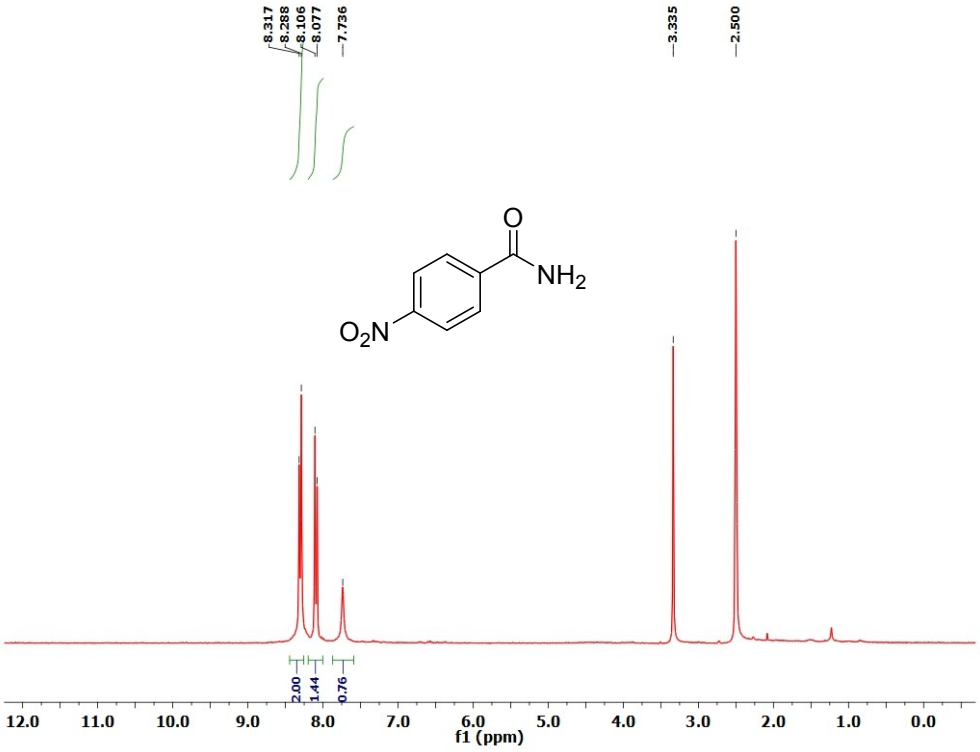
^{13}C-NMR spectrum of **7e** (75 MHz, DMSO)



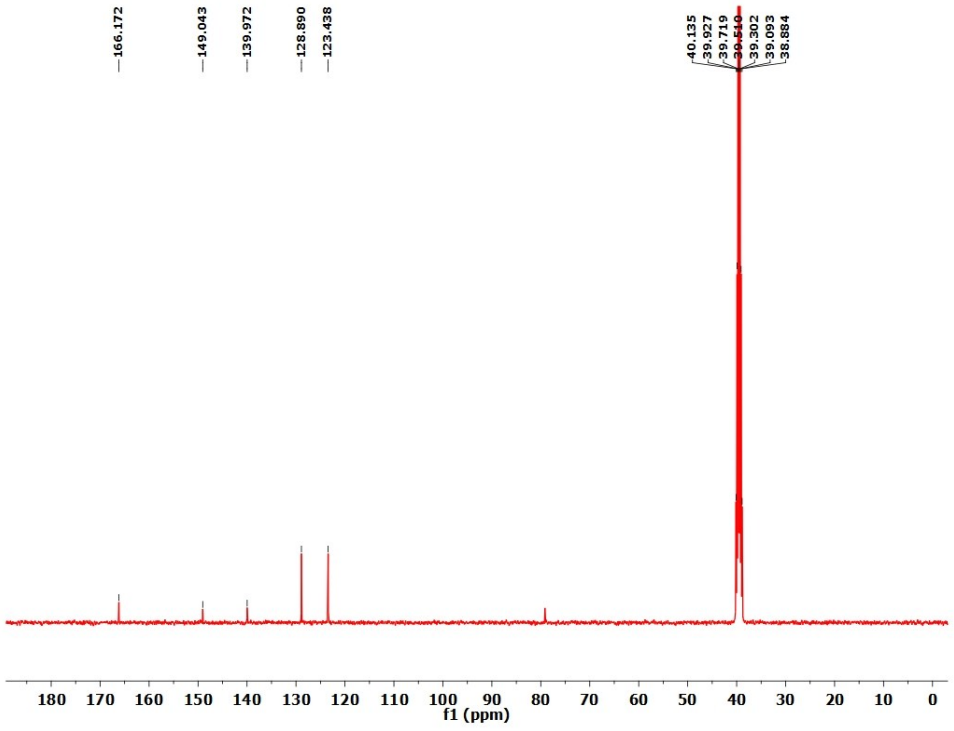
^{1}H-NMR spectrum of **7f** (75 MHz, $CDCl_3$ + DMSO)



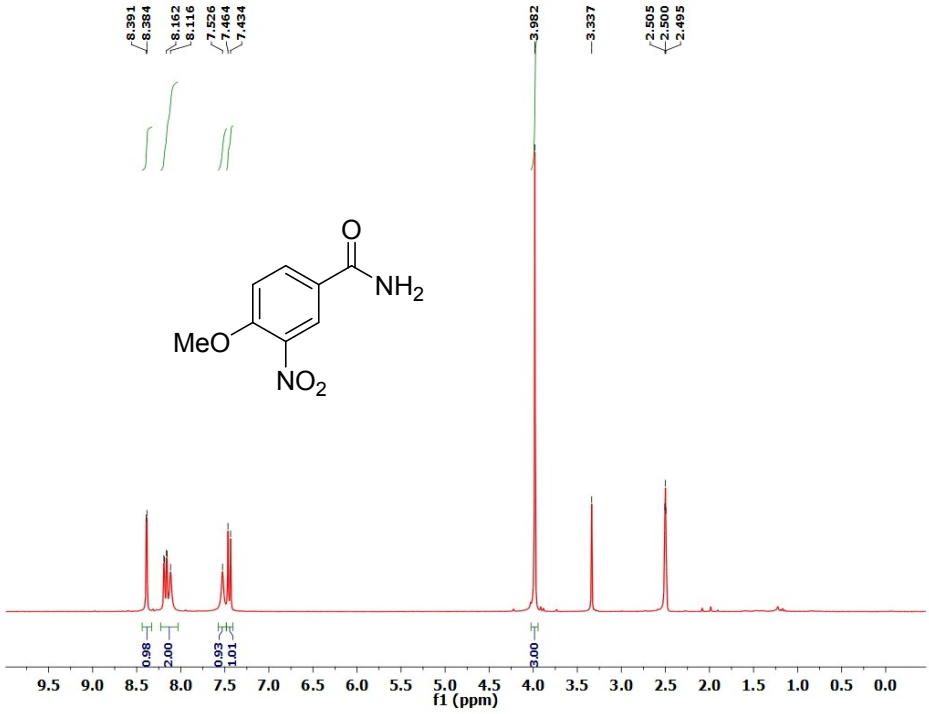
^{13}C-NMR spectrum of **7f** (75 MHz, $CDCl_3$ + DMSO)



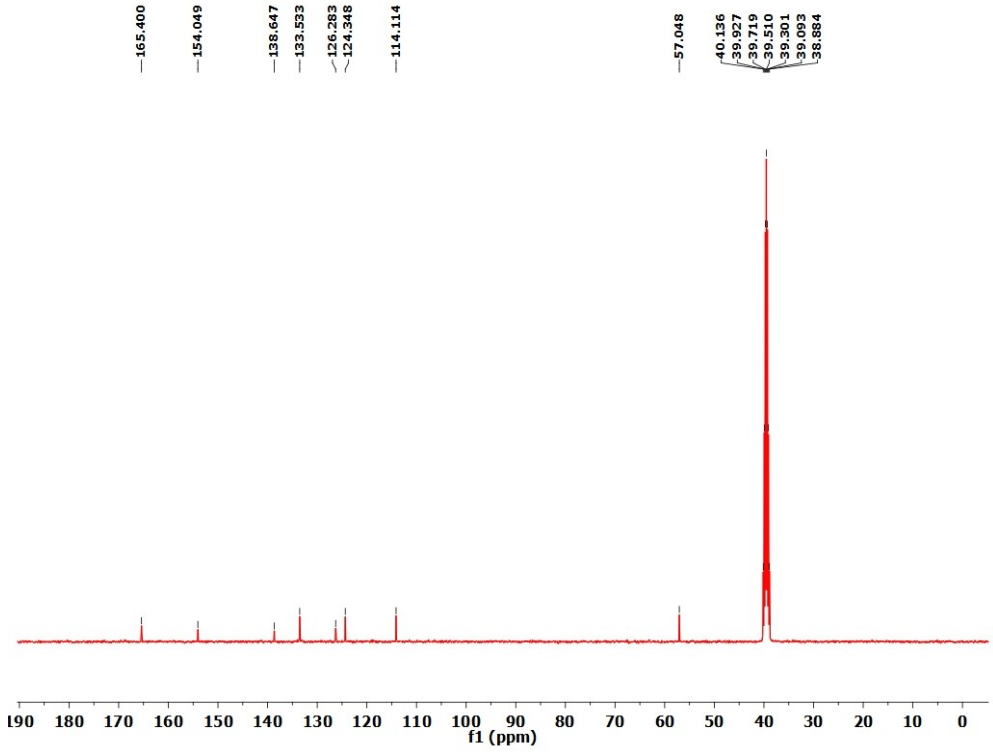
^{1}H-NMR spectrum of **7g** (75 MHz, DMSO)



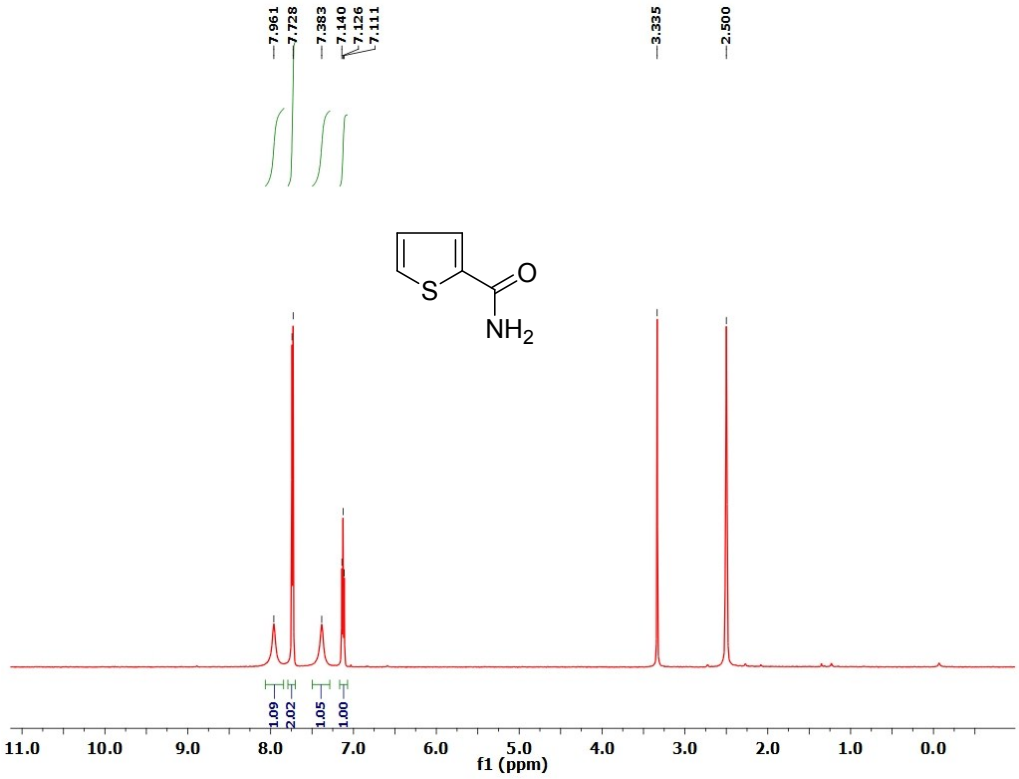
^{13}C-NMR spectrum of **7g** (75 MHz, DMSO)



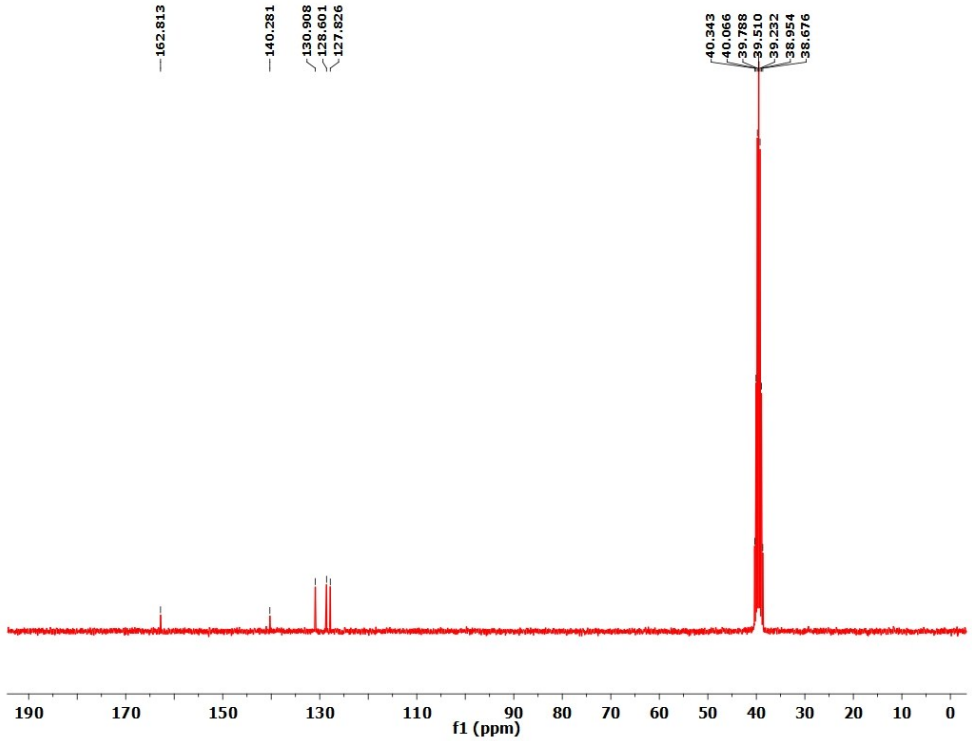
^{1}H-NMR spectrum of **7h** (75 MHz, DMSO)



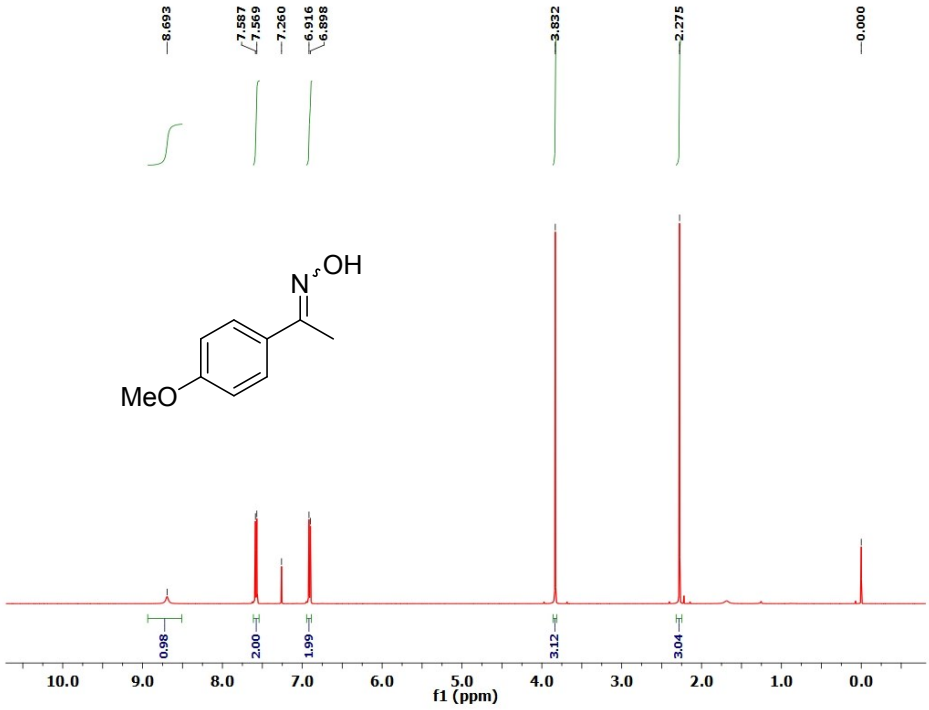
^{13}C-NMR spectrum of **7h** (75 MHz, DMSO)



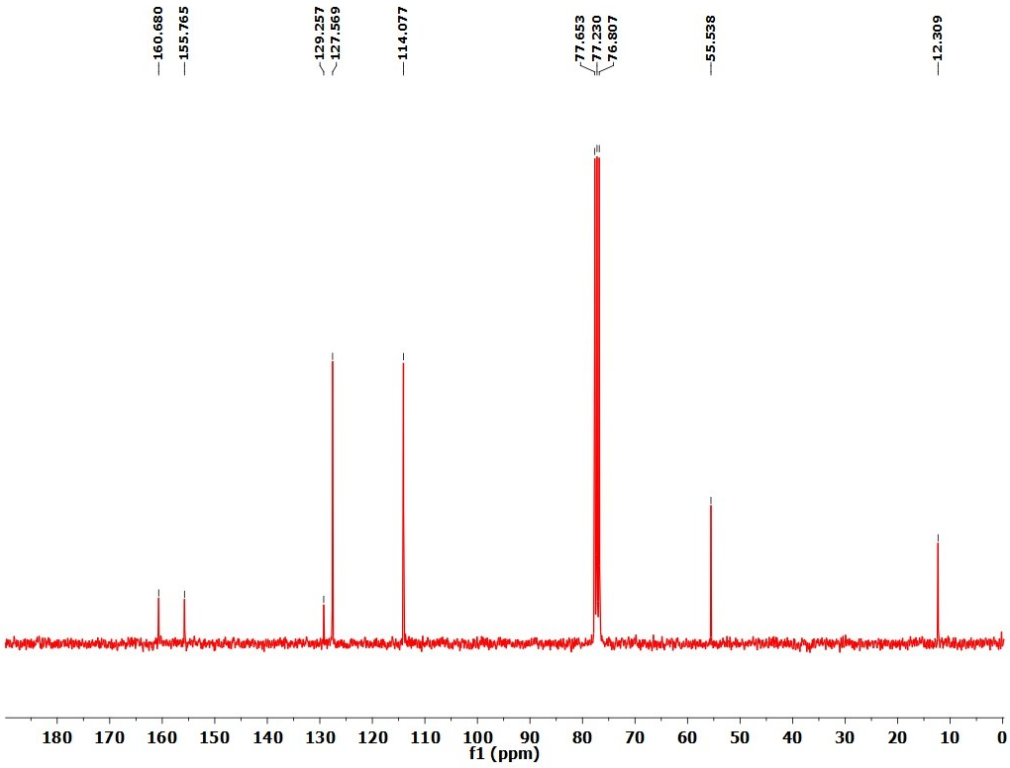
^{1}H-NMR spectrum of **7i** (75 MHz, DMSO)



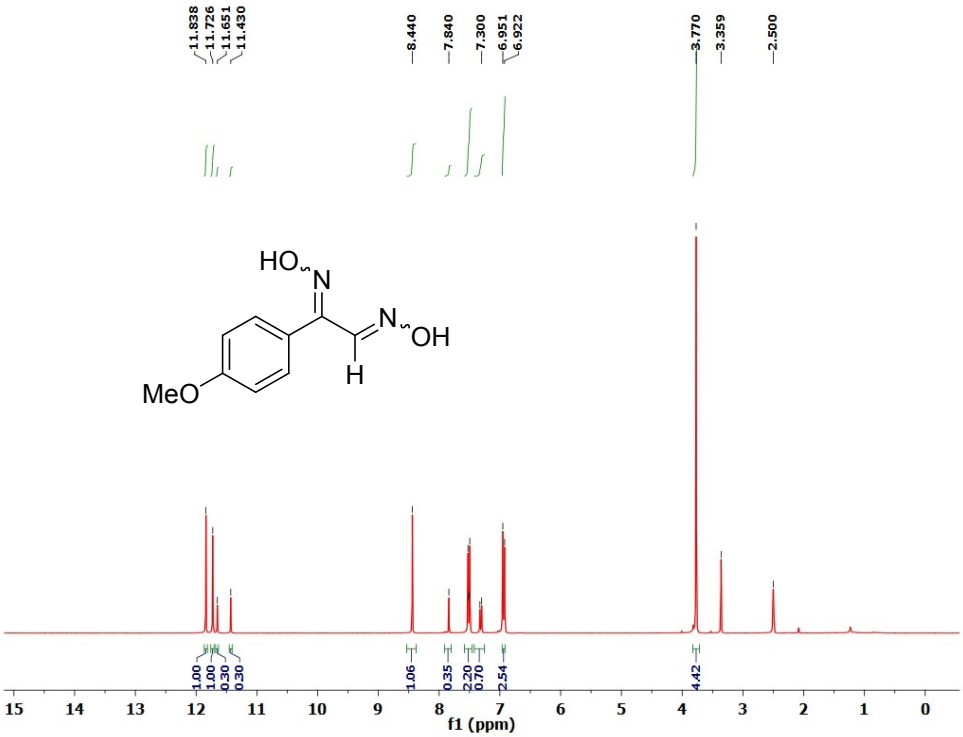
^{13}C-NMR spectrum of **7i** (75 MHz, DMSO)



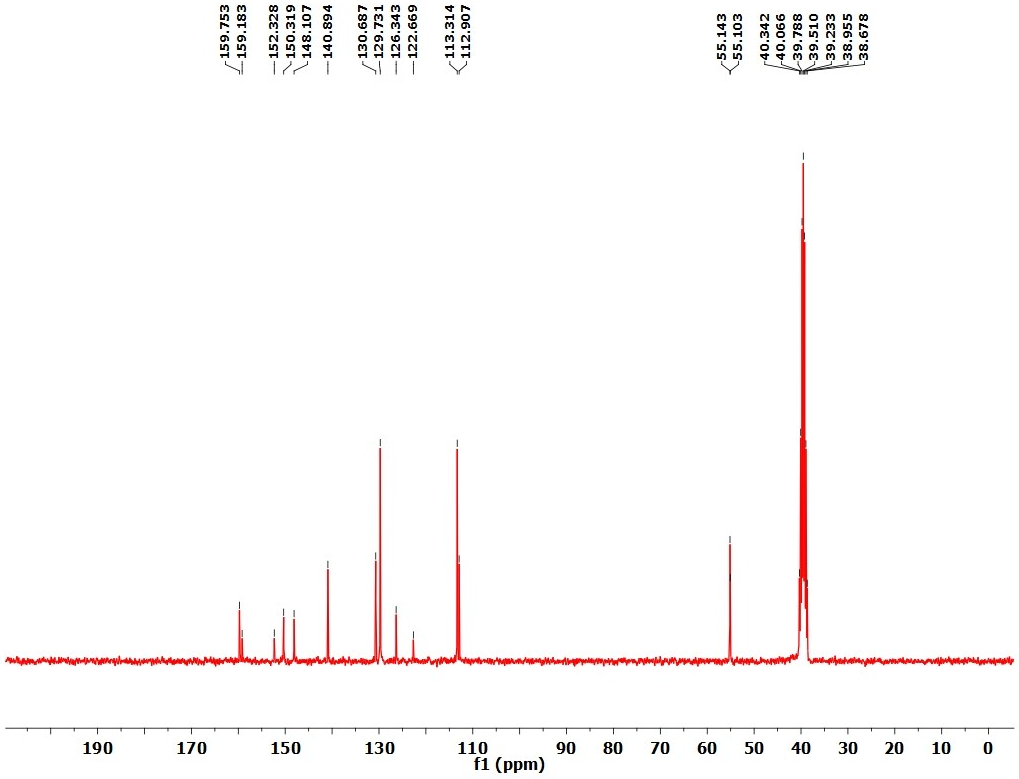
^{1}H-NMR spectrum of **2j** (75 MHz, $CDCl_3$)



^{13}C-NMR spectrum of **2j** (75 MHz, $CDCl_3$)



^{1}H-NMR spectrum of **9** (75 MHz, DMSO)



^{13}C-NMR spectrum of **9** (75 MHz,DMSO)

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