SUPPLEMENTARY MATERIAL

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Chemoselective Oxidation of Aromatic Aldehydes to Carboxylic Acids: Potassium *tert*-butoxide as an Anomalous Source of Oxygen

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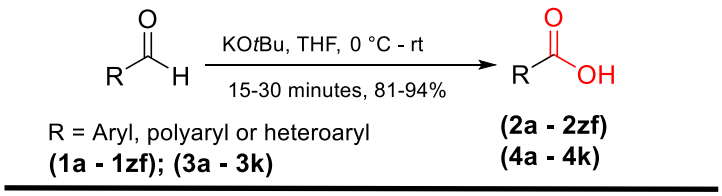
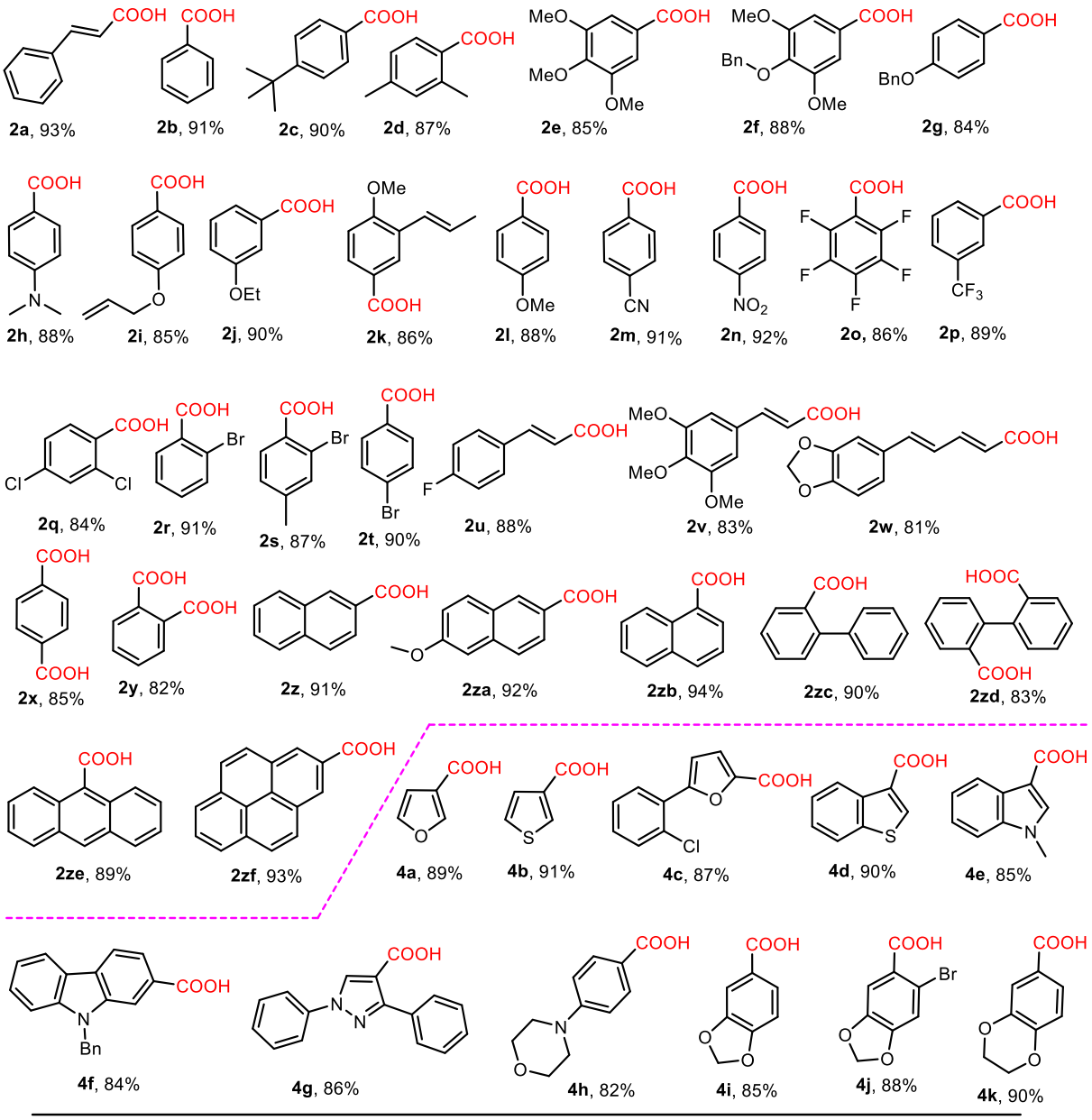
Table of Contents

Section-I: General information.

All reagents (purchased from Sigma Aldrich, Alfa-Aesar, TCI and Spectrochem) were used without further purification unless otherwise stated. Tetrahydrofuran was distilled from sodium benzophenone ketyl radical, and Benzene was distilled over CaH_2. Analytical thin layer chromatography (TLC) was performed on 60 F_{254} (0.25 mm) plates and visualization was done under UV light (254 nm). Further visualization was done with p-anisaldehyde-sulphuric acid mixture and heating the plates at ~120 °C. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded at room temperature in $CDCl_3$, CD_3OD, DMSO-d_6 on 400 MHz Bruker-Asced instrument and chemical shifts are reported in parts per million (δ) scale using tetramethylsilane (TMS) as an internal standard. Standard abbreviations like s, d, t, q, dd, and m represent singlet, doublet, triplet, quartet, doublet of doublet, and multiplet respectively. Coupling constant (J) was measured in Hz. Optical rotations were recorded on an Rudolph research analytical instrument with cell volume of 2 ml using methanol as solvent, and sample concentration was taken as c = 5 mg/mL. High resolution mass spectral data were obtained from electrospray ionization (ESI) apparatus using the time-of-flight (TOF) mass spectrometry.

Section-II: General oxidation procedures.



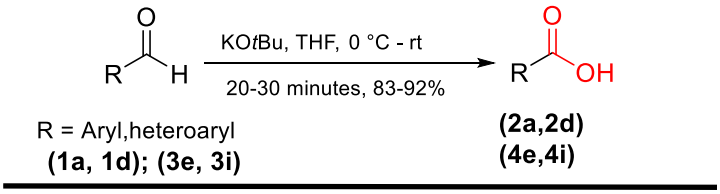


An oven dried round bottom flask was charged with potassium *t*-butoxide (2 equiv.) under ultra-high purity (UHP) grade nitrogen atmosphere. Dry tetrahydrofuran (2.5mL/mmol of potassium *t*-butoxide) was added to this vessel through a syringe and the solution was degassed by purging UHP grade nitrogen gas into solution for 15 minutes. A solution of corresponding aldehyde (1 equiv.) in dry tetrahydrofuran (approx. 1.5mL/mmol of aldehyde) was also degassed in a similar way for 15 minutes and then was added to this solution of potassium *t*-butoxide through cannula at 0°C. After the addition was complete, the ice bath was removed and the reaction mixture was allowed to stir for 15-30 minutes at room temperature until complete consumption of starting material occurred, as monitored by TLC analysis. After completion of the reaction, workup with water and subsequent acidification of the aqueous layer with HCl (10%) resulted in the precipitation of the required compound which was filtered under vacuum, washed with cold water and dried under vacuum to yield the corresponding acids (**2a-2zf** and **4a-4k**). [Note: Degassing was performed to avoid any possible interference from the air/oxygen which might be present in the solid reagents, solvents or

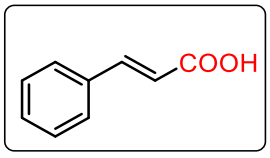
might creep in during the additions. When reactions were carried out without degassing, it was found that there was no change in the reaction outcome as far as the yield of corresponding acids and the time required for the reaction are concerned. Therefore we decided to stick to the non-degassing procedure. Further, addition through cannula was no more required, and simple addition using the syringe-septa technique was found to be equally good.]

Procedure for gram scale synthesis.

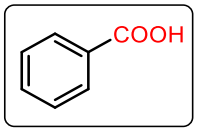
An oven dried round bottom flask was charged with potassium *t*-butoxide (8.5 g, 75.66 mmol, 2 equiv.) under nitrogen atmosphere. Dry tetrahydrofuran (60 mL) was added to this vessel through a syringe and the mixture was allowed to stir at 0 °C. A solution of cinnamaldehyde (5 g, 37.83 mmol, 1 equiv.) in dry tetrahydrofuran (25 mL) was slowly added to the solution of potassium *t*-butoxide through syringe at 0 °C. After the addition, ice bath was removed and the reaction mixture was allowed to stir for 20 minutes at room temperature until complete consumption of starting material occurred, as monitored by TLC analysis. After completion of the reaction, workup with water and subsequent acidification of the aqueous layer with 10% HCl (70 mL) resulted in the precipitation of the required compound which was filtered under vacuum, washed with cold water and dried under vacuum to yield the corresponding acid **2a** (5.153 g) in 92% yield. Similar procedure was followed for the synthesis of **2d, 4e** and **4i** (Corresponding acids obtained in 85%, 85% and 83% yield respectively).



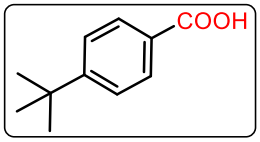
Section-III: Analytical data for general substrate scope:[1]



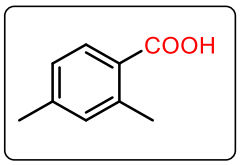
Cinnamic acid (**2a**)[1a, 1s, 1g] [White Solid, Yield = 93% (5.210 g from 5g of **1a**)]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.69–7.64 (m, 2H), 7.60 (d, J = 16.0 Hz, 1H), 7.42–7.37 (m, 3H), 6.53 (d, J = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.8, 144.1, 134.4, 130.4, 129.0, 128.3, 119.3.



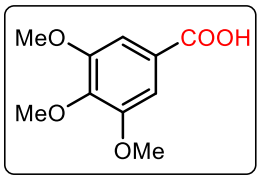
Benzoic acid (**2b**)[1a, 1b, 1e, 1g] [White Solid, Yield = 91% (635 mg from 500 mg of **1b**)]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.99 –7.95 (m, 2H), 7.60 –7.54 (m, 1H), 7.49 –7.43 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.7, 133.0, 131.0, 129.5, 128.7.



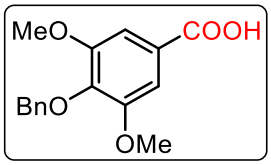
4-(tert-butyl) benzoic acid (**2c**)[1e, 1f] [White Solid, Yield = 90% (1.48 g from 1.5 g of **1c**)]; ^{1}H NMR (400 MHz, CD_3OD) δ 7.93 –7.88 (m, 2H), 7.48 –7.43 (m, 2H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, CD_3OD) δ 172.6, 156.4, 132.2, 130.4, 126.1, 35.8, 31.6.



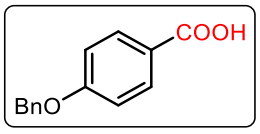
2,4-dimethylbenzoic acid (**2d**)[1o] [White Solid, Yield = 87% (3.78 g from 4 g of **1d**)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.97 (m, 1H), 7.11 –7.07 (m, 2H), 2.64 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 143.8, 141.7, 132.9, 132.0, 126.8, 125.6, 22.3, 21.6.



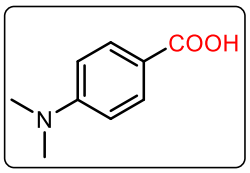
3,4,5-trimethoxybenzoic acid (**2e**)[1f,1g] [White Solid, Yield = 85% (624 mg from 500 mg of **1e**)]; ^{1}H NMR (400 MHz, CD_3OD) δ 7.33 (s, 2H), 3.87 (s, 6H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, CD_3OD) δ 169.4, 154.3, 143.3, 127.2, 108.1, 61.1, 56.6.



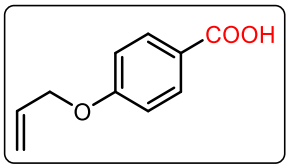
4-(benzyloxy)-3,5-dimethoxybenzoic acid (**2f**)[1p] [White Solid, mp = 159-161 °C, Yield = 88% (930 mg from 1 g of **1f**)]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.44 –7.43 (m, 2H), 7.39 –7.29 (m, 3H), 7.24 (s, 2H), 4.98 (s, 1H), 3.82 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.0, 152.9, 140.2, 137.6, 128.2, 128.0, 127.9, 126.1, 106.6, 74.0, 56.0.



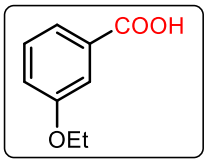
4-(benzyloxy) benzoic acid (**2g**)[1b, 1j] [White Solid, mp = 186-189 °C, Yield = 84% (450 mg from 500 mg of **1g**)]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.91–7.87 (m, 2H), 7.48 –7.44 (m, 2H), 7.43 –7.37 (m, 2H), 7.37 –7.31 (m, 1H), 7.11–7.07 (m, 2H), 5.18 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.2, 162.0, 136.6, 131.5, 128.6, 128.1, 127.9, 123.3, 114.7, 69.6.



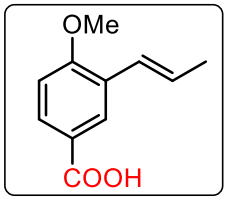
4-(dimethylamino) benzoic acid (**2h**)[1a] [Off-White Solid, Yield = 88% (487 mg from 500 mg of **1h**)]; ^{1}H NMR (400 MHz, CD_3OD) δ 7.88 –7.81 (m, 2H), 6.73 – 6.68 (m, 2H), 3.03 (s, 6H). ^{13}C NMR (100 MHz, CD_3OD) δ 170.8, 155.2, 132.5, 118.0, 111.8, 40.2.



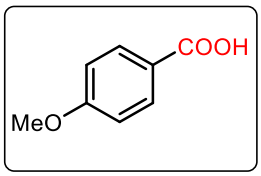
4-(allyloxy) benzoic acid (**2i**)[1g] [White Solid, mp = 163-165 °C, Yield = 85% (466 mg from 500 mg of **1i**)]; ^{1}H NMR (400 MHz, MeOD) δ 11.70 (s, 1H), 6.93 (d, J = 8.6 Hz, 2H), 6.07 (d, J = 8.6 Hz, 2H), 5.14 – 5.03 (m, 1H), 4.38 (dd, J = 51.3, 13.9 Hz, 2H), 3.68 (d, J = 5.0 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.1, 161.8, 133.2, 131.4, 123.1, 117.9, 114.5, 68.4.



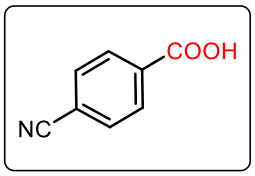
3-ethoxybenzoic acid (**2j**)[1q] [White Solid, mp = 136-139 °C, Yield = 90% (387 mg from 390 mg of **1j**)]; ^{1}H NMR (400 MHz, CD_3OD) δ 7.61 –7.56 (m, 1H), 7.53 –7.50 (m, 1H), 7.38 –7.32 (m, 1H), 7.15 –7.10 (m, 1H), 4.07 (q, J = 7.0 Hz, 2H), 1.40 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, CD_3OD) δ 169.7, 160.4, 133.2, 130.5, 122.9, 120.6, 116.0, 64.7, 15.1.



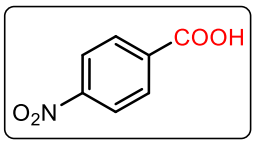
(E)-4-methoxy-3-(prop-1-en-1-yl)benzoic acid (**2k**) [White Solid, mp = 193-195 °C Yield = 86% (469 mg from 500 of **1k**)]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.95 (d, J = 2.0 Hz, 1H), 7.82 –7.77 (m, 1H), 7.05 (d, J = 8.7 Hz, 1H), 6.64 – 6.57 (m, 1H), 6.31 – 6.24 (m, 1H), 3.85 (s, 3H), 1.87 – 1.83 (m, 3H). ^{13}C NMR (100 MHz, CD_3OD) δ 170.0, 161.4, 131.1, 128.9, 128.1, 128.1, 126.2, 123.9, 111.4, 56.2, 19.0.



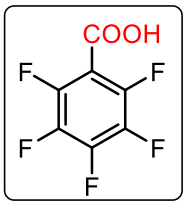
4-methoxybenzoic acid (**2l**)[1b, 1e, 1f] [White Solid, Yield = 88% (491 mg from 500 mg of **1l**)]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.63 (s, 1H), 7.89 (d, J = 8.4 Hz, 2H), 7.01 (d, J = 8.4 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.1, 162.9, 131.4, 123.0, 113.9, 55.5.



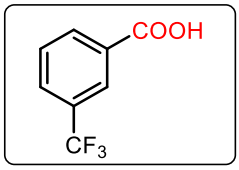
4-cyanobenzoic acid (**2m**)[1e,1g] [White Solid, Yield = 91% (510 mg from 500 mg of **1m**)]; ^{1}H NMR (400 MHz, CD_3OD) δ 8.14 (d, J = 8.3 Hz, 2H), 7.83 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, CD_3OD) δ 167.9, 136.1, 133.4, 131.3, 119.0, 117.2.



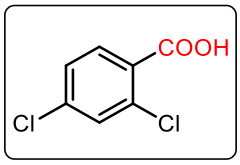
4-nitrobenzoic acid (**2n**)[1a, 1b, 1c] [Off-White Solid, Yield = 92% (1.016 g from 1 g of **1n**)]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.30 (d, J = 8.8 Hz, 2H), 8.15 (d, J = 8.9 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.9, 150.1, 136.4, 130.8, 123.8.



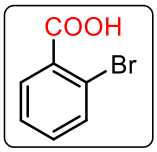
2,3,4,5,6-pentafluorobenzoic acid (**2o**)[1i] [White Solid, mp = 106-10 °C, Yield = 86% (930 mg from 1 g of **1o**)]; ^{19}F NMR (377 MHz, DMSO-d_6) δ -140.6 – -140.7 (m, 2F), -151.3 – -151.4 (m, 1F), -161.7 – -161.9 (m, 2F). ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.0 (s), 145.9 (m), 143.4 (m), 141.1 (m), 138.7 (m), 136.2, 109.4 (m).



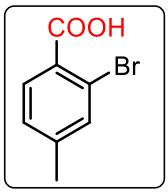
3-(trifluoromethyl)benzoic acid (**2p**)[1a] [White Solid, Yield = 89% (745 mg from 1 g of **1p**)]; ^{1}H NMR (400 MHz, CD_3OD) δ 8.29 – 8.24 (m, 2H), 7.92 – 7.87 (m, 1H), 7.72 – 7.65 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.2, 133.3, 132.0, 130.1, 129.7, 129.4, (m) 125.6 (m), 123.9 (d, J = 272.7 Hz)



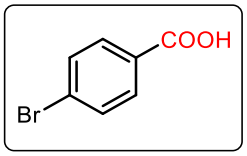
2,4-dichlorobenzoic acid (**2q**)[1e] [White Solid, Yield = 84% (455 mg from 500 mg of **1q**)]; ^{1}H NMR (400 MHz, CD_3OD) δ 7.86 (d, J = 8.4 Hz, 1H), 7.57 (d, J = 2.0 Hz, 1H), 7.44 –7.39 (m, 1H). ^{13}C NMR (100 MHz, CD_3OD) δ 167.8, 139.0, 135.6, 133.7, 131.7, 130.8, 128.3.



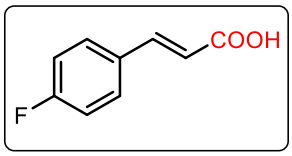
2-bromobenzoic acid (**2r**)[1a, 1c] [Off-White Solid, Yield = 91% (494 mg from 500 mg of **1r**)]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.76 – 7.67 (m, 2H), 7.49 –7.39 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.6, 133.9, 133.9, 132.7, 130.7, 127.8, 120.1.



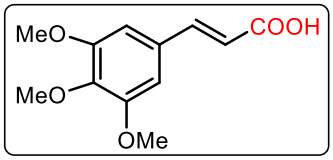
2-bromo-4-methylbenzoic acid (**2s**)[1r] [Off-White Solid, Yield = 87% (470 mg from 500 mg of **1s**)]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.67 (d, J = 7.9 Hz, 1H), 7.53 (s, 1H), 7.24 (d, J = 7.8 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.2, 143.4, 134.4, 131.0, 130.3, 128.4, 120.5, 20.6.



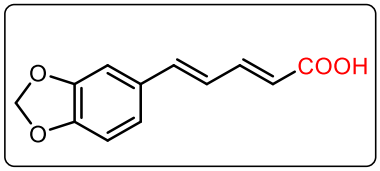
4-bromobenzoic acid (**2t**)[1a, 1b, 1c] [White Solid, Yield = 90% (971 mg from 1 g of **1t**)]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.85 (d, J = 8.5 Hz, 2H), 7.69 (d, J = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.8, 131.8, 131.4, 130.1, 127.1.



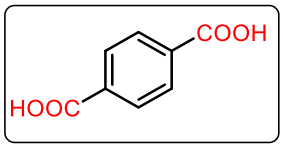
(*E*)-3-(4-fluorophenyl) acrylic acid (**2u**)[1s] [Off-White Solid, Yield = 88% (934 mg from 1 g of **1u**)]; ^{1}H NMR (400 MHz, CD_3OD) δ 7.70 – 7.59 (m, 3H), 7.18 – 7.10 (m, 2H), 6.43 (d, J = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, CD_3OD) δ 170.2, 165.3 (d, J = 250.5 Hz), 145.0, 132.3 (d, J = 3.0 Hz), 131.3 (d, J = 9.1 Hz), 119.3 (d, J = 3.0 Hz), 116.9 (d, J = 22.2 Hz).



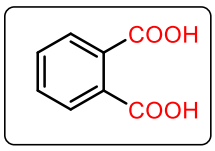
(*E*)-3-(3,4,5-trimethoxyphenyl)acrylic acid (**2v**)[1m] [Off-White Solid, mp = 126-128 °C, Yield = 83% (445 mg from 500 of **1v**)]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.52 (d, J = 15.9 Hz, 1H), 7.02 (s, 2H), 6.53 (d, J = 15.9 Hz, 1H), 3.81 (s, 6H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.9, 153.2, 144.3, 139.4, 130.0, 118.6, 105.8, 60.2, 56.1.



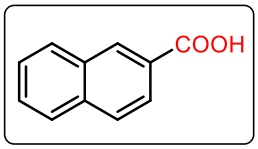
(2*E*,4*E*)-5-(benzo[d][1,3]dioxol-5-yl)penta-2,4-dienoic acid (**2w**)[1h] [White Solid, mp = 200-202 °C, Yield = 81% (262 mg from 300 mg of **1w**)]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.34–7.22 (m, 1H), 7.23 (d, J = 1.4 Hz, 1H), 7.01 (dd, J = 8.1, 1.5 Hz, 1H), 6.98 – 6.94 (m, 2H), 6.92 (d, J = 8.0 Hz, 1H), 6.05 (s, 2H), 5.92 (d, J = 15.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.7, 148.1, 148.0, 144.6, 139.8, 130.5, 124.9, 123.1, 121.2, 108.5, 105.7, 100.4.



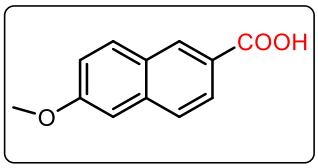
Terephthalic acid (**2x**)[1d,1e] [White Solid, Yield = 85% (1.051 g from 1 g of **1x**)]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.04 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.8, 134.5, 129.5.



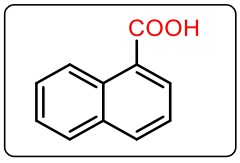
Phthalic acid (**2y**)[1d, 1e] [White Solid, Yield = 82% (508 mg from 500 mg of **1y**)]; ^{1}H NMR (400 MHz, DMSO) δ 7.69 – 7.64 (m, 2H), 7.61 – 7.55 (m, 2H). ^{13}C NMR (100 MHz, DMSO) δ 168.8, 132.9, 130.9, 128.4.



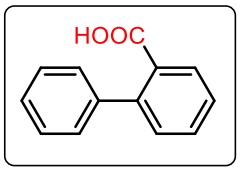
2-naphthoic acid (**2z**)[1a, 1b, 1j] [White Solid, Yield = 91% (1.298 g from 1.3 g of **1z**)]; ^{1}H NMR (400 MHz, CD_3OD) δ 8.60 (s, 1H), 8.02 (dd, J = 8.6, 1.6 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.7 Hz, 2H), 7.56 (m, J = 16.2, 6.9, 1.2 Hz, 2H). ^{13}C NMR (100 MHz, CD_3OD) δ 170.0, 137.0, 134.0, 132.1, 130.3, 129.3, 129.2, 129.1, 128.8, 127.8, 126.3.



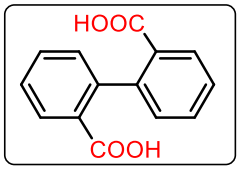
6-methoxy-2-naphthoic acid (**2za**)[1j] [White Solid, mp = 202-204 °C, Yield = 92% (985 mg from 1 g of **1za**)]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.51 (s, 1H), 8.00 (d, J = 9.0 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.6 Hz, 1H), 7.38 (s, 1H), 7.23 (d, J = 8.8 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.7, 159.3, 136.9, 131.0, 130.5, 127.6, 127.1, 125.9, 125.8, 119.6, 106.1, 55.5.



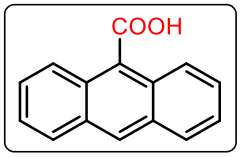
1-naphthoic acid (**2zb**)[1j, 1n, 1s] [Off-White Solid, Yield = 94% (518 mg from 500 mg of **1zb**)]; ^{1}H NMR (400 MHz, CD_3OD) δ 8.94–8.89 (m, 1H), 8.20 (dd, J = 7.2, 1.3 Hz, 1H), 8.05 (d, J = 8.2 Hz, 1H), 7.94 – 7.89 (m, 1H), 7.61–7.55 (m, 1H), 7.55 – 7.48 (m, 2H). ^{13}C NMR (100 MHz, CD_3OD) δ 171.0, 135.4, 134.3, 132.7, 131.3, 129.6, 128.8, 128.5, 127.2, 126.9, 125.6.



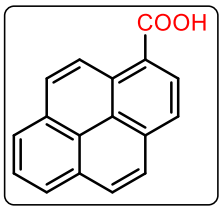
[1,1'-biphenyl]-2-carboxylic acid (**2zc**)[1j] [Off-White Solid, Yield = 90% (265 mg from 270 mg of **1zc**)]; ^{1}H NMR (400 MHz, CD_3OD) δ 7.80 (dd, J = 7.7, 1.1 Hz, 1H), 7.53 –7.48 (m, 1H), 7.42 –7.28 (m, 7H). ^{13}C NMR (100 MHz, CD_3OD) δ 172.4, 143.4, 142.6, 133.0, 132.1, 131.8, 130.5, 129.5, 129.0, 128.2, 128.1.



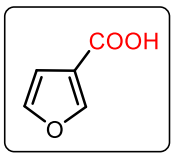
[1,1'-biphenyl]-2,2'-dicarboxylic acid (**2zd**)[1k] [White Solid, mp = 230-232 °C, Yield = 83% (191 mg from 200 mg of **1zd**)]; ^{1}H NMR (400 MHz, CD_3OD) δ 8.00 – 7.99 (m, 1H), 7.98 –7.97 (m, 1H), 7.56 –7.50 (m, 2H), 7.44 – 7.39 (m, 2H), 7.19 –7.15 (m, 2H). ^{13}C NMR (100 MHz, CD_3OD) δ 170.4, 170.3, 145.1, 145.0, 132.4, 132.3, 131.5, 131.4, 131.2, 131.1, 131.0, 130.9, 128.0, 127.9.



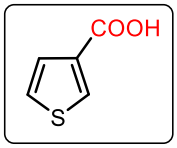
anthracene-9-carboxylic acid (**2ze**)[1l] [Off-White Solid, Yield = 89% (286 mg from 300 mg of **1ze**)]; ^{1}H NMR (400 MHz, CD_3OD) δ 8.60 (s, 1H), 8.16 – 8.04 (m, 4H), 7.60–7.49 (m, 4H). ^{13}C NMR (100 MHz, CD_3OD) δ 173.2, 132.5, 130.5, 129.9, 129.7, 129.0, 127.9, 127.0, 126.6, 126.1.



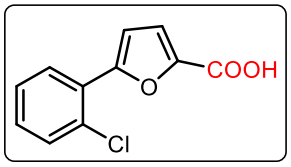
pyrene-1-carboxylic acid (**2zf**) [Off-White Solid, mp = 270-272 °C, Yield = 93% (497 mg from 500 mg of **1zf**)]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.22 (d, J = 9.4 Hz, 1H), 8.61 (d, J = 8.1 Hz, 1H), 8.36–8.26 (m, 5H), 8.20 (d, J = 8.9 Hz, 1H), 8.14–8.08 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.2, 133.7, 130.7, 130.2, 129.9, 129.6, 129.3, 128.5, 127.3, 126.8, 126.6, 126.3, 124.7, 124.6, 124.1, 123.5.



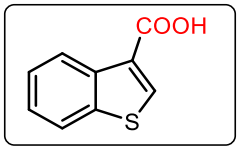
furan-3-carboxylic acid (**4a**)[1a] [Off-White Solid, Yield = 89% (1.038 g from 1 g of **3a**)]; ^{1}H NMR (400 MHz, CD_3OD) δ 8.13 – 8.10 (m, 1H), 7.57–7.54 (m, 1H), 6.74–6.72 (m, 1H). ^{13}C NMR (100 MHz, CD_3OD) δ 166.5, 149.5, 145.4, 120.9, 110.8.



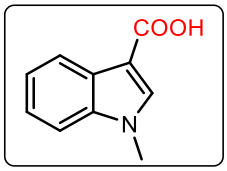
thiophene-3-carboxylic acid (**4b**)[1a] [White Solid, Yield = 91% (1.036 g from 1 g of **3b**)]; ^{1}H NMR (400 MHz, CD_3OD) δ 8.21 – 8.16 (m, 1H), 7.51–7.47 (m, 1H), 7.46 –7.43 (m, 1H). ^{13}C NMR (100 MHz, CD_3OD) δ 166.1, 135.4, 134.2, 128.9, 127.4.



5-(2-chlorophenyl)furan-2-carboxylic acid (**4c**)[1u] [Off-White Solid, mp = > 300 °C Yield = 87% (373 mg from 400 mg of **3c**)]; ^{1}H NMR (400 MHz, CD_3OD) δ 7.99 (dd, J = 7.9, 1.7 Hz, 1H), 7.52 (dd, J = 8.0, 1.2 Hz, 1H), 7.46–7.39 (m, 1H), 7.38 – 7.33 (m, 1H), 7.32 (d, J = 3.7 Hz, 1H), 7.25 (d, J = 3.7 Hz, 1H). ^{13}C NMR (100 MHz, CD_3OD) δ 159.3, 152.5, 144.5, 131.0, 130.4, 130.1, 128.8, 127.9, 127.6, 119.4, 112.8.

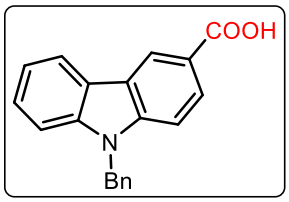


benzo[b]thiophene-3-carboxylic acid (**4d**)[1a] [Off-White Solid, mp = 176-178 °C, Yield = 90% (393 mg from 400 mg of **3d**)]; ^{1}H NMR (400 MHz, CD_3OD) δ 8.56 (d, J = 7.8 Hz, 1H), 8.51 (s, 1H), 7.93 (d, J = 7.9 Hz, 1H), 7.51 – 7.37 (m, 2H). ^{13}C NMR (100 MHz, CD_3OD) δ 165.9, 141.6, 138.3, 138.2, 128.7, 126.3, 126.0, 125.6, 123.6.

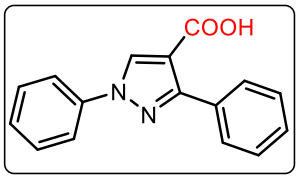


1-methyl-1H-indole-3-carboxylic acid (**4e**)[1t] [Off-White Solid, mp = 209-211 °C, Yield = 85% (2.525 g from 2.7 g of **3e**)]; ^{1}H NMR (400 MHz, CD_3OD) δ 8.07 (d, J = 7.7 Hz, 1H), 7.90 (s, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.29–7.18 (m, 2H), 3.84 (s, 3H).

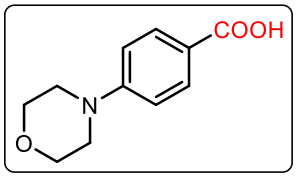
^{13}C NMR (100 MHz, CD_3OD) δ 168.8, 138.9, 137.3, 128.2, 123.7, 122.7, 122.2, 111.1, 107.6, 33.5.



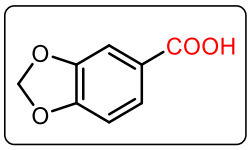
9-benzyl-9H-carbazole-3-carboxylic acid (**4f**) [Off-White Solid, mp = 260-262 °C, Yield = 84% (266 mg from 300 mg of **3f**)]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.81 (d, J = 1.4 Hz, 1H), 8.30 (d, J = 7.7 Hz, 1H), 8.04 (dd, J = 8.6, 1.6 Hz, 1H), 7.68 (dd, J = 18.6, 8.5 Hz, 2H), 7.50 – 7.45 (m, 1H), 7.26 – 7.20 (m, 4H), 7.18 – 7.14 (m, 2H), 5.71 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.1, 142.8, 140.9, 137.5, 128.7, 127.5, 127.3, 126.8, 126.7, 122.6, 122.4, 122.1, 121.6, 120.9, 120.1, 110.1, 109.4, 45.9.



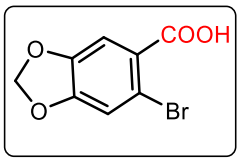
1,3-diphenyl-1H-pyrazole-4-carboxylic acid (**4g**)[1v] [White Solid, mp = 208-210 °C, Yield = 86% (365 mg from 400 mg of **3g**)]; ^{1}H NMR (400 MHz, CD_3OD) δ 8.80 (s, 1H), 7.89 – 7.80 (m, 4H), 7.57 – 7.49 (m, 2H), 7.46 – 7.35 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.9, 152.9, 138.9, 133.6, 132.2, 129.7, 129.2, 128.6, 127.9, 127.4, 119.1, 114.0.



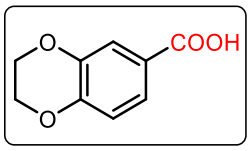
4-morpholinobenzoic acid (**4h**)[1a] [Off-White Solid, mp = 280-285 °C, Yield = 82% (445 mg from 500 mg of **3h**)]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.79 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.9 Hz, 2H), 3.76 – 3.68 (m, 4H), 3.25 –3.18 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.4, 154.0, 131.0, 120.0, 113.3, 66.0, 47.1.



benzo[d][1,3]dioxole-5-carboxylic acid (**4i**)[1a,1g, 1s] [White Solid, mp = 234-237 °C, Yield = 85% (2.820 g from 3 g of **3i**)]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.53 (dd, J = 8.1, 1.7 Hz, 1H), 7.34 (d, J = 1.6 Hz, 1H), 6.96 (d, J = 8.1 Hz, 1H), 6.10 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.8, 151.3, 147.6, 125.1, 124.8, 108.9, 108.1, 102.1.



6-bromobenzo[d][1,3]dioxole-5-carboxylic acid (**4j**)[1w] [White Solid, mp = 198-200 °C, Yield = 88% (469 mg from 500 mg of **3j**)]; ^{1}H NMR (400 MHz, CD_3OD) δ 7.33 (s, 1H), 7.14 (s, 1H), 6.07 (s, 2H). ^{13}C NMR (100 MHz, CD_3OD,) δ 168.6, 152.5, 148.7, 126.6, 115.2, 115.1, 111.7, 104.2.



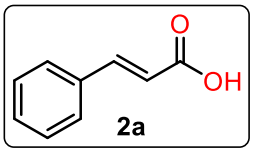
2,3-dihydrobenzo[b][1,4]dioxine-6-carboxylic acid (**4k**)[1l] [Off-White Solid, mp = 133-135 °C, Yield = 90% (494 mg from 500 mg of **3k**)]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.45 – 7.41 (m, 1H), 7.38 (d, J = 2.0 Hz, 1H), 6.92 (d, J = 8.4 Hz, 1H), 4.31–4.24 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.9, 147.6, 143.1, 123.9, 123.1, 118.3, 117.2, 64.5, 64.0.

Section-IV: Evidence for Mechanism:

(a) HPLC analysis of reaction performed under different conditions.

The reaction mixture was analyzed by using RP-HPLC (Reverse-Phase High Performance Liquid Chromatography). The RP-HPLC was equipped with Agilent 1260 series having PDA detector (UV detection at 254 nm), RP-18 endcapped (5µm) column bearing column temp 30℃ with flow rate of 1.5 ml/min and the gradient elution was performed with 40 to 60% MeOH in water as mobile phase for 20 minutes.

Chromatogram of pure cinnamic acid (2a).



2a

Area % Report

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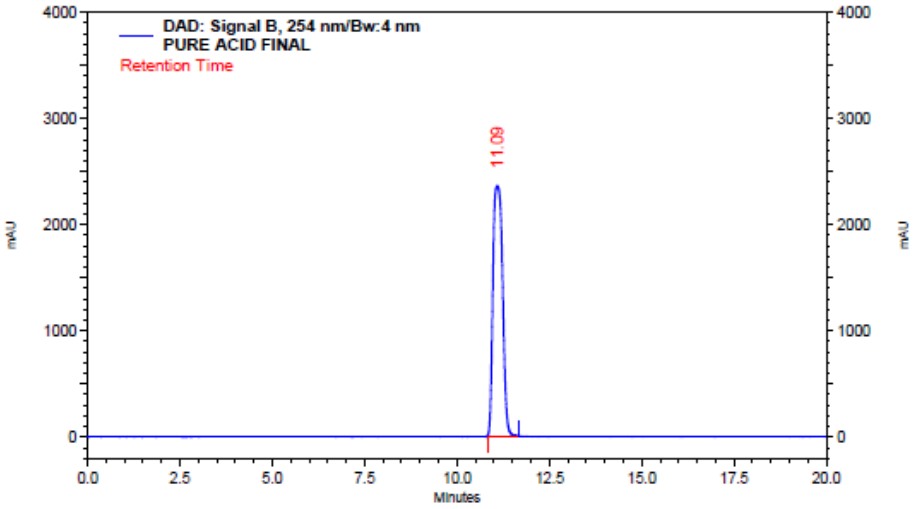

DAD: Signal B, 254 nm/Bw:4 nm
Results

Retention Time	Area	Area %	Height	Height %
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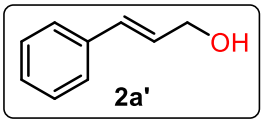
Totals	89457935	100.00	4934416	100.00

Chromatogram of pure cinnamyl alcohol (2a').



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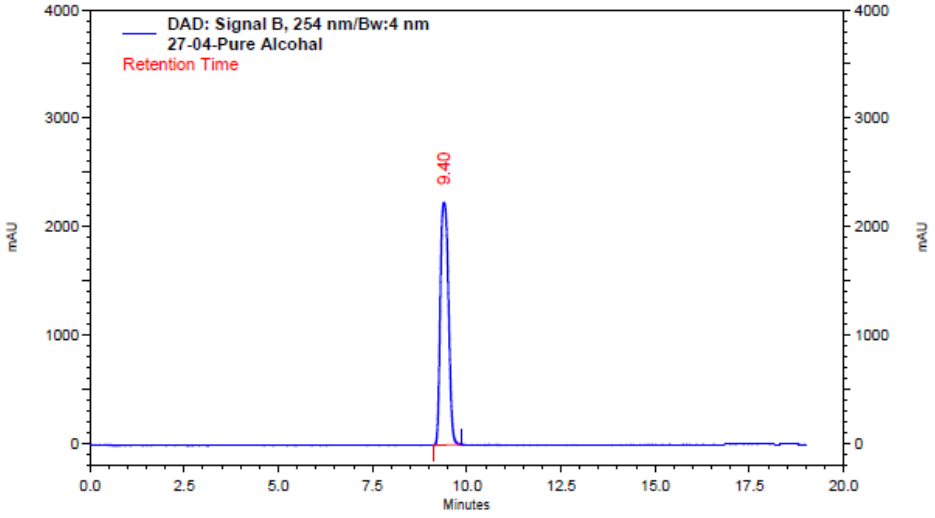

DAD: Signal B, 254 nm/Bw:4 nm
Results

Retention Time	Area	Area %	Height	Height %
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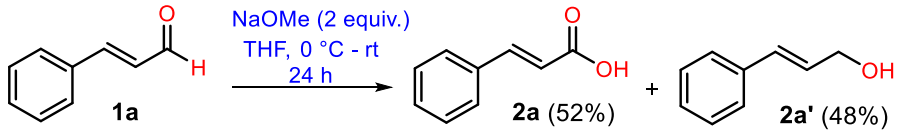
Totals	70326839	100.00	4688399	100.00

Chromatogram of reaction mixture performed by using 2 equivalents of sodium methoxide



Area % Report

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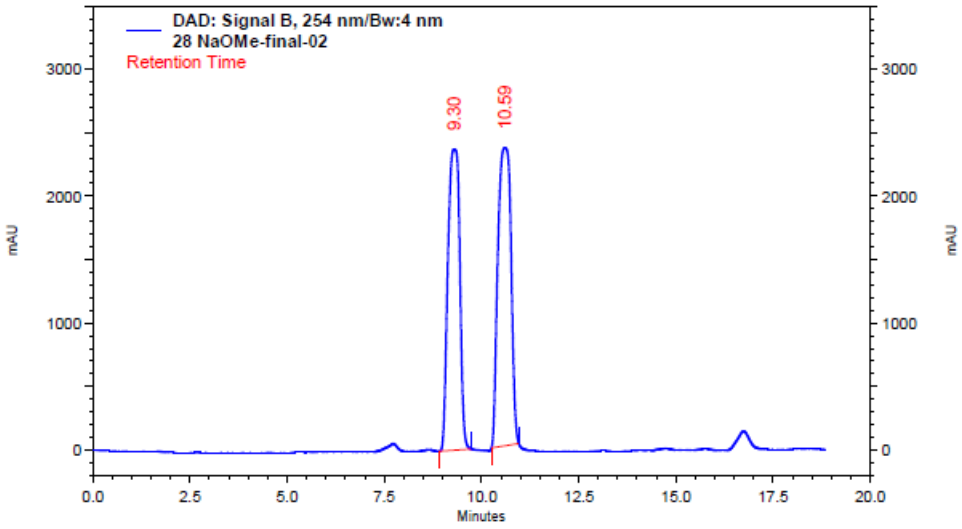
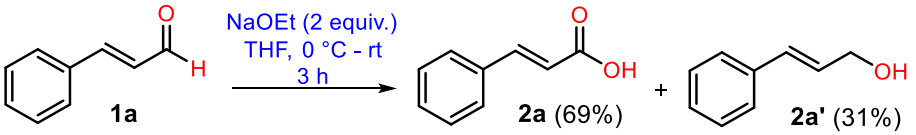


DAD: Signal B,
254 nm/Bw:4 nm
Results

Retention Time	Area	Area %	Height	Height %
9.300	105596813	47.81	4976481	50.26
10.593	115268756	52.19	4924871	49.74
Totals	220865569	100.00	9901352	100.00

Chromatogram of reaction mixture performed by using 2 equivalents of sodium ethoxide.



Area % Report

Data File: C:\Documents and Settings\user\Desktop\PK-NEW\28-NaOET-final-01.rslt\28-NaOET-final-01.dat
Method: untitled.met
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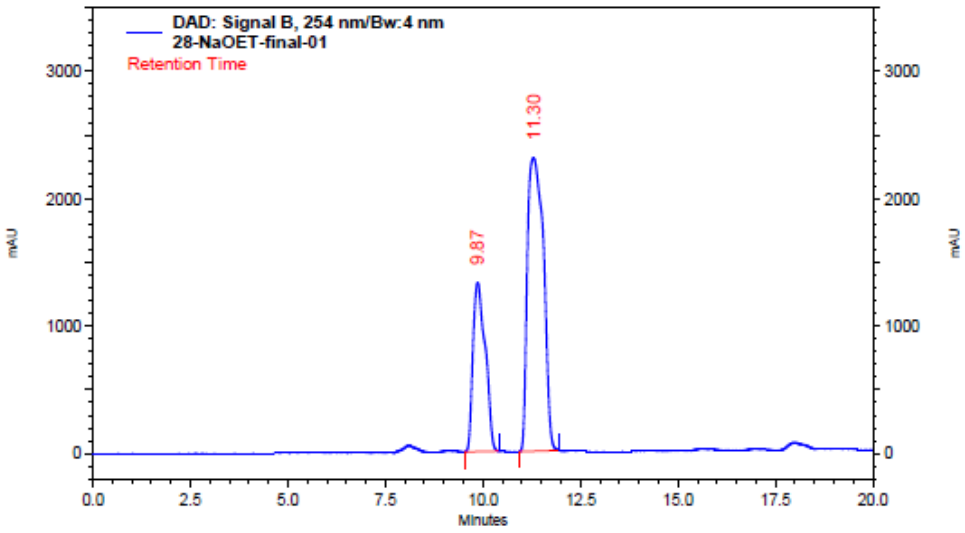
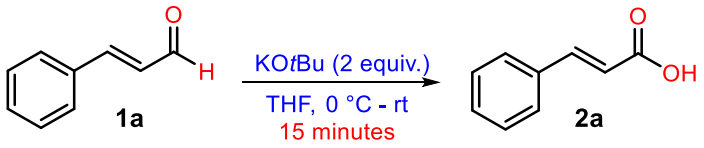


DAD: Signal B, 254 nm/Bw:4 nm
Results

Retention Time	Area	Area %	Height	Height %
9.867	61116051	30.66	2778340	36.52
11.300	138227951	69.34	4828813	63.48
Totals	199344002	100.00	7607153	100.00

Chromatogram of reaction mixture performed by using 2 equivalents of potassium tert-butoxide.



Area % Report

Data File: C:\Documents and Settings\user\Desktop\PK-NEW\28-POT-2 Eq.rslt\28-POT-2 Eq.dat
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Acquired: 4/28/2024 5:13:45 PM (GMT +05:30)
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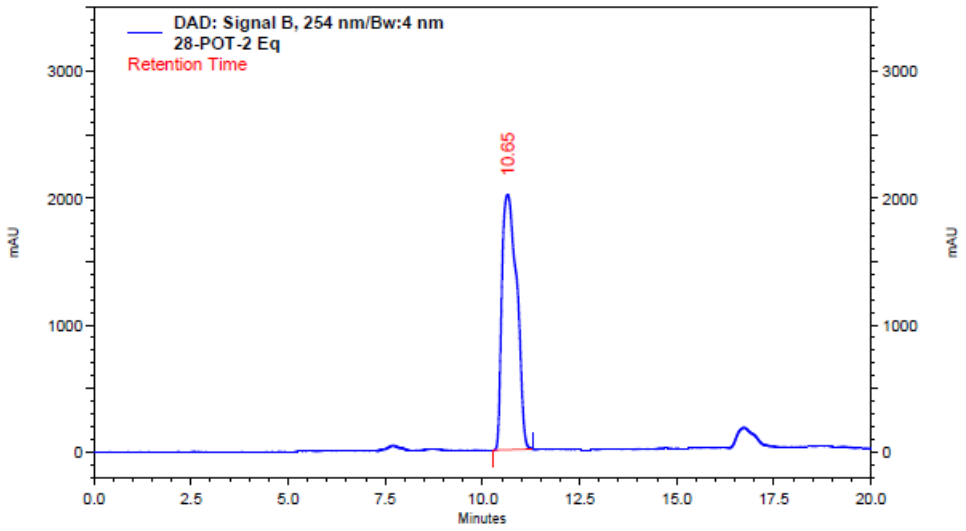
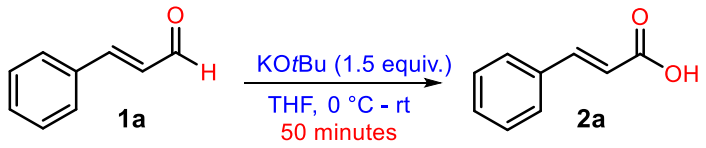


DAD: Signal B,
254 nm/Bw:4 nm
Results

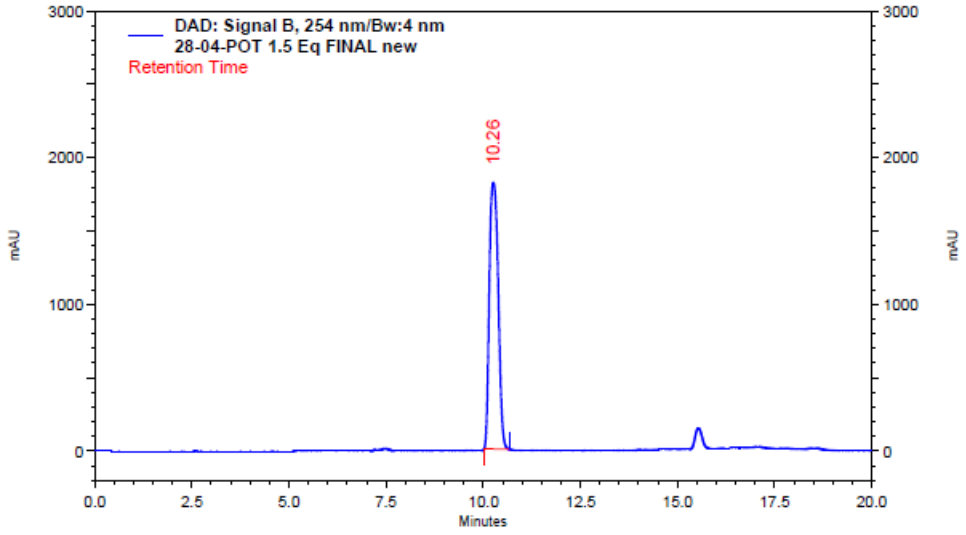
Retention Time	Area	Area %	Height	Height %
10.653	111924477	100.00	4215763	100.00
Totals	111924477	100.00	4215763	100.00

Chromatogram of reaction mixture performed by using 1.5 equivalents of potassium tert-butoxide.



Area % Report

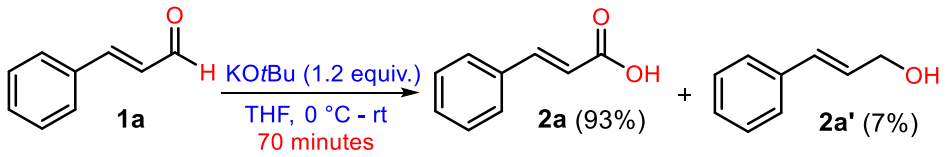
Data File: C:\Documents and Settings\user\Desktop\PK-NEW\28-04-POT 1.5 Eq FINAL new-01.rslt\28-04-POT 1.5 Eq FINAL new.dat
Method: untitled.met
Acquired: 4/28/2024 11:53:20 AM (GMT +05:30)
Printed: 4/28/2024 3:24:12 PM (GMT +05:30)



DAD: Signal B,
254 nm/Bw:4 nm
Results

Retention Time	Area	Area %	Height	Height %
10.260	60660167	100.00	3805964	100.00
Totals	60660167	100.00	3805964	100.00

Chromatogram of reaction mixture performed by using 1.2 equivalents of potassium tert-butoxide.



Area % Report

Data File: C:\Documents and Settings\user\Desktop\PK-NEW\28 POT-1.2 Eq-01.rslt\28 POT-1.2 Eq-01.dat
Method: untitled.met
Acquired: 4/28/2024 1:04:34 PM (GMT +05:30)
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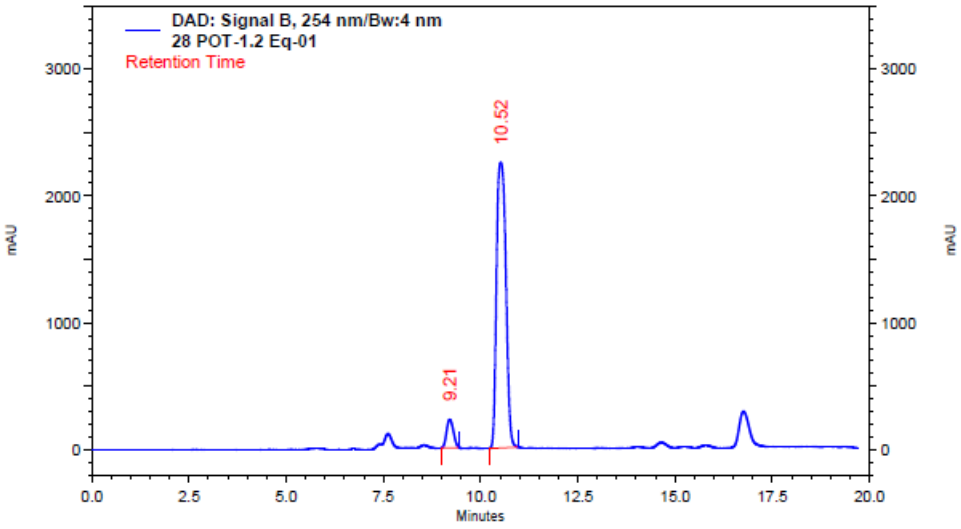
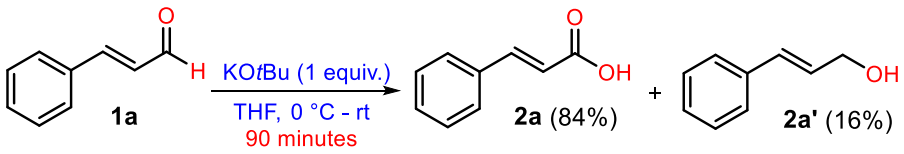


DAD: Signal B, 254 nm/Bw:4 nm
Results

Retention Time	Area	Area %	Height	Height %
9.207	5702864	6.77	466913	9.01
10.520	78549027	93.23	4716341	90.99
Totals	84251891	100.00	5183254	100.00

Chromatogram of reaction mixture performed by using 1 equivalent of potassium tert-butoxide.



Area % Report

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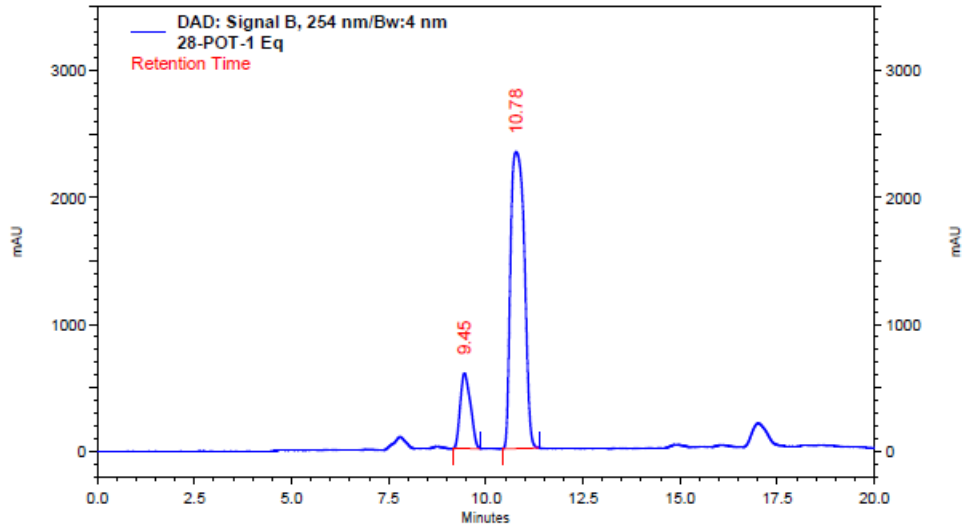
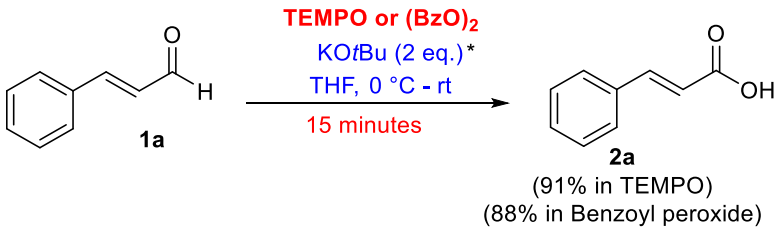
Method: untitled.met
Acquired: 4/28/2024 3:59:23 PM (GMT +05:30)
Printed: 4/28/2024 4:22:51 PM (GMT +05:30)



DAD: Signal B,
254 nm/Bw:4 nm
Results

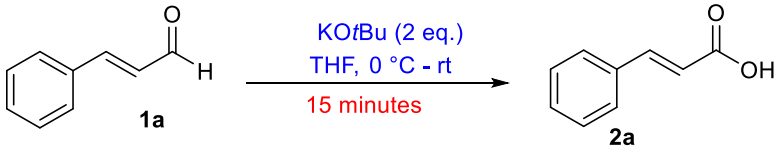
Retention Time	Area	Area %	Height	Height %
9.453	22705171	15.77	1244776	20.25
10.780	121252696	84.23	4903619	79.75
Totals	143957867	100.00	6148395	100.00

(b) Reactions in presence of radical scavengers.



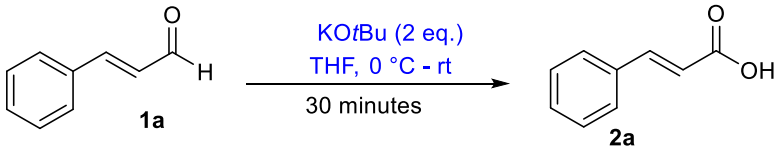
An oven-dried round bottom flask was charged with potassium *t*-butoxide (850 mg, 7.56 mmol, 2 equiv.) and 2,2,6,6-tetramethylpiperidine-N-oxyl (1180 mg, 7.56 mmol, 2.1 equiv.) under ultra-high purity (UHP) grade nitrogen atmosphere. Dry tetrahydrofuran (20 mL) was added to this vessel through a syringe and the solution was degassed by purging nitrogen gas into the solution for 15 minutes. A solution of cinnamaldehyde (500 mg, 3.78 mmol, 1 equiv.) in dry tetrahydrofuran (5 mL) was also degassed by purging UHP grade nitrogen gas into it for 15 minutes and then was added to the solution of potassium *t*-butoxide and 2,2,6,6-tetramethylpiperidine-N-oxyl through cannula at 0°C. The reaction mixture was allowed to stir for 15 minutes at room temperature until complete consumption of starting material occurred, as monitored by TLC analysis. After completion of the reaction, workup with water/EtOAc and subsequent acidification of the aqueous layer with 10% HCl (10 mL) resulted in the precipitation of the required compound which was filtered under vacuum, washed with cold water and dried under vacuum to yield the corresponding acid, **2a** [510 mg, 91%]. Similar procedure was followed for the use of benzoyl peroxide as radical scavenger and **2a** was isolated as an exclusive product [492 mg, 88%]. [Note: Organic layer was discarded since TLC analysis showed some very minor yellow colored impurities].

(c) Reactions in presence of heavy inert gas (Argon).



An oven dried round bottom flask was charged with potassium *t*-butoxide (338.8 mg, 3.02 mmol, 2 equiv.) under argon atmosphere. Dry tetrahydrofuran (10 mL) was added to this vessel through a syringe and the solution was degassed by purging argon gas into solution for 15 minutes. A solution of cinnamaldehyde (200 mg, 1.51 mmol, 1 equiv.) in dry tetrahydrofuran (4 mL) was also degassed in a similar way for 15 minutes and then was added to this solution of potassium *t*-butoxide through cannula at 0°C. After the addition was complete, the ice bath was removed and the reaction mixture was allowed to stir for 15 minutes at room temperature until complete consumption of starting material occurred, as monitored by TLC analysis. After completion of the reaction, workup with water and subsequent acidification of the aqueous layer with HCl (10%) resulted in the precipitation of the required compound **2a** which was filtered, washed with cold water and dried under vacuum.

(d) GC-MS Analysis of crude reaction mixture.[2]



An oven dried round bottom flask was charged with potassium *t*-butoxide (849 mg, 7.56 mmol, 2 equiv.) under nitrogen atmosphere and tetrahydrofuran (15 mL) was added to this vessel through a syringe. A solution of cinnamaldehyde (500 mg, 3.78 mmol, 1 equiv.) in dry tetrahydrofuran (6 mL) was added to this solution of potassium *t*-butoxide at 0ºC. After the addition, the reaction mixture was allowed to stir for 30 minutes at the same temperature until complete consumption of starting material occurred, as monitored by TLC analysis. After completion, the crude reaction mixture was injected into the sample vial through a syringe and subjected to GC-MS analysis separately in THF as well as *t*-BuOH (Note: in both the cases, we were able to successfully detect the isobutylene peak).

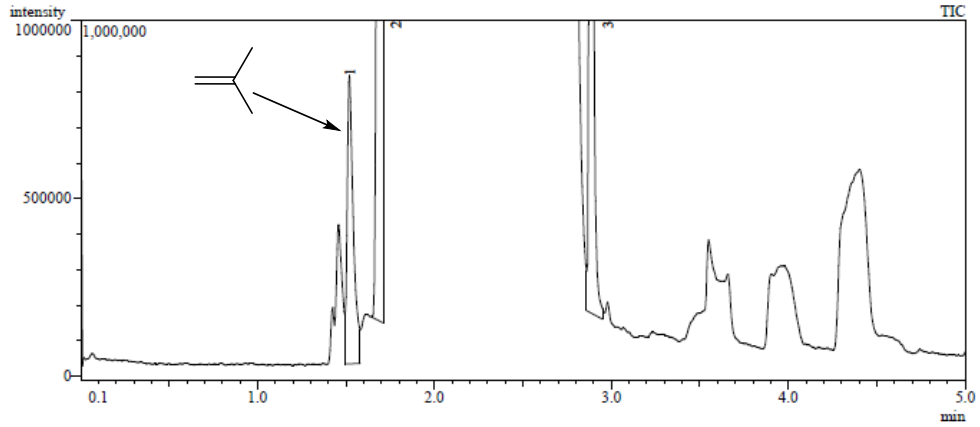
11-05-2024

Qualitative Analysis Report

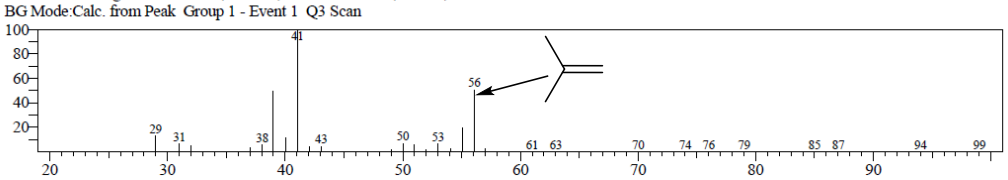
CSIR-INDIAN INSTITUTE OF INTEGRATIVE MEDICINE
Quality Management and Instrumentation Division
GCMS ANALYSIS REPORT

Sample Information

Analyzed by	: System Administrator
Analyzed	: 10-05-2024 14:50:37
Level #	: 1
Sample Name	: WIL-01-15
Sample ID	: WIL-01-15
Sample Amount	: 1
Vial #	: 5
Injection Volume	: 1.00
Data File	: D:\GCMS-2024\DATA\MAY-2024\10.05.2024-08.qgd
Method File	: D:\GCMS-2024\METHODS\GCMS_LIQ_1_5ms_ISOBUTYLENE.qgm
Tuning File	: D:\GCMS-2024\TUNNING\03.01.2024-LIQ-5MS.qgt
$EndIf$Modified by	: System Administrator
Modified	: 10-05-2024 15:32:13

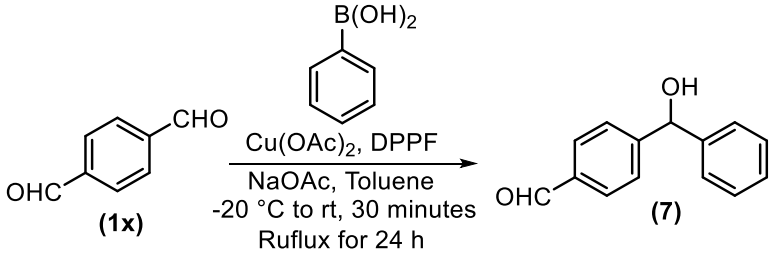


<< Target >>
Line#:1 R.Time:1.520(Scan#:305) MassPeaks:52
RawMode:Averaged 1.515-1.525(304-306) BasePeak:41.05(224107)
BG Mode:Calc. from Peak Group 1 - Event 1 Q3 Scan



Section-V: Synthesis of designer substrates for selectivity experiments:

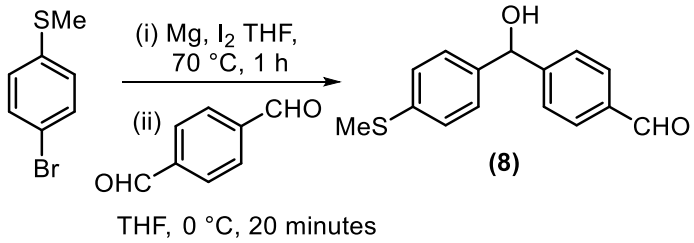
(a) Synthesis of 4-(hydroxy (phenyl)methyl) benzaldehyde (7):



A Round bottomed flask was charged with $Cu(OAc)_2 \cdot H_2O$ (135 mg, 0.75 mmol, 10 mol%) DPPF (620 mg, 1.12 mmol, 15 mol %), arylboronic acid (1815 mg, 14.91 mmol, 2 equiv.), terephthaldehyde **1x** (1000 mg, 7.46 mmol, 1 equiv.), NaOAc (1818 mg, 22.37 mmol, 3 equiv.) and toluene (60 mL). The resulting mixture was stirred under open atmosphere for 0.5 h at room temperature and then refluxed for 24 h. After complete consumption of starting material, the reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 × 70 mL). The combined organic layer was washed with water (100 mL), dried over Na_2SO_4, concentrated under vacuum and purified by flash column chromatography (80: 20, v/v Hexane: EtOAc as eluent) to yield the desired product, **7** [1.450 g, 85%].

4-(hydroxy(phenyl)methyl)benzaldehyde (**7**) [Gummy Solid]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.96 (s, 1H), 7.86 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 7.2 Hz, 2H), 7.31 (t, J = 7.5 Hz, 2H), 7.22 (t, J = 7.3 Hz, 1H), 6.18 (d, J = 4.0 Hz, 1H), 5.83 (d, J = 3.9 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.8, 152.6, 145.0, 135.0, 129.7, 128.4, 127.2, 126.9, 126.5, 74.1.

(b) Synthesis of 4-(hydroxy(4-(methylthio) phenyl)methyl) benzaldehyde (8):



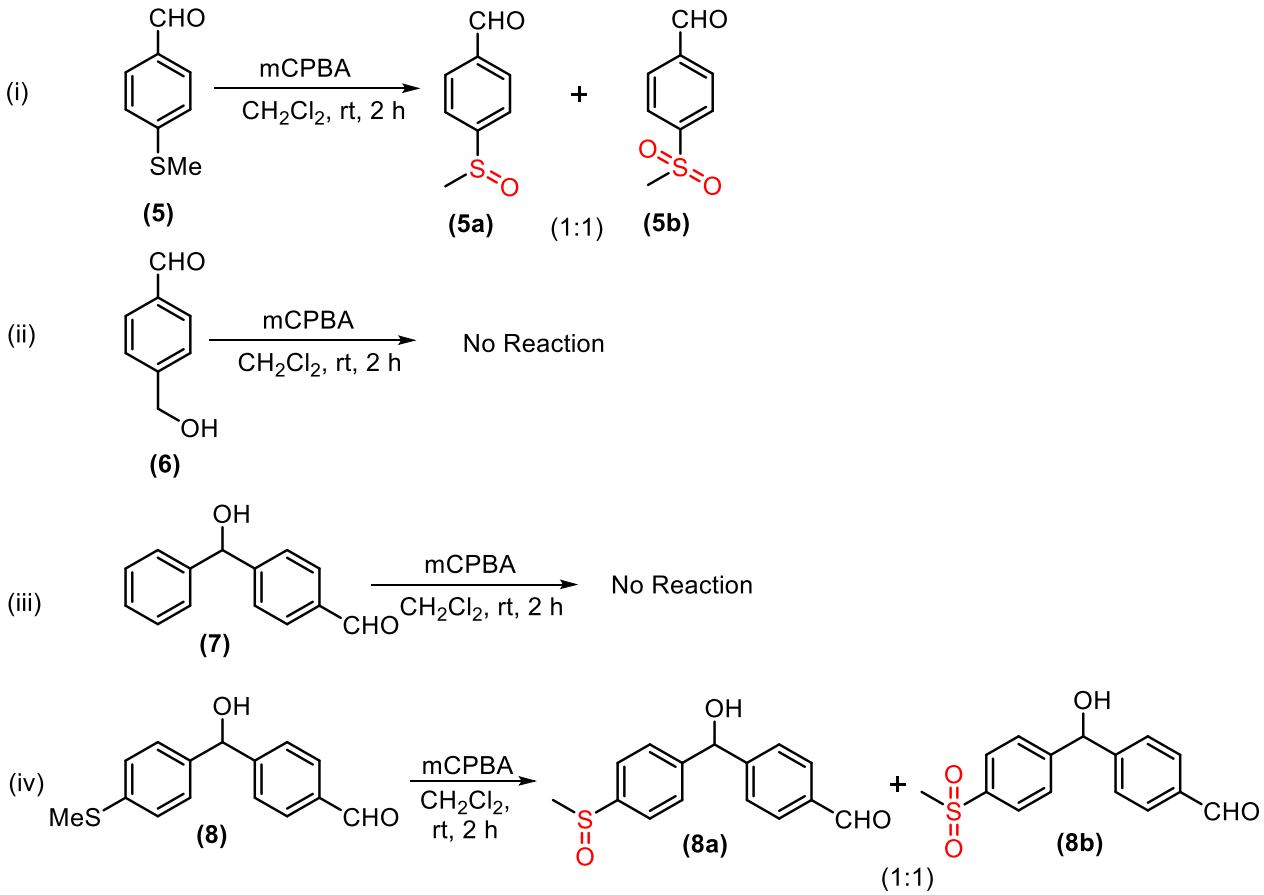
Two neck oven dried round bottom flask was charged with a magnetic stir bar, magnesium turnings (71.73 mg, 2.95 mmol, 1.2 equiv.) and few iodine crystals under nitrogen. Dry tetrahydrofuran (15 mL) was added using syringe septa technique and the mixture was allowed to stir at room temperature for few minutes. 4-bromothioanisole (500 mg, 2.46 mmol, 1.0 equiv.) dissolved in dry tetrahydrofuran (3 mL/mmol of 4-bromothioanisole) was added drop wise to this mixture over 30 minutes and reaction mixture was refluxed for another one hour. Reaction progress was monitored by TLC and upon complete consumption of starting material, the reaction mixture was cooled to obtain a grayish black solution of Grignard reagent. This Grignard reagent was slowly added through syringe to the solution of terephthaldehyde (363 mg, 2.71 mmol, 1.1 equiv.) in dry tetrahydrofuran

10 mL taken in another oven dried round bottom flask under nitrogen atmosphere at 0°C. The reaction mixture was allowed to stir for 20 minutes at the same temperature. The progress of the reaction was monitored by TLC and upon completion, the reaction mixture was quenched with aq. NH_4Cl solution. The mixture was extracted with ethyl acetate (3 x 60 mL) and the combined organic layer was washed with water, dried over Na_2SO_4, concentrated under vacuum and purified by column chromatography (90: 10, v/v Hexane: EtOAc as eluent) on silica gel to give the desired product **8** [496 mg, 78%].

4-(hydroxy(4-(methylthio)phenyl)methyl)benzaldehyde (**8**) [Gummy Solid]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.96 (s, 1H), 7.86 –7.84 (m, 2H), 7.61–7.59 (m, 2H), 7.34-7.32 (m, 2H), 7.22 – 7.19 (m, 2H), 6.13 (d, J = 3.7 Hz, 1H), 5.78 (d, J = 2.7 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.9, 152.5, 141.7, 136.8, 135.0, 129.7, 127.1, 126.8, 126.0, 73.6, 14.9. ESI HRMS m/z calcd. for $C_{15}H_{15}O_2S$ $[M+H]^+$: 259.0799, Found: 259.0793

(c) Selectivity experiments:

(i) Oxidation using weak oxidant (mCPBA)



To a stirred solution of corresponding aldehyde (**5** or **6** or **7** or **8**) (1 equiv.) in CH_2Cl_2 (4 mL/mmol of corresponding aldehyde) at 0 °C was slowly added mCPBA (2 equiv.). The reaction mixture was warmed up to room temperature and allowed to stir for 2 h and monitored by TLC. After complete consumption of starting material, the reaction mixture was washed with saturated solution of $NaHCO_3$ and extracted with ethyl acetate (3 times). The combined organic phase was dried over

$MgSO_4$, solvent was removed under vacuum and residue was purified by column chromatography (using Hexane-Ethyl acetate as eluent) to give the desired products.

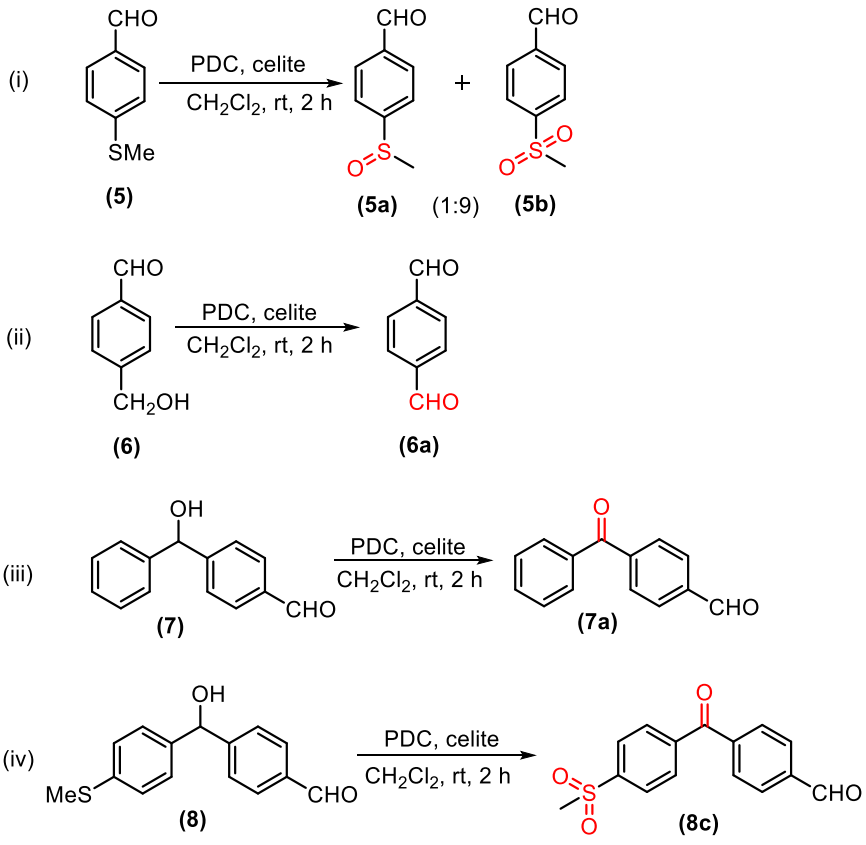
4-*(methylsulfinyl)benzaldehyde* (**5a**) [White Solid, mp = 162-164]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.13 (s, 1H), 8.15 (s, 4H), 3.30 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.7, 145.3, 139.4, 130.3, 127.9, 43.2. ESI HRMS m/z calcd. for $C_8H_9O_2S$ $[M+H]^+$: 169.0318, Found: 169.0329

4-(methylsulfonyl)benzaldehyde (**5b**) [White Solid, mp = 92-94]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.07 (s, 1H), 8.08 (d, J = 8.5 Hz, 2H), 7.89 (d, J = 8.1 Hz, 2H), 2.80 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.8, 152.9, 137.7, 130.2, 124.4, 43.0. ESI HRMS m/z calcd. for $C_8H_9O_3S$ $[M+H]^+$: 185.0267, Found: 185.0272

(4-(hydroxy(4-(methylsulfinyl)phenyl)methyl)benzylidene)oxonium (**8a**) [Gummy Solid]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.96 (s, 1H), 7.89 –7.85 (m, 4H), 7.71–7.63 (m, 4H), 6.41 (d, J = 4.0 Hz, 1H), 5.95 (d, J = 3.9 Hz, 1H), 3.17 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.8, 151.4, 150.6, 139.5, 135.3, 129.8, 127.2, 127.1, 127.0, 73.3, 43.6. ESI HRMS m/z calcd. for $C_{15}H_{15}O_3S$ $[M+H]^+$: 275.0736, Found: 275.0744

4-(hydroxy(4-(methylsulfonyl)phenyl)methyl)benzaldehyde (**8b**) [Gummy Solid]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.96 (s, 1H), 7.86 (d, J = 8.1 Hz, 2H), 7.69 – 7.58 (m, 6H), 6.30 (d, J = 3.6 Hz, 1H), 5.90 (d, J = 3.4 Hz, 1H), 2.69 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 193.2, 152.3, 148.2, 145.2, 135.5, 130.1, 127.6, 127.3, 124.2, 73.9, 49.0. ESI HRMS m/z calcd. for $C_{15}H_{15}O_4S$ $[M+H]^+$: 291.0686, Found: 291.0696

(ii) Oxidation using moderate oxidant (PDC)



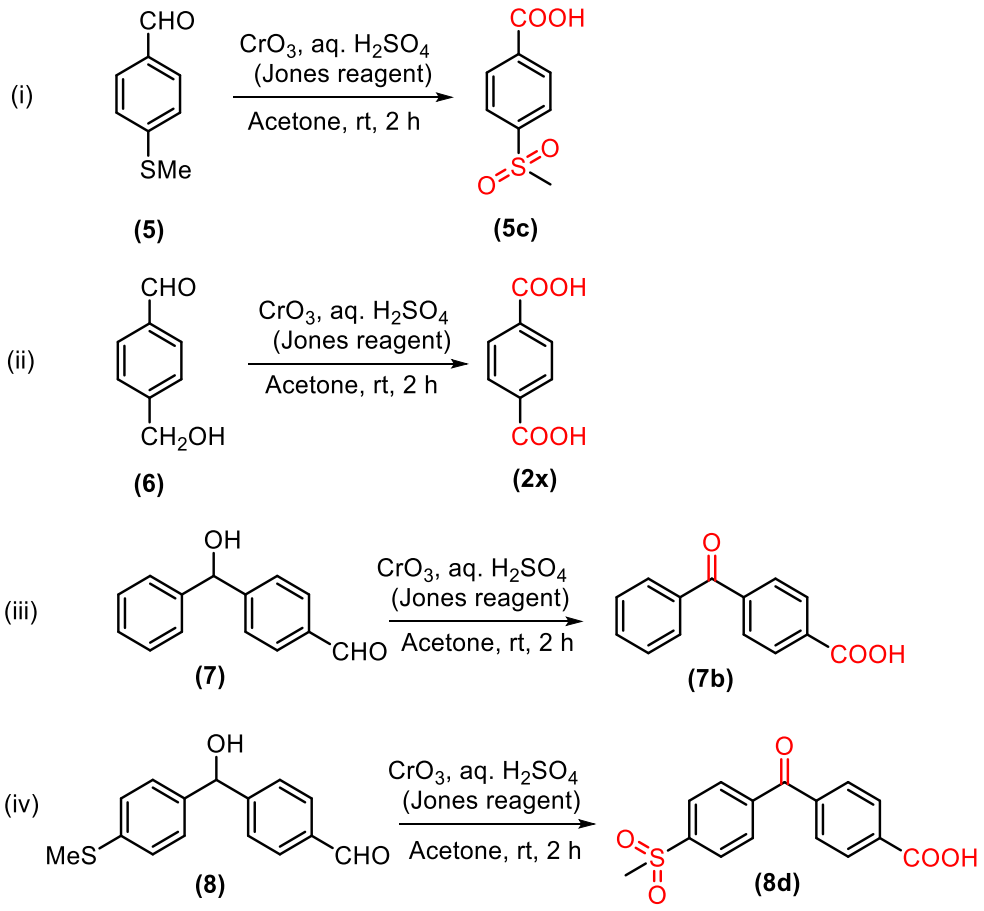
To a stirred solution of corresponding aldehyde (**5** or **6** or **7** or **8**) (1 equiv.) in CH_2Cl_2 (4 mL/mmol of corresponding aldehyde) at 0 °C, was added PDC (2 equiv.) and celite (1:1 w/w of PDC). The reaction mixture was stirred at room temperature for 2 h and monitored by TLC. After completion, the reaction mixture was filtered and the filtrate was evaporated under reduced pressure. Toluene was added 3 times to remove pyridine as an azeotropic mixture. The resulting dark brown residue was subjected to column chromatography to give pure product.

Terephthalaldehyde (**6a**) [Off-White Solid]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.12 (s, 2H), 8.10 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 193.4, 140.0, 130.3.

4-benzoylbenzaldehyde (**7a**) [White Solid, mp = 75-77]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.14 (s, 1H), 8.10 – 8.06 (m, 2H), 7.93 – 7.89 (m, 2H), 7.79–7.75 (m, 2H), 7.74 – 7.69 (m, 1H), 7.62 – 7.56 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 196.2, 193.7, 142.3, 138.8, 136.7, 134.0, 130.5, 130.3, 130.1, 129.3.

4-(4-(methylsulfonyl)benzoyl)benzaldehyde (**8c**) [Off-White Solid, mp = 116-118]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.13 (s, 1H), 8.10 – 8.02 (m, 2H), 7.90 – 7.86 (m, 2H), 7.72 – 7.68 (m, 2H), 7.44 – 7.40 (m, 2H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 194.4, 193.1, 146.1, 142.3, 138.2, 132.2, 130.5, 129.9, 129.6, 124.9, 14.0. ESI HRMS m/z calcd. for $C_{15}H_{13}O_4S$ $[M+H]^+$: 273.0580, Found: 273.0581

(iii) Oxidation using strong oxidant (Jones reagent)



A clean round bottom flask was charged with corresponding aldehyde (**5** or **6** or **7** or **8**) (1 equiv.) in acetone (4 mL/mmol of corresponding aldehyde) and allowed to stir at 0 °C in an ice bath. A freshly prepared Jones reagent (2 equiv.) was added drop wise to the reaction mixture with continuous stirring for 10-15 minutes at the same temperature. The Reaction mixture was then allowed to stir at room temperature for 2 h and progress of reaction was monitored with TLC. Upon completion, the reaction was quenched by slowly adding an aqueous $NaHCO_3$ solution. The mixture was extracted with ethyl acetate (3 times) and the organic layer was washed with water, dried over Na_2SO_4, concentrated under reduced pressure and purified by column chromatography on silica gel to give the desired product.

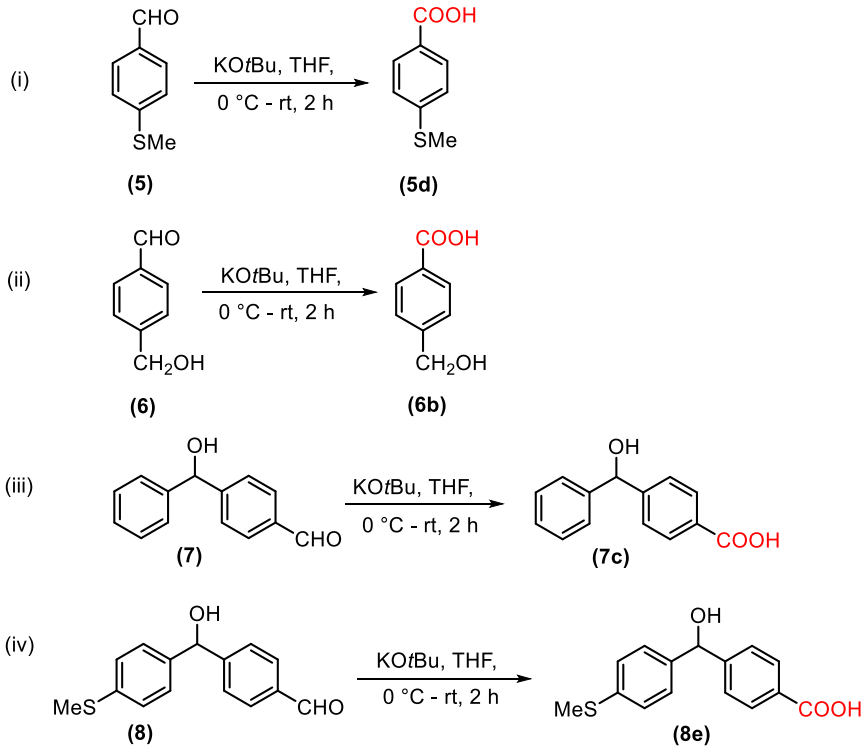
4-(methylsulfonyl)benzoic acid (**5c**) [Off-White Solid, mp = 228-230] [1a]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.10 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 8.2 Hz, 2H), 2.78 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.6, 151.3, 132.8, 130.0, 123.9, 43.1. ESI HRMS m/z calcd. for $C_8H_9O_4S$ $[M+H]^+$: 201.0216, Found: 201.0586

Terephthalic acid (**2x**) (NMR data on page **S7**).

4-benzoylbenzoic acid (**7b**) [Off-White Solid, mp = 200-202][1f]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.10 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 8.4 Hz, 2H), 7.78 – 7.74 (m, 2H), 7.73 – 7.68 (m, 1H), 7.61–7.55) (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 195.4, 166.7, 140.6, 136.5, 134.0, 133.1, 129.8, 129.7, 129.4, 128.7. ESI HRMS m/z calcd. for $C_{14}H_{11}O_3$[M+H] $^+$: 227.0703, Found: 227.0710

4-(4-(methylsulfonyl)benzoyl)benzoic acid (**8d**) [Gummy Solid]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.10 (d, J = 8.2 Hz, 1H), 7.93 (d, J = 8.3 Hz, 1H), 7.89 – 7.83 (m, 4H), 2.83 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 195.2, 167.1, 151.8, 140.5, 138.8, 134.7, 130.9, 130.3, 130.0, 124.4, 43.4. ESI HRMS m/z calcd. for $C_{15}H_{13}O_5S$ $[M+H]^+$: 305.0478, Found: 305.0652

(iv) Oxidation using our method (KO*t*Bu)



An oven dried round bottomed flask was charged with potassium *t*-butoxide (2 equiv.) under nitrogen atmosphere. Dry Tetrahydrofuran (2.5 mL/mmol of potassium *t*-butoxide) was added to this through a syringe and the solution was allowed to stir at 0°C for 5-10 minutes till the base dissolves. A solution of corresponding aldehyde (1 equiv.) in dry tetrahydrofuran (3 mL/mmol of aldehyde) was added drop wise to this solution at the same temperature and the reaction mixture was allowed to stir for 2 h at room temperature till the complete consumption of starting material, as monitored by TLC analysis. After completion of the reaction, workup with water and subsequent acidification of the aqueous layer with HCl (10%) resulted in the precipitation of the required compound which was filtered under vacuum, washed with cold water and dried under vacuum. [Note: As already mentioned in the manuscript, the reaction gets completed with 15-30 minutes, it is kept for 2 h in order to have uniform set of conditions as compared to other selectivity experiments]

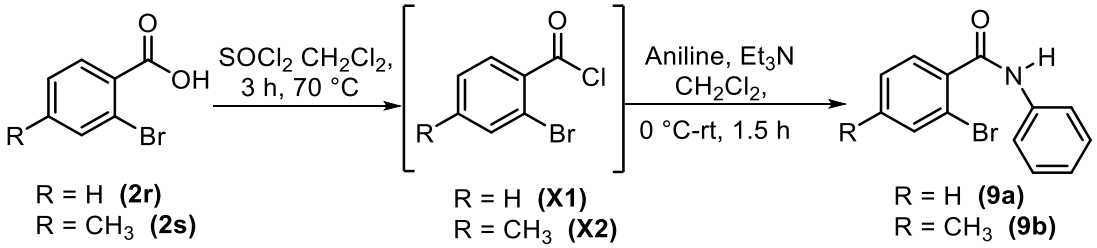
4-(methylthio) benzoic acid (**5d**) [White Solid, mp = 190-192 °C, Yield = 88% (485 mg from 500 mg of 5)] [1a]; ^{1}H NMR (400 MHz, CD_3OD) δ 7.94 – 7.89 (m, 2H), 7.31 – 7.25 (m, 2H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, CD_3OD) δ 169.7, 147.3, 131.1, 127.8, 125.9, 14.6.
4-(hydroxymethyl) benzoic acid (**6b**) [White Solid, mp = 184-186 °C, Yield = 85% (475 mg from 500 mg of 6)] [1a]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.84 (s, 1H), 7.90 (d, J = 8.2 Hz, 2H), 7.43 (d, J = 8.3 Hz, 2H), 5.35 (s, 1H), 4.57 (d, J = 2.6 Hz, 2H). ^{13}C NMR (100 MHz DMSO-d_6) δ 167.3, 147.8, 129.2, 126.2, 62.5.

4-(hydroxy (phenyl) methyl) benzoic acid (**7c**) [Off-White Solid, mp = 164-166 °C, Yield = 88% (378 mg from 400 mg of 7)]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.86 (s, 1H), 7.88 (d, J = 8.2 Hz, 2H), 7.50 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 7.3 Hz, 2H), 7.33–7.27 (m, 2H), 7.23–7.18 (m, 1H), 6.05 (d, J = 3.9 Hz, 1H), 5.77 (d, J = 3.7 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.3, 150.7, 145.1, 129.3, 128.3, 127.0, 126.4, 126.3, 74.0.

4-(hydroxy(4-(methylthio) phenyl)methyl) benzoic acid (**8e**) [White Solid, mp = > 300 °C, Yield = 85% (252 mg from 280 mg of 8)]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.87 (d, J = 8.3 Hz, 2H), 7.47 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 7.22 – 7.18 (m, 2H), 5.73 (s, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.5, 150.5, 142.0, 136.6, 129.8, 129.4, 127.1, 126.3, 126.0, 73.6, 14.9. ESI HRMS m/z calcd. for $C_{15}H_{13}O_3S$ $[M-H]^+$: 273.0560 Found: 273.0585

Section-VI: Synthesis of related natural products:

(a) Synthesis of PARP inhibitor and Phenaglydon:
(i) Synthesis of 2-Bromo-N-phenylbenzamide (9a) and 2-Bromo-4-methyl-N-phenylbenzamide (9b):



R = H **(2r)**
R = CH_3 **(2s)**

R = H **(X1)**
R = CH_3 **(X2)**

R = H **(9a)**
R = CH_3 **(9b)**

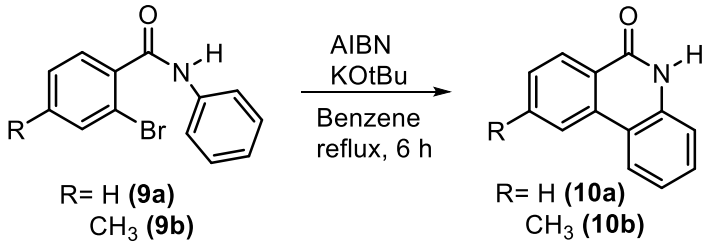
To a solution of acid **2r** (1000 mg, 4.97 mmol, 1 equiv.) in dry CH_2Cl_2 (4 mL/mmol of acid) was added thionyl chloride (1109 µl, 14.97 mmol, 3 equiv.) at room temperature. The reaction mixture was stirred at 70 °C for 3 hours before the solvent was removed. The residue containing acid chloride **X1** was dried under high vacuum and used for next step without further purification.

To the stirred solution of corresponding acid chloride **X1** in CH_2Cl_2 (30 mL), a solution of aniline (555.42 µl, 5.96 mmol, 1.2 equiv.) and triethyl amine (861 µl, 5.96 mmol, 1.2 equiv.) in CH_2Cl_2 (10 mL) was added drop wise using dropping funnel at 0 °C. After complete addition, reaction mixture was stirred for 1.5 h at room temperature. 10% aqueous HCl solution (50 mL) was added to the reaction mixture and resulting solution was extracted with CH_2Cl_2 (3 × 30 mL), combined organic layer was washed with water (100 mL), dried over Na_2SO_4, concentrated in vacuum and purified by column chromatography (80 : 20, v/v Hexane : EtOAc as eluent) to give the desired product **9a** in 88% yield. Similar procedure was followed for the synthesis of **9b** (obtained in 92% yield).

2-Bromo-N-phenylbenzamide (**9a**) [White Solid, mp = 118-120 °C, Yield = 88%]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.48 (s, 1H), 7.75 – 7.70 (m, 3H), 7.56 (dd, J = 7.5, 1.8 Hz, 1H), 7.52–7.48 (m, 1H), 7.44 – 7.40 (m, 1H), 7.39 – 7.32 (m, 2H), 7.14 – 7.08 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.9, 139.2, 139.0, 132.8, 131.3, 128.9, 128.9, 127.8, 123.9, 119.7, 119.1. ESI HRMS m/z calcd. for $C_{13}H_{11}$ BrNO $[M+H]^+$: 276.0004, Found: 276.0024

2-Bromo-4-methyl-N-phenylbenzamide (**9b**) [White Solid, mp = 156-158 °C, Yield = 92%]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.42 (s, 1H), 7.74 (d, J = 7.6 Hz, 2H), 7.57 (s, 1H), 7.45 (d, J = 7.7 Hz, 1H), 7.40 – 7.29 (m, 3H), 7.13-7.9 (m, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.0, 141.5, 139.1, 136.4, 133.0, 128.9, 128.8, 128.3, 123.9, 119.7, 119.0, 20.5. ESI HRMS m/z calcd. for $C_{14}H_{14}$ BrNO $[M+H]^+$: 290.0161, Found: 290.0181

(ii) Synthesis of Phenanthridin-6(5H)-one (10a) and 9-Methylphenanthridin-6(5H)-one (10b):



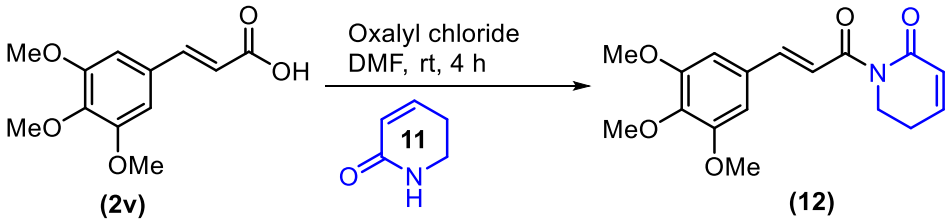
An oven dried round bottom flask was charged with 2-Bromo-N-phenylbenzamide **9a** (200 mg, 0.73 mmol, 1 equiv.), potassium *t*-butoxide (408 mg, 3.63 mmol, 5 equiv.), AIBN (42 mg, 0.25 mmol, 35 mol %) and benzene (10 mL). The reaction mixture was refluxed for 6 h and the progress of reaction was monitored by TLC. After completion, the reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 × 20 mL). The combined organic layer was washed with water (50 mL), dried over Na_2SO_4, concentrated in vacuum and purified by column chromatography (70 : 30,

v/v Hexane : EtOAc as eluent) to give the desired product **10a** in 78% yield. Similar procedure was followed for the synthesis of compound **10b** (obtained in 85% yield).

Phenanthridin-6(5H)-one (**10a**) [Off-White Solid, mp = 278-280 °C, Yield = 85% (111 mg from 200 mg of **9a**]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.68 (s, 1H), 8.50 (d, J = 8.1 Hz, 1H), 8.38 (d, J = 7.5 Hz, 1H), 8.34–8.30 (m, 1H), 7.89 – 7.82 (m, 1H), 7.68 – 7.61 (m, 1H), 7.52 – 7.46 (m, 1H), 7.39–7.35 (m, 1H), 7.29 – 7.24 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.3, 137.0, 134.7, 133.3, 130.1, 128.4, 127.9, 126.1, 123.7, 123.1, 122.8, 118.0, 116.6.

9-Methylphenanthridin-6(5H)-one (**10b**) [Off-White Solid, mp = 250-251 °C, Yield = 85% (123 mg from 200 mg of **9b**)]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.58 (s, 1H), 8.36 (d, J = 7.5 Hz, 1H), 8.31 (s, 1H), 8.20 (d, J = 8.1 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.37–7.33 (m, 1H), 7.28–7.22 (m, 1H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.9, 143.1, 136.8, 134.3, 129.5, 129.2, 127.5, 123.4, 123.3, 122.6, 122.2, 117.6, 116.1, 21.6.

(b) Synthesis of Piperlongumine (12):



To a solution of acid **2v** (200 mg, 0.84 mmol, 1.0 equiv.) and oxalyl chloride (319 mg, 2.5 mmol, 3 equiv.) in DMF (10 mL) was added lactam (98 mg, 1 mmol, 1.2 equiv.). The reaction mixture was stirred at room temperature for 4 h before it was quenched with saturated aqueous NH_4Cl (30 mL) and extracted with ethyl acetate (3 x 20 mL). The combined organic phase was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (50: 50, v/v Hexane: EtOAc as eluent) to provide the desired amide **12** in 82% yield.

(E)-1-(3-(3,4,5-trimethoxyphenyl)acryloyl)-5,6-dihydropyridin-2(1H)-one (**12**) [White Solid, mp = 122-125 °C, (219 mg, 85%)]; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.53 (d, J = 15.6 Hz, 1H), 7.28 (d, J = 15.6 Hz, 1H), 7.10 – 7.06 (m, 1H), 6.96 (s, 2H), 5.96 (d, J = 9.7 Hz, 1H), 3.88 (t, J = 6.4 Hz, 2H), 3.81 (s, 6H), 3.69 (s, 3H), 2.48 – 2.41 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.51, 165.5, 153.2, 147.5, 141.9, 139.4, 130.4, 124.5, 122.0, 105.6, 60.2, 56.0, 41.7, 24.4.

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1. (a) Y. Lu, W. Y. Tan, Ding, Y. Ding, W. Chen and H. Zhang, *J. Org. Chem.*, 2023, **88**, 8114-8122; (b) C. S. Batsika, C. Koutsilieris, G. S. Koutoulogenis, M. G. Kokotou, C. G. Kokotos and G. Kokotos, *Green Chem.*, 2022, **24**, 6224-6231; (c) V. Nair, V. Varghese, R. R. Paul, A. Jose, C. R. Sinu and R. S. Menon, *Org. Lett.,* 2010, **12**, 2653-2655; (d) I. Yavari and E. Karimi, *Synth. Commun.,* 2009, **39**, 3420; (e) J. Wu, J. Chen, L. Wang, H. Zhu, R. Liu, G. Song and Y. Li, *Green Chem.,* 2023, **25**, 940-945; (f) N. Xu, X. Peng, C. Luo, L. Huang, C. Wang, Z. Chen and J. Li, *Adv. Synth. Cat.*, 2023, **365,** 142-147; (g) M. Liu and C. J. Li, *Angew. Chem. Int. Ed.*, 2016, **128,** 10964-10968; (h) G. Meng, L. Hu, H. S. S. Chan, J. X. Qiao and J. Q. Yu, *J. Am. Chem. Soc.*, 2023, **145**, 13003-13007; (i) J. Xu, X. Yue, L. He, J. Shen, Y. Ouyang, C. Liang and W. Li, *ACS Sustainable Chem. Eng.,* 2022, **10**, 14119-14125; (j) S. K. Bhunia, P. Das, S. Nandi and R. Jana, *Org. lett.*, 2019, **21**, 4632-4637; (k) B. W. Zhao, L. Yang, C. Y. Long, Li, H. L. Li, Y. T. He and X. Q. Wang, *Org. Lett.,* 2023, **25**, 4700-4704; (l) Z. Zhao, Y. Liu, S. Wang, S. Tang, D. Ma, Z. Zhu and Y. Qiu, *Angew. Chem. Int. Ed.*, 2023, **135**, e202214710; (m) L. Gao, J. C. Meiring, C. Heise, A. Rai, A. Müller-Deku, A. Akhmanova and, O.Thorn-Seshold, *Angew. Chem. Int. Ed.*, 2022, **134**, e202114614; (n) R. P. Singh, S. Shee, M. Soni, A. Kale, L. Shukla, T. Ghoshal and V. Mishra, *Tetrahedron Lett.*, 2024, **137**, 154930; (o) K. Zeng, A. C. Stückl, J. Qin, M. Simon, C. J. Spyra, J. Li and K. Zhang, *Mol. Catal.*, 2023, **537**, 112919; (p) E. Orlowska, A. Roller, H. Wiesinger, M. Pignitter, F. Jirsa, R. Krachler and B. K. Keppler, *RSC Adv.,* 2016, **6**, 40238-40249; (q) H. E. Master, S. I. Khan and K. A. Poojari, *Bioorg. Med. Chem.*, 2005, **13**, 4891-4899; (r). F. Chacón-Huete, C. Messina, F. Chen, L. Cuccia, X. Ottenwaelder and P. Forgione, *Green Chem.,* 2018, **20**, 5261-5265; (s) H. Yu, J. Ren, Y. Xie, X. Su, A. Wang, L. Yan and Y. Wei, *Green Chem.,* 2022, **24**, 6511-6516; (t) W. Y. Tan, Y. Lu, J. F. Zhao, W. Chen and H. Zhang, *Org. Lett.,* 2021, **23**, 6648-6653; (u) D. K. Hu, D. S. Zhao, M. He, H. W. Jin, Y. M. Tang, L. H. Zhang and Z. N. Cui, *Bioorg. Med. Chem. Let.*, 2018, **28**, 3276-3280; (v) C. Loro, L. Molteni, M. Papis, L. Lo Presti, F. Foschi, E. M. Beccalli and G. Broggini, *Org. Lett.*, 2022, **24**, 3092-3096; (w) V. Rys, A. Couture, E. Deniau, S. Lebrun and P. Grandclaudon, *Tetrahedron,* 2005, **61**, 665–671.
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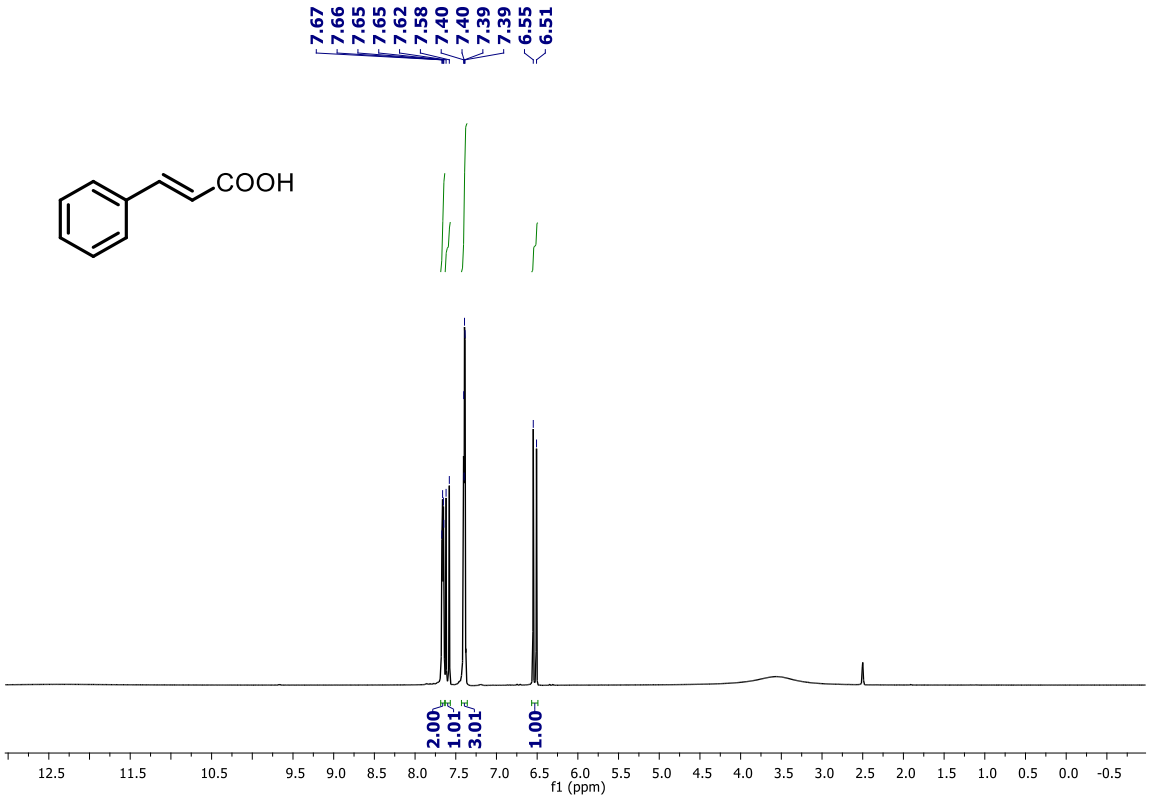
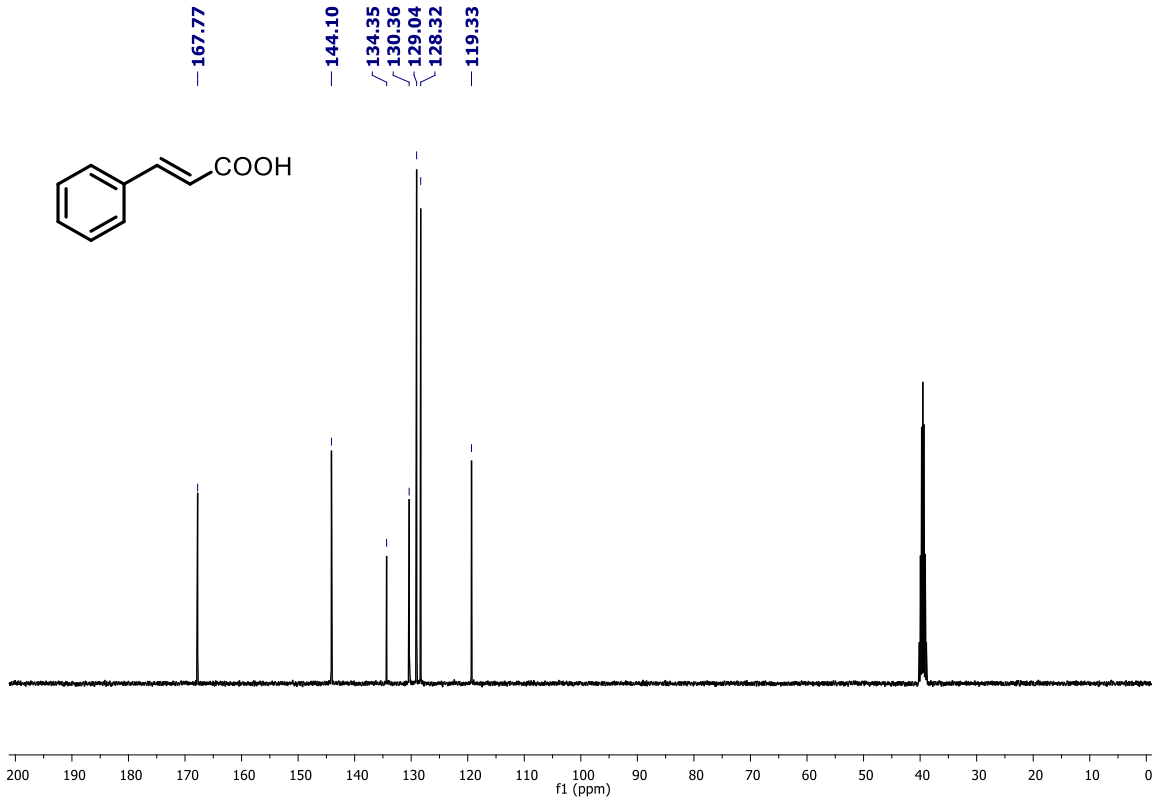
Section-VII: NMR Spectra:

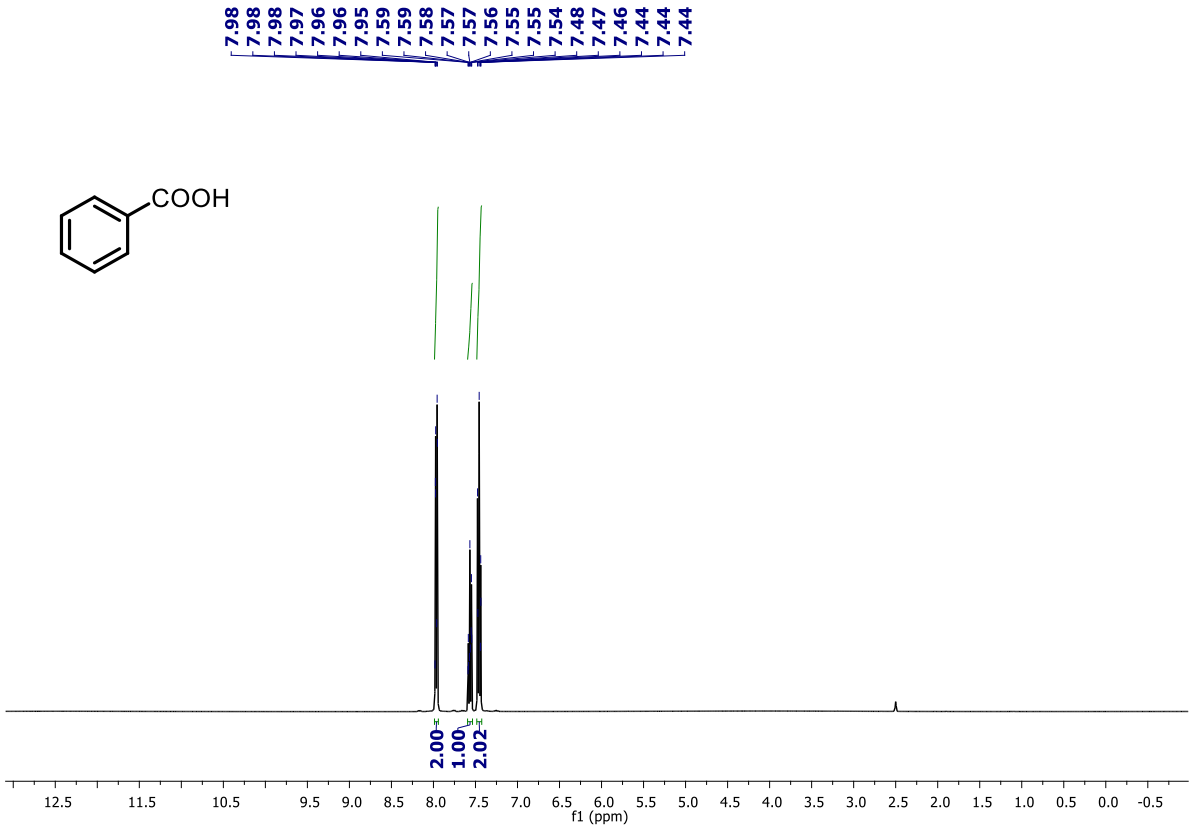
^{1}H NMR Spectrum of **2a** (DMSO-d_6, 400 MHz)



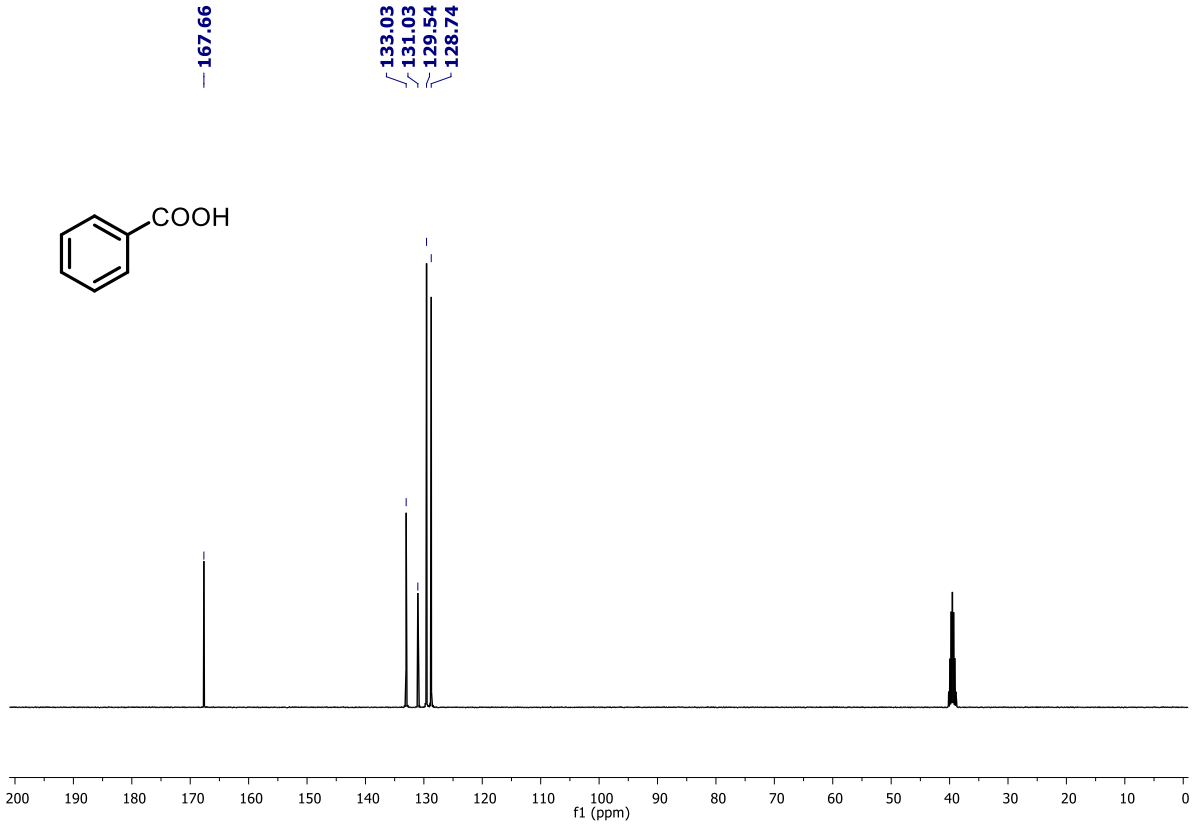
^{13}C {^{1}H} NMR Spectrum of **2a** (DMSO-d_6, 100 MHz)



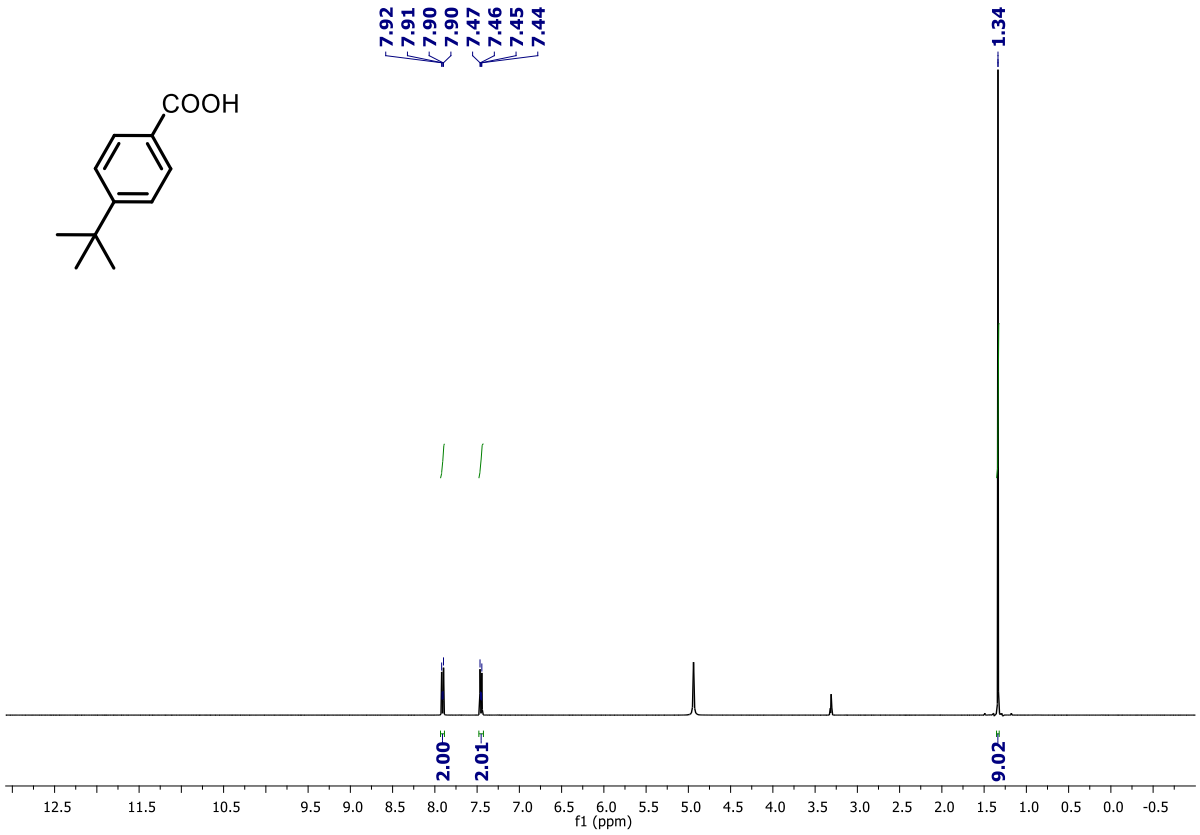
^{1}H NMR Spectrum of **2b** (DMSO-d_6, 400 MHz)



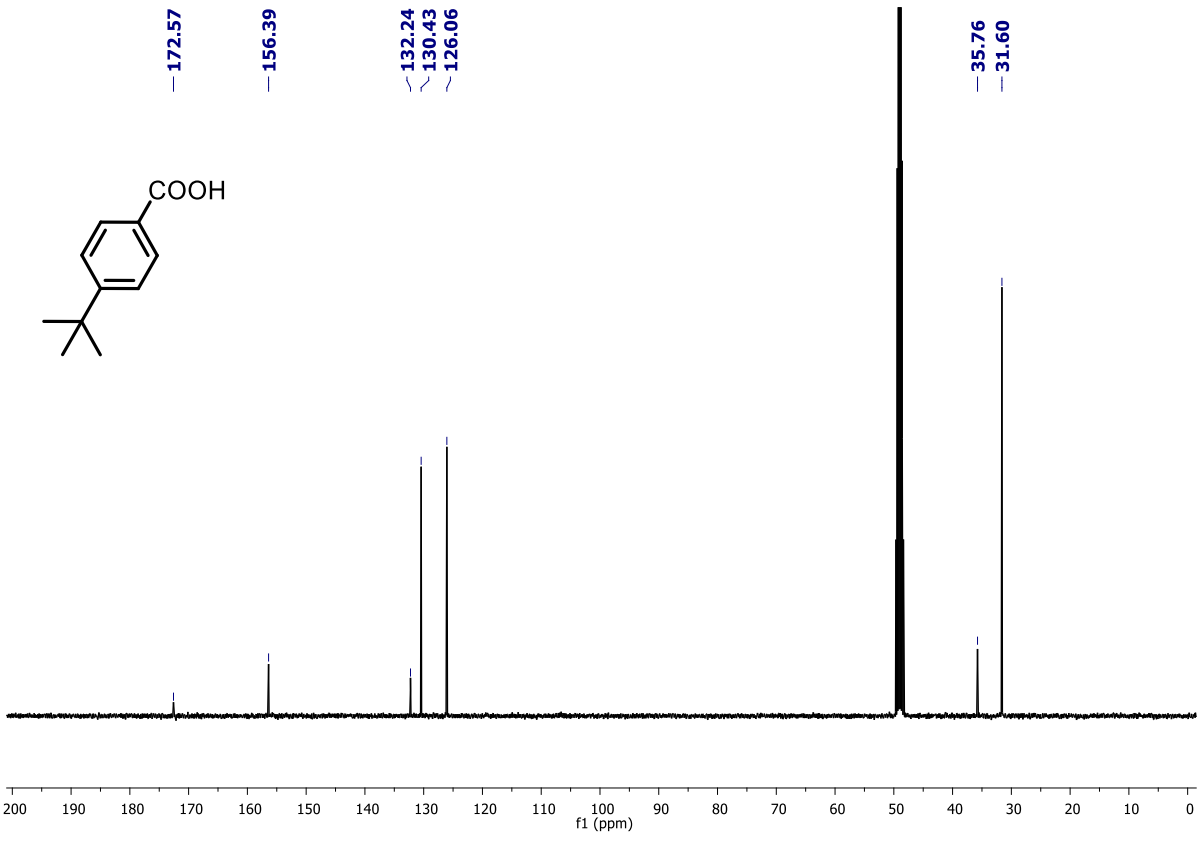
^{13}C {^{1}H} NMR Spectrum of **2b** (DMSO-d_6, 100 MHz)



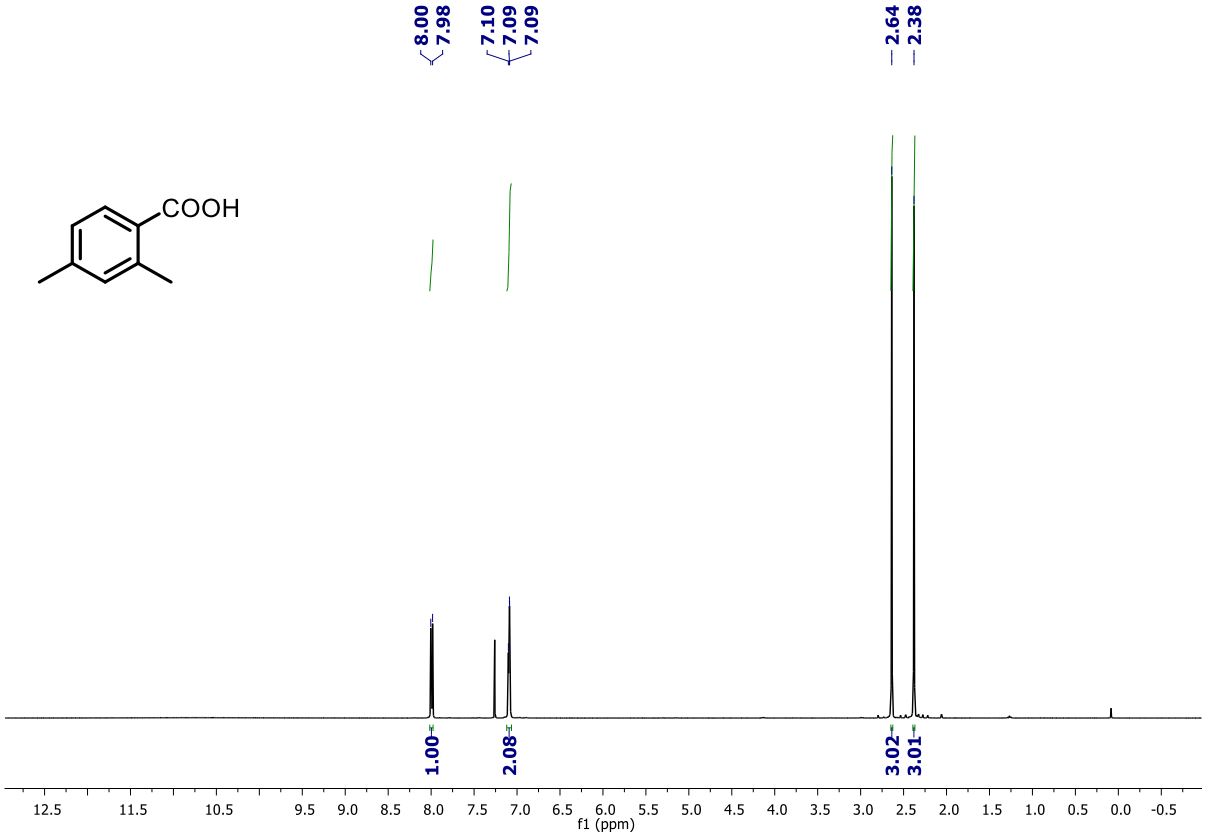
^{1}H NMR Spectrum of **2c** (CD_3OD, 400 MHz)



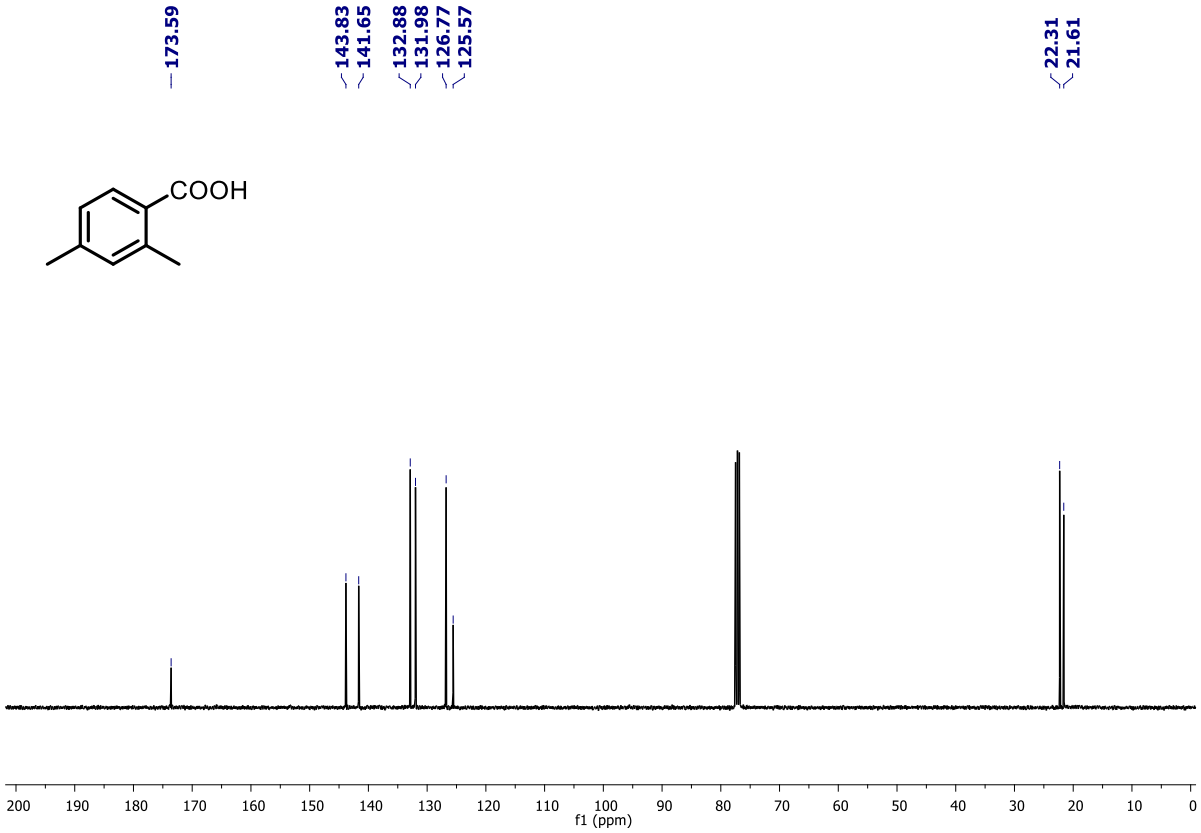
^{13}C {^{1}H} NMR Spectrum of **2c** (CD_3OD, 100 MHz)



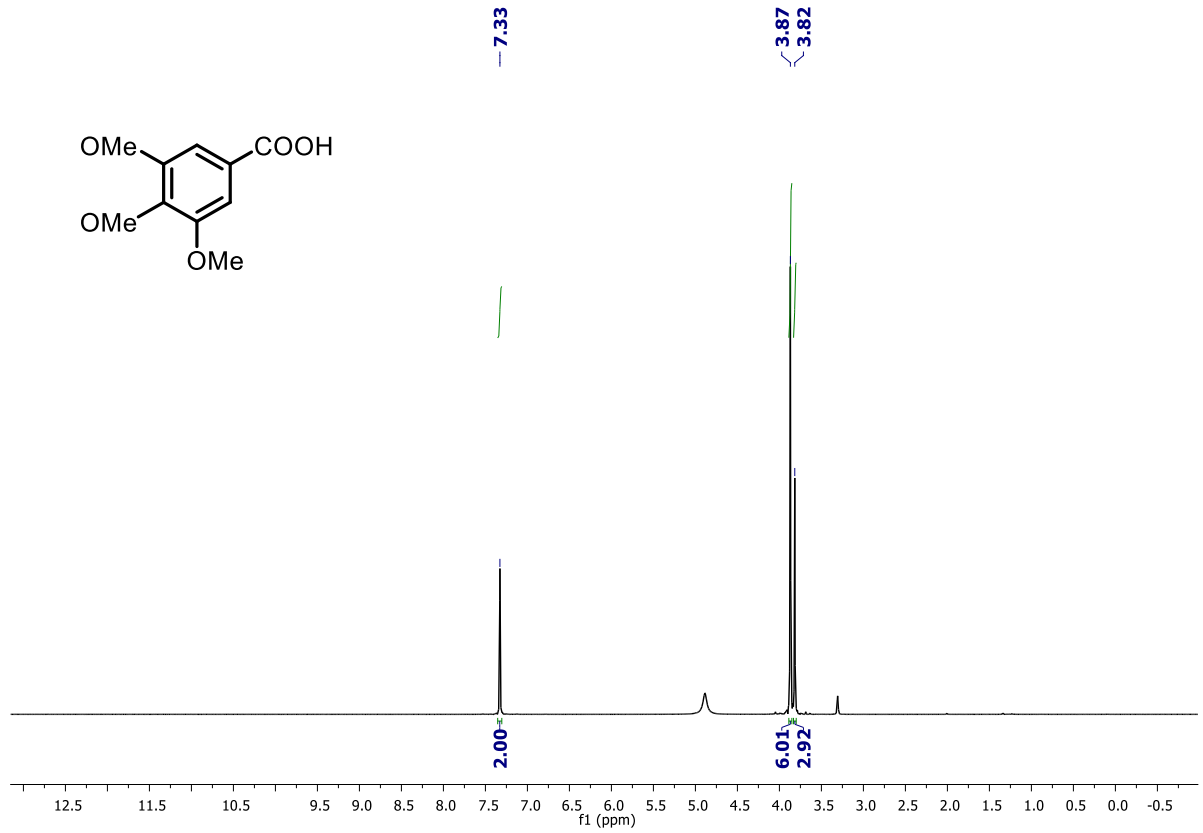
^{1}H NMR Spectrum of **2d** ($CDCl_3$, 400 MHz)



^{13}C {^{1}H} NMR Spectrum of **2d** ($CDCl_3$, 100 MHz)



^{1}H NMR Spectrum of **2e** (CD_3OD, 400 MHz)



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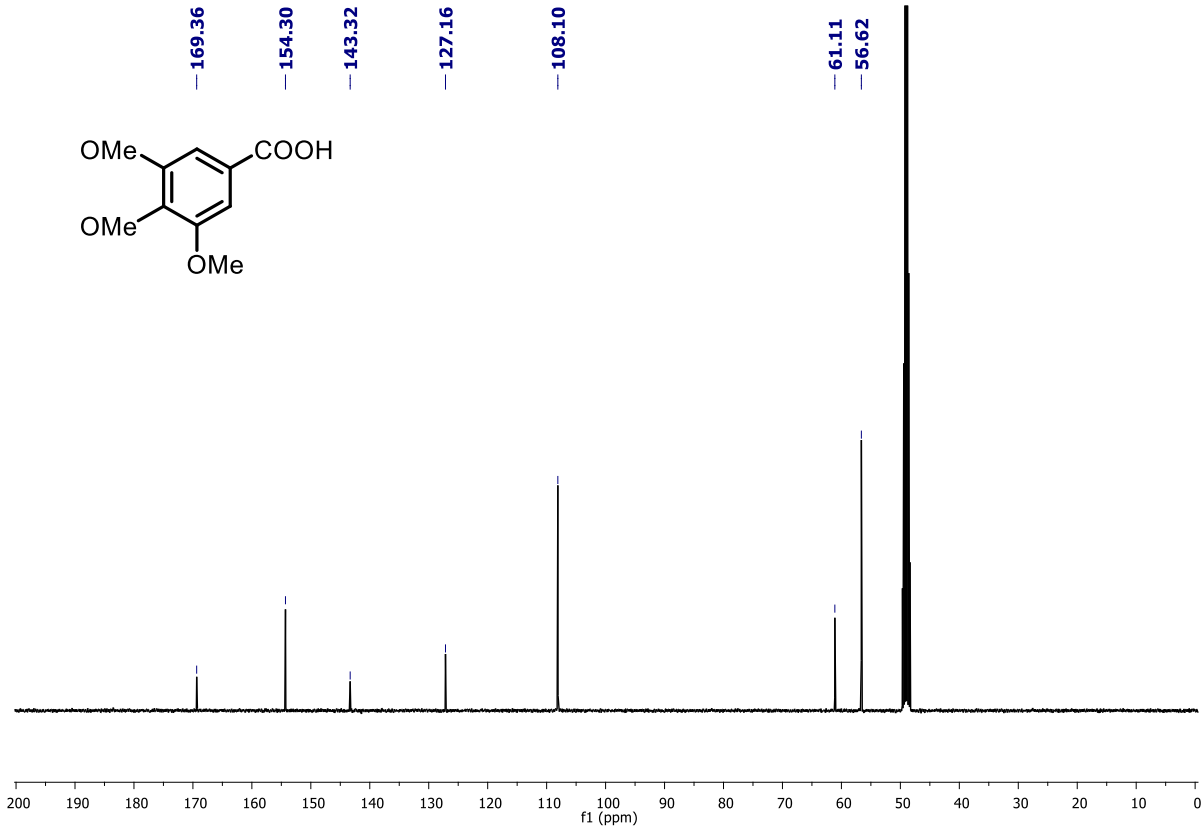
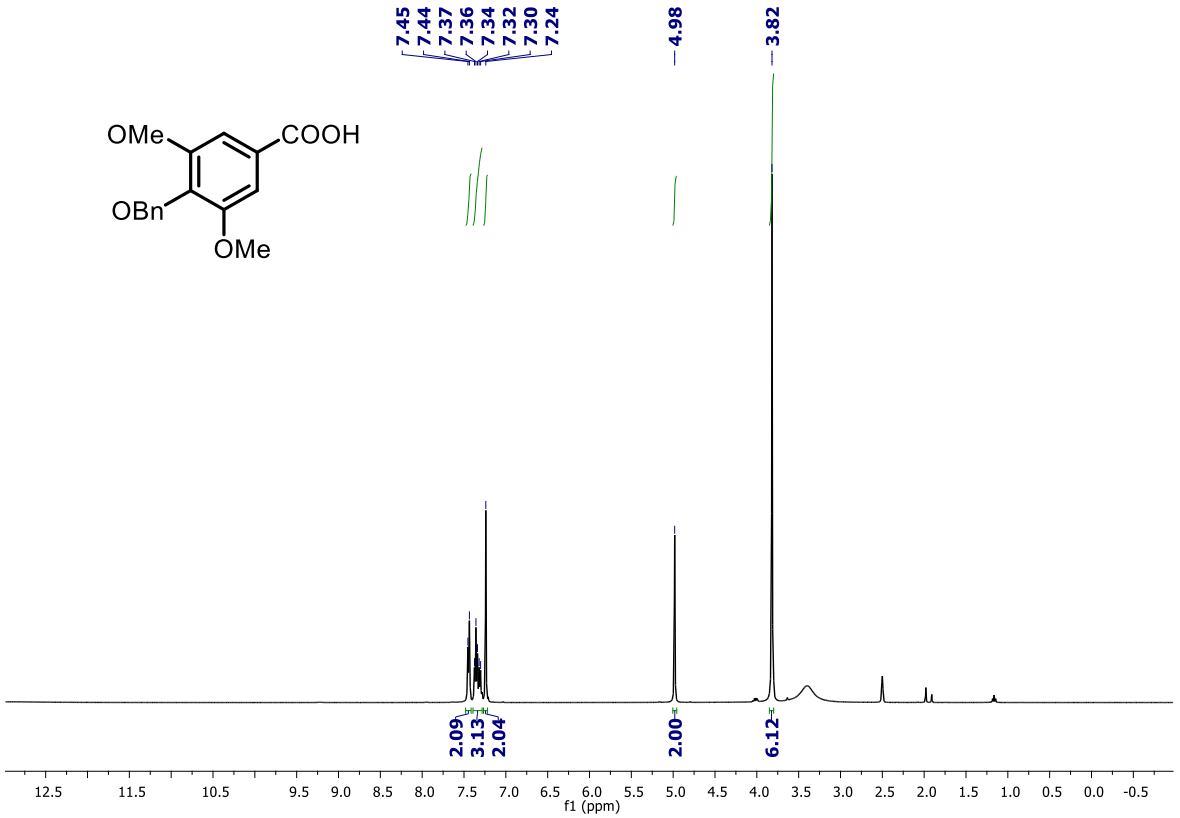
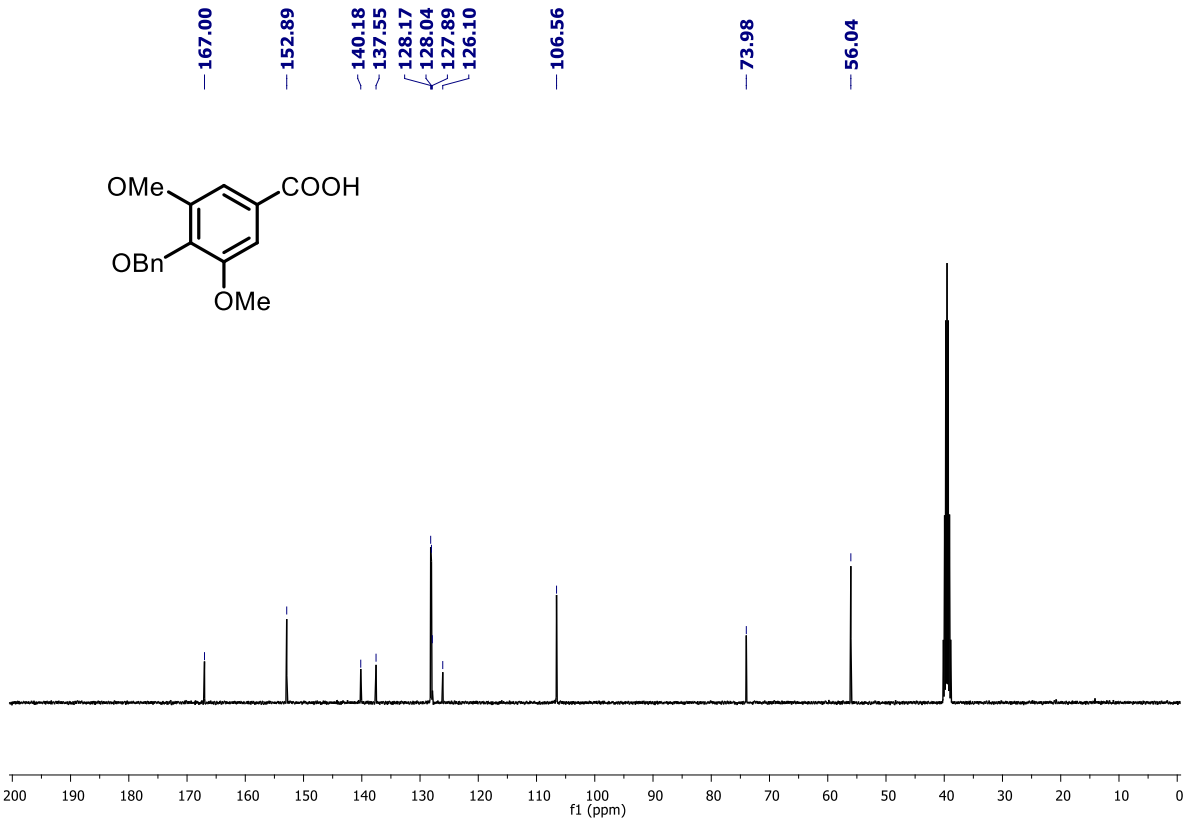


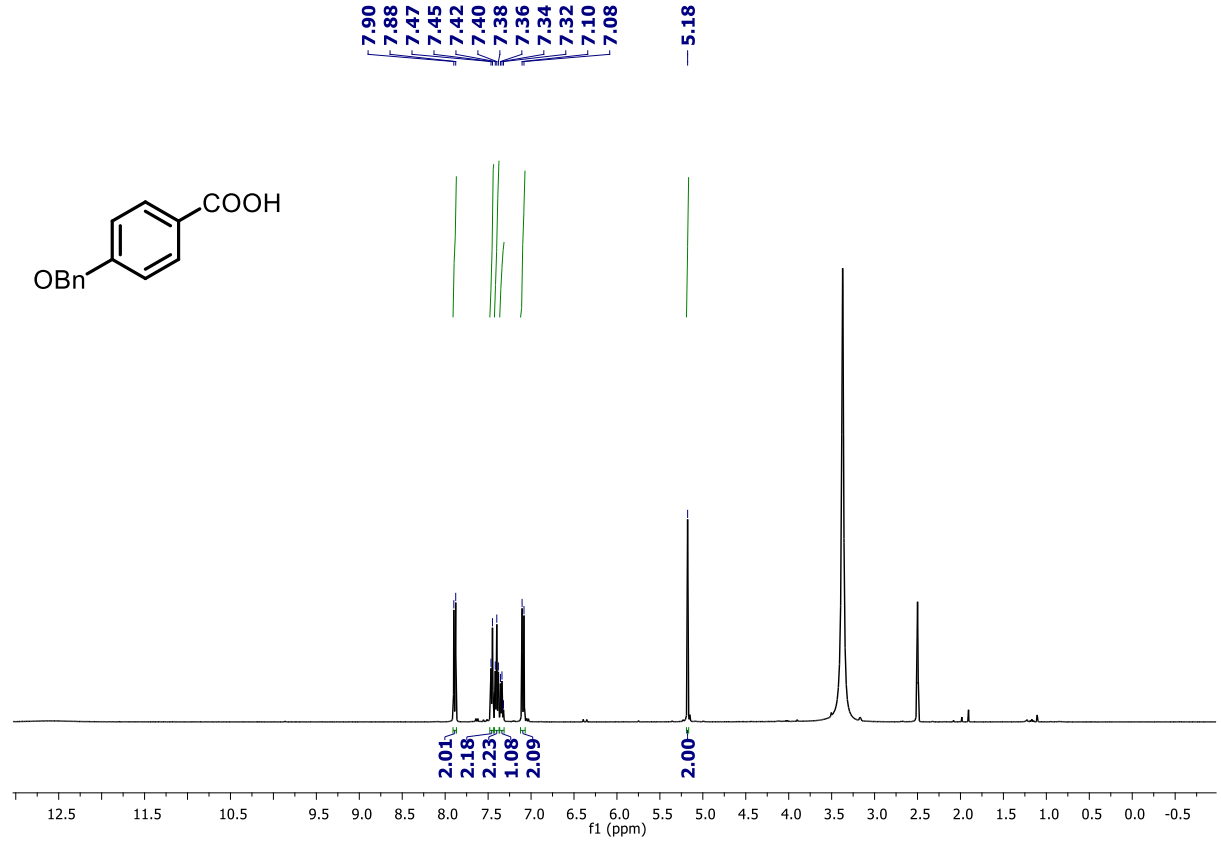
^{1}H NMR Spectrum of **2f** (DMSO-d_6, 400 MHz)



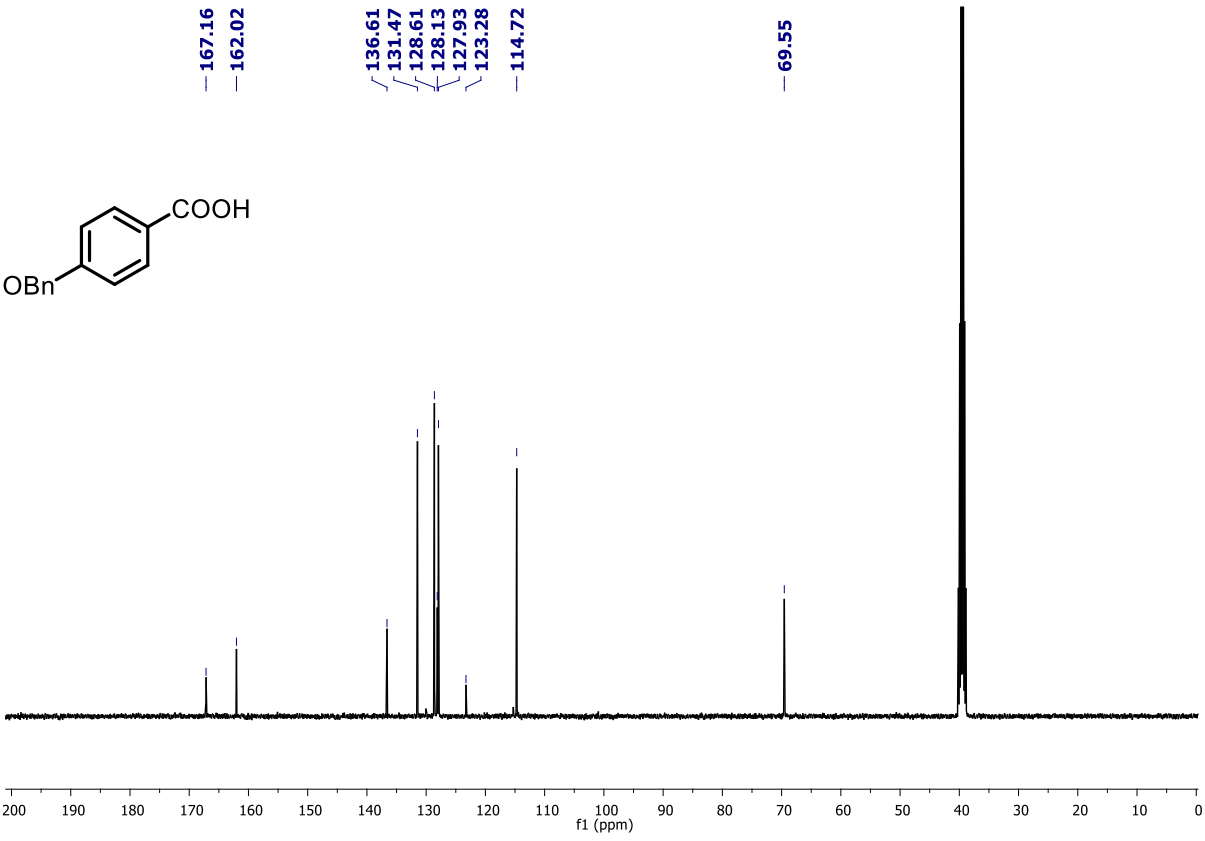
^{13}C {^{1}H} NMR Spectrum of **2f** (DMSO-d_6, 100 MHz)



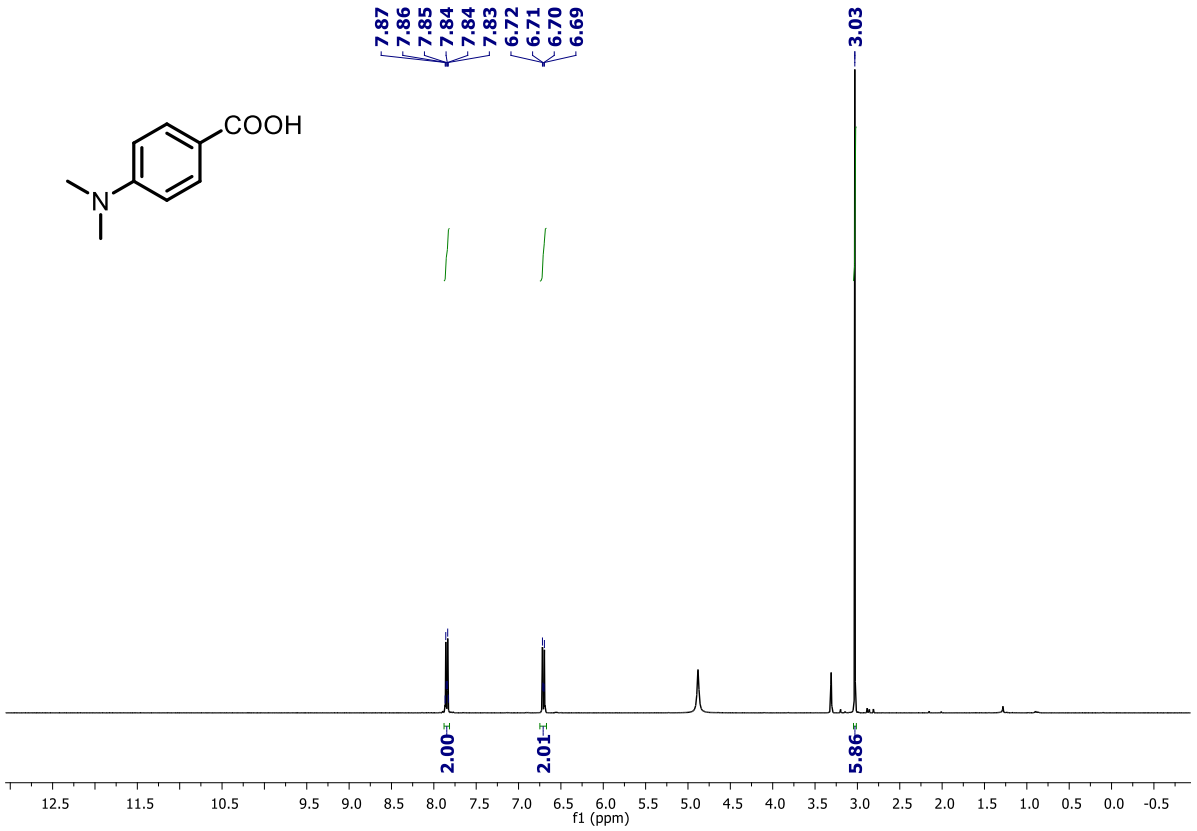
^{1}H NMR Spectrum of **2g** (DMSO-d_6, 400 MHz)



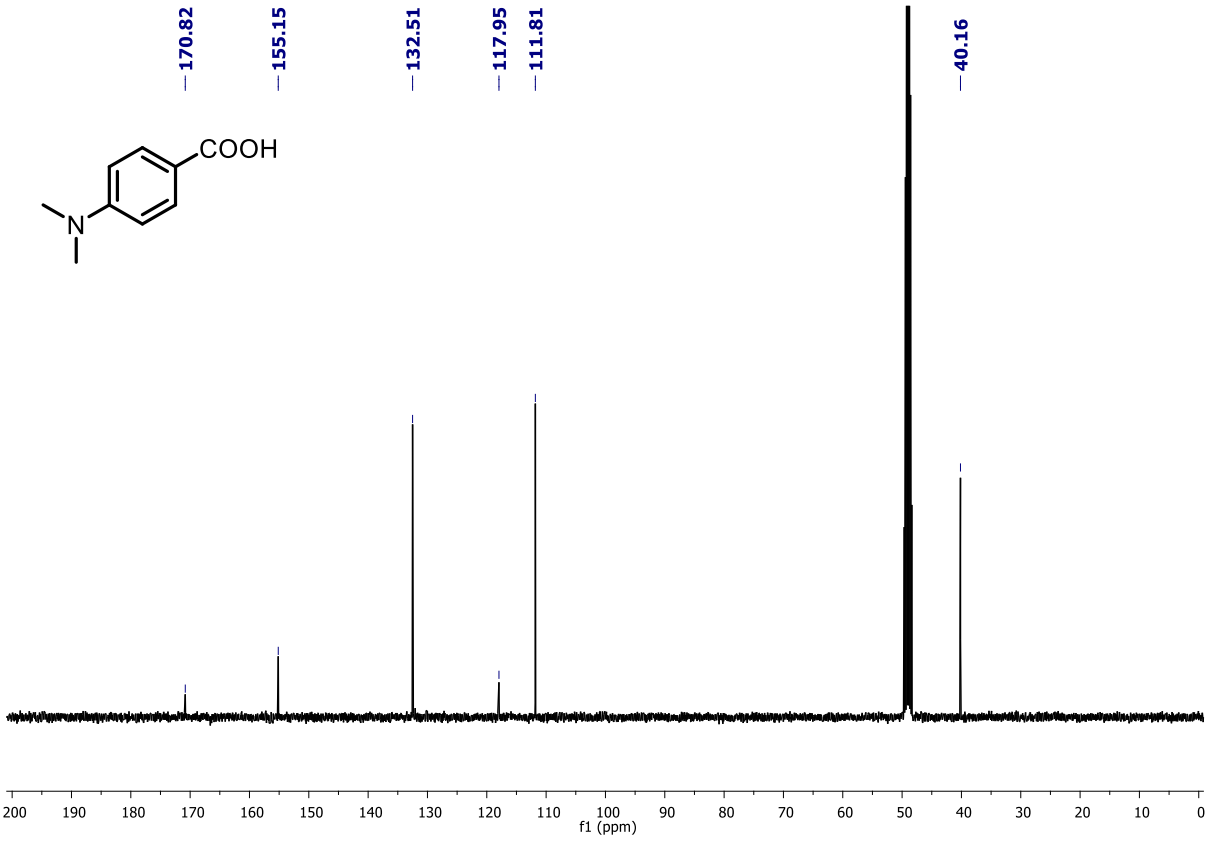
^{13}C {^{1}H} NMR Spectrum of **2g** (DMSO-d_6, 100 MHz)



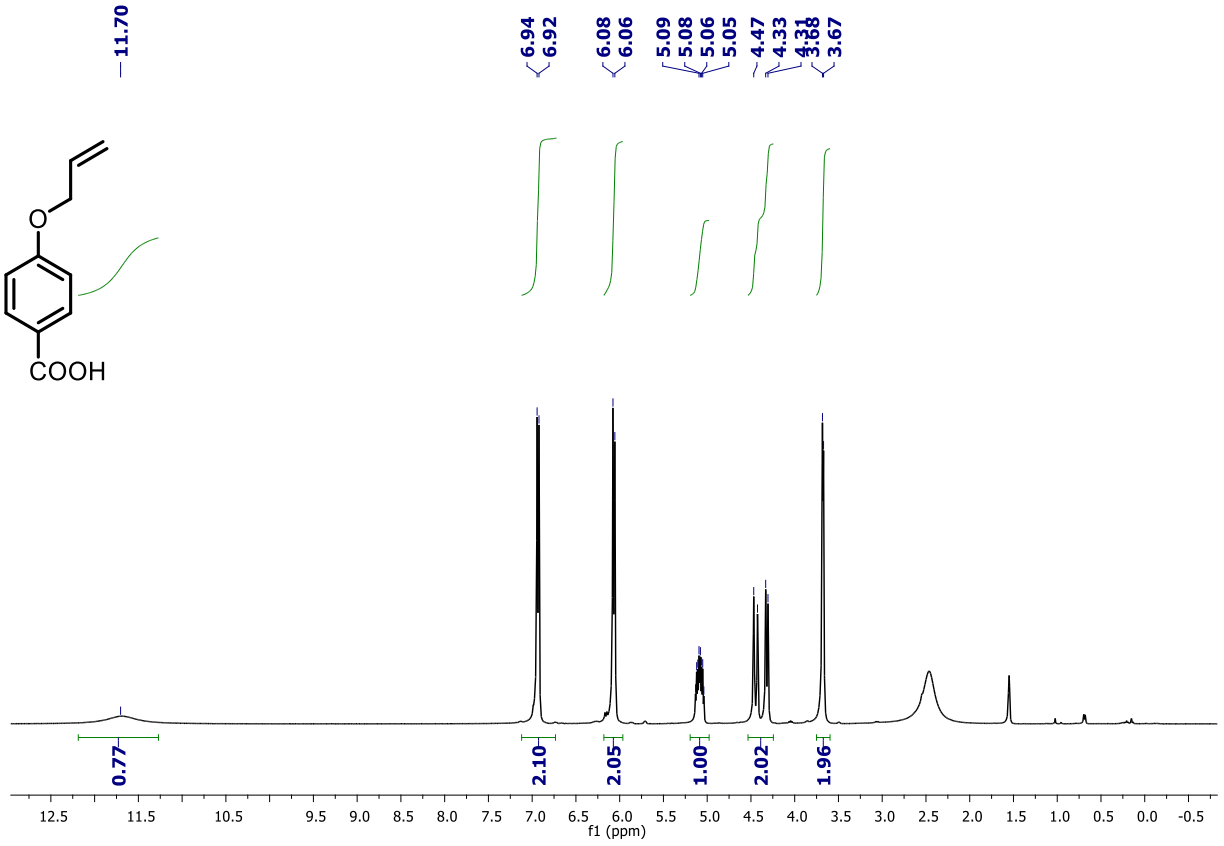
^{1}H NMR Spectrum of **2h** (CD_3OD, 400 MHz)



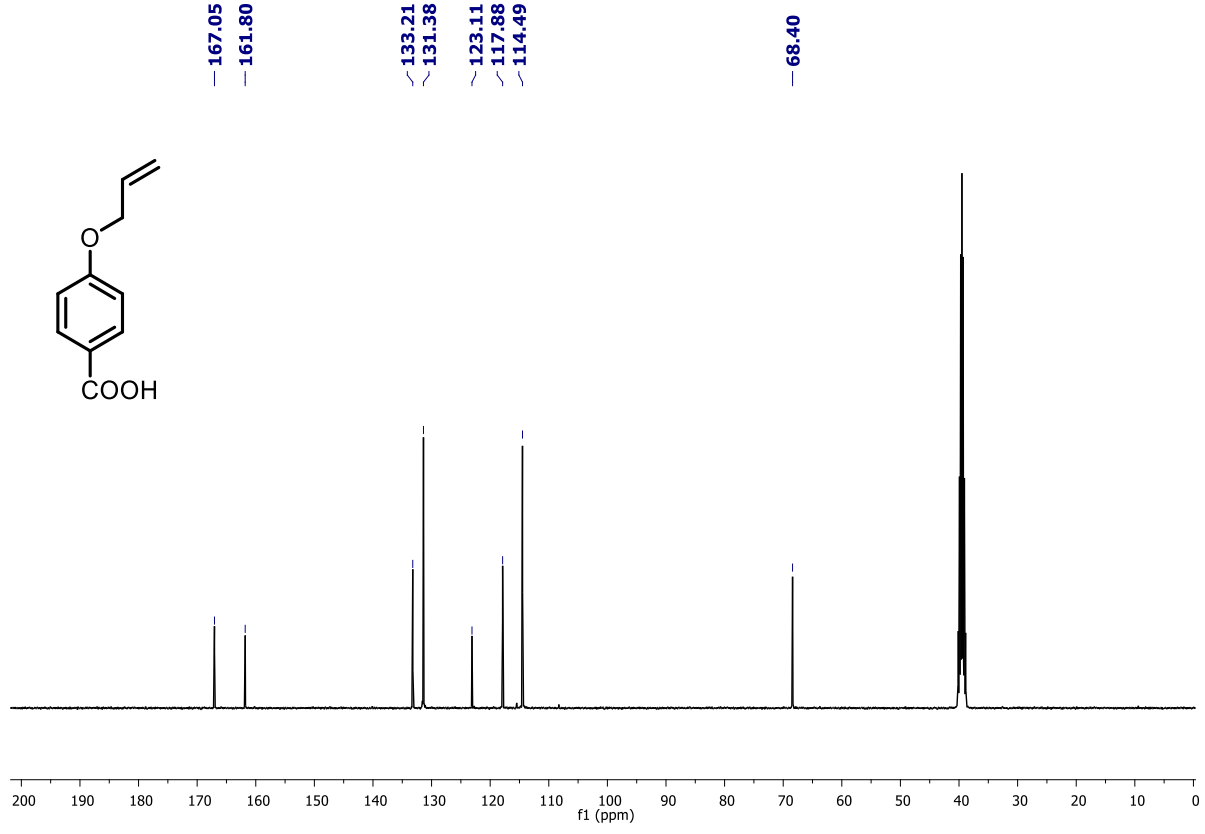
^{13}C {^{1}H} NMR Spectrum of **2h** (CD_3OD, 100 MHz)



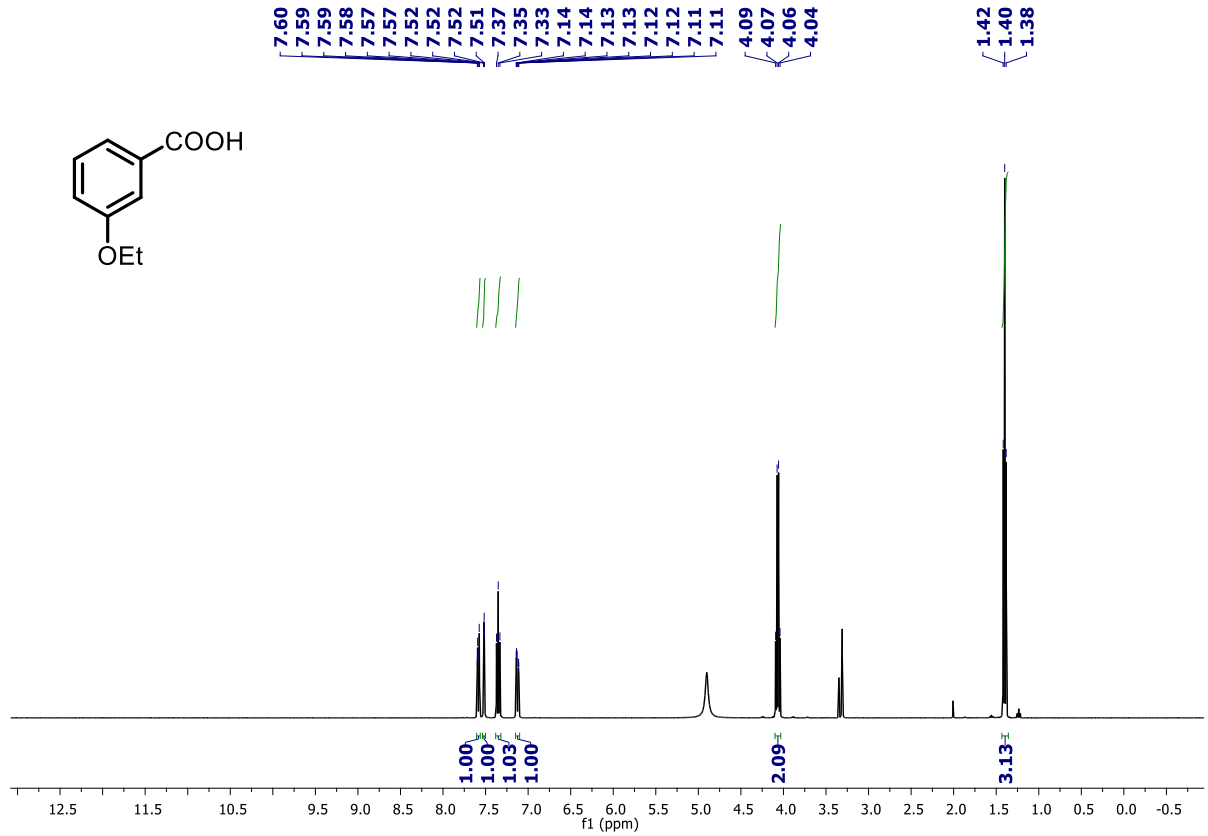
^{1}H NMR Spectrum of **2i** (CD_3OD, 400 MHz)



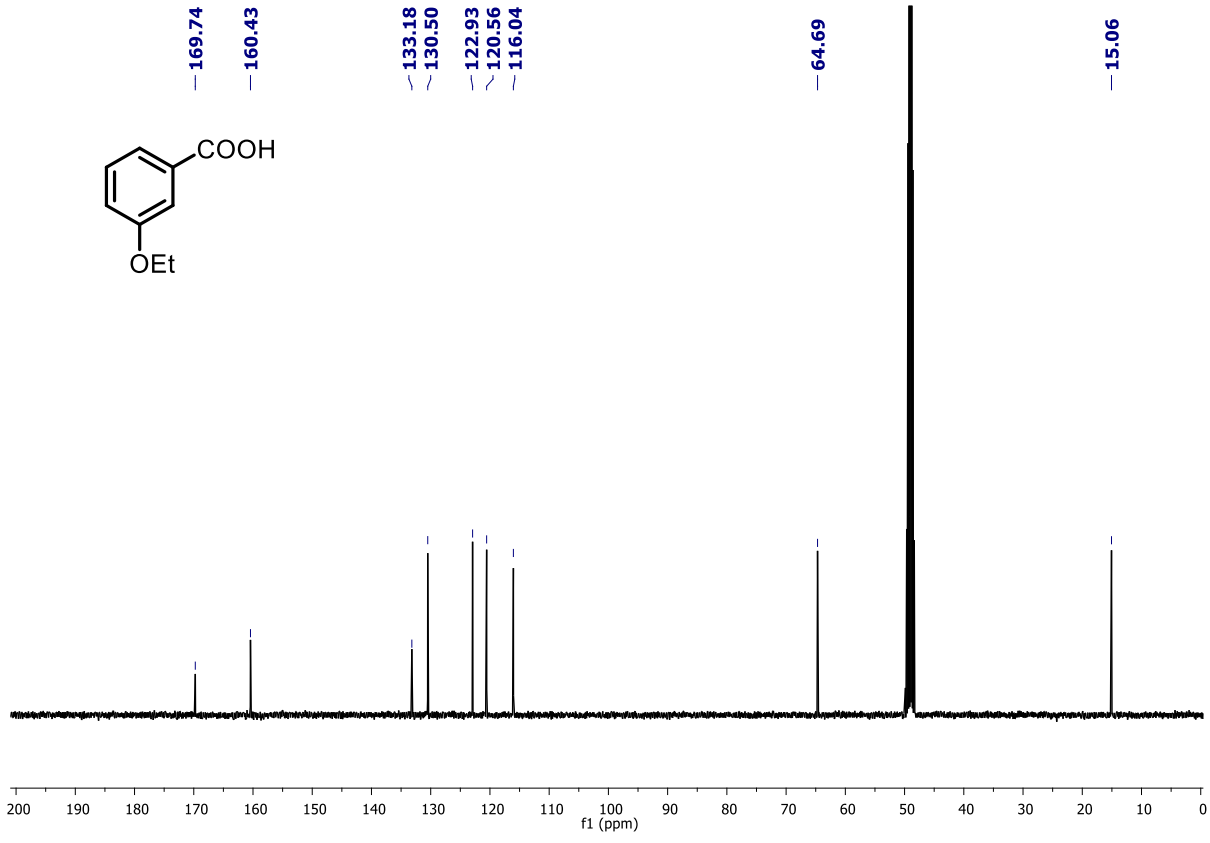
^{13}C {^{1}H} NMR Spectrum of **2i** (DMSO-d_6, 100 MHz)



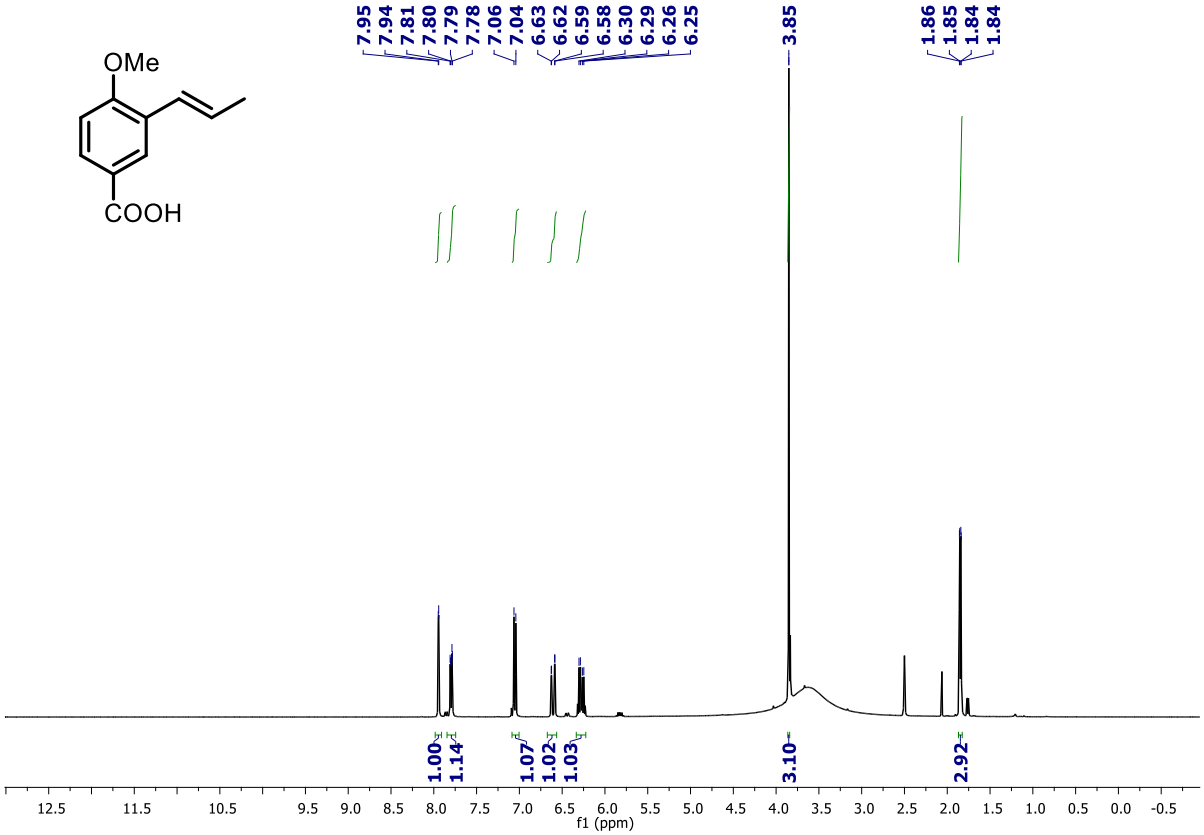
^{1}H NMR Spectrum of **2j** (CD_3OD, 400 MHz)



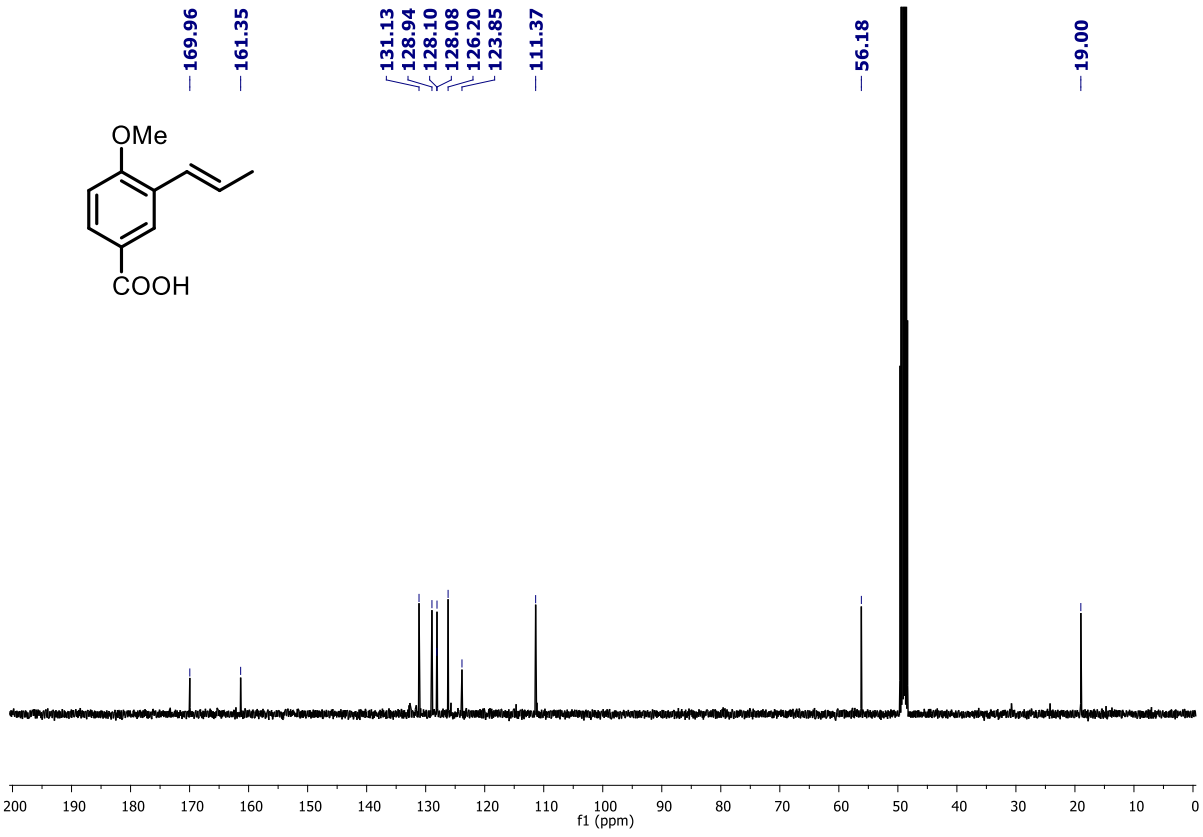
^{13}C {^{1}H} NMR Spectrum of **2j** (CD_3OD, 100 MHz)



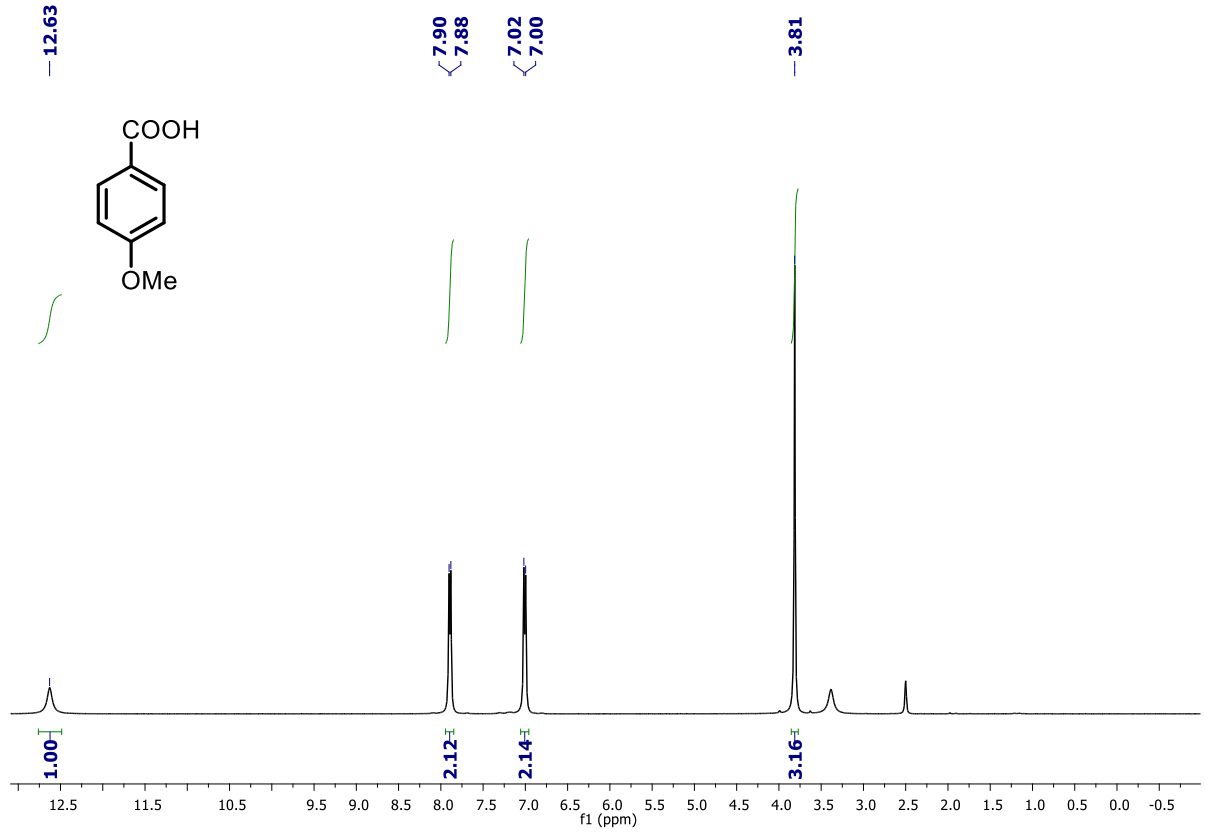
^{1}H NMR Spectrum of **2k** (DMSO-d_6, 400 MHz)



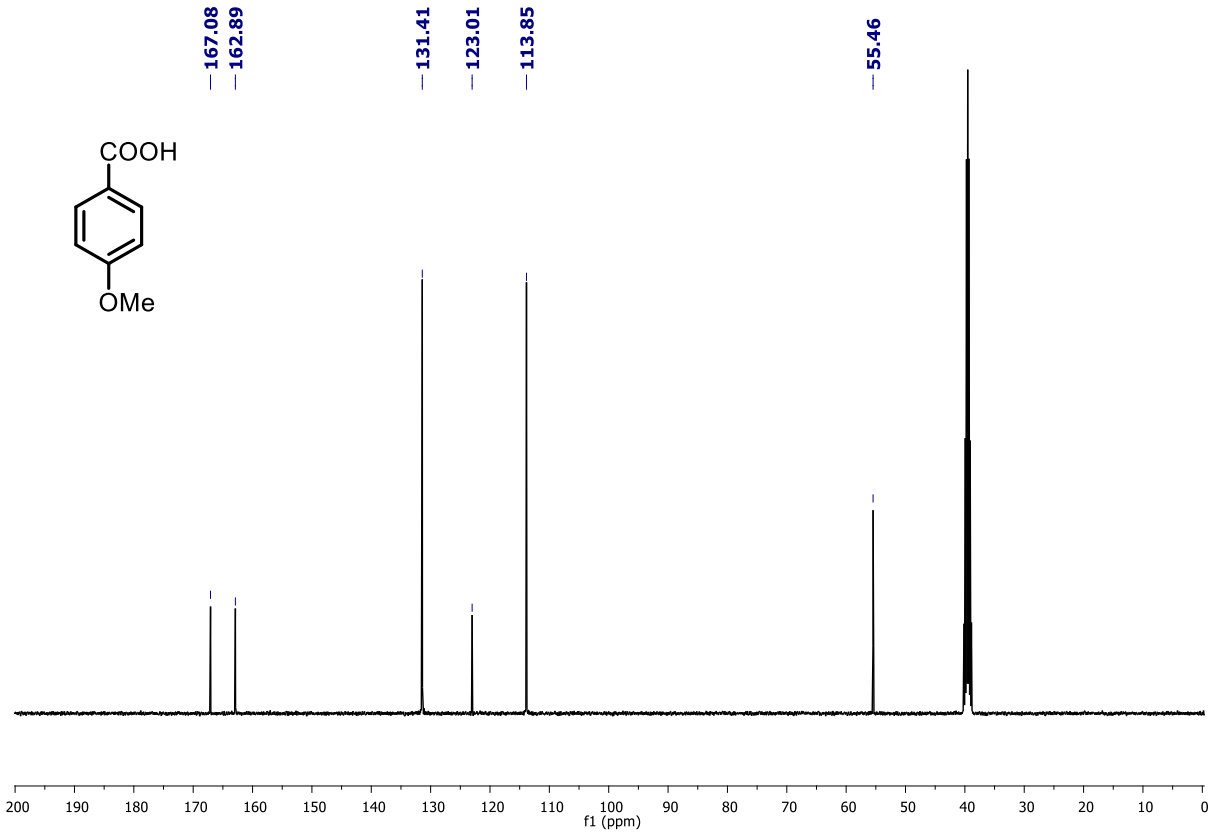
^{13}C {^{1}H} NMR Spectrum of **2k** (CD_3OD, 100 MHz)



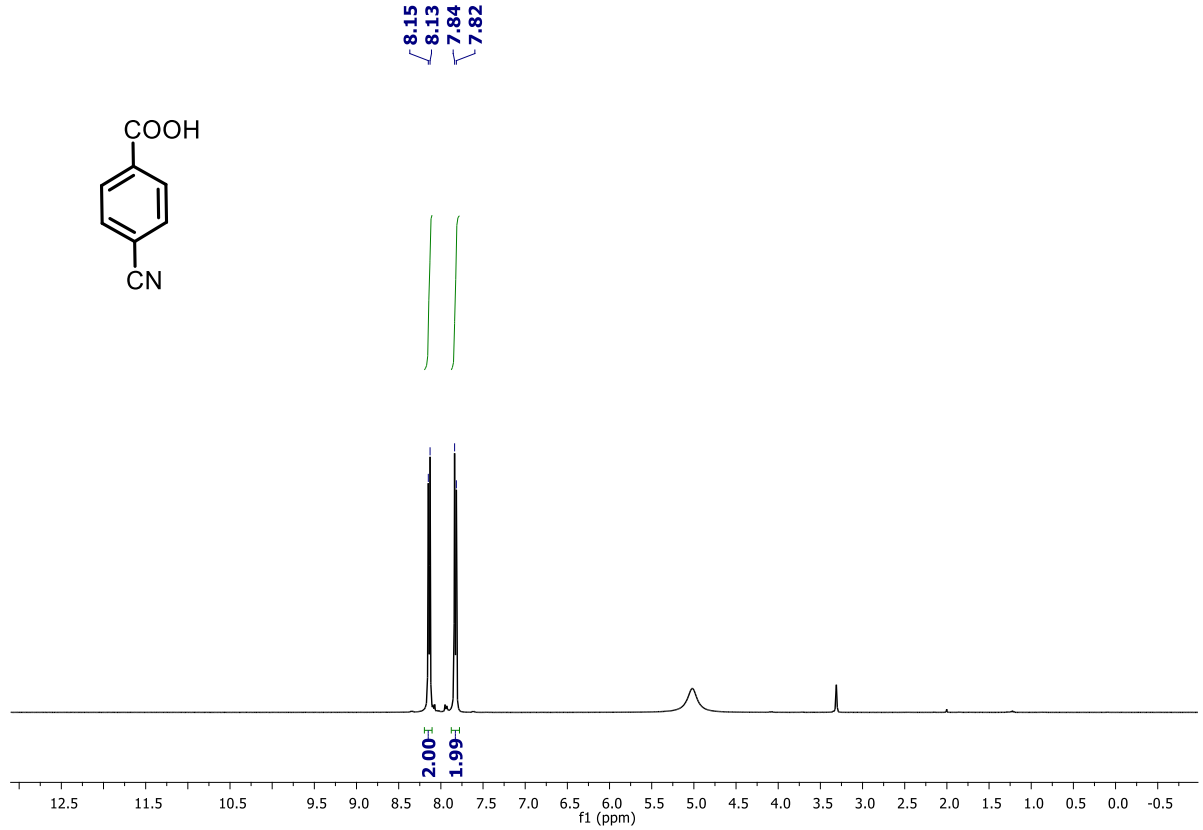
^{1}H NMR Spectrum of **2l** (DMSO-d_6, 400 MHz)



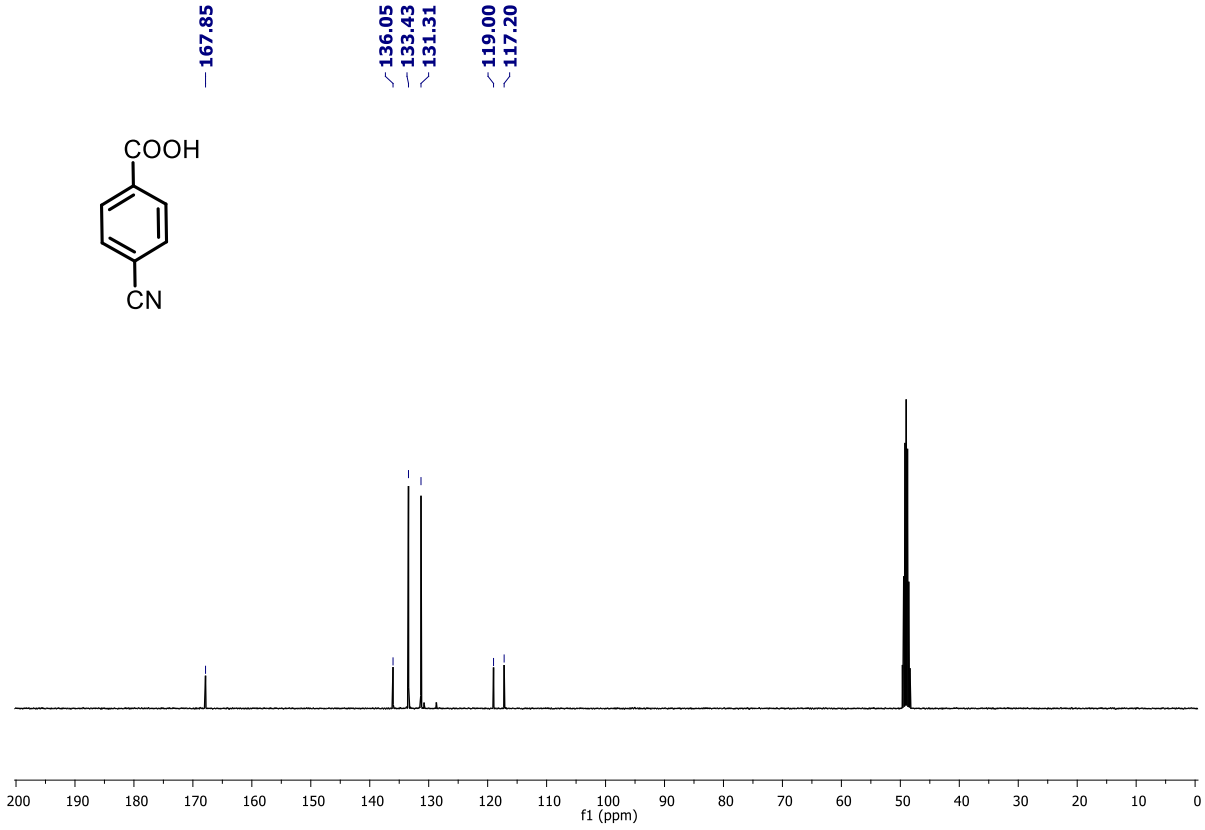
^{13}C {^{1}H} NMR Spectrum of **2l** (DMSO-d_6, 100 MHz)



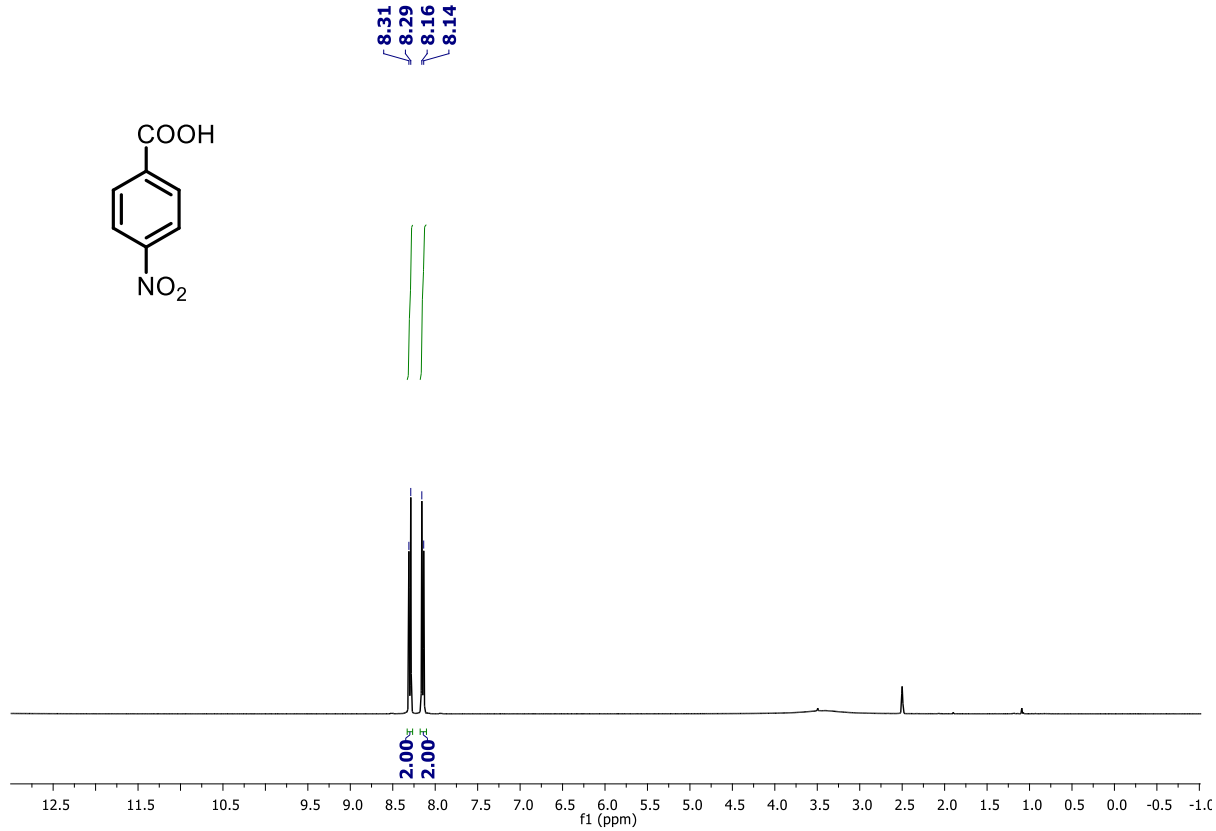
^{1}H NMR Spectrum of **2m** (CD_3OD, 400 MHz)



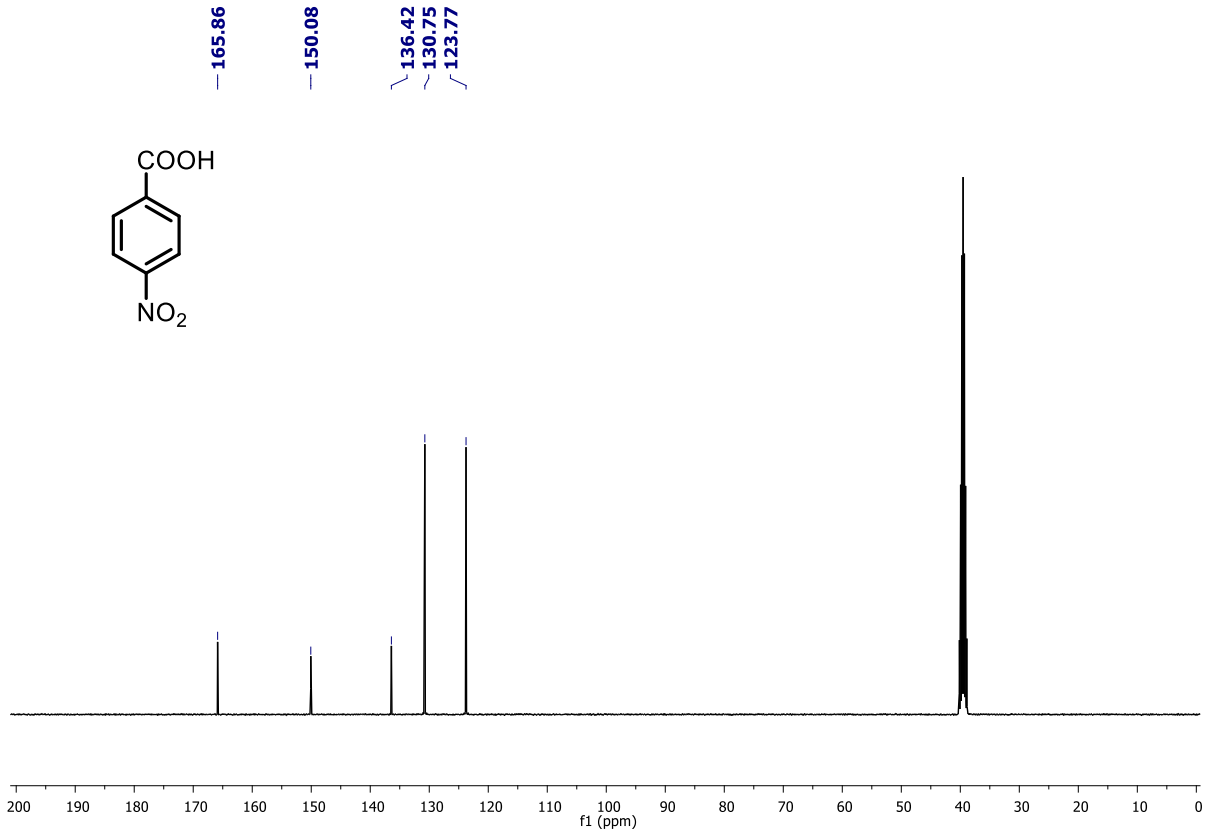
^{13}C {^{1}H} NMR Spectrum of **2m** (CD_3OD, 100 MHz)



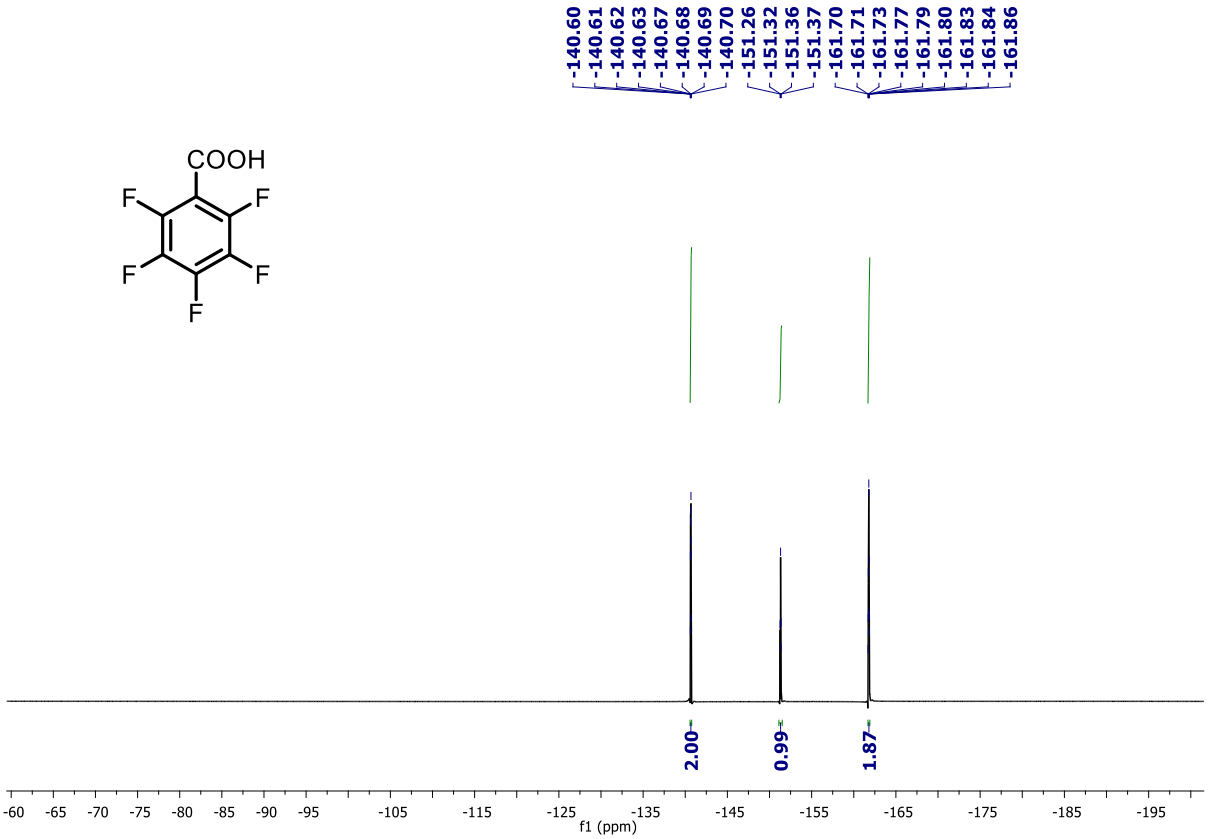
^{1}H NMR Spectrum of **2n** (DMSO-d_6, 400 MHz)



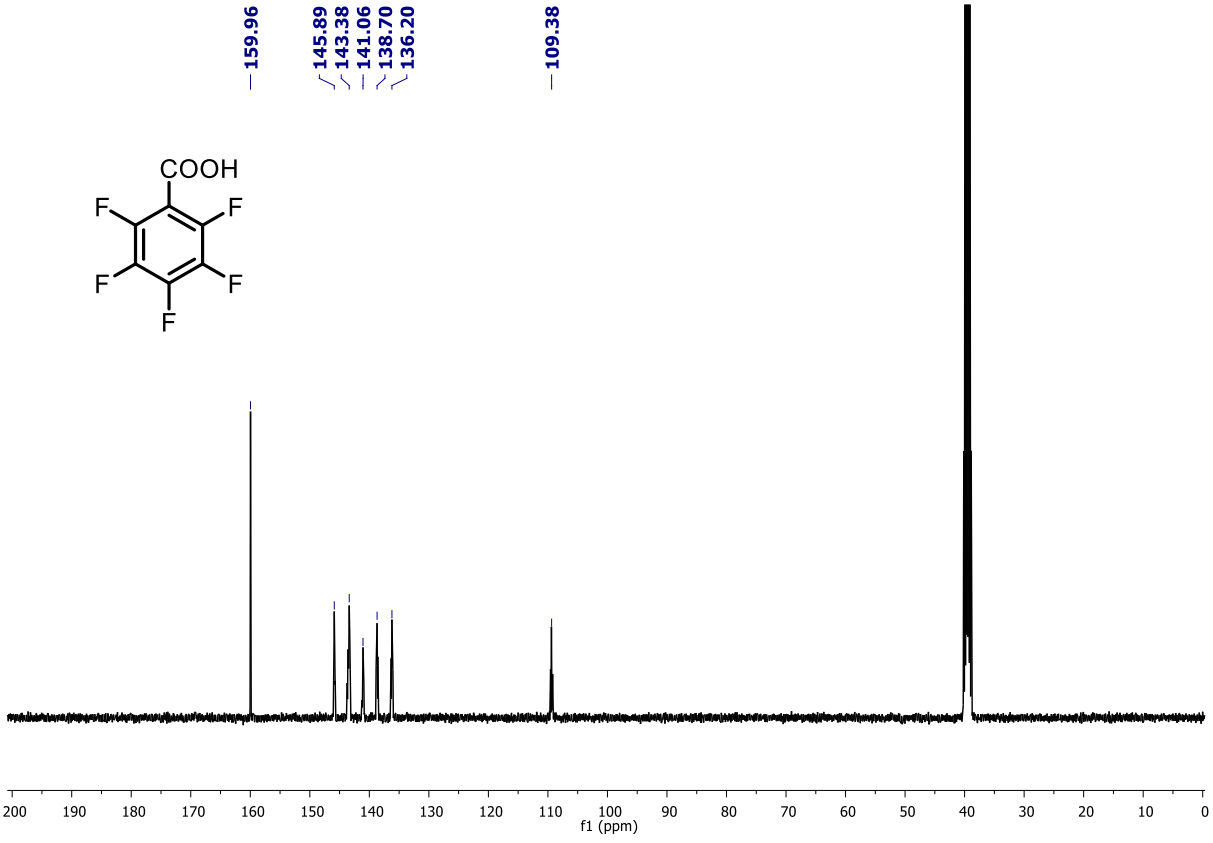
^{13}C {^{1}H} NMR Spectrum of **2n** (DMSO-d_6, 100 MHz)



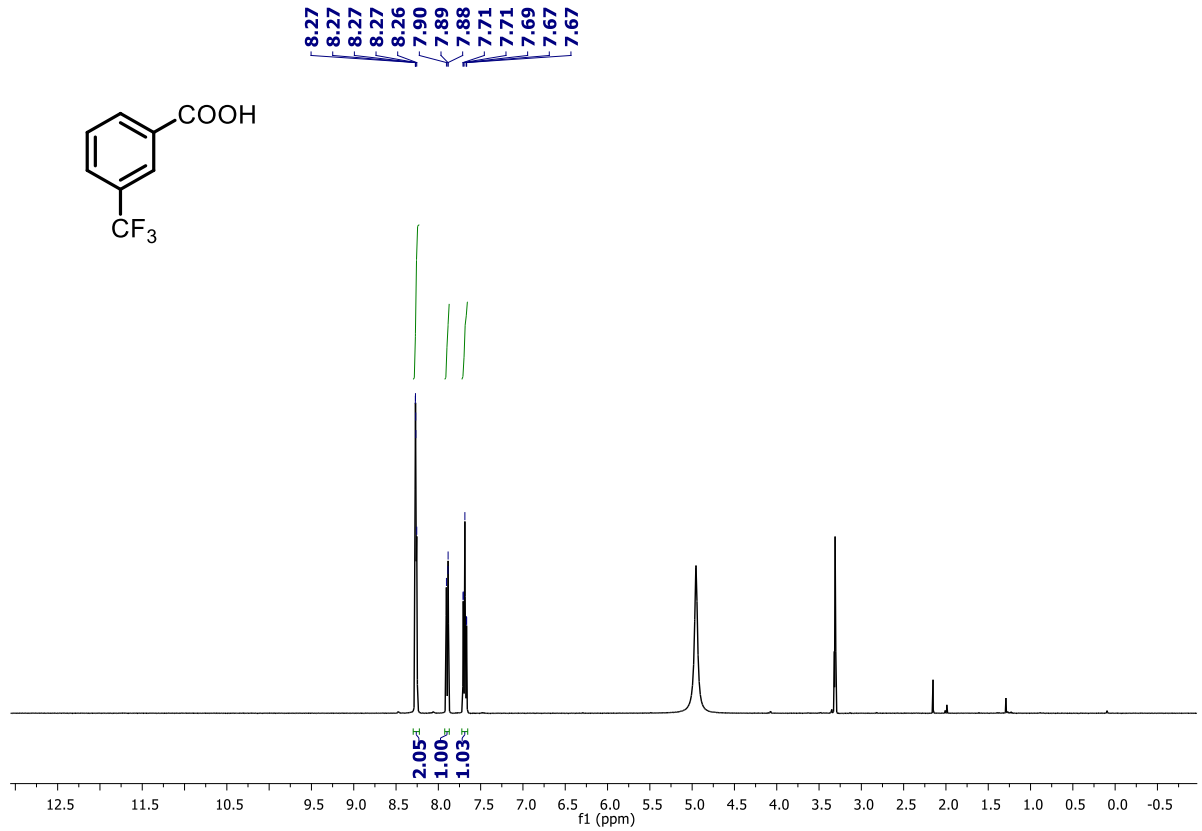
^{19}F NMR Spectrum of **2o** (DMSO-d_6, 377 MHz)



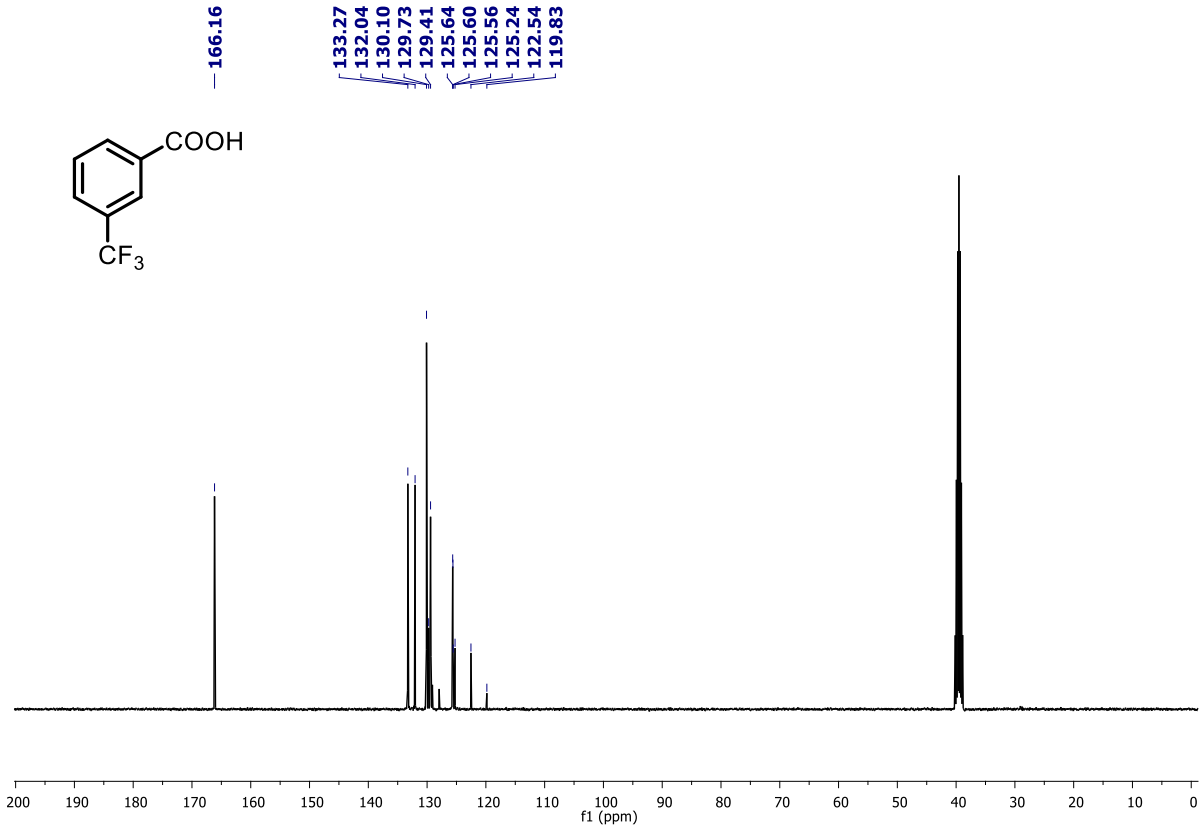
^{13}C {^{1}H} NMR Spectrum of **2o** (DMSO-d_6, 100 MHz)



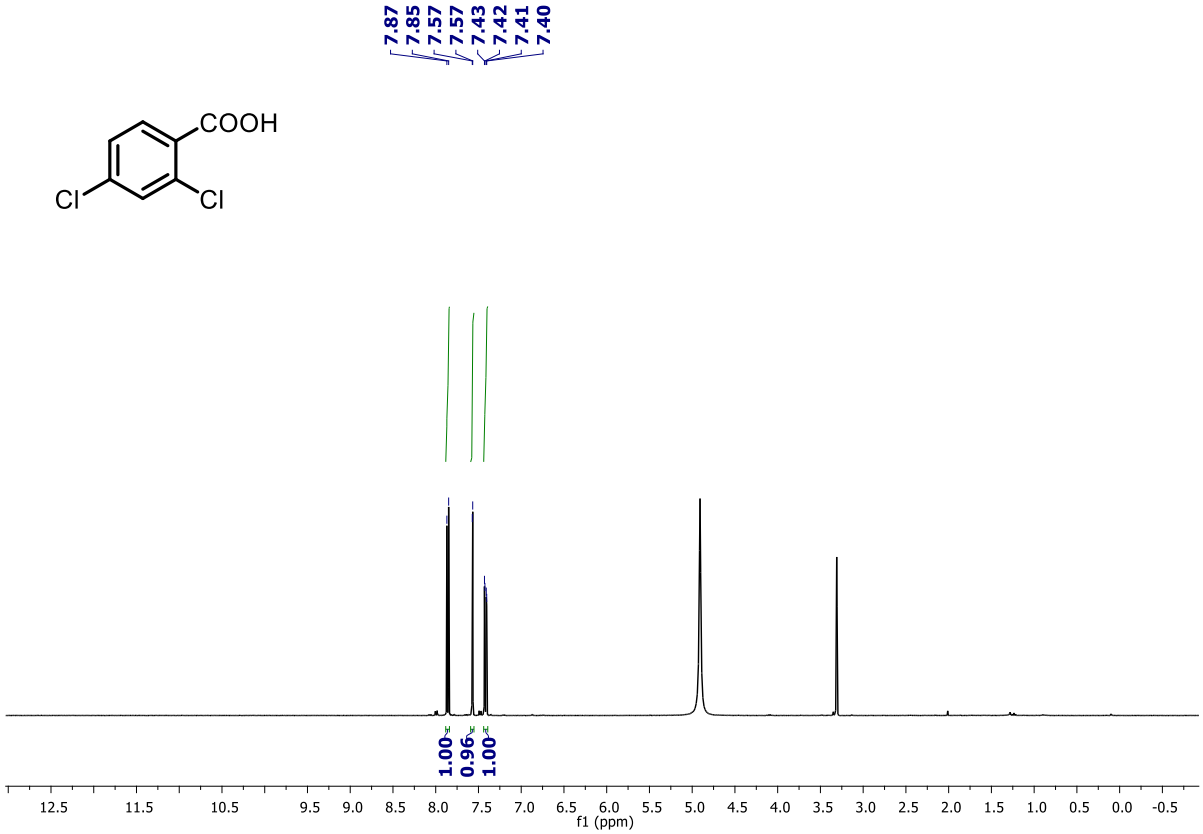
^{1}H NMR Spectrum of **2p** (CD_3OD, 400 MHz)



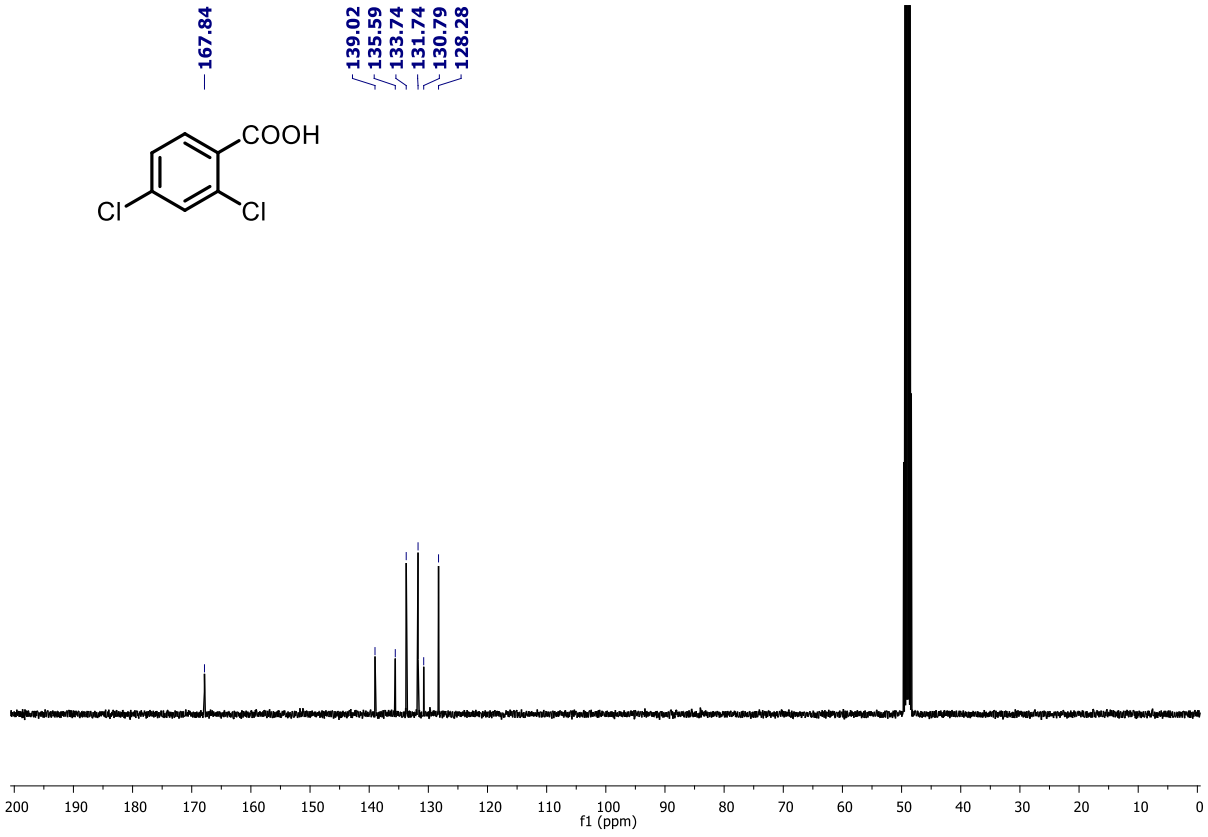
^{13}C {^{1}H} NMR Spectrum of **2p** (DMSO-d_6, 100 MHz)



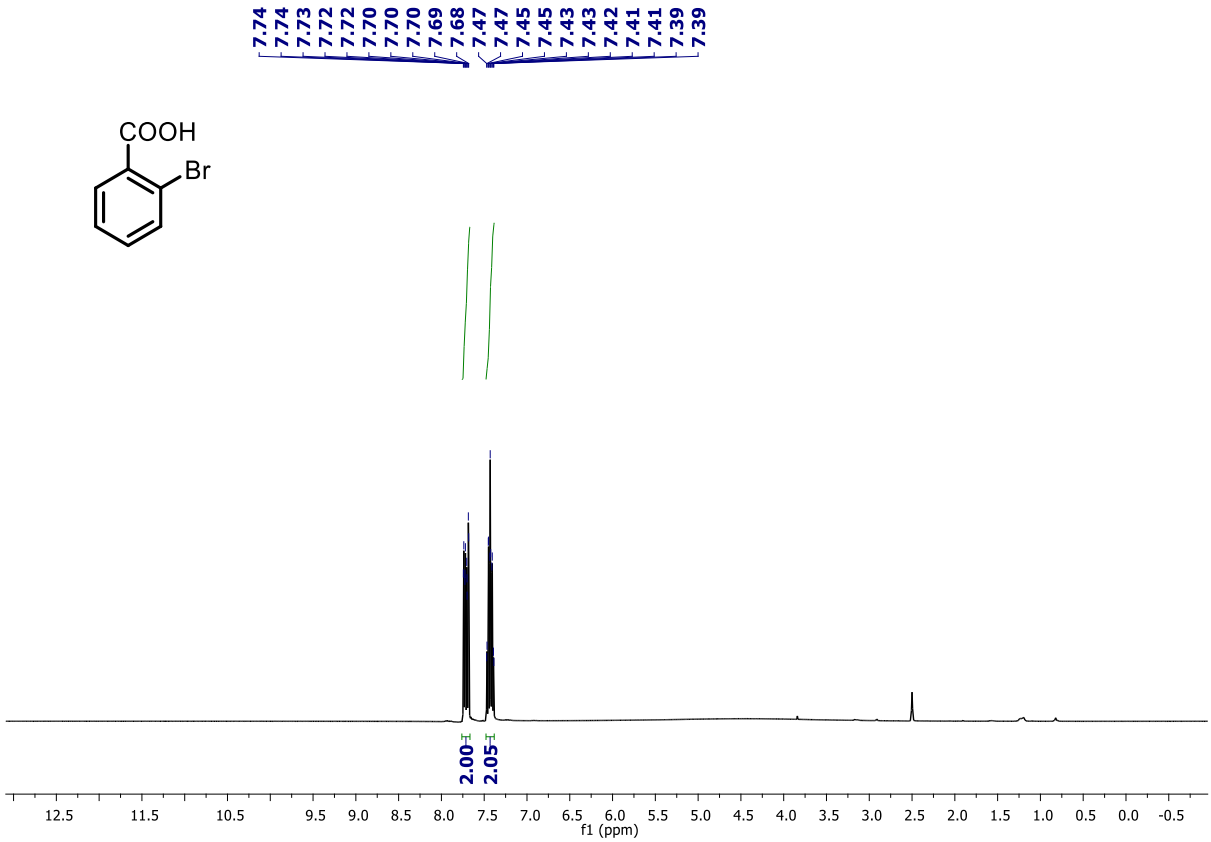
^{1}H NMR Spectrum of **2q** (CD_3OD, 400 MHz)



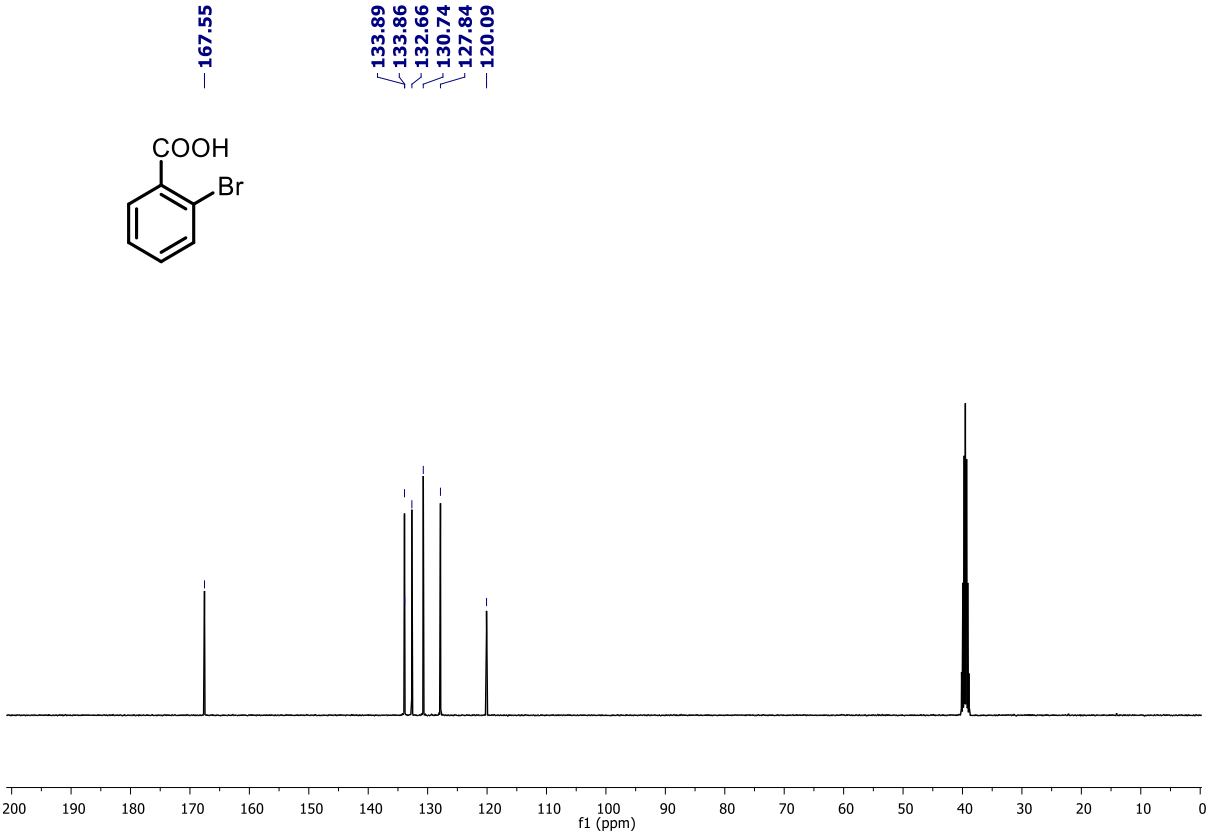
^{13}C {^{1}H} NMR Spectrum of **2q** (CD_3OD, 100 MHz)



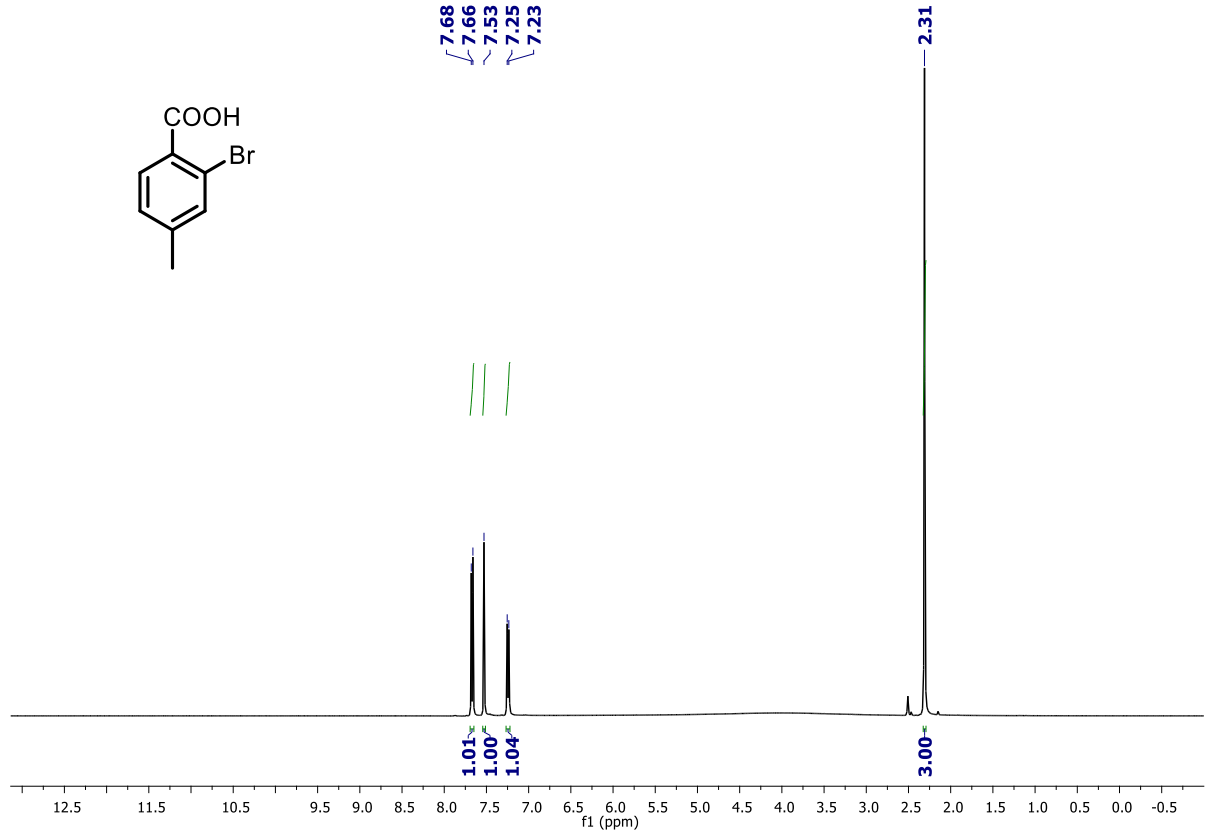
^{1}H NMR Spectrum of **2r** (DMSO-d_6, 400 MHz)



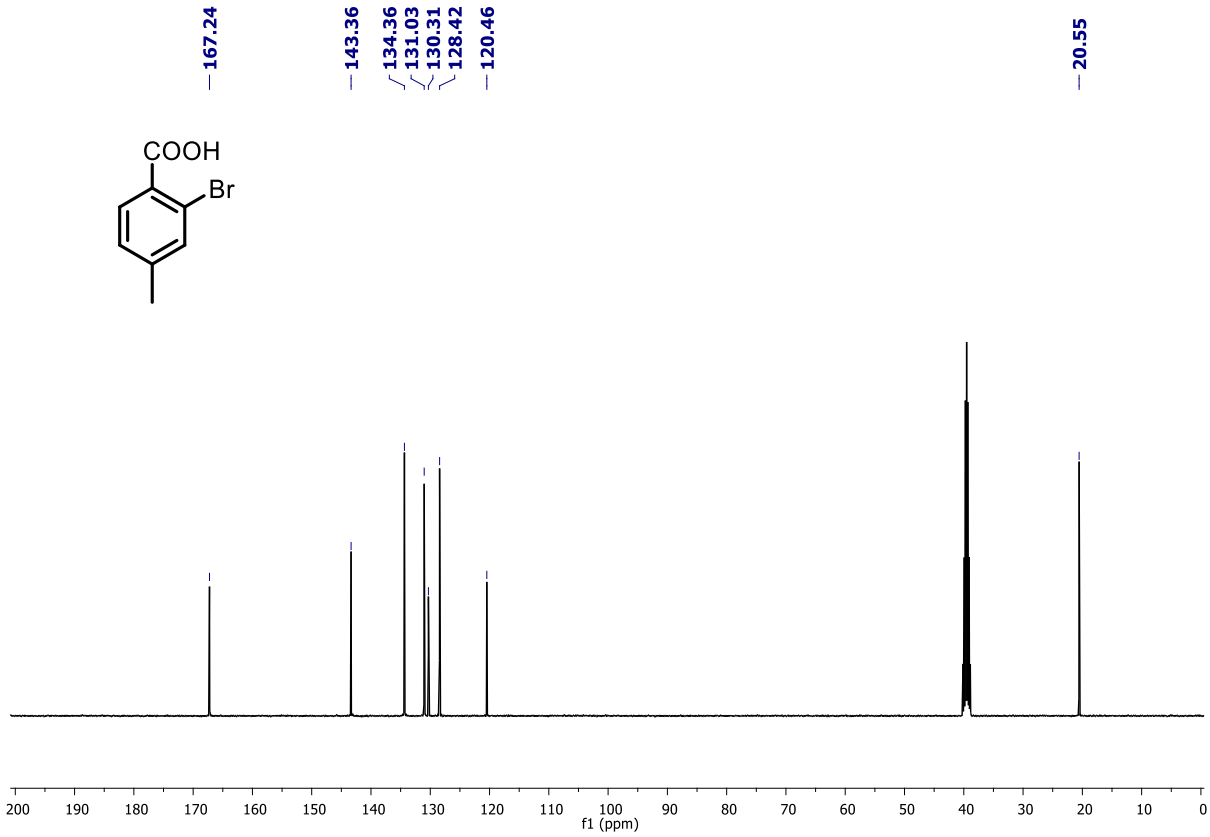
^{13}C {^{1}H} NMR Spectrum of **2r** (DMSO-d_6, 100 MHz)



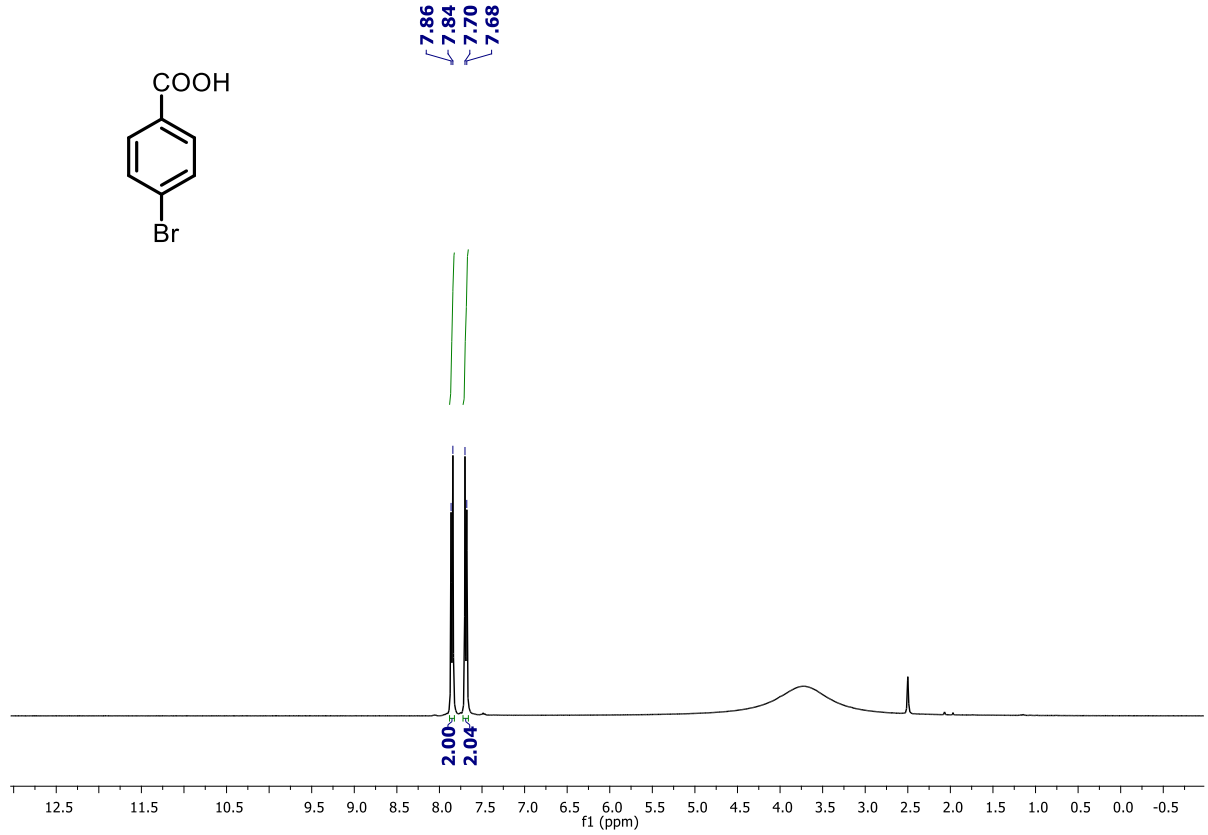
^{1}H NMR Spectrum of **2s** (DMSO-d_6, 400 MHz)



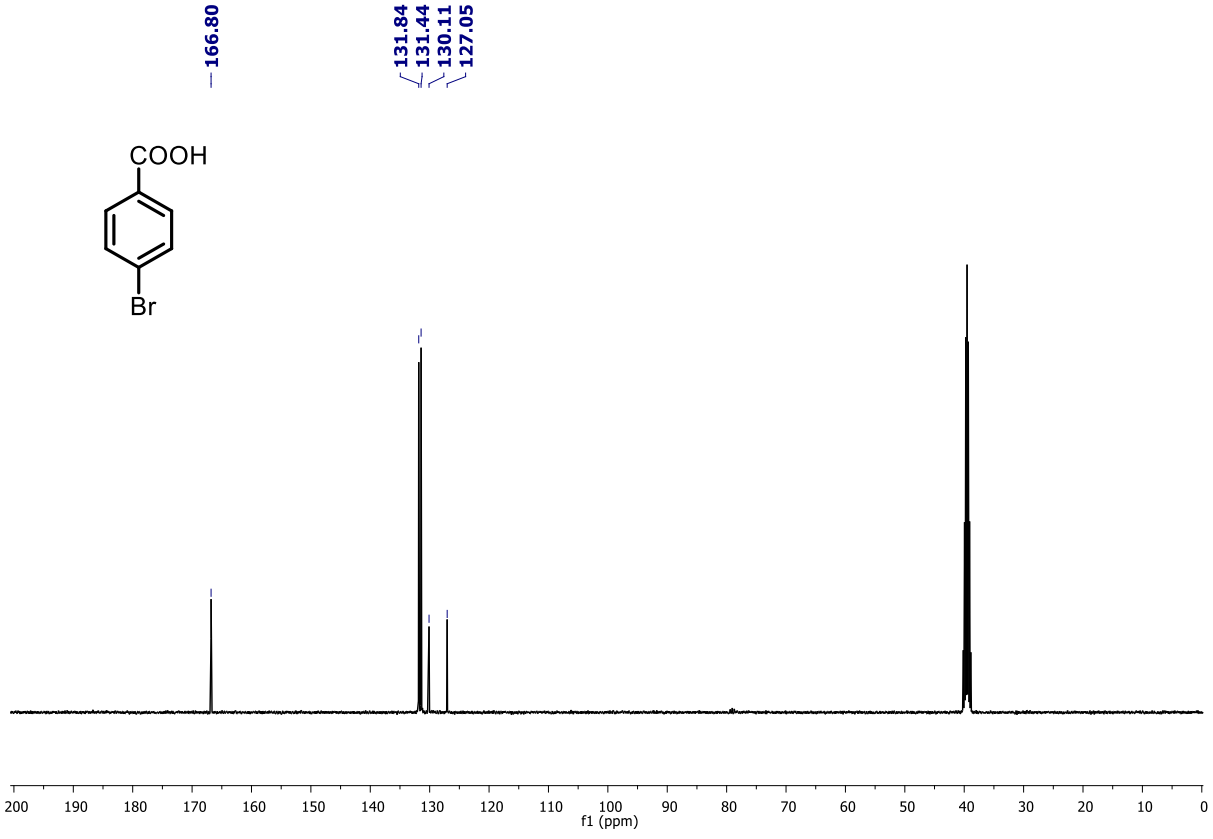
^{13}C {^{1}H} NMR Spectrum of **2s** (DMSO-d_6, 100 MHz)



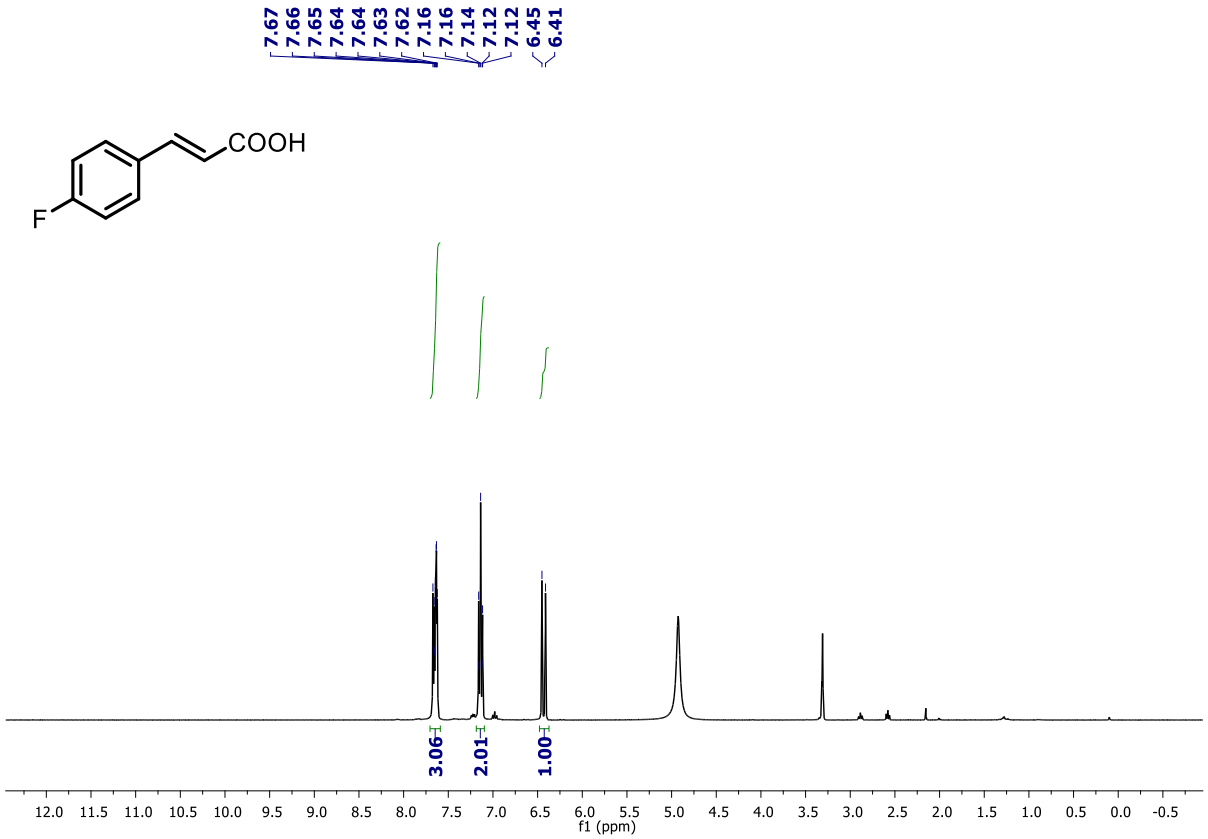
^{1}H NMR Spectrum of **2t** (DMSO-d_6, 400 MHz)



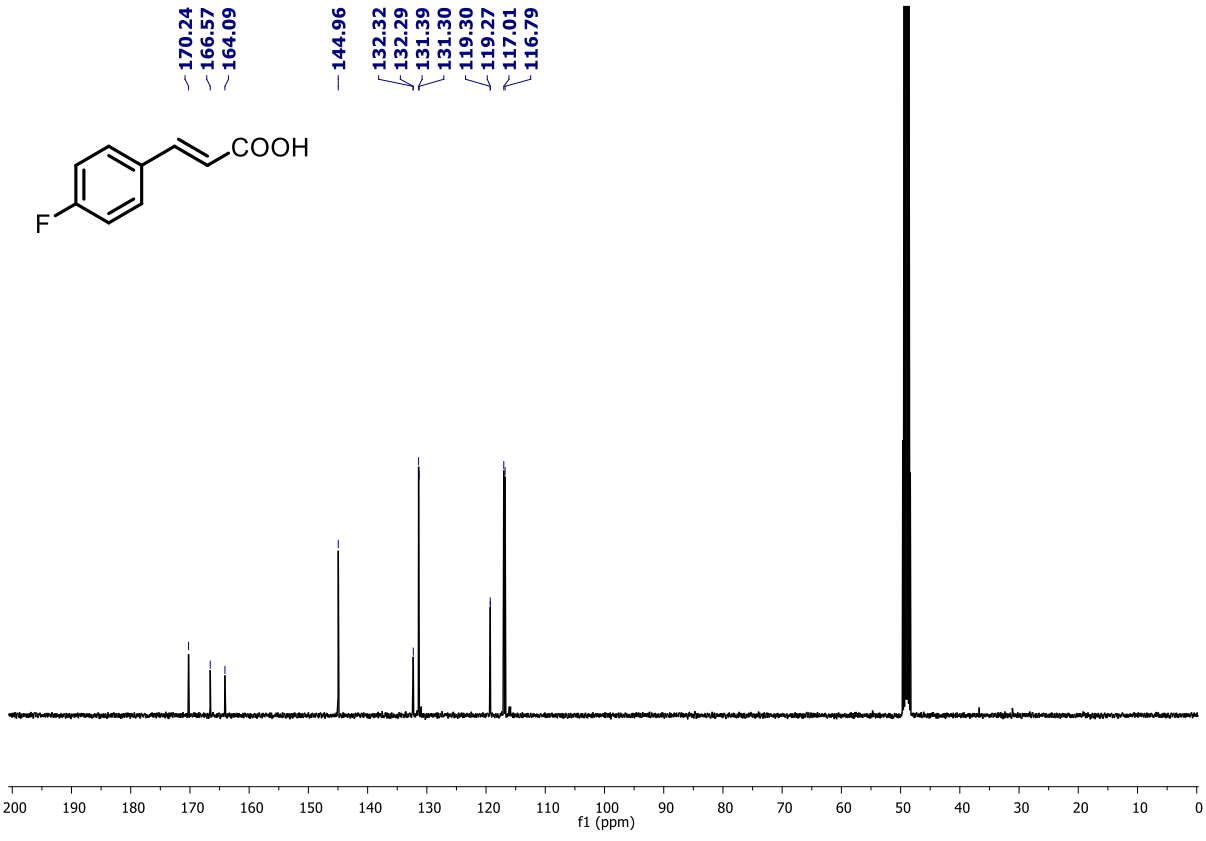
^{13}C {^{1}H} NMR Spectrum of **2t** (DMSO-d_6, 100 MHz)



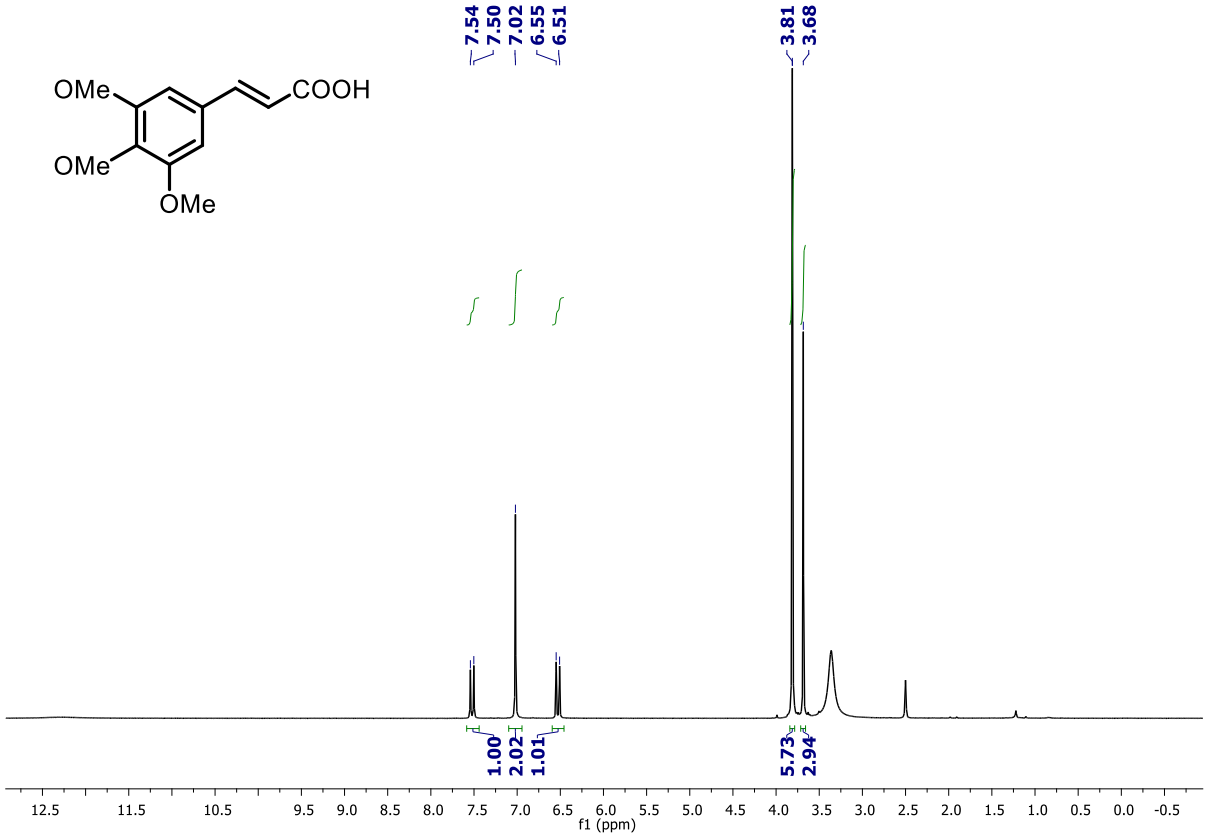
^{1}H NMR Spectrum of **2u** (CD_3OD, 400 MHz)



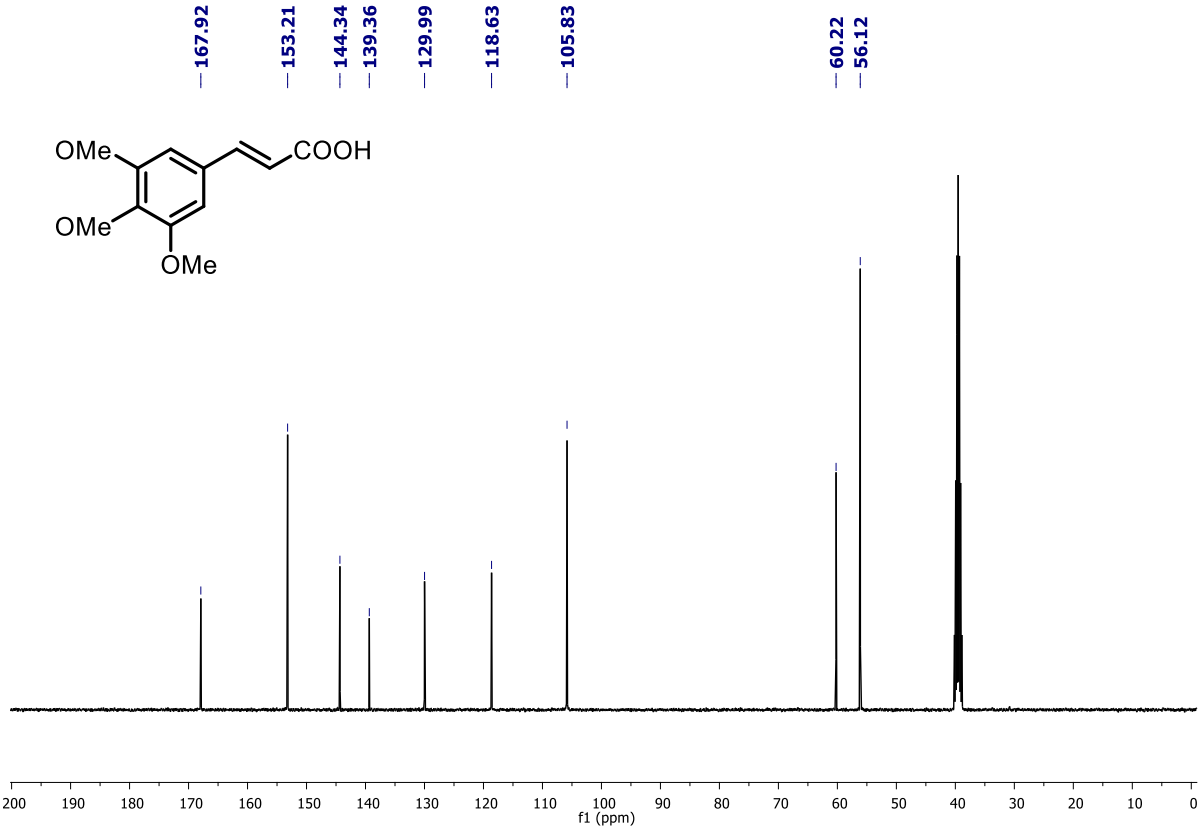
^{13}C {^{1}H} NMR Spectrum of **2u** (CD_3OD, 100 MHz)



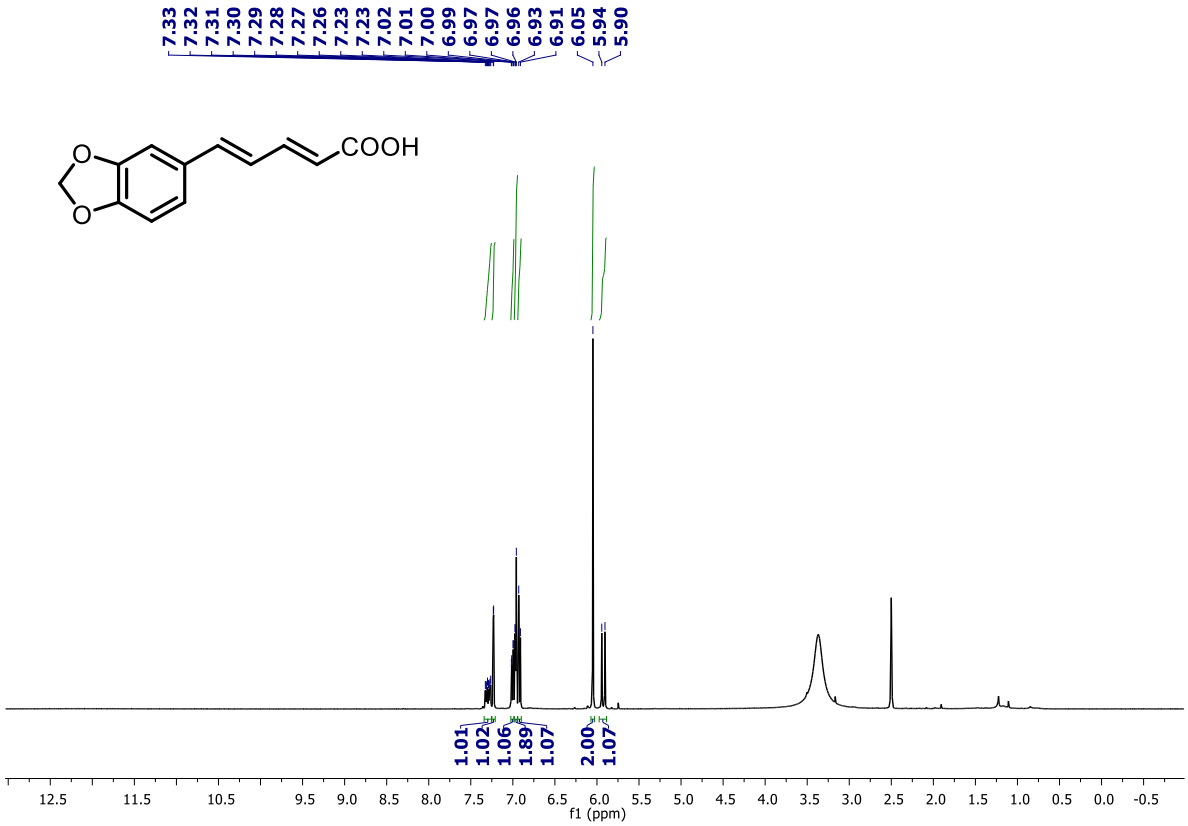
^{1}H NMR Spectrum of **2v** (DMSO-d_6, 400 MHz)



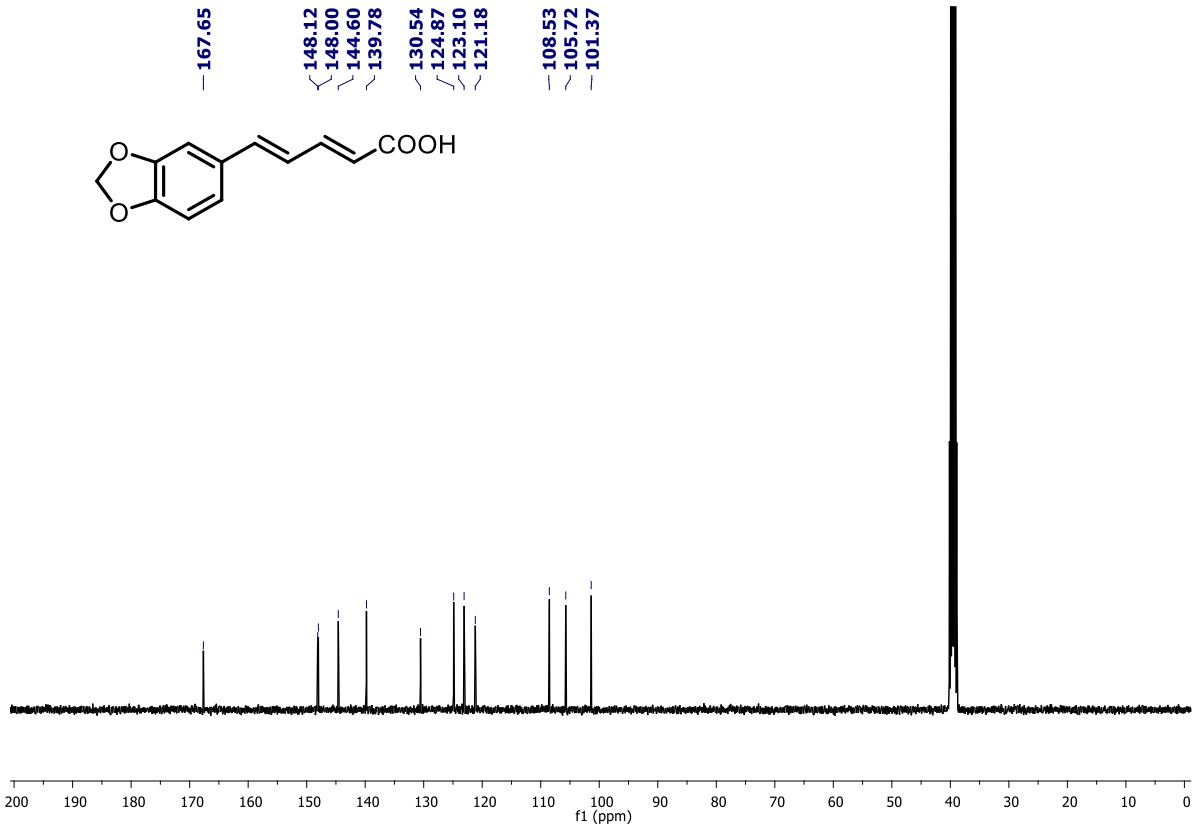
^{13}C {^{1}H} NMR Spectrum of **2v** (DMSO-d_6, 100 MHz)



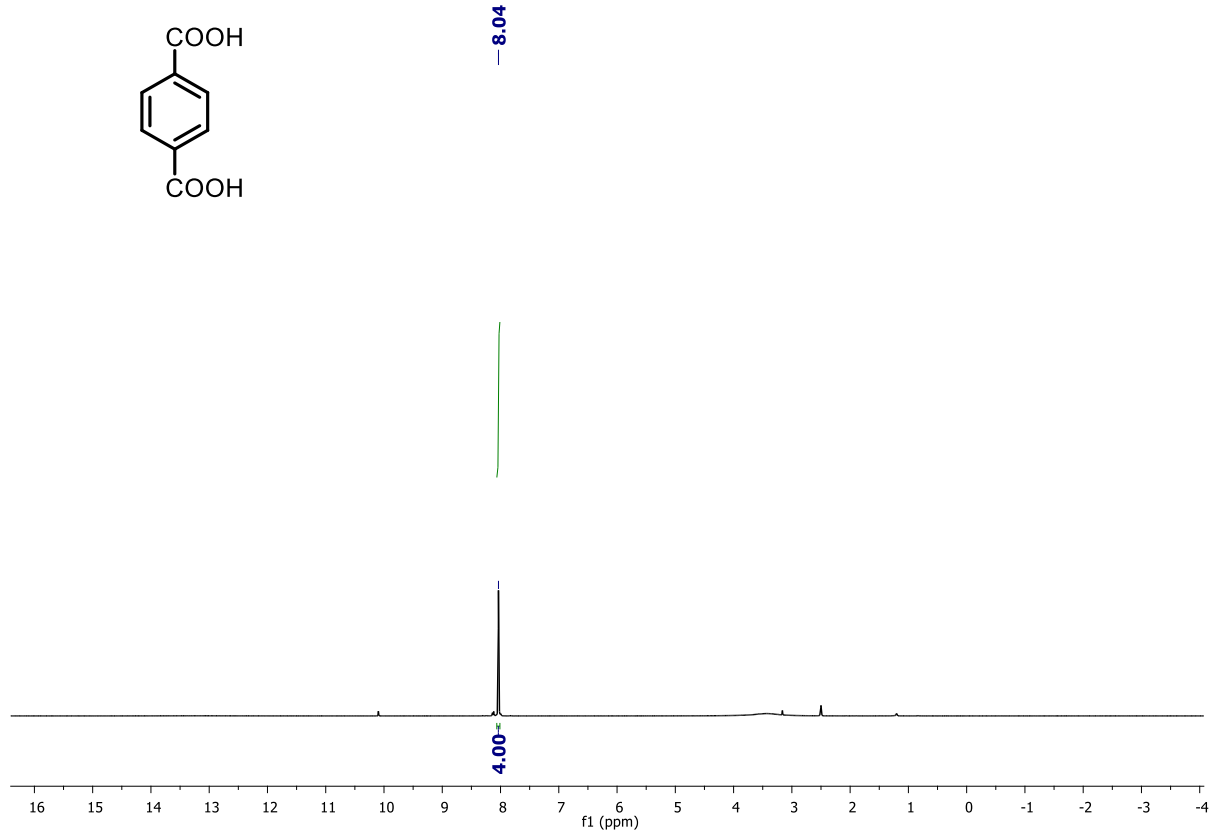
^{1}H NMR Spectrum of **2w** (DMSO-d_6, 400 MHz)



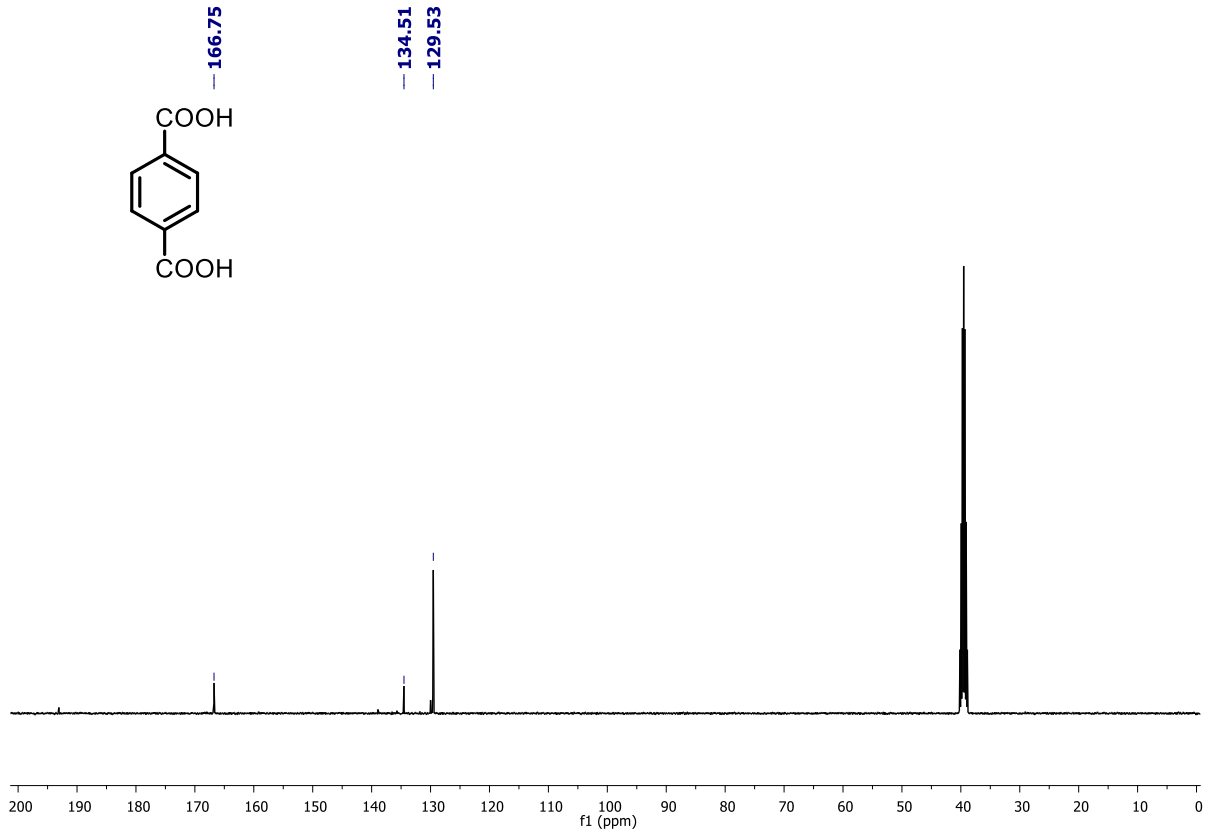
^{13}C {^{1}H} NMR Spectrum of **2w** (DMSO-d_6, 100 MHz)



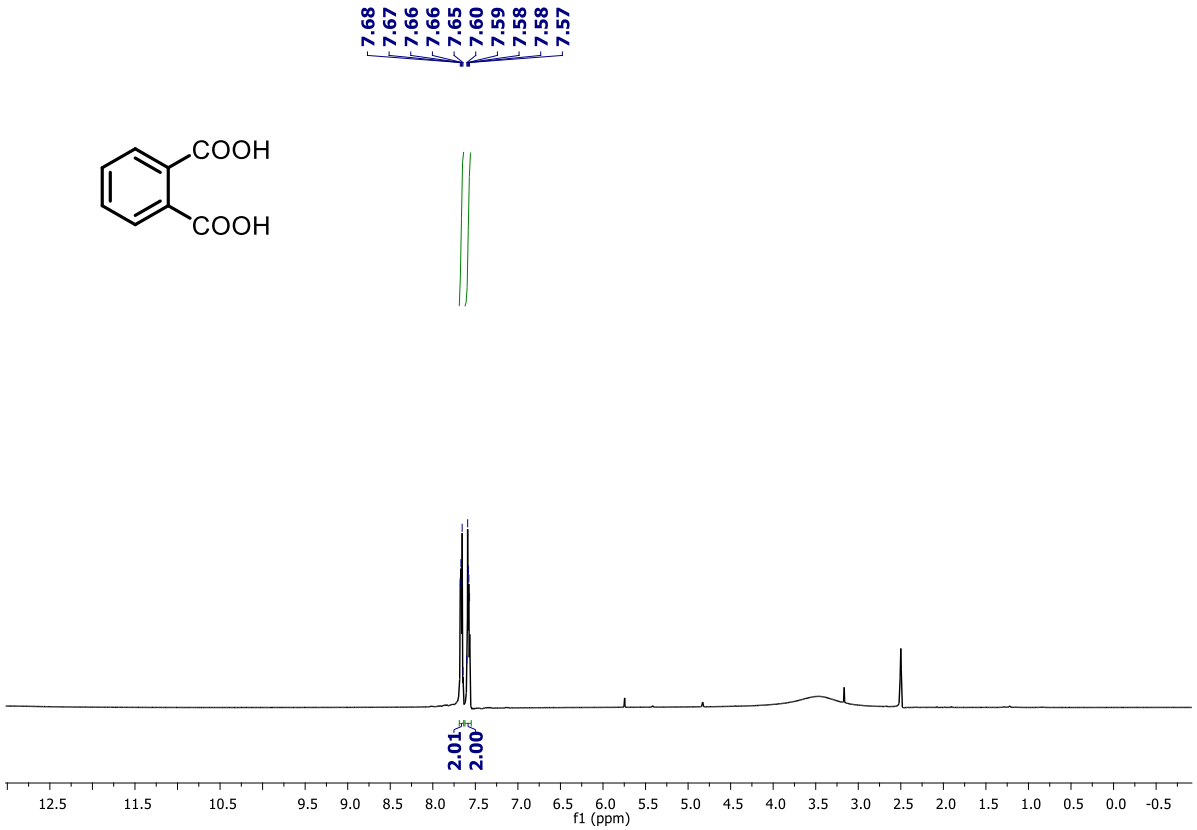
^{1}H NMR Spectrum of **2x** (DMSO-d_6, 400 MHz)



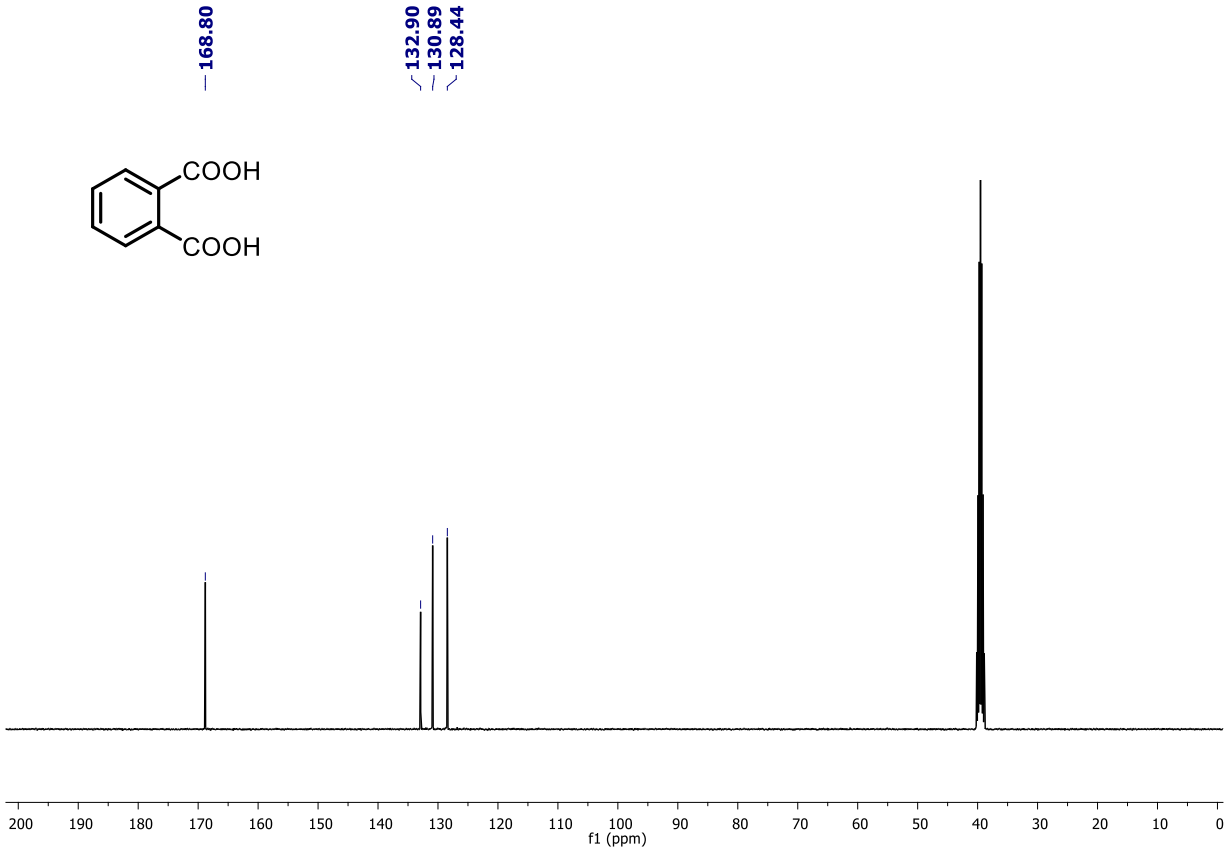
^{13}C {^{1}H} NMR Spectrum of **2x** (DMSO-d_6, 100 MHz)



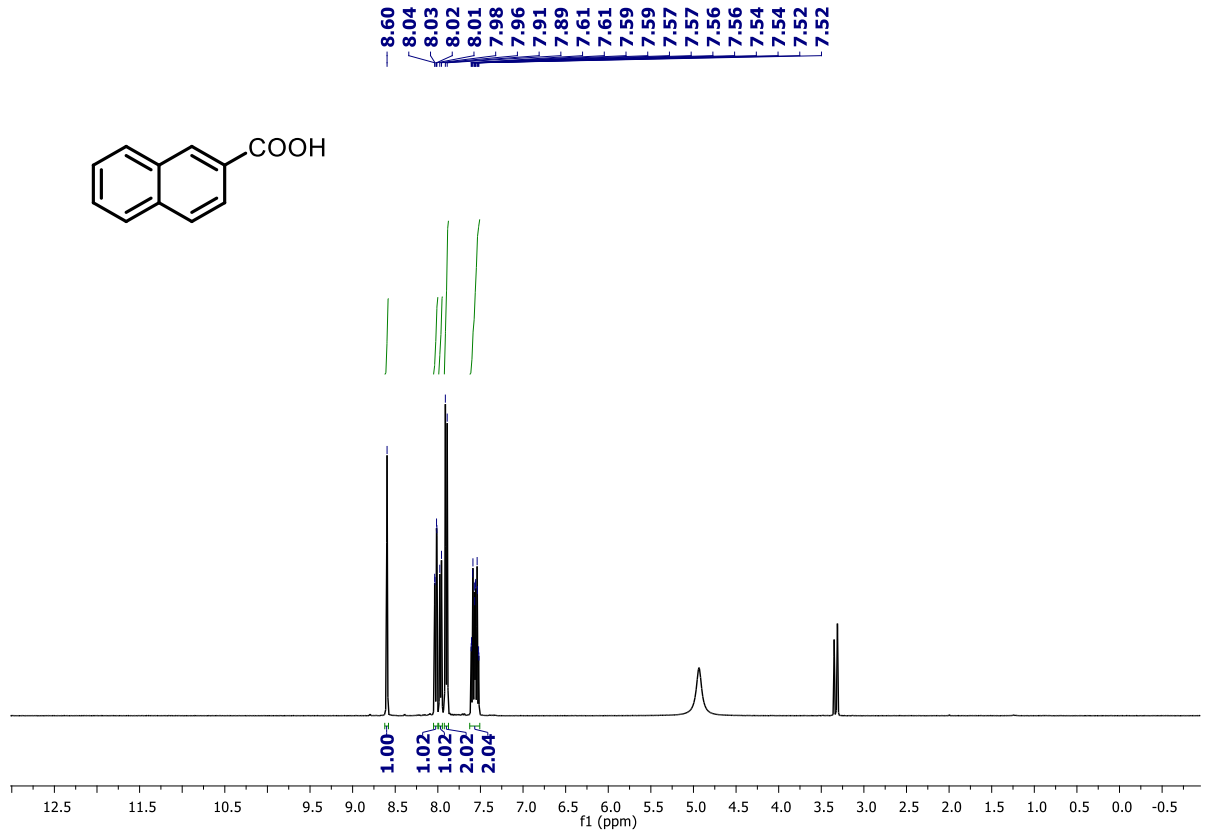
^{1}H NMR Spectrum of **2y** (DMSO-d_6, 400 MHz)



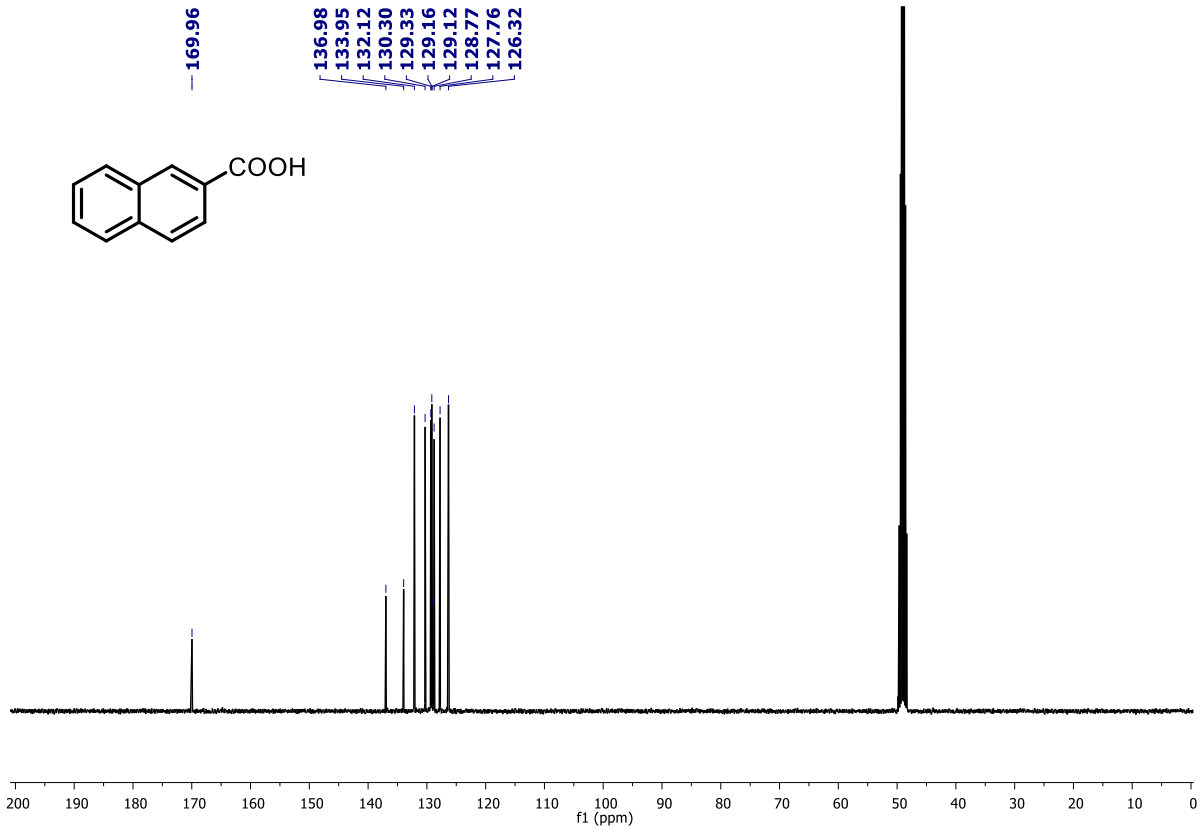
^{13}C {^{1}H} NMR Spectrum of **2y** (DMSO-d_6, 100 MHz)



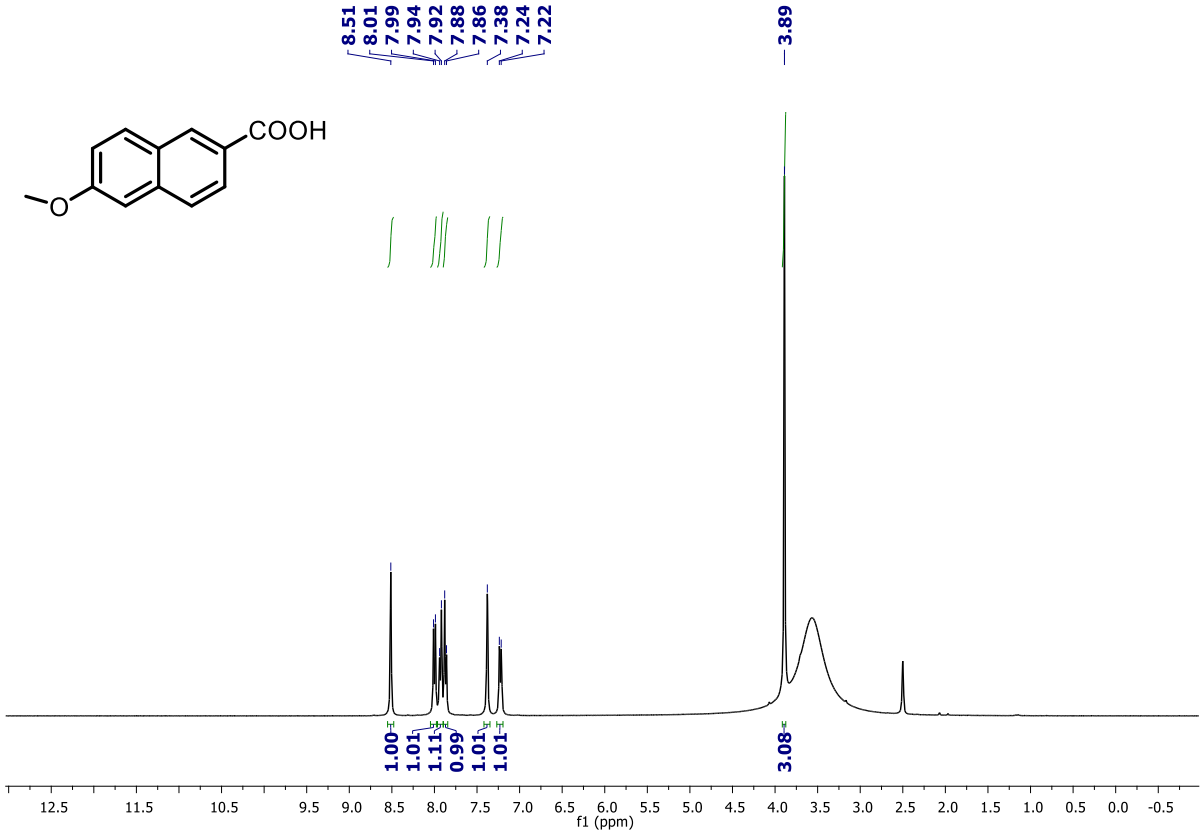
^{1}H NMR Spectrum of **2z** (CD_3OD, 400 MHz)



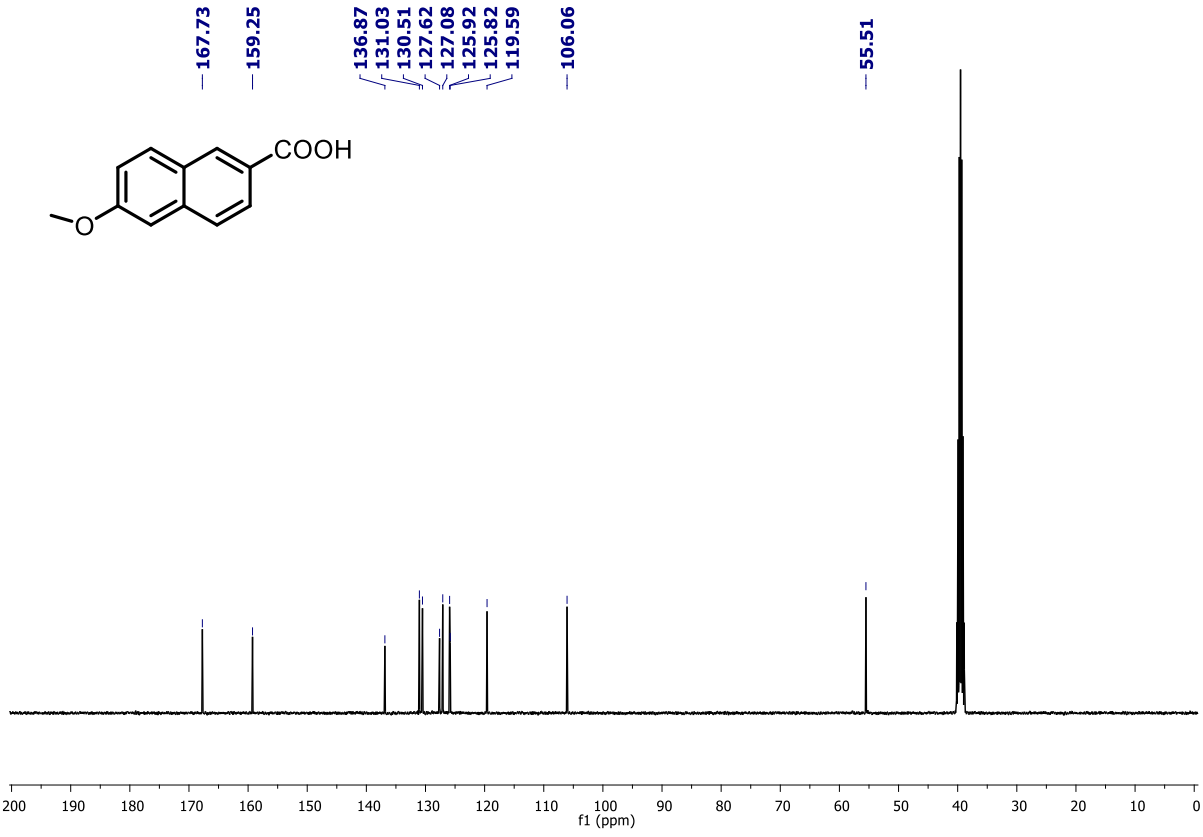
^{13}C {^{1}H} NMR Spectrum of **2z** (CD_3OD, 100 MHz)



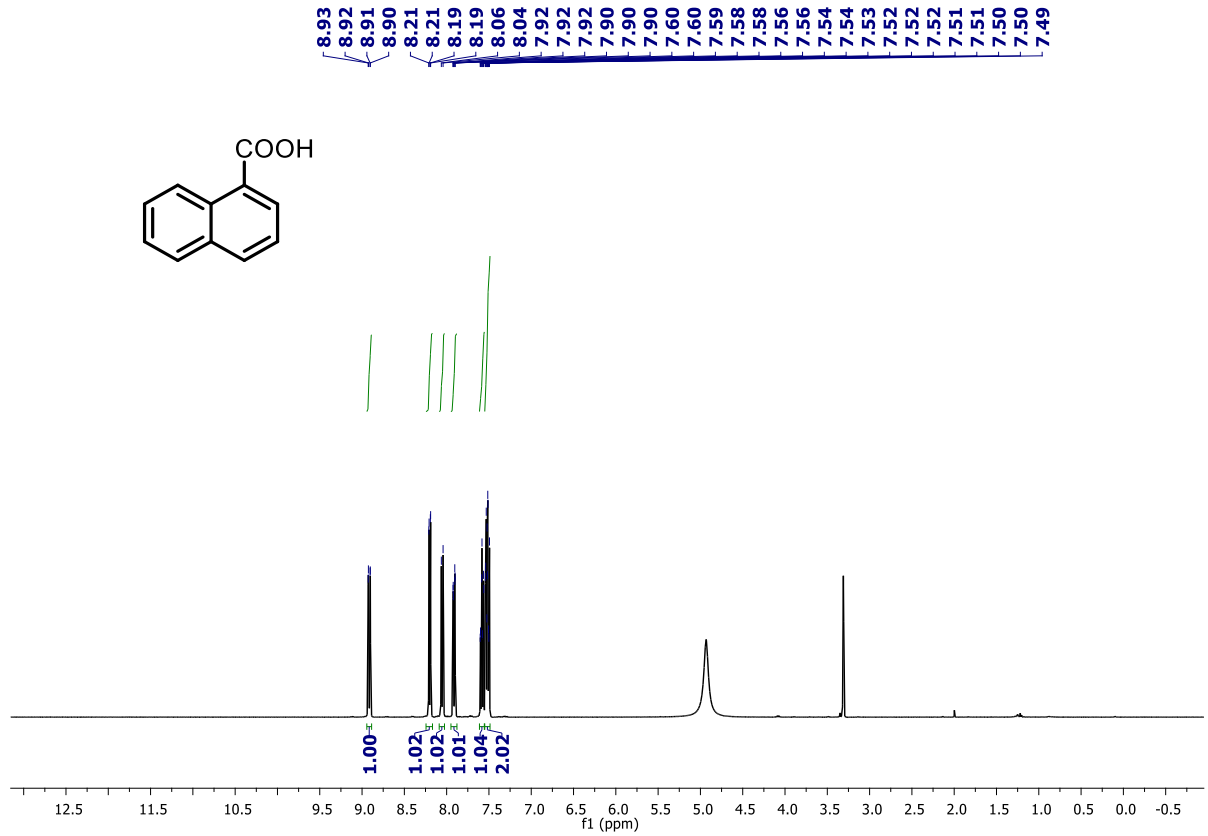
^{1}H NMR Spectrum of **2za** (DMSO-d_6, 400 MHz)



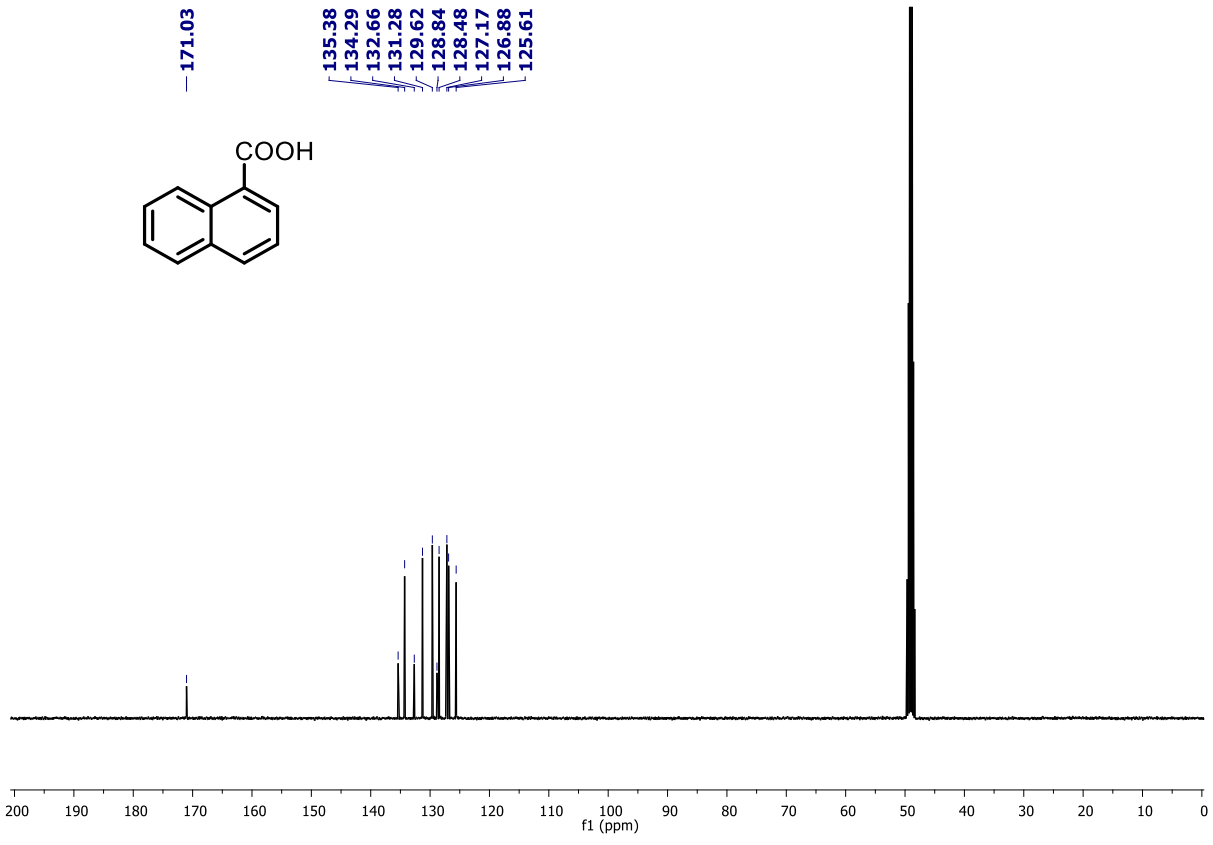
^{13}C {^{1}H} NMR Spectrum of **2za** (DMSO-d_6, 100 MHz)



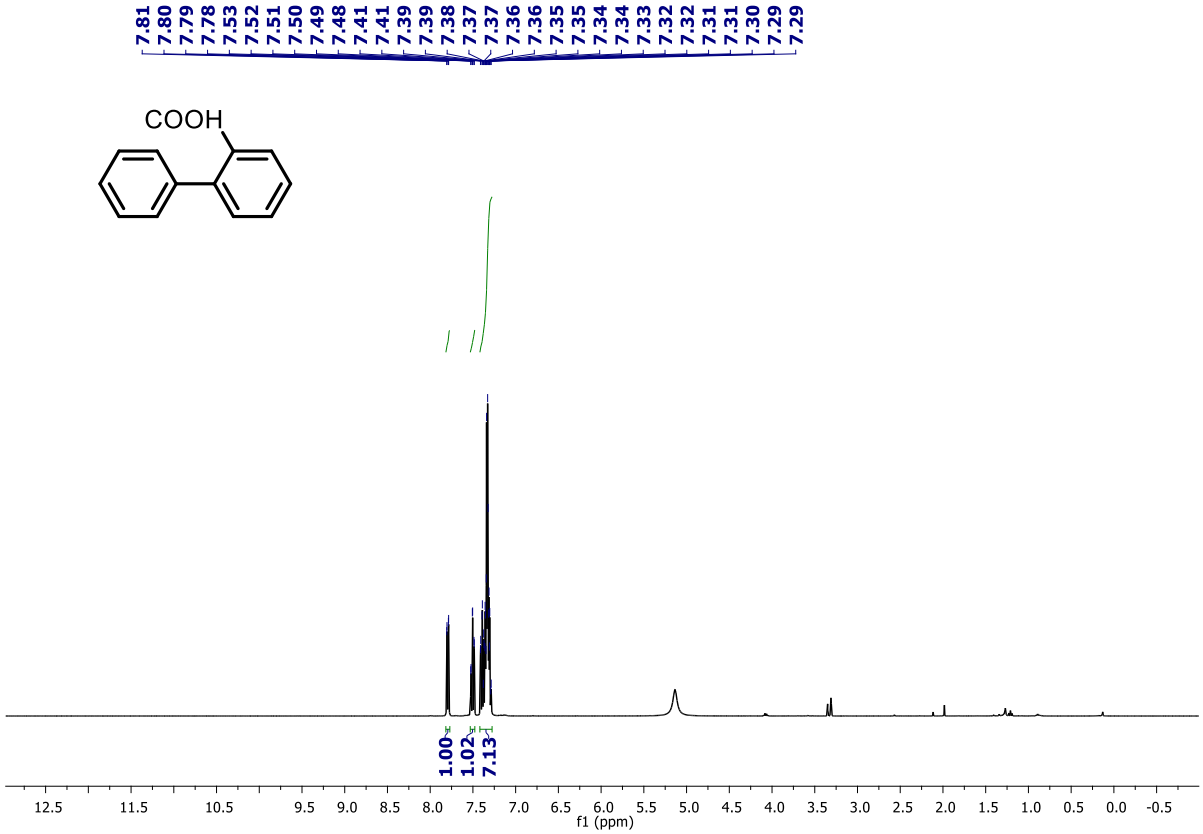
^{1}H NMR Spectrum of **2zb** (CD_3OD, 400 MHz)



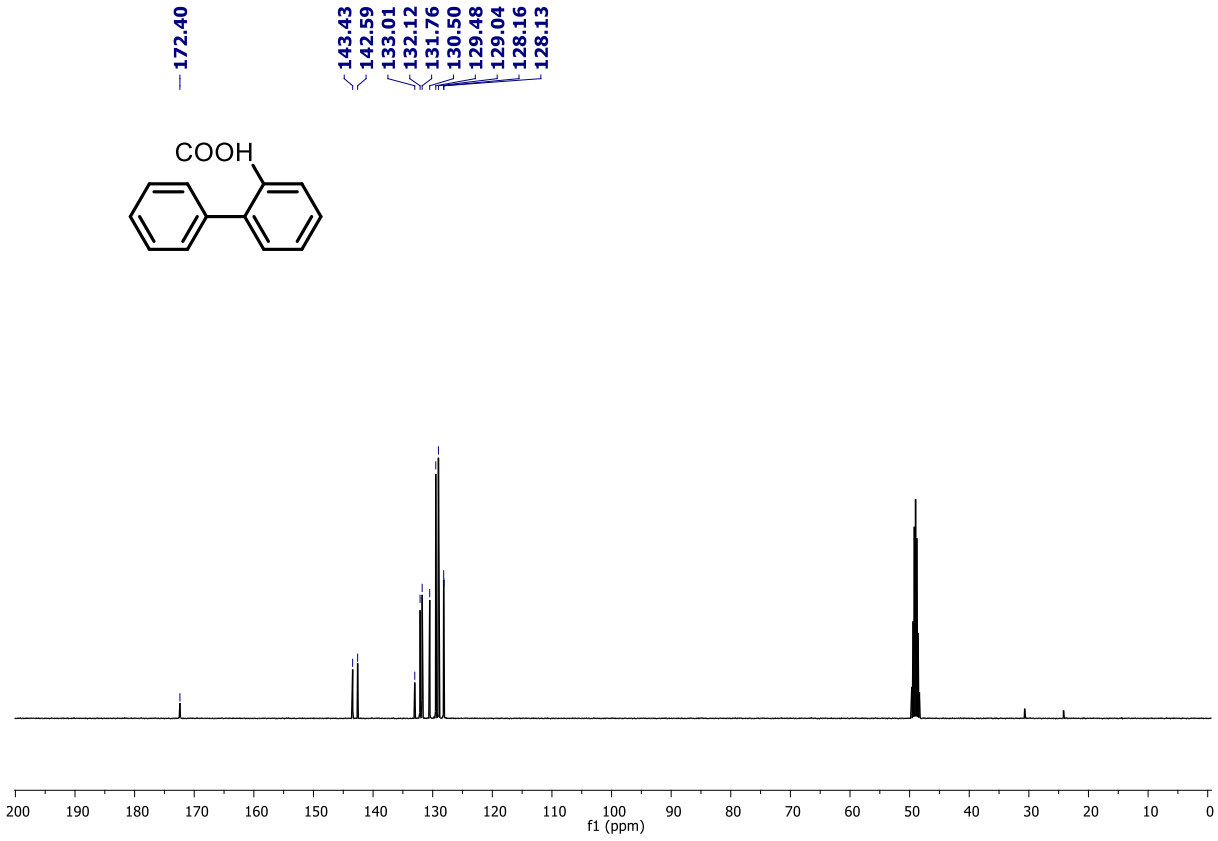
^{13}C {^{1}H} NMR Spectrum of **2zb** (CD_3OD, 100 MHz)



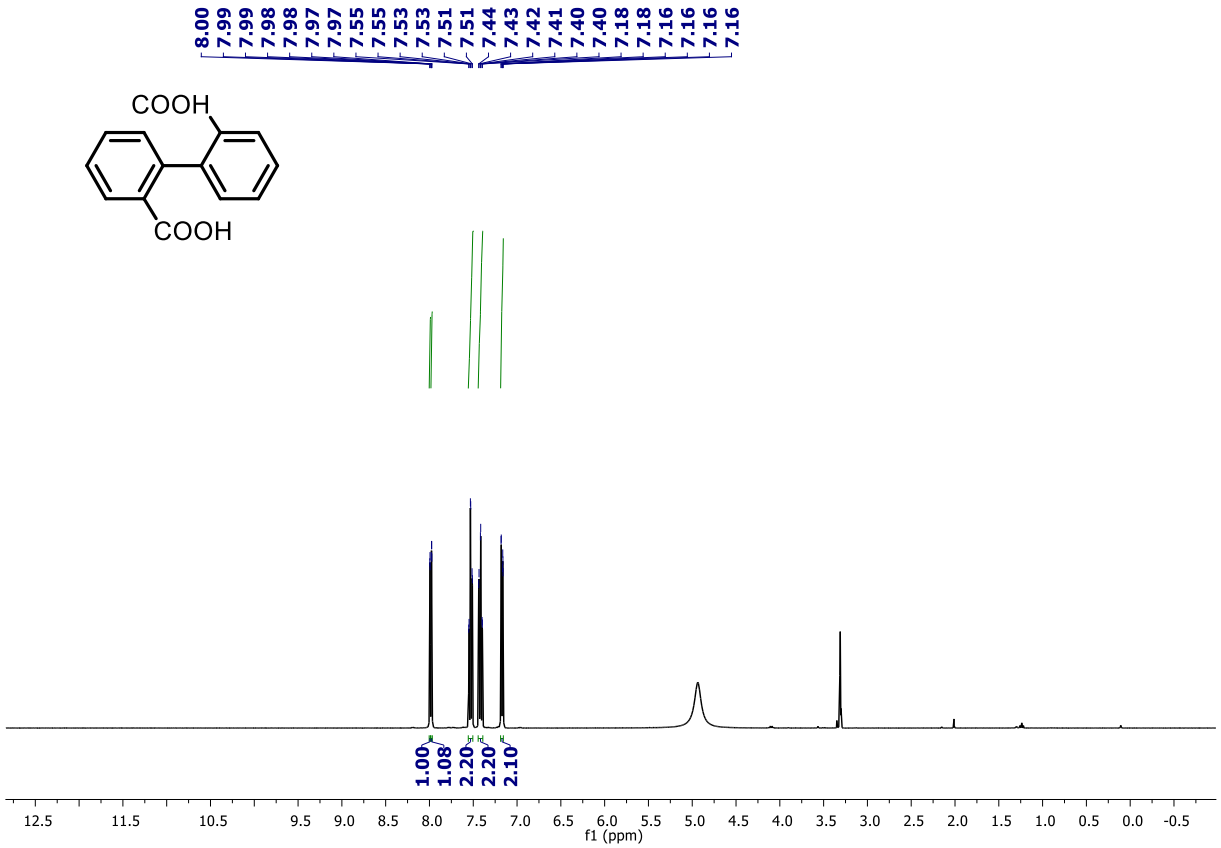
^{1}H NMR Spectrum of **2zc** (CD_3OD, 400 MHz)



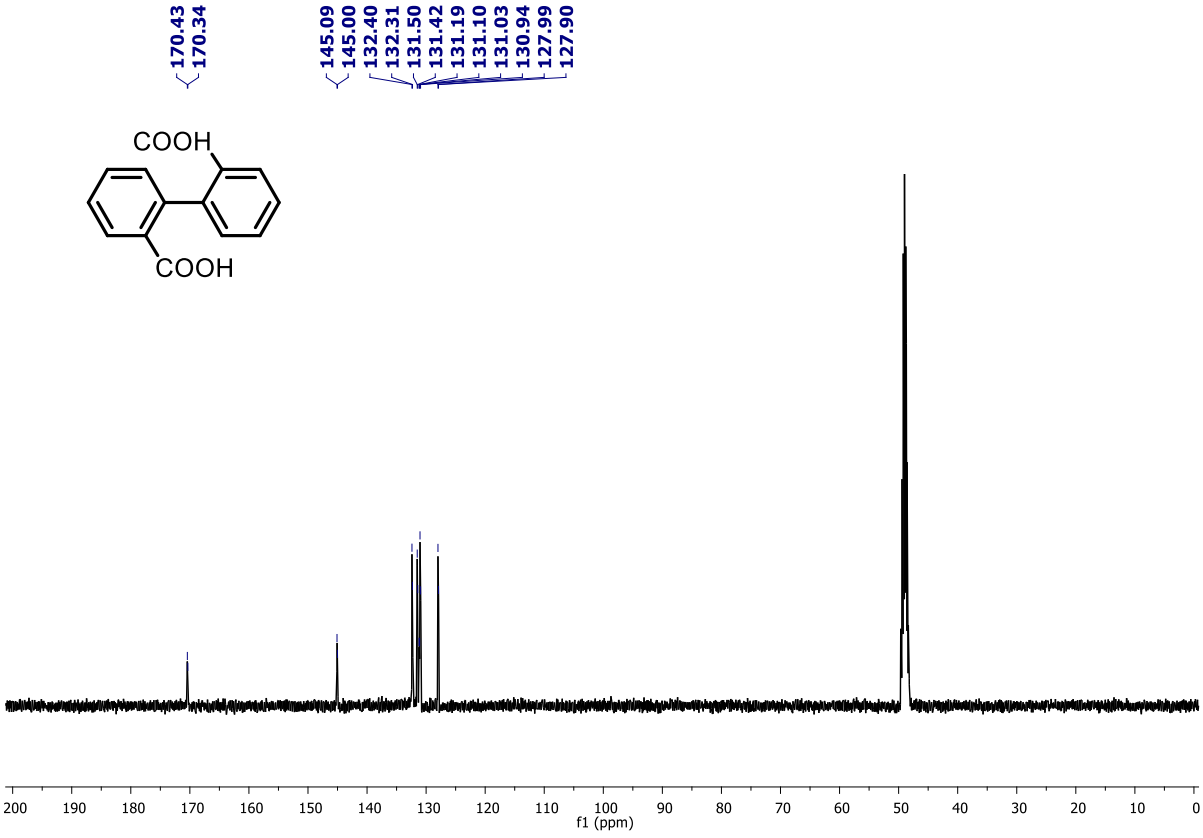
^{13}C {^{1}H} NMR Spectrum of **2zc** (CD_3OD, 100 MHz)



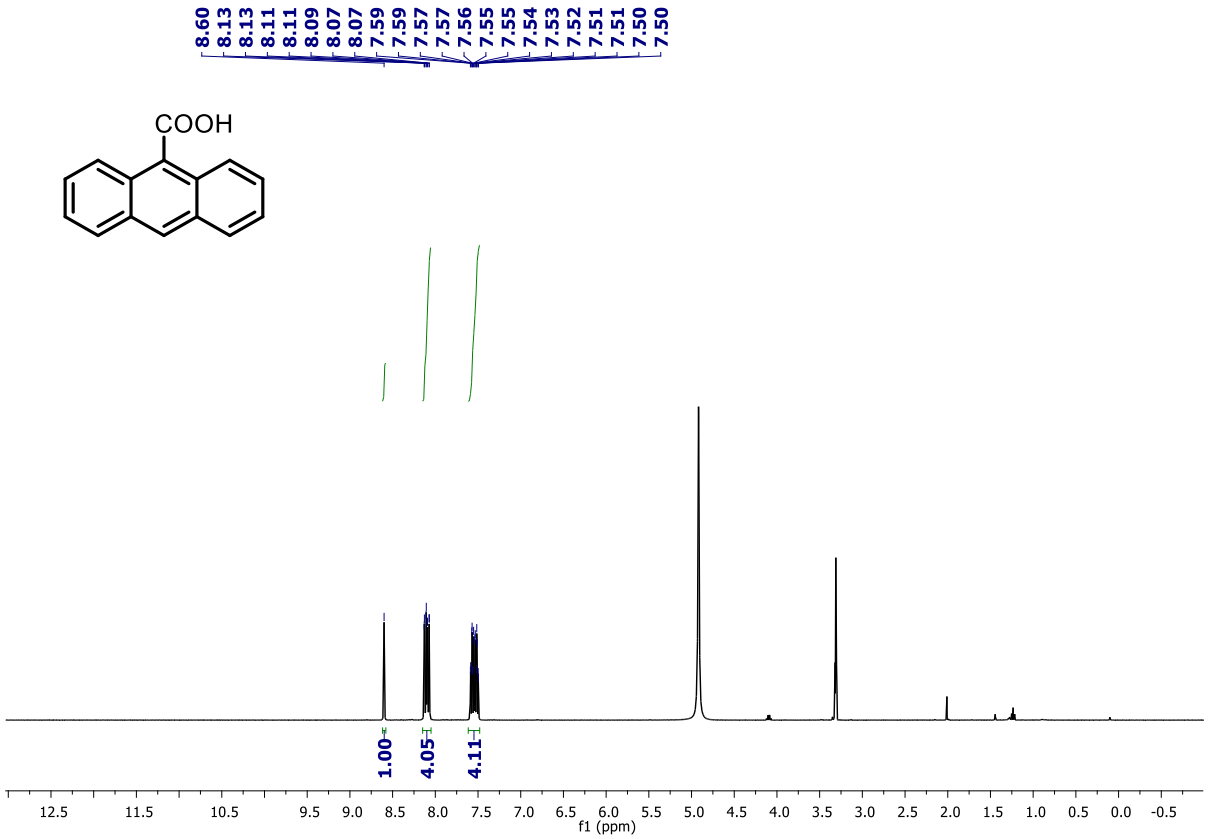
^{1}H NMR Spectrum of **2zd** (CD_3OD, 400 MHz)



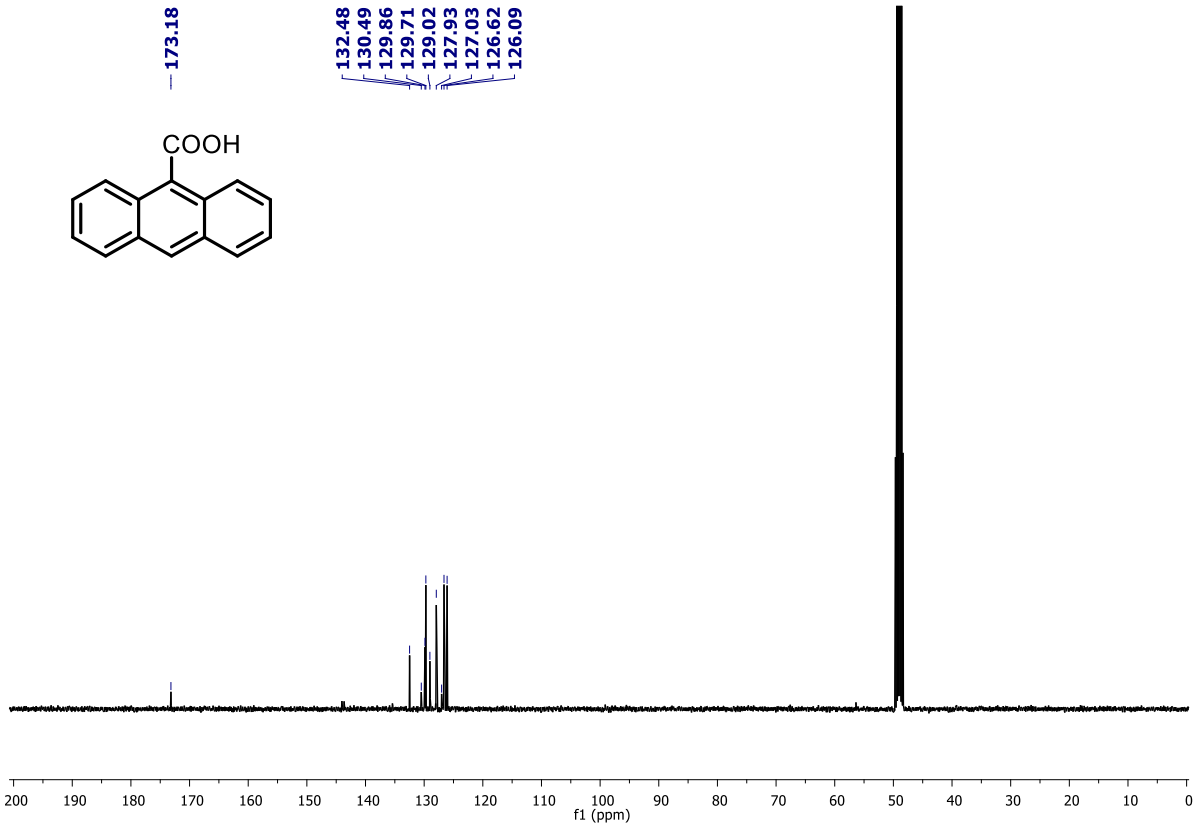
^{13}C {^{1}H} NMR Spectrum of **2zd** (CD_3OD, 100 MHz)



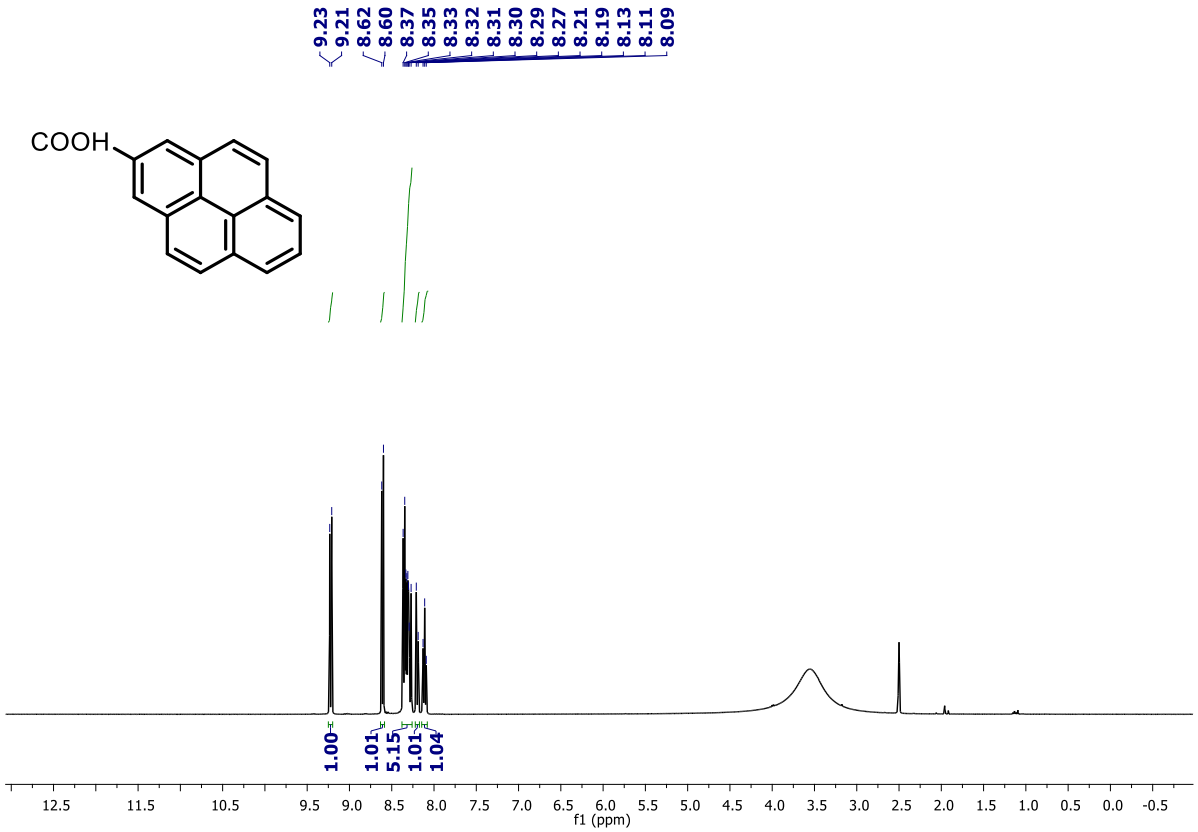
^{1}H NMR Spectrum of **2ze** (CD_3OD, 400 MHz)



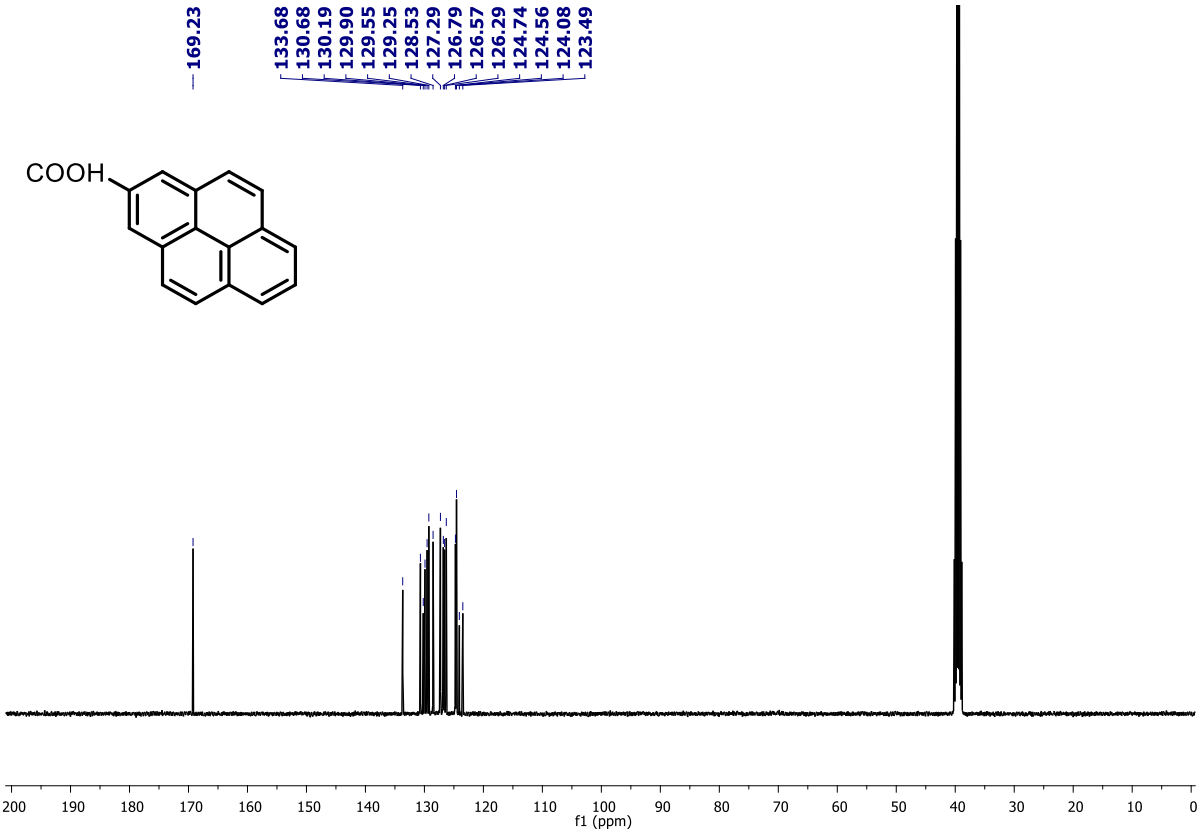
^{13}C {^{1}H} NMR Spectrum of **2ze** (CD_3OD, 100 MHz)



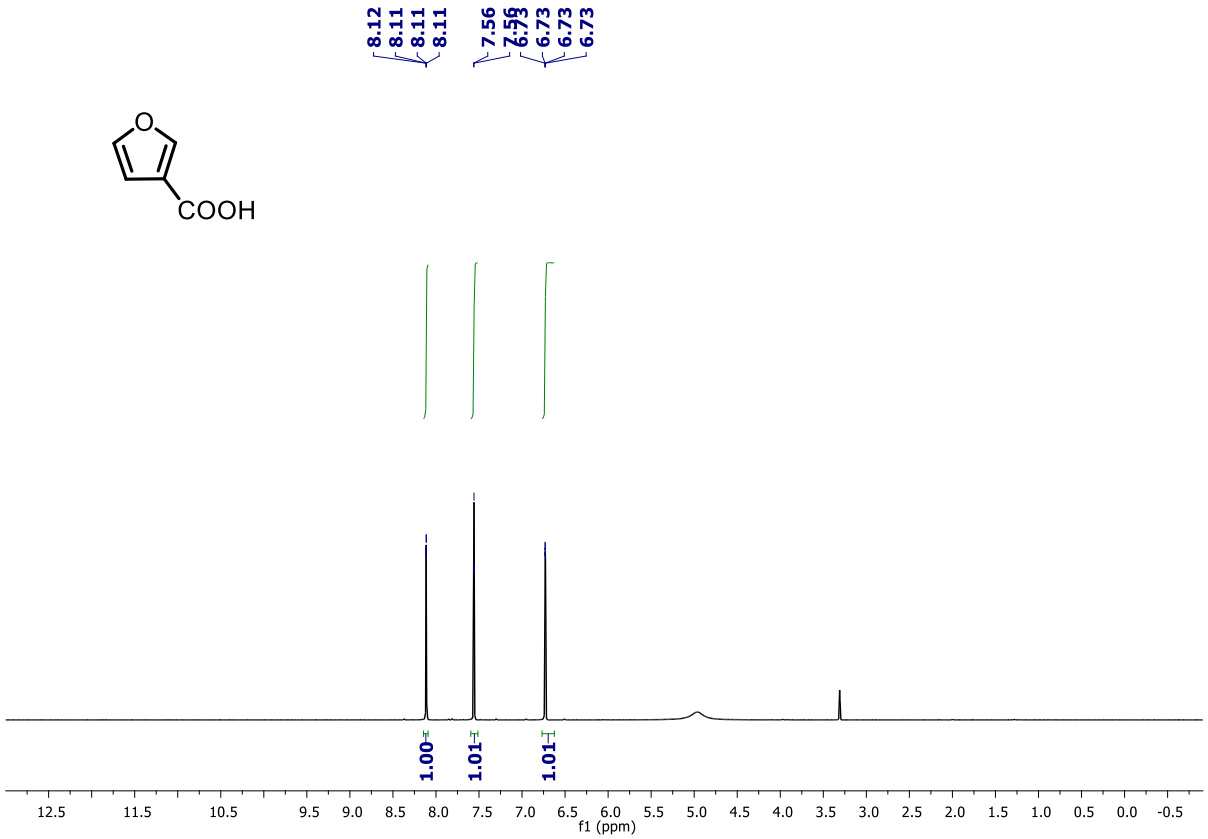
^{1}H NMR Spectrum of **2zf** (DMSO-d_6, 400 MHz)



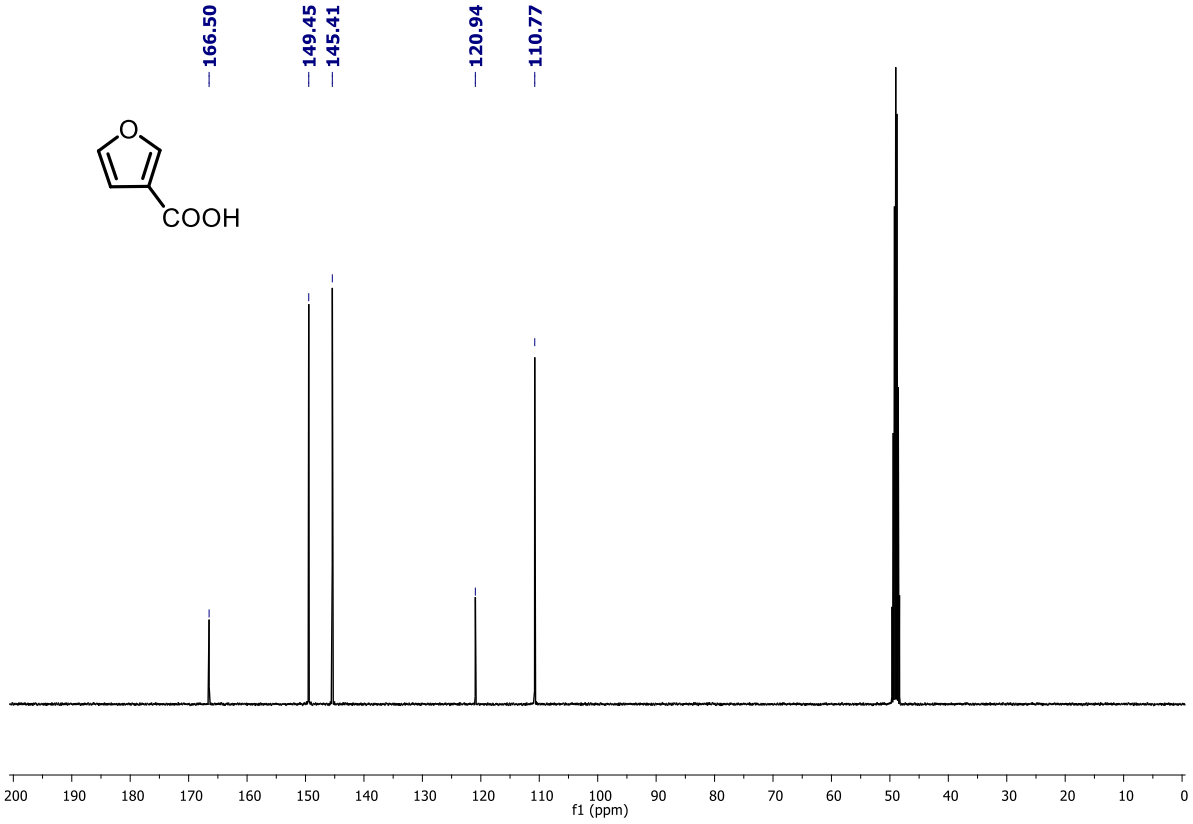
^{13}C {^{1}H} NMR Spectrum of **2zf** (DMSO-d_6, 100 MHz)



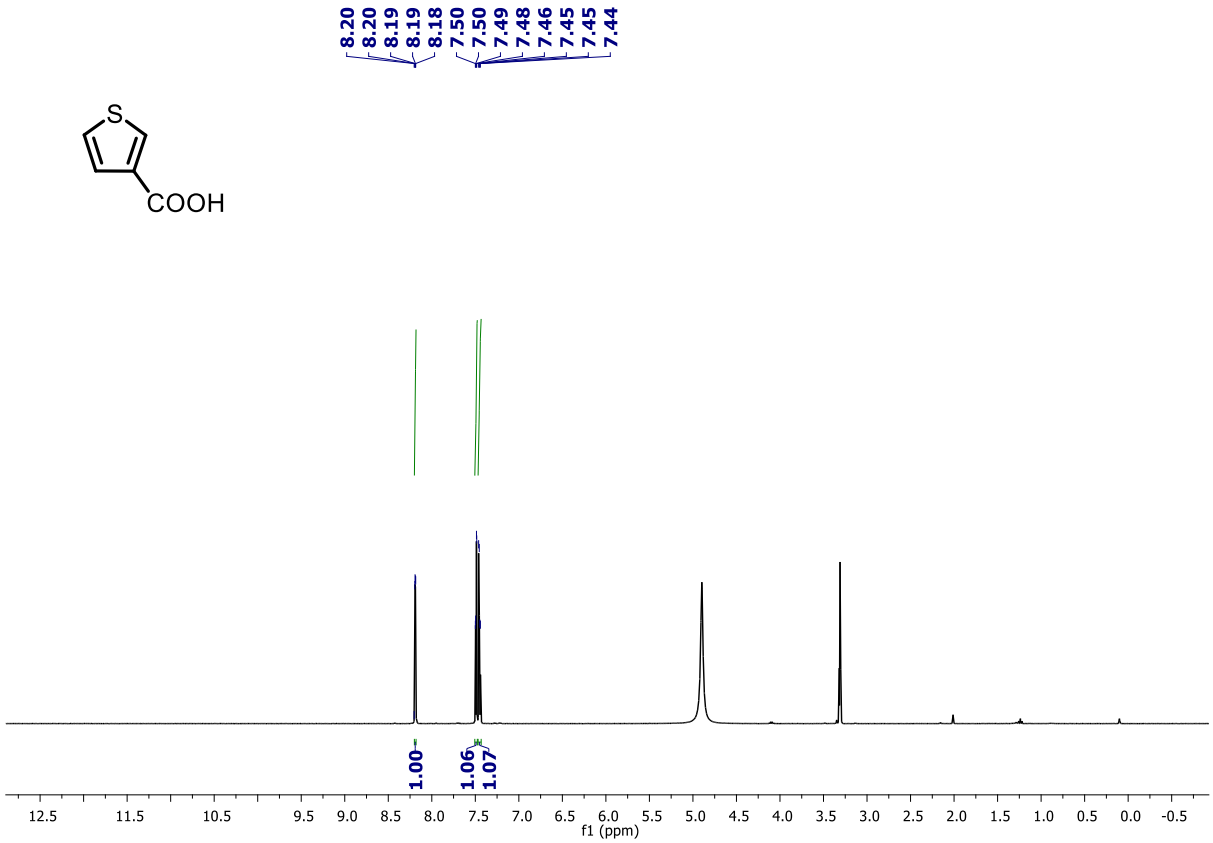
^{1}H NMR Spectrum of **4a** (CD_3OD, 400 MHz)



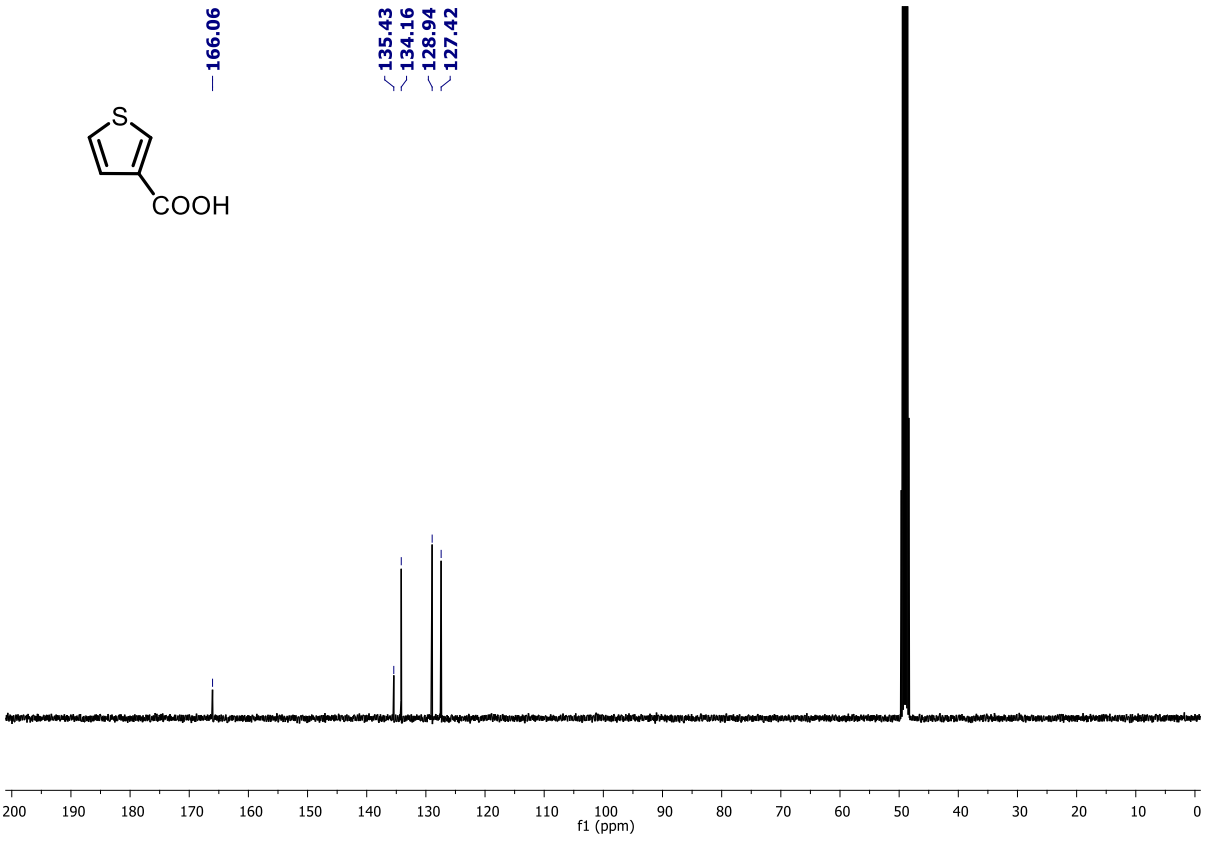
^{13}C {^{1}H} NMR Spectrum of **4a** (CD_3OD, 100 MHz)



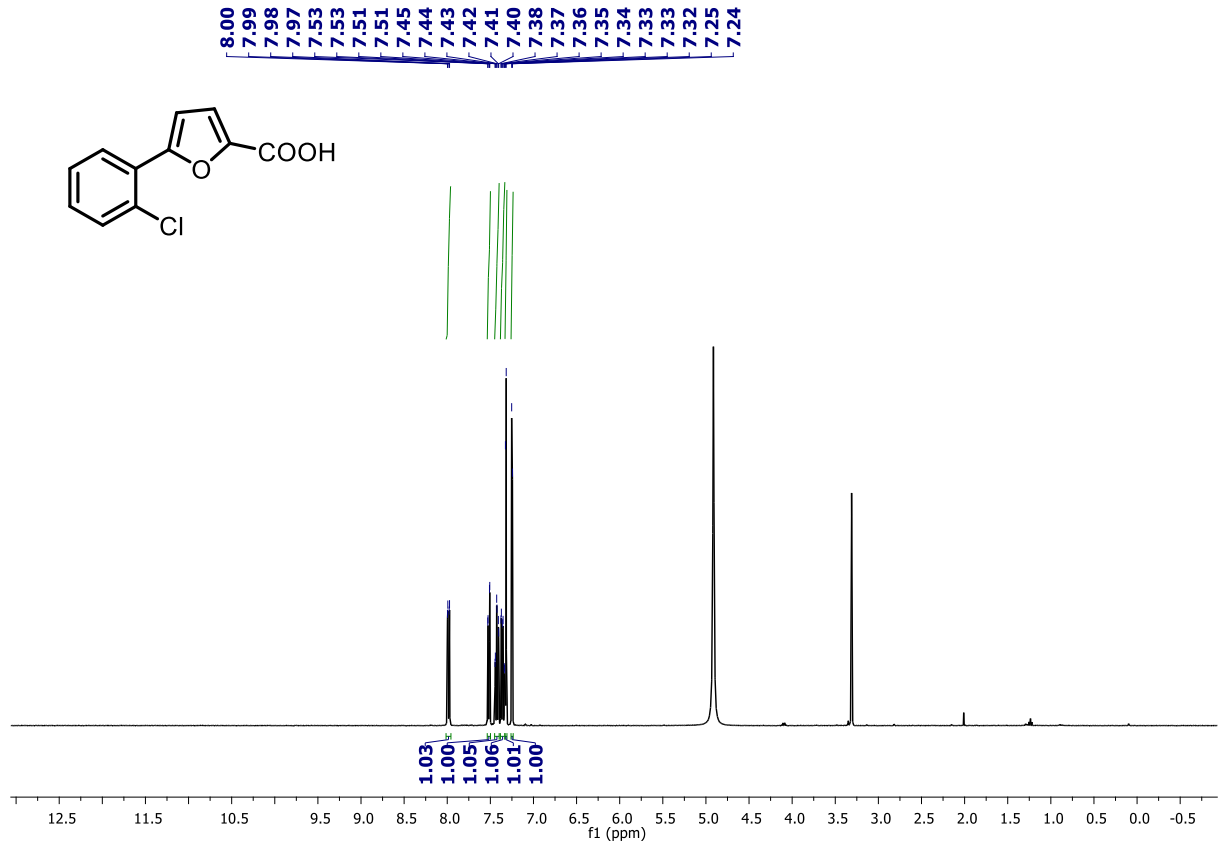
^{1}H NMR Spectrum of **4b** (CD_3OD, 400 MHz)



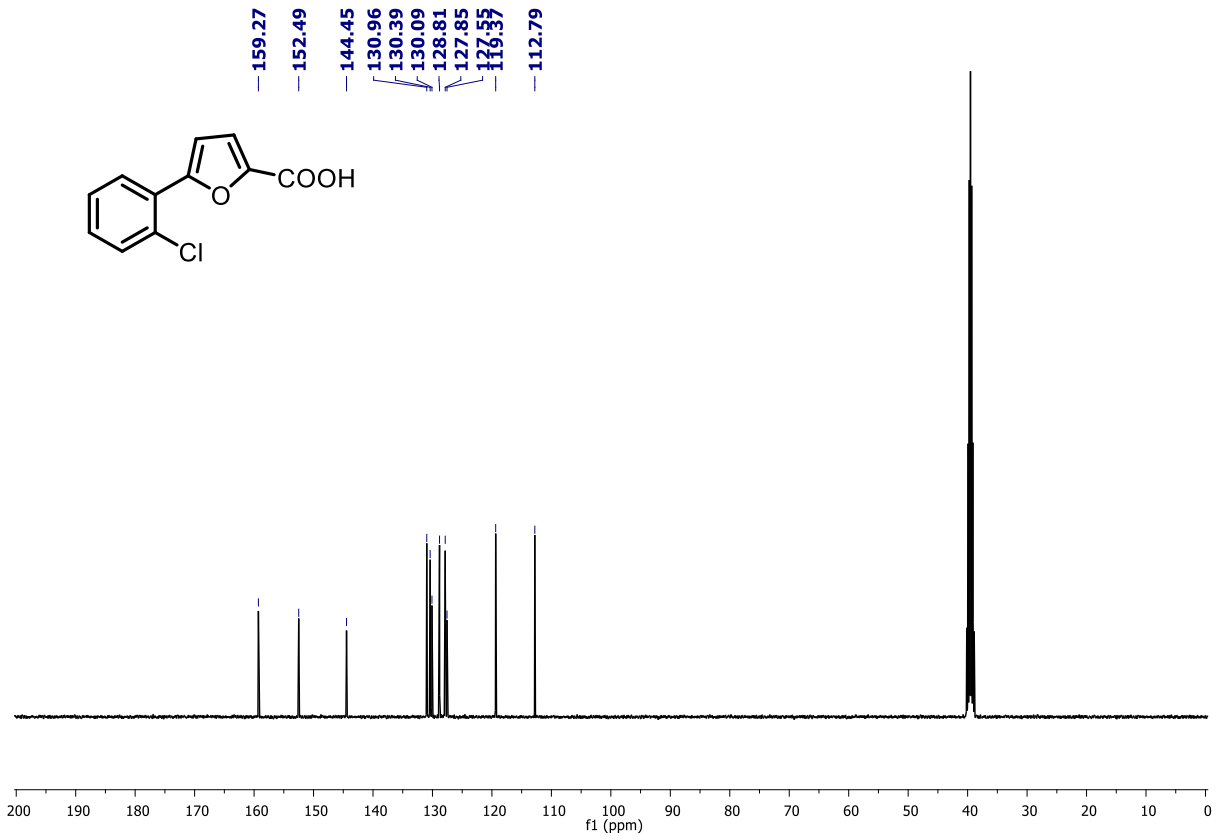
^{13}C {^{1}H} NMR Spectrum of **4b** (CD_3OD, 100 MHz)



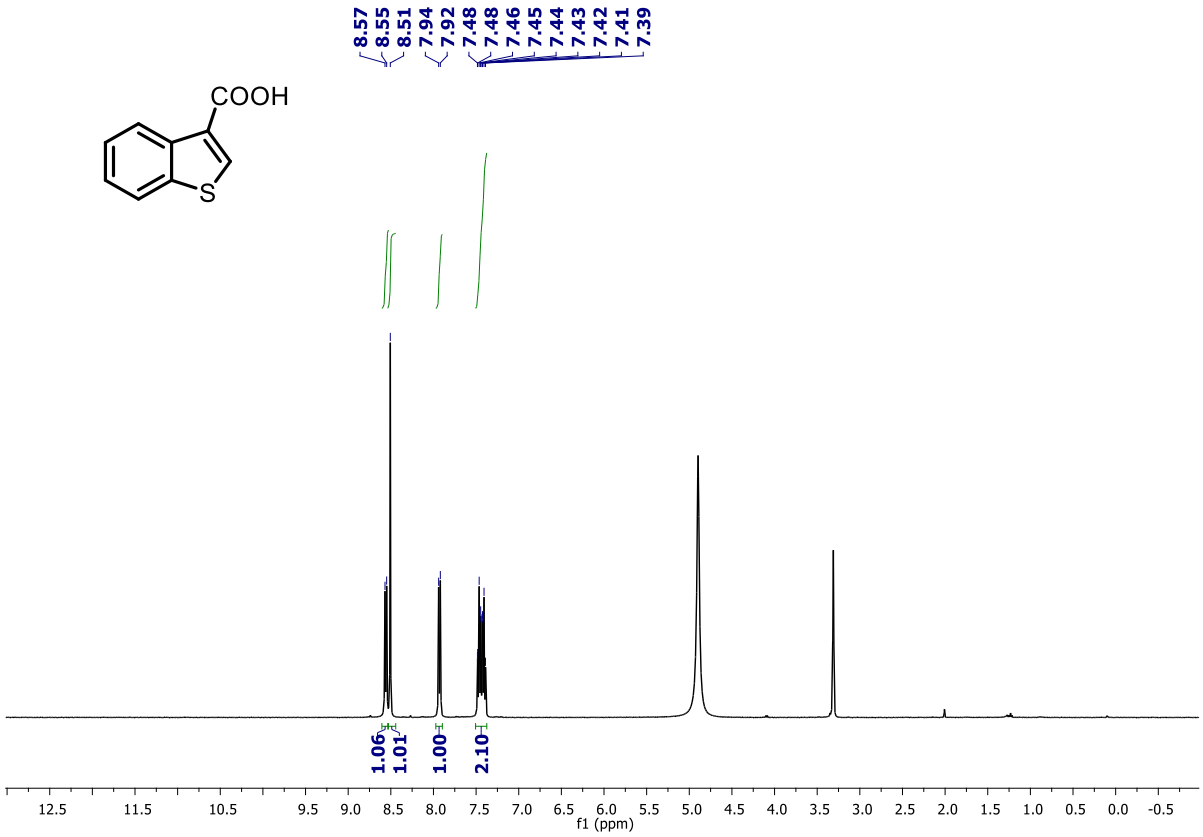
^{1}H NMR Spectrum of **4c** (CD_3OD, 400 MHz)



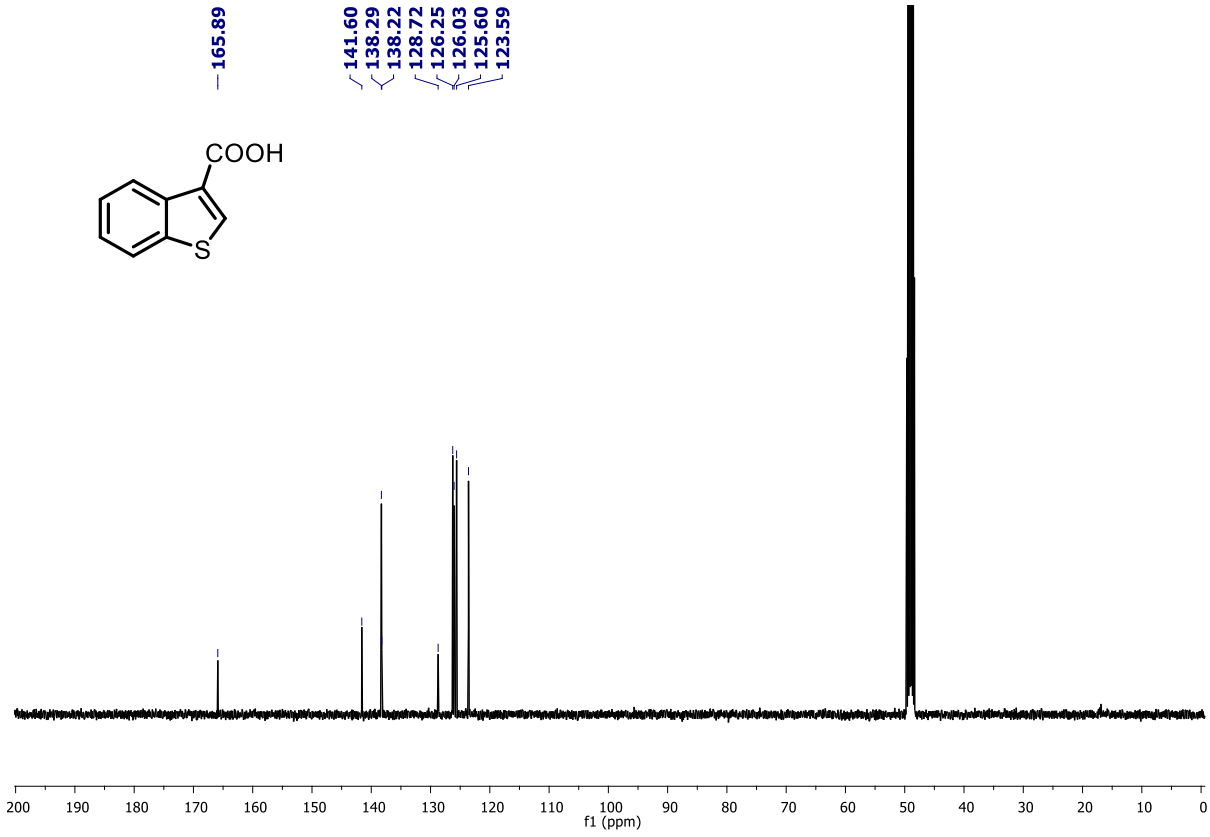
^{13}C {^{1}H} NMR Spectrum of **4c** (DMSO-d_6, 100 MHz)



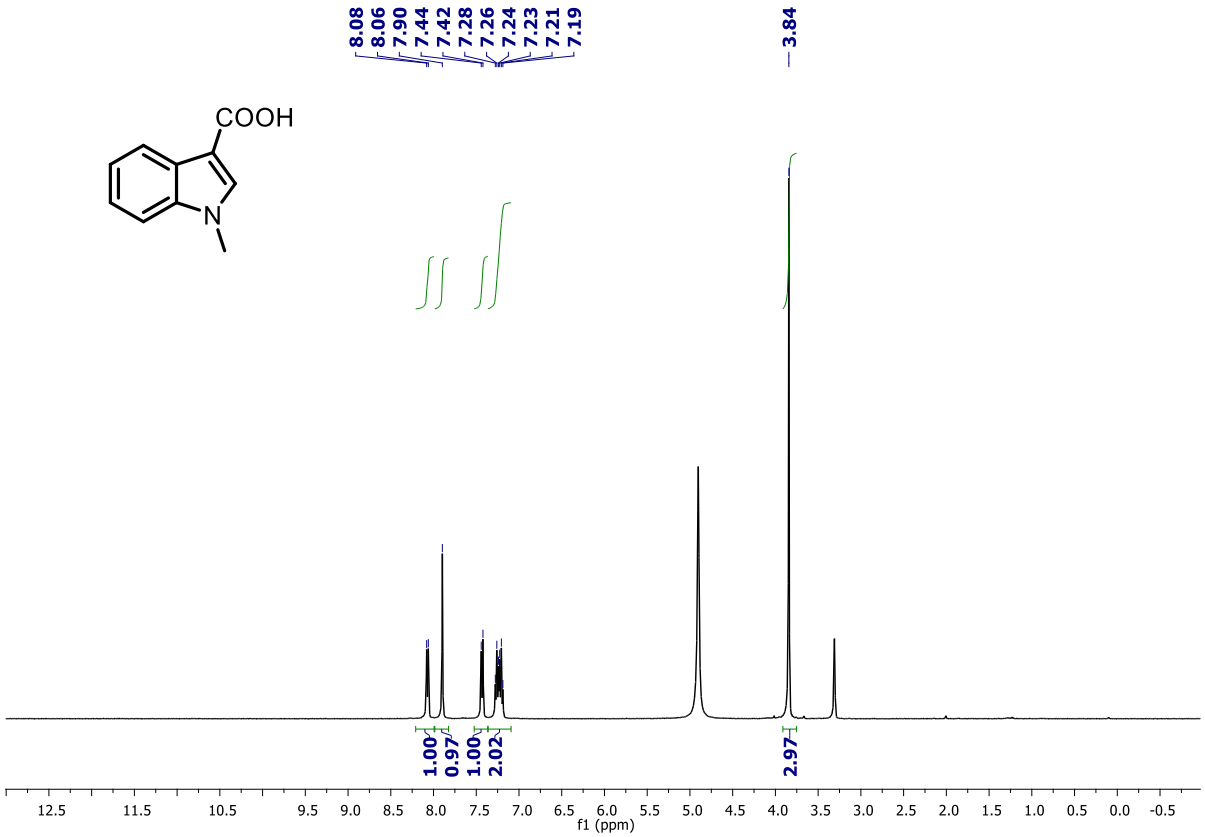
^{1}H NMR Spectrum of **4d** (CD_3OD, 400 MHz)



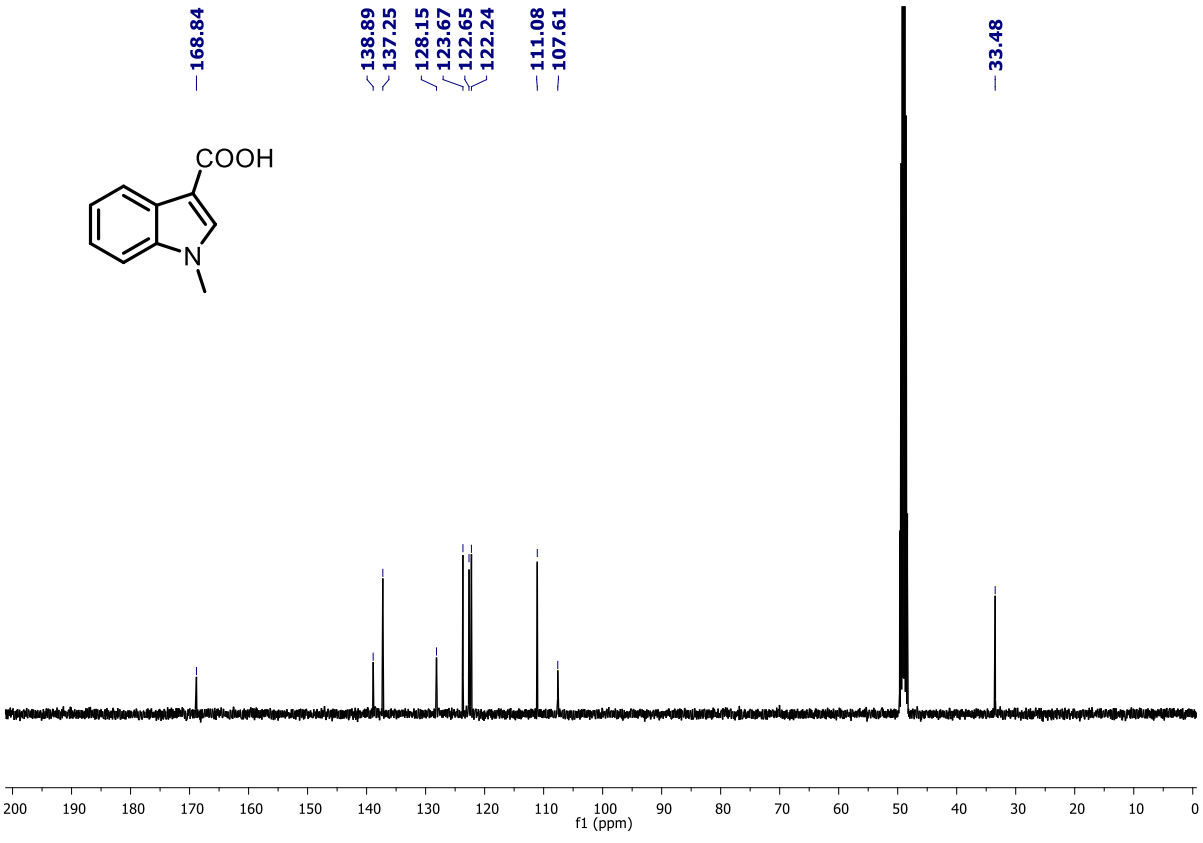
^{13}C {^{1}H} NMR Spectrum of **4d** (CD_3OD, 100 MHz)



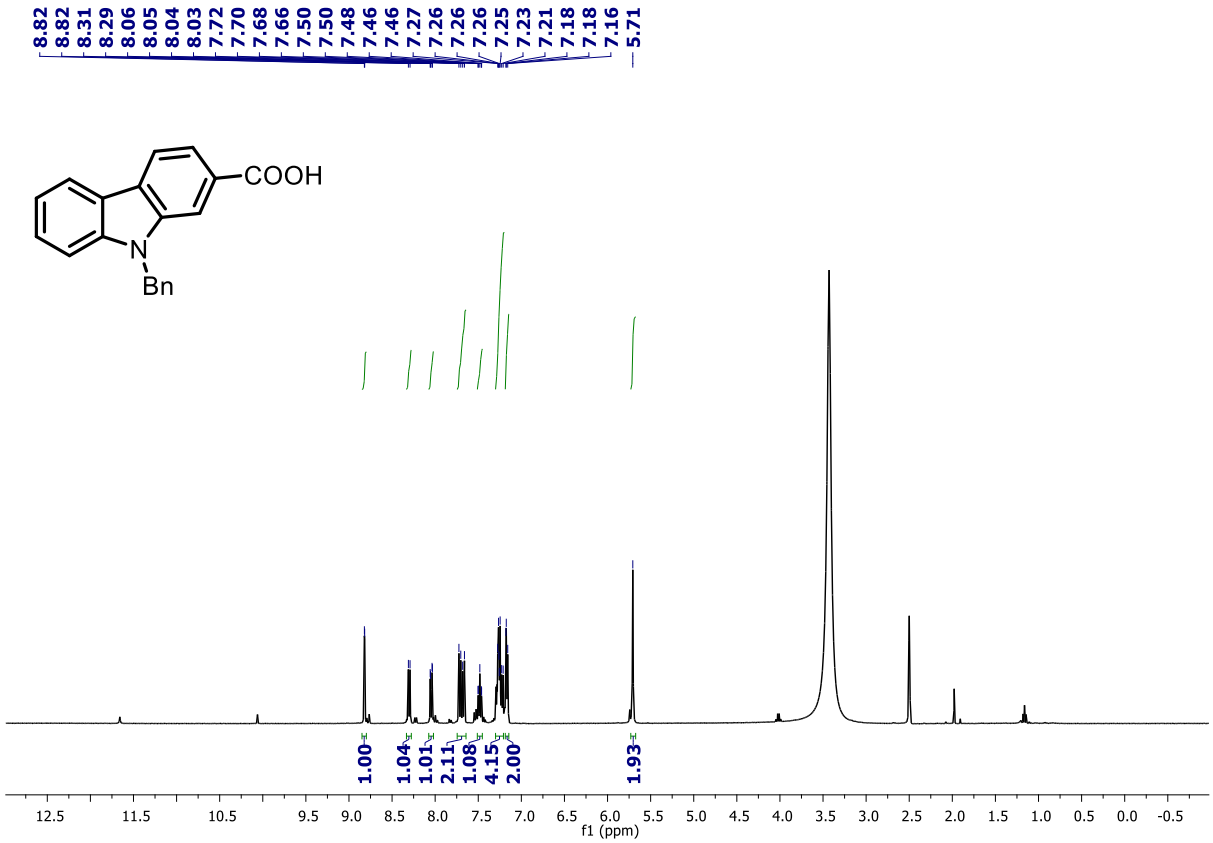
^{1}H NMR Spectrum of **4e** (CD_3OD, 400 MHz)



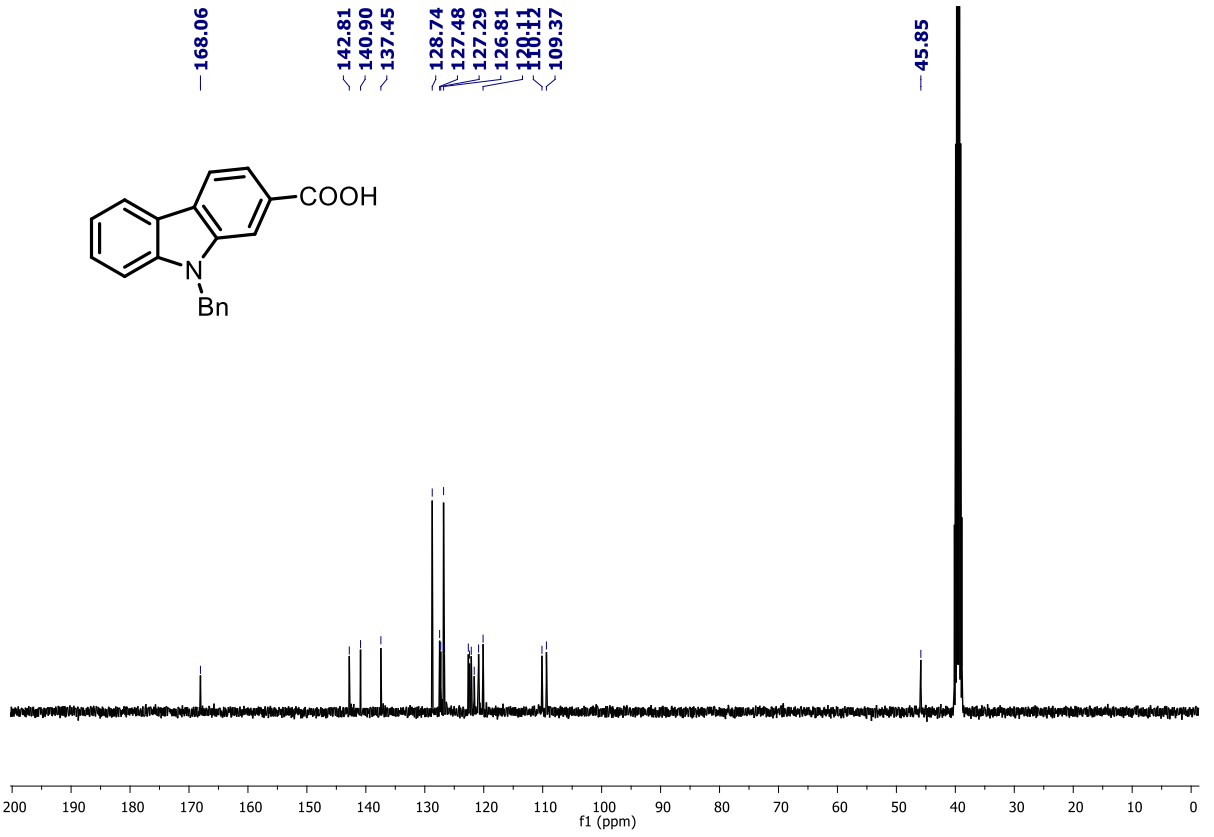
^{13}C {^{1}H} NMR Spectrum of **4e** (CD_3OD, 100 MHz)



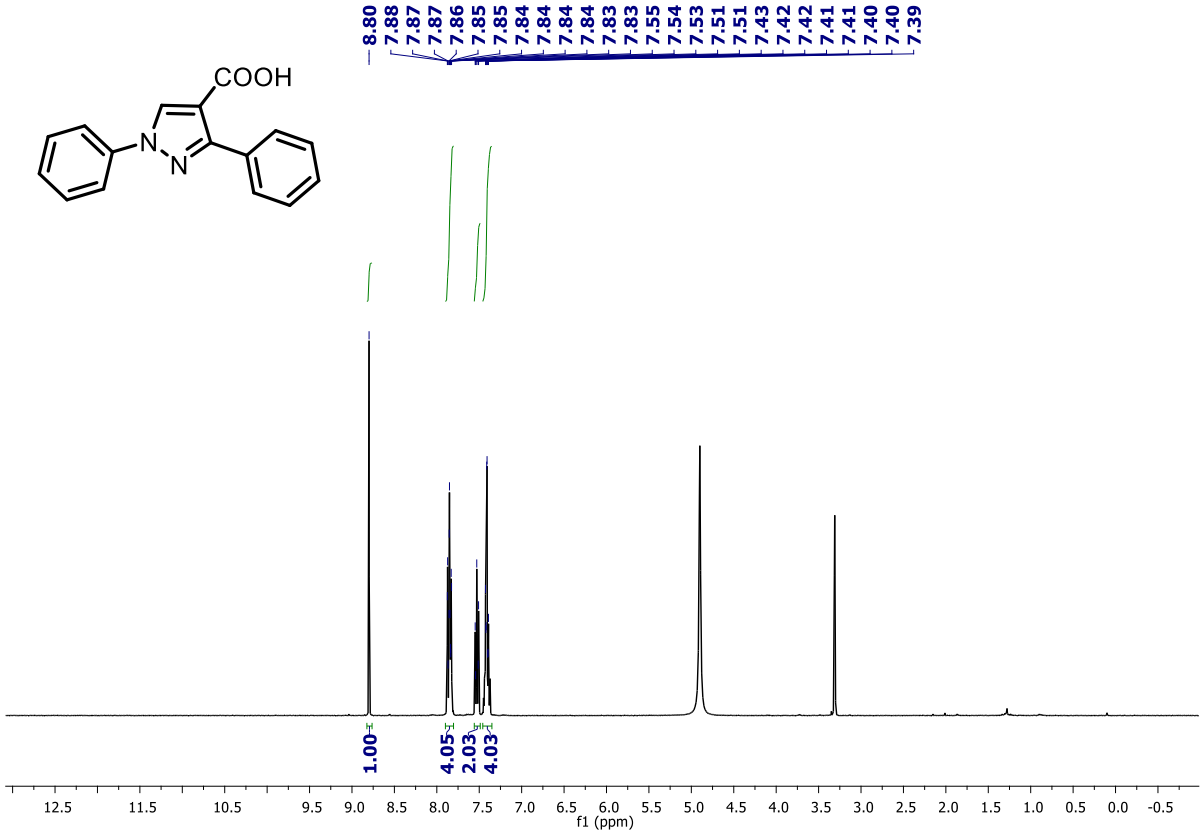
^{1}H NMR Spectrum of **4f** (DMSO-d_6, 400 MHz)



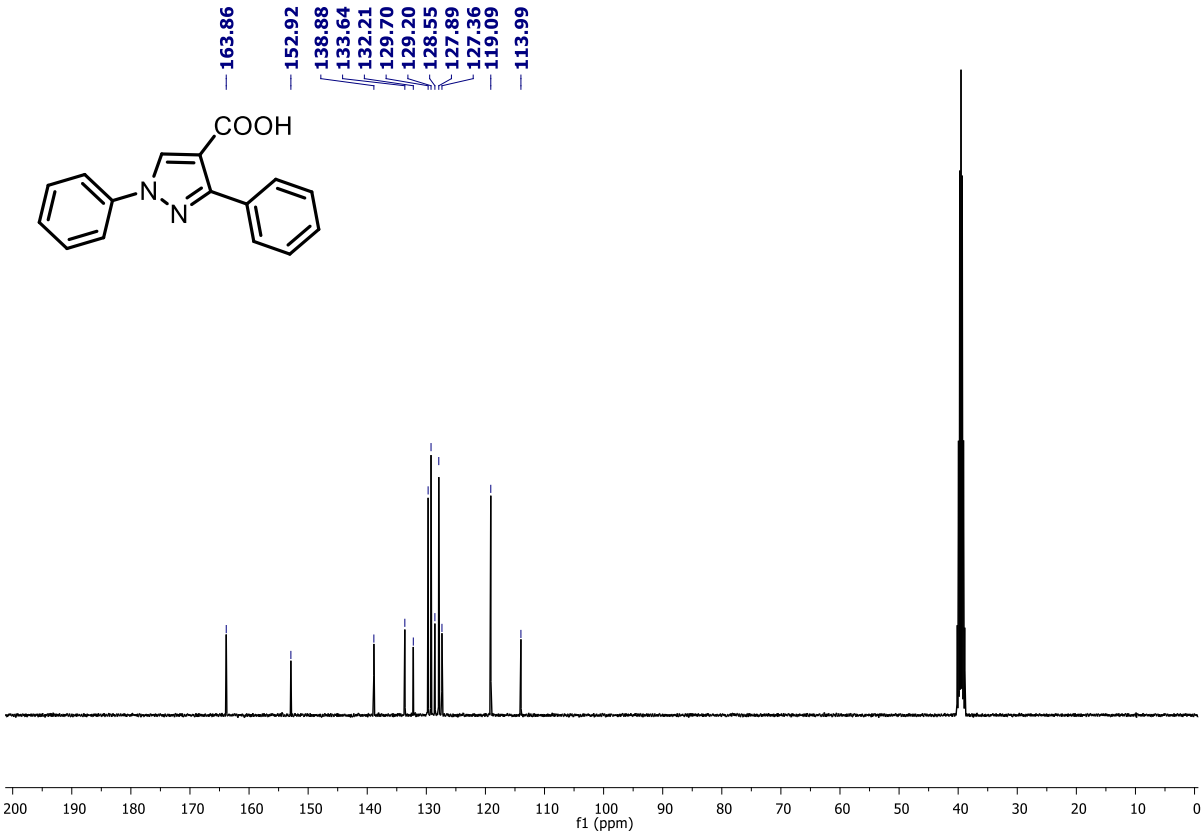
^{13}C {^{1}H} NMR Spectrum of **4f** (DMSO-d_6, 100 MHz)



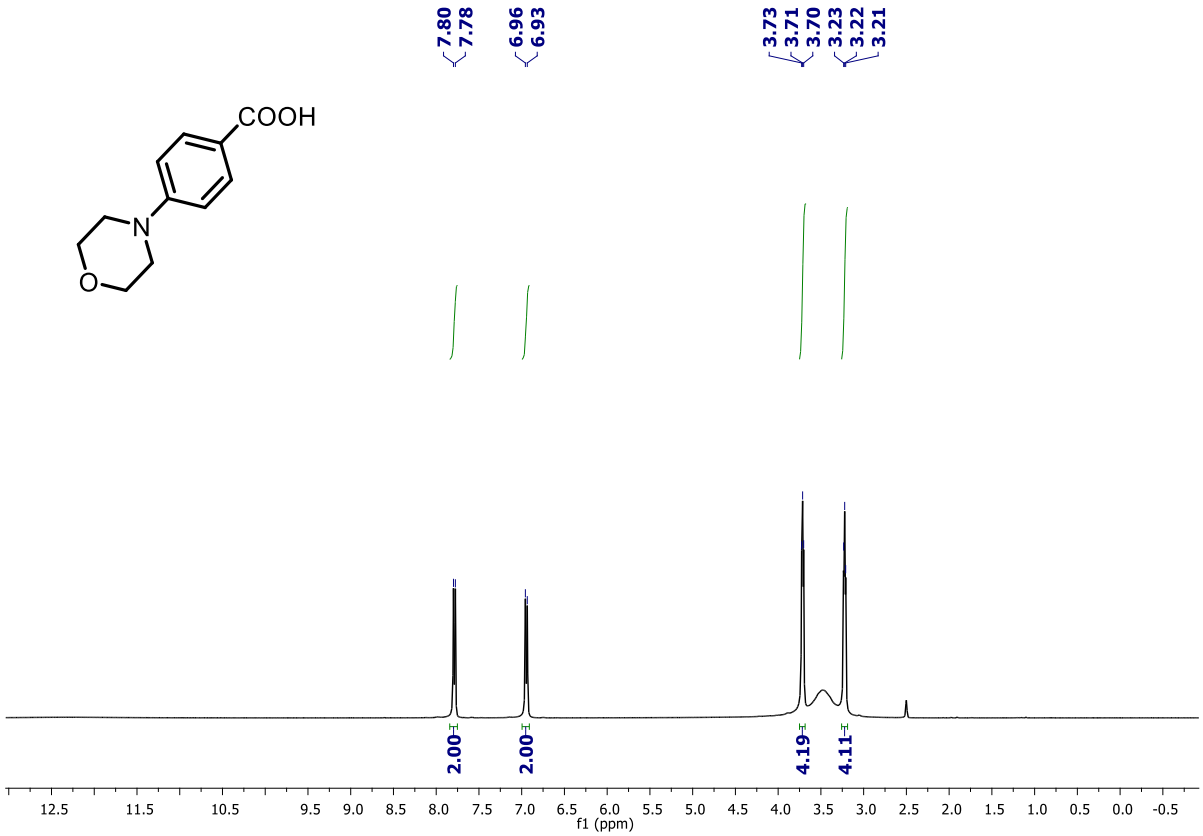
^{1}H NMR Spectrum of **4g** (CD_3OD, 400 MHz)



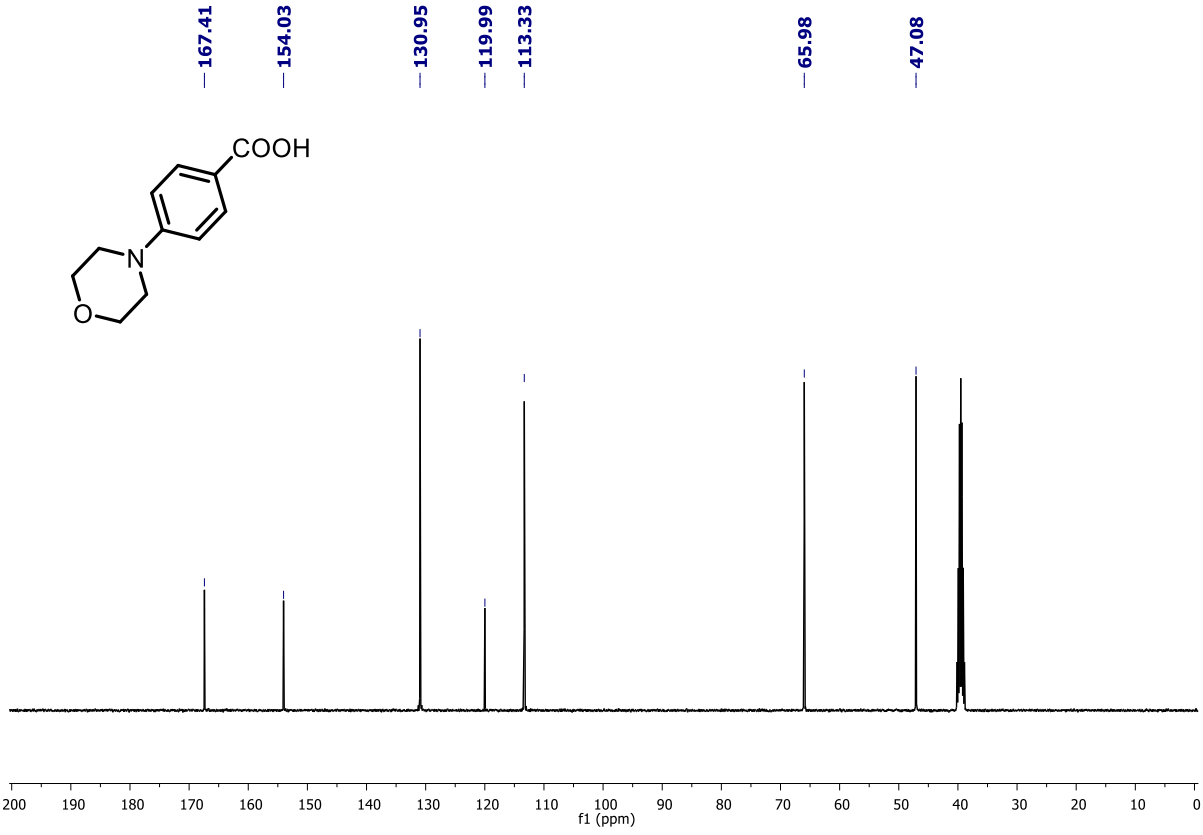
^{13}C {^{1}H} NMR Spectrum of **4g** (DMSO-d_6, 100 MHz)



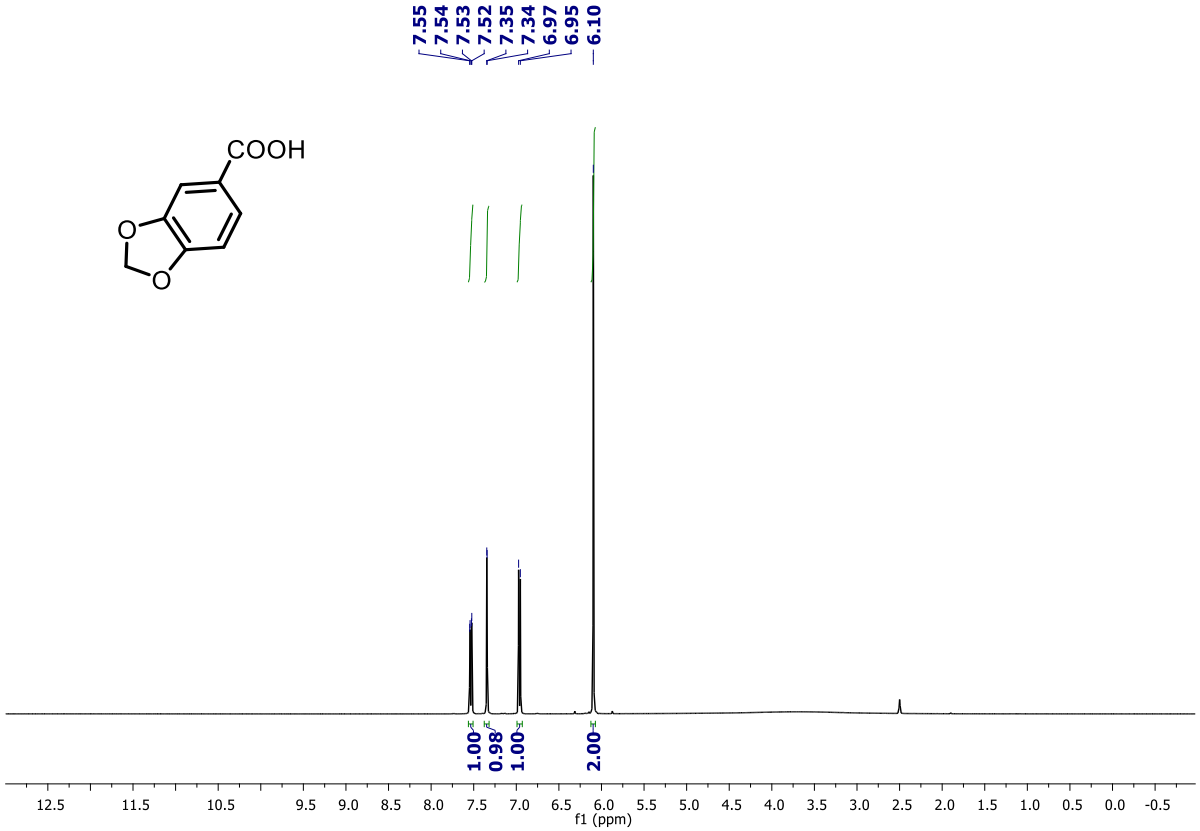
^{1}H NMR Spectrum of **4h** (DMSO-d_6, 400 MHz)



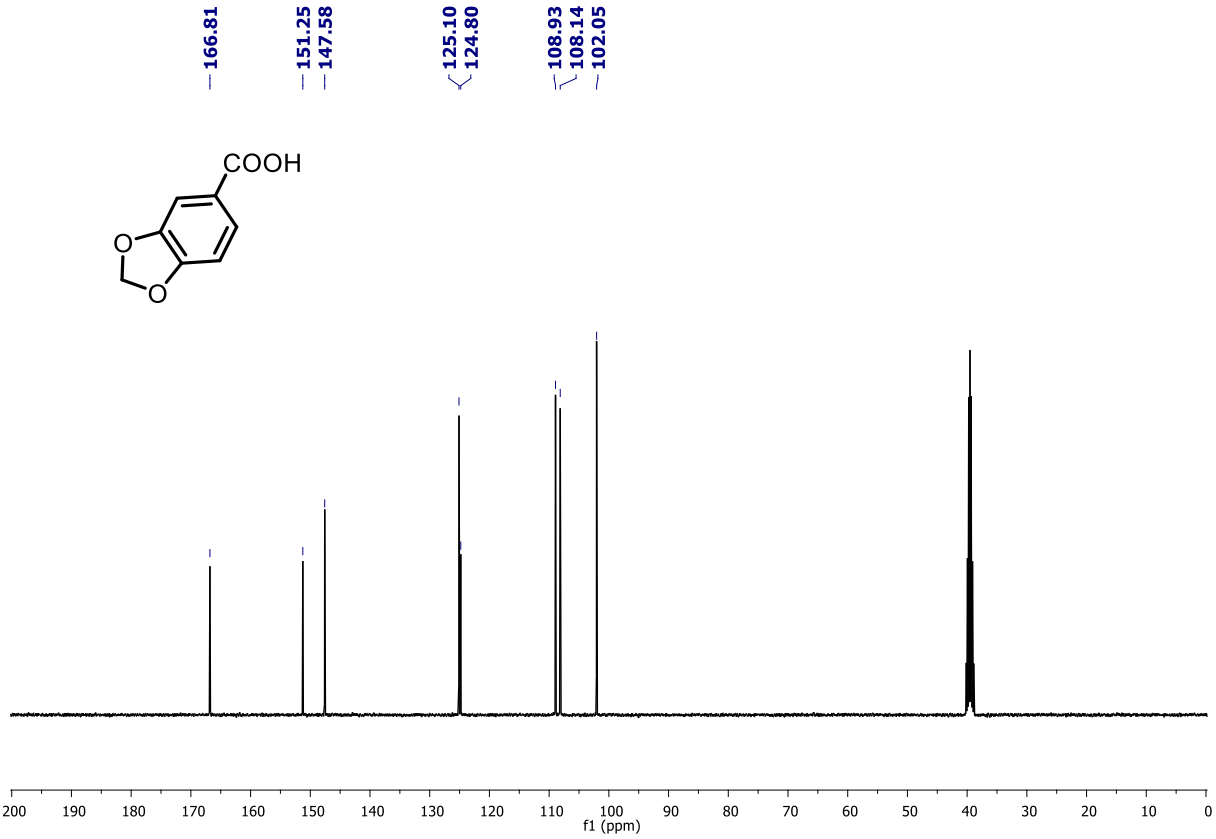
^{13}C {^{1}H} NMR Spectrum of **4h** (DMSO-d_6, 100 MHz)



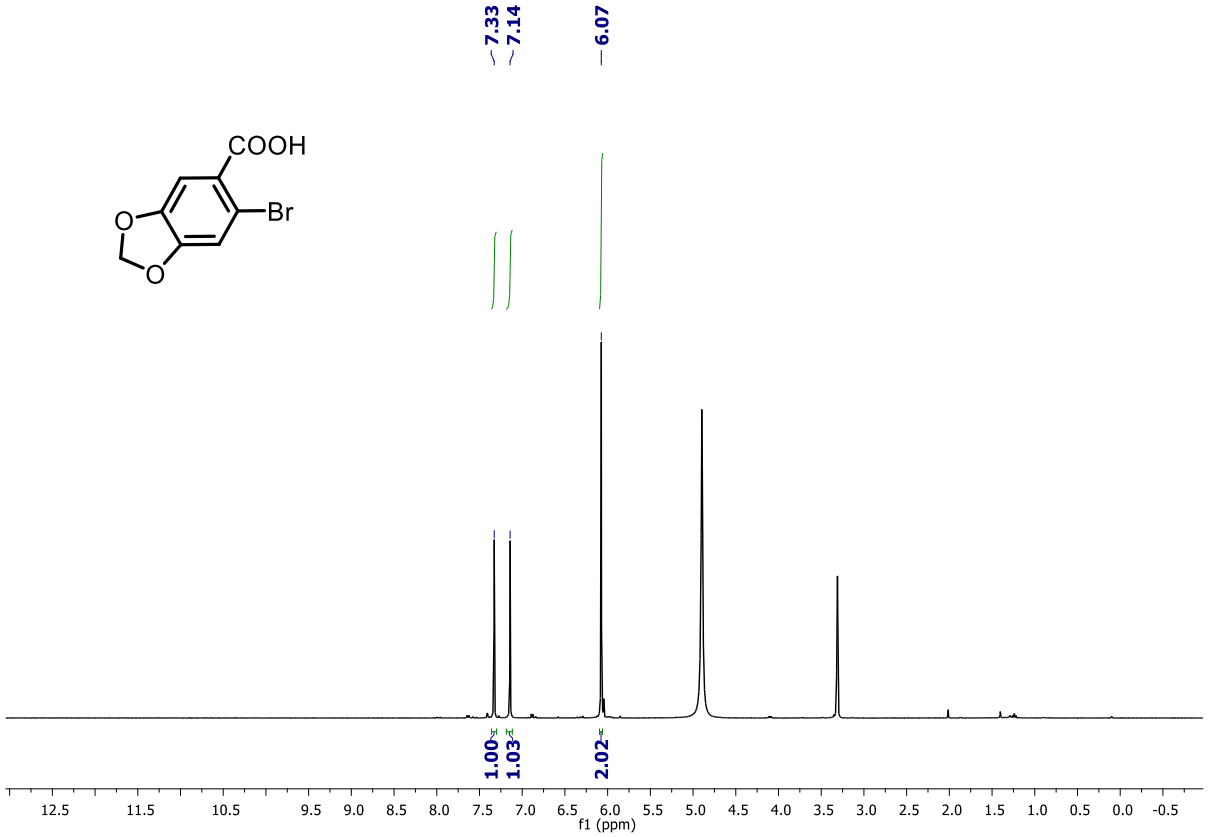
^{1}H NMR Spectrum of **4i** (DMSO-d_6, 400 MHz)



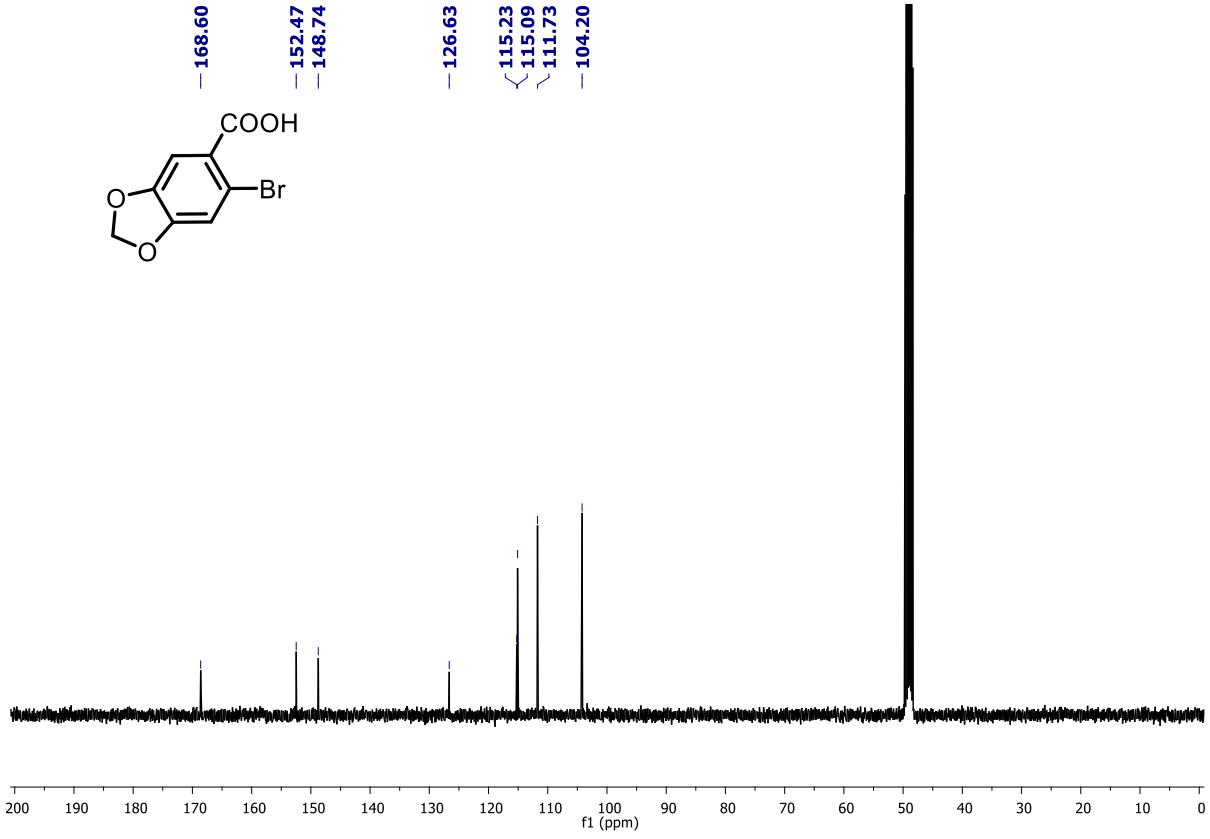
^{13}C {^{1}H} NMR Spectrum of **4i** (DMSO-d_6, 100 MHz)



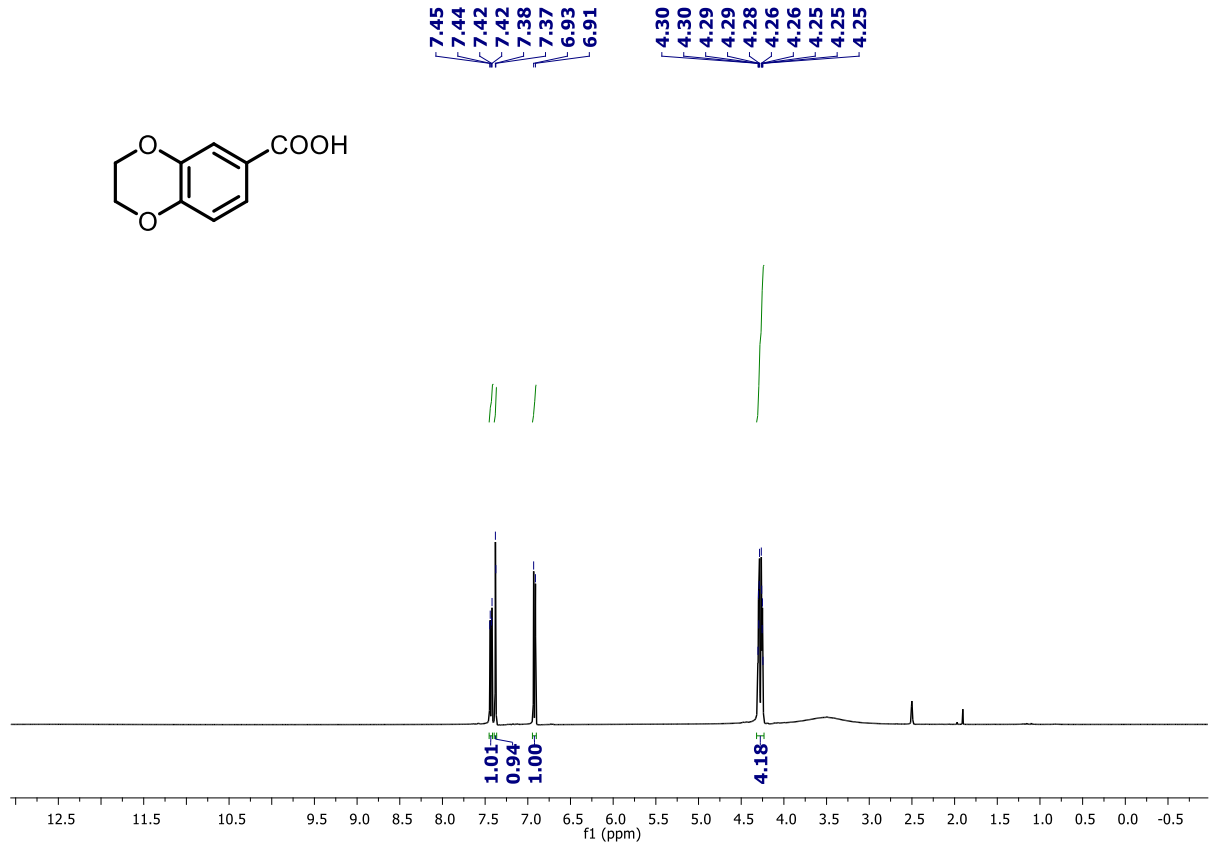
^{1}H NMR Spectrum of **4j** (CD_3OD, 400 MHz)



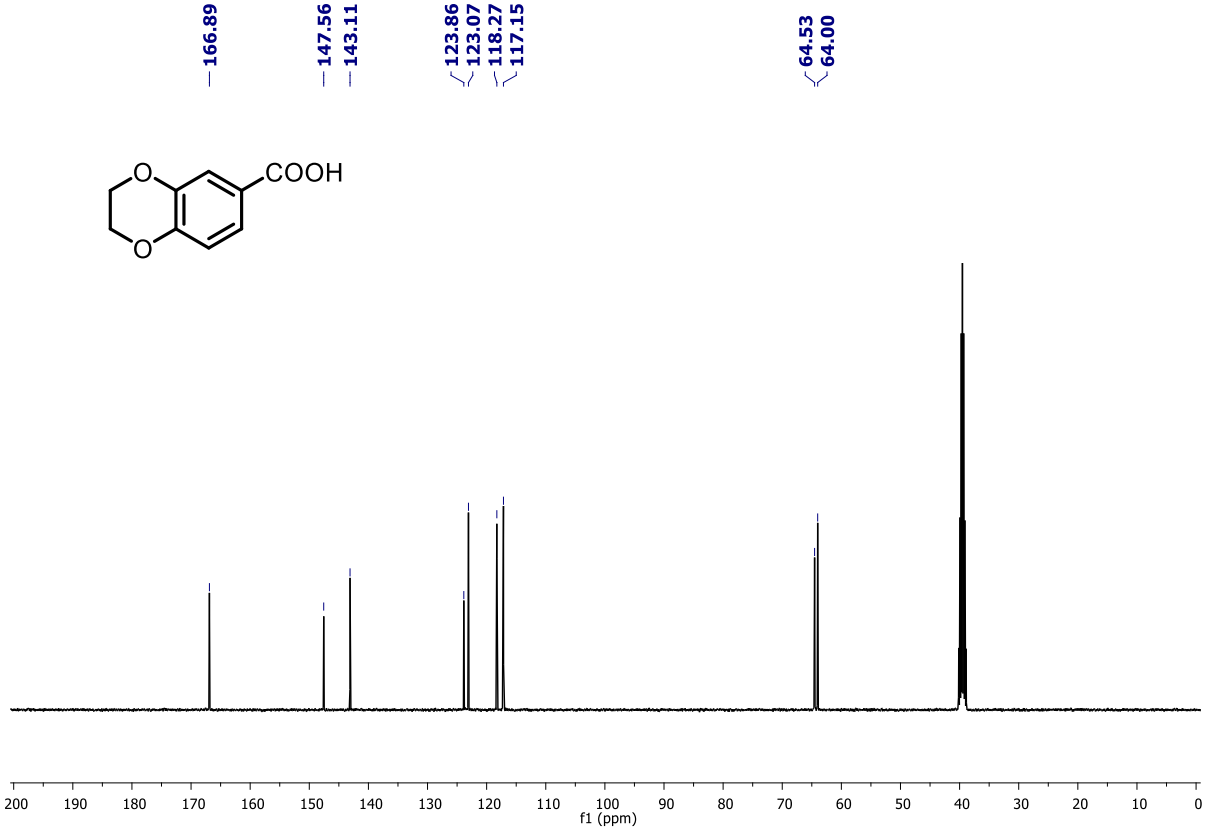
^{13}C {^{1}H} NMR Spectrum of **4j** (CD_3OD, 100 MHz)



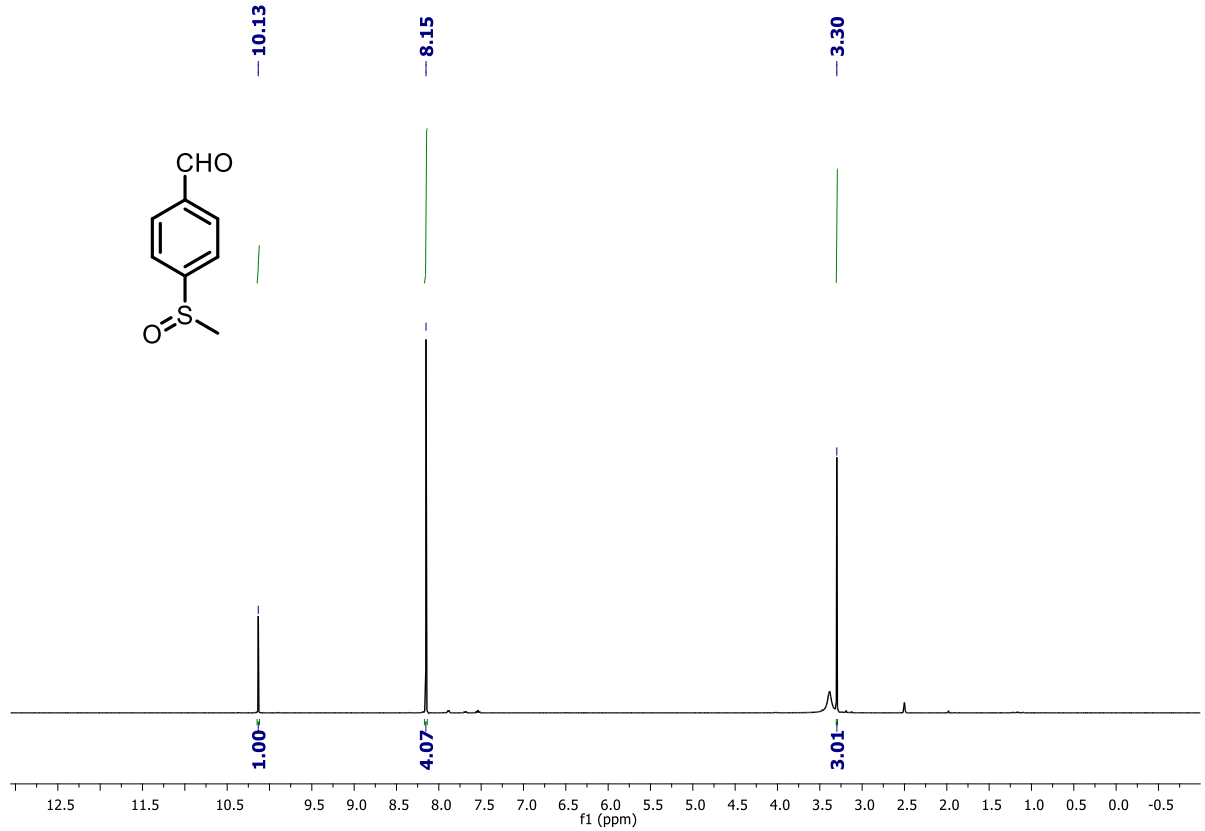
^{1}H NMR Spectrum of **4k** (DMSO-d_6, 400 MHz)



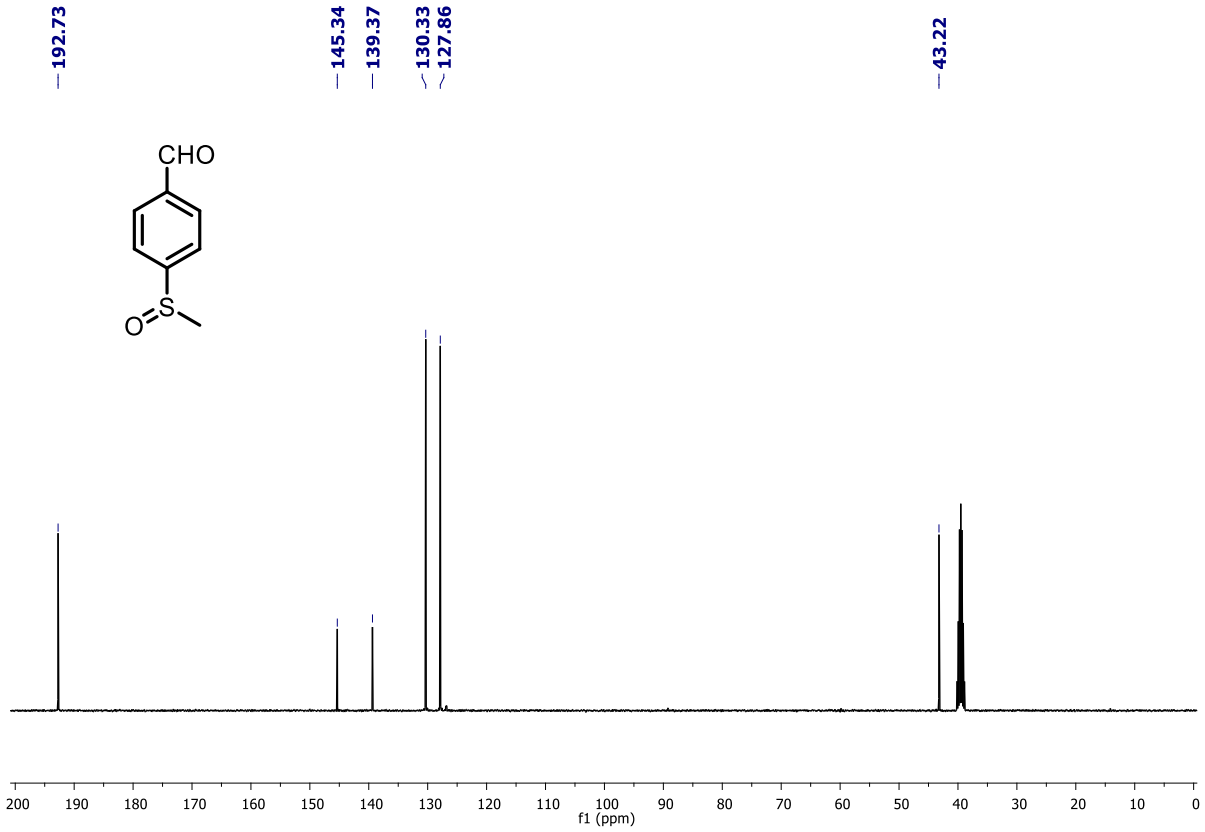
^{13}C {^{1}H} NMR Spectrum of **4k** (DMSO-d_6, 100 MHz)



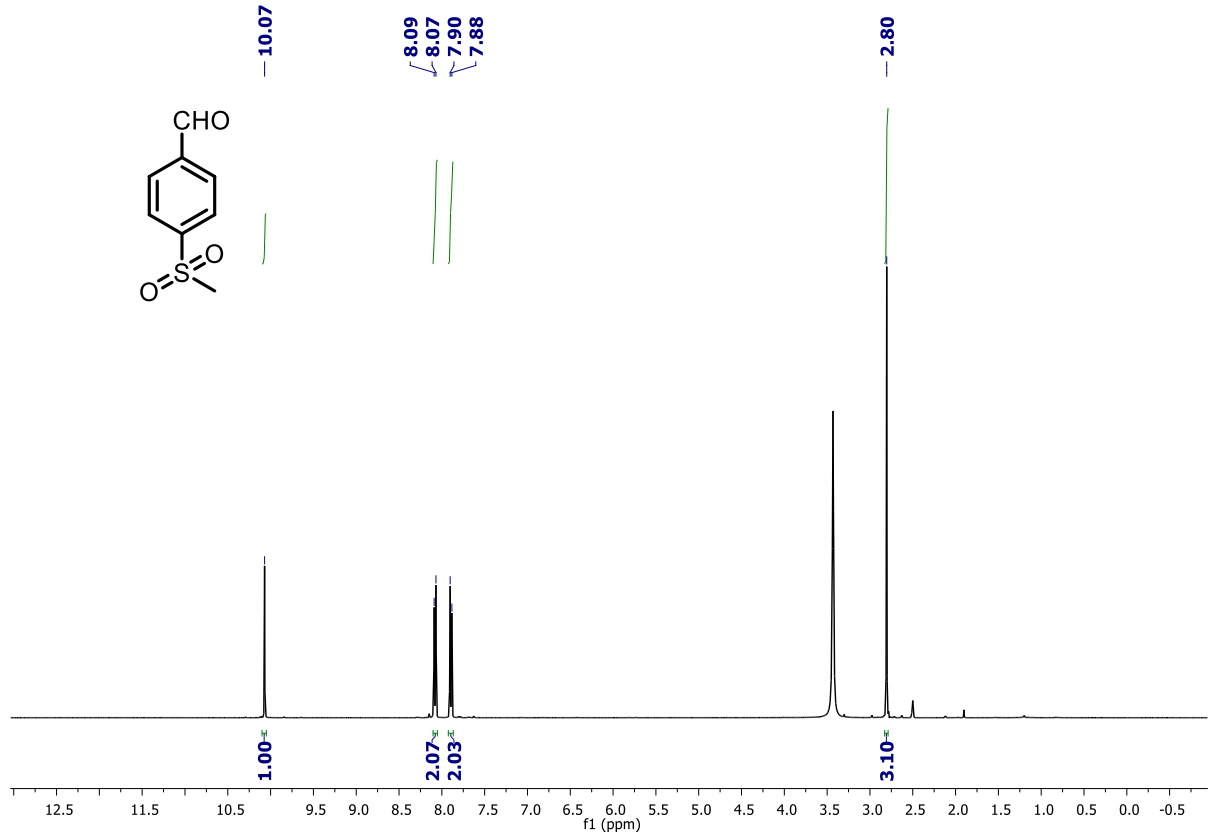
^{1}H NMR Spectrum of **5a** (DMSO-d_6, 400 MHz)



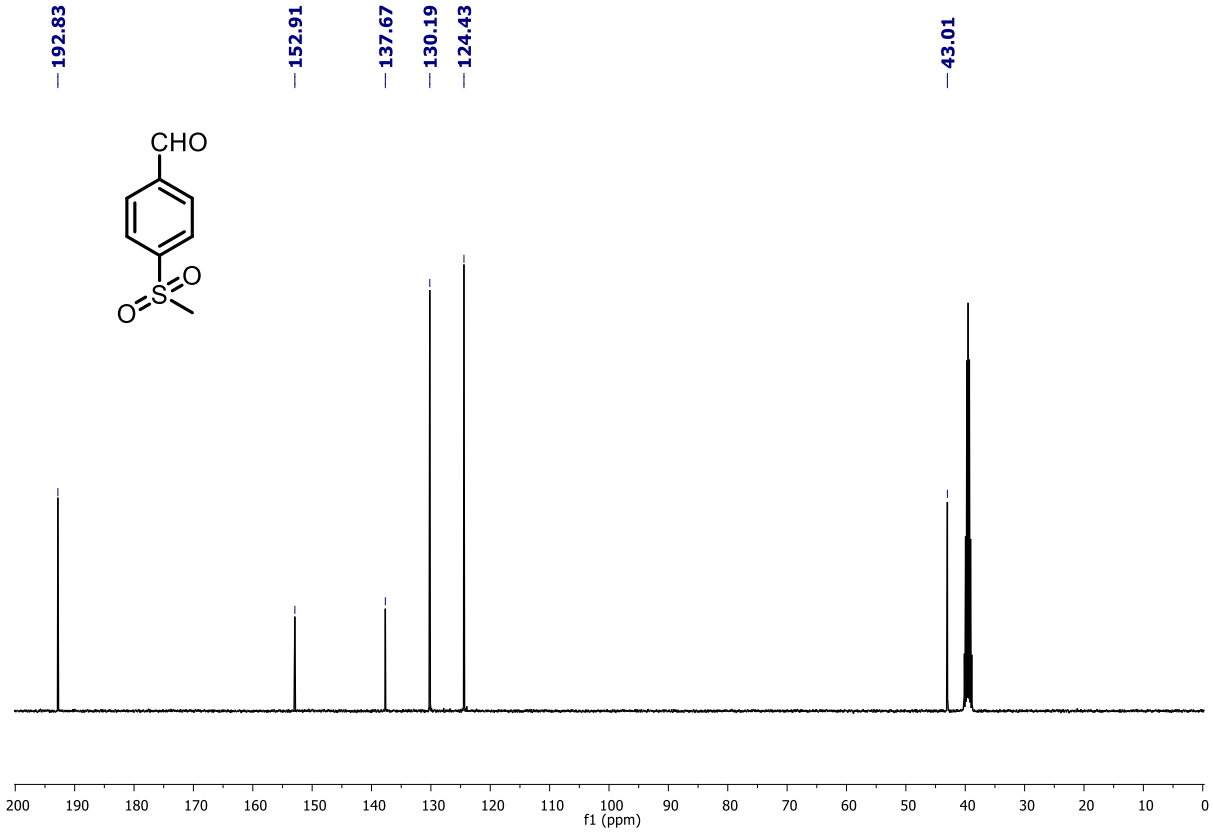
^{13}C {^{1}H} NMR Spectrum of **5a** (DMSO-d_6, 100 MHz)



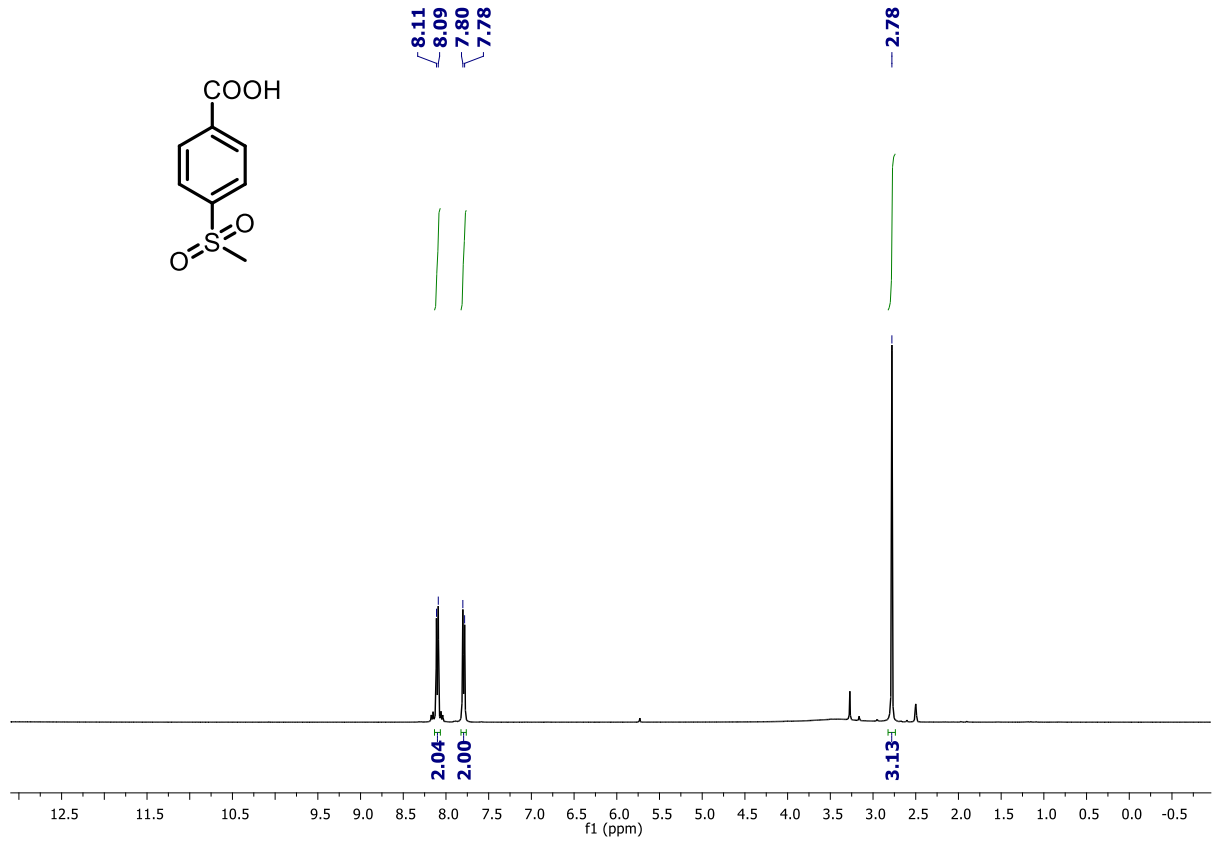
^{1}H NMR Spectrum of **5b** (DMSO-d_6, 400 MHz)



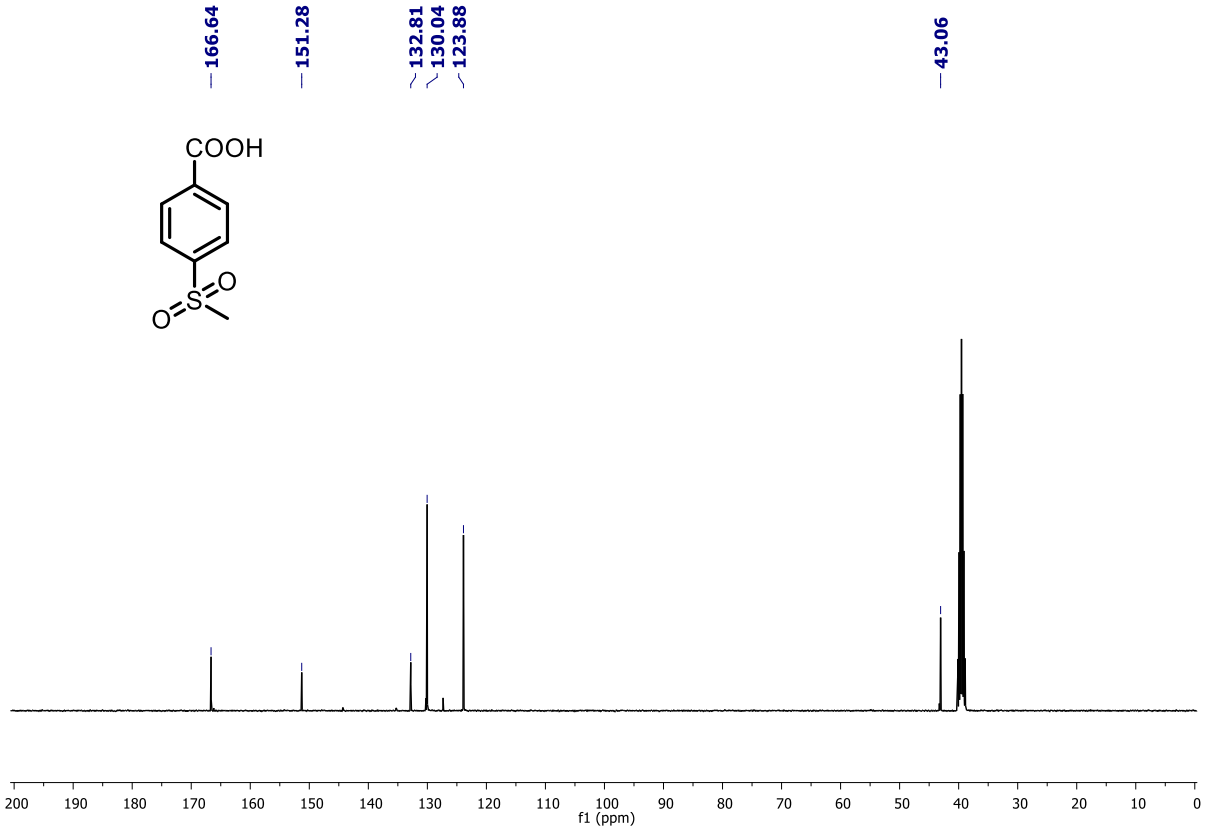
^{13}C {^{1}H} NMR Spectrum of **5b** (DMSO-d_6, 100 MHz)



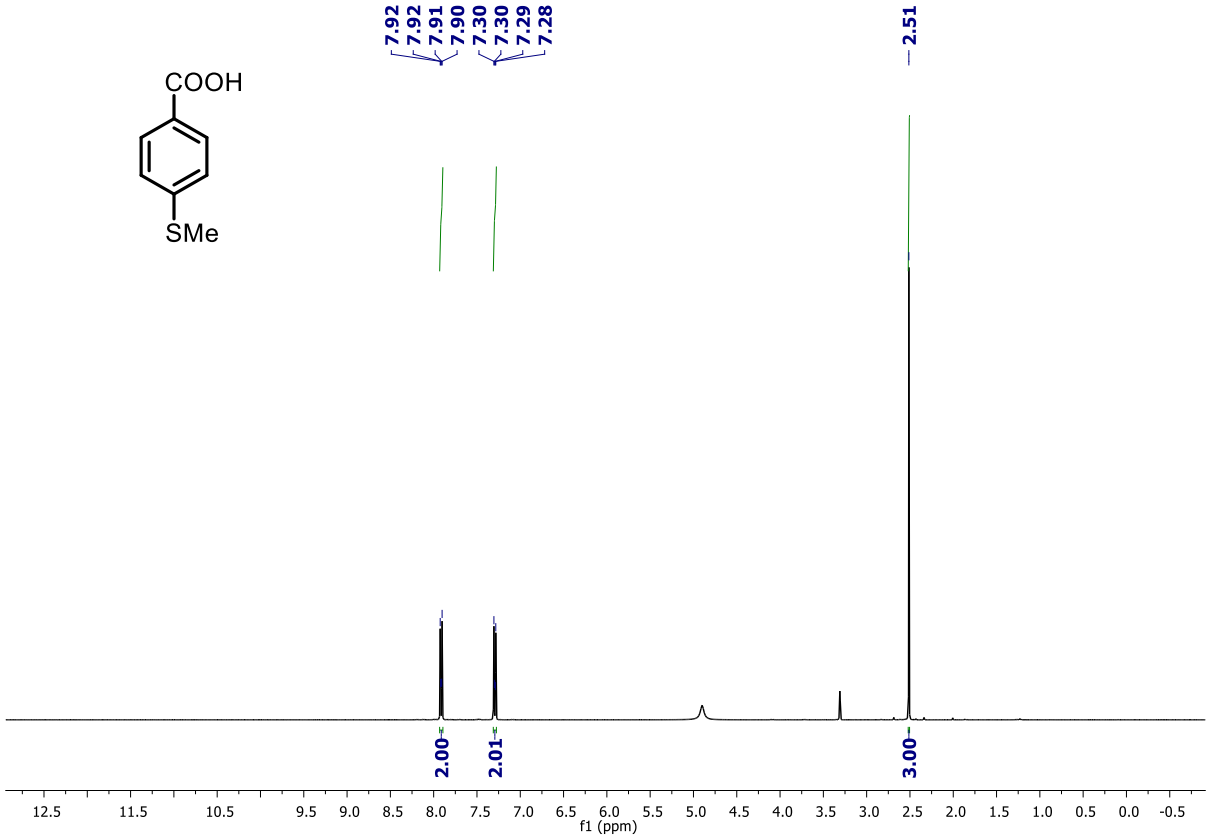
^{1}H NMR Spectrum of **5c** (DMSO-d_6, 400 MHz)



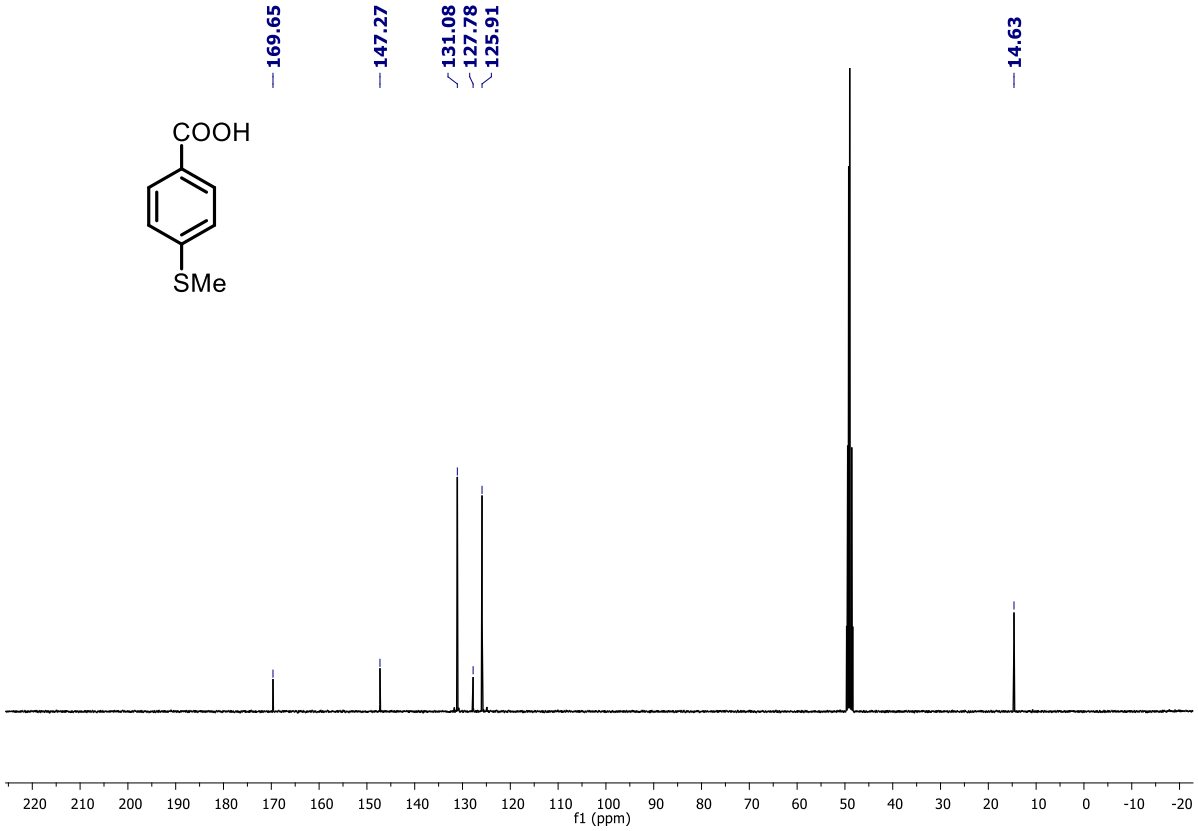
^{13}C {^{1}H} NMR Spectrum of **5c** (DMSO-d_6, 100 MHz)



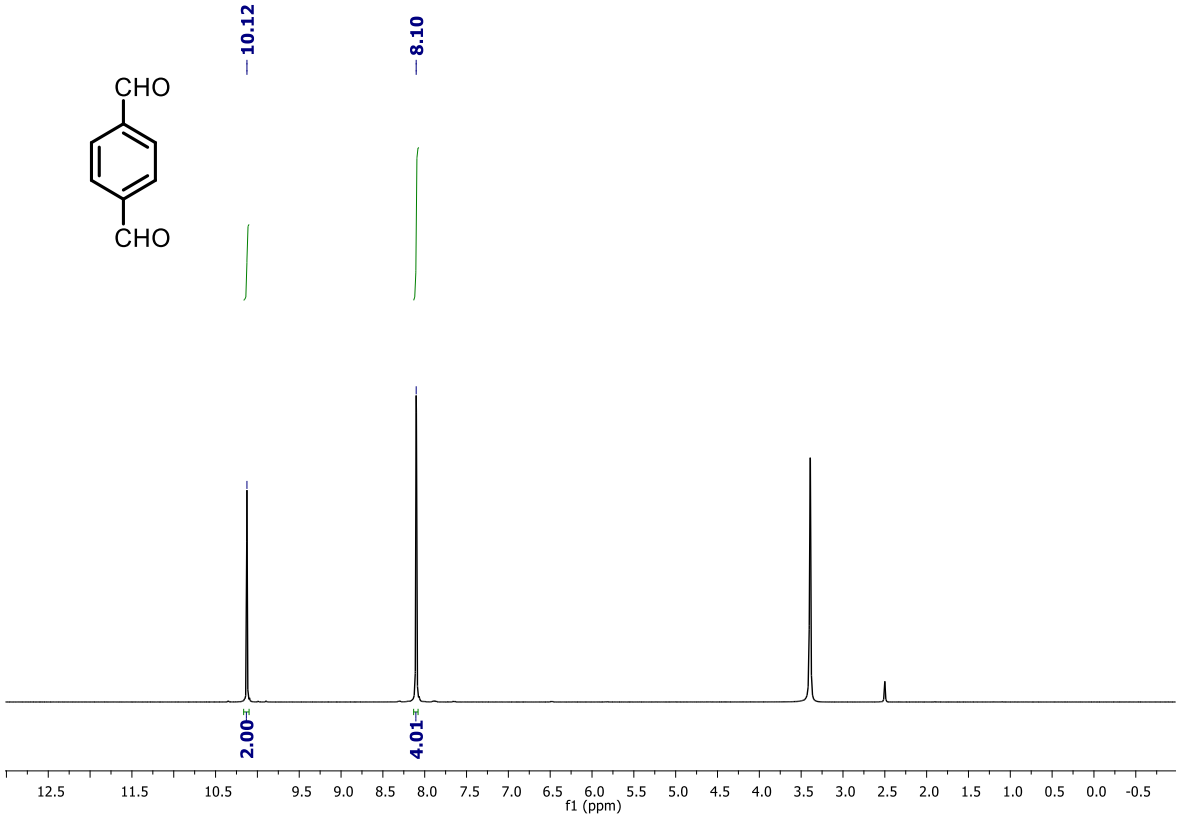
^{1}H NMR Spectrum of **5d** (CD_3OD, 400 MHz)



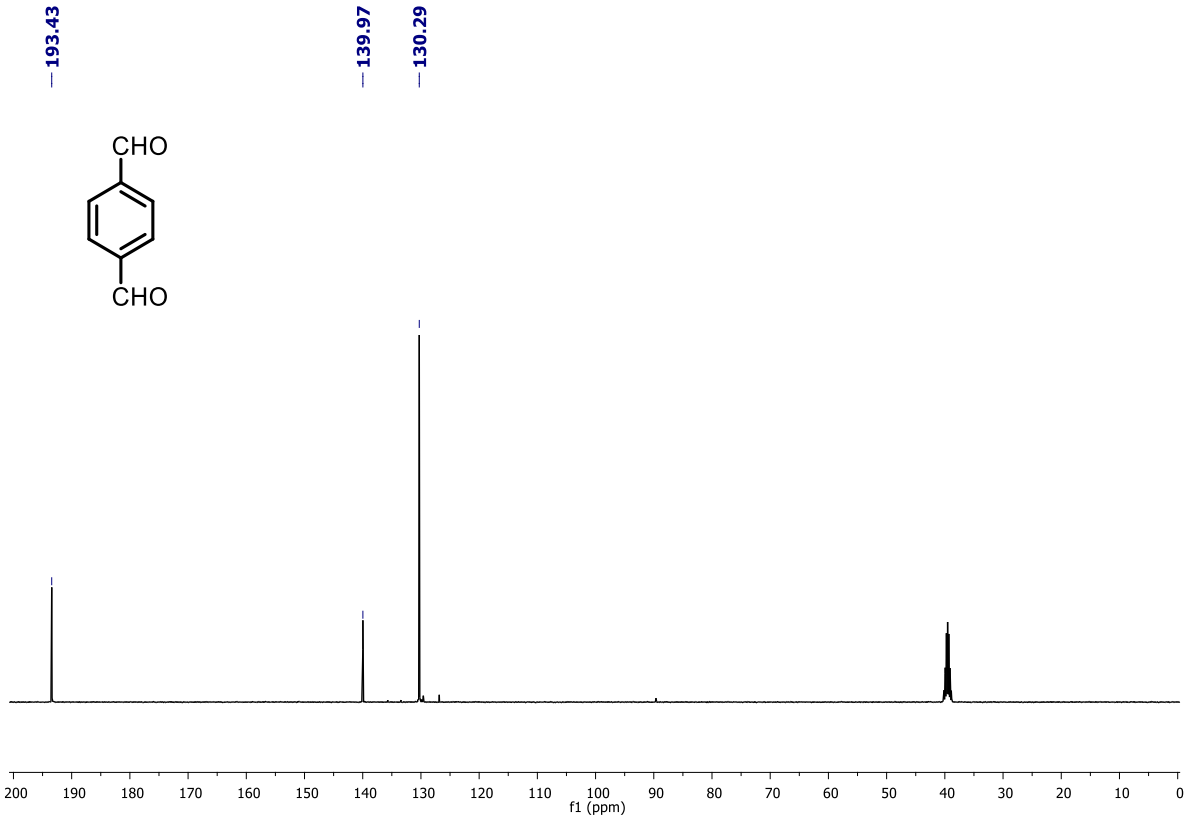
^{13}C {^{1}H} NMR Spectrum of **5d** (CD_3OD, 100 MHz)



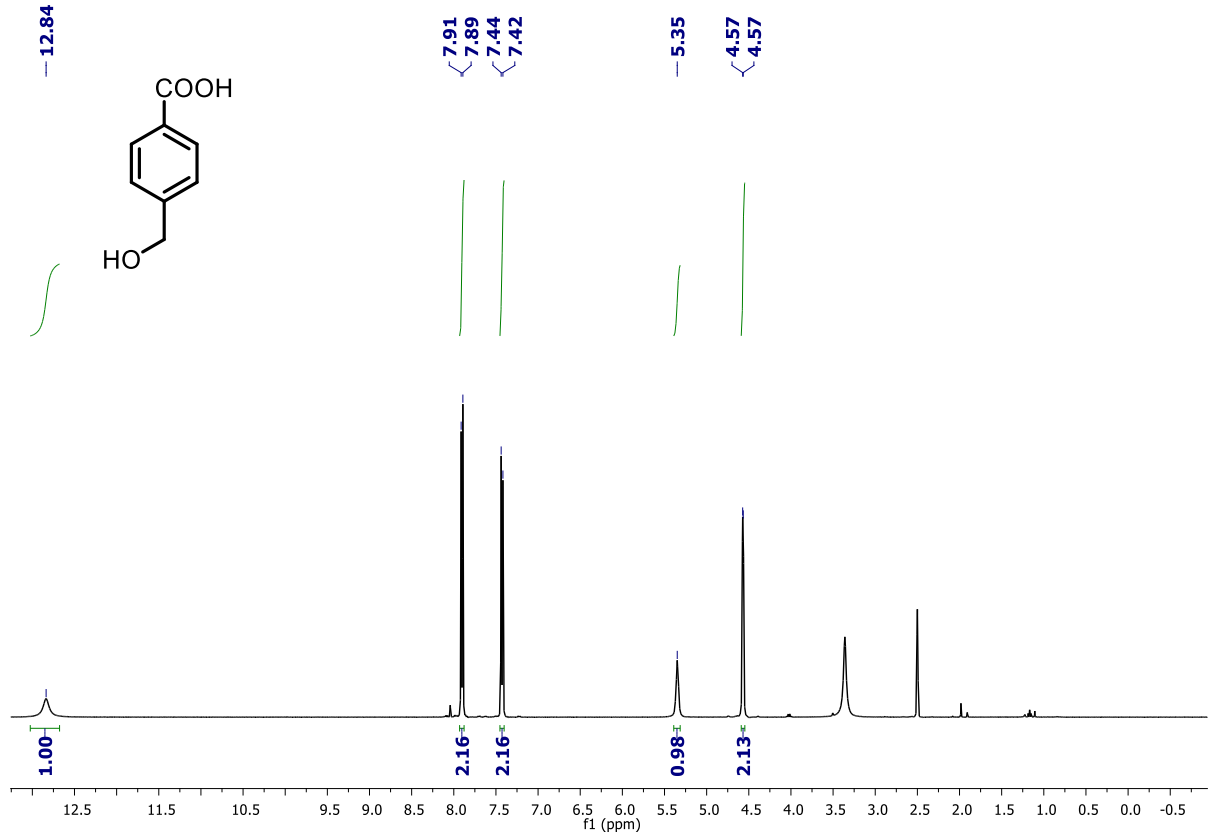
^{1}H NMR Spectrum of **6a** (DMSO-d_6, 400 MHz)



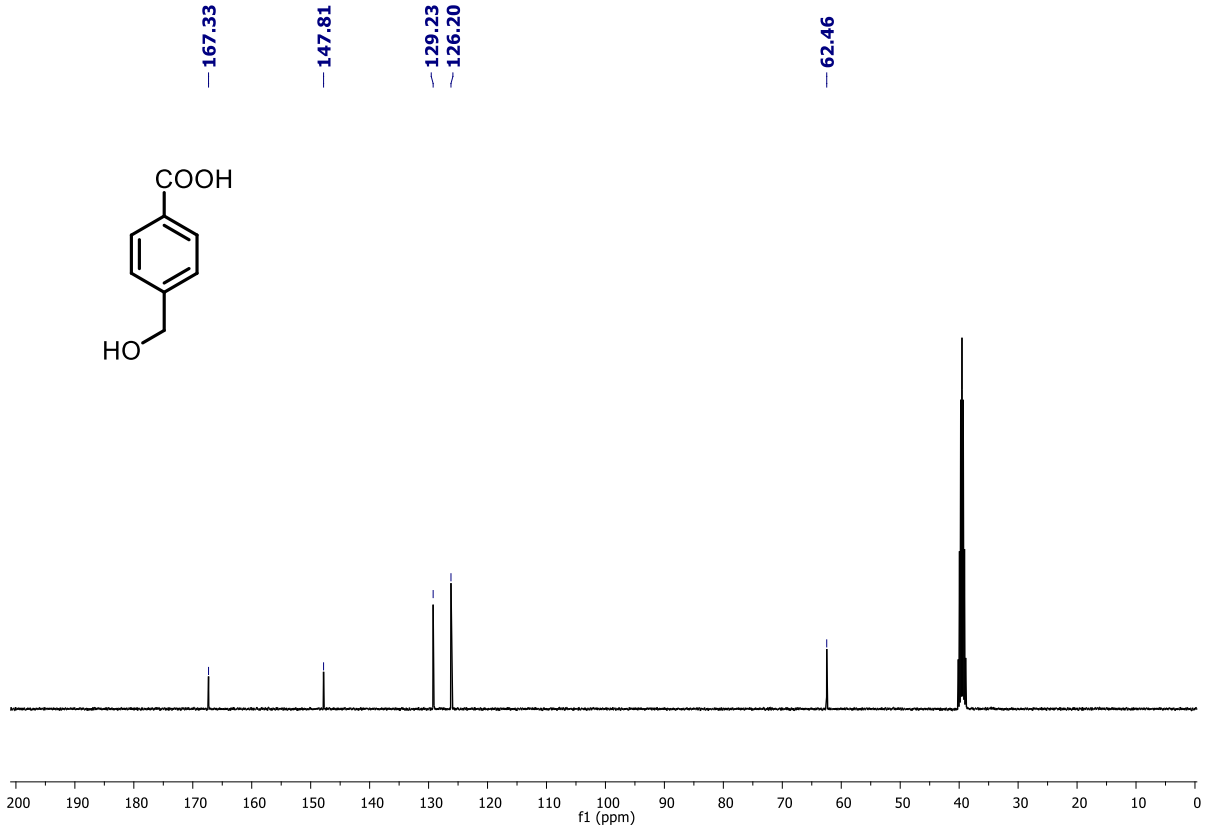
^{13}C {^{1}H} NMR Spectrum of **6a** (DMSO-d_6, 100 MHz)



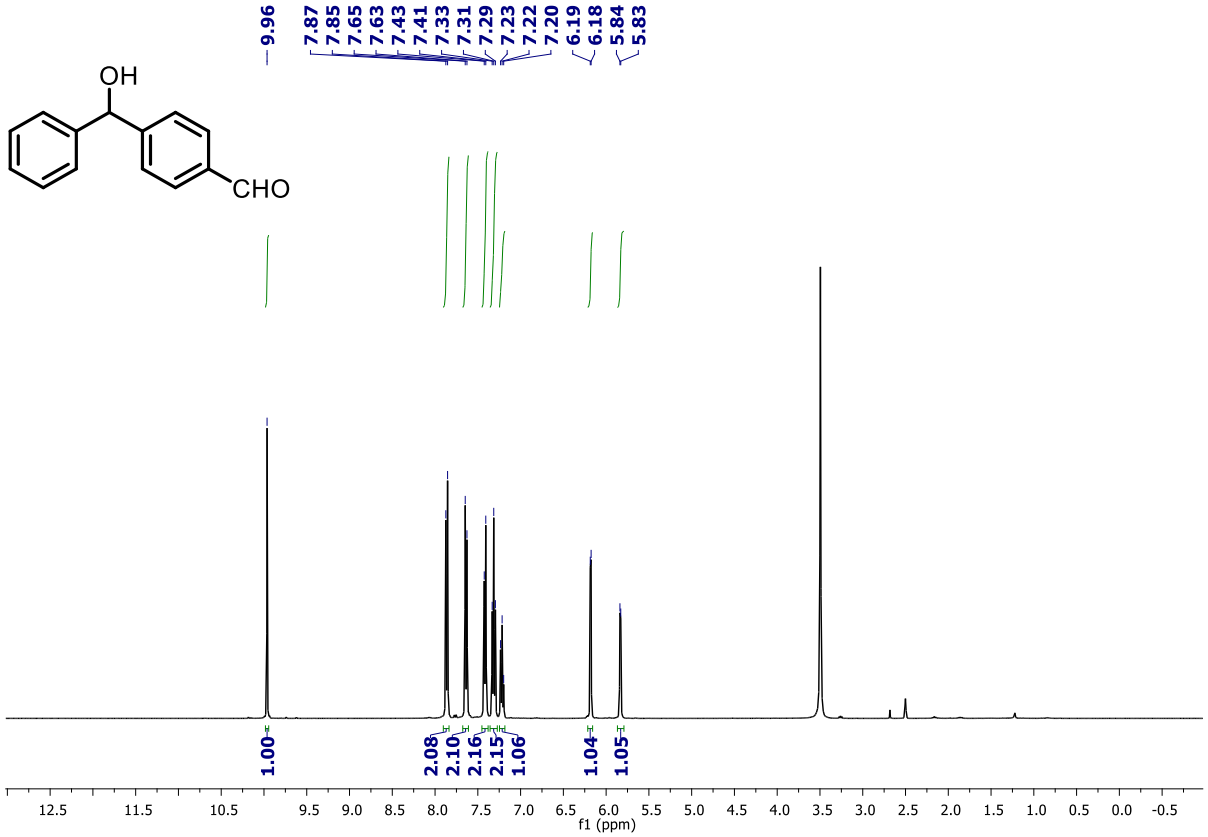
^{1}H NMR Spectrum of **6b** (DMSO-d_6, 400 MHz)



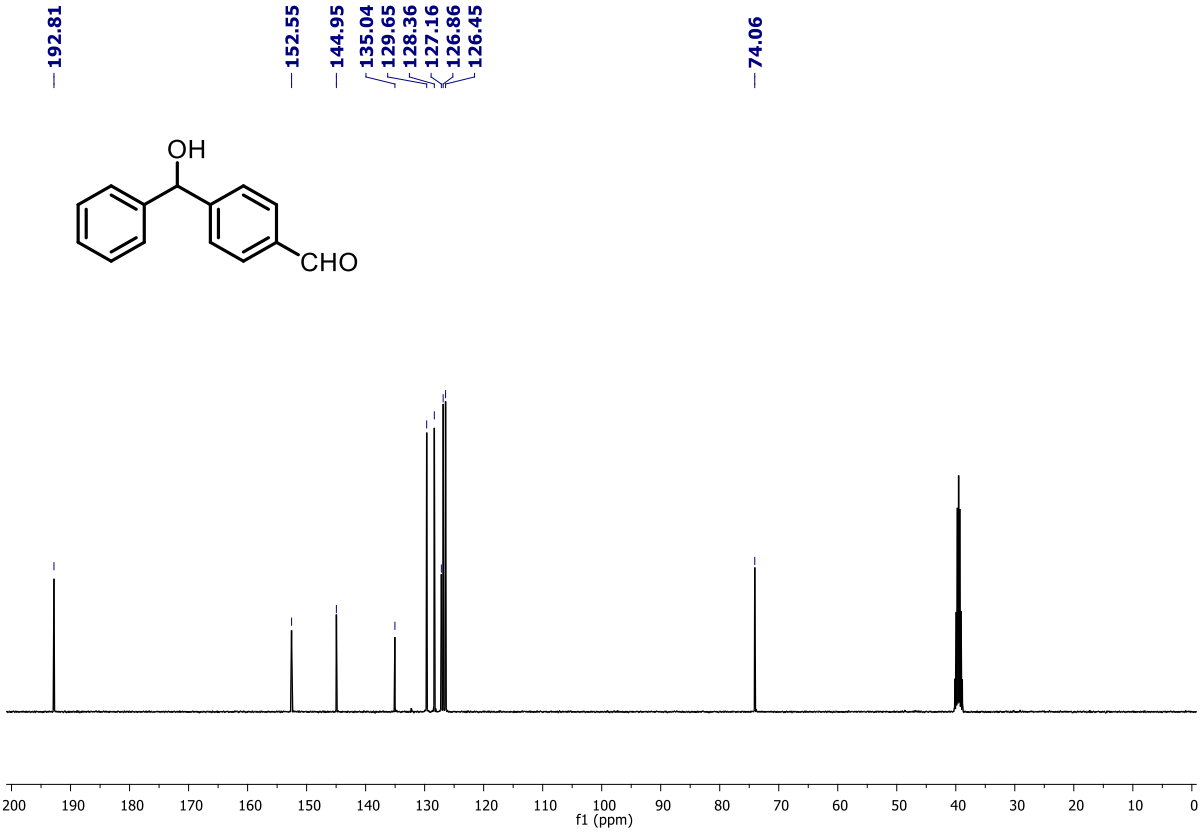
^{13}C {^{1}H} NMR Spectrum of **6b** (DMSO-d_6, 100 MHz)



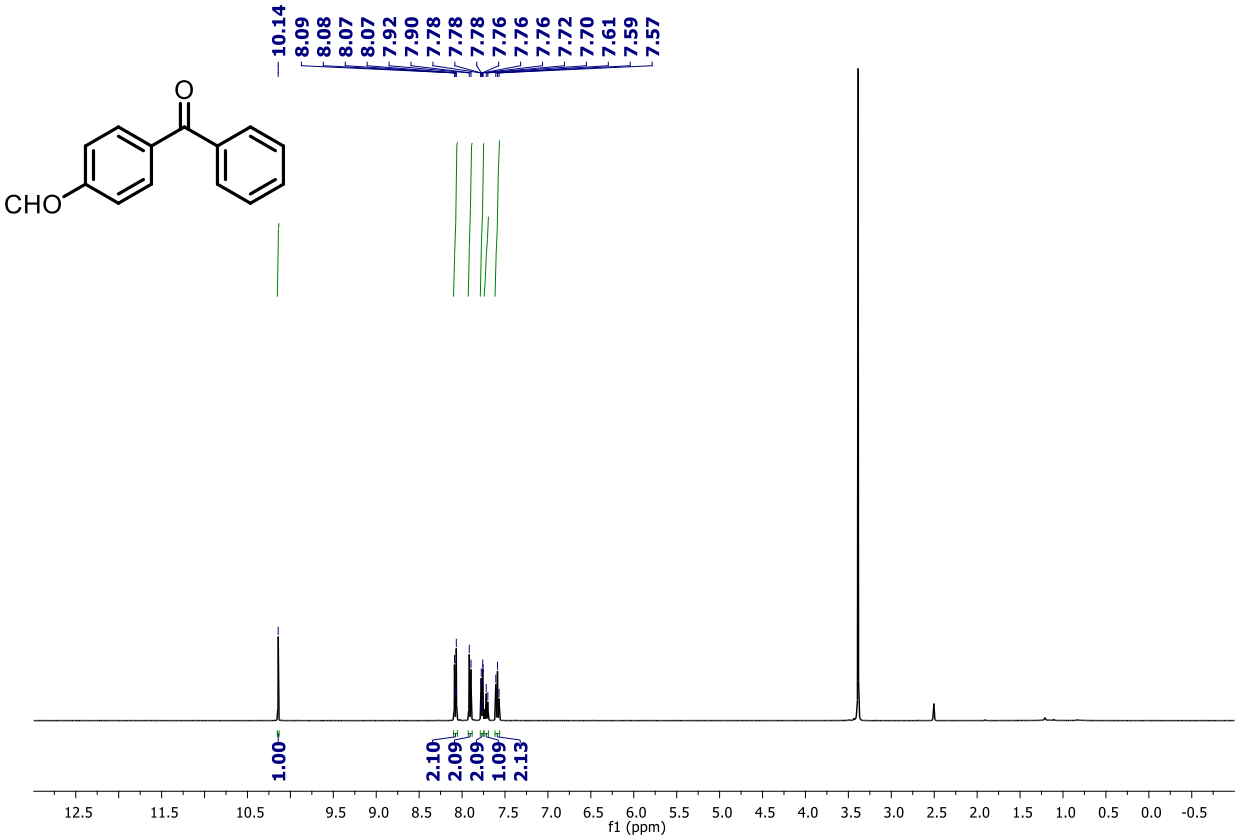
^{1}H NMR Spectrum of **7** (DMSO-d_6, 400 MHz)



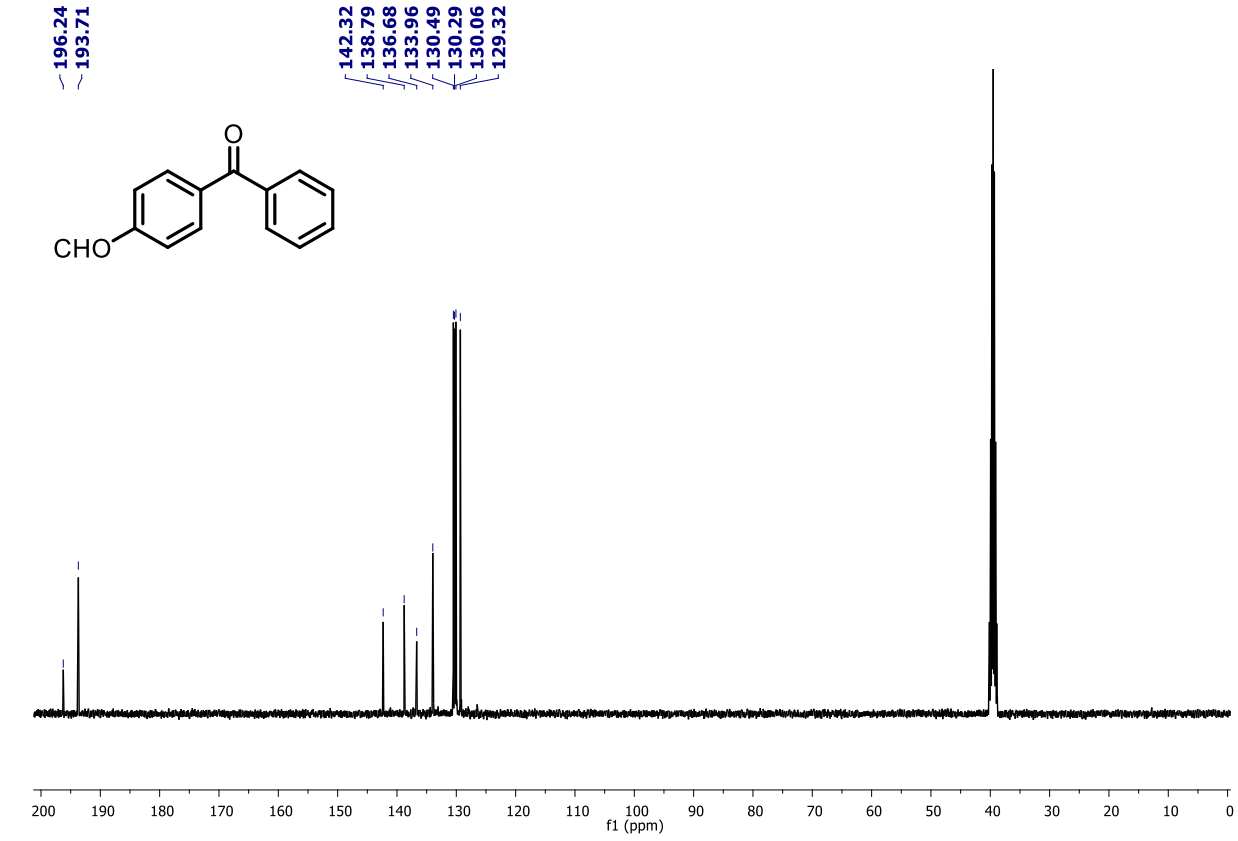
^{13}C {^{1}H} NMR Spectrum of **7** (DMSO-d_6, 100 MHz)



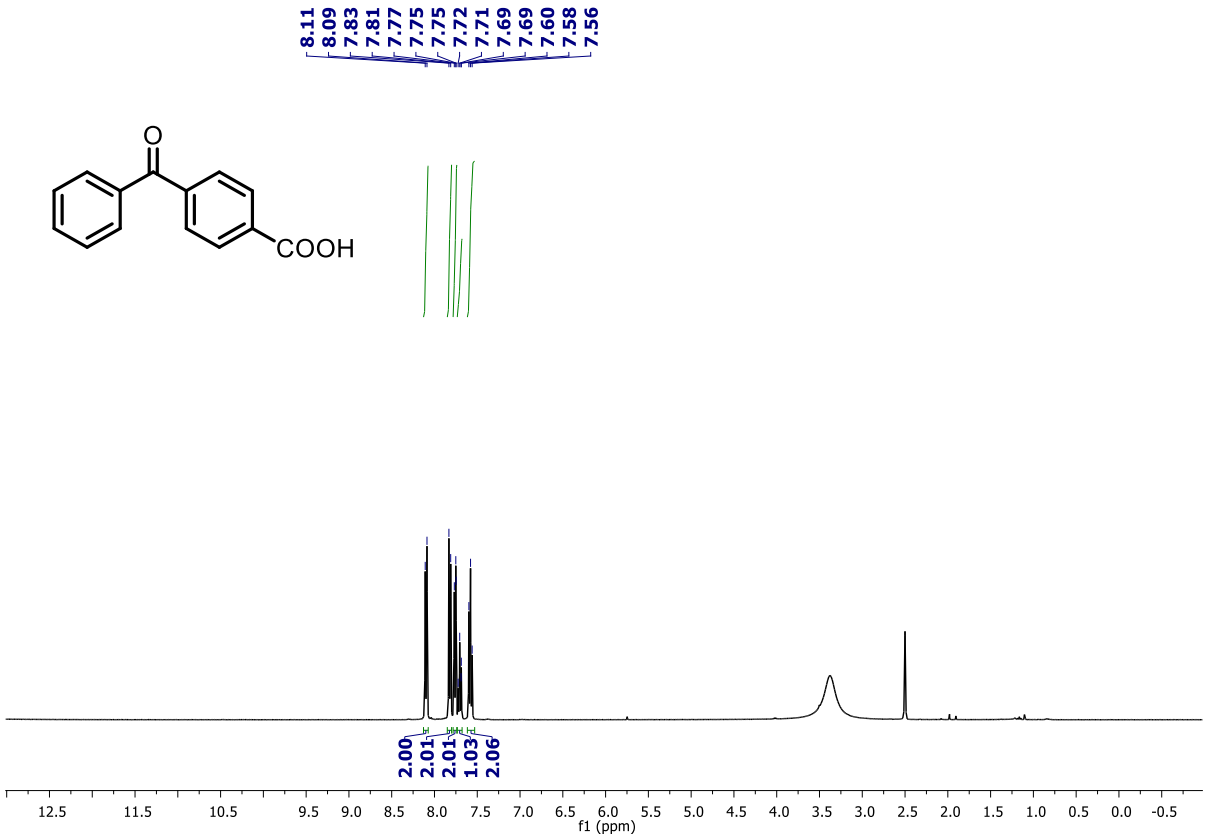
^{1}H NMR Spectrum of **7a** (DMSO-d_6, 400 MHz)



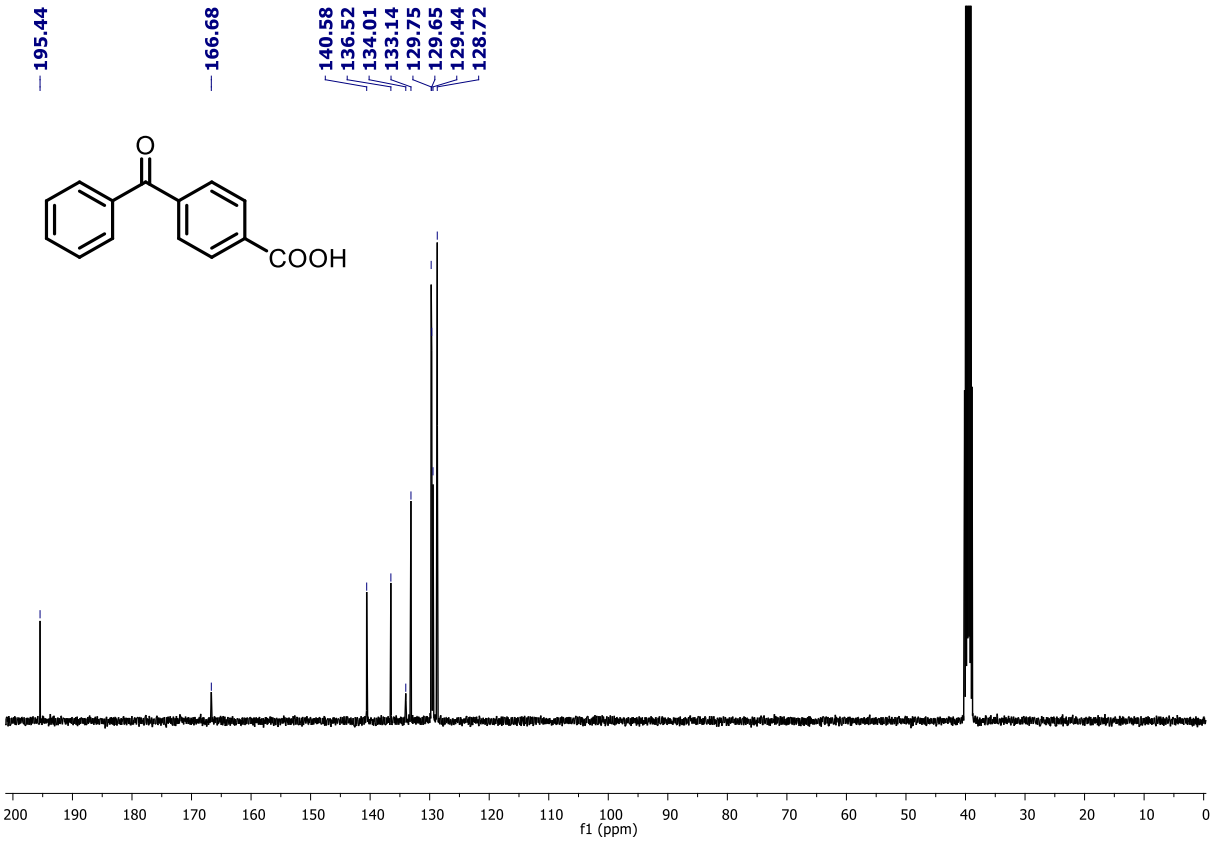
^{13}C {^{1}H} NMR Spectrum of **7a** (DMSO-d_6, 100 MHz)



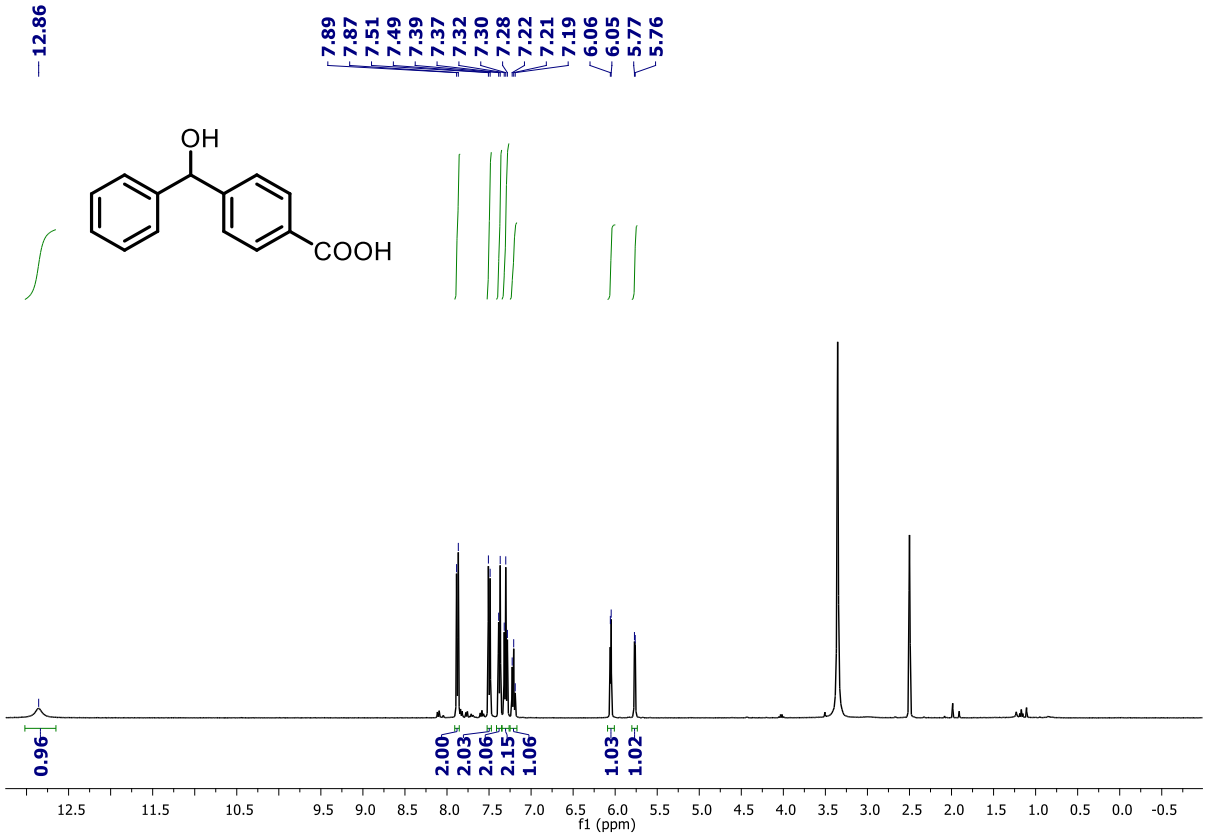
^{1}H NMR Spectrum of **7b** (DMSO-d_6, 400 MHz)



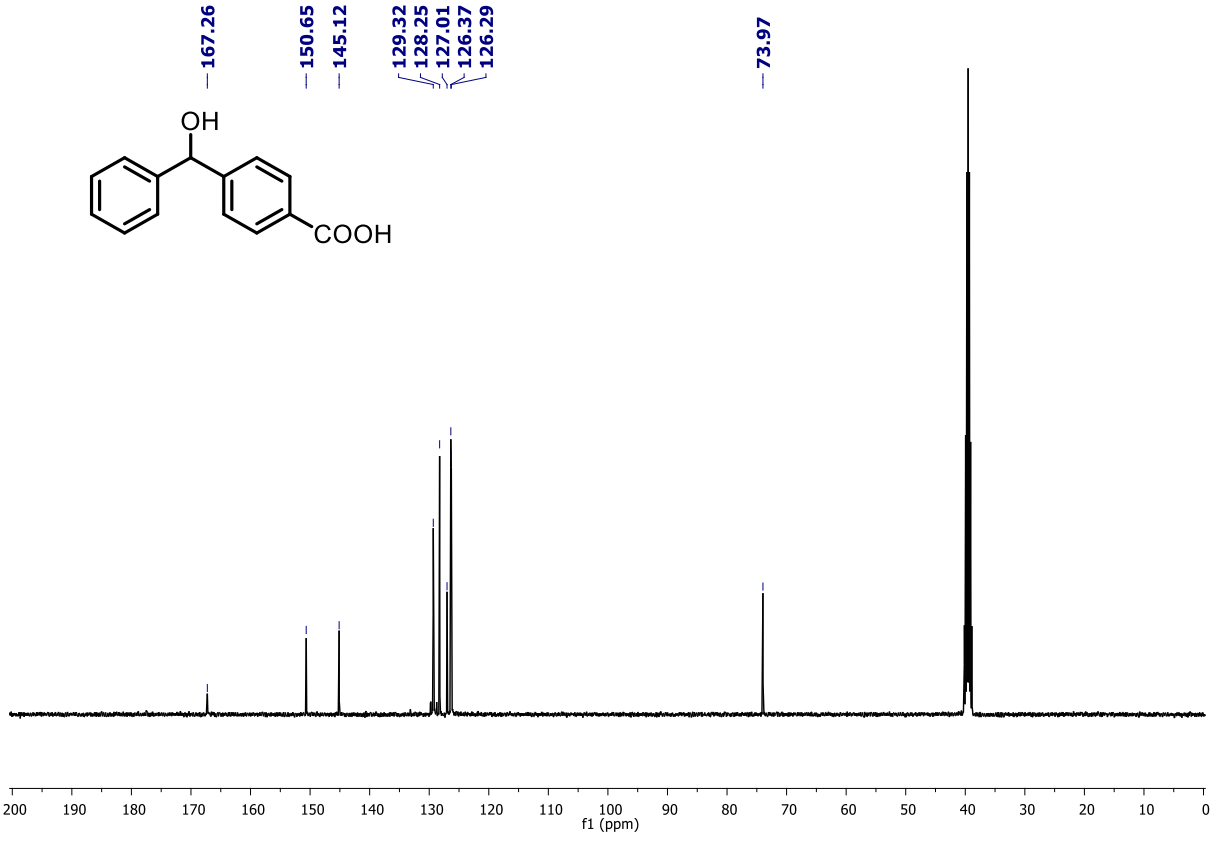
^{13}C {^{1}H} NMR Spectrum of **7b** (DMSO-d_6, 100 MHz)



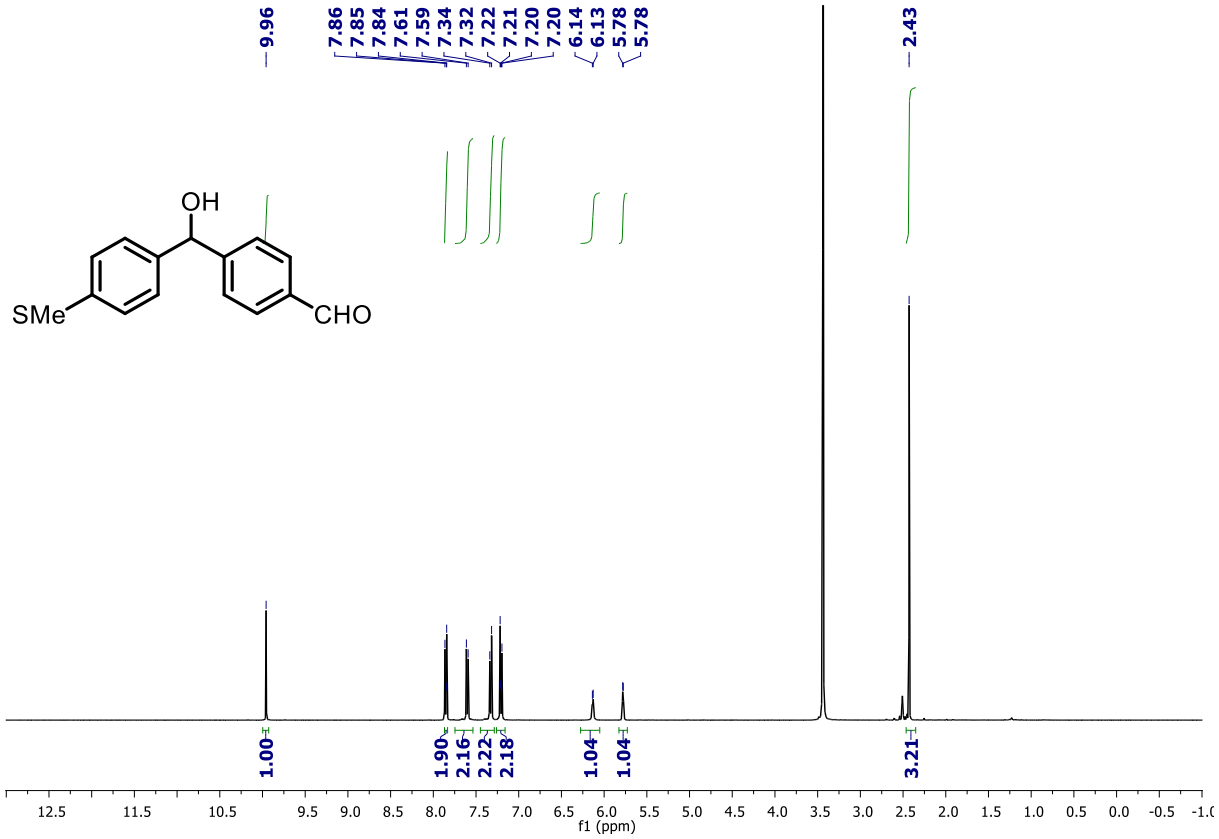
^{1}H NMR Spectrum of **7c** (DMSO-d_6, 400 MHz)



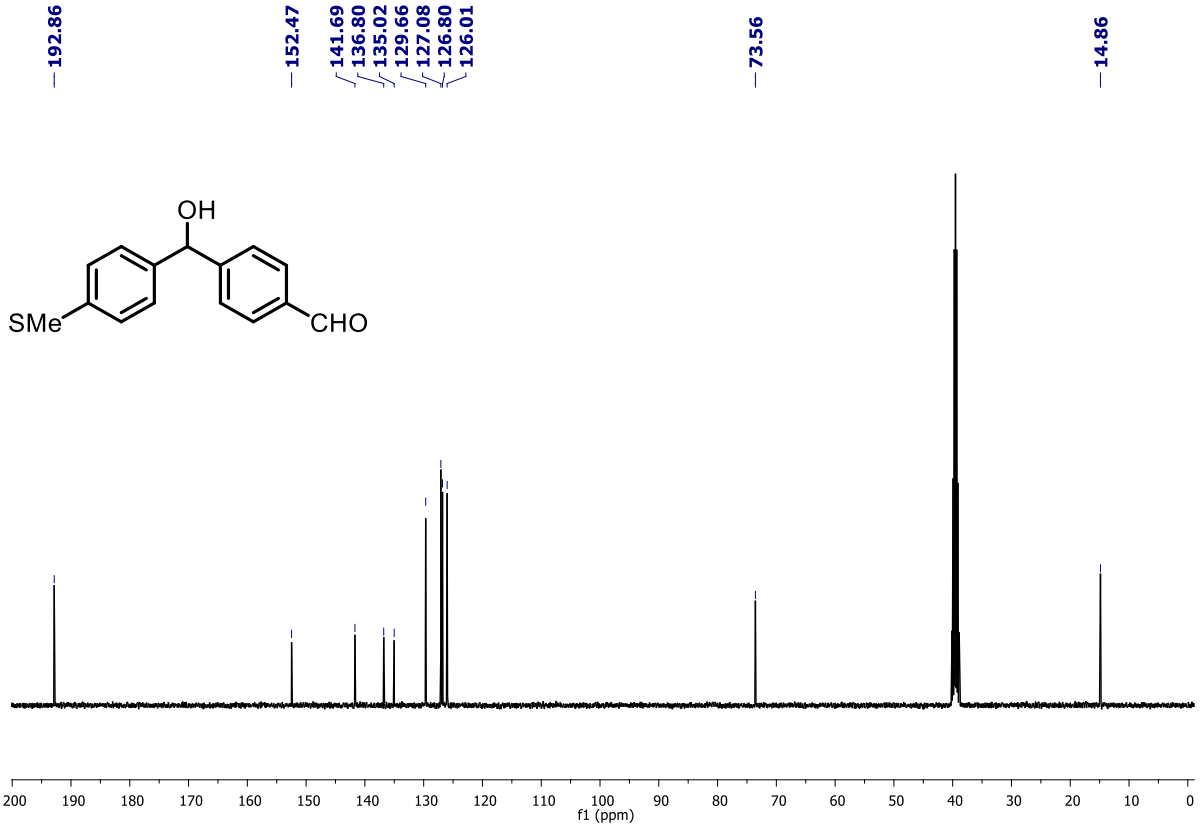
^{13}C {^{1}H} NMR Spectrum of **7c** (DMSO-d_6, 100 MHz)



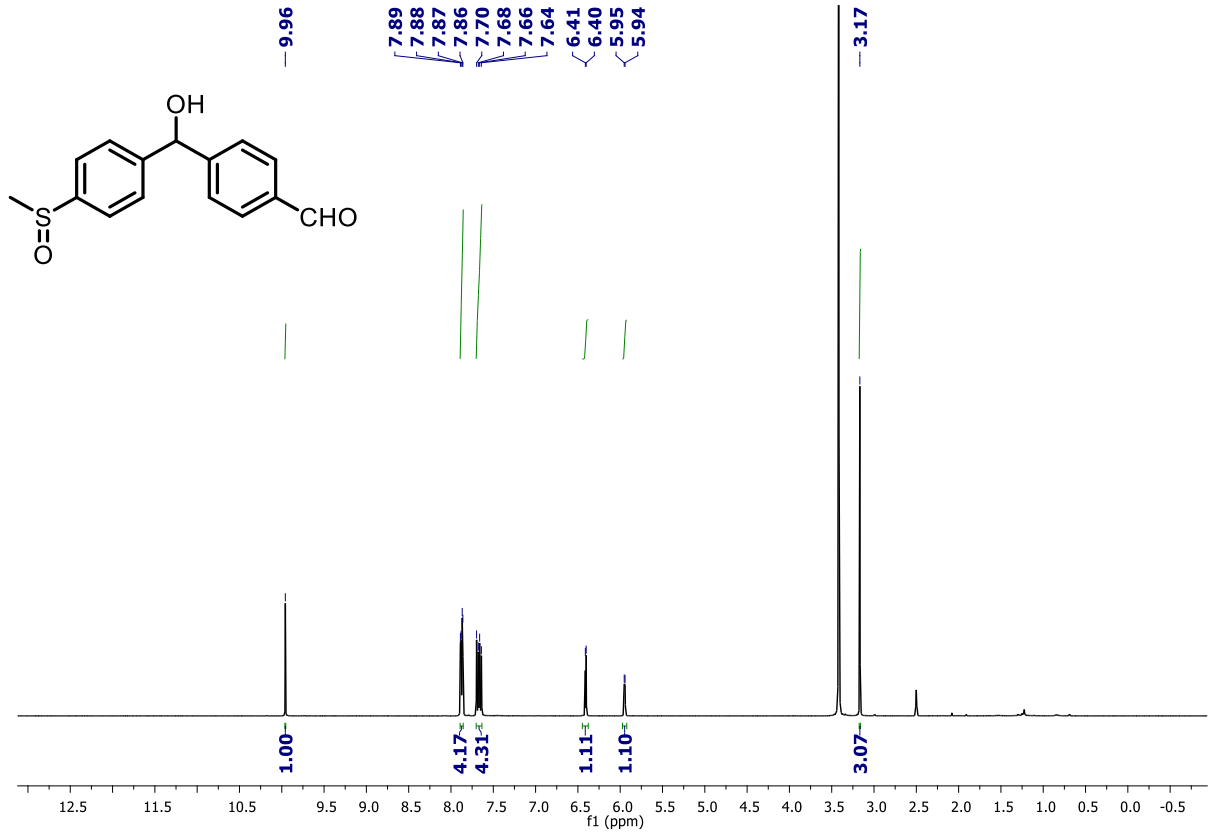
^{1}H NMR Spectrum of **8** (DMSO-d_6, 400 MHz)



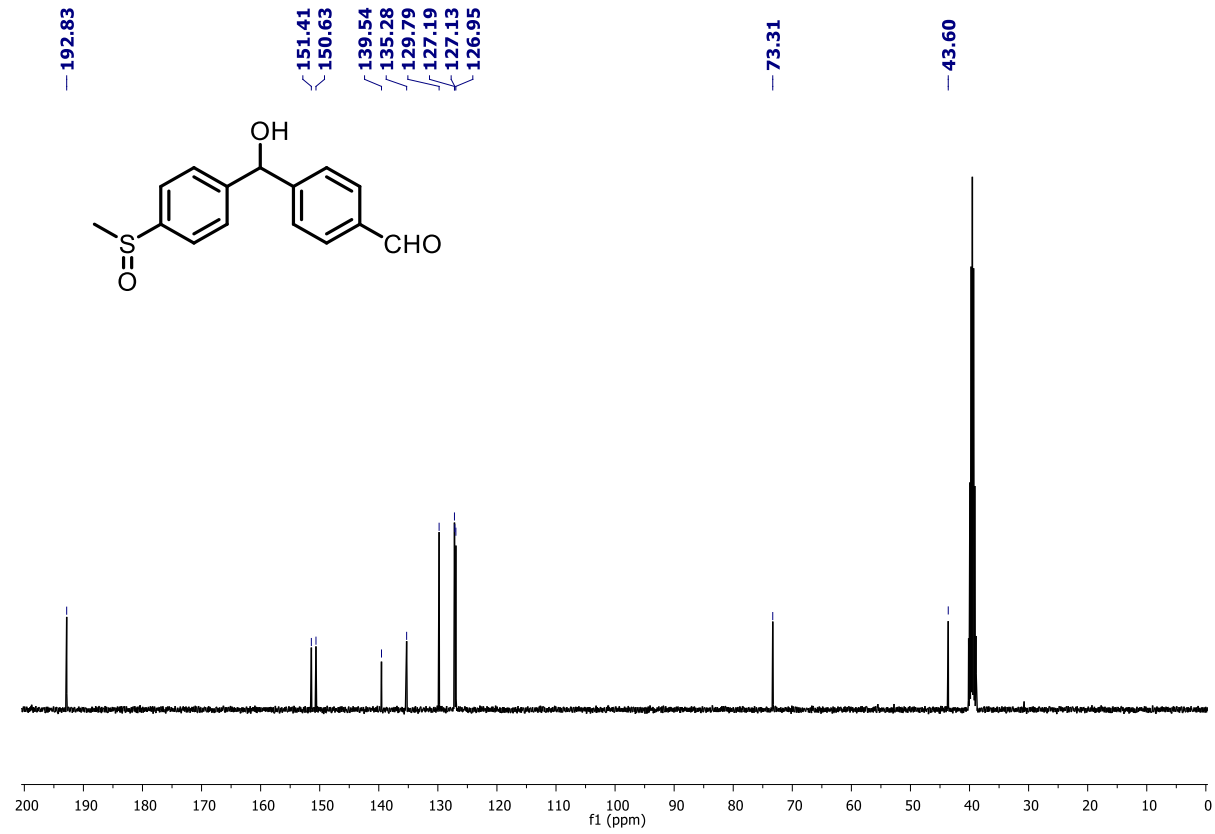
^{13}C {^{1}H} NMR Spectrum of **8** (DMSO-d_6, 100 MHz)



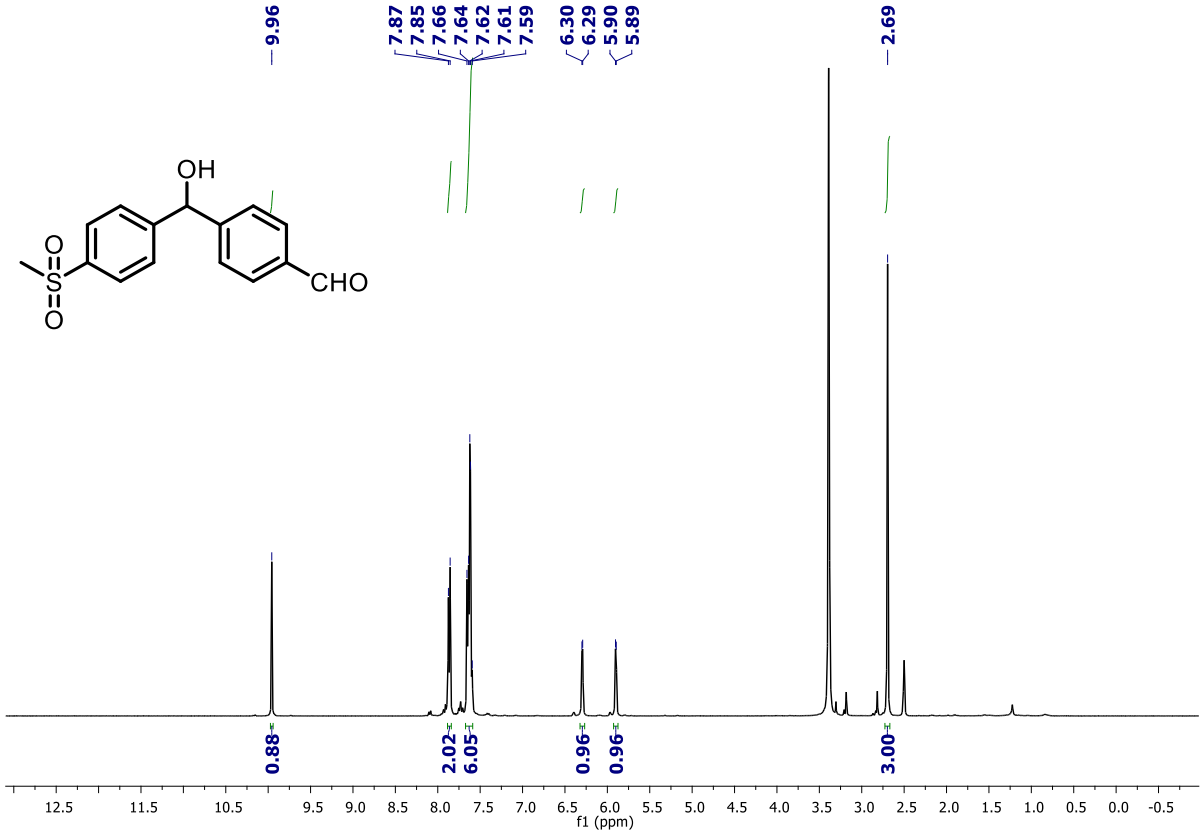
^{1}H NMR Spectrum of **8a** (DMSO-d_6, 400 MHz)



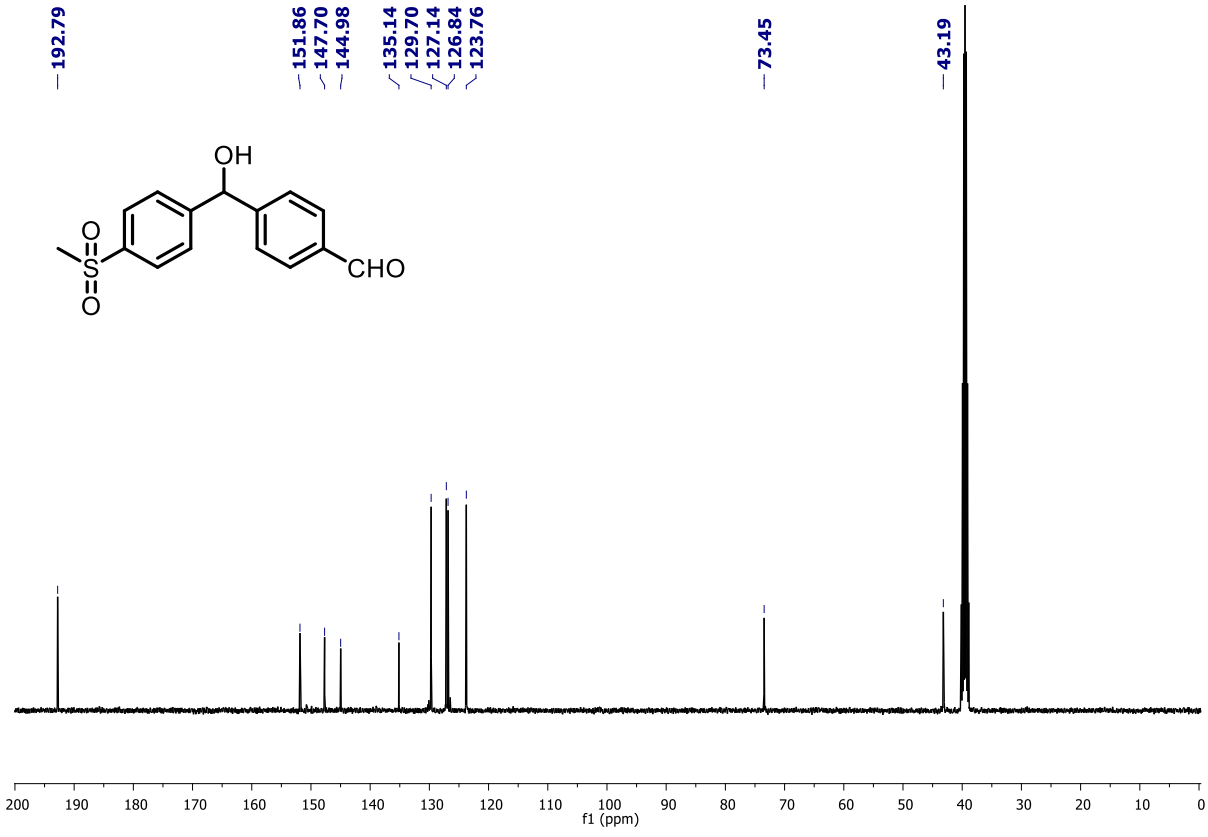
^{13}C {^{1}H} NMR Spectrum of **8a** (DMSO-d_6, 100 MHz)



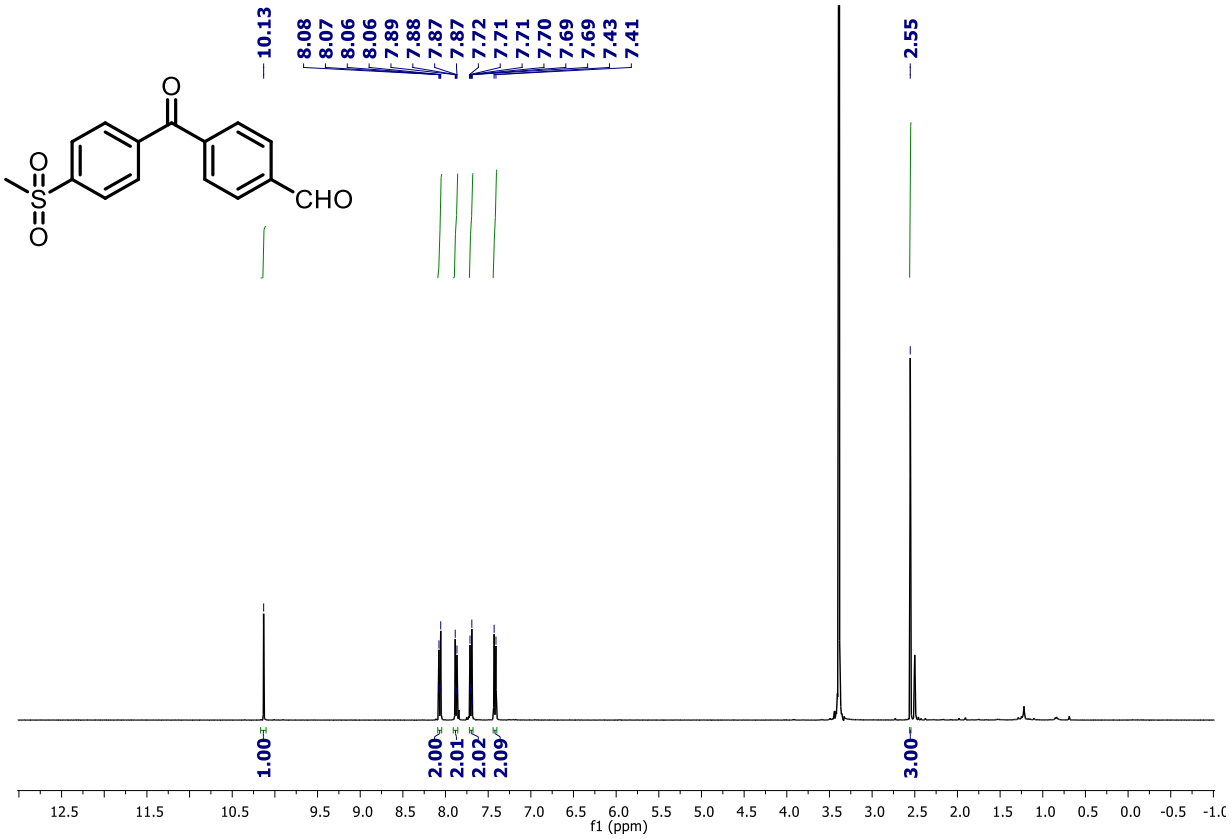
^{1}H NMR Spectrum of **8b** (DMSO-d_6, 400 MHz)



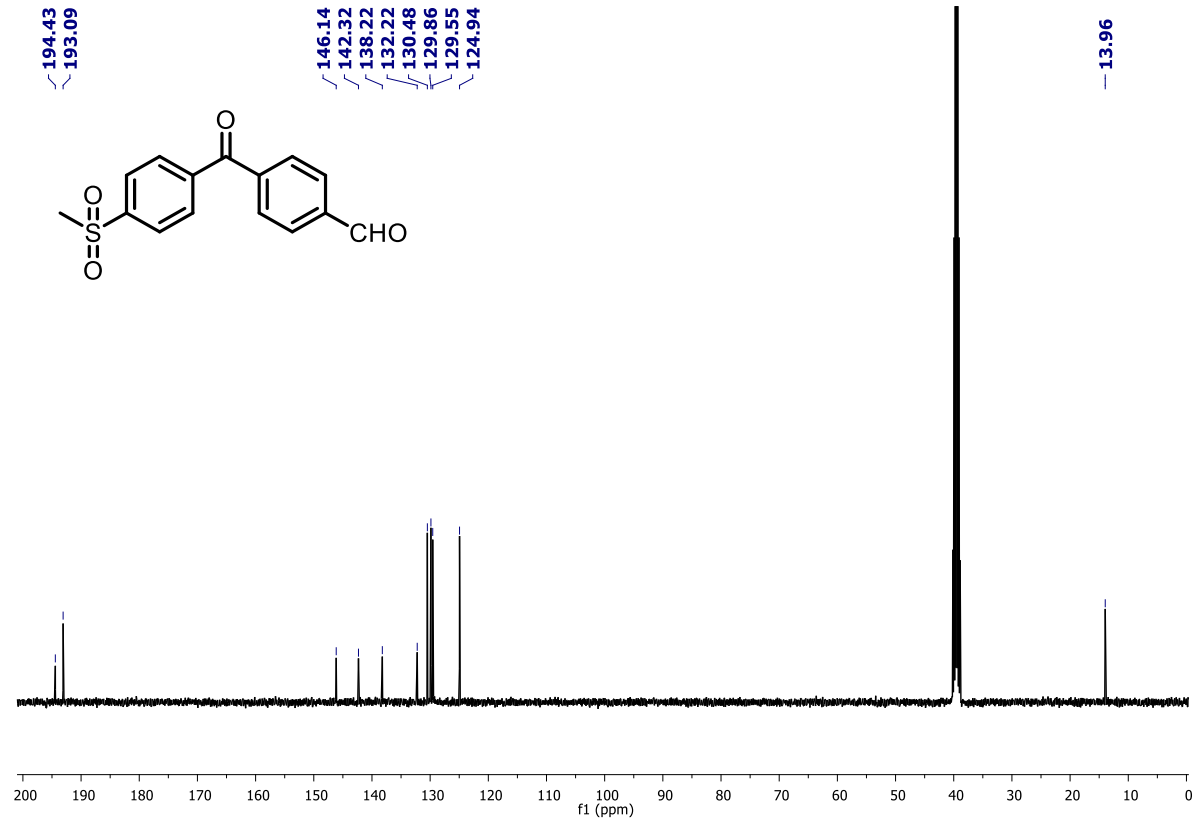
^{13}C {^{1}H} NMR Spectrum of **8b** (DMSO-d_6, 100 MHz)



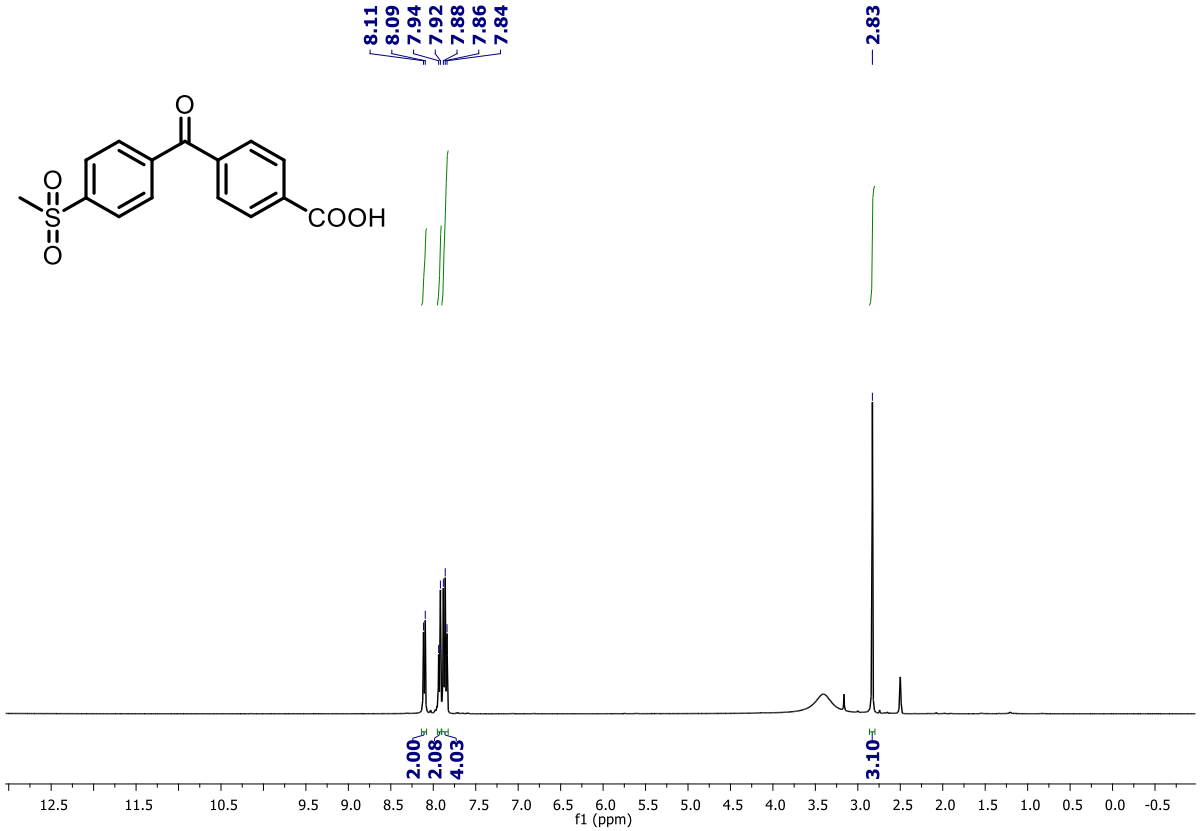
^{1}H NMR Spectrum of **8c** (DMSO-d_6, 400 MHz)



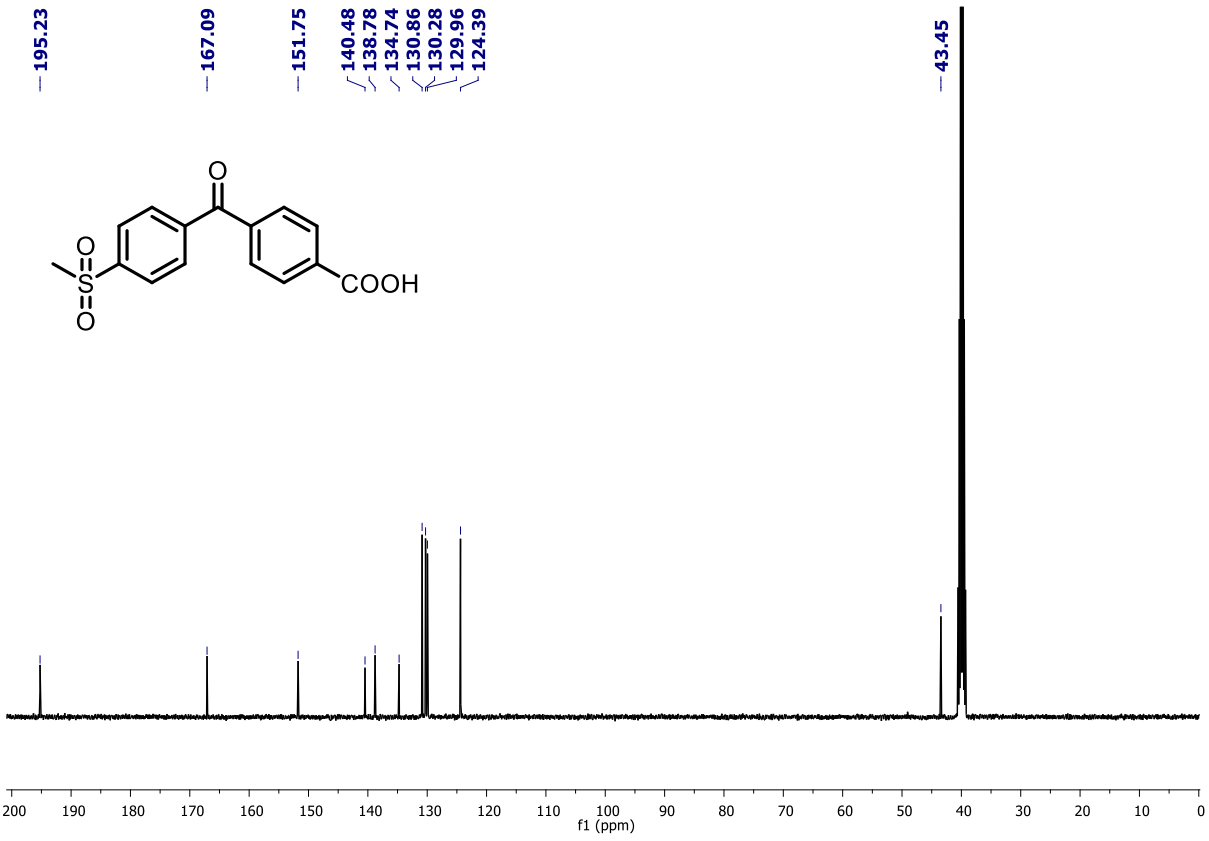
^{13}C {^{1}H} NMR Spectrum of **8c** (DMSO-d_6, 100 MHz)



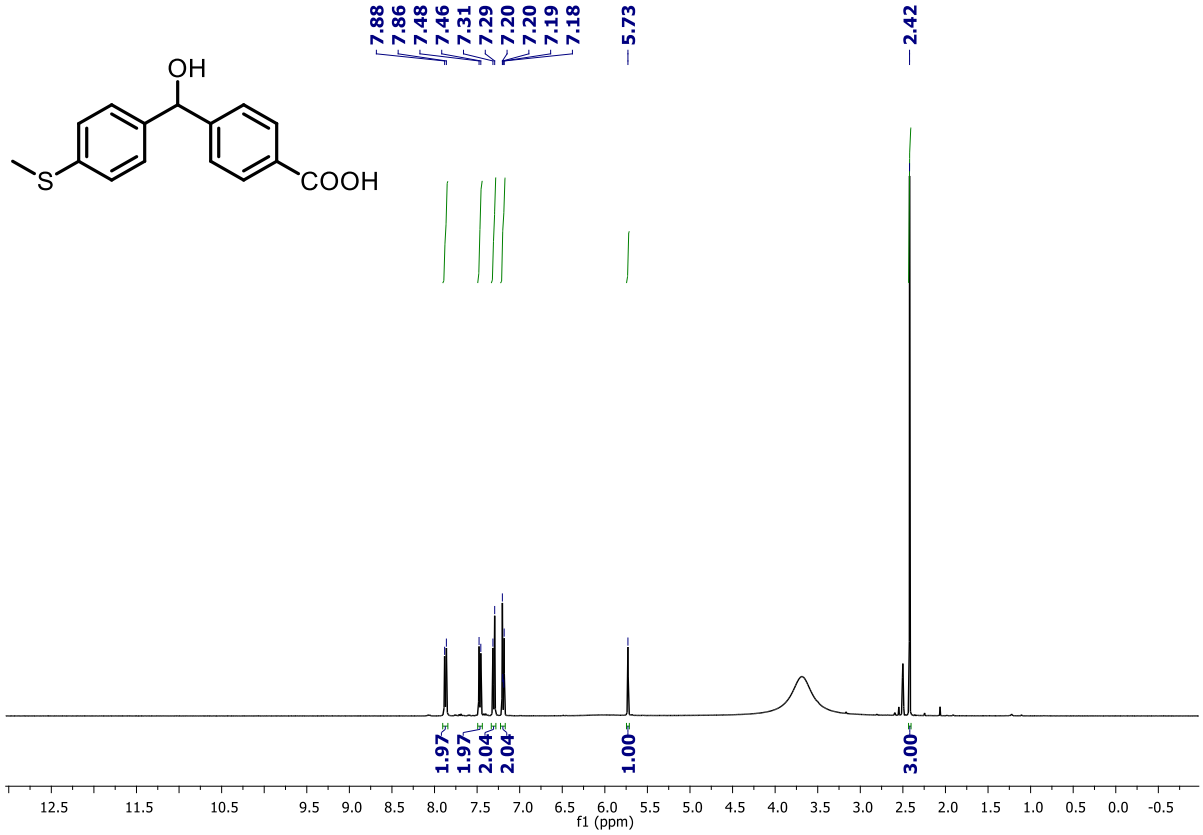
^{1}H NMR Spectrum of **8d** (DMSO-d_6, 400 MHz)



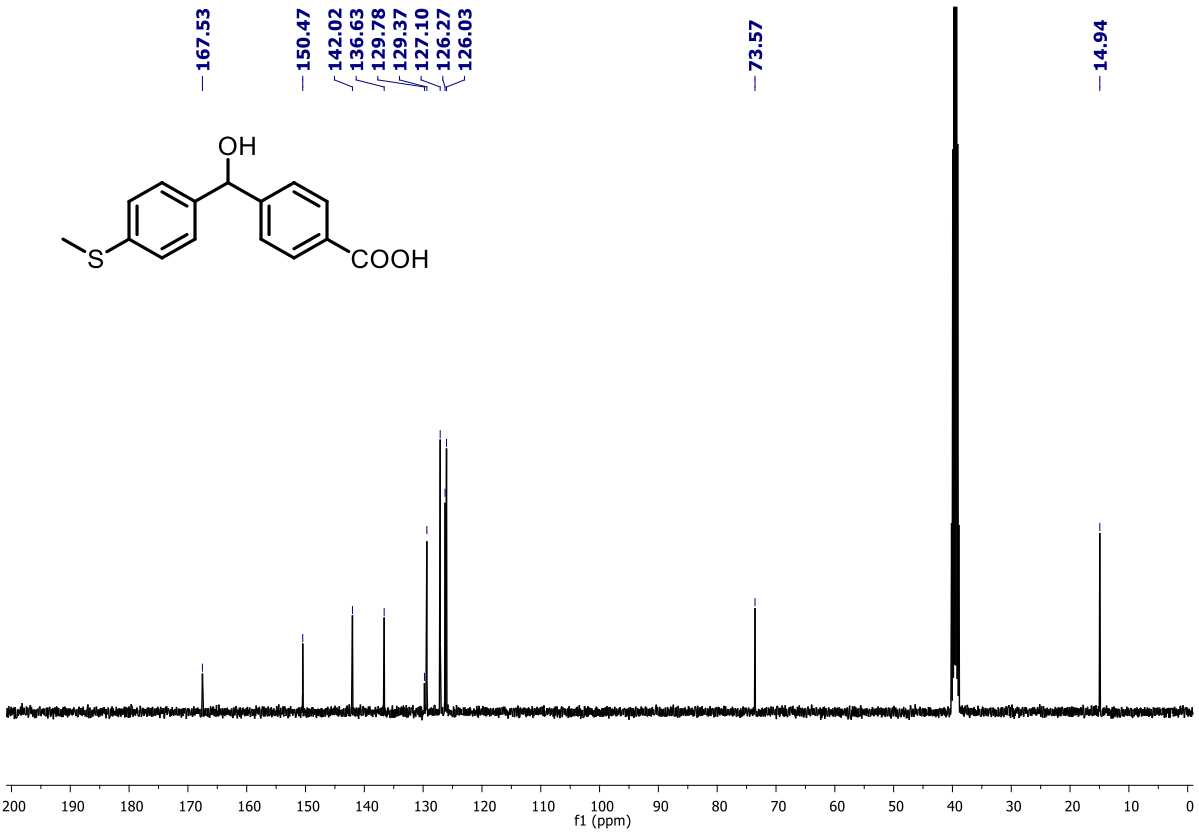
^{13}C {^{1}H} NMR Spectrum of **8d** (DMSO-d_6, 100 MHz)



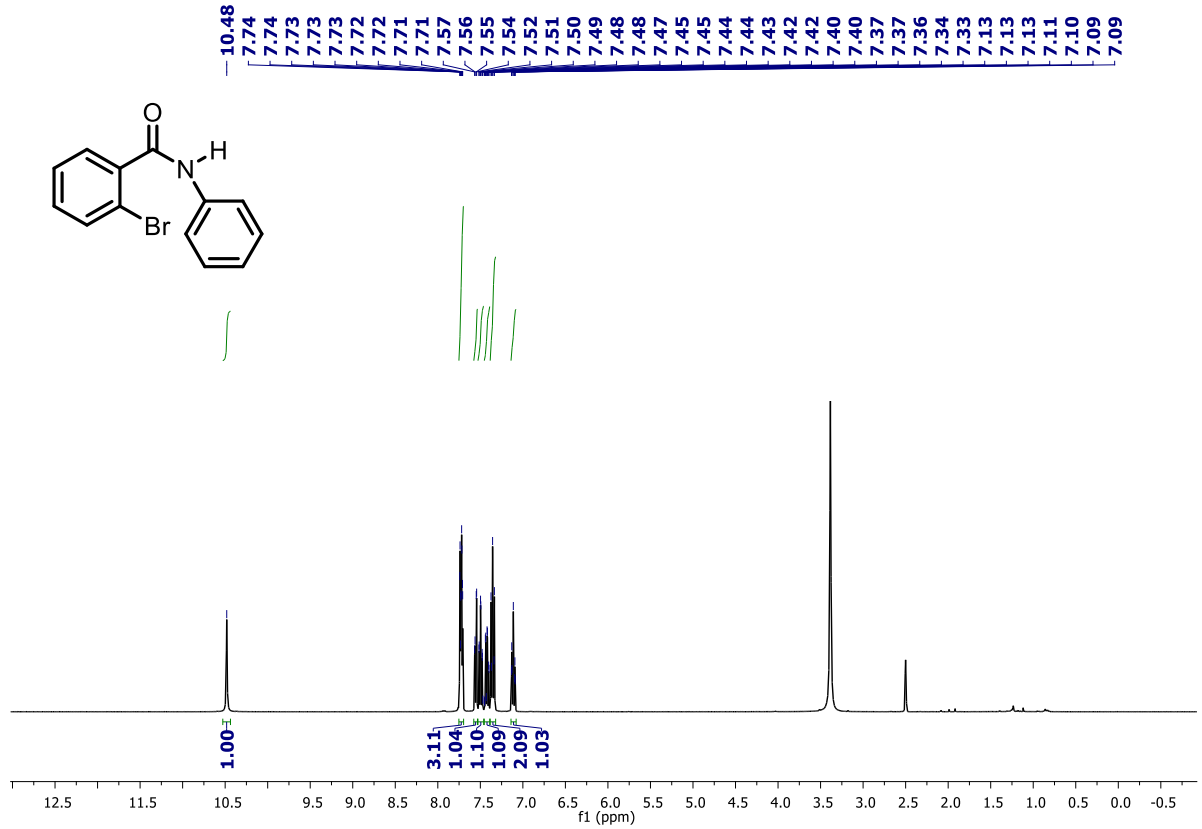
^{1}H NMR Spectrum of **8e** (DMSO-d_6, 400 MHz)



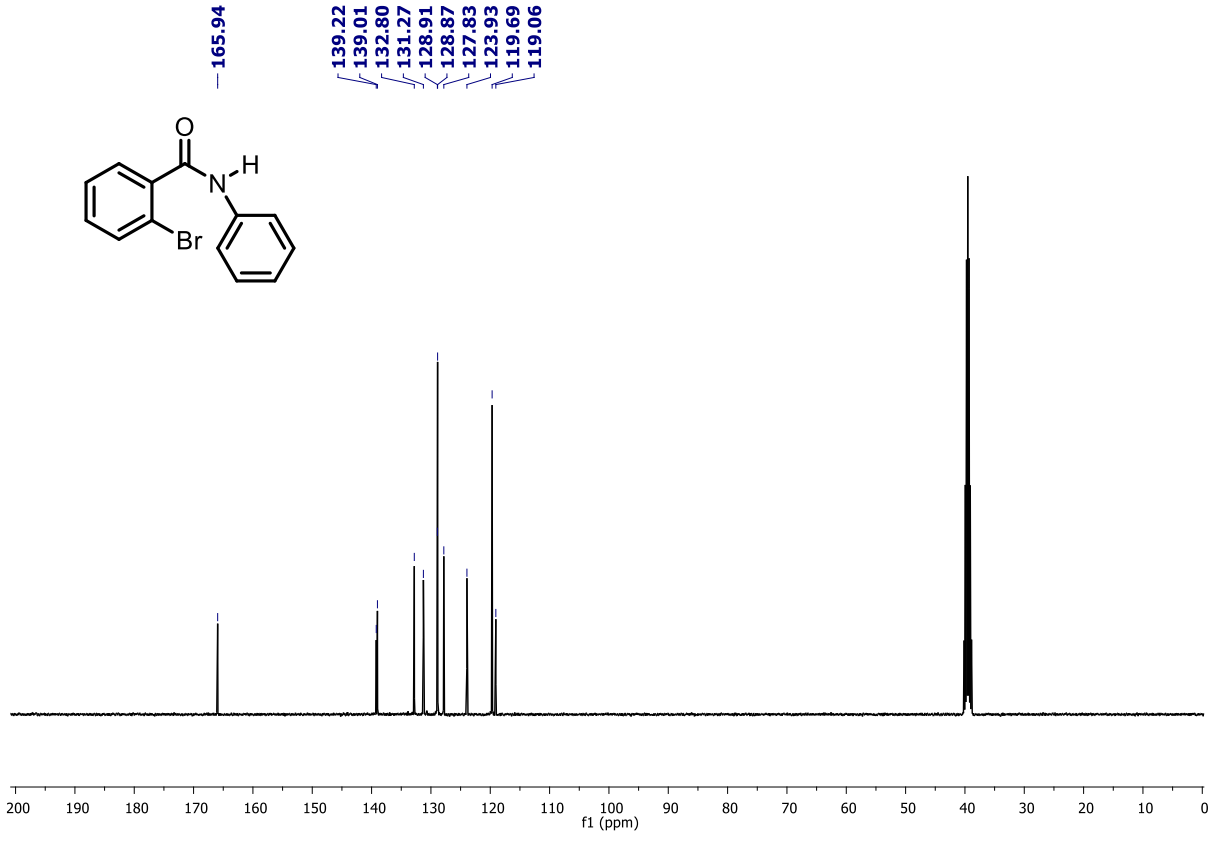
^{13}C {^{1}H} NMR Spectrum of **8e** (DMSO-d_6, 100 MHz)



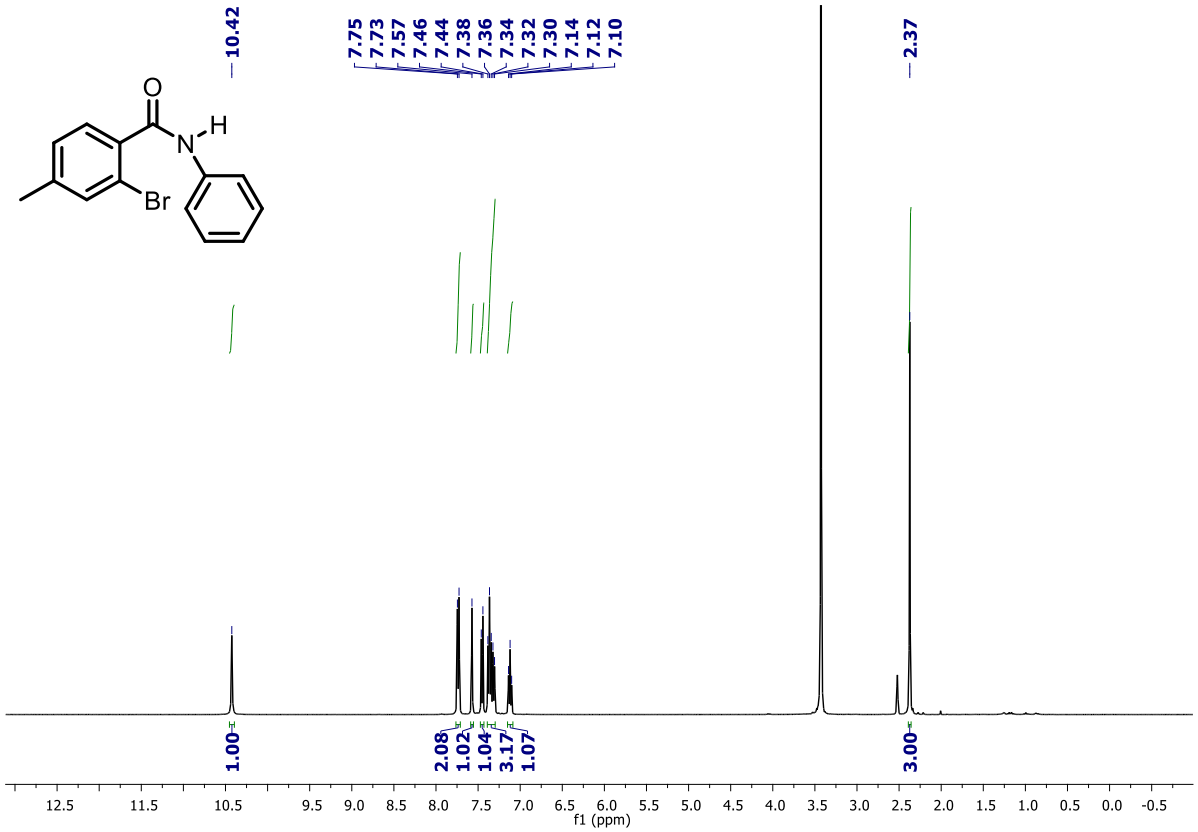
^{1}H NMR Spectrum of **9a** (DMSO-d_6, 400 MHz)



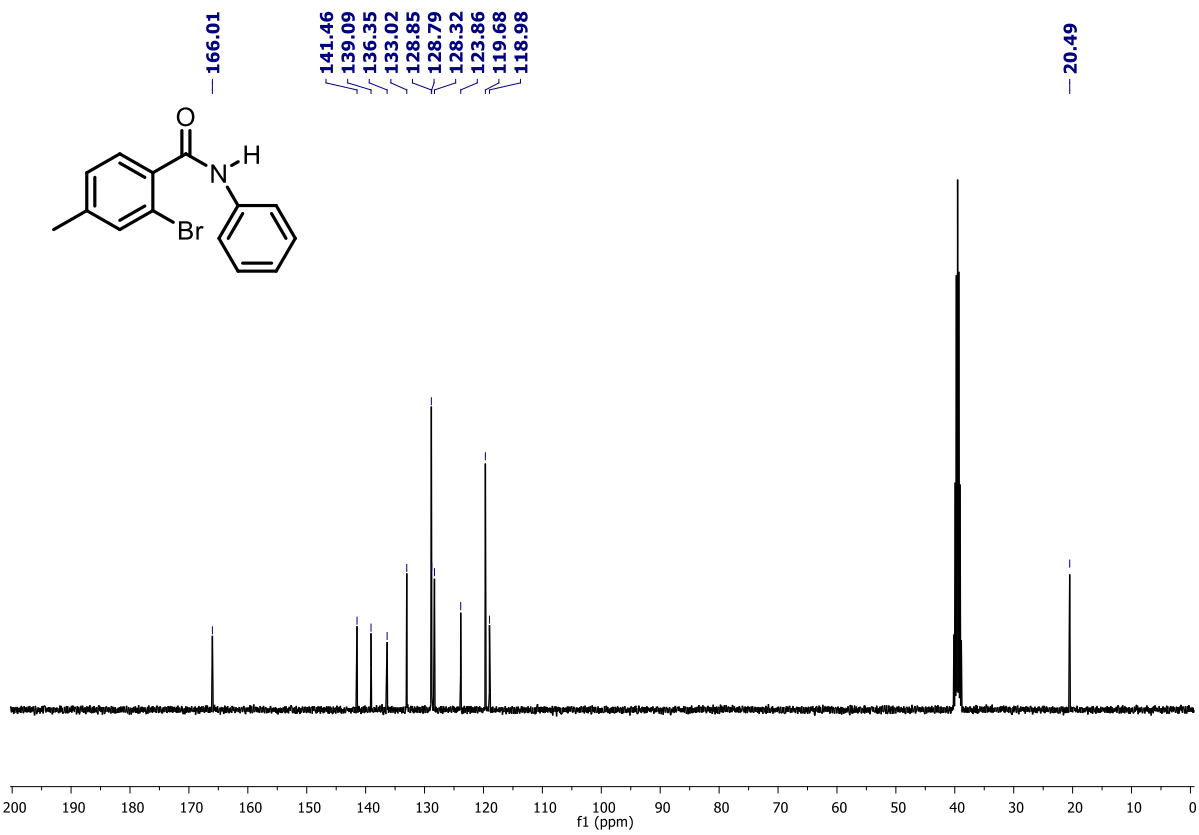
^{13}C {^{1}H} NMR Spectrum of **9a** (DMSO-d_6, 100 MHz)



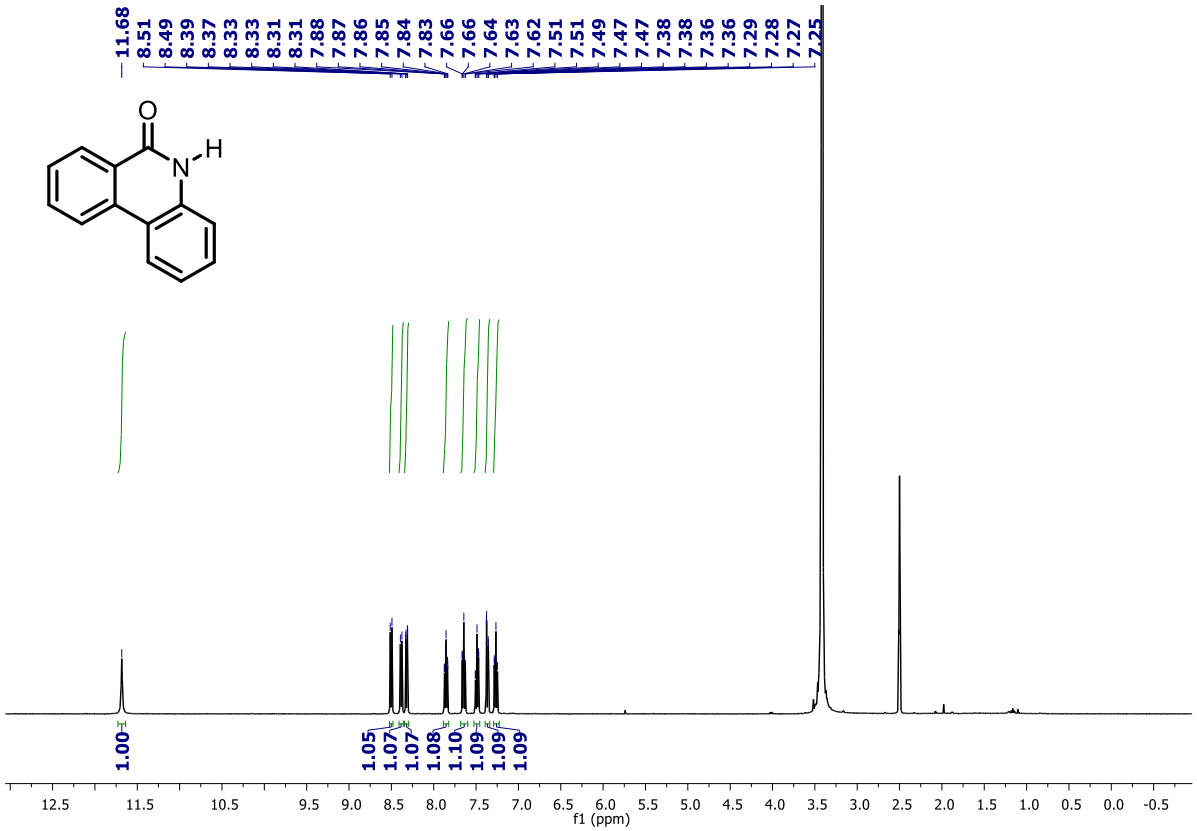
^{1}H NMR Spectrum of **9b** (DMSO-d_6, 400 MHz)



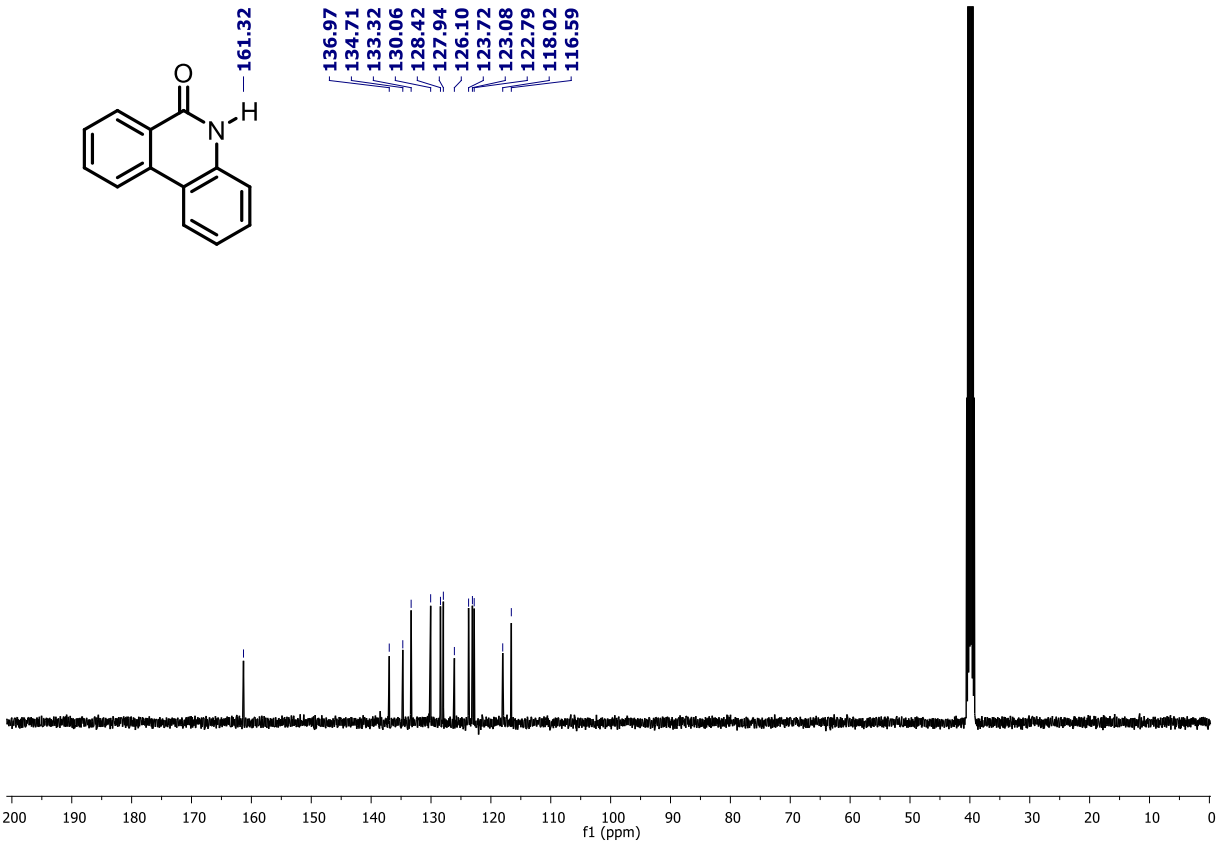
^{13}C {^{1}H} NMR Spectrum of **9b** (DMSO-d_6, 100 MHz)



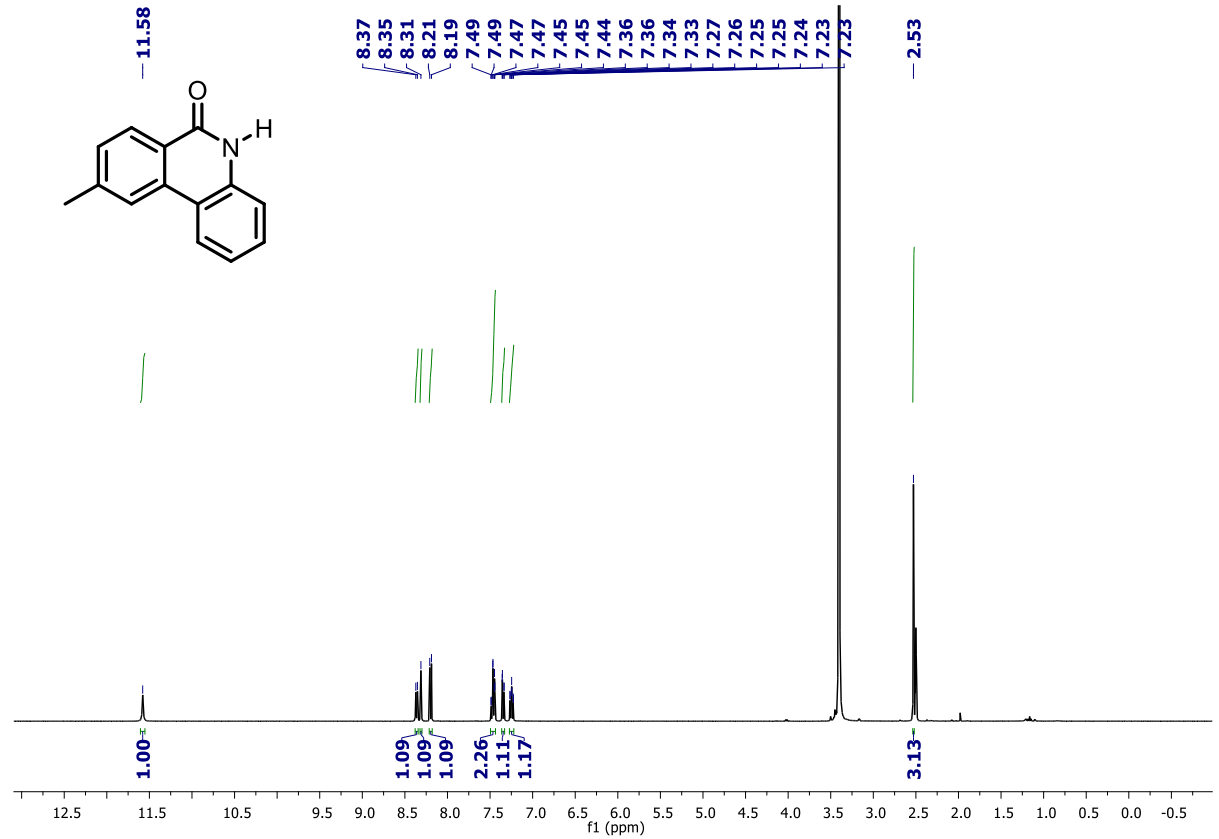
^{1}H NMR Spectrum of **10a** (DMSO-d_6, 400 MHz)



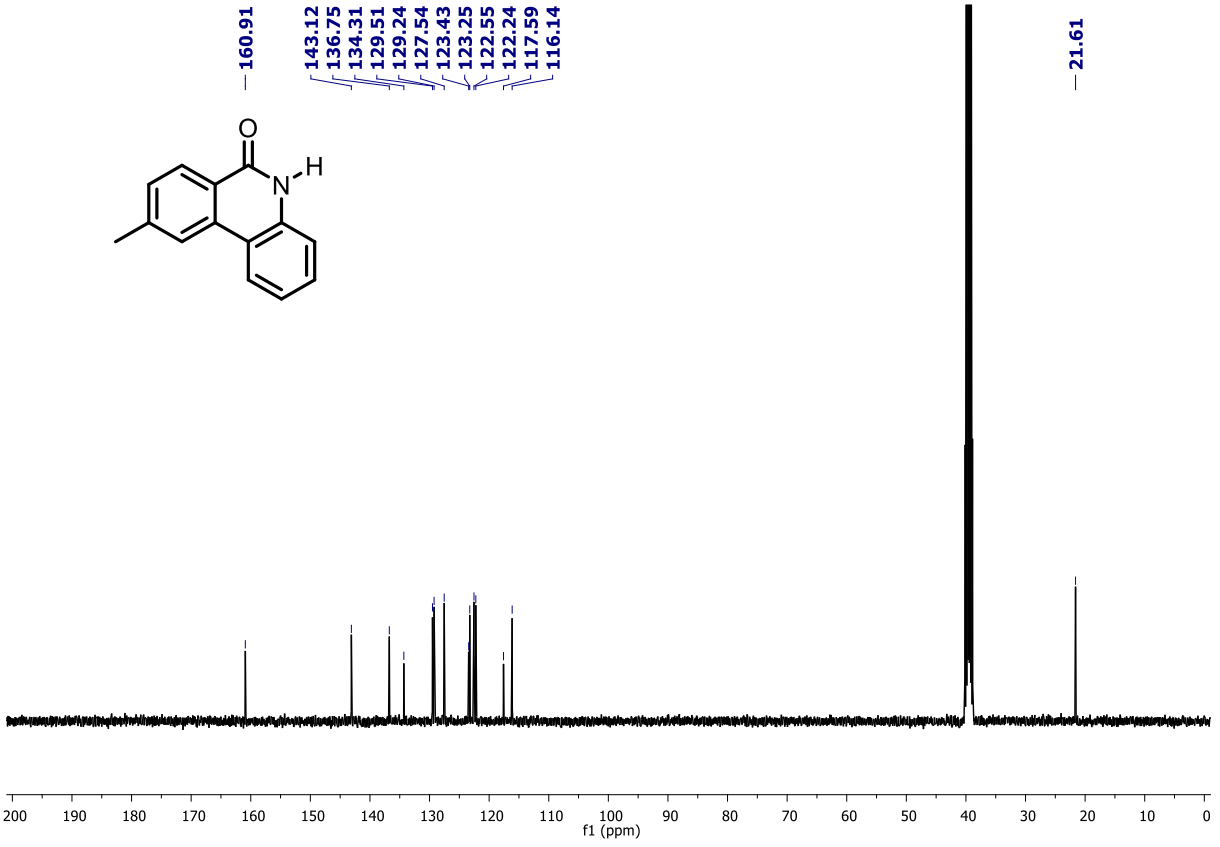
^{13}C {^{1}H} NMR Spectrum of **10a** (DMSO-d_6, 100 MHz)



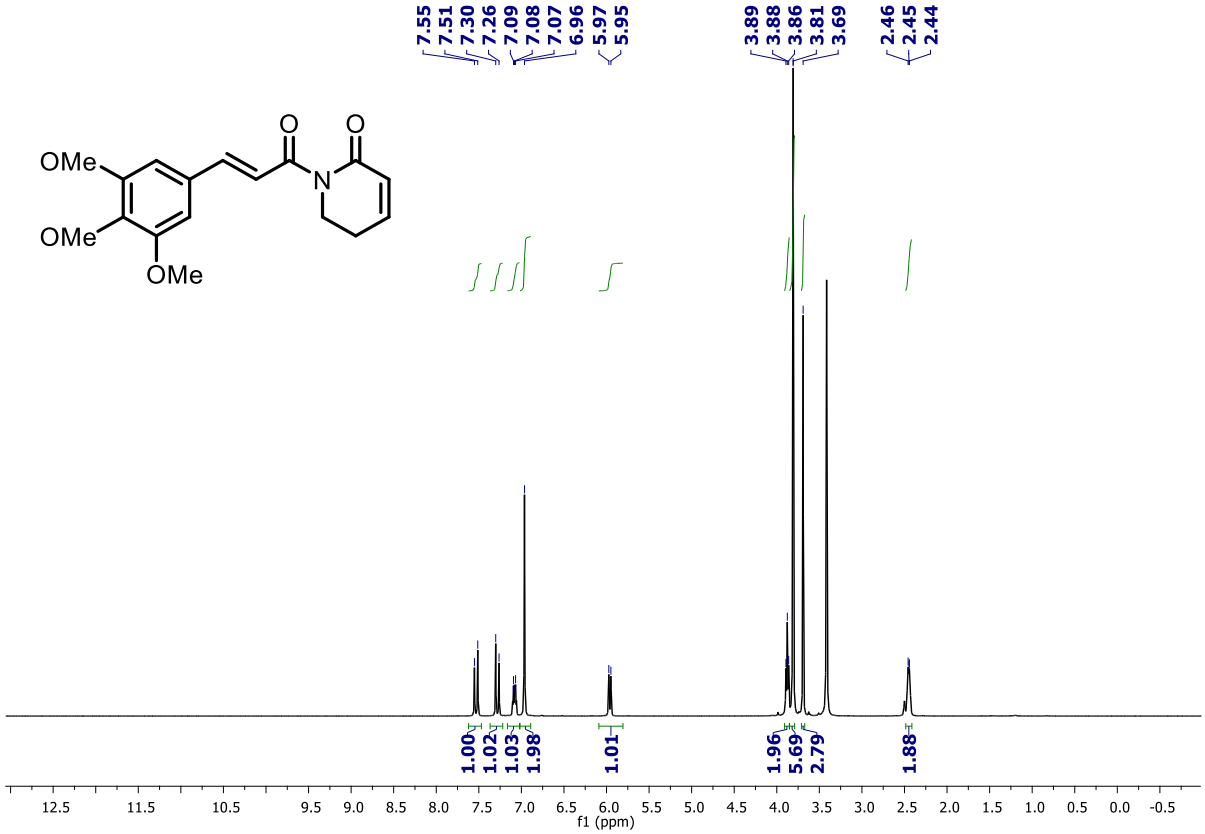
^{1}H NMR Spectrum of **10b** (DMSO-d_6, 400 MHz)



^{13}C {^{1}H} NMR Spectrum of **10b** (DMSO-d_6, 100 MHz)



^{1}H NMR Spectrum of **12** (DMSO-d_6, 400 MHz)



^{13}C {^{1}H} NMR Spectrum of **12** (DMSO-d_6, 100 MHz)