**Supporting Information**

# Remarkably Efficient Novel Synthesis of 2H-Indazole 1-oxides and 2-H-Indazoles via Tandem Carbon-Carbon Followed by Nitrogen-Nitrogen Bonds Formations

Isabelle Bouillon, Jaroslav Zajíček, Naděžda Pudelová and Viktor Krchňák*

*Department of Chemistry and Biochemistry, 251 Nieuwland Science Hall, University of Notre Dame, Notre Dame, Indiana 46556, USA*

*vkrchnak@nd.edu*

**Table of Contents**

**Material and Methods**

Solvents were used without further purification. The Rink resin (100-200 mesh, 1% DVB, 0.75 mmol/g) and Wang resin (100-200 mesh, 1% DVB, 1.0 mmol/g) were used. Synthesis was carried out on Domino Blocks in disposable polypropylene reaction vessels. Labquake Tube Rotator was used for gentle but efficient tumbling of resin slurry.

All reactions were carried out at ambient temperature (~21 $^{o}$C) unless stated otherwise. The volume of wash solvent was 10 mL per 1 g of resin. For washing, resin slurry was shaken with the fresh solvent for at least 1 min before changing the solvent. After adding a reagent solution, the resin slurry was manually vigorously shaken to break any potential resin clumps. Resin-bound intermediates were dried by a stream of nitrogen for prolonged storage and/or quantitative analysis.

For the LC/MS analysis a sample of resin (~5 mg) was treated by 50% TFA in DCM, the cleavage cocktail was evaporated by a stream of nitrogen, and cleaved compounds extracted into 0.5 mL of MeOH.

The LC/MS analyses were carried out using a 3 x 50 mm C18 reverse phase column. Mobile phases: 10 mM ammonium acetate in HPLC grade water (A) and HPLC grade acetonitrile (B). A gradient was formed from 5% to 80% of B in 10 minutes at 0.7 mL/min. The MS electrospray source operated at capillary voltage 3.5 kV and a desolvation temperature 300 $^{o}$C.

Purification was carried out on C18 column 19 x 100 mm, 5 um particles, gradient was formed from 10 mM aqueous ammonium acetate and acetonitrile, flow rate 15 mL/min.

*NMR spectroscopy.* All $^{1}$H and $^{13}$C-NMR experiments were performed at magnetic field strengths of 7.05 or 14.09 T corresponding to $^{1}$H resonance frequencies of 299.89 and 599.89 MHz, respectively, and at ambient temperature (~21 $^{o}$C). Various 1D and 2D homo- and heteronuclear NMR techniques, $^{1}$H, $^{13}$C-APT, $^{1}$H-$^{1}$H DQF-COSY, $^{1}$H-$^{13}$C gHSQC and $^{1}$H-$^{13}$C

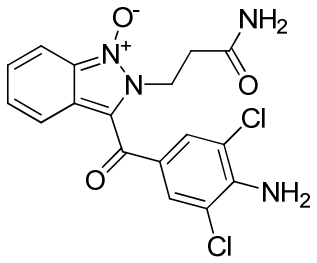
gHMBC, were employed to elucidate the structure of **6(8,2,1)**. The standard pulse sequences[1-6] were used in these experiments.

Time domain data ($t_2$ and $t_1$) for all 2D experiments were recorded as 2048x256 complex matrices with 8, 24, and 96 scans per $t_1$ increment for the DQF-COSY, gHSQC and gHMBC experiments, respectively. The relaxation delay between individual scans was 1.2 sec. In homonuclear 2D experiments, linear prediction to the 1024 complex data points was applied in the $t_1$ domain, which were zero filled to 2048 to obtain final 2kx2k complex time domain data. In heteronuclear 2D experiments, linear prediction to the 2048 complex data points was applied in the $t_1$ domain, which were zero filled to 4096 to obtain final 2kx4k complex time domain data. Shifted sine bell weighting functions were applied in both domains prior to double Fourier transformation. Spectra were processed using Varian VNMR 6.1C or VnmrJ 2.2C software.

$^1$H spectra, the $^1$H dimension in 2D heteronuclear spectra, and $^{13}$C spectra were referenced relative to the signal of DMSO ($^1$H δ=2.49 ppm, $^{13}$C δ=39.50 ppm ). The $^{13}$C dimension in the 2D heteronuclear spectra was referenced indirectly[7].

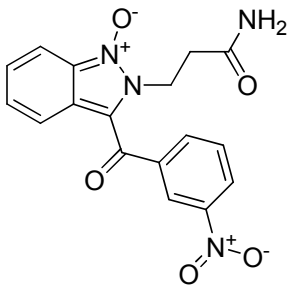
**Analytical data of synthetic compounds**

**2-(3-amino-3-oxopropyl)-3-(4-amino-3,5-dichlorobenzoyl)-2H-indazole 1-oxide 6(1,1,3)**



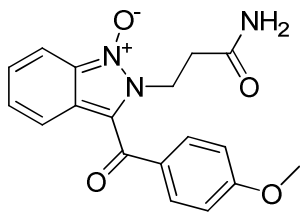
Yield 24.4 mg (52%). ESI-MS *m/z* = 393, $[M+H]^+$. $^1$H NMR (300 MHz, DMSO-$d_6$) δ: 7.75 (d, 1 H) 7.67 (s, 2 H) 7.42 (br. s., 1 H) 7.33 - 7.40 (m, 1 H) 7.24 - 7.33 (m, 1 H) 7.14 (d, *J*=8.29 Hz, 1 H) 6.92 (br. s., 1 H) 6.56 (br. s., 2 H) 4.86 (t, *J*=7.18 Hz, 2 H) 2.71 (t, *J*=7.18 Hz, 2 H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ: 178.2, 171.0, 145.6, 129.9, 128.2, 127.4, 126.5, 126.3, 120.1, 119.0, 117.3, 117.2, 113.3, 41.8, 32.5. HRMS (FAB) *m/z* calcd for $C_{17}H_{15}N_3O_4Cl_2$ $[M + H]^+$ 393.0521, found 393.0520

**3-[3-(3-Nitro-benzoyl)-1-oxy-indazol-2-yl]-propionamide 6(1,1,4)**



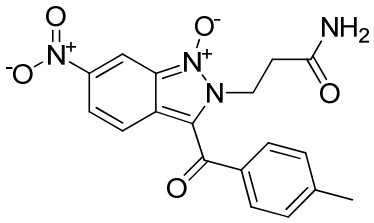
Yield 7.6 mg (47%). ESI-MS *m/z* = 355, $[M+H]^+$. $^1$H NMR (300 MHz, DMSO-$d_6$) δ: 8.49 - 8.60 (m, 2 H) 8.19 (d, *J*=7.73 Hz, 1 H) 7.90 (t, *J*=7.87 Hz, 1 H) 7.81 (d, *J*=8.56 Hz, 1 H) 7.47 (br. s., 1 H) 7.37 (d, *J*=8.29 Hz, 1 H) 7.27 (d, *J*=8.29 Hz, 1 H) 6.96 (br. s., 1 H) 6.81 (d, *J*=8.56 Hz, 1 H) 4.99 (t, *J*=7.18 Hz, 2 H) 2.75 (t, *J*=7.18 Hz, 2 H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ: 179.2, 171.0, 147.8, 140.5, 135.2, 130.6, 128.8, 128.3, 126.9, 126.5, 123.6, 120.2, 119.9, 116.6, 113.5, 42.2, 32.3. HRMS (FAB) *m/z* calcd for $C_{17}H_{15}N_4O_5$ $[M + H]^+$ 355.1042, found 355.1037

**3-[3-(4-Methoxy-benzoyl)-1-oxy-indazol-2-yl]-propionamide 6(1,1,5)**



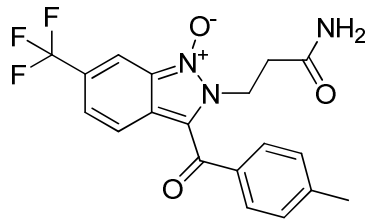
Yield 20.0 mg (58%). ESI-MS *m/z* = 340, $[M+H]^+$. HRMS (FAB) m/z calcd for $C_{18}H_{18}N_3O_4$ [M + H]+ 340.1297, found 340.1304

**3-[3-(4-Methyl-benzoyl)-6-nitro-1-oxy-indazol-2-yl]-propionamide 6(1,2,1)**



Yield 40.4 mg (97%). ESI-MS *m/z* = 369, $[M+H]^+$. $^1$H NMR (300 MHz, DMSO-$d_6$) δ: 8.65 (d, *J*=1.38 Hz, 1 H) 7.99 (dd, *J*=9.39, 1.93 Hz, 1 H) 7.76 (d, *J*=8.01 Hz, 2 H) 7.50 (br. s., 1 H) 7.47 (d, *J*=7.73 Hz, 2 H) 7.11 (d, *J*=9.39 Hz, 1 H) 6.99 (br. s., 1 H) 5.00 (t, *J*=7.04 Hz, 2 H) 2.80 (t, *J*=7.18 Hz, 2 H) 2.50 (s, 3 H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ: 181.8, 170.8, 145.1, 143.9, 135.8, 129.6, 129.4, 126.9, 122.1, 120.7, 120.2, 118.3, 111.4, 42.8, 32.1, 21.4. HRMS (FAB) *m/z* calcd for $C_{18}H_{17}N_4O_5$ $[M + H]^+$ 369.1199, found 369.1186

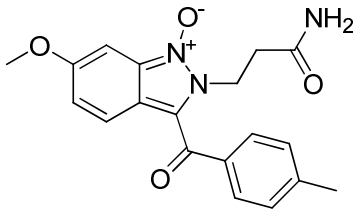
**3-[3-(4-Methyl-benzoyl)-1-oxy-6-trifluoromethyl-indazol-2-yl]-propionamide 6(1,3,1)**



Yield 42 mg (95%). ESI-MS *m/z* = 392, $[M+H]^+$. $^1$H NMR (300 MHz, DMSO-$d_6$) δ: 8.15 (s, 1 H) 7.71 (d, *J*=8.01 Hz, 2 H) 7.49 (dd, *J*=9.12, 1.38 Hz, 1 H) 7.45 (br. s., 1 H) 7.42 (d, *J*=7.73 Hz, 2

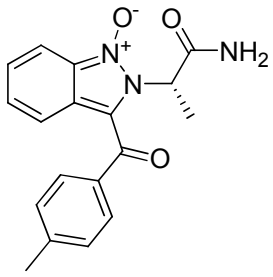
H) 7.07 (d, *J*=9.12 Hz, 1 H) 6.94 (br. s., 1 H) 4.96 (t, *J*=7.18 Hz, 2 H) 2.75 (t, *J*=7.18 Hz, 2 H) 2.45 (s, 3 H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ: 181.7, 170.9, 143.6, 136.0, 129.5, 129.4, 127.0, 122.7, 122.4, 120.0, 117.9, 112.1, 112.0, 42.5, 32.3, 21.3. HRMS (FAB) *m/z* calcd for $C_{19}H_{17}N_3O_3F_3$ $[M + H]^+$ 392.1222, found 392.1242

**3-[6-Methoxy-3-(4-methyl-benzoyl)-1-oxy-indazol-2-yl]-propionamide 6(1,4,1)**



Yield 9.8 mg (59%). ESI-MS *m/z* = 354, $[M+H]^+$. $^1$H NMR (300 MHz, DMSO-$d_6$) δ: 7.67 (d, *J*=8.01 Hz, 2 H) 7.44 (br. s., 1 H) 7.39 (d, *J*=8.01 Hz, 2 H) 7.00 (d, *J*=2.21 Hz, 1 H) 6.92 (br. s., 0 H) 6.92 (dd, *J*=9.25, 2.35 Hz, 1 H) 6.73 (d, *J*=9.12 Hz, 1 H) 4.89 (t, *J*=7.18 Hz, 2 H) 3.85 (s, 3 H) 2.70 (t, *J*=7.04 Hz, 2 H) 2.44 (s, 3 H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ: 181.6, 171.0, 158.3, 143.2, 136.4, 129.4, 129.23, 129.17, 122.0, 121.3, 117.9, 115.5, 90.9, 55.8, 41.9, 32.8, 21.3. HRMS (FAB) *m/z* calcd for $C_{19}H_{20}N_3O_4$ $[M + H]^+$ 354.1453, found 354.1443

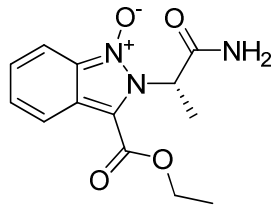
**(S)-2-(1-amino-1-oxopropan-2-yl)-3-(4-methylbenzoyl)-2H-indazole 1-oxide 6(2,1,1)**



Yield 24.5 mg (54%). ESI-MS *m/z* = 324, $[M+H]^+$. $^1$H NMR (300 MHz, DMSO-$d_6$) δ: 7.75 (d, *J*=8.56 Hz, 1 H) 7.71 (d, *J*=8.29 Hz, 2 H) 7.41 (d, *J*=8.01 Hz, 2 H) 7.20 - 7.39 (m, 4 H) 6.83 (d, *J*=8.56 Hz, 1 H) 6.00 - 6.17 (m, 1 H) 2.44 (s, 3 H) 1.78 (d, *J*=6.91 Hz, 3 H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ: 181.6, 168.4, 143.1, 136.6, 129.3, 128.7, 128.6, 127.6, 126.4, 120.3, 120.2, 117.3,

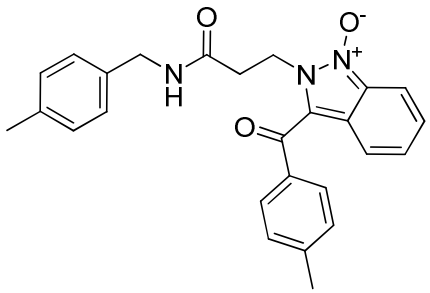
113.5, 55.5, 21.3, 14.7. HRMS (FAB) *m/z* calcd for $C_{18}H_{18}N_3O_3$ $[M + H]^+$ 324.1348, found 324.1370

**(S)-2-(1-amino-1-oxopropan-2-yl)-3-(ethoxycarbonyl)-2H-indazole 1-oxide 6(2,1,5)**



Yield 28.8 mg (74%). ESI-MS *m/z* = 278, $[M+H]^+$. $^1$H NMR (300 MHz, DMSO-$d_6$) δ: 8.05 (d, *J*=8.01 Hz, 1 H) 7.72 (d, *J*=8.56 Hz, 1 H) 7.40 - 7.53 (m, 2 H) 7.39 (br. s., 1 H) 7.29 (br. s., 1 H) 6.31 (q, *J*=6.91 Hz, 1 H) 4.38 (q, *J*=7.18 Hz, 2 H) 1.72 (d, *J*=6.91 Hz, 3 H) 1.39 (t, *J*=7.04 Hz, 3 H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ: 168.5, 157.9, 128.6, 128.0, 126.7, 121.3, 119.8, 113.4, 108.4, 60.9, 54.8, 14.6, 14.2. HRMS (FAB) *m/z* calcd for $C_{13}H_{16}N_3O_4$ $[M + H]^+$ 278.1141, found 278.1144

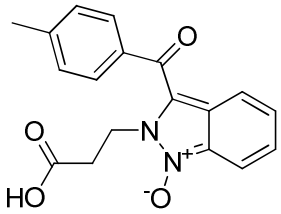
**3-[3-(4-Methyl-benzoyl)-1-oxy-2-indazolyl]-N-(4-methyl-benzyl)-propionamide 6(3,1,1)**



Yield (HPLC purified) 12.3 mg (65%). ESI-MS *m/z* = 428, $[M+H]^+$. $^1$H NMR (300 MHz, DMSO-$d_6$) δ: 8.46 (t, *J*=6.08 Hz, 1 H) 7.77 (d, *J*=9.67 Hz, 1 H) 7.57 (d, *J*=8.01 Hz, 2 H) 7.30 - 7.42 (m, 3 H) 7.25 (d, *J*=7.73 Hz, 1 H) 6.96 (s, 4 H) 6.82 (d, *J*=8.84 Hz, 1 H) 5.01 (t, *J*=6.91 Hz, 2 H) 4.07 - 4.17 (m, 2 H) 2.83 (t, *J*=7.04 Hz, 2 H) 2.43 (s, 3 H) 2.23 (s, 3 H). $^{13}$C NMR (300 MHz, DMSO-$d_6$) δ: 181.6, 168.6, 143.2, 136.4, 136.2, 135.8, 129.4, 129.2, 128.7, 128.5, 127.5, 127.0, 126.4,

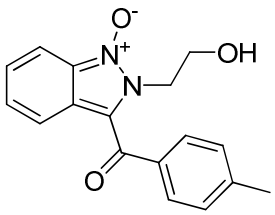
120.2, 119.6, 117.5, 113.3, 42.2, 41.8, 32.8, 21.3, 20.7. HRMS (FAB) *m/z* calcd for $C_{26}H_{26}N_3O_3$ $[M + H]^+$ 428.1974, found 428.1990

**3-[3-(4-Methyl-benzoyl)-1-oxy-indazol-2-yl]-propionic acid 6(4,1,1)**



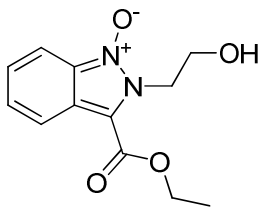
Yield 15.1 mg (37%). ESI-MS *m/z* = 325, $[M+H]^+$. 1H NMR (300 MHz, DMSO-$d_6$) d ppm 2.44 (s, 3 H) 2.80 (t, *J*=7.46 Hz, 2 H) 4.92 (t, *J*=7.32 Hz, 2 H) 6.85 (d, *J*=8.56 Hz, 1 H) 7.19 - 7.28 (m, 1 H) 7.29 - 7.37 (m, 1 H) 7.40 (d, *J*=8.01 Hz, 2 H) 7.68 (d, *J*=8.01 Hz, 2 H) 7.75 (d, *J*=8.56 Hz, 1 H). $^{13}$C NMR (300 MHz, DMSO-$d_6$) δ: 21.26, 32.58, 42.01, 113.31, 117.19, 119.63, 120.10, 126.23, 127.52, 128.43, 129.21, 129.25, 136.44, 143.05, 171.87, 181.63. HRMS (FAB) m/z calcd for $C_{18}H_{17}N_2O_4$ [M + H]+ 325.1188, found 325.1204

**[2-(2-Hydroxy-ethyl)-1-oxy-2H-indazol-3-yl]-p-tolyl-methanone 6(5,1,1**)



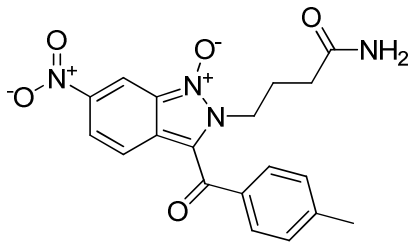
Yield 22.7 mg (80%). ESI-MS *m/z* = 297, $[M+H]^+$. $^1$H NMR (300 MHz, DMSO-$d_6$) δ: 7.76 (d, *J*=8.56 Hz, 1 H) 7.69 (d, *J*=8.01 Hz, 2 H) 7.40 (d, *J*=7.73 Hz, 2 H) 7.33 (d, *J*=8.84 Hz, 1 H) 7.23 (td, *J*=7.67, 0.97 Hz, 1 H) 6.85 (d, *J*=8.56 Hz, 1 H) 5.00 (t, *J*=5.94 Hz, 1 H) 4.92 (t, *J*=5.66 Hz, 2 H) 3.76 (q, *J*=5.80 Hz, 2 H) 2.44 (s, 3 H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ: 181.9, 143.2, 136.5, 129.3, 129.3, 128.5, 127.4, 126.3, 120.2, 119.6, 118.0, 113.4, 57.8, 47.3, 21.3. HRMS (FAB) *m/z* calcd for $C_{17}H_{17}N_2O_3$ $[M + H]^+$ 297.1239, found 297.1251

**2-(2-Hydroxy-ethyl)-1-oxy-2H-indazole-3-carboxylic acid ethyl ester 6(5,1,5**)



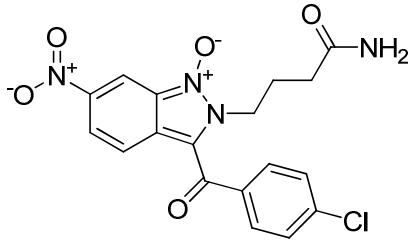
Yield 5.5 mg (23%). ESI-MS *m/z* = 251, $[M+H]^+$. $^1H$ NMR (300 MHz, DMSO-$d_6$) δ: 8.03 (d, *J*=8.01 Hz, 1 H) 7.74 (d, *J*=8.29 Hz, 1 H) 7.31 - 7.53 (m, 2 H) 4.99 (t, *J*=5.94 Hz, 1 H) 4.93 (t, *J*=5.94 Hz, 2 H) 4.40 (q, *J*=7.18 Hz, 2 H) 3.76 (q, *J*=6.08 Hz, 2 H) 1.40 (t, *J*=7.04 Hz, 3 H). $^{13}C$ NMR (75 MHz, DMSO-$d_6$) δ: 157.8, 128.6, 127.8, 126.5, 121.1, 119.2, 113.3, 108.7, 60.8, 57.8, 47.2, 14.2. HRMS (FAB) *m/z* calcd for $C_{12}H_{15}N_2O_4$ $[M + H]^+$ 251.1032, found 251.1030

**4-[3-(4-Methyl-benzoyl)-6-nitro-1-oxy-indazol-2-yl]-butyramide 6(6,2,1)**



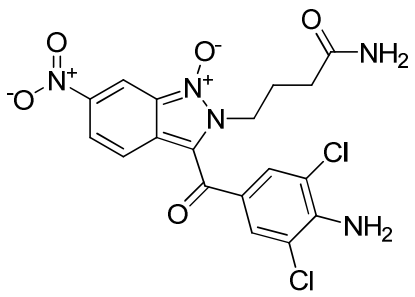
Yield (HPLC purified) 16.6 mg (39%). ESI-MS *m/z* = 383, $[M+H]^+$. HRMS (FAB) m/z calcd for $C_{19}H_{19}N_4O_5$ [M + H]+ 383.1355, found 383.1353

**4-[3-(4-Chloro-benzoyl)-6-nitro-1-oxy-indazol-2-yl]-butyramide 6(6,2,2)**



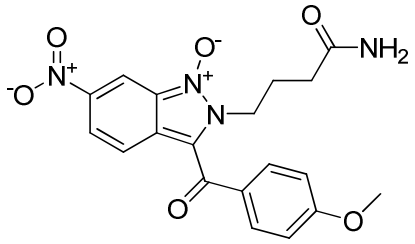
Yield (HPLC purified) 7.7 mg (17%). ESI-MS *m/z* = 403, $[M+H]^+$. HRMS (FAB) m/z calcd for $C_{18}H_{16}N_4O_5Cl$ [M + H]+ 403.0809, found 403.0818

**4-[3-(4-Amino-3,5-dichloro-benzoyl)-6-nitro-1-oxy-indazol-2-yl]-butyramide 6(6,2,3)**



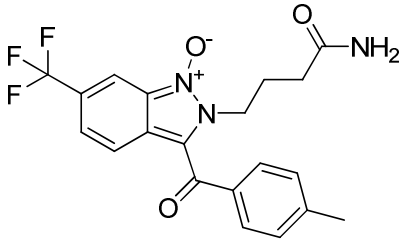
Yield (HPLC purified) 11.7 mg (23%). ESI-MS *m/z* = 452, $[M+H]^+$. HRMS (FAB) m/z calcd for $C_{18}H_{16}N_5O_5Cl_2$ [M + H]+ 452.0528, found 452.0526

**4-[3-(4-Methoxy-benzoyl)-6-nitro-1-oxy-indazol-2-yl]-butyramide 6(6,2,5)**



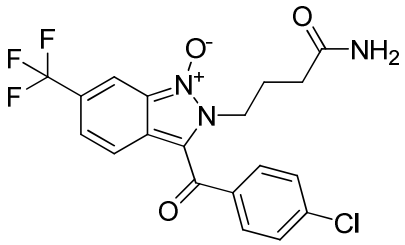
Yield (HPLC purified) 12.8 mg (29%). ESI-MS *m/z* = 399, $[M+H]^+$. HRMS (FAB) m/z calcd for $C_{19}H_{17}N_4O_6$ [M - H]+ 397.1148, found 397.4140

**4-[3-(4-Methyl-benzoyl)-1-oxy-6-triflouromethyl-indazol-2-yl]-butyramide 6(6,3,1)**



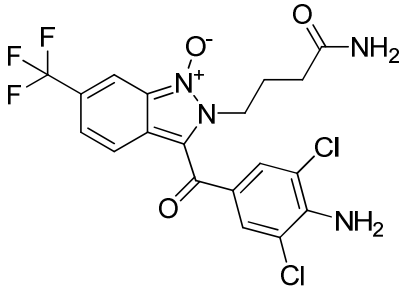
Yield 13.9 mg (30%). ESI-MS *m/z* = 406, $[M+H]^+$. HRMS (FAB) m/z calcd for $C_{20}H_{19}N_30_3F_3$ [M + H]+ 406.1379, found 406.1371

**4-[3-(4-Chloro-benzoyl)-1-oxy-6-triflouromethyl-indazol-2-yl]-butyramide 6(6,3,2)**



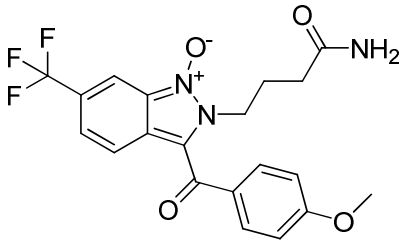
Yield (HPLC purified) 13.6 mg (28%). ESI-MS *m/z* = 426, $[M+H]^+$. HRMS (FAB) m/z calcd for $C_{19}H_{16}N_3O_3ClF_3$ [M + H]+ 426.0832, found 426.0823

**4-[3-(4-Amino-3,5-dichloro-benzoyl)-1-oxy-6-triflouromethyl-indazol-2-yl]-butyramide 6(6,3,3)**



Yield 34.3 mg (64%).ESI-MS *m/z* = 475, $[M+H]^+$. HRMS (FAB) m/z calcd for $C_{19}H_{16}N_4O_3Cl_2F_3$ [M + H]+ 475.0552, found 475.0578

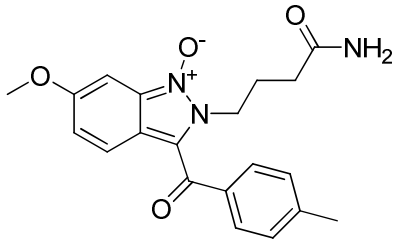
**4-[3-(4-Methoxy-benzoyl)-1-oxy-6-triflouromethyl-indazol-2-yl]-butyramide 6(6,3,5)**



Yield 32.8 mg (69%). ESI-MS *m/z* = 422, $[M+H]^+$. 1H NMR (300 MHz, DMSO-$d_6$) d ppm 2.03 - 2.20 (m, 4 H) 3.89 (s, 3 H) 4.80 (t, *J*=6.49 Hz, 2 H) 6.75 (br. s., 1 H) 7.10 - 7.21 (m, 3 H) 7.27 (br. s., 1 H) 7.49 (dd, *J*=9.12, 1.66 Hz, 1 H) 7.80 - 7.87 (m, 2 H) 8.15 (s, 1 H). $^{13}C$ NMR (300 MHz, DMSO-$d_6$) δ: 180.7, 172.9, 163.3, 131.8, 131.0, 127.0, 126.3, 125.9, 125.5, 122.5, 120.0,

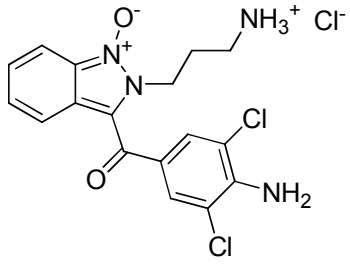
117.3, 116.1, 114.1, 55.6, 45.4, 32.0, 23.9. HRMS (FAB) m/z calcd for $C_{20}H_{19}N_3O_4F_3$ [M + H]+ 422.1328, found 422.1346

**4-[6-Methoxy-3-(4-methyl-benzoyl)-1-oxy-indazol-2-yl]-butyramide 6(6,4,1)**



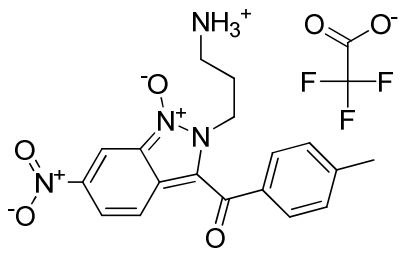
Yield (HPLC purified) 8.5 mg (21%). ESI-MS *m/z* = 368, $[M+H]^+$. HRMS (FAB) m/z calcd for $C_{20}H_{22}N_3O_4$ [M + H]+ 368.1610, found 368.1595

**3-[3-(4-Amino-3,5-dichloro-benzoyl)-1-oxy-indazol-2-yl]-propyl-ammonium chloride 6(7,1,3)**



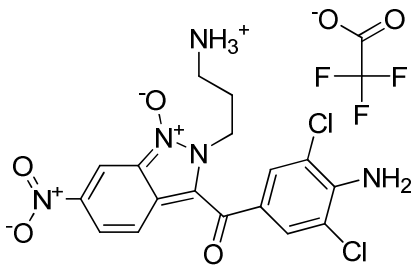
Yield 53.0 mg (81%). ESI-MS *m/z* = 379, $[M+H]^+$. HRMS (FAB) m/z calcd for $C_{17}H_{17}N_4O_2Cl_2$ [M + H]+ 379.0729, found 379.0719

**2-(3-Ammoniopropyl)-3-(4-methylbenzoyl)-6-nitro-2H-indazole 1-oxide 2,2,2-trifluoroacetate 6(7,2,1)**



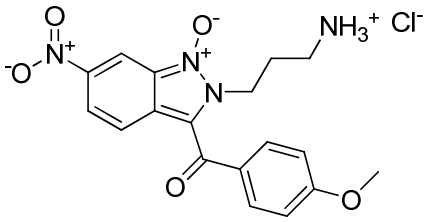
Yield 68.5 mg (93%). ESI-MS *m/z* = 355, $[M+H]^+$. HRMS (FAB) m/z calcd for $C_{18}H_{19}N_4O_4$ [M + H]+ 355.1406, found 355.1404

**3-(4-Amino-3,5-dichlorobenzoyl)-2-(3-ammoniopropyl)-6-nitro-2H-indazole 1-oxide 2,2,2-trifluoroacetate 6(7,2,3)**



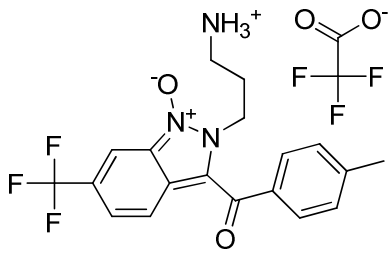
Yield 83.7 mg (99%). ESI-MS *m/z* = 424, $[M+H]^+$. HRMS (FAB) m/z calcd for $C_{17}H_{16}N_5O_4Cl_2$ [M + H]+ 424.0579, found 424.0534

**3-[3-(4-Methoxy-benzoyl)-6-nitro-1-oxy-indazol-2-yl]-propyl-ammonium chloride 6(7,2,5)**



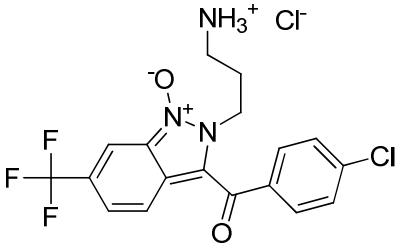
Yield 59.1 mg (92%). ESI-MS m/z = 371, $[M+H]^+$. 1H NMR (300 MHz, DMSO-$d_6$) d ppm 2.20 - 2.33 (m, 2 H) 2.95 (br. s., 2 H) 3.87 - 3.92 (m, 3 H) 4.81 (t, J=6.77 Hz, 2 H) 7.11 - 7.22 (m, 3 H) 7.76 - 7.94 (m, 6 H) 7.98 (dd, J=9.39, 2.21 Hz, 1 H). $^{13}$C NMR (300 MHz, DMSO-$d_6$) δ: 181.53, 164.32, 145.88, 132.69, 131.43, 127.79, 123.10, 121.41, 121.02, 118.86, 114.98, 112.08, 56.45, 44.61, 37.22, 26.99. HRMS (FAB) m/z calcd for $C_{18}H_{19}N_4O_5$ [M + H]+ 371.1355, found 371.1402

**2-(3-Ammoniopropyl)-3-(4-methylbenzoyl)-6-(trifluoromethyl)-2H-indazole 1-oxide 2,2,2-trifluoroacetate 6(7,3,1)**



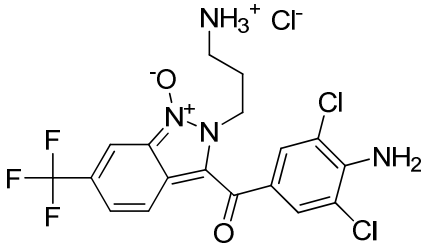
Yield 65.9 mg (81%). ESI-MS *m/z* = 378, $[M+H]^+$. HRMS (FAB) m/z calcd for $C_{19}H_{19}N_3O_2F_3$ [M + H]+ 378.1429, found 378.1430

**3-[3-(4-Chloro-benzoyl)-1-oxy-6-triflouromethyl-indazol-2-yl]-propyl-ammonium chloride 6(7,3,2)**



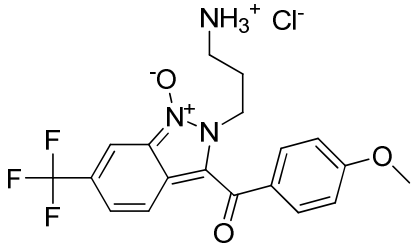
Yield 65.4 mg (90%). ESI-MS *m/z* = 398, $[M+H]^+$. HRMS (FAB) m/z calcd for $C_{18}H_{16}N_3O_2ClF_3$ [M + H]+ 398.0883, found 398.0854

**3-[3-(4-Amino-3,5-dichloro-benzoyl)-1-oxy-6-trifluoromethyl-indazol-2-yl]-propyl-ammonium chloride 6(7,3,3)**



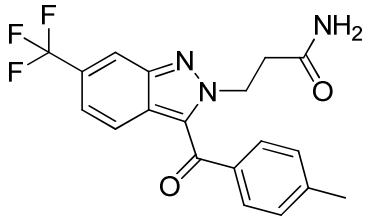
Yield 63.6 mg (84%). ESI-MS *m/z* = 447, $[M+H]^+$. HRMS (FAB) m/z calcd for $C_{18}H_{16}N_4O_2Cl_2F_3$ [M + H]+ 447.0602, found 447.0580

**3-[3-(4-Methoxy-benzoyl)-1-oxy-6-triflouromethyl-indazol-2-yl]-propyl-ammonium chloride 6(7,3,5)**



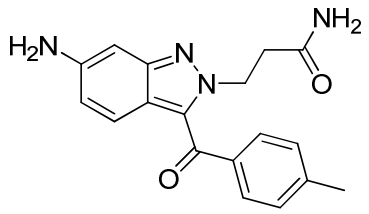
Yield 67.0 mg (99%). ESI-MS *m/z* = 394, $[M+H]^+$. HRMS (FAB) m/z calcd for $C_{19}H_{19}N_3O_3F_3$ [M + H]+ 394.1379, found 394.1389

**3-[3-(4-Methyl-benzoyl)-6-trifluoromethyl-indazol-2-yl]-propionamide 8(1,3,1)**



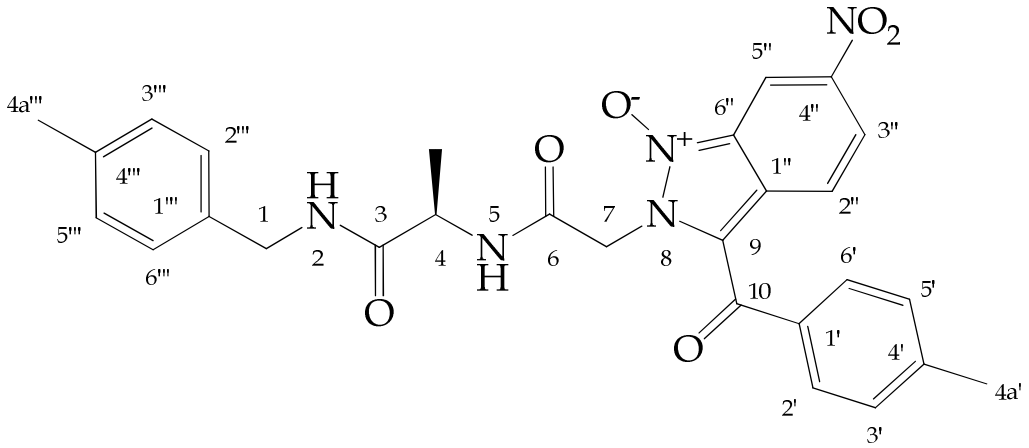
Yield 10.8 mg (48%). ESI-MS *m/z* = 376, $[M+H]^+$. $^1$H NMR (300 MHz, DMSO-$d_6$) δ: 8.26 (s, 1 H) 7.71 (d, *J*=8.01 Hz, 2 H) 7.42 (d, *J*=8.01 Hz, 3 H) 7.38 (dd, *J*=8.98, 1.52 Hz, 1 H) 7.16 (d, *J*=8.84 Hz, 1 H) 6.88 (br. s., 1 H) 4.94 (t, *J*=6.77 Hz, 2 H) 2.85 (t, *J*=6.91 Hz, 2 H) 2.45 (s, 3 H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ: 185.3, 171.2, 145.0, 144.5, 135.2, 132.7, 130.0, 129.5, 123.5, 122.2, 119.6, 119.5, 116.5, 116.4, 49.1, 35.5, 21.4. HRMS (FAB) *m/z* calcd for $C_{19}H_{17}F_3N_3O_2$ [M + H]$^+$ 376.1273, found 376.1287

**3-[6-Amino-3-(4-methyl-benzoyl)-indazol-2-yl]-propionamide 8(1,5,1)**



Yield (HPLC purified) x mg (x%). ESI-MS m/z = 323, [M+H]+. 1H NMR (300 MHz, DMSO-d6) δ: 7.67 (d, J=8.01 Hz, 2 H) 7.38 (d, J=8.29 Hz, 3 H) 6.85 (br. s., 1 H) 6.54 - 6.65 (m, 3 H) 5.26 (br. s., 2 H) 4.73 (t, J=7.04 Hz, 2 H) 2.74 (t, J=7.18 Hz, 2 H) 2.44 (s, 3 H). 13C NMR (75 MHz, DMSO-d6) δ: 185.4, 171.3, 148.9, 146.9, 143.6, 135.8, 131.3, 129.6, 129.1, 120.0, 118.9, 116.5, 94.2, 48.0, 35.8, 21.3. HRMS (FAB) *m/z* calcd for $C_{18}H_{19}N_4O_2$ $[M + H]^+$ 323.1518, found 323.1523

**(R)-3-(4-methylbenzoyl)-2-(2-(1-(4-methylbenzylamino)-1-oxopropan-2-ylamino)-2-oxoethyl)-6-nitro-2H-indazole 1-oxide 6(8,2,1)**

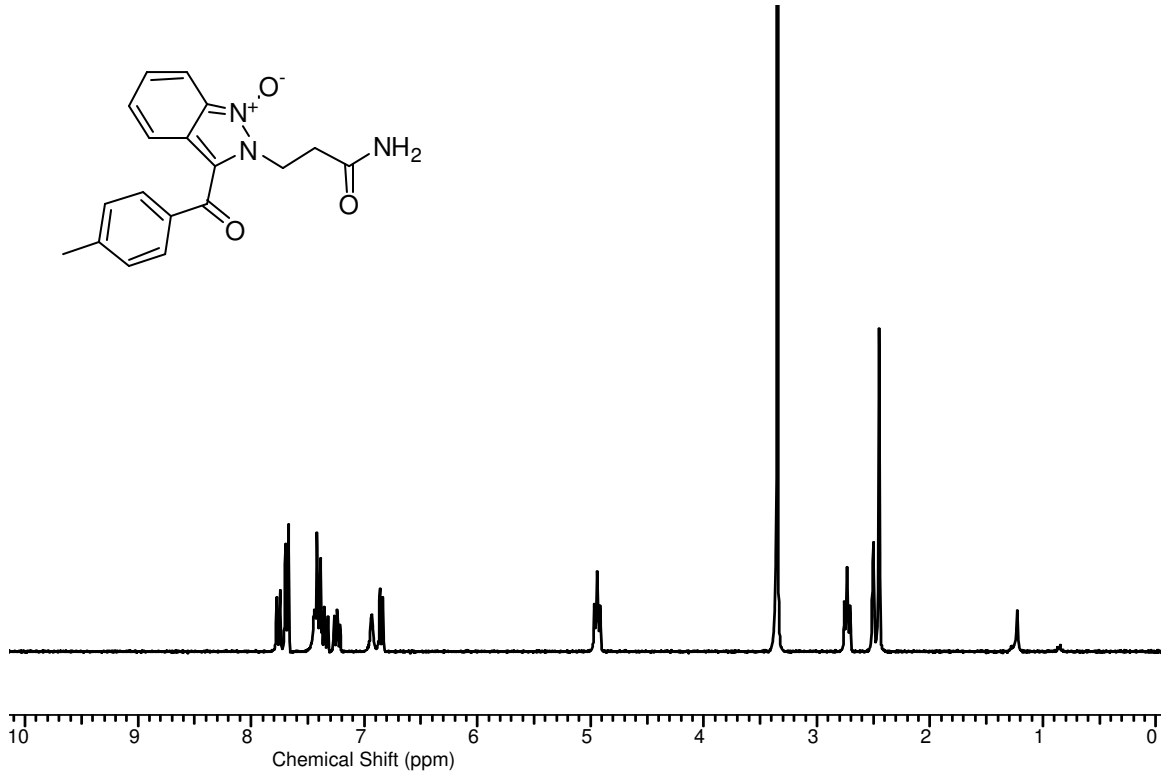


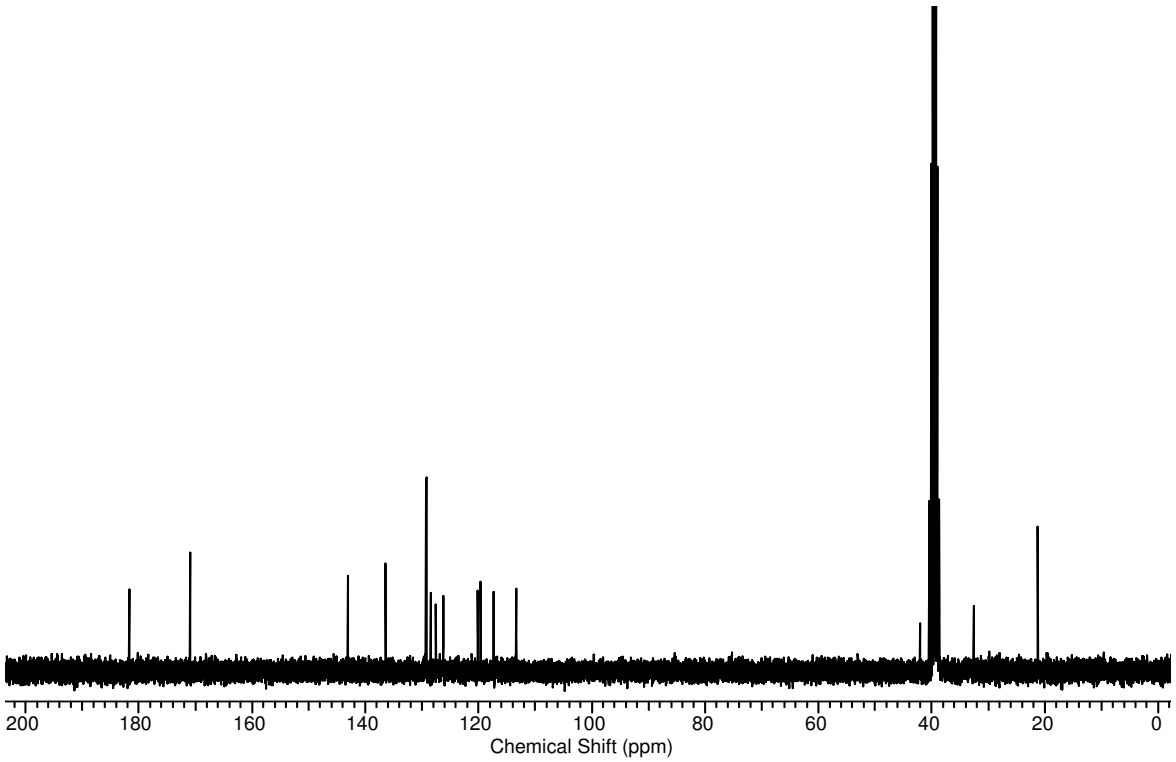

$^1$H NMR (600 MHz, DMSO): δ ppm 8.84 (1H, d, $^3J_{H\text{-}5,H\text{-}4}$=7.4 Hz, H-5), 8.61 (1H, d, $^3J_{H\text{-}5'',H\text{-}3''}$=1.9 Hz, H-5''), 8.39 (1H, t, $^3J_{H\text{-}2,CH2\text{-}1}$=6.0 Hz, H-2), 8.00 (1H, dd, $^3J_{H\text{-}3'',H\text{-}2''}$=9.5 Hz, $^3J_{H\text{-}3'',H\text{-}5''}$=1.9 Hz, H-3''), 7.67 (2H, d, $^3J_{H\text{-}2',H\text{-}3'}$=8.1 Hz, H-2' and H-6'), 7.43 (2H, d, $J_{H\text{-}3',H\text{-}2'}$=8.1 Hz, H-3' and H-5'), 7.15 (1H, d, $^3J_{H\text{-}2'',H\text{-}3''}$=9.5 Hz, H-2''), 7.09 (2H, d, $^3J_{H\text{-}2''',H\text{-}3'''}$=7.9 Hz, H-2''' and H-6'''), 7.04 (2H, d, $^3J_{H\text{-}3''',H\text{-}2'''}$=7.9 Hz, H-3''' and H-5'''), 5.61 (1H, d, $^2J_{Ha\text{-}7,Hb\text{-}7}$=16.4 Hz, $H_a$-7), 5.53 (1H, d, $^2J_{Ha\text{-}7,Hb\text{-}7}$=16.4 Hz, $H_b$-7), 4.31 (1H, dq, $^3J_{H\text{-}4,H\text{-}4a}$=7.2 Hz, $^3J_{H\text{-}4,H\text{-}5}$=7.4 Hz H-4), 4.24 (2H, d, $^3J_{CH2\text{-}1,H\text{-}2}$=6.0 Hz, $CH_2$-1), 2.46 (3H, 2, $CH_3$-$4_a$'), 2.23 (3H, s, $CH_3$-$4_a$'''), 1.27 (3H, d, $^3J_{H\text{-}4a,H\text{-}4}$=7.2 Hz, $CH_3$-$4_a$).

$^{13}$C NMR (150 MHz, DMSO): δ ppm 181.67 (C-10), 171.57 (C-3), 163.64 (C-6), 145.29 (C-4''), 143.90 (C-4'), 136.09 (C-1'''), 135.74 (C-4'), 135.62 (C-1'), 129.50 (C-3', C-5'), 129.40 (C-2', C-6'), 128.79 (C-3''', C-5'''), 126.96 (C-2''', C-6'''), 126.77 (C-6''), 122.24 (C-2''), 121.08 (C-3''),

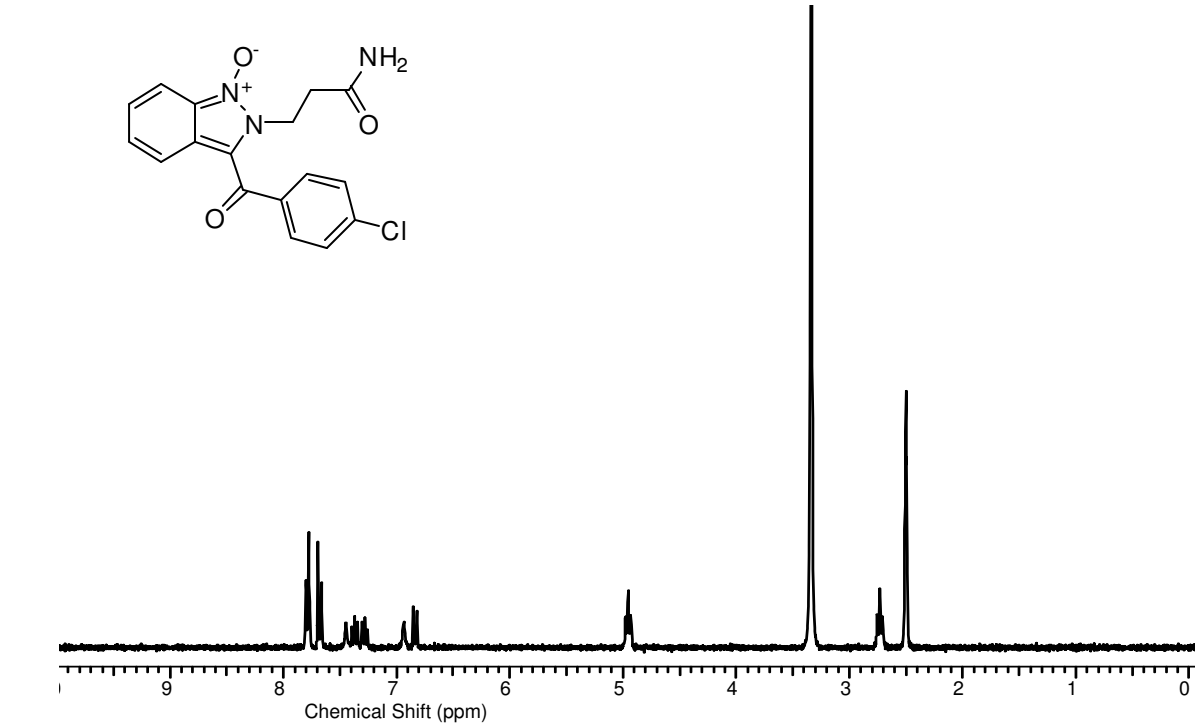
120.05 (C-1''), 118.23 (C-9), 111.54 (C-5''), 48.76 (C-4), 47.91 (C-7), 41.71 (C-1), 21.35 (C-$4_a$'), 20.65 (C-$4_a$'''), 18.43 (C-$4_a$).

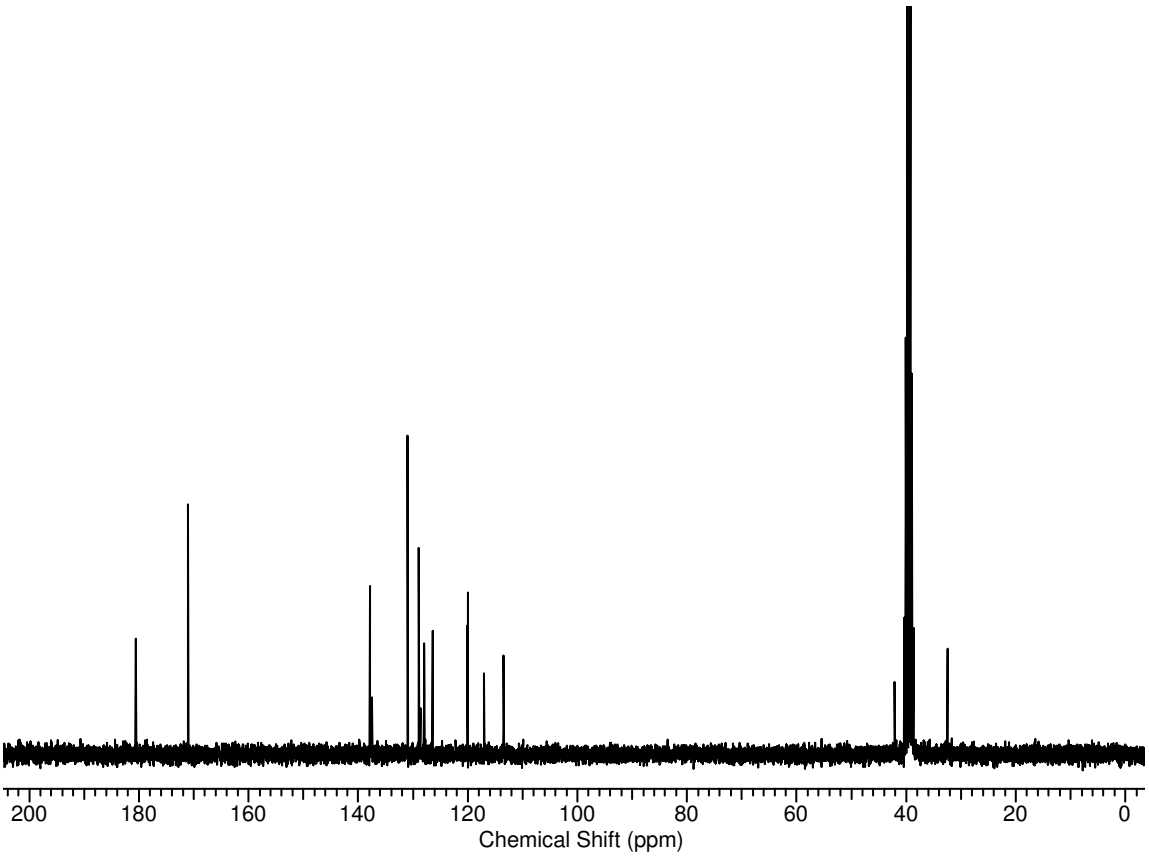
**$^{1}$H and $^{13}$C NMR spectra ($d_6$-DMSO) for compound 6(1,1,1)**



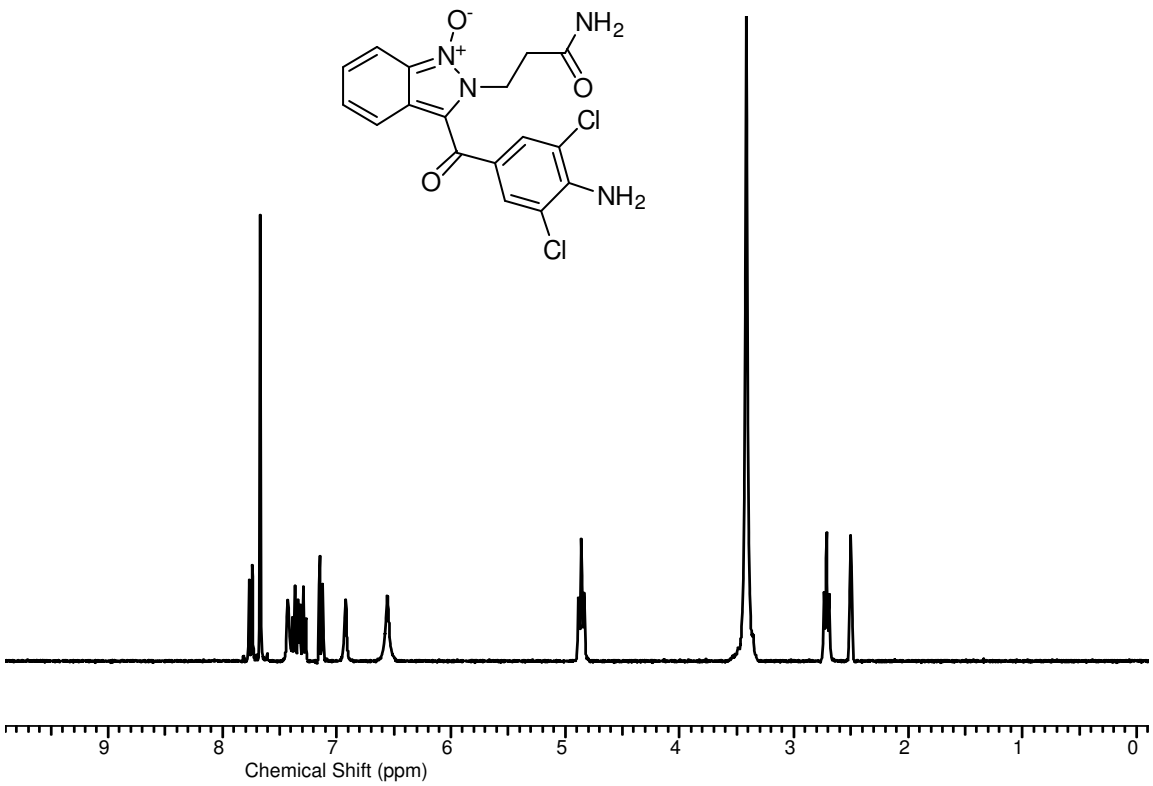



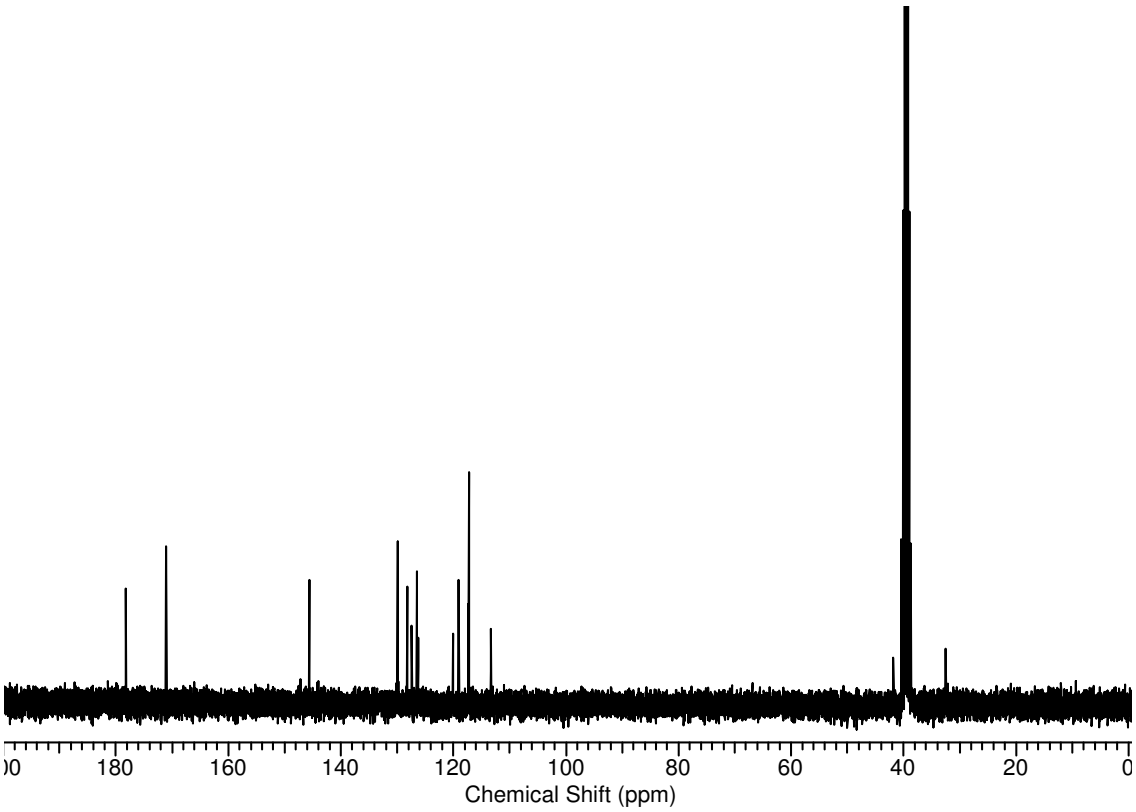
**$^{1}$H and $^{13}$C NMR spectra ($d_6$-DMSO) for compound 6(1,1,2)**



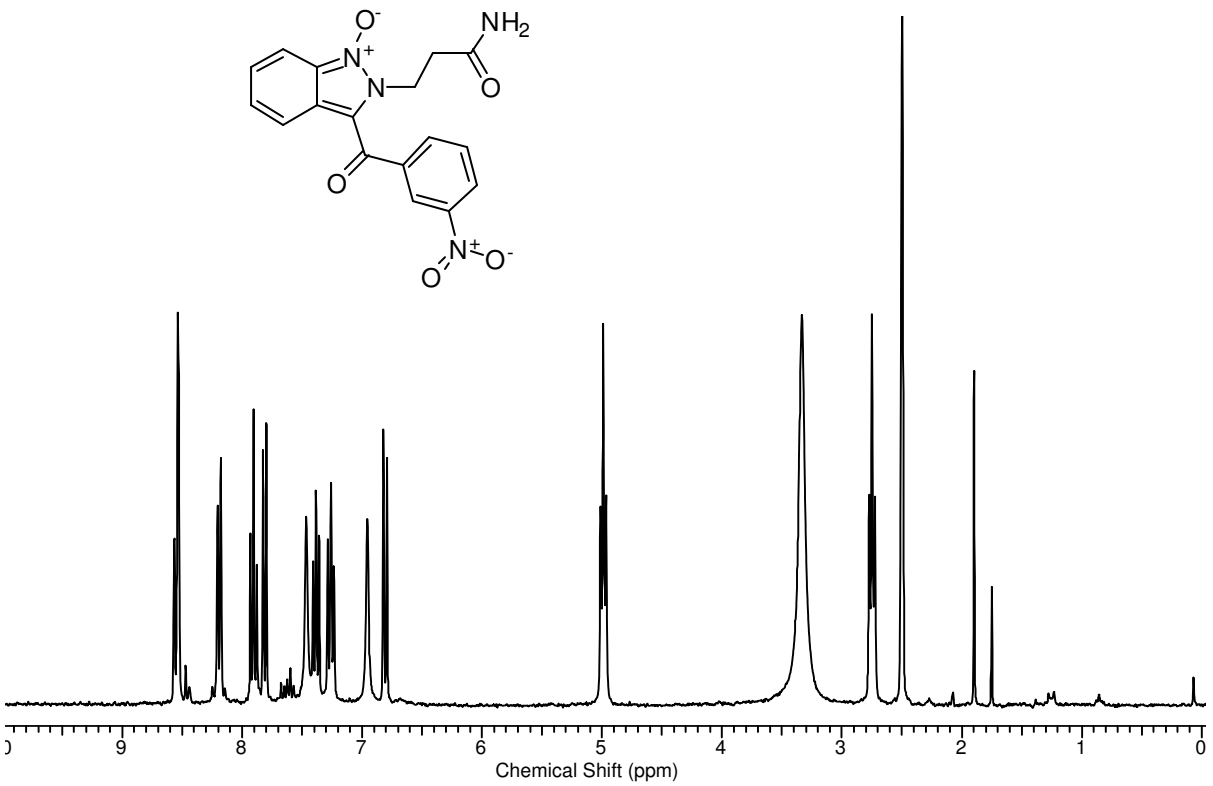



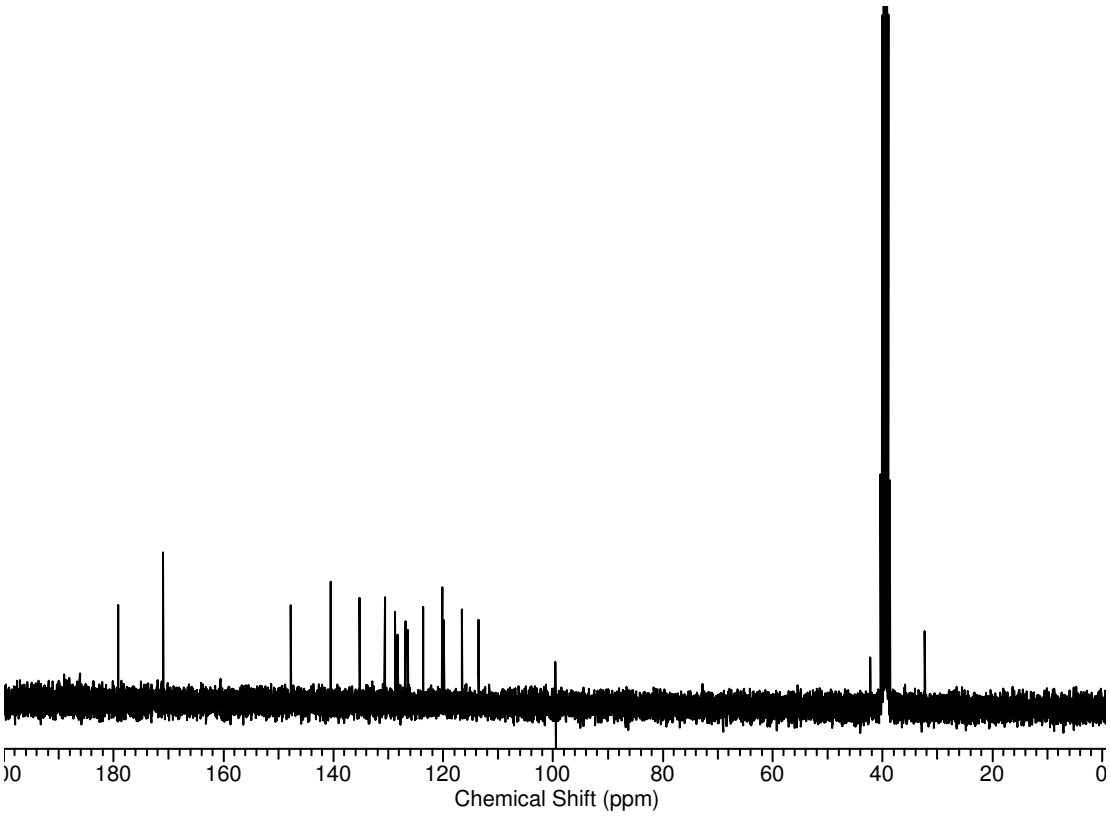
**$^{1}H$ and $^{13}C$ NMR spectra ($d_6$-DMSO) for compound 6(1,1,3)**



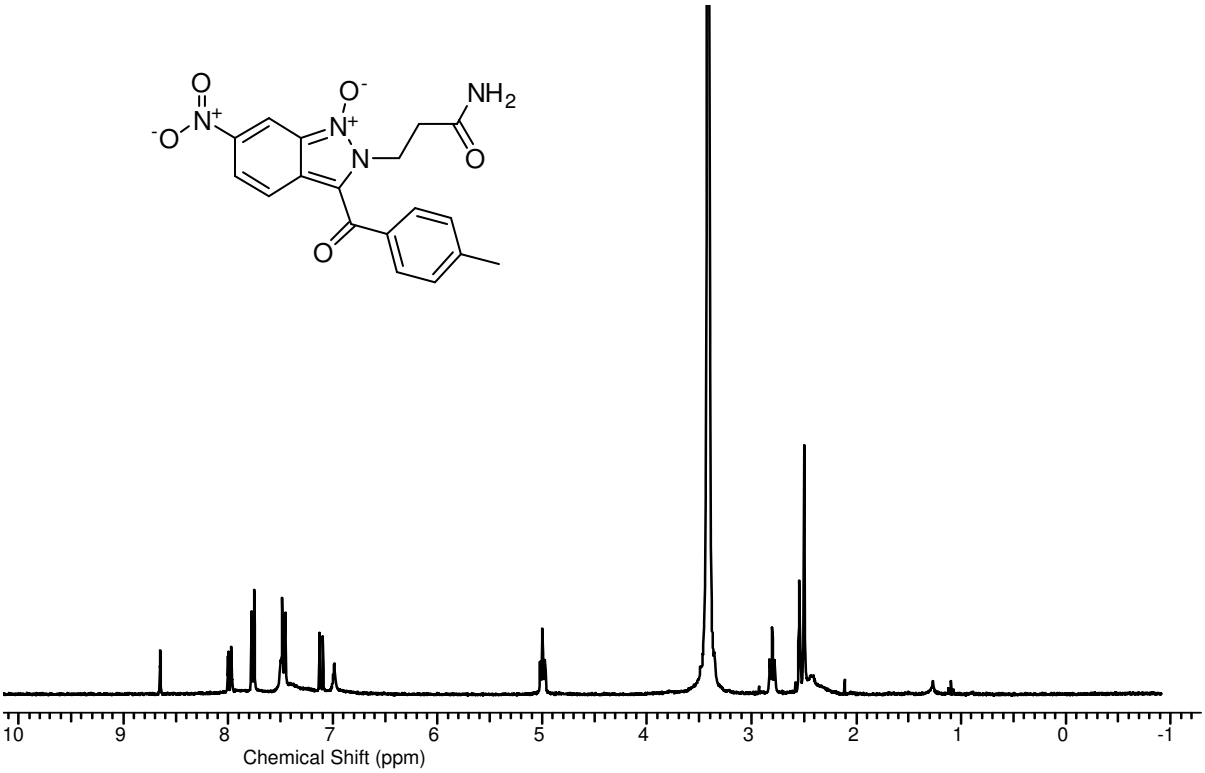



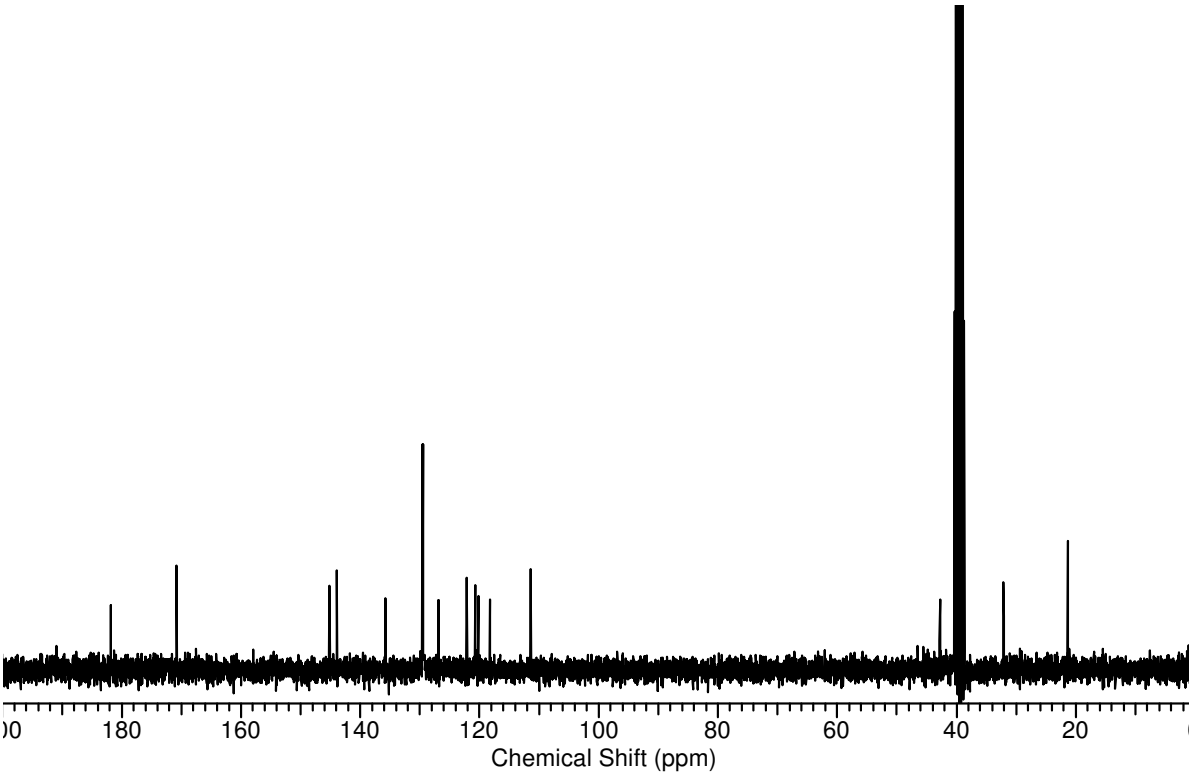
**$^{1}H$ and $^{13}C$ NMR spectra ($d_6$-DMSO) for compound 6(1,1,4)**



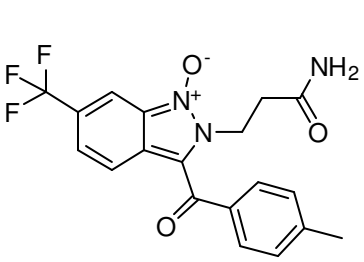



**$^{1}H$ and $^{13}C$ NMR spectra ($d_6$-DMSO) for compound 6(1,2,1)**



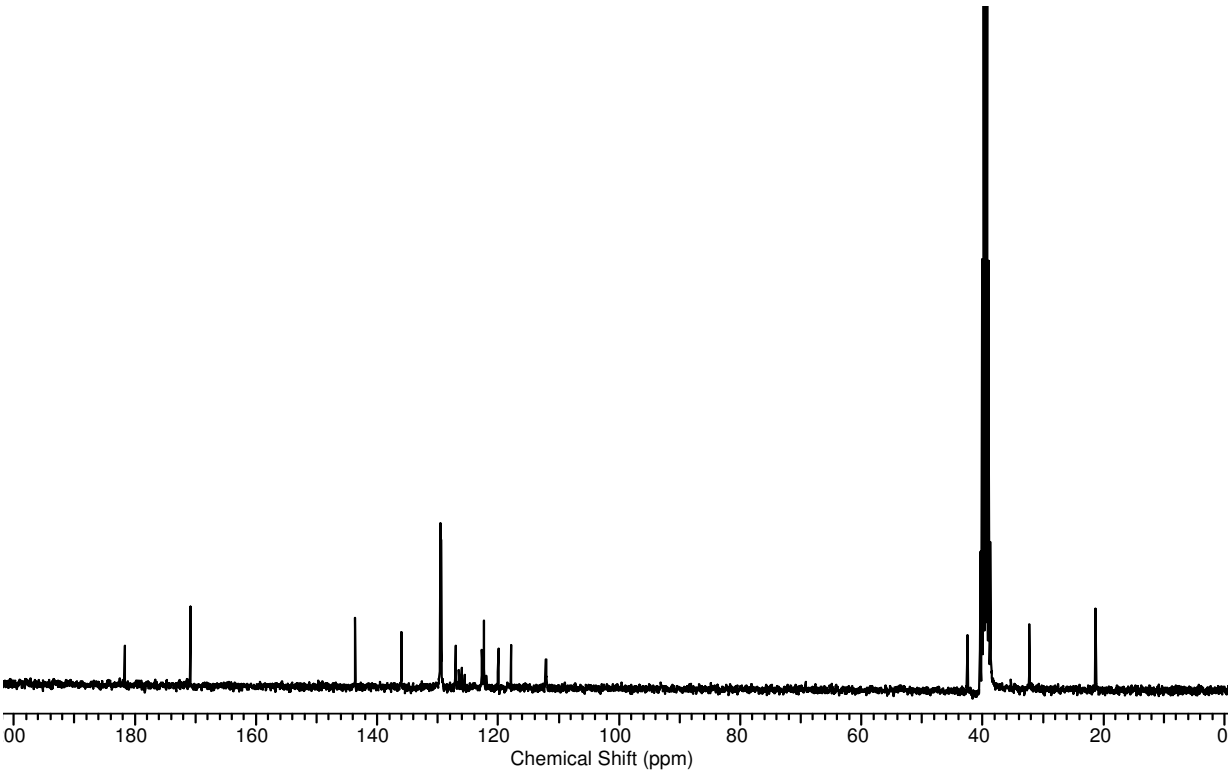



**$^{1}H$ and $^{13}C$ NMR spectra ($d_6$-DMSO) for compound 6(1,3,1)**

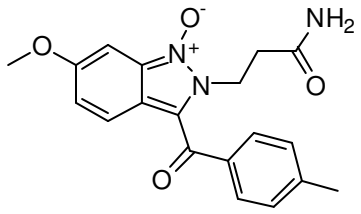






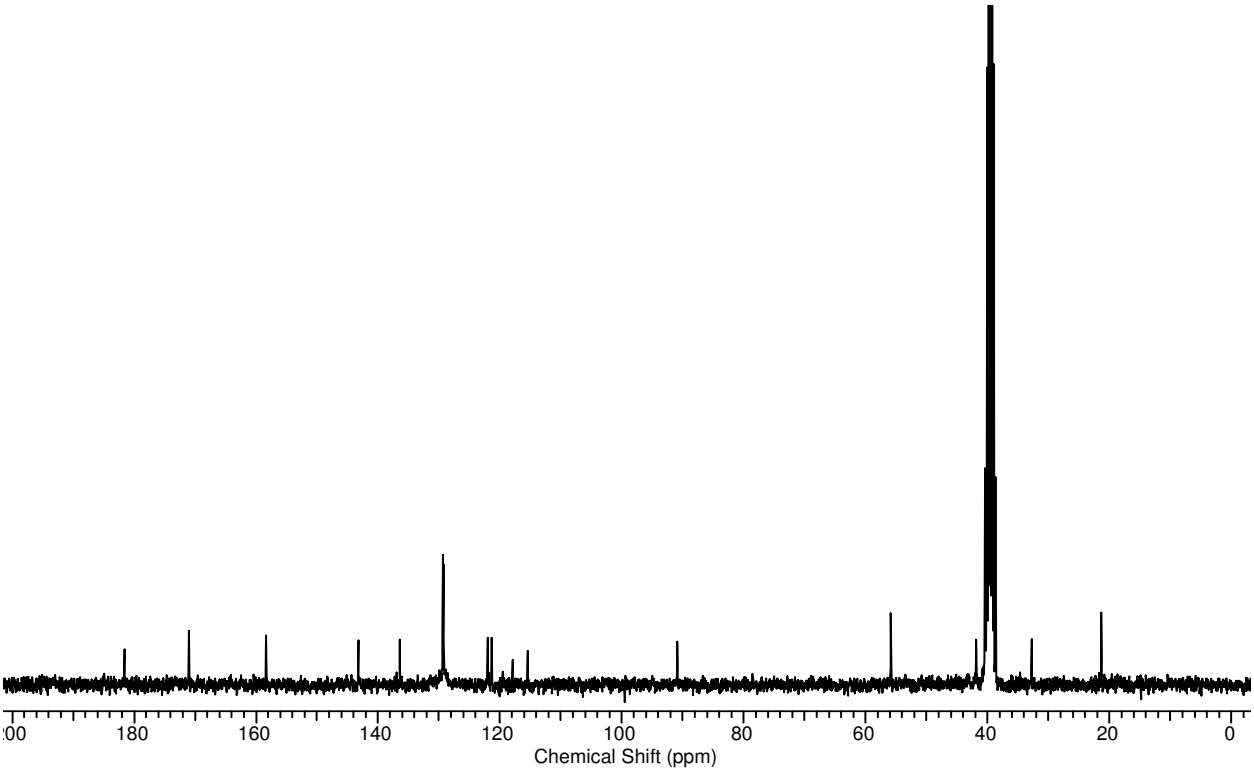


**$^{1}$H and $^{13}$C NMR spectra ($d_6$-DMSO) for compound 6(1,4,1)**

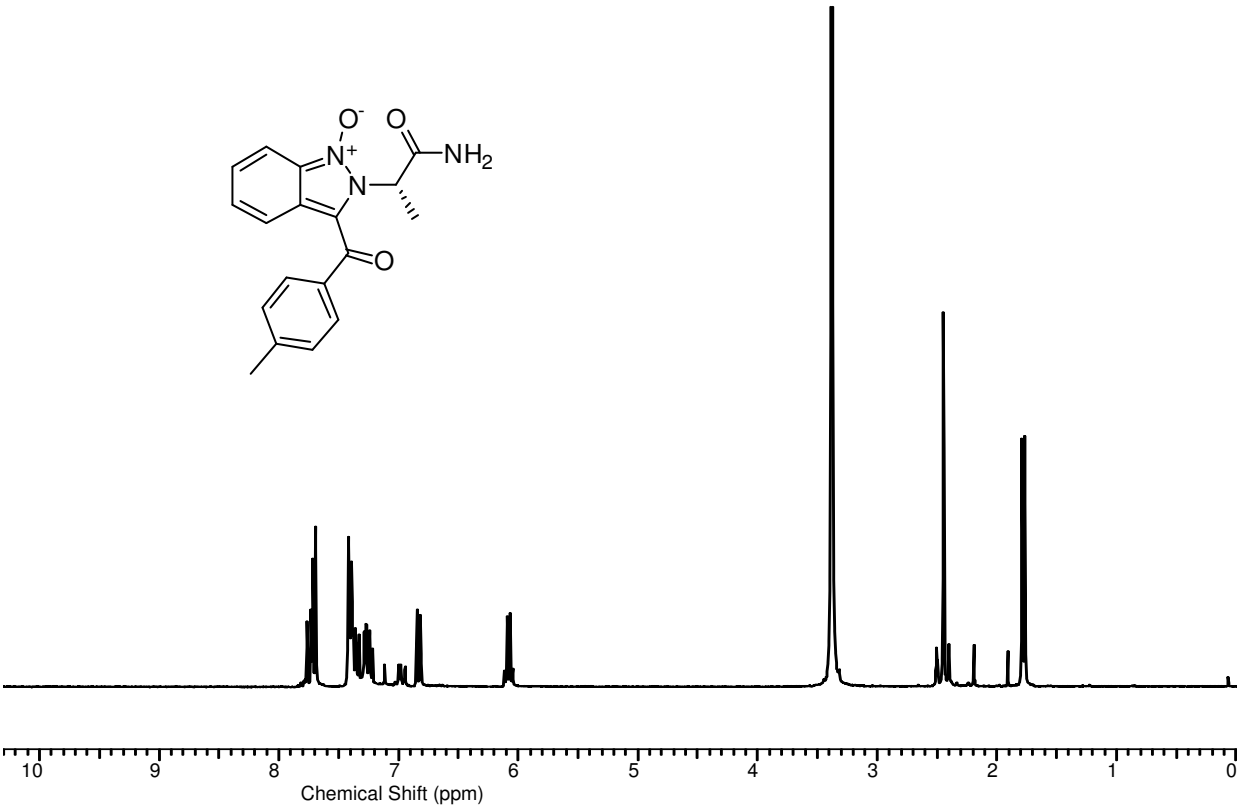


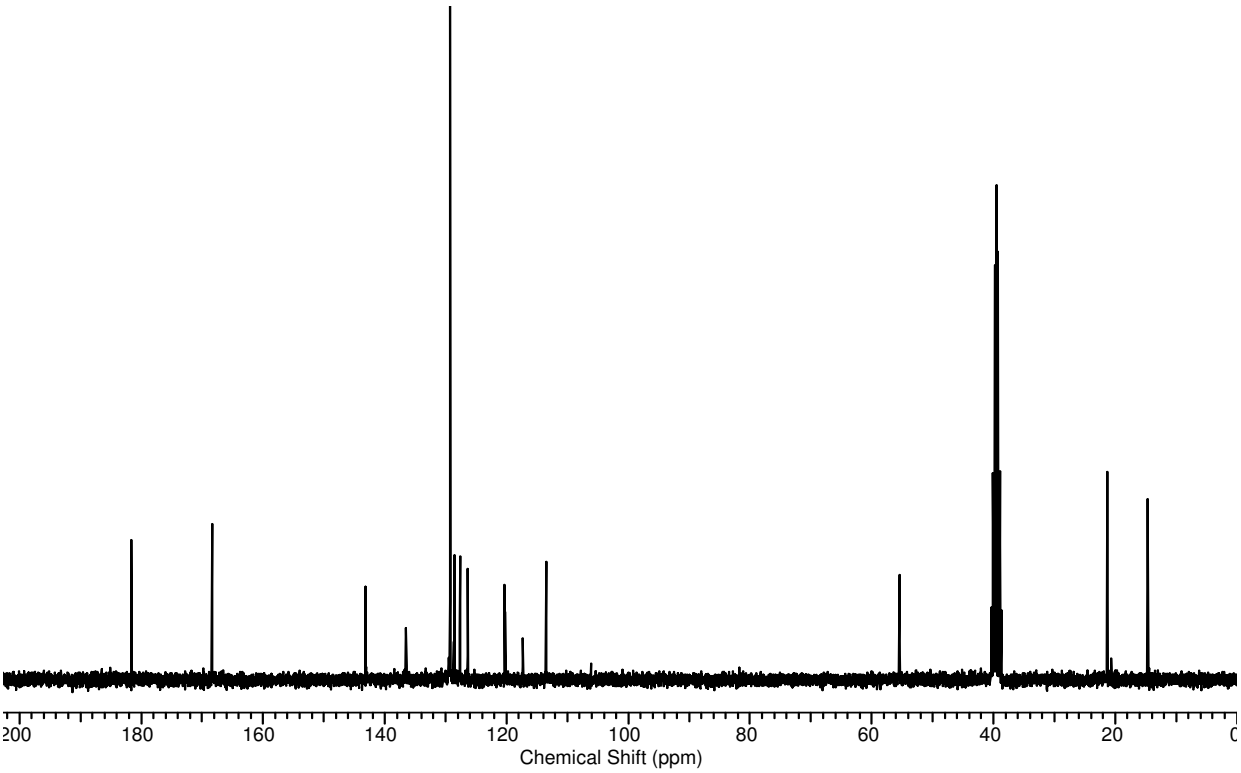




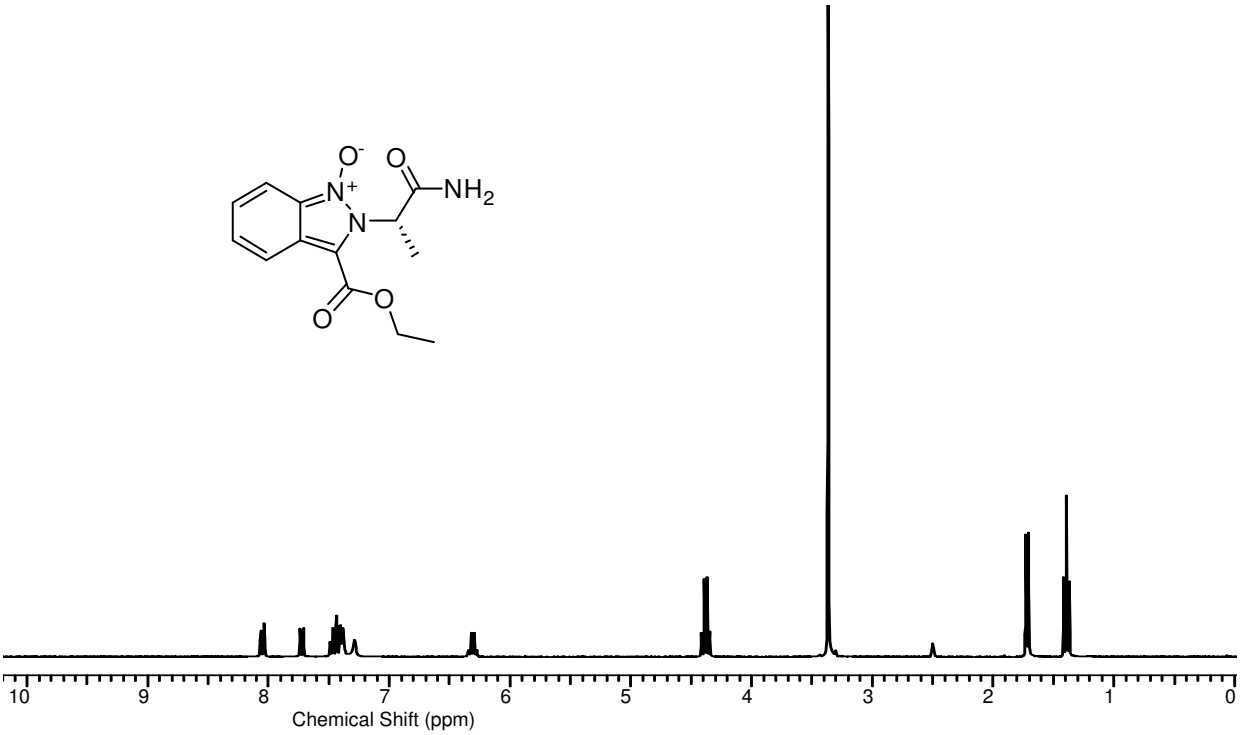


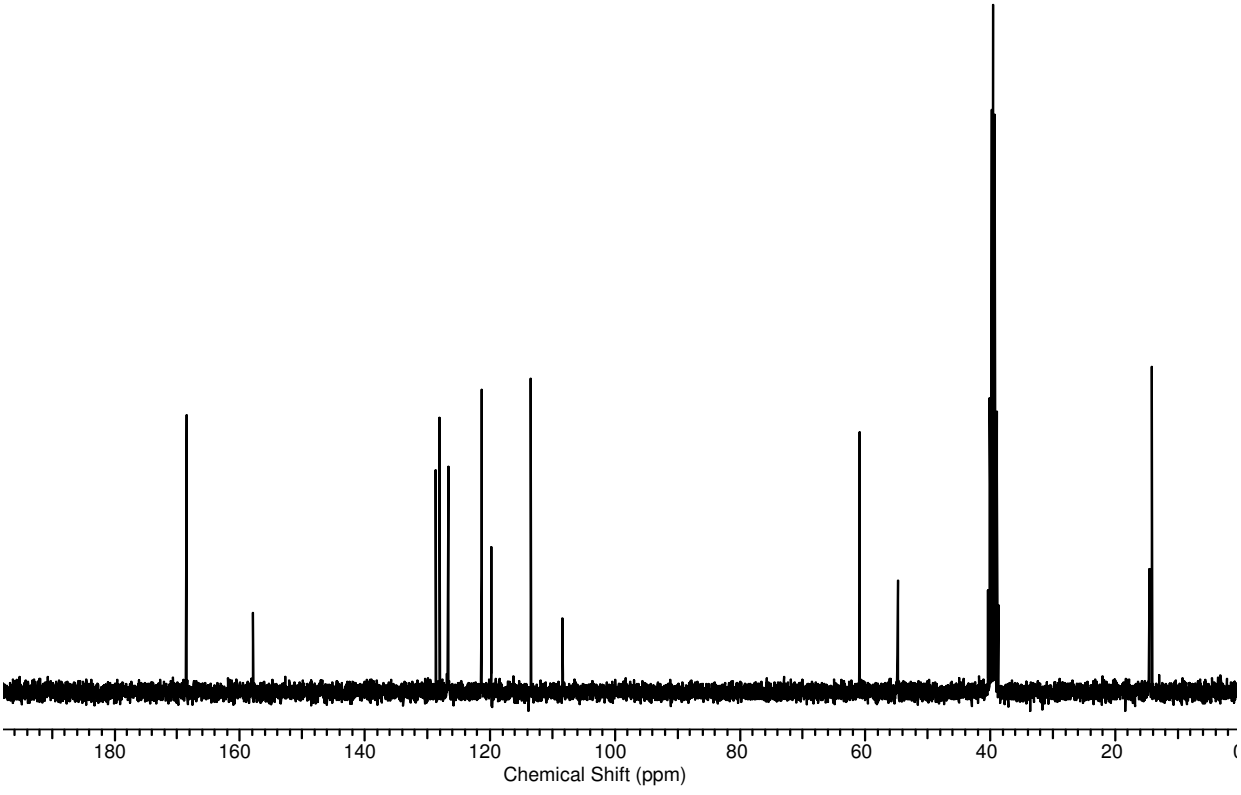
**$^{1}$H and $^{13}$C NMR spectra ($d_6$-DMSO) for compound 6(2,1,1)**



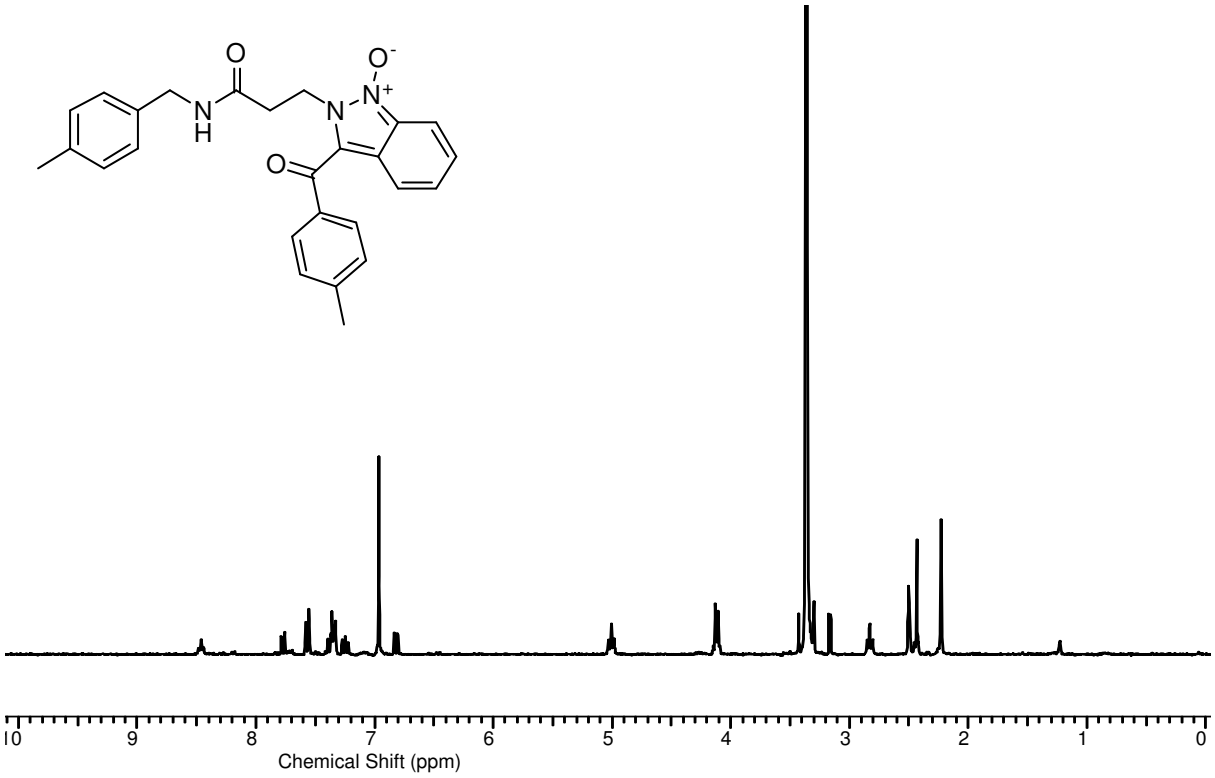



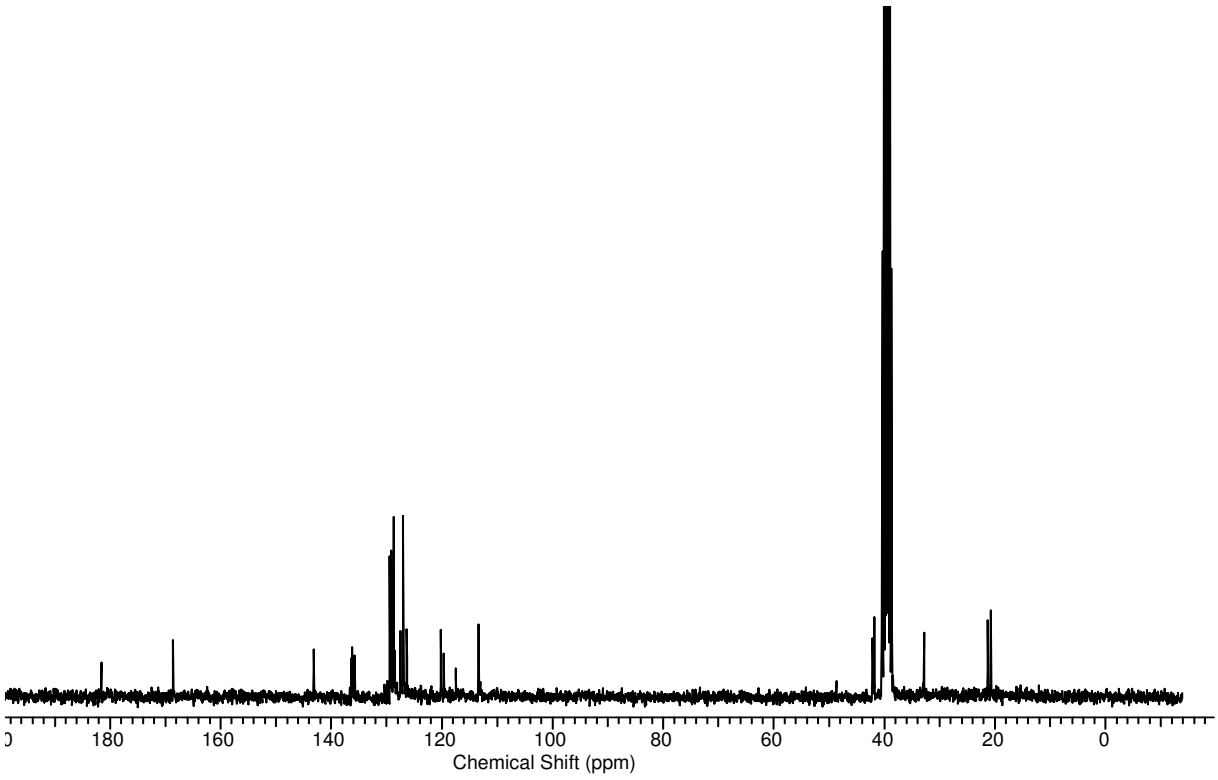
**$^{1}H$ and $^{13}C$ NMR spectra ($d_6$-DMSO) for compound 6(2,1,5)**



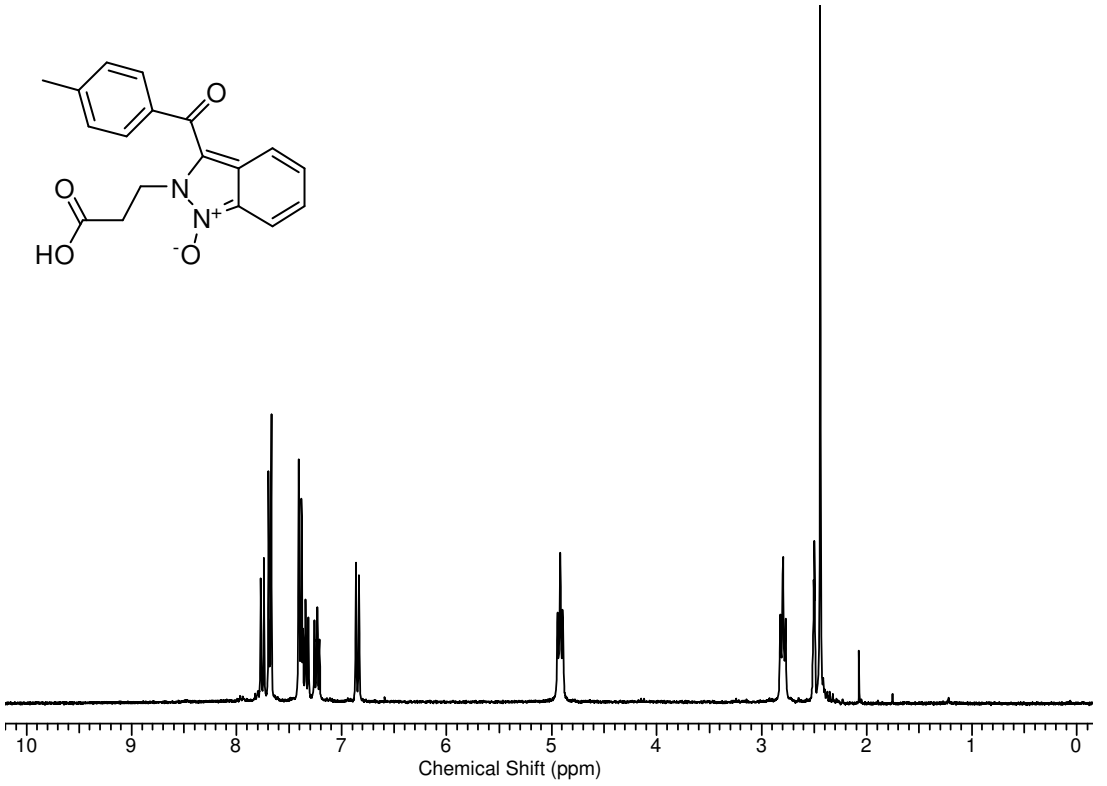



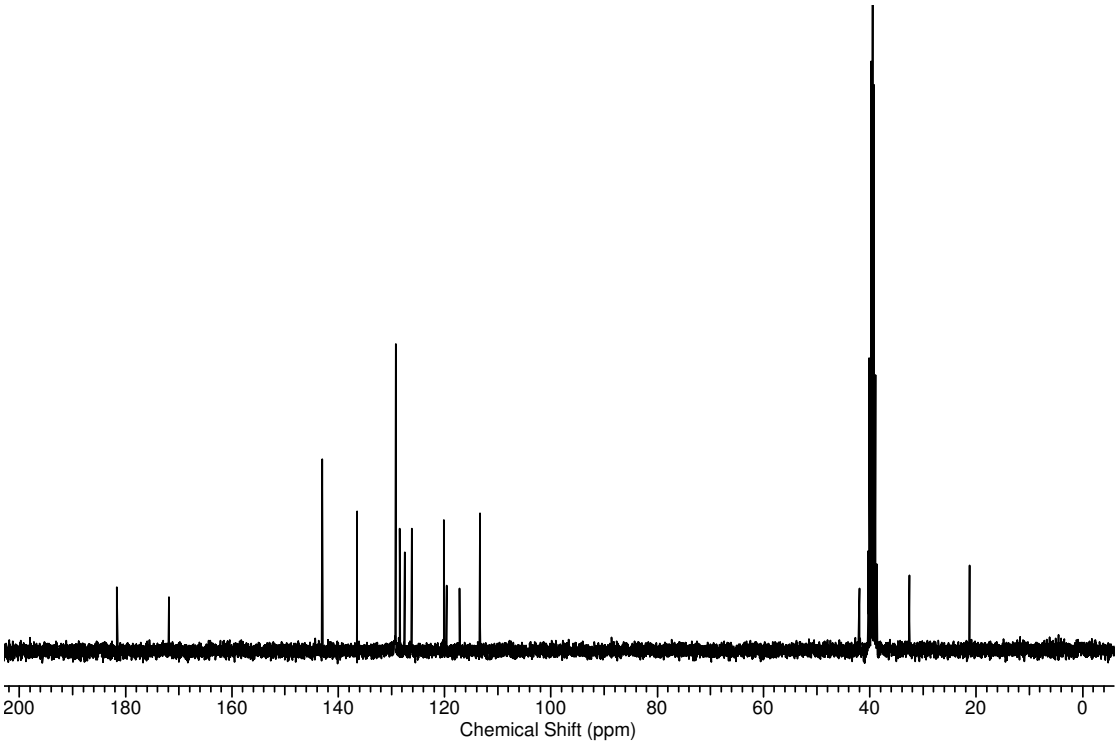
**$^{1}H$ and $^{13}C$ NMR spectra ($d_6$-DMSO) for compound 6(3,1,1)**



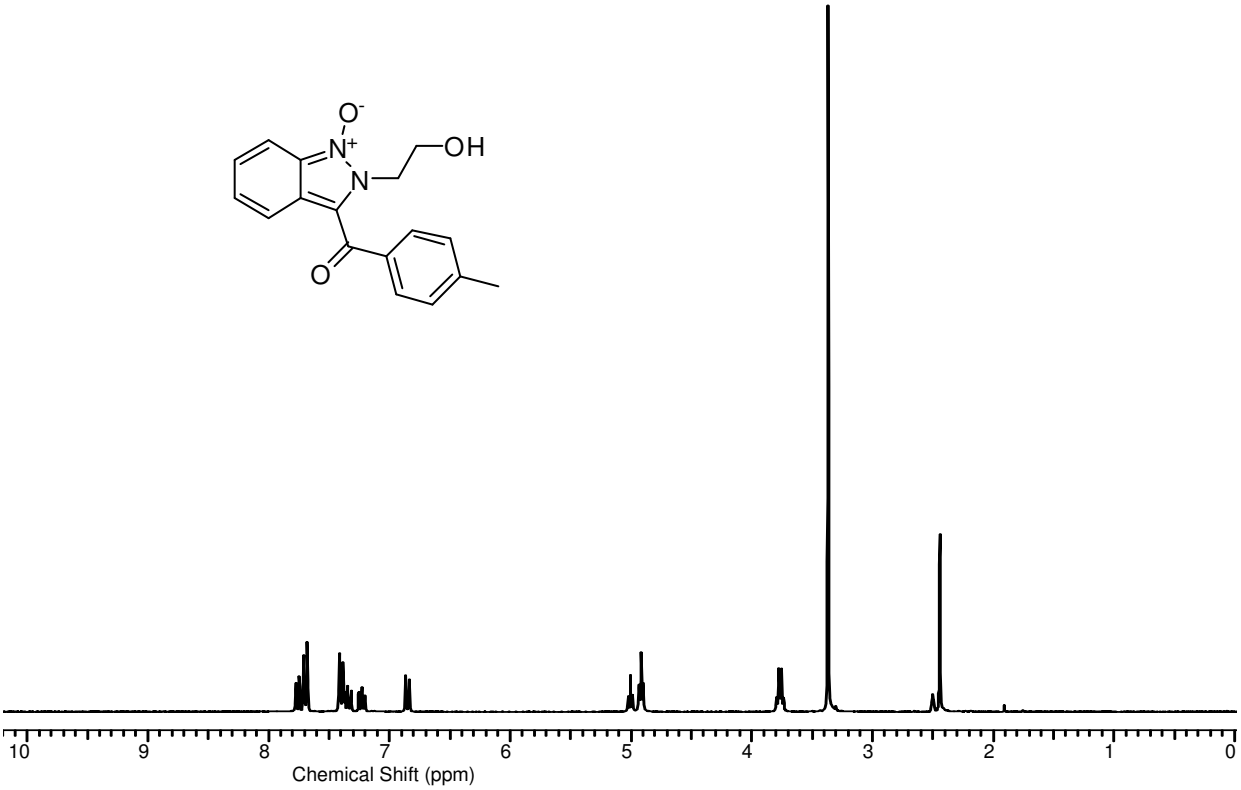



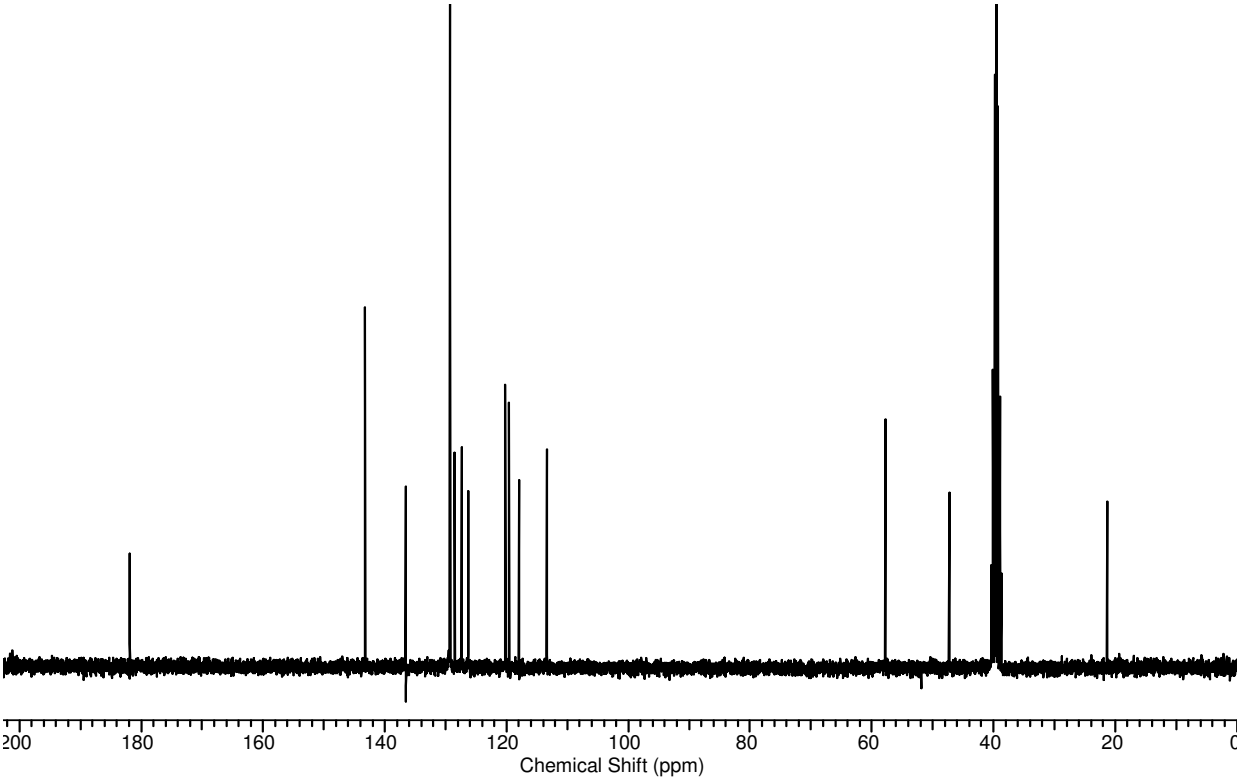
**$^{1}$H and $^{13}$C NMR spectra ($d_6$-DMSO) for compound 6(4,1,1)**



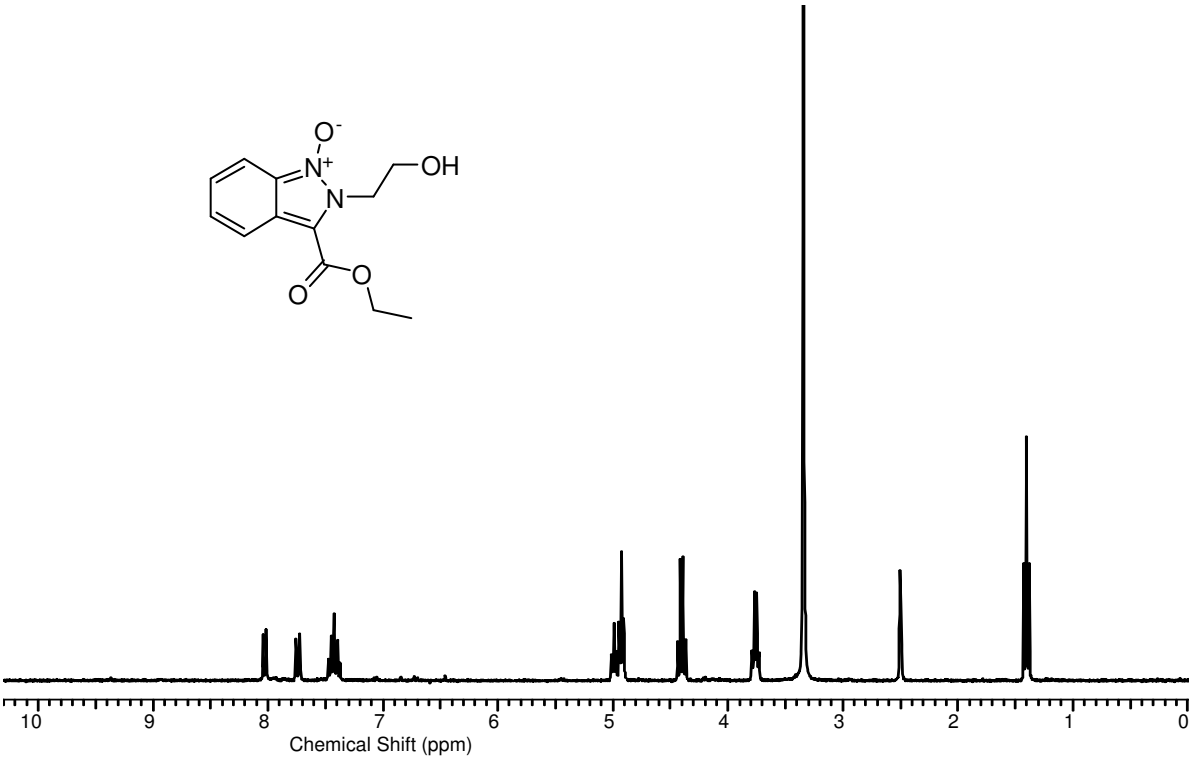



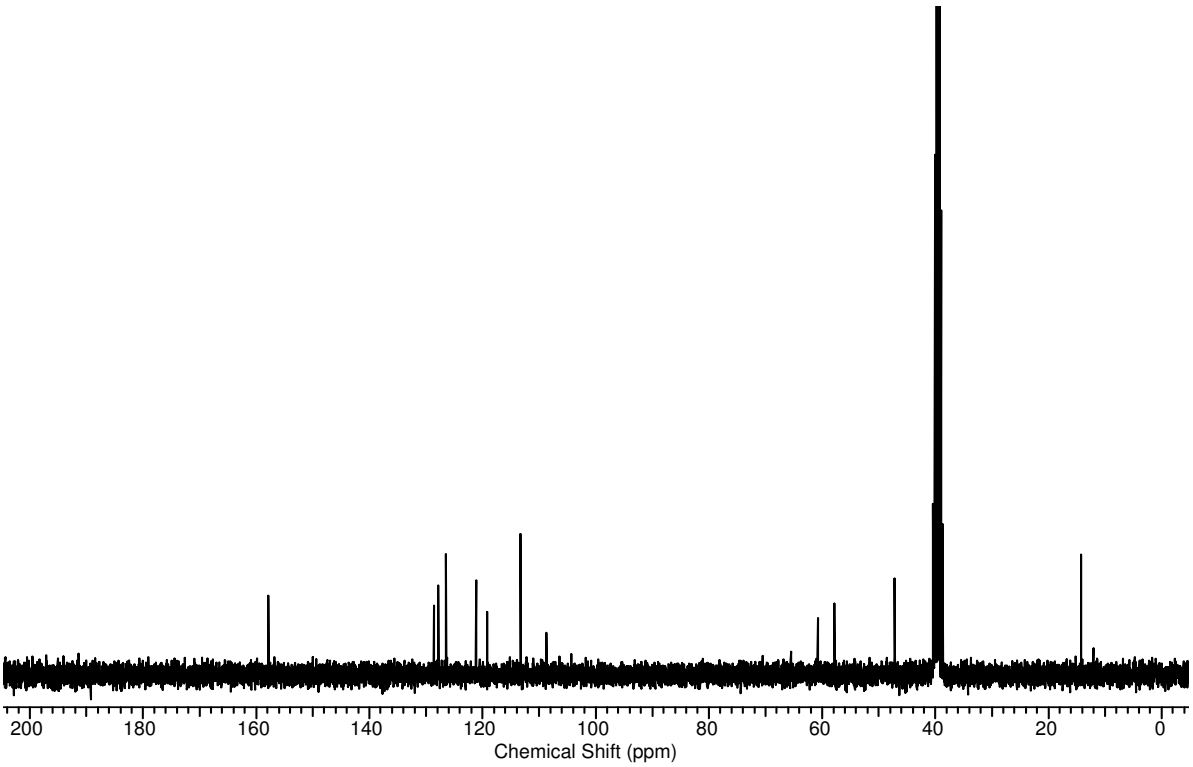
**$^{1}$H and $^{13}$C NMR spectra ($d_6$-DMSO) for compound 6(5,1,1)**



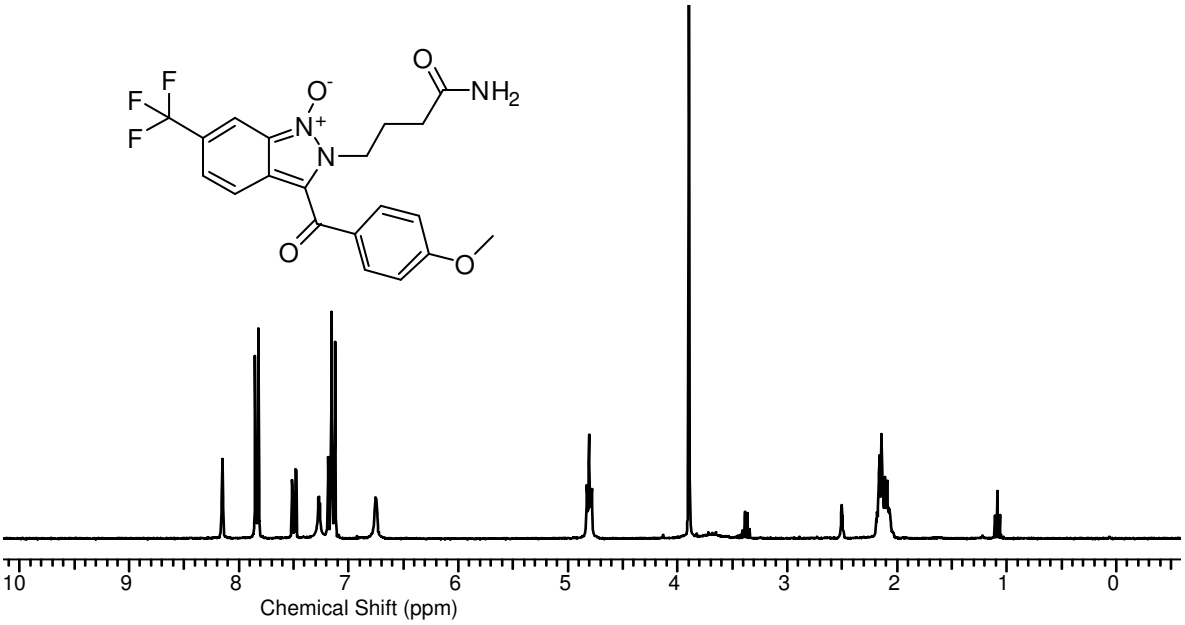



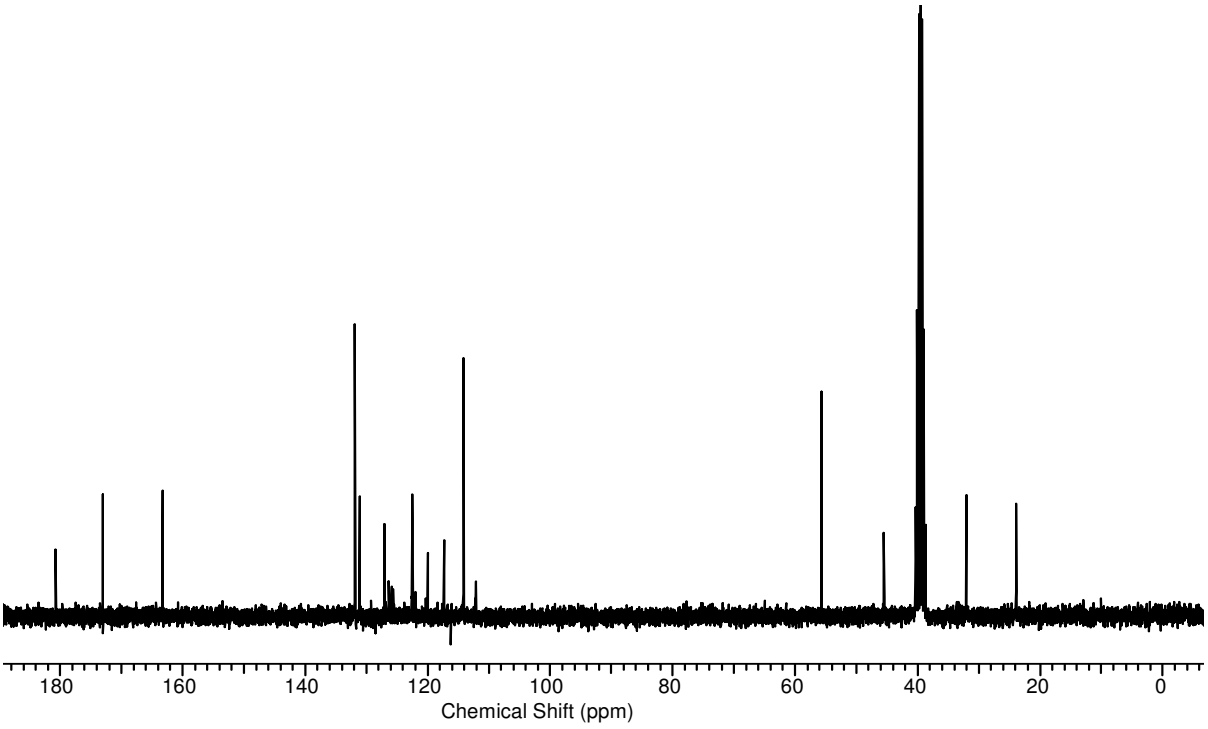
**$^{1}H$ and $^{13}C$ NMR spectra ($d_6$-DMSO) for compound 6(5,1,5)**



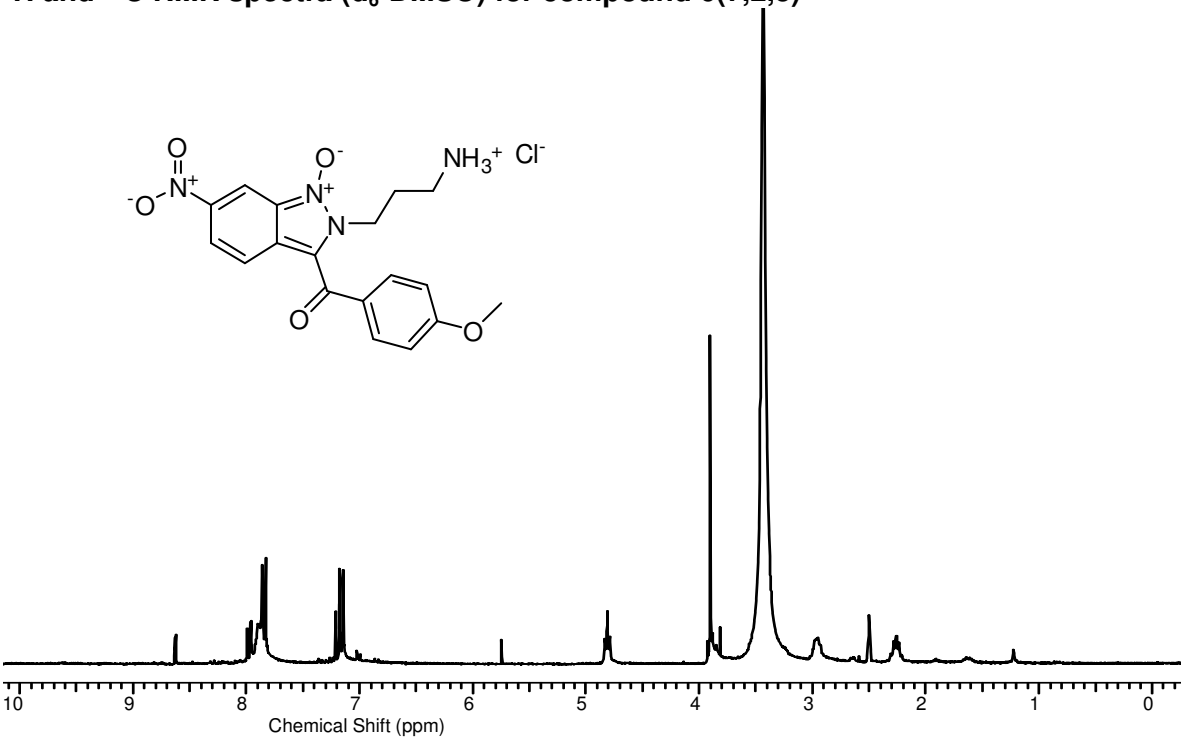



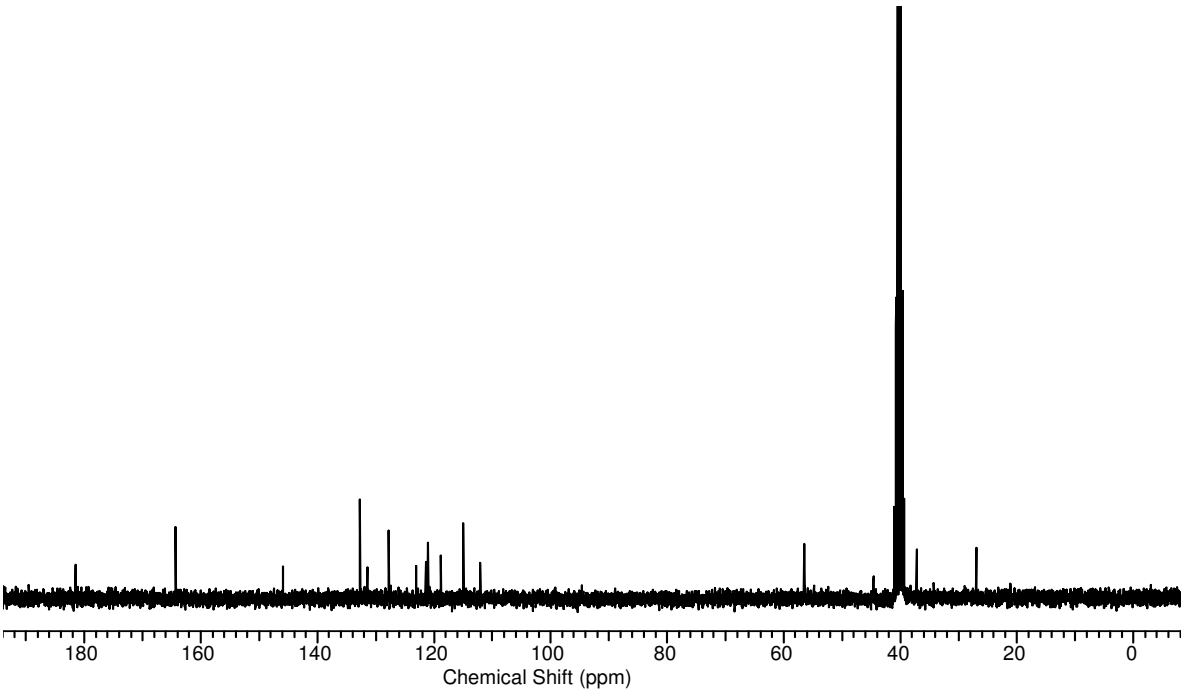
**$^{1}H$ and $^{13}C$ NMR spectra ($d_6$-DMSO) for compound 6(6,3,5)**



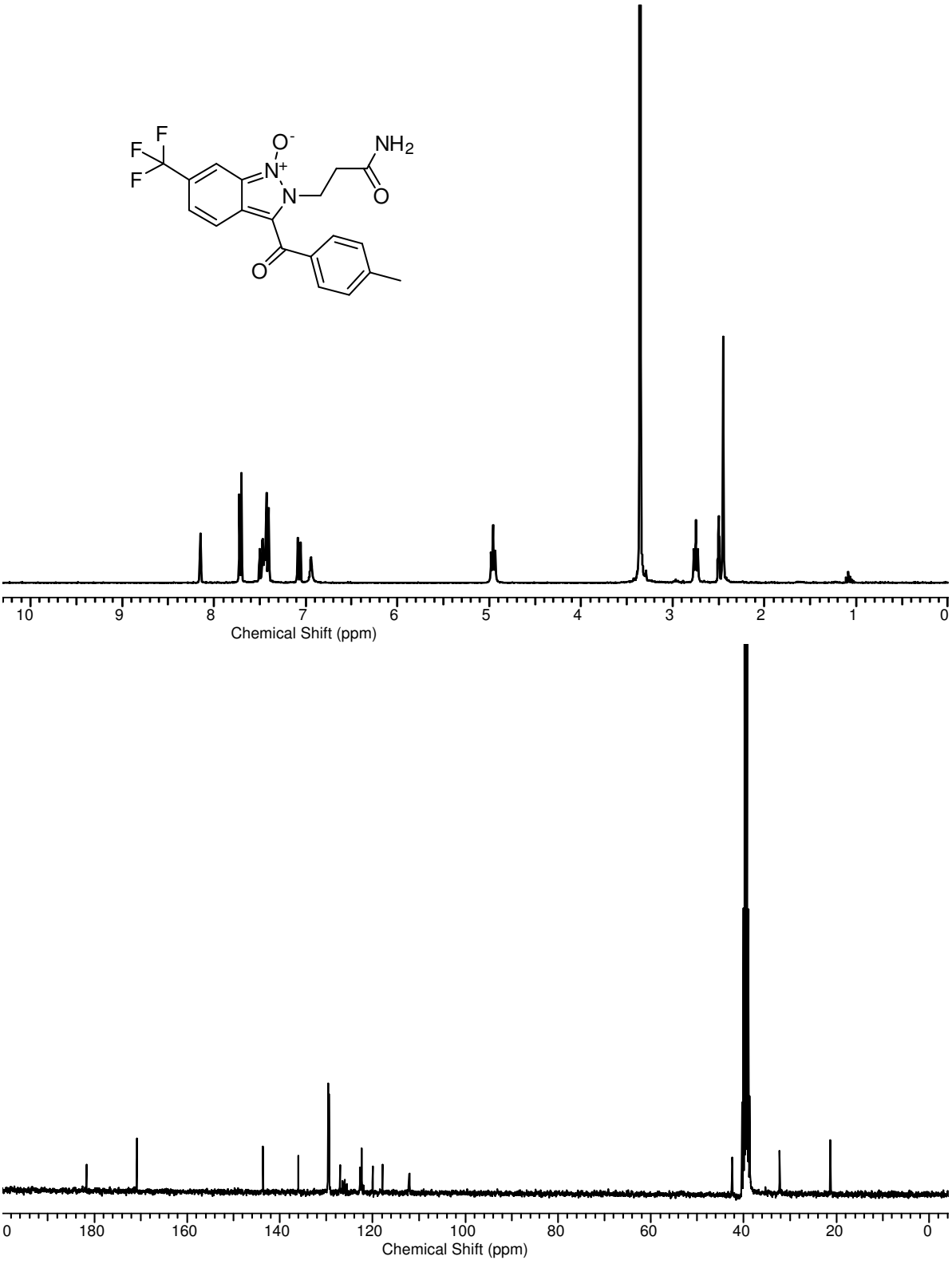



**$^{1}$H and $^{13}$C NMR spectra ($d_6$-DMSO) for compound 6(7,2,5)**

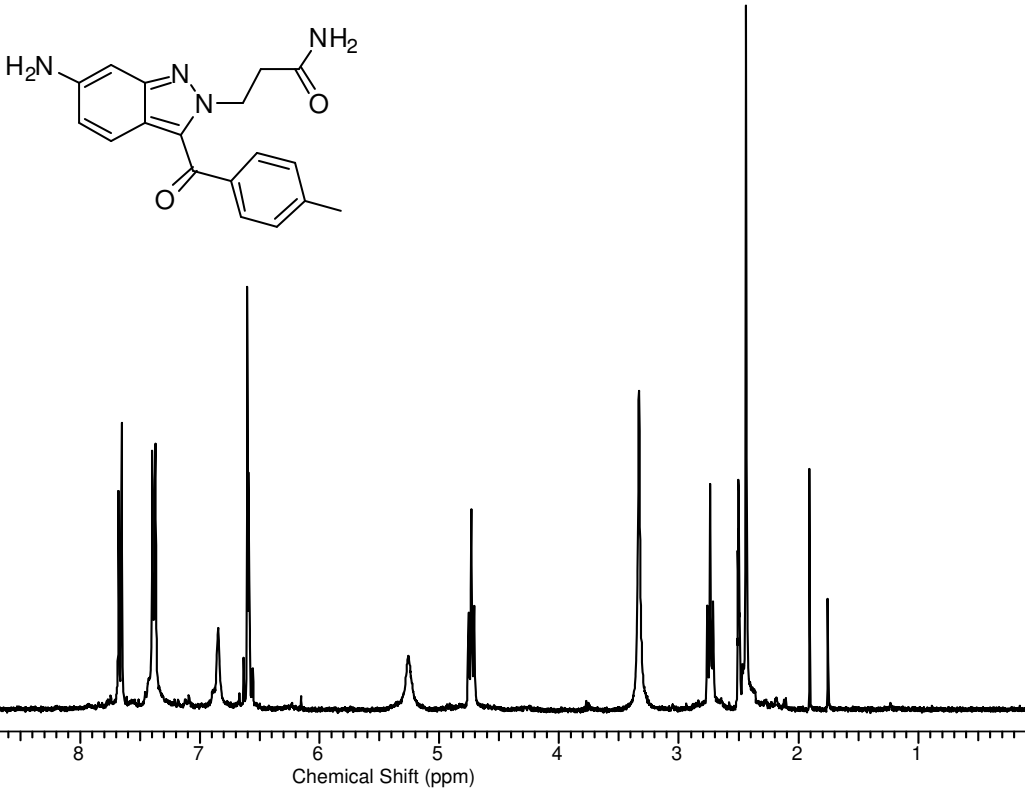


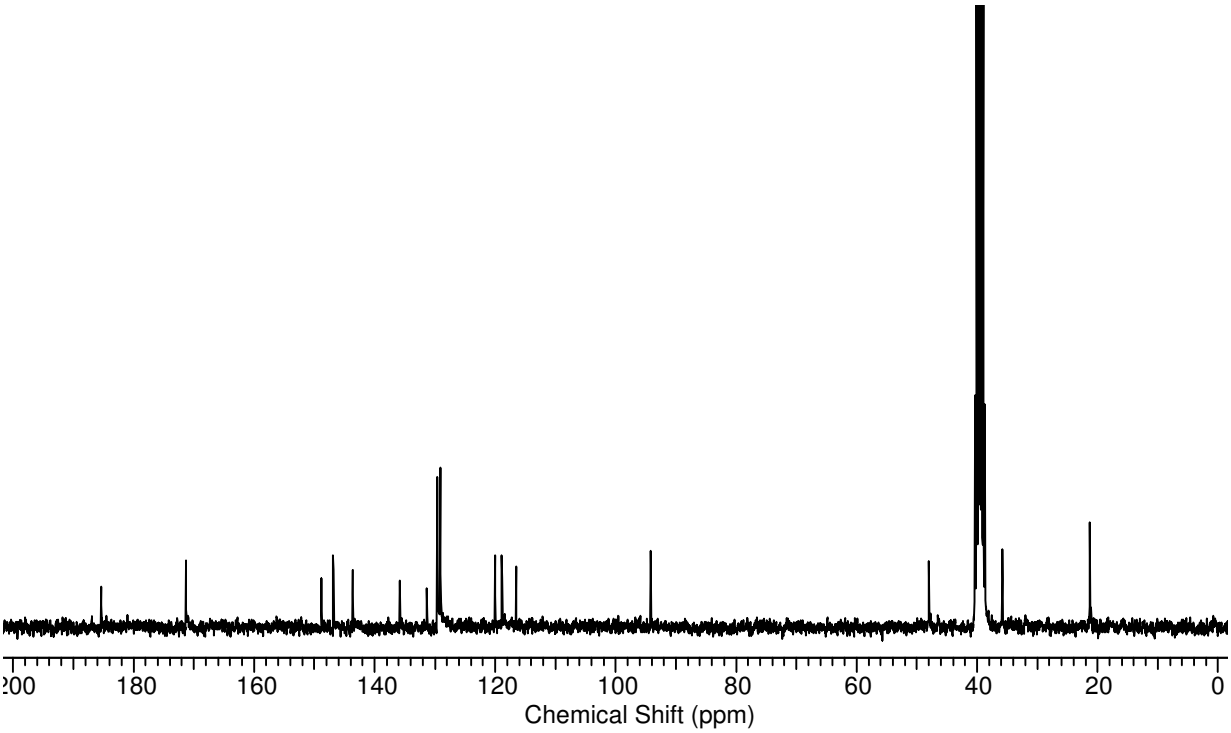



**$^{1}$H and $^{13}$C NMR spectra ($d_6$-DMSO) for compound 8(1,3,1)**



**$^{1}$H and $^{13}$C NMR spectra ($d_6$-DMSO) for compound 8(1,5,1)**



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