Supporting Information

Access to Polycyclic Sulfonyl Indolines via Fe(II)-Catalyzed or UV-Driven Formal [2+2+1] Cyclization Reactions of *N*-((1*H*-indol-3-yl)methyl)propiolamides with $NaHSO_3$

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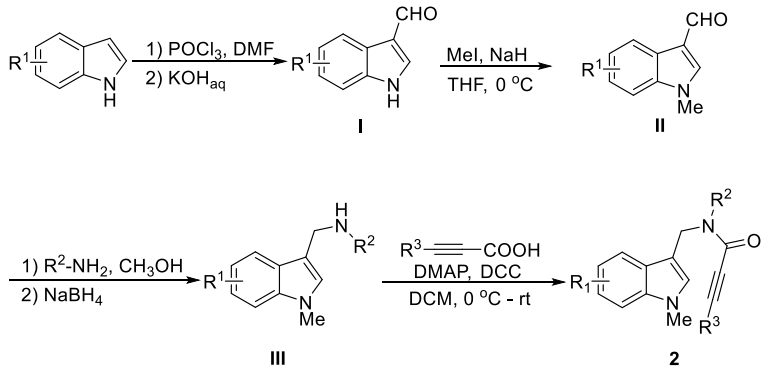
1. General information.

All reactions were carried out in flame-dried sealed tubes with magnetic stirring. Unless otherwise noted, all experiments were performed under N_2 atmosphere. Purifications of reaction products were carried out by flash chromatography using Qingdao Haiyang Chemical Co. Ltd silica gel (200-300 mesh). Infrared spectra (IR) were recorded on a Brucker TENSOR 27 FTIR spectrophotometer and are reported as wavelength numbers (cm^{-1}). ^1H, ^{13}C, ^{19}F NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz for ^1H; 100 MHz for ^{13}C; 376 MHz for ^{19}F), ^1H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 and 19F NMR chemical shifts were determined relative to $CFCl_3$ as external standard. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Mass spectra (MS) were obtained using ESI, DART mass spectrometer. Melting points were determined using a hot stage apparatus. All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature.

2. General Procedure for the Synthesis of the starting materials



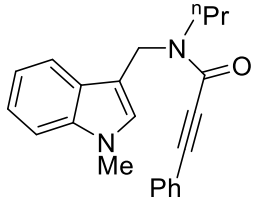
Step 1: Procedure for the synthesis of **I** was identical to the literature.[1]

Step 2: Procedure for the synthesis of **II** from **I:** To a tetrahydrofuran solution of **I** (6.0 mmol, 1.0 equiv) NaH (480.0 mg, 12.0 mmol, 2.0 equiv) was added in portion at 0 °C, and the mixture was stirred for further 0.5 h. Then MeI (1.7 g, 12 mmol, 2.0 equiv) was added to the mixture at 0 °C. The reaction mixture was stirred for 6 hours at room temperature and quenched by water (3 mL). The solvent was removed after reduced pressure and the residue was extracted with ethyl acetate. The organic layer was concentrated in *vacuo* to furnish the desired product **II** that required no further purification.[2]

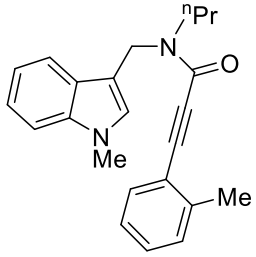
Step 3: Procedure for the synthesis of **III** from **II:** A MeOH (20 mL) solution of **II** and amine (9 mmol, 1.5 equiv) was stirred at room temperature for 24 h. Then the temperature was reduced to 0 °C. To the mixture was added $NaBH_4$ (12 mmol, 453.9 mg, 2.0 equiv) in portion. The reaction was warmed to room temperature. After stirring at the same temperature for 6 h, the solvent was removed after reduced pressure and the residue was extracted with ethyl acetate. The organic layer was concentrated in *vacuo* to furnish the desired product **III** that required no further purification.[3]

Step 4: Procedure for the synthesis of **2** from **III:** To a mixture of **III** and propiolic acid (7.2 mmol, 1.2 equiv) in CH_2Cl_2 (20 mL) was added a solution of DMAP (73.2 mg, 0.6 mmol, 10 mol %) and DCC (1.8 g, 9 mmol, 1.5 equiv) in CH_2Cl_2 (10 mL) at 0 ℃. The reaction mixture was stirred for 6 hours at room temperature and filtered through a short plug of silica gel, which was rinsed with ethyl acetate. The filtrate was concentrated in *vacuo* and the residue was purified by column chromatography on silica gel (petroleum ether /ethyl acetate = 4/1) to afford compound **2** (56-86% yield).[3]

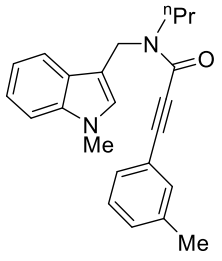
3. Characterization data for the starting materials



***N*-((1-Methyl-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2a)**: 1.60 g, 81% yield, Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (t, J = 8.0 Hz, 1H), 7.56 – 7.44 (m, 2H), 7.40 – 7.29 (m, 3H), 7.27 – 7.18 (m, 2H), 7.17 – 7.09 (m, 1H), 7.09 – 7.00 (m, 1H), 5.03 (s, 1H), 4.81 (s, 1H), 3.80 – 3.64 (m, 3H), 3.54 – 3.44 (m, 1H), 3.39 – 3.27 (m, 1H), 1.73 – 1.52 (m, 2H), 0.94 (t, J = 7.4 Hz, 2H), 0.86 (t, J = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 154.2, 137.2, 137.0, 132.3, 132.2, 129.9, 129.9, 128.9, 128.5, 128.1, 127.4, 127.1, 122.1, 121.9, 120.8, 120.7, 119.6, 119.5, 119.4, 119.0, 109.9, 109.8, 109.5, 109.3, 90.3, 89.5, 82.5, 82.2, 77.4, 49.2, 45.1, 44.5, 38.3, 32.8, 32.7, 21.7, 20.3, 11.4, 11.3. IR (KBr): 3057, 2930, 1620, 1430, 748. HRMS (ESI) *m/z* calcd for $C_{22}H_{23}N_2O$ $[M+H]^+$: 331.1810; found: 331.1807.

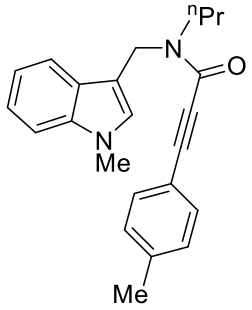


***N*-((1-Methyl-1H-indol-3-yl)methyl)-*N*-propyl-3-(o-tolyl)propiolamide (2b):** 1.63 g, 81% yield, White solid, m.p. 104-105 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 1H), 7.55 – 7.46 (m, 1H), 7.33 – 7.22 (m, 3H), 7.21 – 7.11 (m, 3H), 7.11 – 7.00 (m, 1H), 5.06 (s, 1H), 4.82 (s, 1H), 3.75 (d, J = 1.6 Hz, 3H), 3.58 – 3.46 (m, 1H), 3.42 – 3.30 (m, 1H), 2.51 – 2.36 (m, 3H), 1.82 – 1.41 (m, 2H), 0.93 (t, J = 7.4 Hz, 2H), 0.87 (t, J = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 154.5, 141.4, 141.2, 137.3, 137.0, 133.1, 133.0, 129.9, 129.9, 129.7, 129.7, 128.9, 128.0, 127.5, 127.1, 125.8, 122.1, 121.9, 120.7, 120.6, 119.6, 119.5, 119.4, 119.1, 110.0, 109.8, 109.5, 109.3, 89.4, 88.7, 86.2, 86.0, 49.3, 45.2, 44.6, 38.3, 32.8, 32.8, 21.8, 20.8, 20.8, 20.4, 11.4, 11.3. IR (KBr): 3058, 2928, 1619, 1428, 746. HRMS (ESI) *m/z* calcd for $C_{23}H_{25}N_2O$ $[M+H]^+$: 345.1967; found: 345.1959.

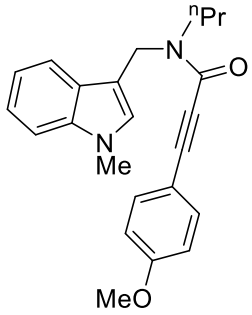


***N*-((1-Methyl-1H-indol-3-yl)methyl)-*N*-propyl-3-(m-tolyl)propiolamide (2c):** 1.49 g, 72% yield, Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.67 (m, 1H), 7.45 – 7.33 (m, 2H), 7.26 – 7.17 (m, 2H), 7.15 – 7.06 (m, 3H), 7.06 – 7.00 (m, 1H), 5.03 (s, 1H), 4.80 (s, 1H), 3.74 – 3.62 (m, 3H), 3.55 – 3.42 (m, 1H), 3.39 – 3.25 (m, 1H), 2.30 (s, 3H), 1.73 – 1.61 (m, 1H), 1.61 – 1.50 (m, 1H), 0.93 (t, J = 7.4 Hz, 2H), 0.86 (t, J = 7.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 154.2, 140.3, 140.2, 137.1, 136.9, 132.2, 132.1, 129.2, 128.8, 128.1, 127.3, 127.0, 121.9, 121.8, 119.5, 119.3, 119.3, 118.9, 117.5,

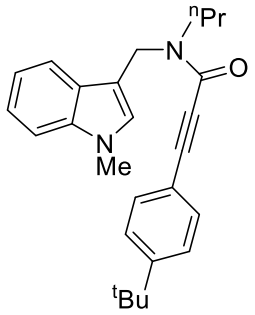
117.5, 109.8, 109.6, 109.4, 109.1, 90.6, 89.8, 82.0, 81.7, 49.1, 44.9, 44.3, 38.1, 32.6, 32.5, 21.6, 21.5, 20.1, 11.3, 11.2. IR (KBr): 3054, 2928, 1618, 1429, 742. HRMS (ESI) *m/z* calcd for $C_{23}H_{25}N_2O$ $[M+H]^+$: 345.1967; found: 345.1961.



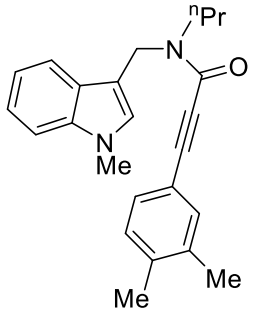
***N*-((1-Methyl-1H-indol-3-yl)methyl)-*N*-propyl-3-(p-tolyl)propiolamide (2d):** 1.67 g, 81% yield, Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.65 (m, 1H), 7.45 – 7.33 (m, 2H), 7.28 – 7.18 (m, 2H), 7.16 – 7.07 (m, 3H), 7.07 – 7.00 (m, 1H), 5.03 (s, 1H), 4.80 (s, 1H), 3.74 – 3.65 (m, 3H), 3.50 (t, *J* = 7.3 Hz, 1H), 3.34 (t, *J* = 7.3 Hz, 1H), 2.32 (s, 3H), 1.72 – 1.62 (m, 1H), 1.62 – 1.50 (m, 1H), 0.93 (t, *J* = 7.4 Hz, 2H), 0.86 (t, *J* = 7.4 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 154.3, 140.4, 140.3, 137.2, 136.9, 132.3, 132.2, 129.2, 128.8, 128.1, 127.3, 127.1, 122.0, 121.9, 119.5, 119.4, 119.4, 118.9, 117.6, 117.5, 109.9, 109.8, 109.5, 109.2, 90.7, 89.9, 82.1, 81.7, 49.2, 45.0, 44.4, 38.2, 32.7, 32.6, 21.6, 21.5, 20.2, 11.3, 11.3. IR (KBr): 3054, 2961, 1620, 1428, 741. HRMS (ESI) *m/z* calcd for $C_{23}H_{25}N_2O$ $[M+H]^+$: 345.1967; found: 345.1964.



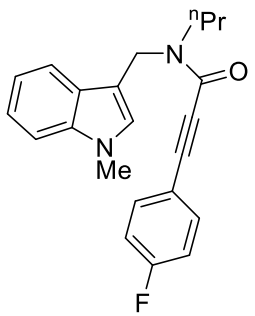
3-(4-Methoxyphenyl)-*N*-((1-methyl-1H-indol-3-yl)methyl)-*N*-propylpropiolamide (2e) : 1.77 g, 82% yield, Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.66 (m, 1H), 7.51 – 7.38 (m, 2H), 7.31 – 7.22 (m, 2H), 7.15 – 7.08 (m, 1H), 7.07 – 7.01 (m, 1H), 6.86 – 6.77 (m, 2H), 5.03 (s, 1H), 4.80 (s, 1H), 3.80 – 3.74 (m, 3H), 3.73 – 3.66 (m, 3H), 3.50 (t, *J* = 7.3 Hz, 1H), 3.39 – 3.23 (m, 1H), 1.74 – 1.62 (m, 1H), 1.61 – 1.49 (m, 1H), 0.94 (t, *J* = 7.4 Hz, 2H), 0.86 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 160.7, 154.8, 154.5, 137.2, 136.9, 134.1, 133.9, 128.8, 128.1, 127.3, 127.1, 121.9, 121.8, 119.5, 119.4, 119.0, 114.2, 112.6, 112.5, 109.9, 109.8, 109.4, 109.2, 90.8, 90.0, 81.7, 81.4, 77.4, 55.23, 49.2, 44.9, 44.4, 38.2, 32.7, 32.6, 21.6, 20.2, 11.3, 11.3. IR (KBr): 3057, 2930, 1614, 1430, 741. HRMS (ESI) *m/z* calcd for $C_{23}H_{25}N_2O_2$ $[M+H]^+$: 361.1916; found: 361.1915.



3-(4-(Tert-butyl)phenyl)-*N*-((1-methyl-1H-indol-3-yl)methyl)-*N*-propylpropiolamide (2f): 1.83 g, 79% yield, Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.67 (m, 1H), 7.52 – 7.42 (m, 2H), 7.40 – 7.32 (m, 2H), 7.31 – 7.27 (m, 1H), 7.27 – 7.21 (m, 1H), 7.17 – 7.10 (m, 1H), 7.10 – 7.03 (m, 1H), 5.04 (s, 1H), 4.81 (s, 1H), 3.79 – 3.70 (m, 3H), 3.55 – 3.44 (m, 1H), 3.40 – 3.27 (m, 1H), 1.74 – 1.63 (m, 1H), 1.62 – 1.52 (m, 1H), 1.32 – 1.27 (m, 9H), 0.94 (t, J = 7.4 Hz, 2H), 0.87 (t, J = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 154.5, 153.5, 153.5, 137.3, 137.0, 132.3, 132.2, 128.9, 128.2, 127.5, 127.2, 125.6, 122.1, 121.9, 119.7, 119.5, 119.5, 119.1, 117.8, 117.7, 110.1, 109.9, 109.5, 109.3, 90.7, 89.9, 82.1, 81.8, 49.4, 45.2, 44.52, 38.4, 35.0, 32.9, 32.8, 31.1, 21.8, 20.4, 11.5, 11.4. IR (KBr): 3055, 2961, 1620, 1427, 741. HRMS (ESI) *m/z* calcd for $C_{26}H_{31}N_2O$ $[M+H]^+$: 387.2436; found: 387.2435.

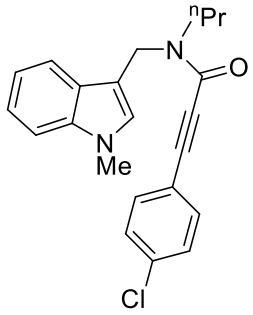


3-(3, 4-Dimethylphenyl)-*N*-((1-methyl-1H-indol-3-yl)methyl)-*N*-propylpropiolamide (2g) : 1.70 g, 79% yield, Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.66 (m, 1H), 7.30 – 7.19 (m, 4H), 7.17 – 7.09 (m, 1H), 7.09 – 7.01 (m, 2H), 5.03 (s, 1H), 4.80 (s, 1H), 3.80 – 3.65 (m, 3H), 3.59 – 3.44 (m, 1H), 3.41 – 3.25 (m, 1H), 2.30 – 2.11 (m, 6H), 1.74 – 1.62 (m, 1H), 1.61 – 1.50 (m, 1H), 0.95 (d, J = 7.4 Hz, 2H), 0.86 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 154.4, 139.2, 139.1, 137.2, 137.0, 136.9, 133.3, 133.2, 129.9, 129.8, 128.8, 128.1, 127.4, 127.2, 122.0, 121.9, 119.6, 119.4, 119.4, 119.0, 117.9, 117.8, 109.9, 109.9, 109.4, 109.2, 90.9, 90.2, 81.9, 81.6, 49.23, 45.1, 44.5, 38.2, 32.7, 21.7, 20.3, 19.8, 19.5, 19.5, 11.4, 11.3. IR (KBr): 3055, 2929, 1619, 1430, 742. HRMS (ESI) *m/z* calcd for $C_{24}H_{27}N_2O$ $[M+H]^+$: 359.2123; found: 359.2120.

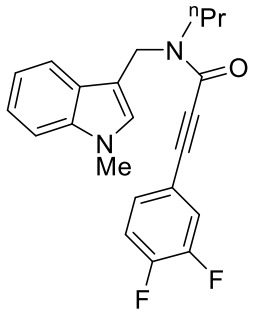


3-(4-Fluorophenyl)-*N*-((1-methyl-1H-indol-3-yl)methyl)-*N*-propylpropiolamide (2h) : 1.59 g, 76%

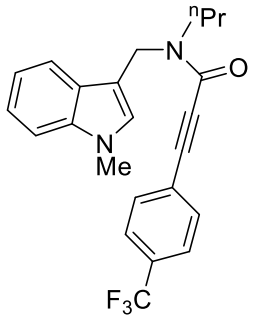
yield, Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.68 (m, 1H), 7.55 – 7.42 (m, 2H), 7.32 – 7.20 (m, 2H), 7.16 – 7.09 (m, 1H), 7.08 – 6.94 (m, 3H), 5.02 (s, 1H), 4.81 (s, 1H), 3.77 – 3.65 (m, 3H), 3.54 – 3.44 (m, 1H), 3.41 – 3.28 (m, 1H), 1.75 – 1.62 (m, 1H), 1.61 – 1.49 (m, 1H), 0.94 (t, J = 7.4 Hz, 2H), 0.86 (t, J = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 164.6, 162.1, 162.1, 154.3, 154.0, 137.2, 136.9, 134.5, 134.4, 134.4, 134.3, 128.8, 128.0, 127.3, 127.0, 122.0, 121.9, 119.5, 119.4, 119.3, 118.9, 116.8, 116.8, 116.7, 116.7, 116.0, 115.7, 109.7, 109.6, 109.5, 109.2, 89.2, 88.4, 82.3, 81.9, 49.1, 45.1, 44.5, 38.2, 32.7, 32.6, 21.6, 20.2, 11.3, 11.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.71, -107.83. IR (KBr): 3059, 2930, 1620, 1430, 741. HRMS (ESI) *m/z* calcd for $C_{22}H_{22}FN_2O$ $[M+H]^+$: 349.1716; found: 349.1710.



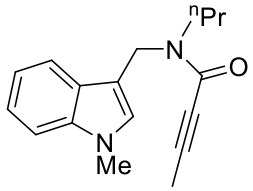
3-(4-Chlorophenyl)-N-((1-methyl-1H-indol-3-yl)methyl)-N-propylpropiolamide (2i) : 1.64 g, 75% yield, Red solid, m.p. 70-72 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 1H), 7.48 – 7.39 (m, 2H), 7.36 – 7.29 (m, 3H), 7.27 – 7.23 (m, 1H), 7.18 – 7.11 (m, 1H), 7.11 – 7.02 (m, 1H), 5.02 (s, 1H), 4.81 (s, 1H), 3.81 – 3.73 (m, 3H), 3.54 – 3.45 (m, 1H), 3.40 – 3.29 (m, 1H), 1.71 – 1.65 (m, 1H), 1.63 – 1.51 (m, 1H), 0.94 (t, J = 7.4 Hz, 2H), 0.87 (t, J = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 154.1, 137.3, 137.1, 136.3, 136.2, 133.7, 133.6, 129.1, 128.1, 127.5, 127.2, 122.2, 122.1, 119.8, 119.6, 119.5, 119.4, 119.3, 119.1, 109.9, 109.8, 109.6, 109.4, 89.2, 88.4, 83.3, 83.1, 49.4, 45.3, 44.7, 38.4, 32.9, 32.9, 21.8, 20.4, 11.5, 11.5. IR (KBr): 3060, 2930, 1621, 1430, 742. HRMS (ESI) *m/z* calcd for $C_{22}H_{22}ClN_2O$ $[M+H]^+$: 365.1421; found: 365.1412.



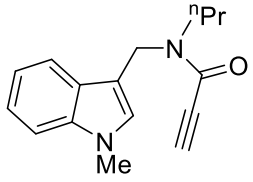
3-(3,4-Difluorophenyl)-*N*-((1-methyl-1H-indol-3-yl)methyl)-*N*-propylpropiolamide (2j) : 1.60 g, 71% yield, Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 7.9 Hz, 1H), 7.34 – 7.21 (m, 4H), 7.10 (m, 3H), 5.01 (s, 1H), 4.80 (s, 1H), 3.74 (d, J = 7.6 Hz, 3H), 3.48 (t, J = 7.3 Hz, 1H), 3.40 – 3.30 (m, 1H), 1.74 – 1.63 (m, 1H), 1.63 – 1.52 (m, 1H), 0.94 (t, J = 7.4 Hz, 2H), 0.87 (t, J = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 153.7, 137.2, 137.0, 129.3, 129.3, 129.3, 129.2, 129.2, 129.12, 129.1, 129.1, 128.9, 128.0, 127.3, 127.0, 122.1, 121.9, 121.3, 121.2, 121.1, 121.0, 119.6, 119.5, 119.3, 118.8, 117.9, 117.7, 117.5, 117.5, 109.6, 109.6, 109.5, 109.3, 87.8, 87.1, 82.7, 82.5, 49.2, 45.2, 44.6, 38.3, 32.7, 32.7, 21.6, 20.2, 11.4, 11.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -132.72, -132.83, -136.09, -136.14. IR (KBr): 3058, 2930, 1620, 1427, 742. HRMS (ESI) *m/z* calcd for $C_{22}H_{20}F_2N_2NaO$ $[M+Na]^+$: 389.1441; found: 389.1442.



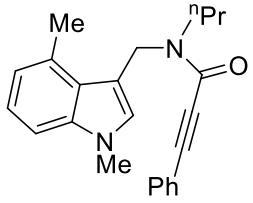
***N*-((1-Methyl-1H-indol-3-yl)methyl)-*N*-propyl-3-(4-(trifluoromethyl)phenyl)propiolamide (2k) :** 1.67 g, 70% yield, Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.67 (m, 1H), 7.67 – 7.53 (m, 4H), 7.36 – 7.27 (m, 1H), 7.27 – 7.20 (m, 1H), 7.18 – 7.11 (m, 1H), 7.11 – 7.01 (m, 1H), 5.03 (s, 1H), 4.82 (s, 1H), 3.84 – 3.70 (m, 3H), 3.57 – 3.46 (m, 1H), 3.41 – 3.31 (m, 1H), 1.78 – 1.64 (m, 1H), 1.64 – 1.52 (m, 1H), 0.95 (t, J = 7.4 Hz, 2H), 0.88 (t, J = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 153.8, 137.3, 137.1, 132.7, 132.5, 131.9, 131.7, 131.7, 131.4, 131.4, 130.6, 129.0, 128.1, 127.4, 127.1, 125.5, 125.5, 125.1, 124.7, 124.6, 122.3, 122.1, 119.8, 119.6, 119.41, 118.9, 109.7, 109.7, 109.4, 88.5, 87.7, 84.3, 84.0, 49.3, 45.3, 44.7, 38.4, 32.9, 32.8, 21.8, 20.3, 11.4, 11.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.03. IR (KBr): 3060, 2931, 1623, 1430, 742. HRMS (ESI) *m/z* calcd for $C_{23}H_{22}F_3N_2O$ $[M+H]^+$: 399.1684; found: 399.1676.



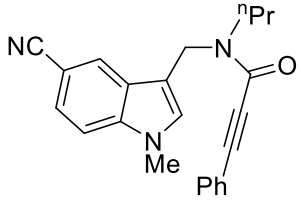
***N*-((1-methyl-1H-indol-3-yl)methyl)-*N*-propylbut-2-ynamide (2l) :** 1.16 g, 73% yield, Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.59 (m, 1H), 7.33 – 7.25 (m, 1H), 7.25 – 7.18 (m, 1H), 7.16 – 7.08 (m, 1H), 7.04 – 6.96 (m, 1H), 4.94 (s, 1H), 4.74 (s, 1H), 3.81 – 3.63 (m, 3H), 3.48 – 3.33 (m, 1H), 3.31 – 3.18 (m, 1H), 2.04 – 1.92 (m, 3H), 1.67 – 1.57 (m, 1H), 1.56 – 1.46 (m, 1H), 0.89 (t, J = 7.4 Hz, 2H), 0.83 (t, J = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 154.36, 137.2, 136.9, 128.7, 127.9, 127.3, 127.1, 122.0, 121.8, 119.5, 119.4, 119.3, 119.0, 109.9, 109.8, 109.45, 109.2, 89.1, 88.4, 74.1, 73.8, 48.9, 44.8, 44.3, 37.9, 32.7, 32.6, 21.5, 20.2, 11.3, 11.2, 4.1, 3.9. IR (KBr): 3057, 2962, 1617, 1430, 743. HRMS (ESI) *m/z* calcd for $C_{17}H_{21}N_2O$ $[M+H]^+$: 269.1654; found: 269.1643.



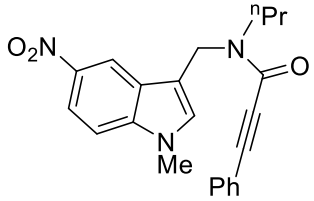
***N*-((1-methyl-1H-indol-3-yl)methyl)-*N*-propylpropiolamide (2m) :** 1.07 g, 70% yield, Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.65 (m, 1H), 7.39 – 7.25 (m, 2H), 7.23 – 7.14 (m, 1H), 7.12 – 7.04 (m, 1H), 5.01 (s, 1H), 4.81 (s, 1H), 3.84 – 3.72 (m, 3H), 3.55 – 3.43 (m, 1H), 3.38 – 3.30 (m, 1H), 3.28 (s, 1H), 3.13 (s, 1H), 1.75 – 1.63 (m, 1H), 1.63 – 1.52 (m, 1H), 0.96 (t, J = 7.4 Hz, 2H), 0.90 (t, J = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 153.0, 137.1, 136.9, 128.9, 128.1, 127.2, 126.9, 122.0, 121.9, 119.5, 119.4, 119.2, 118.8, 109.5, 109.4, 109.3, 109.3, 79.2, 78.4, 76.5, 76.2, 48.9, 44.9, 44.3, 38.1, 32.7, 32.6, 21.4, 20.1, 11.3, 11.1. IR (KBr): 3057, 2930, 1622, 1431, 743. HRMS (ESI) *m/z* calcd for $C_{16}H_{19}N_2O$ $[M+H]^+$: 255.1497; found: 255.1488.



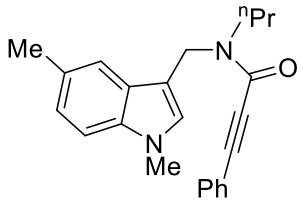
***N*-((1, 4-dimethyl-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2n) :** 1.70 g, 83% yield, Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 1H), 7.47 – 7.41 (m, 1H), 7.40 – 7.31 (m, 2H), 7.31 – 7.21 (m, 1H), 7.16 – 7.07 (m, 2H), 6.98 – 6.91 (m, 1H), 6.89 – 6.83 (m, 1H), 5.22 (s, 1H), 4.98 (s, 1H), 3.71 (s, 3H), 3.60 – 3.51 (m, 1H), 3.46 – 3.38 (m, 1H), 2.70 (s, 1H), 2.64 (s, 2H), 1.71 – 1.54 (m, 2H), 0.96 – 0.83 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 154.7, 137.8, 137.7, 132.4, 132.3, 130.8, 130.4, 130.0, 129.9, 128.9, 128.6, 128.5, 127.7, 126.1, 125.9, 122.1, 122.0, 121.1, 121.0, 120.8, 120.7, 110.9, 109.7, 107.4, 107.3, 89.6, 89.6, 82.4, 82.3, 49.1, 46.3, 45.6, 40.5, 32.9, 32.8, 22.1, 20.9, 20.7, 20.3, 11.4, 11.3. IR (KBr): 3052, 2962, 1622, 1430, 749. HRMS (ESI) *m/z* calcd for $C_{23}H_{25}N_2O$ $[M+H]^+$: 345.1967; found: 345.1963.



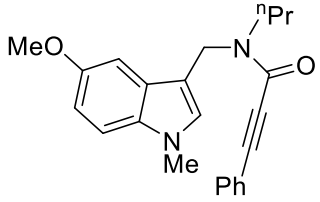
***N*-((5-cyano-1-methyl-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2o) :** 1.62 g, 76% yield, Pale yellow solid, 100-101 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.03 (m, 1H), 7.57 – 7.47 (m, 2H), 7.47 – 7.29 (m, 5H), 7.26 – 7.18 (m, 1H), 5.03 (s, 1H), 4.77 (s, 1H), 3.87 – 3.73 (m, 3H), 3.53 (t, J = 7.1 Hz, 1H), 3.34 (t, J = 7.4 Hz, 1H), 1.77 – 1.64 (m, 1H), 1.63 – 1.50 (m, 1H), 0.97 (t, J = 7.2 Hz, 2H), 0.89 (t, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 154.2, 138.7, 138.4, 132.3, 132.2, 131.1, 130.4, 130.1, 130.0, 128.6, 128.5, 127.0, 126.8, 125.0, 124.9, 124.8, 124.5, 120.7, 120.5, 120.3, 111.4, 111.3, 110.6, 110.3, 102.7, 102.5, 90.7, 90.0, 82.1, 81.8, 49.6, 45.4, 44.0, 38.2, 33.1, 33.0, 21.76, 20.3, 11.4, 11.30. IR (KBr): 3059, 2962, 1620, 1428, 753. HRMS (ESI) *m/z* calcd for $C_{23}H_{22}N_3O$ $[M+H]^+$: 356.1763; found: 356.1758.



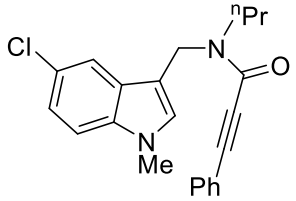
***N*-((1-methyl-5-nitro-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2p):** 1.62 g, 72% yield, Pale yellow solid, 105-107 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 – 8.61 (m, 1H), 8.14 – 8.02 (m, 1H), 7.59 – 7.54 (m, 1H), 7.53 – 7.46 (m, 1H), 7.40 – 7.27 (m, 5H), 5.06 (s, 1H), 4.80 (s, 1H), 3.88 – 3.79 (m, 3H), 3.58 (t, J = 7.3 Hz, 1H), 3.43 – 3.29 (m, 1H), 1.79 – 1.67 (m, 1H), 1.65 – 1.55 (m, 1H), 0.98 (t, J = 7.4 Hz, 2H), 0.89 (t, J = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 154.2, 141.6, 139.9, 139.6, 132.3, 132.2, 131.9, 131.3, 130.0, 128.5, 126.5, 126.2, 120.5, 120.4, 117.6, 117.4, 116.5, 116.2, 113.1, 113.0, 109.6, 109.4, 90.8, 90.0, 82.1, 81.8, 49.99, 45.5, 43.9, 38.4, 33.3, 33.2, 21.9, 20.3, 11.3, 11.2. IR (KBr): 3059, 2962, 1620, 1428, 753. HRMS (ESI) *m/z* calcd for $C_{22}H_{21}N_3NaO_3$ $[M+Na]^+$: 398.1475; found: 398.1479.



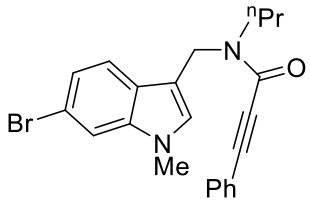
***N*-((1, 5-dimethyl-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2q) :** 1.69 g, 82% yield, Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.44 (m, 3H), 7.41 – 7.29 (m, 3H), 7.24 – 7.14 (m, 1H), 7.10 – 6.97 (m, 2H), 5.00 (s, 1H), 4.79 (s, 1H), 3.78 – 3.65 (m, 3H), 3.51 (t, *J* = 7.2 Hz, 1H), 3.35 (t, *J* = 7.5 Hz, 1H), 2.50 – 2.35 (m, 3H), 1.77 – 1.64 (m, 1H), 1.64 – 1.52 (m, 1H), 0.95 (t, *J* = 7.3 Hz, 2H), 0.88 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 154.3, 135.7, 135.5, 132.4, 132.3, 129.9, 129.9, 129.0, 128.9, 128.8, 128.6, 128.2, 127.7, 127.4, 123.7, 123.6, 120.9, 120.8, 118.9, 118.7, 109.3, 109.2, 109.0, 90.3, 89.5, 82.6, 82.3, 49.2, 45.1, 44.5, 38.3, 32.9, 32.8, 21.7, 21.6, 20.3, 11.5, 11.4. IR (KBr): 3057, 2926, 1620, 1430, 753. HRMS (ESI) *m/z* calcd for $C_{23}H_{25}N_2O$ $[M+H]^+$: 345.1967; found: 345.1965.



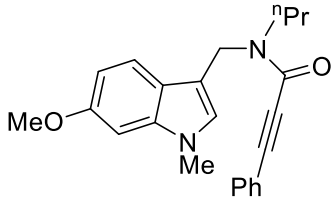
***N*-((5-methoxy-1-methyl-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2r) :** 1.73 g, 80% yield, Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.47 (m, 2H), 7.43 – 7.28 (m, 3H), 7.24 – 7.14 (m, 2H), 7.06 – 6.98 (m, 1H), 6.93 – 6.85 (m, 1H), 5.00 (s, 1H), 4.78 (s, 1H), 3.93 – 3.65 (m, 6H), 3.51 (t, *J* = 7.0 Hz, 1H), 3.34 (t, *J* = 7.3 Hz, 1H), 1.77 – 1.64 (m, 1H), 1.63 – 1.50 (m, 1H), 0.95 (t, *J* = 7.2 Hz, 2H), 0.88 (t, *J* = 7.2 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 154.3, 154.2, 154.1, 132.6, 132.5, 132.4, 132.3, 130.1, 129.9, 129.4, 128.7, 128.6, 128.6, 127.7, 127.5, 120.8, 120.7, 112.6, 112.4, 110.4, 110.1, 109.5, 109.2, 101.1, 100.6, 90.4, 89.5, 82.6, 82.2, 55.9, 55.7, 49.2, 45.0, 44.6, 38.4, 33.0, 32.9, 21.7, 20.3, 11.5, 11.4. IR (KBr): 3062, 2939, 1619, 1431, 750. HRMS (ESI) *m/z* calcd for $C_{23}H_{25}N_2O_2$ $[M+H]^+$: 361.1916; found: 361.1915.



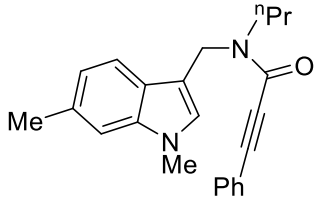
***N*-((5-chloro-1-methyl-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2s) :** 1.77 g, 81% yield, Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.62 (m, 1H), 7.59 – 7.47 (m, 2H), 7.42 – 7.29 (m, 3H), 7.23 – 7.12 (m, 2H), 7.12 – 7.04 (m, 1H), 4.97 (s, 1H), 4.74 (s, 1H), 3.78 – 3.64 (m, 3H), 3.51 (t, *J* = 7.2 Hz, 1H), 3.34 (t, *J* = 7.5 Hz, 1H), 1.75 – 1.63 (m, 1H), 1.62 – 1.51 (m, 1H), 0.95 (t, *J* = 7.3 Hz, 2H), 0.88 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 154.2, 135.7, 135.4, 132.4, 132.3, 130.2, 130.0, 129.9, 129.4, 128.6, 128.4, 128.1, 125.6, 125.5, 122.4, 122.3, 120.7, 120.6, 118.8, 118.5, 110.7, 110.5, 109.8, 109.7, 90.6, 89.8, 82.4, 82.1, 49.5, 45.3, 44.3, 38.3, 33.1, 32.9, 21.8, 20.3, 11.4, 11.3. IR (KBr): 3063, 2962, 1620, 1428, 755. HRMS (ESI) *m/z* calcd for $C_{22}H_{22}ClN_2O$ $[M+H]^+$: 365.1421; found: 365.1416.



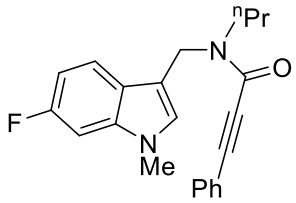
***N*-((6-bromo-1-methyl-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2t) :** 1.91 g, 78% yield, Pale yellow solid, m.p. 69-71 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 1H), 7.55 – 7.47 (m, 2H), 7.47 – 7.42 (m, 1H), 7.42 – 7.28 (m, 3H), 7.24 – 7.18 (m, 1H), 7.07 – 7.00 (m, 1H), 5.00 (s, 1H), 4.76 (s, 1H), 3.77 – 3.63 (m, 3H), 3.49 (t, *J* = 7.2 Hz, 1H), 3.32 (t, *J* = 7.4 Hz, 1H), 1.74 – 1.61 (m, 1H), 1.61 – 1.49 (m, 1H), 0.94 (t, *J* = 7.3 Hz, 2H), 0.86 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 154.3, 138.1, 137.9, 132.4, 132.3, 130.1, 130.0, 129.5, 128.7, 128.6, 128.6, 126.2, 126.0, 122.9, 122.8, 120.9, 120.7, 120.6, 120.3, 115.9, 115.8, 112.7, 112.4, 110.5, 110.3, 90.5, 89.8, 82.4, 82.1, 49.4, 45.3, 44.4, 38.3, 33.0, 32.9, 21.8, 20.4, 11.4, 11.4. IR (KBr): 3062, 2962, 1620, 1434, 755. HRMS (ESI) *m/z* calcd for $C_{22}H_{22}BrN_2O$ $[M+H]^+$: 409.0916; found: 409.0908.



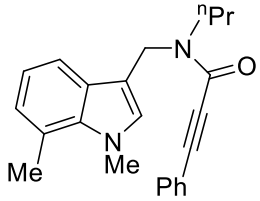
***N*-((6-methoxy-1-methyl-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2u) :** 1.79 g, 83% yield, Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.57 (m, 1H), 7.55 – 7.44 (m, 2H), 7.38 – 7.25 (m, 3H), 6.93 (s, 1H), 6.83 – 6.70 (m, 2H), 4.99 (s, 1H), 4.77 (s, 1H), 3.89 – 3.76 (m, 3H), 3.70 – 3.59 (m, 3H), 3.50 (t, *J* = 7.1 Hz, 1H), 3.34 (t, *J* = 7.4 Hz, 1H), 1.73 – 1.61 (m, 1H), 1.60 – 1.49 (m, 1H), 0.93 (t, *J* = 7.3 Hz, 2H), 0.86 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 154.3, 154.0, 137.9, 137.7, 132.2, 132.0, 129.8, 129.7, 128.3, 127.5, 126.9, 121.5, 121.3, 120.6, 120.5, 120.1, 119.5, 109.7, 109.5, 109.4, 109.2, 92.9, 92.7, 90.2, 89.3, 82.4, 82.1, 55.5, 48.9, 44.9, 44.5, 38.20, 32.6, 32.5, 21.5, 20.1, 11.2, 11.1. IR (KBr): 3066, 2959, 1623, 1432, 754. HRMS (ESI) *m/z* calcd for $C_{23}H_{25}N_2O_2$ $[M+H]^+$: 361.1916; found: 361.1910.



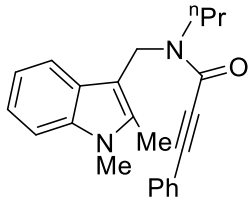
***N*-((1,6-dimethyl-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2v) :** 1.49 g, 72% yield, Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.43 (m, 3H), 7.42 – 7.26 (m, 3H), 7.13 – 7.05 (m, 1H), 7.02 – 6.92 (m, 2H), 5.01 (s, 1H), 4.79 (s, 1H), 3.70 (s, 3H), 3.50 (t, *J* = 7.0 Hz, 1H), 3.33 (t, *J* = 7.3 Hz, 1H), 2.48 (s, 3H), 1.75 – 1.62 (m, 1H), 1.62 – 1.48 (m, 1H), 0.94 (t, *J* = 7.1 Hz, 2H), 0.87 (t, *J* = 7.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 154.3, 137.7, 137.5, 132.5, 132.3, 132.0, 131.9, 130.0, 129.9, 128.6, 128.4, 127.6, 125.3, 125.1, 121.5, 121.3, 120.9, 119.2, 118.8, 109.8, 109.7, 109.5, 109.3, 90.3, 89.5, 82.5, 82.2, 49.2, 45.1, 44.6, 38.4, 32.8, 32.7, 21.9, 21.8, 20.3, 11.5, 11.4. IR (KBr): 3061, 2927, 1621, 1431, 753. HRMS (ESI) *m/z* calcd for $C_{23}H_{25}N_2O$ $[M+H]^+$: 345.1967; found: 345.1964.



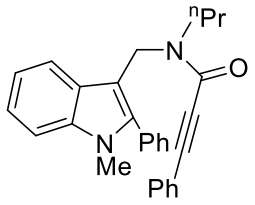
***N*-((6-fluoro-1-methyl-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2w) :** 1.59 g, 76% yield, Pale yellow solid, m.p. 78-79 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.63 (m, 1H), 7.59 – 7.48 (m, 2H), 7.42 – 7.30 (m, 3H), 7.10 – 7.03 (m, 1H), 7.00 – 6.85 (m, 2H), 5.04 (s, 1H), 4.80 (s, 1H), 3.75 – 3.60 (m, 3H), 3.53 (t, *J* = 7.2 Hz, 1H), 3.36 (t, *J* = 7.2 Hz, 1H), 1.76 – 1.64 (m, 1H), 1.63 – 1.53 (m, 1H), 0.97 (t, *J* = 7.3 Hz, 2H), 0.89 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 158.7, 154.4, 154.0, 137.3, 137.2, 137.1, 136.9, 132.2, 132.1, 129.9, 129.8, 129.0, 128.4, 123.7, 123.5, 120.6, 120.5, 120.4, 120.3, 119.8, 119.7, 110.1, 109.9, 108.3, 108.1, 108.0, 107.8, 94.0, 95.7, 95.4, 90.3, 89.6, 82.3, 82.0, 49.1, 45.0, 44.4, 38.2, 32.7, 32.6, 21.5, 20.1, 11.2, 11.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.05, -120.39. IR (KBr): 3065, 2963, 1620, 1432, 753. HRMS (ESI) *m/z* calcd for $C_{22}H_{22}FN_2O$ $[M+H]^+$: 349.1716; found: 349.1710.



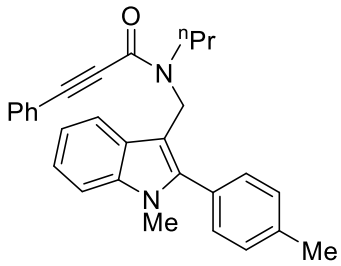
***N*-((1, 7-dimethyl-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2x) :** 1.69 g, 82% yield, Red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.45 (m, 3H), 7.41 – 7.24 (m, 3H), 7.03 – 6.85 (m, 3H), 5.00 (s, 1H), 4.77 (s, 1H), 4.02 – 3.89 (m, 3H), 3.50 (t, *J* = 7.1 Hz, 1H), 3.34 (t, *J* = 7.1 Hz, 1H), 2.71 (s, 3H), 1.75 – 1.62 (m, 1H), 1.62 – 1.49 (m, 1H), 0.94 (t, *J* = 7.3 Hz, 2H), 0.87 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 154.2, 135.9, 13567, 132.3, 132.2, 130.5, 129.9, 129.8, 129.7, 128.5, 128.2, 124.7, 124.5, 121.5, 121.3, 120.8, 120.7, 119.9, 119.8, 117.3, 116.9, 109.5, 109.4, 90.2, 89.5, 82.5, 82.2, 49.2, 45.1, 44.4, 38.1, 36.7, 36.6, 21.7, 20.3, 19.6, 11.4, 11.3. IR (KBr): 3057, 2961, 1619, 1455, 752. HRMS (ESI) *m/z* calcd for $C_{23}H_{25}N_2O$ $[M+H]^+$: 345.1967; found: 345.1963.



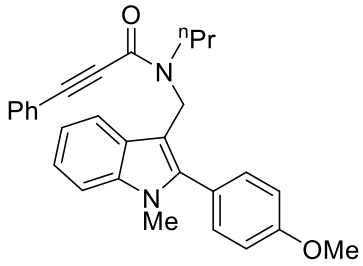
***N*-((1, 2-dimethyl-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2y) :** 1.44 g, 70% yield, Red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.45 (m, 3H), 7.41 – 7.27 (m, 3H), 7.25 – 7.21 (m, 1H), 7.20 – 7.13 (m, 1H), 7.13 – 7.06 (m, 1H), 5.06 (s, 1H), 4.85 (s, 1H), 3.70 – 3.57 (m, 3H), 3.46 – 3.37 (m, 1H), 3.26 – 3.15 (m, 1H), 2.52 – 2.35 (m, 3H), 1.74 – 1.61 (m, 1H), 1.59 – 1.47 (m, 1H), 0.93 (t, *J* = 7.4 Hz, 2H), 0.83 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 153.9, 136.7, 136.6, 135.9, 135.5, 132.3, 132.2, 129.9, 129.8, 128.5, 128.4, 127.7, 127.5, 121.2, 121.1, 120.8, 120.7, 119.7, 119.6, 118.3, 118.1, 108.9, 108.7, 106.2, 105.4, 90.8, 89.5, 82.6, 82.2, 48.6, 44.3, 43.5, 36.8, 29.6, 21.7, 20.2, 11.5, 11.4, 10.3, 10.2. IR (KBr): 3053, 2930, 1620, 1430, 747. HRMS (ESI) *m/z* calcd for $C_{23}H_{25}N_2O$ $[M+H]^+$: 345.1967; found: 345.1959.



***N*-((1-methyl-2-phenyl-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2z):** 1.75 g, 72% yield, Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.80 (m, 1H), 7.59 – 7.43 (m, 5H), 7.42 – 7.25 (m, 7H), 7.21 – 7.14 (m, 1H), 5.04 (s, 1H), 4.86 (s, 1H), 3.66 – 3.51 (m, 3H), 3.25 – 3.14 (m, 1H), 3.13 – 3.04 (m, 1H), 1.23 – 1.06 (m, 2H), 0.70 – 0.58 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 153.9, 140.6, 137.3, 132.5, 132.4, 131.3, 131.0, 130.8, 130.7, 129.9, 129.8, 129.0, 128.8, 128.8, 128.6, 128.6, 127.2, 127.1, 122.5, 122.4, 121.0, 120.9, 120.4, 120.2, 119.5, 109.7, 109.3, 108.4, 107.5, 90.7, 89.4, 82.6, 82.2, 48.4, 44.2, 43.7, 36.7, 30.9, 21.2, 19.8, 11.3, 11.2. IR (KBr): 3056, 2931, 1620, 1436, 750. HRMS (ESI) *m/z* calcd for $C_{28}H_{26}N_2NaO$ $[M+Na]^+$: 429.1937; found: 429.1935.

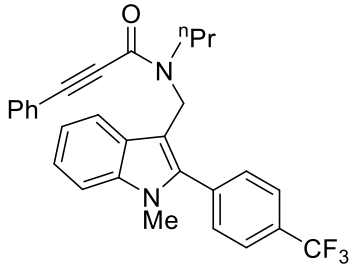


***N*-((1-methyl-2-(p-tolyl)-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2aa):** 1.84 g, 73% yield, White solid; m.p. 126-128 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.79 (m, 1H), 7.58 – 7.51 (m, 1H), 7.49 – 7.42 (m, 1H), 7.41 – 7.23 (m, 9H), 7.20 – 7.12 (m, 1H), 5.03 (s, 1H), 4.86 (s, 1H), 3.57 (s, 3H), 3.25 – 3.16 (m, 1H), 3.15 – 3.06 (m, 1H), 2.48 – 2.37 (m, 3H), 1.26 – 1.11 (m, 2H), 0.66 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 153.8, 140.8, 140.7, 138.8, 138.6, 137.2, 132.4, 132.3, 130.5, 130.5, 129.9, 129.8, 129.4, 129.4, 128.5, 128.1, 127.9, 127.2, 127.1, 122.3, 122.2, 120.9, 120.2, 120.1, 119.3, 109.6, 109.2, 108.1, 107.2, 90.6, 89.4, 82.6, 82.2, 48.4, 44.2, 43.7, 36.8, 30.8, 21.4, 21.2, 19.8, 11.3, 11.1. IR (KBr): 3060, 2932, 1621, 1435, 755. HRMS (ESI) *m/z* calcd for $C_{29}H_{28}N_2NaO$ $[M+Na]^+$: 443.2094; found: 443.2101.

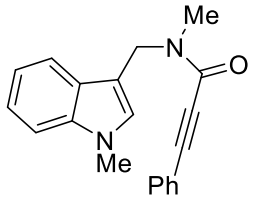


***N*-((2-(4-methoxyphenyl)-1-methyl-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2ab):** 1.86 g, 71% yield, White solid; m.p. 89-91 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.79 (m, 1H), 7.57 – 7.51 (m, 1H), 7.49 – 7.42 (m, 1H), 7.40 – 7.23 (m, 7H), 7.19 – 7.12 (m, 1H), 7.07 – 6.98 (m, 2H), 5.03 (s, 1H), 4.85 (s, 1H), 3.89 – 3.79 (m, 3H), 3.57 (s, 3H), 3.26 – 3.17 (m, 1H), 3.16 – 3.07 (m, 1H), 1.28 – 1.13 (m, 2H), 0.73 – 0.57 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 159.9, 154.3, 153.8, 140.5, 140.5, 137.1, 132.3, 132.2, 131.9, 129.9, 129.8, 128.5, 127.1, 127.0, 123.2, 122.9, 122.2, 122.1, 120.8, 120.2, 120.0, 119.1, 114.2, 114.1, 109.6, 109.2, 108.0, 107.2, 90.6, 89.5, 82.6, 82.2, 55.4, 48.3, 44.2, 43.7, 36.8, 30.7, 21.1, 19.8, 11.3, 11.2. IR (KBr): 3056, 2936, 1626, 1433, 756. HRMS (ESI) *m/z*

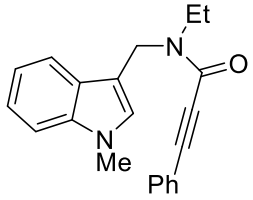
calcd for $C_{29}H_{28}N_2NaO_2$ $[M+Na]^+$: 459.2043; found: 459.2050.



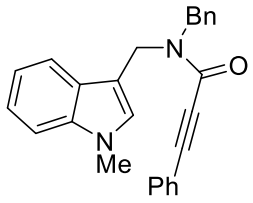
***N*-((1-methyl-2-(4-(trifluoromethyl)phenyl)-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2ac):** 1.99 g, 70% yield, White solid; m.p. 141-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.73 (m, 3H), 7.57 – 7.49 (m, 3H), 7.48 – 7.42 (m, 1H), 7.42 – 7.25 (m, 5H), 7.22 – 7.15 (m, 1H), 5.04 (s, 1H), 4.86 (s, 1H), 3.60 (s, 3H), 3.25 – 3.14 (m, 1H), 3.14 – 3.05 (m, 1H), 1.28 – 1.11 (m, 2H), 0.73 – 0.59 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 153.8, 138.7, 138.6, 137.5, 137.4, 135.0, 134.8, 132.3, 132.3, 131.1, 131.0, 130.0, 129.9, 128.5, 127.1, 127.0, 125.7, 125.7, 125.6, 125.4, 123.0, 122.9, 120.7, 120.6, 120.6, 120.5, 120.3, 119.4, 109.8, 109.5, 109.2, 108.3, 90.7, 89.7, 82.3, 81.9, 48.5, 44.3, 43.5, 36.7, 31.0, 21.2, 20.0, 11.3, 11.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.55, -62.61. IR (KBr): 3058, 2938, 1622, 1437, 751. HRMS (ESI) *m/z* calcd for $C_{29}H_{25}F_3N_2NaO$ $[M+Na]^+$: 497.1811; found: 497.1809.



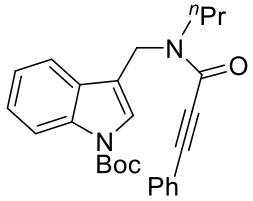
***N*-methyl-*N*-((1-methyl-1H-indol-3-yl)methyl)-3-phenylpropiolamide (2ad)** : 1.54 g, 85% yield, Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.49 (d, *J* = 7.3 Hz, 1H), 7.42 – 7.21 (m, 5H), 7.17 – 7.09 (m, 1H), 7.05 (d, *J* = 9.0 Hz, 1H), 5.02 (s, 1H), 4.79 (s, 1H), 3.81 – 3.62 (m, 3H), 3.16 (s, 1.5H), 2.92 (s, 1.5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 154.3, 137.3, 137.1, 132.4, 132.3, 130.0, 129.9, 128.9, 128.6, 128.5, 128.3, 127.4, 127.1, 122.1, 122.0, 120.7, 120.6, 119.7, 119.5, 119.0, 109.6, 109.4, 109.3, 90.6, 90.1, 82.2, 82.0, 46.7, 40.9, 35.5, 32.8, 32.7, 31.4. IR (KBr): 3057, 2924, 1621, 1438, 748. HRMS (ESI) *m/z* calcd for $C_{20}H_{19}N_2O$ $[M+H]^+$: 303.1497; found: 303.1495.



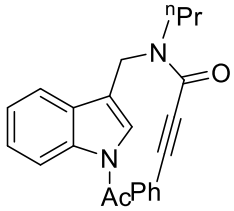
***N*-ethyl-*N*-((1-methyl-1H-indol-3-yl)methyl)-3-phenylpropiolamide (2ae) :** 1.63 g, 86% yield, Pale yellow solid, m.p. 89-90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.67 (m, 1H), 7.60 – 7.47 (m, 2H), 7.43 – 7.23 (m, 5H), 7.17 – 7.11 (m, 1H), 7.10 – 7.04 (m, 1H), 5.04 (s, 1H), 4.82 (s, 1H), 3.85 – 3.70 (m, 3H), 3.60 (q, *J* = 7.1 Hz, 1H), 3.44 (q, *J* = 7.1 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 2H), 1.10 (t, *J* = 7.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 154.1, 137.3, 137.1, 132.5, 132.4, 130.0, 129.9, 128.9, 128.6, 128.6, 128.2, 127.5, 127.2, 122.2, 122.0, 120.9, 120.8, 119.7, 119.6, 119.5, 119.2, 110.1, 109.9, 109.6, 109.3, 90.3, 89.4, 82.5, 82.1, 44.2, 42.6, 38.5, 38.1, 32.8, 13.9, 12.3. IR (KBr): 3057, 2930, 1620, 1432, 746. HRMS (ESI) *m/z* calcd for $C_{21}H_{21}N_2O$ $[M+H]^+$: 317.1654; found: 317.1653.



***N*-benzyl-*N*-((1-methyl-1H-indol-3-yl)methyl)-3-phenylpropiolamide (2af) :** 1.61 g, 71% yield, Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.65 (m, 1H), 7.61 – 7.50 (m, 1H), 7.47 – 7.40 (m, 1H), 7.40 – 7.20 (m, 10H), 7.17 – 7.08 (m, 1H), 6.97 (s, 1H), 4.96 (s, 1H), 4.77 – 4.70 (m, 2H), 4.59 (s, 1H), 3.79 – 3.63 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 154.6, 137.3, 137.1, 136.7, 136.6, 132.4, 132.4, 130.1, 130.0, 129.2, 128.9, 128.6, 128.6, 128.5, 128.3, 127.8, 127.6, 127.5, 127.2, 122.2, 122.0, 120.5, 120.5, 119.7, 119.6, 119.1, 109.5, 109.4, 109.3, 109.1, 91.2, 90.2, 82.2, 82.0, 51.0, 45.8, 43.5, 37.7, 32.7. IR (KBr): 3057, 2925, 1622, 1432, 744. HRMS (ESI) *m/z* calcd for $C_{26}H_{23}N_2O$ $[M+H]^+$: 379.1810; found: 379.1803.

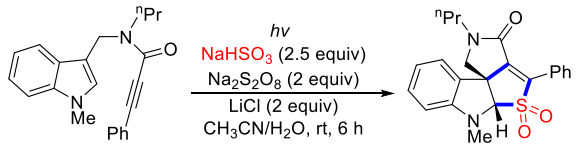


tert-butyl 3-((3-phenyl-N-propylpropiolamido)methyl)-1H-indole-1-carboxylate (2ag): 1.16 g, 56% yield, Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.06 (m, 1H), 7.71 – 7.64 (m, 1H), 7.58 (s, 1H), 7.55 – 7.49 (m, 2H), 7.44 – 7.30 (m, 4H), 7.26 (t, *J* = 7.5 Hz, 1H), 5.00 (s, 1H), 4.80 (s, 1H), 3.53 (t, *J* = 7.4 Hz, 1H), 3.44 – 3.33 (m, 1H), 1.76 – 1.65 (m, 11H), 1.63 – 1.53 (m, 1H), 0.96 (t, *J* = 7.4 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 154.6, 149.8, 135.7, 132.5, 132.4, 130.2, 130.1, 129.5, 129.3, 128.6, 125.2, 125.0, 124.9, 124.6, 123.1, 123.0, 120.7, 120.6, 119.9, 119.2, 116.2, 116.1, 115.6, 115.3, 90.8, 90.2, 84.2, 84.1, 82.2, 81.9, 81.1, 49.4, 45.63, 44.6, 38.3, 28.3, 28.3, 28.0, 21.77, 20.4, 11.4, 11.4. IR (KBr): 3052, 2926, 1622, 1432, 752. HRMS (ESI) *m/z* calcd for $C_{26}H_{29}N_2O_3$ $[M+H]^+$: 417.2178; found: 417.2173.



***N*-((1-acetyl-1*H*-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2ah)**: 1.09 g, 61% yield, yellow solid, m.p. 76-77 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 – 8.29 (m, 1H), 7.73 – 7.59 (m, 1H), 7.56 – 7.41 (m, 3H), 7.41 – 7.25 (m, 5H), 5.02 (s, 1H), 4.78 (s, 1H), 3.57 (t, *J* = 6.6 Hz, 1H), 3.41 (t, *J* = 6.9 Hz, 1H), 2.61 (d, *J* = 6.8 Hz, 3H), 1.77 – 1.66 (m, 1H), 1.64 – 1.50 (m, 1H), 0.97 (t, *J* = 7.0 Hz, 2H), 0.90 (t, *J* = 7.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 168.3, 154.7, 154.4, 136.0, 135.8, 132.3, 132.2, 130.1, 130.1, 129.3, 129.0, 128.5, 125.7, 125.5, 124.5, 123.8, 123.8, 123.7, 120.3, 120.2, 119.3, 118.9, 118.0, 117.9, 116.7, 116.5, 90.7, 90.2, 81.9, 81.7, 49.7, 45.7, 44.4, 38.3, 23.9, 21.7, 20.4, 11.3, 11.2. IR (KBr): 2965, 2218, 1607, 1429, 743. HRMS (ESI) *m/z* calcd for $C_{23}H_{23}N_2O_2$ $[M+H]^+$: 359.1760; found: 359.1756.

4. Optimization of the reaction conditions driven by *hv*

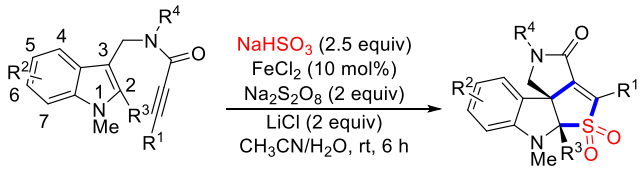


2a 1a

entry	light	Yield/%
1	UV (254 nm), 16 W	72
2	UV (380-385 nm), 18 W	33
3	blue LED (450-470 nm), 18 W	40
4	green LED (520-530 nm), 18 W	38
5	yellow LED (580-585 nm), 18 W	13
6	reddish orange LED (600-610 nm), 18 W	63
7	red LED (620-630 nm), 18 W	46

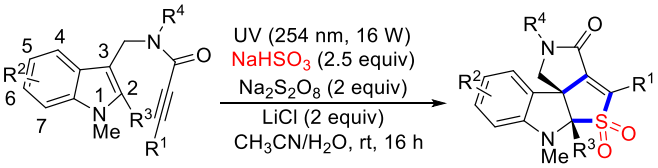
[a] Reaction conditions, unless otherwise noted: 2a (0.2 mmol), $NaHSO_3$ (2.5 equiv), $Na_2S_2O_8$ (2.0 equiv), LiCl (2.0 equiv), CH_3CN/H_2O=3/1 (2 mL), *hv*, room temperature, N_2 atmosphere, 12 h.

5. General Procedure for the Synthesis of products 1



2 1

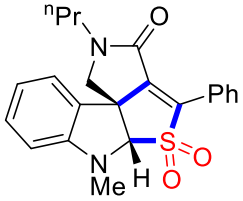
To an oven-dried 25 mL Schlenk tube under N_2 atmosphere equipped with a magnetic bar were added $FeCl_2$ (10 mol %, 2.5 mg), $NaHSO_3$ (0.5 mmol, 52.0 mg), $Na_2S_2O_8$ (0.4 mmol, 95.2 mg), and LiCl (0.4 mmol, 17.0 mg), and then H_2O (0.5 mL), substrate **2** (0.2 mol, 1.0 equiv) and CH_3CN (1.5 mL) were added. The mixture was stirred at room temperature for 6 h. The corresponding reaction mixture was filtered through a pad of celite, washed with EtOAc and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether /ethyl acetate = 5/1) to give corresponding product.



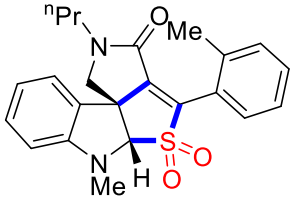
2 1

To an oven-dried 25 mL Schlenk tube under N_2 atmosphere equipped with a magnetic bar were added $FeCl_2$ (10 mol%, 2.5 mg), $NaHSO_3$ (0.5 mmol, 52.0 mg), $Na_2S_2O_8$ (0.4 mmol, 95.2 mg), and LiCl (0.4 mmol, 17.0 mg), and then H_2O (0.5 mL), substrate **2** (0.2 mol, 1.0 equiv) and CH_3CN (1.5 mL) were added. The mixture was stirred at room temperature and irradiated by UV lamp (254 nm, 16 W) for 16 h. The corresponding reaction mixture was filtered through a pad of celite, washed with EtOAc and concentrated under reduced pressure. The residue was purified by silica gel column chromatography ((petroleum ether /ethyl acetate = 5/1) to give corresponding product.

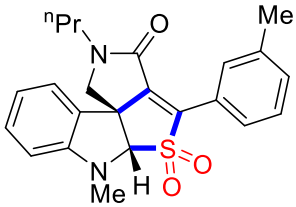
6. Characterization data for 1



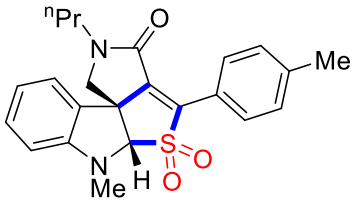
6-Methyl-4-phenyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1a) : 67.8 mg, 86% yield, (56.8 mg, 72% yield), yellow solid, m.p. 187-188 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 5.4 Hz, 2H), 7.40 (d, *J* = 5.5 Hz, 3H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.4 Hz, 1H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 7.9 Hz, 1H), 4.97 (s, 1H), 3.76 (d, *J* = 9.4 Hz, 1H), 3.60 (d, *J* = 9.4 Hz, 1H), 3.57 – 3.46 (m, 1H), 3.40 – 3.21 (m, 4H), 1.67 – 1.58 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 162.9, 147.9, 145.4, 136.8, 131.0, 130.5, 130.4, 129.7, 128.6, 125.4, 121.5, 119.9, 107.4, 90.6, 58.5, 52.9, 45.6, 31.9, 20.8, 11.6. IR (KBr): 3061, 2963, 1690, 1483, 1302, 1126, 748. HRMS (ESI) *m/z* calcd for $C_{22}H_{23}N_2O_3S$ $[M+H]^+$: 395.1429; found: 395.1428.



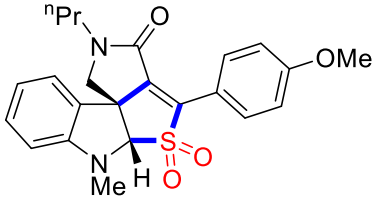
6-Methyl-2-propyl-4-(o-tolyl)-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1b) : 75.2 mg, 92% yield, (66.2 mg, 81% yield), yellow solid, m.p. 215-217 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.34 (d, *J* = 7.5 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.24 – 7.16 (m, 2H), 7.13 (d, *J* = 7.4 Hz, 1H), 6.80 (t, *J* = 7.5 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 5.02 (s, 1H), 3.72 (d, *J* = 9.5 Hz, 1H), 3.55 (d, *J* = 9.5 Hz, 1H), 3.52 – 3.42 (m, 1H), 3.32 – 3.18 (m, 4H), 2.19 (s, 3H), 1.62 – 1.52 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 162.5, 147.9, 143.9, 140.0, 138.6, 130.4, 130.3, 130.1, 129.3, 125.7, 124.6, 121.2, 119.8, 107.5, 91.4, 58.4, 52.3, 45.2, 31.8, 20.7, 19.8, 11.5. IR (KBr): 3061, 2963, 1694, 1481, 1303, 1125, 747. HRMS (ESI) *m/z* calcd for $C_{23}H_{25}N_2O_3S$ $[M+H]^+$: 409.1586; found: 409.1583.



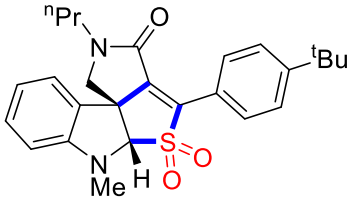
6-Methyl-2-propyl-4-(m-tolyl)-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1c) : 76.8 mg, 94% yield, (58.8 mg, 72% yield), yellow solid, m.p. 172-173 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.87 (d, *J* = 8.2 Hz, 2H), 7.23 (m, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 7.4 Hz, 1H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 4.94 (s, 1H), 3.70 (d, *J* = 9.4 Hz, 1H), 3.56 – 3.42 (m, 2H), 3.36 – 3.21 (m, 4H), 2.33 (s, 3H), 1.65 – 1.52 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 163.0, 147.9, 145.3, 141.4, 135.9, 130.5, 130.3, 129.5, 129.2, 122.5, 121.4, 119.7, 107.3, 90.4, 58.3, 52.7, 45.5, 31.8, 21.6, 20.7, 11.5. IR (KBr): 3063, 2963, 1690, 1481, 1302, 1126, 748. HRMS (ESI) *m/z* calcd for $C_{23}H_{25}N_2O_3S$ $[M+H]^+$: 409.1586; found: 409.1584.



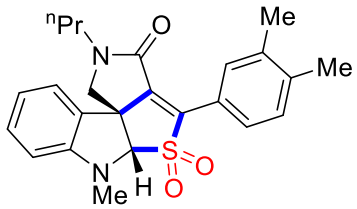
6-Methyl-2-propyl-4-(p-tolyl)-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1d) : 75.2 mg, 92% yield, (61.3 mg, 75% yield), yellow solid, m.p. 149-150 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.1 Hz, 2H), 7.25 – 7.21 (m, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 7.5 Hz, 1H), 6.76 (t, J = 7.5 Hz, 1H), 6.63 (d, J = 7.9 Hz, 1H), 4.94 (s, 1H), 3.70 (d, J = 9.4 Hz, 1H), 3.56 – 3.42 (m, 2H), 3.35 – 3.22 (m, 4H), 2.33 (s, 3H), 1.64 – 1.51 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 147.8, 145.3, 141.4, 135.9, 130.5, 130.3, 129.5, 129.2, 122.5, 121.4, 119.7, 107.27, 90.4, 58.3, 52.7, 45.5, 31.7, 21.6, 20.7, 11.5. IR (KBr): 3055, 2927, 1687, 1420, 1299, 1123, 745. HRMS (ESI) *m/z* calcd for C23H25N2O3S $[M+H]^+$: 409.1586; found: 409.1581.



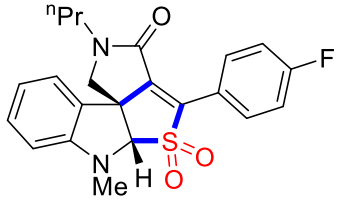
4-(4-Methoxyphenyl)-6-methyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1e) : 79.8 mg, 94% yield, (63.7 mg, 75% yield), yellow solid, m.p. 208-209 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.7 Hz, 2H), 7.22 (d, J = 7.7 Hz, 1H), 7.12 (d, J = 7.5 Hz, 1H), 6.90 (d, J = 8.7 Hz, 2H), 6.76 (t, J = 7.5 Hz, 1H), 6.63 (d, J = 7.9 Hz, 1H), 4.93 (s, 1H), 3.78 (s, 3H), 3.70 (d, J = 9.4 Hz, 1H), 3.58 – 3.43 (m, 2H), 3.37 – 3.21 (m, 4H), 1.64 – 1.52 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 161.7, 147.8, 145.0, 134.3, 131.4, 130.6, 130.3, 121.4, 119.6, 117.8, 114.0, 107.3, 90.2, 58.4, 55.3, 52.7, 45.5, 31.8, 20.7, 11.5. IR (KBr): 3063, 2961, 1686, 1420, 1299, 1123, 745. HRMS (ESI) *m/z* calcd for $C_{23}H_{25}N_2O_4S$ $[M+H]^+$: 425.1535; found: 425.1526.



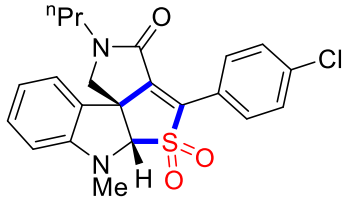
4-(4-(Tert-butyl)phenyl)-6-methyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1f) : 81.1 mg, 90% yield, (78.4 mg, 87% yield), yellow solid, m.p. 200-201 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 7.25 – 7.21 (m, 1H), 7.12 (d, J = 7.4 Hz, 1H), 6.76 (t, J = 7.5 Hz, 1H), 6.63 (d, J = 7.9 Hz, 1H), 4.95 (s, 1H), 3.73 (d, J = 9.4 Hz, 1H), 3.57 – 3.42 (m, 2H), 3.38 – 3.22 (m, 4H), 1.65 – 1.54 (m, 2H), 1.27 (d, J = 9.1 Hz, 9H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 154.3, 147.8, 145.3, 135.8, 130.5, 130.3, 129.3, 125.5, 122.5, 121.4, 119.7, 107.3, 90.4, 58.3, 52.8, 45.5, 34.9, 31.8, 31.1, 20.7, 11.5. IR (KBr): 3061, 2960, 1686, 1416, 1304, 1126, 742. HRMS (ESI) *m/z* calcd for $C_{26}H_{31}N_2O_3S$ $[M+H]^+$: 451.2055; found: 451.2046.



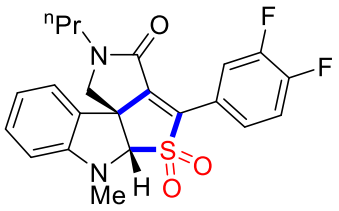
4-(3,4-Dimethylphenyl)-6-methyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1g) : 76.9 mg, 91% yield, (75.2 mg, 89% yield), yellow solid, m.p. 182-183 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.69 (d, J = 7.9 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.14 (t, J = 7.6 Hz, 2H), 6.77 (t, J = 7.4 Hz, 1H), 6.63 (d, J = 7.9 Hz, 1H), 4.94 (s, 1H), 3.72 (d, J = 9.4 Hz, 1H), 3.59 – 3.43 (m, 2H), 3.38 – 3.19 (m, 4H), 2.24 (d, J = 3.0 Hz, 6H), 1.65 – 1.51 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 147.9, 145.5, 140.2, 136.8, 135.7, 130.5, 130.3, 129.8, 127.1, 122.8, 121.5, 119.7, 107.3, 90.4, 58.4, 52.7, 45.5, 31.8, 20.8, 19.9, 19.8, 11.5. IR (KBr): 3077, 2928, 1692, 1483, 1303, 1124, 745. HRMS (ESI) *m/z* calcd for $C_{24}H_{27}N_2O_3S$ $[M+H]^+$: 423.1742; found: 423.1736.



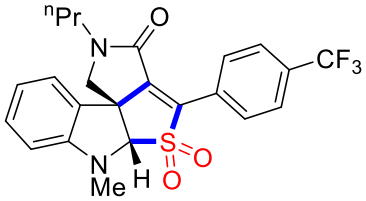
4-(4-Fluorophenyl)-6-methyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1h) : 69.3 mg, 84% yield, (66.0 mg, 80% yield), yellow solid, m.p. 185-186 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.94 (m, 2H), 7.26 – 7.23 (m, 1H), 7.17 – 7.02 (m, 3H), 6.79 (t, J = 7.5 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 4.97 (s, 1H), 3.76 (d, J = 9.4 Hz, 1H), 3.59 (d, J = 9.4 Hz, 1H), 3.56 – 3.45 (m, 1H), 3.39 – 3.25 (m, 4H), 1.66 – 1.57 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 163.0, 162.9, 147.8, 144.3, 136.7, 132.1, 132.0, 130.5, 130.3, 121.6, 121.6, 121.5, 119.9, 115.9, 115.7, 107.4, 90.6, 58.4, 52.8, 45.6, 31.8, 20.8, 11.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.10. IR (KBr): 3066, 2963, 1690, 1489, 1303, 1126, 746. HRMS (ESI) *m/z* calcd for $C_{22}H_{22}FN_2O_3S$ $[M+H]^+$: 413.1335; found: 413.1325.



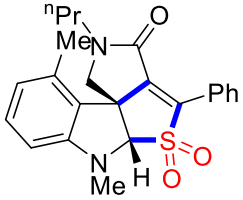
4-(4-Chlorophenyl)-6-methyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1i) : 75.5 mg, 88% yield, (63.5 mg, 74% yield), yellow solid, m.p. 181-183 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.6 Hz, 2H), 7.37 (d, J = 8.6 Hz, 2H), 7.29 – 7.25 (m, 1H), 7.13 (d, J = 7.5 Hz, 1H), 6.79 (t, J = 7.5 Hz, 1H), 6.66 (d, J = 8.0 Hz, 1H), 4.97 (s, 1H), 3.76 (d, J = 9.4 Hz, 1H), 3.59 (d, J = 9.4 Hz, 1H), 3.56 – 3.46 (m, 1H), 3.39 – 3.25 (m, 4H), 1.66 – 1.56 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 147.8, 144.3, 137.4, 137.3, 131.0, 130.5, 130.2, 128.9, 123.9, 121.5, 119.9, 107.5, 90.7, 58.45, 52.9, 45.6, 31.8, 20.8, 11.6. IR (KBr): 3039, 2927, 1687, 1482, 1304, 1125, 744. HRMS (ESI) *m/z* calcd for $C_{22}H_{22}ClN_2O_3S$ $[M+H]^+$: 429.1040; found: 429.1032.



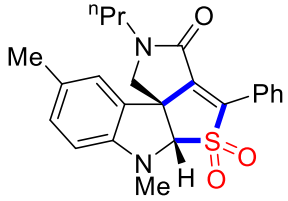
4-(3,4-Difluorophenyl)-6-methyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1j) : 64.6 mg, 75% yield, (43.0 mg, 50% yield), yellow solid, m.p. 175-177 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.92 (m, 1H), 7.86 – 7.74 (m, 1H), 7.28 – 7.23 (m, 1H), 7.22 – 7.15 (m, 1H), 7.13 (d, J = 7.5 Hz, 1H), 6.80 (t, J = 7.5 Hz, 1H), 6.66 (d, J = 7.9 Hz, 1H), 4.98 (s, 1H), 3.78 (d, J = 9.5 Hz, 1H), 3.62 (d, J = 9.5 Hz, 1H), 3.58 – 3.48 (m, 1H), 3.41 – 3.24 (m, 4H), 1.68 – 1.58 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 147.8, 143.4, 137.8, 130.6, 130.1, 126.8, 126.8, 126.7, 122.4, 121.5, 120.0, 119.3, 119.1, 117.6, 117.4, 107.5, 90.7, 58.5, 52.9, 45.7, 31.8, 20.8, 11.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -132.79, -136.11. IR (KBr): 3085, 2967, 1692, 1480, 1300, 1127, 745. HRMS (ESI) *m/z* calcd for $C_{22}H_{21}F_2N_2O_3S$ $[M+H]^+$: 431.1241; found: 431.1246.



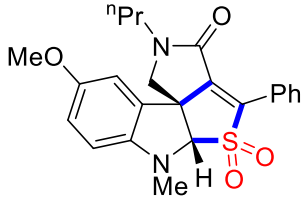
6-Methyl-2-propyl-4-(4-(trifluoromethyl)phenyl)-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1k) : 60.1 mg, 65% yield, (57.3 mg, 62% yield), yellow solid, m.p. 198-200 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 7.9 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.7 Hz, 1H), 7.14 (d, J = 7.4 Hz, 1H), 6.81 (t, J = 7.4 Hz, 1H), 6.67 (d, J = 7.9 Hz, 1H), 5.02 (s, 1H), 3.79 (d, J = 9.5 Hz, 1H), 3.61 (d, J = 9.4 Hz, 1H), 3.57 – 3.45 (m, 1H), 3.41 – 3.23 (m, 4H), 1.67 – 1.58 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 147.8, 144.0, 139.2, 130.63, 130.1, 129.9, 129.0, 125.5, 125.4, 125.4, 125.4, 121.5, 120.0, 107.5, 91.0, 58.5, 53.0, 45.6, 31.8, 20.8, 11.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.05. IR (KBr): 3056, 2930, 1692, 1481, 1319, 1125, 746. HRMS (ESI) *m/z* calcd for $C_{23}H_{22}F_3N_2O_3S$ $[M+H]^+$: 463.1303; found: 463.1299.



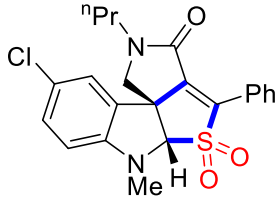
6,10-Dimethyl-4-phenyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1n) : 61.3 mg, 75% yield, (54.7 mg, 67% yield), yellow solid, m.p. 192-193 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 7.7, 1.5 Hz, 2H), 7.48 – 7.34 (m, 3H), 7.14 (t, J = 7.8 Hz, 1H), 6.60 (d, J = 7.6 Hz, 1H), 6.52 (d, J = 7.9 Hz, 1H), 4.91 (s, 1H), 3.84 (d, J = 10.4 Hz, 1H), 3.59 (d, J = 10.4 Hz, 1H), 3.53 – 3.40 (m, 1H), 3.34 – 3.21 (m, 4H), 2.23 (s, 3H), 1.66 – 1.54 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 149.0, 147.0, 137.2, 133.8, 131.1, 130.2, 130.0, 128.5, 128.4, 125.6, 122.9, 105.5, 94.1, 58.0, 52.2, 45.5, 31.9, 20.5, 19.7, 11.6. IR (KBr): 3061, 2963, 1691, 1426, 1301, 1128, 752. HRMS (ESI) *m/z* calcd for $C_{23}H_{25}N_2O_3S$ $[M+H]^+$: 409.1586; found: 409.1576.



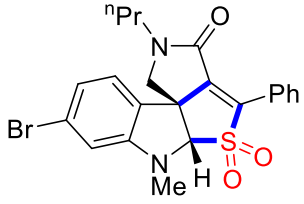
6,9-Dimethyl-4-phenyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1q) : 63.7 mg, 78% yield, (63.7 mg, 78% yield), yellow solid, m.p. 210-212 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.88 (m, 2H), 7.40 (d, J = 5.0 Hz, 3H), 7.06 (d, J = 8.0 Hz, 1H), 6.94 (s, 1H), 6.55 (d, J = 8.0 Hz, 1H), 4.95 (s, 1H), 3.75 (d, J = 9.4 Hz, 1H), 3.56 (d, J = 9.4 Hz, 1H), 3.54 – 3.45 (m, 1H), 3.41 – 3.31 (m, 1H), 3.27 (s, 3H), 2.23 (s, 3H), 1.67 – 1.55 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 145.8, 145.2, 137.0, 130.9, 130.8, 130.5, 129.6, 129.3, 128.5, 125.4, 122.2, 107.2, 91.0, 58.3, 52.7, 45.5, 31.9, 20.8, 20.7, 11.5. IR (KBr): 3062, 2927, 1690, 1490, 1298, 1123, 748. HRMS (ESI) *m/z* calcd for $C_{23}H_{25}N_2O_3S$ $[M+H]^+$: 409.1586; found: 409.1577.



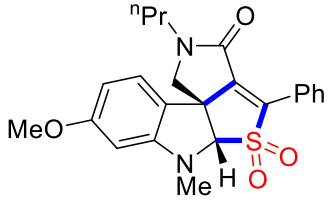
9-Methoxy-6-methyl-4-phenyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1r) : 47.5 mg, 56% yield, (30.6 mg, 36% yield), yellow solid, m.p. 183-185 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.0 Hz, 2H), 7.41 (d, J = 5.1 Hz, 3H), 6.82 (d, J = 8.5 Hz, 1H), 6.75 (s, 1H), 6.57 (d, J = 8.5 Hz, 1H), 4.96 (s, 1H), 3.76 (d, J = 9.4 Hz, 1H), 3.71 (s, 3H), 3.60 (d, J = 9.3 Hz, 1H), 3.58 – 3.48 (m, 1H), 3.37 – 3.22 (m, 4H), 1.68 – 1.58 (m, 2H), 0.98 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 154.2, 145.4, 142.2, 136.6, 131.4, 131.0, 129.7, 128.5, 125.4, 115.3, 108.7, 107.8, 91.4, 58.2, 56.1, 52.8, 45.6, 32.1, 20.8, 11.6. IR (KBr): 3064, 2959, 1691, 1491, 1296, 1125, 753. HRMS (ESI) *m/z* calcd for $C_{23}H_{25}N_2O_4S$ $[M+H]^+$: 425.1535; found: 425.1526.



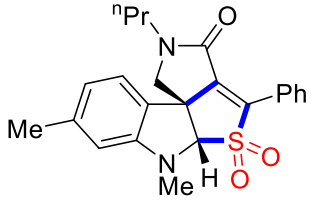
9-Chloro-6-methyl-4-phenyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1s) : 62.6 mg, 73% yield, (15.4 mg, 18% yield), yellow solid, m.p. 175-177 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 6.8 Hz, 2H), 7.41 (d, J = 6.3 Hz, 3H), 7.21 (d, J = 8.4 Hz, 1H), 7.09 (s, 1H), 6.56 (d, J = 8.4 Hz, 1H), 4.96 (s, 1H), 3.75 (d, J = 9.5 Hz, 1H), 3.56 (d, J = 9.5 Hz, 1H), 3.53 – 3.44 (m, 1H), 3.42 – 3.32 (m, 1H), 3.27 (s, 3H), 1.66 – 1.57 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 146.6, 145.8, 136.0, 131.8, 131.2, 130.3, 129.7, 128.6, 125.2, 124.6, 122.0, 108.3, 90.4, 58.2, 52.5, 45.6, 32.0, 20.8, 11.5. IR (KBr): 3065, 2963, 1692, 1483, 1303, 1127, 750. HRMS (ESI) *m/z* calcd for $C_{22}H_{22}ClN_2O_3S$ $[M+H]^+$: 429.1040; found: 429.1033.



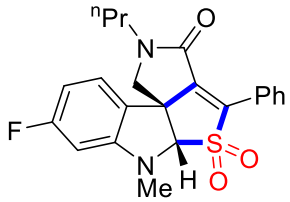
8-Bromo-6-methyl-4-phenyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1t) : 69.1 mg, 73% yield, (26.5 mg, 28% yield), yellow solid, m.p. 215-217 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 5.5 Hz, 2H), 7.43 (s, 3H), 6.99 (d, J = 7.5 Hz, 1H), 6.91 (d, J = 7.5 Hz, 1H), 6.79 (s, 1H), 4.95 (s, 1H), 3.77 (d, J = 8.3 Hz, 1H), 3.65 – 3.44 (m, 2H), 3.40 – 3.18 (m, 4H), 1.68 – 1.57 (m, 2H), 0.97 (t, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 149.1, 145.6, 136.1, 131.2, 129.7, 129.5, 128.6, 125.2, 124.3, 122.7, 122.6, 110.8, 90.3, 58.3, 52.4, 45.6, 32.0, 20.8, 11.6. IR (KBr): 3065, 2963, 1692, 1483, 1303, 1129, 749. HRMS (ESI) *m/z* calcd for $C_{22}H_{22}BrN_2O_3S$ $[M+H]^+$: 473.0535; found: 473.0526.



8-Methoxy-6-methyl-4-phenyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1u) : 63.7 mg, 75% yield, (60.3 mg, 71% yield), yellow solid, m.p. 187-188 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 5.4 Hz, 2H), 7.39 (d, J = 4.7 Hz, 3H), 7.01 (d, J = 8.2 Hz, 1H), 6.28 (d, J = 8.2 Hz, 1H), 6.19 (s, 1H), 4.96 (s, 1H), 3.76 (s, 3H), 3.72 (d, J = 9.4 Hz, 1H), 3.58 – 3.42 (m, 2H), 3.35 – 3.20 (m, 4H), 1.66 – 1.55 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 162.2, 149.4, 144.7, 137.2, 130.9, 129.6, 128.5, 125.4, 123.0, 122.0, 104.3, 94.5, 91.0, 58.6, 55.5, 52.3, 45.5, 31.8, 20.8, 11.5. IR (KBr): 3064, 2961, 1690, 1483, 1301, 1128, 751. HRMS (ESI) *m/z* calcd for $C_{23}H_{25}N_2O_4S$ $[M+H]^+$: 425.1535; found: 425.1534.

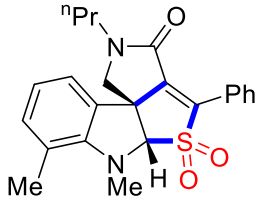


6,8-Dimethyl-4-phenyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1v) : 78.4 mg, 96% yield, (49.8 mg, 61% yield), yellow solid, m.p. 150-152 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.87 (m, 2H), 7.39 (d, J = 5.1 Hz, 3H), 7.00 (d, J = 7.5 Hz, 1H), 6.59 (d, J = 7.6 Hz, 1H), 6.47 (s, 1H), 4.95 (s, 1H), 3.72 (d, J = 9.3 Hz, 1H), 3.58 – 3.44 (m, 2H), 3.37 – 3.19 (m, 4H), 2.31 (s, 3H), 1.66 – 1.55 (m, 2H), 0.95 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 148.0, 145.0, 140.7, 137.1, 130.9, 129.6, 128.5, 127.7, 125.4, 121.2, 120.5, 108.2, 90.9, 58.4, 52.6, 45.5, 31.7, 21.9, 20.8, 11.5. IR (KBr): 3061, 2925, 1692, 1443, 1302, 1126, 751. HRMS (ESI) *m/z* calcd for $C_{23}H_{25}N_2O_3S$ $[M+H]^+$: 409.1586; found: 409.1585.

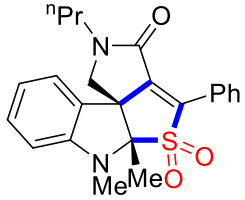


8-Fluoro-6-methyl-4-phenyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1w) : 68.5 mg, 83% yield, (41.2 mg, 50% yield), yellow solid, m.p. 155-156 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 6.9 Hz, 2H), 7.41 (d, J = 6.2 Hz, 3H), 7.05 (dd, J = 7.8, 5.5 Hz, 1H), 6.45 (t, J = 8.7 Hz, 1H), 6.35 (d, J = 9.4 Hz, 1H), 4.97 (s, 1H), 3.73 (d, J = 9.4 Hz, 1H), 3.61 – 3.44 (m, 2H), 3.39 – 3.20 (m, 4H), 1.66 – 1.54 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz,

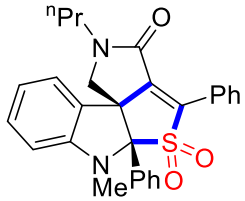
$CDCl_3$) δ 166.2, 163.8, 162.7, 149.7, 149.6, 145.2, 136.6, 131.1, 129.6, 128.6, 126.0, 125.2, 122.5, 122.4, 106.1, 105.9, 95.8, 95.6, 90.6, 58.4, 52.2, 45.6, 31.9, 20.8, 11.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.49. IR (KBr): 3066, 2928, 1692, 1488, 1303, 1127, 751. HRMS (ESI) *m/z* calcd for $C_{22}H_{22}FN_2O_3S$ $[M+H]^+$: 413.1335; found: 413.1328.



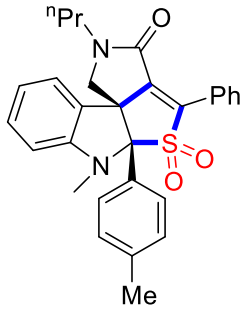
6,7-Dimethyl-4-phenyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1x) : 69.4 mg, 85% yield, (53.9 mg, 66% yield), yellow solid, m.p. 207-209 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.87 (m, 2H), 7.40 (s, 3H), 6.96 (d, *J* = 7.3 Hz, 2H), 6.69 (t, *J* = 7.4 Hz, 1H), 4.86 (s, 1H), 3.72 (d, *J* = 9.4 Hz, 1H), 3.59 – 3.42 (m, 5H), 3.36 – 3.22 (m, 1H), 2.50 (s, 3H), 1.65 – 1.53 (m, 2H), 0.95 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 145.8, 144.6, 137.0, 133.6, 131.4, 130.9, 129.6, 128.5, 125.5, 120.8, 119.9, 119.4, 92.6, 58.6, 52.2, 45.5, 36.6, 20.7, 19.0, 11.5. IR (KBr): 3061, 2963, 1690, 1458, 1300, 1125, 746. HRMS (ESI) *m/z* calcd for $C_{23}H_{25}N_2O_3S$ $[M+H]^+$: 409.1586; found: 409.1581.



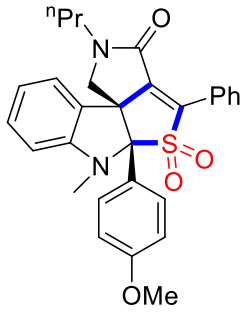
5a,6-Dimethyl-4-phenyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1y) : 40.9 mg, 50% yield, (49.8 mg, 61% yield), yellow solid, m.p. 205-207 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 4.8 Hz, 2H), 7.40 (s, 3H), 7.28 – 7.23 (m, 1H), 7.15 (d, *J* = 7.3 Hz, 1H), 6.79 (t, *J* = 7.2 Hz, 1H), 6.66 (d, *J* = 7.7 Hz, 1H), 3.76 (d, *J* = 9.3 Hz, 1H), 3.63 – 3.51 (m, 1H), 3.42 (d, *J* = 9.2 Hz, 1H), 3.37 – 3.24 (m, 1H), 3.19 (s, 3H), 1.82 (s, 3H), 1.69 – 1.57 (m, 2H), 0.98 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 148.7, 146.3, 137.1, 130.9, 130.5, 130.2, 129.7, 128.4, 125.6, 121.3, 120.0, 107.3, 93.3, 56.1, 55.1, 45.6, 29.2, 20.8, 15.6, 11.6. IR (KBr): 3063, 2927, 1692, 1481, 1290, 1137, 748. HRMS (ESI) *m/z* calcd for $C_{23}H_{25}N_2O_3S$ $[M+H]^+$: 409.1586; found: 409.1583.



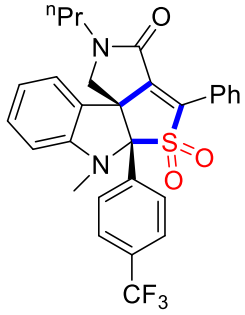
6-Methyl-4,5a-diphenyl-2-propyl-1,2,5a,6-tetrahydro-3H-pyrrolo[3',4':3,4]thieno[2,3-b]indol-3-one 5,5-dioxide (1z): 58.3 mg, 62% yield, (79.9 mg, 85% yield), yellow solid, m.p. 200-201 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 2.5 Hz, 2H), 7.55 (s, 2H), 7.45 (s, 6H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 7.3 Hz, 1H), 6.91 – 6.75 (m, 2H), 3.49 – 3.38 (m, 1H), 3.33 (s, 3H), 3.19 – 3.01 (m, 2H), 2.72 (d, *J* = 9.7 Hz, 1H), 1.52 – 1.39 (m, 2H), 0.84 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 149.4, 149.0, 138.4, 131.8, 131.0, 130.6, 130.2, 129.8, 129.7, 129.1, 128.5, 125.5, 121.4, 120.4, 107.9, 101.9, 58.6, 56.5, 45.2, 32.0, 20.5, 11.3. IR (KBr): 3062, 2928, 1696, 1480, 1291, 1138, 750. HRMS (ESI) *m/z* calcd for $C_{28}H_{26}N_2NaO_3S$ $[M+Na]^+$: 493.1556; found: 493.1555.



6-Methyl-4-phenyl-2-propyl-5a-(p-tolyl)-1,2,5a,6-tetrahydro-3H-pyrrolo[3',4':3,4]thieno[2,3-b]indol-3-one 5,5-dioxide (1aa): 69.7 mg, 72% yield, (87.1 mg, 90% yield), yellow solid, m.p. 192-193 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 3.2 Hz, 2H), 7.43 (d, J = 7.4 Hz, 5H), 7.31 (t, J = 7.7 Hz, 1H), 7.23 (d, J = 7.9 Hz, 2H), 7.17 (d, J = 7.4 Hz, 1H), 6.91 – 6.73 (m, 2H), 3.50 – 3.39 (m, 1H), 3.31 (s, 3H), 3.16 – 3.01 (m, 2H), 2.77 (d, J = 9.8 Hz, 1H), 2.37 (s, 3H), 1.54 – 1.39 (m, 2H), 0.85 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 149.3, 148.9, 139.8, 138.5, 130.9, 130.6, 130.2, 129.7, 129.7, 128.6, 128.5, 128.3, 125.5, 121.3, 120.2, 107.8, 102.0, 58.5, 56.4, 45.2, 32.0, 21.2, 20.5, 11.3. IR (KBr): 3060, 2926, 1695, 1480, 1291, 1137, 751. HRMS (ESI) *m/z* calcd for $C_{29}H_{28}N_2NaO_3S$ $[M+Na]^+$: 507.1713; found: 507.1718.

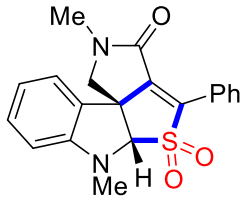


5a-(4-Methoxyphenyl)-6-methyl-4-phenyl-2-propyl-1,2,5a,6-tetrahydro-3H-pyrrolo[3',4':3,4]thieno[2,3-b]indol-3-one 5,5-dioxide (1ab): 43.0 mg, 43% yield, (75.2 mg, 75% yield), yellow solid, m.p. 182-183 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 4.5 Hz, 2H), 7.57 – 7.38 (m, 5H), 7.32 (t, J = 7.7 Hz, 1H), 7.17 (d, J = 7.4 Hz, 1H), 6.97 (d, J = 8.6 Hz, 2H), 6.90 – 6.75 (m, 2H), 3.82 (s, 3H), 3.53 – 3.39 (m, 1H), 3.29 (d, J = 14.9 Hz, 3H), 3.18 – 3.03 (m, 2H), 2.79 (d, J = 9.8 Hz, 1H), 1.54 – 1.39 (m, 2H), 0.86 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 160.4, 149.3, 149.0, 138.5, 130.9, 130.7, 130.2, 129.8, 129.7, 128.5, 125.5, 123.4, 121.4, 120.3, 114.4, 107.8, 102.0, 58.6, 56.4, 55.5, 45.2, 31.9, 20.5, 11.4. IR (KBr): 3066, 2925, 1696, 1482, 1295, 1138, 749. HRMS (ESI) *m/z* calcd for $C_{29}H_{28}N_2NaO_4S$ $[M+Na]^+$: 523.1662; found: 523.1666.

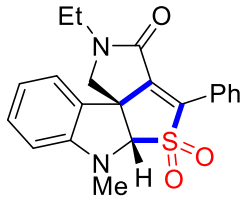


6-Methyl-4-phenyl-2-propyl-5a-(4-(trifluoromethyl)phenyl)-1,2,5a,6-tetrahydro-3H-pyrrolo[3',4':3,4]thieno[2,3-b]indol-3-one 5,5-dioxide (1ac): 21.5 mg, 20% yield, (53.8 mg, 50% yield), yellow

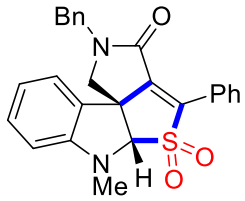
solid, m.p. 196-197 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 5.1 Hz, 2H), 7.78 – 7.67 (m, 4H), 7.46 (d, J = 5.1 Hz, 3H), 7.35 (t, J = 7.7 Hz, 1H), 7.19 (d, J = 7.4 Hz, 1H), 6.89 (t, J = 7.5 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 3.55 – 3.43 (m, 1H), 3.33 (s, 3H), 3.17 (d, J = 9.8 Hz, 1H), 3.14 – 3.04 (m, 1H), 2.71 (d, J = 9.8 Hz, 1H), 1.53 – 1.38 (m, 2H), 0.86 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 149.1, 148.8, 138.1, 136.0, 132.0, 131.7, 131.3, 130.5, 130.4, 129.8, 129.1, 128.7, 126.1, 126.1, 126.0, 125.2, 122.4, 121.4, 120.8, 108.2, 101.0, 58.7, 56.4, 45.4, 32.1, 20.6, 11.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.88. IR (KBr): 3065, 2920, 1693, 1481, 1292, 1136, 746. HRMS (ESI) *m/z* calcd for $C_{29}H_{25}F_3N_2NaO_3S$ $[M+Na]^+$: 561.1430; found: 561.1425.



2,6-Dimethyl-4-phenyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1ad): 53.5 mg, 73% yield, (51.3 mg, 70% yield), yellow solid, m.p. 226-227 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.82 (dd, J = 7.5, 1.7 Hz, 2H), 7.55 – 7.40 (m, 3H), 7.26 (t, J = 7.6 Hz, 1H), 7.07 (d, J = 7.1 Hz, 1H), 6.78 (t, J = 7.3 Hz, 2H), 5.60 (s, 1H), 4.07 (d, J = 9.7 Hz, 1H), 3.54 (d, J = 9.5 Hz, 1H), 3.25 (s, 3H), 3.00 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 162.6, 148.4, 143.8, 138.9, 131.2, 131.1, 130.3, 129.5, 128.9, 126.0, 121.6, 119.6, 107.6, 90.2, 59.8, 53.1, 31.8, 30.9. IR (KBr): 3064, 2962, 1693, 1486, 1301, 1127, 747. HRMS (ESI) *m/z* calcd for $C_{20}H_{18}N_2NaO_3S$ $[M+Na]^+$: 389.0936; found: 389.0929.



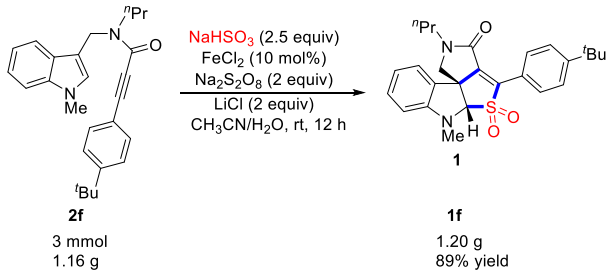
2-Ethyl-6-methyl-4-phenyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1ae) : 60.9 mg, 80% yield, (60.9 mg, 80% yield), yellow solid, m.p. 285-287 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, J = 6.8, 1.5 Hz, 2H), 7.45 – 7.35 (m, 3H), 7.25 (t, J = 7.7 Hz, 1H), 7.12 (d, J = 7.5 Hz, 1H), 6.78 (t, J = 7.5 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 4.97 (s, 1H), 3.74 (d, J = 9.4 Hz, 1H), 3.67 – 3.51 (m, 2H), 3.48 – 3.34 (m, 1H), 3.29 (s, 3H), 1.19 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 147.8, 145.2, 137.0, 130.9, 130.4, 130.4, 129.6, 128.5, 125.4, 121.4, 119.8, 107.3, 90.4, 57.7, 52.8, 38.4, 31.8, 12.5. IR (KBr): 3061, 2932, 1688, 1483, 1301, 1126, 747. HRMS (ESI) *m/z* calcd for $C_{21}H_{20}N_2NaO_3S$ $[M+Na]^+$: 403.1092; found: 403.1090.



2-Benzyl-6-methyl-4-phenyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1af) : 15.0 mg, 17% yield, (50.7 mg, 60% yield), yellow solid, m.p. 254-256 °C. ^{1}H NMR (400 MHz, DMSO) δ 7.90 – 7.81 (m, 2H), 7.51 (d, J = 6.7 Hz, 3H), 7.41 – 7.30 (m, 5H), 7.21 (t, J = 7.6 Hz, 1H), 6.92 (d, J = 7.4 Hz, 1H), 6.75 (d, J = 7.9 Hz, 1H), 6.67 (t, J = 7.4 Hz, 1H), 5.61 (s, 1H), 4.70 (d, J = 14.5 Hz, 1H), 4.56 (d, J = 14.5 Hz, 1H), 4.01 (d, J = 9.6 Hz, 1H), 3.43 (d, J = 9.6 Hz, 1H),

3.21 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 162.3, 148.4, 144.5, 138.8, 136.2, 131.2, 130.9, 130.2, 129.5, 129.2, 129.1, 129.0, 128.3, 125.9, 121.5, 119.4, 107.6, 90.3, 57.5, 53.0, 47.4, 31.8. IR (KBr): 3063, 2924, 1686, 1484, 1301, 1129, 747. HRMS (ESI) *m/z* calcd for $C_{26}H_{22}N_2NaO_3S$ $[M+Na]^+$: 465.1249; found: 465.1248.

7. Gram-scale reaction

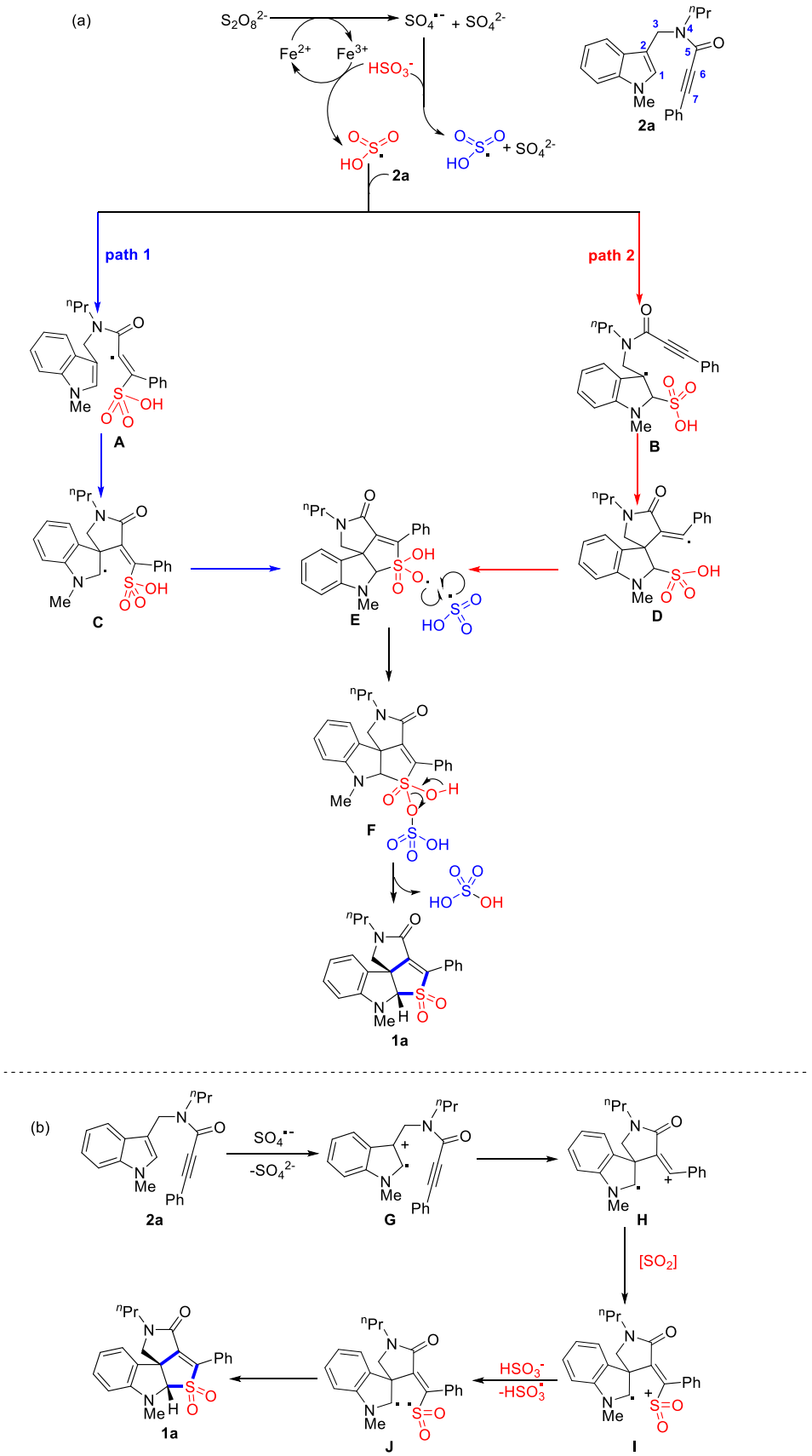


2f
3 mmol
1.16 g

1f
1.20 g
89% yield

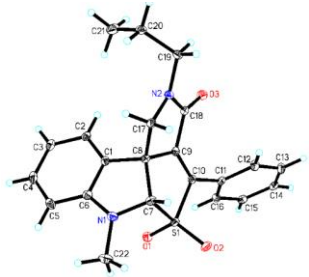
To an oven-dried 50 mL Schlenk tube under N_2 atmosphere equipped with a magnetic bar were added $FeCl_2$ (10 mol %, 37.8 mg), $NaHSO_3$ (7.5 mmol, 780.0 mg), $Na_2S_2O_8$ (6 mmol, 1.40 mg), and LiCl (6 mmol, 252.0 mg), and then H_2O (7.0 mL), substrate **2f** (3 mmol, 1.0 equiv) and CH_3CN (20.0 mL) were added. The mixture was stirred at room temperature for 12 h. The corresponding reaction mixture was filtered through a pad of celite, washed with EtOAc and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether /ethyl acetate = 5/1) to give corresponding product **1f** in 89% yield (1.20 g).

8. Proposed Mechanisms for Formation of 1a.



Scheme 1 Proposed Mechanisms for Formation of 1a

9. X-Ray diffraction analysis



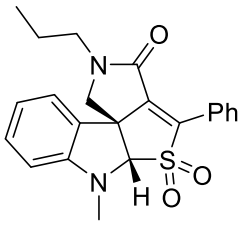


Table S3. Crystal data and structure refinement for **1a** (CCDC 1889285)

Identification code	**1a**
Empirical formula	$C_{22}H_{22}N_2O_3S$
Formula weight	394.47
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.7874(2)
b/Å	12.0670(2)
c/Å	14.6568(3)
α/°	90
β/°	92.032(2)
γ/°	90
Volume/Å^3	1906.70(6)
Z	4
ρ_{calc}g/cm^3	1.374
μ/mm^{-1}	1.724
F(000)	832.0
Crystal size/mm^3	0.14 × 0.12 × 0.11
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.496 to 146.9
Index ranges	-12 ≤ h ≤ 13, -13 ≤ k ≤ 14, -18 ≤ l ≤ 9
Reflections collected	7614
Independent reflections	3736 [R_{int} = 0.0184, R_{sigma} = 0.0225]
Data/restraints/parameters	3736/0/255
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0393, wR_2 = 0.1069
Final R indexes [all data]	R_1 = 0.0405, wR_2 = 0.1083
Largest diff. peak/hole / e Å^{-3}	0.37/-0.45

Table S4. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **1a**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**

S1	5529.3(3)	7184.0(3)	1673.0(2)	16.63(12)
O1	4505.5(9)	6576.6(9)	1256.6(7)	21.7(2)
O3	5765.8(11)	7198.1(9)	4959.6(7)	24.9(3)
O2	5918(1)	8184.9(9)	1230.0(7)	24.4(3)
N2	7298.8(12)	6056.7(10)	4421.8(8)	19.0(3)
N1	6799.4(12)	5261.3(11)	1333.8(8)	20.5(3)
C18	6274.1(14)	6709.2(12)	4342.8(10)	17.9(3)
C9	5924.2(13)	6729.0(12)	3345.4(9)	16.0(3)
C11	4592.6(13)	8477.5(12)	3092(1)	17.1(3)
C10	5282.6(13)	7467.1(12)	2850.5(10)	16.6(3)
C1	5979.3(13)	4749.4(12)	2690.1(10)	16.2(3)
C8	6656.1(13)	5837.7(12)	2877.1(9)	15.7(3)
C16	3360.6(13)	8620.8(13)	2795.6(10)	19.4(3)
C2	5368.9(13)	4053.6(12)	3274.4(10)	18.9(3)
C17	7785.7(13)	5692.1(12)	3547.7(10)	17.4(3)
C15	2738.7(14)	9596.0(13)	2999.8(10)	20.9(3)
C6	6097.7(13)	4467.9(13)	1770.9(10)	19.2(3)
C7	6879.2(13)	6223.4(12)	1894.1(10)	18.1(3)
C14	3344.1(14)	10429.2(12)	3484.9(10)	20.8(3)
C20	8398.8(14)	4807.2(13)	5546.1(10)	21.1(3)
C3	4854.3(14)	3074.0(13)	2925.9(11)	22.8(3)
C4	4954.2(15)	2810.0(13)	2010.1(12)	25.0(4)
C5	5580.9(14)	3495.4(13)	1413.9(11)	23.9(3)
C12	5192.2(14)	9311.4(13)	3594.2(11)	23.9(3)
C13	4569.4(15)	10287.8(13)	3789.1(12)	24.8(3)
C19	8049.6(15)	5989.0(13)	5270(1)	23.8(3)
C22	6883.6(16)	5329.9(16)	347.1(10)	28.9(4)
C21	7288.7(17)	4059.7(16)	5687.4(13)	32.4(4)

Table S5. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **1a**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	$\mathbf{U_{11}}$	$\mathbf{U_{22}}$	$\mathbf{U_{33}}$	$\mathbf{U_{23}}$	$\mathbf{U_{13}}$	$\mathbf{U_{12}}$
S1	16.4(2)	16.1(2)	17.3(2)	3.84(12)	-1.11(13)	-0.08(12)
O1	19.2(5)	21.2(5)	24.3(5)	-0.4(4)	-3.8(4)	0.8(4)
O3	32.0(6)	23.4(6)	19.2(5)	-2.0(4)	1.0(5)	6.7(5)
O2	28.0(6)	21.3(6)	24.0(5)	8.2(4)	-0.1(4)	-2.6(5)
N2	22.8(6)	16.9(6)	16.9(6)	-0.8(5)	-4.1(5)	2.7(5)
N1	21.5(6)	24.5(7)	15.5(6)	-0.4(5)	0.9(5)	4.4(5)
C18	21.5(7)	13.5(7)	18.6(7)	1.5(5)	-0.6(5)	0.2(5)

C9	14.8(6)	14.9(7)	18.1(7)	0.0(5)	0.7(5)	-2.0(5)
C11	17.6(7)	14.6(7)	19.0(7)	3.9(5)	1.2(5)	-0.1(5)
C10	15.0(6)	15.7(7)	18.9(7)	1.4(5)	-0.1(5)	-3.3(6)
C1	14.1(6)	14.8(7)	19.7(7)	-0.7(5)	-1.8(5)	2.9(5)
C8	15.4(6)	15.6(7)	16.1(7)	1.9(5)	0.2(5)	0.4(5)
C16	18.9(7)	19.3(7)	19.9(7)	0.8(6)	-1.5(5)	-0.8(6)
C2	17.1(7)	17.8(7)	21.4(7)	2.4(6)	-1.4(5)	2.5(6)
C17	16.5(7)	17.0(7)	18.6(7)	0.5(5)	-1.9(5)	1.3(5)
C15	16.7(7)	23.7(8)	22.5(7)	4.4(6)	1.0(5)	3.4(6)
C6	16.9(7)	20.6(7)	19.9(7)	-0.3(6)	-1.7(5)	5.7(6)
C7	14.1(6)	21.4(7)	18.9(7)	3.8(6)	0.6(5)	1.1(5)
C14	22.6(7)	17.1(7)	22.9(7)	4.8(6)	5.8(6)	3.6(6)
C20	22.8(7)	22.6(8)	17.5(7)	0.3(6)	-3.9(6)	4.9(6)
C3	18.6(7)	15.9(7)	33.7(8)	2.9(6)	-1.4(6)	0.5(6)
C4	20.1(7)	16.5(7)	37.9(9)	-5.6(6)	-7.5(7)	2.8(6)
C5	23.5(8)	23.3(8)	24.3(8)	-8.0(6)	-6.3(6)	8.1(6)
C12	18.3(7)	18.8(7)	34.3(9)	1.1(6)	-6.2(6)	0.2(6)
C13	25.2(8)	16.9(7)	31.9(8)	-1.4(6)	-3.3(6)	-2.3(6)
C19	29.4(8)	20.7(8)	20.4(7)	-3.8(6)	-9.9(6)	3.3(6)
C22	29.4(8)	41.3(10)	16.3(7)	0.8(7)	2.1(6)	5.4(7)
C21	29.3(9)	34.6(9)	32.7(9)	10.8(7)	-7.3(7)	-3.2(7)

Table S6. Bond Lengths for **1a**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
S1	O1	1.4428(11)	C11	C12	1.392(2)
S1	O2	1.4406(11)	C1	C8	1.5227(19)
S1	C10	1.7885(15)	C1	C2	1.383(2)
S1	C7	1.8803(15)	C1	C6	1.400(2)
O3	C18	1.2252(19)	C8	C17	1.5482(19)
N2	C18	1.3587(19)	C8	C7	1.5410(19)
N2	C17	1.4691(18)	C16	C15	1.392(2)
N2	C19	1.4617(18)	C2	C3	1.395(2)
N1	C6	1.391(2)	C15	C14	1.382(2)
N1	C7	1.4230(19)	C6	C5	1.393(2)
N1	C22	1.4546(19)	C14	C13	1.390(2)
C18	C9	1.4970(19)	C20	C19	1.526(2)
C9	C10	1.328(2)	C20	C21	1.519(2)
C9	C8	1.5132(19)	C3	C4	1.387(2)
C11	C10	1.478(2)	C4	C5	1.395(2)

C11	C16	1.394(2)	C12	C13	1.391(2)

Table S7. Bond Angles for **1a.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	S1	C10	111.56(6)	C6	C1	C8	108.85(12)
O1	S1	C7	109.65(7)	C9	C8	C1	116.11(11)
O2	S1	O1	117.76(7)	C9	C8	C17	101.79(11)
O2	S1	C10	109.30(7)	C9	C8	C7	108.11(11)
O2	S1	C7	111.01(7)	C1	C8	C17	112.20(11)
C10	S1	C7	95.30(7)	C1	C8	C7	100.48(11)
C18	N2	C17	114.47(12)	C7	C8	C17	118.84(11)
C18	N2	C19	121.96(13)	C15	C16	C11	119.94(14)
C19	N2	C17	121.36(12)	C1	C2	C3	118.67(14)
C6	N1	C7	108.57(12)	N2	C17	C8	102.83(11)
C6	N1	C22	123.46(13)	C14	C15	C16	120.19(14)
C7	N1	C22	121.52(13)	N1	C6	C1	110.25(13)
O3	C18	N2	126.88(14)	N1	C6	C5	128.60(14)
O3	C18	C9	127.51(13)	C5	C6	C1	121.13(14)
N2	C18	C9	105.59(12)	N1	C7	S1	111.89(10)
C18	C9	C8	108.30(12)	N1	C7	C8	106.56(12)
C10	C9	C18	130.75(13)	C8	C7	S1	101.63(9)
C10	C9	C8	119.95(13)	C15	C14	C13	120.15(14)
C16	C11	C10	120.68(13)	C21	C20	C19	113.75(14)
C12	C11	C10	119.63(13)	C4	C3	C2	120.35(15)
C12	C11	C16	119.65(14)	C3	C4	C5	121.72(14)
C9	C10	S1	107.85(11)	C6	C5	C4	117.41(14)
C9	C10	C11	132.82(13)	C13	C12	C11	120.14(14)
C11	C10	S1	118.82(10)	C14	C13	C12	119.91(14)
C2	C1	C8	130.40(13)	N2	C19	C20	113.70(12)
C2	C1	C6	120.69(13)				

Table S8. Hydrogen Atom Coordinates ($Å \times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **1a.**

Atom	*x*	*y*	*z*	U(eq)
H16	2954.53	8065.56	2461.9	23
H2	5302.62	4235.07	3887.41	23
H17A	8051.85	4924.69	3577.12	21

H17B	8476.24	6150.82	3372.5	21
H15	1913.52	9686.97	2809.14	25
H7	7676.96	6603.58	1845.83	22
H14	2931.05	11085.9	3608.1	25
H20A	8900.23	4487.32	5076.95	25
H20B	8902.17	4831.29	6107.46	25
H3	4442.28	2595.37	3309.43	27
H4	4593.99	2159.19	1787.85	30
H5	5650.87	3310.32	801.91	29
H12	6010.69	9215.3	3799.75	29
H13	4972.04	10845.27	4122.53	30
H19A	7594.01	6325.44	5757.07	29
H19B	8803.28	6414.63	5200.76	29
H22A	7059.03	4608.88	106.69	43
H22B	7536.51	5832.18	198.68	43
H22C	6110.85	5593.85	84.61	43
H21A	6814.03	3990.41	5123.8	49
H21B	6778.88	4375.23	6144.14	49
H21C	7571.64	3341.07	5883.62	49

Crystal structure determination of 1a

Crystal Data for $C_{22}H_{22}N_2O_3S$ (*M* =394.47 g/mol): monoclinic, space group $P2_1/n$ (no. 14), *a* = 10.7874(2) Å, *b* = 12.0670(2) Å, *c* = 14.6568(3) Å, *β* = 92.032(2) °, *V* = 1906.70(6) $Å^3$, *Z* = 4, *T* = 100.00(10) K, μ(CuKα) = 1.724 mm^{-1}, *Dcalc* = 1.374 g/cm^3, 7614 reflections measured (9.496° ≤ 2Θ ≤ 146.9 °), 3736 unique (R_{int} = 0.0184, R_{sigma} = 0.0225) which were used in all calculations. The final R_1 was 0.0393 (I > 2σ(I)) and wR_2 was 0.1083 (all data).

10. References

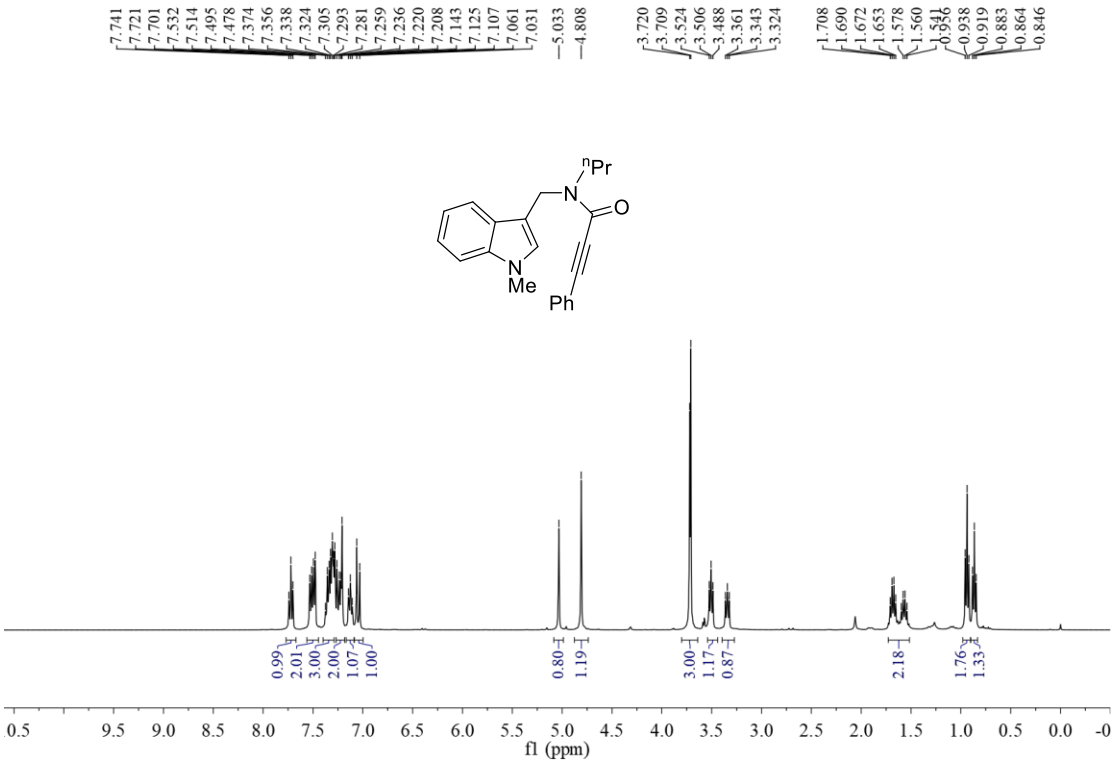
(1) Muratore, M. E.; Holloway, C. A.; Pilling, A. W.; Storer, R. L.; Trevitt, G.; Dixon, D. J.; *J. Am. Chem. Soc.*, **2009**, *131*, 10796.

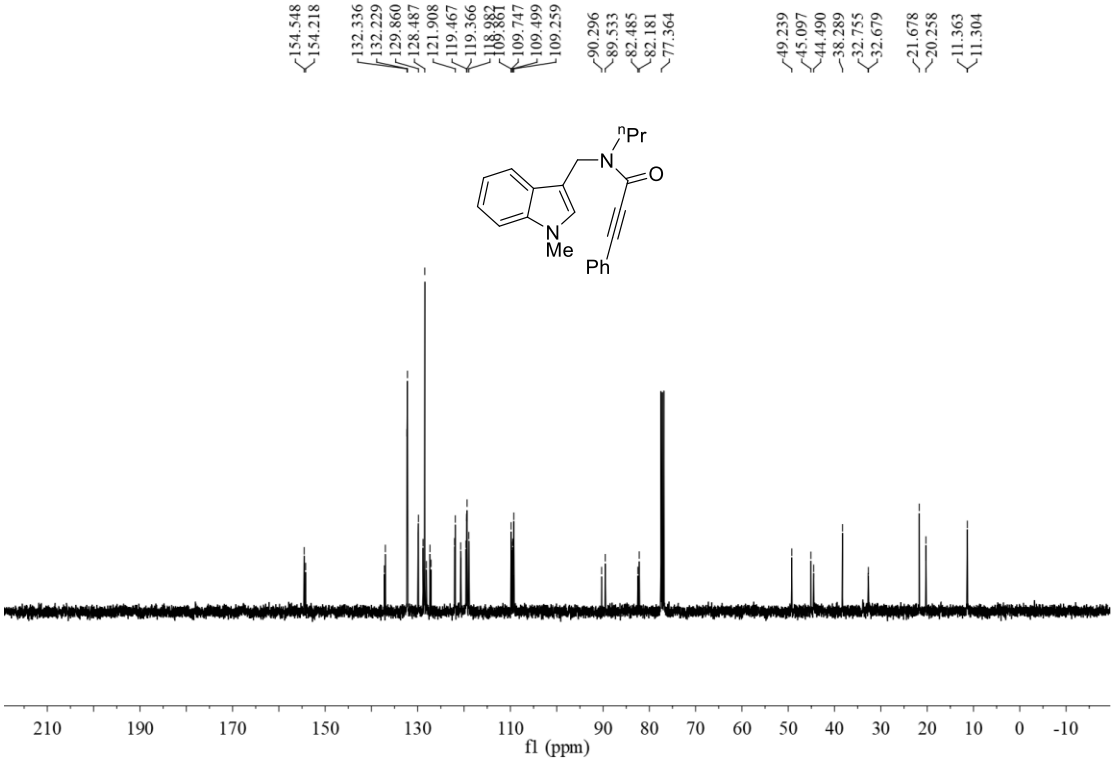
(2) (a) Chen, K.; Zhang, Y.-L.; Fan, J.; Ma, X.; Qin, Y.-J.; Zhu, H.-L. *Eur. J. Med. Chem.*, **2018**, *156*, 722; (b) Zhang, S.; An, B.; Li, J.; Hu, J.; Huang, L.; Li, X.; Chan, A. S. C. *Org. Biomol. Chem.*, **2017**, *15*, 7404; (c) Yang, M.-R.; Qin, Y.-J.; Chen, C.; Zhang, Y.-L.; Li, B.-Y.; Liu, T.-B.; Gong, H.-B.; Wang, B.-Z.; Zhu, H.-L. *RSC Adv.*, **2016**, *6*, 30412.

(3) Yang, Y.; Fei, C.; Wang, K.; Liu, B.; Jiang, D.; Yin, B. *Org. Lett.*, **2018**, *20*, 2273.

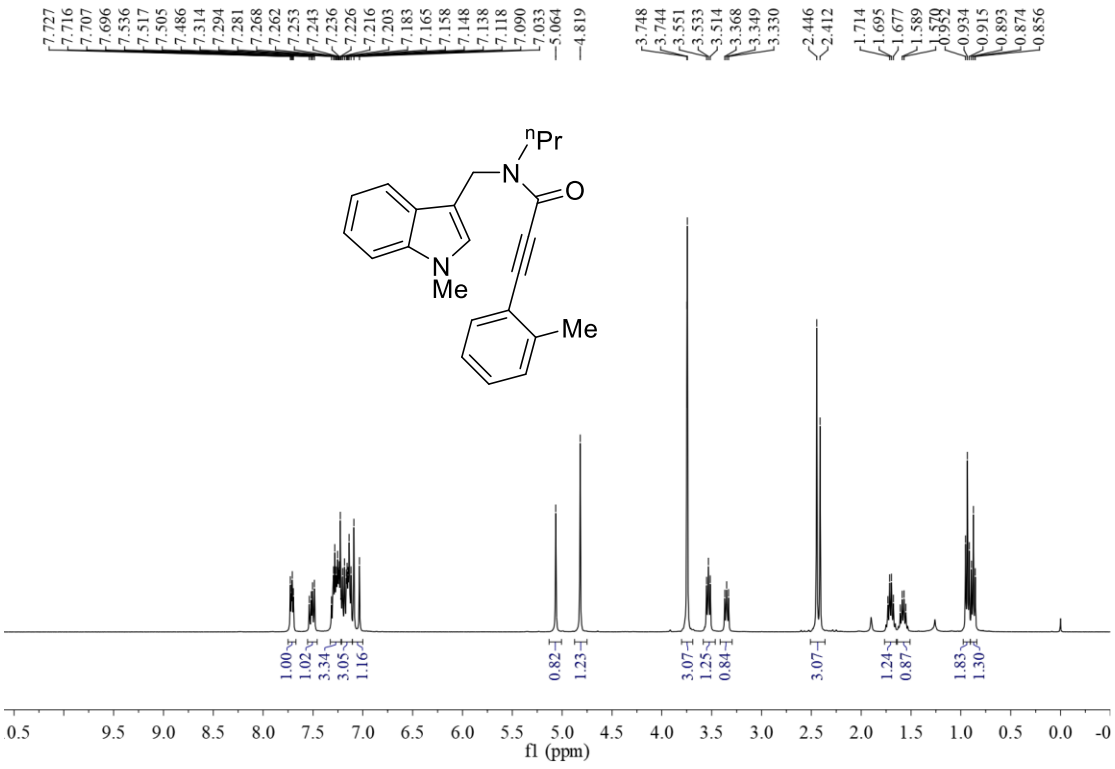
11. NMR spectra of compounds

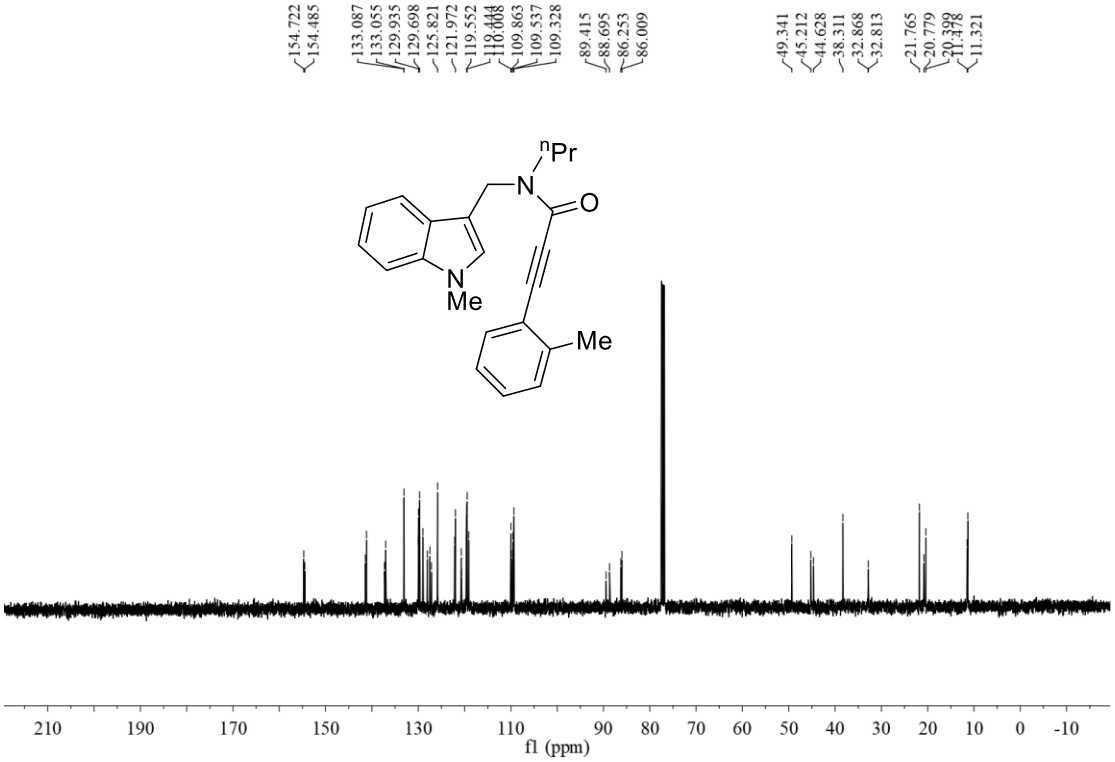
N-((1-methyl-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2a)





***N*-((1-methyl-1H-indol-3-yl)methyl)-*N*-propyl-3-(o-tolyl)propiolamide (2b) :**





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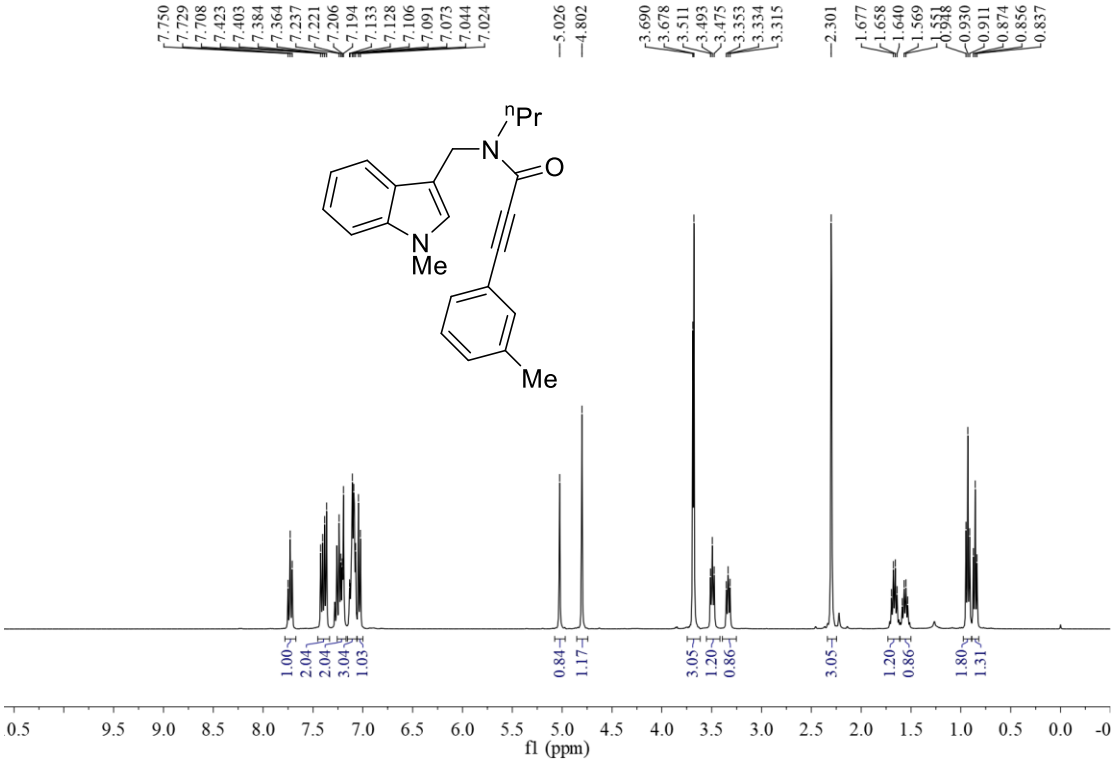

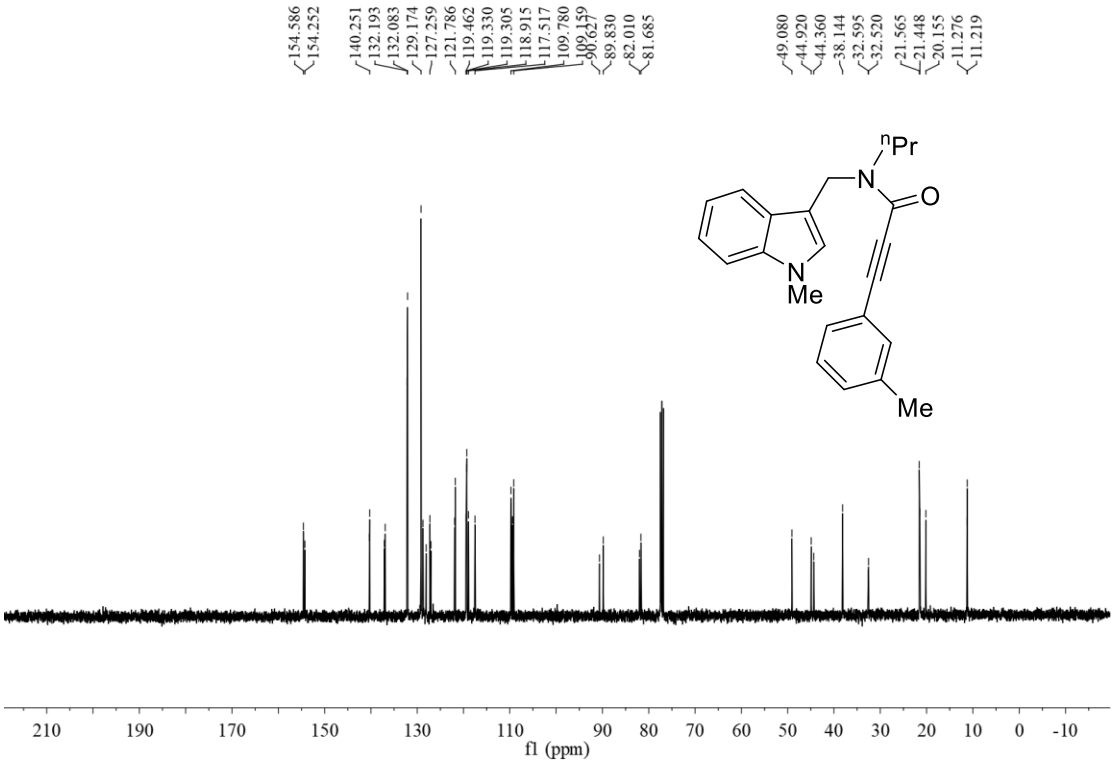

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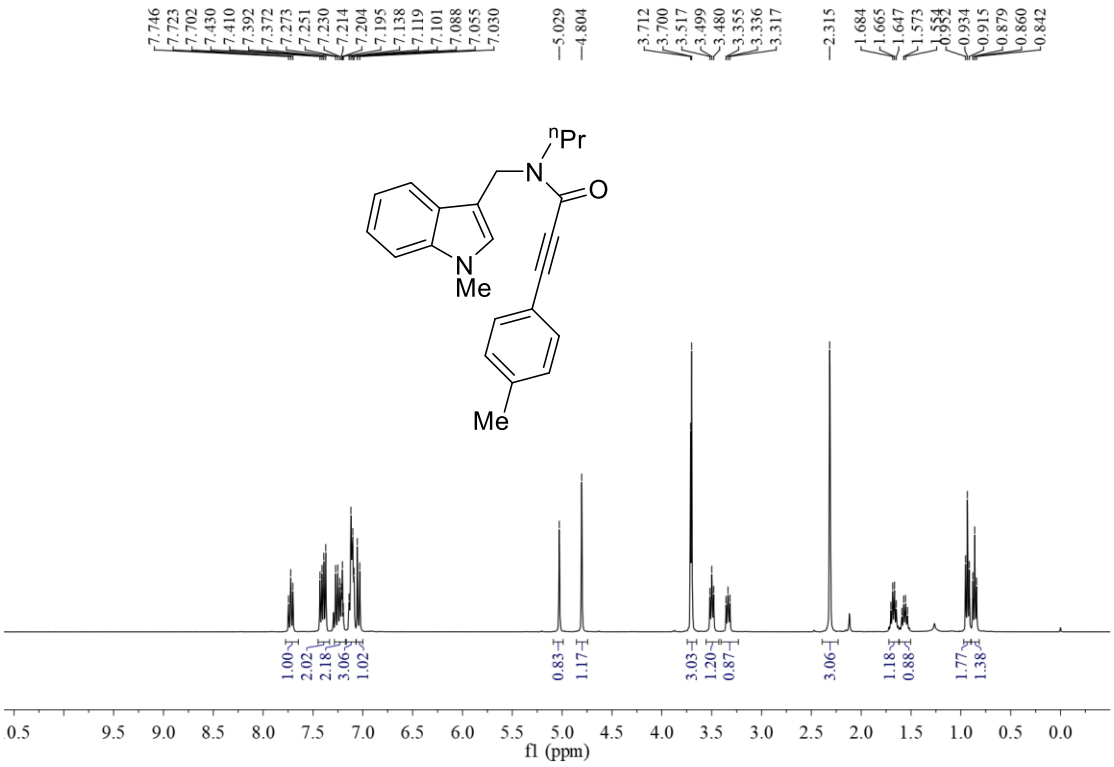

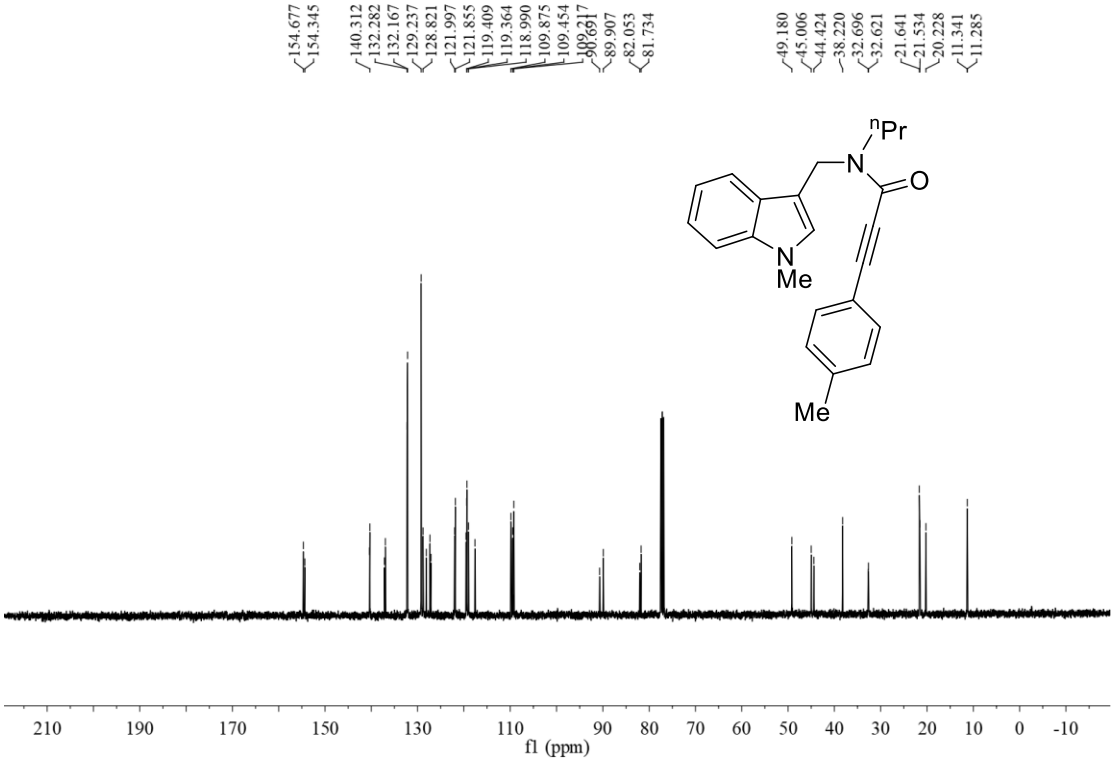

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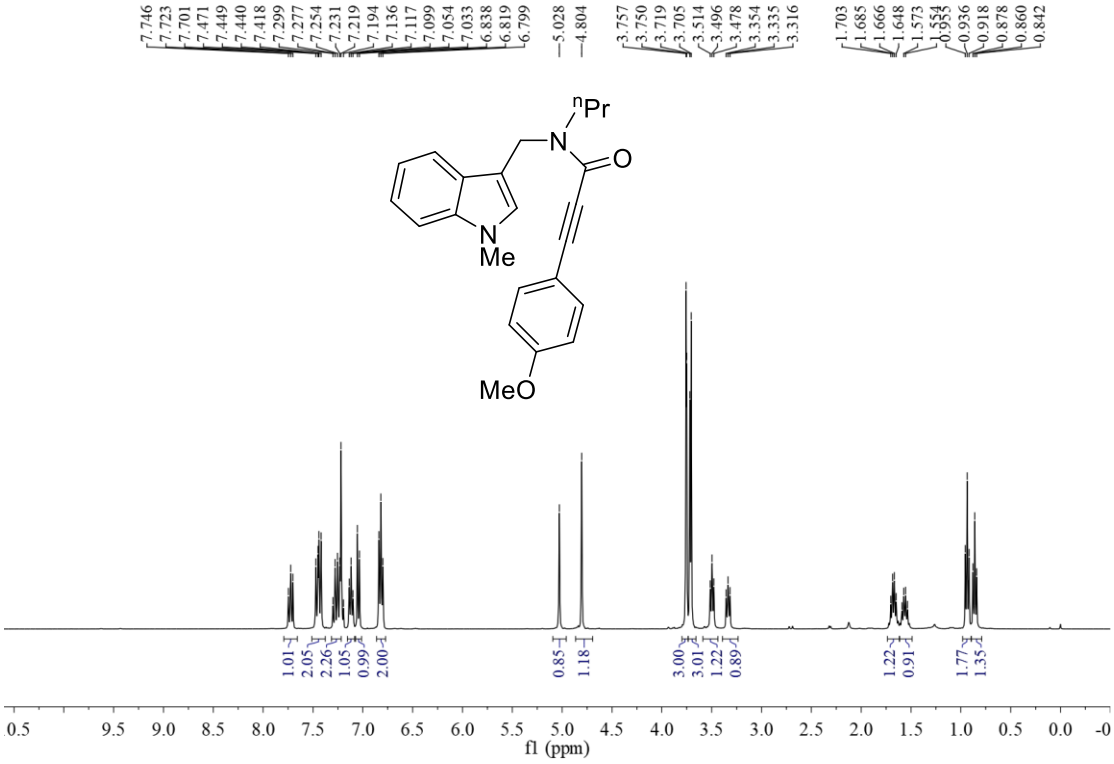

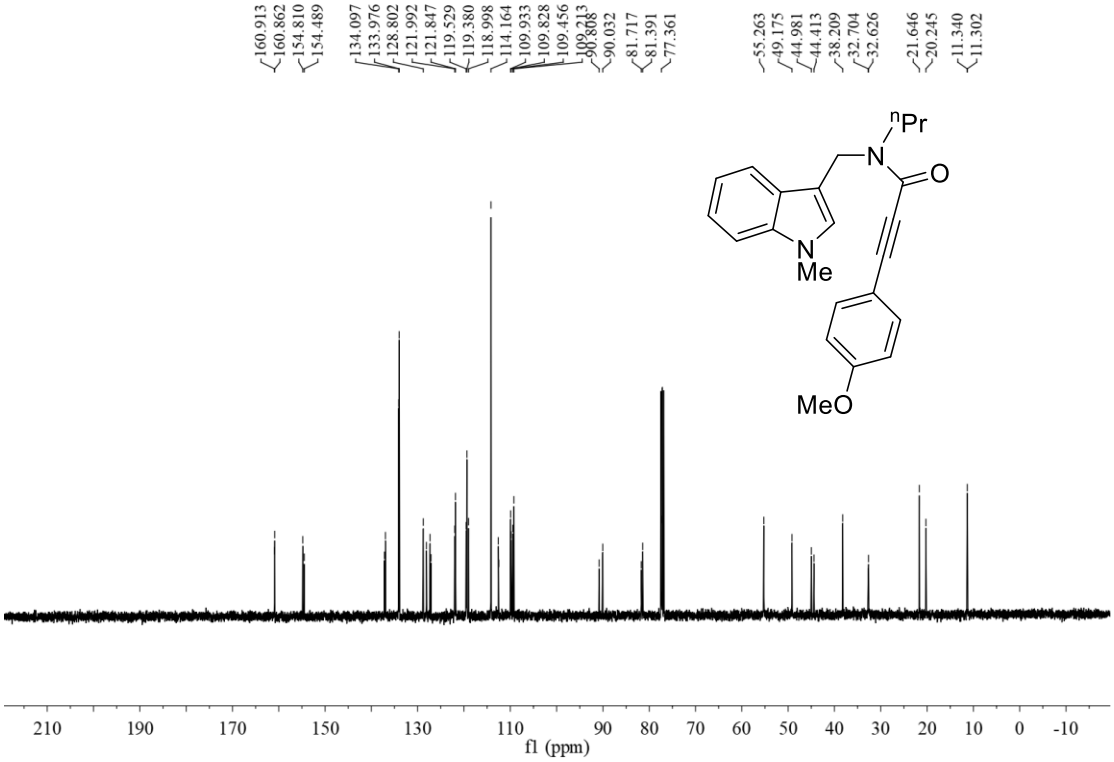

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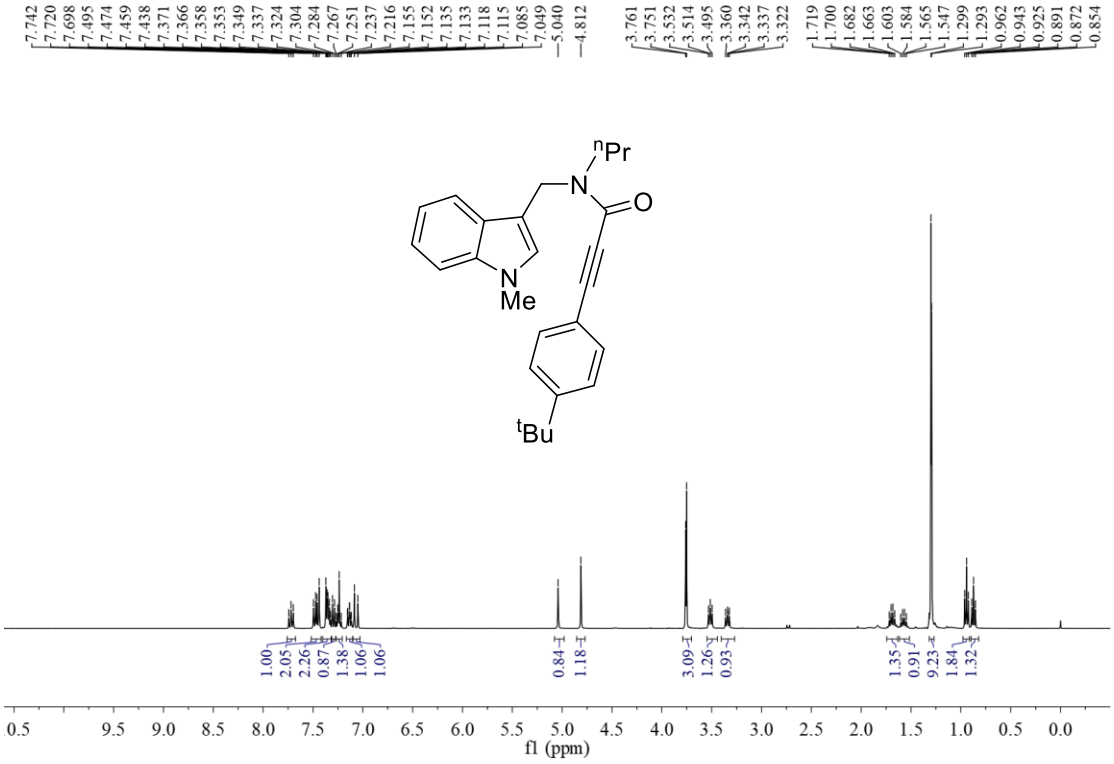

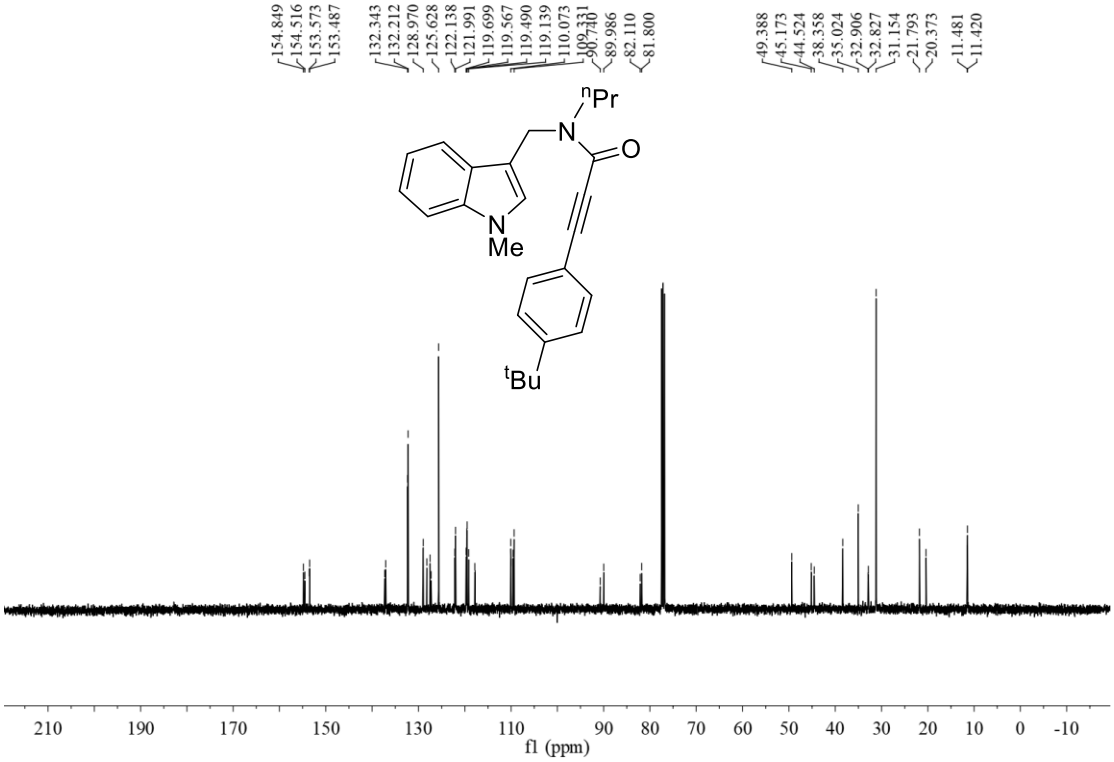

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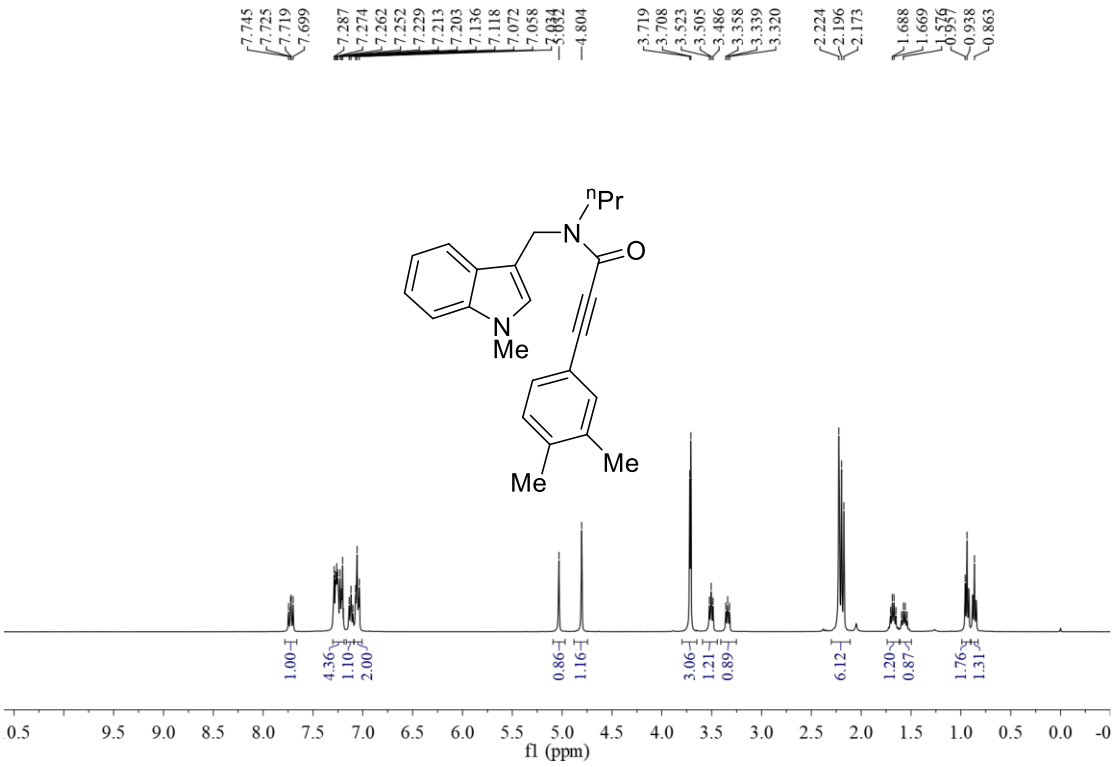

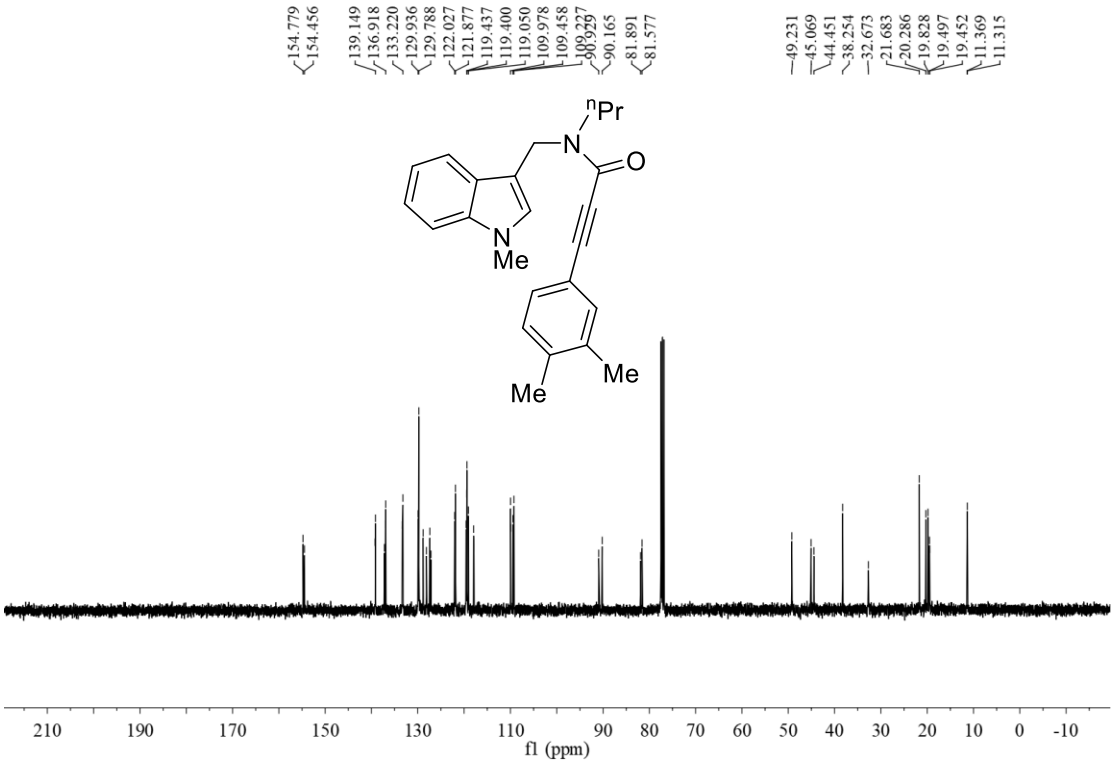

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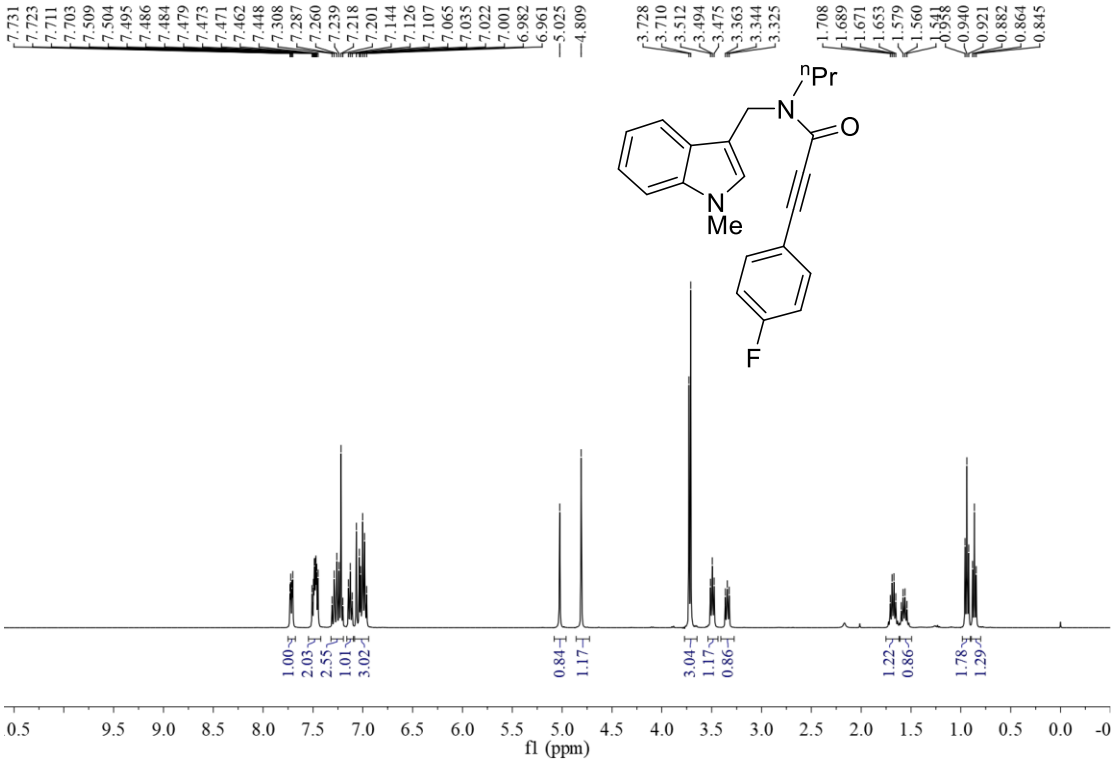

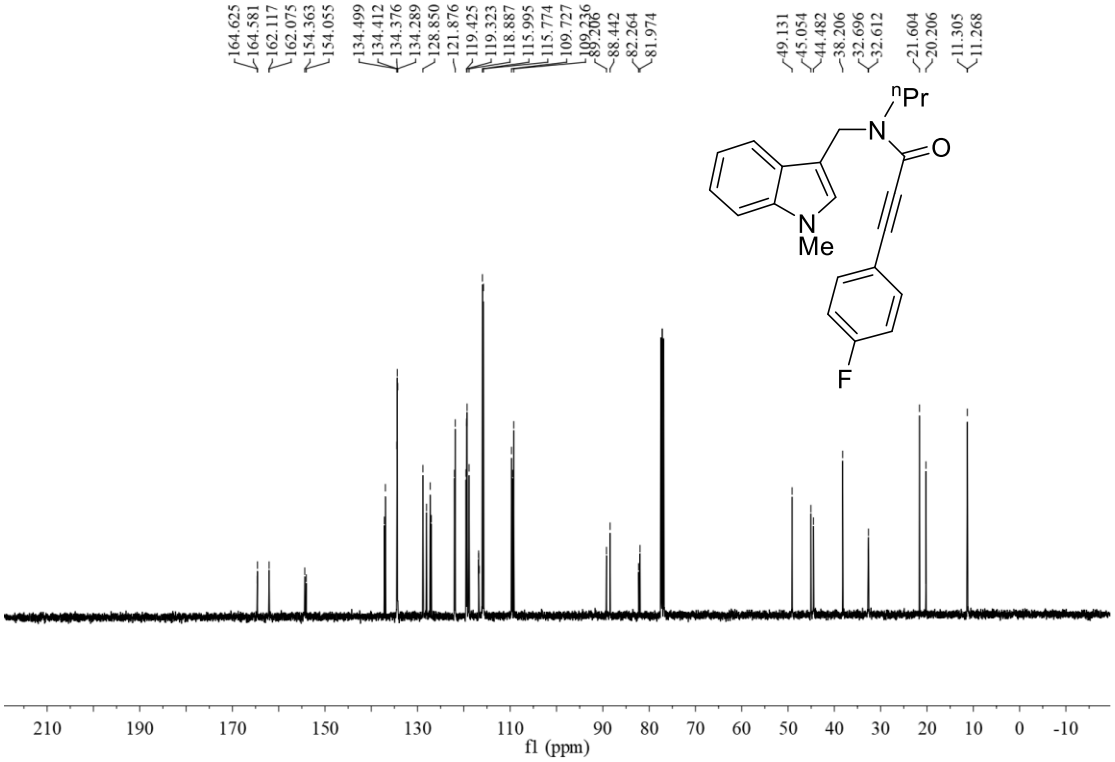

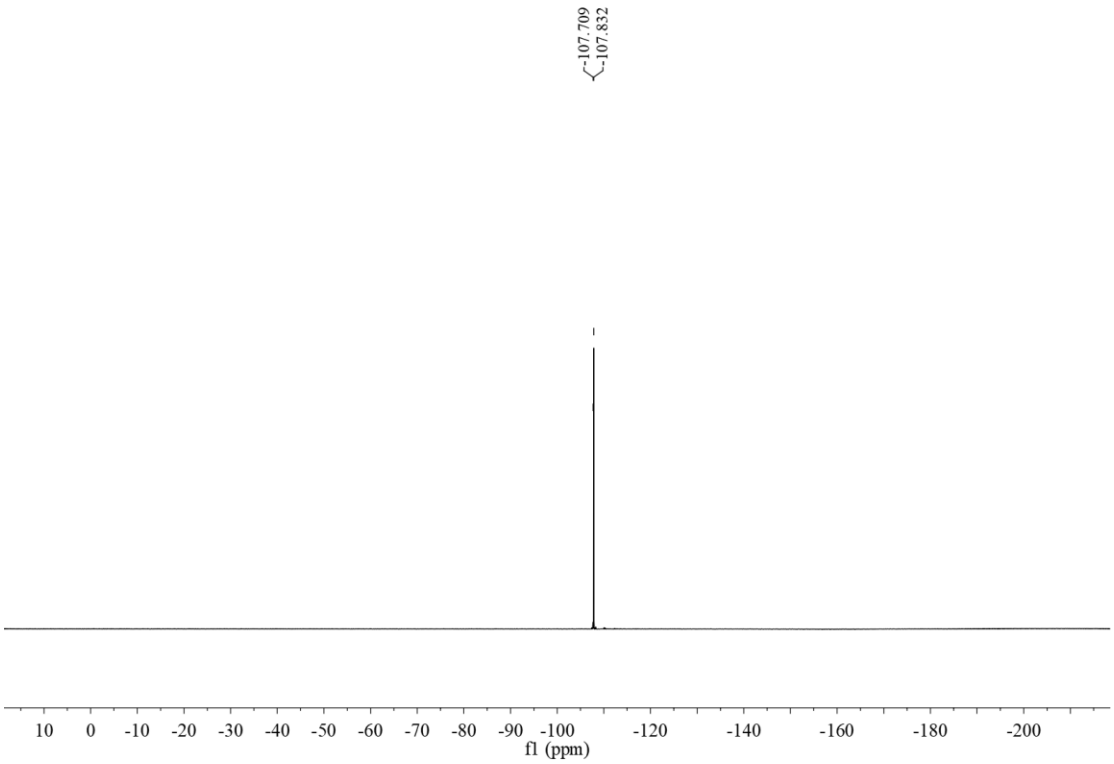
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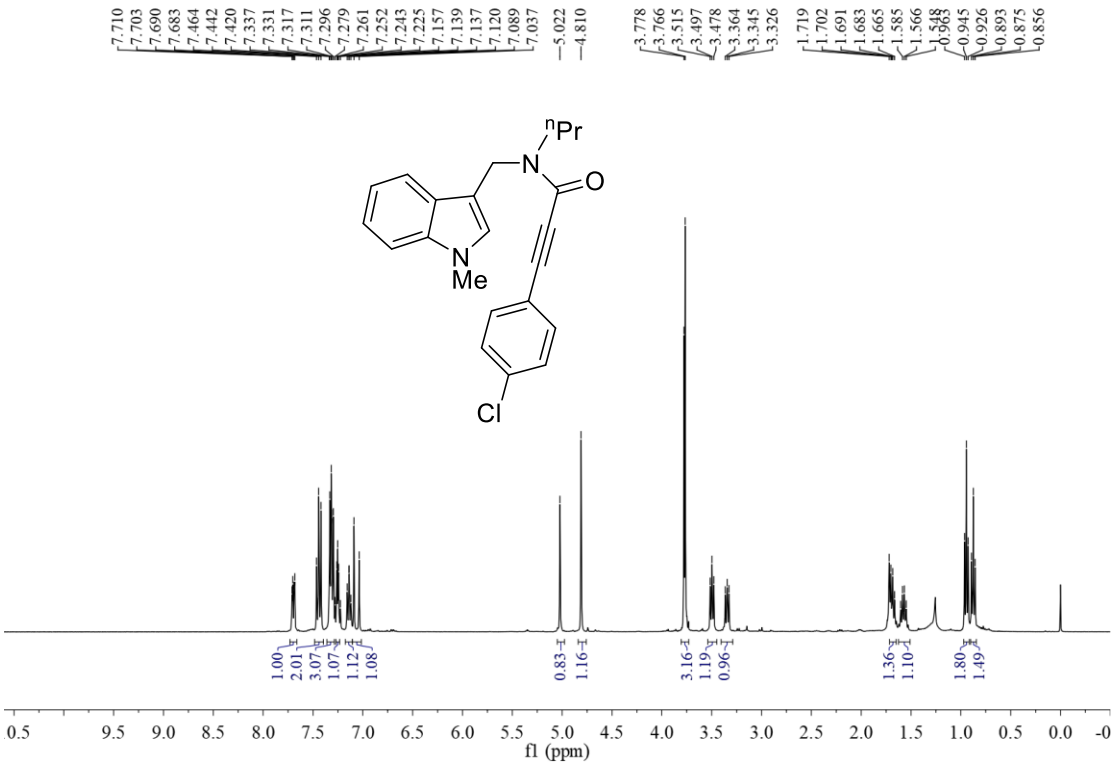
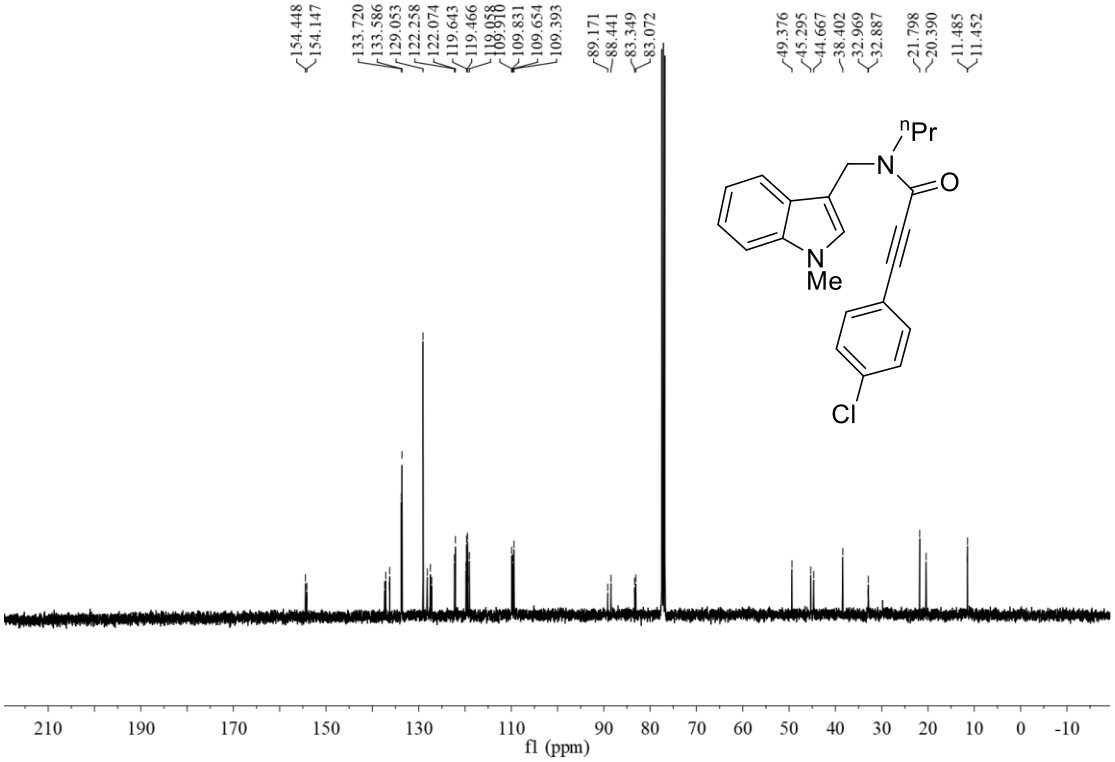
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

3-(4-chlorophenyl)-N-((1-methyl-1H-indol-3-yl)methyl)-N-propylpropiolamide (2i)





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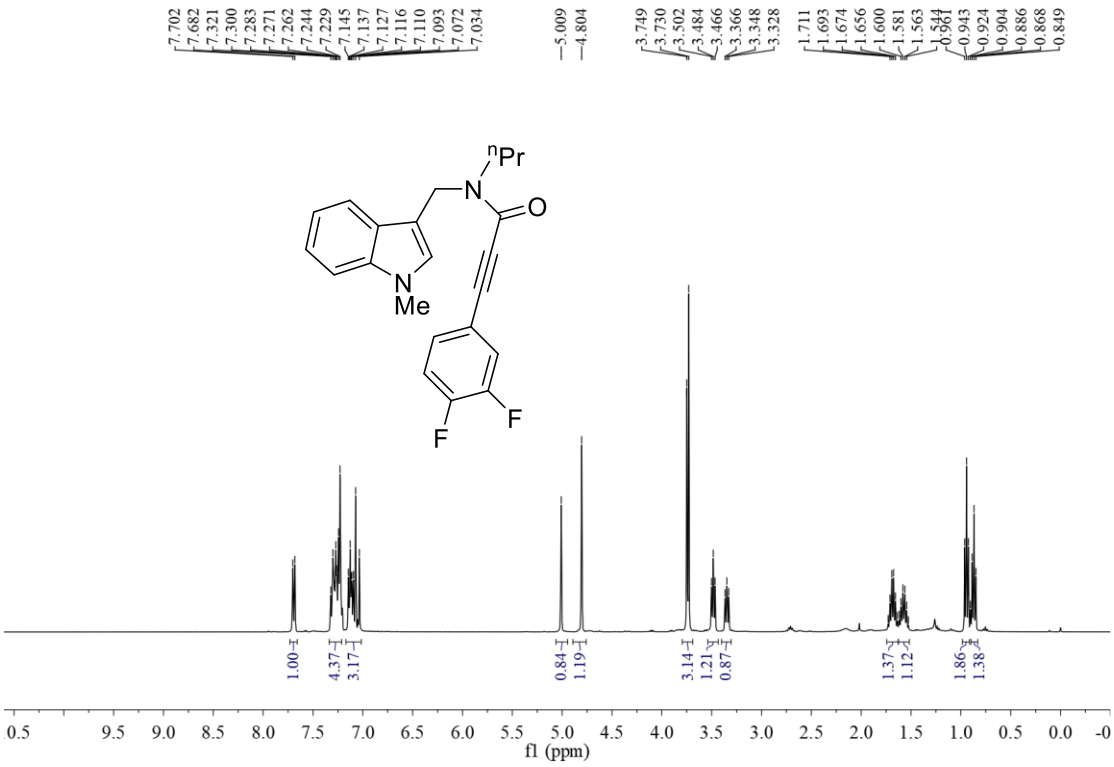

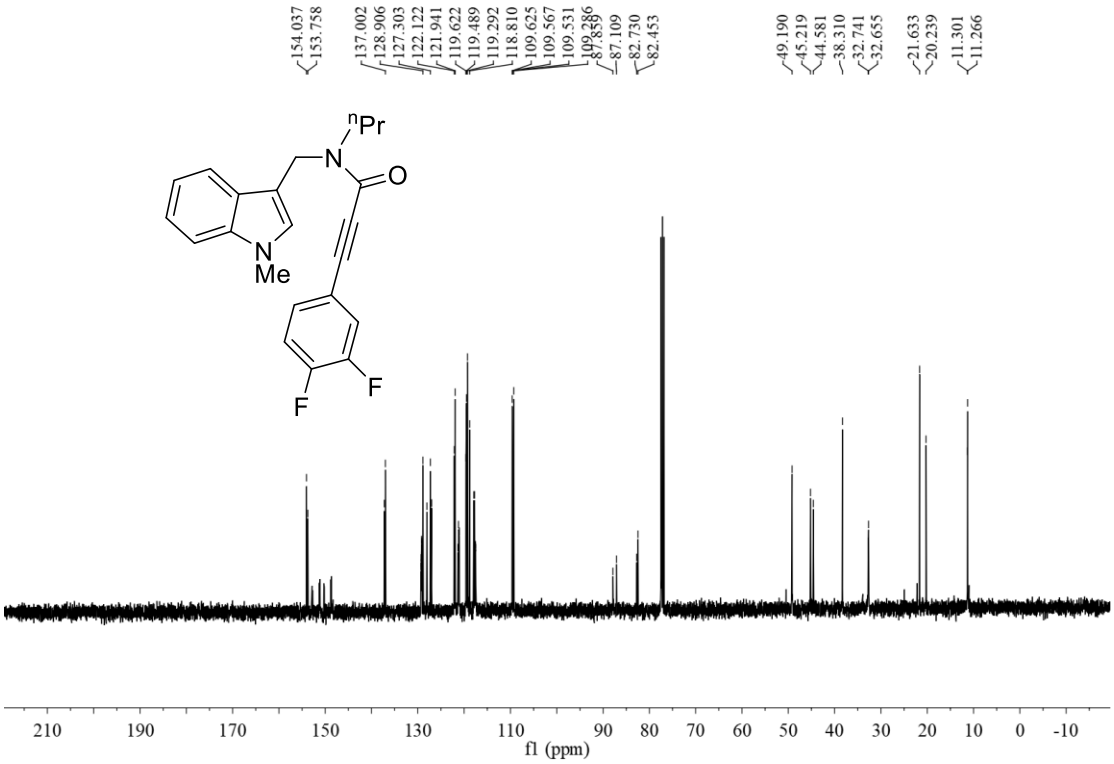

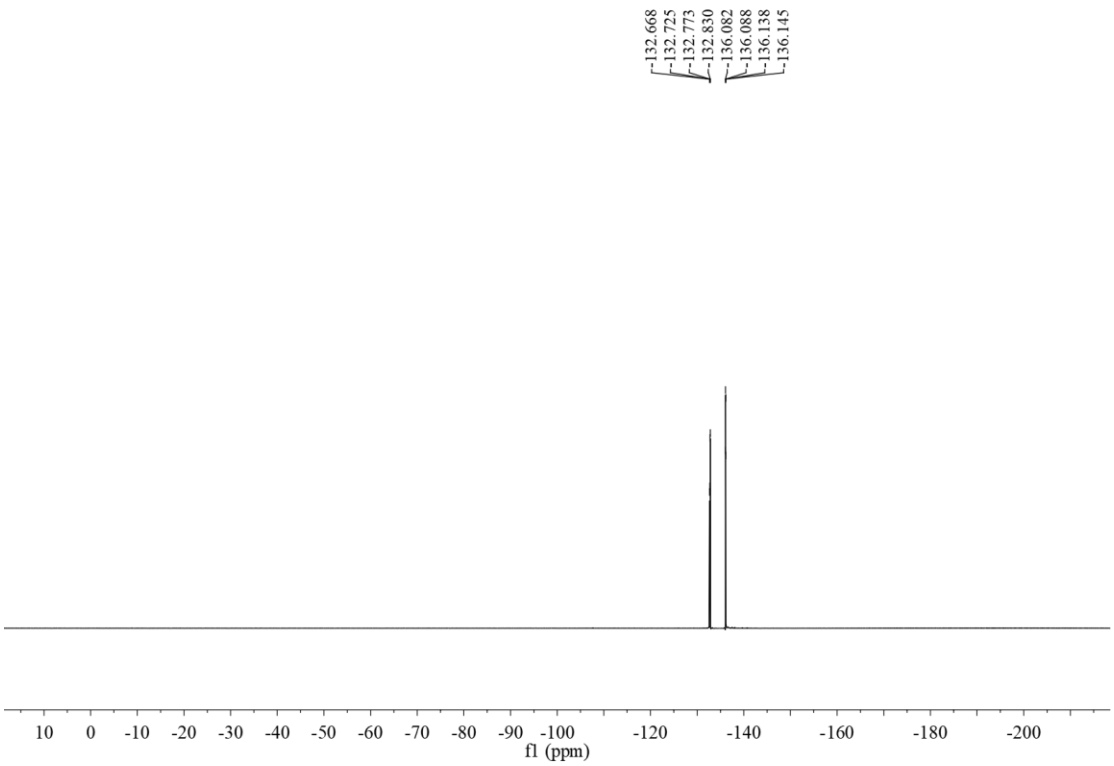
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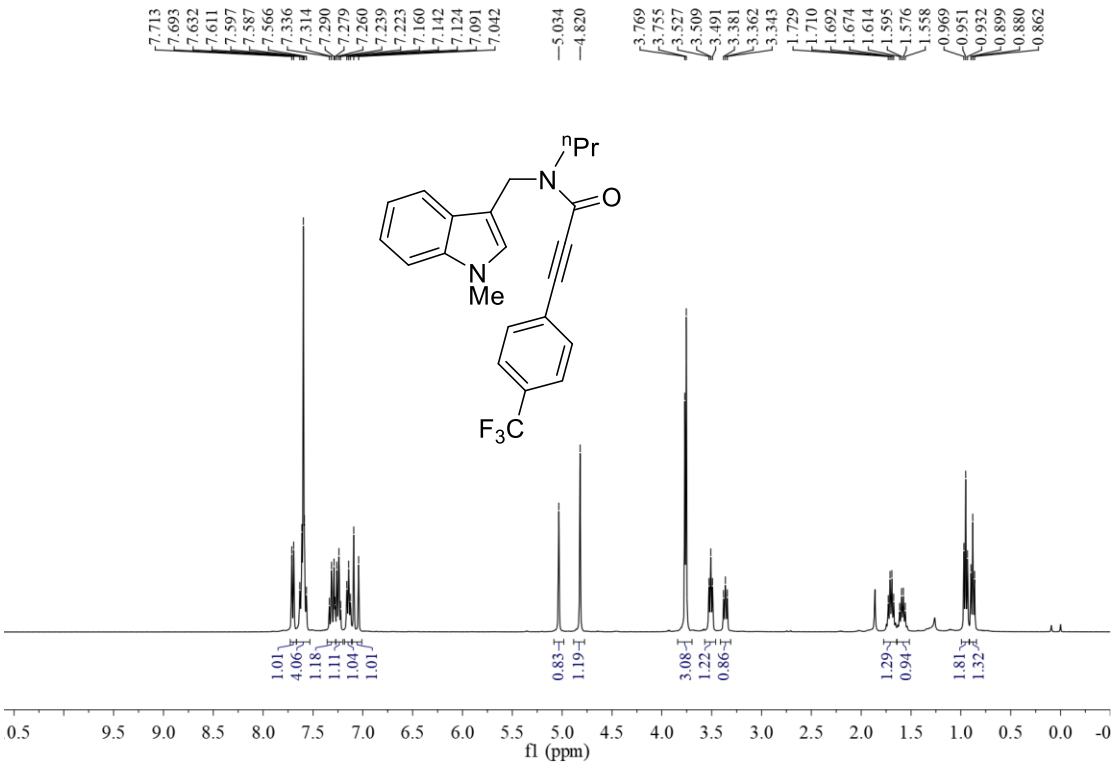
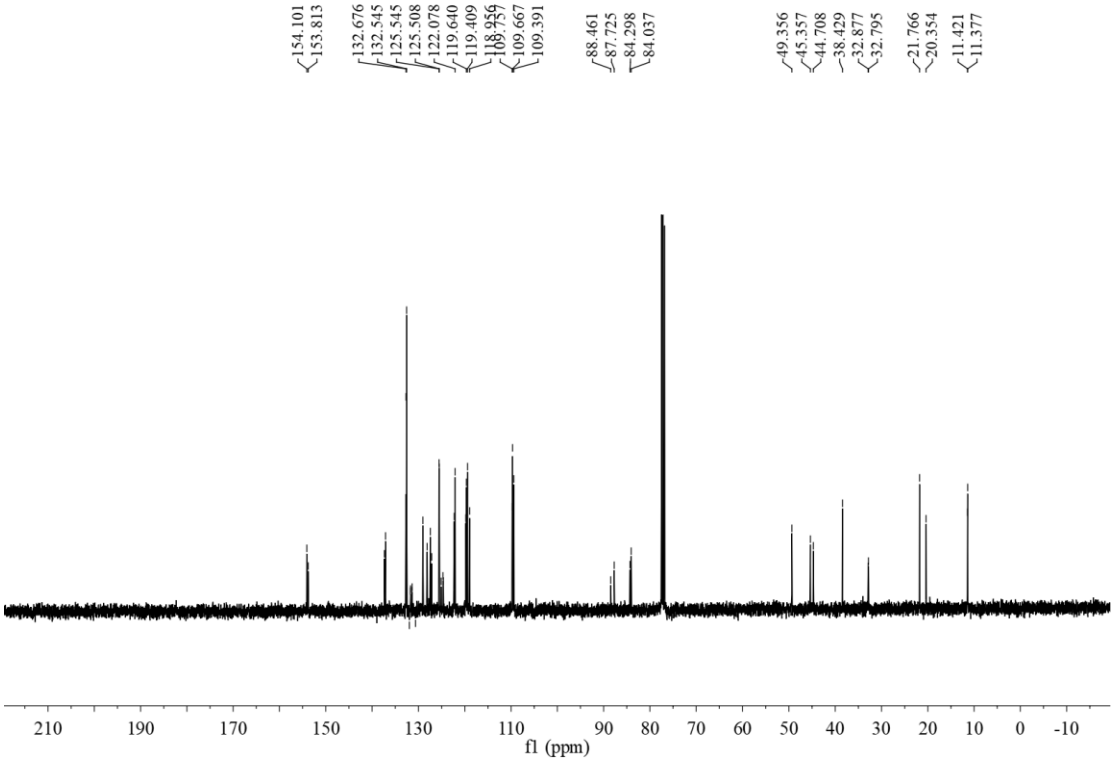
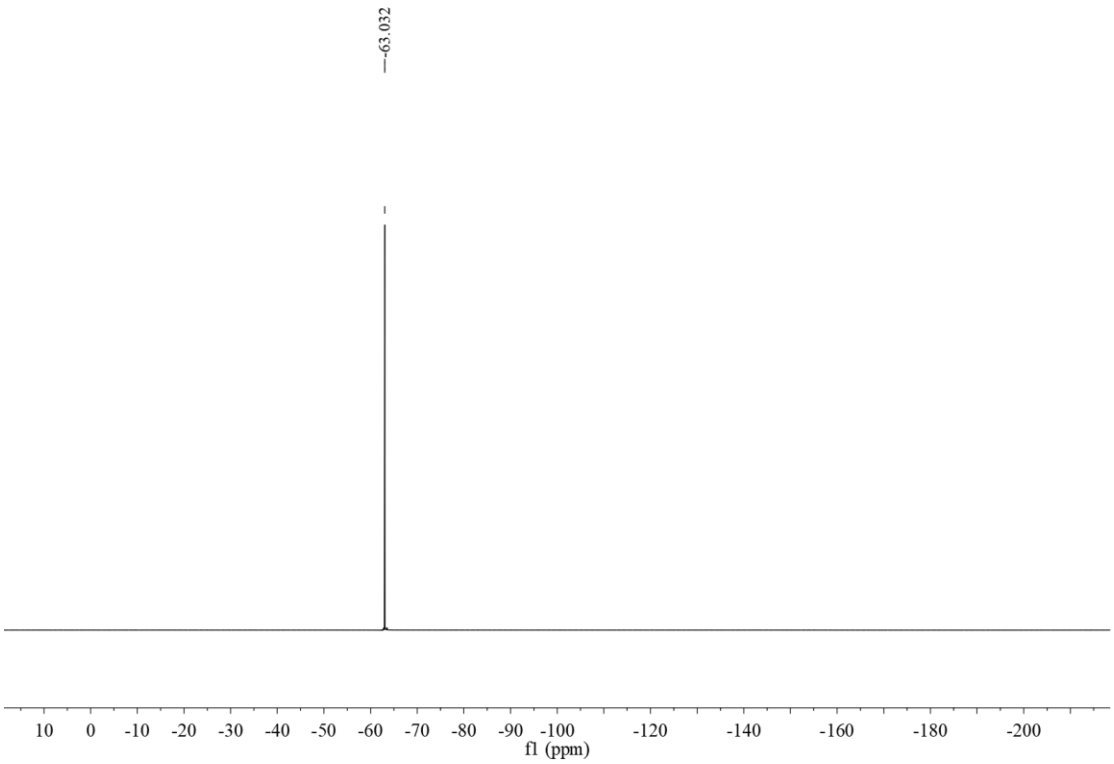
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

_N_-((1-methyl-1H-indol-3-yl)methyl)-_N_-propyl-3-(4-(trifluoromethyl)phenyl)propiolamide (2k)



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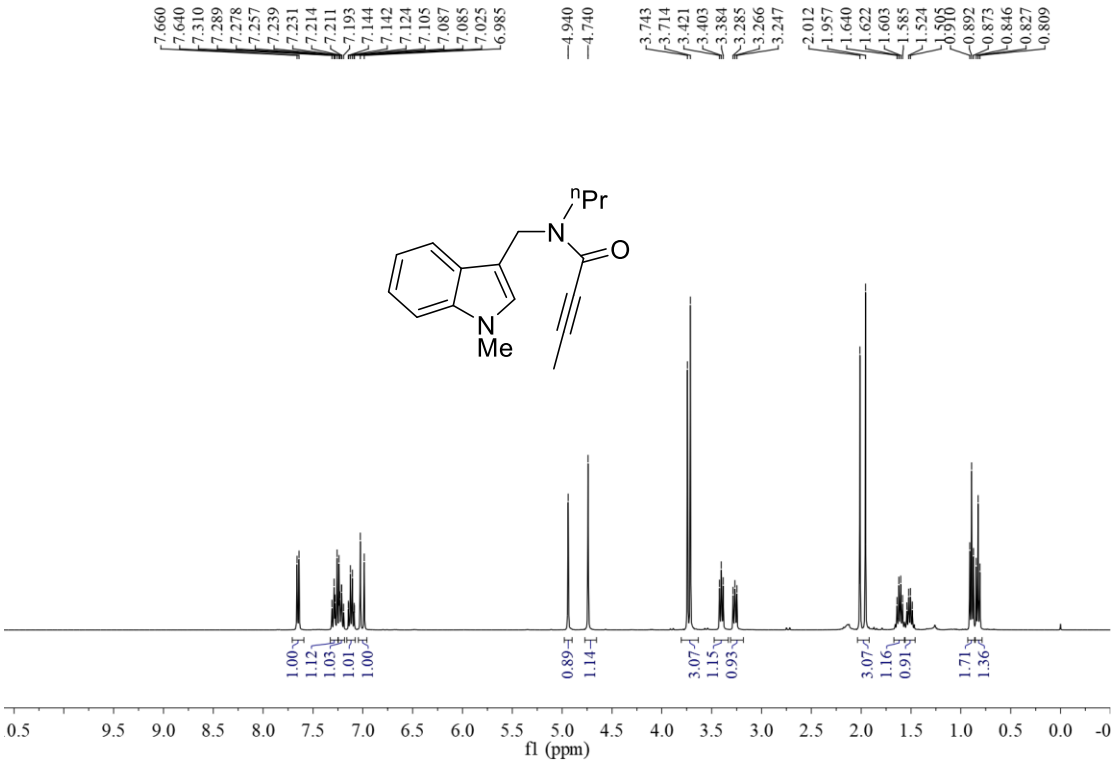
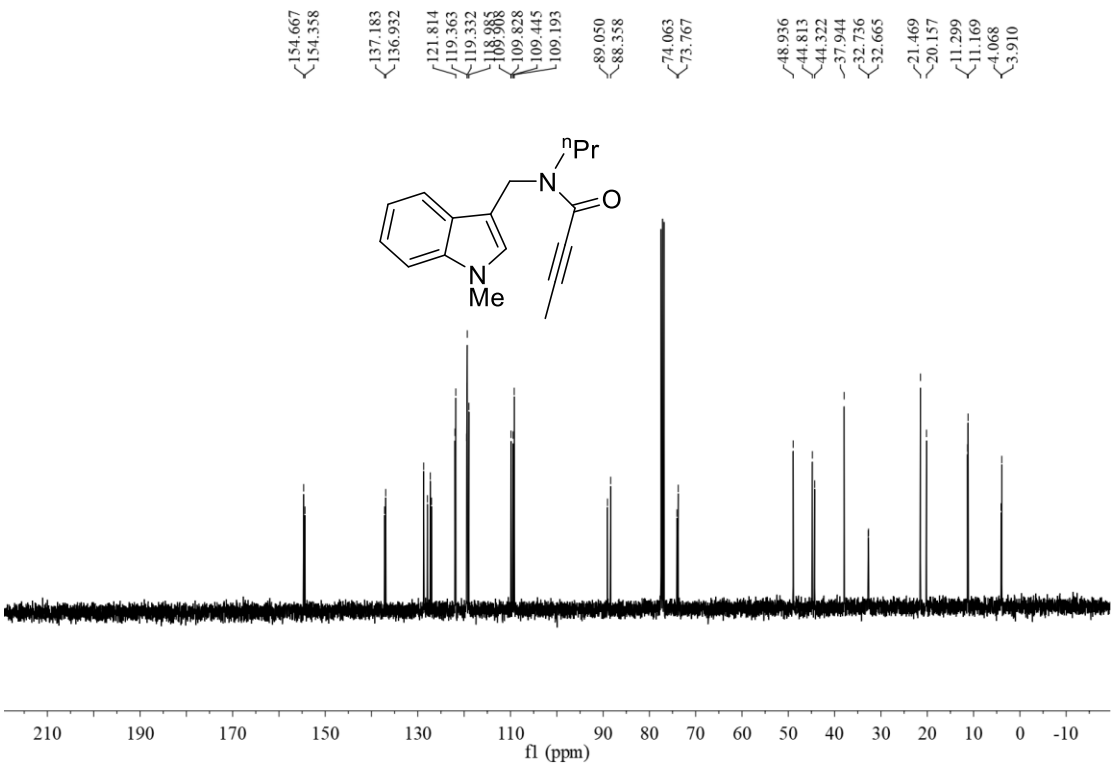
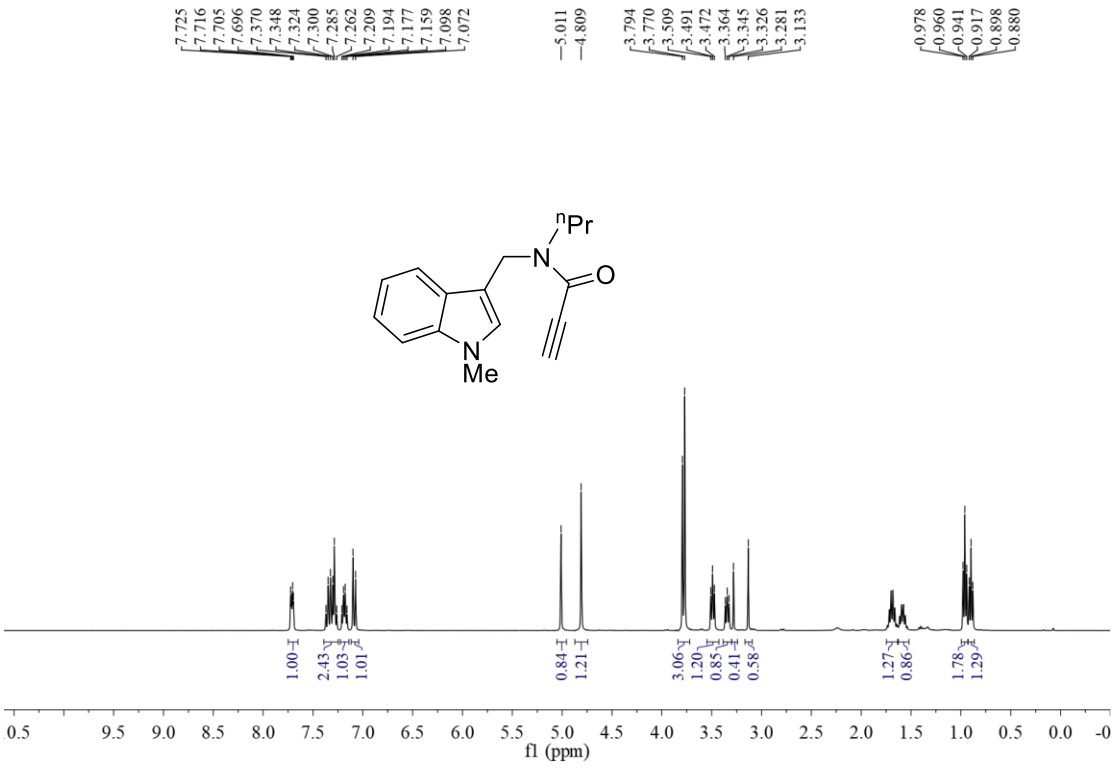
-200
f1 (ppm)

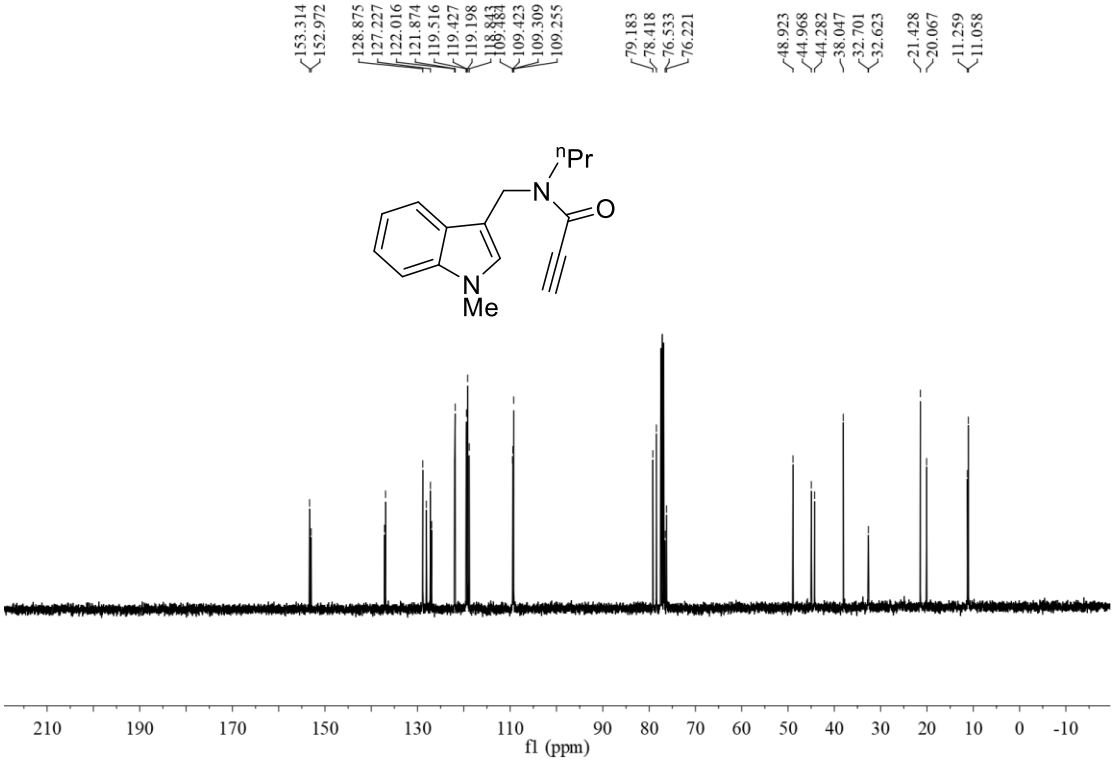
***N*-((1-methyl-1H-indol-3-yl)methyl)-*N*-propylbut-2-ynamide (2l)**





_N_-((1-methyl-1H-indol-3-yl)methyl)-_N_-propylpropiolamide (2m)





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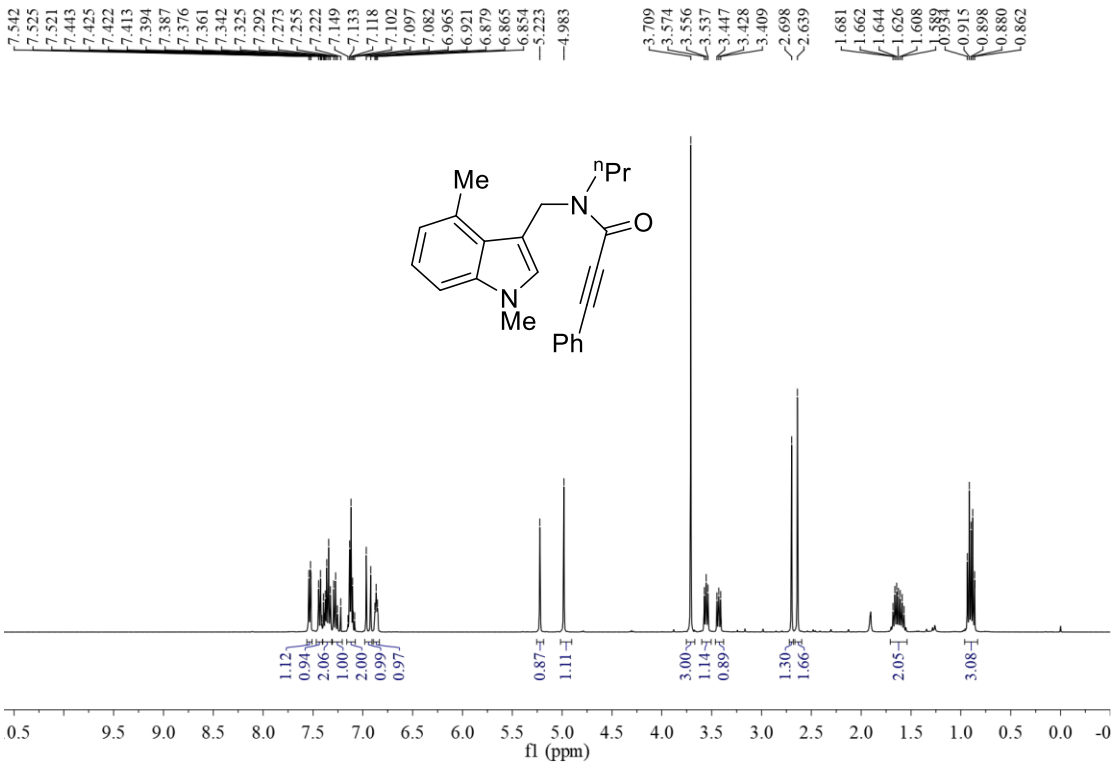
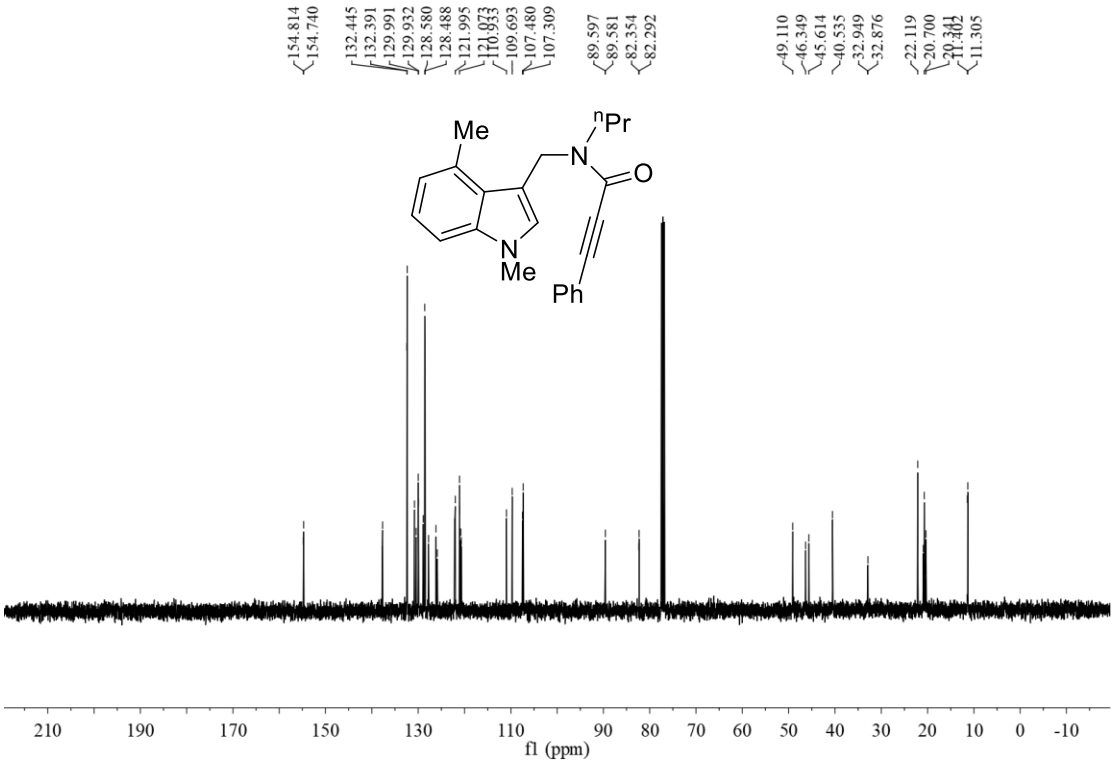
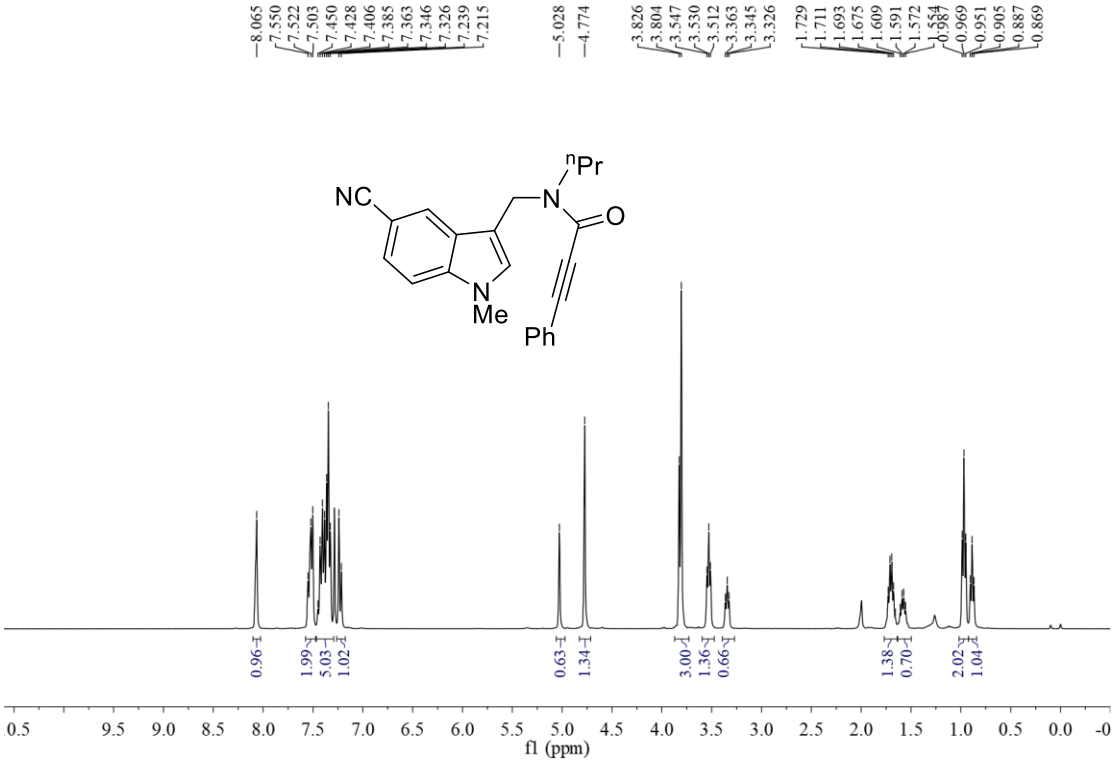
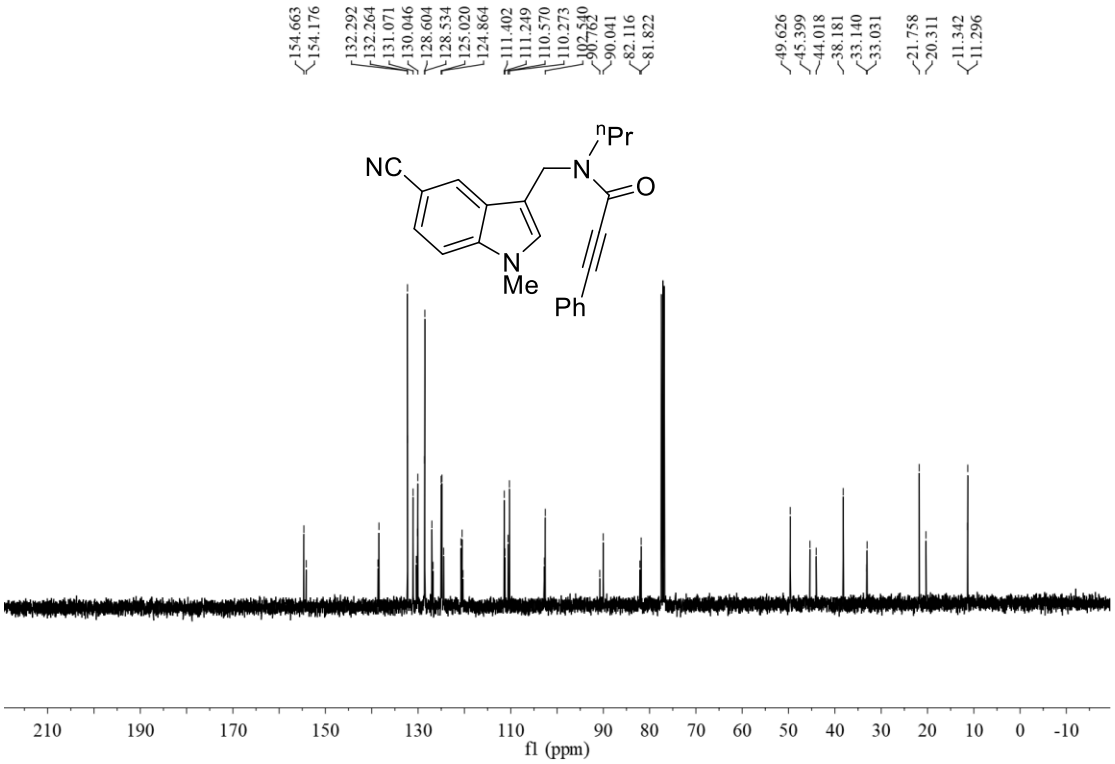


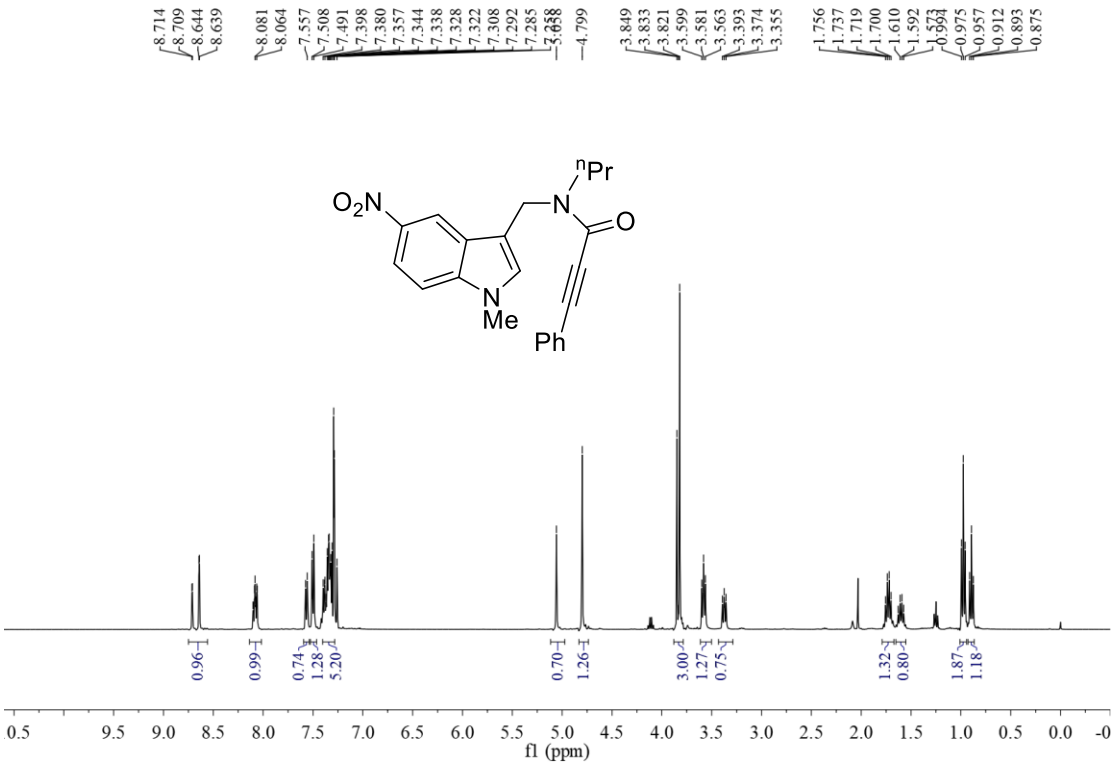


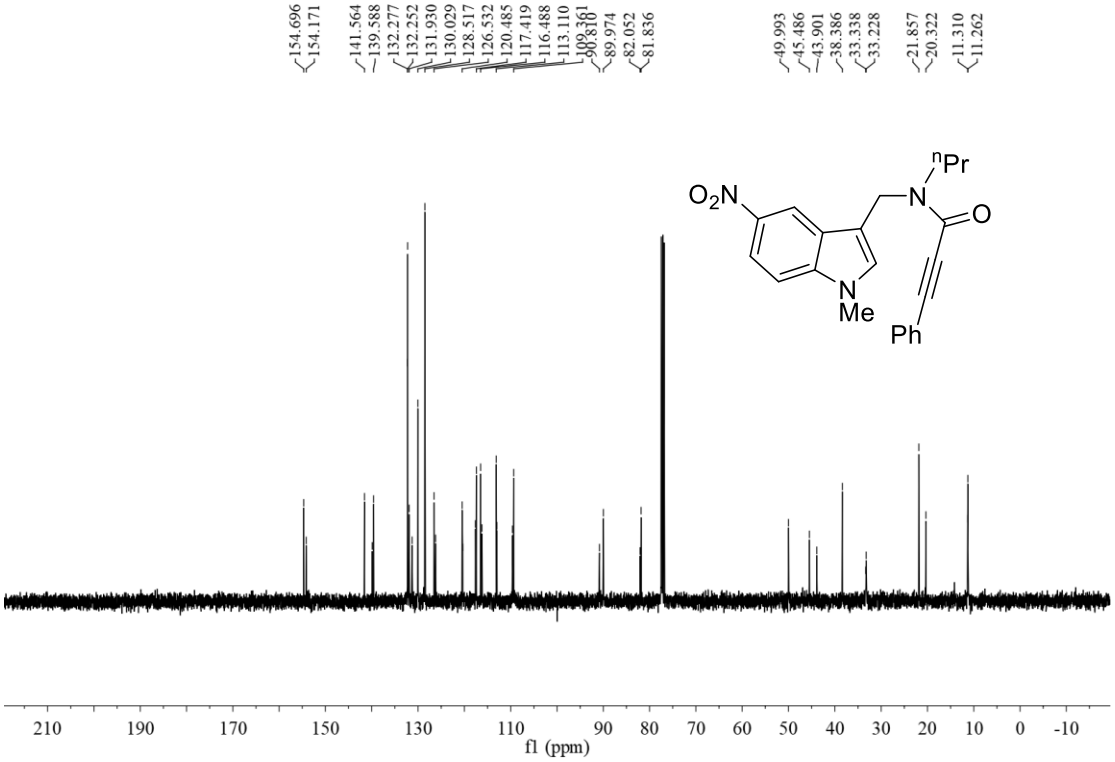
***N*-((5-cyano-1-methyl-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2o) :**



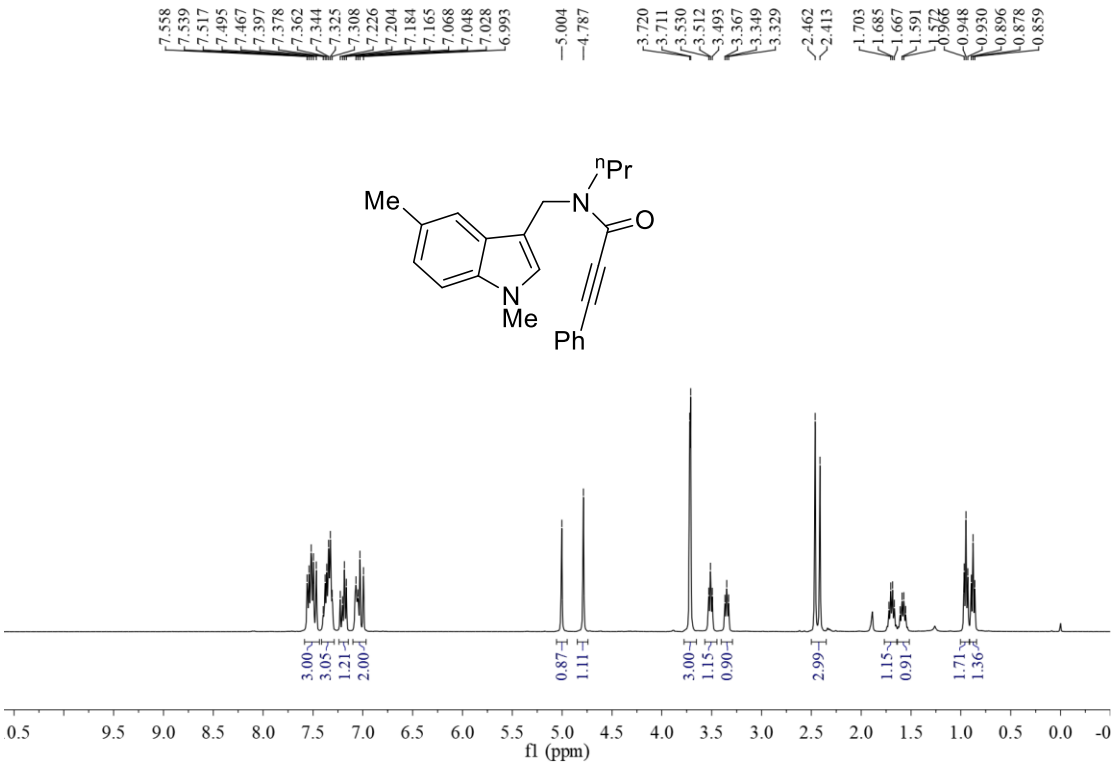


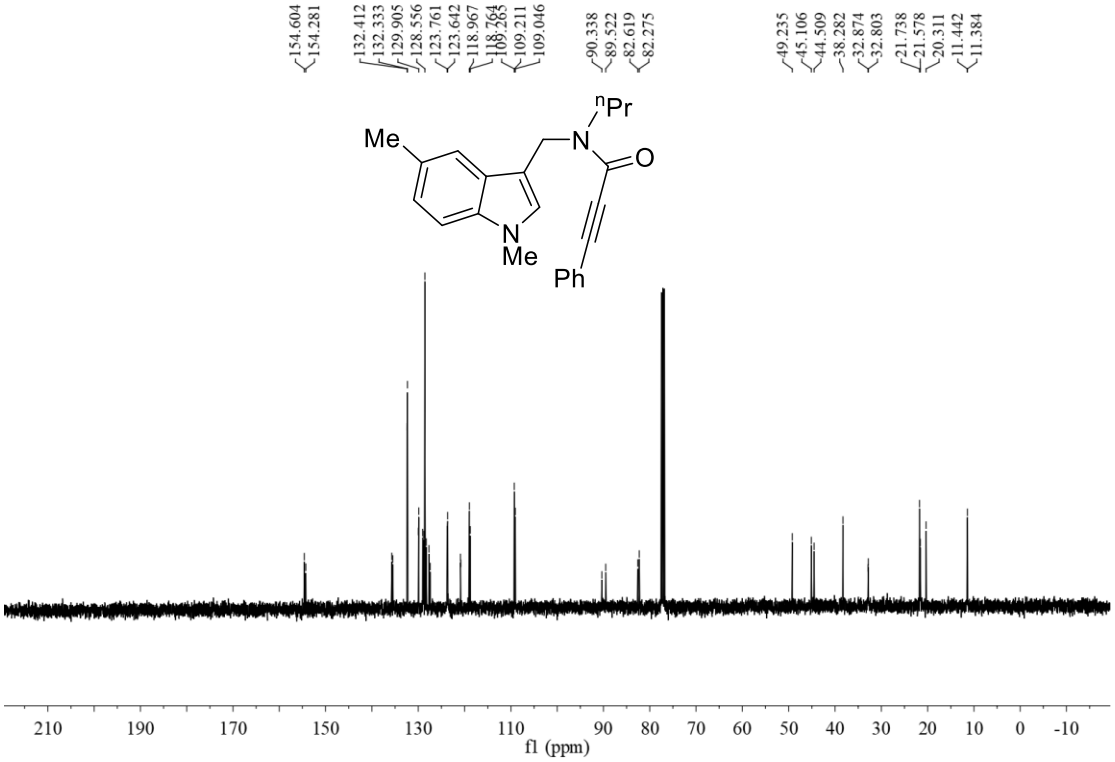
***N*-((1-methyl-5-nitro-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide(2p):**



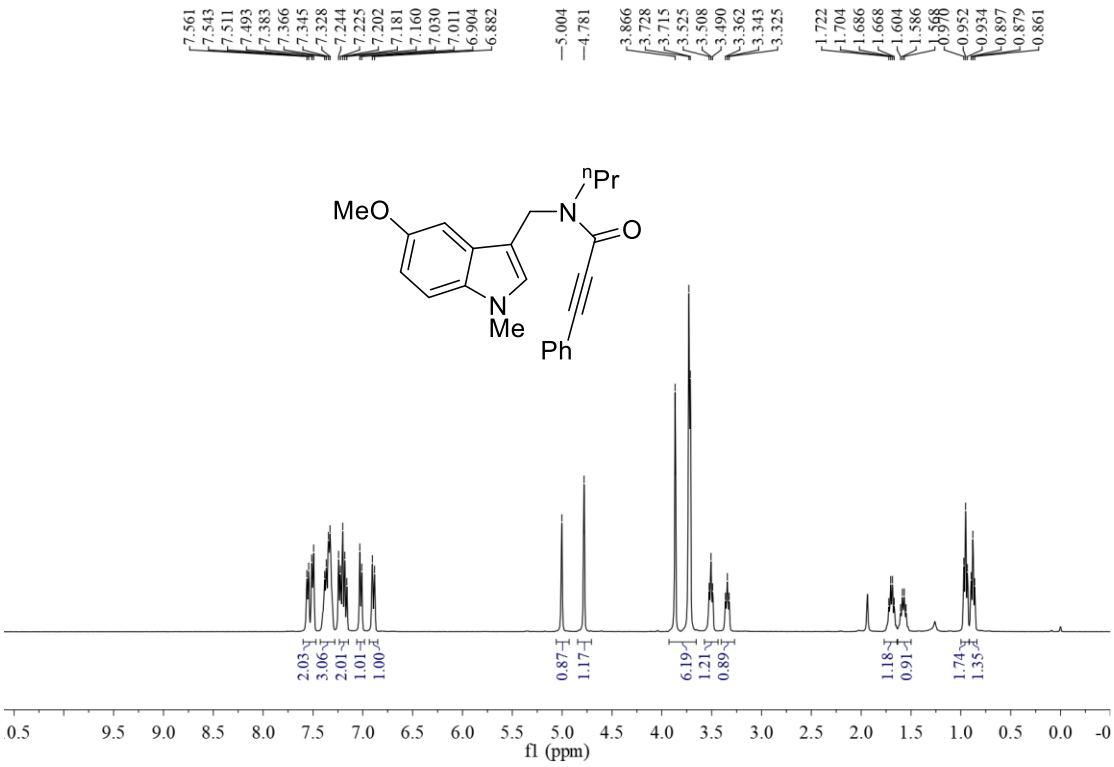


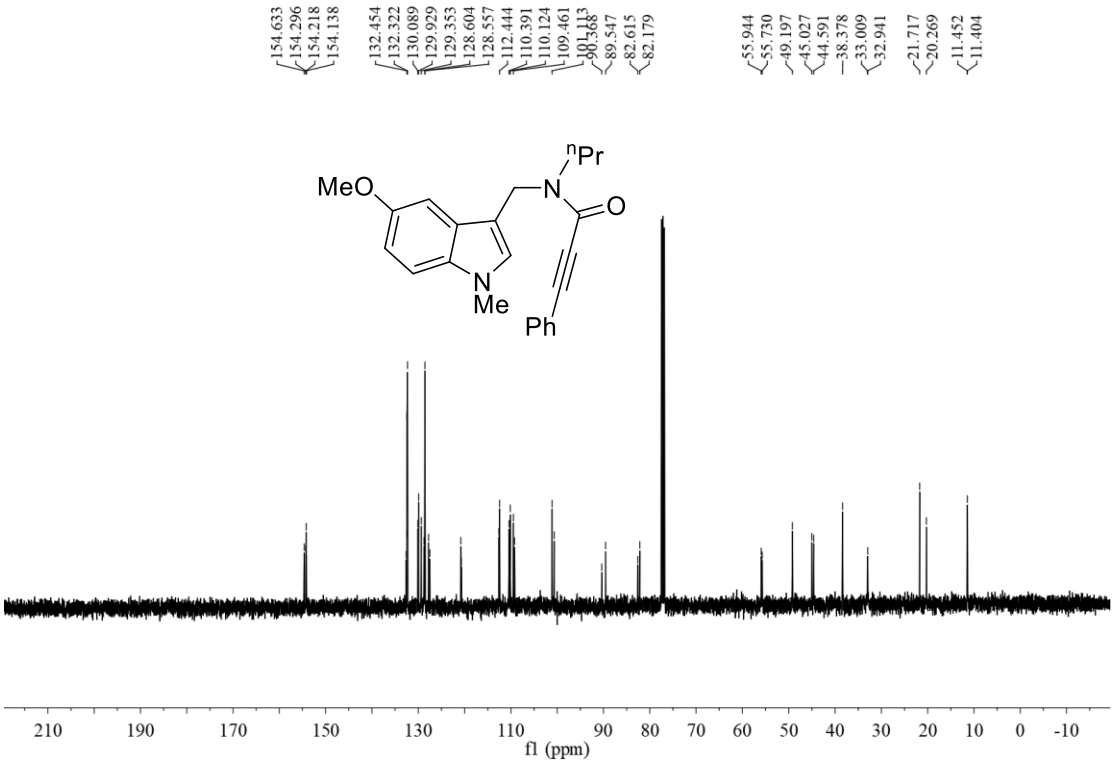
***N*-((1, 5-dimethyl-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2q) :**



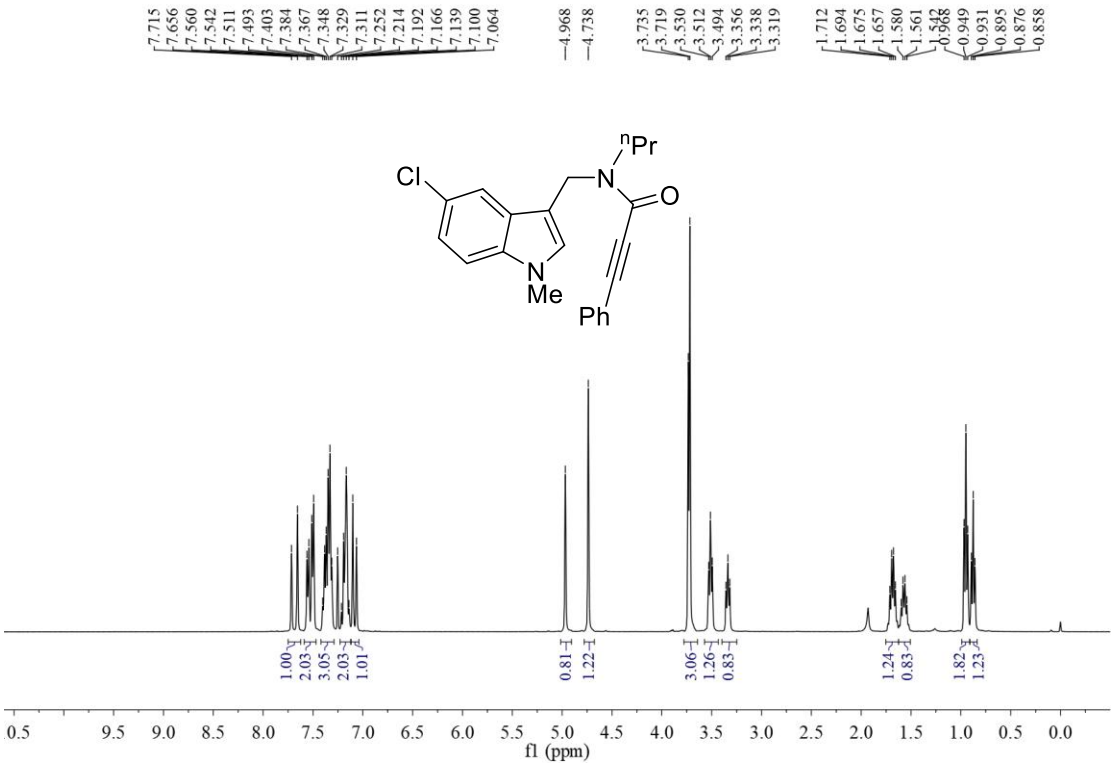


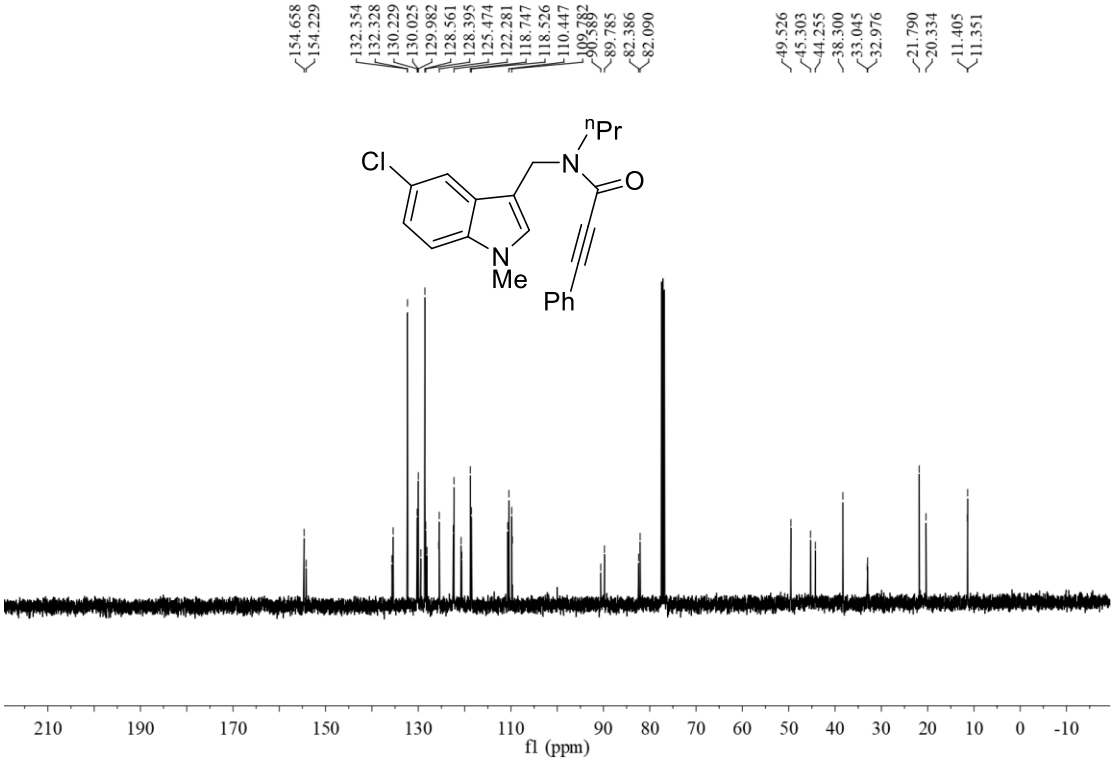
_N_-((5-methoxy-1-methyl-1H-indol-3-yl)methyl)-3-phenyl-_N_-propylpropiolamide (2r)



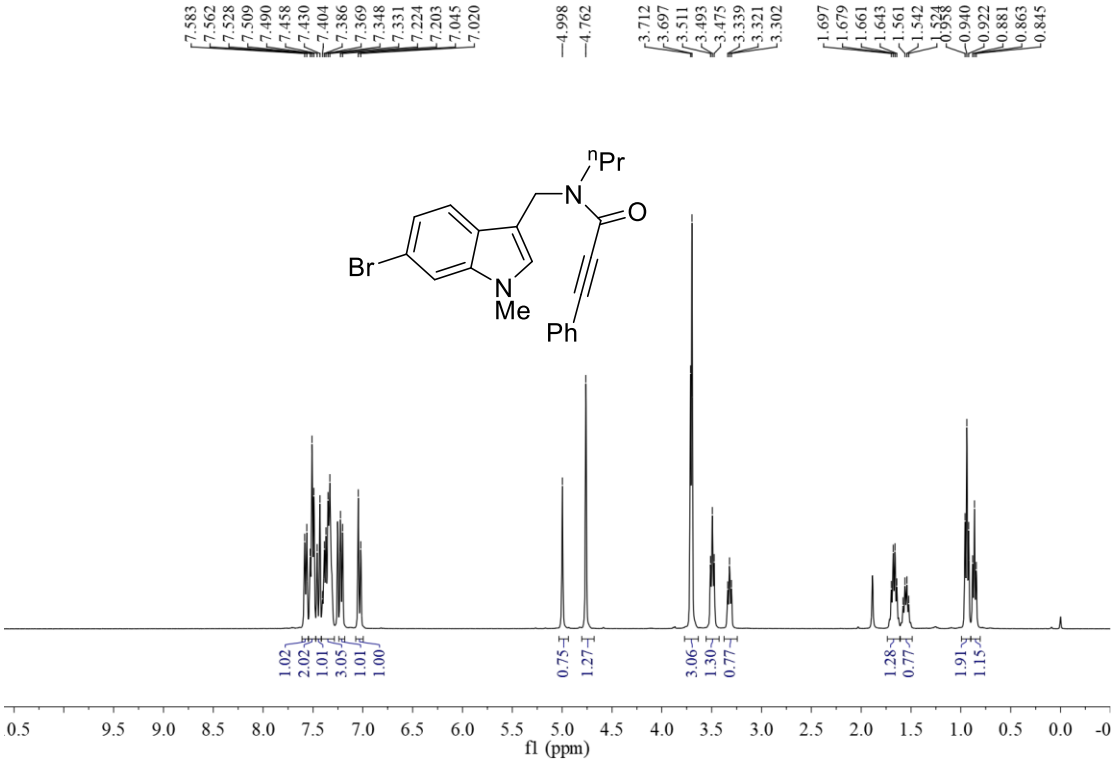


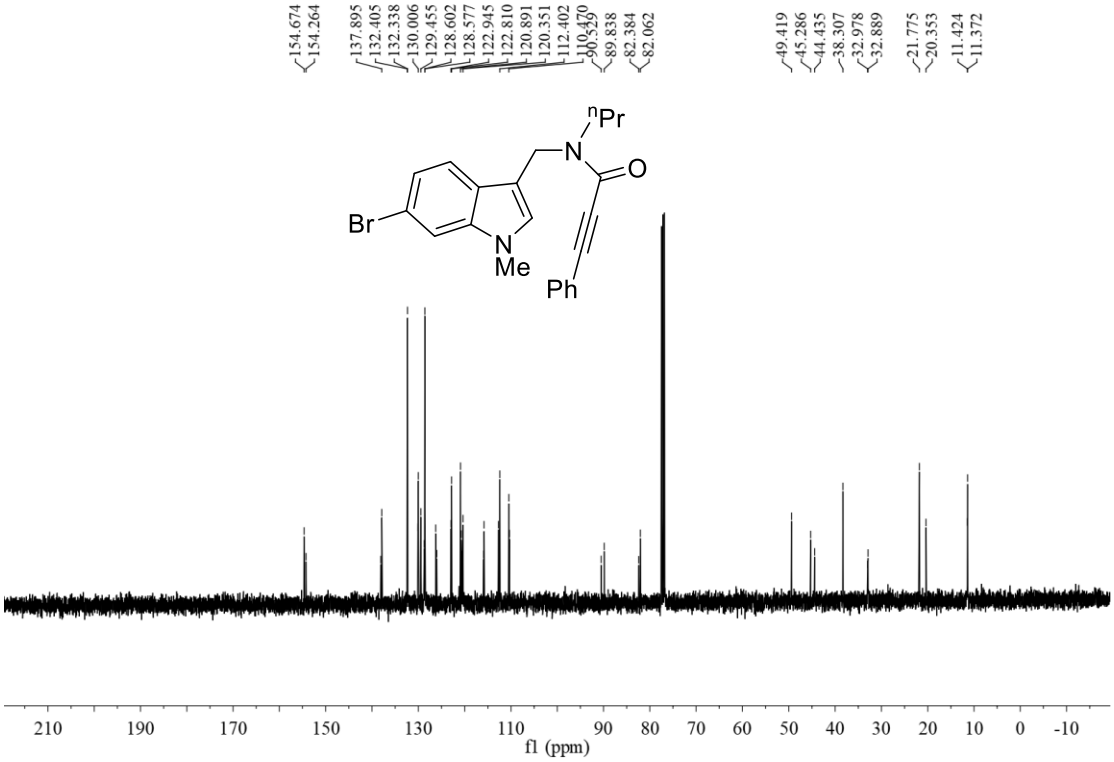
_N_-((5-chloro-1-methyl-1H-indol-3-yl)methyl)-3-phenyl-_N_-propylpropiolamide (2s)



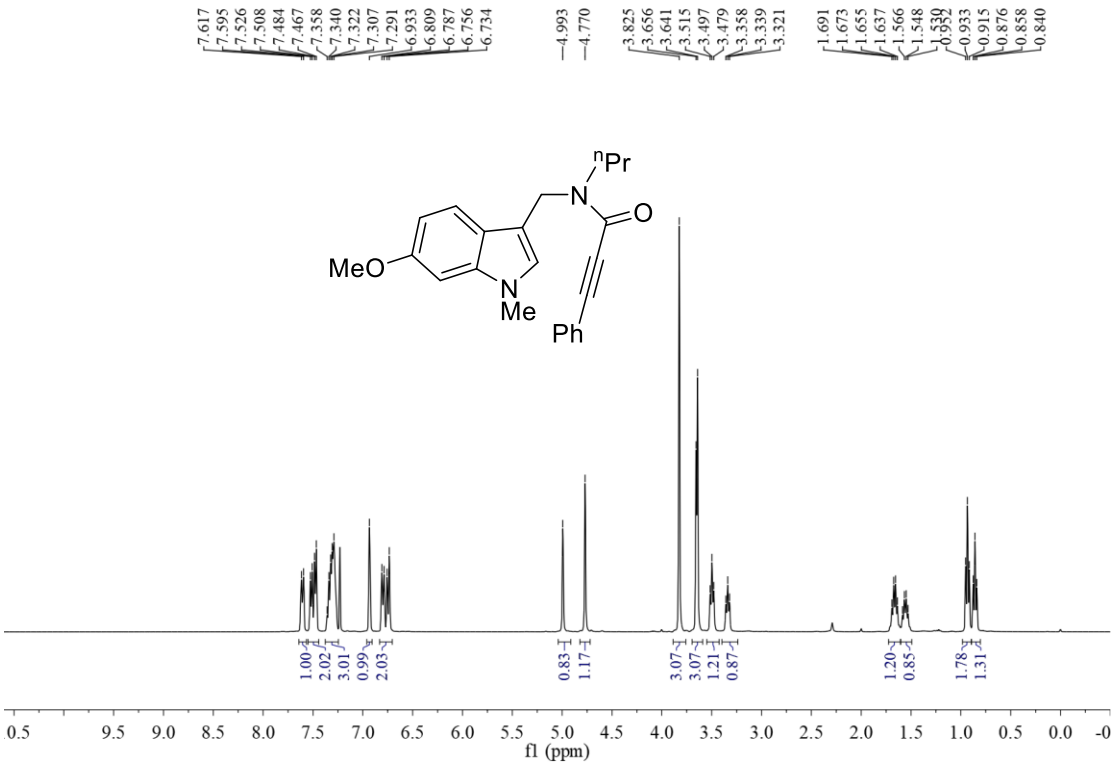


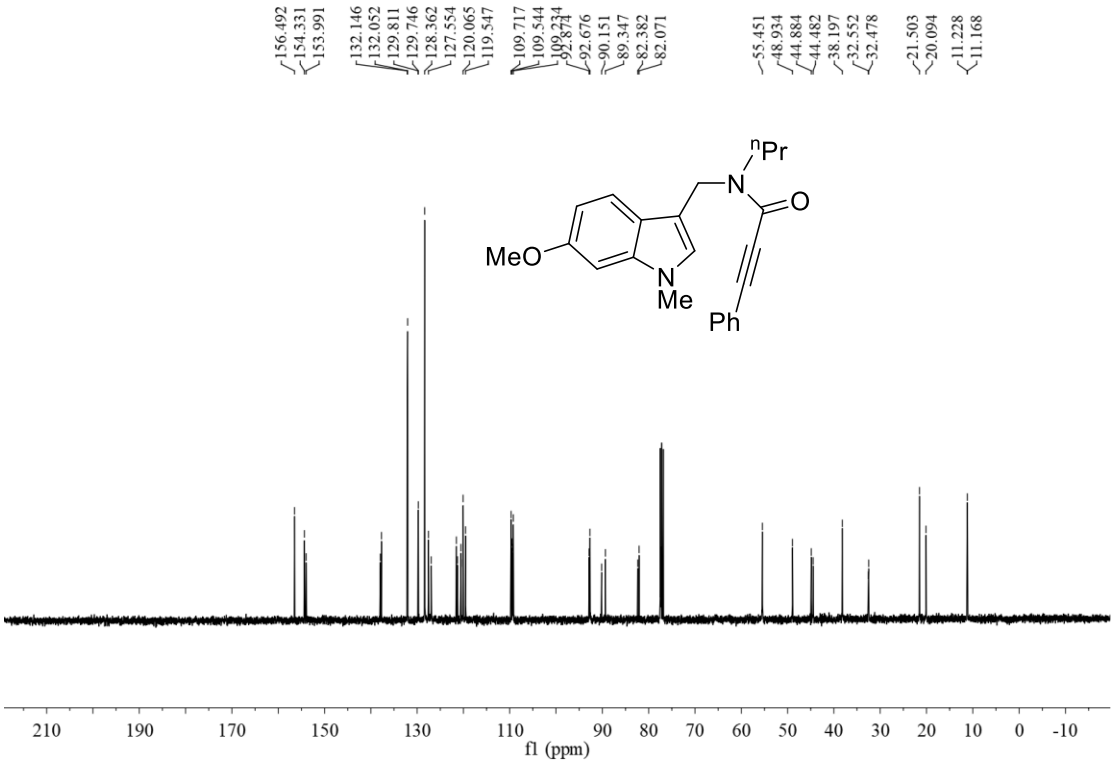
***N*-((6-bromo-1-methyl-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2t) :**



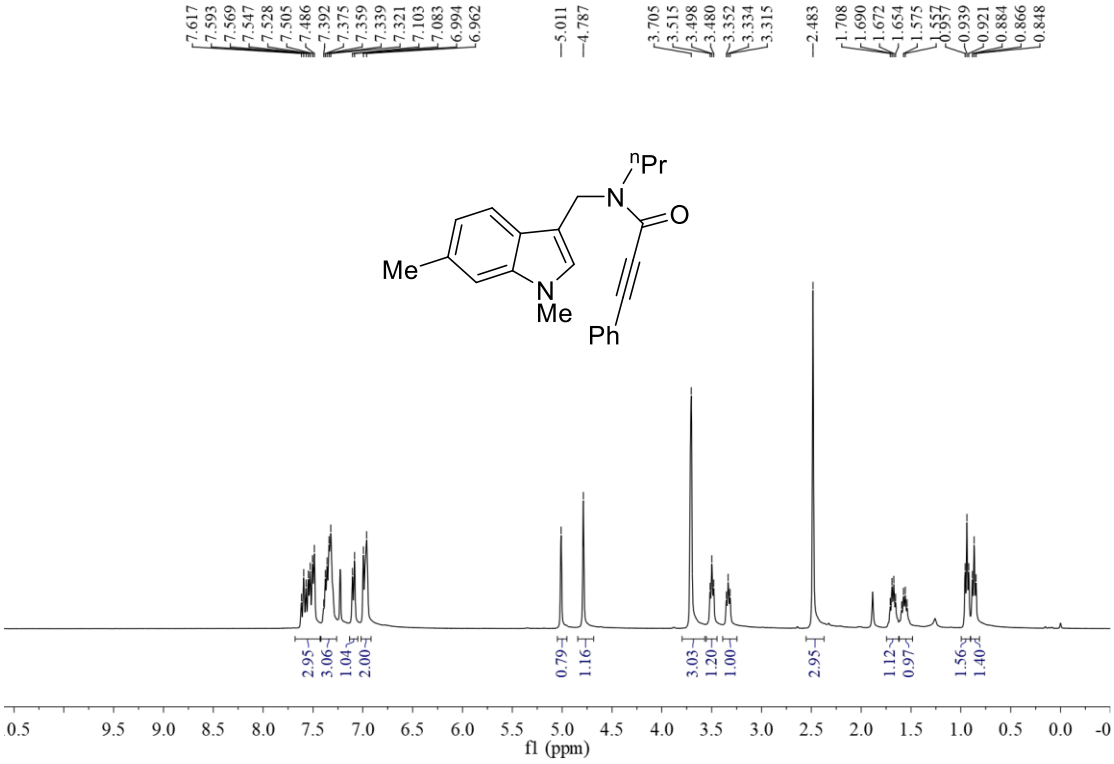


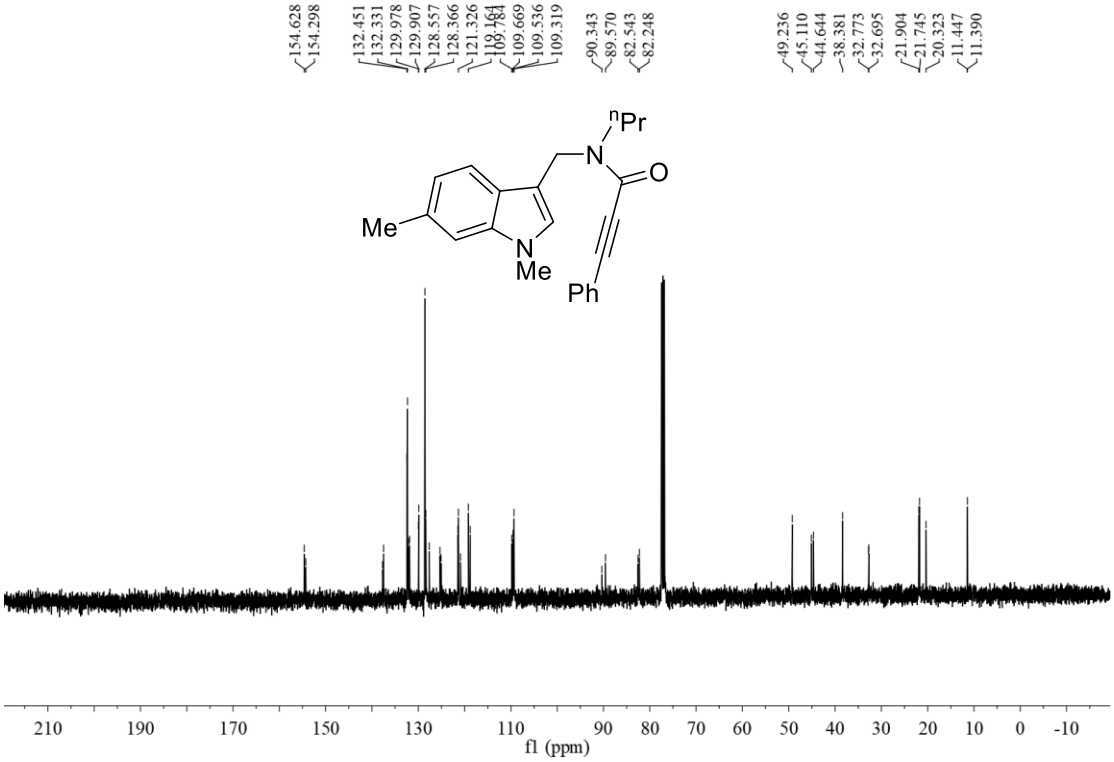
***N*-((6-methoxy-1-methyl-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2u)**



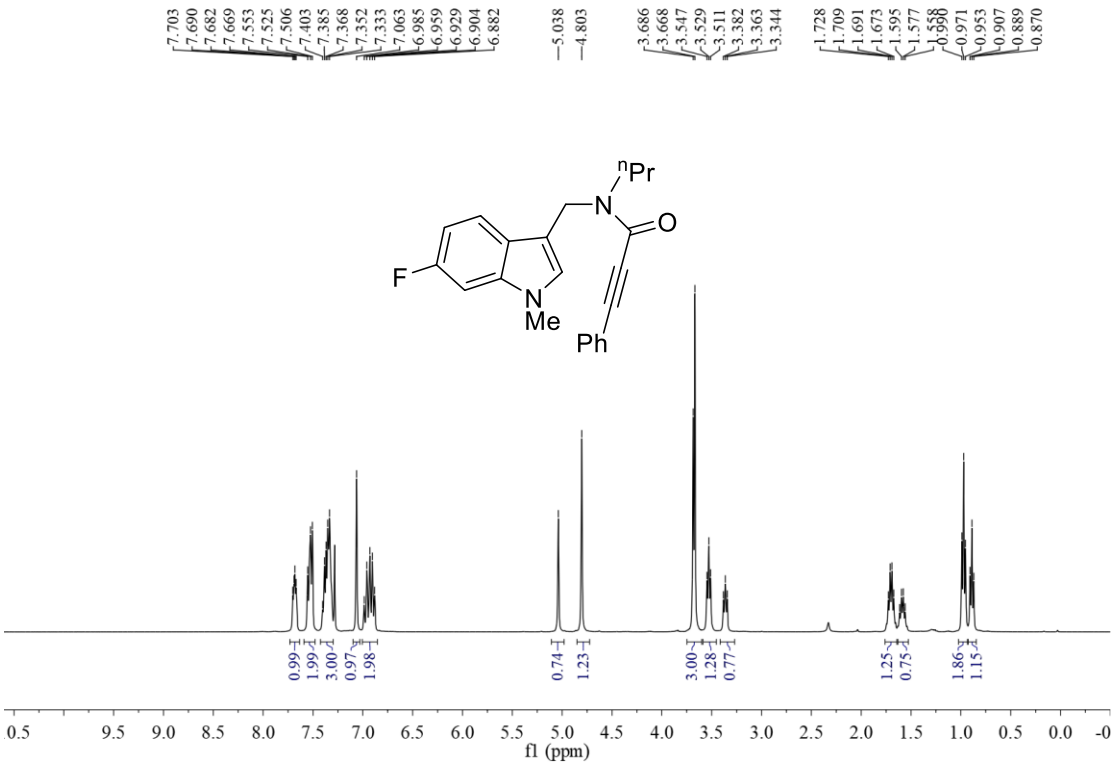


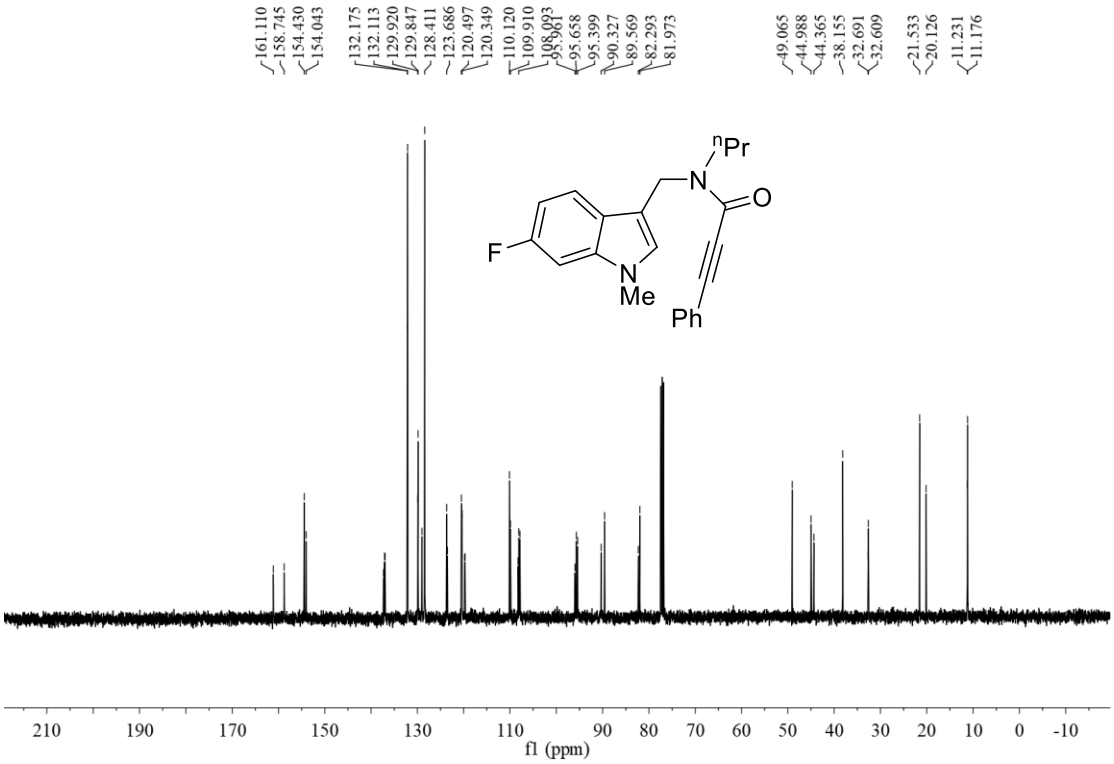
***N*-((1,6-dimethyl-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2v) :**

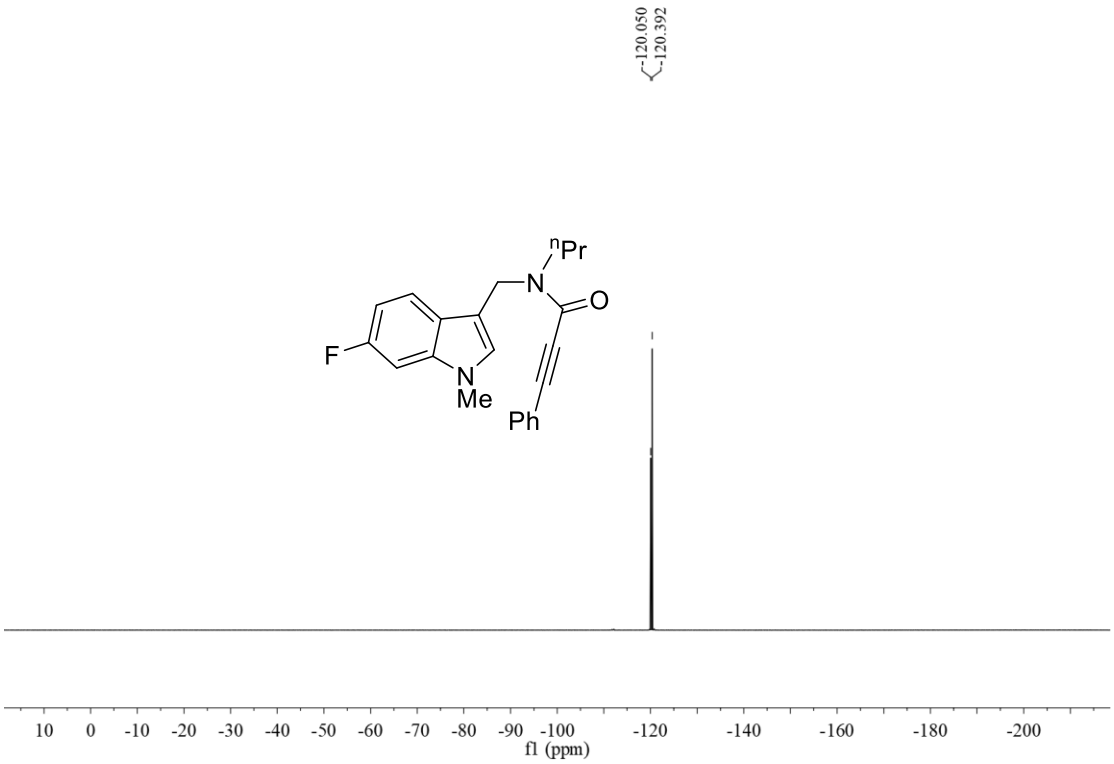




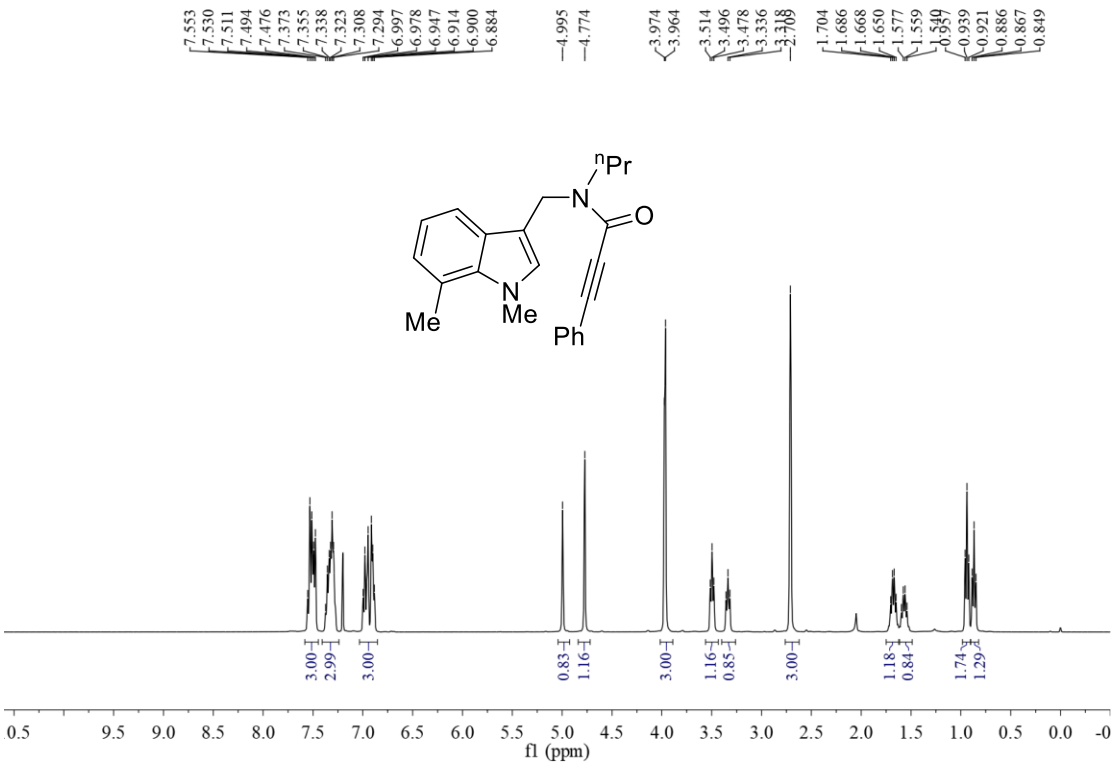
_N_-((6-fluoro-1-methyl-1H-indol-3-yl)methyl)-3-phenyl-_N_-propylpropiolamide (2w)

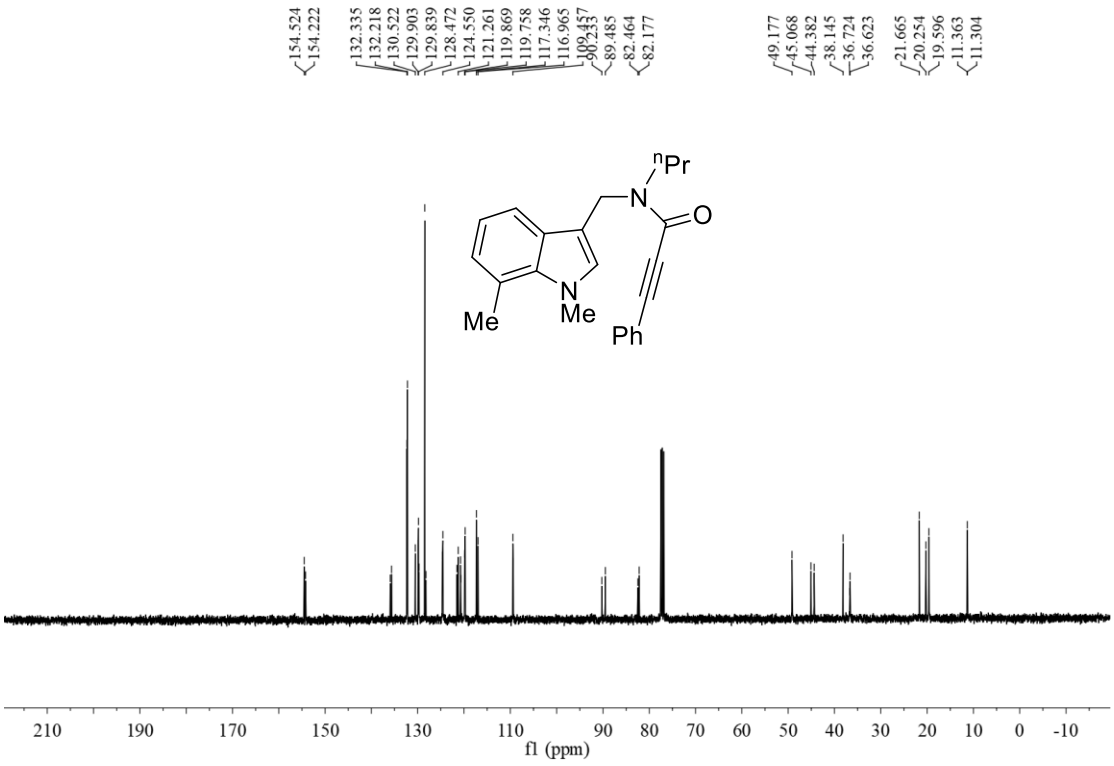




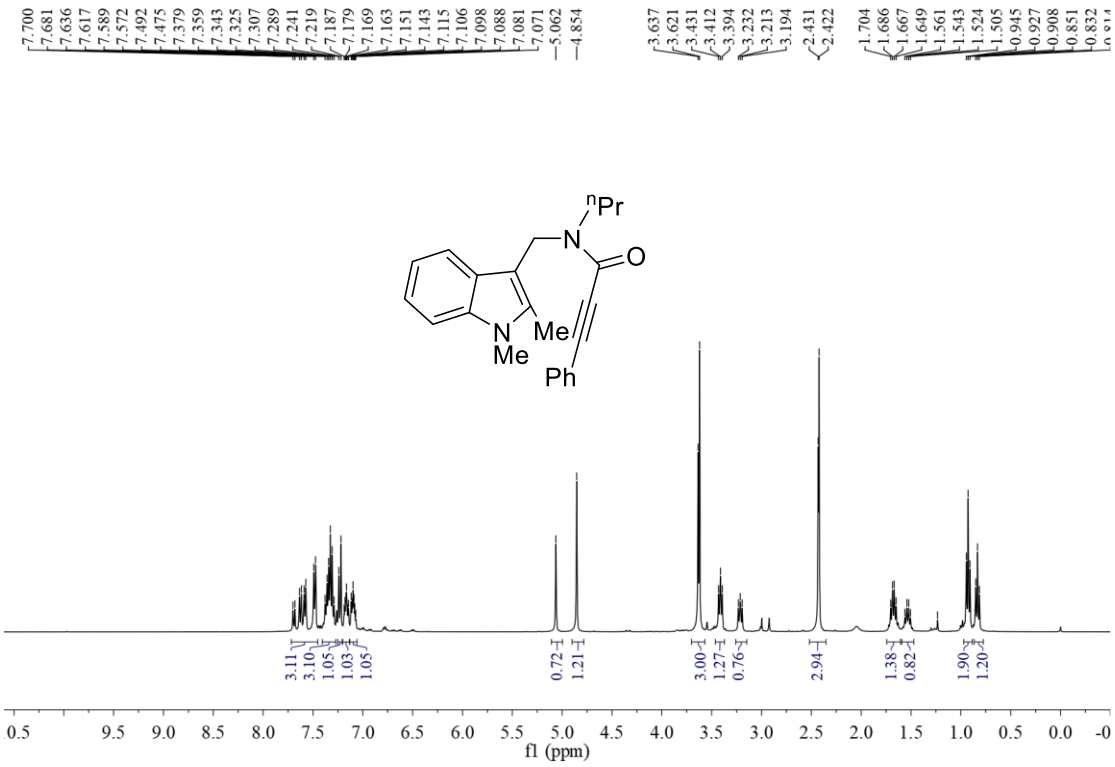

-120.050
-120.392
nPr
N
O
F
N
Me
Ph
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

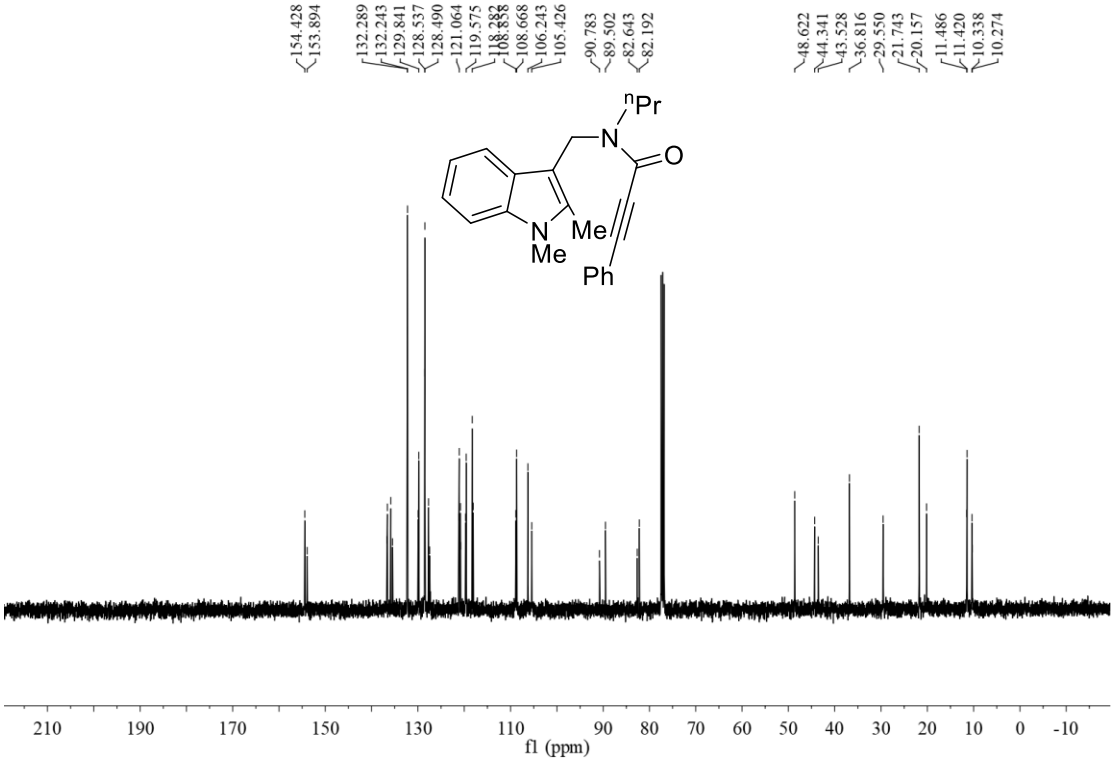
***N*-((1, 7-dimethyl-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2x) :**



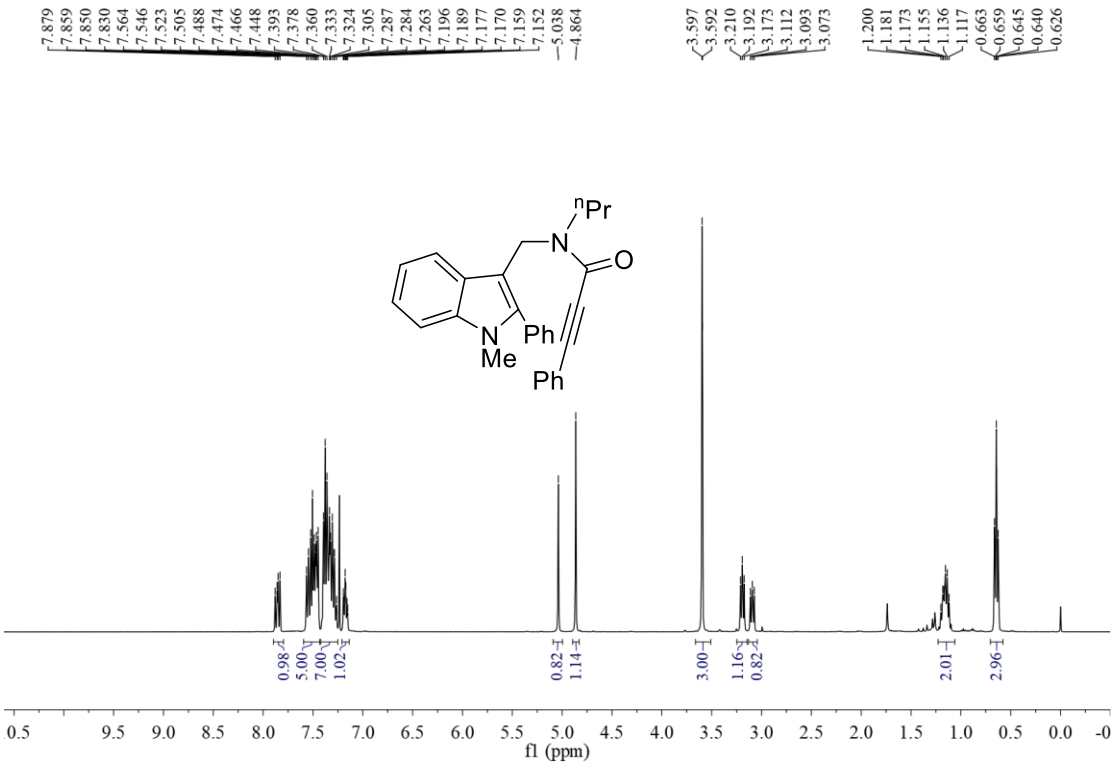


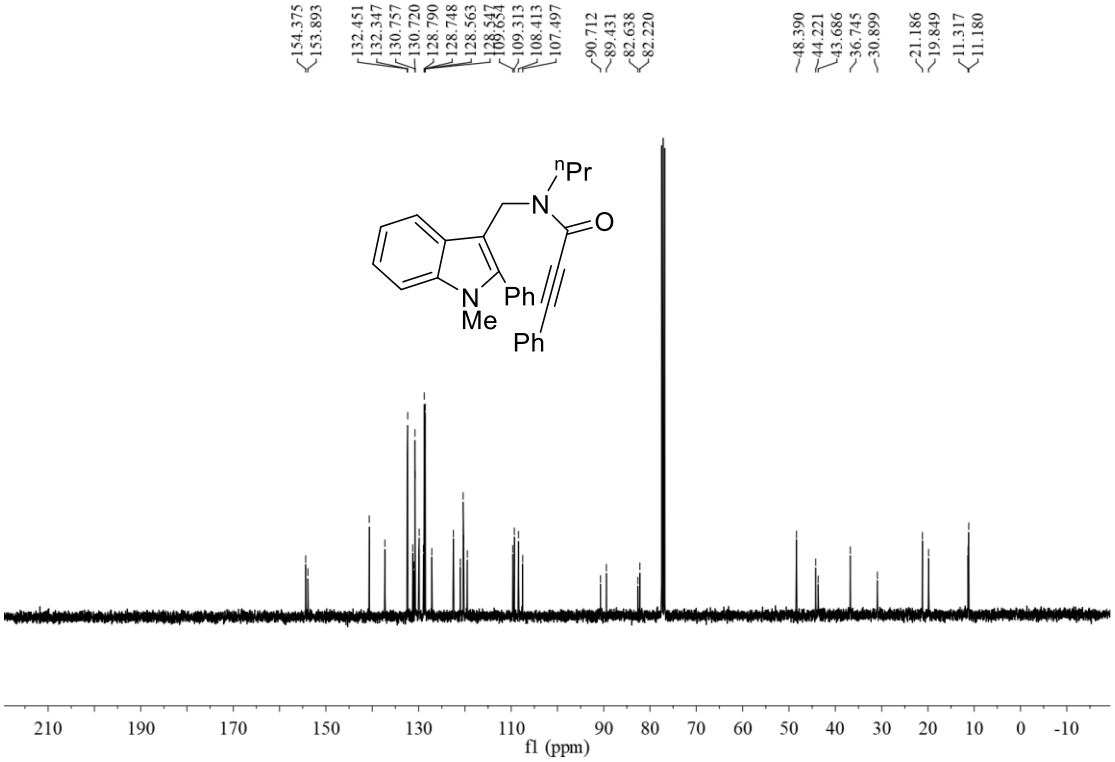
***N*-((1, 2-dimethyl-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2y) :**



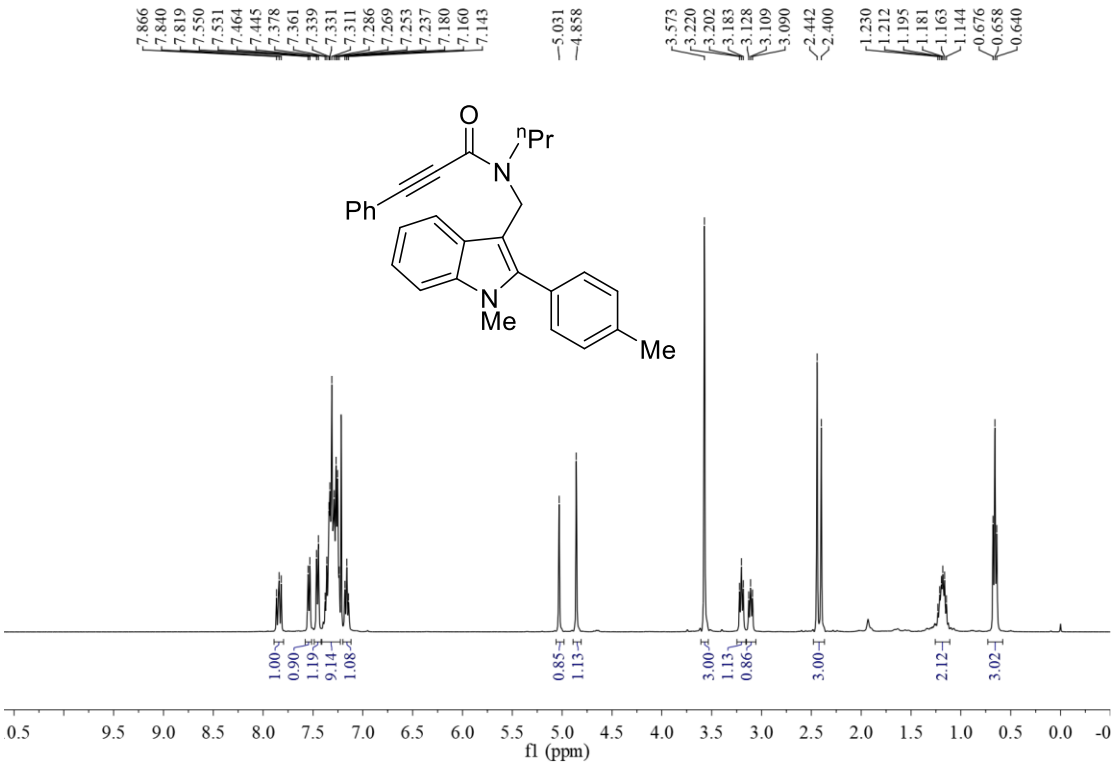


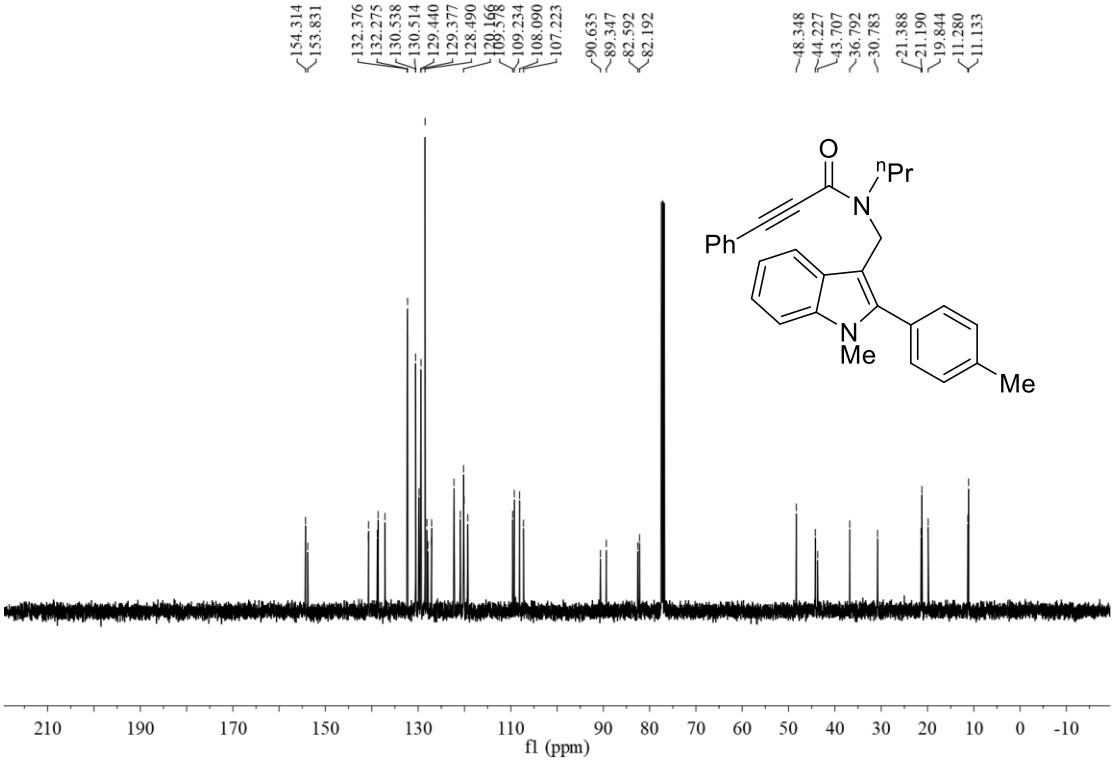
***N*-((1-methyl-2-phenyl-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2z):**



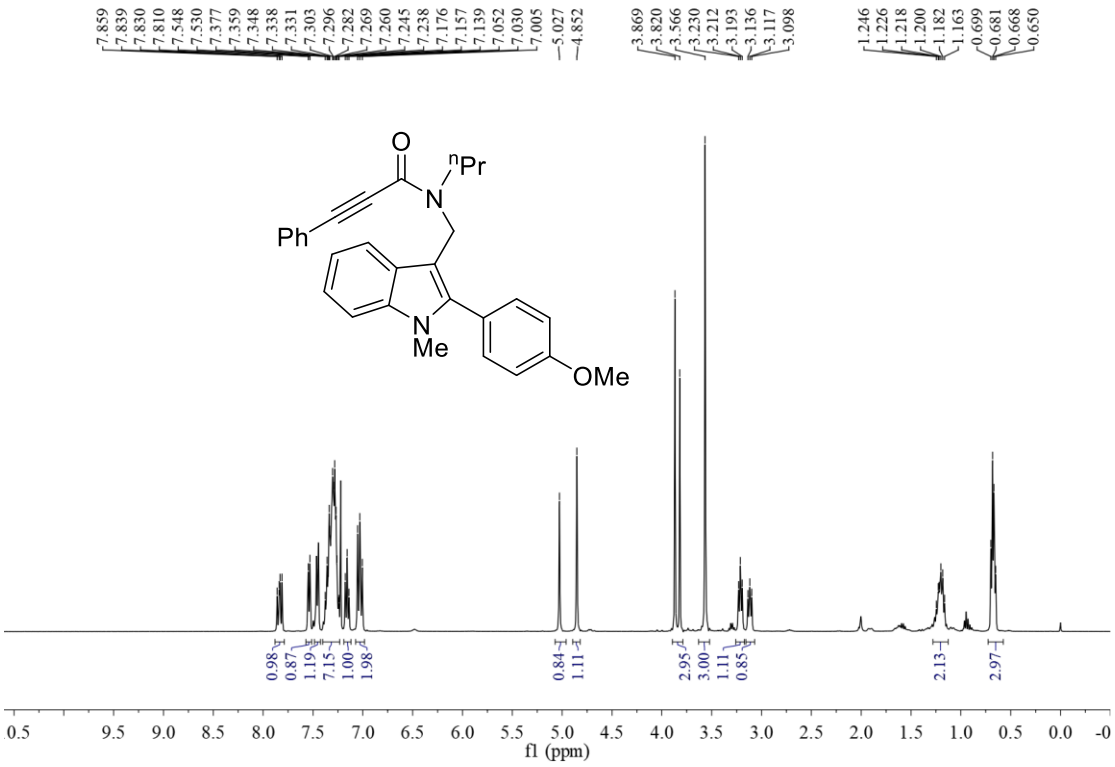


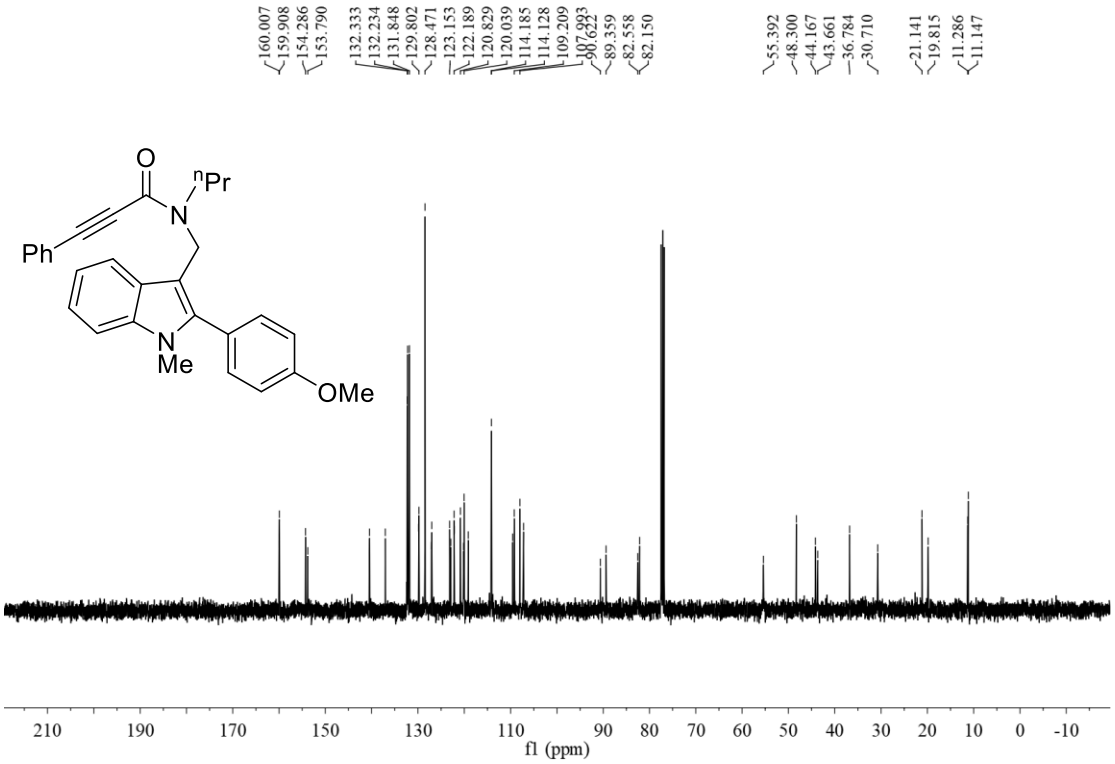
***N*-((1-methyl-2-(p-tolyl)-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2aa):**



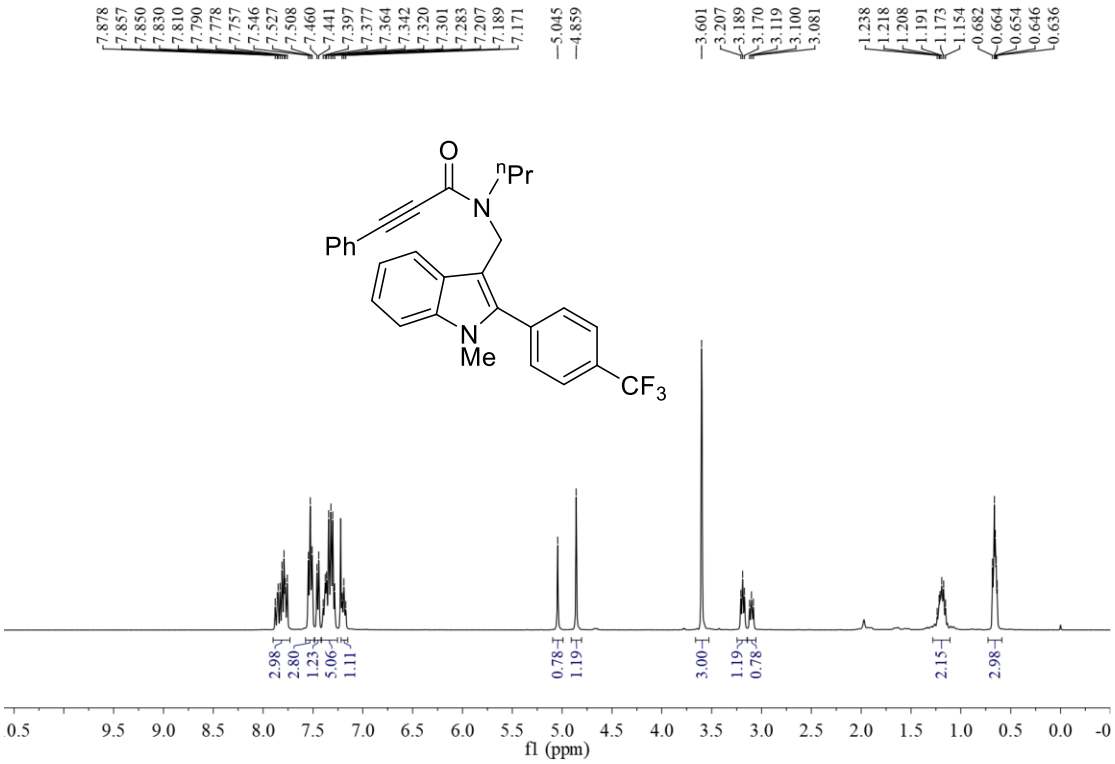


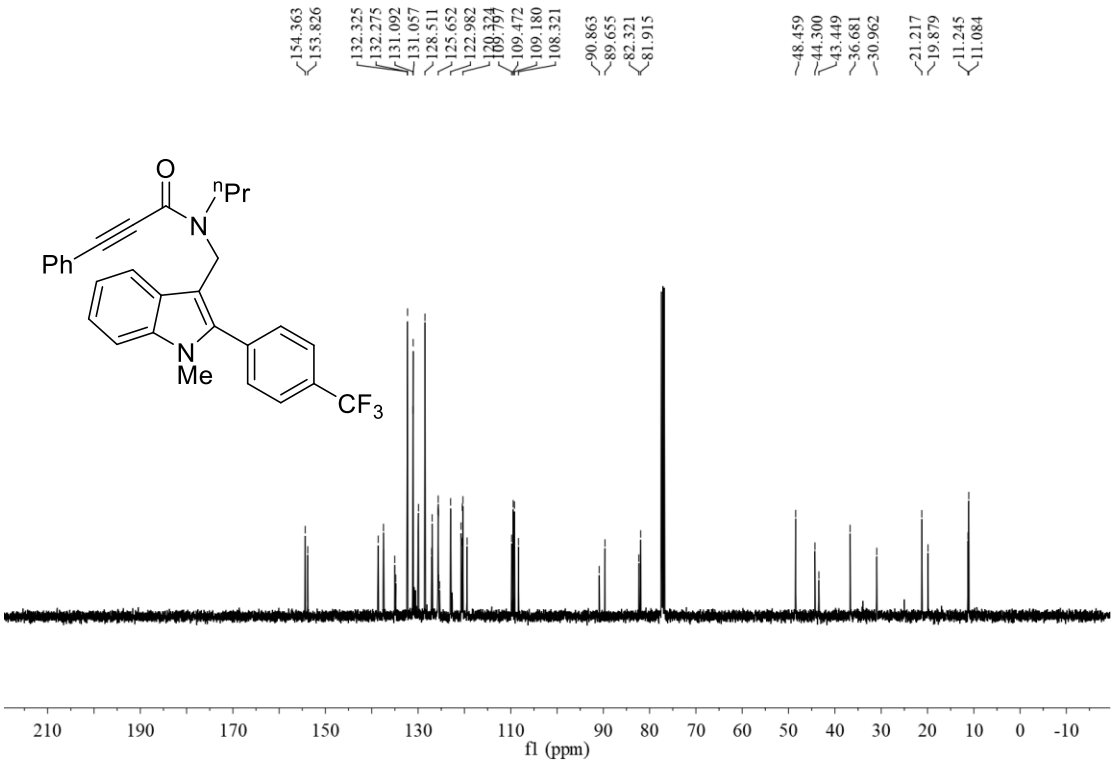
***N*-((2-(4-methoxyphenyl)-1-methyl-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2ab):**

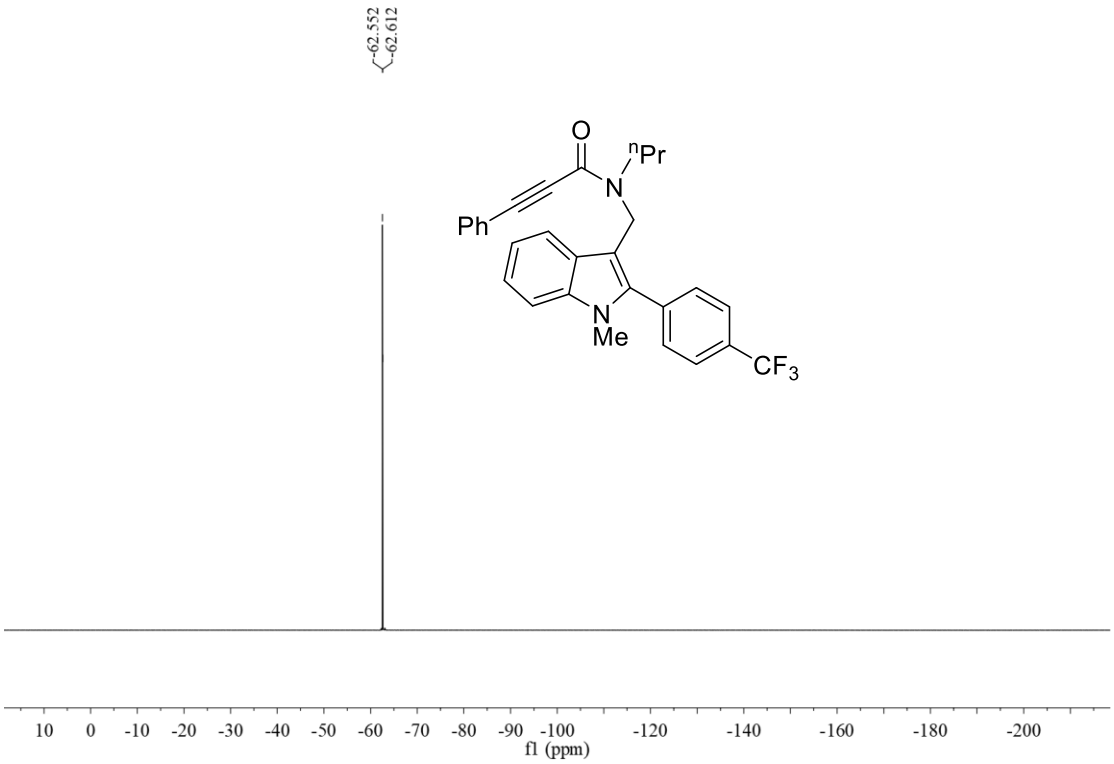




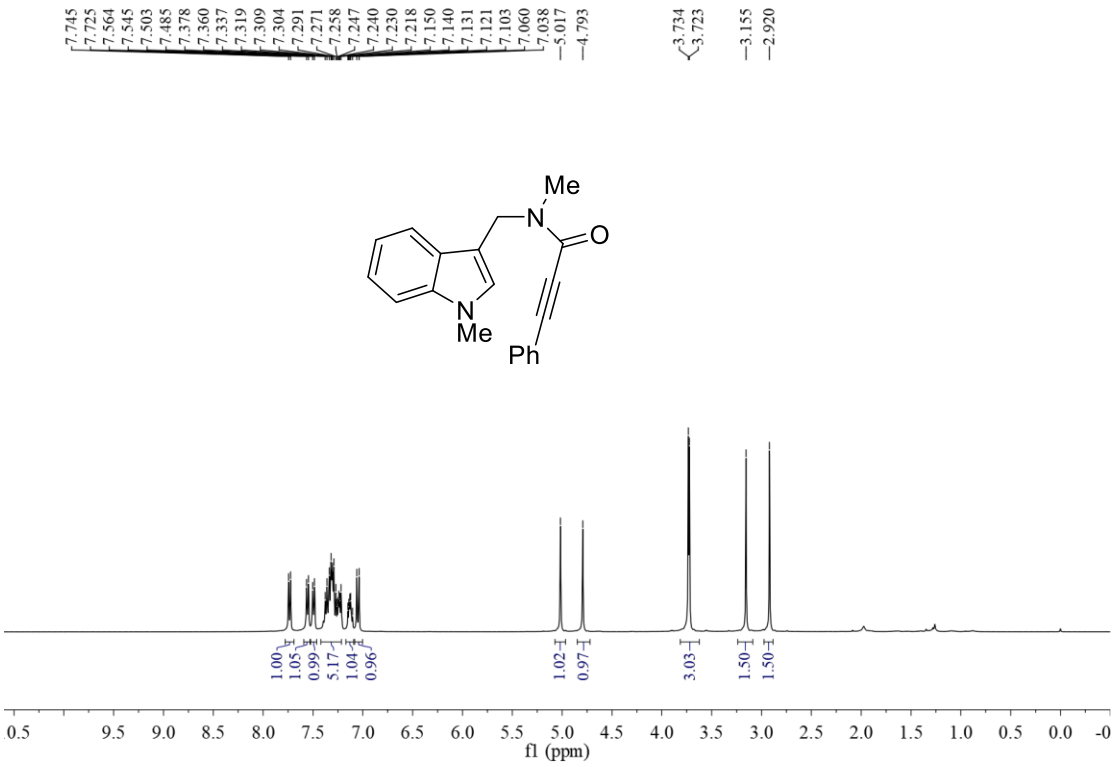
***N*-((1-methyl-2-(4-(trifluoromethyl)phenyl)-1H-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2ac):**

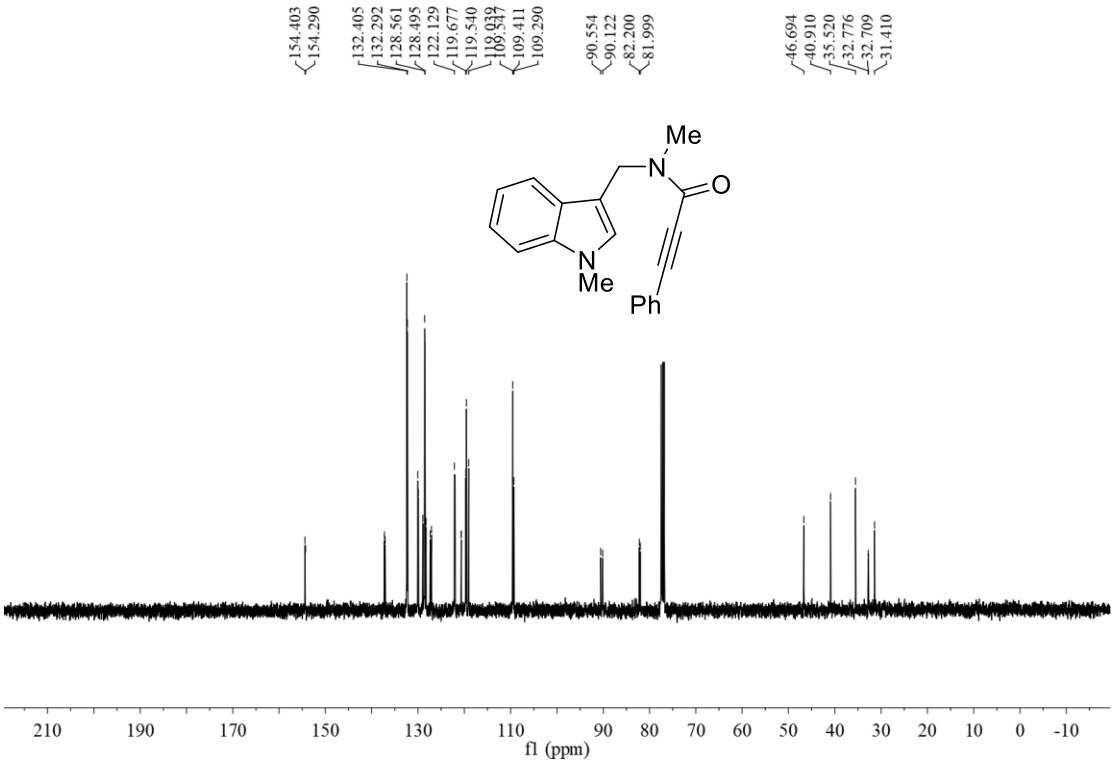




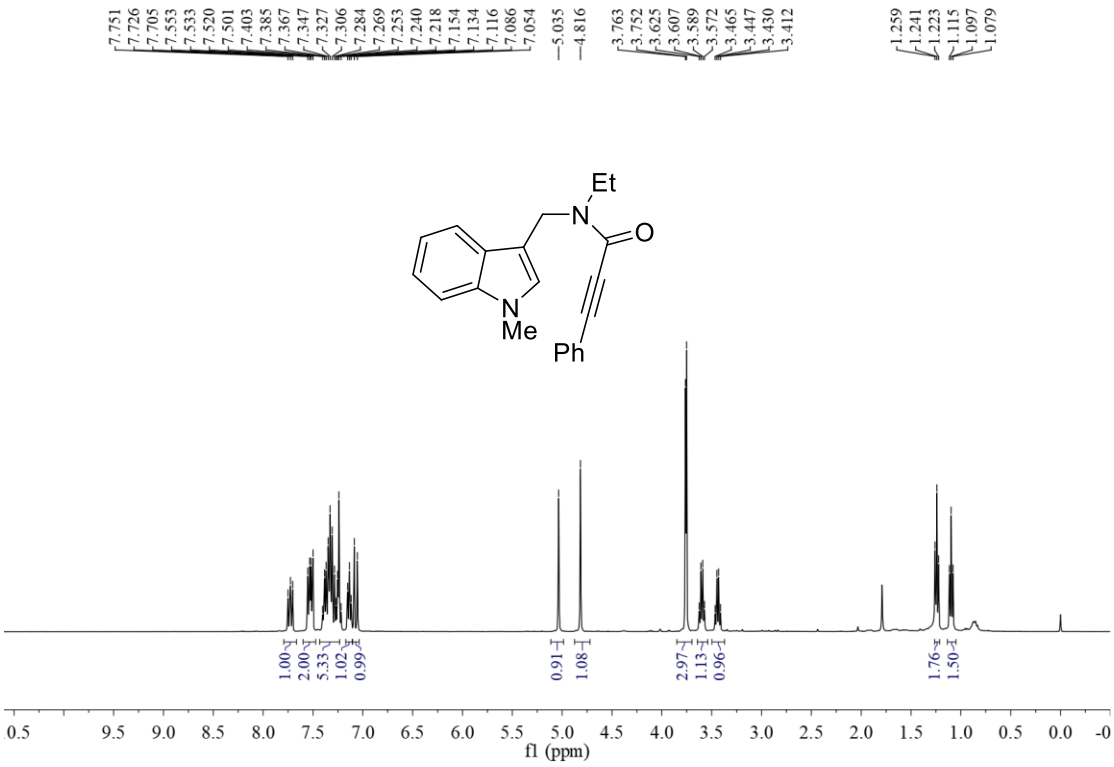

-62.552
-62.612
O
nPr
N
Ph
N
Me
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

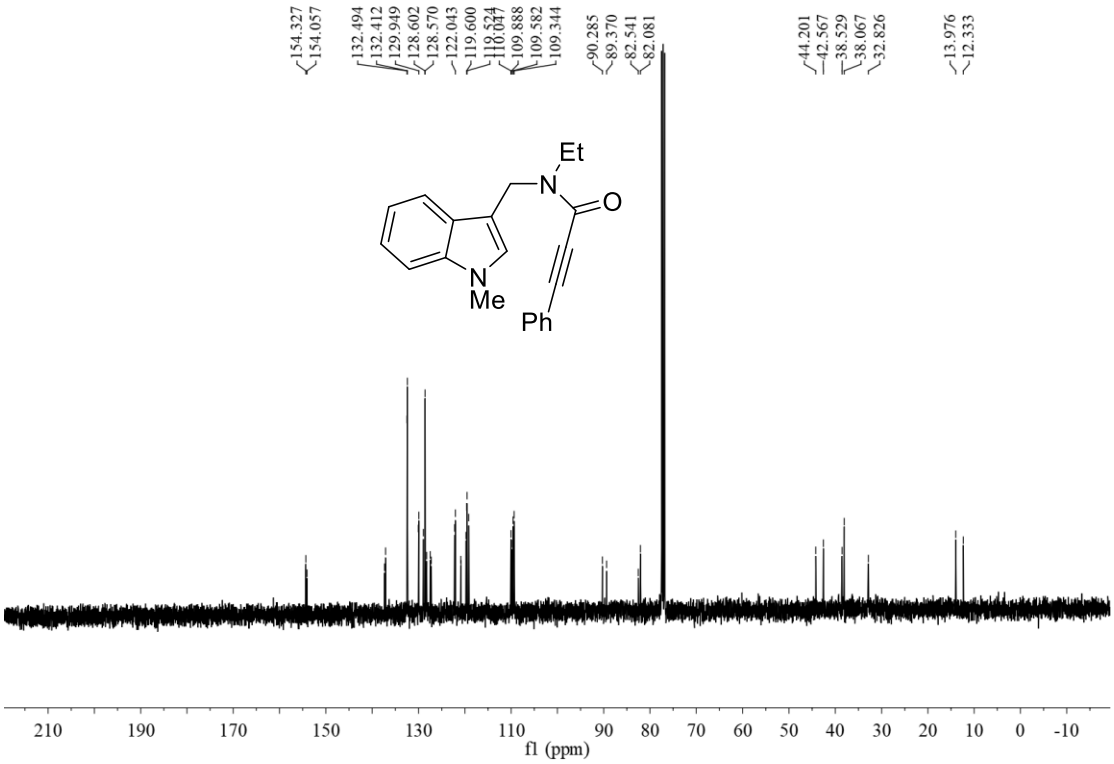
_N_-methyl-_N_-((1-methyl-1H-indol-3-yl)methyl)-3-phenylpropiolamide (2ad)



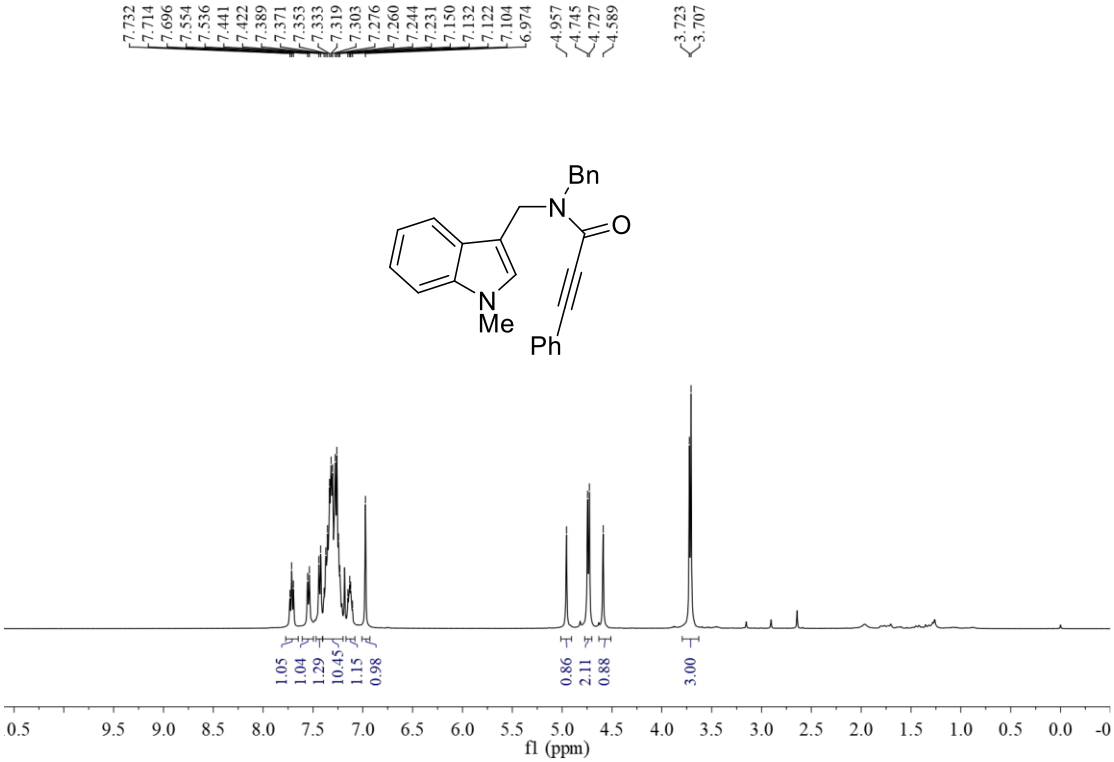


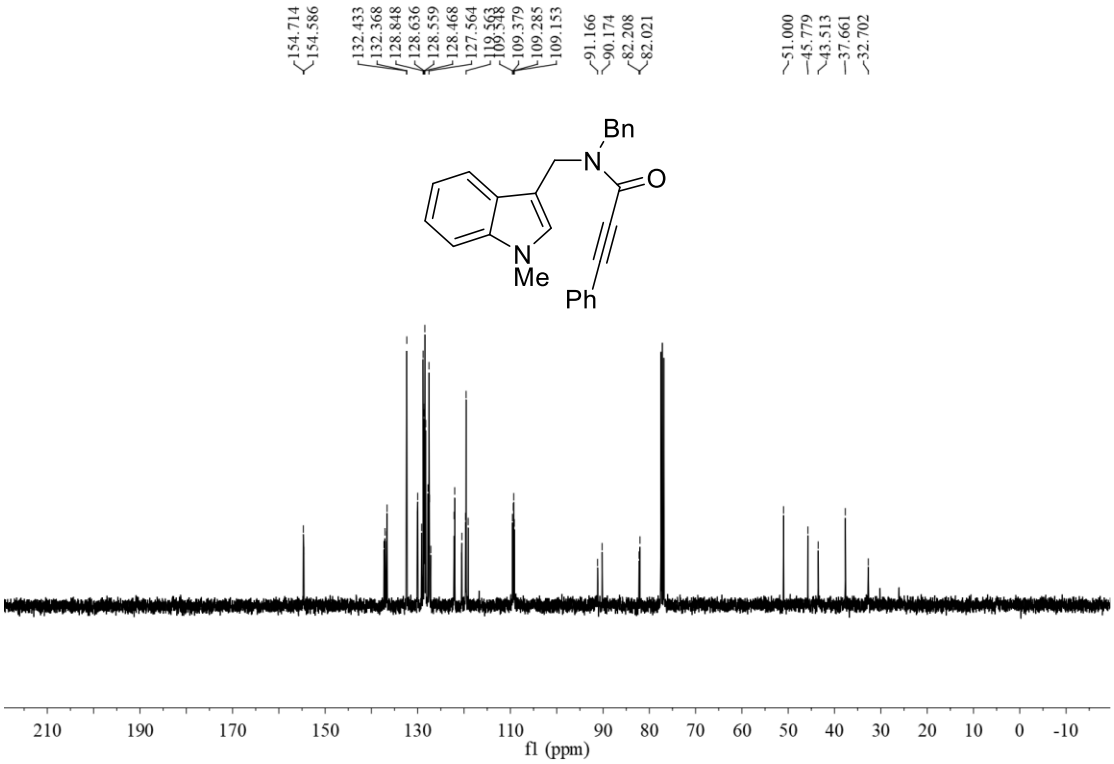
_N_-ethyl-_N_-((1-methyl-1H-indol-3-yl)methyl)-3-phenylpropiolamide (2ae)



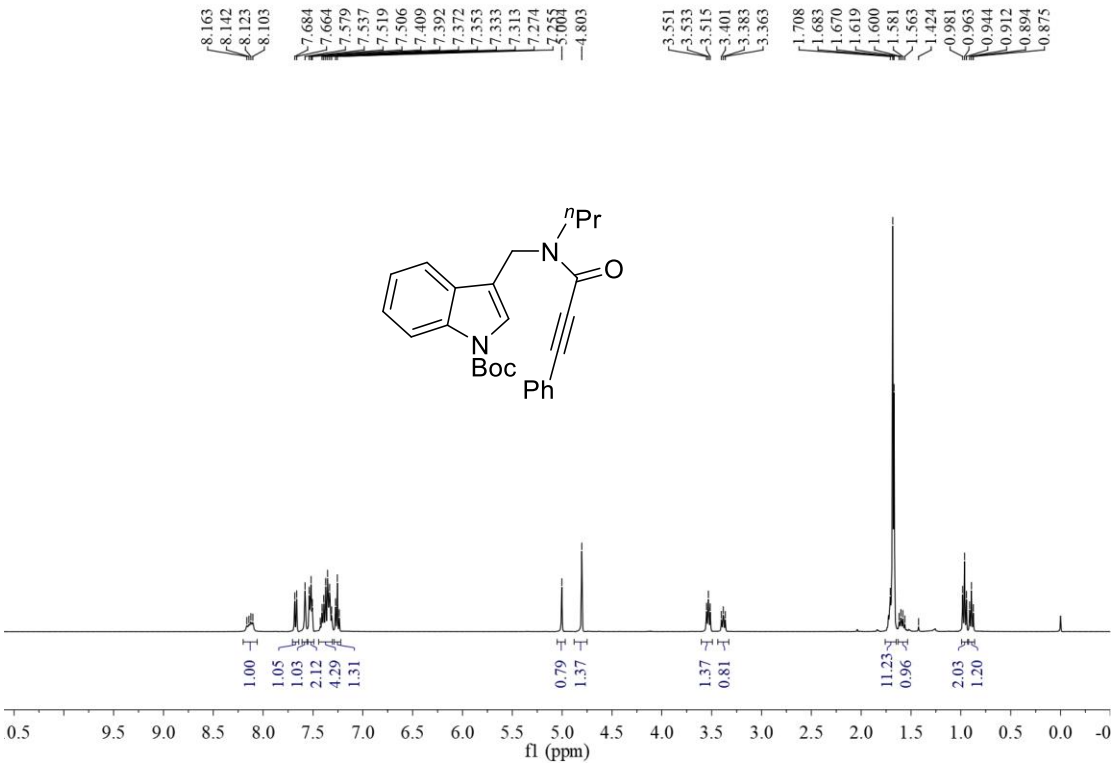


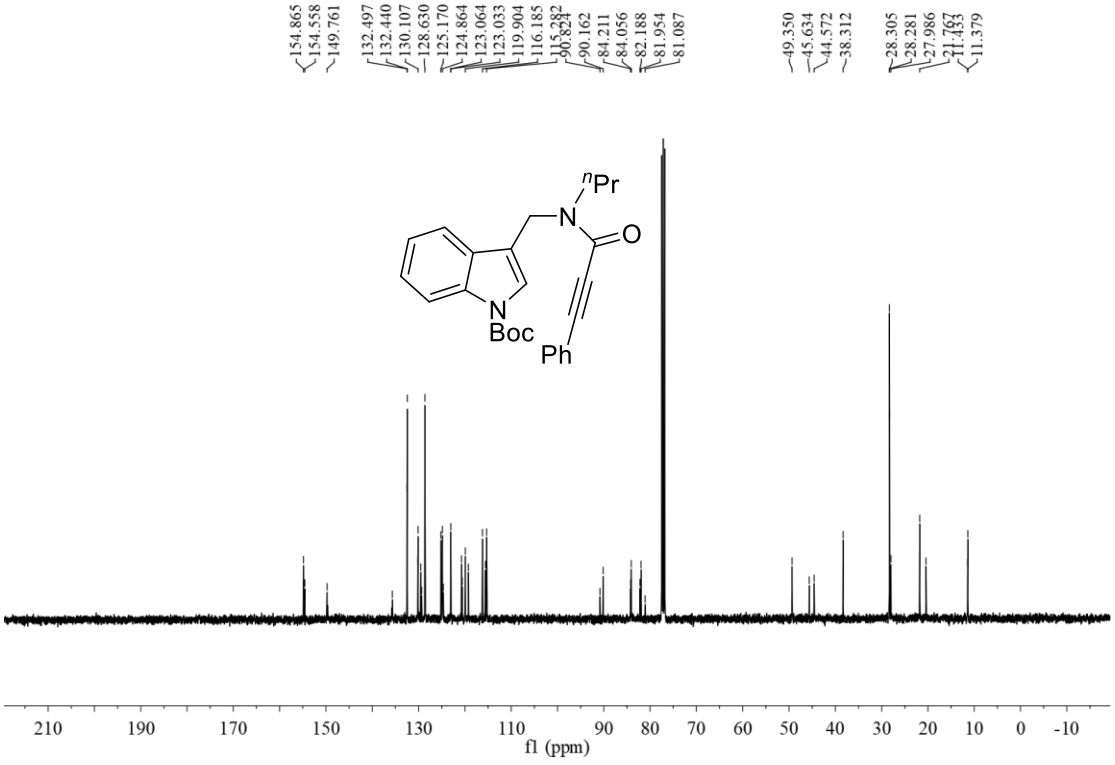
_N_-benzyl-_N_-((1-methyl-1H-indol-3-yl)methyl)-3-phenylpropiolamide (2af)



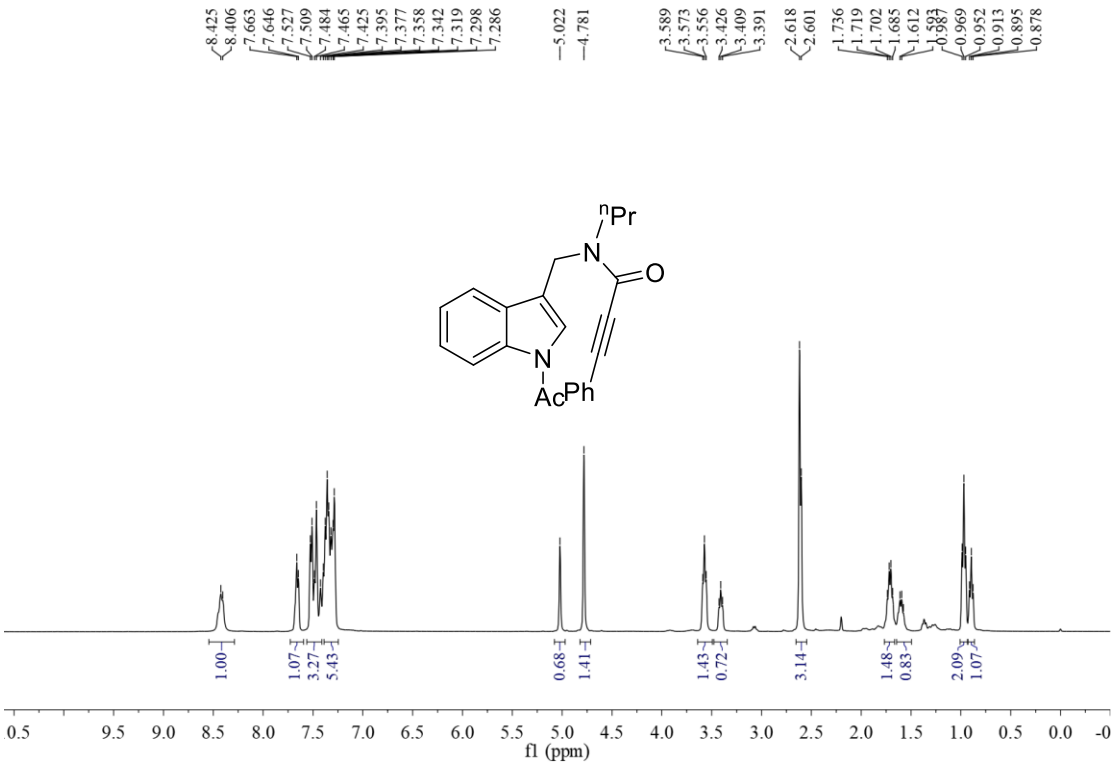


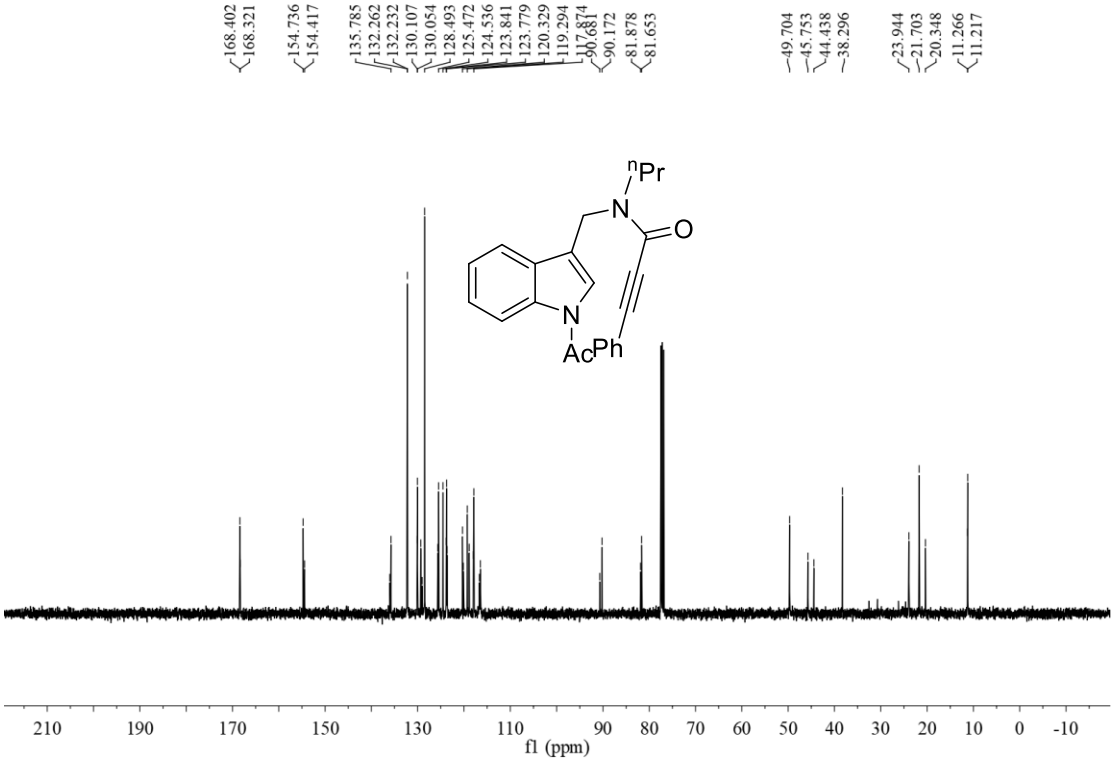
tert-butyl 3-((3-phenyl-N-propylpropiolamido)methyl)-1H-indole-1-carboxylate (2ag):



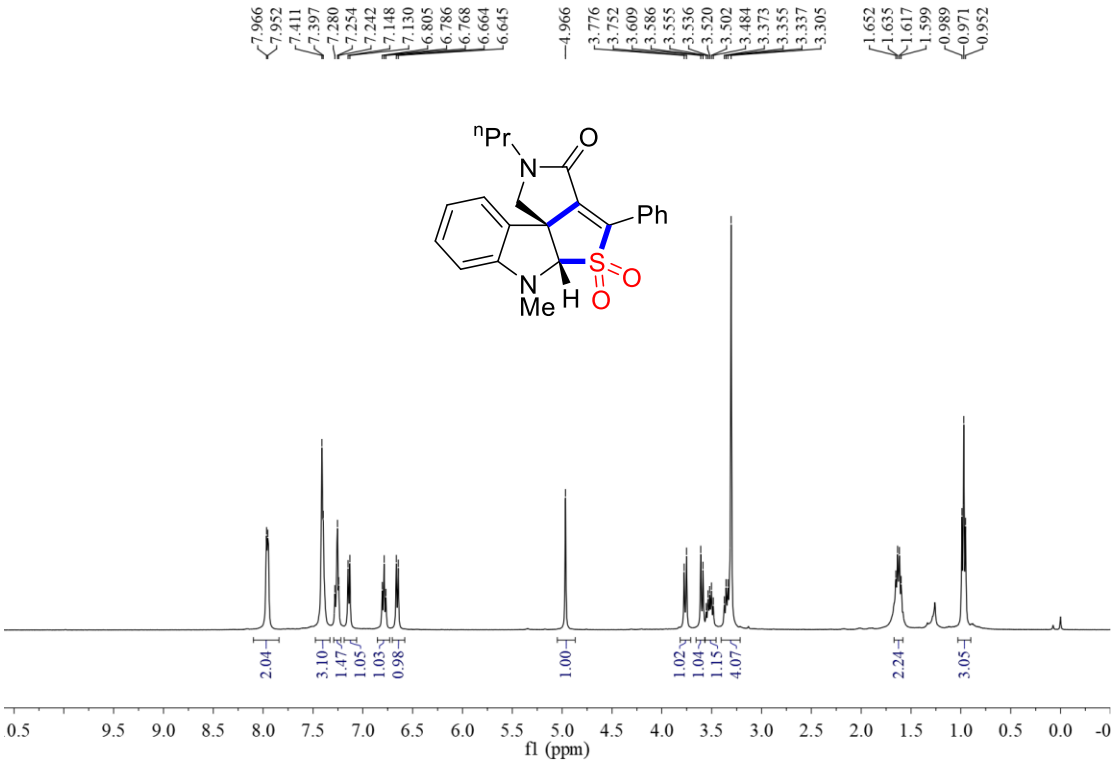


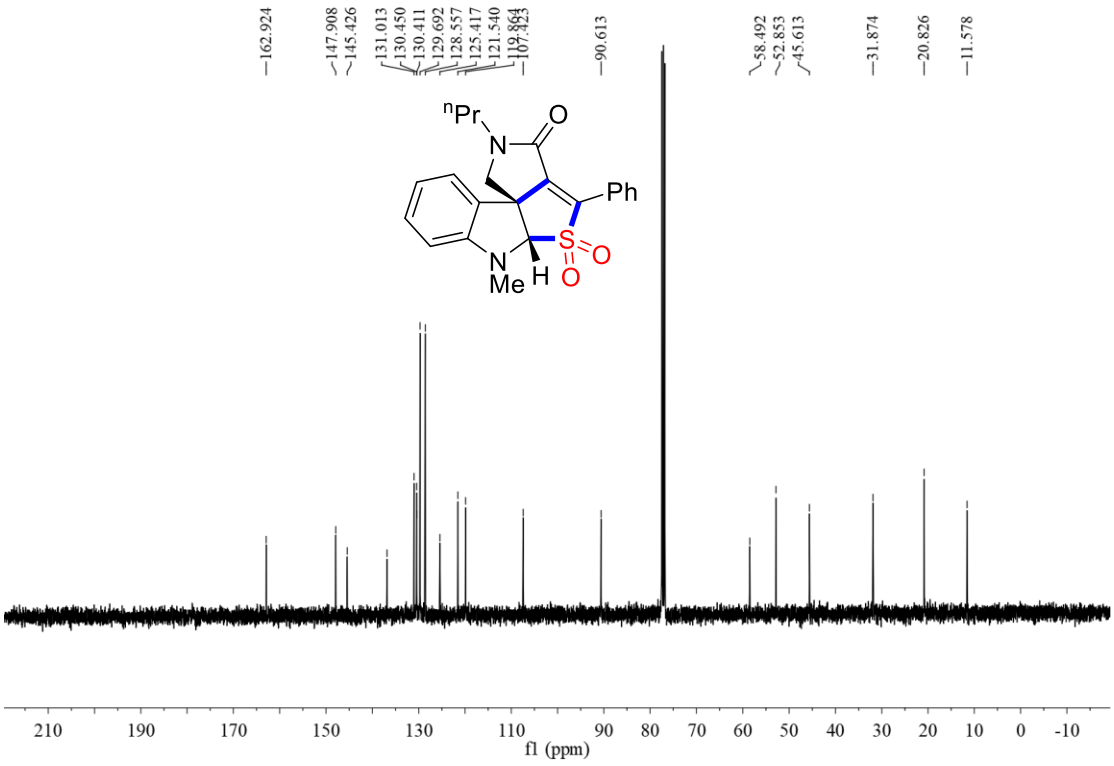
***N*-((1-acetyl-1*H*-indol-3-yl)methyl)-3-phenyl-*N*-propylpropiolamide (2ah)**:



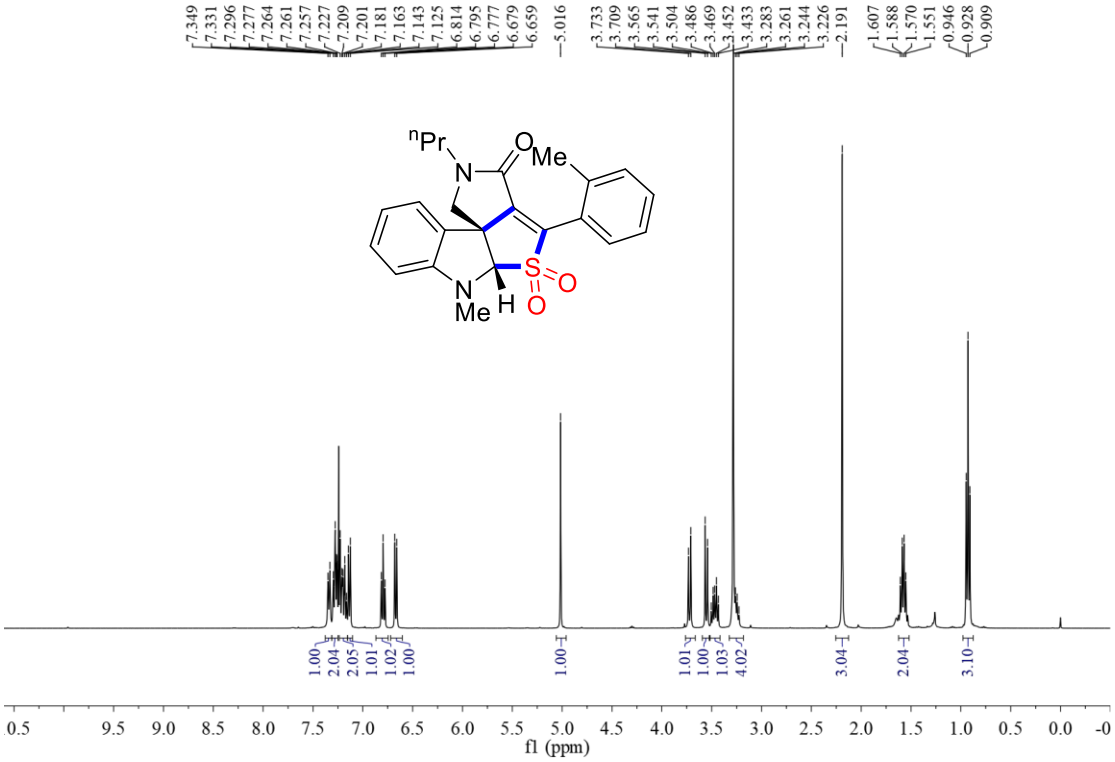


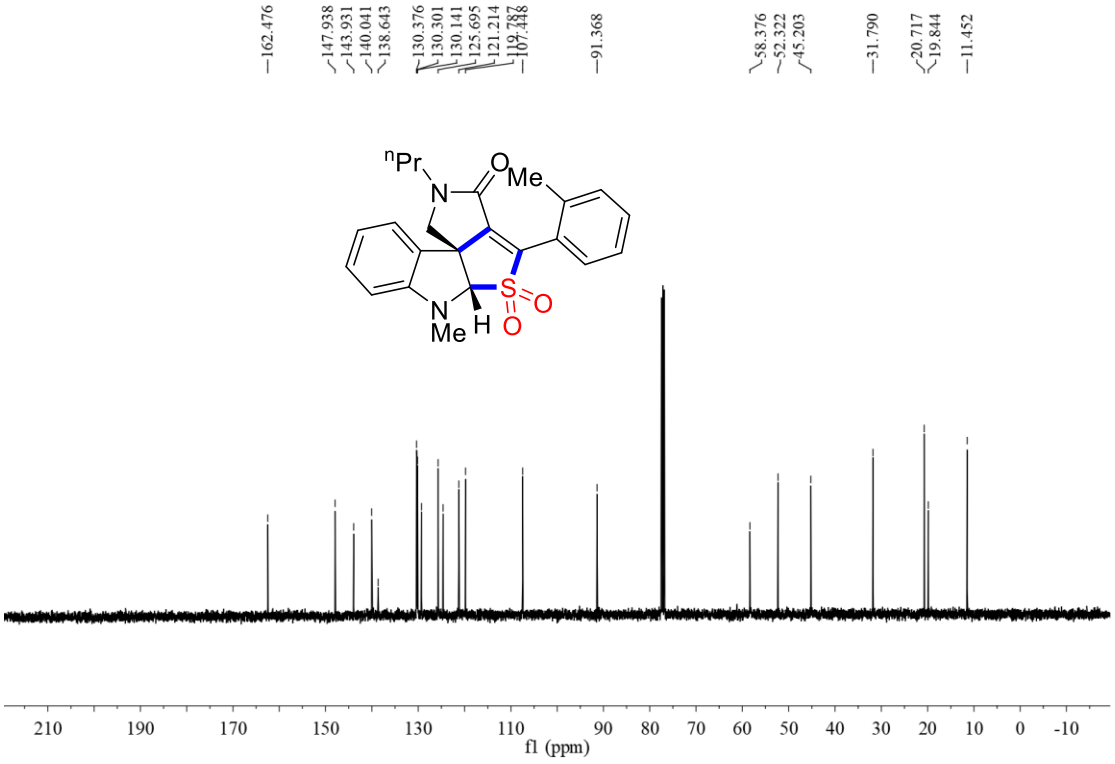
6-methyl-4-phenyl-2-propyl-1,2,5a,6-tetrahydro-3H-pyrrolo[3',4':3,4]thieno[2,3-b]indol-3-one 5,5-dioxide (1a) :



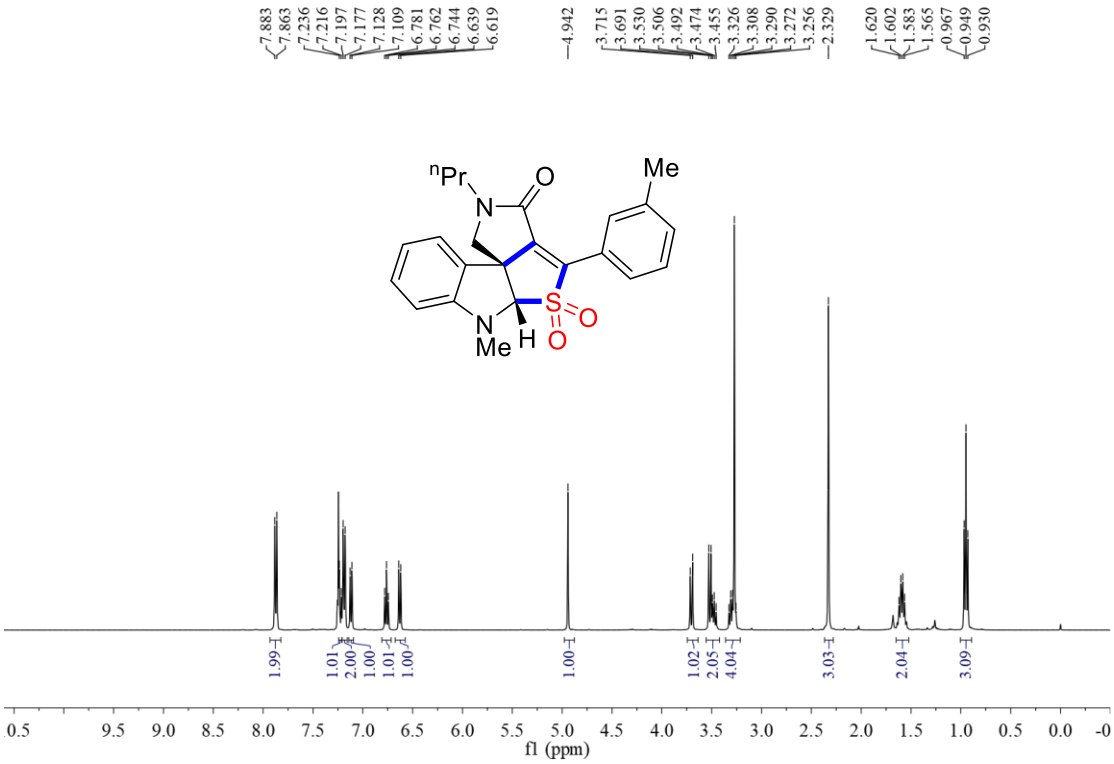


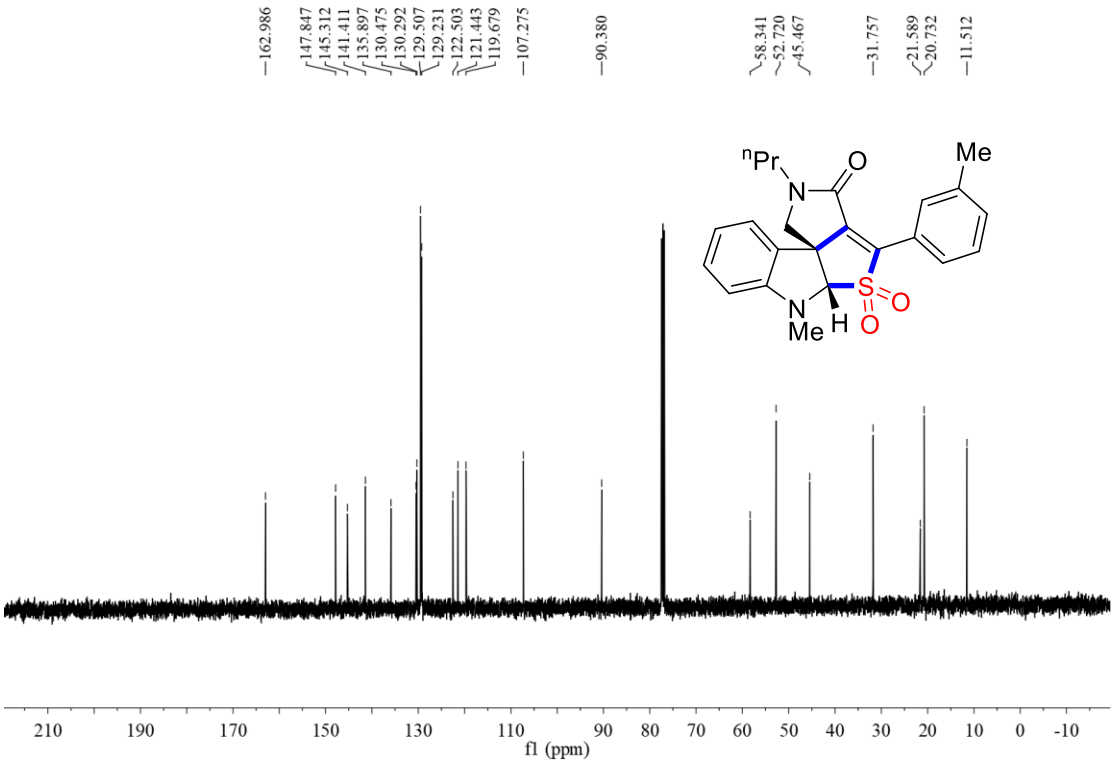
6-methyl-2-propyl-4-(o-tolyl)-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1b) :



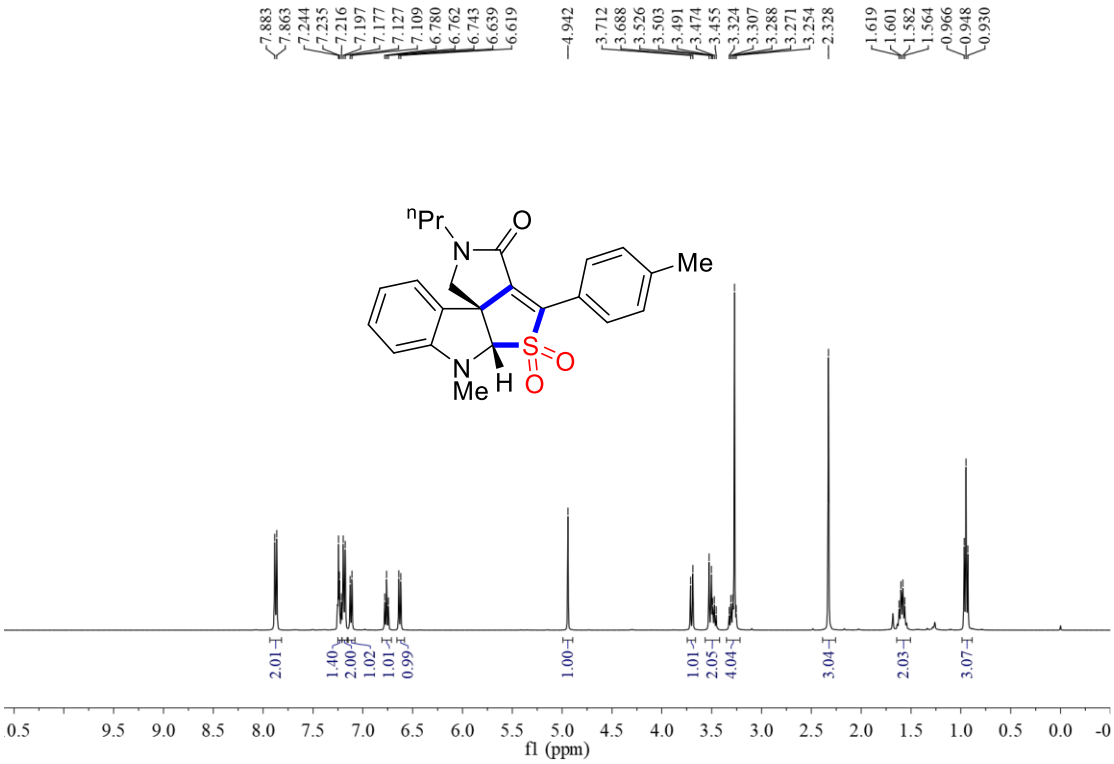


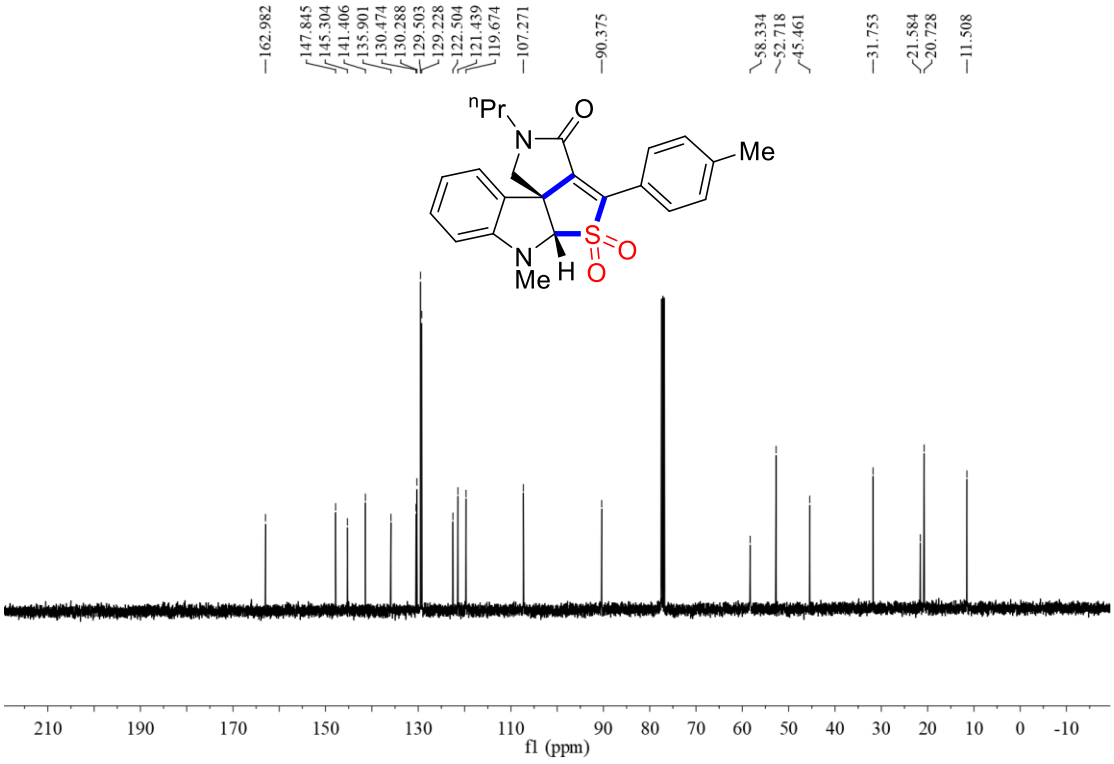
6-methyl-2-propyl-4-(m-tolyl)-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1c)



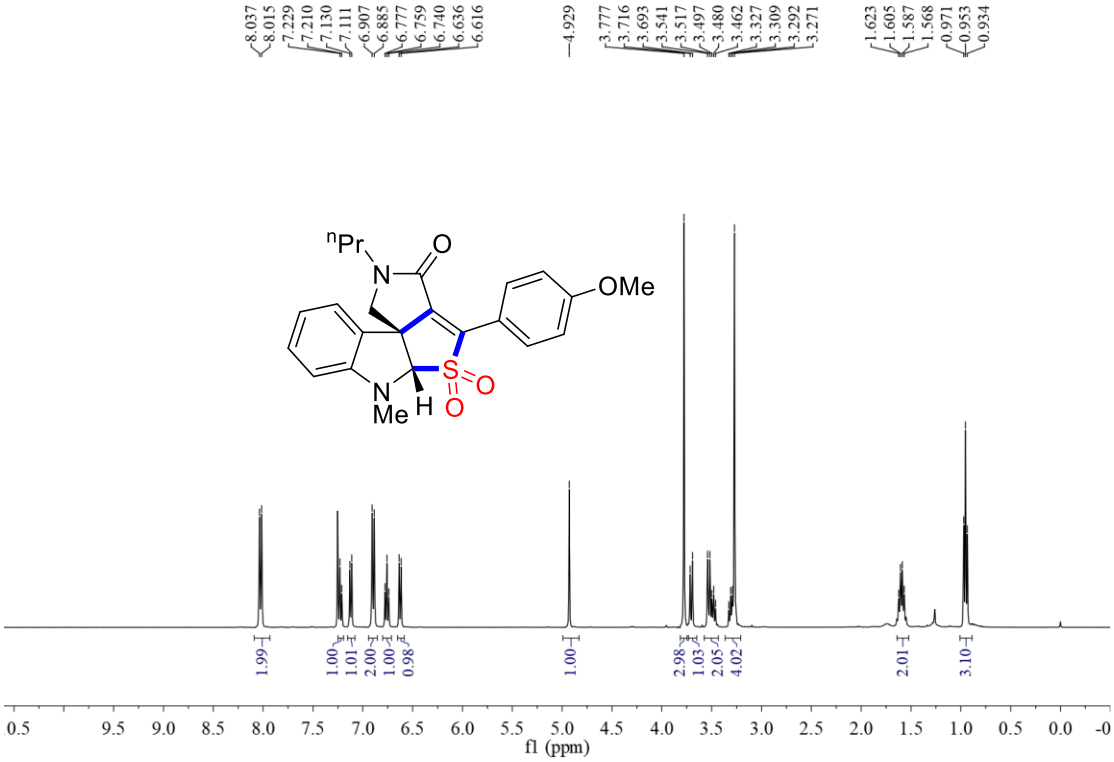


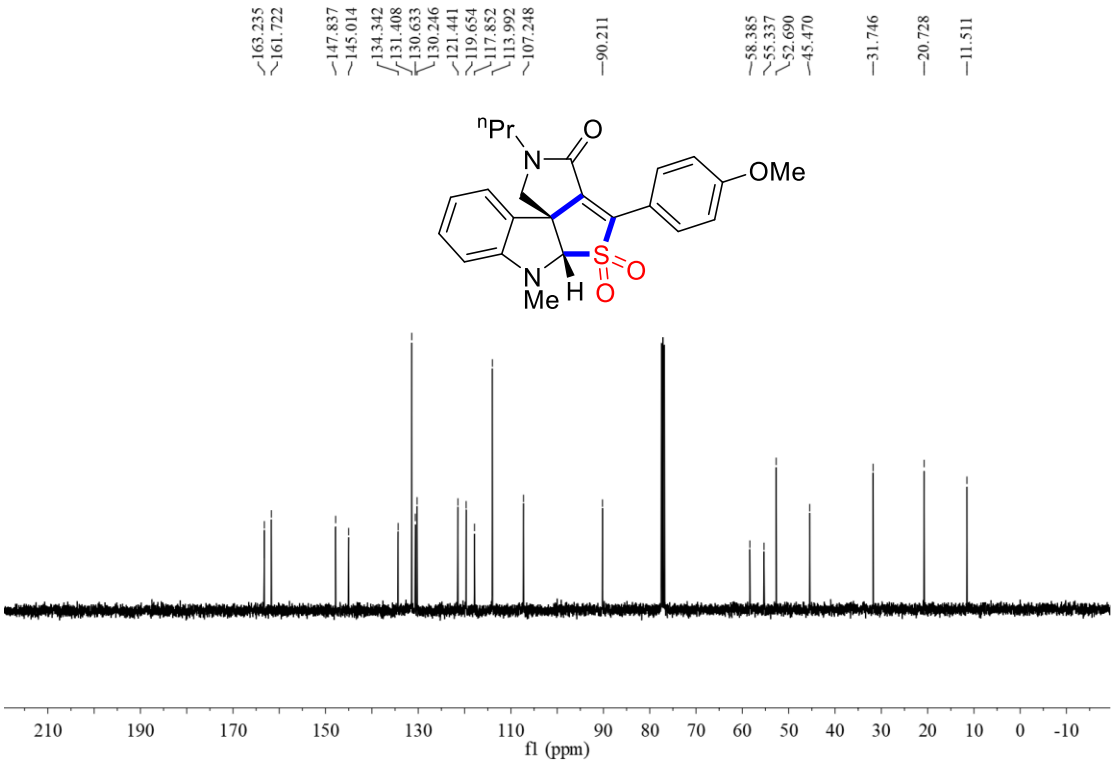
6-methyl-2-propyl-4-(p-tolyl)-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1d) :



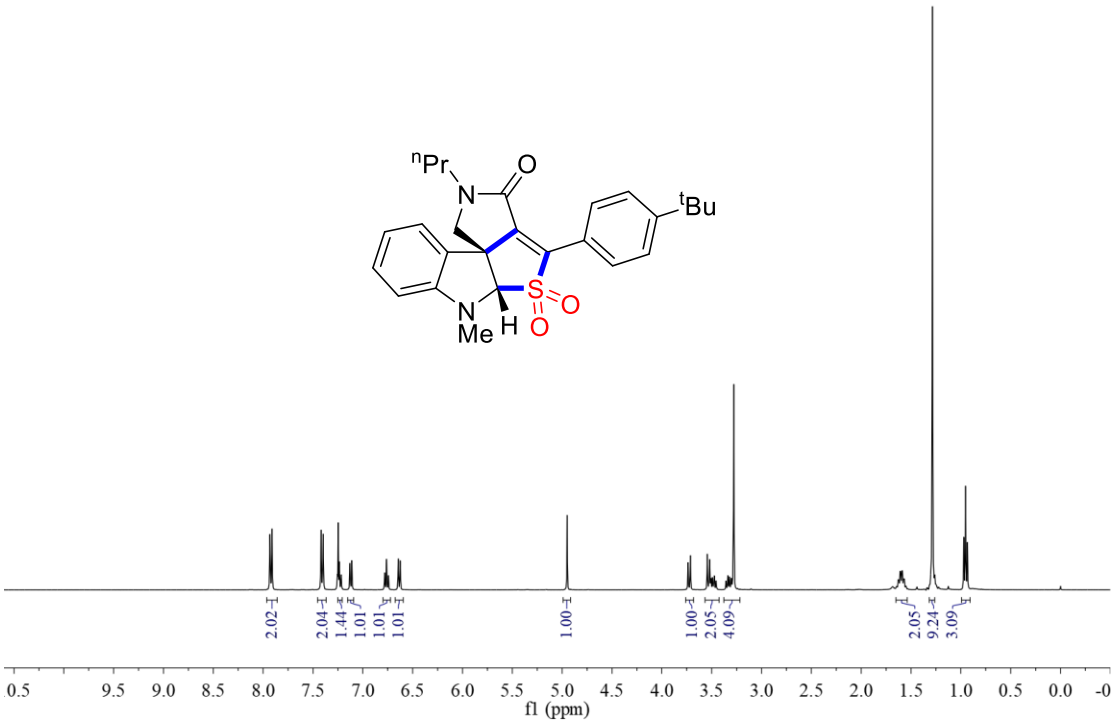


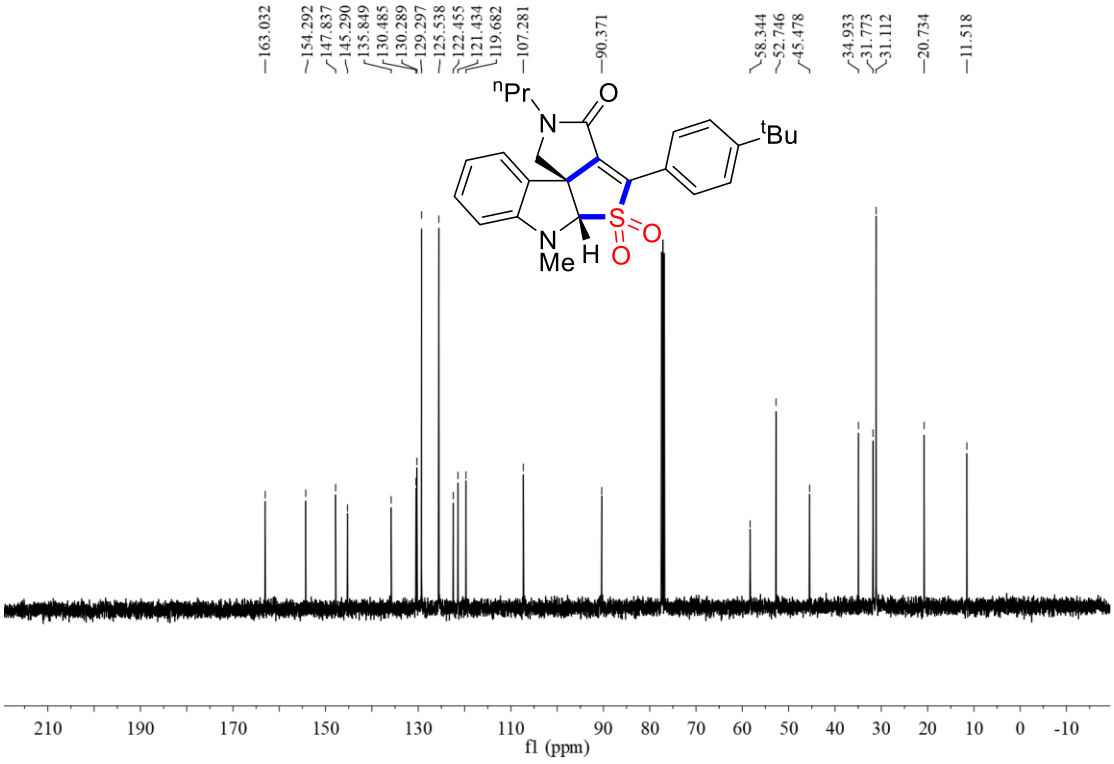
4-(4-methoxyphenyl)-6-methyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1e)



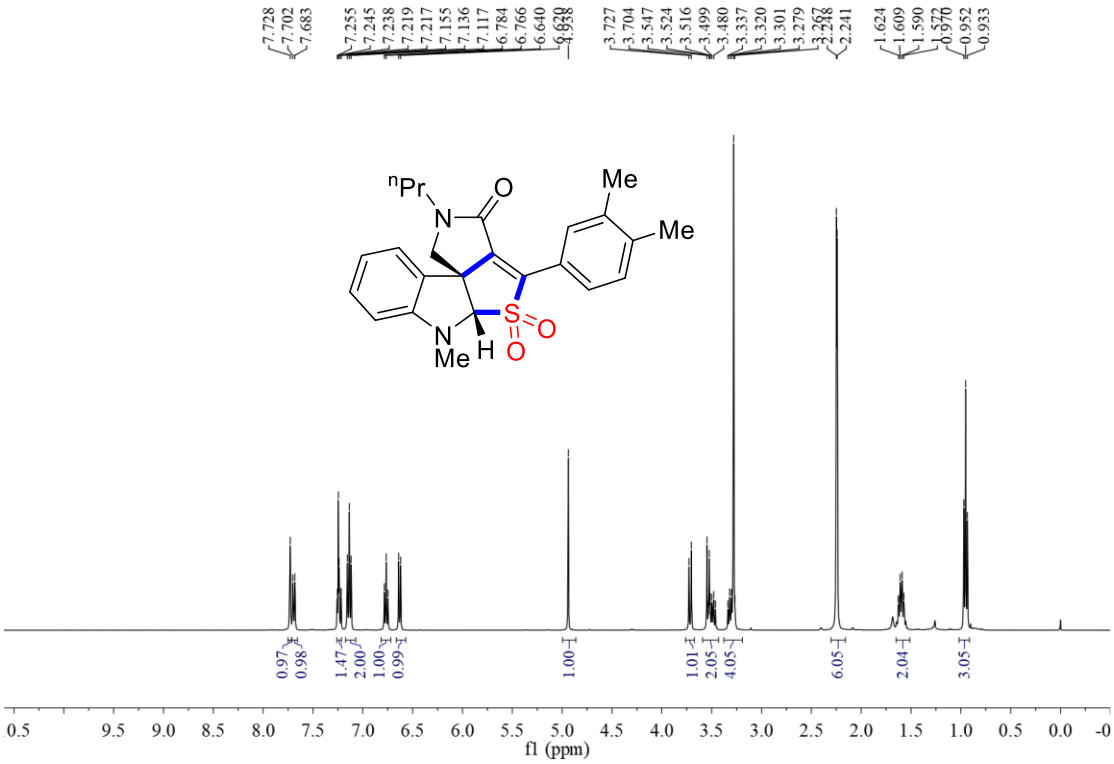


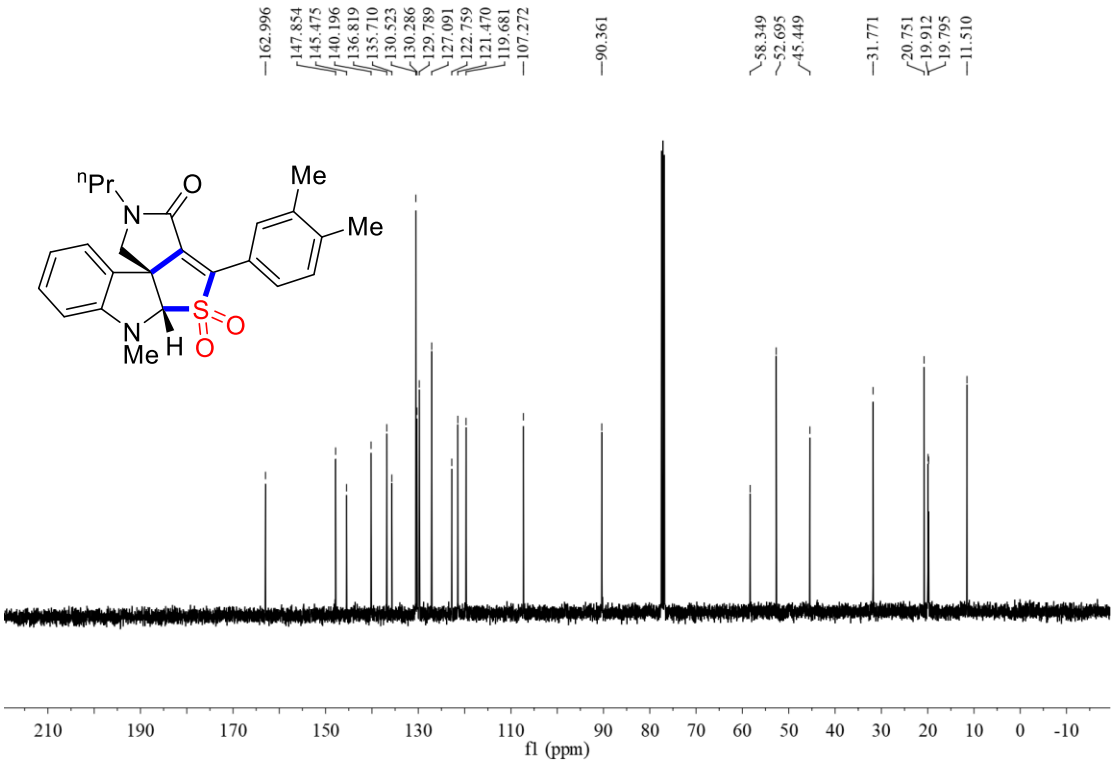
4-(4-(tert-butyl)phenyl)-6-methyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1f)



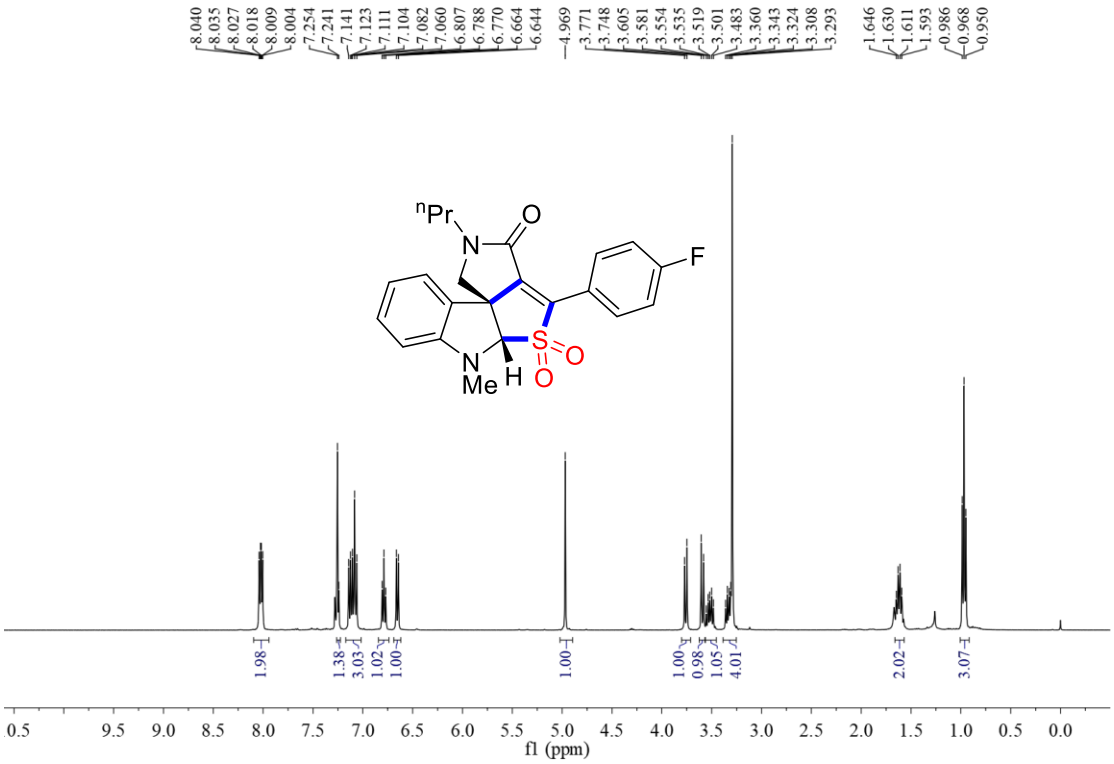


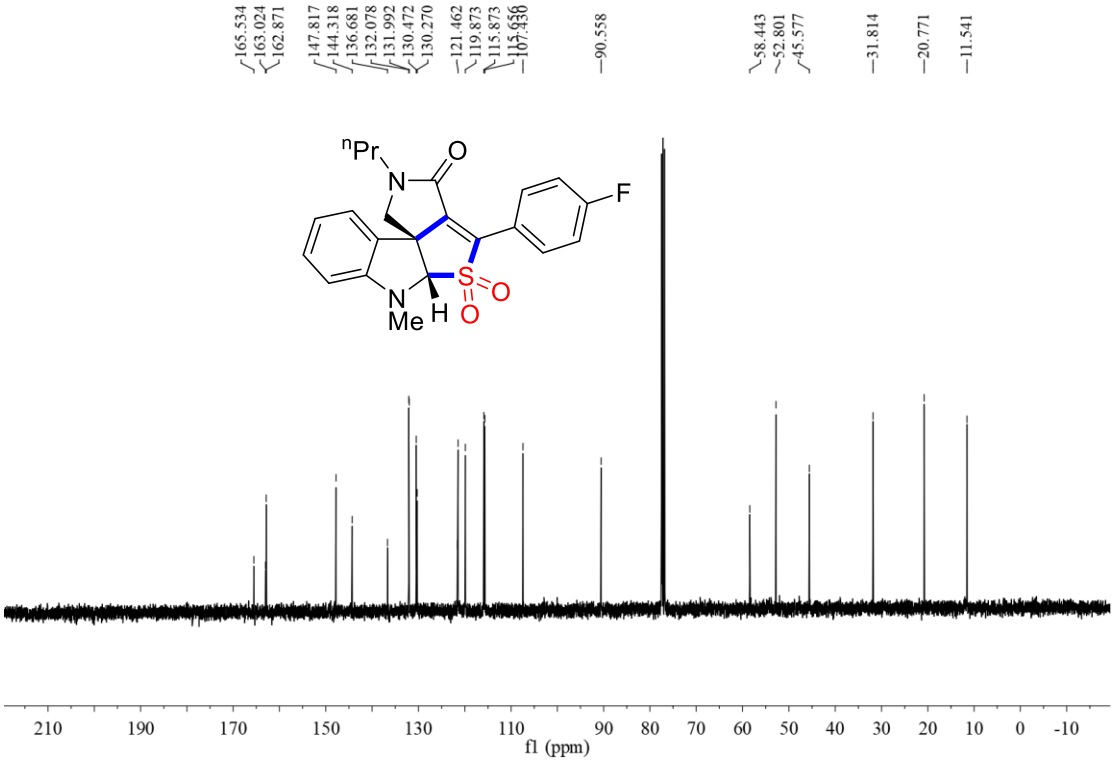
4-(3,4-dimethylphenyl)-6-methyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1g)

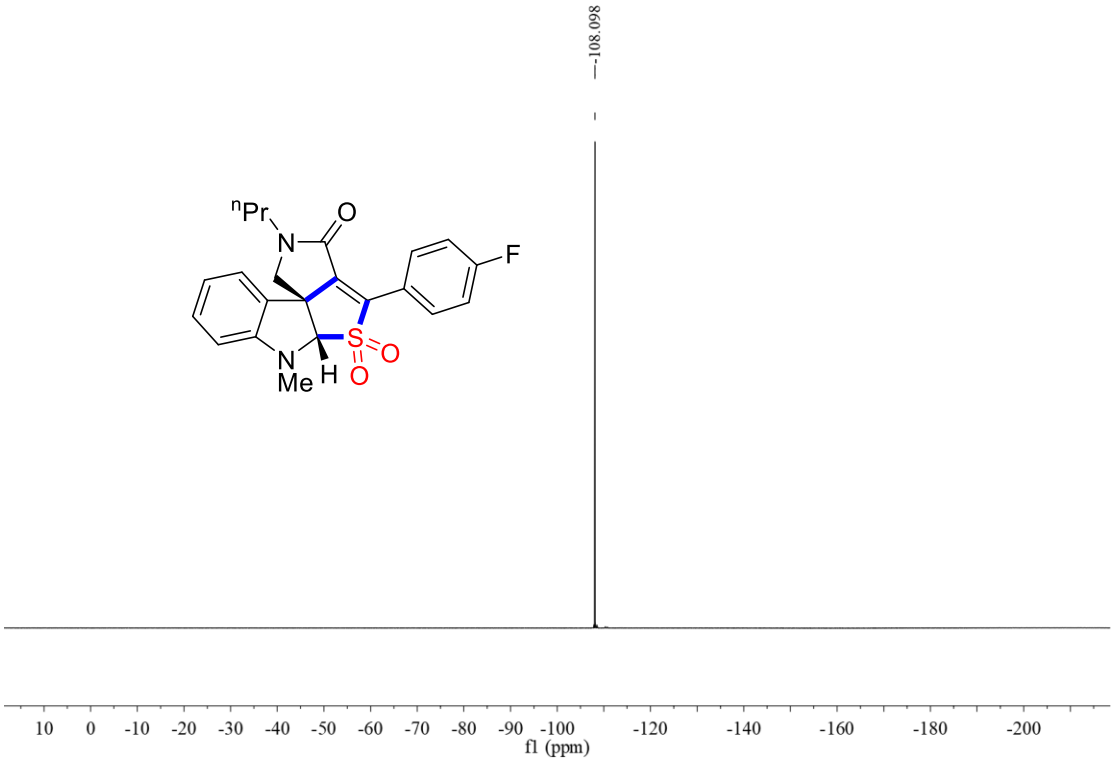




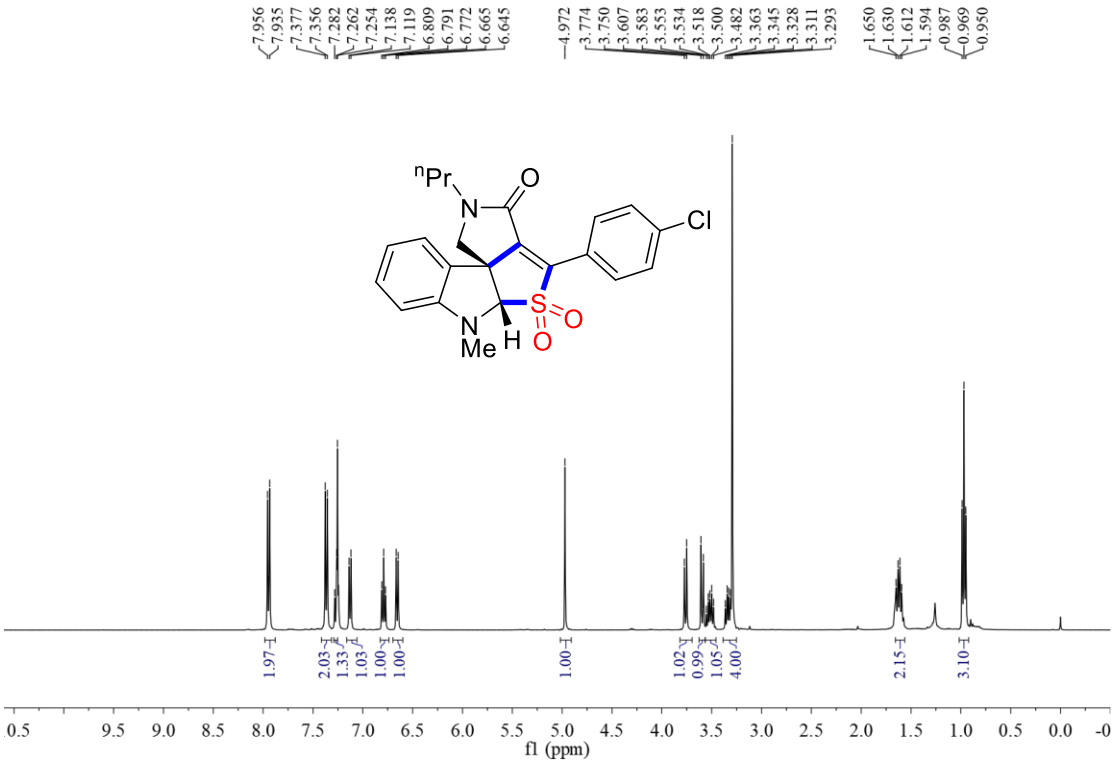
4-(4-fluorophenyl)-6-methyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1h)

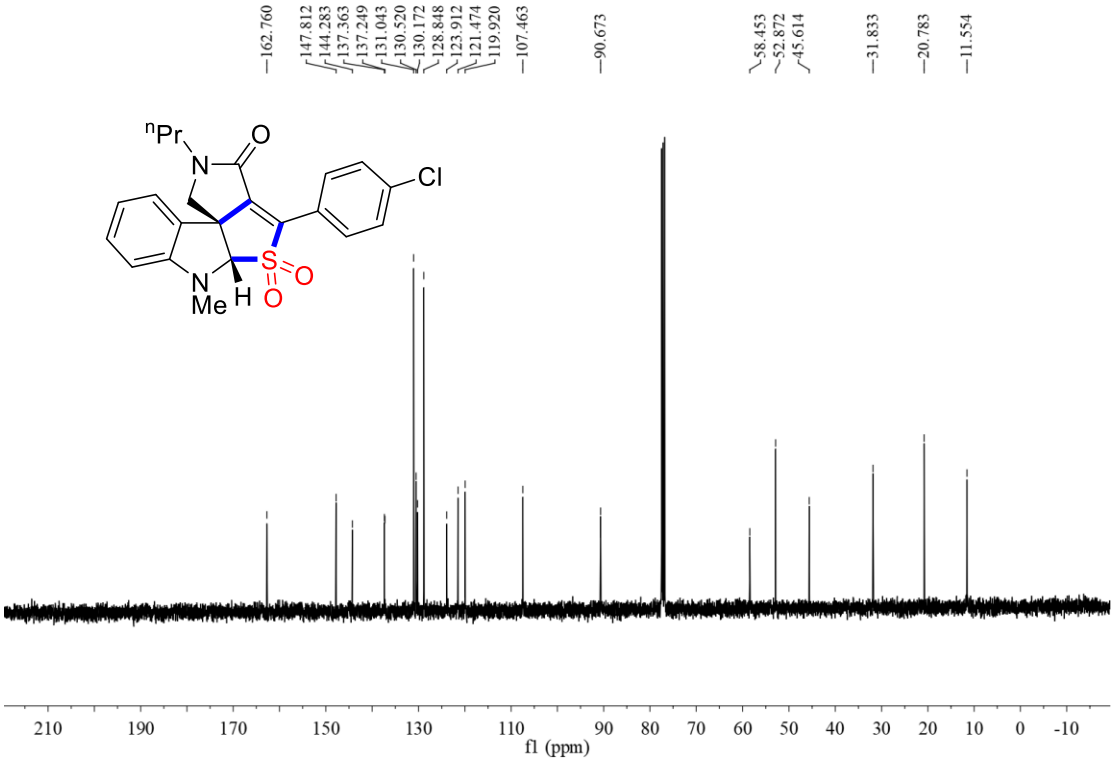




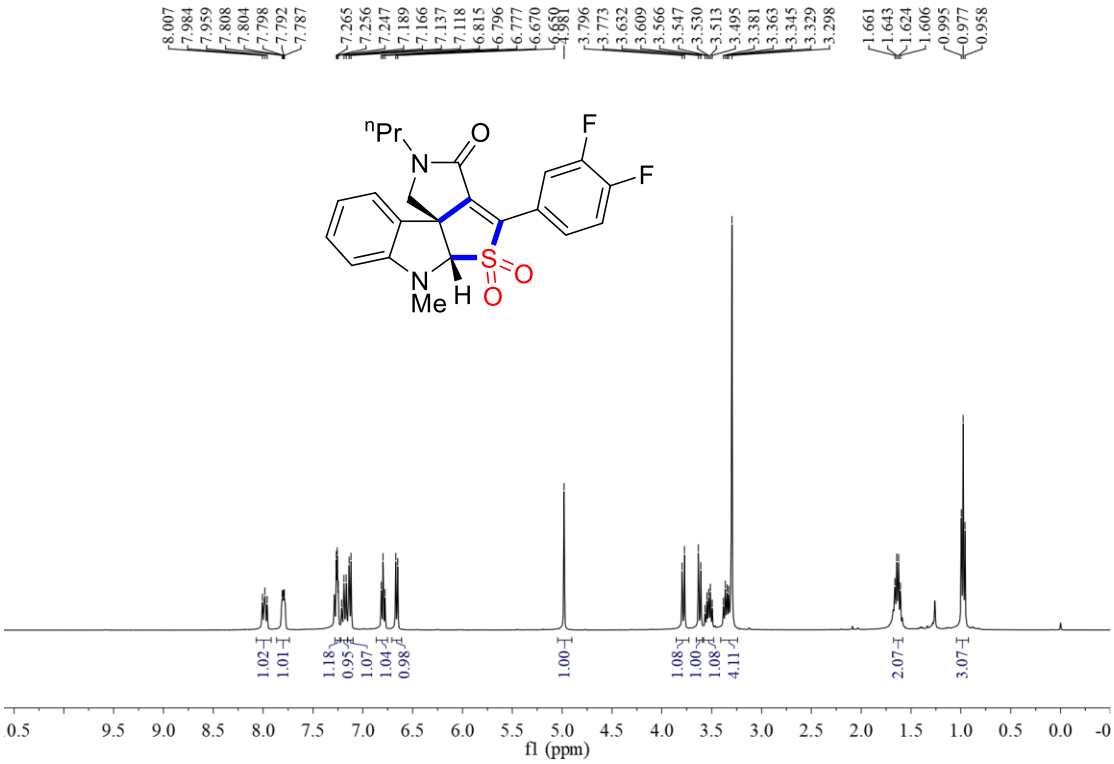

-108.098
nPr
N
O
F
S
O
O
N
Me
H
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

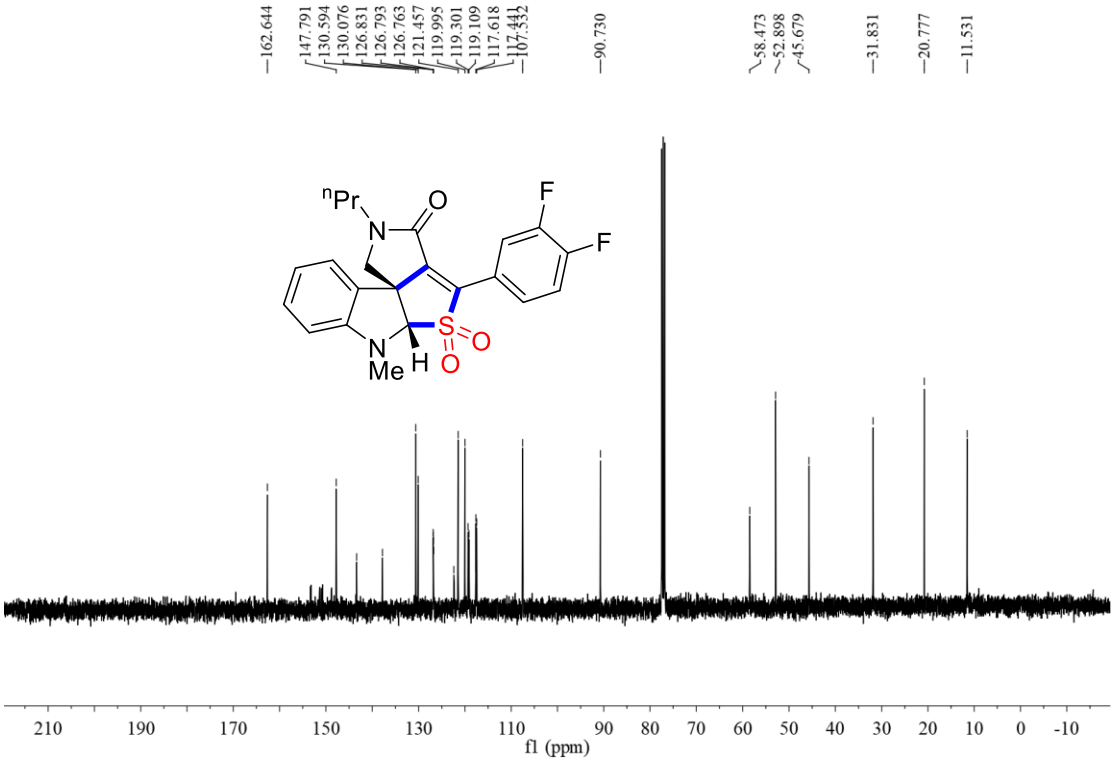
4-(4-chlorophenyl)-6-methyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1i)

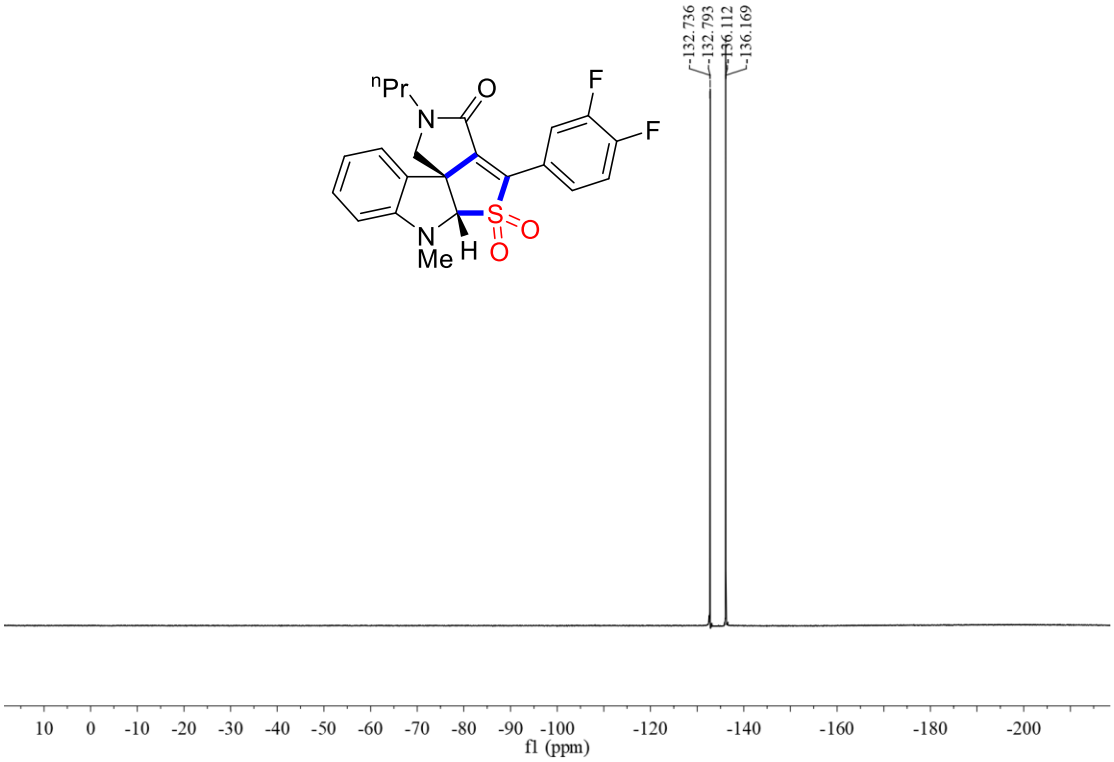




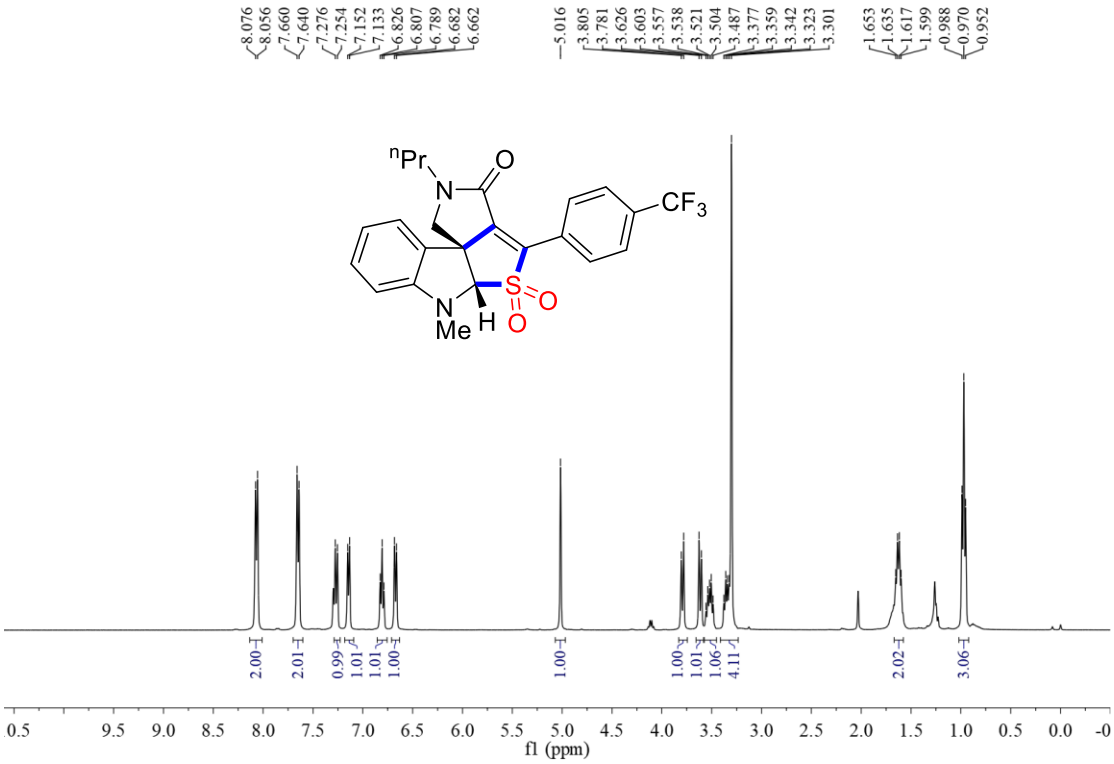
4-(3,4-difluorophenyl)-6-methyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1j)

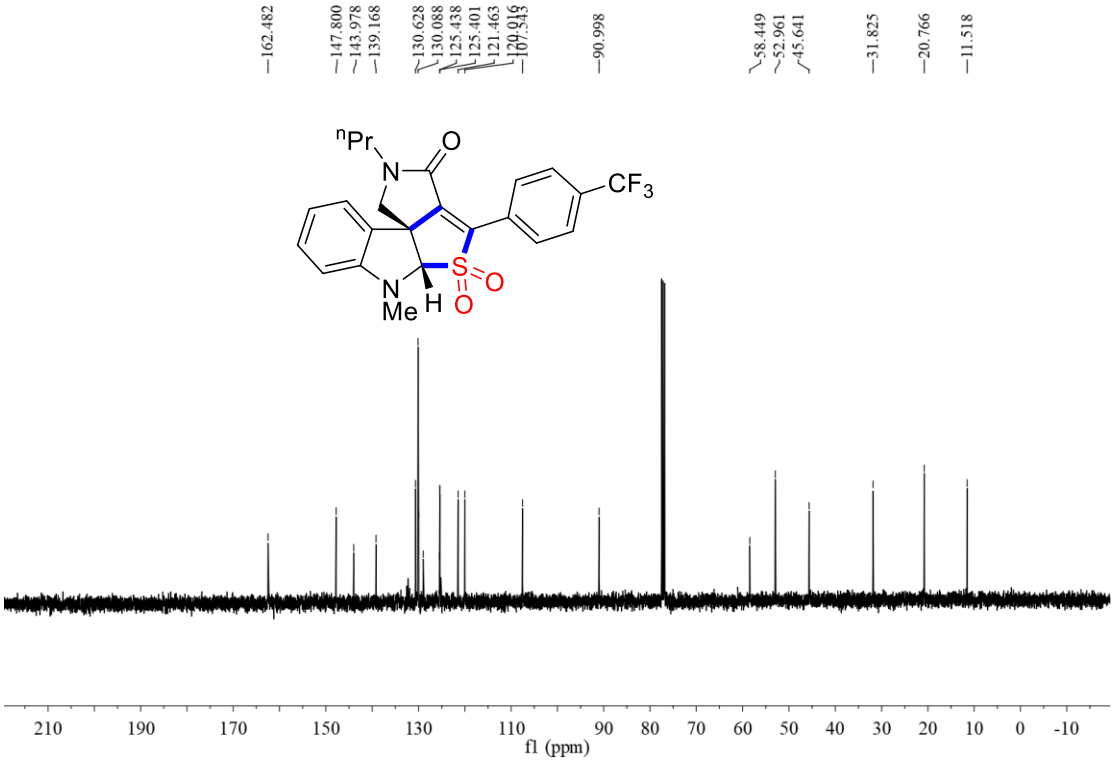


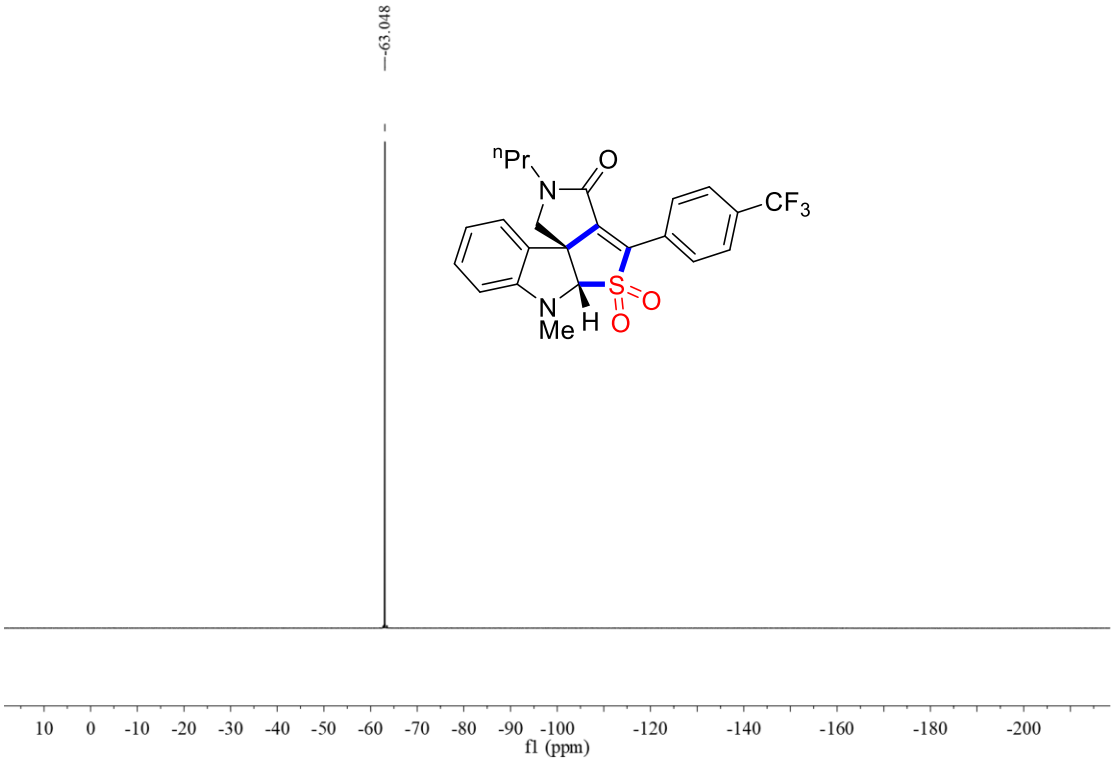



-132.736
-132.793
-136.112
-136.169
nPr
N
O
F
F
N
Me
H
S
O
O
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

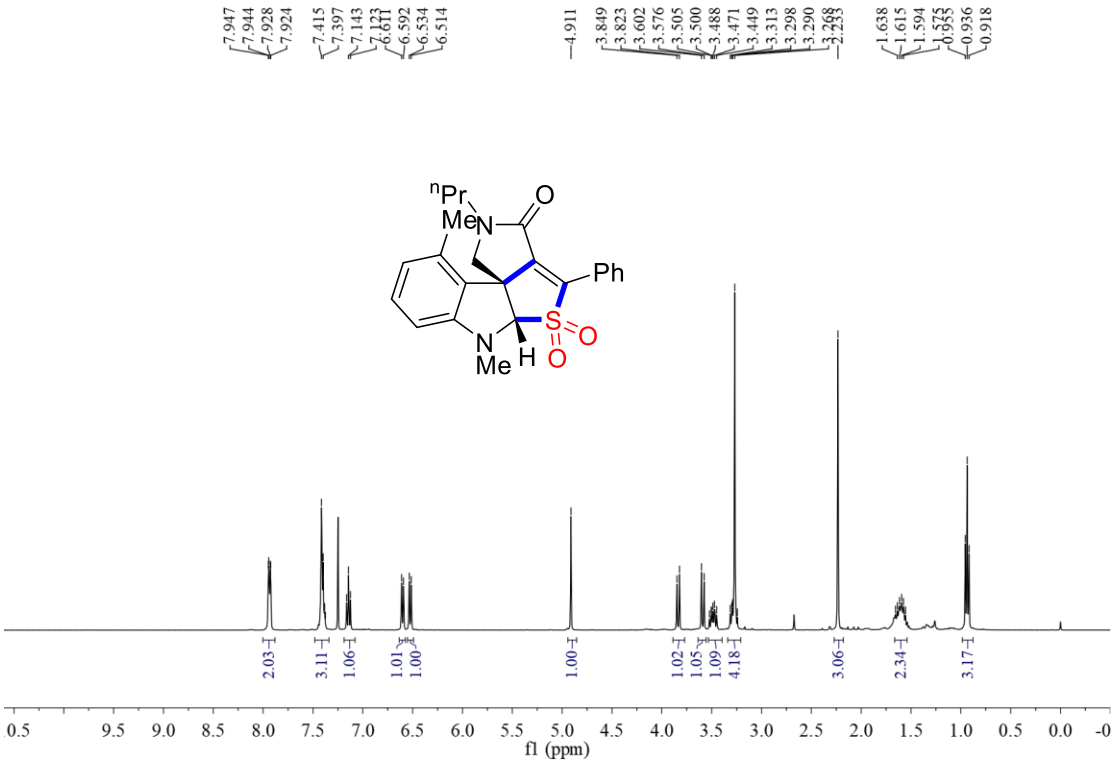
6-methyl-2-propyl-4-(4-(trifluoromethyl)phenyl)-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1k)

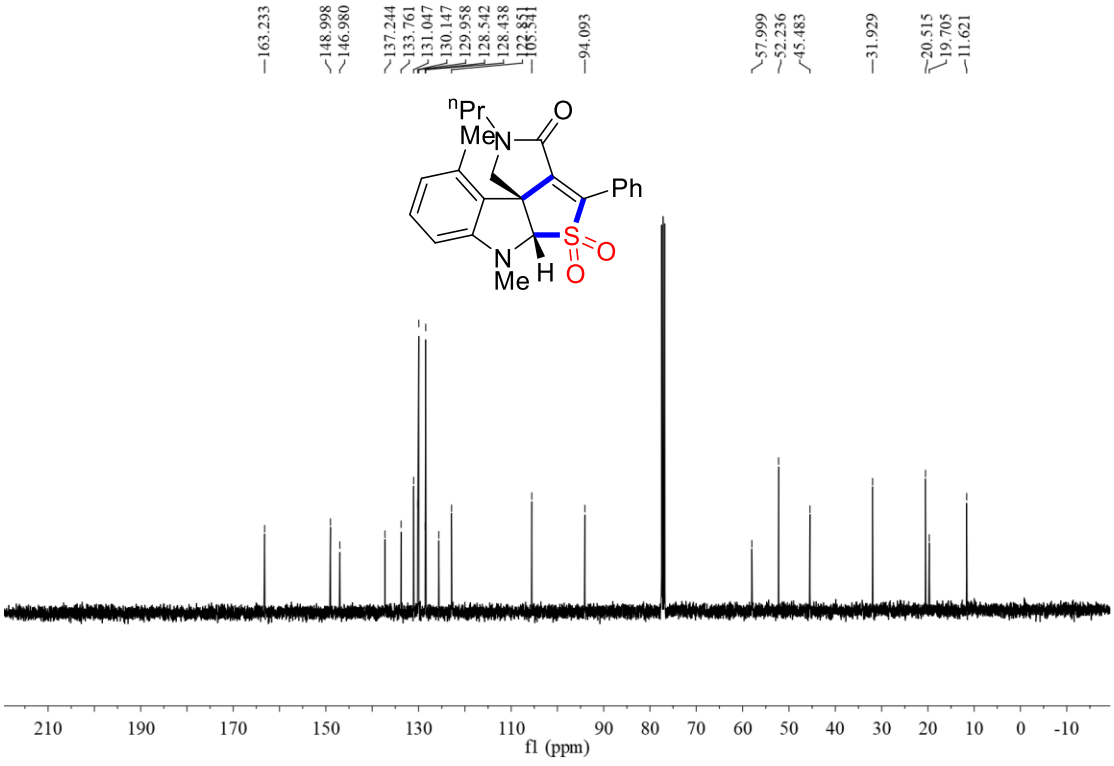




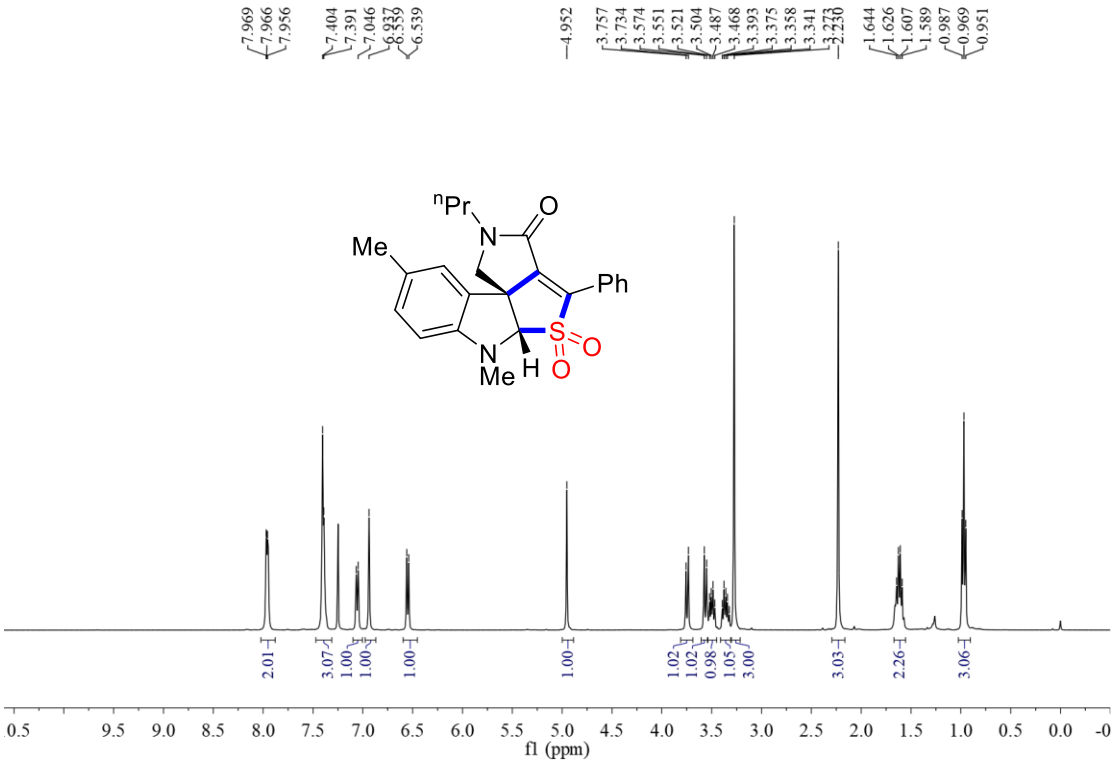

-63.048
nPr
N
O
CF3
S
O
O
N
Me
H
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

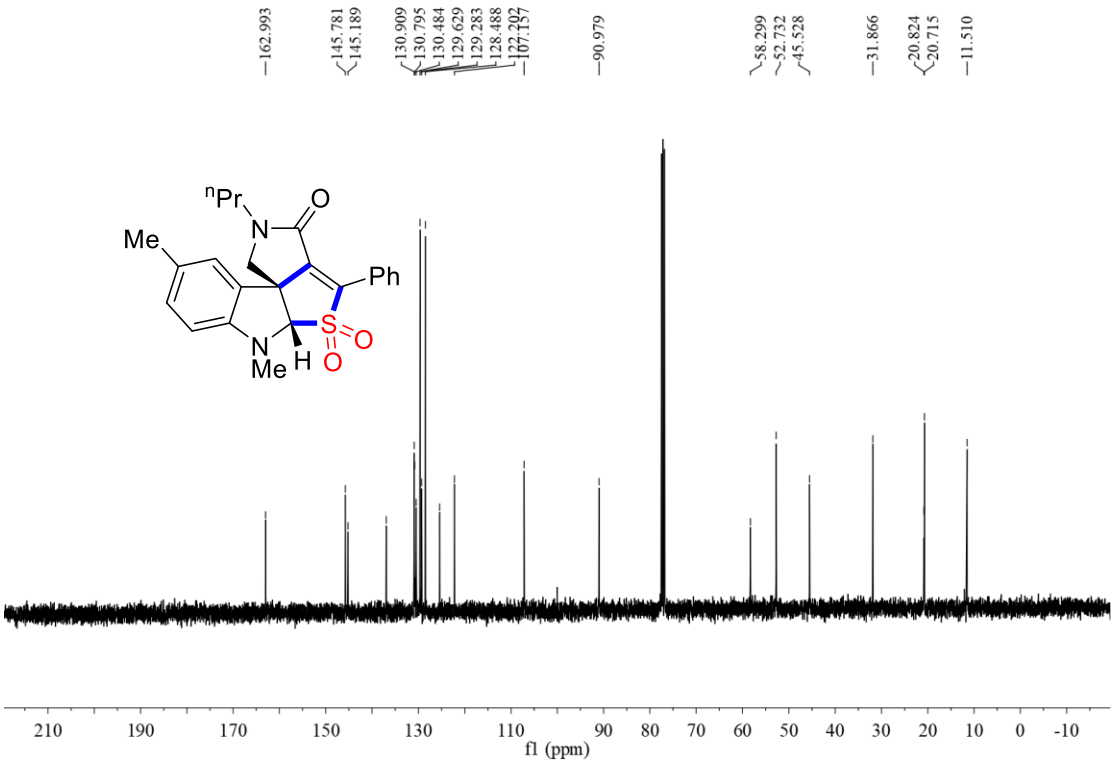
6,10-dimethyl-4-phenyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1n)



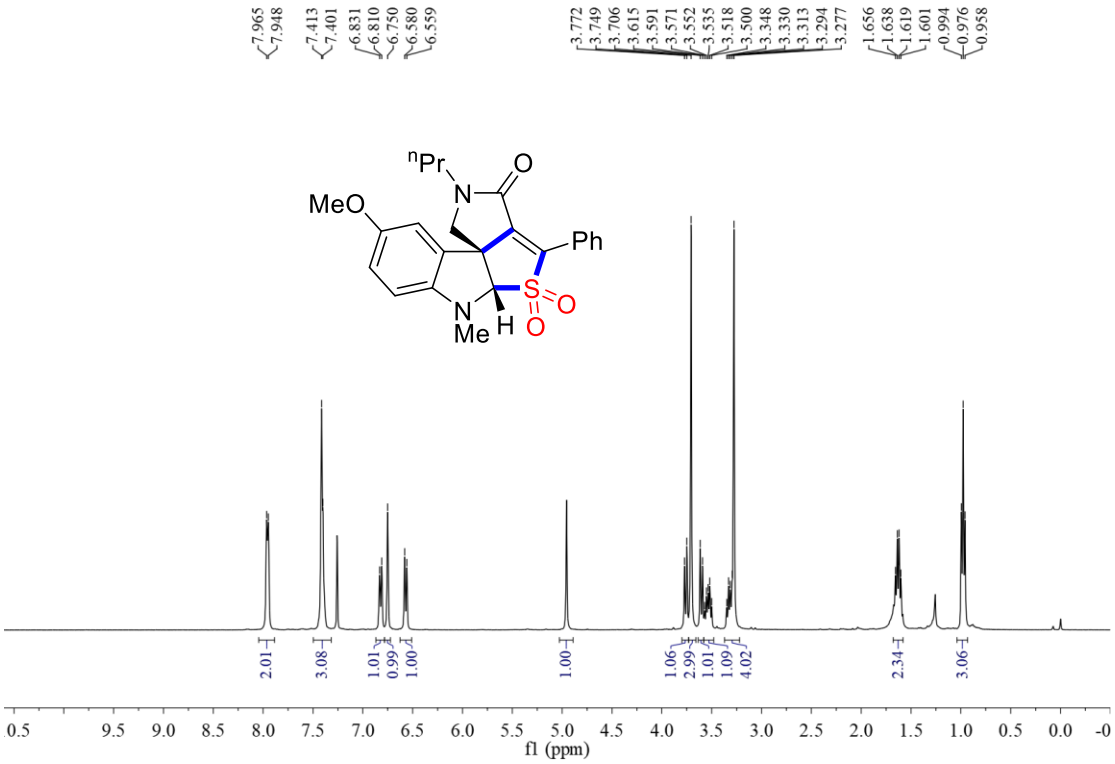


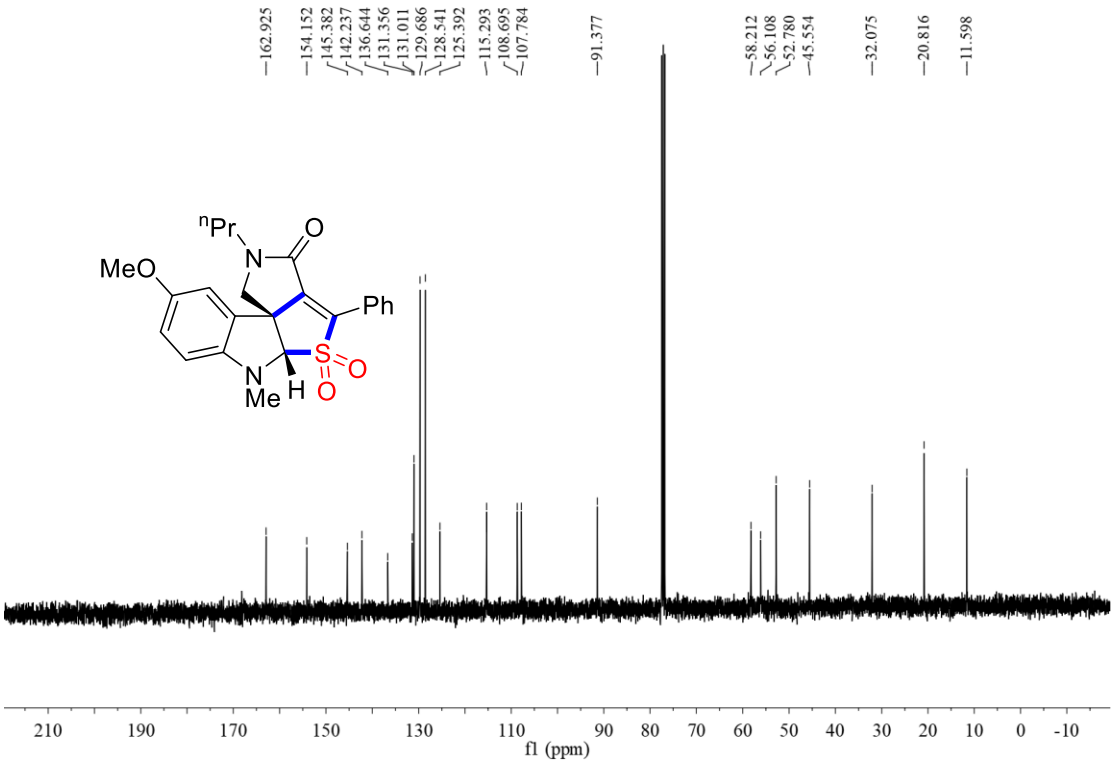
6,9-dimethyl-4-phenyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1q)



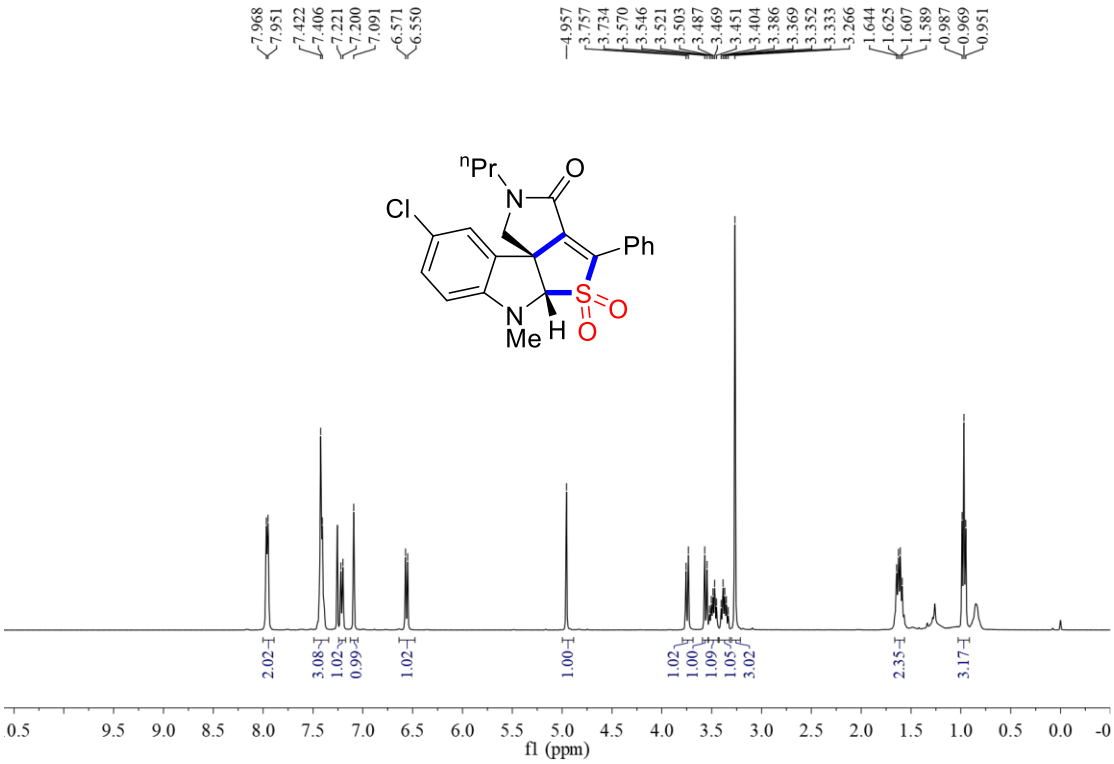


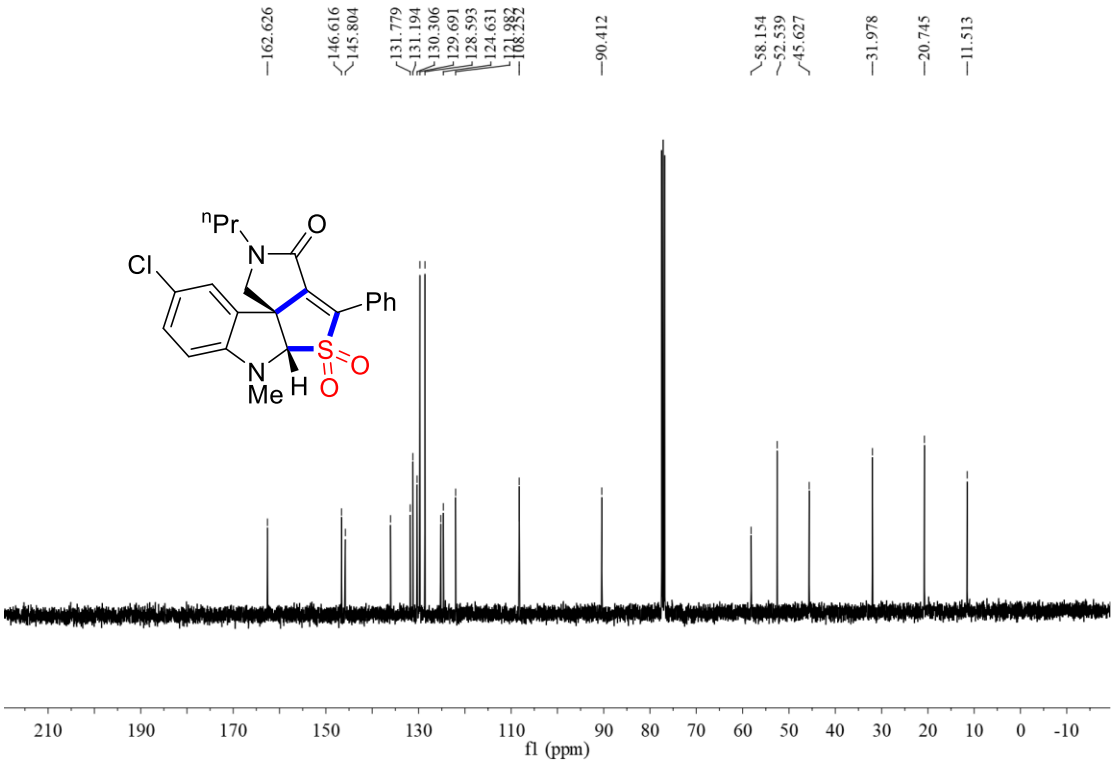
9-methoxy-6-methyl-4-phenyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1r) :



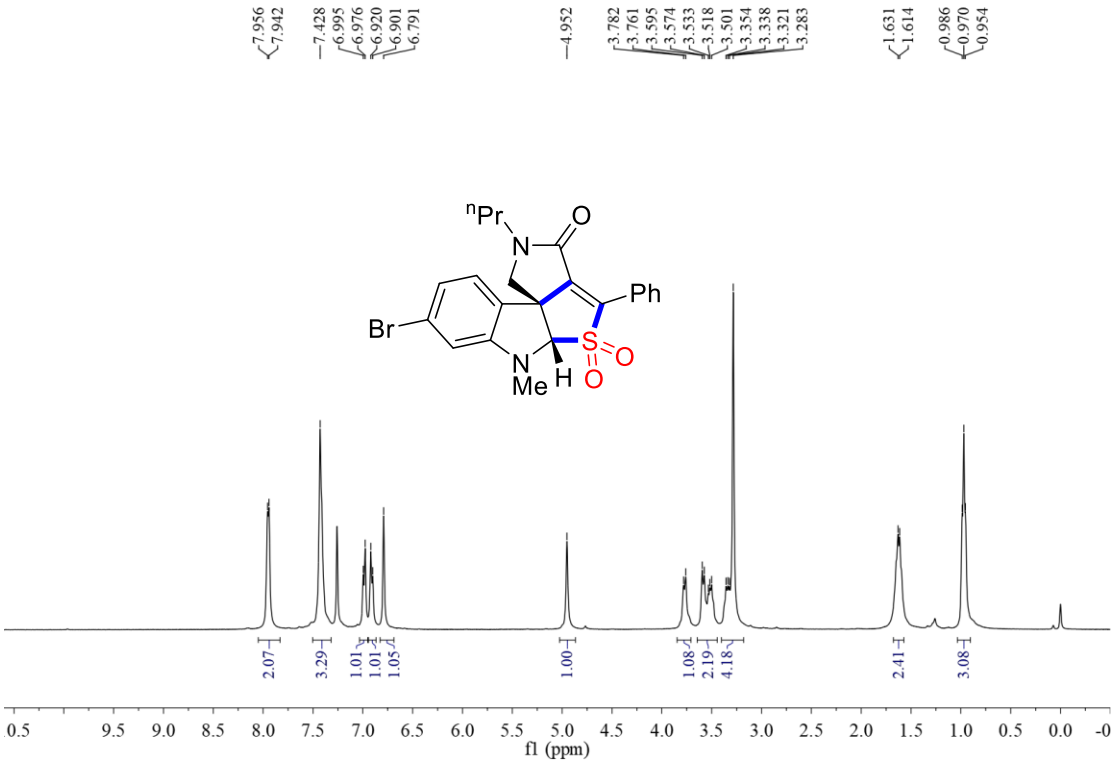


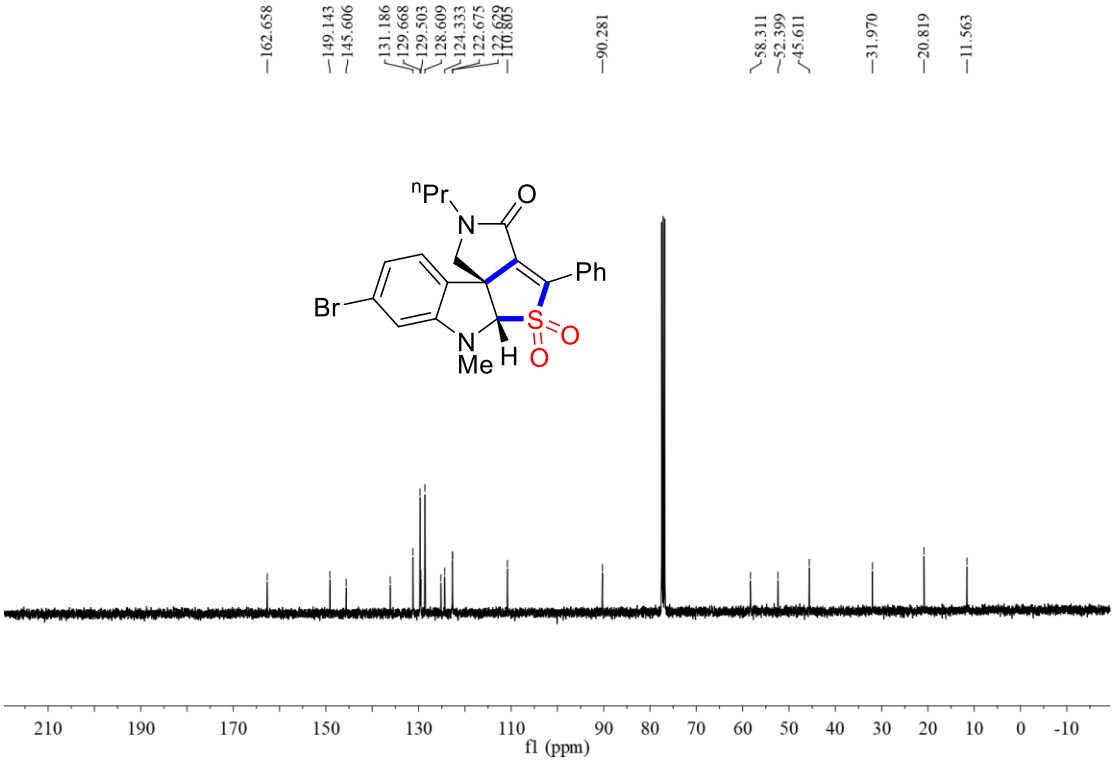
9-chloro-6-methyl-4-phenyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1s)



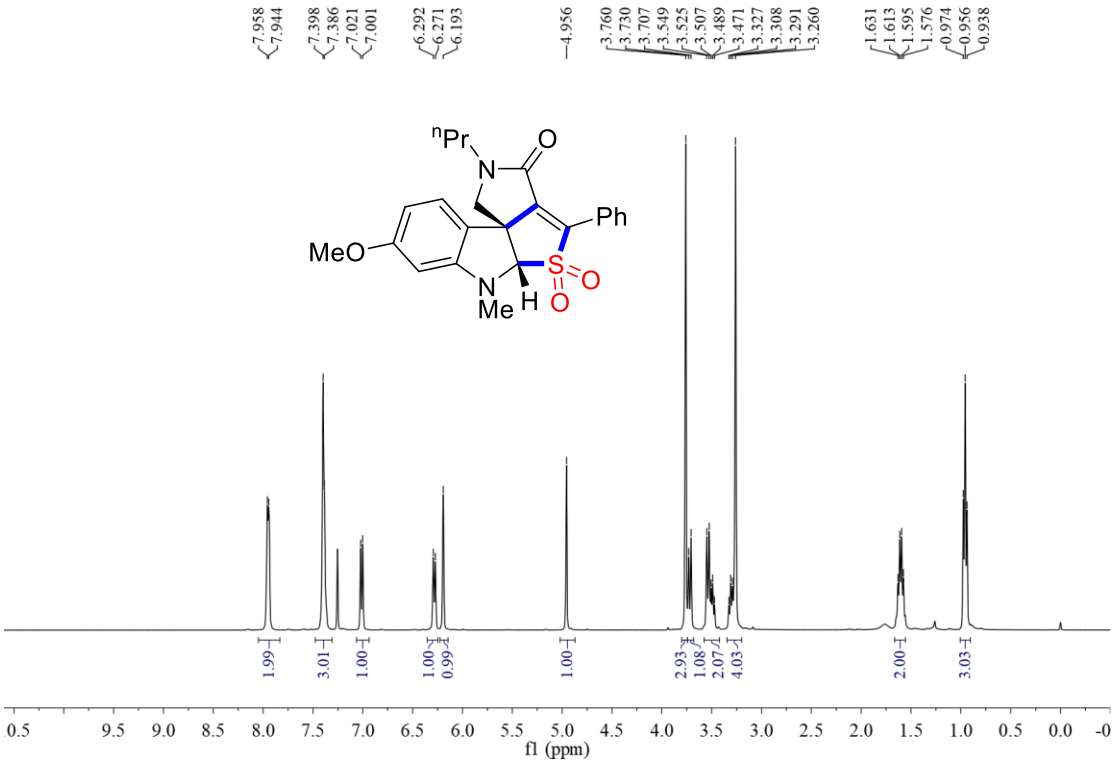


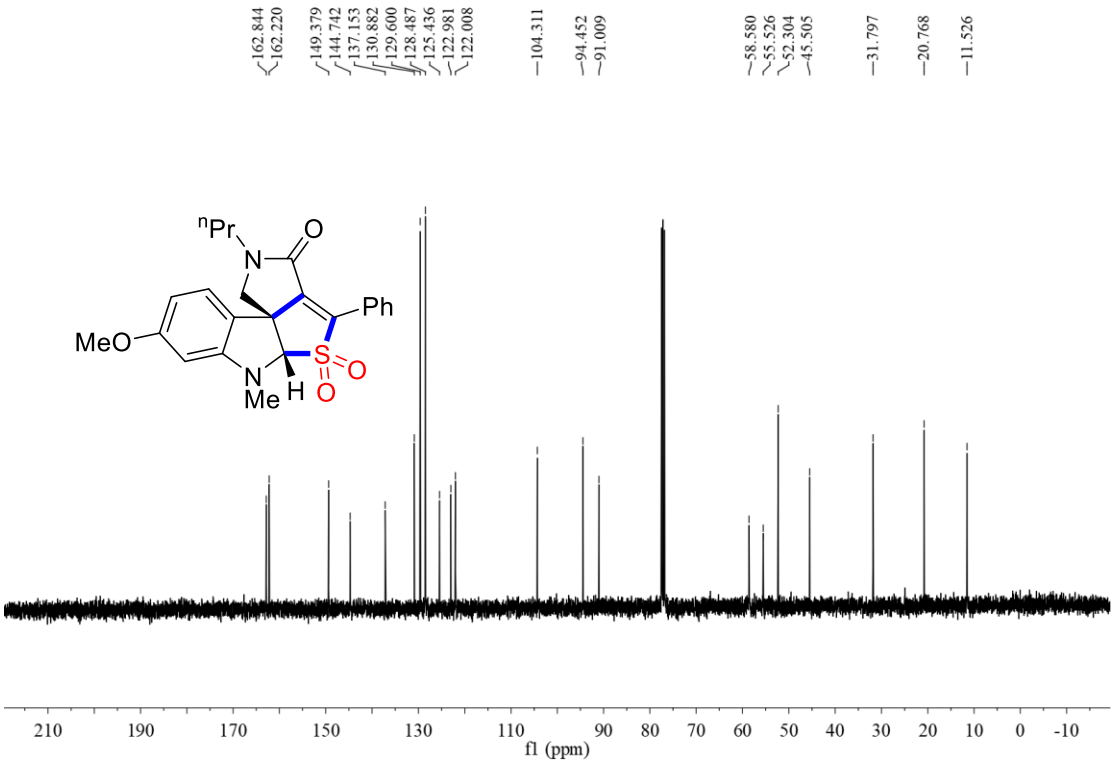
8-bromo-6-methyl-4-phenyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1t)



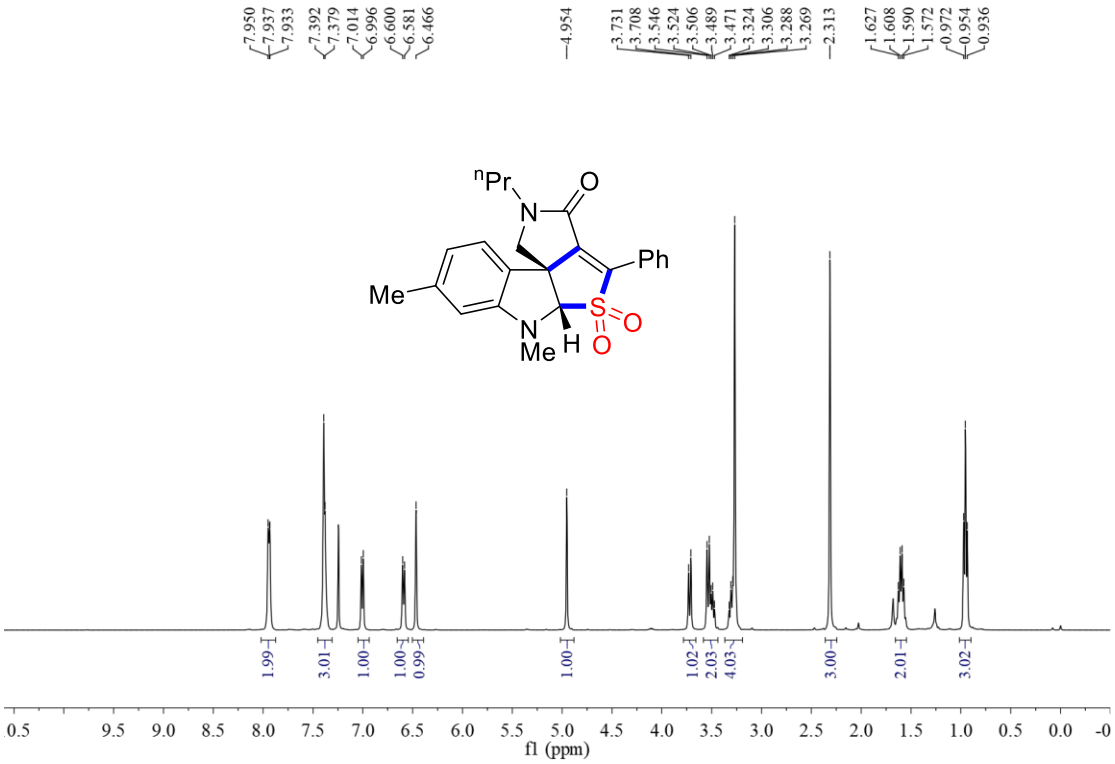


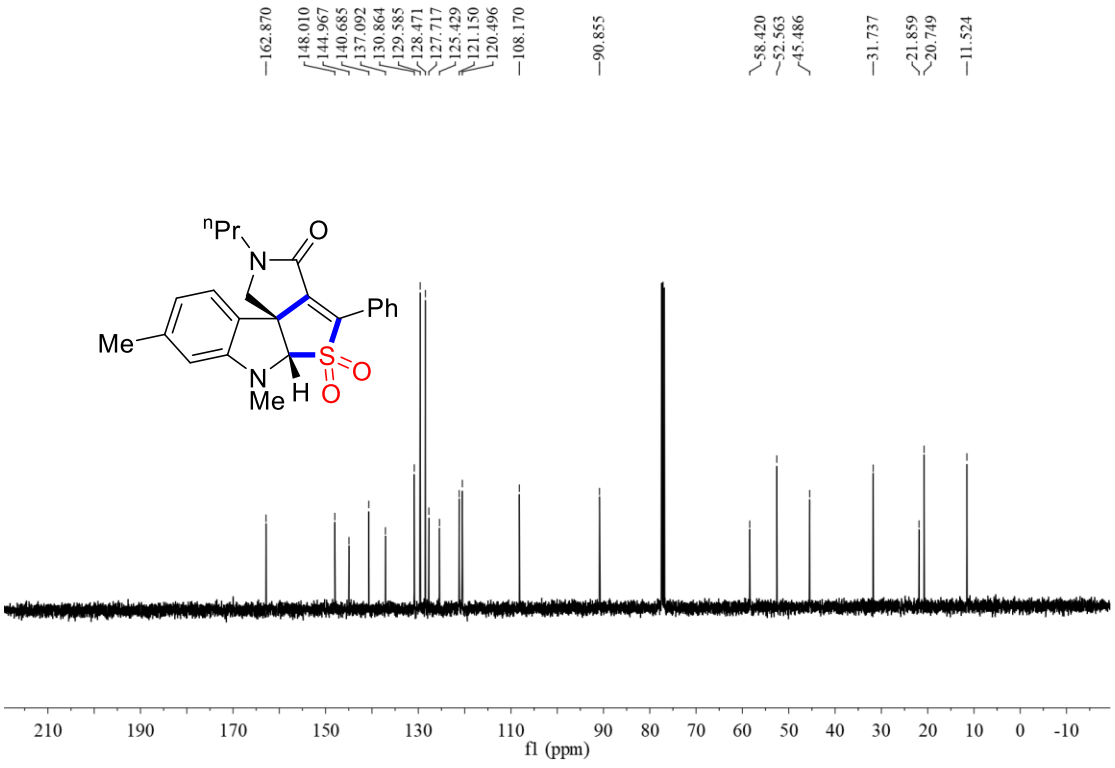
8-methoxy-6-methyl-4-phenyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1u)



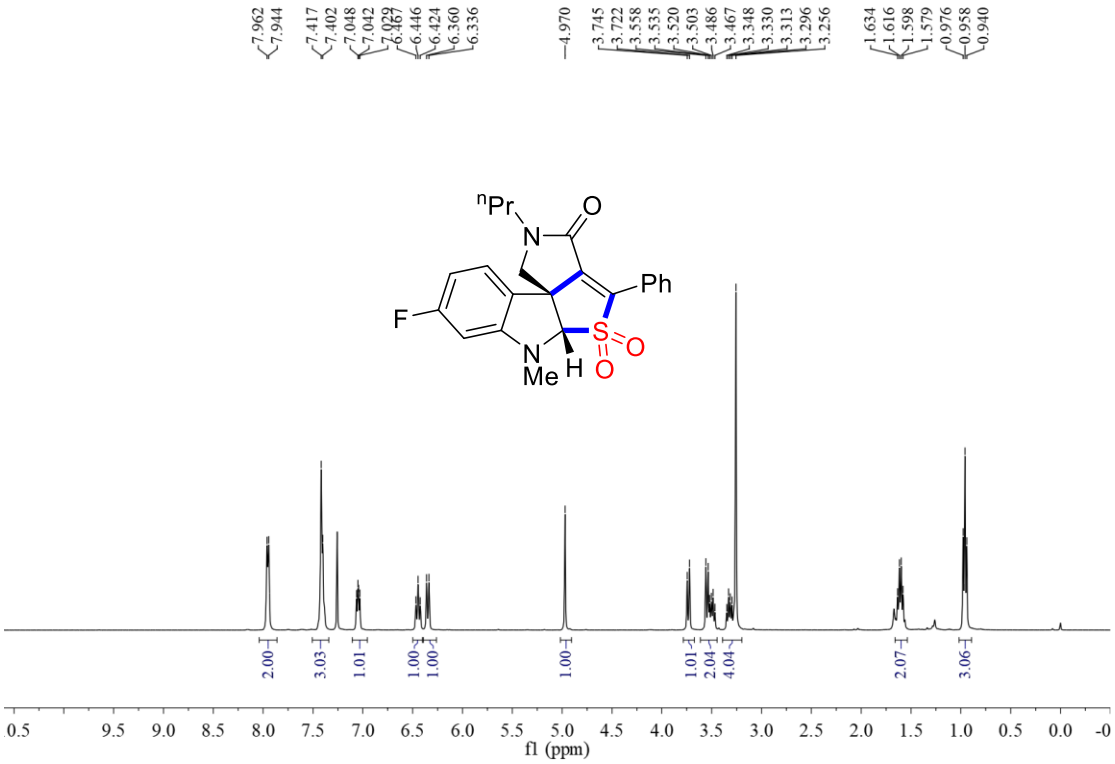


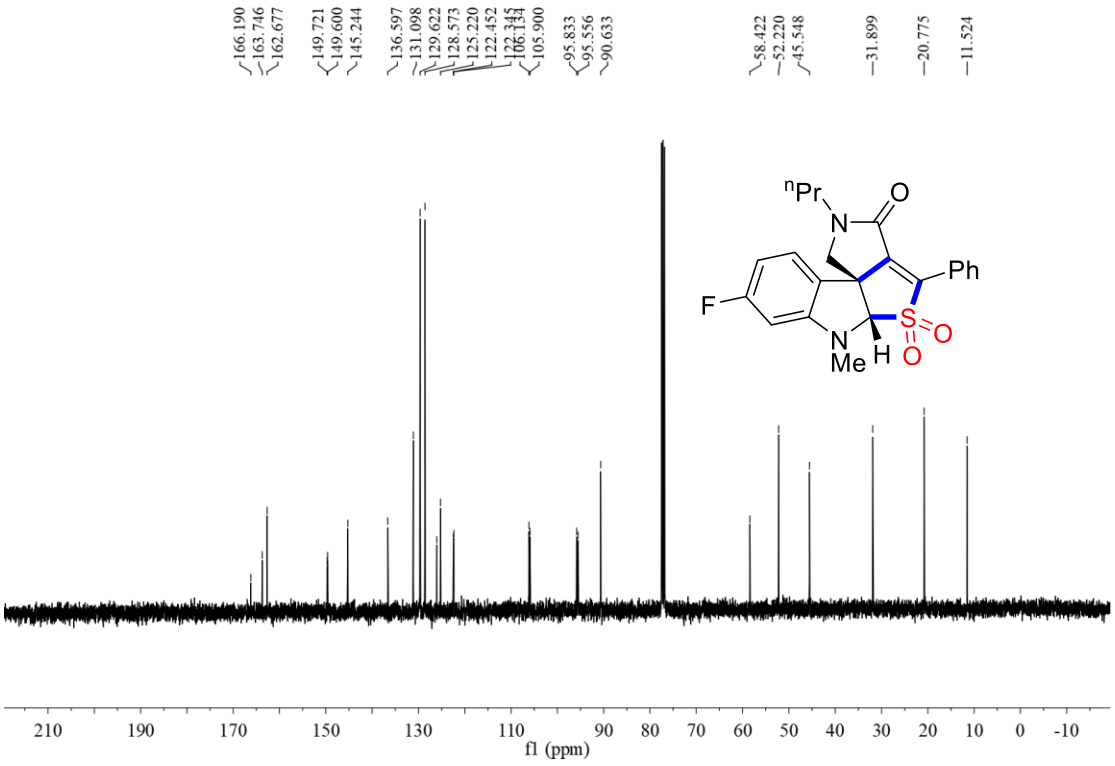
6,8-dimethyl-4-phenyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1v)

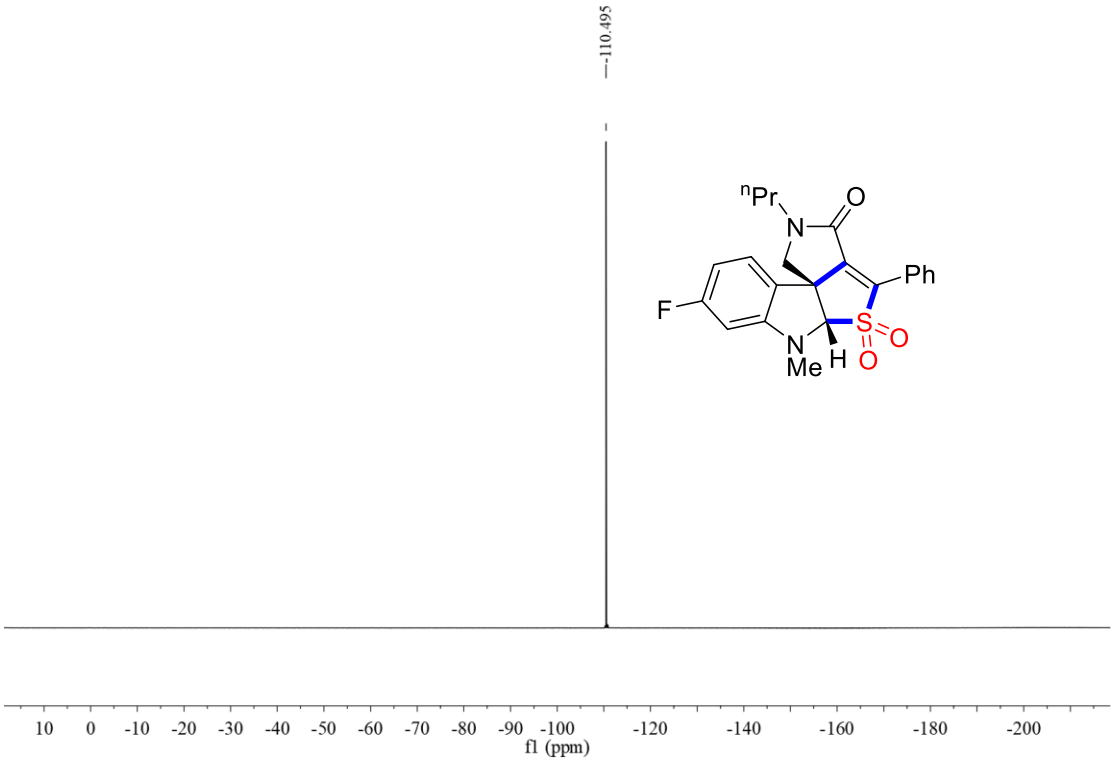




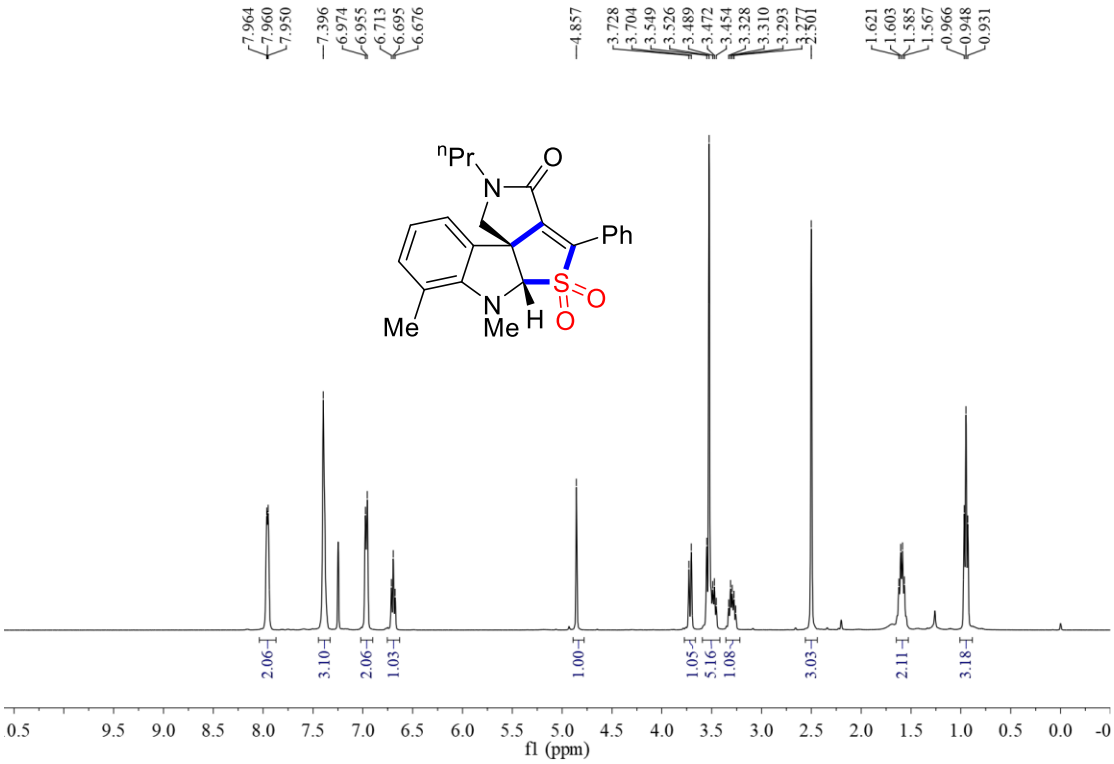
8-fluoro-6-methyl-4-phenyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1w)

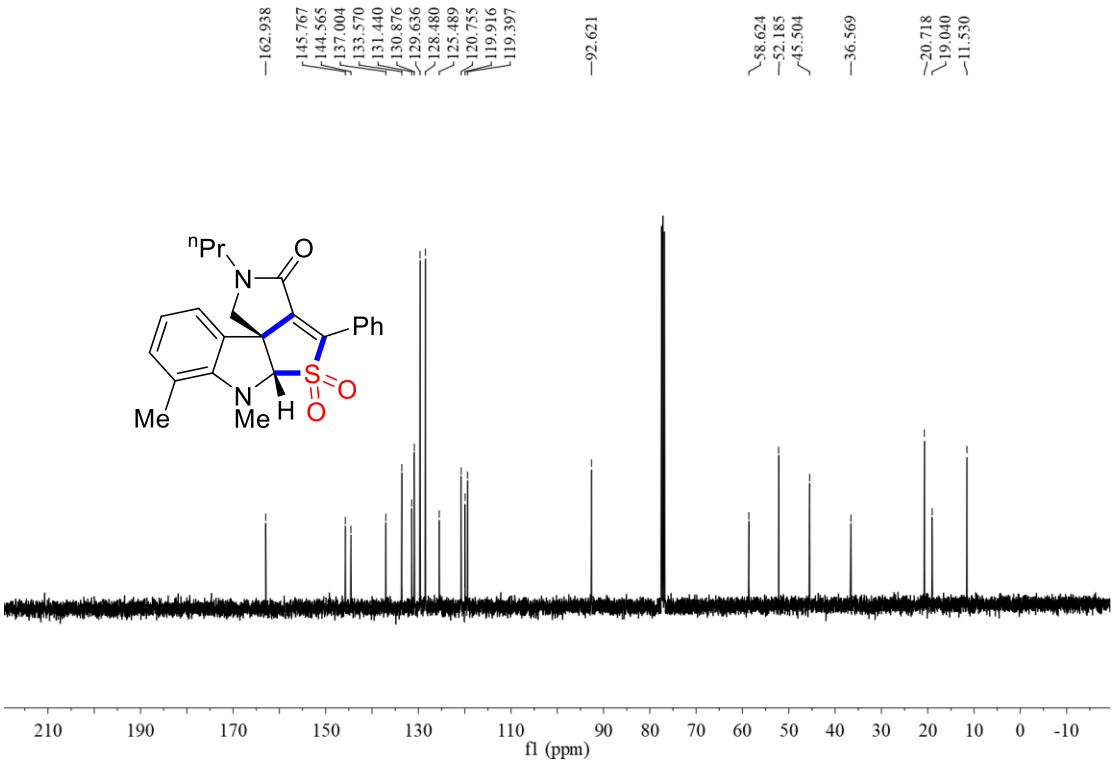




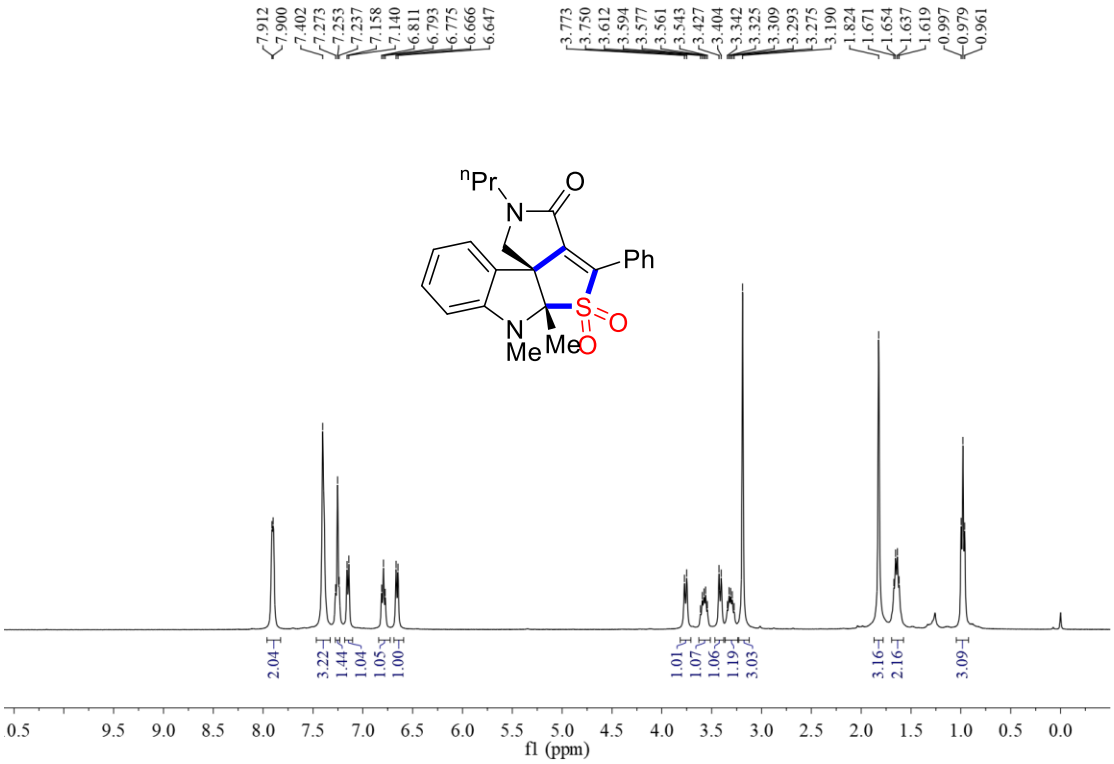

-110.495
nPr
N
O
Ph
F
S
O
N
Me
H
O
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

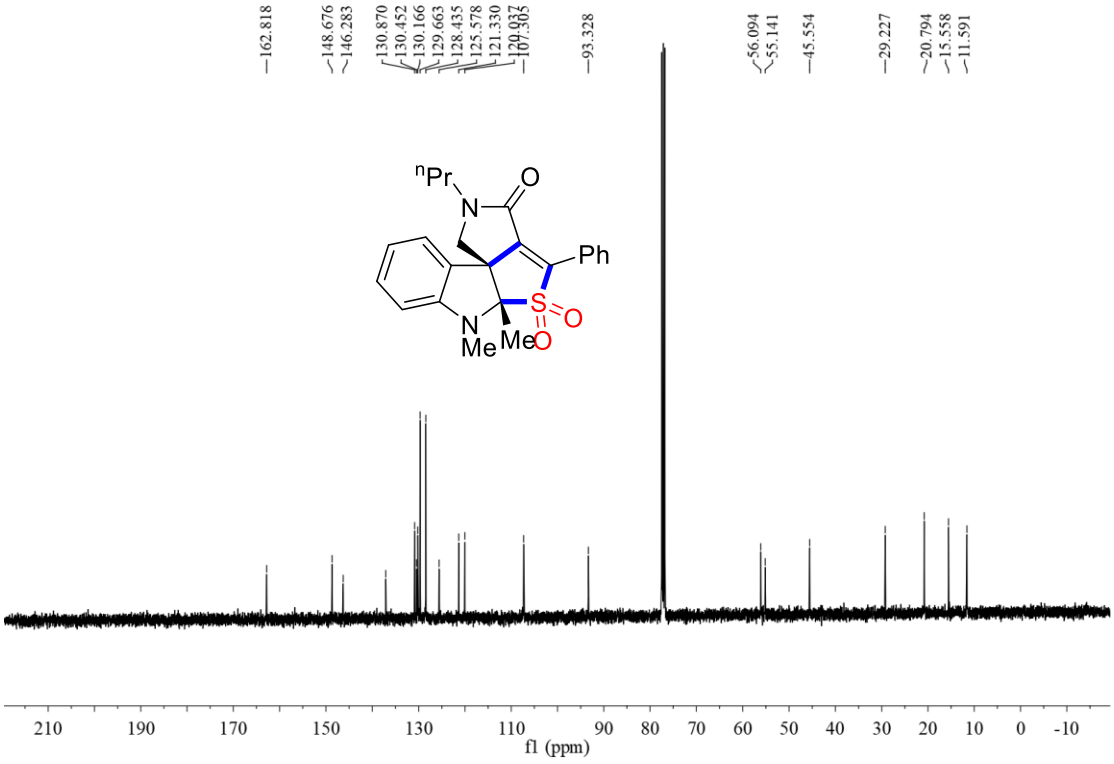
6,7-dimethyl-4-phenyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1x)



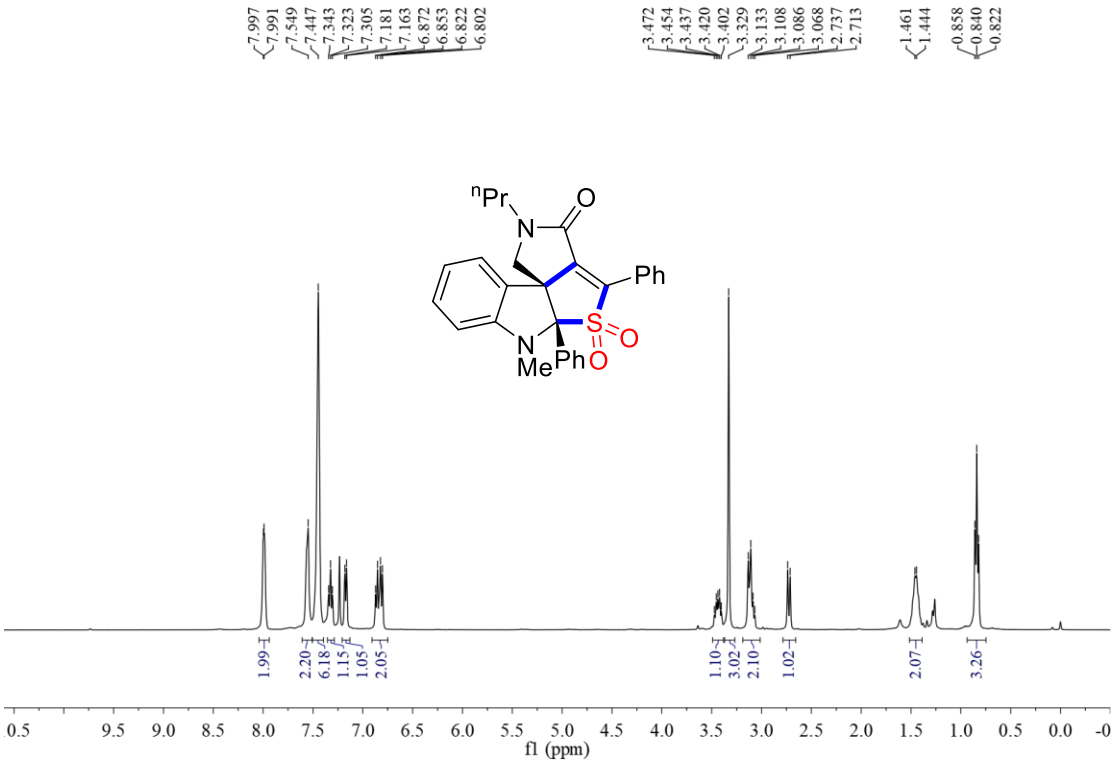


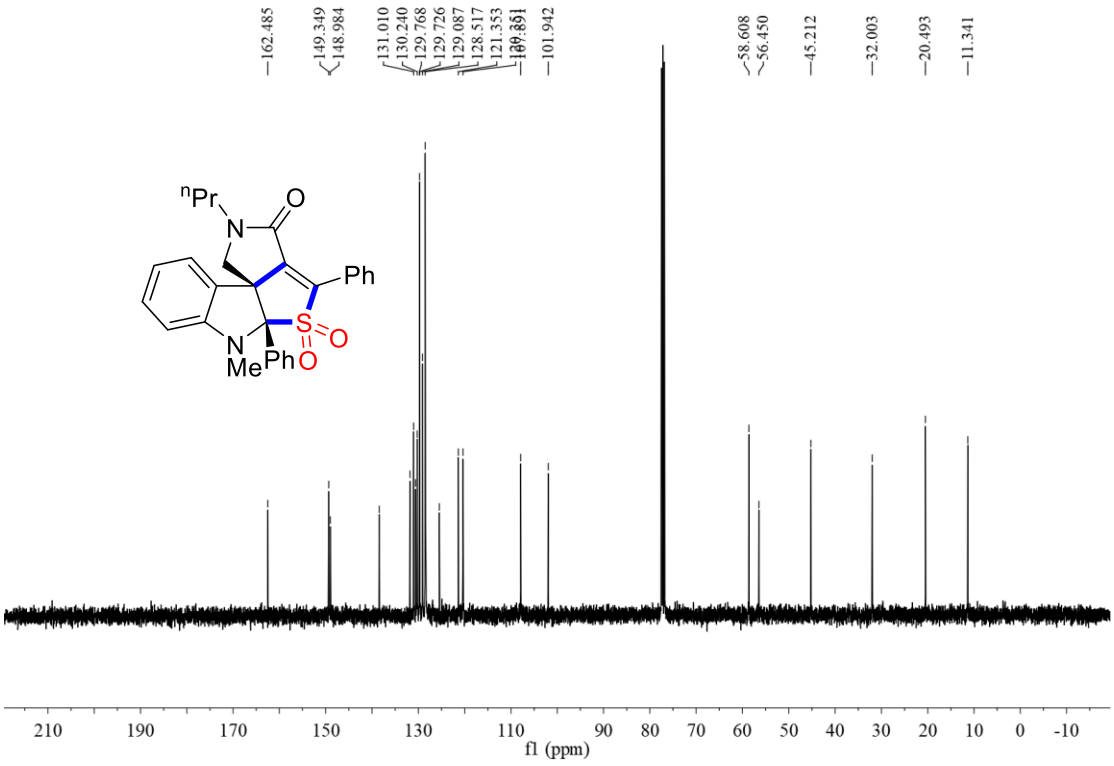
5a,6-dimethyl-4-phenyl-2-propyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1y)



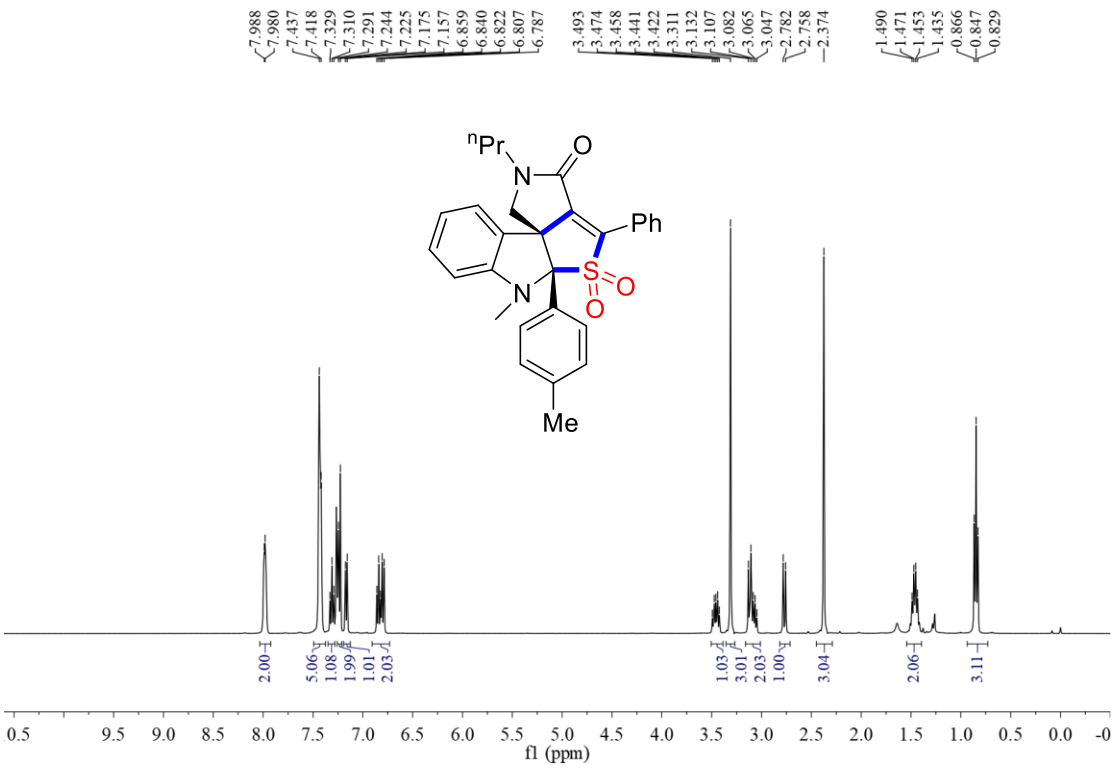


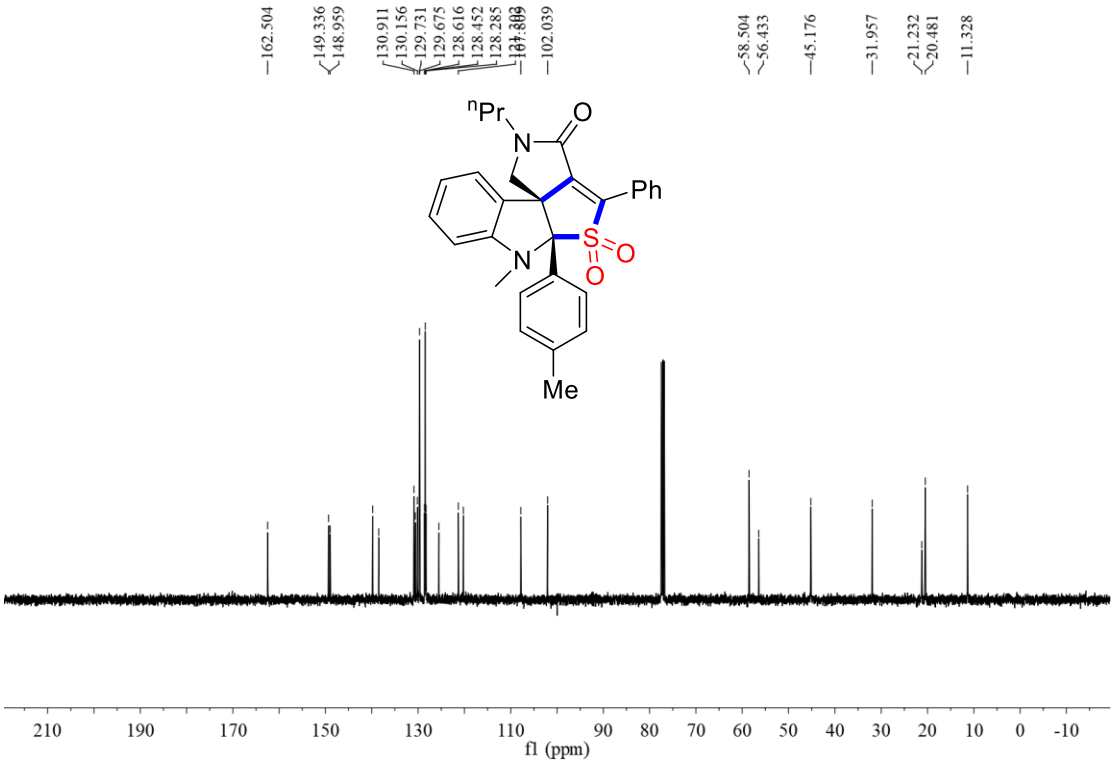
6-methyl-4,5a-diphenyl-2-propyl-1,2,5a,6-tetrahydro-3H-pyrrolo[3',4':3,4]thieno[2,3-b]indol-3-one 5,5-dioxide (1z):



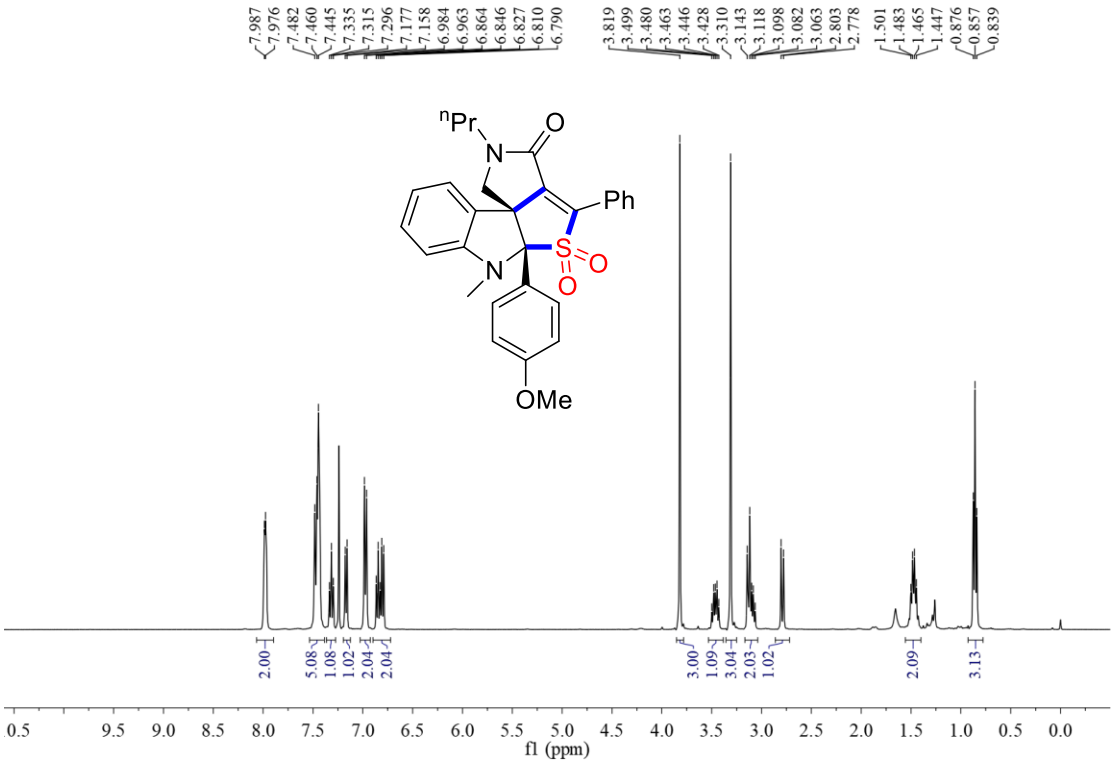


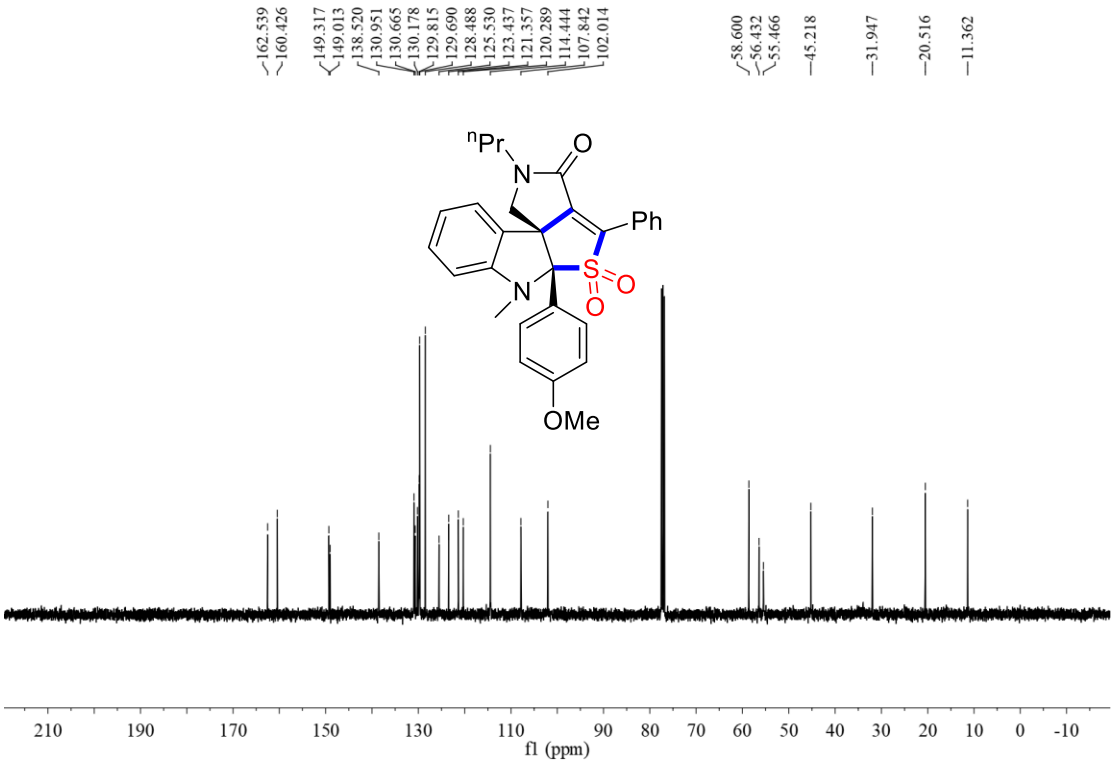
6-methyl-4-phenyl-2-propyl-5a-(p-tolyl)-1,2,5a,6-tetrahydro-3H-pyrrolo[3',4':3,4]thieno[2,3-b]indol-3-one 5,5-dioxide (1aa):



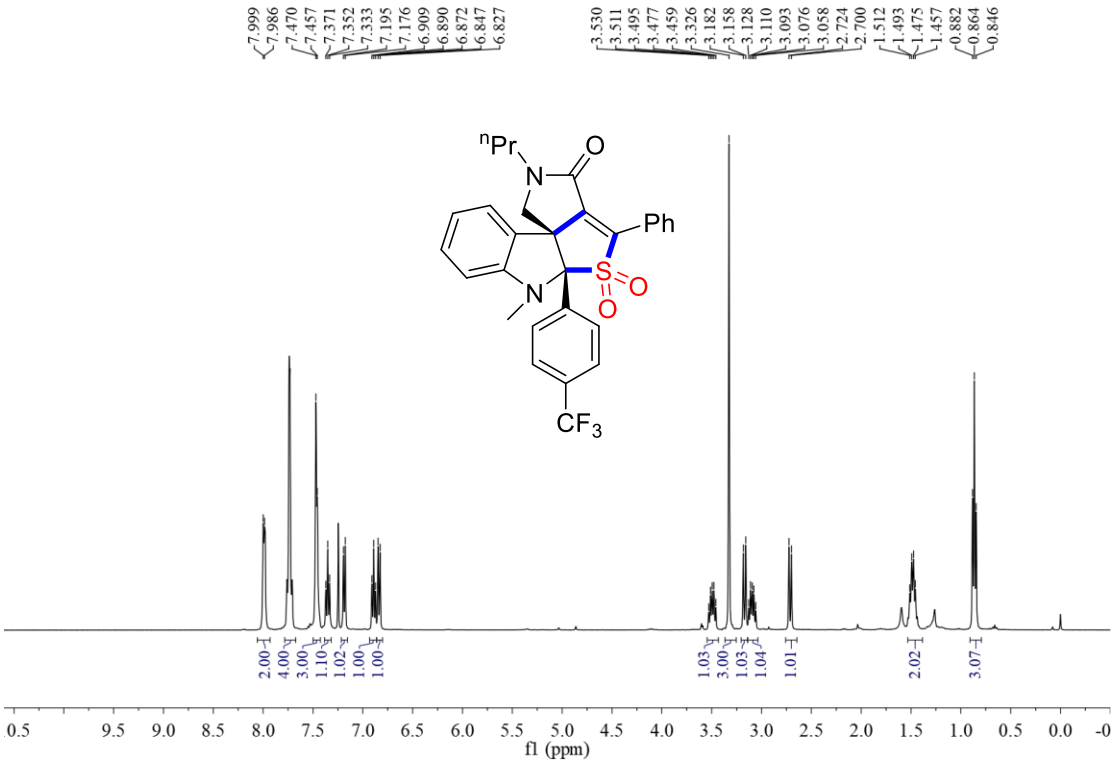


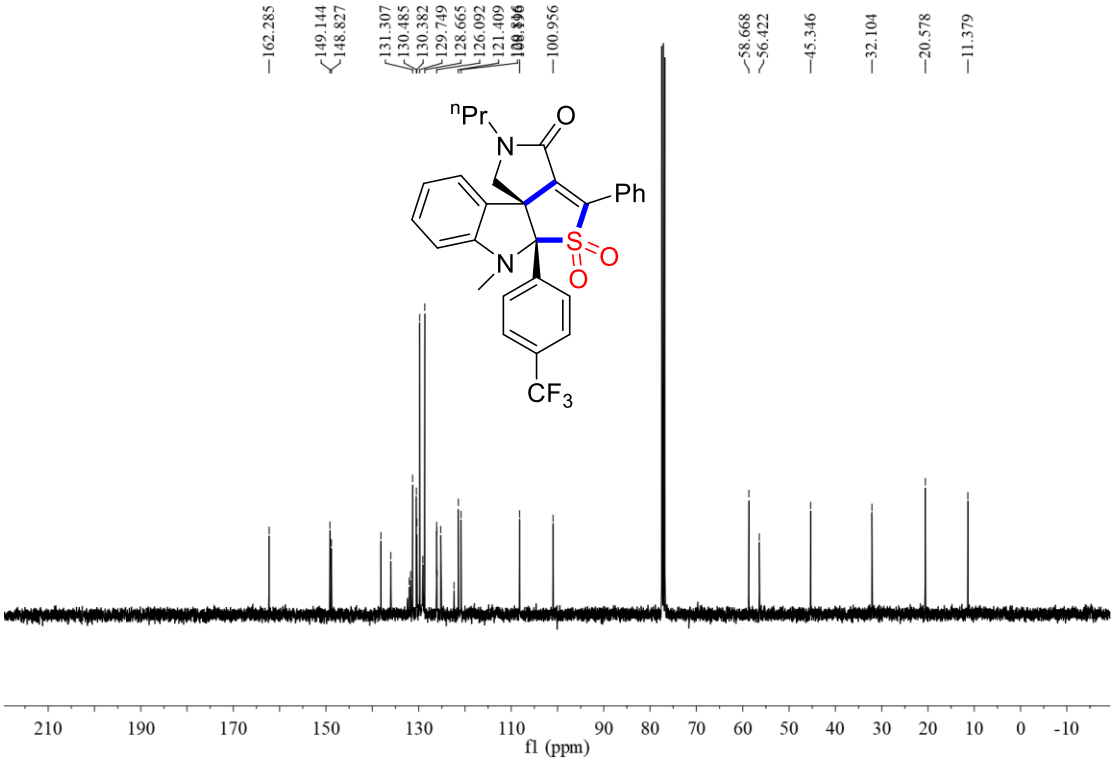
5a-(4-methoxyphenyl)-6-methyl-4-phenyl-2-propyl-1,2,5a,6-tetrahydro-3H-pyrrolo[3',4':3,4]thieno[2,3-b]indol-3-one 5,5-dioxide (1ab):

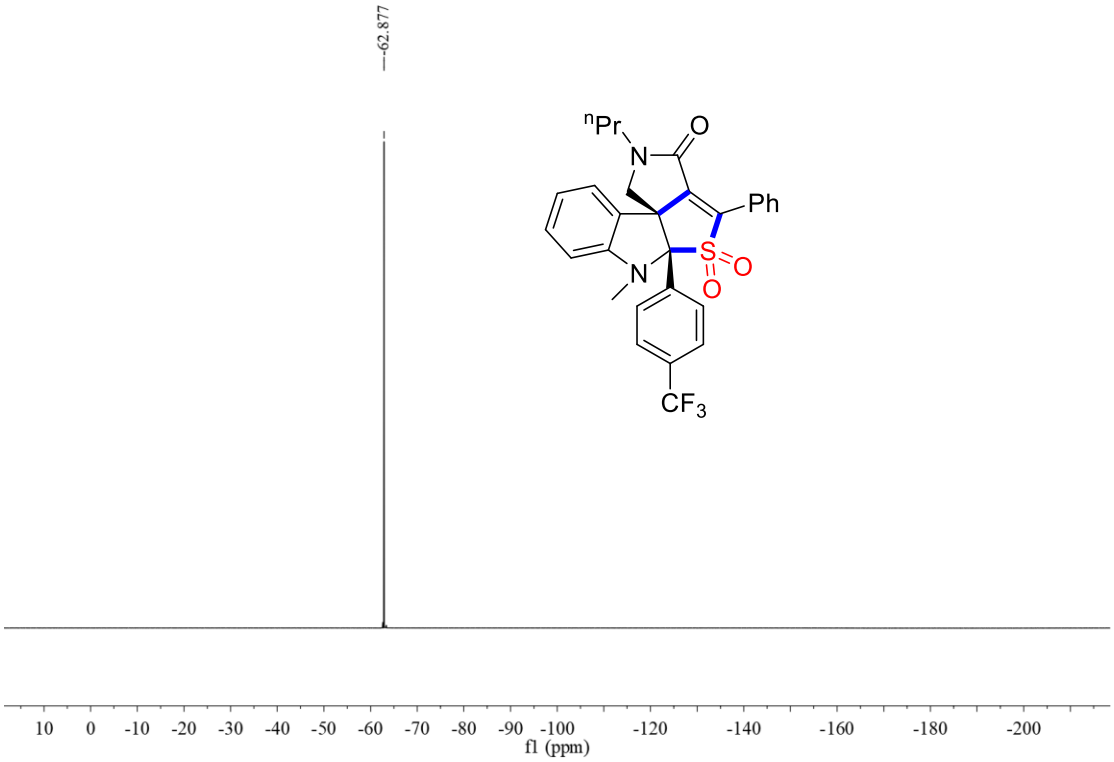




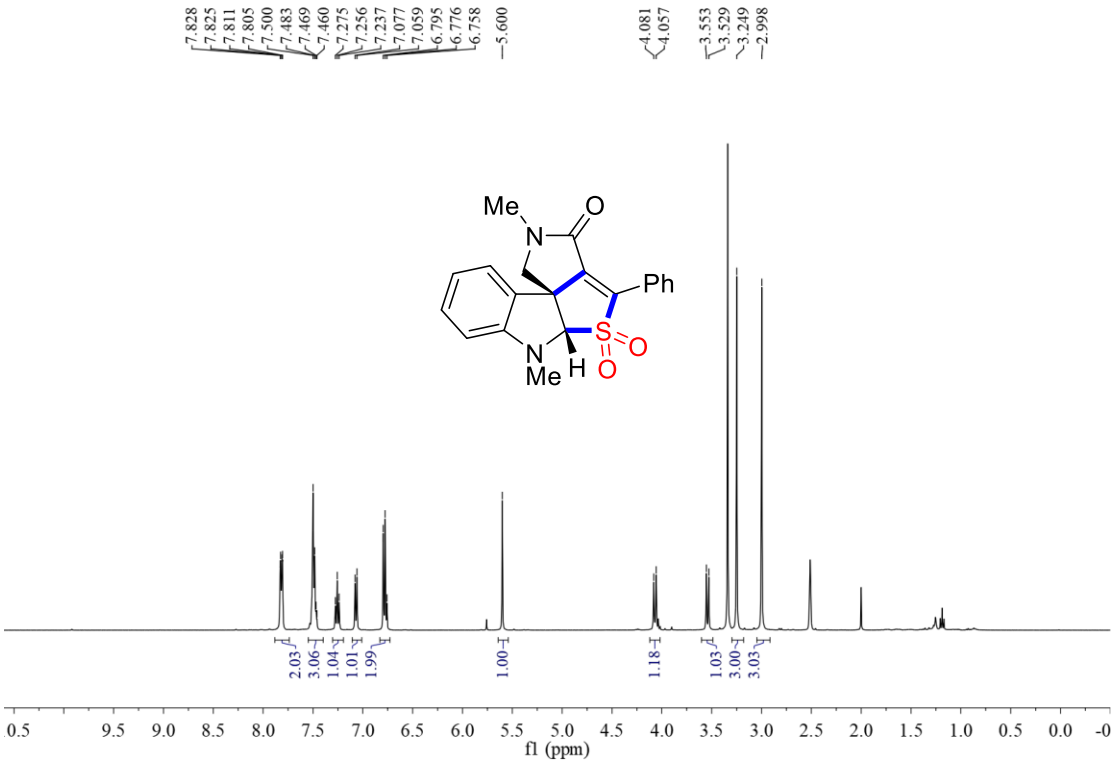
6-methyl-4-phenyl-2-propyl-5a-(4-(trifluoromethyl)phenyl)-1,2,5a,6-tetrahydro-3H-pyrrolo[3',4':3,4]thieno[2,3-b]indol-3-one 5,5-dioxide (1ac):

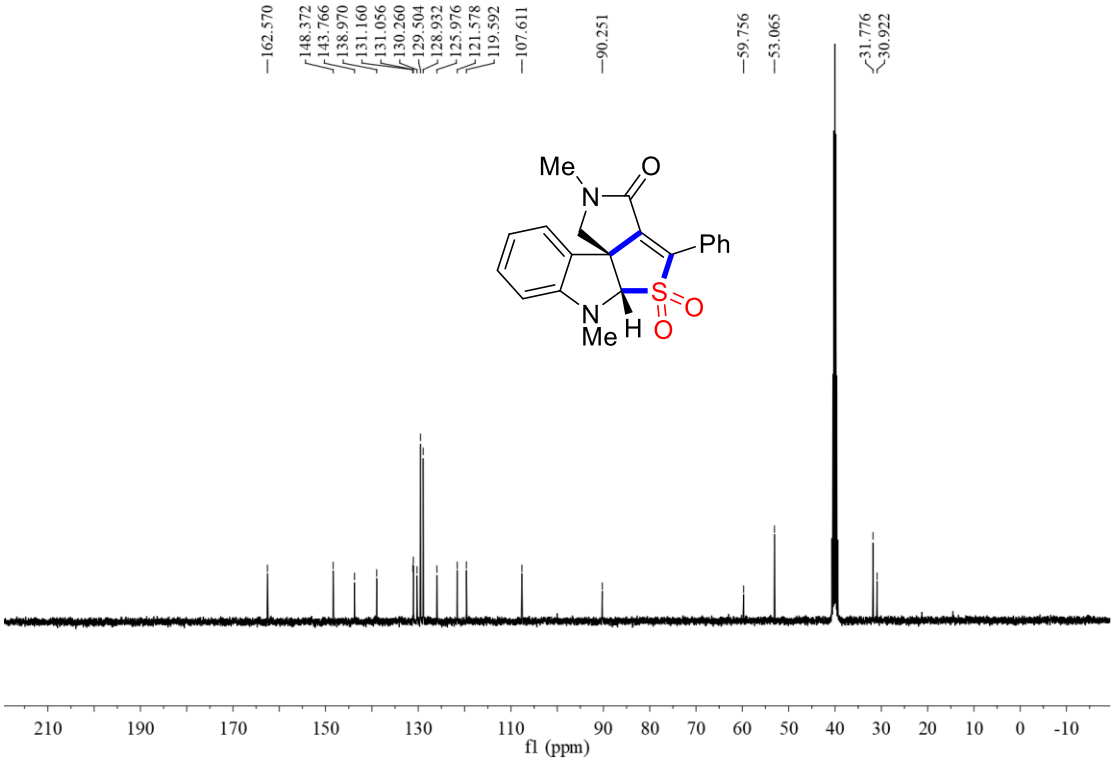




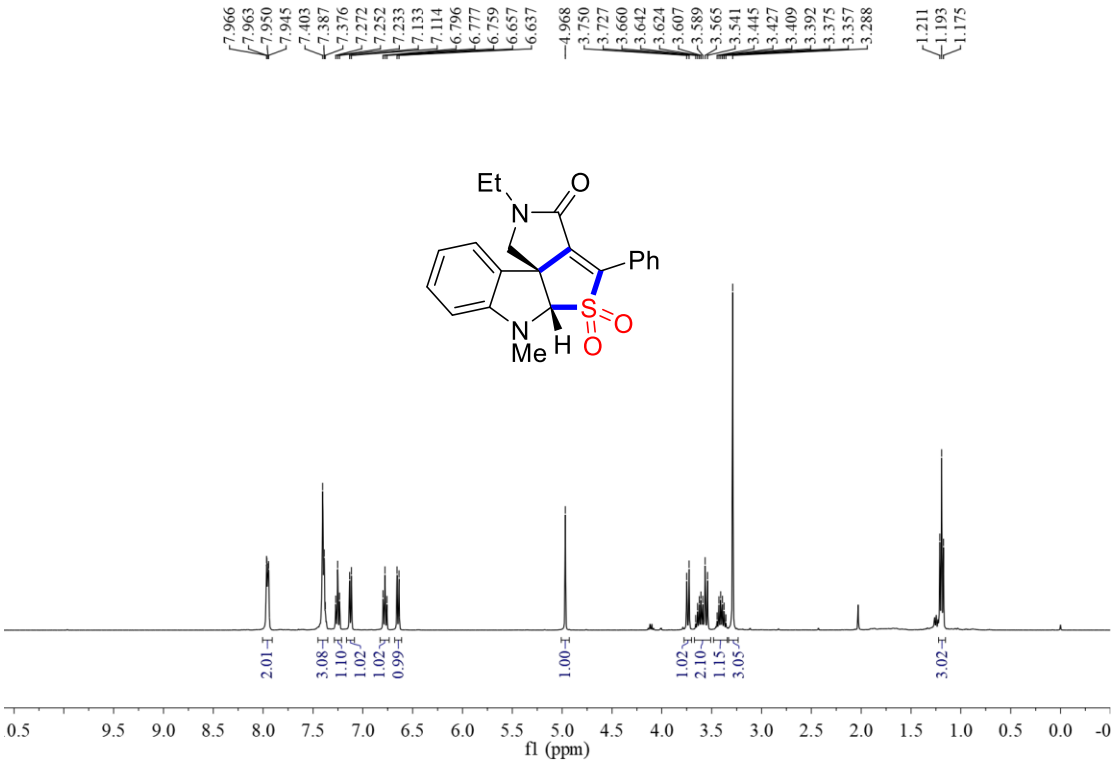

-62.877
nPr
N
O
Ph
S
O
O
N
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

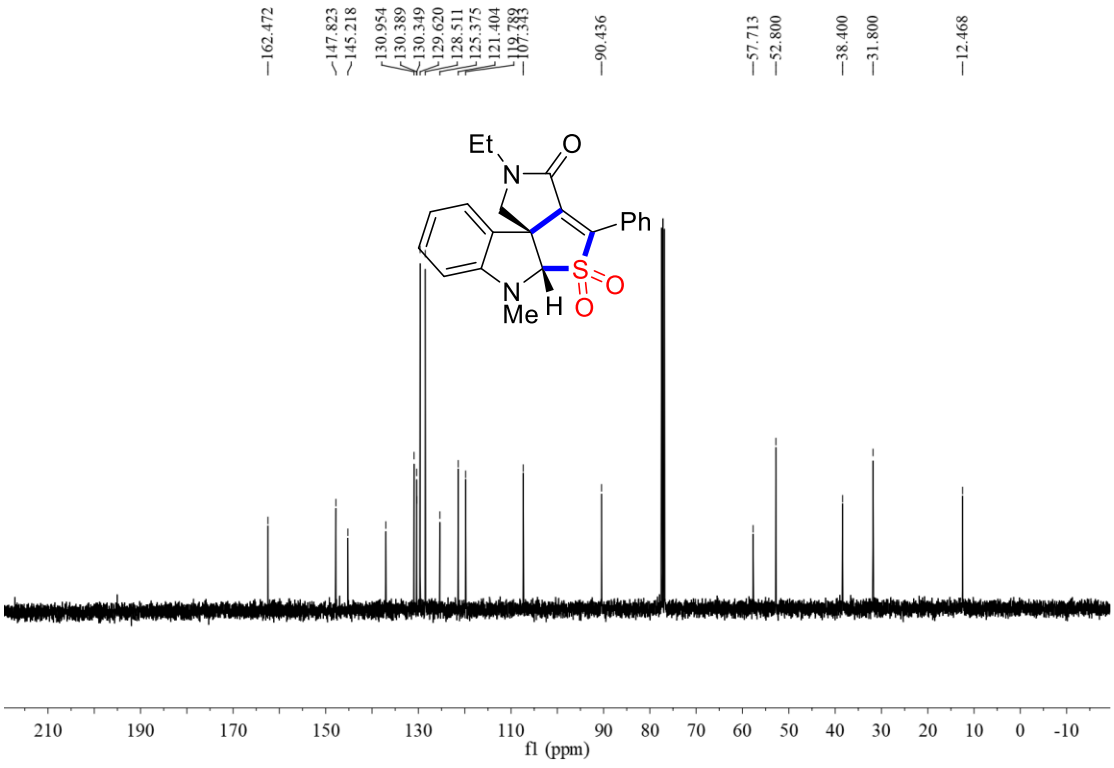
2,6-dimethyl-4-phenyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1ad):





2-ethyl-6-methyl-4-phenyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1ae)





2-benzyl-6-methyl-4-phenyl-1,2,5a,6-tetrahydro-3*H*-pyrrolo[3',4':3,4]thieno[2,3-*b*]indol-3-one 5,5-dioxide (1af) :