Synthesis of triazole fused tetracyclic spirooxindole derivatives via metal-free Huisgen cycloaddition

Sandip Maiti, Nabin Parui, Joydev Halder and Jyotirmayee Dash*
School of Chemical Sciences, Indian Association for the Cultivation of Science, Kolkata 700032, India
Correspondence should be addressed to J.D. (ocjd@iacs.res.in)

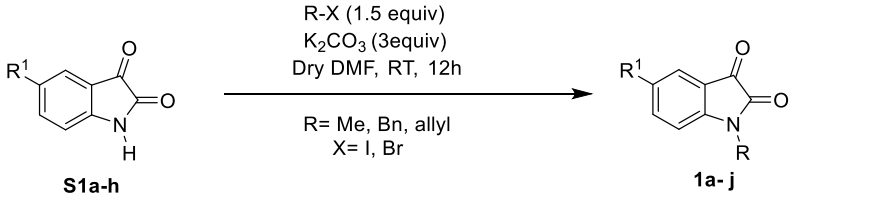
Contents

1.0 General information

All solvents and reagents were purified by standard techniques as reported in Armarego, W. L. F., Chai, C. L. L., Purification of Laboratory Chemicals, 5th edition, Elsevier, 2003; or used as supplied from commercial sources (Sigma-Aldrich Corporation® unless stated otherwise). All reactions were generally carried out under inert atmosphere unless otherwise noted. TLC was performed on Merck Kieselgel 60 F254 plates, and spots were visualized under UV light. Products were purified by column chromatography on silica gel (100-200 mesh, Merck). ^{1}H and ^{13}C NMR spectra were recorded on either Brüker AVANCE 600 (600 MHz and 175 MHz) Brüker AVANCE 400 (400 MHz and 100 MHz), Brüker AVANCE 500 (500 MHz and 125 MHz) or Brüker AVANCE 300 (300 MHz and 75 MHz) instruments using deuterated solvents as detailed and at ambient probe temperature (300 K). Chemical shifts are reported in parts per million (ppm) and are referred to the residual solvent peak. Chemical shifts are reported in parts per million (ppm) relative to the residual solvent peak ($CDCl_3$, 7.26 ppm for ^{1}H NMR and 77.2 ppm for ^{13}C NMR; DMSO-d_6, 2.50 ppm for ^{1}H NMR, 39.6 ppm for ^{13}C NMR). The following notations are used: singlet (s); doublet (d); triplet (t); quartet (q); multiplet (m); broad (br). Coupling constants are quoted in Hertz and are denoted as J. Mass spectra were recorded on a Micromass® Q-Tof (ESI) spectrometer. Single Crystal XRD was recorded on Bruker D8VENTURE Micro-focus diffractometer equipped with PHOTON II Detector. IR Spectrum was recorded in a Perkin Elmer Spectrum Version 10.5.3 instrument.

2.0 Synthesis of N-protected isatins 1a-j:

N-alkylated isatin derivatives **1a-j** were prepared using reported procedures[1] from commercially available isatins **S1**. Isatin derivatives **S1** were stirred with different alkyl halides in the presence of K_2CO_3 in DMF at room temperature for 12 h (**Scheme S1**).



S1a; R^1= H
S1b; R^1= Me
S1c; R^1= 5,7-Me
S1d; R^1= OMe
S1e; R^1= OCF_3
S1f; R^1= Cl
S1g; R^1= 6-Cl
S1h; R^1= 7-F

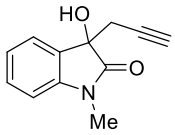
1a; R^1= H, R= Me; 90%
1b; R^1= H, R= Bn; 95%
1c; R^1= H, R= allyl; 92%
1d; R^1= Me, R= Bn; 85%
1e; R^1= 5,7-Me, R= Me; 83%
1f; R^1= OMe, R= Bn; 90%
1g; R^1= OCF_3, R= Bn; 86%
1h; R^1= Cl, R= Me; 85%
1i; R^1= 6-Cl, R= Me; 87%
1j; R^1= 7-F, R= Me; 82%

Scheme S1. Synthesis of N-protected isatins **1a-j**.

3.0 General procedure for the synthesis of 3-substituted 3-hydroxyindolin-2-ones 2a-k (GP-1)[2]:

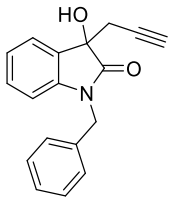
Propargyl bromide (6 mmol, 3 equiv.) was added to a well-stirred suspension of the corresponding N-protected 2, 3-indolinediones **1a-k** (2 mmol, 1 equiv.), zinc powder (12 mmol, 6 equiv.), and hafnium (IV) chloride (0.4 mmol, 0.2 equiv.) in THF/NH_4Cl (aq. satd.) (1:5, 20 mL) at 0 °C. The mixture was stirred at the same temperature until complete disappearance of the α-keto-γ-lactam (TLC). Saturated aqueous $NaHCO_3$ (10 mL) was added, and the mixture was allowed to warm to room temperature before being extracted with ethyl acetate (3 × 15 mL). The organic extract was washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure to give a crude material. The crude material was purified by silica gel column chromatography (Hexane/EtOAc: 7:3) to give product **2a-k** in good to excellent yield.

3-Hydroxy-1-methyl-3-(prop-2-yn-1-yl)indolin-2-one (2a)[2]: Using the general procedure



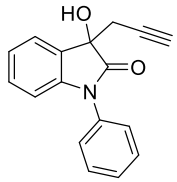
GP-1, propargyl bromide (714 mg, 6 mmol), compound **1a** (322 mg, 2 mmol), zinc powder (784 mg, 12 mmol), and hafnium (IV) chloride (128 mg, 0.4 mmol) in THF/NH_4Cl (aq. satd.) (1:5, 20 mL) provided the compound **2a** (366 mg, 91%) as a white crystalline solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.3 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 3.68 (s, 1H), 3.20 (s, 3H), 2.92 (d, *J* = 19.0 Hz, 1H), 2.73 (d, *J* = 16.5 Hz, 1H), 1.98 (s, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 176.9, 143.4, 130.2, 129.2, 124.3, 123.4, 108.6, 77.8, 74.6, 71.5, 28.9, 26.4. **HRMS (ESI)** calcd. for $C_{12}H_{12}NO_2$ $[M+H]^+$: 202.0868; Found: 202.0866.

1-Benzyl-3-hydroxy-3-(prop-2-yn-1-yl)indolin-2-one (2b): Using the general procedure

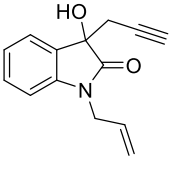


GP-1, propargyl bromide (714 mg, 6 mmol), compound **1b** (475 mg, 2 mmol), zinc powder (780 mg, 12 mmol), and hafnium (IV) chloride (128 mg, 0.4 mmol) in THF/NH_4Cl (aq. satd.) (1:5, 20 mL) provided the compound **2b** (483mg, 87%) as a white crystalline solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 5.9 Hz, 2H), 7.23 (d, *J* = 10.7 Hz, 3H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 7.9 Hz, 1H), 5.00 (d, *J* = 15.7 Hz, 1H), 4.72 (d, *J* = 15.7 Hz, 1H), 3.08 (s, 1H), 2.93 (d, *J* = 18.9 Hz, 1H), 2.78 (d, *J* = 16.5 Hz, 1H), 1.91 (s, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 176.8, 142.8, 135.4, 130.3, 129.1, 128.9, 127.9, 127.5, 124.3, 123.4, 109.7, 77.7, 74.6, 71.8, 44.1, 29.1. **HRMS (ESI)** calcd. for $C_{18}H_{16}NO_2$ $[M+H]^+$: 278.1181; Found: 278.1180.

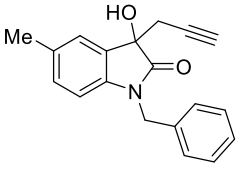
3-Hydroxy-1-phenyl-3-(prop-2-yn-1-yl)indolin-2-one (2c): Using the general procedure **GP-1**, propargyl bromide (714 mg, 6 mmol), compound **1c** (446 mg, 2 mmol), zinc powder (780 mg, 12 mmol), and hafnium (IV) chloride (128 mg, 0.4 mmol) in THF/NH_4Cl (aq. Satd.) (1:5, 20 mL) provided the compound **2c** (500 mg, 95%) as a white crystalline solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 3H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 7.9 Hz, 1H), 3.41 (s, 1H), 3.01 (d, *J* = 16.3 Hz, 1H), 2.90 (d, *J* = 16.3 Hz, 1H), 2.01 (s, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 176.3, 143.7, 1334, 130.2, 129.8, 128.8, 128.5, 126.5, 124.5, 123.9, 109.9, 77.6, 74.84, 71.7, 29.5. **HRMS (ESI)** calcd. for $C_{17}H_{14}NO_2$ $[M+H]^+$: 264.1025; Found: 264.1023.



1-Allyl-3-hydroxy-3-(prop-2-yn-1-yl)indolin-2-one (2d): Using the general procedure **GP-1**, propargyl bromide (714 mg, 6 mmol), compound **1d** (374mg, 2 mmol), zinc powder (780 mg, 12 mmol), and hafnium (IV) chloride (128 mg, 0.4 mmol) in THF/NH_4Cl (aq. satd.) (1:5, 20 mL) provided the compound **2d** (391mg, 86%) as a white crystalline solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.4 Hz, 1H), 7.33 (t, 1H), 7.12 (t, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 5.91 – 5.77 (m, 1H), 5.33 – 5.18 (m, 2H), 4.44 (dd, *J* = 16.4, 5.1 Hz, 1H), 4.22 (dd, *J* = 16.4, 5.3 Hz, 1H), 3.42 (s, 1H), 2.94 (d, *J* = 13.8 Hz, 1H), 2.78 (d, *J* = 16.4 Hz, 1H), 1.97 (s, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 176.6, 142.8, 131.0, 130.2, 129.1, 124.3, 123.4, 118.0, 109.6, 77.8, 74.6, 71.6, 42.6, 29.0. **HRMS (ESI)** calcd. for $C_{14}H_{14}NO_2$ $[M+H]^+$: 228.1025; Found: 228.1024.



1-Benzyl-3-hydroxy-5-methyl-3-(prop-2-yn-1-yl)indolin-2-one (2e): Using the general procedure **GP-1**, propargyl bromide (714 mg, 6 mmol), compound **1e** (503mg, 2 mmol), zinc powder (780 mg, 12 mmol), and hafnium (IV) chloride (128 mg, 0.4 mmol) in THF/NH_4Cl (aq satd) (1:5, 20 mL) provided the compound **2e** (489mg, 84%) as a white crystalline solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 (s, 1H), 7.18 (d, *J* = 6.2 Hz, 3H), 7.14 (d, *J* = 10.1 Hz, 2H), 6.91 (d, *J* = 7.9 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 4.91 (d, *J* = 15.6 Hz, 1H), 4.62 (d, *J* = 15.7 Hz, 1H), 3.27 (s, 1H), 2.85 (d, *J* = 16.4 Hz, 1H), 2.72 (d, *J* = 16.4 Hz, 1H), 2.20 (s, 3H), 1.82 (s, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 176.9, 140.3, 135.5, 133.1, 130.4, 129.1, 128.8, 127.8, 127.5, 125.0, 109.5, 77.9, 74.8, 71.6, 44.1, 29, 21.2. **HRMS (ESI)** calcd. for $C_{19}H_{18}NO_2$ $[M+H]^+$: 292.1338; Found: 292.1336.



3-Hydroxy-1,5,7-trimethyl-3-(prop-2-yn-1-yl)indolin-2-one (2f): Using the general procedure **GP-1**, propargyl bromide (714 mg, 6 mmol), compound **1f** (378mg, 2 mmol), zinc powder (780 mg, 12 mmol), and hafnium (IV) chloride (128 mg, 0.4 mmol) in THF/NH_4Cl (aq. satd.) (1:5, 20 mL) provided the compound **2f** (353mg, 77%) as a white crystalline solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (s, 1H), 6.89 (s, 1H), 3.45 (s, 3H), 3.14 (s, 1H), 2.85 (d, *J* = 16.5 Hz, 1H), 2.71 (d, *J* = 18.7 Hz, 1H), 2.52 (s, 3H), 2.30 (s, 3H), 2.01 (s, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 177.4, 138.7, 134.4, 132.9, 129.9, 122.8, 120, 77.9, 73.8, 71.6, 29.8, 29.2, 20.9, 19.0. **HRMS (ESI)** calcd for $C_{14}H_{16}NO_2$ $[M+H]^+$: 230.1181; Found: 230.1179.

1-Benzyl-3-hydroxy-5-methoxy-3-(prop-2-yn-1-yl)indolin-2-one (2g): Using the general procedure **GP-1**, propargyl bromide (714 mg, 6 mmol), compound **1g** (535 mg, 2 mmol), zinc powder (780 mg, 12 mmol), and hafnium (IV) chloride (128 mg, 0.4 mmol) in THF/NH_4Cl (aq. satd.) (1:5, 20 mL) provided the compound **2g** (504 mg, 82%) as a white crystalline solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 4.2 Hz, 3H), 7.14 (d, *J* = 5.6 Hz, 2H), 7.06 (d, *J* = 2.4 Hz, 1H), 6.63 (d, *J* = 8.5 Hz, 1H), 6.49 (d, *J* = 8.5 Hz, 1H), 4.89 (d, *J* = 15.7 Hz, 1H), 4.61 (d, *J* = 15.7 Hz, 1H), 3.65 (s, 3H), 3.37 (s, 1H), 2.85 (d, *J* = 16.4 Hz, 1H), 2.70 (d, *J* = 18.9 Hz, 1H), 1.84 (s, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 176.8, 156.6, 135.9, 135.4, 130.4, 128.9, 127.9, 127.5, 114.7, 111.4, 110.2, 77.8, 75.0, 71.7, 55.9, 44.2, 29.0. **HRMS (ESI)** calcd. for $C_{19}H_{18}NO_3$ $[M+H]^+$: 308.1287; Found: 308.1285.

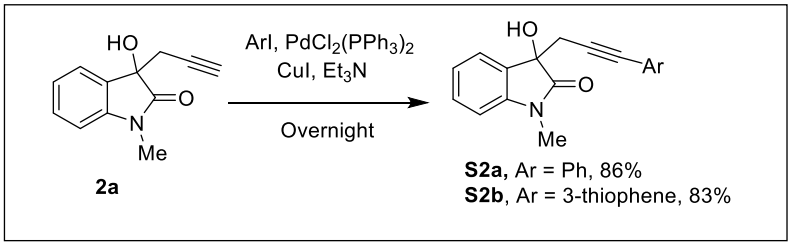
1-Benzyl-3-hydroxy-3-(prop-2-yn-1-yl)-5-(trifluoromethoxy)indolin-2-one (2h): Using the general procedure **GP-1**, propargyl bromide (714 mg, 6 mmol), compound **1h** (642 mg, 2 mmol), zinc powder (780 mg, 12 mmol), and hafnium (IV) chloride (128 mg, 0.4 mmol) in THF/NH_4Cl (aq satd) (1:5, 20 mL) provided the compound **2h** (556 mg, 77%) as a white crystalline solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.23 – 7.15 (m, 5H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.61 (d, *J* = 8.5 Hz, 1H), 4.94 (d, *J* = 15.7 Hz, 1H), 4.65 (d, *J* = 15.7 Hz, 1H), 3.42 (s, 1H), 2.89 (d, *J* = 19.0 Hz, 1H), 2.71 (d, *J* = 19.0 Hz, 1H), 1.88 (s, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 176.9, 145.3, 141.2, 134.8, 130.6, 129.0, 128.2, 127.5, 123.2, 120.6 (q, $J_{C\text{-}F}$ = 226.5 Hz),118.5, 110.3, 74.6, 72.2, 44.3, 29.0. One peak is masked by the solvent peak. **HRMS (ESI)** calcd. for $C_{19}H_{15}F_3NO_3$ $[M+H]^+$: 362.1004; Found: 362.1002.

5-Chloro-3-hydroxy-1-methyl-3-(prop-2-yn-1-yl)indolin-2-one (2i): Using the general procedure **GP-1**, propargyl bromide (714 mg, 6 mmol), compound **1i** (391 mg, 2 mmol), zinc powder (780 mg, 12 mmol), and hafnium (IV) chloride (128 mg, 0.4 mmol) in THF/NH_4Cl (aq. satd.) (1:5, 20 mL) provided the compound **2i** (434mg, 92%) as a white crystalline solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 6.78 (d, *J* = 8.3 Hz, 1H), 3.96 (s, 1H), 3.18 (s, 3H), 2.90 (d, *J* = 16.5 Hz, 1H), 2.72 (d, *J* = 16.5 Hz, 1H), 1.99 (s, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 176.7, 141.9, 130.8, 130.1, 128.9, 124.9, 109.6, 77.3, 74.7, 71.9, 28.8, 26.5; **HRMS (ESI)** calcd. for $C_{12}H_{11}ClNO_2$ $[M+H]^+$: 236.0478; Found: 236.0476 & 238.0464.

6-Chloro-3-hydroxy-1-methyl-3-(prop-2-yn-1-yl)indolin-2-one (2j): Using the general procedure **GP-1**, propargyl bromide (714 mg, 6 mmol), compound **1j** (391mg, 2 mmol), zinc powder (780 mg, 12 mmol), and hafnium (IV) chloride (128 mg, 0.4 mmol) in THF/NH_4Cl (aq. satd.) (1:5, 20 mL) provided the compound **2j** (424mg, 90%) as a white crystalline solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.9 Hz, 1H), 7.09 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.85 (d, *J* = 1.8 Hz, 1H), 3.96 (s, 1H), 3.17 (s, 3H), 2.94 – 2.86 (m, 1H), 2.75 – 2.68 (m, 1H), 1.96 (t, *J* = 2.7 Hz, 1H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 177.0, 144.7, 136.0, 127.6, 125.3, 123.3, 109.4, 77.4, 74.4, 71.7, 28.8, 26.5; **HRMS (ESI)** calcd. for $C_{12}H_{11}ClNO_2$ $[M+H]^+$: 236.0478; Found: 236.0475 & 238.0440.

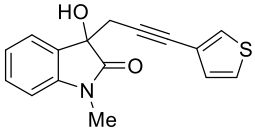
7-Fluoro-3-hydroxy-1-methyl-3-(prop-2-yn-1-yl)indolin-2-one (2k): Using the general procedure **GP-1**, propargyl bromide (714 mg, 6 mmol), compound **1k** (358mg, 2 mmol), zinc powder (780 mg, 12 mmol), and hafnium (IV) chloride (128 mg, 0.4 mmol) in THF/NH_4Cl (aq. satd.) (1:5, 20 mL) provided the compound **2k** (403 mg, 92%) as a white crystalline solid; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 1H), 7.12 – 7.01 (m, 2H), 3.86 (s, 1H), 3.40 (d, *J* = 2.7 Hz, 3H), 2.90 (d, *J* = 19.1 Hz, 1H), 2.75 (d, *J* = 19.1 Hz, 1H), 1.97 (s, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 176.5, 147.9 (d, $J_{C\text{-}F}$ = 241.6 Hz), 131.9, 130.0 (d, $J_{C\text{-}F}$ = 7.6 Hz), 124.2, 120.1, 118.3 (d, $J_{C\text{-}F}$ = 30.2 Hz), 77.3, 74.6, 71.9, 29.1, 29.0 (d, $J_{C\text{-}F}$ = 15.1 Hz). **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -135.99. **HRMS (ESI)** calcd. for $C_{12}H_{11}FNO_2$ $[M+H]^+$: 220.0774; Found: 220.0775.

4.0 Synthesis of internal alkyne containing oxindole S2a-b from 2a[3]:



Scheme S2. Sonogashira coupling for the synthesis of **S2a-b** from **2a**.

3-hydroxy-1-methyl-3-(3-phenylprop-2-yn-1-yl)indolin-2-one (S2a): A round-bottomed flask containing a magnetic stirrer bar and iodobenzene (367mg, 1.8 mmol, 1.2 equiv) was added with $PdCl_2(PPh_3)_2$ (21 mg, 0.03 mmol, 0.02 equiv.), CuI (29 mg, 0.15 mmol, 0.1equiv) and 5.0 mL of Et_3N. The resulted mixture was thoroughly degassed by a steady stream of argon for 15 min before 3-hydroxy-1-methyl-3-(prop-2-yn-1-yl) indolin-2-one **2a** (302mg, 1.5mmol, 1 equiv.) was added. Then the reaction mixture was allowed to stir at room temperature under argon overnight. After removal of Et_3N under reduced pressure, the reaction mixture was diluted with saturated aqueous NH_4Cl and the separated aqueous layer was extracted with EtOAc (3x15 mL). Combined organic phases were washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo to give a crude material. The crude material was purified by silica gel column chromatography eluting with 30% EtOAc-hexane to give the desired product **S2a** as colourless solid (358 mg, 86%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 6.9 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.23 (s, 5H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 4.71 (s, 1H), 3.19 (s, 1H), 3.15 (d, *J* = 3.2 Hz, 3H), 3.01 (d, *J* = 16.4 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 177.4, 143.3, 131.6, 129.9, 129.7, 128.1, 127.9, 124.15, 123.3, 123.1, 108.3, 83.5, 83.1, 75.4, 29.8, 26.3. **HRMS (ESI)** calcd. for $C_{18}H_{16}NO_2$ $[M+H]^+$: 278.1181; Found: 278.1180.



3-hydroxy-1-methyl-3-(3-(thiophen-3-yl)prop-2-yn-1-yl)indolin-2-one (S2b): As above mentioned procedure for **S2a,** 3-hydroxy-1-methyl-3-(prop-2-yn-1-yl) indolin-2-one **2a** (302 mg, 1.5 mmol, 1 equiv.), 3- iodothiophene (378 mg, 1.8 mmol, 1.2 equiv), $PdCl_2(PPh_3)_2$ (21 mg, 0.03 mmol, 0.02 equiv.), CuI (29 mg, 0.15 mmol, 0.1equiv) and 5.0 mL of Et_3N provided compound **S2b** as a colourless solid (353 mg, 83%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.1 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 4.1 Hz, 1H), 7.20 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 6.1 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 3.57 (s, 1H), 3.20 (s, 3H), 3.11 (d, *J* = 16.5 Hz,

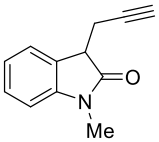
1H), 2.91 (d, *J* = 16.5 Hz, 1H). **$^{13}C\{^{1}H\}$ NMR** (151 MHz, $CDCl_3$) δ 177.1, 143.5, 130.1, 130.0, 129.5, 128.6, 125.2, 124.3, 123.4, 122.14, 108.5, 82.8, 78.7, 75.0, 30.1, 26.4. **HRMS (ESI)** calcd. for $C_{16}H_{14}NO_2S$ $[M+H]^+$: 284.0745; Found: 284.0744.

5.0 General procedure for the synthesis of 3-propargyl 2-oxindoles 3a-m (GP-2)[4,5]:

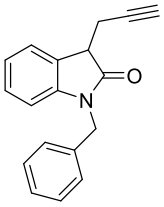
Step 1: A solution of hydroxyoxindole **2a-k, S2a-b** (1 mmol, 1 equiv.) and DIPEA (0.523 mL, 3 mmol, 3 equiv) in DCM (10 mL) was cooled to 0 °C, and thionyl chloride (diluted with 10 mL DCM, 0.087 mL, 1.2 mmol, 1.2 equiv) was added dropwise. The reaction solution was stirred at 0 °C for 1 hour then at RT for another 1 hour. The entire reaction mixture was poured into saturated $NaHCO_3$ solution, extracted with DCM (3x10 mL). The combined extracts were washed with saturated aqueous NaCl, dried with anhydrous Na_2SO_4 and concentrated. It was used for the next step without any further purification.

Step 2: The chlorooxindole compound as obtained from **step1** (1 mmol, 1 equiv.) was dissolved in THF (10 mL) and acetic acid (3 mL). zinc dust (390 mg, 6 mmol, 6 equiv.) was then added. The reaction mixture was stirred at ambient temperature for 3 h, and then it was filtered. The filtrate was concentrated in vacuo to dryness. The residue was dissolved in ethyl acetate (10 mL). The organic phase was washed with saturated $NaHCO_3$ solution (10 mL) and brine, then dried with anhydrous Na_2SO_4, filtered and concentrated in vacuo to dryness. The residue was purified by column chromatography (petroleum ether/ EtOAc, 9:1) to give pure compounds **3a-m** as colourless solids.

1-Methyl-3-(prop-2-yn-1-yl)indolin-2-one (3a): Using the **step 1** of general procedure **GP-2**, DIPEA(0.523 mL, 3 mmol), $SOCl_2$ (diluted in 10 mL DCM, 0.087mL, 1.2 mmol), compound **2a** (201mg, 1 mmol) in 10 mL DCM provided the corresponding chlorooxindole derivative. Then using **step 2** of **GP-2**, zinc dust (390 mg, 6 mmol), acetic acid (3 mL) in THF (10 mL) provided the compound **3a** (120mg, 65%) as a colourless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.3 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 3.55 (dd, *J* = 8.8, 4.3 Hz, 1H), 3.21 (s, 3H), 3.02 – 2.95 (m, 1H), 2.63 – 2.55 (m, 1H), 1.99 (s, 1H). **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$) δ 176.1, 144.5, 128.6, 128.0, 124.5, 122.7, 108.1, 80.8, 70.3, 44.2, 26.4, 20.6. **HRMS (ESI)** calcd. for $C_{12}H_{12}NO$ $[M+H]^+$: 186.0919; Found: 186.0918.

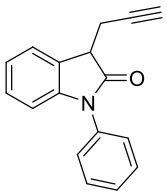


1-Benzyl-3-(prop-2-yn-1-yl)indolin-2-one (3b): Using the **step1** of general procedure **GP-2**,



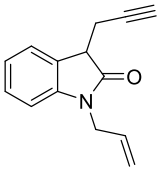
DIPEA (0.523mL, 3mmol), $SOCl_2$ (diluted in 10 mL DCM, 0.087 mL, 1.2 mmol), compound **2b** (277mg, 1 mmol) in 10 mL DCM provided the corresponding chlorooxindole derivative. Then using **step2** of **GP-2**, zinc dust (390 mg, 6 mmol), acetic acid (3 mL) in THF (10 mL) provided the compound **3b** (162 mg, 62%) as a colourless solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.4 Hz, 1H), 7.35 – 7.26 (m, 5H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 7.7 Hz, 1H), 5.01 (d, *J* = 15.7 Hz, 1H), 4.84 (d, *J* = 15.7 Hz, 1H), 3.65 (dd, *J* = 8.0, 4.5 Hz, 1H), 3.11 – 2.97 (m, 1H), 2.74 (dd, *J* = 19.4, 8.1 Hz, 1H), 1.96 (s, 1H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 176.2, 143.6, 135.8, 128.9, 128.8, 128.5, 127.9, 127.7, 127.5, 124.4, 122.7, 109.2, 80.6, 70.5, 44.2, 43.9, 20.6. **HRMS (ESI)** calcd. for $C_{18}H_{16}NO$ $[M+H]^+$: 262.1232; Found: 262.1233.

1-Phenyl-3-(prop-2-yn-1-yl)indolin-2-one (3c): Using the **step1** of general procedure **GP-2**,



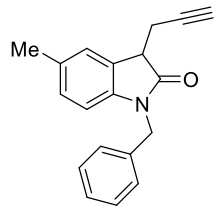
DIPEA(0.523mL, 3mmol), $SOCl_2$ (diluted in 10 mL DCM, 0.087mL, 1.2mmol), compound **2c** (263mg, 1mmol) in 10 mL DCM provided the corresponding chlorooxindole derivative. Then using **step2** of **GP-2**, zinc dust (390 mg, 6 mmol), acetic acid (3 mL) in THF (10 mL) provided the compound **3c** (173mg,70%) as a colourless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.4 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 2H), 7.60 (d, *J* = 6.9 Hz, 3H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 7.9 Hz, 1H), 3.91 (dd, *J* = 8.1, 4.4 Hz, 1H), 3.28 – 3.19 (m, 1H), 3.01 – 2.93 (m, 1H), 2.20 (s, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 175.5, 144.5, 134.4, 129.7, 128.4, 128.2, 127.7, 126.6, 124.6, 123.0, 109.4, 80.3, 70.5, 44.2, 20.9; **HRMS (ESI)** calcd. for $C_{17}H_{14}NO$ $[M+H]^+$: 248.1075; Found: 248.1076.

1-Allyl-3-(prop-2-yn-1-yl)indolin-2-one (3d): Using the **step1** of general procedure **GP-2**,

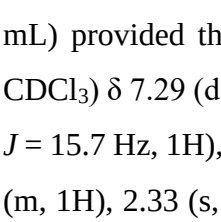


DIPEA (0.523 mL, 3 mmol), $SOCl_2$ (diluted in 10 mL DCM, 0.087mL, 1.2 mmol), compound **2d** (227mg, 1mmol) in 10 mL DCM provided the corresponding chlorooxindole derivative. Then using **Step2** of **GP-2**, zinc dust (390 mg, 6 mmol), acetic acid (3 mL) in THF (10 mL) provided the compound **3d** (129 mg, 61%) as a colourless solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.3 Hz, 1H), 7.27 (t, *J* = 7.2 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 5.83 (ddd, *J* = 22.4, 10.3, 5.2 Hz, 1H), 5.28 – 5.17 (m, 2H), 4.34 (qd, *J* = 16.4, 5.2 Hz, 2H), 3.58 (dd, *J* = 8.3, 4.5 Hz, 1H), 3.04 – 2.94 (m, 1H), 2.71 – 2.60 (m, 1H), 1.96 (s, 1H); **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 175.8, 143.6, 131.3, 128.4, 127.9, 124.4, 122.6, 117.6, 109.0, 80.6, 70.4, 44.1, 42.4, 20.5; **HRMS (ESI)** calcd. for $C_{14}H_{14}NO$ $[M+H]^+$: 212.1075; Found: 212.1073.

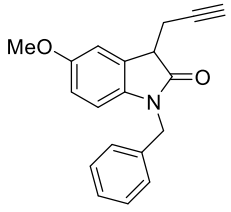
1-Benzyl-5-methyl-3-(prop-2-yn-1-yl)indolin-2-one (3e): Using the **step1** of general procedure **GP-2**, DIPEA (0.523 mL, 3 mmol), $SOCl_2$ (diluted in 10 mL DCM, 0.087 mL, 1.2 mmol), compound **2e** (291mg, 1 mmol) in 10 mL DCM provided the corresponding chlorooxindole derivative. Then using **step2** of **GP-2**, Zinc dust (390 mg, 6 mmol), acetic acid (3 mL) in THF (10 mL) provided the compound **3e** (162 mg, 59%) as colourless solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.29 (d, *J* = 13.6 Hz, 6H), 7.00 (d, *J* = 7.9 Hz, 1H), 6.62 (d, *J* = 7.9 Hz, 1H), 5.01 (d, *J* = 15.7 Hz, 1H), 4.82 (d, *J* = 14.1 Hz, 1H), 3.62 (s, 1H), 3.02 (d, *J* = 16.7 Hz, 1H), 2.81 – 2.67 (m, 1H), 2.33 (s, 3H), 1.98 (s, 1H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 176.1, 141.1, 135.8, 132.1, 128.7, 128.6, 127.8, 127.6, 127.4, 125.2, 108.8, 80.6, 70.4, 44.2, 43.8, 21.2, 20.5; **HRMS (ESI)** calcd. for $C_{19}H_{18}NO$ $[M+H]^+$: 276.1388; Found: 276.1388.



1,5,7-Trimethyl-3-(prop-2-yn-1-yl)indolin-2-one (3f): Using the **step1** of general procedure **GP-2**, DIPEA (0.523mL, 3mmol), $SOCl_2$ (diluted in 10 mL DCM, 0.087 mL, 1.2 mmol), compound **2f** (229 mg, 1 mmol) in 10 mL DCM provided the corresponding chlorooxindole derivative. Then using **step2** of **GP-2**, zinc dust (390 mg, 6 mmol), acetic acid (3 mL) in THF (10 mL) provided compound **3f** (117 mg, 55%) as a colourless solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.17 (s, 1H), 6.84 (s, 1H), 3.46 (s, 3H), 3.46 – 3.43 (m, 1H), 2.93 (dd, *J* = 16.8, 7.1 Hz, 1H), 2.58 (dd, *J* = 19.4, 8.5 Hz, 1H), 2.53 (s, 3H), 2.29 (s, 3H), 1.98 (s, 1H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 176.8, 139.7, 132.7, 132.0, 128.7, 123.0, 119.4, 80.9, 70.2, 43.9, 29.7, 21.0, 20.8, 19.0; **HRMS (ESI)** calcd. for $C_{19}H_{16}NO$ $[M+H]^+$: 214.1232; Found: 214.1230.



1-Benzyl-5-methoxy-3-(prop-2-yn-1-yl)indolin-2-one (3g): Using the **step1** of general procedure **GP-2**, DIPEA (0.523mL, 3 mmol), $SOCl_2$ (diluted in 10 mL DCM, 0.087 mL, 1.2 mmol), compound **2g** (307 mg, 1 mmol) in 10 mL DCM provided the corresponding chlorooxindole derivative. Then using **step2** of **GP-2**, zinc dust (390 mg, 6 mmol), acetic acid (3 mL) in THF (10 mL) provided the compound **3c** (166 mg, 57%) as a colourless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.21 (m, 5H), 7.14 (s, 1H), 6.71 (d, *J* = 10.9 Hz, 1H), 6.60 (d, *J* = 8.5 Hz, 1H), 4.98 (d, *J* = 15.6 Hz, 1H), 4.81 (d, *J* = 15.6 Hz, 1H), 3.76 (s, 3H), 3.62 (dd, *J* = 8.2, 4.4 Hz, 1H), 3.02 (d, *J* = 16.8 Hz, 1H), 2.71 (dd, *J* = 16.8, 8.3 Hz, 1H), 1.98 (s, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 175.9, 156.1, 137.1, 135.9, 129.2, 128.8, 127.7, 127.5, 112.7, 112.1,



109.5, 80.6, 70.5, 55.9, 44.5, 44.0, 20.7. **HRMS (ESI)** calcd. for $C_{19}H_{18}NO_2$ $[M+H]^+$: 292.1338; Found: 292.1339 & 294.1321.

1-Benzyl-3-(prop-2-yn-1-yl)-5-(trifluoromethoxy)indolin-2-one (3h): Using the **step1** of general procedure **GP-2**, DIPEA(0.523mL, 3 mmol), $SOCl_2$ (diluted in 10 mL DCM, 0.087 mL, 1.2 mmol), compound **2h** (361 mg, 1 mmol) in 10 mL DCM provided the corresponding chlorooxindole derivative. Then using **step2** of **GP-2**, zinc dust (390 mg, 6 mmol), acetic acid (3 mL) in THF (10 mL) provided the compound **3h** (179 mg, 52%) as a colourless solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.37 – 7.22 (m, 5H), 7.07 (d, *J* = 7.8 Hz, 1H), 6.69 (d, *J* = 8.5 Hz, 1H), 5.00 (d, *J* = 15.7 Hz, 1H), 4.83 (d, *J* = 15.7 Hz, 1H), 3.67 (dd, *J* = 8.4, 4.5 Hz, 1H), 3.11 – 2.97 (m, 1H), 2.78 – 2.64 (m, 1H), 2.00 (s, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 175.9, 144.8, 142.3, 135.3, 129.3, 129.0, 128.0, 127.5, 121.6, 120.7 (q, J_{C-F} = 258.2 Hz), 118.6, 109.5, 80.0, 71.0, 44.1, 20.5. **HRMS (ESI)** calcd. for $C_{19}H_{15}F_3NO_2$ $[M+H]^+$: 346.1055; Found: 346.1056.

5-Chloro-1-methyl-3-(prop-2-yn-1-yl)indolin-2-one (3i): Using the **step1** of general procedure **GP-2**, DIPEA (0.523mL, 3 mmol), $SOCl_2$ (diluted in 10 mL DCM, 0.087 mL, 1.2 mmol), compound **2i** (236 mg, 1 mmol) in 10 mL DCM provided the corresponding chlorooxindole derivative. Then using **step2** of **GP-2**, zinc dust (390 mg, 6 mmol), acetic acid (3 mL) in THF (10 mL) provided the compound **3h** (158 mg, 72%) as a colourless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.28 (d, *J* = 8.3 Hz, 1H), 6.75 (d, *J* = 8.3 Hz, 1H), 3.53 (dd, *J* = 8.7, 4.2 Hz, 1H), 3.18 (s, 3H), 3.00 – 2.93 (m, 1H), 2.60 – 2.52 (m, 1H), 2.01 (s, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 175.5, 143.0, 129.5, 128.5, 128.0, 125.0, 109.0, 80.2, 70.8, 44.1, 26.5, 20.4. **HRMS (ESI)** calcd. for $C_{12}H_{11}NOCl$ $[M+H]^+$: 220.0529; Found: 220.0529 & 222.0519.

6-Chloro-1-methyl-3-(prop-2-yn-1-yl)indolin-2-one (3j): Using the **step1** of general procedure **GP-2**, DIPEA (0.523 mL, 3 mmol), $SOCl_2$ (diluted in 10 mL DCM, 0.087 mL, 1.2 mmol), compound **2j** (236 mg, 1 mmol) in 10 mL DCM provided the corresponding chlorooxindole derivative. Then using **step2** of **GP-2**, zinc dust (390 mg, 6 mmol), acetic acid (3 mL) in THF (10 mL) provided compound **3h** (162 mg, 74%) as a colourless solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.8 Hz, 1H), 7.03 (d, *J* = 7.9 Hz, 1H), 6.82 (s, 1H), 3.50 (dd, *J* = 8.6, 4.3 Hz, 1H), 2.99 – 2.88 (m, 1H), 2.62 – 2.51 (m, 1H), 1.98 (t, *J* = 2.7 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ

175.9, 145.6, 134.4, 126.2, 125.3, 122.4, 108.9, 80.3, 70.6, 43.7, 26.4, 20.4. **HRMS (ESI)** calcd. for $C_{12}H_{11}NOCl$ $[M+H]^+$: 220.0529; Found: 220.0527 & 222.0492.

7-Fluoro-1-methyl-3-(prop-2-yn-1-yl)indolin-2-one (3k): Using the **step1** of general procedure **GP-2**, DIPEA (0.523 mL, 3 mmol), $SOCl_2$ (diluted in 10 mL DCM, 0.087 mL, 1.2 mmol), compound **2k** (219mg, 1 mmol) in 10 mL DCM provided the corresponding chlorooxindole derivative. Then using **step2** of **GP-2**, zinc dust (390 mg, 6 mmol), acetic acid (3 mL) in THF (10 mL) provided the compound **3k** (140 mg, 69%) as a colourless solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 1H), 7.09 – 7.02 (m, 1H), 7.02 – 6.96 (m, 1H), 3.56 (dd, *J* = 8.5, 4.4 Hz, 1H), 3.43 (d, *J* = 2.7 Hz, 3H), 3.03 – 2.90 (m, 1H), 2.68 – 2.54 (m, 1H), 1.99 (s, 1H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 175.5, 147.7 (d, $J_{C\text{-}F}$ = 241.6 Hz), 131.0 (d, $J_{C\text{-}F}$ = 7.5 Hz), 130.7 (d, $J_{C\text{-}F}$ = 3.0 Hz), 123.1 (d, $J_{C\text{-}F}$ = 3.0 Hz), 120.2 (d, $J_{C\text{-}F}$ = 3.0 Hz), 116.5 (d, $J_{C\text{-}F}$ = 18 Hz), 80.2, 70.5, 44.4, 28.7 (d, $J_{C\text{-}F}$ = 15.1 Hz), 20.5. **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -136.9. **HRMS (ESI)** calcd. for $C_{12}H_{11}FNO[M+H]^+$: 204.0825; Found: 204.0826.

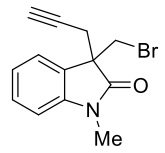
1-Methyl-3-(3-phenylprop-2-yn-1-yl)indolin-2-one (3l): Using the **step1** of general procedure **GP-2**, DIPEA (0.523 mL, 3 mmol), $SOCl_2$ (diluted in 10 mL DCM, 0.087 mL, 1.2 mmol), compound **S2a** (277 mg, 1 mmol) in 10 mL DCM provided the corresponding chlorooxindole derivative. Then using **step2** of **GP-2**, zinc dust (390 mg, 6 mmol), acetic acid (3 mL) in THF (10 mL) provided compound **3k** (172 mg, 66%) as a colourless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.4 Hz, 1H), 7.36 – 7.30 (m, 3H), 7.30 – 7.25 (m, 3H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 3.64 (dd, *J* = 9.1, 4.3 Hz, 1H), 3.26 – 3.19 (m, 4H), 2.77 (dd, *J* = 16.8, 9.1 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 176.2, 144.5, 131.6, 128.5, 128.3, 128.3, 128.0, 124.5, 123.4, 122.6, 108.1, 86.4, 82.4, 44.6, 26.3, 21.7. **HRMS (ESI)** calcd. for $C_{18}H_{16}NO[M+H]^+$: 262.1232; Found: 262.1230.

1-methyl-3-(3-(thiophen-3-yl)prop-2-yn-1-yl)indolin-2-one (3m): Using the **step1** of general procedure **GP-2**, DIPEA (0.523 mL, 3 mmol), $SOCl_2$ (diluted in 10 mL DCM, 0.087 mL, 1.2 mmol), compound **S2b** (283 mg, 1 mmol) in 10 mL DCM provided the corresponding chlorooxindole derivative. Then using **step2** of **GP-2**, zinc dust (390 mg, 6 mmol), acetic acid (3 mL) in THF (10 mL) provided compound **3m** (163 mg, 61%) as a colourless solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.4 Hz, 1H), 7.37 – 7.28 (m, 2H), 7.26 – 7.19 (m, 1H), 7.08 (t, *J* =

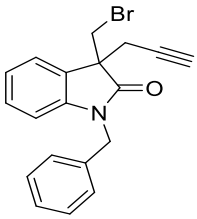
7.5 Hz, 1H), 7.01 (d, *J* = 5.0 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 3.62 (dd, *J* = 9.1, 4.4 Hz, 1H), 3.27 – 3.15 (m, 4H), 2.73 (dd, *J* = 16.8, 9.2 Hz, 1H). **$^{13}C\{^{1}H\}$ NMR** (75 MHz, $CDCl_3$) δ 176.2, 144.4, 130.0, 128.5, 128.27, 125.2, 124.5, 122.6, 122.4, 108.1, 86.0, 77.5, 44.6, 26.4, 21.7. **HRMS (ESI)** calcd. for $C_{16}H_{14}NOS[M+H]^+$: 268.0796; Found: 268.0795.

6.0 General procedure to prepare compound 3, 3-disubstuted 2-oxindole 4, 5, 6a-m (GP-3)[6]: A solution of **3a-m** (0.25 mmol, 1equiv.) and dibromoalkane (0.50 mmol, 2 eqiv.)) in DMF (0.5 mL) was degassed and bubbled with argon under ice-cooling. Powdered KOH (0.50 mmol, 2 eqiv.) was added to the solution in one portion, and the reaction mixture was stirred at room temperature for 2 h, diluted with H_2O, and extracted with EtOAc. The organic layer was washed with H_2O and brine and dried with Na_2SO_4 and the solvents were evaporated. The residue was purified on a silica gel column (petroleum ether/ EtOAc, 9:1) to give compounds **4, 5, 6a-m** in good to excellent yields.

3-(Bromomethyl)-1-methyl-3-(prop-2-yn-1-yl)indolin-2-one (4a): Using **GP-3**, 3-substituted oxindole **3a** (46 mg, 0.25 mmol), dibromomethane (87 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **4a** (59 mg, 85%) as a brown sticky liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.7 Hz, 1H), 7.37 (t, J=7.7Hz, 1H), 7.13(t, J=7.8Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 3.87 (d, *J* = 10.2 Hz, 1H), 3.74 (d, *J* = 10.2 Hz, 1H), 3.25 (s, 3H), 2.87 (d, *J* = 16.8 Hz, 1H), 2.61 (d, *J* = 19.4 Hz, 1H), 2.03(s, 1H). **$^{13}C\{^{1}H\}$ NMR** (151 MHz, $CDCl_3$) δ 176.0, 143.9, 129.3, 129.2, 123.9, 122.9, 108.4, 78.4, 71.9, 51.4, 34.9, 26.5, 26.3. **HRMS (ESI)** calcd. for $C_{13}H_{13}NOBr$ $[M+H]^+$: 278.0181; Found: 278.0182 & 280.0147.



1-Benzyl-3-(bromomethyl)-3-(prop-2-yn-1-yl)indolin-2-one (4b): Using **GP-3**, 3-substituted oxindole **3b** (65 mg, 0.25 mmol), dibromomethane (87 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **4b** (73 mg, 82%) as a brown sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.4 Hz, 1H), 7.29 – 7.15 (m, 6H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 1H), 4.91 (d, *J* = 15.6 Hz, 1H), 4.84 (d, *J* = 15.7 Hz, 1H), 3.83 (d, *J* = 10.2 Hz, 1H), 3.73 (d, *J* = 10.2 Hz, 1H), 2.84 (d, *J* = 16.7 Hz, 1H), 2.61 (d, *J* = 14.6 Hz, 1H), 1.93 (s, 1H). **$^{13}C\{^{1}H\}$ NMR** (151 MHz, $CDCl_3$) δ 176.2, 143.0, 135.5, 129.2, 129.1, 128.8, 127.8, 127.5, 123.9, 122.9, 109.5, 78.4, 72.0, 51.5, 44.2, 35.0, 26.6. **HRMS (ESI)** calcd. for $C_{19}H_{17}NOBr$ $[M+H]^+$: 354.0494; Found: 354.0492 & 356.0472



3-(Bromomethyl)-1-phenyl-3-(prop-2-yn-1-yl)indolin-2-one (4c): Using **GP-3**, 3-substituted oxindole **3c** (62 mg, 0.25 mmol), dibromomethane (87 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **4c** (68 mg, 80%) as a brown sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.4 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.43 (d, *J* = 8.2 Hz, 3H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.9 Hz, 1H), 3.94 (d, *J* = 10.1 Hz, 1H), 3.86 (d, *J* = 10.1 Hz, 1H), 2.95 (d, *J* = 16.6 Hz, 1H), 2.78 (d, *J* = 16.6 Hz, 1H), 2.08 (s, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 175.6, 144.2, 134.3, 129.8, 129.2, 128.9, 128.5, 126.8,124.0, 123.4, 109.7, 78.3, 72.0, 51.6, 35.3, 26.6. HRMS (ESI) calcd. for $C_{18}H_{15}NOBr$ $[M+H]^+$: 340.0337; Found: 340.0338 & 342.0305.

1-Allyl-3-(bromomethyl)-3-(prop-2-yn-1-yl)indolin-2-one (4d): Using **GP-3**, 3-substituted oxindole **3d** (53 mg, 0.25 mmol), dibromomethane (87 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **4d** (62 mg, 81%) as a brown sticky liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 8.4 Hz, 1H), 7.16 – 7.09 (m, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 5.91 – 5.75 (m, 1H), 5.33 – 5.19 (m, 2H), 4.44 – 4.30 (m, 2H), 3.88 (d, *J* = 10.1 Hz, 1H), 3.76 (d, *J* = 10.2 Hz, 1H), 2.87 (d, *J* = 16.7 Hz, 1H), 2.64 (d, *J* = 16.7 Hz, 1H), 2.02 (s, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 175.8, 143.1, 131.1, 129.2 (two peaks), 123.9, 122.9, 117.9, 109.4, 78.4, 71.9, 51.4, 42.7, 35.0, 26.5. **HRMS (ESI)** calcd. for $C_{15}H_{15}NOBr$ $[M+H]^+$: 304.0337; Found: 304.0335 & 306.0345.

1-Benzyl-3-(bromomethyl)-5-methyl-3-(prop-2-yn-1-yl) indolin-2-one (4e): Using **GP-3**, 3-substituted oxindole **3e** (69 mg, 0.25 mmol), dibromomethane (87 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **4e** (80 mg, 87%) as a brown sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 3H), 7.32 – 7.21 (m, 3H), 7.04 (d, *J* = 7.9 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 4.98 (d, *J* = 15.7 Hz, 1H), 4.91 (d, *J* = 15.7 Hz, 1H), 3.90 (d, *J* = 10.1 Hz, 1H), 3.81 (d, *J* = 10.2 Hz, 1H), 2.90 (d, *J* = 19.2 Hz, 1H), 2.69 (d, *J* = 16.6 Hz, 1H), 2.35 (s, 3H), 2.02 (s, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 176.1, 140.6, 135.6, 132.4, 129.5, 129.1, 128.7, 127.7, 127.5, 124.6, 109.2, 78.4, 71.9, 51.5, 44.2, 35.1, 26.5, 21.3. **HRMS (ESI)** calcd. for $C_{20}H_{19}NOBr$ $[M+H]^+$: 368.0650; Found: 368.0648 & 370.0594.

3-(Bromomethyl)-1,5,7-trimethyl-3-(prop-2-yn-1-yl)indolin-2-one (4f): Using **GP-3**, 3-substituted oxindole **3f** (53 mg, 0.25 mmol), dibromomethane (87 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **4f** (67 mg, 88%) as a brown sticky liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.15 (s, 1H), 6.89 (s, 1H), 3.80 (d, *J* = 10.1 Hz, 1H), 3.72 (d, *J* = 10.0 Hz, 1H), 3.49 (s, 3H), 2.81 (d, *J* = 16.7 Hz, 1H), 2.58 (d, *J* = 16.8 Hz, 1H), 2.55 (s, 3H), 2.32 (s, 3H), 2.04 (s, 1H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 176.7, 139.3, 133.6, 132.3, 129.9, 122.3, 119.7, 78.6, 71.8, 50.7, 35.3, 29.9, 26.6, 21.1, 19.1. **HRMS (ESI)** calcd. for $C_{20}H_{19}NOBr$ $[M+H]^+$: 306.0494; Found: 306.0495 & 308.0505.

1-Benzyl-3-(bromomethyl)-5-methoxy-3-(prop-2-yn-1-yl)indolin-2-one (4g): Using **GP-3**, 3-substituted oxindole **3g** (73 mg, 0.25 mmol), dibromomethane (87 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **4g** (86 mg, 89%) as a brown sticky liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.29 – 7.18 (m, 5H), 7.07 (s, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 6.56 (d, *J* = 8.6 Hz, 1H), 4.90 (d, *J* = 15.6 Hz, 1H), 4.82 (d, *J* = 15.7 Hz, 1H), 3.82 (d, *J* = 10.2 Hz, 1H), 3.74 (s, 4H), 2.83 (d, *J* = 19.3 Hz, 1H), 2.60 (d, *J* = 16.8 Hz, 1H), 1.96 (s, 1H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 175.8, 156.1, 136.4, 135.6, 130.5, 128.8, 127.8, 127.5, 113.2, 111.6, 109.8, 78.4, 72.1, 55.8, 51.8, 44.3, 34.9, 26.6. **HRMS (ESI)** calcd. for $C_{20}H_{19}NO_2Br$ $[M+H]^+$: 384.0599; Found: 384.0599 & 386.0581.

1-Benzyl-3-(bromomethyl)-3-(prop-2-yn-1-yl)-5-(trifluoromethoxy)indolin-2-one (4h): Using **GP-3**, 3-substituted oxindole **3h** (86 mg, 0.25 mmol), dibromomethane (87 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **4h** (79 mg, 72%) as a brown sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.33 (d, *J* = 6.2 Hz, 4H), 7.31 – 7.27 (m, 1H), 7.11 (d, *J* = 8.6 Hz, 1H), 6.72 (d, *J* = 8.5 Hz, 1H), 4.99 (d, *J* = 15.7 Hz, 1H), 4.91 (d, *J* = 15.7 Hz, 1H), 3.90 (d, *J* = 10.3 Hz, 1H), 3.80 (d, *J* = 10.3 Hz, 1H), 2.92 (d, *J* = 16.8 Hz, 1H), 2.68 (d, *J* = 16.7 Hz, 1H), 2.06 (s, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 176.0, 144.9, 141.7, 135.0, 130.6, 129.0, 128.0, 127.5, 122.2,120.4 (q, J_{C-F} = 256.7 Hz), 118.1,109.9, 77.8, 72.5, 51.8, 44.4, 34.2, 26.5. **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -58.29. **HRMS (ESI)** calcd. for $C_{20}H_{16}NO_2F_3Br$ $[M+H]^+$: 438.0317; Found: 438.0318 & 440.0285.

3-(Bromomethyl)-5-chloro-1-methyl-3-(prop-2-yn-1-yl)indolin-2-one (4i): Using **GP-3**, 3-substituted oxindole **3i** (55 mg, 0.25 mmol), dibromomethane (87 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **4i** (63mg, 81%) as a brown sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.34 (d, *J* = 10.2 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 3.83 (d, *J* = 10.2 Hz, 1H), 3.71 (d, *J* = 10.2 Hz, 1H), 3.23 (s, 3H), 2.85 (d, *J* = 19.1 Hz, 1H), 2.60 (d, *J* = 19.2 Hz, 1H), 2.07 (s, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 175.6, 142.5, 130.8, 129.3, 128.4, 124.5, 109.3, 77.9, 72.3, 51.6, 34.4, 26.7, 26.2. **HRMS (ESI)** calcd. for $C_{13}H_{12}NOClBr$ $[M+H]^+$: 311.9791; Found: 311.9792 & 313.9759.

3-(Bromomethyl)-6-chloro-1-methyl-3-(prop-2-yn-1-yl)indolin-2-one (4j): Using **GP-3**, 3-substituted oxindole **3e** (55 mg, 0.25 mmol), dibromomethane (87 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **4d** (66 mg, 84%) as a brown sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 9.6 Hz, 1H), 6.89 (s, 1H), 3.83 (d, *J* = 10.2 Hz, 1H), 3.71 (d, *J* = 10.2 Hz, 1H), 3.23 (s, 3H), 2.85 (d, *J* = 16.7 Hz, 1H), 2.59 (d, *J* = 16.7 Hz, 1H), 2.04 (s, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 176.0, 145.1, 135.2, 127.5, 124.9, 122.8, 109.2, 78.0, 72.1, 51.3, 34.5, 26.7, 26.2. **HRMS (ESI)** calcd. for $C_{13}H_{12}NOClBr$ $[M+H]^+$: 311.9791; Found: 311.9792 & 313.9770.

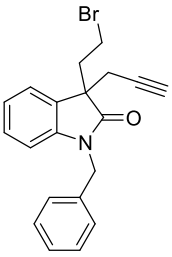
3-(Bromomethyl)-7-fluoro-1-methyl-3-(prop-2-yn-1-yl)indolin-2-one (4k): Using **GP-3**, 3-substituted oxindole **3k** (51 mg, 0.25 mmol), dibromomethane (87 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **4d** (58 mg, 79%) as a brown sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.2 Hz, 1H), 7.15 – 7.00 (m, 2H), 3.82 (d, *J* = 10.2 Hz, 1H), 3.72 (d, *J* = 10.2 Hz, 1H), 3.45 (d, $J_{C\text{-}F}$ = 2.7 Hz, 3H), 2.84 (d, *J* = 16.7 Hz, 1H), 2.61 (d, *J* = 16.7 Hz, 1H), 2.04 (s, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 175.7, 147.9 (d, $J_{C\text{-}F}$ = 244.6 Hz), 132.01(d, $J_{C\text{-}F}$ = 3 Hz), 130.58 (d, $J_{C\text{-}F}$ =7.6 Hz), 123.50 (d, $J_{C\text{-}F}$ = 6 Hz),119.66 (d, $J_{C\text{-}F}$ = 4.5 Hz),117.32 (d, $J_{C\text{-}F}$ = 19.6 Hz), 77.99, 72.12, 51.80, 34.63, 29.01(d, J= 6Hz) 26.45. **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -136.15. **HRMS (ESI)** calcd. for $C_{13}H_{12}NOFBr$ $[M+H]^+$: 296.0086; Found: 296.0084 & 298.0094.

3-(Bromomethyl)-1-methyl-3-(3-phenylprop-2-yn-1-yl)indolin-2-one (4l): Using **GP-3**, 3-substituted oxindole **3l** (65 mg, 0.25 mmol), dibromomethane (87 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **4l** (72 mg, 87%) as a brown sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.30 (s, 5H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 3.95 (d, *J* = 10.1 Hz, 1H), 3.83 (d, *J* = 10.1 Hz, 1H), 3.26 (s, 3H), 3.08 (d, *J* = 16.7 Hz, 1H), 2.82 (d, *J* = 16.7 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 176.2, 144.0, 131.8, 131.7, 129.4, 129.2, 128.4, 128.3, 123.9, 123.0, 122.9, 108.3, 83.9, 52.0, 35.0, 27.4, 26.5. **HRMS (ESI)** calcd. for $C_{19}H_{17}NOBr$ $[M+H]^+$: 354.0494; Found: 354.0493 & 356.0441.

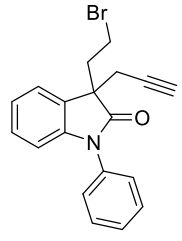
3-(bromomethyl)-1-methyl-3-(3-(thiophen-3-yl)prop-2-yn-1-yl)indolin-2-one (4m): Using **GP-3**, 3-substituted oxindole **3m** (67 mg, 0.25 mmol), dibromomethane (87 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **4m** (80 mg, 89%) as a brown sticky liquid.**^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.1 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 4.1 Hz, 1H), 7.23 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.17 – 7.10 (m, 1H), 6.98 (d, *J* = 6.1 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 3.93 (d, *J* = 10.1 Hz, 1H), 3.81 (d, *J* = 10.1 Hz, 1H), 3.25 (s, 3H), 3.05 (d, *J* = 16.8 Hz, 1H), 2.79 (d, *J* = 16.8 Hz, 1H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 176.1, 143.9, 129.8, 129.4, 129.2, 128.6, 125.4, 123.9, 122.9, 121.9, 108.3, 83.4, 79.0, 51.9, 34.9, 27.4, 26.5. **HRMS (ESI)** calcd. for $C_{17}H_{15}NOSBr$ $[M+H]^+$: 360.0058; Found: 360.0057 & 362.0047.

3-(2-Bromoethyl)-1-methyl-3-(prop-2-yn-1-yl)indolin-2-one (5a): Using **GP-3**, 3-substituted oxindole **3a** (46 mg, 0.25 mmol), 1,2-dibromoethane (94 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **5a** (55 mg, 75%) as a brown sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 3.20 (s, 3H), 3.07 – 2.94 (m, 2H), 2.71 (d, *J* = 16.6 Hz, 1H), 2.54 (t, *J* = 8.1 Hz, 2H), 2.45 (d, *J* = 19.0 Hz, 1H), 2.00 (s, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 177.4, 143.6, 129.6, 128.9, 123.6, 122.9, 108.4, 78.9, 50.8, 38.6, 27.3, 27.0, 26.4. **HRMS (ESI)** calcd. for $C_{14}H_{15}NOBr$ $[M+H]^+$: 292.0337; Found: 292.0335 & 294.0302.

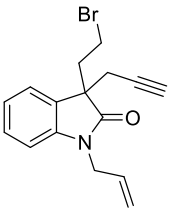
1-Benzyl-3-(2-bromoethyl)-3-(prop-2-yn-1-yl)indolin-2-one (5b): Using **GP-3**, 3-substituted oxindole **3b** (65 mg, 0.25 mmol), 1,2-dibromoethane (94 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **5b** (66 mg, 72%) as a brown sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.3 Hz, 1H), 7.33 – 7.26 (m, 5H), 7.22 (t, *J* = 7.9 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 5.00 (d, *J* = 15.6 Hz, 1H), 4.84 (d, *J* = 15.6 Hz, 1H), 3.14 – 3.06 (m, 1H), 3.03 – 2.95 (m, 1H), 2.79 (d, *J* = 18.6 Hz, 1H), 2.66 – 2.53 (m, 3H), 1.97 (s, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 177.6, 142.8, 135.7, 129.6, 128.9, 127.9, 127.5, 123.7, 123.0, 109.5, 78.9, 71.7, 51.0, 44.1, 39.0, 27.6, 26.9. **HRMS (ESI)** calcd. for $C_{20}H_{19}NOBr$ $[M+H]^+$: 368.0650; Found: 368.0651 & 370.0631.



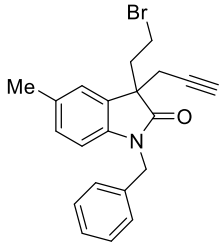
3-(2-Bromoethyl)-1-phenyl-3-(prop-2-yn-1-yl)indolin-2-one (5c): Using **GP-3**, 3-substituted oxindole **3c** (62 mg, 0.25 mmol), 1,2-dibromoethane (94 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **5c** (62 mg, 70%) as a brown sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (dt, *J* = 14.9, 7.5 Hz, 3H), 7.42 (t, *J* = 9.4 Hz, 3H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 3.25 – 3.09 (m, 2H), 2.82 (d, *J* = 19.0 Hz, 1H), 2.73 – 2.58 (m, 3H), 2.03 (s, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 177.1, 143.9, 134.4, 129.8, 129.4, 128.9, 128.4, 126.7, 123.9, 123.4, 109.8, 78.8, 71.7, 51.1, 39.0, 28.1, 27.1. **HRMS (ESI)** calcd. for $C_{19}H_{17}NOBr$ $[M+H]^+$: 354.0494; Found: 354.0492 & 356.0459.



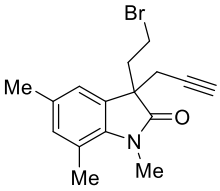
1-Allyl-3-(2-bromoethyl)-3-(prop-2-yn-1-yl)indolin-2-one (5d): Using **GP-3**, 3-substituted oxindole **3d** (53 mg, 0.25 mmol), 1,2-dibromoethane (94 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **5d** (56 mg, 71%) as a brown sticky liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.4 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.14 – 7.07 (m, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 5.90 – 5.74 (m, 1H), 5.30 – 5.17 (m, 2H), 4.35 (t, *J* = 5.0 Hz, 2H), 3.14 – 2.92 (m, 2H), 2.74 (d, *J* = 16.6 Hz, 1H), 2.63 – 2.48 (m, 3H), 1.99 (s, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 177.2, 142.9, 131.3, 129.6, 128.9, 123.7, 123.0, 117.9, 109.4, 78.9, 71.6, 51.0, 42.6, 38.9, 27.6, 26.9. **HRMS (ESI)** calcd. for $C_{16}H_{17}NOBr$ $[M+H]^+$: 318.0494; Found: 318.0495 & 320.0505.



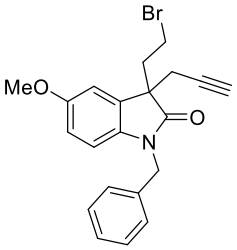
1-Benzyl-3-(2-bromoethyl)-5-methyl-3-(prop-2-yn-1-yl)indolin-2-one (5e): Using **GP-3**, 3-substituted oxindole **3e** (69 mg, 0.25 mmol), 1,2-dibromoethane (94 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **5e** (76 mg, 79%) as a brown sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 4.3 Hz, 4H), 7.27 (d, *J* = 4.9 Hz, 1H), 7.23 (s, 1H), 7.01 (d, *J* = 7.9 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 4.98 (d, *J* = 15.6 Hz, 1H), 4.82 (d, *J* = 15.5 Hz, 1H), 3.14 – 3.05 (m, 1H), 3.03 – 2.93 (m, 1H), 2.77 (d, *J* = 16.5 Hz, 1H), 2.66 – 2.49 (m, 3H), 2.34 (s, 3H), 1.97 (s, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 177.5, 140.4, 135.8, 132.6, 129.6, 129.2, 128.8, 127.8, 127.5, 124.4, 109.2, 79.0, 71.6, 51.1, 44.1, 39.2, 27.6, 27.0, 21.3. **HRMS (ESI)** calcd. for $C_{21}H_{21}NOBr$ $[M+H]^+$: 382.0807; Found: 382.0808 & 384.0752.



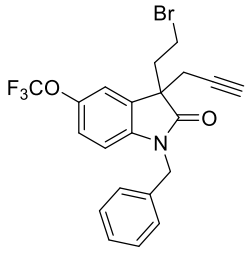
3-(2-Bromoethyl)-1,5,7-trimethyl-3-(prop-2-yn-1-yl)indolin-2-one (5f): Using **GP-3**, 3-substituted oxindole **3f** (53 mg, 0.25 mmol), 1,2-dibromoethane (94 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **5f** (61 mg, 76%) as a brown sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.06 (s, 1H), 6.85 (s, 1H), 3.46 (s, 3H), 3.08 – 2.91 (m, 2H), 2.68 (d, *J* = 16.6 Hz, 1H), 2.56 – 2.49 (m, 4H), 2.48 – 2.41 (m, 2H), 2.30 (s, 3H), 2.00 (s, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 178.2, 139.0, 133.1, 132.4, 130.4, 122.1, 119.7, 79.1, 71.5, 50.3, 39.1, 29.8, 27.7, 27.2, 21.0, 19.0. **HRMS (ESI)** calcd. for $C_{16}H_{19}NOBr$ $[M+H]^+$: 320.0650; Found: 320.0648 & 322.0656.



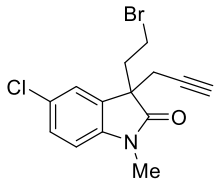
3-(2-Bromoethyl)-5-methoxy-1-methyl-3-(prop-2-yn-1-yl)indolin-2-one (5g): Using **GP-3**, 3-substituted oxindole **3g** (73 mg, 0.25 mmol), 1,2-dibromoethane (94 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **5g** (80mg, 80%) as a brown sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 3.0 Hz, 5H), 7.05 (s, 1H), 6.73 (d, *J* = 8.5 Hz, 1H), 6.66 (d, *J* = 8.5 Hz, 1H), 4.97 (d, *J* = 15.6 Hz, 1H), 4.81 (d, *J* = 15.6 Hz, 1H), 3.77 (s, 3H), 3.14 – 3.06 (m, 1H), 3.03 – 2.96 (m, 1H), 2.78 (d, *J* = 14.0 Hz, 1H), 2.66 – 2.59 (m, 1H), 2.58 – 2.52 (m, 2H), 1.99 (s, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 177.2, 156.2, 136.2, 135.8, 131.0, 128.9, 127.8, 127.5, 112.9, 111.3, 109.8, 78.9, 71.8, 55.8, 51.3, 44.2, 39.1, 27.6, 26.8. **HRMS (ESI)** calcd. for $C_{21}H_{21}NO_2Br$ $[M+H]^+$: 398.0756; Found: 398.0754 & 400.0736.



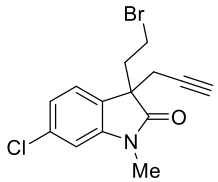
3-(2-Bromoethyl)-1-methyl-3-(prop-2-yn-1-yl)-5-(trifluoromethoxy)indolin-2-one (5h): Using **GP-3**, 3-substituted oxindole **3h** (86 mg, 0.25 mmol), 1,2-dibromoethane (94 mg, 0.50 mmol), powdered KOH (28 mg, 0.50mmol) in 0.5 mL DMF provided compound **5h** (78 mg, 69%) as a brown sticky liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40 – 7.22 (m, 6H), 7.09 (d, *J* = 9.9 Hz, 1H), 6.75 (d, *J* = 8.5 Hz, 1H), 5.00 (d, *J* = 15.6 Hz, 1H), 4.83 (d, *J* = 15.6 Hz, 1H), 3.17 – 2.97 (m, 2H), 2.80 (d, *J* = 16.6 Hz, 1H), 2.71 – 2.48 (m, 3H), 2.03 (s, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 177.5, 145.0, 141.4, 135.2, 131.2, 129.1, 128.1, 127.5, 121.9, 120.6 (q, $J_{C\text{-}F}$ = 256.7 Hz), 117.9, 109.9, 78.3, 72.3, 51.1, 44.4, 38.6, 27.6, 26.4. **HRMS (ESI)** calcd. for $C_{21}H_{18}F_3NO_2Br$ $[M+H]^+$: 452.0473; Found: 452.0471 & 454.0506.



3-(2-Bromoethyl)-5-chloro-1-methyl-3-(prop-2-yn-1-yl)indolin-2-one (5i): Using **GP-3**, 3-substituted oxindole **3i** (55 mg, 0.25 mmol), 1,2-dibromoethane (94 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **5i** (60 mg, 73%) as a brown sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.31 (d, *J* = 8.3 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 3.20 (s, 3H), 3.09 – 2.97 (m, 2H), 2.73 (d, *J* = 16.7 Hz, 1H), 2.60 – 2.51 (m, 2H), 2.45 (d, *J* = 16.7 Hz, 1H), 2.05 (s, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 177.1, 142.3, 131.4, 129.0, 128.4, 124.3, 109.4, 78.4, 72.1, 51.0, 38.4, 27.3, 26.6. **HRMS (ESI)** calcd. for $C_{14}H_{14}NOClBr$ $[M+H]^+$: 325.9947; Found: 325.9945 & 327.9910.

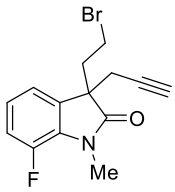


3-(2-Bromoethyl)-6-chloro-1-methyl-3-(prop-2-yn-1-yl)indolin-2-one (5j): Using **GP-3**, 3-substituted oxindole **3j** (55 mg, 0.25 mmol), 1,2-dibromoethane (94 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **5j** (61 mg, 74%) as brown sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.9 Hz, 1H), 7.09 (d, *J* = 9.3 Hz, 1H), 6.88 (s, 1H), 3.20 (s, 3H), 3.07 – 2.98 (m, 2H), 2.72 (d, *J* = 16.6 Hz, 1H), 2.55 (m, 2H), 2.46 (d, *J* = 16.6 Hz, 1H), 2.02 (s, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 177.5, 144.9, 134.9, 124.7, 122.8, 109.3, 78.6, 71.9, 50.7, 38.5, 27.5, 26.7. **HRMS (ESI)** calcd. for $C_{14}H_{14}NOClBr$ $[M+H]^+$: 325.9947; Found: 325.9946 & 327.9924.

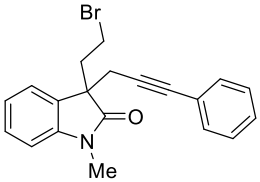


3-(2-Bromoethyl)-7-fluoro-1-methyl-3-(prop-2-yn-1-yl)indolin-2-one (5k): Using **GP-3**, 3-substituted oxindole **3k** (51 mg, 0.25 mmol), 1,2-dibromoethane (94 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **5k** (54 mg, 70%) as a brown sticky liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.24 – 7.18 (m, 1H), 7.09 – 6.98 (m, 2H),

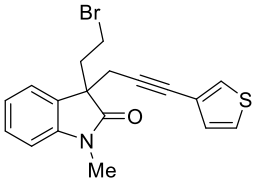
3.41 (d, *J* = 2.7 Hz, 3H), 3.10 – 2.91 (m, 2H), 2.70 (d, *J* = 16.6 Hz, 1H), 2.61 – 2.42 (m, 3H), 2.01 (s, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 177.1, 147.8 (d, $J_{C\text{-}F}$ = 244.62 Hz), 132.52 (d, $J_{C\text{-}F}$ = 3.0 Hz), 130.3 ($J_{C\text{-}F}$ = 7.5 Hz), 123.51 (d, $J_{C\text{-}F}$ = 6.0 Hz), 119.4 (d, $J_{C\text{-}F}$= 3.0Hz), 117.0, 116.8, 78.5, 71.8, 51.2, 38.7, 28.9 (d, $J_{C\text{-}F}$ = 6.04 Hz), 27.6, 26.7. **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -136.0. **HRMS (ESI)** calcd. for $C_{14}H_{14}NOFBr$ $[M+H]^+$: 310.0243; Found: 310.0244 & 312.0254.



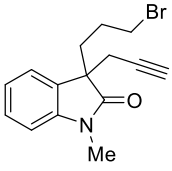
3-(2-Bromoethyl)-1-methyl-3-(3-phenylprop-2-yn-1-yl)indolin-2-one (5l): Using **GP-3**, 3-substituted oxindole **3l** (65 mg, 0.25 mmol), 1,2-dibromoethane (94 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **5l** (71 mg, 77%) as a brown sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 8.3 Hz, 1H), 7.29 (s, 5H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 3.23 (s, 3H), 3.14 – 3.01 (m, 2H), 2.96 (d, *J* = 16.6 Hz, 1H), 2.71 – 2.60 (m, 3H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 177.7, 143.8, 131.7, 130.0, 128.9, 128.4, 128.2, 123.8, 123.2, 123.0, 108.4, 84.5, 83.66, 51.5, 38.7, 28.6, 27.2, 26.5. **HRMS (ESI)** calcd. for $C_{20}H_{19}NOBr$ $[M+H]^+$: 368.0650; Found: 368.0652 & 370.0596.



3-(2-bromoethyl)-1-methyl-3-(3-(thiophen-3-yl)prop-2-yn-1-yl)indolin-2-one (5m): Using **GP-3**, 3- substituted oxindole **3m** (67 mg, 0.25 mmol), 1,2-dibromoethane (94 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **5m** (76 mg, 81%) as a brown sticky liquid.**^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.1 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 4.3 Hz, 1H), 7.22 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 5.0 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 3.22 (s, 3H), 3.14 – 2.98 (m, 2H), 2.93 (d, *J* = 16.7 Hz, 1H), 2.70 – 2.58 (m, 3H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 177.7, 143.7, 129.9, 129.9, 128.9, 128.5, 125.3, 123.8, 123.0, 122.1, 108.4, 84.1, 78.8, 77.6, 77.2, 76.7, 51.4, 38.7, 28.6, 27.2, 26.5. **HRMS (ESI)** calcd. for $C_{18}H_{17}NOSBr$ $[M+H]^+$: 374.0214; Found: 374.0215 & 376.0195.



3-(3-Bromopropyl)-1-methyl-3-(prop-2-yn-1-yl)indolin-2-one (6a): Using **GP-3**, 3-substituted oxindole **3a** (46 mg, 0.25 mmol), 1,3-dibromopropane (101 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **6a** (54 mg, 70%) as a brown sticky liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.1 Hz, 1H), 7.32 (t, *J* = 8.4 Hz, 1H), 7.14 – 7.07 (m, 1H), 6.86 (d, *J* = 7.7



Hz, 1H), 3.29 – 3.20 (m, 5H), 2.71 (d, *J* = 16.6 Hz, 1H), 2.50 (d, *J* = 16.6 Hz, 1H), 2.21 – 1.99 (m, 2H), 1.96 (s, 1H), 1.61 – 1.51 (m, 1H), 1.47 – 1.33 (m, 1H). **$^{13}C\{^{1}H\}$ NMR** (75 MHz, $CDCl_3$) δ 178.3, 143.7, 130.8, 128.7, 123.6, 122.9, 108.2, 79.3, 71.1, 50.5, 34.6, 33.1, 27.8, 27.6, 26.4. **HRMS (ESI)** calcd. for $C_{15}H_{17}NOBr$ $[M+H]^+$: 306.0494; Found: 306.0492 & 308.0464.

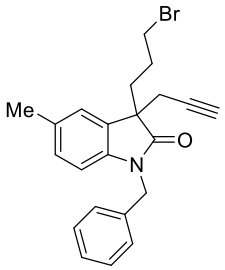
1-Benzyl-3-(3-bromopropyl)-3-(prop-2-yn-1-yl)indolin-2-one (6b): Using **GP-3**, 3-substituted oxindole **3b** (65 mg, 0.25 mmol), 1,3-dibromopropane (101 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **6b** (65 mg, 68%) as a brown sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.3 Hz, 1H), 7.31 (d, *J* = 3.4 Hz, 5H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 4.97 (d, *J* = 15.6 Hz, 1H), 4.88 (d, *J* = 15.6 Hz, 1H), 3.26 (q, *J* = 6.4 Hz, 2H), 2.77 (d, *J* = 16.6 Hz, 1H), 2.61 (d, *J* = 14.1 Hz, 1H), 2.20 – 2.06 (m, 2H), 1.92 (s, 1H), 1.67 – 1.59 (m, 2H), 1.48 – 1.39 (m, 1H). **$^{13}C\{^{1}H\}$ NMR** (151 MHz, $CDCl_3$) δ 178.5, 142.9, 135., 130.7, 128., 128.6, 127.8, 127.5, 123.6, 123.0, 109.3, 79.4, 71.2, 50.6, 44.0, 34.9, 33.1, 27.8, 27.7. **HRMS (ESI)** calcd. for $C_{21}H_{21}NOBr$ $[M+H]^+$: 382.0807; Found: 382.0808 & 384.0788.

3-(3-Bromopropyl)-1-phenyl-3-(prop-2-yn-1-yl)indolin-2-one (6c): Using **GP-3**, 3-substituted oxindole **3c** (62 mg, 0.25 mmol), 1,3-dibromopropane (101 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **6c** (59 mg, 64%) as a brown sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (t, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 6.6 Hz, 3H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 3.32 (d, *J* = 6.4 Hz, 1H), 3.29 (d, *J* = 7.3 Hz, 1H), 2.80 (d, *J* = 16.4 Hz, 1H), 2.70 (d, *J* = 18.9 Hz, 1H), 2.25 – 2.10 (m, 2H), 1.98 (s, 1H), 1.81 – 1.68 (m, 1H), 1.55 (s, 3H), 1.33 – 1.23 (m, 1H), 0.92 – 0.78 (m, 1H). **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$) δ 177.9, 143.9, 134.5, 130.5, 129.8, 128.6, 128.4, 126.7, 123.7, 123.4, 109.6, 79.2, 71.2, 50.8, 35.1, 33.1, 28.1, 27.9. **HRMS (ESI)** calcd. for $C_{20}H_{19}NOBr$ $[M+H]^+$: 368.0650; Found: 368.0648 & 370.0620.

1-Allyl-3-(3-bromopropyl)-3-(prop-2-yn-1-yl)indolin-2-one (6d): Using **GP-3**, 3-substituted oxindole **3d** (53 mg, 0.25 mmol), 1,3-dibromopropane (101 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **6d** (59 mg, 71%) as a brown sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.4 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* =

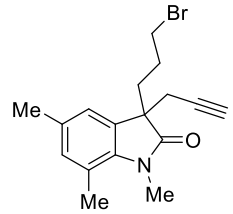
7.8 Hz, 1H), 5.87 – 5.76 (m, 1H), 5.27 – 5.18 (m, 2H), 4.35 (s, 2H), 3.25 (q, *J* = 6.4 Hz, 2H), 2.73 (d, *J* = 16.5 Hz, 1H), 2.55 (d, *J* = 16.5 Hz, 1H), 2.20 – 2.10 (m, 1H), 2.04 (t, *J* = 12.4 Hz, 1H), 1.94 (s, 1H), 1.61 (dd, *J* = 19.5, 5.9 Hz, 1H), 1.46 – 1.34 (m, 1H). **$^{13}C\{^{1}H\}$ NMR** (151 MHz, $CDCl_3$) δ 178.0, 142.9, 131.4, 130.7, 128.5, 123.5, 122.9, 117.8, 109.2, 79.3, 71.2, 50.5, 42.5, 34.8, 33.1, 27.8, 27.7. **HRMS (ESI)** calcd. for $C_{17}H_{19}NOBr$ $[M+H]^+$: 332.0650; Found: 332.0648 & 334.0660.

1-Benzyl-3-(3-bromopropyl)-5-methyl-3-(prop-2-yn-1-yl)indolin-2-one (6e): Using **GP-3**,



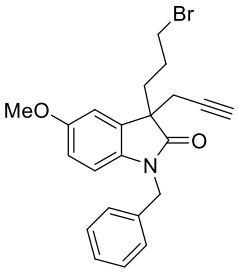
3-substituted oxindole **3e** (69 mg, 0.25mmol), 1,3-dibromopropane (101 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **6e** (67 mg, 68%) as a brown sticky liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 5H), 7.20 (s, 1H), 7.00 (d, *J* = 7.2 Hz, 1H), 6.64 (d, *J* = 7.9 Hz, 1H), 5.00 – 4.85 (m, 2H), 3.29 – 3.22 (m, 2H), 2.75 (d, *J* = 19.2 Hz, 1H), 2.60 (d, *J* = 13.9 Hz, 1H), 2.33 (s, 3H), 2.16 – 2.06 (m, 2H), 1.92 (s, 1H), 1.67 – 1.59 (m, 1H), 1.49 – 1.40 (m, 1H). **$^{13}C\{^{1}H\}$ NMR** (151 MHz, $CDCl_3$) δ 178.3, 140.5, 136.0, 132.5, 130.7, 128.8, 128.79, 127.7, 127.5, 124.3, 109.0, 79.5, 71.1, 50.6, 44.0, 35.0, 33.1, 27.8, 27.7, 21.3. **HRMS (ESI)** calcd. for $C_{22}H_{23}NOBr$ $[M+H]^+$: 396.0963; Found: 396.0964 & 398.0912.

3-(3-Bromopropyl)-1,5,7-trimethyl-3-(prop-2-yn-1-yl)indolin-2-one (6f): Using **GP-3**, 3-

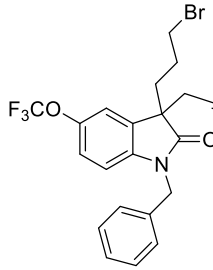


substituted oxindole **3f** (53 mg, 0.25 mmol), 1,3-dibromopropane(101 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **4d** (57 mg, 68%) as brown sticky liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.03 (s, 1H), 6.83 (s, 1H), 3.47 (s, 3H), 3.30 – 3.18 (m, 2H), 2.66 (d, *J* = 16.5 Hz, 1H), 2.53 (s, 3H), 2.48 (d, *J* = 13.9 Hz, 1H), 2.30 (s, 3H), 2.09 – 1.98 (m, 2H), 1.96 (s, 1H), 1.63 – 1.49 (m, 1H), 1.46 – 1.31 (m, 1H). **$^{13}C\{^{1}H\}$ NMR** (151 MHz, $CDCl_3$) δ 179.0, 139.0, 132.9, 132.2, 131.5, 122.0, 119.4, 79.5, 71.0, 49.9, 34.9, 33.2, 29.7, 27.9, 27.8, 21.0, 19.0. **HRMS (ESI)** calcd. for $C_{17}H_{21}NOBr$ $[M+H]^+$: 334.0807; Found: 334.0808 & 336.0814.

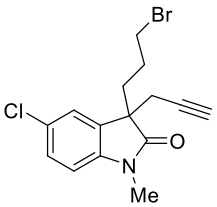
1-Benzyl-3-(3-bromopropyl)-5-methoxy-3-(prop-2-yn-1-yl)indolin-2-one (6g): Using **GP-3**, 3-substituted oxindole **3g** (73 mg, 0.25 mmol), 1,3-dibromopropane (101 mg, 0.50 mmol), powdered KOH (28mg, 0.50mmol) in 0.5 mL DMF provided compound **6g** (69mg, 67%) as a brown sticky liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.30 – 7.22 (m, 5H), 7.01 (s, 1H), 6.69 (d, *J* = 11.0 Hz, 1H), 6.61 (d, *J* = 8.5 Hz, 1H), 4.92 (d, *J* = 15.6 Hz, 1H), 4.83 (d, *J* = 15.6 Hz, 1H), 3.75 (s, 3H), 3.23 (td, *J* = 6.6, 3.2 Hz, 2H), 2.73 (d, *J* = 16.5 Hz, 1H), 2.57 (d, *J* = 16.5 Hz, 1H), 2.15 – 2.02 (m, 2H), 1.92 (s, 1H), 1.65 – 1.57 (m, 1H), 1.49 – 1.37 (m, 1H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 178.1, 156.2, 136.3, 135.9, 132.1, 128.8, 127.8, 127.5, 112.6, 111.2, 109.6, 79.4, 71.3, 55.8, 50.9, 44.1, 34.9, 33.1, 27.9, 27.7**. HRMS (ESI)** calcd. for $C_{22}H_{23}NO_2Br$ $[M+H]^+$: 412.0912; Found: 412.0913 & 414.0894.



1-Benzyl-3-(3-bromopropyl)-3-(prop-2-yn-1-yl)-5-(trifluoromethoxy)indolin-2-one (6h): Using **GP-3**, 3-substituted oxindole **3h** (86 mg, 0.25 mmol), 1,3-dibromopropane (101 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **6h** (72 mg, 62%) as a brown sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 6H), 7.07 (d, *J* = 9.7 Hz, 1H), 6.73 (d, *J* = 8.5 Hz, 1H), 4.96 (d, *J* = 15.6 Hz, 1H), 4.88 (d, *J* = 15.6 Hz, 1H), 3.34 – 3.20 (m, 2H), 2.78 (d, *J* = 16.6 Hz, 1H), 2.60 (d, *J* = 16.6 Hz, 1H), 2.22 – 2.08 (m, 2H), 1.98 (s, 1H), 1.68 – 1.61 (m, 1H), 1.49 – 1.37 (m, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 178.2, 141.5, 135.4, 132.3, 129.0, 128.0, 127.5, 121.6, 120.6 (q, $J_{C\text{-}F}$ = 256.7 Hz), 117.7, 109.7, 78.7, 71.8, 50.8, 44.2, 34.6, 32.8, 27.7, 27.6. **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -58.29. **HRMS (ESI)** calcd. for $C_{22}H_{20}NO_2F_3Br$ $[M+H]^+$: 466.0630; Found: 466.0628 & 468.0596.

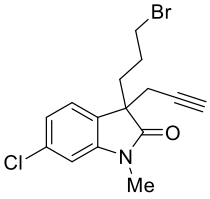


3-(3-Bromopropyl)-5-chloro-1-methyl-3-(prop-2-yn-1-yl)indolin-2-one (6i): Using **GP-3**, 3-substituted oxindole **3i** (55 mg, 0.25 mmol), 1,3-dibromopropane (101 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **6i** (57 mg, 67%) as a brown sticky liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.39 (s, 1H), 7.28 (d, *J* = 10.3 Hz, 1H), 6.78 (d, *J* = 8.3 Hz, 1H), 3.25 (t, *J* = 6.7 Hz, 2H), 3.19 (s, 3H), 2.69 (d, *J* = 14.4 Hz, 1H), 2.48 (d, *J* = 19.8 Hz, 1H), 2.16 – 2.02 (m, 2H), 1.99 (s, 1H), 1.63 – 1.49 (m, 1H), 1.47 – 1.30 (m, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 177.8, 142.3, 132.5, 128.6, 128.3, 124.0, 109.1, 78.8, 71.6, 50.7, 34.5,

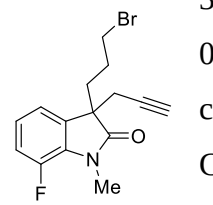


32.8, 27.6, 27.4, 26.5. **HRMS (ESI)** calcd. for $C_{15}H_{16}NOClBr$ $[M+H]^+$: 340.0104; Found: 340.0102 & 342.0067.

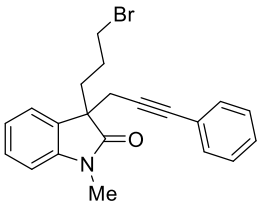
3-(3-Bromopropyl)-6-chloro-1-methyl-3-(prop-2-yn-1-yl)indolin-2-one (6j): Using **GP-3**, 3-substituted oxindole **3j** (55 mg, 0.25 mmol), 1,3-dibromopropane(101 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **6j** (58 mg, 68%) as a brown sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.9 Hz, 1H), 7.08 (d, *J* = 9.7 Hz, 1H), 6.86 (s, 1H), 3.30 – 3.22 (m, 2H), 3.20 (s, 3H), 2.70 (d, *J* = 16.6 Hz, 1H), 2.49 (d, *J* = 16.6 Hz, 1H), 2.16 – 2.00 (m, 2H), 1.96 (s, 1H), 1.59 – 1.50 (m, 1H), 1.45 – 1.33 (m, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 178.3, 145.0, 134.5, 129.1, 124.5, 122.8, 109.0, 79.0, 71.4, 50.4, 34.5, 33.0, 27.7, 27.5, 26.5. **HRMS (ESI)** calcd. for $C_{15}H_{16}NOClBr$ $[M+H]^+$: 340.0104; Found: 340.0105 & 342.0085.



3-(3-Bromopropyl)-7-fluoro-1-methyl-3-(prop-2-yn-1-yl)indolin-2-one (6k): Using **GP-3**, 3-substituted oxindole **3k** (51 mg, 0.25 mmol), 1,3-dibromopropane (101 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **6k** (53 mg, 66%) as a brown sticky liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.22 – 7.15 (m, 1H), 7.04 (d, *J* = 2.3 Hz, 1H), 7.03 – 6.99 (m, 1H), 3.42 (d, *J* = 2.7 Hz, 3H), 3.31 – 3.19 (m, 2H), 2.69 (d, *J* = 13.9 Hz, 1H), 2.52 (d, *J* = 13.9 Hz, 1H), 2.17 – 1.99 (m, 2H), 1.96 (s, 1H), 1.65 – 1.51 (m, 1H), 1.46 – 1.30 (m, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 177.9, 147.8 (d, J_{C-F} = 244.6 Hz), 133.7, 130.3(d, J_{C-F} = 9.1 Hz), 123.5 (d, J_{C-F} = 6.0 Hz), 119.3 (d, J_{C-F} = 3.0 Hz), 116.6 (d, J_{C-F} = 18.1 Hz), 78.9, 71.3, 51.0, 34.7, 33.0, 28.8(d, J_{C-F} = 6.0 Hz), 27.7 (d, J_{C-F} = 4.5 Hz). **HRMS (ESI)** calcd. for $C_{15}H_{16}NFOBr$ $[M+H]^+$: 324.0399; Found: 324.0397 & 326.0407.

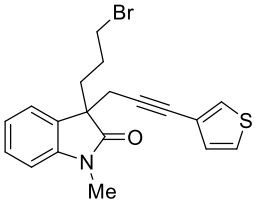


3-(3-Bromopropyl)-1-methyl-3-(3-phenylprop-2-yn-1-yl)indolin-2-one (6l): Using **GP-3**, 3-substituted oxindole **3l** (65 mg, 0.25 mmol), 1,3-dibromopropane (101 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **6l** (68 mg, 71%) as a brown sticky liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.4 Hz, 1H), 7.17 (t, *J* = 8.3 Hz, 1H), 7.12 (s, 5H), 6.96 (t, *J* = 7.9 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 3.12 (t, *J* = 5.5 Hz, 2H), 3.07 (s, 3H), 2.78 (d, *J* = 16.6 Hz, 1H), 2.55 (d, *J* = 16.6 Hz, 1H), 2.13 – 2.03 (m, 1H), 2.02 – 1.92 (m, 1H), 1.53 – 1.41 (m, 1H), 1.36 – 1.24 (m, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 178.5, 143.8, 131.6, 131.0, 128.6, 128.3, 128.1, 123.6, 123.4, 122.9, 108.1, 85.0, 83.2, 51.1,



34.5, 33.2, 28.7, 27.9, 26.4. **HRMS (ESI)** calcd. for $C_{21}H_{21}NOBr$ $[M+H]^+$: 382.0807; Found: 382.0805 & 384.0749.

3-(3-bromopropyl)-1-methyl-3-(3-(thiophen-3-yl)prop-2-yn-1-yl)indolin-2-one (6m):



Using **GP-3**, 3- substituted oxindole **3m** (67 mg, 0.25 mmol), 1,3-dibromopropane (101 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **6m** (69 mg, 71%) as a brown sticky liquid.**^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.23 – 7.19 (m, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 6.1 Hz, 1H), 6.87 (d, *J* = 7.7 Hz, 1H), 3.27 (t, *J* = 6.8 Hz, 2H), 3.22 (s, 3H), 2.91 (d, *J* = 16.6 Hz, 1H), 2.67 (d, *J* = 16.6 Hz, 1H), 2.24 – 2.07 (m, 2H), 1.67 – 1.54 (m, 1H), 1.50 – 1.37 (m, 1H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 178.5, 143.7, 131.0, 130.0, 128.6, 128.3, 125.2, 123.6, 122.9, 122.3, 108.1, 84.6, 78.4, 51.0, 34.5, 33.3, 28.7, 27.9, 26.4. **HRMS (ESI)** calcd. for $C_{19}H_{19}NOSBr$ $[M+H]^+$: 388.0371; Found: 388.0370 & 390.0314.

7.0 Optimization for the synthesis of cycloaddition products:

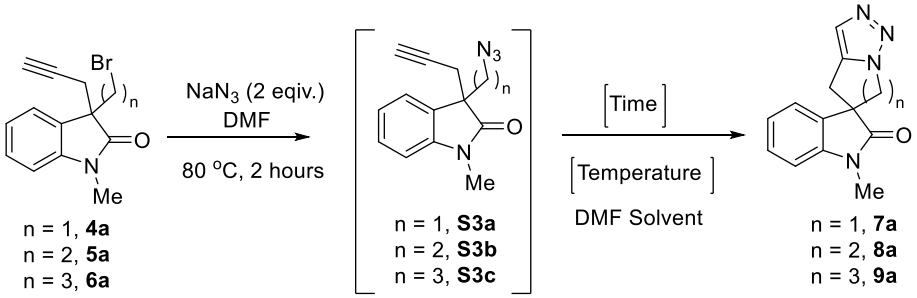


Table S1: Optimization table for the synthesis of **7a, 8a, 9a** from the corresponding azides of bromo derivatives **4a**, **5a**, **6a**

Entry	Reactant	Solvent	Time (h)	Temperature	Product	Isolated Yield (%)
1	Azide of **4a**	DMF	4	80 °C	**7a**	8
2	Azide of **4a**	DMF	4	100 °C	**7a**	32
3	Azide of **4a**	DMF	10	100 °C	**7a**	74
4	Azide of **4a**	DMF	22	100 °C	**7a**	86
5	Azide of **4a**	DMF	22	120 °C	**7a**	84
6	Azide of **5a**	DMF	4	80 °C	**8a**	61

7	Azide of **5a**	DMF	4	100 °C	**8a**	92
8	Azide of **6a**	DMF	4	80 °C	**9a**	No reaction
9	Azide of **6a**	DMF	10	80 °C	**9a**	No reaction
10	Azide of **6a**	DMF	10	100 °C	**9a**	10
11	Azide of **6a**	DMF	22	100 °C	**9a**	45
12	Azide of **6a**	DMF	22	120 °C	**9a**	56
13	Azide of **6a**	DMF	46	120 °C	**9a**	72

A solution of 3, 3-disubstituted oxindole **4a, 5a, 6a** (0.15 mmol, 1 eqiv.) and NaN_3 (0.30 mmol, 2 eqiv.) in DMF (1 mL) was taken in a 10 mL round-bottom flask. The reaction mixture was heated on an oil bath at 80 °C for the first 2 hours. Complete conversion of bromo derivatives to azide derivatives were indicated by TLC. To get further confirmation on it, we isolated corresponding azides of **4a, 5a, 6a**. IR spectra as well as NMR were recorded. In IR a strong peak at 2100 cm^{-1} region confirmed the formation of azide from bromo derivatives.

We also carried out series of reactions taking exactly same amount of bromo derivatives (**4a, 5a, 6a),** NaN_3 and DMF solvent. In each case for first two hours we keep the temperature at 80 °C to allow complete conversion of bromo to azide. Interestingly, for **5a** some product formation was observed at the bottom of the TLC along with the complete conversion of bromo to azide. If temperature was kept at 80 °C for another 4 hours 61% yield of **8a** was obtained. When the temperature is increased to 100 °C from 80 °C after 2 hours and continued for 4 hours, the yield improved to 92% and also no unreacted azide was left in the reaction mixture as indicated by TLC (**Entry 7**). However for **4a,** if heating was continued for another 4 hours only 8% yield of **7a** was obtained (**Entry 1**). Best result was obtained when heating at 100 °C was continued for 22 hours (**Entry 4**) with 86% yield of **8a**. For **6a**, even heating at 100 °C for 22 hours was not enough for the complete consumption of azide (**Entry 11**). Complete conversion of azide of **6a** along with highest yield of 76% was observed when the temperature was increased to 120 °C for 46 hours (**Entry 13**).

8.0 General procedure for the synthesis of 5, 6, 7-membered ring containing spirooxindoles 7, 8, 9a-l (GP-4): A solution of 3,3-disubstituted oxindole **4, 5, 6a-m** (0.15 mmol, 1 eqiv.) and NaN_3 (0.30 mmol, 2 eqiv.) in DMF (1 mL) was taken in a 10 mL round-bottom flask. The reaction mixture was heated on an oil bath at 80 °C for the first 2 hours.

Now taking **Entry 4, 7, 13** of **Table S2** as the optimal reaction conditions

(i) for compound **4a-m,** the heating was raised to 100 °C and maintained for 22 hours,

(ii) for compounds **5a-m**, the heating was increased to 100 °C and maintained for 4 hours.

(iii) for compounds **6a-m**, the heating was increased to 120 °C and maintained for 46 hours.

Upon completion of the reaction, as indicated by thin-layer chromatography (TLC), the DMF was removed from the reaction mixture under reduced pressure. The reaction mixture was then diluted with water and extracted with ethyl acetate (EtOAc). The organic layer was washed with brine, dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated. The residue was purified by column chromatography on silica gel using a dichloromethane/methanol (CH_2Cl_2/MeOH) mixture (99:1) as the eluent to give compounds **7, 8, 9a-m** in good to excellent yields.

3-(azidomethyl)-1-methyl-3-(prop-2-yn-1-yl)indolin-2-one (S3a): A solution of 3,3-disubstituted oxindole **4a** (42mg, 0.15 mmol, 1 eqiv.) and NaN_3 (0.30 mmol, 2 eqiv.) in DMF (1 mL) was taken in a 10 mL round-bottom flask. The reaction mixture was heated on an oil bath at 80 °C for 2 hours. Upon completion of the reaction, as indicated by thin-layer chromatography (TLC), the DMF was removed from the reaction mixture under reduced pressure. The reaction mixture was then diluted with water and extracted with ethyl acetate (EtOAc). The organic layer was washed with brine, dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated. The residue was purified by column chromatography (Hexane/EtOAc, 9:1) to give compound **S3a** as colourless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 8.3 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 3.89 (d, *J* = 12.1 Hz, 1H), 3.72 (d, *J* = 12.1 Hz, 1H), 3.25 (s, 3H), 2.78 (d, *J* = 19.4 Hz, 1H), 2.51 (d, *J* = 16.8 Hz, 1H), 2.03 (s, 1H)**. ^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 176.4, 144.0, 129.4, 128.8, 124.0, 123.0, 108.5, 78.4, 71.8, 55.4, 50.8, 26.6, 24.7. In IR a strong peak at 2102.22 cm^{-1} indicates the presence of azide group.

3-(2-azidoethyl)-1-methyl-3-(prop-2-yn-1-yl)indolin-2-one (S3b): A solution of 3,3-disubstituted oxindole **5a** (44mg, 0.15 mmol, 1 eqiv.) and NaN_3 (0.30 mmol, 2 eqiv.) in DMF (1 mL) was taken in a 10 mL round-bottom flask. The reaction mixture was heated on an oil bath at 80 °C for 2 hours. Upon completion of the reaction, as indicated by thin-layer chromatography (TLC), the DMF was removed from the reaction mixture under reduced pressure. The reaction mixture was then diluted with water and extracted with ethyl acetate (EtOAc). The organic layer was washed with brine, dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated. The

residue was purified by column chromatography (Hexane/EtOAc, 9:1) to give compound **S3b** as colourless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 6.9 Hz, 1H), 7.33 (t, *J* = 7.1 Hz, 1H), 7.15 – 7.07 (m, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 3.23 (s, 3H), 3.06 – 2.93 (m, 2H), 2.73 (d, *J* = 16.6 Hz, 1H), 2.46 (d, *J* = 19.2 Hz, 1H), 2.33 – 2.24 (m, 2H), 2.01 (s, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 177.9, 143.6, 129.9, 128.9, 123.7, 122.9, 108.5, 79.1, 71.5, 49.2, 47.5, 34.4, 27.8, 26.5. In IR a strong peak at 2097.08 cm^{-1} indicates the presence of azide group.

3-(3-azidopropyl)-1-methyl-3-(prop-2-yn-1-yl)indolin-2-one (S3c): A solution of 3,3-disubstituted oxindole **6a** (46 mg, 0.15 mmol, 1 eqiv.) and NaN_3 (0.30 mmol, 2 eqiv.) in DMF (1 mL) was taken in a 10 mL round-bottom flask. The reaction mixture was heated on an oil bath at 80 °C for 2 hours. Upon completion of the reaction, as indicated by thin-layer chromatography (TLC), the DMF was removed from the reaction mixture under reduced pressure. The reaction mixture was then diluted with water and extracted with ethyl acetate (EtOAc). The organic layer was washed with brine, dried over anhydrous sodium sulfate (Na_2SO_4), and the solvent was evaporated. The residue was purified by column chromatography (Hexane/EtOAc, 9:1) to give compound **S3c** as colourless liquid.**^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.1 Hz, 1H), 7.35 – 7.27 (m, 1H), 7.13 – 7.05 (m, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 3.21 (s, 3H), 3.14 (q, *J* = 7.1 Hz, 2H), 2.70 (d, *J* = 16.6 Hz, 1H), 2.48 (d, *J* = 16.6 Hz, 1H), 2.02 (dt, *J* = 10.0, 5.4 Hz, 2H), 1.96 (s, 1H), 1.27 (dt, *J* = 11.3, 5.5 Hz, 1H), 1.19 – 1.06 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 178.3, 143.7, 130.7, 128.6, 123.4, 122.9, 108.2, 79.3, 51.3, 50.6, 33.0, 27.5, 26.3, 24.0. In IR a strong peak at 2094.86 cm^{-1} indicates the presence of azide group.

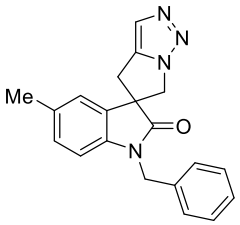
1-Methyl-4'H,6'H-spiro[indoline-3,5'-pyrrolo[1,2-c][1,2,3]triazol]-2-one (7a): Using **GP-4**, 3,3-disubstituted oxindole **4a** (42 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **7a** (31 mg, 86%) as a colourless solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.36 (t, *J* = 8.3 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.93 (dd, *J* = 7.4, 5.2 Hz, 2H), 4.72 (d, *J* = 11.6 Hz, 1H), 4.47 (d, *J* = 11.6 Hz, 1H), 3.50 (d, *J* = 16.0 Hz, 1H), 3.28 (s, 3H), 3.06 (d, *J* = 15.8 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 175.5, 142.7, 140.0, 132.0, 129.8, 127.6, 123.9, 122.1, 109.0, 57.6, 55.1, 32.8, 26.8. **HRMS (ESI)** calcd. for $C_{13}H_{13}N_4O$ $[M+H]^+$: 241.1089; Found: 241.1088.

1-Benzyl-4'H,6'H-spiro[indoline-3,5'-pyrrolo[1,2-c][1,2,3]triazol]-2-one (7b): Using **GP-4**, 3,3-disubstituted oxindole **4b** (53 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **7b** (40 mg, 85%) as a colourless solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.32 – 7.07 (m, 6H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 7.1 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 4.92 – 4.77 (m, 2H), 4.68 (d, *J* = 11.6 Hz, 1H), 4.42 (d, *J* = 11.6 Hz, 1H), 3.45 (d, *J* = 15.8 Hz, 1H), 3.01 (d, *J* = 15.8 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 175.8, 141.9, 140.0, 135.3 131.8, 129.7, 129.1, 128.2, 127.6, 127.5, 123.9, 122.2, 110.0, 57.6, 55.1, 44.4, 33.0. **HRMS (ESI)** calcd. for $C_{19}H_{17}N_4O$ $[M+H]^+$: 317.1402; Found: 317.1401.

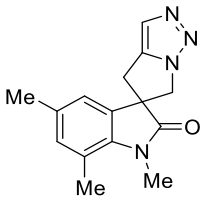
1-Phenyl-4'H,6'H-spiro[indoline-3,5'-pyrrolo[1,2-c][1,2,3]triazol]-2-one (7c): Using **GP-4**, 3,3-disubstituted oxindole **4c** (51 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **7c** (40 mg, 88%) as a colourless solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2H), 7.54 (s, 1H), 7.50 – 7.42 (m, 3H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.09 (t, *J* = 7.9 Hz, 1H), 7.00 (d, *J* = 6.6 Hz, 1H), 6.91 (d, *J* = 7.9 Hz, 1H), 4.84 (d, *J* = 11.6 Hz, 1H), 4.61 (d, *J* = 11.6 Hz, 1H), 3.63 (d, *J* = 15.8 Hz, 1H), 3.20 (d, *J* = 15.8 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 175.0, 142.7, 140.0, 133.8, 131.8, 129.9, 129.6, 128.7, 127.6, 126.4, 124.4, 122.4, 110.3, 57.8, 55.5, 33.4. **HRMS (ESI)** calcd. for $C_{18}H_{15}N_4O$ $[M+H]^+$: 303.1246; Found: 303.1244.

1-Allyl-4'H,6'H-spiro[indoline-3,5'-pyrrolo[1,2-c][1,2,3]triazol]-2-one (7d): Using **GP-4**, 3,3-disubstituted oxindole **4d** (46 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **7c** (34 mg, 85%) as a colourless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 7.9 Hz, 1H), 5.94 – 5.79 (m, 1H), 5.32 – 5.21 (m, 2H), 4.73 (d, *J* = 11.6 Hz, 1H), 4.49 (d, *J* = 11.6 Hz, 1H), 4.45 – 4.32 (m, 2H), 3.51 (d, *J* = 15.8 Hz, 1H), 3.08 (d, *J* = 15.8 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 175.3, 141.9, 140.0, 131.90, 131.9, 129.6, 127.6, 123.9, 122.2, 118.4, 109.9, 57.5, 55.1, 42.9, 33.0. **HRMS (ESI)** calcd. for $C_{15}H_{15}N_4O$ $[M+H]^+$: 267.1246; Found: 267.1247.

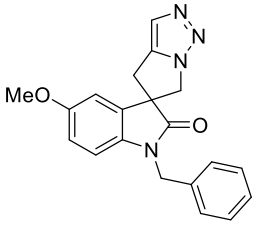
1-Benzyl-5-methyl-4'H,6'H-spiro[indoline-3,5'-pyrrolo[1,2-c][1,2,3]triazol]-2-one (7e): Using **GP-4**, 3, 3-disubstituted oxindole **4e** (55 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **7e** (45 mg, 90%) as a colourless solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.38 – 7.27 (m, 5H), 7.03 (d, *J* = 8.8 Hz, 1H), 6.75 (s, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 5.01 – 4.88 (m, 2H), 4.77 (d, *J* = 11.5 Hz, 1H), 4.51 (d, *J* = 11.5 Hz, 1H), 3.55 (d, *J* = 16.4 Hz, 1H), 3.10 (d, *J* = 15.9 Hz, 1H), 2.23 (s, 3H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 175.7, 140.1, 139.4, 135.4, 133.8, 132.0, 129.9, 129.1, 128.1, 127.6, 127.5, 122.9, 109.7, 57.7, 55.2, 44.4, 33.0, 21.1. **HRMS (ESI)** calcd. for $C_{20}H_{19}N_4O$ $[M+H]^+$: 331.1559; Found: 331.1557.



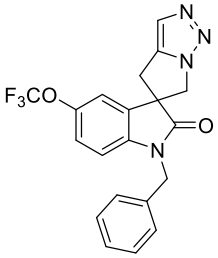
1,5,7-Trimethyl-4'H,6'H-spiro[indoline-3,5'-pyrrolo[1,2-c][1,2,3]triazol]-2-one (7f): Using **GP-4**, 3, 3-disubstituted oxindole **4f** (46 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **7f** (37 mg, 91%) as a colourless solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.54 (s, 1H), 6.88 (s, 1H), 6.54 (s, 1H), 4.69 (d, *J* = 11.5 Hz, 1H), 4.42 (d, *J* = 11.5 Hz, 1H), 3.52 (s, 3H), 3.47 (d, *J* = 15.9 Hz, 1H), 3.01 (d, *J* = 15.8 Hz, 1H), 2.55 (s, 3H), 2.20 (s, 3H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 176.2, 140.2, 137.9, 133.7, 133.6, 133.0, 127.6, 120.5, 120.4, 57.2, 55.57, 33.2, 30.1, 20.8, 18.9. **HRMS (ESI)** calcd. for $C_{15}H_{17}N_4O$ $[M+H]^+$: 269.1402; Found: 269.1403.



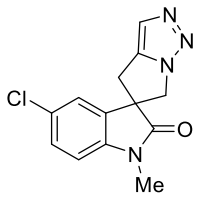
1-Benzyl-5-methoxy-4'H,6'H-spiro[indoline-3,5'-pyrrolo[1,2-c][1,2,3]triazol]-2-one (7g): Using **GP-4**, 3, 3-disubstituted oxindole **4g** (58 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **7g** (48 mg, 93%) as a colourless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.36 – 7.31 (m, 2H), 7.28 (d, *J* = 6.4 Hz, 3H), 6.71 (t, *J* = 7.3 Hz, 2H), 6.55 (s, 1H), 4.94 (d, *J* = 15.6 Hz, 1H), 4.88 (d, *J* = 15.5 Hz, 1H), 4.76 (d, *J* = 11.6 Hz, 1H), 4.50 (d, *J* = 11.6 Hz, 1H), 3.66 (s, 3H), 3.54 (d, *J* = 15.8 Hz, 1H), 3.10 (d, *J* = 15.8 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 175.5, 156.9, 139.9, 135.3, 135.0, 132.9, 129.0, 128.0, 127.5, 127.4, 113.8, 110.5, 109.5, 109.5, 57.9, 55.9, 55.0, 44.3, 32.9. **HRMS (ESI)** calcd. for $C_{20}H_{19}N_4O_2$ $[M+H]^+$: 347.1508; Found: 347.1509.



1-Benzyl-5-(trifluoromethoxy)-4'H,6'H-spiro[indoline-3,5'-pyrrolo[1,2-c][1,2,3]triazol]-2-one (7h): Using **GP-4**, 3, 3-disubstituted oxindole **4h** (66 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **7h** (45 mg, 75%) as a colourless solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.42 – 7.26 (m, 5H), 7.12 (d, *J* = 8.6 Hz, 1H), 6.84 (s, 1H), 6.81 (d, *J* = 8.6 Hz, 1H), 4.99 (d, *J* = 15.6 Hz, 1H), 4.91 (d, *J* = 15.6 Hz, 1H), 4.80 (d, *J* = 11.7 Hz, 1H), 4.54 (d, *J* = 11.7 Hz, 1H), 3.58 (d, *J* = 15.9 Hz, 1H), 3.14 (d, *J* = 16.0 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 175.6, 145.6, 140.6, 139.6, 134.8, 133.0, 129.3, 128.4, 127.7, 127.5, 120.4 (q, $J_{C\text{-}F}$ = 256.7 Hz), 116.4, 110.6, 57.7, 54.9, 44.6, 33.0. **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -58.39. **HRMS (ESI)** calcd. for $C_{20}H_{16}F_3N_4O_2$ $[M+H]^+$: 401.1225; Found: 401.1226.

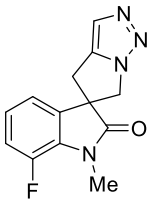


5-Chloro-1-methyl-4'H,6'H-spiro[indoline-3,5'-pyrrolo[1,2-c][1,2,3]triazol]-2-one (7i): Using **GP-4**, 3, 3-disubstituted oxindole **4i** (47 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **7i** (37 mg, 91%) as a colourless solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.34 (d, *J* = 10.4 Hz, 1H), 6.90 (s, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 4.72 (d, *J* = 11.7 Hz, 1H), 4.47 (d, *J* = 11.7 Hz, 1H), 3.51 (d, *J* = 15.3 Hz, 1H), 3.27 (s, 3H), 3.06 (d, *J* = 15.9 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 175.0, 141.3, 139.7, 133.5, 129.7, 129.3, 127.7, 122.7, 110.0, 57.7, 54.9, 32.8, 27.0. **HRMS (ESI)** calcd. for $C_{13}H_{12}ClN_4O$ $[M+H]^+$: 275.0700; Found: 275.0701 & 277.0666 .



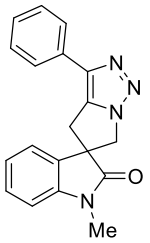
6-Chloro-1-methyl-4'H,6'H-spiro[indoline-3,5'pyrrolo[1,2c][1,2,3]triazol]-2-one (7j): Using **GP-4**, 3,3-disubstituted oxindole **4j** (47 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **7j** (38 mg, 93%) as a colourless solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.02 (d, *J* = 9.7 Hz, 1H), 6.92 (s, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 4.70 (d, *J* = 11.6 Hz, 1H), 4.45 (d, *J* = 11.7 Hz, 1H), 3.49 (d, *J* = 15.9 Hz, 1H), 3.26 (s, 3H), 3.03 (d, *J* = 15.9 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 175.4, 144.0, 139.8, 135.7, 130.2, 127.6, 123.7, 123.0, 109.8, 57.3, 55.0, 32.8, 26.9. **HRMS (ESI)** calcd. for $C_{13}H_{12}ClN_4O$ $[M+H]^+$: 275.0700; Found: 275.0700 & 277.0666.

7-Fluoro-1-methyl-4'H,6'H-spiro[indoline-3,5'-pyrrolo[1,2-c][1,2,3]triazol]-2-one (7k):



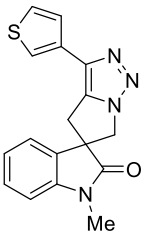
Using **GP-4**, 3, 3-disubstituted oxindole **4k** (44 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **7k** (31 mg, 81%) as a colourless solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.12 – 7.03 (m, 1H), 7.02 – 6.92 (m, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 4.69 (d, *J* = 11.6 Hz, 1H), 4.45 (d, *J* = 11.6 Hz, 1H), 3.47 (d, *J* = 2.7 Hz, 4H), 3.04 (d, *J* = 15.9 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 175.1,147.9 (d, J_{C-F} = 246.1 Hz), 139.8, 134.6 (d, J_{C-F} = 3.0 Hz), 129.4 (d, J_{C-F} = 9.1 Hz), 127.6, 124.6 (d, J_{C-F} = 6.0 Hz), 117.9 (d, J_{C-F}= 3.0 Hz), 117.75, 117.6, 57.7, 55.1, 33.0, 29.2 (d, J_{C-F} = 6.04 Hz). **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -135.34. **HRMS (ESI)** calcd. for $C_{13}H_{12}N_4FO$ $[M+H]^+$: 259.0995; Found: 259.0993.

1-Methyl-3'-phenyl-4'H,6'H-spiro[indoline-3,5'-pyrrolo[1,2-c][1,2,3]triazol]-2-one (7l) :



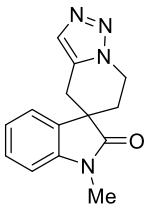
Using **GP-4**, 3, 3-disubstituted oxindole **4l** (53 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **7l** (36 mg, 75%) as a colourless solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.82 – 7.73 (m, 2H), 7.46 – 7.28 (m, 4H), 7.07 (d, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 6.1 Hz, 1H), 6.93 (d, *J* = 7.9 Hz, 1H), 4.77 (d, *J* = 11.6 Hz, 1H), 4.52 (d, *J* = 11.6 Hz, 1H), 3.71 (d, *J* = 15.9 Hz, 1H), 3.30 (s, 3H), 3.26 (d, *J* = 15.9 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 175.5, 142.7, 140.4, 136.4, 132.1, 130.9, 129.8, 129.0, 128.0, 125.5, 124.0, 122.2, 109.0, 57.8, 55.19, 34.0, 26.8. **HRMS (ESI)** calcd. for $C_{19}H_{17}N_4O$ $[M+H]^+$: 317.1402; Found: 317.1400.

1-methyl-3'-(thiophen-3-yl)-4'H,6'H-spiro[indoline-3,5'-pyrrolo[1,2-c][1,2,3]triazol]-2-one (7m):



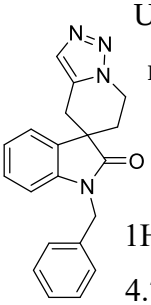
Using **GP-4**, 3, 3-disubstituted oxindole **4m** (54 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **7m** (37 mg, 77%) as a white solid.**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.44 (d, *J* = 5.0 Hz, 1H), 7.39 (s, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 6.9 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 4.75 (d, *J* = 11.6 Hz, 1H), 4.50 (d, *J* = 11.6 Hz, 1H), 3.64 (d, *J* = 15.8 Hz, 1H), 3.29 (s, 3H), 3.19 (d, *J* = 15.8 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 175.5, 142.7, 137.1, 135.8, 132.0, 132.0, 129.8, 126.6, 125.5, 124.0, 122.2, 120.8, 109.0, 57.7, 55.3, 33.4, 26.8. **HRMS (ESI)** calcd. for $C_{17}H_{15}N_4OS$ $[M+H]^+$: 323.0967; Found: 323.0965.

1-Methyl-6',7'-dihydro-4'H-spiro[indoline-3,5'-[1,2,3]triazolo[1,5-a]pyridin]-2-one (8a):



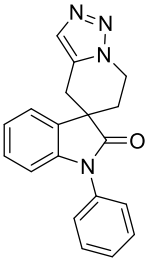
Using **GP-4**, 3, 3-disubstituted oxindole **5a** (44 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **8a** (35 mg, 92%) as a colourless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.62 (d, *J* = 7.4 Hz, 1H), 4.88 – 4.79 (m, 1H), 4.59 – 4.51 (m, 1H), 3.32 (d, *J* = 16.5 Hz, 1H), 3.28 (s, 3H), 2.93 (d, *J* = 16.5 Hz, 1H), 2.59 – 2.49 (m, 1H), 2.08 (m, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 177.8, 143.0, 131.7, 131.5, 130.7, 129.2, 123.2, 123.2, 108.9, 45.0, 42.4, 30.3, 28.1, 26.7. **HRMS (ESI)** calcd. for $C_{14}H_{15}N_4O$ $[M+H]^+$: 255.1246; Found: 255.1244.

1-Benzyl-6',7'-dihydro-4'H-spiro[indoline-3,5'-[1,2,3]triazolo[1,5-a]pyridin]-2-one (8b):



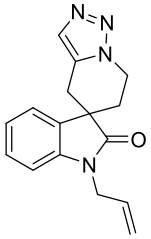
Using **GP-4**, 3,3-disubstituted oxindole **5b** (55 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **8a** (45 mg, 90%) as a colourless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.17 (d, *J* = 6.3 Hz, 2H), 7.13 (d, *J* = 6.9 Hz, 3H), 7.06 (t, *J* = 7.7 Hz, 1H), 6.78 (t, *J* = 7.5 Hz, 1H), 6.68 (d, *J* = 7.9 Hz, 1H), 6.45 (d, *J* = 7.4 Hz, 1H), 4.86 (d, *J* = 15.6 Hz, 1H), 4.74 (d, *J* = 15.6 Hz, 1H), 4.71 – 4.66 (m, 1H), 4.46 – 4.37 (m, 1H), 3.21 (d, *J* = 16.5 Hz, 1H), 2.83 (d, *J* = 16.5 Hz, 1H), 2.50 – 2.40 (m, 1H), 2.01 – 1.93 (m, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 178.0, 142.0, 135.6, 131.7, 131.5, 130.6, 129.1, 129.1, 128.0, 127.3, 123.3, 123.2, 110.0, 45.0, 44.0, 42.4, 30.5, 28.1. **HRMS (ESI)** calcd. for $C_{20}H_{19}N_4O$ $[M+H]^+$: 331.1559; Found: 331.1557.

1-Phenyl-6',7'-dihydro-4'H-spiro[indoline-3,5'-[1,2,3]triazolo[1,5-a]pyridin]-2-one (8c):



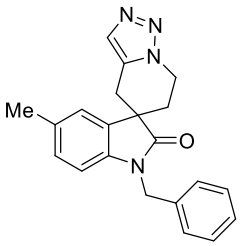
Using **GP-4**, 3,3-disubstituted oxindole **5c** (53 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **8c** (45 mg, 95%) as a colourless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.40 (t, *J* = 8.8 Hz, 3H), 7.21 (s, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 7.9 Hz, 1H), 6.64 (d, *J* = 7.5 Hz, 1H), 4.87 – 4.80 (m, 1H), 4.61 – 4.52 (m, 1H), 3.38 (d, *J* = 16.5 Hz, 1H), 3.05 (d, *J* = 16.5 Hz, 1H), 2.65 – 2.55 (m, 1H), 2.24 – 2.16 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 177.3, 142.9, 134.0, 131.7, 131.4, 130.5, 129.9, 129.1, 128.6, 126.6, 123.6, 123.5, 110.3, 45.2, 42.4, 30.7, 28.3. **HRMS (ESI)** calcd. for $C_{19}H_{17}N_4O$ $[M+H]^+$: 317.1402; Found: 317.1403.

1-Allyl-6',7'-dihydro-4'H-spiro[indoline-3,5'-[1,2,3]triazolo[1,5-a]pyridin]-2-one (8d) :



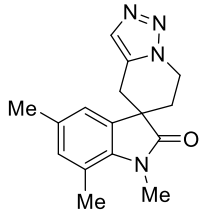
Using **GP-4**, 3, 3-disubstituted oxindole **5d** (48 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **8d** (38 mg, 91%) as a colourless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 7.9 Hz, 1H), 6.62 (d, *J* = 7.4 Hz, 1H), 5.92 – 5.78 (m, 1H), 5.29 – 5.20 (m, 2H), 4.88 – 4.79 (m, 1H), 4.60 – 4.50 (m, 1H), 4.43 (dd, *J* = 16.3, 5.2 Hz, 1H), 4.34 (dd, *J* = 16.3, 5.3 Hz, 1H), 3.31 (d, *J* = 16.5 Hz, 1H), 2.95 (d, *J* = 16.6 Hz, 1H), 2.60 – 2.49 (m, 1H), 2.14 – 2.07 (m, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 177.6, 142.1, 131.6, 131.5, 131.1, 130.7, 129.1, 123.2, 123.1, 118.0, 109.8, 44.9, 42.6, 42.4, 30.5, 28.1. **HRMS (ESI)** calcd. for $C_{16}H_{17}N_4O$ $[M+H]^+$: 281.1402; Found: 281.1400.

1-Benzyl-5-methyl-6',7'-dihydro-4'H-spiro[indoline-3,5'-[1,2,3]triazolo[1,5-a]pyridin]-2-one (8e):



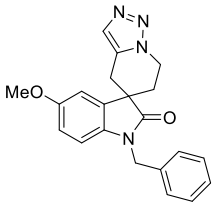
Using **GP-4**, 3, 3-disubstituted oxindole **5e** (57 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **8e** (48 mg, 92%) as a colourless solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.21 (q, *J* = 7.2, 6.4 Hz, 5H), 6.93 (d, *J* = 8.7 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 6.35 (s, 1H), 4.92 (d, *J* = 15.6 Hz, 1H), 4.80 (d, *J* = 7.7 Hz, 1H), 4.78 – 4.72 (m, 1H), 4.57 – 4.41 (m, 1H), 3.27 (d, *J* = 16.6 Hz, 1H), 2.90 (d, *J* = 17.5 Hz, 1H), 2.57 – 2.43 (m, 1H), 2.11 (s, 3H), 2.07 – 1.99 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.7, 140.1, 139.4, 135.4, 133.8, 132.0, 129.9, 129.1, 128.1, 127.6, 127.4, 122.91, 109.72, 57.69, 55.20, 44.36, 33.02, 21.08. **HRMS (ESI)** calcd. for $C_{21}H_{21}N_4O$ $[M+H]^+$: 345.1715; Found: 345.1714.

1,5,7-Trimethyl-6',7'-dihydro-4'H-spiro[indoline-3,5'-[1,2,3]triazolo[1,5-a]pyridin]-2-one (8f):

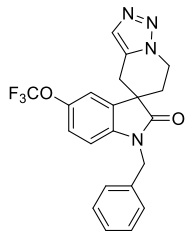


Using **GP-4**, 3,3-disubstituted oxindole **5f** (48 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **8f** (40 mg, 94%) as a colourless solid.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 6.87 (s, 1H), 6.29 (s, 1H), 4.87 – 4.75 (m, 1H), 4.60 – 4.48 (m, 1H), 3.52 (s, 3H), 3.26 (d, *J* = 16.7 Hz, 1H), 2.90 (d, *J* = 16.7 Hz, 1H), 2.56 (s, 3H), 2.50 – 2.41 (m, 1H), 2.17 (s, 3H), 2.09 – 2.00 (m, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 178.5, 138.2, 133.3, 132.7, 131.7, 131.7, 131.5, 121.6, 120.3, 44.2, 42.3, 30.7, 30.0, 28.1, 20.9, 19.1. **HRMS (ESI)** calcd. for $C_{16}H_{19}N_4O$ $[M+H]^+$: 283.1559; Found: 283.1558.

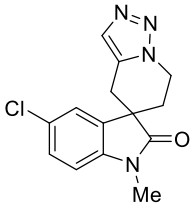
1-Benzyl-5-methoxy-6',7'-dihydro-4'H-spiro[indoline-3,5'-[1,2,3]triazolo[1,5-a]pyridin]-2-one (8g): Using **GP-4**, 3, 3-disubstituted oxindole **5g** (60 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **8g** (52 mg, 96%) as a colourless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.37 – 7.26 (m, 5H), 6.72 (s, 2H), 6.24 (s, 1H), 4.99 (d, *J* = 15.6 Hz, 1H), 4.89 (s, 1H), 4.87 – 4.82 (m, 1H), 4.63 – 4.54 (m, 1H), 3.64 (s, 3H), 3.36 (d, *J* = 16.6 Hz, 1H), 2.99 (d, *J* = 16.5 Hz, 1H), 2.63 – 2.55 (m, 1H), 2.17 – 2.08 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 177.6, 156.3, 135.7, 135.4, 132.1, 131.6, 131.4, 129.1, 128.0, 127.4, 112.8, 111.2, 110.3, 55.9, 45.4, 44.1, 42.3, 30.6, 28.1. **HRMS (ESI)** calcd. for $C_{21}H_{21}N_4O_2$ $[M+H]^+$: 361.1665; Found: 361.1663.

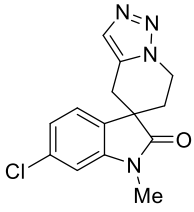


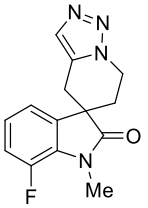
1-Benzyl-5-(trifluoromethoxy)-6',7'-dihydro-4'H-spiro[indoline-3,5'-[1,2,3]triazolo[1,5-a]pyridin]-2-one (8h): Using **GP-4**, 3, 3-disubstituted oxindole **5h** (68 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **8h** (50 mg, 80%) as a colourless solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.44 – 7.26 (m, 5H), 7.10 (d, *J* = 9.7 Hz, 1H), 6.81 (d, *J* = 8.6 Hz, 1H), 6.54 (s, 1H), 5.01 (d, *J* = 15.6 Hz, 1H), 4.95 – 4.82 (m, 2H), 4.62 – 4.47 (m, 1H), 3.37 (d, *J* = 16.7 Hz, 1H), 3.03 (d, *J* = 16.6 Hz, 1H), 2.65 – 2.51 (m, 1H), 2.26 – 2.11 (m, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 177.7, 145.0, 140.7, 135.1, 132.2, 131.6, 130.8, 129.2, 128.3, 127.4, 122.2, 120.4(q, $J_{C\text{-}F}$ = 256.7 Hz), 117.4, 110.4, 45.2, 44.2, 42.2, 30.5, 28.0. **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -58.43. **HRMS (ESI)** calcd. for $C_{21}H_{18}F_3N_4O_2$ $[M+H]^+$: 415.1382; Found: 415.1380.



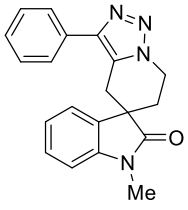
5-Chloro-1-methyl-6',7'-dihydro-4'H-spiro[indoline-3,5'-[1,2,3]triazolo[1,5-a]pyridin]-2-one (8i): Using **GP-4**, 3, 3-disubstituted oxindole **5i** (49 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **8i** (40 mg, 93%) as a colourless solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.31 (d, *J* = 10.4 Hz, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 6.64 (s, 1H), 4.88 – 4.78 (m, 1H), 4.61 – 4.50 (m, 1H), 3.25 (s, 4H), 2.94 (d, *J* = 16.3 Hz, 1H), 2.58 – 2.45 (m, 1H), 2.11 (td, *J* = 10.5, 9.8, 4.9 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 177.3, 141.5, 132.3, 131.6, 130.9, 129.2, 128.6, 123.6, 109.8, 45.1, 42.2, 30.2, 27.9, 26.8. **HRMS (ESI)** calcd. for $C_{14}H_{14}ClN_4O$ $[M+H]^+$: 289.0856; Found: 289.0854 & 291.0797.



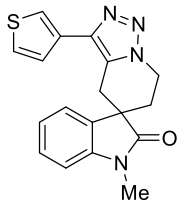
6-Chloro-1-methyl-6',7'-dihydro-4'H-spiro[indoline-3,5'-[1,2,3]triazolo[1,5-a]pyridin]-2-one (8j):  Using **GP-4**, 3, 3-disubstituted oxindole **5j** (49 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **8d** (41 mg, 95%) as a colourless solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.54 (s, 1H), 6.95 (d, *J* = 7.8 Hz, 2H), 6.52 (d, *J* = 7.8 Hz, 1H), 4.91 – 4.75 (m, 1H), 4.57 – 4.43 (m, 1H), 3.25 (s, 4H), 2.91 (d, *J* = 17.7 Hz, 1H), 2.58 – 2.47 (m, 1H), 2.11 – 2.03 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 177.7, 144.2, 135.2, 131.7, 131.2, 128.9, 124.1, 122.9, 109.7, 44.8, 42.3, 30.3, 28.0, 26.8. **HRMS (ESI)** calcd. for $C_{14}H_{14}ClN_4O$ $[M+H]^+$: 289.0856; Found: 289.0856 & 291.0792.

7-Fluoro-1-methyl-6',7'-dihydro-4'H-spiro[indoline-3,5'-[1,2,3]triazolo[1,5-a]pyridin]-2-one (8k):  Using **GP-4**, 3,3-disubstituted oxindole **5k** (47 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **8k** (35 mg, 85%) as a colourless solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.06 (dd, *J* = 12.3, 8.5 Hz, 1H), 6.95 – 6.86 (m, 1H), 6.40 (d, *J* = 8.3 Hz, 1H), 4.89 – 4.76 (m, 1H), 4.60 – 4.44 (m, 1H), 3.47 (d, *J* = 2.8 Hz, 3H), 3.28 (d, *J* = 16.6 Hz, 1H), 2.93 (d, *J* = 16.6 Hz, 1H), 2.56 – 2.45 (m, 1H), 2.09 (dt, *J* = 14.0, 4.8 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 177.4, 148.2 (d, $J_{C\text{-}F}$ = 244.6 Hz), 133.5 (d, $J_{C\text{-}F}$ =3.0 Hz), 131.6, 131.2, 129.7 (d, $J_{C\text{-}F}$ = 7.6 Hz), 123.8 (d, $J_{C\text{-}F}$ = 6.0 Hz), 119.0 (d, $J_{C\text{-}F}$ = 4.5 Hz), 117.3 (d, $J_{C\text{-}F}$ = 19.6 Hz), 45.3, 42.2, 30.5, 29.2 (d, $J_{C\text{-}F}$ = 4.5 Hz), 28.1. **^{19}F{^{1}H} NMR** (565 MHz, $CDCl_3$) δ -135.2. **HRMS (ESI)** calcd. for $C_{14}H_{14}FN_4O$ $[M+H]^+$: 273.1152; Found: 273.1151.

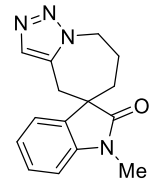
1-Methyl-3'-phenyl-6',7'-dihydro-4'H-spiro[indoline-3,5'-[1,2,3]triazolo[1,5-a]pyridin]-2-one (8l): Using **GP-4**, 3,3-disubstituted oxindole **5l** (55 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **8l** (40 mg, 80%) as a colourless solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.36 – 7.27 (m, 2H), 7.02 – 6.95 (m, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 4.95 – 4.84 (m, 1H), 4.70 – 4.54 (m, 1H), 3.51 (d, *J* = 16.6 Hz, 1H), 3.28 (s, 3H), 3.10 (d, *J* = 16.6 Hz, 1H), 2.65 – 2.51 (m, 1H), 2.11 (dt, *J* = 15.5, 4.6 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 177.9, 143.6, 143.0, 131.3, 130.7, 129.2, 128.9, 128.0, 127.8, 126.6, 123.3, 123.2, 108.9, 45.1, 42.7, 29.9, 29.6, 26.7. **HRMS (ESI)** calcd. for $C_{20}H_{19}N_4O$ $[M+H]^+$: 330.3910; Found: 330.3906.



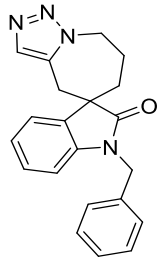
1-methyl-3'-(thiophen-3-yl)-6',7'-dihydro-4'H-spiro[indoline-3,5'-[1,2,3]triazolo[1,5-a]pyridin]-2-one (8m): Using **GP-4**, 3,3-disubstituted oxindole **5m** (56 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **8m** (42 mg, 83%) as a white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.51 (d, *J* = 5.9 Hz, 1H), 7.44 (s, 1H), 7.36 (d, *J* = 2.9 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.73 (d, *J* = 7.4 Hz, 1H), 4.93 – 4.79 (m, 1H), 4.67 – 4.52 (m, 1H), 3.44 (d, *J* = 16.6 Hz, 1H), 3.28 (s, 3H), 3.06 (d, *J* = 16.6 Hz, 1H), 2.63 – 2.46 (m, 1H), 2.18 – 2.04 (m, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 177.9, 142.9, 140.3, 132.2, 130.8, 129.2, 127.4, 126.2, 126.1, 123.3, 123.2, 120.9, 109.0, 45.0, 42.6, 30.0, 29.1, 26.7. **HRMS (ESI)** calcd. for $C_{18}H_{17}N_4OS$ $[M+H]^+$: 337.1123; Found: 337.1122.



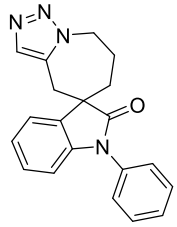
1-Methyl-7',8'-dihydro-4'H,6'H-spiro[indoline-3,5'-[1,2,3]triazolo[1,5-a]azepin]-2-one (9a): Using **GP-4**, 3,3-disubstituted oxindole **6a** (46 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **9a** (29 mg, 72%) as a colourless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (s, 1H), 7.26 (t, *J* = 7.7 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.83 (t, *J* = 7.6 Hz, 1H), 5.99 (d, *J* = 7.4 Hz, 1H), 5.07 (d, *J* = 14.4 Hz, 1H), 4.36 (t, *J* = 12.8 Hz, 1H), 3.31 (d, *J* = 15.4 Hz, 1H), 3.24 (s, 3H), 2.84 (d, *J* = 15.3 Hz, 1H), 2.36 (t, *J* = 14.9 Hz, 1H), 2.13 (d, *J* = 18.1 Hz, 1H), 2.03 (t, *J* = 13.4 Hz, 1H), 1.86 – 1.81 (m, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 178.7, 142.9, 135.23, 134.2, 130.1, 128.6, 124.9, 122.5, 108.6, 50.4, 48.4, 37.5, 29.2, 26.5, 23.1. **HRMS (ESI)** calcd. for $C_{15}H_{17}N_4O$ $[M+H]^+$: 269.1402; Found: 269.1400.



1-Benzyl-7',8'-dihydro-4'H,6'H-spiro[indoline-3,5'-[1,2,3]triazolo[1,5-a]azepin]-2-one (9b): Using **GP-4**, 3,3-disubstituted oxindole **6b** (57 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **9b** (35 mg, 68%) as a colourless solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.33 – 7.23 (m, 5H), 7.15 (t, *J* = 7.8 Hz, 1H), 6.83 – 6.75 (m, 2H), 5.99 (d, *J* = 7.1 Hz, 1H), 5.10 (d, *J* = 16.1 Hz, 1H), 5.00 (d, *J* = 15.6 Hz, 1H), 4.86 (d, *J* = 15.6 Hz, 1H), 4.38 (t, *J* = 11.9 Hz, 1H), 3.38 (d, *J* = 15.3 Hz, 1H), 2.90 (d, *J* = 15.3 Hz, 1H), 2.50 – 2.38 (m, 1H), 2.19 – 2.10 (m, 1H), 2.09 – 2.00 (m, 1H), 1.91 (d, *J* = 17.3 Hz, 1H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 178.9, 142.0, 135.8, 135.3, 134.2, 130.1, 129.0, 128.5, 127.9, 127.3, 125.0, 122.5, 109.6, 50.4, 48.4, 43.8, 37.8, 29.3, 23.1. **HRMS (ESI)** calcd. for $C_{21}H_{21}N_4O$ $[M+H]^+$: 345.1715; Found: 345.1716.



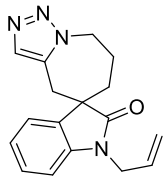
1-Phenyl-7',8'-dihydro-4'H,6'H-spiro[indoline-3,5'-[1,2,3]triazolo[1,5-a]azepin]-2-one



(9c): Using **GP-4**, 3,3-disubstituted oxindole **6c** (55 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **9c** (37 mg, 74%) as a colourless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (t, *J* = 7.7 Hz, 2H), 7.47 – 7.38 (m, 4H), 7.19 (t, *J* = 7.7 Hz, 1H), 6.87 (t, *J* = 7.9 Hz, 2H), 6.05 (d, *J* = 7.4 Hz, 1H), 5.12 (d, *J* = 14.8 Hz, 1H), 4.40 (t, *J* = 12.8 Hz, 1H), 3.42 (d, *J* = 15.3 Hz, 1H), 3.03 (d, *J* = 15.3 Hz, 1H), 2.46 (t, *J* = 13.2 Hz, 1H), 2.17 (t, *J* = 11.6 Hz, 1H), 2.10 – 2.00 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 178.1, 142.9, 135.3, 134.2, 134.1, 129.9, 129.9, 128.5, 128.5, 126.7, 125.2, 122.9, 110.0, 50.5, 48.5, 37.9, 29.4, 23.1. **HRMS (ESI)** calcd. for $C_{20}H_{19}N_4O$ $[M+H]^+$: 331.1559; Found: 331.1557.

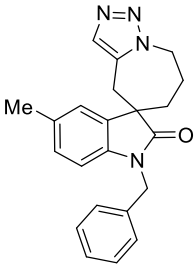
1-Allyl-7',8'-dihydro-4'H,6'H-spiro[indoline-3,5'-[1,2,3]triazolo[1,5-a]azepin]-2-one

(9d): Using **GP-4**, 3,3-disubstituted oxindole **6d** (50 mg, 0.15 mmol), NaN_3(20 mg, 0.30 mmol) in 1 mL DMF provided compound **9d** (31 mg, 70%) as a colourless solid.



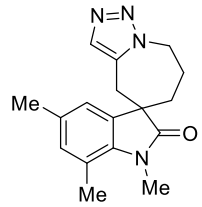
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.23 (t, *J* = 7.9 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.83 (t, *J* = 7.5 Hz, 1H), 6.00 (d, *J* = 7.4 Hz, 1H), 5.92 – 5.77 (m, 1H), 5.29 – 5.18 (m, 2H), 5.09 (d, *J* = 16.1 Hz, 1H), 4.48 – 4.26 (m, 3H), 3.34 (d, *J* = 15.3 Hz, 1H), 2.86 (d, *J* = 15.3 Hz, 1H), 2.38 (t, *J* = 13.5 Hz, 1H), 2.12 (t, *J* = 14.4 Hz, 1H), 2.04 (d, *J* = 14.2 Hz, 1H), 1.86 (d, *J* = 13.7 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 178.5, 142.1, 135.30, 134.2, 131.3, 130.1, 128.5, 125.0, 122.5, 117.9, 109.5, 50.5, 48.3, 42.4, 37.7, 29.3, 23.2. **HRMS (ESI)** calcd. for $C_{17}H_{19}N_4O$ $[M+H]^+$: 295.1559; Found: 295.1558

1-Benzyl-5-methyl-7',8'-dihydro-4'H,6'H-spiro[indoline-3,5'-[1,2,3]triazolo[1,5-a]azepin]-2-one (9e): Using **GP-4**, 3,3-disubstituted oxindole **6e** (59 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **9e** (40 mg, 74%) as a colourless solid.

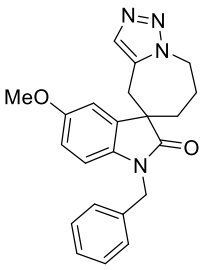


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.35 – 7.23 (m, 5H), 6.94 (d, *J* = 7.1 Hz, 1H), 6.67 (d, *J* = 7.3 Hz, 1H), 5.81 (s, 1H), 5.09 (d, *J* = 13.0 Hz, 1H), 4.97 (d, *J* = 15.5 Hz, 1H), 4.85 (d, *J* = 15.3 Hz, 1H), 4.38 (t, *J* = 12.6 Hz, 1H), 3.37 (d, *J* = 15.2 Hz, 1H), 2.89 (d, *J* = 15.1 Hz, 1H), 2.42 (t, *J* = 13.6 Hz, 1H), 2.36 – 2.21 (m, 1H), 2.13 (t, *J* = 15.2 Hz, 4H), 1.90 (d, *J* = 12.3 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 178.8, 139.6, 135.9, 135.3, 134.2, 132.1, 130.3, 129.1, 129.0, 128.8, 128.8, 127.9, 127.5, 127.3, 125.7, 109.4, 50.5, 48.5, 43.9, 37.8, 29.4, 23.2, 21.2. **HRMS (ESI)** calcd. for $C_{22}H_{23}N_4O$ $[M+H]^+$: 359.1872; Found: 359.1873.

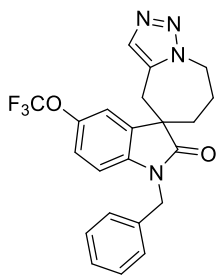
1,5,7-Trimethyl-3a',4',7',8'-tetrahydro-3'H,6'H-spiro[indoline-3,5'-[1,2,3]triazolo[1,5-a]azepin]-2-one (9f): Using **GP-4**, 3,3-disubstituted oxindole **6f** (50 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **9f** (33 mg, 75%) as a colourless solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.33 (s, 1H), 6.81 (s, 1H), 5.67 (s, 1H), 5.03 (d, *J* = 17.7 Hz, 1H), 4.38 (t, *J* = 13.6 Hz, 1H), 3.50 (s, 3H), 3.28 (d, *J* = 15.3 Hz, 1H), 2.81 (d, *J* = 15.3 Hz, 1H), 2.54 (s, 3H), 2.32 (t, *J* = 13.1 Hz, 1H), 2.09 (s, 5H), 1.81 (d, *J* = 16.7 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 179.4, 138.2, 135.2, 134.3, 132.8, 131.9, 131.2, 123.4, 120.0, 50.5, 47.6, 37.8, 29.9, 29.5, 22.9, 20.9, 19.2. **HRMS (ESI)** calcd. for $C_{17}H_{21}N_4O$ $[M+H]^+$: 297.1715; Found: 297.1716.



1-Benzyl-5-methoxy-7',8'-dihydro-4'H,6'H-spiro[indoline-3,5'-[1,2,3]triazolo[1,5-a]azepin]-2-one (9g): Using **GP-4**, 3,3-disubstituted oxindole **6g** (62mg, 0.15mmol), NaN_3(20mg, 0.30mmol) in 1 mL DMF provided compound **9g** (43 mg, 77%) as a colourless solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.36 – 7.21 (m, 5H), 6.67 (d, *J* = 1.4 Hz, 2H), 5.58 (s, 1H), 5.09 (dq, *J* = 14.0, 2.2 Hz, 1H), 4.97 (d, *J* = 15.6 Hz, 1H), 4.84 (d, *J* = 15.6 Hz, 1H), 4.47 – 4.32 (m, 1H), 3.54 (s, 3H), 3.39 (d, *J* = 15.3 Hz, 1H), 2.90 (d, *J* = 17.1 Hz, 1H), 2.51 – 2.38 (m, 1H), 2.23 – 2.01 (m, 2H), 1.91 (d, *J* = 13.1 Hz, 1H). **^{13}C{1H} NMR** (151 MHz, $CDCl_3$) δ 178.5, 155.6, 135.8, 135.4, 135.3, 134.1, 131.3, 129.0, 127.9, 127.3, 113.2, 112.1, 110.0, 55.7, 50.4, 48.7, 43.9, 37.7, 29.3, 23.1. **HRMS (ESI)** calcd. for $C_{22}H_{23}N_4O_2$ $[M+H]^+$: 375.1821; Found: 375.1820.

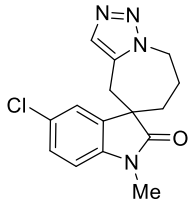


1-Benzyl-5-(trifluoromethoxy)-7',8'-dihydro-4'H,6'H-spiro[indoline-3,5'-[1,2,3]triazolo[1,5-a]azepin]-2-one (9h): Using **GP-4**, 3,3-disubstituted oxindole **6h** (70 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **9h** (40 mg, 62%) as a colourless solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.37 – 7.26 (m, 5H), 7.03 (d, *J* = 9.8 Hz, 1H), 6.76 (d, *J* = 8.6 Hz, 1H), 5.90 (s, 1H), 5.09 (d, *J* = 14.1 Hz, 1H), 5.00 (d, *J* = 15.6 Hz, 1H), 4.85 (d, *J* = 15.6 Hz, 1H), 4.46 – 4.33 (m, 1H), 3.40 (d, *J* = 15.2 Hz, 1H), 2.91 (d, *J* = 16.9 Hz, 1H), 2.53 – 2.37 (m, 1H), 2.26 – 2.14 (m, 1H), 2.05 – 1.91 (m, 2H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 178.6, 144.4, 140.6, 135.3, 133.5, 131.6, 129.2, 128.2, 127.4, 121.8, 120.4 (q, $J_{C\text{-}F}$ = 256.7 Hz), 119.1, 110.0, 50.3, 48.6, 44.1, 37.6, 29.3, 23.1. **^{19}F{^{1}H}**



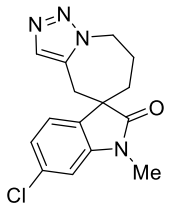
NMR (565 MHz, $CDCl_3$) δ -58.5. **HRMS (ESI)** calcd. for $C_{22}H_{20}F_3N_4O_2$ $[M+H]^+$: 429.1538; Found: 429.1536.

5-Chloro-1-methyl-7',8'-dihydro-4'H,6'H-spiro[indoline-3,5'-[1,2,3]triazolo[1,5-a]azepin]-2-one (9i): Using **GP-4**, 3,3-disubstituted oxindole **6i** (51 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **9i** (33 mg, 72%) as a colourless solid.



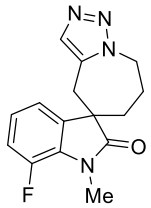
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.25 (d, *J* = 6.3 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 6.06 (s, 1H), 5.05 (d, *J* = 17.9 Hz, 1H), 4.47 – 4.31 (m, 1H), 3.30 (d, *J* = 15.4 Hz, 1H), 3.22 (s, 3H), 2.86 (d, *J* = 15.3 Hz, 1H), 2.35 (t, *J* = 12.0 Hz, 1H), 2.18 (d, *J* = 13.1 Hz, 1H), 2.08 – 1.95 (m, 1H), 1.85 (d, *J* = 13.9 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 178.1, 141.4, 135.2, 133.6, 131.9, 128.6, 128.0, 125.1, 109.5, 50.3, 48.6, 37.4, 29.1, 26.6, 23.1. **HRMS (ESI)** calcd. for $C_{15}H_{16}N_4OCl$ $[M+H]^+$: 303.1013; Found: 303.1014 & 305.1002.

6-Chloro-1-methyl-7',8'-dihydro-4'H,6'H-spiro[indoline-3,5'-[1,2,3]triazolo[1,5-a]azepin]-2-one (9j): Using **GP-4**, 3,3-disubstituted oxindole **6j** (51 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **9j** (34 mg, 74%) as colourless solid.



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (s, 1H), 6.88 (s, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 5.89 (d, *J* = 8.0 Hz, 1H), 5.08 (d, *J* = 18.6 Hz, 1H), 4.36 (t, *J* = 13.9 Hz, 1H), 3.32 (d, *J* = 15.4 Hz, 1H), 3.23 (s, 3H), 2.83 (d, *J* = 17.1 Hz, 1H), 2.39 (d, *J* = 12.8 Hz, 1H), 2.15 (d, *J* = 11.1 Hz, 1H), 2.00 (t, 2H), 1.84 (d, *J* = 14.3 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 178.7, 144.2, 135.3, 134.8, 134.0, 128.4, 125.7, 122.3, 109.5, 50.4, 48.2, 37.5, 29.2, 26.7, 23.2. **HRMS (ESI)** calcd. for $C_{15}H_{16}N_4OCl$ $[M+H]^+$: 303.1013; Found: 303.1014 & 305.1000.

7-Fluoro-1-methyl-7',8'-dihydro-4'H,6'H-spiro[indoline-3,5'-[1,2,3]triazolo[1,5-a]azepin]-2-one (9k): Using **GP-4**, 3,3-disubstituted oxindole **6k** (49 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF provided compound **9j** (25 mg, 58%) as a colourless solid.



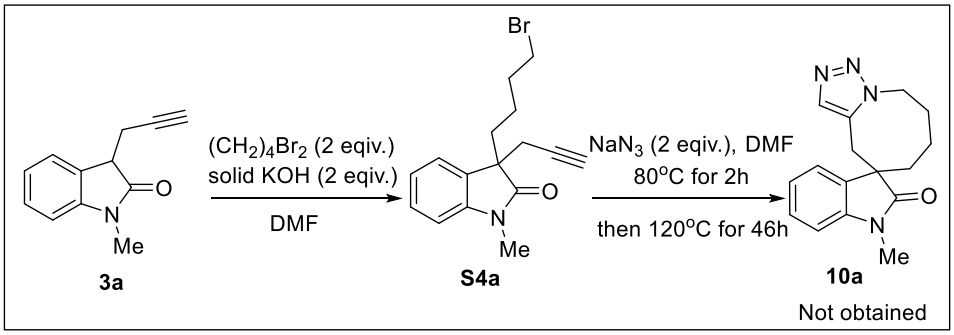
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (s, 1H), 7.00 (dd, *J* = 12.4, 8.5 Hz, 1H), 6.82 – 6.70 (m, 1H), 5.77 (d, *J* = 7.1 Hz, 1H), 5.05 (d, *J* = 14.2 Hz, 1H), 4.44 – 4.29 (m, 1H), 3.45 (d, *J* = 3.0 Hz, 3H), 3.31 (d, *J* = 14.9 Hz, 1H), 2.85 (d, *J* = 17.2 Hz, 1H), 2.42 – 2.29 (m, 1H), 2.13 (d, *J* = 15.2 Hz, 1H), 2.06 – 1.94 (m, 1H), 1.84 (d, *J* = 14.2 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ 178.3, 148.1 (d, $J_{C\text{-}F}$ = 244.6 Hz), 135.3, 133.9, 132.9, 129.7 (d, $J_{C\text{-}F}$ = 9.0 Hz), 123.0 (d, $J_{C\text{-}F}$ = 6.0 Hz), 120.7 (d, $J_{C\text{-}F}$ = 4.5 Hz), 116.7 (d, $J_{C\text{-}F}$ = 19.6 Hz), 50.3, 48.6, 37.6, 29.3, 29.0 (d, $J_{C\text{-}F}$ = 6.0 Hz), 23.0.

$^{19}F\{^1H\}$ NMR (565 MHz, $CDCl_3$) δ -135.55. **HRMS (ESI)** calcd. for $C_{15}H_{16}FN_4O$ $[M+H]^+$: 287.1308; Found: 287.1305.

1-Methyl-3'-phenyl-7',8'-dihydro-4'H,6'H-spiro[indoline-3,5'-[1,2,3]triazolo[1,5-a]azepin]-2-one (9l): Using **GP-4**, 3,3-disubstituted oxindole **6l** (57 mg, 0.15mmol), NaN_3(20 mg, 0.30 mmol) in 1 mL DMF provided compound **9l** (27 mg, 53%) as colourless solid. **^1H NMR** (300 MHz, $CDCl_3$) δ 7.28 – 7.18 (m, 4H), 7.08 (dd, *J* = 3.8, 1.9 Hz, 2H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.82 (t, *J* = 7.6 Hz, 1H), 6.14 (d, *J* = 7.5 Hz, 1H), 5.12 (dt, *J* = 15.7, 3.0 Hz, 1H), 4.42 (t, *J* = 12.5 Hz, 1H), 3.36 (d, *J* = 15.4 Hz, 1H), 3.25 (s, 3H), 3.02 (d, *J* = 15.4 Hz, 1H), 2.42 (t, *J* = 15.1 Hz, 1H), 2.26 – 2.07 (m, 2H), 1.88 (d, *J* = 14.4 Hz, 1H). **$^{13}C\{^1H\}$ NMR** (151 MHz, $CDCl_3$) δ 178.8, 147.6, 142.9, 131.0, 130.9, 130.0, 128.7, 128.6, 128.0, 127.9, 124.9, 122.7, 108.7, 50.8, 48.5, 37.7, 29.1, 26.6, 23.3. **HRMS (ESI)** calcd for $C_{21}H_{21}N_4O$ $[M+H]^+$: 345.1715; Found: 345.1716.

1-methyl-3'-(thiophen-3-yl)-7',8'-dihydro-4'H,6'H-spiro[indoline-3,5'-[1,2,3]triazolo[1,5-a]azepin]-2-one (9m): Using **GP-4**, 3,3-disubstituted oxindole **6m** (58 mg, 0.15 mmol), NaN_3(20 mg, 0.30 mmol) in 1 mL DMF provided compound **9m** (26 mg, 50%) as a white solid. **^1H NMR** (300 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.8 Hz, 1H), 7.23 – 7.17 (m, 1H), 6.91 (d, *J* = 7.9 Hz, 1H), 6.88 (d, *J* = 6.2 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 2.9 Hz, 1H), 6.14 (d, *J* = 7.4 Hz, 1H), 5.10 (d, *J* = 17.0 Hz, 1H), 4.40 (t, *J* = 13.9 Hz, 1H), 3.35 (d, *J* = 15.3 Hz, 1H), 3.27 (s, 3H), 2.99 (d, *J* = 15.3 Hz, 1H), 2.49 – 2.34 (m, 1H), 2.15 (t, *J* = 14.2 Hz, 2H), 1.88 (d, *J* = 14.2 Hz, 1H). **$^{13}C\{^1H\}$ NMR** (151 MHz, $CDCl_3$) δ 178.8, 143.5, 142.8, 131.6, 130.7, 130.1, 128.8, 127.1, 126.0, 124.8, 122.8, 122.4, 108.7, 50.6, 48.3, 37.5, 29.3, 26.6, 23.4. **HRMS (ESI)** calcd for $C_{19}H_{19}N_4OS$ $[M+H]^+$: 351.1280; Found: 351.1281.

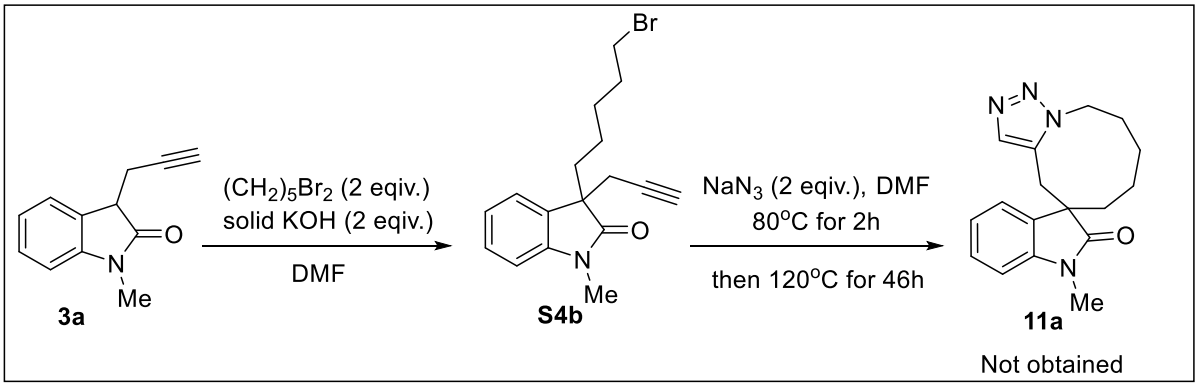
9.0 Synthesis of 3, 3-disubstituted 2-oxindole S4a-b from 3a:



Scheme S3. synthesis of **S4a** from **3a**

3-(4-bromobutyl)-1-methyl-3-(prop-2-yn-1-yl)indolin-2-one (S4a): Using **GP-2**, 3-substituted oxindole **3a** (67 mg, 0.25 mmol), 1,4-dibromobutane (108 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **S4a** (50 mg, 63%) as a brown sticky liquid.**^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.0 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.08 (t, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 3.24 (t, *J* = 6.9 Hz, 2H), 3.21 (s, 3H), 2.69 (d, *J* = 19.2 Hz, 1H), 2.47 (d, *J* = 19.2 Hz, 1H), 2.05 – 1.87 (m, 3H), 1.81 – 1.67 (m, 2H), 1.18 – 1.05 (m, 1H), 1.03 – 0.90 (m, 1H). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$) δ 178.5, 143.8, 131.0, 128.4, 123.4, 122.7, 108.1, 79.5, 71.0, 50.8, 35.0, 33.0, 32.8, 27.5, 26.3, 23.0. **HRMS (ESI)** calcd. for $C_{16}H_{19}NOBr$ $[M+H]^+$: 320.0650; Found: 320.0651 & 322.0602.

1-methyl-6',7',8',9'-tetrahydro-4'H-spiro[indoline-3,5'-[1,2,3]triazolo[1,5-a]azocin]-2-one (10a): 3,3-disubstituted oxindole **S4a** (48 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF were taken in a R.B flask. We followed exactly the same reaction condition (**GP-3**) as used for the synthesis of seven membered ring fused spirooxindole **9a-m**. But no product **10a** formation observed.



Scheme S4. synthesis of **S4b** from **3a**

3-(5-bromopentyl)-1-methyl-3-(prop-2-yn-1-yl)indolin-2-one (S4b): Using **GP-2**, 3-substituted oxindole **3a** (67 mg, 0.25 mmol), 1,4-dibromopentane (115 mg, 0.50 mmol), powdered KOH (28 mg, 0.50 mmol) in 0.5 mL DMF provided compound **S4b** (51 mg, 61%) as a brown sticky liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.1 Hz, 1H), 7.30 (t, *J* = 8.3 Hz, 1H), 7.08 (t, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 3.27 (t, *J* = 6.8 Hz, 2H), 3.21 (s, 3H), 2.68 (d, *J* = 19.2 Hz, 1H), 2.48 (d, *J* = 19.2 Hz, 1H), 1.97 – 1.94 (m, 1H), 1.93 (s, 1H), 1.71 (dt, *J* = 14.3, 6.9 Hz, 2H), 1.31 (dq, *J* = 13.5, 7.1 Hz, 2H), 1.00 (tt, *J* = 16.5, 7.5 Hz, 1H), 0.90 – 0.79 (m,

1H). **$^{13}C\{^{1}H\}$ NMR** (151 MHz, $CDCl_3$) δ 178.7, 143.8, 131.2, 128.4, 123.4, 122.7, 108.0, 79.6, 70.8, 51.0, 35.8, 33.7, 32.4, 28.2, 27.5, 26.3, 23.5. **HRMS (ESI)** calcd. for $C_{17}H_{21}NOBr$ $[M+H]^+$: 320.0650; Found: 334.0808 & 334.0808 & 334.0817.

1-methyl-7',8',9',10'-tetrahydro-4'H,6'H-spiro[indoline-3,5'-[1,2,3]triazolo[1,5-a]azonin]-2-one (11a): 3,3-disubstituted oxindole **S4b** (50 mg, 0.15 mmol), NaN_3 (20 mg, 0.30 mmol) in 1 mL DMF were taken in a R.B flask. We followed exactly the same reaction condition (**GP-3**) as used for the synthesis of seven membered ring fused spirooxindole **9a-m**. But no product **11a** formation observed.

10.0. X-Ray Crystal Analysis Data:

10.0.1 X-Ray Crystal Structure of 7g:

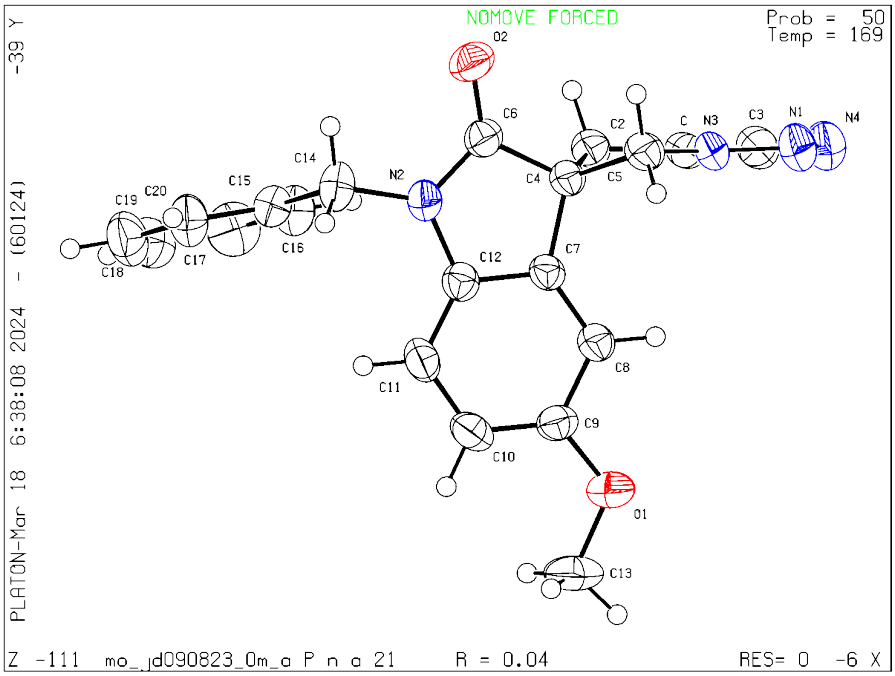


Figure S1. ORTEP illustration of **7g** (thermal ellipsoids are drawn at 50% probability). O: Red , N: Blue, H: White, C: Black.

Single crystals for X-ray studies were grown by slow evaporation of a solution of compound **7g** in MeOH in small glass vial at room temperature. The X-ray data of **7g** is deposited in the Cambridge Crystallograpic Data Centre (CCDC No.-2356047-). Crystal data for the compound **7g** was collected at 169.04 K on a Bruker D8VENTURE Micro-focus diffractometer equipped with PHOTON II Detector, with MoKα radiation (0.71073 Å), controlled by the APEX3 (v2017.3-0) software package. The raw data was integrated and corrected for Lorentz and

polarization effects with the aid of the Bruker Apex III program suite. Absorption corrections were performed by using SADABS. Space groups were assigned by systematic absences (determined by XPREP) and analysis of metric chemistry and were further checked by PLATON[7,8], for additional symmetry. Structure was solved by direct methods and refined against all data in the reported 2Θ ranges by full-matrix least square on F2 using the SHELXL program suite[9] in the OLEX2[10] interface. Hydrogen atoms at idealized position were included in final refinements. The OLEX2 interface was used for structure visualization as well as for drawing ORTEP7[11] plots.

Table S2. Crystal data and structure refinement for 7g	
Identification code	mo_JD090823_0m_a
CCDC No.	2356047
Empirical formula	$C_{20}H_{18}N_4O_2$
Formula weight	346.38
Temperature/K	169.04
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	16.083(15)
b/Å	19.232(17)
c/Å	5.595(5)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	1731(3)
Z	4
$\rho_{calc}g/cm^3$	1.329
μ/mm^{-1}	0.089
F(000)	728.0
Crystal size/mm^3	0.2 × 0.2 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.936 to 51.422
Index ranges	$-19 \leq h \leq 19$, $-23 \leq k \leq 23$, $-5 \leq l \leq 6$
Reflections collected	17927
Independent reflections	2941 [R_{int} = 0.0787, R_{sigma} = 0.0521]
Data/restraints/parameters	2941/1/250
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0384, wR_2 = 0.0895
Final R indexes [all data]	R_1 = 0.0524, wR_2 = 0.1001
Largest diff. peak/hole / e $Å^{-3}$	0.14/-0.15
Flack parameter	-0.3(10)

10.0.2 X-Ray Crystal Structure of 9d:

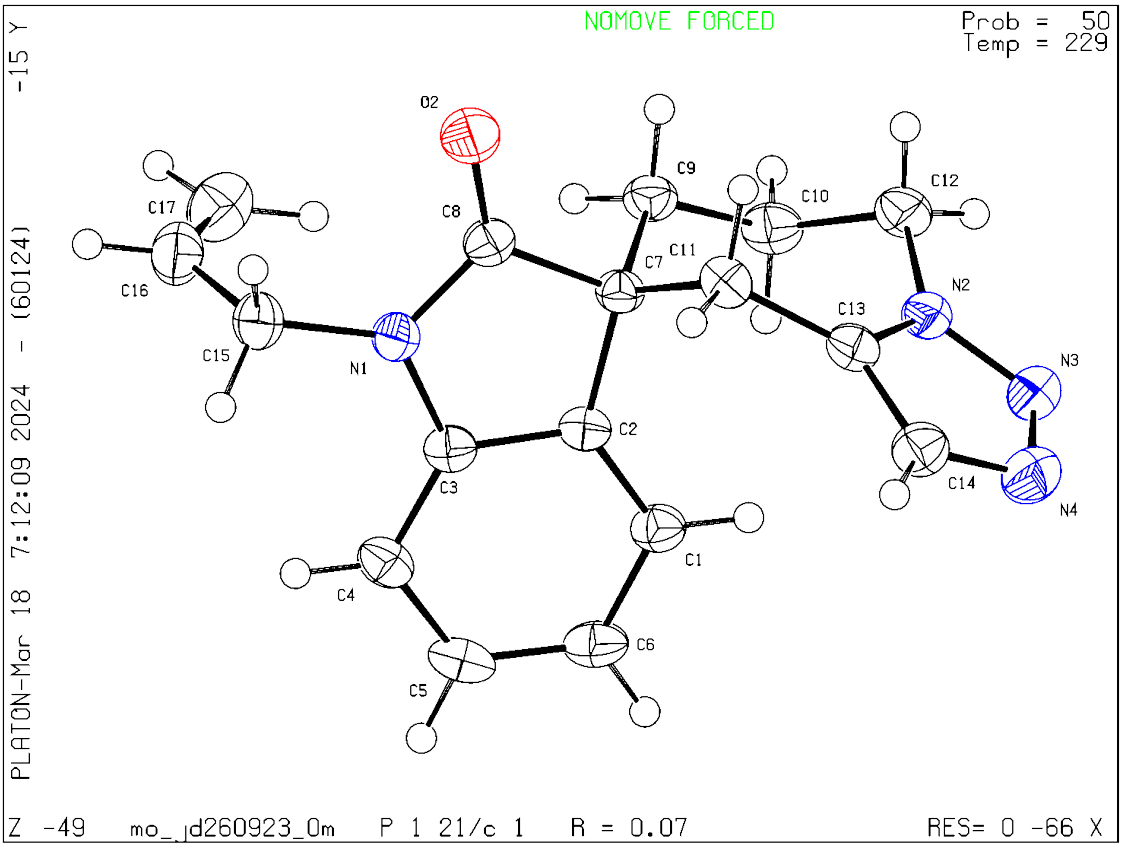


Figure S2. ORTEP illustration of **9d** (thermal ellipsoids are drawn at 50% probability). O: Red , N: Blue, H: White, C: Black.

Single crystals for X-ray studies were grown by slow evaporation of a solution of compound **9d** in MeOH in small glass vial at room temperature. The X-ray data of **9d** is deposited in the Cambridge Crystallograpic Data Centre (CCDC No. 2356048). Crystal data for the compound **9d** was collected at 229.07 K on a Bruker D8VENTURE Micro-focus diffractometer equipped with PHOTON II Detector, with MoKα radiation (0.71073 Å), controlled by the APEX3 (v2017.3-0) software package. The raw data was integrated and corrected for Lorentz and polarization effects with the aid of the Bruker Apex III program suite. Absorption corrections were performed by using SADABS. Space groups were assigned by systematic absences (determined by XPREP) and analysis of metric chemistry and were further checked by PLATON[7,8], for additional symmetry. Structure was solved by direct methods and refined against all data in the reported 2Θ ranges by full-matrix least square on F2 using the SHELXL program suite[9] in the OLEX2[10] interface. Hydrogen atoms at idealized position were included in final refinements. The OLEX2 interface was used for structure visualization as well as for drawing ORTEP7[11] plots.

Table S3. Crystal data and structure refinement for 9d	
Identification code	9d
CCDC No.	2356048
Empirical formula	$C_{17}H_{18}N_4O$
Formula weight	294.35
Temperature/K	229.07
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.422(4)
b/Å	20.895(10)
c/Å	7.919(4)
α/°	90
β/°	106.630(18)
γ/°	90
Volume/Å^3	1493.7(13)
Z	4
ρ_{calc}g/cm^3	1.309
μ/mm^{-1}	0.085
F(000)	624.0
Crystal size/mm^3	0.2 × 0.2 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.512 to 56.776
Index ranges	$-11 \leq h \leq 12$, $-27 \leq k \leq 27$, $-10 \leq l \leq 10$
Reflections collected	16226
Independent reflections	3717 [R_{int} = 0.1031, R_{sigma} = 0.0890]
Data/restraints/parameters	3717/0/207
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0672, wR_2 = 0.1686
Final R indexes [all data]	R_1 = 0.0904, wR_2 = 0.1874
Largest diff. peak/hole / e Å^{-3}	0.32/-0.27

11.0 References:

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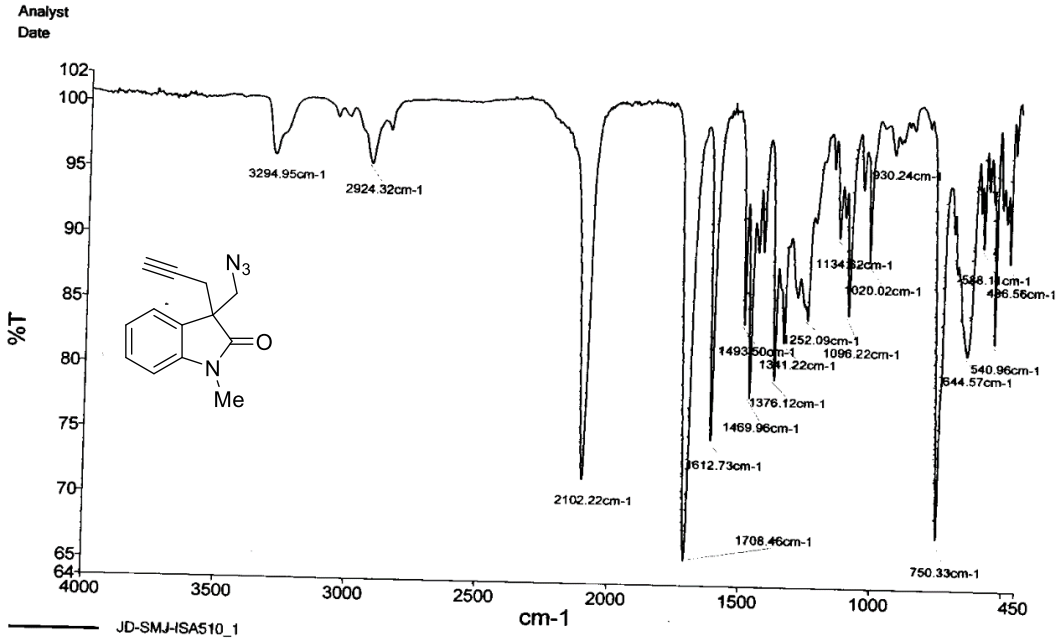
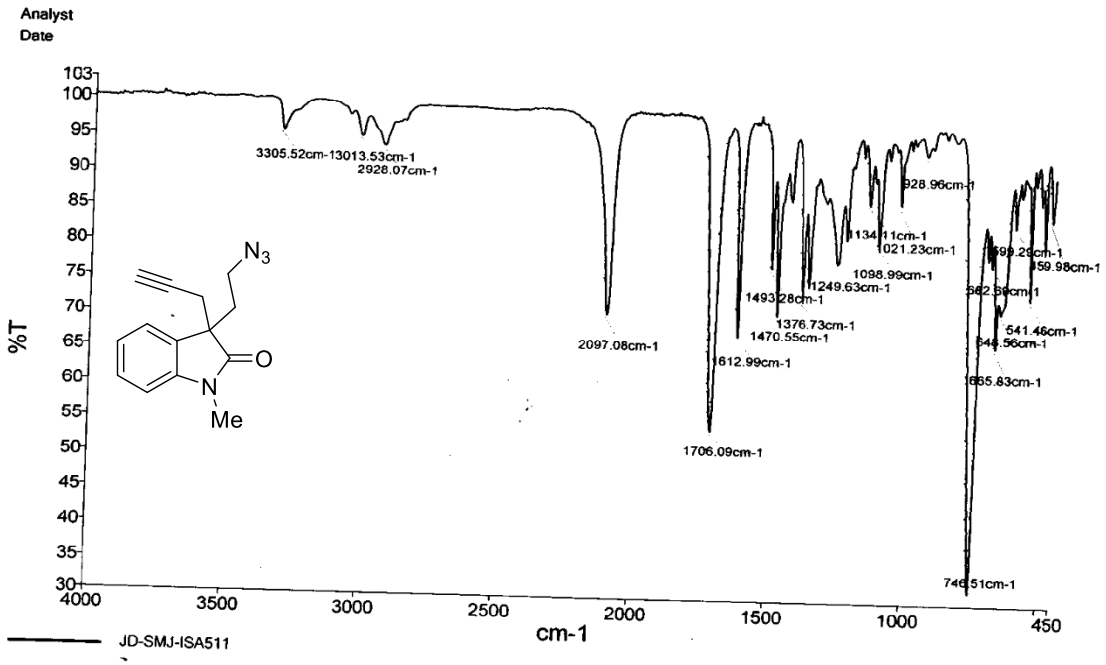
12.0 IR Spectrum of compound S3-c:

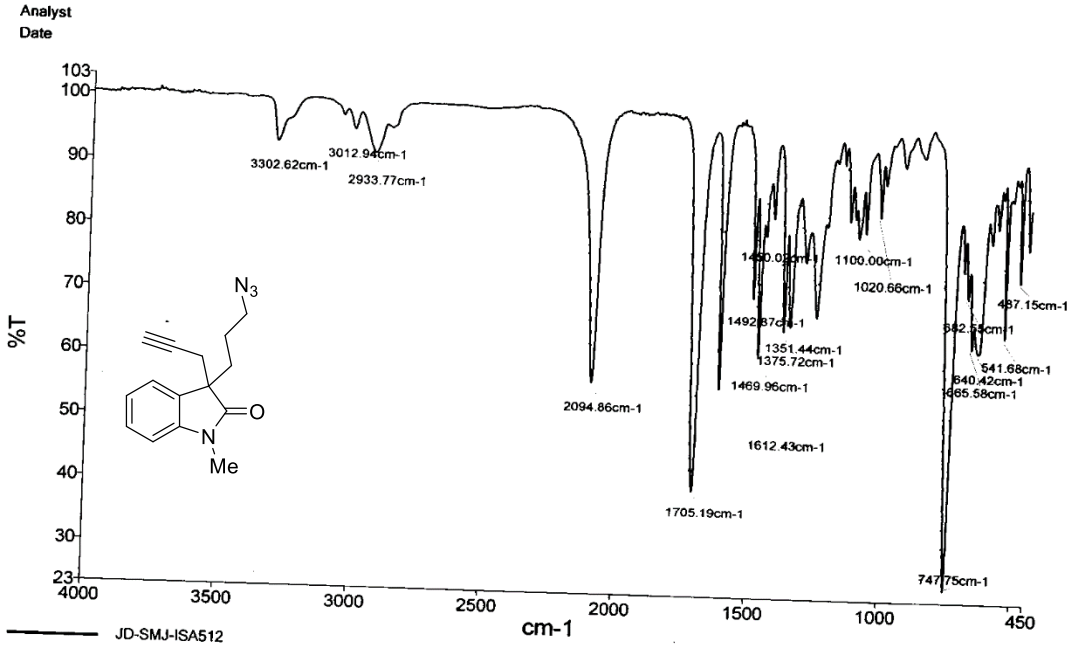
IR Spectrum of S3a:



IR Spectrum of S3b:

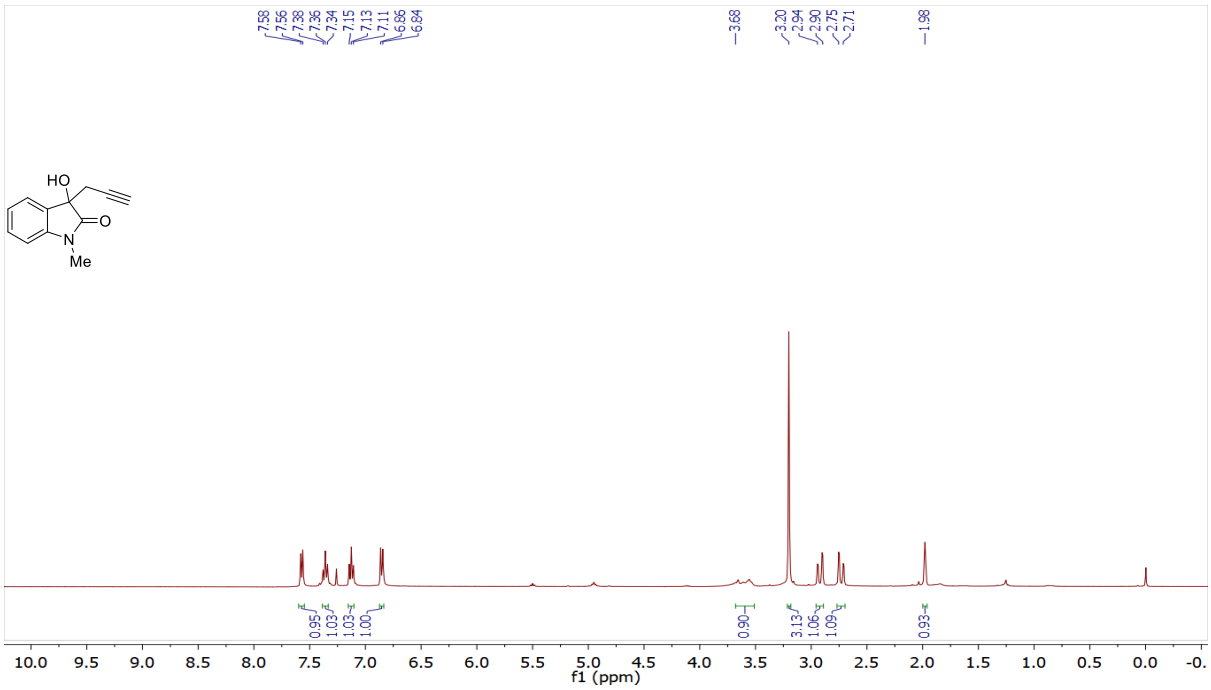


IR Spectrum of S3c:

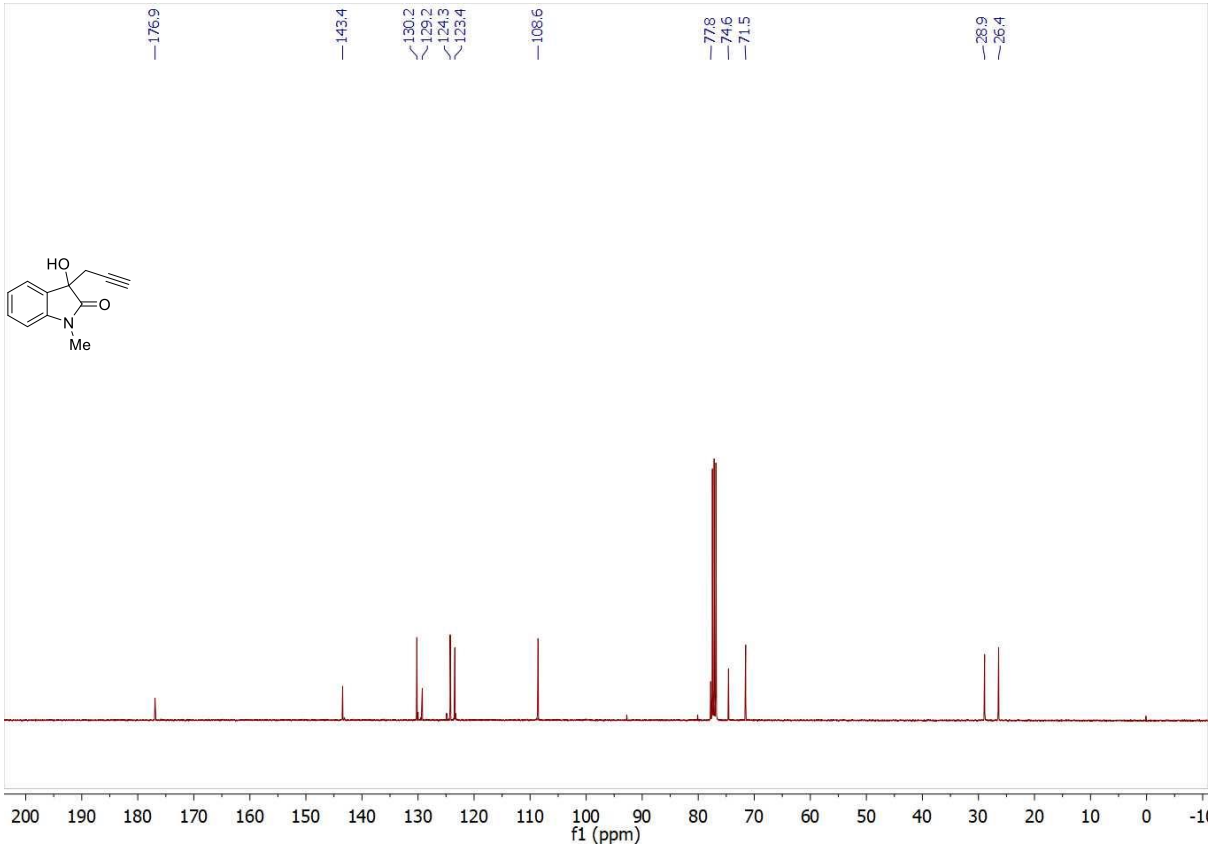


13.0 NMR spectra of all the synthesized compounds:

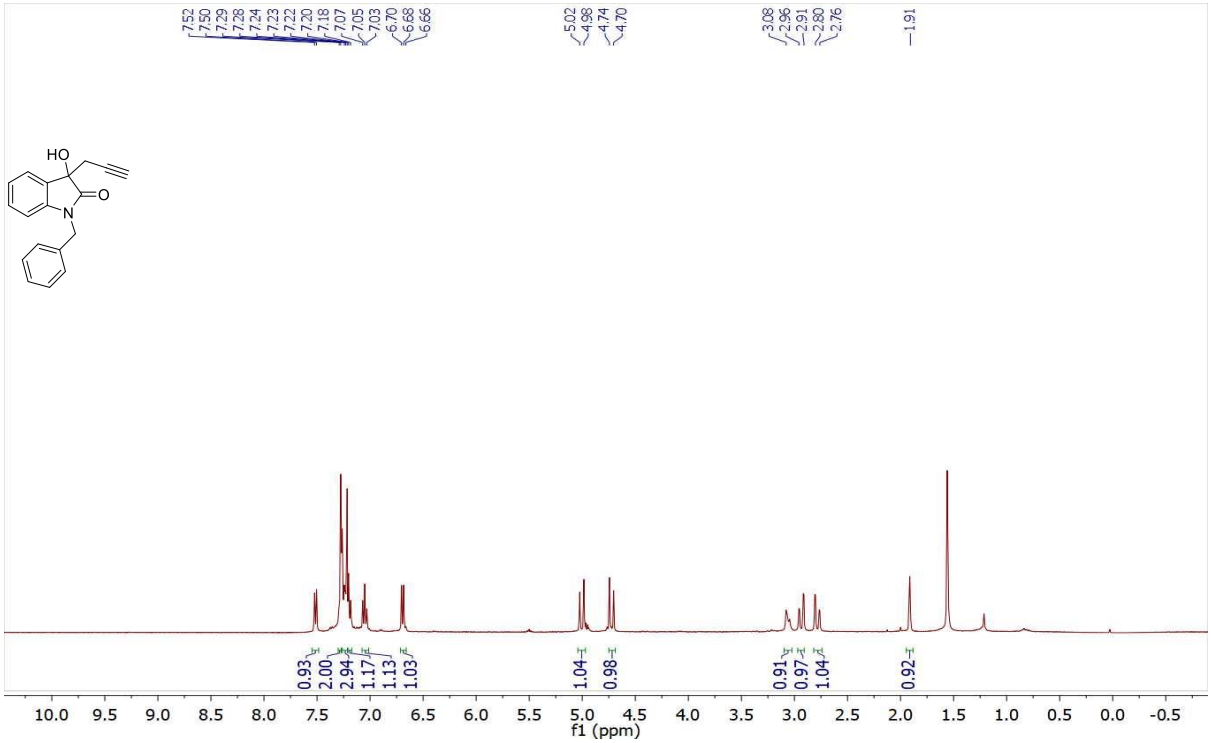
^{1}H NMR of 2a (400 MHz, $CDCl_3$):



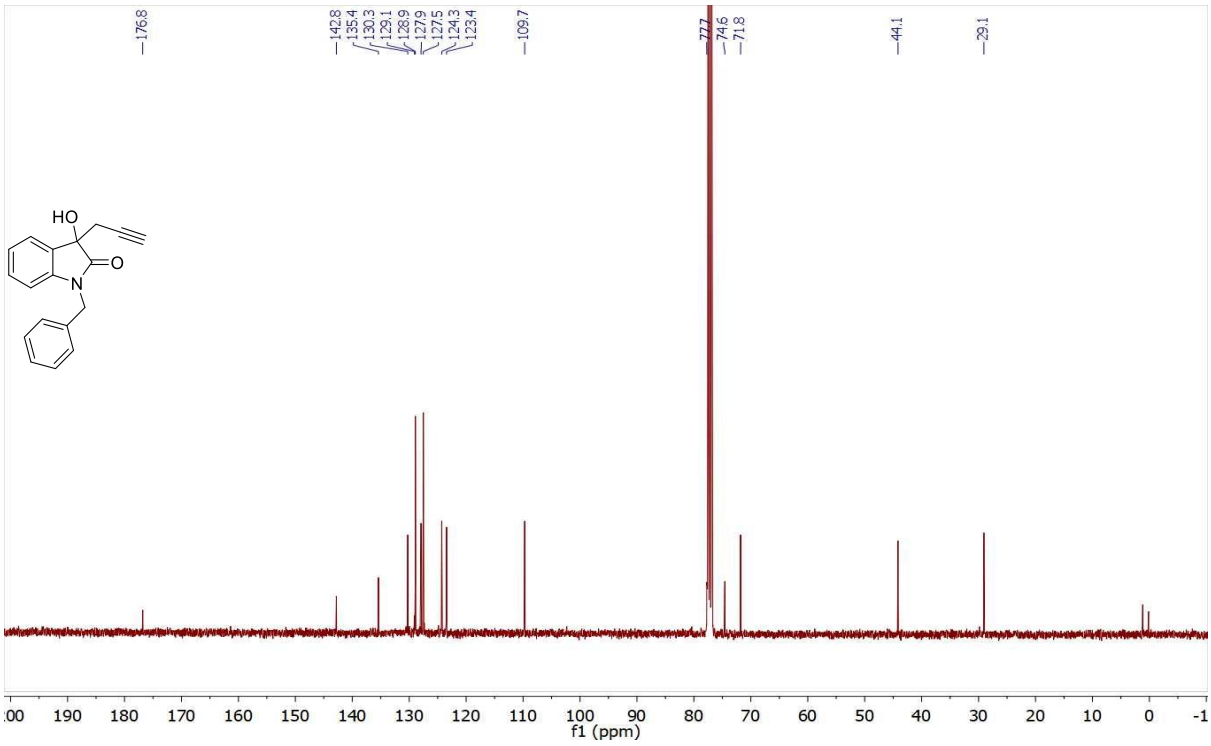
^{13}C{^{1}H} NMR of 2a (101 MHz, $CDCl_3$):



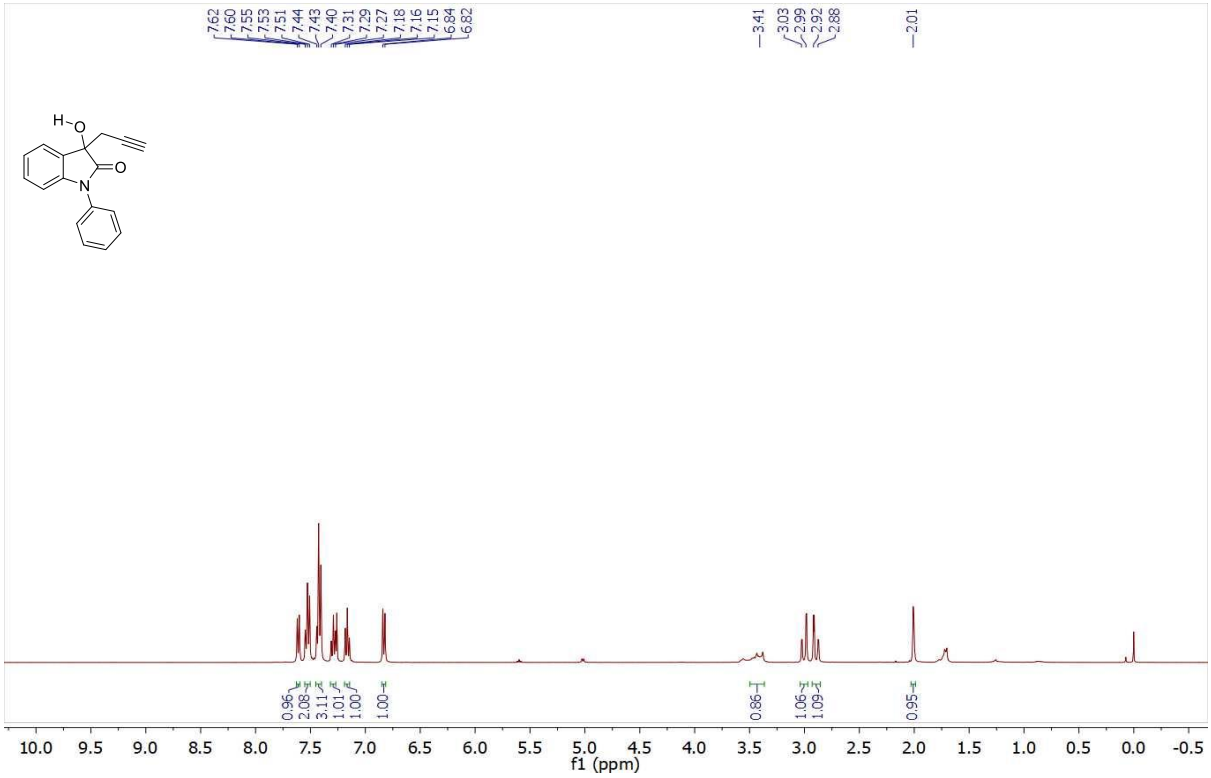
^{1}H NMR of 2b (400 MHz, $CDCl_3$):



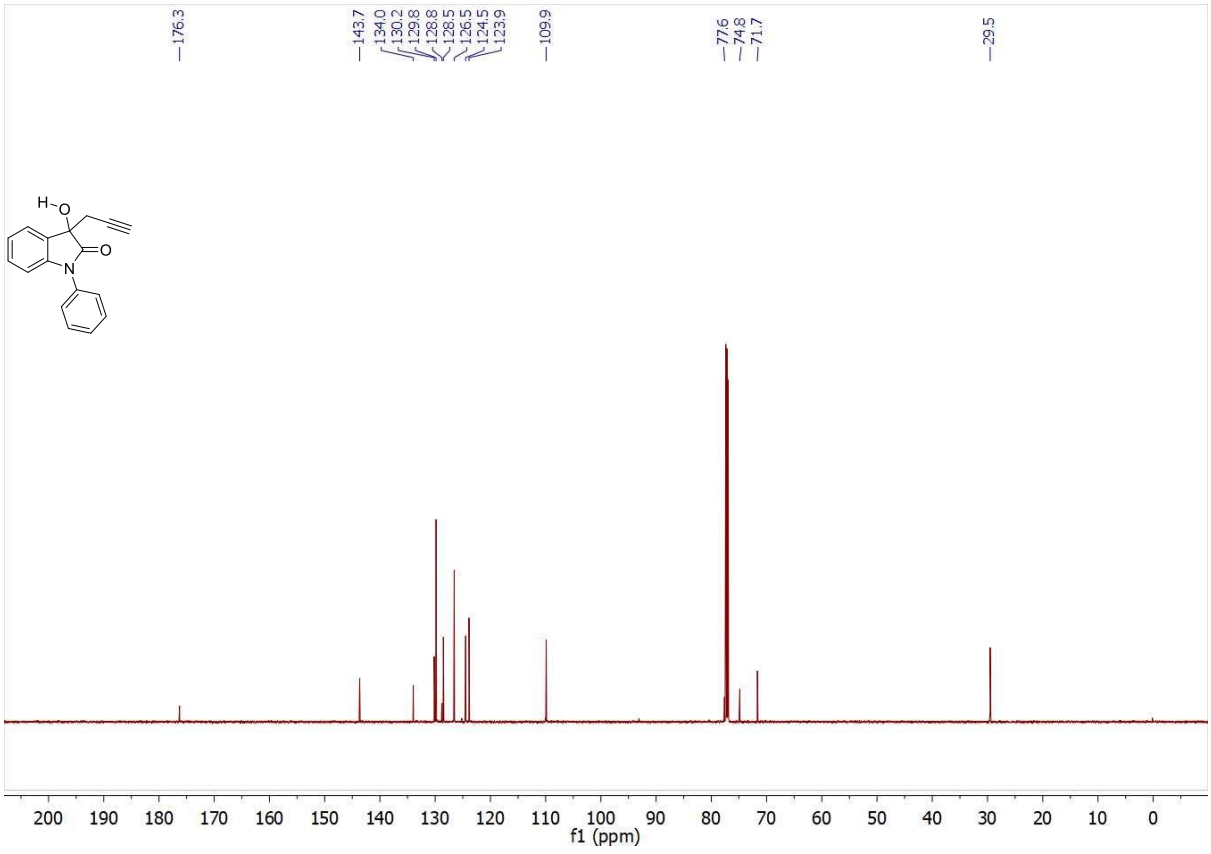
^{13}C{^{1}H} NMR of 2b (101 MHz, $CDCl_3$):



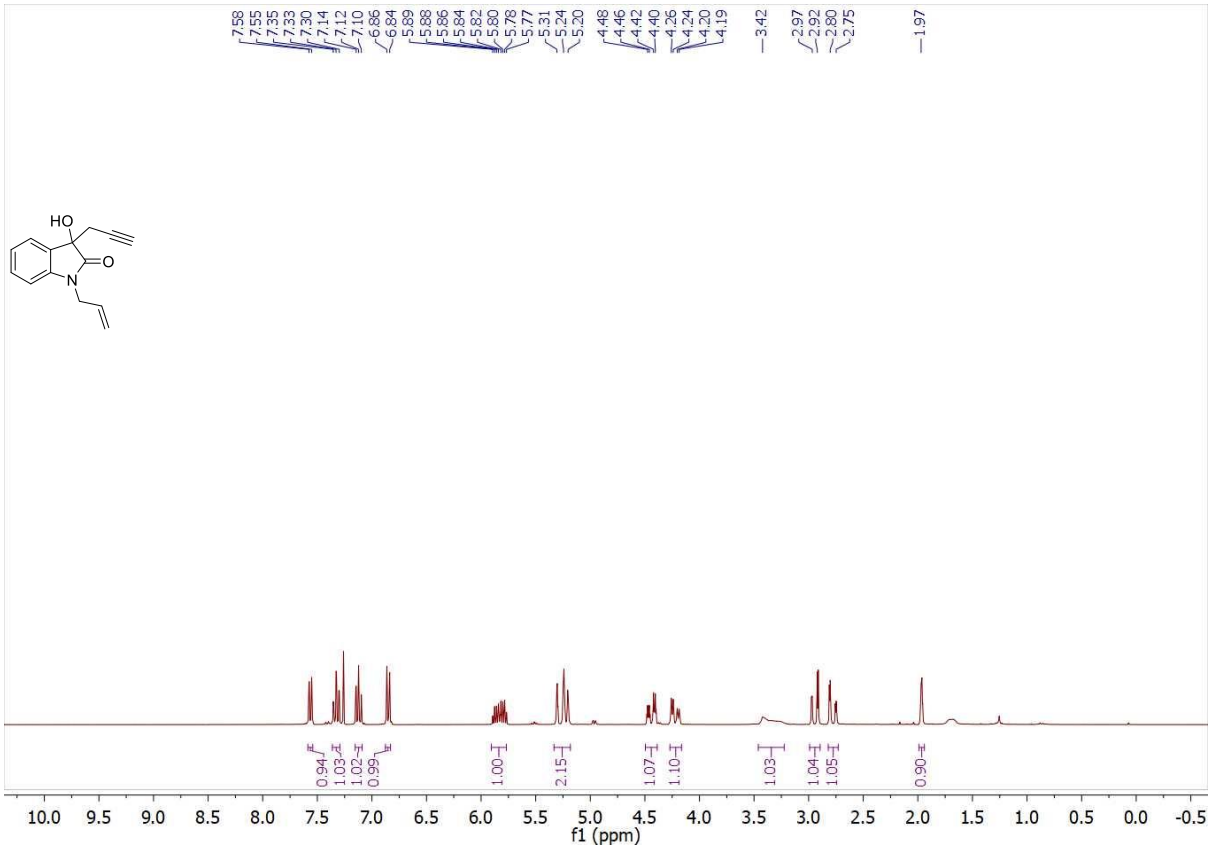
^{1}H NMR of 2c (400 MHz, $CDCl_3$):



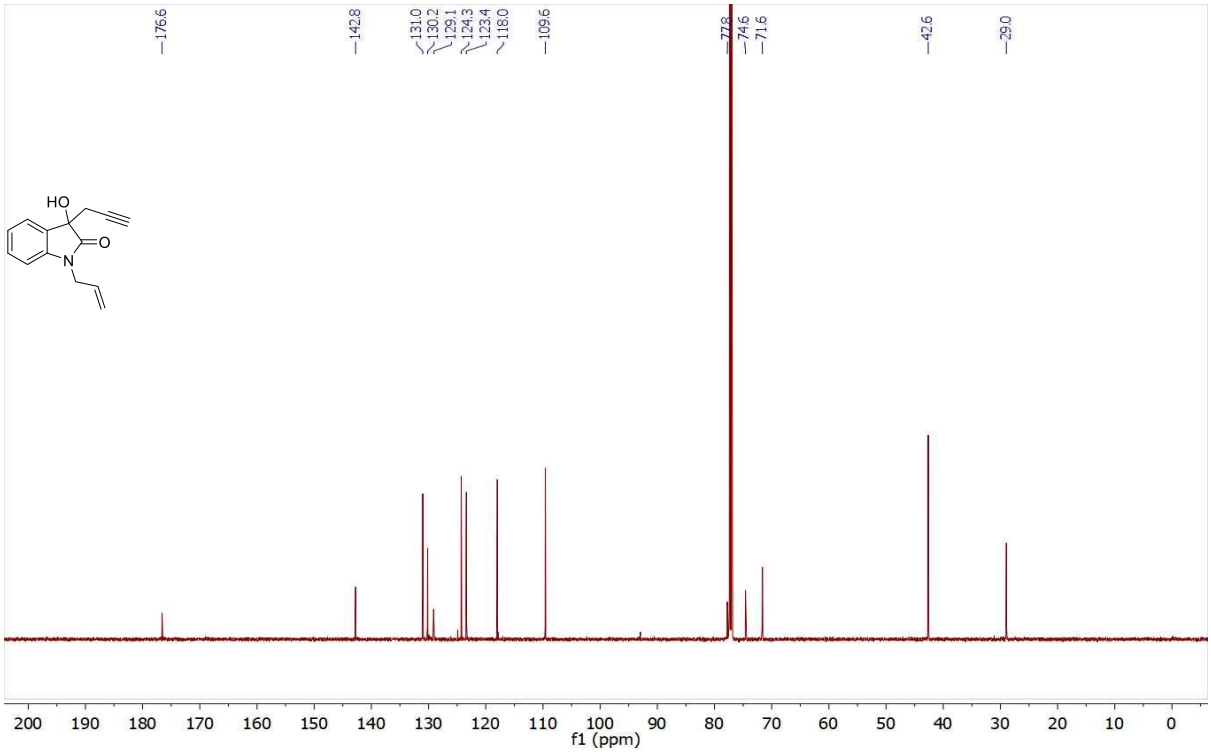
^{13}C{1H} NMR of 2c (151 MHz, $CDCl_3$):



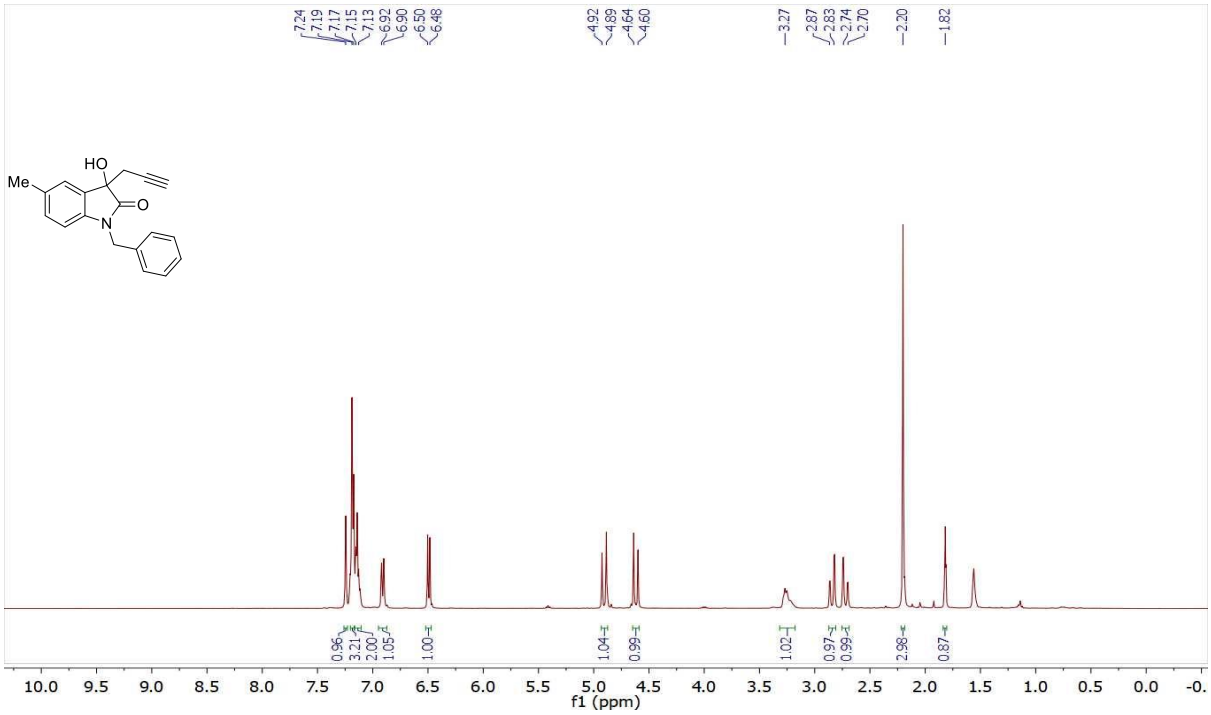
^{1}H NMR of 2d (300 MHz, $CDCl_3$):



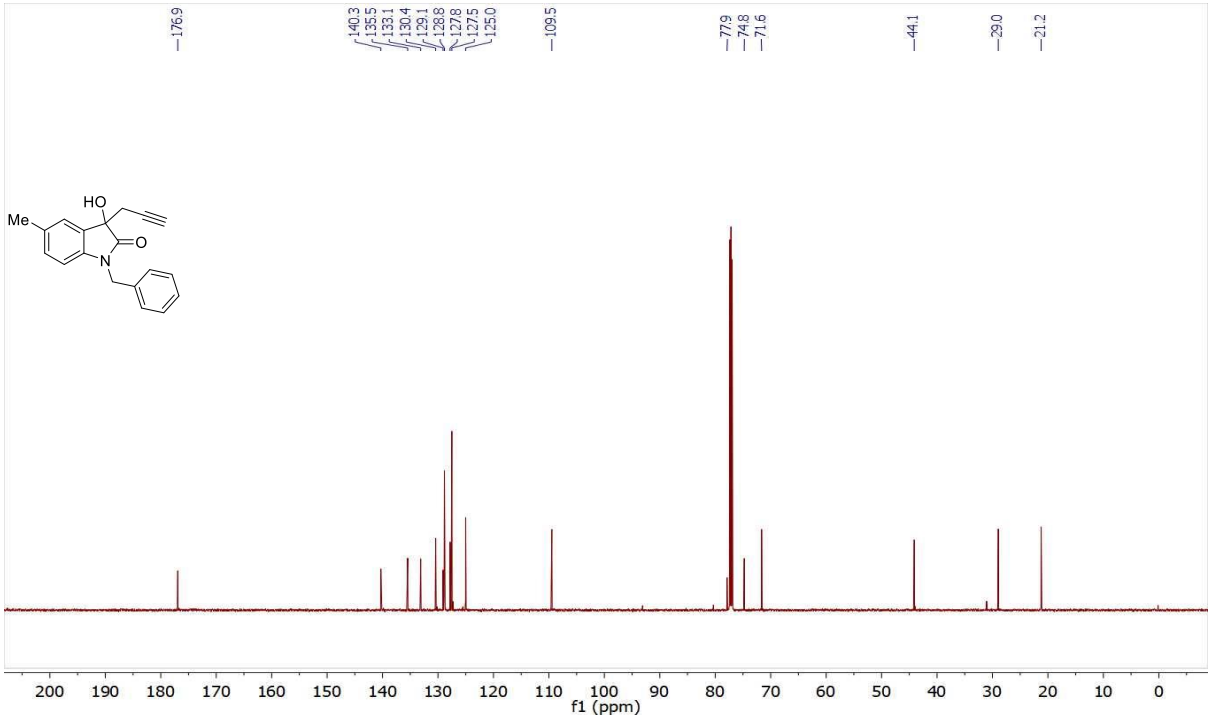
^{13}C{^{1}H} NMR of 2d (151 MHz, $CDCl_3$):



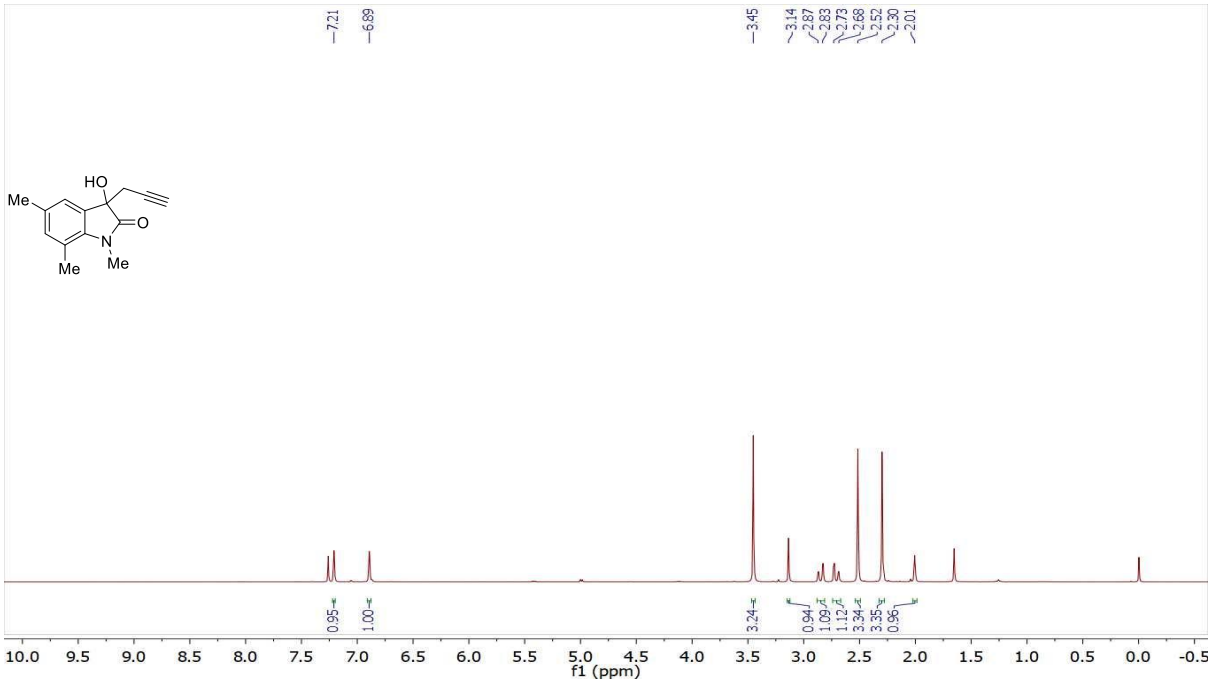
^{1}H NMR of 2e (400 MHz, $CDCl_3$):



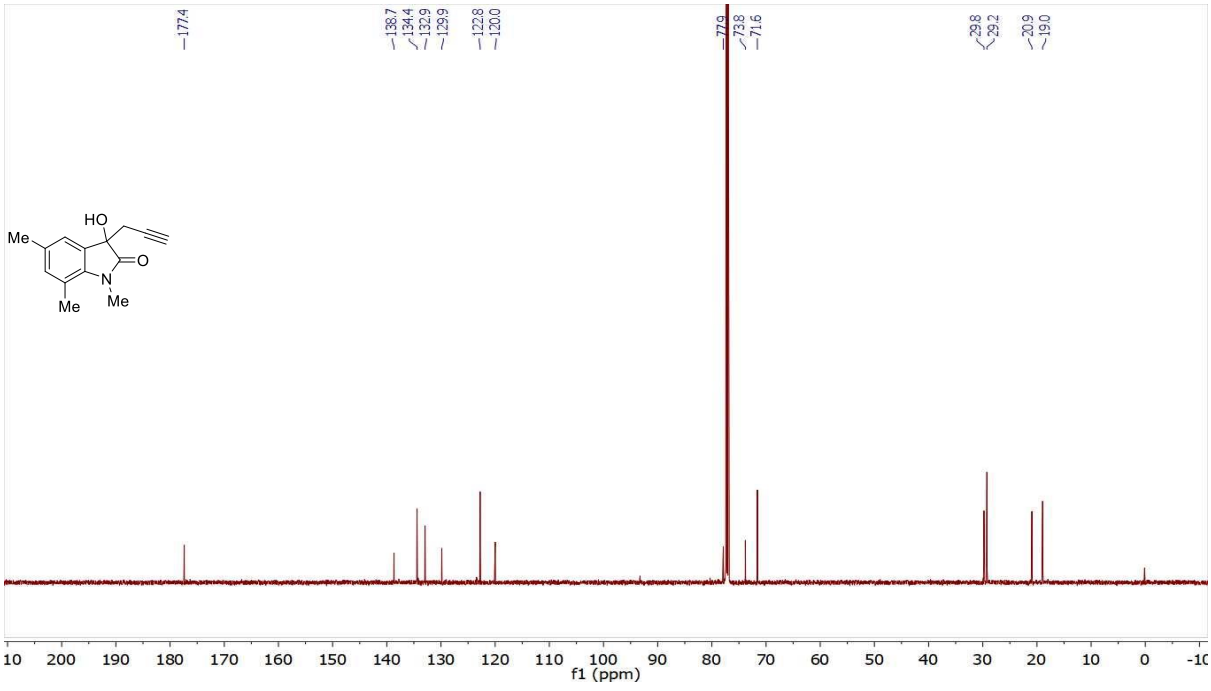
^{13}C{1H} NMR of 2e (151 MHz, $CDCl_3$):



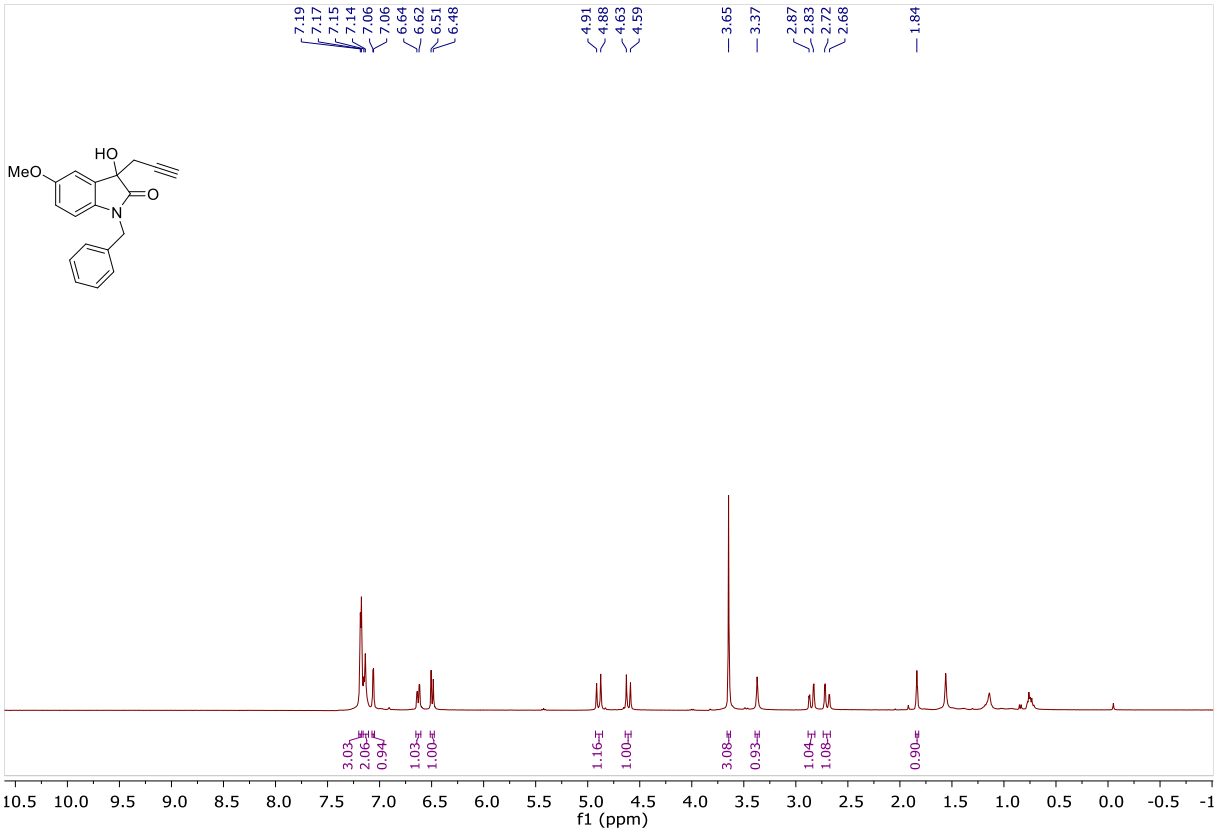
^{1}H NMR of 2f (400 MHz, $CDCl_3$):



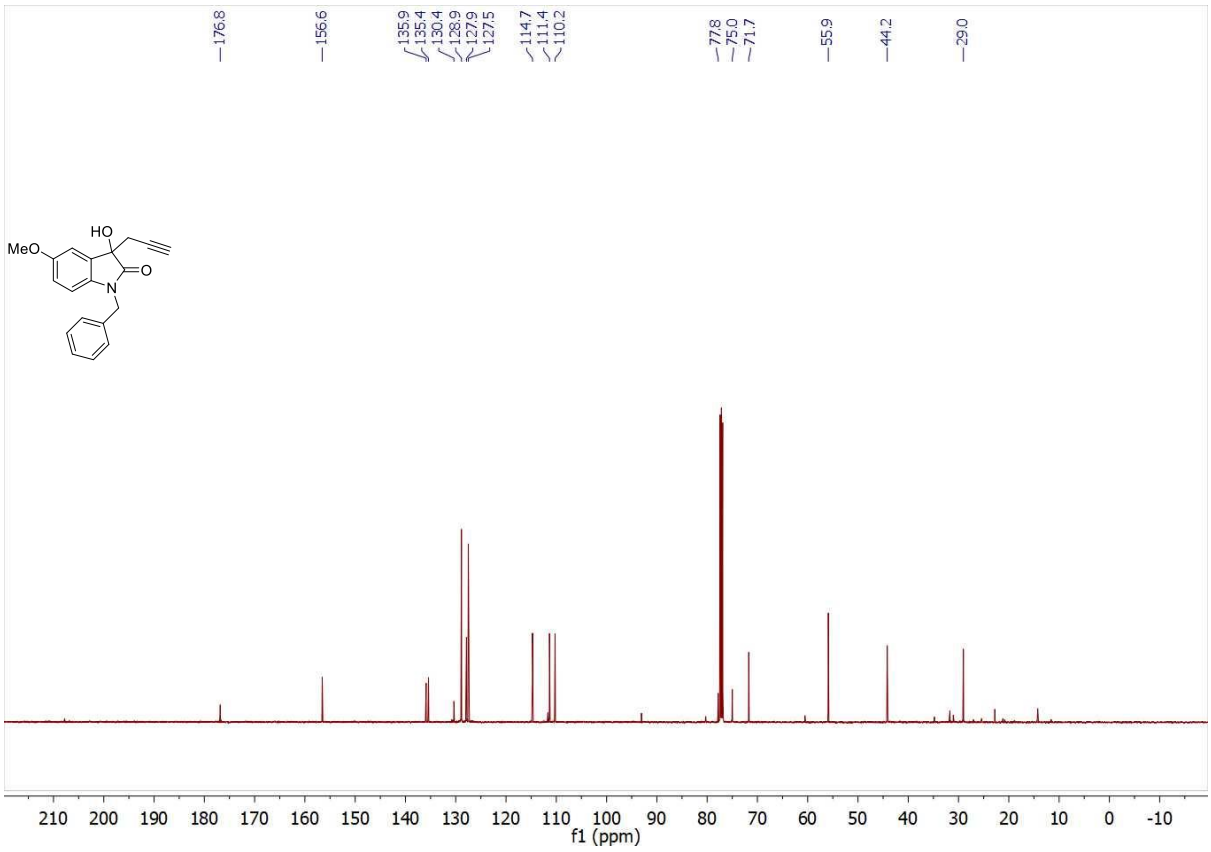
^{13}C{1H} NMR of 2f (151 MHz, $CDCl_3$):



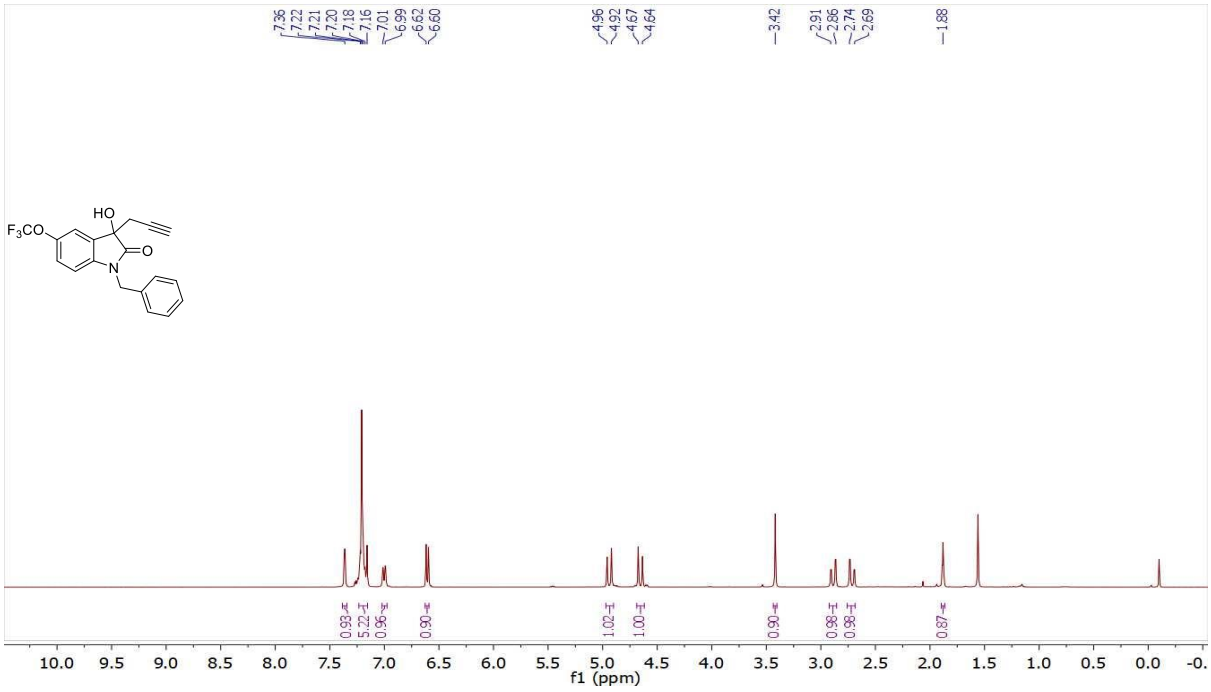
^{1}H NMR of 2g (400 MHz, $CDCl_3$):



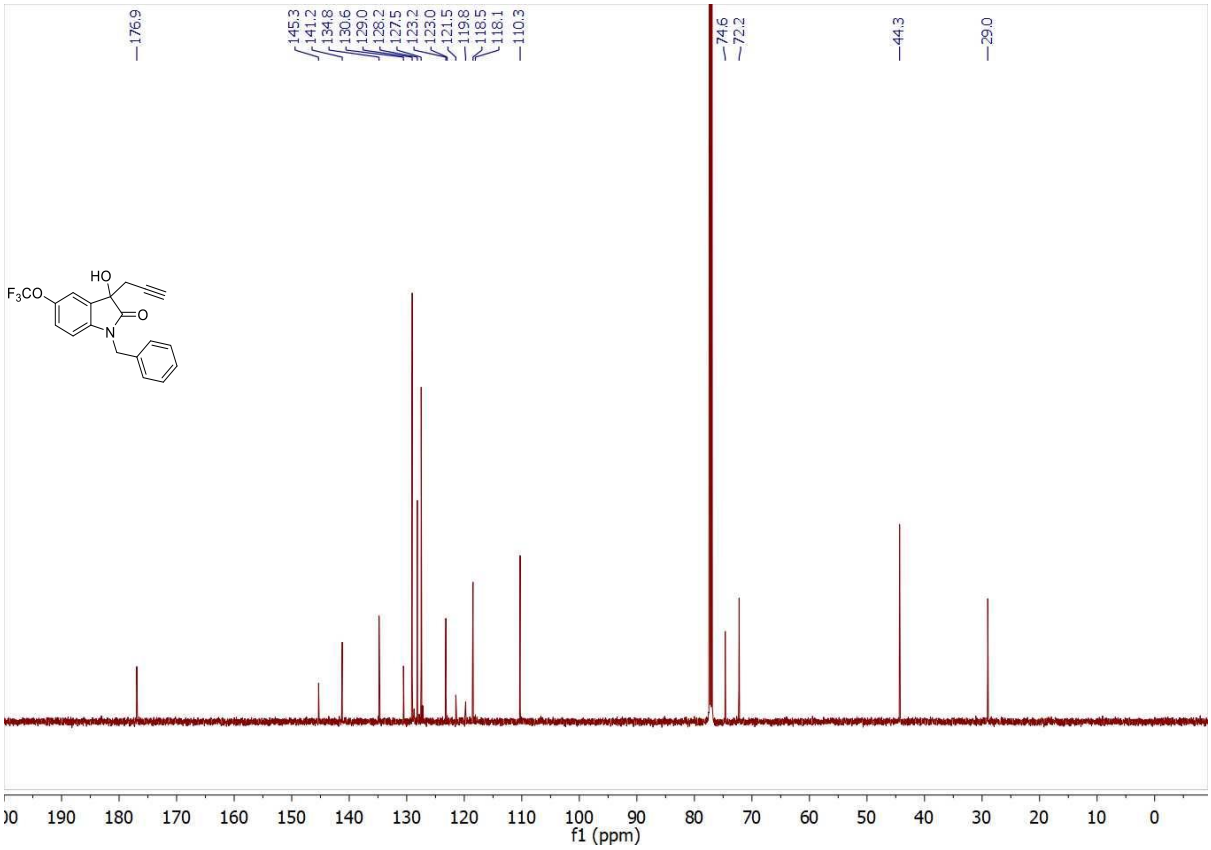
^{13}C{^{1}H} NMR of 2g (126 MHz, $CDCl_3$):



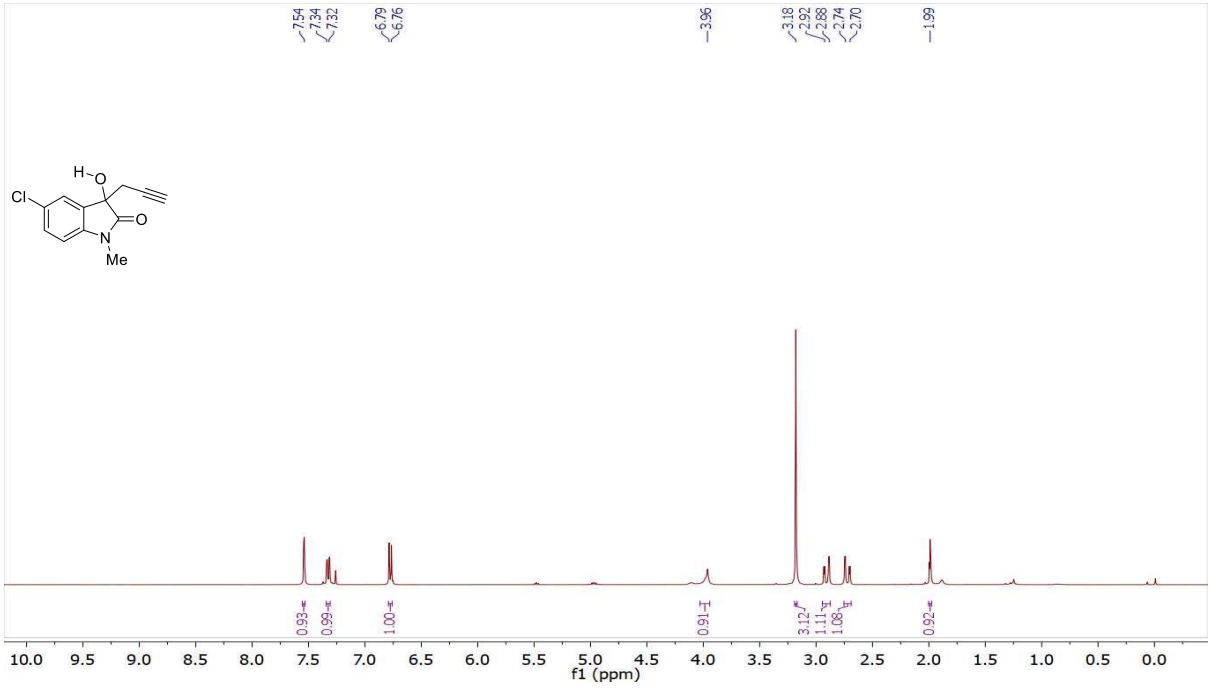
1H NMR of 2h (400 MHz, CDCl3):



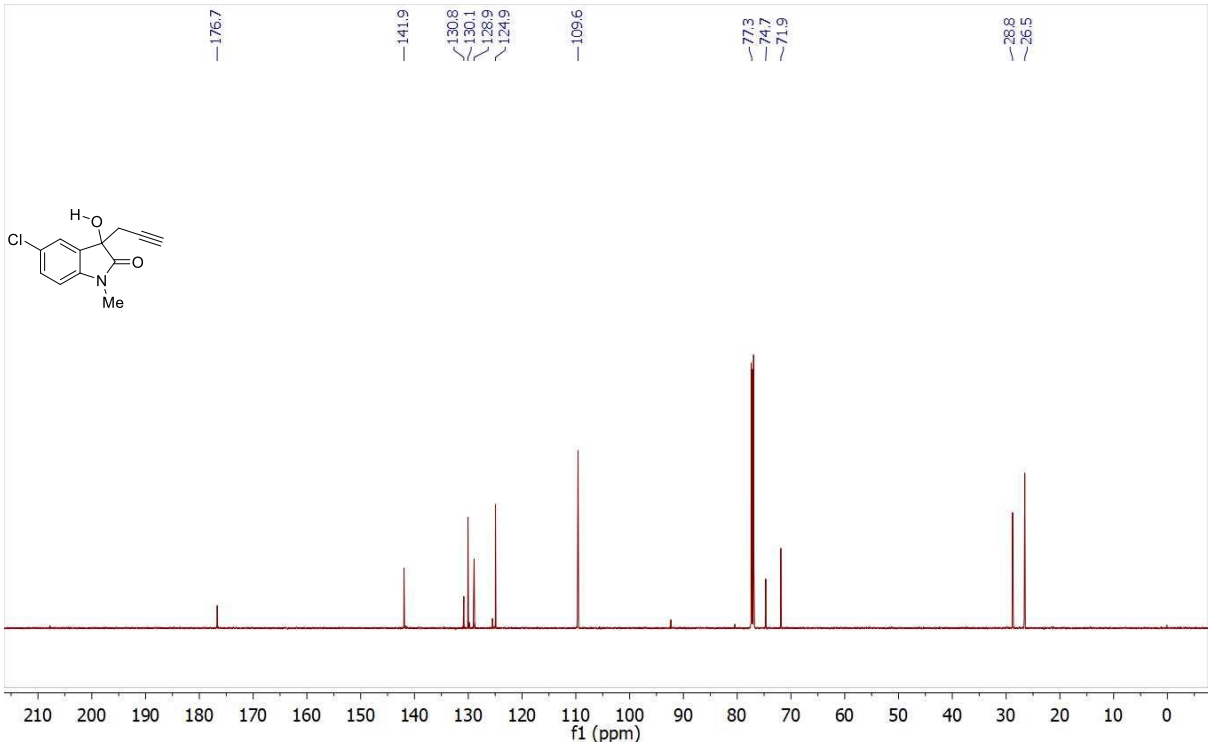
^{13}C{1H} NMR of 2h (151 MHz, $CDCl_3$):



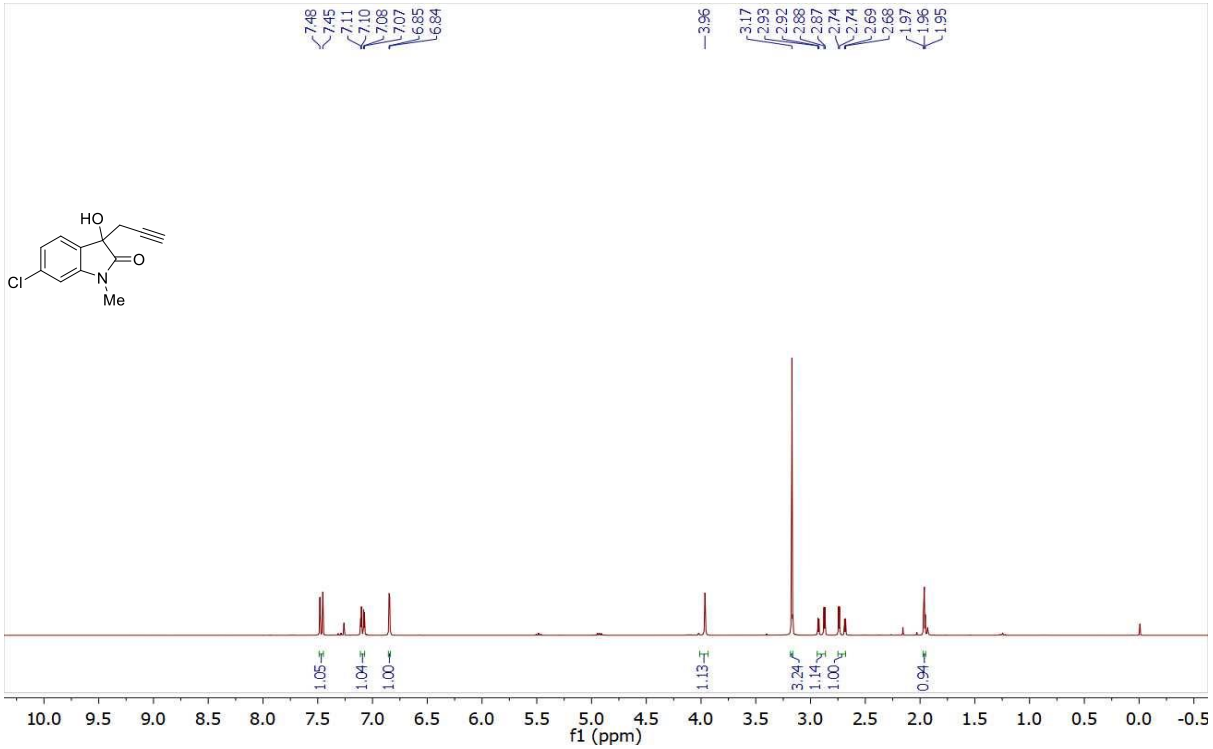
^{1}H NMR of 2i (400 MHz, $CDCl_3$):



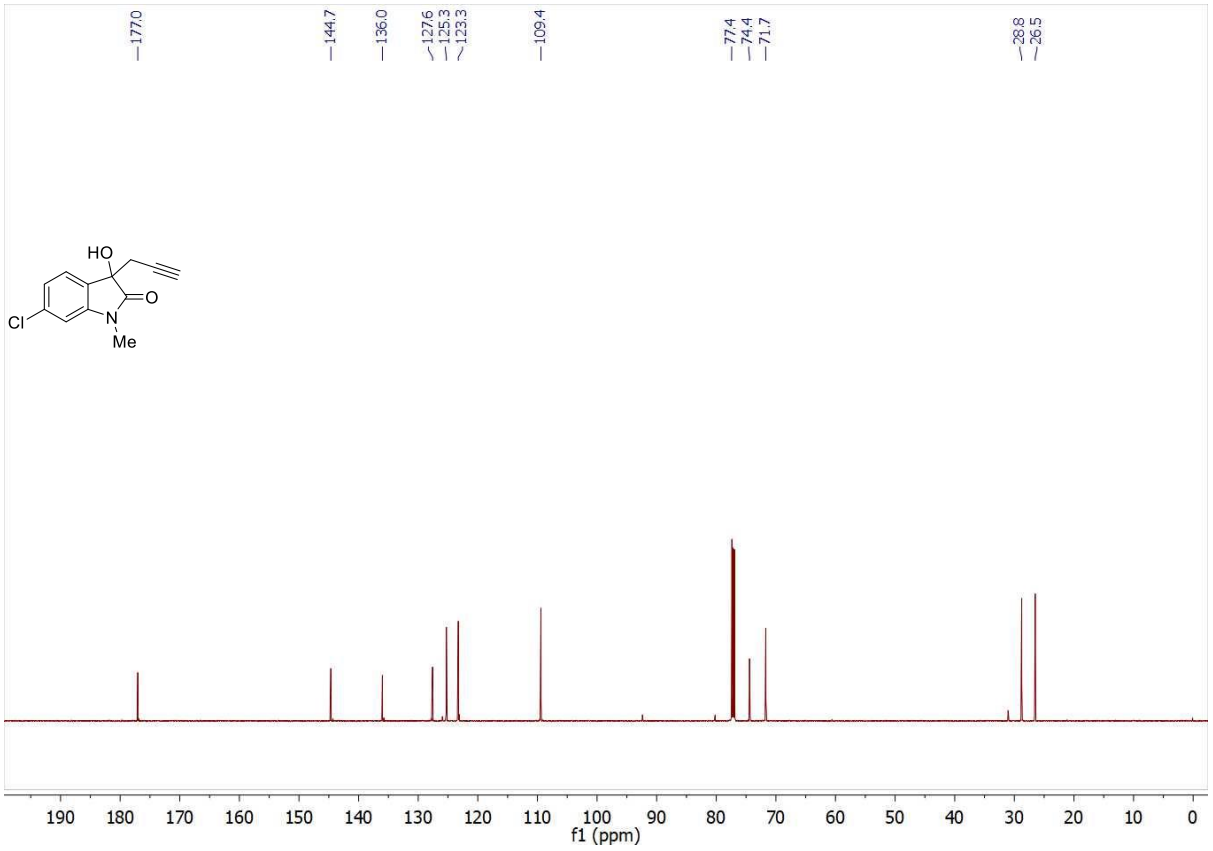
^{13}C{^{1}H} NMR of 2i (151 MHz, $CDCl_3$):



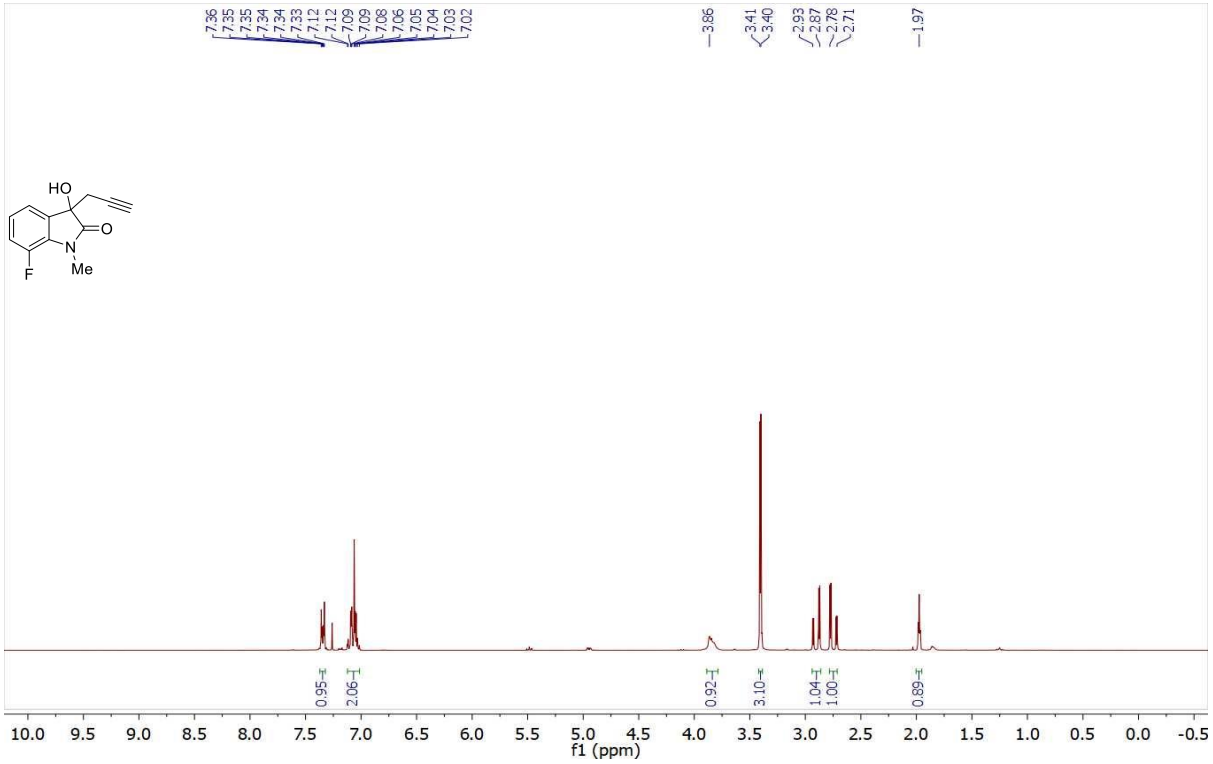
^{1}H NMR of 2j (300 MHz, $CDCl_3$):



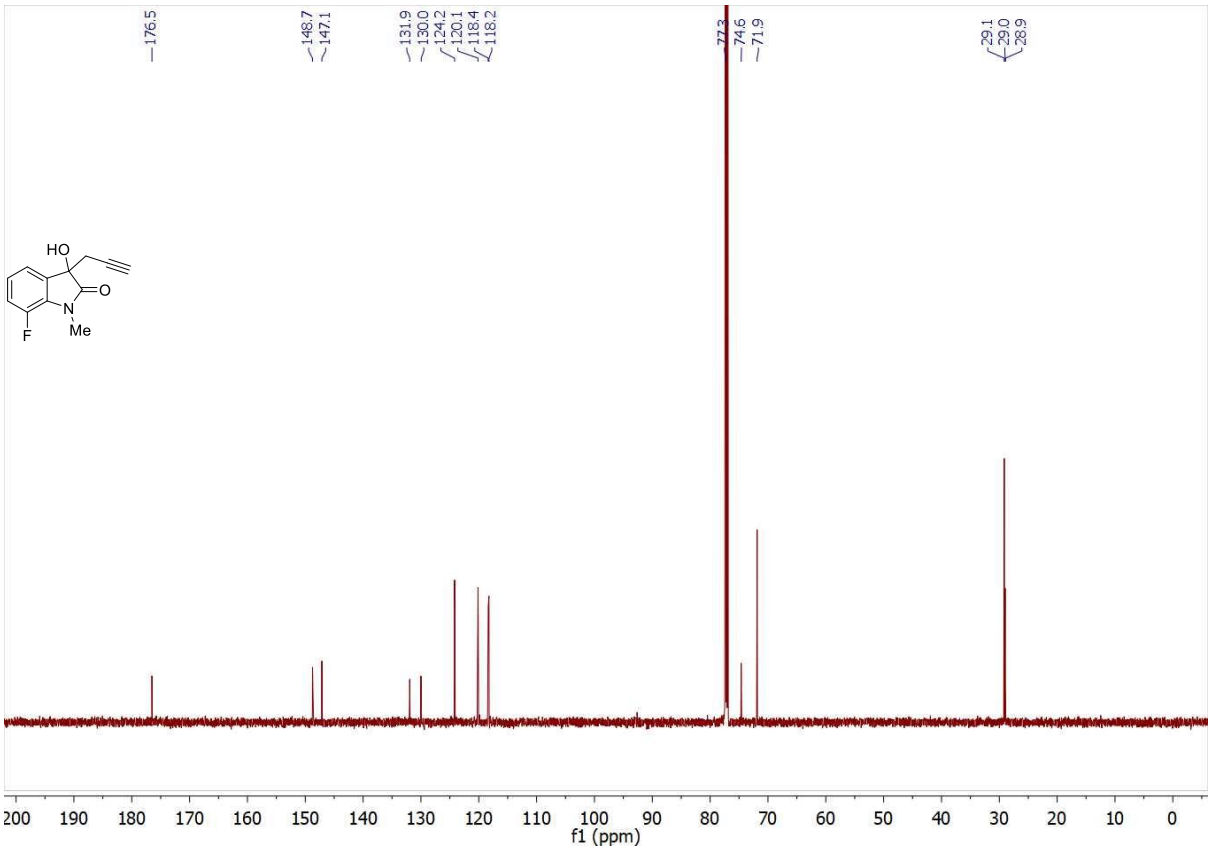
^{13}C{^{1}H} NMR of 2j (151 MHz, $CDCl_3$):



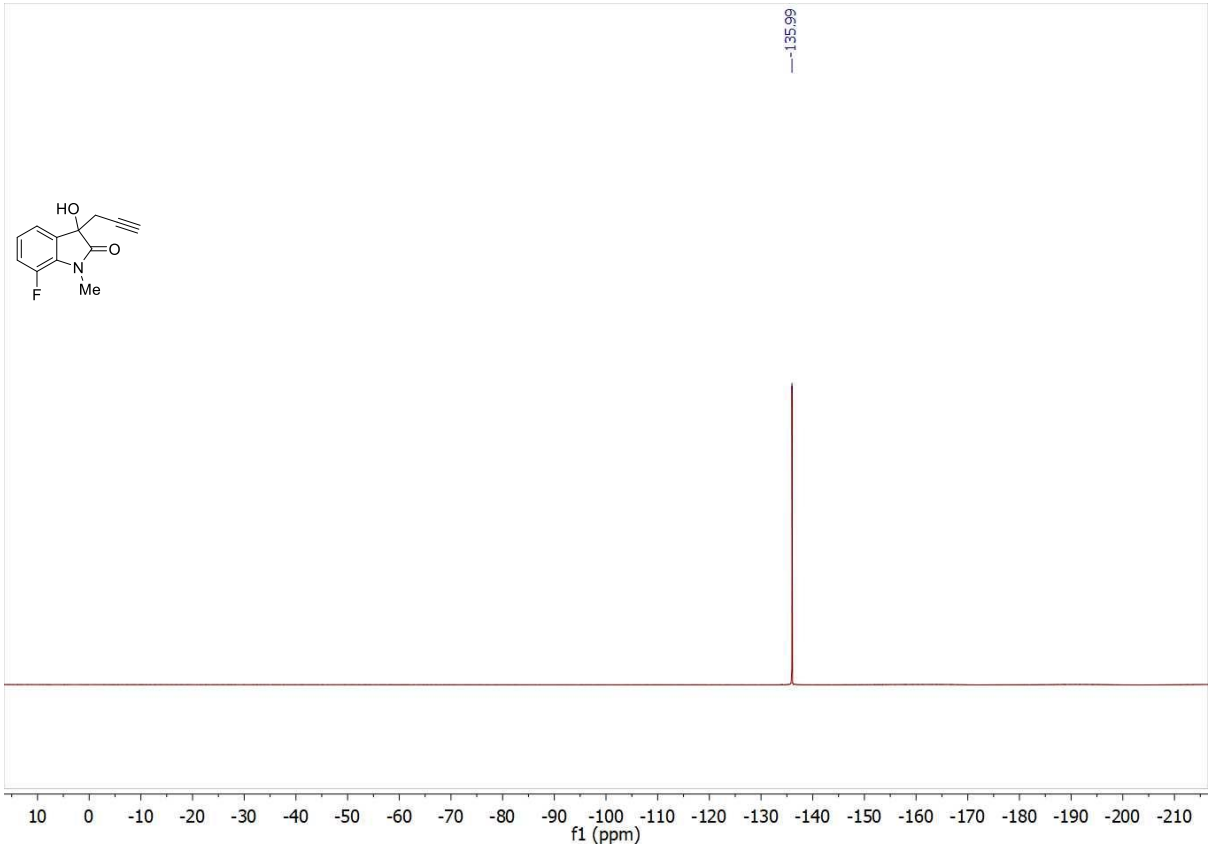
^{1}H NMR of 2k (300 MHz, $CDCl_3$):



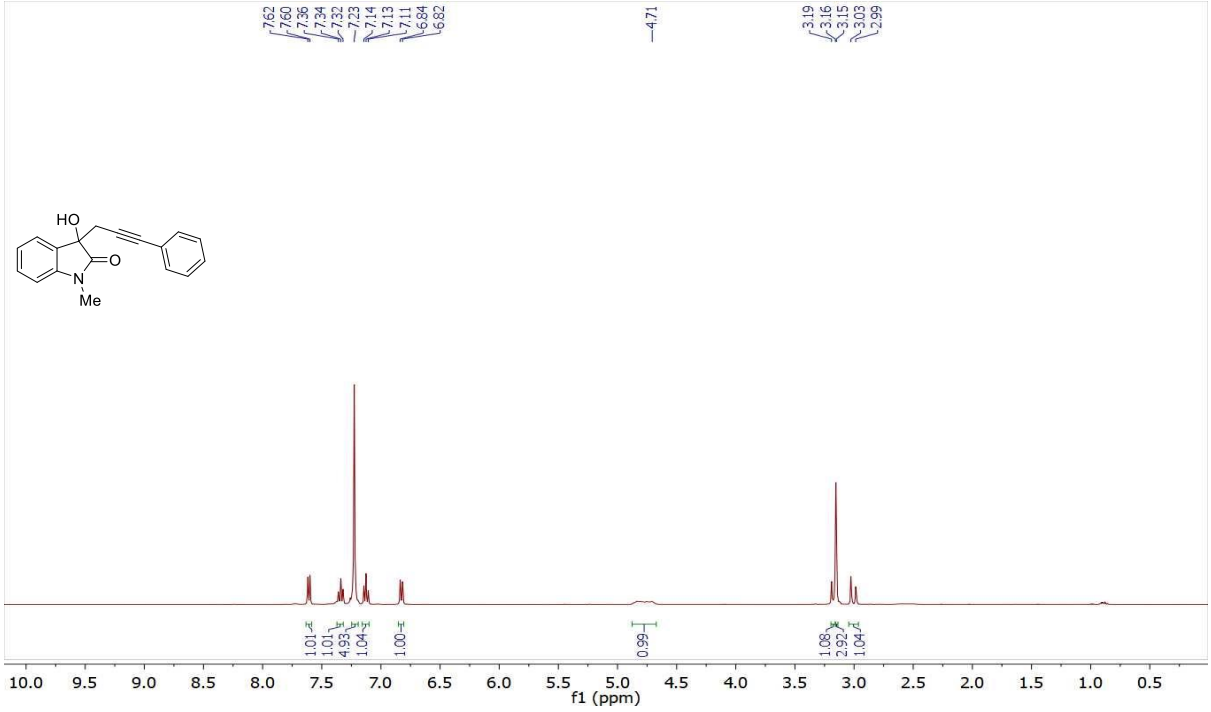
^{13}C{1H} NMR of 2k (151 MHz, $CDCl_3$):



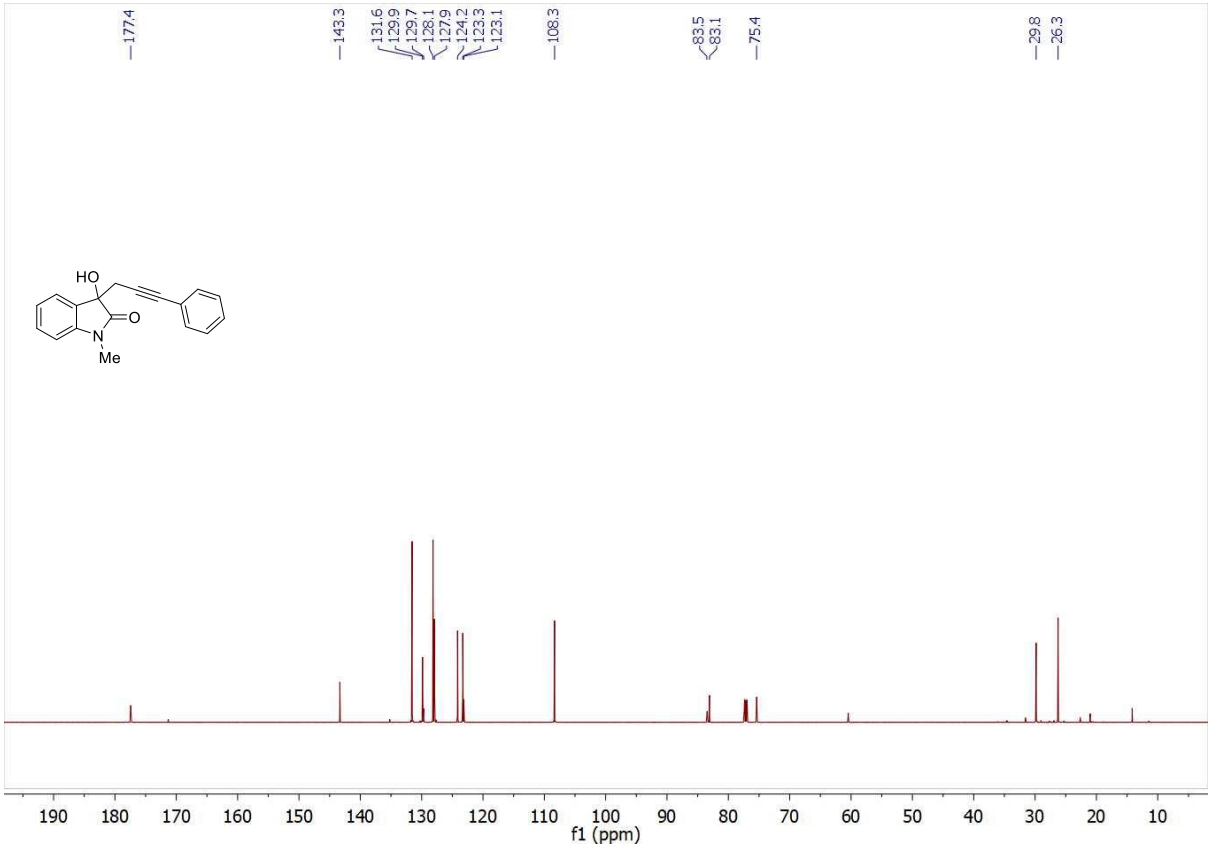
$^{19}F\{^{1}H\}$ NMR of 2k (565 MHz, $CDCl_3$):



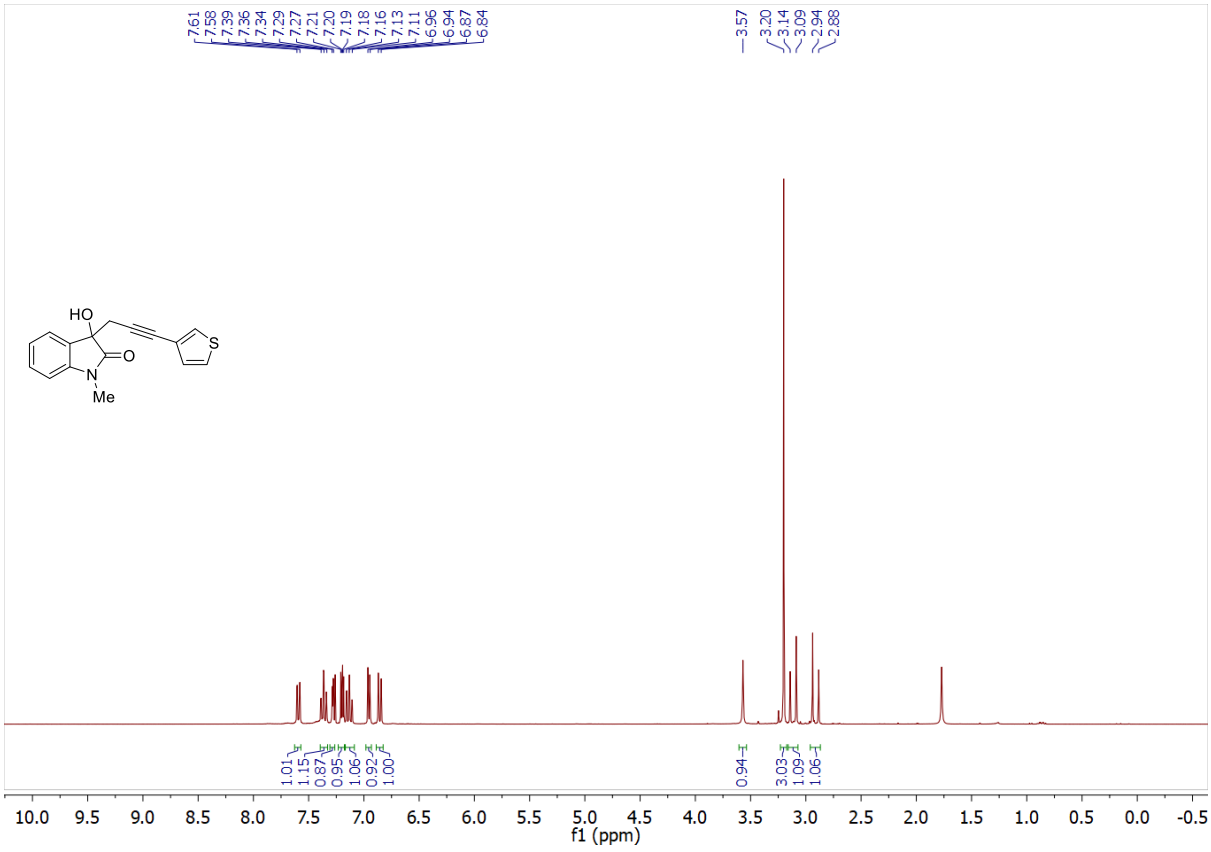
^{1}H NMR of S2a (400 MHz, $CDCl_3$):



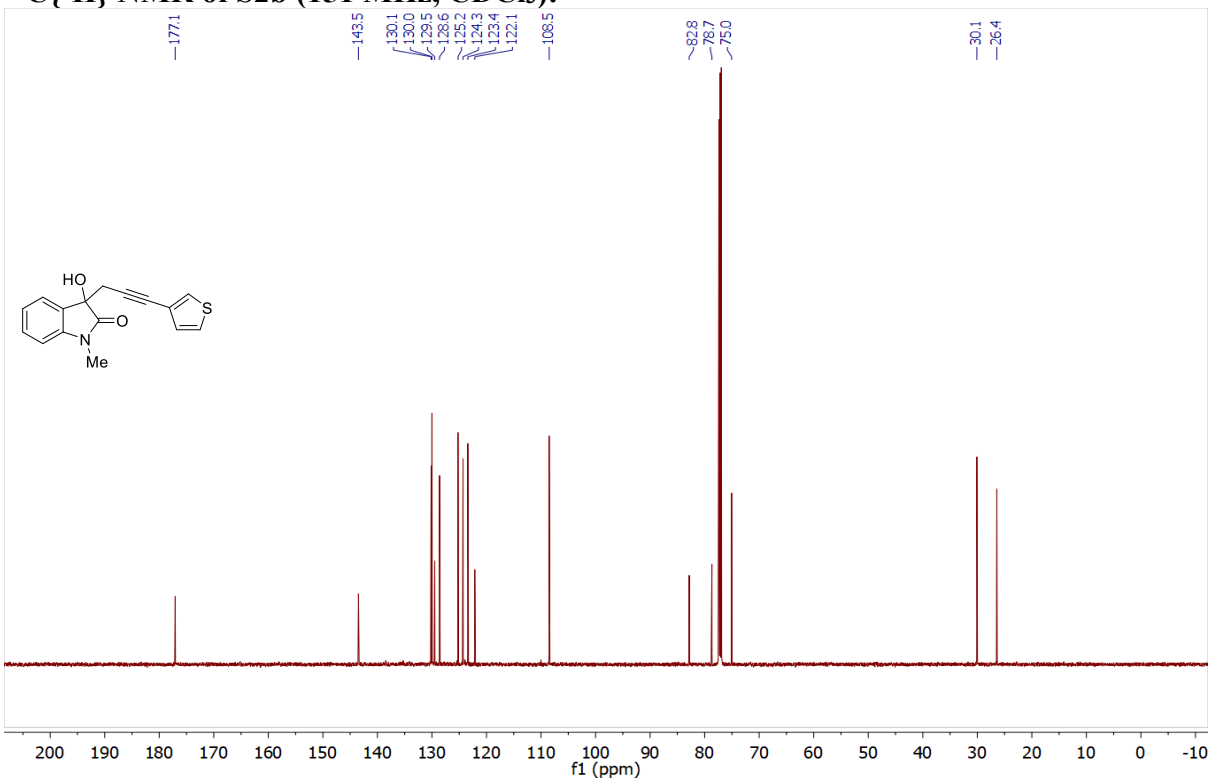
$^{13}C\{^{1}H\}$ NMR of S2a (151 MHz, $CDCl_3$):



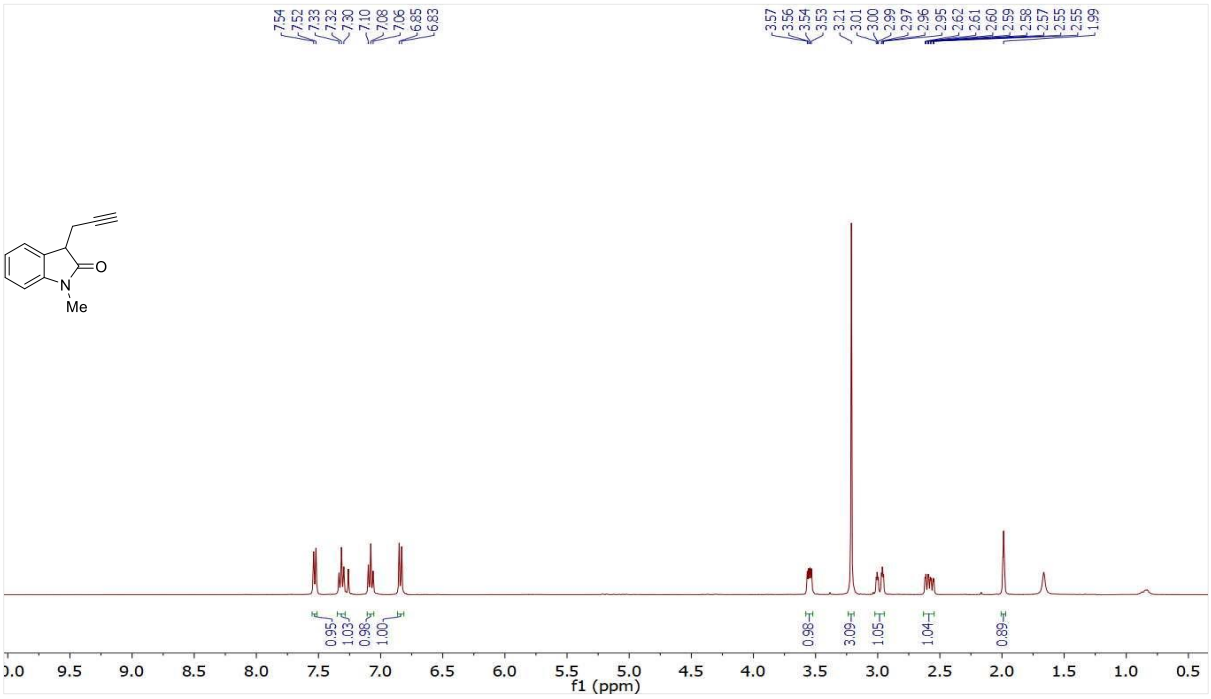
^{1}H NMR of S2a (300 MHz, $CDCl_3$):



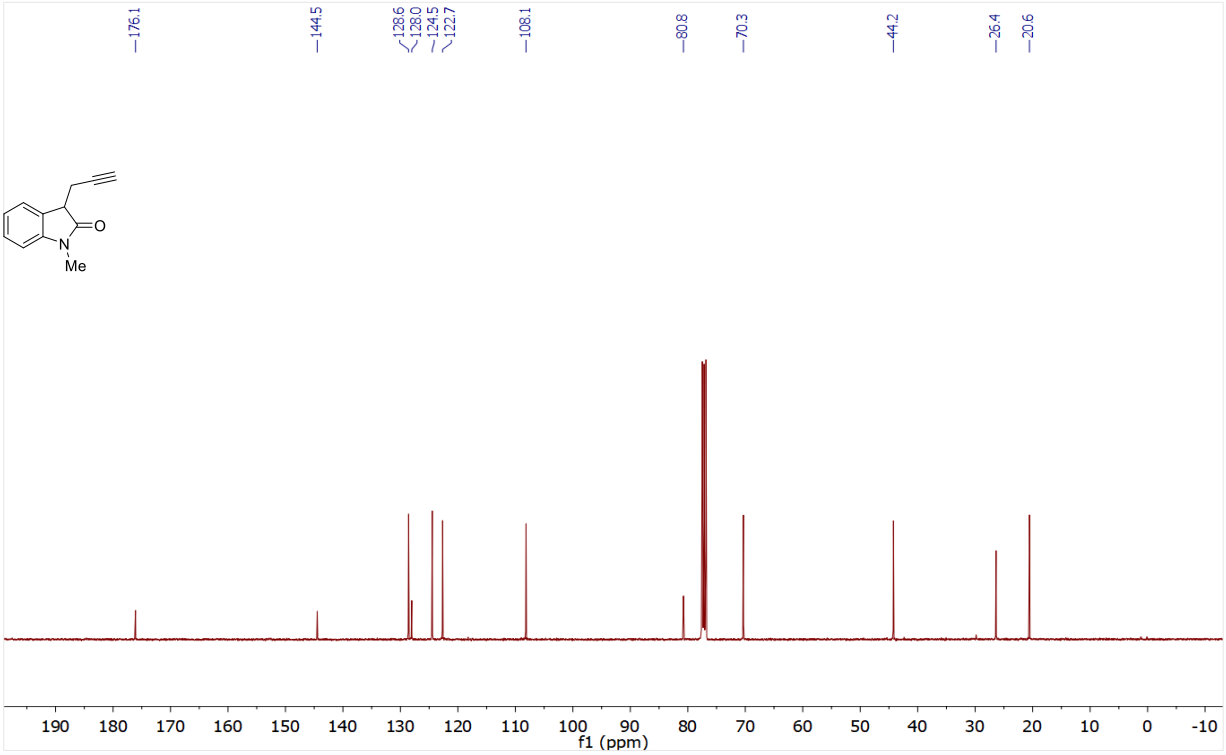
$^{13}C\{^{1}H\}$ NMR of S2b (151 MHz, $CDCl_3$):



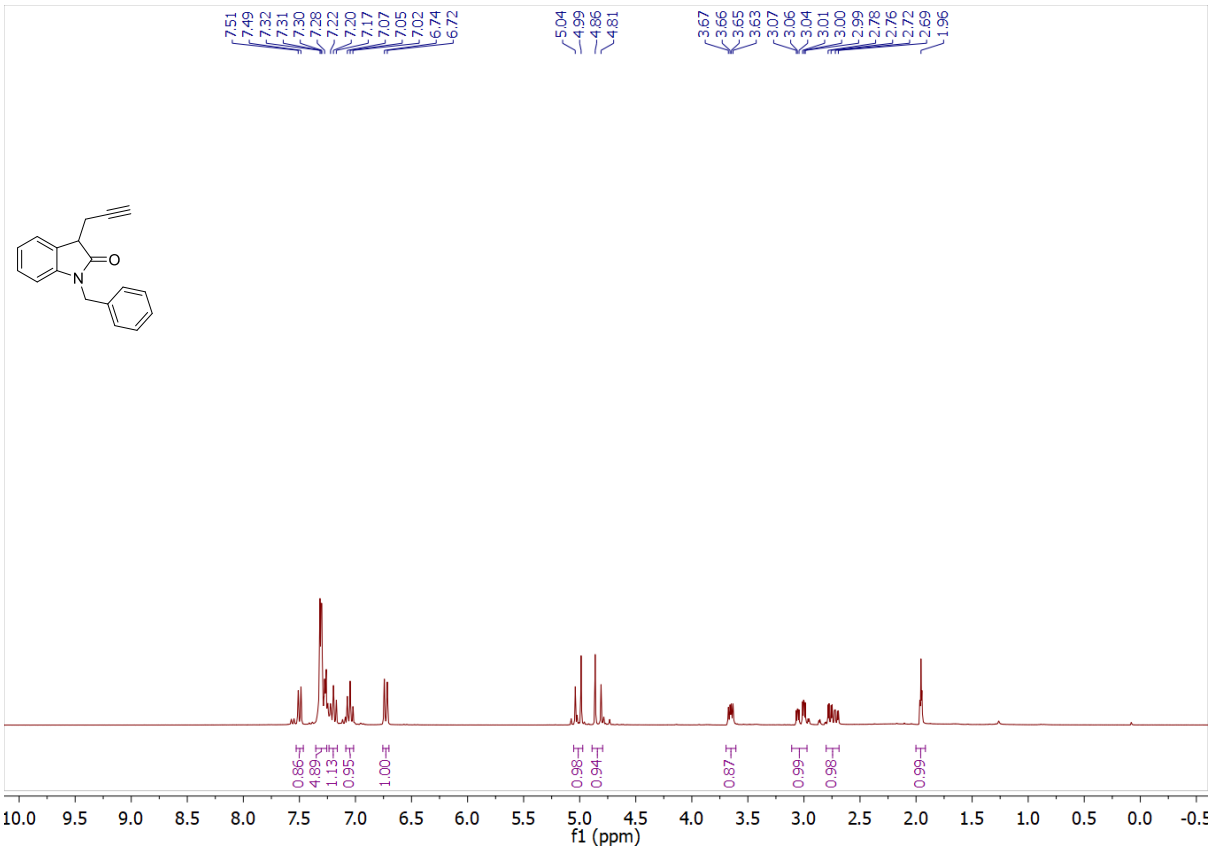
^{1}H NMR of 3a (400 MHz, $CDCl_3$):



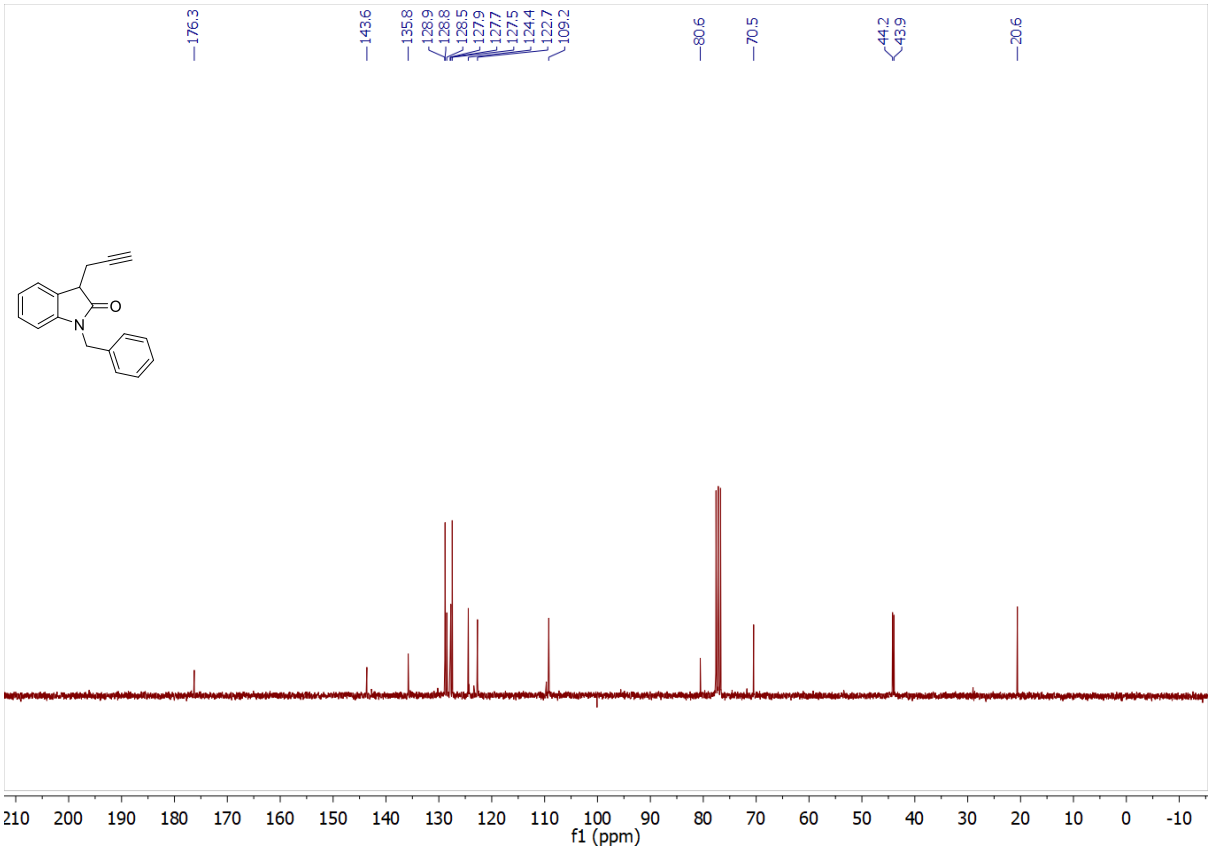
$^{13}C\{^{1}H\}$ NMR of 3a (101 MHz, $CDCl_3$):



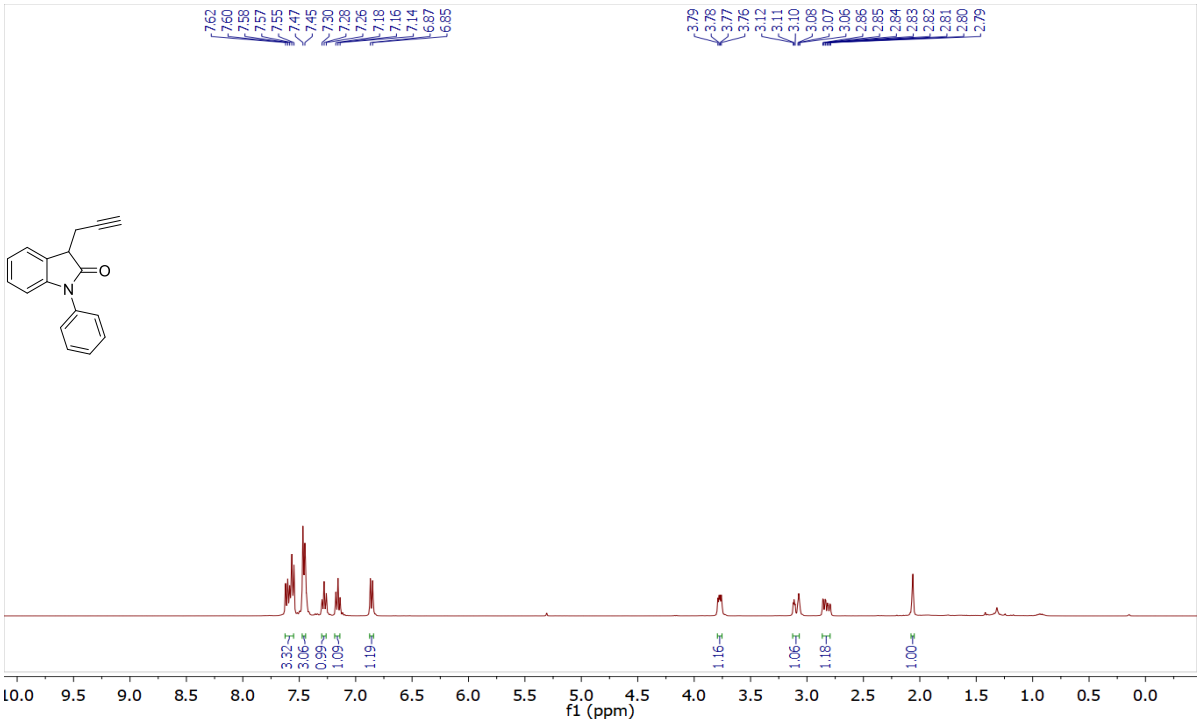
^{1}H NMR of 3b (300 MHz, $CDCl_3$):



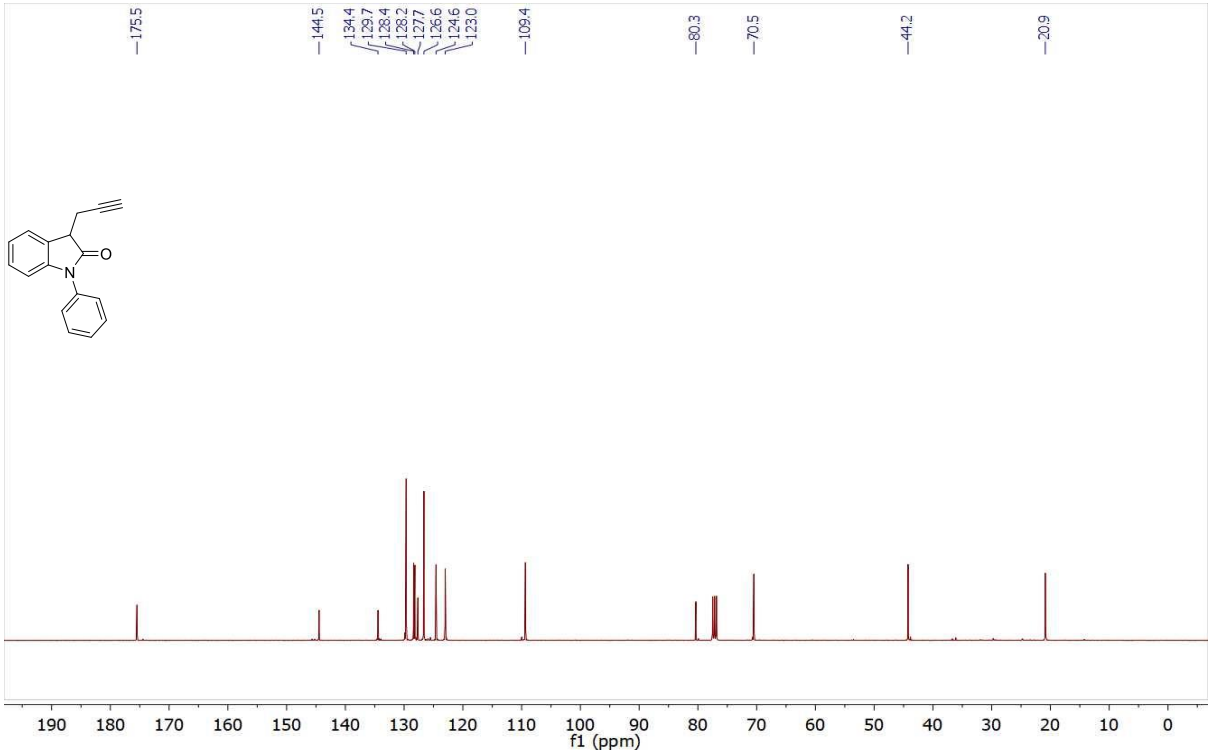
$^{13}C\{^{1}H\}$ NMR of 3b (75 MHz, $CDCl_3$):



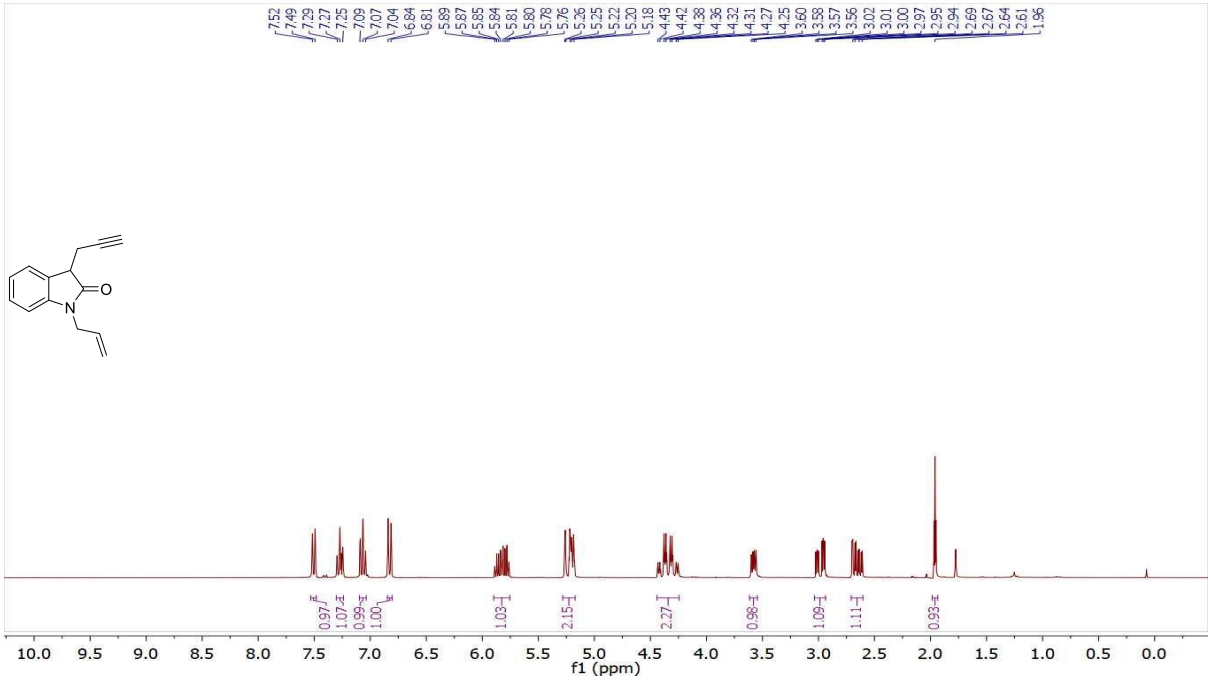
^{1}H NMR of 3c (400 MHz, $CDCl_3$):



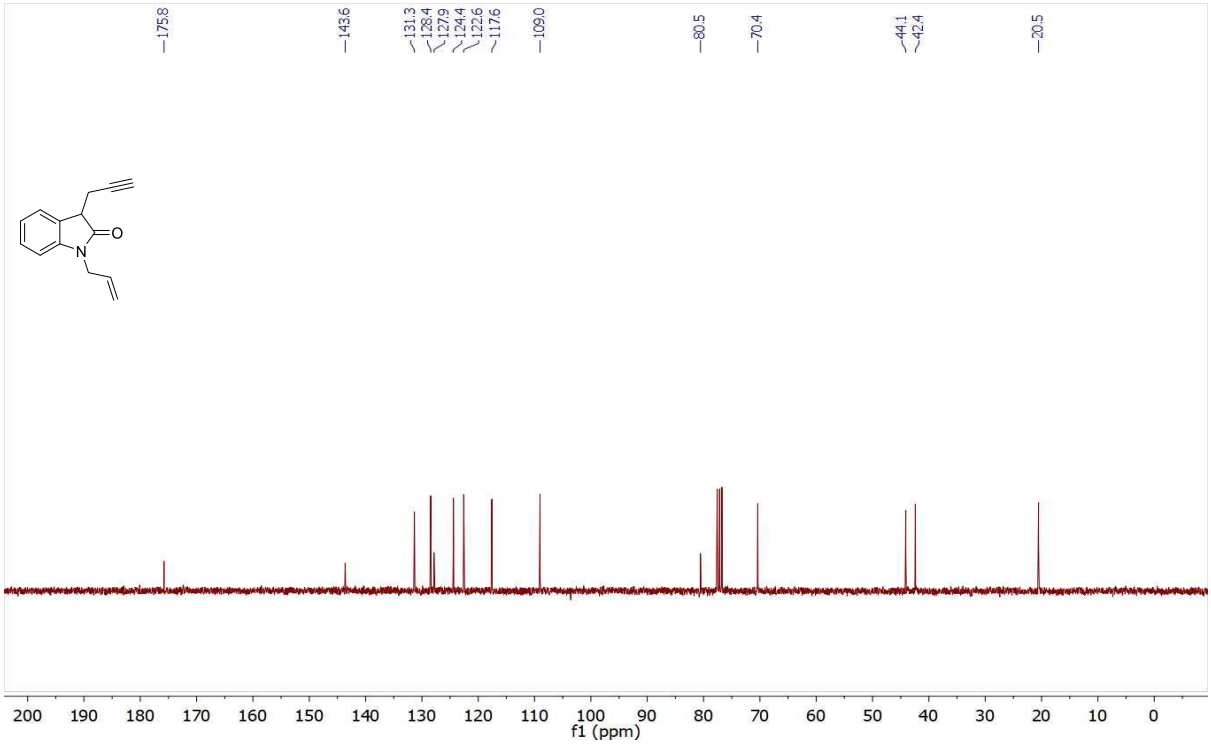
$^{13}C\{^{1}H\}$ NMR of 3c (101 MHz, $CDCl_3$):



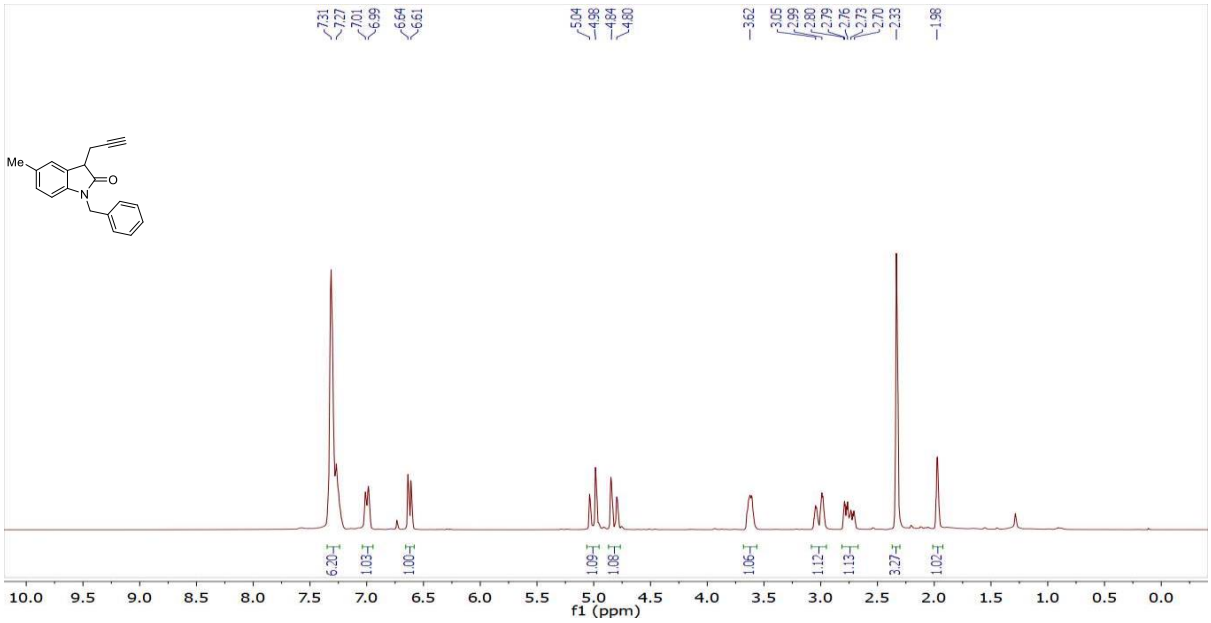
^{1}H NMR of 3d (300 MHz, $CDCl_3$):



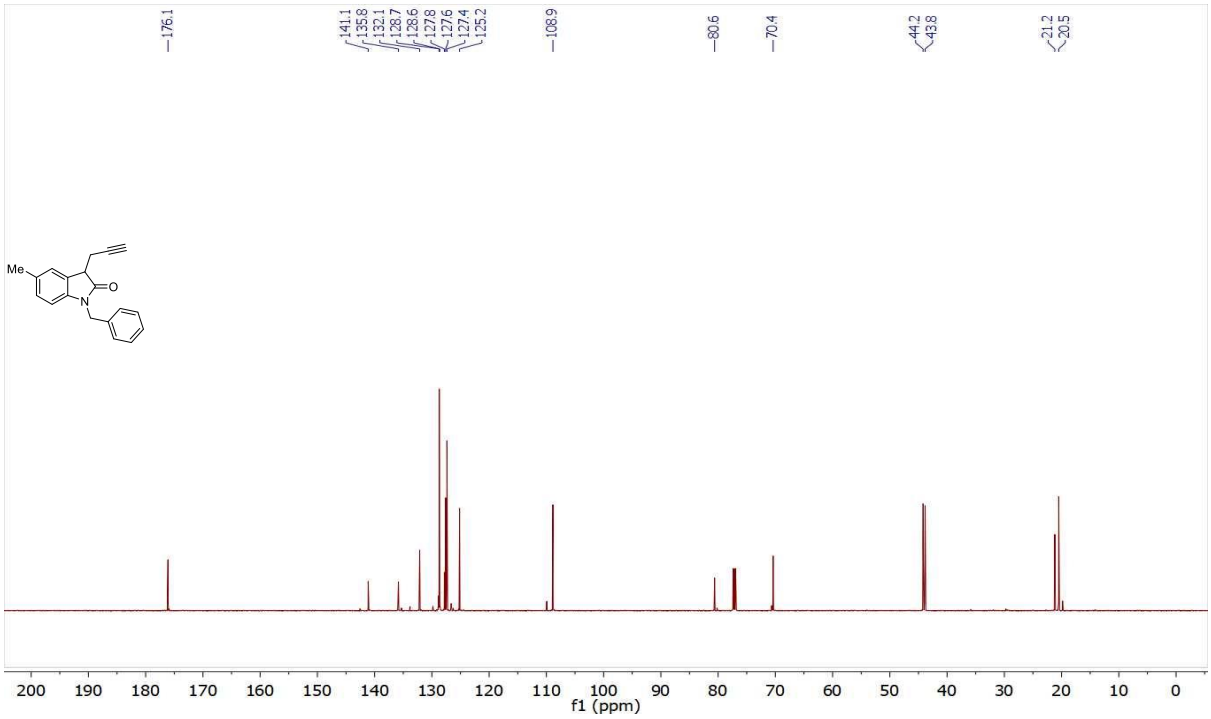
$^{13}C\{^{1}H\}$ NMR of 3d (75 MHz, $CDCl_3$):



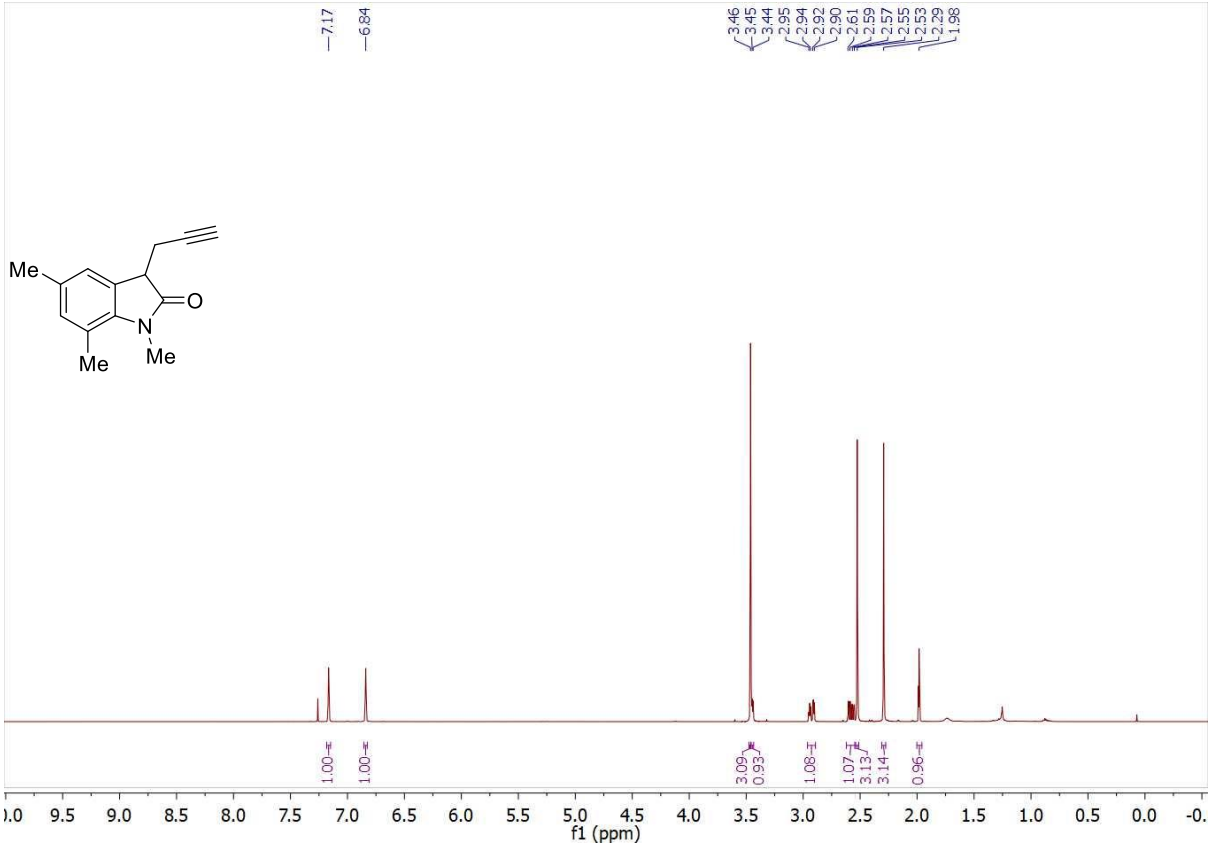
^{1}H NMR of 3e (300 MHz, $CDCl_3$):



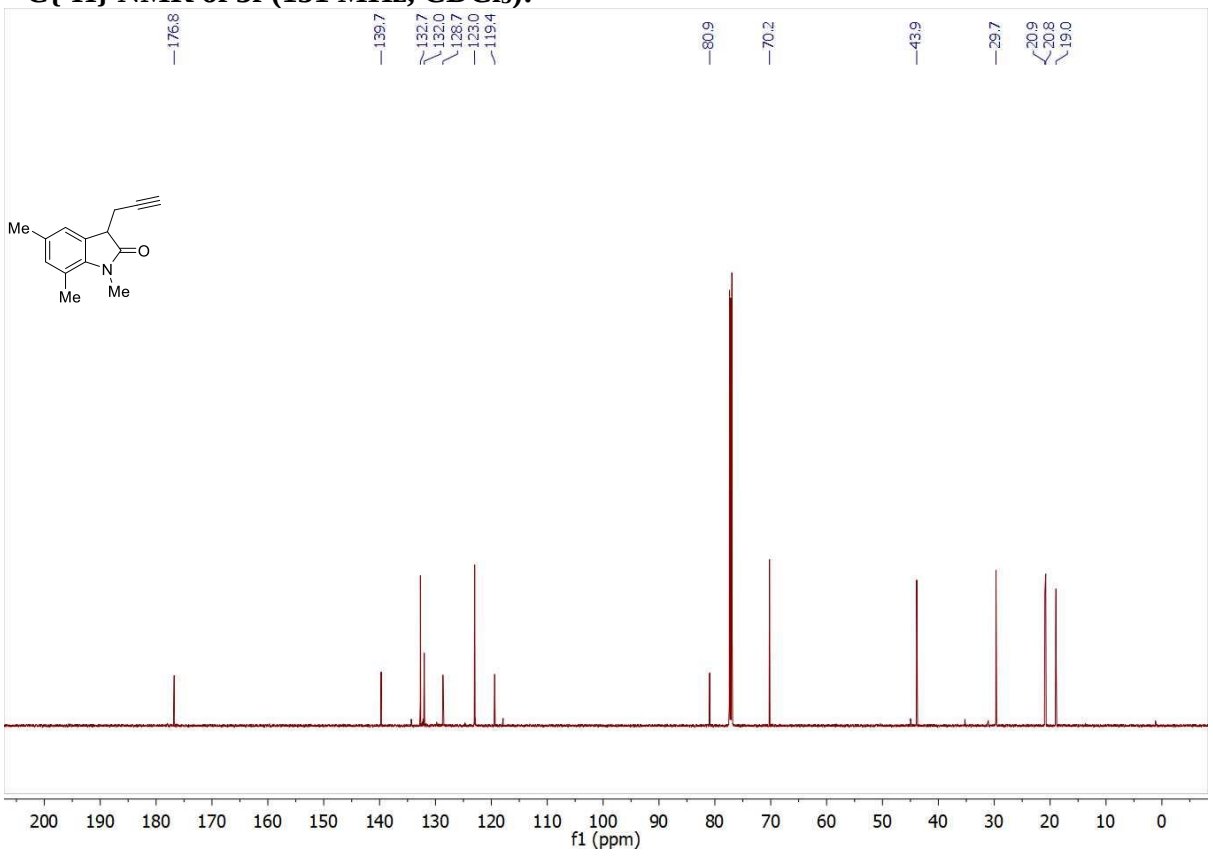
$^{13}C\{^{1}H\}$ NMR of 3e (151 MHz, $CDCl_3$):



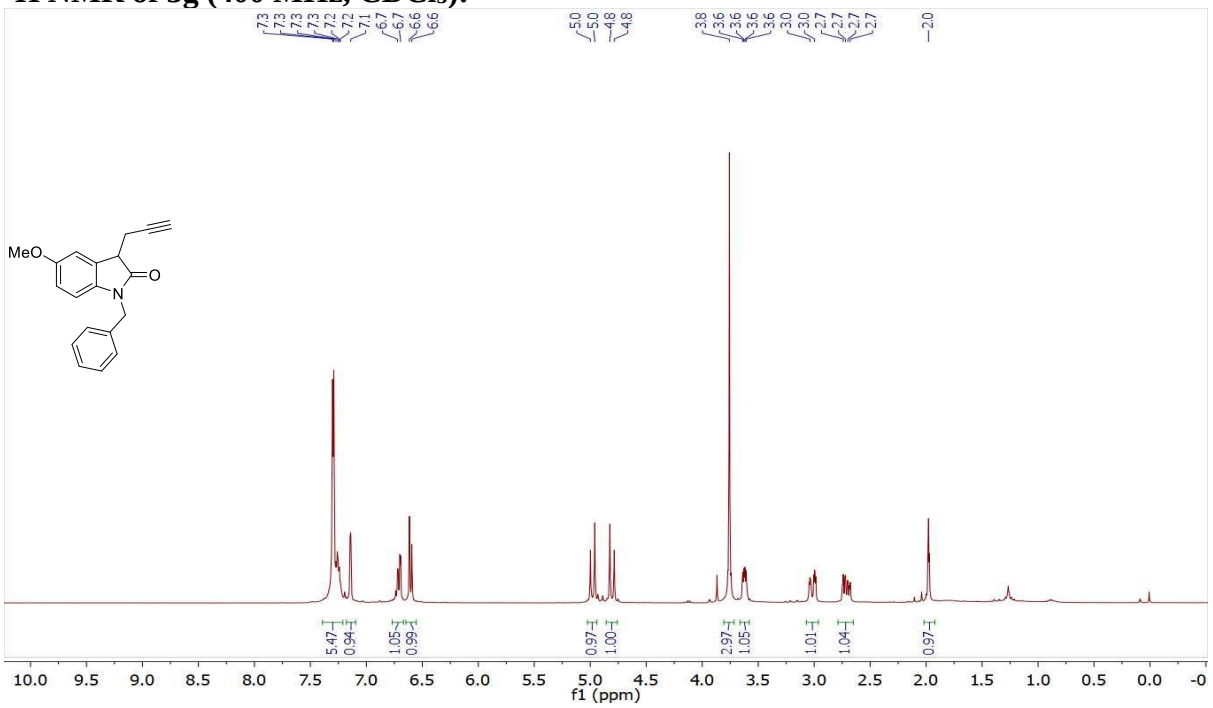
^{1}H NMR of 3f (500 MHz, $CDCl_3$):



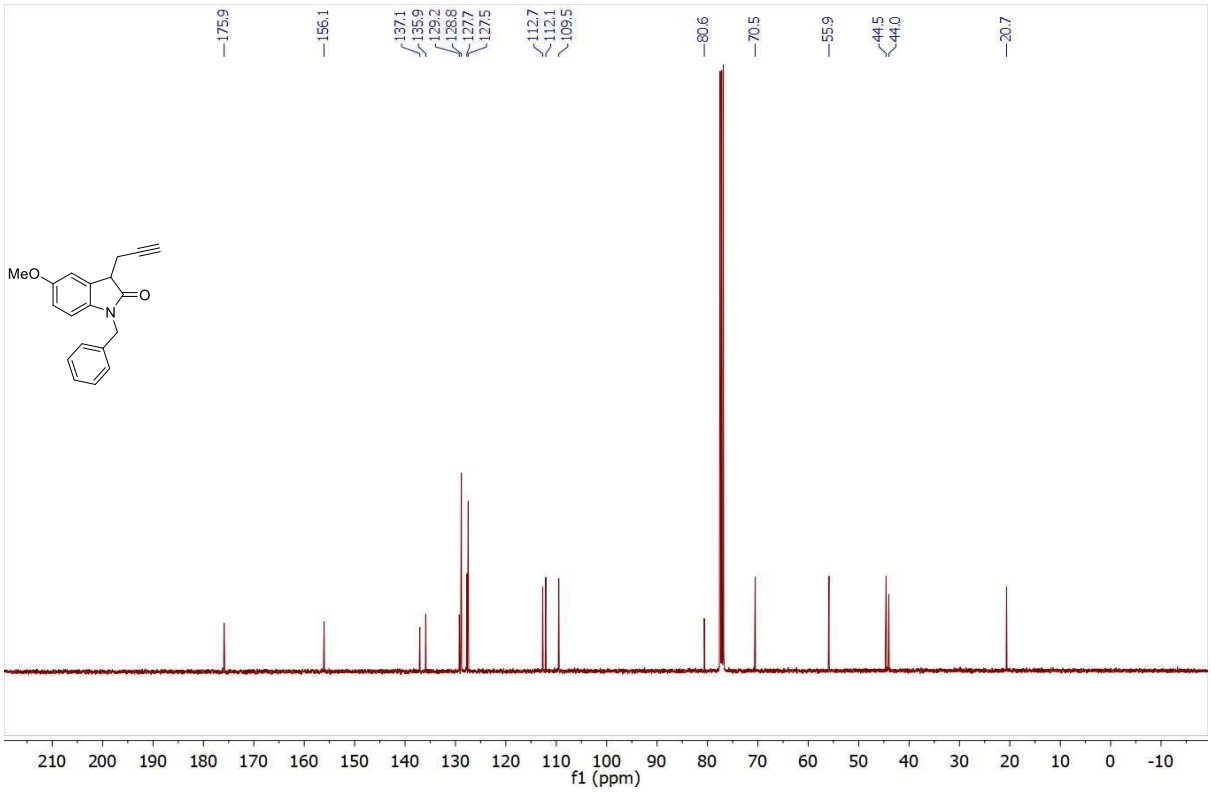
$^{13}C\{^{1}H\}$ NMR of 3f (151 MHz, $CDCl_3$):



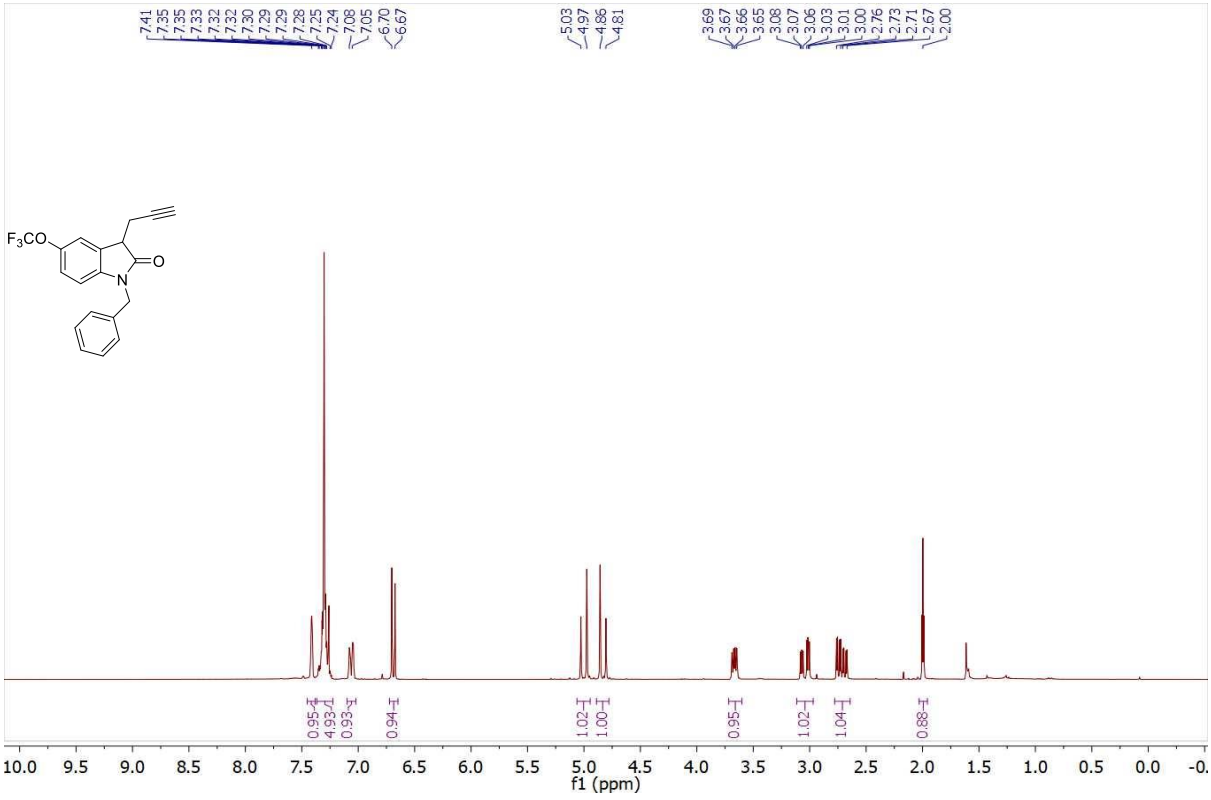
^{1}H NMR of 3g (400 MHz, $CDCl_3$):



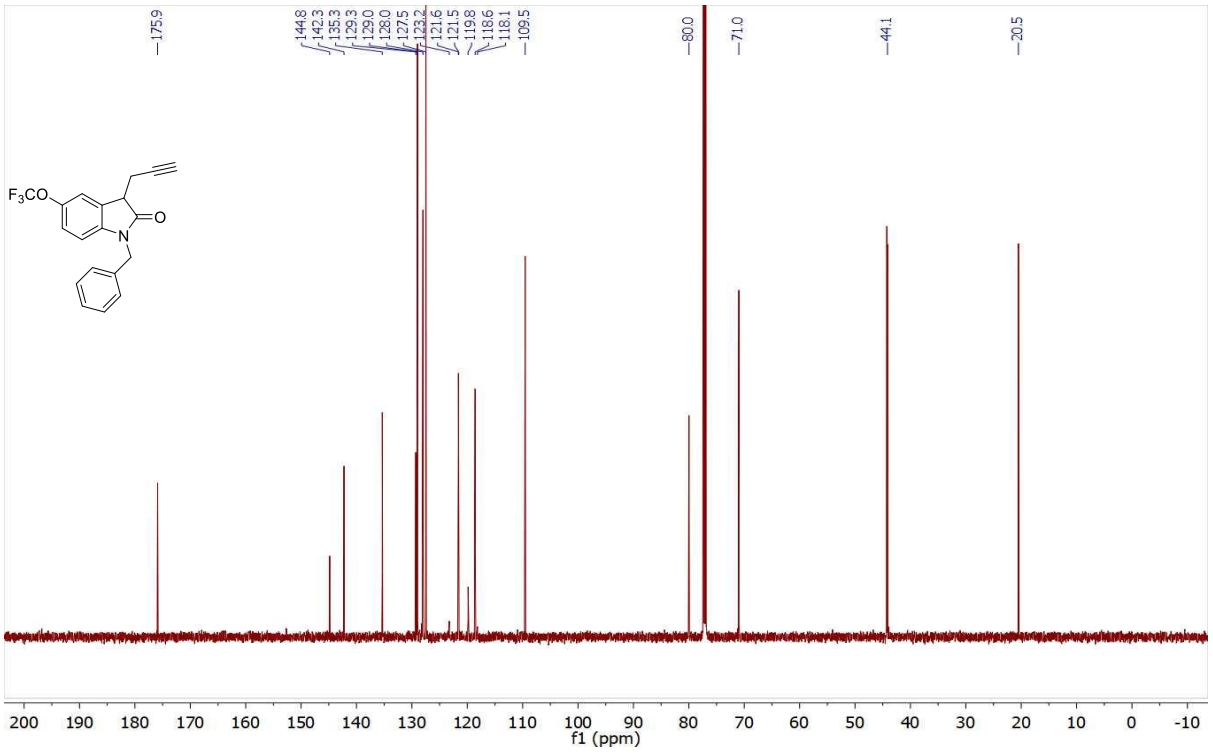
$^{13}C\{^{1}H\}$ NMR of 3g (151 MHz, $CDCl_3$):



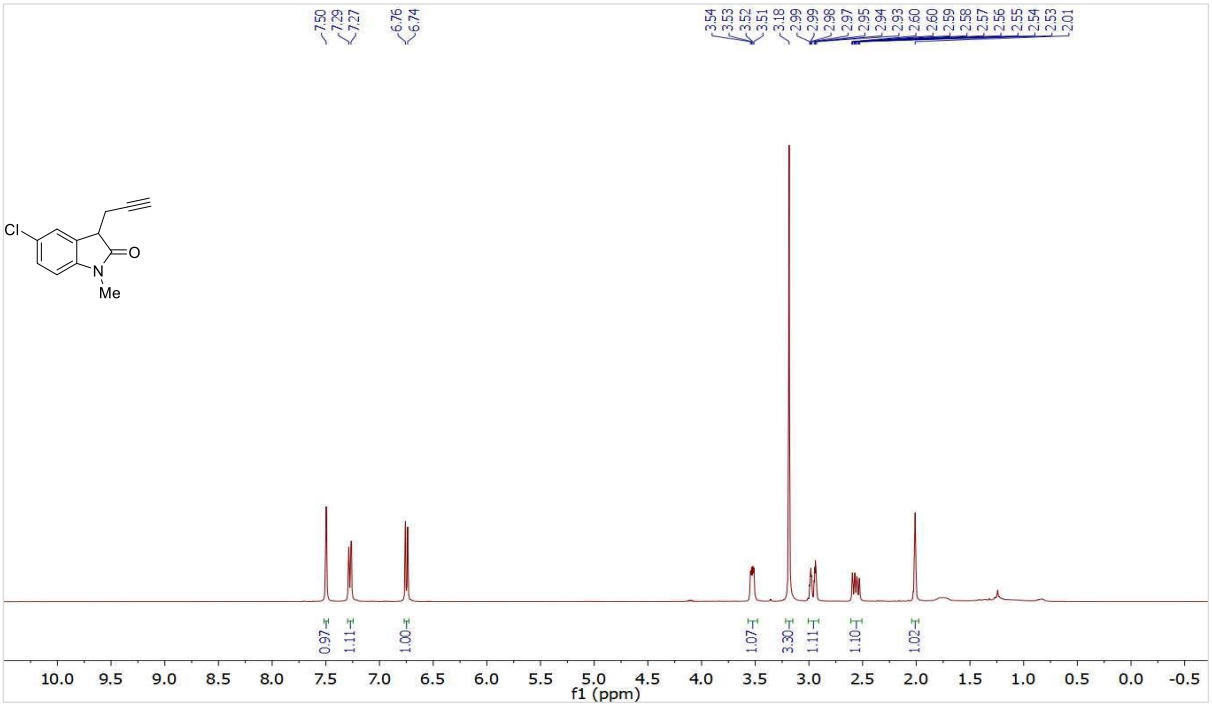
^{1}H NMR of 3h (300 MHz, $CDCl_3$):



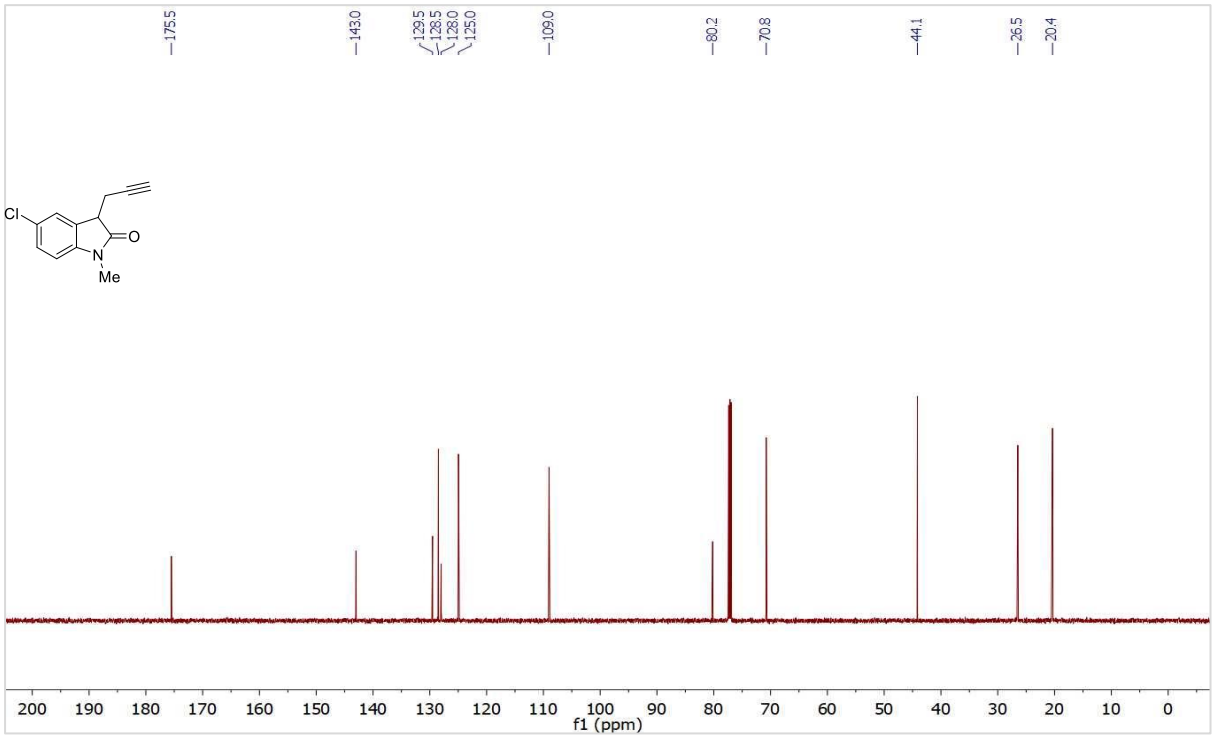
$^{13}C\{^{1}H\}$ NMR of 3h (151 MHz, $CDCl_3$):



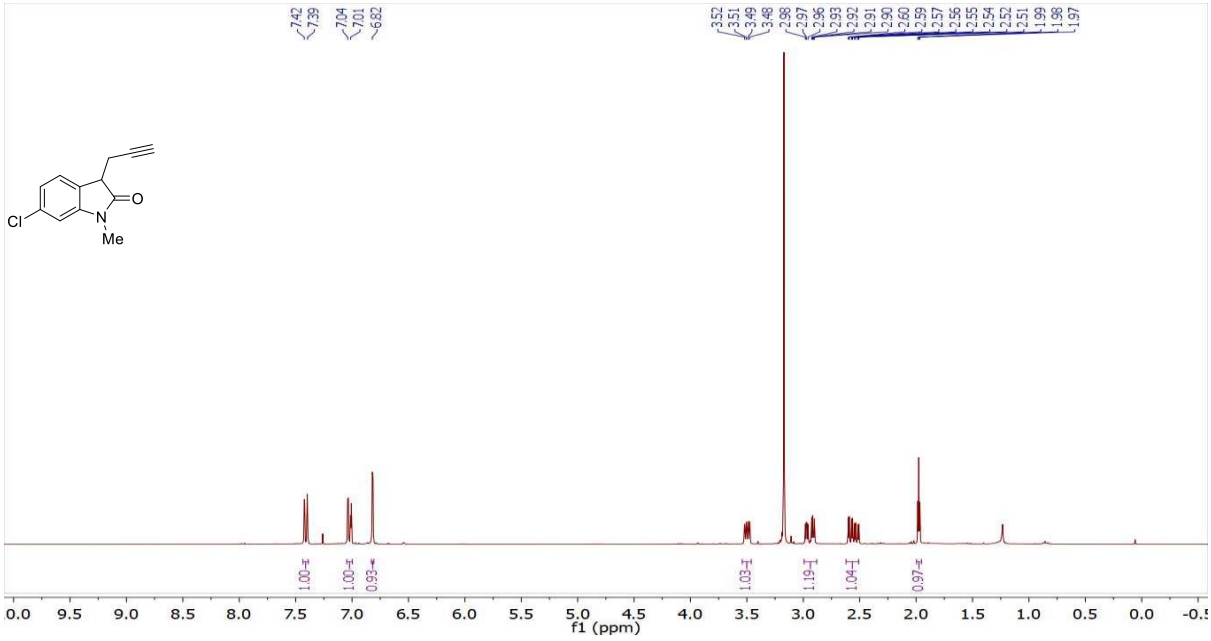
^{1}H NMR of 3i (400 MHz, $CDCl_3$):



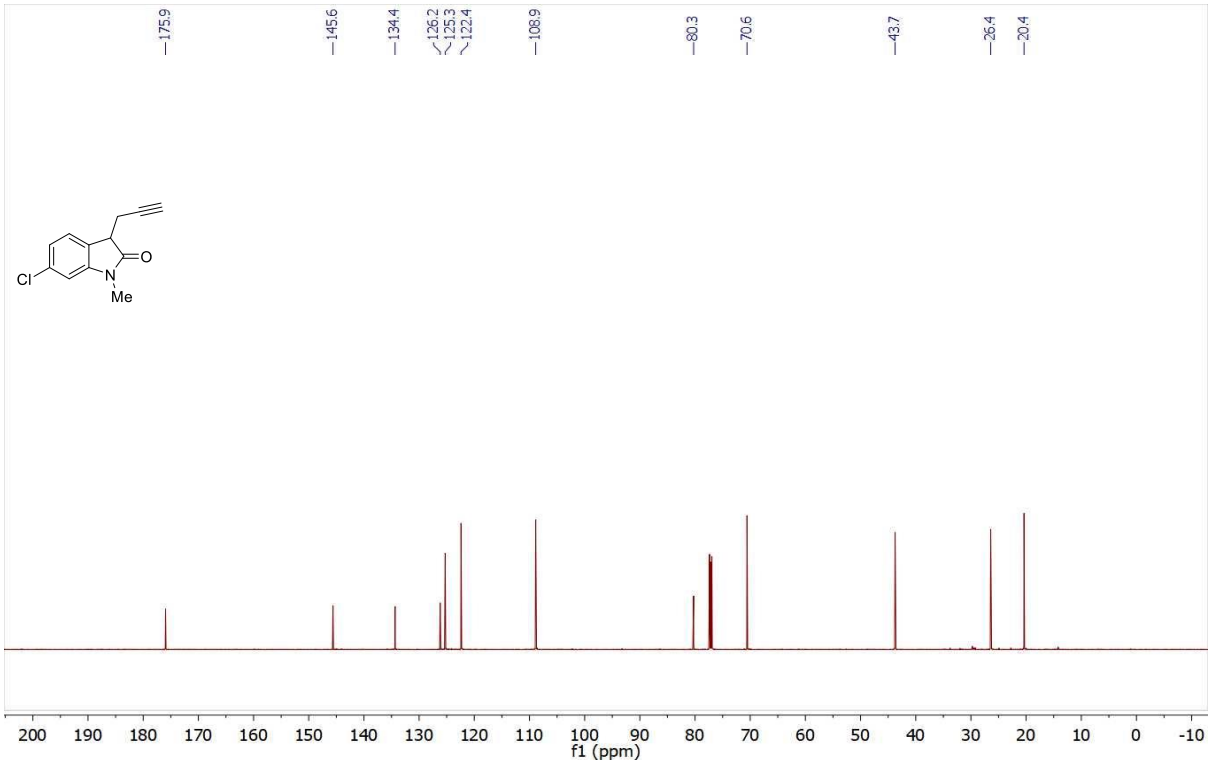
$^{13}C\{^{1}H\}$ NMR of 3i (151 MHz, $CDCl_3$):



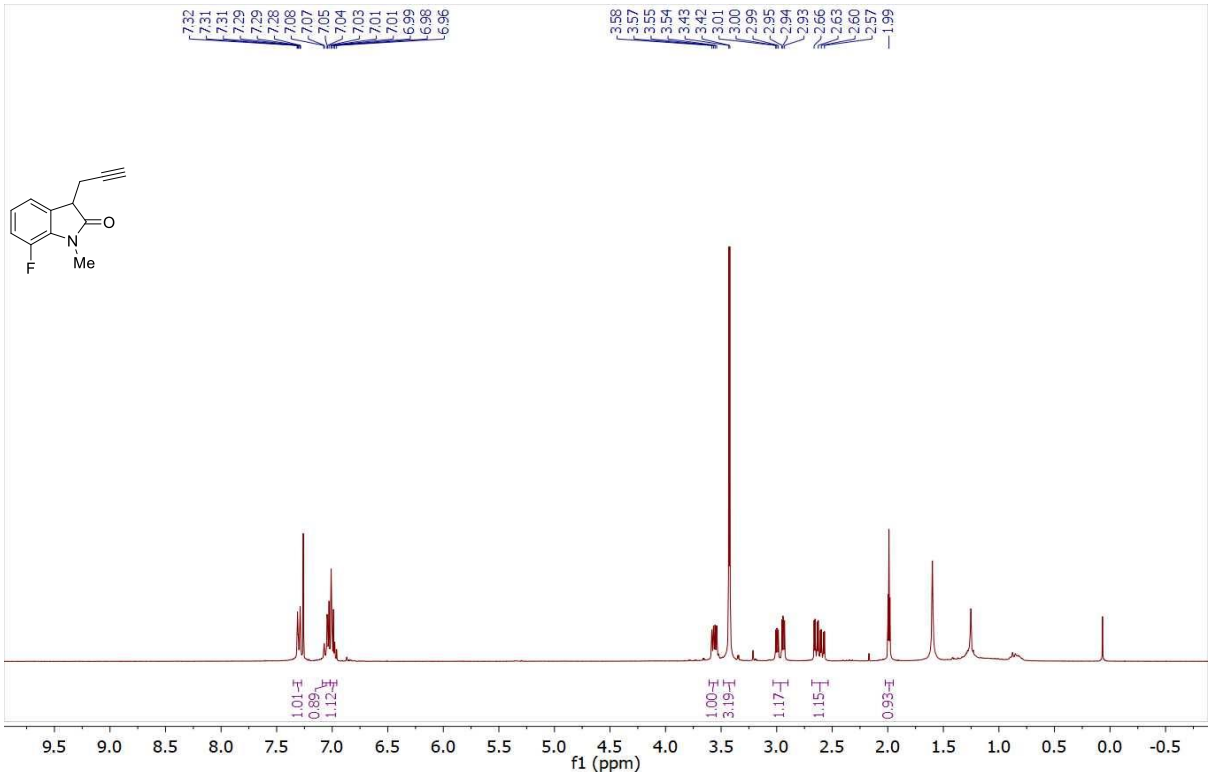
^{1}H NMR of 3j (300 MHz, $CDCl_3$):



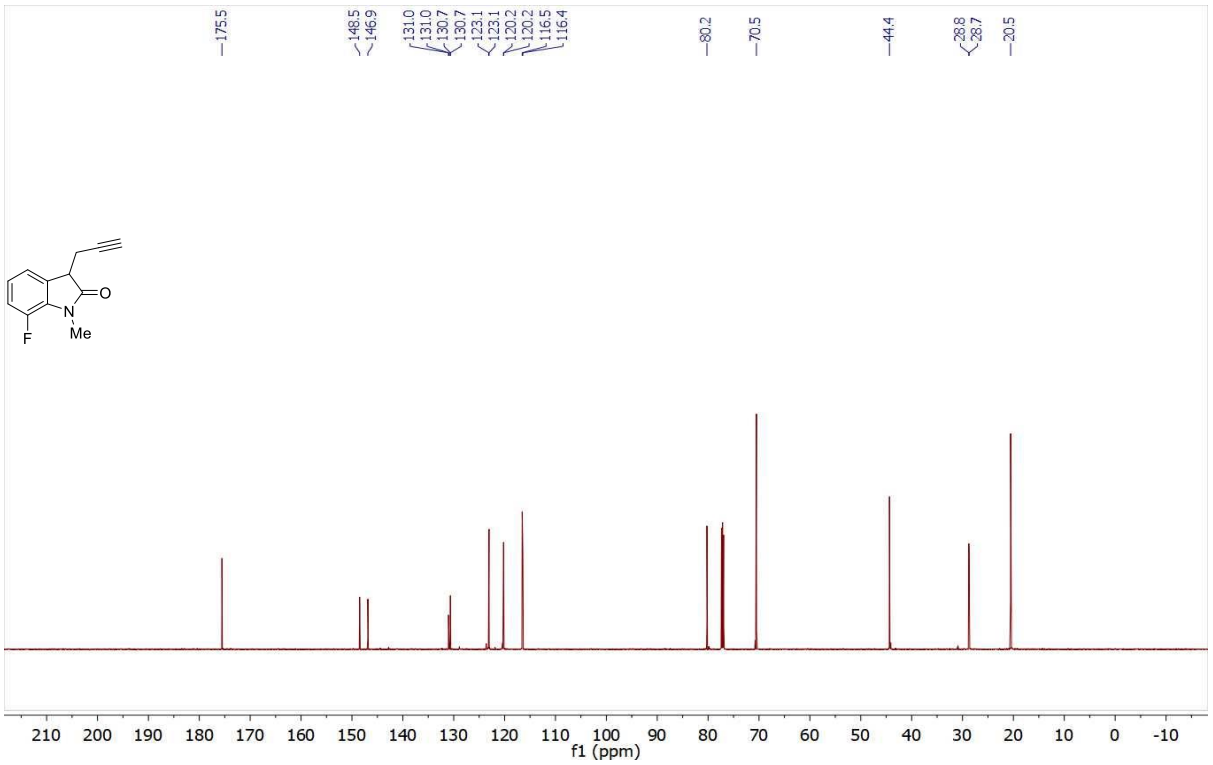
$^{13}C\{^{1}H\}$ NMR of 3j (151 MHz, $CDCl_3$):



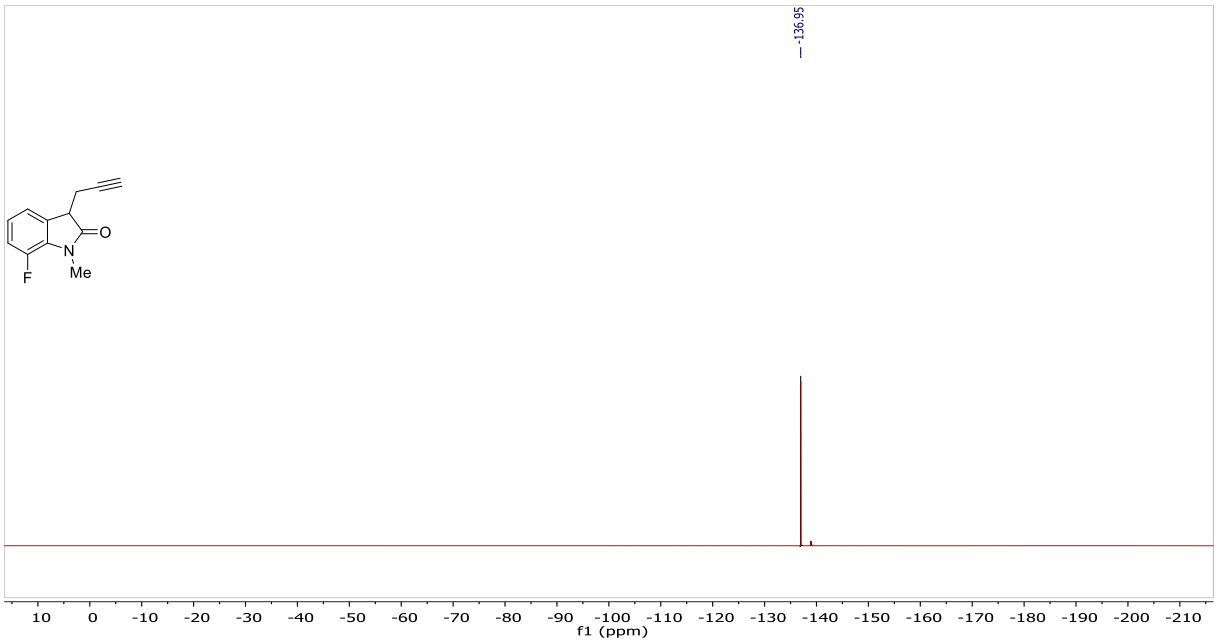
^{1}H NMR of 3k (300 MHz, $CDCl_3$):



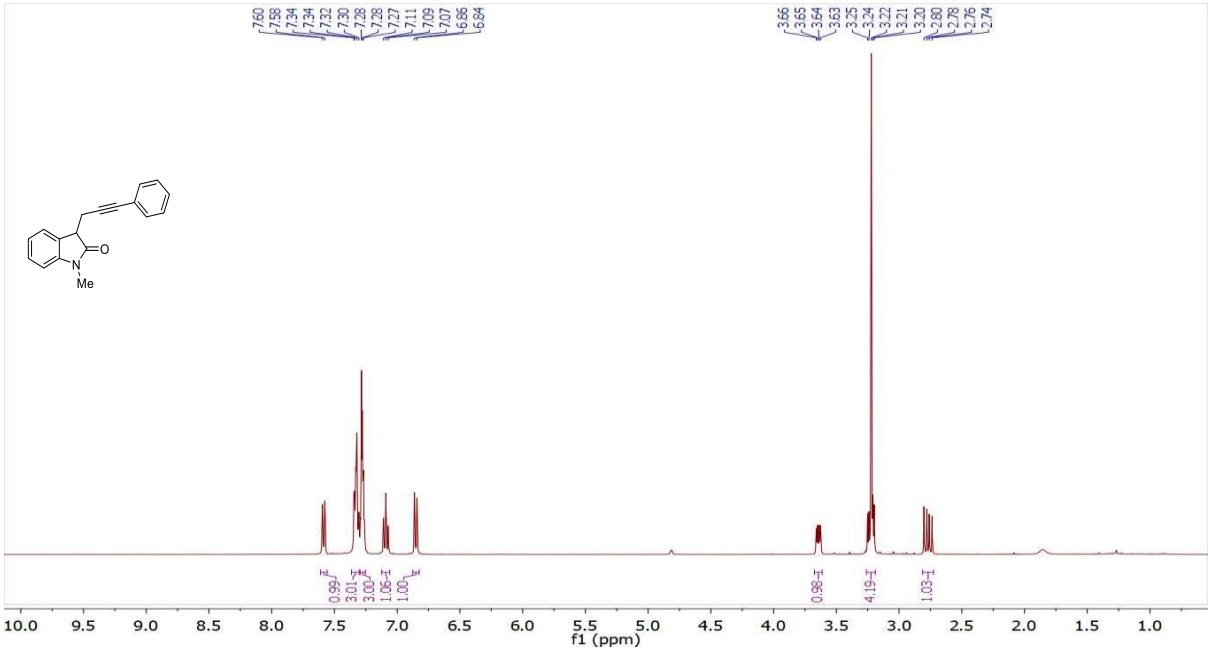
$^{13}C\{^{1}H\}$ NMR of 3k (151 MHz, $CDCl_3$):



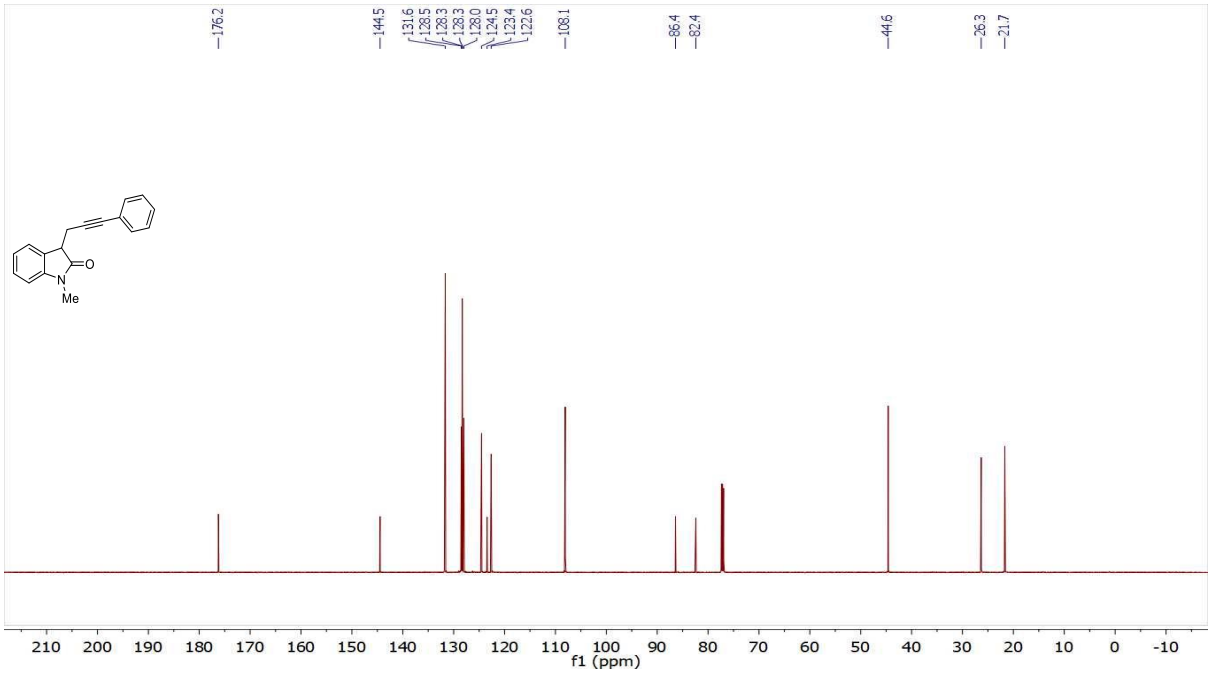
^{19}F NMR of 3k (565 MHz, $CDCl_3$):



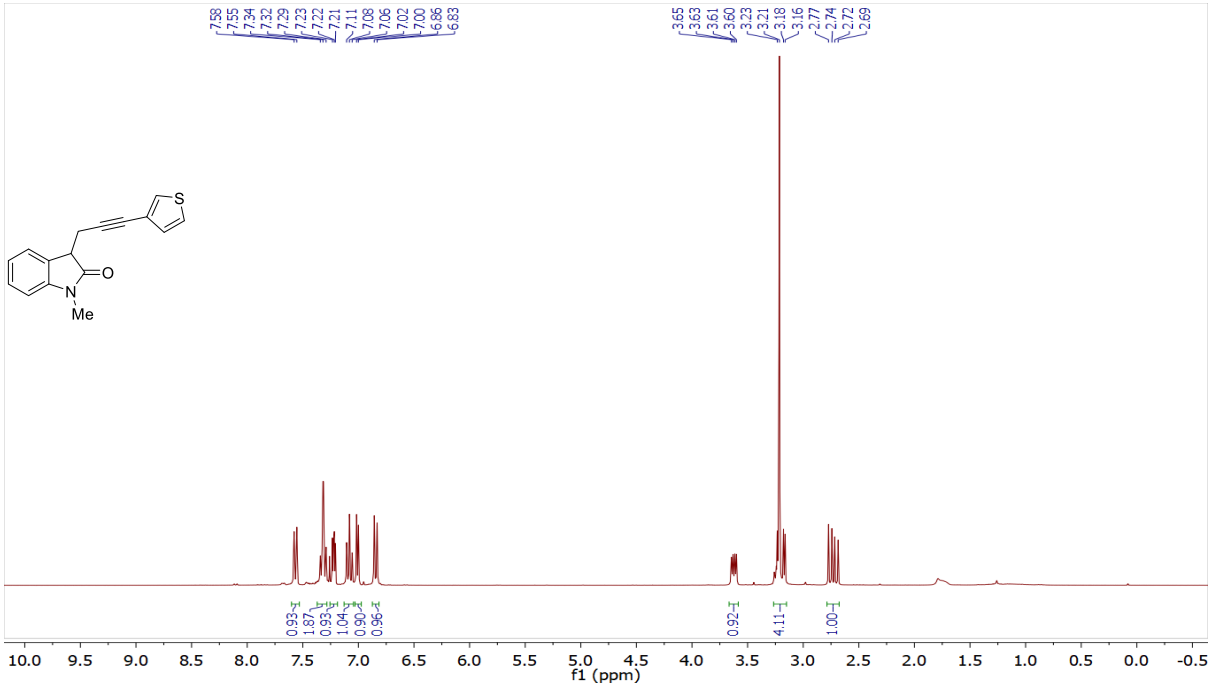
^{1}H NMR of 3l (400 MHz, $CDCl_3$):



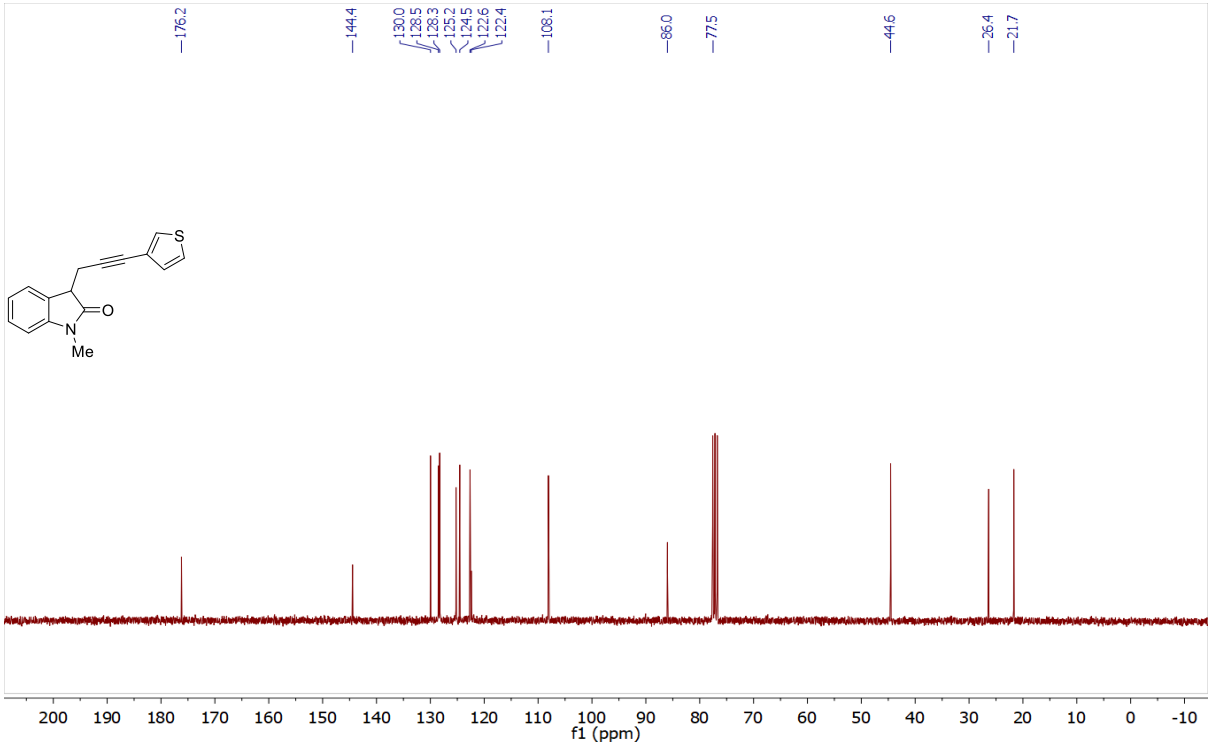
^{13}C{^{1}H} NMR of 3l (151 MHz, $CDCl_3$):



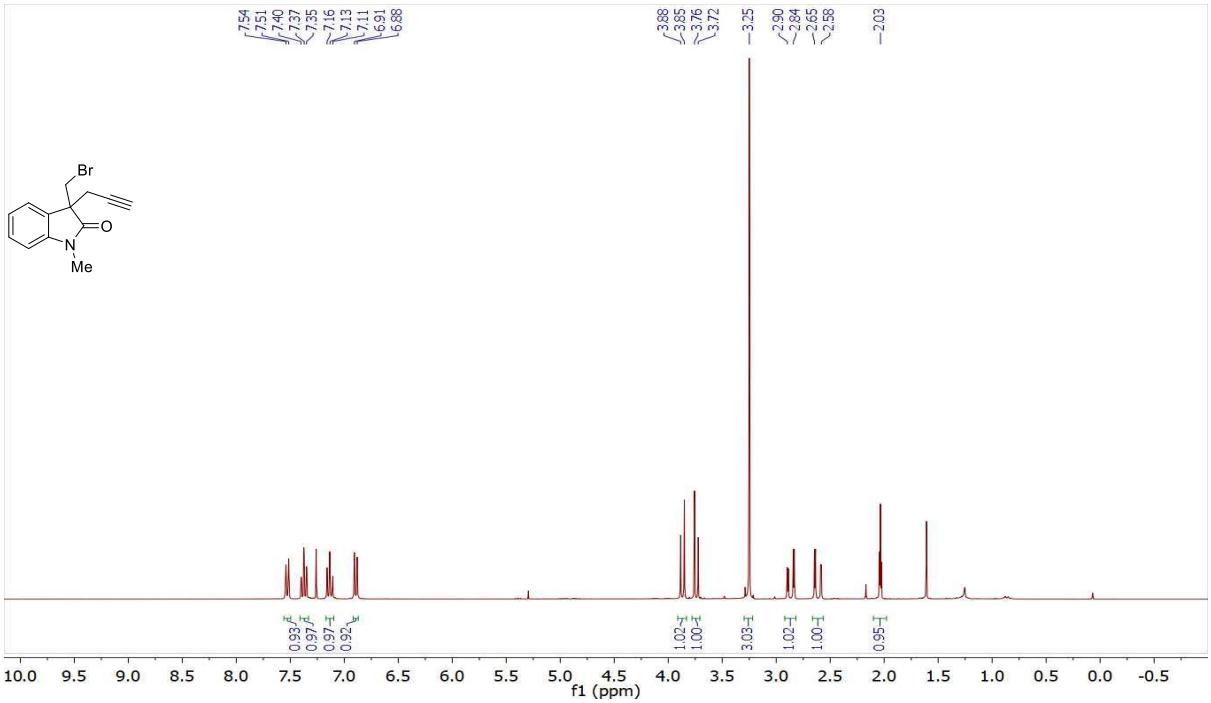
^{1}H NMR of 3m (300 MHz, $CDCl_3$):



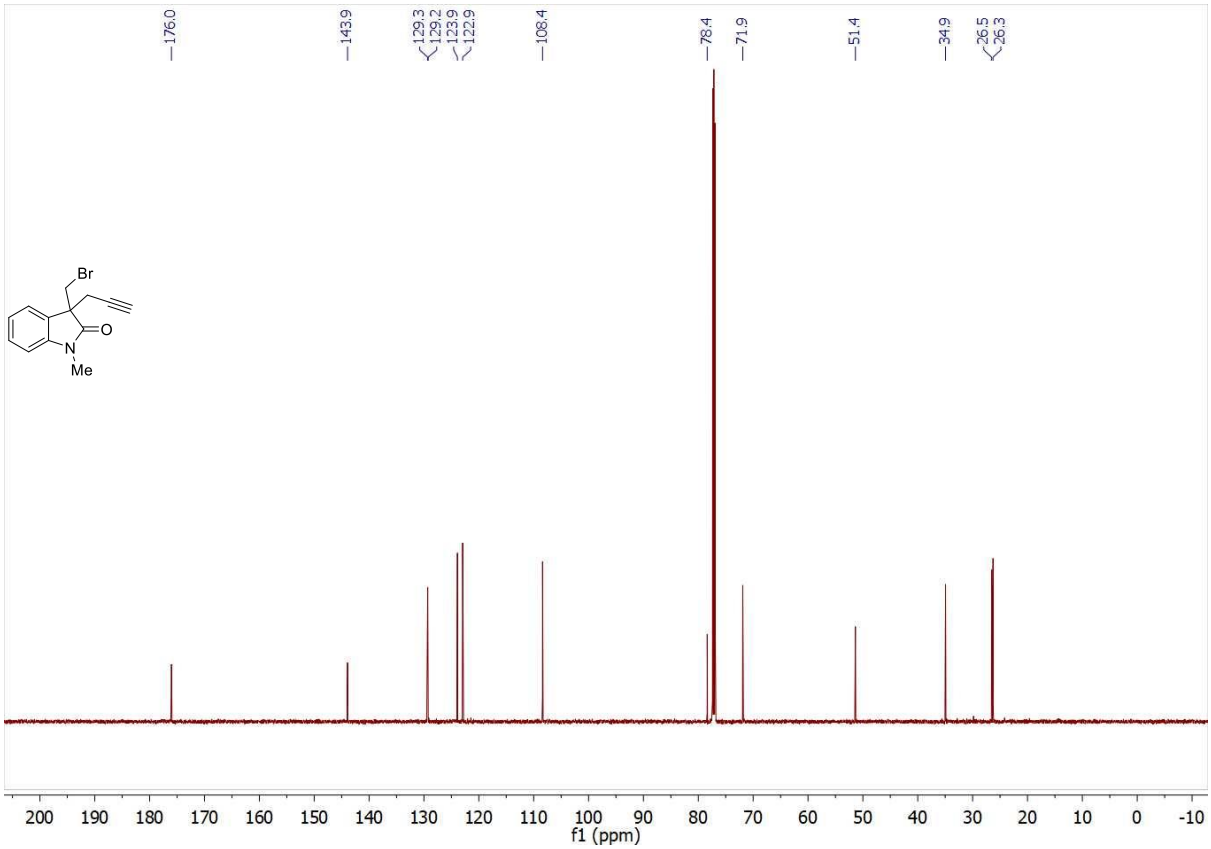
^{13}C{^{1}H} NMR of 3m (75 MHz, $CDCl_3$):



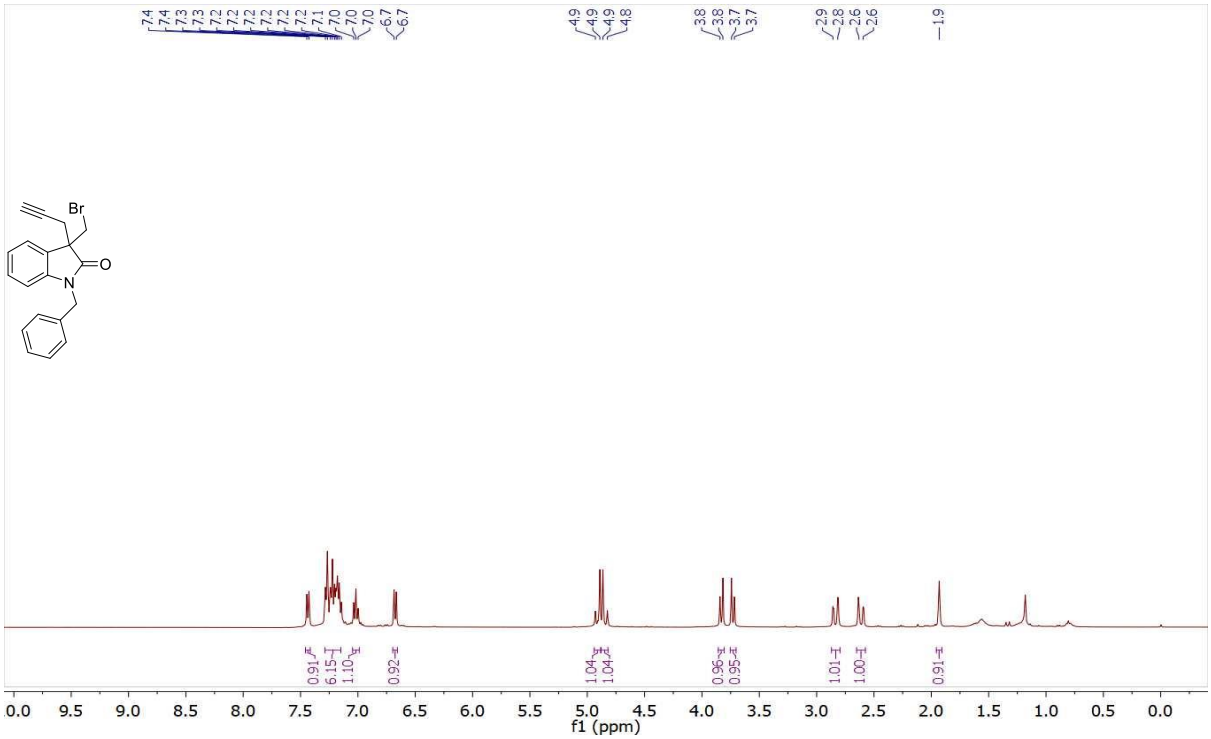
^{1}H NMR of 4a (300 MHz, $CDCl_3$):



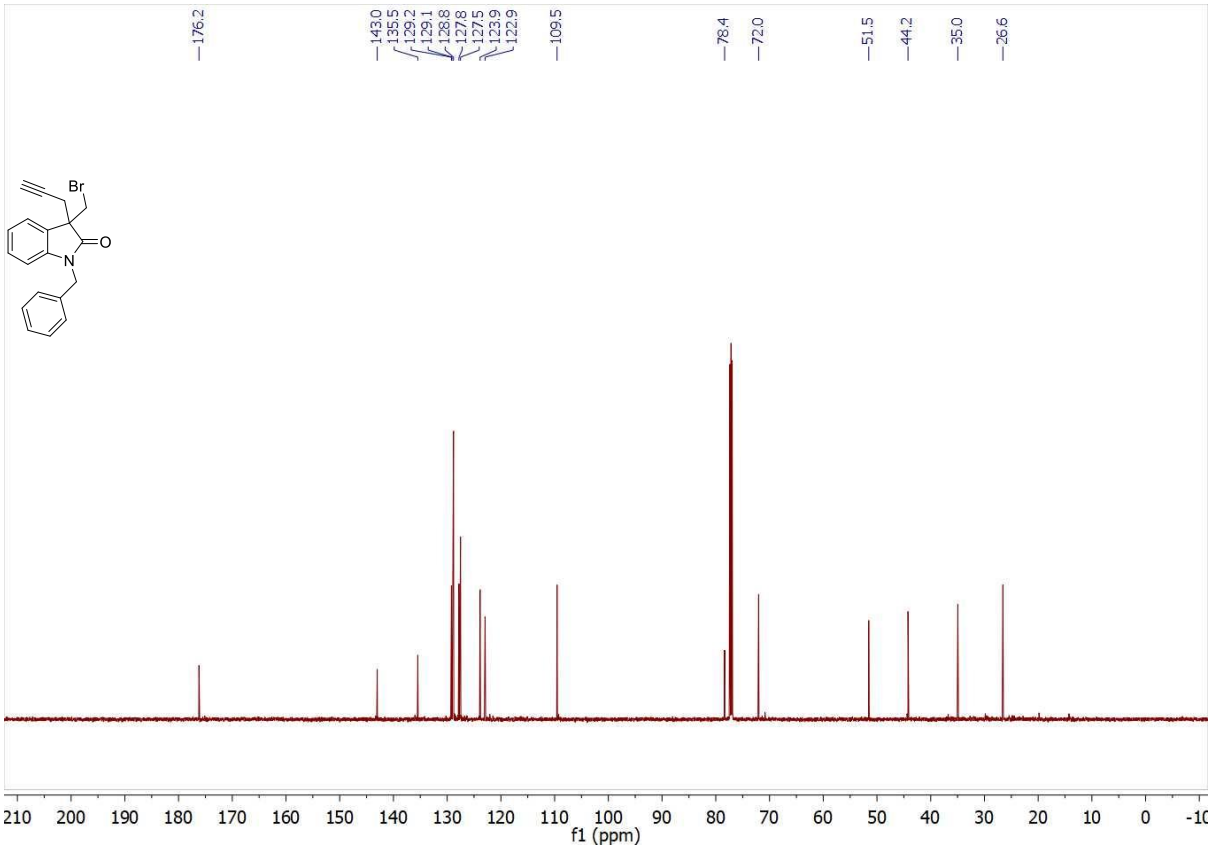
^{13}C{^{1}H} NMR of 4a (151 MHz, $CDCl_3$):



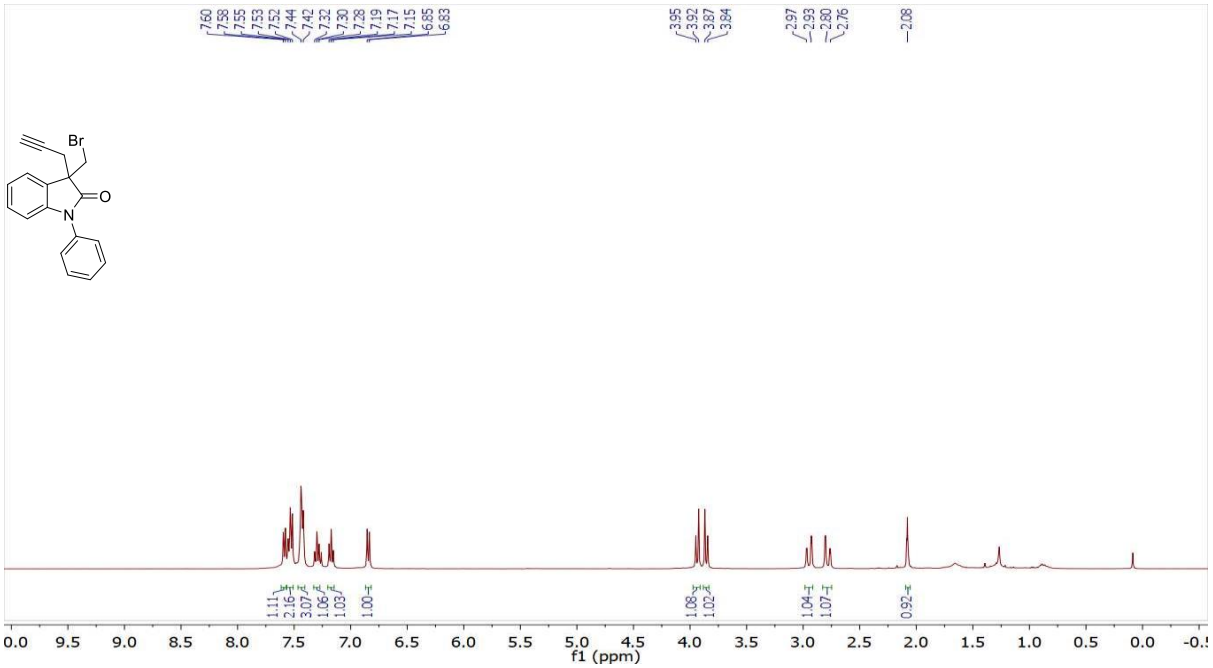
^{1}H NMR of 4b (400 MHz, $CDCl_3$):



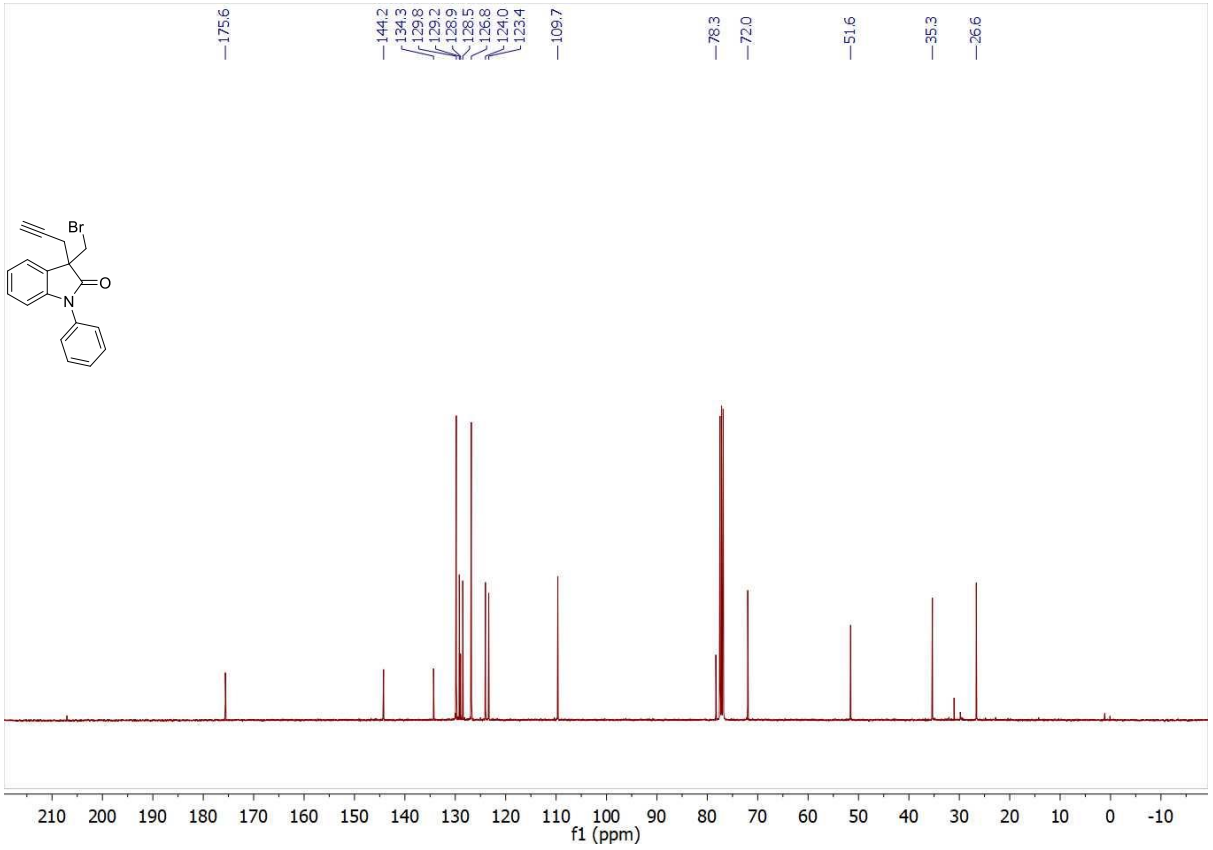
^{13}C{^{1}H} NMR of 4b (151 MHz, $CDCl_3$):



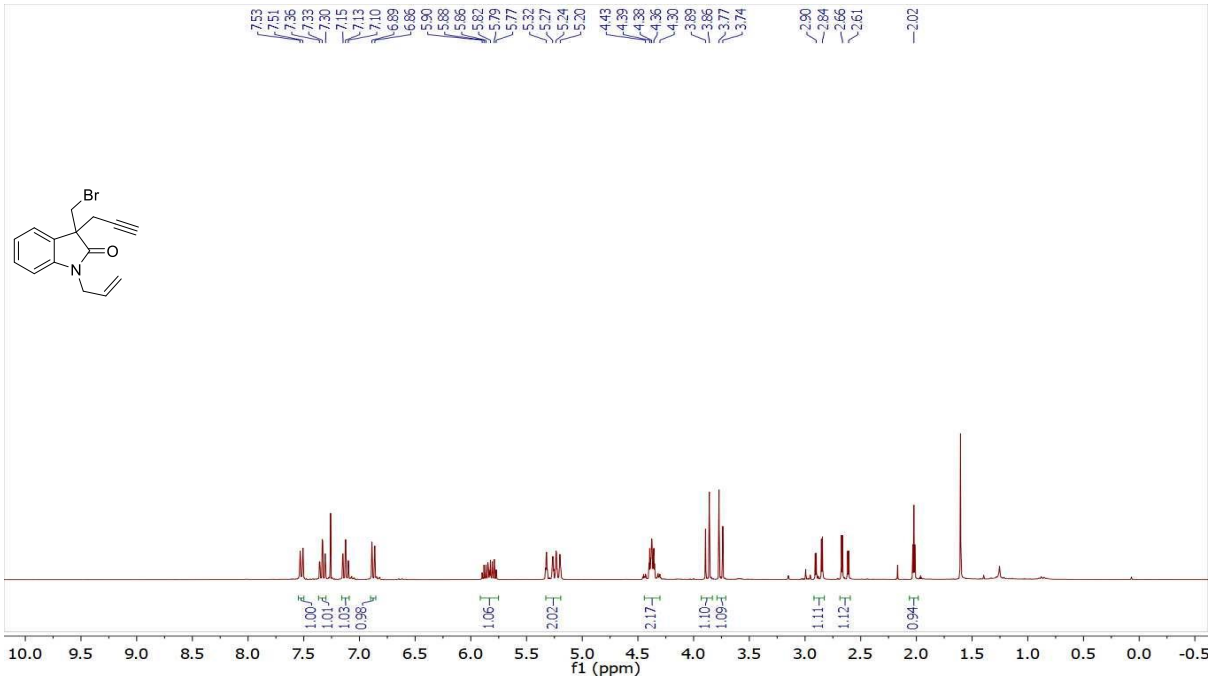
^{1}H NMR of 4c (400 MHz, $CDCl_3$):



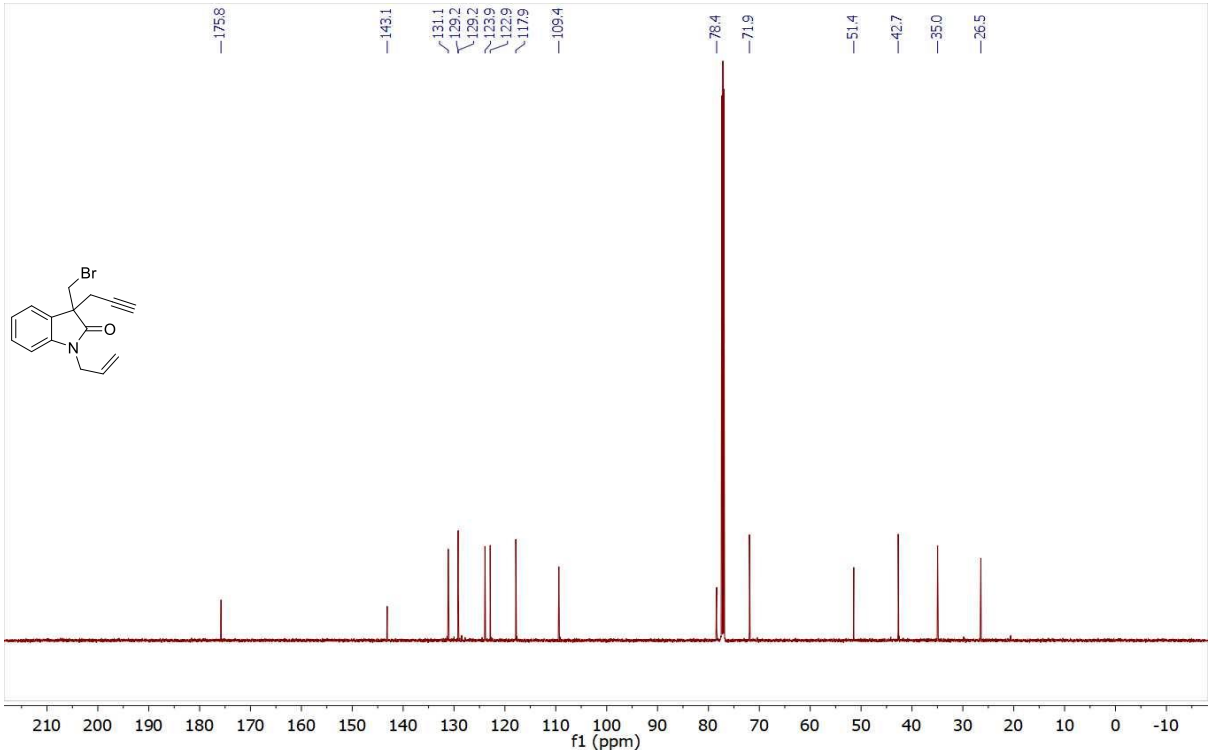
^{13}C{^{1}H} NMR of 4c (101 MHz, $CDCl_3$):



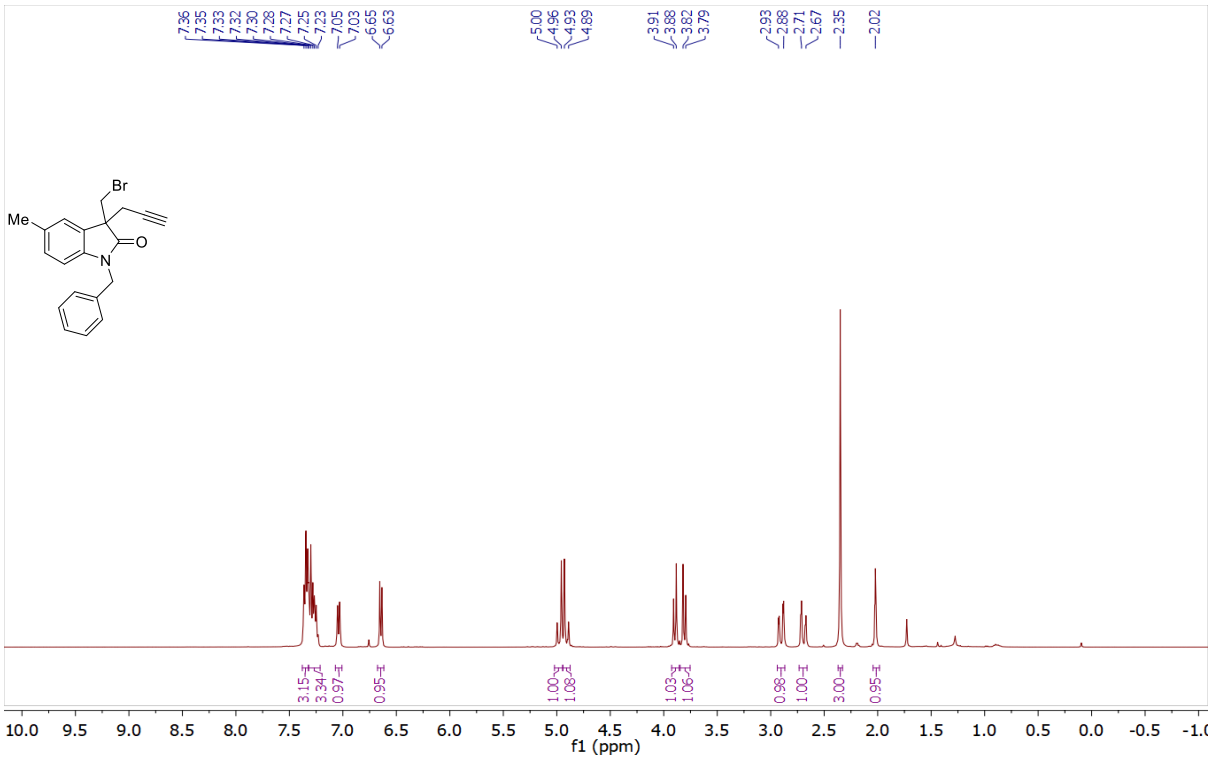
^{1}H NMR of 4d (300 MHz, $CDCl_3$):



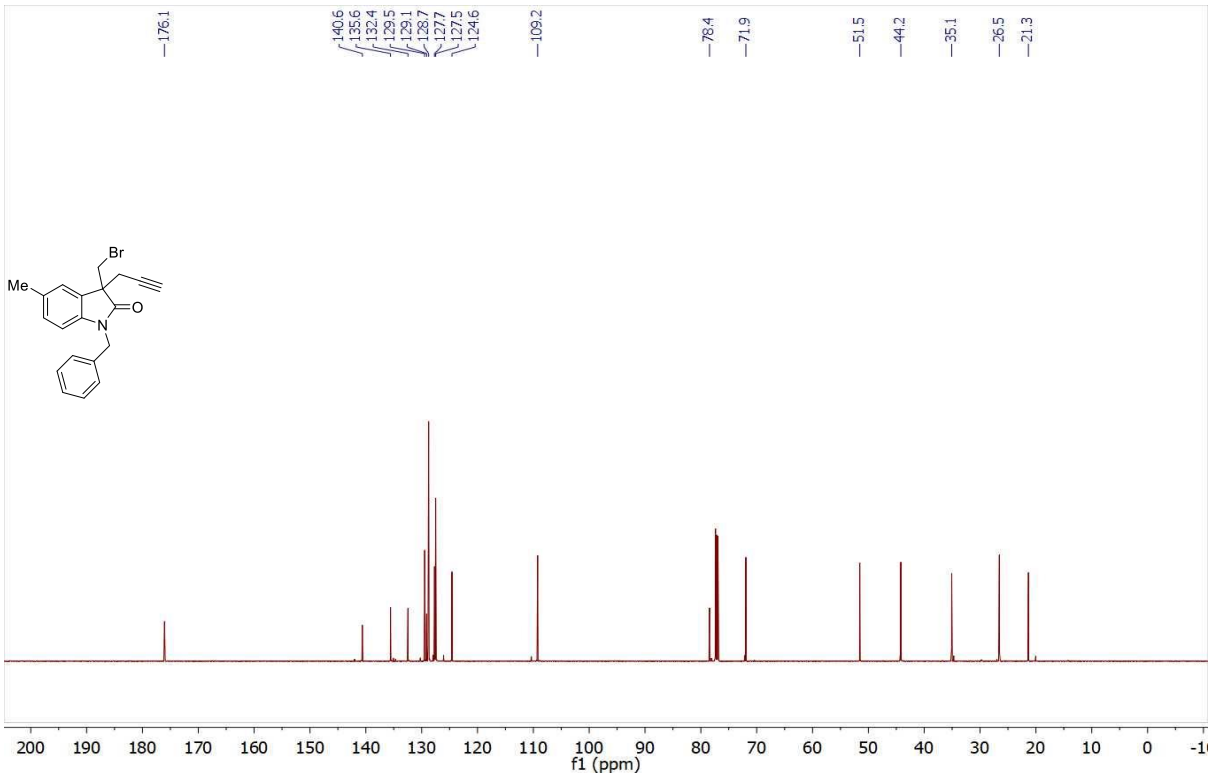
^{13}C{^{1}H} NMR of 4d (151 MHz, $CDCl_3$):



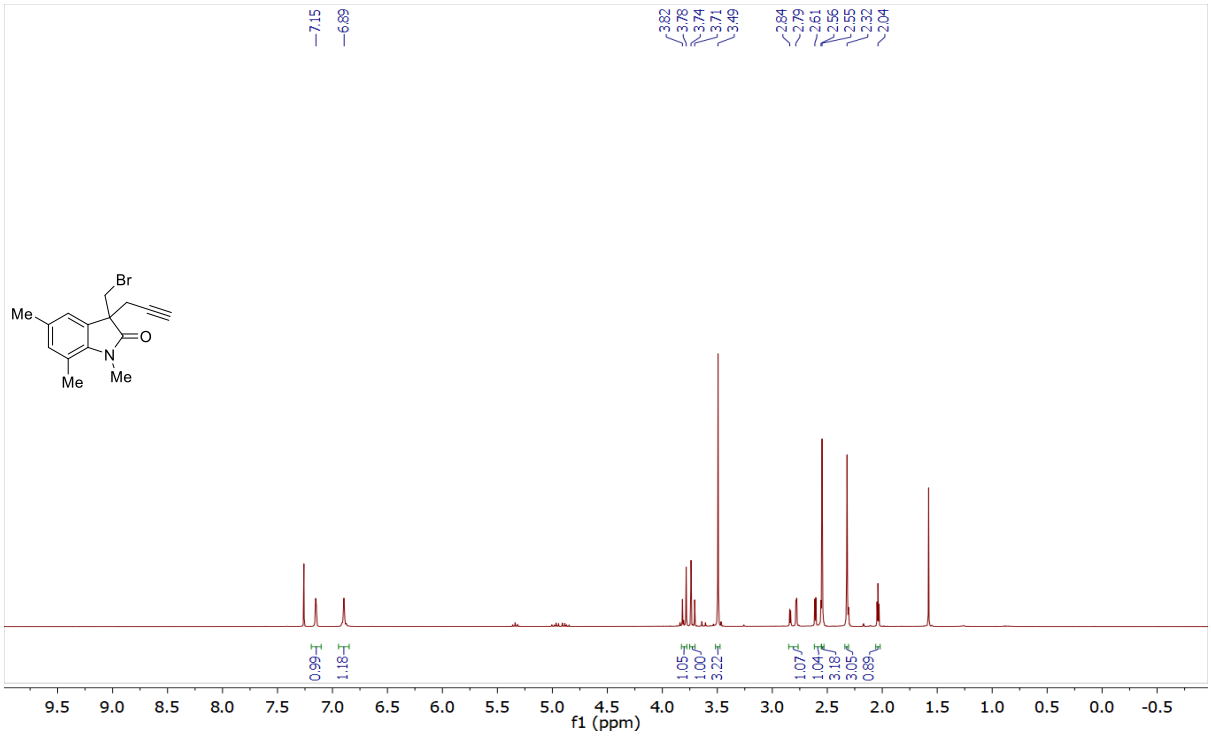
^{1}H NMR of 4e (400 MHz, $CDCl_3$):



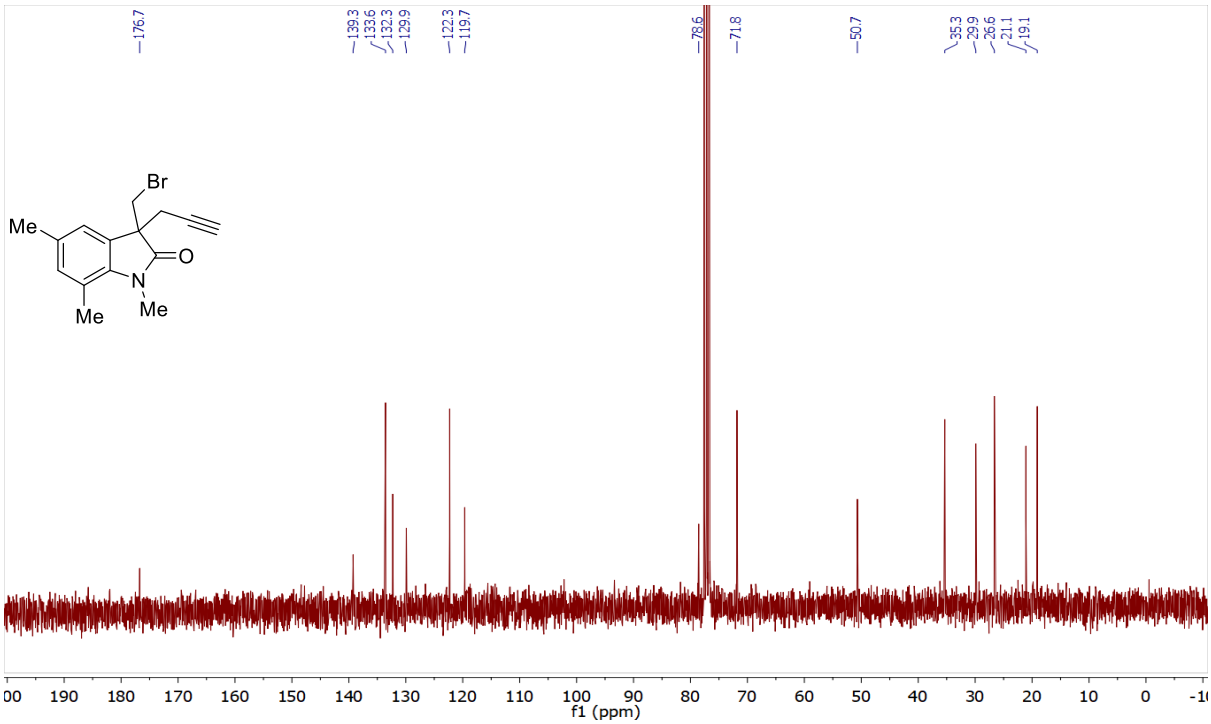
^{13}C{^{1}H} NMR of 4e (151 MHz, $CDCl_3$):



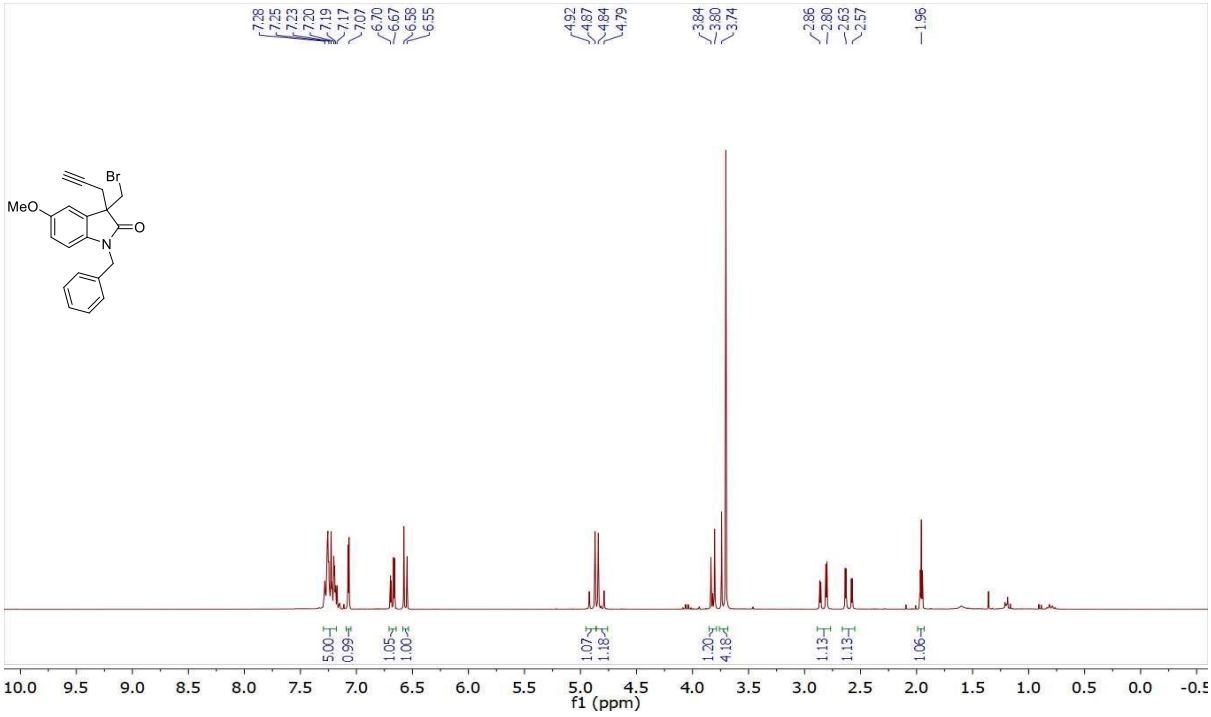
^{1}H NMR of 4f (300 MHz, $CDCl_3$):



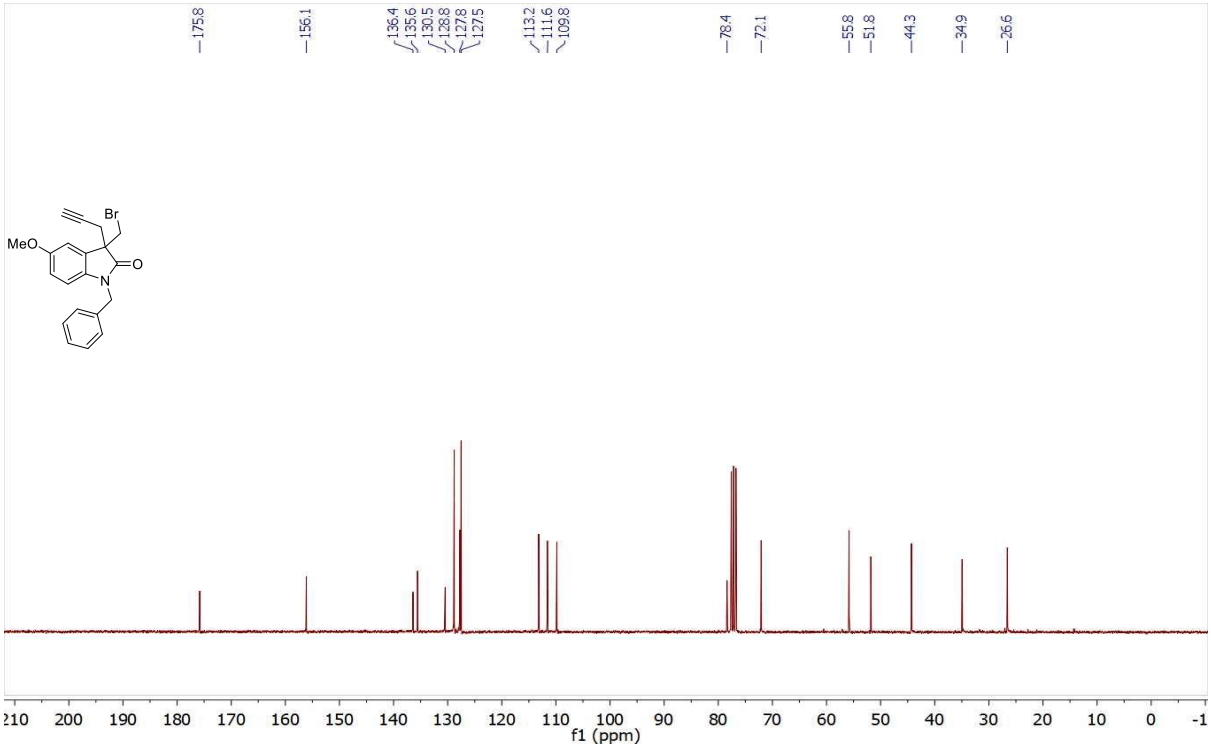
^{13}C{^{1}H} NMR of 4f (75 MHz, $CDCl_3$):



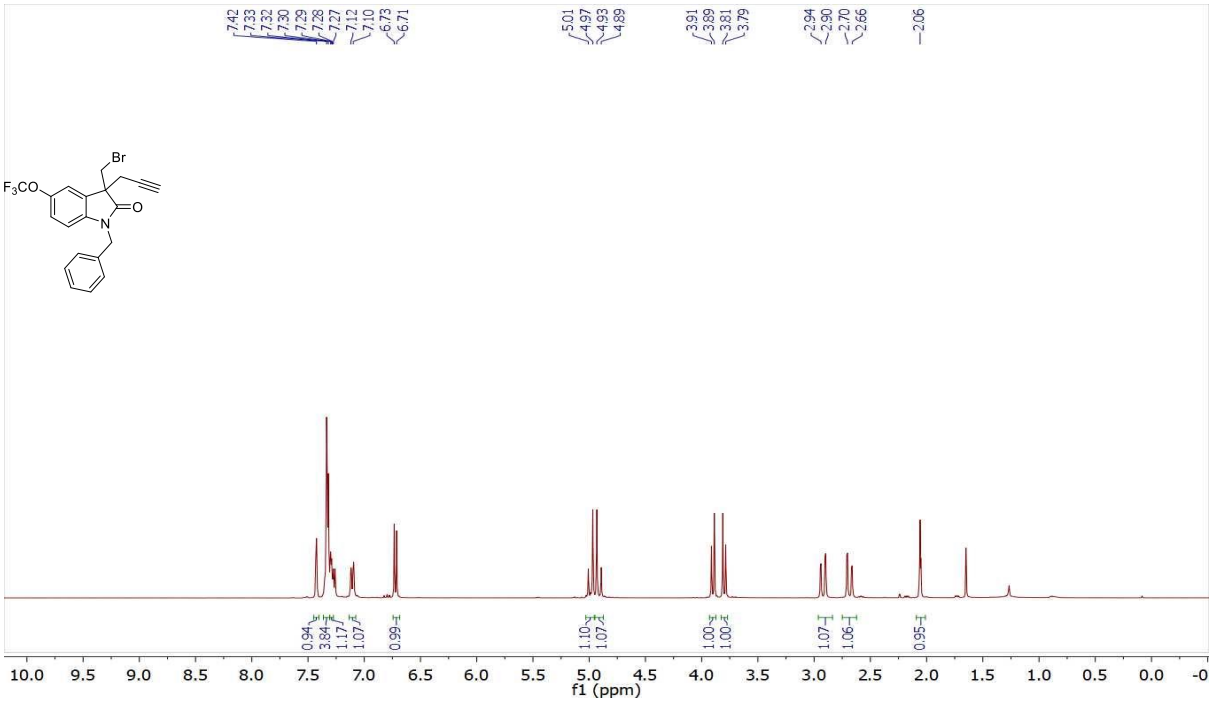
^{1}H NMR of 4g (300 MHz, $CDCl_3$):



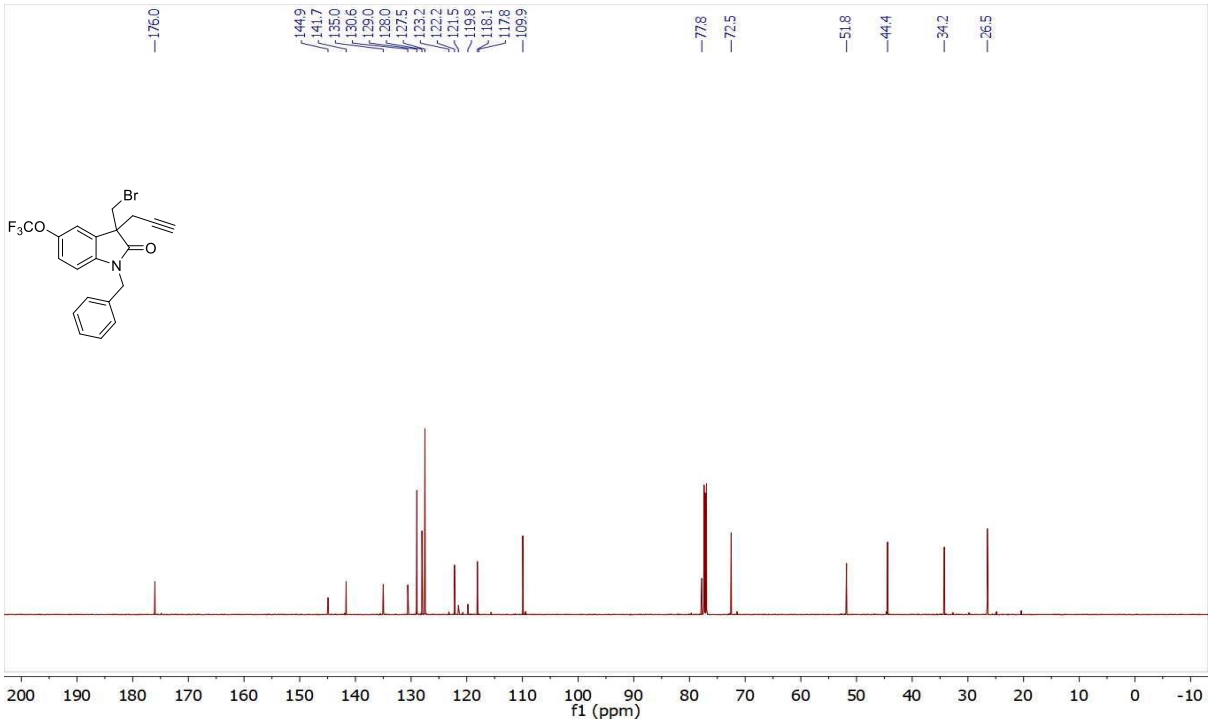
^{13}C{^{1}H} NMR of 4g (75 MHz, $CDCl_3$):



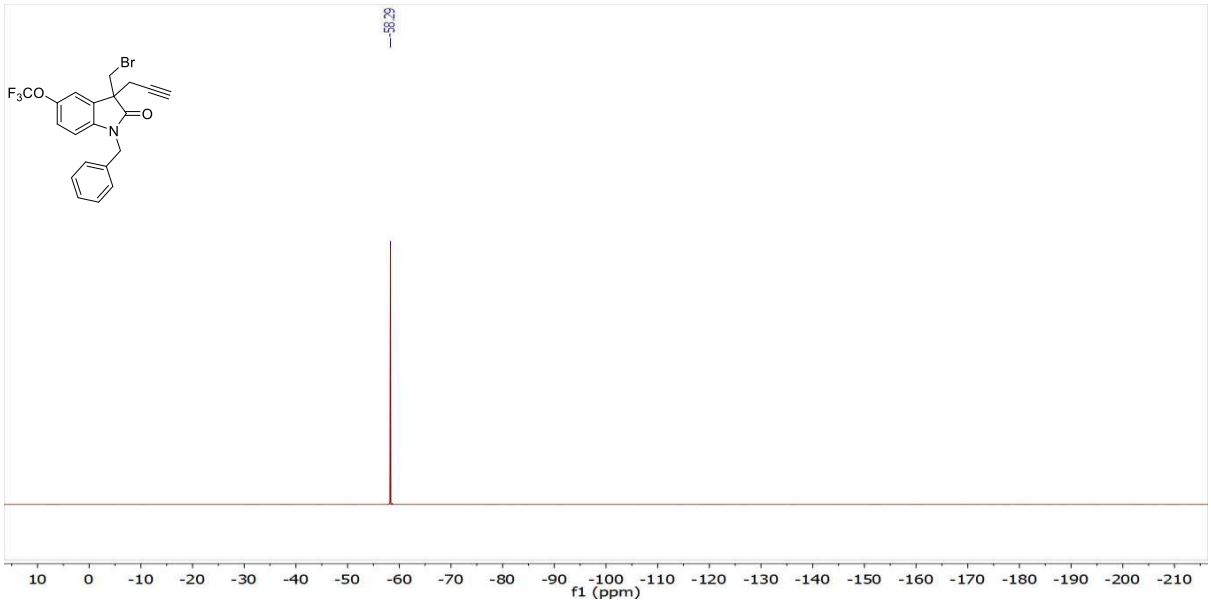
^{1}H NMR of 4h (400 MHz, $CDCl_3$):



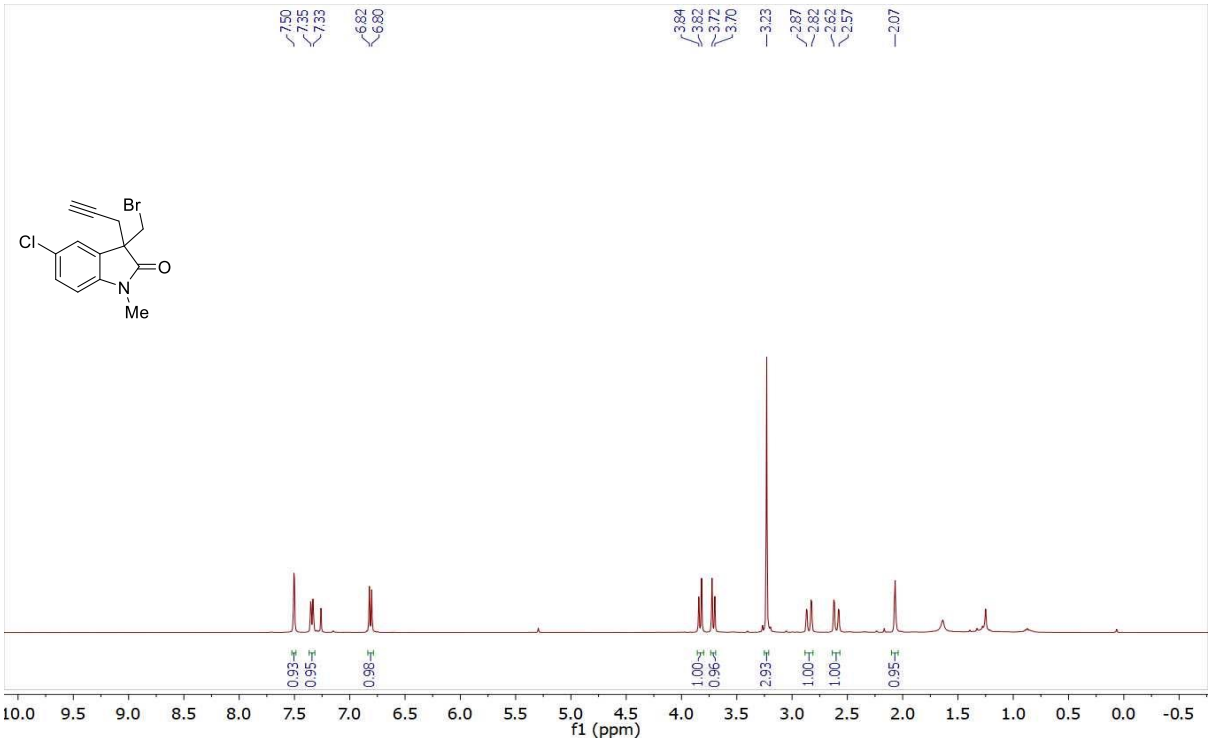
^{13}C{^{1}H} NMR of 4h (151 MHz, $CDCl_3$):



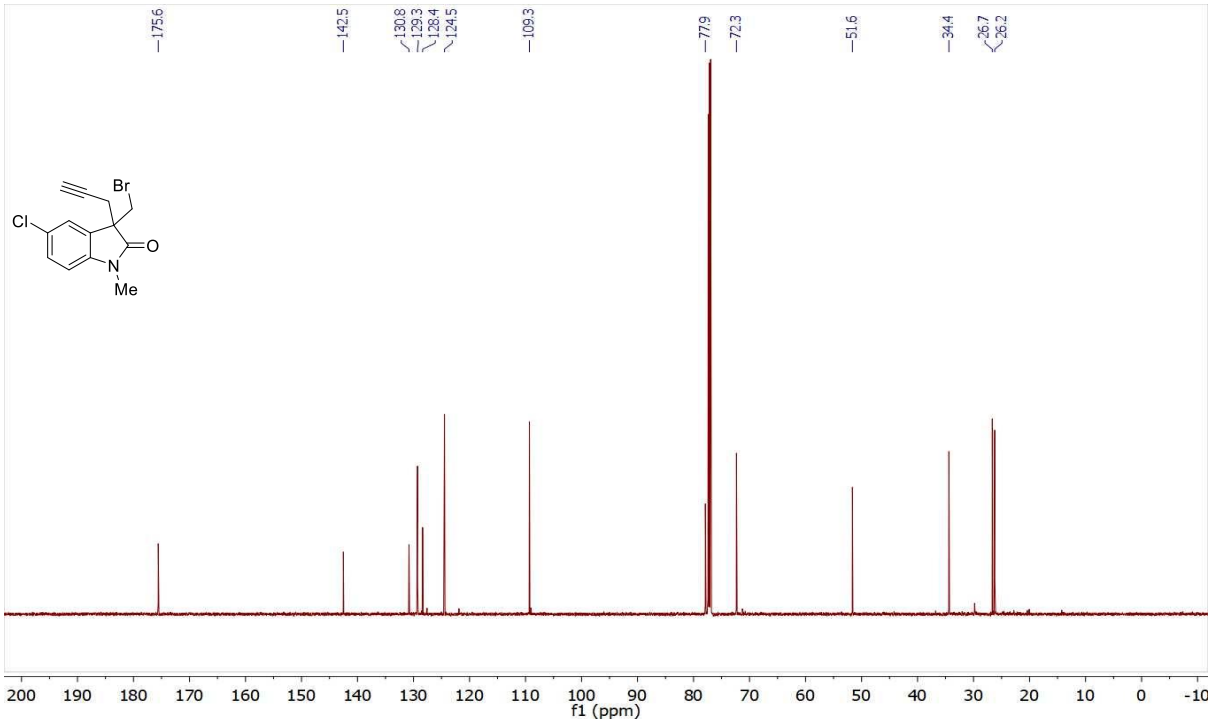
$^{19}F\{^{1}H\}$ NMR of 4h (565 MHz, $CDCl_3$):



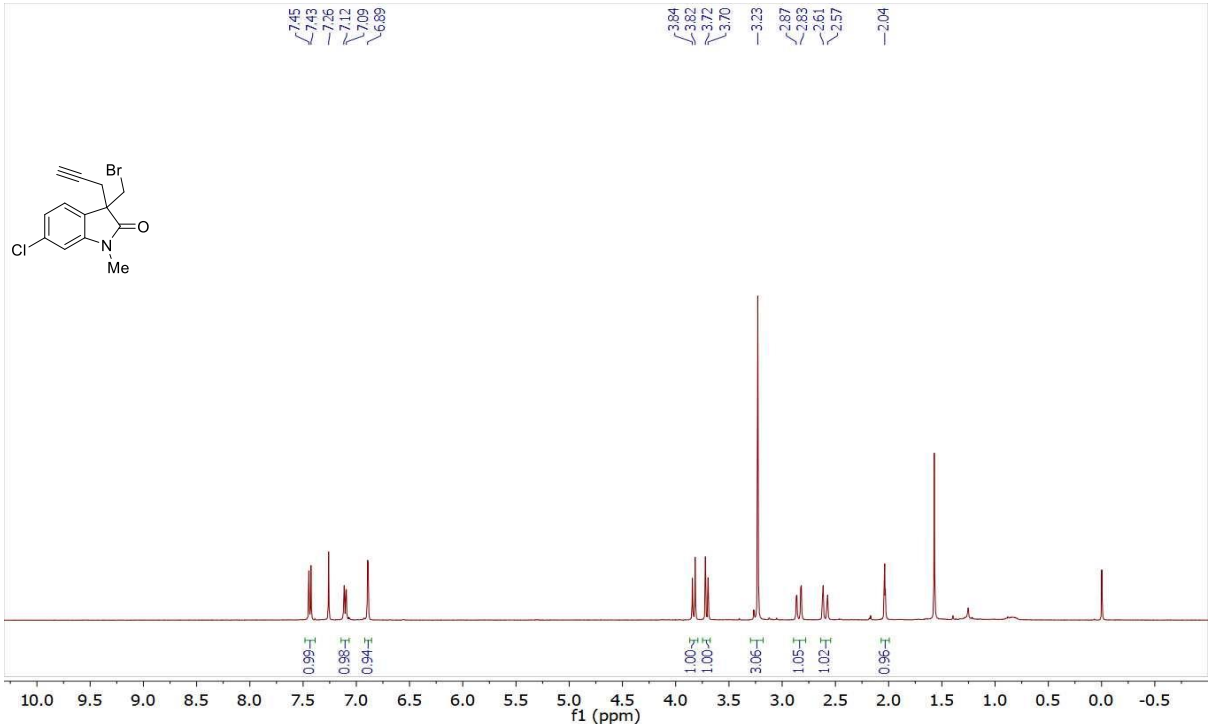
^{1}H NMR of 4i (400 MHz, $CDCl_3$):



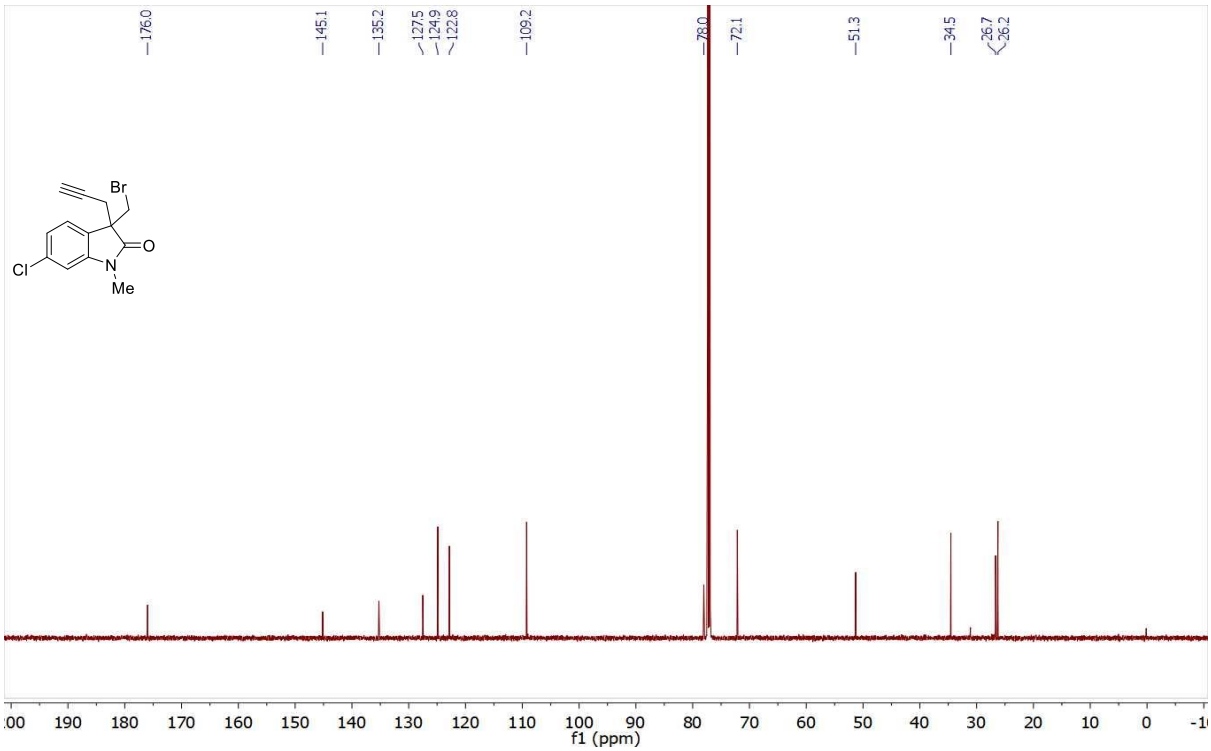
$^{13}C\{^{1}H\}$ NMR of 4i (151 MHz, $CDCl_3$):



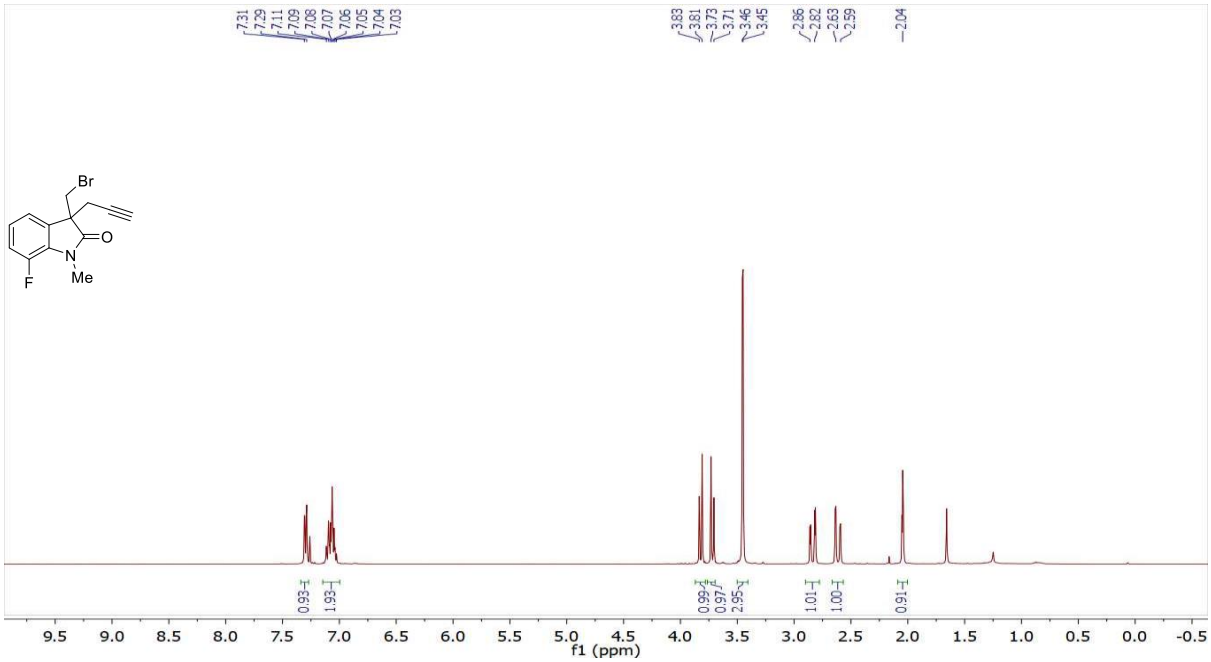
^{1}H NMR of 4j (400 MHz, $CDCl_3$):



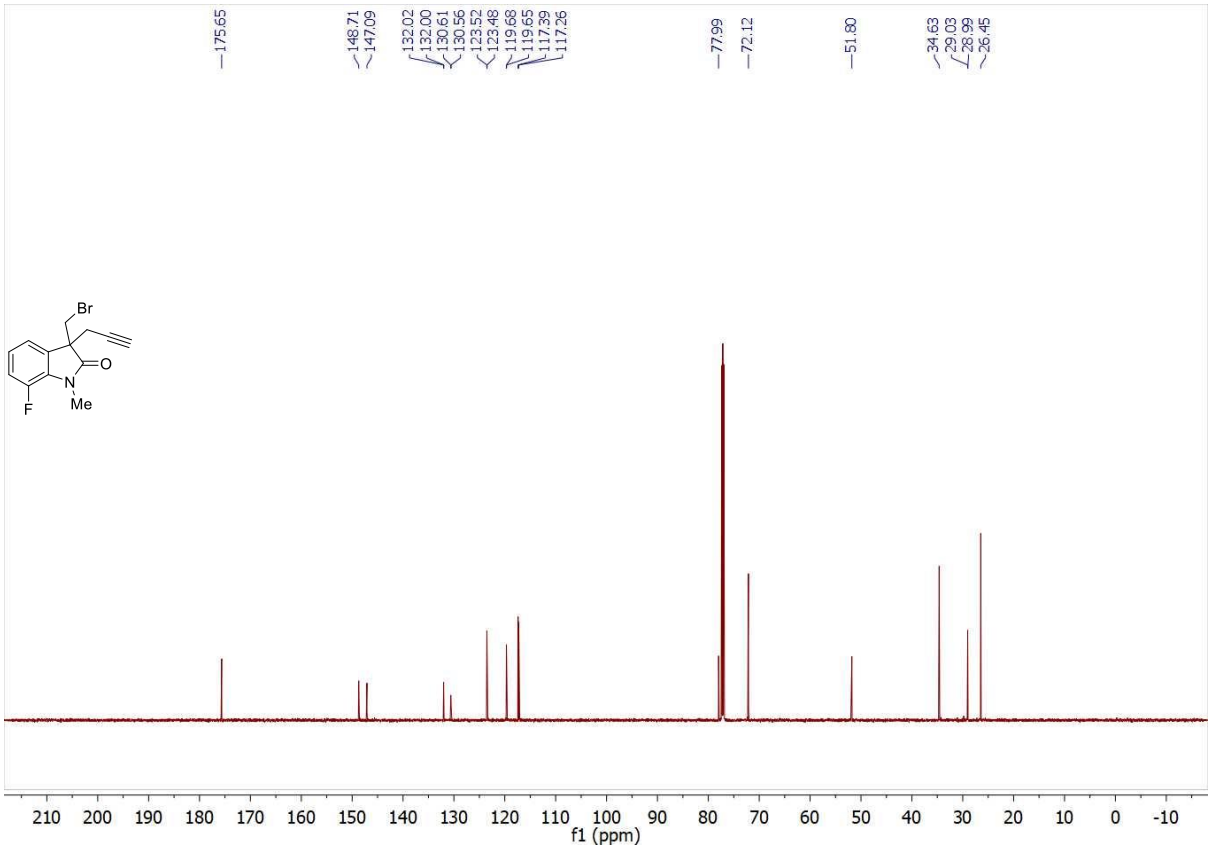
$^{13}C\{^{1}H\}$ NMR of 4j (151 MHz, $CDCl_3$):



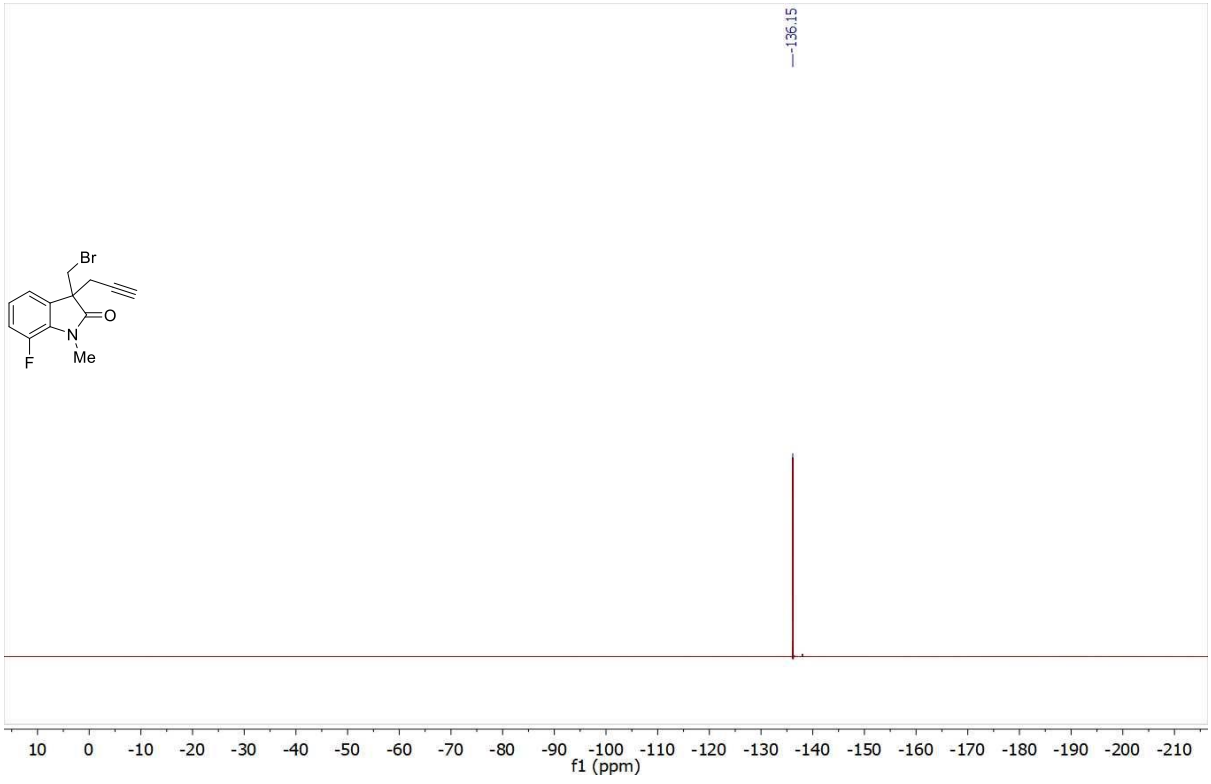
^{1}H NMR of 4k (400 MHz, $CDCl_3$):



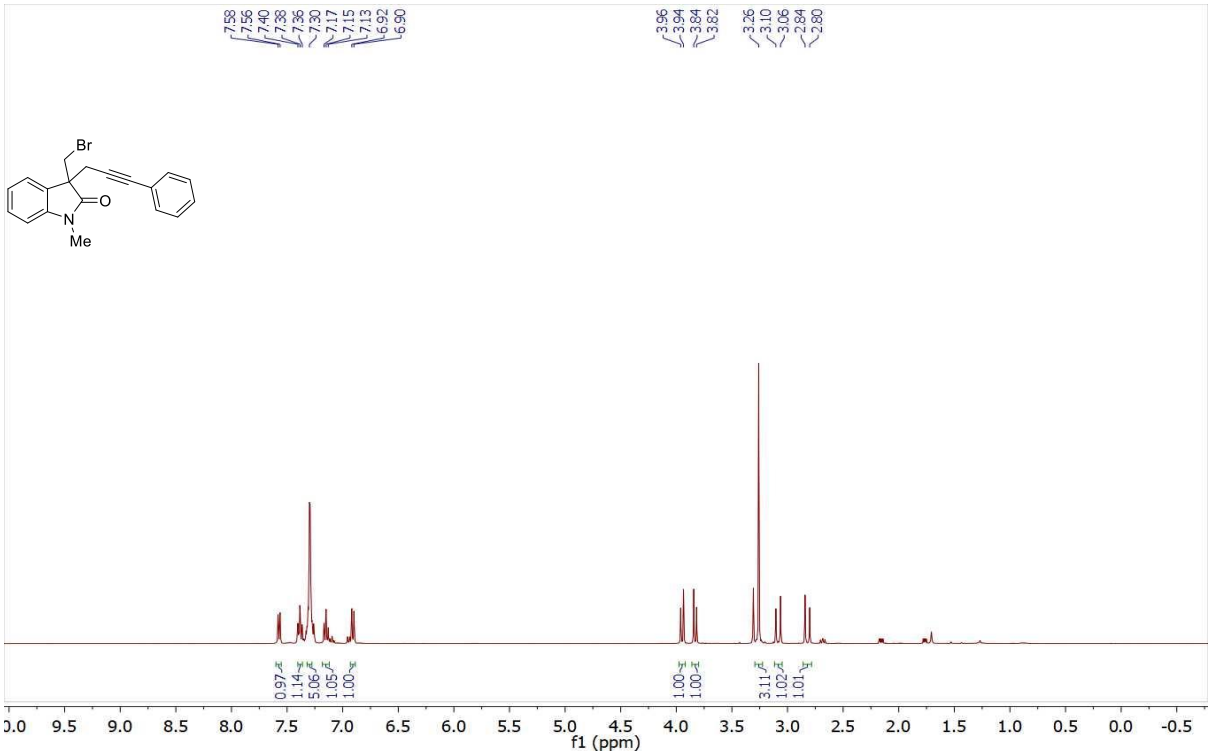
$^{13}C\{^{1}H\}$ NMR of 4k (151 MHz, $CDCl_3$):



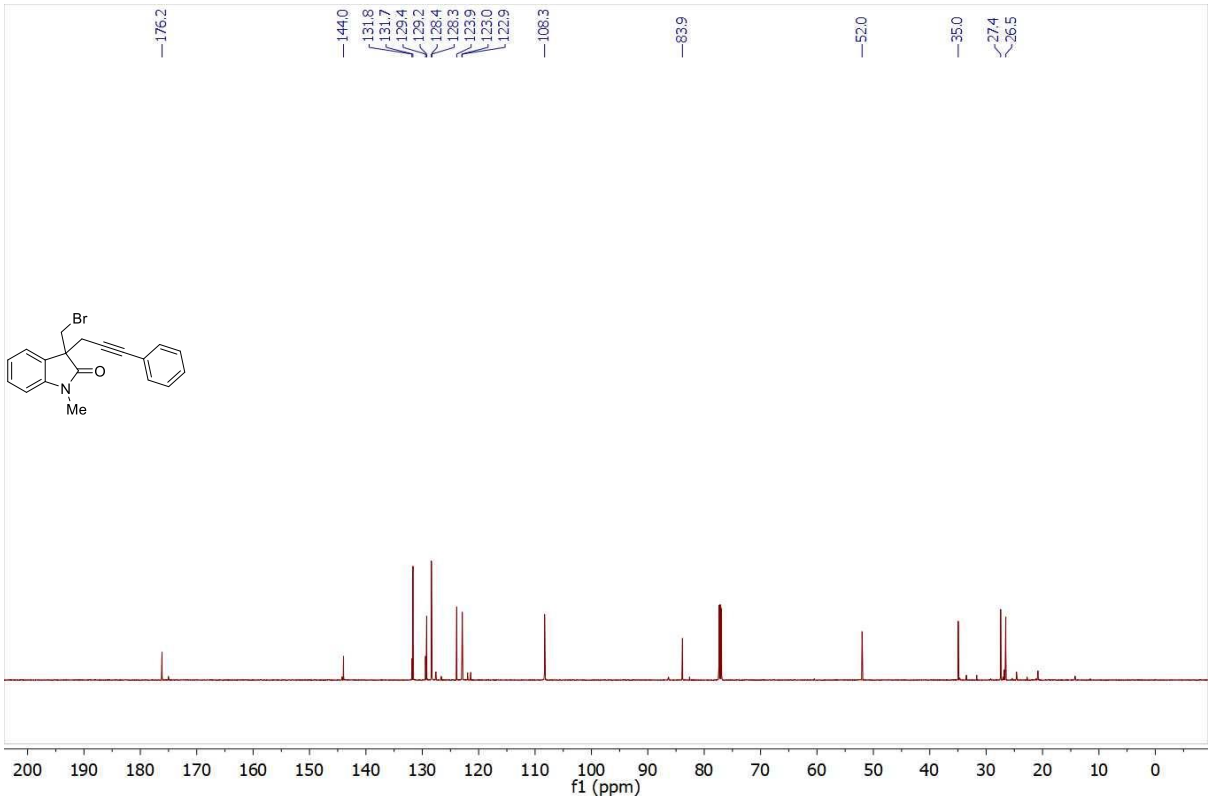
$^{19}F\{^{1}H\}$ NMR of 4k (565 MHz, $CDCl_3$):



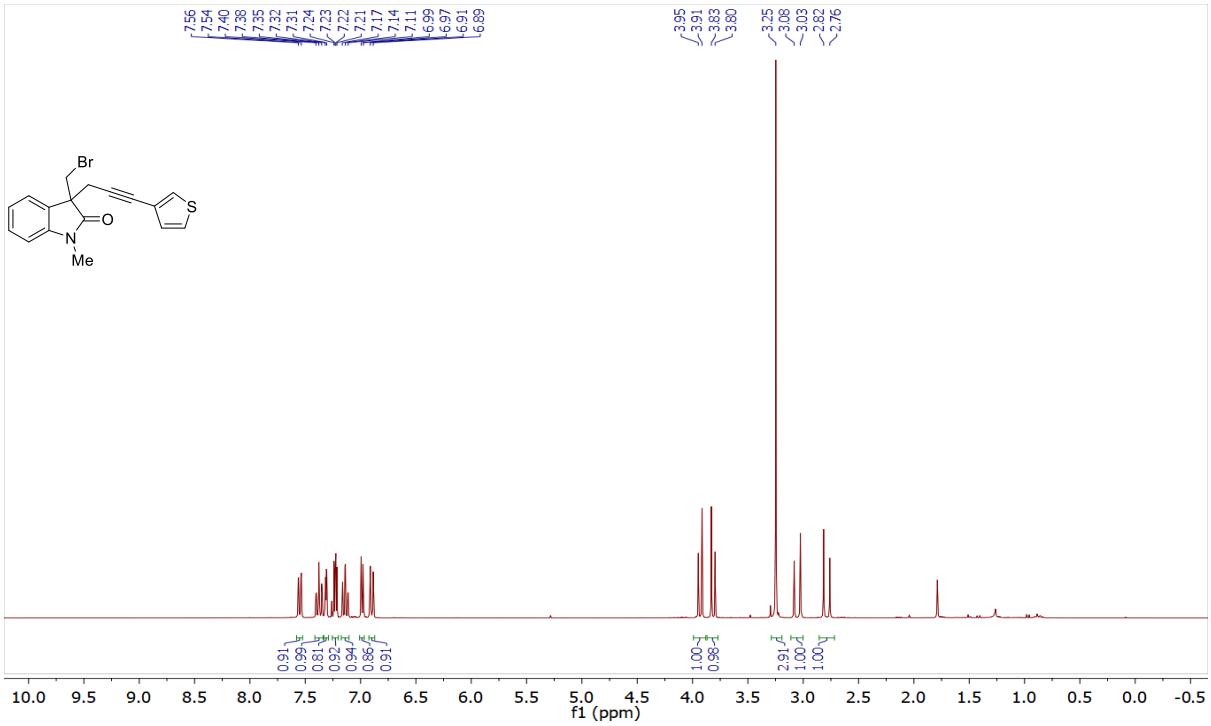
^{1}H NMR of 4l (400 MHz, $CDCl_3$):



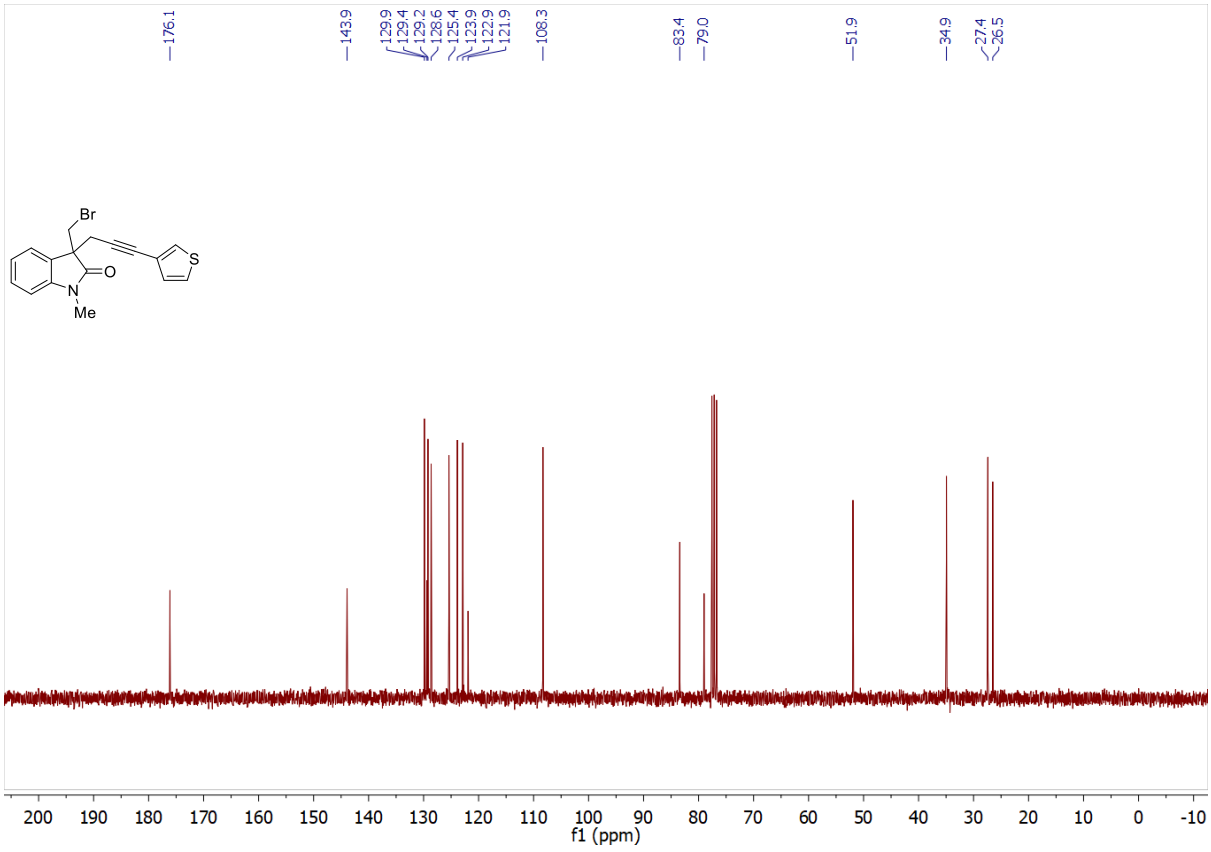
^{13}C{^{1}H} NMR of 4l (151 MHz, $CDCl_3$):



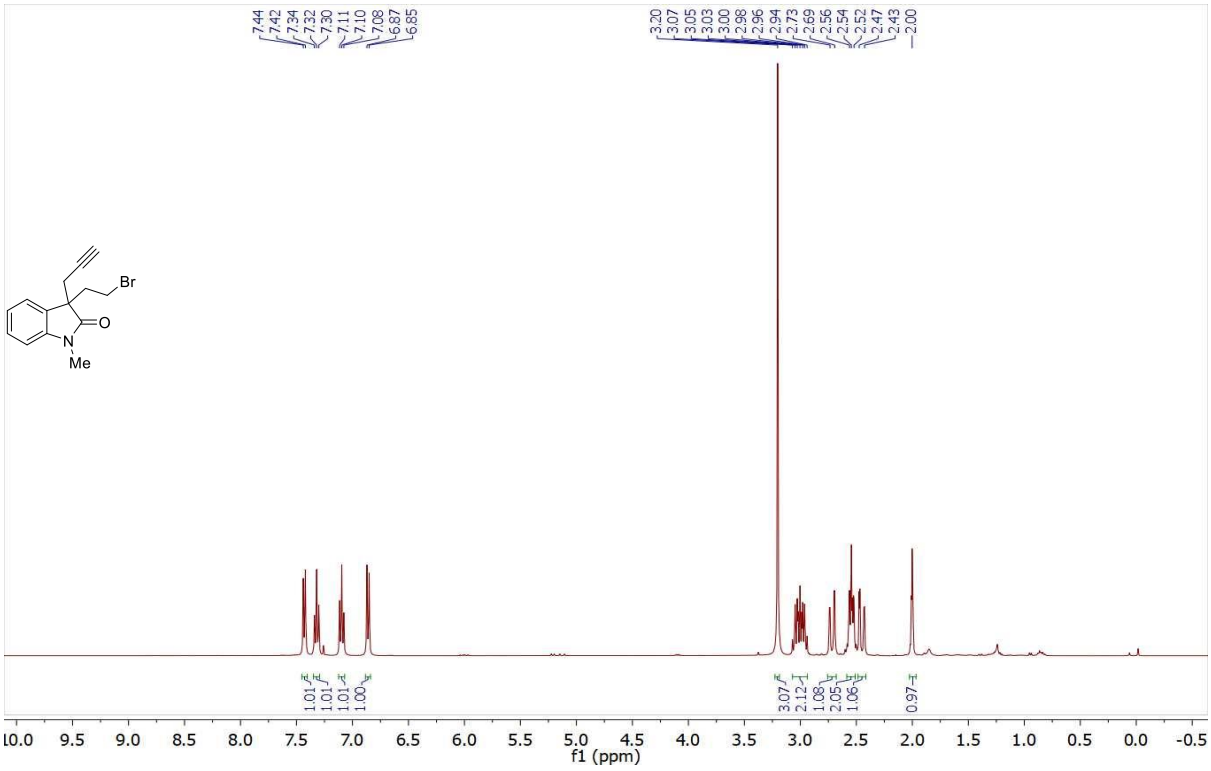
^{1}H NMR of 4m (300 MHz, $CDCl_3$):



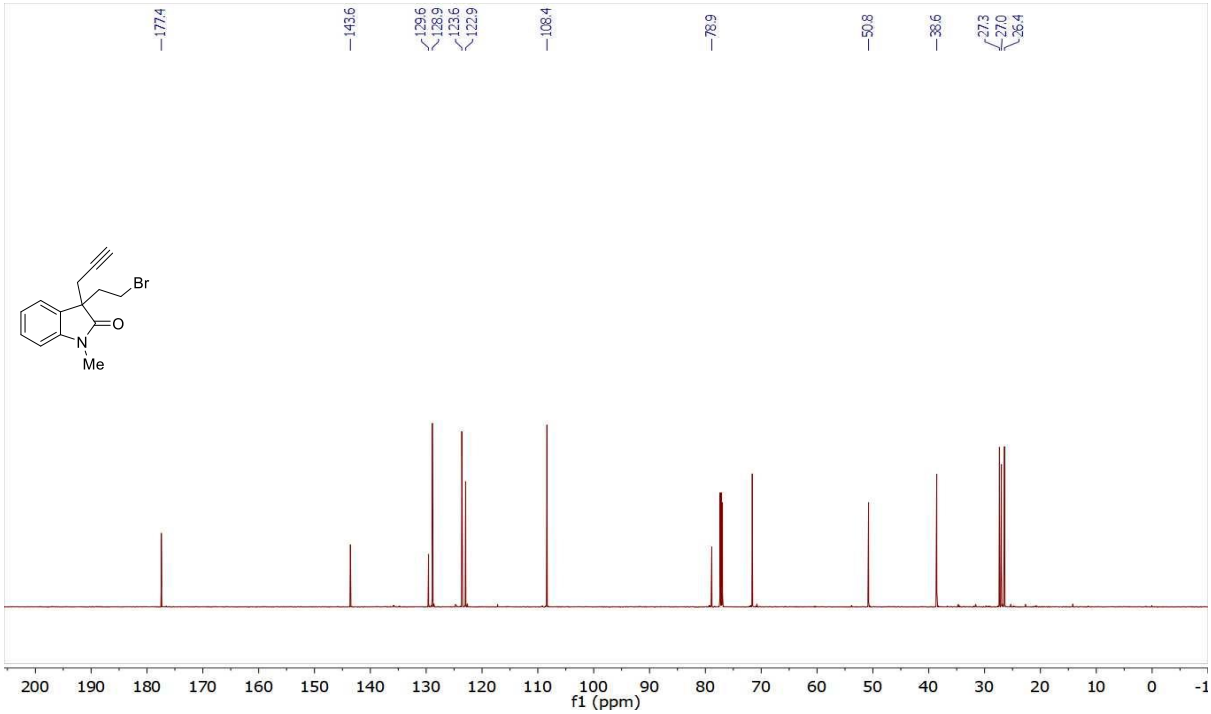
^{13}C{^{1}H} NMR of 4m (75 MHz, $CDCl_3$):



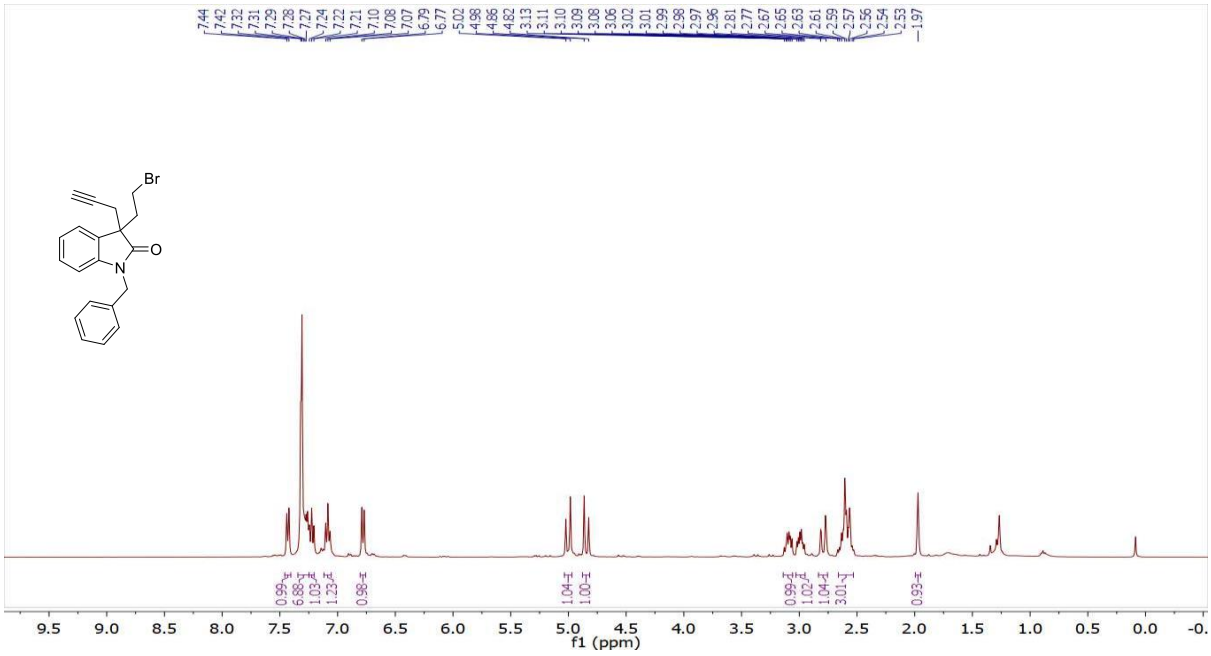
^{1}H NMR of 5a (400 MHz, $CDCl_3$):



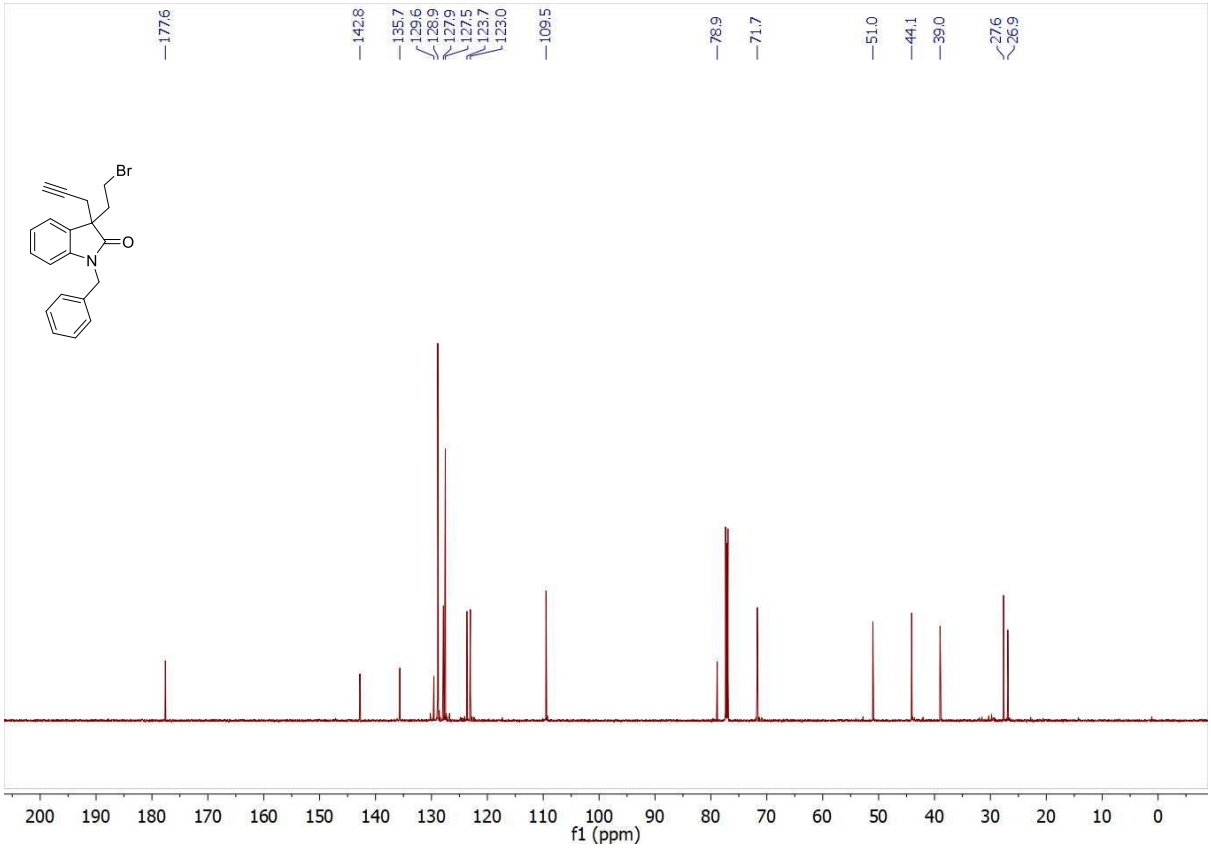
^{13}C{^{1}H} NMR of 5a (151 MHz, $CDCl_3$):



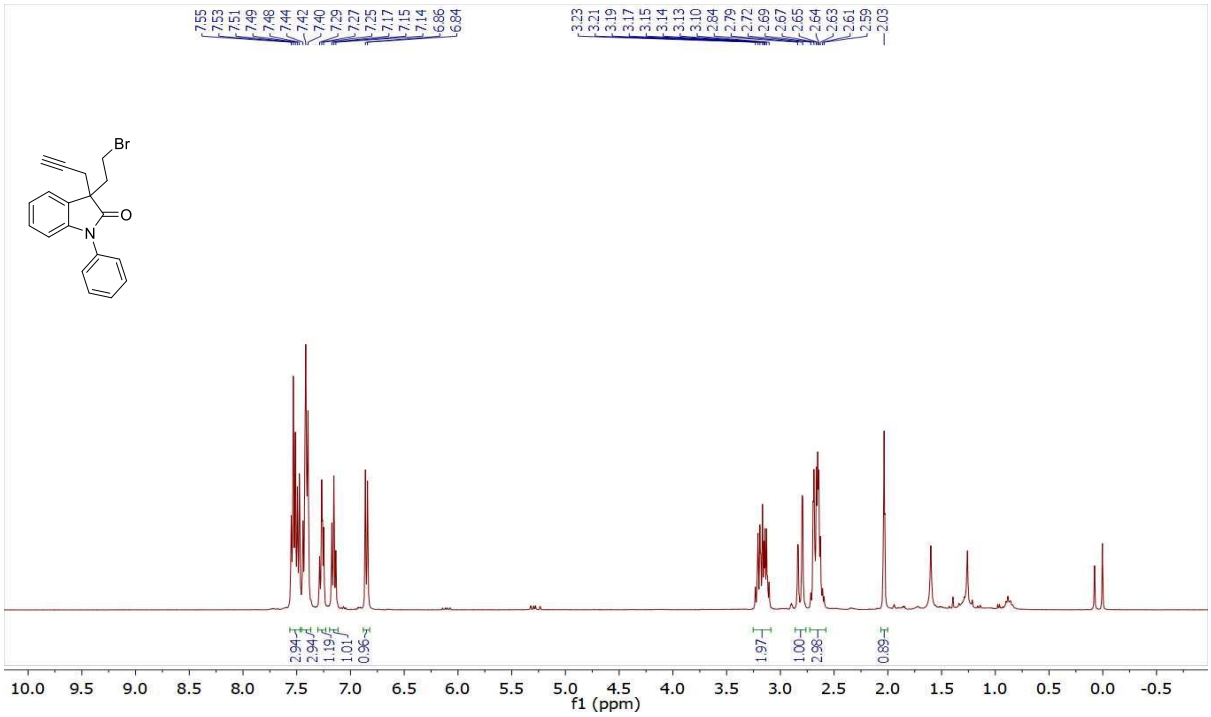
^{1}H NMR of 5b (400 MHz, $CDCl_3$):



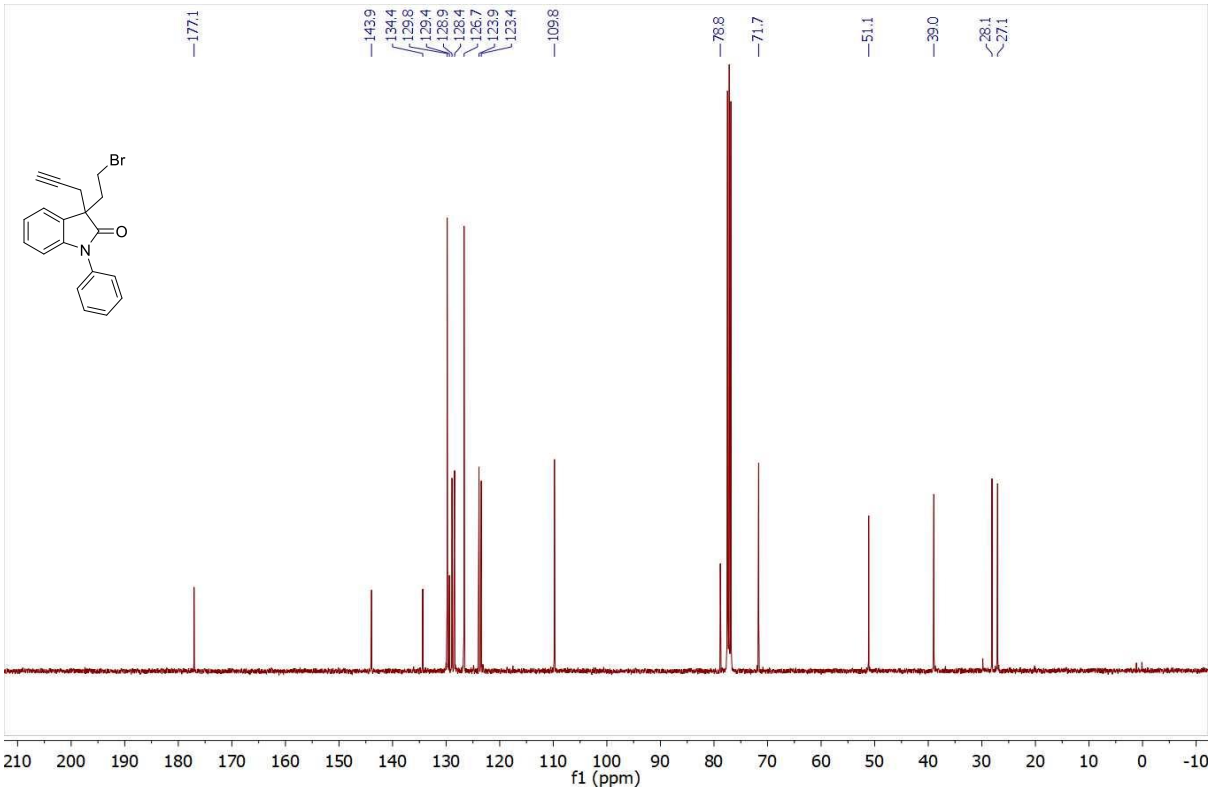
^{13}C{^{1}H} NMR of 5b (151 MHz, $CDCl_3$):



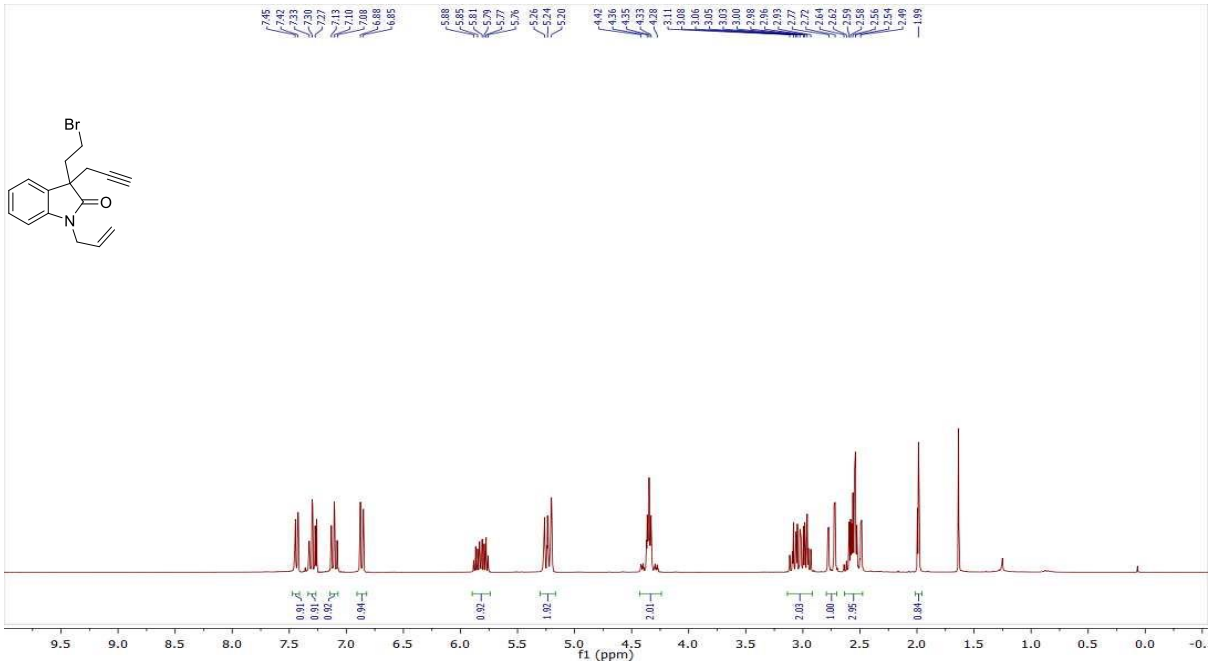
^{1}H NMR of 5c (400 MHz, $CDCl_3$):



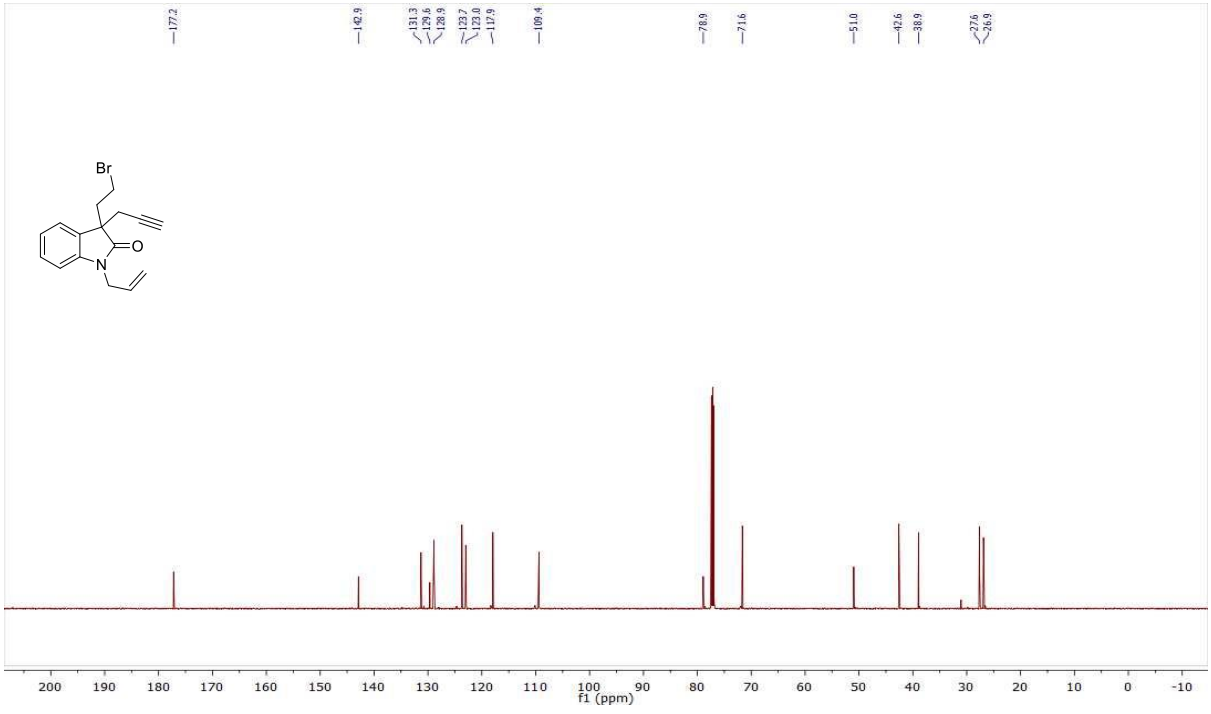
^{13}C{^{1}H} NMR of 5c (101 MHz, $CDCl_3$):



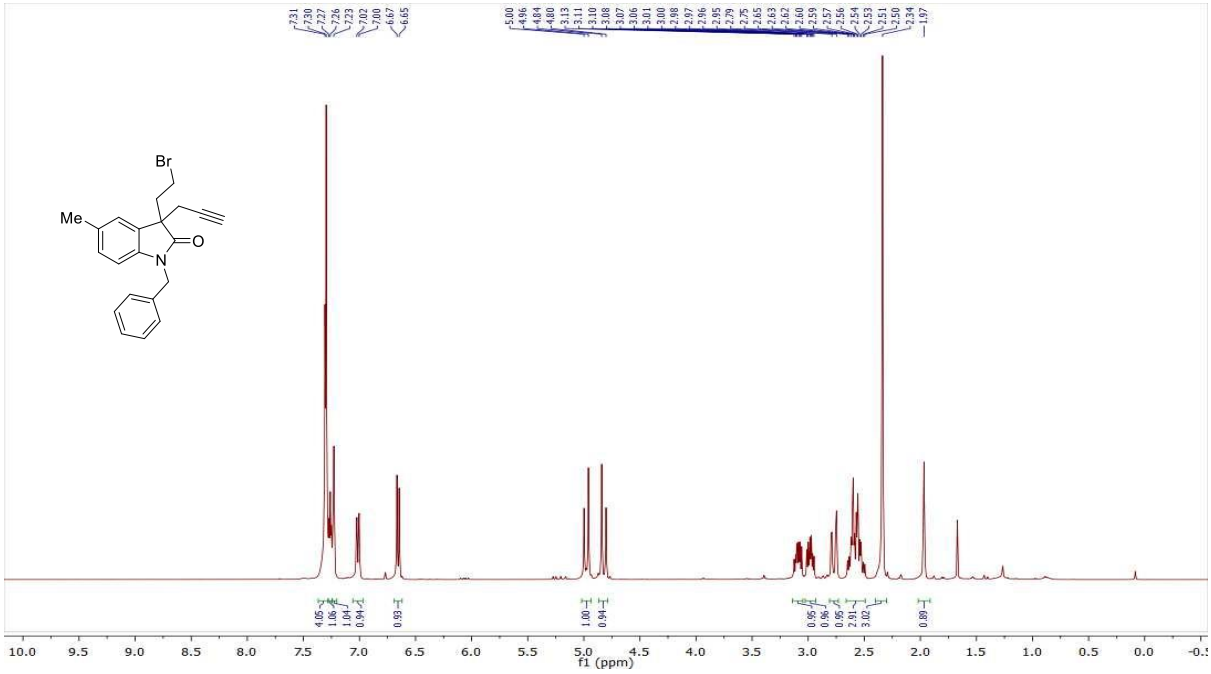
^{1}H NMR of 5d (300 MHz, $CDCl_3$):



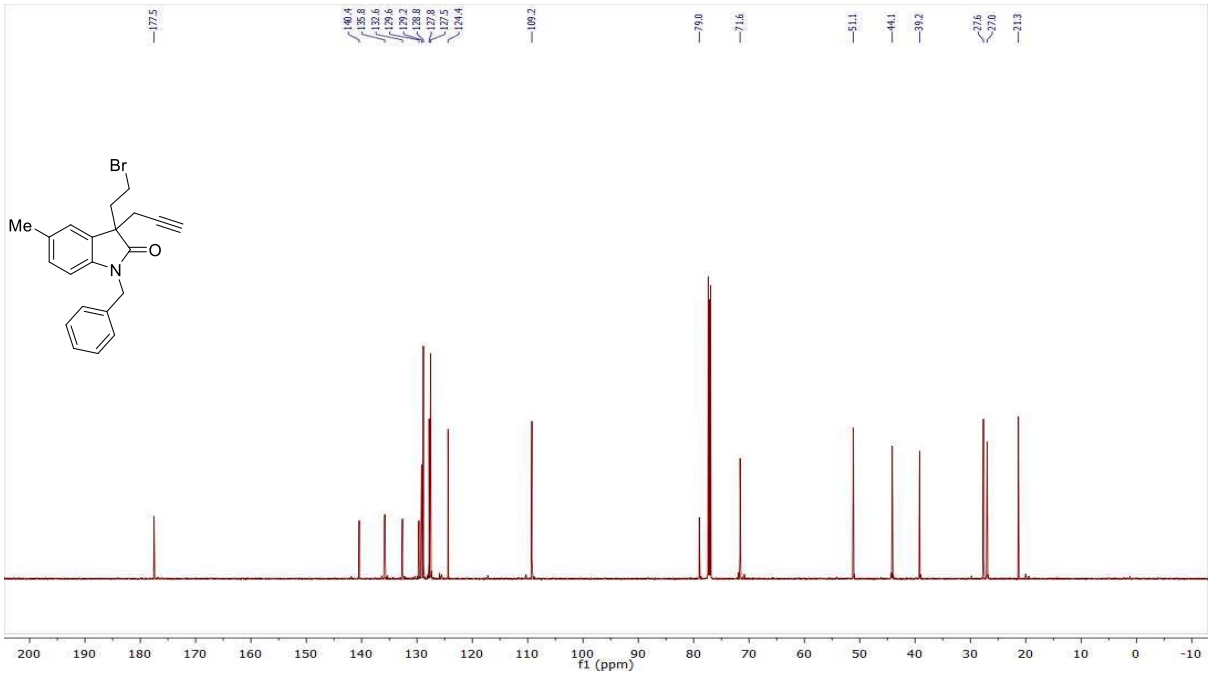
$^{13}C\{^{1}H\}$ NMR of 5d (151 MHz, $CDCl_3$):



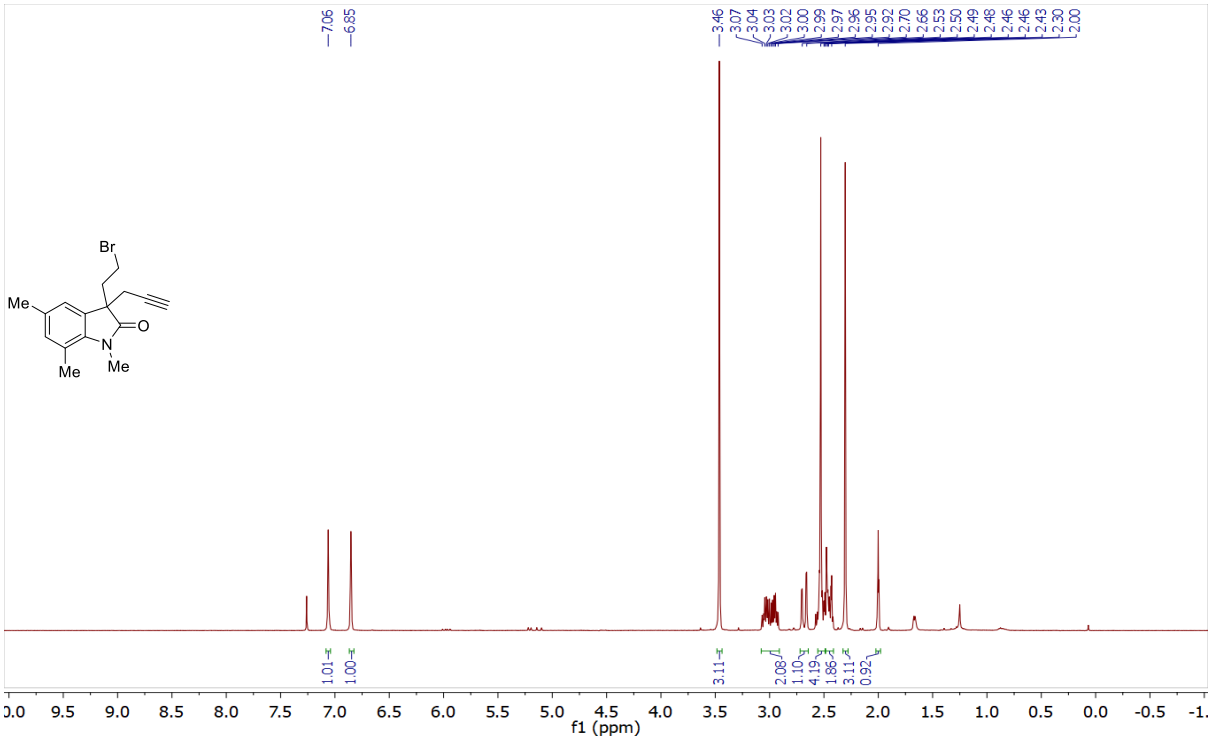
^{1}H NMR of 5e (400 MHz, $CDCl_3$):



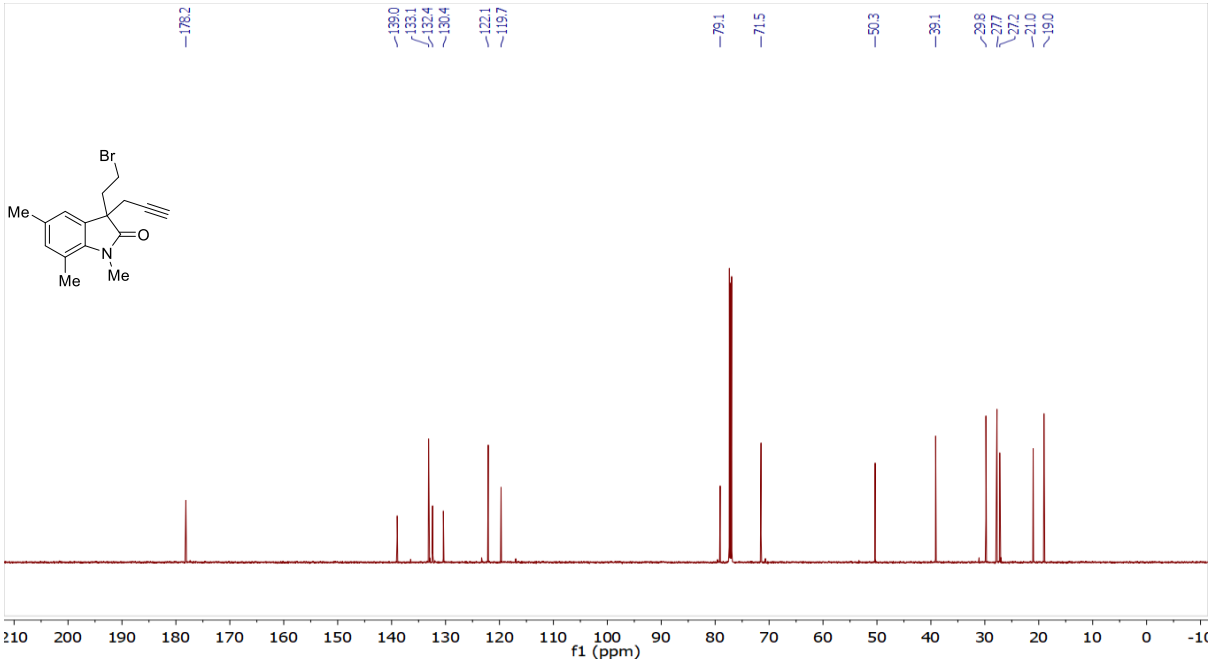
$^{13}C\{^{1}H\}$ NMR of 5e (151 MHz, $CDCl_3$):



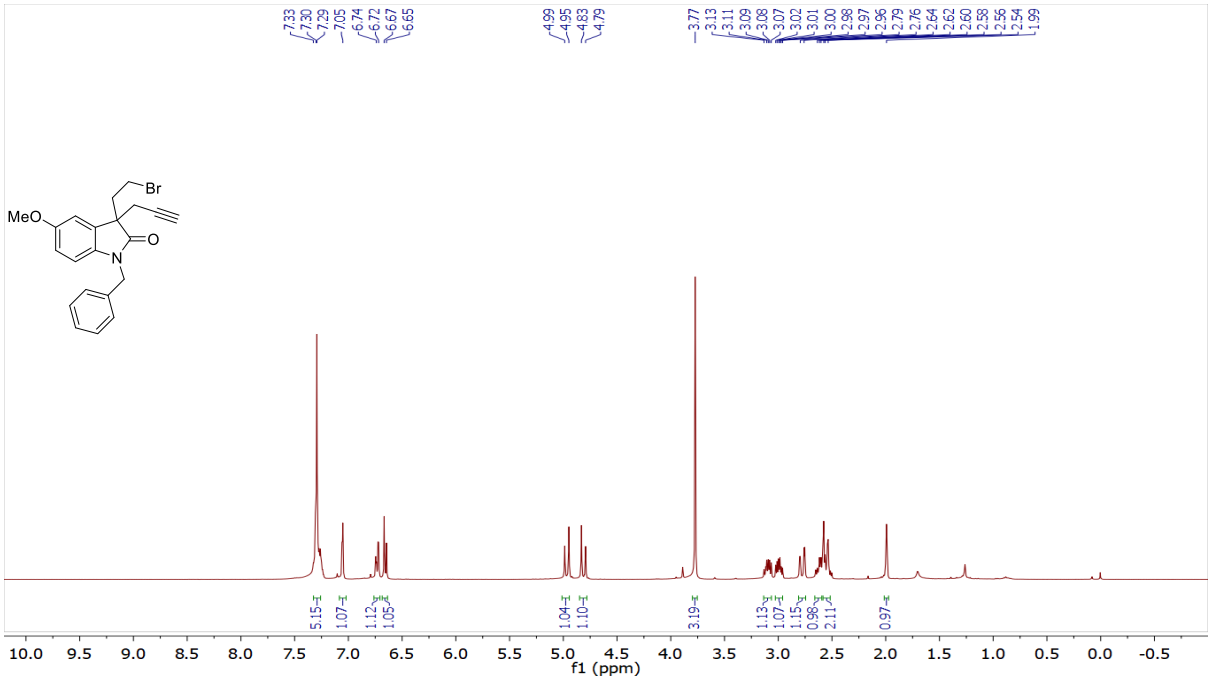
^{1}H NMR of 5f (400 MHz, $CDCl_3$):



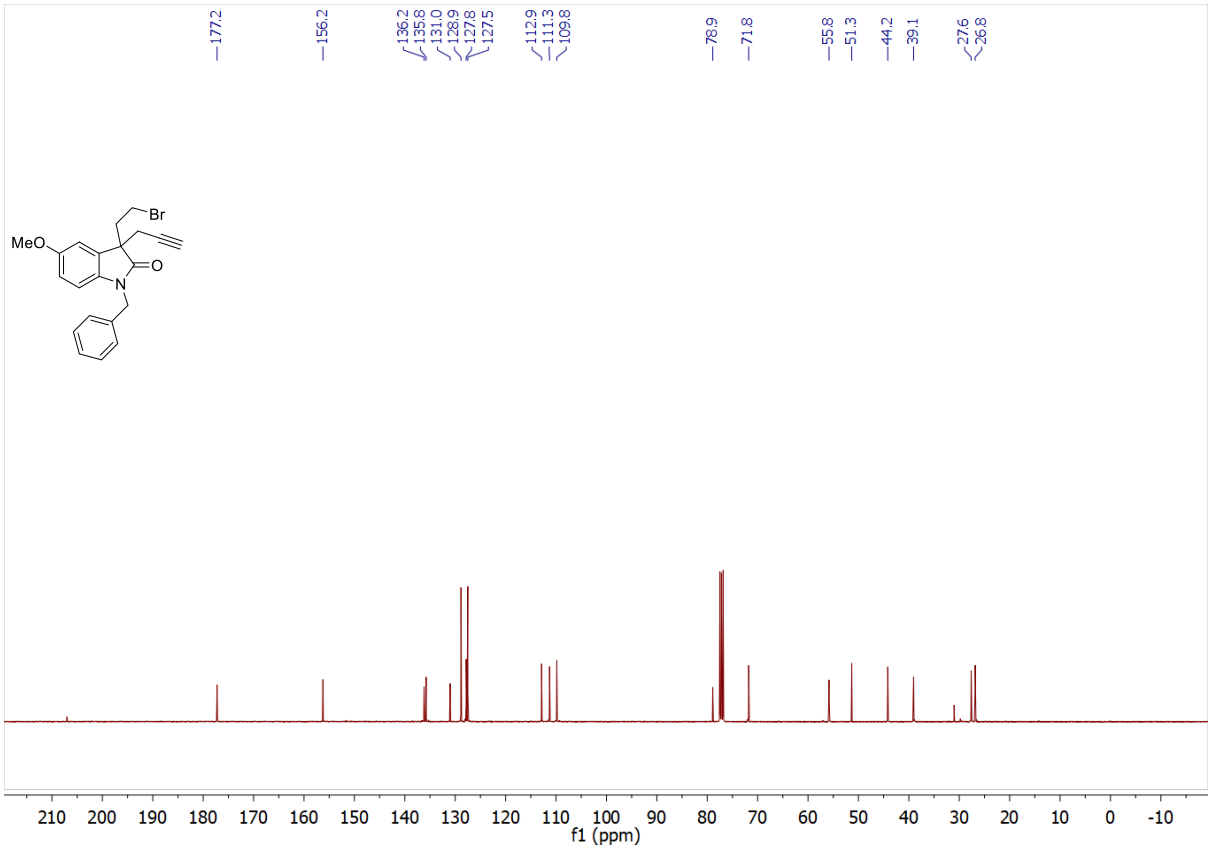
^{13}C{^{1}H} NMR of 5f (151 MHz, $CDCl_3$):



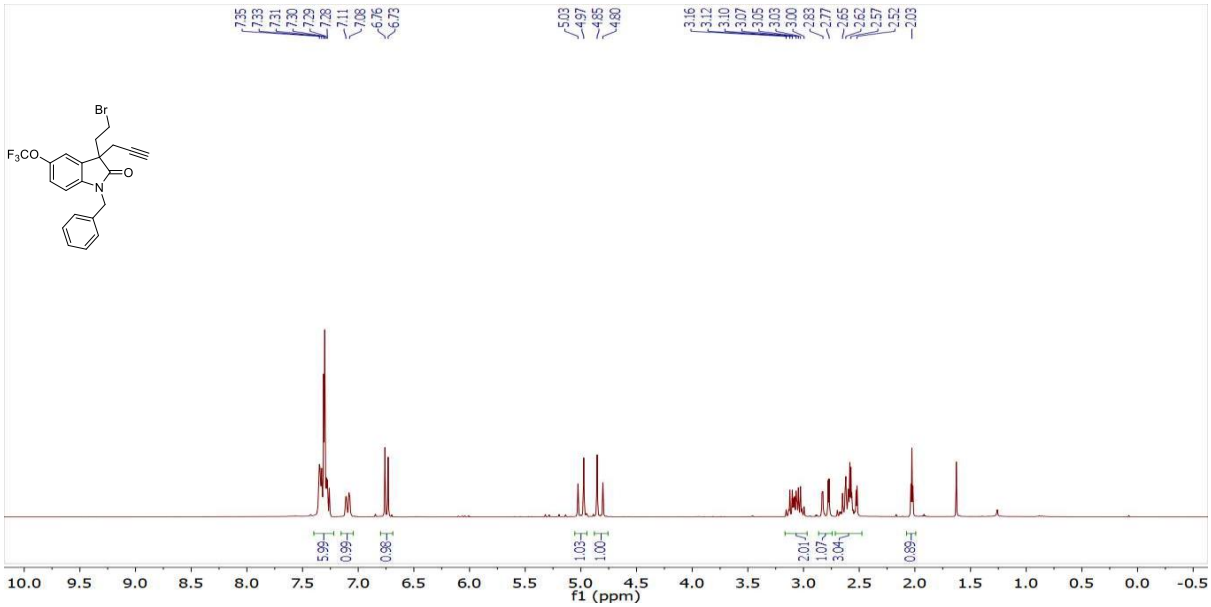
^{1}H NMR of 5g (400 MHz, $CDCl_3$):



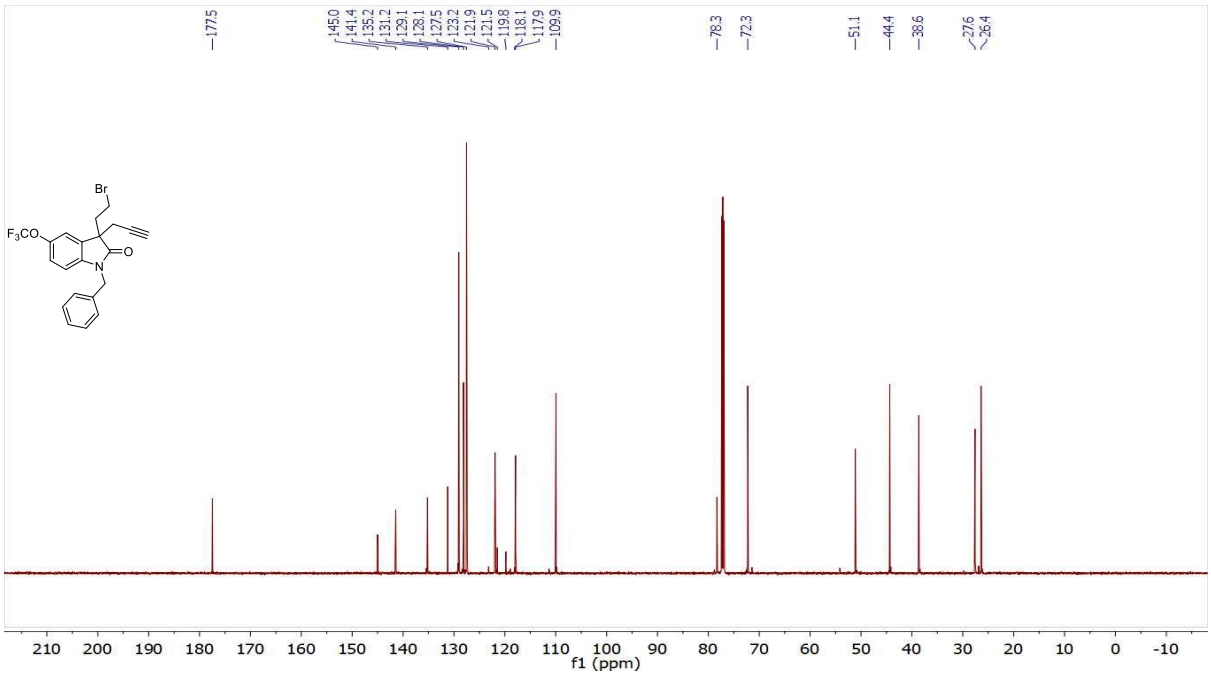
^{13}C{^{1}H} NMR of 5g (101 MHz, $CDCl_3$):



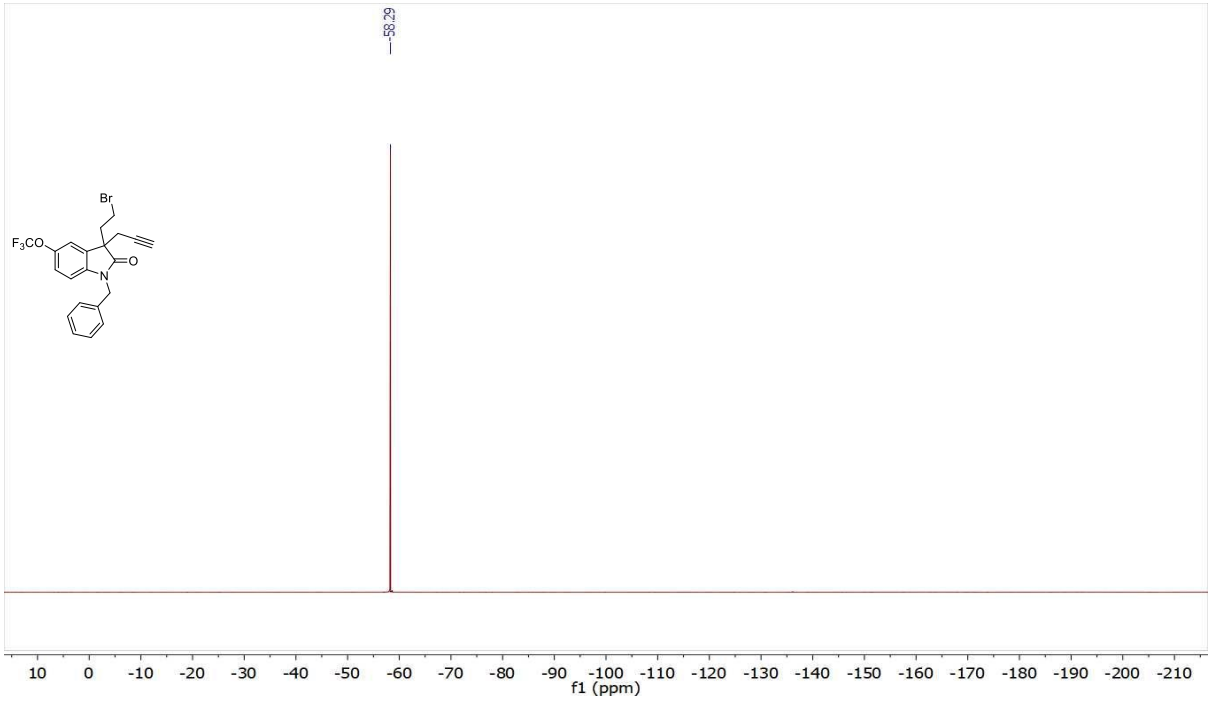
^{1}H NMR of 5h (300 MHz, $CDCl_3$):



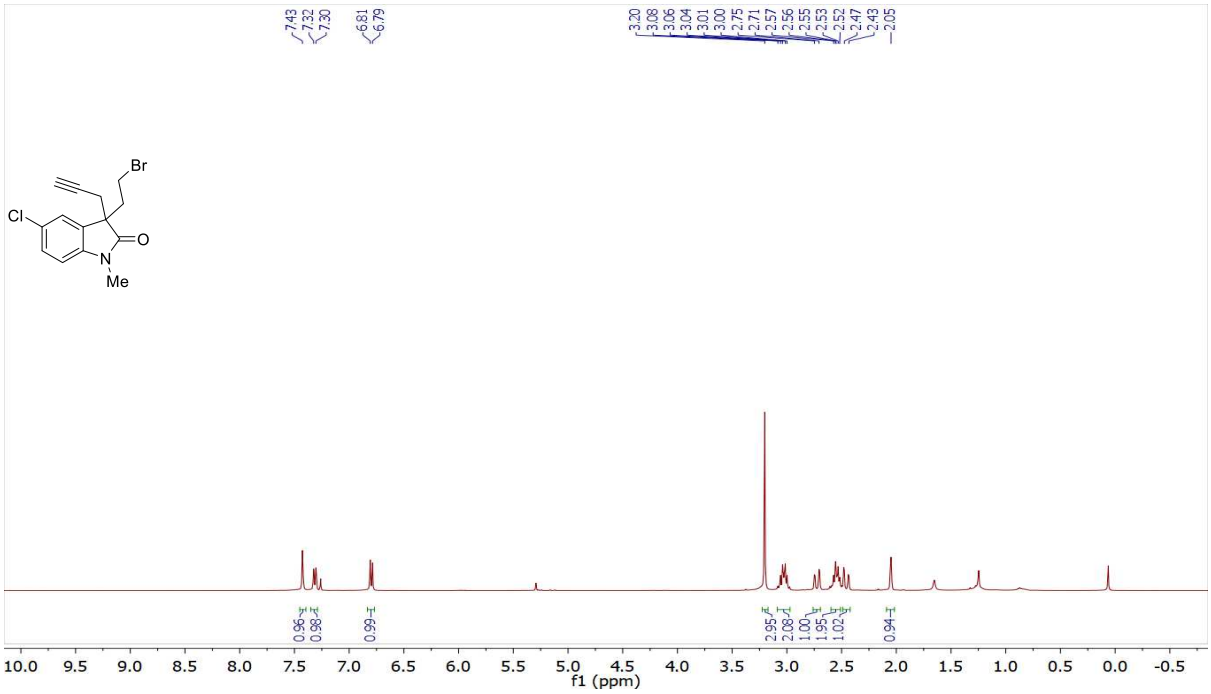
^{13}C{^{1}H} NMR of 5h (151 MHz, $CDCl_3$):



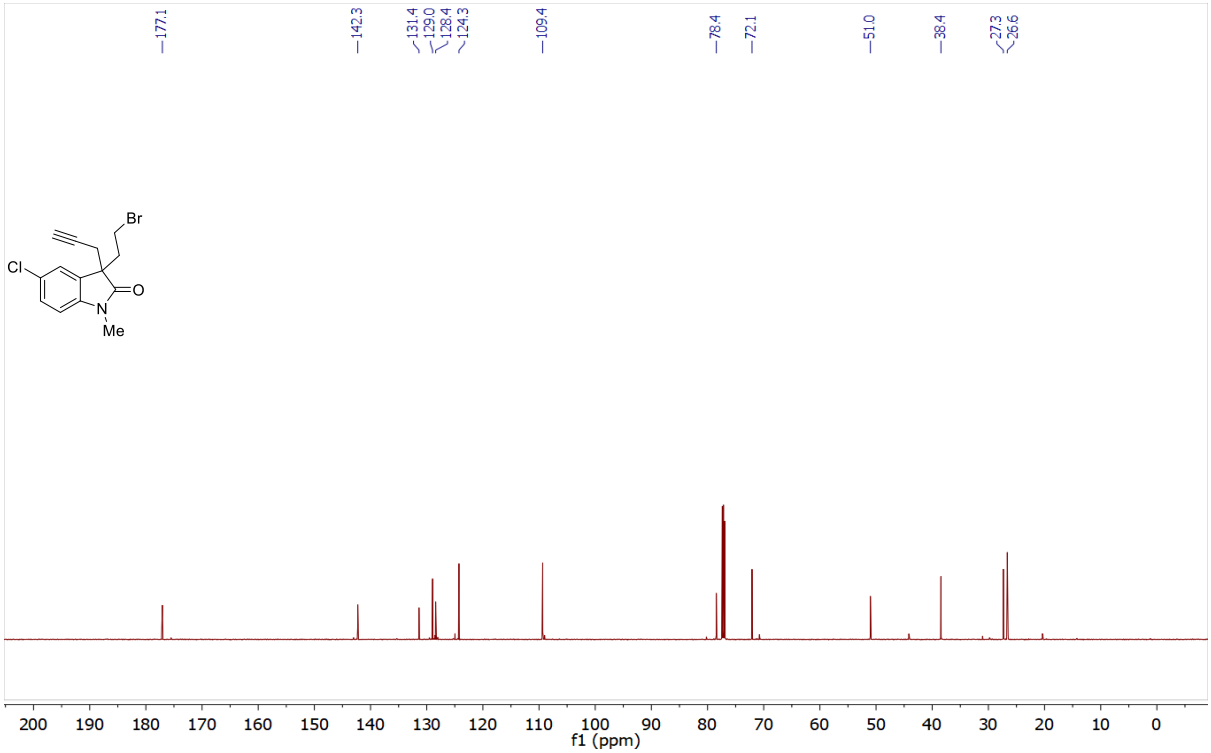
$^{19}F\{^{1}H\}$ NMR of 5h (565 MHz, $CDCl_3$):



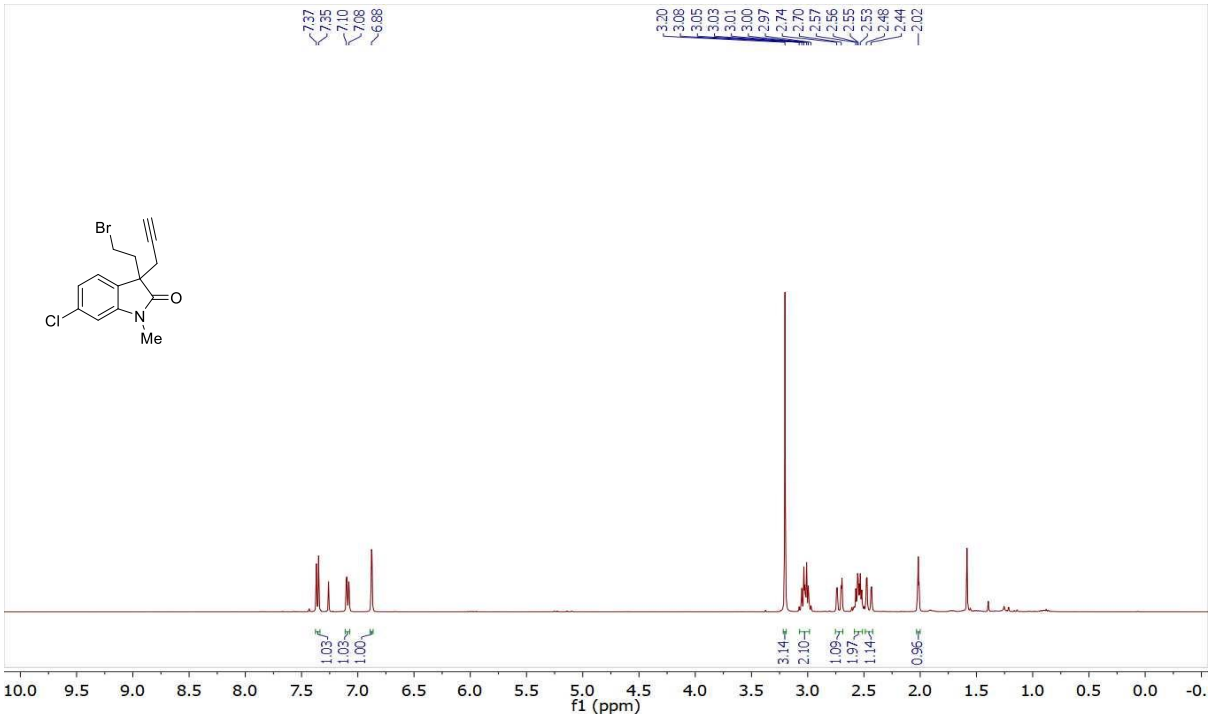
^{1}H NMR of 5i (400 MHz, $CDCl_3$):



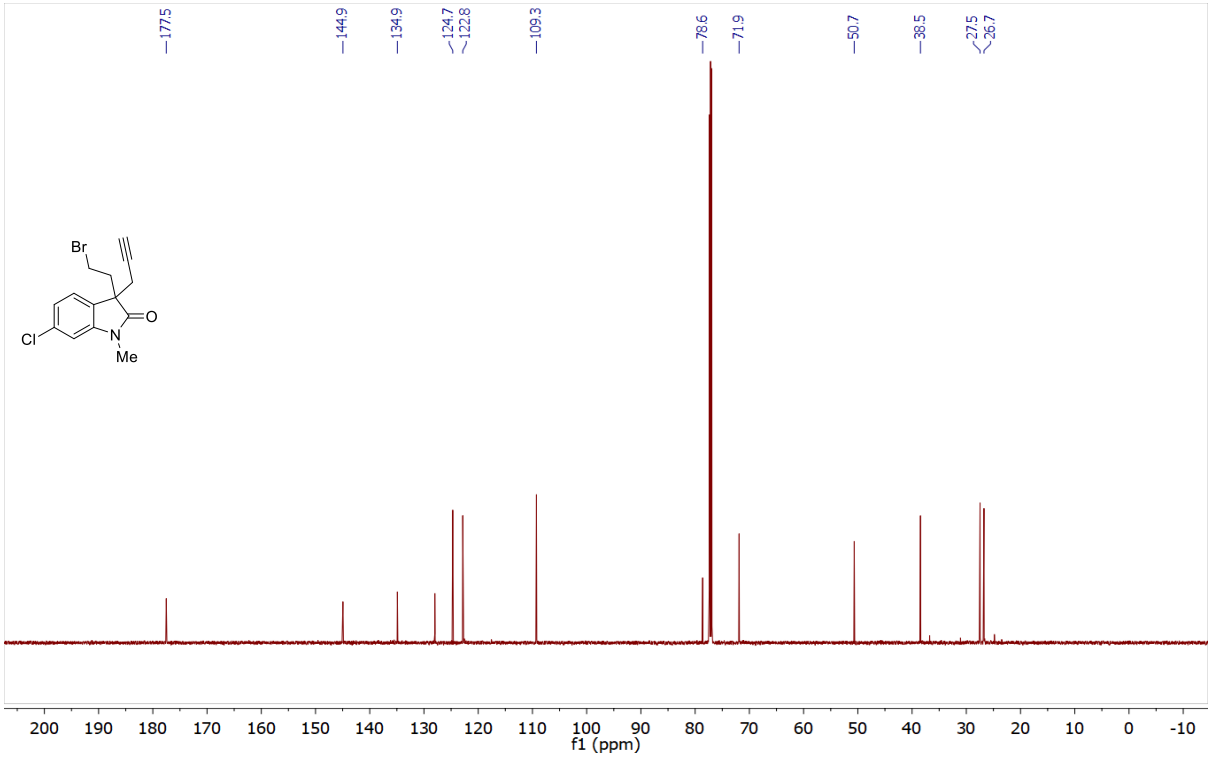
$^{13}C\{^{1}H\}$ NMR of 5i (151 MHz, $CDCl_3$):



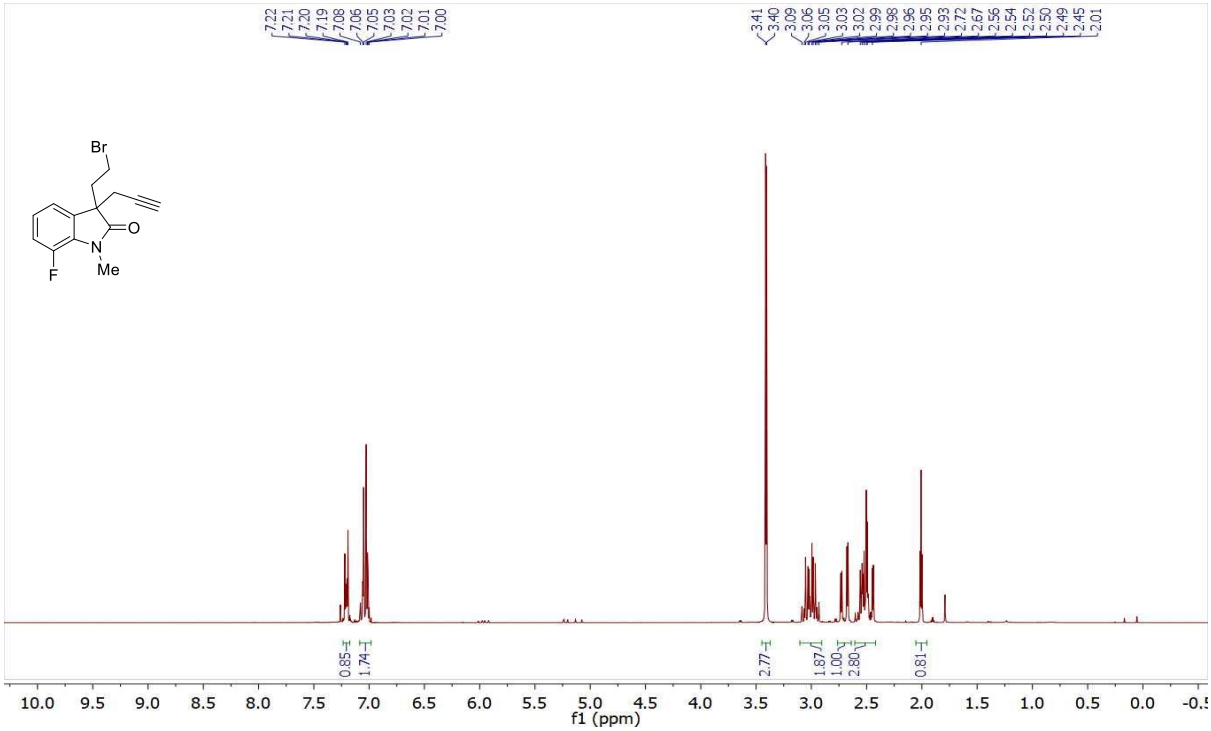
^{1}H NMR of 5j (400 MHz, $CDCl_3$):



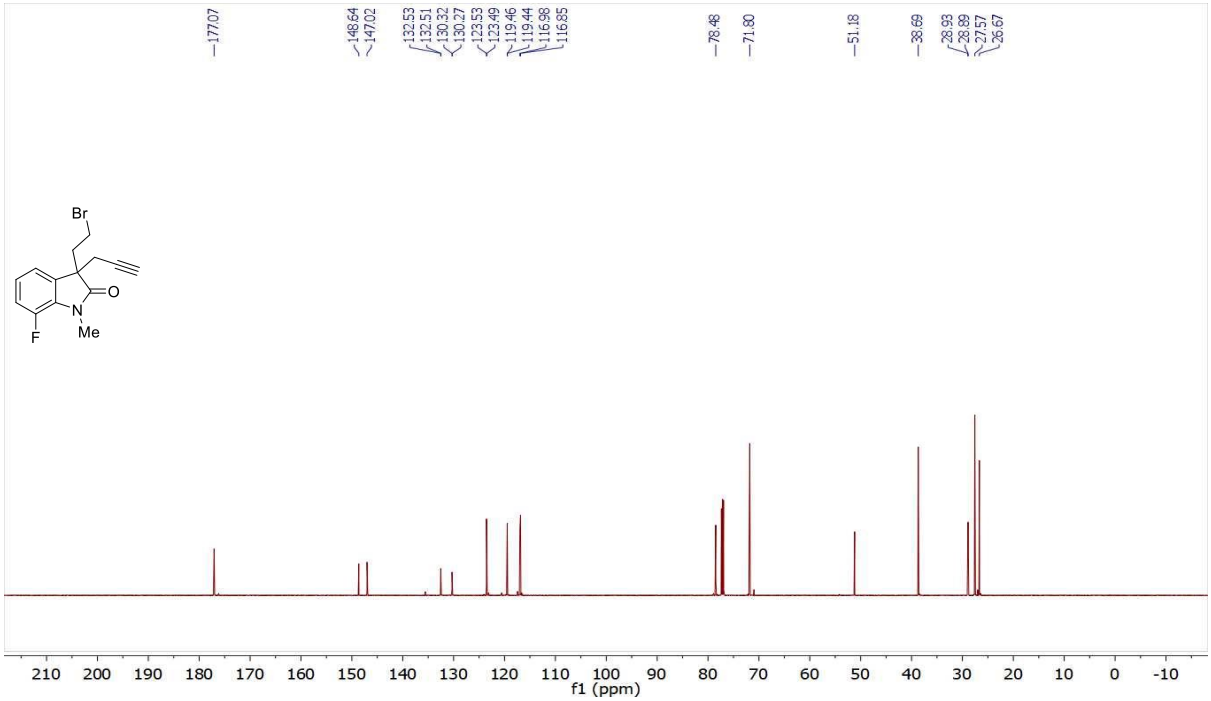
$^{13}C\{^{1}H\}$ NMR of 5j (151 MHz, $CDCl_3$):



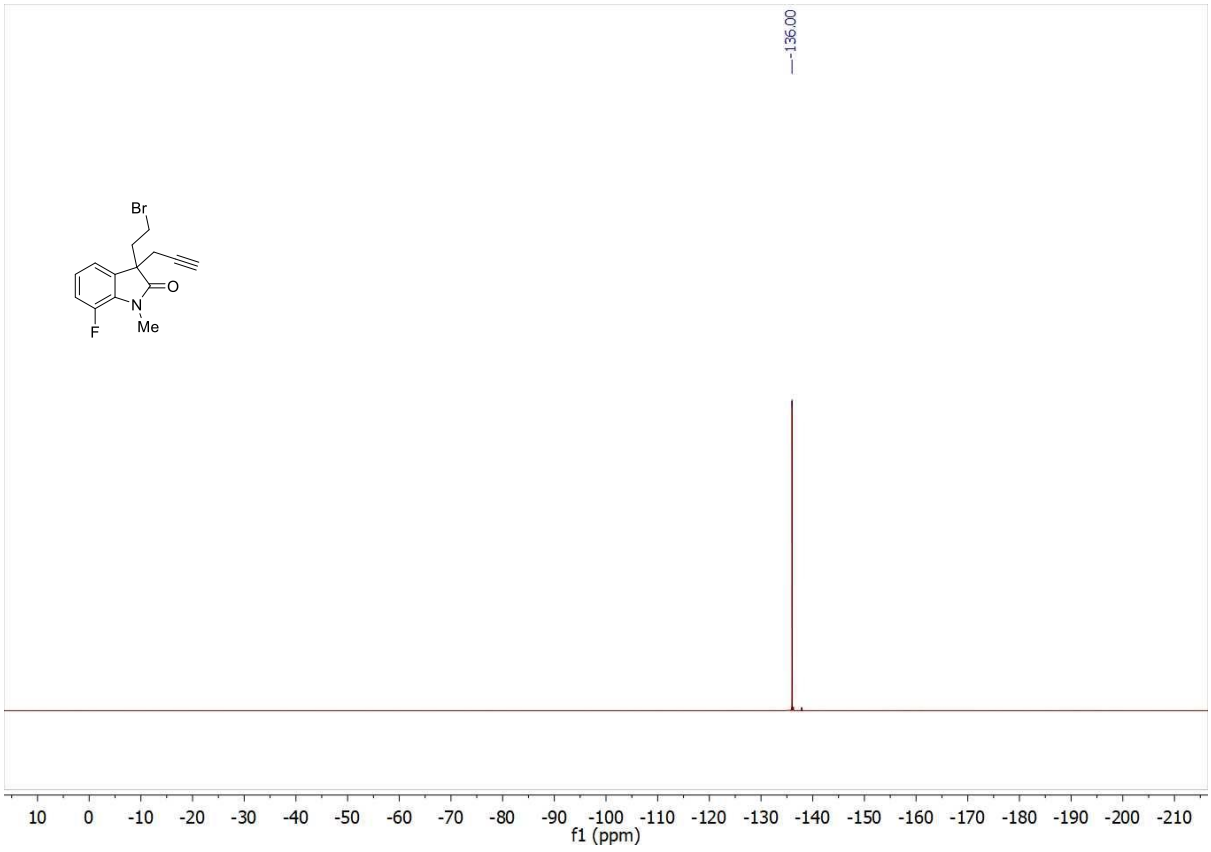
^{1}H NMR of 5k (300 MHz, $CDCl_3$):



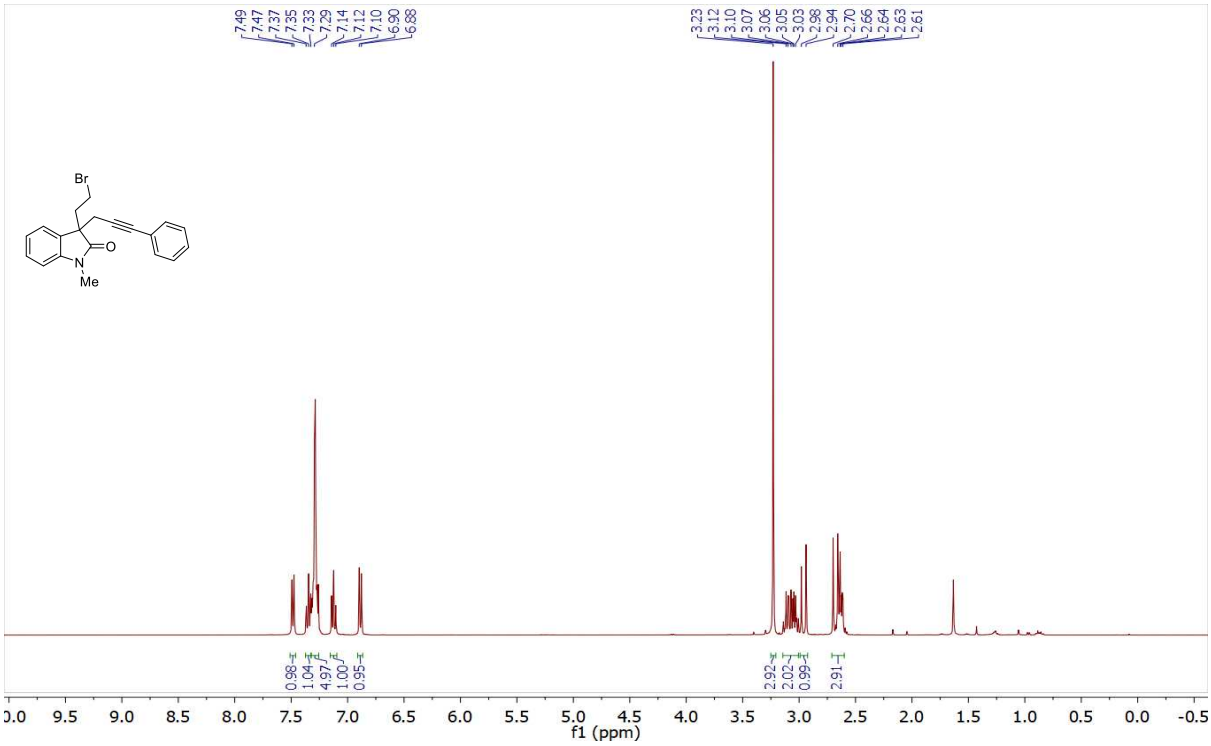
$^{13}C\{^{1}H\}$ NMR of 5k (151 MHz, $CDCl_3$):



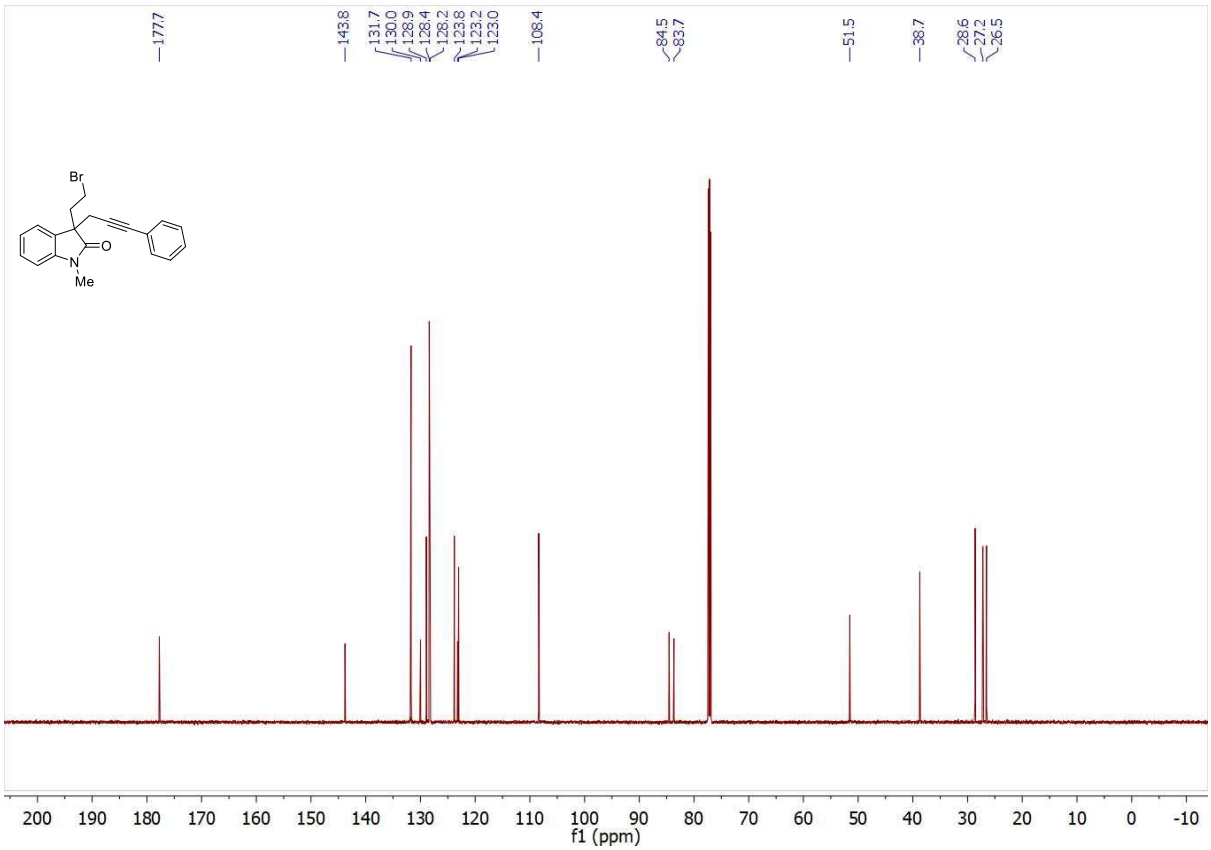
$^{19}F\{^{1}H\}$ NMR of 5k (565 MHz, $CDCl_3$):



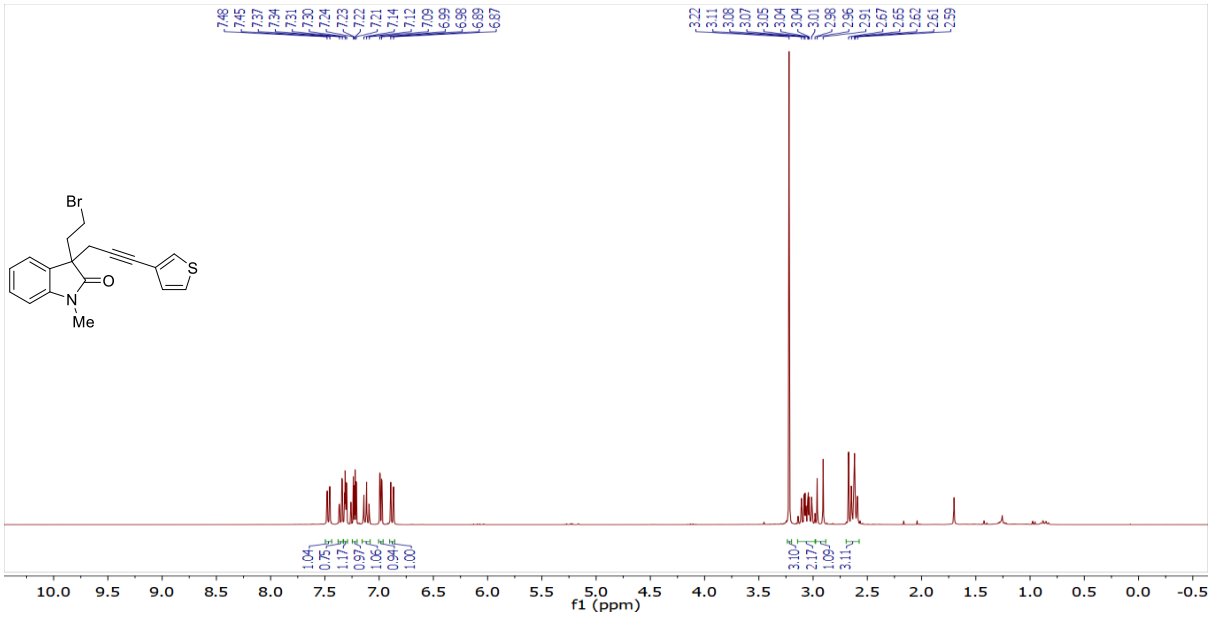
^{1}H NMR of 5l (400 MHz, $CDCl_3$):



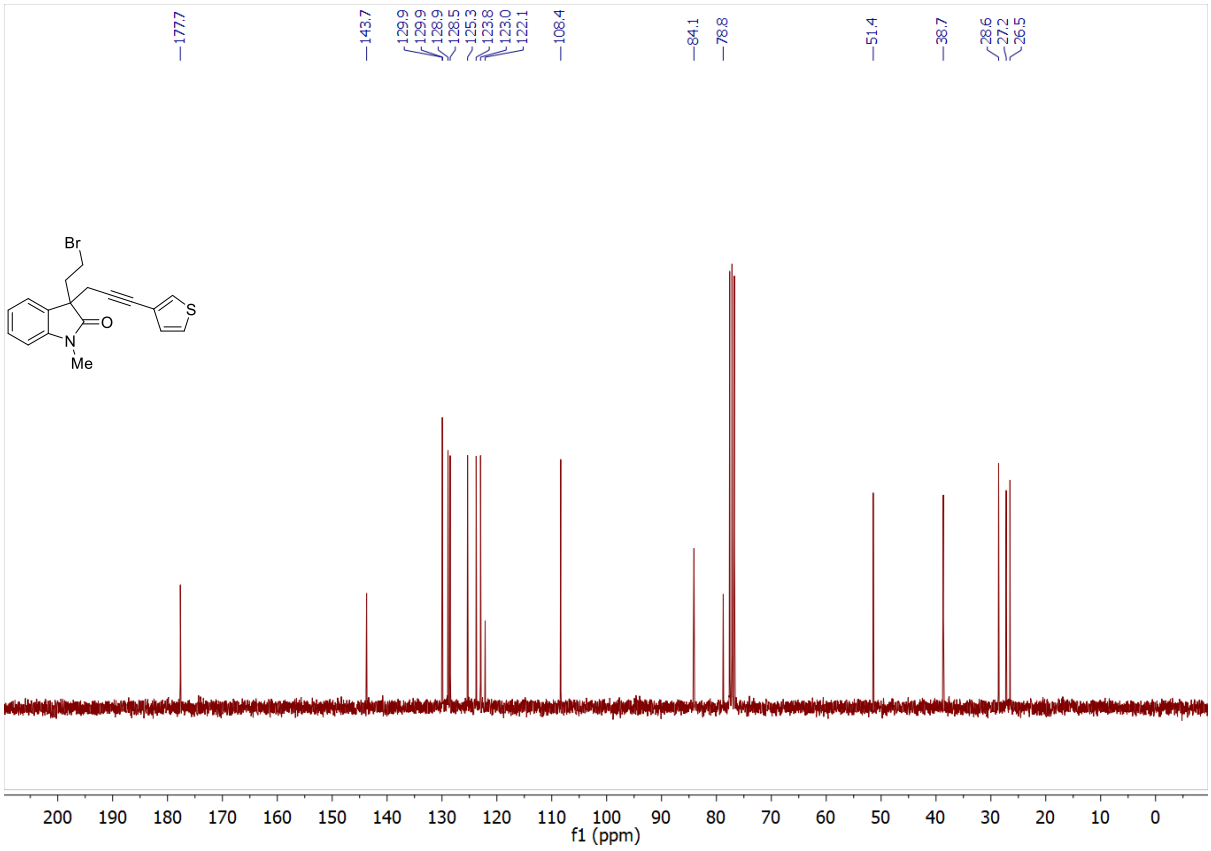
^{13}C{^{1}H} NMR of 5l (151 MHz, $CDCl_3$):



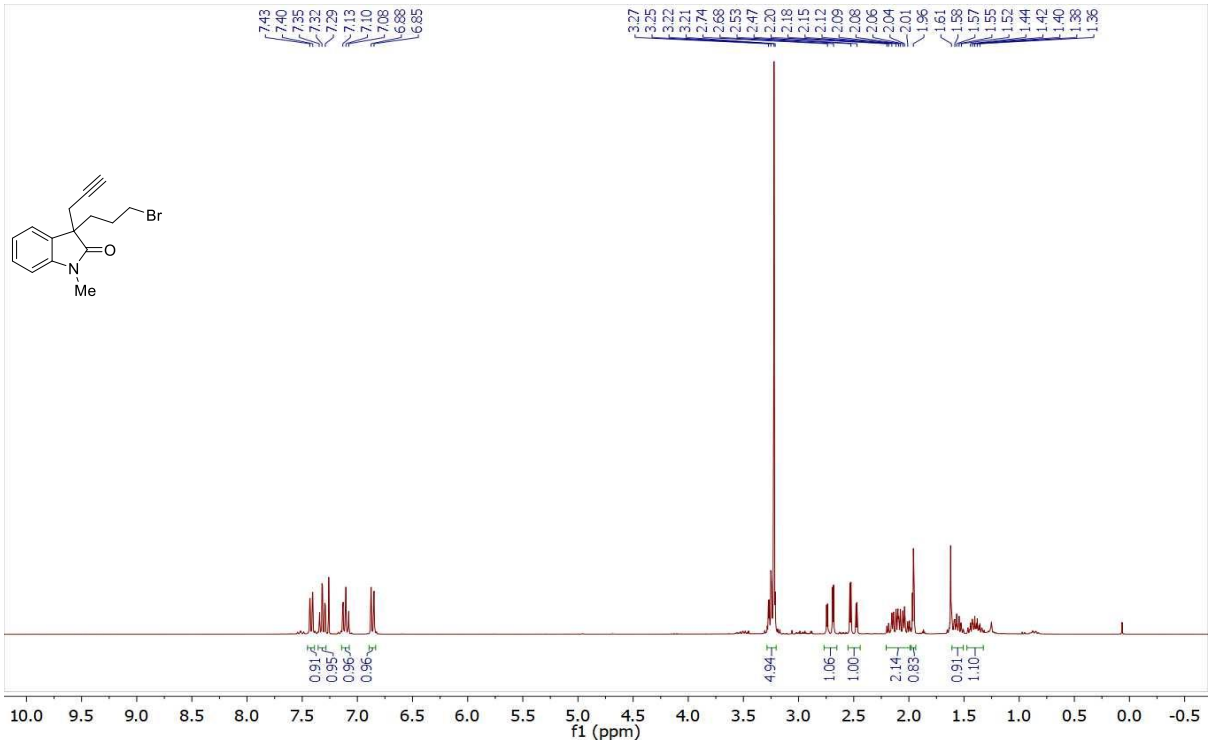
^{1}H NMR of 5m (300 MHz, $CDCl_3$):



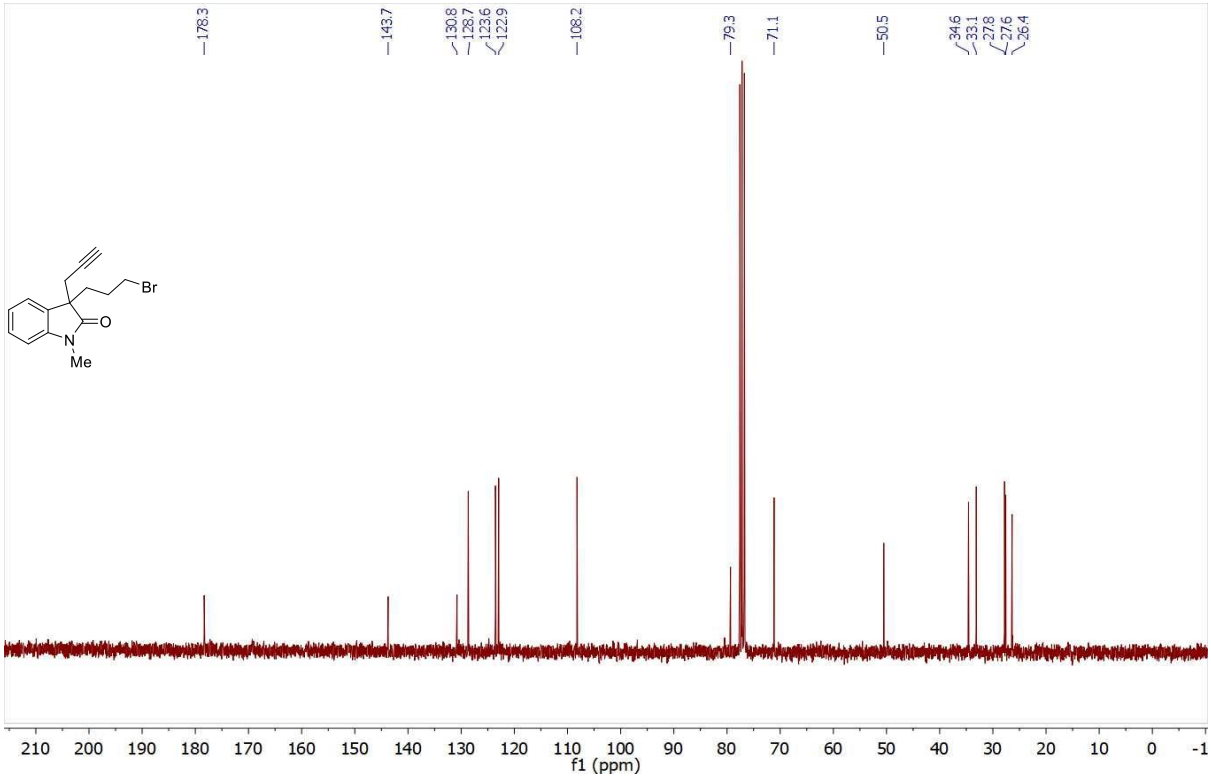
^{13}C{^{1}H} NMR of 5m (75 MHz, $CDCl_3$):



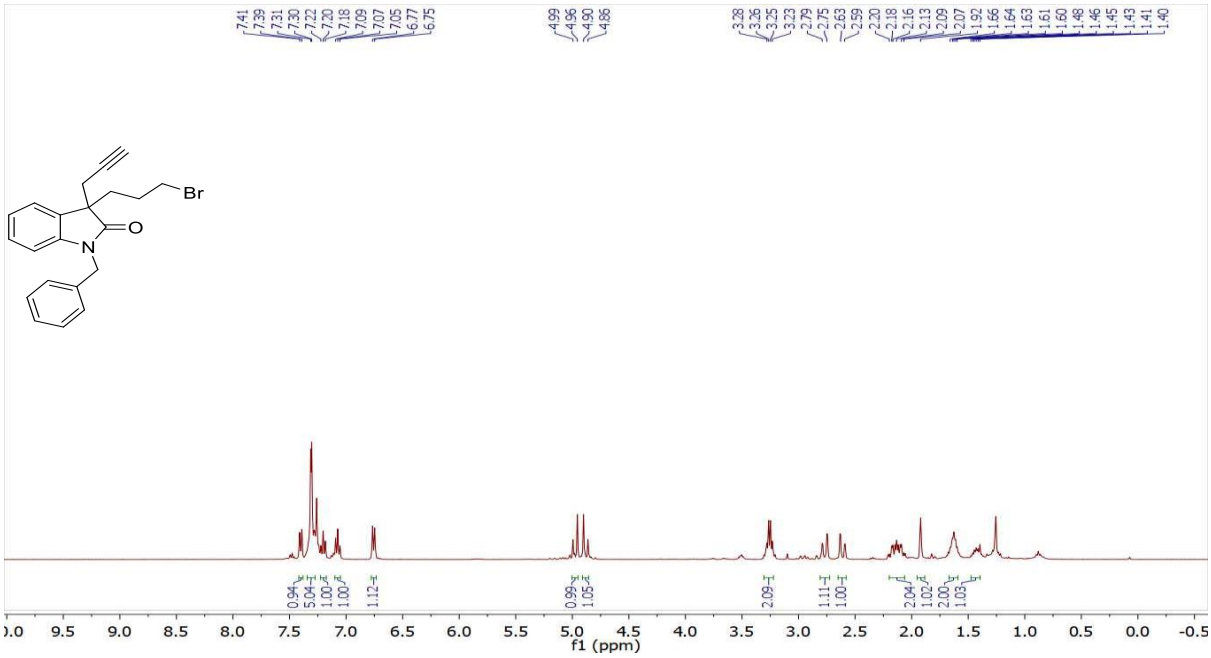
^{1}H NMR of 6a (300 MHz, $CDCl_3$):



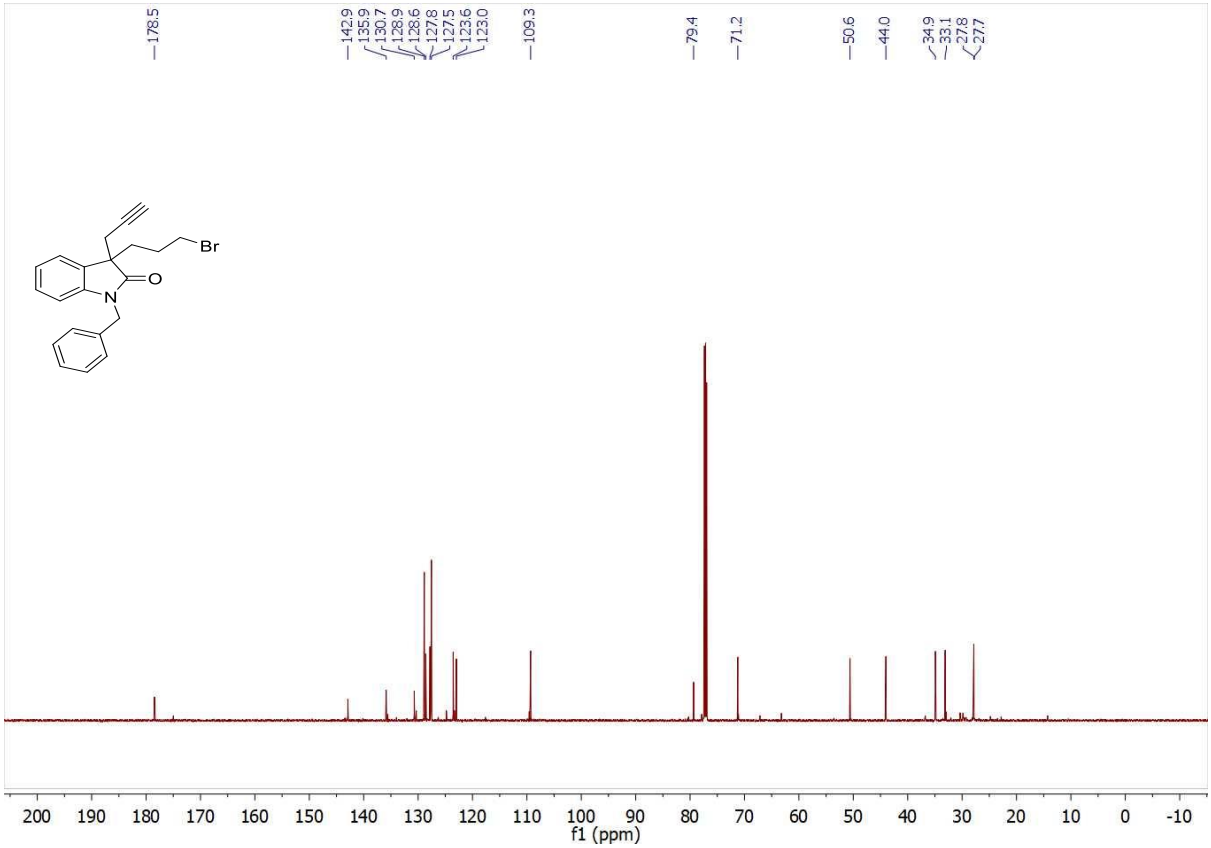
^{13}C{^{1}H} NMR of 6a (75 MHz, $CDCl_3$):



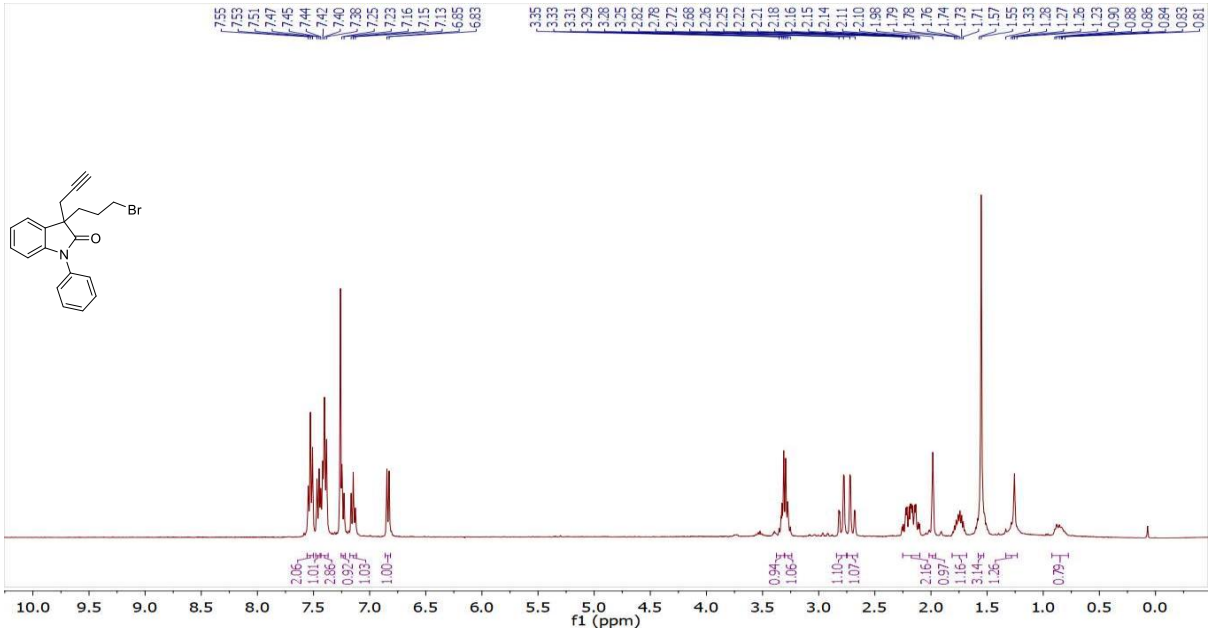
^{1}H NMR of 6b (400 MHz, $CDCl_3$):



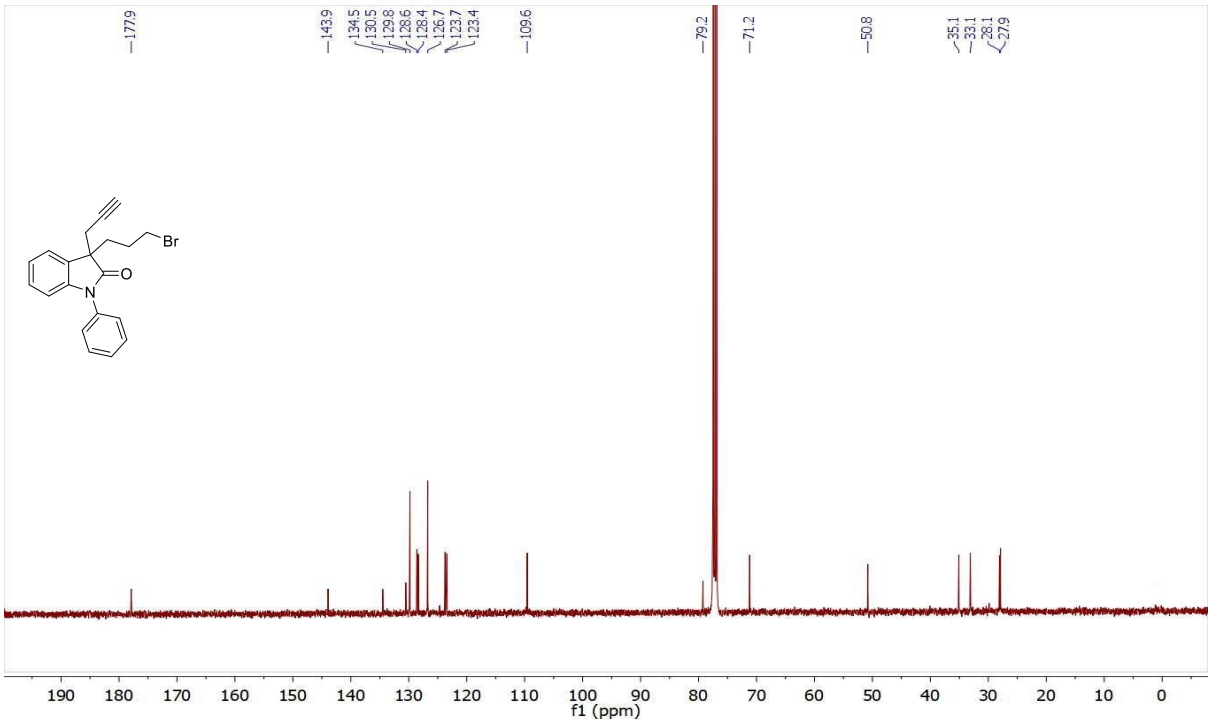
^{13}C{^{1}H} NMR of 6b (151 MHz, $CDCl_3$):



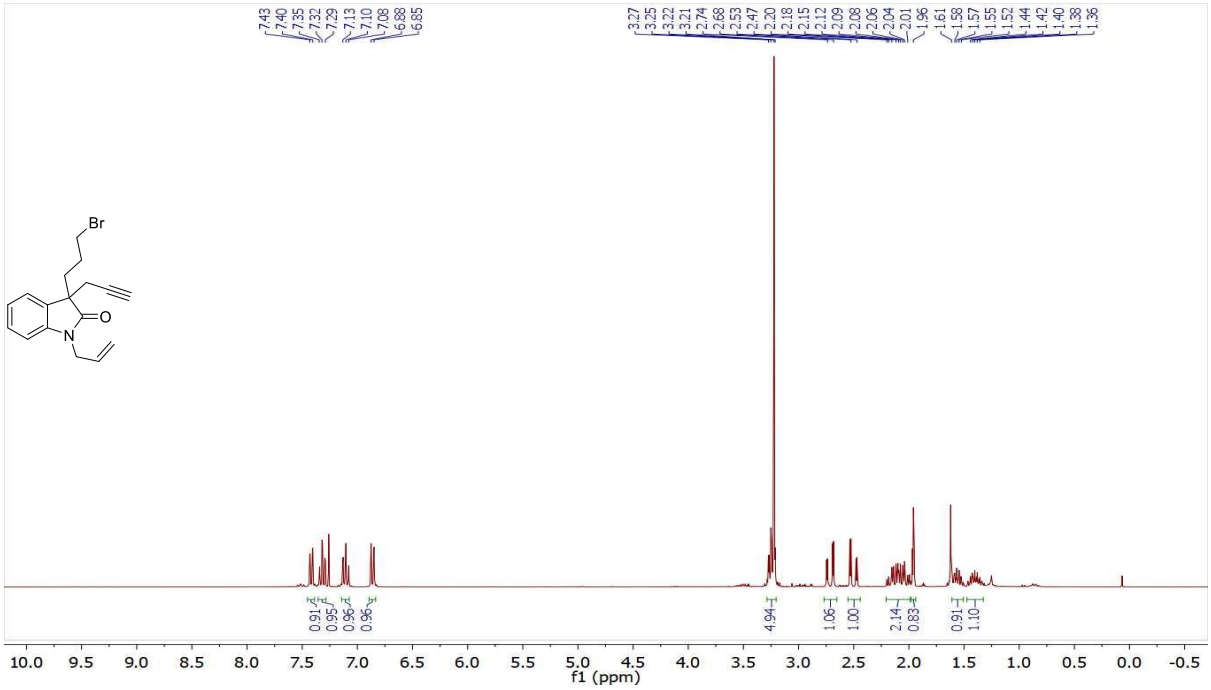
^{1}H NMR of 6c (400 MHz, $CDCl_3$):



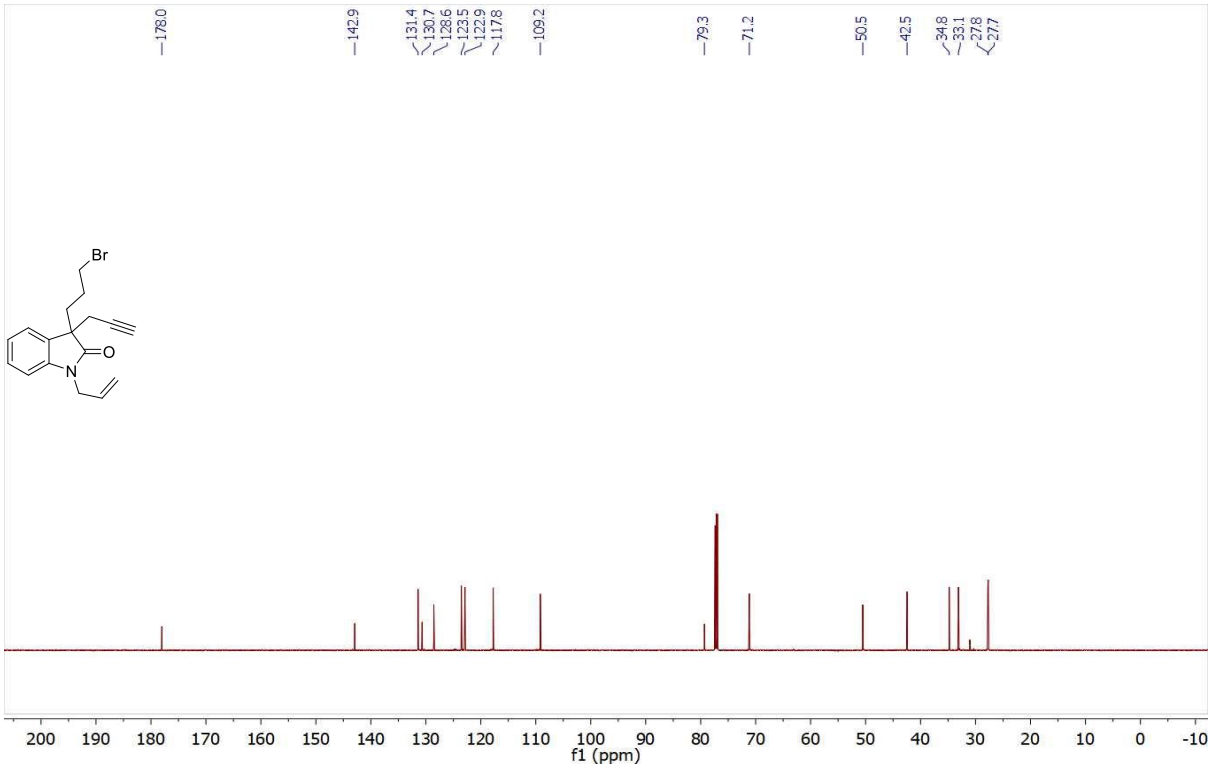
^{13}C{^{1}H} NMR of 6c (101 MHz, $CDCl_3$):



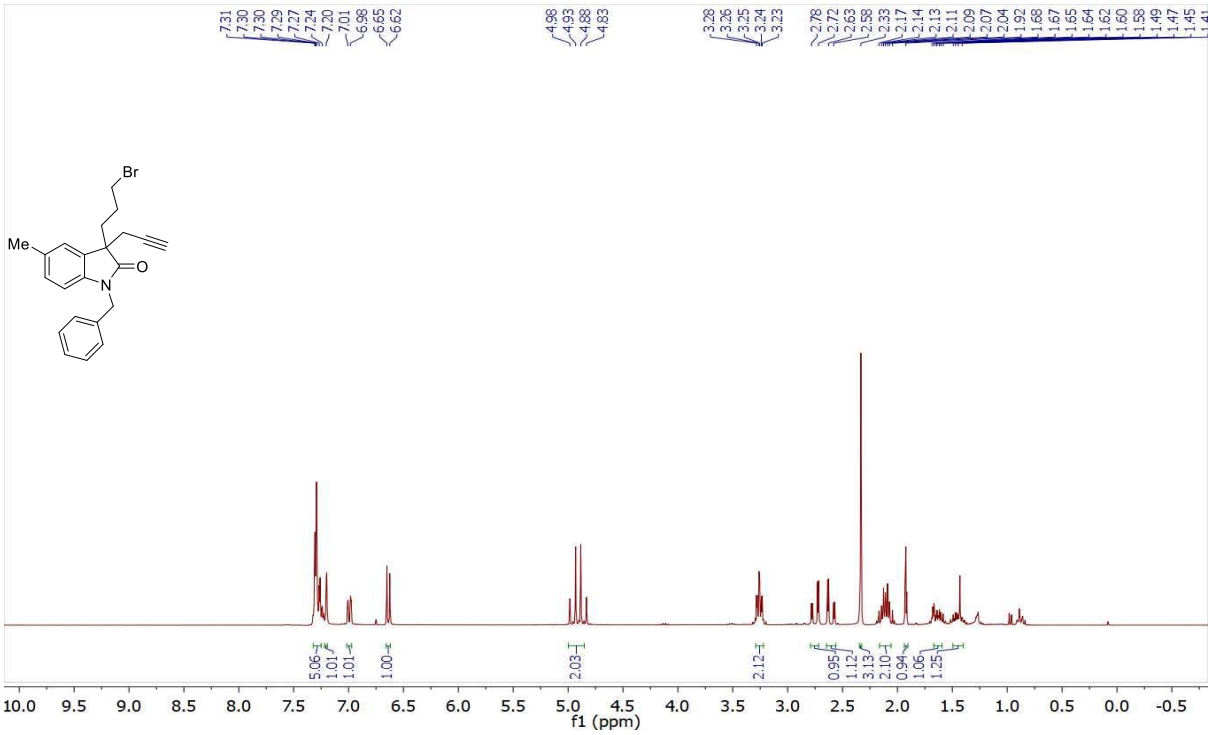
^{1}H NMR of 6d (400 MHz, $CDCl_3$):



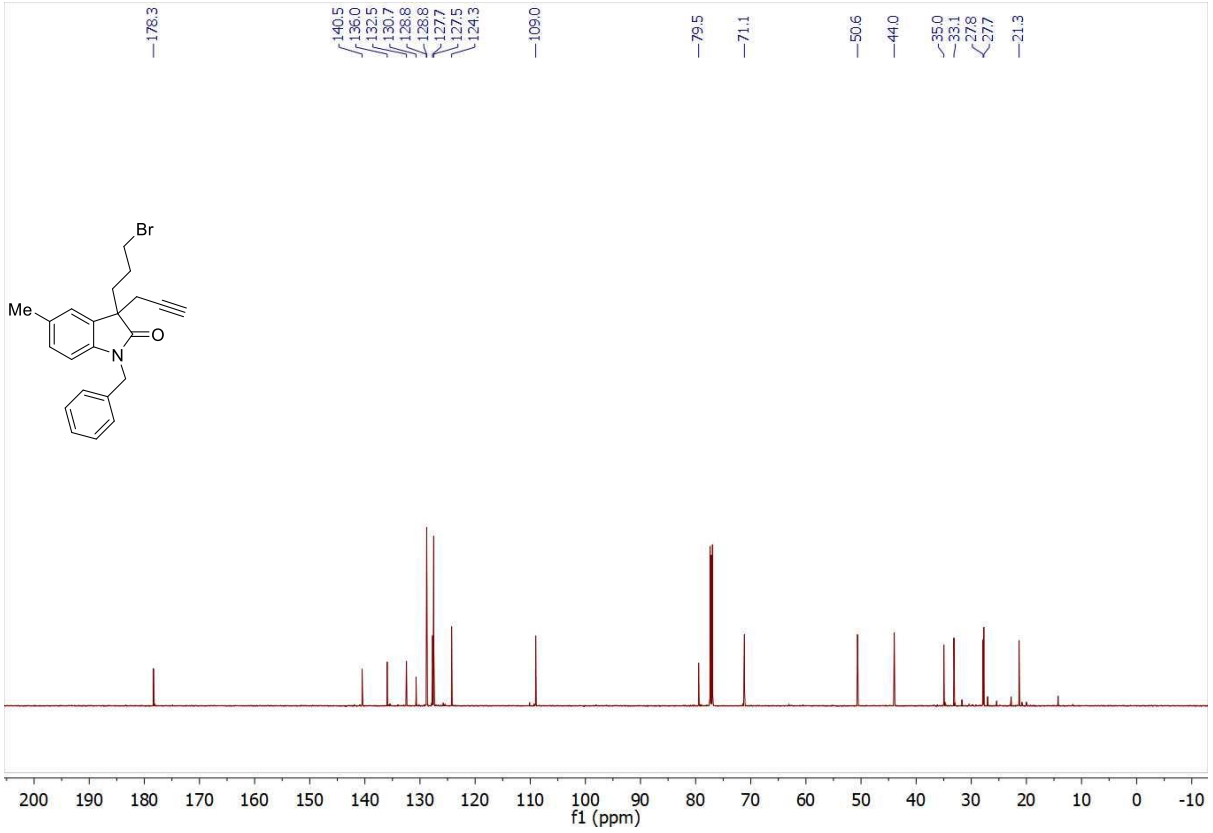
^{13}C{^{1}H} NMR of 6d (151 MHz, $CDCl_3$):



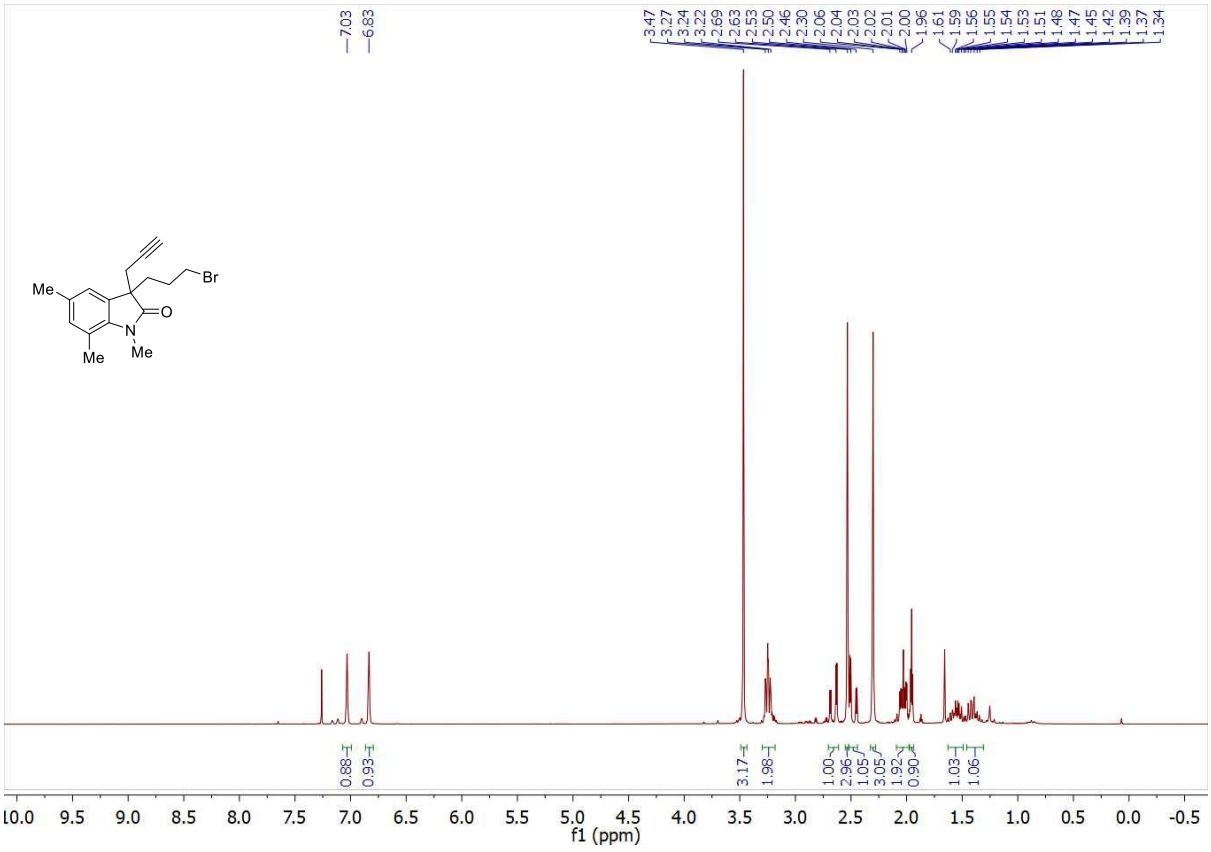
^{1}H NMR of 6e (300 MHz, $CDCl_3$):



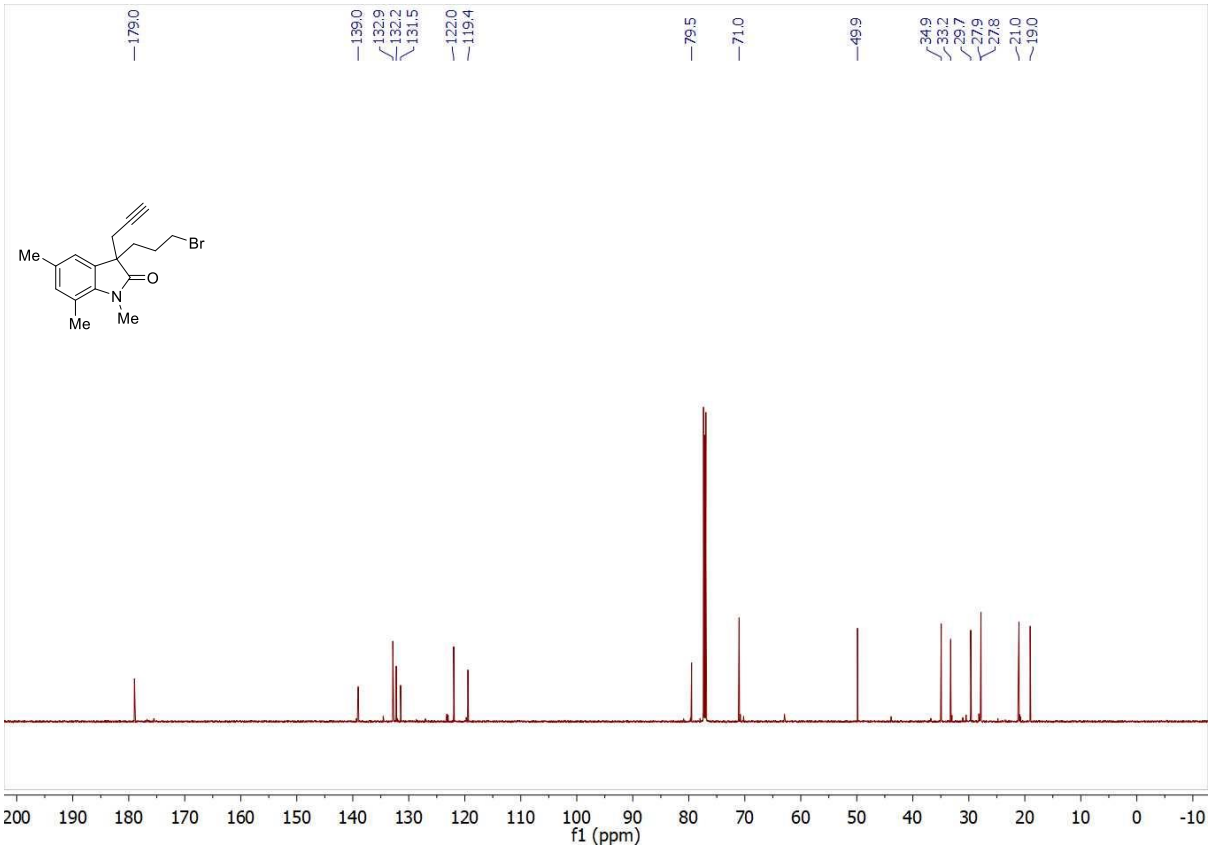
^{13}C{^{1}H} NMR of 6e (151 MHz, $CDCl_3$):



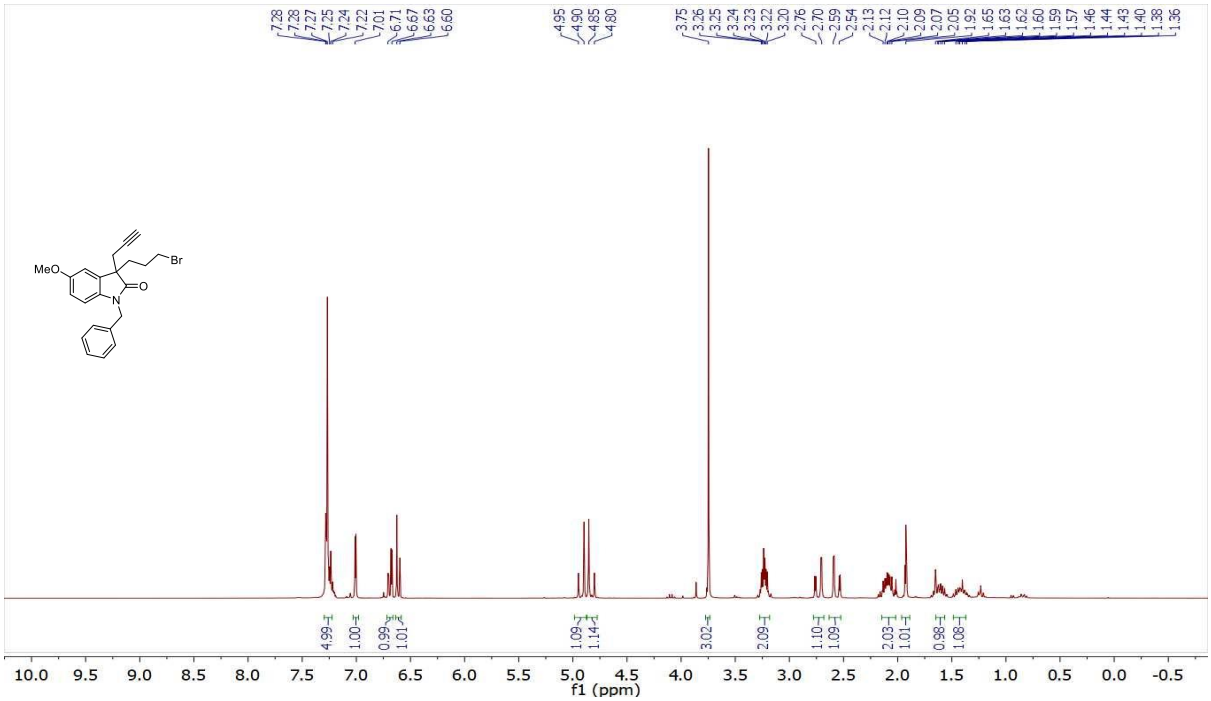
^{1}H NMR of 6f (300 MHz, $CDCl_3$):



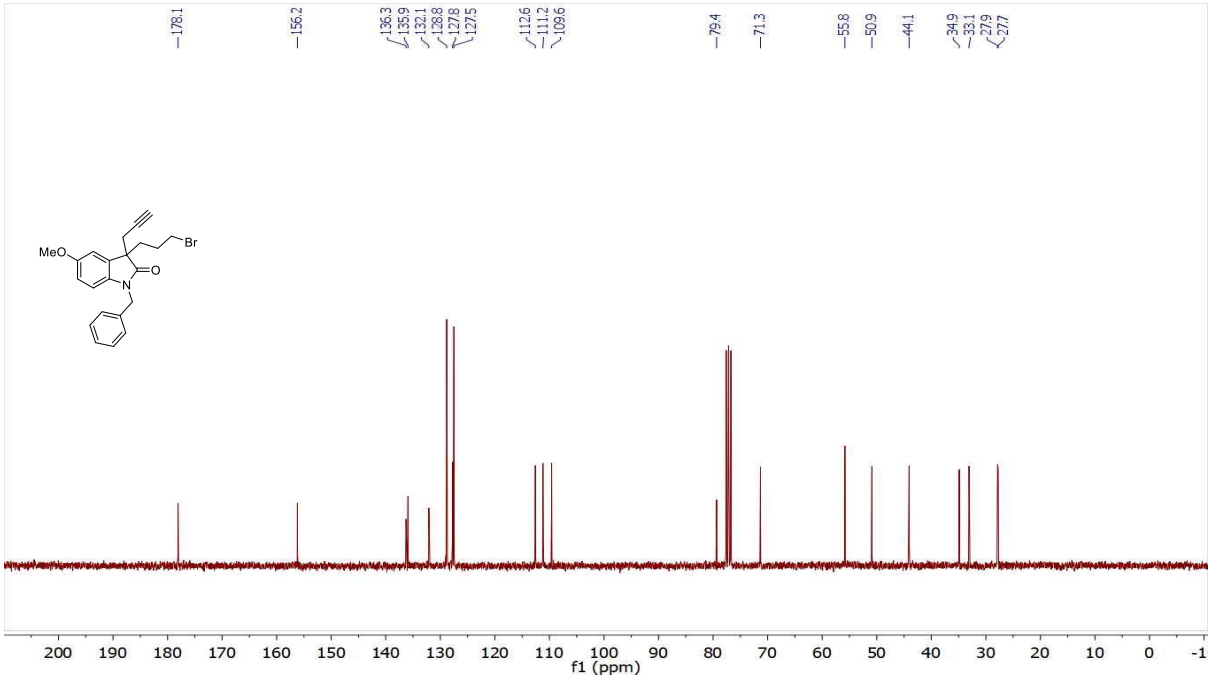
^{13}C{^{1}H} NMR of 6f (151 MHz, $CDCl_3$):



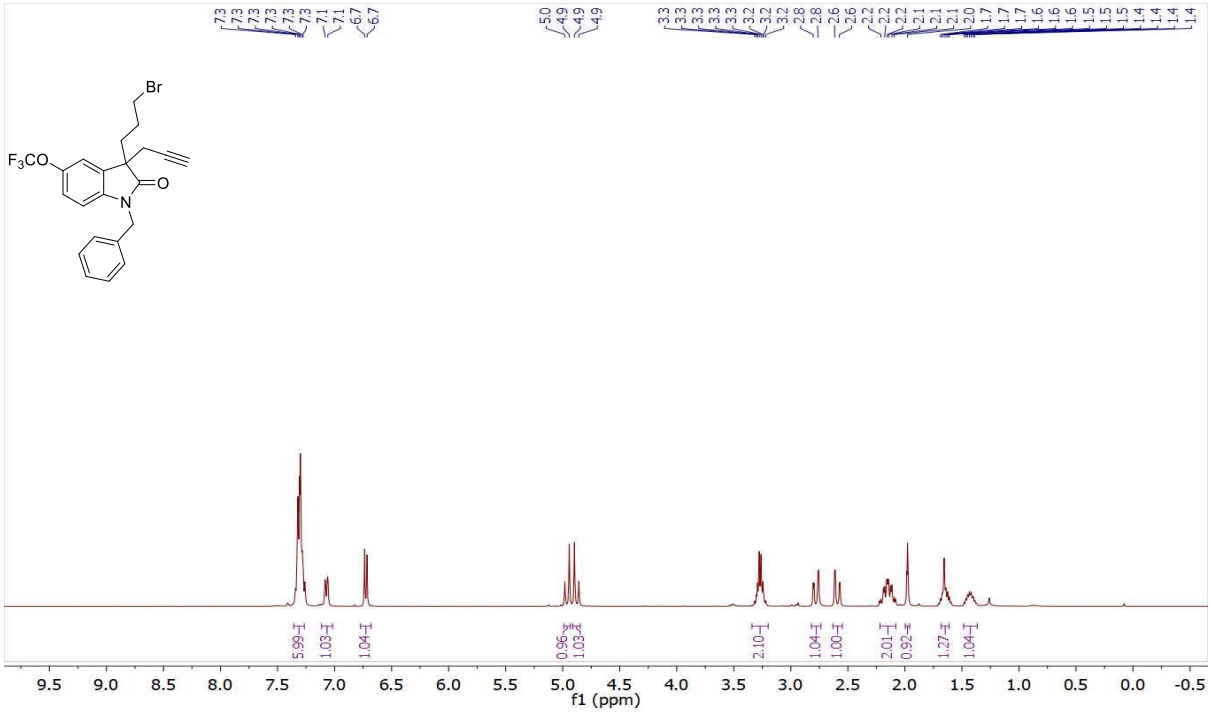
^{1}H NMR of 6g (300 MHz, $CDCl_3$):



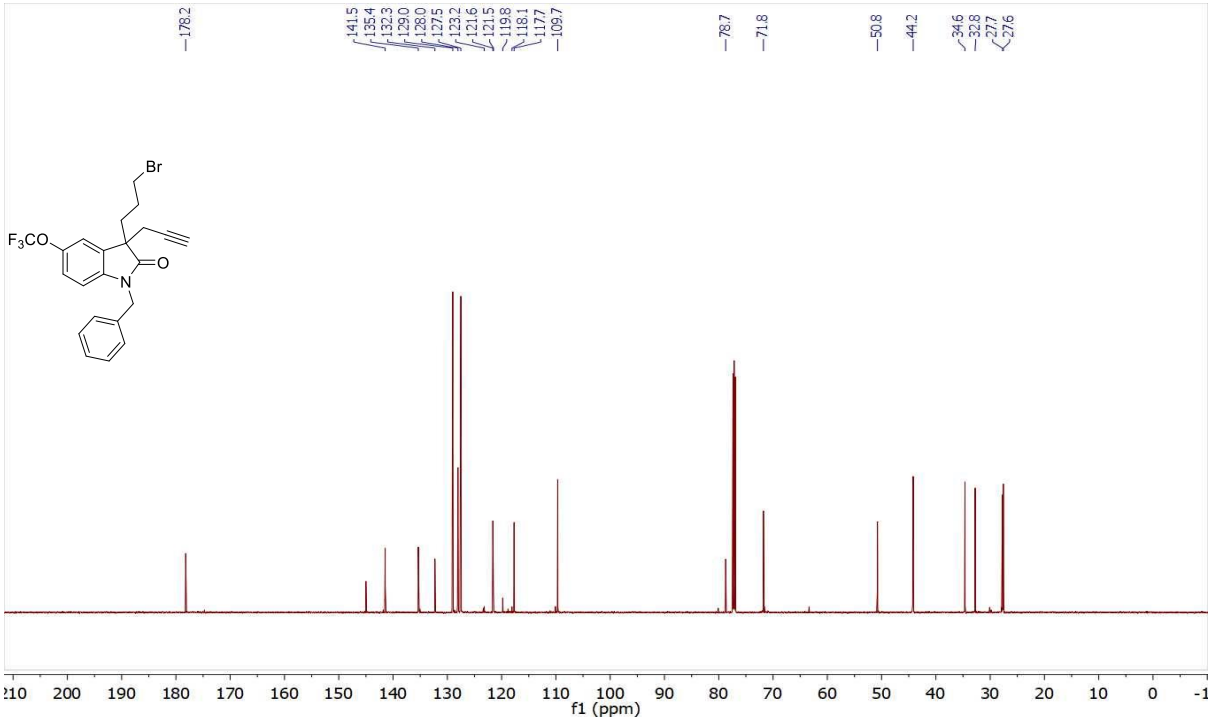
^{13}C{^{1}H} NMR of 6g (75 MHz, $CDCl_3$):



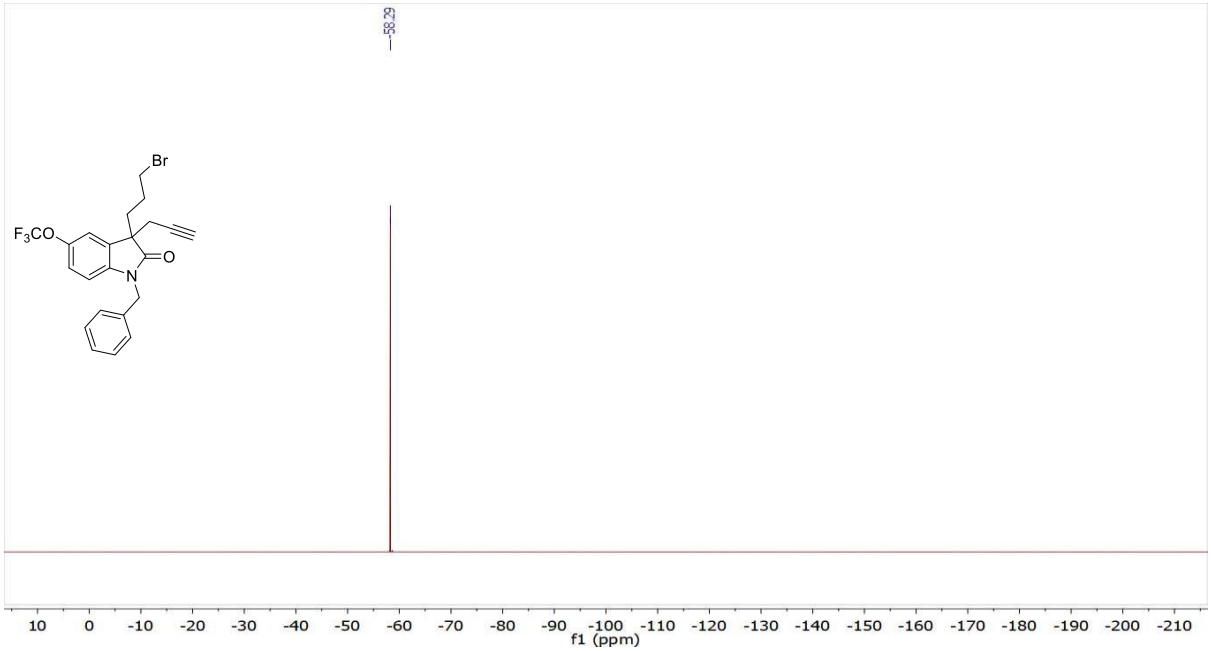
^{1}H NMR of 6h (400 MHz, $CDCl_3$):



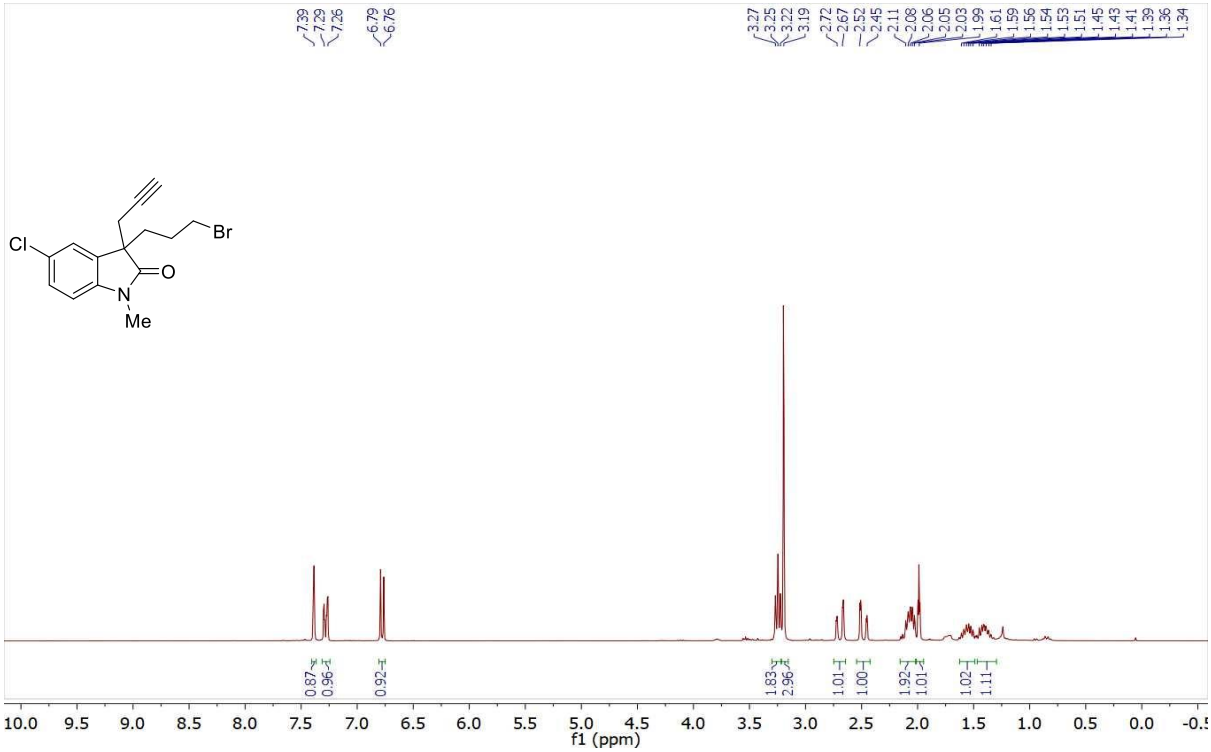
^{13}C{^{1}H} NMR of 6h (151 MHz, $CDCl_3$):



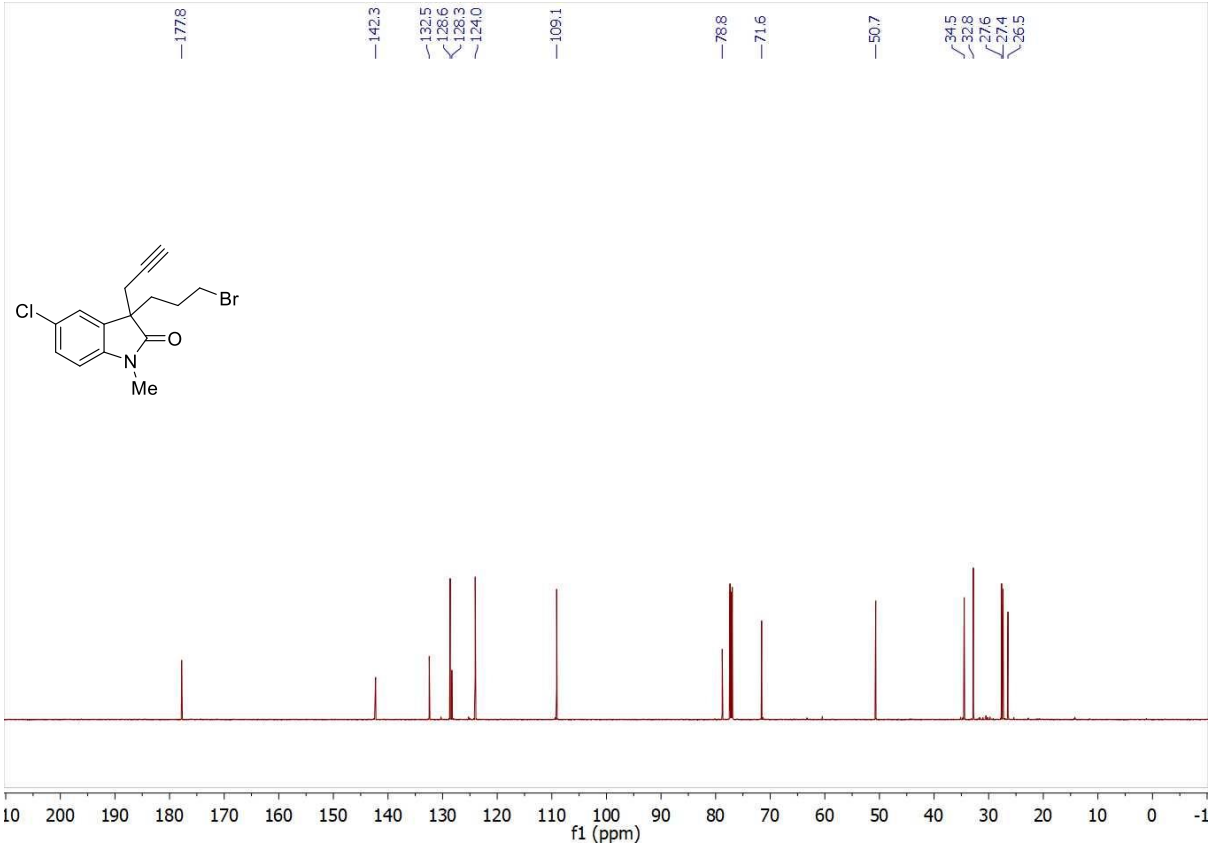
^{19}F NMR of 6h (565 MHz, $CDCl_3$):



^{1}H NMR of 6i (300 MHz, $CDCl_3$):



$^{13}C\{^{1}H\}$ NMR of 6i (151 MHz, $CDCl_3$):



^{1}H NMR of 6j (400 MHz, $CDCl_3$):

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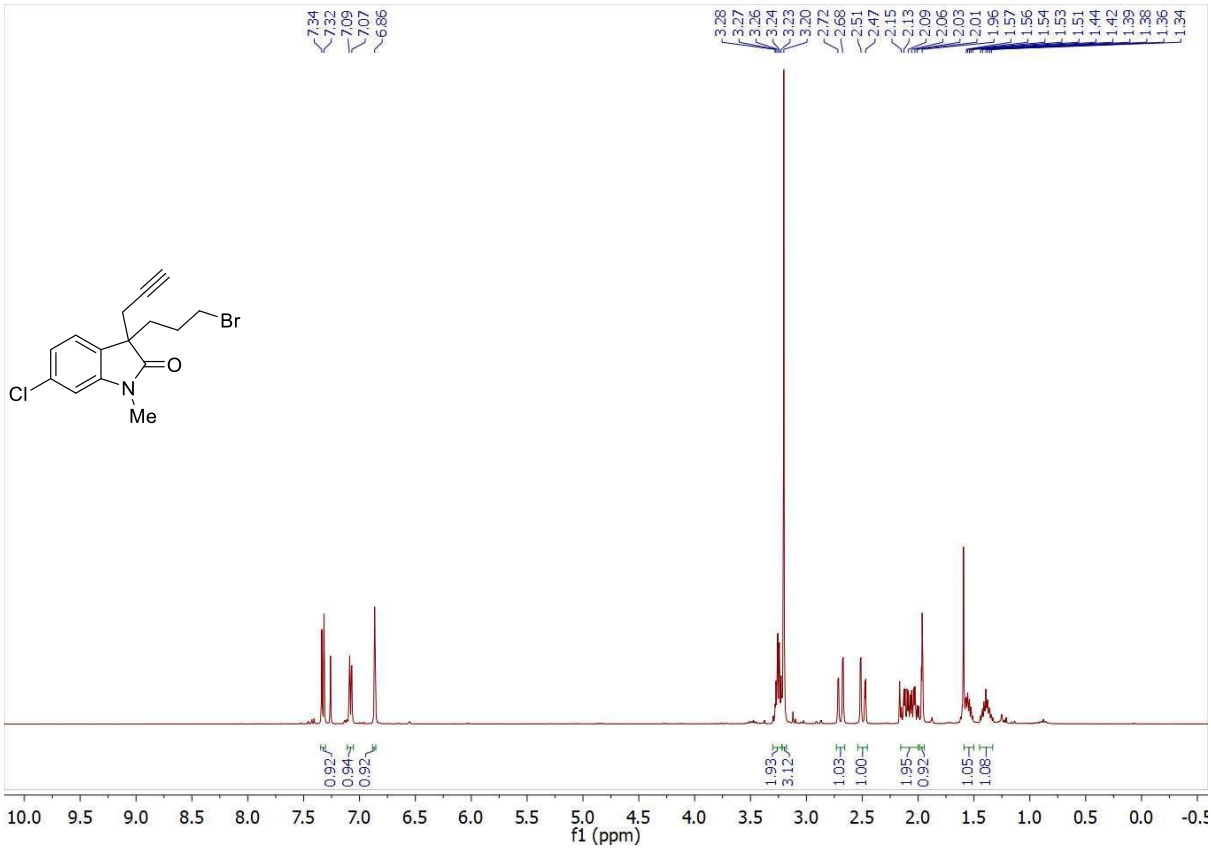
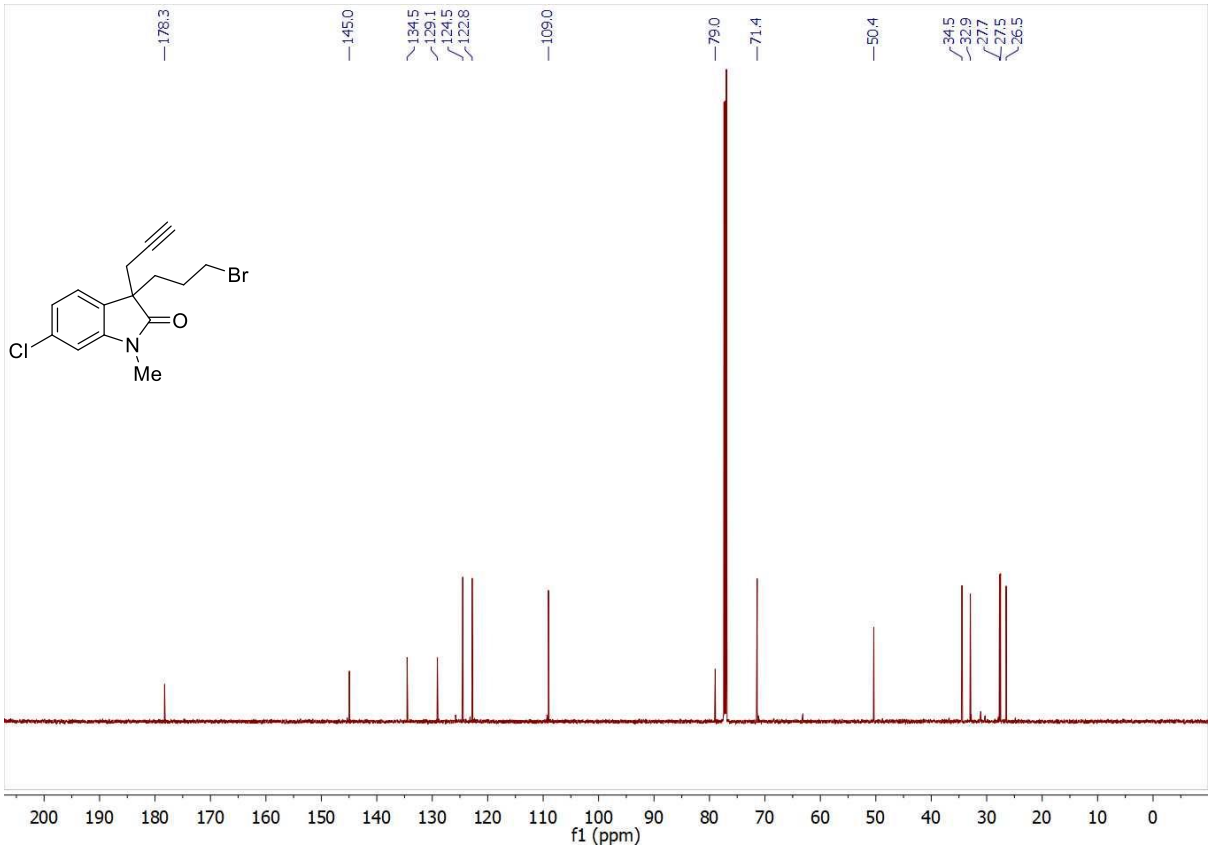
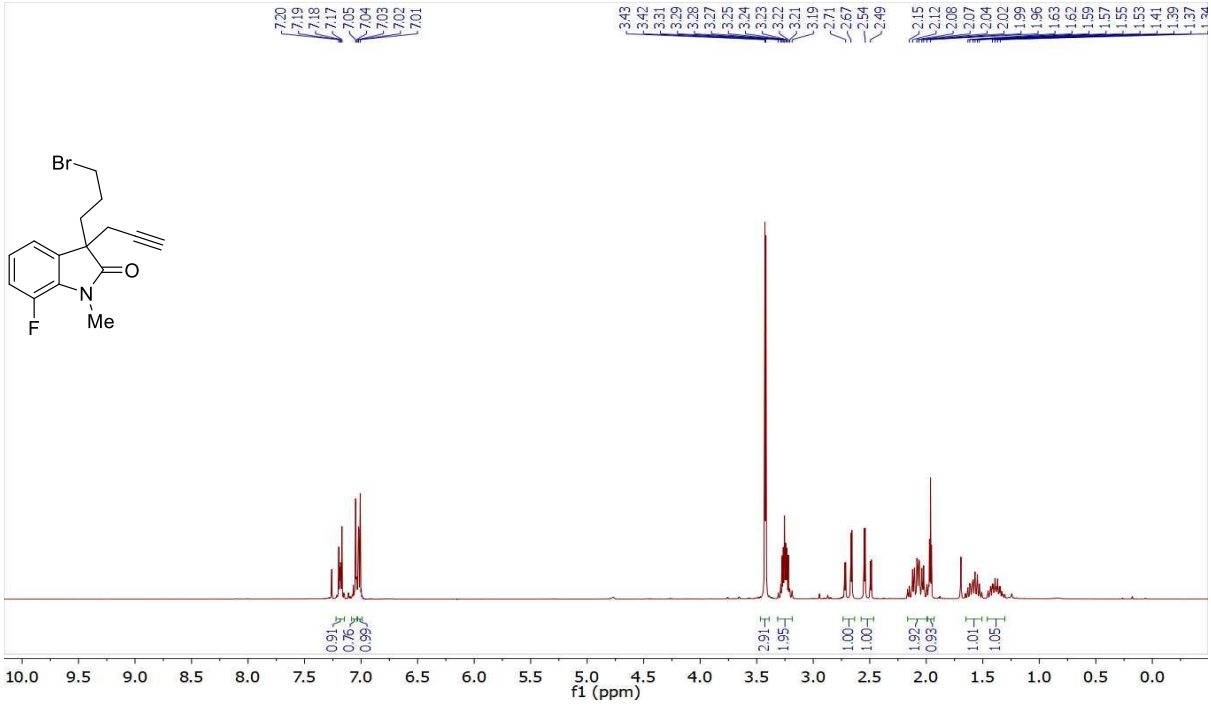


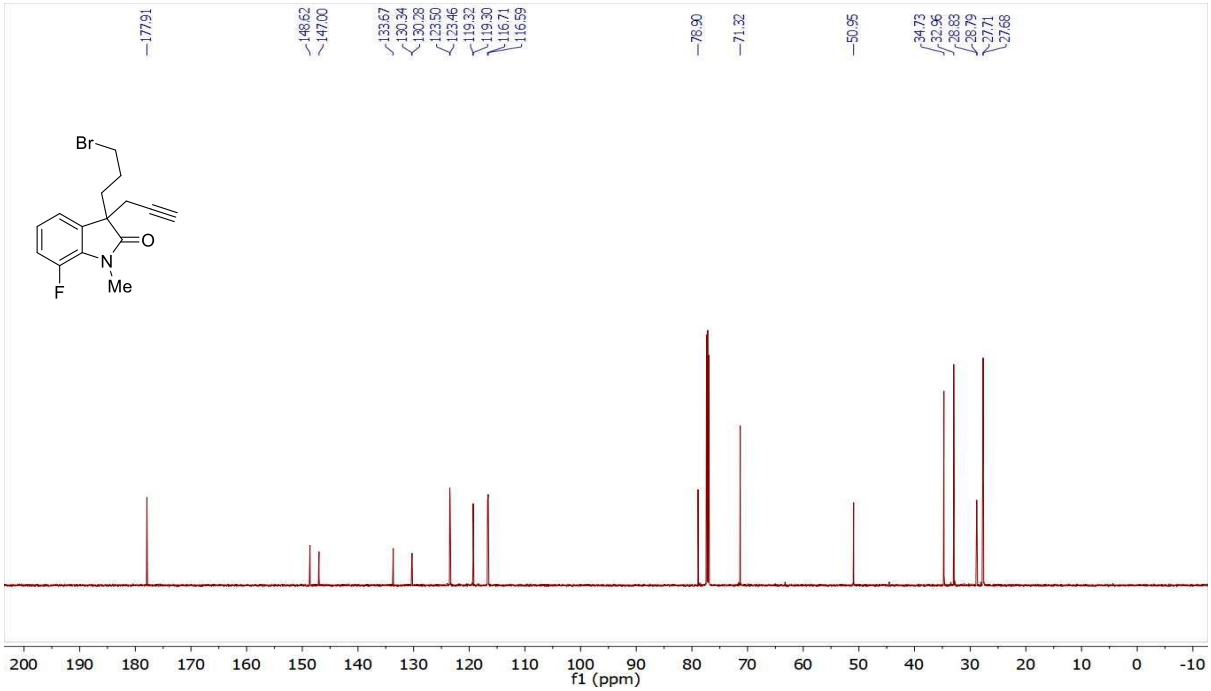
$^{13}C\{^{1}H\}$ NMR of 6j (151 MHz, $CDCl_3$):



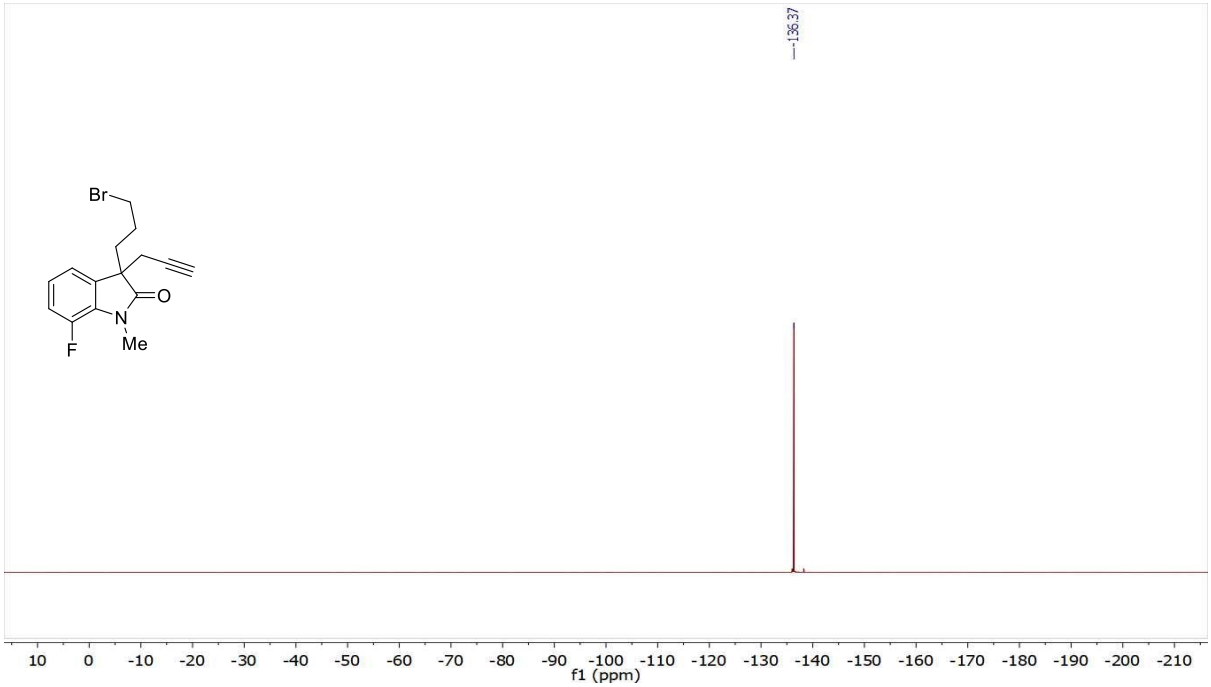
^{1}H NMR of 6k (300 MHz, $CDCl_3$):



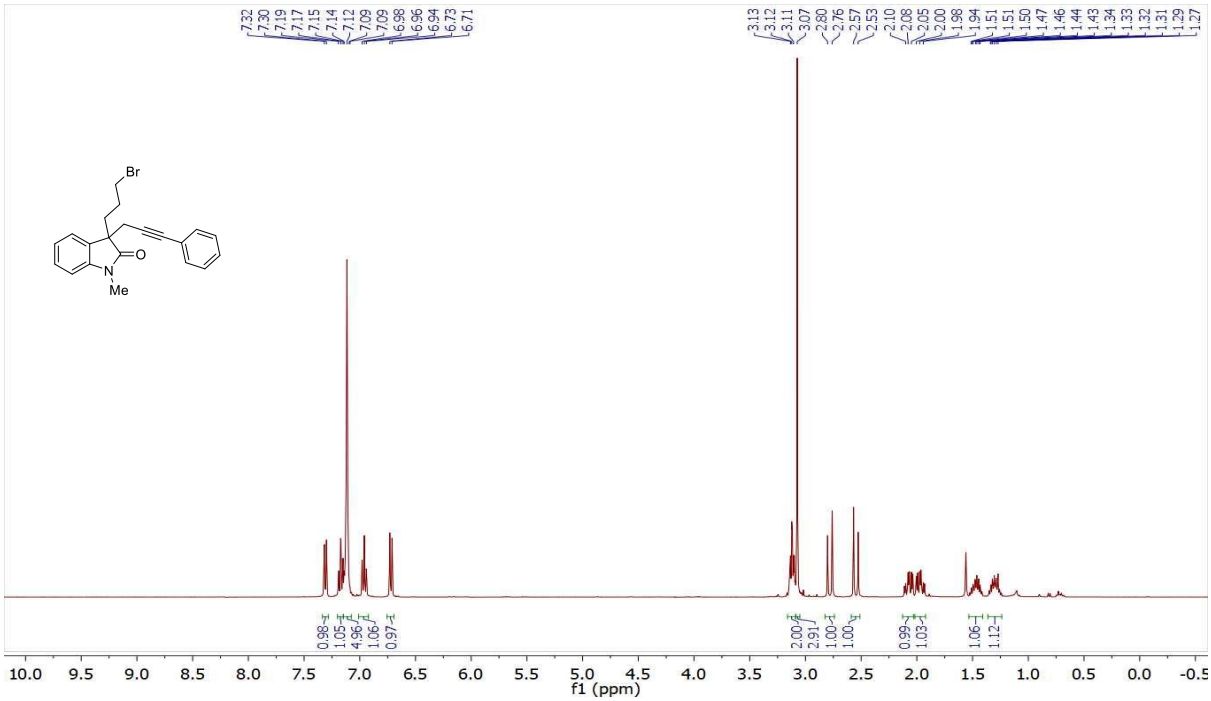
$^{13}C\{^{1}H\}$ NMR of 6k (151 MHz, $CDCl_3$):



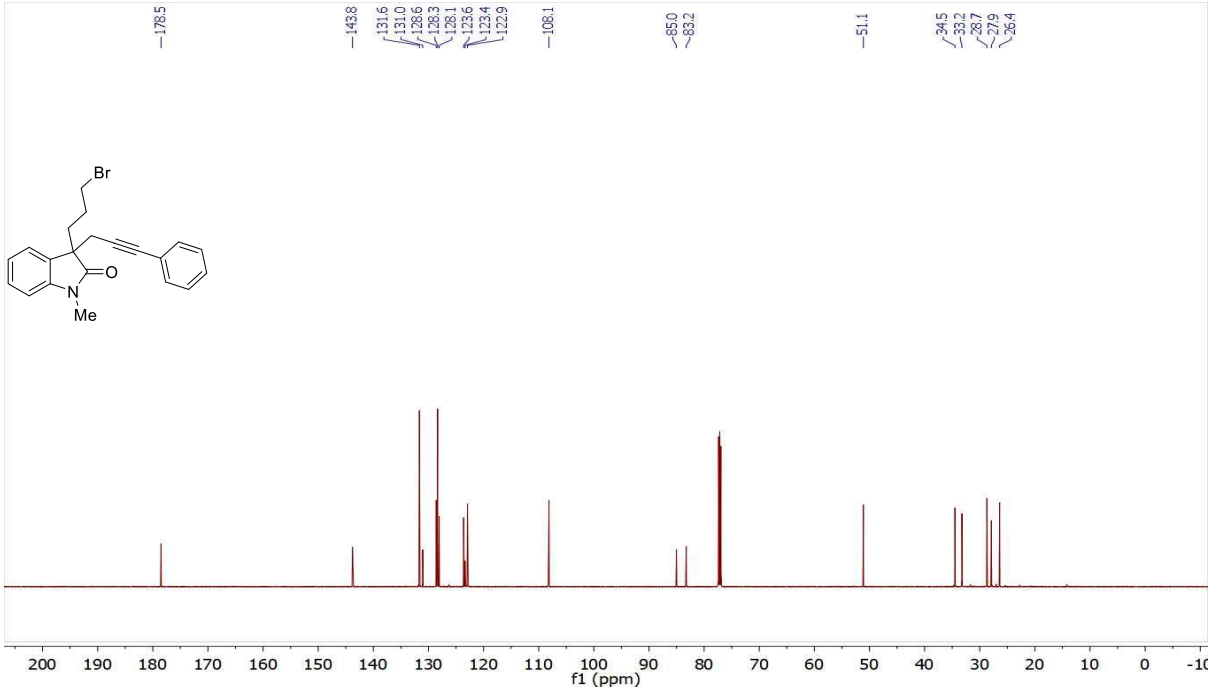
$^{19}F\{^{1}H\}$ NMR of 6k (565 MHz, $CDCl_3$):



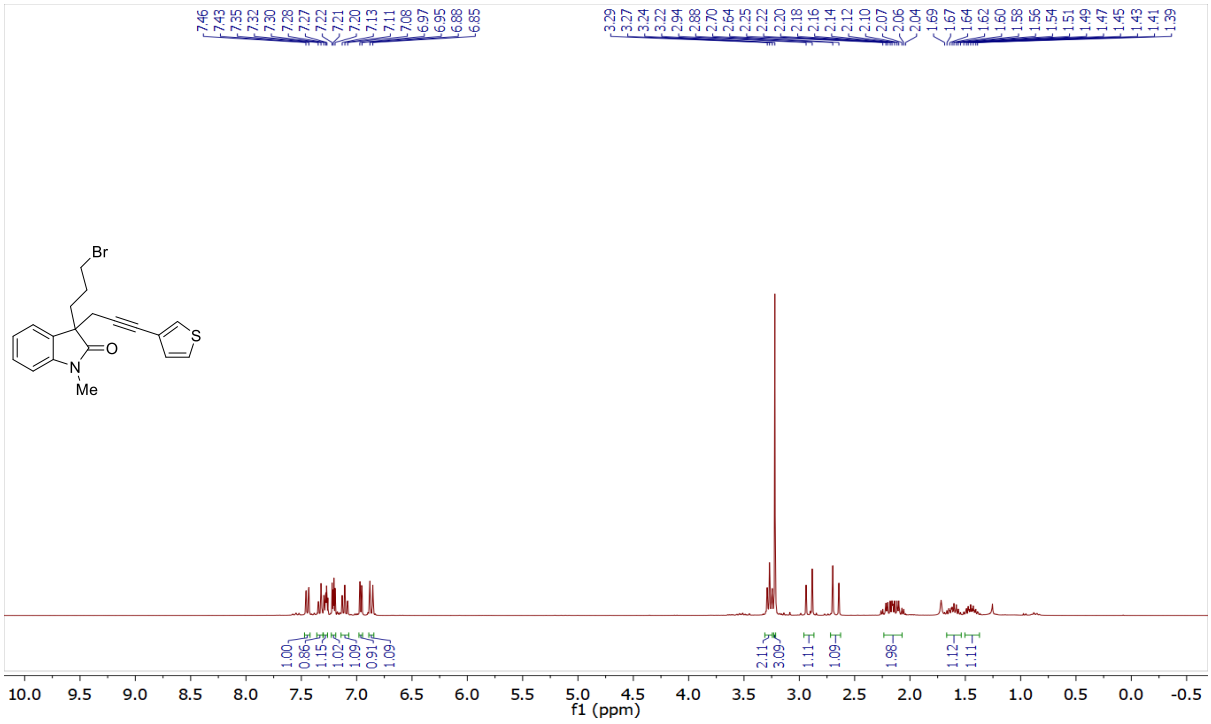
^{1}H NMR of 6l (400 MHz, $CDCl_3$):



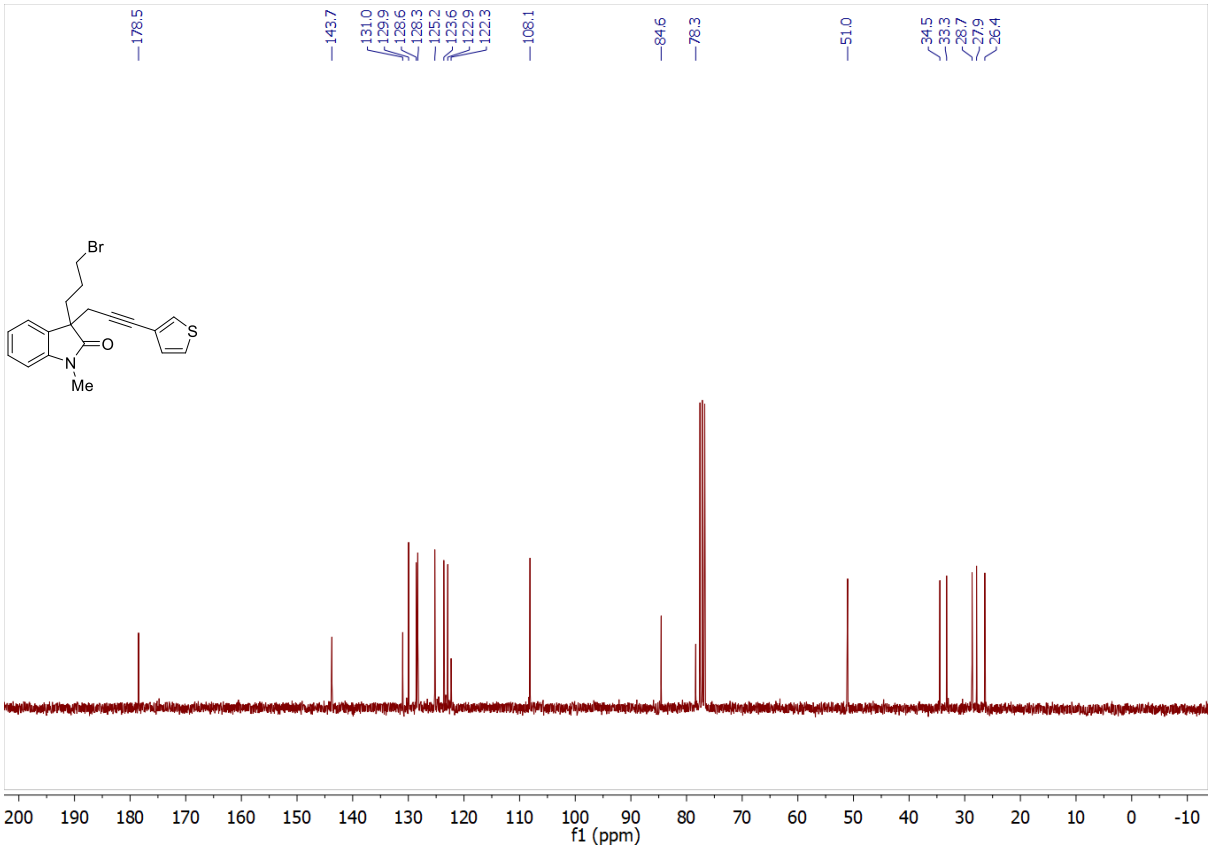
^{13}C{^{1}H} NMR of 6l (151 MHz, $CDCl_3$):



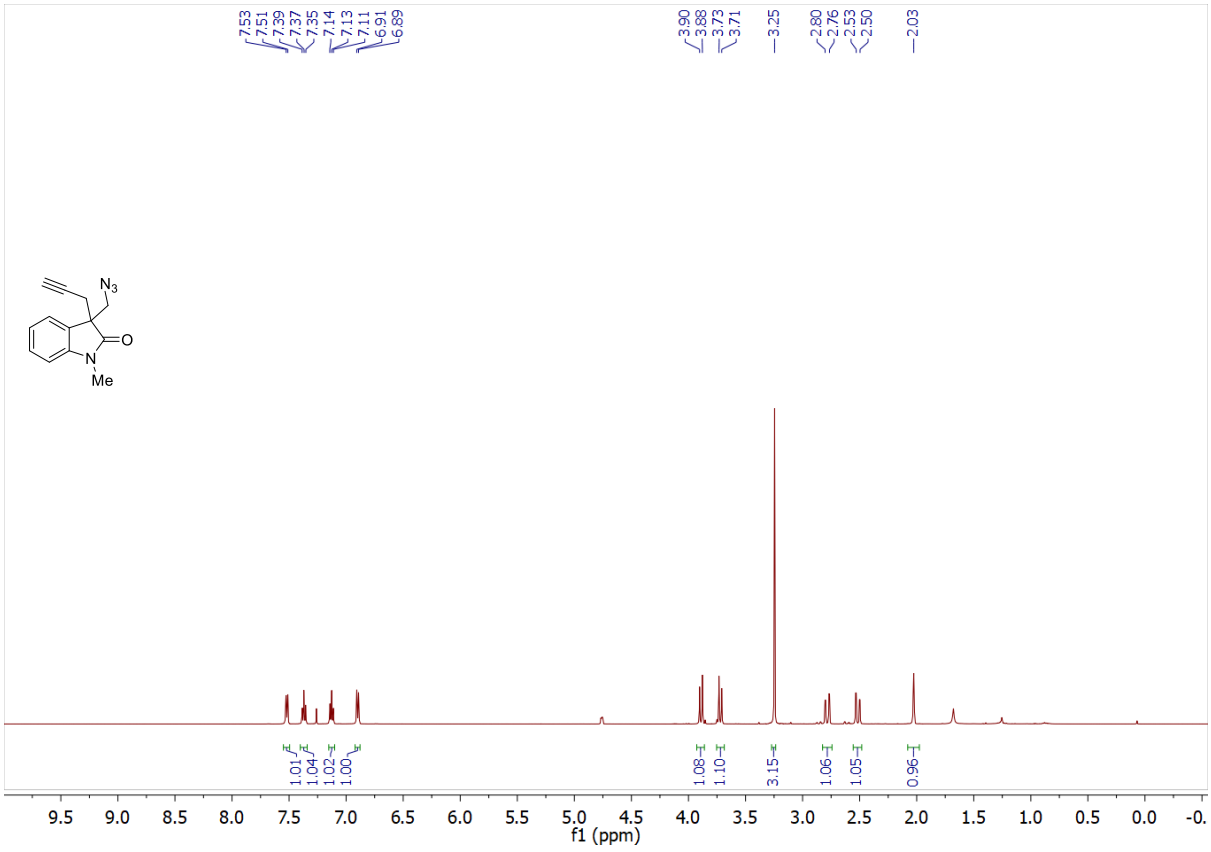
^{1}H NMR of 6m (300 MHz, $CDCl_3$):



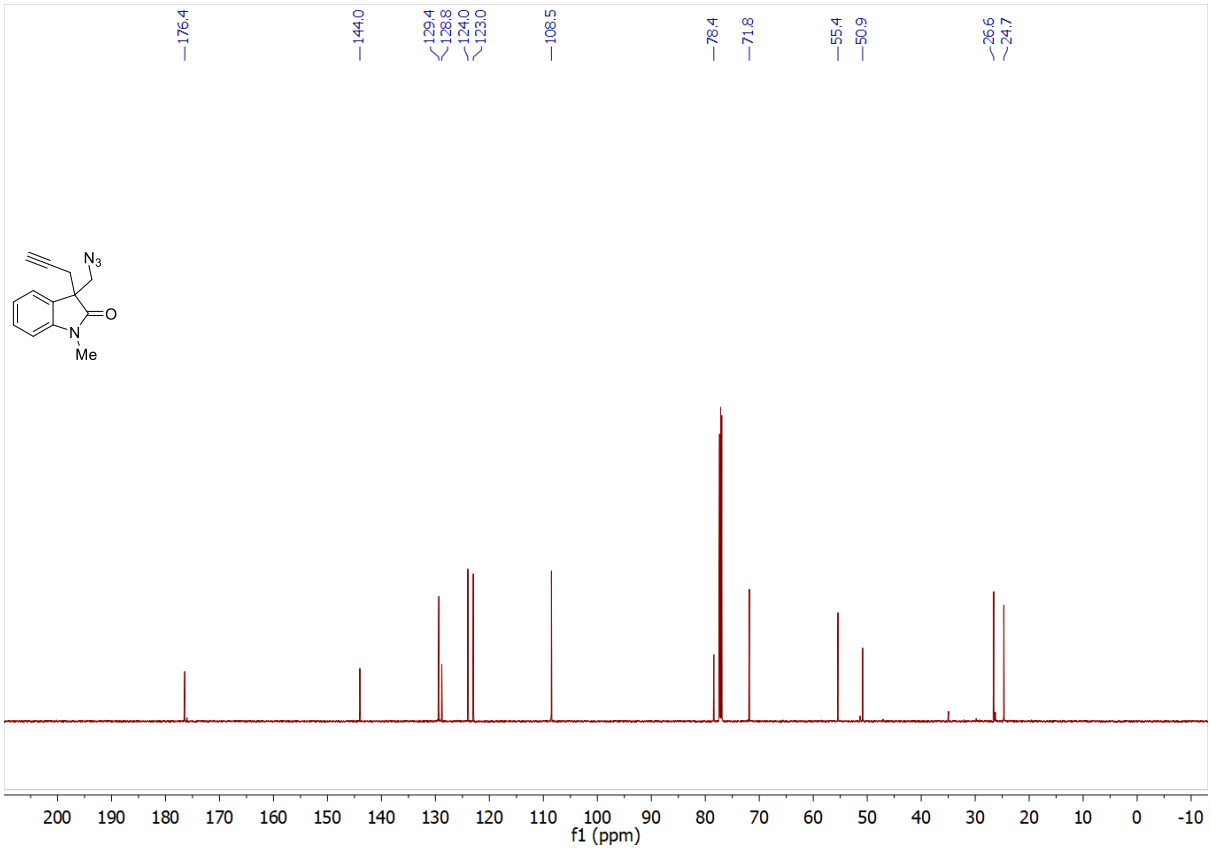
^{13}C{^{1}H} NMR of 6m (75 MHz, $CDCl_3$):



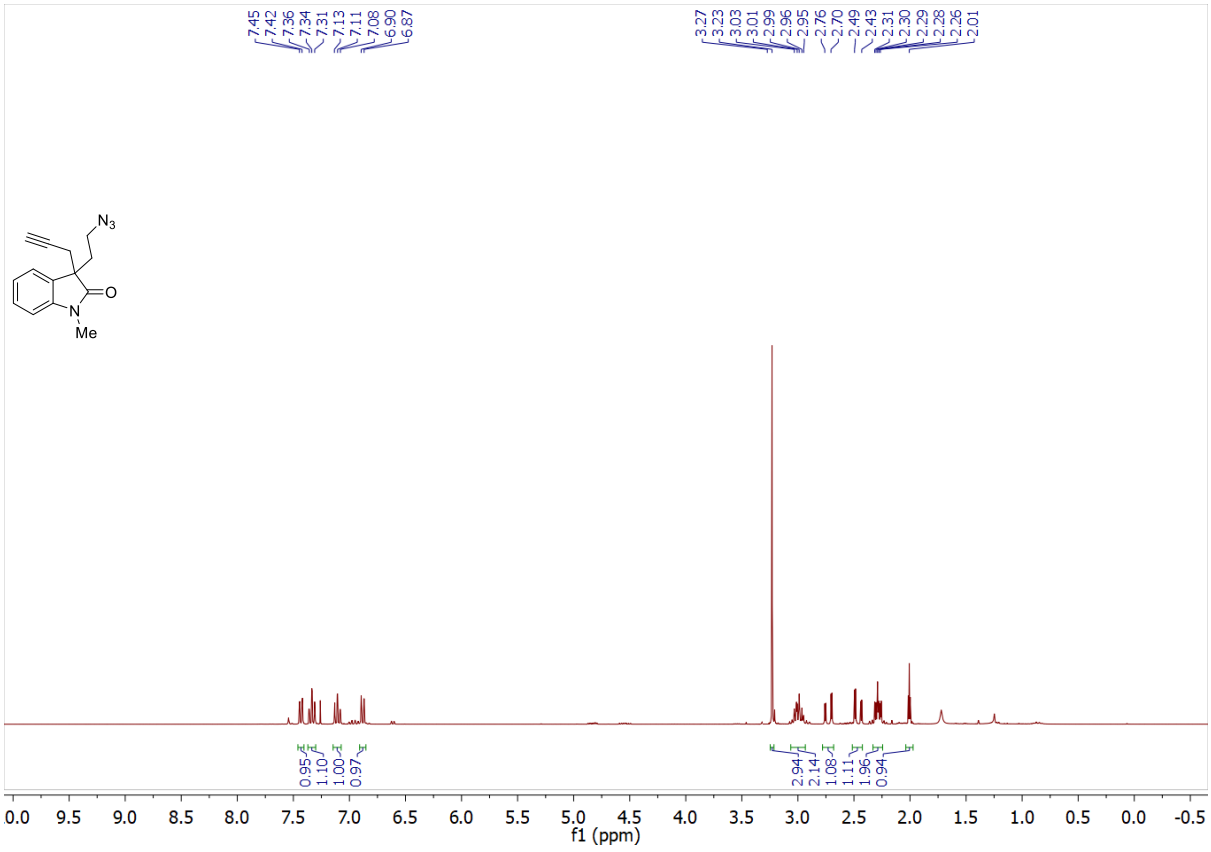
^{1}H NMR of S3a (500 MHz, $CDCl_3$):



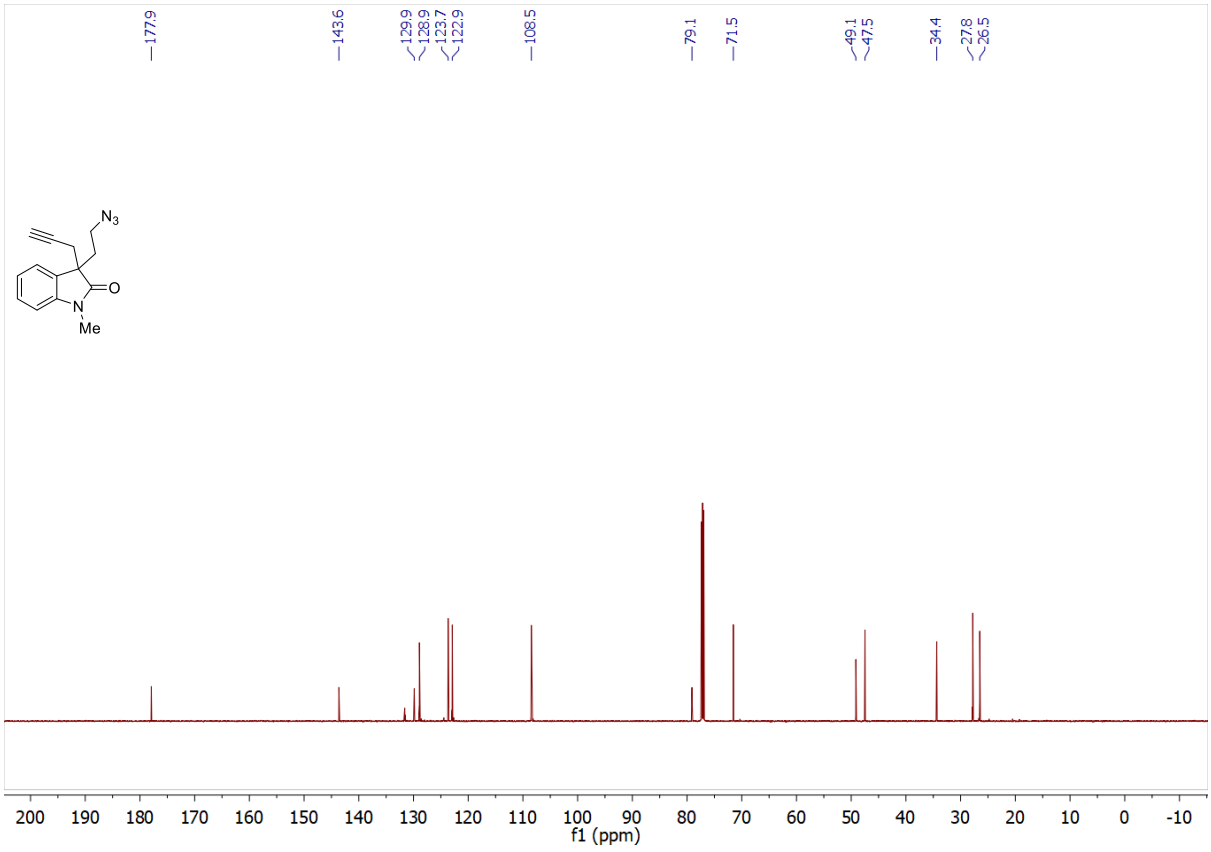
^{13}C{^{1}H} NMR of S3a (151 MHz, $CDCl_3$):



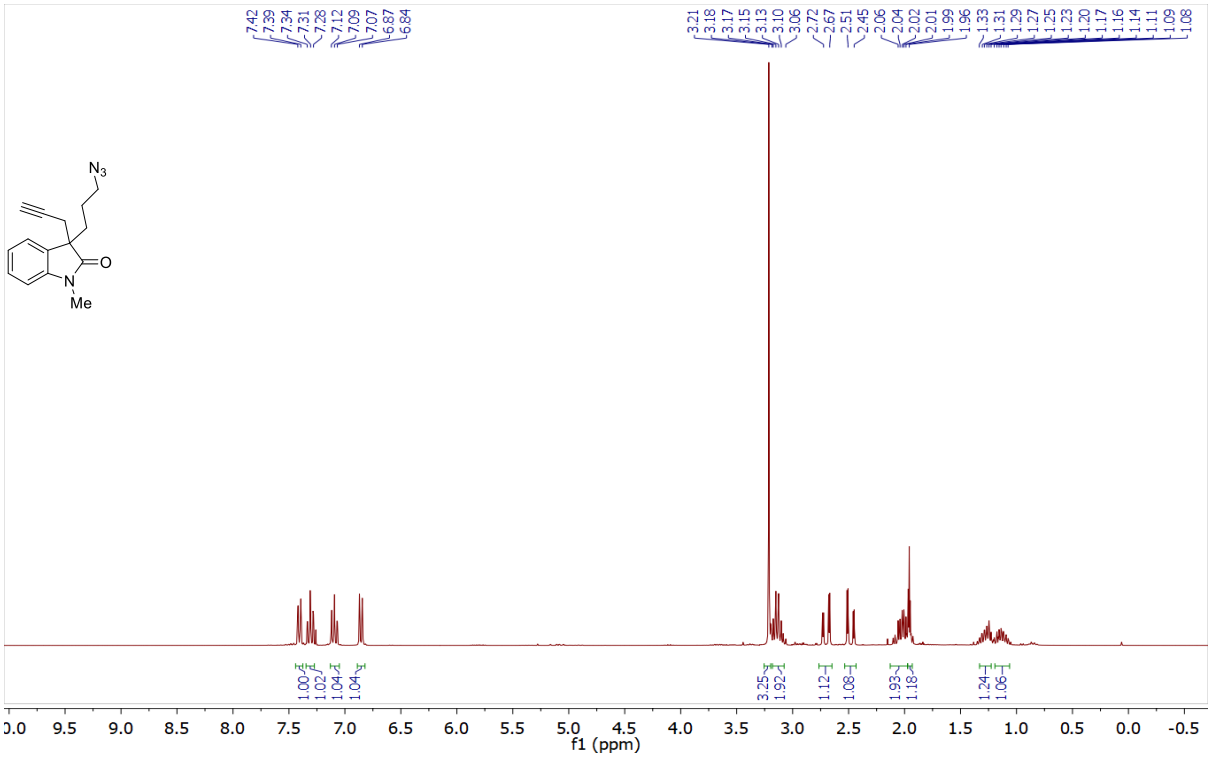
^{1}H NMR of S3b (300 MHz, $CDCl_3$):



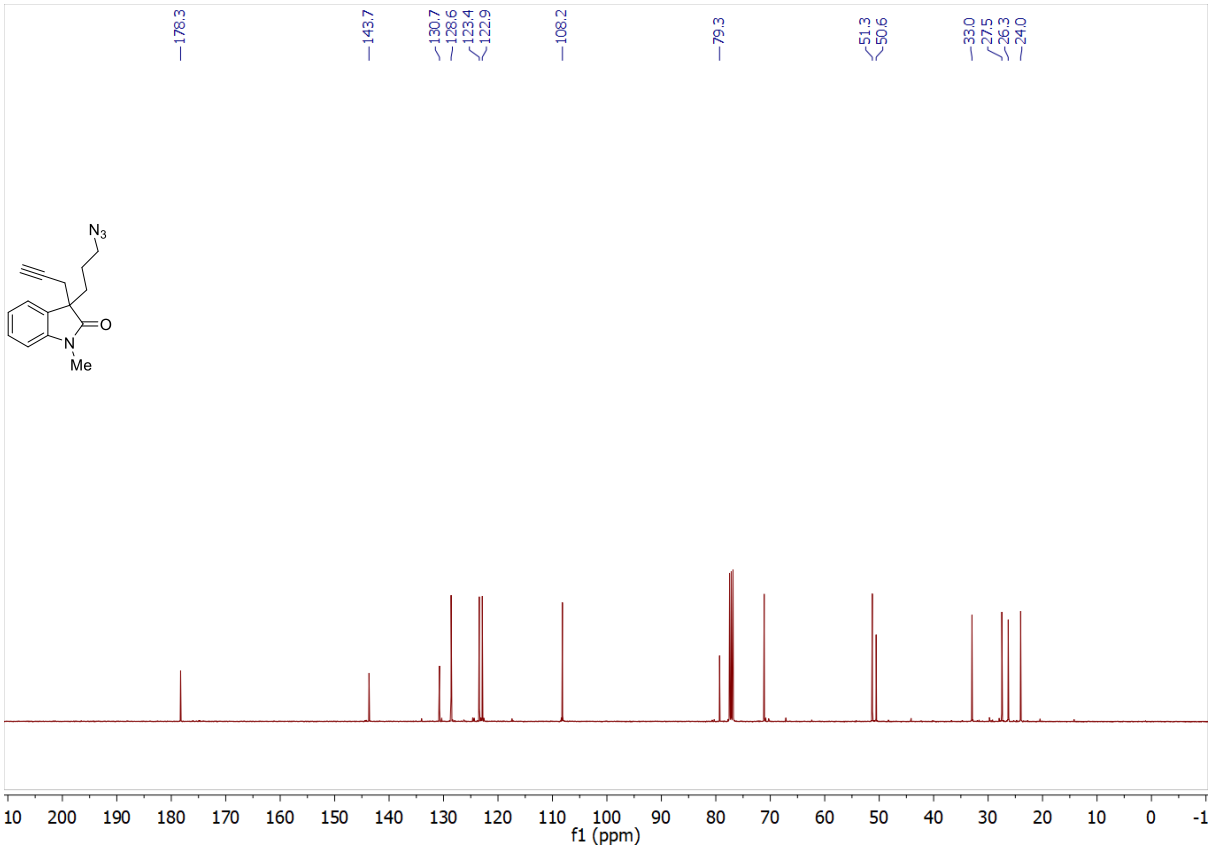
^{13}C{^{1}H} NMR of S3b (151 MHz, $CDCl_3$):



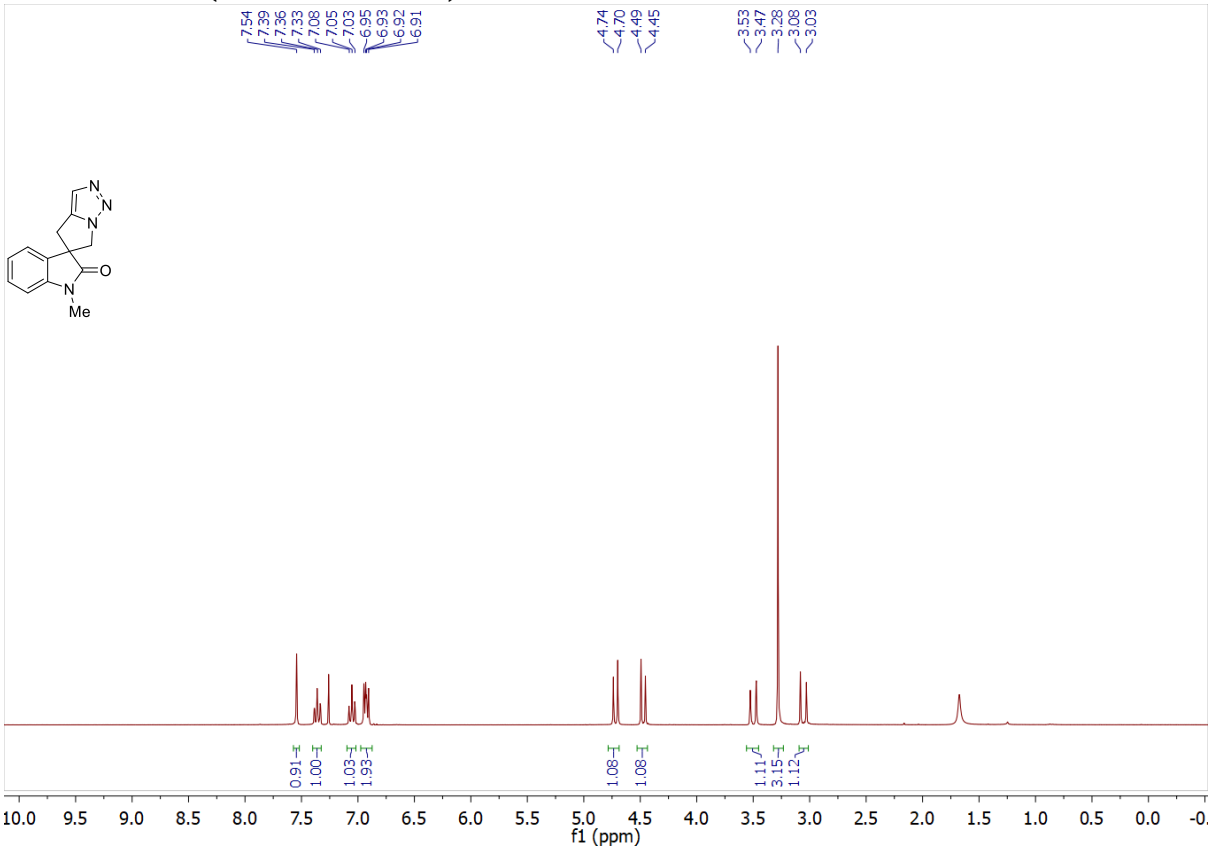
^{1}H NMR of S3c (300 MHz, $CDCl_3$):



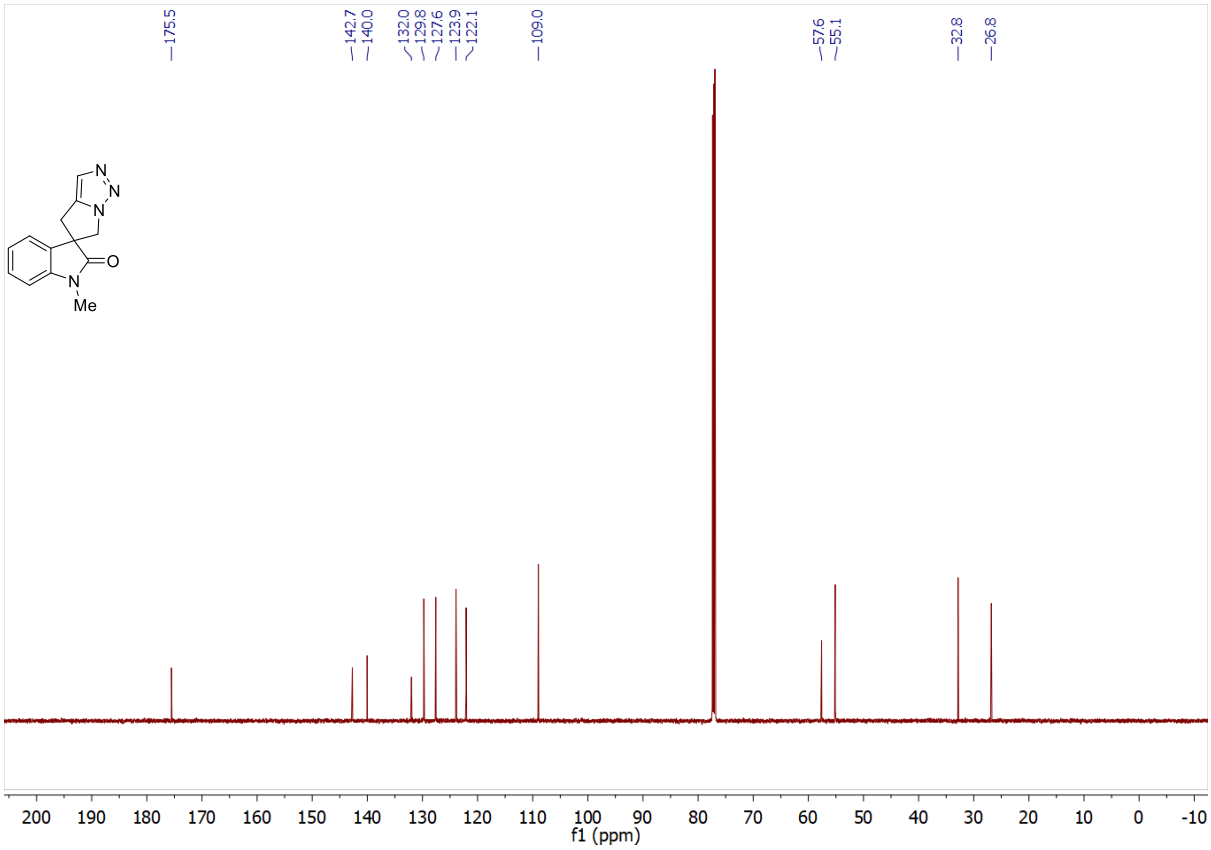
^{13}C{^{1}H} NMR of S3c (101 MHz, $CDCl_3$):



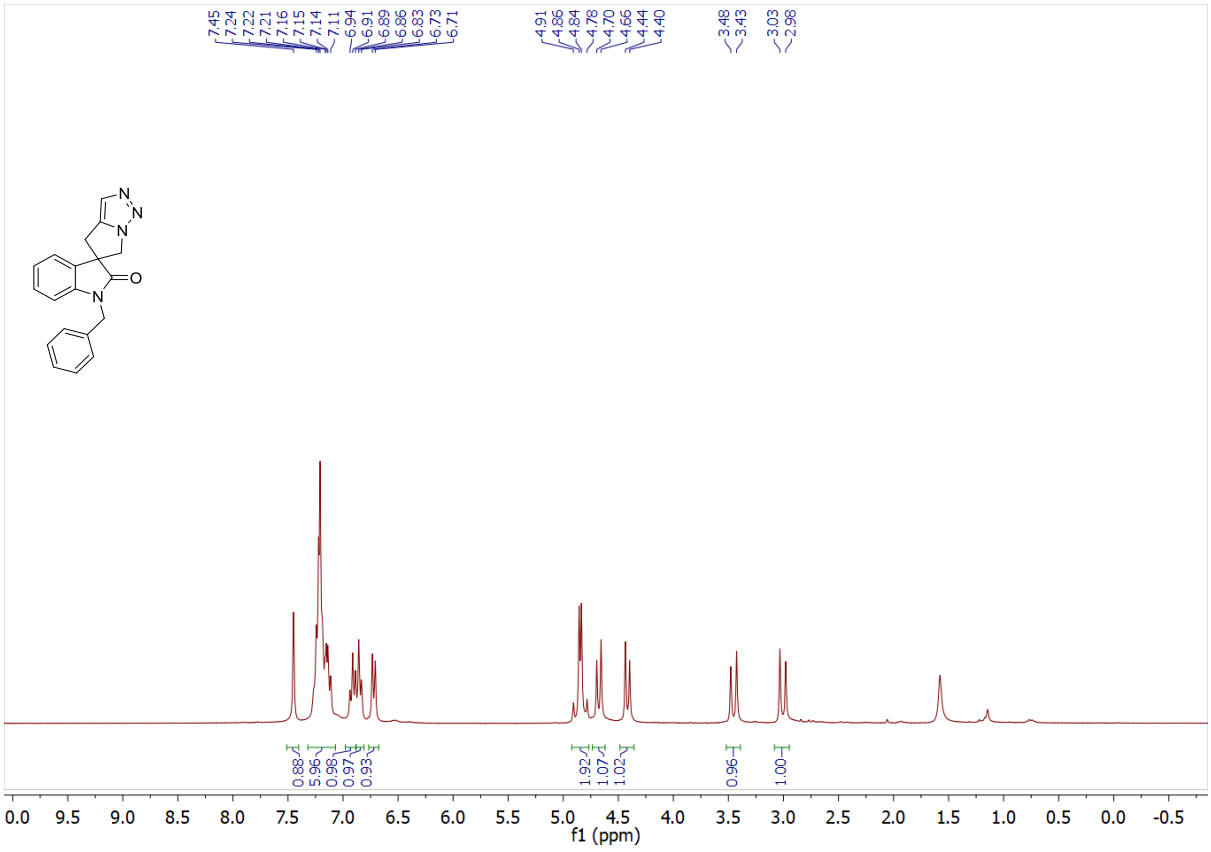
^{1}H NMR of 7a (300 MHz, $CDCl_3$):



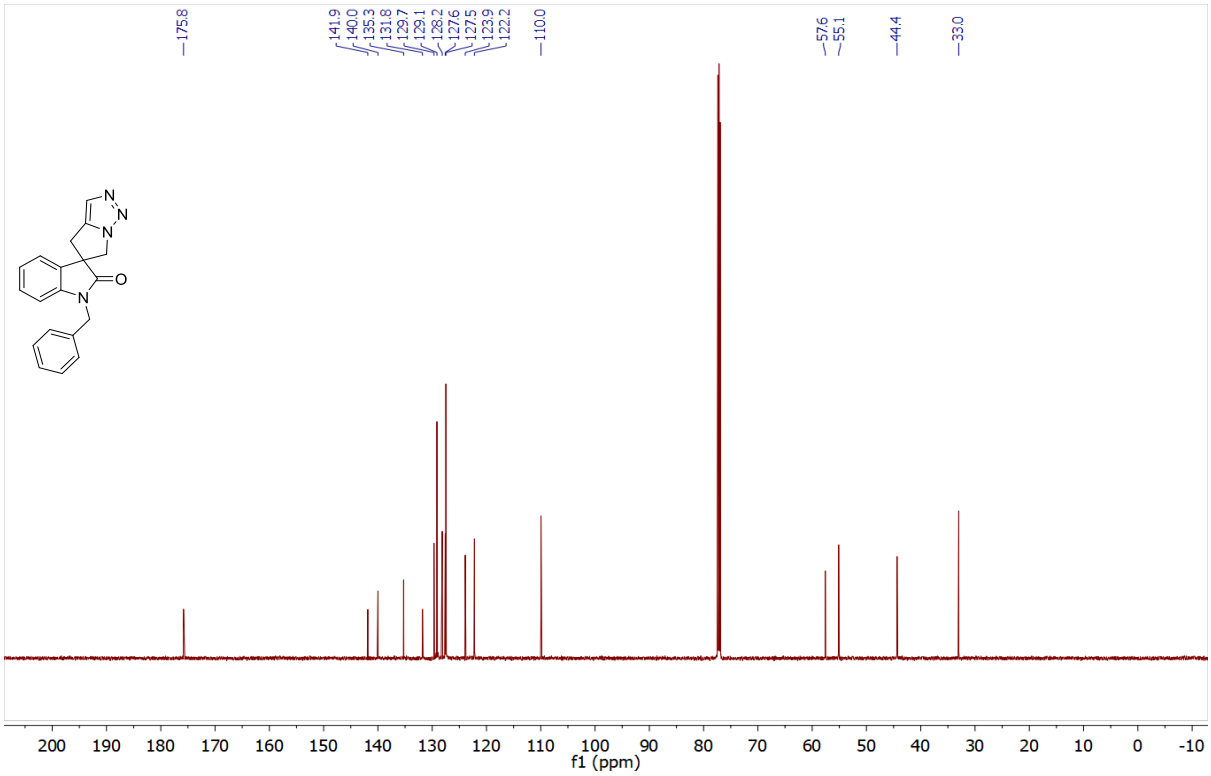
^{13}C{^{1}H} NMR of 7a (151 MHz, $CDCl_3$):



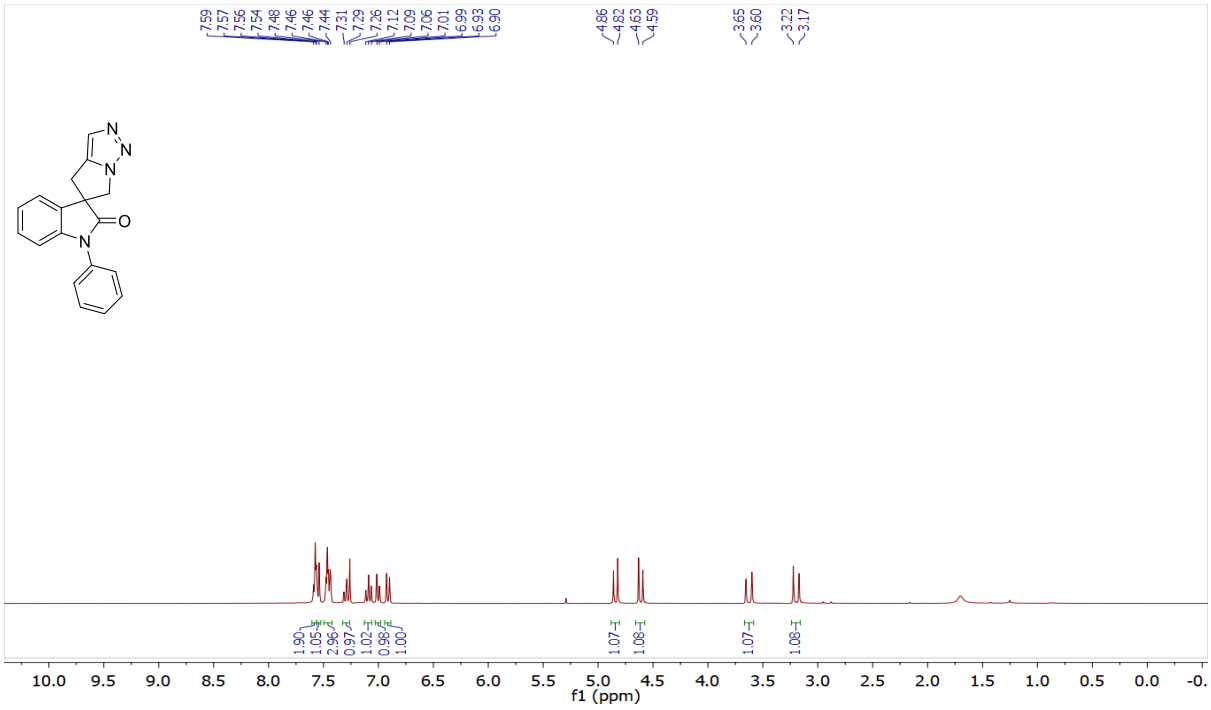
^{1}H NMR of 7b (300 MHz, $CDCl_3$):



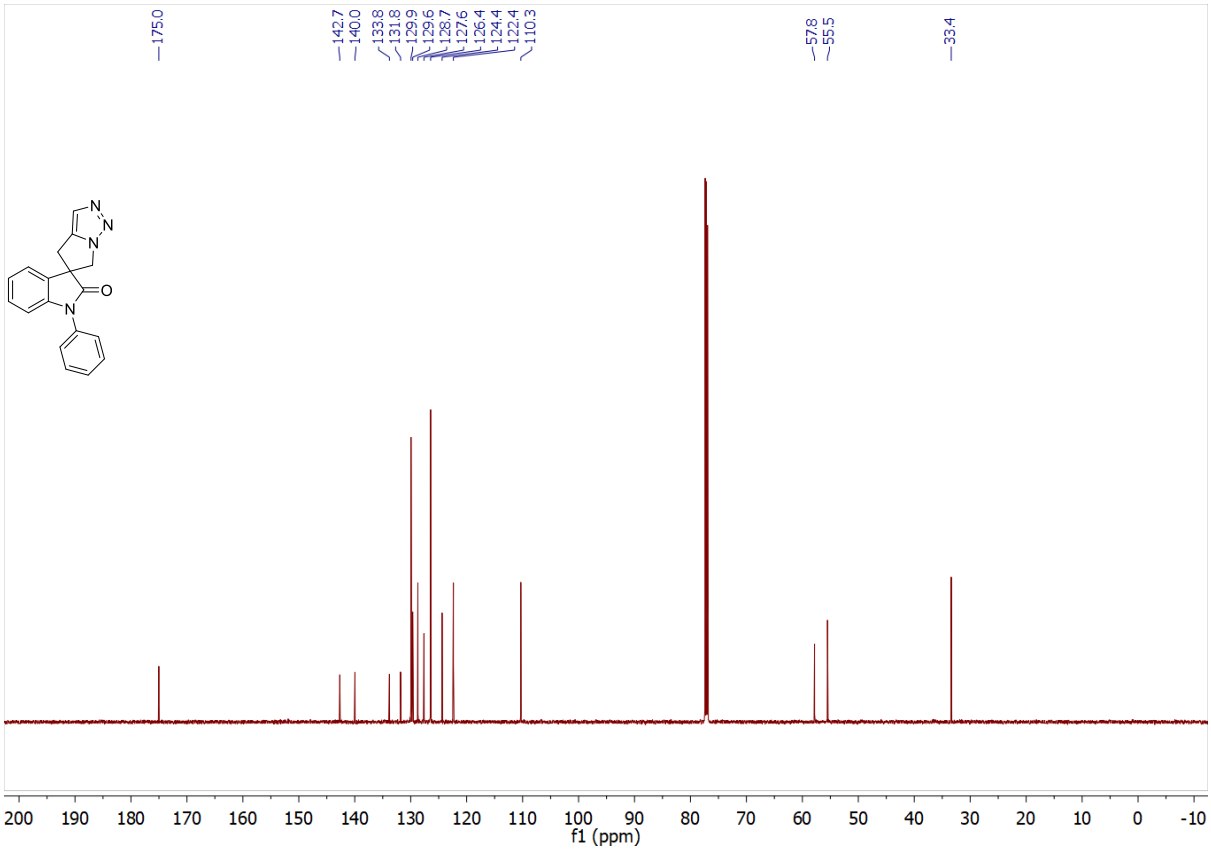
^{13}C{^{1}H} NMR of 7b (151 MHz, $CDCl_3$):



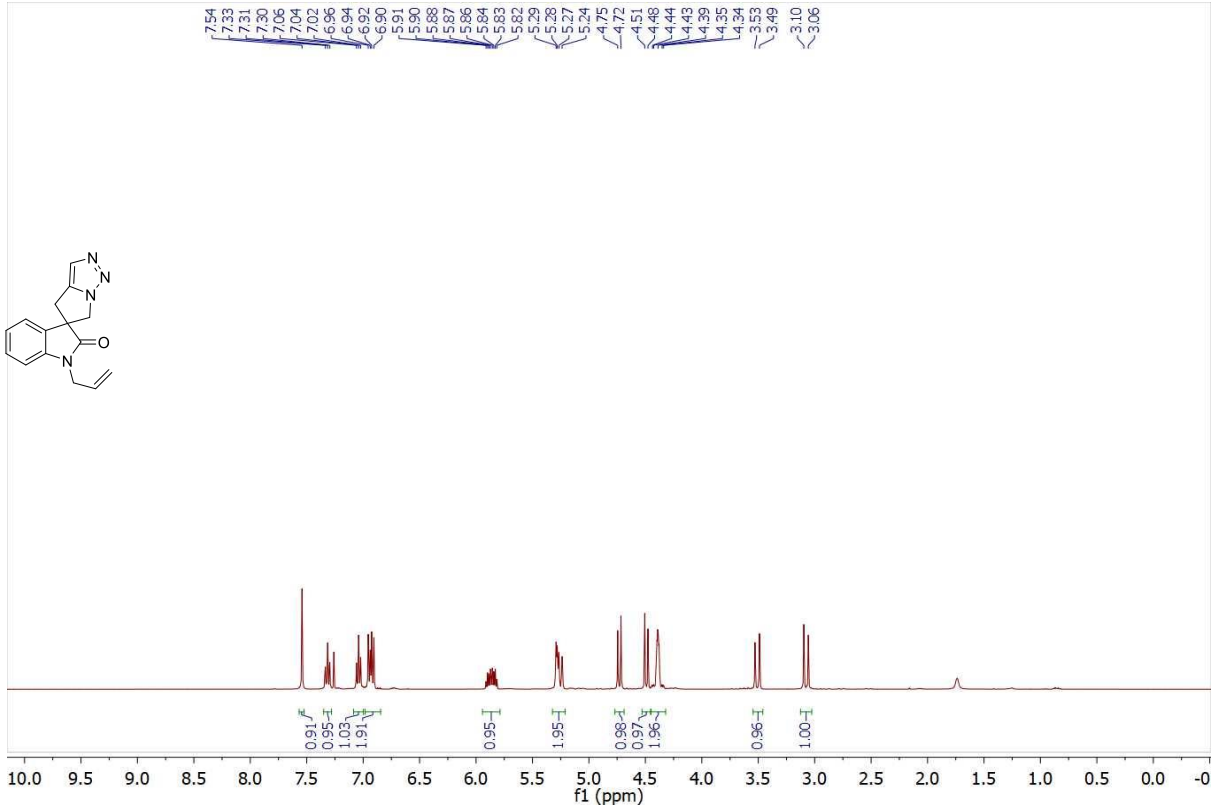
^{1}H NMR of 7c (300 MHz, $CDCl_3$):



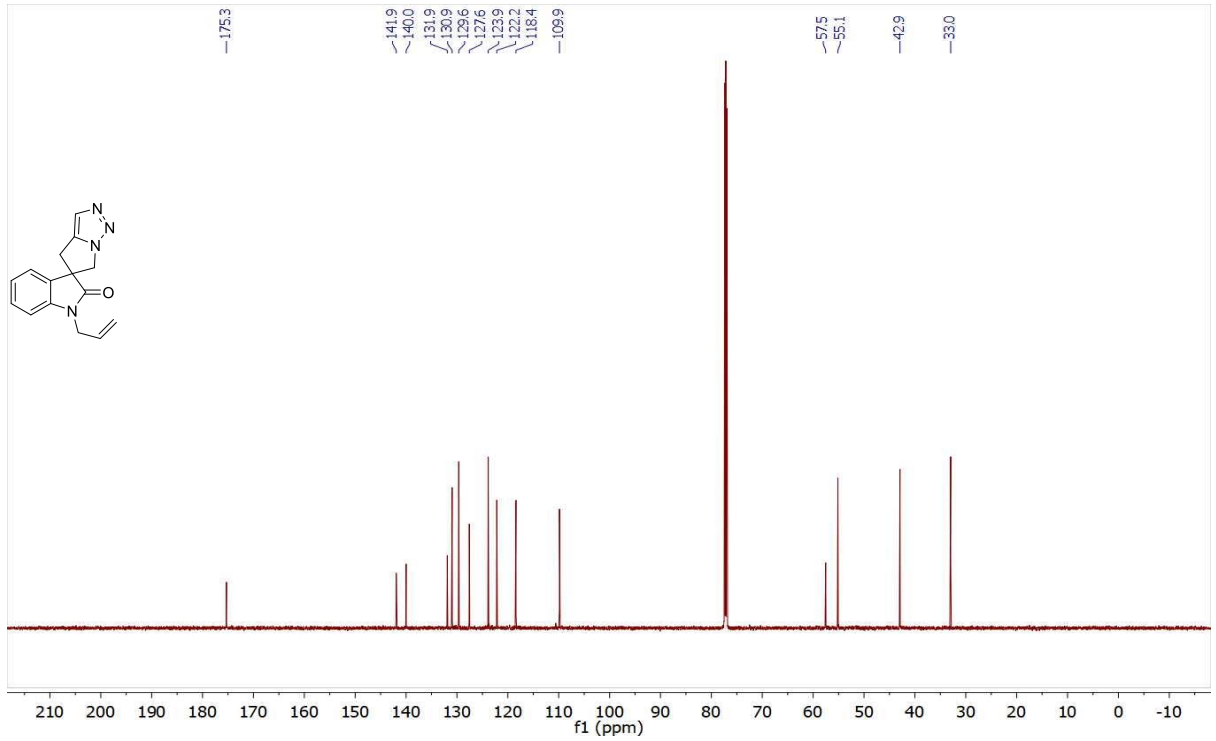
^{13}C{^{1}H} NMR of 7c (151 MHz, $CDCl_3$):



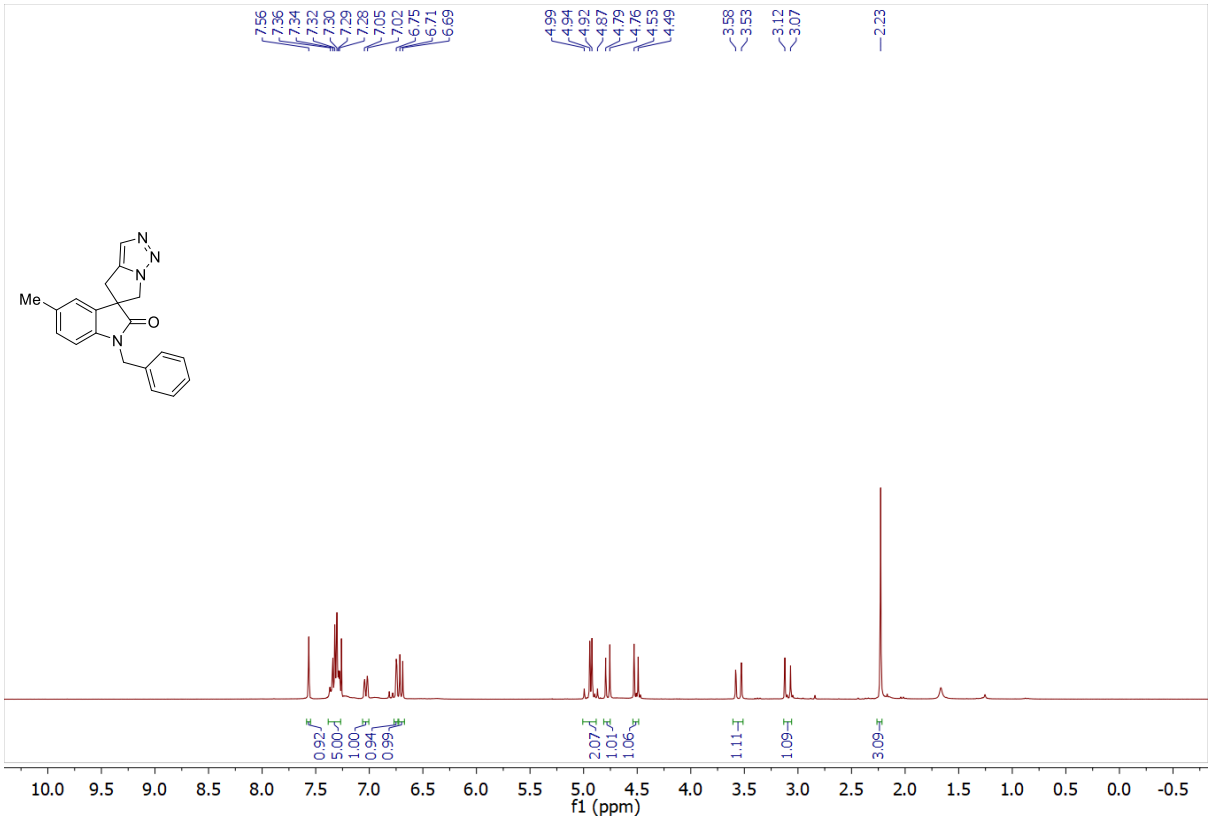
^{1}H NMR of 7d (400 MHz, $CDCl_3$):



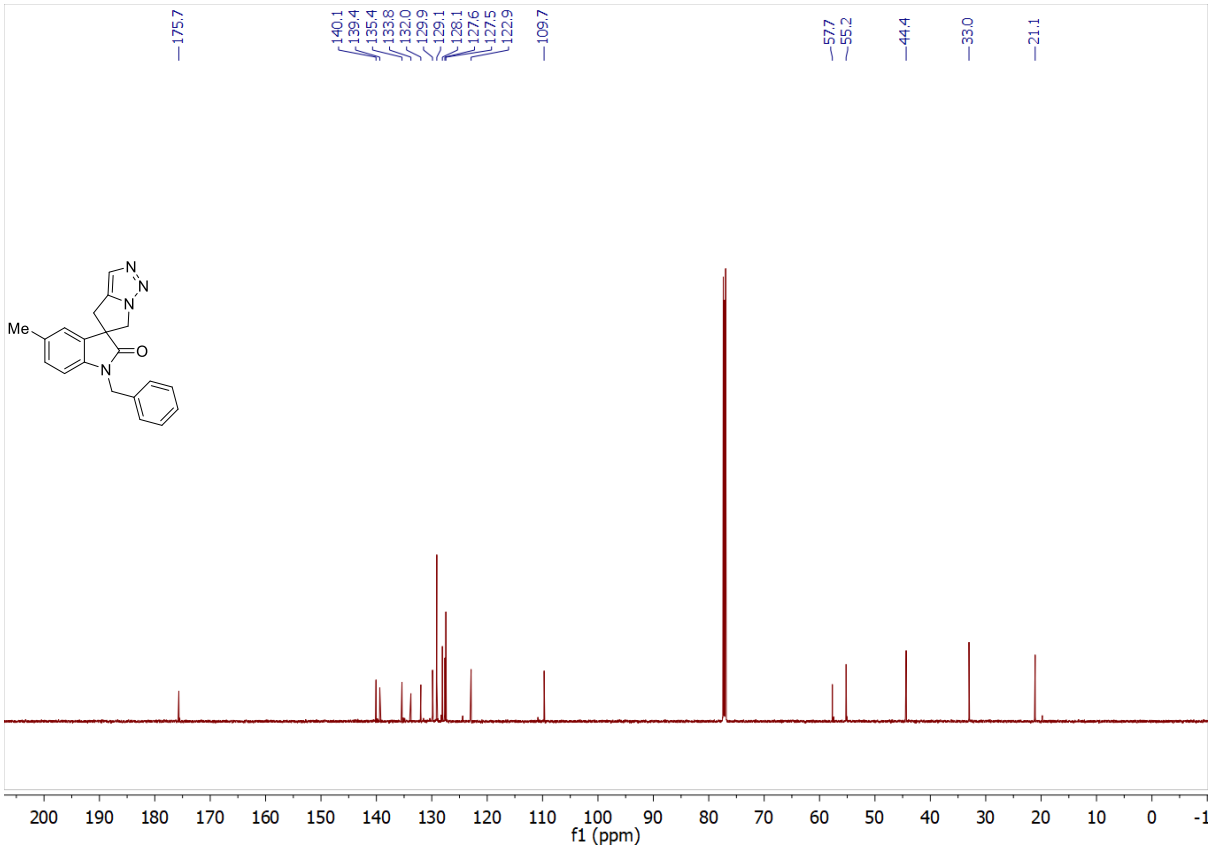
^{13}C{^{1}H} NMR of 7d (151 MHz, $CDCl_3$):



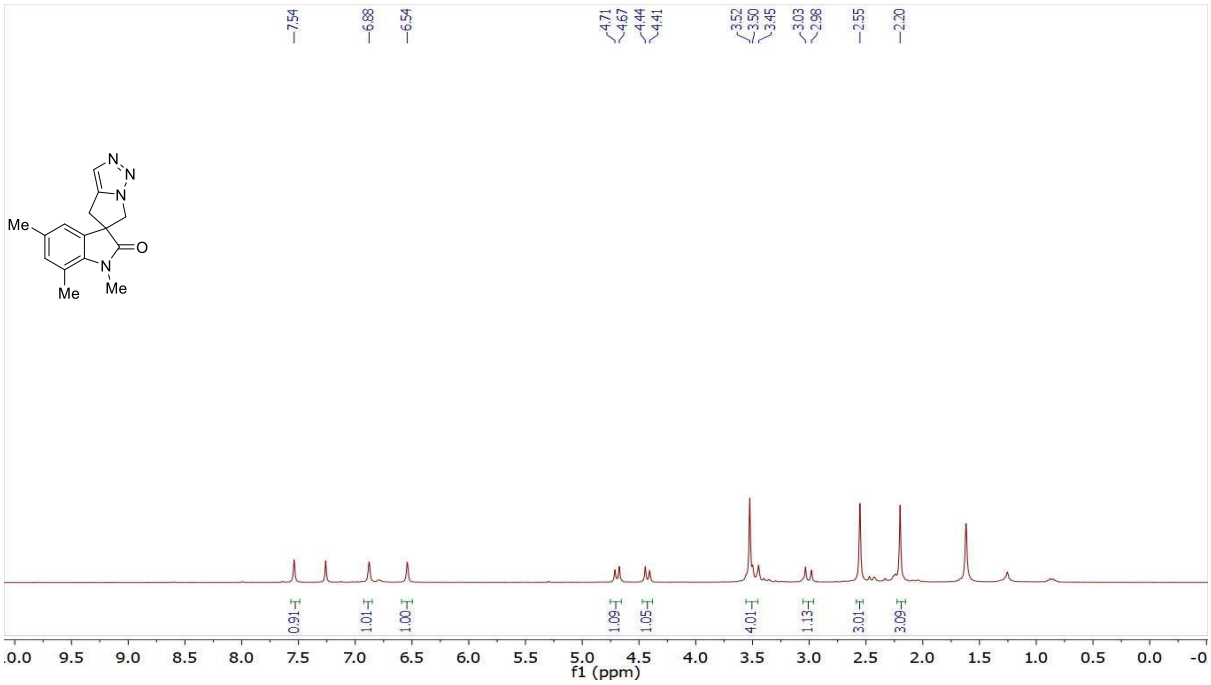
^{1}H NMR of 7e (300 MHz, $CDCl_3$):



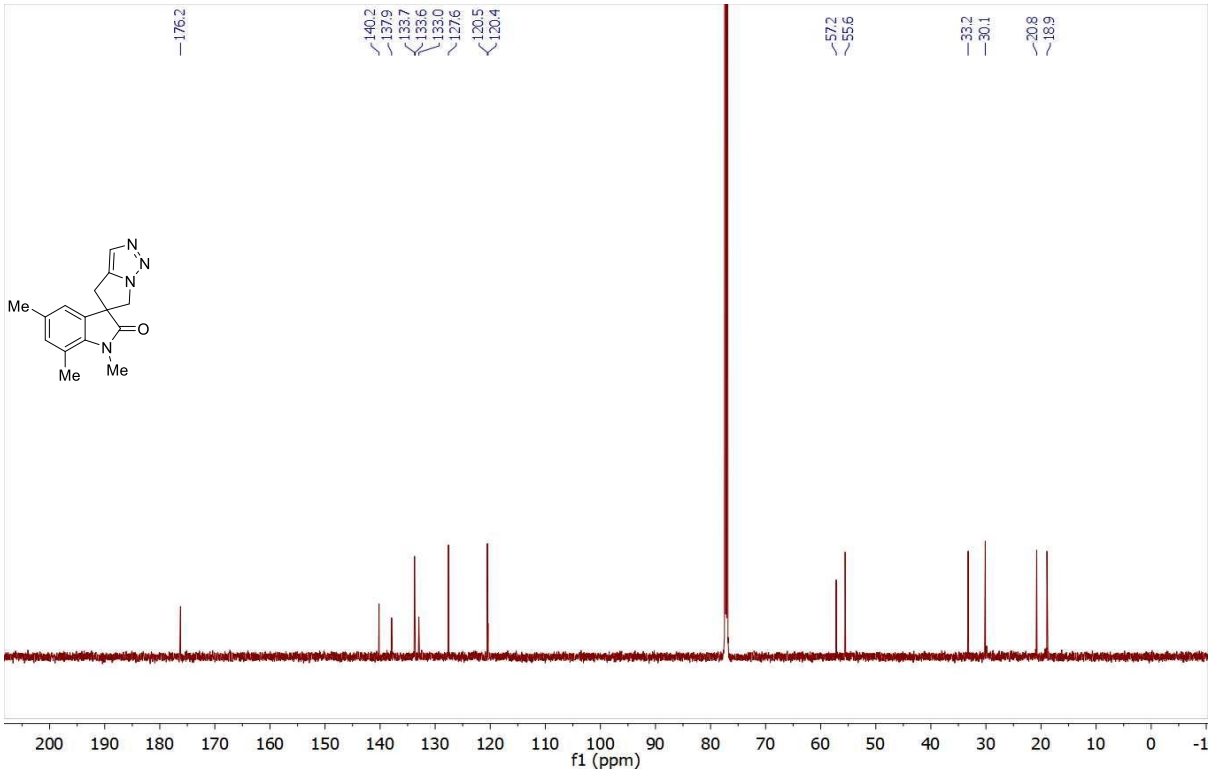
^{13}C{^{1}H} NMR of 7e (151 MHz, $CDCl_3$):



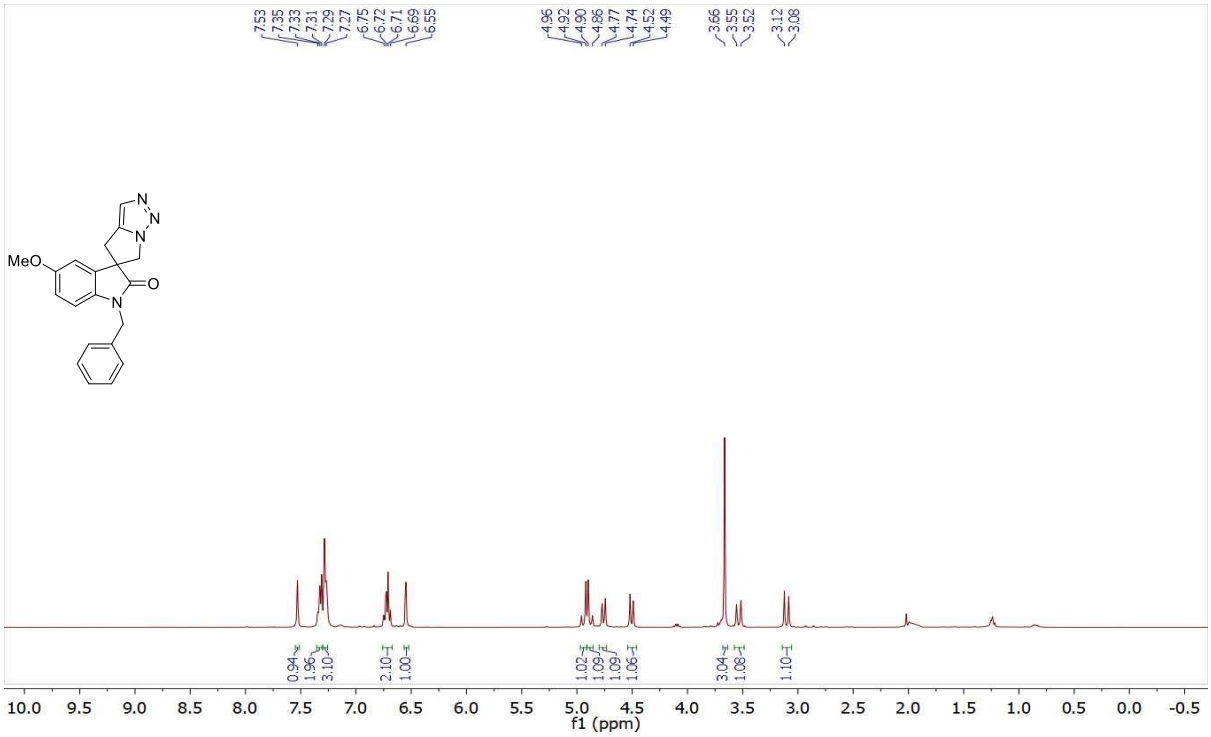
^{1}H NMR of 7f (300 MHz, $CDCl_3$):



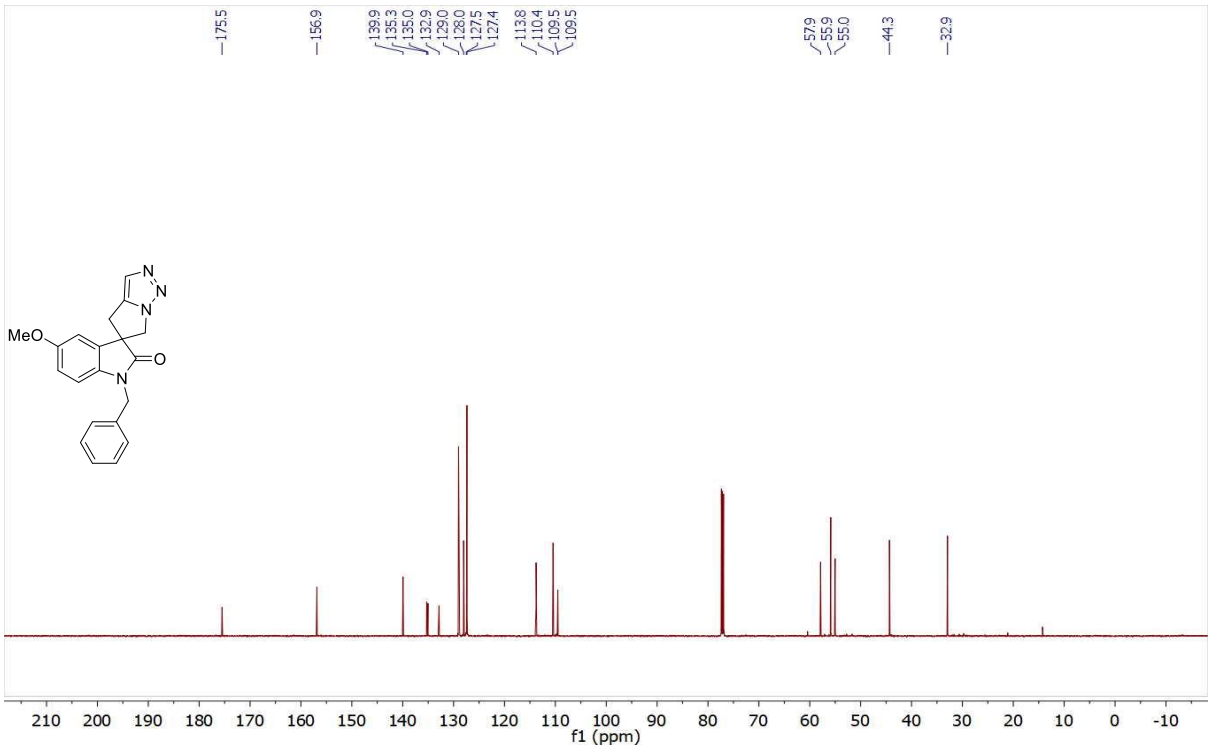
^{13}C{^{1}H} NMR of 7f (151 MHz, $CDCl_3$):



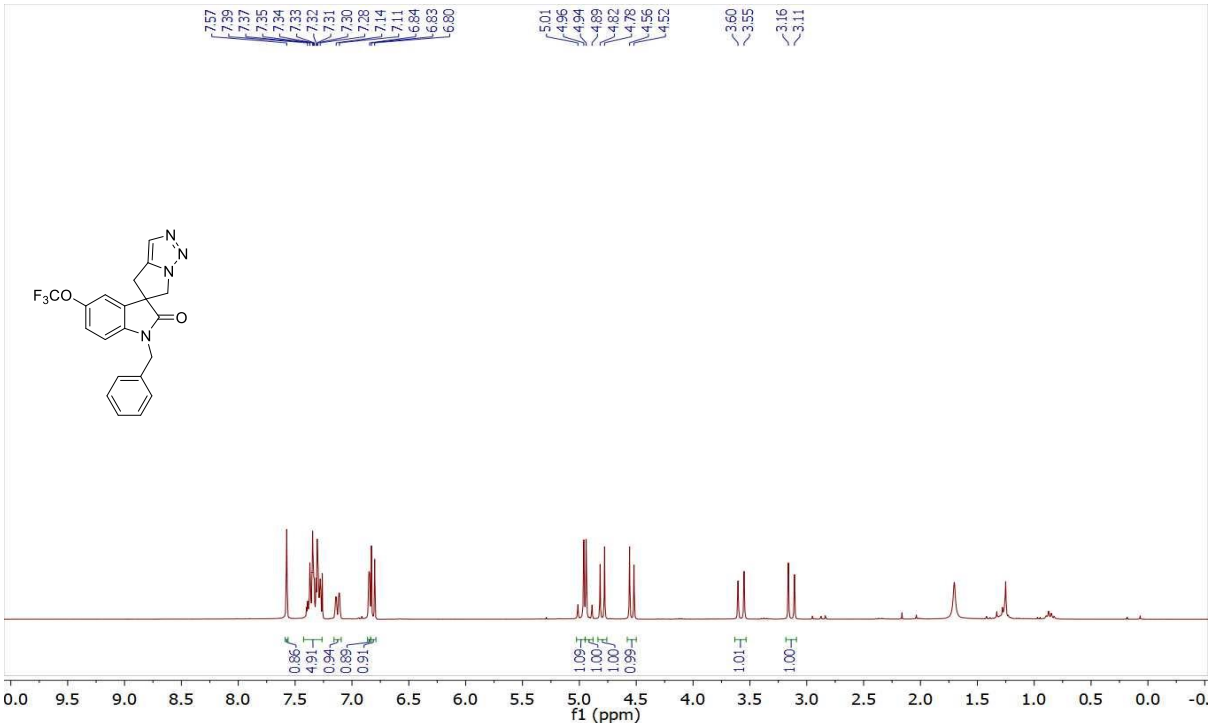
^{1}H NMR of 7g (400 MHz, $CDCl_3$):



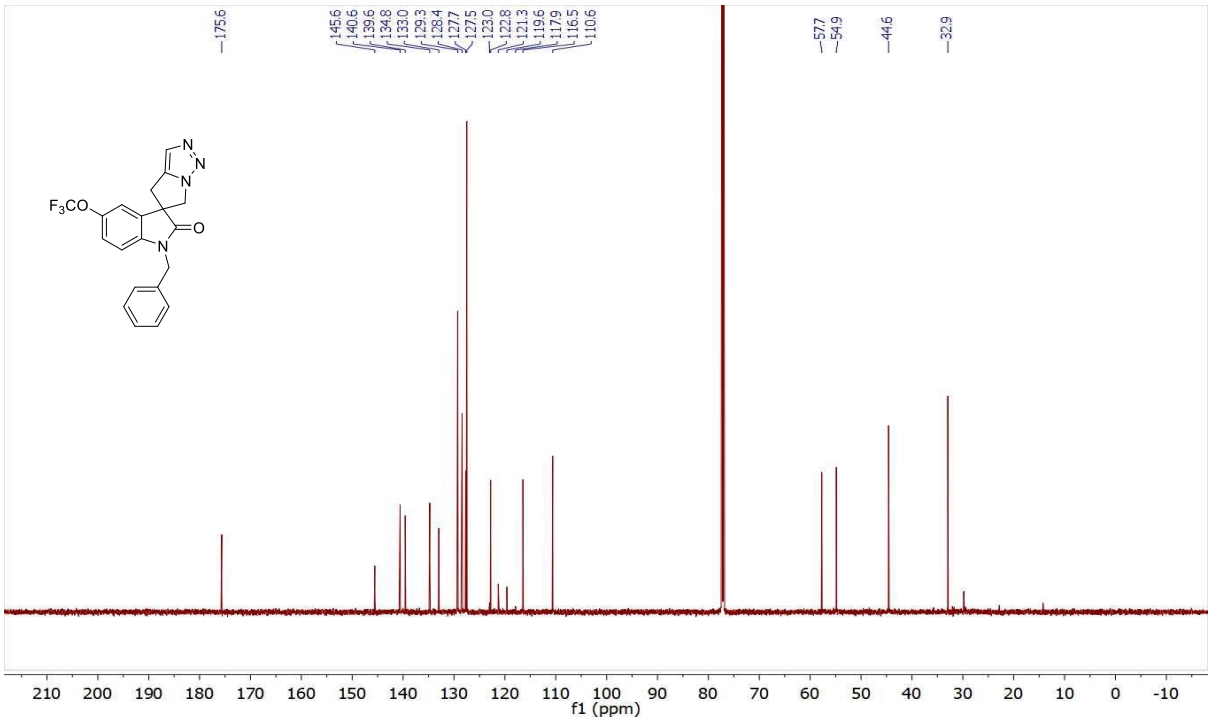
^{13}C{^{1}H} NMR of 7g (151 MHz, $CDCl_3$):



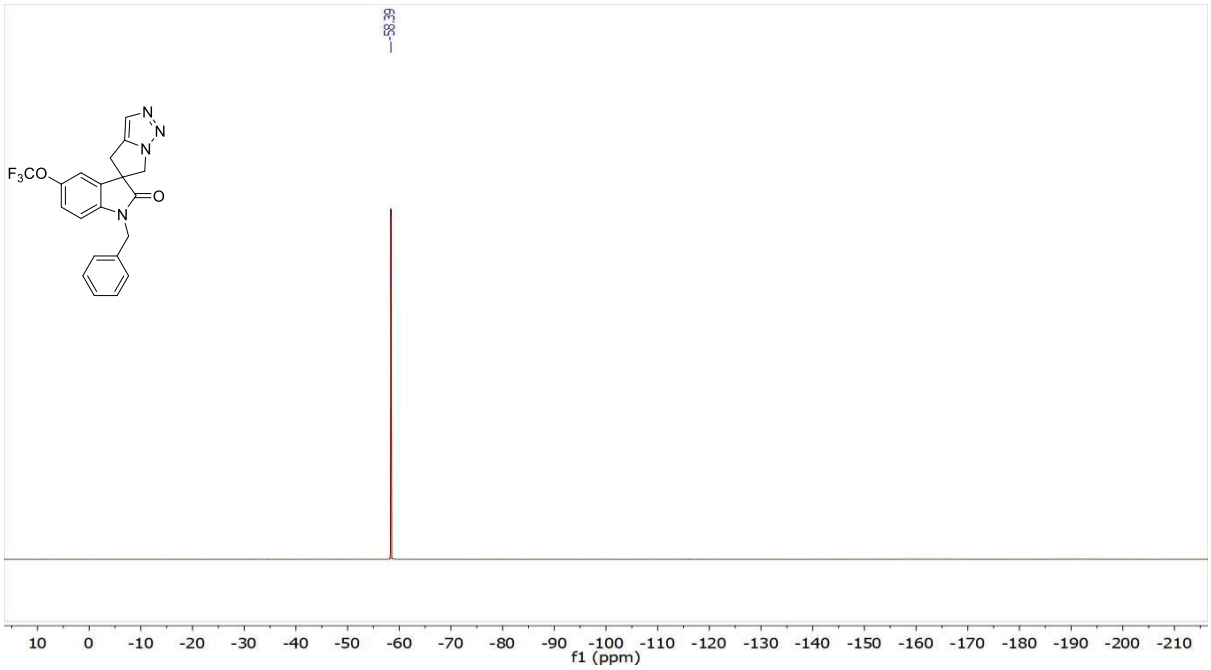
^{1}H NMR of 7h (300 MHz, $CDCl_3$):



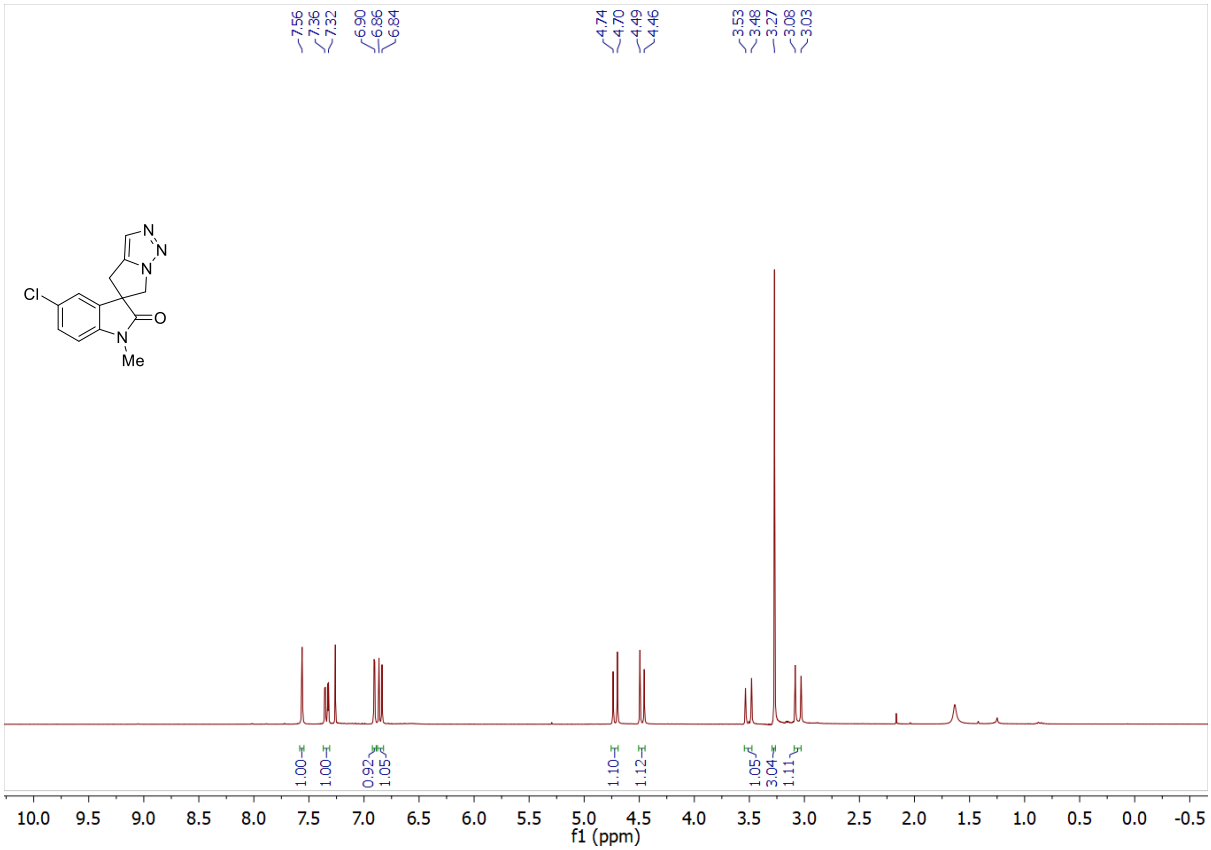
^{13}C{^{1}H} NMR of 7h (151 MHz, $CDCl_3$):



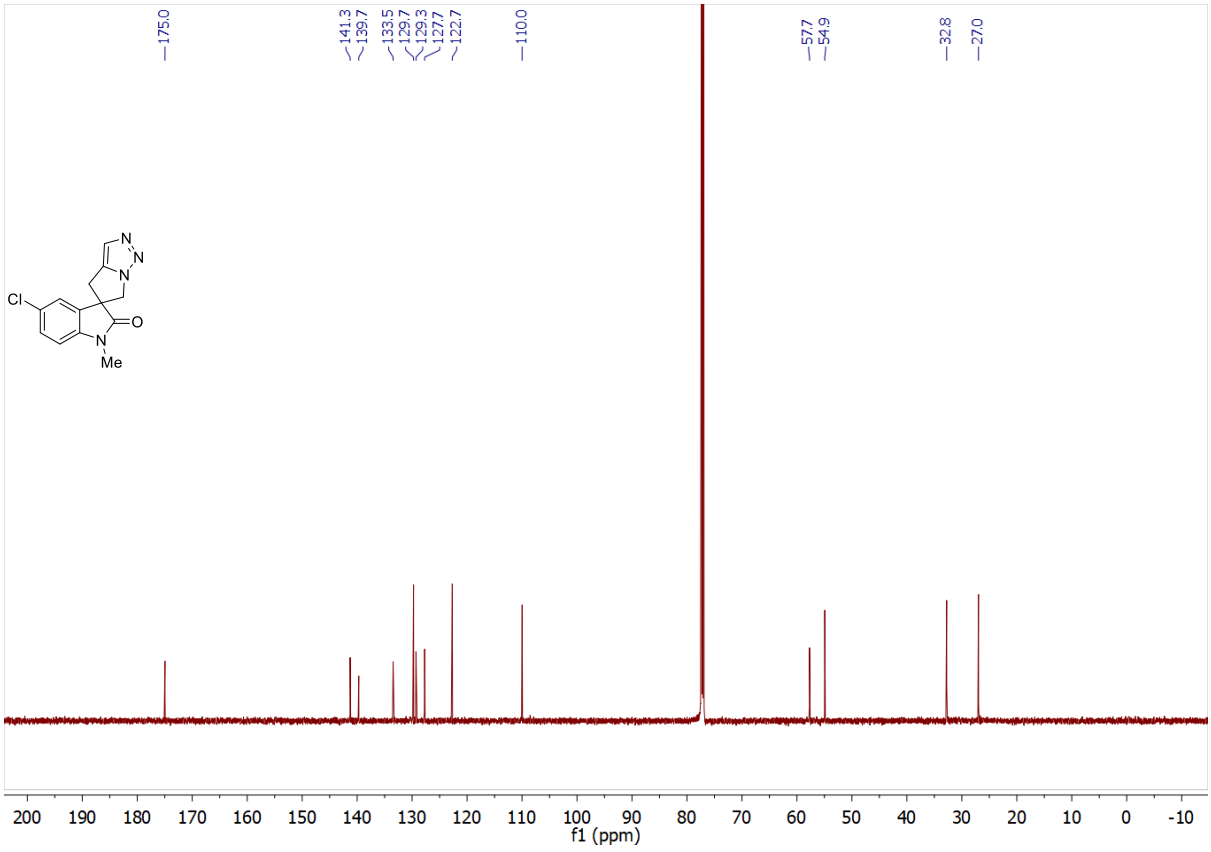
$^{19}F\{^{1}H\}$ NMR of 7h (565 MHz, $CDCl_3$):



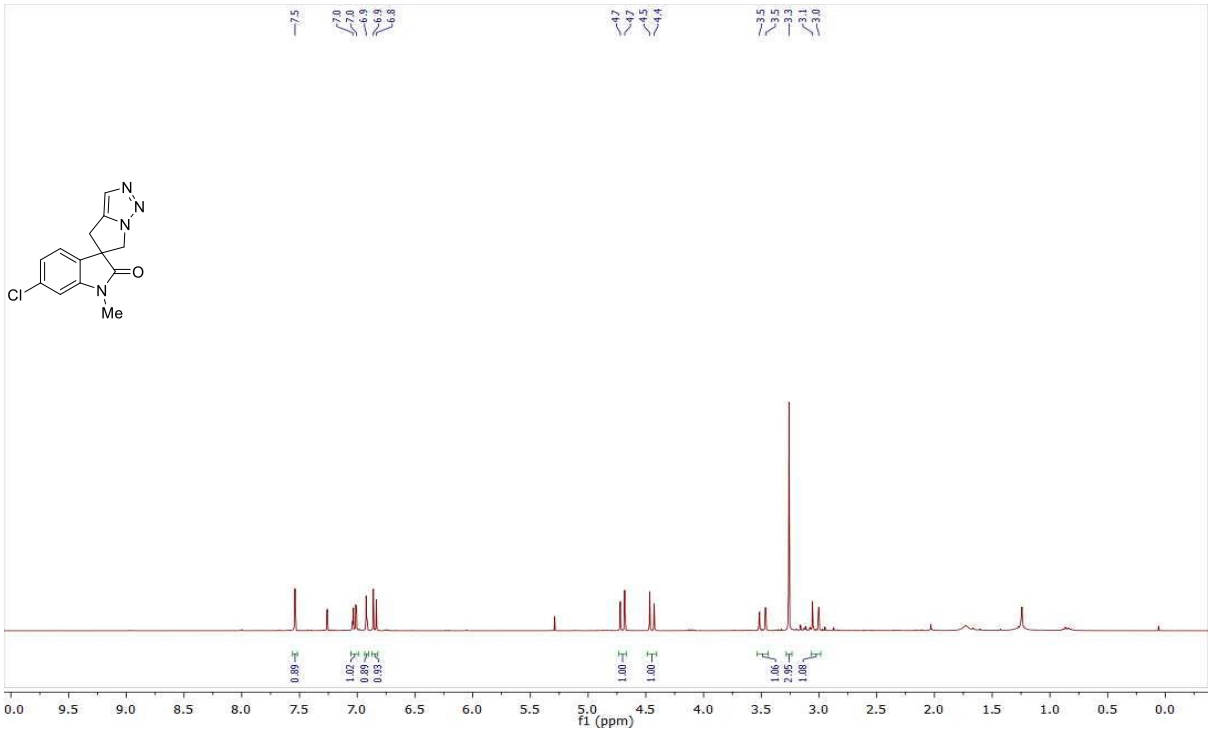
^{1}H NMR of 7i (300 MHz, $CDCl_3$):



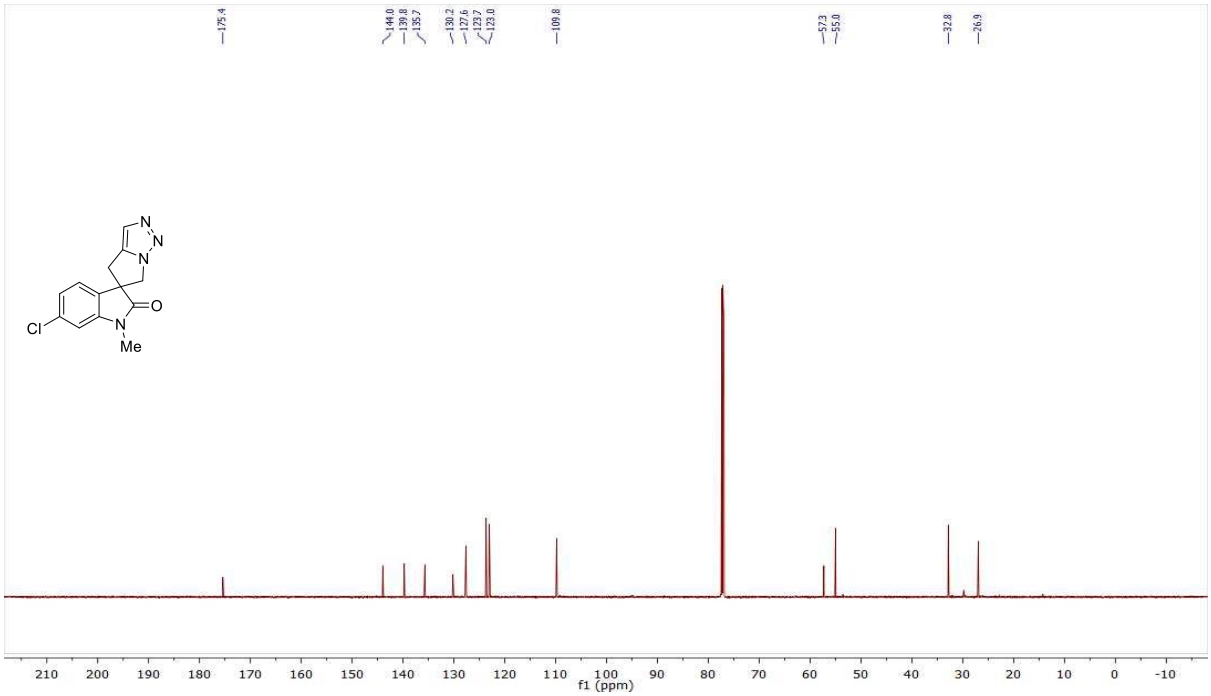
$^{13}C\{^{1}H\}$ NMR of 7i (151 MHz, $CDCl_3$):



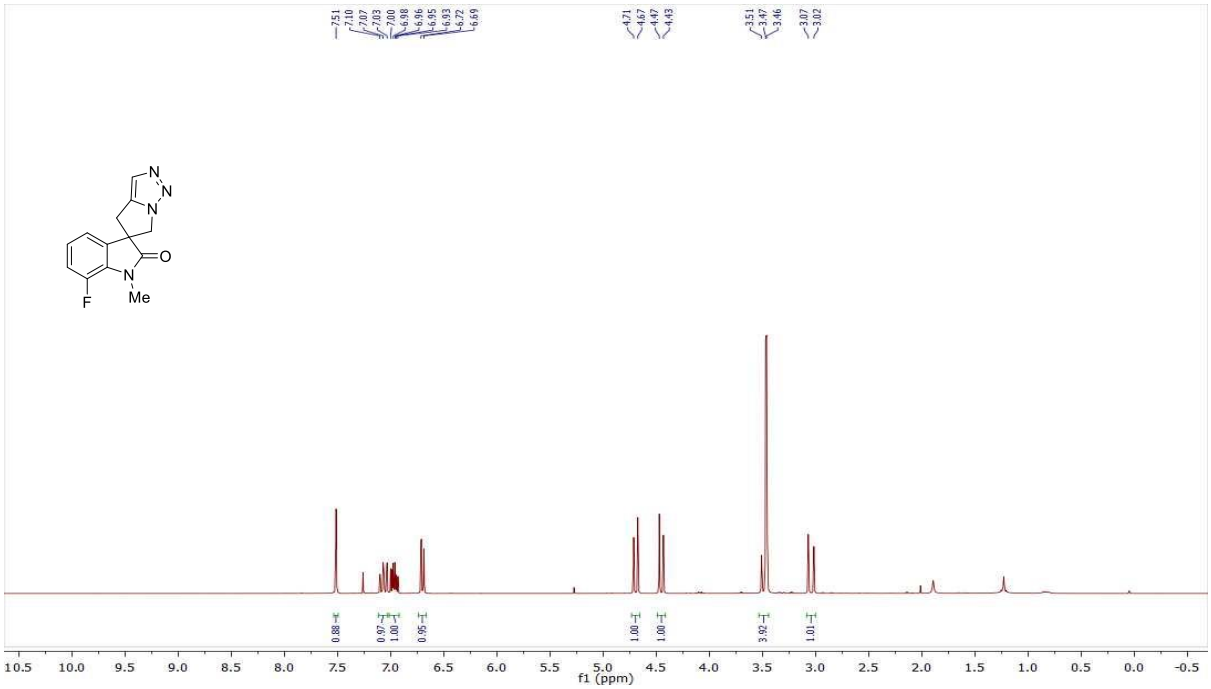
^{1}H NMR of 7j (300 MHz, $CDCl_3$):



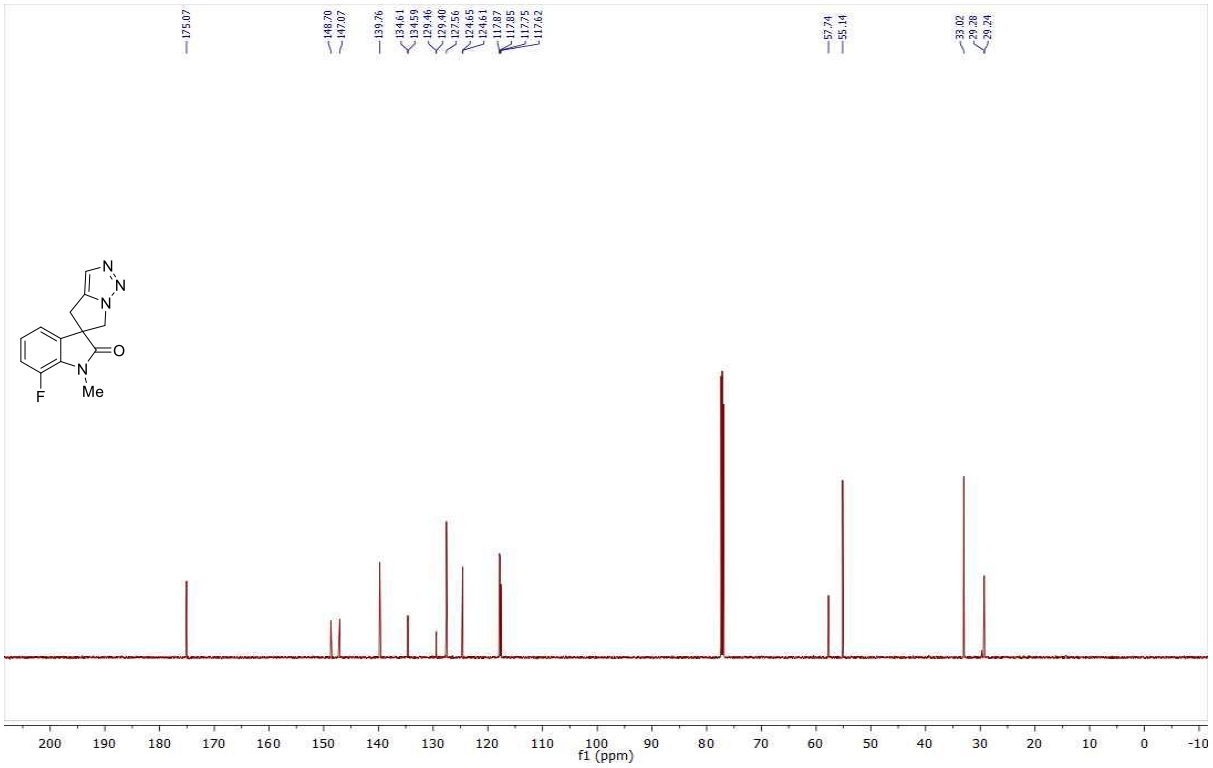
$^{13}C\{^{1}H\}$ NMR of 7j (151 MHz, $CDCl_3$):



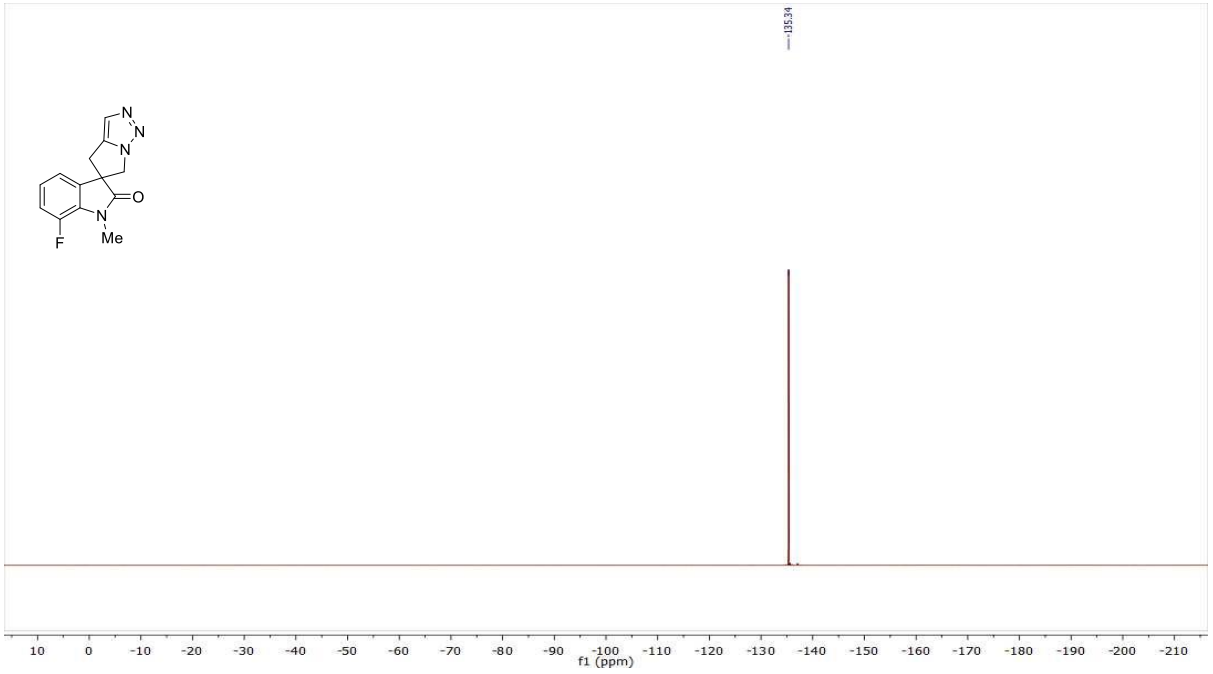
^{1}H NMR of 7k (300 MHz, $CDCl_3$):



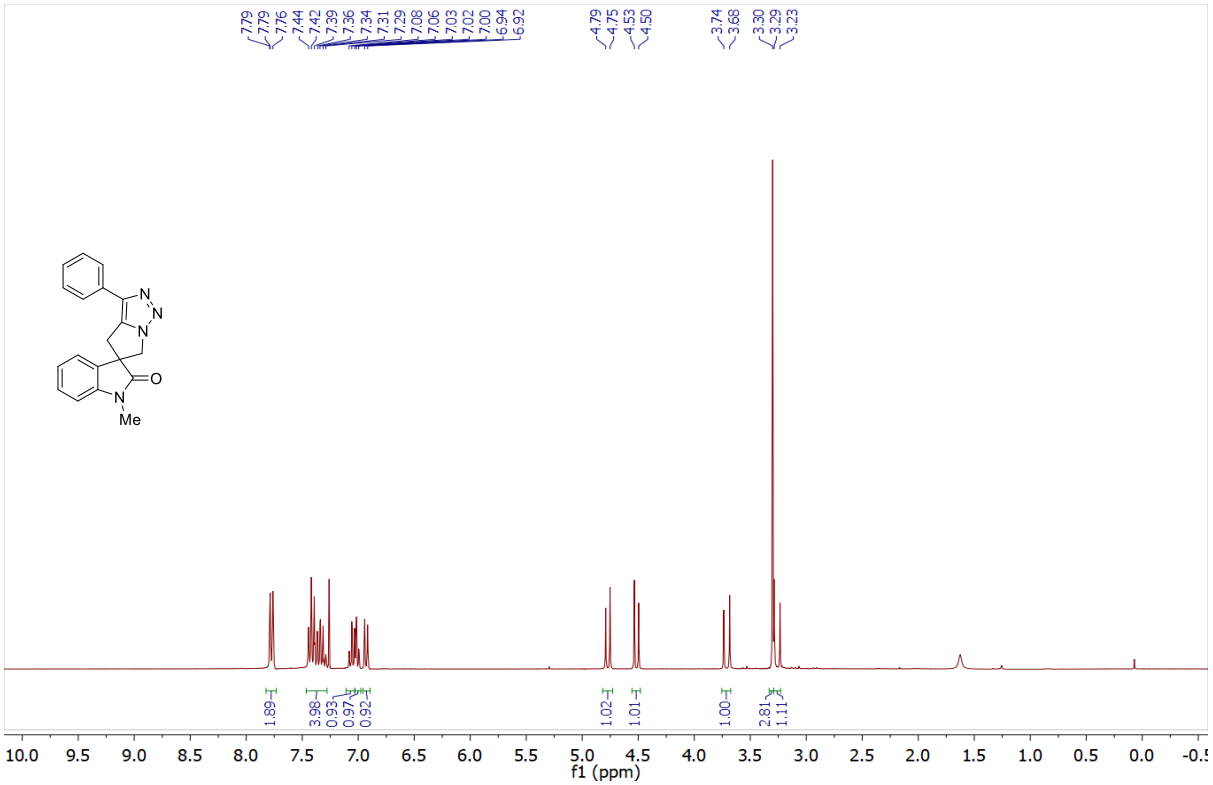
$^{13}C\{^{1}H\}$ NMR of 7k (151 MHz, $CDCl_3$):



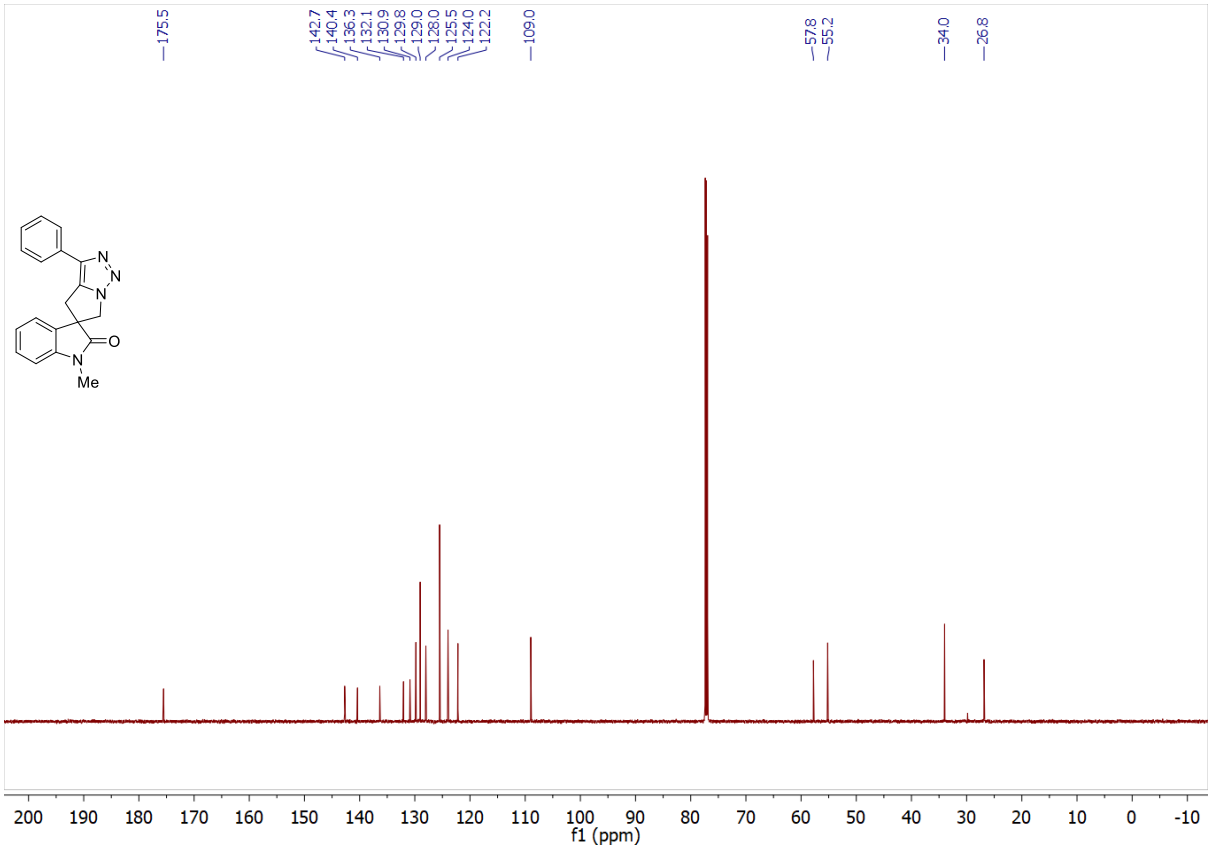
$^{19}F\{^{1}H\}$ NMR of 7k (565 MHz, $CDCl_3$):



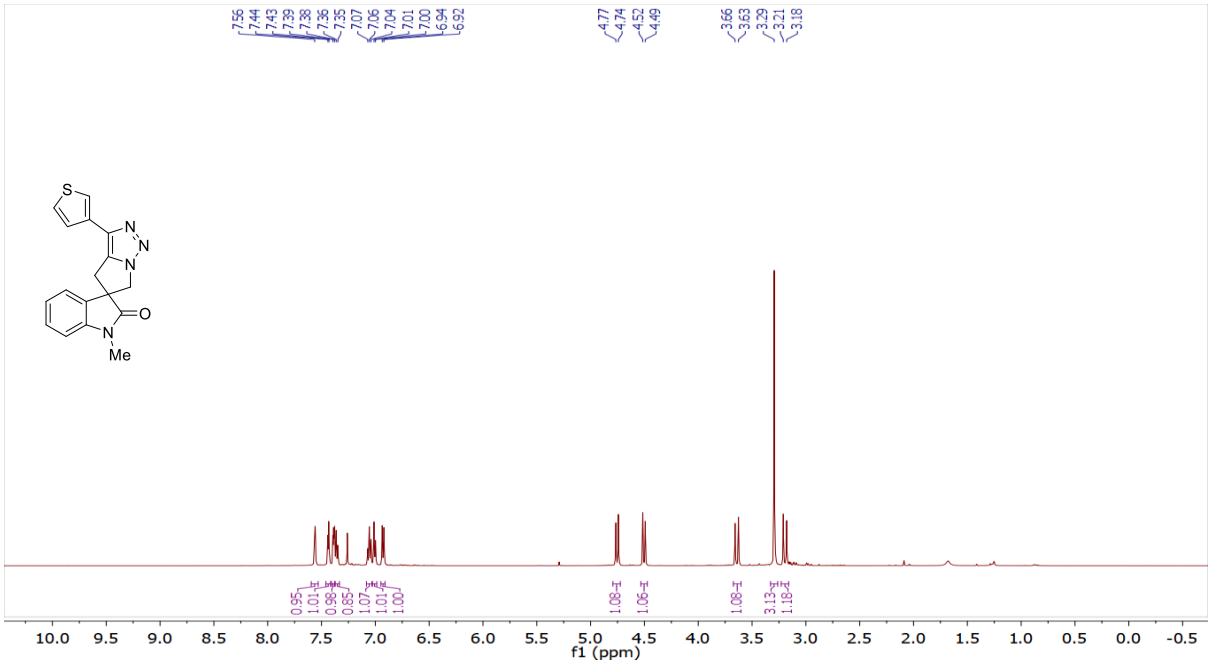
^{1}H NMR of 7l (300 MHz, $CDCl_3$):



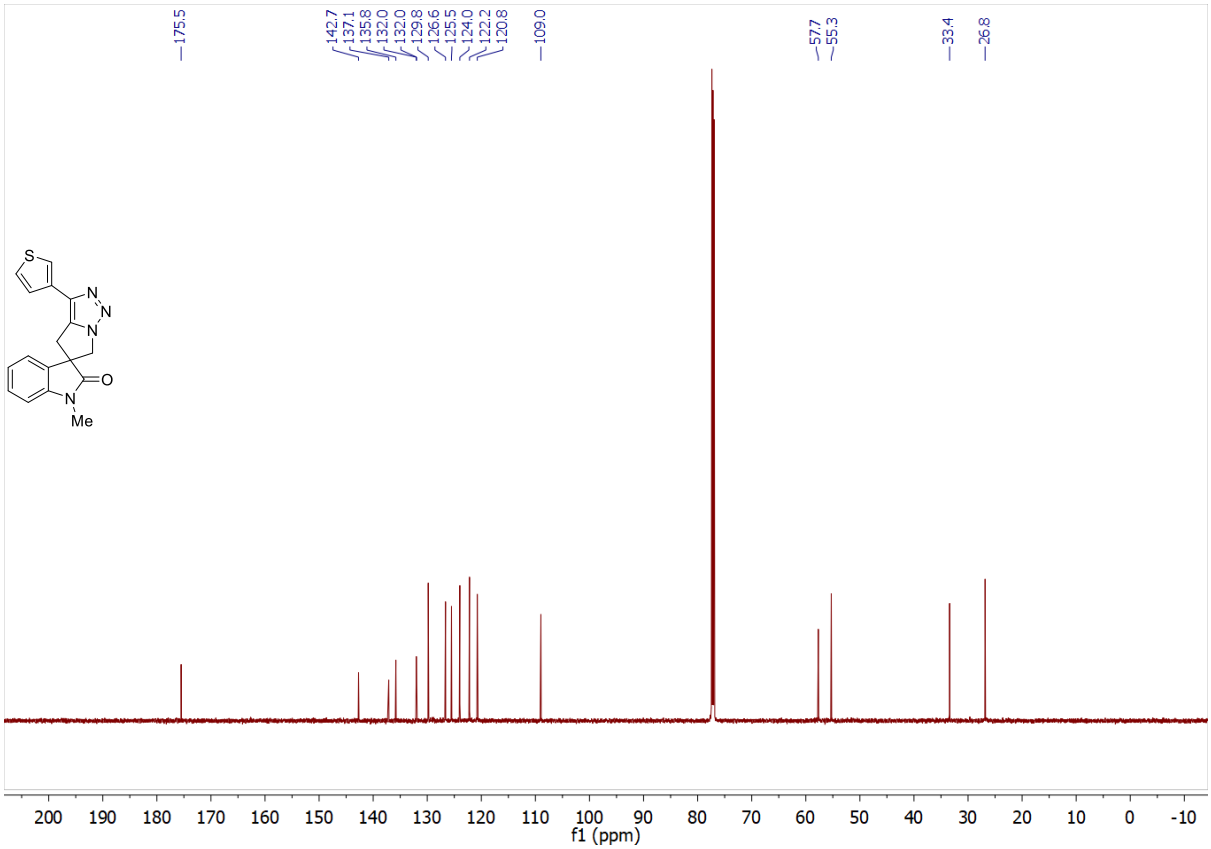
^{13}C{^{1}H} NMR of 7l (151 MHz, $CDCl_3$):



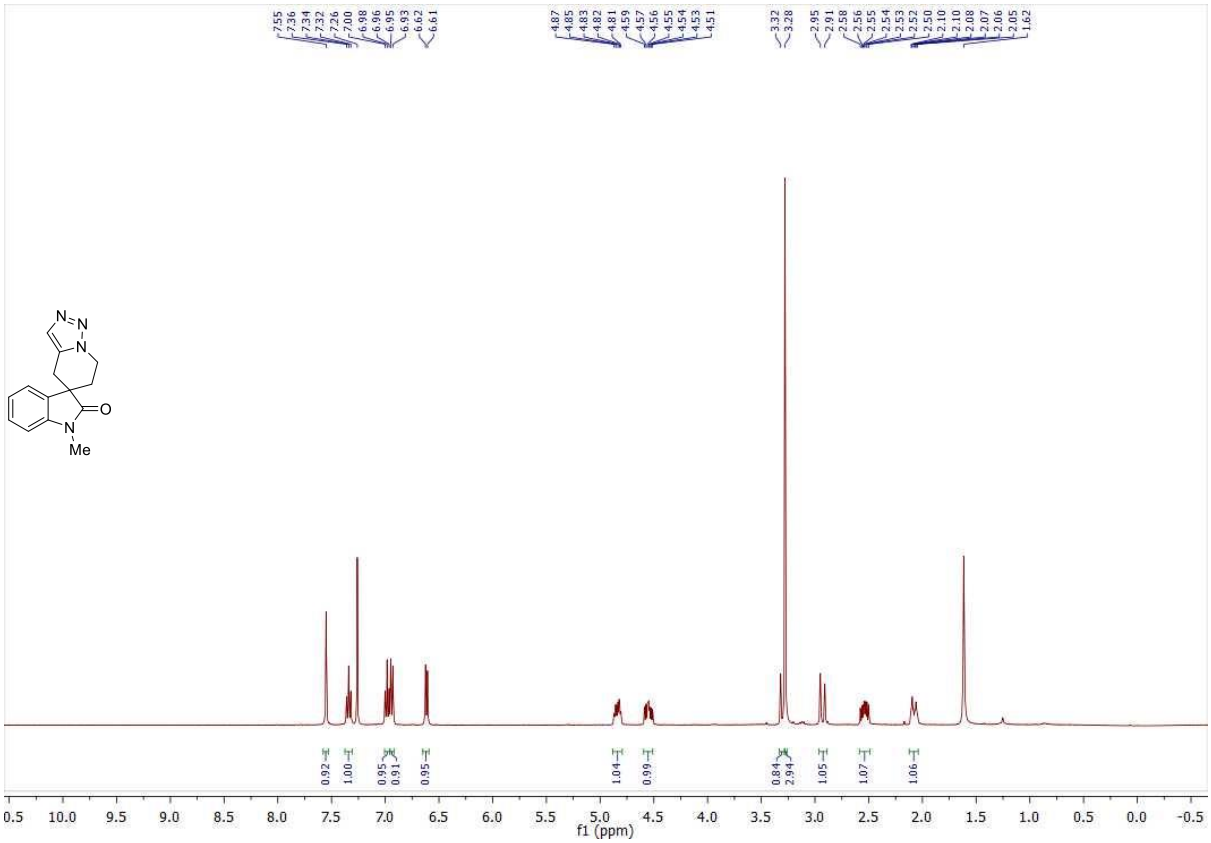
^{1}H NMR of 7m (500 MHz, $CDCl_3$):



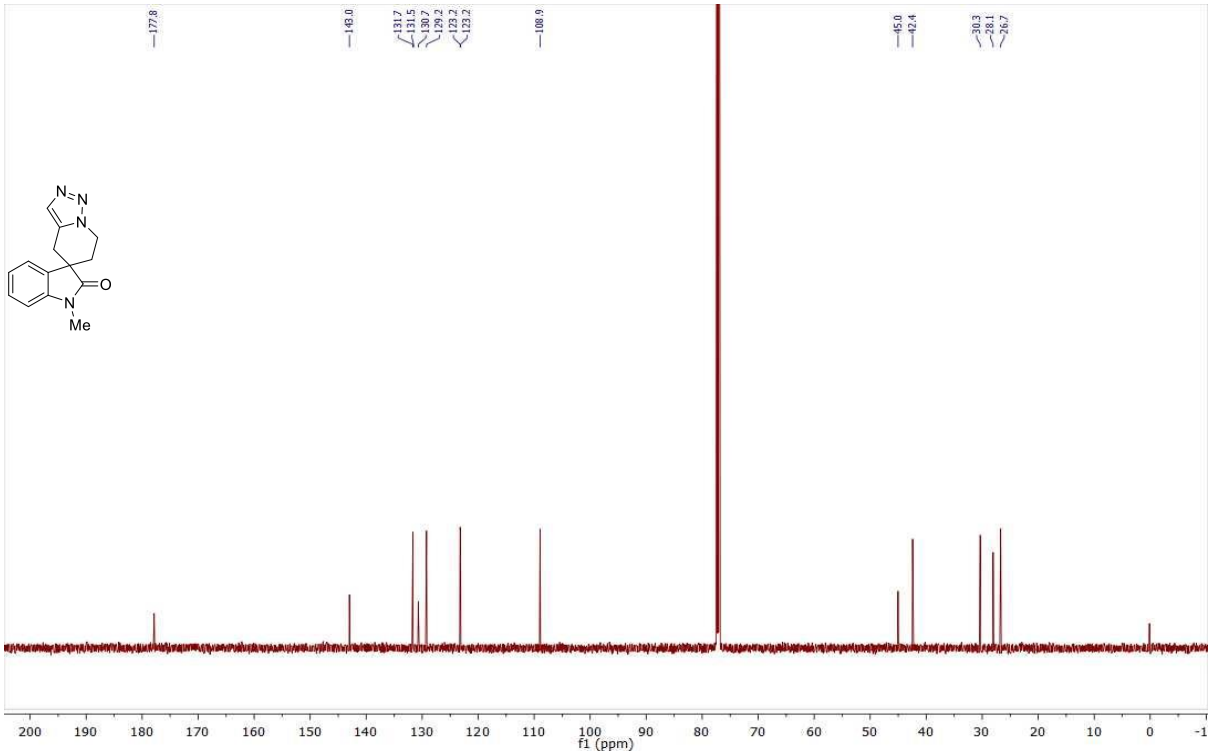
^{13}C{^{1}H} NMR of 7m (151 MHz, $CDCl_3$):



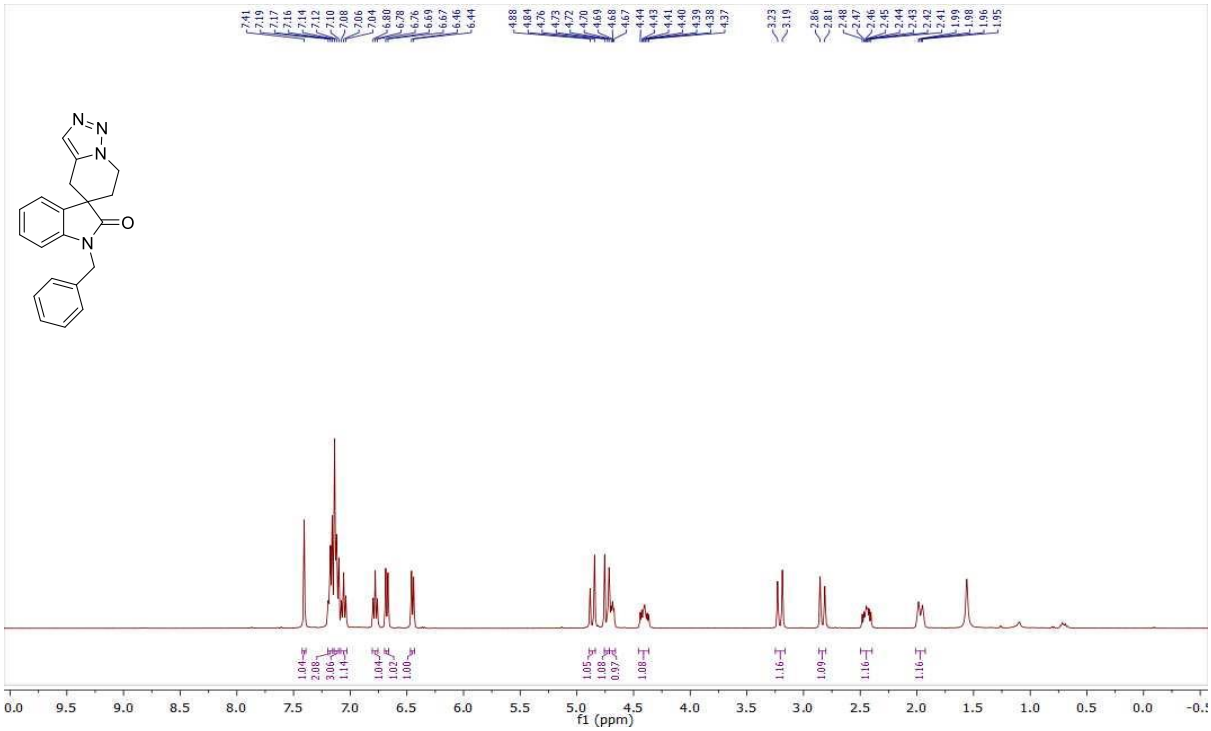
^{1}H NMR of 8a (400 MHz, $CDCl_3$):



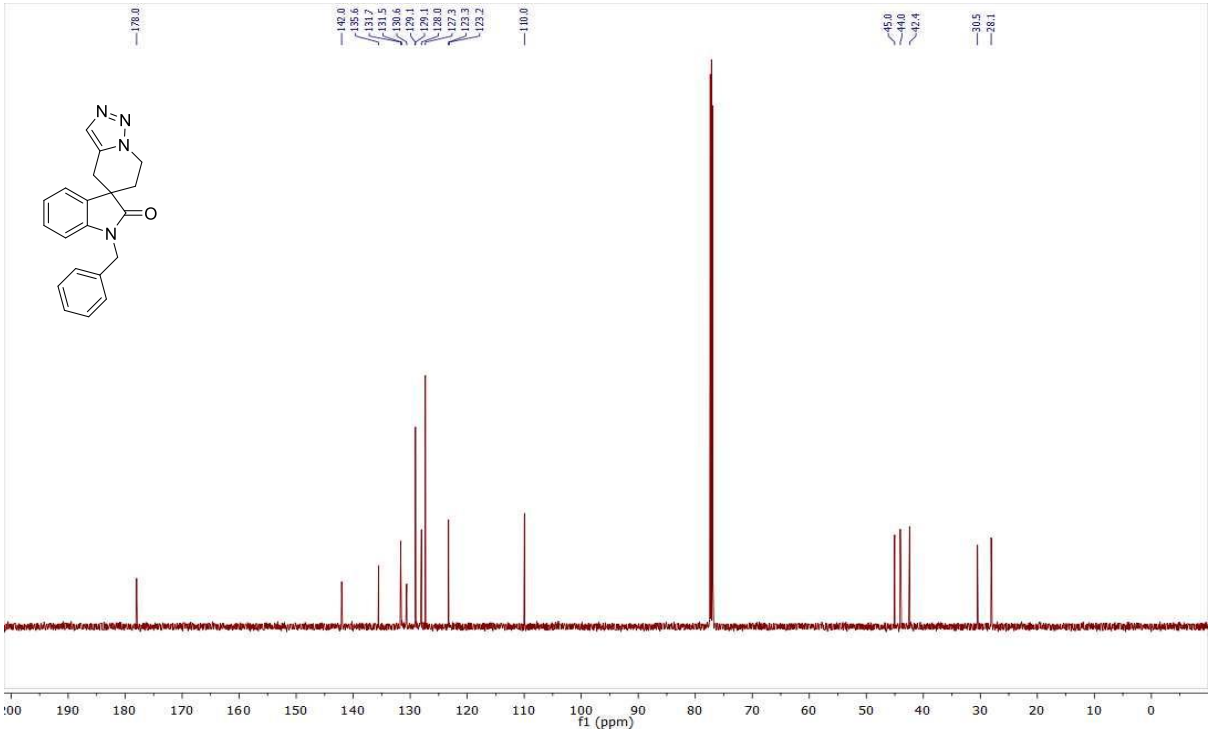
^{13}C{^{1}H} NMR of 8a (151 MHz, $CDCl_3$):



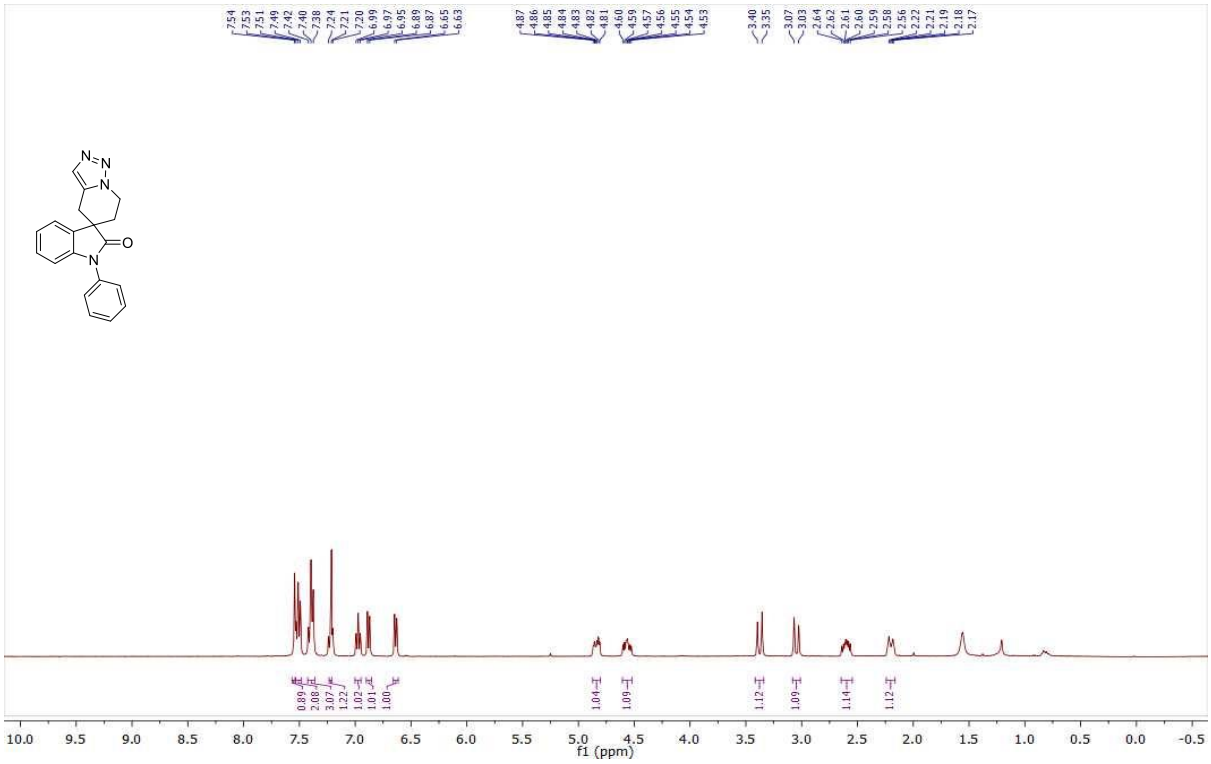
^{1}H NMR of 8b (400 MHz, $CDCl_3$):



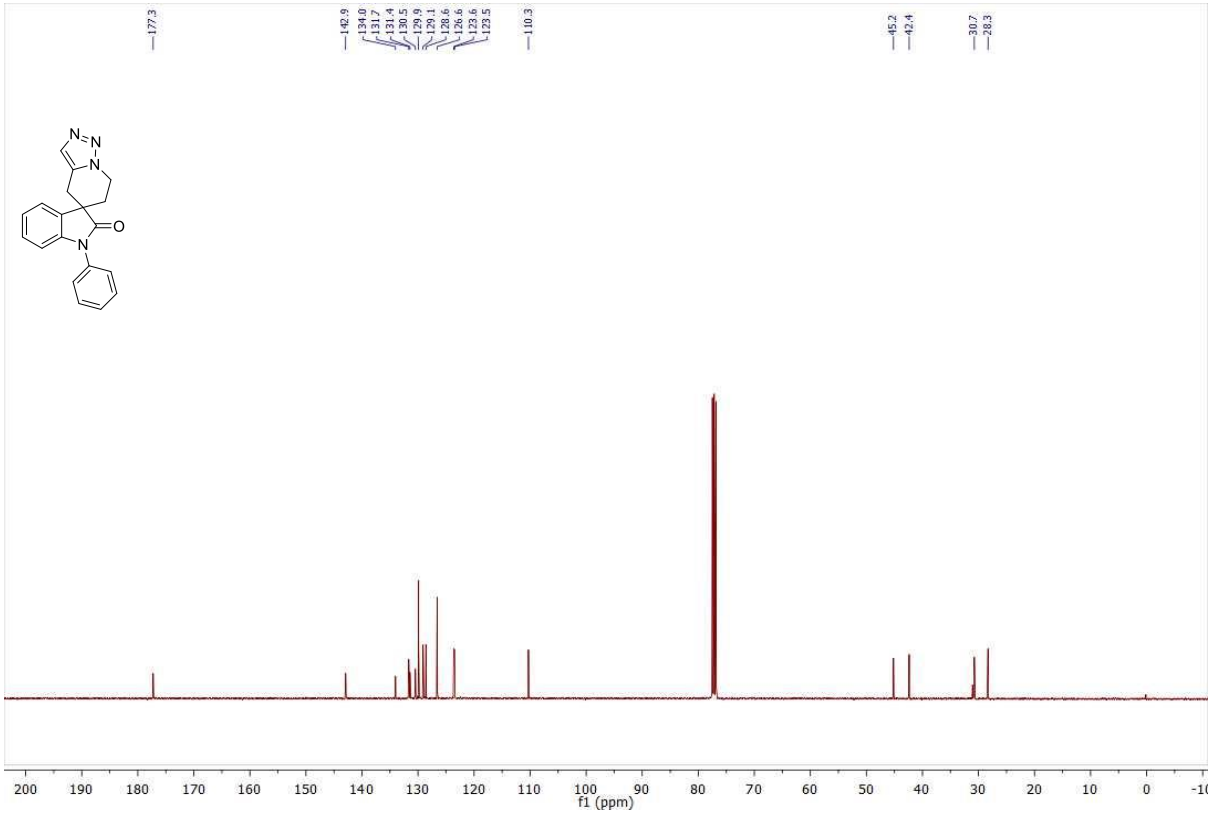
$^{13}C\{^{1}H\}$ NMR of 8b (151 MHz, $CDCl_3$):



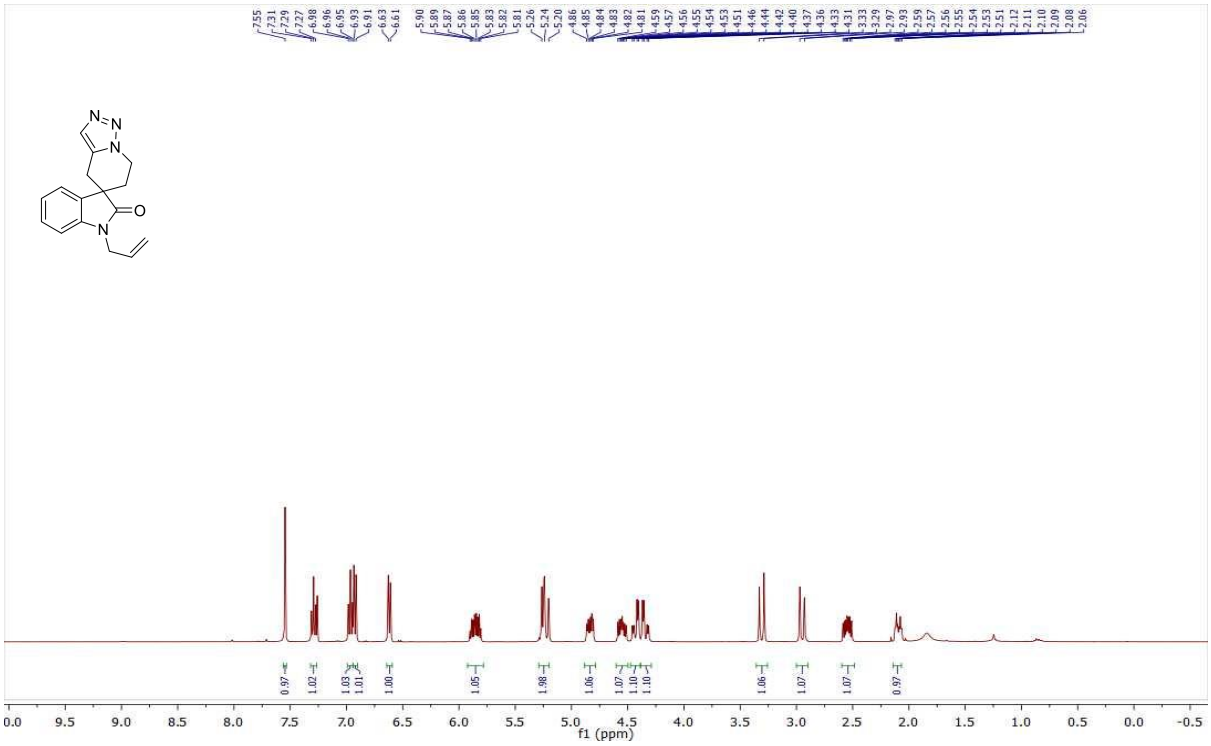
^{1}H NMR of 8c (400 MHz, $CDCl_3$):



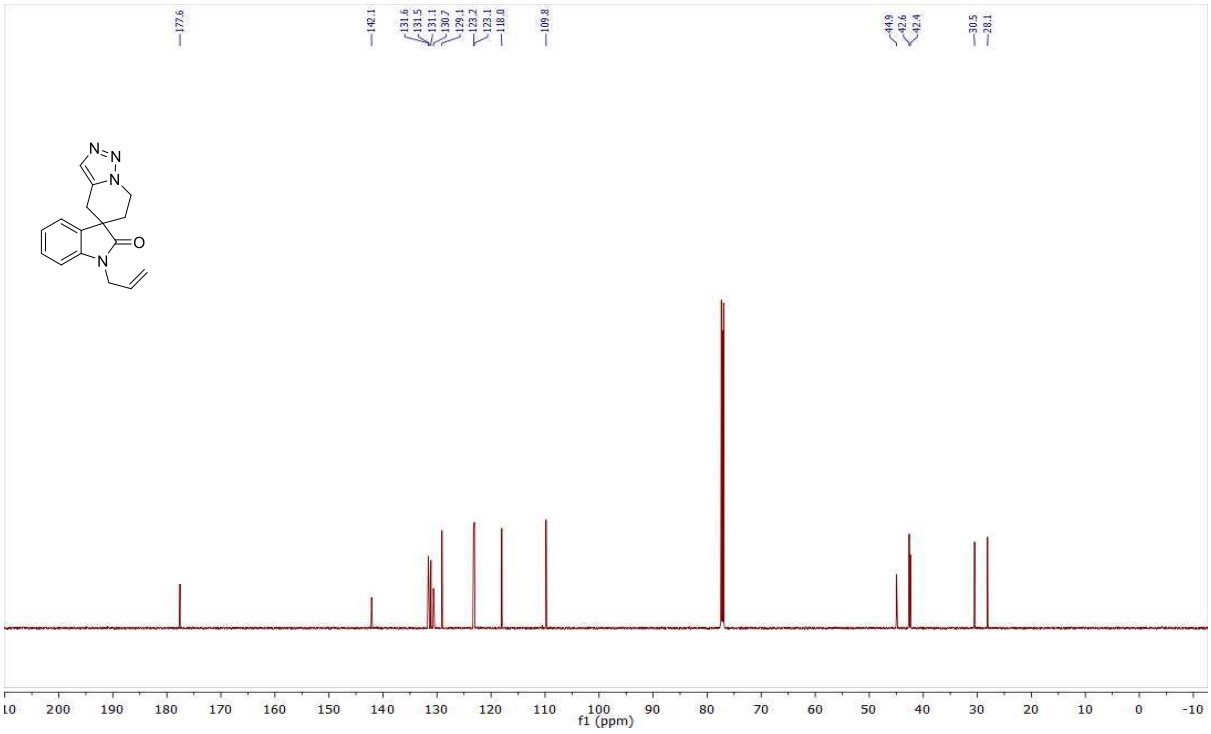
^{13}C{^{1}H} NMR of 8c (101 MHz, $CDCl_3$):



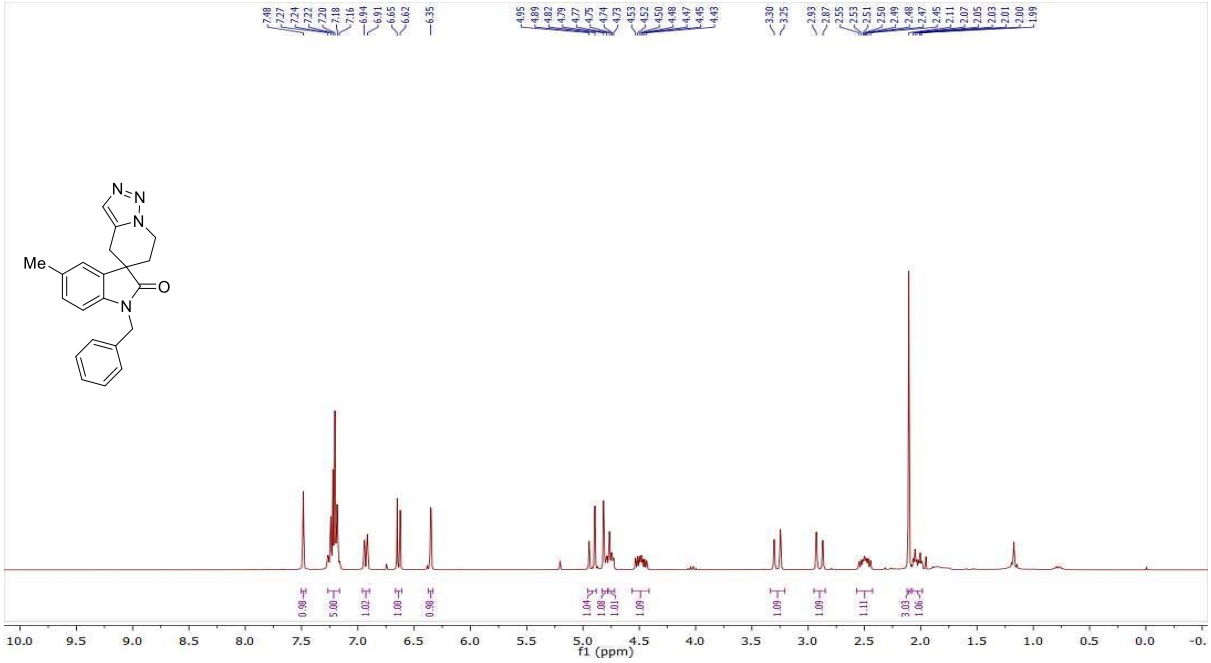
^{1}H NMR of 8d (400 MHz, $CDCl_3$):



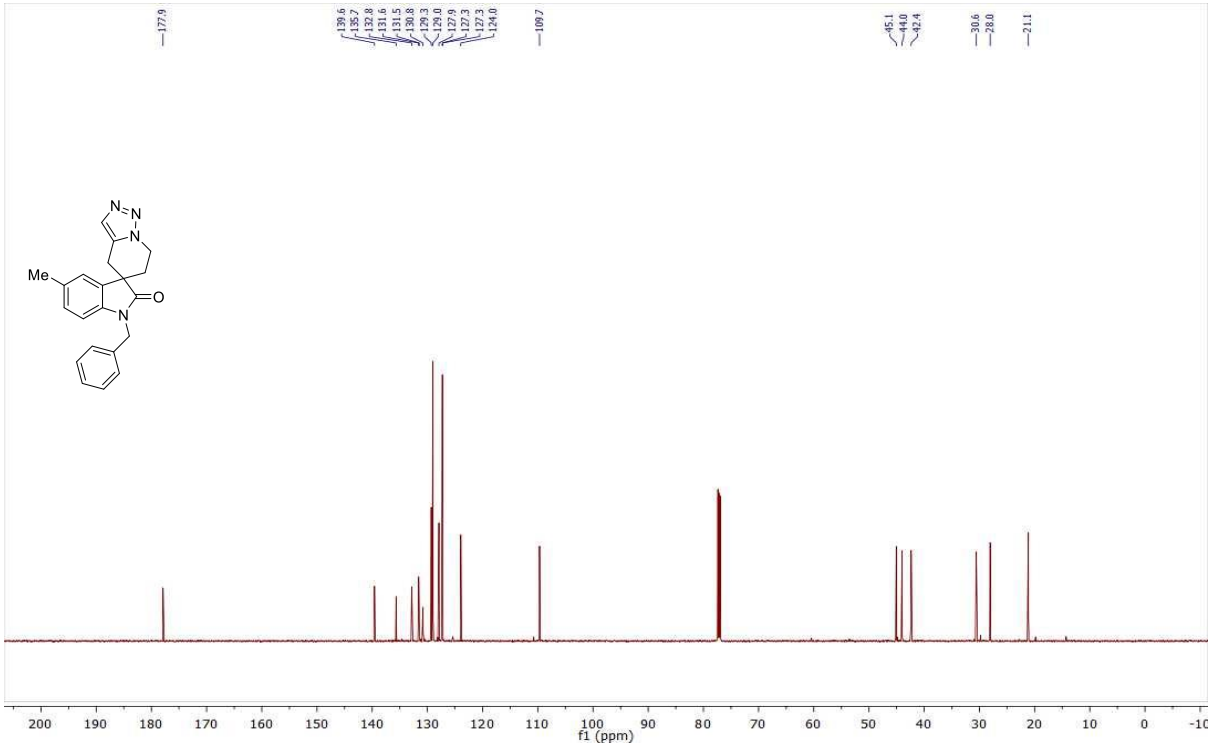
^{13}C{^{1}H} NMR of 8d (151 MHz, $CDCl_3$):



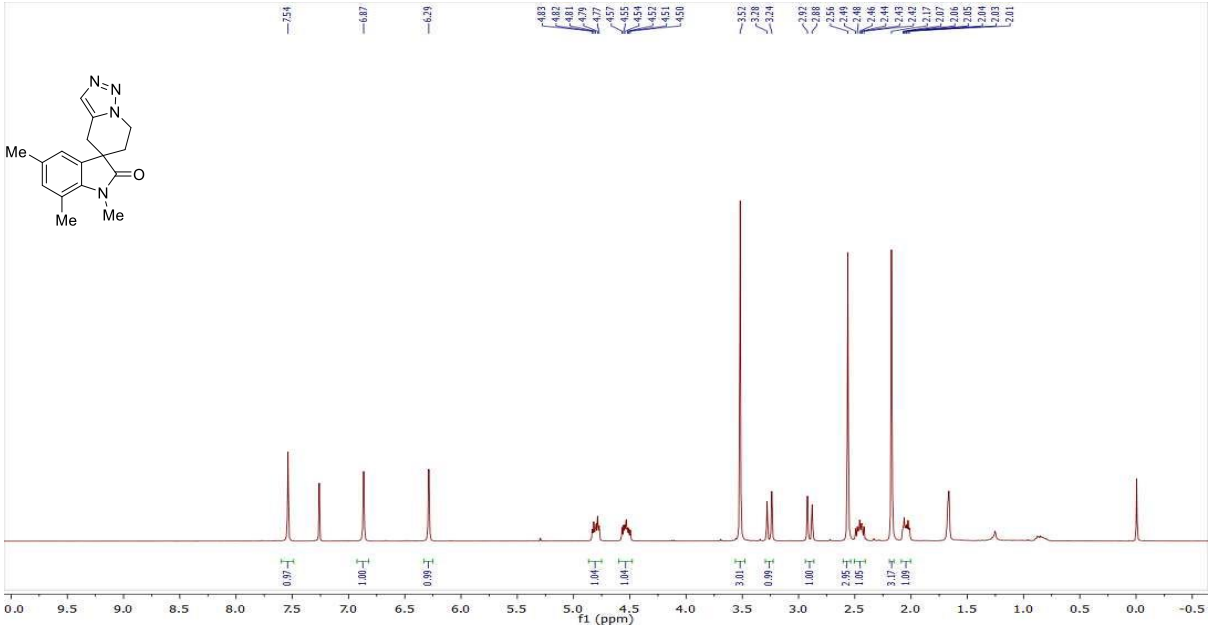
^{1}H NMR of 8e (300 MHz, $CDCl_3$):



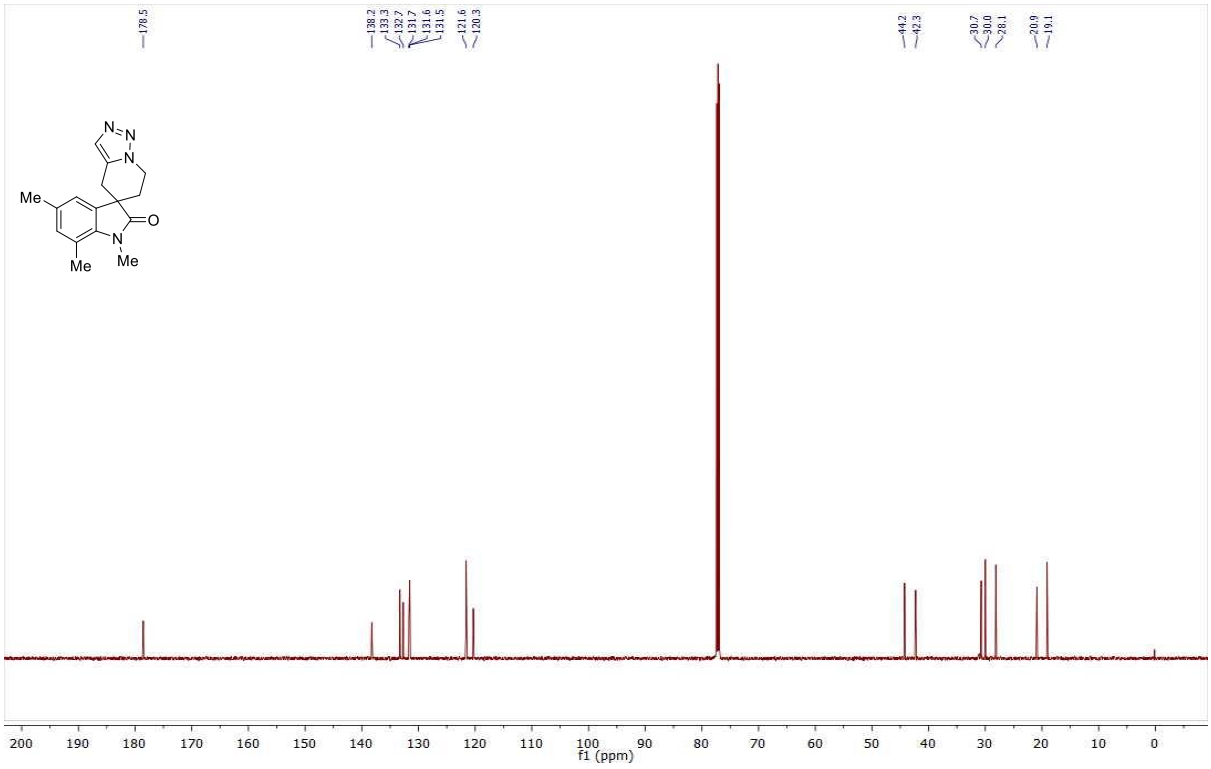
^{13}C{^{1}H} NMR of 8e (151 MHz, $CDCl_3$):



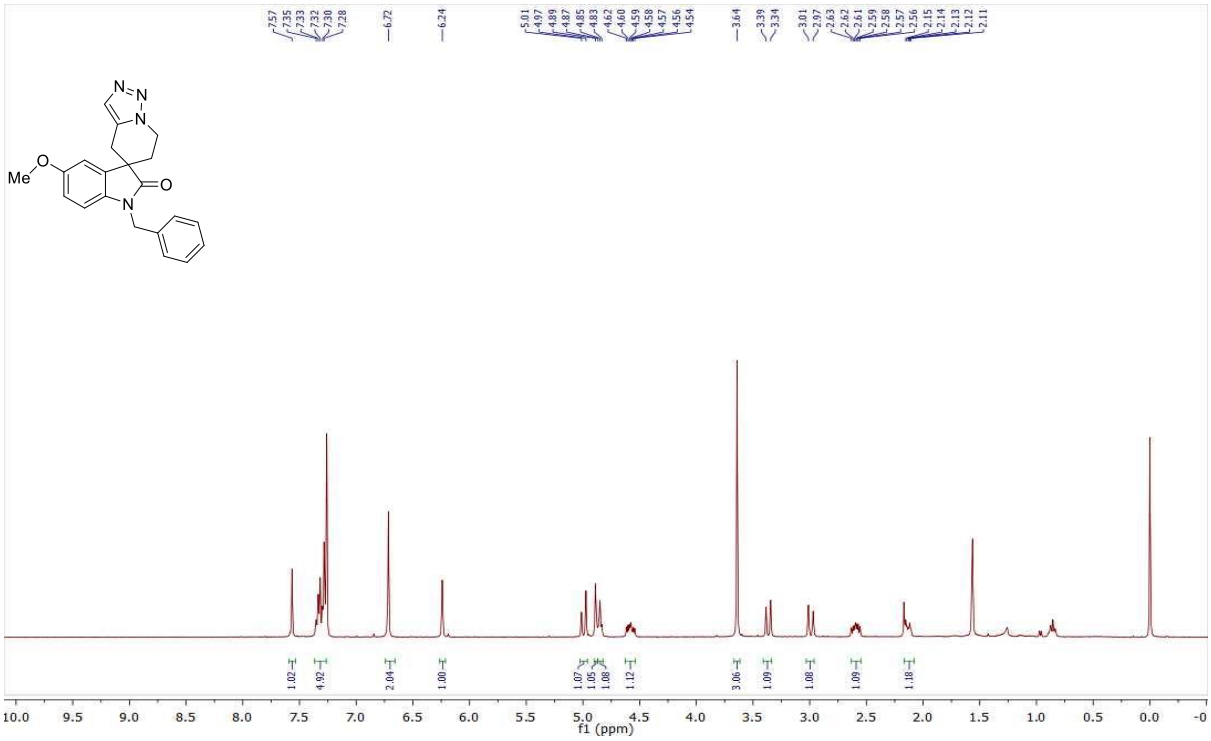
^{1}H NMR of 8f (400 MHz, $CDCl_3$):



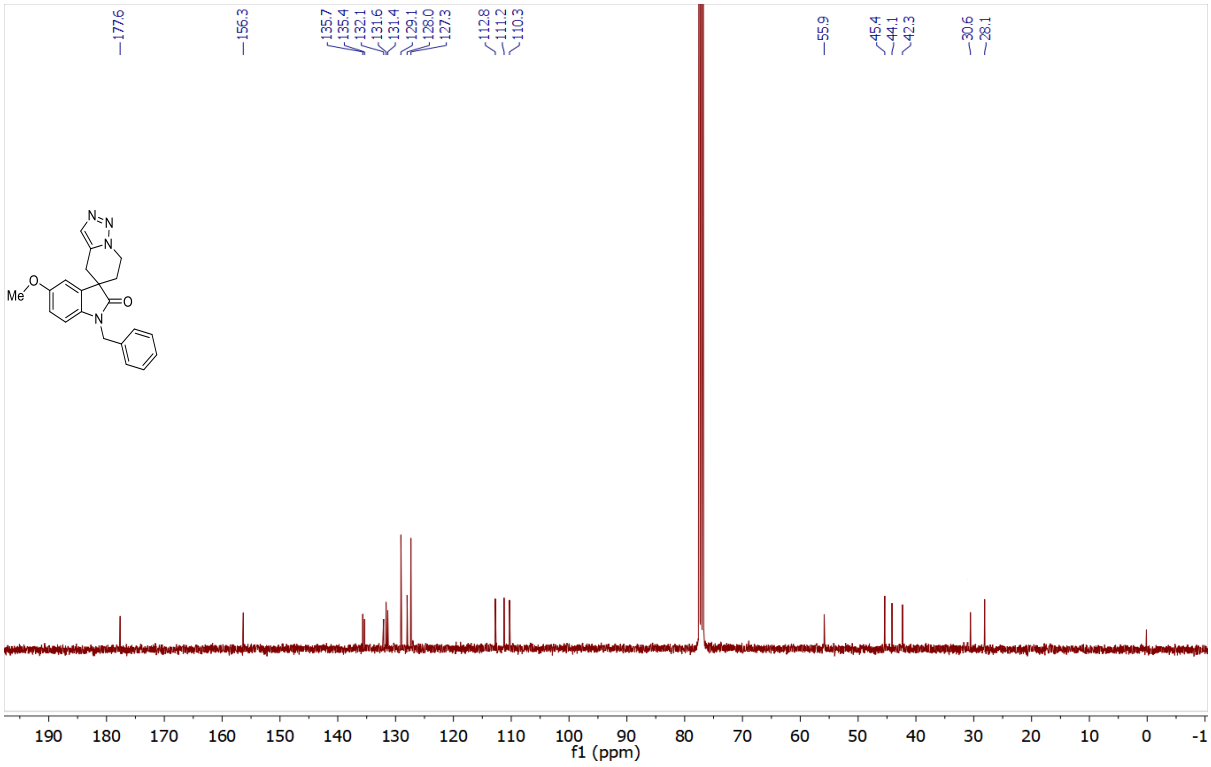
^{13}C{^{1}H} NMR of 8f (151 MHz, $CDCl_3$):



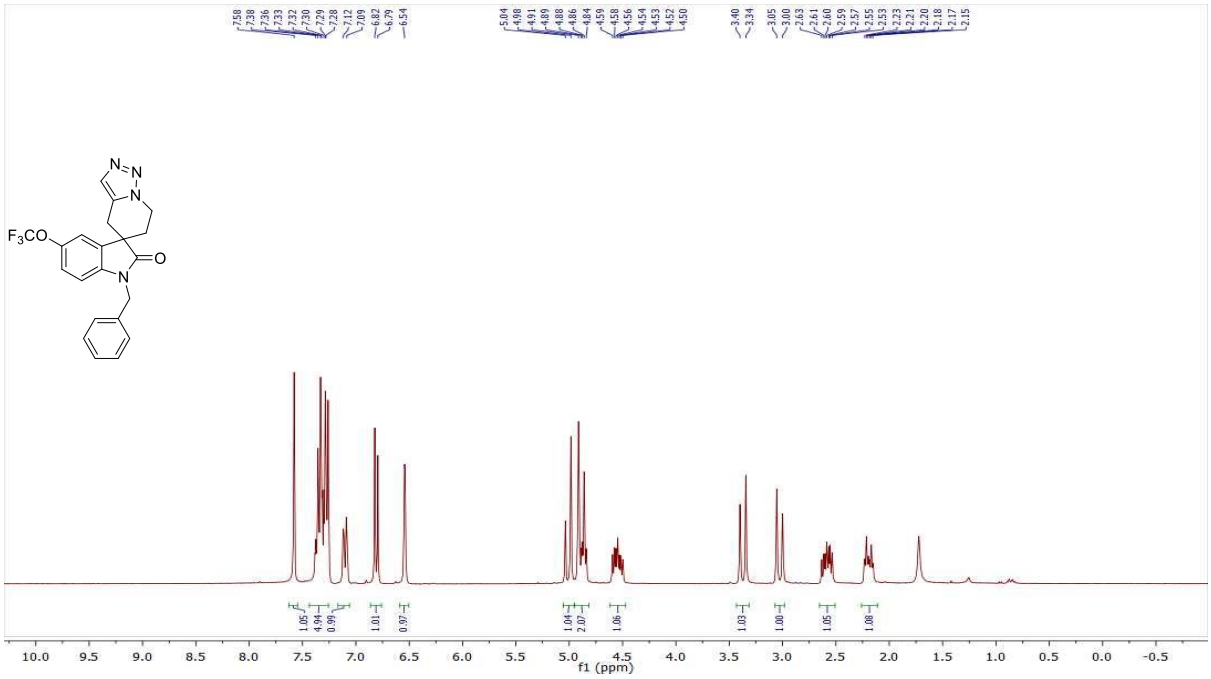
^{1}H NMR of 8g (400 MHz, $CDCl_3$):



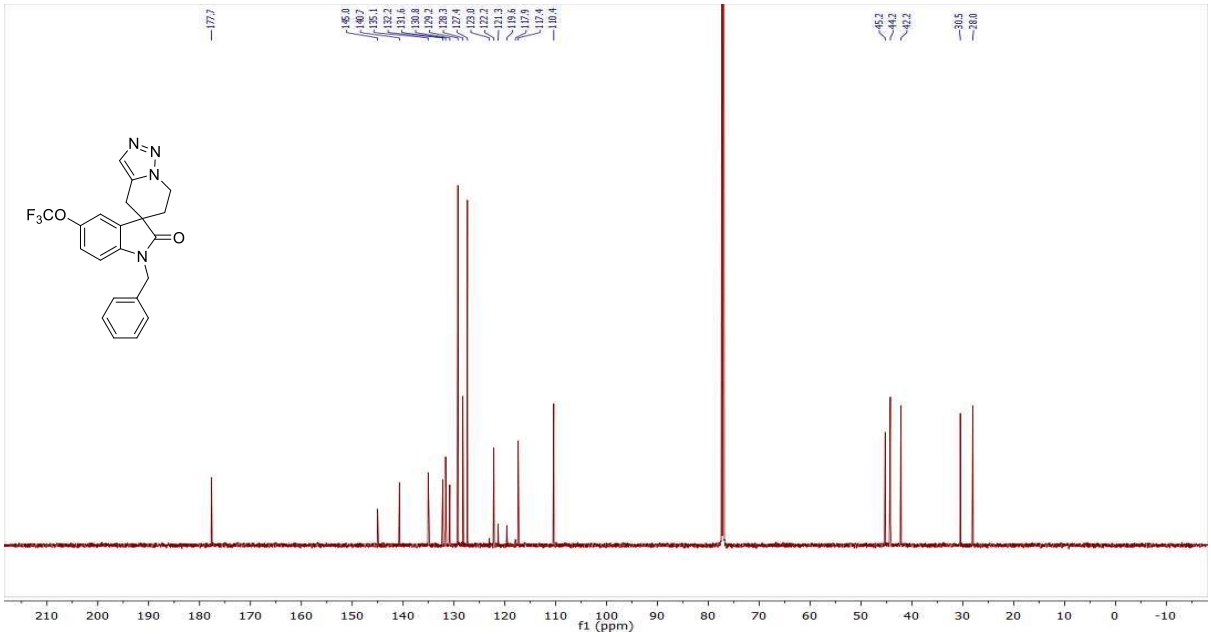
^{13}C{^{1}H} NMR of 8g (101 MHz, $CDCl_3$):



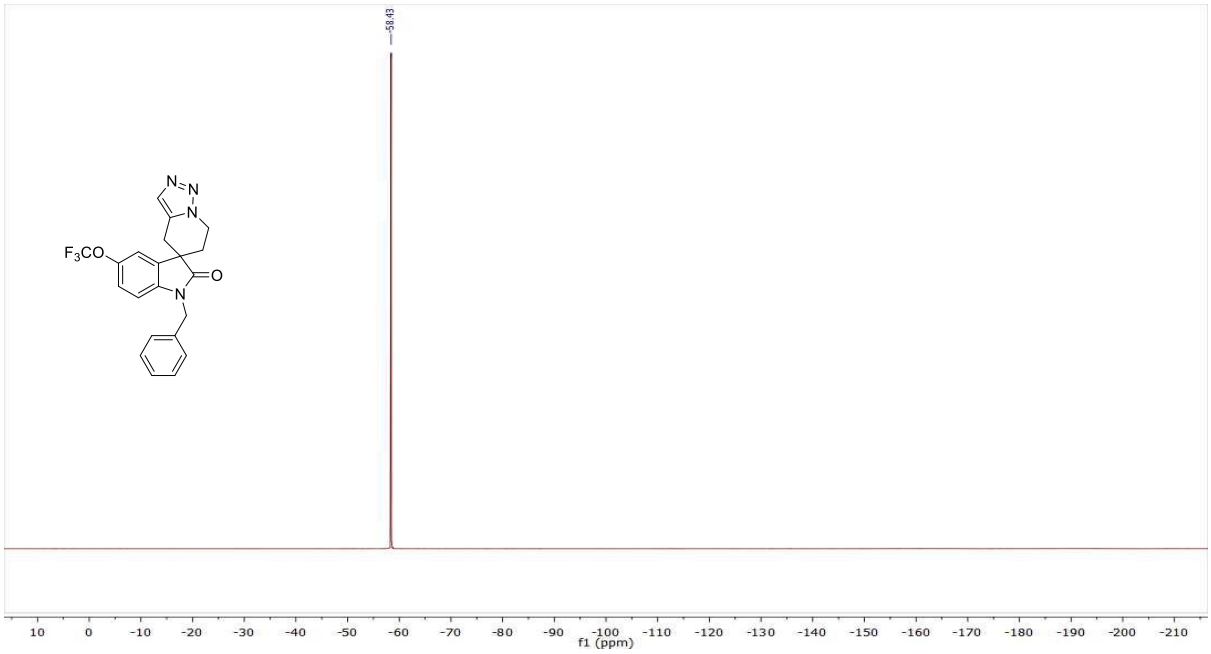
^{1}H NMR of 8h (300 MHz, $CDCl_3$):



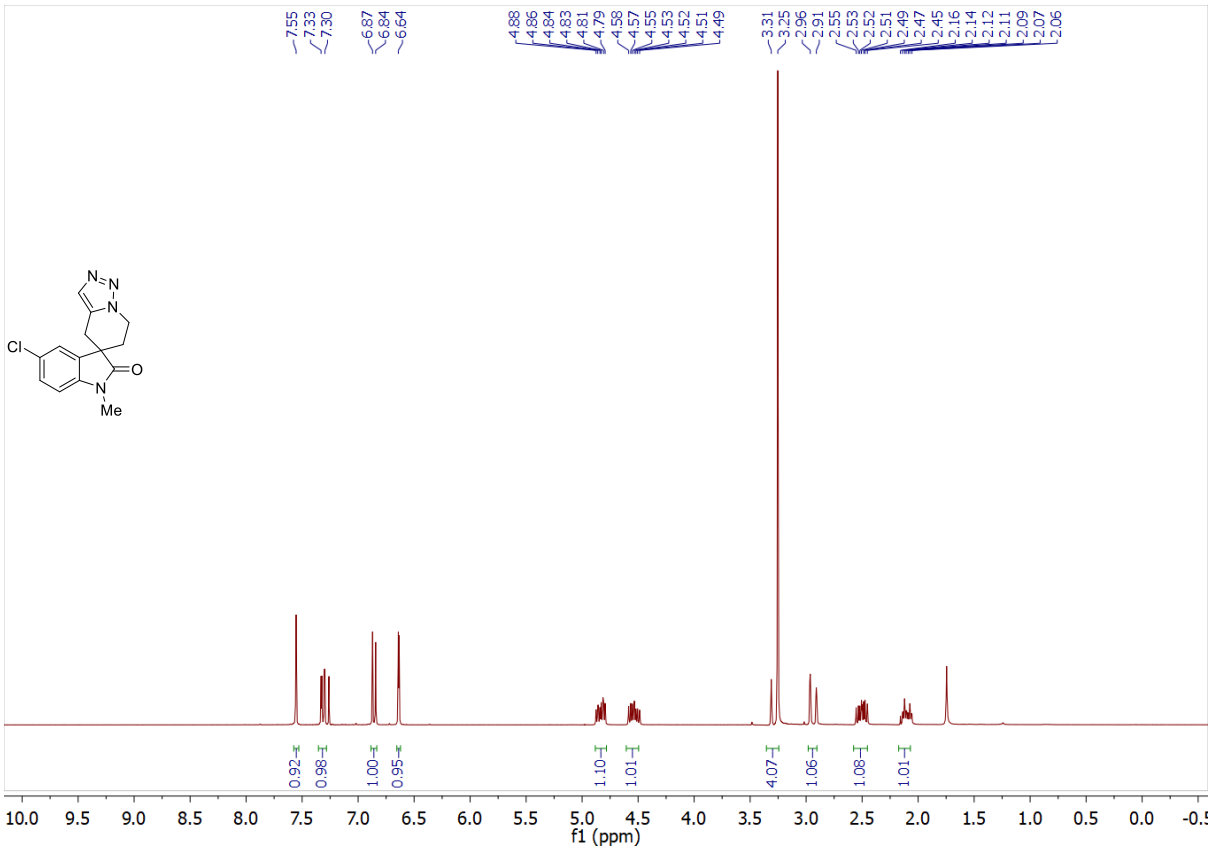
$^{13}C\{^{1}H\}$ NMR of 8h (151 MHz, $CDCl_3$):



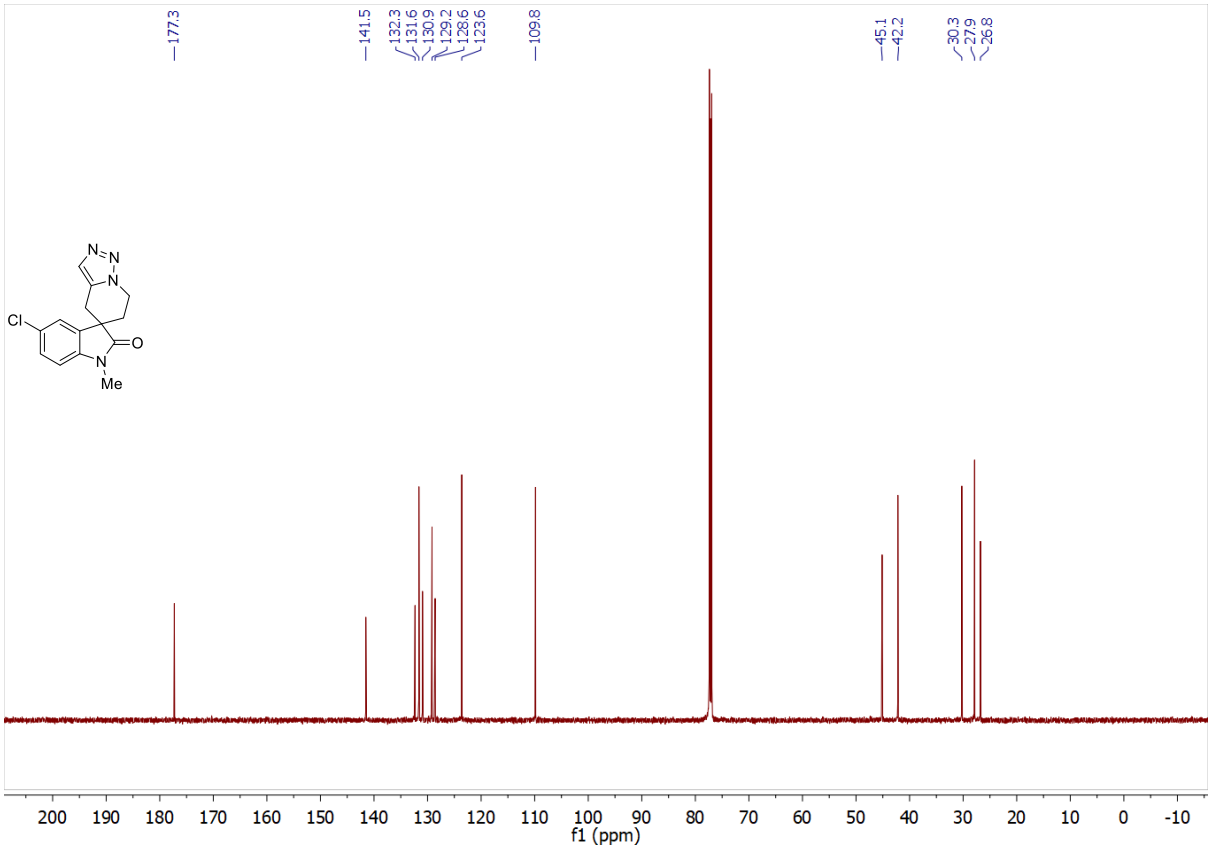
$^{19}F\{^{1}H\}$ NMR of 8h (565 MHz, $CDCl_3$):



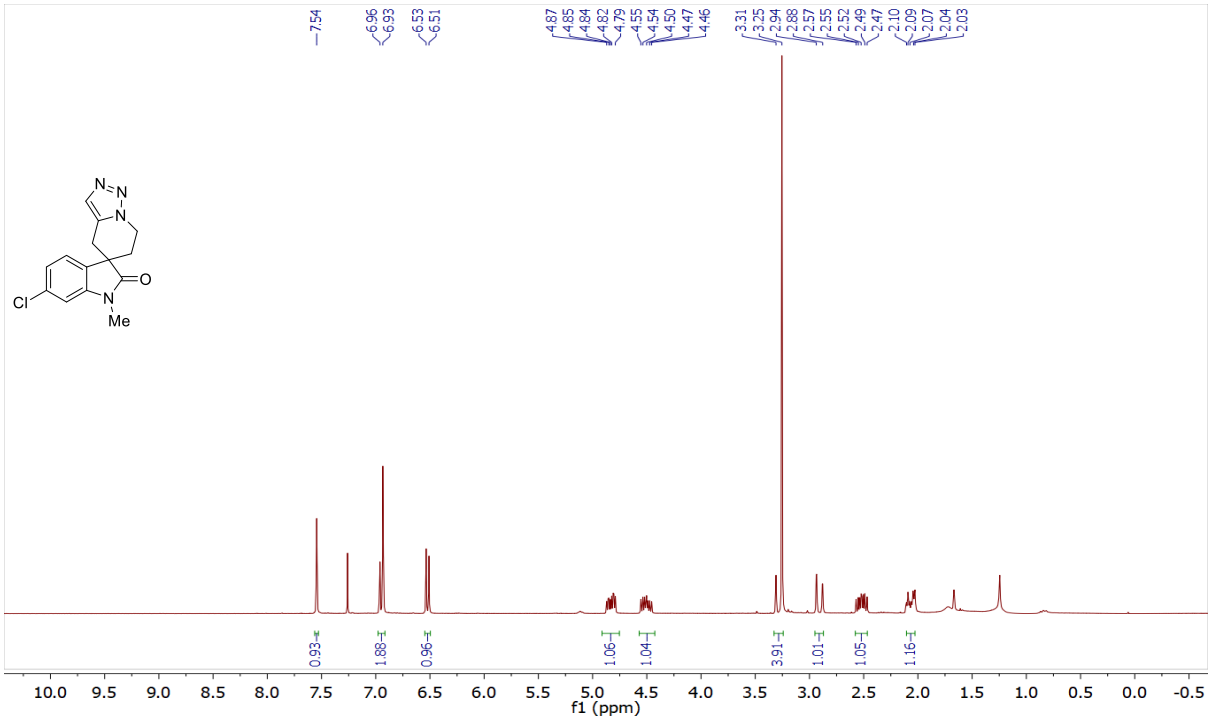
^{1}H NMR of 8i (300 MHz, $CDCl_3$):



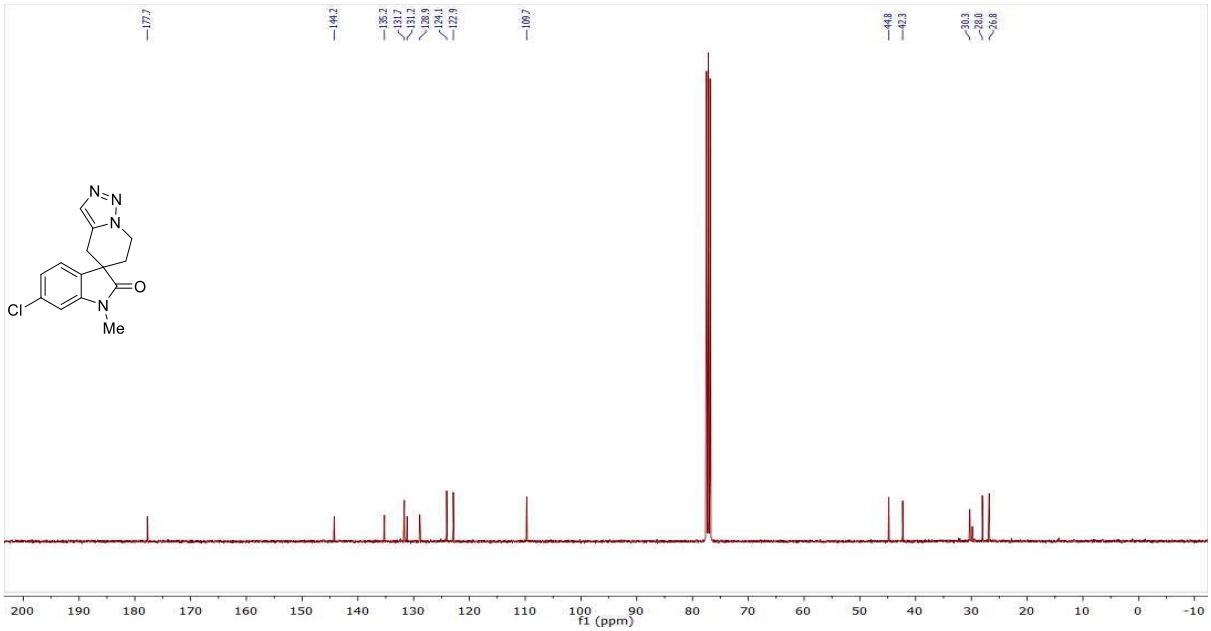
$^{13}C\{^{1}H\}$ NMR of 8i (151 MHz, $CDCl_3$):



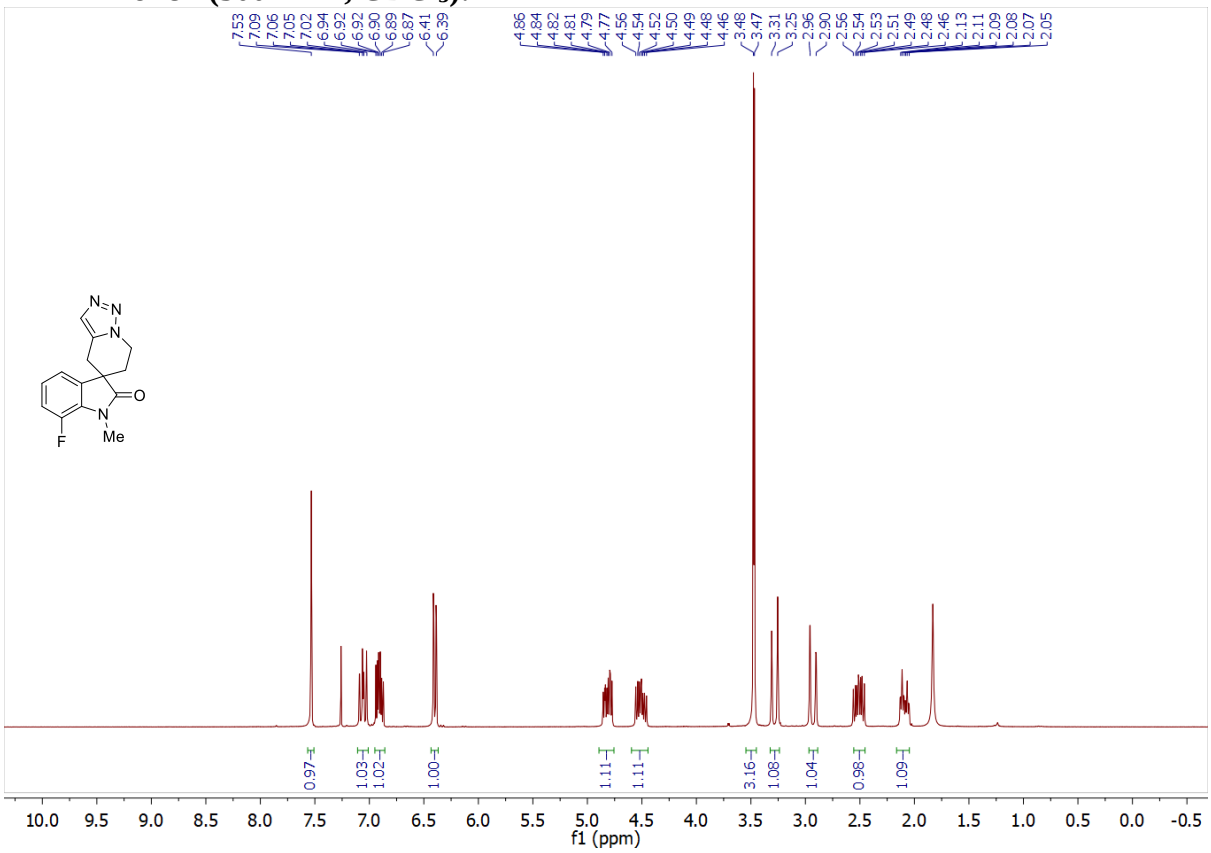
^{1}H NMR of 8j (300 MHz, $CDCl_3$):



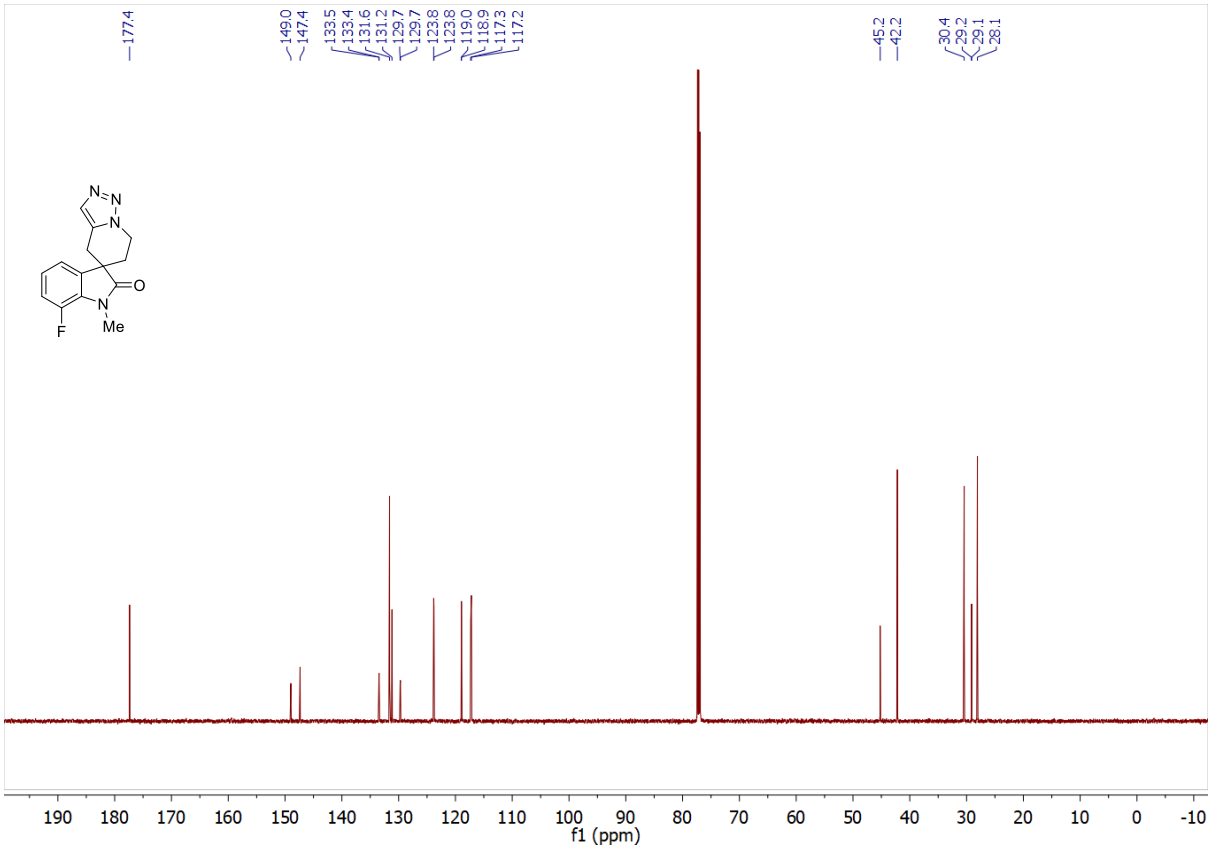
$^{13}C\{^{1}H\}$ NMR of 8j (101 MHz, $CDCl_3$):



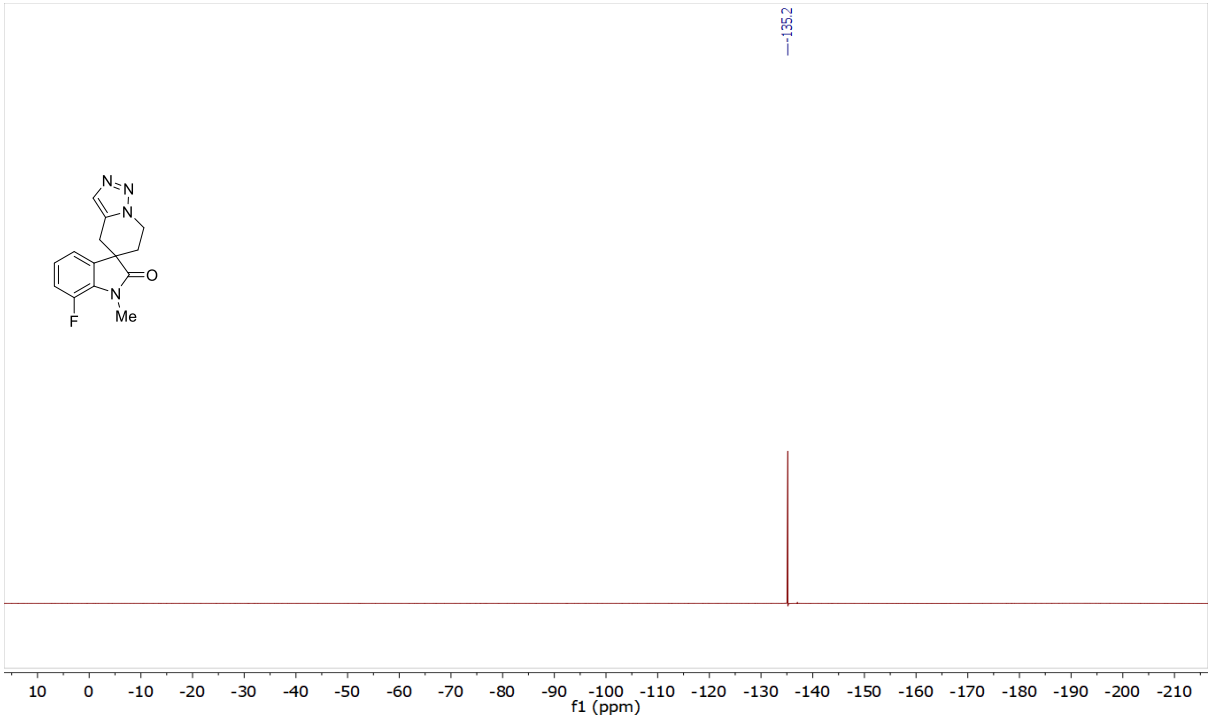
^{1}H NMR of 8k (300 MHz, $CDCl_3$):



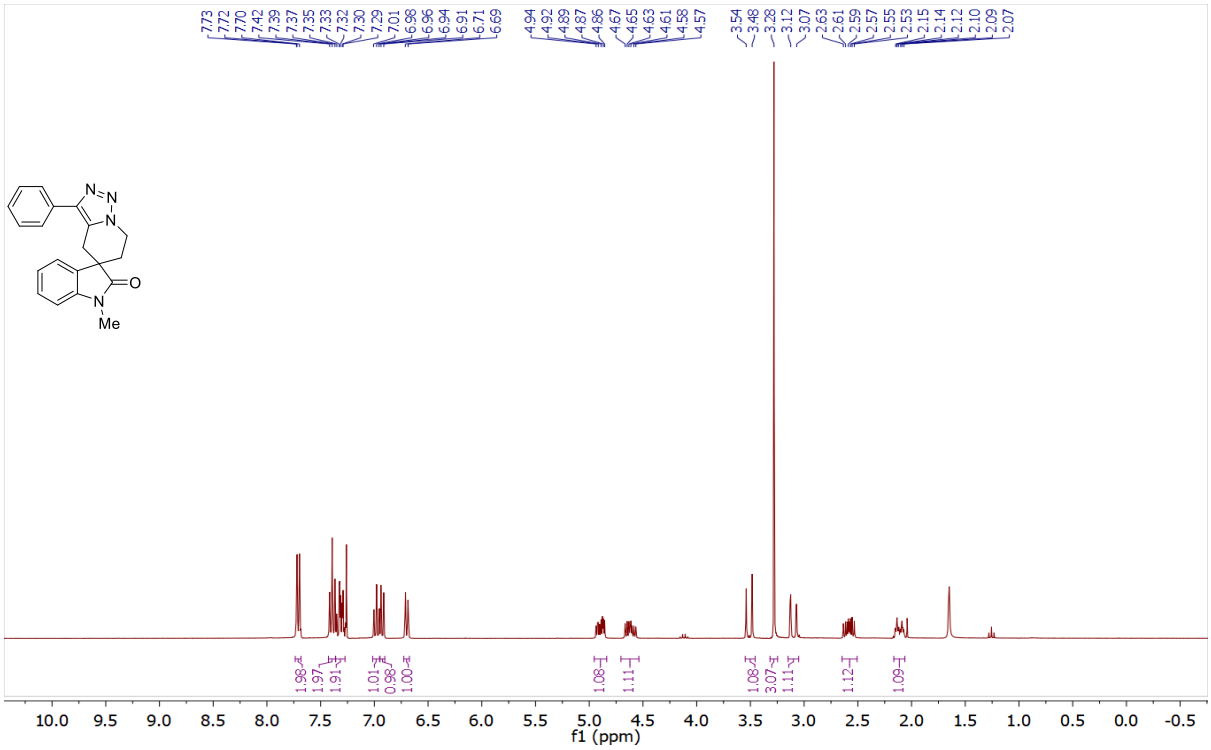
$^{13}C\{^{1}H\}$ NMR of 8k (151 MHz, $CDCl_3$):



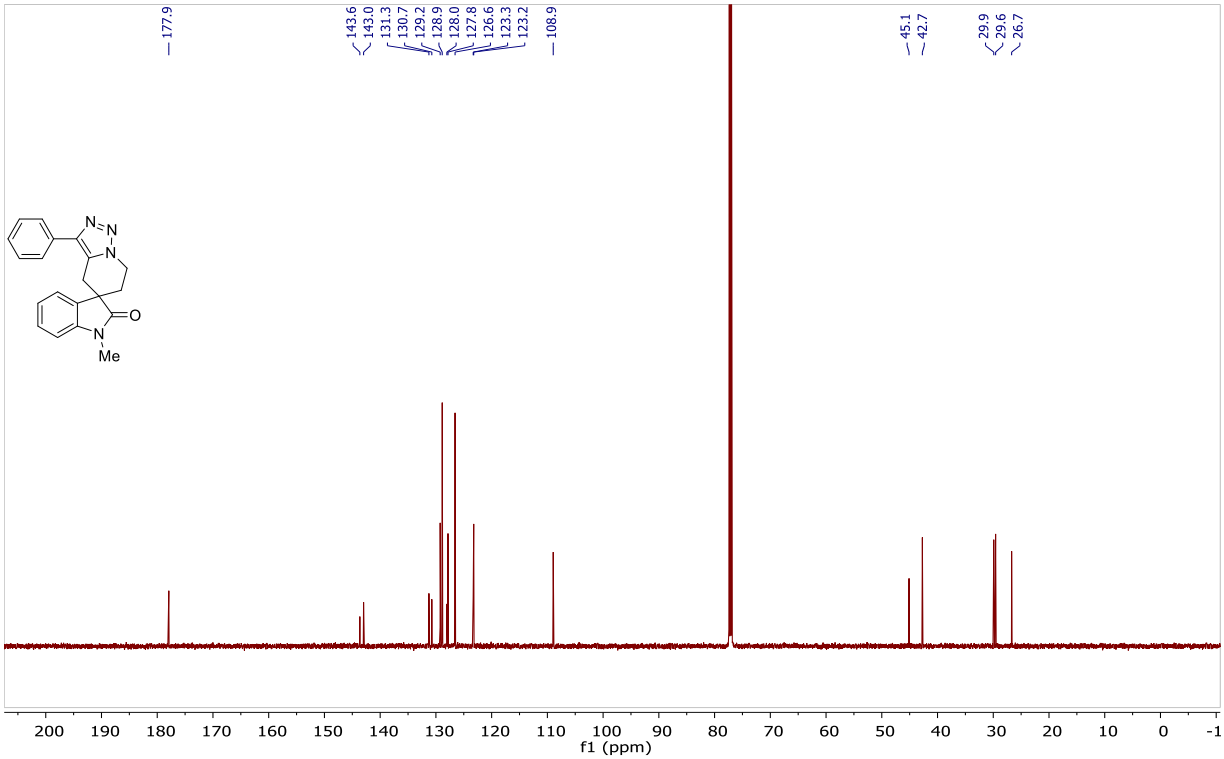
$^{19}F\{^{1}H\}$ NMR of 8k (565 MHz, $CDCl_3$):



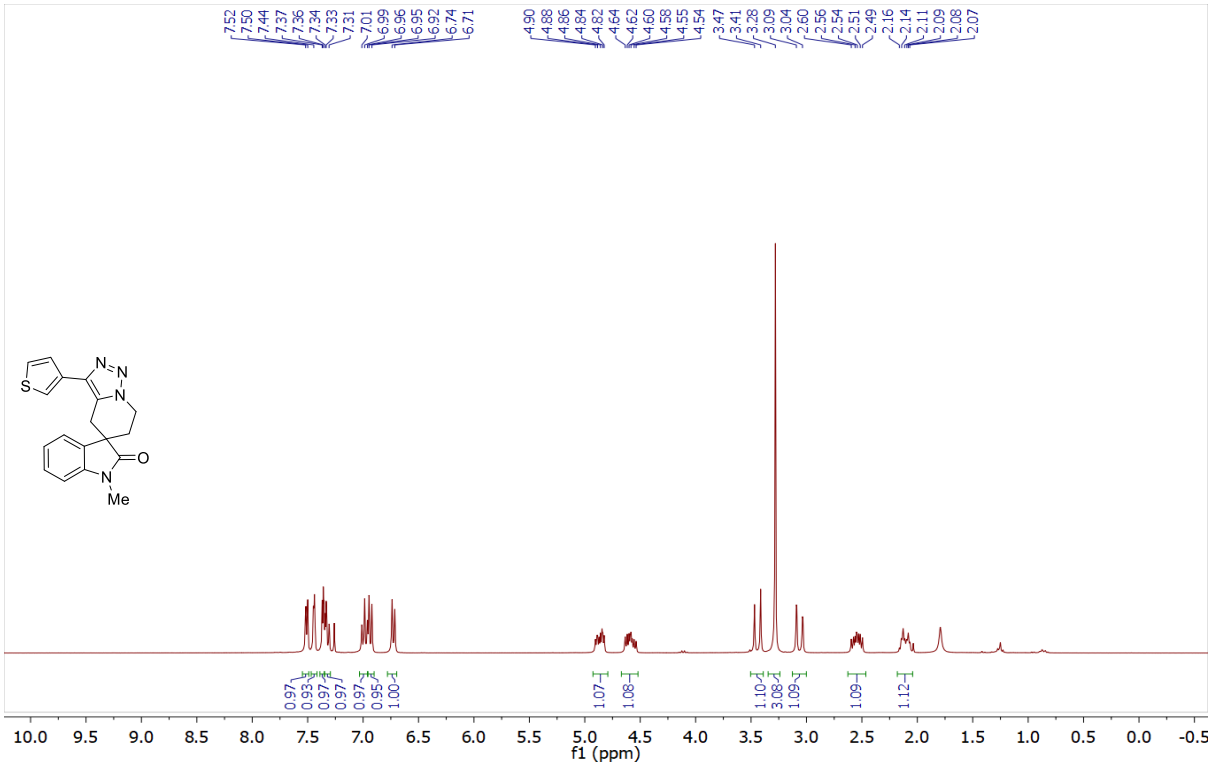
^{1}H NMR of 8l (300 MHz, $CDCl_3$):



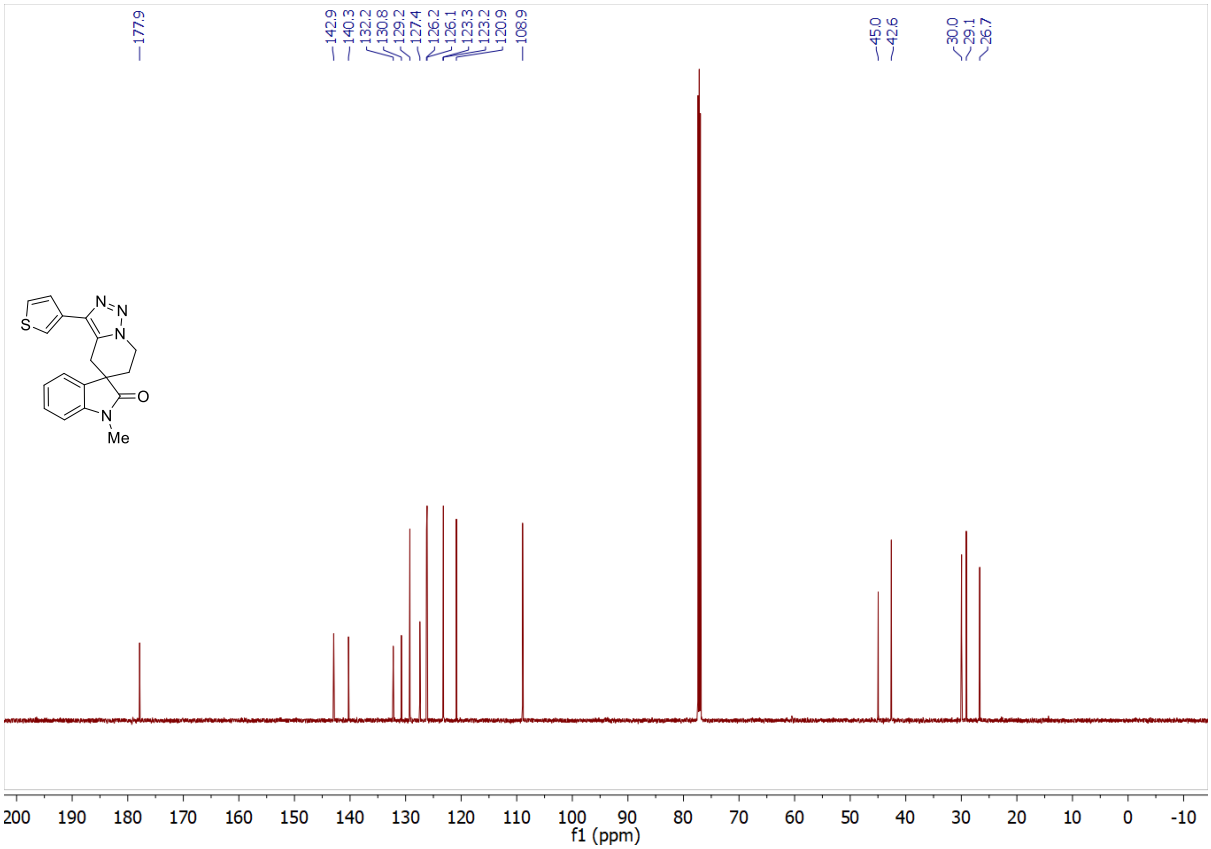
^{13}C{^{1}H} NMR of 8l (151 MHz, $CDCl_3$):



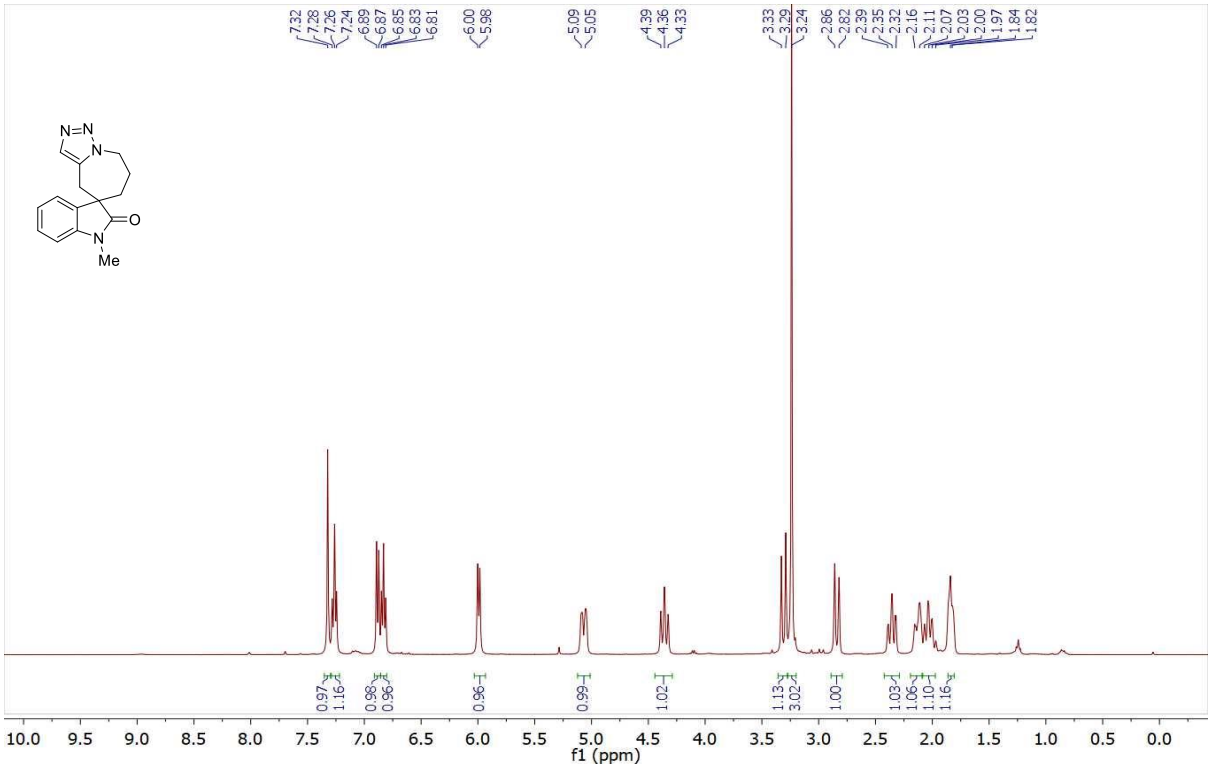
^{1}H NMR of 8m (300 MHz, $CDCl_3$):



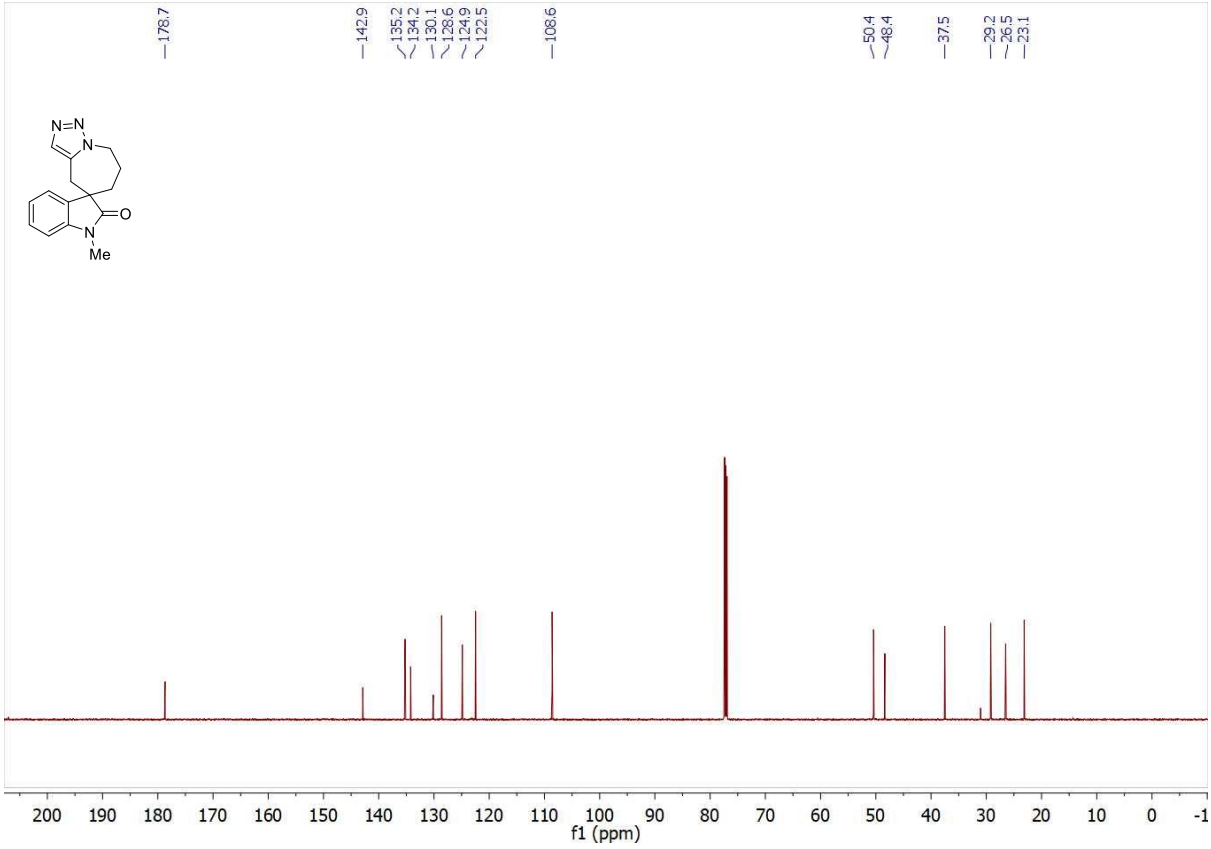
^{13}C{^{1}H} NMR of 8m (151 MHz, $CDCl_3$):



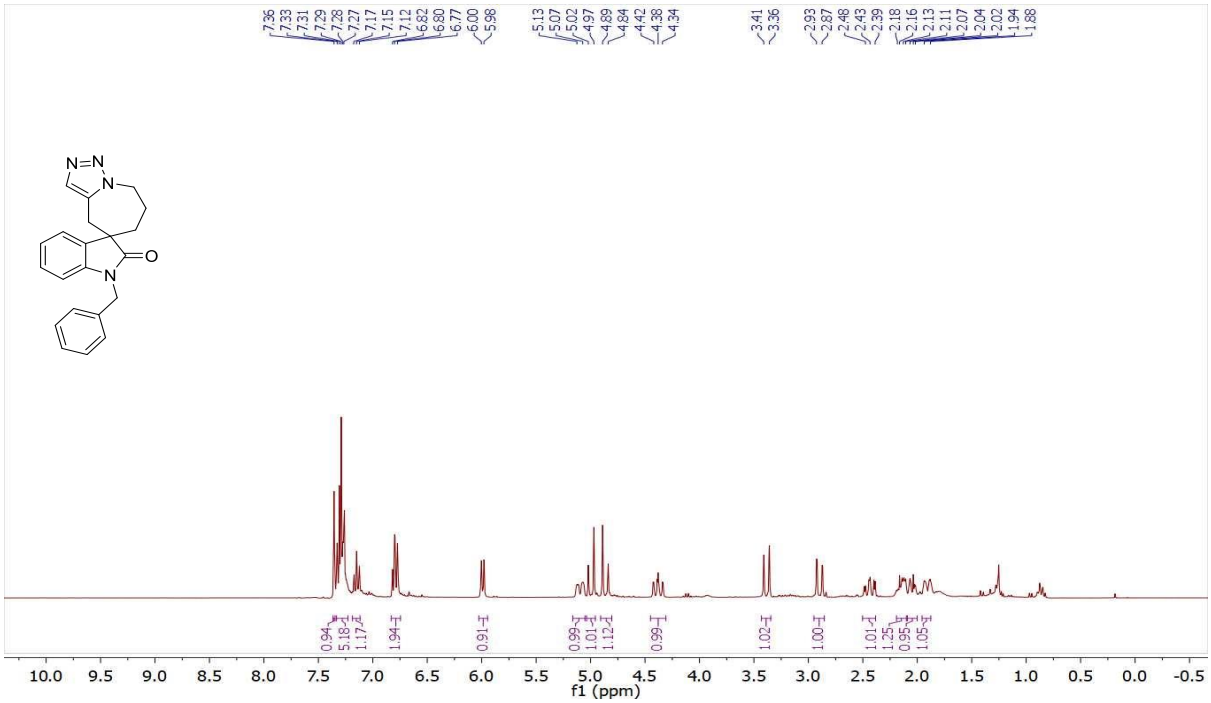
^{1}H NMR of 9a (400 MHz, $CDCl_3$):



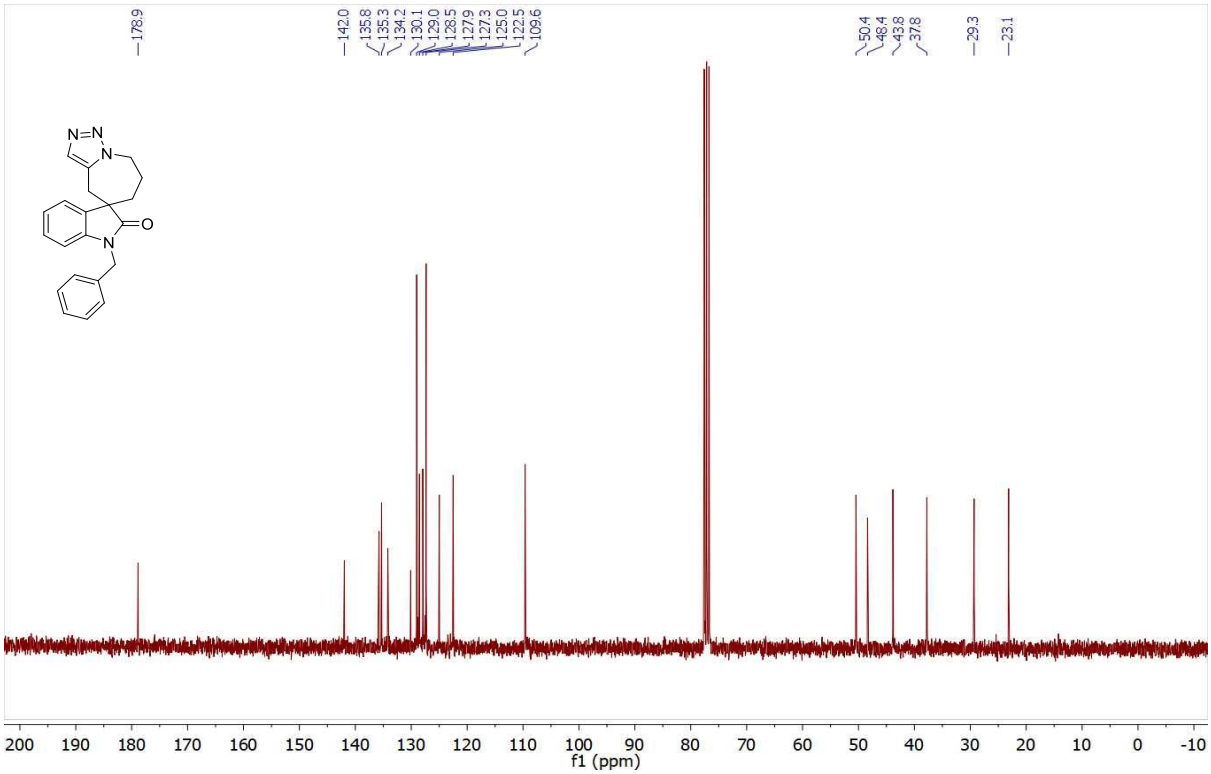
^{13}C{^{1}H} NMR of 9a (151 MHz, $CDCl_3$):



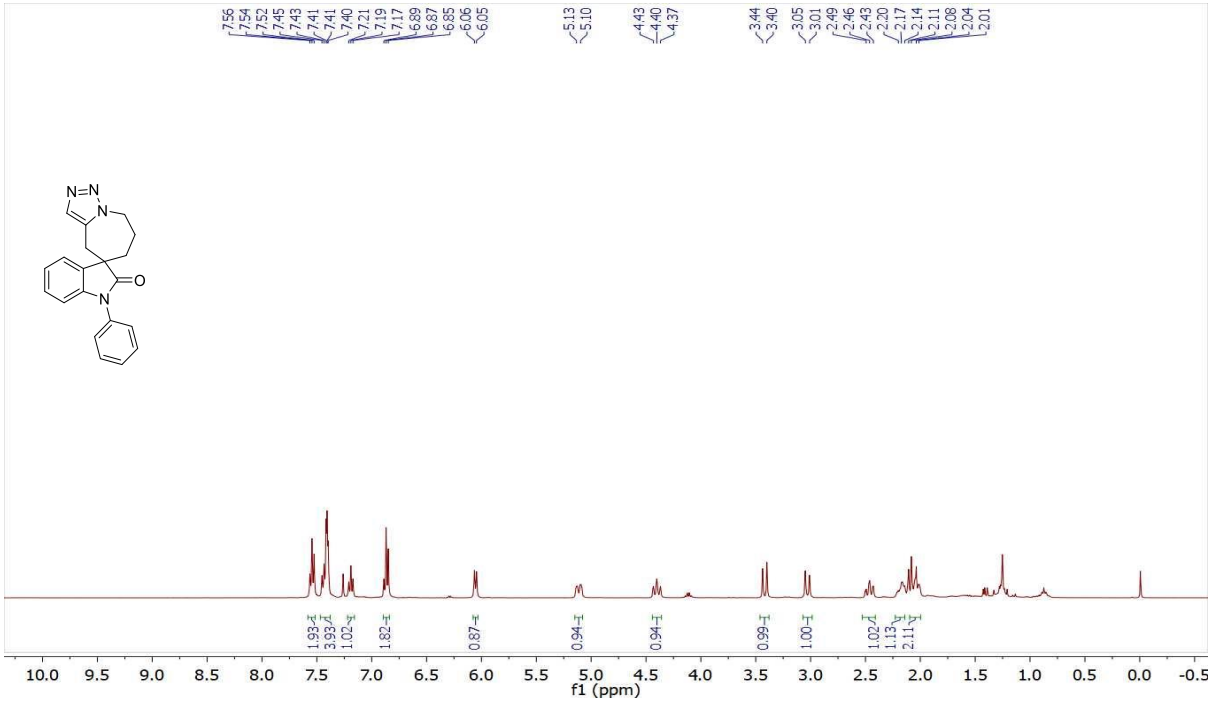
^{1}H NMR of 9b (300 MHz, $CDCl_3$):



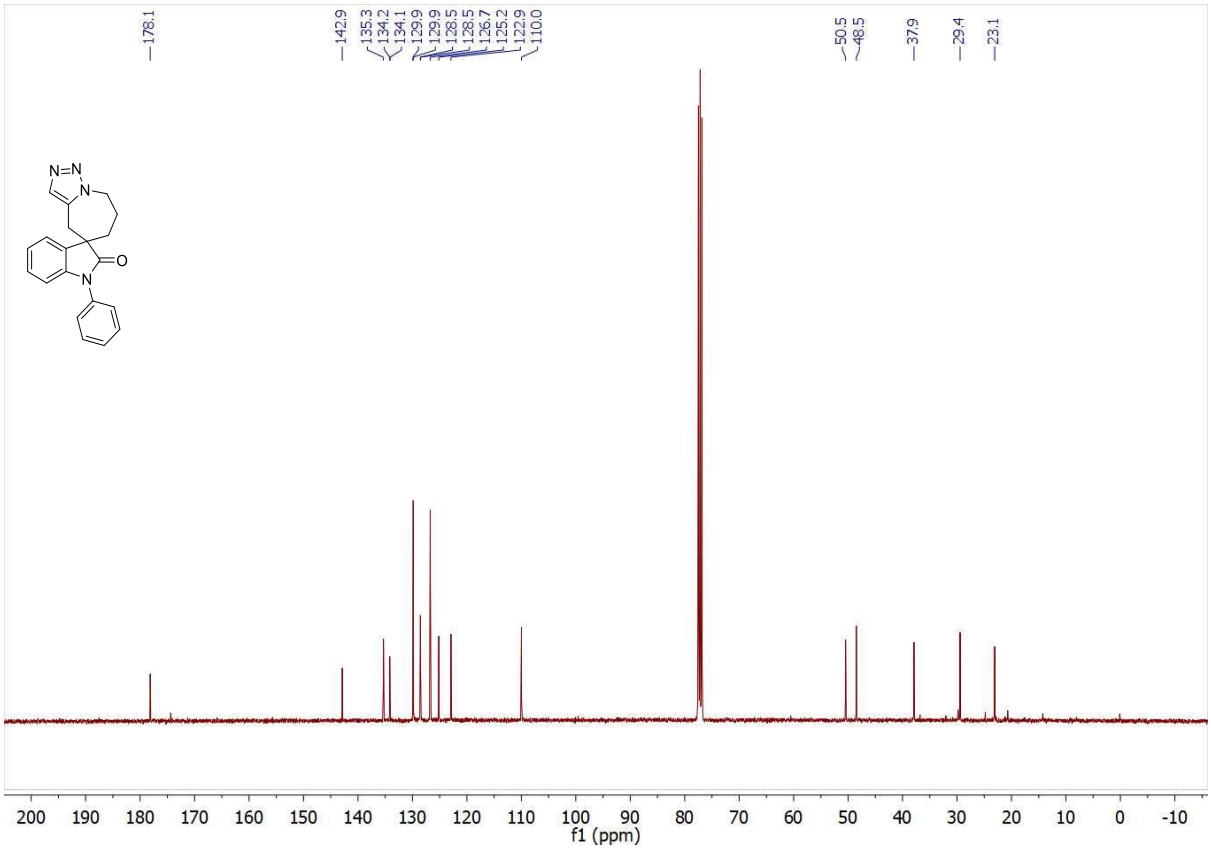
^{13}C{^{1}H} NMR of 9b (75 MHz, $CDCl_3$):



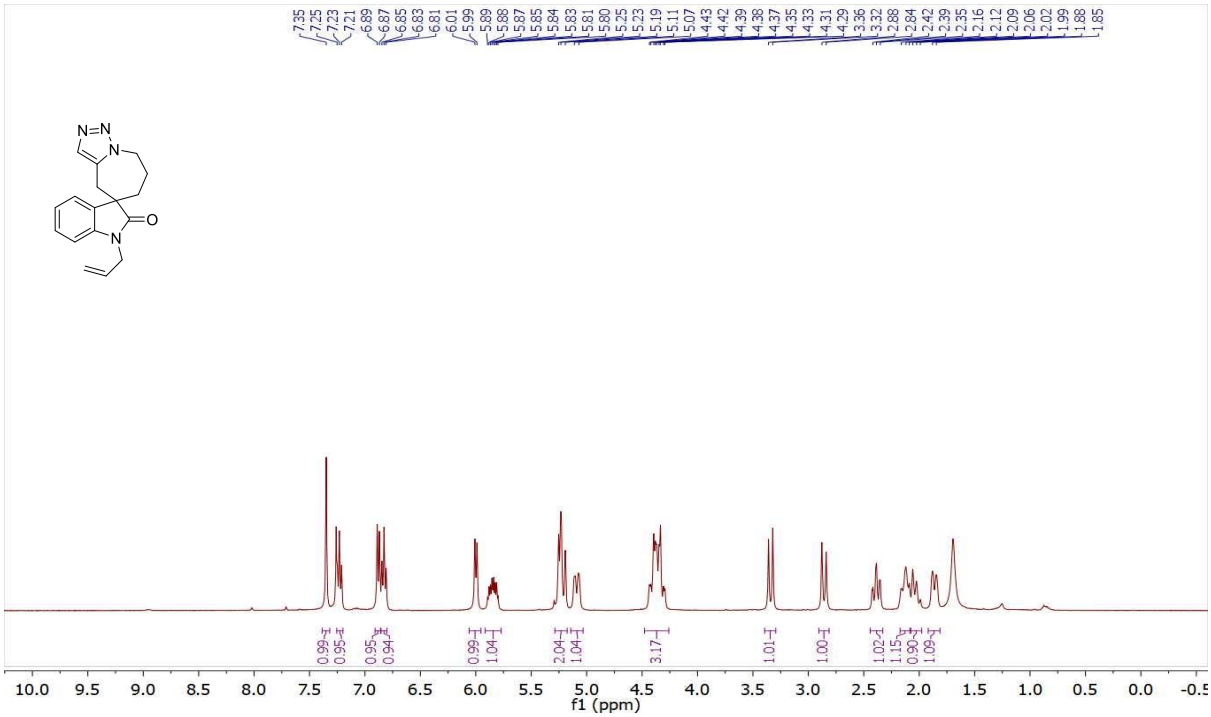
^{1}H NMR of 9c (400 MHz, $CDCl_3$):



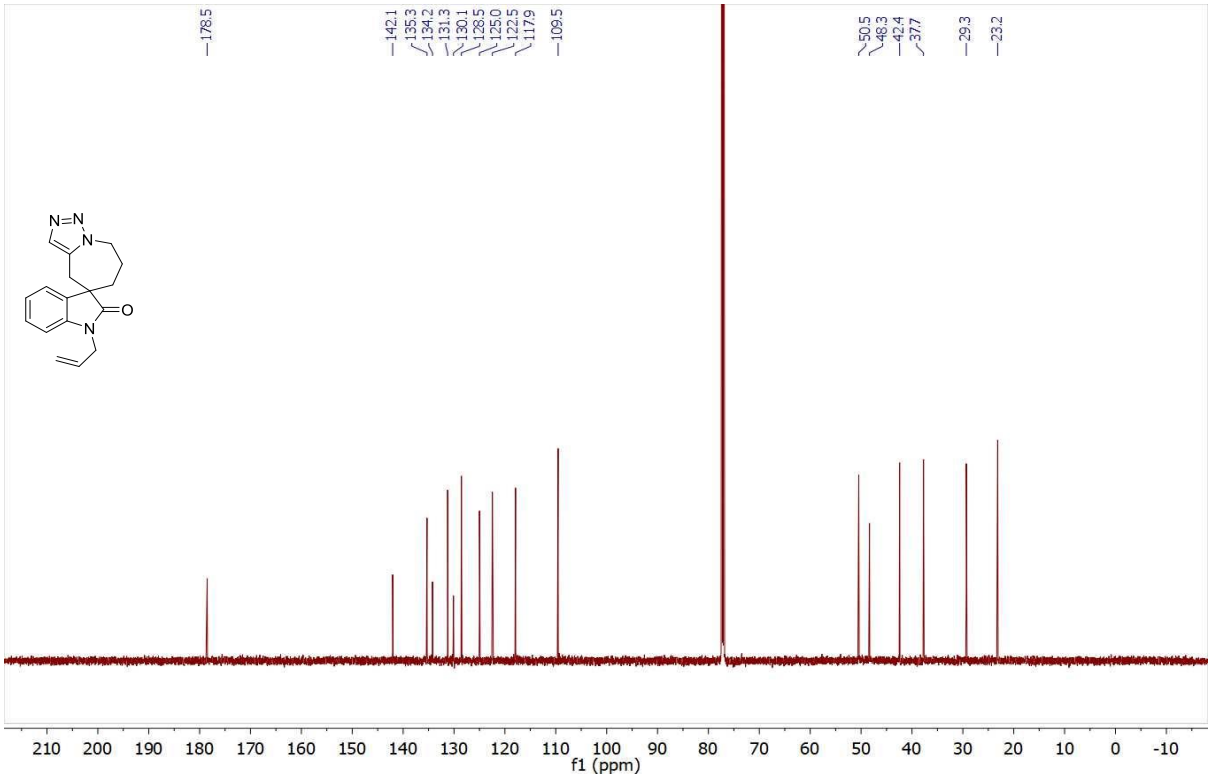
^{13}C{^{1}H} NMR of 9c (101 MHz, $CDCl_3$):



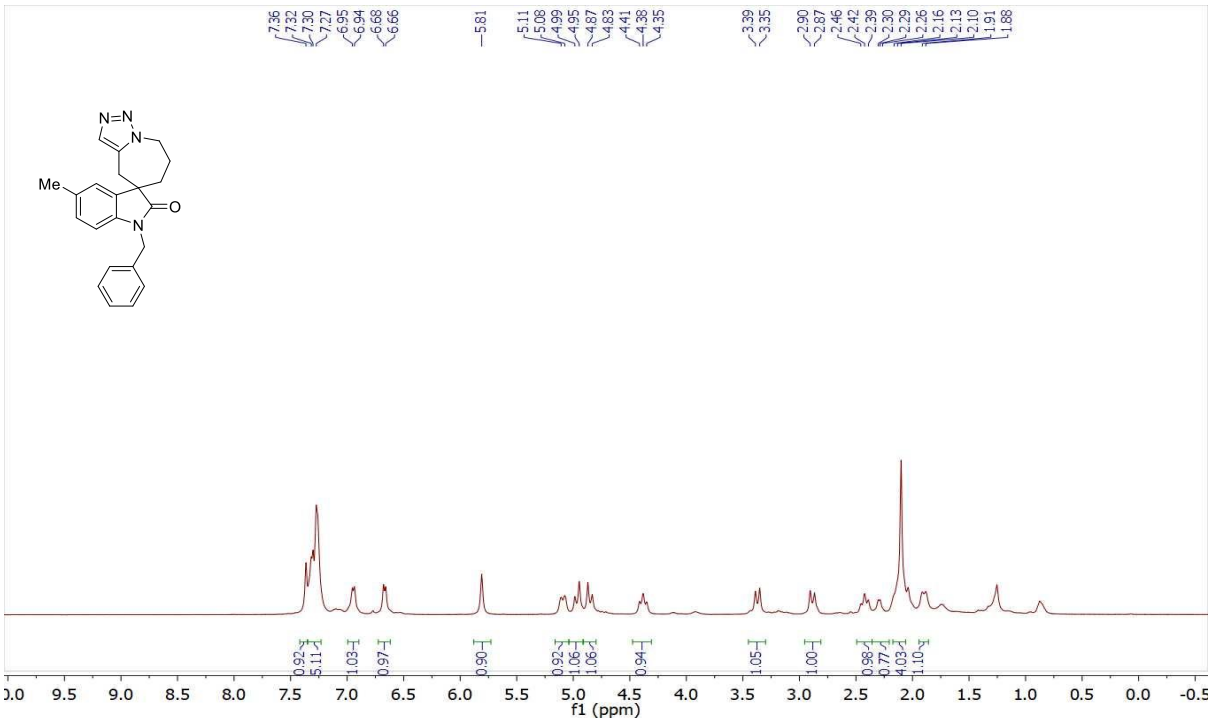
^{1}H NMR of 9d (400 MHz, $CDCl_3$):



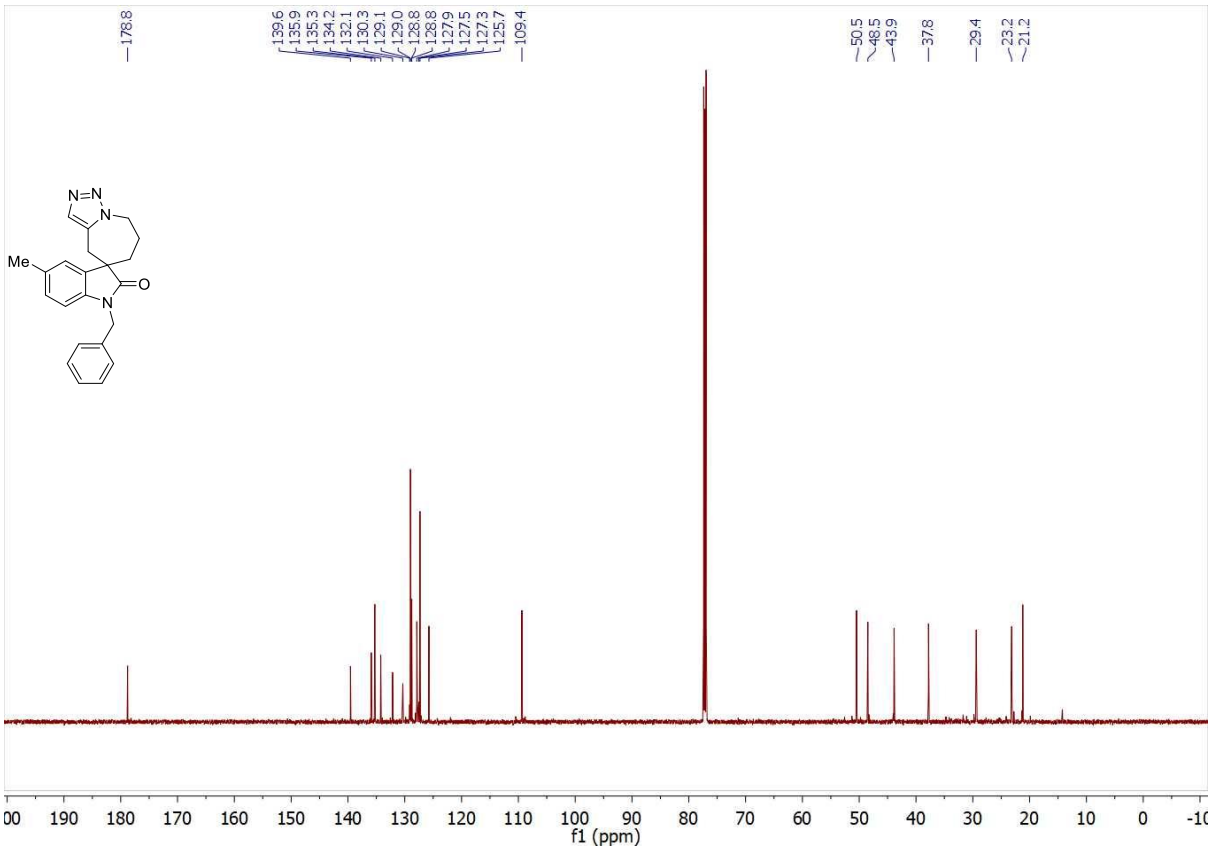
^{13}C{^{1}H} NMR of 9d (151 MHz, $CDCl_3$):



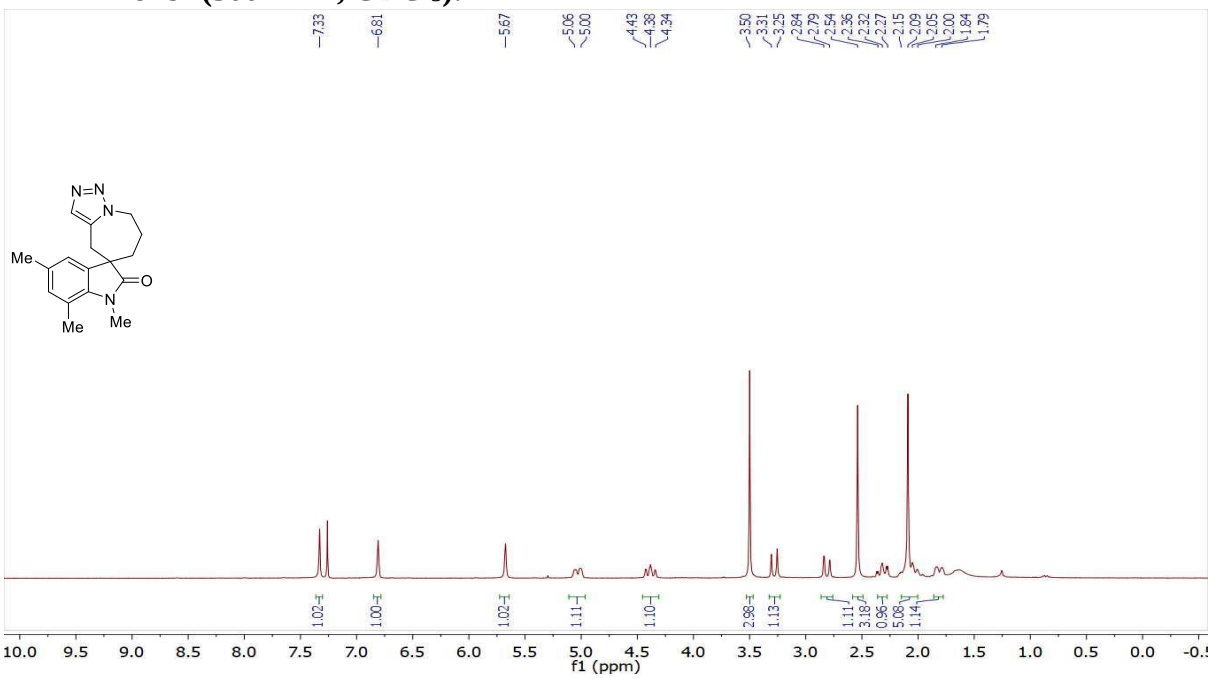
^{1}H NMR of 9e (400 MHz, $CDCl_3$):



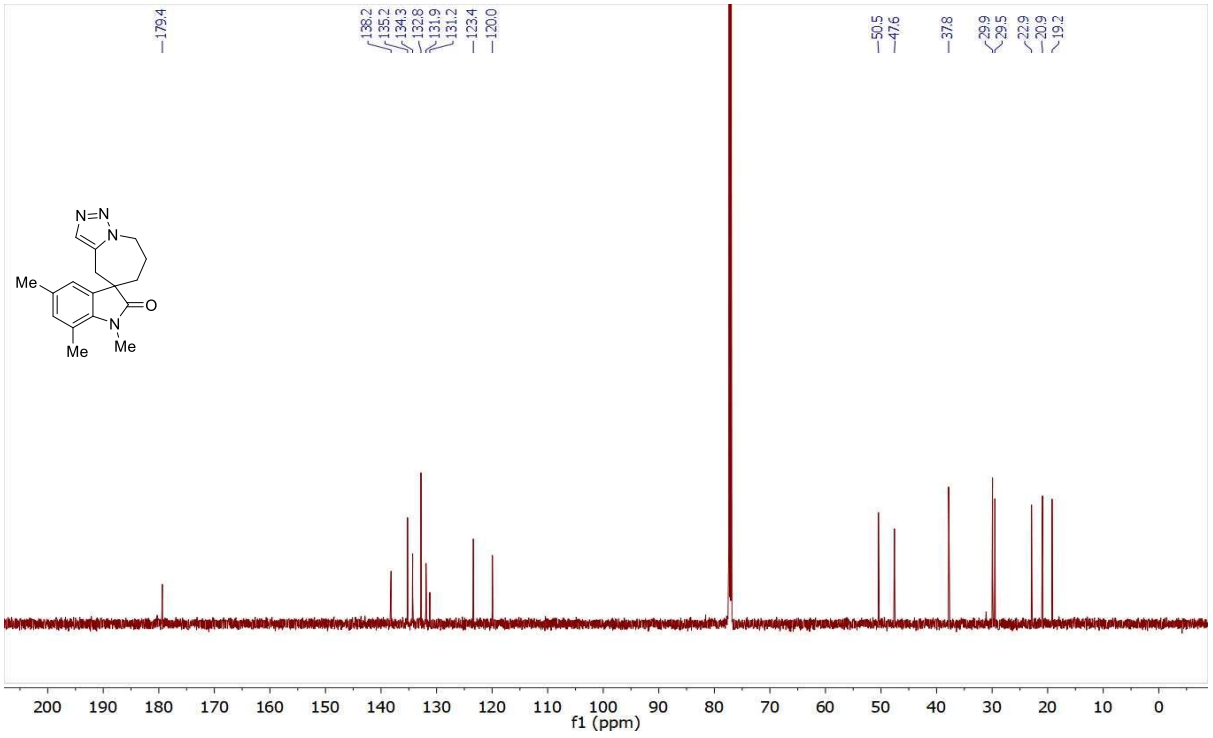
^{13}C{^{1}H} NMR of 9e (151 MHz, $CDCl_3$):



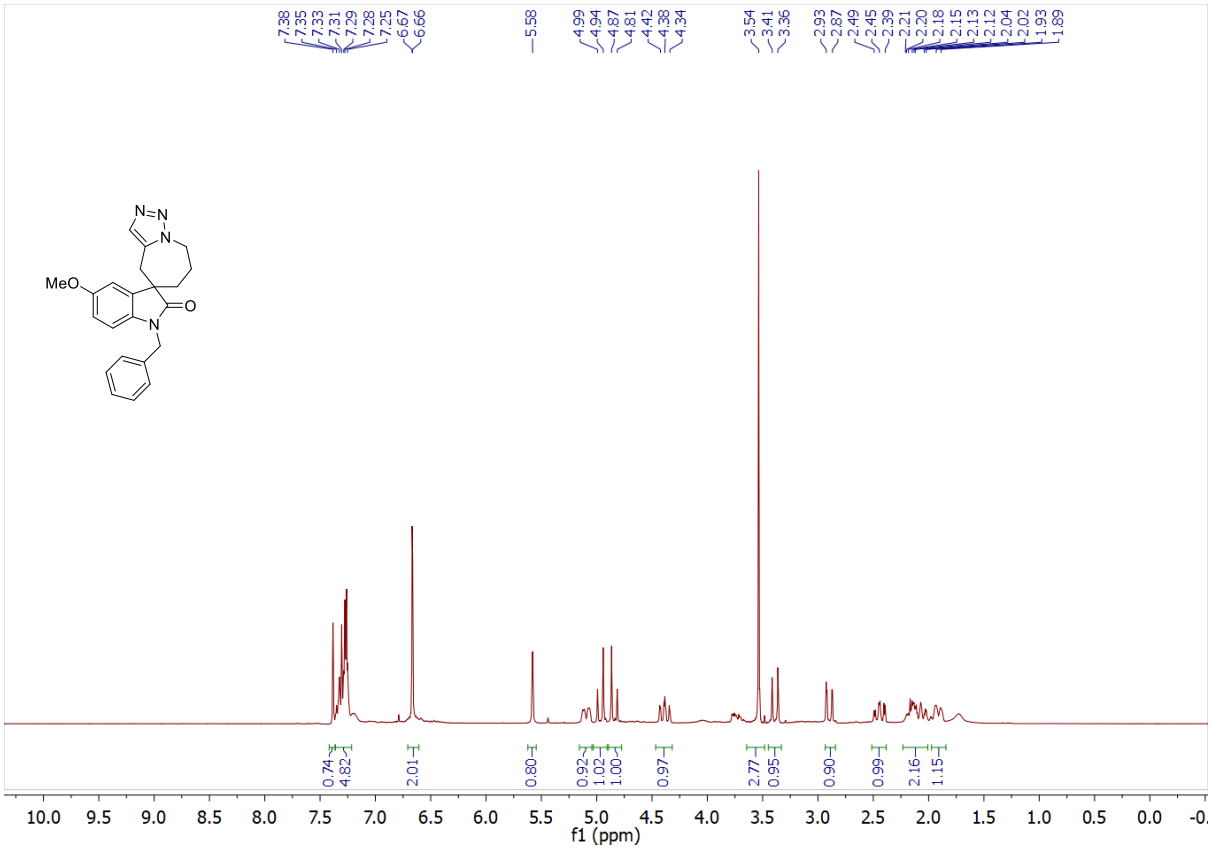
^{1}H NMR of 9f (300 MHz, $CDCl_3$):



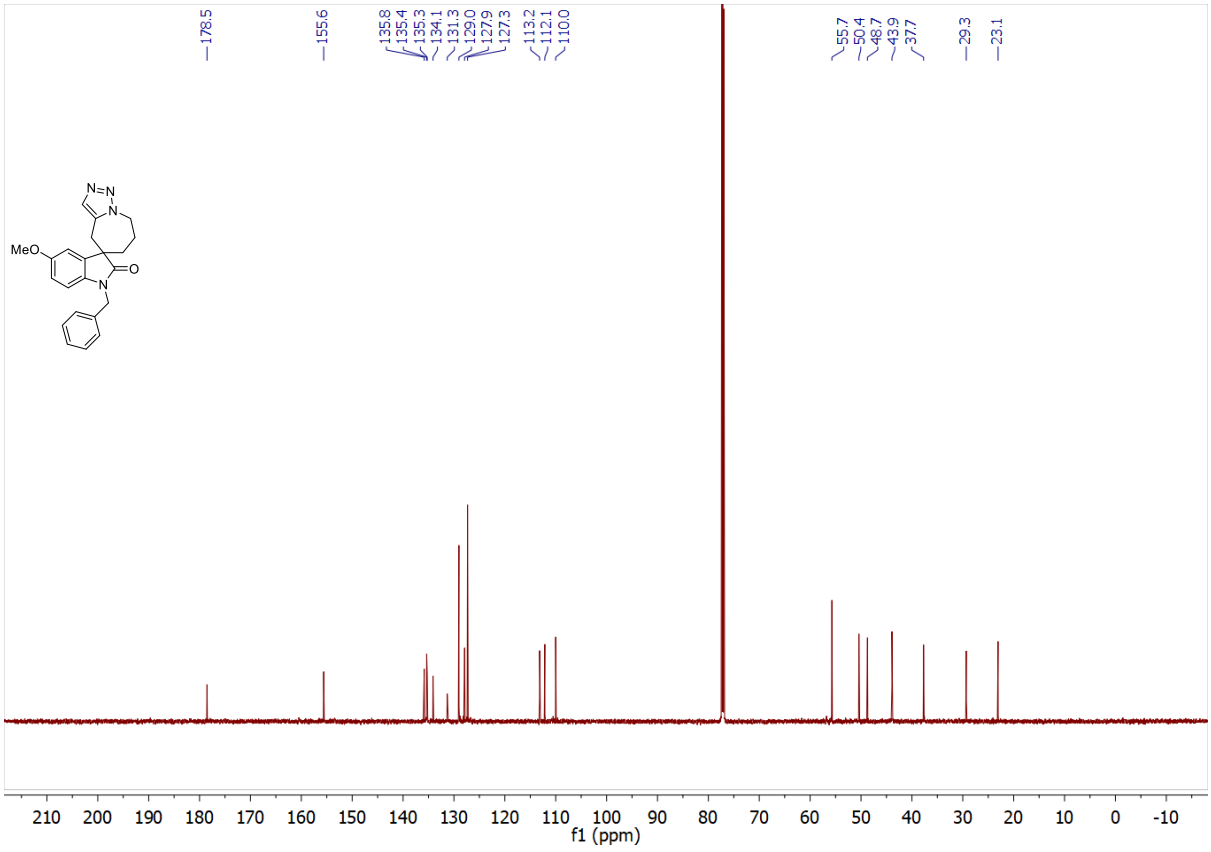
^{13}C{^{1}H} NMR of 9f (151 MHz, $CDCl_3$):



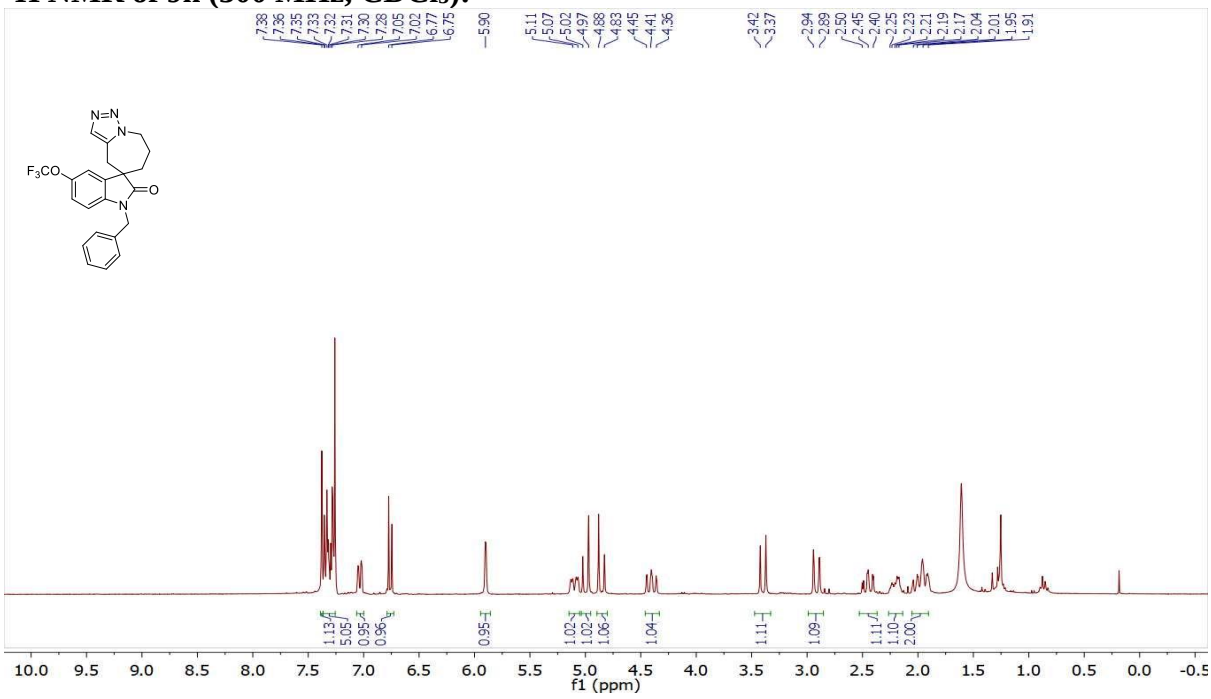
^{1}H NMR of 9g (300 MHz, $CDCl_3$):



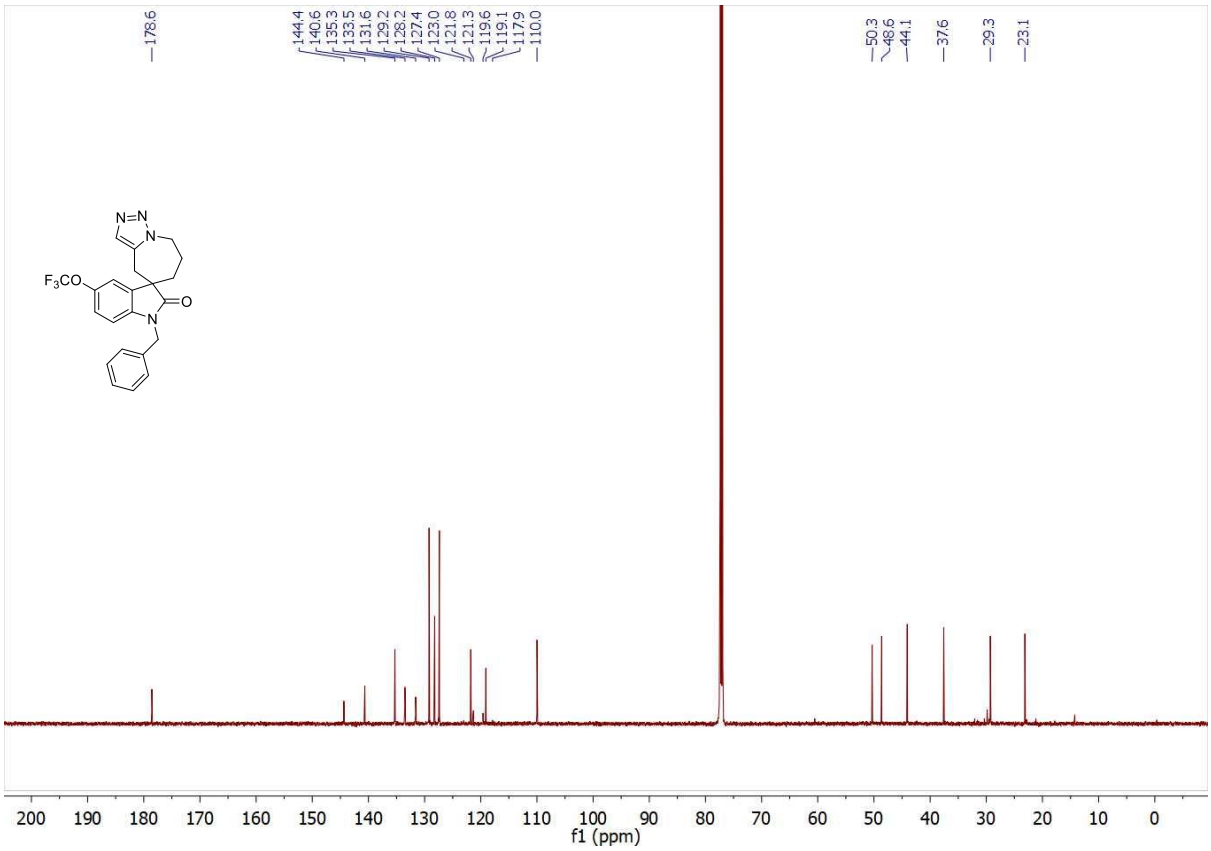
^{13}C{^{1}H} NMR of 9g (151 MHz, $CDCl_3$):



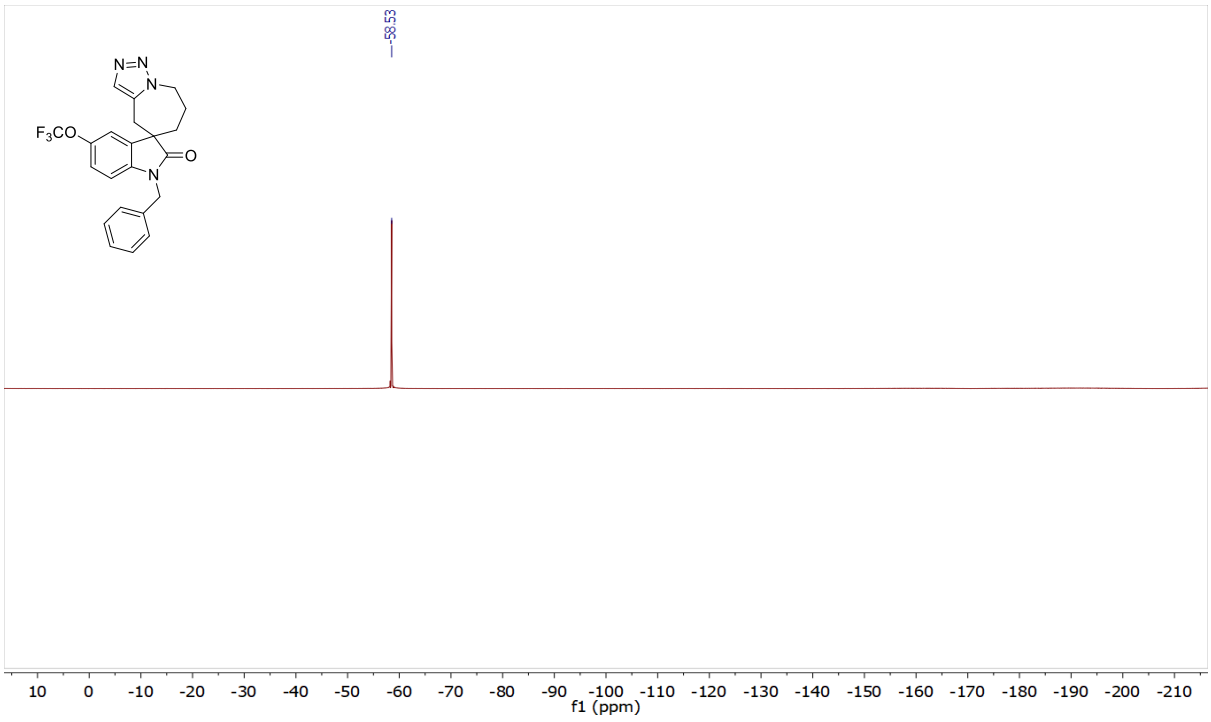
^{1}H NMR of 9h (300 MHz, $CDCl_3$):



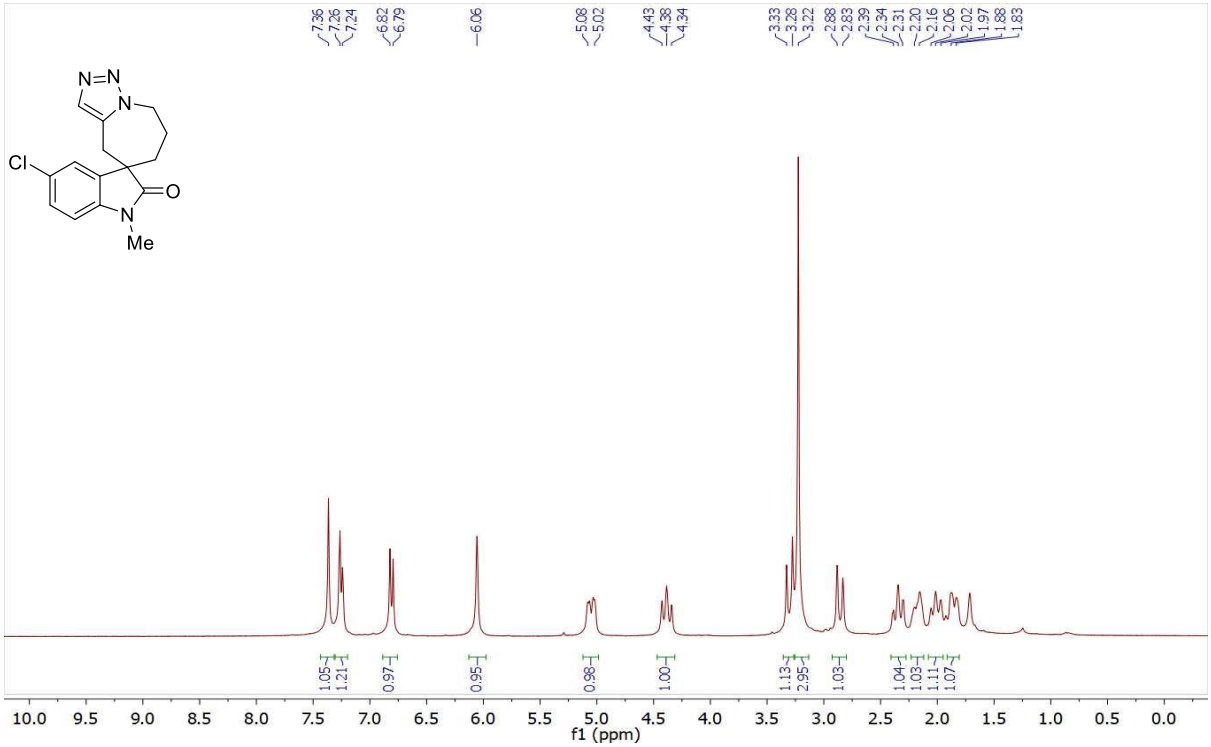
^{13}C{^{1}H} NMR of 9h (151 MHz, $CDCl_3$):



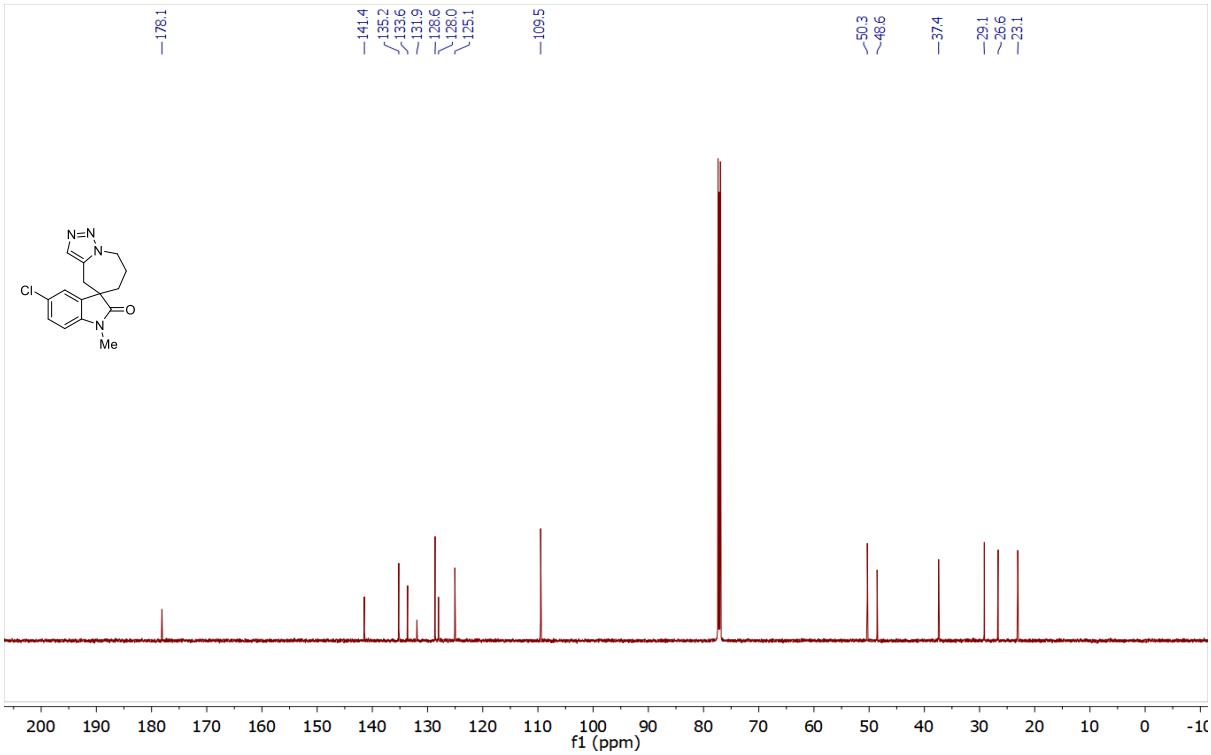
$^{19}F\{^{1}H\}$ NMR of 9h (565 MHz, $CDCl_3$):



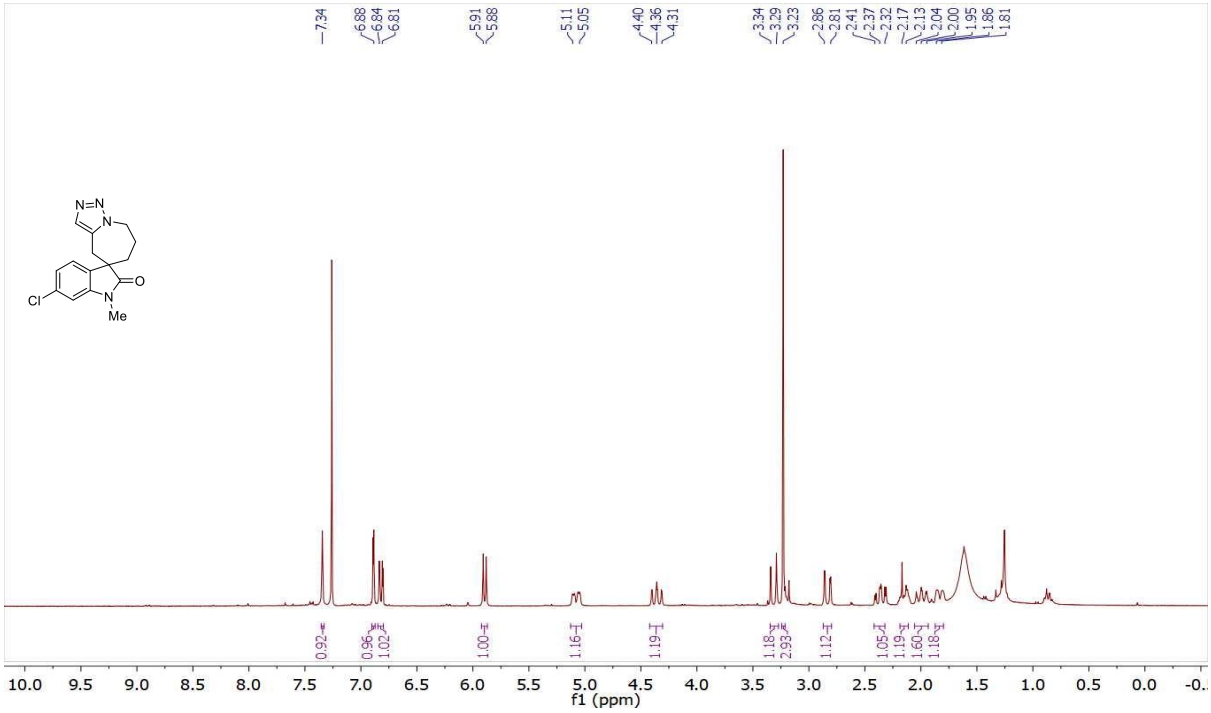
^{1}H NMR of 9i (300 MHz, $CDCl_3$):



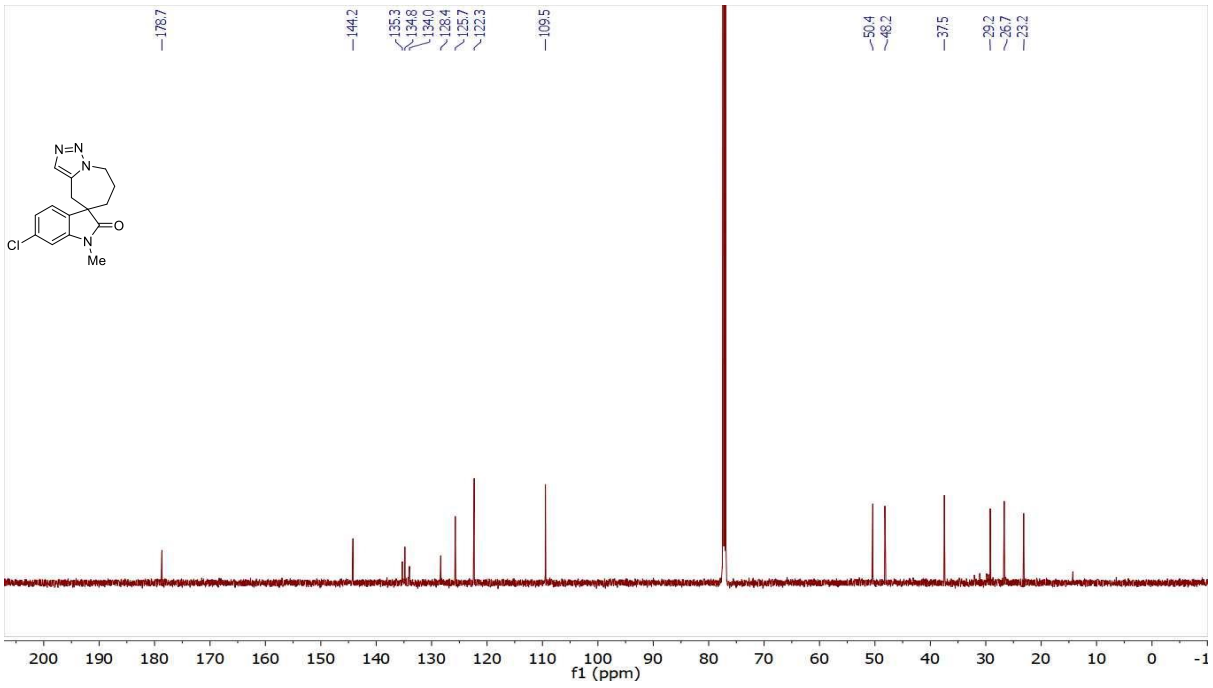
$^{13}C\{^{1}H\}$ NMR of 9i (151 MHz, $CDCl_3$):



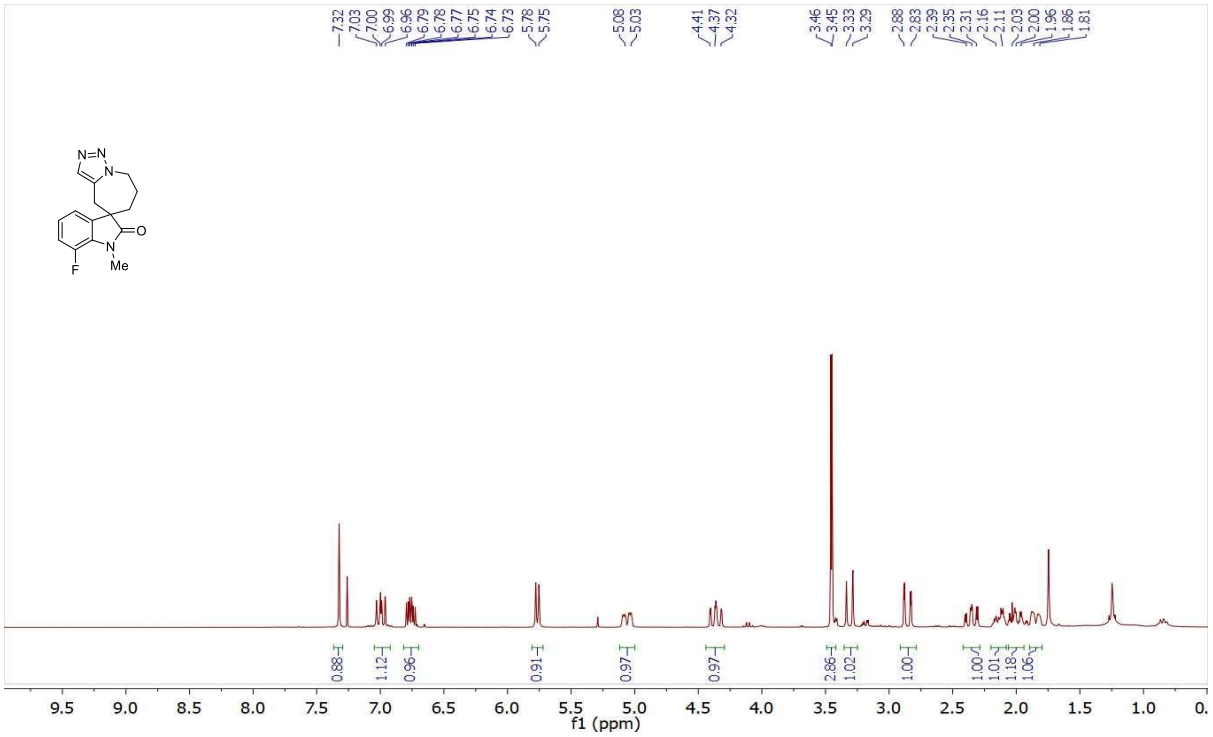
^{1}H NMR of 9j (300 MHz, $CDCl_3$):



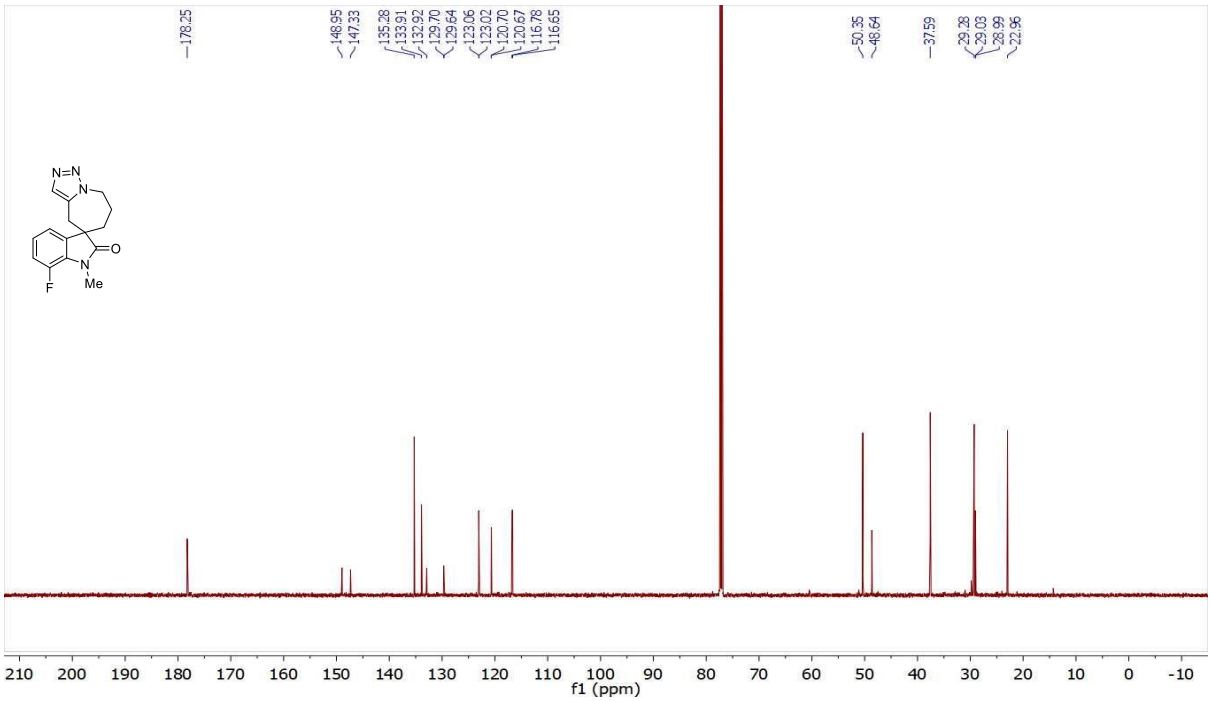
$^{13}C\{^{1}H\}$ NMR of 9j (151 MHz, $CDCl_3$):



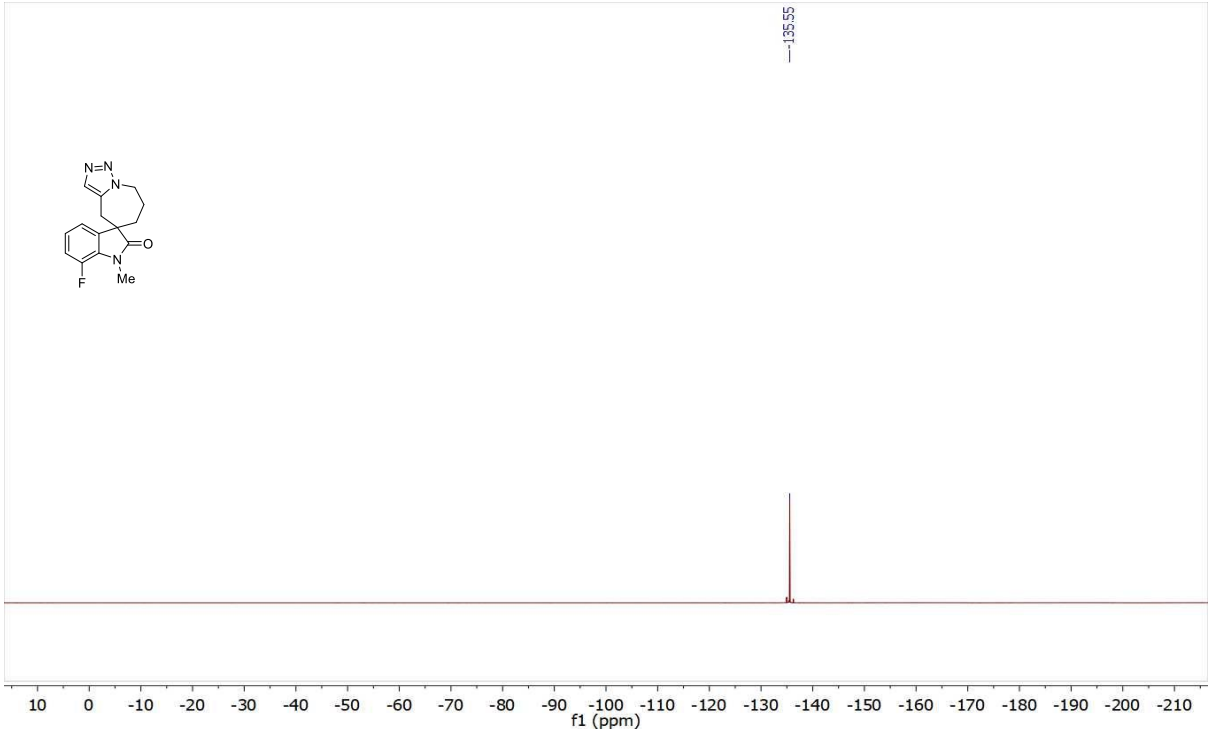
^{1}H NMR of 9k (300 MHz, $CDCl_3$):



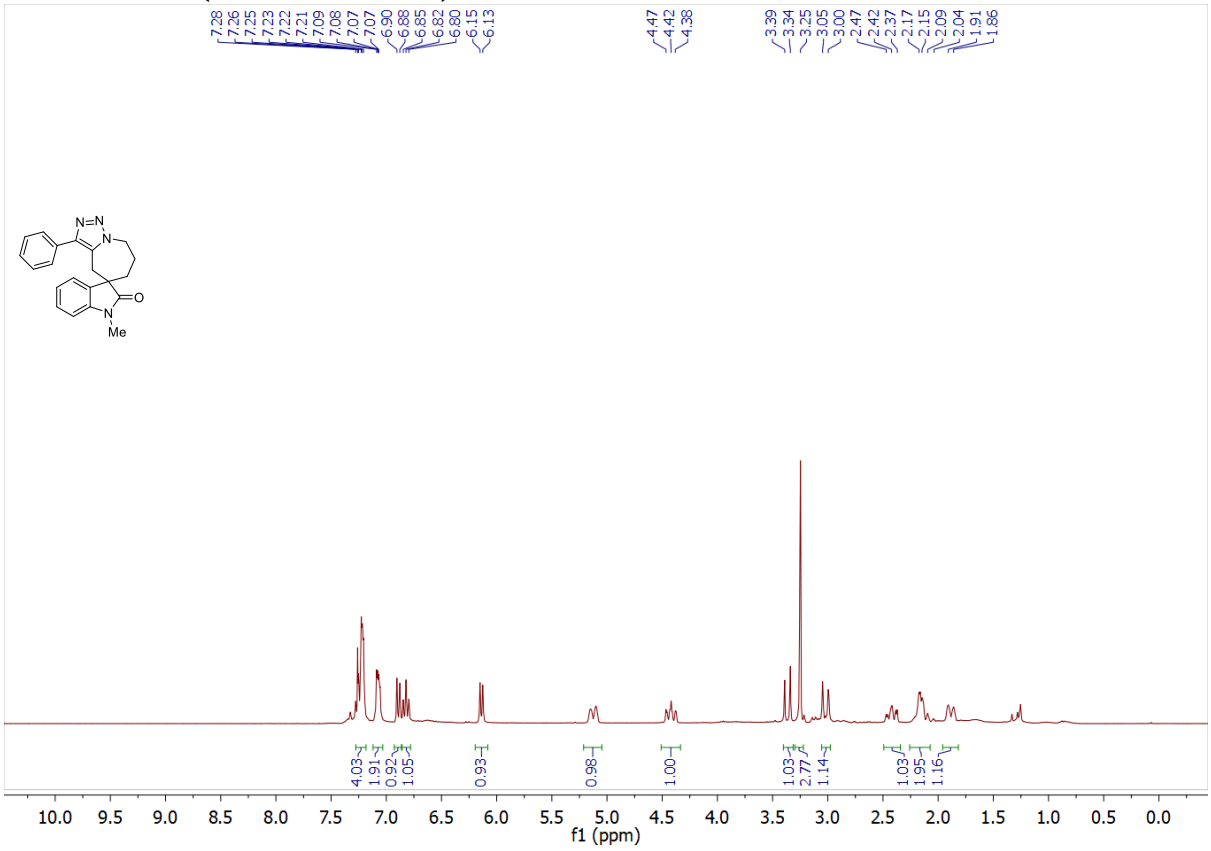
$^{13}C\{^{1}H\}$ NMR of 9k (151 MHz, $CDCl_3$):



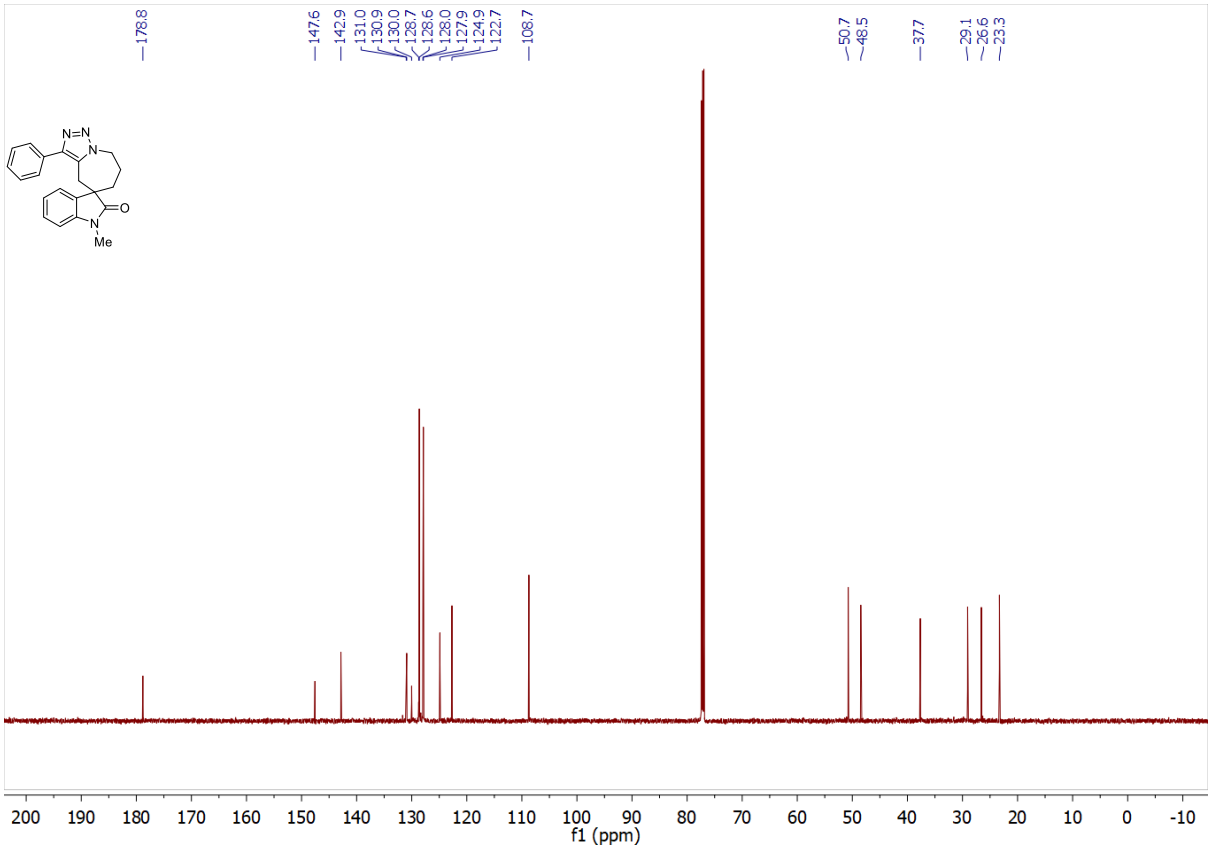
$^{19}F\{^{1}H\}$ NMR of 9k (565 MHz, $CDCl_3$):



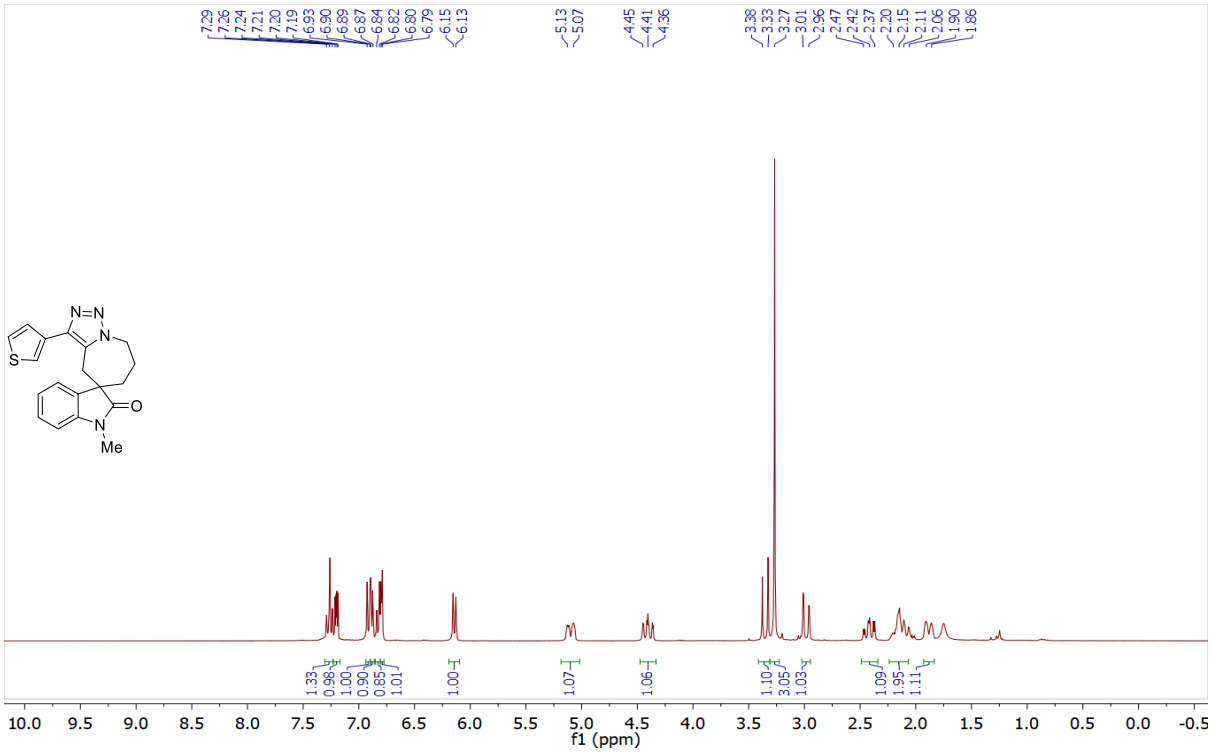
^{1}H NMR of 9l (300 MHz, $CDCl_3$):



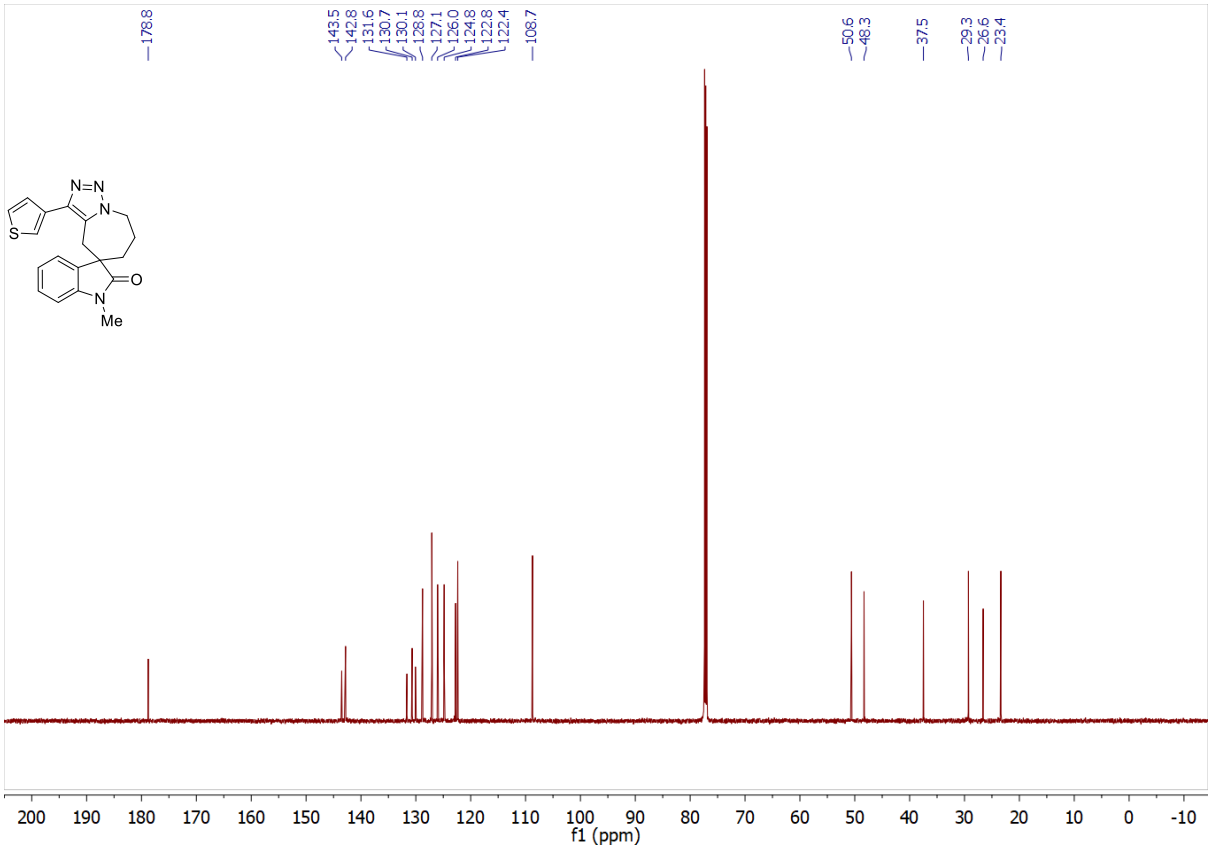
^{13}C{^{1}H} NMR of 9l (151 MHz, $CDCl_3$):



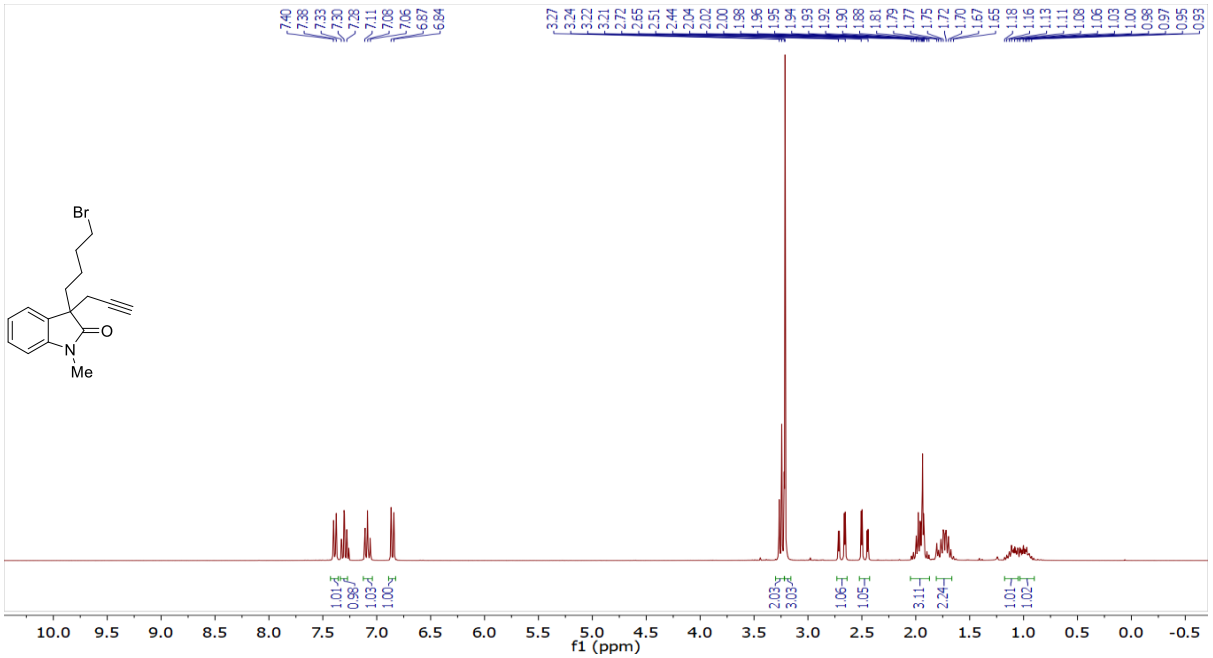
^{1}H NMR of 9m (300 MHz, $CDCl_3$):



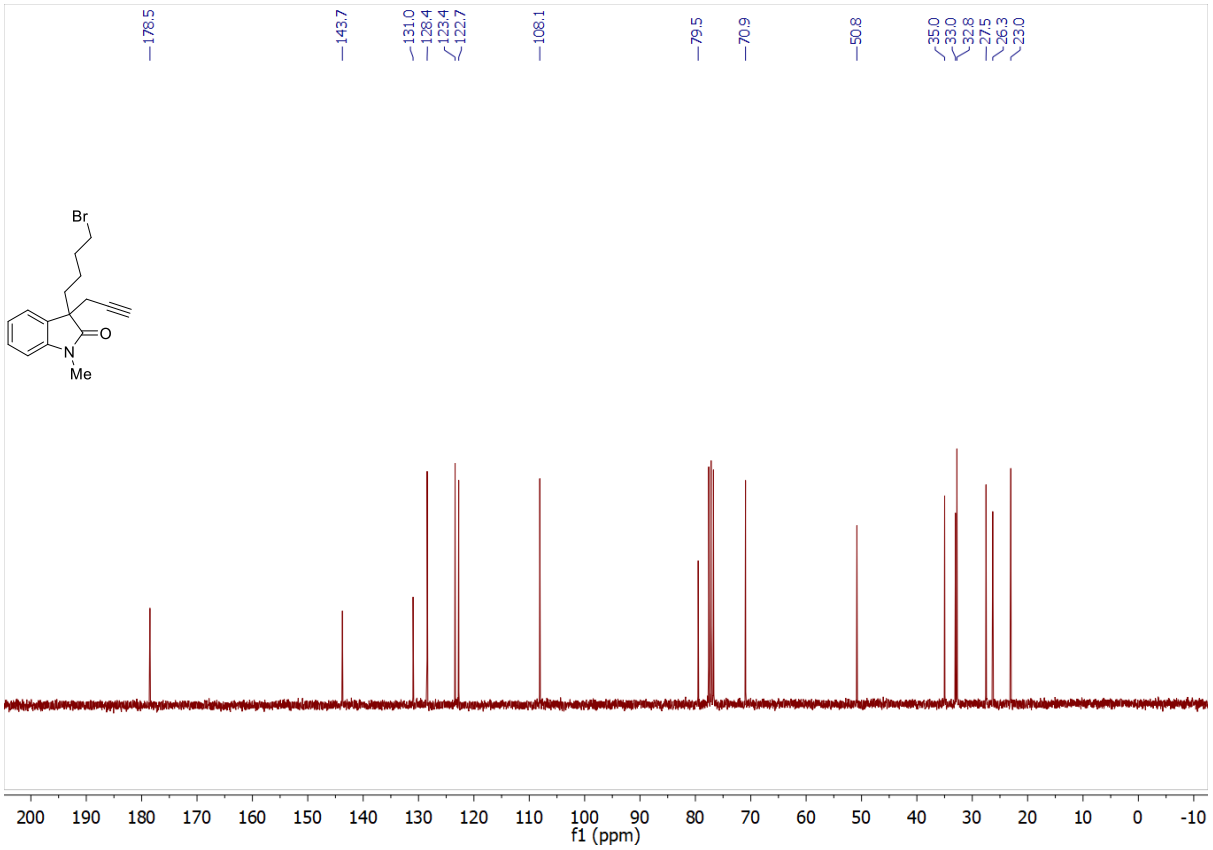
^{13}C{^{1}H} NMR of 9m (151 MHz, $CDCl_3$):



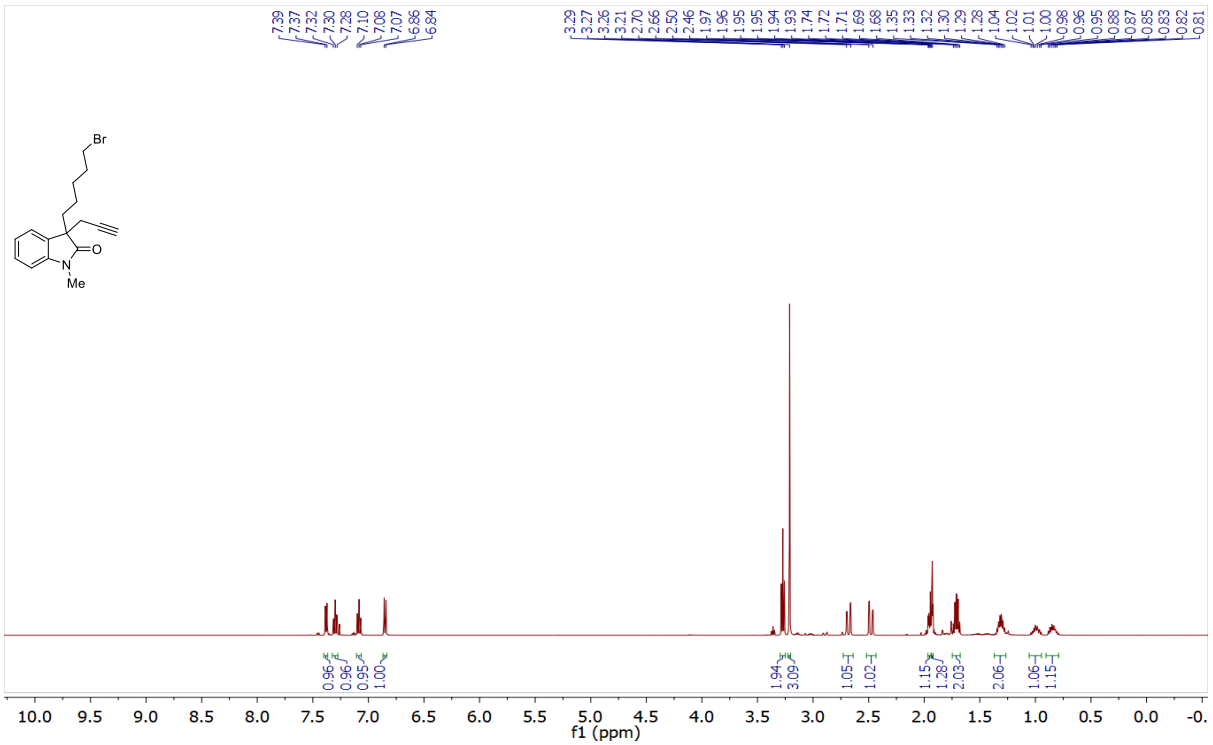
^{1}H NMR of S4a (300 MHz, $CDCl_3$):



^{13}C{^{1}H} NMR of S4a (75 MHz, $CDCl_3$):



^{1}H NMR of S4b (500 MHz, $CDCl_3$):



^{13}C{^{1}H} NMR of S4b (151 MHz, $CDCl_3$):