

## Supporting Information

# **Palladium-Catalyzed Tandem C(sp<sup>2</sup>)-H Nitration and Annulation of Sulfonyl hydrazide with Co(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O: Synthesis of 3-nitro-1-(phenylsulfonyl)-1H-indazole Derivatives.**

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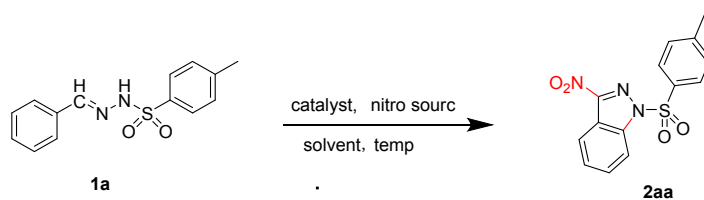
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## 1. General Information

All the chemicals were obtained commercially and used without any prior purification.  $^1\text{H}$  NMR spectra were recorded on a BrukerAvanceII 400 spectrometer. All products were isolated by short chromatography on a silica gel (200–300 mesh) column using petroleum ether (60-90°C) and ethyl acetate. Unless otherwise noted. All compounds were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and HRGC- HRMS, which are consistent with those reported in the literature.

## 2. Experimental Section

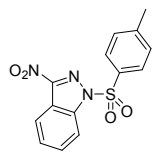
### General procedure for Synthesis of 3-nitro-1-(phenylsulfonyl)-1H-indazole Derivatives.



A mixture of the **1a** (0.2 mmol),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (1.5 equiv.),  $\text{Pd}(\text{OAc})_2$  (20 mol %) in  $\text{CH}_2\text{ClCH}_2\text{Cl}$  (2.0 mL) was stirred at sealed tube, 110 °C for 4 h. After cooling down to room temperature and concentrating in vacuum, the residue was purified by flash chromatography on a short silica gel to afford the product.

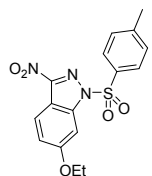
### 3. Characterization data of the products

#### 3-nitro-1-tosyl-1H-indazole (2aa)



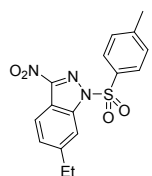
Obtained as a white solid in 96% yield; M.p.173-175 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.30 (d, *J* = 8.6 Hz, 1H), 8.25 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 2H), 7.71 (t, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 2H), 2.41 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 147.02, 142.08, 133.35, 130.89, 130.39, 128.27, 127.01, 121.78, 117.21, 113.59, 21.76. HRMS(ESI<sup>+</sup>): Calculated for C<sub>14</sub>H<sub>11</sub>N<sub>3</sub>O<sub>4</sub>S, [M+H]<sup>+</sup> 318.0543. Found 318.0547.

#### 6-ethoxy-3-nitro-1-tosyl-1H-indazole (2ab)



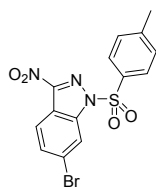
Obtained as a white solid in 91% yield; M.p.188-190 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.04 (d, *J* = 8.9 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 2.1 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.12 (dd, *J* = 9.1, 2.2 Hz, 1H), 4.19 (q, *J* = 7.0 Hz, 2H), 2.40 (s, 3H), 1.51 (t, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.89, 146.95, 144.11, 133.51, 130.42, 128.23, 122.37, 119.20, 111.32, 95.40, 64.60, 21.86, 14.61. HRMS(ESI<sup>+</sup>): Calculated for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>O<sub>5</sub>S, [M+H]<sup>+</sup> 362.0805. Found 362.0802.

#### 6-ethyl-3-nitro-1-tosyl-1H-indazole (2ac)



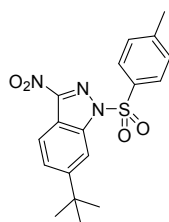
Obtained as a white solid in 86% yield; M.p.168-170 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.10 (dd, *J* = 8.5, 1.1 Hz, 1H), 8.07-8.06 (m, 1H), 7.97 (d, *J* = 8.7 Hz, 2H), 7.40 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.32 (dd, *J* = 8.6, 1.1 Hz, 2H), 2.88 (q, *J* = 7.8 Hz, 2H), 2.39 (s, 3H), 1.34 (t, *J* = 7.6 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 148.66, 146.99, 142.87, 133.48, 130.44, 128.29, 128.23, 121.40, 115.52, 111.90, 29.63, 21.85, 15.61. HRMS(ESI<sup>+</sup>): Calculated for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>O<sub>4</sub>S, [M+H]<sup>+</sup> 346.0856. Found 346.0853.

#### 6-bromo-3-nitro-1-tosyl-1H-indazole (2ad)



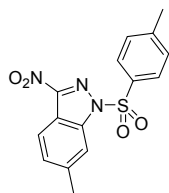
Obtained as a white solid in 81% yield; M.p.206-208 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.51 (s, 1H), 8.11 (d, *J* = 8.7 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 2H), 7.67 (dd, *J* = 8.7, 1.5 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 2.43 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 147.48, 142.53, 133.02, 130.92, 130.61, 128.49, 126.02, 122.82, 116.67, 116.07, 21.91. HRMS(ESI<sup>+</sup>): Calculated for C<sub>14</sub>H<sub>10</sub>BrN<sub>3</sub>O<sub>4</sub>S, [M+H]<sup>+</sup> 395.9648. Found 395.9643.

#### 6-(tert-butyl)-3-nitro-1-tosyl-1H-indazole (2ae)



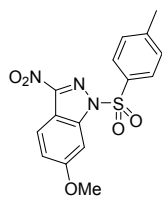
Obtained as a white solid in 85% yield; M.p.107-109 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.24-8.23 (m, 1H), 8.12 (dd, *J* = 8.7, 0.8 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.62 (dd, *J* = 8.7, 1.5 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H), 1.43 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.60, 146.97, 142.90, 133.51, 130.42, 128.32, 125.96, 121.08, 115.21, 109.41, 35.88, 31.35, 21.86. HRMS(ESI<sup>+</sup>): Calculated for C<sub>18</sub>H<sub>19</sub>N<sub>3</sub>O<sub>4</sub>S, [M+H]<sup>+</sup> 374.1169. Found 374.1166.

#### 6-methyl-3-nitro-1-tosyl-1H-indazole (2af)



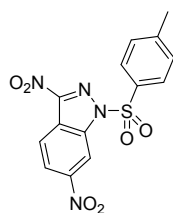
Obtained as a white solid in 83% yield; M.p.155-157 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.13 – 8.03 (m, 2H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.36 (dd, *J* = 8.5, 1.3 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 2.59 (s, 3H), 2.39 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.98, 142.79, 142.35, 133.49, 130.44, 129.22, 128.29, 121.23, 115.36, 113.06, 22.40, 21.86. HRMS(ESI<sup>+</sup>): Calculated for C<sub>15</sub>H<sub>13</sub>N<sub>3</sub>O<sub>4</sub>S, [M+H]<sup>+</sup> 332.0700. Found 332.0703.

#### 6-methoxy-3-nitro-1-tosyl-1H-indazole (2ag)



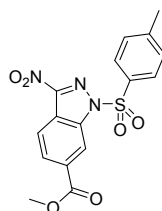
Obtained as a white solid in 85% yield; M.p.196-198 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.05 (d, *J* = 9.0 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 2.2 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.14 (dd, *J* = 9.0, 2.2 Hz, 1H), 3.98 (s, 3H), 2.40 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.55, 147.00, 144.08, 133.49, 130.43, 128.26, 122.43, 118.97, 111.46, 94.87, 56.12, 21.87. HRMS(ESI<sup>+</sup>): Calculated for C<sub>15</sub>H<sub>13</sub>N<sub>3</sub>O<sub>5</sub>S, [M+H]<sup>+</sup>348.0649. Found 348.0645.

### 3,6-dinitro-1-tosyl-1H-indazole (2ah)



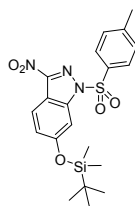
Obtained as a white solid in 86% yield; M.p.146-148 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.18 (d, *J* = 2.0 Hz, 1H), 8.44 – 8.37 (m, 2H), 8.04 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 2.43 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 148.07, 140.93, 132.54, 130.82, 128.74, 123.23, 121.64, 120.25, 110.21, 100.00, 21.97. HRMS(ESI<sup>+</sup>): Calculated for C<sub>14</sub>H<sub>10</sub>N<sub>4</sub>O<sub>6</sub>S, [M+H]<sup>+</sup>363.0394. Found 363.0391.

### methyl 3-nitro-1-tosyl-1H-indazole-6-carboxylate (2ai)



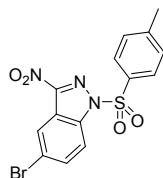
Obtained as a white solid in 83% yield; M.p.142-144 °C <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.96 (s, 1H), 8.31 (d, *J* = 8.6 Hz, 1H), 8.21 (d, *J* = 8.6 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 4.04 (s, 3H), 2.42 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.68, 147.41, 141.63, 132.96, 132.58, 130.54, 128.45, 127.51, 121.84, 119.60, 115.38, 52.98, 21.84. HRMS(ESI<sup>+</sup>): Calculated for C<sub>16</sub>H<sub>13</sub>N<sub>3</sub>O<sub>6</sub>S, [M+H]<sup>+</sup>376.0598. Found 376.0594.

### 6-((tert-butyldimethylsilyloxy)-3-nitro-1H-indazole (2aj)



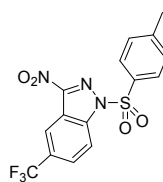
Obtained as a white solid in 80% yield; M.p.154-156 °C  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (d,  $J = 8.9$  Hz, 1H), 7.96 (d,  $J = 8.4$  Hz, 2H), 7.66 (d,  $J = 1.7$  Hz, 1H), 7.34 (d,  $J = 7.9$  Hz, 2H), 7.08 (dd,  $J = 8.9, 2.0$  Hz, 1H), 2.42 (s, 3H), 1.04 (s, 9H), 0.32 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.77, 151.30, 146.95, 143.66, 133.29, 130.39, 128.18, 122.48, 122.36, 111.88, 102.94, 25.64, 21.84, 18.38, -4.32. HRMS(ESI+): Calculated for  $\text{C}_{20}\text{H}_{25}\text{N}_3\text{O}_5\text{SSi}$ ,  $[\text{M}+\text{H}]^+448.1357$ . Found 448.1355.

### 5-bromo-3-nitro-1-tosyl-1H-indazole (2am)



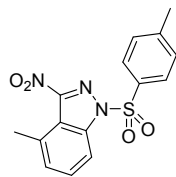
Obtained as a white solid in 92% yield; M.p.178-180 °C  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.41 (dd,  $J = 1.9, 0.7$  Hz, 1H), 8.17 (dd,  $J = 9.1, 0.7$  Hz, 1H), 7.96 (d,  $J = 8.5$  Hz, 2H), 7.77 (dd,  $J = 9.0, 1.9$  Hz, 1H), 7.34 (d,  $J = 7.9$  Hz, 2H), 2.41 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.49, 140.83, 134.34, 133.00, 130.60, 128.43, 124.34, 121.07, 118.66, 115.04, 21.90. HRMS(ESI+): Calculated for  $\text{C}_{14}\text{H}_{10}\text{BrN}_3\text{O}_4\text{S}$ ,  $[\text{M}+\text{H}]^+395.9648$ . Found 395.9645.

### 3-nitro-1-tosyl-5-(trifluoromethyl)-1H-indazole (2an)



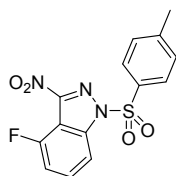
Obtained as a white solid in 89% yield; M.p.164-166 °C  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.58 (s, 1H), 8.44 (d,  $J = 9.0$  Hz, 1H), 8.00 (d,  $J = 8.2$  Hz, 2H), 7.93 (d,  $J = 9.5$  Hz, 1H), 7.37 (d,  $J = 8.1$  Hz, 2H), 2.43 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.64, 142.88, 132.76, 130.61, 128.44, 127.50(q,  $J = 3.3$  Hz), 121.84(q,  $J = 210.1$  Hz), 120.04(q,  $J = 4.6$  Hz), 116.72, 114.62, 107.62, 21.87.  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -61.89. HRMS(ESI+): Calculated for  $\text{C}_{15}\text{H}_{10}\text{F}_3\text{N}_3\text{O}_4\text{S}$ ,  $[\text{M}+\text{H}]^+386.0417$ . Found 386.0415.

### 4-methyl-3-nitro-1-tosyl-1H-indazole (2ap)



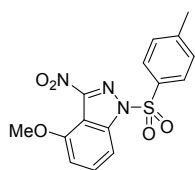
Obtained as a white solid in 80% yield; M.p.191-193 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.13 (d, *J* = 8.7 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 2H), 7.57 – 7.53 (m, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 5.4 Hz, 1H), 2.61 (s, 3H), 2.40 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.88, 142.19, 133.50, 132.44, 130.98, 130.40, 130.39, 128.22, 128.15, 115.87, 111.15, 21.84, 20.54. HRMS(ESI<sup>+</sup>): Calculated for C<sub>15</sub>H<sub>13</sub>N<sub>3</sub>O<sub>4</sub>S, [M+H]<sup>+</sup>332.0700. Found 332.0702.

#### 4-fluoro-3-nitro-1-tosyl-1H-indazole (2aq)



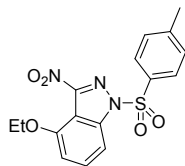
Obtained as a white solid in 84% yield; M.p.161-163 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.10 (dd, *J* = 8.7, 0.5 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 2H), 7.65 (ddd, *J* = 8.6, 8.1, 4.6 Hz, 1H), 7.35 – 7.32 (m, 2H), 7.21 – 7.16 (m, 1H), 2.41 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 154.03(d, *J* = 263.6 Hz), 147.43, 143.85(d, *J* = 5.1 Hz), 133.04, 132.38(d, *J* = 8.1 Hz), 130.57, 128.40, 112.25(d, *J* = 19.2 Hz), 109.71(d, *J* = 6.1 Hz), 107.10(d, *J* = 20.2 Hz), 21.89. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -108.38. HRMS(ESI<sup>+</sup>): Calculated for C<sub>14</sub>H<sub>10</sub>FN<sub>3</sub>O<sub>4</sub>S, [M+H]<sup>+</sup>336.0449. Found 336.0444.

#### 4-methoxy-3-nitro-1-tosyl-1H-indazole (2ar)



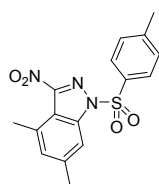
Obtained as a white solid in 86% yield; M.p.138-140 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 (d, *J* = 8.1 Hz, 2H), 7.82 (d, *J* = 8.6 Hz, 1H), 7.59 (t, *J* = 8.3 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 1H), 3.93 (s, 3H), 2.40 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 153.03, 146.83, 143.25, 133.49, 132.75, 130.37, 128.15, 107.60, 105.71, 105.58, 56.17, 21.83. HRMS(ESI<sup>+</sup>): Calculated for C<sub>15</sub>H<sub>13</sub>N<sub>3</sub>O<sub>5</sub>S, [M+H]<sup>+</sup>348.0649. Found 348.0644.

#### 4-ethoxy-3-nitro-1-tosyl-1H-indazole (2as)



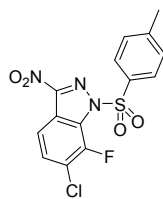
Obtained as a white solid in 82% yield; M.p.153-155 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (d,  $J = 8.5$  Hz, 2H), 7.78 (d,  $J = 8.6$  Hz, 1H), 7.57 – 7.52 (m, 1H), 7.29 (d,  $J = 9.2$  Hz, 2H), 6.76 (s, 1H), 4.14 (q,  $J = 7.0$  Hz, 2H), 2.39 (s, 3H), 1.43 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.41, 146.75, 143.27, 133.54, 132.74, 130.34, 128.14, 107.69, 106.30, 105.33, 100.00, 64.77, 21.82, 14.35. HRMS(ESI<sup>+</sup>): Calculated for  $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}_5\text{S}$ ,  $[\text{M}+\text{H}]^+$ 349.0722. Found 349.0720.

#### 4,6-dimethyl-3-nitro-1-tosyl-1H-indazole (2at)



Obtained as a white solid in 70% yield; M.p.167-169 °C  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J = 8.5$  Hz, 2H), 7.90 (s, 1H), 7.31 (d,  $J = 9.2$  Hz, 2H), 7.07 (s, 1H), 2.56 (s, 3H), 2.52 (s, 3H), 2.39 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.74, 142.92, 142.19, 133.62, 131.70, 130.36, 130.30, 128.18, 114.00, 110.65, 100.00, 29.78, 22.16, 20.50. HRMS(ESI<sup>+</sup>): Calculated for  $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}_4\text{S}$ ,  $[\text{M}+\text{H}]^+$ 346.0856. Found 346.0855.

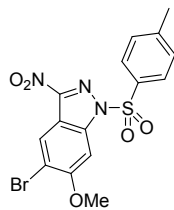
#### 6-chloro-7-fluoro-3-nitro-1-tosyl-1H-indazole (2au)



Obtained as a white solid in 42% yield; M.p.219-221 °C  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.40 (d,  $J = 5.9$  Hz, 1H), 7.99-7.97 (m, 3H), 7.37 (d,  $J = 7.9$  Hz, 2H), 2.42 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.95(d,  $J = 252.5$  Hz), 155.70, 147.70, 138.19(d,  $J = 3.1$  Hz), 132.78, 130.68, 128.54, 127.41, 116.30(d,  $J = 11.1$  Hz), 115.65, 107.61(d,  $J = 26.3$  Hz), 21.93.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -113.37. HRMS(ESI<sup>+</sup>): Calculated for  $\text{C}_{14}\text{H}_9\text{ClFN}_3\text{O}_4\text{S}$ ,  $[\text{M}+\text{H}]^+$ 370.0059. Found 370.0055.

#### 5-bromo-6-methoxy-3-nitro-1-tosyl-1H-indazole (2av)





Obtained as a white solid in 62% yield; M.p.219-221 °C <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

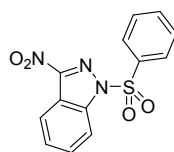
δ 8.40 (s, 1H), 7.95 (d, *J* = 8.5 Hz, 2H), 7.68 (s, 1H), 7.35 – 7.33 (m, 2H), 4.08 (s, 3H), 2.41 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.34, 147.34, 142.81, 133.17, 130.53, 128.32, 125.50, 114.42,

111.90, 94.77, 57.08, 21.90. HRMS(ESI<sup>+</sup>): Calculated for C<sub>15</sub>H<sub>12</sub>BrN<sub>3</sub>O<sub>5</sub>S, [M+H]<sup>+</sup>425.9754. Found

425.9755.

### 3-nitro-1-(phenylsulfonyl)-1H-indazole (2ba)



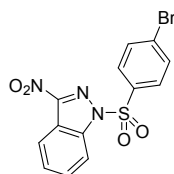
Obtained as a white solid in 91% yield; M.p.145-147 °C <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

δ 8.29 (dd, *J* = 20.4, 8.5 Hz, 2H), 8.12 (d, *J* = 7.6 Hz, 2H), 7.70 (dt, *J* = 15.3, 7.8 Hz, 2H), 7.57 (q, *J* =

7.2 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 142.23, 136.41, 135.51, 131.13, 129.87, 128.28, 127.21,

121.93, 117.29, 113.62. HRMS(ESI<sup>+</sup>): Calculated for C<sub>13</sub>H<sub>9</sub>N<sub>3</sub>O<sub>4</sub>S, [M+H]<sup>+</sup>304.0387. Found 304.0385.

### 1-((4-bromophenyl)sulfonyl)-3-nitro-1H-indazole (2bb)



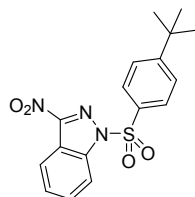
Obtained as a white solid in 87% yield; M.p.195-197 °C <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

δ 8.50 – 8.48 (m, 2H), 8.29 (dd, *J* = 8.2, 2.2 Hz, 2H), 7.96 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.70 (t, *J* = 8.0 Hz,

2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 142.23, 135.23, 133.28, 131.33, 131.32, 127.36, 127.35, 122.06,

117.32, 113.53. HRMS(ESI<sup>+</sup>): Calculated for C<sub>13</sub>H<sub>8</sub>BrN<sub>3</sub>O<sub>4</sub>S, [M+H]<sup>+</sup>381.9492. Found 381.9490.

### 1-((4-(tert-butyl)phenyl)sulfonyl)-3-nitro-1H-indazole (2bc)



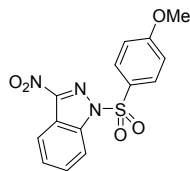
Obtained as a white solid in 83% yield; M.p.153-155 °C <sup>1</sup>H NMR (400 MHz,

CDCl<sub>3</sub>) δ 8.30 (dt, *J* = 8.8, 1.1 Hz, 1H), 8.24 (dt, *J* = 8.3, 1.4 Hz, 1H), 8.01 (d, *J* = 9.0 Hz, 2H), 7.72-

7.68 (m, 1H), 7.59 – 7.50 (m, 3H), 1.28 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.90, 142.15, 133.27,

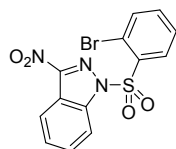
131.00, 128.20, 127.10, 126.95, 121.84, 117.29, 113.68, 35.57, 30.94. HRMS(ESI<sup>+</sup>): Calculated for C<sub>17</sub>H<sub>17</sub>N<sub>3</sub>O<sub>4</sub>S, [M+H]<sup>+</sup>360.1013. Found 360.1011.

#### 1-((4-methoxyphenyl)sulfonyl)-3-nitro-1H-indazole (2bd)



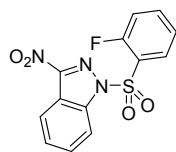
Obtained as a white solid in 88% yield; M.p.167-169 °C <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.29 (dt, *J* = 8.7, 0.9 Hz, 1H), 8.24 (dt, *J* = 8.3, 1.0 Hz, 1H), 8.03 (d, *J* = 9.1 Hz, 2H), 7.71-7.67 (m, 1H), 7.57-7.53 (m, 1H), 6.97 (d, *J* = 9.1 Hz, 2H), 3.84 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.24, 142.04, 130.91, 130.83, 127.43, 127.04, 121.83, 117.25, 115.09, 113.67, 55.96. HRMS(ESI<sup>+</sup>): Calculated for C<sub>14</sub>H<sub>11</sub>N<sub>3</sub>O<sub>5</sub>S, [M+H]<sup>+</sup>334.0492. Found 334.0495.

#### 1-((2-bromophenyl)sulfonyl)-3-nitro-1H-indazole (2be)



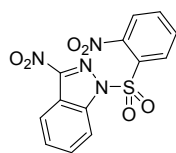
Obtained as a white solid in 83% yield; M.p.177-179 °C <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.35 – 8.22 (m, 4H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.75 (dd, *J* = 7.3, 1.0 Hz 1H), 7.74 – 7.71 (m, 1H), 7.62-7.58 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.71, 136.27, 136.04, 135.99, 133.70, 130.99, 128.42, 127.11, 121.88, 121.81, 116.58, 114.65. HRMS(ESI<sup>+</sup>): Calculated for C<sub>13</sub>H<sub>8</sub>BrN<sub>3</sub>O<sub>4</sub>S, [M+H]<sup>+</sup>381.9492. Found 381.9495.

#### 1-((2-fluorophenyl)sulfonyl)-3-nitro-1H-indazole (2bf)



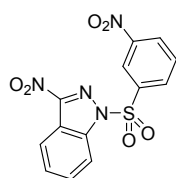
Obtained as a white solid in 82% yield; M.p.165-167 °C <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.33 (d, *J* = 8.7 Hz, 1H), 8.28 (d, *J* = 8.3Hz,1H),8.23 (td, *J* = 7.7,1.7Hz,1H),7.75–7.67 (m,2H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.18 – 7.12 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ159.72(d, *J* = 262.6Hz), 142.80, 138.06(d, *J* = 9.1Hz), 131.66, 131.14, 127.26, 125.30(d, *J* = 4.1Hz), 124.73(d, *J* = 13.1Hz), 121.77, 117.81(d, *J* = 20.2Hz), 116.97, 114.27(d, *J* = 2.0Hz), 100.00. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -106.48. HRMS(ESI<sup>+</sup>): Calculated for C<sub>13</sub>H<sub>8</sub>FN<sub>3</sub>O<sub>4</sub>S, [M+H]<sup>+</sup>322.0293. Found 322.0295.

### 3-nitro-1-((2-nitrophenyl)sulfonyl)-1H-indazole (2bg)



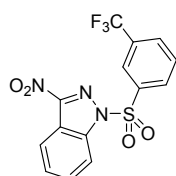
Obtained as a white solid in 32% yield; M.p.176-178 °C  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.33 (dd,  $J$  = 8.7, 1.3 Hz, 1H), 8.28 (dt,  $J$  = 8.2, 1.0 Hz, 1H), 8.24 (ddd,  $J$  = 8.1, 6.9, 1.8 Hz, 1H), 7.77 – 7.68 (m, 2H), 7.61 – 7.57 (m, 1H), 7.41 (td,  $J$  = 7.8, 1.1 Hz, 1H), 7.15 (ddd,  $J$  = 9.7, 8.4, 1.0 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  171.52, 143.27, 136.69, 133.85, 133.74, 133.18, 131.42, 130.28, 128.57, 127.43, 125.31, 121.64, 114.66. HRMS(ESI+): Calculated for  $\text{C}_{13}\text{H}_8\text{N}_4\text{O}_6\text{S}$ ,  $[\text{M}+\text{H}]^+$ 349.0238. Found 349.0233.

### 3-nitro-1-((3-nitrophenyl)sulfonyl)-1H-indazole (2bh)



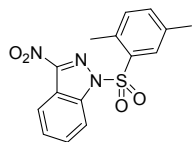
Obtained as a white solid in 84% yield; M.p.190-192 °C  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.51-8.50 (m, 2H), 8.31 (d,  $J$  = 6.1 Hz, 2H), 7.98 (d,  $J$  = 8.3 Hz, 2H), 7.71 (t,  $J$  = 8.0 Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.69, 142.44, 138.35, 133.94, 131.82, 131.51, 129.80, 127.70, 123.33, 122.22, 117.31, 113.50. HRMS(ESI+): Calculated for  $\text{C}_{13}\text{H}_8\text{N}_4\text{O}_6\text{S}$ ,  $[\text{M}+\text{H}]^+$ 349.0238. Found 349.0236.

### 3-nitro-1-((3-(trifluoromethyl)phenyl)sulfonyl)-1H-indazole (2bi)



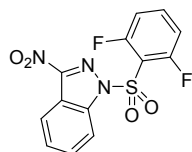
Obtained as a white solid in 78% yield; M.p.152-154 °C  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.38 – 8.31 (m, 2H), 8.30 (d,  $J$  = 8.7 Hz, 1H), 8.27 (d,  $J$  = 8.2 Hz, 1H), 7.93 (d,  $J$  = 7.0 Hz, 1H), 7.76 (dd,  $J$  = 7.2, 1.3 Hz, 1H), 7.74 – 7.71 (m, 1H), 7.60 (ddd,  $J$  = 8.1, 7.2, 0.8 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.36, 137.61, 132.32(q,  $J$  = 34.3Hz), 132.12, 131.72(q,  $J$  = 1.3Hz), 131.55, 130.85, 130.52, 127.51, 125.20(q,  $J$  = 3.9Hz), 122.15, 117.32, 113.48.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.96. HRMS(ESI+): Calculated for  $\text{C}_{14}\text{H}_8\text{F}_3\text{N}_3\text{O}_4\text{S}$ ,  $[\text{M}+\text{H}]^+$ 372.0261. Found 372.0266.

### 1-((2,5-dimethylphenyl)sulfonyl)-3-nitro-1H-indazole (2bj)



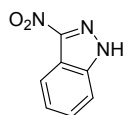
Obtained as a white solid in 93% yield; M.p.173-175 °C <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.33 – 8.24 (m, 2H), 8.04 (d, *J* = 2.2 Hz, 1H), 7.74 – 7.66 (m, 1H), 7.56 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 1H), 7.35 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 1H), 2.58 (s, 3H), 2.40 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 142.39, 137.27, 136.62, 136.43, 134.52, 133.36, 131.07, 130.91, 127.03, 121.85, 117.01, 113.82, 20.93, 20.39. HRMS(ESI<sup>+</sup>): Calculated for C<sub>15</sub>H<sub>13</sub>N<sub>3</sub>O<sub>4</sub>S, [M+H]<sup>+</sup>332.0700. Found 332.0702.

### 1-(2,6-difluorophenyl)sulfonyl-3-nitro-1H-indazole (2bk)



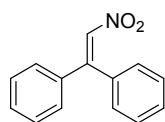
Obtained as a white solid in 76% yield; M.p.183-185 °C <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.29 (d, *J* = 9.4 Hz, 2H), 7.76 – 7.71 (m, 1H), 7.67 – 7.58 (m, 2H), 7.05 (t, *J* = 8.4 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.18 (dd, *J* = 266.3 Hz, 2.6 Hz), 142.75, 137.79(t, *J* = 11.3 Hz), 131.33, 127.36, 121.87, 116.91, 114.14(t, *J* = 1.2 Hz), 113.80(d, *J* = 26.2Hz), 113.82(dd, *J* = 18.2 Hz, 3.3 Hz), 100.00. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -103.66. HRMS(ESI<sup>+</sup>): Calculated for C<sub>13</sub>H<sub>7</sub>F<sub>2</sub>N<sub>3</sub>O<sub>4</sub>S, [M+H]<sup>+</sup>340.0198. Found 340.0192.

### 3-nitro-1H-indazole (3a)



Obtained as a white solid in 91% yield; M.p.203-205 °C <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 12.90 (s, 1H), 8.35 (d, *J* = 8.2 Hz, 1H), 7.98 (d, *J* = 8.6 Hz, 1H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 149.02, 142.15, 129.28, 126.12, 120.82, 115.77, 112.40. HRMS(ESI<sup>+</sup>): Calculated for C<sub>7</sub>H<sub>5</sub>N<sub>3</sub>O<sub>2</sub>, [M+H]<sup>+</sup>164.0455. Found 164.0452.

### (2-nitroethene-1,1-diyl)dibenzene (6a)



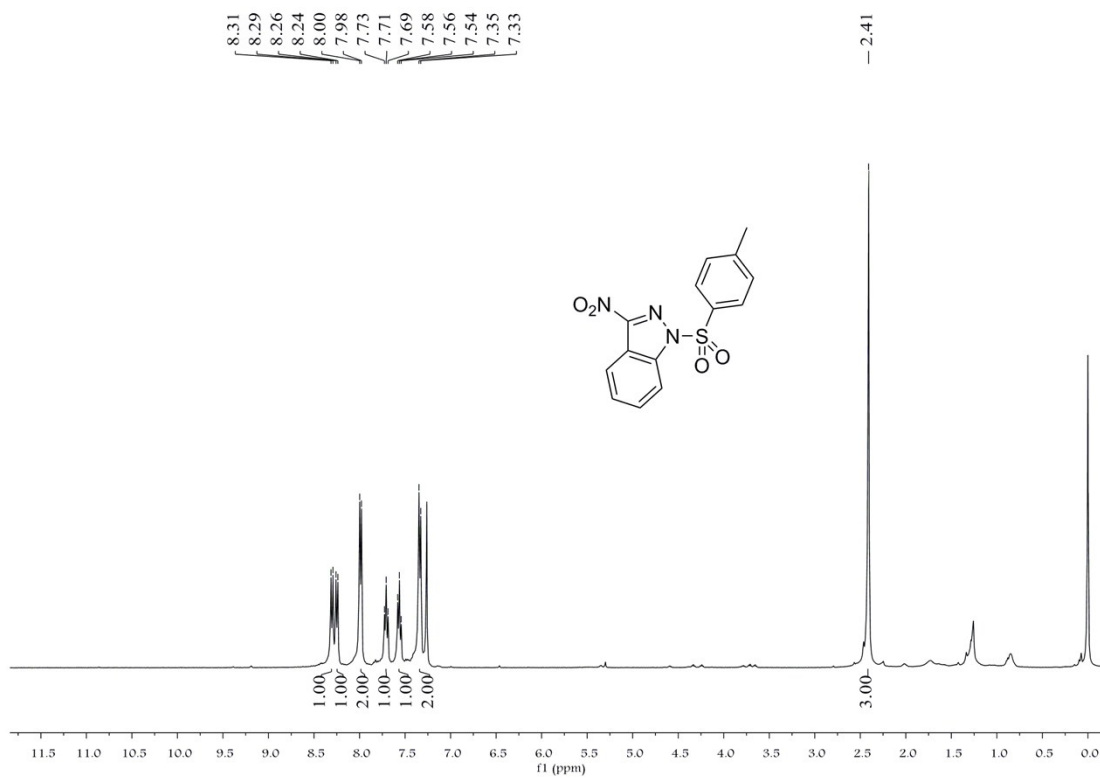
Obtained as a Light yellow liquid in 48% yield; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.81 (d, *J* = 1.2 Hz, 2H), 7.79 (d, *J* = 1.5 Hz, 2H), 7.61 – 7.56 (m, 2H), 7.48 (d, *J* = 7.8 Hz, 3H), 7.46-7.43 (m,

2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.85, 137.70, 132.52, 130.15, 128.38, 121.82. HRMS(ESI+):

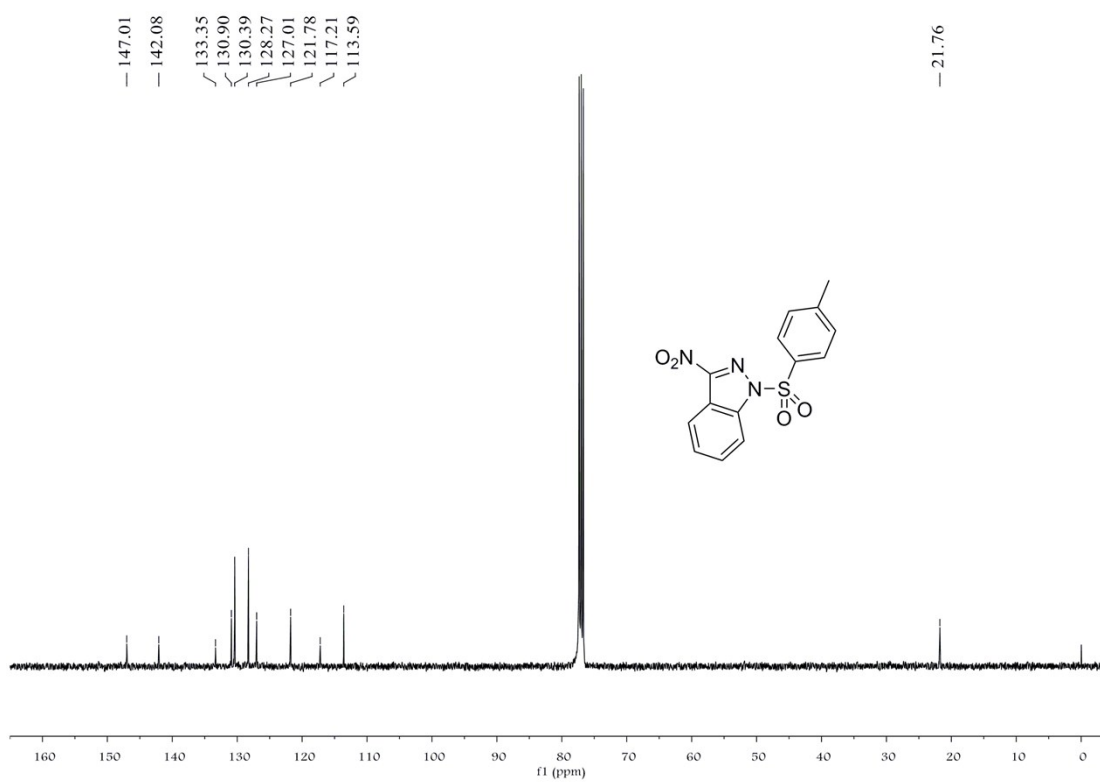
Calculated for  $\text{C}_{14}\text{H}_{11}\text{NO}_2$ ,  $[\text{M}+\text{H}]^+$  226.0863. Found 226.0862.

#### 4. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of the products

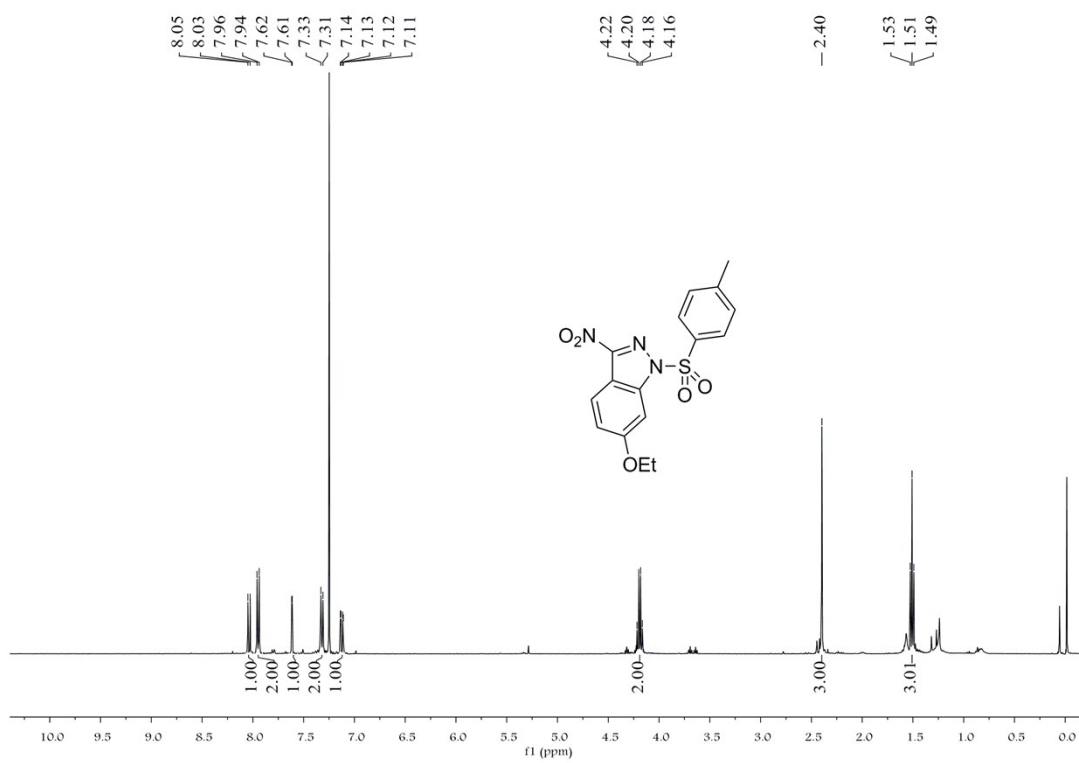
2aa  $^1\text{H}$  NMR



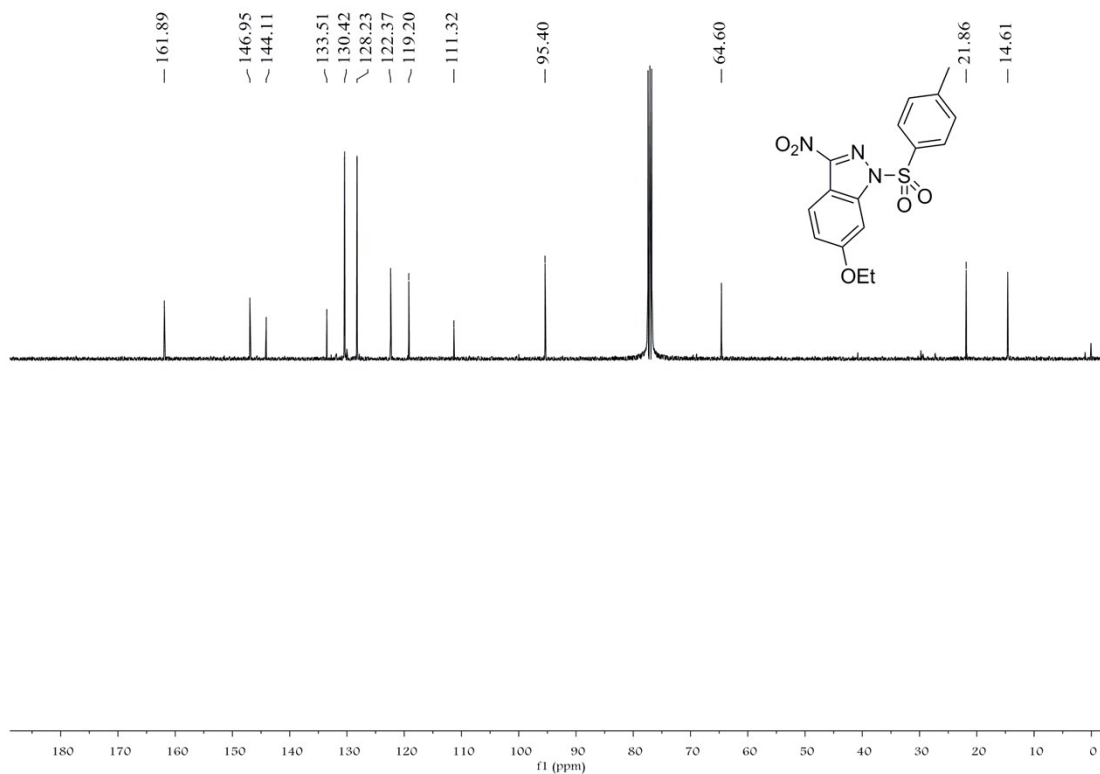
2aa <sup>13</sup>C NMR



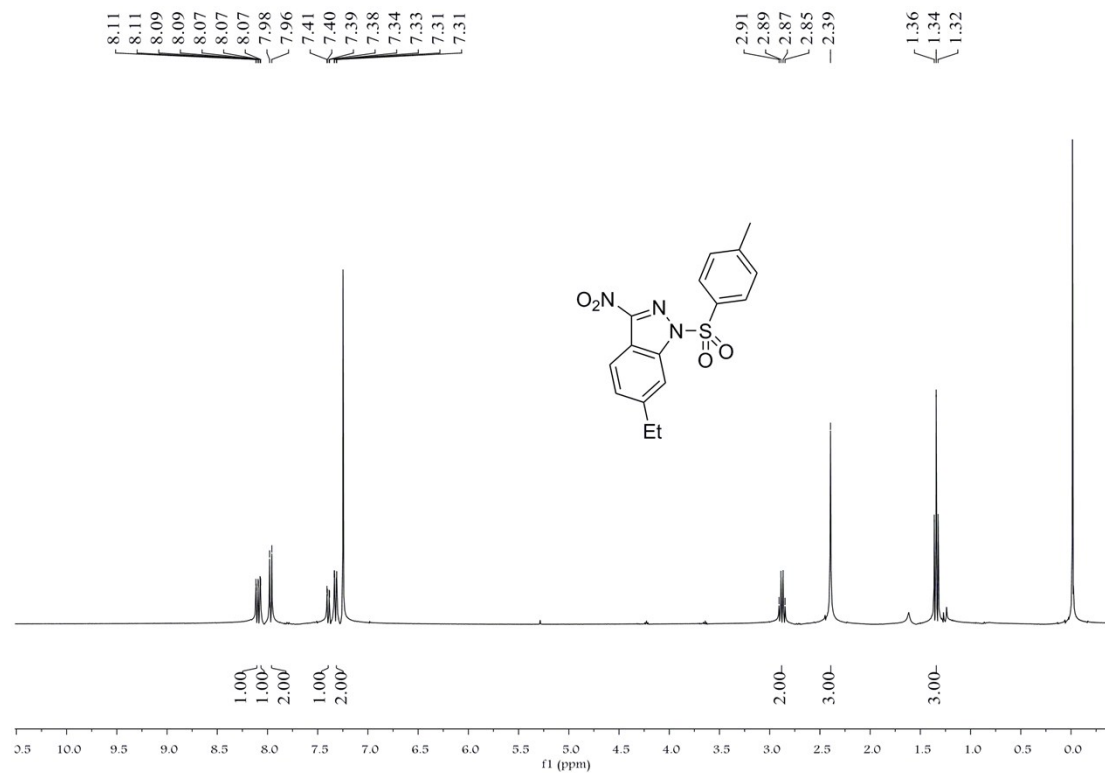
2ab <sup>1</sup>H NMR



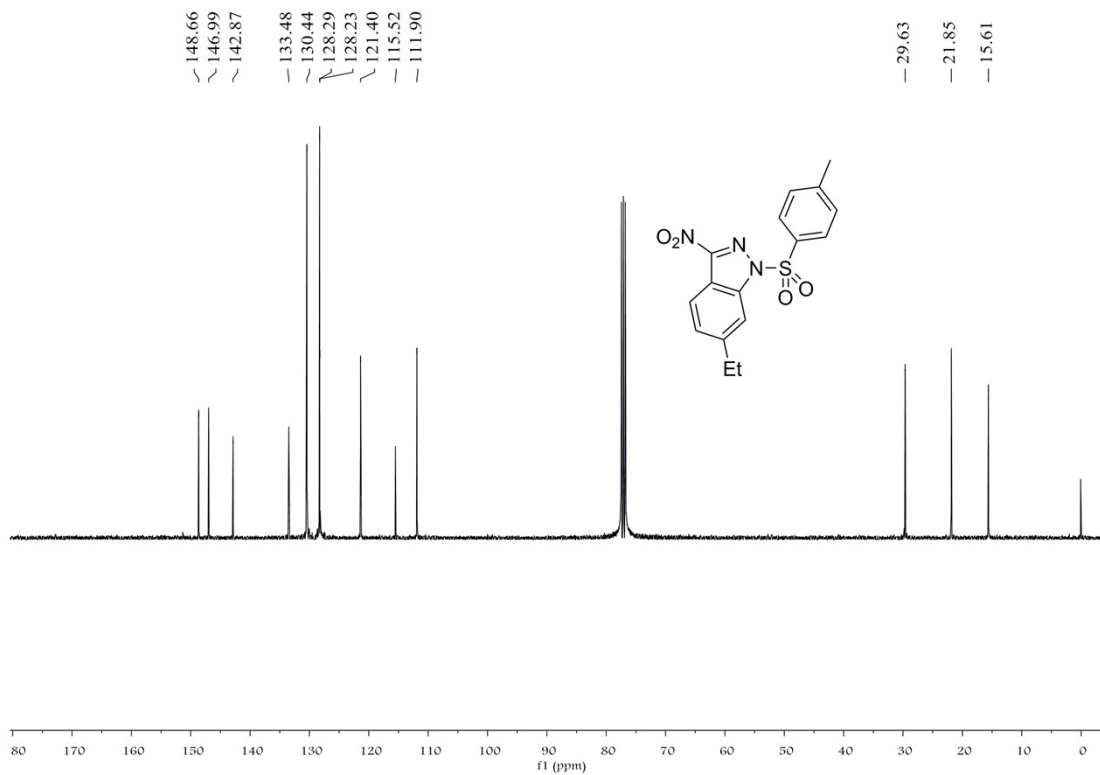
2ab <sup>13</sup>C NMR



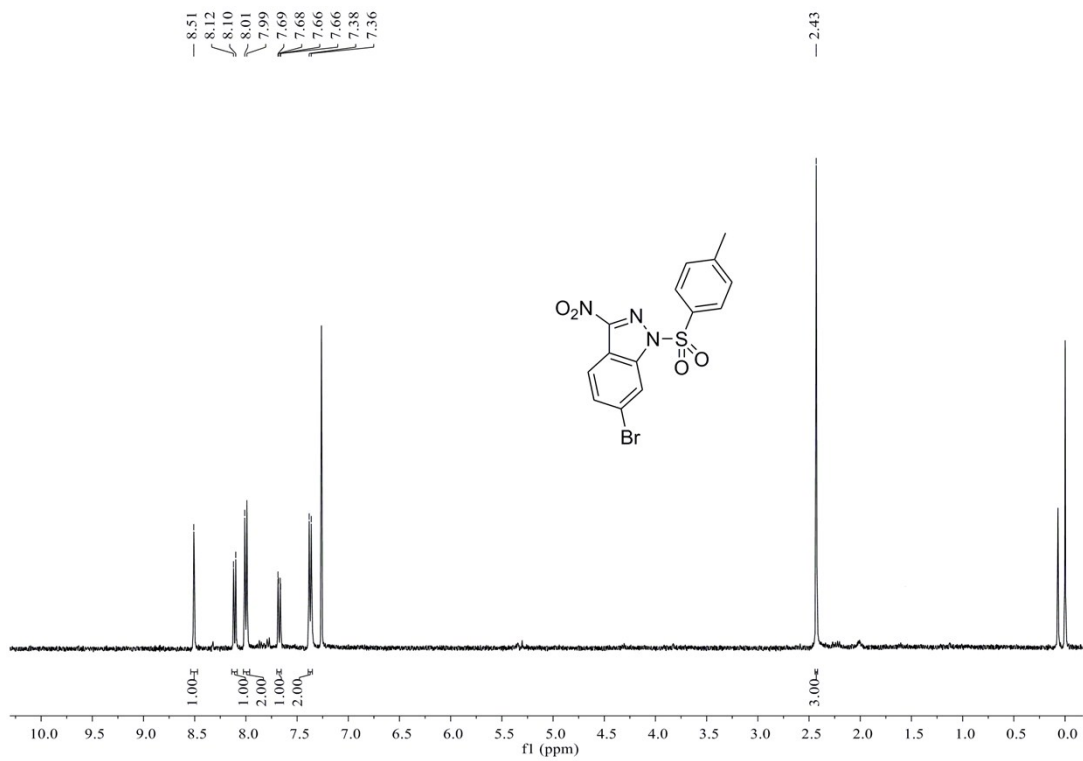
2ac <sup>1</sup>H NMR



### 2ac <sup>13</sup>C NMR

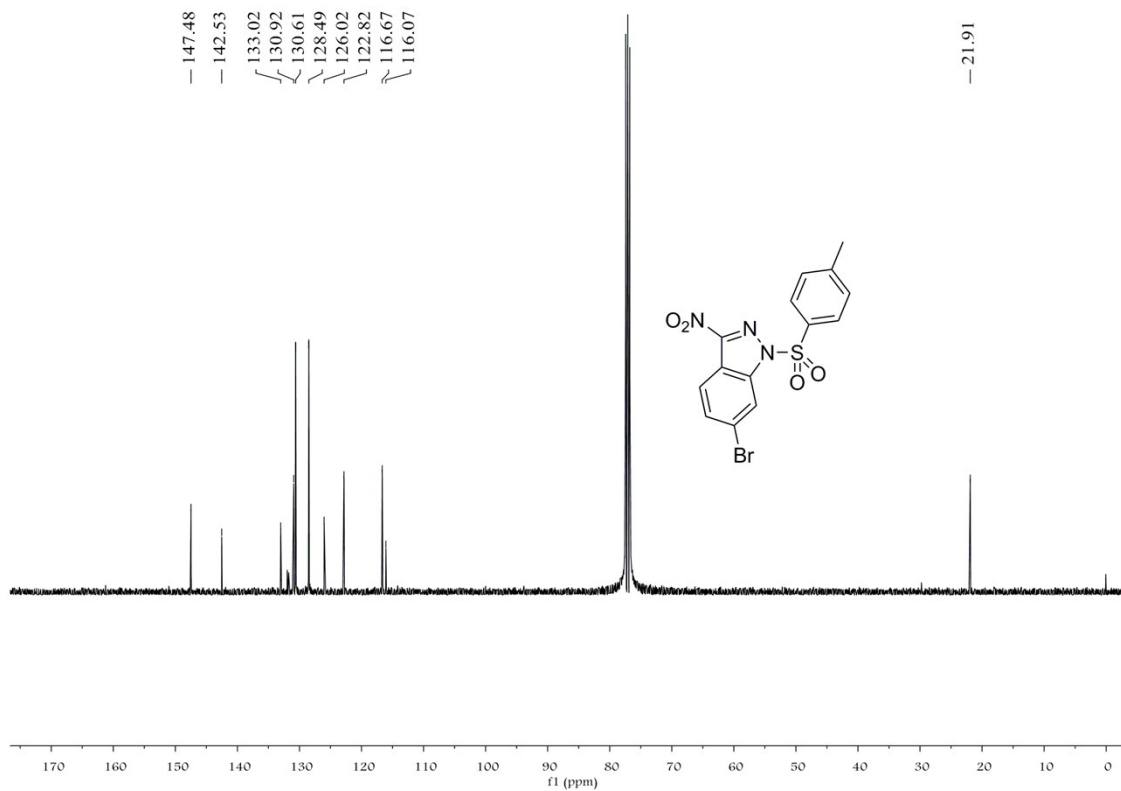


### 2ad <sup>1</sup>H NMR

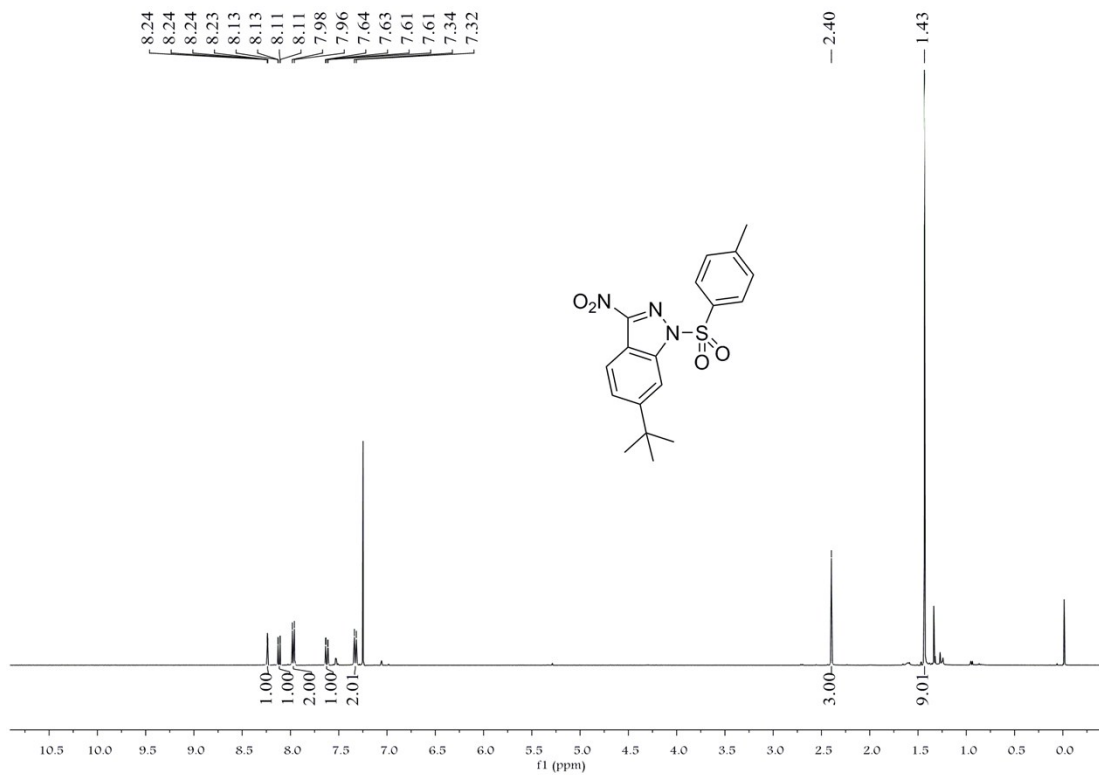




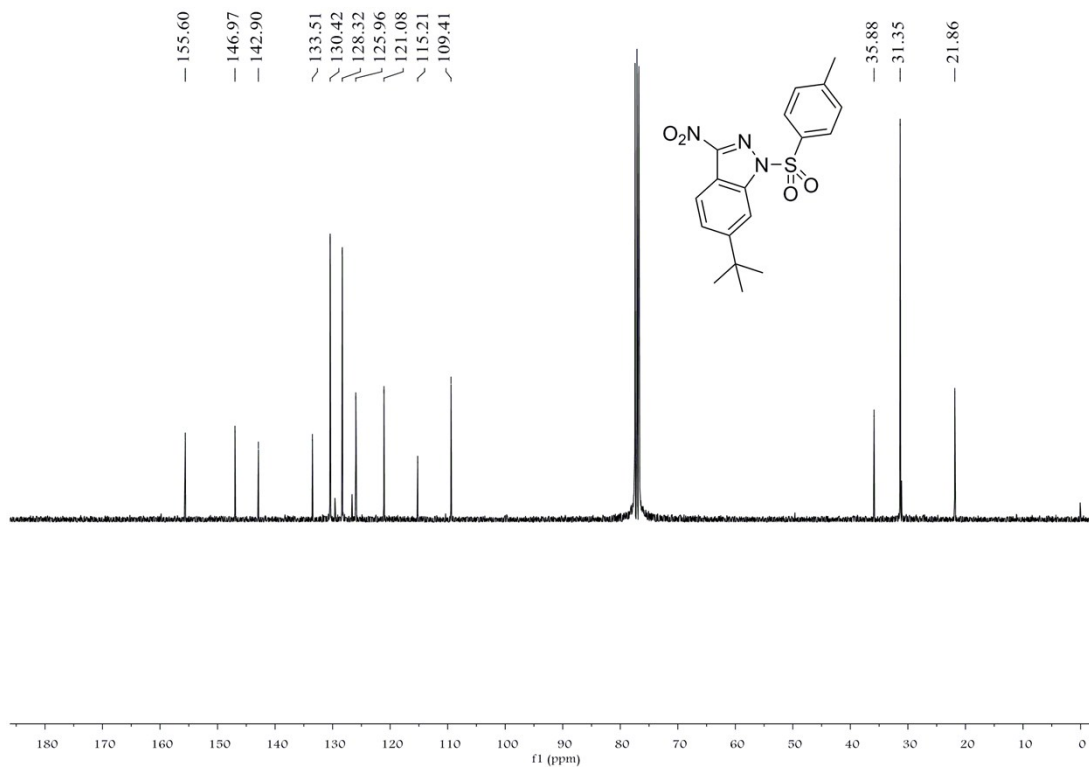
2ad <sup>13</sup>C NMR



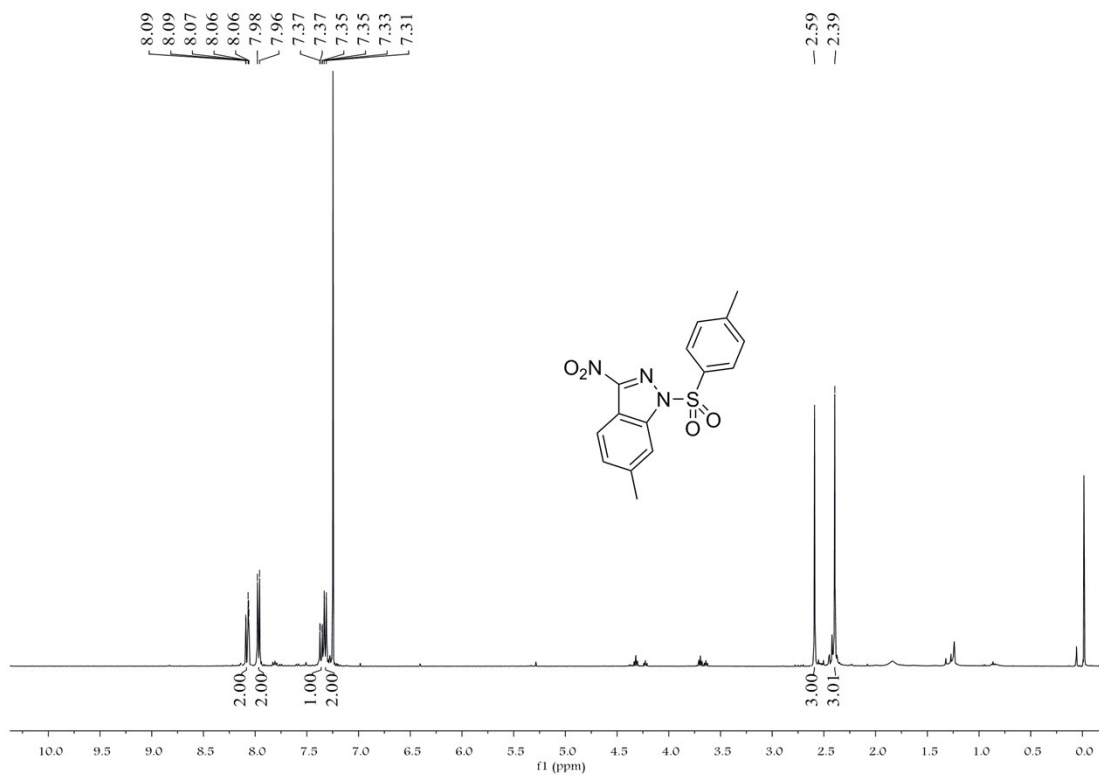
2ae <sup>1</sup>H NMR



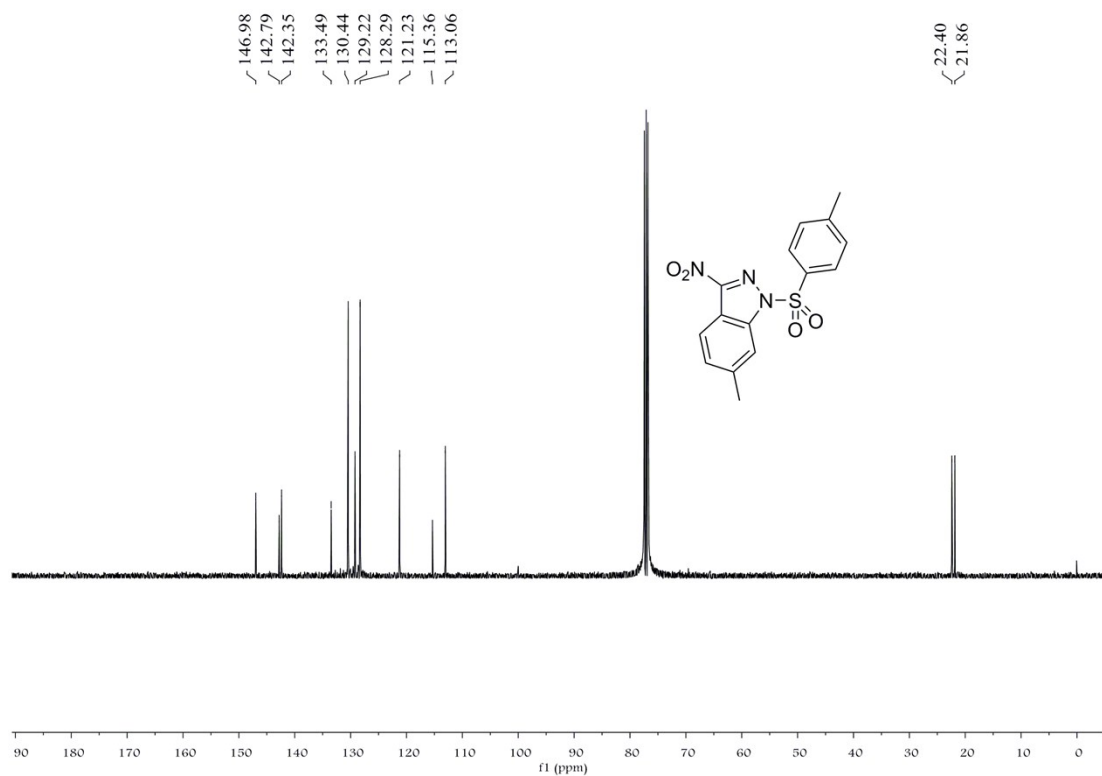
2ae <sup>13</sup>C NMR



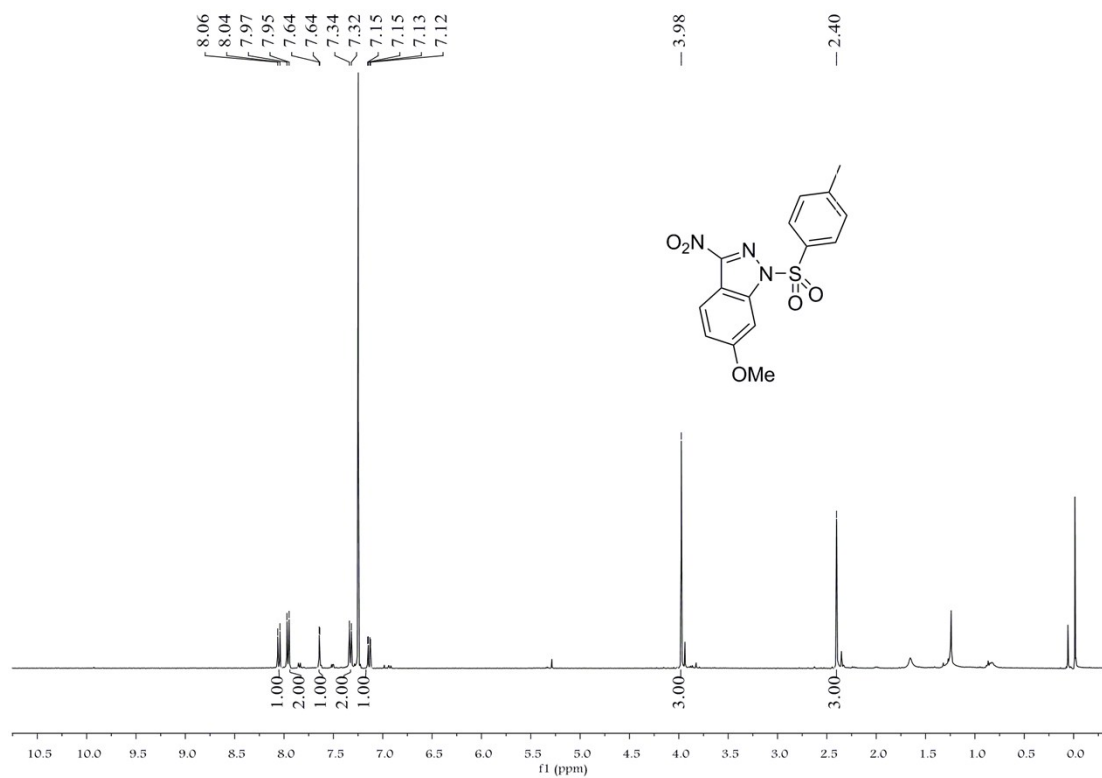
2af <sup>1</sup>H NMR



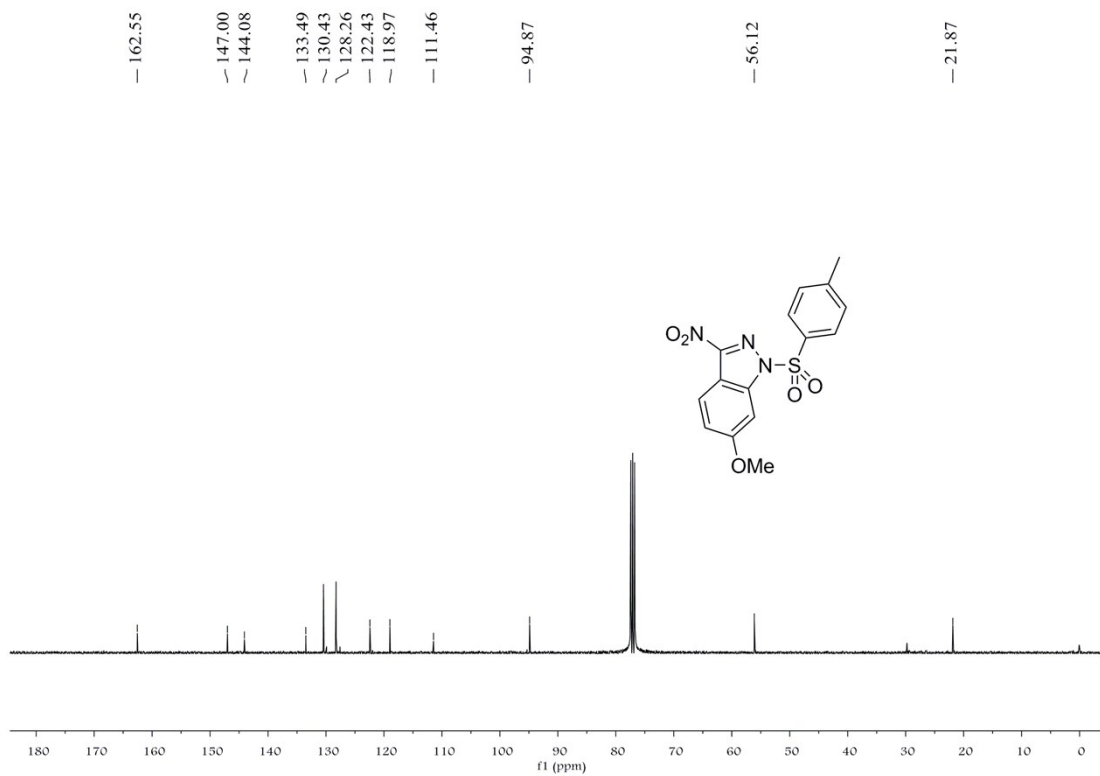
### 2af <sup>13</sup>C NMR



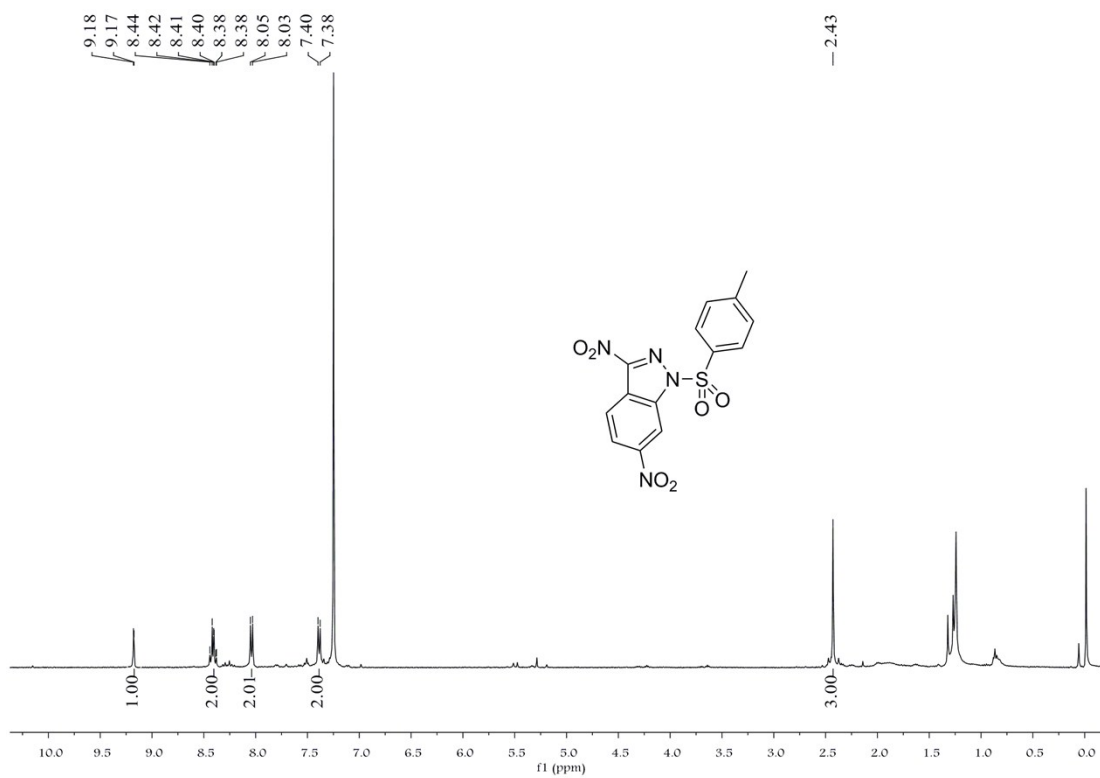
### 2ag <sup>1</sup>H NMR



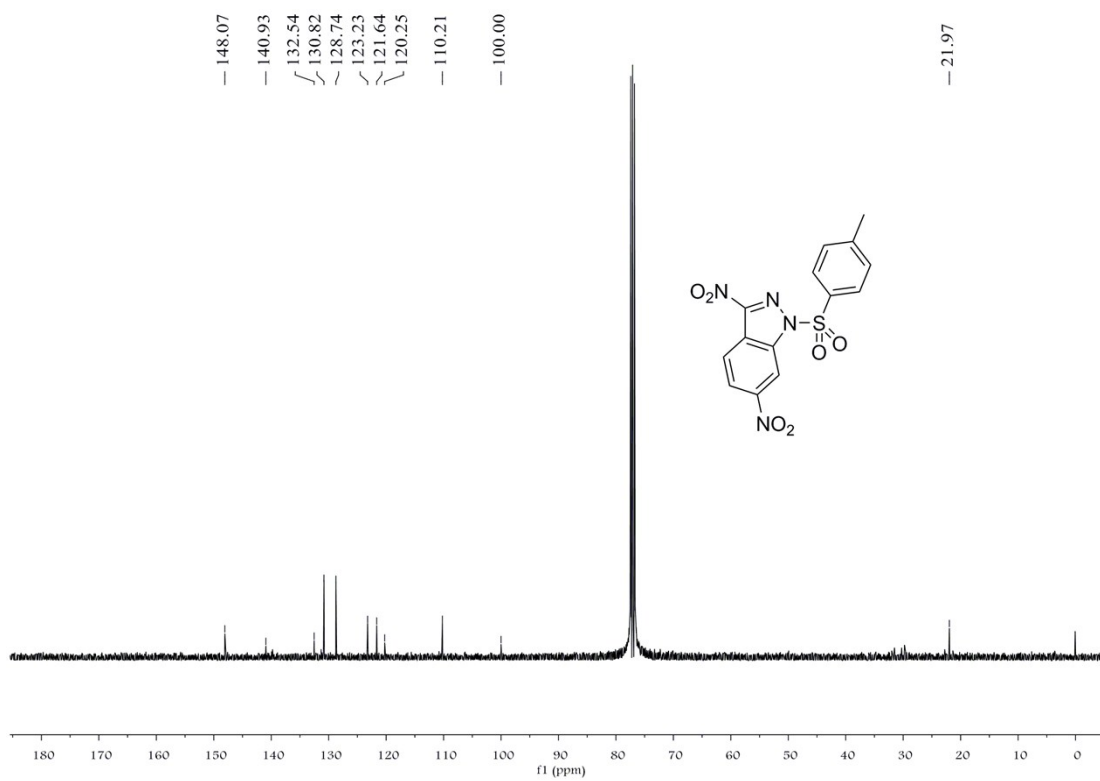
2ag <sup>13</sup>C NMR



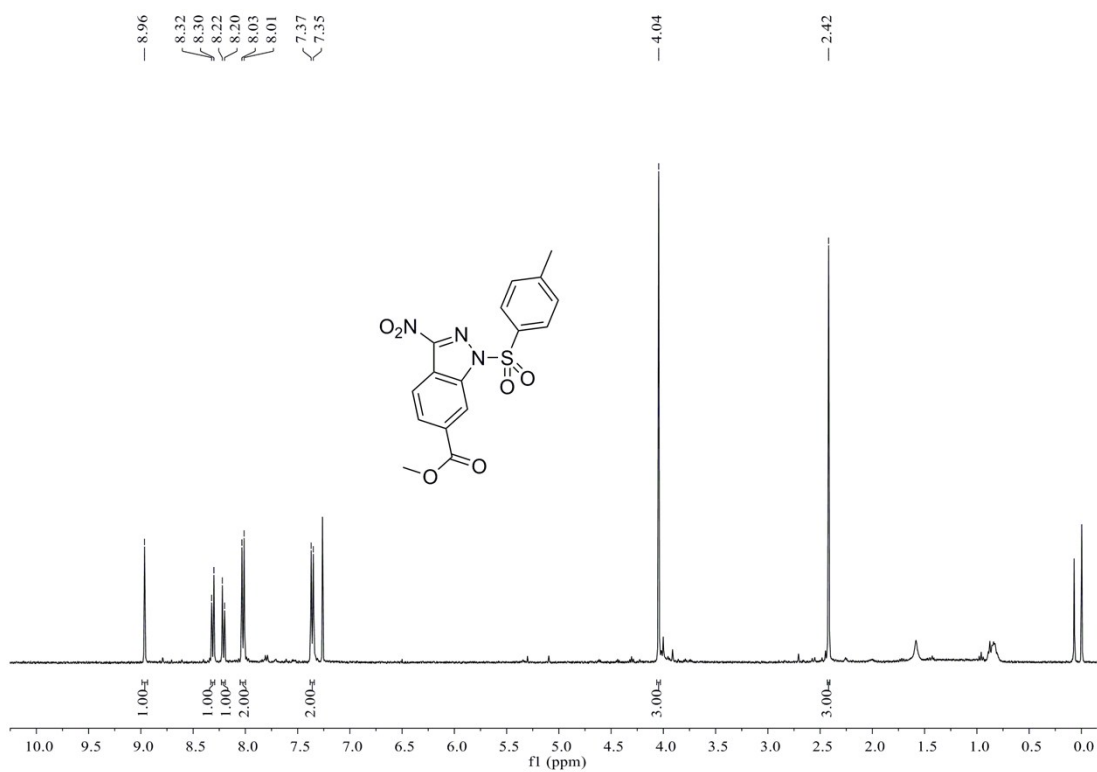
2ah <sup>1</sup>H NMR



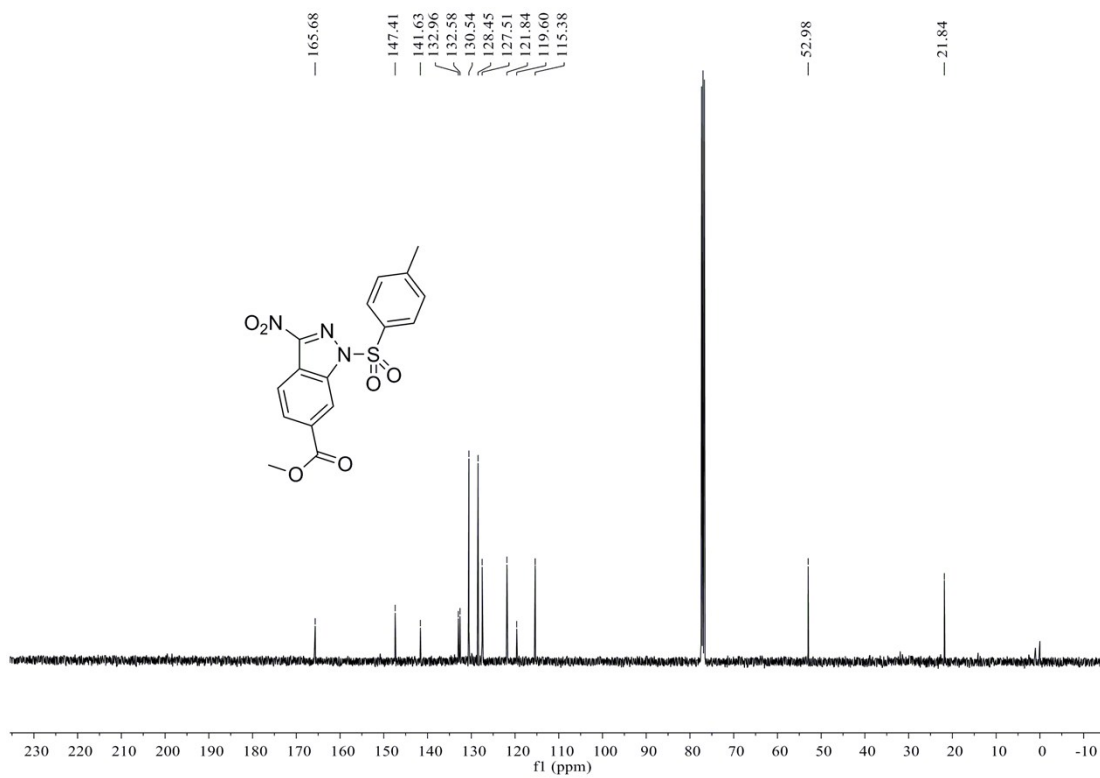
### 2ah <sup>13</sup>C NMR



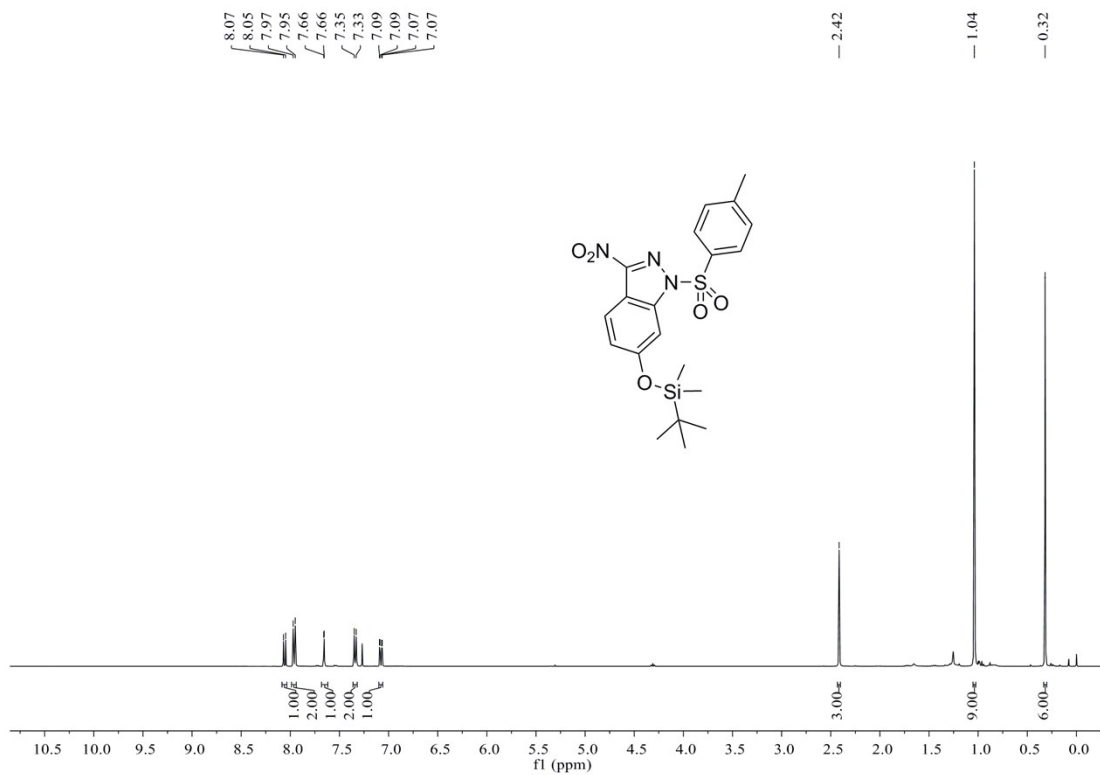
### 2ai <sup>1</sup>H NMR



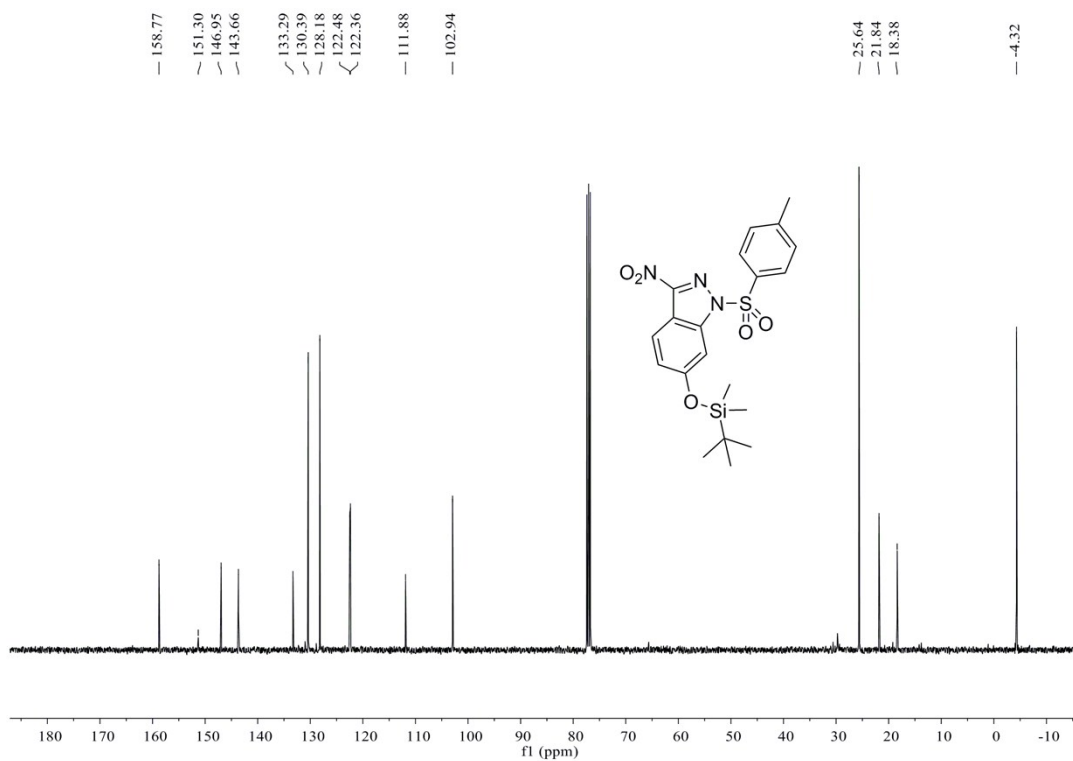
2ai <sup>13</sup>C NMR



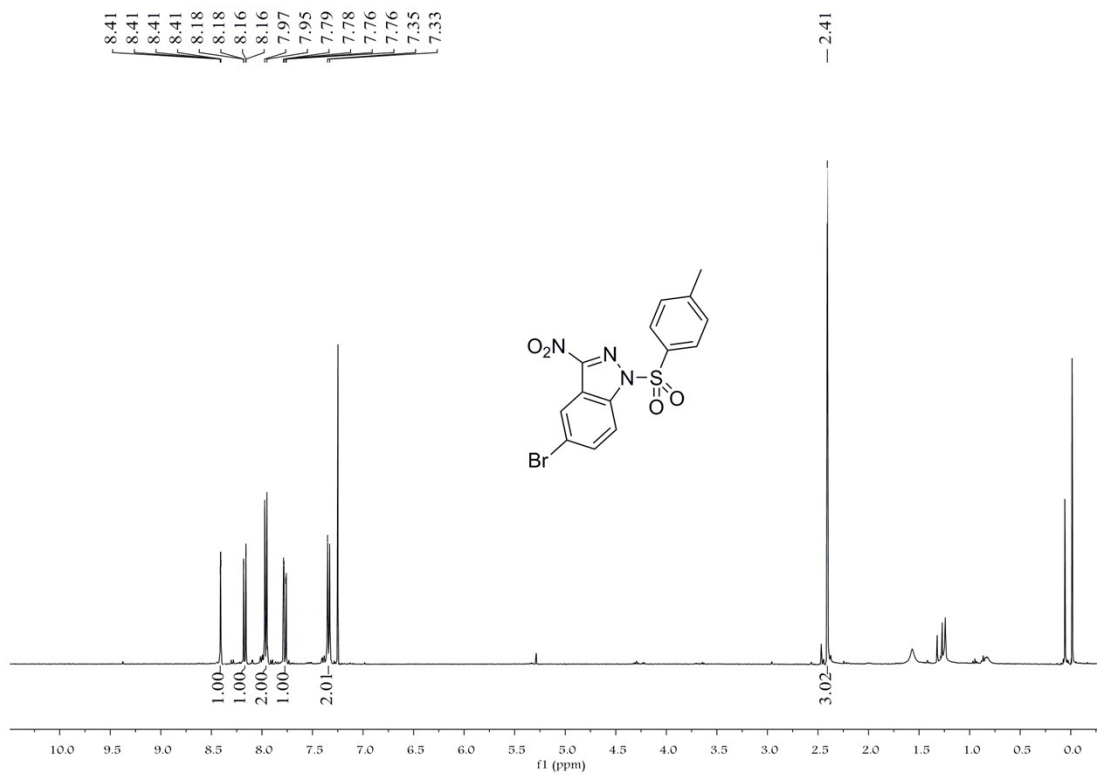
2aj <sup>1</sup>H NMR



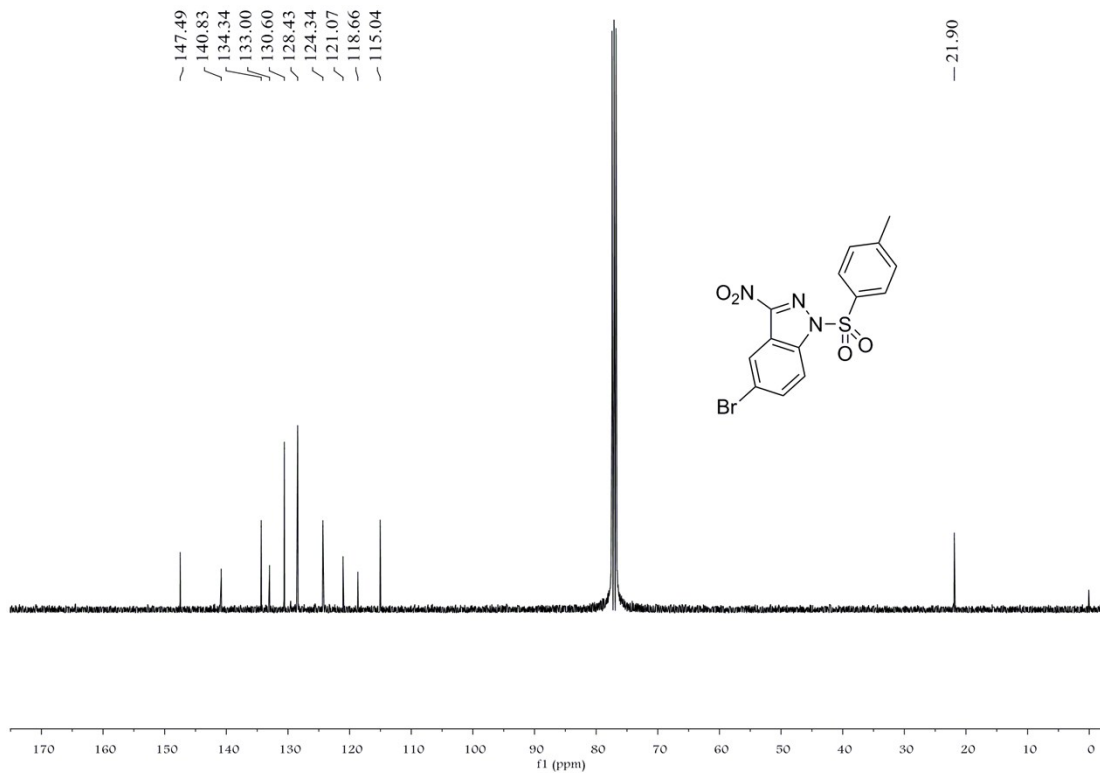
2aj <sup>13</sup>C NMR



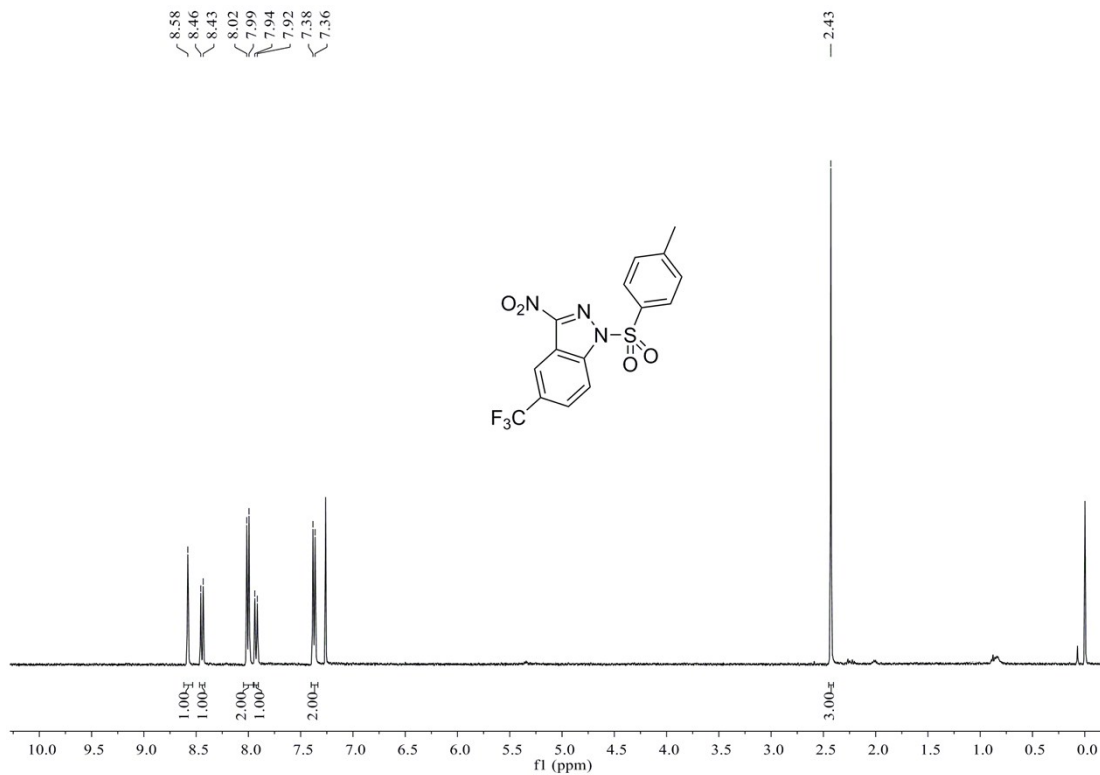
2am <sup>1</sup>H NMR



2am <sup>13</sup>C NMR

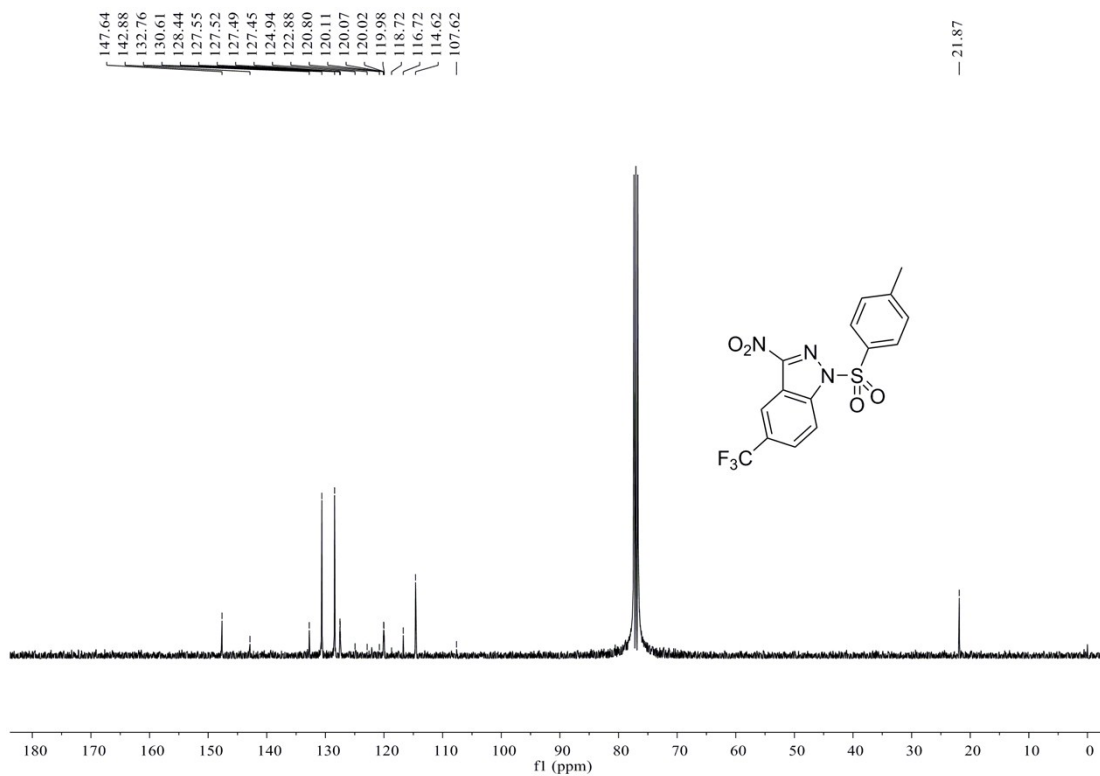


2an <sup>1</sup>H NMR

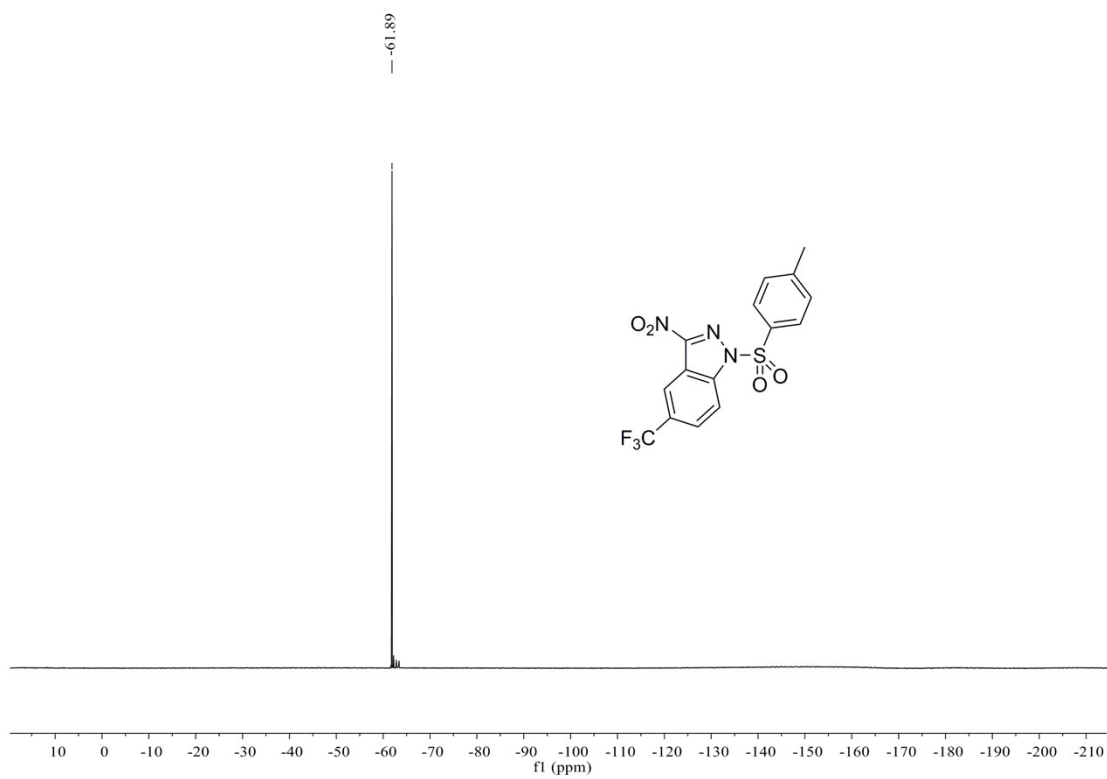




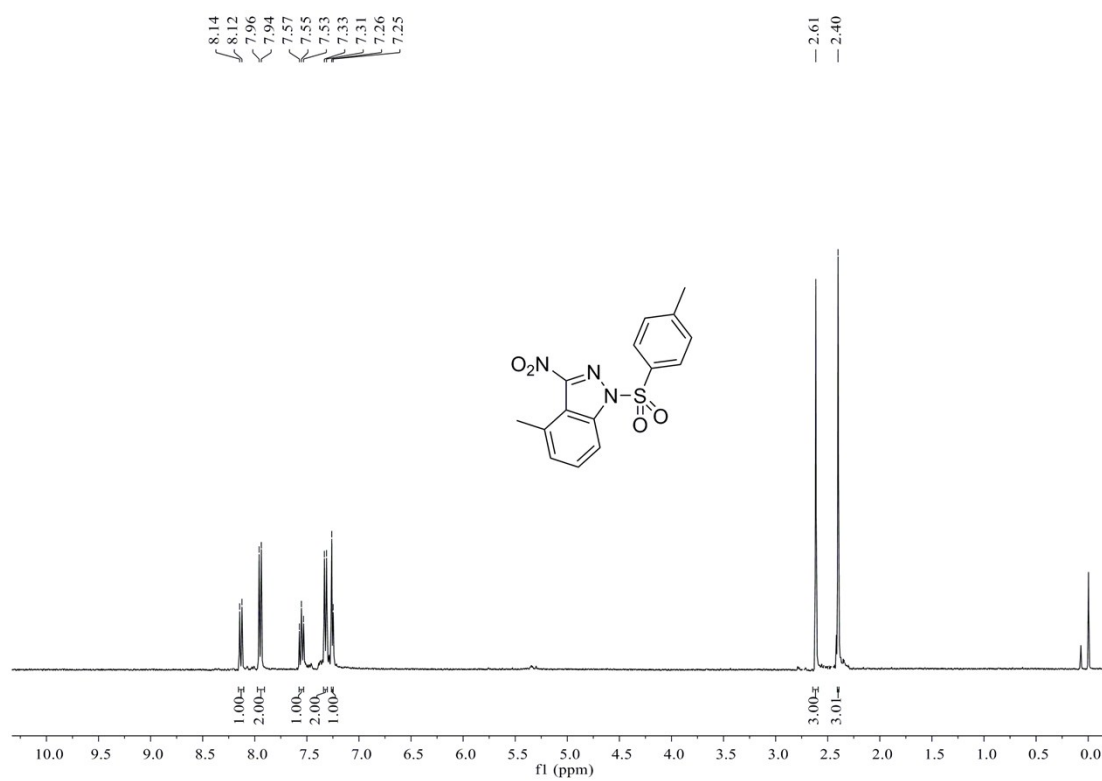
### 2an <sup>13</sup>C NMR



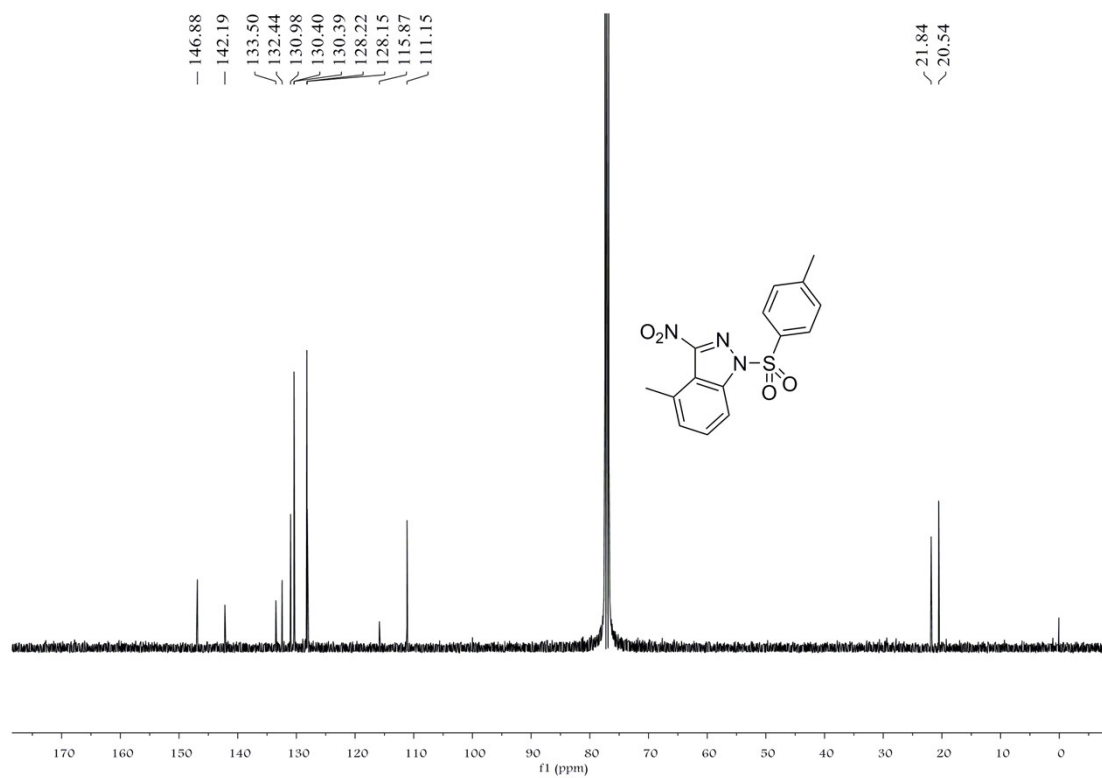
### 2an <sup>19</sup>F NMR



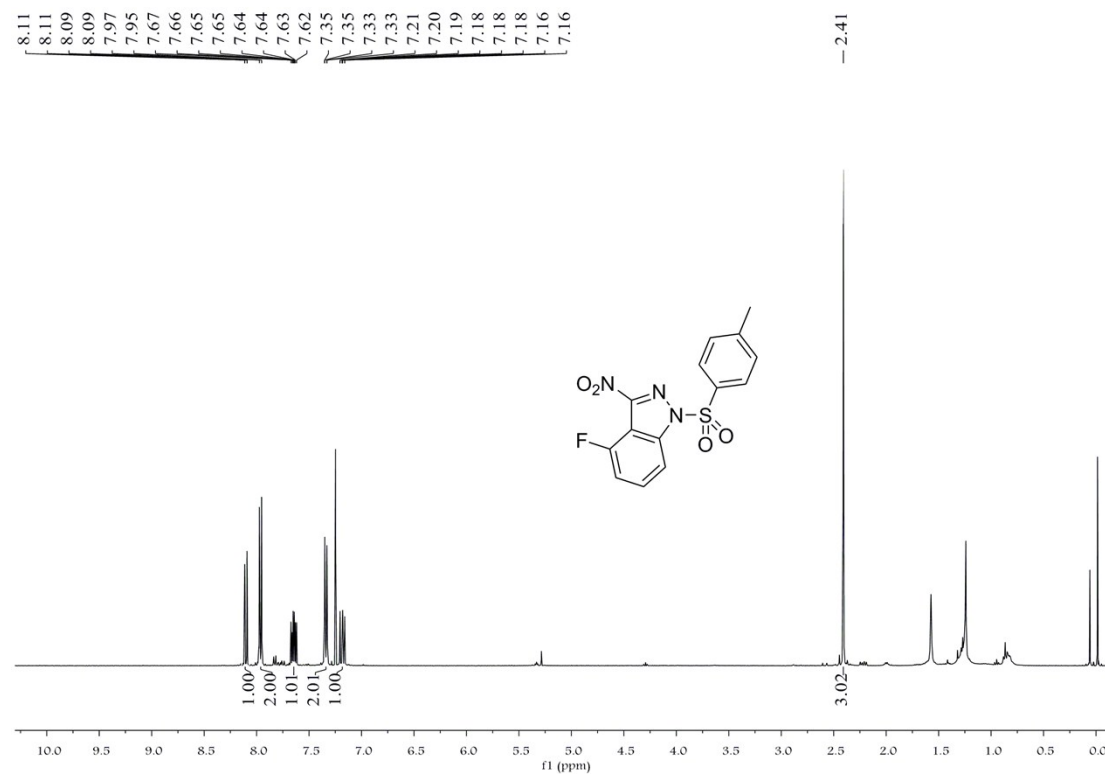
## 2ap <sup>1</sup>H NMR



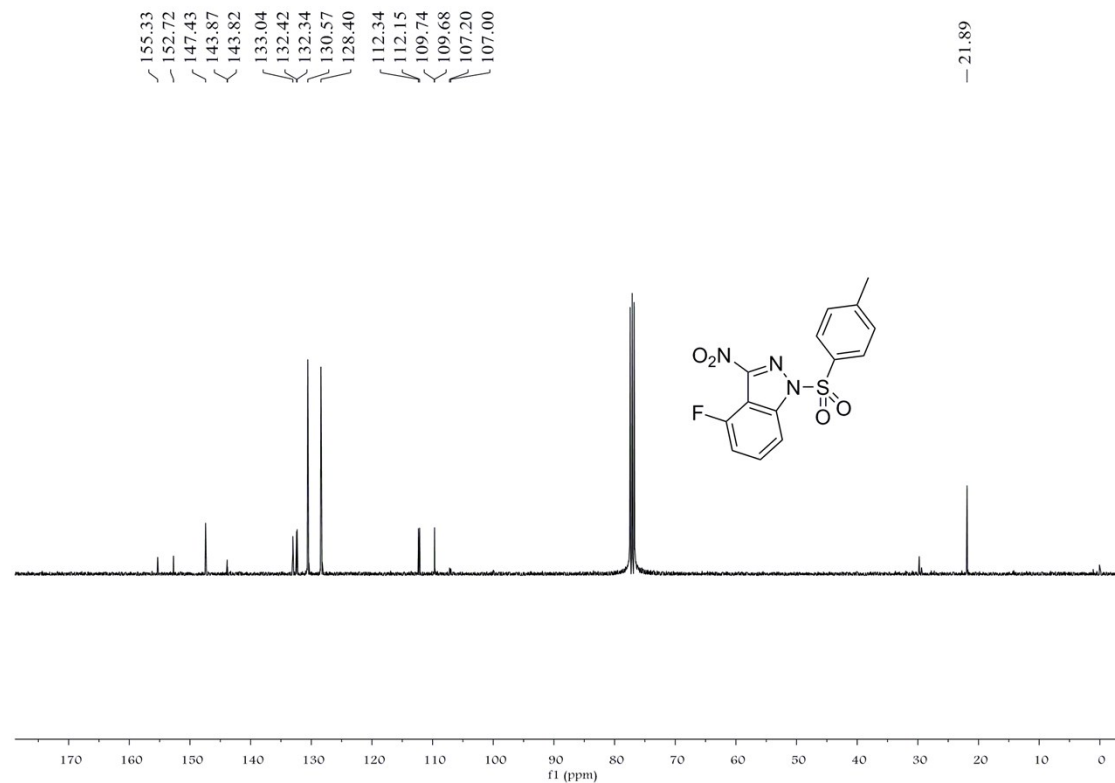
## 2ap <sup>13</sup>C NMR



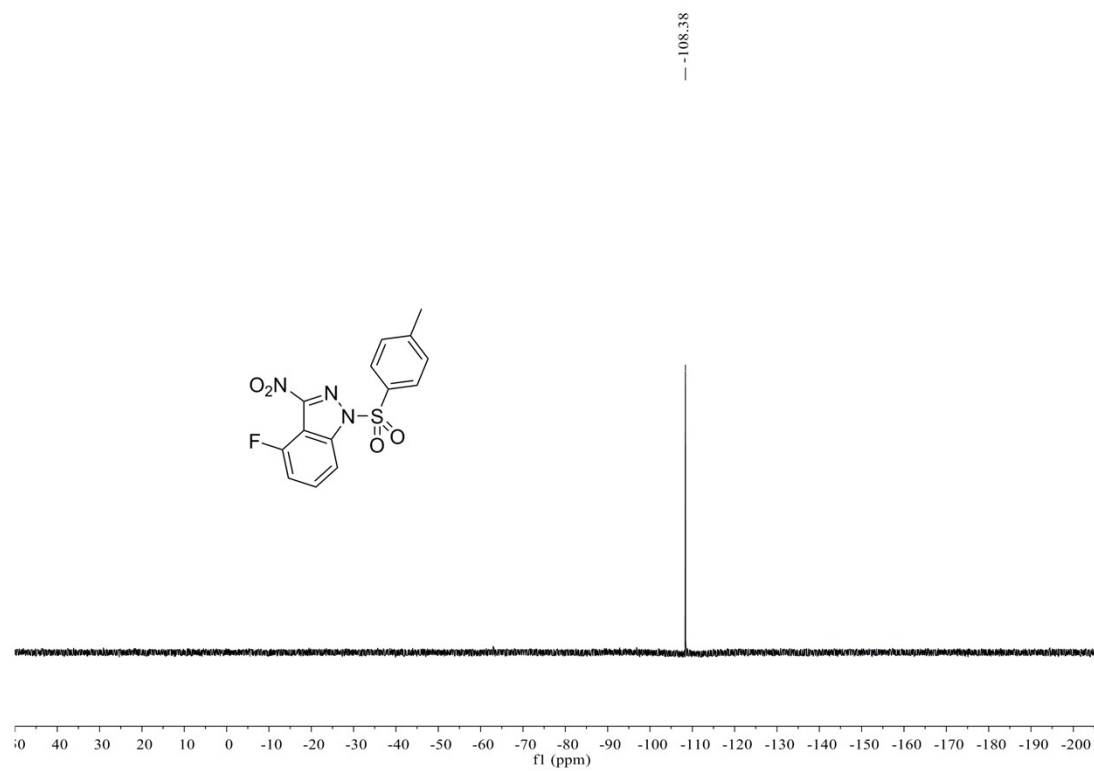
### 2aq <sup>1</sup>H NMR



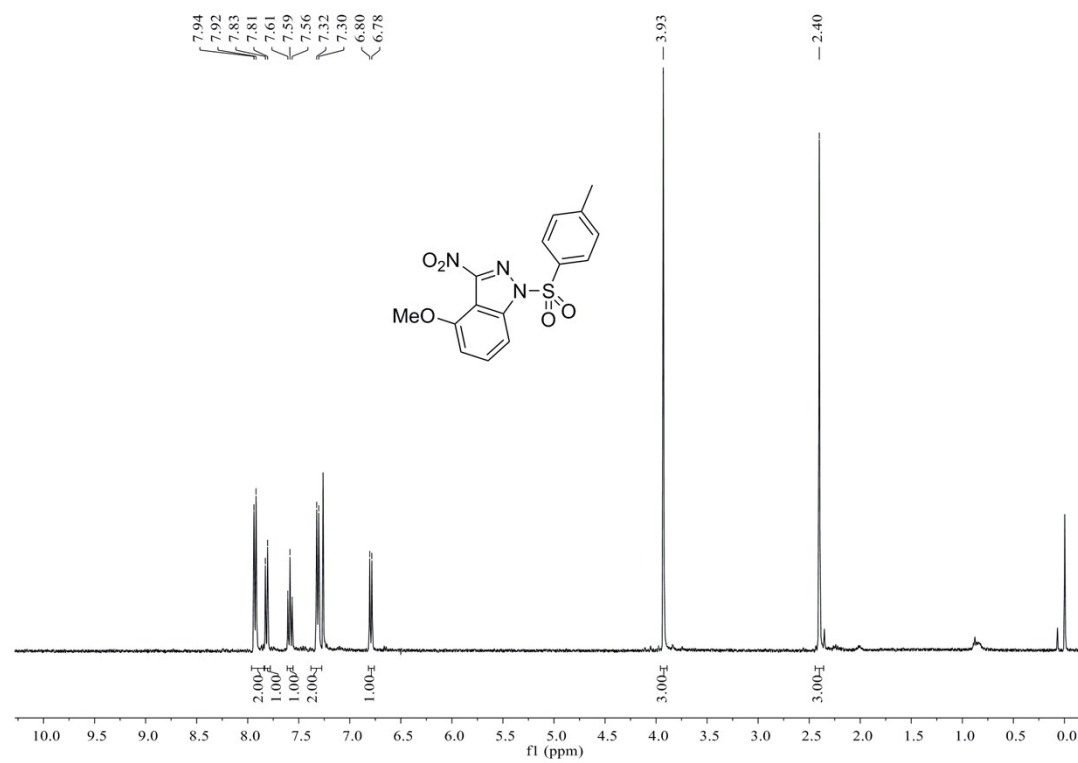
### 2aq <sup>13</sup>C NMR



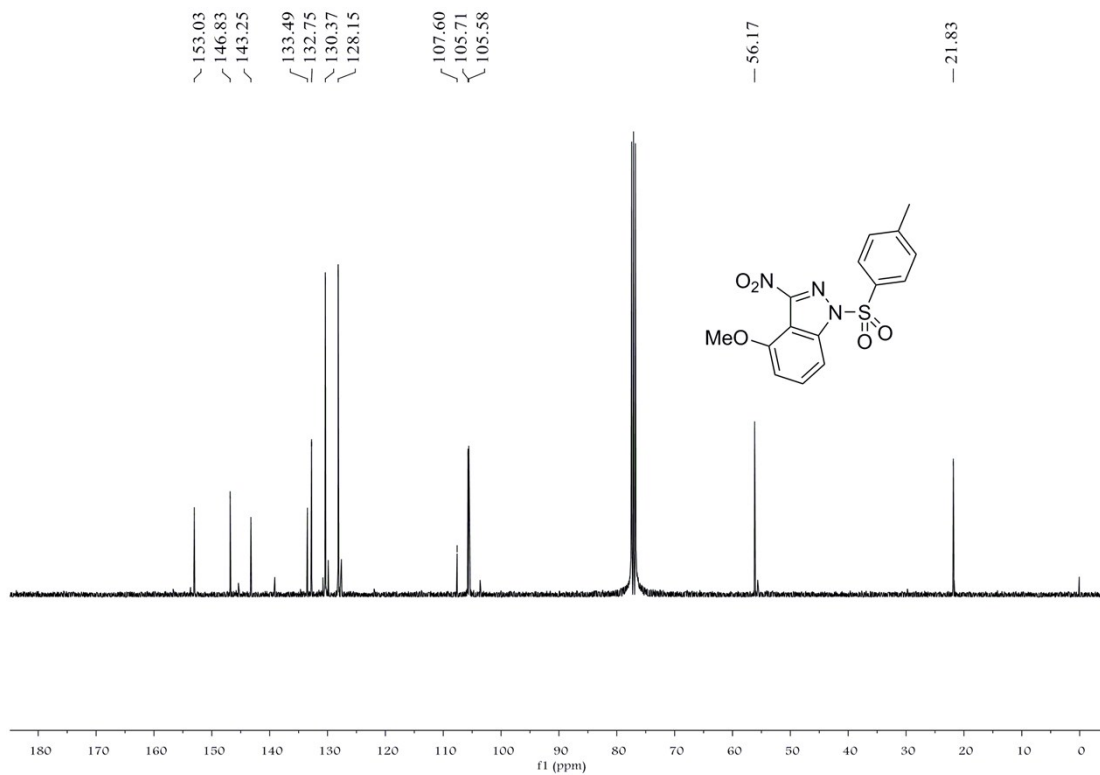
2aq <sup>19</sup>F NMR



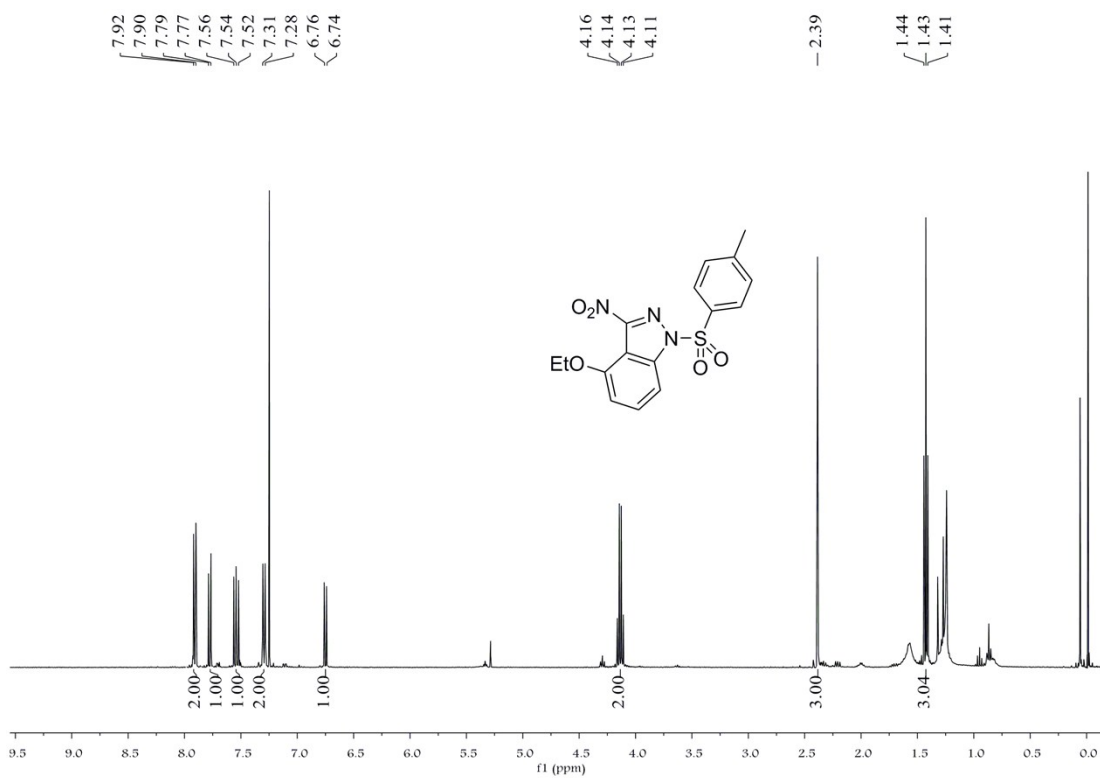
2ar <sup>1</sup>H NMR



2ar <sup>13</sup>C NMR



2as <sup>1</sup>H NMR



2as <sup>13</sup>C NMR

~ 152.41  
~ 146.75  
~ 143.27

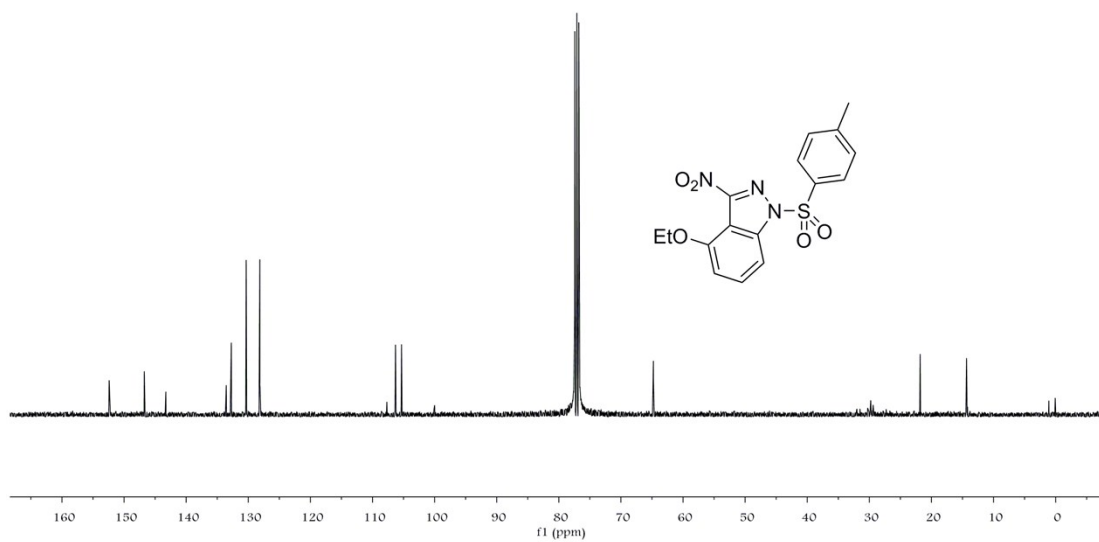
~ 133.54  
~ 132.74  
~ 130.34  
~ 128.14

~ 107.69  
~ 106.30  
~ 105.33  
~ 100.00

- 64.77

- 21.82

- 14.35

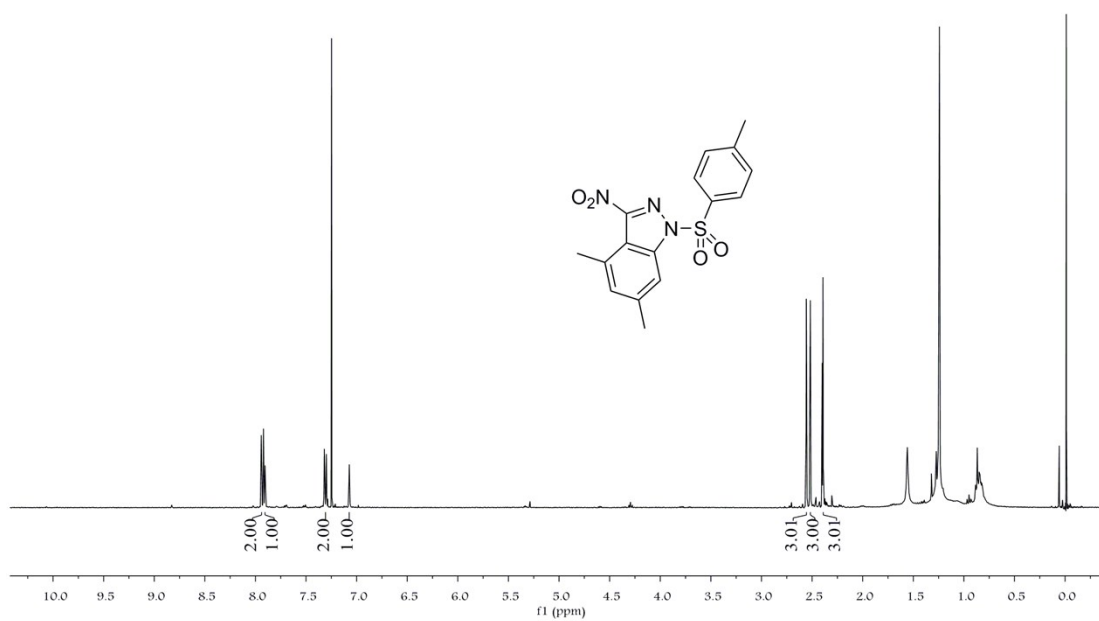


2at <sup>1</sup>H NMR

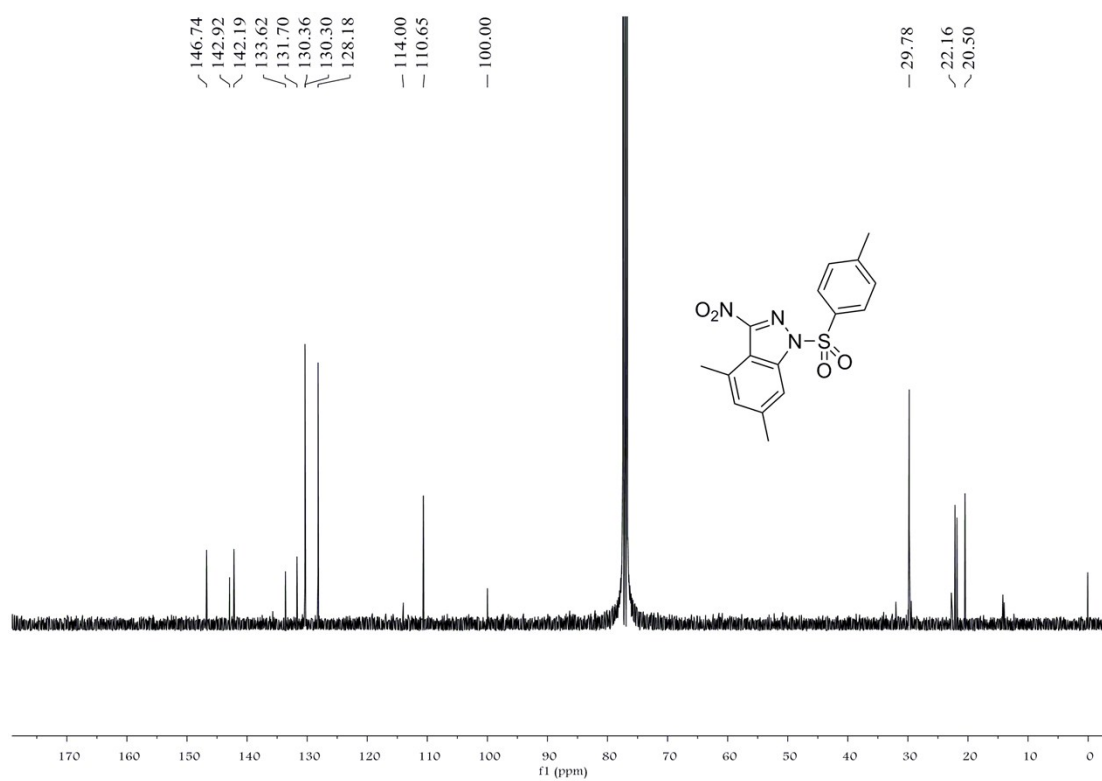
~ 7.94  
~ 7.92  
~ 7.90

~ 7.32  
~ 7.30  
~ 7.07

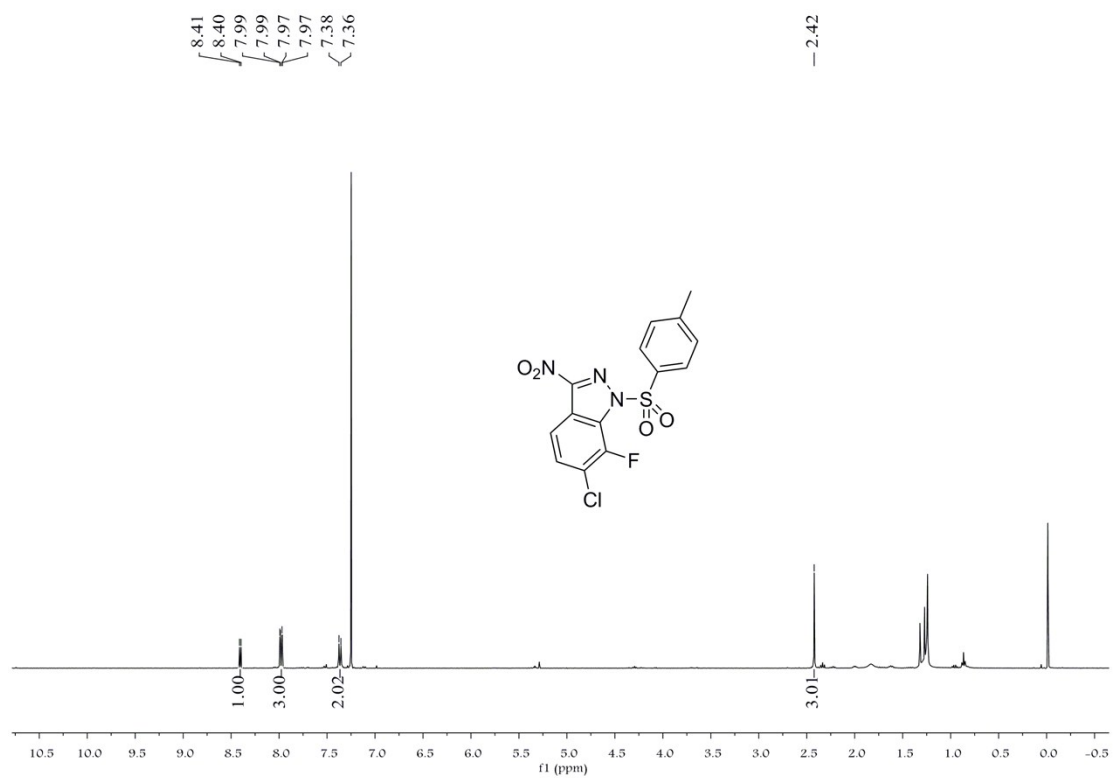
~ 2.56  
~ 2.52  
~ 2.40



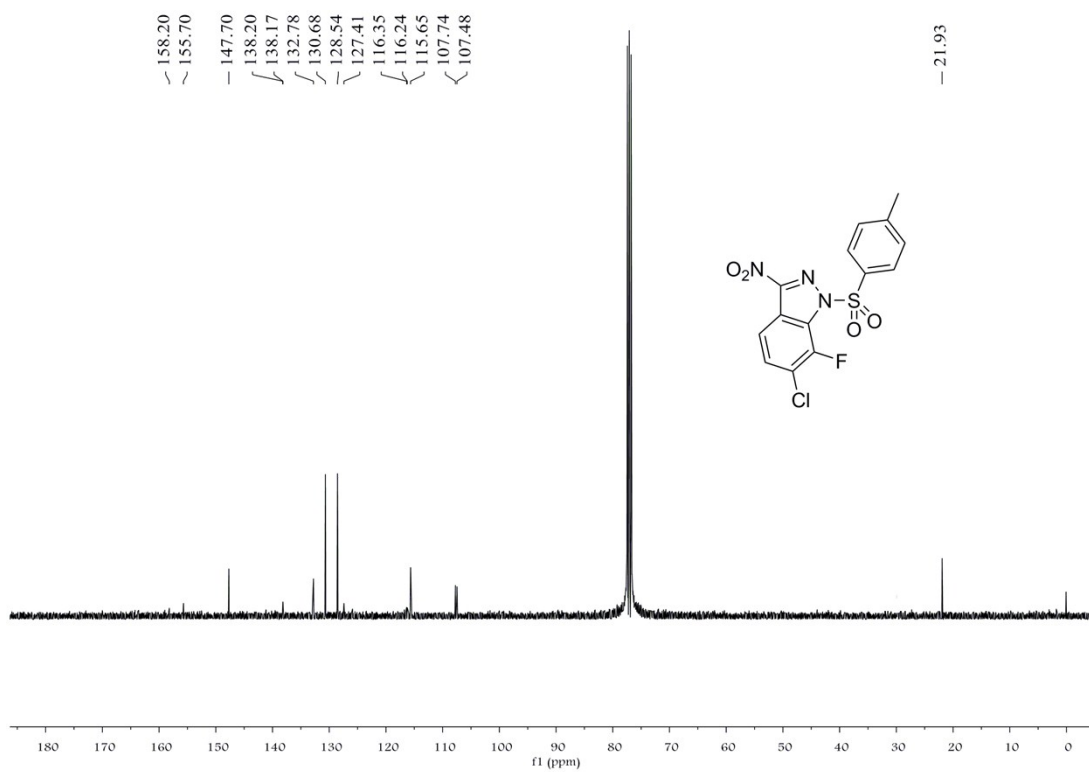
2at <sup>13</sup>C NMR



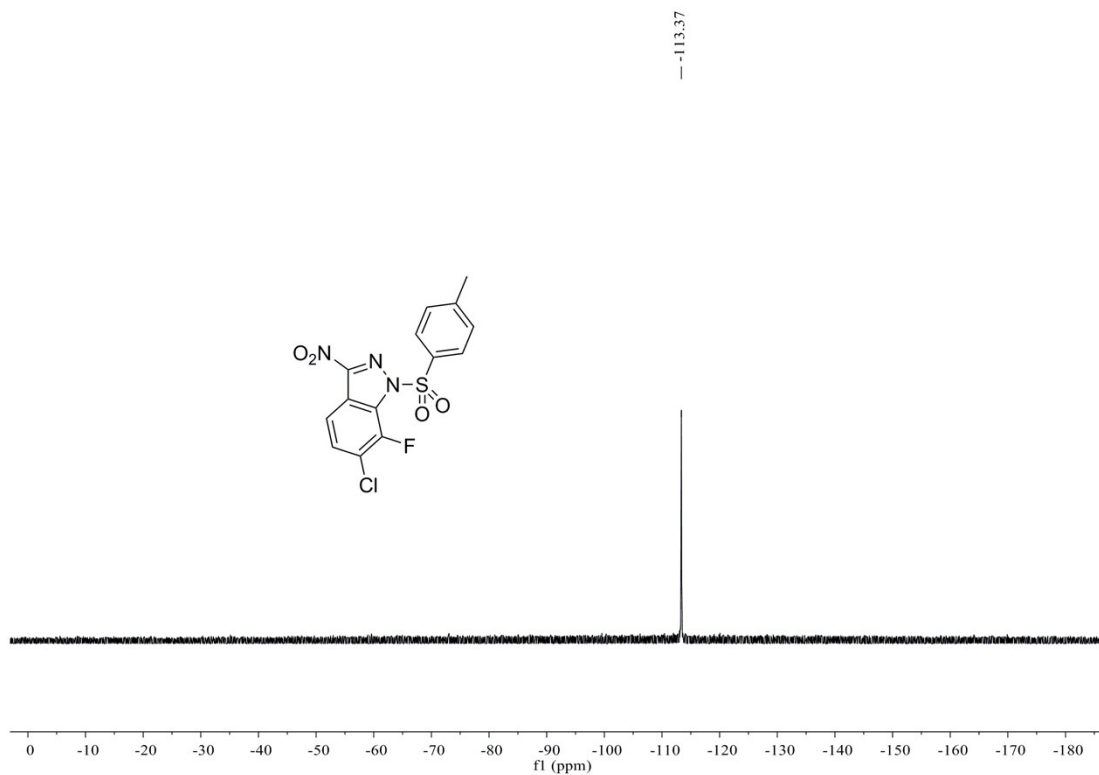
2au <sup>1</sup>H NMR



## 2au <sup>13</sup>C NMR

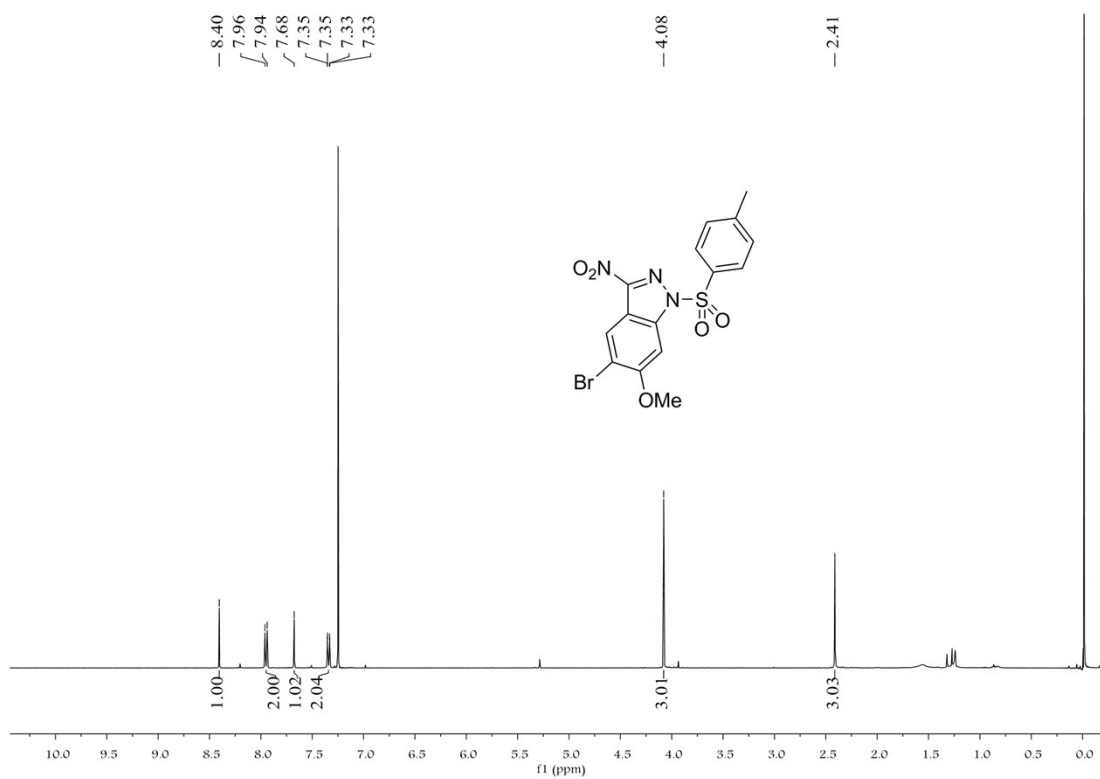


## 2au <sup>19</sup>F NMR

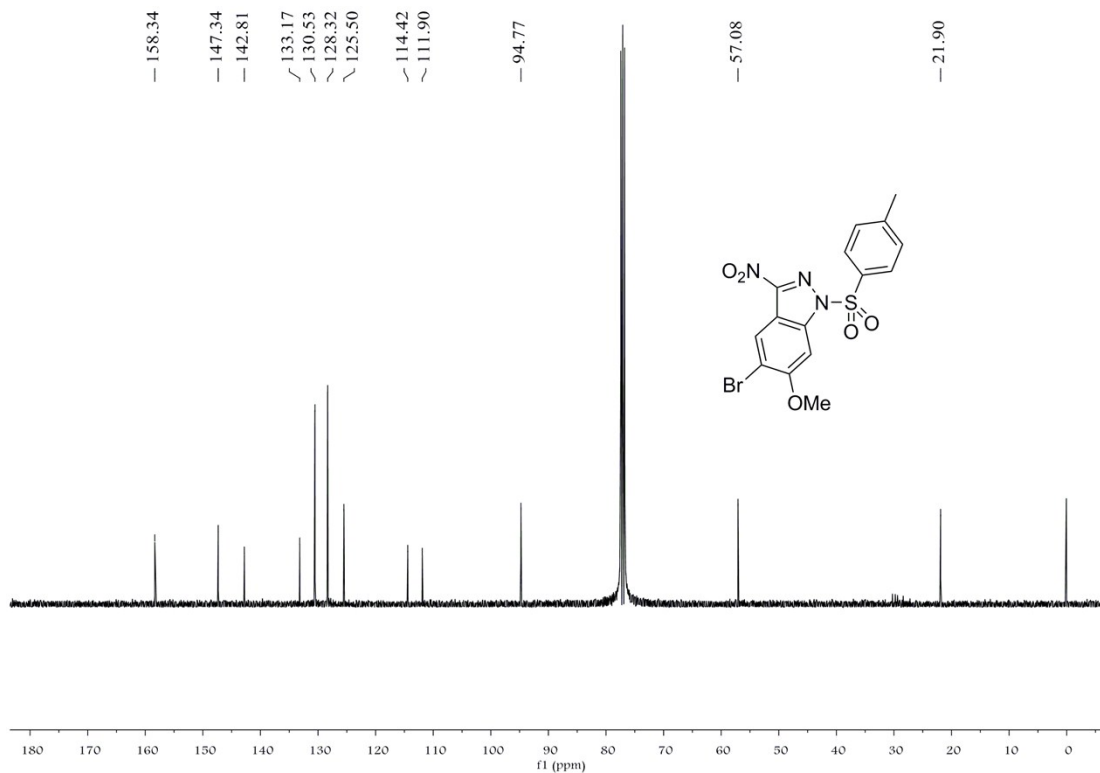




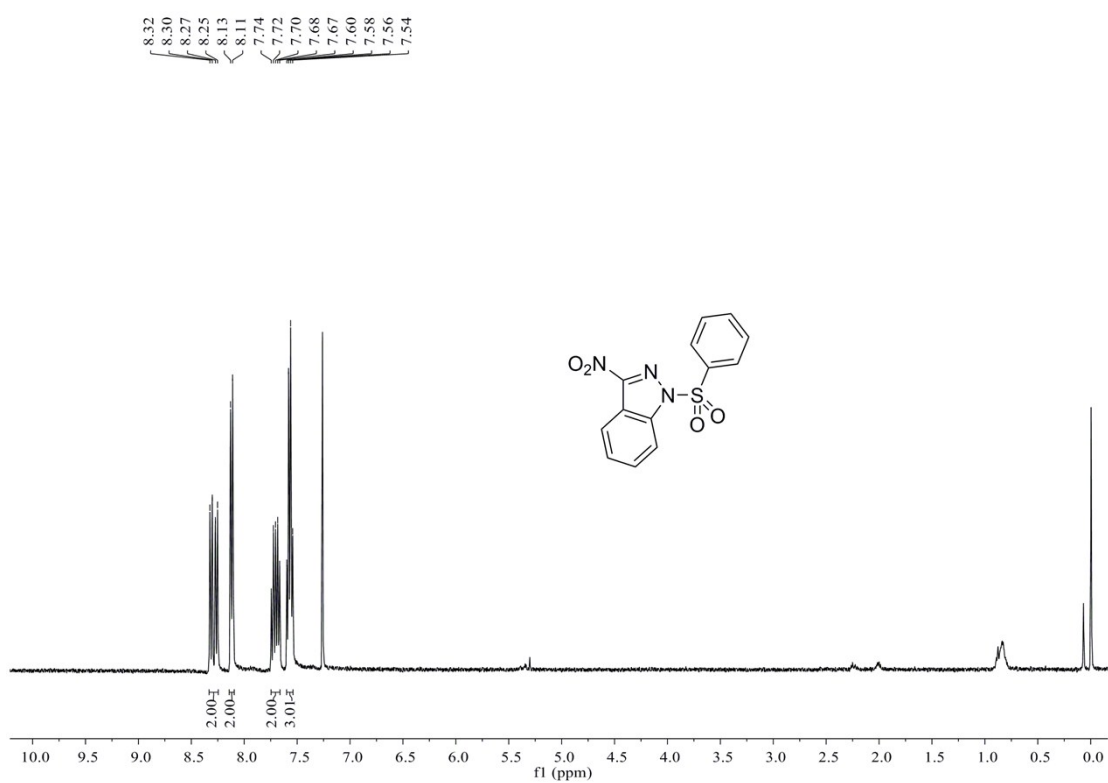
2av <sup>1</sup>H NMR



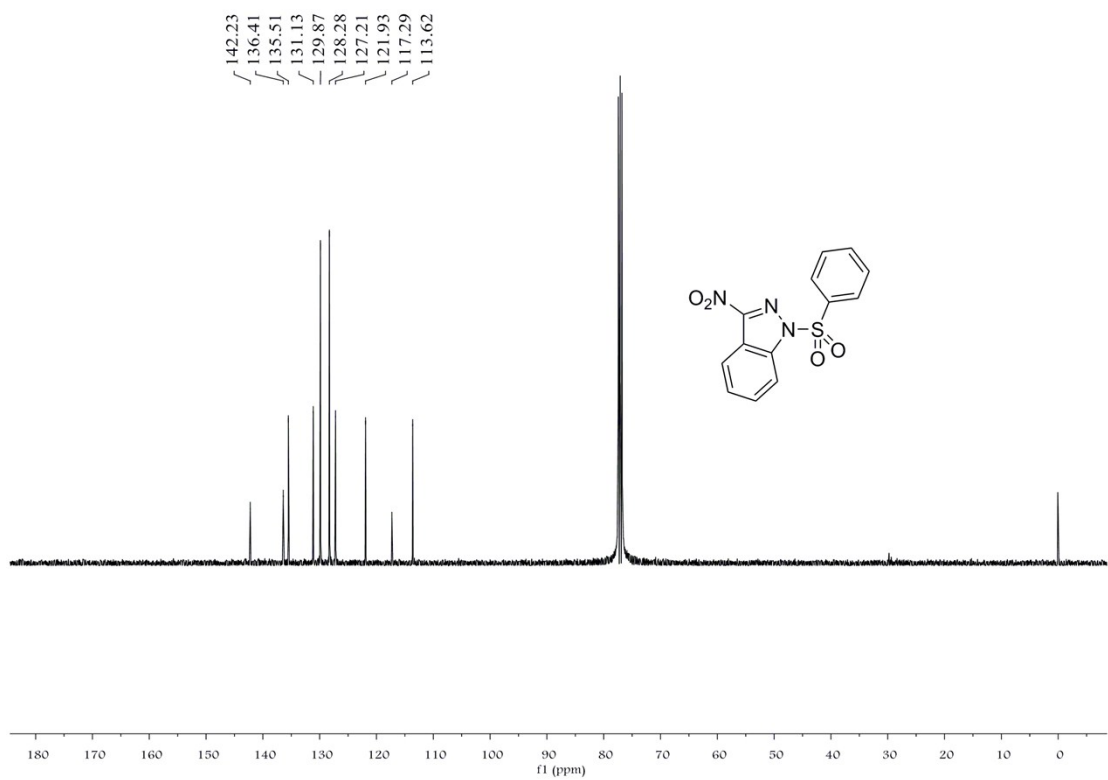
2av <sup>13</sup>C NMR



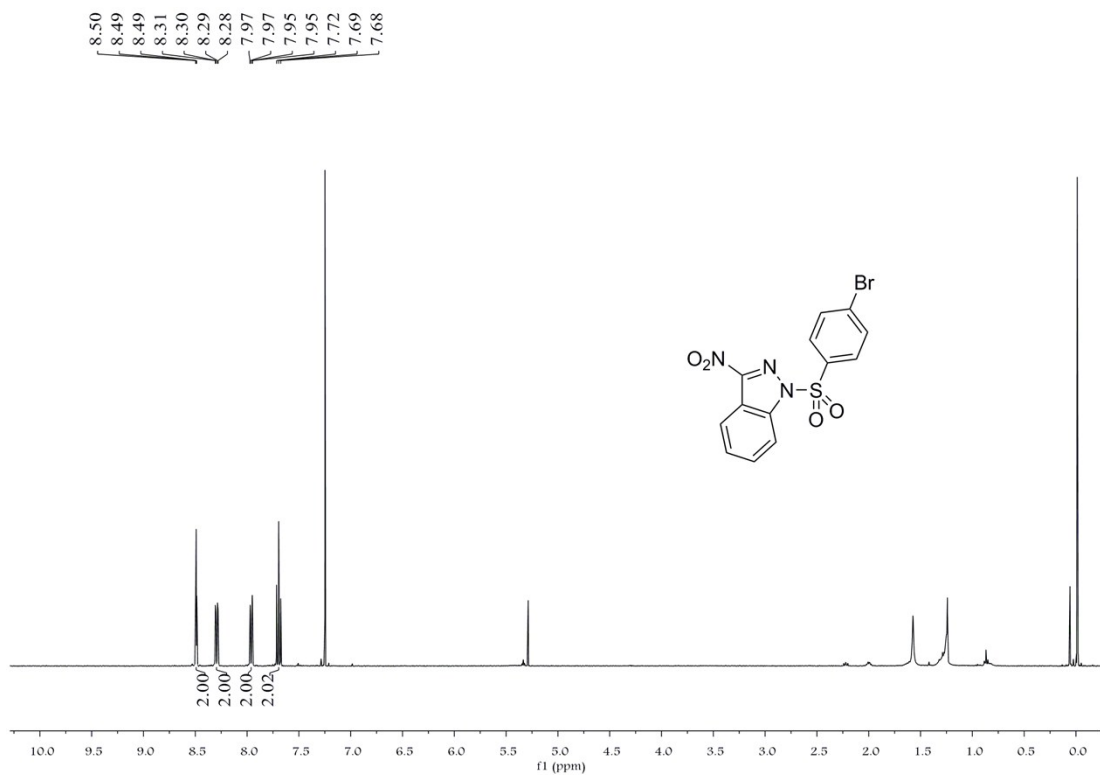
### 2ba <sup>1</sup>H NMR



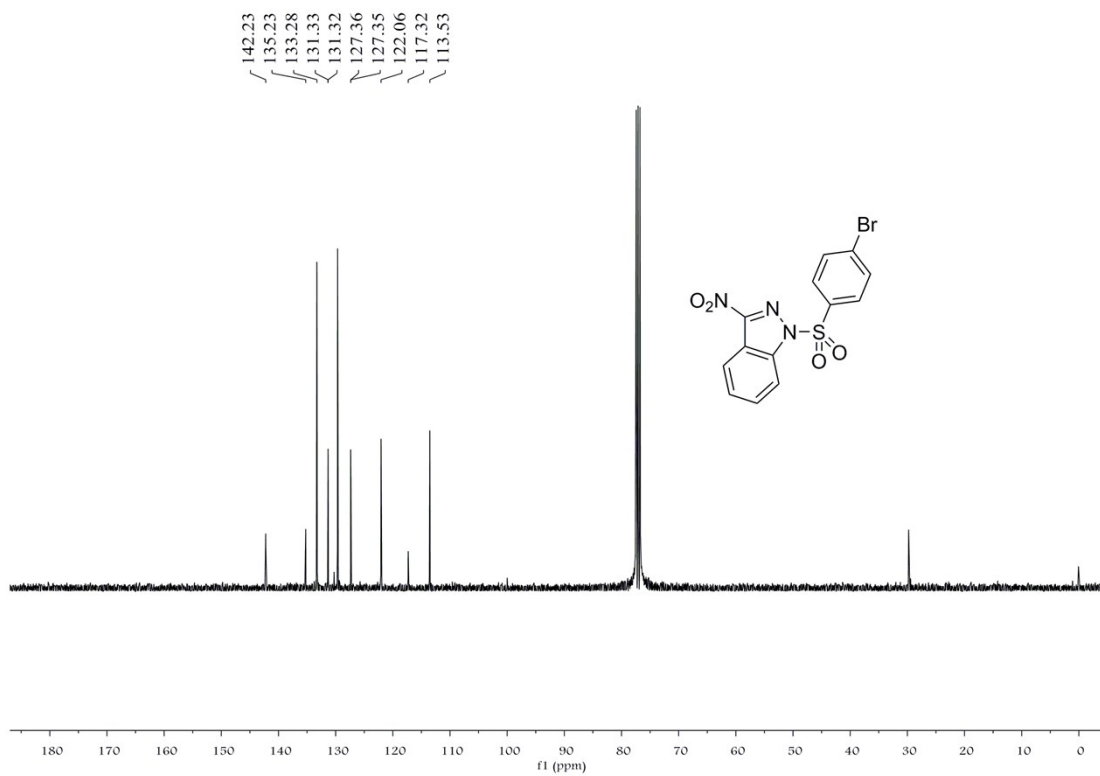
### 2ba <sup>13</sup>C NMR



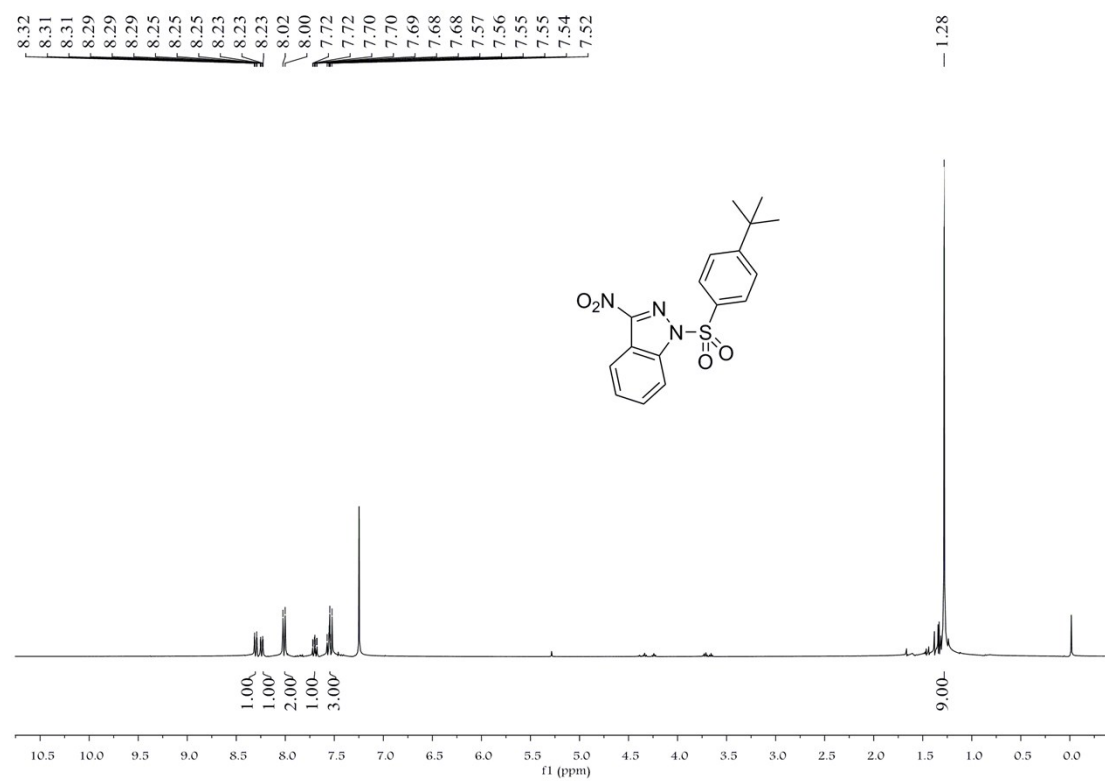
### 2bb <sup>1</sup>H NMR



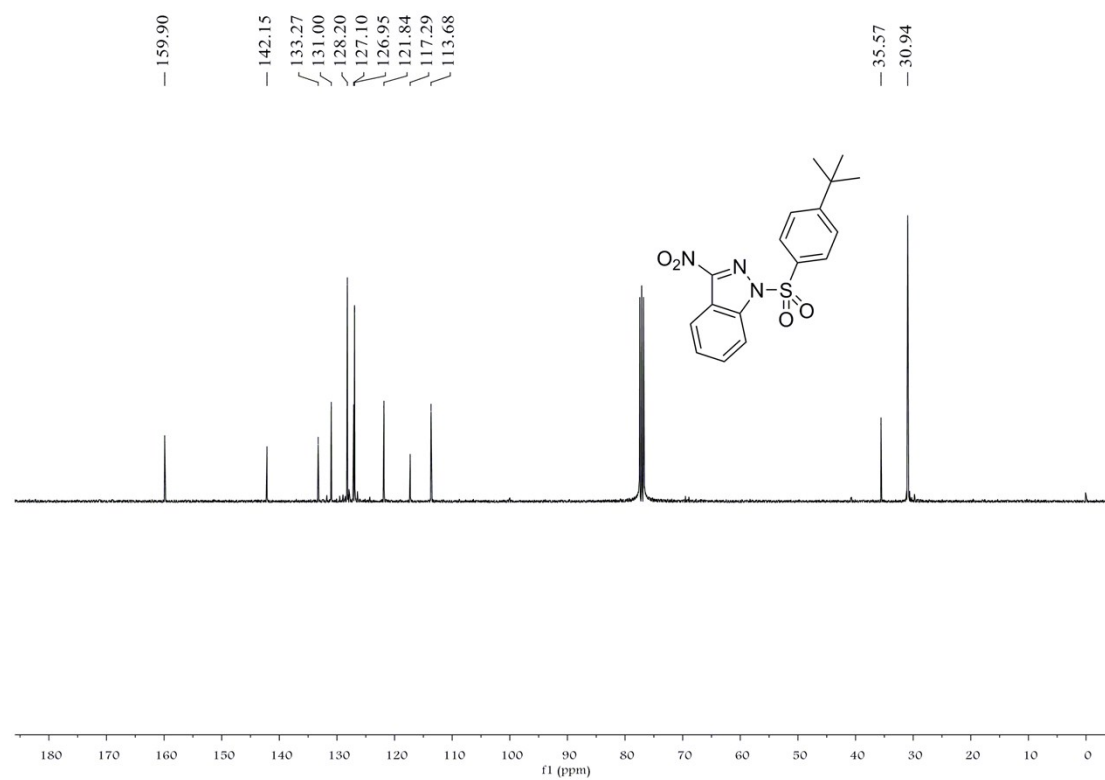
### 2bb <sup>13</sup>C NMR



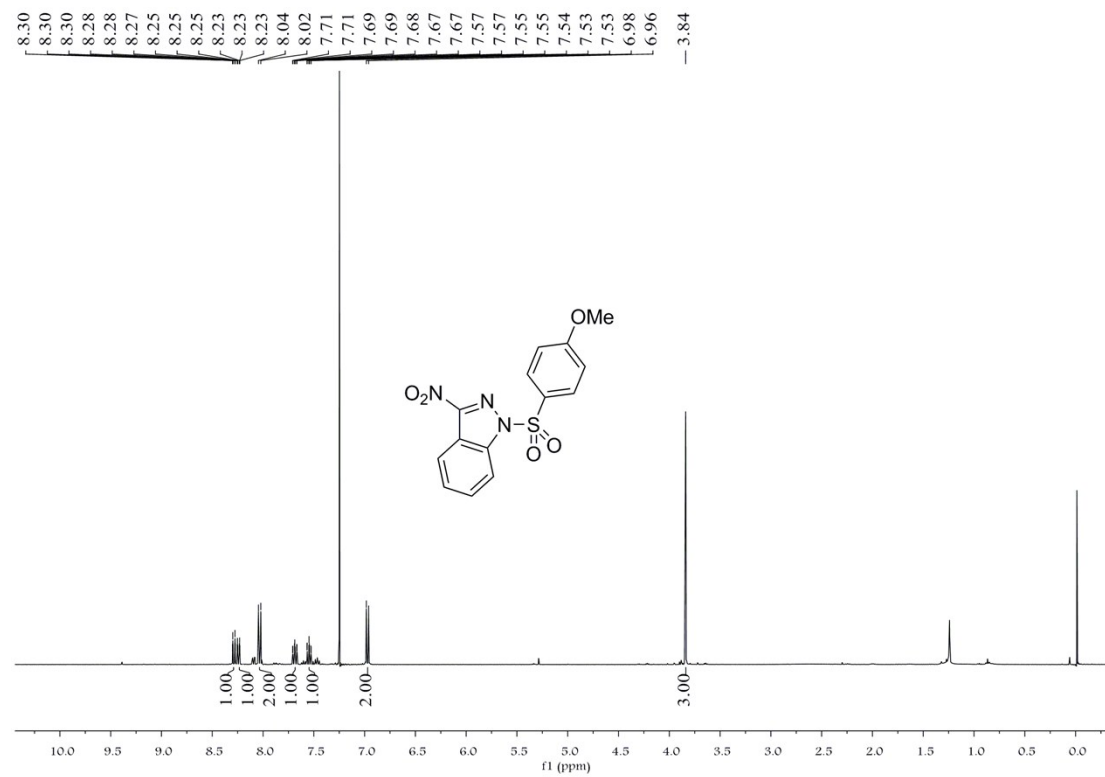
### 2bc <sup>1</sup>H NMR



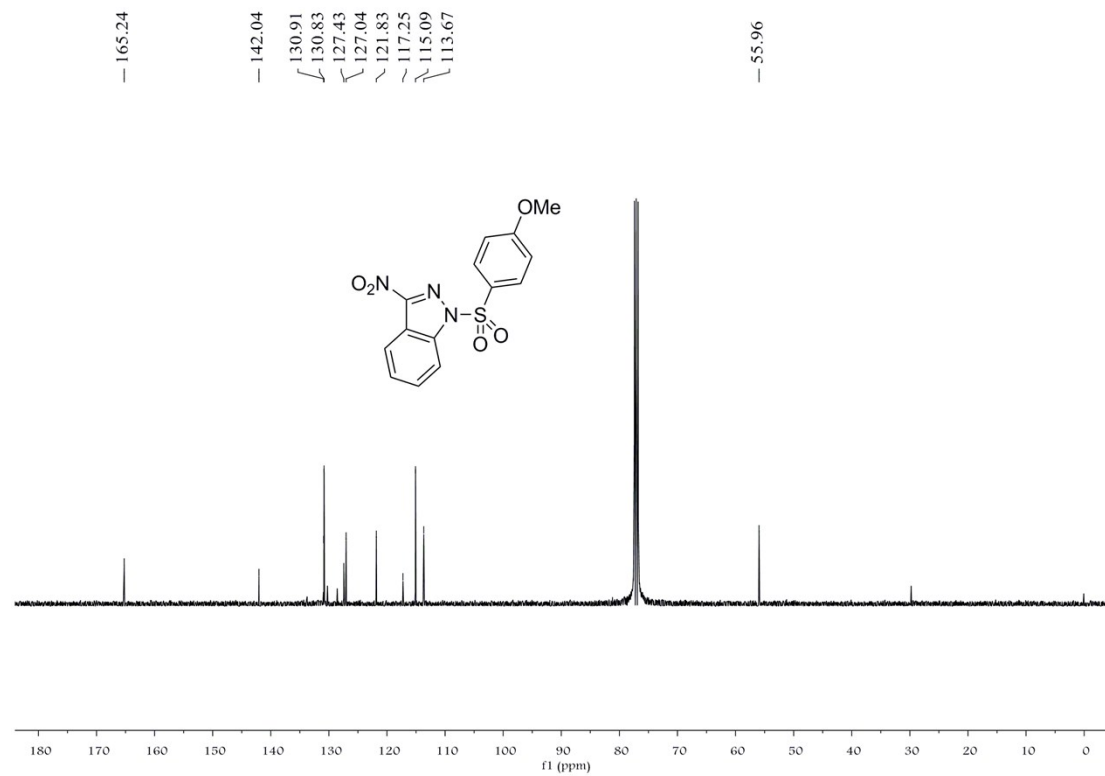
### 2bc <sup>13</sup>C NMR



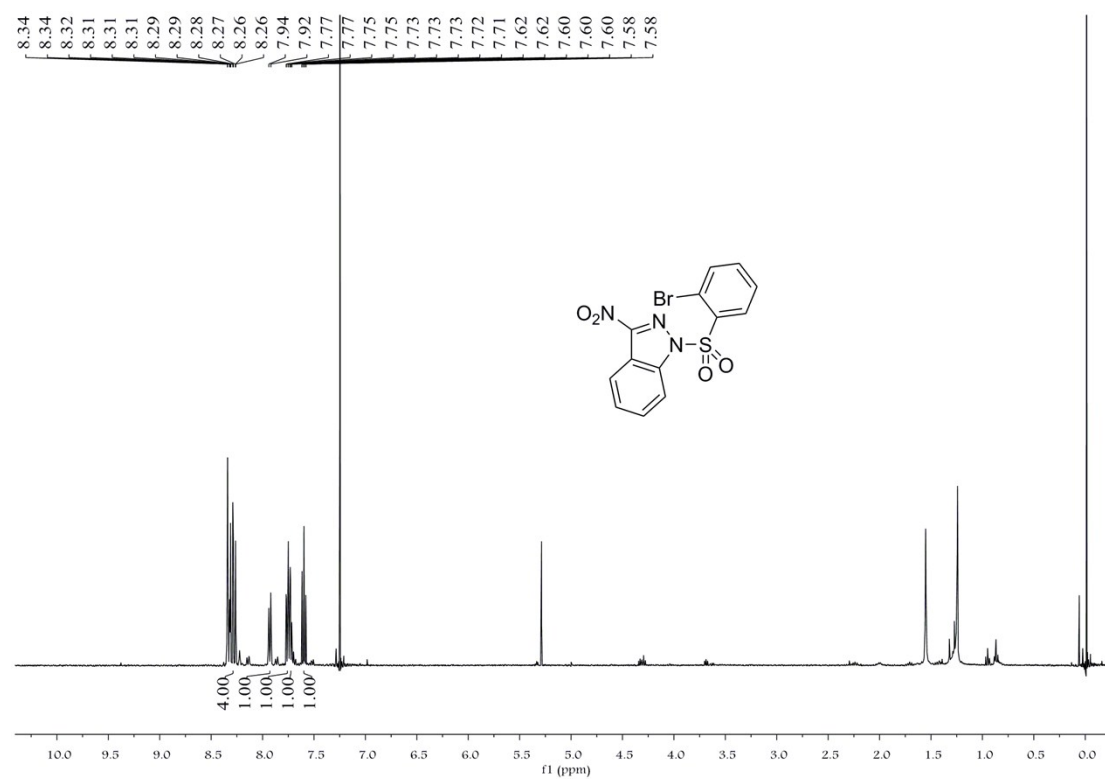
2bd <sup>1</sup>H NMR



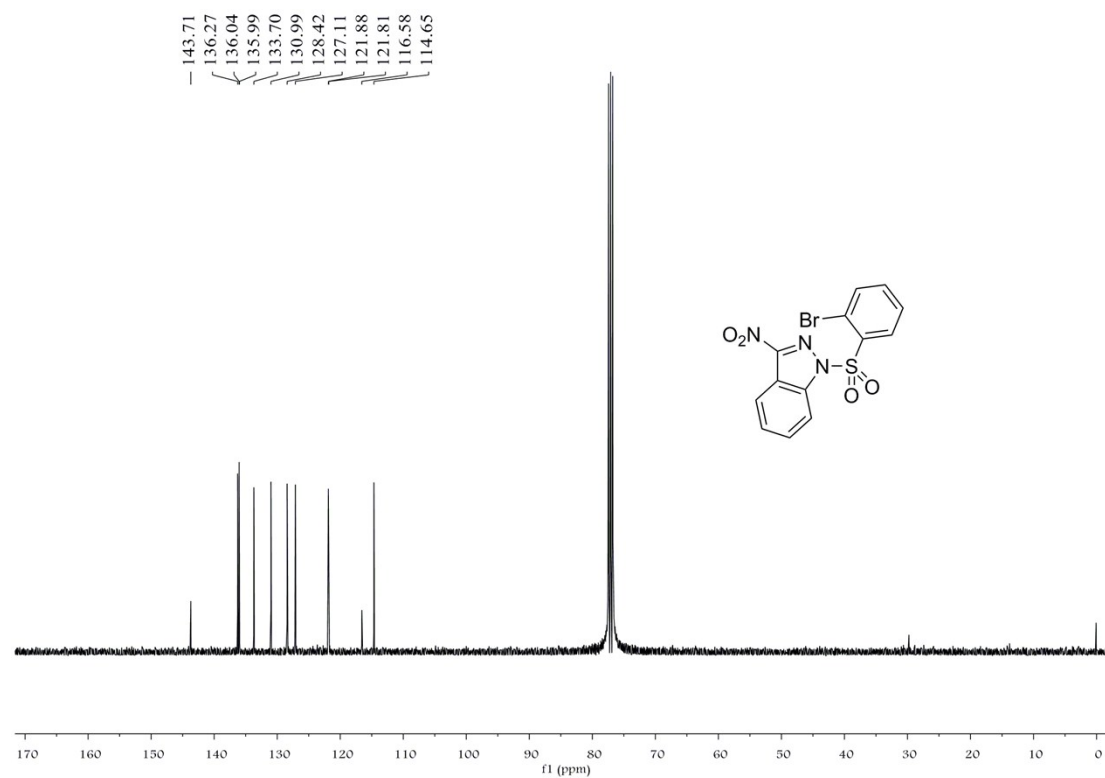
2bd <sup>13</sup>C NMR



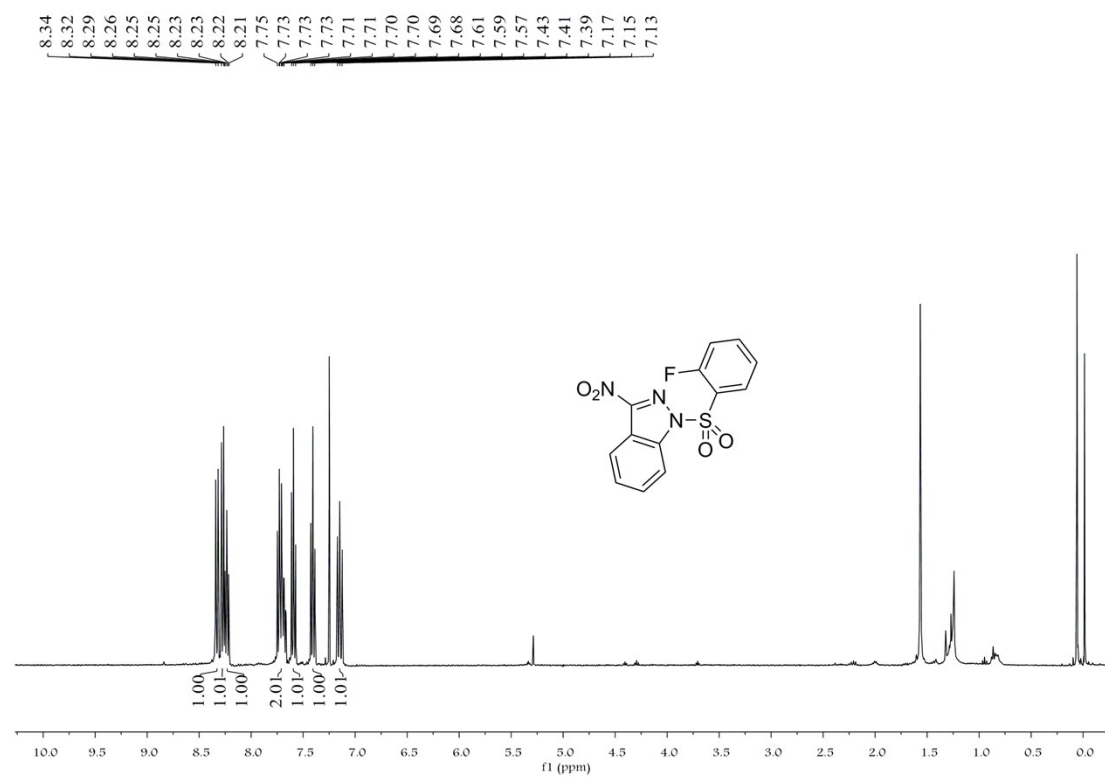
### 2be <sup>1</sup>H NMR



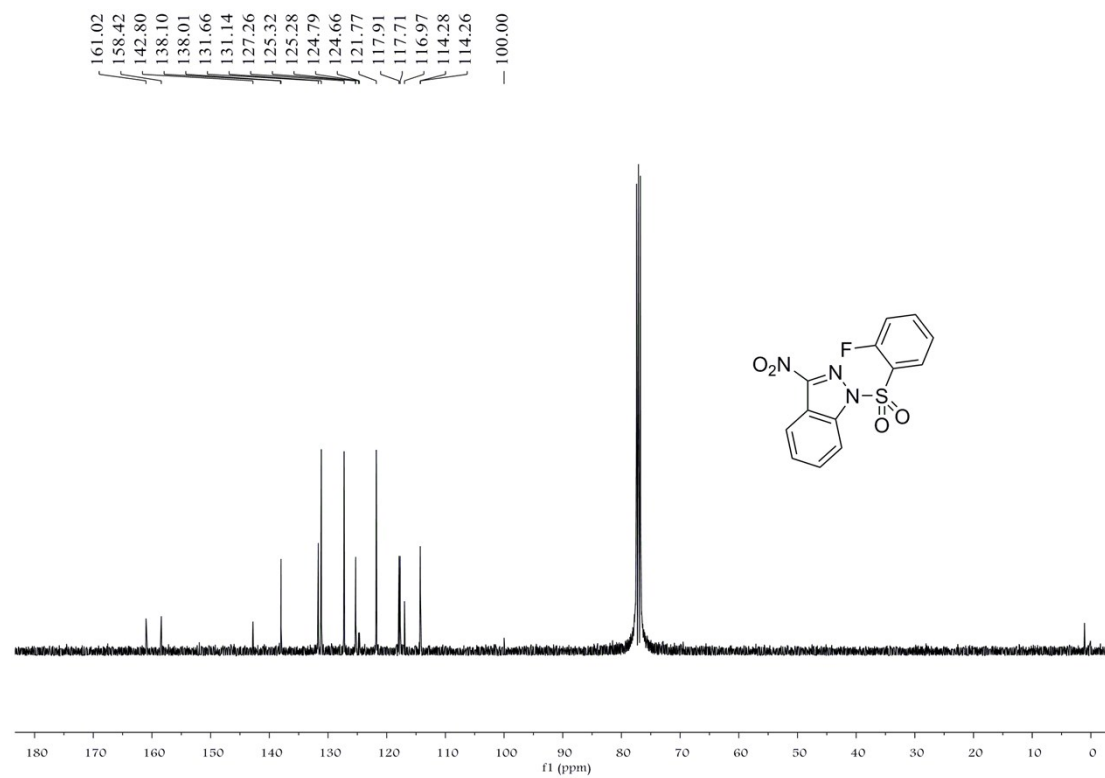
### 2be <sup>13</sup>C NMR



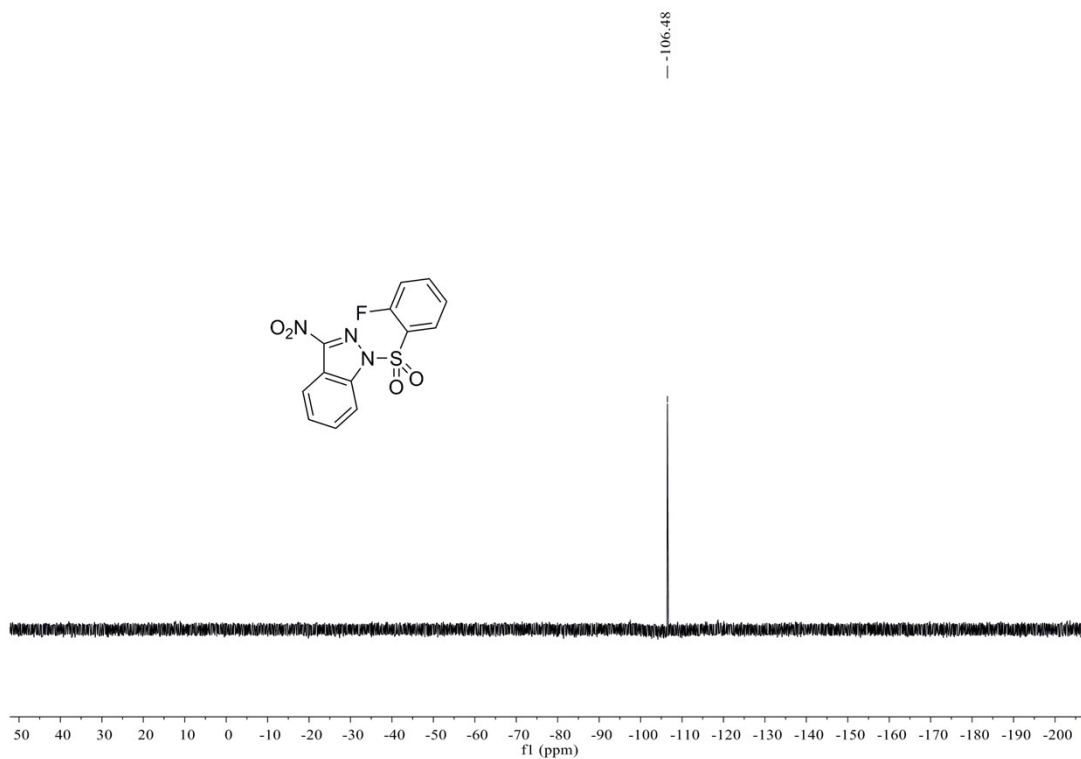
### 2bf <sup>1</sup>H NMR



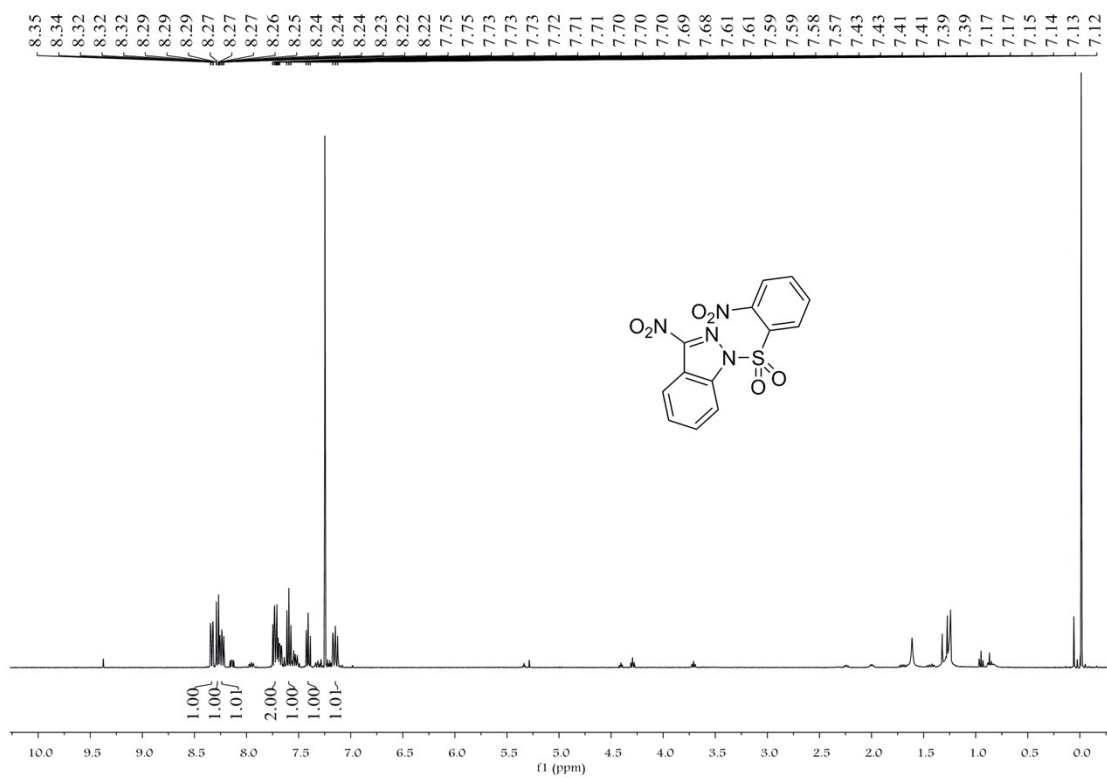
### 2bf <sup>13</sup>C NMR



### 2bf <sup>19</sup>F NMR

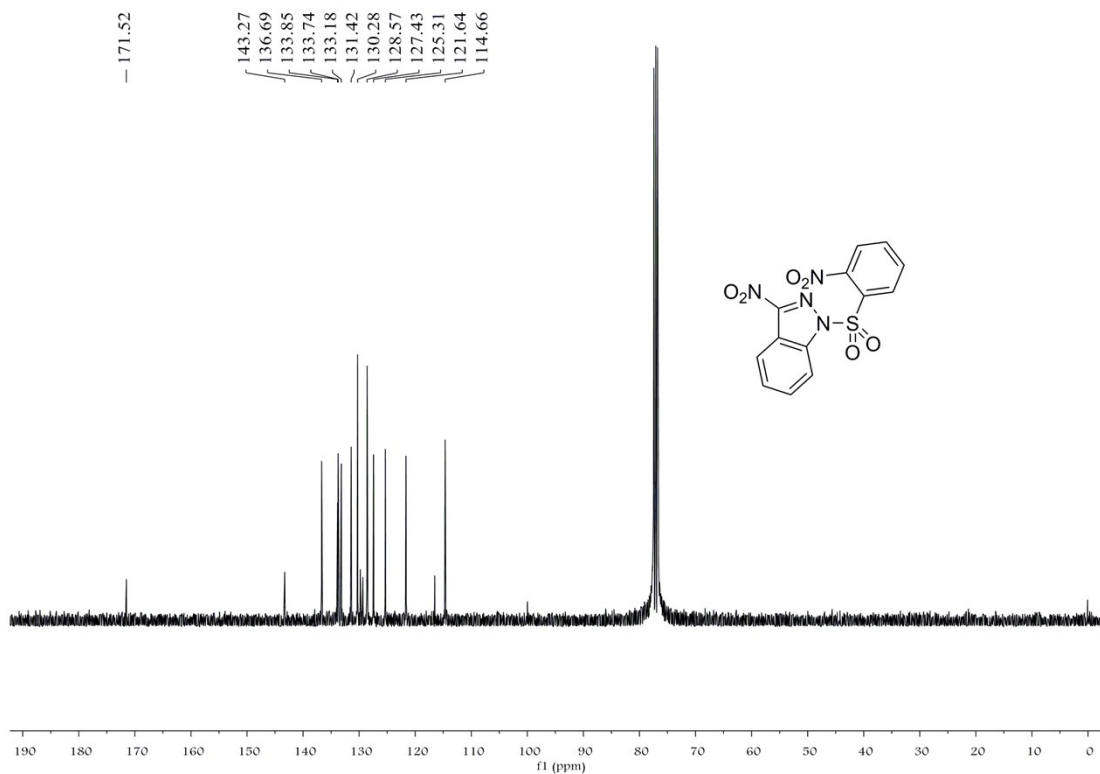


### 2bg <sup>1</sup>H NMR

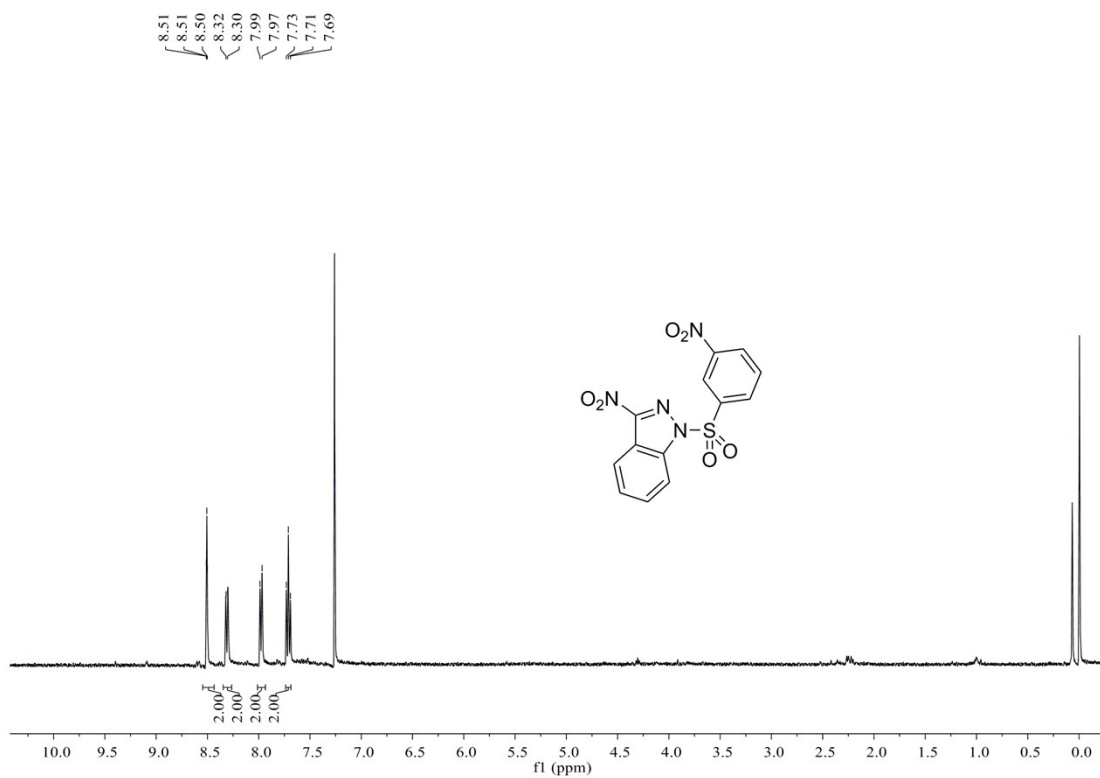




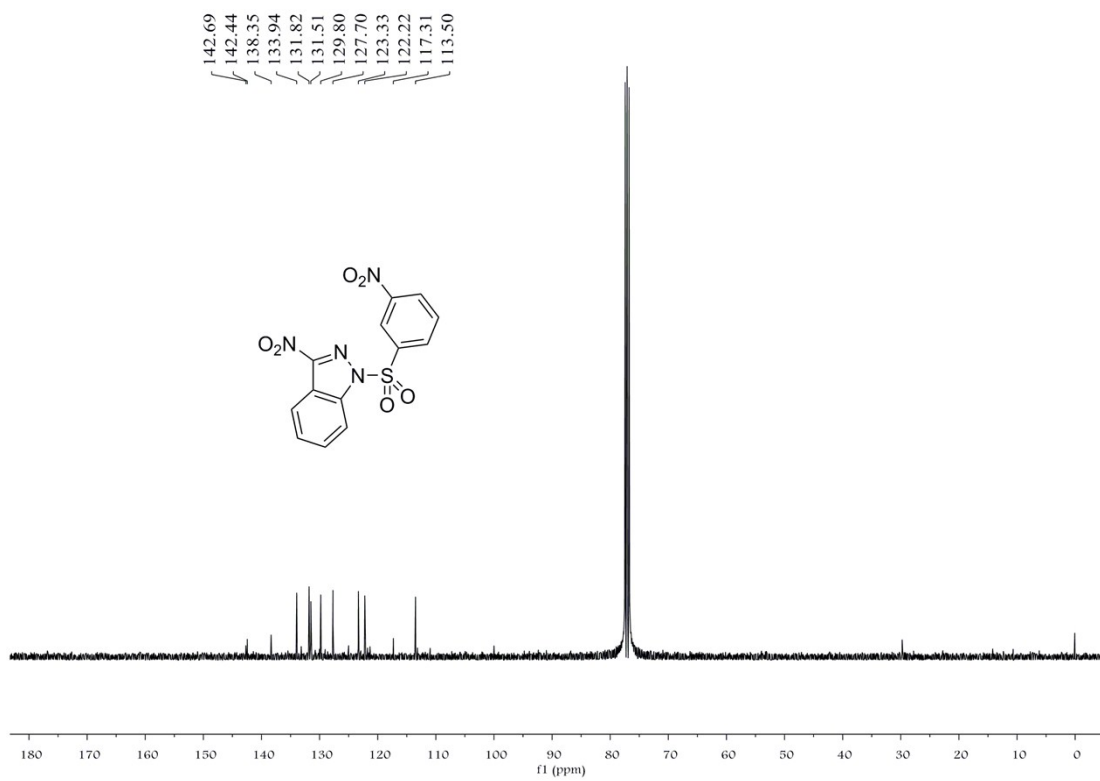
### 2bg <sup>13</sup>C NMR



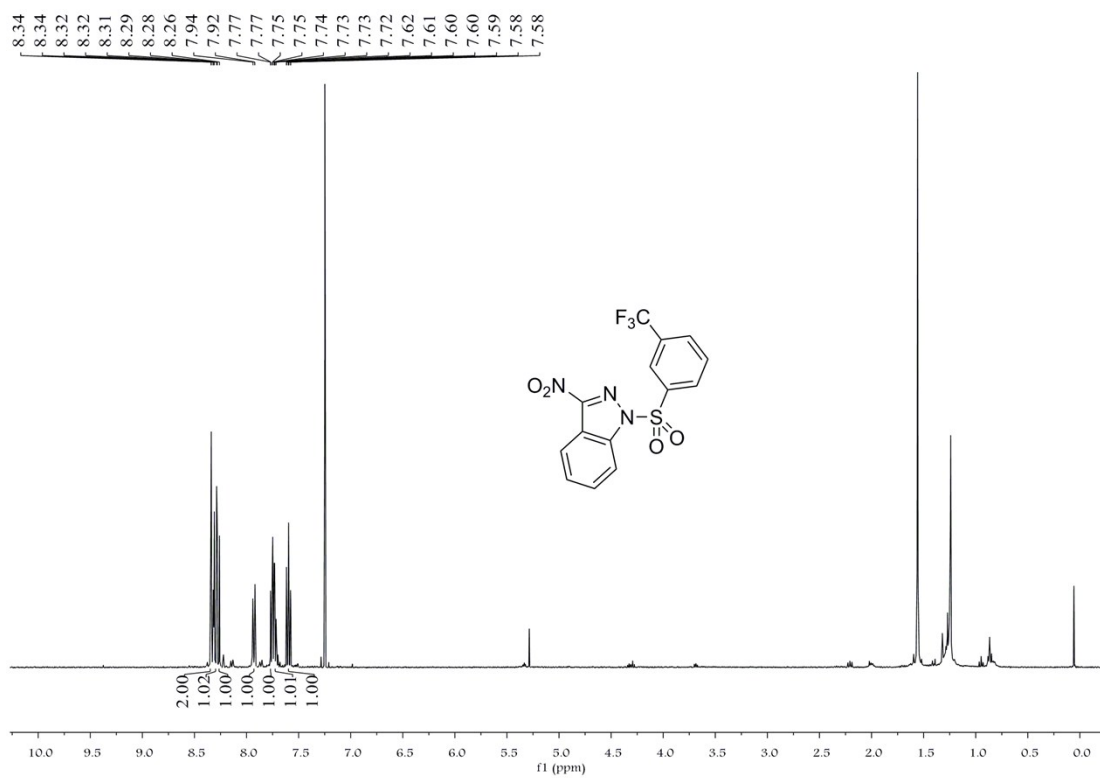
### 2bh <sup>1</sup>H NMR



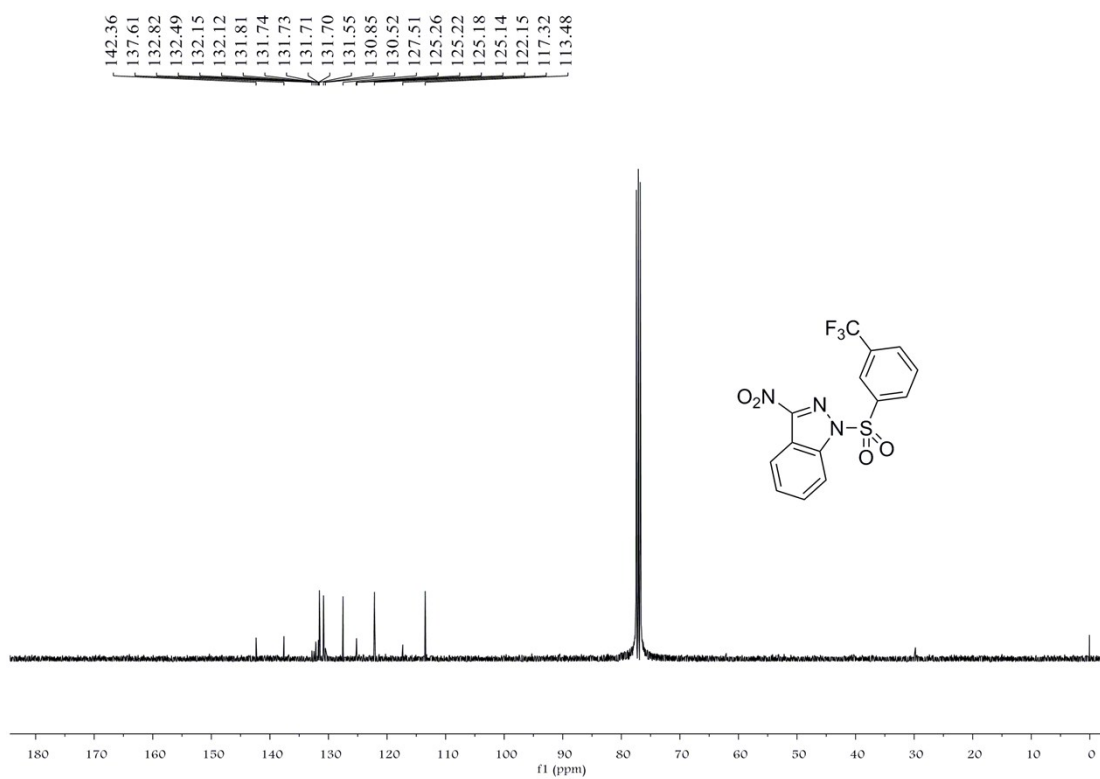
### 2bh <sup>13</sup>C NMR



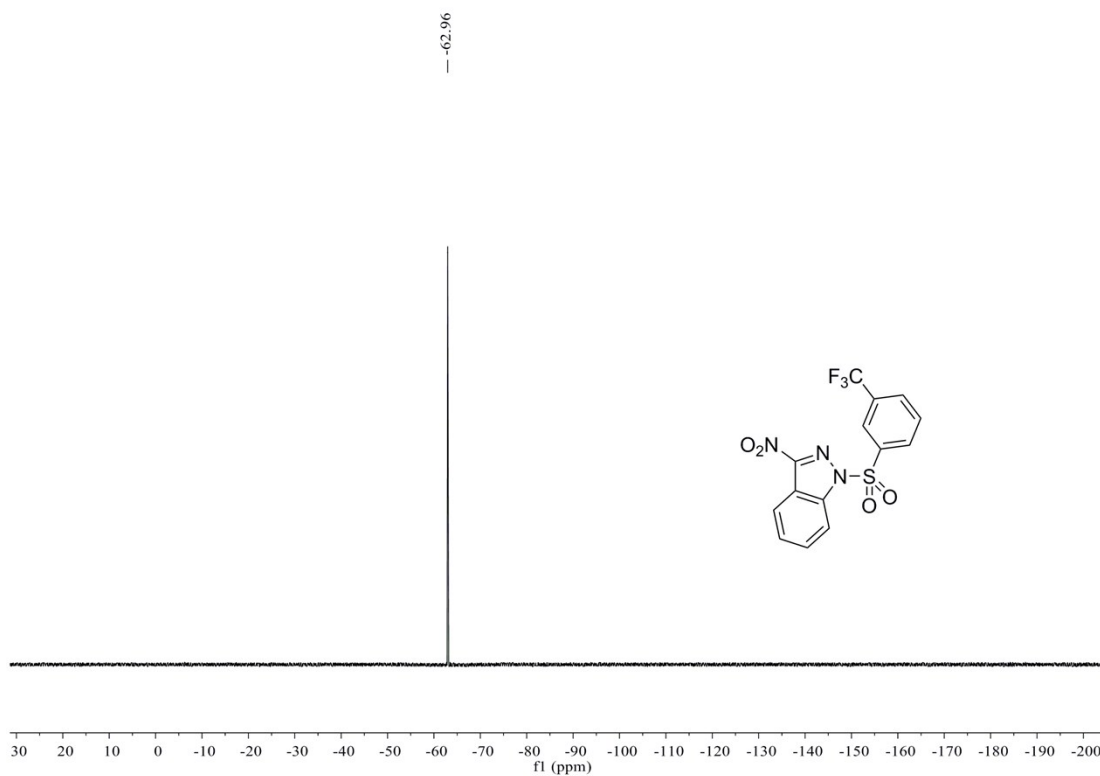
### 2bi <sup>1</sup>H NMR



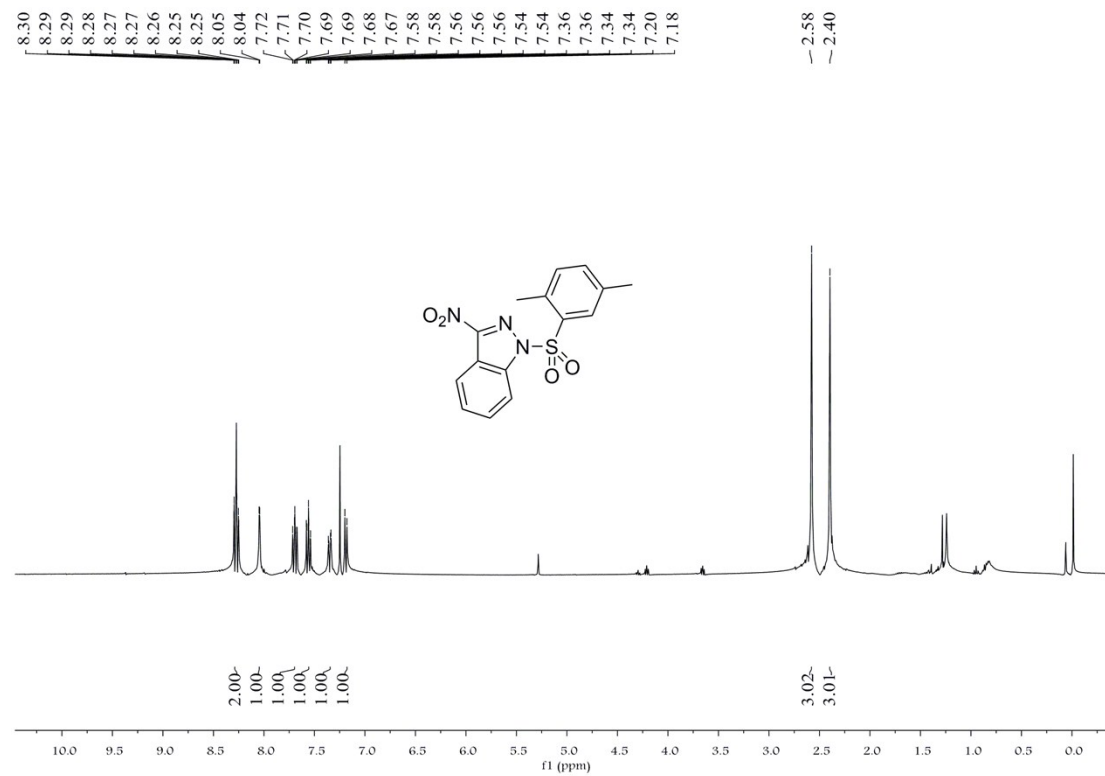
### 2bi <sup>13</sup>C NMR



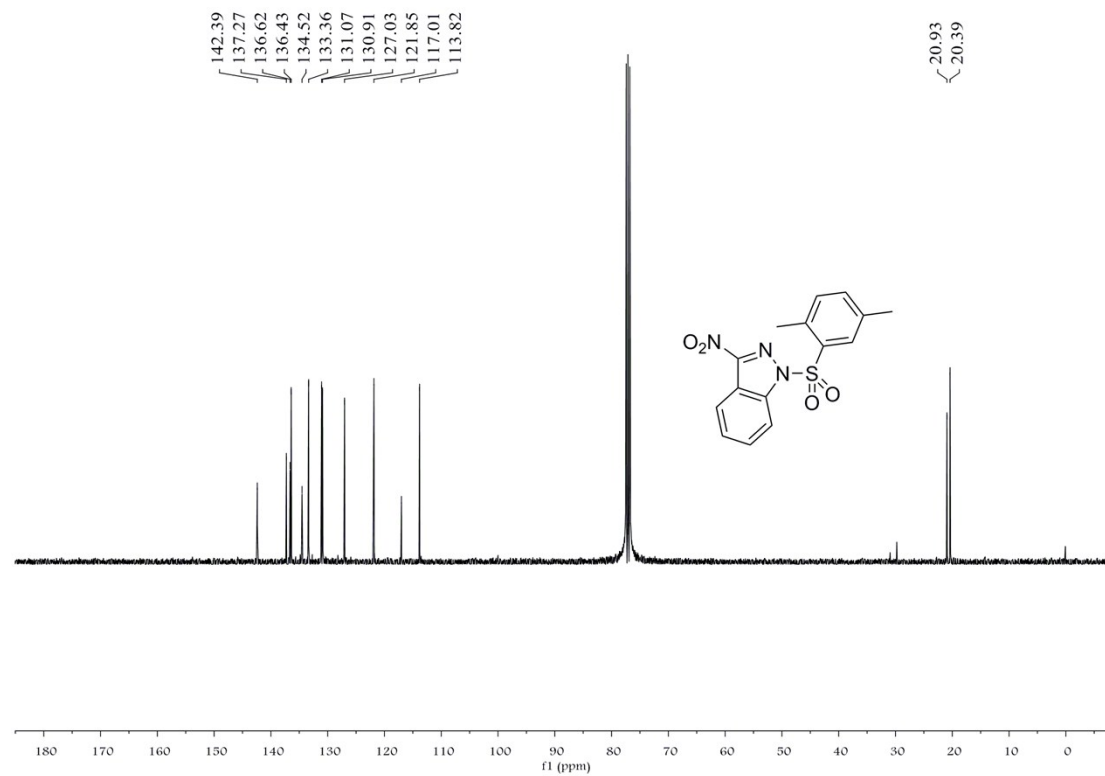
### 2bi <sup>19</sup>F NMR



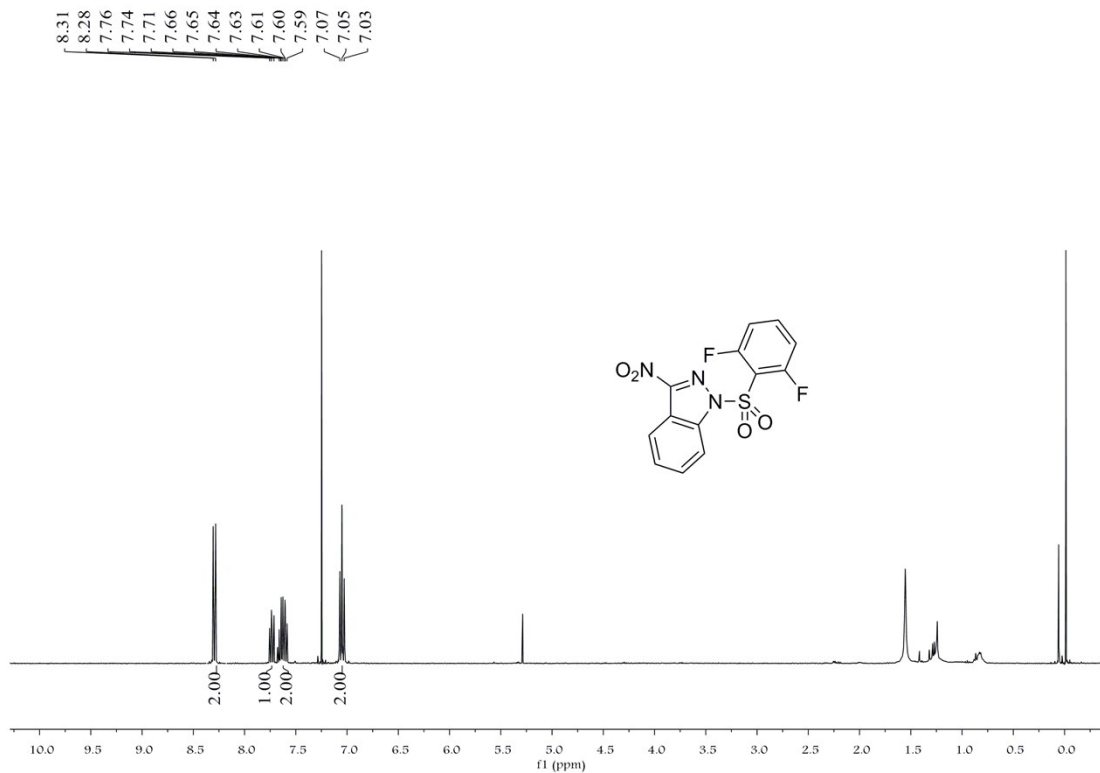
### 2bj <sup>1</sup>H NMR



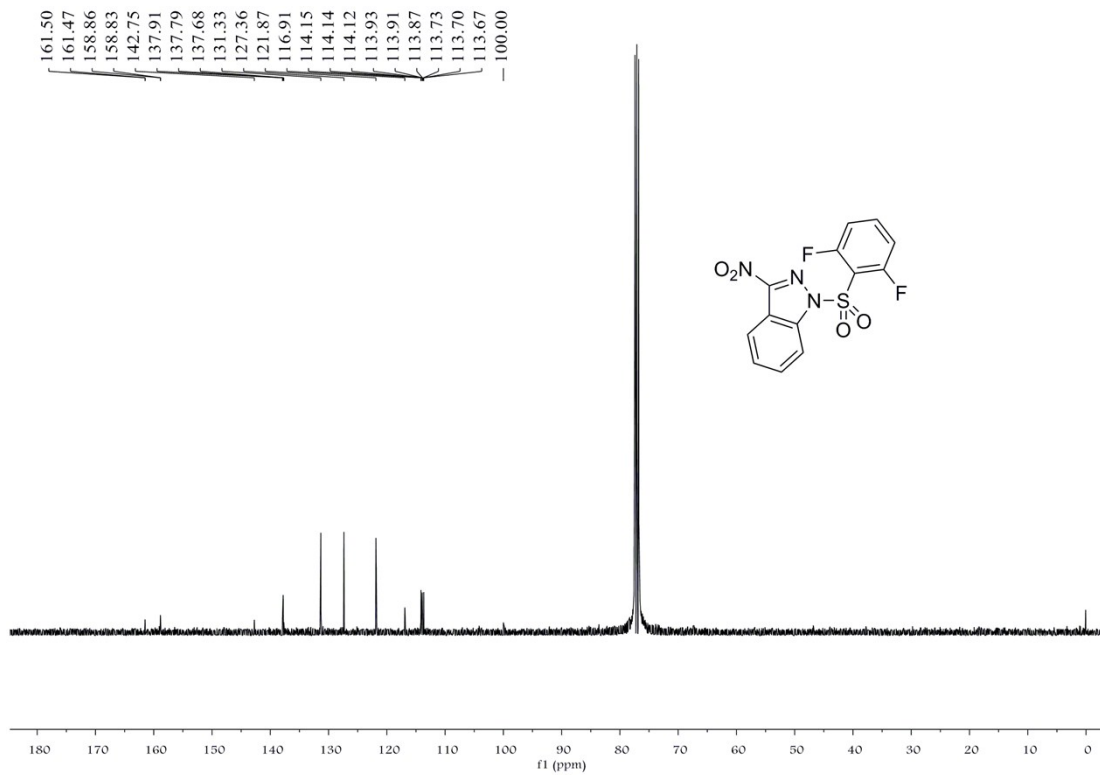
### 2bj <sup>13</sup>C NMR



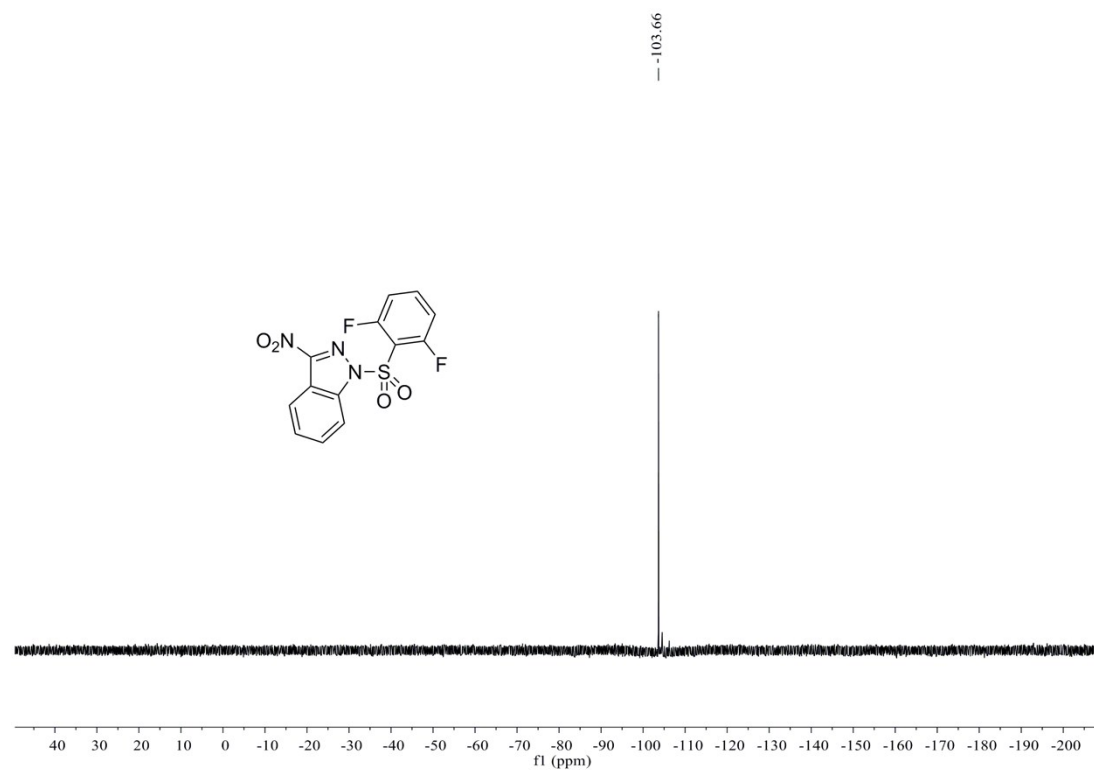
### 2bk <sup>1</sup>H NMR



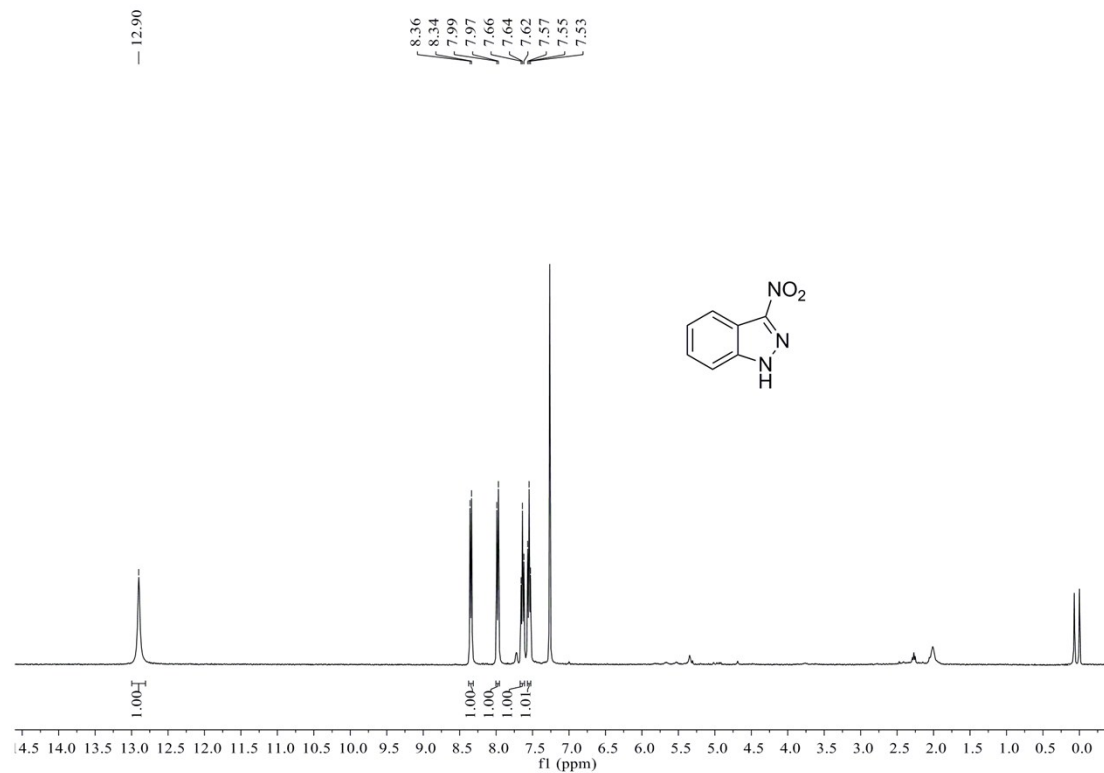
### 2bk <sup>13</sup>C NMR



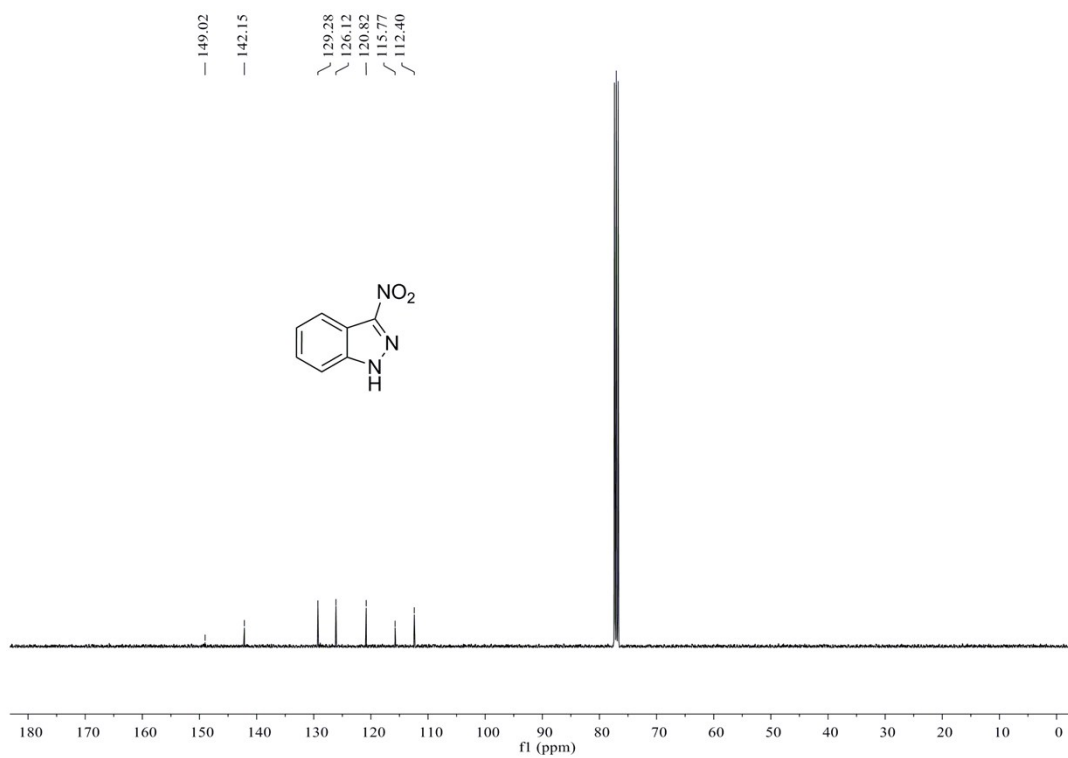
### 2bk <sup>19</sup>F NMR



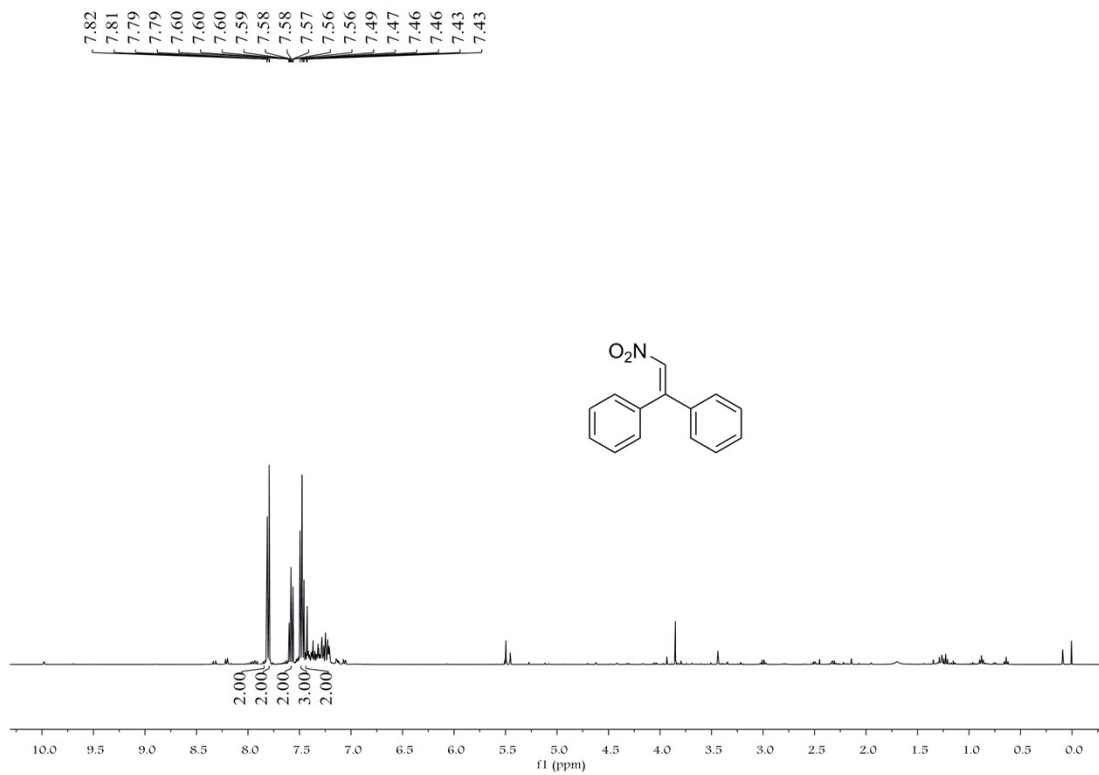
### 3a <sup>1</sup>H NMR



### 3a <sup>13</sup>C NMR



### 6a <sup>1</sup>H NMR



6a <sup>13</sup>C NMR

