

## Supporting Information

### **Photoredox-catalyzed Trifluoromethylation of 2*H*-Indazoles Using TT-CF<sub>3</sub><sup>+</sup>OTf<sup>-</sup> in Ionic Liquids**

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86609135)

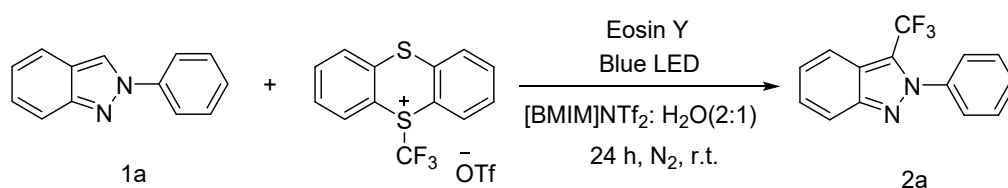
### **Contents of Supporting Information**

1. Materials and measurements.....	S2
2. General experimental procedure .....	S2
3. Preparation of TT-CF <sub>3</sub> <sup>+</sup> OTf <sup>-</sup> reagent .....	S3
4. Structures and data of target compounds.....	S3
5. NMR spectra.....	S15

## 1. Materials and measurements

All starting materials and the reagents were purchased from TCI or J&K Chemical Company and used without further purification unless specified. All the reactions were monitored by thin layer chromatography (TLC), and column chromatography were carried out on silica gel (300 ~ 400 mesh).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Ultrashield™ 400 spectrometer operating at 400 MHz and 100 MHz in  $\text{CDCl}_3$  or DMSO.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were reported in ppm with tetramethylsilane (TMS) as internal standard.  $^{19}\text{F}$  NMR was reported in ppm with trifluoroacetic acid (TFA) as internal standard. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiple. Coupling constants ( $J$ ) were reported in Hertz (Hz). Melting points were recorded on a WRR melting point apparatus. Infrared spectra were recorded with the Perkin-Elmer Spectrum100 Fourier transform infrared spectroscopy. UV-visible spectra were measured by Shimadzu UV-2501PC UV-visible spectrophotometer. Elemental analyses of C, H, N were performed on a Elementar Vario MICRO cube. High resolution mass spectrum was accomplished on Agilent 1100 (VL) mass spectrometer.

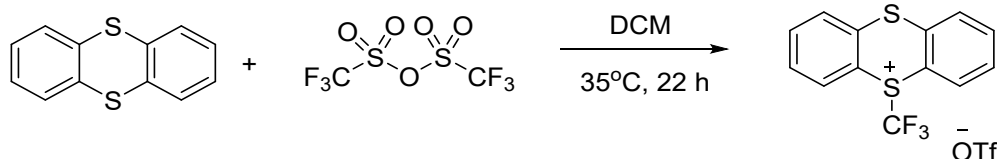
## 2. General experimental procedure



In the  $\text{N}_2$  atmosphere, **1a** (0.10 mmol, 1 equiv), TT- $\text{CF}_3^+\text{OTf}^-$  (0.20 mmol, 2 equiv), Eosin Y (0.0125 mmol, 5 mol%) were added to a 10 mL round-bottomed flask with a magnetic stirrer with 2 mL of [BMIM]NTf<sub>2</sub> (1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide): H<sub>2</sub>O (2:1). The reaction mixture was stirred at room temperature for 24 hours under irradiation of blue LED (monitored by TLC). When the reaction was completed, extraction was performed with  $\text{CH}_2\text{Cl}_2$  (10 mL×3) and the aqueous layer was collected to recover the ionic liquid. The organic extracts were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure. The

resulting mixture was then purified by flash column chromatography.

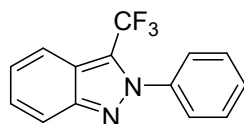
### 3. Preparation of TT-CF<sub>3</sub><sup>+</sup>OTf<sup>-</sup> reagent



In ambient atmosphere, thianthrene (17.3 g, 80.00 mmol, 1 equiv) and 200 ml dichloromethane (DCM) were added to a 500 ml two-necked round bottom flask which equipped with magnetic stirring. Then, trifluoromethanesulfonic anhydride (24.8 g, 88.0 mmol, 1.1 equiv) was added dropwise with magnetic stirring at room temperature. After the addition was complete, the reaction mixture was stirred at 35°C for 22 hours. At this time, the reaction liquid was dark purple. Subsequently, saturated aqueous sodium bicarbonate solution was slowly added dropwise to the reaction mixture until the color of the reaction mixture changed to light brown. The reaction solution was then extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL × 3). The organic extract was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give a dark brown solid material. The dark brown solid was washed with diethyl ether (20 mL × 3), and the product was finally obtained as a yellow solid after suction filtration (21.1g, 63%).

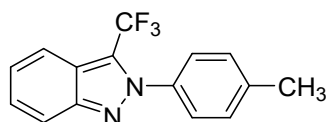
### 4. Structures and data of target compounds

#### 2-phenyl-3-(trifluoromethyl)-2H-indazole (2a)



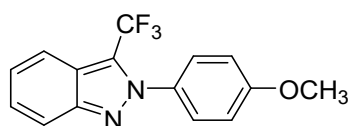
The pure product was obtained as a white solid (83%, 22.3mg). m.p:40.2~42.3°C <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 9.0 Hz, 2H), 7.61 – 7.52 (m, 5H), 7.44 – 7.38 (m, 1H), 7.33 – 7.27 (m, 1H). (**Figure S1**). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 148.2, 139.6, 130.0, 129.1, 127.3, 126.1, 125.1, 123.7(q, *J*<sub>C-F</sub> = 39.1 Hz), 121.6, 121.0(q, *J*<sub>C-F</sub> = 267.4 Hz), 119.4(q, *J*<sub>C-F</sub> = 14.5 Hz), 118.4. (**Figure S2**). <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ 21.57. (**Figure S3**) HRMS: C<sub>14</sub>H<sub>9</sub>F<sub>3</sub>N<sub>2</sub> for [M+H]<sup>+</sup>: 263.0750, Found: 263.0747. Anal.calcd for: C<sub>14</sub>H<sub>9</sub>F<sub>3</sub>N<sub>2</sub>: C 74.12, H 3.46, F 21.73, N 10.68; Found: C 74.11, H 3.47, F 21.72, N 10.66.

#### 2-(*p*-tolyl)-3-(trifluoromethyl)-2H-indazole (2b)



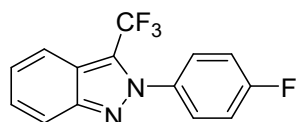
The pure product was obtained as a white solid (84%, 23.7mg). m.p:83.5~84.7°C <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 9.1 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.42 – 7.37 (m, 1H), 7.31 (dd, *J* = 14.3, 8.1 Hz, 3H), 2.45 (s, 3H). (**Figure S4**). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 148.1, 140.2, 137.1, 129.6, 127.1, 125.9, 124.9, 123.8, 121.5, 121.2(q, *J*<sub>C-F</sub> = 267.4 Hz), 121.5, 119.4(q, *J*<sub>C-F</sub> = 8.1 Hz), 21.3. (**Figure S5**). <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ 21.50. (**Figure S6**). HRMS: C<sub>15</sub>H<sub>11</sub>F<sub>3</sub>N<sub>2</sub> for [M+H]<sup>+</sup>: 277.0908, Found: 277.0909. Anal.calcd for: C<sub>15</sub>H<sub>11</sub>F<sub>3</sub>N<sub>2</sub>: C 65.22, H 4.01, F 20.63, N 10.14; Found: C 65.23, H 4.02, F 20.62, N 10.13.

### 2-(4-methoxyphenyl)-3-(trifluoromethyl)-2H-indazole (2c)



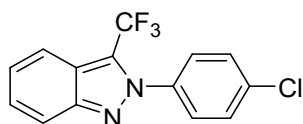
The pure product was obtained as a white solid (81%, 24.2mg). m.p:74.1~76.5°C <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 9.0 Hz, 2H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.44 – 7.37 (m, 1H), 7.32 – 7.26 (m, 1H), 7.03 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H). (**Figure S7**). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 160.6, 157.5, 148.0, 132.5, 127.4, 127.1, 124.9, 121.4, 121.0(q, *J*<sub>C-F</sub> = 267.3 Hz), 119.4(q, *J*<sub>C-F</sub> = 10.2 Hz), 118.3, 114.2, 55.6. (**Figure S8**). <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ 21.37. (**Figure S9**). HRMS: C<sub>15</sub>H<sub>11</sub>F<sub>3</sub>N<sub>2</sub>O for [M+H]<sup>+</sup>: 293.0857, Found: 293.0852. Anal.calcd for: C<sub>15</sub>H<sub>11</sub>F<sub>3</sub>N<sub>2</sub>O: C 61.65, H 3.79, F 19.50, N 9.59, O 5.47; Found: C 61.62, H 3.77, F 19.53, N 9.54, O 5.48.

### 2-(4-fluorophenyl)-3-(trifluoromethyl)-2H-indazole (2d)



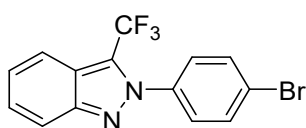
The pure product was obtained as a white solid (71%, 21.0mg). m.p:68.3~70.1°C <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.85 (dd, *J* = 18.0, 8.7 Hz, 2H), 7.75 (dd, *J* = 8.6, 4.8 Hz, 2H), 7.50 (q, *J* = 8.5, 7.0 Hz, 3H), 7.43 – 7.38 (m, 1H). (**Figure S10**). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 163.2(d, *J*<sub>C-F</sub> = 249.2 Hz), 148.2, 135.6(d, *J*<sub>C-F</sub> = 3.2 Hz), 128.1(d, *J*<sub>C-F</sub> = 9.5 Hz), 127.4, 125.2, 123.6, 122.9(q, *J*<sub>C-F</sub> = 267.4 Hz), 121.5(d, *J*<sub>C-F</sub> = 1.1 Hz), 119.4(q, *J*<sub>C-F</sub> = 14.2 Hz), 118.4, 116.2(d, *J*<sub>C-F</sub> = 23.1 Hz). (**Figure S11**). <sup>19</sup>F NMR (376 MHz, DMSO-*d*<sub>6</sub>) δ 21.50, -34.14. (**Figure S12**). HRMS: C<sub>14</sub>H<sub>8</sub>F<sub>4</sub>N<sub>2</sub> for [M+H]<sup>+</sup>: 281.0657, Found: 281.0651. Anal.calcd for: C<sub>14</sub>H<sub>8</sub>F<sub>4</sub>N<sub>2</sub>: C 60.01, H 2.88, F 27.12, N 10.00; Found: C 60.00, H 2.87, F 27.11, N 10.00

### 2-(4-chlorophenyl)-3-(trifluoromethyl)-2H-indazole (2e)



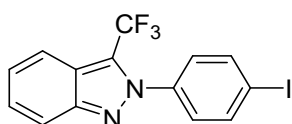
The pure product was obtained as a white solid (72%, 23.4mg). m.p:81.4~83.6°C  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.83 (dd,  $J = 8.6, 2.8$  Hz, 2H), 7.55 (s, 4H), 7.46 – 7.41 (m, 1H), 7.35 – 7.29 (m, 1H). **(Figure S13)**.  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  148.3, 138.0, 136.1, 129.4, 127.5, 127.4, 125.3, 123.5, 121.7, 120.8(q,  $J_{\text{C-F}} = 267.3$  Hz), 119.4(q,  $J_{\text{C-F}} = 12.2$  Hz), 118.4. **(Figure S14)**.  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  21.64. **(Figure S15)**. HRMS:  $\text{C}_{14}\text{H}_8\text{ClF}_3\text{N}_2$  for  $[\text{M}+\text{H}]^+$ : 298.0299, Found: 298.0299. Anal.calcd for:  $\text{C}_{14}\text{H}_8\text{ClF}_3\text{N}_2$ : C 56.68, H 2.72, Cl 11.95, F 19.21, N 9.44; Found: C 56.67, H 2.71, Cl 11.94, F 19.20, N 9.44

### 2-(4-bromophenyl)-3-(trifluoromethyl)-2H-indazole (2f)



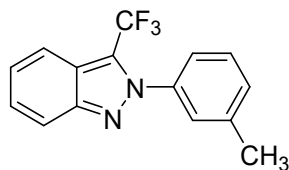
The pure product was obtained as a white solid (73%, 27.2mg). m.p:80.2~82.3°C  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.81 (d,  $J = 8.8$  Hz, 2H), 7.69 (d,  $J = 8.5$  Hz, 2H), 7.47 (d,  $J = 8.5$  Hz, 2H), 7.45 – 7.39 (m, 1H), 7.34 – 7.28 (m, 1H). **(Figure S16)**.  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  148.4, 138.5, 132.4, 127.6, 127.5, 125.3, 124.2, 120.6(q,  $J_{\text{C-F}} = 215.7$  Hz), 119.4(q,  $J_{\text{C-F}} = 12.4$  Hz), 118.4, 109.5, 100.0. **(Figure S17)**.  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  21.68. **(Figure S18)**. HRMS:  $\text{C}_{14}\text{H}_8\text{BrF}_3\text{N}_2$  for  $[\text{M}+\text{H}]^+$ : 341.9802, Found: 341.9806. Anal.calcd for:  $\text{C}_{14}\text{H}_8\text{BrF}_3\text{N}_2$ : C 49.29, H 2.36, Br 23.42, F 16.71, N 8.21; Found: C 49.28, H 2.35, Br 23.41, F 16.73, N 8.22

### 2-(4-iodophenyl)-3-(trifluoromethyl)-2H-indazole (2g)



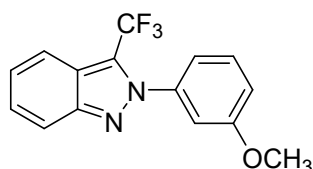
The pure product was obtained as a white solid (70%, 31.4mg). m.p:104.1~106.4°C  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.89 (d,  $J = 8.6$  Hz, 2H), 7.81 (d,  $J = 9.0$  Hz, 2H), 7.45 – 7.39 (m, 1H), 7.31 (dd,  $J = 17.1, 7.8$  Hz, 3H). **(Figure S19)**.  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  148.4, 139.3, 138.3, 127.7, 127.5, 125.3, 121.7, 120.8(q,  $J_{\text{C-F}} = 267.3$  Hz), 119.4(q,  $J_{\text{C-F}} = 13.2$  Hz), 118.4, 100.0, 95.8. **(Figure S20)**.  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  21.71. **(Figure S21)**. HRMS:  $\text{C}_{14}\text{H}_8\text{IF}_3\text{N}_2$  for  $[\text{M}+\text{H}]^+$ : 388.9718, Found: 388.9717. Anal.calcd for:  $\text{C}_{14}\text{H}_8\text{IF}_3\text{N}_2$ : C 43.32, H 2.08, I 32.70, F 14.68, N 7.22; Found: C 43.31, H 2.07, I 32.72, F 14.67, N 7.21

### 2-(*m*-tolyl)-3-(trifluoromethyl)-2H-indazole (2h)



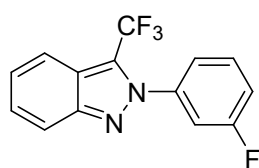
The pure product was obtained as a white solid (80%, 22.6mg). m.p:81.2~83.4°C  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  6.91 (d,  $J$  = 8.8 Hz, 1H), 6.84 (d,  $J$  = 8.5 Hz, 1H), 6.53 (dd,  $J$  = 17.2, 9.9 Hz, 5H), 6.43 – 6.37 (m, 1H), 1.45 (s, 3H). **(Figure S22)**.  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  147.9, 139.5(d,  $J_{\text{C-F}}$  = 2.5 Hz), 131.3, 129.3, 127.7, 127.0, 125.9, 123.6, 123.3, 122.9, 121.2(q,  $J_{\text{C-F}}$  = 264.8 Hz), 121.3, 119.2(q,  $J_{\text{C-F}}$  = 19.8 Hz), 118.7, 21.1. **(Figure S23)**.  $^{19}\text{F}$  NMR (376 MHz, DMSO- $d_6$ )  $\delta$  20.30. **(Figure S24)**. HRMS:  $\text{C}_{15}\text{H}_{11}\text{F}_3\text{N}_2$  for  $[\text{M}+\text{H}]^+$ : 277.0908, Found: 277.0921. Anal.calcd for:  $\text{C}_{15}\text{H}_{11}\text{F}_3\text{N}_2$ : C 65.22, H 4.01, F 20.63, N 10.14; Found: C 65.21, H 4.03, F 20.61, N 10.13.

### 2-(3-methoxyphenyl)-3-(trifluoromethyl)-2H-indazole (2i)



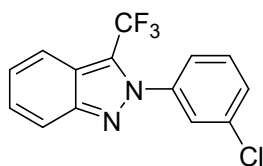
The pure product was obtained as a white solid (78%, 23.3mg). m.p:74.1~76.5°C  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.82 (d,  $J$  = 8.6 Hz, 2H), 7.43 (q,  $J$  = 8.5 Hz, 2H), 7.33 – 7.27 (m, 1H), 7.18 (d,  $J$  = 7.7 Hz, 1H), 7.14 – 7.07 (m, 2H), 3.86 (s, 3H). **(Figure S25)**.  $^{13}\text{C}$  NMR (100 MHz, Chloroform- $d$ )  $\delta$  159.9, 148.1, 140.5, 129.9, 127.3, 125.1, 122.6(q,  $J_{\text{C-F}}$  = 271.1 Hz), 121.5, 119.4(q,  $J_{\text{C-F}}$  = 8.3Hz), 118.4, 118.3, 116.2, 114.7, 111.7, 55.6. **(Figure S26)**.  $^{19}\text{F}$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  21.49. **(Figure S27)**. HRMS:  $\text{C}_{15}\text{H}_{11}\text{F}_3\text{N}_2\text{O}$  for  $[\text{M}+\text{H}]^+$ : 293.0857, Found: 293.0852. Anal.calcd for:  $\text{C}_{15}\text{H}_{11}\text{F}_3\text{N}_2\text{O}$ : C 61.65, H 3.79, F 19.50, N 9.59, O 5.47; Found: C 61.62, H 3.77, F 19.53, N 9.54, O 5.48.

### 2-(3-fluorophenyl)-3-(trifluoromethyl)-2H-indazole (2j)



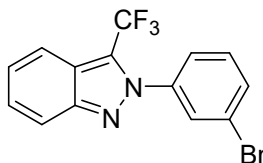
The pure product was obtained as a white solid (68%, 21.0mg). m.p:38.0~40.5°C.  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.81 (d,  $J$  = 9.2 Hz, 2H), 7.56 – 7.48 (m, 1H), 7.42 (t,  $J$  = 7.4 Hz, 2H), 7.36 (d,  $J$  = 8.8 Hz, 1H), 7.33 – 7.25 (m, 2H). **(Figure S28)**.  $^{13}\text{C}$  NMR (100 MHz, Chloroform- $d$ )  $\delta$  163.6, 161.1, 148.35, 140.7(d,  $J_{\text{C-F}}$  = 9.6 Hz), 134.4, 130.4(d,  $J_{\text{C-F}}$  = 8.8 Hz), 127.6, 125.4, 123.4, 120.8(q,  $J_{\text{C-F}}$  = 267.4 Hz), 119.4(q,  $J_{\text{C-F}}$  = 4.9 Hz), 118.4, 117.2(d,  $J_{\text{C-F}}$  = 21.0 Hz), 114.0(d,  $J_{\text{C-F}}$  = 24.7 Hz). **(Figure S29)**.  $^{19}\text{F}$  NMR (376 MHz, Chloroform- $d$ )  $\delta$  21.59, -34.57. **(Figure S30)**. HRMS:  $\text{C}_{14}\text{H}_8\text{F}_4\text{N}_2$  for  $[\text{M}+\text{H}]^+$ : 281.0657, Found: 281.0652. Anal.calcd for:  $\text{C}_{14}\text{H}_8\text{F}_4\text{N}_2$ : C 60.01, H 2.88, F 27.12, N 10.00; Found: C 60.02, H 2.87, F 27.11, N 10.01

### 2-(3-chlorophenyl)-3-(trifluoromethyl)-2H-indazole (2k)



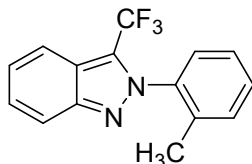
The pure product was obtained as a white solid (70%, 23.1mg). m.p:52.2~54.1°C  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.82 (dd,  $J = 8.4, 3.2$  Hz, 2H), 7.63 (s, 1H), 7.55 (d,  $J = 6.7$  Hz, 1H), 7.49 (d,  $J = 6.6$  Hz, 2H), 7.45 – 7.39 (m, 1H), 7.34 – 7.29 (m, 1H). **(Figure S31)**.  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  148.4, 140.4, 134.9, 130.2, 130.1, 127.6, 126.6, 125.4, 124.6, 124.3, 121.7, 120.8(q,  $J_{\text{C-F}} = 267.5$  Hz), 119.4(q,  $J_{\text{C-F}} = 7.0$  Hz), 118.4. **(Figure S32)**.  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  21.66. **(Figure S33)**. HRMS:  $\text{C}_{14}\text{H}_8\text{ClF}_3\text{N}_2$  for  $[\text{M}+\text{H}]^+$ : 298.0299, Found: 298.0294. Anal.calcd for:  $\text{C}_{14}\text{H}_8\text{ClF}_3\text{N}_2$ : C 56.68, H 2.72, Cl 11.95, F 19.21, N 9.44; Found: C 56.67, H 2.72, Cl 11.96, F 19.20, N 9.45

### 2-(3-bromophenyl)-3-(trifluoromethyl)-2H-indazole (2l)



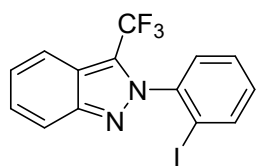
The pure product was obtained as a white solid (71%, 26.6mg). m.p:50.2~52.3°C  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.85 – 7.76 (m, 2H), 7.70 (d,  $J = 8.0$  Hz, 1H), 7.55 (d,  $J = 8.2$  Hz, 1H), 7.42 (t,  $J = 7.8$  Hz, 3H), 7.35 – 7.28 (m, 1H). **(Figure S34)**.  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  148.4, 140.5, 133.2, 130.3, 129.4, 127.6, 125.4, 124.7, 123.5, 122.5, 121.7, 120.8(q,  $J_{\text{C-F}} = 267.1$  Hz), 119.4(q,  $J_{\text{C-F}} = 1.5$  Hz), 118.4. **(Figure S35)**.  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  21.68. **(Figure S36)**. HRMS:  $\text{C}_{14}\text{H}_8\text{BrF}_3\text{N}_2$  for  $[\text{M}+\text{H}]^+$ : 341.9802, Found: 341.9806. Anal.calcd for:  $\text{C}_{14}\text{H}_8\text{BrF}_3\text{N}_2$ : C 49.29, H 2.36, Br 23.42, F 16.71, N 8.21; Found: C 49.28, H 2.35, Br 23.41, F 16.73, N 8.22

### 2-(*o*-tolyl)-3-(trifluoromethyl)-2H-indazole (2m)



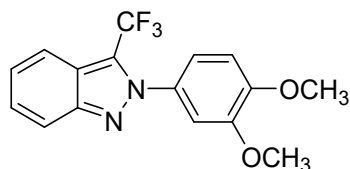
The pure product was obtained as a white solid (65%, 19.8mg). m.p:52.3~54.1°C  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.83 (dd,  $J = 8.2, 5.3$  Hz, 2H), 7.49 – 7.39 (m, 2H), 7.38 – 7.28 (m, 4H), 2.02 (s, 3H). **(Figure S37)**.  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  148.2, 138.3, 135.8, 130.8, 130.5, 127.3, 127.1, 126.3, 125.0, 124.1, 120.8(q,  $J_{\text{C-F}} = 267.3$  Hz), 120.8, 119.4(q,  $J_{\text{C-F}} = 14.0$  Hz), 118.5, 16.8. **(Figure S38)**.  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  19.81. **(Figure S39)**. HRMS:  $\text{C}_{15}\text{H}_{11}\text{F}_3\text{N}_2$  for  $[\text{M}+\text{H}]^+$ : 277.0908, Found: 277.0913. Anal.calcd for:  $\text{C}_{15}\text{H}_{11}\text{F}_3\text{N}_2$ : C 65.22, H 4.01, F 20.63, N 10.14; Found: C 65.23, H 4.02, F 20.62, N 10.13.

## 2-(2-iodophenyl)-3-(trifluoromethyl)-2H-indazole (2n)



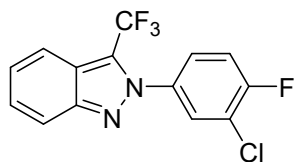
The pure product was obtained as a white solid (60%, 27.1mg). m.p.:58.7~60.7°C  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.00 (d,  $J = 7.9$  Hz, 1H), 7.89 – 7.81 (m, 2H), 7.48 (tt,  $J = 16.0, 8.0$  Hz, 3H), 7.31 (dd,  $J = 16.9, 8.8$  Hz, 2H). (**Figure S40**).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  148.3, 142.11, 139.7, 131.8, 128.7, 128.5, 127.5, 125.3, 122.6, 120.5(q,  $J_{\text{C-F}} = 267.6$  Hz), 121.0, 119.4(q,  $J_{\text{C-F}} = 16.1$  Hz), 118.6, 96.4. (**Figure S41**).  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  20.21. (**Figure S42**). HRMS:  $\text{C}_{14}\text{H}_8\text{IF}_3\text{N}_2$  for  $[\text{M}+\text{H}]^+$ : 388.9718, Found: 388.9713. Anal.calcd for:  $\text{C}_{14}\text{H}_8\text{IF}_3\text{N}_2$ : C 43.32, H 2.08, I 14.68, F 32.70, N 7.22; Found: C 43.31, H 2.07, I 14.69, F 32.71, N 7.22 FT-IR (KBr disc):  $\nu = 1489, 1435, 1303, 1219, 1180, 1049, 995, 748$   $\text{cm}^{-1}$ .

## 2-(3,4-dimethoxyphenyl)-3-(trifluoromethyl)-2H-indazole (2o)



The pure product was obtained as a white solid (83%, 27.4mg). m.p.:125.3~126.7°C  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.82 (d,  $J = 9.3$  Hz, 2H), 7.44 – 7.38 (m, 1H), 7.32 – 7.27 (m, 1H), 7.16 (dd,  $J = 8.5, 2.0$  Hz, 1H), 7.10 (d,  $J = 2.2$  Hz, 1H), 6.98 (d,  $J = 8.6$  Hz, 1H), 3.97 (s, 3H), 3.92 (s, 3H). (**Figure S43**).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  150.3, 149.1, 148.0, 132.5, 131.2, 127.2, 125.0, 121.4, 121.0(q,  $J_{\text{C-F}} = 267.1$  Hz), 119.4(q,  $J_{\text{C-F}} = 12.4$  Hz), 118.4, 118.3, 110.5, 109.7, 56.2, 56.1. (**Figure S44**).  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  21.37. (**Figure S45**). HRMS:  $\text{C}_{16}\text{H}_{13}\text{F}_3\text{N}_2\text{O}_2$  for  $[\text{M}+\text{H}]^+$ : 323.0963, Found: 323.0958. Anal.calcd for:  $\text{C}_{16}\text{H}_{13}\text{F}_3\text{N}_2\text{O}_2$ : C 59.63, H 4.07, F 17.68, N 8.69, O 9.93; Found: C 59.64, H 4.05, F 17.66, N 8.68, O 9.95. FT-IR (KBr disc):  $\nu = 1604, 1519, 1473, 1427, 1334, 1234, 1180, 1010, 740$   $\text{cm}^{-1}$ .

## 2-(3-chloro-4-fluorophenyl)-3-(trifluoromethyl)-2H-indazole (2p)

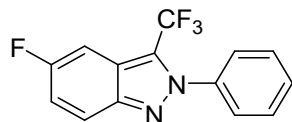


The pure product was obtained as a white solid (65%, 23.3mg). m.p.:84.2~86.1°C  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.84 – 7.78 (m, 2H), 7.70 (dd,  $J = 6.2, 2.4$  Hz, 1H), 7.50 (dt,  $J = 6.4, 3.1$  Hz, 1H), 7.46 – 7.40 (m, 1H), 7.35 – 7.28 (m, 2H). (**Figure S46**).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  160.1, 157.6, 148.4, 135.9(d,  $J_{\text{C-F}} = 3.6$  Hz), 128.8, 127.7, 126.1(d,  $J_{\text{C-F}} = 4.3$ Hz), 126.0(d,  $J_{\text{C-F}} = 1.0$  Hz), 125.5, 121.7(d,  $J_{\text{C-F}} = 25.5$  Hz), 120.7(q,  $J_{\text{C-F}} = 265.2$  Hz), 119.3(d,  $J_{\text{C-F}} = 12.7$  Hz), 118.4, 116.9(d,  $J_{\text{C-F}} = 22.7$  Hz). (**Figure S47**).  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  21.61, -36.13. (**Figure**



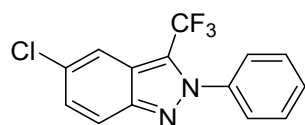
**S48).** HRMS:  $C_{14}H_7ClF_4N_2$  for  $[M+H]^+$ : 316.0204, Found: 316.0198. Anal.calcd for:  $C_{14}H_7ClF_4N_2$ : C 53.44, H 2.24, Cl 11.27, F 24.15, N 8.90; Found: C 53.43, H 2.23, Cl 11.28, F 24.14, N 8.91

**5-fluoro-2-phenyl-3-(trifluoromethyl)-2H-indazole (2q)**



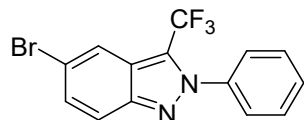
The pure product was obtained as a white solid (71%, 21.8mg). m.p:56.0~58.1°C.  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.81 (dd,  $J = 9.4, 4.6$  Hz, 1H), 7.60 – 7.52 (m, 5H), 7.40 (d,  $J = 8.9$  Hz, 1H), 7.21 (td,  $J = 9.2, 2.3$  Hz, 1H). (**Figure S49**).  $^{13}C$  NMR (100 MHz, Chloroform-*d*)  $\delta$  160.1(d,  $J_{C-F} = 243.3$  Hz), 145.6, 139.4, 130.1, 129.1, 126.0, 121.3(q,  $J_{C-F} = 1.2$  Hz), 120.8(d,  $J_{C-F} = 1.4$  Hz), 120.7(q,  $J_{C-F} = 267.3$  Hz), 119.3, 119.0, 102.3(q,  $J_{C-F} = 24.2$  Hz). (**Figure S50**).  $^{19}F$  NMR (376 MHz, Chloroform-*d*)  $\delta$  21.33, -38.47. (**Figure S51**). HRMS:  $C_{14}H_8F_4N_2$  for  $[M+H]^+$ : 281.0657, Found: 281.0655. Anal.calcd for:  $C_{14}H_8F_4N_2$ : C 60.01, H 2.88, F 27.12, N 10.00; Found: C 60.02, H 2.87, F 27.11, N 10.01 FT-IR (KBr disc):  $\nu = 1643, 1597, 1527, 1504, 1473, 1280, 1111, 995, 840, 771$   $cm^{-1}$ .

**5-chloro-2-phenyl-3-(trifluoromethyl)-2H-indazole (2r)**



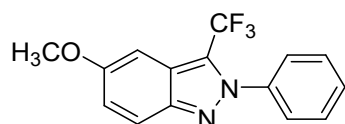
The pure product was obtained as a white solid (73%, 23.4mg). m.p:90.2~92.1°C  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.82 – 7.73 (m, 2H), 7.60 – 7.51 (m, 5H), 7.34 (dd,  $J = 9.2, 1.7$  Hz, 1H). (**Figure S52**).  $^{13}C$  NMR (100 MHz, Chloroform-*d*)  $\delta$  146.5, 139.3, 131.0, 130.2, 129.2, 128.9, 126.0, 122.4(q,  $J_{C-F} = 229.1$  Hz), 121.9(q,  $J_{C-F} = 8.9$  Hz), 120.0, 119.3, 118.2(d,  $J_{C-F} = 1.9$  Hz). (**Figure S53**).  $^{19}F$  NMR (376 MHz, Chloroform-*d*)  $\delta$  21.42. (**Figure S54**). HRMS:  $C_{14}H_8ClF_3N_2$  for  $[M+H]^+$ : 298.0299, Found: 298.0293. Anal.calcd for:  $C_{14}H_8ClF_3N_2$ : C 56.68, H 2.72, Cl 11.95, F 19.21, N 9.44; Found: C 56.67, H 2.72, Cl 11.96, F 19.20, N 9.45

**5-bromo-2-phenyl-3-(trifluoromethyl)-2H-indazole (2s)**



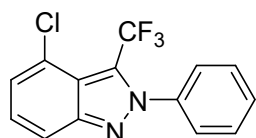
The pure product was obtained as a yellow solid (70%, 27.2mg). m.p:112.1~113.2°C  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.00 (s, 1H), 7.70 (d,  $J = 9.2$  Hz, 1H), 7.58 – 7.53 (m, 5H), 7.47 (dd,  $J = 9.2, 1.7$  Hz, 1H). (**Figure S55**).  $^{13}C$  NMR (100 MHz, Chloroform-*d*)  $\delta$  146.6, 139.2, 131.2, 130.2, 129.2, 126.0, 123.0, 122.6, 121.6(q,  $J_{C-F} = 11.1$  Hz), 120.6(q,  $J_{C-F} = 267.5$  Hz), 120.1, 119.1. (**Figure S56**).  $^{19}F$  NMR (376 MHz, Chloroform-*d*)  $\delta$  21.42. (**Figure S57**). HRMS:  $C_{14}H_8BrF_3N_2$  for  $[M+H]^+$ : 341.9802, Found: 341.9805. Anal.calcd for:  $C_{14}H_8BrF_3N_2$ : C 49.29, H 2.36, Br 23.42, F 16.71, N 8.21; Found: C 49.28, H 2.35, Br 23.41, F 16.73, N 8.22

### 5-methoxy-2-phenyl-3-(trifluoromethyl)-2H-indazole (2t)



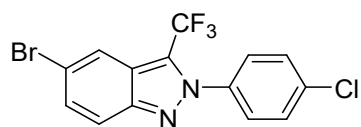
The pure product was obtained as a white solid (81%, 24.8mg). m.p:107.1~109.2°C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 9.4 Hz, 1H), 7.61 – 7.48 (m, 5H), 7.09 (dd, *J* = 9.4, 2.3 Hz, 1H), 6.95 (s, 1H), 3.88 (s, 3H). (**Figure S58**). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 157.3, 145.1, 139.7, 129.7, 129.0, 128.6, 126.1, 122.7, 122.2, 121.2(q, *J*<sub>C-F</sub> = 266.7 Hz), 119.8, 95.1(q, *J*<sub>C-F</sub> = 6.0 Hz), 55.5. (**Figure S59**). <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ 21.69. (**Figure S60**). HRMS: C<sub>15</sub>H<sub>11</sub>F<sub>3</sub>N<sub>2</sub>O for [M+H]<sup>+</sup>: 293.0855, Found: 293.0850. Anal.calcd for: C<sub>15</sub>H<sub>11</sub>F<sub>3</sub>N<sub>2</sub>O: C 61.65, H 3.79, F 19.50, N 9.59, O 5.47; Found: C 61.65, H 3.75, F 19.52, N 9.59, O 5.45

### 4-chloro-2-phenyl-3-(trifluoromethyl)-2H-indazole (2u)



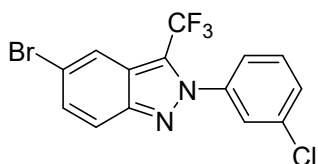
The pure product was obtained as a yellow solid (45%, 13.4mg). m.p:87.1~89.2°C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.58 (s, 1H), 7.96 (d, *J* = 7.7 Hz, 2H), 7.56 (dt, *J* = 10.6, 5.6 Hz, 3H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H). (**Figure S61**). <sup>13</sup>C NMR (100MHz, Chloroform-*d*) δ 145.2, 139.9, 130.2, 129.7, 128.8, 127.3, 125.6(q, *J*<sub>C-F</sub> = 16.6 Hz), 124.0, 123.6(q, *J*<sub>C-F</sub> = 270.2 Hz), 121.4, 121.0, 120.2. (**Figure S62**). <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ 13.92. (**Figure S63**). HRMS: C<sub>14</sub>H<sub>8</sub>ClF<sub>3</sub>N<sub>2</sub> for [M+H]<sup>+</sup>: 298.0295, Found: 298.0290. Anal.calcd for: C<sub>14</sub>H<sub>8</sub>ClF<sub>3</sub>N<sub>2</sub>: C 56.68, H 2.72, Cl 11.95, F 19.21, N 9.44; Found: C 56.66, H 2.75, Cl 11.90, F 19.25, N 9.44 FT-IR (KBr disc): ν=3673, 3525, 3068, 2926, 2854, 2355, 1695, 1634, 1596, 1470, 1439, 1314, 1290, 1104, 999, 768 cm<sup>-1</sup>.

### 5-bromo-2-(4-chlorophenyl)-3-(trifluoromethyl)-2H-indazole (2v)



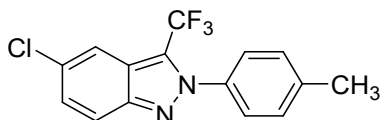
The pure product was obtained as a yellow solid (69%, 28.9mg). m.p:103.0~105.3°C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.68 (d, *J* = 9.2 Hz, 1H), 7.52 (s, 4H), 7.47 (d, *J* = 9.2 Hz, 1H). (**Figure S64**). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 146.7, 137.7, 136.4, 131.4, 129.4, 127.2, 122.7, 121.5(q, *J*<sub>C-F</sub> = 15.9 Hz), 120.5(q, *J*<sub>C-F</sub> = 267.6 Hz), 120.1, 119.3, 117.0(d, *J*<sub>C-F</sub> = 36.9 Hz). (**Figure S65**). <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ 21.49. (**Figure S66**). HRMS: C<sub>14</sub>H<sub>7</sub>BrClF<sub>3</sub>N<sub>2</sub> for [M+H]<sup>+</sup>: 375.9413, Found: 375.9417. Anal.calcd for: C<sub>14</sub>H<sub>7</sub>BrClF<sub>3</sub>N<sub>2</sub>: C 44.77, H 1.88, Br 21.28, Cl 9.44, F 15.18, N 7.46; Found: C 44.76, H 1.86, Br 21.29, Cl 9.45, F 15.18, N 7.46 FT-IR (KBr disc): ν=1504, 1419, 1342, 1273, 1219, 1118, 1041, 995, 833, 802 cm<sup>-1</sup>.

### 5-bromo-2-(3-chlorophenyl)-3-(trifluoromethyl)-2H-indazole (2w)



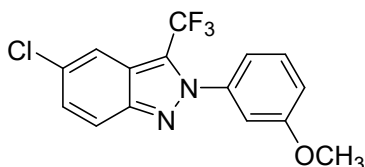
The pure product was obtained as a white solid (66%, 28.2mg). m.p:76.8~78.0°C  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.00 (s, 1H), 7.69 (d,  $J = 9.2$  Hz, 1H), 7.62 (s, 1H), 7.58 – 7.53 (m, 1H), 7.49 (d,  $J = 5.1$  Hz, 3H). **(Figure S67)**.  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  146.8, 140.1, 135.0, 131.5, 130.5, 130.1, 126.5, 124.1, 123.4, 123.0, 122.7, 121.6(q,  $J_{\text{C-F}} = 16.4$  Hz), 120.6(q,  $J_{\text{C-F}} = 238.7$  Hz), 120.1. **(Figure S68)**.  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  21.50. **(Figure S69)**. HRMS:  $\text{C}_{14}\text{H}_7\text{BrClF}_3\text{N}_2$  for  $[\text{M}+\text{H}]^+$ : 375.9413, Found: 375.9417. Anal.calcd for:  $\text{C}_{14}\text{H}_7\text{BrClF}_3\text{N}_2$ : C 44.77, H 1.88, Br 21.28, Cl 9.44, F 15.18, N 7.46; Found: C 44.76, H 1.86, Br 21.29, Cl 9.45, F 15.18, N 7.46 FT-IR (KBr disc):  $\nu=1589, 1489, 1419, 1265, 1219, 1162, 1120, 1041, 1002, 948, 864$   $\text{cm}^{-1}$ .

#### 5-chloro-2-(p-tolyl)-3-(trifluoromethyl)-2H-indazole (2x)



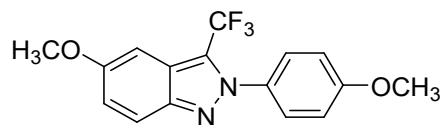
The pure product was obtained as a white solid (70%, 25.1mg). m.p:98.2~99.0°C  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.80 (s, 1H), 7.75 (d,  $J = 9.2$  Hz, 1H), 7.44 (d,  $J = 8.2$  Hz, 2H), 7.34 (d,  $J = 7.8$  Hz, 3H), 2.46 (s, 3H). **(Figure S70)**.  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  146.4, 140.5, 136.8, 130.9, 129.7, 128.7, 125.7, 122.0, 121.9, 121.7(q,  $J_{\text{C-F}} = 288.1$  Hz), 119.9, 118.2(q,  $J_{\text{C-F}} = 7.3$  Hz), 21.3. **(Figure S71)**.  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  21.31. **(Figure S72)**. HRMS:  $\text{C}_{15}\text{H}_{10}\text{ClF}_3\text{N}_2$  for  $[\text{M}+\text{H}]^+$ : 312.0455, Found: 312.0456. Anal.calcd for:  $\text{C}_{15}\text{H}_{10}\text{ClF}_3\text{N}_2$ : C 57.99, H 3.24, Cl 11.41, F 18.34, N 9.02; Found: C 57.98, H 3.23, Cl 11.42, F 18.33, N 9.01

#### 5-chloro-2-(3-methoxyphenyl)-3-(trifluoromethyl)-2H-indazole (2y)



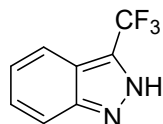
The pure product was obtained as a yellow solid (71%, 27.1mg). m.p:99.3~101.4°C  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.84 – 7.74 (m, 2H), 7.47 – 7.41 (m, 1H), 7.35 (dd,  $J = 9.2, 1.7$  Hz, 1H), 7.16 (d,  $J = 8.0$  Hz, 1H), 7.13 – 7.07 (m, 2H), 3.86 (s, 3H). **(Figure S73)**.  $^{13}\text{C}$  NMR (100MHz, Chloroform-*d*)  $\delta$  160.0, 146.4, 140.2, 131.1, 129.9, 128.9, 124.9, 123.2, 120.6(q,  $J_{\text{C-F}} = 263.3$  Hz), 120.0, 118.2(q,  $J_{\text{C-F}} = 11.1$  Hz), 116.6, 116.4, 111.6, 55.6. **(Figure S74)**.  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  21.33. **(Figure S75)**. HRMS:  $\text{C}_{15}\text{H}_{10}\text{ClF}_3\text{N}_2\text{O}$  for  $[\text{M}+\text{H}]^+$ : 328.0404, Found: 328.0399. Anal.calcd for:  $\text{C}_{15}\text{H}_{10}\text{ClF}_3\text{N}_2\text{O}$ : C 55.15, H 3.09, Cl 10.85, O 4.90, F 17.45, N 8.57; Found: C 55.14, H 3.09, Cl 10.84, O 4.91, F 17.46, N 8.58 FT-IR (KBr disc):  $\nu=1604, 1496, 1473, 1280, 1172, 1056, 848, 762$   $\text{cm}^{-1}$ .

### 5-methoxy-2-(4-methoxyphenyl)-3-(trifluoromethyl)-2H-indazole (2z)



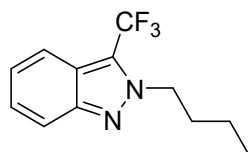
The pure product was obtained as a white solid (83%, 27.4mg). m.p:99.3~101.4°C <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.74 (d, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 9.3 Hz, 1H), 7.00 (t, *J* = 9.4 Hz, 3H), 6.87 (s, 1H), 3.83 (d, *J* = 4.2 Hz, 6H). (**Figure S76**). <sup>13</sup>C NMR (100MHz, Chloroform-*d*) δ 160.5, 157.2, 144.9, 132.6, 127.3, 123.0(q, *J*<sub>C-F</sub> = 275.6 Hz), 122.5, 122.0(q, *J*<sub>C-F</sub> = 8.7 Hz), 119.7, 114.1, 95.1, 93.3, 55.6, 55.5. (**Figure S77**). <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ 21.50. (**Figure S78**). HRMS: C<sub>16</sub>H<sub>13</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub> for [M+H]<sup>+</sup>: 322.0929, Found: 322.0924. Anal.calcd for: C<sub>16</sub>H<sub>13</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub>: C 59.63, H 4.07, F 17.68, N 8.69, O 9.93; Found: C 59.62, H 4.05, F 17.69, N 8.68, O 9.95.

### 3-(trifluoromethyl)-2H-indazole (2aa)



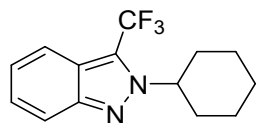
The pure product was obtained as a yellow solid (55%, 10.2mg). m.p:95.5~97.2°C <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 10.92 (s, 1H), 8.21 (s, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H). (**Figure S79**). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 135.4(d, *J*<sub>C-F</sub> = 15.8 Hz), 127.9, 125.2, 124.6(q, *J*<sub>C-F</sub> = 4.4 Hz), 124.3(q, *J*<sub>C-F</sub> = 269.5 Hz), 120.5, 112.9(q, *J*<sub>C-F</sub> = 34.0 Hz), 110.2. (**Figure S80**). <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ 15.21. (**Figure S81**). HRMS: C<sub>8</sub>H<sub>5</sub>F<sub>3</sub>N<sub>2</sub> for [M+H]<sup>+</sup>: 187.0435, Found: 187.0430. Anal.calcd for: C<sub>8</sub>H<sub>5</sub>F<sub>3</sub>N<sub>2</sub>: C 51.62, H 2.71, F 30.62, N 15.05; Found: C 51.60, H 2.73, F 30.64, N 15.02

### 2-butyl-3-(trifluoromethyl)-2H-indazole (2ab)



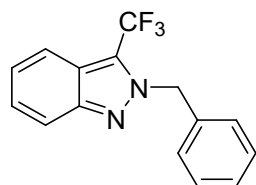
The pure product was obtained as a yellow oil (67%, 16.7mg). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.73 (t, *J* = 9.3 Hz, 2H), 7.34 – 7.28 (m, 1H), 7.22 – 7.15 (m, 1H), 4.50 (t, *J* = 7.5 Hz, 2H), 2.01 (p, *J* = 7.6 Hz, 2H), 1.40 (h, *J* = 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). (**Figure S82**). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 147.5, 126.3, 124.3, 122.2(d, *J*<sub>C-F</sub> = 39.2 Hz), 121.4(q, *J*<sub>C-F</sub> = 266.9 Hz), 120.9, 119.0(q, *J*<sub>C-F</sub> = 14.7 Hz), 118.0, 52.6, 32.6, 19.8, 13.5. (**Figure S83**). <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ 19.64. (**Figure S84**). HRMS: C<sub>12</sub>H<sub>13</sub>F<sub>3</sub>N<sub>2</sub> for [M+H]<sup>+</sup>: 243.1064, Found: 243.1070. Anal.calcd for: C<sub>12</sub>H<sub>13</sub>F<sub>3</sub>N<sub>2</sub>: C 59.50, H 5.41, F 23.53, N 11.56; Found: C 59.51, H 5.40, F 23.52, N 11.55

### 2-cyclohexyl-3-(trifluoromethyl)-2H-indazole (2ac)



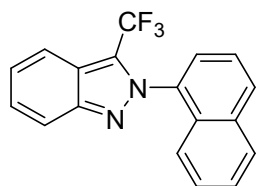
The pure product was obtained as a yellow oil (71%, 19.6mg).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.78 (dd,  $J = 15.5, 8.6$  Hz, 2H), 7.38 – 7.30 (m, 1H), 7.26 – 7.17 (m, 1H), 4.56 (t,  $J = 11.4$  Hz, 1H), 2.18 (dt,  $J = 40.3, 11.4$  Hz, 4H), 1.98 (d,  $J = 13.1$  Hz, 2H), 1.79 (d,  $J = 12.1$  Hz, 1H), 1.47 (dt,  $J = 30.9, 15.1$  Hz, 3H). (**Figure S85**).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  147.4, 126.1, 124.3, 121.6(q,  $J_{\text{C-F}} = 266.8$  Hz), 121.3, 120.4, 119.2(q,  $J_{\text{C-F}} = 15.3$  Hz), 118.2, 61.9, 33.5, 25.6, 25.1. (**Figure S86**).  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  19.80. (**Figure S87**). HRMS:  $\text{C}_{14}\text{H}_{15}\text{F}_3\text{N}_2$  for  $[\text{M}+\text{H}]^+$ : 269.1221, Found: 269.1226. Anal.calcd for:  $\text{C}_{14}\text{H}_{15}\text{F}_3\text{N}_2$ : C 62.68, H 5.64, F 21.24, N 10.44; Found: C 62.69, H 5.63, F 21.23, N 10.45.

### 2-benzyl-3-(trifluoromethyl)-2H-indazole (2ad)



The pure product was obtained as a white solid (73%, 20.7mg). m.p:42.3~44.3°C  $^1\text{H}$  NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.82 (d,  $J = 8.7$  Hz, 1H), 7.74 (d,  $J = 8.5$  Hz, 1H), 7.46 – 7.39 (m, 1H), 7.33 (q,  $J = 10.1, 8.4$  Hz, 4H), 7.21 (d,  $J = 7.2$  Hz, 2H), 5.81 (s, 2H). (**Figure S88**).  $^{13}\text{C}$  NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  147.5, 136.1, 129.1, 128.5, 127.7, 127.3, 125.6, 123.1(q,  $J_{\text{C-F}} = 239.2$  Hz), 121.0, 120.2, 119.0(q,  $J_{\text{C-F}} = 14.2$  Hz), 118.6, 56.3. (**Figure S89**).  $^{19}\text{F}$  NMR (376 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  21.03. (**Figure S90**). HRMS:  $\text{C}_{15}\text{H}_{11}\text{F}_3\text{N}_2$  for  $[\text{M}+\text{H}]^+$ : 277.0908, Found: 277.0904. Anal.calcd for:  $\text{C}_{15}\text{H}_{11}\text{F}_3\text{N}_2$ : C 65.22, H 4.01, F 20.63, N 10.14; Found: C 65.21, H 4.00, F 20.64, N 10.13

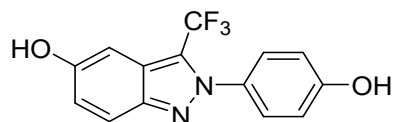
### 2-(naphthalen-1-yl)-3-(trifluoromethyl)-2H-indazole (2ae)



The pure product was obtained as a yellow solid (69%, 22.3mg). m.p:45.3~47.2°C  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.09 (d,  $J = 8.2$  Hz, 1H), 8.01 – 7.91 (m, 3H), 7.69 (d,  $J = 7.2$  Hz, 1H), 7.59 (dt,  $J = 18.5, 7.9$  Hz, 2H), 7.49 (q,  $J = 7.3$  Hz, 2H), 7.42 – 7.35 (m, 1H), 7.15 (d,  $J = 8.4$  Hz, 1H). (**Figure S91**).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  148.4, 135.6, 133.9, 131.0, 130.3, 128.1, 127.9, 127.4, 127.0, 125.8, 125.4, 125.3(d,  $J_{\text{C-F}} = 2.2$  Hz), 124.6, 122.3, 121.0, 120.9(q,  $J_{\text{C-F}} = 267.6$  Hz), 119.4(q,  $J_{\text{C-F}} = 15.2$  Hz), 118.6. (**Figure S92**).  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  20.18. (**Figure S93**). HRMS:  $\text{C}_{18}\text{H}_{11}\text{F}_3\text{N}_2$  for  $[\text{M}+\text{H}]^+$ : 313.0914, Found: 313.0905. Anal.calcd for:  $\text{C}_{18}\text{H}_{11}\text{F}_3\text{N}_2$ : C 69.23, H 3.55, F 18.25, N 8.97; Found: C 69.21, H

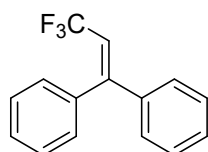
3.58, F 18.22, N 8.97 FT-IR (KBr disc):  $\nu=3731, 3611, 3600, 2960, 2381, 1734, 1700, 1556, 1540, 1521, 1420, 1210, 1120, 933, 757, 665, 628 \text{ cm}^{-1}$ .

**2-(4-hydroxyphenyl)-3-(trifluoromethyl)-2H-indazol-5-ol (highly selective ligand for the ERb)**



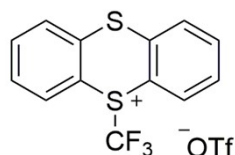
The pure product was obtained as a white solid (72.3%, 24.5mg). m.p:224.3~225.4°C  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.99 (s, 1H), 8.70 (s, 1H), 7.67 (d,  $J = 9.3$  Hz, 1H), 7.46 (d,  $J = 8.2$  Hz, 2H), 7.07 (d,  $J = 9.2$  Hz, 1H), 7.02 – 6.92 (m, 3H). (**Figure S94**).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  156.8, 153.5, 141.2, 128.9, 123.6, 120.0, 119.3(q,  $J_{\text{C-F}} = 275.6$  Hz), 118.8, 118.3(q,  $J_{\text{C-F}} = 8.7$  Hz), 116.0, 110.4, 91.5. (**Figure S95**).  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  21.14. (**Figure S96**). HRMS:  $\text{C}_{14}\text{H}_9\text{F}_3\text{N}_2\text{O}_2$  for  $[\text{M}+\text{H}]^+$ : 294.2323, Found: 294.2329. Anal.calcd for:  $\text{C}_{14}\text{H}_9\text{F}_3\text{N}_2\text{O}_2$ : C 57.15, H 3.08, F 19.37, N 9.52, O 10.88; Found: C 57.14, H 3.07, F 19.38, N 9.51, O 10.87 FT-IR (KBr disc):  $\nu=3640, 3580, 3426, 2969, 2885, 2831, 2355, 2043, 1608, 1513, 1433, 1299, 1252, 1175, 980, 925, 830, 730, 711, 610, 520 \text{ cm}^{-1}$ .

**(3,3,3-trifluoroprop-1-ene-1,1-diyl)dibenzene (3)**



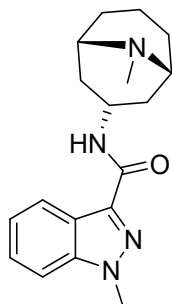
The pure product was obtained as a colourless oil (43%, 53.3mg).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.42 – 7.39 (m, 3H), 7.38 – 7.32 (m, 3H), 7.27 – 7.24 (m, 4H), 6.14 (q,  $J = 8.3$  Hz, 1H). (**Figure S97**).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  152.5(q,  $J_{\text{C-F}} = 7.3$  Hz), 140.3, 137.3, 129.4, 129.1, 129.1, 128.4, 128.0, 128.0, 123.1(q,  $J_{\text{C-F}} = 271.1$  Hz), 115.4(q,  $J_{\text{C-F}} = 33.5$  Hz). (**Figure S98**).  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  20.63. (**Figure S99**). HRMS:  $\text{C}_{15}\text{H}_{11}\text{F}_3$  for  $[\text{M}+\text{H}]^+$ : 248.0813, Found: 248.0814. Anal.calcd for:  $\text{C}_{15}\text{H}_{11}\text{F}_3$ : C 72.57, H 4.47, F 22.96; Found: C 72.56, H 4.46, F 22.95

**Trifluoromethyl Thianthrenium Triflate (TT- $\text{CF}_3^+\text{OTf}^-$ )**



The pure product was obtained as a yellow solid (63%, 21.1g). m.p:142.1~143.5°C  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.52 (d,  $J = 8.1$  Hz, 2H), 7.95 (t,  $J = 7.7$  Hz, 2H), 7.87 (d,  $J = 7.9$  Hz, 2H), 7.76 (t,  $J = 7.7$  Hz, 2H). (**Figure S100**).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  136.9, 136.7, 136.6, 130.3, 129.4, 124.4(q,  $J_{\text{C-F}} = 280.6$  Hz), 120.7(q,  $J_{\text{C-F}} = 252.1$  Hz), 108.8. (**Figure S101**).  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  24.92, -2.32. (**Figure S102**). HRMS:  $\text{C}_{14}\text{H}_8\text{F}_6\text{O}_3\text{S}_3$  for  $[\text{M}+\text{H}]^+$ : 285.0010, Found: 285.0011. Anal.calcd for:  $\text{C}_{14}\text{H}_8\text{F}_6\text{O}_3\text{S}_3$ : C 38.71, H 1.86, F 26.24, O 11.05, S 22.14; Found: C 62.08, H 4.33, F 16.35, N 8.05, O 9.18

**1-Methyl-N-((1R,3r,5S)-9-methyl-9-azabicyclo[3.3.1]nonan-3-yl)-1H-indazole-3-carboxamide (Granisetron)**



The pure product was obtained as a yellow solid. (39%, 21.1mg) m.p.:290.3~292.5°C  
 $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.39 (dt,  $J = 8.2, 1.0$  Hz, 1H), 7.45-7.36 (m, 2H), 6.78 (d,  $J = 8.4$  Hz, 1H), 4.55 (tdt,  $J = 11.3, 8.3, 6.7$  Hz, 1H), 4.07 (s, 3H), 3.18-3.02 (m, 2H), 2.56-2.51 (m, 2H), 2.50 (s, 3H), 2.06-1.88 (m, 3H), 1.60-1.48 (m, 2H), 1.40 (ddd,  $J = 14.2, 11.3, 3.2$  Hz, 2H), 1.15-1.01 (m, 2H). **(Figure S103)**.  $^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  162.0, 141.4, 137.8, 126.9, 123.2, 123.0, 122.6, 109.1, 51.4, 40.8, 40.8, 36.1, 33.1, 25.0, 14.5. **(Figure S104)**. HRMS:  $\text{C}_{18}\text{H}_{24}\text{N}_4\text{O}$  for  $[\text{M}+\text{H}]^+$ : 313.2023, Found: 313.2021. Anal.calcd for:  $\text{C}_{18}\text{H}_{24}\text{N}_4\text{O}$ : C 69.20, H 7.74, N 17.93, O 5.12; Found: C 69.23, H 7.71, N 17.95, O 5.11

**5. NMR spectra for target compounds.**

7.84  
7.81  
7.59  
7.57  
7.55  
7.54  
7.43  
7.41  
7.39  
7.31  
7.29  
7.28  
7.25

$^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.83 (d,  $J=9.0$  Hz, 2H),  
7.61 – 7.52 (m, 5H), 7.44 – 7.38 (m, 1H), 7.33 – 7.27 (m, 1H).

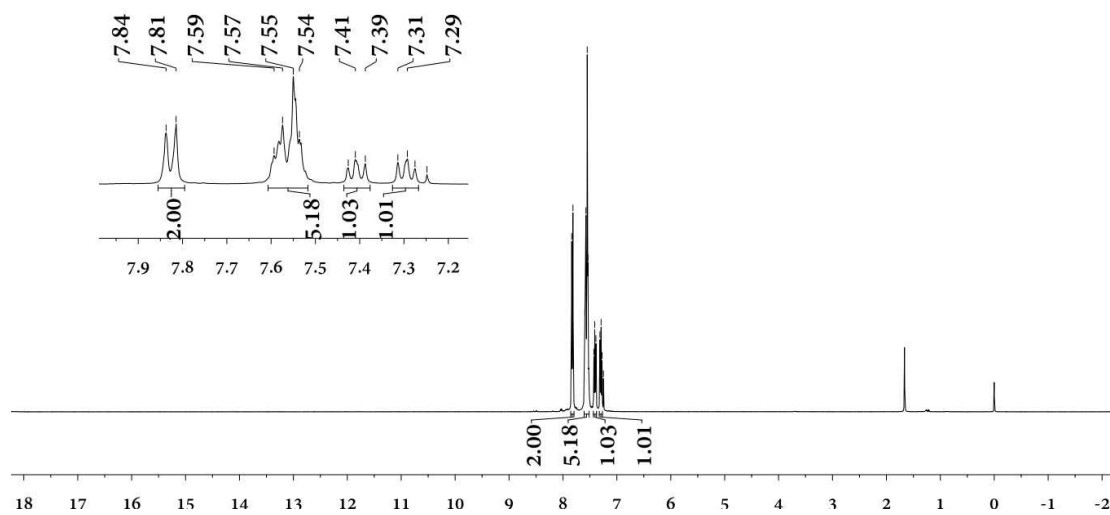
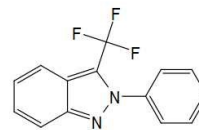


Figure S1.  $^1\text{H NMR}$  of 2-phenyl-3-(trifluoromethyl)-2H-indazole (**2a**)

148.2  
139.6  
130.0  
129.1  
127.3  
126.1  
125.1  
123.9  
123.5  
122.3  
121.6  
119.6  
119.5  
119.4  
119.4  
119.3  
118.4

$^{13}\text{C NMR}$  (100 MHz, Chloroform-*d*)  $\delta$  148.2, 139.6, 130.0, 129.1,  
127.3, 126.1, 125.1, 123.7(q,  $J_{\text{C-F}} = 39.1$  Hz), 121.6, 121.0(q,  
 $J_{\text{C-F}} = 267.4$  Hz), 119.4(q,  $J_{\text{C-F}} = 14.5$  Hz), 118.4.

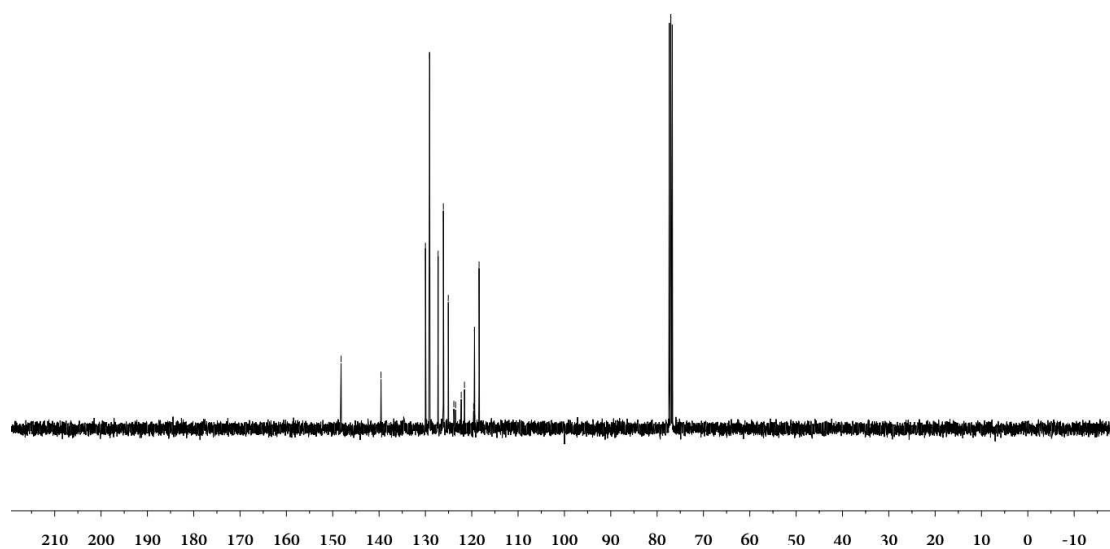


Figure S2.  $^{13}\text{C NMR}$  of 2-phenyl-3-(trifluoromethyl)-2H-indazole (**2a**)



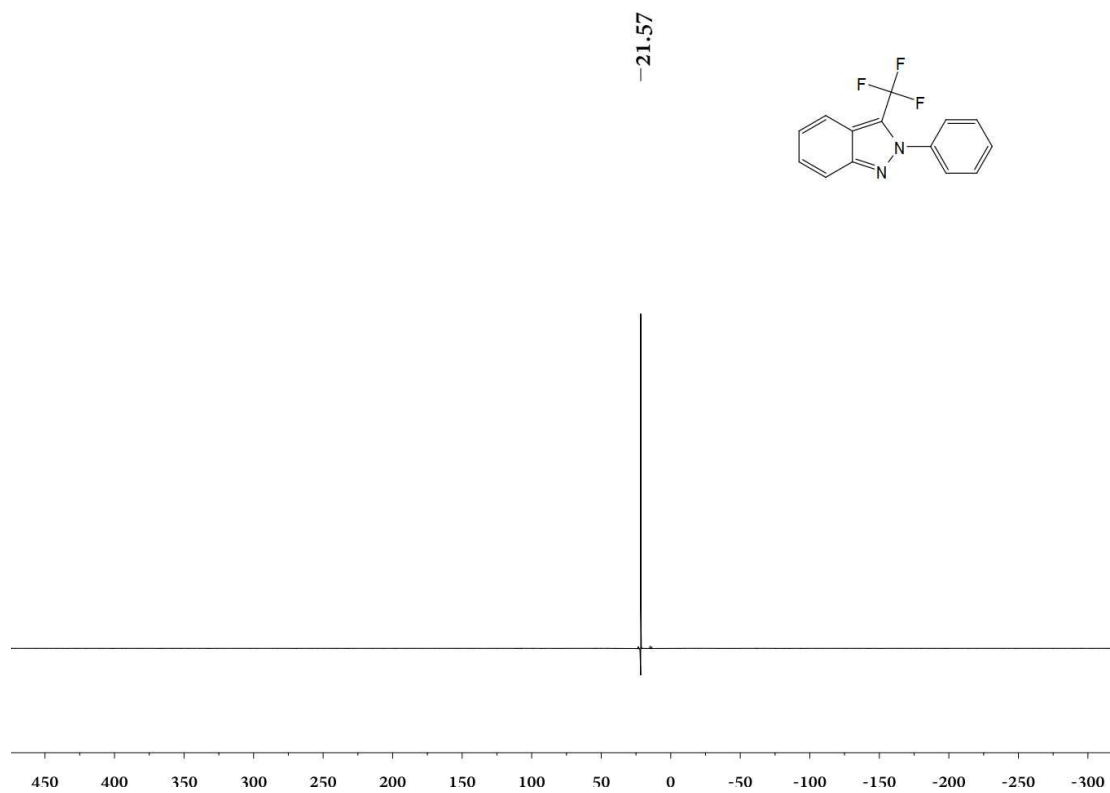


Figure S3.  $^{19}\text{F}$  NMR of 2-phenyl-3-(trifluoromethyl)-2H-indazole (**2a**)

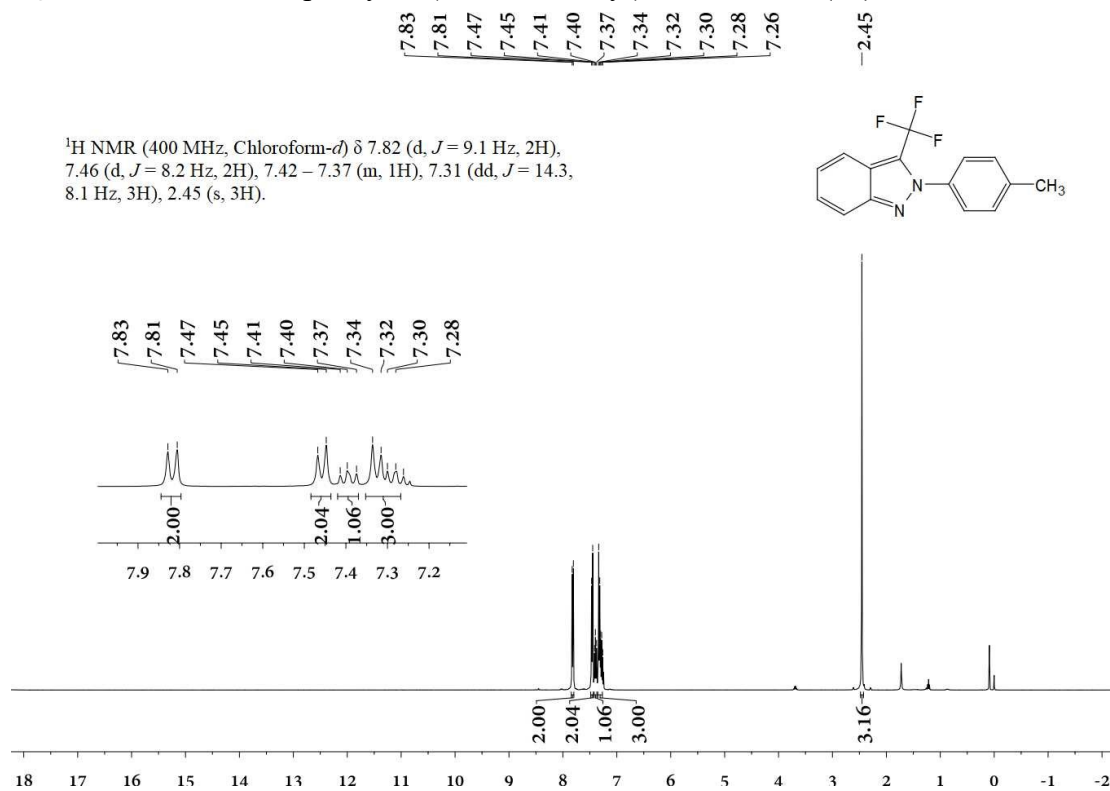


Figure S4.  $^1\text{H}$  NMR of 2-(p-tolyl)-3-(trifluoromethyl)-2H-indazole (**2b**)

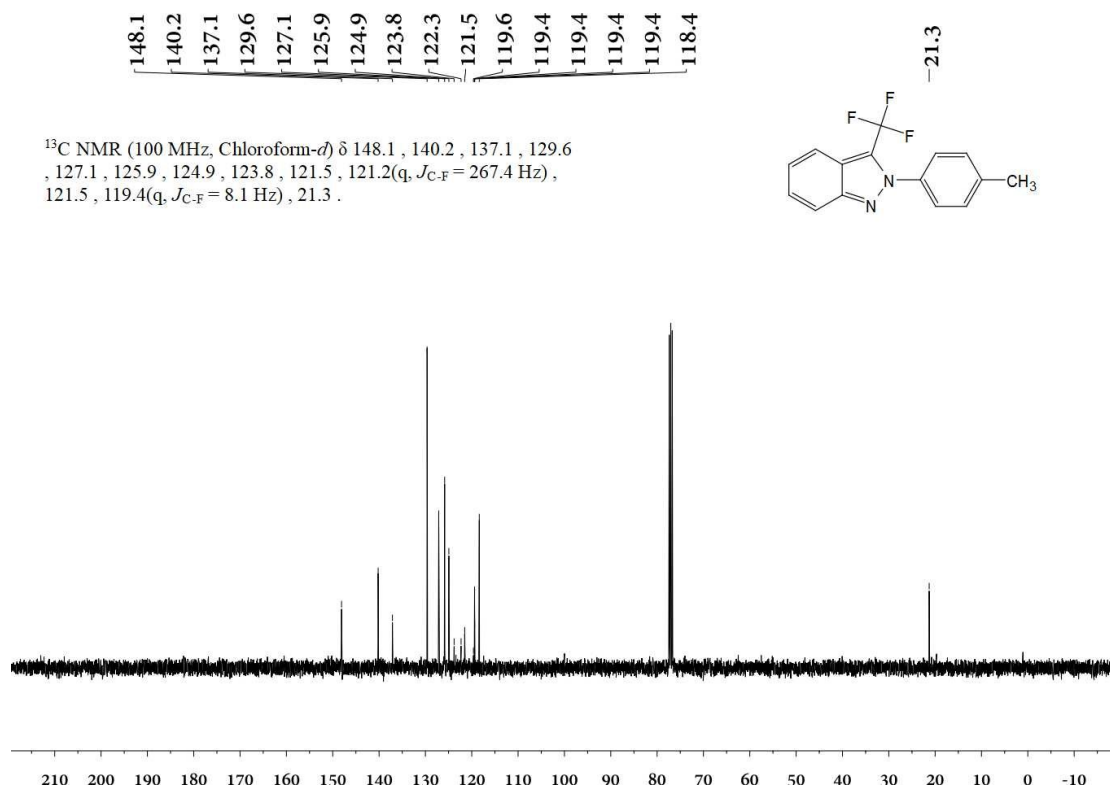


Figure S5.  $^{13}\text{C}$  NMR of 2-(p-tolyl)-3-(trifluoromethyl)-2H-indazole (**2b**)

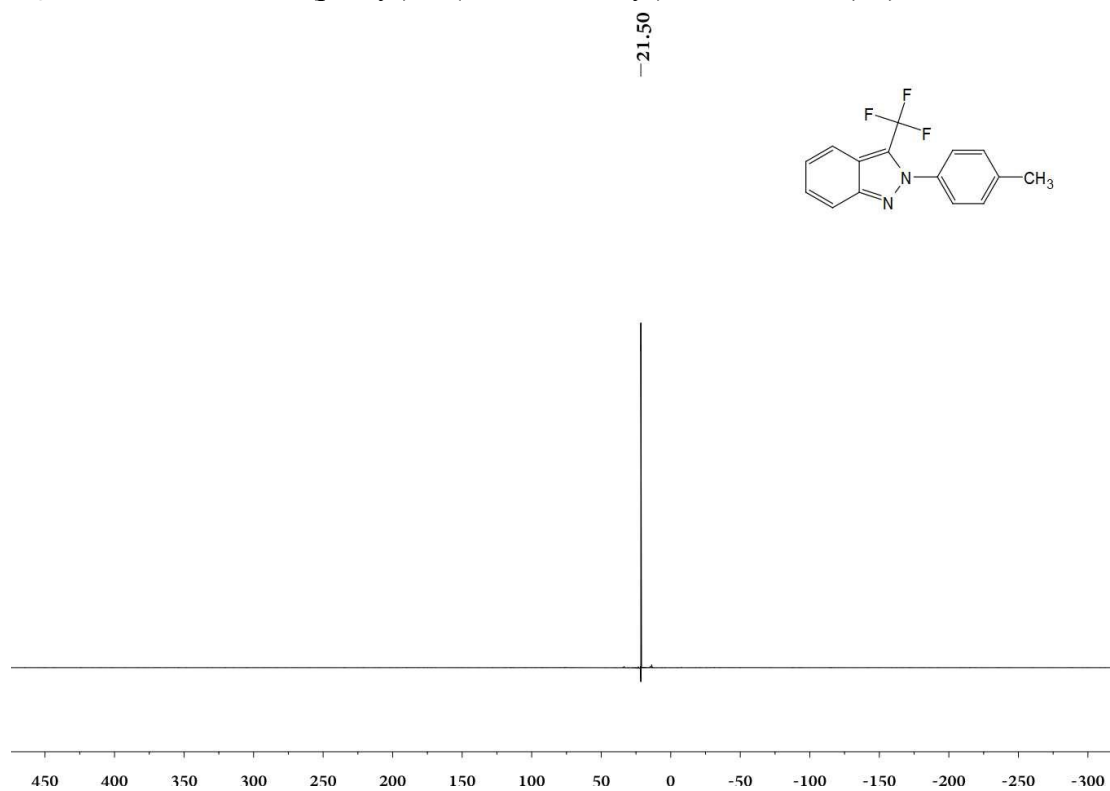


Figure S6.  $^{19}\text{F}$  NMR of 2-(p-tolyl)-3-(trifluoromethyl)-2H-indazole (**2b**)

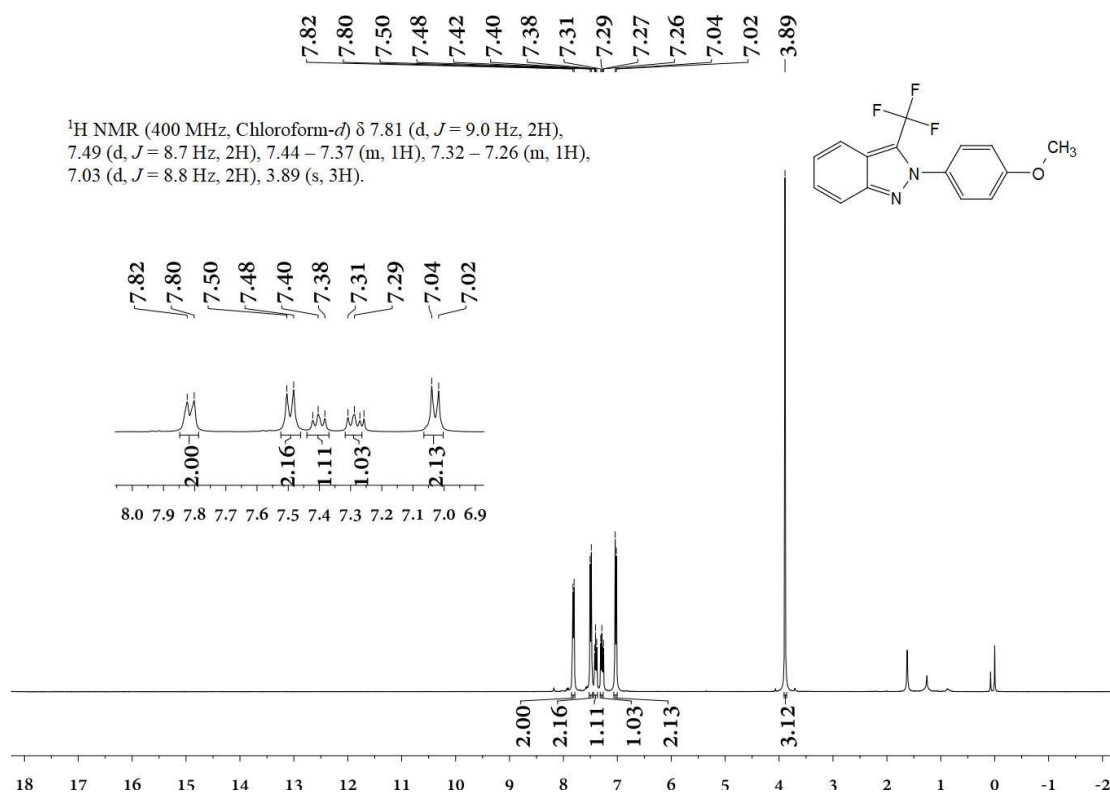


Figure S7. <sup>1</sup>H NMR of 2-(4-methoxyphenyl)-3-(trifluoromethyl)-2H-indazole (**2c**)

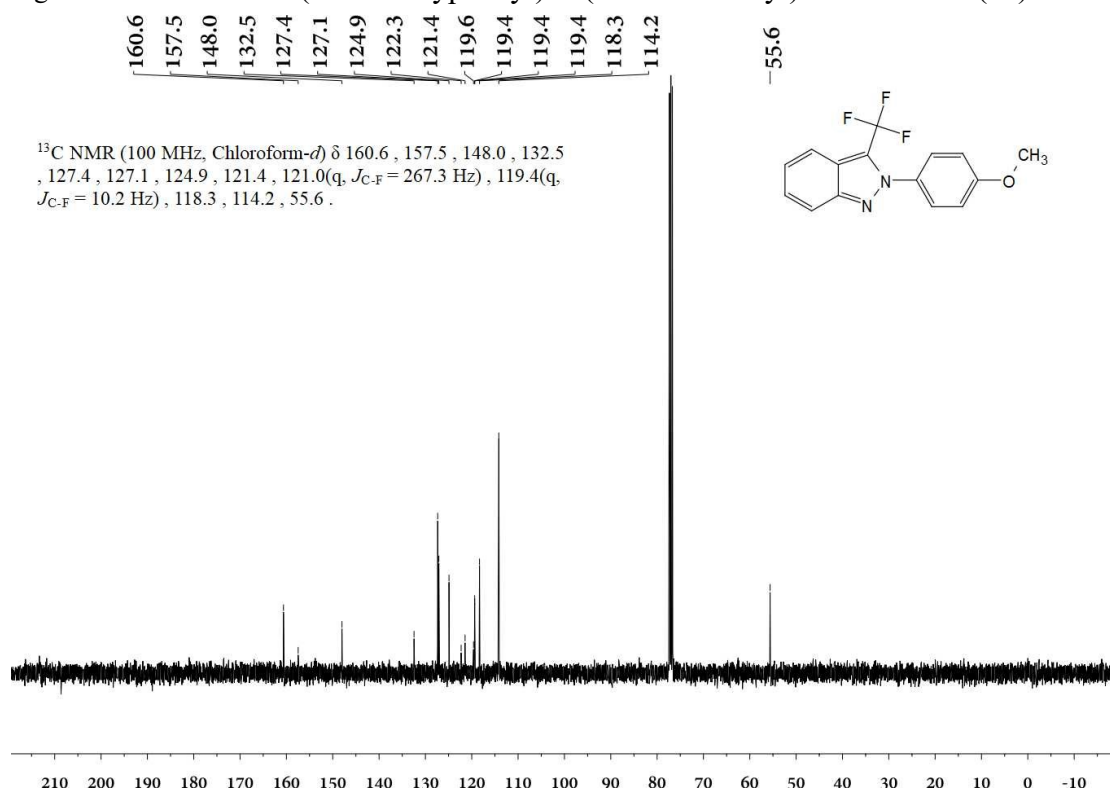


Figure S8. <sup>13</sup>C NMR of 2-(4-methoxyphenyl)-3-(trifluoromethyl)-2H-indazole (**2c**)

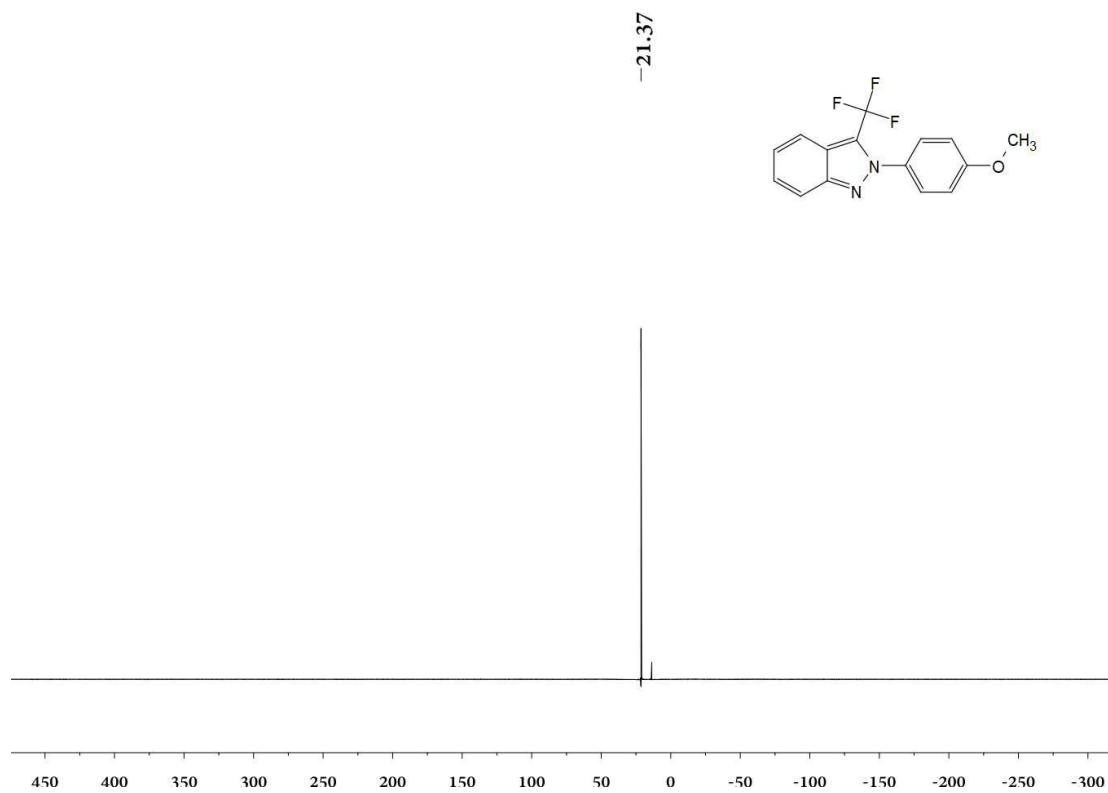
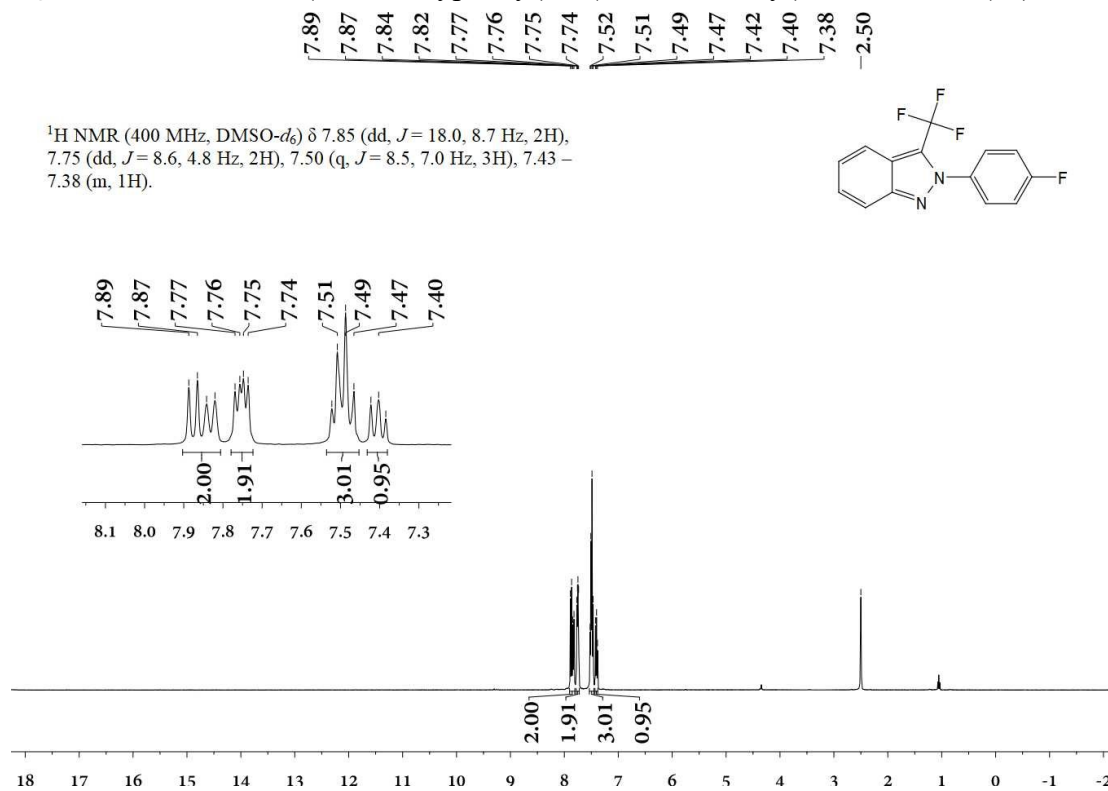


Figure S9.  $^{19}\text{F}$  NMR of 2-(4-methoxyphenyl)-3-(trifluoromethyl)-2H-indazole (**2c**)



$^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  7.85 (dd,  $J = 18.0, 8.7$  Hz, 2H), 7.75 (dd,  $J = 8.6, 4.8$  Hz, 2H), 7.50 (q,  $J = 8.5, 7.0$  Hz, 3H), 7.43 – 7.38 (m, 1H).

Figure S10.  $^1\text{H}$  NMR of 2-(4-fluorophenyl)-3-(trifluoromethyl)-2H-indazole (**2d**)

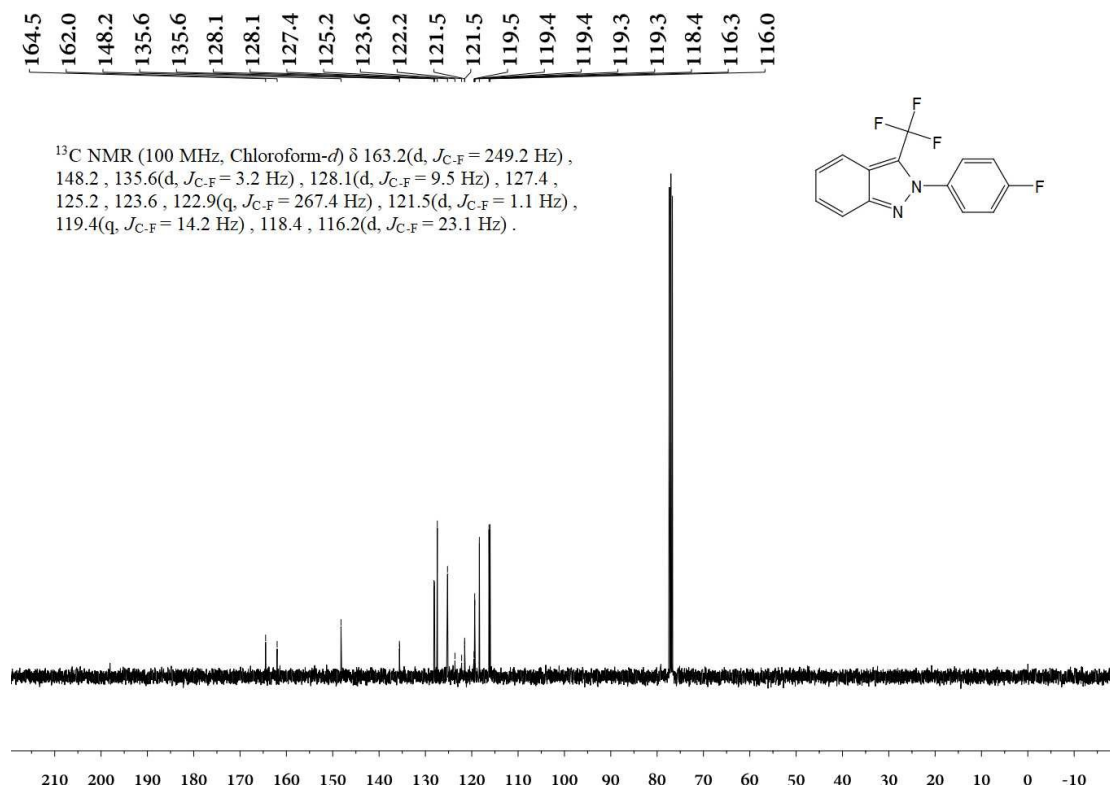


Figure S11. <sup>13</sup>C NMR of 2-(4-fluorophenyl)-3-(trifluoromethyl)-2H-indazole (**2d**)

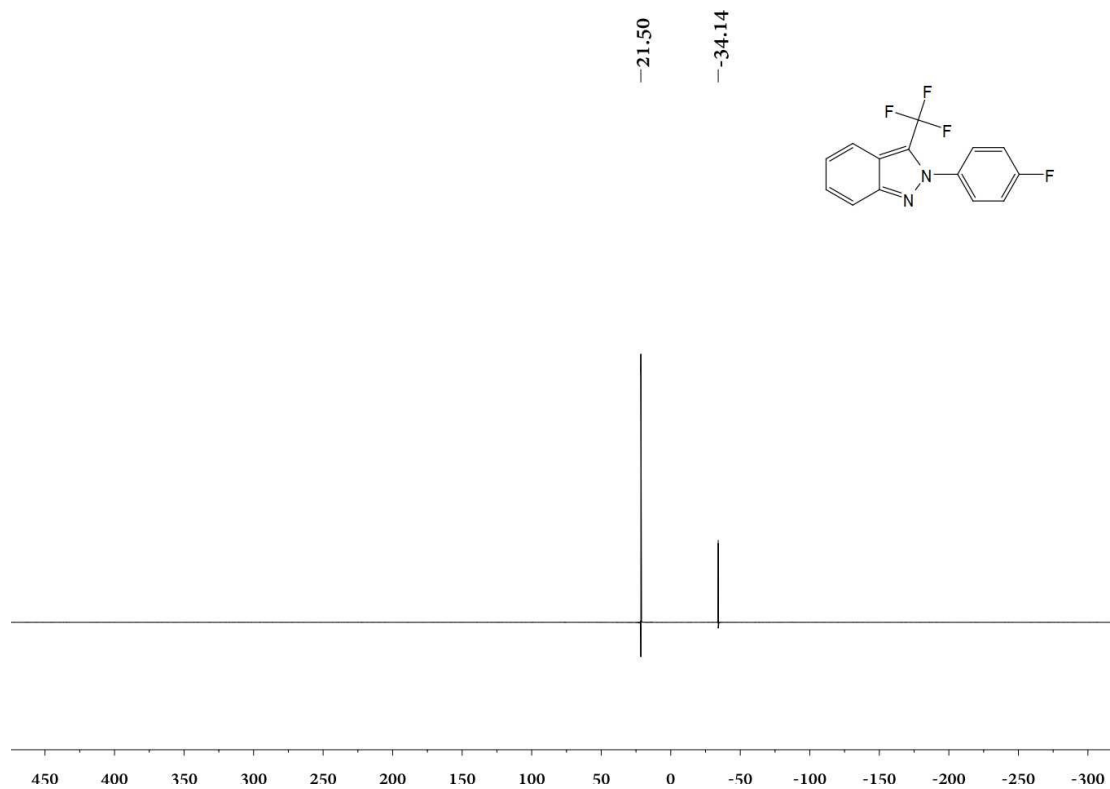


Figure S12. <sup>19</sup>F NMR of 2-(4-fluorophenyl)-3-(trifluoromethyl)-2H-indazole (**2d**)

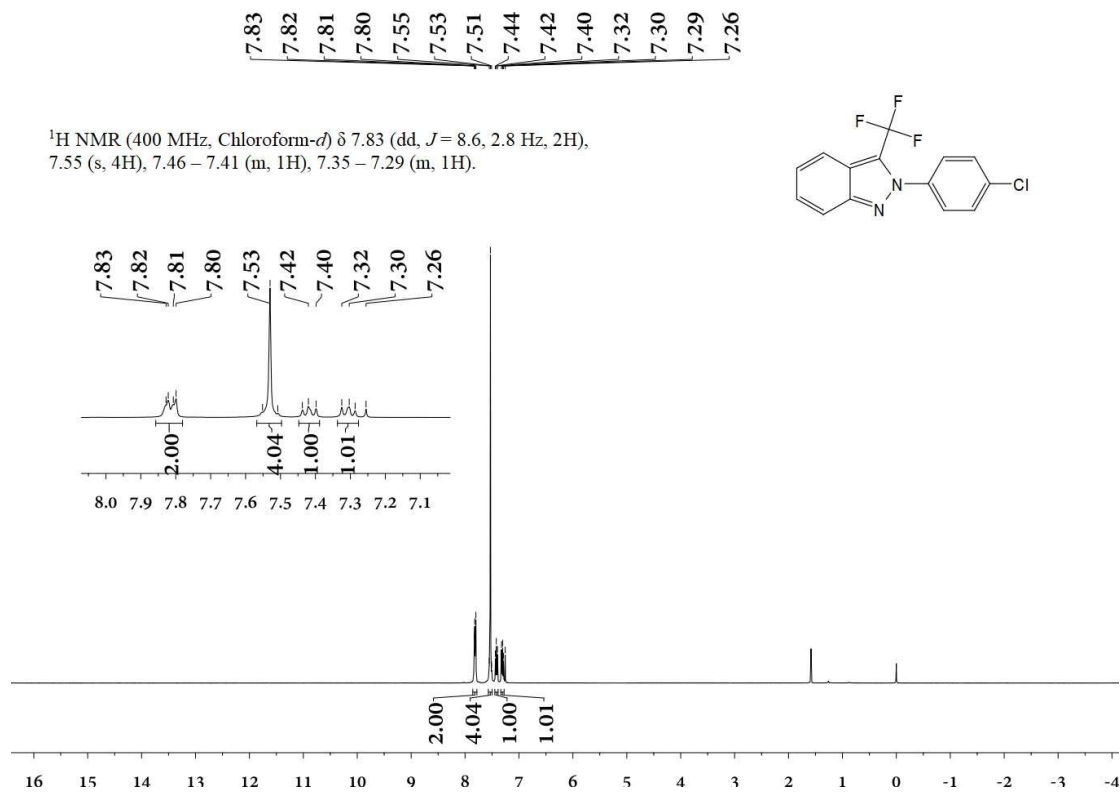


Figure S13. <sup>1</sup>H NMR of 2-(4-chlorophenyl)-3-(trifluoromethyl)-2H-indazole (**2e**)

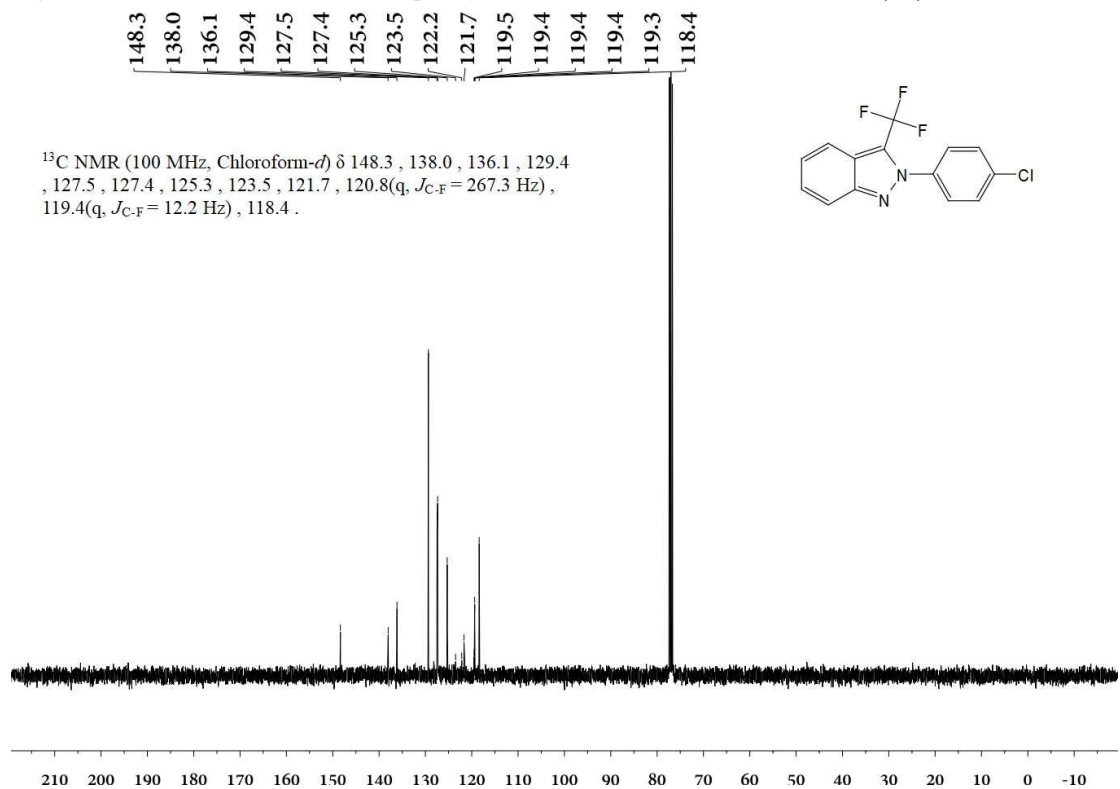


Figure S14. <sup>13</sup>C NMR of 2-(4-chlorophenyl)-3-(trifluoromethyl)-2H-indazole (**2e**)

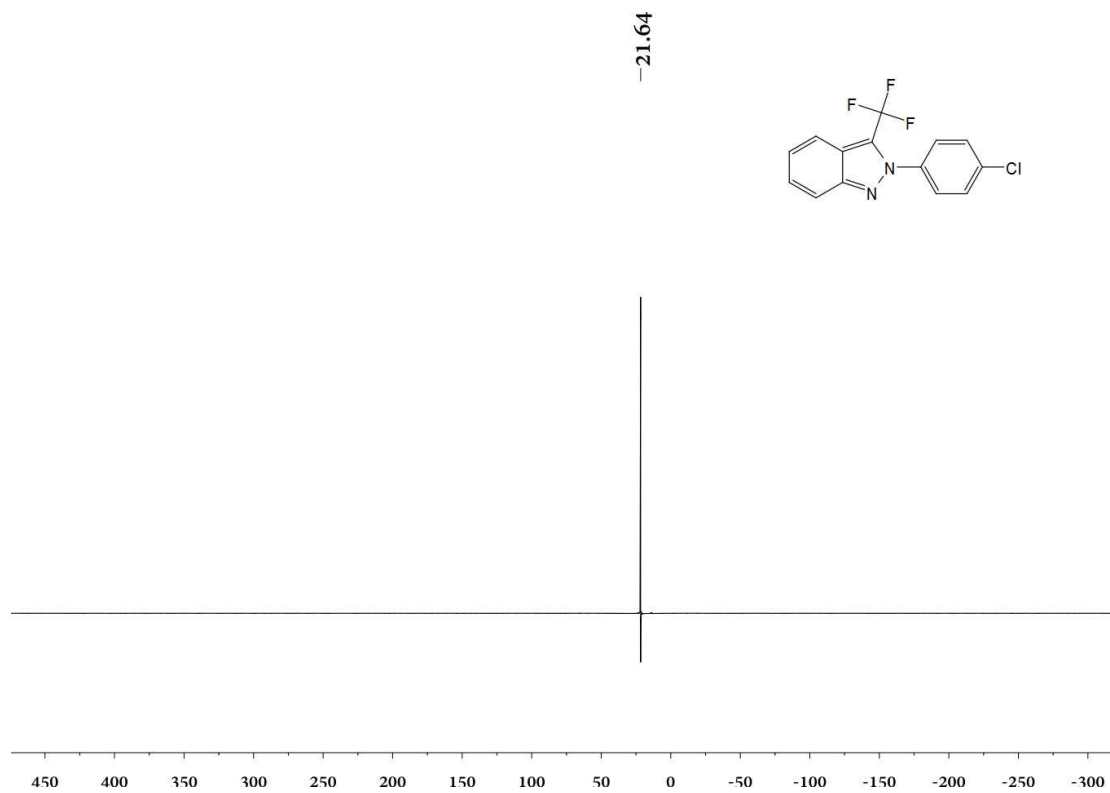


Figure S15.  $^{19}\text{F}$  NMR of 2-(4-chlorophenyl)-3-(trifluoromethyl)-2H-indazole (**2e**)

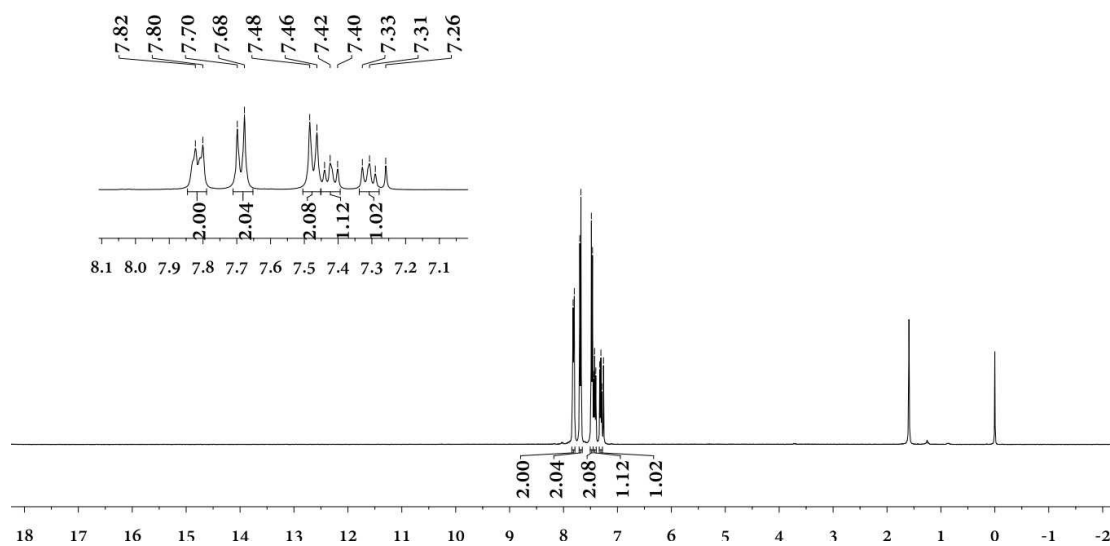
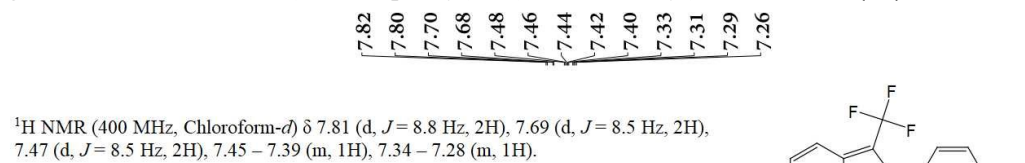


Figure S16.  $^1\text{H}$  NMR of 2-(4-bromophenyl)-3-(trifluoromethyl)-2H-indazole (**2f**)

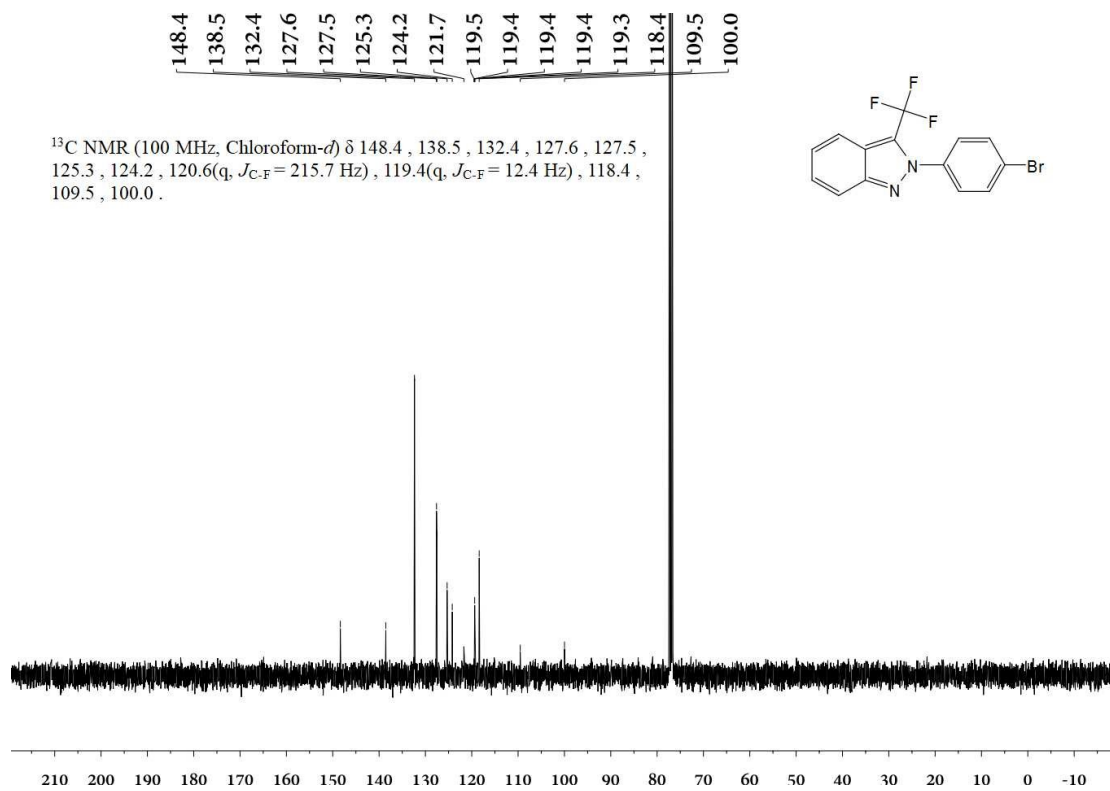


Figure S17. <sup>13</sup>C NMR of 2-(4-bromophenyl)-3-(trifluoromethyl)-2H-indazole (**2f**)

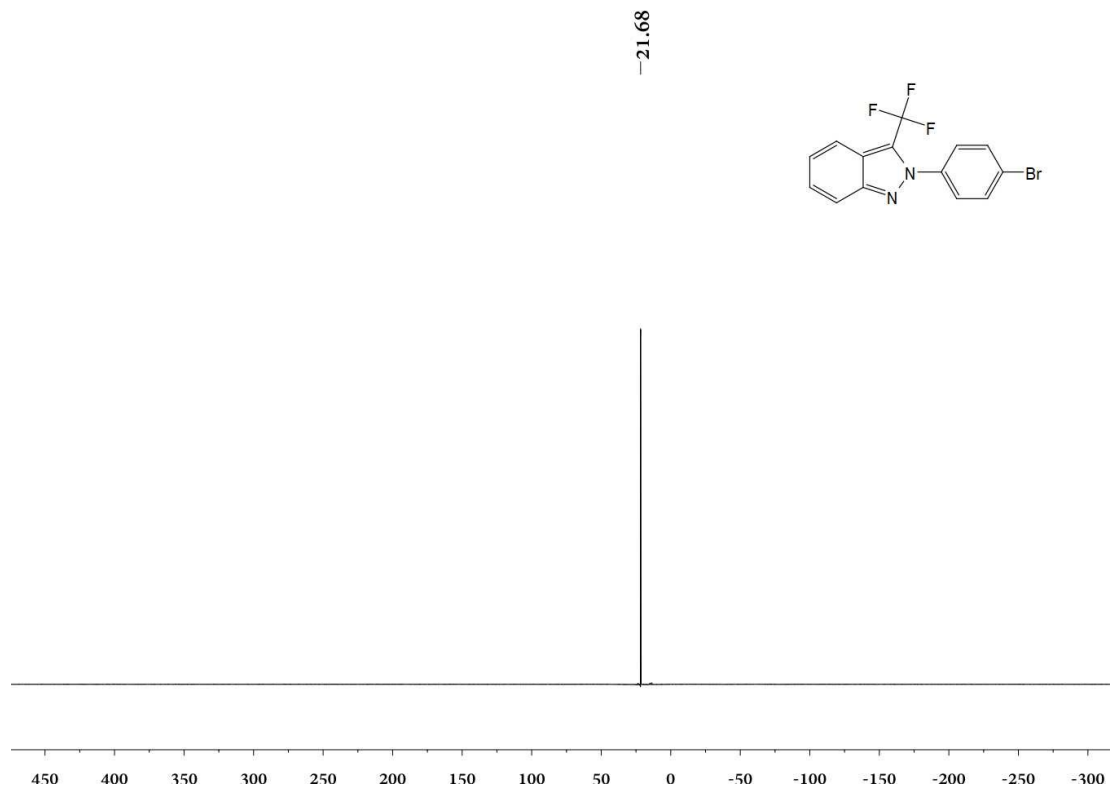


Figure S18. <sup>19</sup>F NMR of 2-(4-bromophenyl)-3-(trifluoromethyl)-2H-indazole (**2f**)



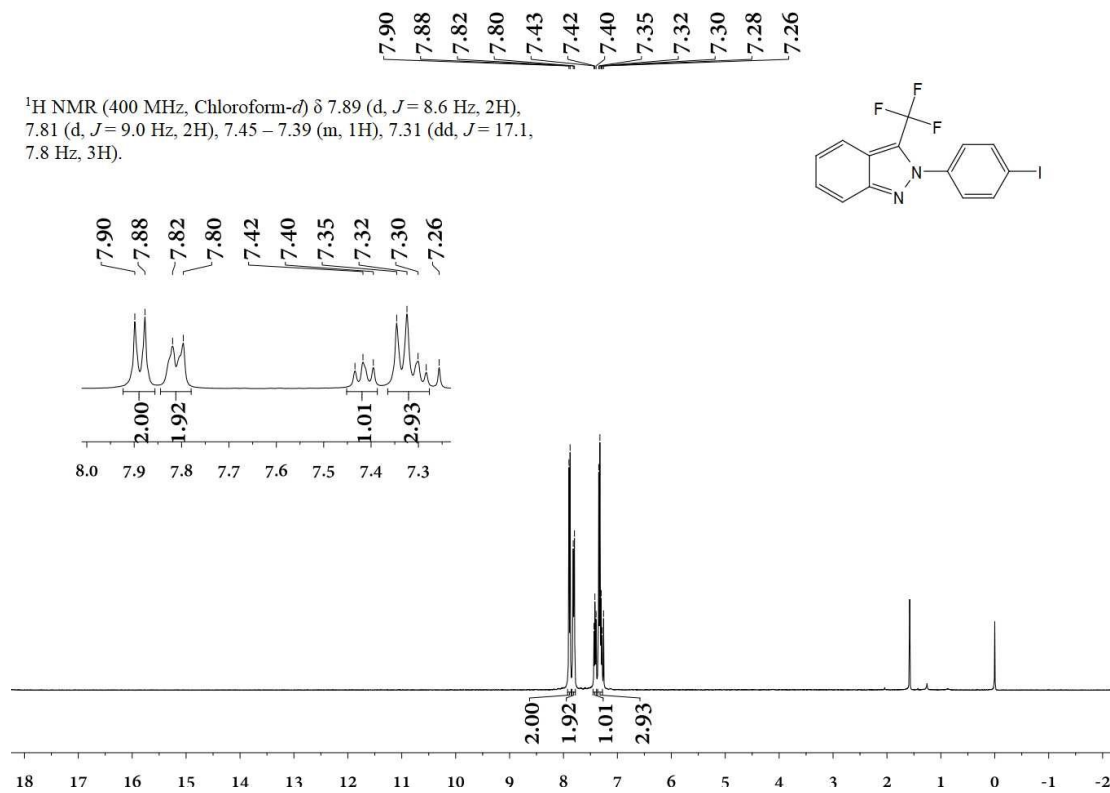


Figure S19. <sup>1</sup>H NMR of 1-(pyridin-2-yl)-2-naphthonitrile (**2g**)

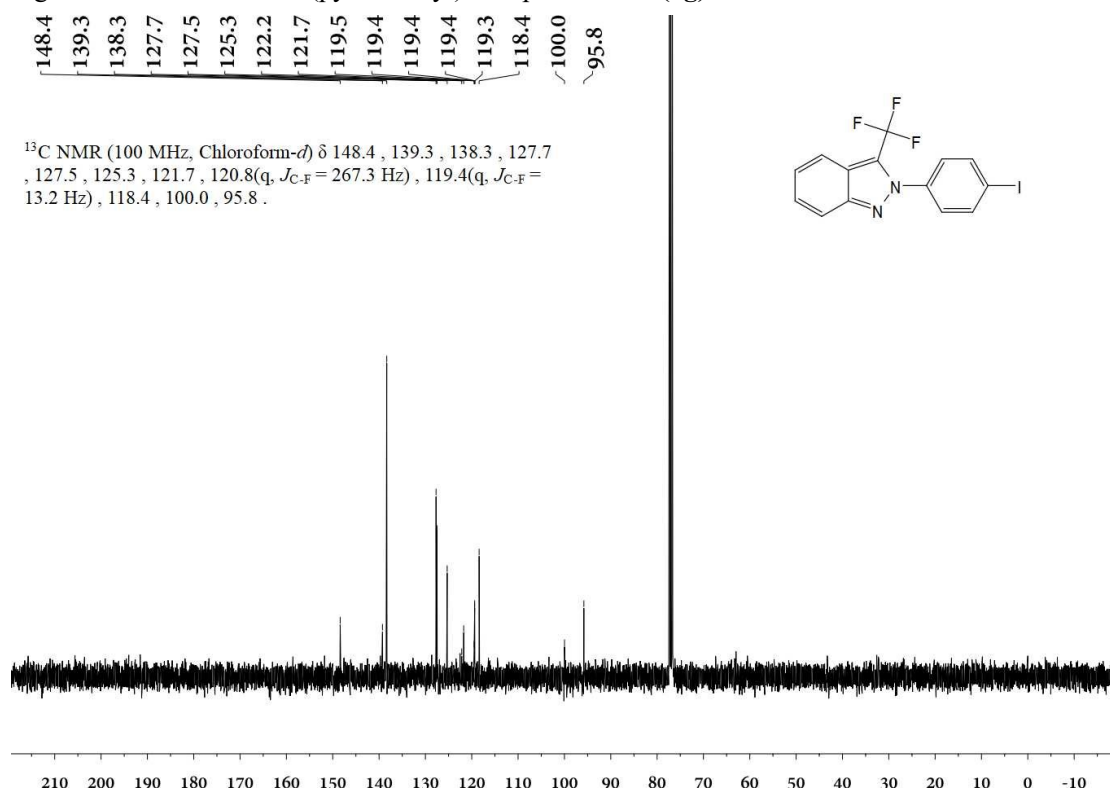


Figure S20. <sup>13</sup>C NMR of 1-(pyridin-2-yl)-2-naphthonitrile (**2g**)

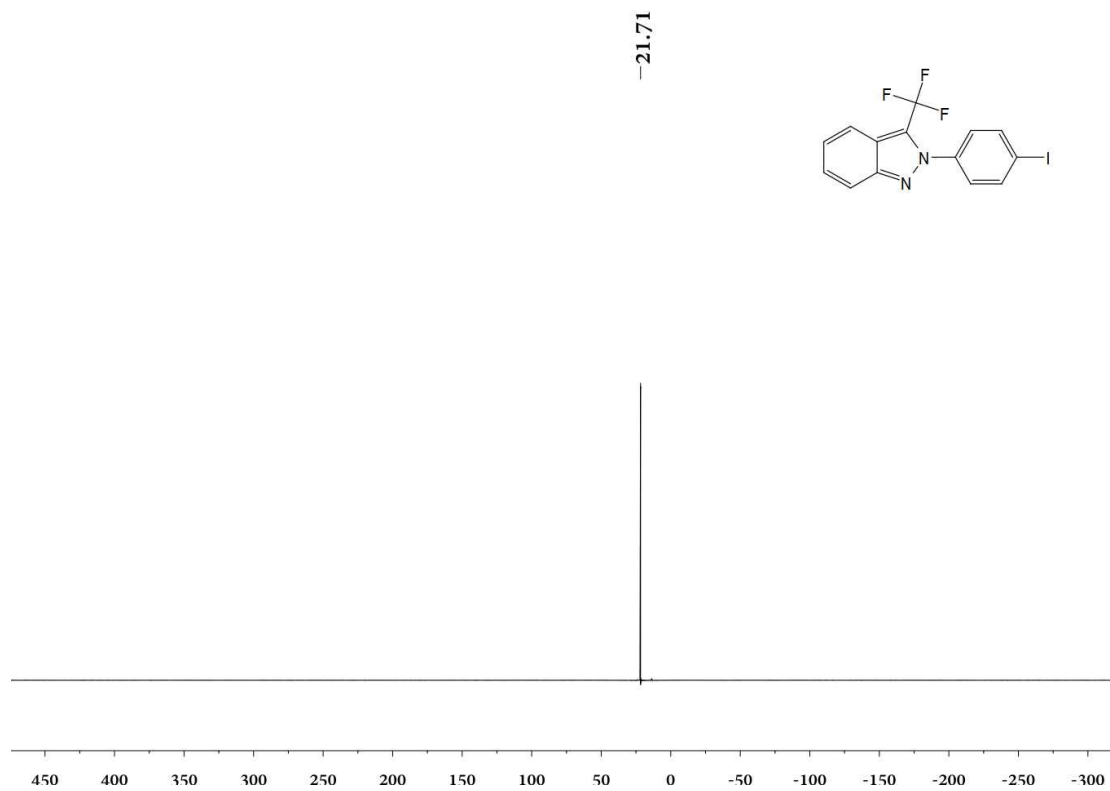


Figure S21.  $^{19}\text{F}$  NMR of 1-(pyridin-2-yl)-2-naphthonitrile (**2g**)

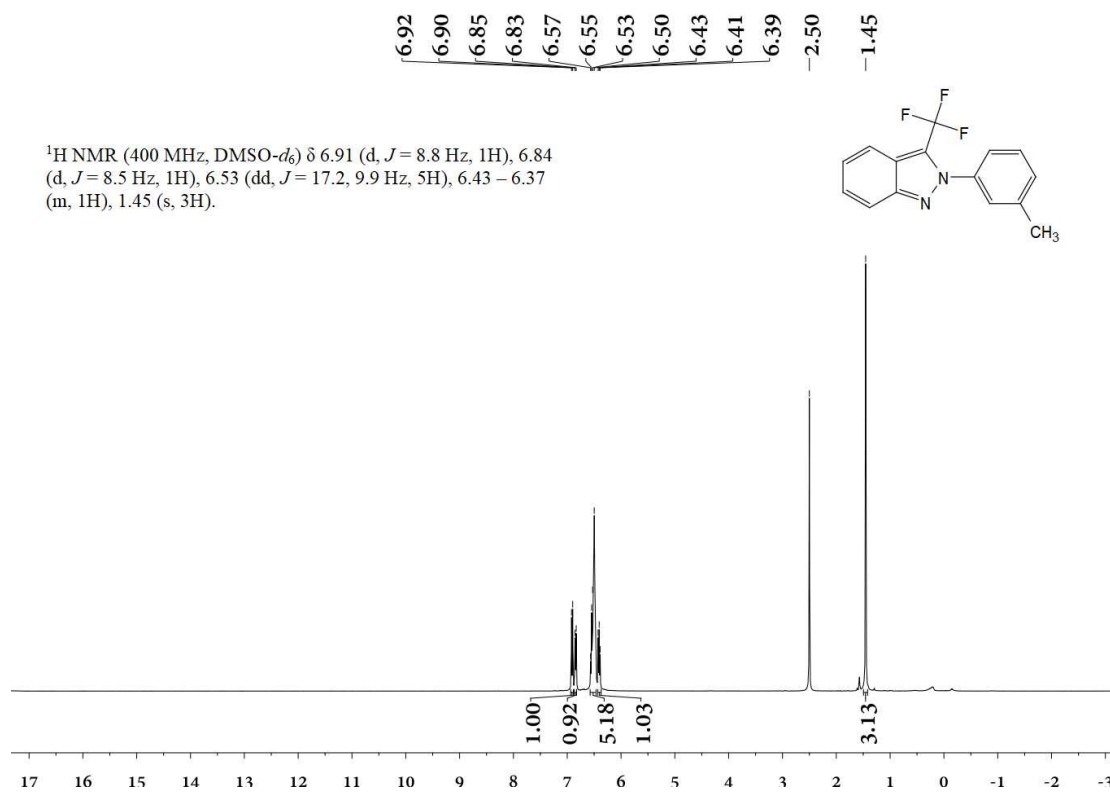


Figure S22.  $^1\text{H}$  NMR of 2-(m-tolyl)-3-(trifluoromethyl)-2H-indazole (**2h**)

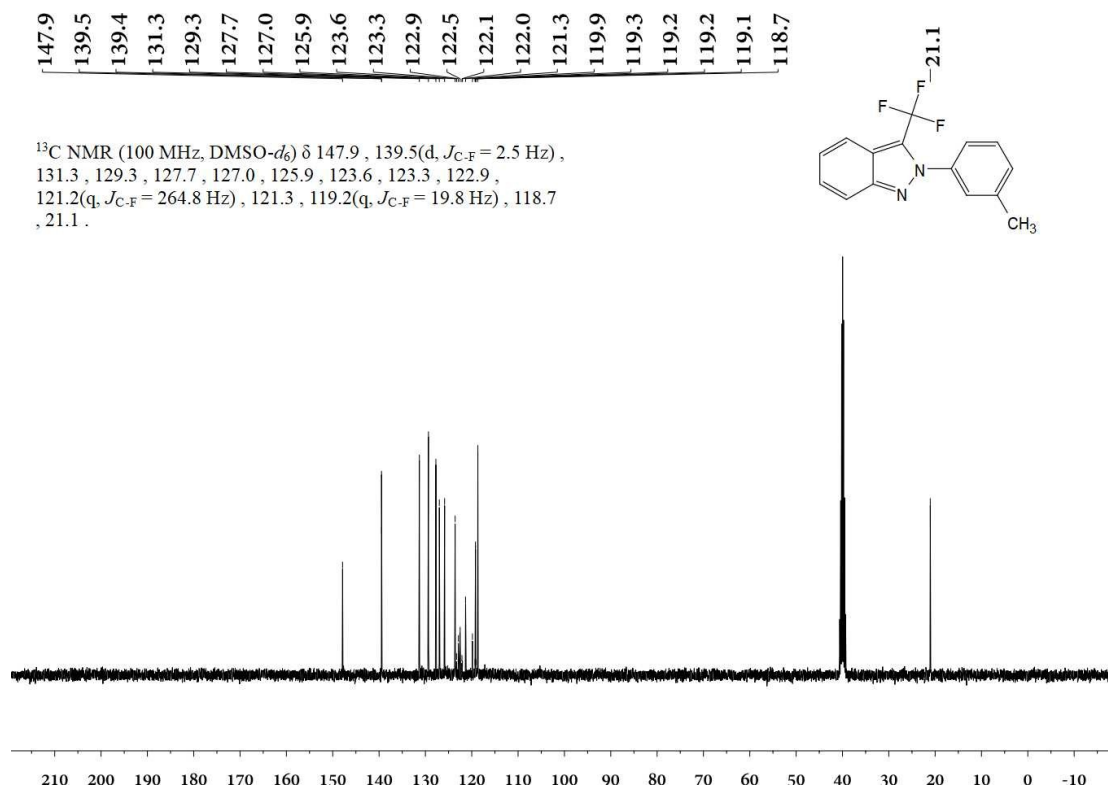


Figure S23. <sup>13</sup>C NMR of 2-(m-tolyl)-3-(trifluoromethyl)-2H-indazole (**2h**)



Figure S24. <sup>19</sup>F NMR of 2-(m-tolyl)-3-(trifluoromethyl)-2H-indazole (**2h**)

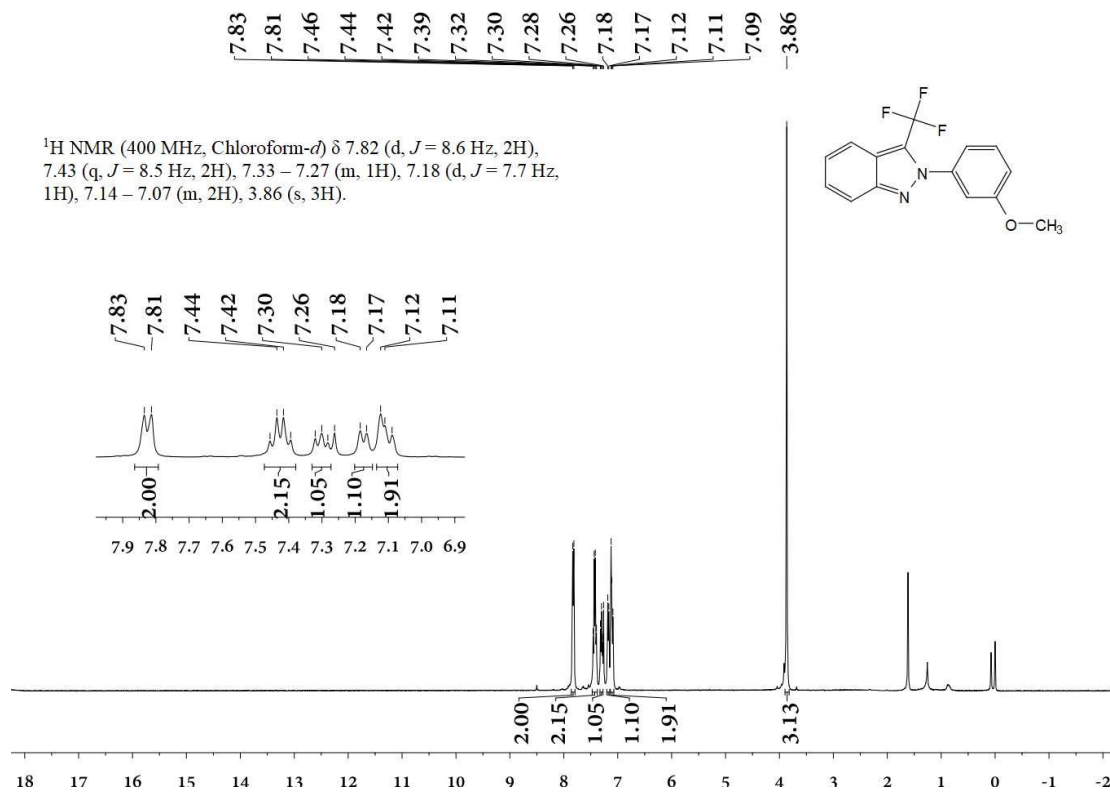


Figure S25. <sup>1</sup>H NMR of 2-(3-methoxyphenyl)-3-(trifluoromethyl)-2H-indazole (**2i**)

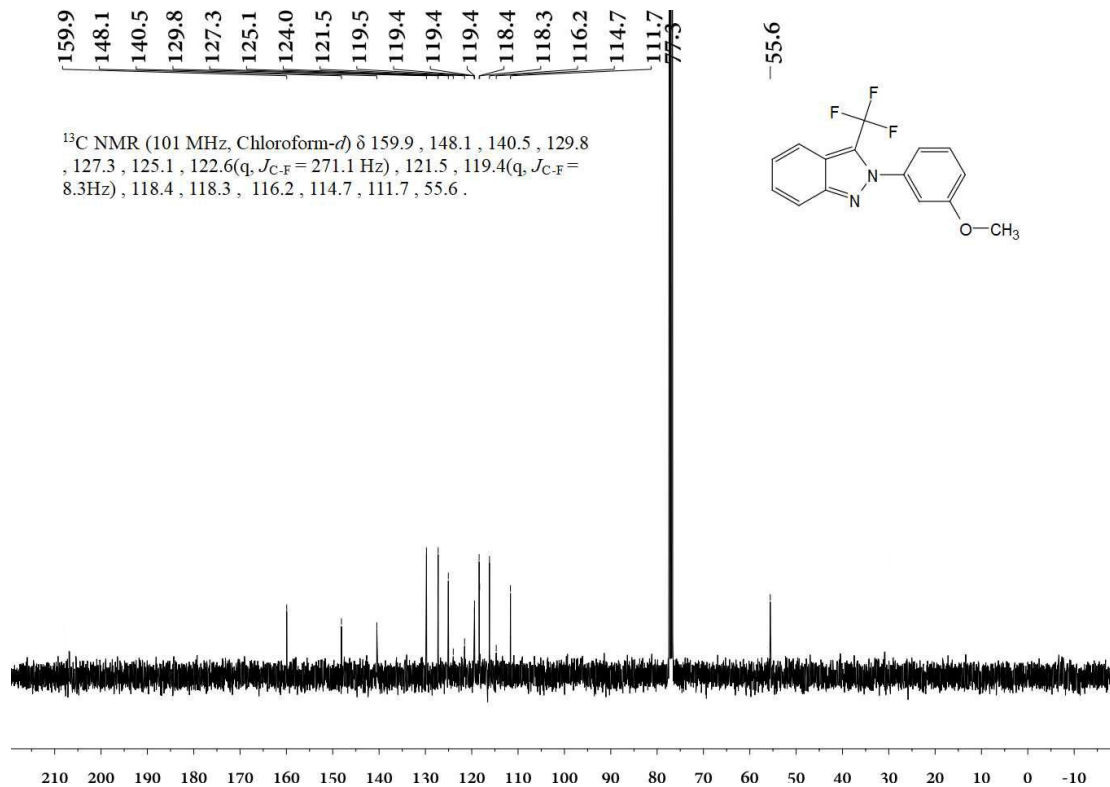


Figure S26. <sup>13</sup>C NMR of 2-(3-methoxyphenyl)-3-(trifluoromethyl)-2H-indazole (**2i**)

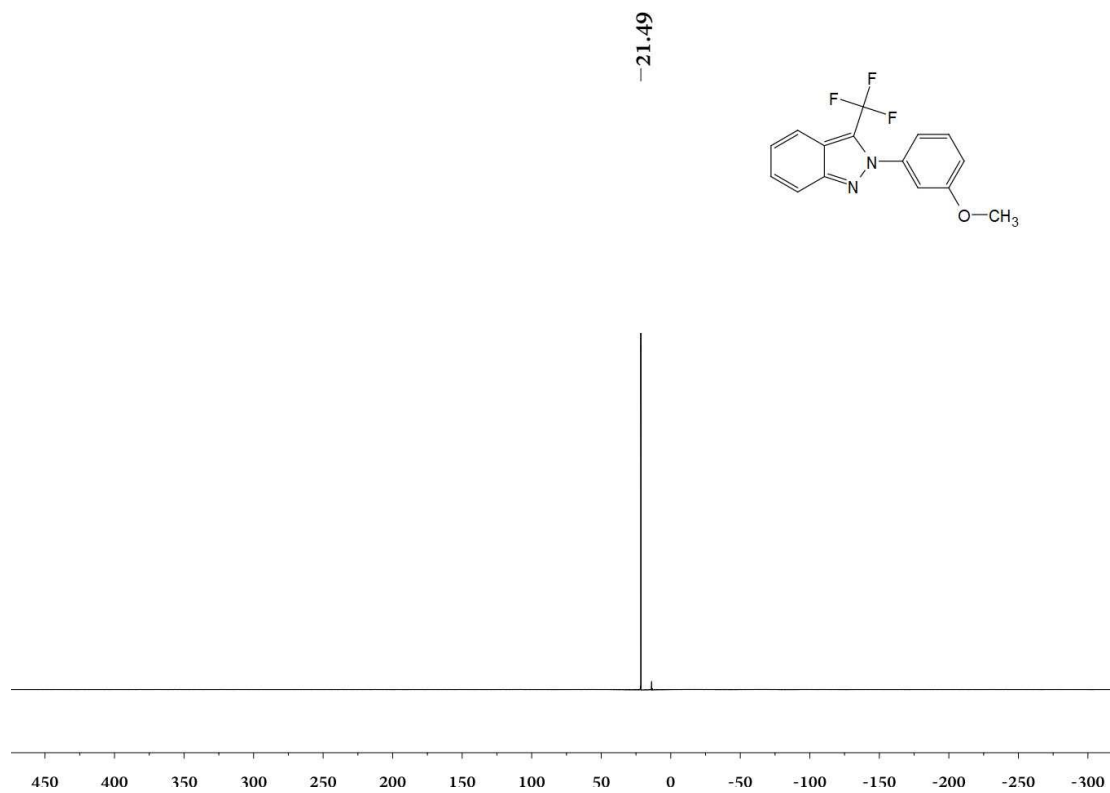


Figure S27.  $^{19}\text{F}$  NMR of 2-(3-methoxyphenyl)-3-(trifluoromethyl)-2H-indazole (**2i**)

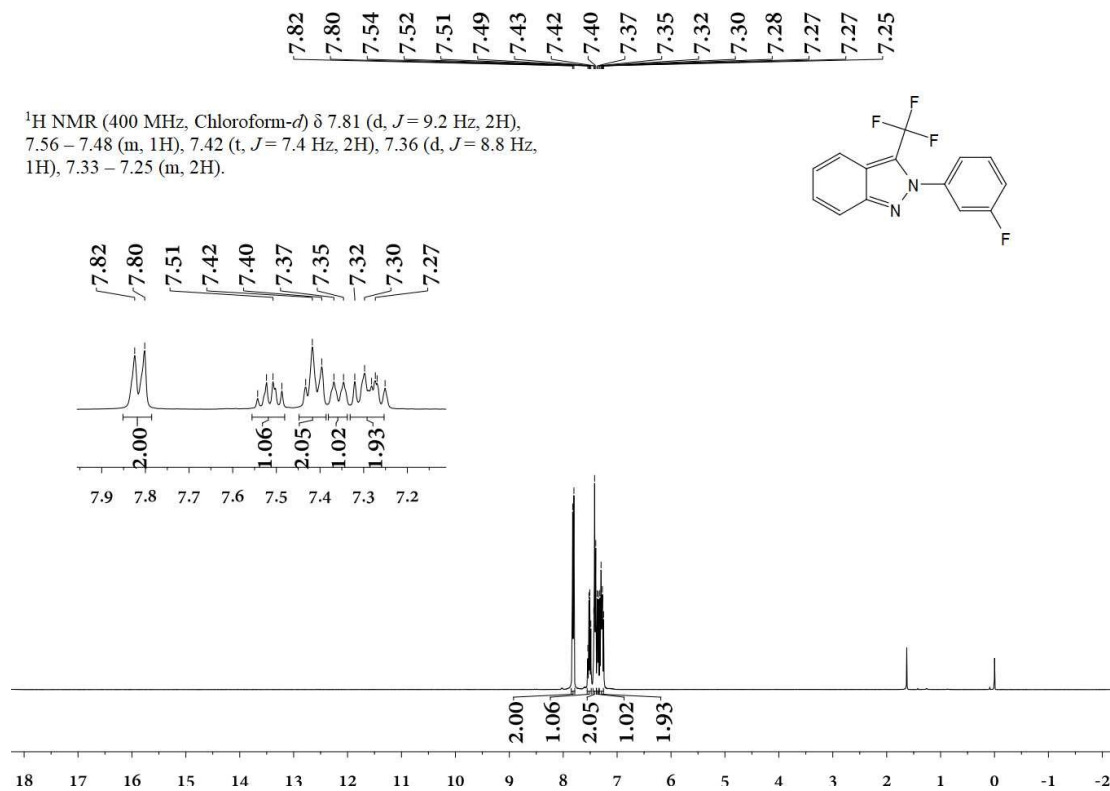
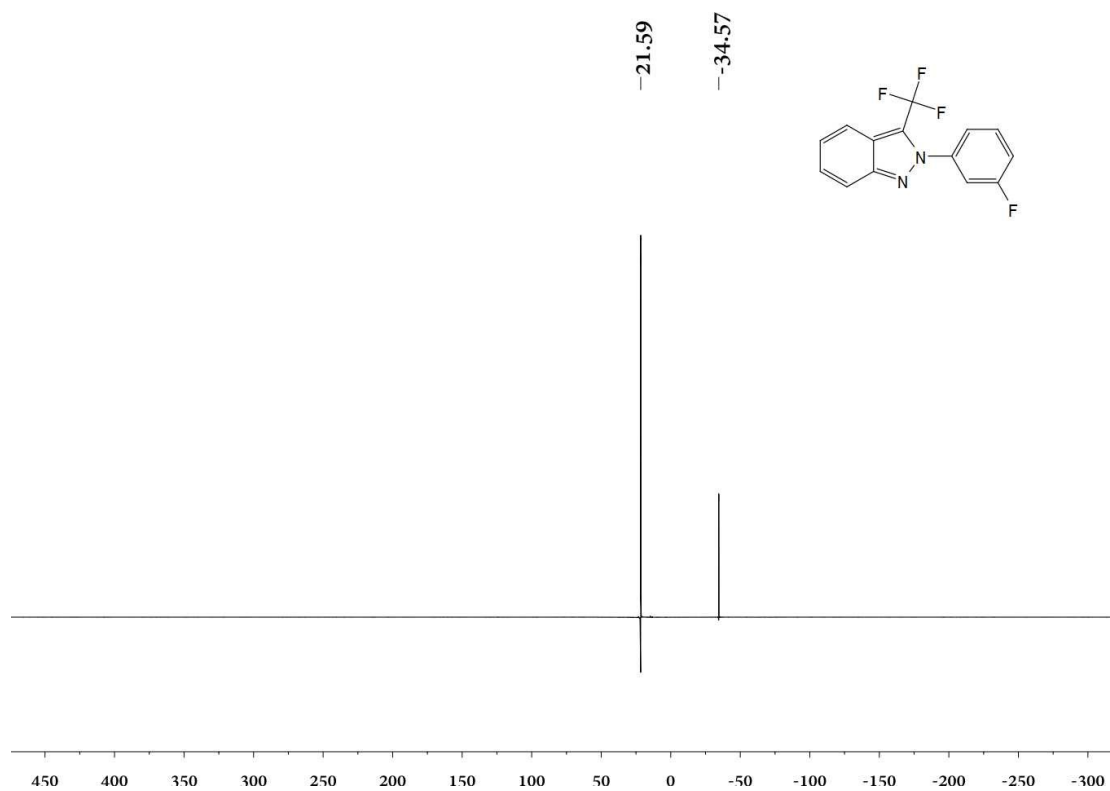
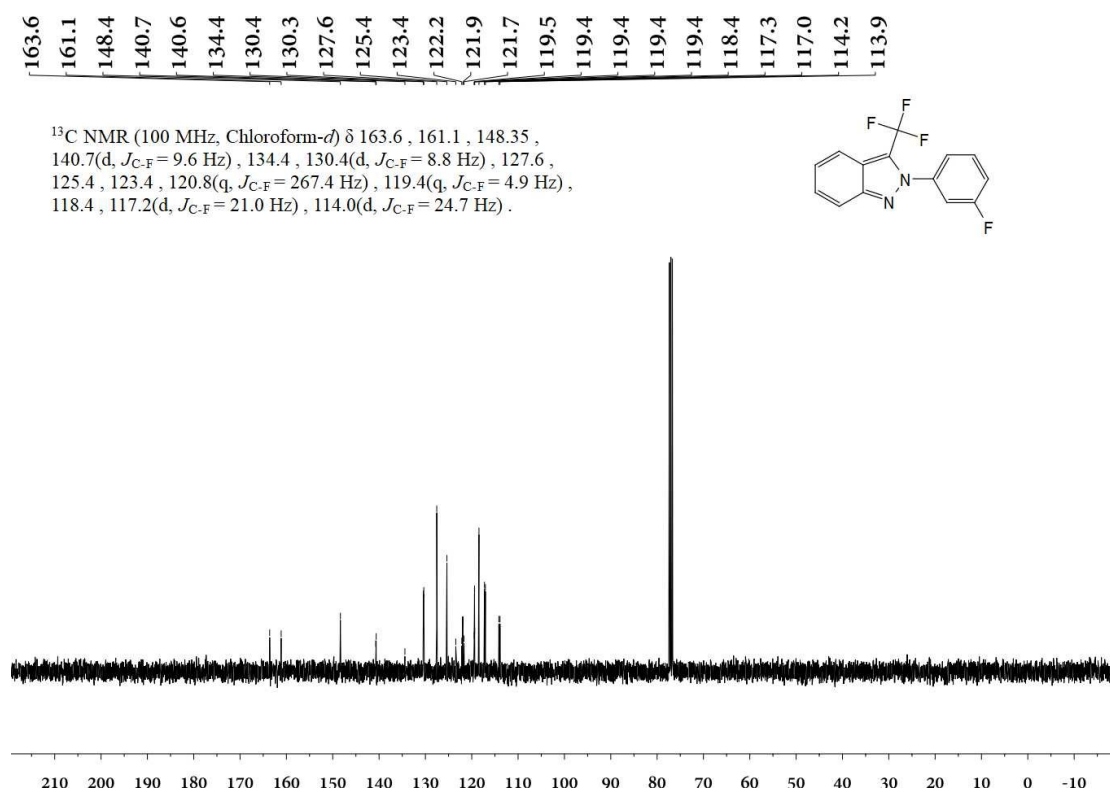


Figure S28.  $^1\text{H}$  NMR of 2-(3-fluorophenyl)-3-(trifluoromethyl)-2H-indazole (**2j**)



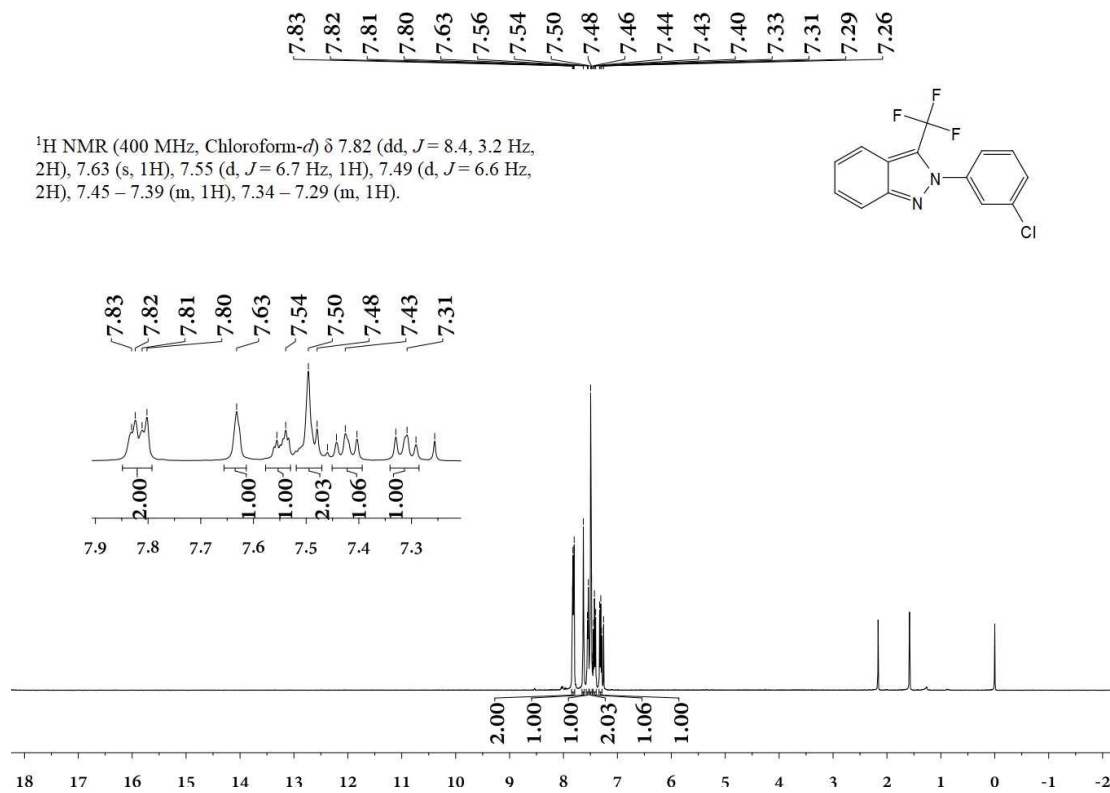


Figure S31. <sup>1</sup>H NMR of 2-(3-chlorophenyl)-3-(trifluoromethyl)-2H-indazole (**2k**)

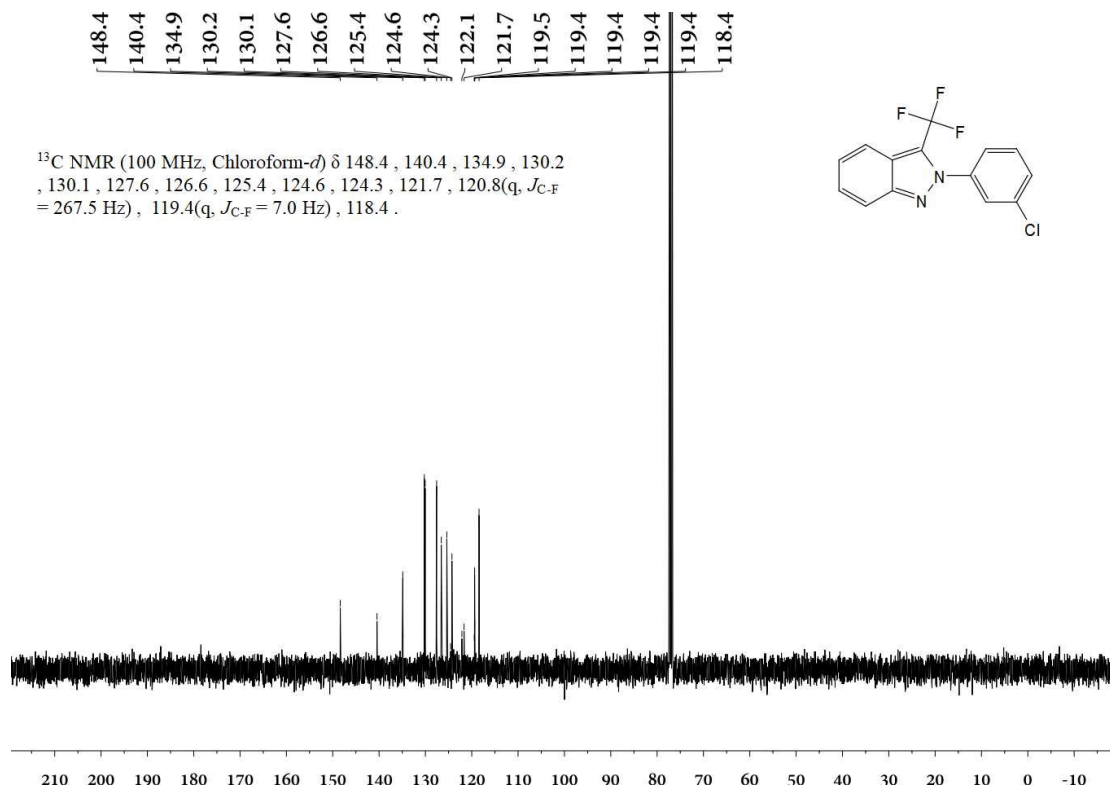


Figure S32. <sup>13</sup>C NMR of 2-(3-chlorophenyl)-3-(trifluoromethyl)-2H-indazole (**2k**)

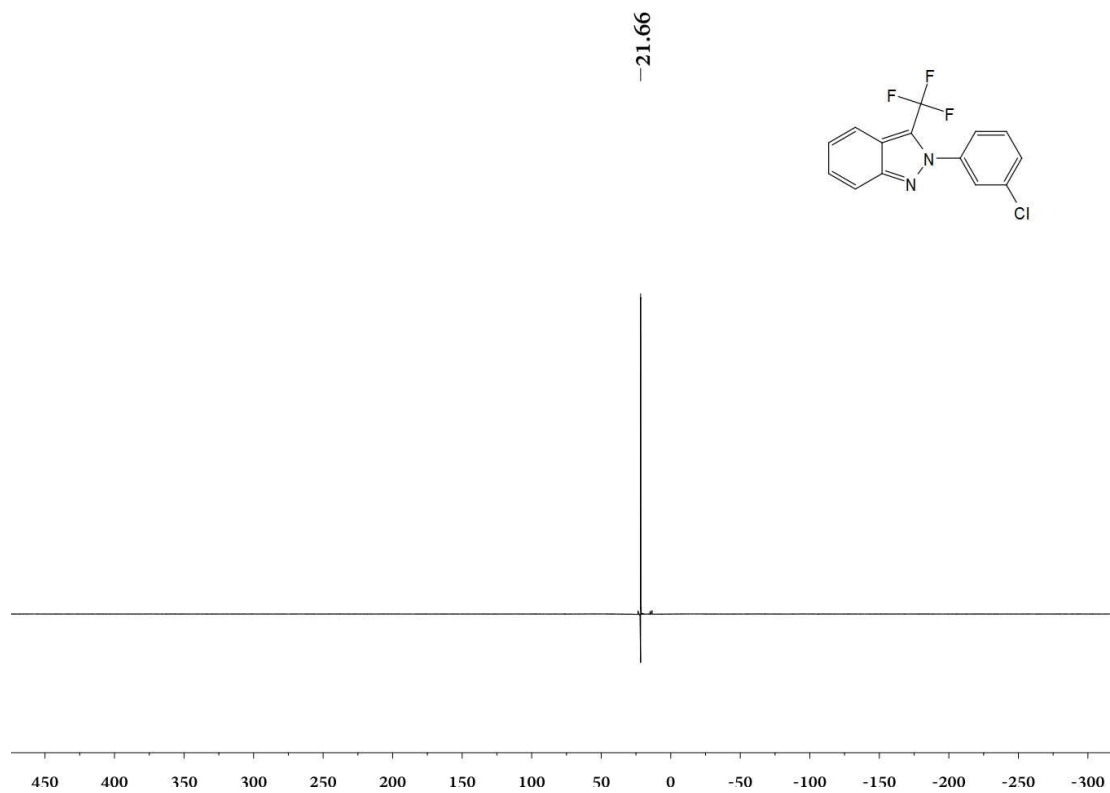


Figure S33.  $^{19}\text{F}$  NMR of 2-(3-chlorophenyl)-3-(trifluoromethyl)-2H-indazole (**2k**)

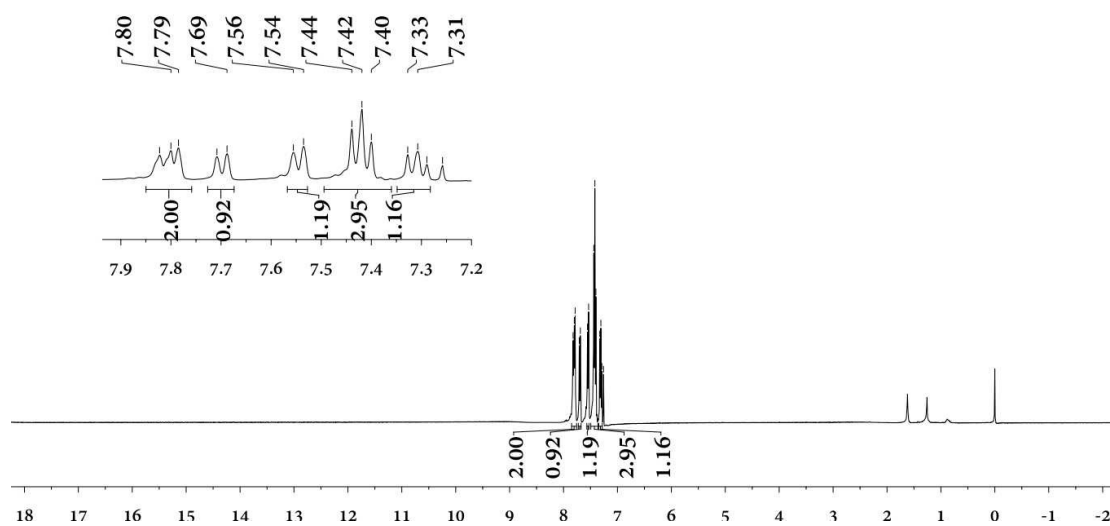
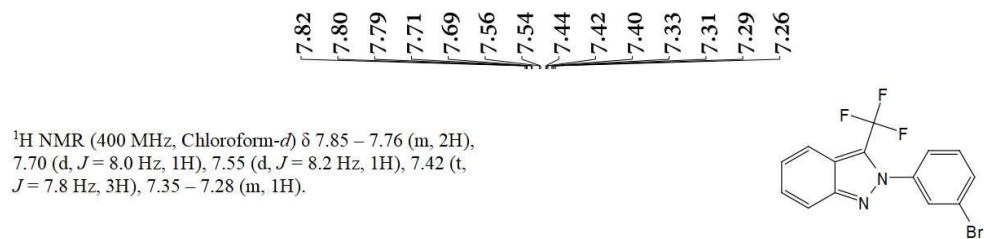


Figure S34.  $^1\text{H}$  NMR of 2-(3-bromophenyl)-3-(trifluoromethyl)-2H-indazole (**2l**)



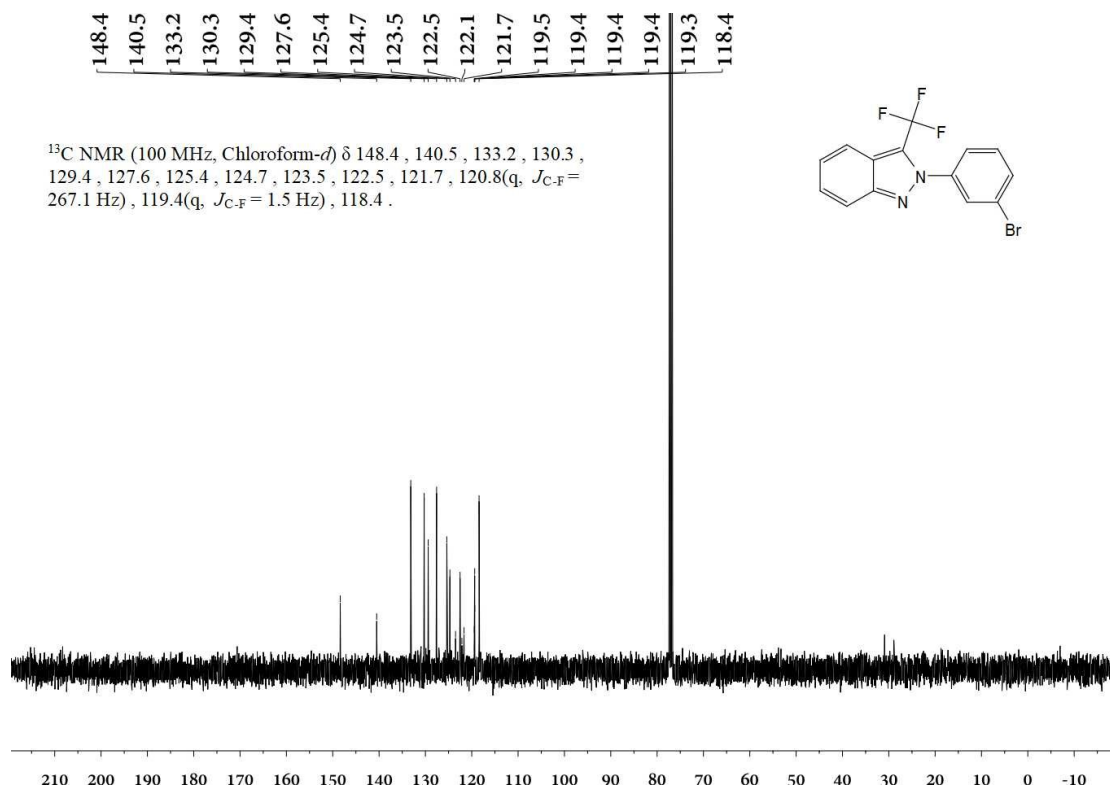


Figure S35.  $^{13}\text{C}$  NMR of 2-(3-bromophenyl)-3-(trifluoromethyl)-2H-indazole (**21**)

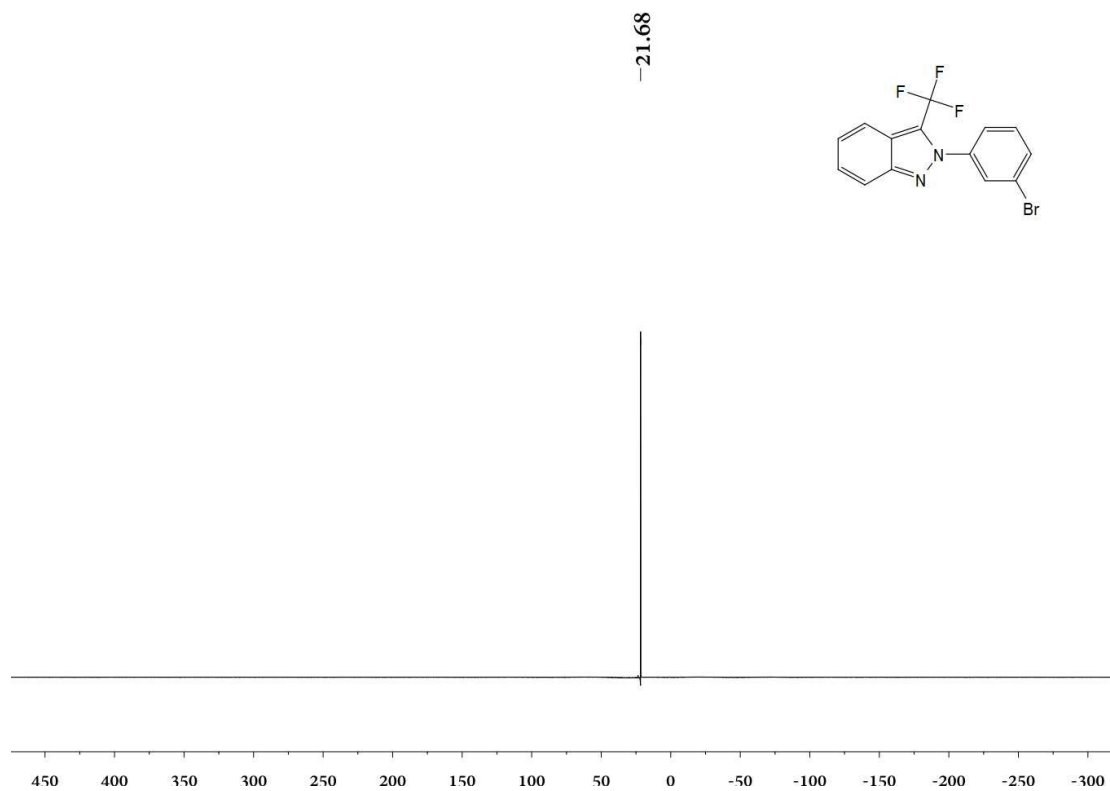


Figure S36.  $^{19}\text{F}$  NMR of 2-(3-bromophenyl)-3-(trifluoromethyl)-2H-indazole (**21**)

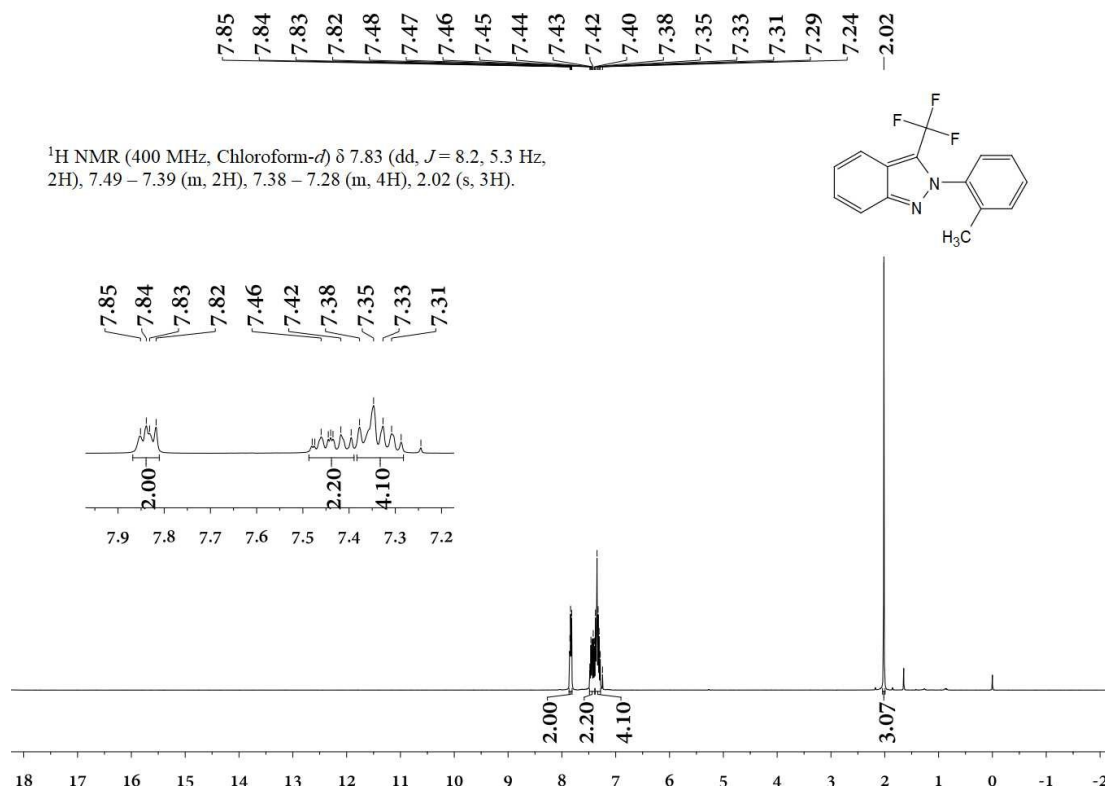


Figure S37. <sup>1</sup>H NMR of 2-(o-tolyl)-3-(trifluoromethyl)-2H-indazole (**2m**)

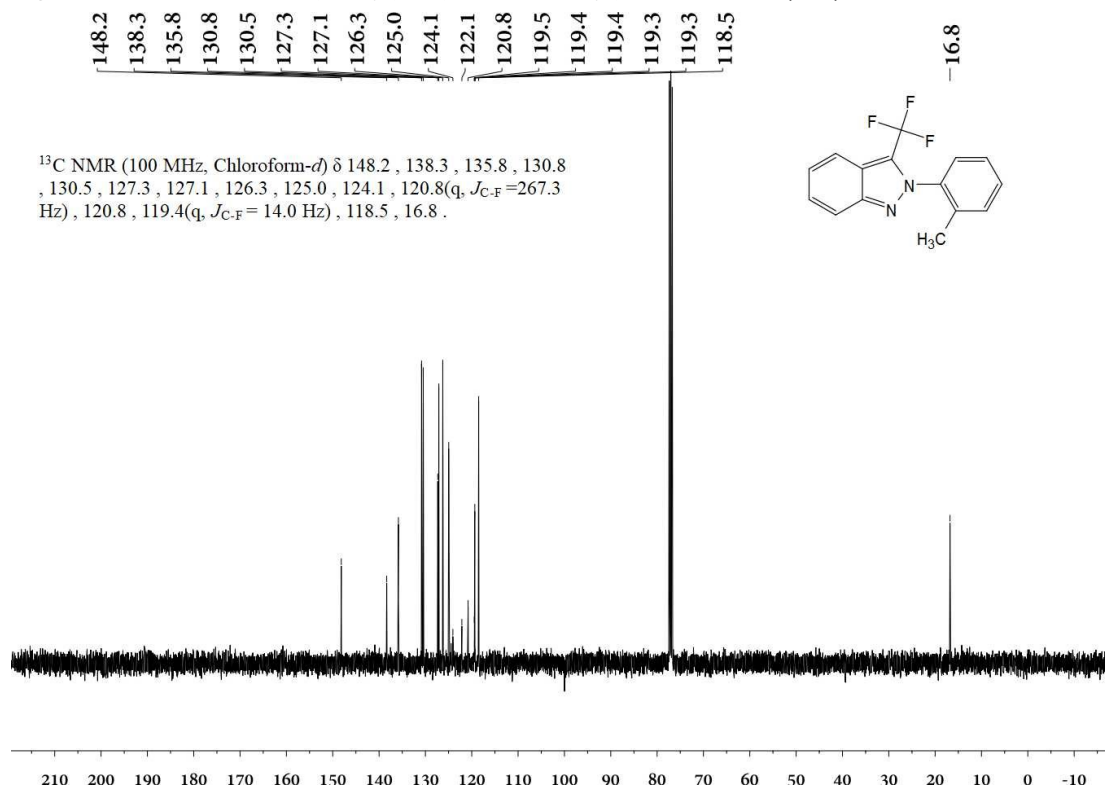


Figure S38. <sup>13</sup>C NMR of 2-(o-tolyl)-3-(trifluoromethyl)-2H-indazole (**2m**)

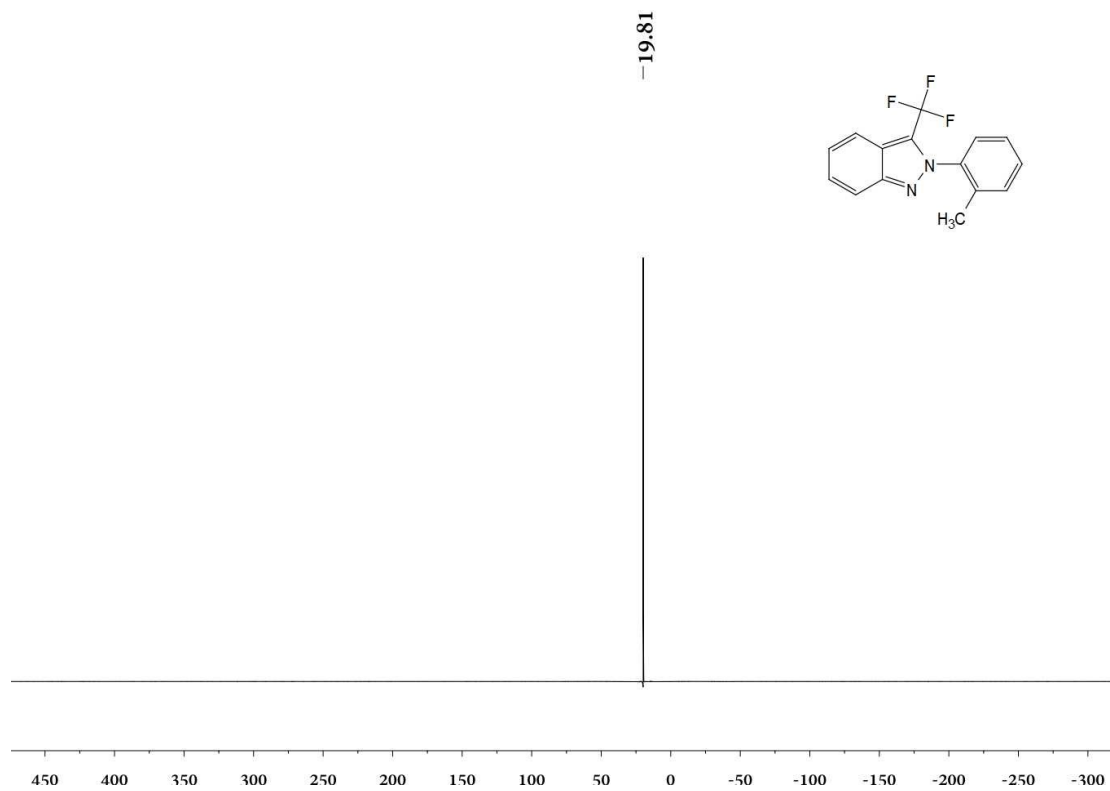


Figure S39.  $^{19}\text{F}$  NMR of 2-(o-tolyl)-3-(trifluoromethyl)-2H-indazole (**2m**)

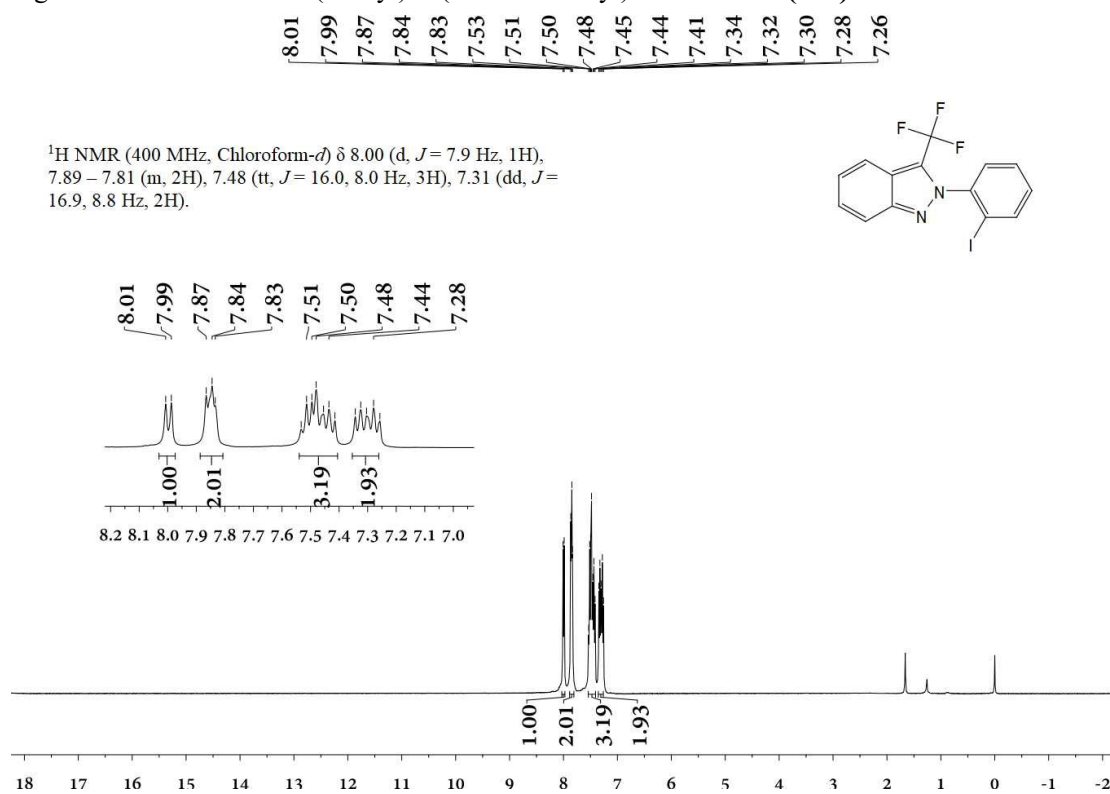


Figure S40.  $^1\text{H}$  NMR of 2-(2-iodophenyl)-3-(trifluoromethyl)-2H-indazole (**2n**)

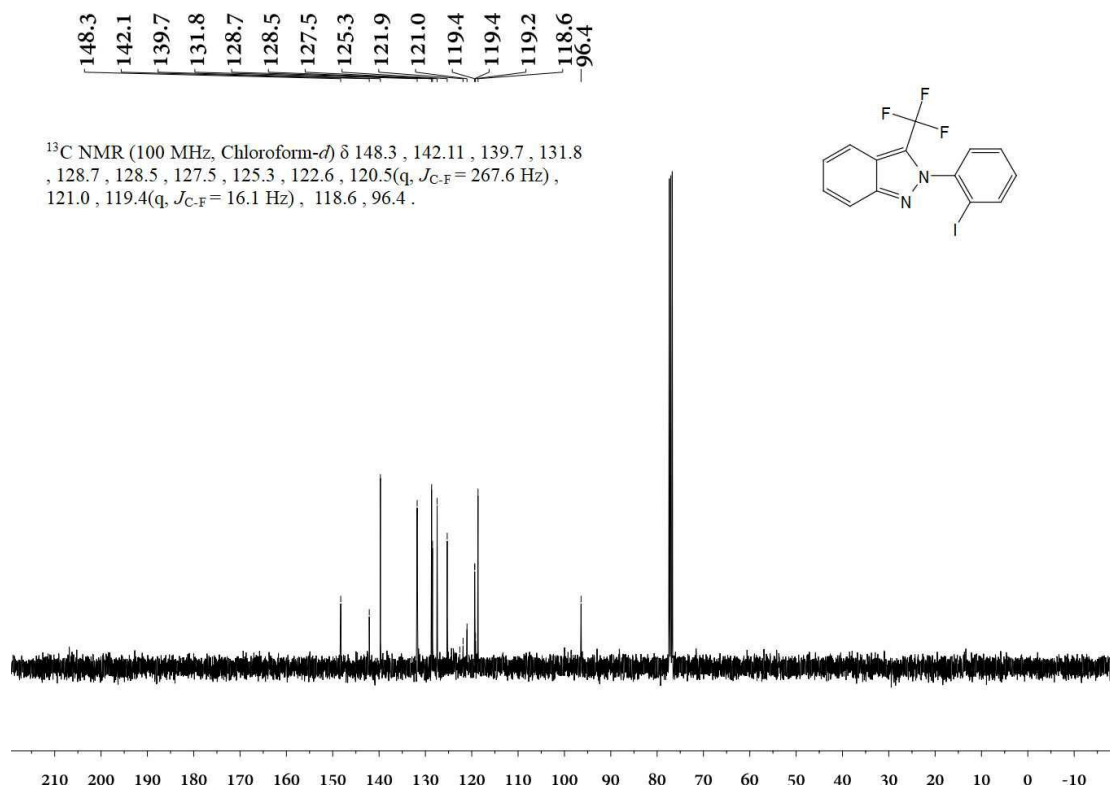


Figure S41. <sup>13</sup>C NMR of 2-(2-iodophenyl)-3-(trifluoromethyl)-2H-indazole (**2n**)

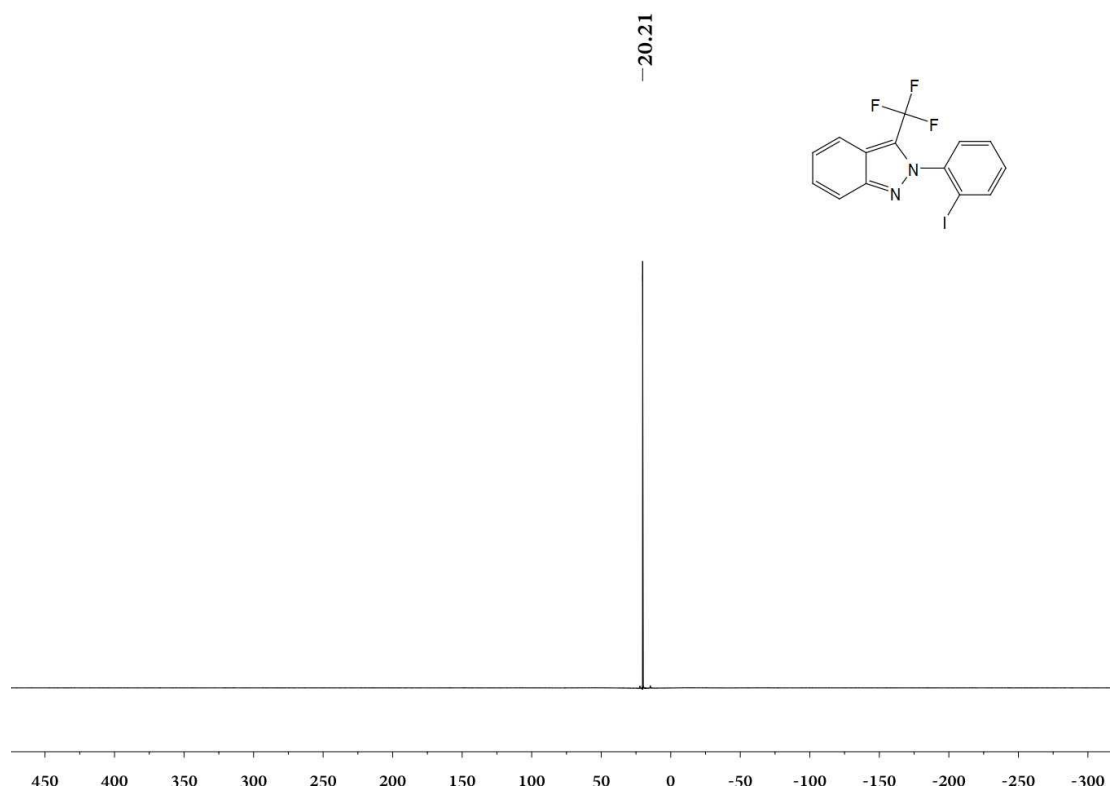


Figure S42. <sup>19</sup>F NMR of 2-(2-iodophenyl)-3-(trifluoromethyl)-2H-indazole (**2n**)

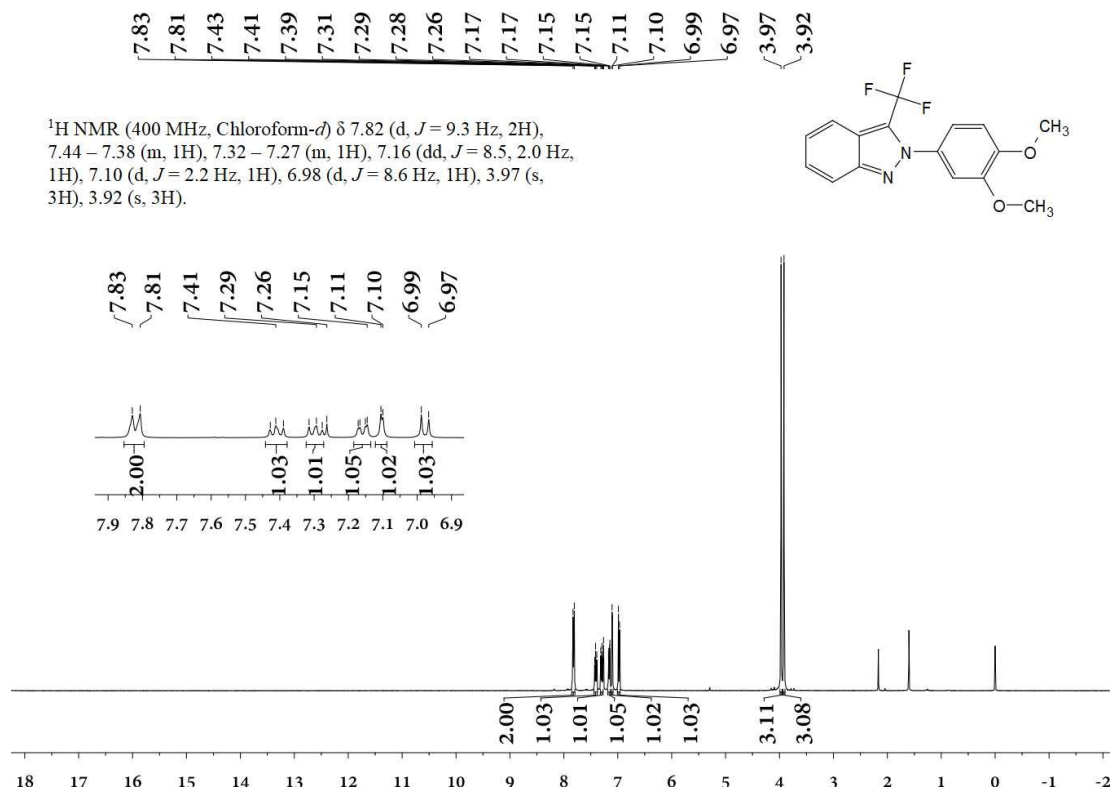


Figure S43. <sup>1</sup>H NMR of 2-(3,4-dimethoxyphenyl)-3-(trifluoromethyl)-2H-indazole (**20**)

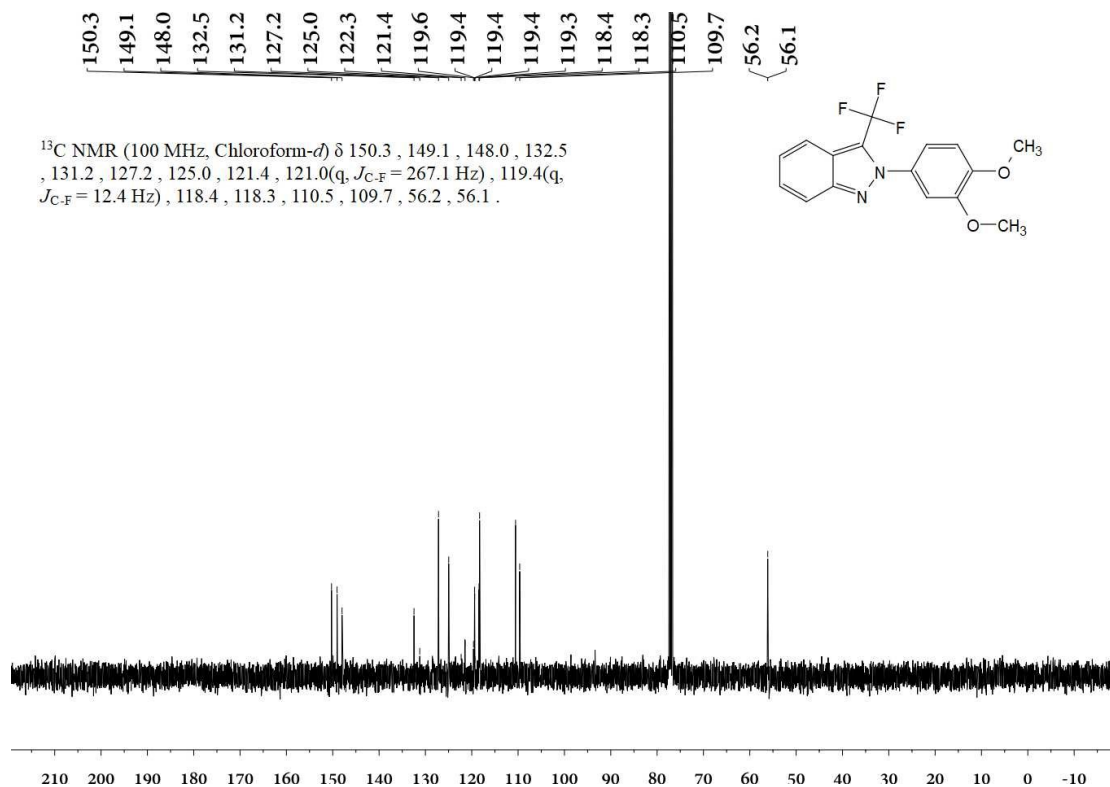


Figure S44. <sup>13</sup>C NMR of 2-(3,4-dimethoxyphenyl)-3-(trifluoromethyl)-2H-indazole (**20**)

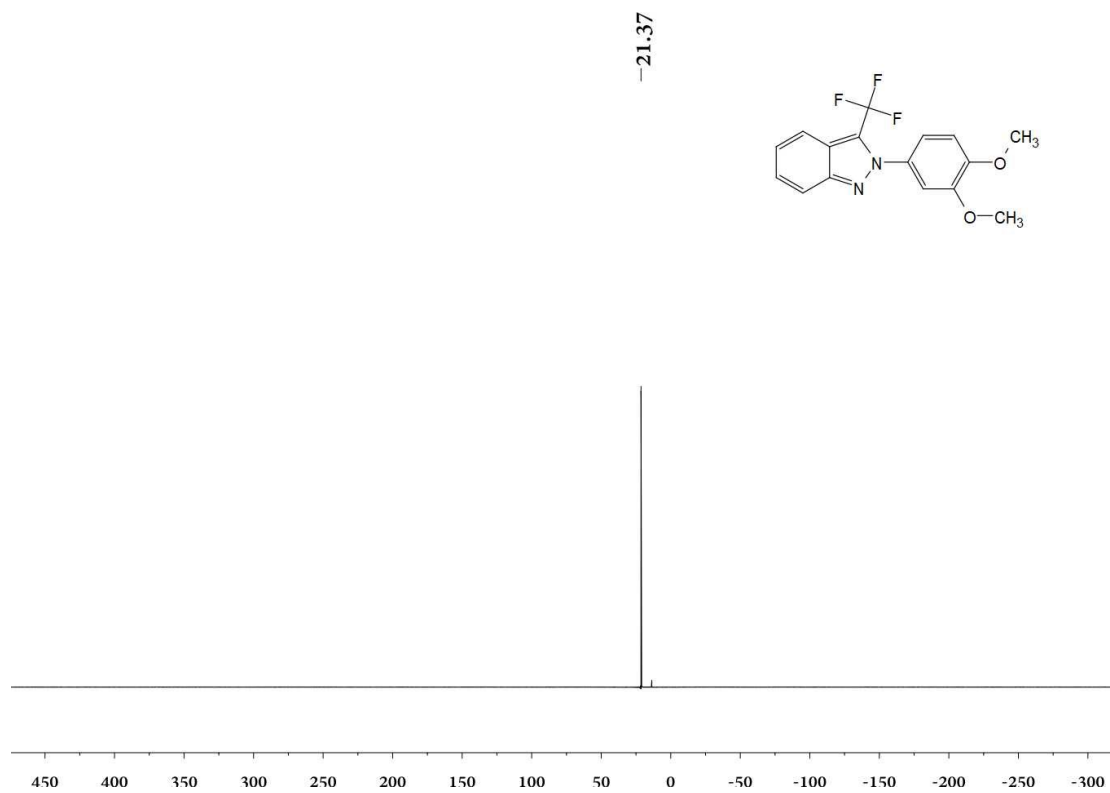


Figure S45.  $^{19}\text{F}$  NMR of 2-(3,4-dimethoxyphenyl)-3-(trifluoromethyl)-2H-indazole (**2o**)

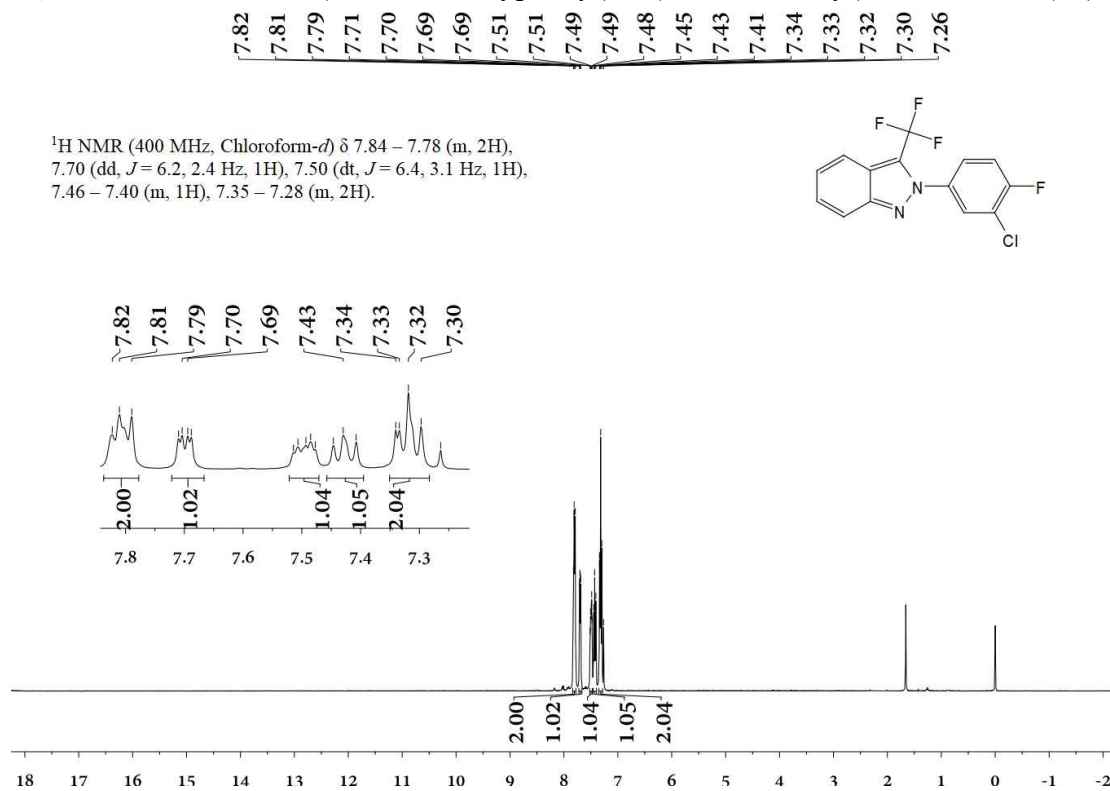


Figure S46.  $^1\text{H}$  NMR of 2-(3-chloro-4-fluorophenyl)-3-(trifluoromethyl)-2H-indazole (**2p**)

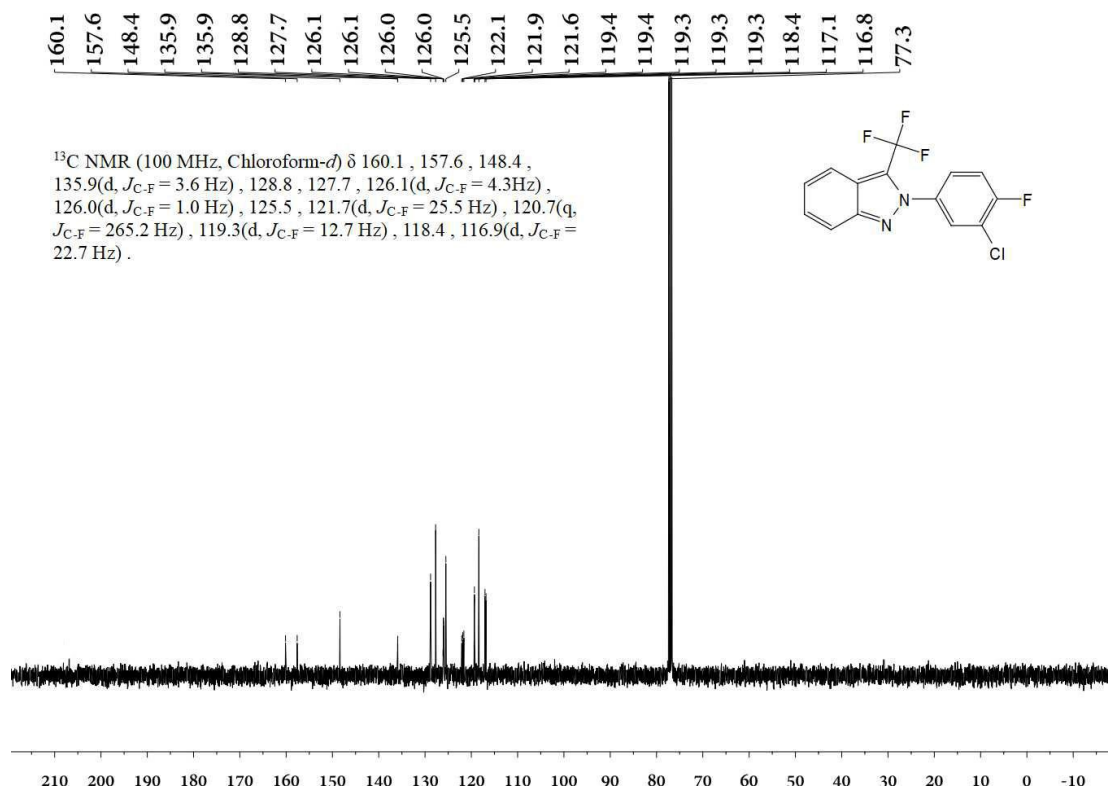


Figure S47. <sup>13</sup>C NMR of 2-(3-chloro-4-fluorophenyl)-3-(trifluoromethyl)-2H-indazole (**2p**)

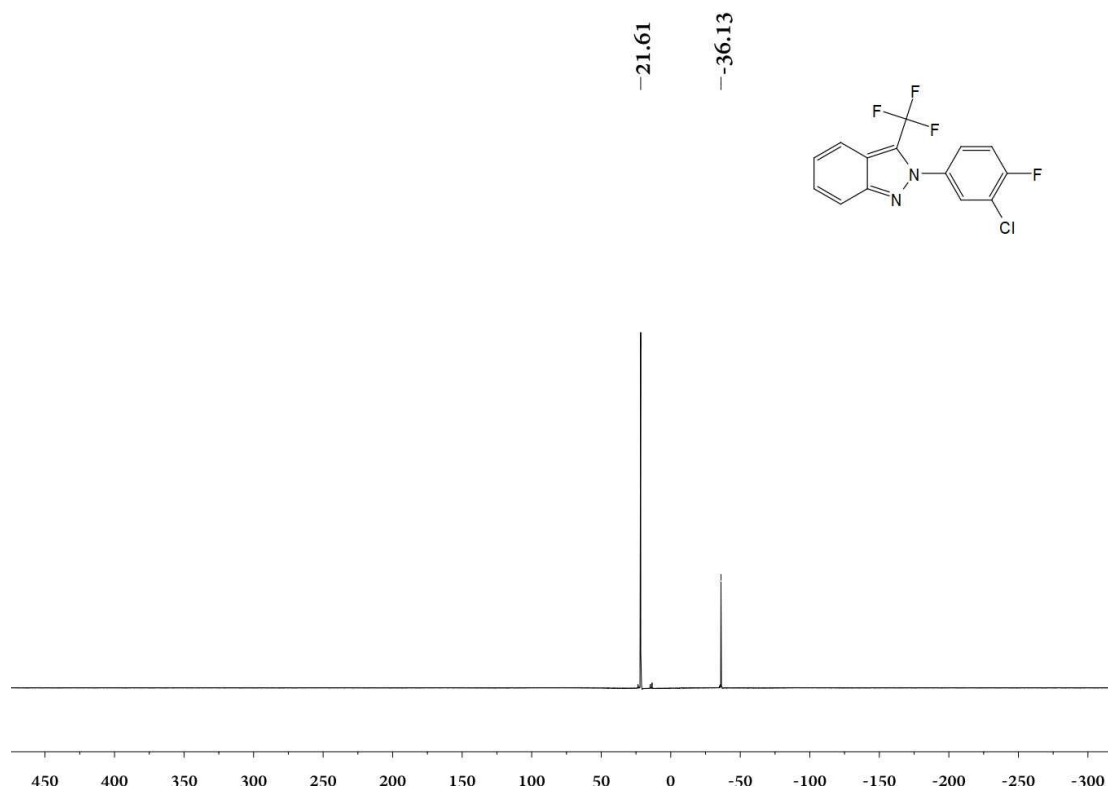


Figure S48. <sup>19</sup>F NMR of 2-(3-chloro-4-fluorophenyl)-3-(trifluoromethyl)-2H-indazole (**2p**)

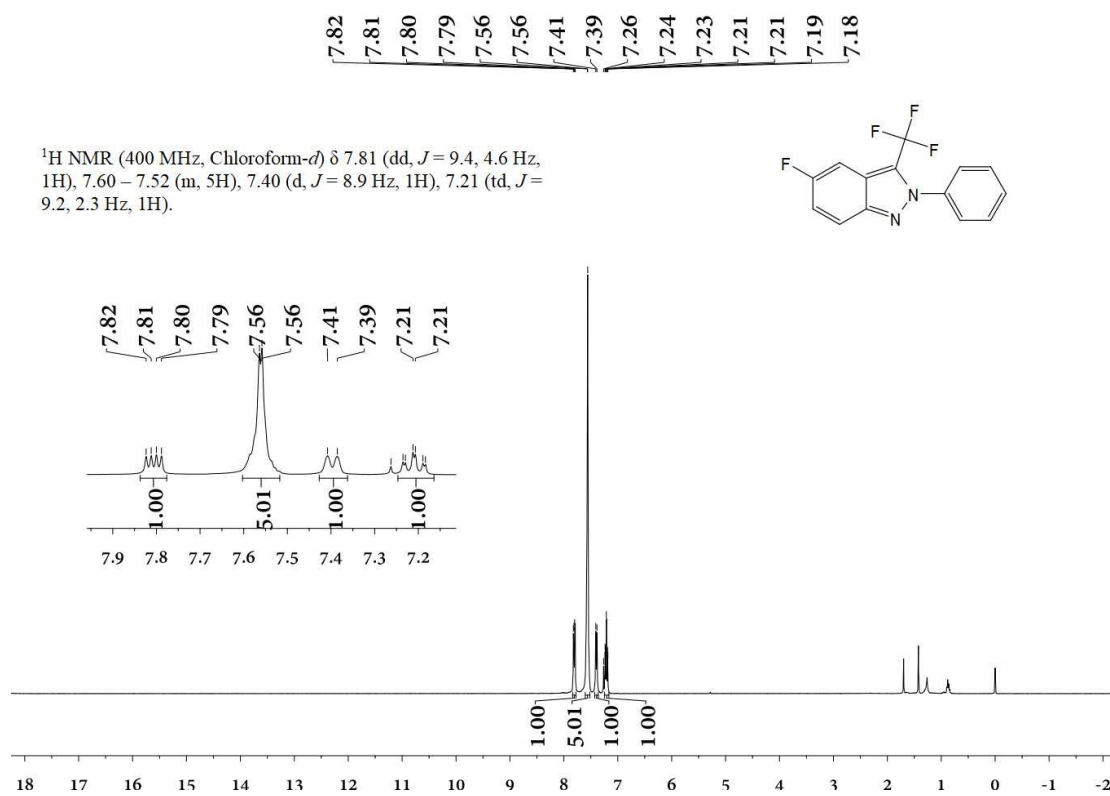


Figure S49. <sup>1</sup>H NMR of 5-fluoro-2-phenyl-3-(trifluoromethyl)-2H-indazole (**2q**)

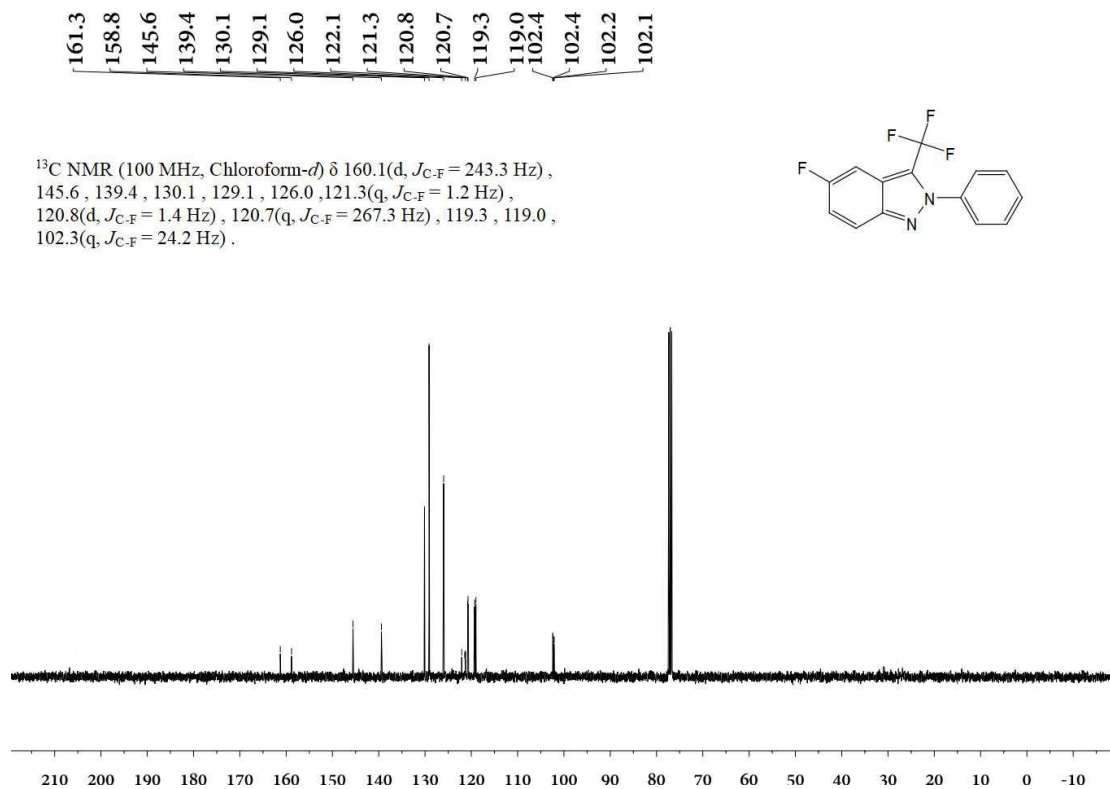


Figure S50. <sup>13</sup>C NMR of 5-fluoro-2-phenyl-3-(trifluoromethyl)-2H-indazole (**2q**)



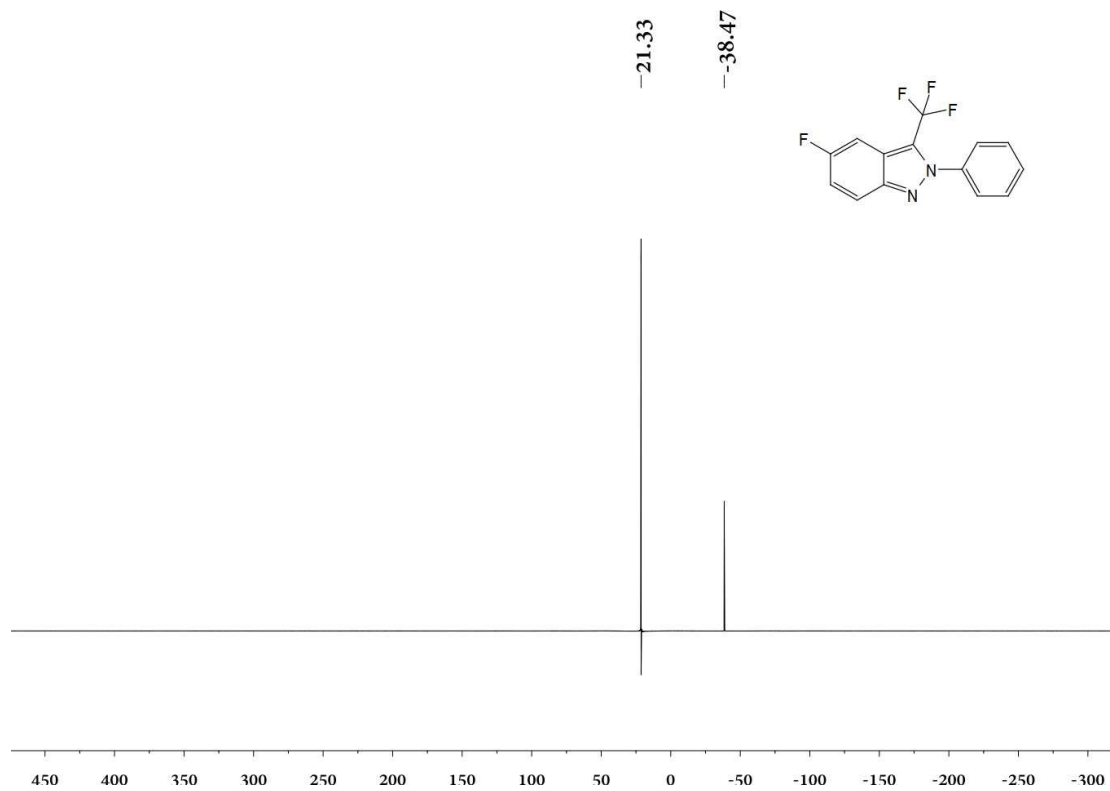


Figure S51.  $^{19}\text{F}$  NMR of 5-fluoro-2-phenyl-3-(trifluoromethyl)-2H-indazole (**2q**)

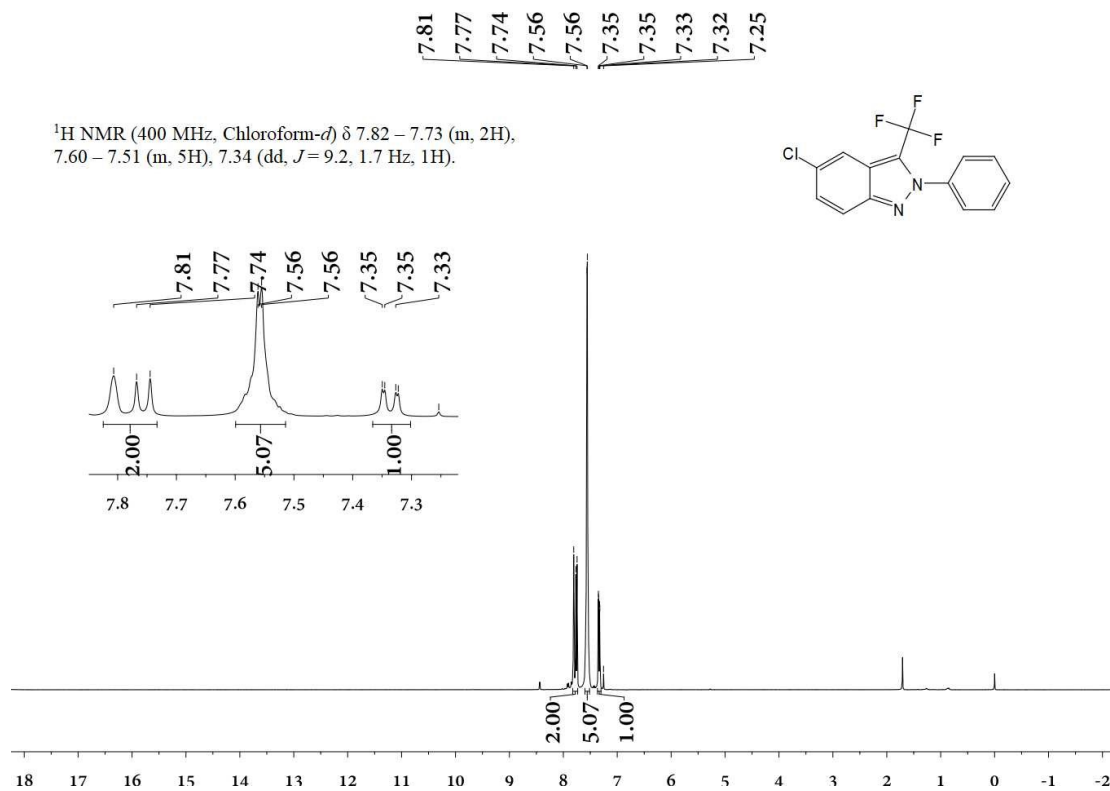


Figure S52.  $^1\text{H}$  NMR of 5-chloro-2-phenyl-3-(trifluoromethyl)-2H-indazole (**2r**)

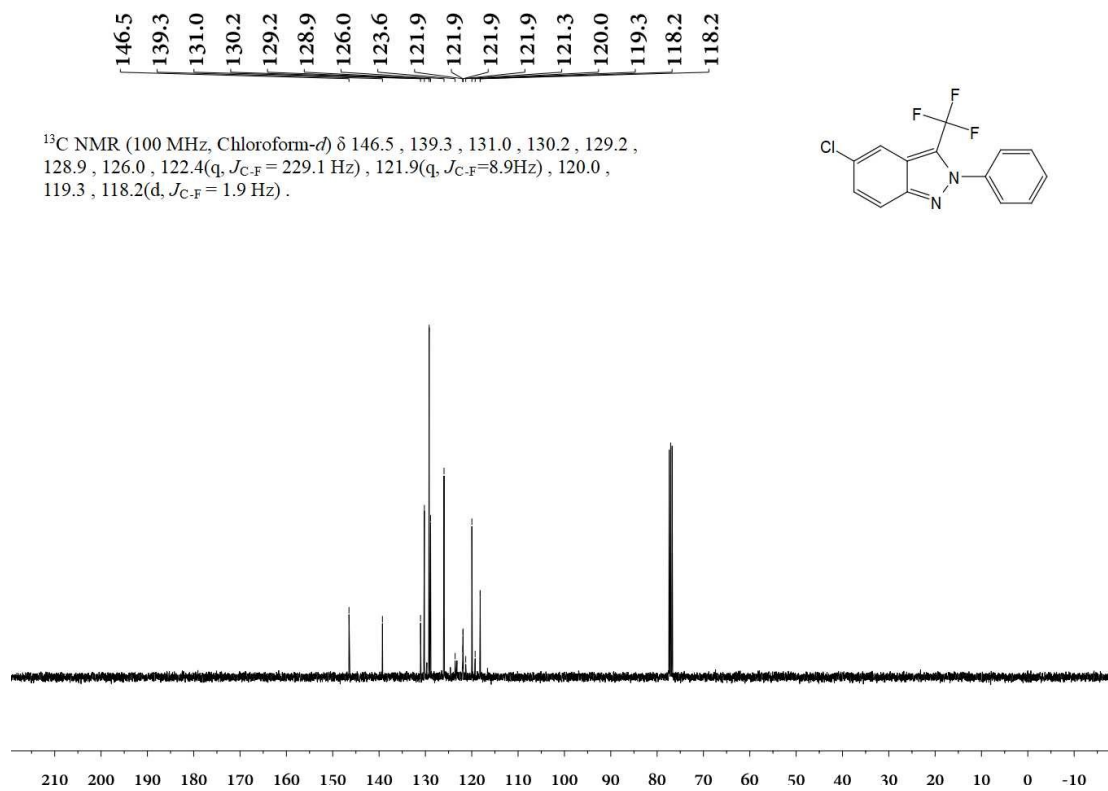


Figure S53. <sup>13</sup>C NMR of 5-chloro-2-phenyl-3-(trifluoromethyl)-2H-indazole (**2r**)

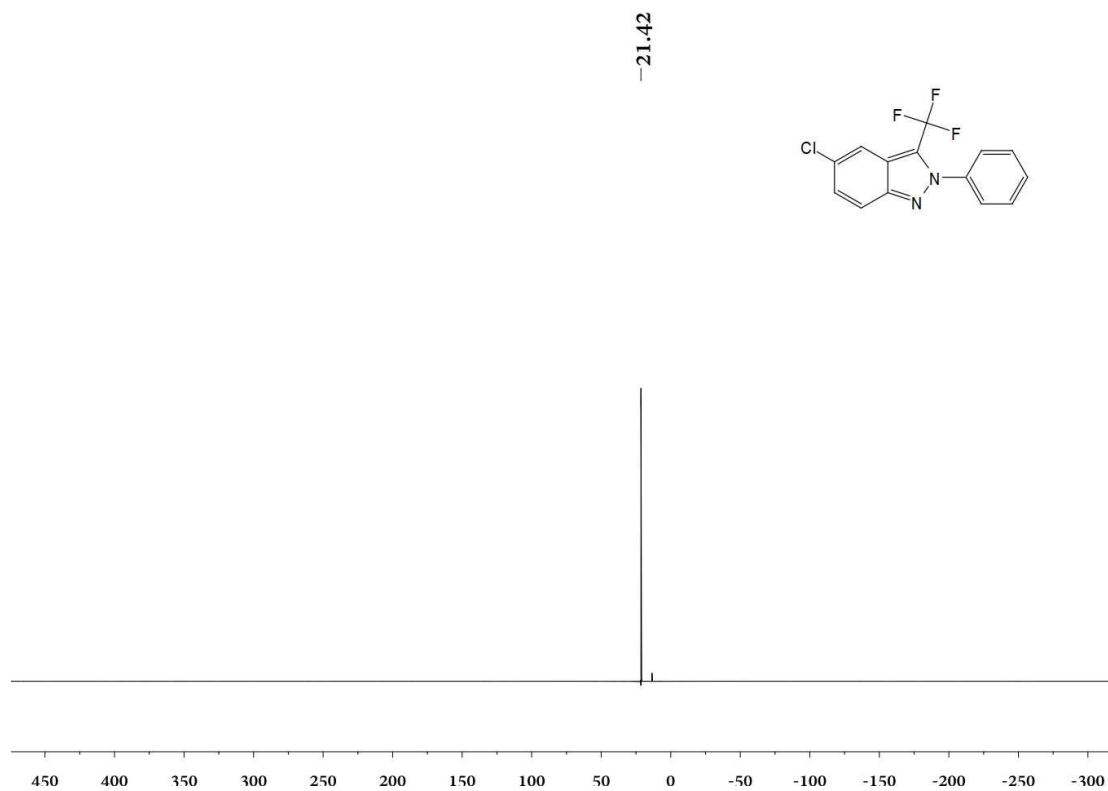


Figure S54. <sup>19</sup>F NMR of 5-chloro-2-phenyl-3-(trifluoromethyl)-2H-indazole (**2r**)

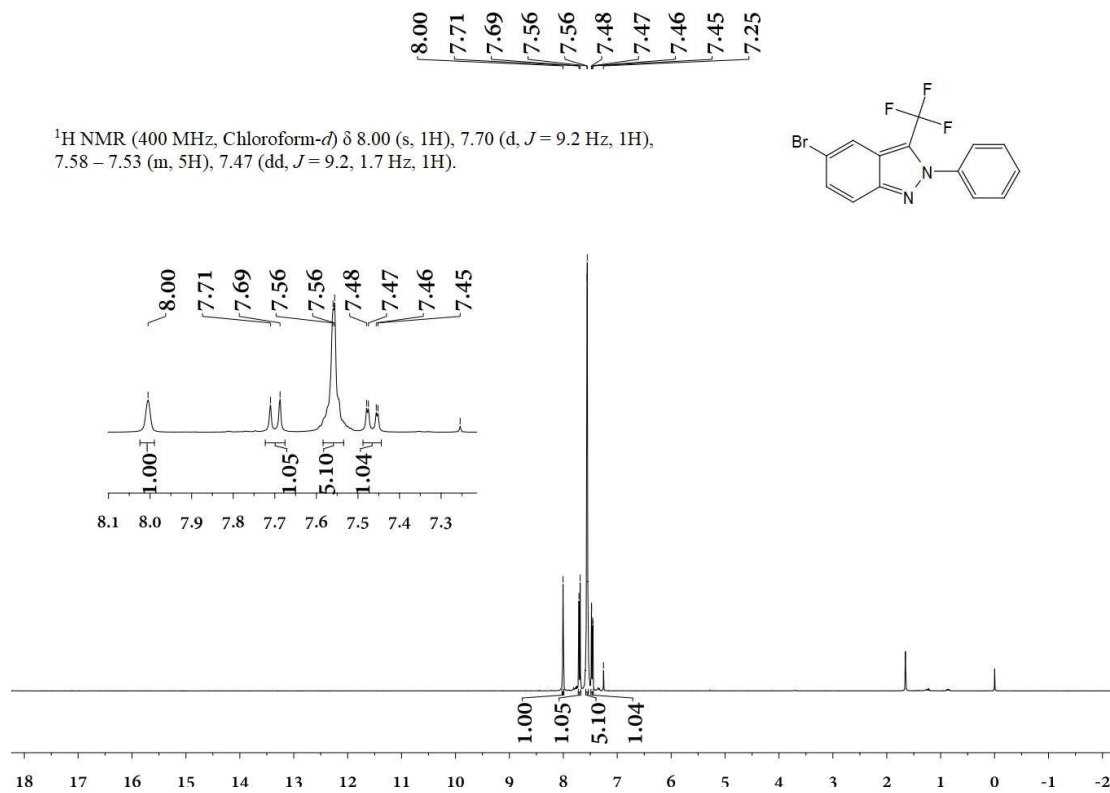


Figure S55. <sup>1</sup>H NMR of 5-bromo-2-phenyl-3-(trifluoromethyl)-2H-indazole (**2s**)

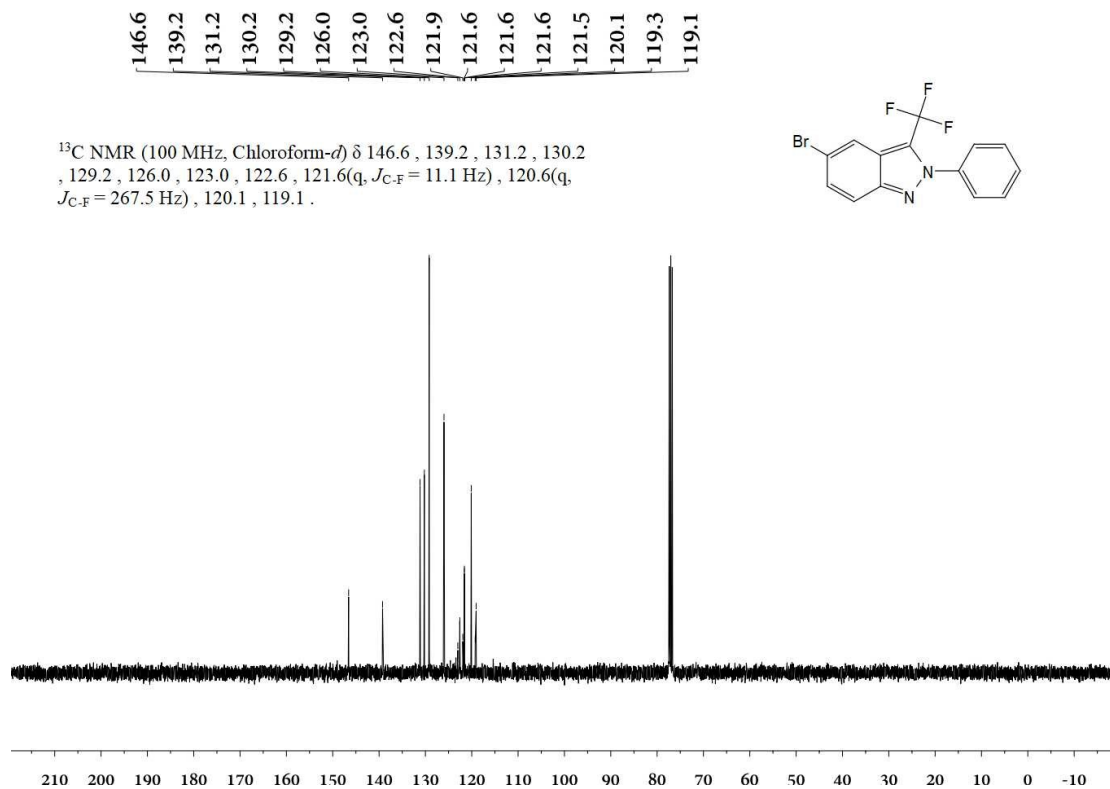


Figure S56. <sup>13</sup>C NMR of 5-bromo-2-phenyl-3-(trifluoromethyl)-2H-indazole (**2s**)



Figure S57.  $^{13}\text{C}$  NMR of 5-methoxy-2-phenyl-3-(trifluoromethyl)-2H-indazole (**2s**)

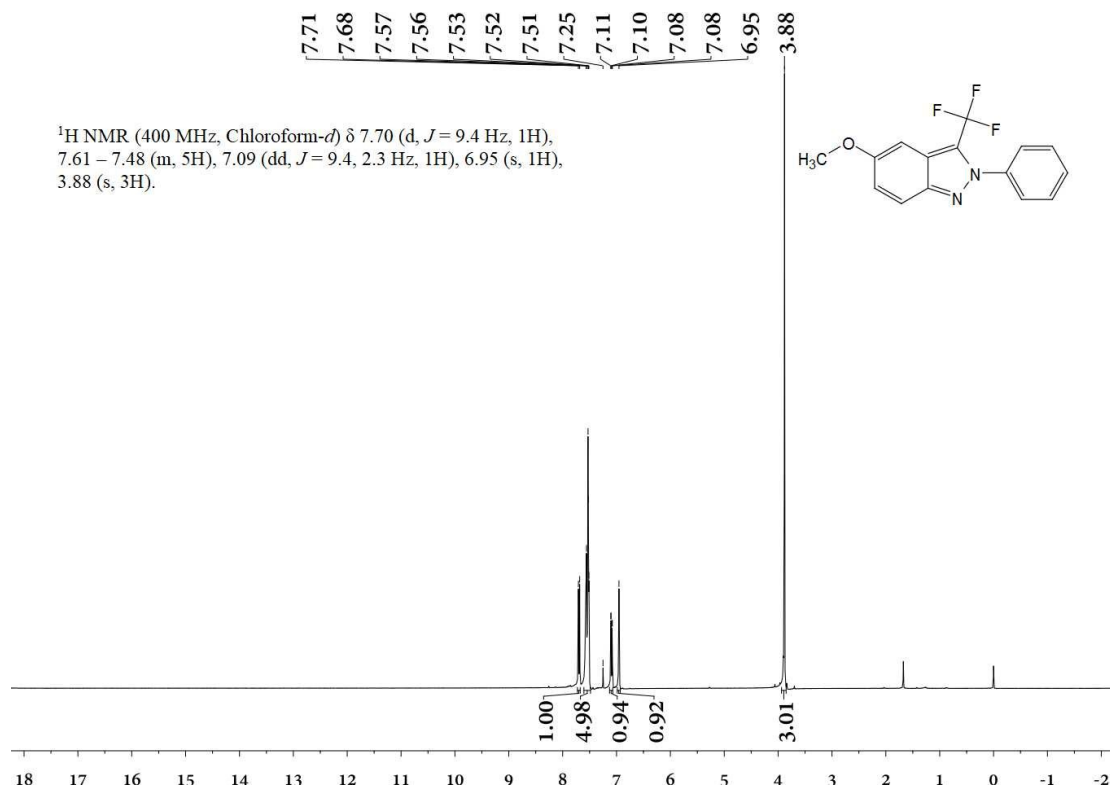


Figure S58.  $^1\text{H}$  NMR of 5-methoxy-2-phenyl-3-(trifluoromethyl)-2H-indazole (**2t**)

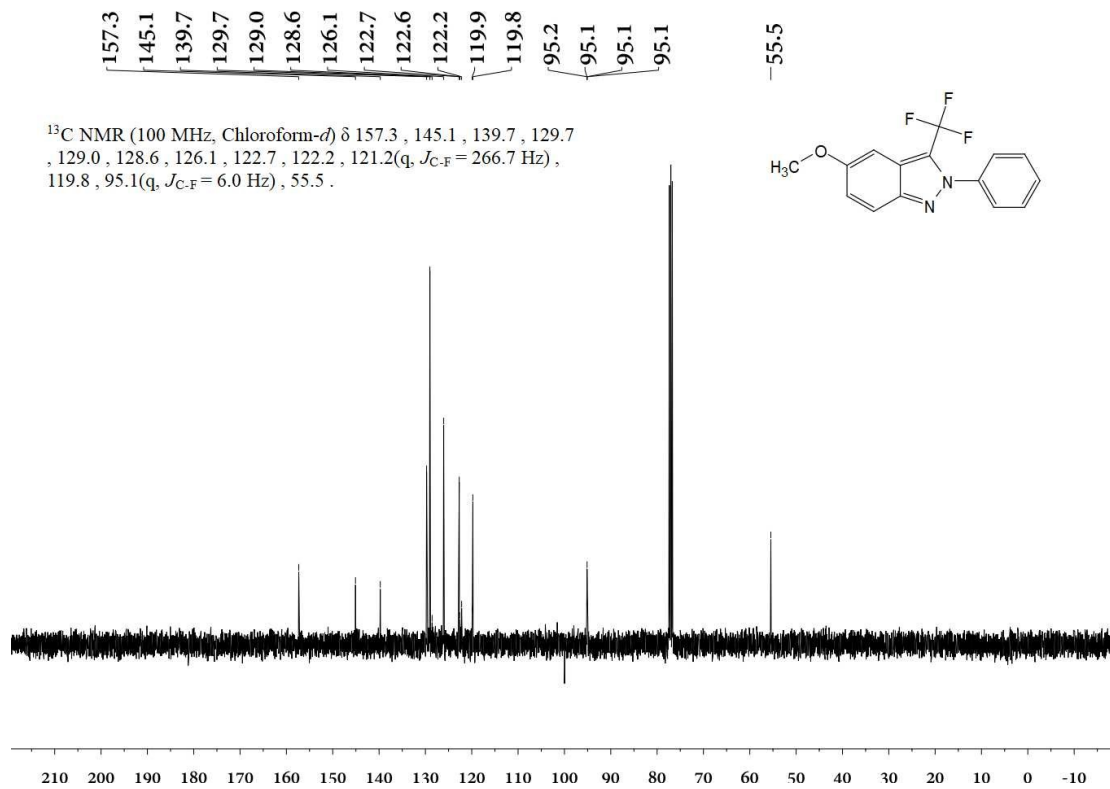


Figure S59. <sup>13</sup>C NMR of 5-methoxy-2-phenyl-3-(trifluoromethyl)-2H-indazole (**2t**)

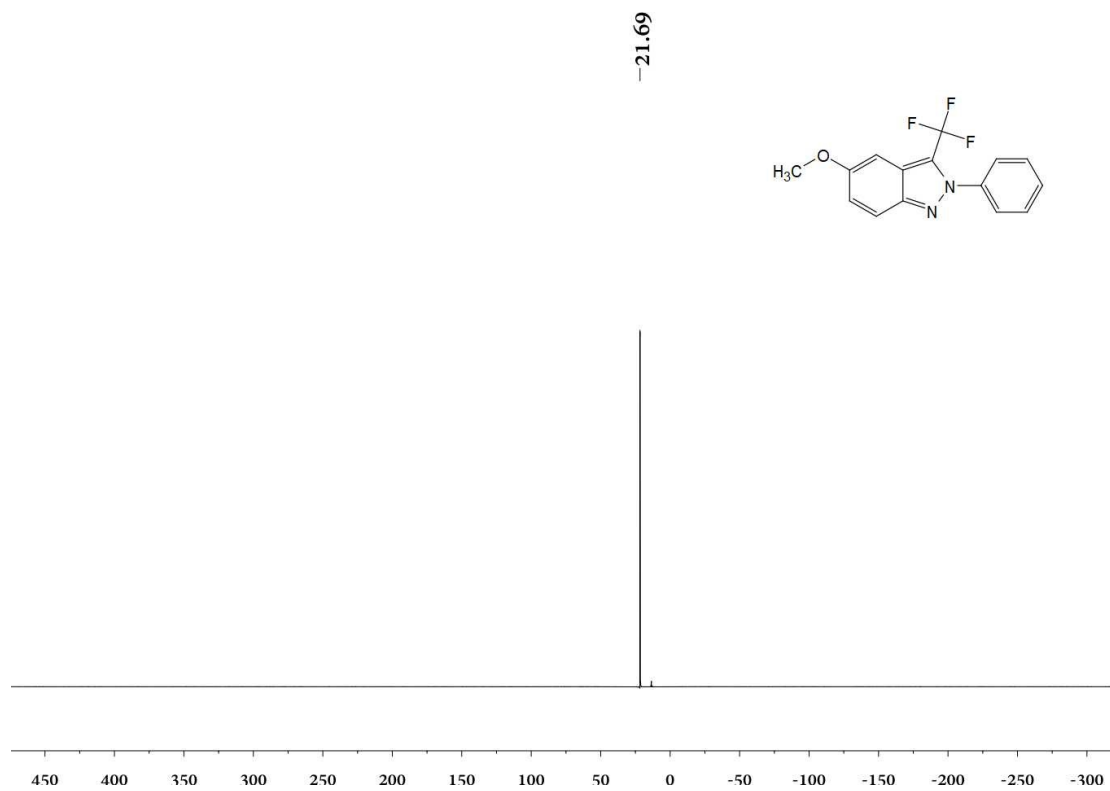


Figure S60. <sup>19</sup>F NMR of 5-methoxy-2-phenyl-3-(trifluoromethyl)-2H-indazole (**2t**)

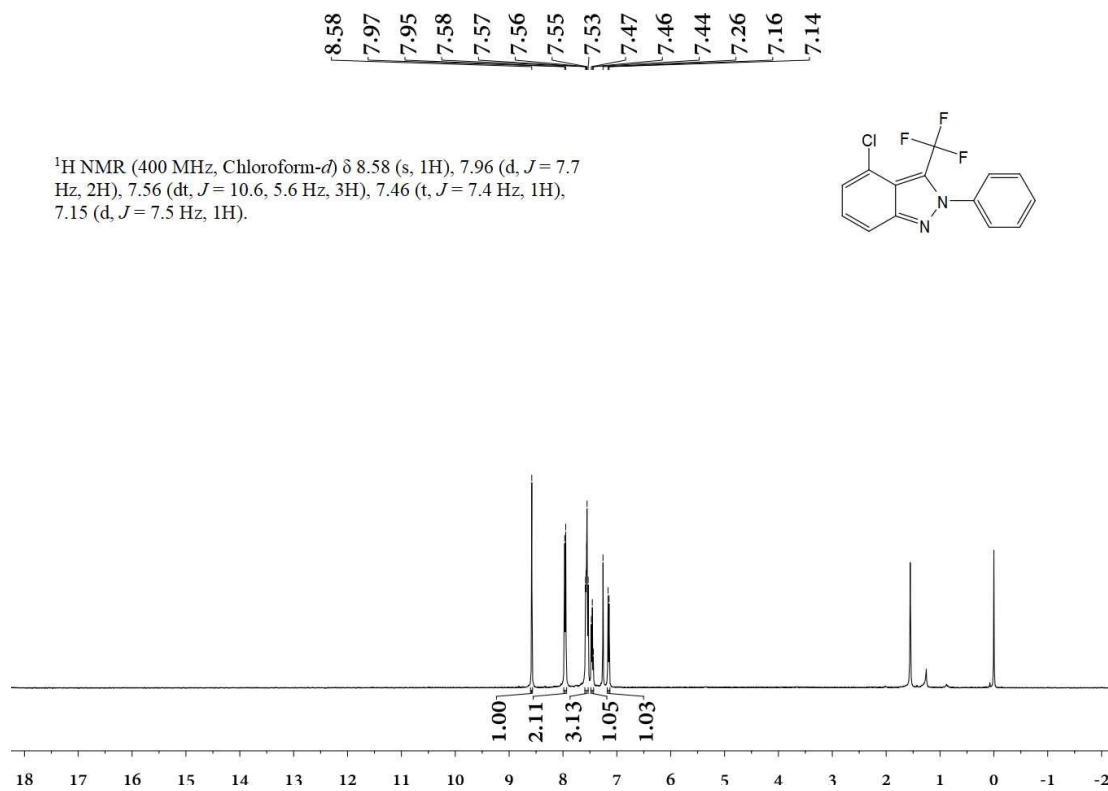


Figure S61. <sup>1</sup>H NMR of 4-chloro-2-phenyl-3-(trifluoromethyl)-2H-indazole (**2u**)

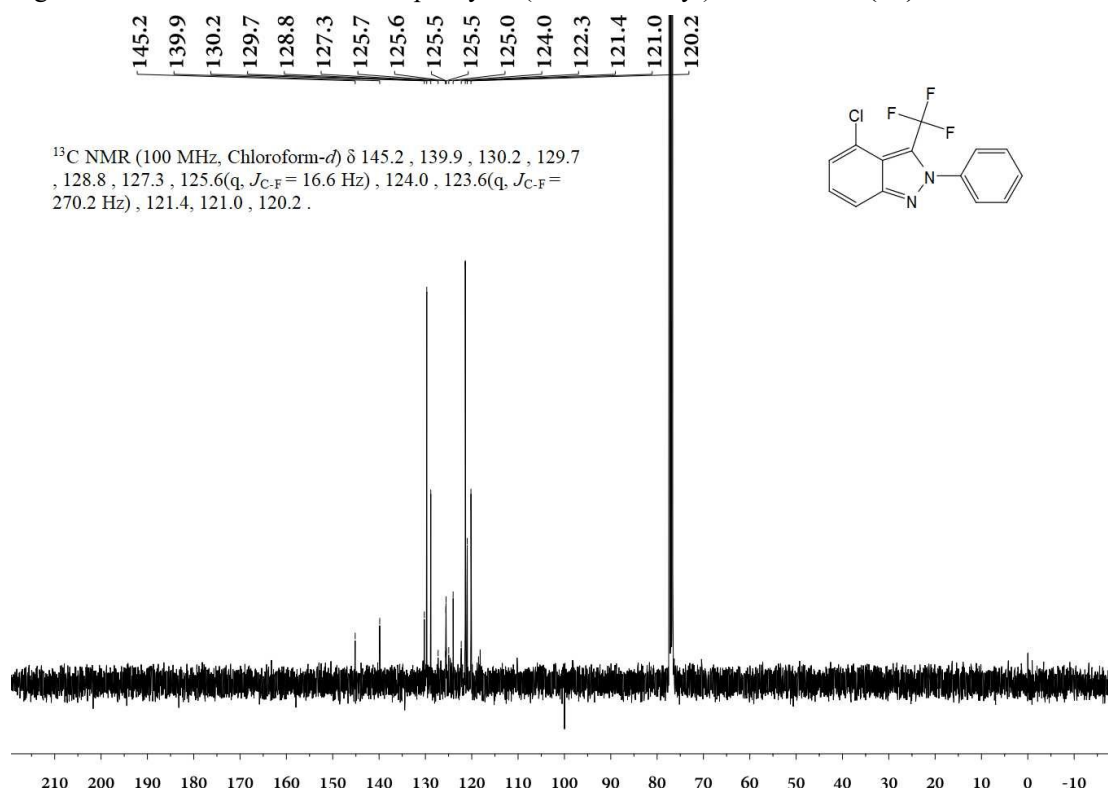


Figure S62. <sup>13</sup>C NMR of 4-chloro-2-phenyl-3-(trifluoromethyl)-2H-indazole (**2u**)

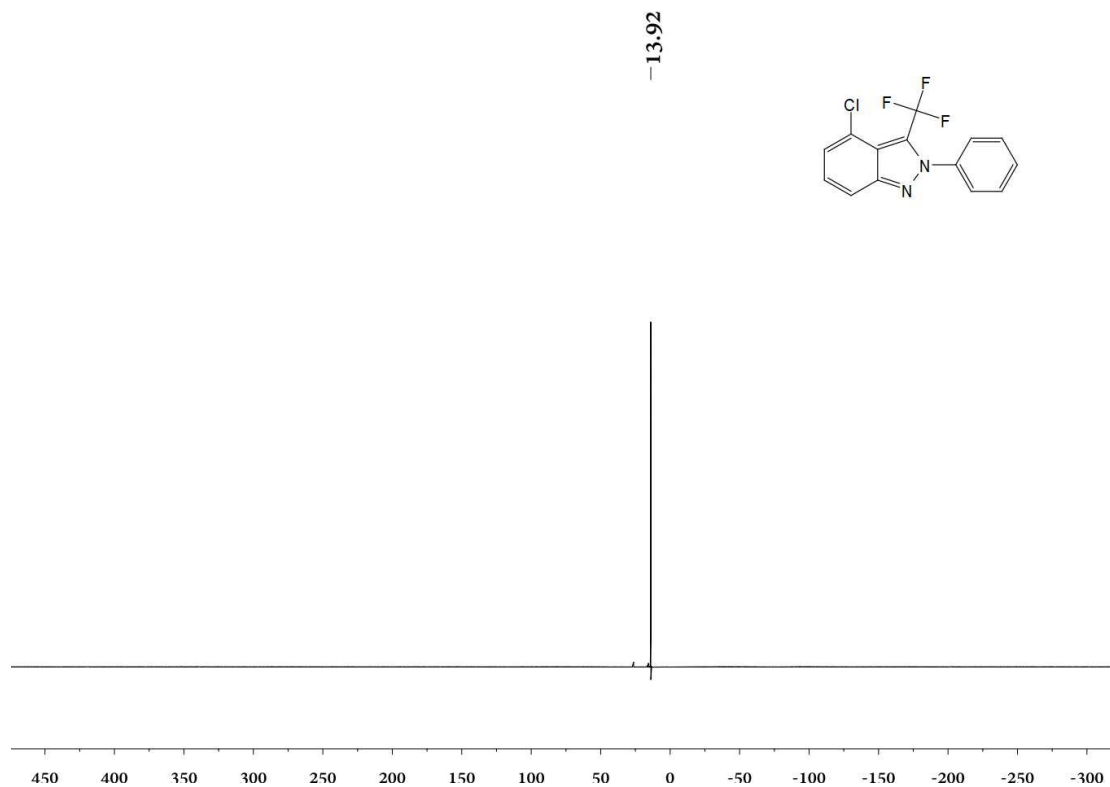


Figure S63.  $^{19}\text{F}$  NMR of 4-chloro-2-phenyl-3-(trifluoromethyl)-2H-indazole (**2u**)

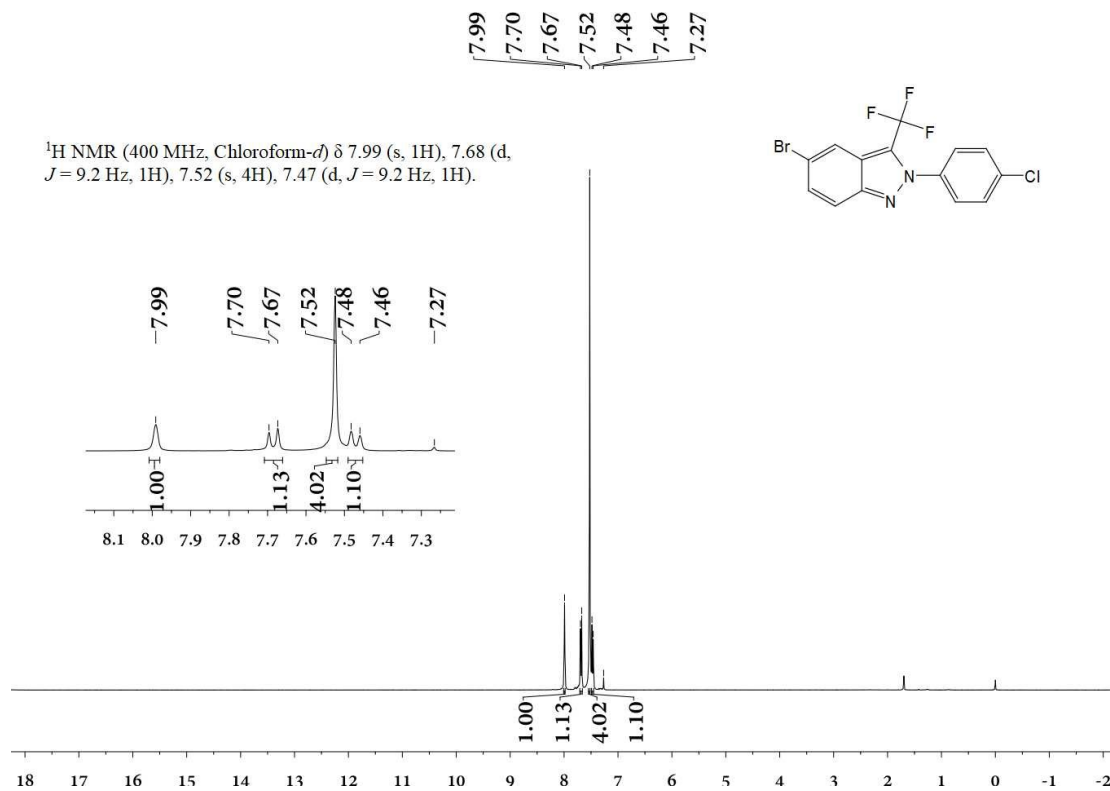
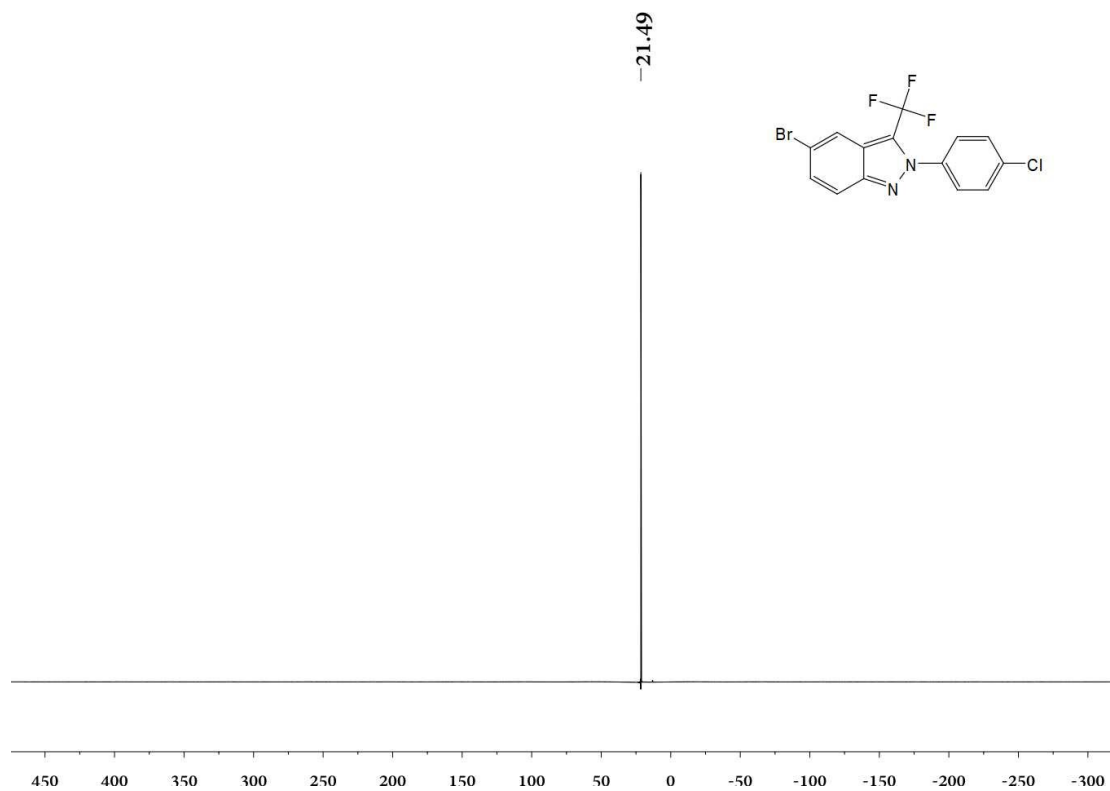
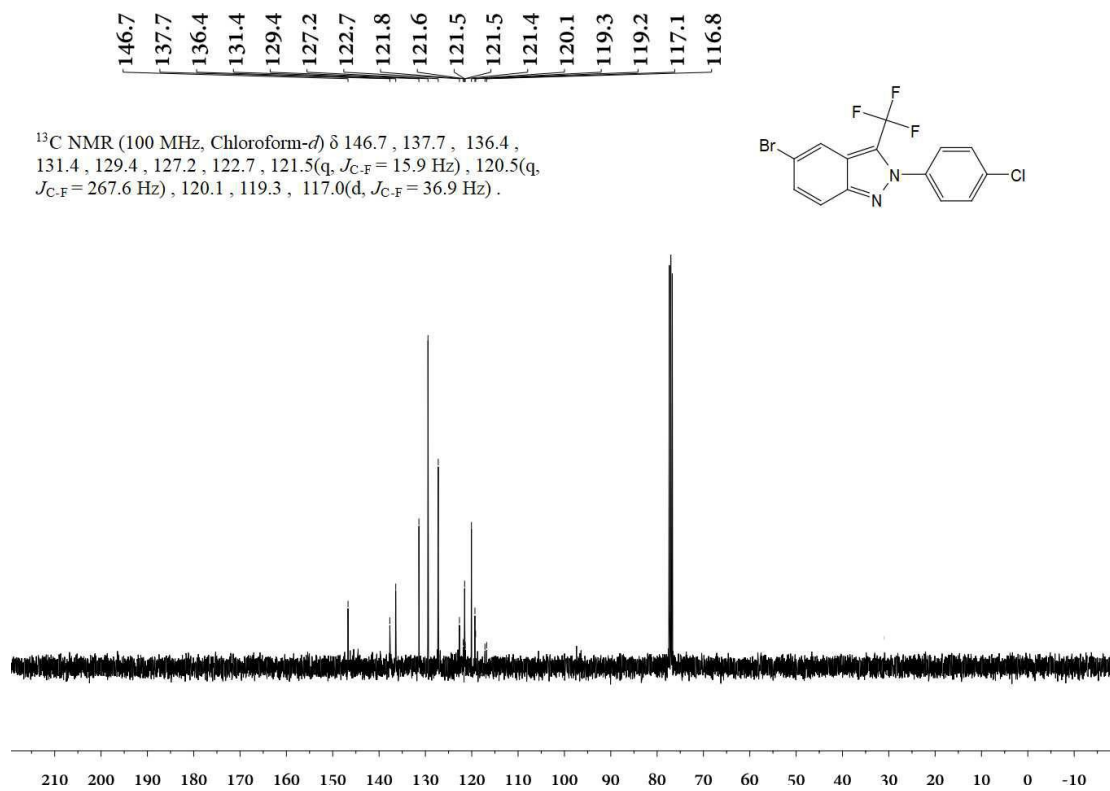


Figure S64.  $^1\text{H}$  NMR of 5-bromo-2-(4-chlorophenyl)-3-(trifluoromethyl)-2H-indazole (**2v**)





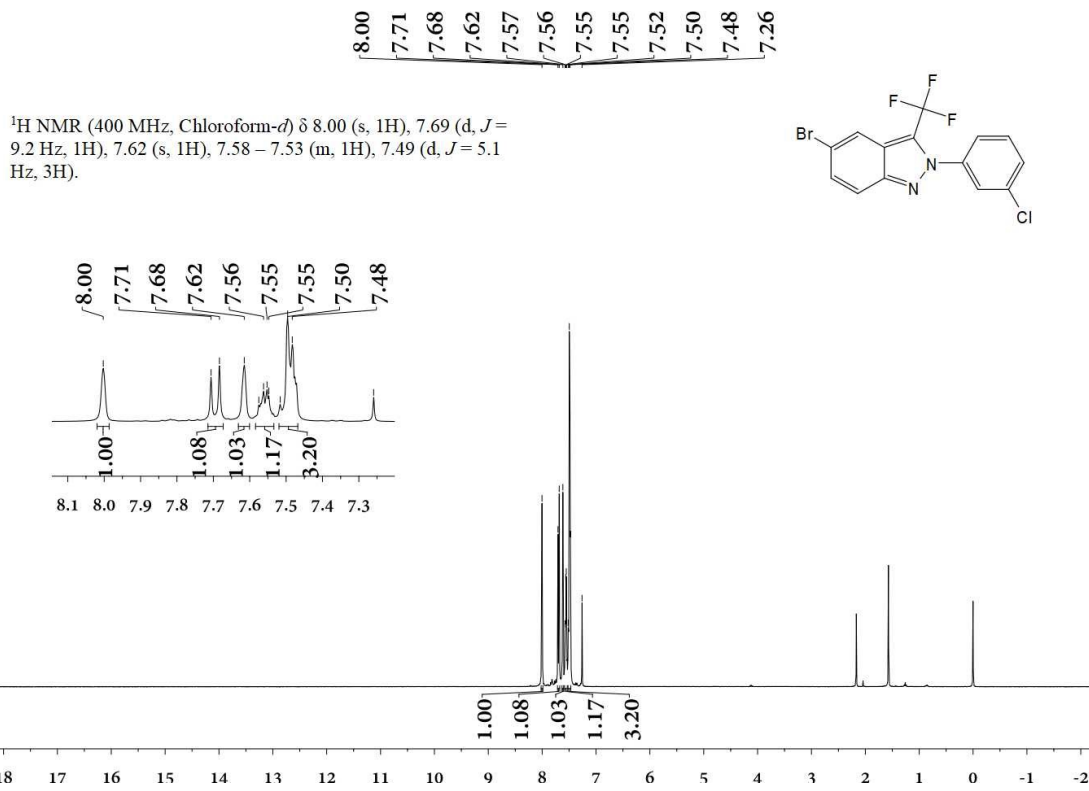


Figure S67. <sup>1</sup>H NMR of 5-bromo-2-(3-chlorophenyl)-3-(trifluoromethyl)-2H-indazole (**2w**)

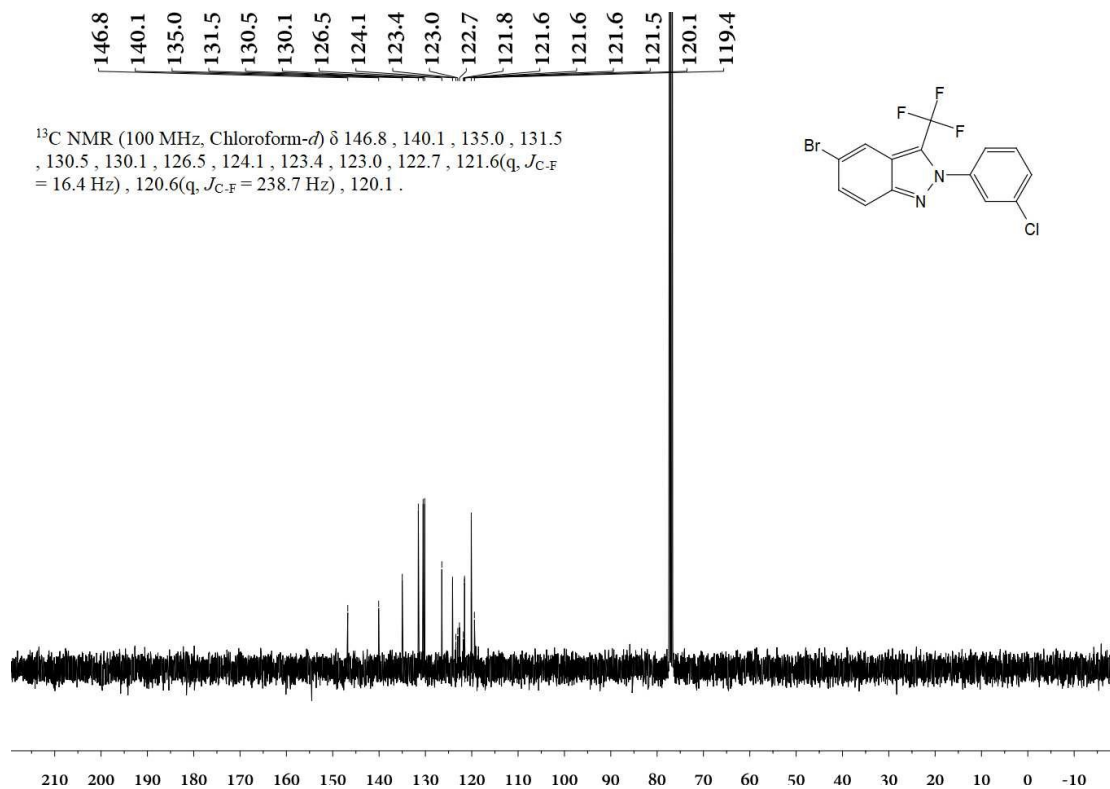


Figure S68. <sup>13</sup>C NMR of 5-bromo-2-(3-chlorophenyl)-3-(trifluoromethyl)-2H-indazole (**2w**)

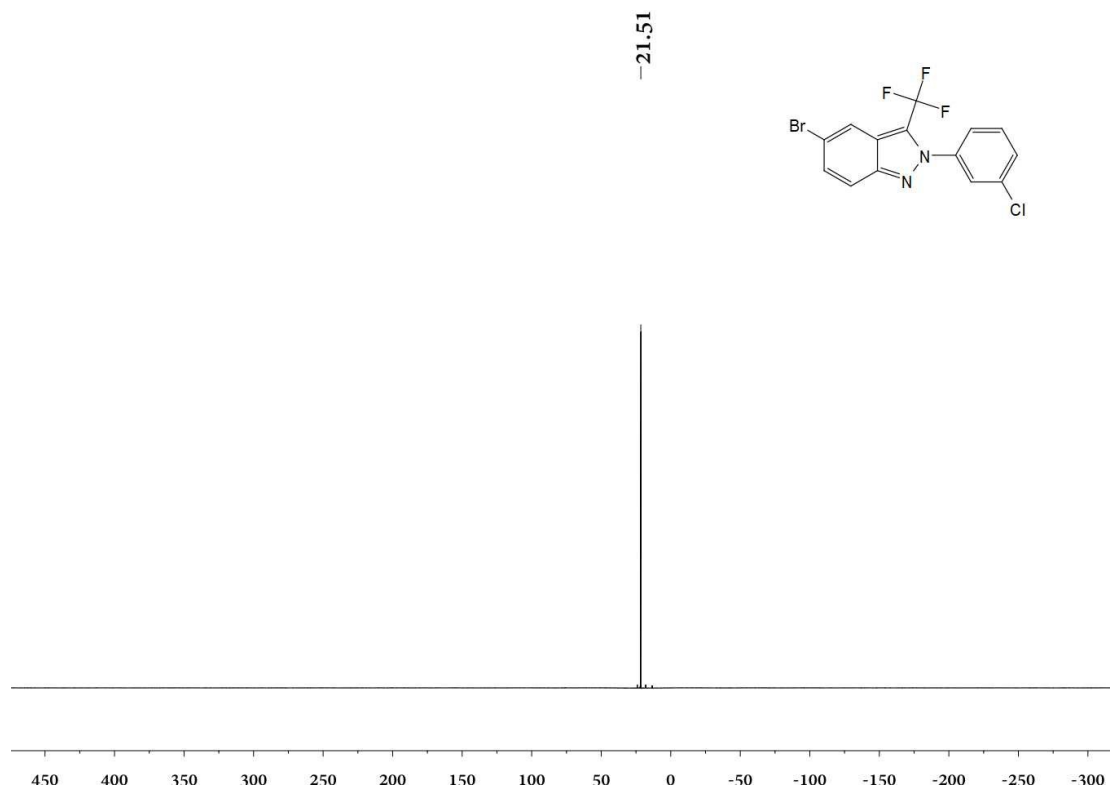


Figure S69.  $^{13}\text{C}$  NMR of 5-bromo-2-(3-chlorophenyl)-3-(trifluoromethyl)-2H-indazole (**2w**)

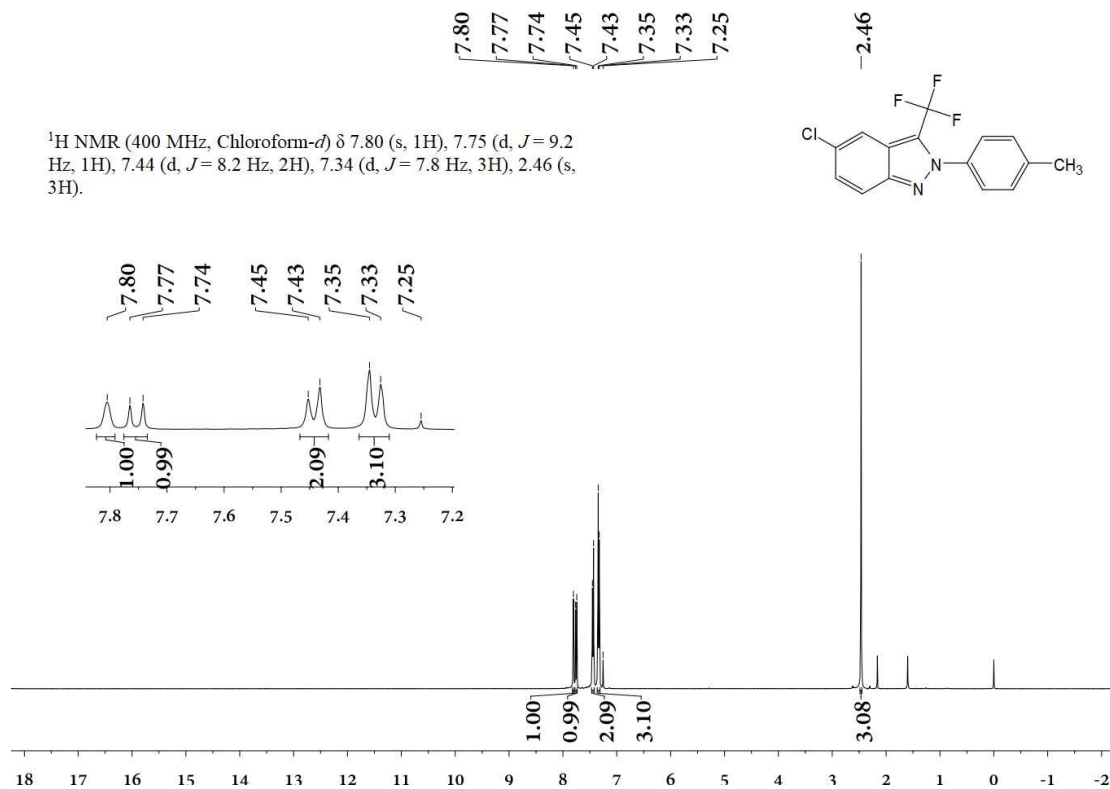


Figure S70.  $^1\text{H}$  NMR of 5-chloro-2-(p-tolyl)-3-(trifluoromethyl)-2H-indazole (**2x**)

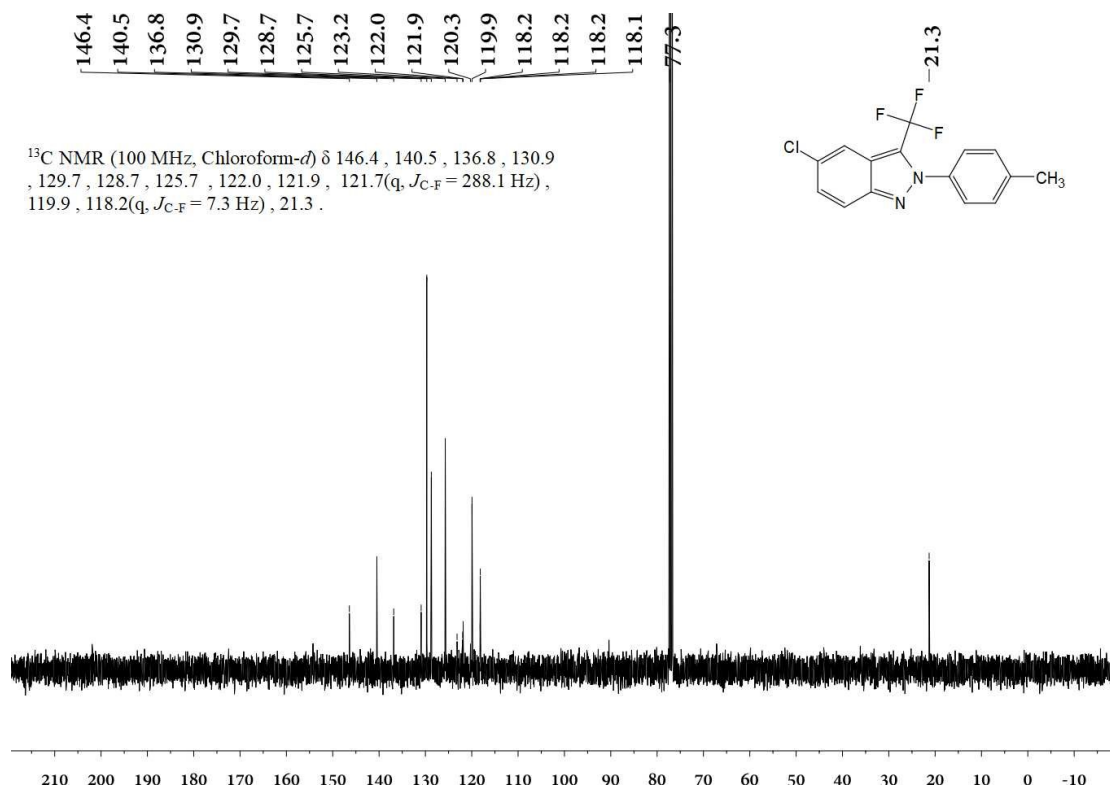


Figure S71. <sup>13</sup>C NMR of 5-chloro-2-(p-tolyl)-3-(trifluoromethyl)-2H-indazole (**2x**)

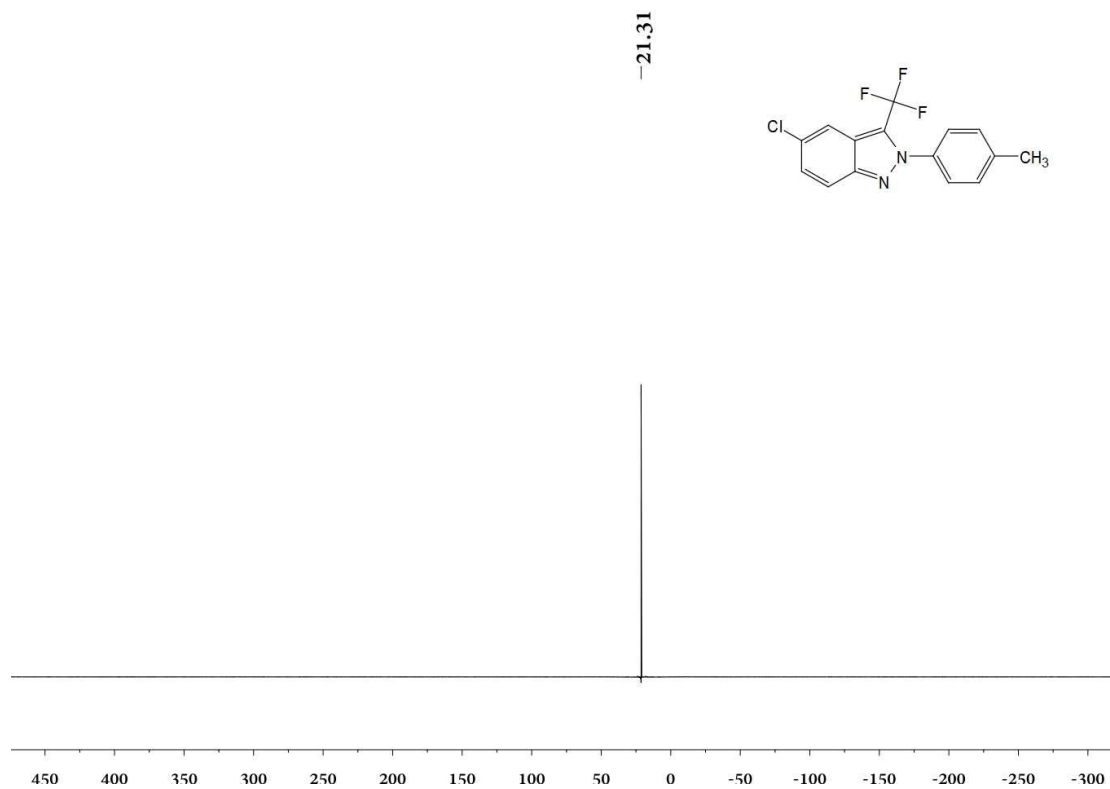


Figure S72. <sup>19</sup>F NMR of 5-chloro-2-(p-tolyl)-3-(trifluoromethyl)-2H-indazole (**2x**)

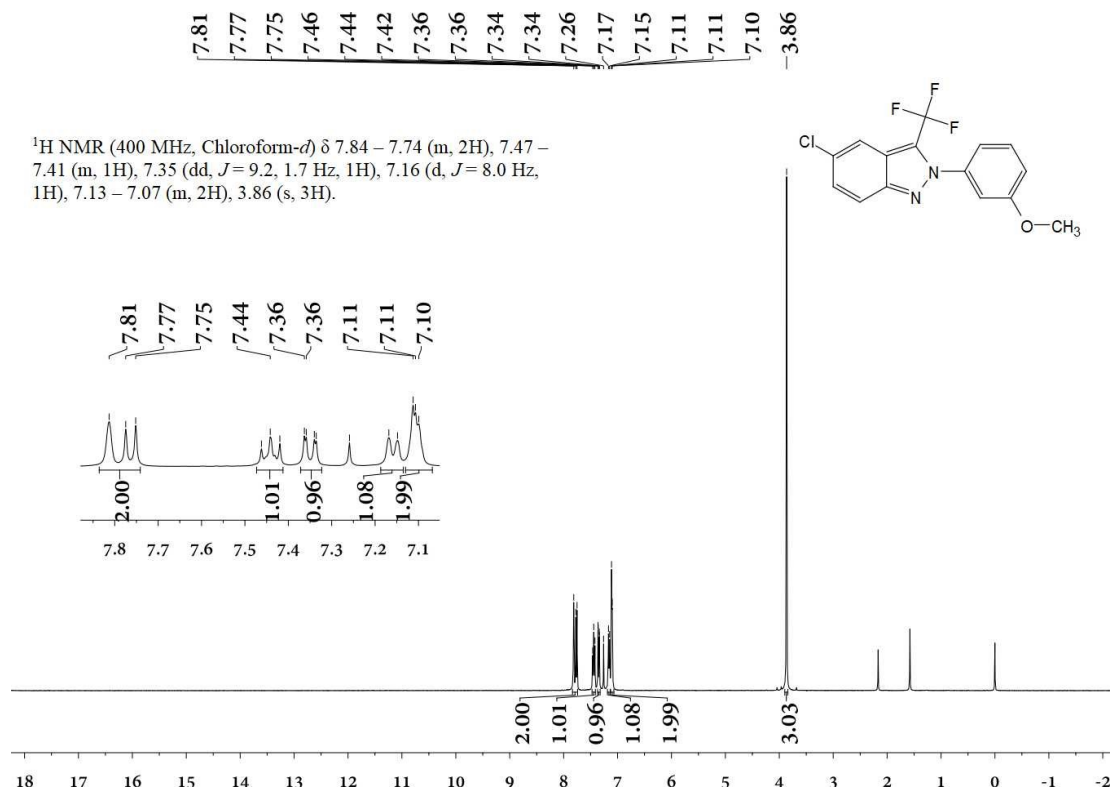


Figure S73. <sup>1</sup>H NMR of 5-chloro-2-(3-methoxyphenyl)-3-(trifluoromethyl)-2H-indazole (**2y**)

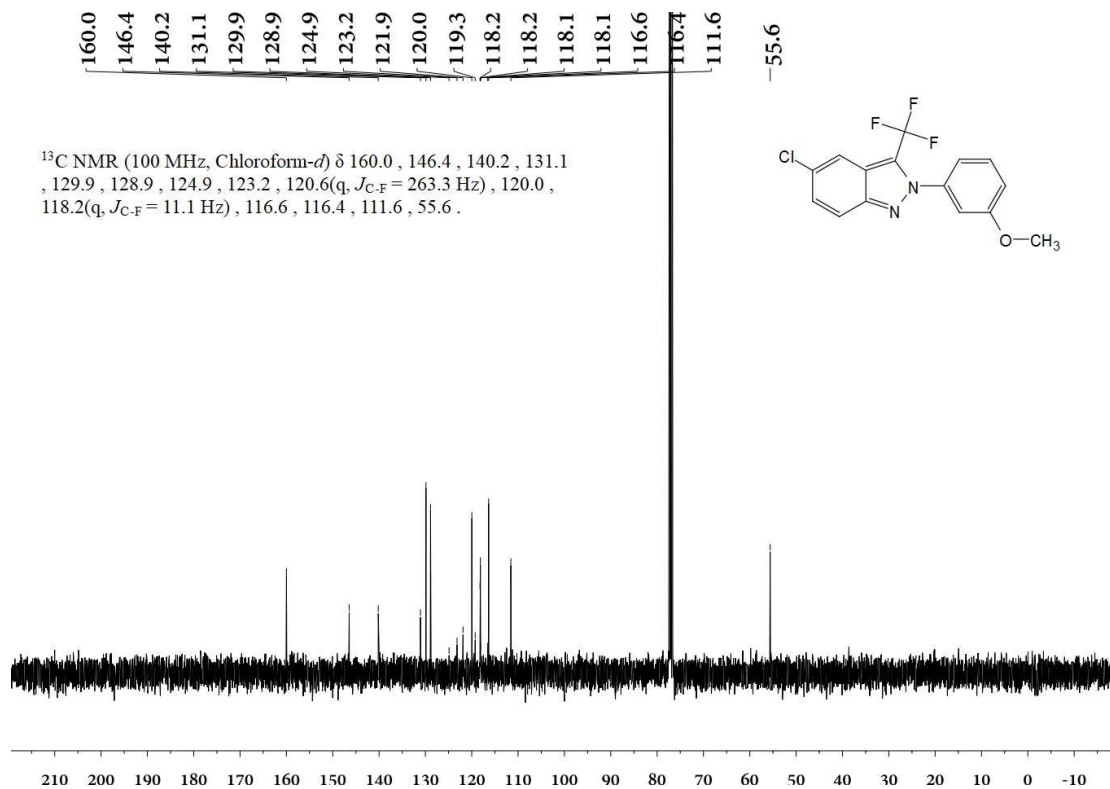


Figure S74. <sup>13</sup>C NMR of 5-chloro-2-(3-methoxyphenyl)-3-(trifluoromethyl)-2H-indazole (**2y**)

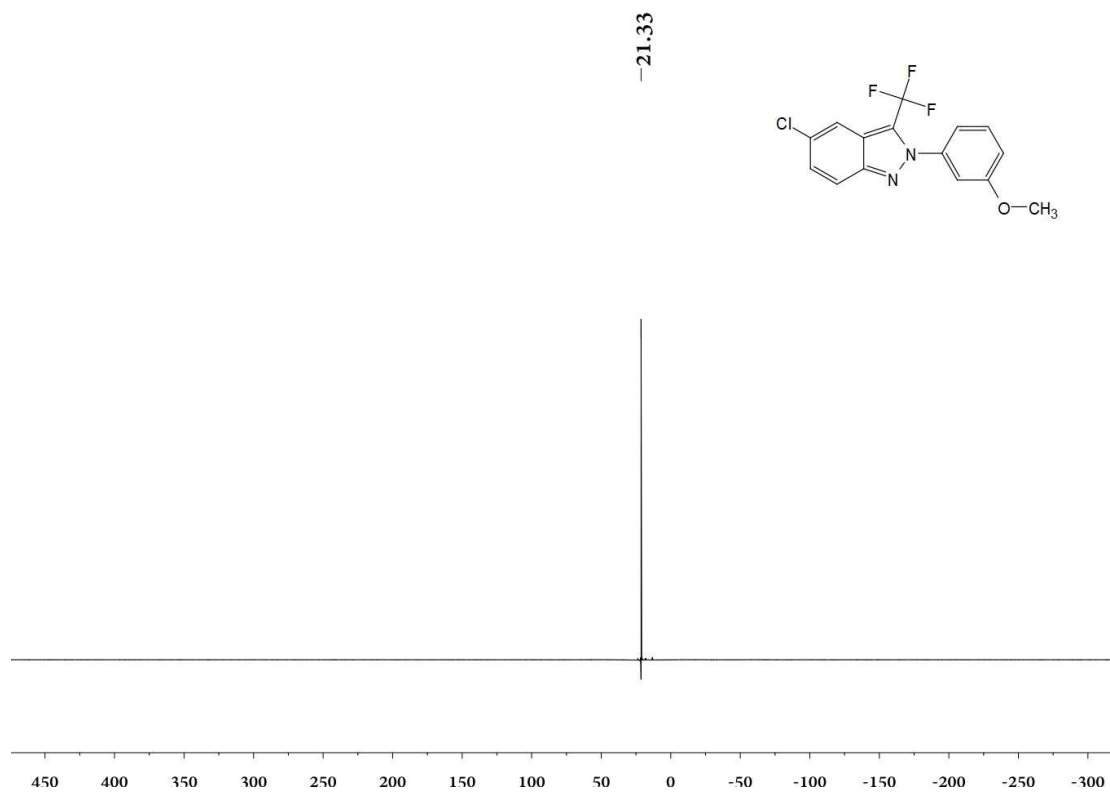


Figure S75.  $^{19}\text{F}$  NMR of 5-chloro-2-(3-methoxyphenyl)-3-(trifluoromethyl)-2H-indazole (**2y**)

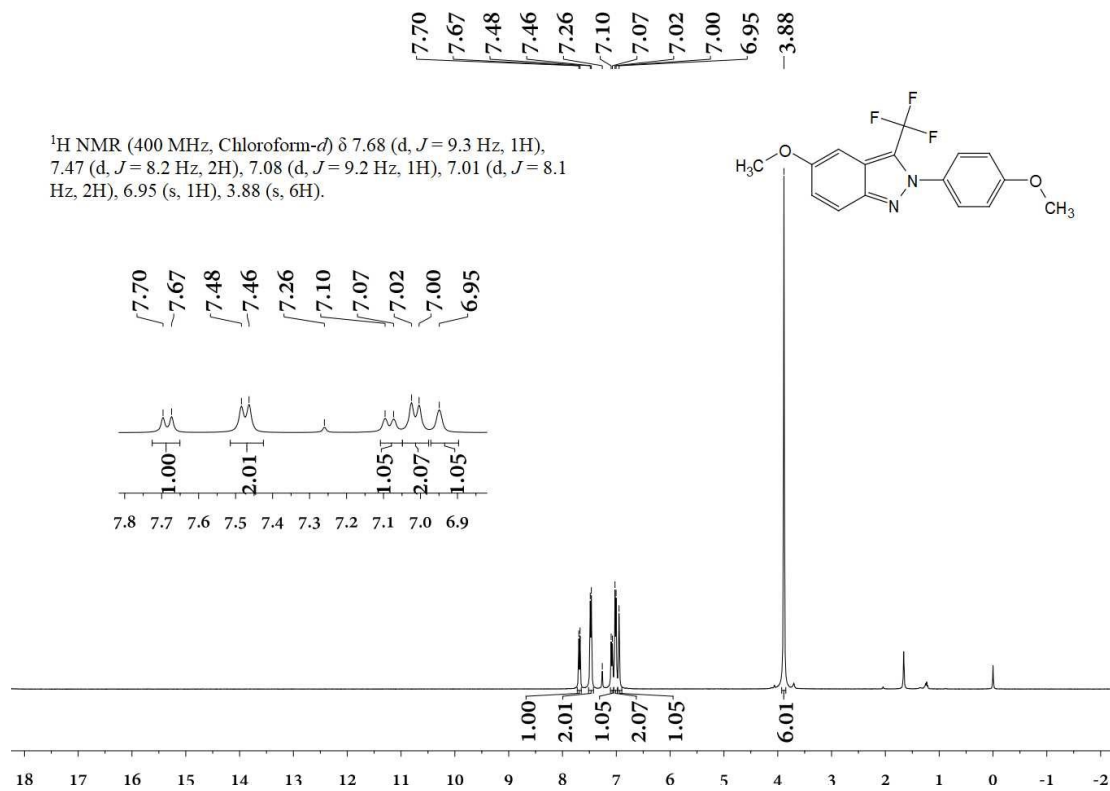


Figure S76.  $^1\text{H}$  NMR of 5-methoxy-2-(4-methoxyphenyl)-3-(trifluoromethyl)-2H-indazole (**2z**)

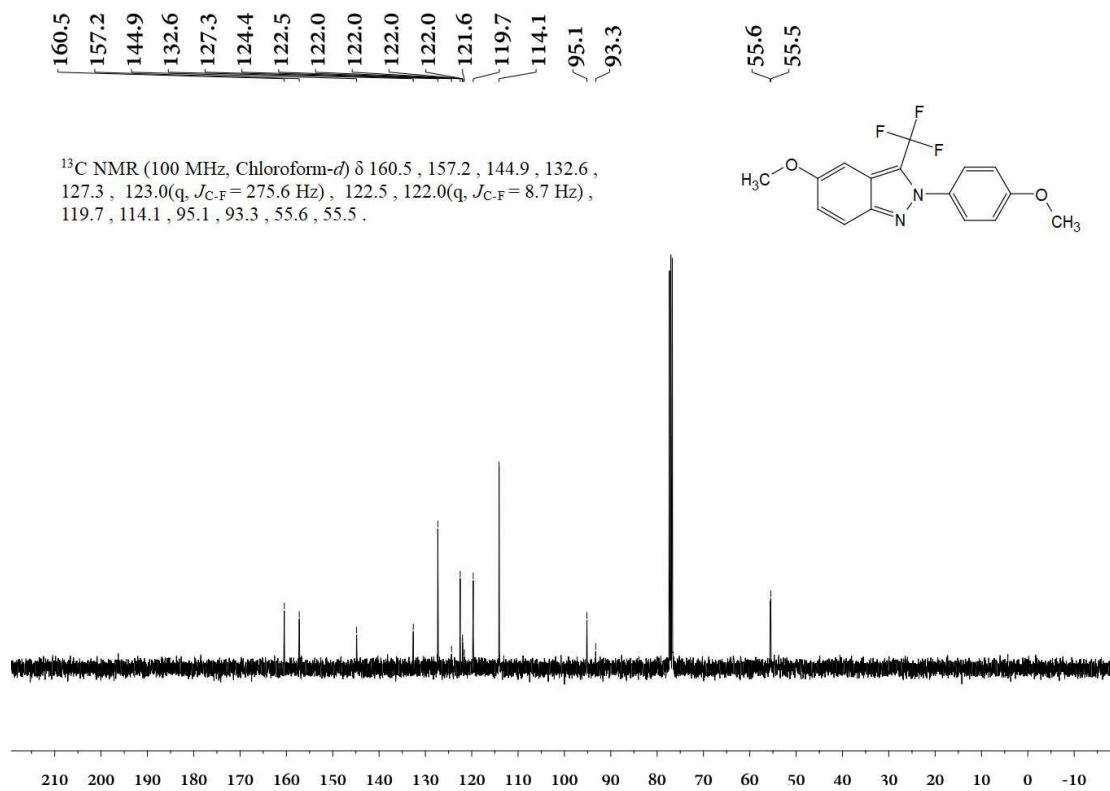


Figure S77. <sup>13</sup>C NMR of 5-methoxy-2-(4-methoxyphenyl)-3-(trifluoromethyl)-2H-indazole (**2z**)

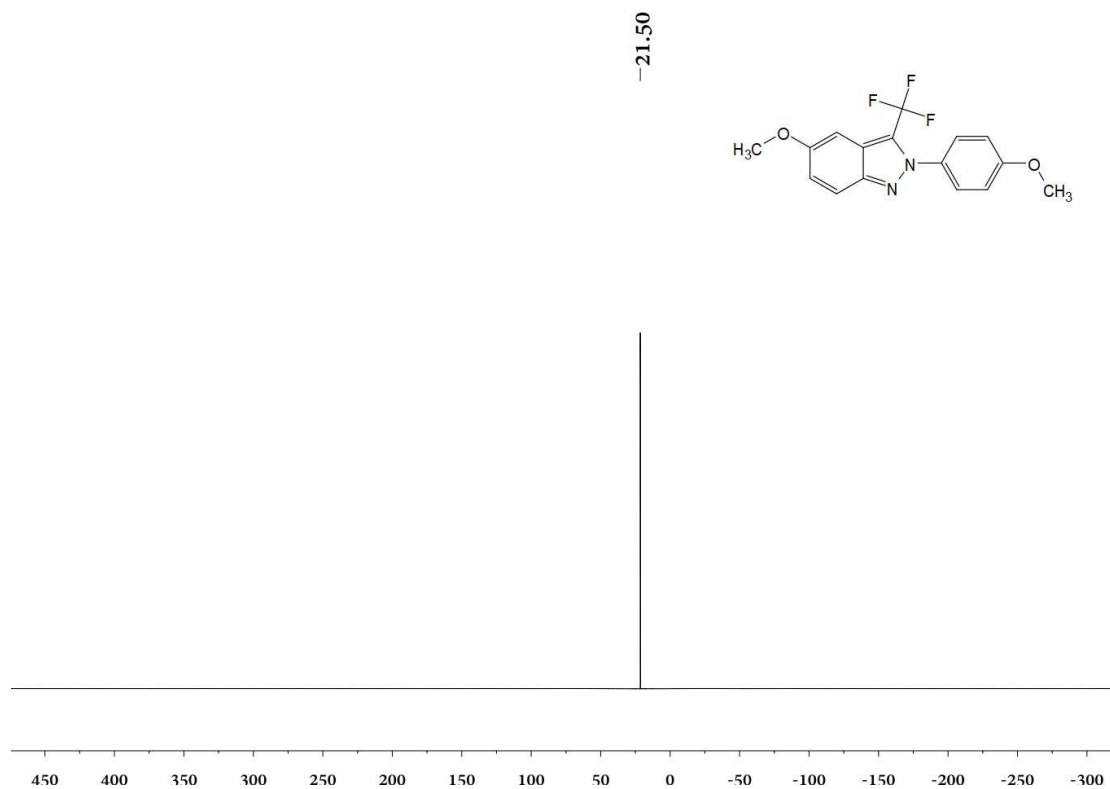


Figure S78. <sup>19</sup>F NMR of 5-methoxy-2-(4-methoxyphenyl)-3-(trifluoromethyl)-2H-indazole (**2z**)

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 10.92 (s, 1H), 8.21 (s, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H).

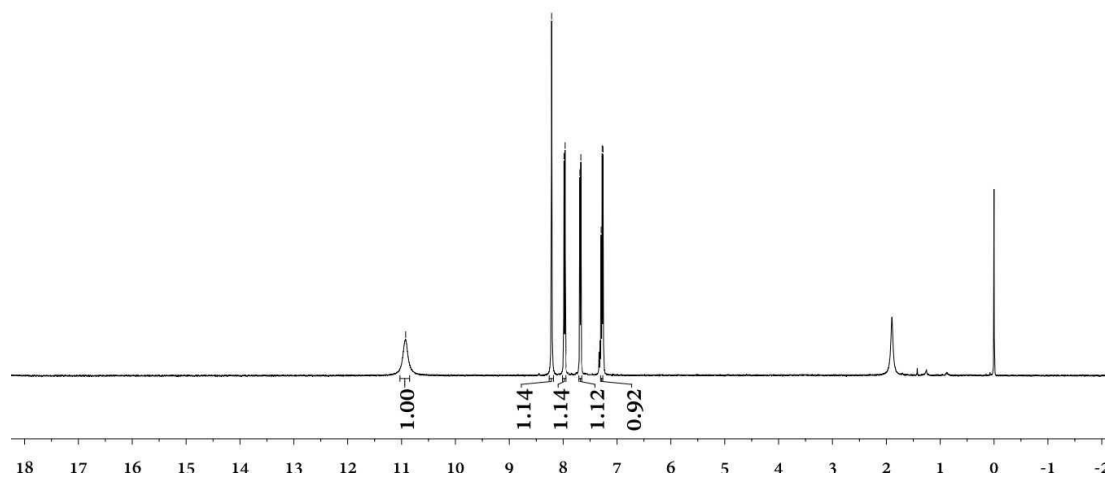


Figure S79. <sup>1</sup>H NMR of 3-(trifluoromethyl)-2H-indazole (**2aa**)

<sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 135.4 (d, *J*<sub>C-F</sub> = 15.8 Hz), 127.9, 125.2, 124.6 (q, *J*<sub>C-F</sub> = 4.4 Hz), 124.3 (q, *J*<sub>C-F</sub> = 269.5 Hz), 120.5, 112.9 (q, *J*<sub>C-F</sub> = 34.0 Hz), 110.2.

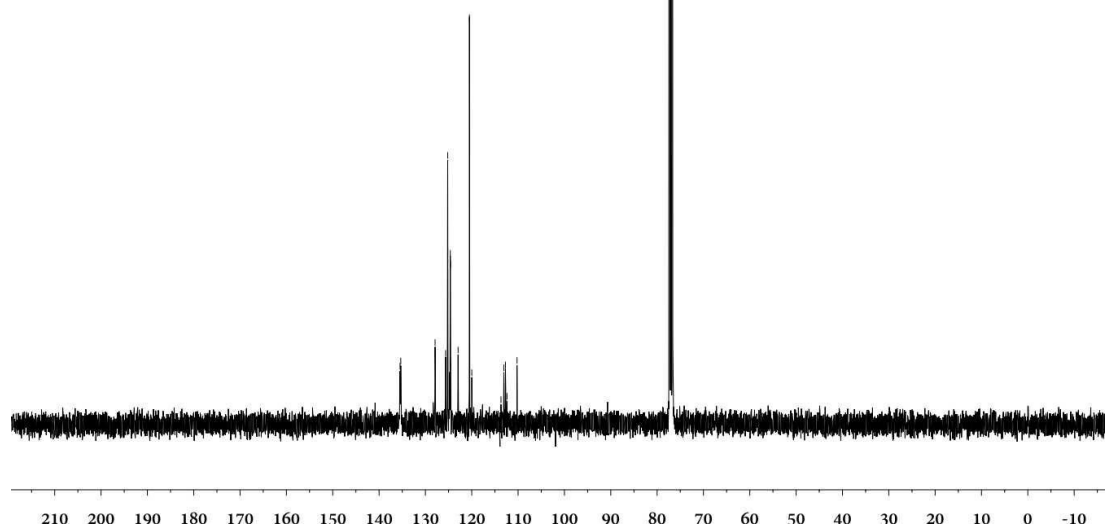


Figure S80. <sup>13</sup>C NMR of 3-(trifluoromethyl)-2H-indazole (**2aa**)

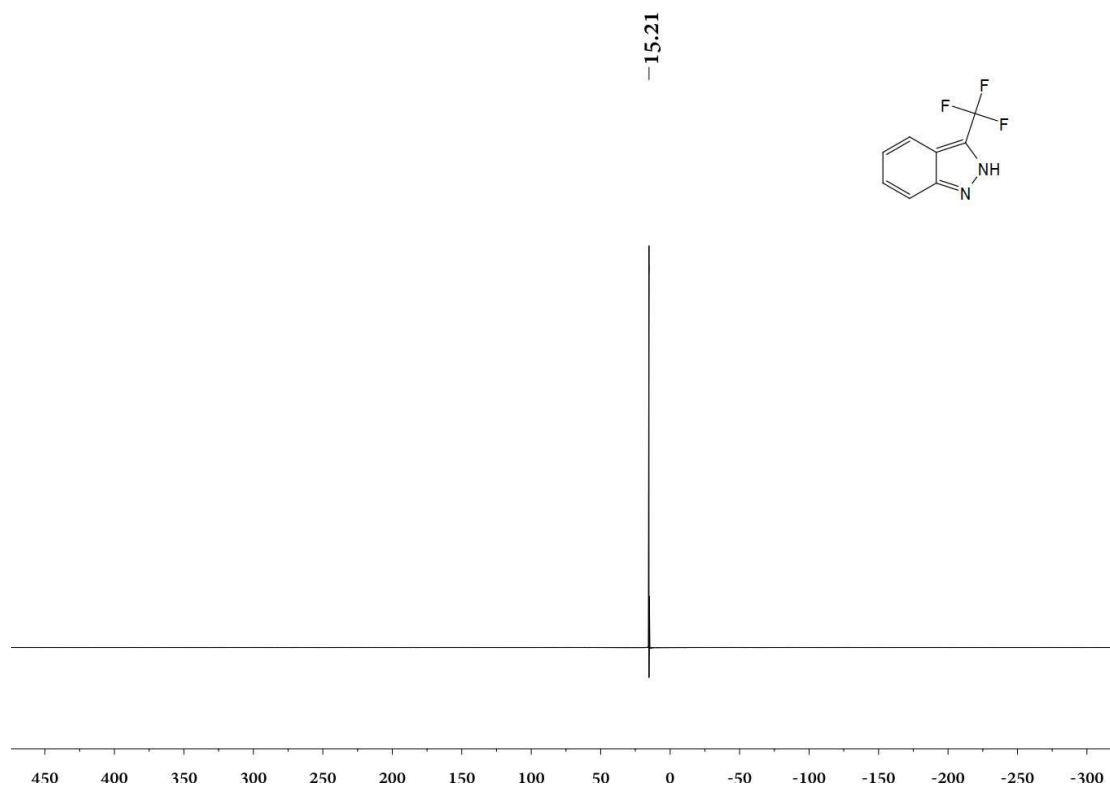


Figure S81.  $^{19}\text{F}$  NMR of 3-(trifluoromethyl)-2H-indazole (**2aa**)

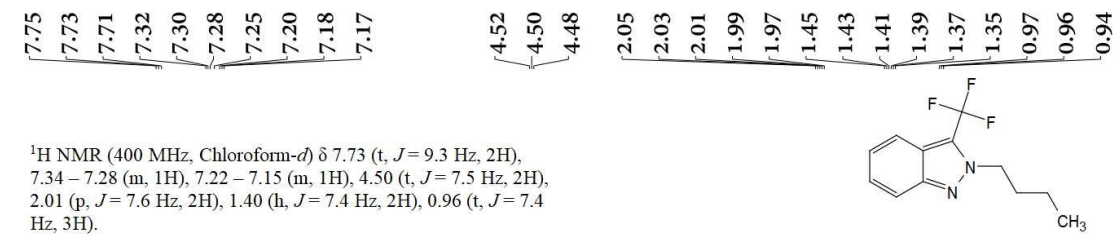
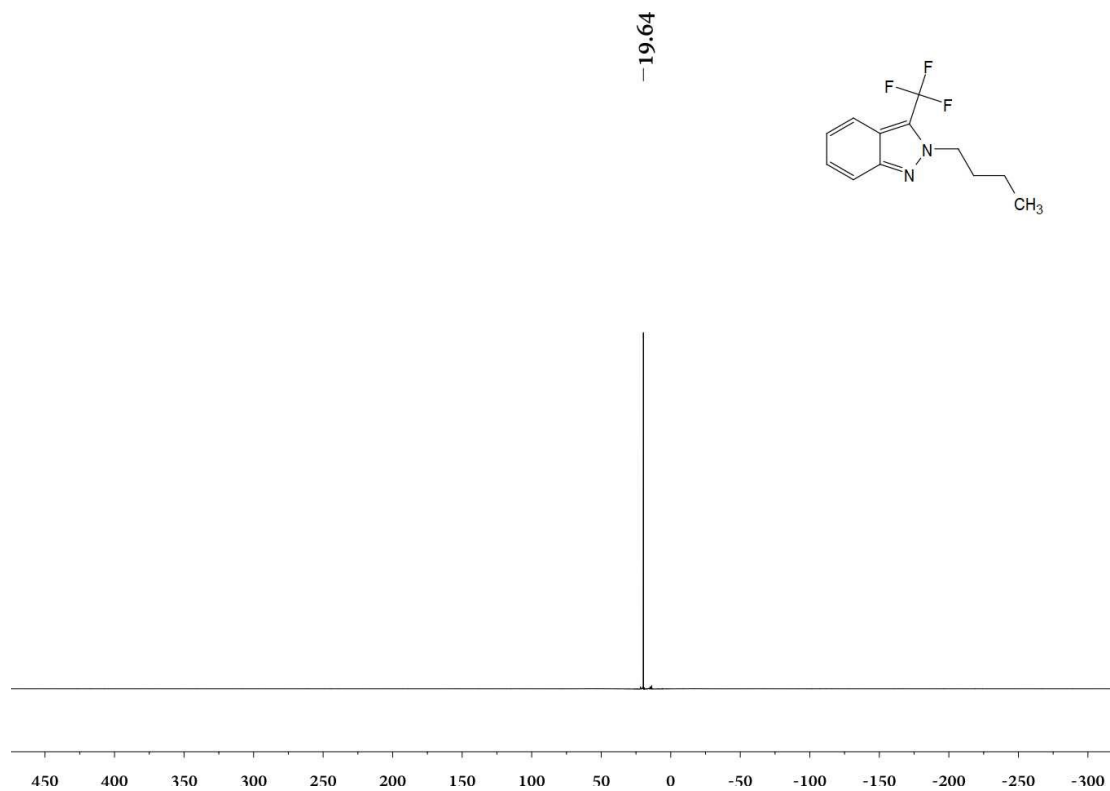
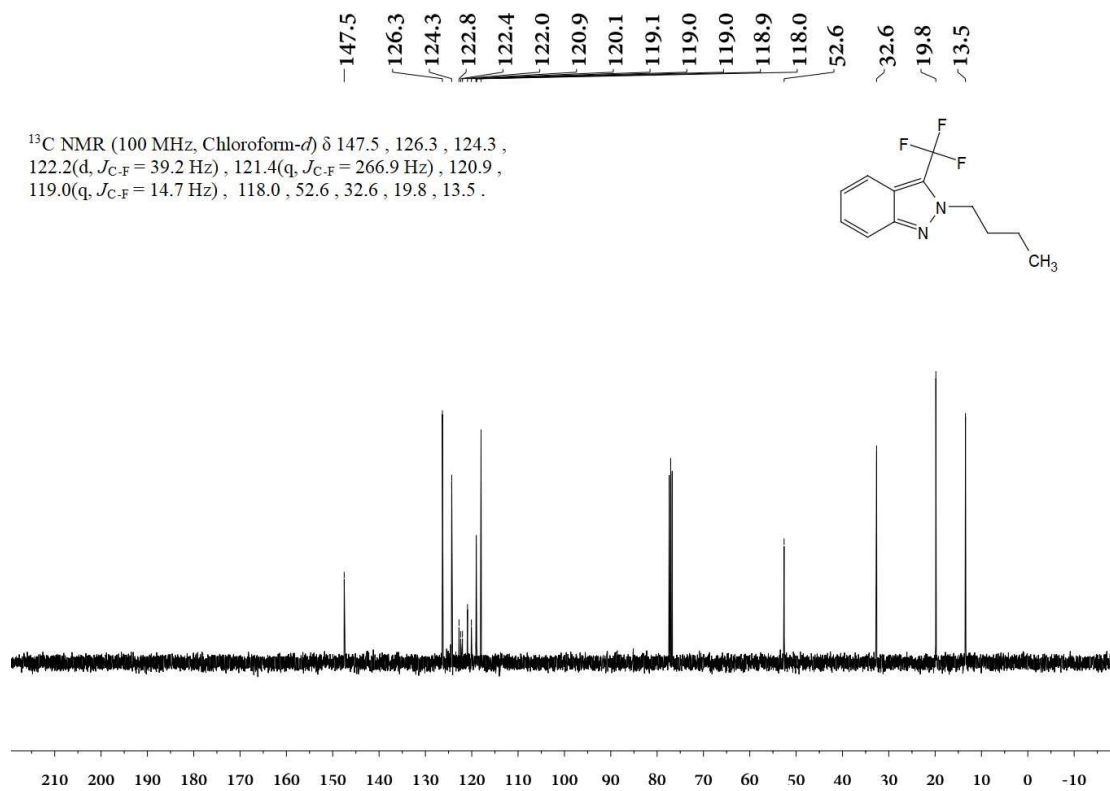


Figure S82.  $^1\text{H}$  NMR of 2-butyl-3-(trifluoromethyl)-2H-indazole (**2ab**)





7.81  
7.79  
7.77  
7.75  
7.36  
7.34  
7.32  
7.27  
7.24  
7.22  
7.20  
4.59  
4.56  
4.53  
2.26  
2.23  
2.20  
2.17  
2.13  
2.10  
2.00  
1.97  
1.80  
1.77  
1.54  
1.51  
1.48  
1.44  
1.40  
1.37

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.78 (dd,  $J = 15.5, 8.6$  Hz, 2H), 7.38 – 7.30 (m, 1H), 7.26 – 7.17 (m, 1H), 4.56 (t,  $J = 11.4$  Hz, 1H), 2.18 (dt,  $J = 40.3, 11.4$  Hz, 4H), 1.98 (d,  $J = 13.1$  Hz, 2H), 1.79 (d,  $J = 12.1$  Hz, 1H), 1.47 (dt,  $J = 30.9, 15.1$  Hz, 3H).

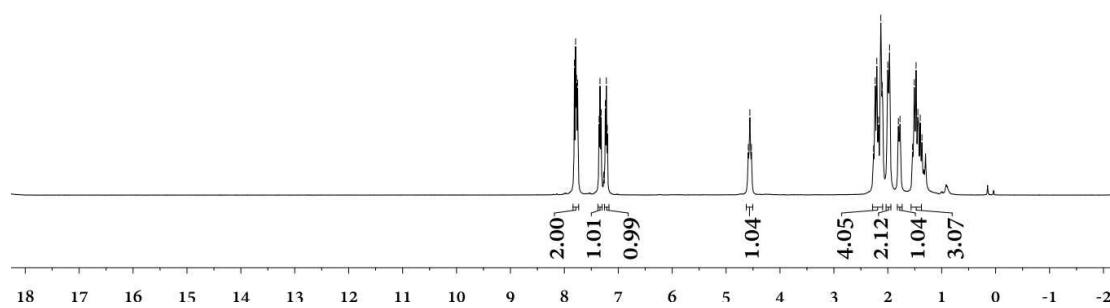


Figure S85.  $^1\text{H}$  NMR of 2-cyclohexyl-3-(trifluoromethyl)-2H-indazole (**2ac**)

147.4  
126.1  
124.3  
122.9  
121.3  
120.4  
120.3  
119.2  
119.1  
119.1  
119.1  
118.2  
61.8  
33.5  
25.6  
25.1

$^{13}\text{C}$  NMR (100 MHz, Chloroform-*d*)  $\delta$  147.4, 126.1, 124.3, 121.6(q,  $J_{\text{C-F}} = 266.8$  Hz), 121.3, 120.4, 119.2(q,  $J_{\text{C-F}} = 15.3$  Hz), 118.2, 61.9, 33.5, 25.6, 25.1.

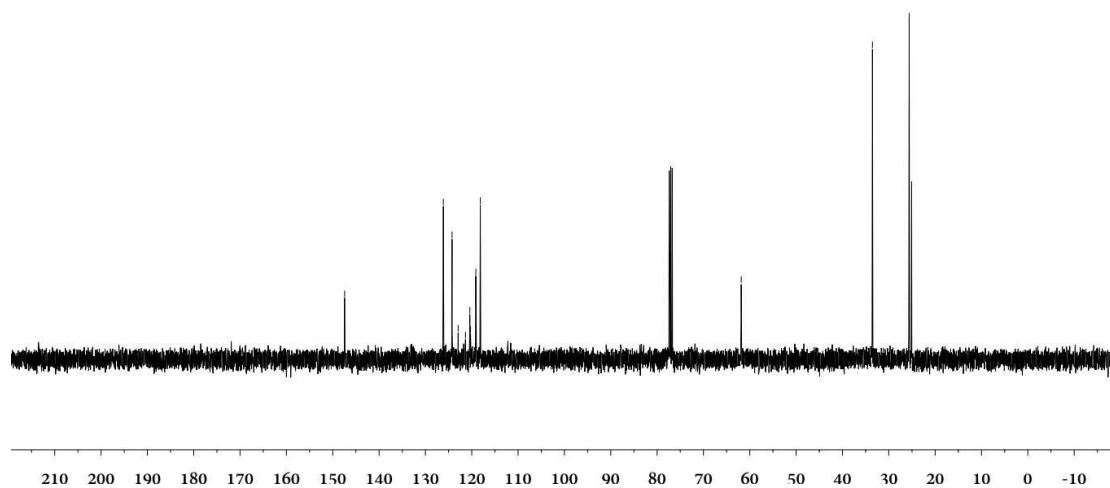
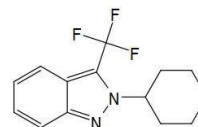


Figure S86.  $^{13}\text{C}$  NMR of 2-cyclohexyl-3-(trifluoromethyl)-2H-indazole (**2ac**)

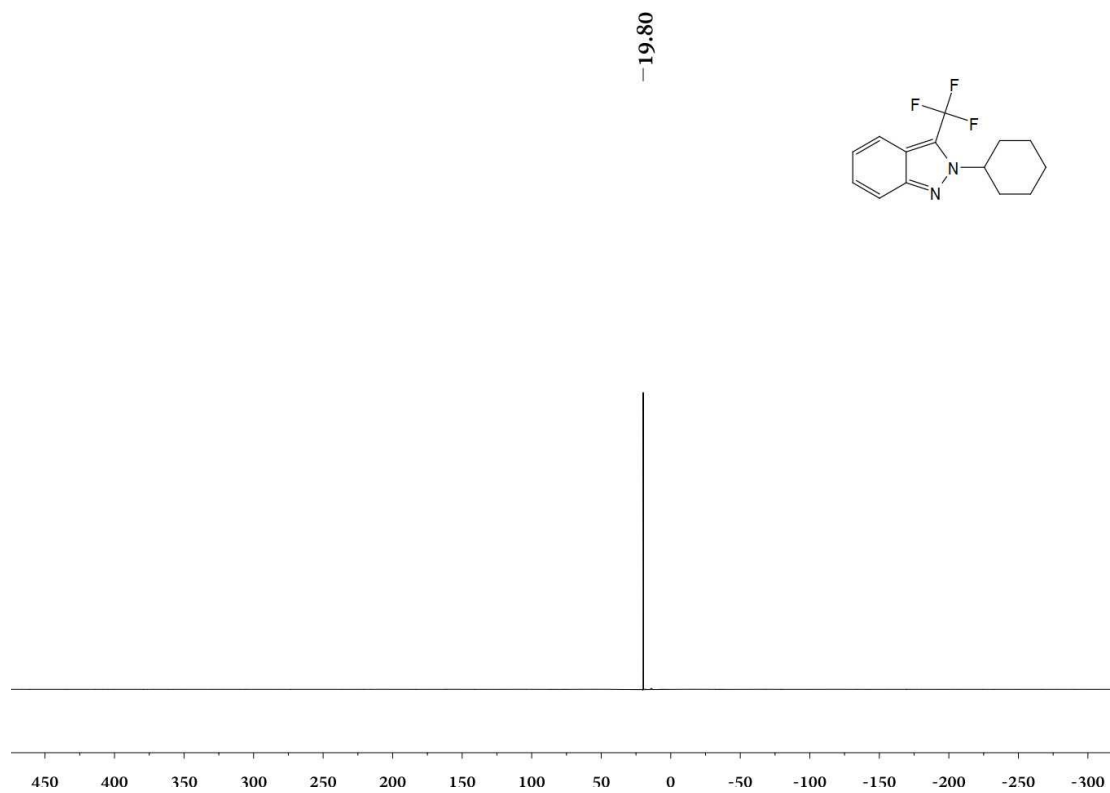


Figure S87.  $^{19}\text{F}$  NMR of 2-cyclohexyl-3-(trifluoromethyl)-2H-indazole (**2ac**)

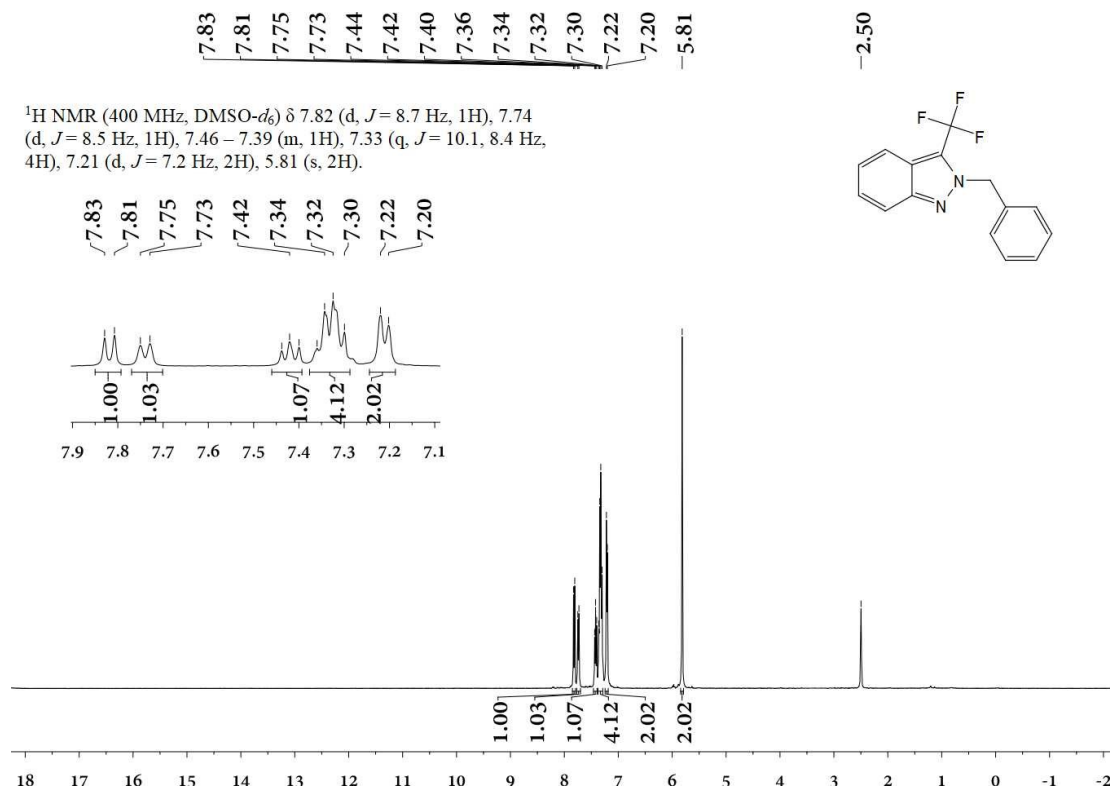


Figure S88.  $^1\text{H}$  NMR of 2-benzyl-3-(trifluoromethyl)-2H-indazole (**2ad**)

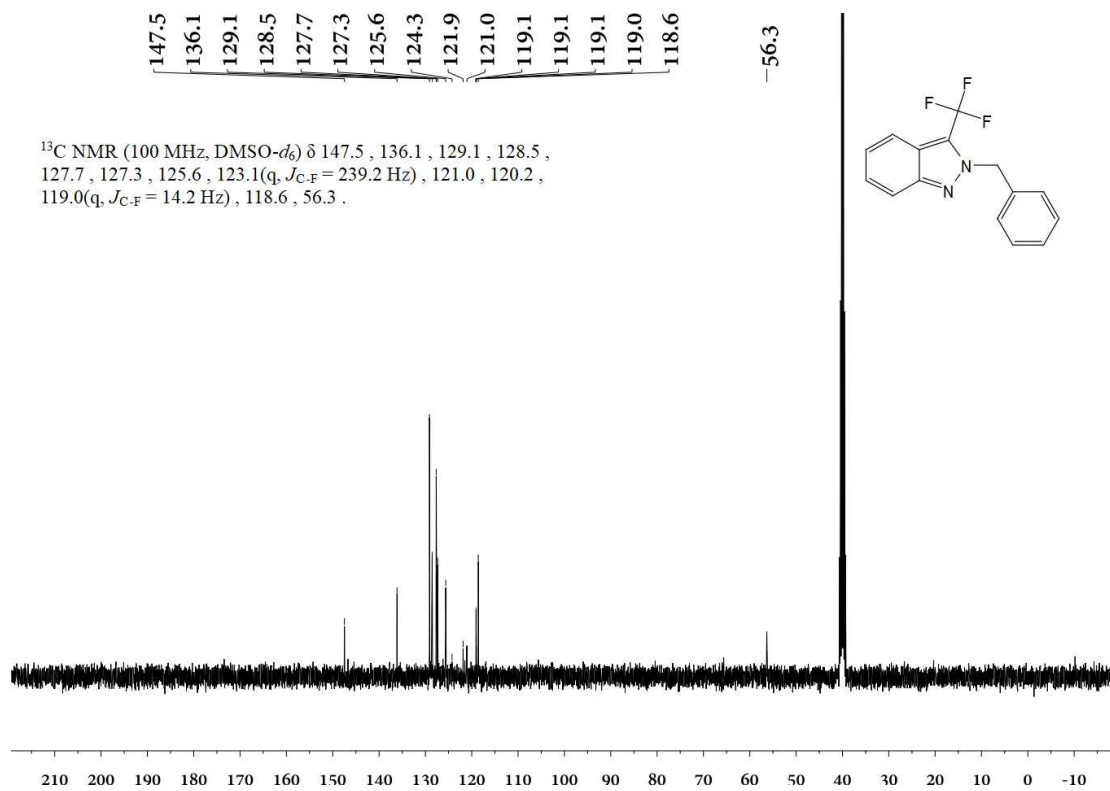


Figure S89. <sup>13</sup>C NMR of 2-(isoquinolin-1-yl)-6-methylbenzonitrile (**2ad**)



Figure S90. <sup>19</sup>F NMR of 2-(isoquinolin-1-yl)-6-methylbenzonitrile (**2ad**)

8.10 8.08 7.99 7.97 7.95 7.94 7.93 7.70 7.68 7.63 7.61 7.60 7.59 7.57 7.55 7.52 7.50 7.48 7.46 7.41 7.39 7.37 7.27 7.16 7.13

$^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.09 (d,  $J = 8.2$  Hz, 1H), 8.01 – 7.91 (m, 3H), 7.69 (d,  $J = 7.2$  Hz, 1H), 7.59 (dt,  $J = 18.5$ , 7.9 Hz, 2H), 7.49 (q,  $J = 7.3$  Hz, 2H), 7.42 – 7.35 (m, 1H), 7.15 (d,  $J = 8.4$  Hz, 1H).

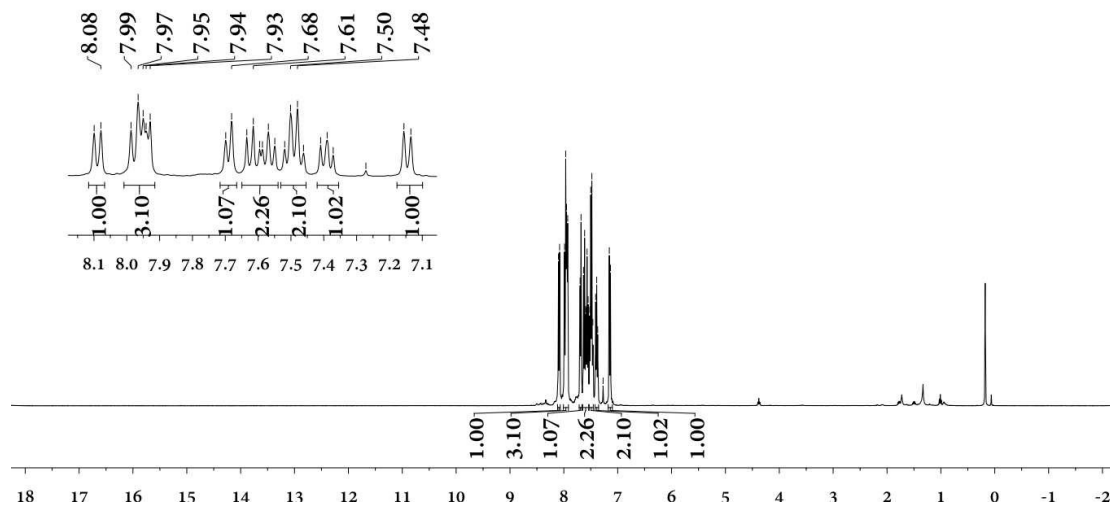
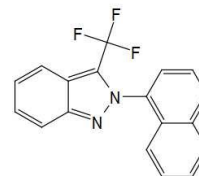


Figure S91.  $^1\text{H NMR}$  of 2-(naphthalen-1-yl)-3-(trifluoromethyl)-2H-indazole (**2ae**)

148.4 135.6 133.9 131.0 130.3 128.1 127.9 127.4 127.0 125.8 125.4 125.3 125.2 124.6 122.3 122.2 121.0 119.5 119.5 119.4 119.4 119.3 118.6

$^{13}\text{C NMR}$  (100 MHz, Chloroform-*d*)  $\delta$  148.4, 135.6, 133.9, 131.0, 130.3, 128.1, 127.9, 127.4, 127.0, 125.8, 125.4, 125.3 (d,  $J_{\text{C-F}} = 2.2$  Hz), 124.6, 122.3, 121.0, 120.9 (q,  $J_{\text{C-F}} = 267.6$  Hz), 119.4 (q,  $J_{\text{C-F}} = 15.2$  Hz), 118.6.

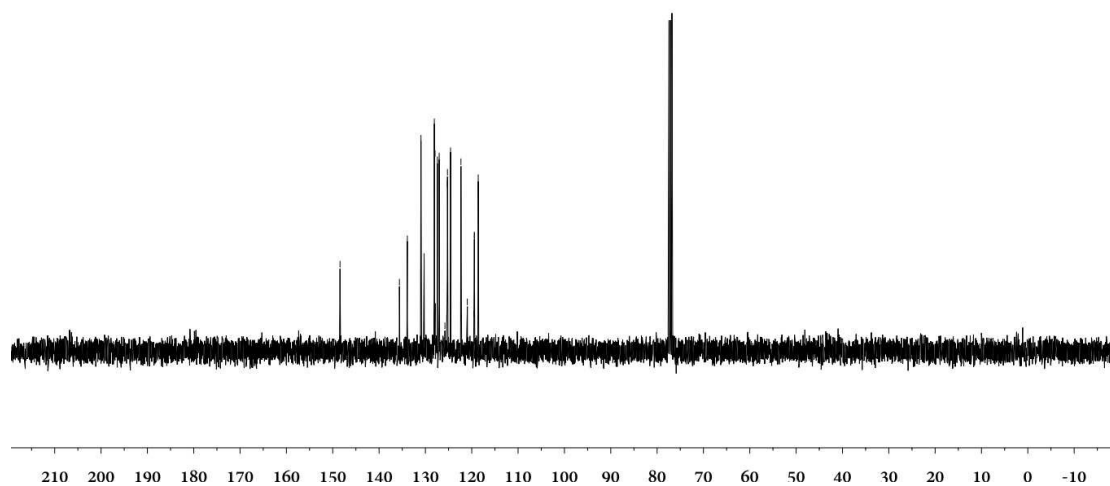
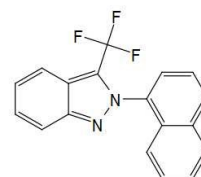


Figure S92.  $^{13}\text{C NMR}$  of 2-(naphthalen-1-yl)-3-(trifluoromethyl)-2H-indazole (**2ae**)

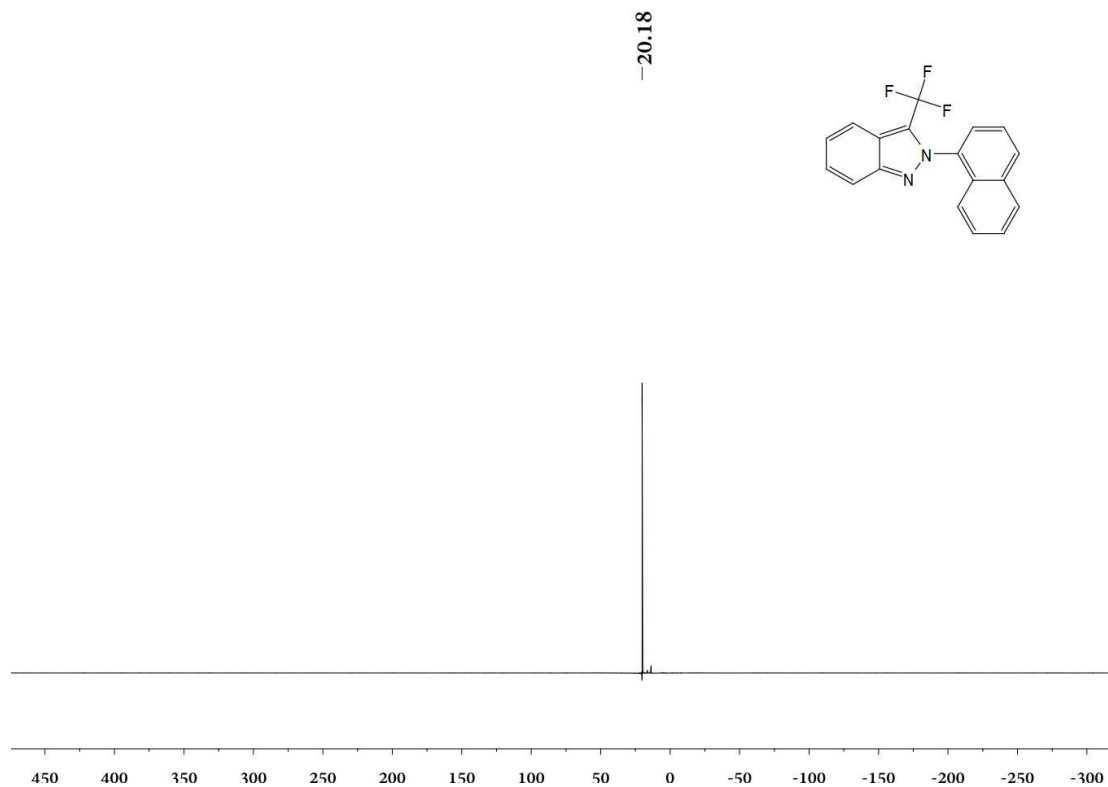
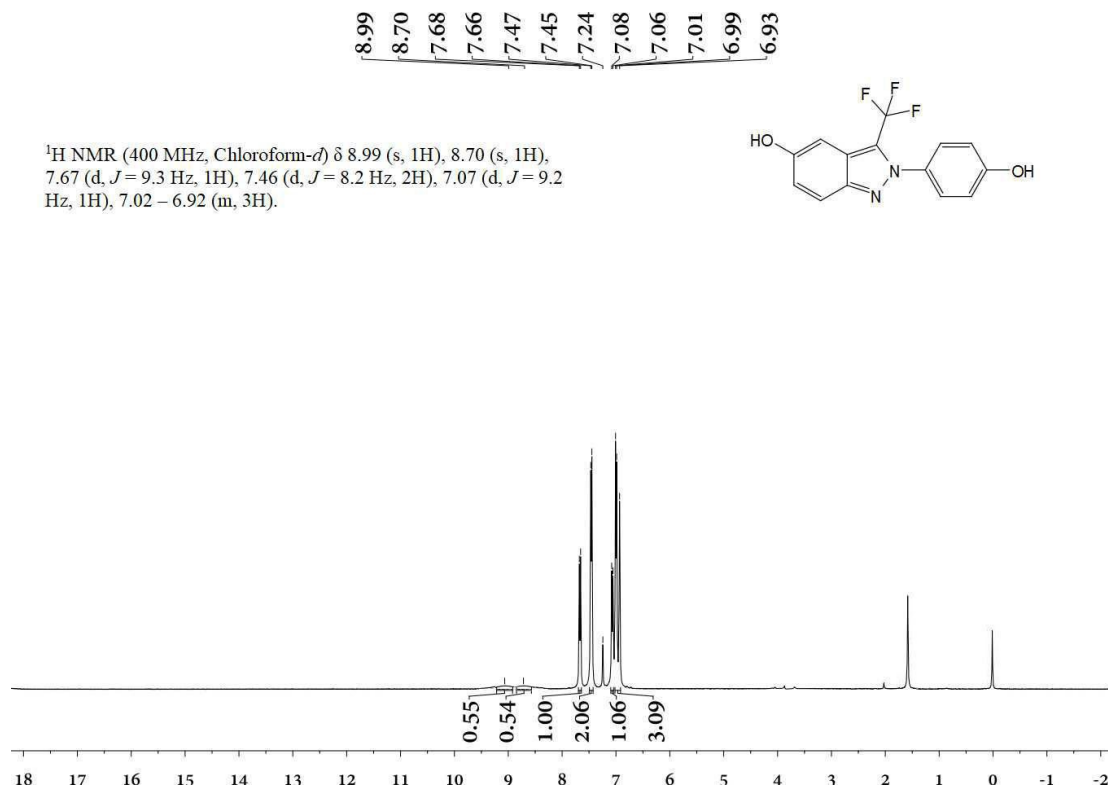


Figure S93.  $^{19}\text{F}$  NMR of 2-(naphthalen-1-yl)-3-(trifluoromethyl)-2H-indazole (**2ae**)



$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.99 (s, 1H), 8.70 (s, 1H), 7.67 (d,  $J = 9.3$  Hz, 1H), 7.46 (d,  $J = 8.2$  Hz, 2H), 7.07 (d,  $J = 9.2$  Hz, 1H), 7.02 – 6.92 (m, 3H).

Figure S94.  $^1\text{H}$  NMR of 2-(4-hydroxyphenyl)-3-(trifluoromethyl)-2H-indazol-5-ol (**highly selective ligand for the ERb**)

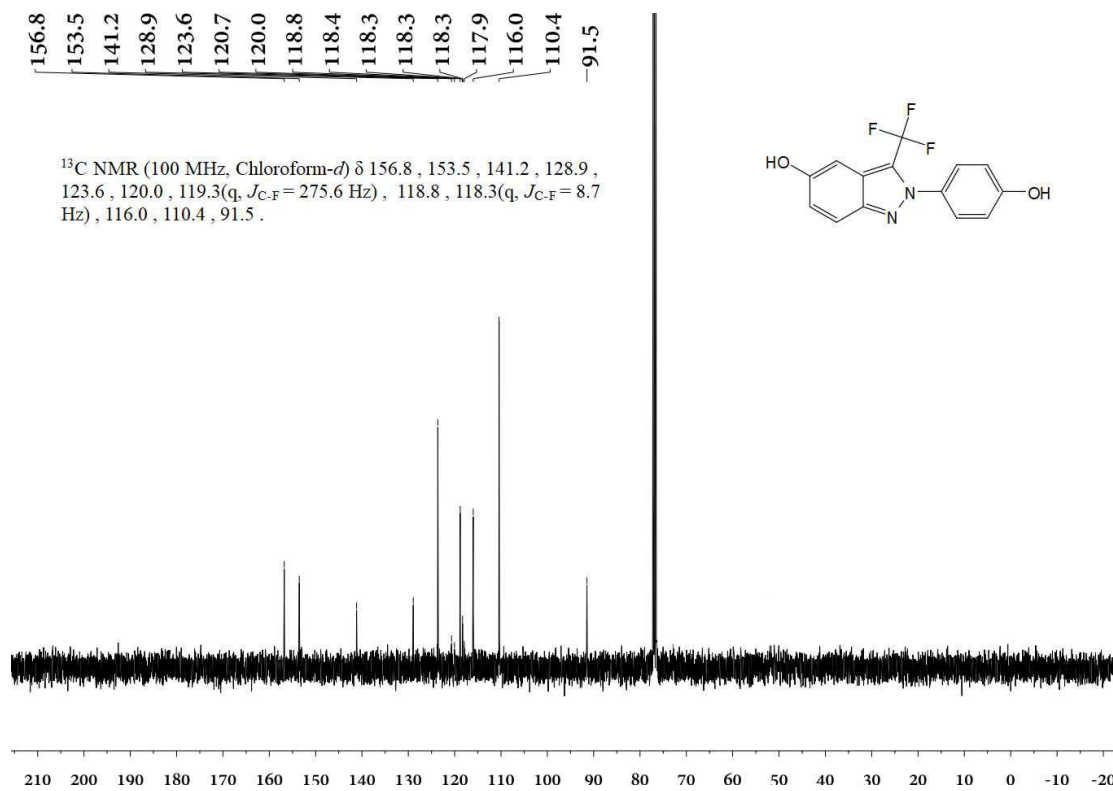


Figure S95.  $^{13}\text{C}$  NMR of 2-(4-hydroxyphenyl)-3-(trifluoromethyl)-2H-indazol-5-ol (**highly selective ligand for the ERb**)



Figure S96.  $^{19}\text{F}$  NMR of 2-(4-hydroxyphenyl)-3-(trifluoromethyl)-2H-indazol-5-ol (**highly selective ligand for the ERb**)

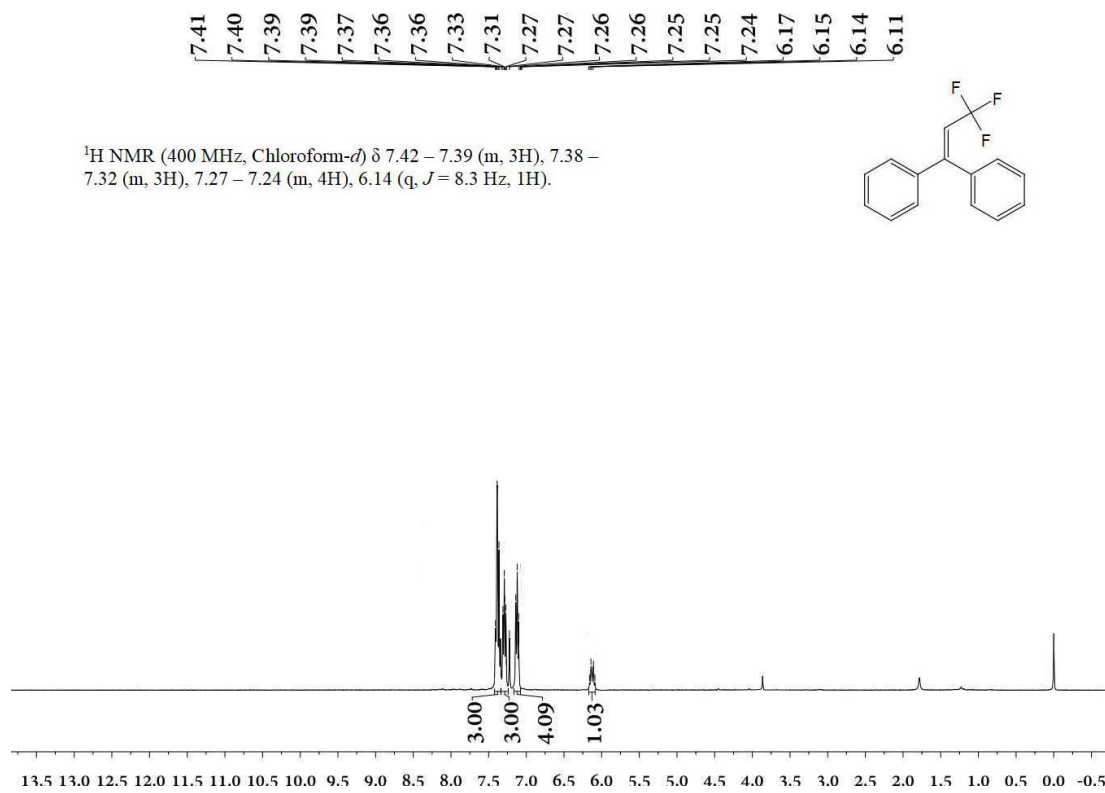


Figure S97. <sup>1</sup>H NMR of (3,3,3-trifluoroprop-1-ene-1,1-diyl)dibenzene (**3**)

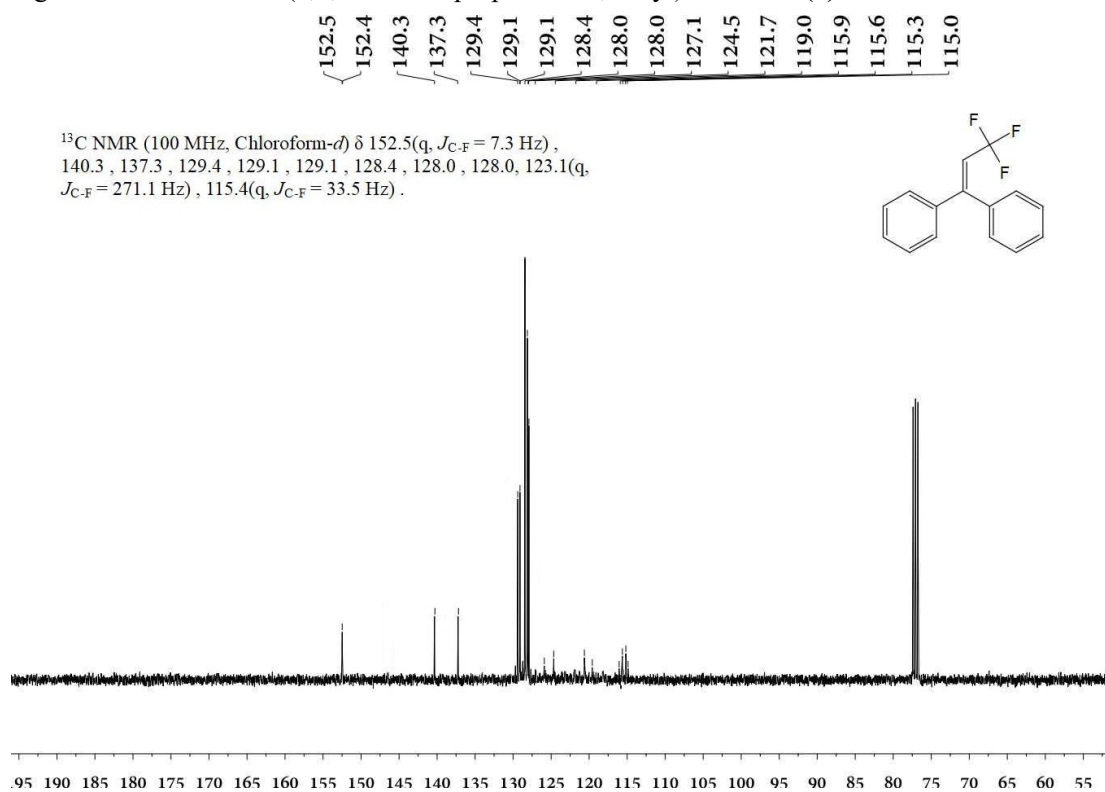


Figure S98. <sup>13</sup>C NMR of (3,3,3-trifluoroprop-1-ene-1,1-diyl)dibenzene (**3**)





Figure S99.  $^{19}\text{F}$  NMR of (3,3,3-trifluoroprop-1-ene-1,1-diyl)dibenzene (**3**)

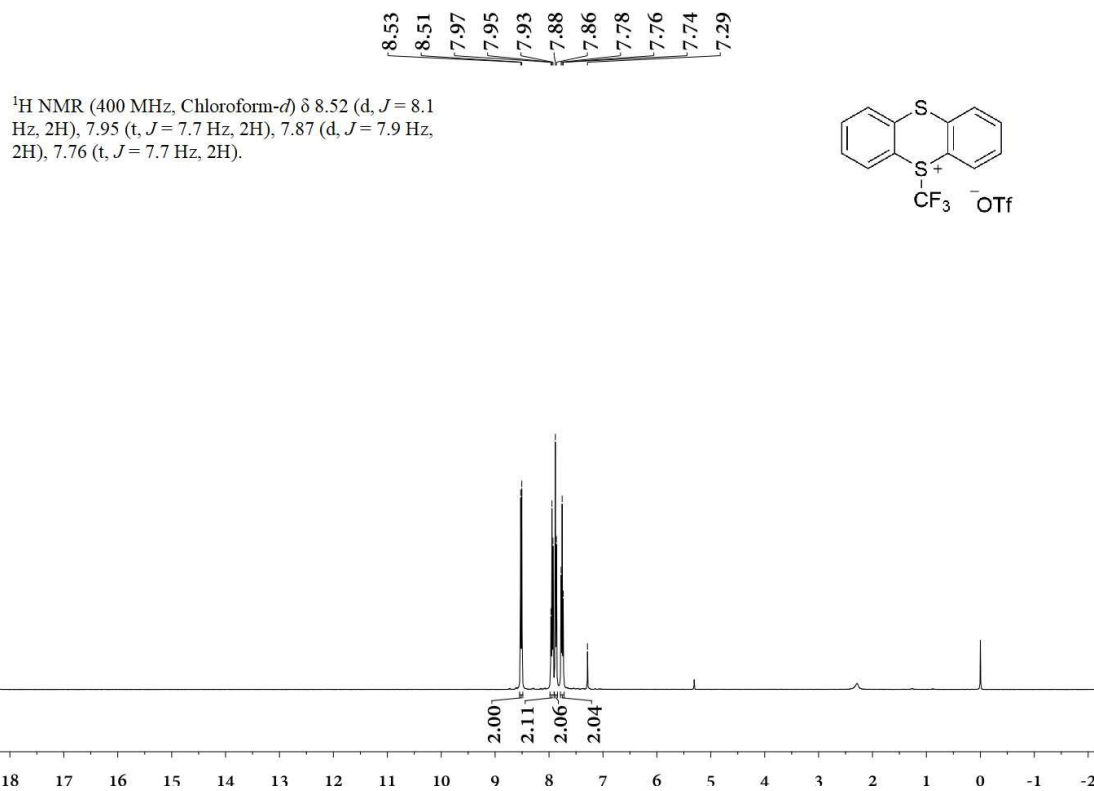


Figure S100.  $^1\text{H}$  NMR of Trifluoromethyl Thianthrenium Triflate ( $\text{TT-CF}_3^+\text{OTf}^-$ )

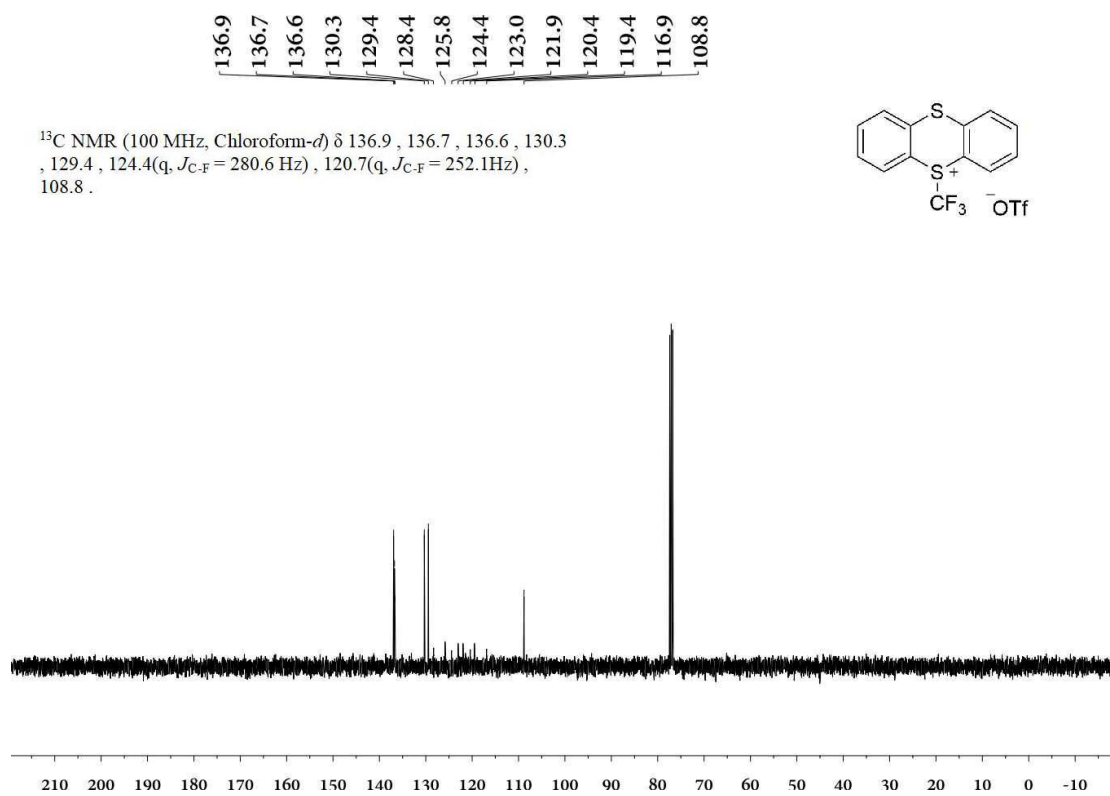


Figure S101. <sup>13</sup>C NMR of Trifluoromethyl Thianthrenium Triflate (TT-CF<sub>3</sub><sup>+</sup>OTf<sup>-</sup>)

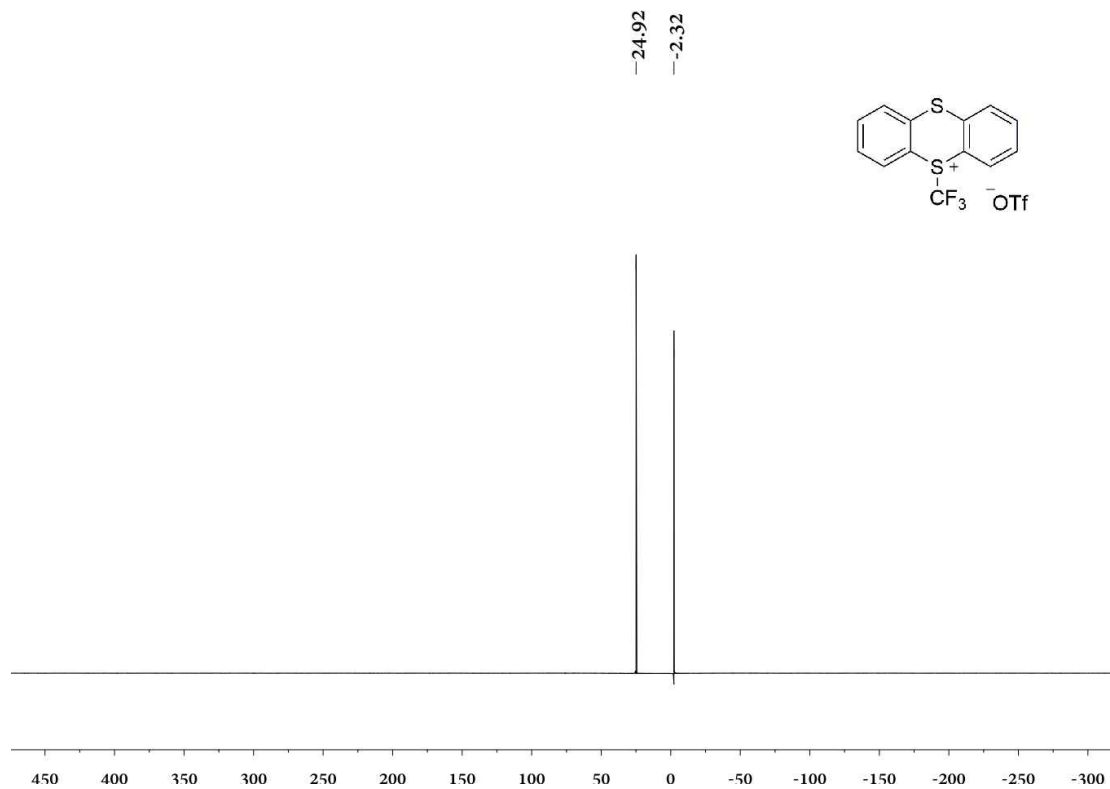


Figure S102. <sup>19</sup>F NMR of Trifluoromethyl Thianthrenium Triflate (TT-CF<sub>3</sub><sup>+</sup>OTf<sup>-</sup>)

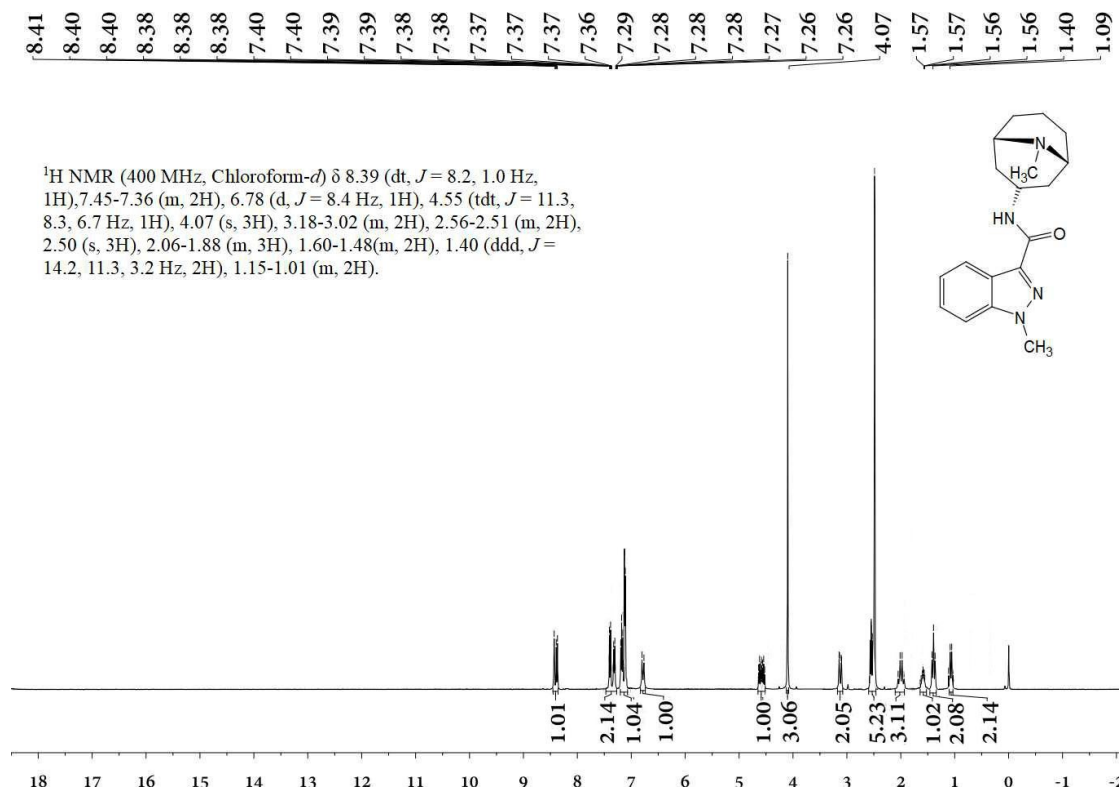


Figure S103. <sup>1</sup>H NMR of 1-Methyl-N-((1R,3r,5S)-9-methyl-9-azabicyclo[3.3.1]nonan-3-yl)-1H-indazole-3-carboxamide (**Granisetron**)

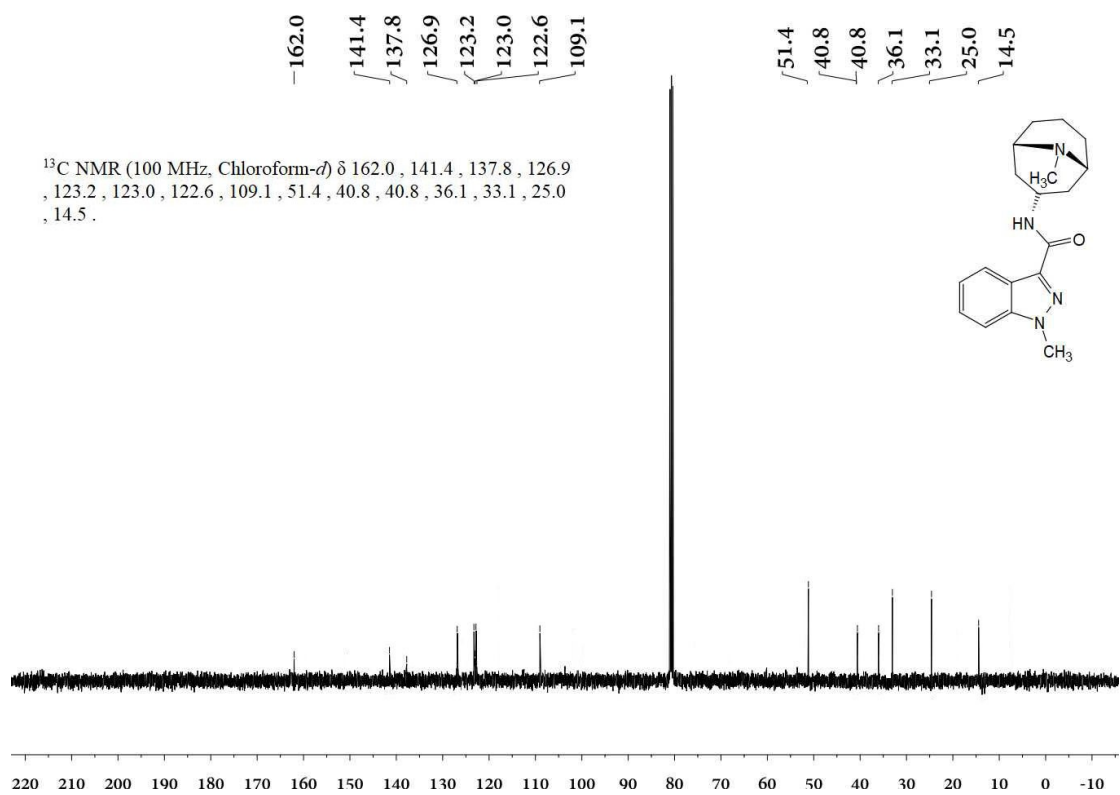


Figure S104. <sup>13</sup>C NMR of 1-Methyl-N-((1R,3r,5S)-9-methyl-9-azabicyclo[3.3.1]nonan-3-yl)-1H-indazole-3-carboxamide (**Granisetron**)