Support Information

Radical-mediated multicomponent cascade reaction for the synthesis of azide-biindole derivatives

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Contents

1. General information 3

2. General Procedure for preparing 3-azido-biindoles **3-4** and triazol product **8** 3

3. Spectroscopic Data of **3-8** 5

4. Reaction Condition Optimizations 24

Table S1. Reaction Condition Optimizations[a,c] 24

5. X-ray Structure and Data of **3a** 26

Figure S1. X-Ray crystal structure of **3a** 26

Table S2. Crystal data and structure refinement for **3a** 27

6. X-ray Structure and Data of **4p** 28

Figure S2. X-Ray crystal structure of **4p** 28

Table S3. Crystal data and structure refinement for **4p** 29

7. X-ray Structure and Data of **6** 30

Figure S3. X-Ray crystal structure of **6**.....30

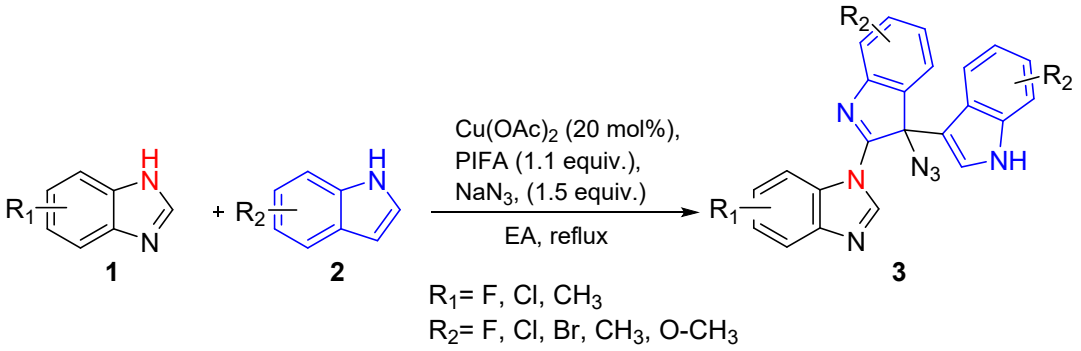
Table S4. Crystal data and structure refinement for **6**.....31

8. ^{1}H NMR and ^{13}C NMR Spectra of These Compounds.....32

1. General information

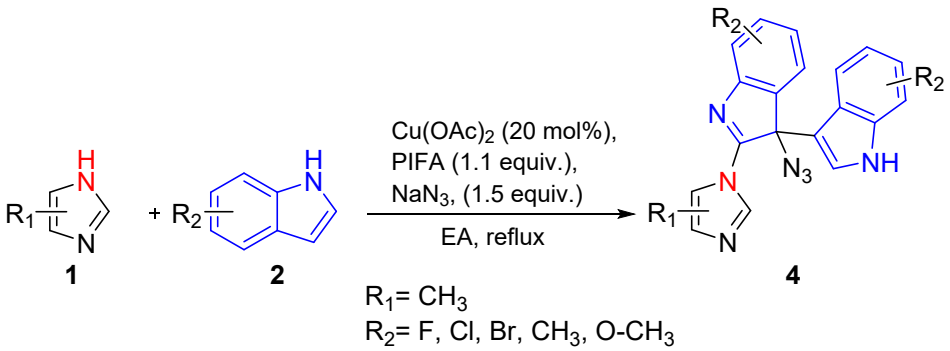
All chemicals and reagents were used of commercial grade and were used without no further purification. The reactions were monitored by thin-layer chromatography (TLC) using silica gel GF254. Column chromatography was performed with 200–300 mesh silica gel. All yields refer to isolated products after purification. The intermediates and the products synthesized were fully characterized by spectroscopic data. The NMR spectra were recorded on Bruker DRX-600 (^{1}H: 600 MHz, ^{13}C: 151 MHz) using DMSO-d_6 as solvents. The following abbreviation were used to explain the multiplicities: (s) = singlet, (d) = doublet, (t) = triplet, (q) = quartet, (sept) = septuplet, (dd) = double doublet, (dt) = double triplet, (dq) = double quartet, (ddd) = double-double doublet, (m) = multiplet; Chemical shifts (δ) are expressed in parts per million (ppm) and J values are given in hertz (Hz). IR spectra were recorded on an FT-IR Thermo Nicolet Avatar 360 using a KBr pellet. HRMS was performed on an Agilent LC/MSD TOF instrument. The melting points were measured by the XT-4A melting point apparatus without correction.

2. General Procedure for preparing 3-azido-biindoles **3-4** and triazol product **8**

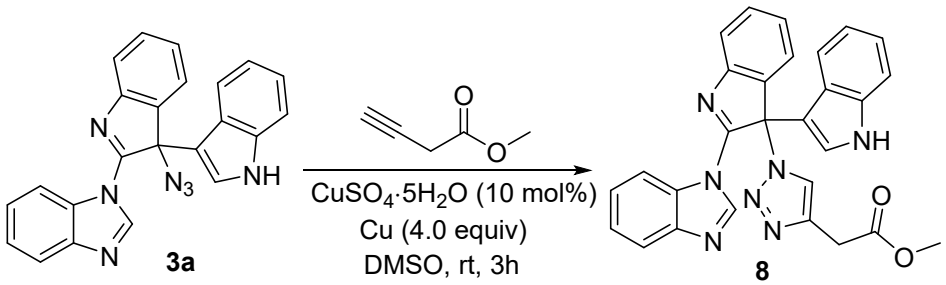


Under air atmosphere, benzimidazole **1** (1 mmol), indole **2** (2.2 mmol), PIFA (1.1 mmol, 473 mg), $Cu(OAc)_2$ (20 mol%, 36.2 mg), NaN_3 (1.5 mmol, 97.5 mg) and EA (30 mL) were added to 100 mL reaction tube. The mixture was stirred at reflux temperature in oil bath for 5 h. After cooling to room temperature, the reaction was quenched with saturated NaCl solution and extracted with 60 mL EtOAc for three times. The organic layers were combined, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residues were purified by flash column chromatography

on silica gel to provide the products **3a-3s**. The products were further identified by FTIR spectroscopy, NMR spectroscopy, and HRMS.



Under air atmosphere, imidazole **1** (1 mmol), indole **2** (2.2 mmol), PIFA (1.1 mmol, 473 mg), $Cu(OAc)_2$ (20 mol%, 36.2 mg), NaN_3 (1.5 mmol, 97.5 mg) and EA (30 mL) were added to 100 mL reaction tube. The mixture was stirred at reflux temperature in oil bath for 5 h. After cooling to room temperature, the reaction was quenched with saturated NaCl solution and extracted with 60 mL EtOAc for three times. The organic layers were combined, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residues were purified by flash column chromatography on silica gel to provide the products **4a-4q**. The products were further identified by FTIR spectroscopy, NMR spectroscopy, and HRMS.

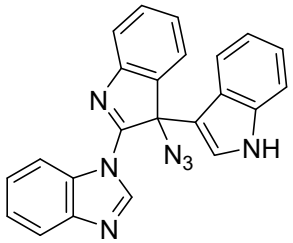


The reaction of 3-azido-biindole product **3a** (7.1 mmol, 2.76 g), methyl but-3-ynoate (8 mmol, 784 mg), $CuSO_4 \cdot 5H_2O$ (10 mol%, 177.5 mg), and Cu powder (28.4 mmol, 1.8 g) were placed in a flame-dried Schlenk tube under air, followed by the addition of DMSO (80 mL). The reaction was conducted at room temperature for 3 h in dark place. After that, 120 mL water was added and the reaction was extracted by ethyl acetate. The crude product was purified by flash column chromatography on silica gel to afford the product **8** as reddish brown solid (3.17 g, 92%). The product **8** was

further identified by FTIR spectroscopy, NMR spectroscopy, and HRMS.

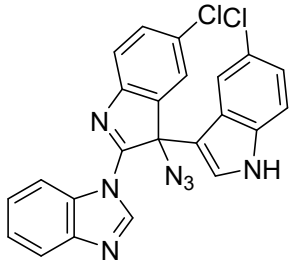
3. Spectroscopic Data of **3-8**

3'-Azido-2'-(1H-benzo[d]imidazol-1-yl)-1H,3'H-3,3'-biindole (**3a**)



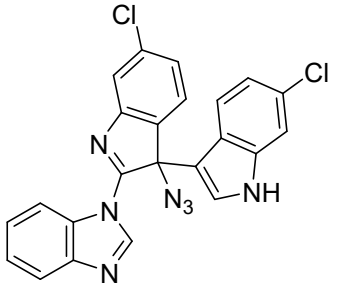
Reddish brown solid; Mp: 213.4 -214.1 °C; 295 mg, yield: 76%; **IR** (KBr): 3440, 2254, 2128, 1662, 826, 763, 633, 603, 550, 503, 454 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.56 (d, *J* = 2.9 Hz, 1H, NH), 8.65 (d, *J* = 8.2 Hz, 1H, ArH), 8.59 (s, 1H, ArH), 8.01 (d, *J* = 2.8 Hz, 1H, ArH), 7.83 (d, *J* = 7.7 Hz, 1H, ArH), 7.72 (d, *J* = 7.9 Hz, 1H, ArH), 7.56 (t, *J* = 7.0 Hz, 1H, ArH), 7.53 – 7.49 (m, 1H, ArH), 7.38 (dt, *J* = 19.4, 7.2 Hz, 3H, ArH), 7.30 (t, *J* = 7.4 Hz, 1H, ArH), 7.01 – 6.95 (m, 1H, ArH), 6.73 (t, *J* = 7.6 Hz, 1H, ArH), 6.64 (d, *J* = 8.2 Hz, 1H, ArH); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 165.26, 151.96, 143.31, 141.51, 137.47, 136.03, 131.79, 131.71, 127.29, 126.03, 125.45, 125.19, 123.68, 123.35, 122.46, 121.39, 120.57, 120.24, 117.30, 116.38, 112.78, 109.16, 74.40. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{16}N_7$ 390.1462; Found 390.1459.

3'-Azido-2'-(1H-benzo[d]imidazol-1-yl)-5,5'-dichloro-1H,3'H-3,3'-biindole (**3b**)



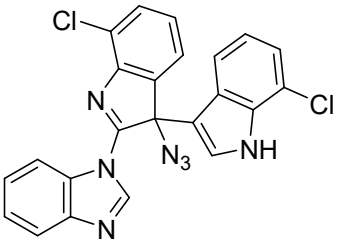
Reddish brown solid; Mp: 221.7 -222.9 °C; 310 mg, yield: 68%; **IR** (KBr): 3436, 2255, 2124, 1660, 1652, 824, 762, 649, 626, 618, 521, 508, 494 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.83 (d, *J* = 2.3 Hz, 1H, NH), 8.64 (d, *J* = 8.2 Hz, 1H, ArH), 8.56 (s, 1H, ArH), 8.07 (d, *J* = 2.8 Hz, 1H, ArH), 7.89 (d, *J* = 8.3 Hz, 1H, ArH), 7.76 (d, *J* = 7.9 Hz, 1H, ArH), 7.67 (dd, *J* = 8.3, 2.2 Hz, 1H, ArH), 7.56 (d, *J* = 7.2 Hz, 1H, ArH), 7.54 (d, *J* = 2.2 Hz, 1H, ArH), 7.45 (d, *J* = 7.7 Hz, 1H, ArH), 7.42 (d, *J* = 8.7 Hz, 1H, ArH), 7.05 (dd, *J* = 8.7, 2.1 Hz, 1H, ArH), 6.66 (s, 1H, ArH); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 165.47, 150.65, 143.35, 141.48, 137.71, 135.96, 131.91, 131.71, 131.68, 127.41, 126.22, 125.68, 124.92, 124.22, 123.97, 122.86, 122.67, 120.69, 116.35, 116.30, 114.60, 108.21, 74.20. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{14}Cl_2N_7$ 458.0682; Found 458.0680.

3'-Azido-2'-(1H-benzo[d]imidazol-1-yl)-6,6'-dichloro-1H,3'H-3,3'-biindole (**3c**)



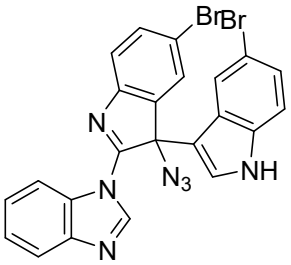
Reddish brown solid; Mp: 226.1 -226.6 °C; 320 mg, yield: 70%; **IR** (KBr): 3437, 2253, 2126, 1659, 823, 763, 625 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.75 (s, 1H, NH), 8.65 (d, *J* = 8.2 Hz, 1H, ArH), 8.60 (s, 1H, ArH), 8.07 (d, *J* = 2.8 Hz, 1H, ArH), 7.97 (d, *J* = 1.9 Hz, 1H, ArH), 7.78 (d, *J* = 7.9 Hz, 1H, ArH), 7.57 (t, *J* = 7.2 Hz, 1H, ArH), 7.48 – 7.44 (m, 3H, ArH), 7.41 (dd, *J* = 8.0, 1.9 Hz, 1H, ArH), 6.87 (dd, *J* = 8.6, 2.0 Hz, 1H, ArH), 6.70 (d, *J* = 8.7 Hz, 1H, ArH); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 166.44, 153.38, 143.37, 141.51, 137.90, 136.12, 134.58, 127.45, 127.12, 126.61, 126.19, 125.72, 125.01, 122.95, 122.03, 121.71, 120.87, 120.69, 118.57, 116.42, 112.50, 109.01, 73.88. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{14}Cl_2N_7$ 458.0682; Found 458.0677.

3'-Azido-2'-(1H-benzo[d]imidazol-1-yl)-7,7'-dichloro-1H,3'H-3,3'-biindole (**3d**)



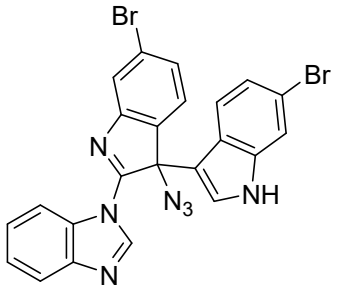
Reddish brown solid; Mp: 244.5 -245.3 °C; 233 mg, yield: 51%; **IR** (KBr): 3445, 2252, 2126, 1661, 824, 762, 624, 551, 500, 453 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 12.05 (s, 1H, NH), 8.66 (d, *J* = 8.1 Hz, 1H, ArH), 8.61 (s, 1H, ArH), 8.12 (d, *J* = 2.9 Hz, 1H, ArH), 7.76 (d, *J* = 7.9 Hz, 1H, ArH), 7.68 (d, *J* = 7.0 Hz, 1H, ArH), 7.62 – 7.54 (m, 1H, ArH), 7.45 (t, *J* = 7.0 Hz, 1H, ArH), 7.40 (d, *J* = 6.3 Hz, 1H, ArH), 7.34 (t, *J* = 7.7 Hz, 1H, ArH), 7.13 (d, *J* = 7.6 Hz, 1H, ArH), 6.83 (t, *J* = 7.9 Hz, 1H, ArH), 6.63 (d, *J* = 8.1 Hz, 1H, ArH); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 165.74, 148.64, 143.37, 141.52, 137.63, 134.32, 132.03, 131.71, 128.88, 126.87, 126.31, 125.79, 125.43, 125.10, 122.56, 122.22, 121.66, 120.72, 117.27, 116.39, 116.18, 109.99, 74.94. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{14}Cl_2N_7$ 458.0682; Found 458.0677.

3'-Azido-2'-(1H-benzo[d]imidazol-1-yl)-5,5'-dibromo-1H,3'H-3,3'-biindole (**3e**)



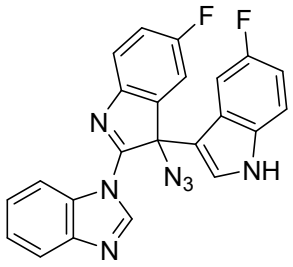
Reddish brown solid; Mp: 236.8 -237.4 °C; 344 mg, yield: 63%; **IR** (KBr): 3444, 2250, 2128, 1660, 829, 757, 621, 544, 486, 456, 414 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.84 (d, *J* = 2.9 Hz, 1H, NH), 8.64 (d, *J* = 8.2 Hz, 1H, ArH), 8.54 (s, 1H, ArH), 8.05 (d, *J* = 2.8 Hz, 1H, ArH), 7.86 – 7.77 (m, 2H, ArH), 7.75 (d, *J* = 7.9 Hz, 1H, ArH), 7.64 (d, *J* = 1.9 Hz, 1H, ArH), 7.55 (t, *J* = 7.7 Hz, 1H, ArH), 7.44 (t, *J* = 7.0 Hz, 1H, ArH), 7.37 (d, *J* = 8.7 Hz, 1H, ArH), 7.15 (dd, *J* = 8.6, 1.9 Hz, 1H, ArH), 6.82 (s, 1H, ArH); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 165.35, 151.03, 143.34, 141.45, 137.95, 136.18, 134.83, 131.69, 127.22, 126.67, 126.24, 125.70, 125.21, 124.90, 123.27, 120.69, 119.74, 119.35, 116.34, 115.02, 112.89, 108.11, 74.16. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{14}Br_2N_7$ 547.9651; Found 547.9654.

3'-Azido-2'-(1H-benzo[d]imidazol-1-yl)-6,6'-dibromo-1H,3'H-3,3'-biindole (**3f**)



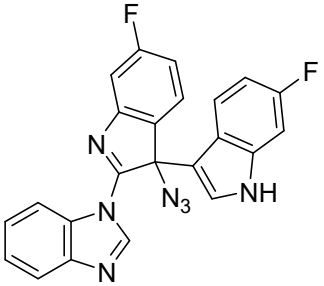
Reddish brown solid; Mp: 201.1 -201.8 °C; 338 mg, yield: 62%; **IR** (KBr): 3444, 2255, 2125, 1657, 823, 762, 701, 654, 630, 609, 592, 534, 510, 492 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.73 (d, *J* = 2.5 Hz, 1H, NH), 8.62 (d, *J* = 8.3 Hz, 1H, ArH), 8.56 (s, 1H, ArH), 8.07 (d, *J* = 1.8 Hz, 1H, ArH), 8.03 (d, *J* = 2.8 Hz, 1H, ArH), 7.76 (d, *J* = 7.8 Hz, 1H, ArH), 7.61 – 7.50 (m, 3H, ArH), 7.44 (t, *J* = 7.0 Hz, 1H, ArH), 7.37 (d, *J* = 7.9 Hz, 1H, ArH), 6.96 (dd, *J* = 8.6, 1.8 Hz, 1H, ArH), 6.64 (d, *J* = 8.7 Hz, 1H, ArH); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 166.27, 153.46, 143.34, 141.46, 138.33, 134.98, 131.68, 130.03, 126.49, 126.19, 125.77, 125.72, 125.34, 124.50, 123.42, 122.26, 120.68, 118.92, 116.42, 115.46, 115.41, 108.97, 73.93. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{14}Br_2N_7$ 547.9651; Found 547.9650.

3'-Azido-2'-(1H-benzo[d]imidazol-1-yl)-5,5'-difluoro-1H,3'H-3,3'-biindole (**3g**)



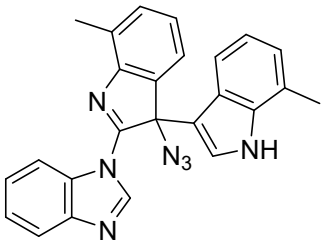
Reddish brown solid; Mp: 214.2 -214.7 °C; 272 mg, yield: 64%; **IR** (KBr): 3435, 2255, 2129, 1664, 825, 762, 700, 668, 623, 547, 541, 511, 451 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.73 (s, 1H, NH), 8.63 (d, J = 8.3 Hz, 1H, ArH), 8.59 (s, 1H, ArH), 8.07 (d, J = 2.9 Hz, 1H, ArH), 7.89 (dd, J = 8.5, 4.4 Hz, 1H, ArH), 7.75 (d, J = 7.9 Hz, 1H, ArH), 7.60 – 7.50 (m, 1H, ArH), 7.47 – 7.37 (m, 4H, ArH), 6.92 (dtd, J = 28.1, 9.2, 2.5 Hz, 1H, ArH), 6.35 (d, J = 7.6 Hz, 1H, ArH); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 165.50, 161.82 (d, J = 243 Hz), 157.81 (d, J = 232.5 Hz), 148.40, 143.71, 141.87, 138.21, 134.53, 132.11, 127.91, 126.53, 125.95, 123.77 (d, J = 10.5 Hz), 123.17 (d, J = 9 Hz), 121.04, 118.75, (d, J = 24 Hz), 116.70, 114.61 (d, J = 10.5 Hz), 112.26 (d, J = 25.5 Hz), 111.33 (d, J = 25.5 Hz), 109.07 (d, J = 4.5 Hz), 102.38 (d, J = 25.5 Hz), 74.77; **^{19}F NMR** (565 MHz, DMSO-d_6) δ -124.27, -125.17. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{14}F_2N_7$ 426.1273; Found 426.1265.

3'-Azido-2'-(1H-benzo[d]imidazol-1-yl)-6,6'-difluoro-1H,3'H-3,3'-biindole (**3h**)



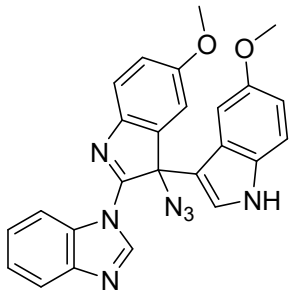
Reddish brown solid; Mp: 250.8 -252.1 °C; 255 mg, yield: 60%; **IR** (KBr): 3437, 2257, 2128, 1663, 824, 762, 665, 618, 535, 512, 463, 426 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.65 (s, 1H, NH), 8.62 (d, J = 8.2 Hz, 1H, ArH), 8.60 (s, 1H, ArH), 8.02 (d, J = 2.7 Hz, 1H, ArH), 7.80 – 7.70 (m, 2H, ArH), 7.59 – 7.52 (m, 1H, ArH), 7.48 – 7.40 (m, 2H, ArH), 7.16 (td, J = 9.2, 8.5, 4.3 Hz, 2H, ArH), 6.69 (td, J = 9.3, 2.4 Hz, 1H, ArH), 6.63 (dd, J = 8.9, 5.2 Hz, 1H, ArH); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 166.80, 164.45 (d, J = 244.5 Hz), 159.46 (d, J = 235.5 Hz), 153.82 (d, J = 12 Hz), 143.34, 141.46, 137.53 (d, J = 13.5 Hz), 131.78 (d, J = 24 Hz), 126.17, 126.12, 125.68, 125.14 (d, J = 10.5 Hz), 120.67, 120.11, 118.32 (d, J = 10.5 Hz), 116.41, 113.72 (d, J = 22.5 Hz), 109.54 (d, J = 24 Hz), 109.21, 109.18, 109.01, 98.87 (d, J = 22.5 Hz), 73.83; **^{19}F NMR** (565 MHz, DMSO-d_6) δ -109.13, -120.30. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{14}F_2N_7$ 426.1273; Found 426.1268.

3'-Azido-2'-(1H-benzo[d]imidazol-1-yl)-7,7'-dimethyl-1H,3'H-3,3'-biindole (**3i**)



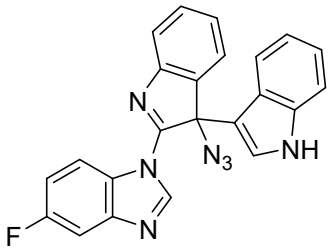
Reddish brown solid; Mp: 204.7 -205.3 °C; 200 mg, yield: 48%; **IR** (KBr): 3444, 2252, 2125, 1666, 822, 769, 625, 583 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.53 (s, 1H, NH), 8.69 (d, J = 8.2 Hz, 1H, ArH), 8.59 (s, 1H, ArH), 7.99 (d, J = 2.9 Hz, 1H, ArH), 7.73 (d, J = 7.9 Hz, 1H, ArH), 7.54 (t, J = 7.8 Hz, 1H, ArH), 7.44 – 7.41 (m, 1H, ArH), 7.40 (d, J = 3.3 Hz, 1H, ArH), 7.20 (t, J = 7.4 Hz, 1H, ArH), 7.16 (d, J = 7.3 Hz, 1H, ArH), 6.79 (d, J = 7.1 Hz, 1H, ArH), 6.64 (t, J = 7.6 Hz, 1H, ArH), 6.46 (d, J = 8.1 Hz, 1H, ArH), 2.71 (s, 3H, CH_3), 2.40 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 164.24, 150.26, 143.31, 141.47, 136.96, 135.86, 132.81, 131.85, 130.79, 127.10, 126.01, 125.38, 124.76, 123.13, 122.91, 122.07, 121.00, 120.52, 120.45, 116.39, 114.94, 109.76, 74.70, 17.09, 16.76. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{20}N_7$ 418.1775; Found 418.1770.

3'-Azido-2'-(1H-benzo[d]imidazol-1-yl)-5,5'-dimethoxy-1H,3'H-3,3'-biindole (**3j**)



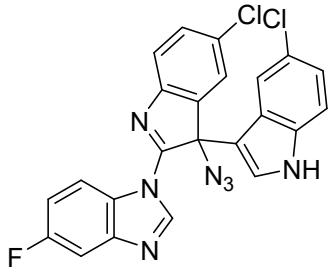
Reddish brown solid; Mp: 248.9 -250.2 °C; 296 mg, yield: 66%; **IR** (KBr): 3655, 3442, 2258, 2122, 2001, 1660, 1220, 824, 768, 626, 566, 554, 499, 420 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.45 (s, 1H, NH), 8.67 (d, J = 8.2 Hz, 1H, ArH), 8.62 (s, 1H, ArH), 7.99 (s, 1H, ArH), 7.82 (d, J = 8.5 Hz, 1H, ArH), 7.78 (d, J = 8.0 Hz, 1H, ArH), 7.57 (t, J = 7.8 Hz, 1H, ArH), 7.46 (t, J = 7.7 Hz, 1H, ArH), 7.30 (d, J = 8.6 Hz, 1H, ArH), 7.17 (d, J = 7.3 Hz, 1H, ArH), 7.01 (s, 1H, ArH), 6.71 (d, J = 8.9 Hz, 1H, ArH), 6.13 (s, 1H, ArH), 3.81 (s, 3H, CH_3), 3.44 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 163.56, 159.04, 153.91, 145.03, 143.27, 141.39, 137.58, 132.50, 131.78, 125.87, 125.71, 125.26, 123.76, 121.95, 120.53, 116.13, 115.82, 113.45, 111.93, 110.46, 108.67, 99.61, 74.50, 56.26, 55.40. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{20}N_7O_2$ 450.1673; Found 450.1665.

3'-Azido-2'-(5-fluoro-1H-benzo[d]imidazol-1-yl)-1H,3'H-3,3'-biindole (**3k**)



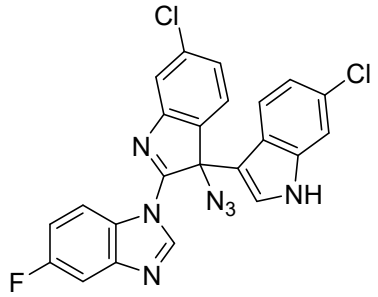
Reddish brown solid; Mp: 265.3 -266.6 °C; 260 mg, yield: 64%; **IR** (KBr): 3447, 2255, 2129, 1659, 1453, 828, 729, 620, 546, 517, 491, 451 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.58 (s, 1H, NH), 8.60 (s, 1H, ArH), 8.41 (dd, J = 9.1, 2.6 Hz, 1H, ArH), 8.02 (d, J = 2.8 Hz, 1H, ArH), 7.87 (d, J = 7.8 Hz, 1H, ArH), 7.76 (dd, J = 8.7, 4.9 Hz, 1H, ArH), 7.59 (t, J = 7.7 Hz, 1H, ArH), 7.38 (t, J = 8.5 Hz, 2H, ArH), 7.35 – 7.27 (m, 2H, ArH), 7.01 (t, J = 7.6 Hz, 1H, ArH), 6.75 (t, J = 7.6 Hz, 1H, ArH), 6.64 (d, J = 8.2 Hz, 1H, ArH); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 165.16, 160.62 (d, J = 238.5 Hz), 151.71, 142.12, 139.84, 138.86, 137.46, 135.96, 131.74, 127.46, 125.28, 123.68, 123.30 (d, J = 10.5 Hz), 122.49, 121.74 (d, J = 10.5 Hz), 121.56, 120.29, 117.31, 113.37 (d, J = 24 Hz), 112.80, 108.89, 103.31 (d, J = 28.5 Hz), 74.32; **^{19}F NMR** (565 MHz, DMSO-d_6) δ -115.38. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{15}FN_7$ 408.1367; Found 408.1361.

3'-Azido-5,5'-dichloro-2'-(5-fluoro-1H-benzo[d]imidazol-1-yl)-1H,3'H-3,3'-biindole (**3l**)



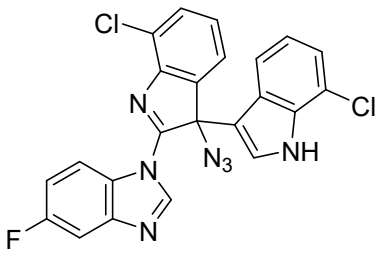
Reddish brown solid; Mp: 244.4 -245.3 °C; 280 mg, yield: 59%; **IR** (KBr): 3442, 2259, 2127, 1660, 1478, 824, 763, 622, 553, 516, 453 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.86 (d, J = 2.3 Hz, 1H, NH), 8.62 (s, 1H, ArH), 8.63 – 8.61 (m, 1H, ArH), 8.08 (d, J = 2.8 Hz, 1H, ArH), 7.87 (d, J = 8.3 Hz, 1H, ArH), 7.65 (dd, J = 8.3, 2.1 Hz, 1H, ArH), 7.62 (dd, J = 9.0, 2.6 Hz, 1H, ArH), 7.54 (d, J = 2.1 Hz, 1H, ArH), 7.44 – 7.37 (m, 2H, ArH), 7.04 (dd, J = 8.7, 2.1 Hz, 1H, ArH), 6.65 (s, 1H, ArH); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 165.23, 159.55, 150.44, 143.18, 137.70, 135.94, 131.93, 131.80, 128.34, 127.48, 124.92, 124.18, 124.00, 122.91, 122.67, 117.29 (d, J = 10.5 Hz), 116.27, 114.61, 114.05, 113.88, 108.09, 106.96 (d, J = 24 Hz), 74.04; **^{19}F NMR** (565 MHz, DMSO-d6) δ -116.74. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{13}Cl_2FN_7$ 476.0588; Found 476.0583.

3'-Azido-6,6'-dichloro-2'-(5-fluoro-1H-benzo[d]imidazol-1-yl)-1H,3'H-3,3'-biindole (**3m**)



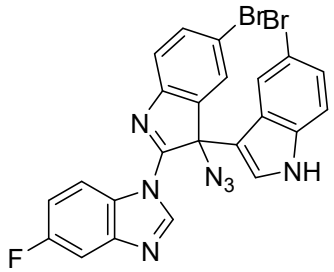
Reddish brown solid; Mp: 249.1 -249.5 °C; 285 mg, yield: 60%; **IR** (KBr): 3442, 2255, 2126, 1651, 823, 763, 624, 585, 533, 486, 434 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.74 (s, 1H, NH), 8.56 (s, 1H, ArH), 8.38 (dd, J = 9.1, 2.6 Hz, 1H, ArH), 8.04 (d, J = 2.8 Hz, 1H, ArH), 7.97 (d, J = 1.9 Hz, 1H, ArH), 7.78 (dd, J = 8.7, 4.8 Hz, 1H, ArH), 7.47 – 7.40 (m, 2H, ArH), 7.39 (dd, J = 7.9, 1.9 Hz, 1H, ArH), 7.31 (td, J = 9.1, 2.6 Hz, 1H, ArH), 6.85 (dd, J = 8.7, 1.9 Hz, 1H, ArH), 6.69 (d, J = 8.7 Hz, 1H, ArH); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 166.33, 159.89, 153.12, 142.07, 139.89, 137.90, 136.15, 134.51, 132.00, 127.48, 127.27, 126.68, 125.00, 122.01, 121.91, 120.90, 118.60, 113.67, 113.51, 112.50, 108.76, 103.47 (d, J = 30 Hz), 73.81; **^{19}F NMR** (565 MHz, DMSO-d_6) δ -115.19. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{13}Cl_2FN_7$ 476.0588; Found 476.0586.

3'-Azido-7,7'-dichloro-2'-(5-fluoro-1H-benzo[d]imidazol-1-yl)-1H,3'H-3,3'-biindole (**3n**)



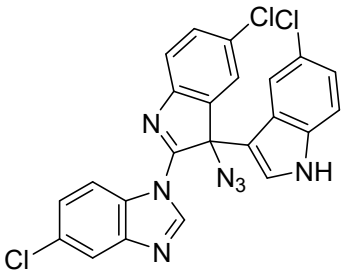
Reddish brown solid; Mp: 277.3 -278.5 °C; 247 mg, yield: 52%; **IR** (KBr): 3447, 2252, 2126, 1666, 826, 766, 624, 590, 529, 501, 479 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 12.06 (d, J = 2.9 Hz, 1H, NH), 8.62 (s, 1H, ArH), 8.39 (dd, J = 9.0, 2.7 Hz, 1H, ArH), 8.12 (d, J = 2.9 Hz, 1H, ArH), 7.80 (dd, J = 8.8, 4.8 Hz, 1H, ArH), 7.69 (dd, J = 8.1, 1.1 Hz, 1H, ArH), 7.41 (dd, J = 7.4, 1.1 Hz, 1H, ArH), 7.39 – 7.31 (m, 2H, ArH), 7.14 (d, J = 6.9 Hz, 1H, ArH), 6.85 (t, J = 7.9 Hz, 1H, ArH), 6.64 (d, J = 8.2 Hz, 1H, ArH); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 165.67, 160.67 (d, J = 238.5 Hz), 148.36, 142.16, 139.90, 137.56, 134.31, 132.05, 131.95 (d, J = 30 Hz), 129.08, 126.96, 125.55, 125.08, 122.58, 122.24, 121.94 (d, J = 9 Hz), 121.72, 117.27, 116.23, 113.68 (d, J = 25.5 Hz), 109.71, 103.37 (d, J = 30 Hz), 74.88; **^{19}F NMR** (565 MHz, DMSO-d_6) δ -114.95. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{13}Cl_2FN_7$ 476.0588; Found 476.0582.

3'-Azido-5,5'-dibromo-2'-(5-fluoro-1H-benzo[d]imidazol-1-yl)-1H,3'H-3,3'-biindole (**3o**)



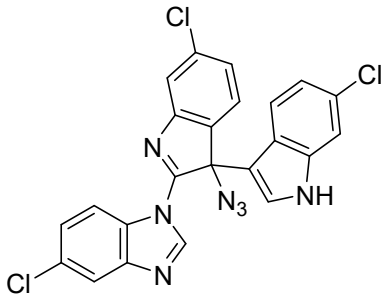
Reddish brown solid; Mp: 269.8 -270.6 °C; 315 mg, yield: 56%; **IR** (KBr): 3442, 2253, 2127, 1660, 1478, 826, 763, 622, 553, 516, 455 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.83 (s, 1H, NH), 8.63 (dd, *J* = 9.0, 4.9 Hz, 1H, ArH), 8.59 (s, 1H, ArH), 8.04 (d, *J* = 2.8 Hz, 1H, ArH), 7.85 – 7.76 (m, 2H, ArH), 7.67 – 7.59 (m, 2H, ArH), 7.42 (tt, *J* = 9.1, 2.6 Hz, 1H, ArH), 7.37 (d, *J* = 8.6 Hz, 1H, ArH), 7.16 (dd, *J* = 8.4, 2.0 Hz, 1H, ArH), 6.81 (s, 1H, ArH); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 165.14, 160.39 (d, *J* = 238.5 Hz), 150.85, 144.19 (d, *J* = 13.5 Hz), 143.16, 137.98, 136.17, 134.87, 128.37, 127.31, 126.71, 125.21, 124.89, 123.34, 119.88, 119.35, 117.30 (d, *J* = 9 Hz), 115.03, 114.00 (d, *J* = 24 Hz), 112.89, 107.99, 106.99 (d, *J* = 25.5Hz), 74.06; **^{19}F NMR** (565 MHz, DMSO-d_6) δ -116.74. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{13}Br_2FN_7$ 565.9557; Found 565.9553.

3'-Azido-5,5'-dichloro-2'-(5-chloro-1H-benzo[d]imidazol-1-yl)-1H,3'H-3,3'-biindole (**3p**)



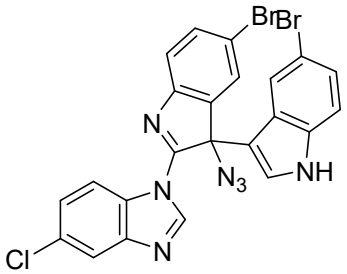
Reddish brown solid; Mp: 255.2 -256.5 °C; 324 mg, yield: 66%; **IR** (KBr): 3439, 2243, 2124, 1656. 829, 759, 617, 571, 527 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.83 (d, *J* = 2.9 Hz, 1H, NH), 8.61 (t, *J* = 4.4 Hz, 2H, ArH), 8.06 (d, *J* = 2.8 Hz, 1H, ArH), 7.88 (d, *J* = 8.3 Hz, 1H, ArH), 7.85 (d, *J* = 2.1 Hz, 1H, ArH), 7.67 (dd, *J* = 8.3, 2.2 Hz, 1H, ArH), 7.59 (dd, *J* = 8.7, 2.2 Hz, 1H, ArH), 7.55 (d, *J* = 2.1 Hz, 1H, ArH), 7.41 (d, *J* = 8.7 Hz, 1H, ArH), 7.05 (dd, *J* = 8.7, 2.1 Hz, 1H, ArH), 6.66 (d, *J* = 2.0 Hz, 1H, ArH); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 165.28, 150.39, 144.36, 142.94, 137.72, 135.96, 131.94, 131.90, 130.58, 129.98, 127.49, 126.29, 124.96, 124.21, 124.00, 122.97, 122.68, 120.38, 117.53, 116.31, 114.61, 107.99, 74.13. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{13}Cl_3N_7$ 492.0293; Found 492.0284.

3'-Azido-6,6'-dichloro-2'-(5-chloro-1H-benzo[d]imidazol-1-yl)-1H,3'H-3,3'-biindole (**3q**)



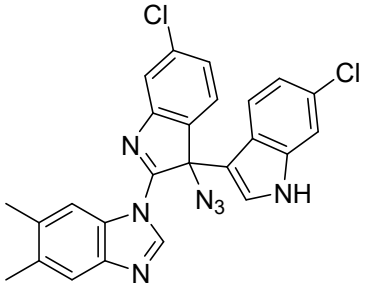
Reddish brown solid; Mp: 272.3 -273.7 °C; 299 mg, yield: 61%; **IR** (KBr): 3441, 2269, 2136, 1656, 1497, 1455, 821, 764, 578, 529, 495, 484, 447 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.73 (d, J = 2.8 Hz, 1H, NH), 8.65 (d, J = 2.1 Hz, 1H, ArH), 8.59 (s, 1H, ArH), 8.04 (d, J = 2.8 Hz, 1H, ArH), 8.02 (d, J = 1.9 Hz, 1H, ArH), 7.77 (d, J = 8.5 Hz, 1H, ArH), 7.48 (dd, J = 8.5, 2.1 Hz, 1H, ArH), 7.43 (d, J = 8.1 Hz, 2H, ArH), 7.39 (dd, J = 7.9, 1.9 Hz, 1H, ArH), 6.85 (dd, J = 8.7, 1.9 Hz, 1H, ArH), 6.70 (d, J = 8.7 Hz, 1H, ArH); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 166.28, 153.06, 142.33, 142.19, 137.90, 136.18, 134.52, 132.38, 130.55, 127.47, 127.32, 126.70, 125.97, 124.98, 122.06, 122.02, 121.99, 120.92, 118.64, 116.20, 112.49, 108.75, 73.81. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{13}Cl_3N_7$ 492.0293; Found 492.0287.

3'-Azido-5,5'-dibromo-2'-(5-chloro-1H-benzo[d]imidazol-1-yl)-1H,3'H-3,3'-biindole (**3r**)



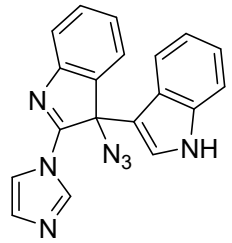
Reddish brown solid; Mp: 240.6 -241.4 °C; 346 mg, yield: 60%; **IR** (KBr): 3443, 2364, 2254, 2127, 1659, 1461, 821, 769, 625, 546, 455, 430 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.84 (d, J = 2.9 Hz, 1H, NH), 8.61 (s, 1H, ArH), 8.60 (s, 1H, ArH), 8.04 (d, J = 2.8 Hz, 1H, ArH), 7.85 – 7.81 (m, 1H, ArH), 7.79 (dd, J = 10.0, 8.1 Hz, 1H, ArH), 7.64 (dd, J = 8.7, 2.0 Hz, 1H, ArH), 7.57 (dd, J = 8.8, 2.1 Hz, 1H, ArH), 7.36 (d, J = 8.7 Hz, 1H, ArH), 7.14 (dd, J = 8.6, 1.9 Hz, 1H, ArH), 6.87 (d, J = 8.3 Hz, 1H, ArH), 6.81 (s, 1H, ArH); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 165.15, 159.42, 150.79, 144.38, 142.94, 140.53, 137.97, 136.19, 134.86, 130.00, 127.35, 126.71, 126.28, 125.22, 123.37, 120.38, 119.96, 119.39, 117.52, 115.01, 112.92, 107.89, 74.10. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{13}Br_2ClN_7$ 579.9282; Found 579.9284.

3'-Azido-6,6'-dichloro-2'-(5,6-dimethyl-1H-benzo[d]imidazol-1-yl)-1H,3'H-3,3'-biindole (**3s**)



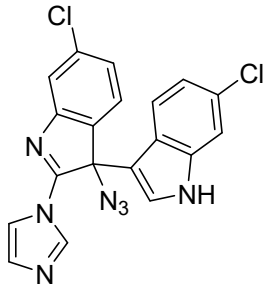
Reddish brown solid; Mp: 229.6 -231.2 °C; 227 mg, yield: 47%; **IR** (KBr): 3448, 2269, 2129, 1662, 829, 768, 626, 550, 511, 422 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.73 (s, 1H, NH), 8.42 (s, 1H, ArH), 8.39 (s, 1H, ArH), 8.03 (d, *J* = 2.7 Hz, 1H, ArH), 7.94 (d, *J* = 1.7 Hz, 1H, ArH), 7.51 (s, 1H, ArH), 7.45 – 7.39 (m, 2H, ArH), 7.38 – 7.34 (m, 1H, ArH), 6.84 (dd, *J* = 8.6, 1.8 Hz, 1H, ArH), 6.66 (d, *J* = 8.7 Hz, 1H, ArH), 2.41 (s, 3H, CH_3), 2.33 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 166.33, 153.51, 141.84, 140.62, 137.88, 136.09, 134.98, 134.54, 134.37, 130.02, 127.44, 126.91, 126.45, 124.95, 122.02, 121.60, 120.85, 120.70, 118.54, 116.47, 112.48, 109.19, 73.81, 20.65, 20.22. **HRMS** (ESI-TOF) m/z: $[M - H]^-$ calcd for $C_{25}H_{18}Cl_2N_7$ 484.0850; Found 484.0847.

3'-Azido-2'-(1H-imidazol-1-yl)-1H,3'H-3,3'-biindole (**4a**)



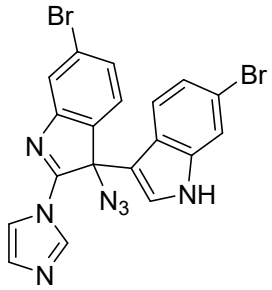
Reddish brown solid; Mp: 142.9 -144.2 °C; 247 mg, yield: 73%; **IR** (KBr): 3448, 2256, 2121, 1655, 1452, 1307, 829, 767, 667, 626, 575, 511, 453, 424 cm^{-1}; **^{1}H NMR** (600 MHz, Acetone-d_6) δ 10.67 (s, 1H, NH), 8.11 (s, 1H, ArH), 7.76 (d, *J* = 2.7 Hz, 1H, ArH), 7.64 (t, *J* = 1.5 Hz, 1H, ArH), 7.58 (d, *J* = 7.7 Hz, 1H, ArH), 7.41 (td, *J* = 7.6, 1.3 Hz, 1H, ArH), 7.28 (d, *J* = 8.2 Hz, 1H, ArH), 7.23 (d, *J* = 6.2 Hz, 1H, ArH), 7.17 (td, *J* = 7.5, 1.0 Hz, 1H, ArH), 6.94 – 6.89 (m, 1H, ArH), 6.87 (d, *J* = 1.6 Hz, 1H, ArH), 6.72 – 6.62 (m, 2H, ArH); **^{13}C NMR** (151 MHz, Acetone-d_6) δ 164.53, 151.60, 137.50, 136.81, 136.21, 131.09, 130.23, 126.90, 124.20, 123.43, 123.37, 122.35, 120.95, 119.92, 117.50, 116.72, 112.14, 109.23, 73.91. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{14}N_7$ 340.1305; Found 340.1302.

3'-Azido-6,6'-dichloro-2'-(1H-imidazol-1-yl)-1H,3'H-3,3'-biindole (**4b**)



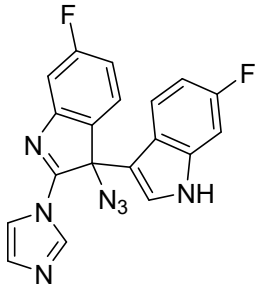
Reddish brown solid; Mp: 202.7 -203.4 °C; 260 mg, yield: 64%; **IR** (KBr): 3448, 2248, 2117, 1648, 826, 769, 630, 568, 534, 480, 435, 412 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.72 (d, J = 2.8 Hz, 1H, NH), 8.30 (s, 1H, ArH), 7.98 (d, J = 2.7 Hz, 1H, ArH), 7.86 (d, J = 1.6 Hz, 1H, ArH), 7.76 (s, 1H, ArH), 7.44 (d, J = 1.9 Hz, 1H, ArH), 7.41 – 7.36 (m, 2H, ArH), 7.15 – 7.06 (m, 1H, ArH), 6.89 (dd, J = 8.6, 1.9 Hz, 1H, ArH), 6.62 (d, J = 8.6 Hz, 1H, ArH); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 165.70, 152.70, 137.84, 136.75, 136.11, 135.38, 131.09, 127.41, 126.71, 125.12, 122.05, 121.75, 120.83, 118.67, 117.43, 116.59, 112.48, 108.31, 73.23. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{12}Cl_2N_7$ 408.0526; Found 408.0520.

3'-Azido-6,6'-dibromo-2'-(1H-imidazol-1-yl)-1H,3'H-3,3'-biindole (**4c**)



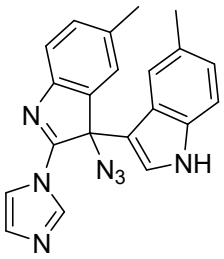
Reddish brown solid; Mp: 191.3 -192.5 °C; 292 mg, yield: 59%; **IR** (KBr): 3448, 2259, 2124, 1658, 1306, 828, 769, 630, 544, 513, 455, 422 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.76 (d, J = 2.8 Hz, 1H, NH), 8.33 (d, J = 1.1 Hz, 1H, ArH), 8.03 (d, J = 1.8 Hz, 1H, ArH), 8.00 (d, J = 2.7 Hz, 1H, ArH), 7.80 (t, J = 1.5 Hz, 1H, ArH), 7.63 (d, J = 1.8 Hz, 1H, ArH), 7.57 (dd, J = 7.9, 1.8 Hz, 1H, ArH), 7.37 (d, J = 7.9 Hz, 1H, ArH), 7.13 (d, J = 1.6 Hz, 1H, ArH), 7.05 (dd, J = 8.6, 1.8 Hz, 1H, ArH), 6.62 (d, J = 8.6 Hz, 1H, ArH); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 165.54, 152.78, 138.28, 136.73, 135.78, 131.08, 130.33, 126.58, 125.45, 124.53, 124.47, 123.39, 122.27, 119.02, 117.42, 115.44, 115.38, 108.28, 73.28. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{12}Br_2N_7$ 497.9495; Found 497.9488.

3'-Azido-6,6'-difluoro-2'-(1H-imidazol-1-yl)-1H,3'H-3,3'-biindole (**4d**)



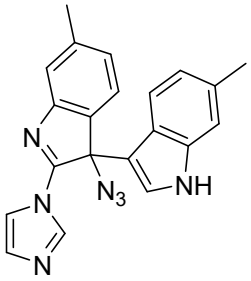
Reddish brown solid; Mp: 130.7 -131.4 °C; 228 mg, yield: 61%; **IR** (KBr): 3442, 2258, 2128, 1998, 1654, 1213, 1150, 821, 768, 632, 573, 513, 456, 424 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.64 (s, 1H, NH), 8.31 (s, 1H, ArH), 7.94 (d, J = 2.7 Hz, 1H, ArH), 7.77 (t, J = 1.5 Hz, 1H, ArH), 7.67 (dd, J = 8.9, 2.4 Hz, 1H, ArH), 7.41 (dd, J = 8.2, 5.2 Hz, 1H, ArH), 7.17 (dd, J = 9.9, 2.4 Hz, 1H, ArH), 7.15 – 7.12 (m, 1H, ArH), 7.09 (s, 1H, C= ArH), 6.73 (td, J = 9.3, 2.4 Hz, 1H, ArH), 6.55 (dd, J = 8.9, 5.2 Hz, 1H, ArH); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 166.05, 164.37 (d, J = 244.5 Hz), 159.46 (d, J = 235.5 Hz), 153.14 (d, J = 12 Hz), 137.46 (d, J = 12 Hz), 136.73, 132.69, 131.04, 126.25, 125.26 (d, J = 9 Hz), 120.14, 118.44 (d, J = 10.5 Hz), 117.40, 113.98 (d, J = 24 Hz), 109.64 (d, J = 24 Hz), 109.04 (d, J = 25.5 Hz), 108.49, 98.84 (d, J = 25.5 Hz), 73.17**; ^{19}F NMR** (565 MHz, DMSO-d_6) δ -109.13, -120.42. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{12}F_2N_7$ 376.1117; Found 376.1112.

3'-Azido-2'-(1H-imidazol-1-yl)-5,5'-dimethyl-1H,3'H-3,3'-biindole (**4e**)



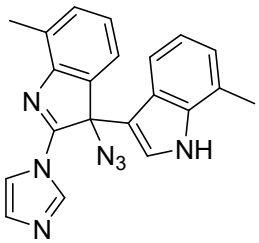
Reddish brown solid; Mp: 205.1 -205.8 °C; 231 mg, yield: 63%; **IR** (KBr): 3448, 2255, 2129, 1665, 1475, 1328, 835, 769, 694, 596, 573, 453 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.40 (s, 1H, NH), 8.25 (s, 1H, ArH), 7.83 (d, J = 2.7 Hz, 1H, ArH), 7.76 (s, 1H, ArH), 7.64 (d, J = 7.9 Hz, 1H, ArH), 7.35 (d, J = 7.9 Hz, 1H, ArH), 7.27 (d, J = 8.3 Hz, 1H, ArH), 7.15 (s, 1H, ArH), 7.05 (s, 1H, ArH), 6.87 (d, J = 8.3 Hz, 1H, ArH), 6.40 (s, 1H, ArH), 2.29 (s, 3H, CH_3), 2.12 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 163.75, 148.95, 137.26, 137.04, 136.48, 135.80, 131.95, 130.66, 128.71, 125.02, 124.19, 124.11, 123.66, 120.98, 117.32, 116.97, 112.46, 108.04, 73.80, 21.70, 21.35. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{18}N_7$ 368.1618; Found 368.1615.

3'-Azido-2'-(1H-imidazol-1-yl)-6,6'-dimethyl-1H,3'H-3,3'-biindole (**4f**)



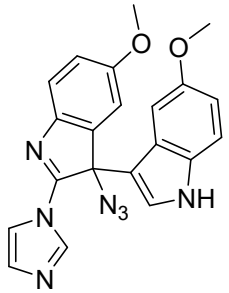
Reddish brown solid; Mp: 171.2 -172.5 °C; 220 mg, yield: 60%; **IR** (KBr): 3441, 2258, 2128, 1997, 1655, 1306, 834, 753, 621, 579, 524, 481, 414 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.34 (s, 1H, NH), 8.25 (t, J = 1.0 Hz, 1H, ArH), 7.79 (d, J = 2.7 Hz, 1H, ArH), 7.75 (t, J = 1.5 Hz, 1H, ArH), 7.59 – 7.52 (m, 1H, ArH), 7.20 (d, J = 7.5 Hz, 1H, ArH), 7.15 (s, 1H, ArH), 7.11 (dt, J = 7.3, 1.2 Hz, 1H, ArH), 7.05 (dd, J = 1.6, 0.8 Hz, 1H, ArH), 6.62 (dd, J = 8.3, 1.5 Hz, 1H, ArH), 6.46 (d, J = 8.3 Hz, 1H, ArH), 2.42 (s, 3H, CH_3), 2.27 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 164.66, 151.51, 141.60, 137.85, 136.53, 133.96, 131.74, 130.69, 127.87, 124.36, 123.40, 122.04, 121.93, 121.35, 117.33, 117.17, 112.39, 108.60, 73.64, 21.70, 21.57. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{18}N_7$ 368.1618; Found 368.1622.

3'-Azido-2'-(1H-imidazol-1-yl)-7,7'-dimethyl-1H,3'H-3,3'-biindole (**4g**)



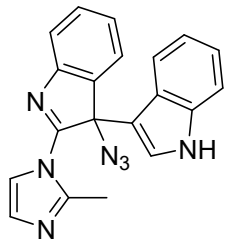
Reddish brown solid; Mp: 180.8 -181.8 °C; 158 mg, yield: 43%; **IR** (KBr): 3439, 2258, 2126, 1659, 1388, 828, 769, 625, 563, 536, 454 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.55 (s, 1H, NH), 8.33 (s, 1H, ArH), 7.95 (d, J = 2.8 Hz, 1H, ArH), 7.82 (t, J = 1.4 Hz, 1H, ArH), 7.44 (d, J = 7.6 Hz, 1H, ArH), 7.25 (t, J = 7.5 Hz, 1H, ArH), 7.18 (d, J = 7.3 Hz, 1H, ArH), 7.13 – 7.05 (m, 1H, ArH), 6.88 (d, J = 7.2 Hz, 1H, ArH), 6.74 (t, J = 7.6 Hz, 1H, ArH), 6.45 (d, J = 8.1 Hz, 1H, ArH), 2.66 (s, 3H, CH_3), 2.47 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 163.47, 149.60, 136.93, 136.76, 136.53, 132.85, 130.93, 130.63, 127.32, 124.83, 123.19, 122.90, 122.04, 121.09, 120.40, 117.34, 115.12, 109.14, 74.07, 17.10, 16.69. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{18}N_7$ 368.1618; Found 368.1613.

3'-Azido-2'-(1H-imidazol-1-yl)-5,5'-dimethoxy-1H,3'H-3,3'-biindole (**4h**)



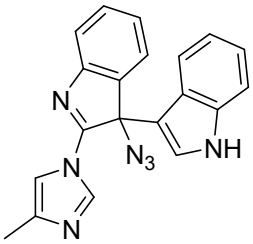
Reddish brown solid; Mp: 121.9 -122.6 °C; 263 mg, yield: 66%; **IR** (KBr): 3491, 2976, 2258, 2129, 1665, 1222, 826, 762, 691, 643, 590, 550, 493, 452 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.38 (d, J = 2.8 Hz, 1H, NH), 8.28 (s, 1H, ArH), 7.87 (d, J = 2.8 Hz, 1H, ArH), 7.76 (t, J = 1.4 Hz, 1H, ArH), 7.69 (d, J = 8.5 Hz, 1H, ArH), 7.28 (d, J = 8.8 Hz, 1H, ArH), 7.10 (dd, J = 8.5, 2.6 Hz, 1H, ArH), 7.05 (s, 1H, ArH), 6.92 (d, J = 2.6 Hz, 1H, ArH), 6.71 (dd, J = 8.8, 2.5 Hz, 1H, ArH), 6.00 (d, J = 2.4 Hz, 1H, ArH), 3.74 (s, 3H, CH_3), 3.48 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 162.63, 159.16, 153.93, 144.36, 138.49, 136.37, 132.48, 130.57, 125.83, 123.83, 121.97, 117.25, 115.73, 113.44, 111.89, 110.61, 107.95, 99.80, 73.85, 56.24, 55.49. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{18}N_7O_2$ 400.1516; Found 400.1512.

3'-Azido-2'-(2-methyl-1H-imidazol-1-yl)-1H,3'H-3,3'-biindole (**4i**)



Reddish brown solid; Mp: 121.3 -122.2 °C; 144 mg, yield: 41%; **IR** (KBr): 3444, 2263, 2129, 1657, 1306, 824, 763, 626, 551, 518, 480, 454, 423 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.47 (d, J = 2.7 Hz, 1H, NH), 7.81 (d, J = 2.7 Hz, 1H, ArH), 7.75 (d, J = 7.8 Hz, 1H, ArH), 7.54 (td, J = 7.4, 1.8 Hz, 1H, ArH), 7.47 (d, J = 1.7 Hz, 1H, ArH), 7.37 (d, J = 8.2 Hz, 1H, ArH), 7.34 – 7.28 (m, 2H, ArH), 7.03 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H, ArH), 6.81 (td, J = 7.5, 7.0, 1.1 Hz, 1H, ArH), 6.78 (d, J = 1.7 Hz, 1H, ArH), 6.64 (d, J = 8.1 Hz, 1H, ArH), 2.71 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 165.51, 151.43, 146.88, 137.35, 136.47, 131.57, 128.34, 127.55, 125.12, 123.67, 123.35, 122.40, 121.50, 120.17, 118.09, 117.38, 112.74, 108.39, 74.96, 17.74. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{16}N_7$ 354.1462; Found 354.1459.

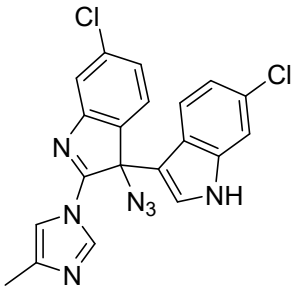
3'-Azido-2'-(4-methyl-1H-imidazol-1-yl)-1H,3'H-3,3'-biindole (**4j**)



Reddish brown solid; Mp: 115.8 -117.3 °C; 208 mg, yield: 59%; **IR** (KBr): 3449, 2262, 2139, 1658, 1451, 821, 759, 629, 572, 455, 429 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.56 (d, J = 2.8 Hz, 1H, NH), 8.20 (d, J = 1.3 Hz, 1H, ArH), 7.94 (d, J = 2.7 Hz, 1H, ArH), 7.75 (d, J = 7.7 Hz, 1H, ArH), 7.57 (td, J = 7.7, 1.4 Hz, 1H, ArH), 7.55 – 7.52 (m, 1H, ArH), 7.42 (d, J = 7.9 Hz, 1H, ArH), 7.36 (dd, J = 7.5, 1.4 Hz, 1H, ArH), 7.32 (td, J = 7.5, 1.1 Hz, 1H, ArH), 7.07 (ddd, J = 8.2, 7.1, 1.1 Hz, 1H, ArH), 6.82 (ddd, J = 8.2, 7.0, 1.1 Hz, 1H, ArH), 6.63 (d, J = 8.1 Hz, 1H, ArH), 2.10 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 164.23, 151.47, 139.64, 137.42, 136.81,

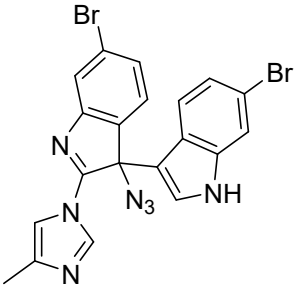
136.12, 131.63, 127.29, 125.12, 123.72, 123.41, 122.43, 121.20, 120.17, 117.46, 113.23, 112.75, 108.70, 73.68, 13.70. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{16}N_7$ 354.1462; Found 354.1464.

3'-Azido-6,6'-dichloro-2'-(4-methyl-1H-imidazol-1-yl)-1H,3'H-3,3'-biindole (**4k**)



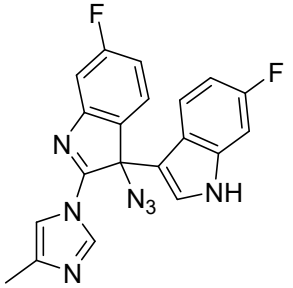
Reddish brown solid; Mp: 123.6 -124.8 °C; 240 mg, yield: 57%; **IR** (KBr): 3448, 2259, 2121, 1655, 834, 773, 631, 572, 517, 483, 452, 424 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.70 (d, J = 2.8 Hz, 1H, NH), 8.16 (s, 1H, ArH), 7.95 (d, J = 2.7 Hz, 1H, ArH), 7.82 (d, J = 1.7 Hz, 1H, ArH), 7.51 – 7.42 (m, 2H, ArH), 7.39 – 7.33 (m, 2H, ArH), 6.89 (dd, J = 8.6, 1.9 Hz, 1H, ArH), 6.64 (d, J = 8.6 Hz, 1H, ArH), 2.08 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 165.46, 152.90, 140.01, 137.85, 136.26, 136.04, 135.33, 127.41, 127.13, 126.54, 125.04, 122.08, 121.53, 120.80, 118.70, 113.22, 112.47, 108.55, 73.16, 13.70. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{14}Cl_2N_7$ 422.0682; Found 422.0680.

3'-Azido-6,6'-dibromo-2'-(4-methyl-1H-imidazol-1-yl)-1H,3'H-3,3'-biindole (**4l**)



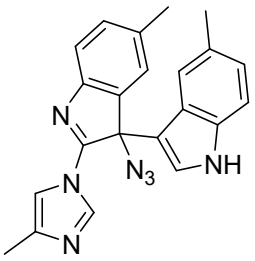
Reddish brown solid; Mp: 154.1 -154.7 °C; 275 mg, yield: 54%; **IR** (KBr): 3447, 2256, 2137, 1996, 1653, 1306, 821, 773, 674, 624, 542, 514, 456, 413 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.70 (d, J = 2.7 Hz, 1H, NH), 8.15 (d, J = 1.3 Hz, 1H, ArH), 7.95 (d, J = 1.8 Hz, 1H, ArH), 7.93 (d, J = 2.7 Hz, 1H, ArH), 7.59 (d, J = 1.8 Hz, 1H, ArH), 7.49 (dd, J = 7.9, 1.8 Hz, 1H, ArH), 7.48 – 7.45 (m, 1H, ArH), 7.30 (d, J = 7.9 Hz, 1H, ArH), 7.00 (dd, J = 8.6, 1.8 Hz, 1H, ArH), 6.58 (d, J = 8.6 Hz, 1H, ArH), 2.07 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 165.29, 152.97, 140.02, 138.28, 136.25, 135.73, 130.07, 126.42, 125.38, 124.42, 124.31, 123.36, 122.30, 119.05, 115.43, 115.36, 113.22, 108.51, 73.20, 13.69. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{14}Br_2N_7$ 511.9651; Found 511.9652.

3'-Azido-6,6'-difluoro-2'-(4-methyl-1H-imidazol-1-yl)-1H,3'H-3,3'-biindole (**4m**)



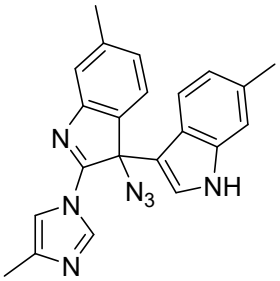
Reddish brown solid; Mp: 162.2 -163.3 °C; 210 mg, yield: 54%; **IR** (KBr): 3462, 3078, 2342, 2256, 2124, 1665, 825, 761, 694, 622, 595, 532, 498, 441 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.61 (d, J = 2.7 Hz, 1H, NH), 8.17 (d, J = 1.4 Hz, 1H, ArH), 7.92 (d, J = 2.7 Hz, 1H, ArH), 7.63 (dd, J = 8.9, 2.4 Hz, 1H, ArH), 7.52 – 7.44 (m, 1H, ArH), 7.38 (dd, J = 8.2, 5.2 Hz, 1H, ArH), 7.17 (dd, J = 9.8, 2.4 Hz, 1H, ArH), 7.12 (ddd, J = 9.4, 8.2, 2.4 Hz, 1H, ArH), 6.73 (td, J = 9.3, 2.4 Hz, 1H, ArH), 6.57 (dd, J = 8.9, 5.2 Hz, 1H, ArH), 2.08 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 165.80, 164.36 (d, J = 244.5 Hz), 159.45 (d, J = 235.5 Hz), 153.32 (d, J = 12 Hz), 139.95, 137.44 (d, J = 12 Hz), 136.26, 132.61, 126.10, 125.19 (d, J = 10.5 Hz), 120.15, 118.45 (d, J = 9 Hz), 113.72 (d, J = 24 Hz), 113.21, 109.42 (d, J = 24 Hz), 109.01 (d, J = 24 Hz), 108.72, 98.83 (d, J = 27 Hz), 73.06, 13.72; **^{19}F NMR** (565 MHz, DMSO-d_6) δ -109.23, -120.44. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{14}F_2N_7$ 390.1273; Found 390.1267.

3'-Azido-5,5'-dimethyl-2'-(4-methyl-1H-imidazol-1-yl)-1H,3'H-3,3'-biindole (**4n**)



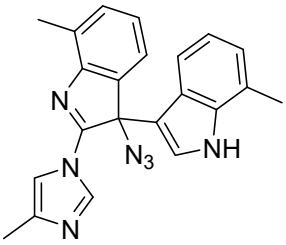
Reddish brown solid; Mp: 107.3 -108.4 °C; 221 mg, yield: 58%; **IR** (KBr): 3444, 2258, 2126, 1655, 814, 762, 621, 574, 530, 454, 418 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.39 (s, 1H, NH), 8.12 (t, J = 1.3 Hz, 1H, ArH), 7.81 (d, J = 2.5 Hz, 1H, ArH), 7.60 (d, J = 7.9 Hz, 1H, ArH), 7.48 (q, J = 1.3 Hz, 1H, ArH), 7.38 – 7.29 (m, 1H, ArH), 7.27 (d, J = 8.3 Hz, 1H, ArH), 7.12 (s, 1H, ArH), 6.87 (d, J = 8.3 Hz, 1H, ArH), 6.42 (s, 1H, ArH), 2.28 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.07 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 163.54, 149.13, 139.50, 136.99, 136.95, 135.98, 135.80, 131.88, 128.65, 124.86, 124.12, 124.07, 123.69, 120.78, 117.03, 113.18, 112.44, 108.27, 73.74, 21.72, 21.33, 13.72. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{20}N_7$ 382.1775; Found 382.1772.

3'-Azido-6,6'-dimethyl-2'-(4-methyl-1H-imidazol-1-yl)-1H,3'H-3,3'-biindole (**4o**)



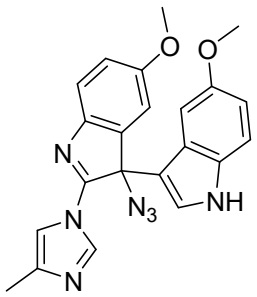
Reddish brown solid; Mp: 128.8 -129.7 °C; 213 mg, yield: 56%; **IR** (KBr): 3445, 2242, 2129, 1660, 1457, 819, 758, 621, 526, 455, 422 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.32 (d, J = 2.7 Hz, 1H, NH), 8.11 (s, 1H, ArH), 7.77 (d, J = 2.7 Hz, 1H, ArH), 7.53 (s, 1H, ArH), 7.47 (s, 1H, ArH), 7.17 (d, J = 7.5 Hz, 1H, ArH), 7.15 (s, 1H, ArH), 7.08 (d, J = 7.6 Hz, 1H, ArH), 6.62 (d, J = 8.3 Hz, 1H, ArH), 6.47 (d, J = 8.2 Hz, 1H, ArH), 2.40 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.06 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 164.44, 151.65, 141.53, 139.54, 137.84, 136.04, 133.88, 131.74, 127.64, 124.17, 123.33, 121.90, 121.84, 121.35, 117.19, 113.18, 112.37, 108.85, 73.56, 21.69, 21.57, 13.68. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{20}N_7$ 382.1775; Found 382.1771.

3'-Azido-7,7'-dimethyl-2'-(4-methyl-1H-imidazol-1-yl)-1H,3'H-3,3'-biindole (**4p**)



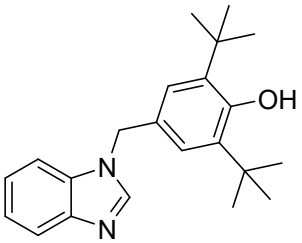
Reddish brown solid; Mp: 144.1 -144.9 °C; 160 mg, yield: 42%; **IR** (KBr): 3444, 2243, 2119, 2009, 1667, 821, 758, 625, 572, 495, 450, 418 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.49 (d, J = 2.8 Hz, 1H, NH), 8.14 (s, 1H, ArH), 7.88 (d, J = 2.8 Hz, 1H, ArH), 7.51 (t, J = 1.4 Hz, 1H, ArH), 7.36 (d, J = 7.7 Hz, 1H, ArH), 7.17 (t, J = 7.5 Hz, 1H, ArH), 7.11 (d, J = 7.3 Hz, 1H, ArH), 6.83 (d, J = 7.1 Hz, 1H, ArH), 6.70 (t, J = 7.6 Hz, 1H, ArH), 6.43 (d, J = 8.1 Hz, 1H, ArH), 2.60 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.08 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 163.26, 149.76, 139.49, 136.91, 136.69, 136.03, 132.78, 130.67, 127.07, 124.69, 123.20, 122.86, 122.01, 121.03, 120.36, 115.15, 113.23, 109.35, 73.96, 17.11, 16.69, 13.70. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{20}N_7$ 382.1775; Found 382.1776.

3'-Azido-5,5'-dimethoxy-2'-(4-methyl-1H-imidazol-1-yl)-1H,3'H-3,3'-biindole (**4q**)



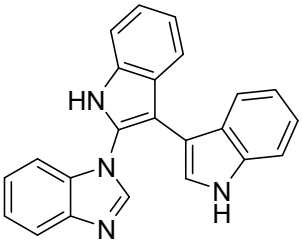
Reddish brown solid; Mp: 123.6 -124.5 °C; 231 mg, yield: 56%; **IR** (KBr): 3446, 2252, 2129, 2001, 1656, 1489, 821, 763, 620, 559, 537, 482, 456, 425 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.36 (d, J = 2.8 Hz, 1H, NH), 8.14 (s, 1H, ArH), 7.84 (d, J = 2.8 Hz, 1H, ArH), 7.65 (d, J = 8.5 Hz, 1H, ArH), 7.52 – 7.43 (m, 1H, ArH), 7.28 (d, J = 8.8 Hz, 1H, ArH), 7.08 (dd, J = 8.5, 2.6 Hz, 1H, ArH), 6.90 (d, J = 2.6 Hz, 1H, ArH), 6.72 (dd, J = 8.8, 2.5 Hz, 1H, ArH), 6.03 (d, J = 2.5 Hz, 1H, ArH), 3.73 (s, 3H, CH_3), 3.48 (s, 3H, CH_3), 2.07 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 162.46, 158.99, 153.92, 144.55, 139.39, 138.42, 135.86, 132.49, 125.68, 123.86, 121.74, 115.68, 113.41, 113.12, 111.86, 110.54, 108.20, 99.89, 73.81, 56.21, 55.51, 13.73. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{20}N_7O_2$ 414.1673; Found 414.1667.

4-((1H-benzo[d]imidazol-1-yl)methyl)-2,6-di-tert-butylphenol (**5**)



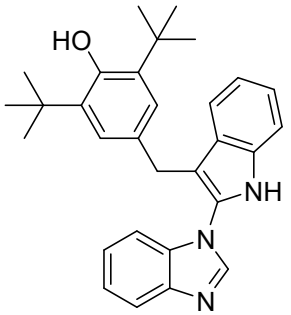
White solid; Mp: 151.4 -152.6 °C; 141 mg, yield: 42%; **IR** (KBr): 3624, 2910, 2746, 2577, 1703, 1628, 1481, 1365, 1197, 964, 847, 732 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 8.40 (s, 1H, ArH), 7.67 (d, J = 8.1 Hz, 1H, ArH), 7.63 (d, J = 8.0 Hz, 1H, ArH), 7.24 (t, J = 7.6 Hz, 1H, ArH), 7.19 (t, J = 7.5 Hz, 1H, ArH), 7.15 (s, 2H, ArH), 7.06 (s, 1H, OH), 5.38 (s, 2H, CH_2), 1.35 (s, 18H, CH_3); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 153.92, 144.46, 143.95, 139.95, 134.25, 128.32, 124.53, 122.76, 121.96, 119.90, 111.20, 48.47, 34.94, 30.75. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{29}N_2O$ 337.2274; Found 337.2269.

2-(1H-benzo[d]imidazol-1-yl)-1H,1'H-3,3'-biindole (**6**)



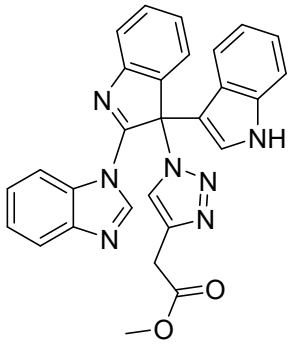
Reddish brown solid; Mp: 282.4 -283.8 °C; 309 mg, yield: 89%; **IR** (KBr): 3767, 3426, 3060, 2355, 1655, 824, 766, 611, 503, 450 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 12.08 (s, 1H, NH), 11.20 (d, J = 2.6 Hz, 1H, NH), 8.45 (s, 1H, ArH), 7.71 (d, J = 7.9 Hz, 1H, ArH), 7.60 (d, J = 8.0 Hz, 1H, ArH), 7.51 (d, J = 8.1 Hz, 1H, ArH), 7.38 – 7.33 (m, 2H, ArH), 7.29 (td, J = 8.0, 2.9 Hz, 2H, ArH), 7.26 – 7.19 (m, 2H, ArH), 7.16 (t, J = 7.5 Hz, 1H, ArH), 7.05 – 7.00 (m, 2H, ArH), 6.77 (t, J = 7.5 Hz, 1H, ArH); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 144.90, 143.14, 136.57, 134.94, 134.49, 127.43, 126.92, 126.38, 124.46, 123.97, 123.12, 122.97, 121.64, 120.45, 120.29, 120.12, 119.29, 119.15, 112.19, 112.12, 111.36, 106.50, 104.74. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{17}N_4$ 349.1448; Found 349.1440.

4-((2-(1H-benzo[d]imidazol-1-yl)-1H-indol-3-yl)methyl)-2,6-di-tert-butylphenol (**7**)



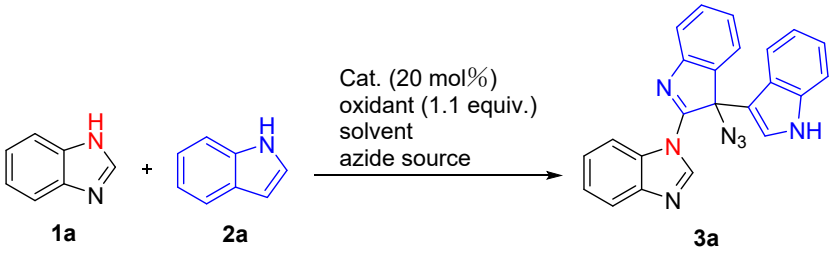
HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{30}H_{34}N_3O$ 452.2696; Found 452.2690.

methyl 2-(1-(2'-(1H-benzo[d]imidazol-1-yl)-1H,3'H-[3,3'-biindol]-3'-yl)-1H-1,2,3-triazol-4-yl)acetate (**8**)



Reddish brown solid; Mp: 267.2 -268.5 °C; 3.17 g, yield: 92%; **IR** (KBr): 3760, 3414, 3018, 2127, 1788, 1651, 826, 760, 613, 504, 453 cm^{-1}; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 9.11 (s, 1H, NH), 8.19 (s, 1H, ArH), 7.94 (dd, J = 7.9, 1.5 Hz, 1H, ArH), 7.85 (t, J = 1.2 Hz, 1H, ArH), 7.76 (s, 1H, ArH), 7.69 – 7.61 (m, 2H, ArH), 7.54 – 7.47 (m, 3H, ArH), 7.40 (td, J = 7.5, 1.3 Hz, 1H, ArH), 7.32 (ddd, J = 8.3, 7.1, 1.4 Hz, 1H, ArH), 7.22 (tdd, J = 7.6, 4.8, 1.4 Hz, 2H, ArH), 7.11 (dtd, J = 11.5, 7.6, 1.5 Hz, 2H, ArH), 3.85 (d, J = 1.2 Hz, 2H, CH_2), 3.75 (s, 3H, CH_3); **^{13}C NMR** (151 MHz, DMSO-d_6) δ 169.72, 155.73, 145.68, 142.87, 140.48, 140.02, 138.47, 138.19, 132.53, 130.56, 130.26, 128.72, 127.26, 124.93, 124.65, 122.19, 122.04, 121.58, 120.88, 120.49, 120.35, 118.68, 116.90, 111.44, 108.98, 61.08, 52.08, 33.28. **HRMS** (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{28}H_{22}N_7O_2$ 488.1829; Found 488.1826.

4. Reaction Condition Optimizations



Entry	Catalyst	Oxidant	Azide source	Solvent	*t* [°C][b]	Yield (%)
1	CuI_2	PIFA	NaN_3	CH_2Cl_2	rt	11
2	CuI	PIFA	NaN_3	CH_2Cl_2	rt	9
3	$CuCl_2$	PIFA	NaN_3	CH_2Cl_2	rt	17
4	$CuBr_2$	PIFA	NaN_3	CH_2Cl_2	rt	14
5	CuBr	PIFA	NaN_3	CH_2Cl_2	rt	8
6	$Cu(OAc)_2$	PIFA	NaN_3	CH_2Cl_2	rt	32
7	$Cu(acac)_2$[d]	PIFA	NaN_3	CH_2Cl_2	rt	17
8	$FeCl_3$	PIFA	NaN_3	CH_2Cl_2	rt	nr
9	$Cu(OAc)_2$	PIFA	NaN_3	MeCN	rt	21
10	$Cu(OAc)_2$	PIFA	NaN_3	$CHCl_3$	rt	15
11	$Cu(OAc)_2$	PIFA	NaN_3	1,4-dioxane	rt	30
12	$Cu(OAc)_2$	PIFA	NaN_3	THF	rt	34
13	$Cu(OAc)_2$	PIFA	NaN_3	Ethyl Acetate	rt	56
14	$Cu(OAc)_2$	PIDA	NaN_3	Ethyl Acetate	rt	25
15	$Cu(OAc)_2$	IBX	NaN_3	Ethyl Acetate	rt	23
16	$Cu(OAc)_2$	DTBP	NaN_3	Ethyl Acetate	rt	19
17	$Cu(OAc)_2$	TBHP	NaN_3	Ethyl Acetate	rt	16
18	$Cu(OAc)_2$	PIFA	$TMSN_3$	Ethyl Acetate	rt	27
19	$Cu(OAc)_2$	PIFA	DPPA	Ethyl Acetate	rt	15
20	$Cu(OAc)_2$	PIFA	NaN_3	Ethyl Acetate	40	59
21	$Cu(OAc)_2$	PIFA	NaN_3	Ethyl Acetate	50	64
22	$Cu(OAc)_2$	PIFA	NaN_3	Ethyl Acetate	reflux	76
23	$Cu(OAc)_2$[e]	PIFA	NaN_3	Ethyl Acetate	reflux	58
24	$Cu(OAc)_2$[f]	PIFA	NaN_3	Ethyl Acetate	reflux	41
25[g]	$Cu(OAc)_2$	PIFA	NaN_3	Ethyl Acetate	reflux	73

[a] Reagents and conditions: In a 25 mL reaction tube, benzimidazole **1a** (0.5 mmol), indole **2a** (1.1 mmol), oxidant (0.55 mmol), catalyst (20 mol%), azide source (0.75 mmol), solvent 10 mL, under aerobic atmosphere (1 atm), stirred for 5 h. [b] rt = room temperature. [c] Isolated yield based on **1a**. [d] acac = acetylacetone. [e] Catalyst (10 mol%). [f] Catalyst (5 mol%). [g] under argon (1 atm) atmosphere.

Table S1. Reaction Condition Optimizations[a,c]

Our initial attempt involved the cascade reaction of benzimidazole (**1a**) and indole (**2a**) was studied in the presence of a series of catalysts by using PIFA as an oxidant in

dichloromethane. Different catalysts were screened for their ability to catalyze the cascade reaction at room temperature (Table S1, entries 1–8). The results indicated that the use of $Cu(OAc)_2$ led to the highest yield (32%) of the model azide-biindole product **3a** (Table S1, entry 6). Encouraged by this result, we sought to enhance the yield of this cascade reaction by screening a variety of different solvents (Table S1, entries 9–13). Using $Cu(OAc)_2$ as the catalyst in the presence of PIFA and sodium azide, the highest yield of **3a** was obtained when using ethyl acetate as the solvent (56% yield, Table S1, entry 13). Subsequent screening of other oxidants indicated that PIFA remained the best oxidant for furnishing **3a** in the highest yield (Table S1, entries 14–17). In addition to NaN_3, azidotrimethylsilane ($TMSN_3$) and diphenyl phosphoryl azide (DPPA) were screened as the azide source (Table S1, entries 18–19). The results showed that NaN_3 was more reactive than the other organic azides (Table S1, entry 13). Then, increasing the reaction temperature from 40°C to reflux afforded increasingly higher yields compared to at r.t., with the highest yield being obtained under refluxing conditions (76% yield, Table S1, entry 22). In addition, the amount of the catalyst was screened, showing that a decrease in the amount of the catalyst decreased the yield of the reaction; approximately 20 mol% was identified as the optimal amount (Table S1, entry 23, 24 vs entry 22). Finally, the reaction proceeded under argon atmosphere to test whether the inert gas (argon) environment affected the yield of this cascade reaction, we found that under inert atmosphere, the reaction yield did not change significantly (Table S1, entry 25). Therefore, the results of the reaction optimization indicated that ethyl acetate as the solvent, 1.1 equiv. of PIFA as the oxidant, 20 mol% $Cu(OAc)_2$ as the catalyst, 1.5 equiv. of NaN_3 as the azide source, a temperature of reflux temperature was best-suited for the synthesis of compound **3a** (Table S1, entry 22).

5. X-ray Structure and Data of **3a**

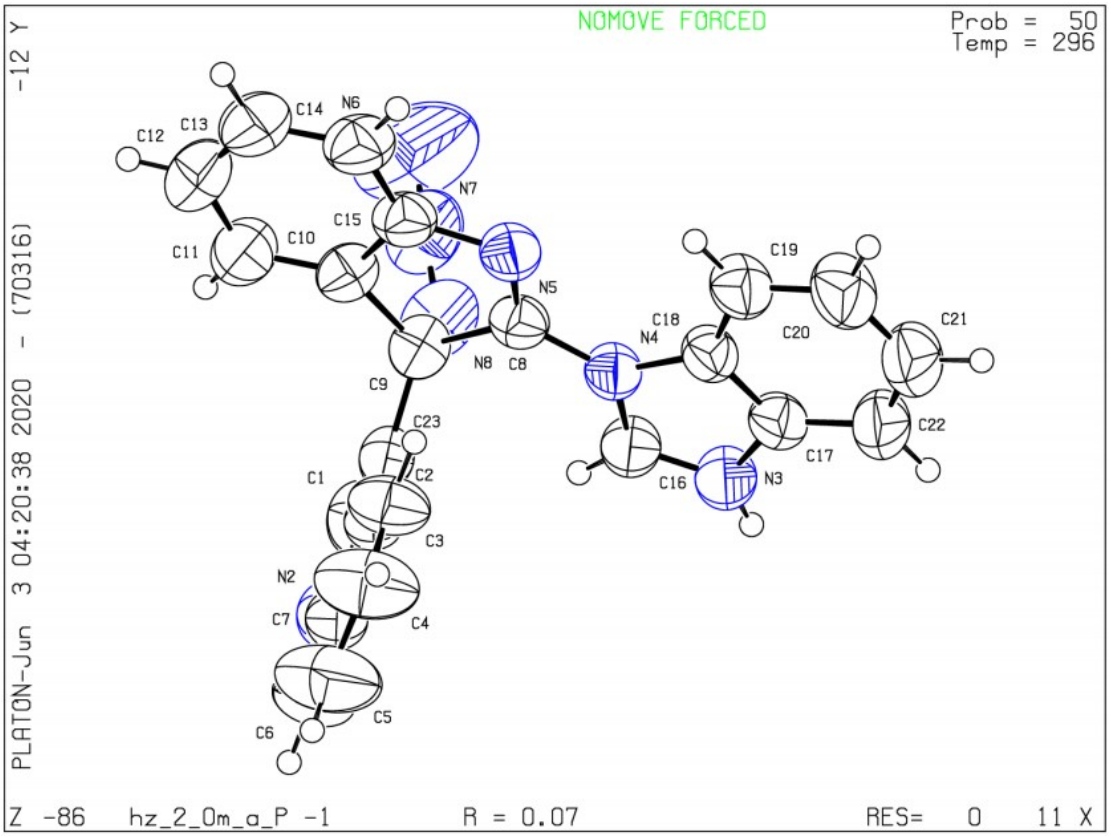


Figure S1. X-Ray crystal structure of **3a**

Table S2. Crystal data and structure refinement for **3a**

Datablock: hz_2_0m_a_sq

```
Bond precision:  C-C = 0.0039 A          Wavelength=0.71073

Cell:          a=10.6842(17)     b=10.8749(17)     c=12.429(2)
               alpha=91.808(2)   beta=111.391(2)   gamma=101.478(2)
Temperature:   296 K

                 Calculated                Reported
Volume           1309.1(4)                 1309.1(4)
Space group      P -1                      P -1
Hall group       -P 1                      -P 1
Moiety formula   C23 H15 N7 [+ solvent]    ?
Sum formula      C23 H15 N7 [+ solvent]    C19.50 H19.50 N19.50 O0
Mr               389.42                    527.04
Dx,g cm-3        0.988                     1.337
Z                2                         2
Mu (mm-1)        0.063                     0.095
F000             404.0                     546.0
F000'            404.12
h,k,lmax         13,14,16                  13,14,16
Nref             5996                      5904
Tmin,Tmax        0.986,0.989
Tmin'            0.986

Correction method= Not given

Data completeness= 0.985          Theta(max)= 27.491

R(reflections)= 0.0669( 3171)     wR2(reflections)= 0.2246( 5904)

S = 1.186                 Npar= 271
```

Compound **3a** (50 mg) was add to a 10 mL sample bottle, following to add DCM (2 mL), n-hexane (2.5 mL) and toluene (0.1 mL), then seal the bottle with a parafilm, and poke 15 small holes on the parafilm, place the sample bottle in a safe place to allow it to volatilize and separate out the single crystal. Take out the single crystal and send it for single crystal diffraction test to obtain relevant data. Instrument model：Intensity data for single crystals of each complex were collected on a BRUKER SMART APEX II CCD detector with graphite-monochromatized Mo Kα radiation (k = 0.071073 nm). The structures were solved by direct method using the program SHELXS-97 and subsequent Fourier difference techniques, and refined anisotropically by full matrix least-squares on F2 using SHELXL-97.

6. X-ray Structure and Data of **4p**

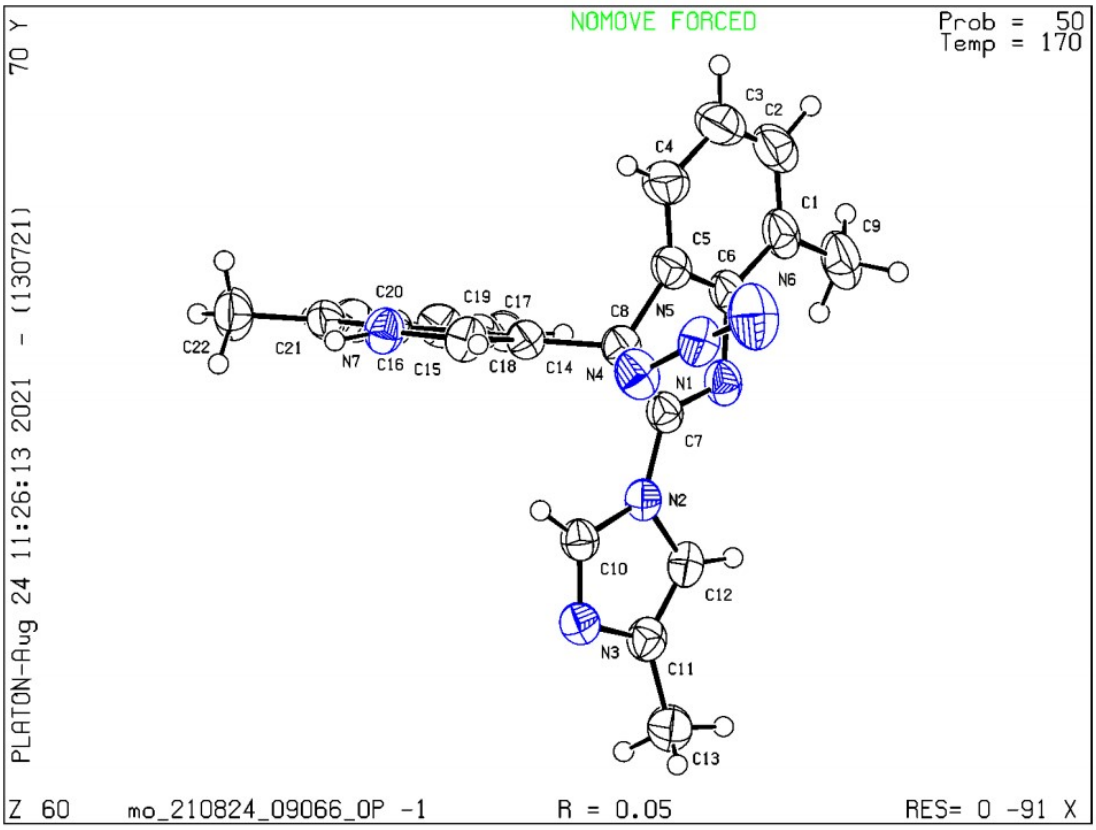


Figure S2. X-Ray crystal structure of **4p**

Table S3. Crystal data and structure refinement for **4p**

Datablock: mo_210824_09066_0m

Bond precision: C-C = 0.0031 A Wavelength=0.71073

Cell: a=8.0191(10) b=10.4708(13) c=13.0070(16)
alpha=68.608(5) beta=84.564(5) gamma=75.181(4)
Temperature: 170 K

	Calculated	Reported
Volume	983.1(2)	983.1(2)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C22 H19 N7	C22 H19 N7
Sum formula	C22 H19 N7	C22 H19 N7
Mr	381.44	381.44
Dx,g cm-3	1.289	1.289
Z	2	2
Mu (mm-1)	0.082	0.082
F000	400.0	400.0
F000'	400.12	
h,k,lmax	10,13,16	10,13,16
Nref	4363	4139
Tmin,Tmax	0.996,0.998	0.673,0.746
Tmin'	0.994	

Correction method= # Reported T Limits: Tmin=0.673 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.949 Theta(max)= 27.147

R(reflections)= 0.0514(2681) wR2(reflections)= 0.1445(4139)

S = 1.040 Npar= 268

Compound **4p** (50 mg) was add to a 10 mL sample bottle, following to add DCM (2 mL), n-hexane (2.5 mL) and toluene (0.1 mL), then seal the bottle with a parafilm, and poke 15 small holes on the parafilm, place the sample bottle in a safe place to allow it to volatilize and separate out the single crystal. Take out the single crystal and send it for single crystal diffraction test to obtain relevant data. Instrument model：
Intensity data for single crystals of each complex were collected on a BRUKER SMART APEX II CCD detector with graphite-monochromatized Mo Kα radiation (k = 0.071073 nm). The structures were solved by direct method using the program SHELXS-97 and subsequent Fourier difference techniques, and refined anisotropically by full matrix least-squares on F2 using SHELXL-97.

7. X-ray Structure and Data of **6**

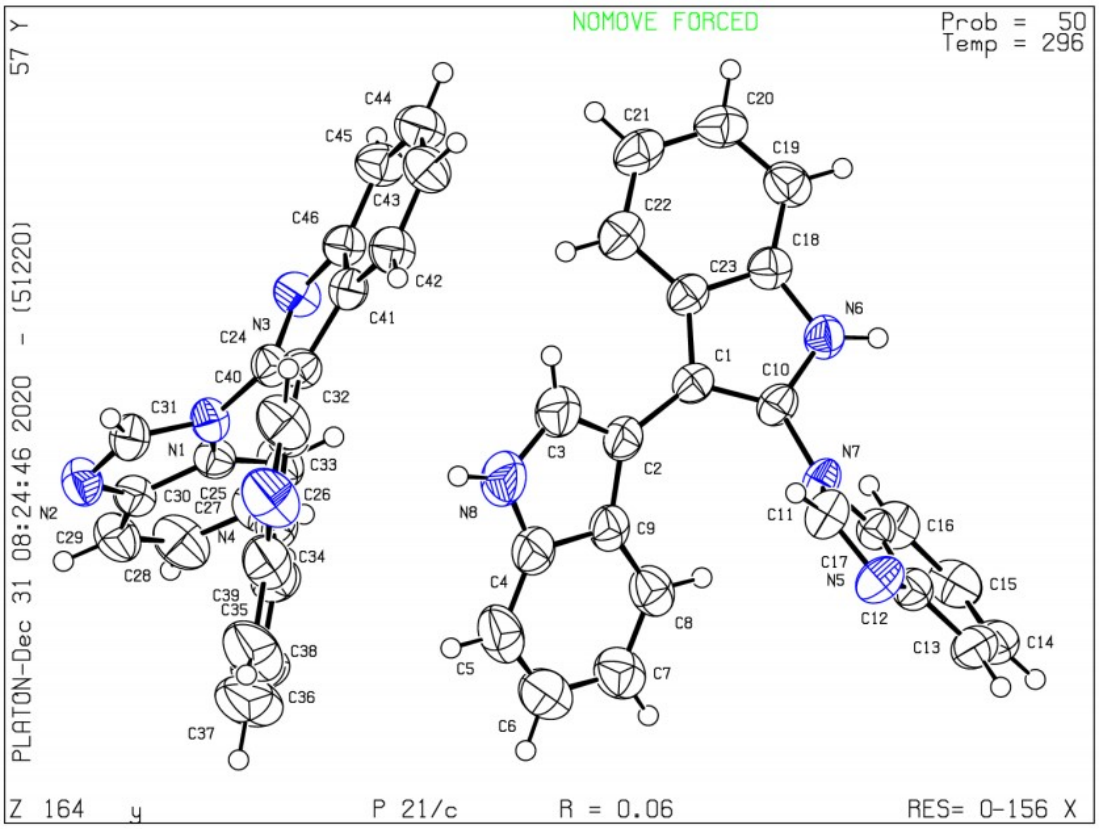


Figure S3. X-Ray crystal structure of **6**

Table S4. Crystal data and structure refinement for **6**

Datablock: y

Bond precision: C-C = 0.0063 A Wavelength=0.71073

Cell: a=7.196(5) b=19.955(15) c=24.468(18)
alpha=90 beta=90.050(1) gamma=90
Temperature: 296 K

	Calculated	Reported
Volume	3514(4)	3514(4)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C23 H15 N4, C23 H16 N4	?
Sum formula	C46 H31 N8	C46 H31 N8
Mr	695.79	695.79
Dx,g cm-3	1.315	1.315
Z	4	4
Mu (mm-1)	0.080	0.080
F000	1452.0	1452.0
F000'	1452.48	
h,k,lmax	8,24,30	8,24,30
Nref	6885	6548
Tmin,Tmax	0.986,0.990	
Tmin'	0.986	

Correction method= Not given

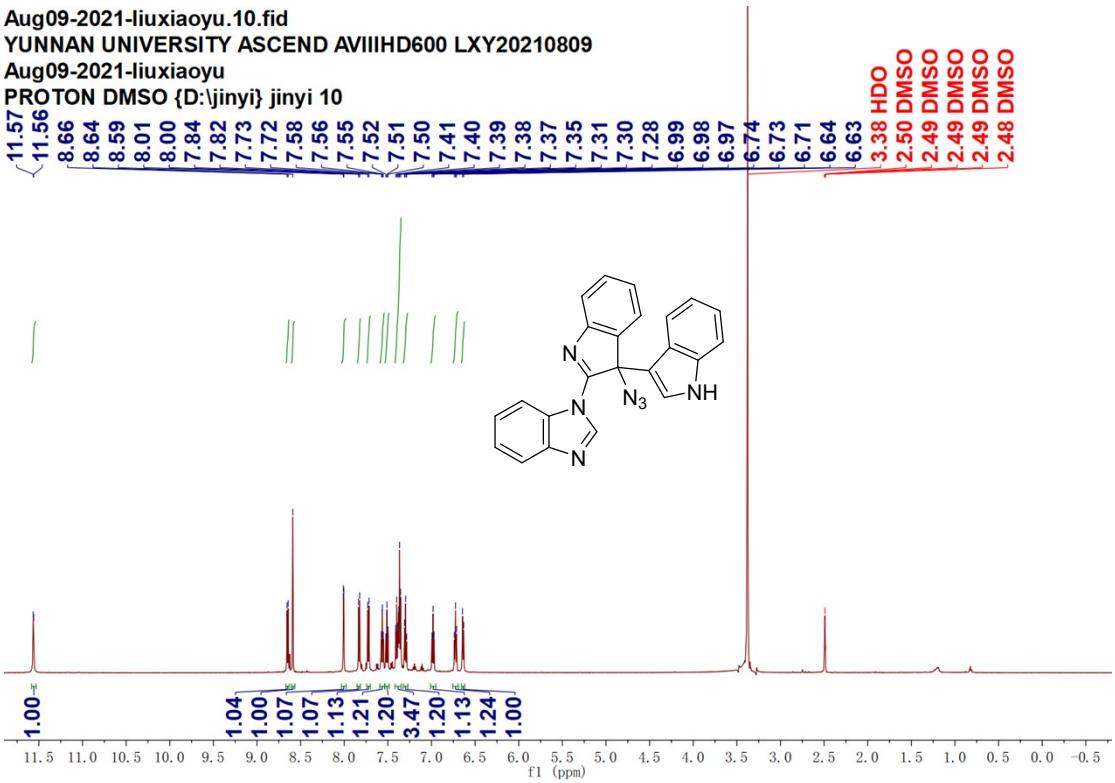
Data completeness= 0.951 Theta(max)= 25.999

R(reflections)= 0.0621(2035) wR2(reflections)= 0.1289(6548)

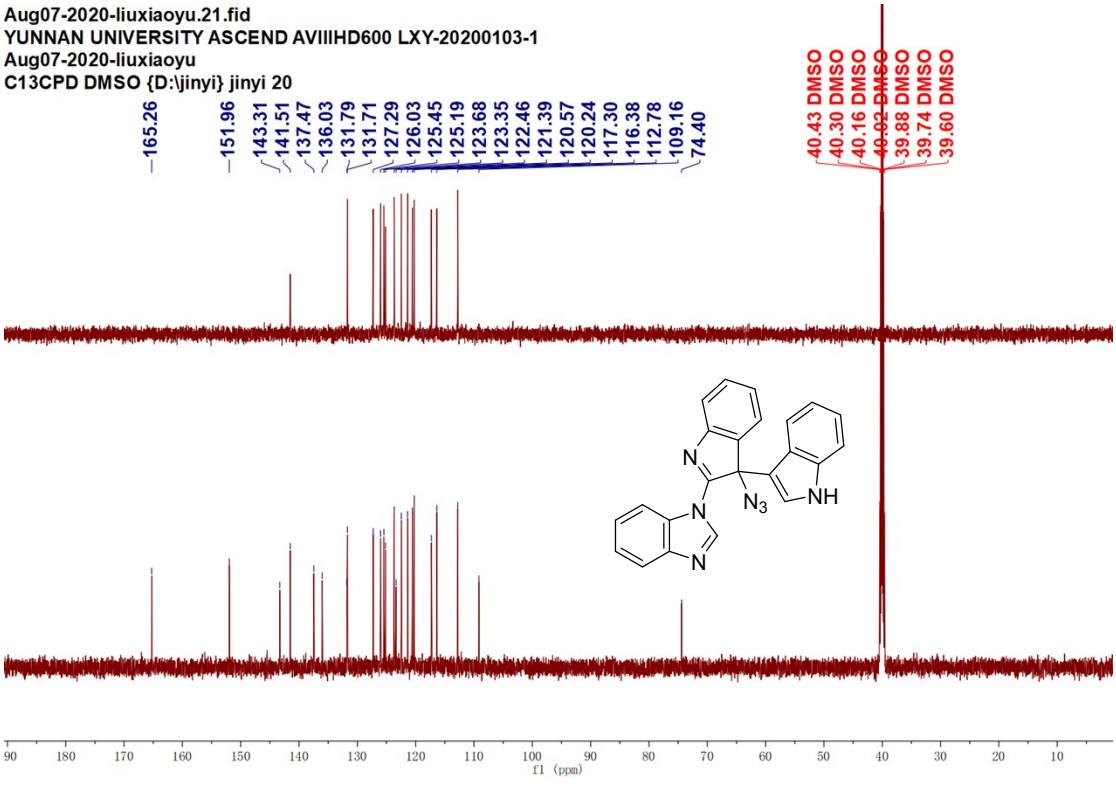
S = 0.757 Npar= 487

Compound **6** (50 mg) was add to a 10 mL sample bottle, following to add DCM (2 mL), n-hexane (2.5 mL) and toluene (0.1 mL), then seal the bottle with a parafilm, and poke 15 small holes on the parafilm, place the sample bottle in a safe place to allow it to volatilize and separate out the single crystal. Take out the single crystal and send it for single crystal diffraction test to obtain relevant data. Instrument model：
Intensity data for single crystals of each complex were collected on a BRUKER SMART APEX II CCD detector with graphite-monochromatized Mo Kα radiation (k = 0.071073 nm). The structures were solved by direct method using the program SHELXS-97 and subsequent Fourier difference techniques, and refined anisotropically by full matrix least-squares on F2 using SHELXL-97.

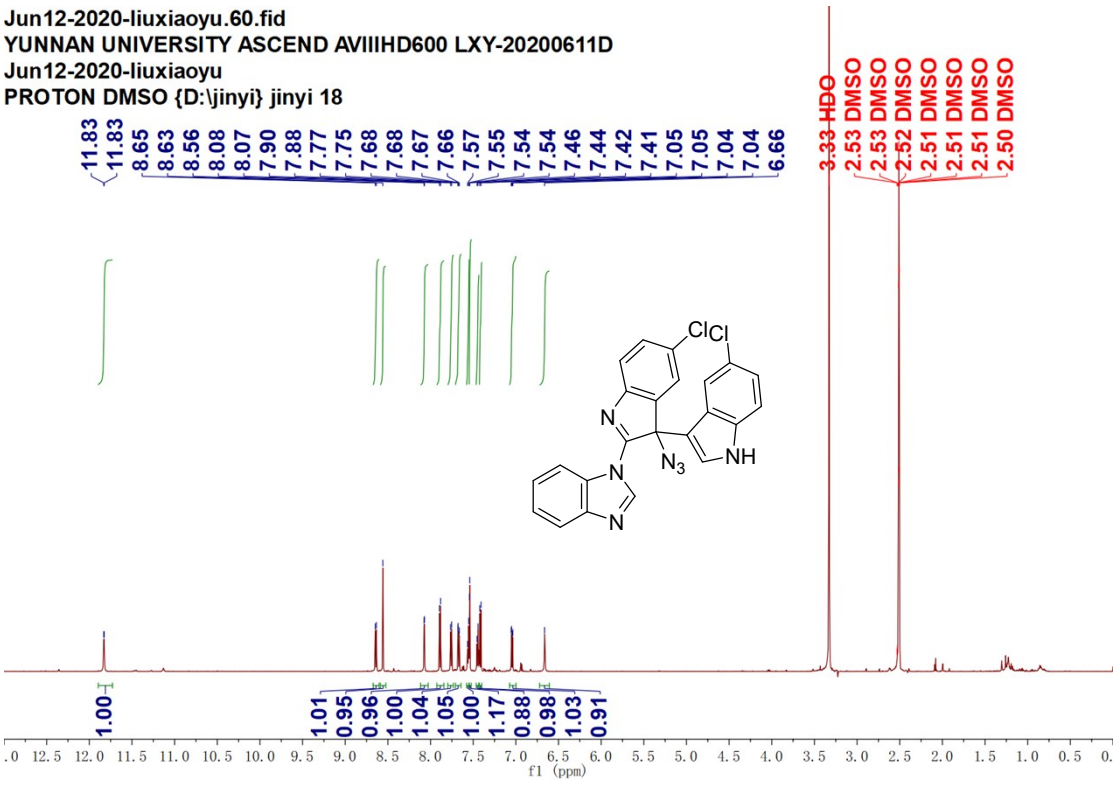
8. ^{1}H NMR and ^{13}C NMR Spectra of These Compounds



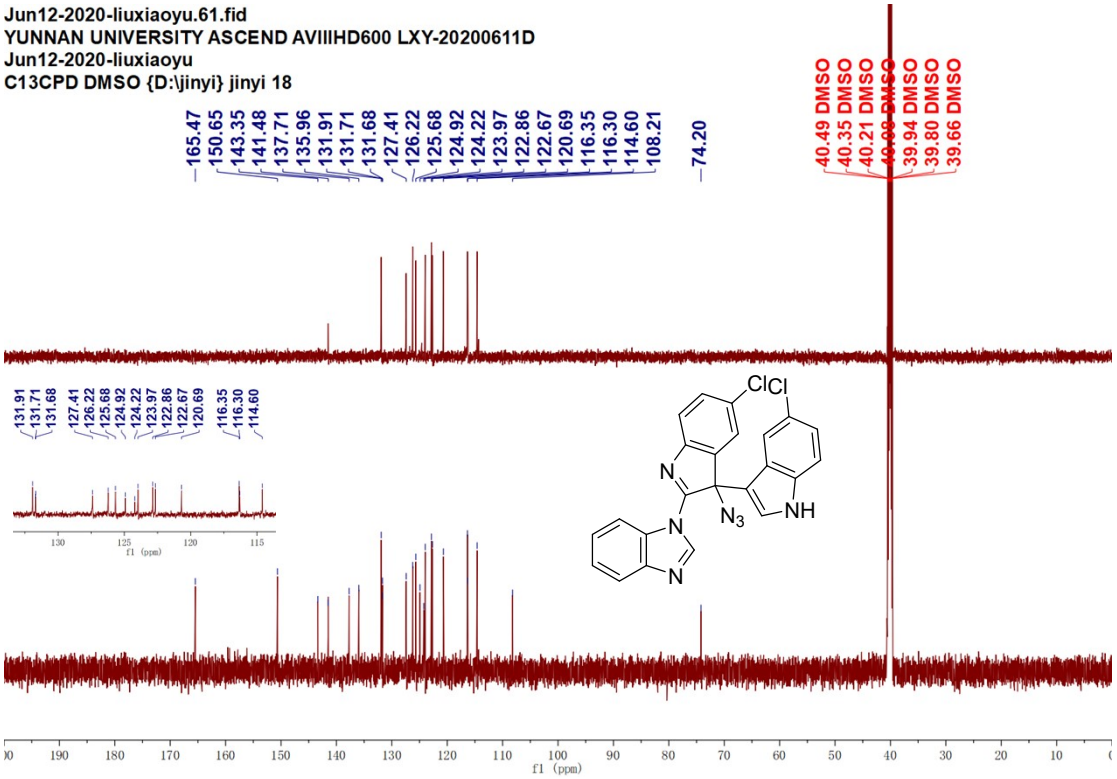
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **3a**



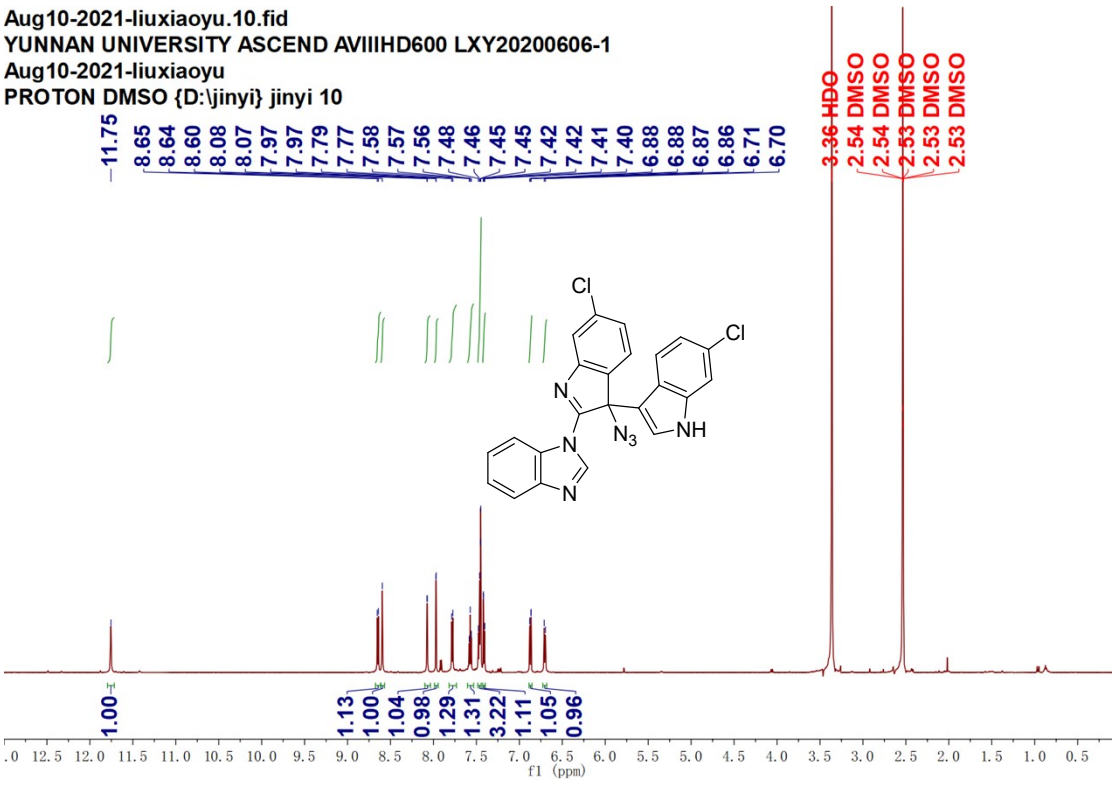
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **3a**



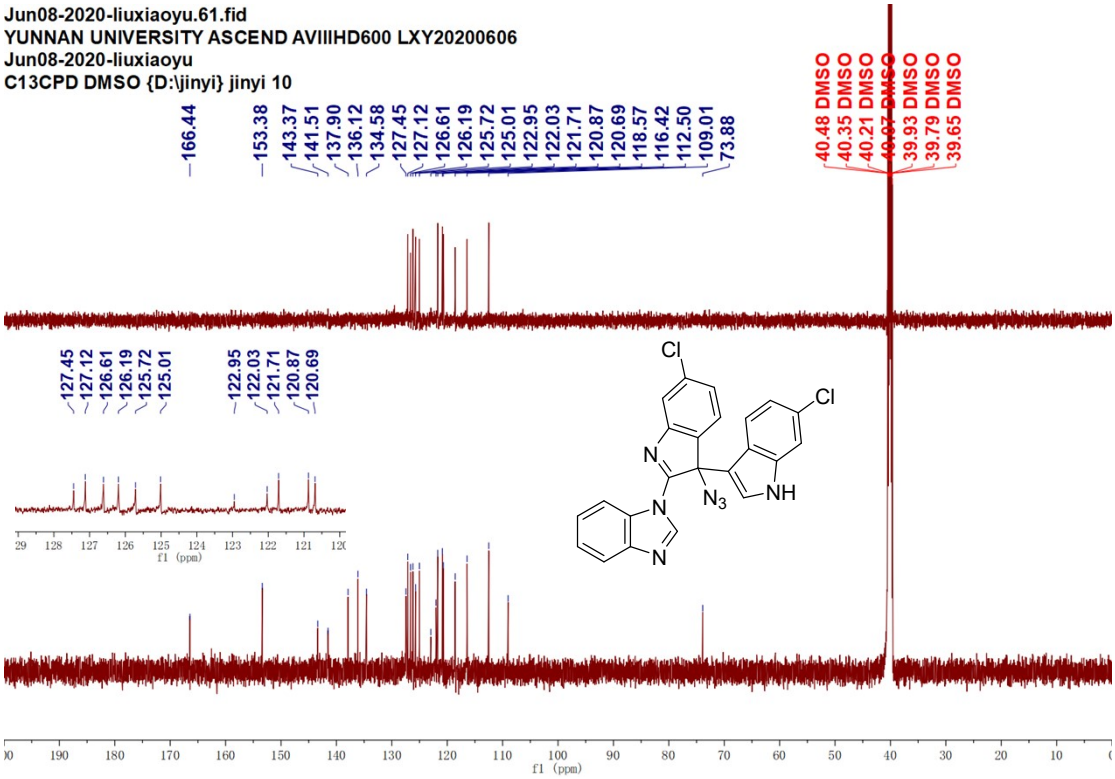
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **3b**



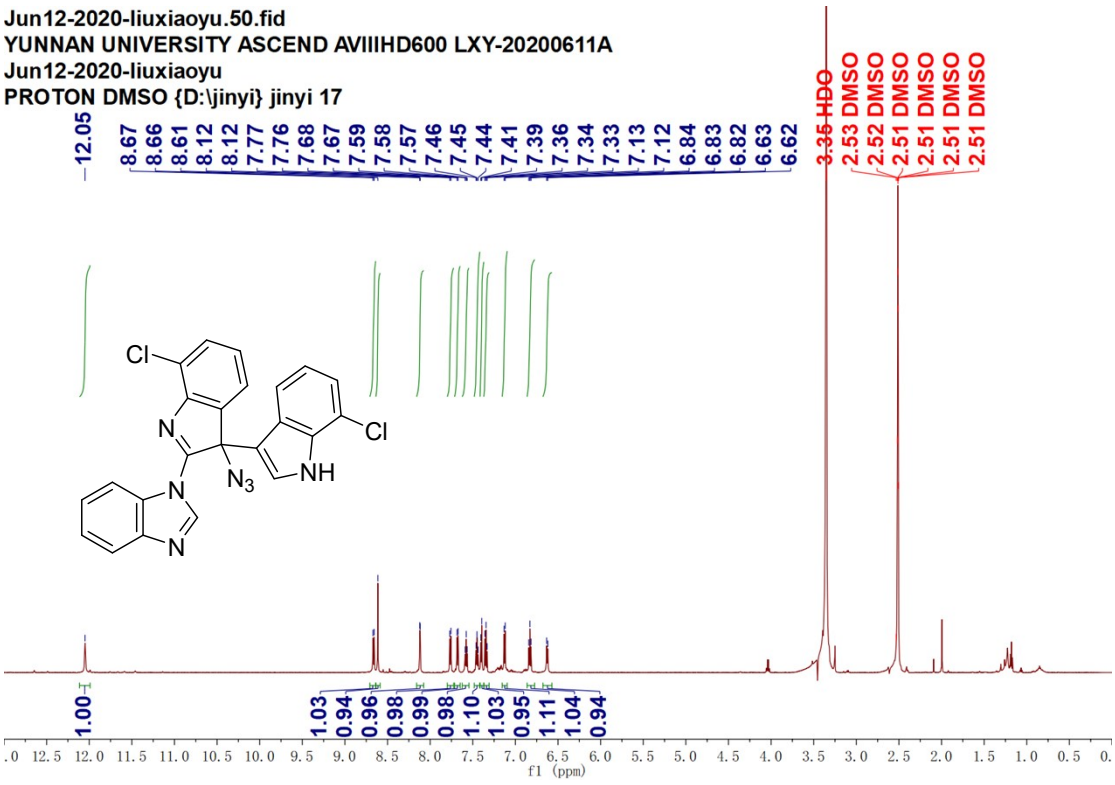
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **3b**



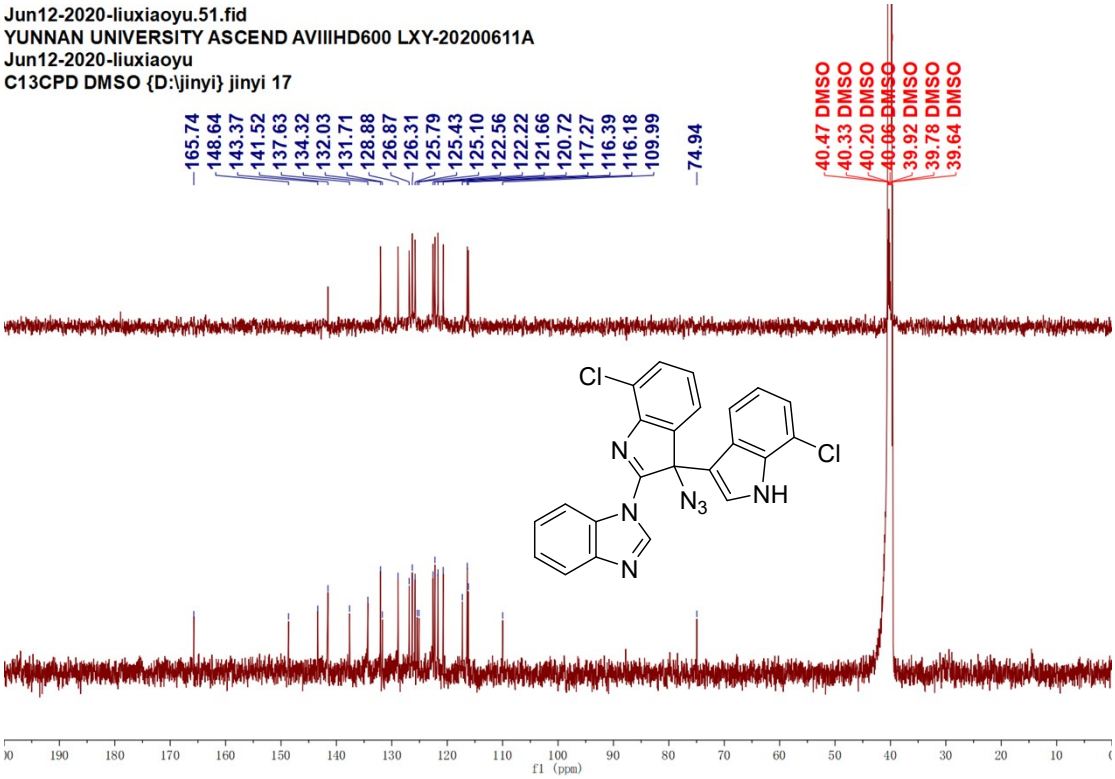
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **3c**



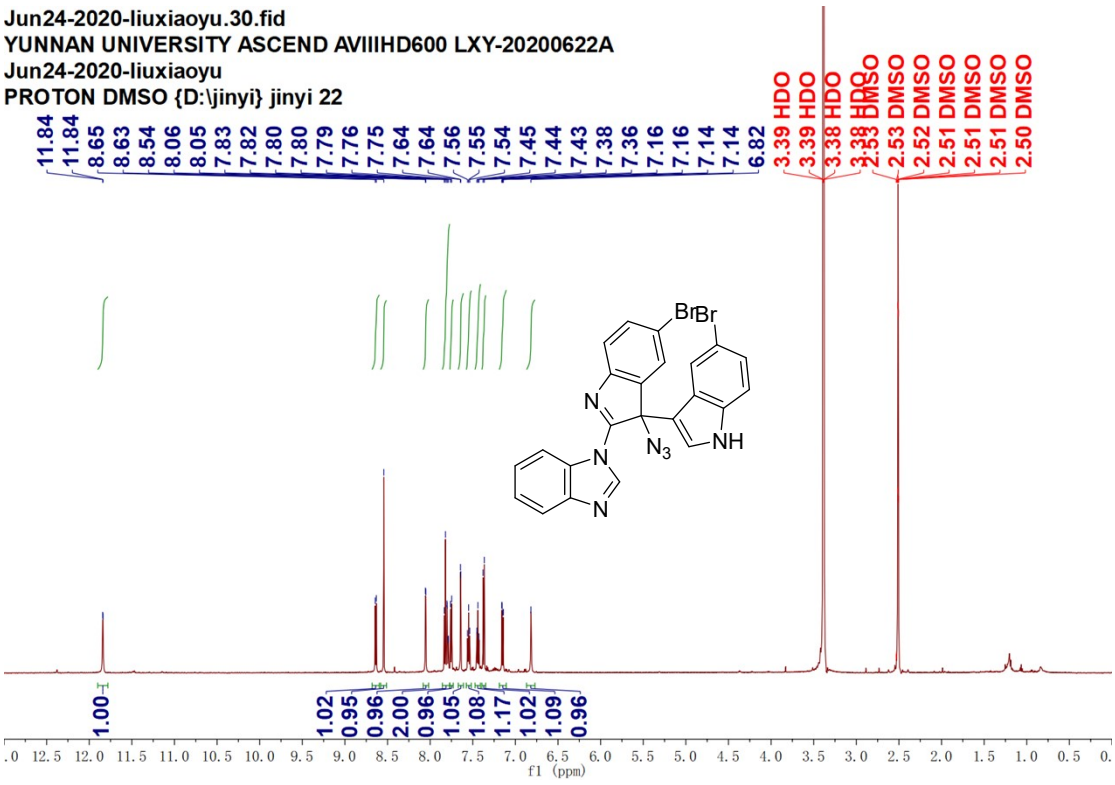
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **3c**



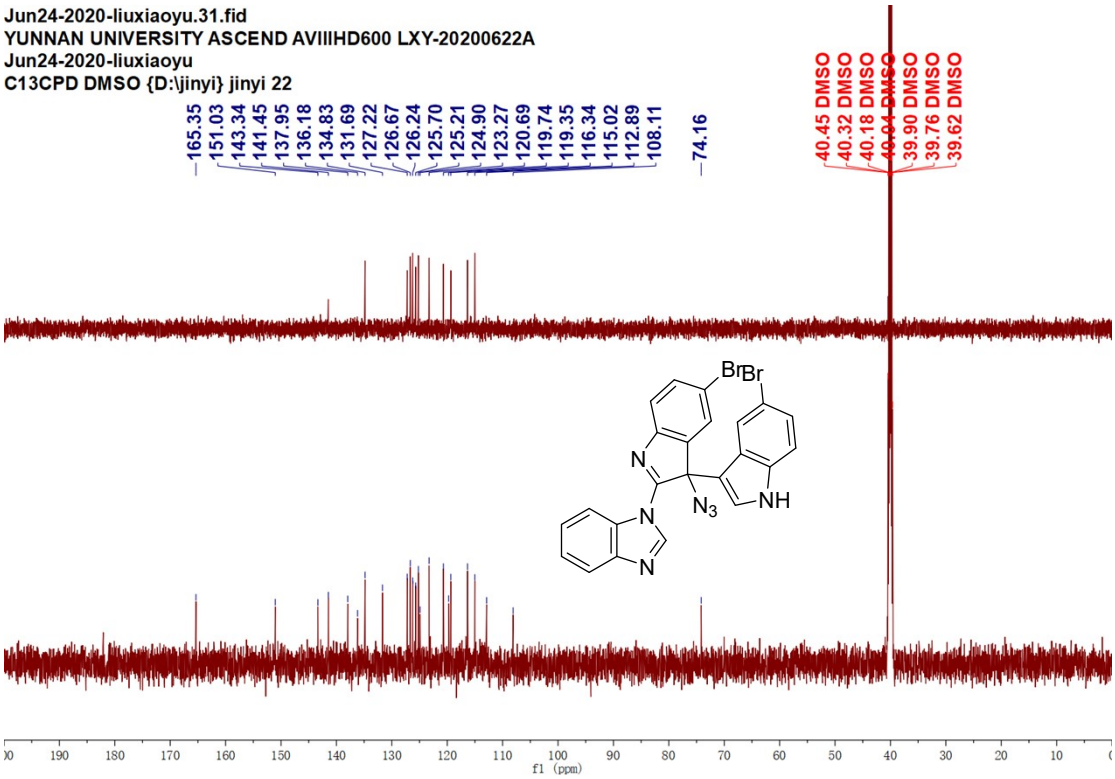
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **3d**



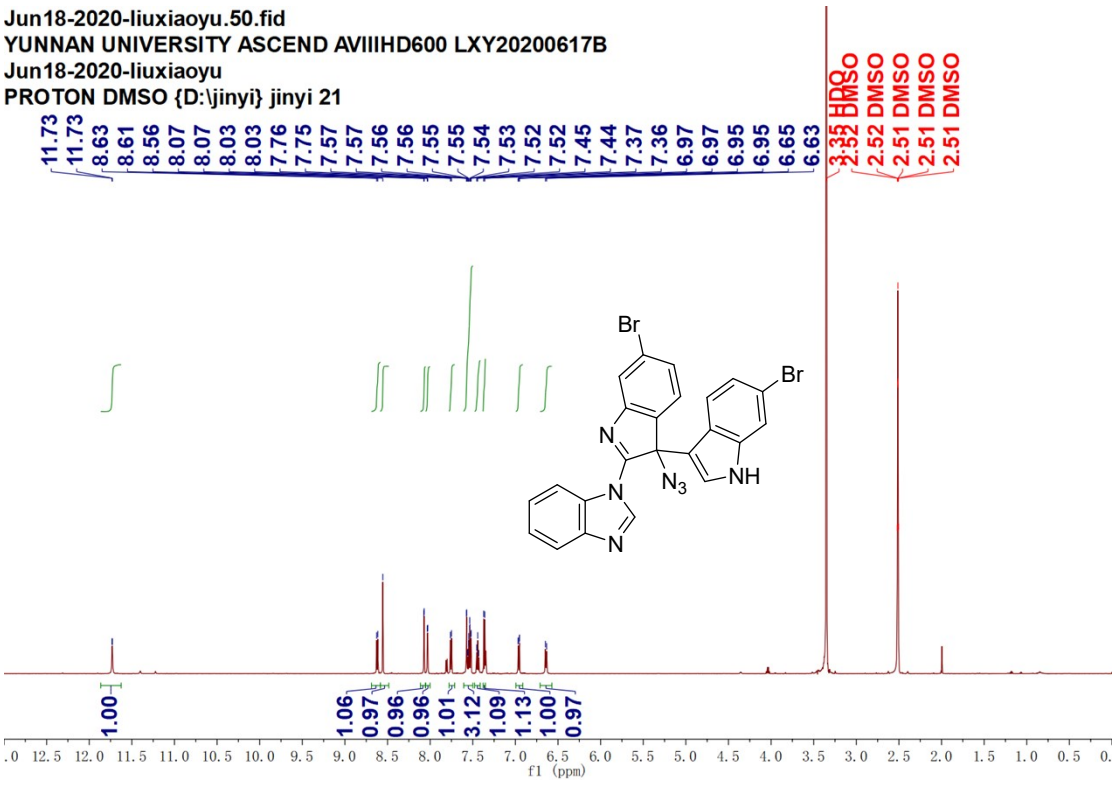
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **3d**



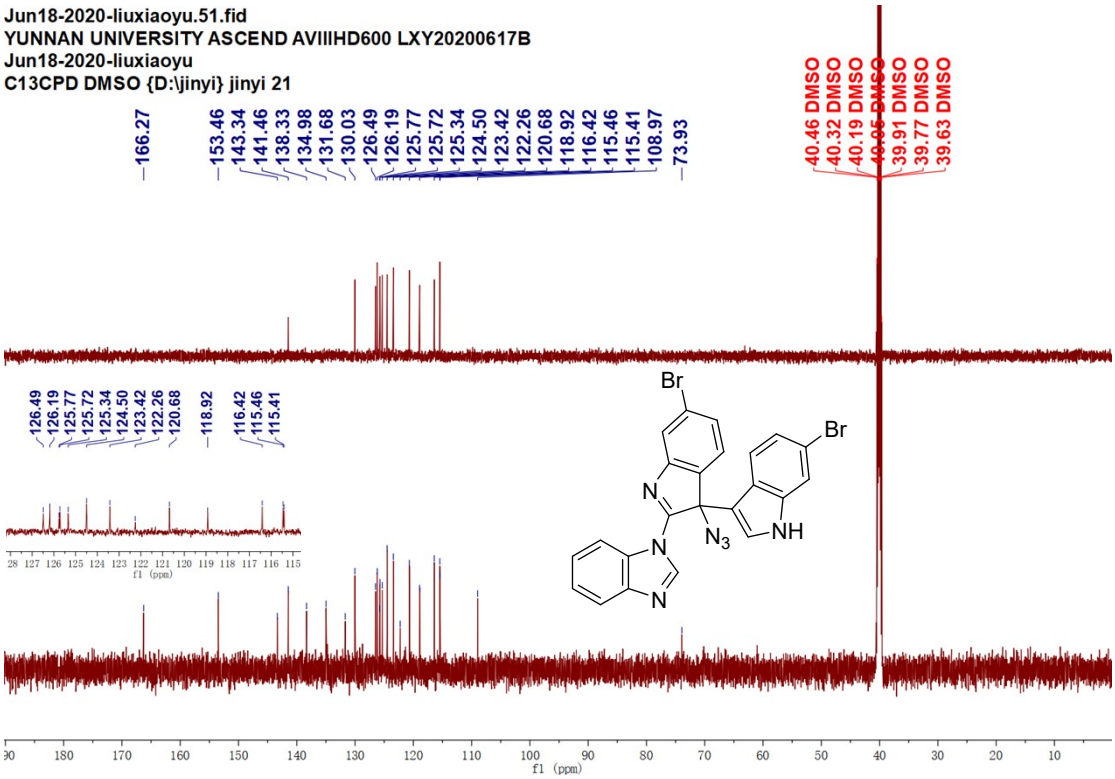
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **3e**



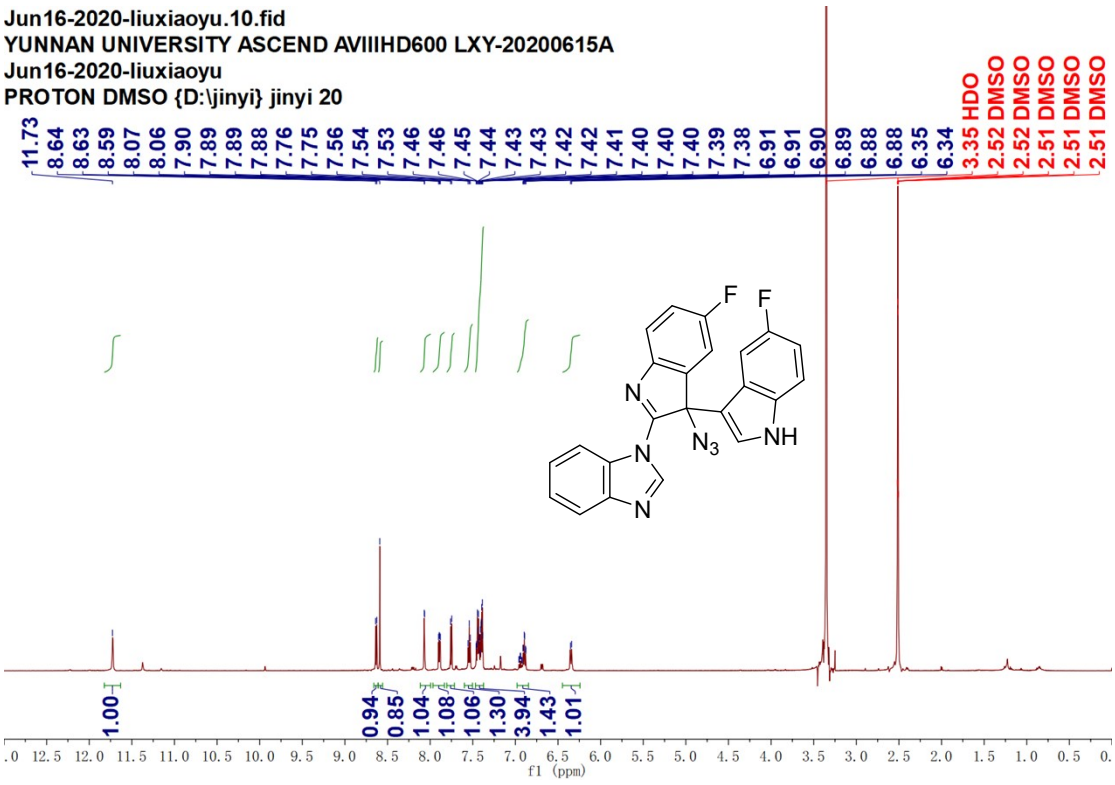
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **3e**



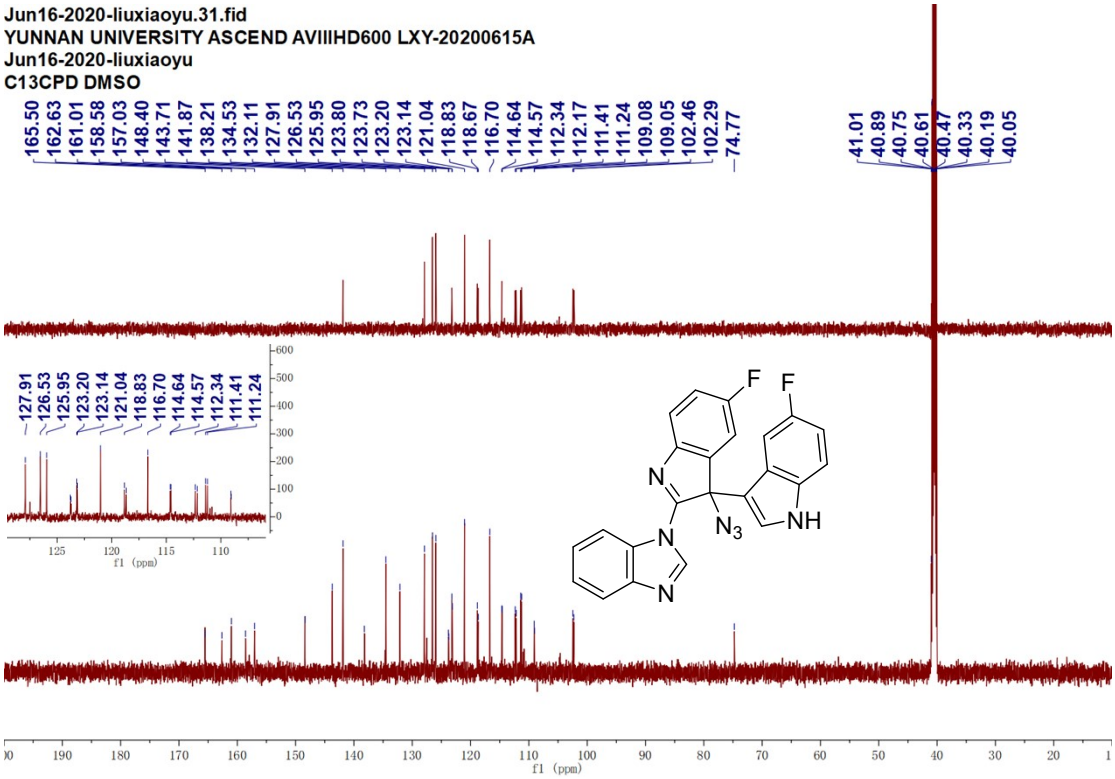
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **3f**



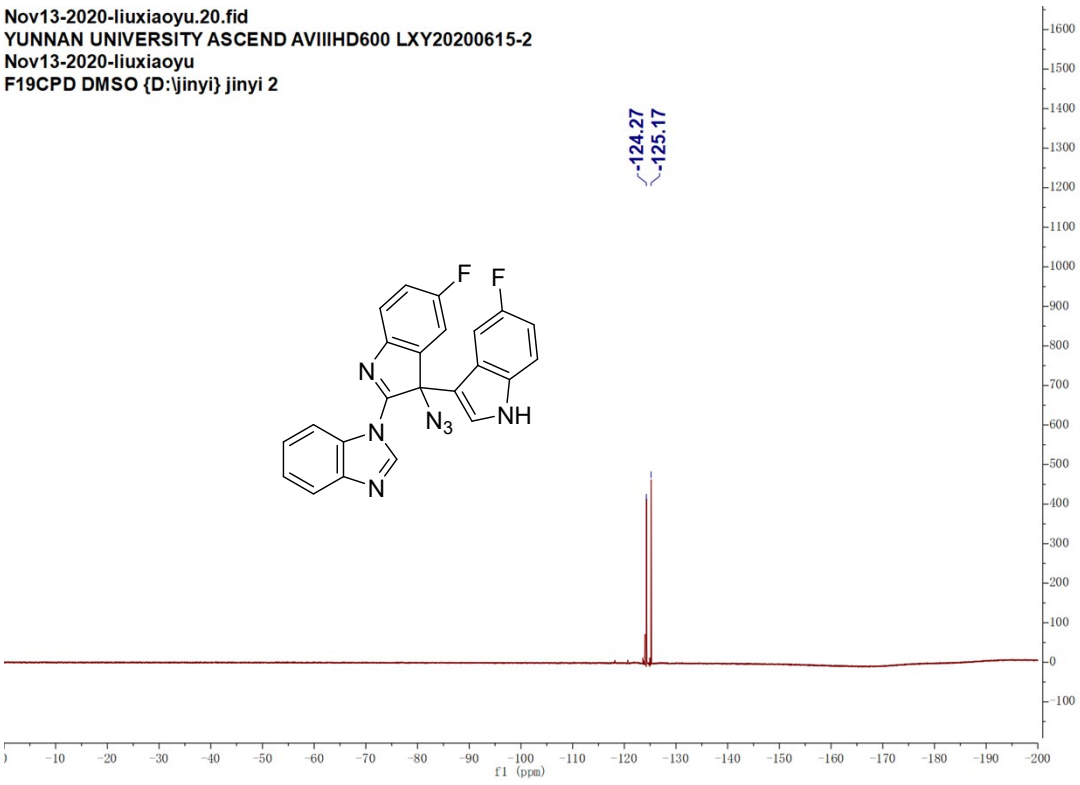
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **3f**



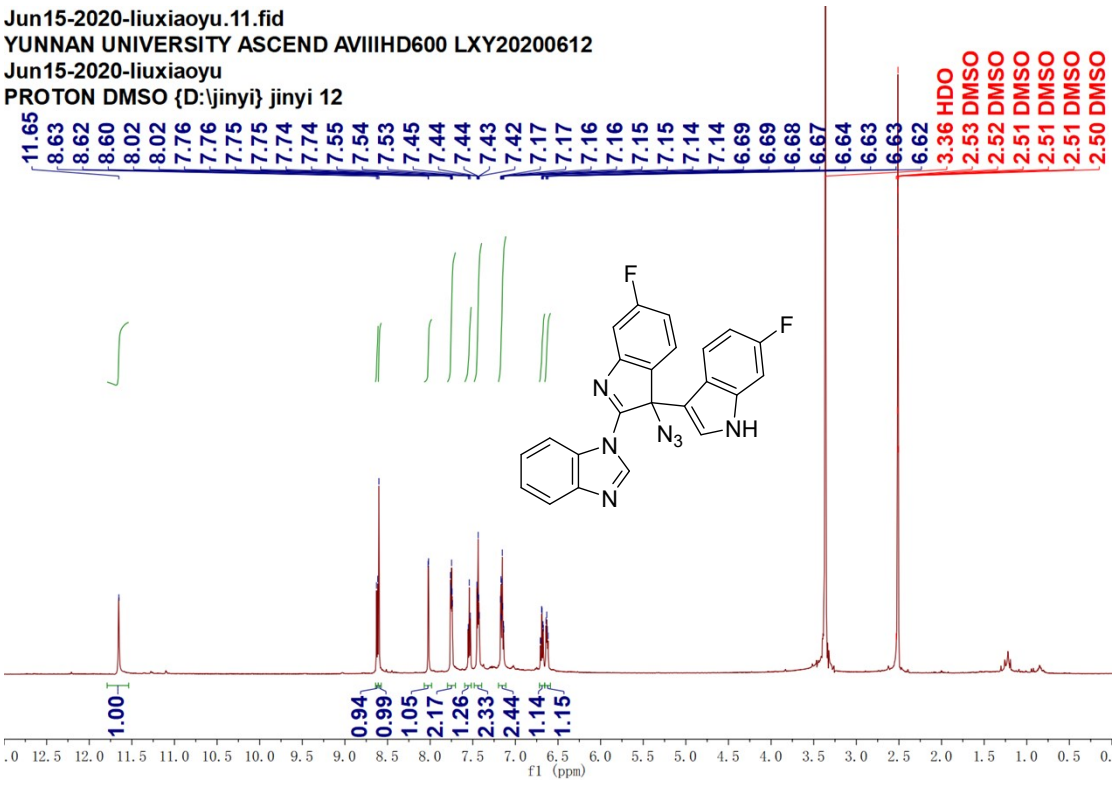
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **3g**



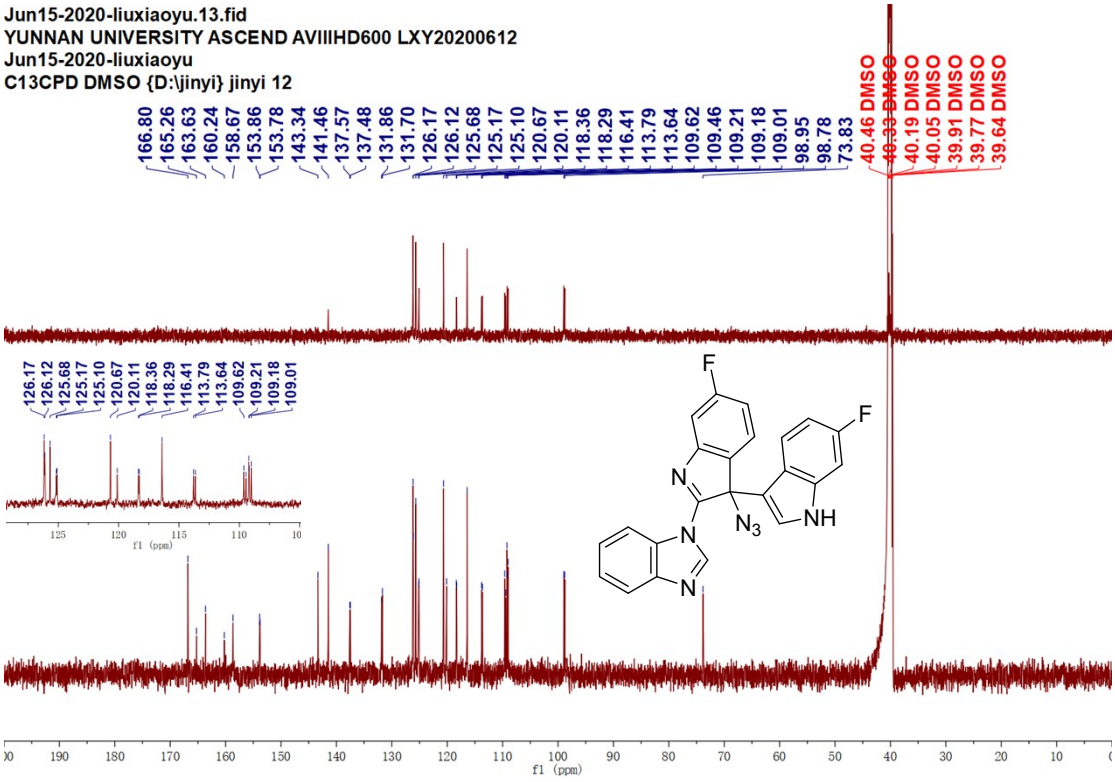
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **3g**



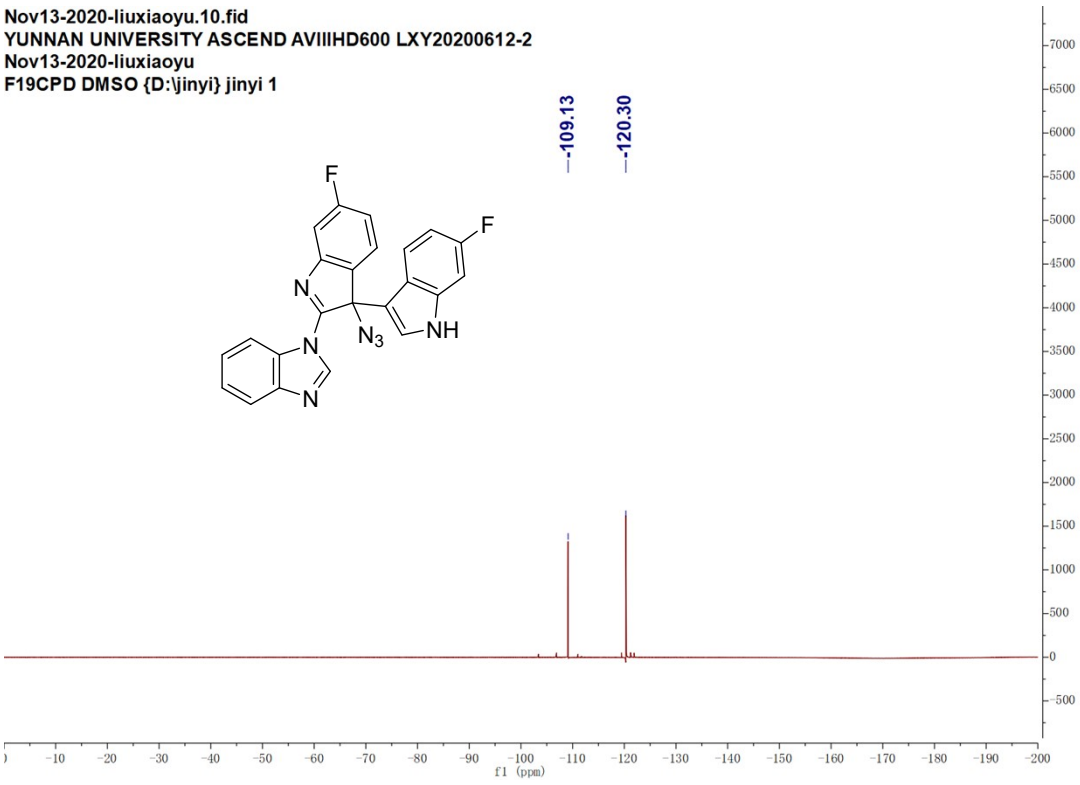
^{19}F-NMR (565MHz, DMSO) spectrum of compound **3g**



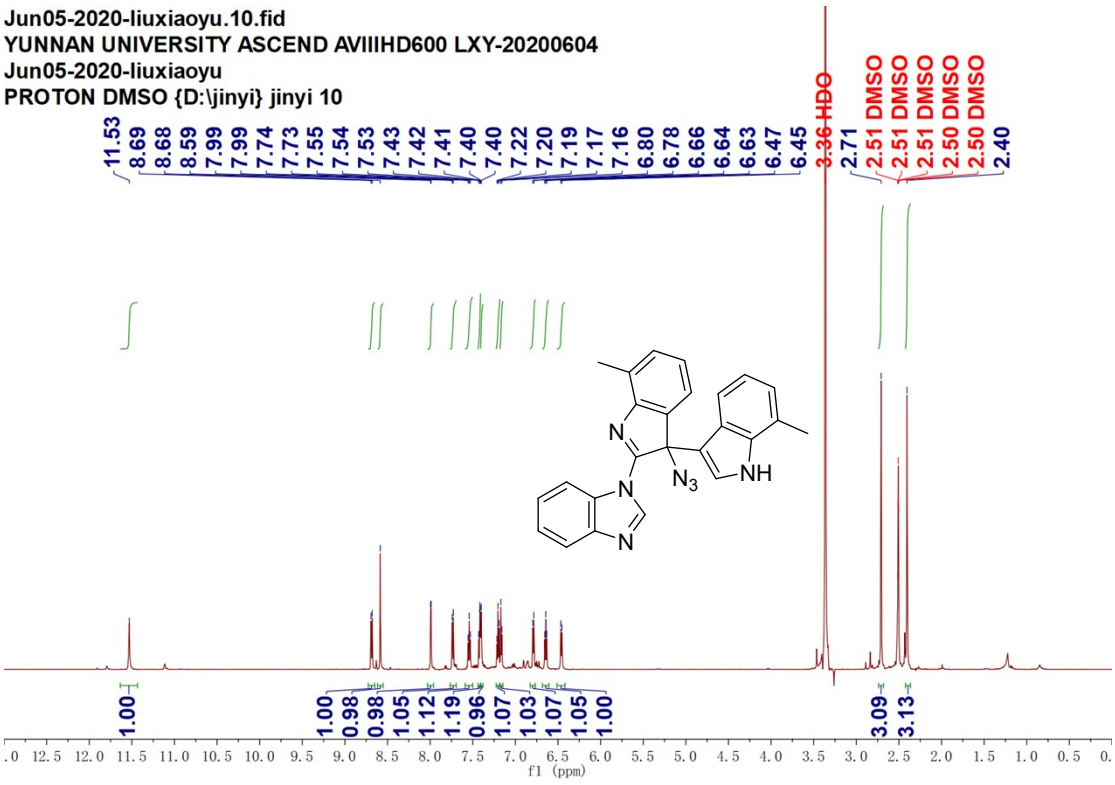
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **3h**



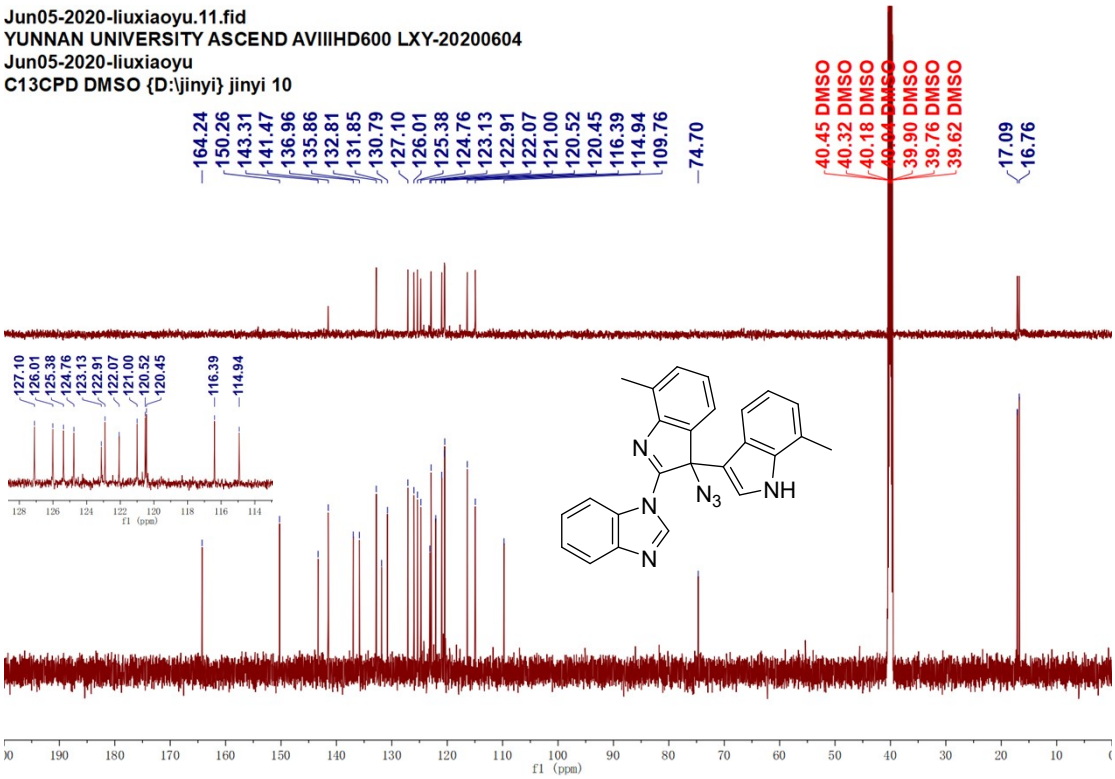
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **3h**



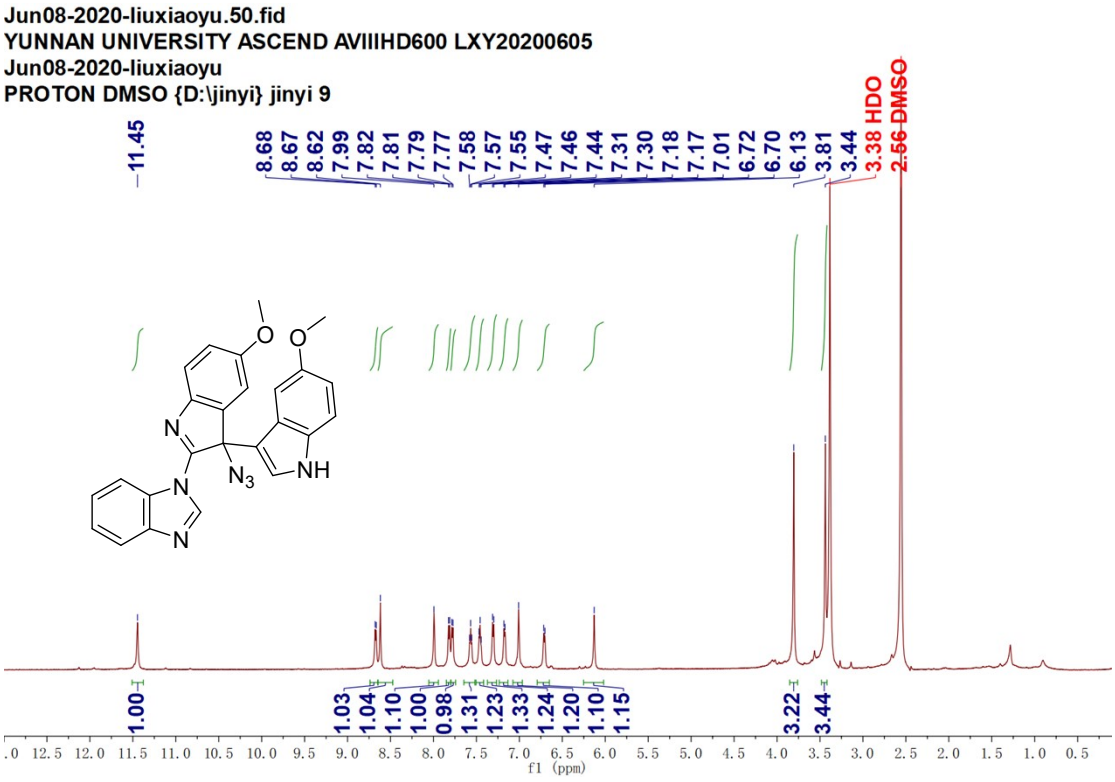
^{19}F-NMR (565MHz, DMSO) spectrum of compound **3h**



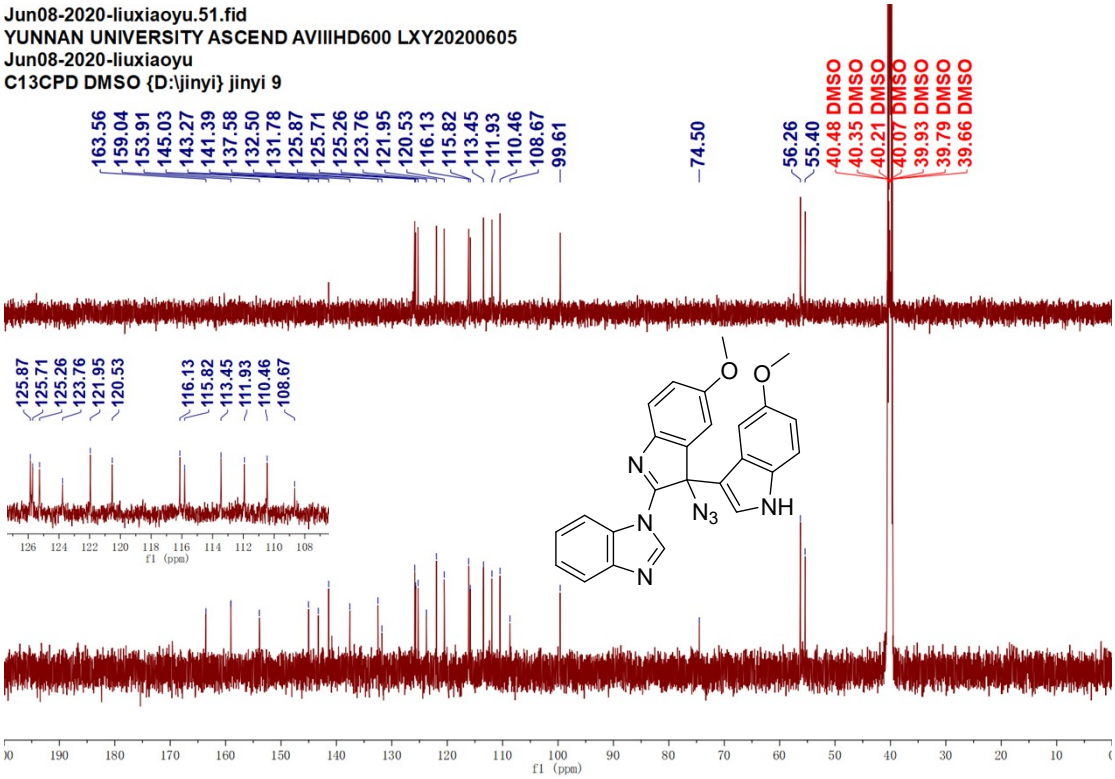
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **3i**



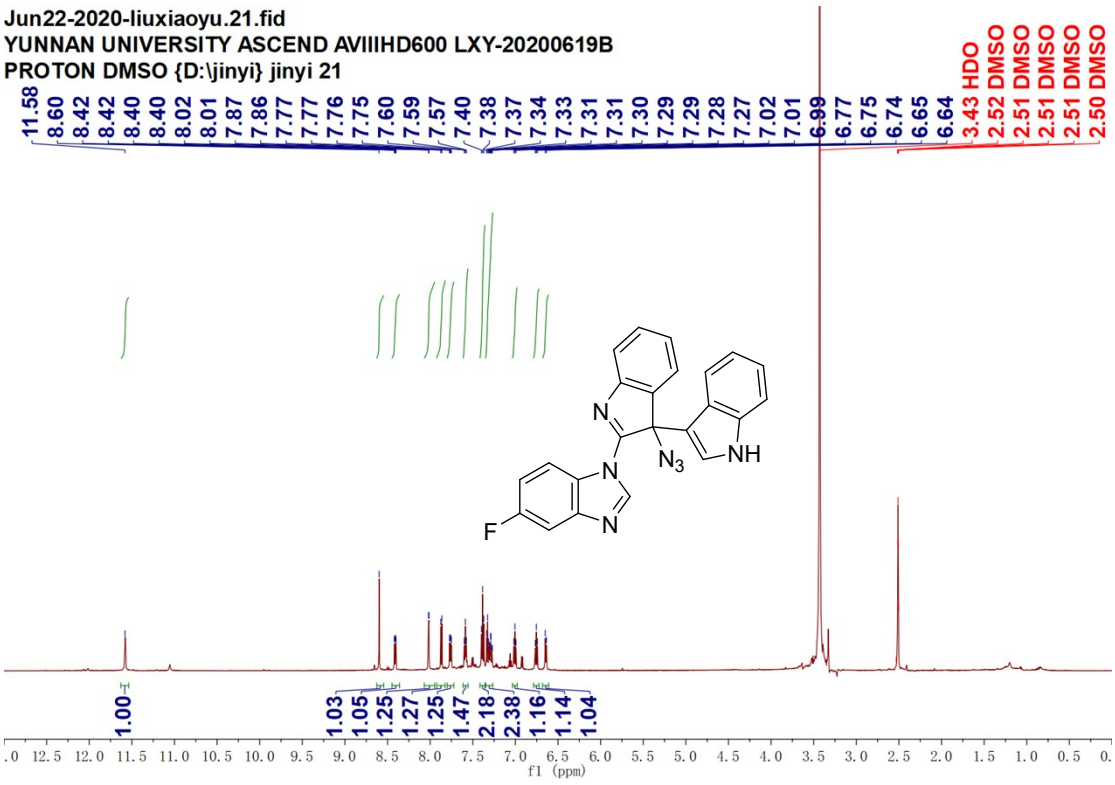
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **3i**



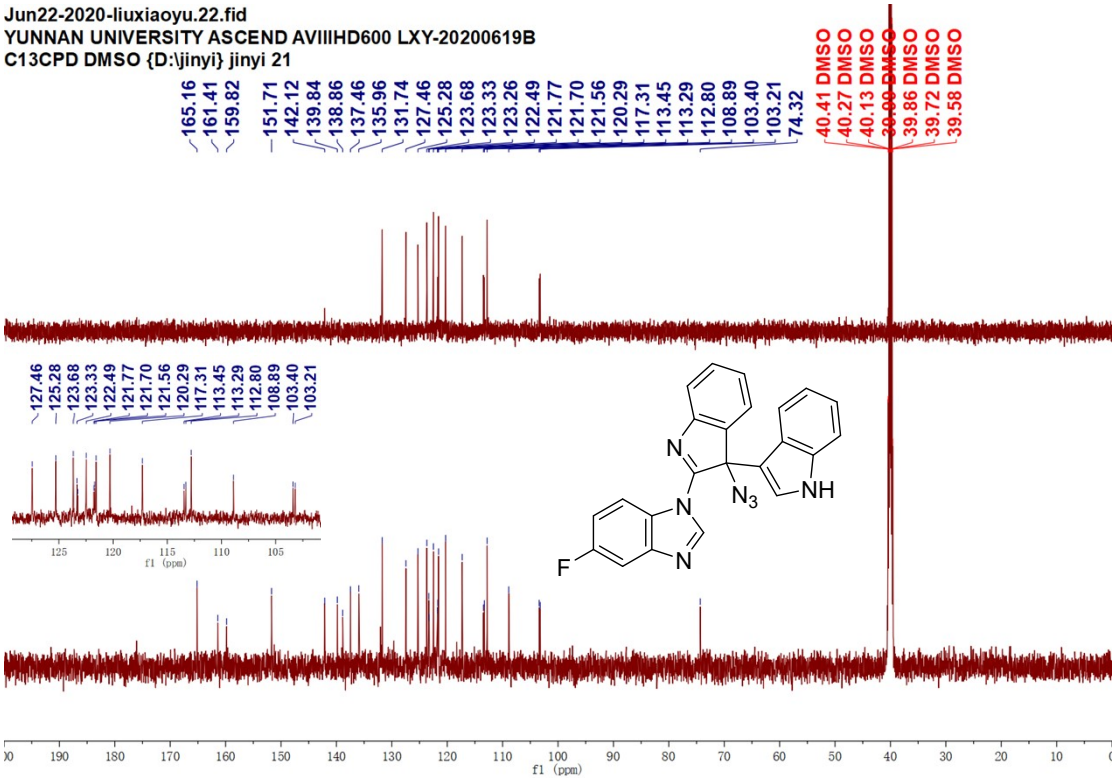
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **3j**



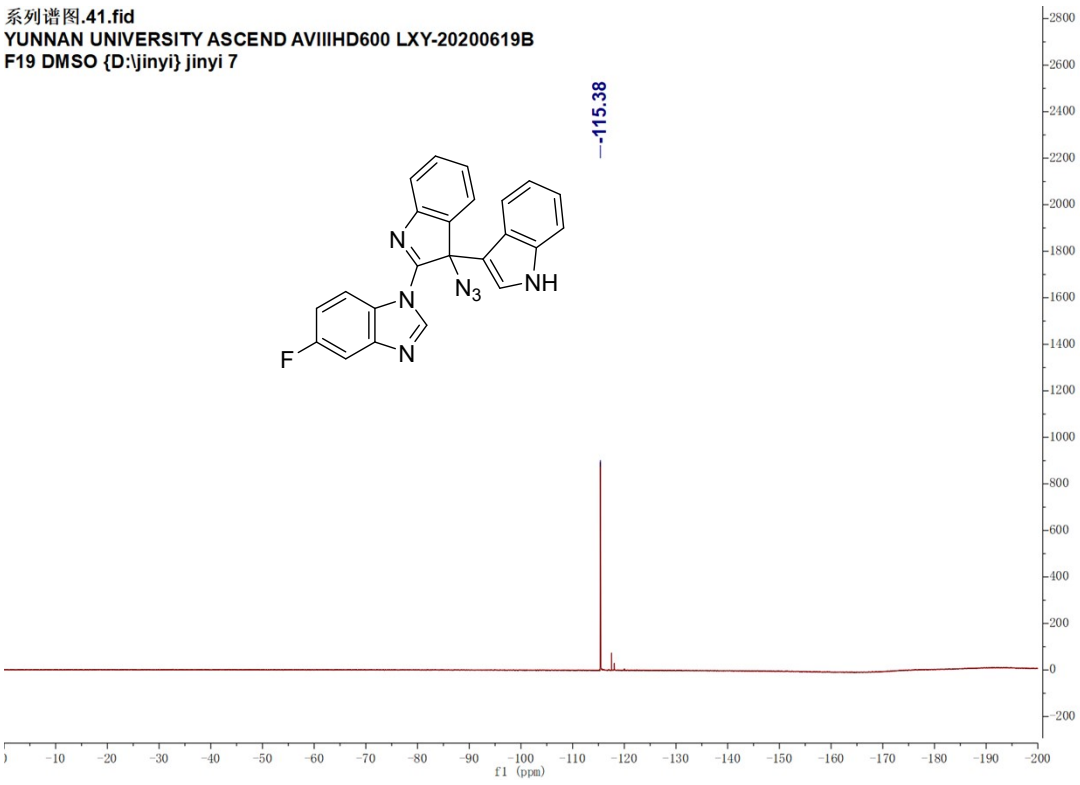
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **3j**



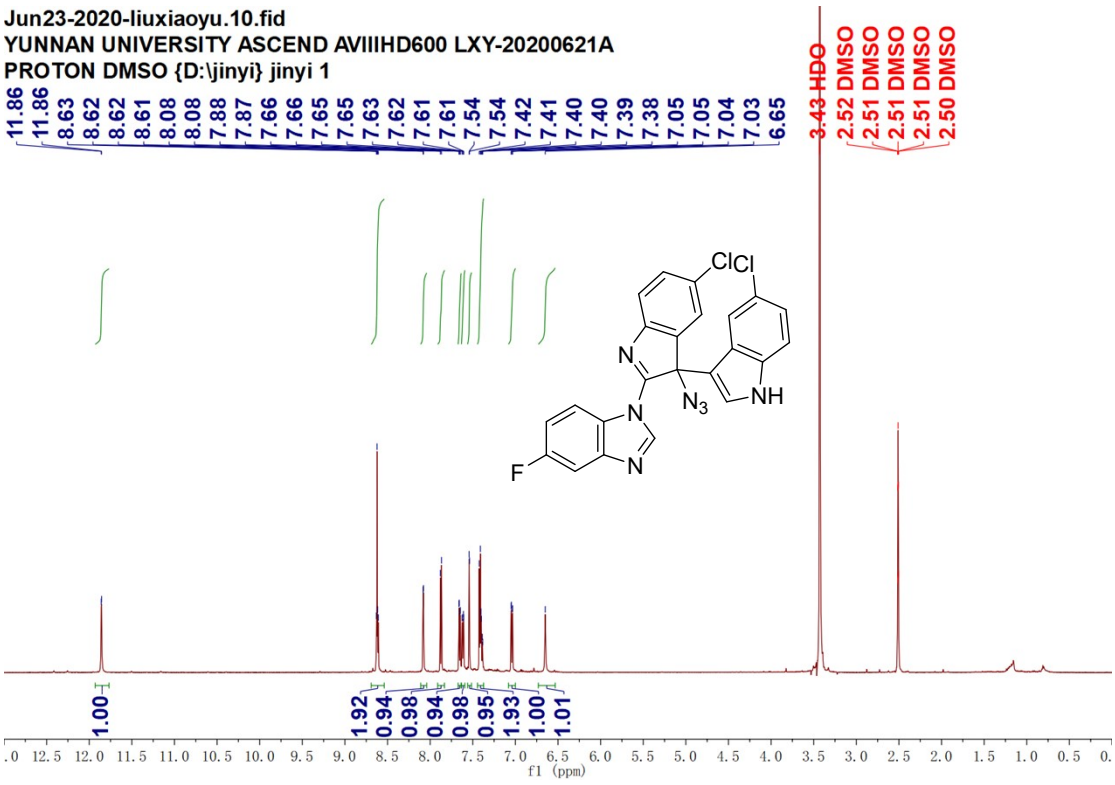
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **3k**



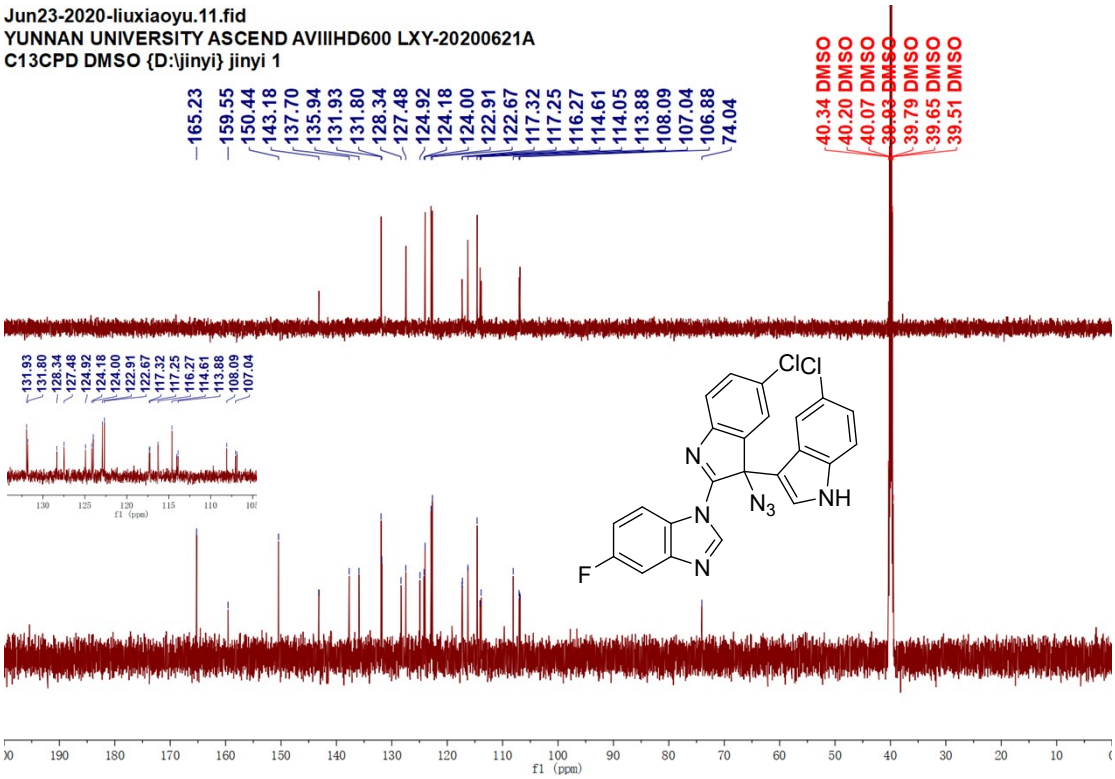
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **3k**



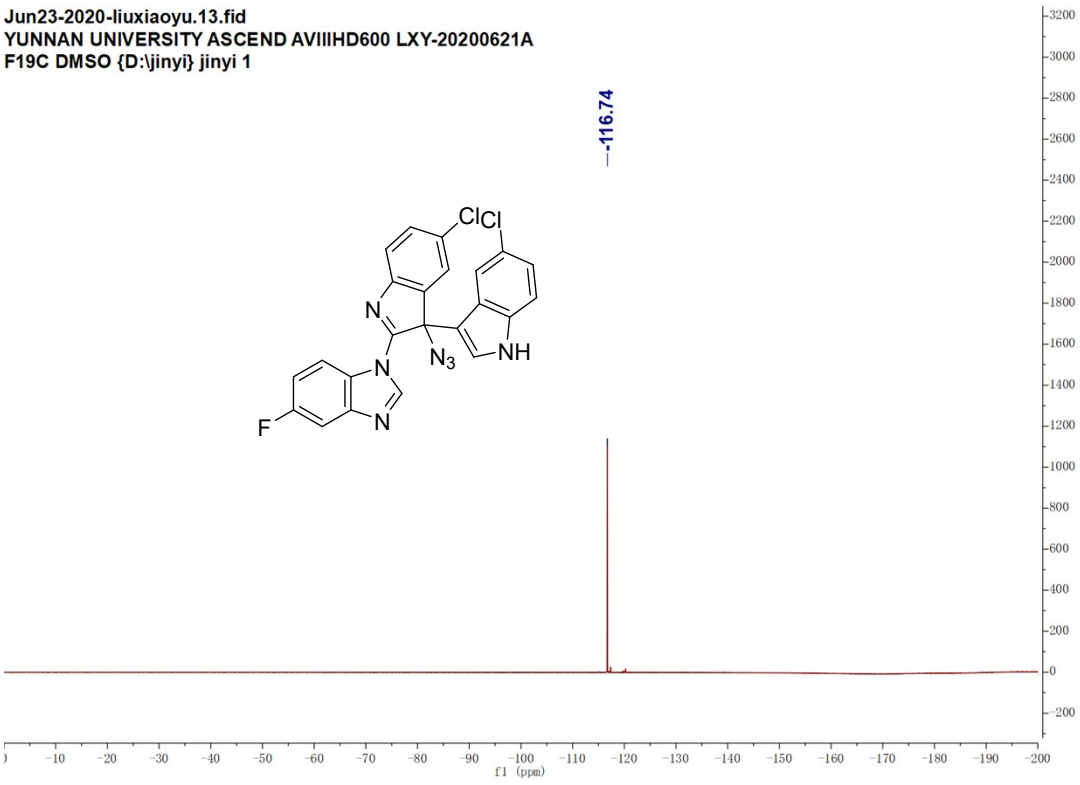
^{19}F-NMR (565MHz, DMSO) spectrum of compound **3k**



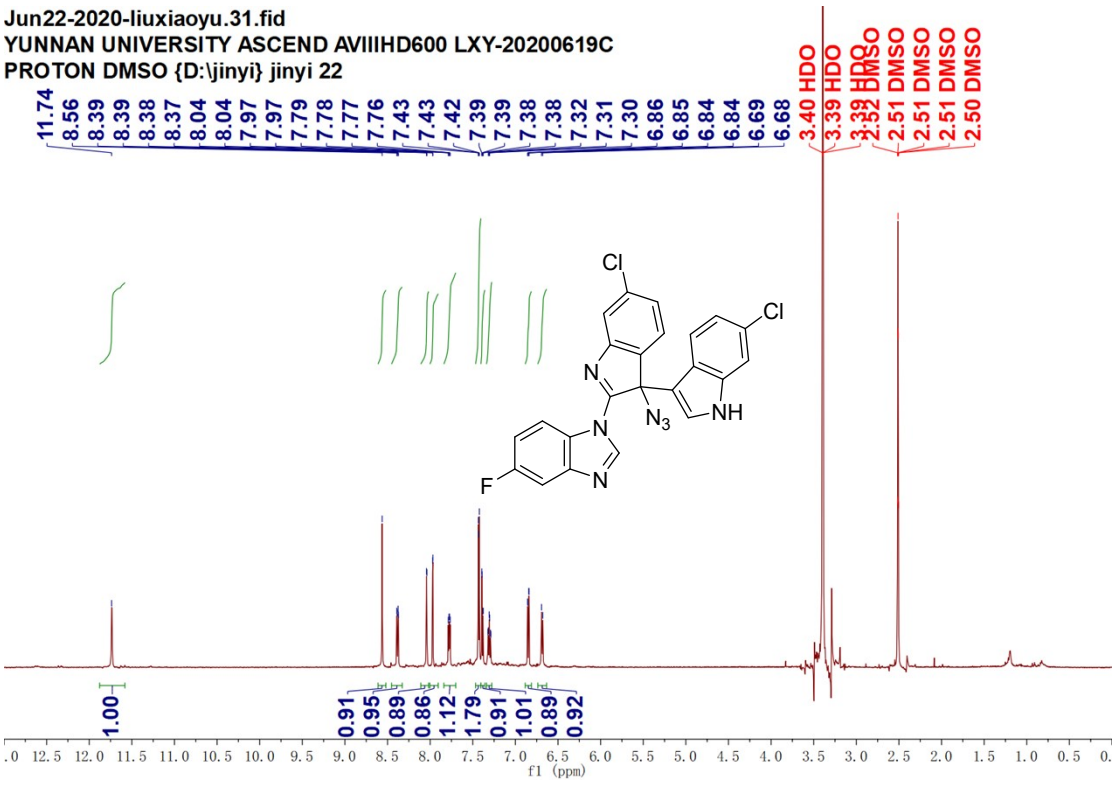
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **3l**



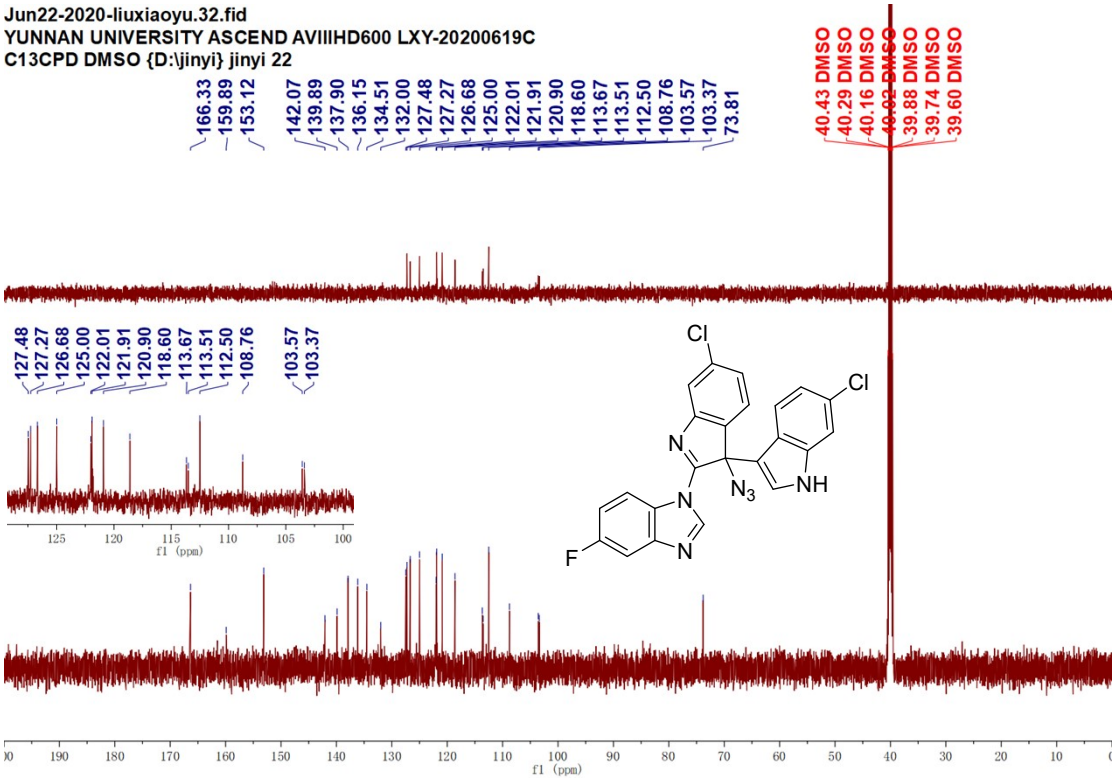
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **3l**



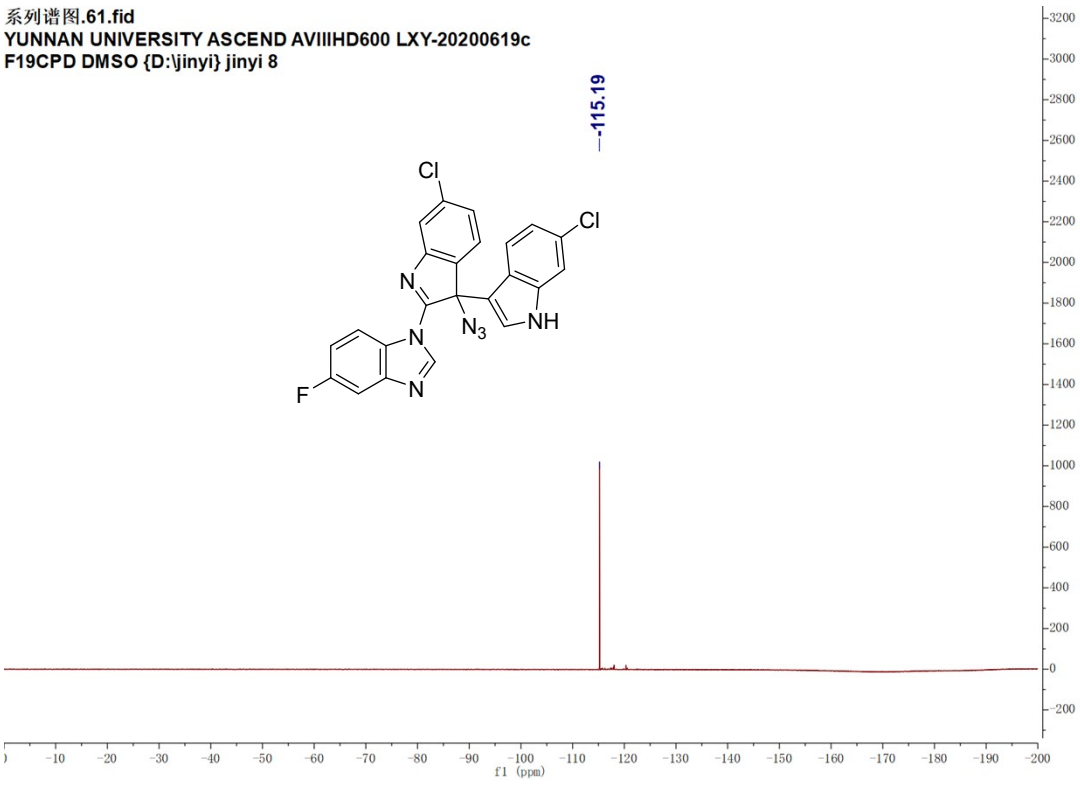
^{19}F-NMR (565MHz, DMSO) spectrum of compound **3l**



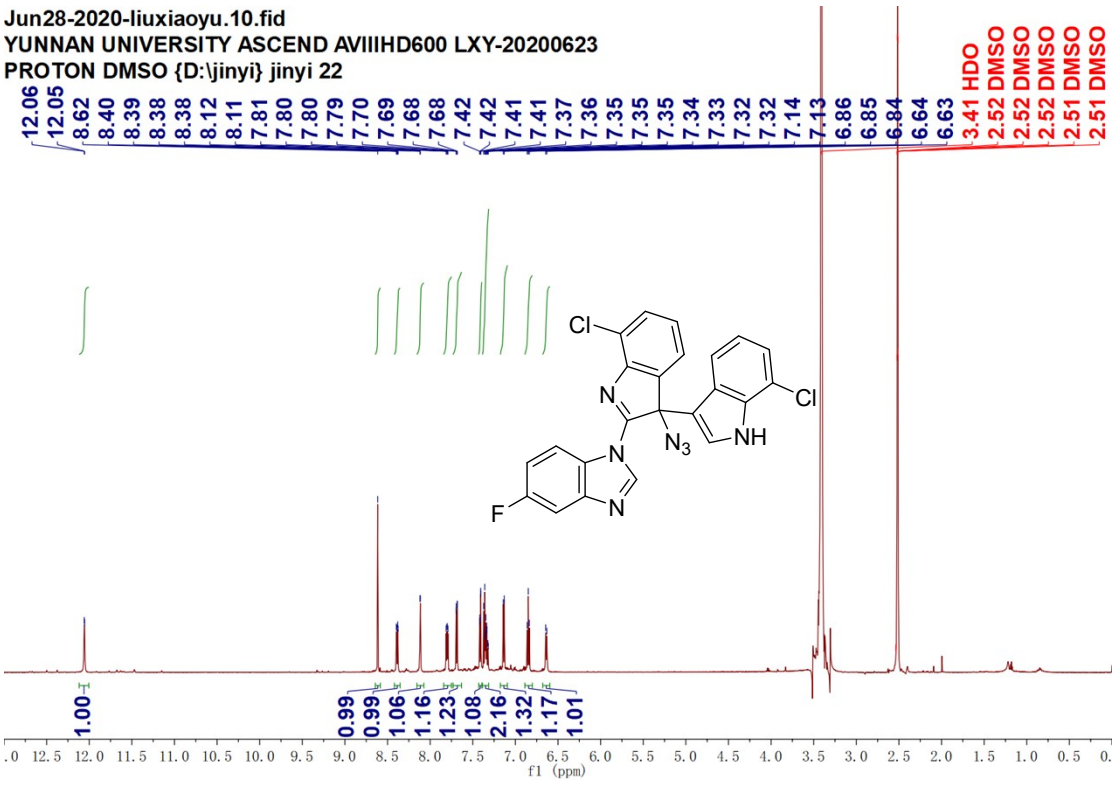
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **3m**



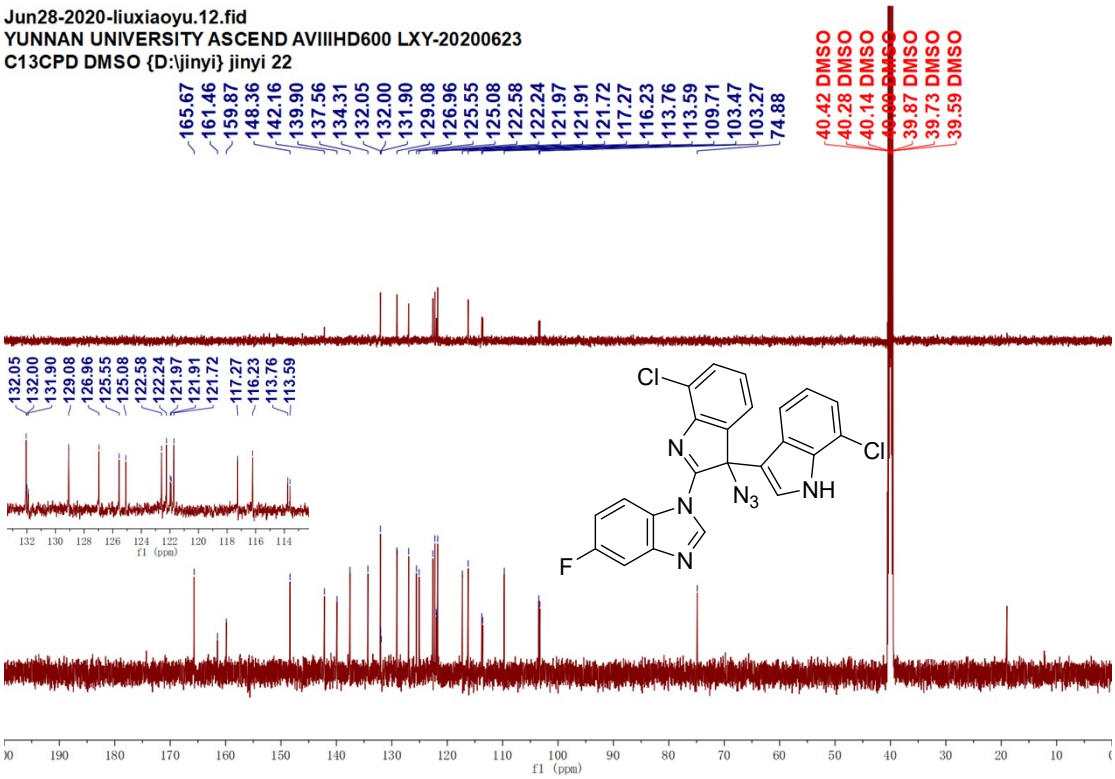
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **3m**



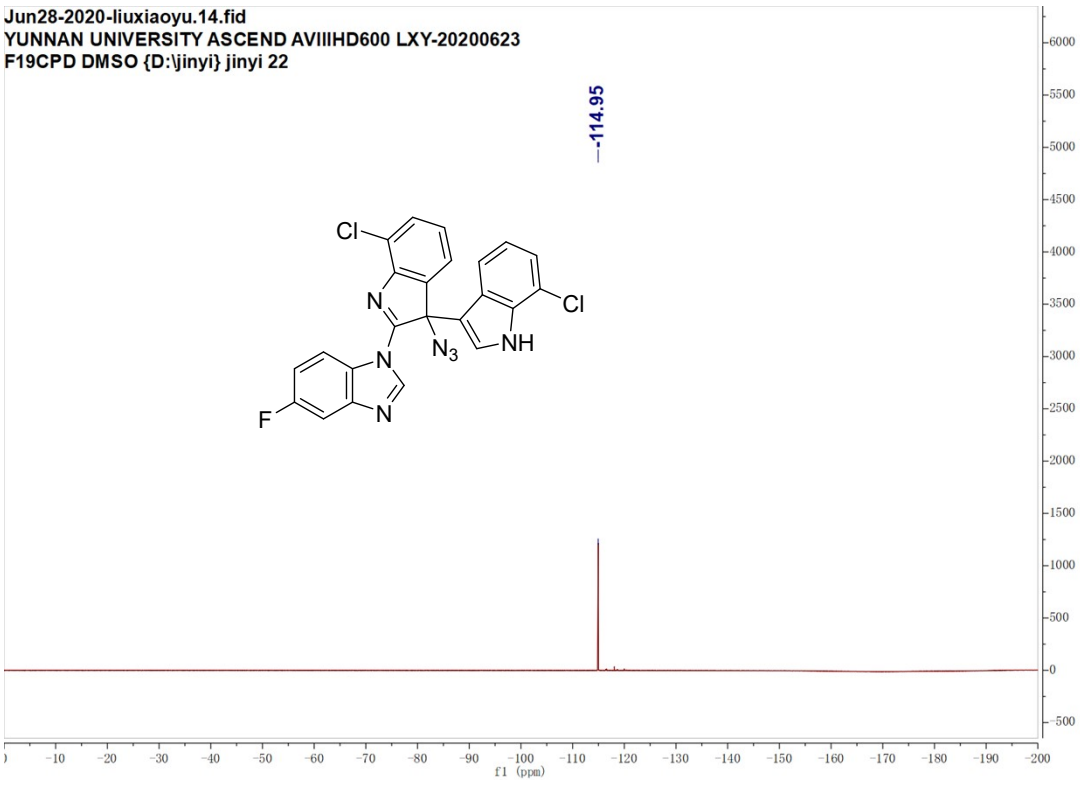
^{19}F-NMR (565MHz, DMSO) spectrum of compound **3m**



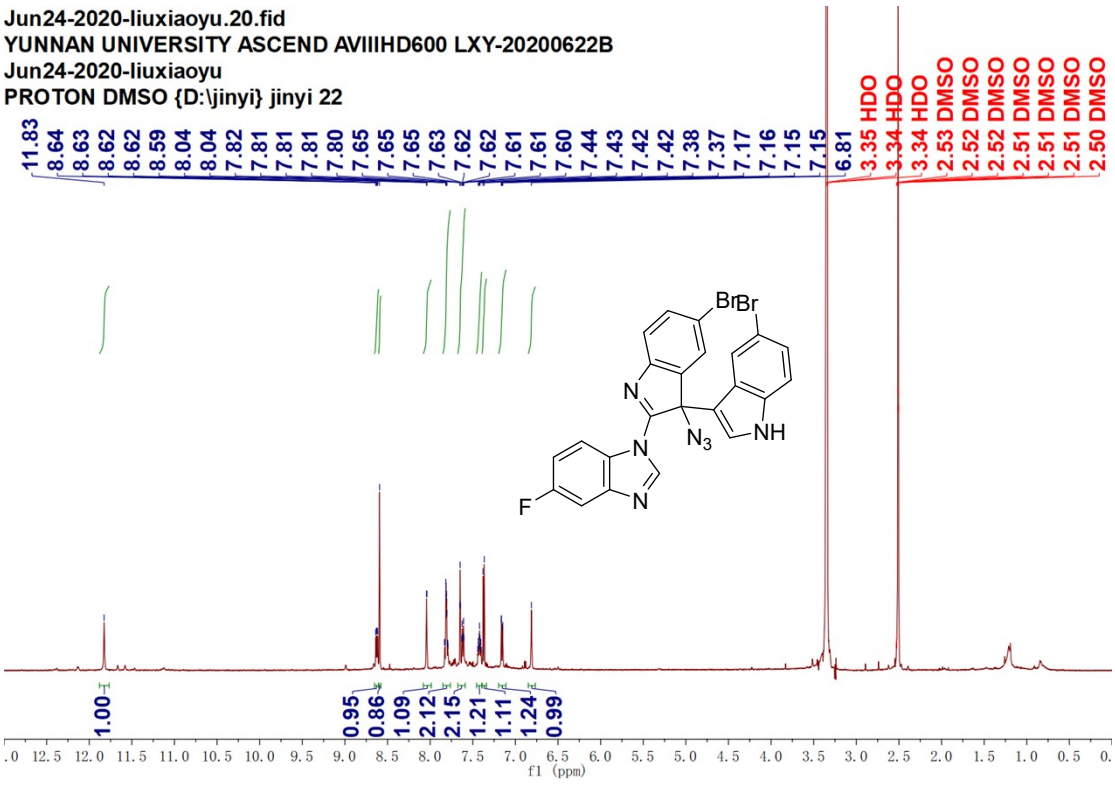
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **3n**



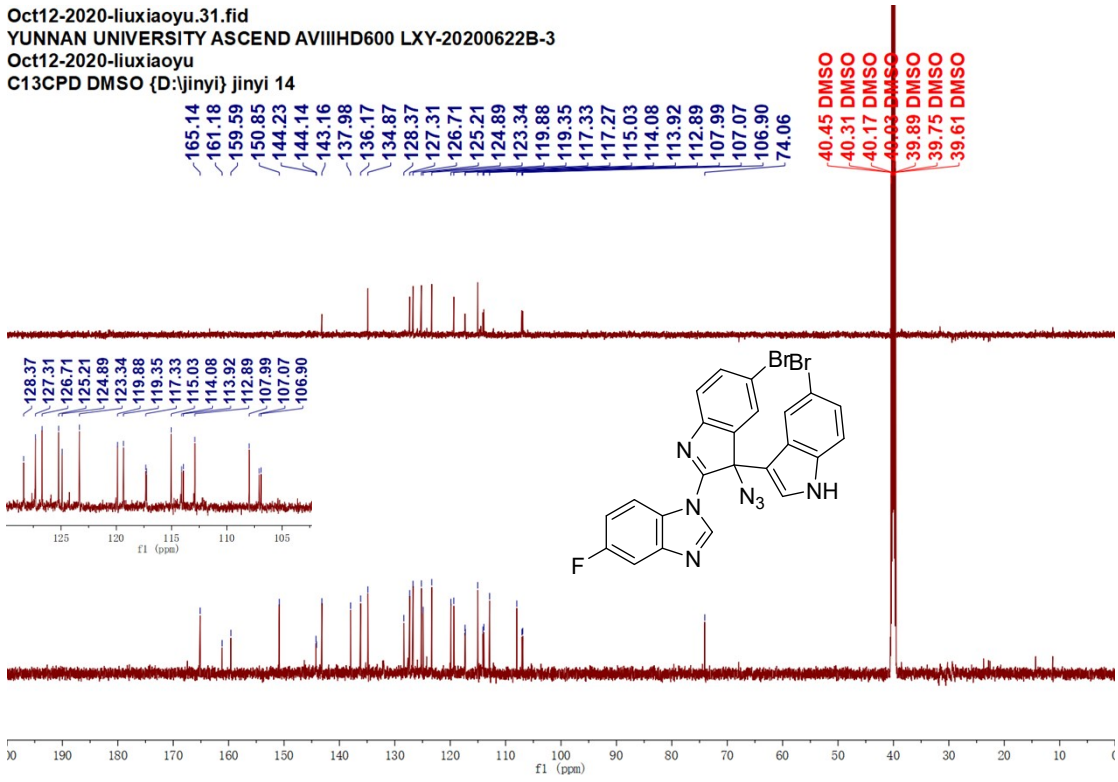
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **3n**



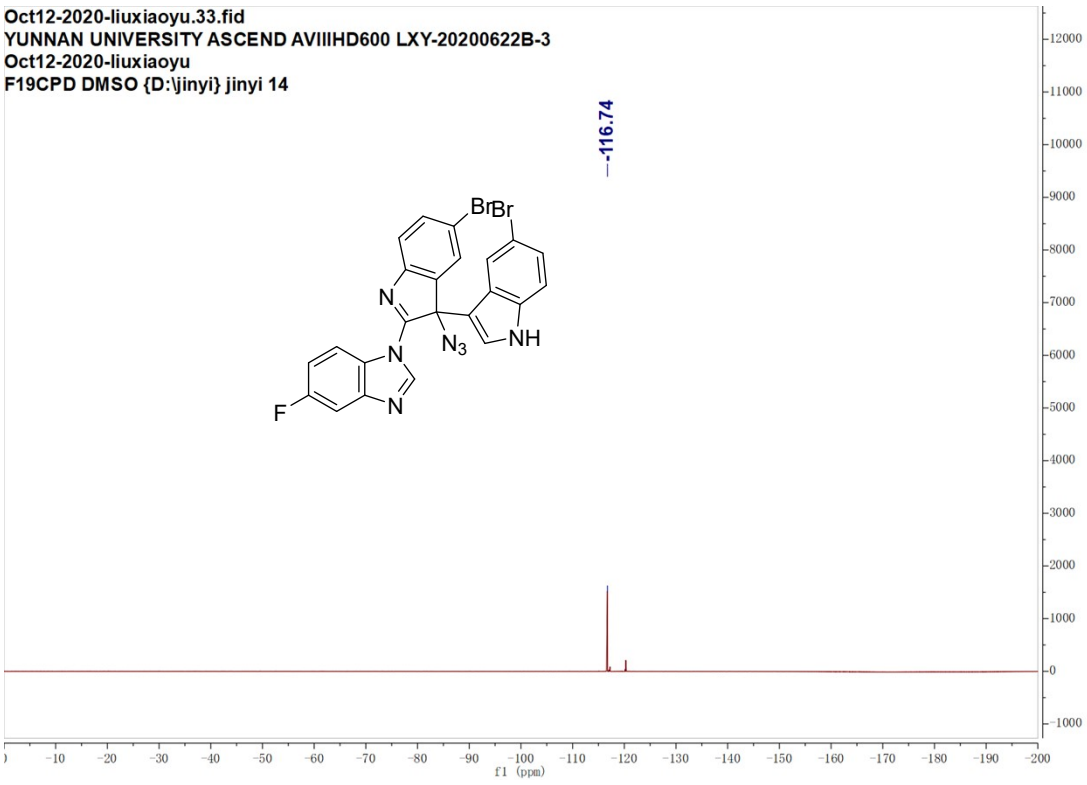
^{19}F-NMR (565MHz, DMSO) spectrum of compound **3n**



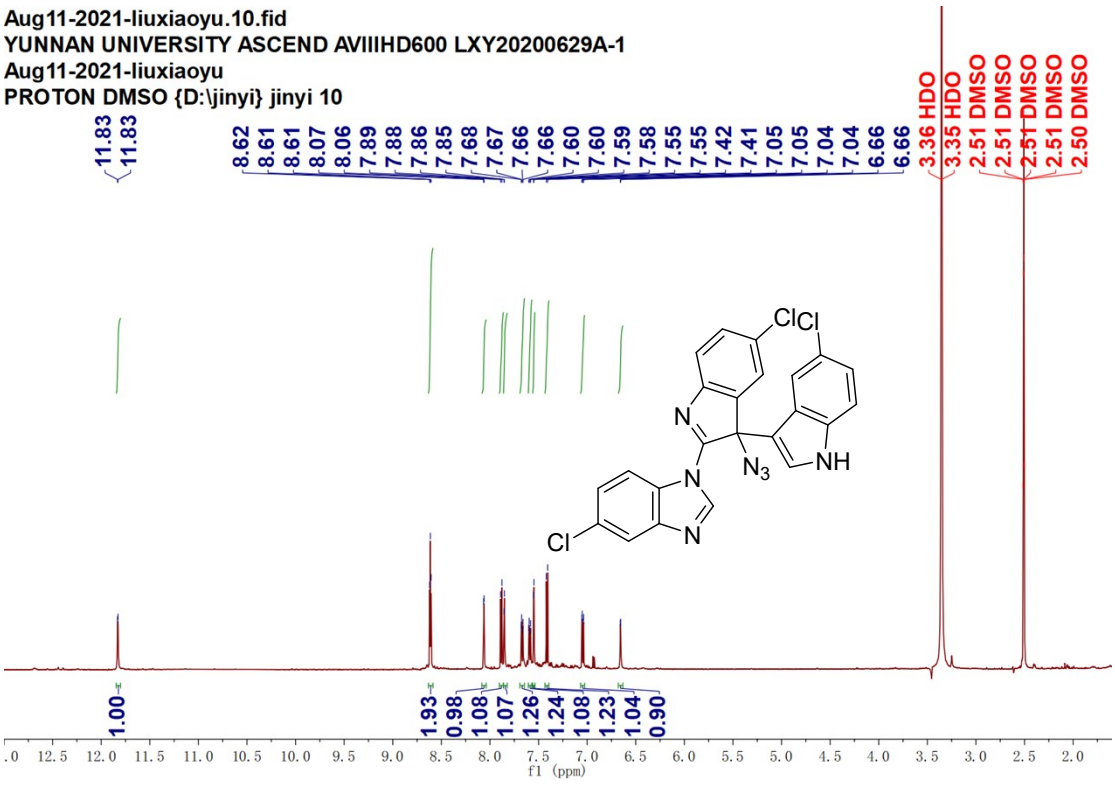
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **3o**



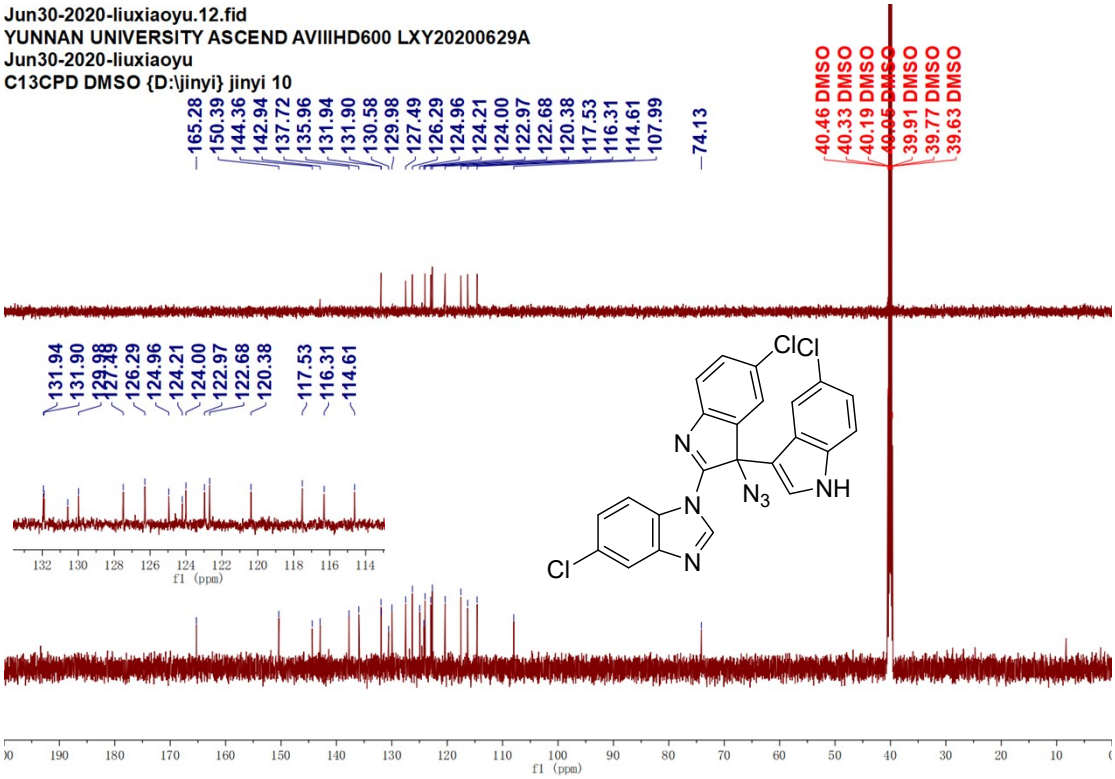
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **3o**



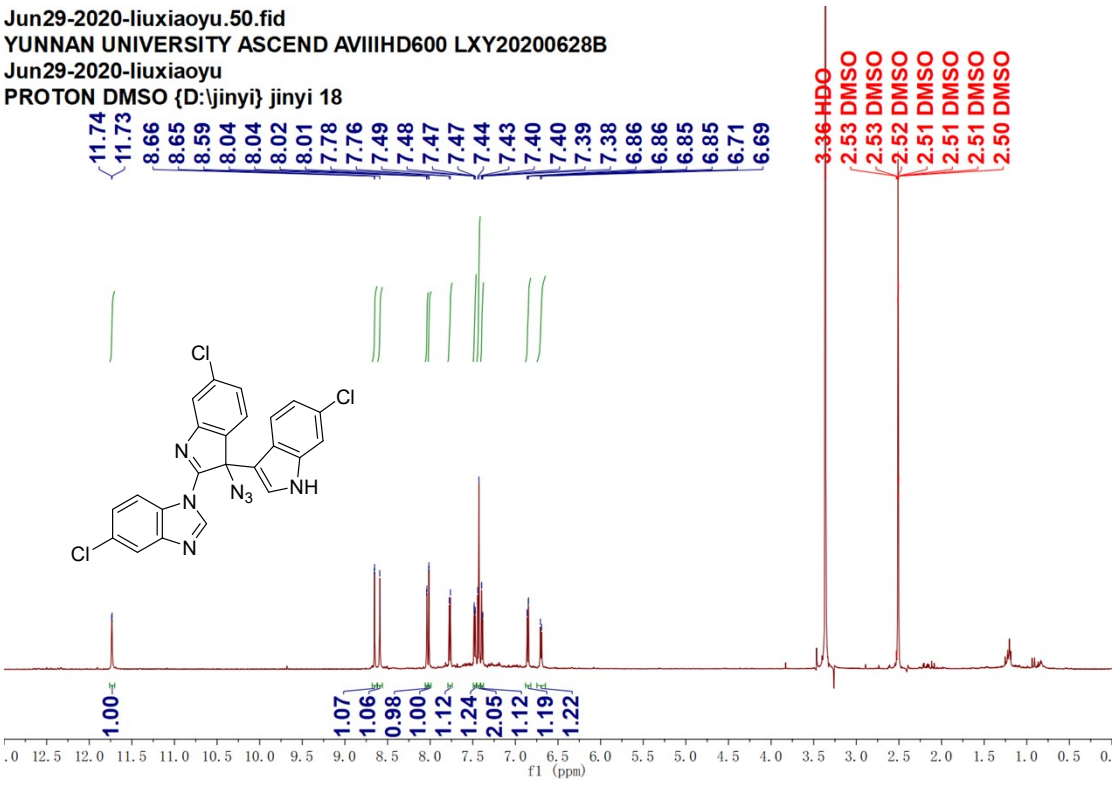
^{19}F-NMR (565MHz, DMSO) spectrum of compound **3o**



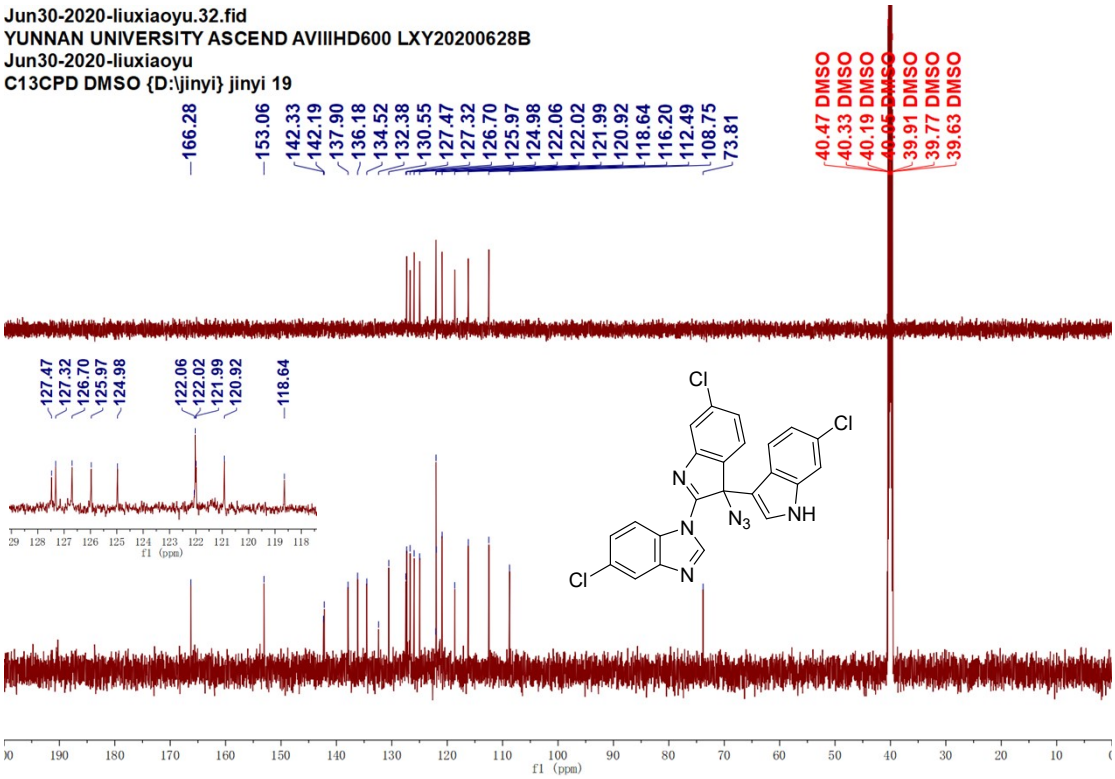
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **3p**



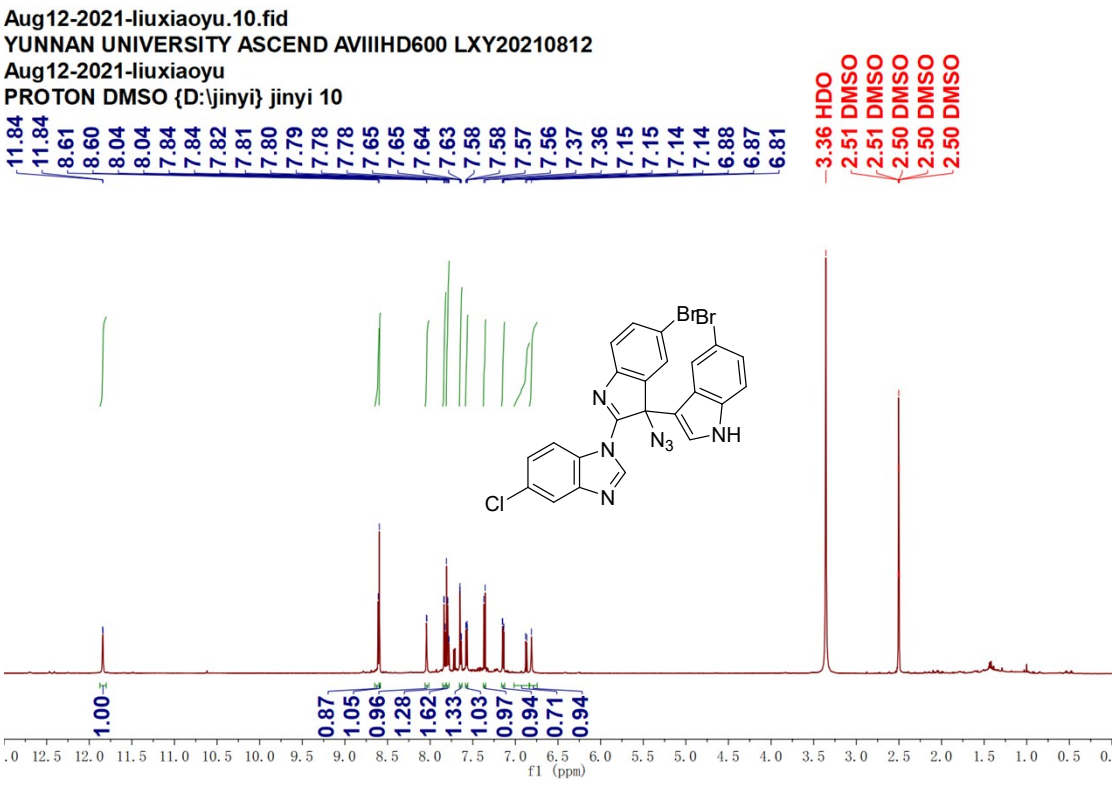
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **3p**



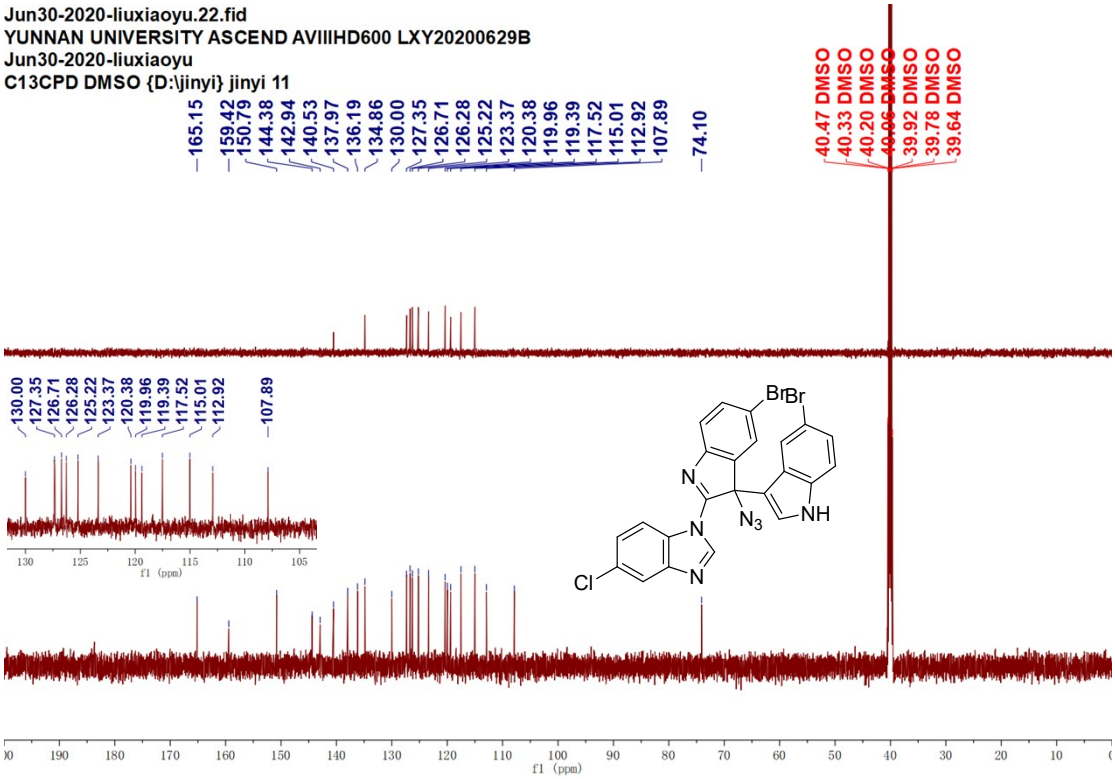
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **3q**



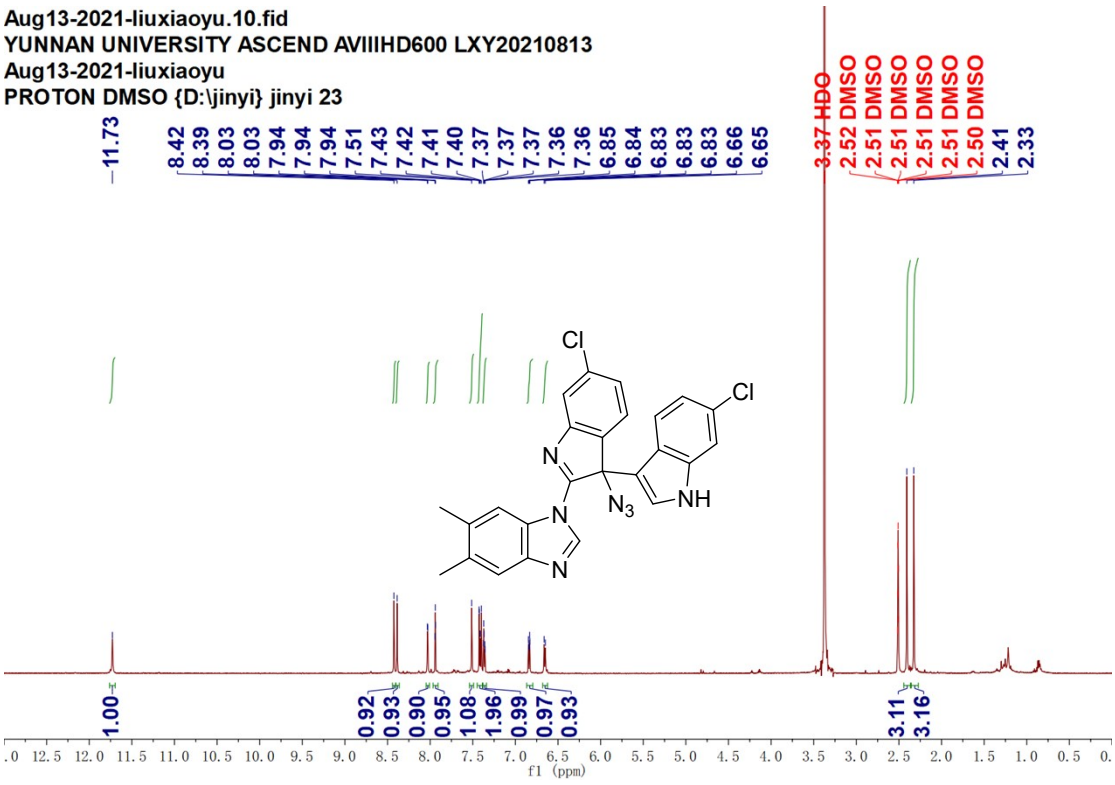
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **3q**



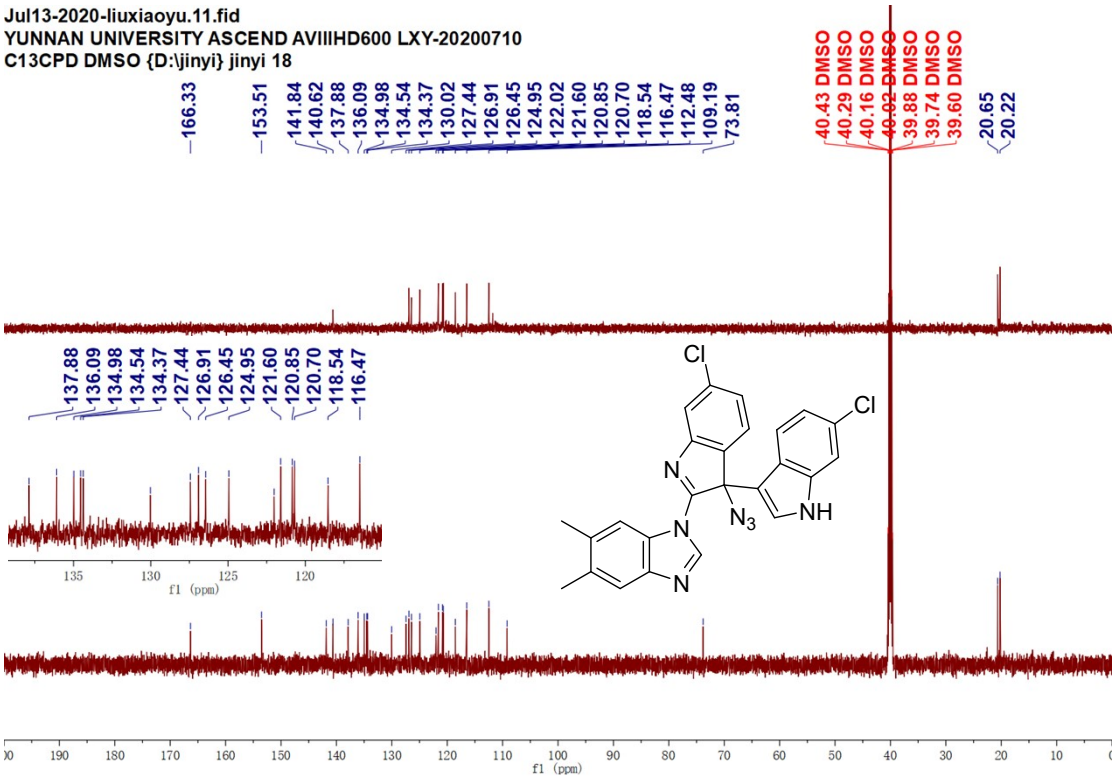
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **3r**



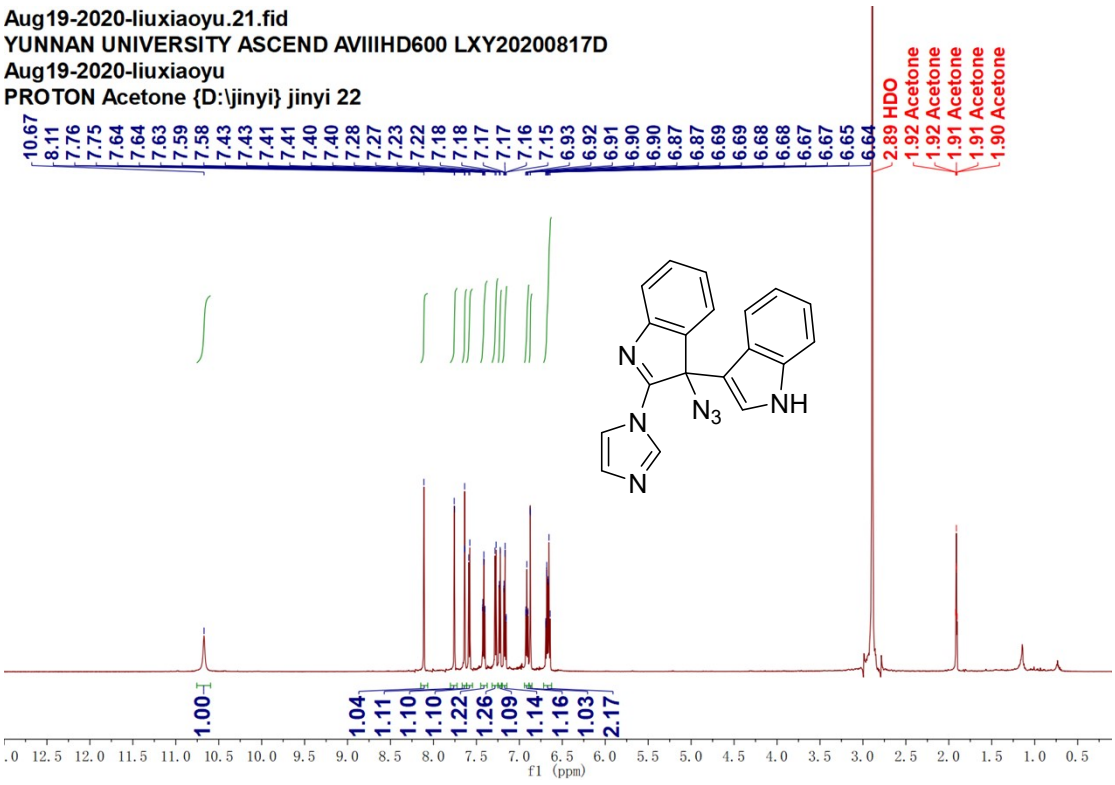
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **3r**



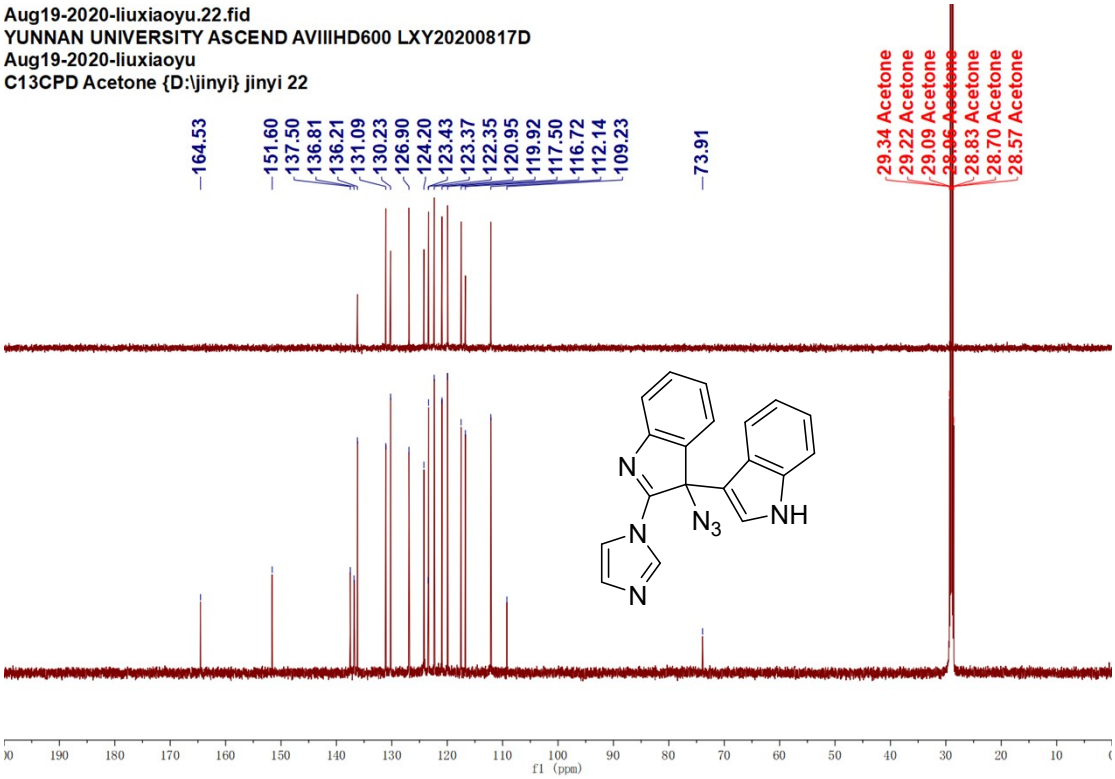
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **3s**



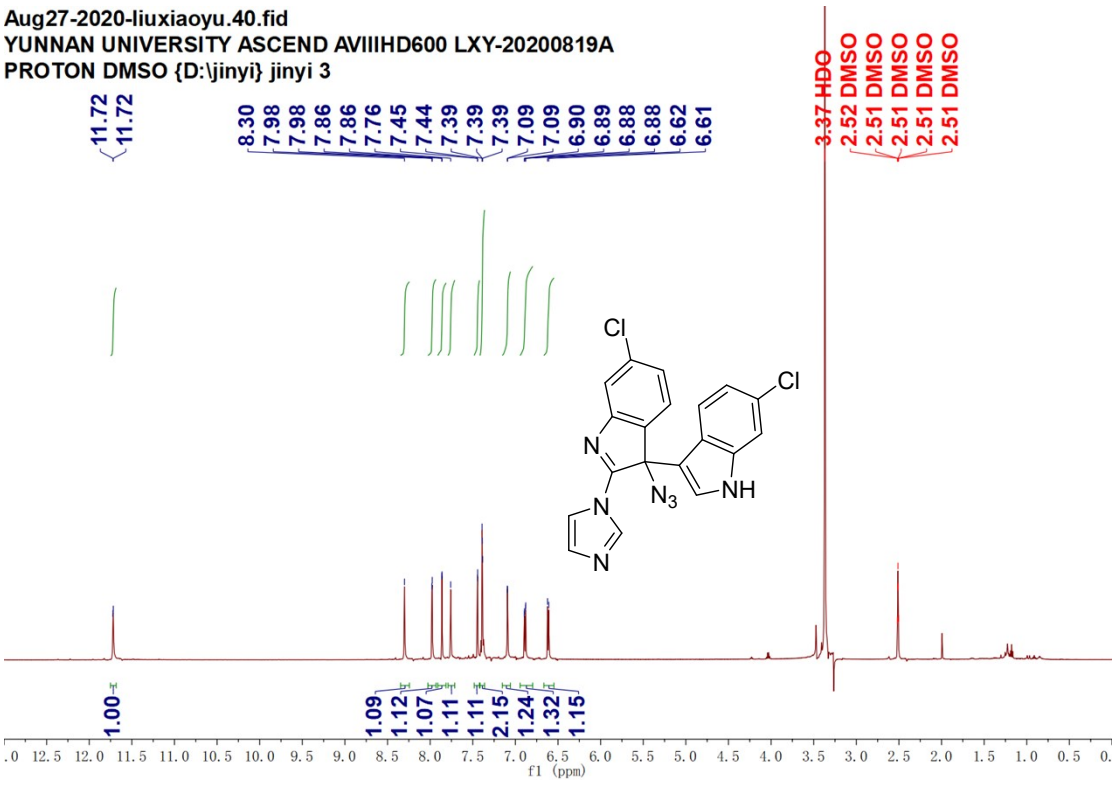
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **3s**



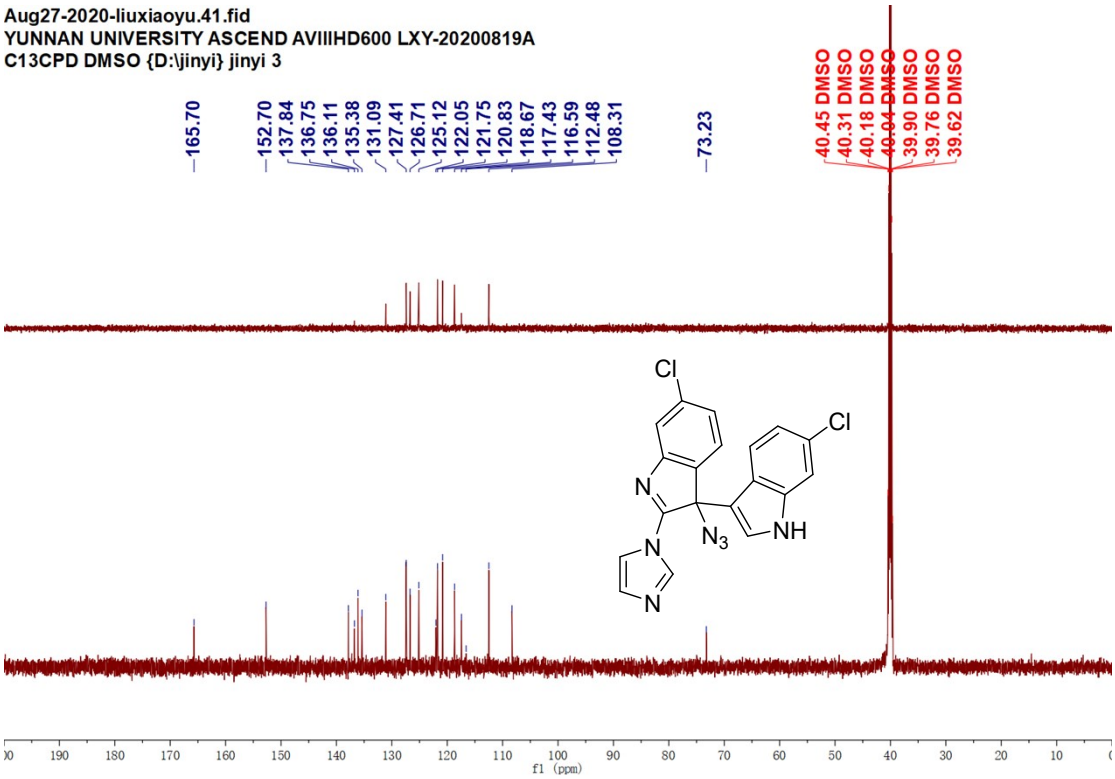
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **4a**



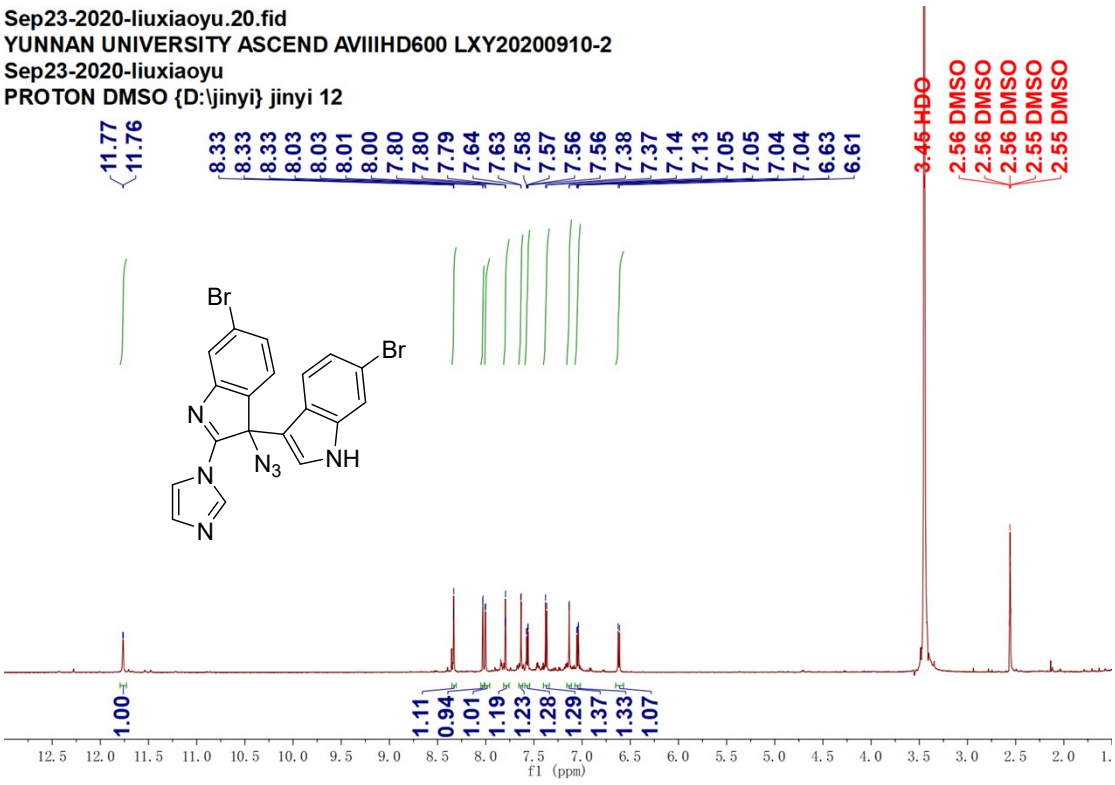
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **4a**



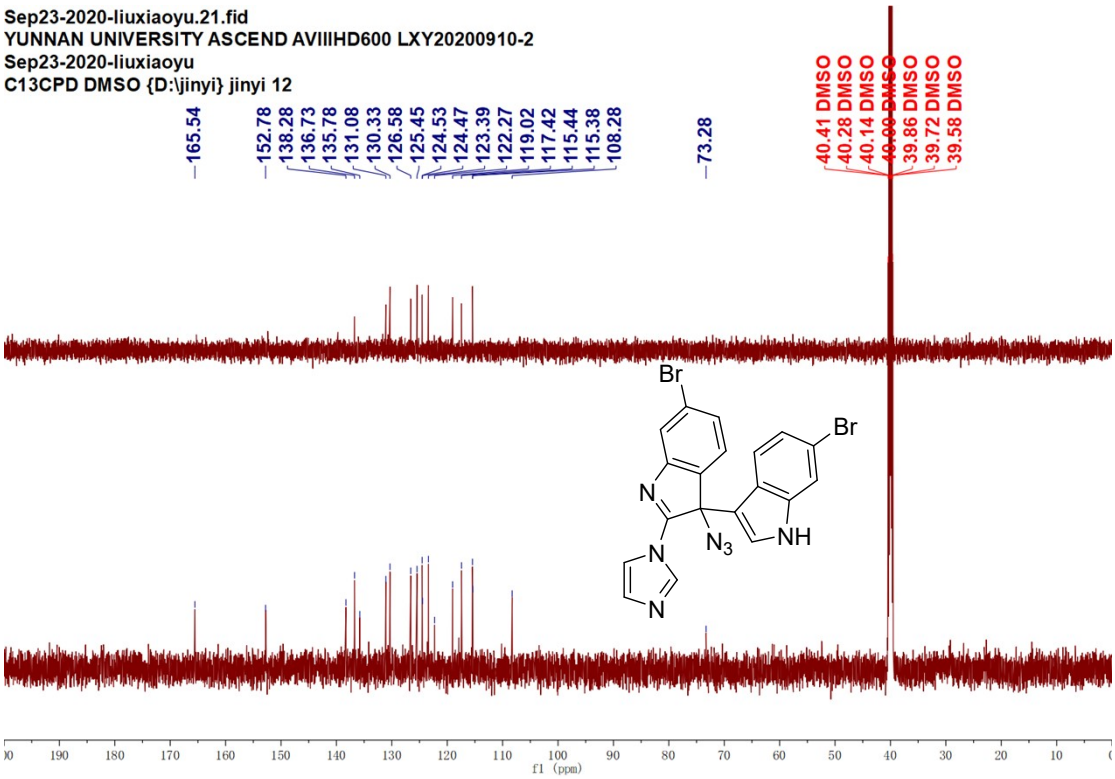
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **4b**



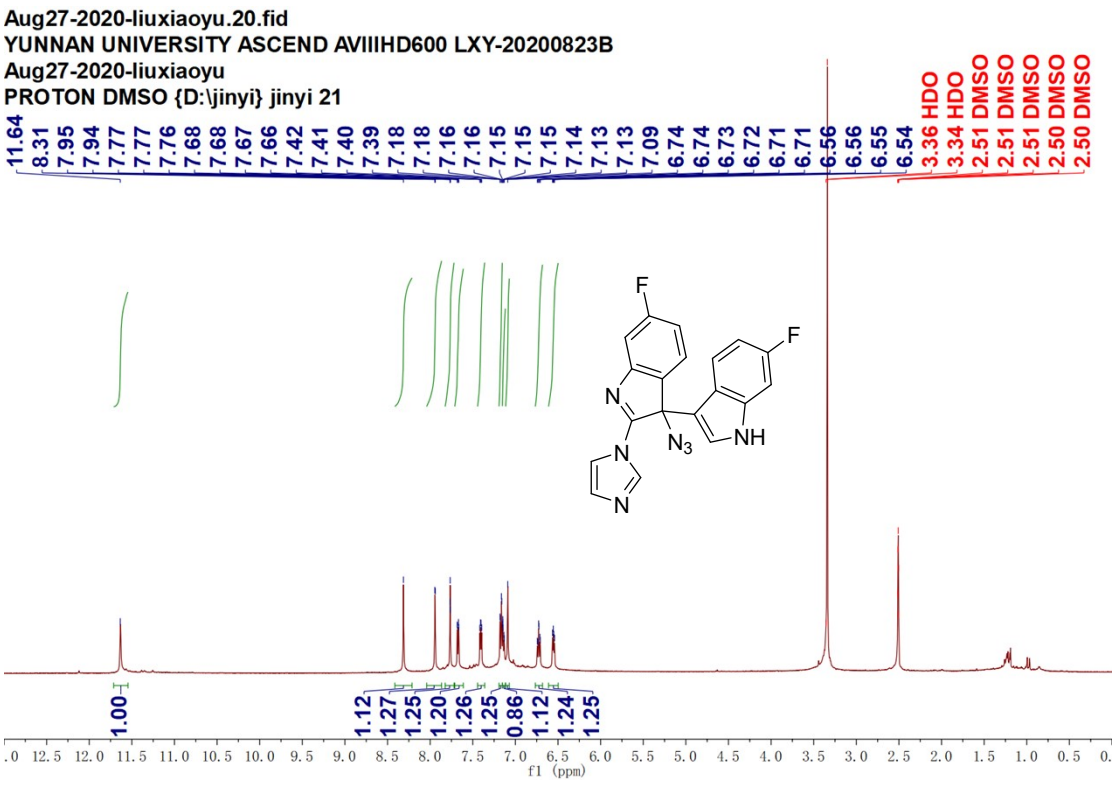
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **4b**



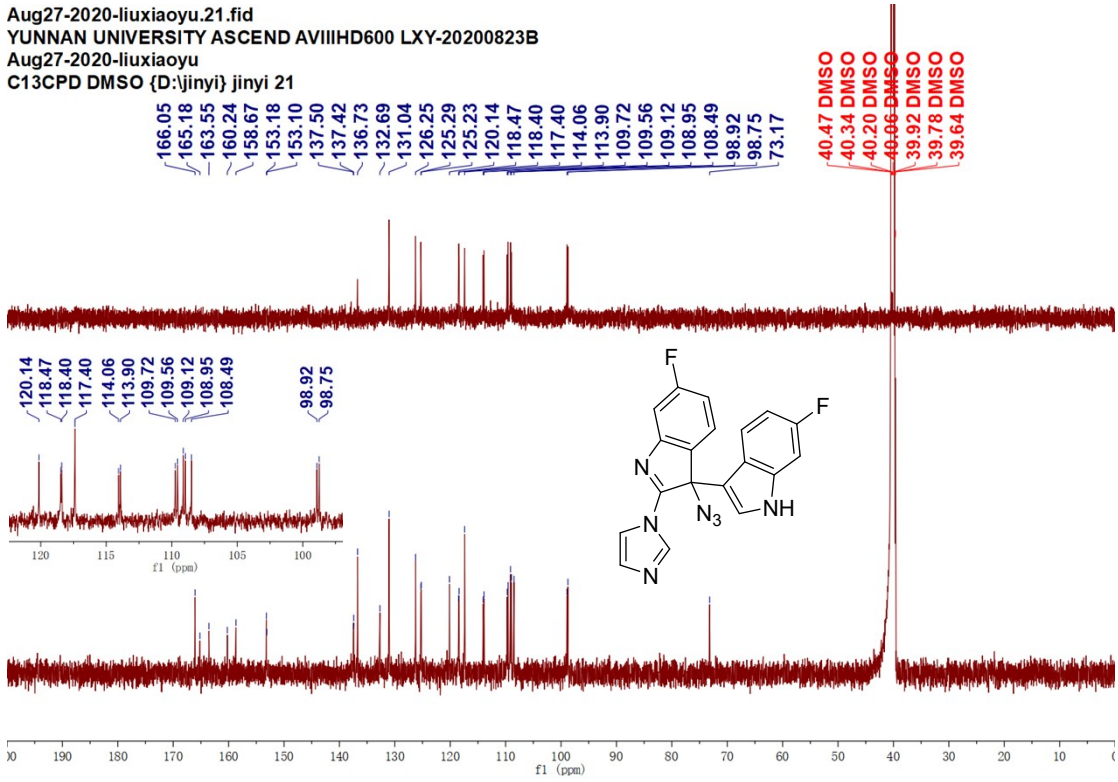
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **4c**



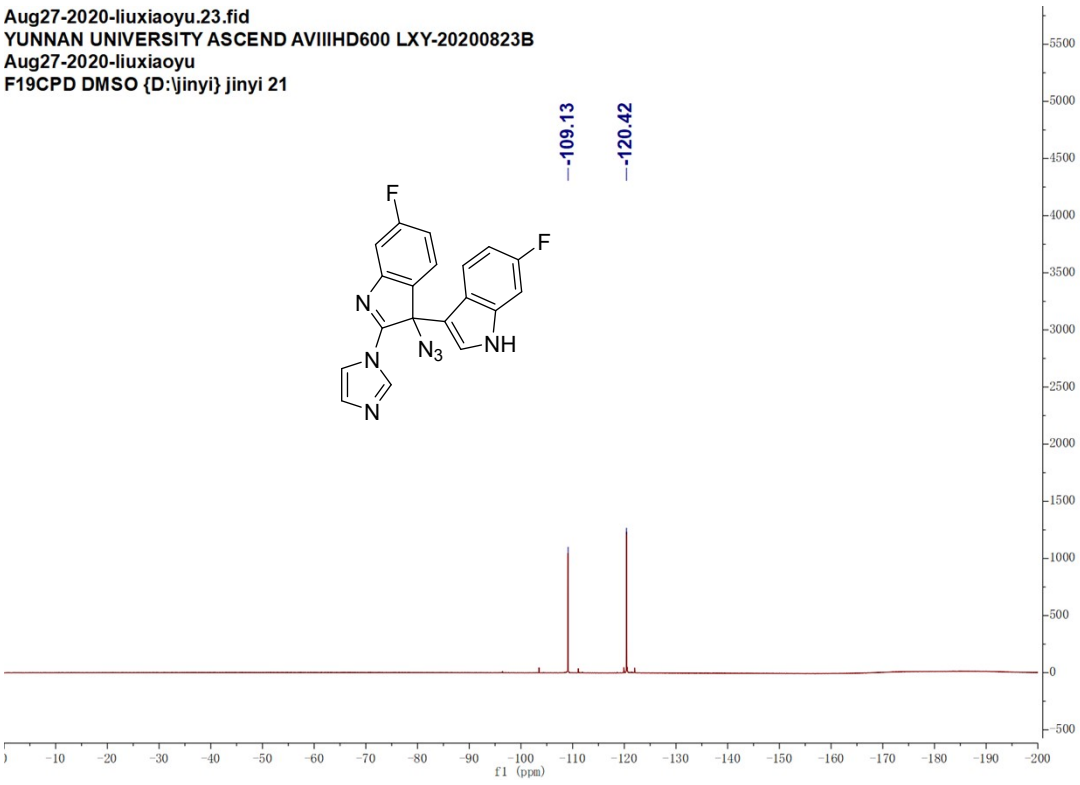
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **4c**



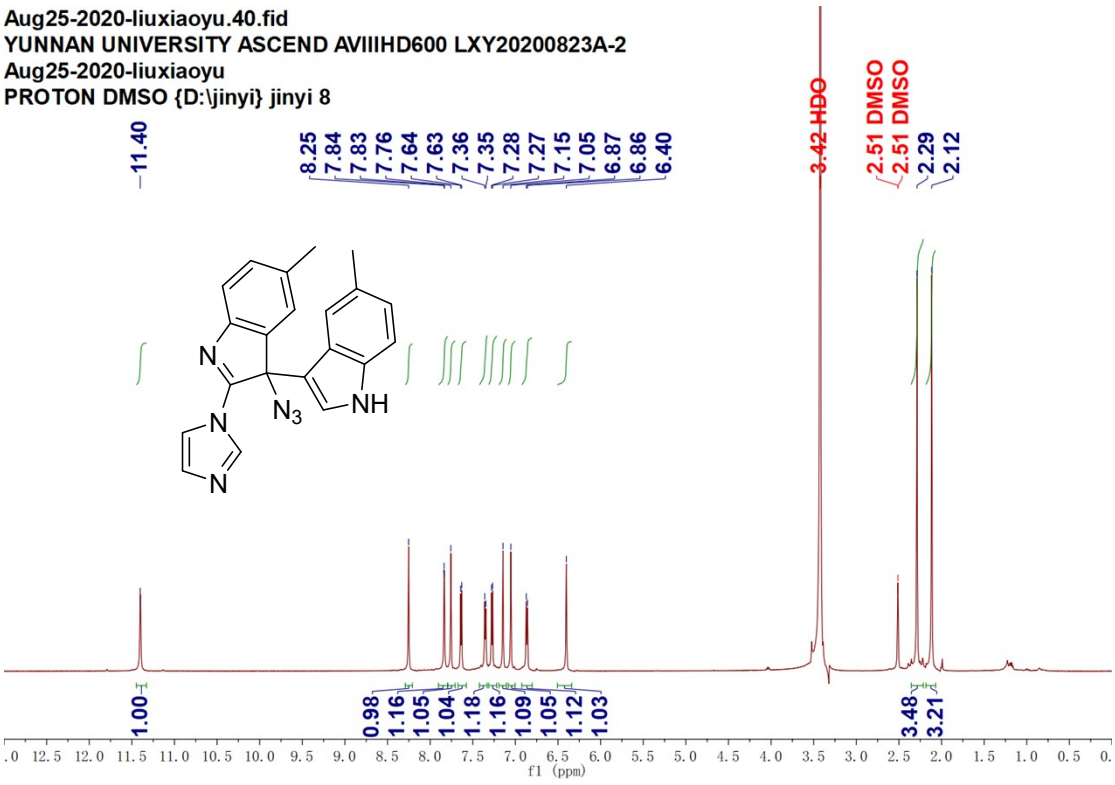
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **4d**



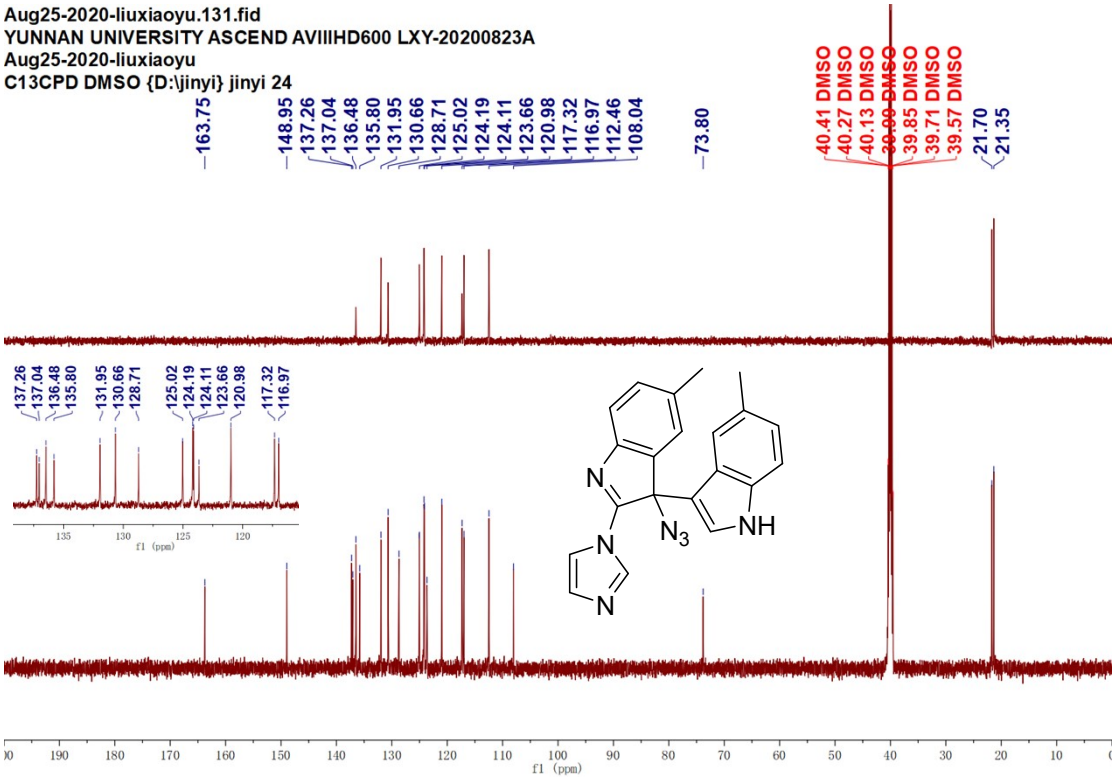
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **4d**



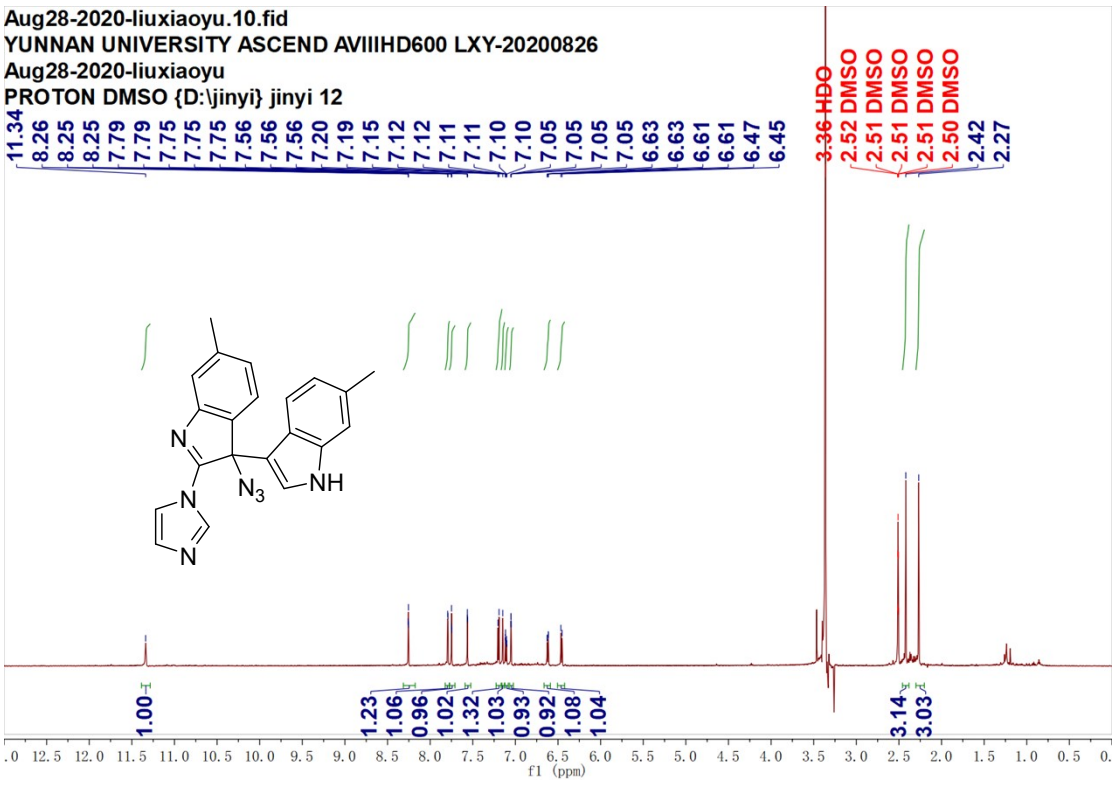
^{19}F-NMR (565MHz, DMSO) spectrum of compound **4d**



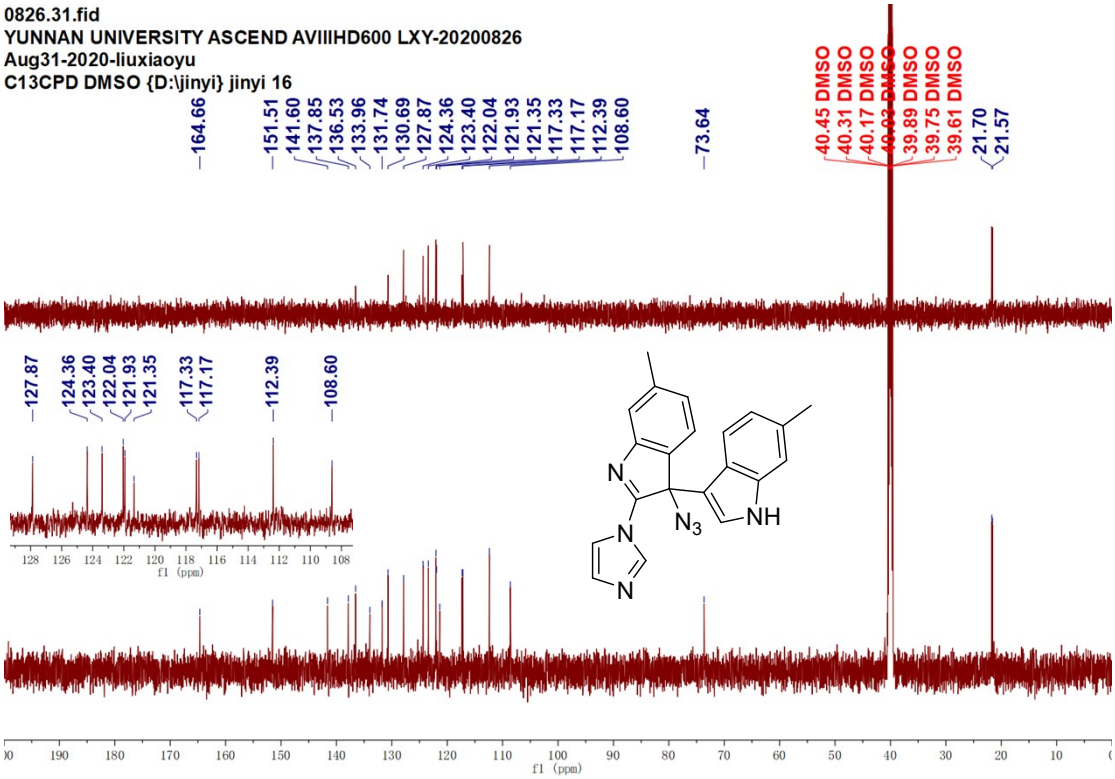
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **4e**



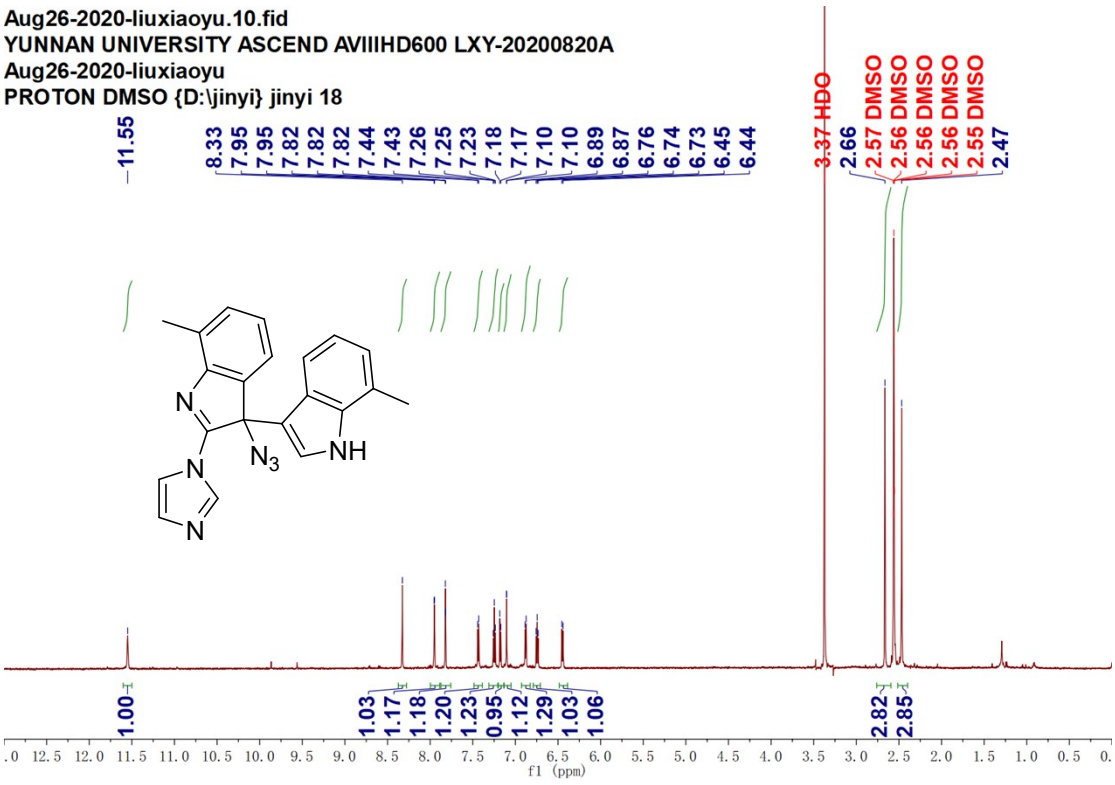
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **4e**



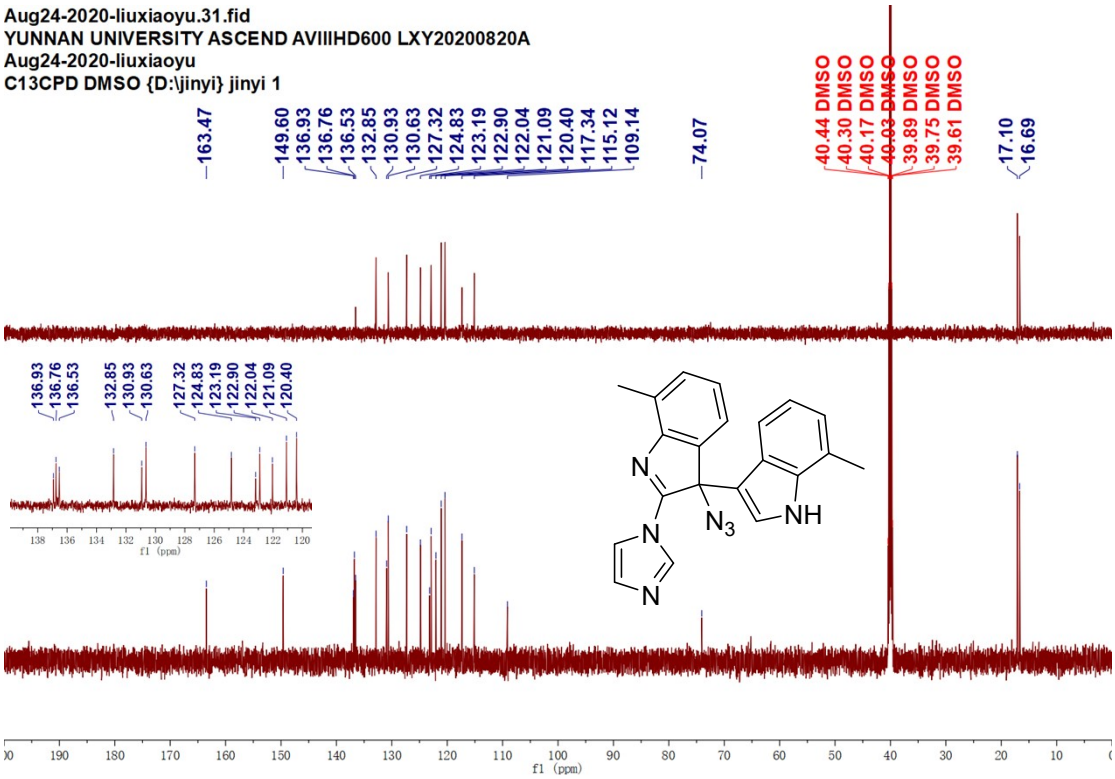
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **4f**



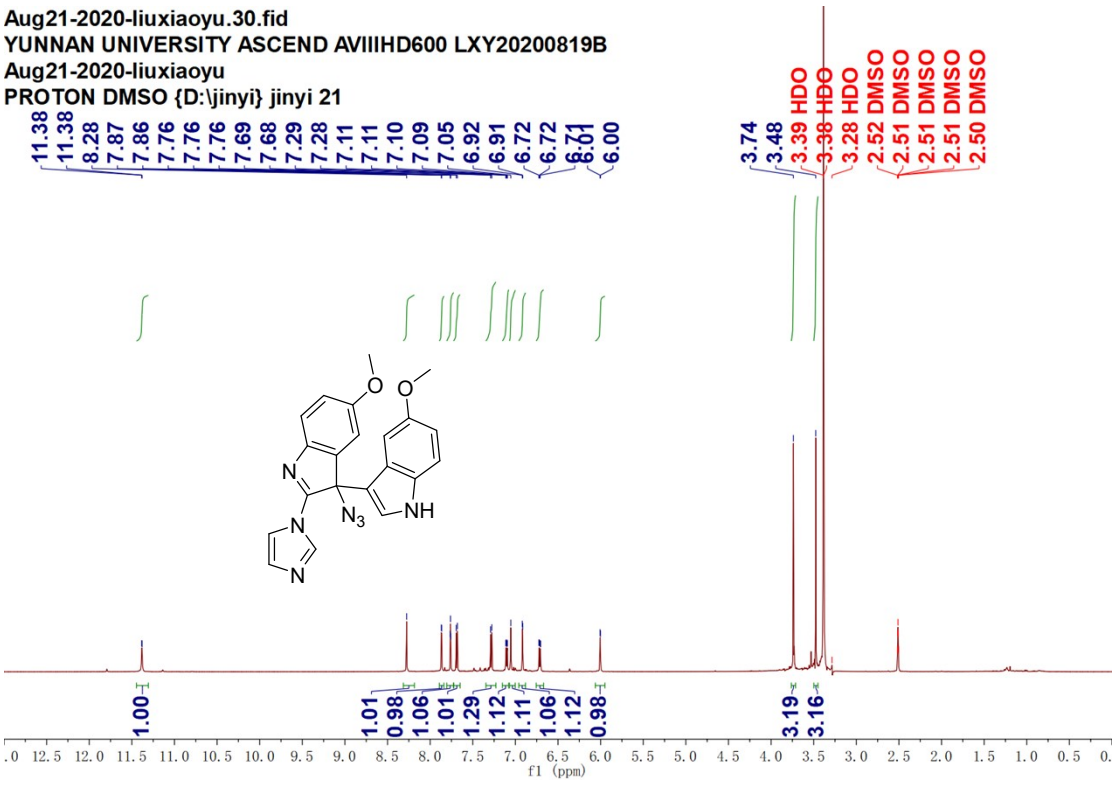
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **4f**



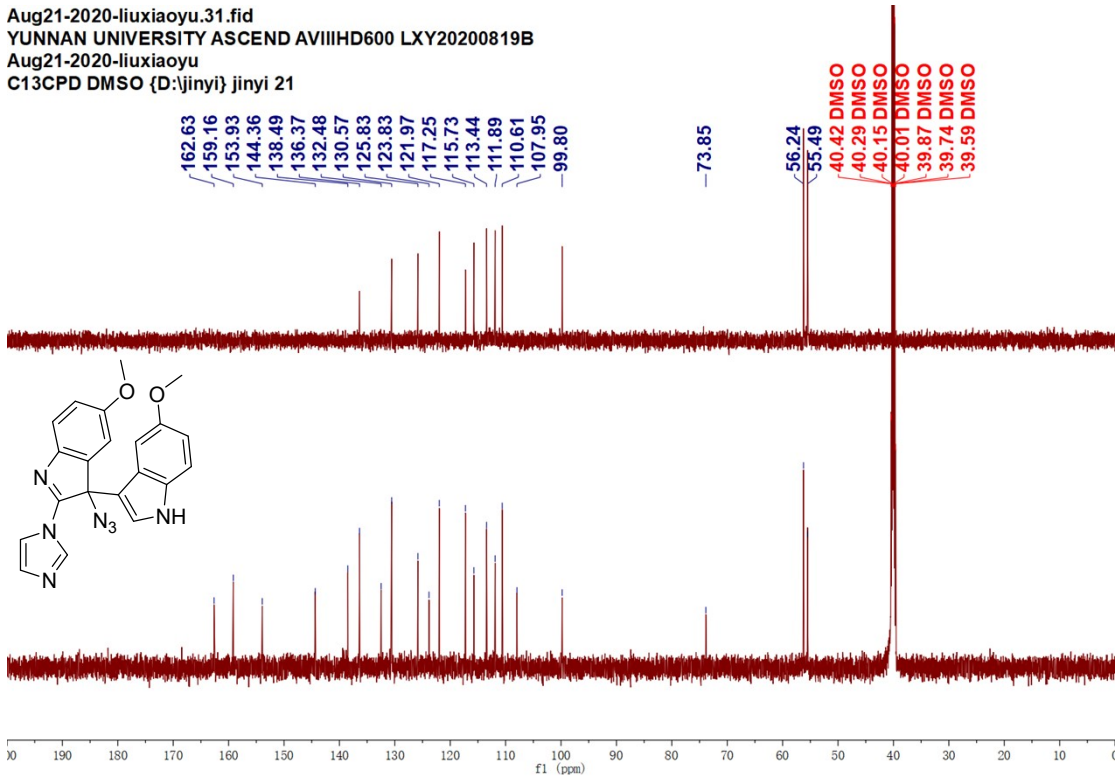
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **4g**



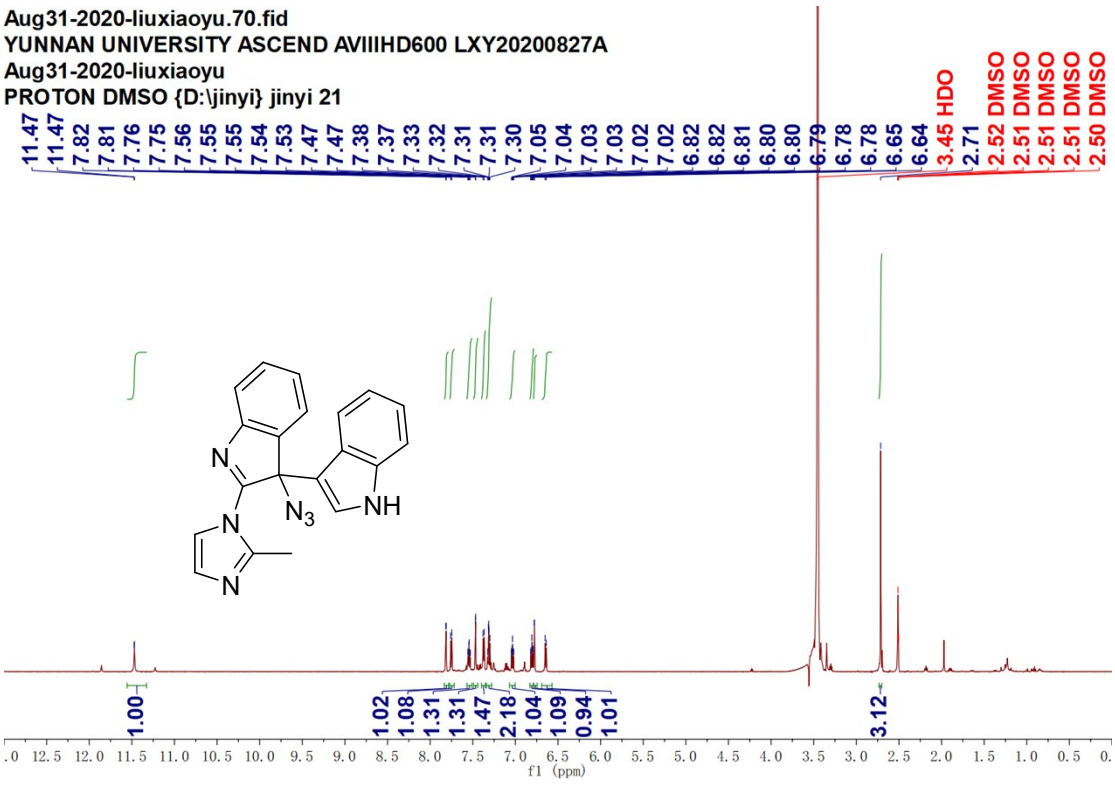
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **4g**



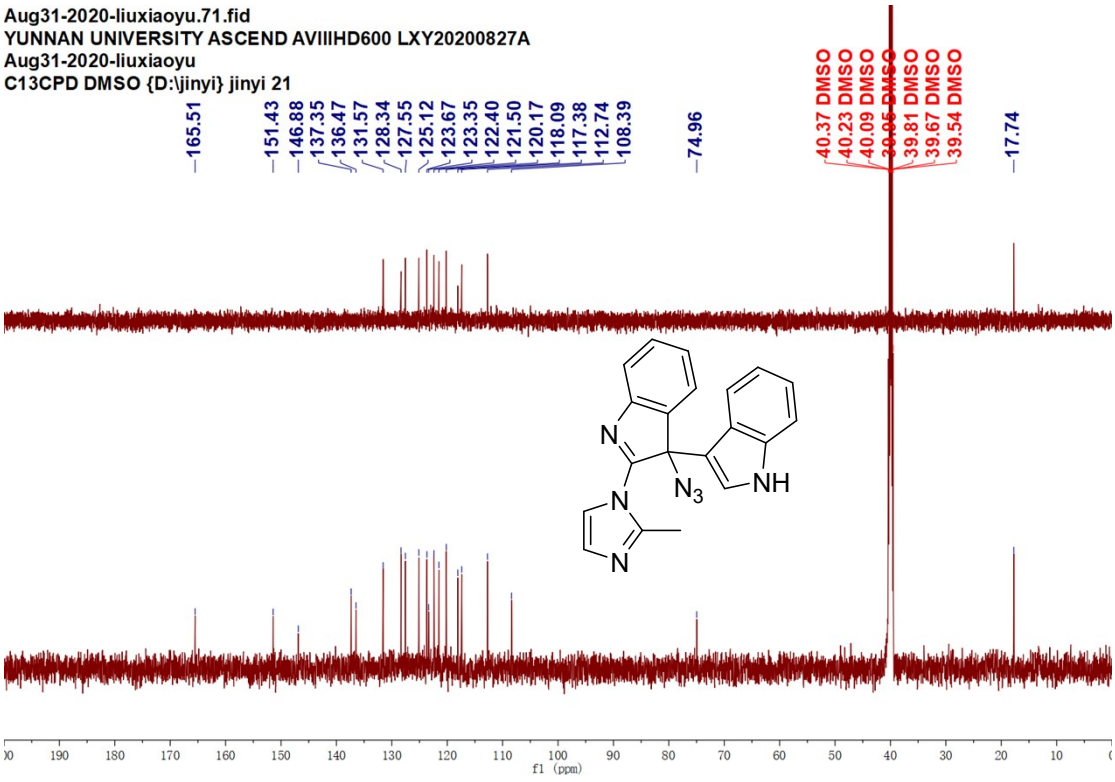
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **4h**



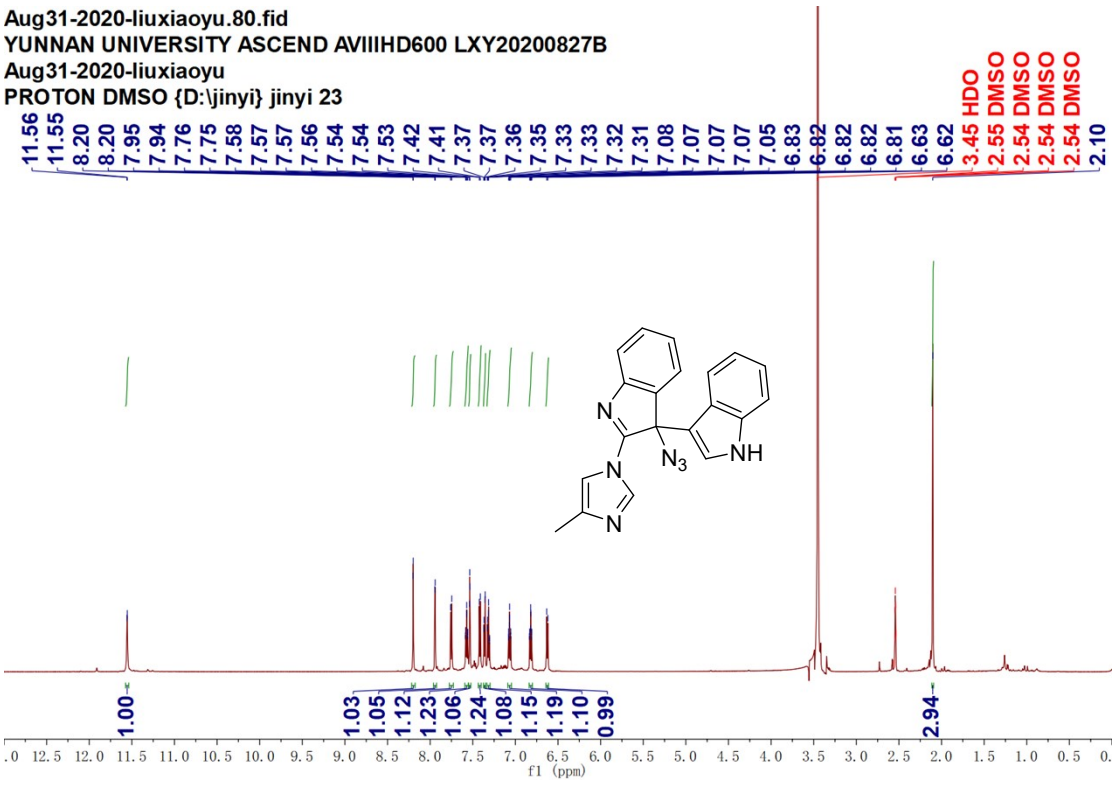
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **4h**



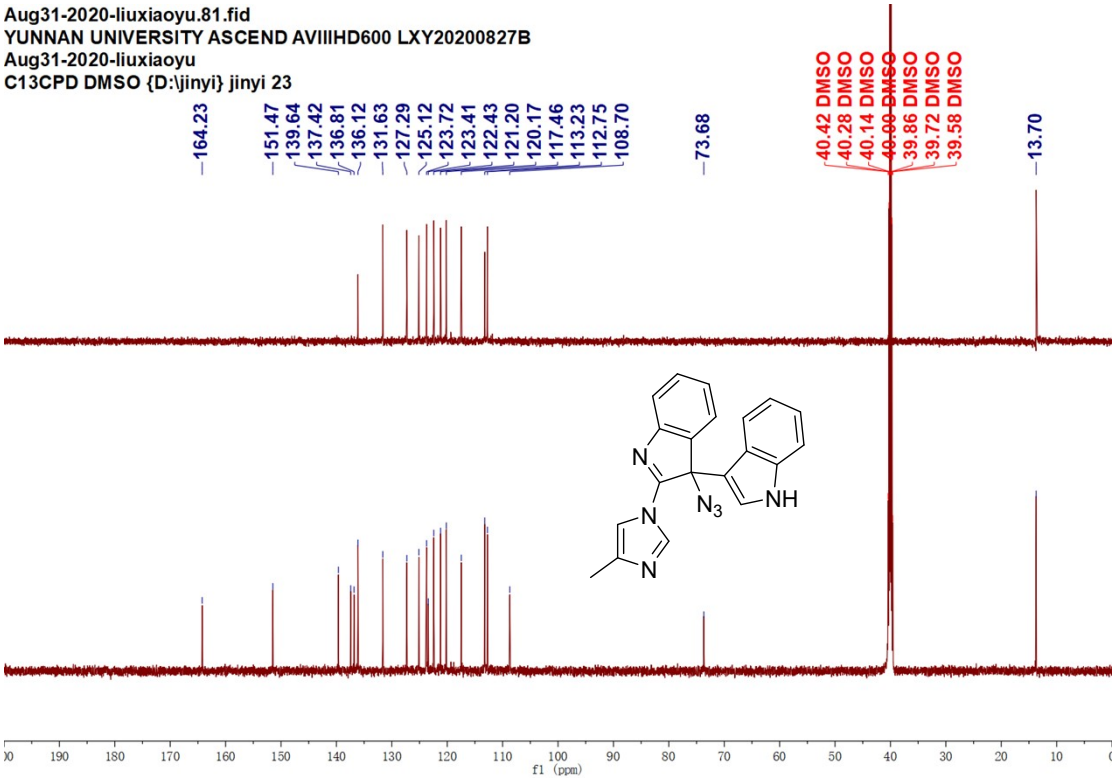
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **4i**



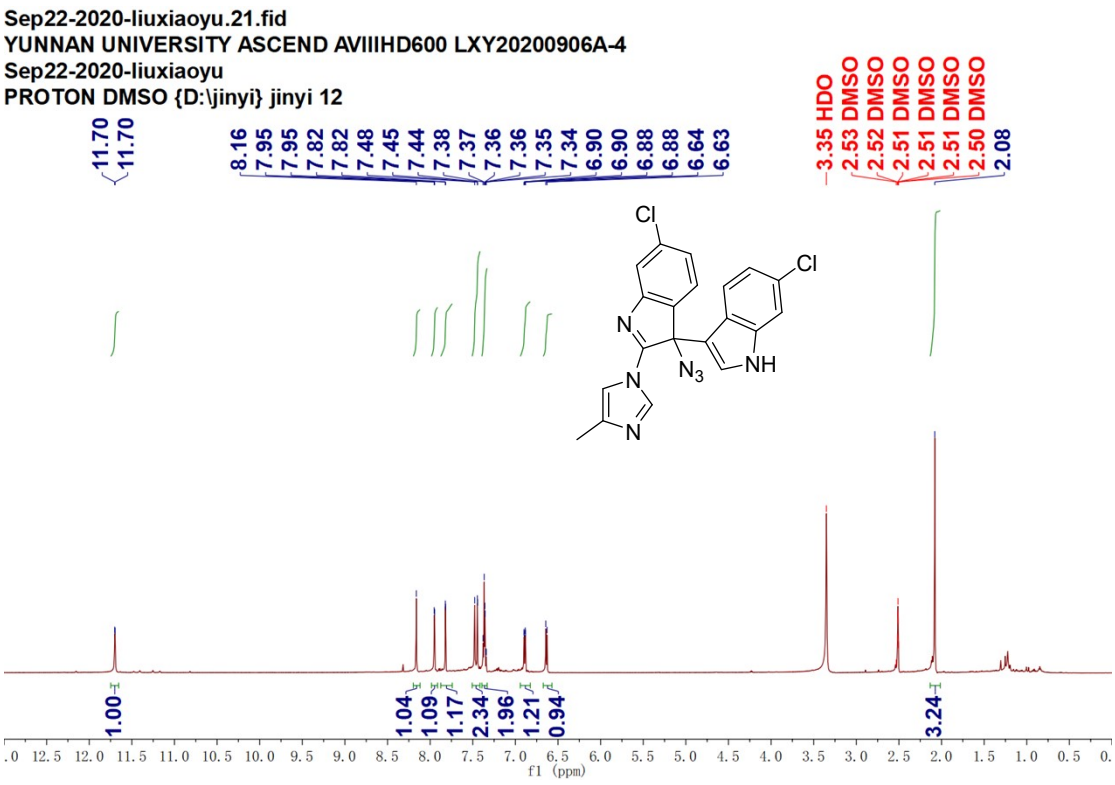
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **4i**



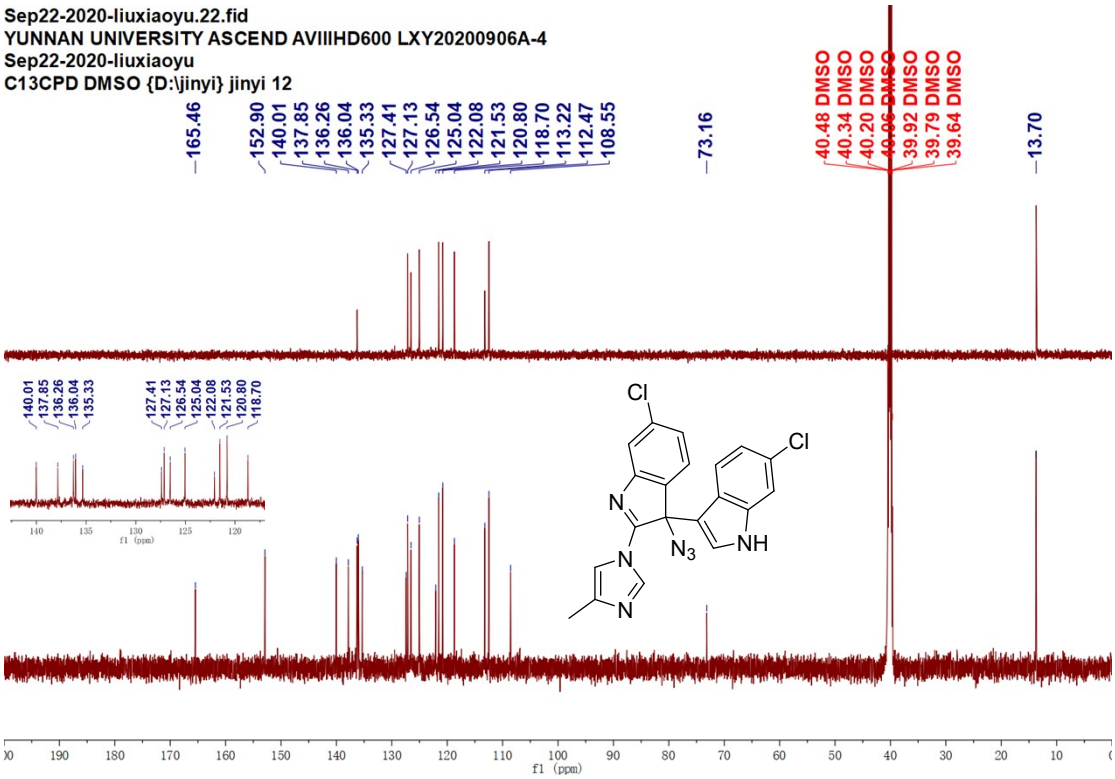
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **4j**



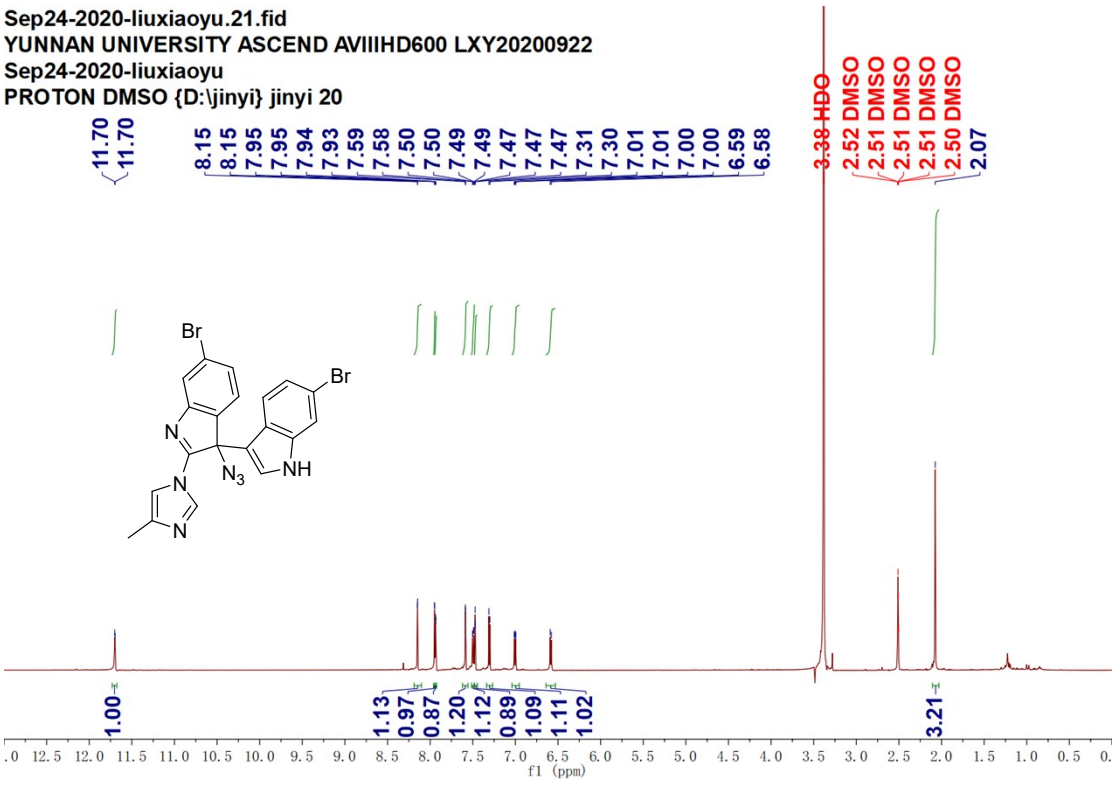
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **4j**



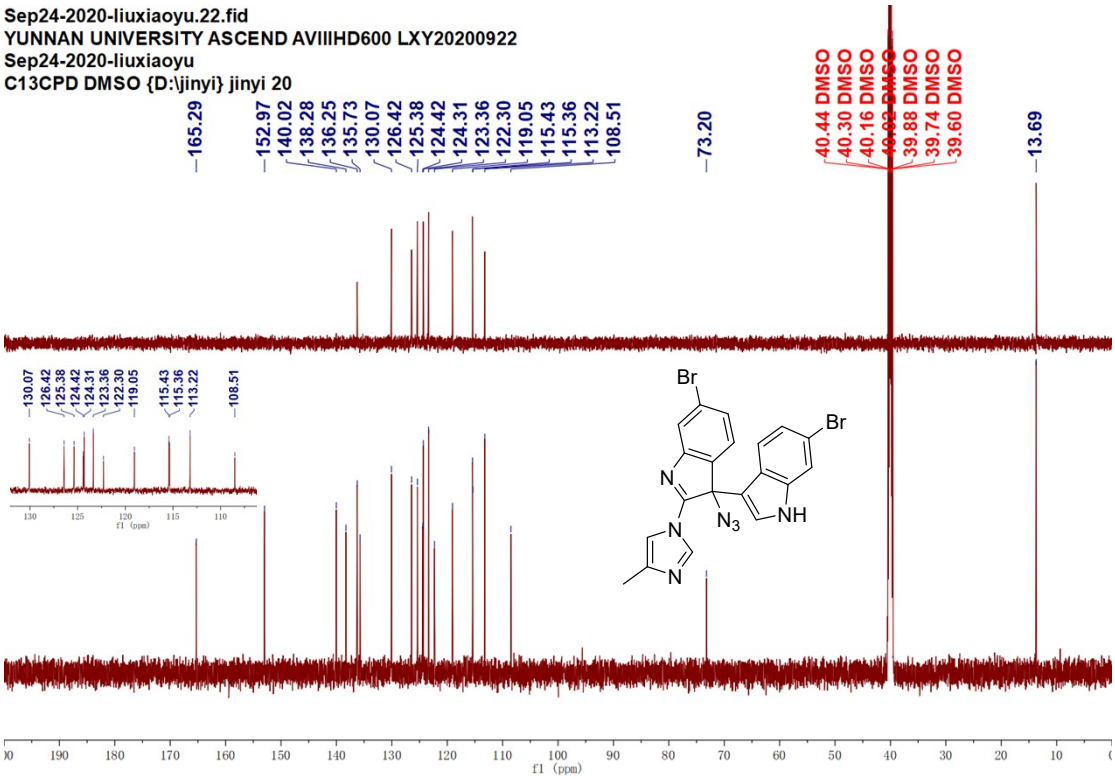
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **4k**



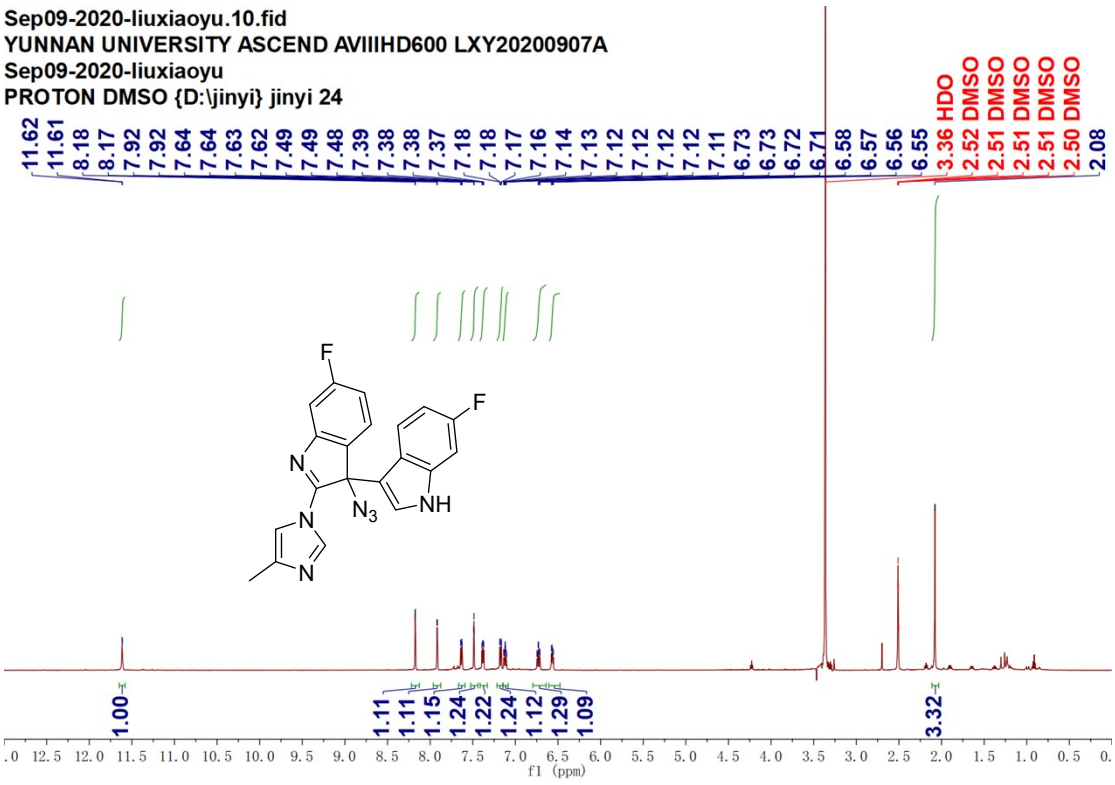
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **4k**



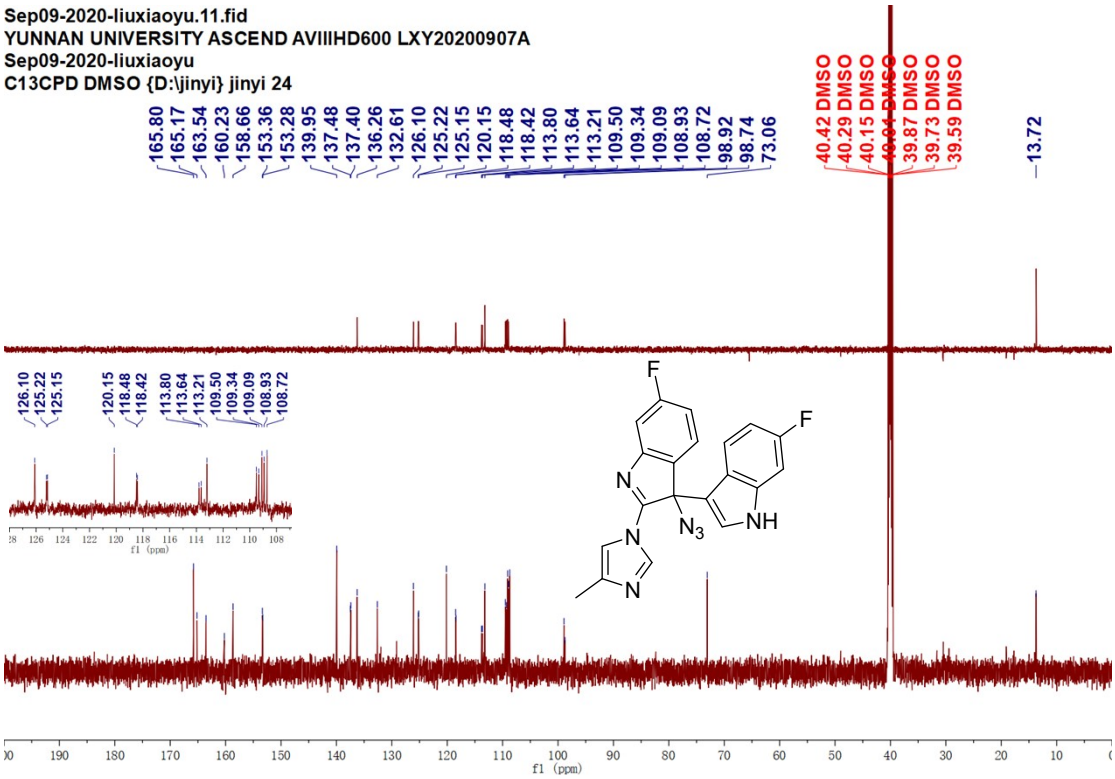
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **4l**



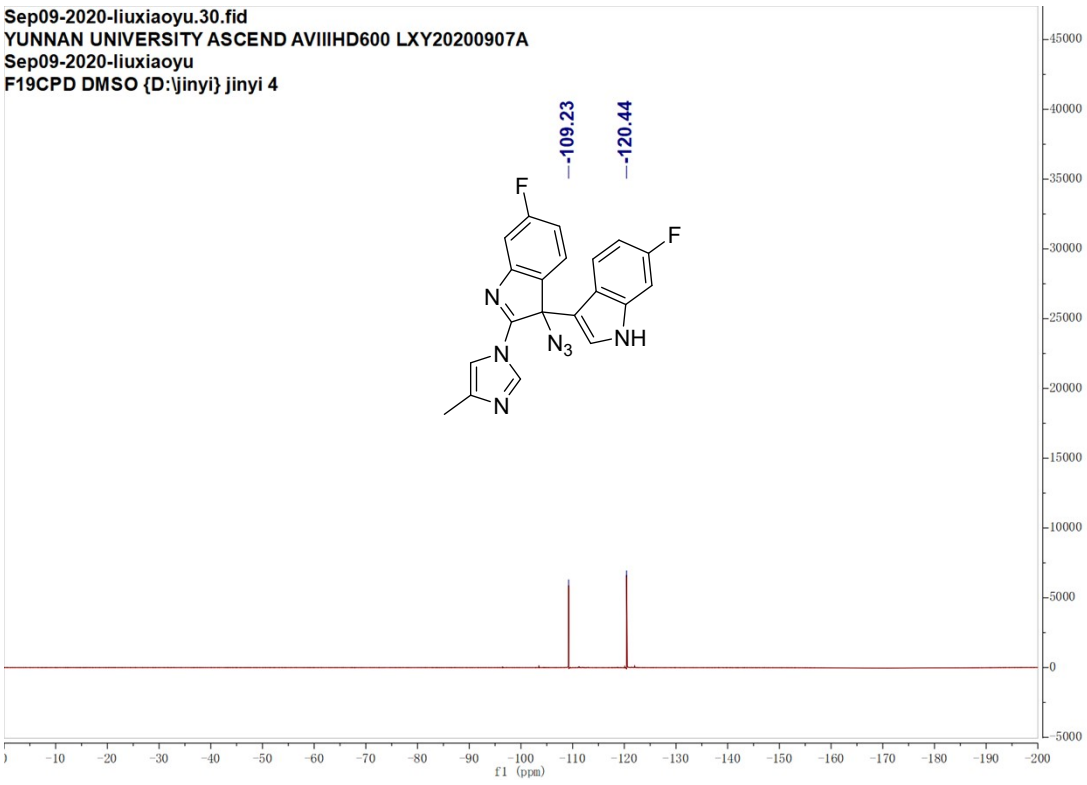
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **4l**



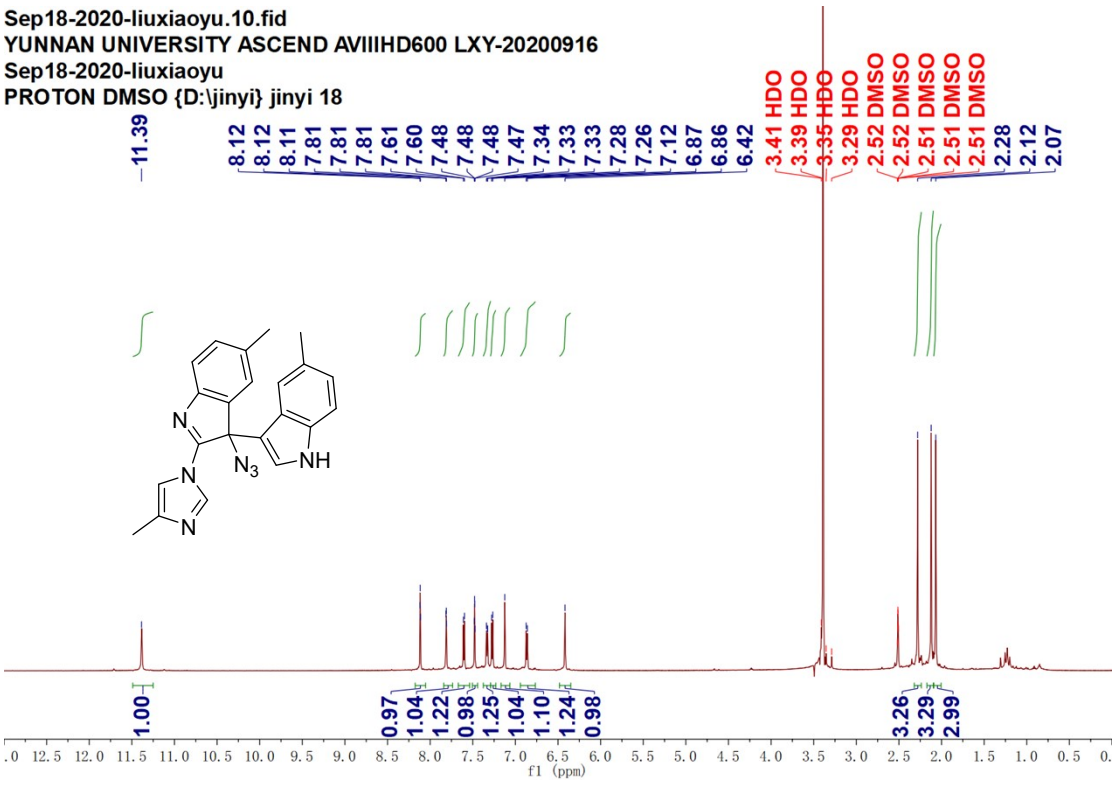
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **4m**



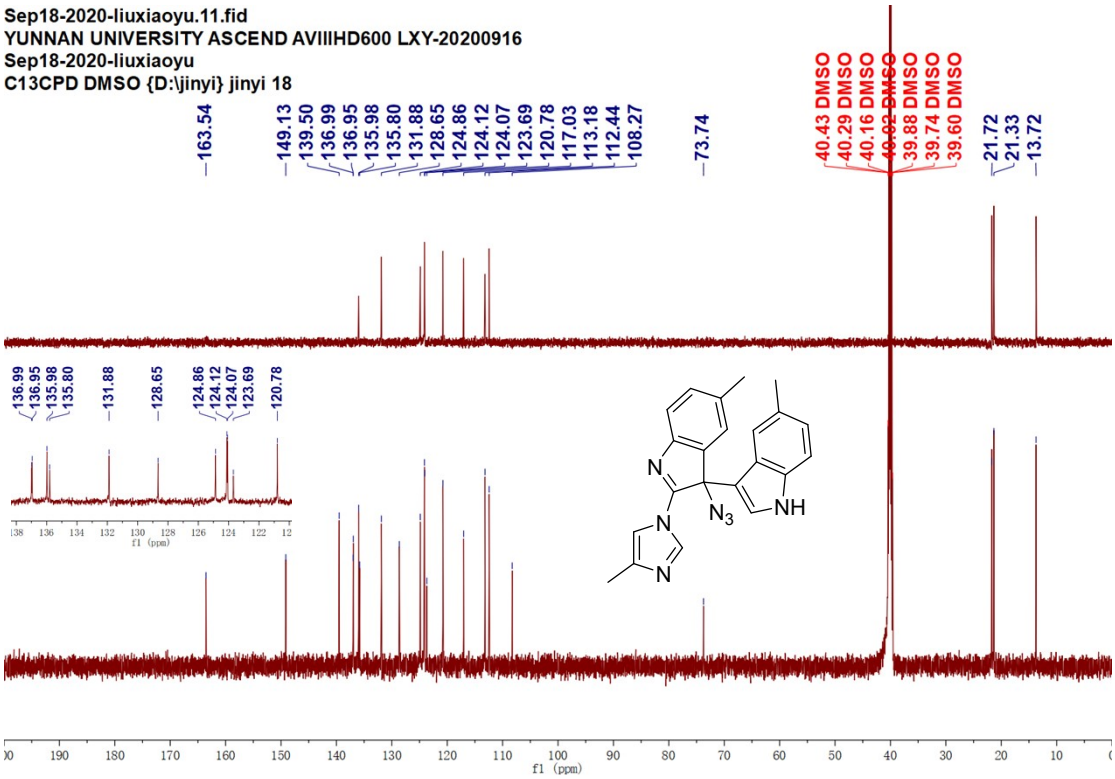
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **4m**



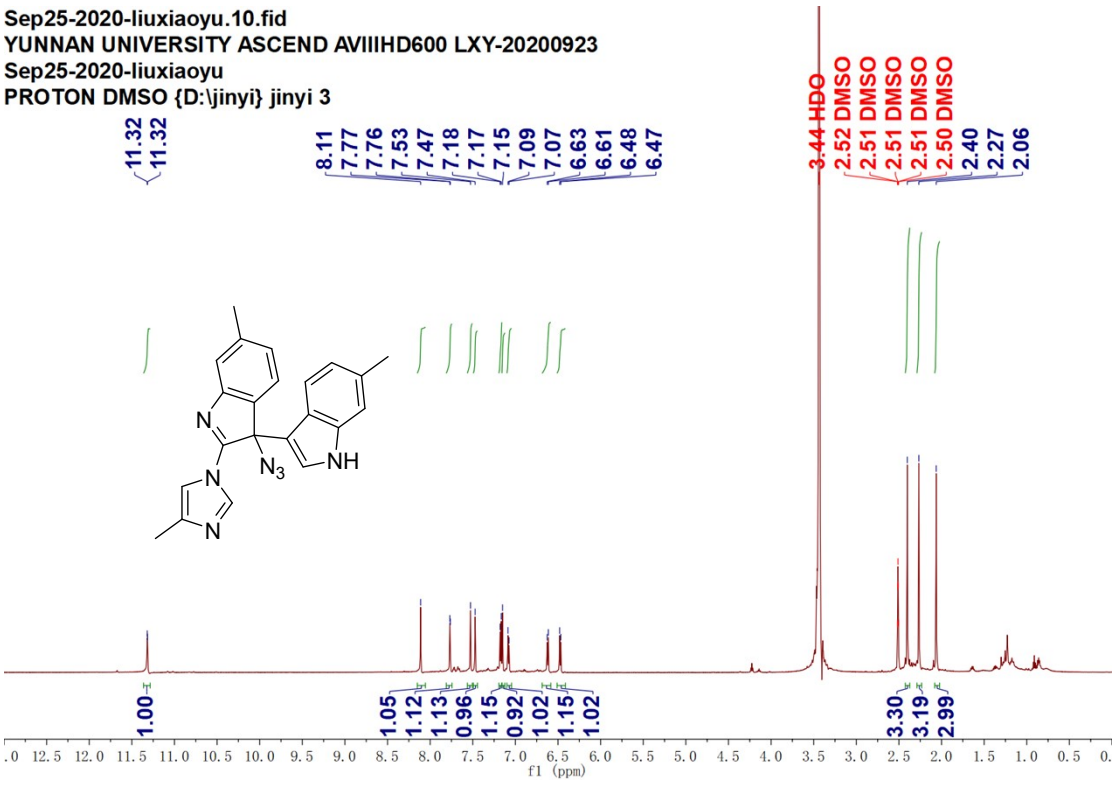
^{19}F-NMR (565MHz, DMSO) spectrum of compound **4m**



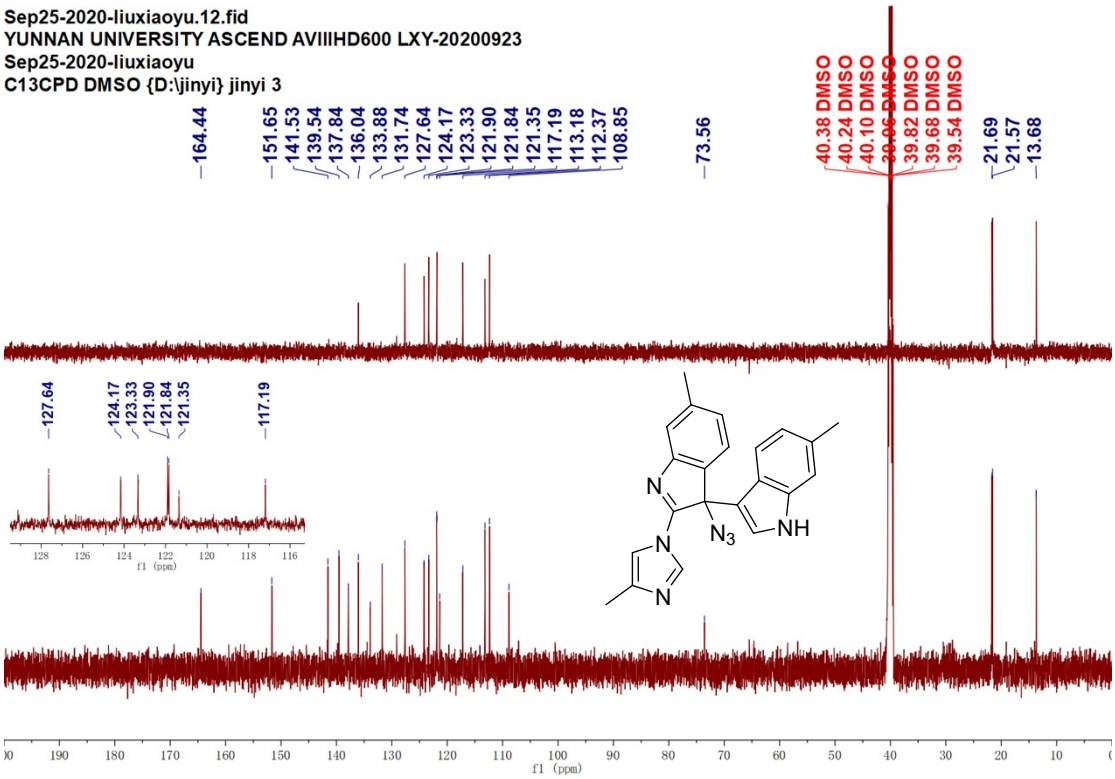
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **4n**



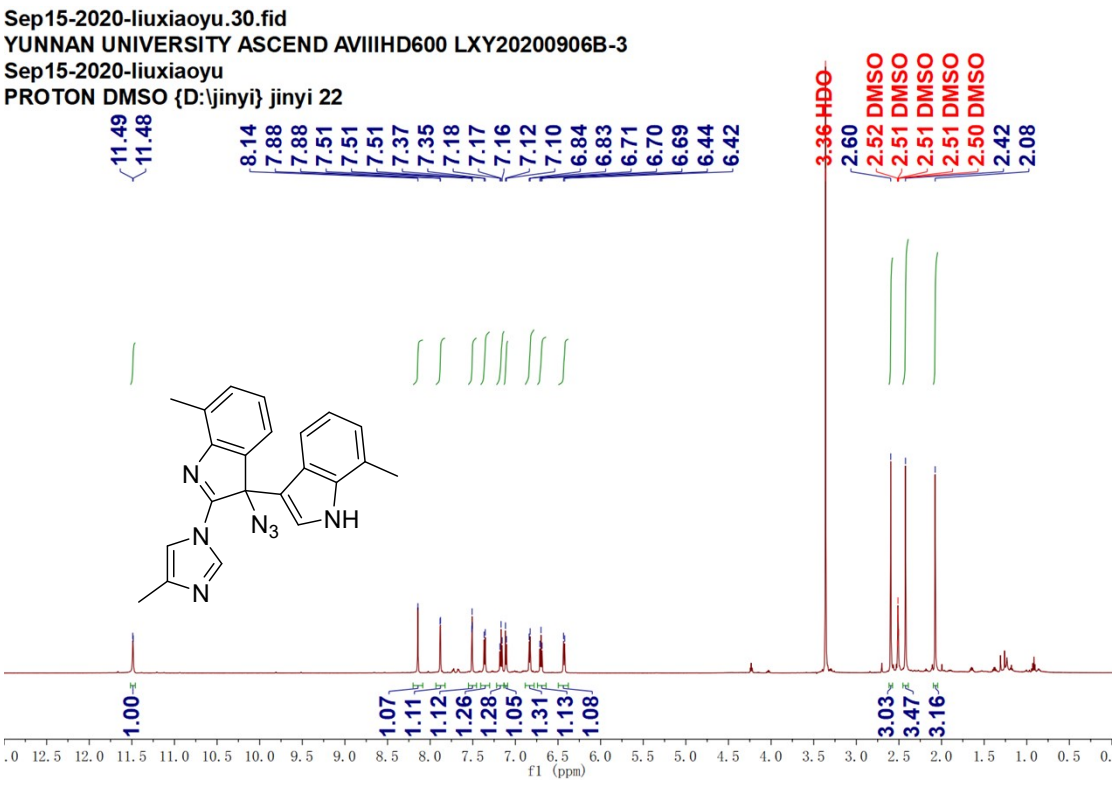
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **4n**



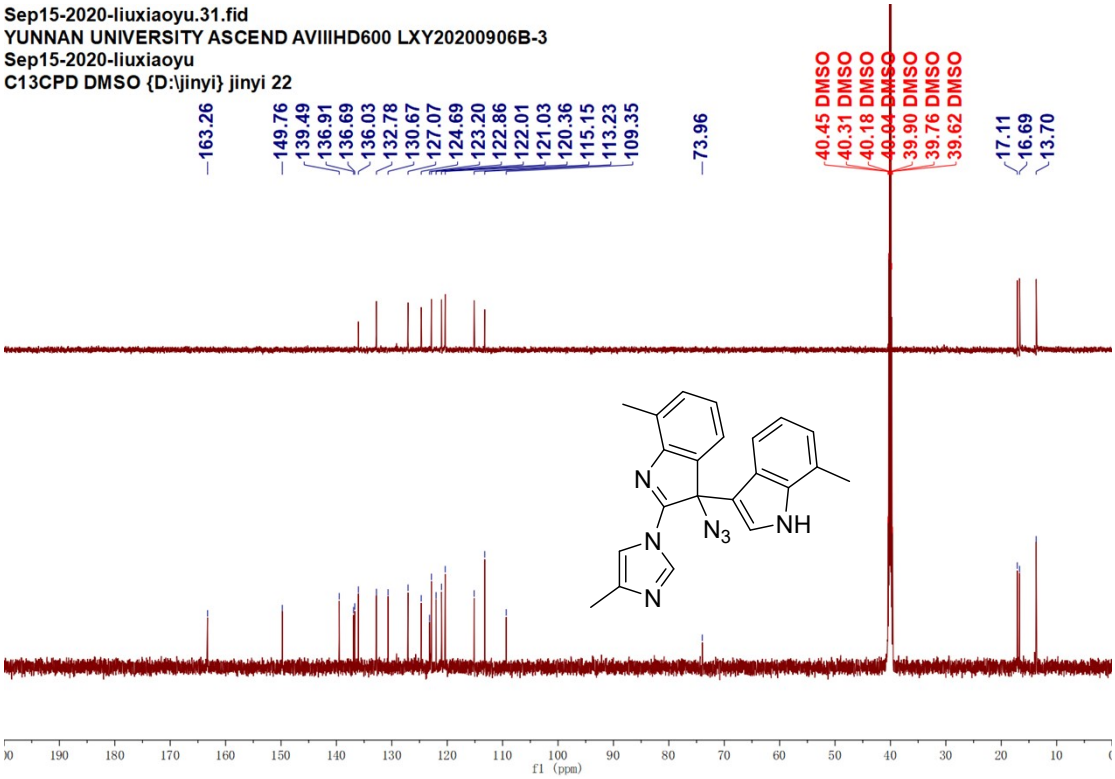
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **4o**



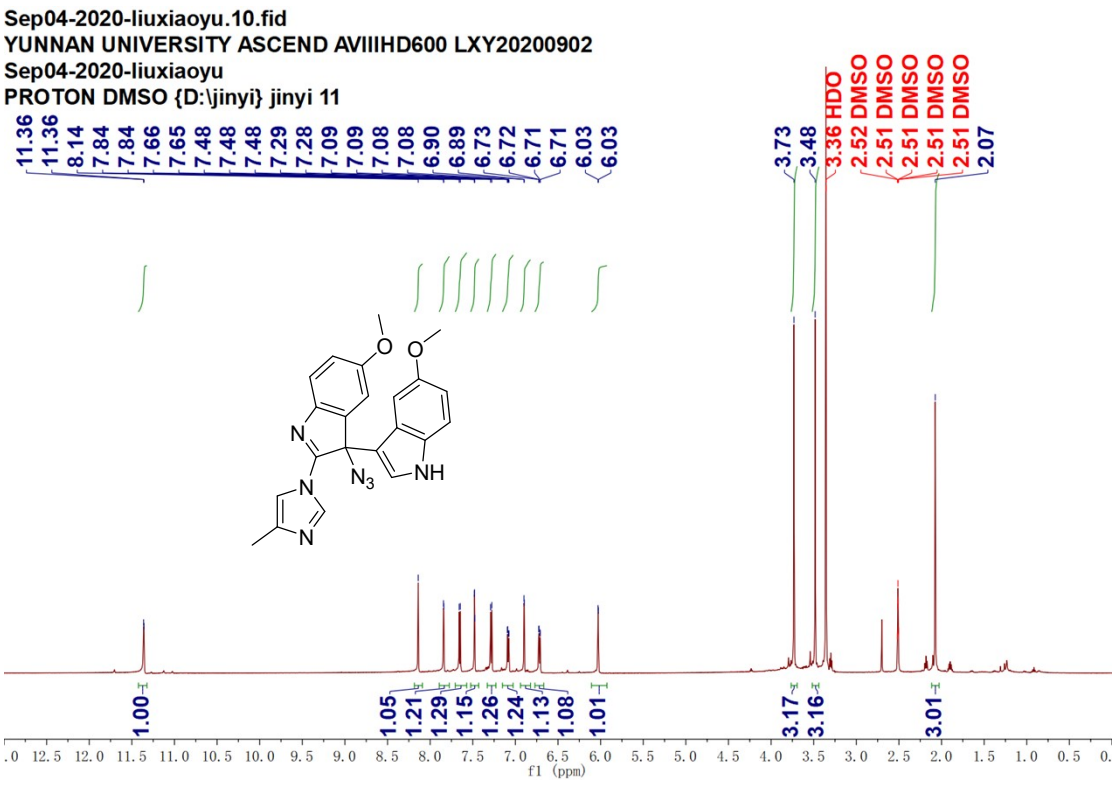
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **4o**



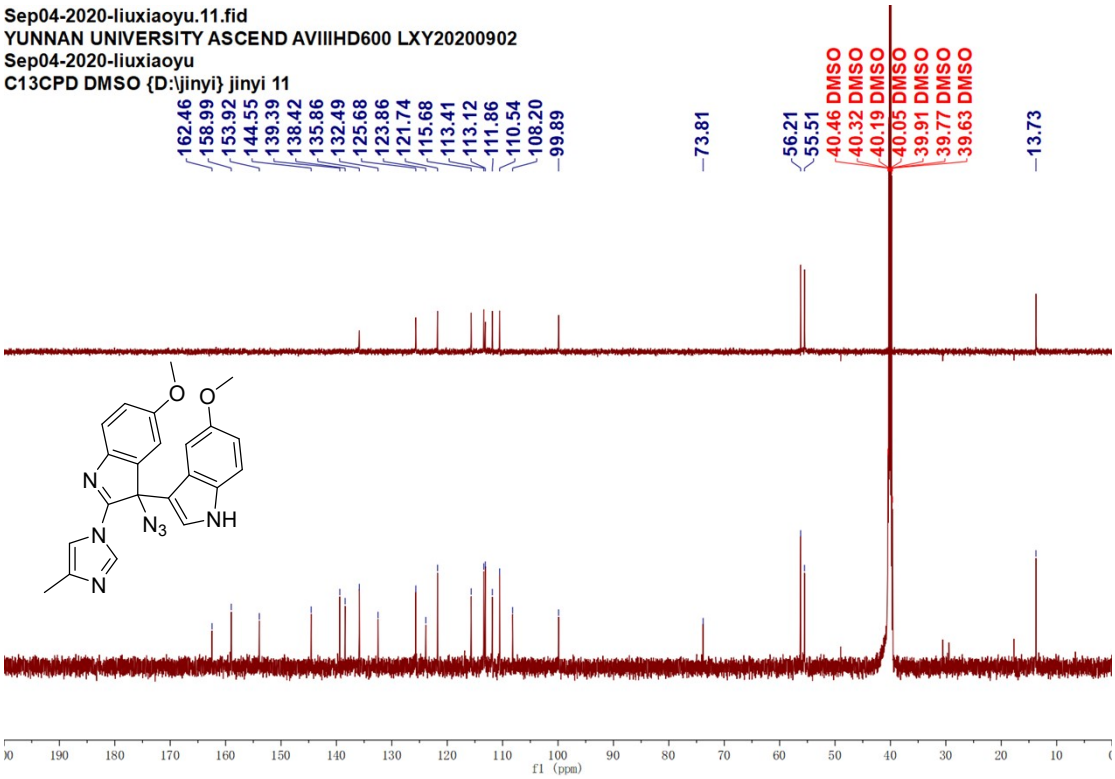
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **4p**



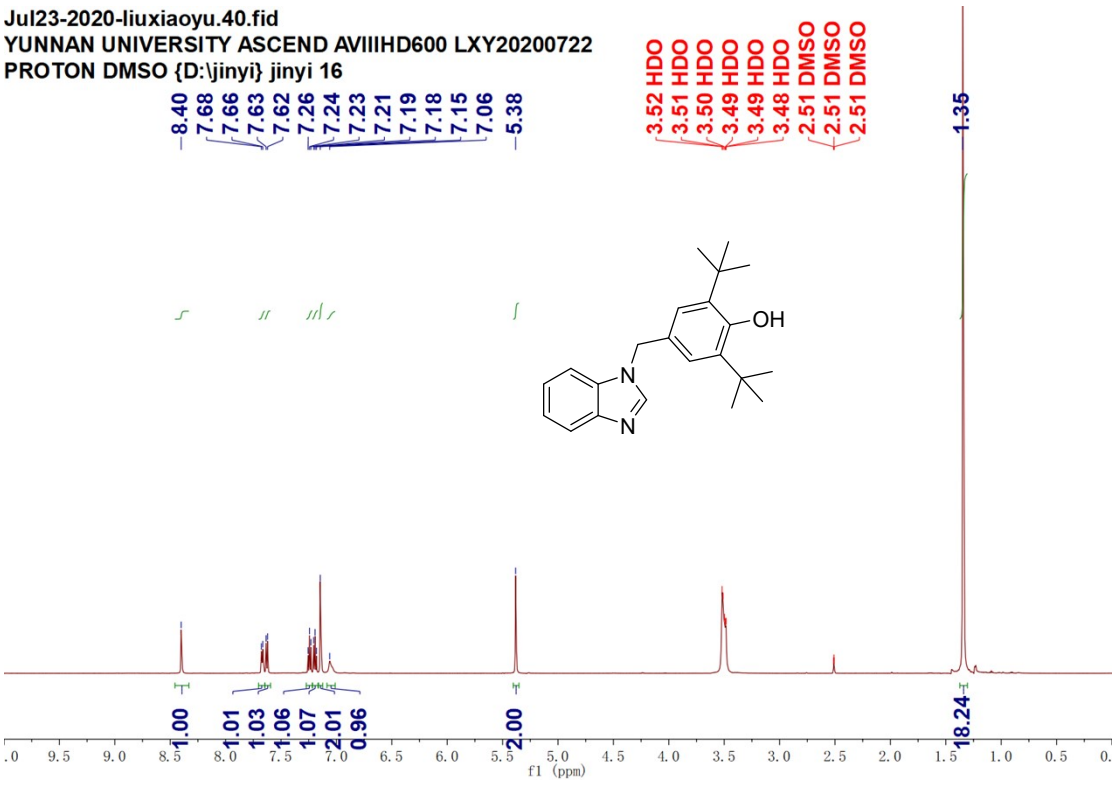
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **4p**



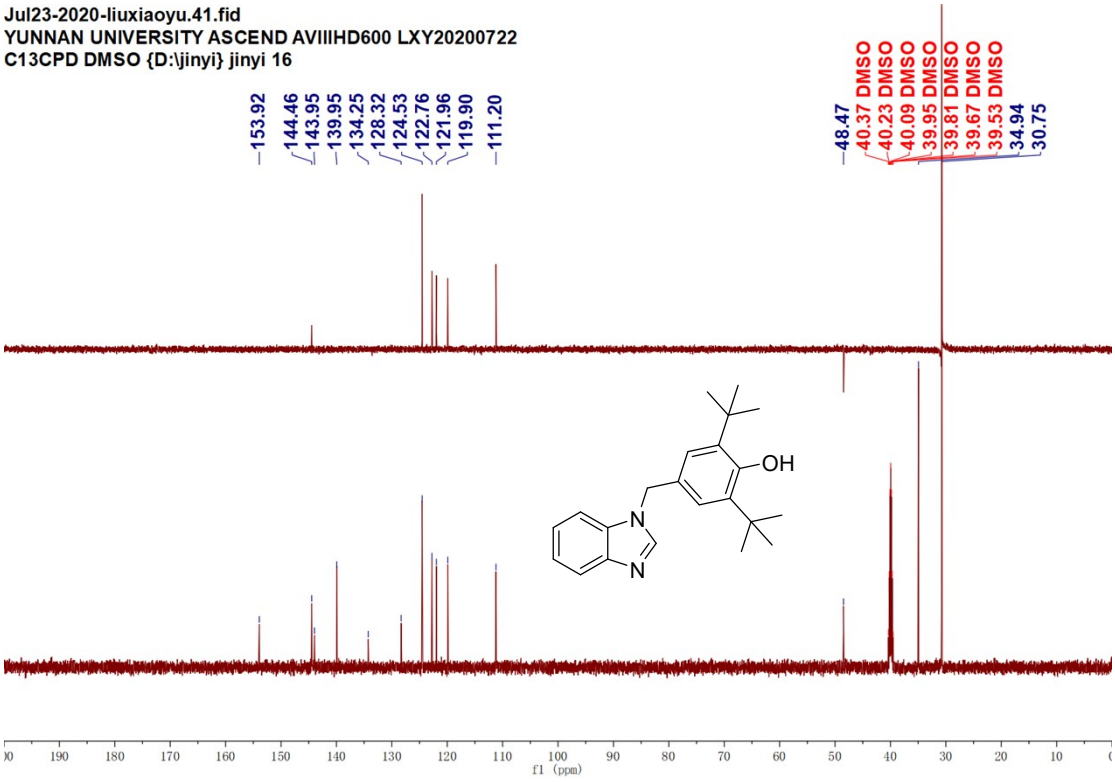
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **4q**



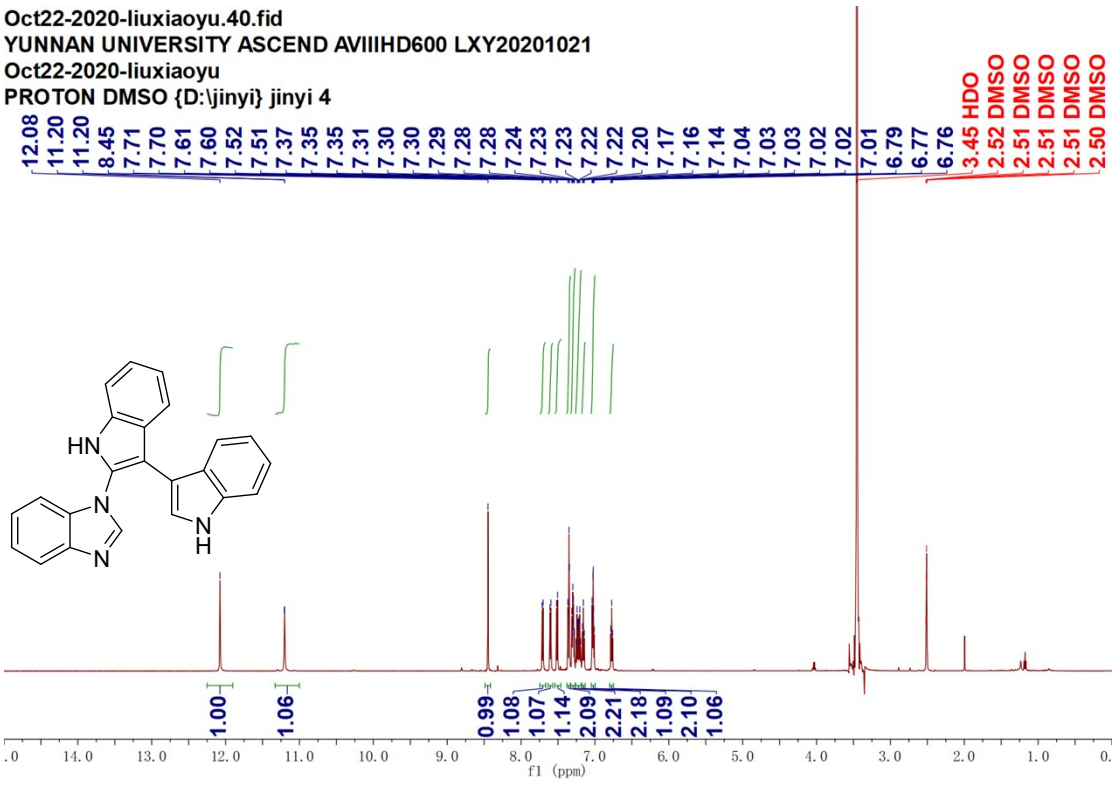
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **4q**



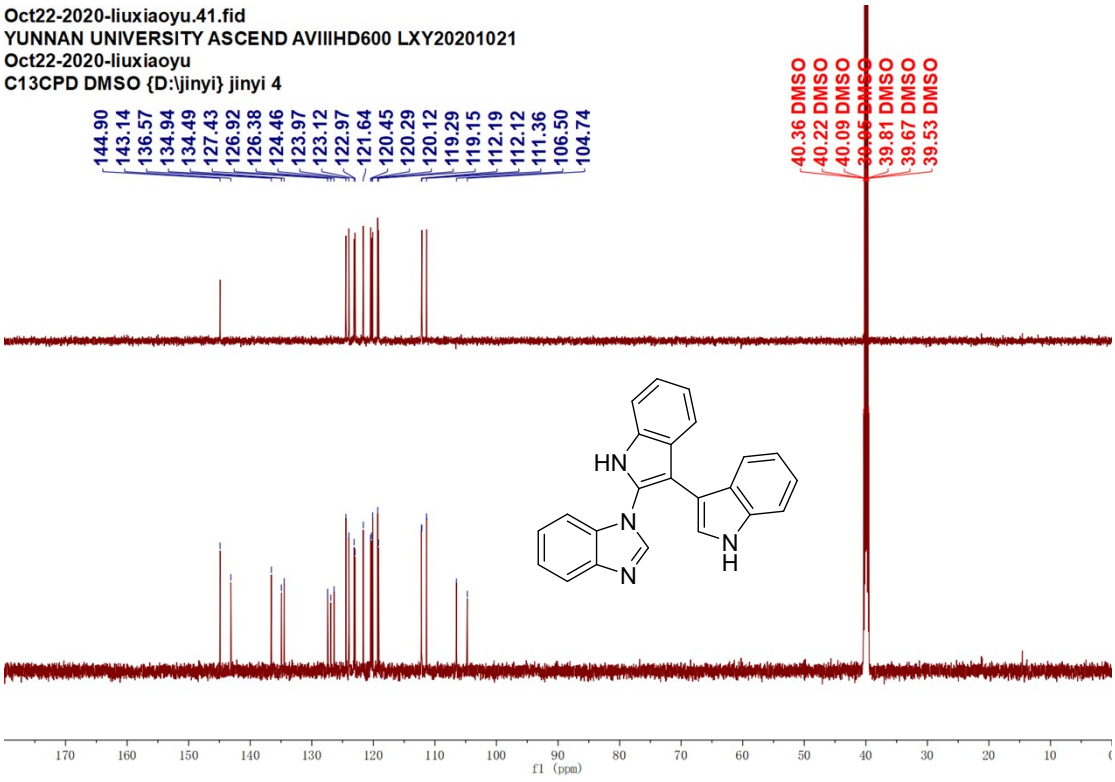
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **5**



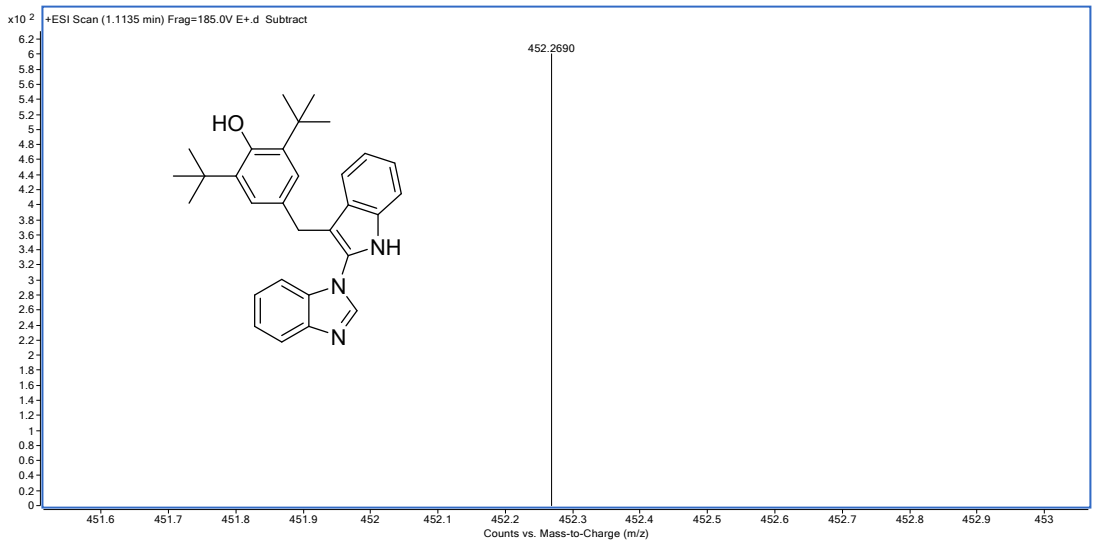
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **5**



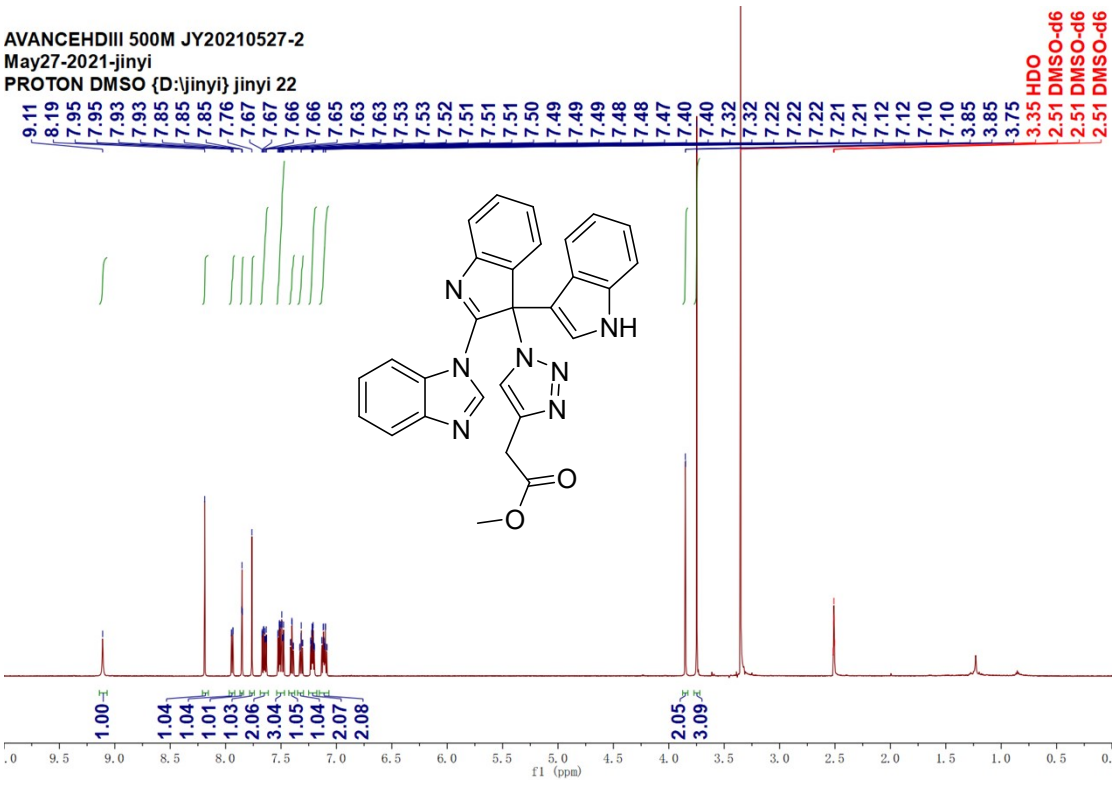
^{1}H-NMR (600 MHz, DMSO) Spectra of compound **6**



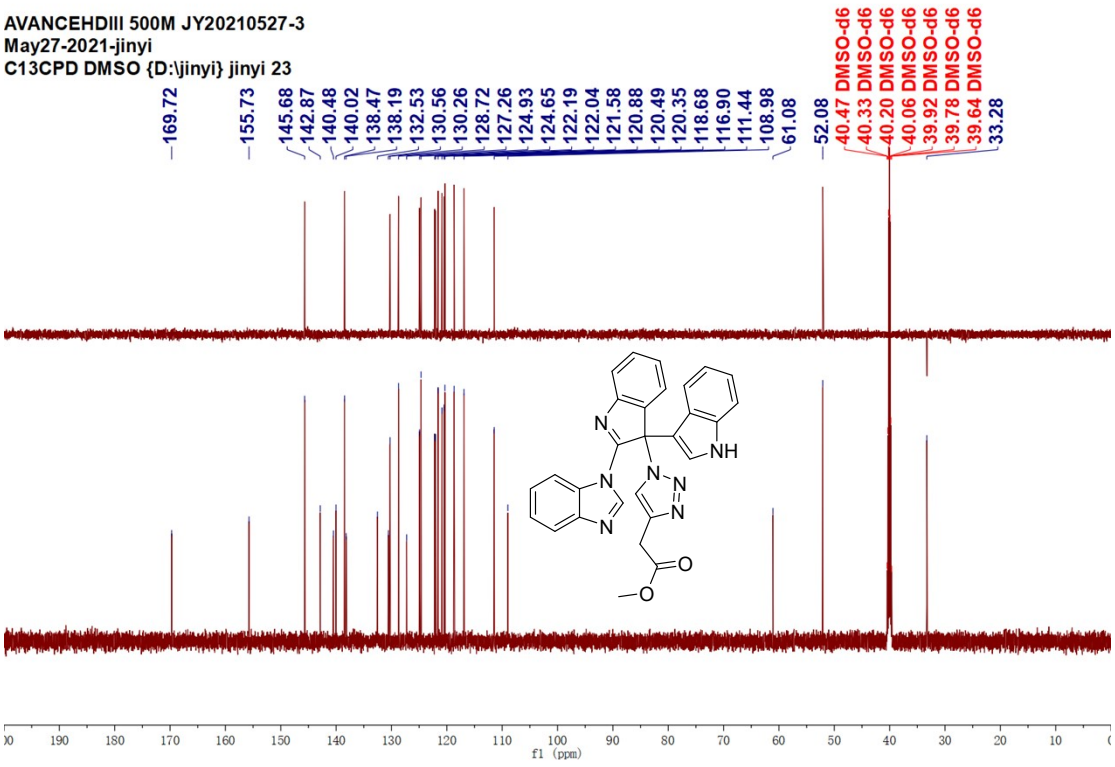
^{13}C-NMR (151 MHz, DMSO) Spectra of compound **6**



HRMS spectrum of compound **7**



^{1}H-NMR (600 MHz, DMSO) Spectra of compound **8**



^{13}C-NMR (151 MHz, DMSO) Spectra of compound **8**