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Supporting Information

A Single-Step Acid Catalyzed Reaction for Rapid Assembly of *NH*-1,2,3-Triazoles

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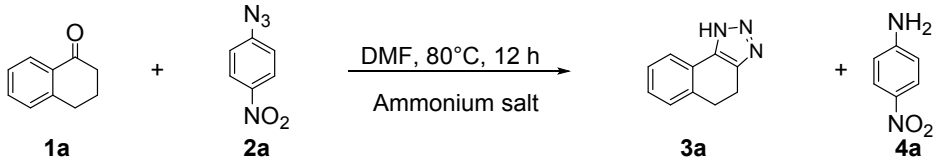
1. General experimental methods

NMR spectra were acquired on commercial instruments (Bruker Avance 300 MHz, Bruker AMX 400 MHz or Bruker Avance II$^+$ 600 MHz) and chemical shifts (δ) are reported in parts per million (ppm) referenced to tetramethylsilane (^{1}H), or the internal (NMR) solvent signal (^{13}C). Mass spectra were run using a HP5989A apparatus (EI, 70 eV ionisation energy) with Apollo 300 data system, a Micromass Quattro II apparatus (ESI) with MASSLYNX data system or a Thermo Finnigan LCQ Advantage apparatus (ESI). Exact mass measurements were acquired on a Kratos MS50TC instrument (performed in the EI mode at a resolution of 10000) or a Bruker Daltonics Apex2 FT-ICR instrument (performed in the ESI mode at a resolution of 60000). Melting points (not corrected) were determined using a Reichert Thermovar apparatus. For column chromatography 70-230 mesh silica 60 (E. M. Merck) was used as the stationary phase. Chemicals received from commercial sources were used without further purification. Reaction solvents DMF were used as received from commercial sources.

2. Experimental Procedures

2.1 Optimization study

We started the optimization of reaction conditions by selecting α-Tetralone **1a** (1 equiv.), and 4-nitrophenyl azide **2a** (1.4 equiv.) as the model reagents with various ammonium salts and solvents to form *NH*-1,2,3 traizole (Table 1). Interestingly, initial screening of NH_4OH (1 equiv.) in toluene at 80 °C afforded the expected product in 13 % yield after 12 h (entry 1). Inspired by this result, several ammonium salt such as NH_4CO_3, NH_4OAc, and NH_4Cl were screened in our model reaction. Among these, to our delight, NH_4OAc (1 equiv.) gave the best result. Further changing the solvent to DMF result in 63 % yield (entry 5). Whereas DMSO and EtOH gave dissatisfactory yield compared to DMF. A gradual increase in yield was observed when the amount of NH_4OAc was increased from 1 equiv. to 5 equiv. (entry 9). Next we investigated the temperature effect on reaction. Decreasing the reaction temperature to 60 °C resulted in lower yield after an extended reaction time of 24 h (entry 11). Similarly, increasing the reaction temperature to 100 °C also resulted in lower yield (entry 12).



1a **2a** **3a** **4a**

Table 1: Optimization of reaction conditions.

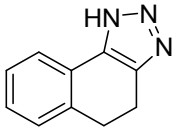
entry	ammonium salts	solvent	Temp (°C)	Time (h)	Yield (%)[a]
1	NH_4OH (1 equiv.)	toluene	80	12	13
2	NH_4CO_3 (1 equiv.)	toluene	80	12	18
3	NH_4OAc (1 equiv.)	toluene	80	12	46
4	NH_4Cl (1 equiv.)	toluene	80	12	18
5	NH_4OAc (1 equiv.)	DMF	80	12	62
6	NH_4OAc (1 equiv.)	DMSO	80	12	51
7	NH_4OAc (1 equiv.)	EtOH	80	12	43
8	NH_4OAc (3 equiv.)	DMF	80	12	77

9	NH_4OAc (5 equiv.)	DMF	80	12	86
10	NH_4OAc (6 equiv.)	DMF	80	12	84
11	NH_4OAc (5 equiv.)	DMF	60	24	77
12	NH_4OAc (5 equiv.)	DMF	100	12	81

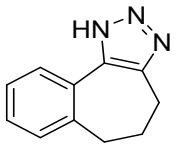
[a] Isolated yield.

2.2 General procedure for the preparation of substituted *NH*-1,2,3-triazoles.

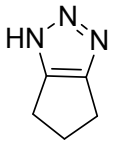
To an oven-dried screw-capped reaction tube equipped with a magnetic stir bar were added the ketone, ammonium acetate, 4-nitrophenyl azide. The mixture was dissolved in DMF and stirred at 80 °C for 12 - 24 h. Upon completion the DMF was removed *in vacuo*. and purified by column chromatography (silica gel), at first with CH_2Cl_2 as eluent to remove all 4-nitroaniline **4** formed during the reaction followed by using a mixture of heptane and ethyl acetate as eluent to afford the corresponding *NH*-1,2,3-triazole as off-white solids or semi-solids.



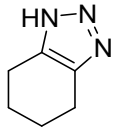
4,5-dihydro-1H-naphtho[1,2-d][1,2,3]triazole (3a): Tetralone (69 mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 5:2) afforded **3a** (69 mg, 86% yield) as an off-white solid. m.p. 113 - 114 ˚C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.90 - 7.88 (m, 1H), 7.34 - 7.27 (m, 3H), 3.12 - 3.05 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 144.0, 143.2, 136.2, 128.7, 128.5, 127.5, 127.4, 123.2, 29.2, 20.2. **HRMS** (ESI^+): m/z calcd for $C_{10}H_{10}N_3$ $[M+H]^+$: 172.0869, found 172.0865. Spectroscopic data for **3a** are consistent with previously reported data for the compound.[1]



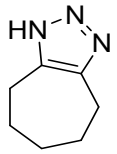
1,4,5,6-tetrahydrobenzo[3,4]cyclohepta[1,2-d][1,2,3]triazole (3b): 6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one (75 mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 5:2) afforded **3b** (70 mg, 81% yield) as an off-white solid. m.p. 173 - 174 ˚C. **^{1}H NMR** (400 MHz, MeOD) δ 7.91 (d, *J* = 7.6 Hz, 1H), 7.19 – 7.07 (m, 3H), 2.96 (t, *J* = 6.7 Hz, 2H), 2.80 (t, *J* = 5.3 Hz, 2H), 1.97 – 1.91 (m, 2H). **^{13}C NMR** (100 MHz, MeOD) δ 141.9, 130.9, 130.0, 129.0, 127.6, 36.2, 26.6, 25.2. **HRMS** (ESI^+): m/z calcd for $C_{11}H_{11}N_3$ $[M+H]^+$: 186.1025, found 186.1033.



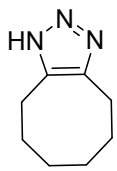
1,4,5,6-tetrahydrocyclopenta[d][1,2,3]triazole (3c): cyclopentanone (40 mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 4:6) afforded **3c** (34 mg, 65% yield) as a colorless solid. m.p. 141 - 142 ˚C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.81 (t, *J* = 7.4 Hz, 4H), 2.62 - 2.52 (m, 2H). **^{13}C NMR** (100 MHz, MeOD) δ 156.1, 29.4, 22.1. **HRMS** (ESI+): m/z calcd for $C_5H_7N_3$ $[M+H]^+$: 110.0712, found 110.0725.



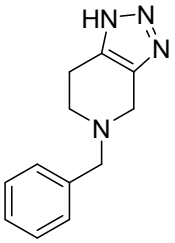
4,5,6,7-tetrahydro-1H-benzo[d][1,2,3]triazole (3d): Cyclohexanone (46 mg, 0.47 mmol), Amonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), DMF (1 mL). Reaction time is 12 h. The product was purified by flash column chromatography (DCM followed by hexane/EtOAc = 5:2) afforded **3d** (48 mg, 84% yield) as a colorless solid. m.p. 77 - 78 ˚C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 2.76 (s, 4H), 1.86 (s, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 142.5, 142.4, 23.2, 21.6. **HRMS** (ESI^+): m/z calcd for $C_6H_{10}N_3$ $[M+H]^+$: 124.0869, found 124.0867.



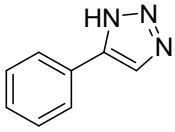
1,4,5,6,7,8-hexahydrocyclohepta[d][1,2,3]triazole (3e): Cycloheptanone (53 mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 4:6) afforded **3e** (47 mg, 72% yield) as a colorless solid. m.p. 83 - 84 ˚C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 2.85 (t, *J* = 5.4 Hz, 4H), 1.89 – 1.85 (m, 2H), 1.73 – 1.69 (m, 4H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 146.6, 31.5, 27.5, 26.6. **HRMS** (ESI+): m/z calcd for $C_7H_{11}N_3$ $[M+H]^+$: 138.1025, found 138.1018.



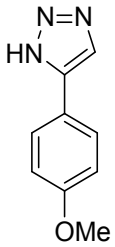
4,5,6,7,8,9-hexahydro-1H-cycloocta[d][1,2,3]triazole (3f): Cyclooctanone (60 mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 4:6) afforded **3f** (65 mg, 91% yield) as a colorless semi-solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.89 (t, *J* = 6.4 Hz, 4H), 1.76 (s_{br}, 4H), 1.48 (s_{br}, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.8, 28.3, 25.5, 23.4. **HRMS** (ESI+): m/z calcd for $C_8H_{13}N_3$ $[M+H]^+$: 152.1182, found 152.1187.



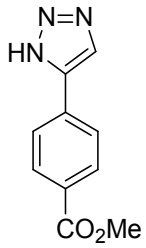
5-benzyl-4,5,6,7-tetrahydro-1H-[1,2,3]triazolo[4,5-c]pyridine (3g): 1-benzylpiperidin-4-one (88 mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 1:1) afforded **3g** (78 mg, 78% yield) as an off white solid. m.p. 245 - 246 ˚C. **^{1}H NMR** (300 MHz, MeOD) δ 7.40 – 7.26 (m, 5H), 3.78 (s, 2H), 3.63 (s, 2H), 2.89 - 2.81(m, 4H). **^{13}C NMR** (75 MHz, MeOD) δ 141.2, 139.8, 138.7, 130.5, 129.5, 128.6, 62.7, 51.2, 49.9, 22.5. **HRMS** (ESI+): m/z calcd for $C_{12}H_{14}N_4$ $[M+H]^+$: 215.1291, found 215.1290.



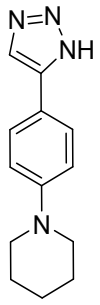
5-phenyl-1H-1,2,3-triazole (3h): Acetophenone (56 mg, 0.47 mmol), ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 12 h. The product was purified by flash column chromatography (DCM followed by heptane/EtOAc = 5:2) afforded **3h** (62 mg, 93% yield) as an off-white solid. m.p. 148 - 149 ˚C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.8 (s, 1H), 7.85 - 7.82 (m, 2H), 7.49 - 7.36 (m, 3H). **^{13}C NMR** (75 MHz, DMSO-d_6) δ 147.5, 129.9, 129.1, 128.9, 126.3. **HRMS** (ESI^+): m/z calcd for $C_8H_8N_3$ $[M+H]^+$: 146.0713, found 146.0716. Spectroscopic data for **3h** are consistent with previously reported data for the compound.[2]



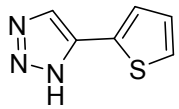
5-(4-methoxyphenyl)-1H-1,2,3-triazole (3i): 1-(4-methoxyphenyl)ethan-1-one (71 mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 4:6) afforded **3i** (73 mg, 89% yield) as an off white semi-solid. m.p. 162 - 163 ˚C. **^{1}H NMR** (300 MHz, MeOD) δ 8.03 (s, 1H), 7.74 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.38 (s, 3H). **^{13}C NMR** (75 MHz, MeOD) δ 161.4, 128.3, 123.5, 115.4, 55.7. **HRMS** (ESI+): m/z calcd for $C_9H_9N_3O$ $[M+H]^+$: 176.0818, found: 176.0827. Spectroscopic data for **3i** are consistent with previously reported data for the compound.[2]



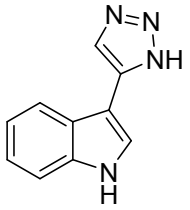
Methyl 4-(1H-1,2,3-triazol-5-yl)benzoate (3j): methyl 4-acetylbenzoate (83mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 4:6) afforded **3j** (75 mg, 80% yield) as an off white solid. m.p. 197.5 – 198.5 ˚C. **^{1}H NMR** (300 MHz, MeOD) δ 8.27 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 2H), 3.92 (s, 3H). **^{13}C NMR** (100 MHz, MeOD) δ 168.1, 136.2, 131.2, 131.0, 126.7, 52.7; **HRMS** (ESI+): m/z calcd for $C_{10}H_9N_3O_2$ $[M+H]^+$: 204.0767, found: 204.0770. Spectroscopic data for **3j** are consistent with previously reported data for the compound.[2]



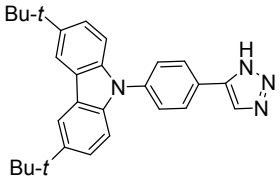
1-(4-(1H-1,2,3-triazol-5-yl)phenyl)piperidine (3k): 1-(4-(piperidin-1-yl)phenyl)ethan-1-one (95 mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 1:1) afforded **3k** (68 mg, 64% yield) as an off white solid. m.p. 222 - 223 ˚C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.09 (s, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 3.18 (S_{br}, 4H), 1.61 – 1.58 (m, 6H). **^{13}C NMR** (75 MHz, DMSO-d_6) δ 151.3, 146.6, 129.9, 126.5, 126.1, 115.6, 49.1, 25.1, 23.9. **HRMS** (ESI+): m/z calcd for $C_{13}H_{16}N_4$ $[M+H]^+$: 229.1447, found 229.1435.



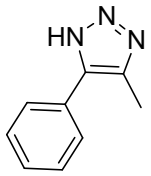
5-(thiophen-2-yl)-1H-1,2,3-triazole (3l): 1-(thiophen-2-yl)ethan-1-one (60 mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 4:6) afforded **3l** (51 mg, 71% yield) as an off white semi-solid. m.p. 67 - 68 ˚C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.44 – 7.43 (m, 1H), 7.36 – 7.34 (m, 1H), 7.12 – 7.09 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 142.5, 132.1, 129.0, 127.9, 126.0, 125.3. **HRMS** (ESI+): m/z calcd for $C_6H_5N_3S$ $[M+H]^+$: 152.02769, found: 152.0276. Spectroscopic data for **3l** are consistent with previously reported data for the compound.[2]



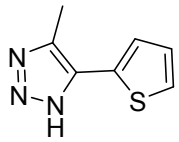
3-(1H-1,2,3-triazol-5-yl)-1H-indole (3m): 1-(1H-indol-3-yl)ethan-1-one (74 mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 4:6) afforded **3m** (80 mg, 92% yield) as an off white solid. m.p. 197.5 – 198.5 ˚C. **^{1}H NMR** (300 MHz, MeOD) δ 8.06 (s, 1H), 7.95 (d, *J* = 7.5 Hz, 1H), 7.70 (s, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.22 – 7.12 (m, 2H). **^{13}C NMR** (75 MHz, MeOD) δ 138.2, 126.3, 126.2, 124.4, 123.2, 121.1, 120.52, 112.6. **HRMS** (ESI+): m/z calcd for $C_{10}H_8N_4$ $[M+H]^+$: 185.08216, found:185.0828. Spectroscopic data for **3m** are consistent with previously reported data for the compound.[2]



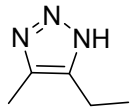
9-(4-(1H-1,2,3-triazol-5-yl)phenyl)-3,6-di-tert-butyl-9H-carbazole (3n): 1-(4-(3, 6-di-tert-butyl-9H-carbazol-9-yl) phenyl) ethan-1-one (186 mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) afforded **3n** (150 mg, 76% yield) as an off white solid. m.p. 130 - 131 ˚C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.15 (s, 2H), 8.06 (t, *J* = 8.4 Hz, 3H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.48 – 7.38 (m, 4H), 1.46 (s, 18 h). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 146.8, 143.2, 139.1, 138.7, 129.6, 128.4, 127.6, 127.2, 123.8, 123.6, 116.4, 109.3, 34.9, 32.1. **HRMS** (ESI^+): m/z calcd for $C_{28}H_{30}N_4$ $[M+H]^+$: 423.2543, found 423.2527.



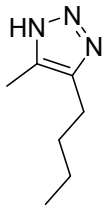
4-methyl-5-phenyl-1H-1,2,3-triazole (3o): propiophenone (62 mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) afforded **3o** (65 mg, 89% yield) as an off white solid. m.p. 142.5 – 143.5 ˚C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.3 Hz, 2H) 7.47 (t, *J* = 7.8 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 2.55 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 130.8, 128.9, 128.3, 127.4, 11.7. **HRMS** (ESI+): m/z calcd for $C_9H_9N_3$ $[M+H]^+$: 160.0869, found 160.0873. Spectroscopic data for **3o** are consistent with previously reported data for the compound.[2]



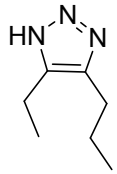
4-methyl-5-(thiophen-2-yl)-1H-1,2,3-triazole (3p): 1-(thiophen-2-yl)propan-1-one (66 mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 4:6) afforded **3p** (55 mg, 71% yield) as an off white semi-solid. m.p. 155 - 156 ˚C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.38 – 7.36 (m, 2H), 7.15 – 7.12 (m, 1H), 2.56 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 132.9, 127.8, 125.8, 125.3, 11.3. **HRMS** (ESI+): m/z calcd for $C_7H_7N_3S$ $[M+H]^+$: 166.04334, found: 166.0435.



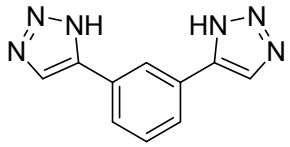
4-ethyl-5-methyl-1H-1,2,3-triazole (3q) pentan-3-one (40 mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) afforded **3q** (38 mg, 72% yield) as a colorless semi-solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 2.73 – 2.66 (m, 2H), 2.31(s, 3H), 1.30 – 1.25(t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 145.4, 139.4, 17.8, 13.4, 9.6. **HRMS** (ESI+): m/z calcd for $C_5H_9N_3$ $[M+H]^+$: 112.0869, found 112.0860. Spectroscopic data for **3q** are consistent with previously reported data for the compound.[3]



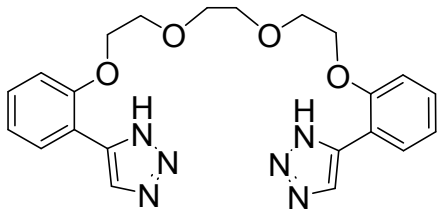
4-butyl-5-methyl-1H-1,2,3-triazole (3r): heptan-2-one (53 mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 4:6) afforded **3r** (57 mg, 88% yield) as an off white semi-solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 2.67 (t, *J* = 7.8 Hz, 2H), 2.30 (s, 3H), 1.67 – 1.61 (m, 2H), 1.37 – 1.32 (m, 2H), 0.94 - 0.89 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 143.9, 139.4, 31.2, 24.0, 22.4, 13.9, 9.6. **HRMS** (ESI+): m/z calcd for $C_7H_{13}N_3$ $[M+H]^+$: 140.11821, found: 140.1190.



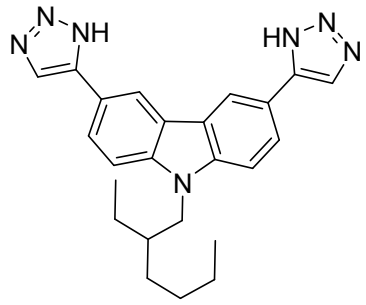
5-ethyl-4-propyl-1H-1,2,3-triazole (3s): heptan-3-one (53 mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) afforded **3s** (62 mg, 95% yield) as a colorless semi-solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 2.73 – 2.62 (m, 4H), 1.76 – 1.64 (m, 2H), 1.29 (t, *J* = 7.6 Hz, 3H), 0.96 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 145.3, 143.6, 26.4, 22.6, 17.9, 13.9, 13.7. **HRMS** (ESI+): m/z calcd for $C_7H_{13}N_3$ $[M+H]^+$: 140.1182, found 140.1196.



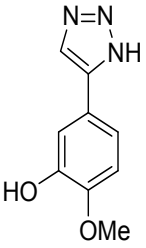
1,3-di(1H-1,2,3-triazol-5-yl)benzene (5): 1,3-diacetylbenzene (76 mg, 0.46 mmol), Ammonium acetate (360 mg, 4.70 mmol), 4-nitrophenyl azide (200 mg, 1.2 mmol), and DMF (1 mL). Reaction time is 48 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) afforded **3s** (mg, 83% yield) as an off white solid. m.p. 238 - 239 ˚C. **^{1}H NMR** (400 MHz, DMSO - d_6) δ 8.45 (s, 2H), 8.40 (s, 2H), 7.88 – 7.86 (m, 2H), 7.57 (t, *J* = 7.7 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO - d_6) δ 162.3, 145.2, 131.1, 129.6, 125.2, 122.6. **HRMS** (ESI+): m/z calcd for $C_{10}H_8N_6$ $[M+H]^+$: 213.08831, found: 213.0887



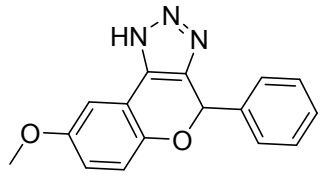
1,2-bis(2-(2-(1H-1,2,3-triazol-5-yl)phenoxy)ethoxy)ethane (6): 1,1'-((((ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl))bis(oxy))bis(2,1-phenylene))bis(ethan-1-one) (80 mg, 0.20 mmol), Ammonium acetate (158 mg, 2 mmol), 4-nitrophenyl azide (90 mg, 0.56 mmol), and DMF (1 mL). Reaction Temperature 60˚C, and Reaction time is 4 d. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 1:4) afforded **6** (36 mg, 41% yield) as an off white oily liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7:85 (s, 2H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.26 – 7.21 (m, 2H), 7.00 – 6.95 (m, 2H), 6.85 (d, *J* = 8.2 Hz, 2H), 4.17 – 4.13 (m, 4H), 4.06 (s, 4H), 4.00 – 3.97 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.7, 154.7, 133.8, 130.0, 127.8, 121.9, 113.7, 70.3, 69.2, 67.4. **HRMS** (ESI+): m/z calcd for $C_{22}H_{24}N_6O_4$ $[M+H]^+$: 437.19316, found: 437.1922.



9-(2-ethylhexyl)-3,6-di(1H-1,2,3-triazol-5-yl)-9H-carbazole (7): 1,1'-(9-(2-ethylhexyl)-9H-carbazole-3,6-diyl)bis(ethan-1-one) (121 mg, 0.335 mmol), Ammonium acetate (257 mg, 3.35 mmol), 4-nitrophenyl azide (139 mg, 0.84 mmol), and DMF (1 mL). Reaction time is 48 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 4:6) afforded **7** (99 mg, 72% yield) as an off white solid. m.p. 94 - 95 ˚C. **^{1}H NMR** (300 MHz, DMSO-d_6) δ 8.74 (s, 2H), 8.37 (s, 2H), 8.01 – 7.98 (m, 2H), 7.67 (d, *J* = 8.6 Hz, 2H), 4.31 (d, *J* = 7.4 Hz, 2H), 1.37 – 1.14 (m, 9H), 0.87 (t, J = 7.3 Hz, 3H) – 0.78 (t, J = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 162.3, 146.1, 140.7, 124.0, 122.4, 121.5, 117.7, 110.1, 46.7, 38.7, 30.2, 28.0, 23.7, 22.5, 13.8, 10.7. **HRMS** (ESI+): m/z calcd for $C_{24\ h27}N_7$ $[M+H]^+$: 414.24005, found 414.2405.

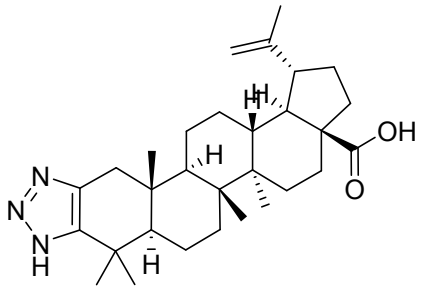


2-methoxy-5-(1H-1,2,3-triazol-5-yl)phenol (9a): 1-(3-hydroxy-4-methoxyphenyl)ethan-1-one (78 mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 4:6) afforded **9a** (74 mg, 82% yield) as an off white solid. m.p. 156 – 157 ˚C. **^{1}H NMR** (300 MHz, DMSO - d_6) δ 8.18 (s, 1H), 7.39 (s, 1H), 7.26 (d, *J* = 8.1 Hz, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 3.83 (s, 3H). **^{13}C NMR** (75 MHz, DMSO - d_6) δ 148.0, 146.8, 118.5, 115.8, 109.7, 55.7. **HRMS** (ESI+): m/z calcd for $C_9H_9N_3O_2$ $[M+H]^+$: 192.07674, found 192.0761.

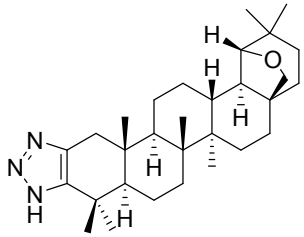


8-methoxy-4-phenyl-1,4-dihydrochromeno[3,4-d][1,2,3]triazole (9b): 6-methoxy-2-phenylchroman-4-one (119 mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) afforded **9b** (112 mg, 85% yield) as an off

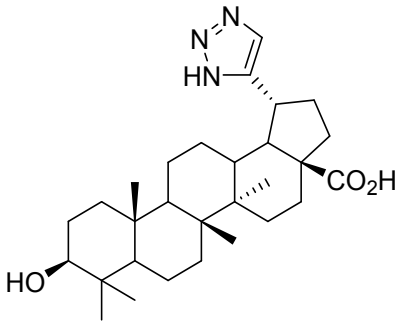
white solid. m.p. 175 - 176 ˚C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.47 – 7.31(m, 6H), 7.00 (d, *J* = 8.9 Hz, 1H), 6.87 – 6.83 (m, 1H), 6.52 (s, 1H), 3.82 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 155.0, 147.6, 142.8, 139.5, 138.6, 129.0, 128.8, 127.2, 118.9, 117.2, 116.3, 107.2, 75.9, 57.0. **HRMS** (ESI+): m/z calcd for $C_{16}H_{13}N_3O_2$ $[M+H]^+$: 280.1080, found 280.1075.



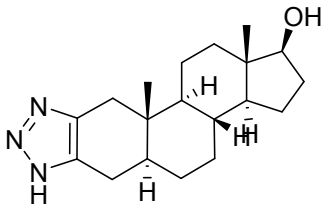
(1R,3aS,5aR,5bR,7aR,12aR,12bR,14aR,14bR)-5a,5b,8,8,12a-Pentamethyl-1-(prop-1-en-2-yl)-2,3,4,5,5a,5b,6,7,7a,8,9,12,12a,12b,13,14,14a,14b-octadecahydrocyclopenta[7,8]chryseno[2,3-d][1,2,3]triazole-3a(1H)-carboxylic acid (9c): Betulonic acid (213 mg, 0.47 mmol), ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 2:8) affording **9c** (195 mg, 87% yield) as an off-white solid. m.p. 146 - 147 ˚C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.76 (s, 1H), 4.63 (s, 1H), 3.06 - 2.87 (m, 2H), 2.33 - 1.98 (m, 6H), 1.79 (s, 3H), 1.71 - 1.43 (m, 14H), 1.31 - 1.29 (m, 4H), 1.20 – 1,22 (m, 4H), 1,01 (s, 3H), 0.99 (s, 3H), 0.78 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 181.0, 150.6, 149.3, 139.9, 109.8, 56.5, 53.6, 49.3, 49.2, 47.0, 42.6, 40.9, 39.2, 38.5, 37.4, 37.2, 33.4, 32.3, 31.0, 30.7, 29.9, 25.6, 23.8, 21.5, 19.5, 19.3, 16.4, 15.8, 14.8. **HRMS** (ESI^+): m/z calcd for $C_{30}H_{46}N_3O_2$ $[M+H]^+$: 480.3584; found 480.3580.



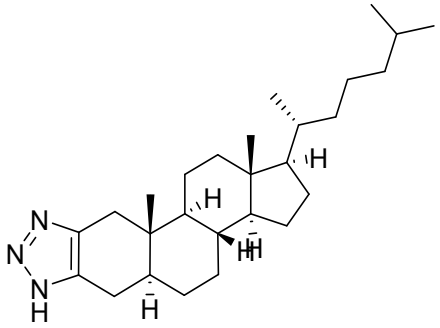
(1R,4aR,6aR,6bR,8aR,13aR,13bR,15aR,15bR)-2,2,6a,6b,9,9,13a-heptamethyl-1,2,3,4,5,6,6a,6b,7,8,8a,9,10,13,13a,13b,14,15,15a,15b-icosahydro-1,4a-(epoxymethano)piceno[2,3-d][1,2,3]triazole (9d): Allobetulone (206 mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 4:6) afforded **9d** (204 mg, 94% yield) as an off white solid. m.p. above 300 ˚C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.81 (d, *J* = 7.2 Hz, 1H), 3.58 (s, 1H), 3.47 (d, *J* = 7.8 Hz, 1H), 2.94 (d, *J* = 15.5 Hz, 1H), 2.16 (d, *J* = 15.5 Hz, 1H), 1.61 – 1.56 (m, 6H), 1.53 – 1.50 (m, 4H), 1.49 – 1.42 (m, 3H), 1.39 – 1.32 (m, 7H), 1.29 – 1.23 (m, 5H), 1.19 – 1.55(m, 1H), 1.04 (s, 3H), 0.95 (d, *J* = 2.4 Hz, 6H), 0.82 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.8, 140.3, 88.1, 71.4, 53.7, 49.8, 46.9, 41.6, 40.9, 40.8, 39.2, 37.7, 36.8, 36.4, 34.4, 33.5, 33.0, 32.8, 31.2, 29.0, 26.6, 26.5, 26.3, 24.7, 23.9, 21.6, 19.2, 16.7, 15.5, 13.6. **HRMS** (ESI+): m/z calcd for $C_{30}H_{47}N_3O$ $[M+H]^+$: 466.3791 , found 466.3799.



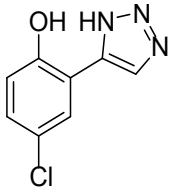
(1R,3aS,5aR,5bR,9S,11aR)-9-hydroxy-5a,5b,8,8,11a-pentamethyl-1-(1H-1,2,3-triazol-5-yl)icosahydro-3aH-cyclopenta[a]chrysene-3a-carboxylic acid (9e): Platanic acid (215 mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 4:6) afforded **9e** (139 mg, 61% yield) as an off white solid. m.p. above 300 ˚C. **^{1}H NMR** (400 MHz, DMSO – d_6) δ 7.57(s, 1H), 4.23 (d, *J* = 4.9 Hz, 1H), 3.62 – 3.57 (m, 1H), 2.96 – 2.89 (m, 1H), 2.24 – 2.03 (m, 3H), 1.90 – 1.82 (m, 2H), 1.76 – 1.67 (m, 1H), 1.50 – 1.41 (m, 7H), 1.33 – 1.31 (m, 2H), 1.18 – 1.05 (m, 5H), 0.89 (s, 3H), 0.86 (s, 6H), 0.81 – 0.76 (m, 1H), 0.73 (s, 3H), 0.64 (s, 3H), 0.61 – 0.59 (m, 1H), 0.46 – 0.43 (m, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6 + TFA, 1drop) δ 177.7, 150.5, 127.4, 77.4, 55.9, 55.3, 53.7, 50.1, 42.3, 40.6, 38.7, 37.9, 37.1, 35.1, 34.3, 33.0, 29.6, 28.4, 27.4, 26.6, 20.8, 18.3, 16.2, 16.1, 16.1, 14.6. **HRMS** (ESI+): m/z calcd for $C_{29}H_{45}N_3O_3$ $[M+H]^+$: 484.35334 , found 484.3522.



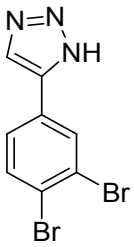
(1S,3aS,3bR,5aS,10aS,10bS,12aS)-10a,12a-dimethyl-1,2,3,3a,3b,4,5,5a,6,7,10,10a,10b,11,12,12a-hexadecahydrocyclopenta[7,8]phenanthro[2,3-d][1,2,3]triazol-1-ol (9f): Dihydrotestosterone (136 mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 4:6) afforded **9f** (142 mg, 96% yield) as an off white semi-solid. m.p. 174 - 175 ˚C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 4.83(s_{br}, 1H), 3.44 (t, *J* = 8.6Hz, 1H), 2.70 – 2.57 (m, 2H), 2.22 – 2.16(m, 2H), 1.88 – 1.76 (m, 2H), 1.67 – 1.47 (m, 5H), 1.39 – 1.30 (m, 4H), 1.23 – 1.13 (m, 2H), 1.04 – 0.97 (m, 1H), 0.93 – 0.85 (m, 3H), 0.67 (s, 3H), 0.65 (s, 3H). **^{13}C NMR** (100 MHz, MeOD) δ 139.8, 138.7, 82.5, 52.1, 49.8, 44.0, 43.2, 38.1, 38.0, 37.9, 37.0, 35.0, 32.2, 30.6, 29.8, 25.2, 24.3, 22.0, 11.9, 11.6. **HRMS** (ESI+): m/z calcd for $C_{19}H_{29}N_3O$ $[M+H]^+$: 316.23832, found 316.2390.



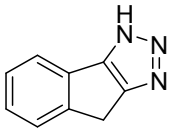
(1R,3aS,3bR,5aS,10aS,10bS,12aR)-10a,12a-dimethyl-1-((R)-6-methylheptan-2-yl)-1,2,3,3a,3b,4,5,5a,6,7,10,10a,10b,11,12,12a-hexadecahydrocyclopenta[7,8]phenanthro[2,3-d][1,2,3]triazole (9g) : Cholestan-3-one (181 mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 4:6) afforded **9g** (169 mg, 88% yield) as an off white solid. m.p. 170 – 171 ˚C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.84 (d, *J* = 15.9 Hz, 1H), 2.74 – 2.69 (m, 1H), 2.37 – 2.29 (m, 2H), 2.07 – 2.02 (m, 1H), 1.86 – 1.80 (m, 1H), 1.75 – 1.71 (m, 1H), 1.63 – 1.57 (m, 3H), 1.54 – 1.47 (m, 2H), 1.39 – 1.32 (m, 4H), 1.27 – 1.22 (m, 4H), 1.16 – 1.09 (m, 5H), 1.06 – 0.98 (m, 3H), 0.95 – 0.91 (m, 4H), 0.87 (d, *J* = 1.7 Hz, 3H), 0.86 (d, *J* = 1.7 Hz, 3H), 0.75 (s, 3H), 0.69 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.7, 141.7, 56.5, 56.4, 53.9, 42.6, 42.6, 40.1, 39.7, 37.0, 36.3, 35.9, 35.7, 35.6, 31.8, 29.3, 28.4, 28.1, 25.9, 24.4, 24.0, 23.0, 22.7, 21.4, 18.8, 12.1, 11.8. **HRMS** (ESI+): m/z calcd for $C_{27}H_{45}N_3$ $[M+H]^+$: 412.36860, found 412.3675.



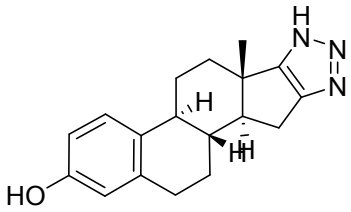
5-chloro-2-(1H-1,2,3-triazol-5-yl)phenol (12a): 1-(4-chloro-2-hydroxyphenyl) ethan-1-one (80 mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) afforded **12a** (71 mg, 77% yield) as an off white solid. m.p. 76 - 77 ˚C. **^{1}H NMR** (300 MHz, DMSO-d_6) δ 8.31 (s, 1H), 7.91 (s, 1H), 7.24 – 7.20 (m, 1H), 6.99 (d, *J* = 8.7 Hz, 1H). **^{13}C NMR** (75 MHz, DMSO-d_6) δ 153.1, 128.4, 126.2, 122.9, 117.8. **HRMS** (ESI+): m/z calcd for $C_8H_6ClN_3O$ $[M+H]^+$: 196.0272, found 196.0268. Spectroscopic data for **12a** are consistent with previously reported data for the compound.[4]



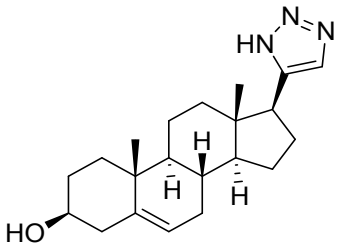
5-(3,4-dibromophenyl)-1H-1,2,3-triazole (12b): 1-(3,4-dibromophenyl)ethan-1-one (129 mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) afforded **12b** (112 mg, 80% yield) as an off white solid. m.p. 163 - 164 ˚C. **^{1}H NMR** (300 MHz, DMSO-d_6) δ 8.52 (s, 1H), 8.25 (s, 1H), 7.87 - 7.80 (m, 2H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 134.3, 131.8, 130.2, 126.1, 124.5, 123.0. **HRMS** (ESI+): m/z calcd for $C_8H_5Br_2N_3$ $[M+H]^+$: 301.8924, found 301.8926. Spectroscopic data for **12b** are consistent with previously reported data for the compound.[5]



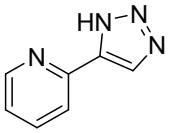
3,8-dihydroindeno[1,2-d][1,2,3]triazole (12c): 1-Indanone (61 mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 4:6) afforded **12c** (55 mg, 75% yield) as an off white semi-solid. m.p. 121 – 122 ˚C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.72 (d, *J* = 7.4 Hz, 1H), 7.60 (d, *J* = 7.4 Hz, 1H), 7.42 – 7.32 (m, 2H), 3.81(s, 2H). **^{13}C NMR** (75 MHz, DMSO-d_6) δ 154.0, 148.2, 133.0, 128.4, 127.3, 121.5, 28.6. **HRMS** (ESI+): m/z calcd for $C_9H_7N_3$ $[M+H]^+$: 158.07127, found 158.0697. Spectroscopic data for **12c** are consistent with previously reported data for the compound.[5]



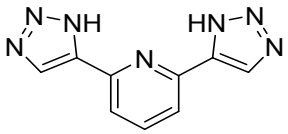
(6bS,8aS,12aS,12bR)-8a-methyl-1,2,6b,7,8,8a,9,12,12a,12b-decahydronaphtho[2',1':4,5]indeno[1,2-d][1,2,3]triazol-4-ol (**12d**): Estrone (127 mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 48 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 4:6) afforded **12c** (112 mg, 81**%** yield) as an off white semi-solid. m.p. 264 – 265 ˚C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.06 (d, *J* = 8.5 Hz, 1H), 6.54 – 6.52 (m, 1H), 6.47 (1H, *J* = 2.4 Hz, 1H), 2.86 – 2.67 (m, 3H), 2.45 – 2.26 (m, 3H), 2.19 – 2.09 (m, 2H), 1.92 – 1.88 (m, 1H), 1.81 – 1.71 (m, 1H), 1.69 – 1.63 (m, 1H), 1.59 – 1.49 (m, 1H), 1.47 – 1.35 (m, 1H), 1.26 – 1.16 (m, 1H), 0.94 (s, 3H). **^{13}C NMR** (100 MHz, MeOD) δ 161.3, 156.0, 151.2, 137.0, 130.1, 125.8, 115.0, 112.8, 60.7, 43.8, 39.2, 37.1, 33.8, 29.0, 27.0, 25.7, 23.1, 18.3. **HRMS** (ESI+): m/z calcd for $C_{18\,h21}N_3O$ $[M+H]^+$: 296.17572, found 296.1757. Spectroscopic data for **12d** are consistent with previously reported data for the compound.[6]



(3S,8S,9S,10R,13S,14S,17S)-17-((S)-4,5-dihydro-1H-1,2,3-triazol-5-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol (12e): Pregnenolone (148 mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 4:6) afforded **12e** (110 mg, 69% yield) as an off white semi-solid. m.p. 237-238 ˚C. **^{1}H NMR** (300 MHz, DMSO – d_6 + TFA, 1 drop) δ 7.85 (s, 1H), 5.31 (s, 1H), 3.32 – 3.23 (m, 1H), 2.82 – 2.75 (m, 1H), 2.20 – 1.92 (m, 4H), 1.77 – 1.55 (m, 5H), 1.45 – 1.18 (m, 7H), 1.03 – 0.86 (m, 6H), 0.49 – 0.43 (m, 3H). **^{13}C NMR** (100 MHz, MeOD) δ 142.3, 142.2, 122.3, 72.4, 57.3, 51.8, 51.4, 44.9, 43.0, 38.6, 37.8, 33.7, 33.3, 33.0, 32.3, 27.7, 25.5, 22.0, 19.9, 13.5. **HRMS** (ESI+): m/z calcd for $C_{21}H_{31}N_3O$ $[M+H]^+$: 342.25397, found 342.2545.

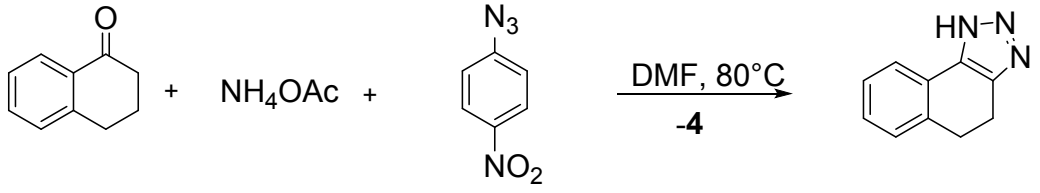


2-(1H-1,2,3-triazol-5-yl)pyridine (12f): 2-Acetopyridine (57 mg, 0.47 mmol), Ammonium acetate (180 mg, 2.35 mmol), 4-nitrophenyl azide (100 mg, 0.61 mmol), and DMF (1 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 4:6) afforded **12f** (61 mg, 89% yield) as an off white solid. m.p. 142 - 143 ˚C. **^{1}H NMR** (300 MHz, MeOD) δ 8.58 (d, J = 8 Hz, 1H), 8.30 (s, 1H), 8.03 (d, J = 8 Hz, 1H), 7.93 – 7.87 (m, 1H), 7.93 – 7.34 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.7, 137.4, 126.1, 124.7, 123.5, 121.1. **HRMS** (ESI+): m/z calcd for $C_7H_6N_4$ $[M+H]^+$: 147.06651, found 147.0663. Spectroscopic data for **12f** are consistent with previously reported data for the compound.[8]



2,6-di(1H-1,2,3-triazol-5-yl)pyridine (12g): 2,6-Diacetylpyridine (77 mg, 0.47 mmol), Ammonium acetate (360 mg, 4.70 mmol), 4-nitrophenyl azide (200 mg, 1.22 mmol), and DMF (1 mL). Reaction time is 48 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 4:6) afforded **12g** (70 mg, 70% yield) as an off white semi-solid. m.p. 158 - 159 ˚C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.53 (s, 2H), 8.03 - 7.94 (m, 3H). **^{13}C NMR** (75 MHz, DMSO-d6) δ 149.6, 145.7, 138.9, 128.6, 119.6. **HRMS** (ESI+): m/z calcd for $C_9H_7N_7$ $[M+H]^+$: 214.0835, found 214.0838. Spectroscopic data for **12g** are consistent with previously reported data for the compound.[9]

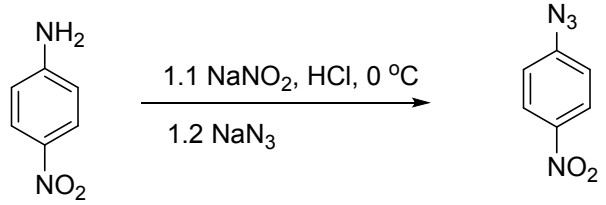
2.2 Bulk synthesis of *NH*-1,2,3-triazole 3a



1a (2 g) (5.2 g) **2** (2.9 g) **3a** (1.92 g, 82%)

To a 100 mL round-bottom flask equipped with a magnetic stir bar was added an equivalent of **1a** (2 g, 13.7 mmol), Ammonium acetate (5.2 g, 68.5 mmol), **2** (2.9 g, 17.7 mmol). The mixture was dissolved in anhydrous DMF (20 mL) and stirred at 80 °C for 12 hr. Upon completion the solvent was evaporated off and the resulting reaction mixture was diluted with ethyl acetate (3x 200 mL), washed with water, dried over $MgSO_4$ and evaporated under reduced pressure. The residue was further purified by column chromatography (silica gel), at first with CH_2Cl_2 as eluent to remove of all 4-nitroaniline **4** formed during the reaction followed by using a mixture of heptane/EtOAc = 5:2 as eluent to afford **3a** (1.92 g, 82%) as an off-white solid.

2.3 A 31 gm scale synthesis of 4-nitrophenyl azide (2):



4 (28 g) **2a** (31 g)

4-Nitroaniline (28.0 g, 0.20 mol) wassuspended in 2.4 N HCl solution (300 mL) and methanol (60 mL) was added to aid the solubility. After cooling the solution to 0 °C, $NaNO_2$ (6 M, 40 mL) in water was added dropwise. The mixture was stirred at 0 °C for 30 minutes, after which a solution of NaN_3 (4.1 M, 60 mL) in water was added dropwise over 20 minutes and the whole reaction mixture was stirred for an hour at room temperature. The reaction mixture was extracted with diethyl ether and the organic fraction was washed with a saturated $NaHCO_3$ solution and brine, dried over $MgSO_4$ and concentrated in under reduced pressure affording the pure compound **3a** as a yellow solid in 95% yield (31 g). Spectroscopic data for 3a was consistent with previously reported data for this compound[2].

3. References

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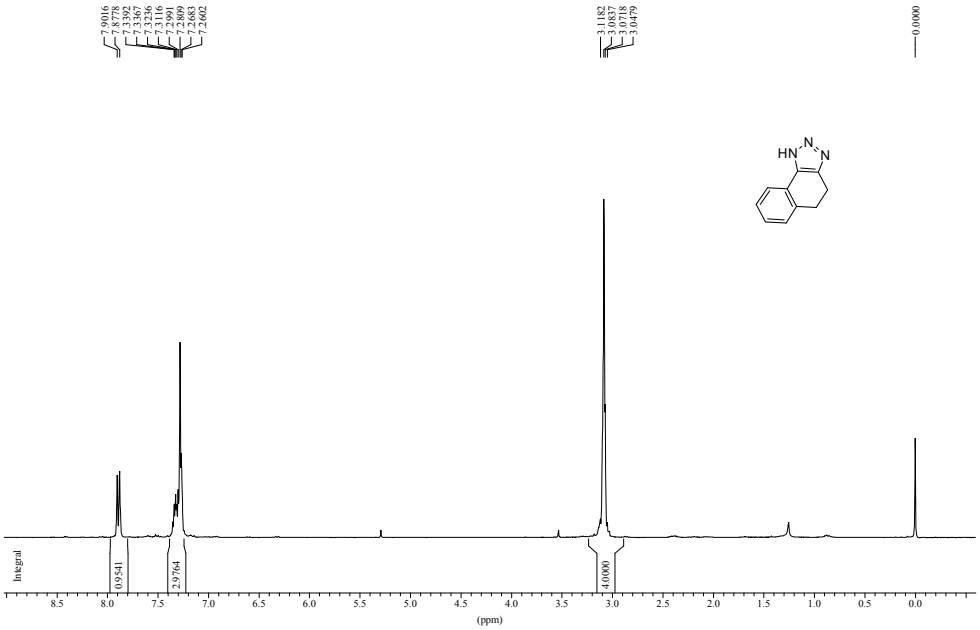
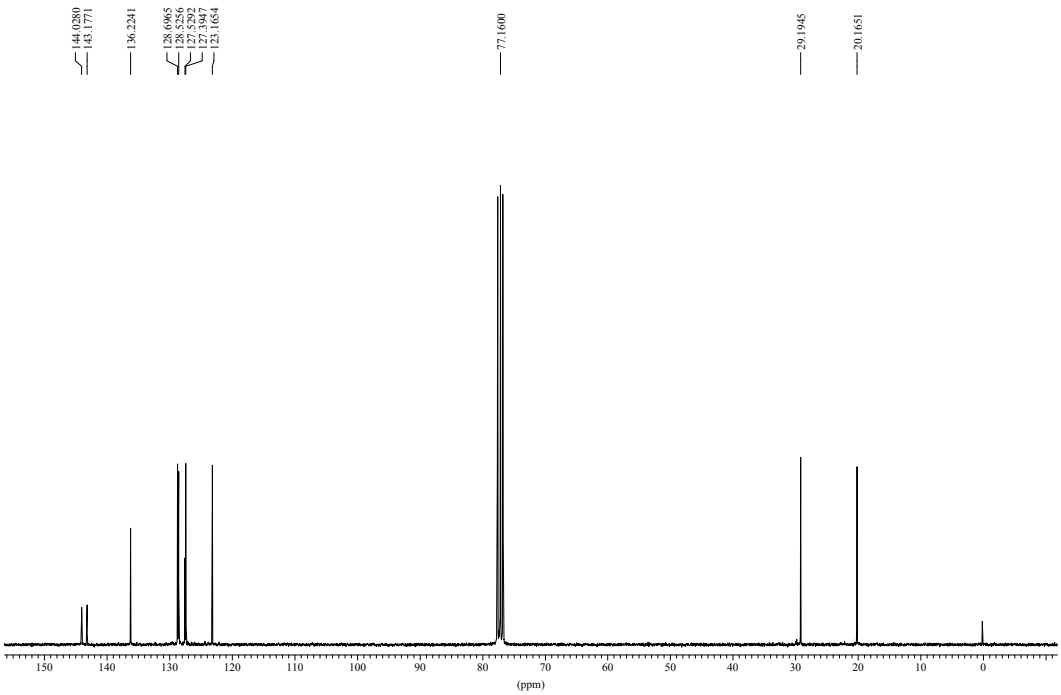
4. ^{1}H and ^{13}C NMR spectra of products

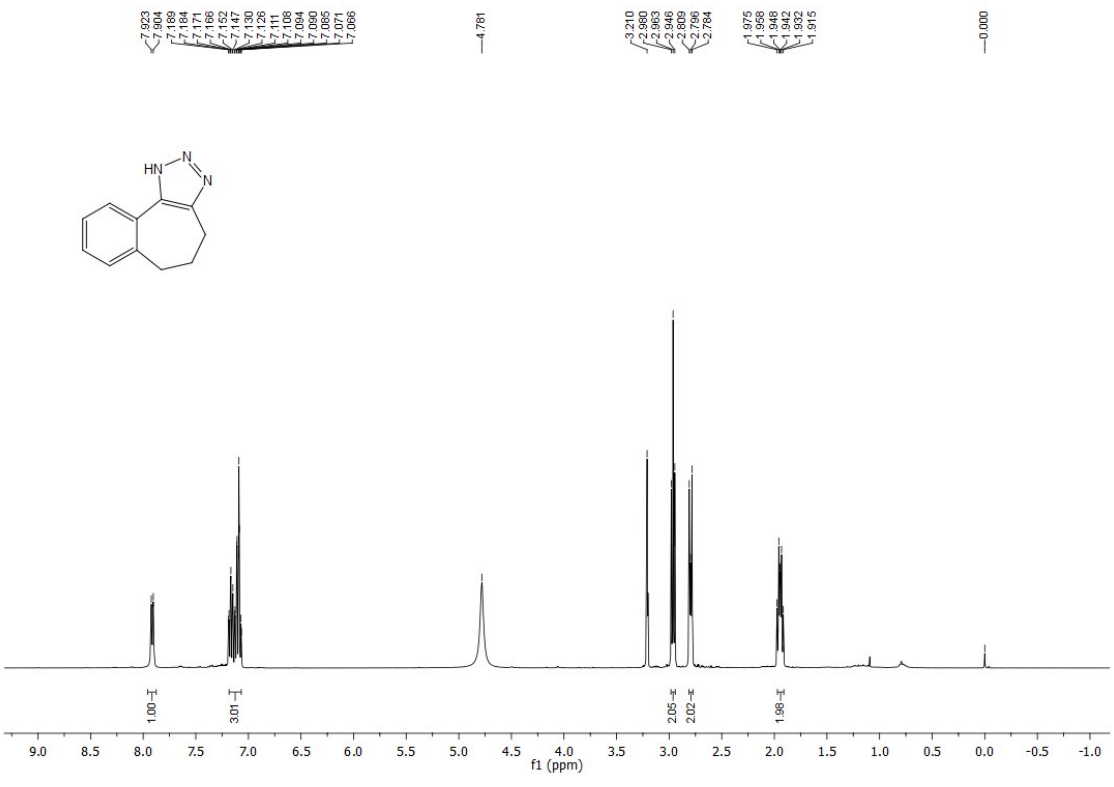
^{1}H NMR spectra of **3a** (300 MHz, $CDCl_3$)



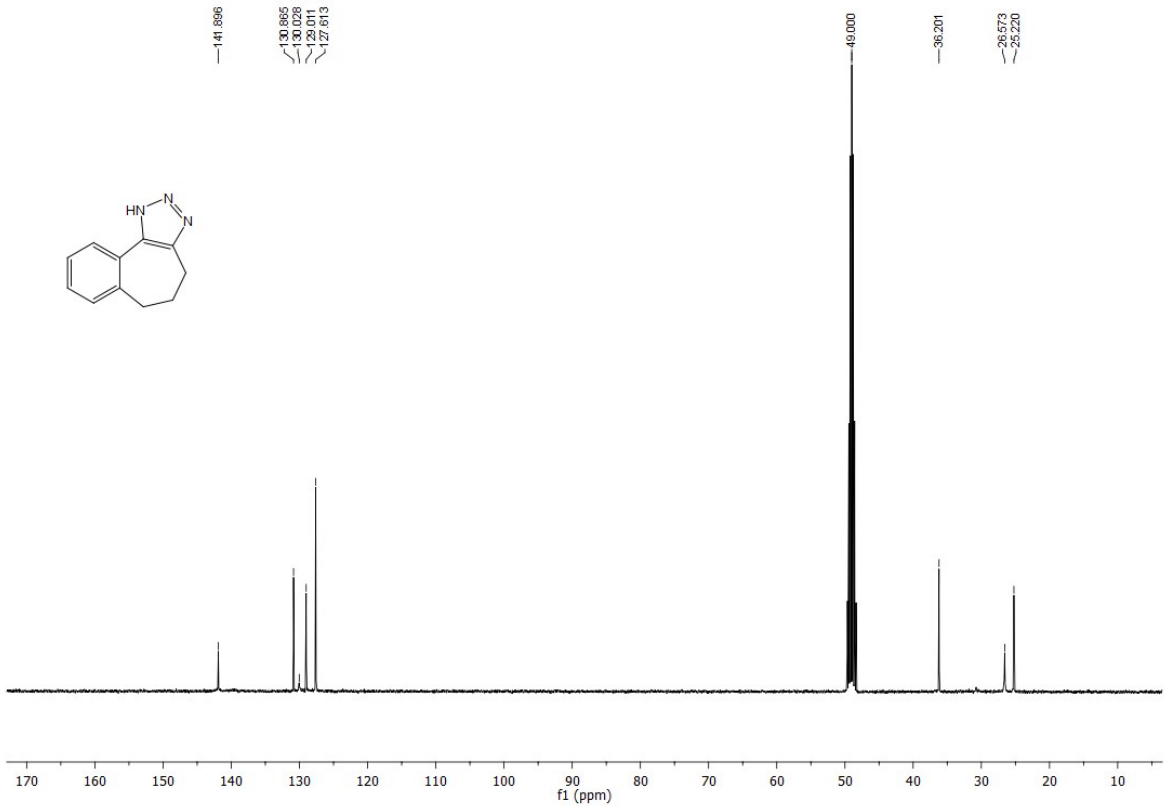
^{13}C NMR Spectra of **3a** (75 MHz, CDCl3):



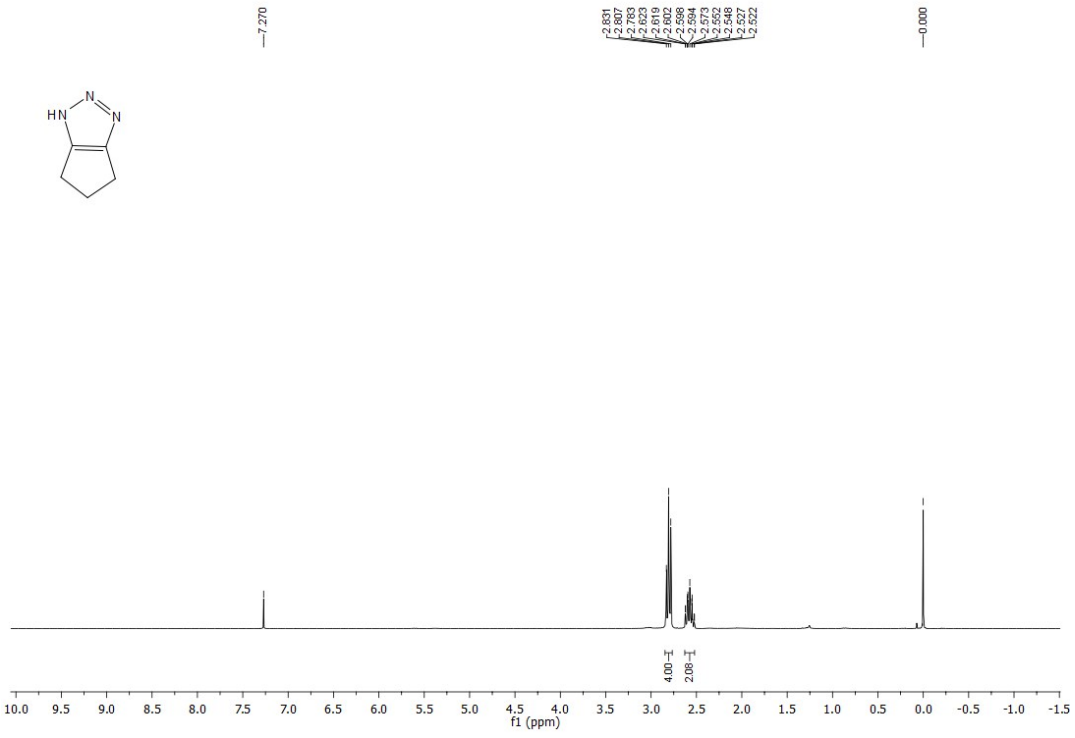
^{1}H NMR spectra of 3b (400 MHz, MeOD):



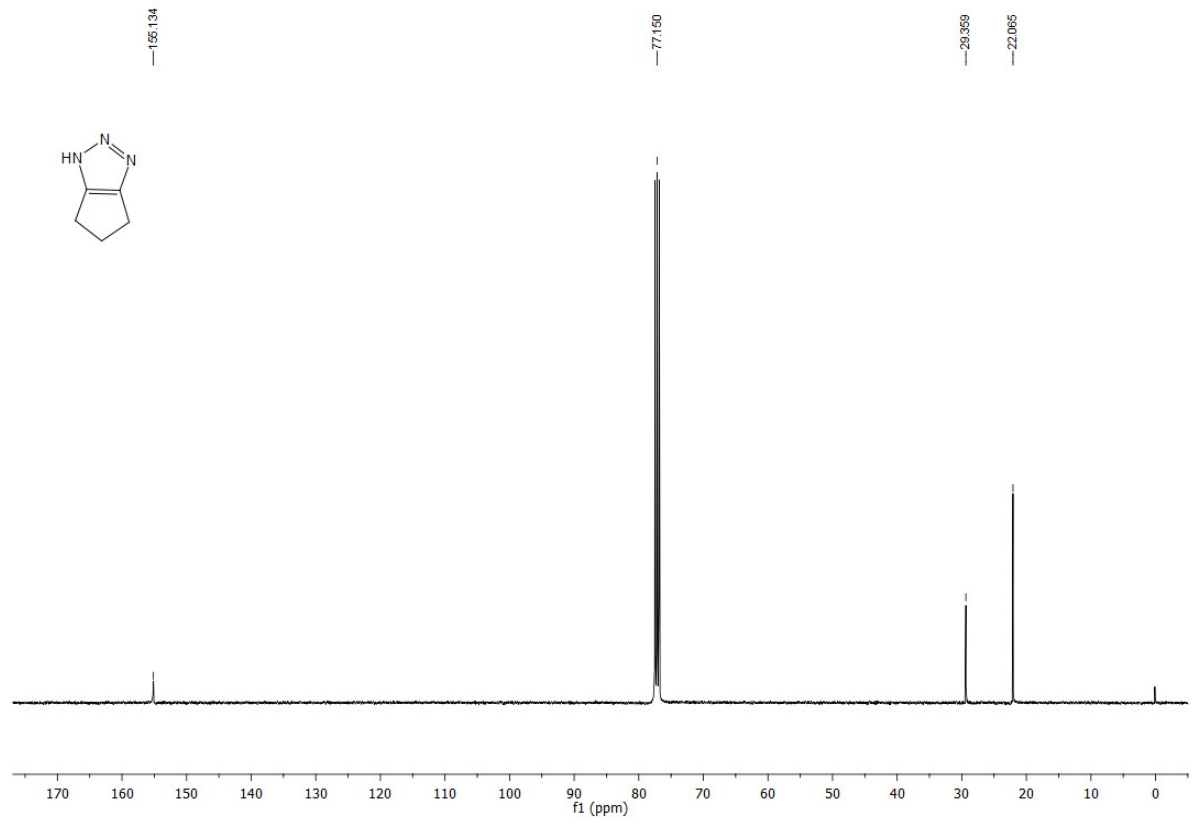
^{13}C NMR spectra of 3b (100 MHz, MeOD):



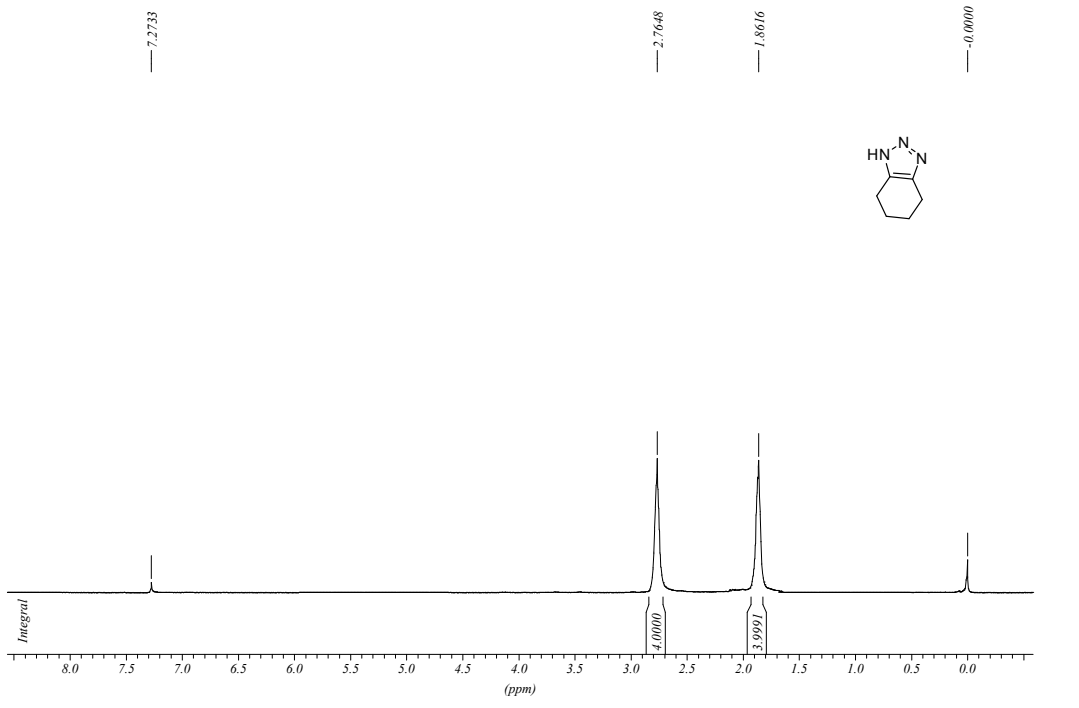
^{1}H NMR of 3c (400 MHz, $CDCl_3$):



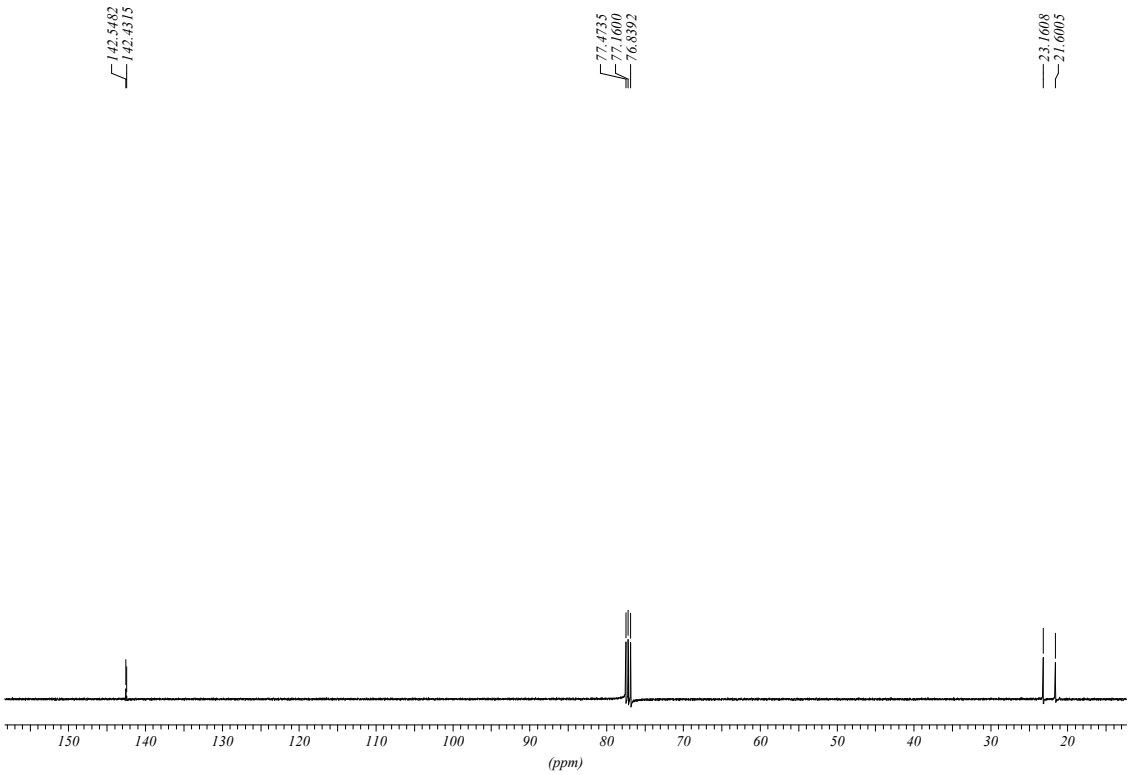
^{13}C NMR of 3c (100 MHz, $CDCl_3$):



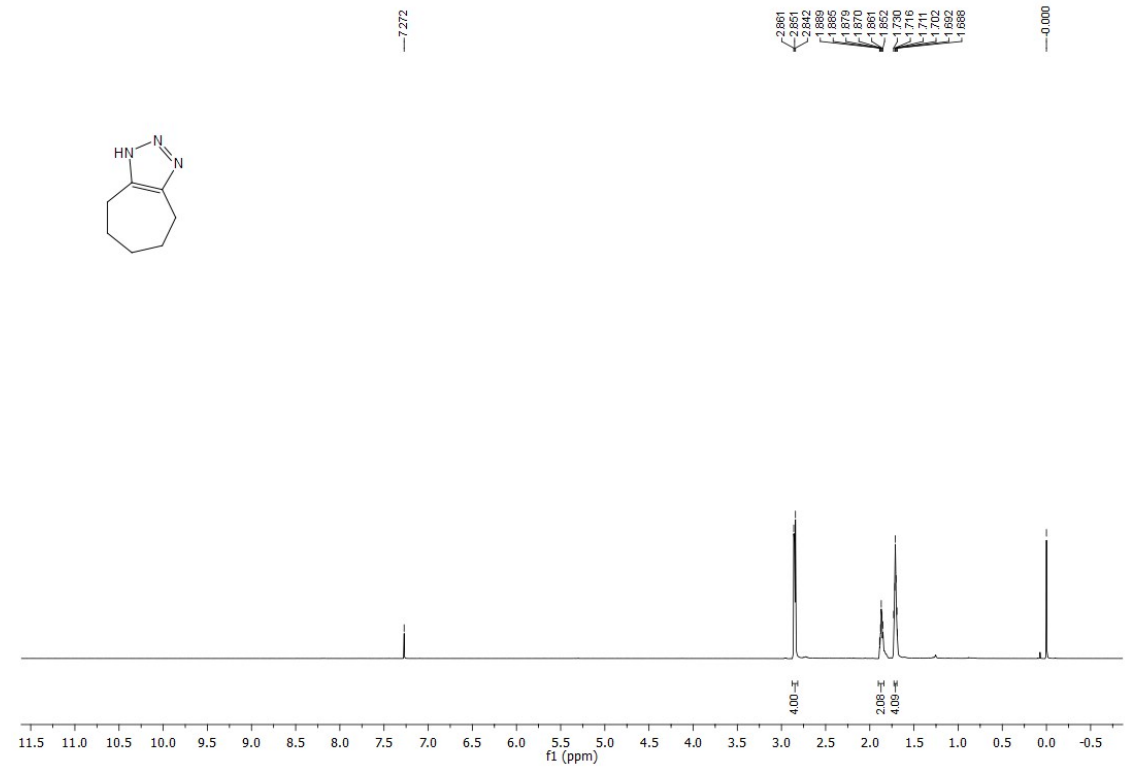
^{1}H NMR spectra of 3d (300 MHz, $CDCl_3$):



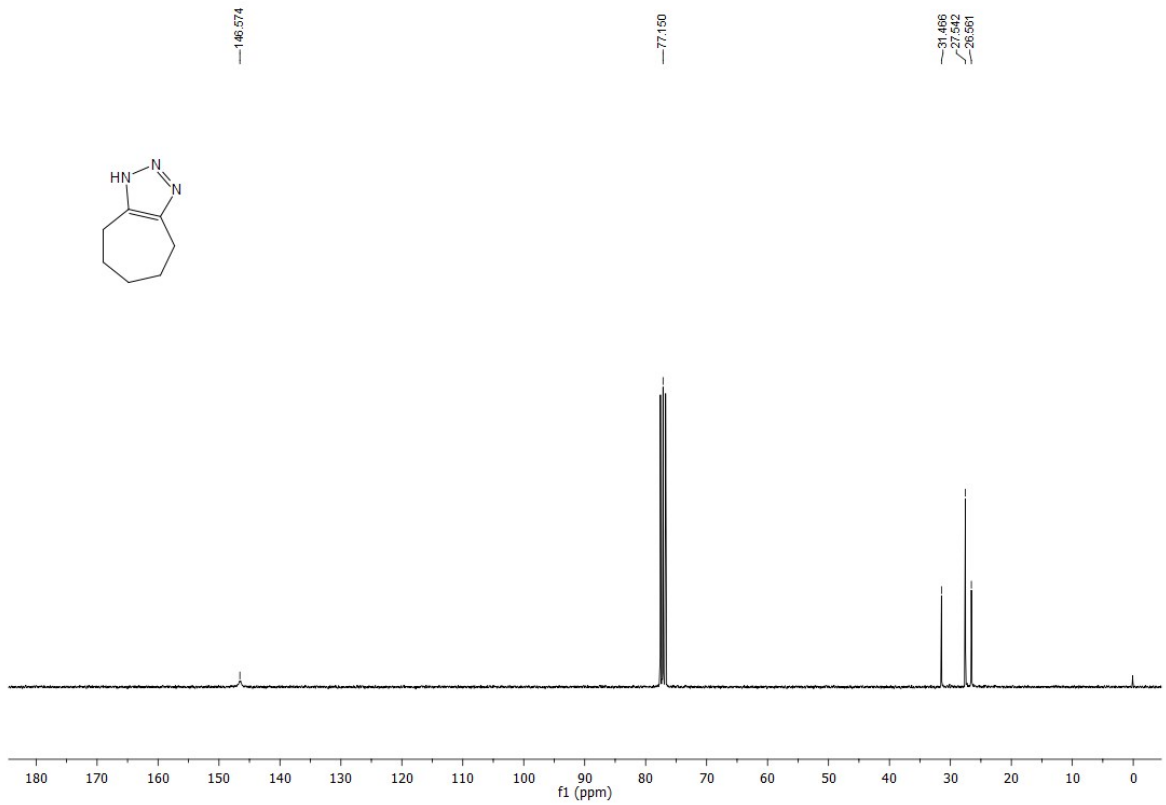
^{13}C NMR spectra of 3d (75 MHz, $CDCl_3$):



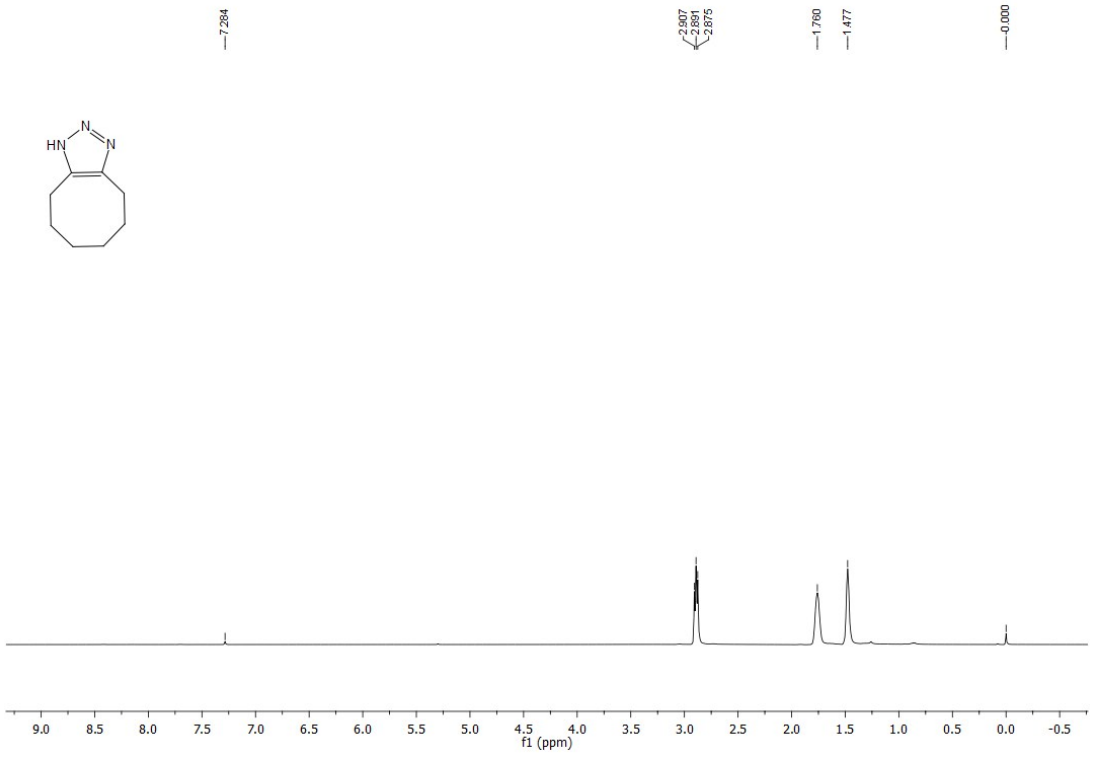
^{1}H NMR spectra of 3e (600 MHz, $CDCl_3$):



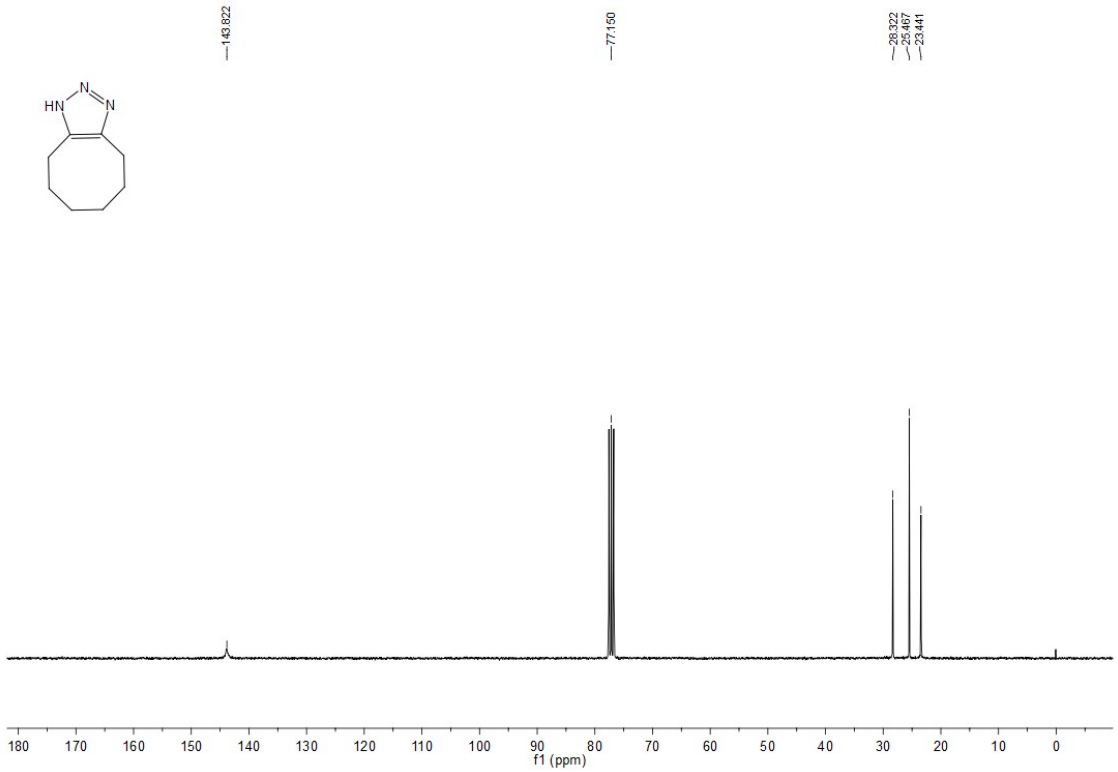
^{13}C NMR spectra of 3e (150 MHz, $CDCl_3$):



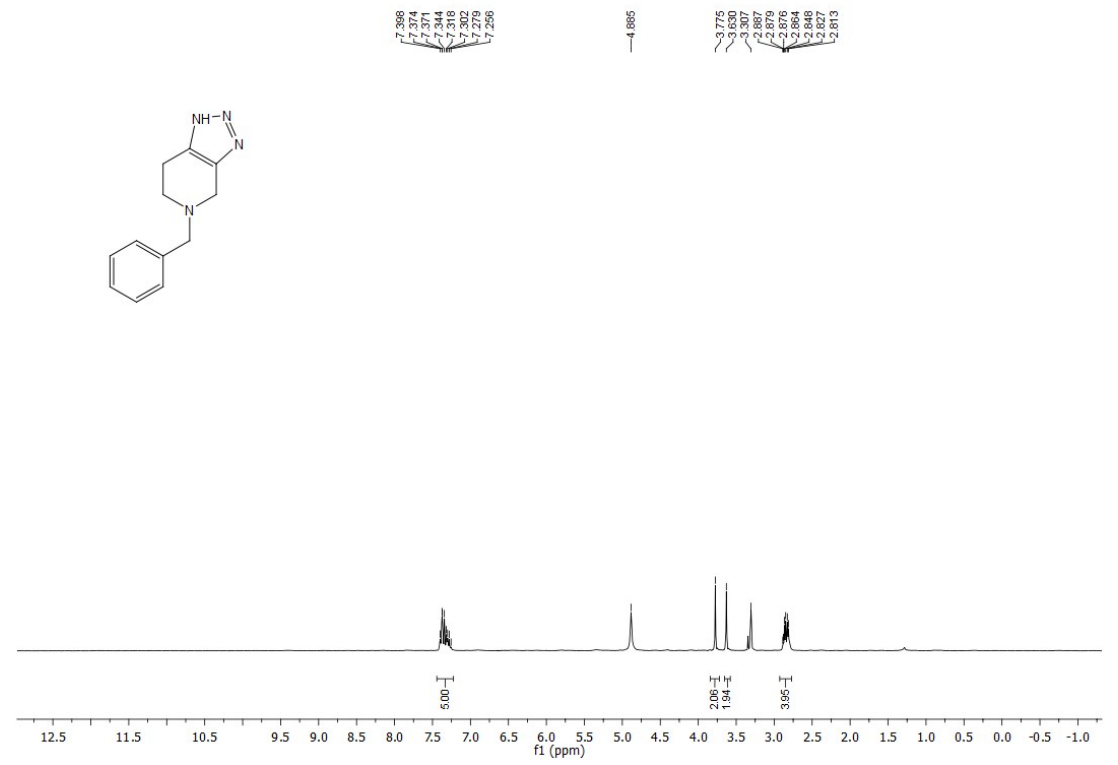
^{1}H NMR spectra of 3f (400 MHz, $CDCl_3$):



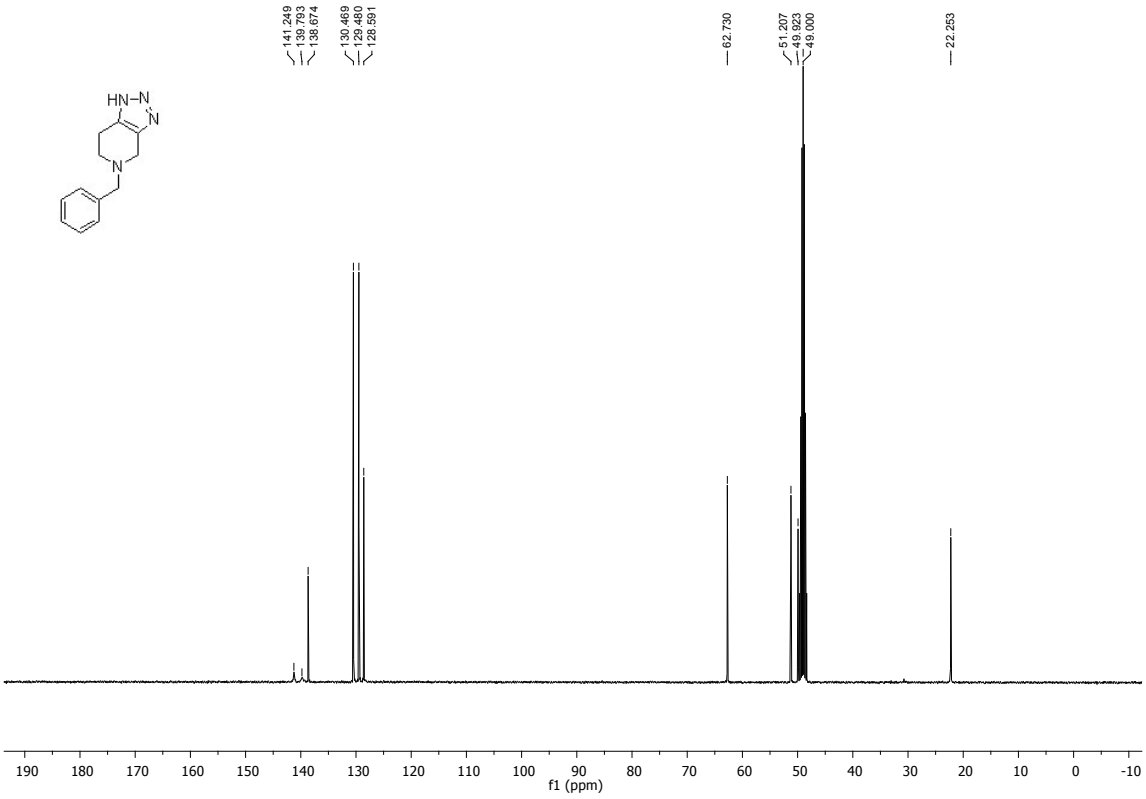
^{13}C NMR spectra of 3f (100 MHz, $CDCl_3$):



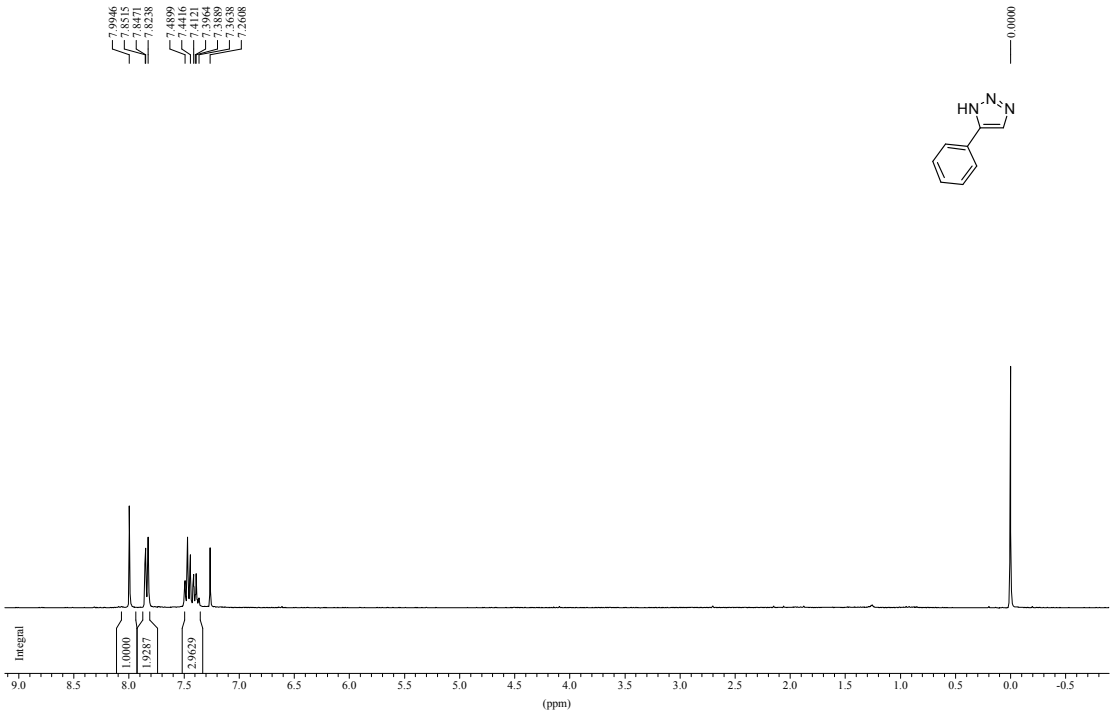
^{1}H NMR spectra of 3g (300 MHz, MeOD):



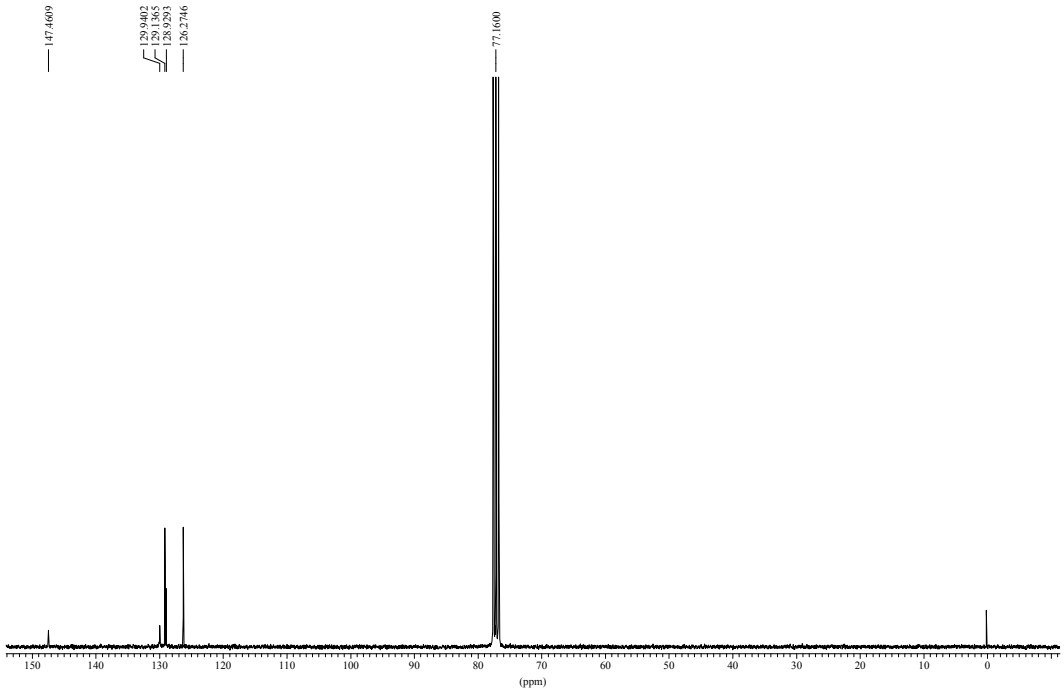
^{13}C NMR nmr spectra of 3g (75 MHz, MeOD):



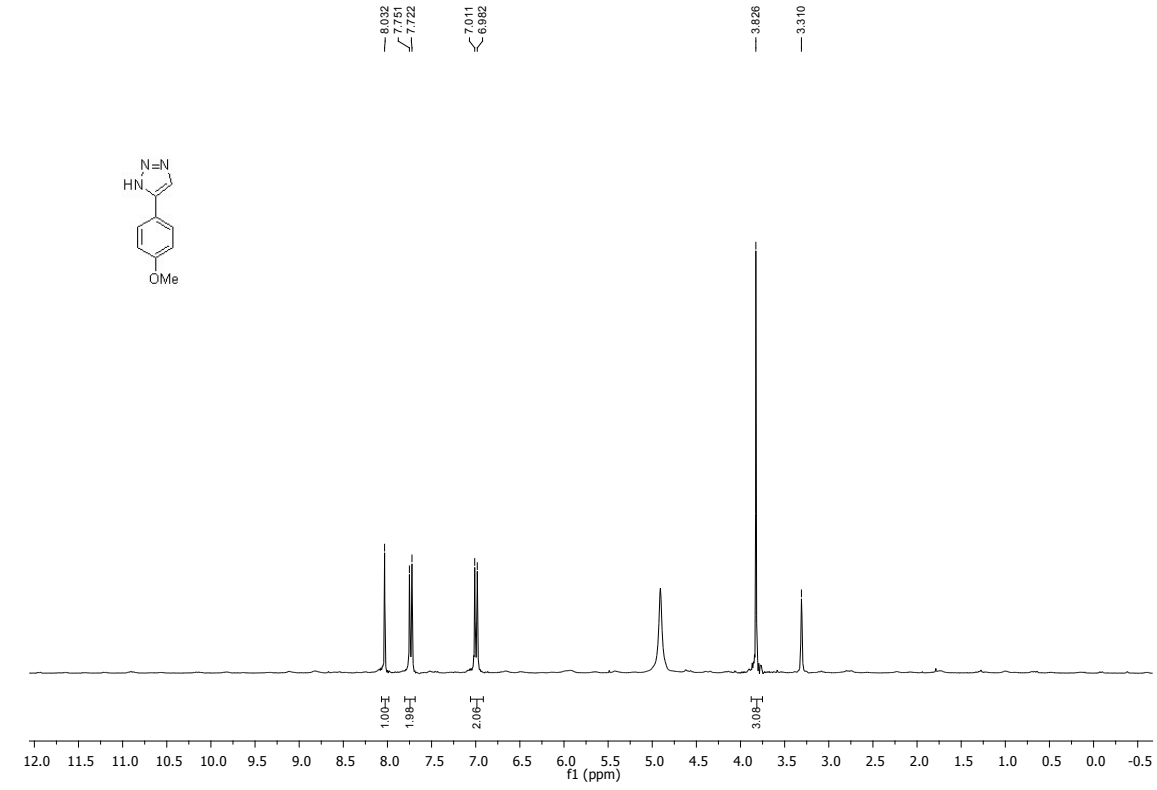
^{1}H NMR spectra of 3h (300 MHz, $CDCl_3$):



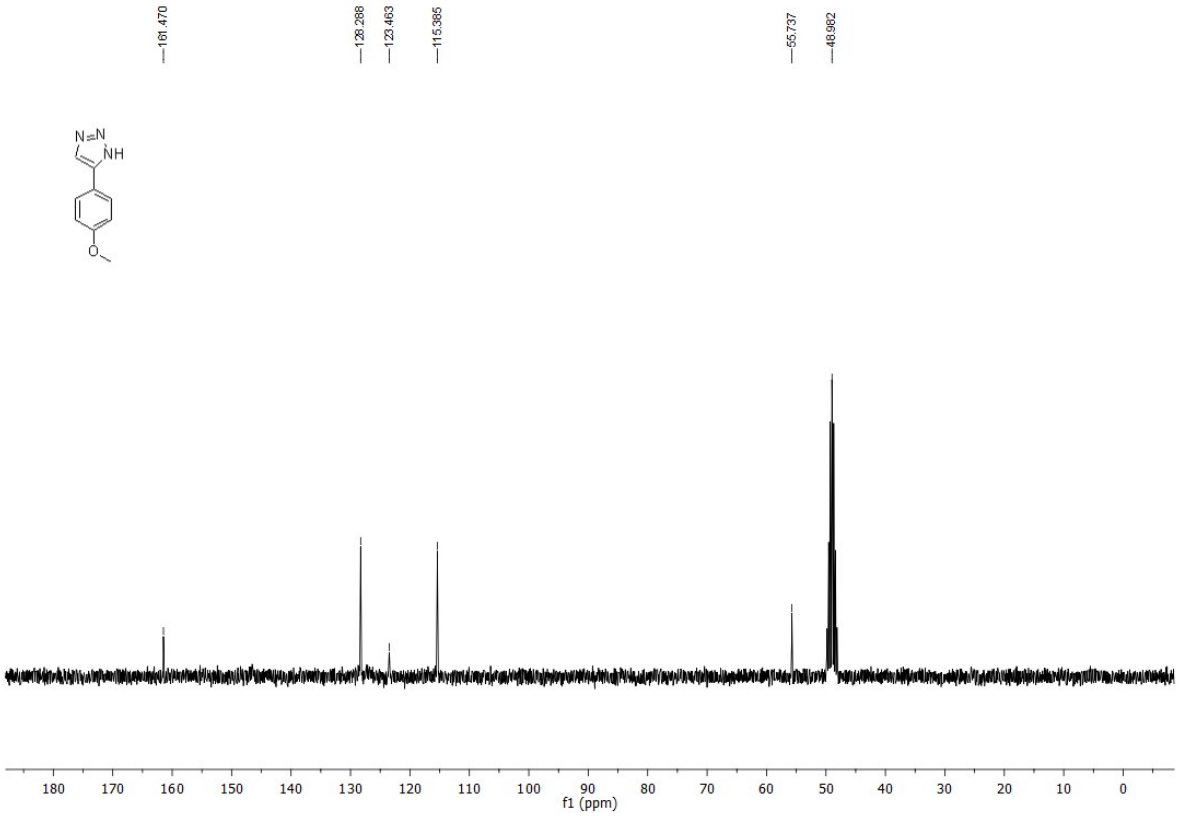
^{13}C NMR spectra of 3h (75 MHz, DMSO-d_6):



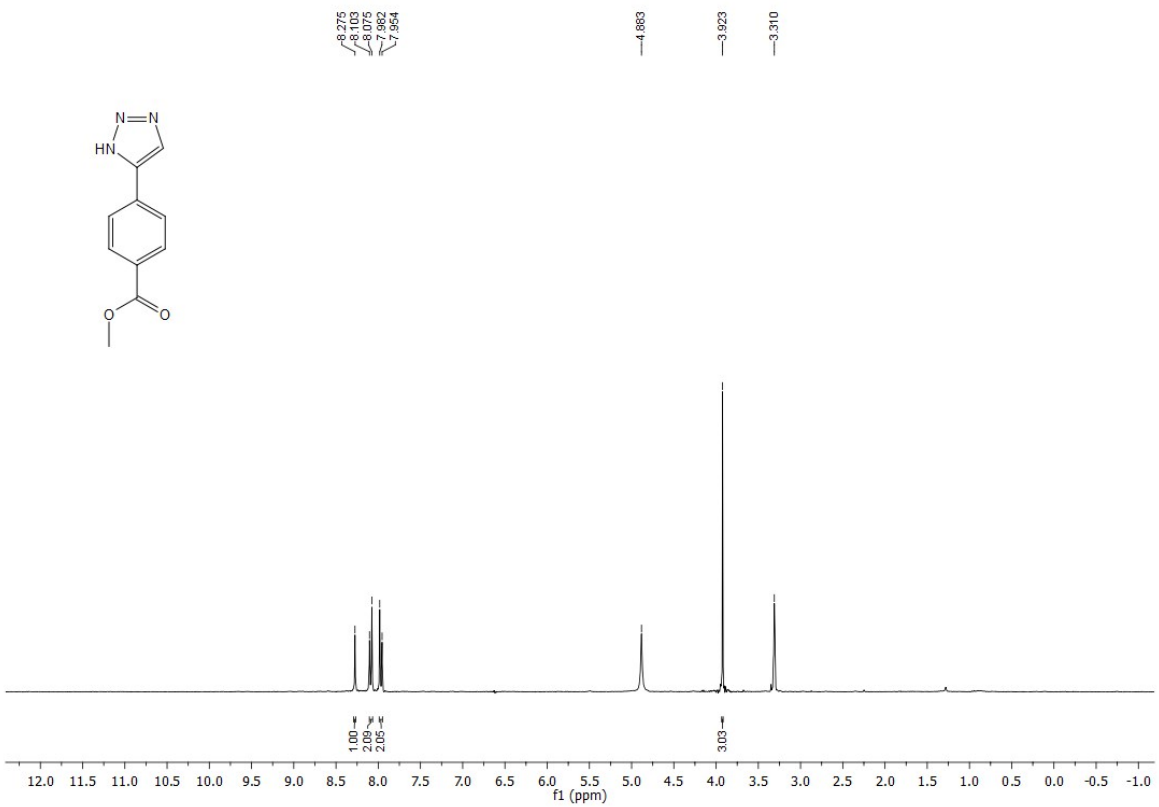
^{1}H NMR spectra of 3i (300 MHz, MeOD):



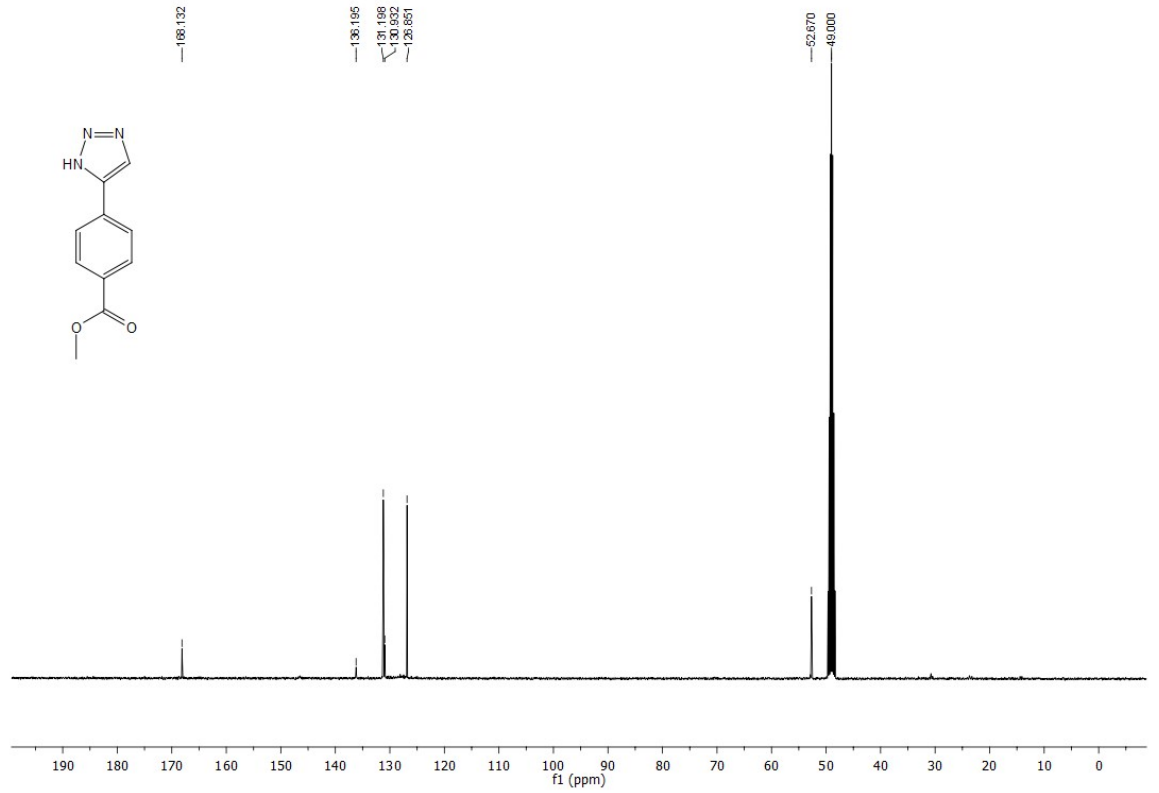
^{13}C NMR spectra of 3i (75 MHz, MeOD):



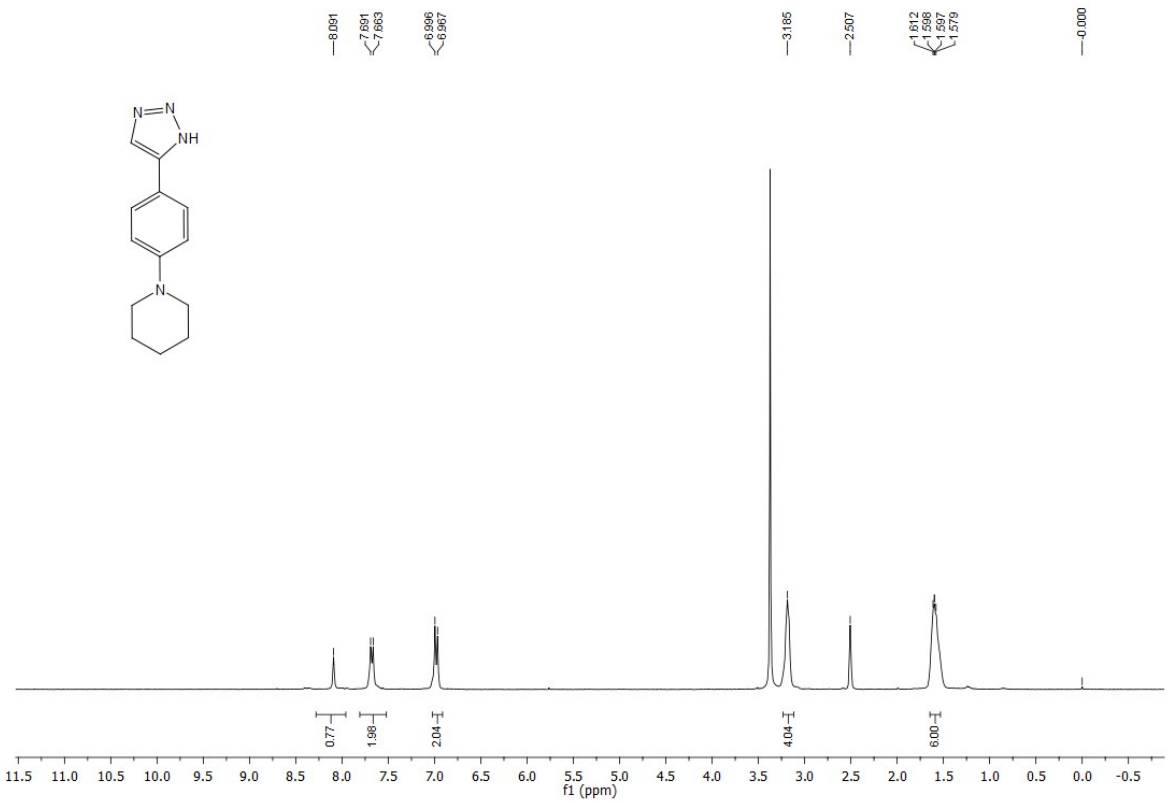
^{1}H NMR spectra of 3j (300 MHz, MeOD):



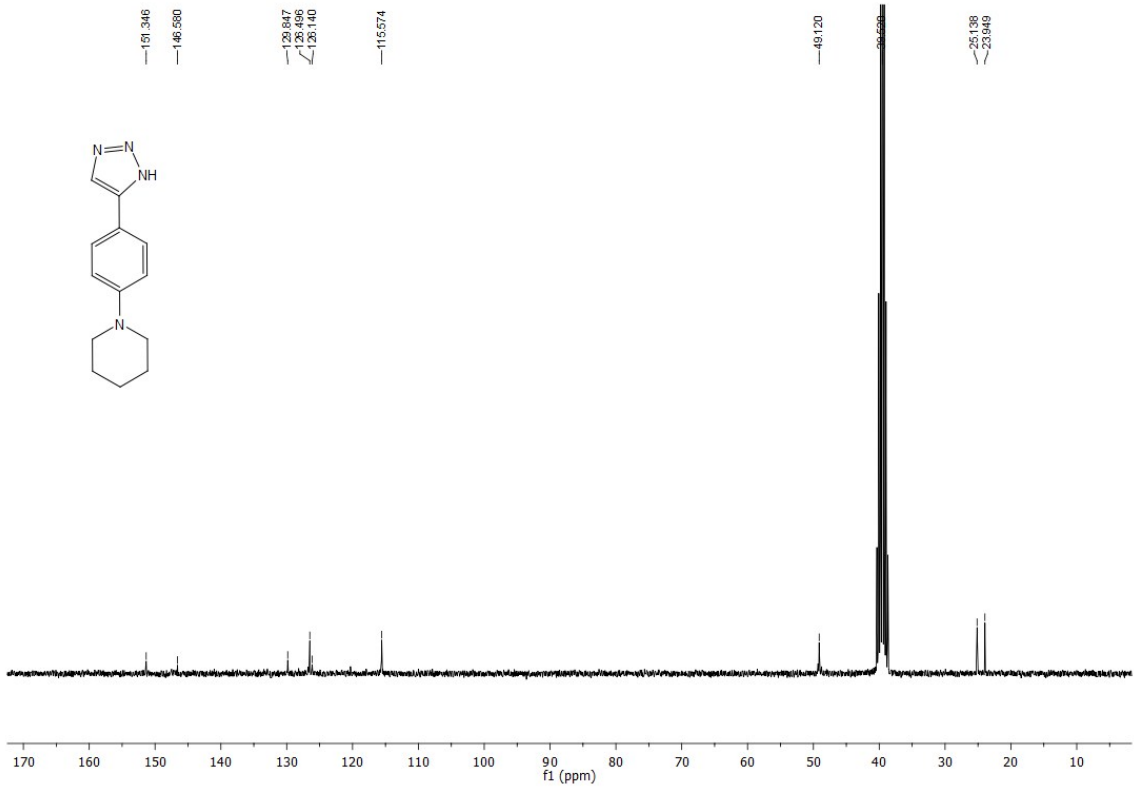
^{13}C NMR spectra of 3j (100 MHz, MeOD):



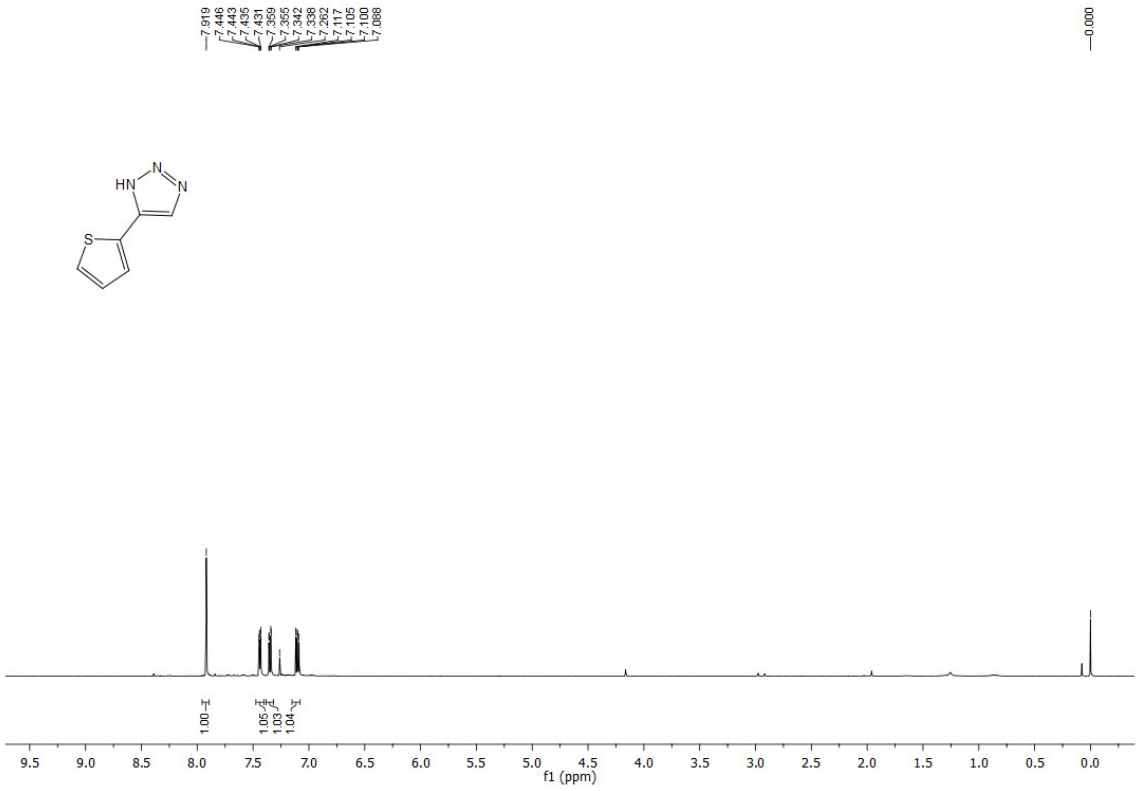
. ^{1}H NMR spectra of 3k (400 MHz, DMSO-d_6):



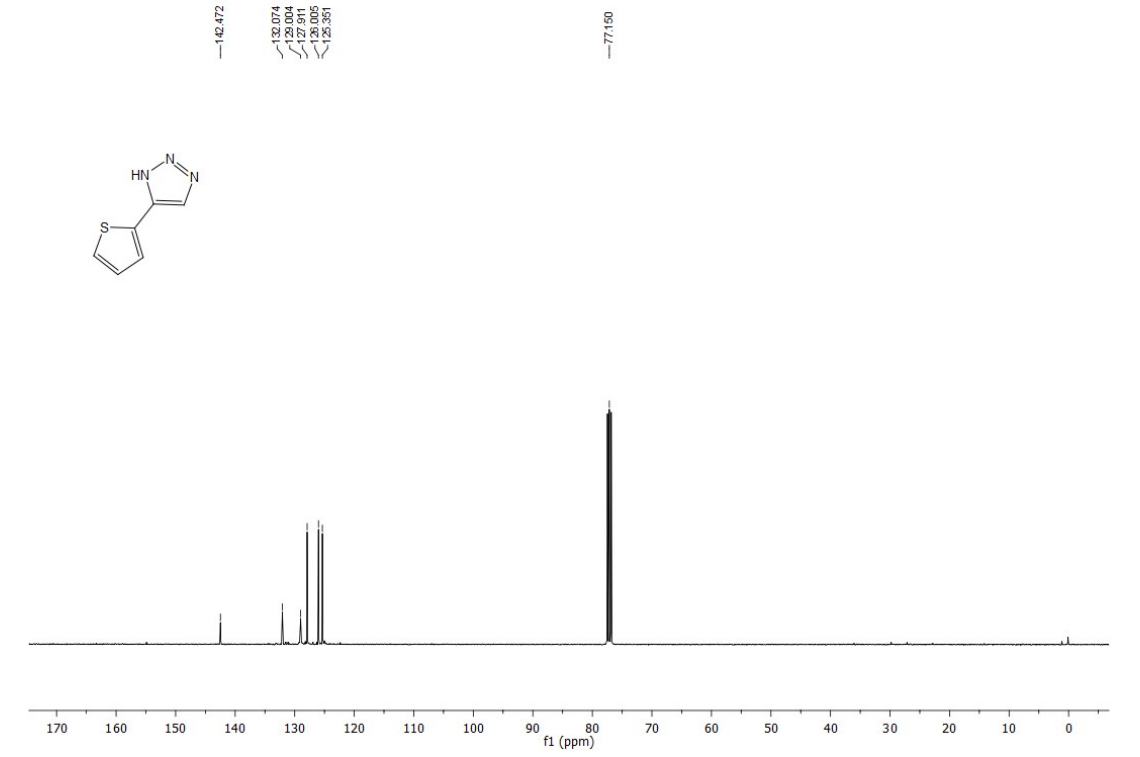
^{13}C NMR spectra of 3k (75 MHz, DMSO-d_6):



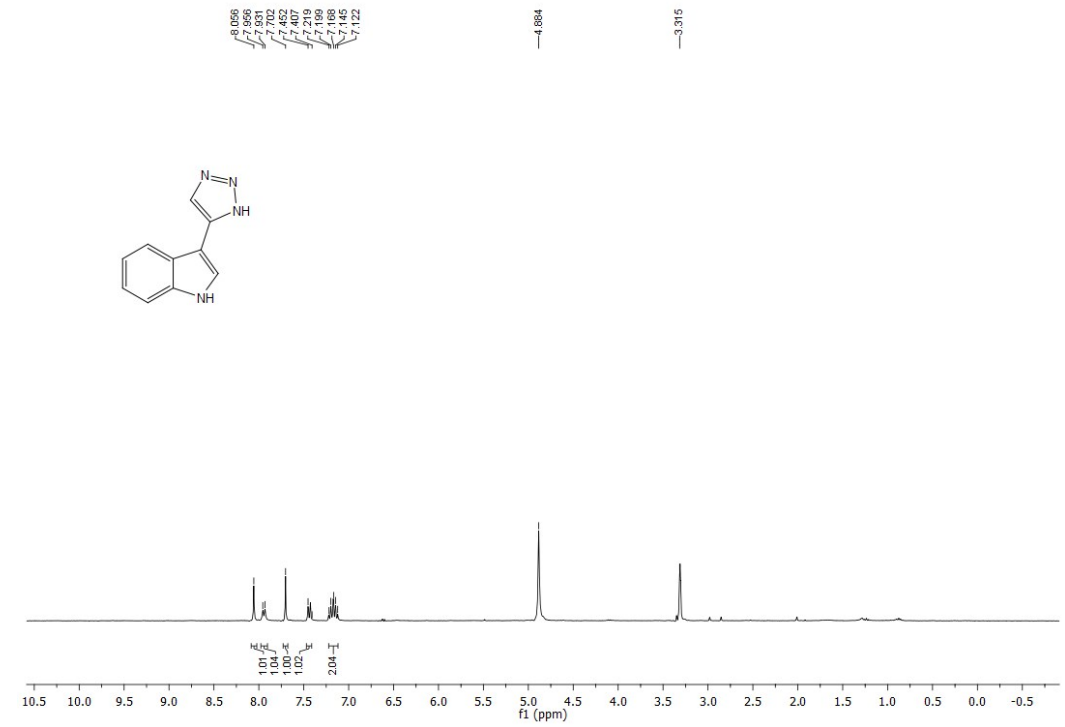
^{1}H NMR spectra of 3l (300 MHz, $CDCl_3$):



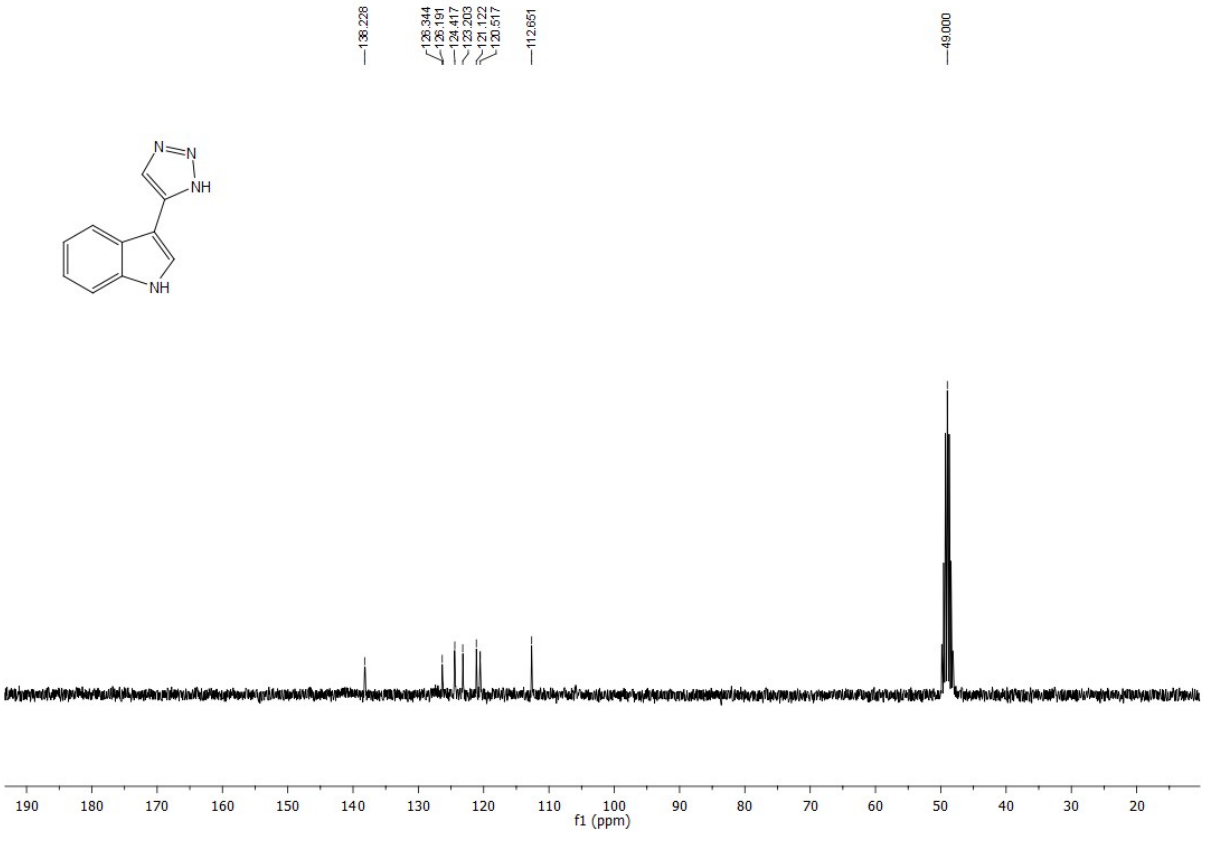
^{13}C NMR spectra of 3l (75 MHz, $CDCl_3$):



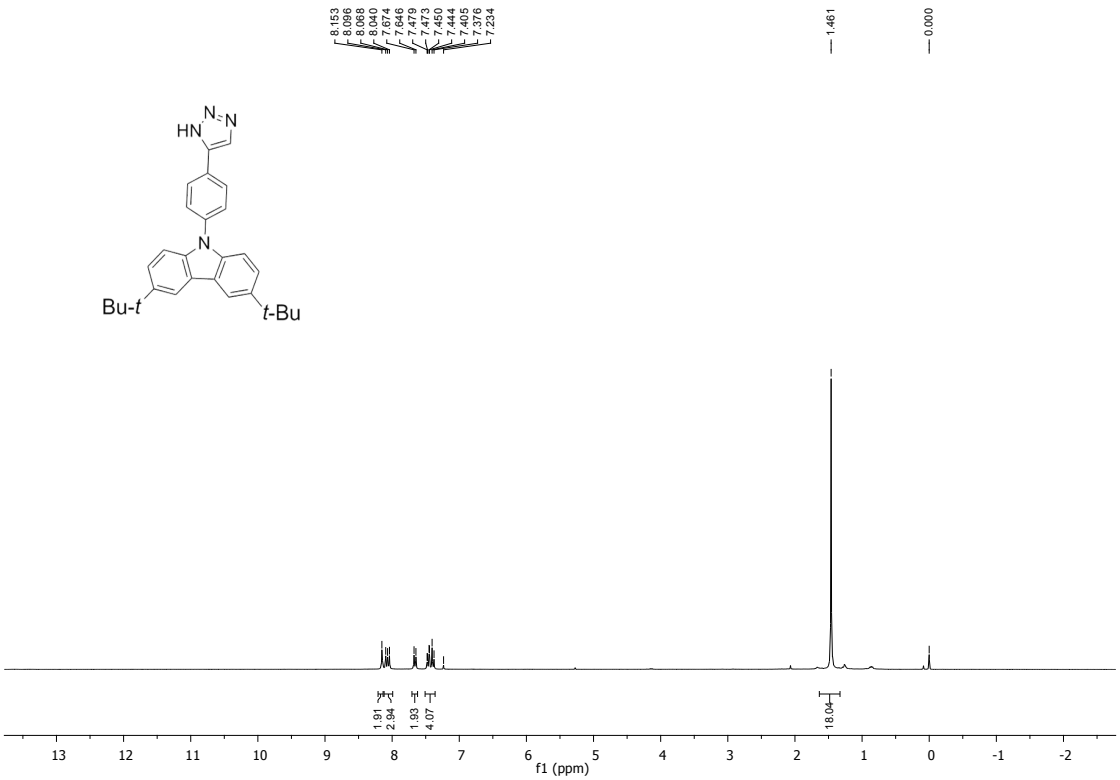
^{1}H NMR spectra of 3m (300 MHz, MeOD):



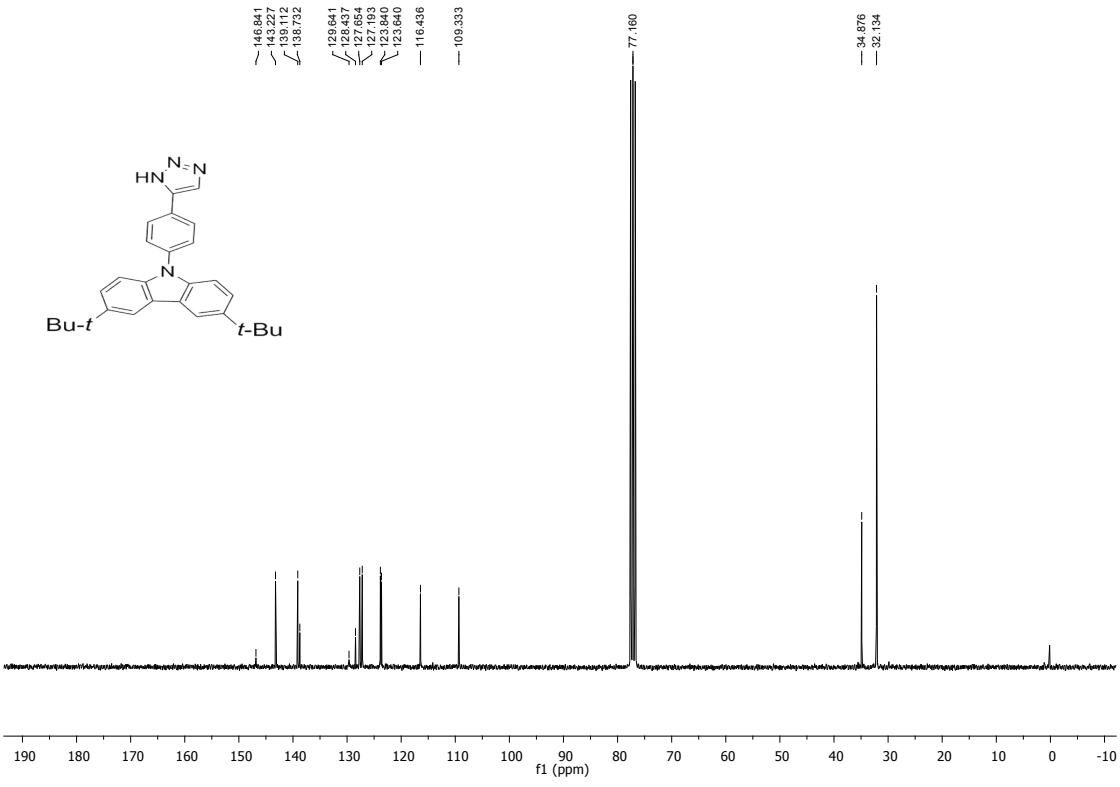
^{13}C NMR spectra of 3m (75 MHz, MeOD):



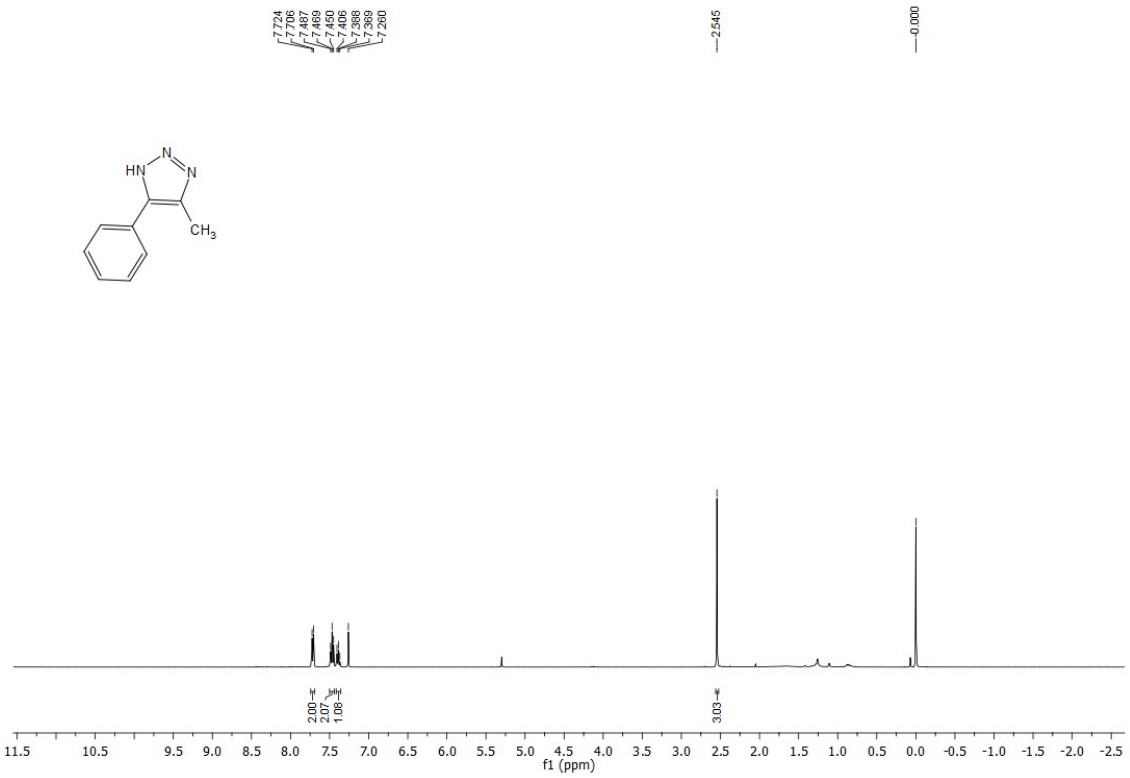
^{1}H NMR spectra of 3n (300 MHz, $CDCl_3$):



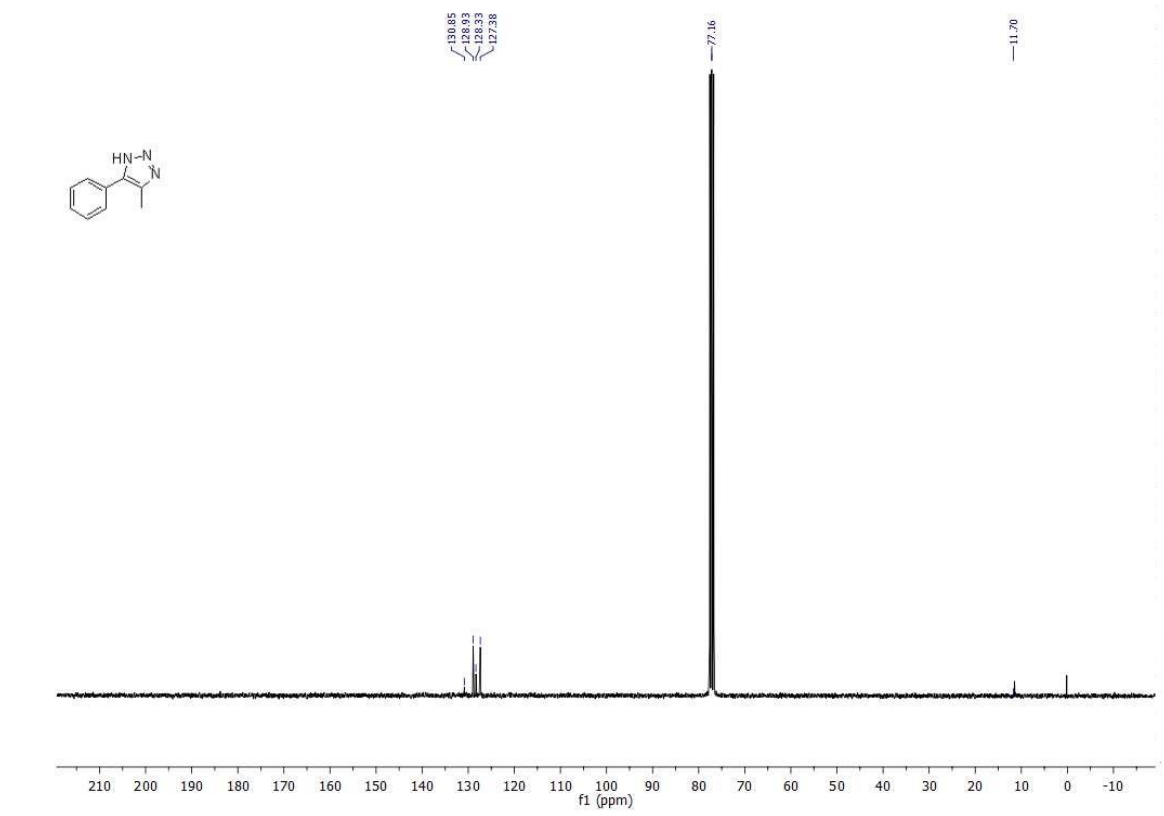
^{13}C NMR spectra of 3n (75 MHz, $CDCl_3$):



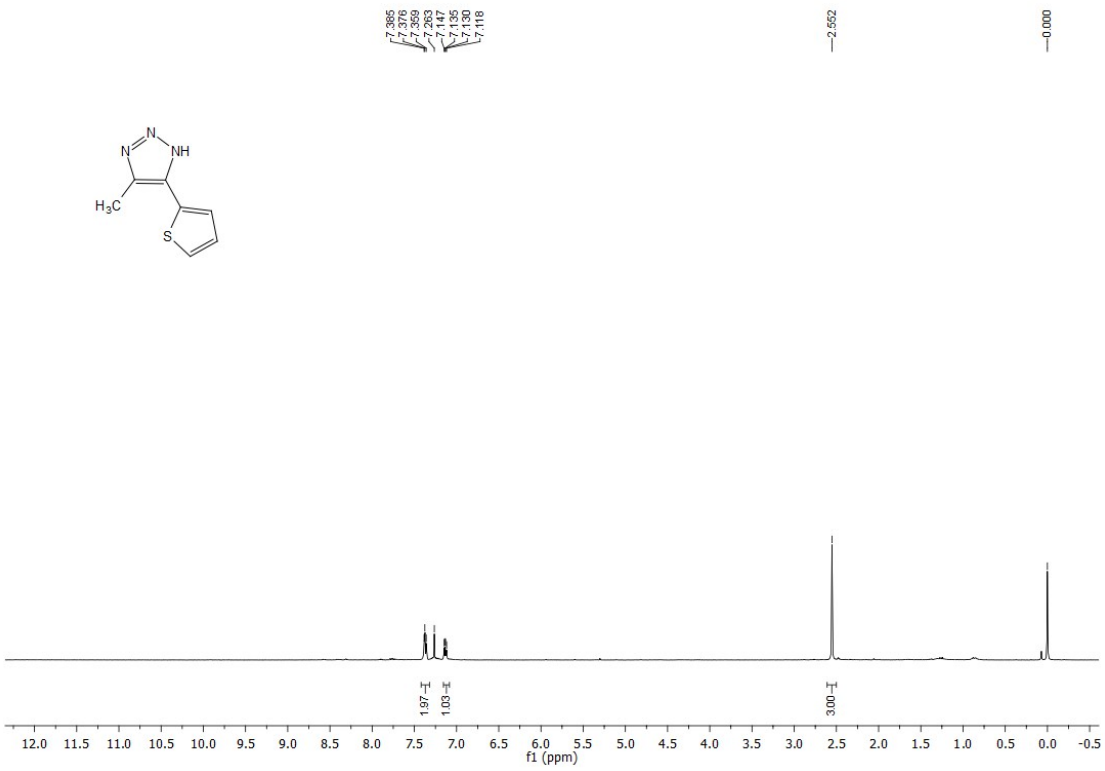
^{1}H NMR spectra of 3o (400 MHz, $CDCl_3$):



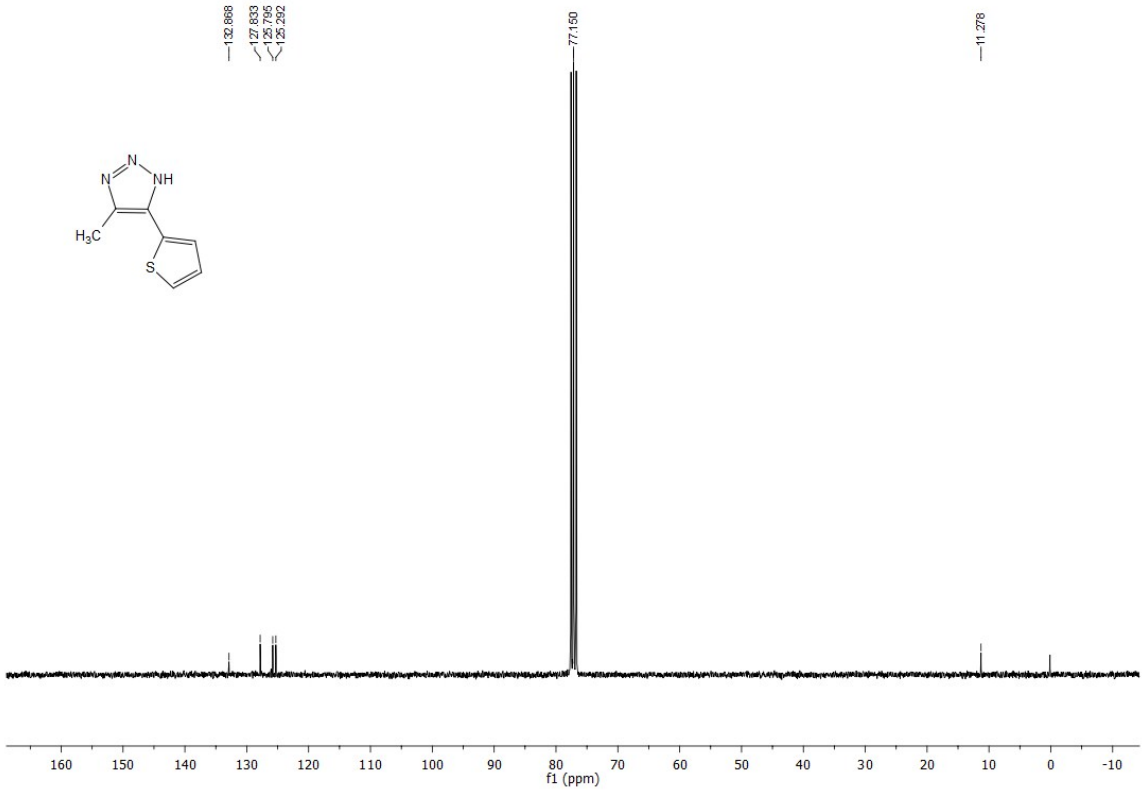
^{13}C NMR spectra of 3o (75 MHz, $CDCl_3$):



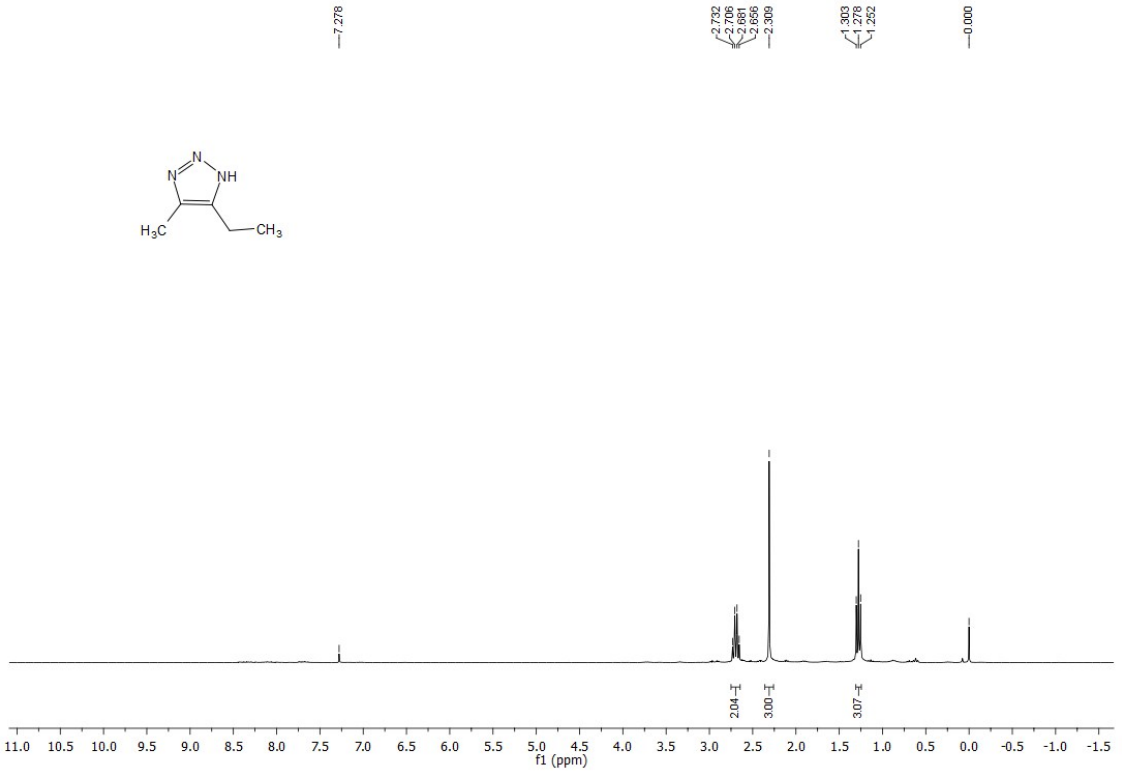
^{1}H NMR spectra of 3p (300 MHz, $CDCl_3$):



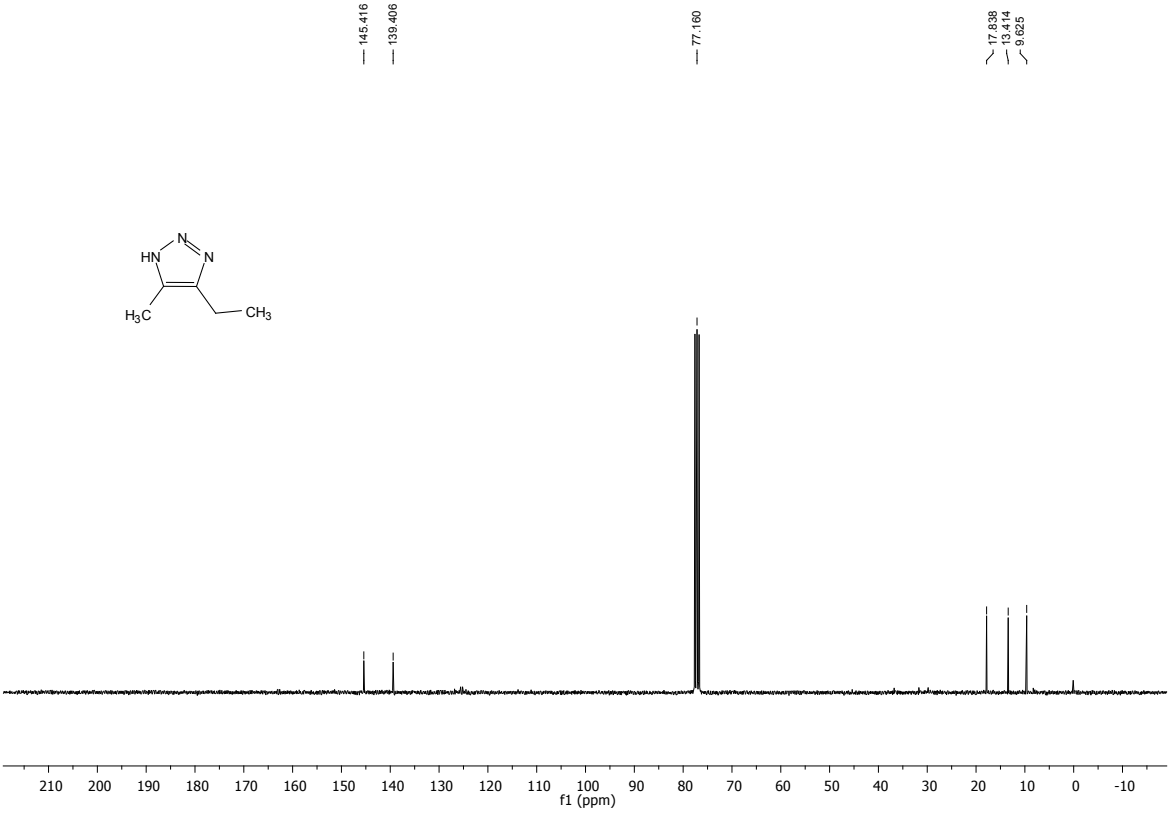
^{13}C NMR spectra of 3p (75 MHz, $CDCl_3$):



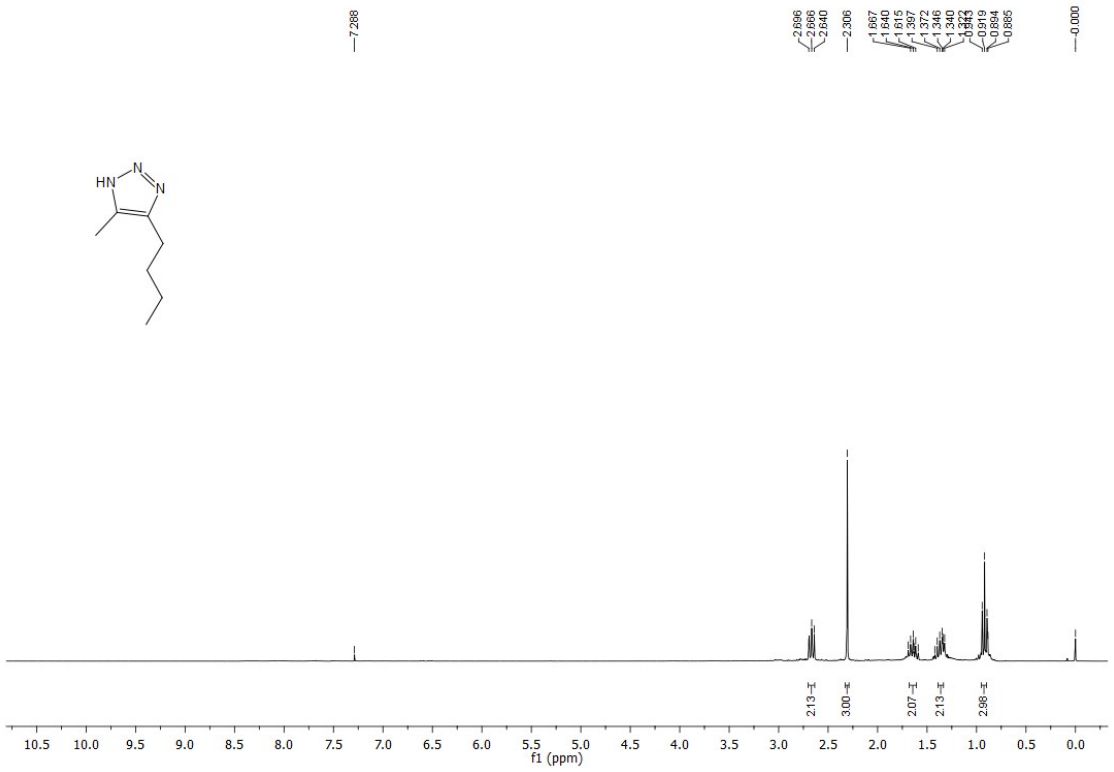
^{1}H NMR spectra of 3q (300 MHz, $CDCl_3$):



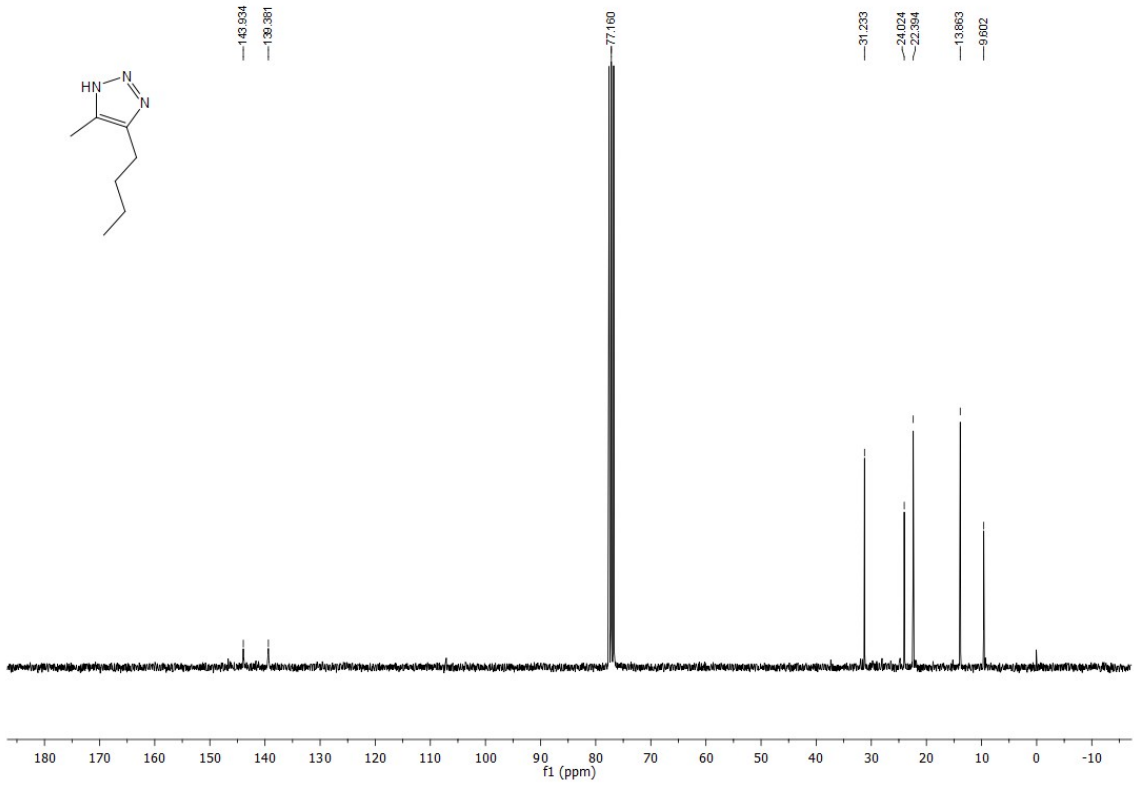
^{13}C NMR spectra of 3q (75 MHz, $CDCl_3$):



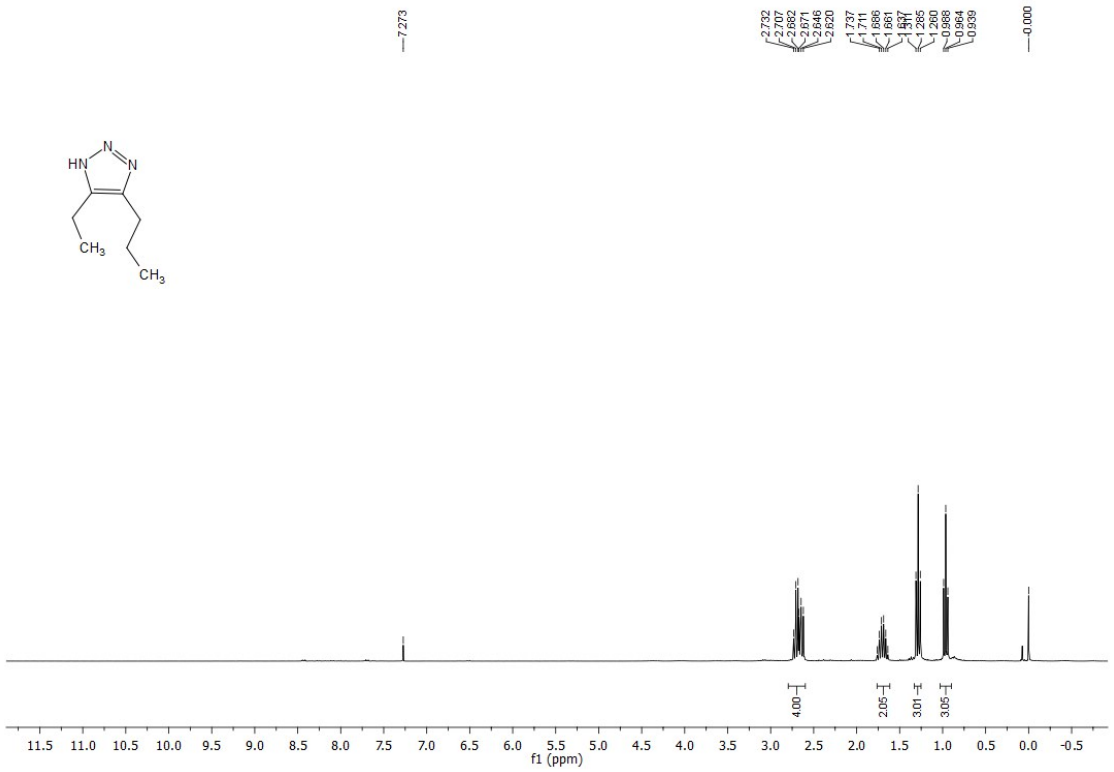
^{1}H NMR spectra of 3r (300 MHz, $CDCl_3$):



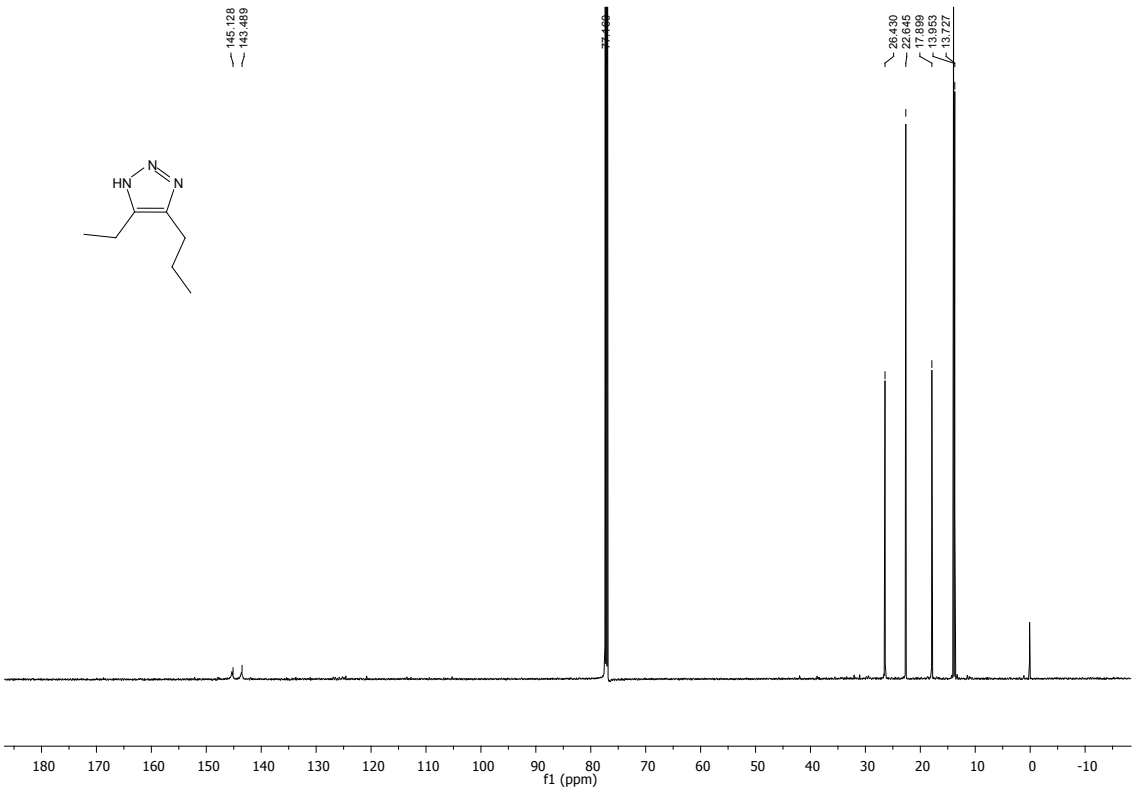
^{13}C NMR spectra of 3r (75 MHz, $CDCl_3$):



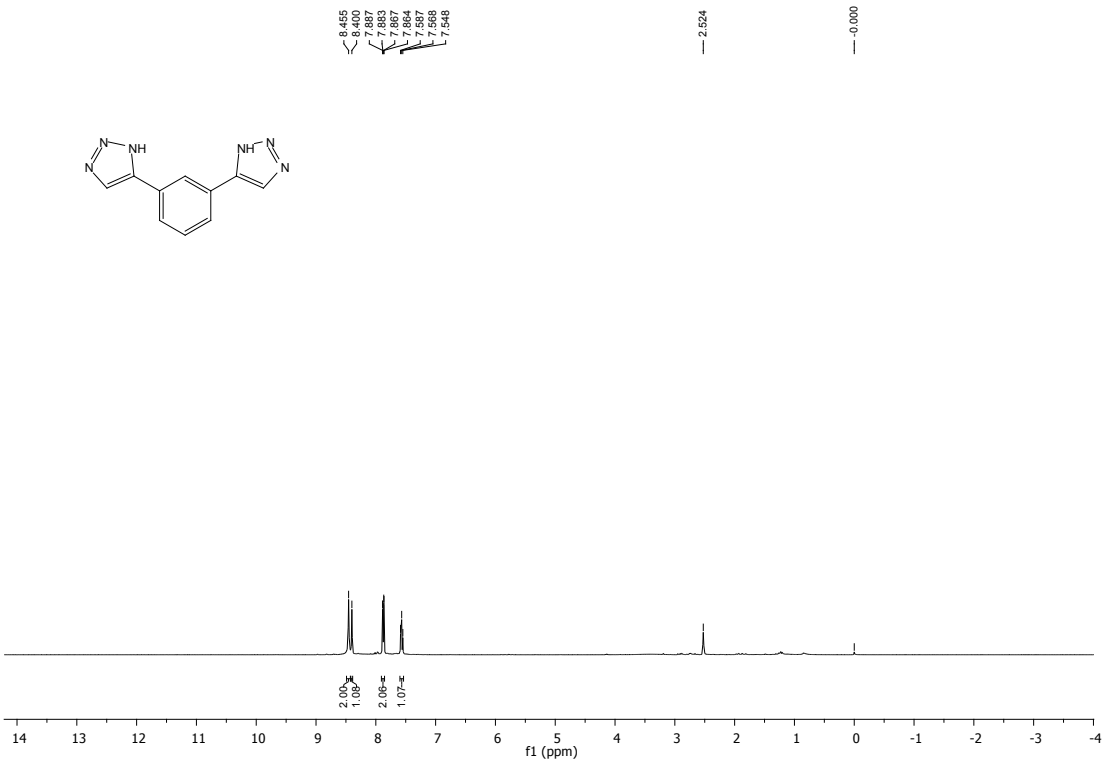
^{1}H NMR spectra of 3s (600 MHz, $CDCl_3$):



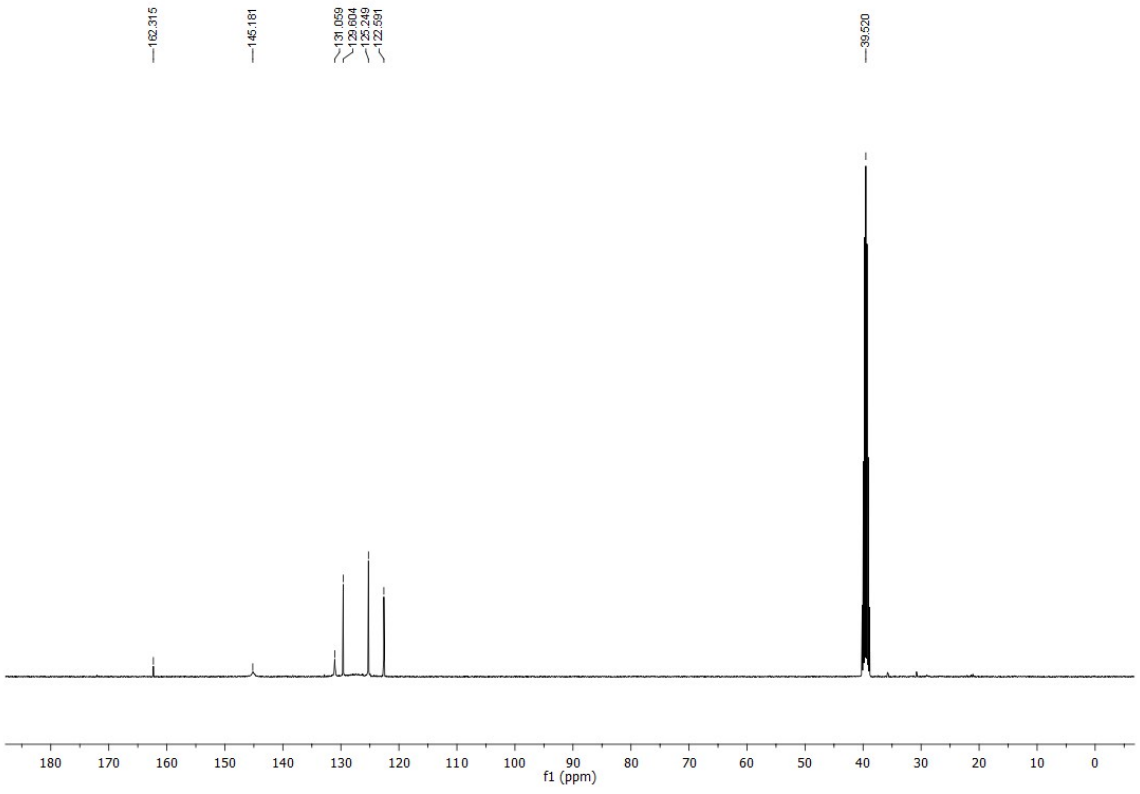
^{13}C NMR spectra of 3s (150 MHz, $CDCl_3$):



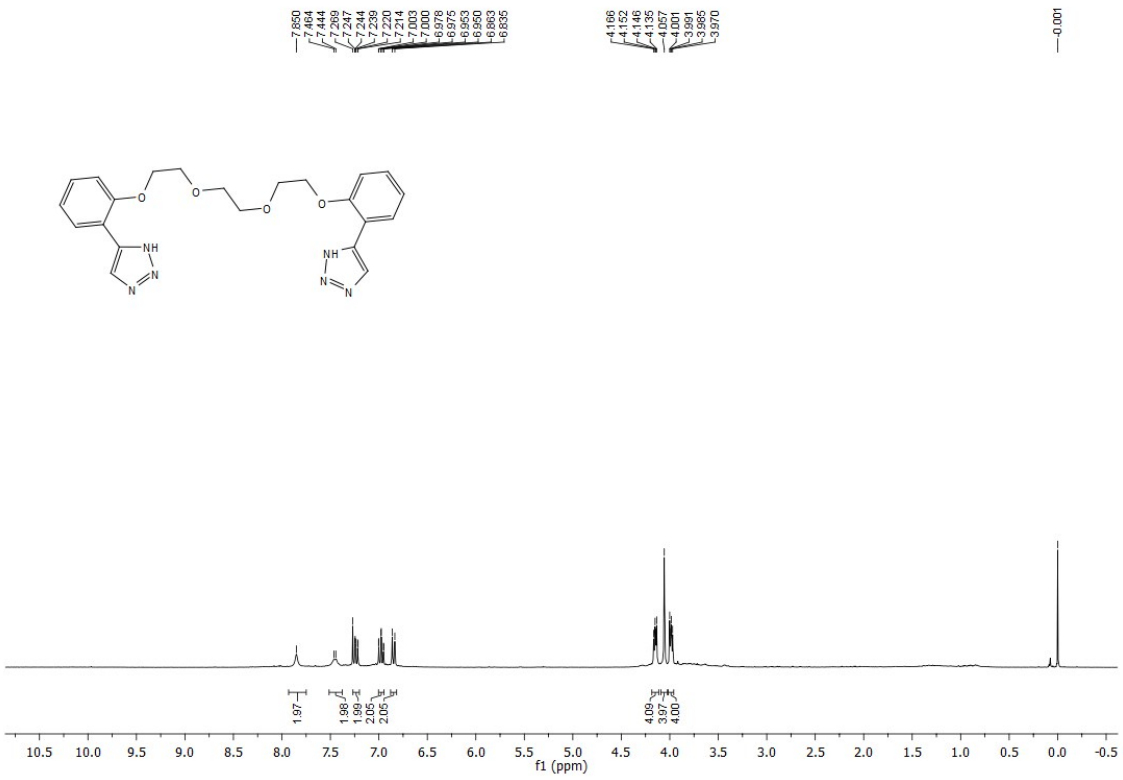
^{1}H NMR spectra of 5 (400 MHz, DMSO – d_6):



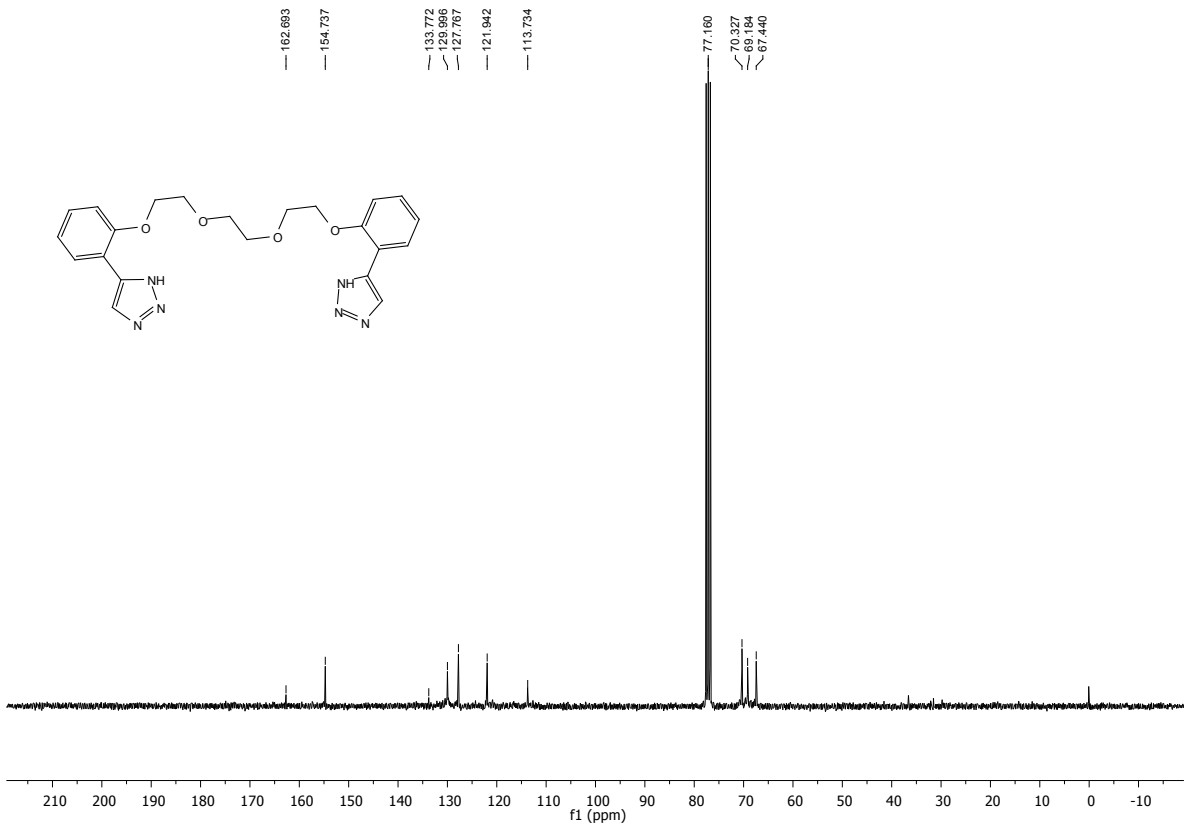
^{13}C NMR spectra of 5 (100 MHz, DMSO – d_6):



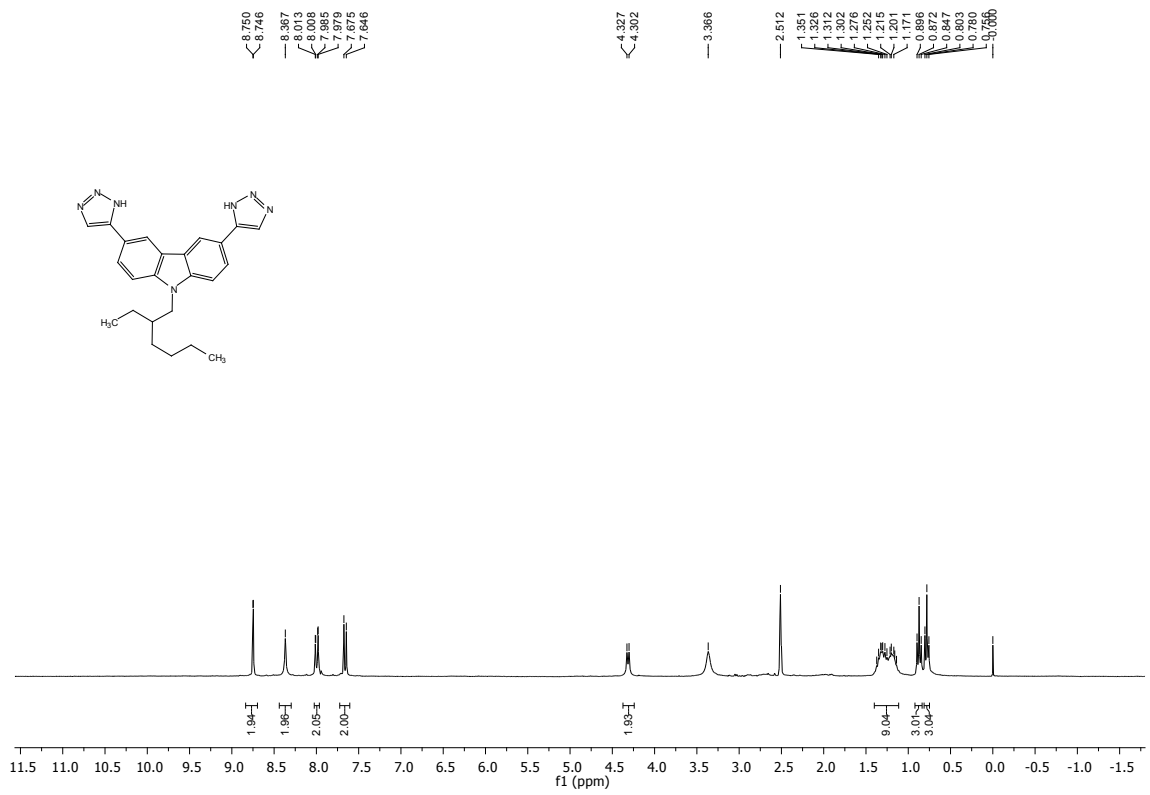
^{1}H NMR spectra of 6 (400 MHz, $CDCl_3$):



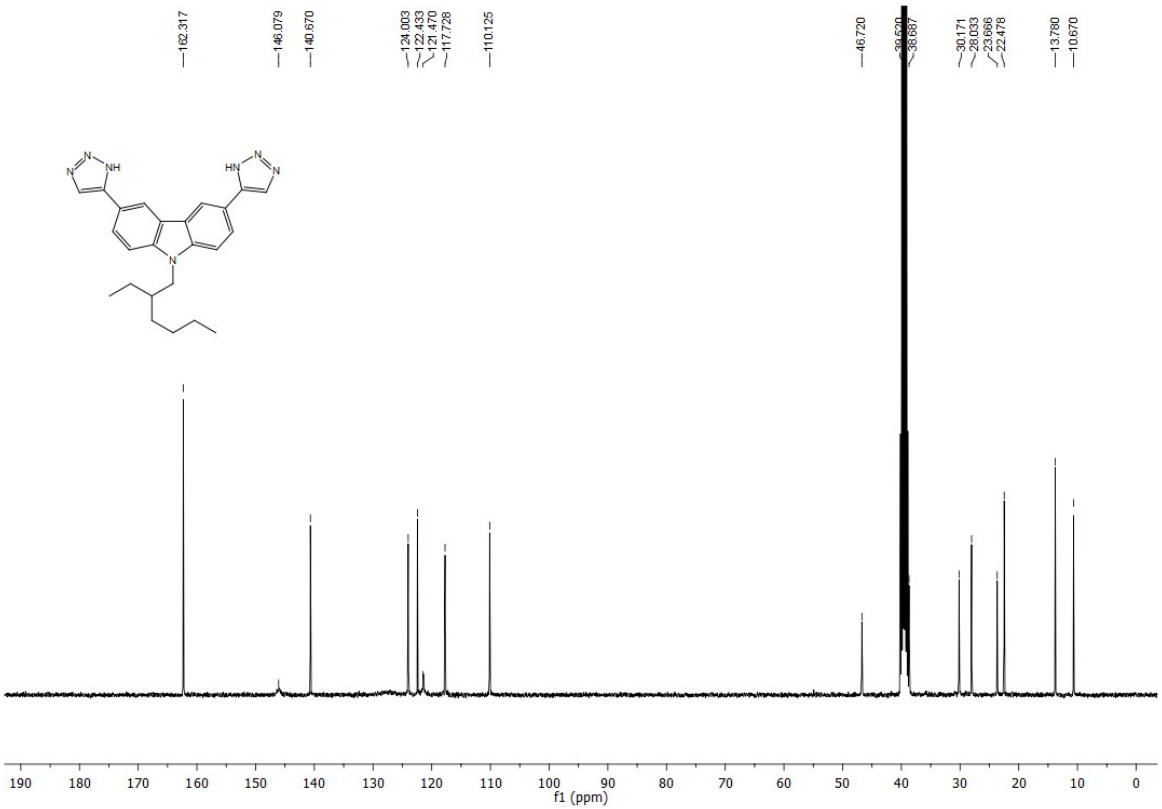
^{13}C NMR spectra of 6 (100 MHz, $CDCl_3$):



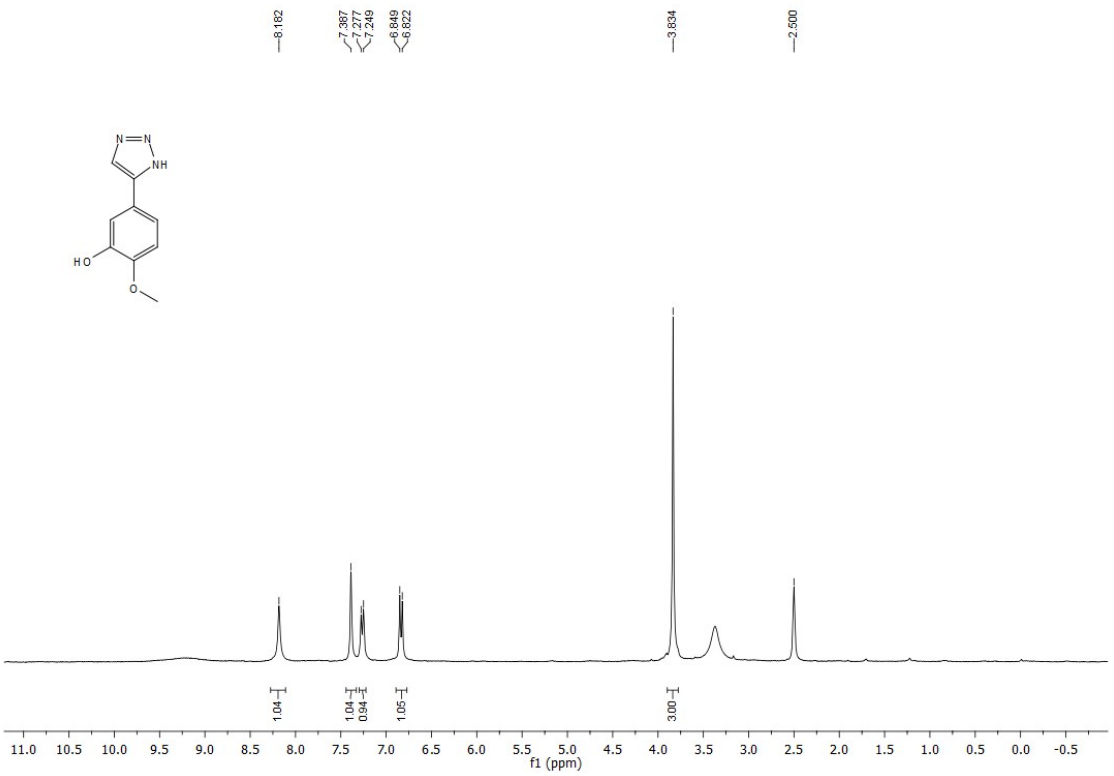
^{1}H NMR spectra of 7 (300 MHz, DMSO-d_6):



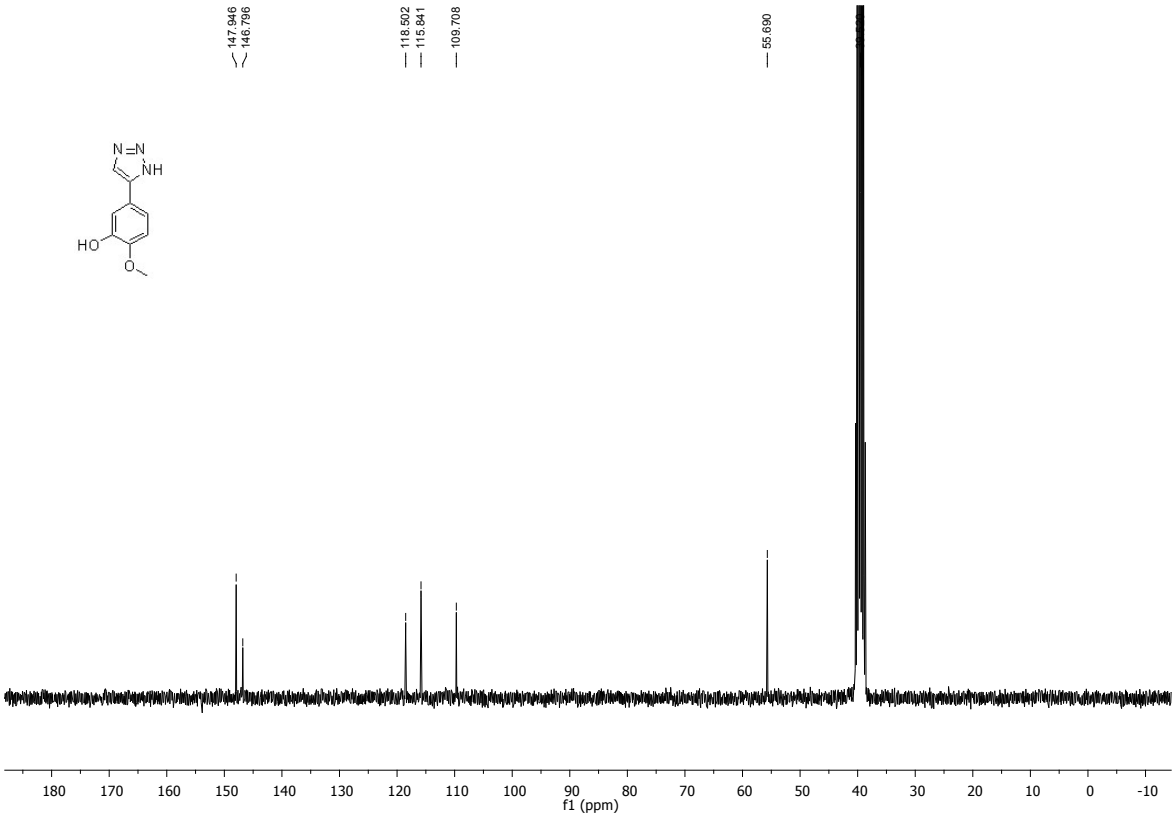
^{13}C NMR spectra of 7 (100 MHz, DMSO-d_6):



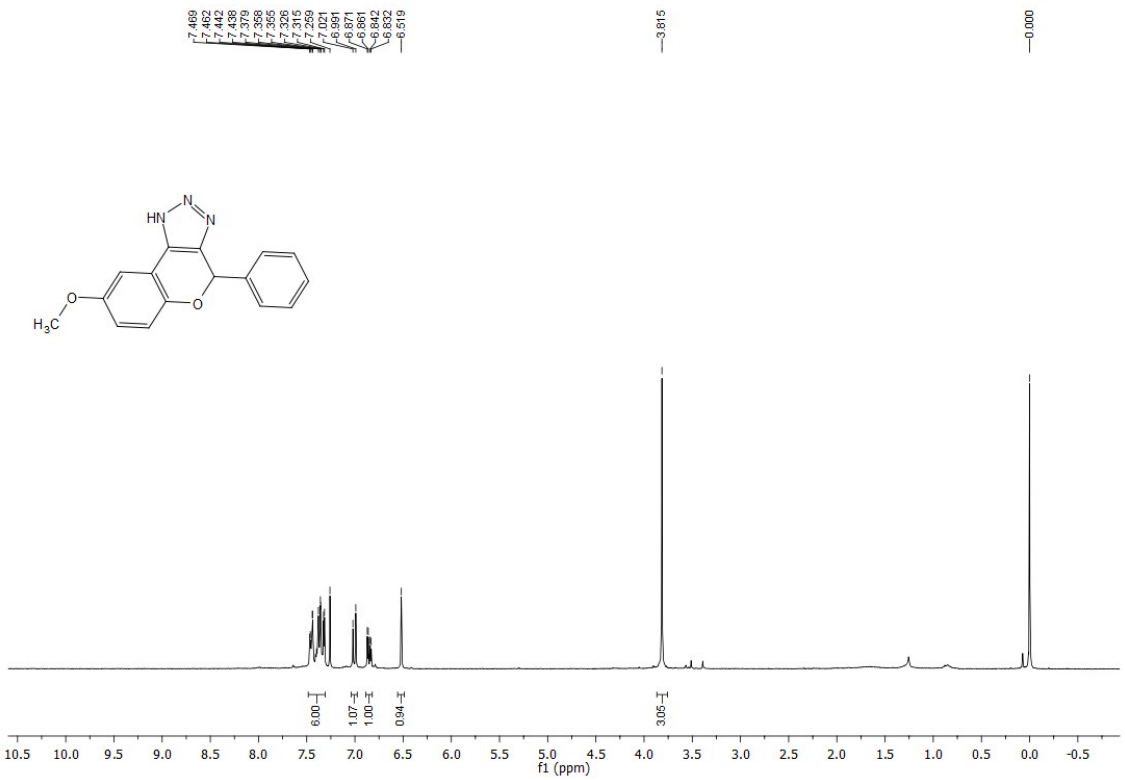
^{1}H NMR spectra of 9a (300 MHz, DMSO - d_6):



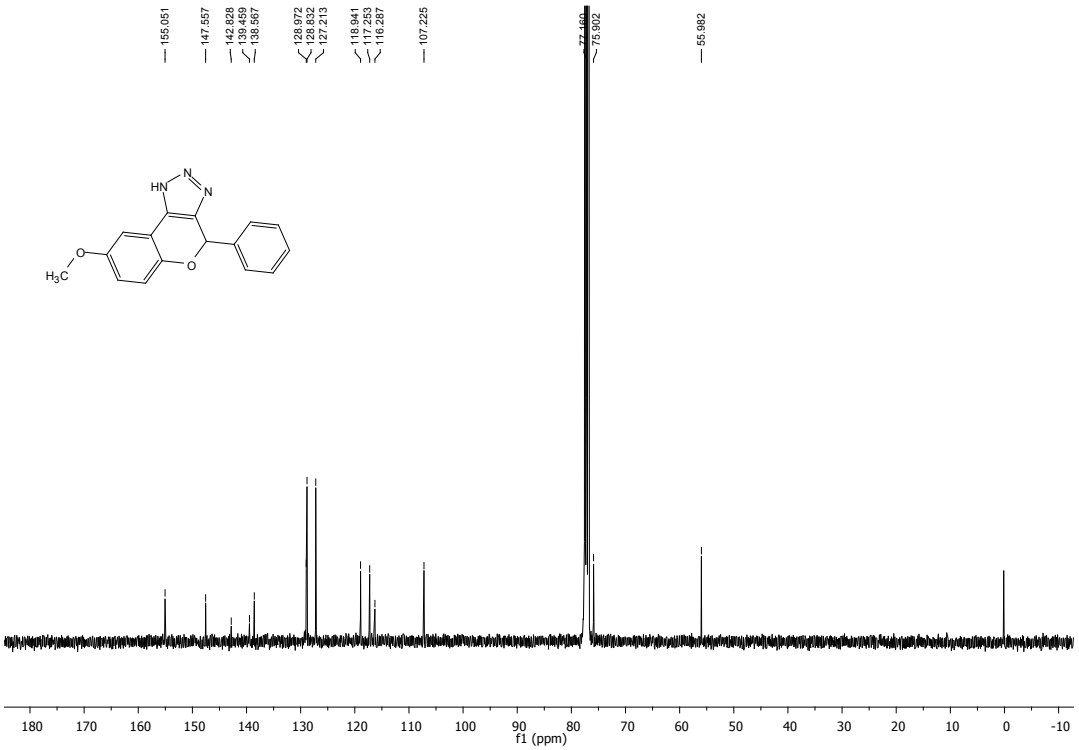
^{13}C NMR spectra of 9a (75 MHz, DMSO - d_6):



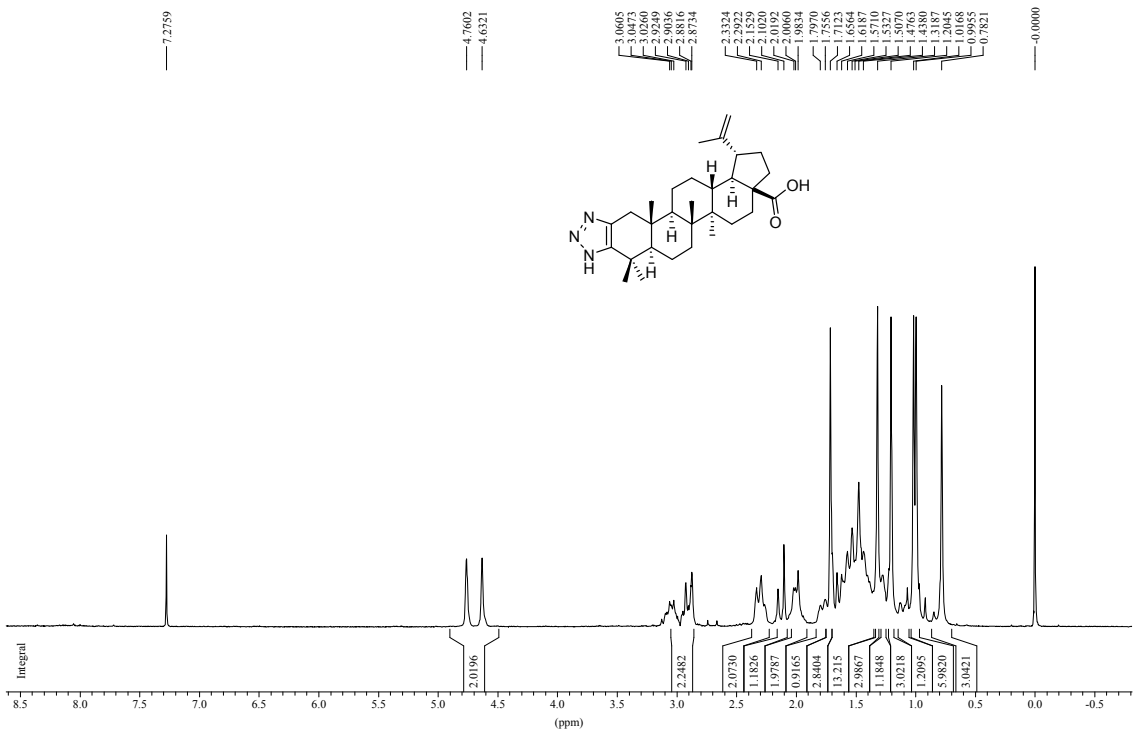
^{1}H NMR spectra of 9b (300 MHz, $CDCl_3$):



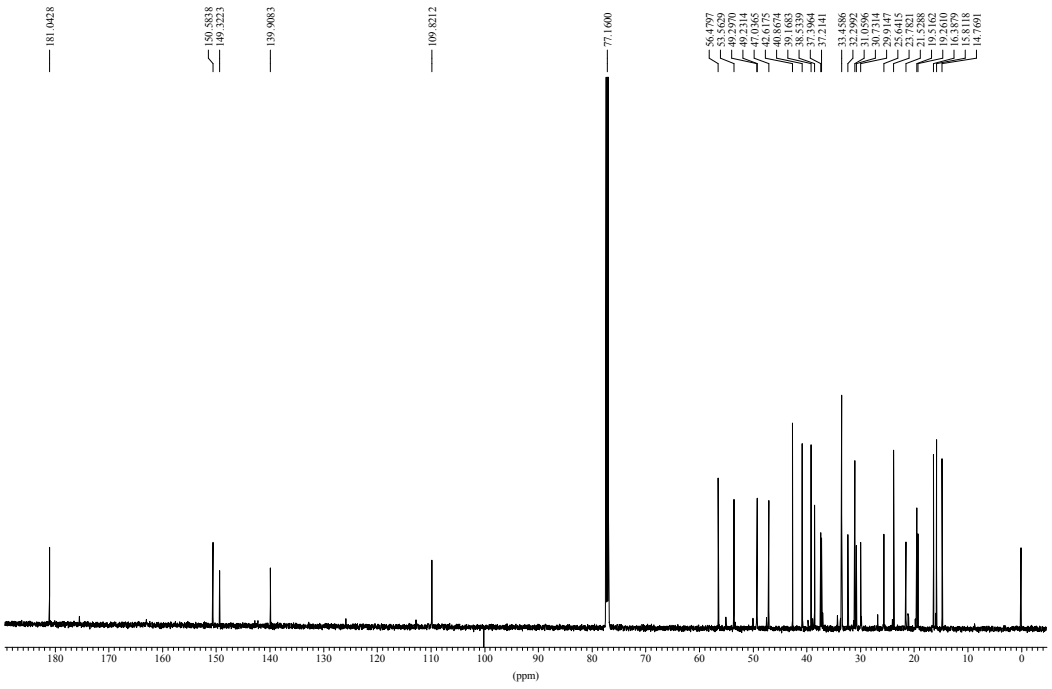
^{13}C NMR spectra of 9b (75 MHz, $CDCl_3$):



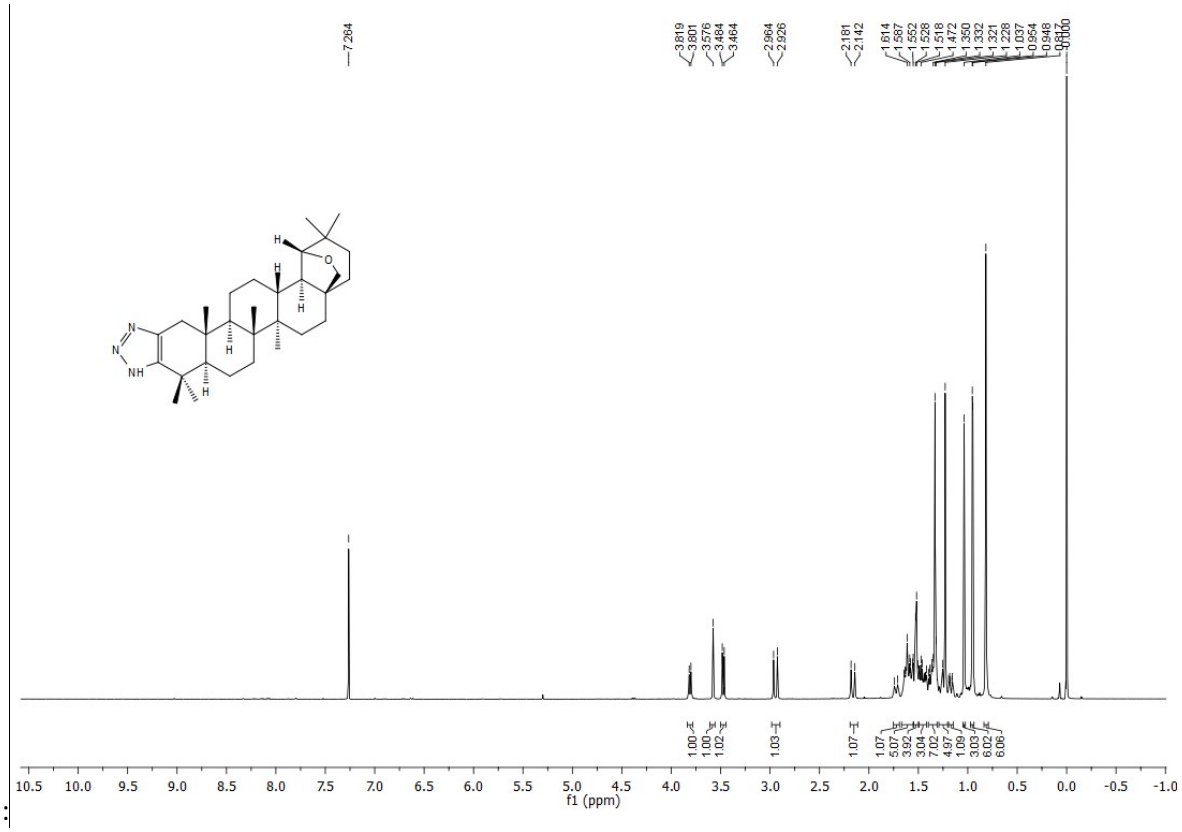
^{1}H NMR spectra of 9c (300 MHz, $CDCl_3$):



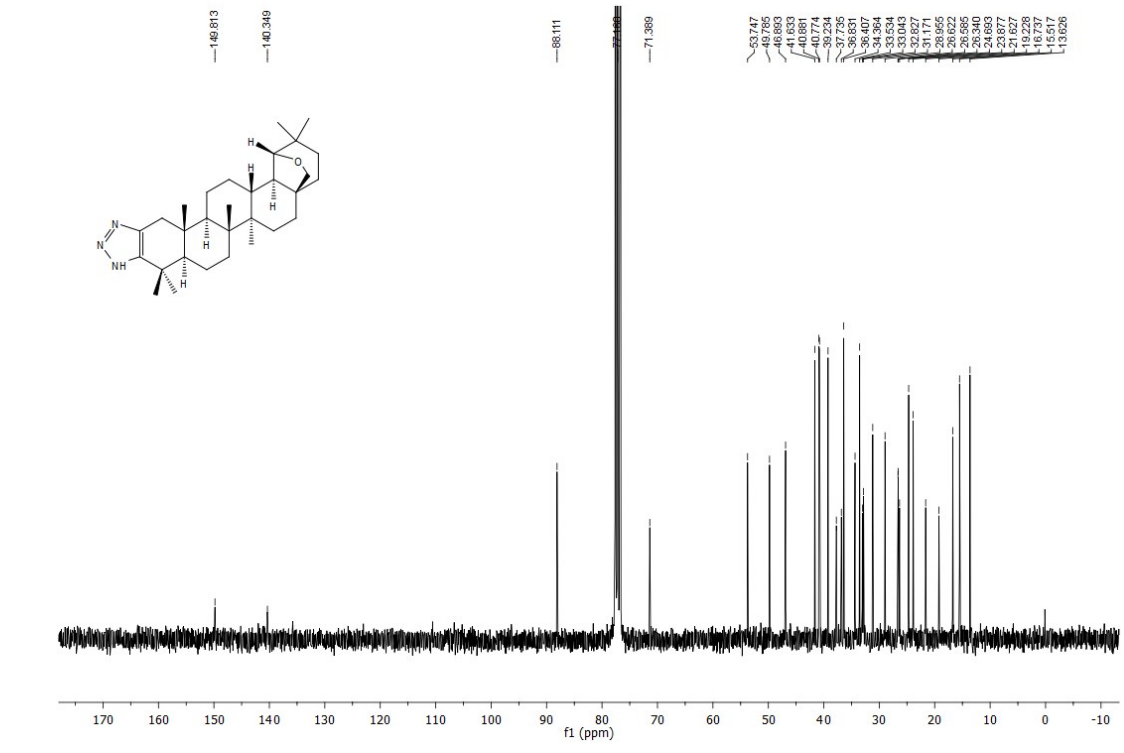
^{13}C NMR spectra of 9c (75 MHz, $CDCl_3$):



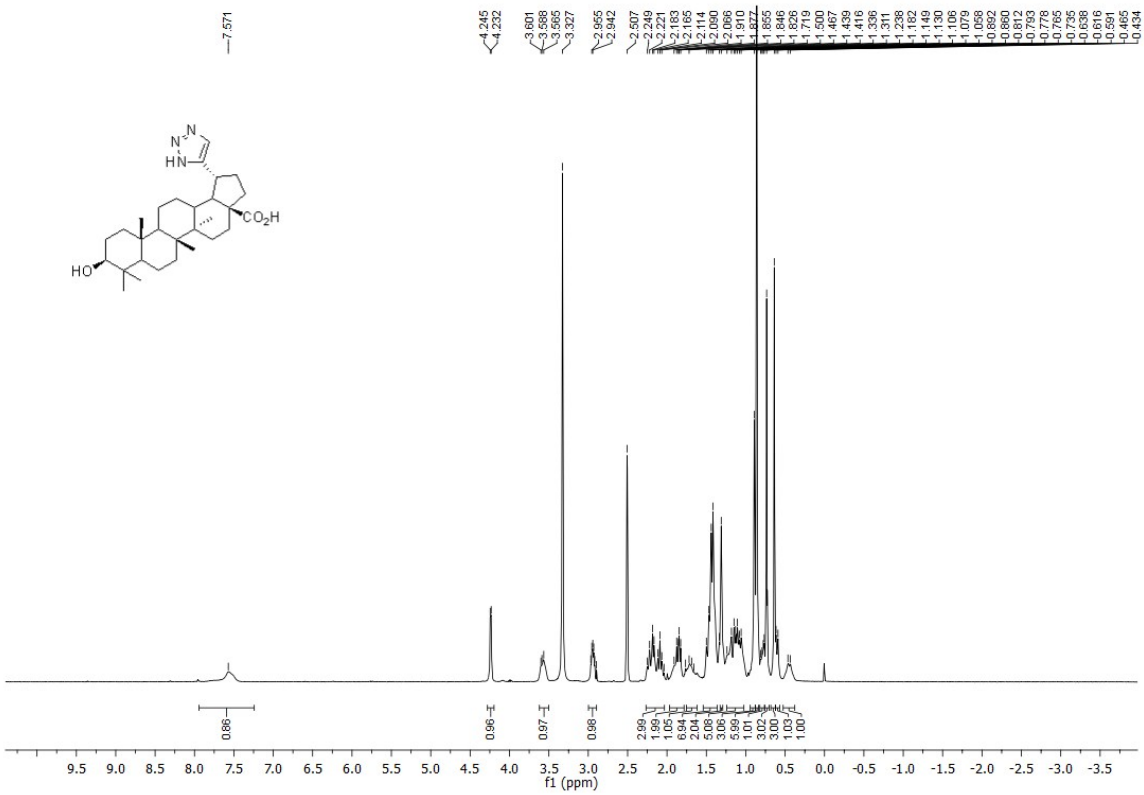
^{1}H NMR spectra of 9d (400 MHz, $CDCl_3$)



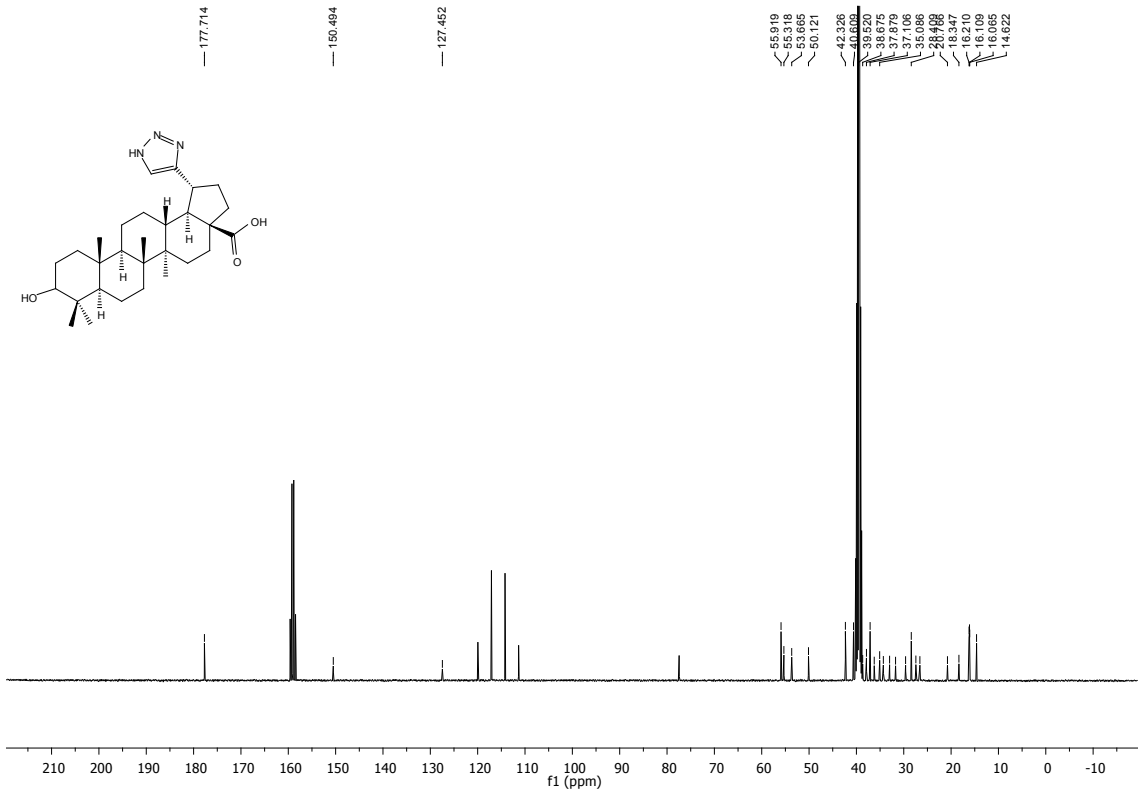
^{13}C NMR spectra of 9d (100 MHz, $CDCl_3$):



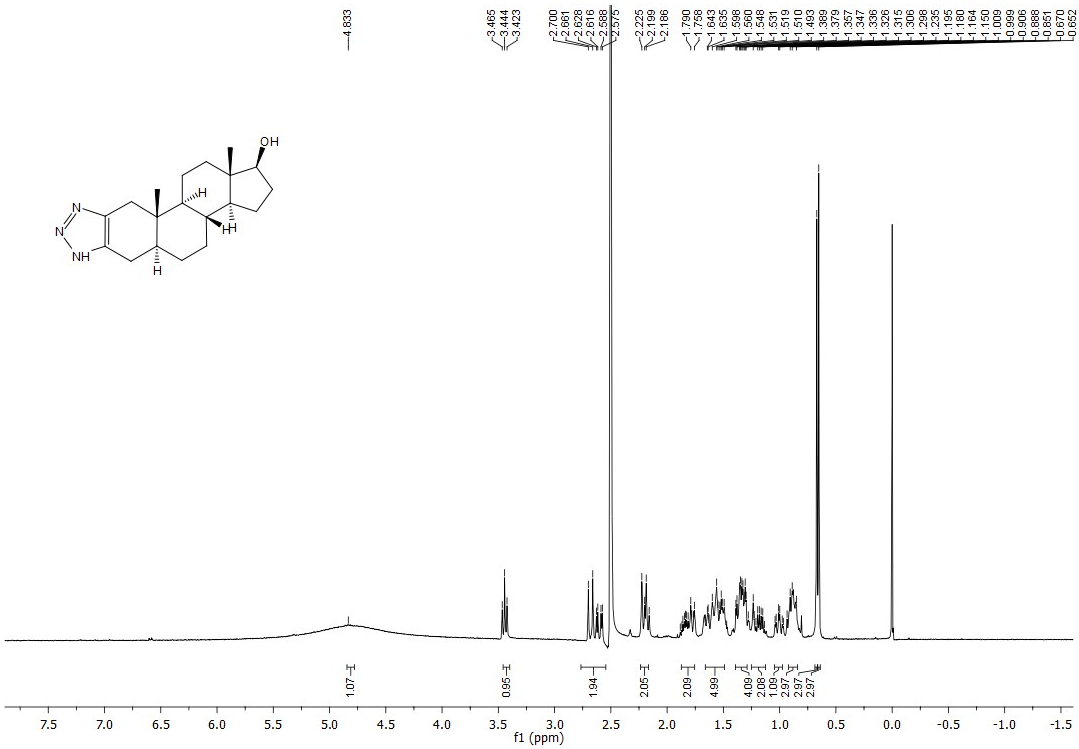
^{1}H NMR spectra of 9e (400 MHz, DMSO – d_6):



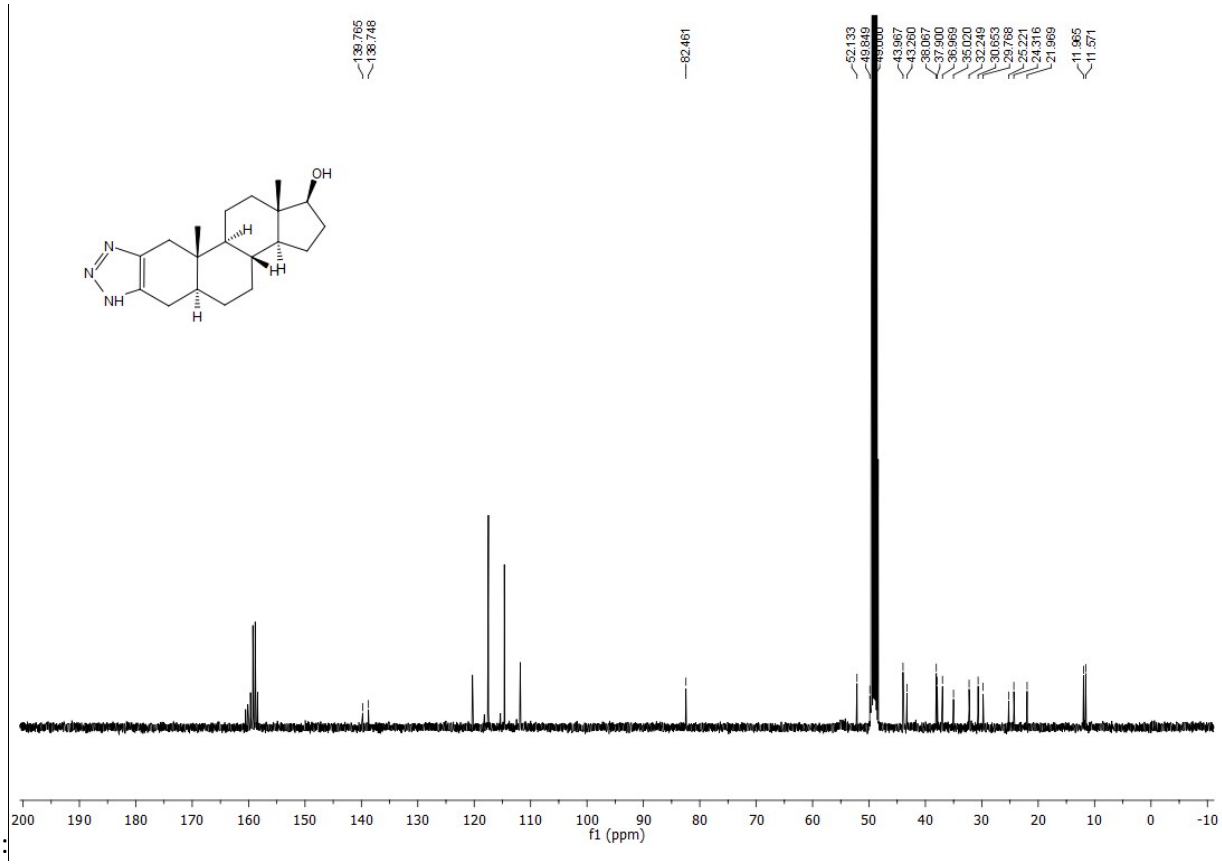
^{13}C NMR spectra of 9e (100 MHz, DMSO - d_6 + TFA, 1drop):



^{1}H NMR spectra of 9f (400 MHz, DMSO – d_6+ TFA, 1drop):



^{13}C NMR spectra of 9f (100 MHz, MeOD + TFA, 1drop)



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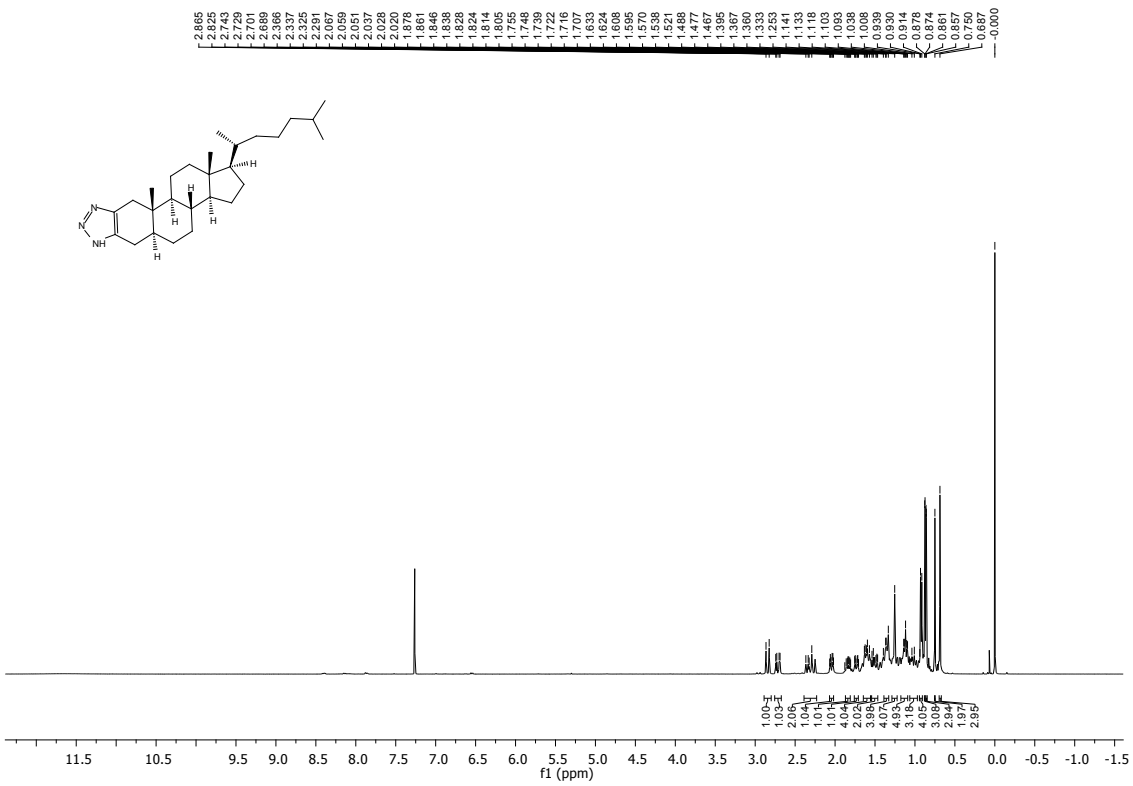
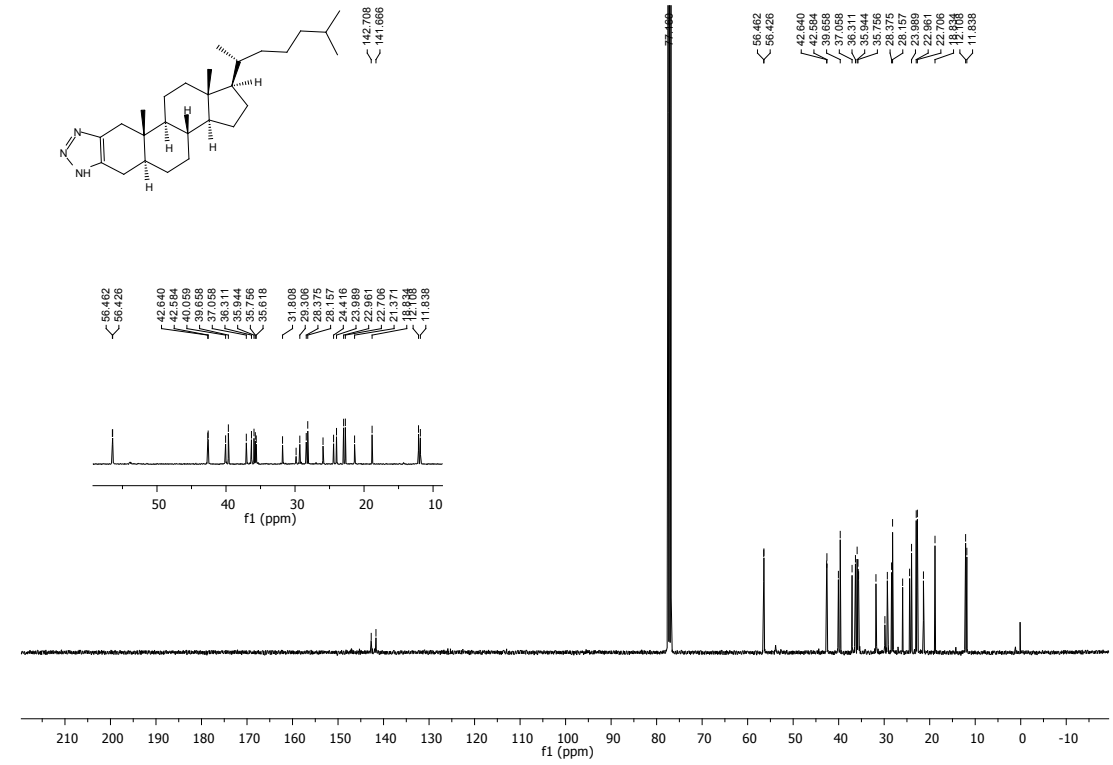
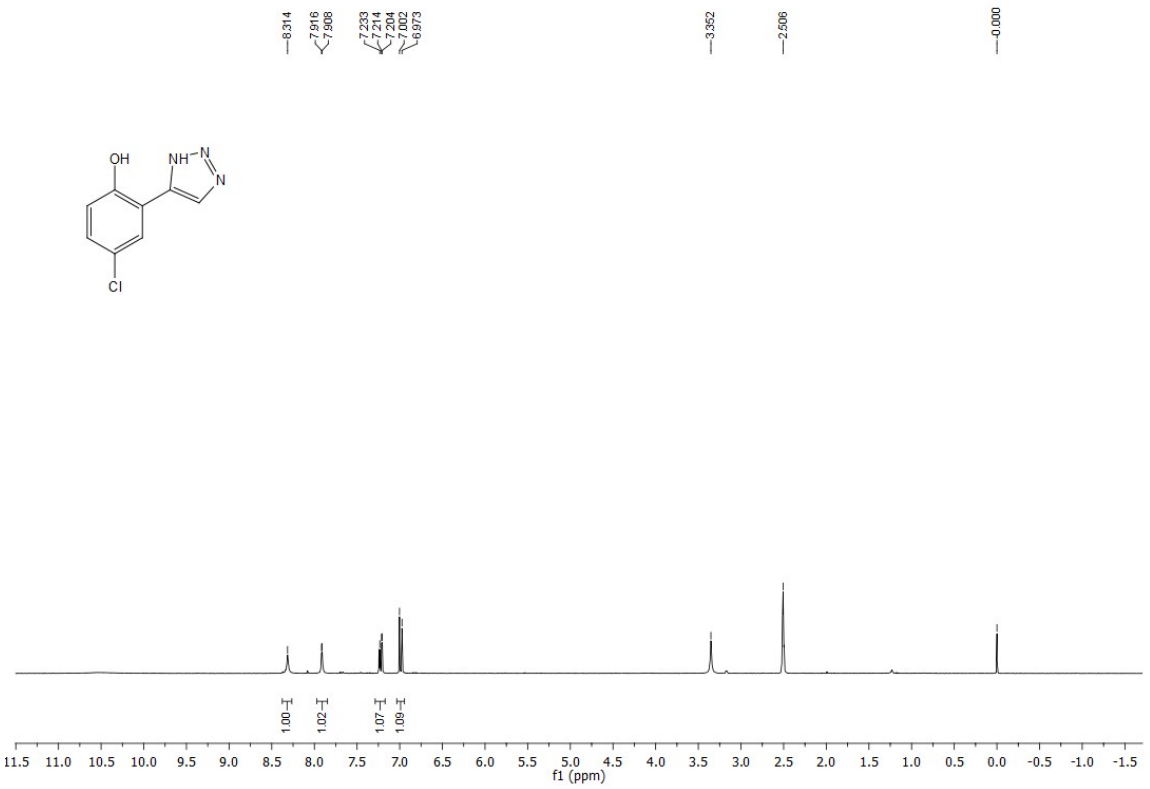
^{1}H NMR spectra of 9g (400 MHz, $CDCl_3$):



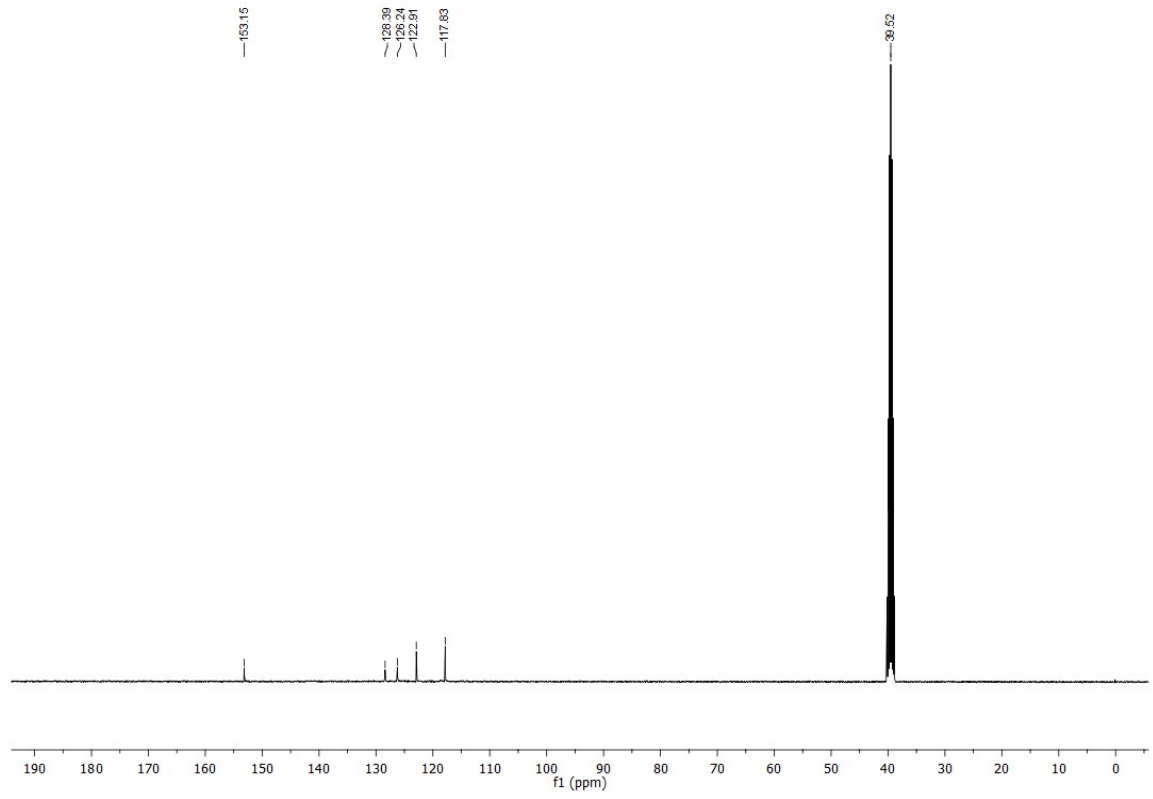
^{13}C NMR spectra of 9g (100 MHz, $CDCl_3$):



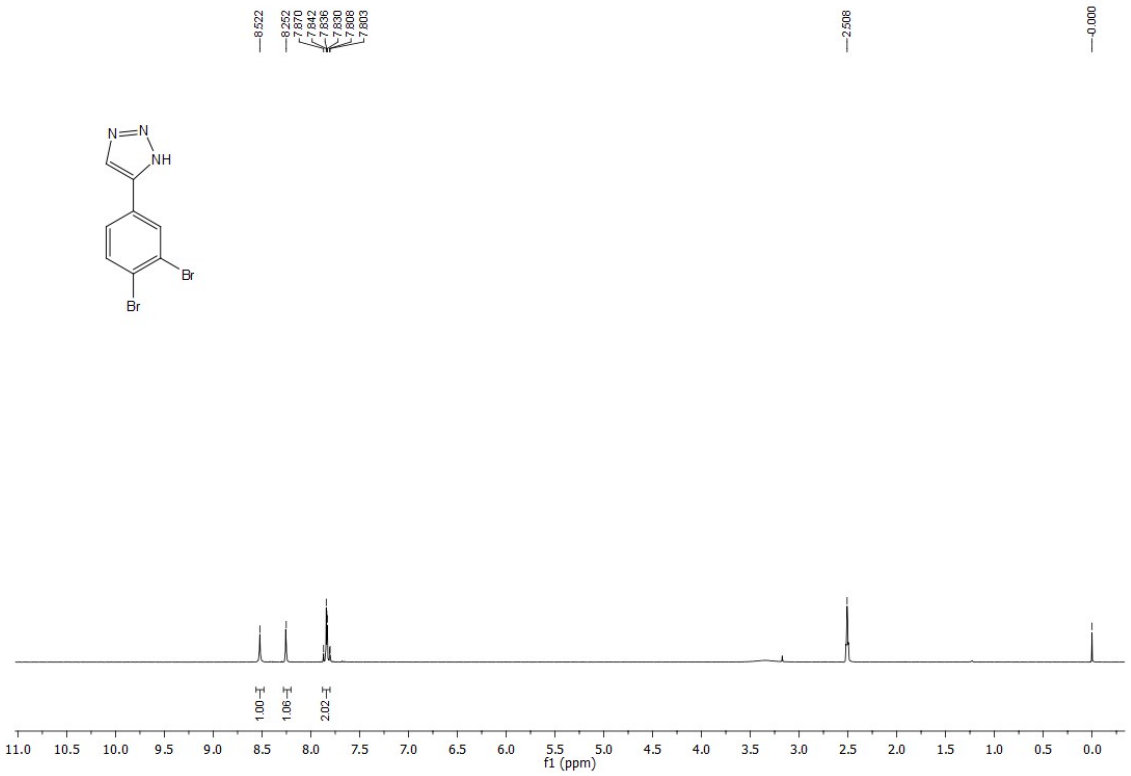
^{1}H NMR spectra of 12a (300 MHz, DMSO-d_6):



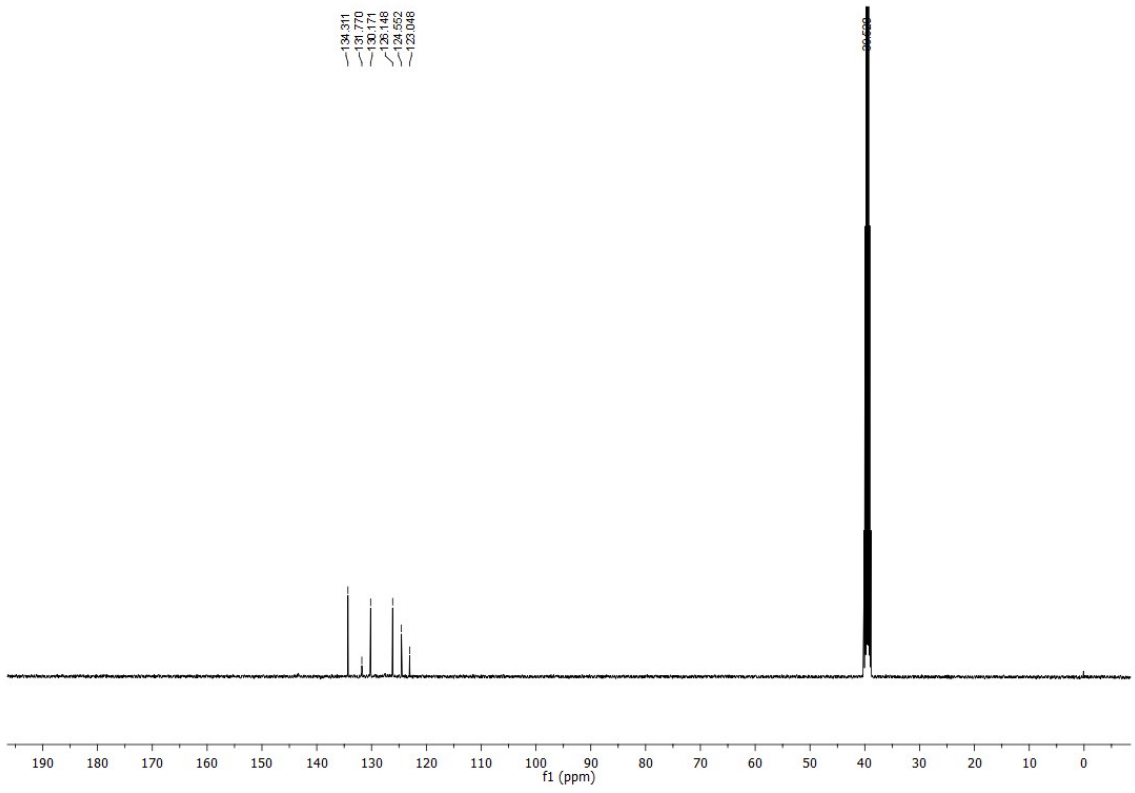
^{13}C NMR spectra of 12a (75 MHz, DMSO-d_6):



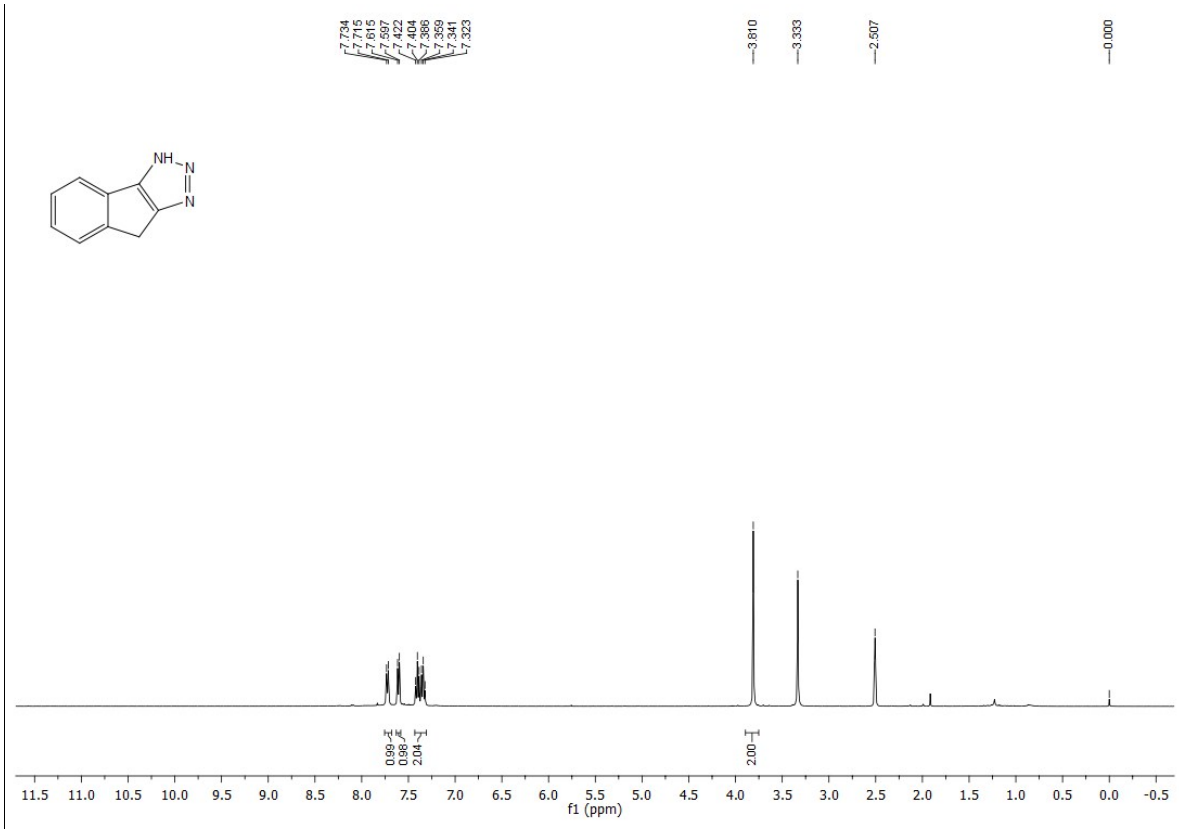
^{1}H NMR spectra of 12b (300 MHz, DMSO-d_6):



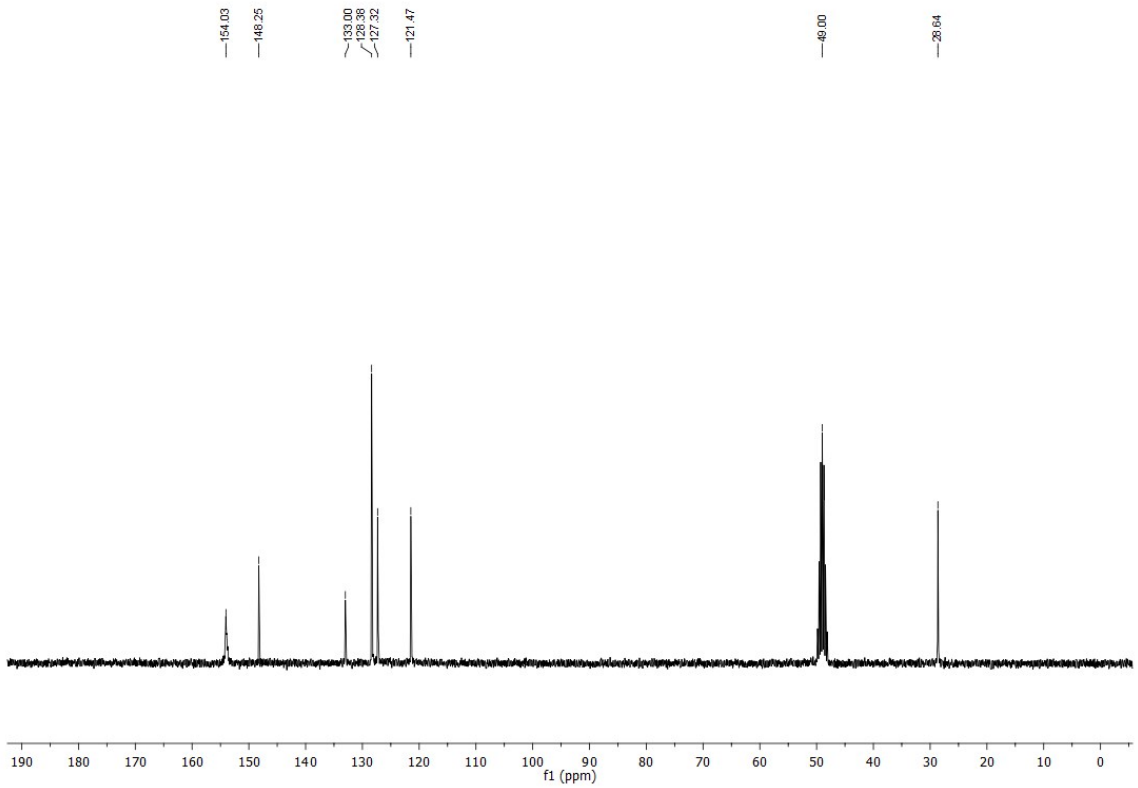
^{13}C NMR spectra of 12b (75 MHz, DMSO-d_6):



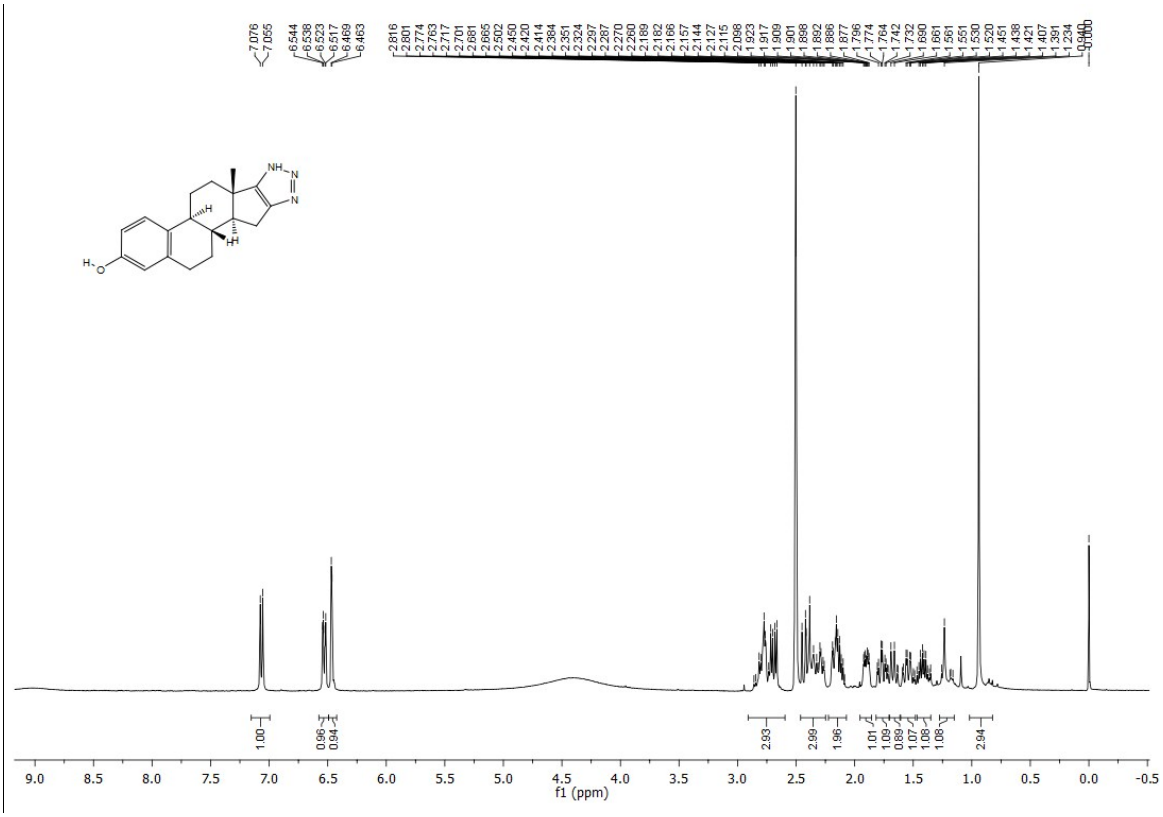
^{1}H NMR spectra of 12c (400 MHz, DMSO-d_6):



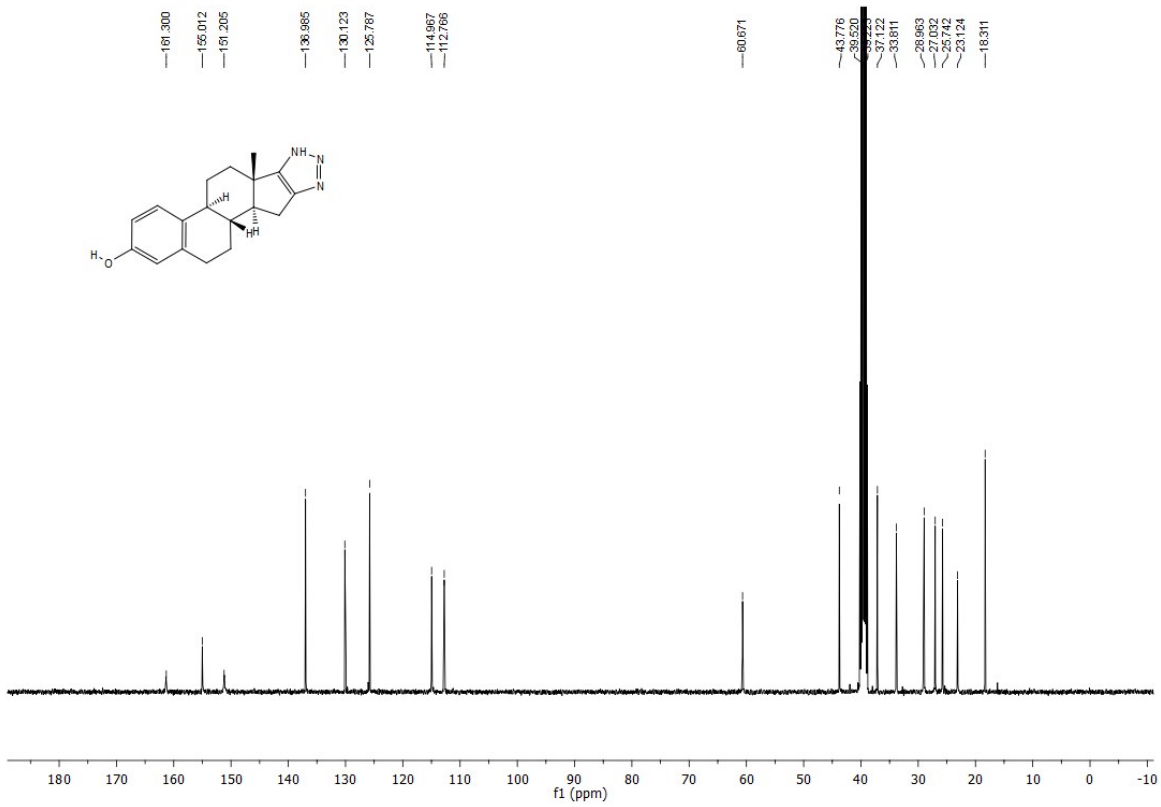
^{13}C NMR spectra of 12c (75 MHz, MeOD):



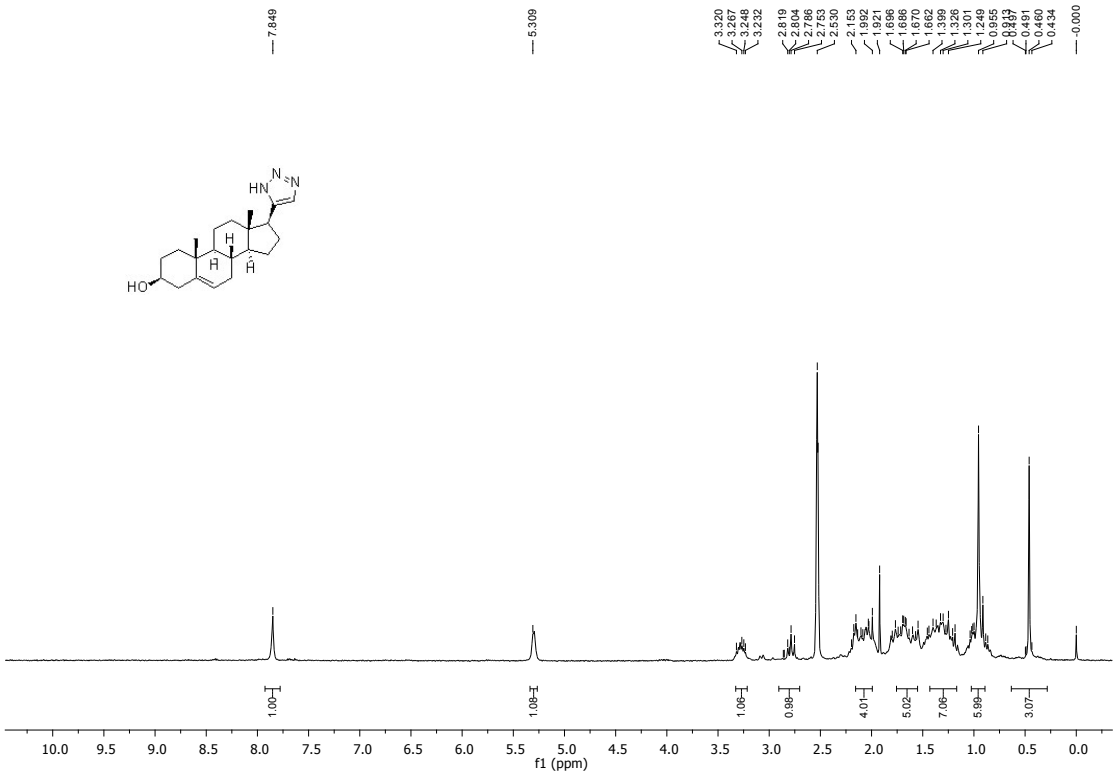
^{1}H NMR spectra of 12d (400 MHz, DMSO-d_6):



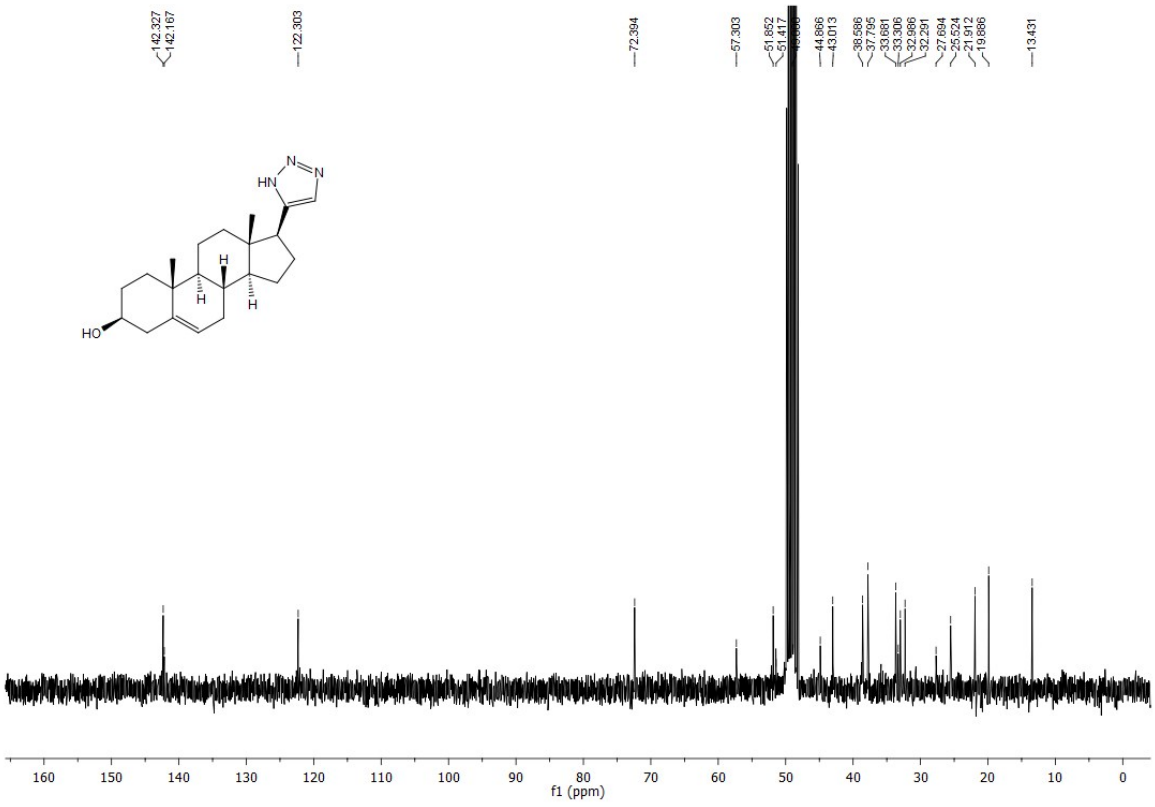
^{13}C NMR spectra of 12d (100 MHz, DMSO-d_6):



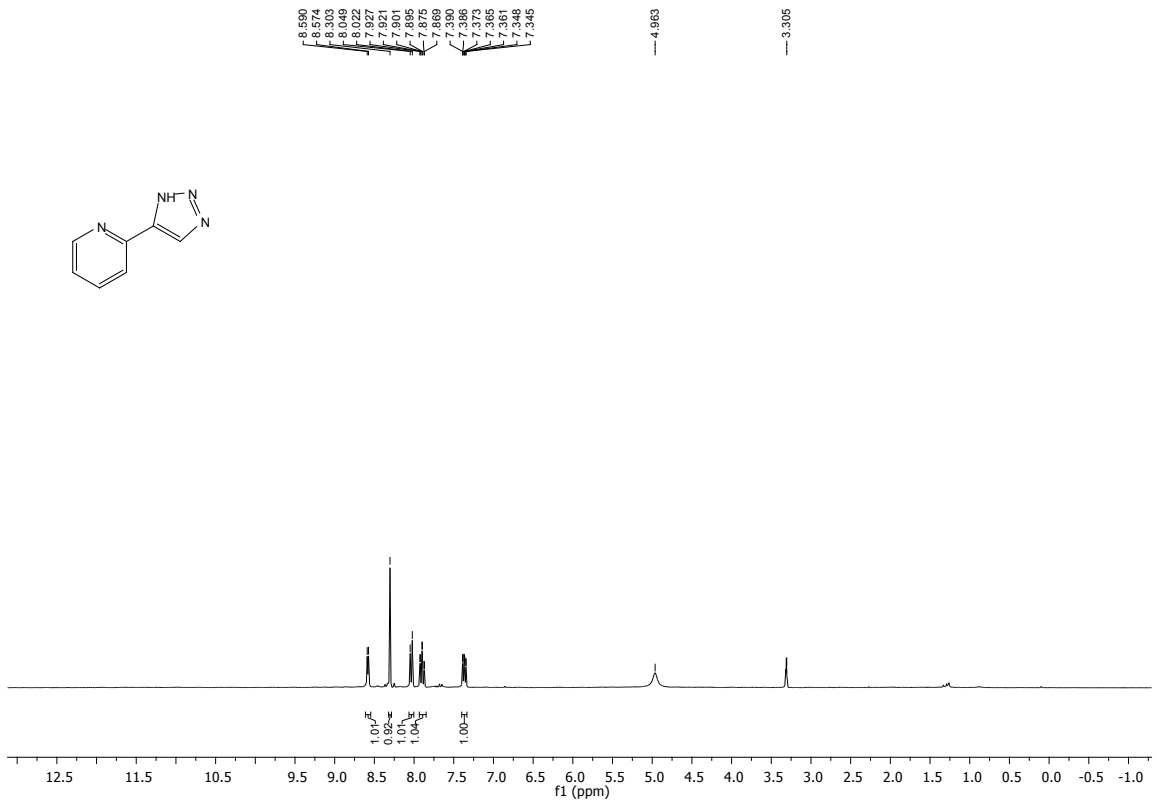
^{1}H NMR spectra of 12e (300 MHz, DMSO-d_6 + TFA, 1 drop):



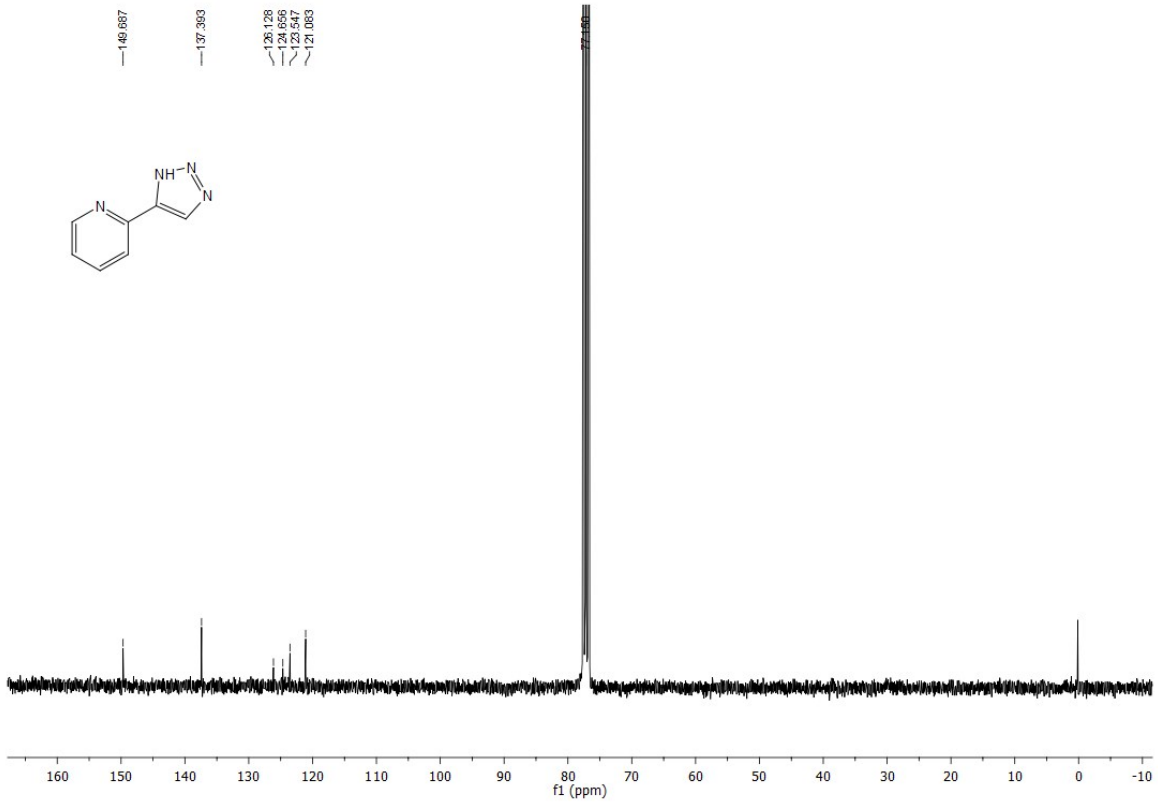
^{13}C NMR spectra of 12e (100 MHz, DMSO-d_6):



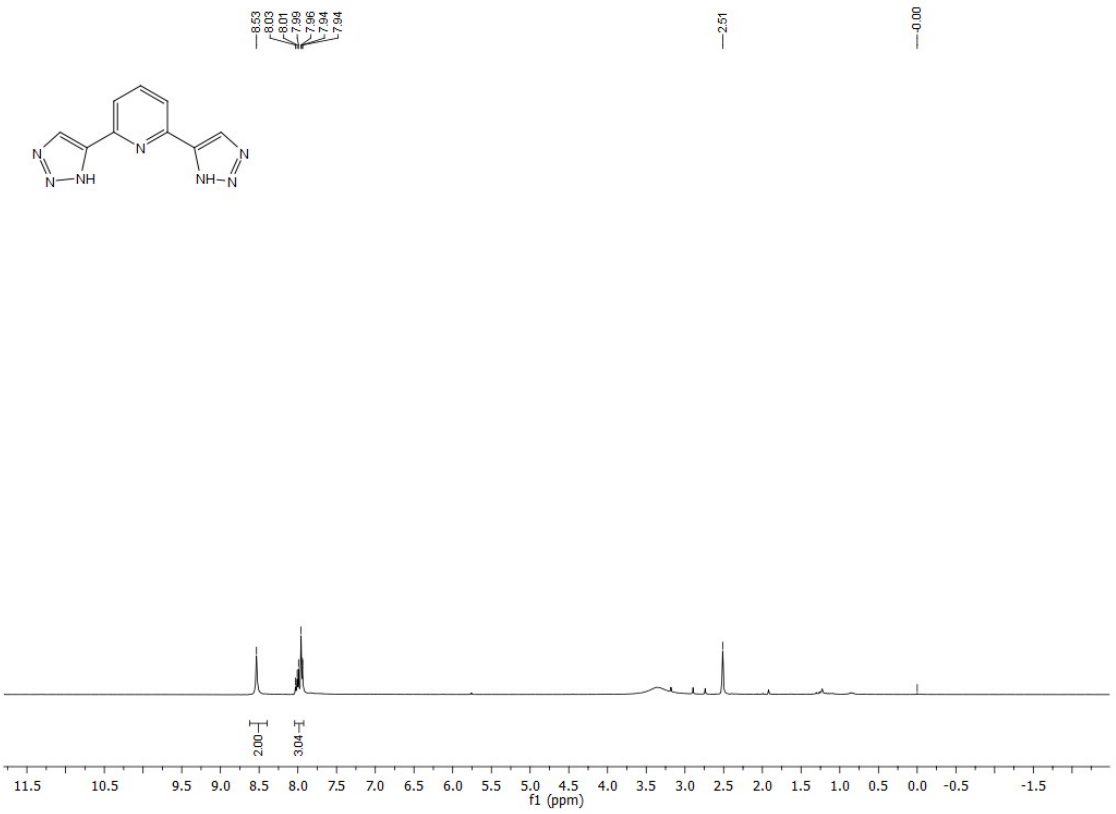
^{1}H NMR spectra of 12f (300 MHz, MeOD):



^{13}C NMR spectra of 12f (75 MHz, $CDCl_3$):



^{1}H NMR spectra of 12g (400 MHz, DMSO-d_6):



^{13}C NMR spectra of 12g (75 MHz, DMSO-d_6):