Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A general metal-free route towards the synthesis of 1,2,3-triazoles from readily available primary amines and ketones

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1. General experimental methods

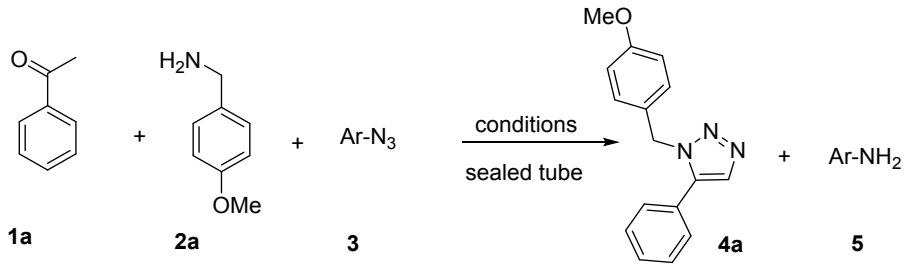
NMR spectra were acquired on commercial instruments (Bruker Avance 300 MHz, Bruker AMX 400 MHz or Bruker Avance II$^+$ 600 MHz) and chemical shifts (δ) are reported in parts per million (ppm) referenced to tetramethylsilane (^{1}H), or the internal (NMR) solvent signal (^{13}C). Mass spectra were acquired 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 (toluene) were used as received from commercial sources.

2. Optimization Studies

We started to investigate the optimization of reaction conditions by selecting acetophenone (**1a**) and 4-methoxybenzylamine (**2a**) as the model reagents with various diazo transfer reagents, catalysts and solvents to form 1,5-disubstituted triazole **4a** as summarized in Table S1. We presumed that the addition of 4 Å molecular sieves favors imine formation by effectively removing water from the carbonyl + amine $\rightleftharpoons$ imine + H_2O equilibrium[1]. Initial experiments were conducted *via* a MCR of these reagents in the presence of 4-nitrophenyl azide (**3a**) as the diazo-transfer reagent and 30 mol% of p-toluenesulfonic acid (TsOH) as the catalyst over 4 Å molecular sieves in toluene (0.4 mL, 1 molar) at 100°C in a sealed tube for 12 h (Table S1, entry 1). To our delight, this combination promoted the reaction with an excellent of yield of 80%. The use of **3b** as diazo transfer agent resulted in a significant reduction in the yield of the title compound **4a** to 25% (Table S1, entry 2). Subsequently, performing the reaction with other azido compounds that are known as diazo transfer reagents, such as **3c** and **3d** resulted in much lower efficiencies (Table S1, entries 3 & 4). One possible reason for this is the formation of corresponding sulfonamide as a side product which derived from the nucleophilic substitution reaction of **2a** with **3c** and **3d**. Interestingly, among the different Bronsted acid catalysts tried, CH_3COOH gave the best result (Table S1, entries 5-7). We then examined various stoichiometries of the building blocks and different loading of CH_3COOH catalyst on the reaction performance (Table S1, entries 8-10). The best result was obtained while using 1.4 equivalents of **2a** and 30 mol% of CH_3COOH catalyst, and the desired three-component-coupling product **4a** was obtained in 93% yield (Table S1, entries 10). When performing the reactions with secondary amine catalysts such as L-proline and morpholine:p-toluenesulfonic acid salt, however, lower yields were obtained (Table S1, entry 12 and 13). Next, we performed the reaction with other azido compounds analogous to **3a** such as 4-

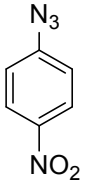
azidobenzonitrile **3e** (Table S1, entry 14) and ethyl 4-azidobenzoate (Table S1, entry 15) **3f.** These reactions of less electron poor aryl azides were less efficient than the ones performed with **3a** and also required longer reaction times for the complete consumption of the starting materials. Remarkably, this reaction also worked fine under acid free conditions without significantly affecting the yield of **4a** (85%) although the required reaction time was longer (24 h) (Table S1, entry 17). This observation can be viewed as an additional advantage as this transformation could also be extended to acid sensitive substrates. The yields of the reactions are also influenced by the solvent (Table S1, entries 18-24): MeCN (85%), THF (70%), $ClCH_2CH_2Cl$ (56%), DMSO (78%), DMF (67%), EtOH (74%), 1,4-dioxane (57%). Therefore, a three-component reaction of **1a**, **2a** and **3a** in a respective molar ratio of 1:1.4:1.1 using 30 mol% of acetic acid (8 mg, 0.13 mmol) as catalyst over 4 Å molecular sieves in 1 molar solution of toluene at 100°C in a sealed tube under argon atmosphere over a period of 12 h proved to be the conditions of choice.

Table S1: Optimization of reaction conditions for the organocatalyzed three-component reaction of acetophenone (**1a**),4-methoxybenzylamine (**2a**) and organic azides (**3a-d**).[a]

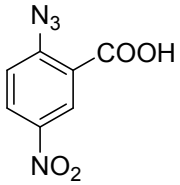


Entry	Ratio **1a**:**2a**:**3a**	Catalyst (mol%)	Ar-N_3	Solvent	isolated Yield[b]
1	1:1:1	TsOH (20)	**3a**	toluene	80
2	1:1:1	TsOH (20)	**3b**	toluene	25
3	1:1:1	TsOH (20)	**3c**	toluene	trace
4	1:1:1	TsOH (20)	**3d**	toluene	trace
5	1:1:1	CF_3COOH (20)	**3a**	toluene	81
6	1:1:1	NEt_3: TsOH (20)	**3a**	toluene	83
7	1:1:1	CH_3COOH (20)	**3a**	toluene	84
8	1:1.2:1	CH_3COOH (20)	**3a**	toluene	86
9	1:1.4:1	CH_3COOH (20)	**3a**	toluene	90
10	**1:1.4:1**	**CH_3COOH (30)**	**3a**	**toluene**	**93**
11[c]	1:1.4:1	CH_3COOH (30)	3a	toluene	90
12	1:1.4:1	*L*-proline (30)	**3a**	toluene	62
13	1:1.4:1	morpholine:TsOH (30)	**3a**	toluene	79
14[d]	1:1.4:1	CH_3COOH (30)	**3e**	toluene	65
15[e]	1:1.4:1	CH_3COOH (30)	**3f**	toluene	43
16	1:1.4:1	None	**3a**	toluene	71
17[f]	**1:1.4:1**	**None**	**3a**	**toluene**	**85**
18	1:1.4:1	CH_3COOH (30)	**3a**	CH_3CN	85
19	1:1.4:1	CH_3COOH (30)	**3a**	THF	70
20	1:1.4:1	CH_3COOH (30)	**3a**	$ClCH_2CH_2Cl$	56
21	1:1.4:1	CH_3COOH (30)	**3a**	DMSO	78
22	1:1.4:1	CH_3COOH (30)	**3a**	DMF	67
23	1:1.4:1	CH_3COOH (30)	**3a**	EtOH	74
24	1:1.4:1	CH_3COOH (30)	**3a**	1,4-dioxane	80

Ar-N_3 =



3a



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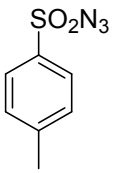

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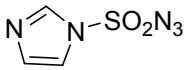

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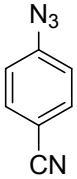
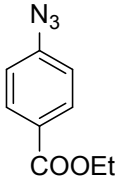


3e



3f

a] Reaction conditions: except where otherwise noted, **1a** is always in 0.42 mmol amount and the molar ratio of **2a** and **3a** is calculated on the basis of this, reaction temperature is 100°C, solvent (0.4 mL, 1 molar), 4 Å molecular sieves (30 mg) and reaction time is 12 h. [b] isolated yield after column chromatography. [c] reaction

performed without molecular sieves and reaction time is 20 h. [e] reaction time is 40 h. [f] reaction time is 56 h. [f] reaction time is 24 h. TsOH is *p*-toluenesulfonic acid.

2. Mechanistic studies

We conducted several control experiments to gain a better understanding about the mechanism of the reaction. After some optimization we found that the reaction of **1a** and **2a** under acid free conditions for 2 hours at 100 °C followed by the addition of an equivalent of **3a** at 50°C afforded the triazoline intermediate **6a** in 75% yield in 6 hours (Fig. S1a). Subjecting the same reaction using 30 mol% of acid yields the triazole **4a** (73%) as the sole product. This observation shows the high reactivity of the aminotriazoline intermediate **6a** under acidic conditions. Then, two separate experiments were conducted and monitored by ^{1}H NMR spectroscopy, with the isolated adduct **6a** in the presence and absence of the catalyst in $CDCl_3$ at 65° C in a NMR tube (Fig. S1b). Interestingly, the reaction in the presence of acid was complete after 3 hours and exclusively yielded the expected products **4a** and **5a** in 1:1 ratio, presumably as a result of protonation of the N-3 of the aminotriazoline intermediate **6a** followed by a ring opening/ring closure sequence (Fig. S1c). On the other hand, in the case of acid-free conditions, the reaction proceeded very slowly and complete conversion at 65°C was observed only after 40 hours. Furthermore, we monitored a one-pot reaction starting from **1a**, **2a** and **3a** under acidic conditions (30% AcOH) at 65°C and the reaction was finished only after 48 hours. This observation demonstrated convincingly that the Schiff base formation is slow at this temperature. Taken together, the results of these experiments are in agreement with the hypothesis that imine/enamine formation is the rate determining step. We presume that the imine/enamine species is in equilibrium with the starting material **1a** and **2a**, and the formation of the key intermediate **6a** from a 3+2 cycloaddition reaction between transiently generated enamine and **3a** displaces this equilibrium. Thus this overall process could be considered as an application of thermodynamically controlled dynamic covalent chemistry.

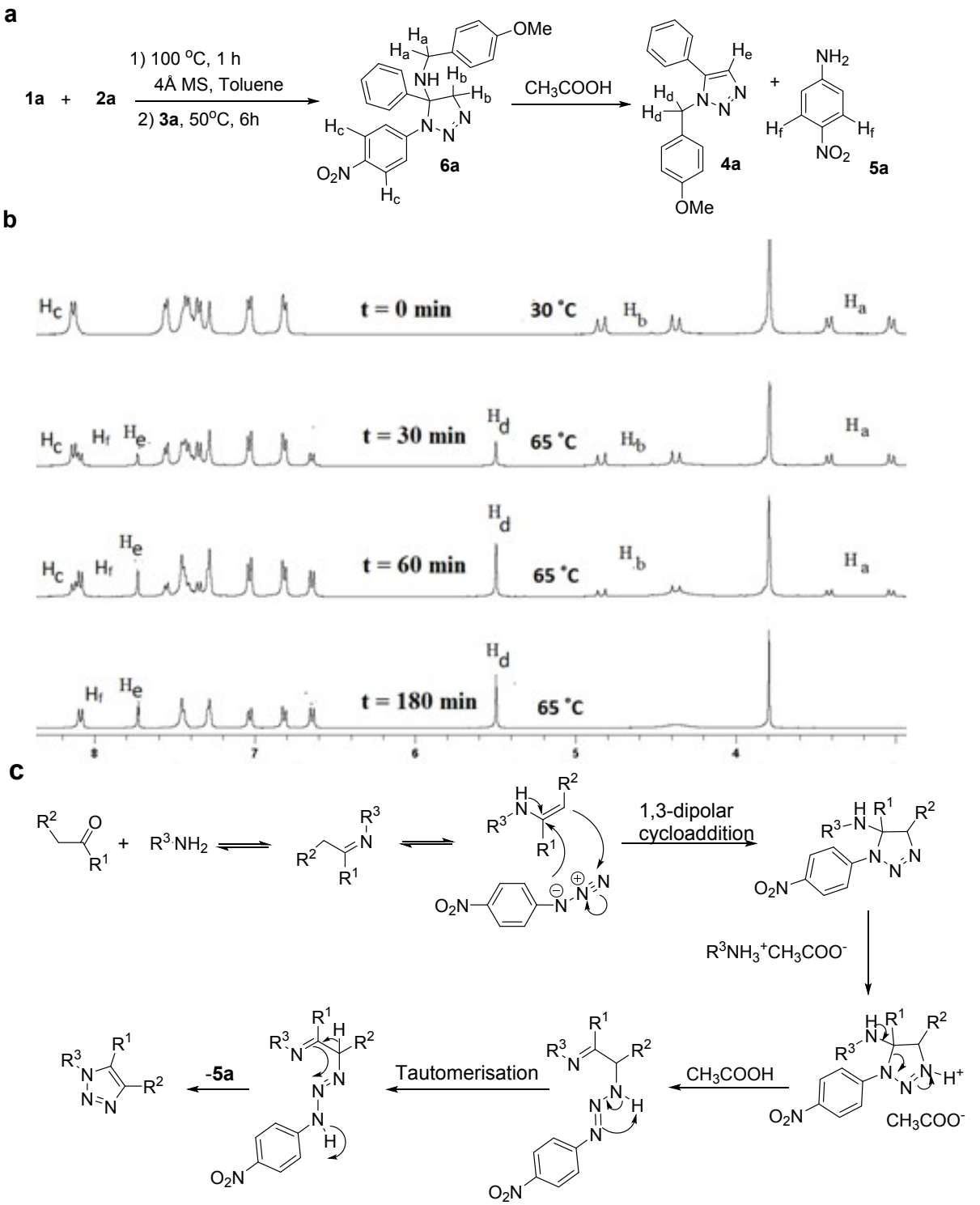


Figure S1. Proposed mechanistic experiments and catalytic cycles. a) Scheme showing the synthesis of the triazoline intermediate **6a** and its subsequent conversion to **4a** and **5a**. b) The ^{1}H NMR spectra showing the clean formation of the triazole **4a** and **5a** upon heating the triazoline intermediate **6a** in presence of 8 mol% of CH_3COOH in $CDCl_3$ at 65 °C. c) Postulated mechanism. $R^3NH_3^+CH_3COO^-$ indicates the *in situ* formation of the organic salt when CH_3COOH reacts with R^3NH_2.

4. Experimental Procedures

4.1 Preparation of azides

4-Nitrophenyl azide, 3a. 4-Nitroaniline (28.0 g, 0.20 mol) was suspended 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 (31.48 g). Spectroscopic data for **3a** was consistent with previously reported data for this compound[2].

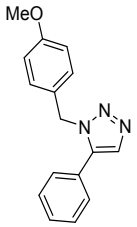
2-Azido-5-nitrobenzoic acid, 3b. This compound has been prepared according to the procedure reported by Smith et al. Material identity was confirmed by MS, ^1H and ^{13}C NMR[3].

Imidazole-1-sulfonyl azide, 3d. This compound has been prepared according to the procedure reported by Goddard-Borger et al. Material identity was confirmed by MS, ^1H and ^{13}C NMR[4].

CAUTION: As organic azides are potentially explosive, all aryl azides have been stored in the freezer in the dark.

4.2 General procedure for the preparation of substituted 1,2,3-triazoles.

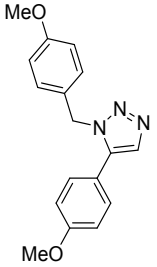
To an oven-dried screw-capped reaction tube equipped with a magnetic stirring bar was added the ketone, amine, 4-nitrophenyl azide (**3a**), acetic acid (0-30 mol%) and 4 Å molecular sieves (50 mg). The mixture was dissolved in the proper solvent and stirred at 100 °C for 12-72 hours. The crude reaction mixture was then directly purified by column chromatography (silica gel) at first with CH_2Cl_2 as eluent to remove all 4-nitroaniline formed during the reaction followed by using a mixture of heptane and ethyl acetate as eluent to afford the corresponding 1,2,3-triazoles as off-white solids or semi-solids.



4a: 93% yield

1-(4-Methoxybenzyl)-5-phenyl-1H-1,2,3-triazole (4a): Acetophenone (50 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) affording **4a** (103 mg, 93% yield) as an off white semi-solid.

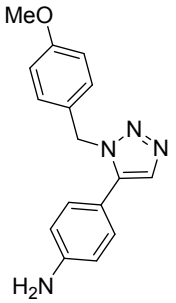
^1H NMR (300 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.45 - 7.42 (m, 3H), 7.28 - 7.25 (m, 2H), 7.01 (d, 2H, *J* = 8.6 Hz), 6.79 (d, 2H, *J* = 8.7 Hz), 5.48 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 138.1, 133.4, 129.6, 129.1, 129.0, 128.8, 127.6, 127.1, 114.3, 55.4, 51.5; MS (EI): m/z: 265 (M^+); HRMS (ESI^+): m/z calcd for $C_{16}H_{16}N_3O$ $[M+H]^+$: 266.1287, found 266.1284. Spectroscopic data for **4a** are consistent with previously reported data for this compound[5].



4b: 89% yield

1-(4-Methoxybenzyl)-5- (4-methoxyphenyl)-1H-1,2,3-triazole (4b): 4-Methoxy acetophenone (63 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) affording **4b** (110 mg, 89% yield) as an off white semi-solid.

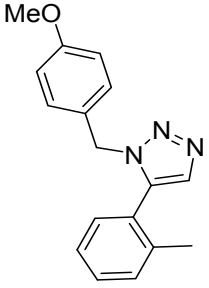
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.18 (d, 2H, *J* = 8.5 Hz), 7.03 (d, 2H, *J* = 8.5 Hz), 6.94 (d, 2H, *J* = 8.6 Hz), 6.81 (d, 2H, *J* = 8.6 Hz), 5.45 (s, 2H), 3.85 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.6, 159.5, 137.8, 133.1, 130.4, 128.7, 127.8, 119.2, 114.5, 114.2, 55.5, 55.3, 51.3; MS (EI): m/z: 295 (M^+); HRMS (ESI$^+$): m/z calcd for $C_{17}H_{18}N_3O_2$ $[M+H]^+$: 296.1393, found 296.1399. Spectroscopic data for **4b** are consistent with previously reported data for this compound[5].



4c: 68% yield

4-(1- (4-Methoxybenzyl)-1H-1,2,3-triazol-5-yl)aniline (4c): 4-Aminoacetophenone (56 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 40 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 4:6) affording **4c** (79 mg, 68% yield) as an off white semi-solid.

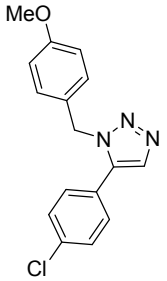
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.06 - 7.03 (m, 4H), 6.81 (d, 2H, *J* = 8.2 Hz), 6.69 (d, 2H, *J* = 7.9 Hz), 5.44 (s, 2H), 3.89 (s_{br}, 1H), 3.78 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 147.7, 138.4, 132.9, 130.2, 128.8, 128.0, 116.5, 115.1, 114.2, 55.4, 51.2; MS (EI): m/z: 280 (M^+); HRMS (ESI$^+$): m/z calcd for $C_{16}H_{17}N_4O$ $[M+H]^+$: 281.1397, found 281.1396.



4d: 88% yield

1-(4-Methoxybenzyl)-5- (o-tolyl)-1H-1,2,3-triazole (4d): 2-Methylacetophenone (56 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) affording **4d** (103 mg, 88% yield) as an off white semi-solid.

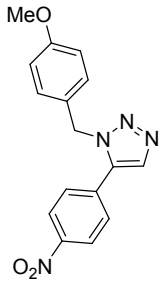
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.40 - 7.35 (m, 1H), 7.23 (d, 2H, *J* = 7.0 Hz), 7.04 (d, 1H, *J* = 7.5 Hz), 6.87 (d, 2H, *J* = 8.95 Hz), 6.71 (d, 2H, *J* = 8.74 Hz), 5.27 (s, 2H), 3.75 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.60, 138.1, 136.5, 133.9, 130.5, 130.0, 129.5, 127.1, 126.7, 126.0, 114.0, 55.4, 51.6, 19.7; MS (EI): m/z: 279 (M^+); HRMS (ESI^+): m/z calcd for $C_{17}H_{18}N_3O$ $[M+H]^+$: 280.1444, found 280.1445.



4e: 79% yield

5-(4-Chlorophenyl)-1- (4-methoxybenzyl)-1H-1,2,3-triazole (4e): 4-Chloroacetophenone (64 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) affording **4e** (98 mg, 79% yield) as an off-white solid. m.p. 56 - 57 ˚C.

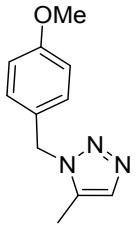
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.40 (d, 2H, *J* = 8.1 Hz), 7.18 (d, 2H, *J* = 8.5 Hz), 6.91 (d, 2H, *J* = 8.6 Hz), 6.80 (d, 2H, *J* = 8.7 Hz), 5.46 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 136.9, 135.9, 133.6, 130.4, 129.3, 128.7, 127.4, 125.6, 114.4, 55.4, 51.6; MS (EI): m/z: 299 (M^+); HRMS (ESI^+): m/z calcd for $C_{16}H_{16}ClN_4O$ $[M+H]^+$: 300.0899, found 300.0896.



4f: 62% yield

1-(4-Methoxybenzyl)-5- (4-nitrophenyl)-1H-1,2,3-triazole (4f): 4-Nitroacetophenone (69 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 40 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) affording **4f** (80 mg, 62% yield) as an off-white solid m.p. 86 - 87 ˚C.

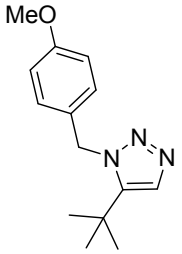
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (d, 2H, *J* = 8.7 Hz), 7.82 (s, 1H), 7.46 (d, 2H, *J* = 8.5 Hz), 7.00 (d, 2H, *J* = 8.5 Hz), 6.81 (d, 2H, *J* = 8.6 Hz), 5.54 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 148.4, 135.9, 134.2, 133.6, 129.9, 128.6, 126.9, 124.2, 114.5, 55.4, 52.1; MS (EI): m/z: 310 (M^+); HRMS (ESI^+): m/z calcd for $C_{16}H_{15}N_4O_3$ $[M+H]^+$: 311.1138, found 311.1130.



4g: 62% yield

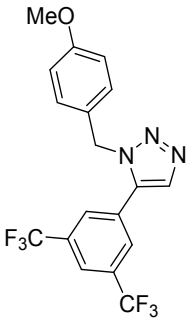
1-(4-Methoxybenzyl)-5-methyl-1H-1,2,3-triazole (4g): Acetone (72 mg, 1.26 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) affording **4g** (52 mg, 62% yield) as an off-white solid. m.p. 69 - 70 ˚C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.12 (d, 2H, *J* = 8.5 Hz), 6.87 (d, 2H, *J* = 8.5 Hz), 5.43 (s, 2H), 3.79 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 133.6, 132.7, 128.8, 126.9, 114.4, 55.4, 51.3, 8.6; MS (EI): m/z: 203 (M^+); HRMS (ESI^+): m/z calcd for $C_{11}H_{14}N_3O$ $[M+H]^+$: 204.1131, found 204.1131.



4h: 83% yield

5-Tert-butyl-1- (4-methoxybenzyl)-1H-1,2,3-triazole (4h): Pinacolone (41 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) affording **4h** (85 mg, 83% yield) as an off white semi-solid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (s, 2H), 7.02 (d, 2H, *J* = 8.8 Hz), 6.84 (d, 2H, *J* = 8.8Hz), 5.63 (s, 2H), 3.78 (s, 3H), 1.29 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 145.5, 131.7, 128.2, 128.0, 114.3, 55.4, 52.6, 30.4, 30.0; MS (EI): m/z: 245 (M^+); HRMS (ESI^+): m/z calcd for $C_{14}H_{20}N_3O$ $[M+H]^+$: 246.1601, found 246.1601.

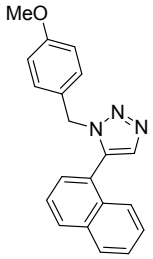


4i: 70% yield

5-(3,5-Bis (trifluoromethyl)phenyl)-1- (4-methoxybenzyl)-1H-1,2,3-triazole (4i): 3´,5´-Bis (trifluoromethyl)acetophenone (107 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-

nitrophenyl azide (68 mg, 0.42 mmol), (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) affording **4i** (117 mg, 70% yield) as an off white solid. m.p. 70 - 71 ˚C.

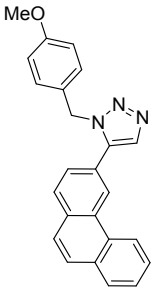
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.82 (s, 1H), 7.63 (s, 2H), 7.02 (d, 2H, *J* = 8.5 Hz), 6.81 (d, 2H, *J* = 8.7 Hz), 5.50 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.0, 135.2, 134.3, 132.8, 132.3, 129.5, 129.3, 128.8, 126.6, 124.7, 123.3, 121.0, 114.6, 55.4, 52.4; MS (EI): m/z: 401 (M^+); HRMS (ESI^+): m/z calcd for $C_{18}H_{14}F_6N_3O$ $[M+H]^+$: 402.1035, found 402.1039.



4J: 80% yield

1-(4-Methoxybenzyl)-5- (1-naphthyl)-1H-1,2,3-triazole (4j): 1-Acetonaphthone (71 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) affording **4j** (105 mg, 80% yield) as an off white semi-solid.

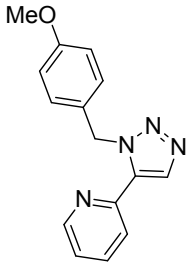
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 - 7.90 (m, 2H), 7.78 (s, 1H), 7.53 - 7.21 (m, 5H), 6.75 (d, 2H, *J* = 8.6 Hz), 6.61 (d, 2H, *J* = 8.6 Hz), 5.26 (s, 2H), 3.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 135.8, 134.9, 133.6, 132.1, 130.4, 129.4, 129.0, 128.6, 127.3, 127.1, 126.6, 125.1, 124.9, 124.6, 113.9, 55.3, 51.9; MS (EI): m/z: 315 (M^+); HRMS (ESI^+): m/z calcd for $C_{20}H_{18}N_3O$ $[M+H]^+$: 316.1444, found 316.1444.



4K: 91% yield

1-(4-Methoxybenzyl)-5- (3-phenanthryl)-1H-1,2,3-triazole (4k): 3-Acetyl phenantherene (92 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) affording **4k** (138 mg, 91% yield) as an off white solid. m.p. 164 - 165 ˚C.

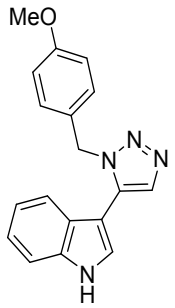
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.24 (d, 1H, *J* = 7.2 Hz), 7.94 (t, 2H, *J* = 8.3 Hz), 7.88 (s, 1H), 7.84 - 7.75 (m, 2H), 7.66 - 7.58 (m, 2H), 7.50 (d, 1H, *J* = 8.3 Hz), 7.11 (d, 2H, *J* = 8.7 Hz), 6.85 (d, 2H, *J* = 8.7 Hz), 5.57 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 138.5, 133.7, 132.4, 132.4, 130.3, 129.9, 129.4, 128.9, 128.8, 128.6, 128.1, 127.4, 127.1, 126.9, 126.4, 124.9, 123.8, 122.8, 114.5, 55.5, 51.8; MS (EI): m/z: 365 (M^+); HRMS (ESI^+): m/z calcd for $C_{24}H_{20}N_3O$ $[M+H]^+$: 366.1601, found 366.1606.



4l: 82% yield

2-(1-(4-Methoxybenzyl)-1H-1,2,3-triazol-5-yl)pyridine(4l): 2- Acetyl pyridine (51 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 3:7) affording **4l** (91 mg, 82% yield) as an off white solid. m.p. 73 - 74 ˚C.

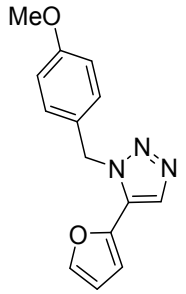
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.72 (d, 1H, *J* = 4.7 Hz), 7.98 (s, 1H), 7.77 - 7.71 (m, 1H), 7.55 - 7.52 (m, 1H), 7.31 - 7.27 (m, 1H), 7.20 (d, 2H, *J* = 8.3), 6.77 - 6.74 (m, 2H), 6.09 (s, 2H), 3.73 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 149.6, 147.2, 137.1, 135.5, 133.8, 129.5, 128.3, 123.4, 122.9, 113.9, 55.3, 52.6; MS (EI): m/z: 266 (M^+); HRMS (ESI^+): m/z calcd for $C_{15}H_{15}N_4O$ $[M+H]^+$: 267.1240, found 267.1241.



4m: 83% yield

3-(1- (4-Methoxybenzyl)-1H-1,2,3-triazol-5-yl)-1H-indole (4m): 3-Acetyl indole (67mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 5:5) affording **4m** (106 mg, 83% yield) as an off white solid. m.p. 192 - 193 ˚C.

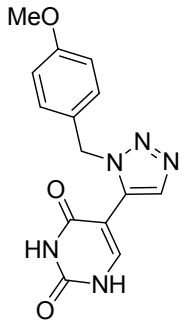
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.57 (s_{br}, 1H), 7.89 (s, 1H), 7.54 (d, 1H, *J* = 7.9 Hz), 7.46 (d, 1H, *J* = 8.1 Hz), 7.33 - 7.19 (m, 3H), 7.05 - 7.00 (m, 3H), 6.80 (d, 2H, *J* = 8.7 Hz), 5.53 (s, 2H), 3.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 136.0, 133.7, 132.6, 131.8, 128.5, 128.2, 126.3, 124.2, 123.4, 121.3, 119.3, 114.3, 111.7, 55.4, 51.4; MS (EI): m/z: 304 (M^+); HRMS (ESI^+): m/z calcd for $C_{18}H_{17}N_4O$ $[M+H]^+$: 305.1397, found 305.1395.



4n: 68% yield

5-(Furan-2-yl)-1- (4-methoxybenzyl)-1H-1,2,3-triazole (4n): 2- Acetyl furan (46 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) affording **4n** (96 mg, 68% yield) as an off white semi-solid.

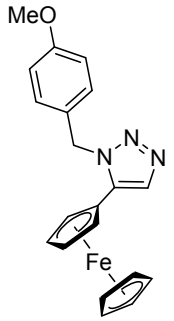
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.55 - 7.54 (m, 1H), 7.13 (d, 2H, *J* = 88 Hz), 6.82 (d, 2H, *J* = 8.8 Hz), 6.53 - 6.48 (m, 2H), 5.71 (s, 2H), 3.77 (s, 3H); ^{13}CNMR (75 MHz, $CDCl_3$) δ 159.6, 143.7, 141.5, 132.5, 128.9, 128.8, 127.3, 114.3, 111.9, 110.5, 55.4, 52.5; MS (EI): m/z: 255 (M^+); HRMS (ESI^+): m/z calcd for $C_{14}H_{14}N_3O_2$ $[M+H]^+$: 256.1080, found 256.1082.



4o: 67% yield

5-(1- (4-Methoxybenzyl)-1H-1,2,3-triazol-5-yl)pyrimidine-2,4 (1H,3H)-dione (4o): 5-Acetyluracil (64 mg, 0.42 mmol), 4-methoxybenzylamine (77 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), 4 Å molecular sieves (50 mg) and DMF (0.6 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by DCM/MeOH = 95:5) affording **4o** (83 mg, 67% yield) as an off-white solid. m.p. 253 - 254 ˚C.

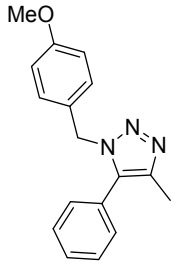
^{1}H NMR (300 MHz, *d6*-DMSO) δ 8.28 (s, 1H), 7.67 (s, 1H), 7.56 (s, 1H), 7.05 (d, 2H, *J* = 8.6 Hz), 6.85 (d, 2H, *J* = 8.6 Hz), 5.45 (s, 2H), 3.71 (s, 3H); ^{13}C NMR (75 MHz *d6*-DMSO) δ 162.3, 158.8, 151.7, 144.8, 137.5, 134.1, 129.7, 129.1, 127.8, 113.9, 55.1, 51.3; MS (EI): m/z: 299 (M^+); HRMS (ESI^+): m/z calcd for $C_{14}H_{14}N_5O_3$ $[M+H]^+$: 300.1091, found 300.1096.



4p: 79% yield

1-(4-Methoxybenzyl)-5-ferrocenyl-1H-1,2,3-triazole (4p): 1-Acetylferrocene (100 mg, 0.42 mmol), 4-methoxybenzylamine (168 mg, 1.2 mmol), 4-nitrophenyl azide (143 mg, 0.88 mmol), 4 Å molecular sieves (50 mg) and toluene (1 mL). Reaction time is 72 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by by heptane/EtOAc = 2:8) affording **4p** (130 mg, 79% yield) as a red semi solid.

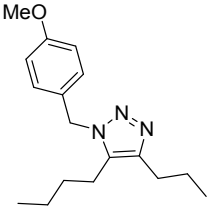
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.03 (d, 2H, *J* = 8.5 Hz), 6.86 (d, 2H, *J* = 8.5 Hz), 5.58 (s, 2H), 4.37 (s, 2H), 4.32 (s, 2H), 4.08 (s, 4H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 136.3, 133.1, 128.1, 127.9, 114.4, 70.9, 69.8, 69.6, 68.6, 55.4, 51.3; MS (EI): m/z: 373 (M^+); HRMS (ESI^+): m/z calcd for $C_{20}H_{20}FeN_3O$ $[M+H]^+$: 374.0950, found 374.0958.



4q: 83% yield

1-(4-Methoxybenzyl)-5-methyl-1H-1,2,3-triazole-4-carbaldehyde (4q): Propiophenone (56 mg,0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) affording **4q** (96 mg, 83% yield) as an off-white solid. m.p. 74 - 75 ˚C.

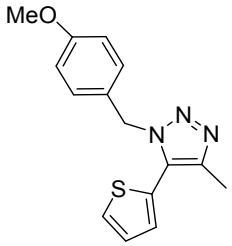
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 -7.42 (m, 3H), 7.17 - 7.13 (m, 2H), 6.99 - 6.94 (m, 2H), 6.79 - 6.74 (m, 2H), 5.35 (s, 2H), 3.76 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 141.7, 134.5, 129.7, 129.3, 129.0, 128.9, 127.8, 127.7, 114.1, 55.4, 51.7, 10.7; MS (EI): m/z: 279 (M^+); HRMS (ESI^+): m/z calcd for $C_{17}H_{18}N_3O$ $[M+H]^+$: 280.1444, found 280.1443.



4r: 78% yield

5-Butyl-1- (4-methoxybenzyl)-4-propyl-1H-1,2,3-triazole (4r): 5-nonanone (59 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) affording **4r** (94 mg, 78% yield) as an off white semi-solid.

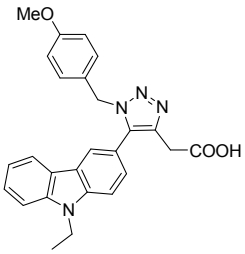
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 (d, 2H, *J* = 8.67 Hz), 6.85 (d, 2H, *J* = 8.67 Hz), 5.40 (s, 2H), 3.79 (s, 3H), 2.56 (t, 2H, *J* = 7.53 Hz), 2.46 (t, 2H, *J* = 7.71 Hz), 1.74 - 1.64 (m, 4H), 1.28 - 1.25 (m, 2H), 0.95 (t, 3H, *J* = 7.35 Hz), 0.87 - 0.82 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 145.5, 133.2, 128.6, 127.7, 114.4, 55.4, 51.62, 31.0, 27.3, 23.0, 22.6, 22.4, 14.1, 13.8; MS (EI): m/z: 287 (M^+); HRMS (ESI^+): m/z calcd for $C_{17}H_{26}N_3O$ $[M+H]^+$:288.2070, found 288.2072.



4s: 89% yield

1-(4-Methoxybenzyl)-4-methyl-5- (thiophen-2-yl)-1H-1,2,3-triazole (4s): 2- Propanoyl thiophene (59 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc =6:4) affording **4s** (106 mg, 89% yield) as an off white semi-solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 - 7.47 (m, 1H), 7.13 - 7.10 (m, 1H), 7.01 (d, 2H, *J* = 8.5 Hz), 6.95 - 6.94 (m, 1H), 6.80 (d, 2H, *J* = 8.7 Hz), 5.46 (s, 2H), 3.76 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 142.9, 129.3, 128.7, 128.3, 128.1, 127.7, 127.6, 127.0, 114.1, 55.3, 51.8, 11.0; MS (EI): m/z: 285 (M^+); HRMS (ESI^+): m/z calcd for $C_{15}H_{16}N_3OS$ $[M+H]^+$: 286.1008, found 286.1009.

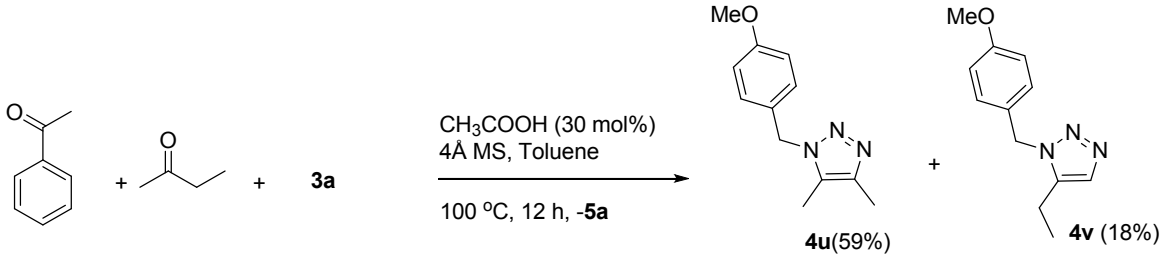


4t: 74% yield

2-(5- (9-Ethyl-9H-carbazol-3-yl)-1- (4-methoxybenzyl)-1H-1,2,3-triazol-4-yl)acetic acid (4t): 4- (9-Ethyl-9H-carbazol-3-yl)-4-oxobutanoic acid (50 mg, 0.17 mmol), 4-methoxybenzylamine (49 mg, 0.35 mmol), 4-nitrophenyl azide (30 mg, 0.0.17 mmol), acetic acid (3 mg, 0.05 mmol), 4 Å molecular sieves (10 mg) and toluene (0.4 mL). Reaction time is 40 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 1:9) affording **4t** (53 mg, 74 %) as an off white solid. m.p. 90 - 91 ˚C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, 1H, *J* = 7.9Hz), 7.80 (s, 1H), 7.52 - 7.44 (m, 3H), 7.28 - 7.23 (m, 2H), 7.03 (d, 2H, *J* = 8.6 Hz), 6.79 (d, 2H, *J* = 8.5 Hz), 5.40 (s, 2H), 4.41 (q, 2H, *J* = 7.2 Hz), 3.78 – 3.76 (m, 5H),

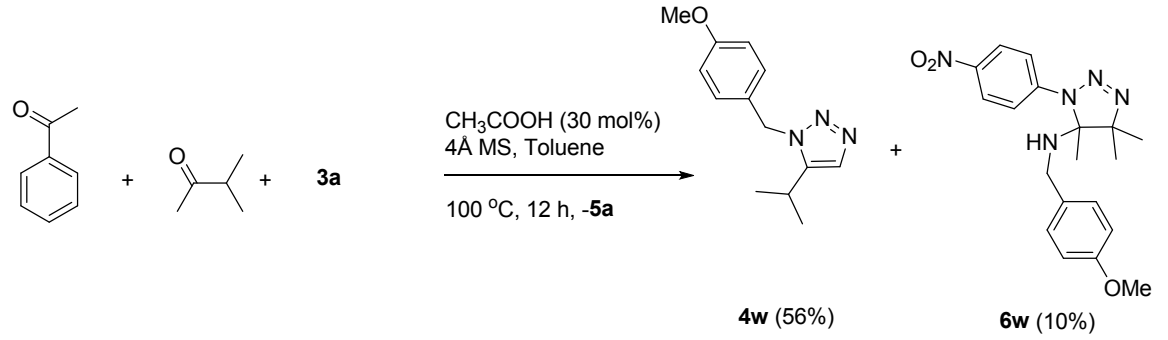
1.47 (t, 3H, *J* = 7.1Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 159.6, 140.5, 138.6, 137.2, 129.3, 127.7, 127.1, 126.7, 123.3, 122.5, 122.3, 120.8, 119.7, 115.9, 114.3, 109.1, 109.0, 55.4, 52.0, 37.2, 29.8, 14.0; MS (EI): m/z: 440 (M^+); HRMS (ESI^+): m/z calcd for $C_{26}H_{25}N_4O_3$ $[M+H]^+$: 441.1921, found 441.1924.



2-Butanone (30mg, 0.44 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The products was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc =7:3) affording **4u** (53 mg, 59% yield) and **4v** (16 mg, 18% yield) as colorless semi-solids.

1-(4-Methoxybenzyl)-4,5-dimethyl-1H-1,2,3-triazole (4u): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (d, 2H, *J* = 8.5 Hz), 6.85 (d, 2H, *J* = 8.5 Hz), 5.38 (s, 2H), 3.78 (s, 3H), 2.24 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 141.2, 129.1, 128.7, 127.1, 114.3, 55.4, 51.6, 10.3, 8.0; MS (EI): m/z: 217 (M^+); HRMS (ESI^+): m/z calcd for $C_{12}H_{16}N_3O$ $[M+H]^+$: 218.1289, found 218.1284.

5-Ethyl-1- (4-methoxybenzyl)-1H-1,2,3-triazole (4v): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.11 (d, 2H, *J* = 8.6 Hz), 6.85 (d, 2H, *J* = 8.6 Hz), 5.43 (s, 2H), 3.79 (s, 3H), 2.51 (q, 2H, *J* = 7.7 Hz), 1.19 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 138.7, 132.2, 128.7, 127.0, 114.4, 55.4, 51.3, 16.9, 12.2; MS (EI): m/z: 217 (M^+); HRMS (ESI^+): m/z calcd for $C_{12}H_{16}N_3O$ $[M+H]^+$: 218.1289, found 218.1282. Spectroscopic data for **4v** are consistent with previously reported data for this compound[6].

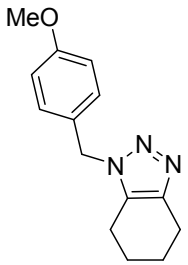


Methyl isopropyl ketone (36 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The products was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 5:5) affording **4w** (54 mg, 56% yield) and **6w** (15 mg, 10% yield) as a colorless semi-solid.

5-Isopropyl-1-(4-methoxybenzyl)-1H-1,2,3-triazole (4w): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.11 (d, 2H, *J* = 8.8 Hz), 6.85 (d, 2H, *J* = 8.6Hz), 5.46 (s, 2H), 3.79 (s, 3H), 2.92 - 2.83 (m, 1H), 1.15 (d, 6H, *J* = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 143.5, 130.9, 128.6, 127.3, 114.4, 55.4, 51.3, 23.9, 22.5; MS (EI): m/z: 231 (M^+); HRMS (ESI^+): m/z calcd for $C_{13}H_{17}N_3O$ $[M+H]^+$: 232.1444, found 232.1449.

N-(4-Methoxybenzyl)-4,4,5-trimethyl-1- (4-nitrophenyl)-4,5-dihydro-1H-1,2,3-triazol-5-amine (6w): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, 2H, *J* = 8.8 Hz), 7.07 (d, 2H, *J* = 8.2 Hz), 6.84 (d, 2H, *J* = 8.5 Hz), 6.75 (d, 2H, *J* = 8.7 Hz), 4.86 (s, 1H), 3.94 (s, 2H), 3.80 (s, 3H), 1.24 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.8,

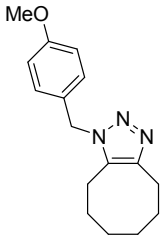
159.3, 141.0, 130.2, 129.0, 124.9, 120.7, 114.3, 71.8, 70.5, 55.4, 48.0, 39.2, 29.7, 29.3; MS (EI): m/z: 369 (M^+); HRMS (ESI): m/z calcd for $C_{19}H_{24}N_5O_3$ $[M+H]^+$: 370.1873, found 370.1877.



4x: 91% yield

1-(4-Methoxybenzyl)-4,5,6,7-tetrahydro-1H-benzo[d][1,2,3]triazole (4x): Cyclohexanone (41 mg, 0.84 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) affording **4x** (91 mg, 91% yield) as a solid. m.p. 91 - 92 ˚C.

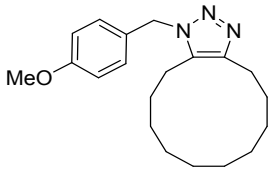
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (d, 2H, *J* = 8.8 Hz), 6.85 (d, 2H, *J* = 8.8Hz), 5.36 (s, 2H), 3.79 (s, 3H), 2.74 - 2.72 (m, 2H), 2.43 - 2.39 (m, 2H), 1.78 - 1.73 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 144.0, 131.9, 129.1, 127.1, 114.3, 55.4, 51.5, 22.6, 22.5, 22.0, 20.2; MS (EI): m/z: 243 (M^+); HRMS (ESI^+): m/z calcd for $C_{14}H_{18}N_3O$ $[M+H]^+$: 244.1444, found 244.1440.



4y: 89% yield

1-(4-Methoxybenzyl)-4,5,6,7,8,9-hexahydro-1H-cycloocta[d][1,2,3]triazole (4y): Cyclooctanone (52 mg, 0.42mmol), 4-methoxybenzylamine (77 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) affording **4y** (101 mg, 89% yield) as a semi-solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 (d, 2H, *J* = 8.8 Hz), 6.84 (d, 2H, *J* = 8.7 Hz), 5.39 (s, 2H), 3.78 (s, 3H), 2.89 (t, 2H, *J* = 6.4 Hz), 2.62 (t, 2H, *J* = 6.2 Hz), 1.74 - 1.72 (m, 2H), 1.54 - 1.50 (m, 2H), 1.39 - 1.37 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 145.3, 133.2, 128.6, 127.6, 114.3, 55.4, 51.4, 28.4, 26.0, 26.0, 24.9, 24.7, 21.9; MS (EI): m/z: 271 (M^+); HRMS (ESI^+): m/z calcd for $C_{16}H_{22}N_3O$ $[M+H]^+$: 272.1757, found 272.1755.

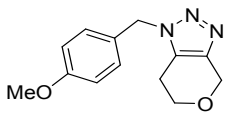


4z: 95% yield

1-(4-Methoxybenzyl)-4,5,6,7,8,9, 10, 11, 12, 13-decahydro-1H-cyclododeca[d][1,2,3]triazole (4z): Cyclododecanone (76 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl

azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) affording **4z** (132 mg, 95% yield as a semisolid.

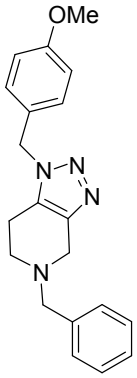
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09 (d, 2H, *J* = 8.7 Hz), 6.84 (d, 2H, *J* = 8.7 Hz), 5.42 (s, 2H), 3.78 (s, 3H), 2.59 (t, 2H, *J* = 7.0 Hz), 2.49 (t, 2H, *J* = 7.2 Hz), 1.88 - 1.80 (m, 2H), 1.61 - 1.52 (m, 2H), 1.42 - 1.19 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 146.1, 133.3, 128.5, 127.5, 114.3, 55.4, 51.7, 27.7, 26.2, 25.3, 24.8, 24.8, 24.5, 22.6, 22.6, 22.0, 19.6; MS (EI): m/z: 327 (M^+); HRMS (ESI^+): m/z calcd for $C_{20}H_{30}N_3O$ $[M+H]^+$: 328.2383, found 328.2382**.**



4aa: 76 % yield

1-(4-Mthoxybenzyl)-1,4,6,7-tetrahydropyrano[3,4-d][1,2,3]triazole (4aa): Tetrahydro-4H-pyran-4-one (42 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) affording **4aa** (78 mg, 76% yield) as an off white solid. m.p. 75 - 76 ˚C.

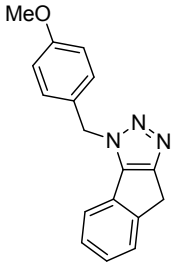
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (d, 2H, *J* = 8.8 Hz), 6.87 (d, 2H, *J* = 8.8 Hz), 5.42 (s, 2H), 4.80 (s, 2H), 3.85 (t, 2H, *J* = 5.5), 3.80 (s, 3H), 2.55 (t, 2H, *J* = 5.5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 142.3, 129.5, 129.3, 126.5, 114.5, 64.2, 64.0, 55.4, 51.9, 22.0; MS (EI): m/z: 245 (M^+); HRMS (ESI^+): m/z calcd for $C_{13}H_{16}N_3O_2$ $[M+H]^+$: 246.1237, found 246.1239.



4ab: 73% yield

5-Benzyl-1-(4-methoxybenzyl)-4,5,6,7-tetrahydro-1H-[1,2,3]triazolo[4,5-c]pyridine (4ab): 1-Benzylpiperidin-4-one (79 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 5:2) affording **4ab (**107 mg, 78% yield) as an off-white solid. m.p. 75 -76 ˚C.

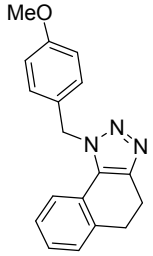
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 - 7.26 (m, 5H), 7.16 (d, 2H, *J* = 8.7 Hz), 6.85 (d, 2H, *J* = 8.6 Hz), 5.36 (s, 2H), 3.78 (s, 3H), 3.70 (s, 2H), 3.67 (s, 2H), 2.71 (t, 2H, *J* = 5.8 Hz), 2.49 (t, 2H, *J* = 5.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 142.9, 138.0, 130.5, 129.3, 129.1, 128.5, 127.4, 126.7, 114.4, 61.9, 55.4, 51.8, 49.9, 49.3, 21.0; MS (EI): m/z: 334 (M^+); HRMS (ESI^+): m/z calcd for $C_{20}H_{23}N_4O$ $[M+H]^+$: 335.1866, found 335.1869.



4ac: 95% yield

3-(4-Methoxybenzyl)-3,8-dihydroindeno[1,2-d][1,2,3]triazole (4ac): 1-indanone (55 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) affording **4ac** (99 mg, 95% yield) as an off white solid. m.p. 110 - 111 ˚C.

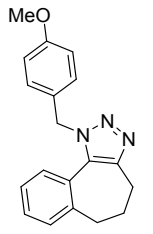
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 - 7.49 (m, 1H), 7.29 - 7.25 (m, 4H), 7.13 (t, 1H, *J* = 8.6 Hz), 6.88 (d, 2H, *J* = 8.6 Hz), 5.70 (s, 2H), 3.78 (s, 3H), 3.79 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8, 155.9, 147.6, 141.3, 129.8, 129.0, 127.3, 127.2, 127.0, 126.7, 120.1, 114.6, 55.4, 53.1, 29.1; MS (EI): m/z: 277 (M^+); HRMS (ESI^+): m/z calcd for $C_{17}H_{16}N_3O$ $[M+H]^+$: 278.1288, found 278.1281.



4ad: 85% yield

1-(4-Methoxybenzyl)-4,5-dihydro-1H-naphtho[1,2-d][1,2,3]triazole (4ad): 1-Tetralone (61 mg, 0.42mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) affording **4ad** (103 mg, 85% yield) as a solid. m.p. 84 ˚C.

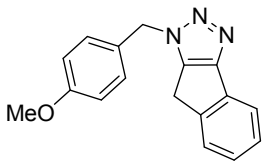
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 - 7.30 (m, 2H), 7.28 - 7.17 (m, 2H), 7.12 (d, 2H, *J* = 8.8 Hz), 6.85 (d, 2H, *J* = 8.8Hz), 5.77 (s, 2H), 3.76 (s, 3H), 3.02 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 145.7, 137.3, 131.4, 129.2, 128.5, 127.9, 127.3, 127.2, 125.0, 122.7, 114.5, 55.3, 52.7, 30.3, 20.8; MS (EI): m/z: 291 (M^+); HRMS (ESI^+): m/z calcd for $C_{18}H_{18}N_3O$ $[M+H]^+$: 292.1444, found 292.1447.



4ae: 94% yield

1-(4-Methoxybenzyl)-1,4,5,6-tetrahydrobenzo[3,4]cyclohepta[1,2-d][1,2,3]triazole (4ae): 1-Benzosuberone (67 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) affording **4ae (**119 mg, 94% yield) as an off white semi-solid.

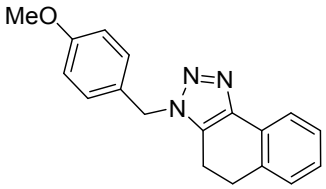
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 - 7.24 (m, 4H), 7.16 (d, 2H, *J* = 8.7 Hz), 6.83 (d, 2H, *J* = 8.7 Hz), 5.59 (s, 2H), 3.77 (s, 3H), 2.93 (t, 2H, *J* = 7.3 Hz), 2.57 (t, 2H, *J* = 6.0 Hz), 2.23 - 2.14 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 146.1, 142.4, 133.1, 130.1, 128.9, 128.3, 127.5, 126.8, 126.6, 114.3, 55.3, 51.7, 32.8, 29.9, 23.3; MS (EI): m/z: 305 (M^+); HRMS (ESI^+): m/z calcd for $C_{19}H_{20}N_3O$ $[M+H]^+$: 306.1601, found 306.1605.



4af: 75% yield

1-(4-Methoxybenzyl)-1,8-dihydroindeno[1,2-d][1,2,3]triazole (4af): 2-Indanone (55 mg, 0.42mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) affording **4af (**86 mg, 75% yield) as an off white semi-solid.

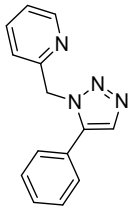
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 - 7.76 (m, 1H), 7.34 - 7.27 (m, 4H), 7.21 - 7.16 (m, 1H), 6.91 (d, 2H, *J* = 8.7 Hz), 5.54 (s, 2H), 3.81 (s, 3H), 3.24 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.1, 156.4, 144.8, 141.9, 133.7, 130.2, 127.6, 126.1, 125.9, 125.8, 119.9, 114.6, 55.5, 53.3, 28.0; MS (EI): m/z: 277 (M^+); HRMS (ESI^+): m/z calcd for $C_{17}H_{16}N_3O$ $[M+H]^+$: 278.1288, found 278.1288.



4ag: 82% yield

3-(4-Methoxybenzyl)-4,5-dihydro-3H-naphtho[1,2-d][1,2,3]triazole (4ag): 2-Tetralone (61 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) affording **4ag (**100 mg, 82% yield) as a semi solid.

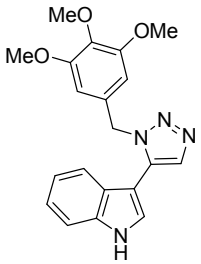
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, 1H, *J* = 7.3 Hz), 7.30 - 7.26 (m, 1H), 7.18 - 7.15 (m, 4H), 6.85 (d, 2H, *J* = 8.6 Hz), 5.47 (s, 2H), 3.78 (s, 3H), 3.0 (t, 2H, *J* = 7.7 Hz), 2.72 (t, 2H, *J* = 7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 144.1, 133.4, 132.6, 129.0, 128.7, 128.2, 127.5,127.4, 126.9, 122.1, 114.5, 55.4, 51.8, 28.5, 19.1; MS (EI): m/z: 291 (M^+); HRMS (ESI^+): m/z calcd for $C_{18}H_{18}N_3O$ $[M+H]^+$: 292.1443, found 292.1445.



4ah: 67% yield

2-((5-Phenyl-1H-1,2,3-triazol-1-yl)methyl)pyridine (4ah): Acetophenone (52 mg, 0.42 mmol), pyridin-2-ylmethanamine (64 mg, 0.59 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc =2:8) affording **4ah** (70 mg, 67% yield) as an off white semi solid.

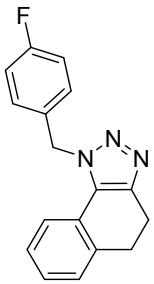
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (d, 1H, *J* = 5), 7.80 (s, 1H), 7.67 – 7.62 (m, 1H), 7.42 -7.40 (m, 5H), 7.27 -7.20 (m, 1H), 7.03 (d, 1H, J = 8), 5.70 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.5, 149.7, 138.8, 137.2, 133.2, 129.6, 129.1, 128.9, 126.7, 123.1, 121.7, 53.4; MS (EI): m/z: 236 (M^+); HRMS (ESI^+): m/z calcd for $C_{14}H_{12}N_4$ $[M+H]^+$: 265.1448, found 265.1442.



4ai: 78% yield

3-(1-(3,4,5-Trimethoxybenzyl)-1H-1,2,3-triazol-5-yl)-1H-indole (4ai): 3-Acetylindole (66 mg, 0.42 mmol), 3,4,5-trimethoxybenzylamine (115 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) affording **4ai (**119 mg, 78% yield) as an off-white solid. m.p. 180 - 181 ˚C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.31 (s, 1H), 7.89 (s, 1H), 7.50 - 7.46 (m, 2H), 7.31 - 7.26 (m, 1H), 7.22 - 7.16 (m, 1H), 7.13 (d, 1H, *J* = 2.6 Hz), 6.23 (s, 2H), 5.52 (s, 2H),3.79 (s, 3H), 3.63 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 137.6, 136.1, 133.7, 132.2, 131.6, 126.3, 124.5, 123.3, 121.2, 119.2, 111.9, 104.3, 102.1, 60.9, 56.0, 52.1; MS (EI): m/z: 364 (M^+); HRMS (ESI^+): m/z calcd for $C_{20}H_{21}N_4O_3$ $[M+H]^+$: 365.1608, found 365.1610.

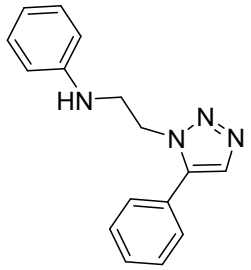


4aj: 79% yeild

1-(4-Fluorobenzyl)-4,5-dihydro-1H-naphtho[1,2-d][1,2,3]triazole (4aj): 1-Tetralone (61 mg, 0.42 mmol), 4-flurobenzylamine (73 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8

mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 5:2) affording **4aj (**92 mg, 79% yield) as an off white semi-solid.

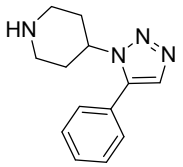
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 - 7.14 (m, 6H), 7.06 - 7.0 (m, 2H), 5.81 (s, 2H), 3.04 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 161.0, 145.9, 137.4, 131.5, 131.1, 131.0, 129.4, 128.7, 128.5, 128.4, 127.2, 124.9, 122.5, 116.4, 116.1, 52.5, 30.4, 20.8; MS (EI): m/z: 279 (M^+); HRMS (ESI^+): m/z calcd for $C_{17}H_{15}FN_3$ $[M+H]^+$: 280.1244, found 280.1242.



4ak: 62% yield

N-(2-(5-Phenyl-1H-1,2,3-triazol-1-yl)ethyl)aniline (4ak): Acetophenone (52 mg, 0.42 mmol), N-phenylmethanediamine (71 mg, 0.59 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by CH_2Cl_2/MeOH = 95:5) affording **4ak** (69 mg, 62% yield) as an off white semi solid.

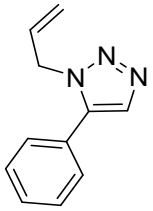
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.48 - 7.45 (m, 3H), 7.41 - 7.35 (m, 2H), 7.30 - 7.21 (m, 5H), 4.45 (t, 2H, *J* = 6 Hz), 3.10 (t, 2H, *J* = 6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.7, 138.3, 133.1, 129.6, 129.2, 129.0, 128.5, 128.1, 127.2, 127.1, 53.3, 48.2; MS (EI): m/z: 264 (M^+); HRMS (ESI^+): m/z calcd for $C_{16}H_{17}N_4$ $[M+H]^+$: 265.1448, found 265.1442.



4al: 56% yield

4-(5-Phenyl-1H-1,2,3-triazol-1-yl)piperidine (4al): Acetophenone (50 mg, 0.42 mmol), 4-piperidineamine (58 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by CH_2Cl_2/MeOH = 95:5) affording **4al** (53 mg, 56% yield) as an off white semi-solid.

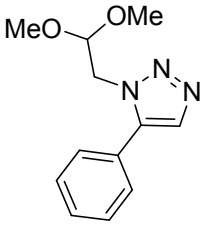
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.53 - 7.50 (m, 3H), 7.36 - 7.33 (m, 2H), 4.39 - 4.32 (m, 1H), 3.29 - 3.24 (m, 2H), 2.72 - 2.64 (m, 2H), 2.36 - 2.30 (m, 2H), 2.28 - 1.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 133.0, 129.6, 129.3, 129.1, 127.5, 56.5, 45.8, 34.1; MS (EI): m/z: 228 (M^+); HRMS (ESI^+): m/z calcd for $C_{13}H_{17}N_4$ $[M+H]^+$: 229.1448, found 229.1445.



4am: 61% yield

1-Allyl-5-phenyl-1H-1,2,3-triazole (4am): Acetophenone (52 mg, 0.42 mmol), allylamine (34 mg, 0.59 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) affording **4am** (49 mg, 61% yield) as an off white semi-solid.

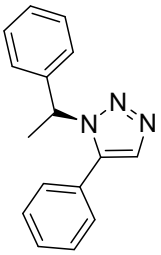
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.50 - 7.40 (m, 5H), 6.09 - 5.96 (m, 1H), 5.27 (d, 1H, *J* = 9.3 Hz), 5.07 - 4.97 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.1, 133.1, 132.2, 129.6, 129.1, 128.8, 127.0, 118.8, 50.6; MS (EI): m/z: 185 (M^+); HRMS (ESI^+): m/z calcd for $C_{11}H_{12}N_3$ $[M+H]^+$: 186.1026, found 186.1028. Spectroscopic data for **4am** is consistent with previously reported data for this compound[7].



4an: 82% yield

1-(2,2-Dimethoxyethyl)-5-phenyl-1H-1,2,3-triazole (4an): Acetophenone (50 mg, 0.42 mmol), 2,2-dimethoxyethanamine (61 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 24 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) affording **4an** (79 mg, 82% yield) as an off-white solid. m.p. 120 - 121 ˚C

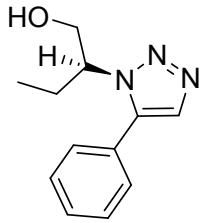
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.49 - 7.48 (m, 5H), 4.89 (t, 1H, *J* = 7.6 Hz), 4.41 (d, 2H, *J* = 7.5 Hz), 3.33 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 132.8, 129.5, 129.2, 129.0, 126.9, 103.4, 55.2, 49.6; MS (EI): m/z: 233 (M^+); HRMS (ESI^+): m/z calcd for $C_{12}H_{16}N_3O_2$ $[M+H]^+$: 234.1237, found 234.1238.



4ao: 87% yield

(S)-5-Phenyl-1- (1-phenylethyl)-1H-1,2,3-triazole (4ao): Acetophenone (50 mg, 0.42 mmol), (S)-(−)-α-methylbenzylamine (71 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 48 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 5:2) affording **4ao** (91 mg, 87% yield) as an off-white solid. m.p. 53 - 54 ˚C.

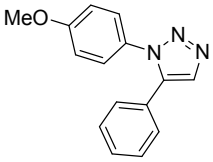
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.42 - 7.40 (m, 3H), 7.31 - 7.26 (m, 3H), 7.20 - 7.17 (m, 4H), 5.57 (q, 1H, *J* = 7.1 Hz), 2.02 (d, 3H, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 138.0, 133.3, 129.5, 129.4, 129.0, 128.9, 128.1, 127.3, 126.3, 58.5, 22.9; MS (EI): m/z: 249 (M^+); HRMS (ESI^+): m/z calcd for $C_{16}H_{16}N_3$ $[M+H]^+$: 250.1339, found 250.1339.
7



4ap: 83% yield

(S)-2-(5-Phenyl-1H-1,2,3-triazol-1-yl)butan-1-ol (4ap): Acetophenone (50 mg, 0.42 mmol), (S)-2-aminobutan-1-ol (51 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 48 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 4:6) affording **4ap** (75 mg, 83% yield) as an off white semi-solid.

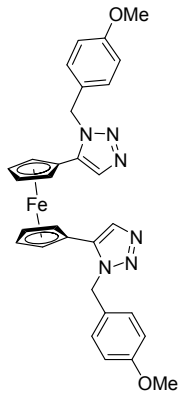
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.50 - 7.44 (m, 5H), 4.46 - 4.31 (m, 2H), 4.0 - 3.97 (m, 1H), 3.73 (s_{br}, 1H), 2.06 - 1.79 (m, 2H), 0.69 (t, 3H, *J* = 7.3Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.6, 132.4, 129.6, 129.6, 129.1, 127.1, 65.0, 62.1, 25.1, 10.4; MS (EI): m/z: 217 (M^+); HRMS (ESI^+): m/z calcd for $C_{12}H_{16}N_3O$ $[M+H]^+$: 218.1288, found 218.1287.



4aq: 25% yield

1-(4-Methoxyphenyl)-5-phenyl-1H-1,2,3-triazole (4aq): Acetophenone (50 mg, 0.42 mmol), 4-methoxyaniline (72 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 48 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) affording **4aq** (26 mg, 25% yield) as an off-white solid. m.p. 160 - 161 ˚C.

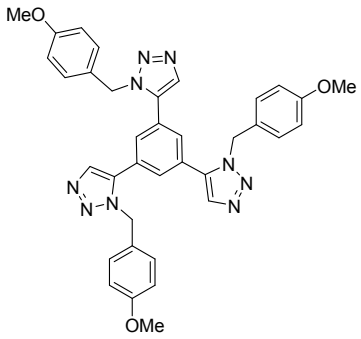
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.36 - 7.24 (m, 7H), 6.93 (d, 2H, *J* = 8.8 Hz), 3.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.2, 137.4, 133.3, 129.7, 129.3, 129.0, 128.7, 127.0, 126.7, 114.6, 55.7; MS (EI): m/z: 251 (M^+); HRMS (ESI^+): m/z calcd for $C_{15}H_{14}N_3O$ $[M+H]^+$: 252.1131, found 252.1132. Spectroscopic data for **4ar** are consistent with previously reported data for this compound[7].



7: 68% yield

1,1'-Bis(1-(4-methoxybenzyl)-1H-1,2,3-triazol-5-yl)ferrocene (7): 1, 1'-Diacetylferrocene (100 mg, 0.37 mmol), 4-methoxybenzylamine (282 mg, 2.07 mmol), 4-nitrophenyl azide (121 mg, 0.74 mmol), 4 Å molecular sieves (50 mg) and toluene (1 mL). Reaction time is 72 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 2:8) affording **7** (140 mg, 68% yield) as a red solid. m.p. 100 - 101 ˚C.

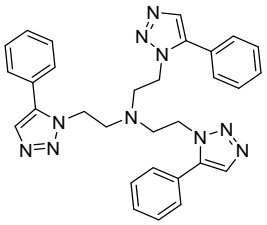
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (s, 2H), 6.96 (d, 4H, *J* = 8.4 Hz), 6.84 (d, 4H, *J* = 8.5 Hz), 5.42 (s, 4H), 4.26 (s, 4H), 4.18 (s, 4H), 3.79 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 135.1, 133.3, 128.1, 127.5, 114.5, 72.2, 71.7, 70.0, 55.5, 51.5; MS (EI): m/z: 560 (M^+); HRMS (ESI^+): m/z calcd for $C_{30}H_{29}FeN_6O_2$ $[M+H]^+$: 561.1695, found 561.1691.



8: 77% yield

1,3,5-Tris (1- (4-methoxybenzyl)-1H-1,2,3-triazol-5-yl)benzene (8): 1,3,5-Triacetylbenzene (50 mg, 0.24 mmol), 4-methoxybenzylamine (140 mg, 1.03 mmol), 4-nitrophenyl azide (144 mg, 0.88 mmol), acetic acid (4 mg, 0.06 mmol), 4 Å molecular sieves (50 mg) and toluene (0.8 mL). Reaction time is 48 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 2:8) affording **8** (118 mg, 77% yield) an off-white solid. m.p. 167 - 168 ˚C.

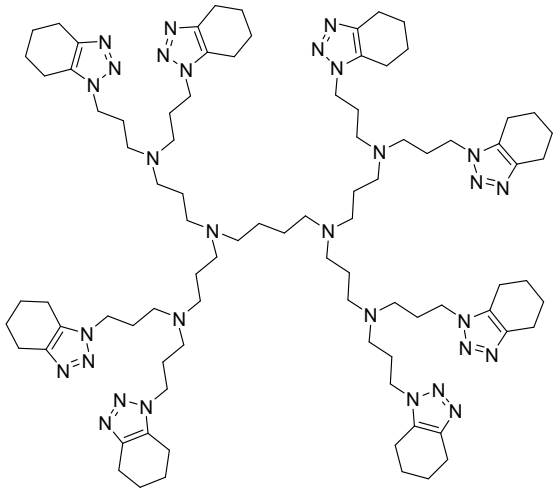
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (s, 3H), 7.28 (s, 3H), 6.84 (d, 6H, *J* = 8.6 Hz), 6.73 (d, 6H, *J* = 8.8Hz), 5.35 (s, 6H), 3.72 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8, 135.7, 133.9, 129.7, 128.8, 128.5, 126.9, 114.4, 55.4, 52.0; MS (EI): m/z: 639 (M^+); HRMS (ESI^+): m/z calcd for $C_{36}H_{34}N_9O_3$ $[M+H]^+$: 640.2779, found 640.2781.



9: 65% yield

Tris (2-(5-phenyl-1H-1,2,3-triazol-1-yl)ethyl)amine (9): Acetophenone (295 mg, 2.4 mmol), tris(2-aminoethyl)amine (100 mg, 0.68 mmol), 4-nitrophenyl azide (370 mg, 2.2 mmol), acetic acid (4 mg, 0.06 mmol) 4 Å molecular sieves (30 mg) and toluene (0.6 mL).Reaction time is 48 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by CH_2Cl_2/MeOH= 95:5) affording **9** (230 mg, 65% yield) an off-white solid. m.p. 167 - 168 ˚C.

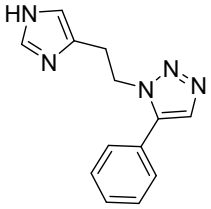
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (s, 3H), 7.48 - 7.46 (m, 9H), 7.29 - 7.27 (m, 6H), 4.08 - 4.03 (t, 6H, *J* = 6.6), 2.74 - 2.70 (t, 6H, *J* = 6.96); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.1, 133.2, 129.8, 129.4, 128.8, 127.0, 53.5, 46.2; MS (EI): m/z: 530 (M^+); HRMS (ESI^+): m/z calcd for $C_{30}H_{31}N_{10}$ $[M+H]^+$: 531.2727, found 531.2728.



11: 73% yield

N1,N1'-(Butane-1,4-diyl)bis(N1-(3-(bis(3-(4,5,6,7-tetrahydro-1H-benzo[d][1,2,3]triazol-1-yl)propyl)amino)propyl)-N3,N3-bis(3-(4,5,6,7-tetrahydro-1H-benzo[d][1,2,3]triazol-1-yl)propyl)propane-1,3-diamine) (11): Poly(propylene imine)-dendrimer of generation 2 (70 mg, 0.09 mmol), cyclohexanone (106 mg, 1.08 mmol), 4-nitrophenyl azide (178 mg, 1.08 mmol), 4 Å molecular sieves (30 mg) and dioxane (1.5 mL). Reaction time is 24 h. The product was precipitated out in diethyl ether and affording **10** (106 mg, 73% yield) as an off white solid. m.p. 101 ˚C.

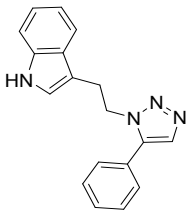
^{1}H NMR (300 MHz, $CDCl_3$) δ 4.21 (s_{br}, 16H), 3.35 (s_{br}, 4H), 2.71 (s_{br}, 16H), 2.60 (s_{br}, 16H), 2.45 (s_{br}, 32H), 1.96 - 1.56 (m, 62H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4, 131.9, 52.2, 50.9, 45.8, 29.8, 27.5, 25.8, 22.8, 22.6, 22.0, 20.2; MS $(ESI)^+$: m/z: 1622 (M^+); HRMS (ESI^+): m/z calcd for $C_{88}H_{145}N_{30}$ $[M+H]^+$: 1622.2262, found 1622.2211.



13a: 61% yield

1-(2-(1H-imidazol-4-yl)ethyl)-5-phenyl-1H-1,2,3-triazole (11a): Acetophenone (52 mg, 0.42 mmol), histamine (65 mg, 0.59 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by CH_2Cl_2/MeOH = 95:5) affording **11a** (61 mg, 61% yield) as an off white semi solid.

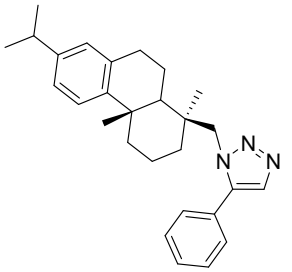
^{1}H NMR (300 MHz, $CDCl_3$) δ7.65 (s, 1H), 7.52 (s, 1H), 7.45 - 7.43 (m, 3H), 7.26 - 7.22 (m, 2H), 6.95 (s_{br}, 1H), 6.64 (s, 1H), 4.61 (t, 2H, *J* = 7.0 Hz), 3.22 (t, 2H, *J* = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.5, 135.1, 134.0, 132.9, 129.2, 128.8, 126.8, 116.5, 48.2, 28.1; MS (EI): m/z: 239 (M^+); HRMS (ESI^+): m/z calcd for $C_{13}H_{14}N_5$ $[M+H]^+$: 240.1243, found 240.1248.



13b: 75% yield

3-(2-(5-Phenyl-1H-1,2,3-triazol-1-yl)ethyl)-1H-indole (11b): Acetophenone (50 mg, 0.42 mmol), tryptamine (94 mg, 0.59 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.4 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 6:4) affording **11b** (90 mg, 75% yield) as an off white solid. m.p. 123 - 124 ˚C.

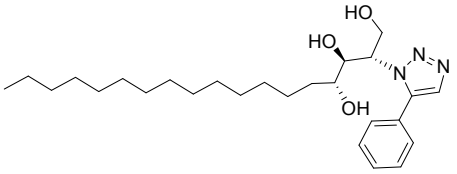
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.63 (s, 1H), 7.41 - 7.14 (m, 6H), 7.06 - 7.00 (m, 3H), 6.83 (s, 1H), 4.60 (t, 2H, *J* = 7.3 Hz), 3.33 (t, 2H, *J* = 7.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.4, 136.3, 133.0, 129.3, 128.9, 128.8, 127.1, 127.0, 122.6, 122.2, 119.6, 118.2, 111.4, 111.2, 48.8, 26.6; MS (EI): m/z: 288 (M^+); HRMS (ESI^+): m/z calcd for $C_{18}H_{17}N_4$ $[M+H]^+$: 289.1445, found 289.1446. Spectroscopic data for **11b** is consistent with previously reported data for this compound[7].



13c: 76% yield

1-(((1S,4aS)-7-Isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-5-phenyl-1H-1,2,3-triazole (11c): Acetophenone (50 mg, 0.42 mmol), dehydroabietylamine (166 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.8 mL). Reaction time is 48 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 5:5) affording **11c** (132 mg, 76% yield) as an off-white solid.

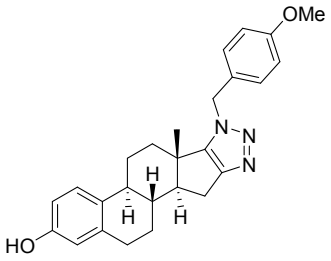
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.48 - 7.46 (m, 3H), 7.35 - 7.32 (m, 2H), 7.08 (d, 1H, *J* = 8.1 Hz), 6.94 (d, 1H, *J* = 8.1 Hz), 6.87 (s, 1H), 4.32 (s, 2H), 2.86 - 2.76 (m, 3H), 2.19 - 2.15 (m, 1H), 1.80 - 1.31 (m, 6H), 1.22 (s, 3H), 1.20 (s, 3H), 1.15 (s, 3H), 1.05 - 1.04 (m, 2H), 0.93 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.0, 145.8, 139.1, 134.7, 133.1, 129.4, 129.3, 129.2, 128.3, 127.0, 124.1, 123.9, 58.4, 45.9, 39.4, 38.1, 37.7, 36.6, 33.6, 29.9, 25.6, 24.1, 24.0, 19.4, 18.7, 18.5; MS (EI): m/z: 413 (M^+); HRMS (ESI^+): m/z calcd for $C_{28}H_{36}N_3$ $[M+H]^+$: 414.2903, found 414.2909.



13d: 81% yield

2-(5-Phenyl-1H-1,2,3-triazol-1-yl)octadecane-1,3,4-triol (13d): Acetophenone (50 mg, 0.42 mmol), phytosphingosine (185 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), 4 Å molecular sieves (50 mg) and toluene (1 mL). Reaction time is 48 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by CH_2Cl_2/MeOH = 95:5) affording **11d** (150 mg, 81% yield) as an off white semi-solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.50 - 7.49 (m, 3H), 7.45 - 7.43 (m, 2H), 4.81 - 4.78 (m, 1H), 4.37 - 4.33 (m, 1H), 4.11 - 4.07 (m, 2H), 3.59 - 3.54 (m, 1H), 2.93 (s_{br}, 1H), 1.38 - 1.08 (m, 26H), 0.88 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.0, 132.8, 130.0, 129.4, 129.3, 126.5, 75.5, 72.3, 62.0, 60.3, 32.1, 29.8, 29.8, 29.8, 29.7, 29.7, 29.5, 25.9, 22.8, 14.2; MS (EI): m/z: 445 (M^+); HRMS (ESI^+): m/z calcd for $C_{26}H_{44}N_3O_3$ $[M+H]^+$: 446.3376, found 446.3372.

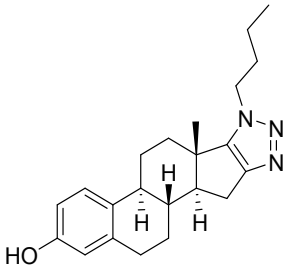


13e1: 71% yield

(6bS,8aS,12aS,12bR)-9-(4-Mthoxybenzyl)-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 (13f1): Estrone (113 mg, 0.42 mmol), 4-methoxybenzylamine (160 mg, 1.18 mmol), 4-nitrophenyl azide (137 mg, 0.84 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (1.5 mL). Reaction time is 72 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 3:7) affording **13e1** (123 mg, 71% yield) as an off white solid. m.p. 210 – 211 ˚C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (d, 2H, *J* = 8.7 Hz), 7.09 (d, 1H, *J* = 8.7 Hz), 6.86 (d, 2H, *J* = 8.7 Hz), 6.65 - 6.58 (m, 2H), 5.49 - 5.31 (m, 2H), 5.08 (s_{br}, 1H), 3.80 (s, 3H), 2.89 - 2.75 (m, 3H), 2.48 - 2.23 (m, 4H), 2.07 - 2.03 (m, 2H), 1.95 - 1.42 (m, 4H), 0.73 (s, 3H); ^{13}C NMR (75 MHz, CDCl3) δ 159.8, 154.0, 149.3, 138.0, 131.7, 129.2, 127.6, 126.2, 115.6, 114.3, 113.0, 61.7, 55.4, 52.7, 44.1, 41.5, 37.3, 34.0, 29.4,

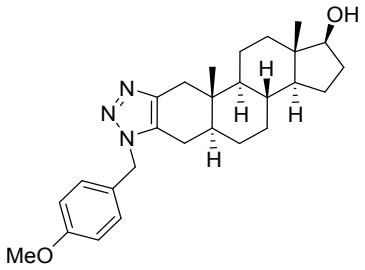
27.4, 25.9, 24.6, 17.2; MS (EI): m/z: 415 (M^+); HRMS (ESI^+): m/z calcd for $C_{26}H_{30}N_3O_2$ $[M+H]^+$: 416.2332, found 416.2332**.**



13e2: 88% yield

(6bS,8aS, 12aS, 12bR)-9-Butyl-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 (**13e2)**: Estrone (113 mg, 0.42 mmol), *n*-butyl amine (120 mg, 1.66 mmol),4-nitrophenyl azide (137 mg, 0.84 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (1.5 mL). Reaction time is 72 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 3:7) affording **13e2** (130 mg, 88% yield) as an off white solid. m.p. 264 - 265 ˚C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 (d, 1H, *J* = 8.6 Hz), 6.70 - 6.66 (m, 1H), 6.62 (s, 1H), 5.61 (s_{br}, 1H), 4.30 - 4.19 (m, 2H), 2.93 - 2.77 (m, 3H), 2.50 - 2.25 (m, 5H), 1.98 - 1.92 (m, 4H), 1.89 - 1.35 (m, 5H), 1.05 (s, 3H), 0.97 (t, 3H, *J* = 7.3 Hz); ^{13}C NMR (75 MHz, CDCl3) δ 154.0, 154.3, 149.2, 138.1, 131.8, 126.2, 115.6, 113.0, 61.7, 49.1, 44.2, 41.4, 37.3, 34.3, 32.8, 29.5, 27.4, 26.0, 24.5, 20.0, 17.9, 13.7; MS (EI): m/z: 351 (M^+); HRMS (ESI^+): m/z calcd for $C_{22}H_{30}N_3O$ $[M+H]^+$: 352.2382, found 352.2381**.**

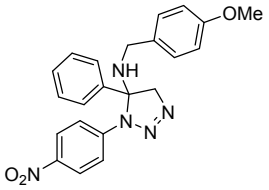


13f: 88% yield

(1S,3aS,3bR,5aS,10aS,10bS,12aS)-7-(4-Methoxybenzyl)-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 (13f): 5α-Dihydrotestosterone (120 mg, 0.42 mmol), 4-methoxybenzylamine (80 mg, 0.58 mmol), 4-nitrophenyl azide (68 mg, 0.42 mmol), acetic acid (8 mg, 0.13 mmol), 4 Å molecular sieves (50 mg) and toluene (0.8 mL). Reaction time is 12 h. The product was purified by flash column chromatography (CH_2Cl_2 followed by heptane/EtOAc = 4:6) affording **13f** (160 mg, 88% yield) as an off-white solid. m.p. 96 - 97 ˚C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 (d, 2H, *J* = 8.5 Hz), 6.86 (d, 2H, *J* = 8.7 Hz), 5.35 (s, 2H), 3.79 (s, 3H), 3.65 (t, 1H, *J* = 8.5 Hz), 2.85 (d, 1H, *J* = 15.6 Hz), 2.40 - 2.24 (m, 2H), 2.09 - 1.83 (m, 3H), 1.72 - 1.22 (m, 11H), 1.15 - 0.85 (m, 4H), 0.75 (s, 3H), 0.66 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 143.8, 130.6, 128.9, 127.1, 114.3, 81.8, 55.4, 53.8, 51.5, 50.9, 42.9, 42.2, 36.8, 36.7, 36.2, 35.6, 31.2, 30.5, 28.9, 24.6,

23.5, 20.8, 11.7, 11.2; MS (EI): m/z: 435 (M^+); HRMS (ESI^+): m/z calcd for $C_{27}H_{38}N_3O_2$ $[M+H]^+$: 436.2958, found 436.2956.

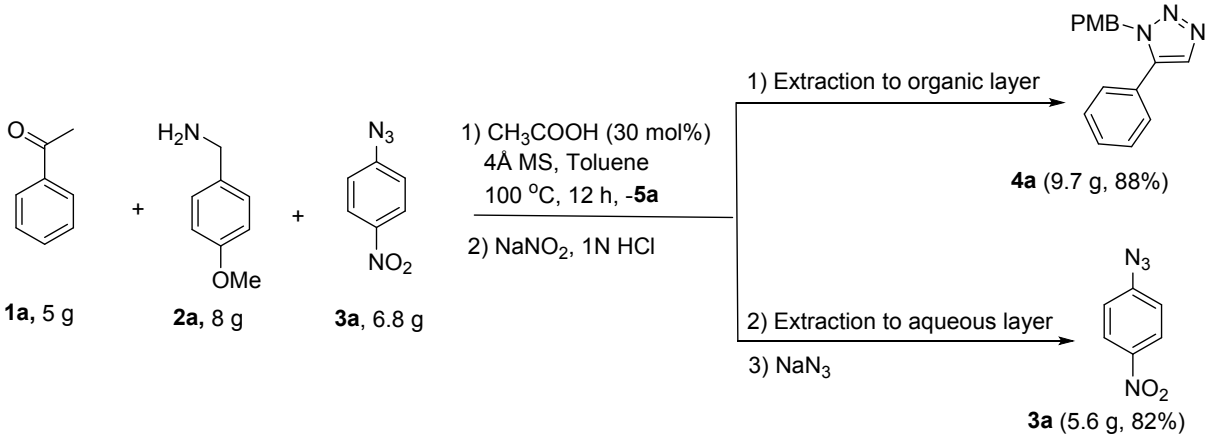


6a: 75% yeild

4.3 Preparation of N- (4-Methoxybenzyl)-1- (4-nitrophenyl)-5-phenyl-4,5-dihydro-1H-1,2,3-triazol-5-amine (6a). To an oven-dried screw-capped reaction tube equipped with a magnetic stir bar was added acetophenone (500 mg, 4.2mmol), 4-methoxybenzylamine (800 mg, 5.8 mmol) and 4 Å molecular sieves (500 mg). The mixture was dissolved in anhydrous toluene (4 mL) and stirred at 100 °C for 2 h. After cooling it down to room temperature, an equivalent of 4-nitrophenyl azide (680 mg, 4.2 mmol) was added and the reaction mixture was stirred for another 6 h at 50°C. The resulting reaction mixture was precipitated in diethyl ether, filtered and dried to afford 1.2 g of the triazoline intermediate **6a** in 75% yield. m.p. 153 – 154 ˚C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, 2H, *J* = 8.7 Hz), 7.54 – 7.26 (m, 7H), 7.01 (d, 2H, *J* = 8.2 Hz), 6.79 (d, 2H, *J* = 8.5 Hz), 4.82 (d, 1H, *J* = 18 Hz), 4.35 (d, 1H, *J* = 18.7 Hz), 3.77 (s, 3H), 3.37 (t, 1H, *J* = 10.9 Hz), 2.96 (d, 1H, *J* = 12.0 Hz), 2.60 (d, 1H, *J* = 10.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 144.7, 142.6, 141.5, 130.1, 129.7, 129.6, 129.0, 125.7, 125.6, 114.7, 114.1, 81.6, 80.2, 55.4, 45.9; MS (EI): m/z: 403 (M^+); HRMS (ESI^+): m/z calcd for $C_{22}H_{22}N_5O_3$ $[M+H]^+$: 404.1717; found 404.1717.

4.4 Bulk synthesis of 1,2,3-triazole (4a) and the regeneration of the 4-nitrophenyl azide (5a)



To a 250 mL round-bottom flask equipped with a magnetic stir bar was added an equivalent of acetophenone (5 g, 42mmol), 1.4 equivalents of4-methoxybenzylamine (8 g, 58mmol), oneequivalent of 4-nitrophenyl azide (6.8 g, 42mmol), 30 mol% of acetic acid (8 mg, 0.13 mmol) (0.8 mL, 12.6mmol) and 4 Å molecular sieves (5 g). The mixture was dissolved in anhydrous toluene (30 mL) and stirred at 100 °C for 12 hr.The solvent was evaporated off and the resulting reaction mixture was suspended in hydrochloric acid (3N, 100mL) and methanol (30 mL) was added to aid the solubility. After cooling the solution to 0 °C, $NaNO_2$ (6g) in water (20 mL) was added dropwise. The resulting solution was stirred at 0 °C for 30 minutes, after which reaction mixture was extracted with ethyl acetate at 0-5 °C. The aqueous layer was collected separately and the organic fraction was washed with a saturated $NaHCO_3$

solution and brine, dried over $MgSO_4$ and concentrated in vacuo to afford 1,5-disubstituted 1,2,3-triazole **4a (**9.7 g)in sufficent purity with an overall yield of 88%. To the aqueous layer, a solution of NaN_3 (4 g) in 20 mL of water was added dropwise at 0 °Cand the whole was stirred for at least 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 vacuo to get the desired azide compound **5a** (5.6 g) in sufficient purity (82% yield).

5. References

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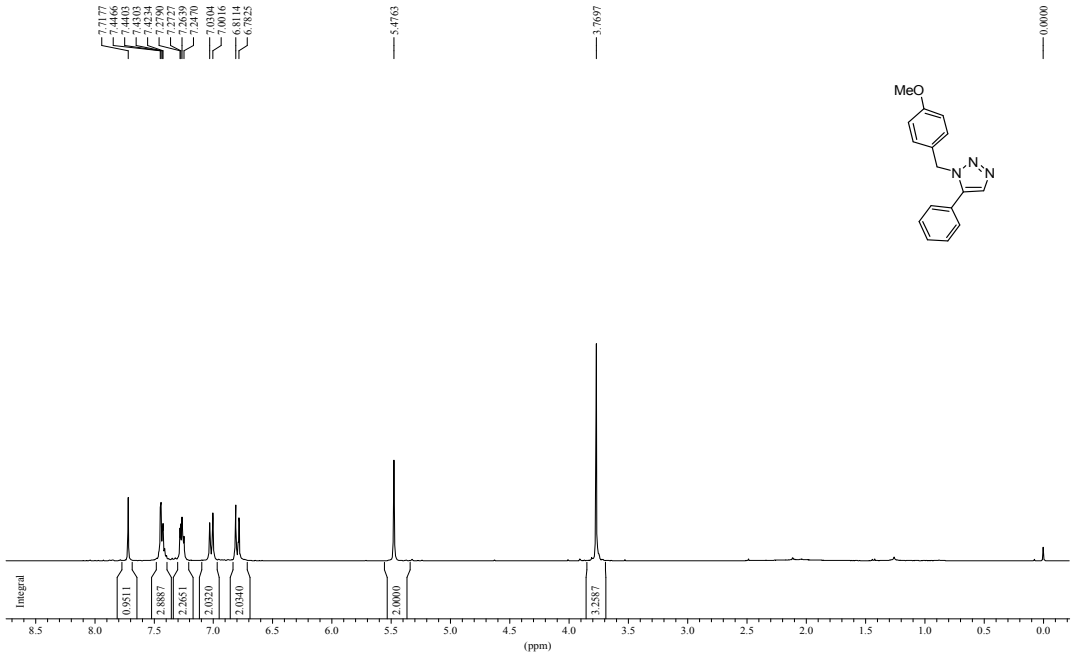
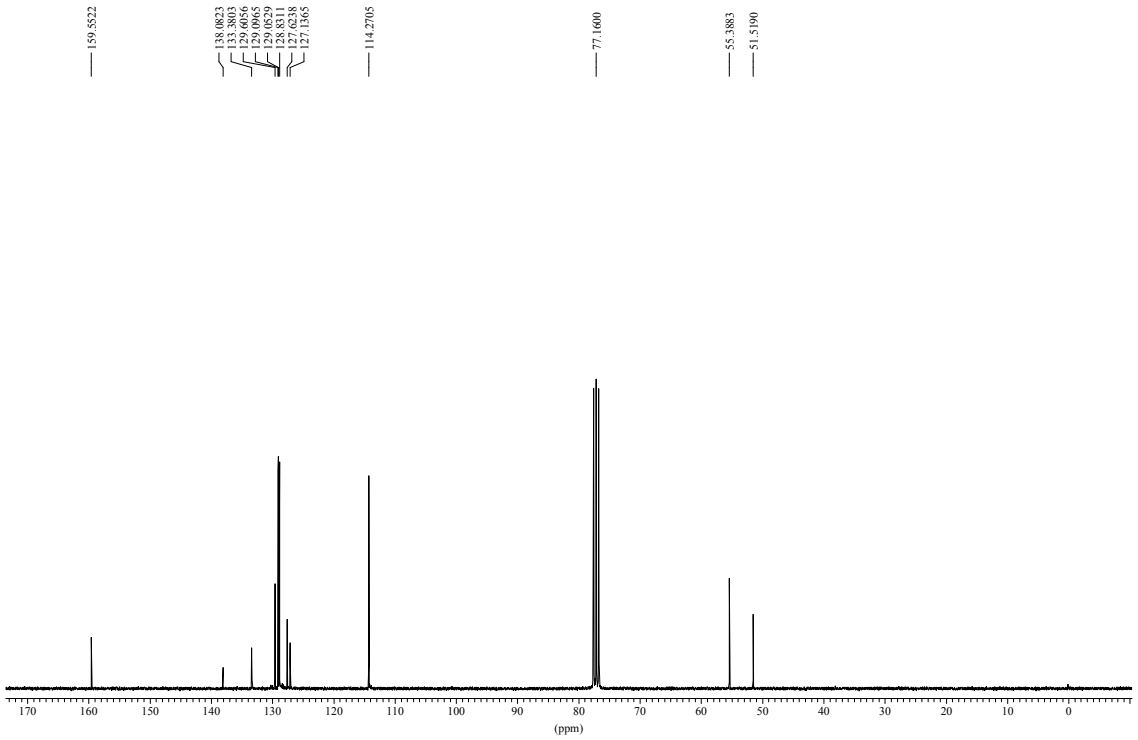
6. ^{1}H and ^{13}C NMR spectra of products

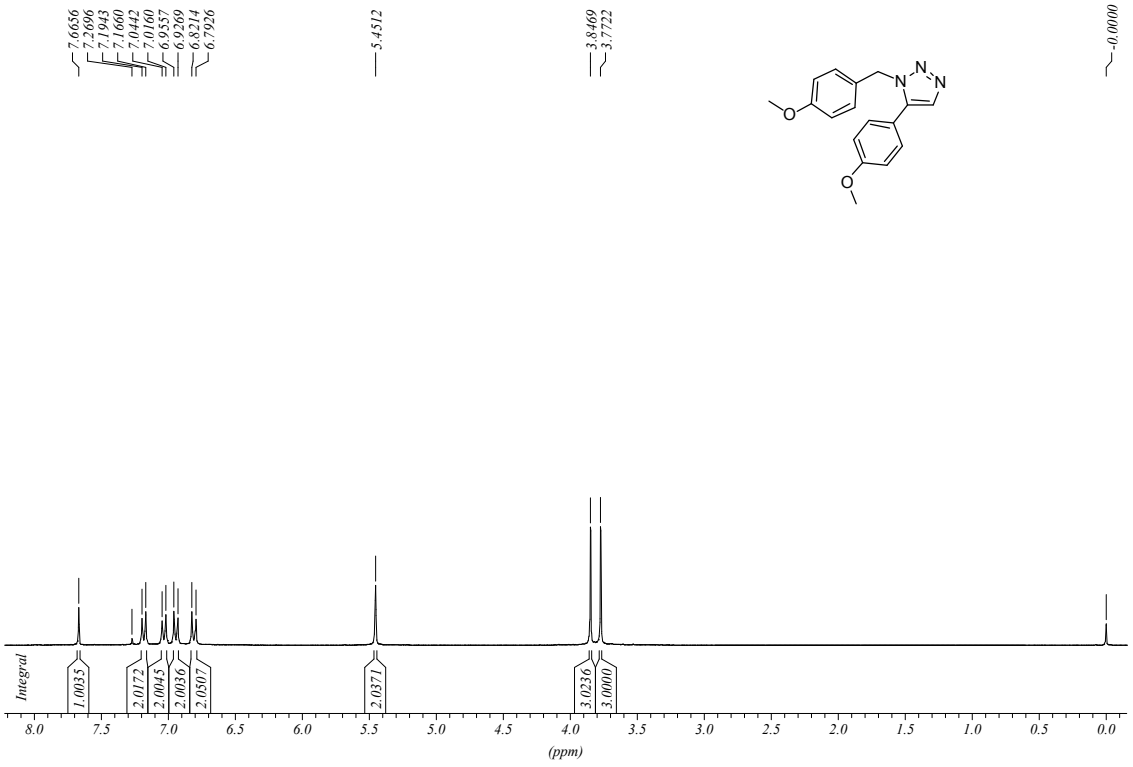
^{1}H NMR Spectra of **4a** (300 MHz, CDCl3):



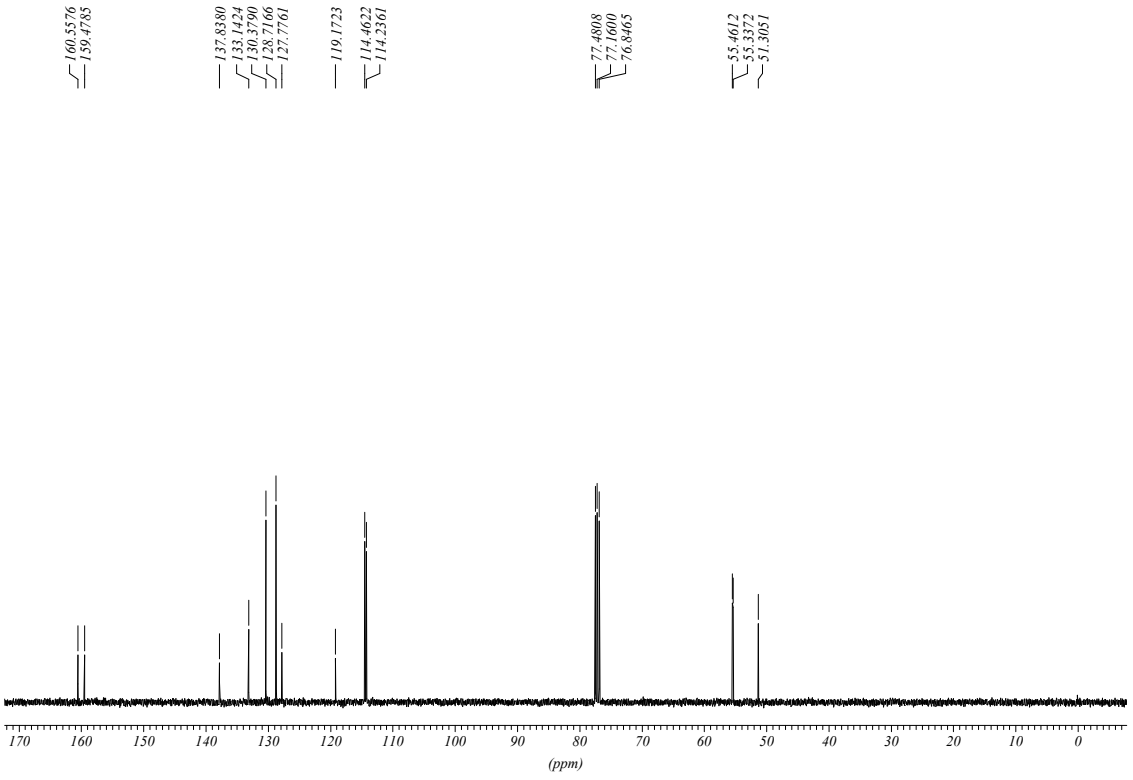
^{13}C NMR Spectra of **4a** (75 MHz, CDCl3):



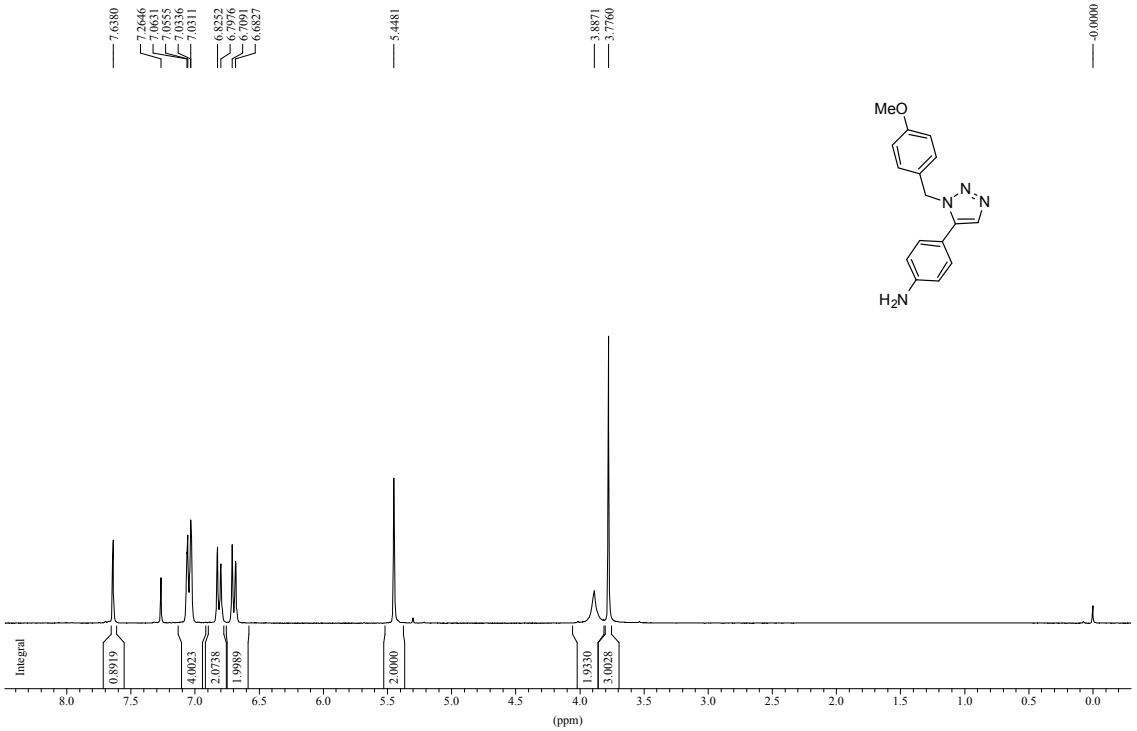
^{1}H NMR Spectra of **4b** (300 MHz, CDCl3):



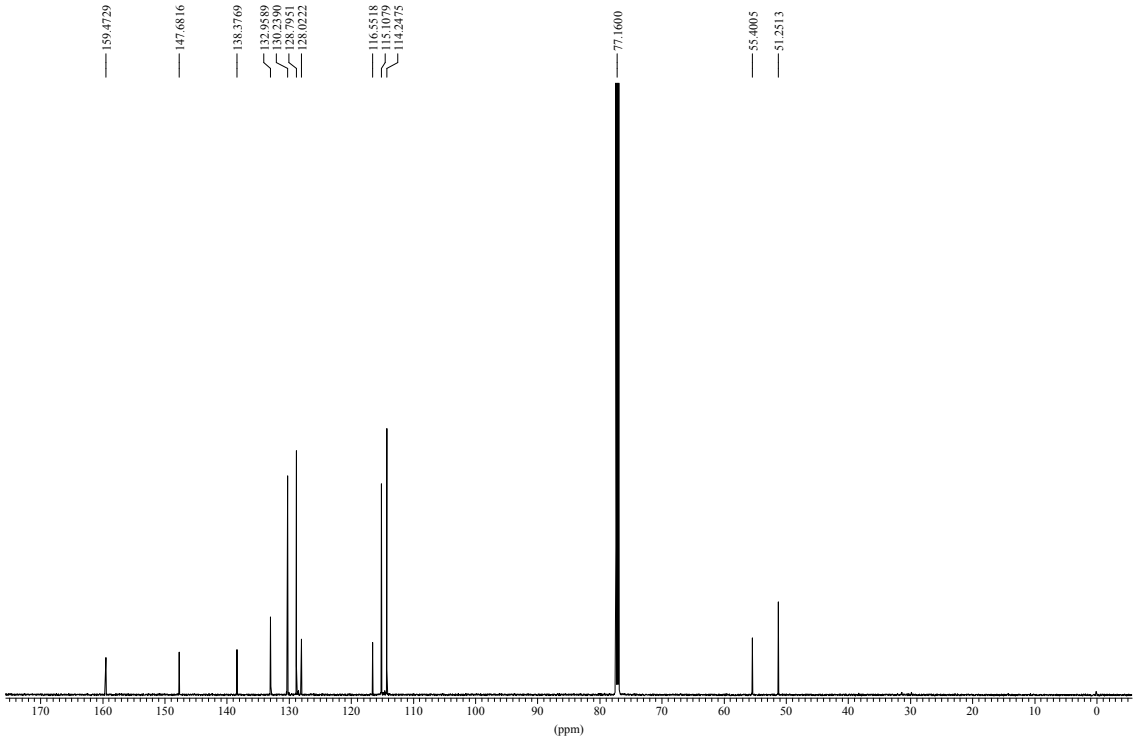
^{13}C NMR Spectra of **4b** (75 MHz, CDCl3):



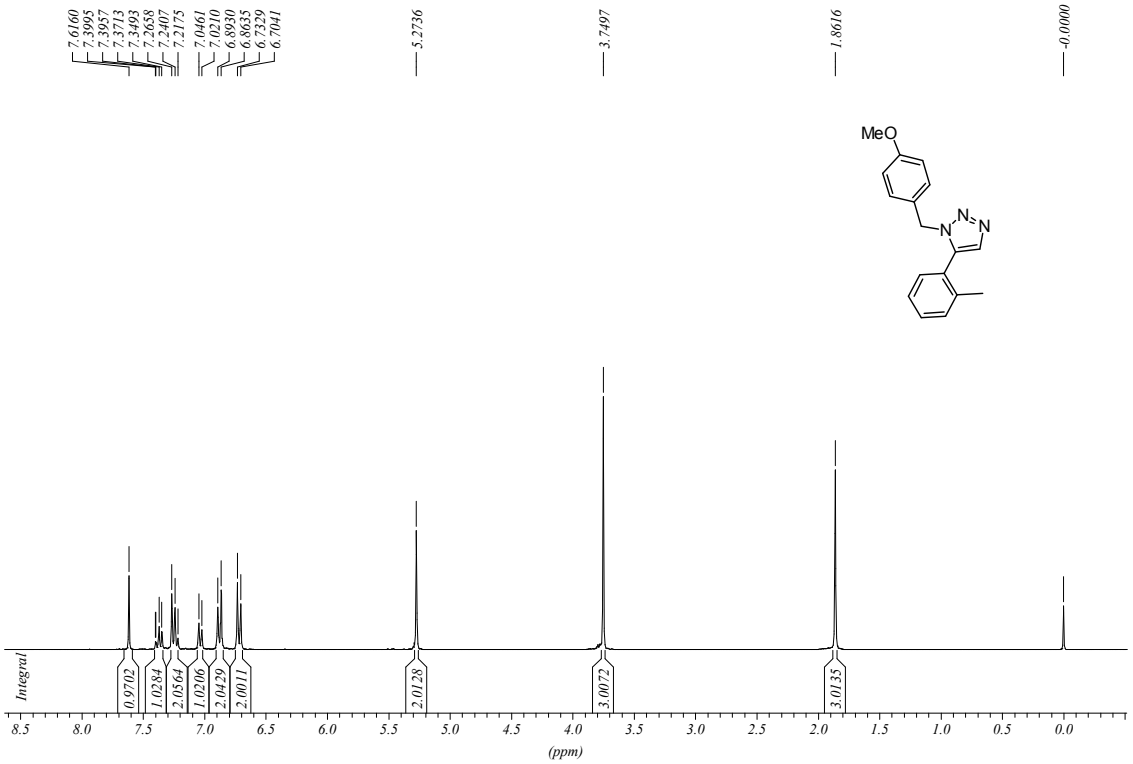
^{1}H NMR Spectra of **4c** (300 MHz, CDCl3):



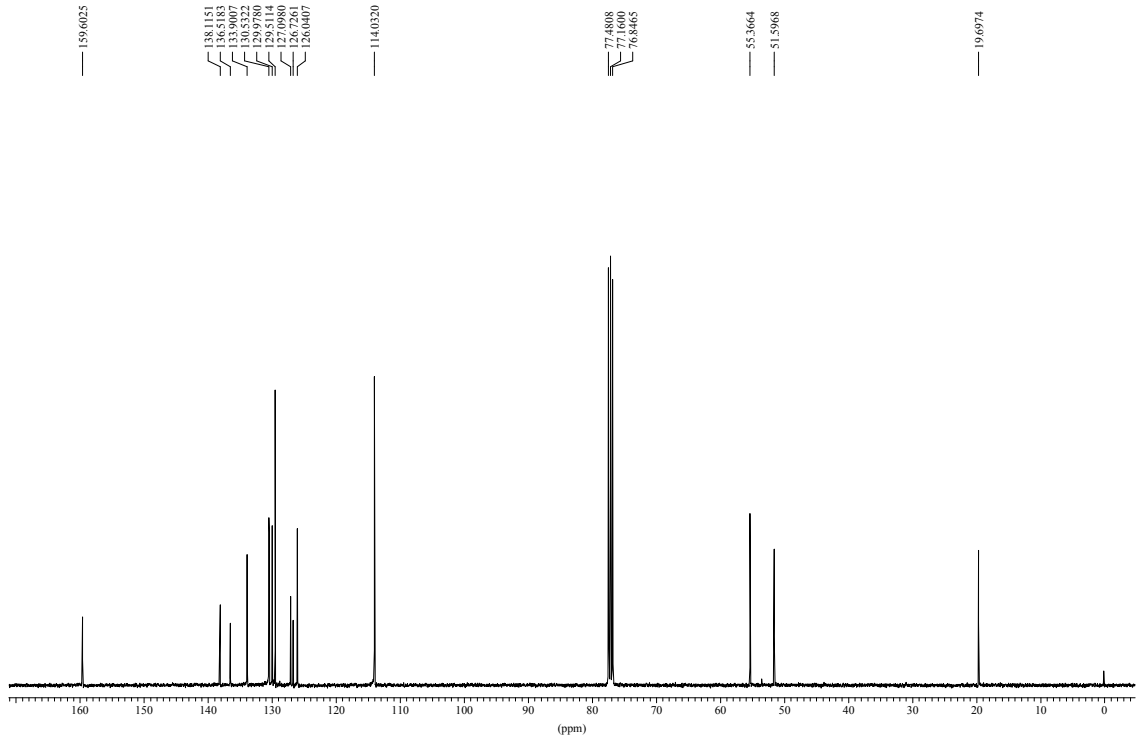
^{13}C NMR Spectra of **4c** (125 MHz, CDCl3):



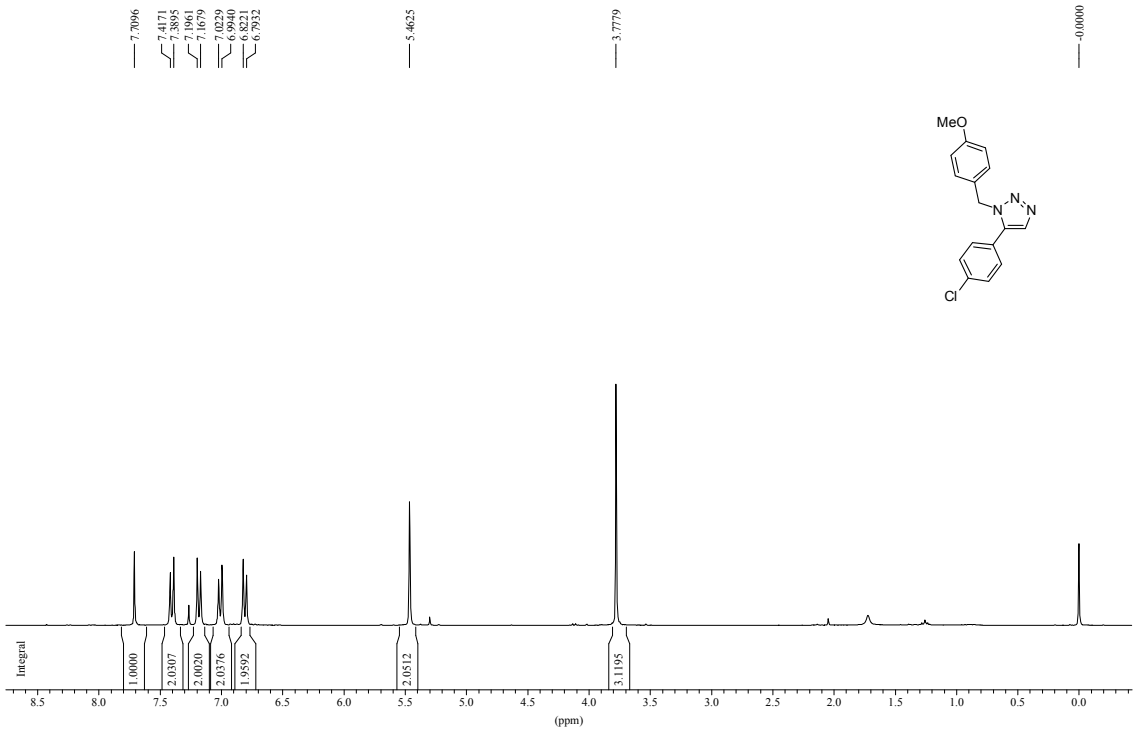
^{1}H NMR Spectra of **4d** (300 MHz, CDCl3):



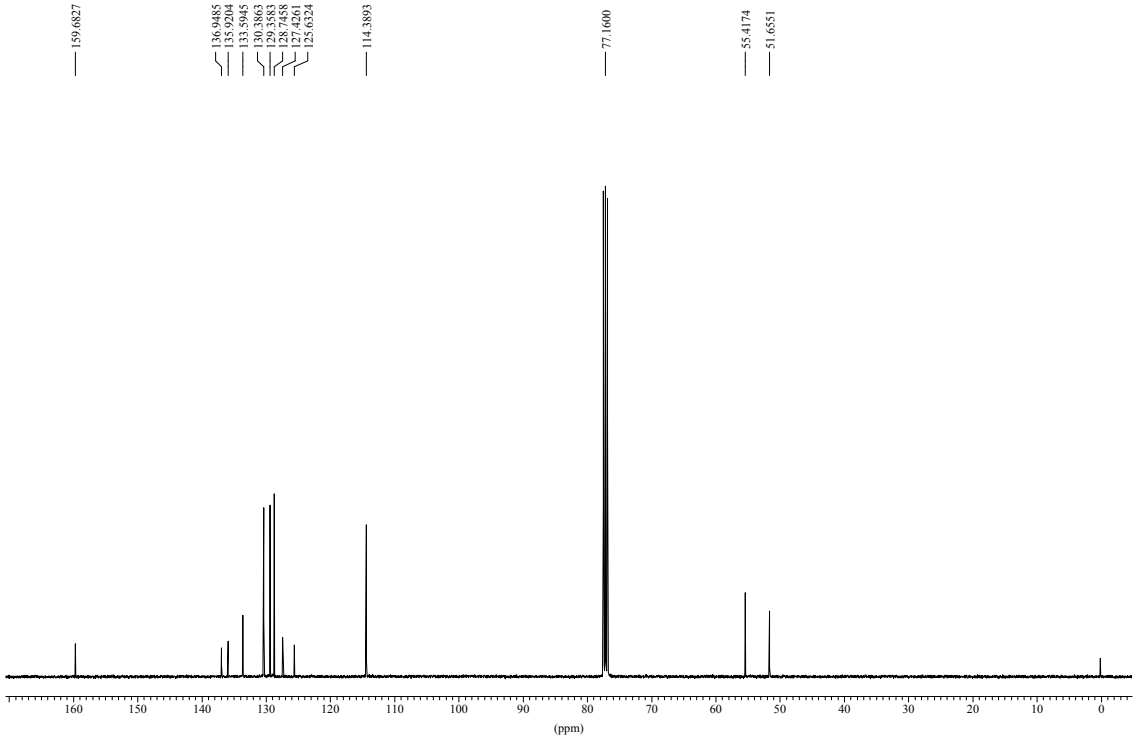
^{13}C NMR Spectra of **4d** (75 MHz, CDCl3):



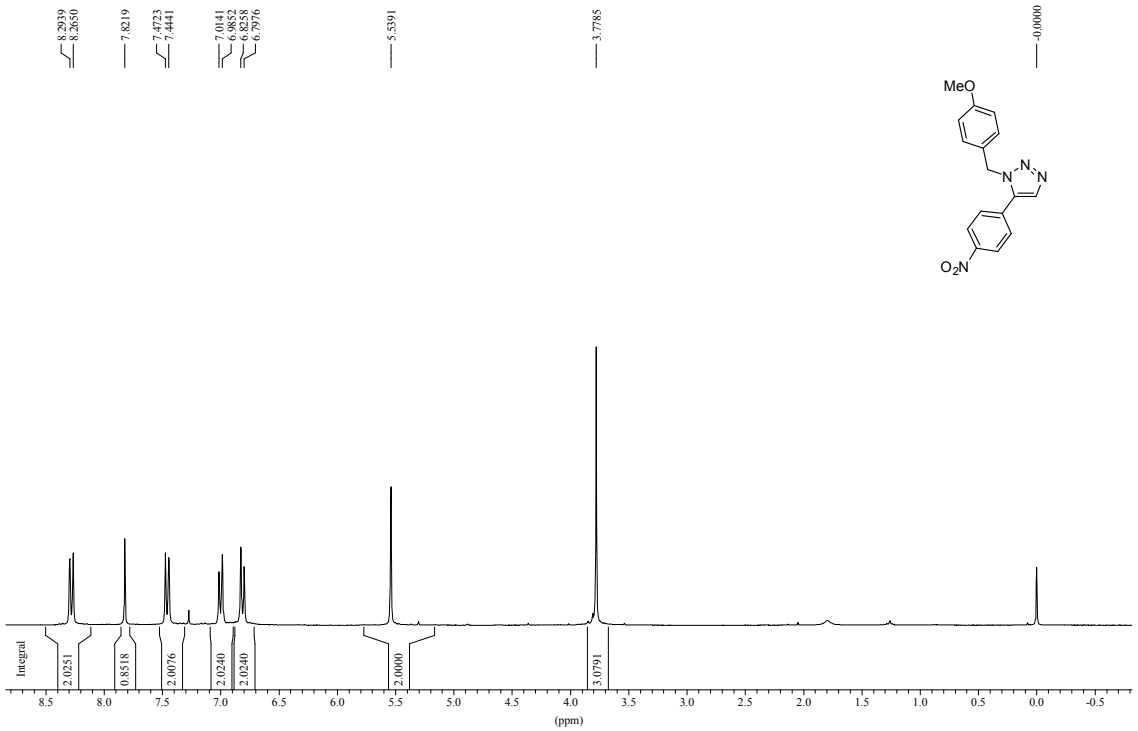
^{1}H NMR Spectra of **4e** (300 MHz, CDCl3):



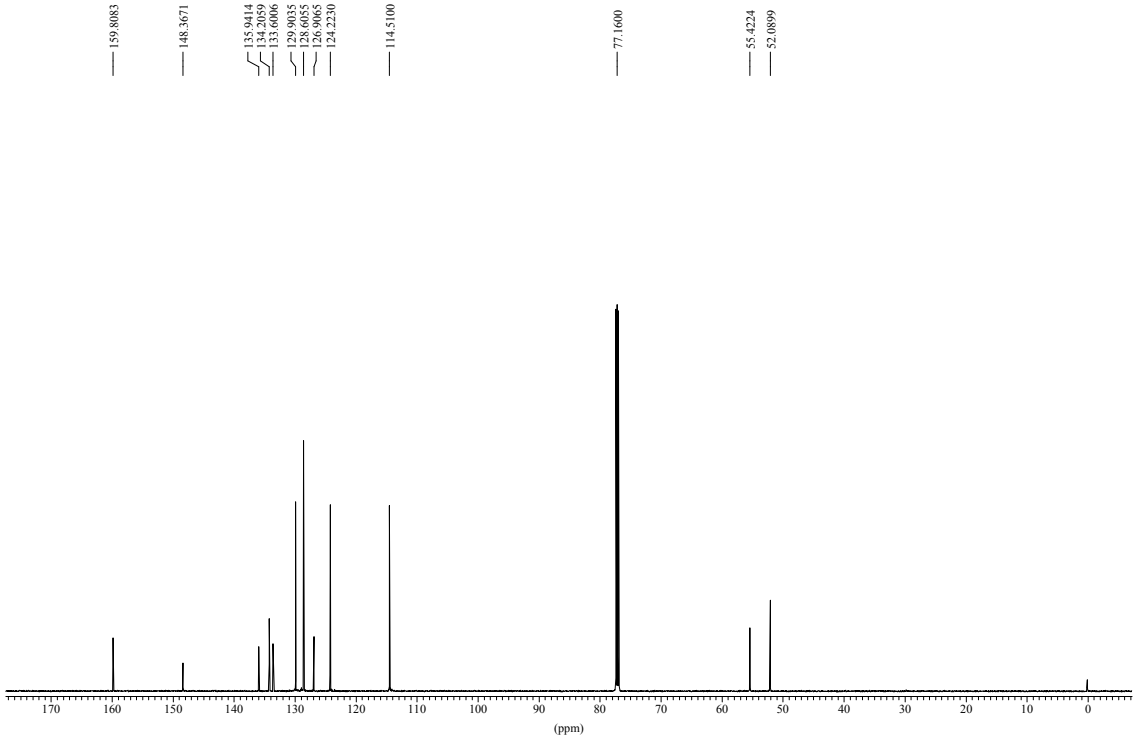
^{13}C NMR Spectra of **4e** (100 MHz, CDCl3):



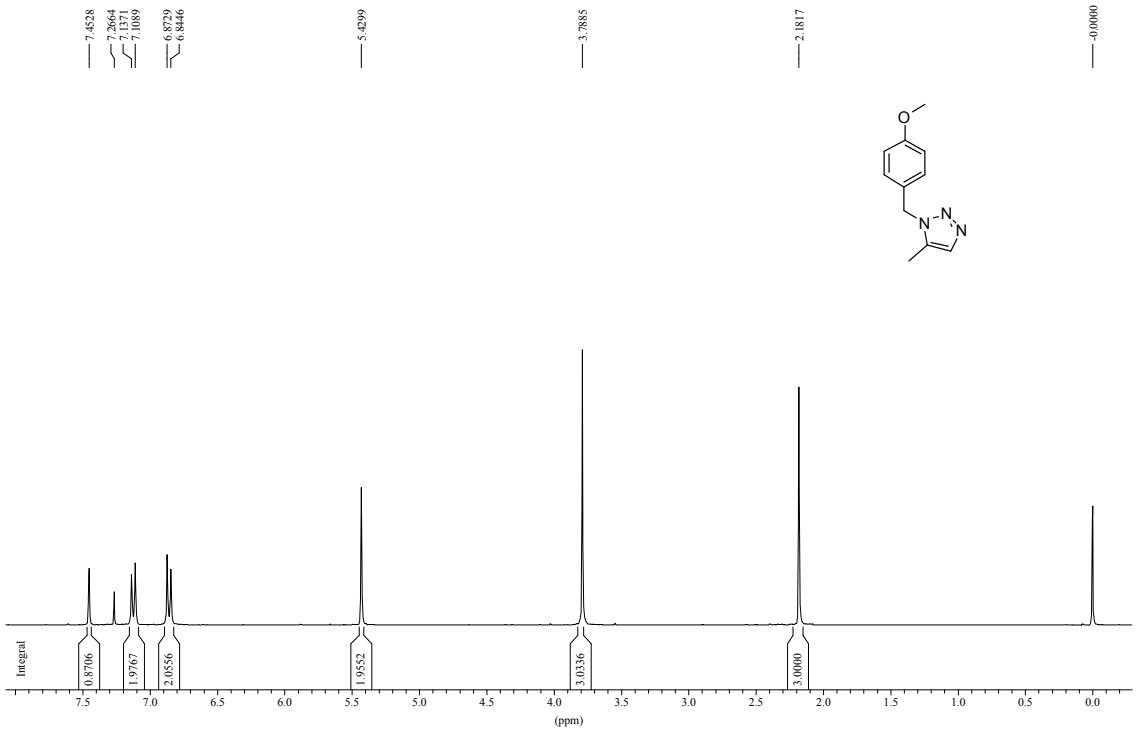
^{1}H NMR Spectra of **4f** (300 MHz, CDCl3):



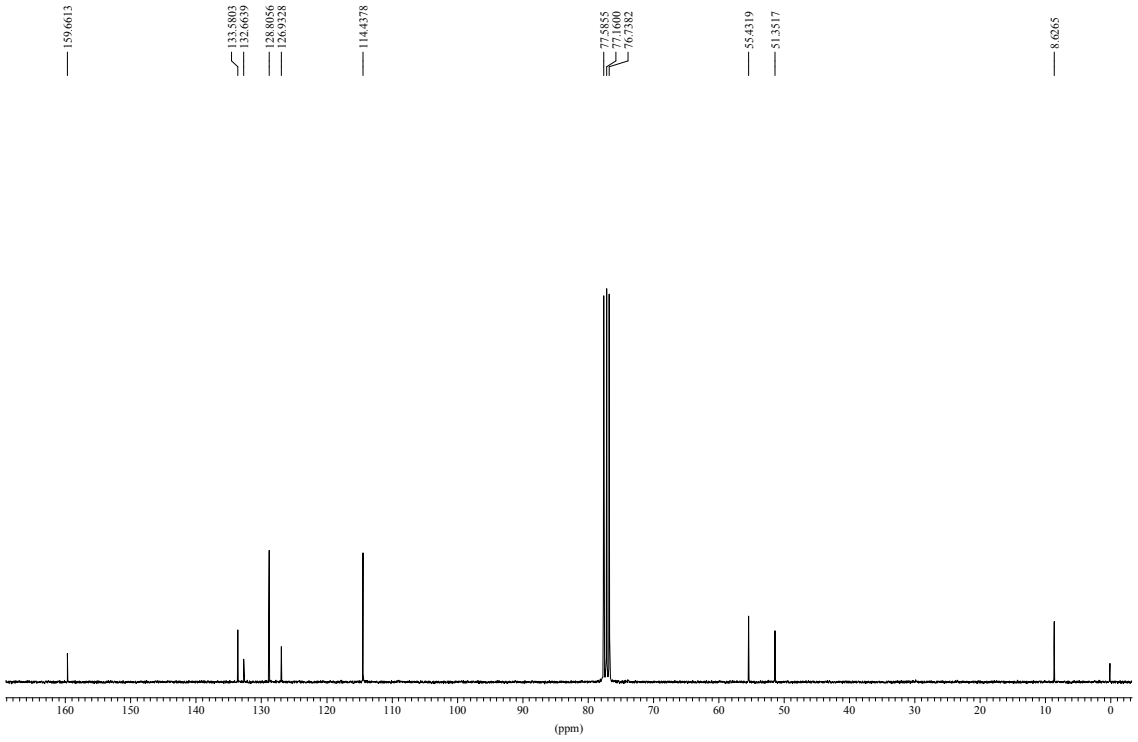
^{13}C NMR Spectra of **4f** (75 MHz, CDCl3):



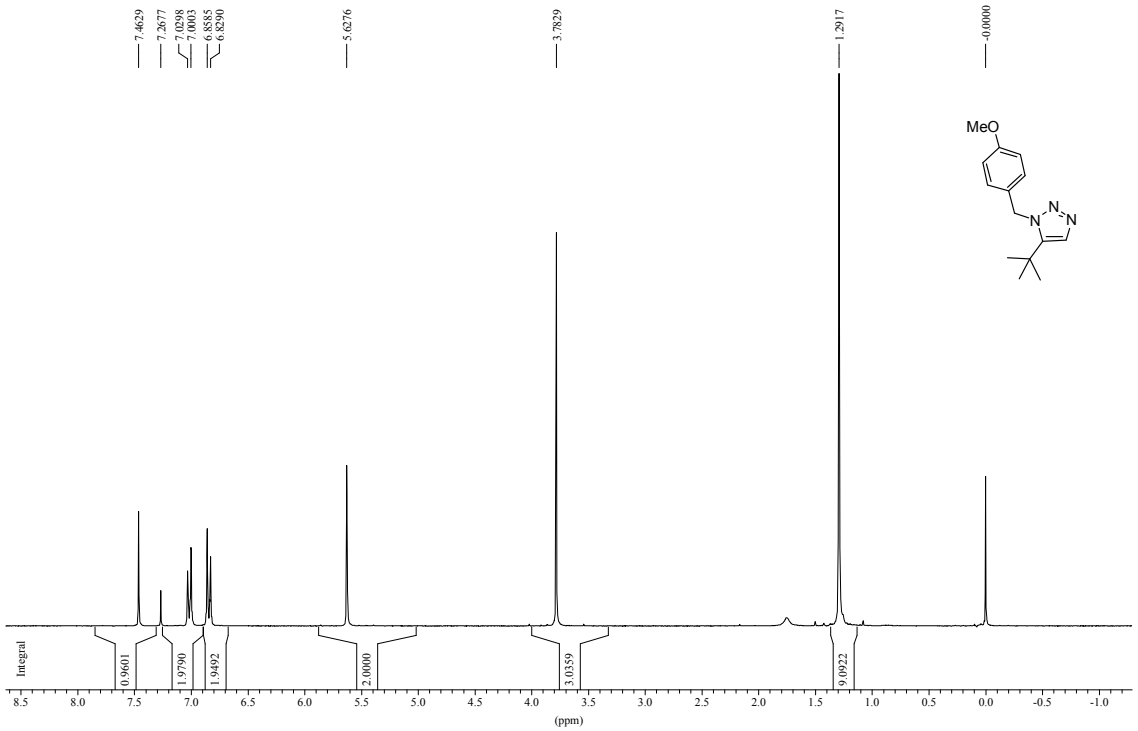
^{1}H NMR Spectra of **4g** (300 MHz, CDCl3):



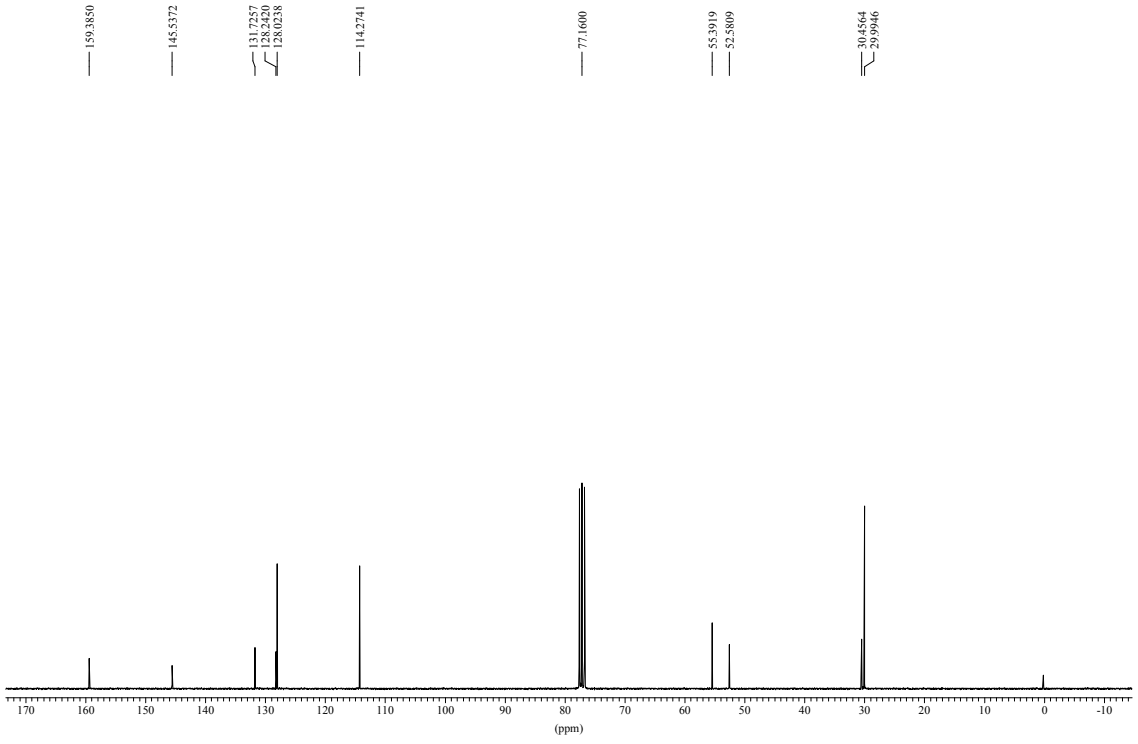
^{13}C NMR Spectra of **4g** (75 MHz, CDCl3):



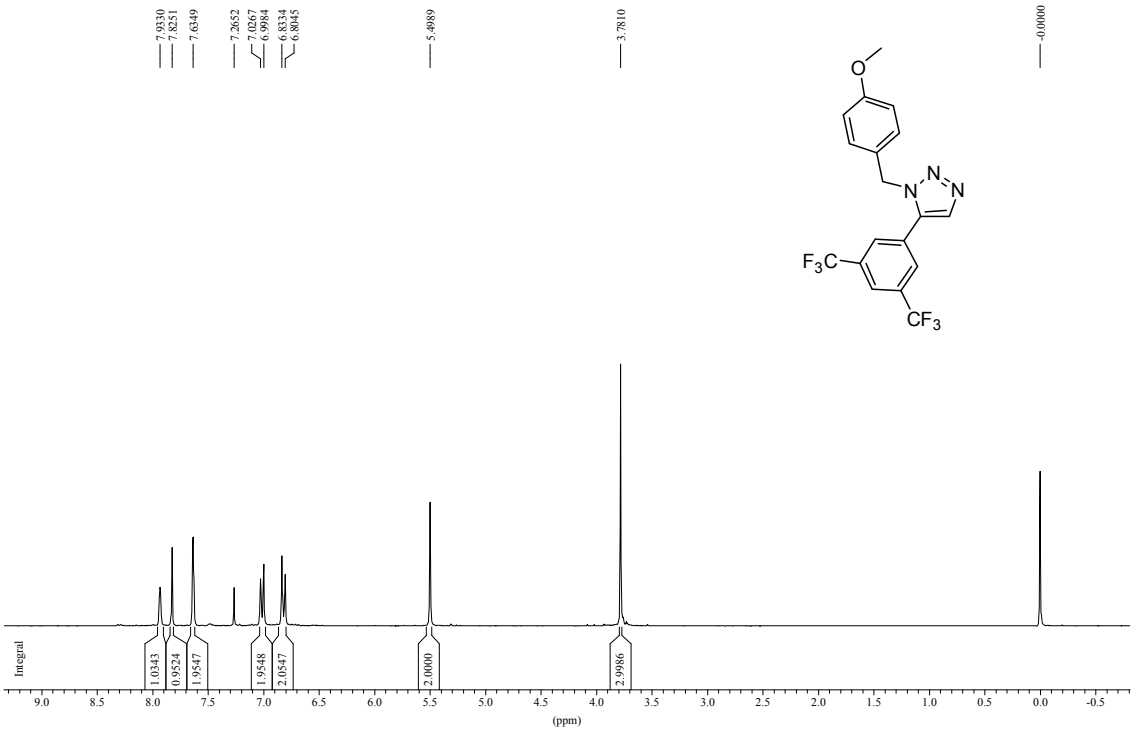
^{1}H NMR Spectra of **4h** (300 MHz, CDCl3):



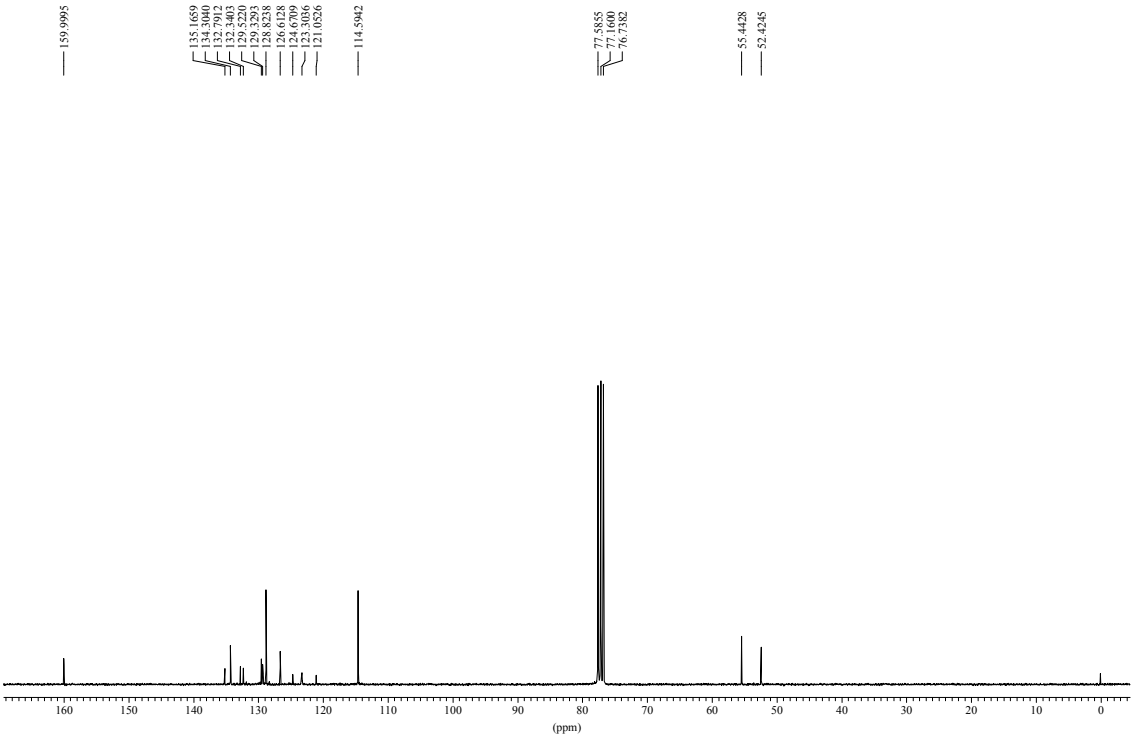
^{13}C NMR Spectra of **4h** (75 MHz, CDCl3):



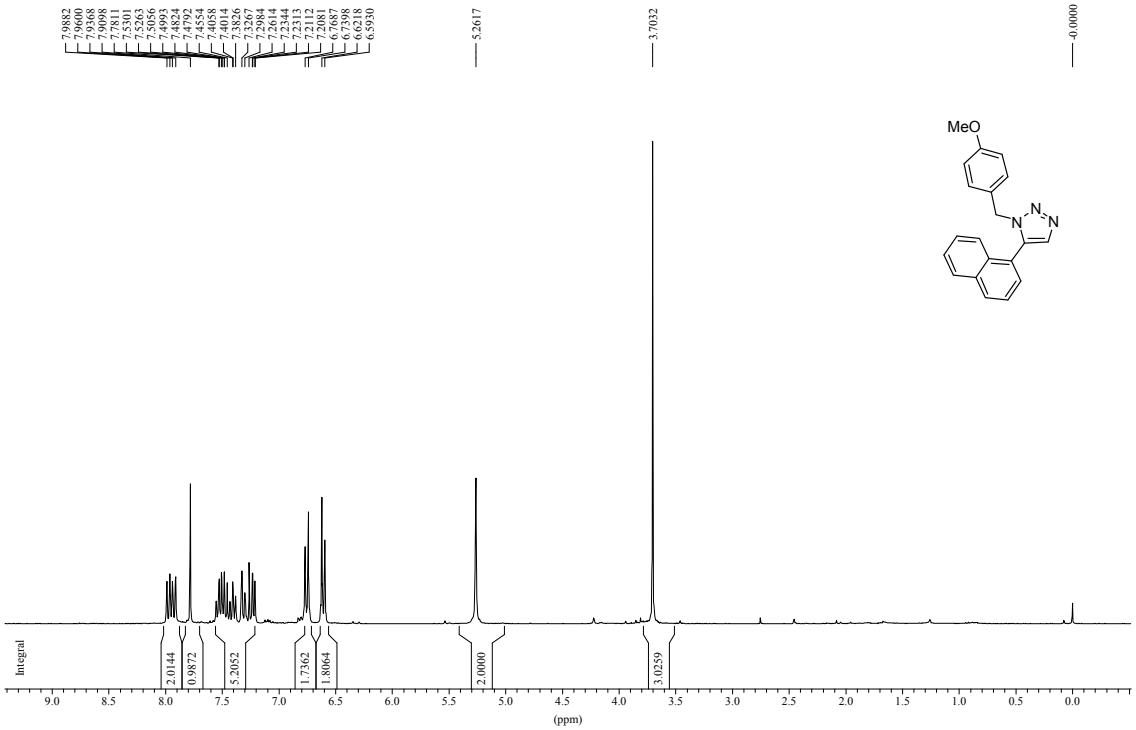
^{1}H NMR Spectra of **4i** (300 MHz, CDCl3):



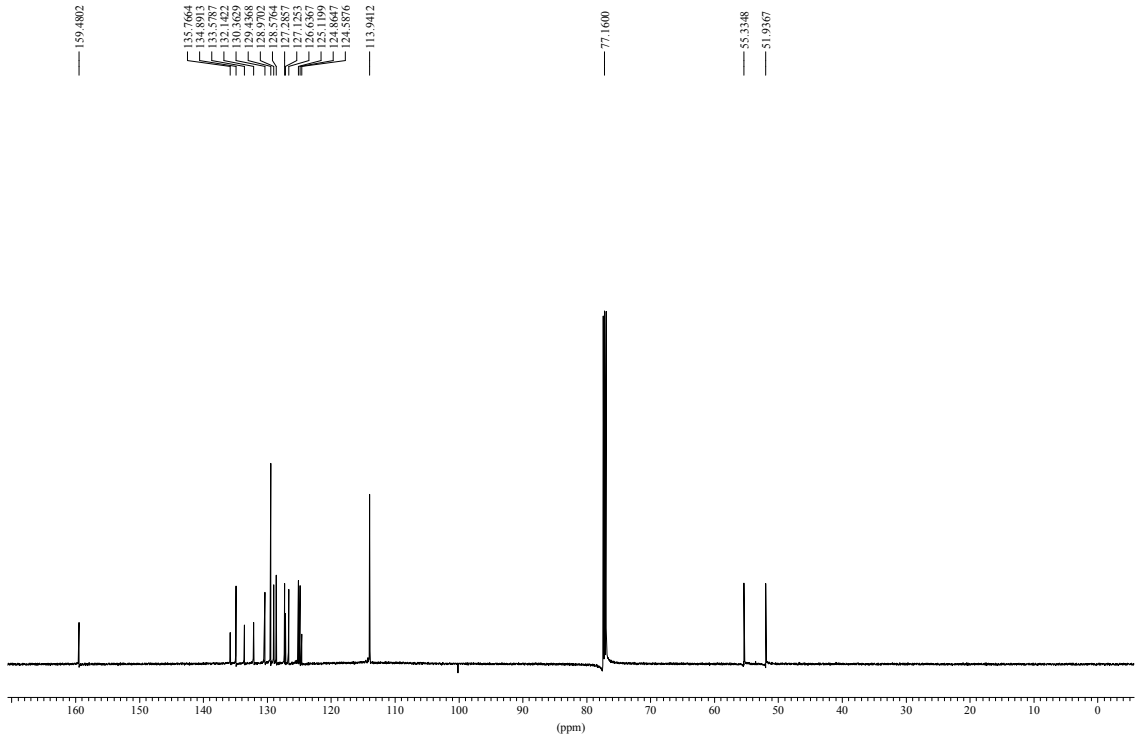
^{13}C NMR Spectra of **4i** (75 MHz, CDCl3):



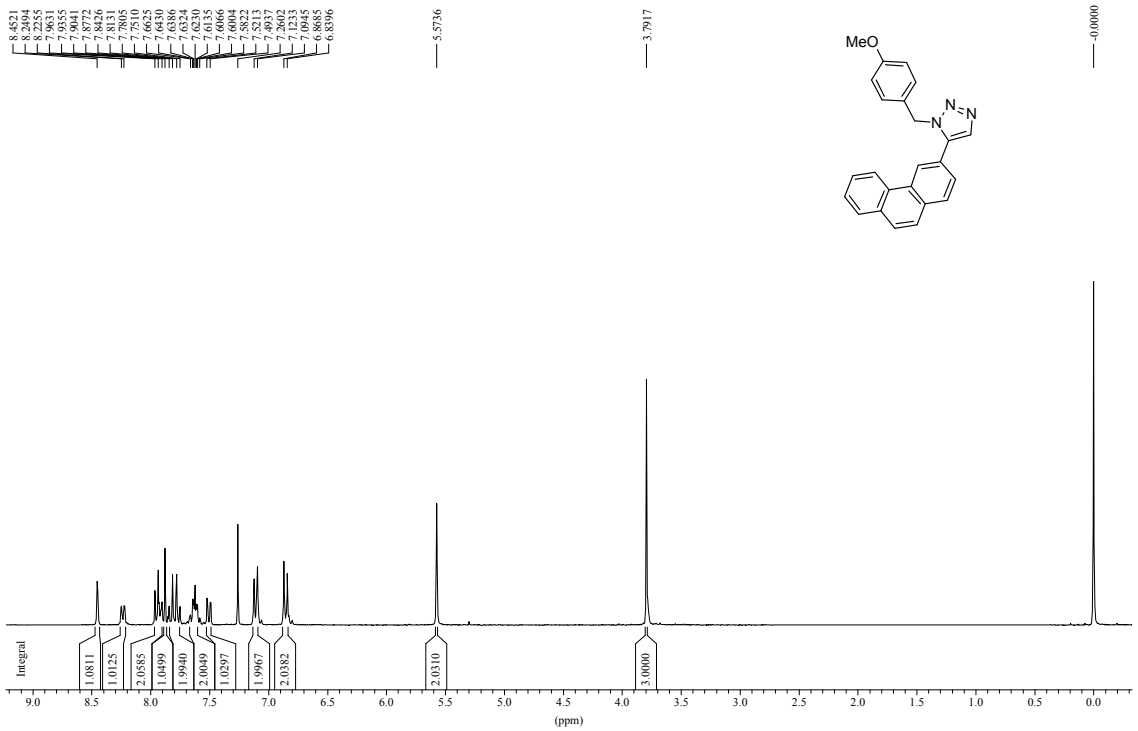
^{1}H NMR Spectra of **4j** (300 MHz, CDCl3):



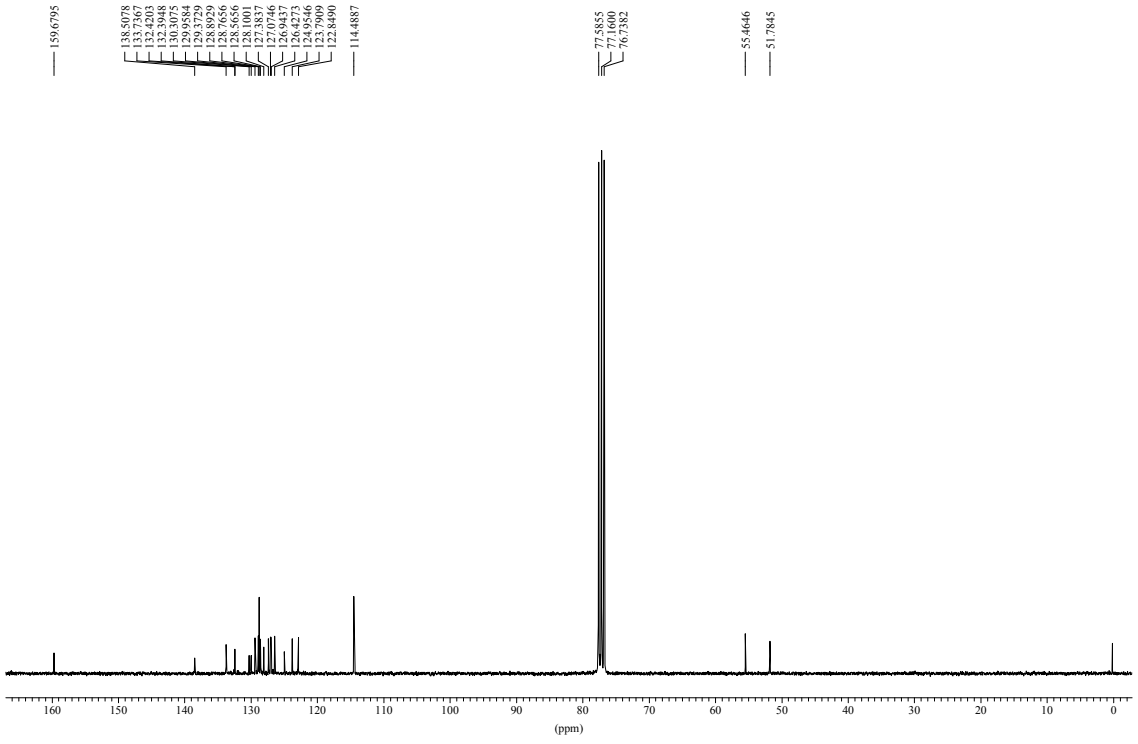
^{13}C NMR Spectra of **4j** (75 MHz, CDCl3):



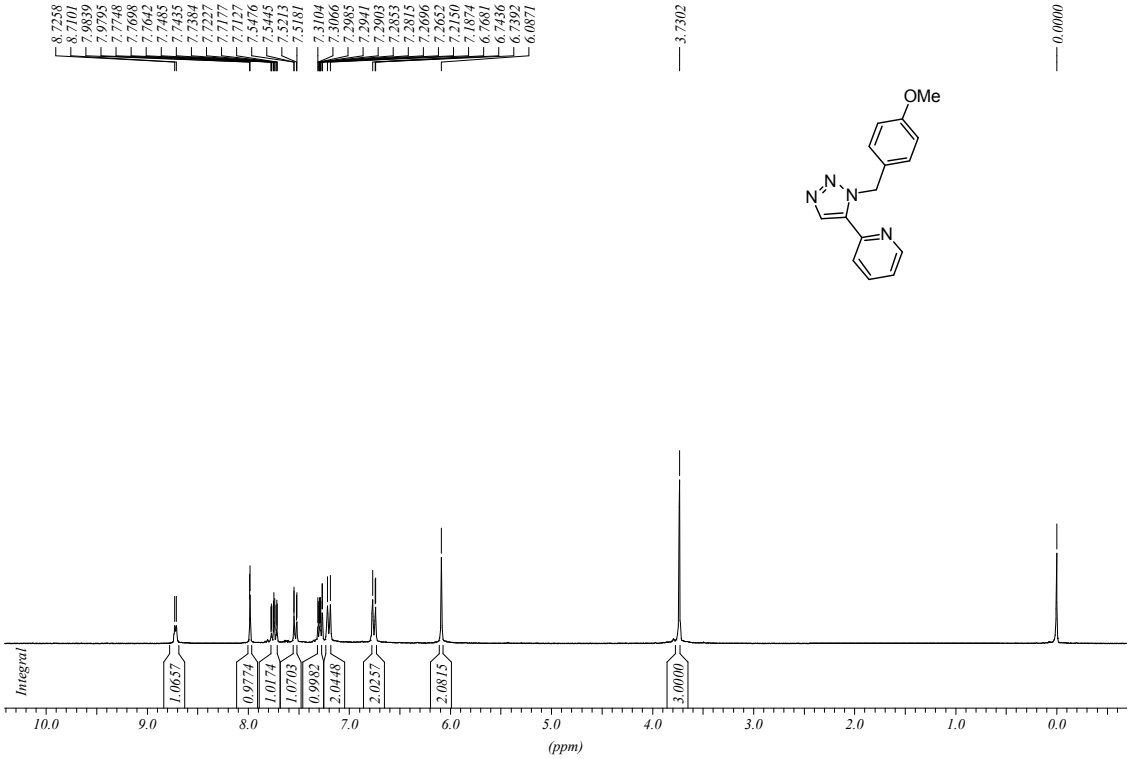
^{1}H NMR Spectra of **4k** (300 MHz, CDCl3):



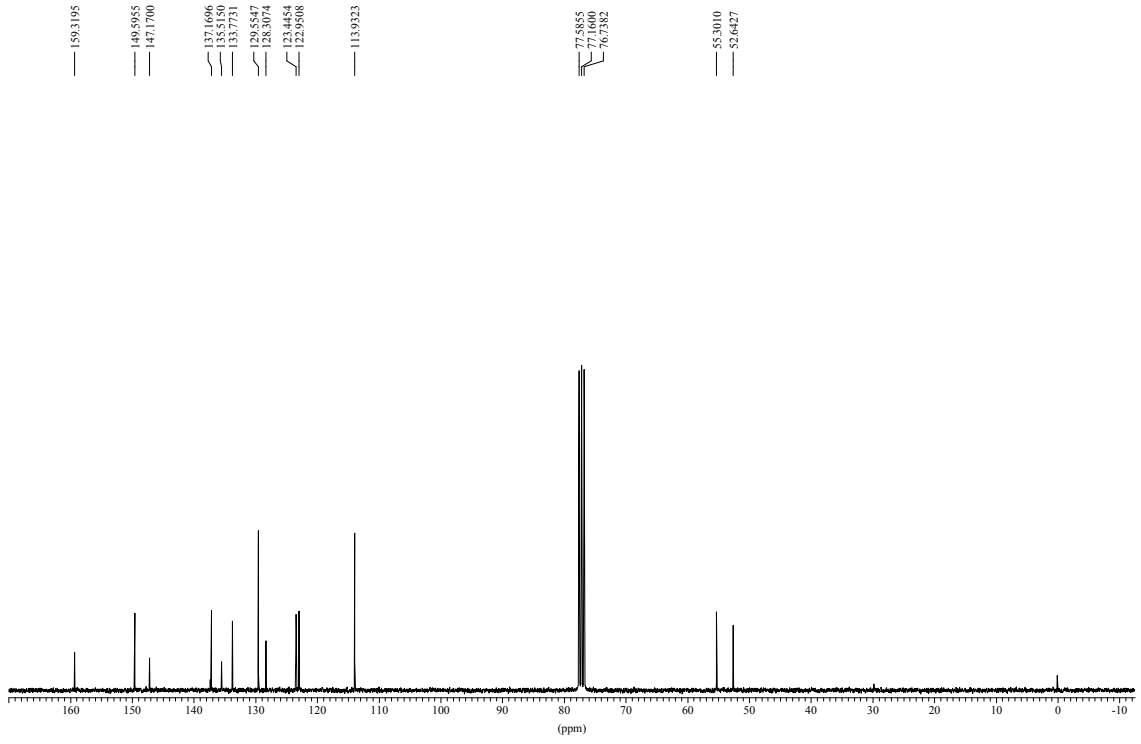
^{13}C NMR Spectra of **4k** (75 MHz, CDCl3):



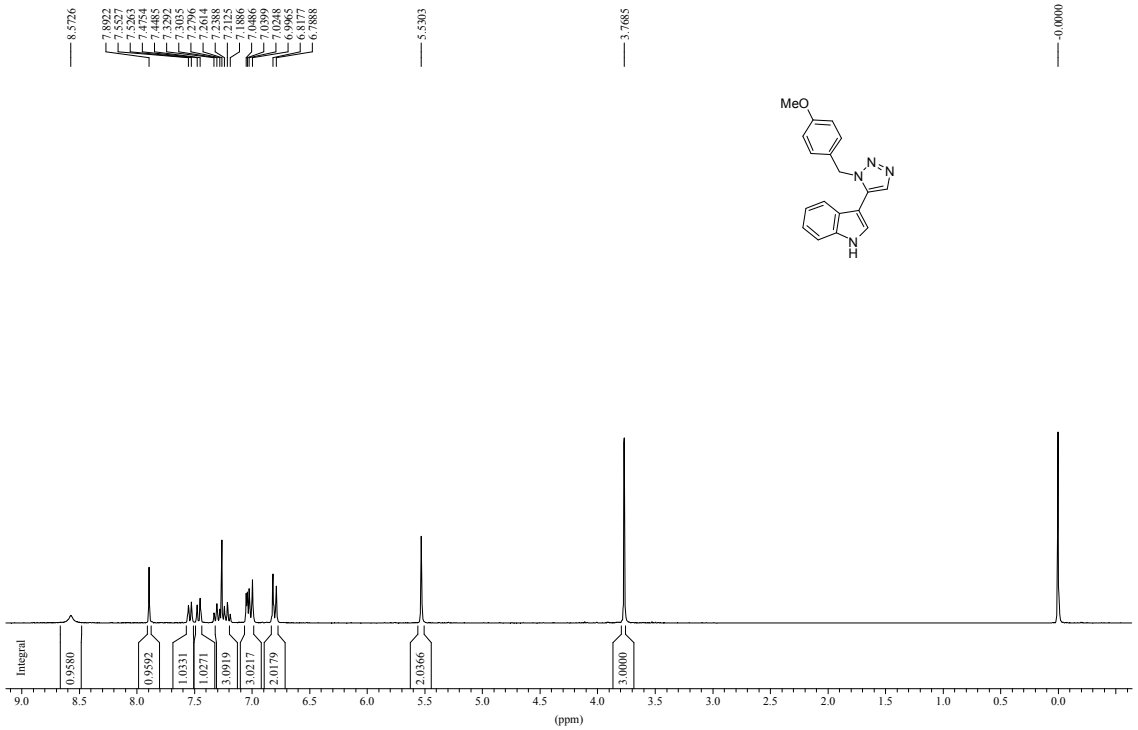
^{1}H NMR Spectra of **4l** (300 MHz, CDCl3):



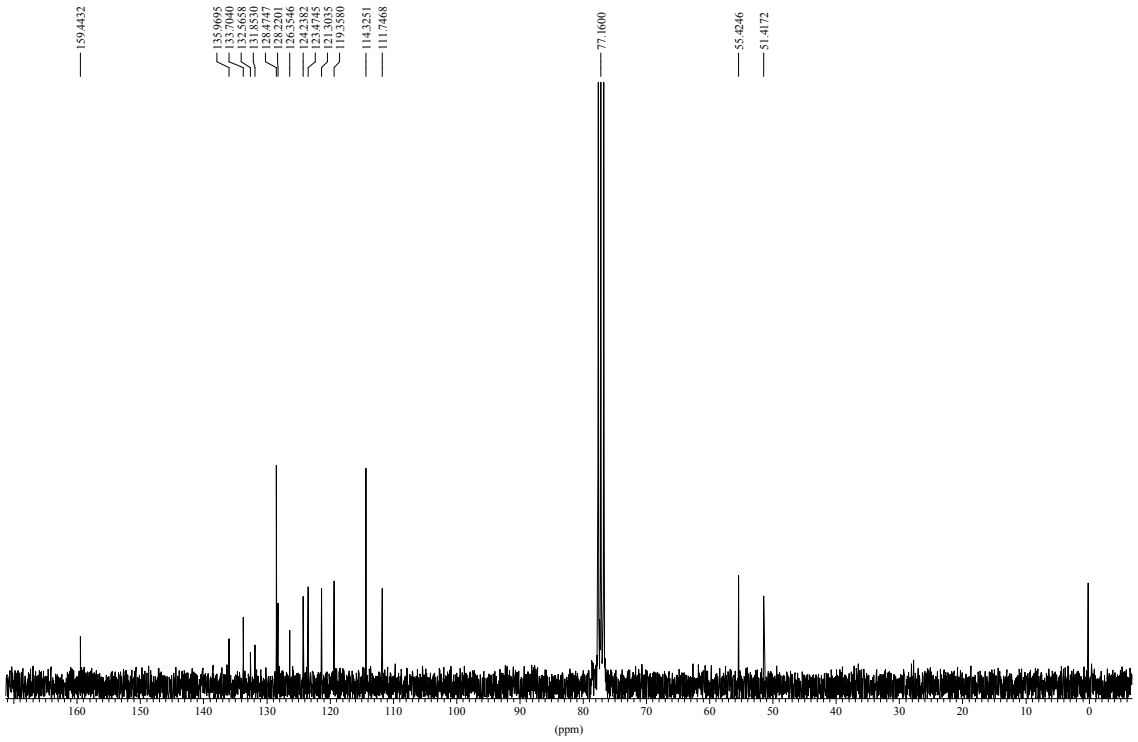
^{13}C NMR Spectra of **4l** (75 MHz, CDCl3):



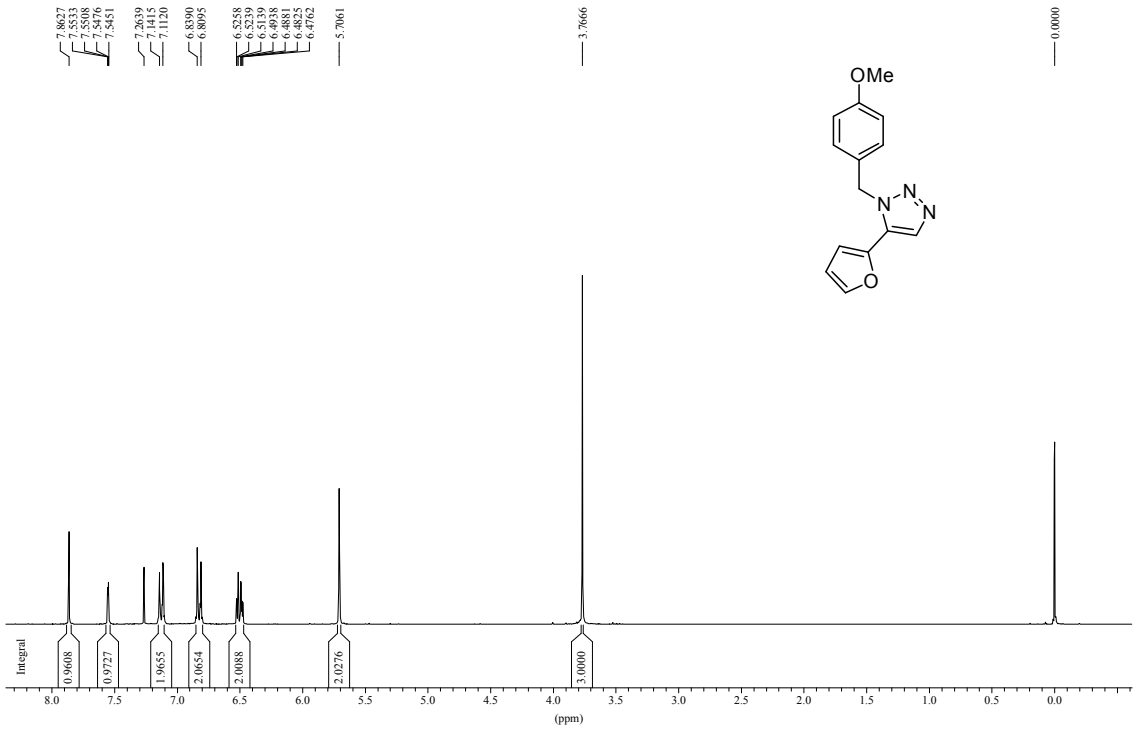
^{1}H NMR Spectra of **4m** (300 MHz, CDCl3):



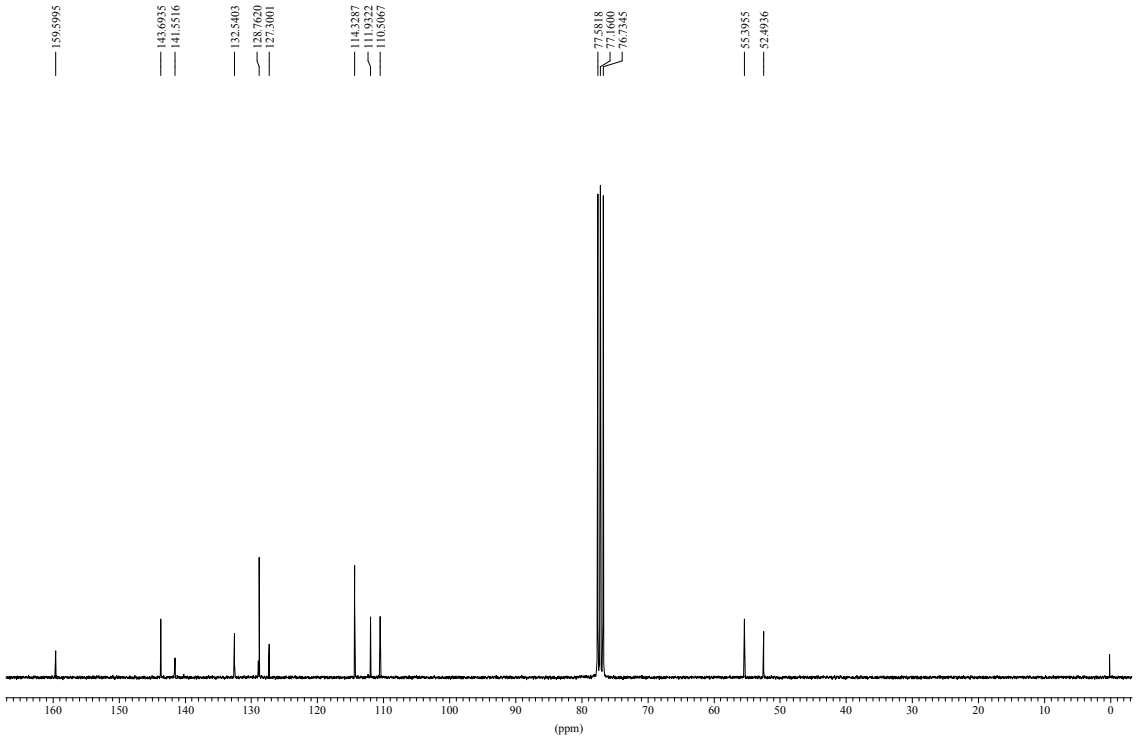
^{13}C NMR Spectra of **4m** (75 MHz, CDCl3):



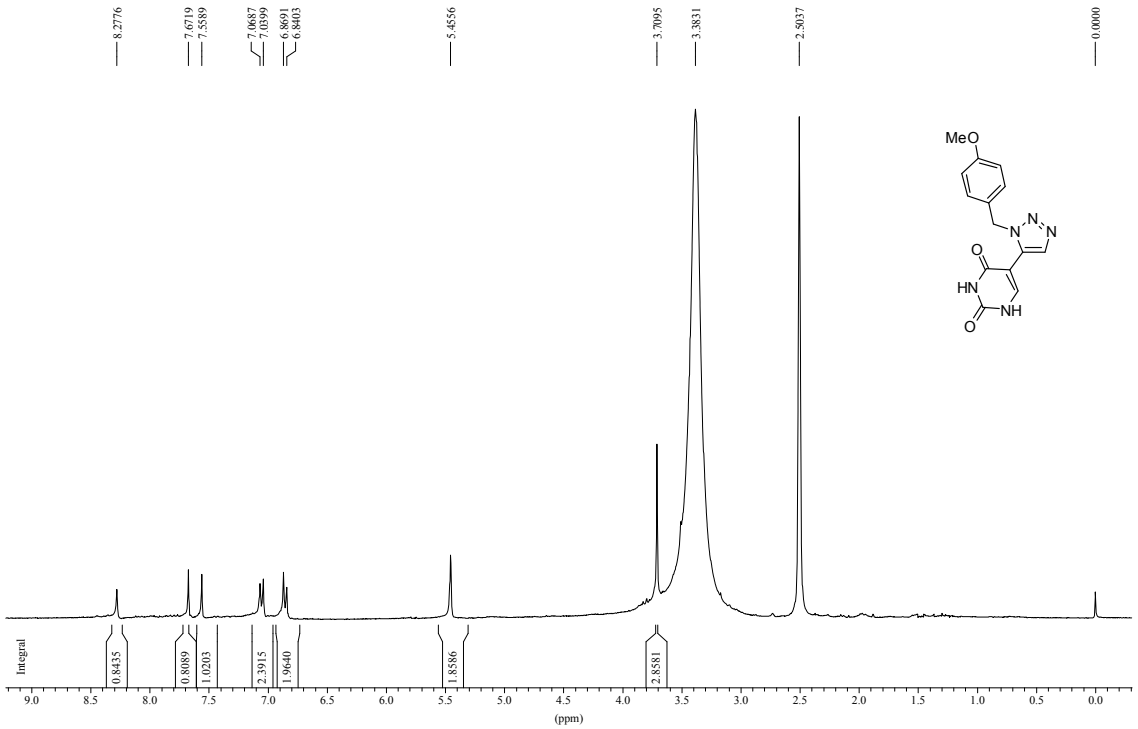
^{1}H NMR Spectra of **4n** (300 MHz, CDCl3):



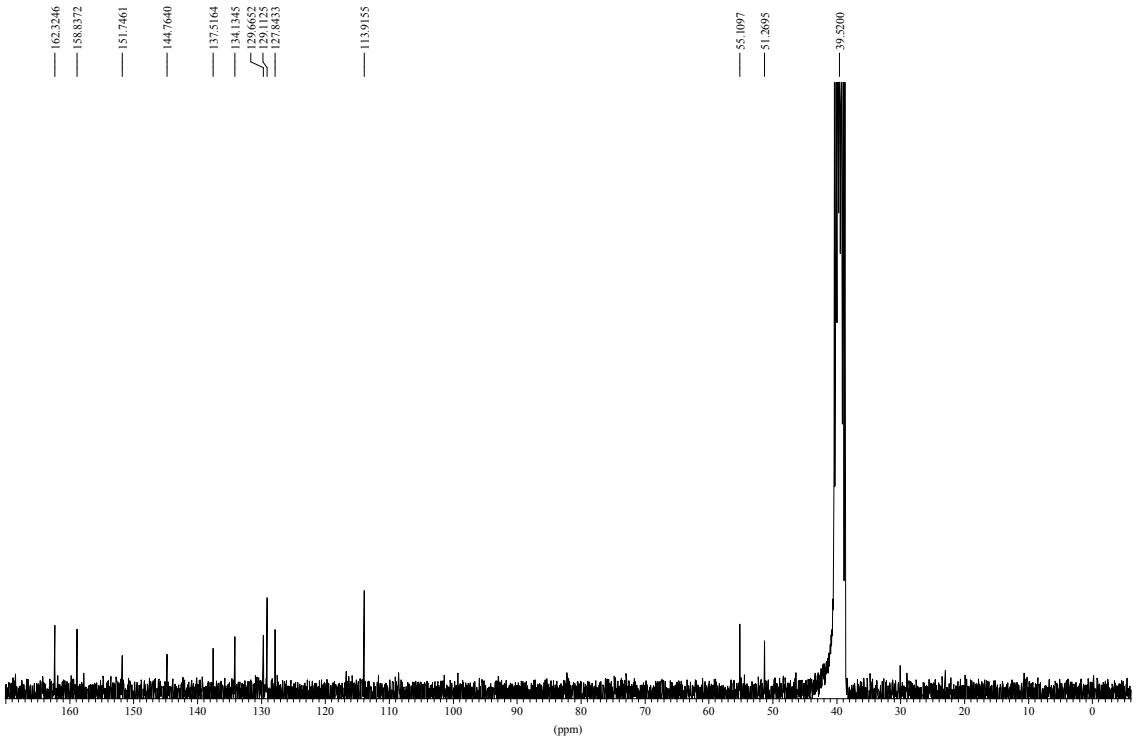
^{13}C NMR Spectra of **4n** (75 MHz, CDCl3):



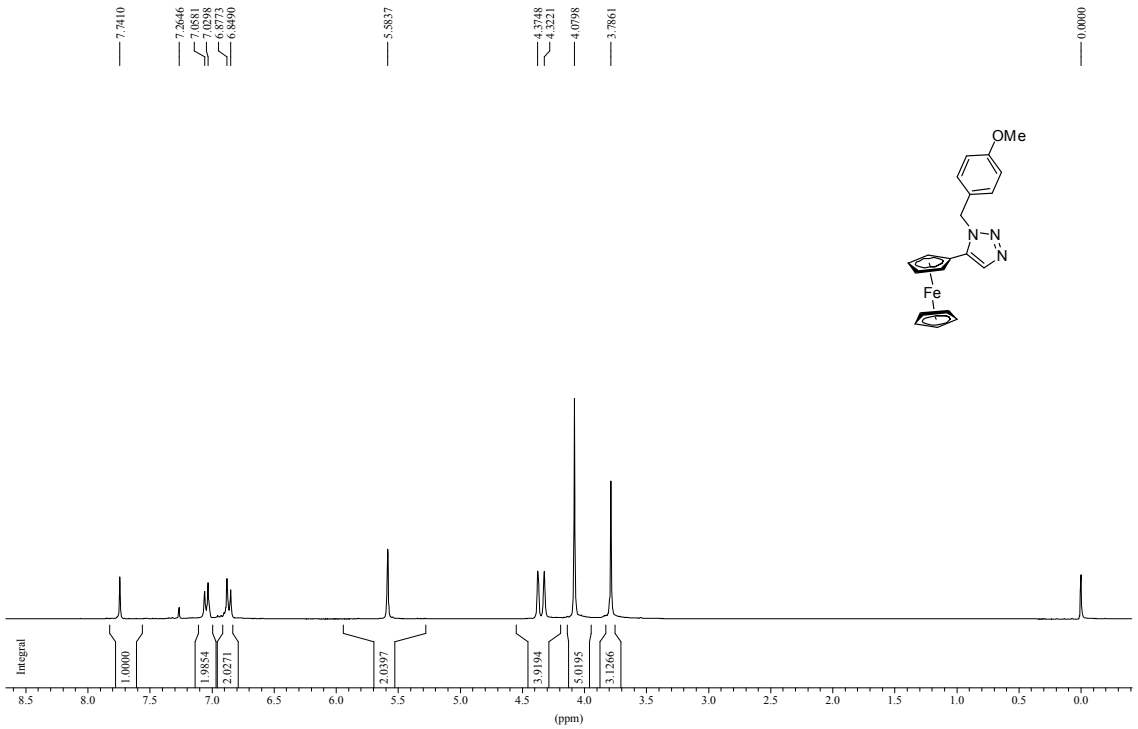
^{1}H NMR Spectra of **4o** (300 MHz, DMSO):



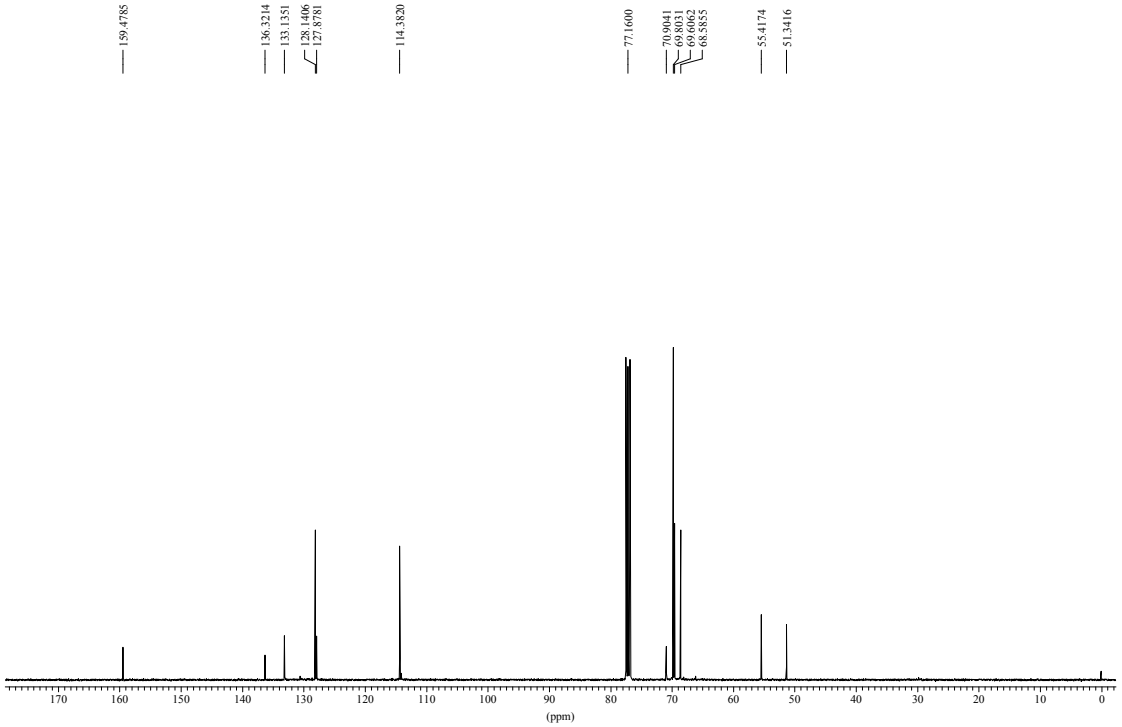
^{13}C NMR Spectra of **4o** (75 MHz, DMSO):



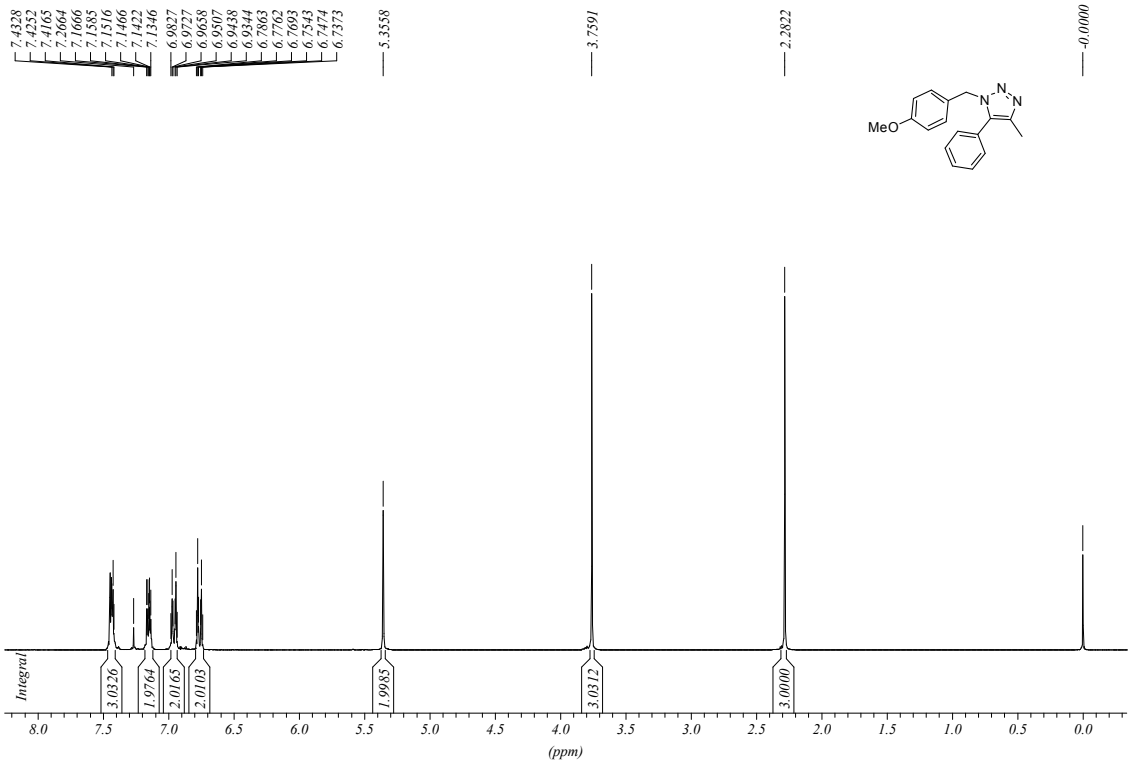
^{1}H NMR Spectra of **4p** (300 MHz, CDCl3):



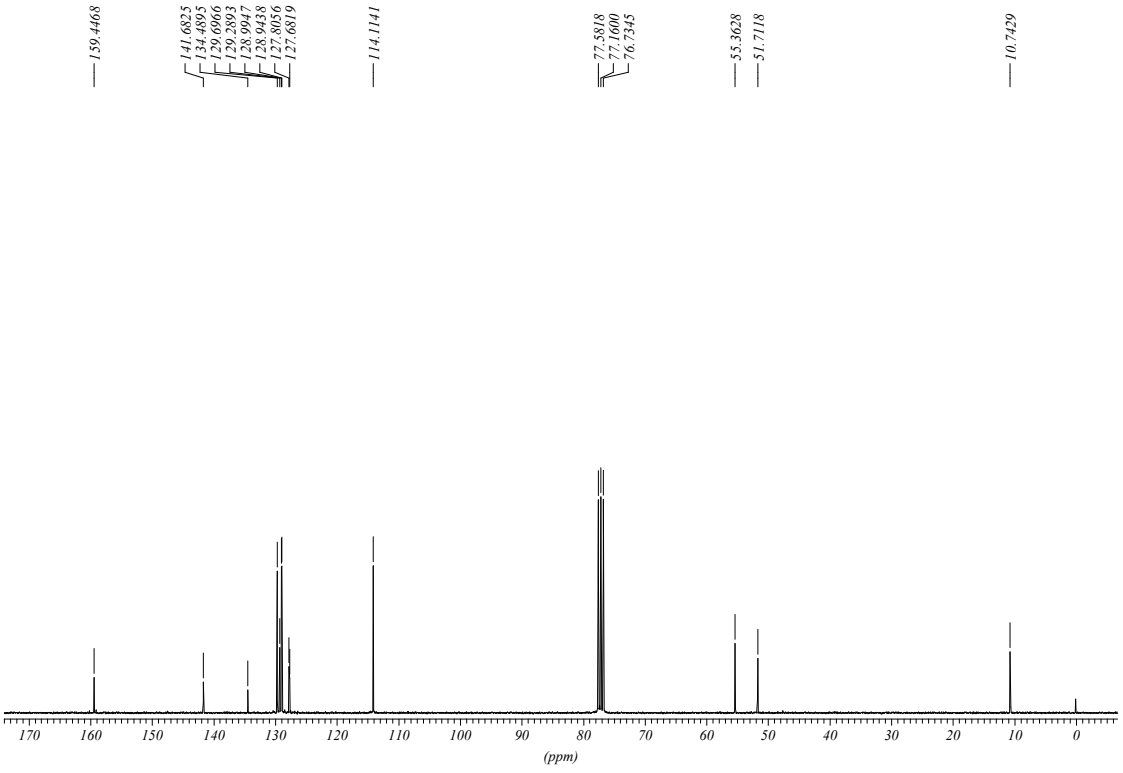
^{13}C NMR Spectra of **4p** (75 MHz, CDCl3):



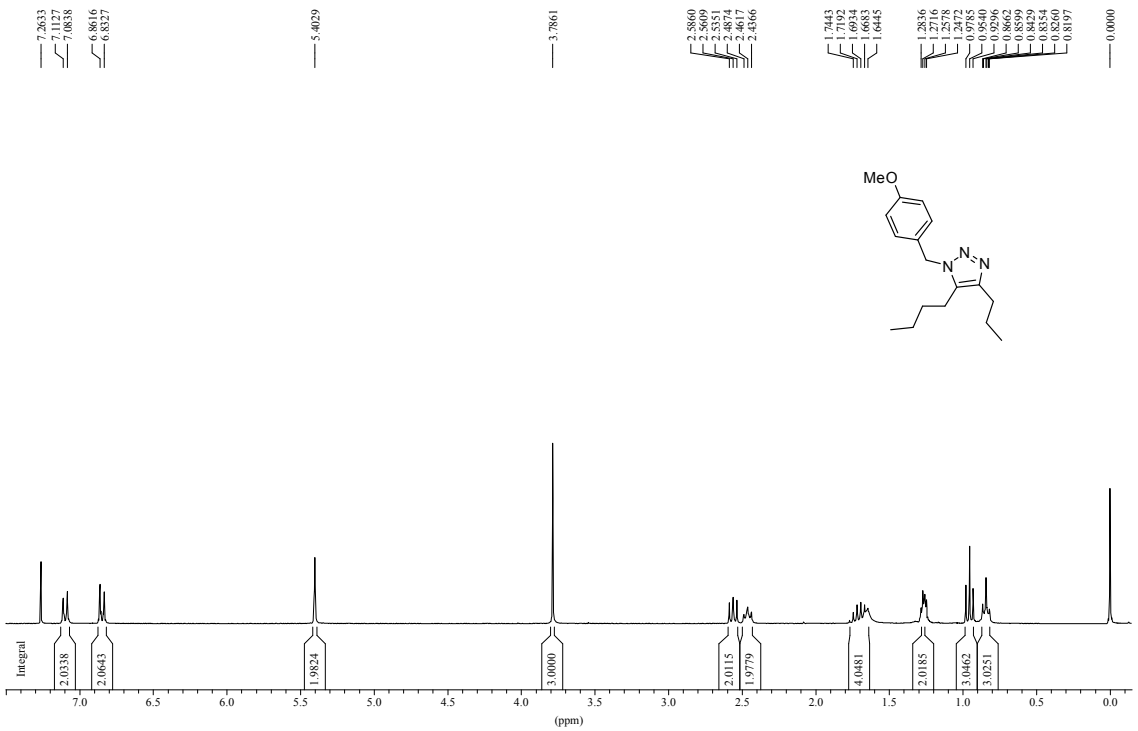
^{1}H NMR Spectra of **4q** (300 MHz, CDCl3):



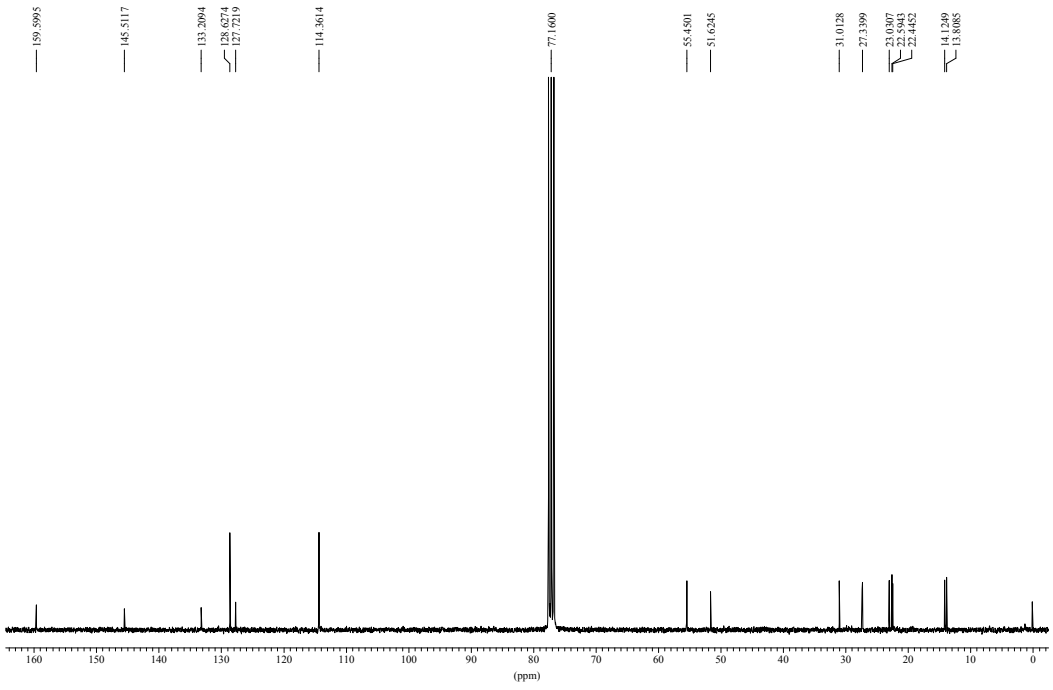
^{13}C NMR Spectra of **4q** (75 MHz, CDCl3):



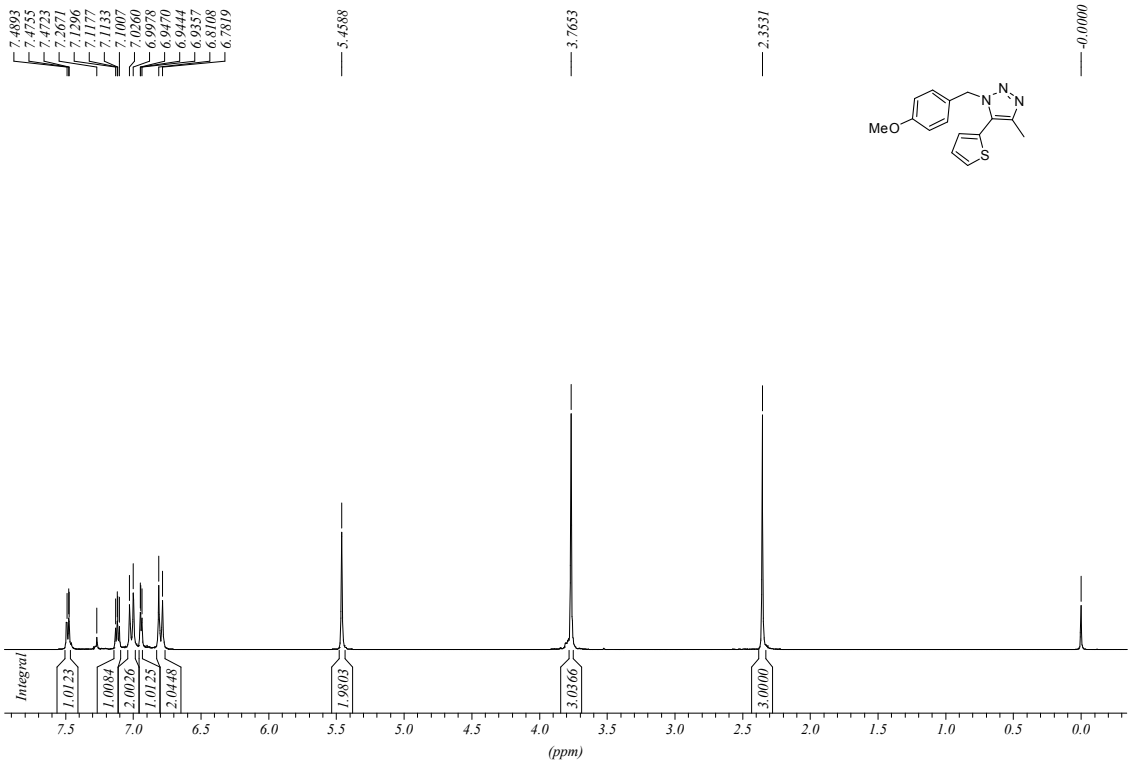
^{1}H NMR Spectra of **4r** (300 MHz, CDCl3):



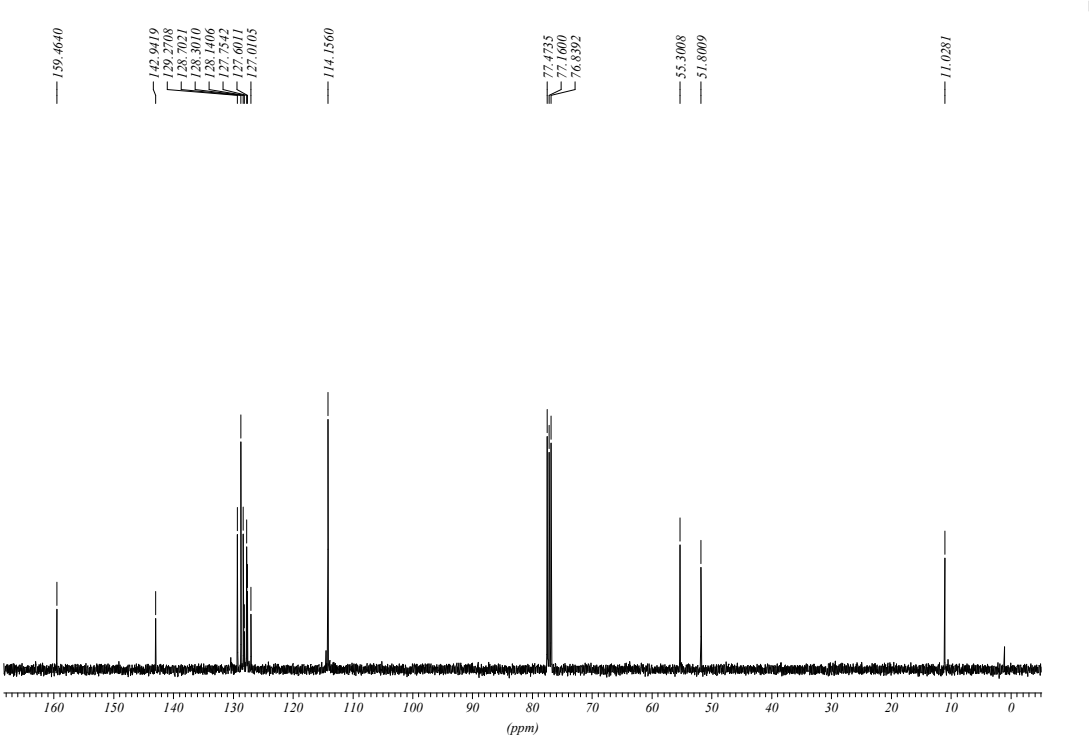
^{13}C NMR Spectra of **4r** (75 MHz, CDCl3):



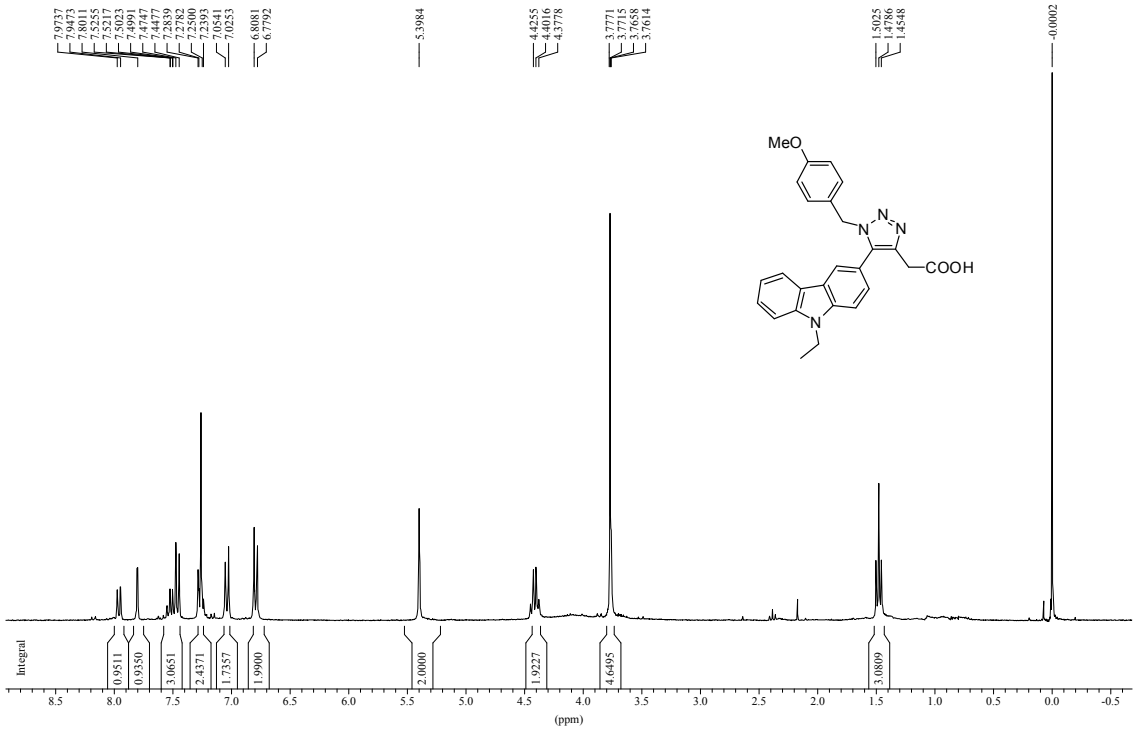
^{1}H NMR Spectra of **4s** (300 MHz, CDCl3):



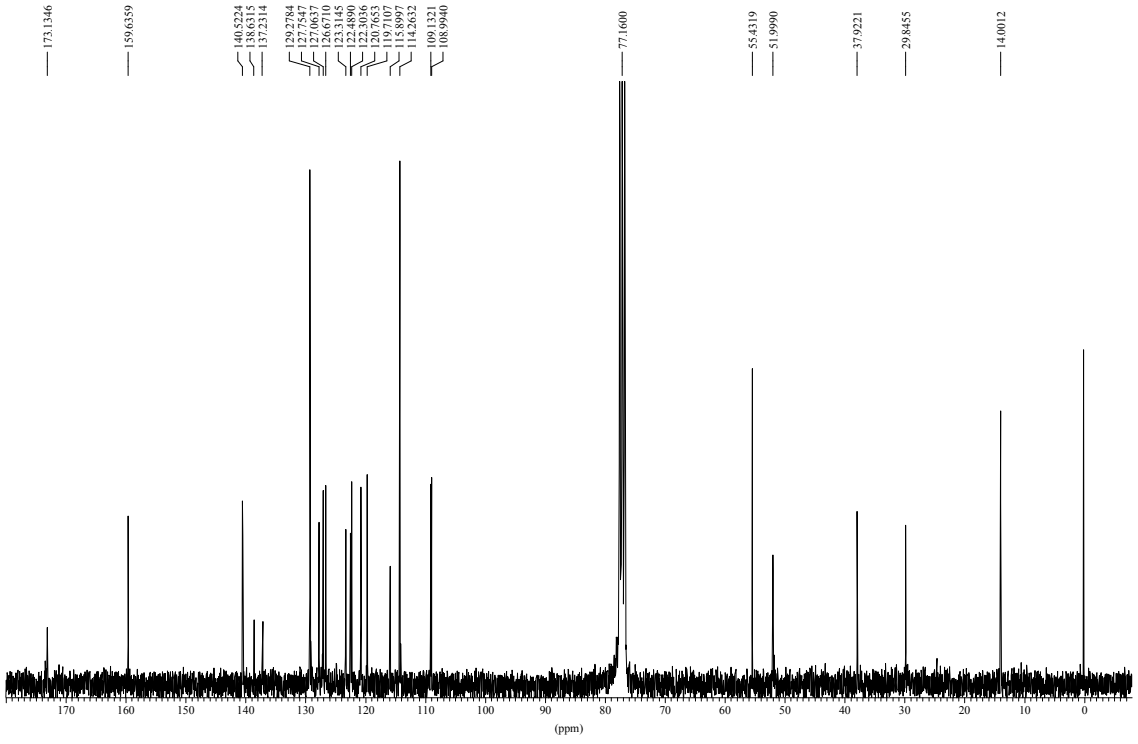
^{13}C NMR Spectra of **4s** (75 MHz, CDCl3):



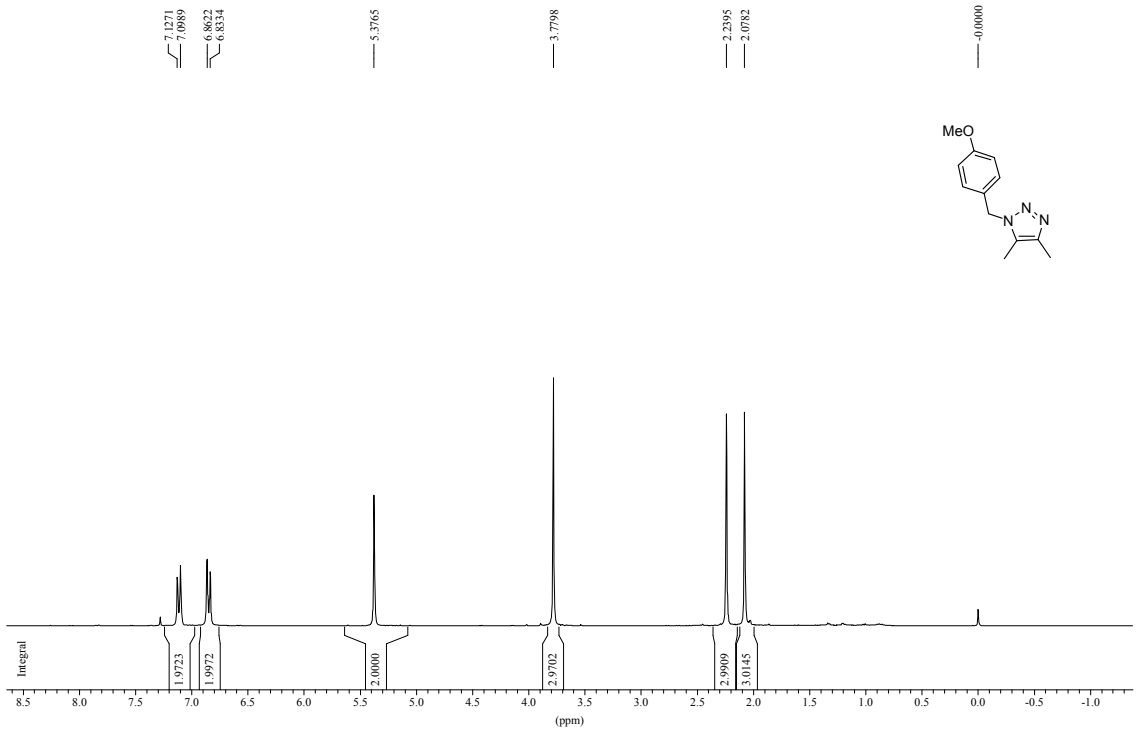
^{1}H NMR Spectra of **4t** (300 MHz, CDCl3):



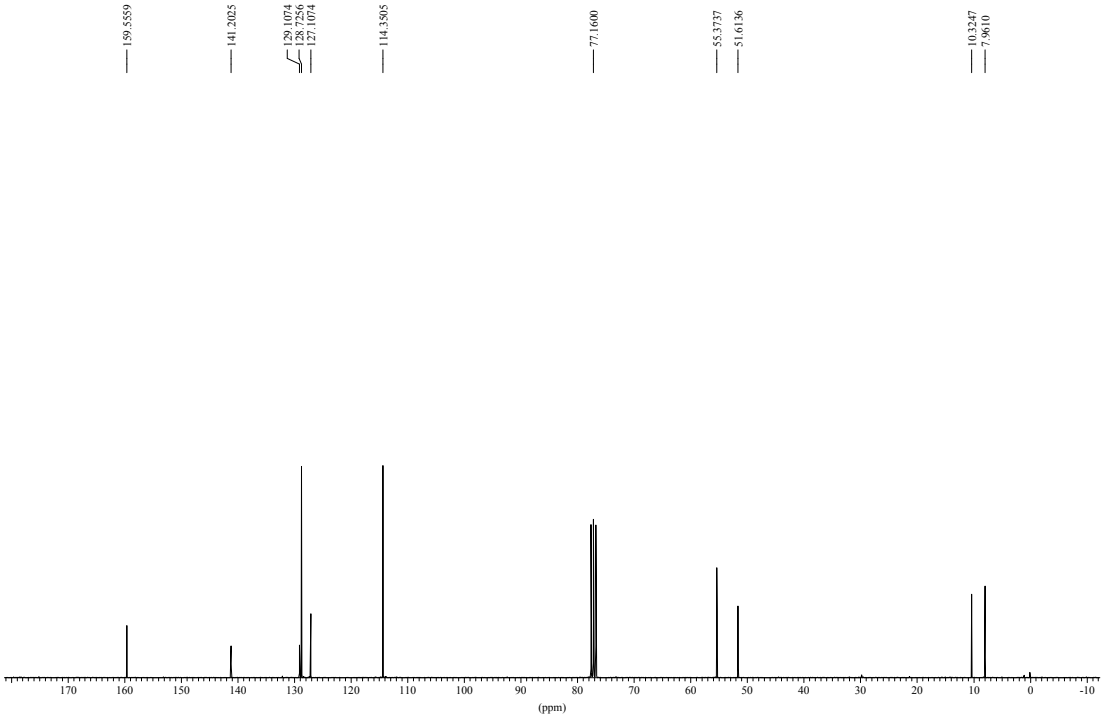
^{13}C NMR Spectra of **4t** (75 MHz, CDCl3):



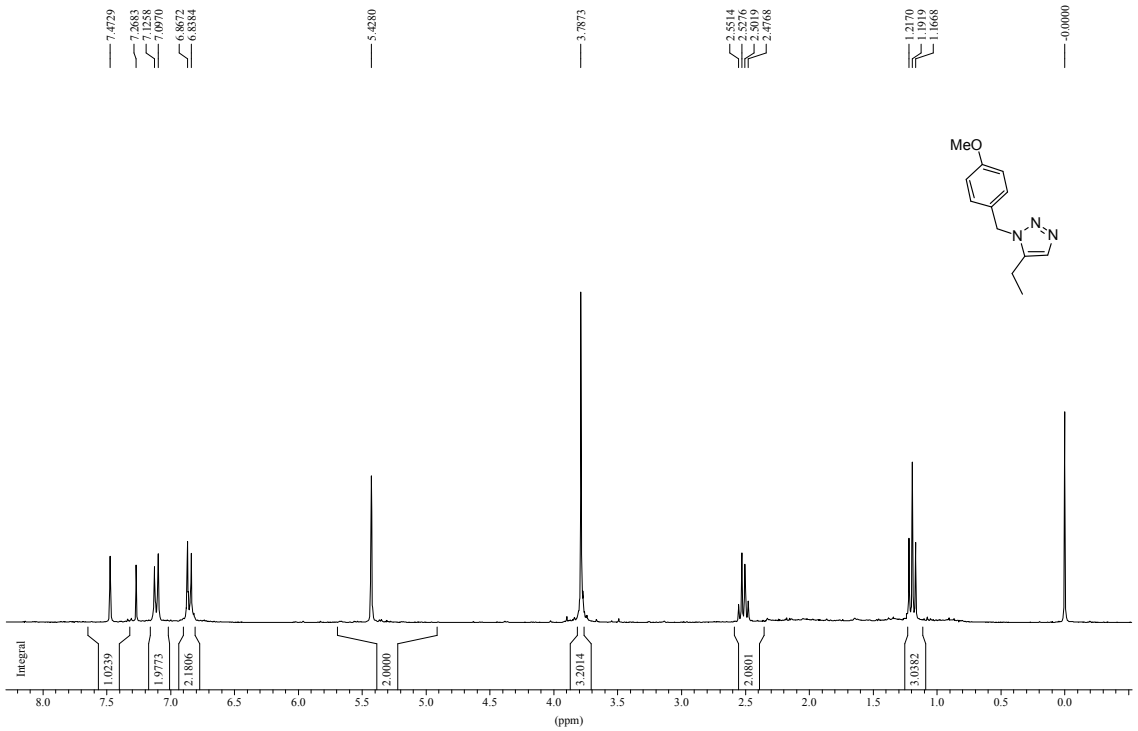
^{1}H NMR Spectra of **4u** (300 MHz, CDCl3):



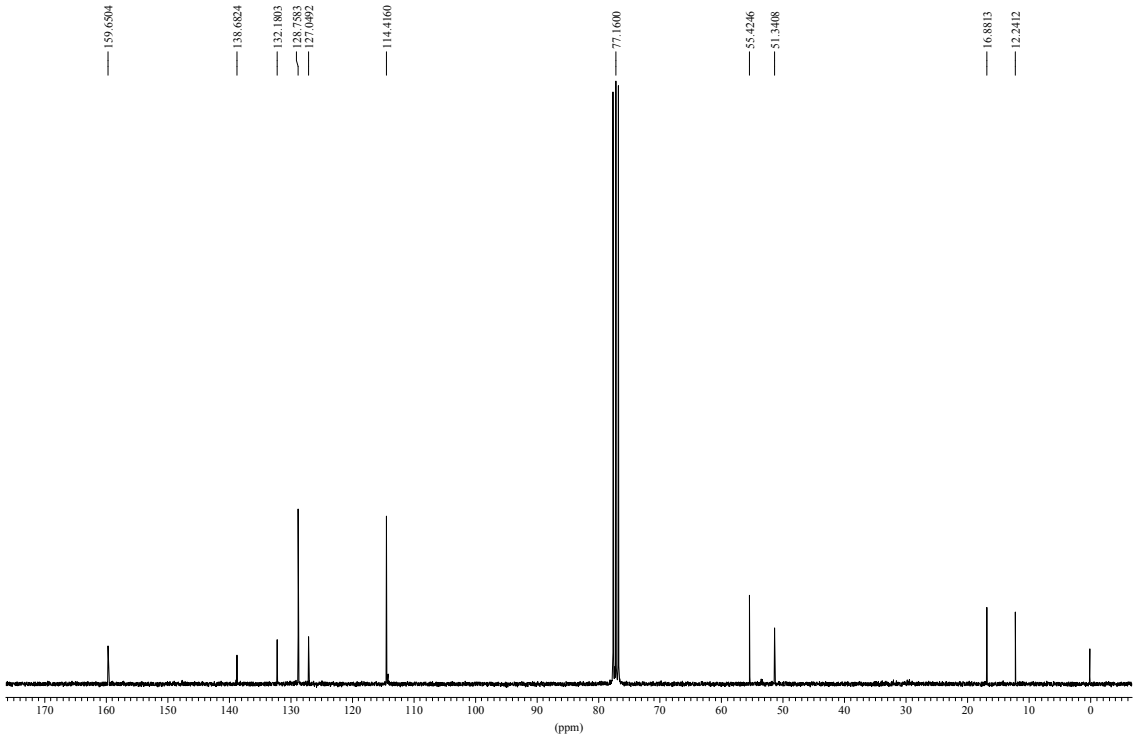
^{13}C NMR Spectra of **4u** (75 MHz, CDCl3):



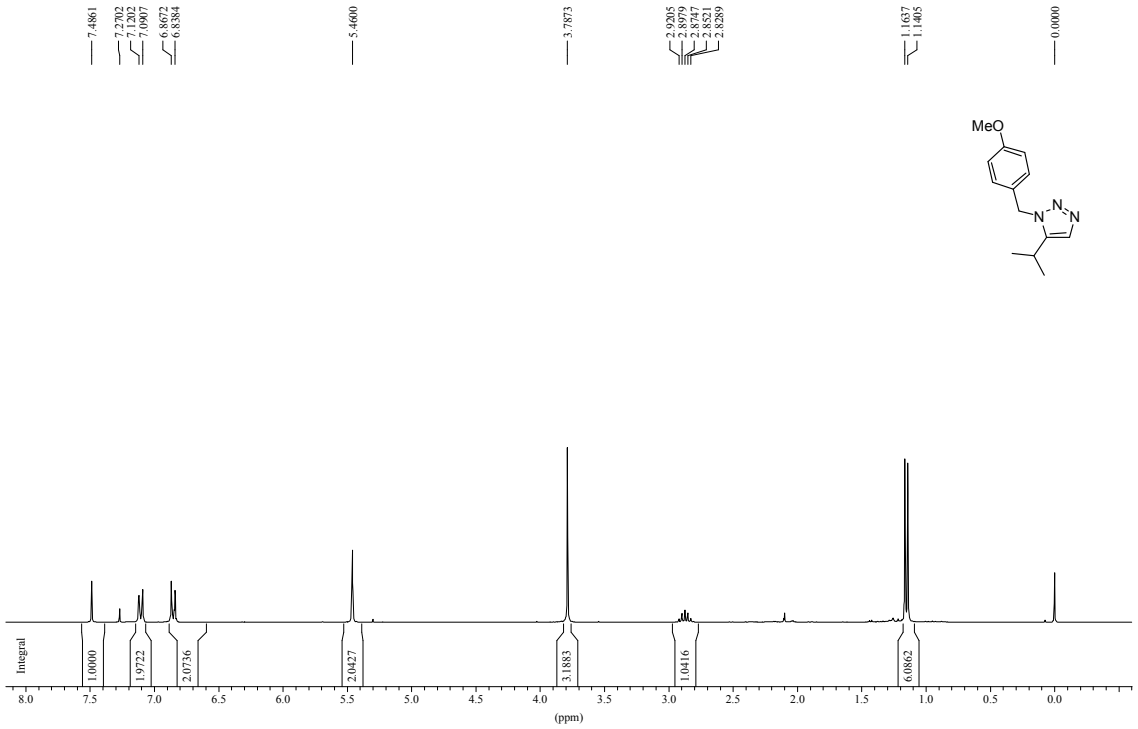
^{1}H NMR Spectra of **4v** (300 MHz, CDCl3):



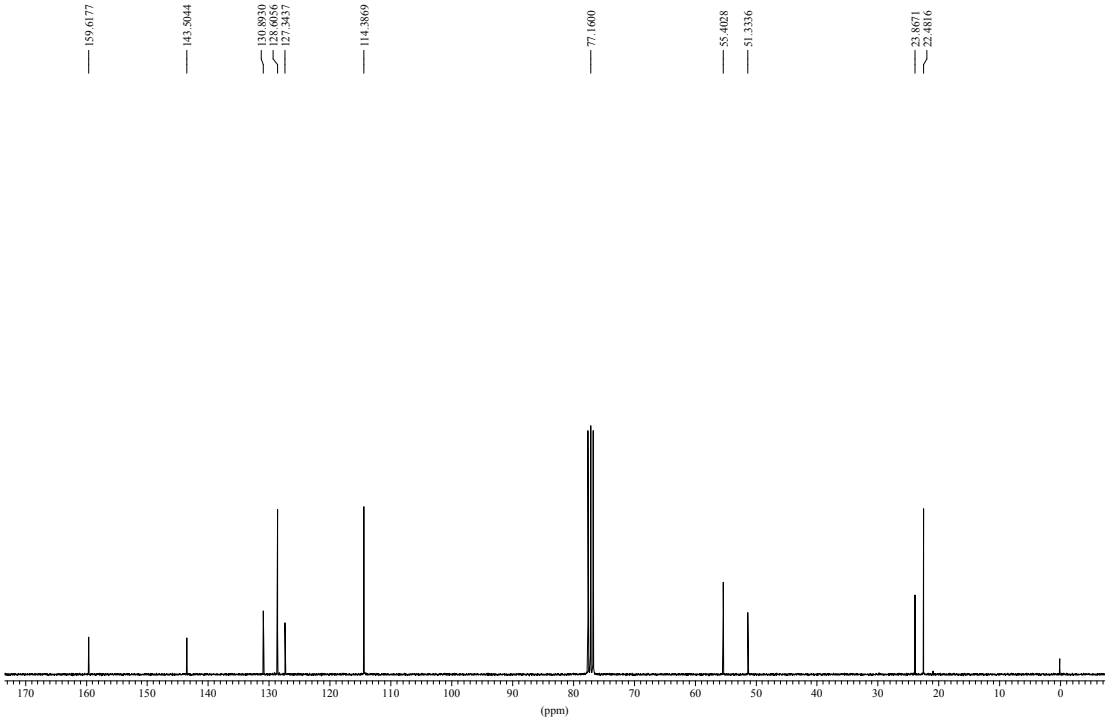
^{13}C NMR Spectra of **4v** (75 MHz, CDCl3):



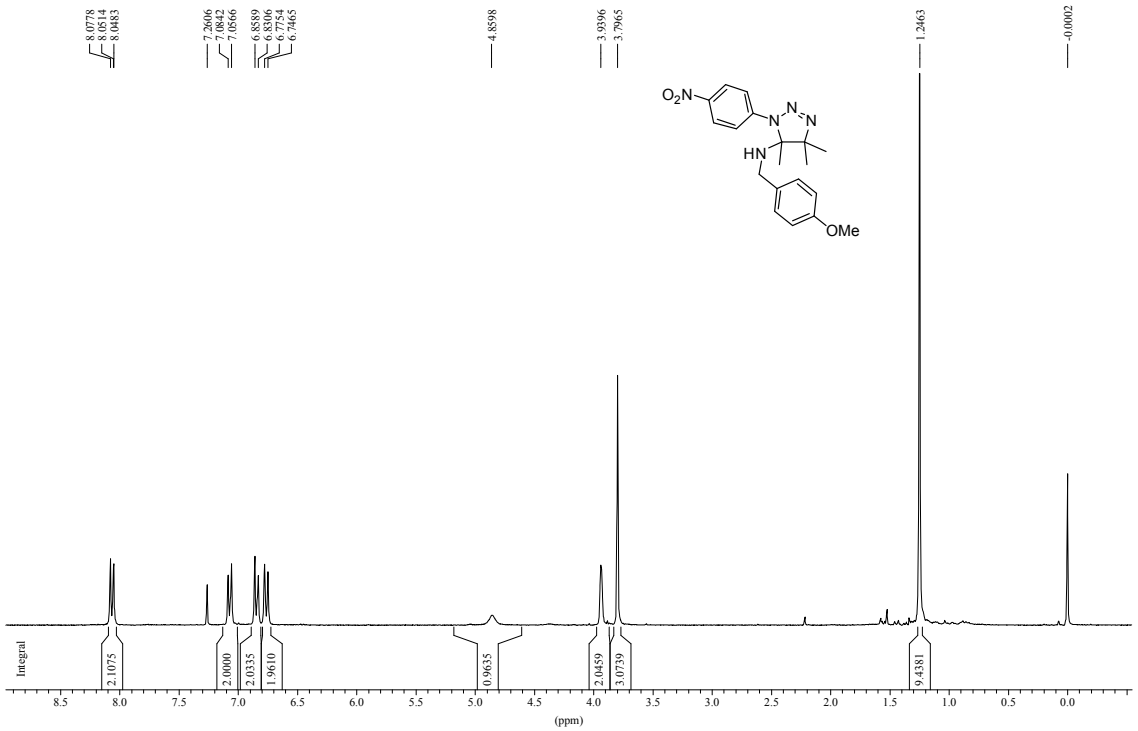
^{1}H NMR Spectra of **4w** (300 MHz, CDCl3):



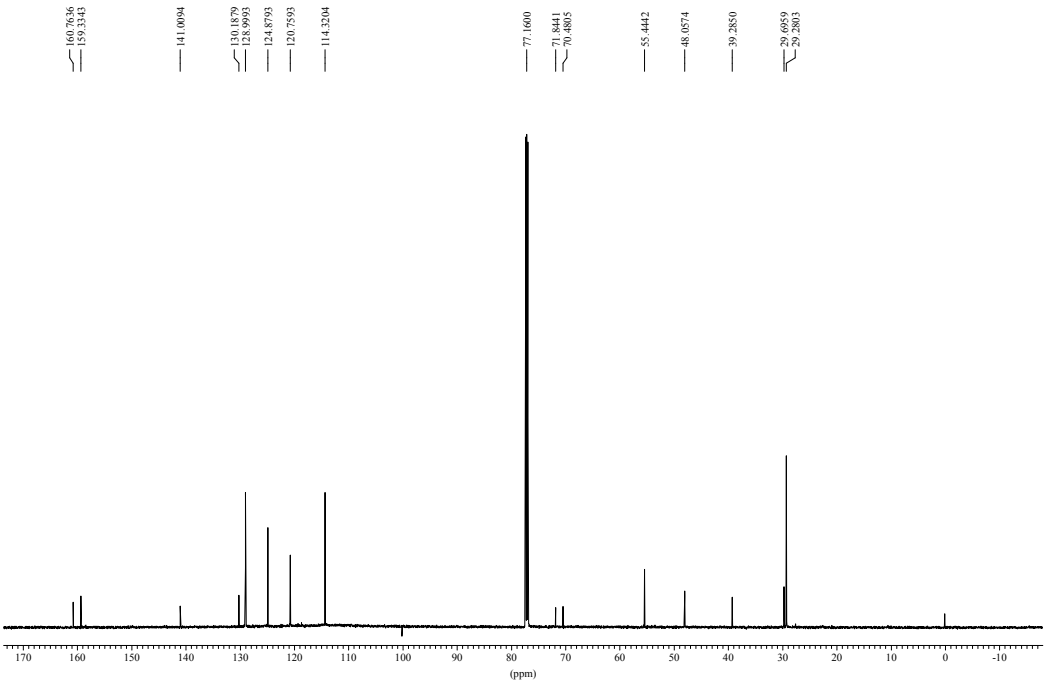
^{13}C NMR Spectra of **4w** (75 MHz, CDCl3):



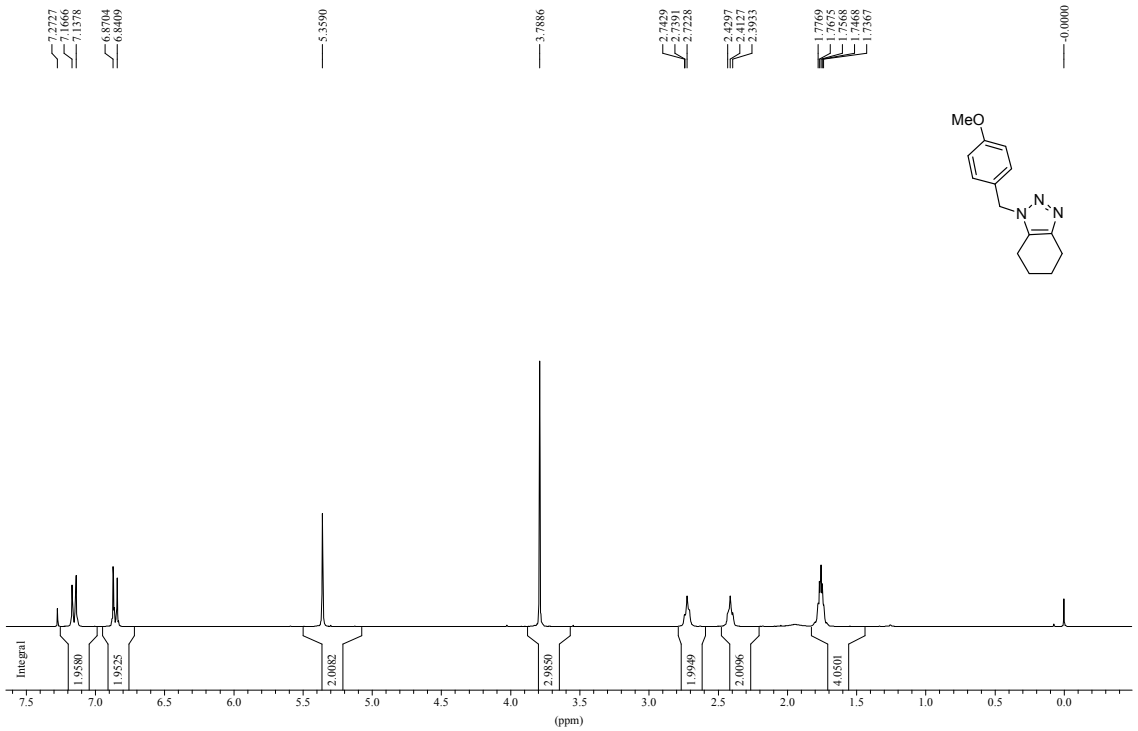
^{1}H NMR Spectra of **6w** (300 MHz, CDCl3):



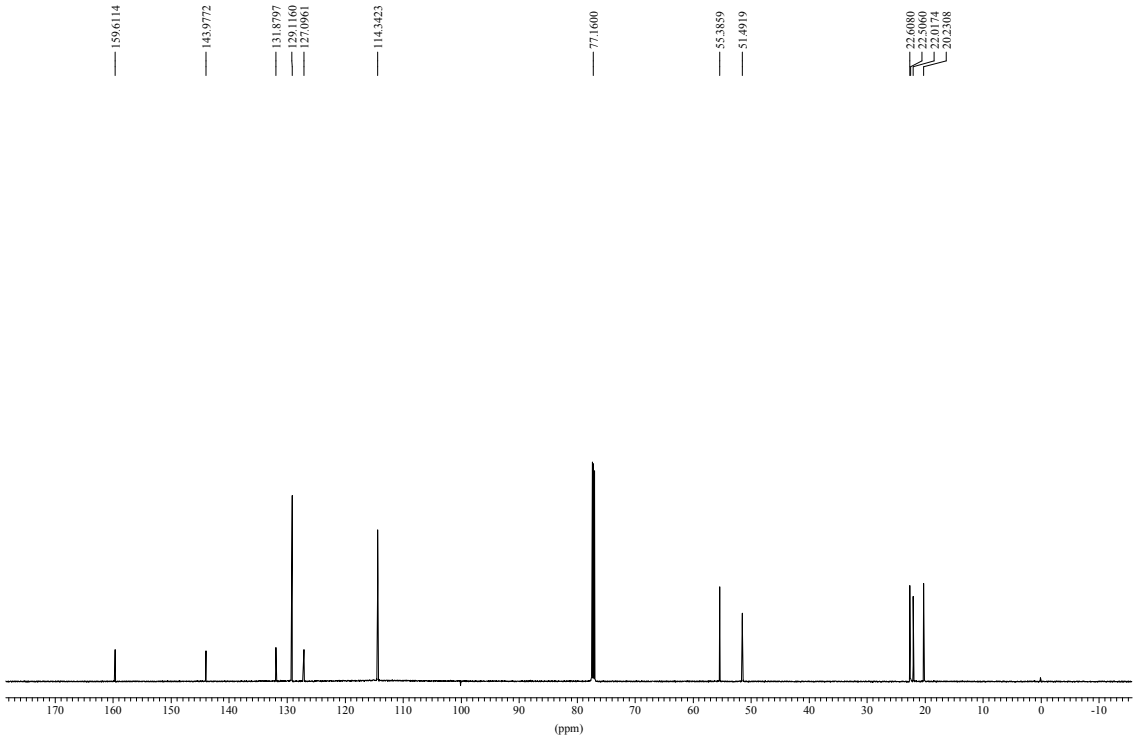
^{13}C NMR Spectra of **6w** (75 MHz, CDCl3):



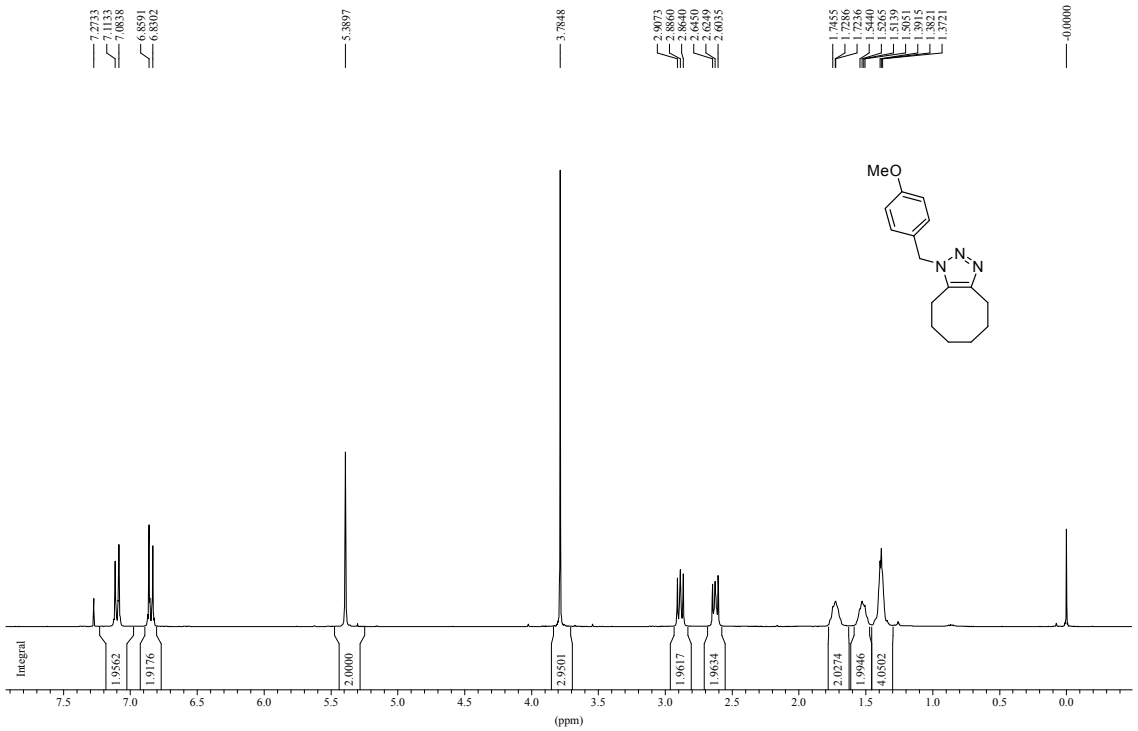
^{1}H NMR Spectra of **4x** (300 MHz, CDCl3):



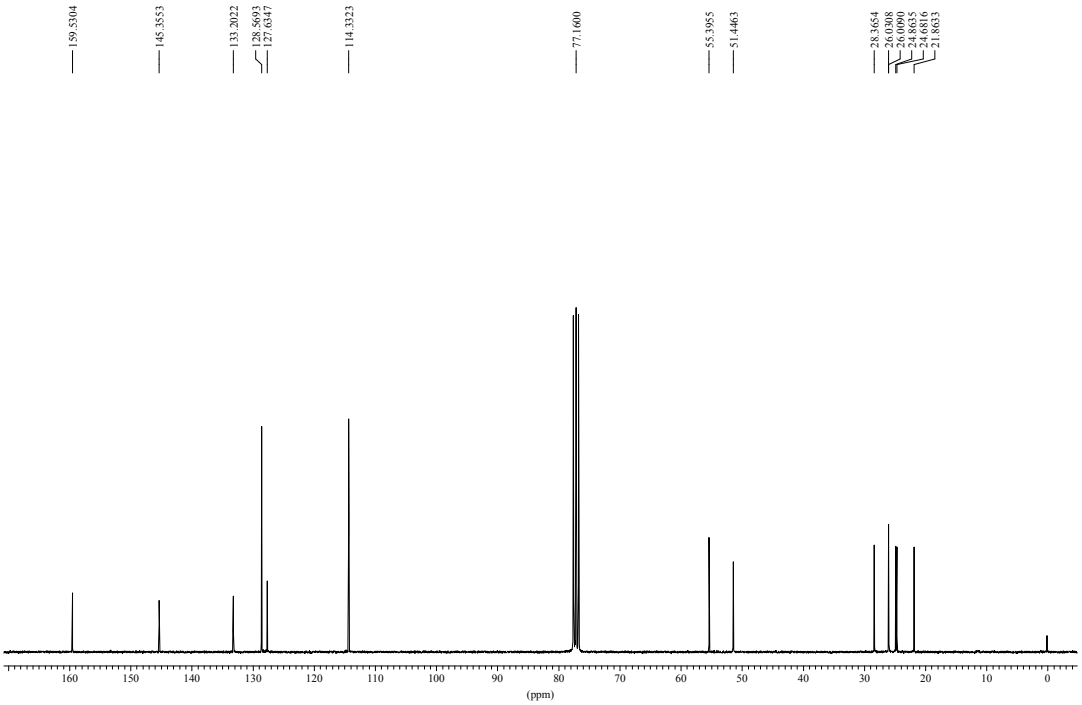
^{13}C NMR Spectra of **4x** (75 MHz, CDCl3):



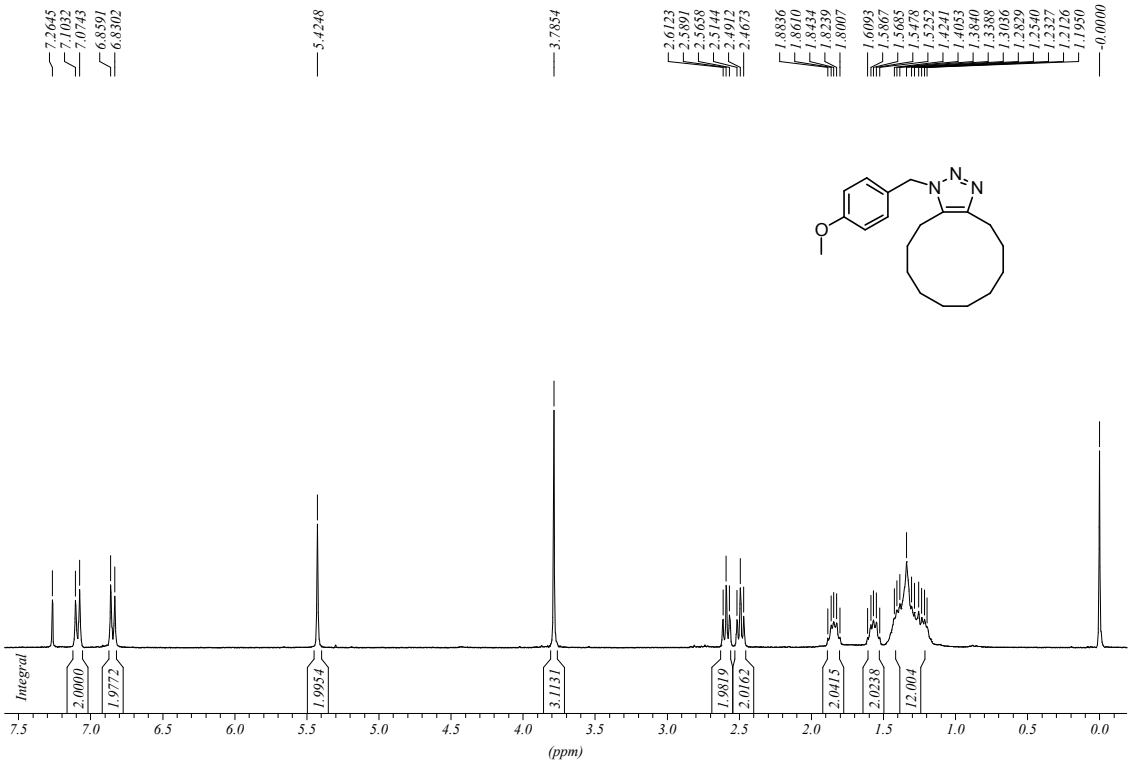
^{1}H NMR Spectra of **4y** (300 MHz, CDCl3):



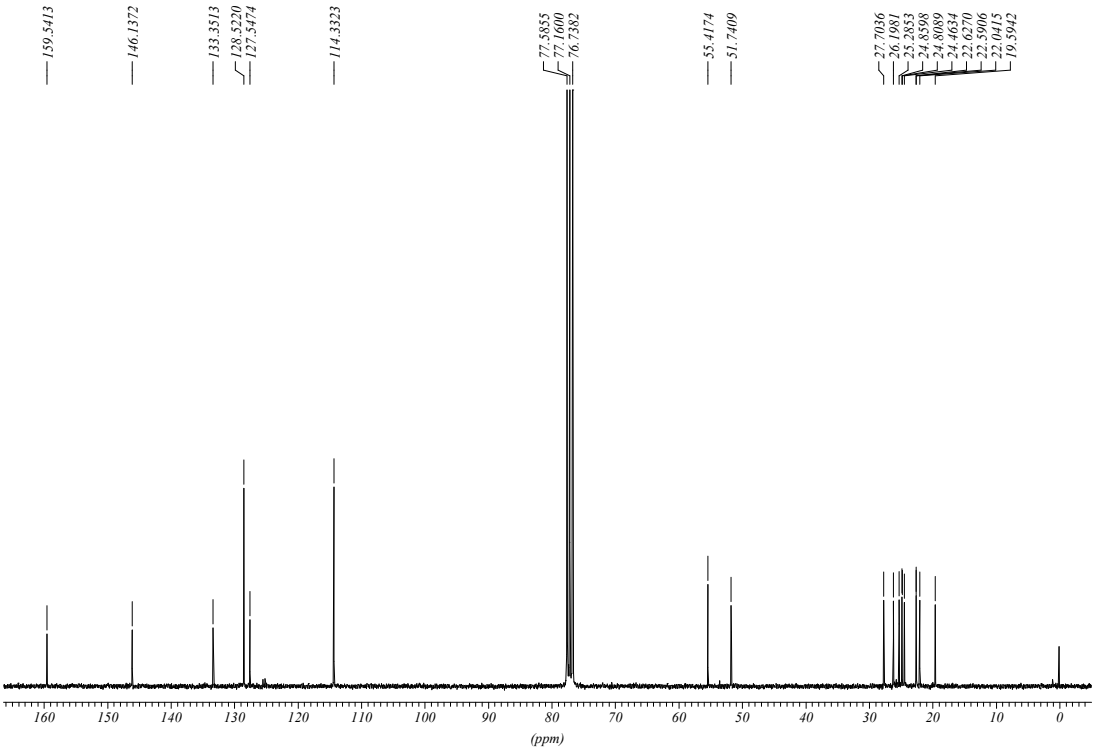
^{13}C NMR Spectra of **4y** (75 MHz, CDCl3):



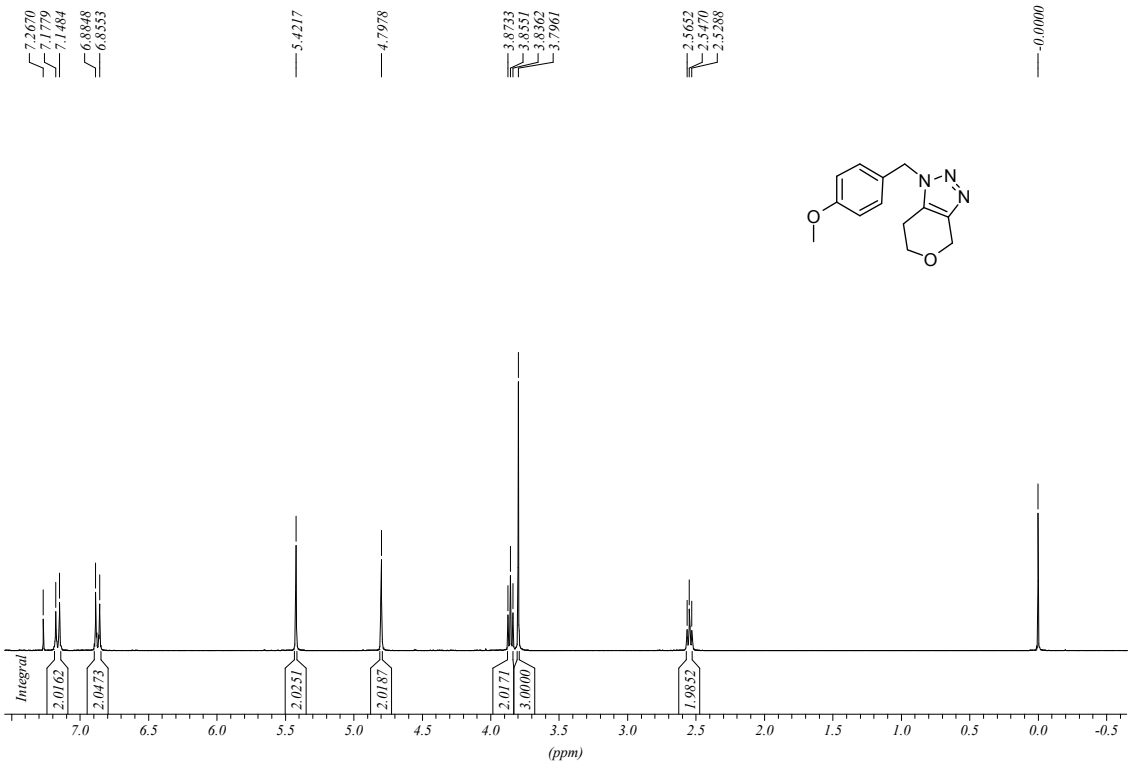
^{1}H NMR Spectra of **4z** (300 MHz, CDCl3):



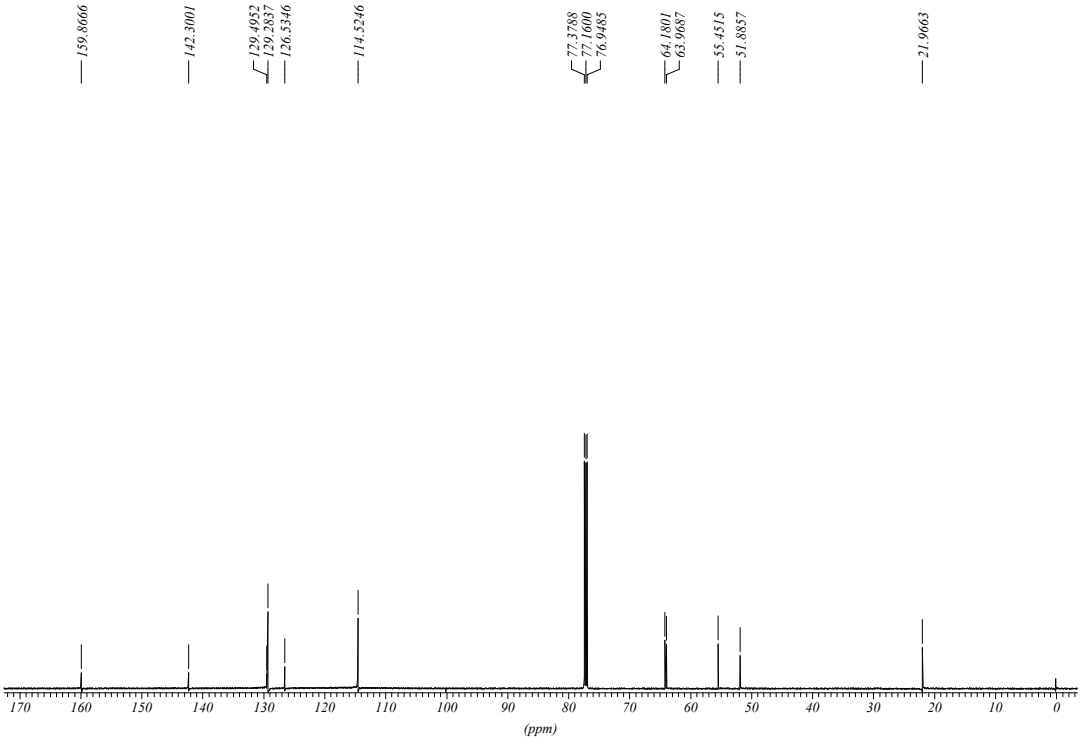
^{13}C NMR Spectra of **4z** (75 MHz, CDCl3):



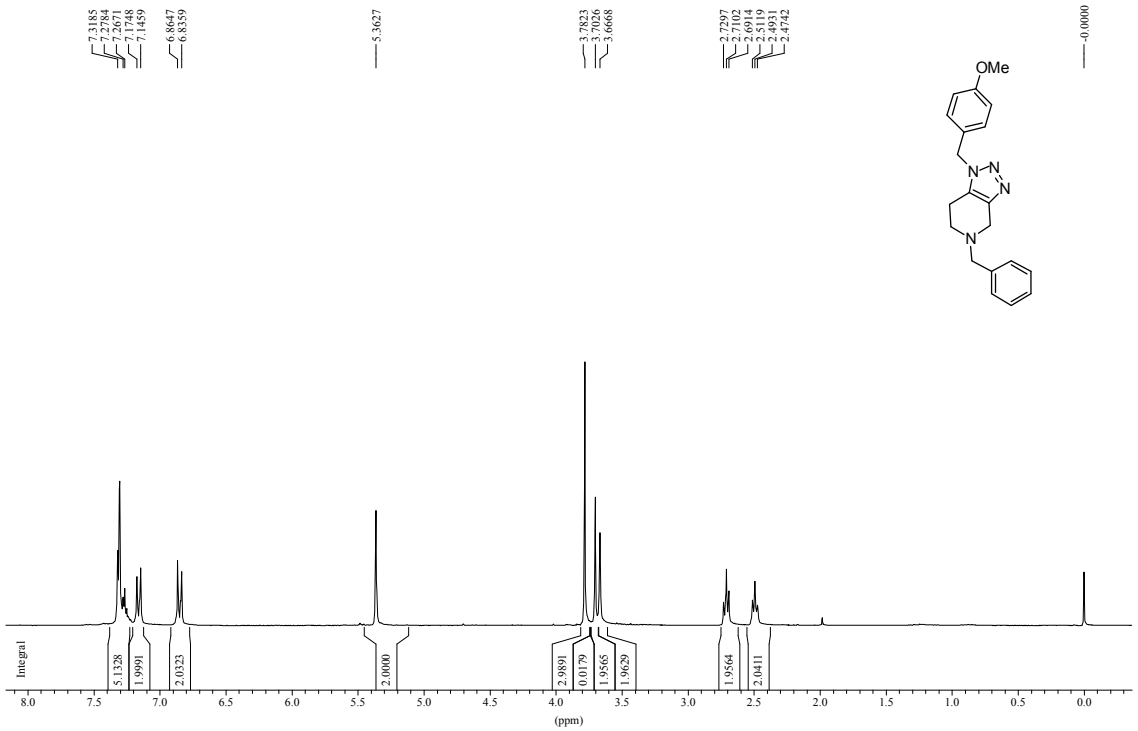
^{1}H NMR Spectra of **4aa** (300 MHz, CDCl3):



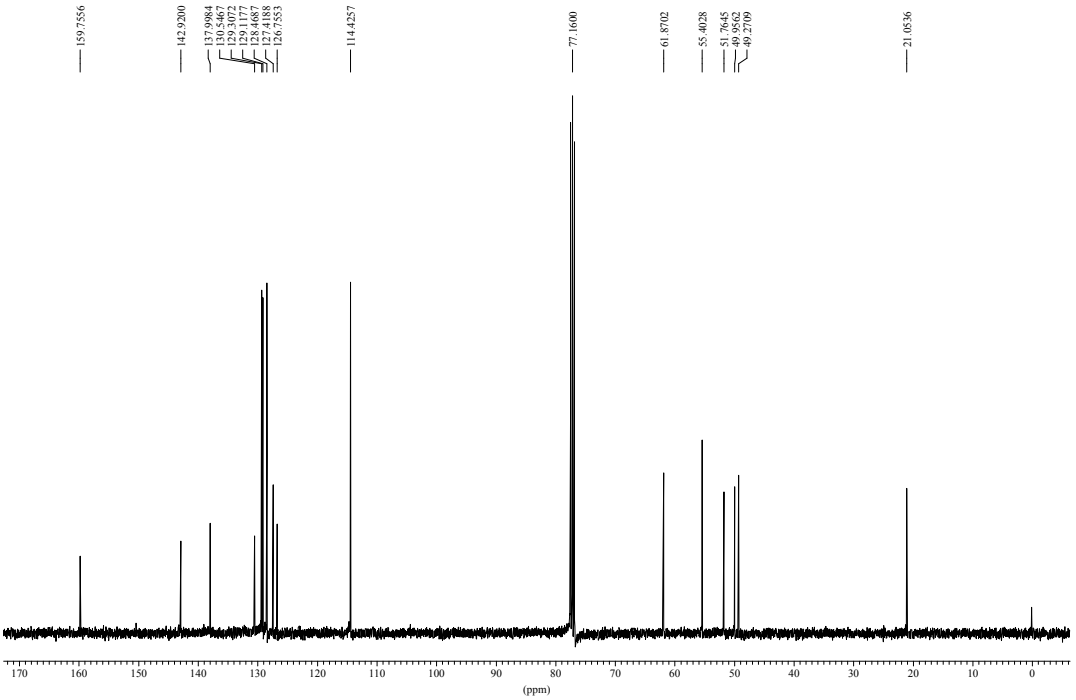
^{13}C NMR Spectra of **4aa** (75 MHz, CDCl3):



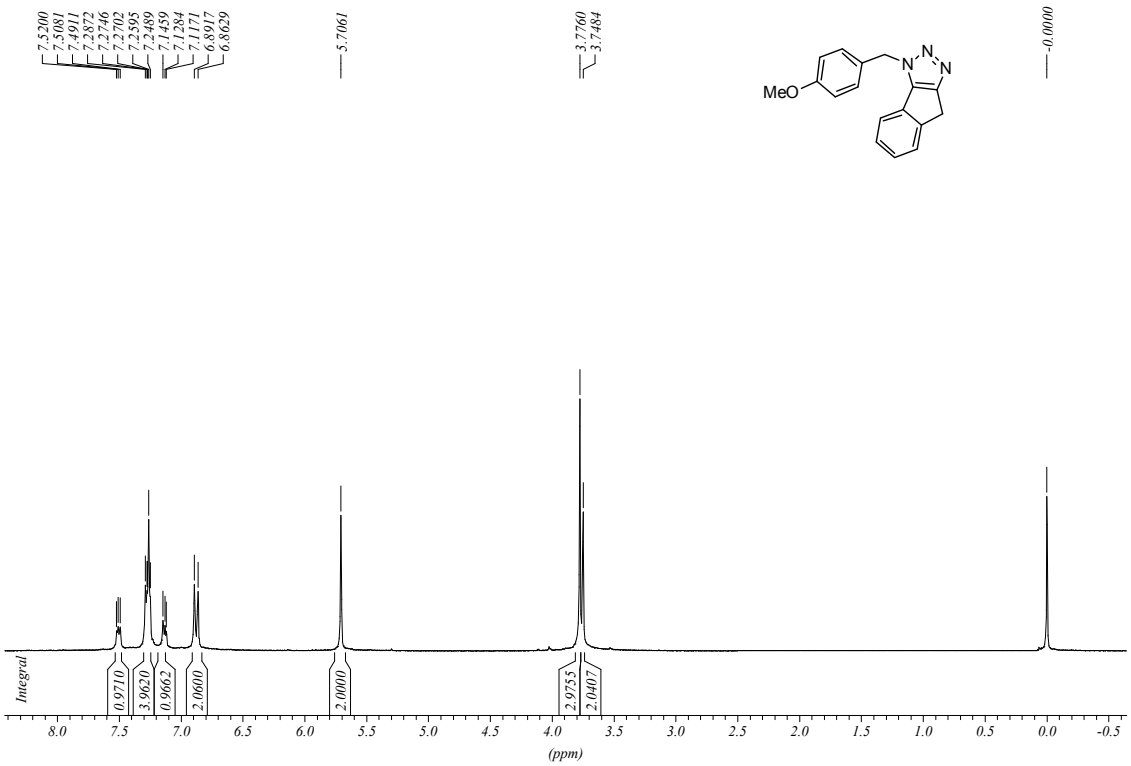
^{1}H NMR Spectra of **4ab** (300 MHz, CDCl3):



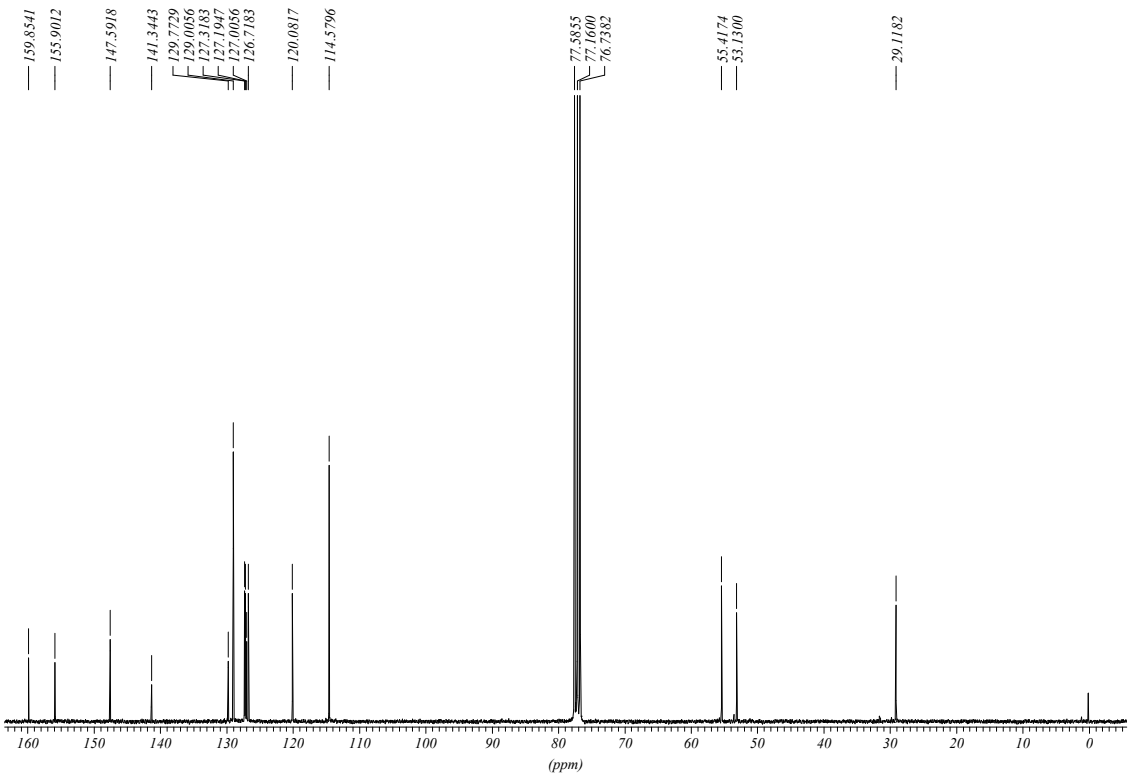
^{13}C NMR Spectra of **4ab** (75 MHz, CDCl3):



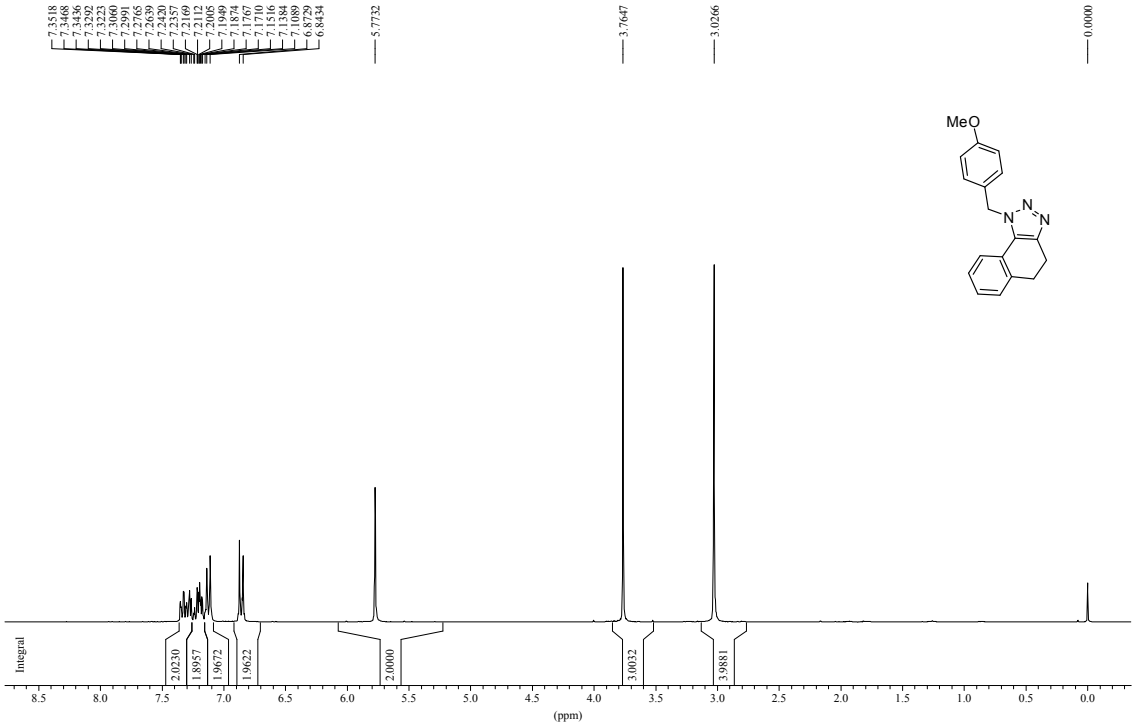
^{1}H NMR Spectra of **4ac** (300 MHz, CDCl3):



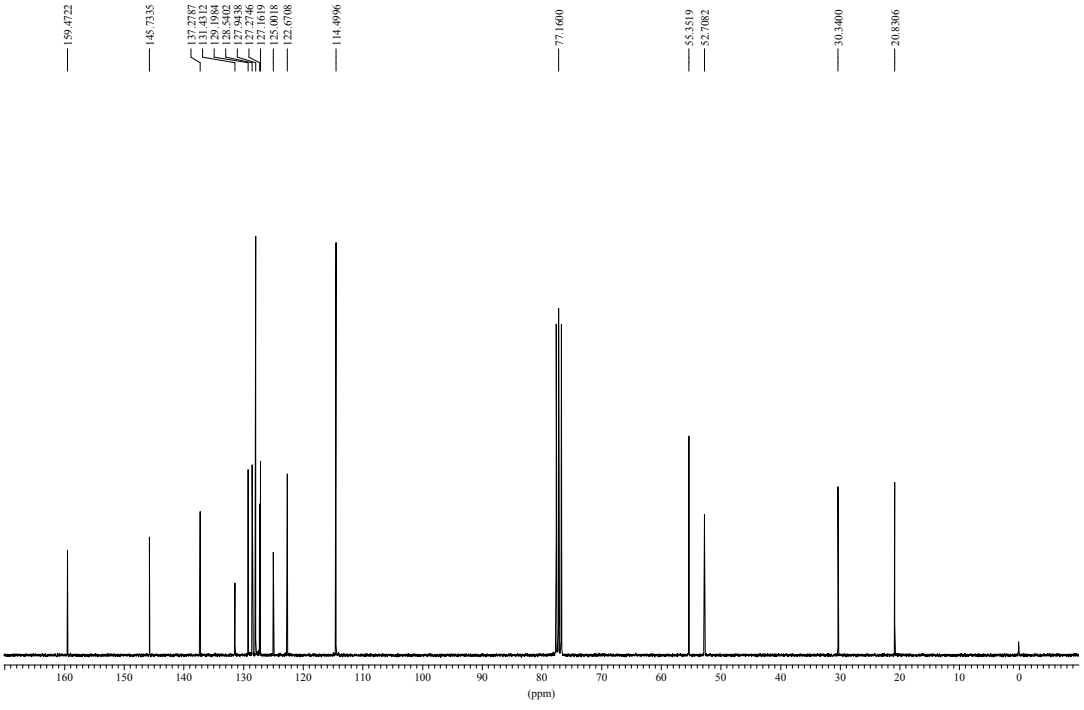
^{13}C NMR Spectra of **4ac** (75 MHz, CDCl3):



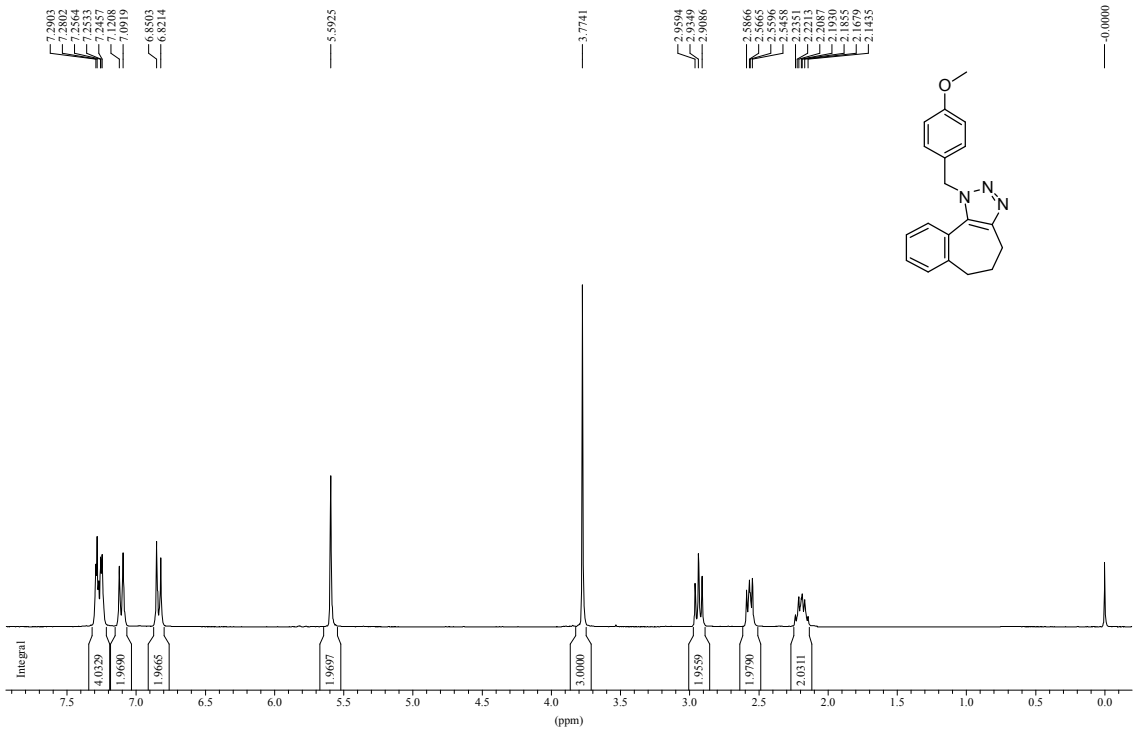
^{1}H NMR Spectra of **4ad** (300 MHz, CDCl3):



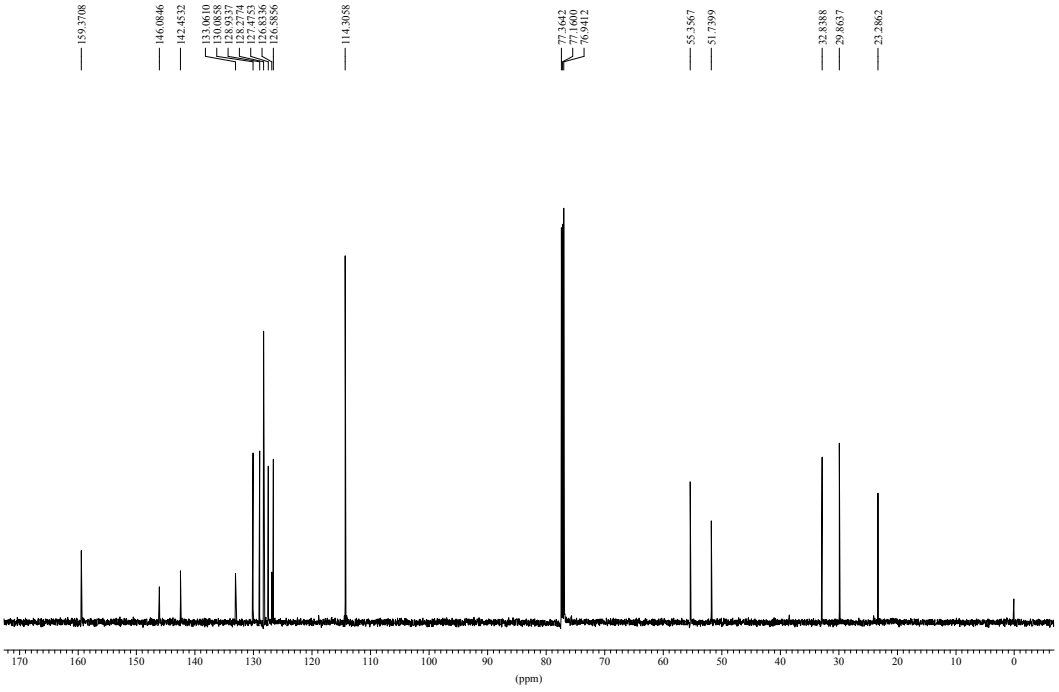
^{13}C NMR Spectra of **4ad** (75 MHz, CDCl3):



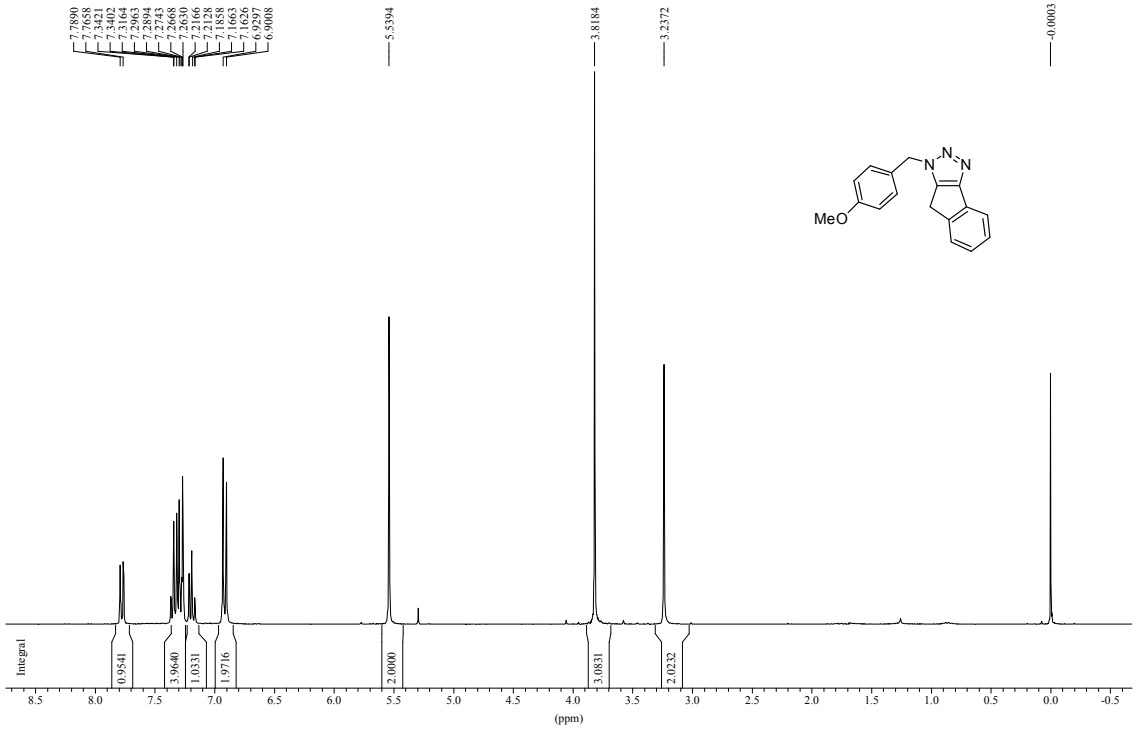
^{1}H NMR Spectra of **4ae** (300 MHz, CDCl3):



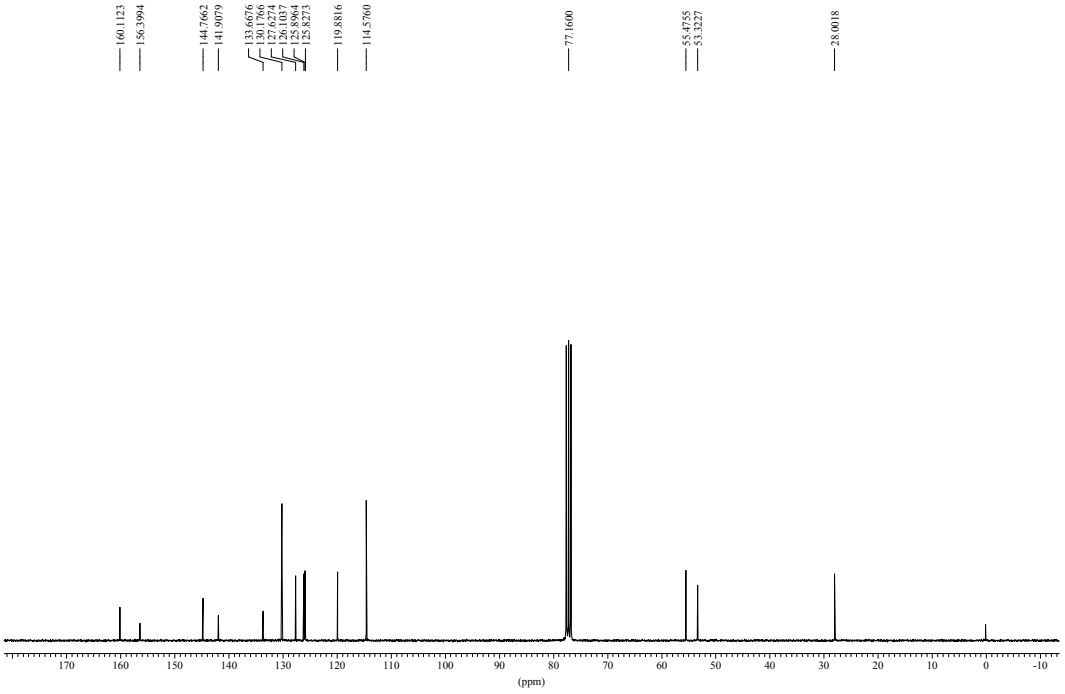
^{13}C NMR Spectra of **4ae** (75 MHz, CDCl3):



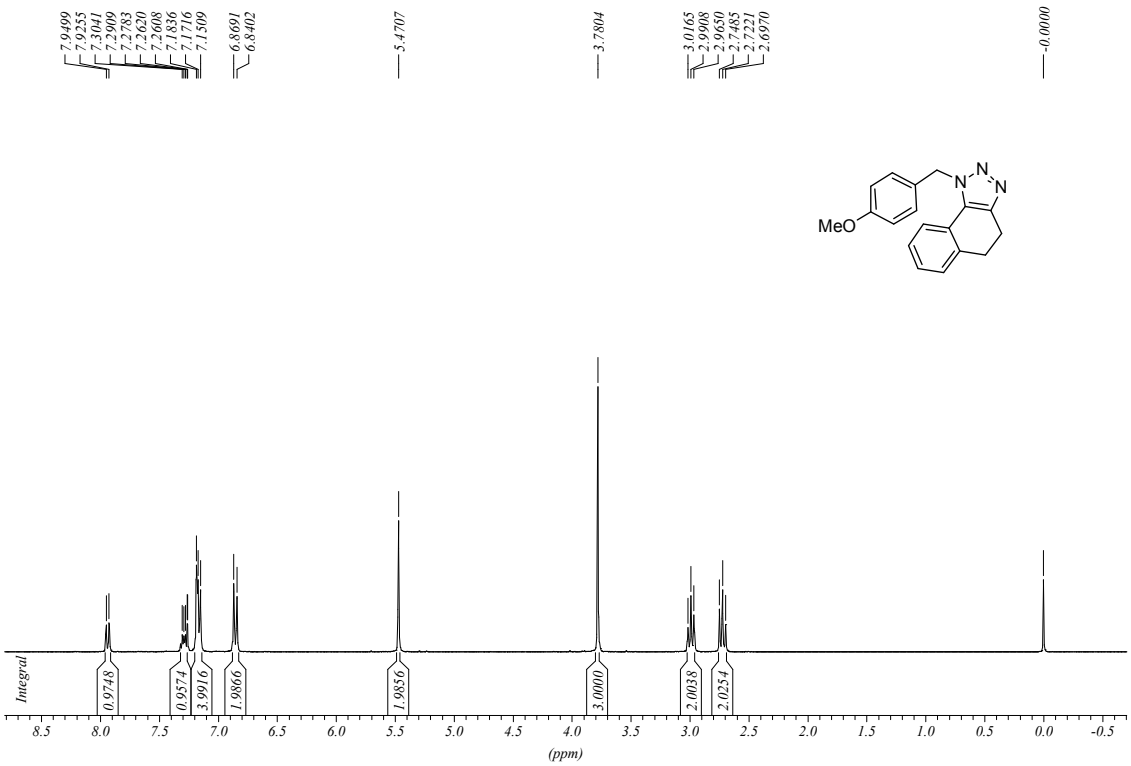
^{1}H NMR Spectra of **4af** (300 MHz, CDCl3):



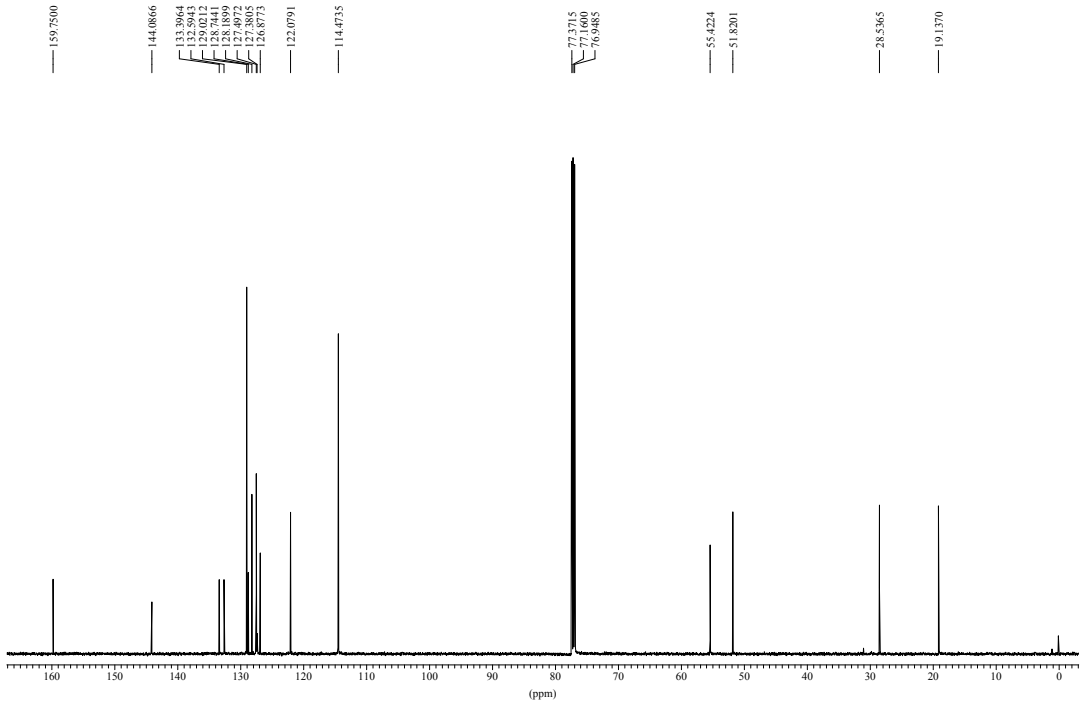
^{13}C NMR Spectra of **4af** (75 MHz, CDCl3):



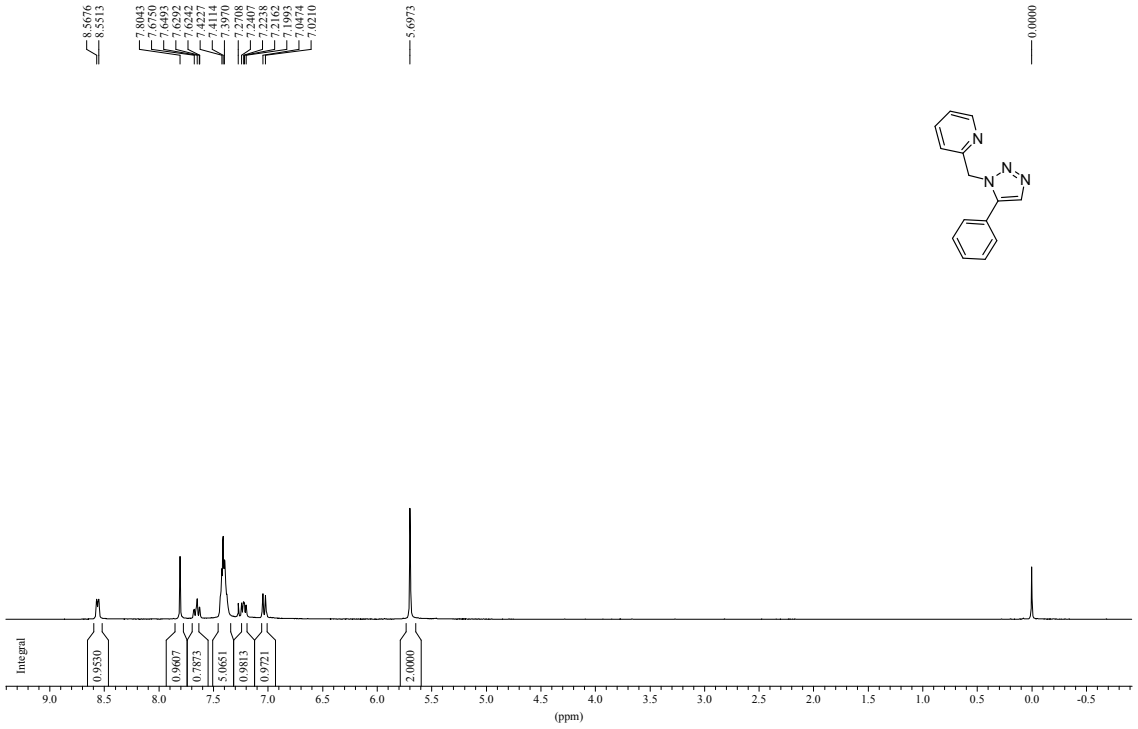
^{1}H NMR Spectra of **4ag** (300 MHz, CDCl3):



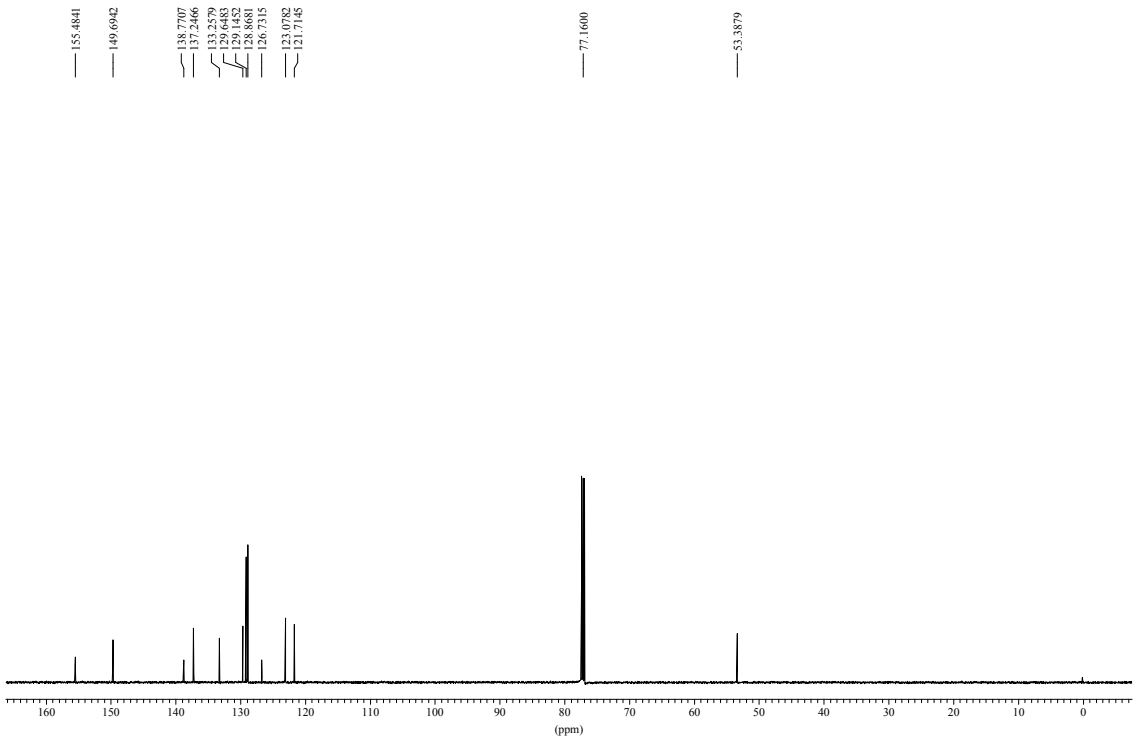
^{13}C NMR Spectra of **4ag** (75 MHz, CDCl3):



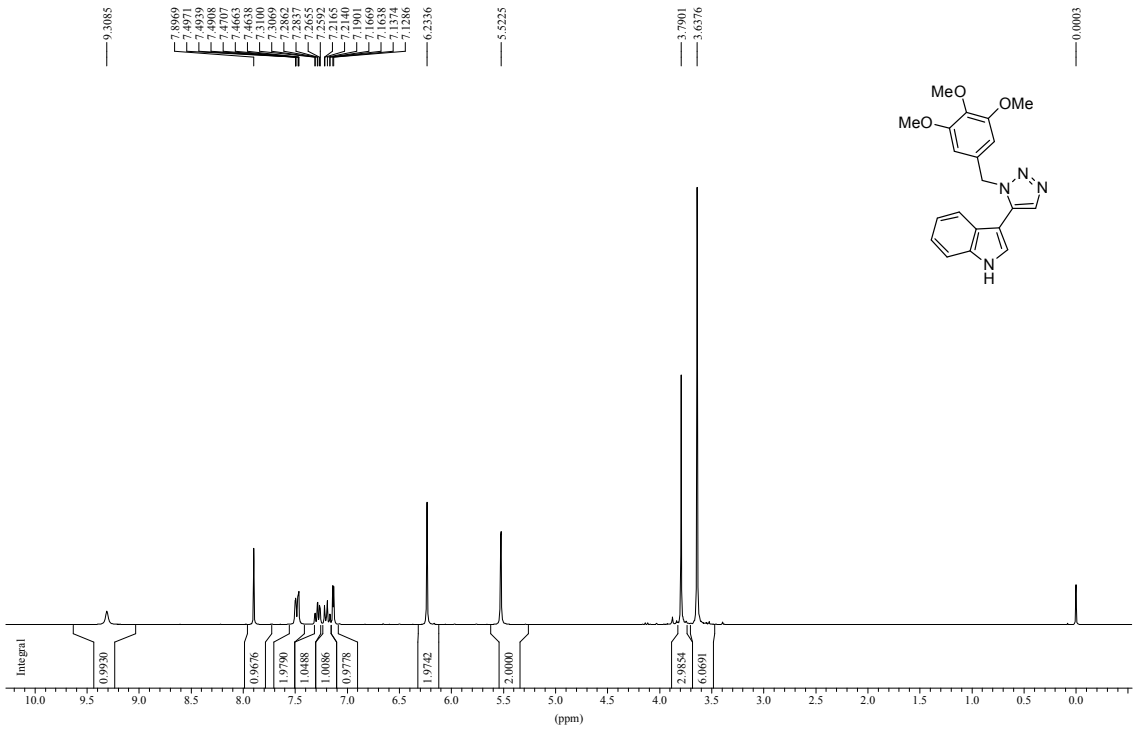
^{1}H NMR Spectra of **4ah** (300 MHz, CDCl3):



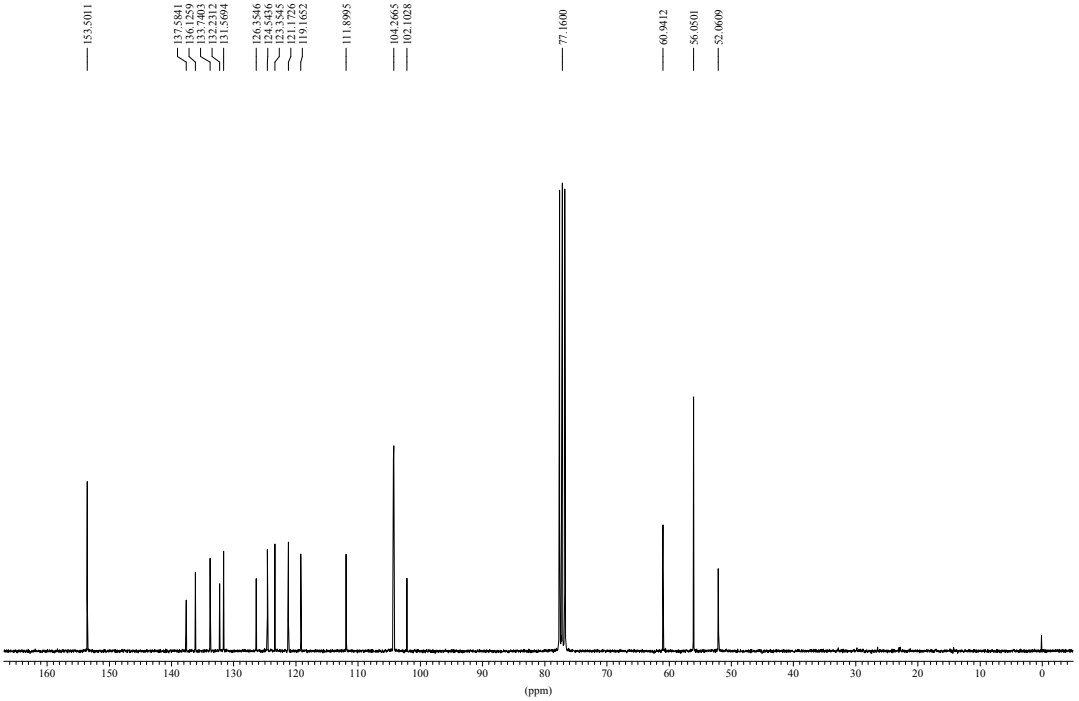
^{13}C NMR Spectra of **4ah** (75 MHz, CDCl3):



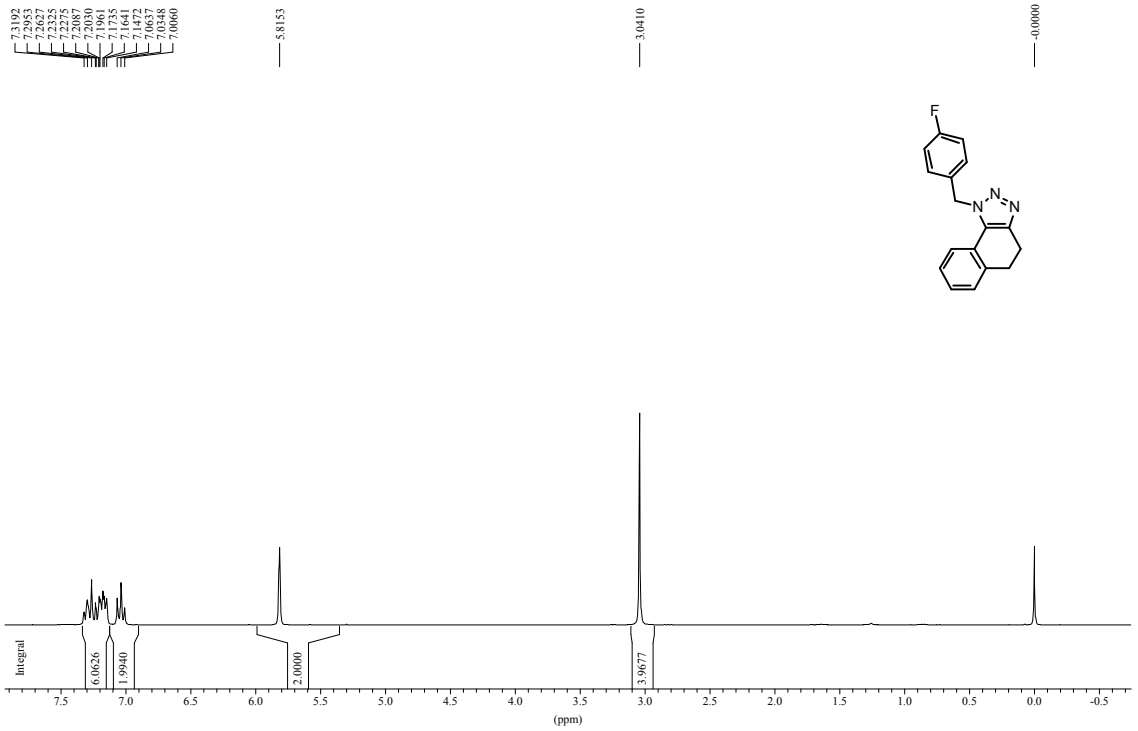
^{1}H NMR Spectra of **4ai** (300 MHz, CDCl3):



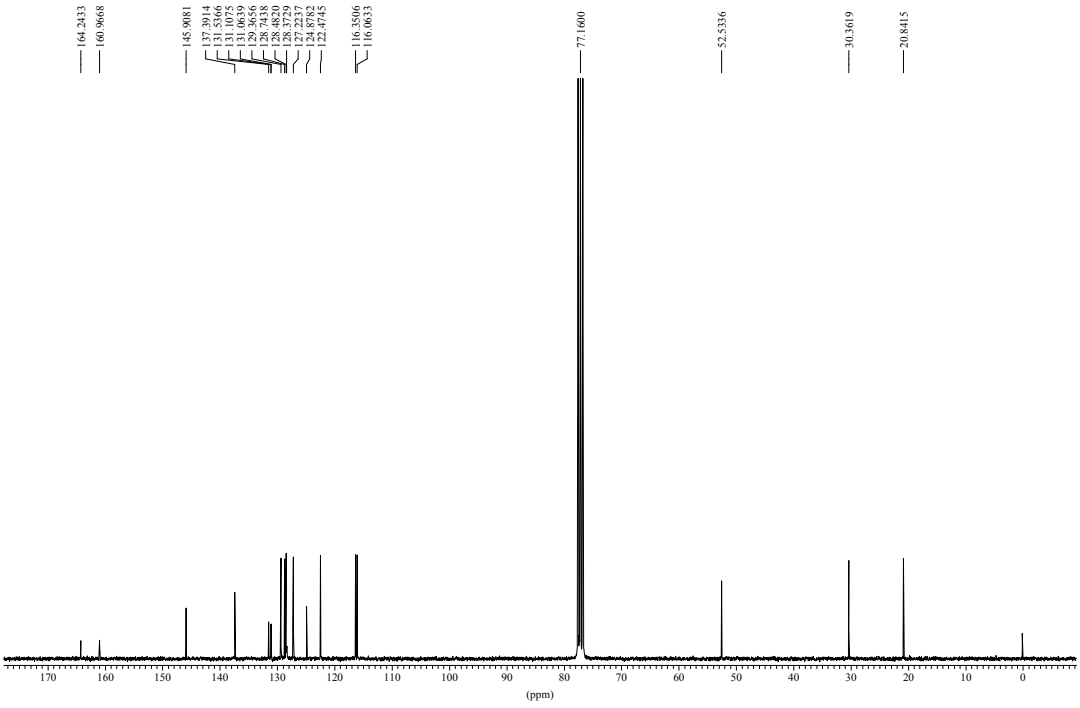
^{13}C NMR Spectra of **4ai** (75 MHz, CDCl3):



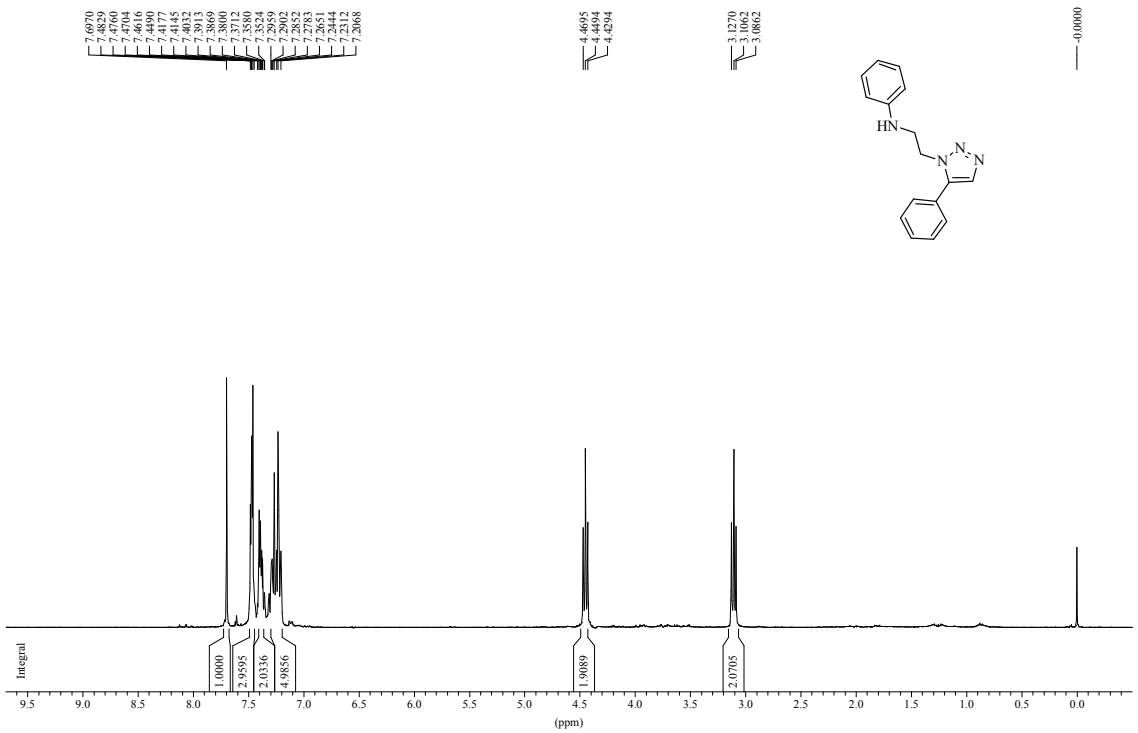
^{1}H NMR Spectra of **4aj** (300 MHz, CDCl3):



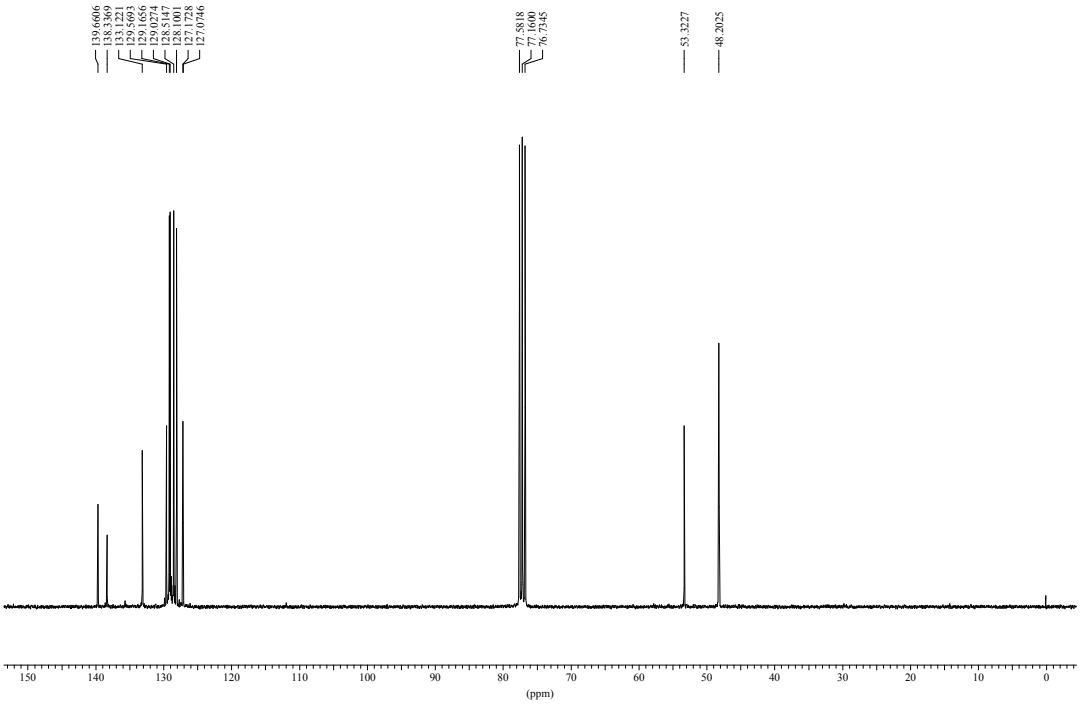
^{13}C NMR Spectra of **4aj** (75 MHz, CDCl3):



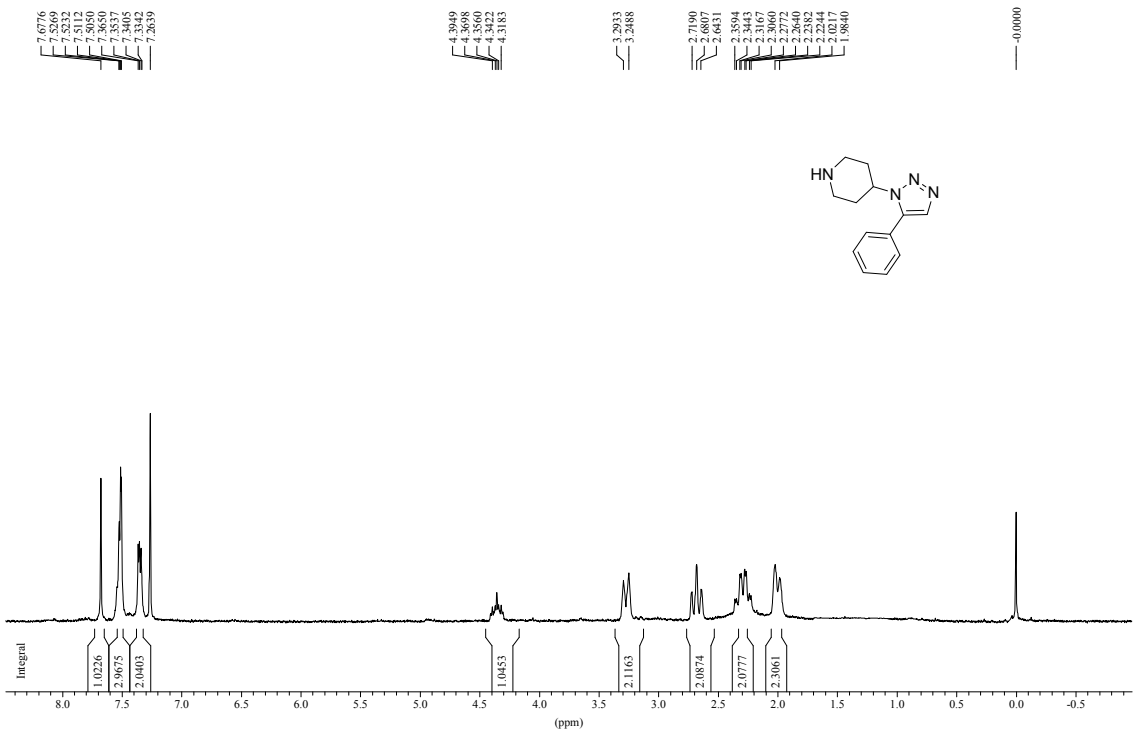
^{1}H NMR Spectra of **4ak**(300 MHz, CDCl3):



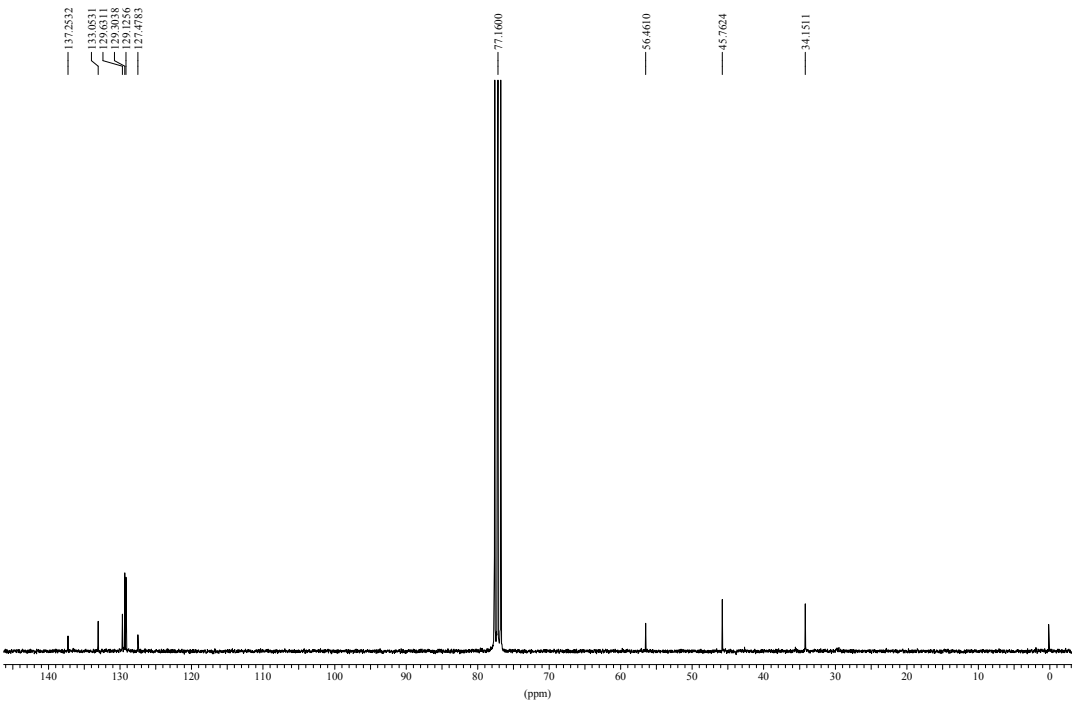
^{13}C NMR Spectra of **4ak** (75 MHz, CDCl3):



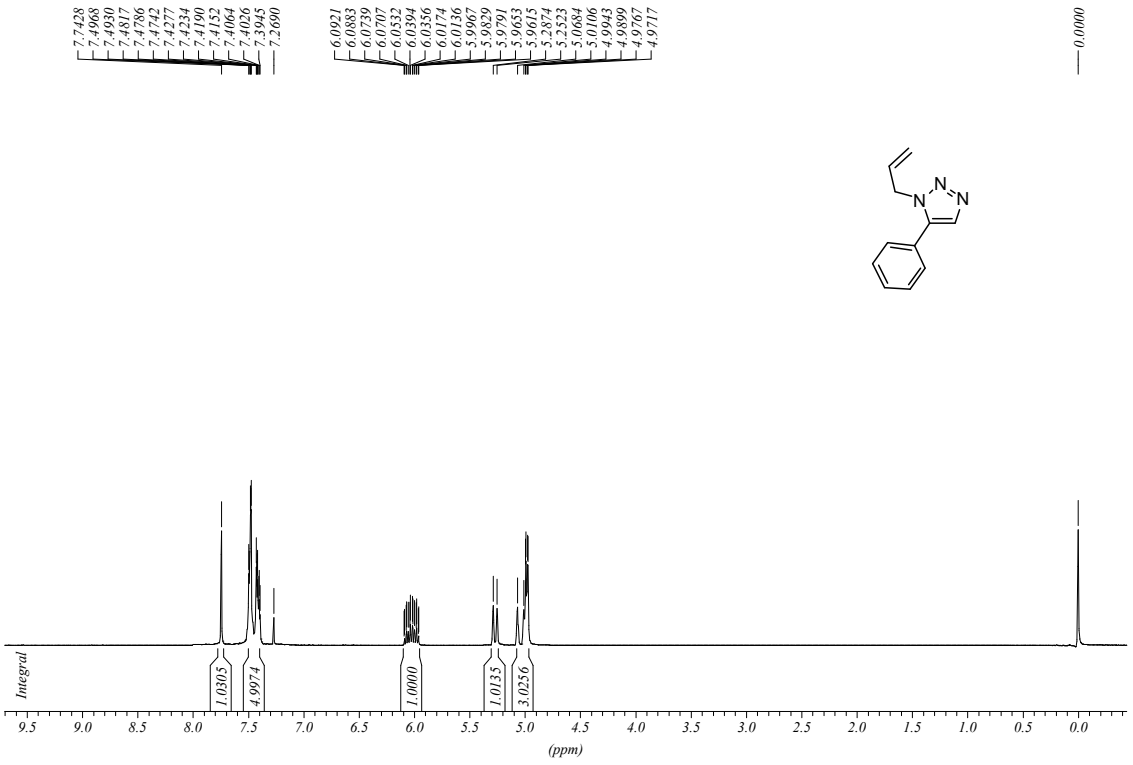
^{1}H NMR Spectra of **4al** (300 MHz, CDCl3):



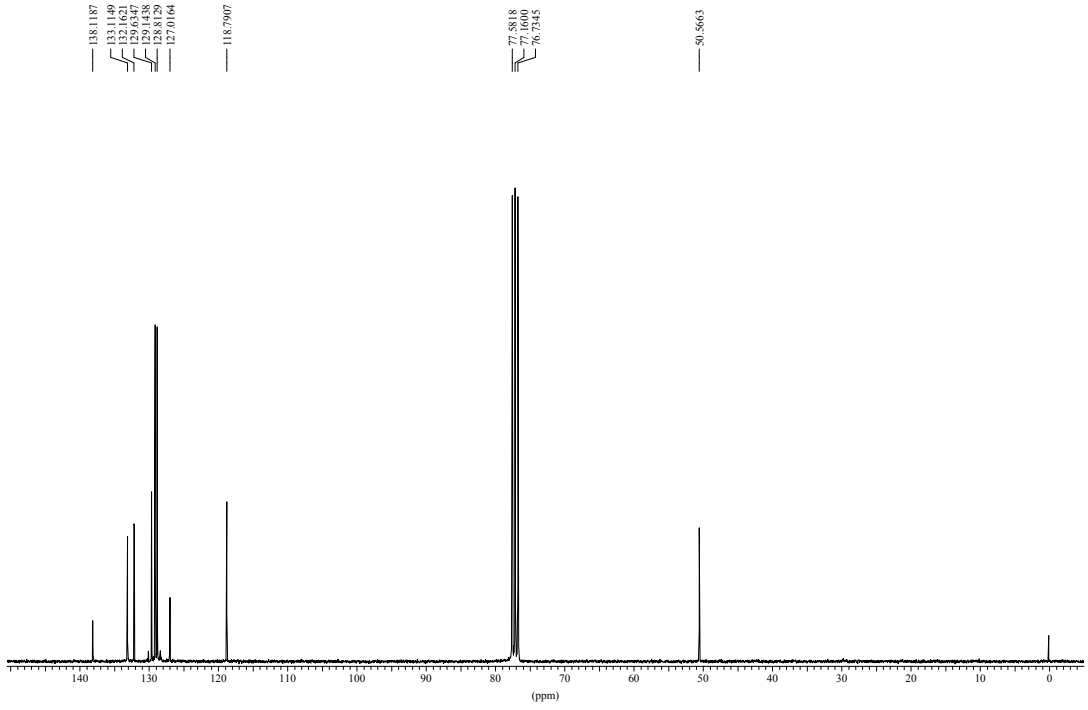
^{13}C NMR Spectra of **4al** (75 MHz, CDCl3):



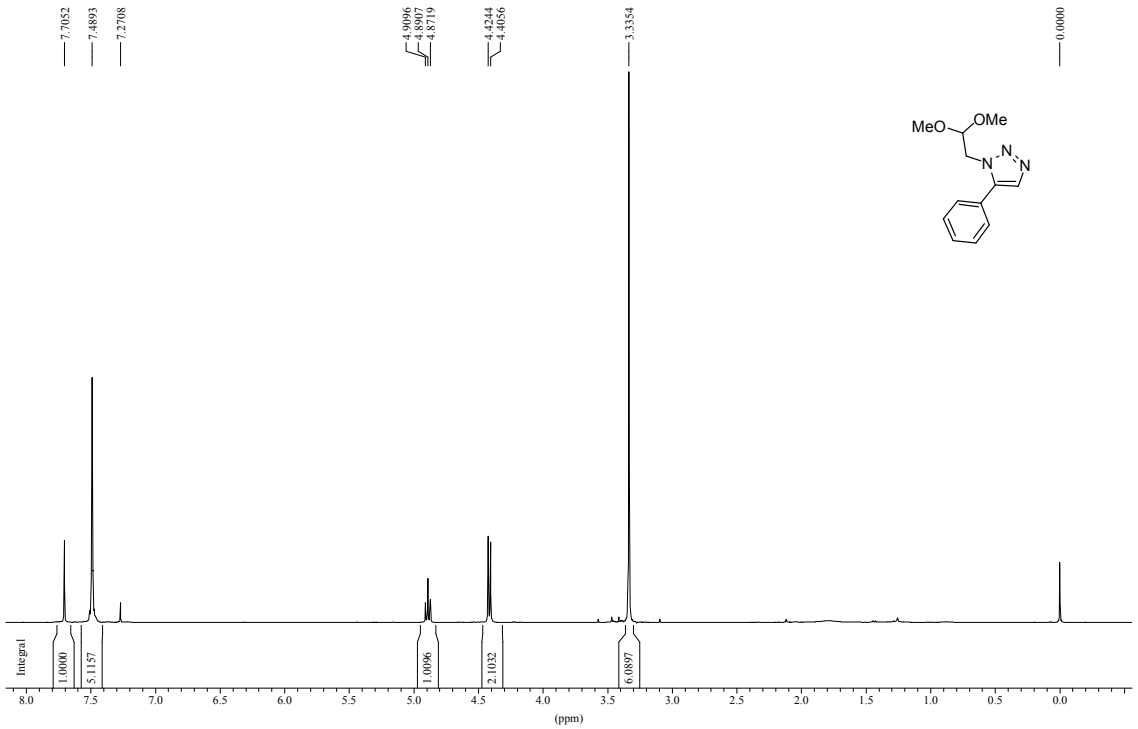
^{1}H NMR Spectra of **4am** (300 MHz, CDCl3):



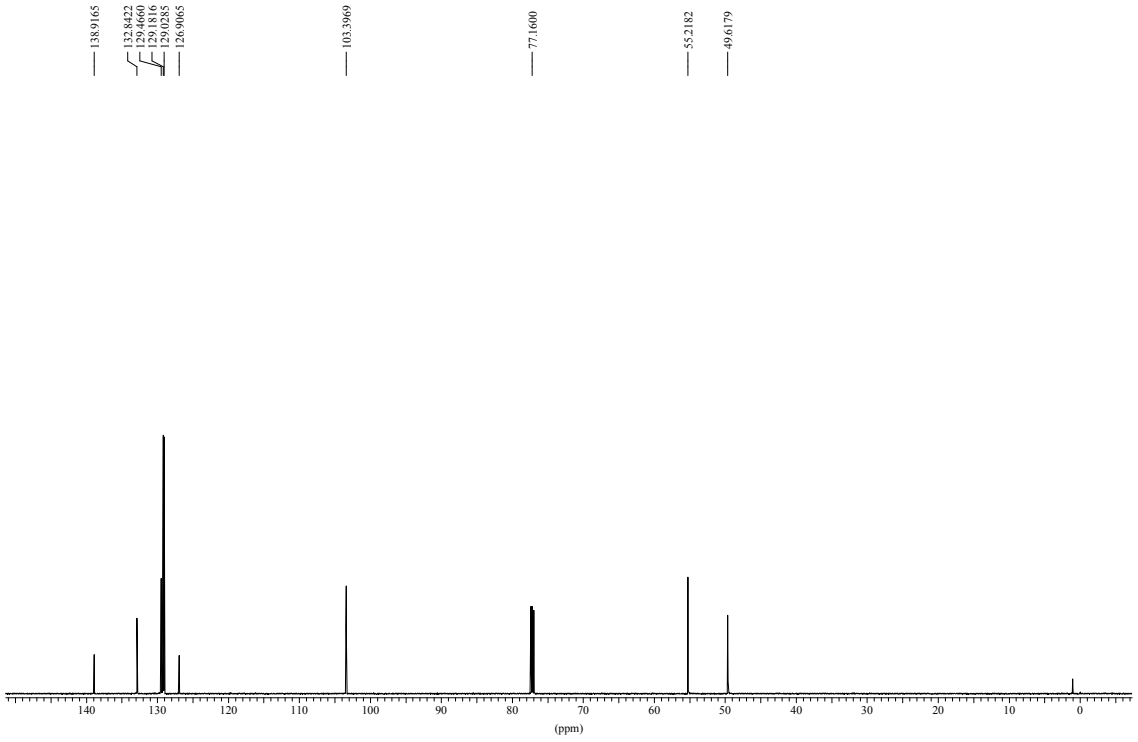
^{13}C NMR Spectra of **4am** (75 MHz, CDCl3):



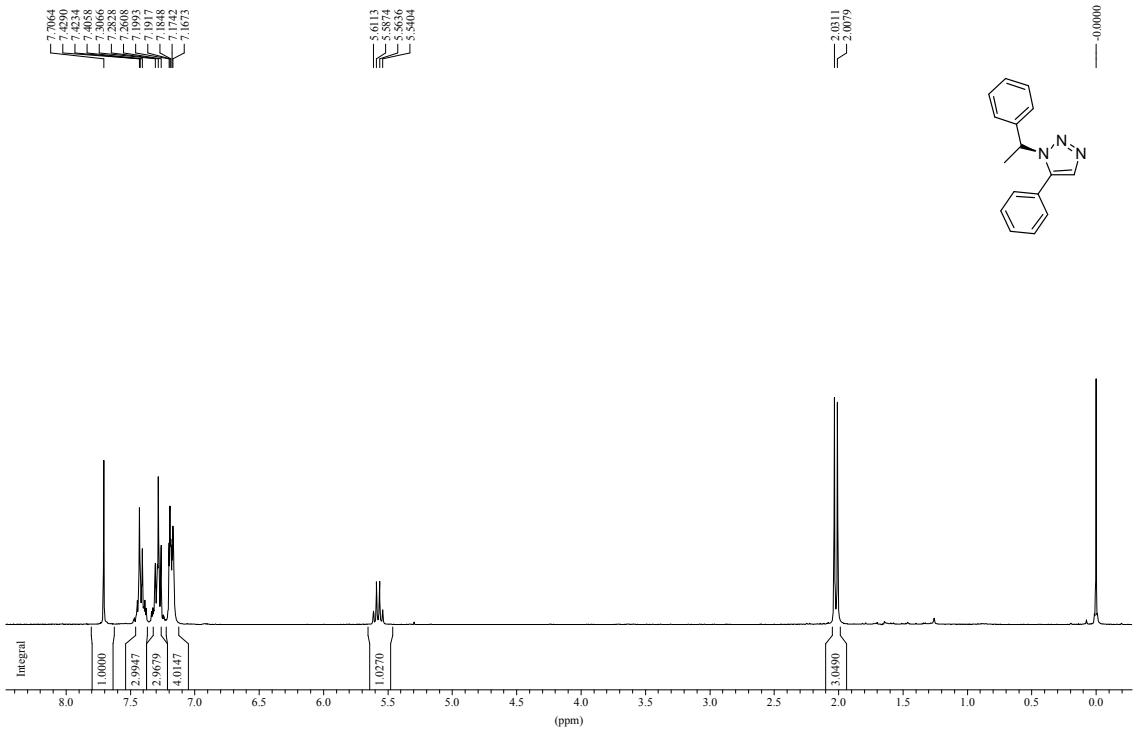
^{1}H NMR Spectra of **4an** (300 MHz, CDCl3):



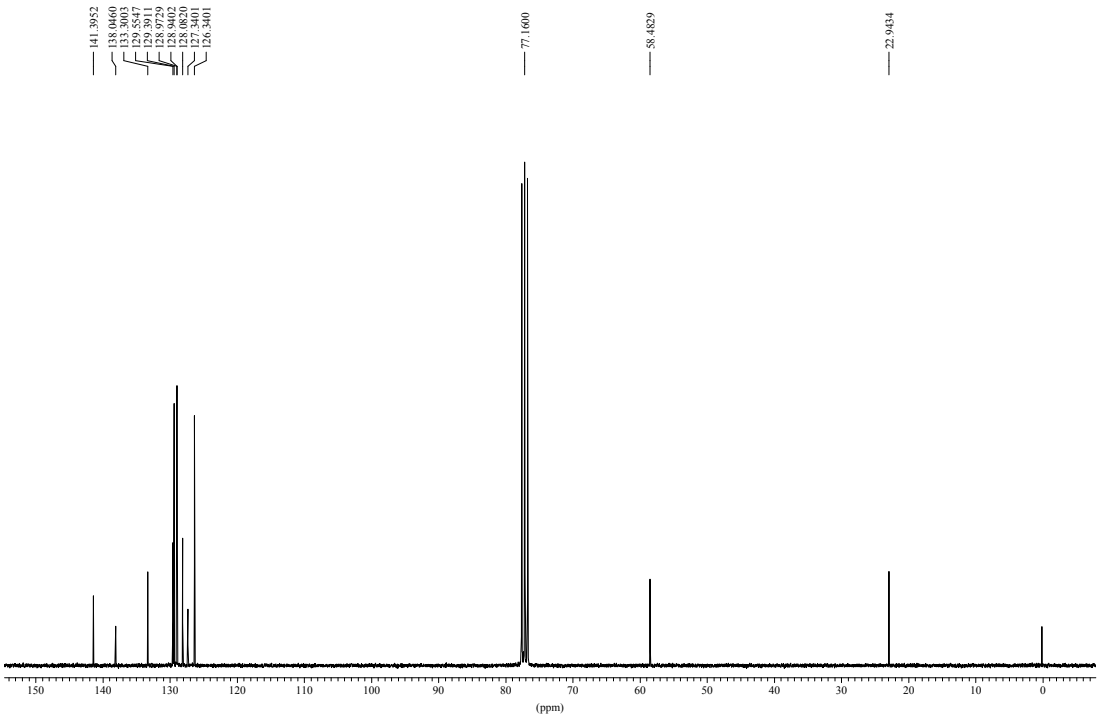
^{13}C NMR Spectra of **4an** (75 MHz, CDCl3):



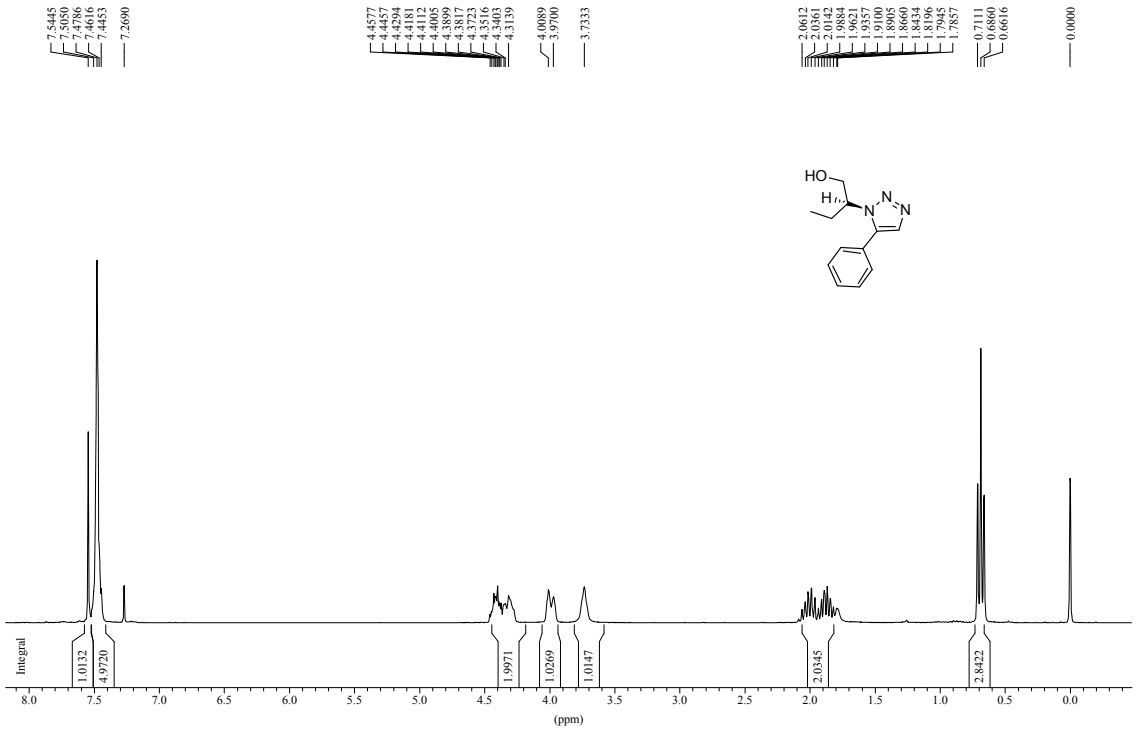
^{1}H NMR Spectra of **4ao** (300 MHz, CDCl3):



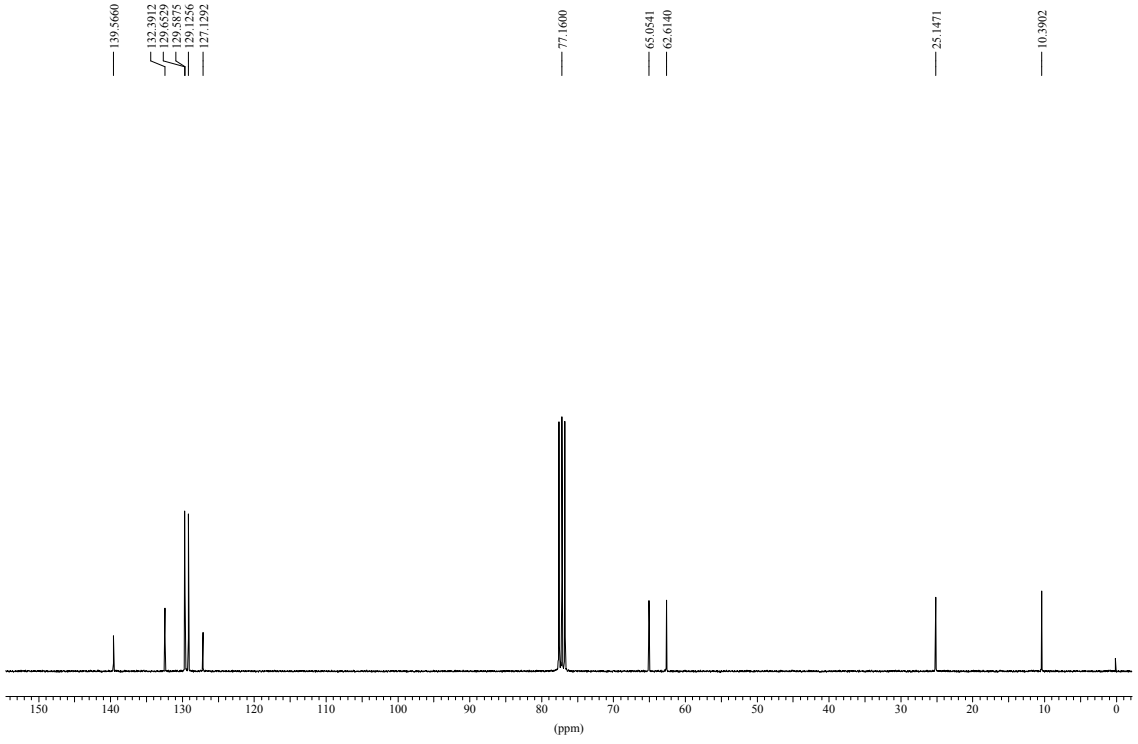
^{13}C NMR Spectra of **4ao** (75 MHz, CDCl3):



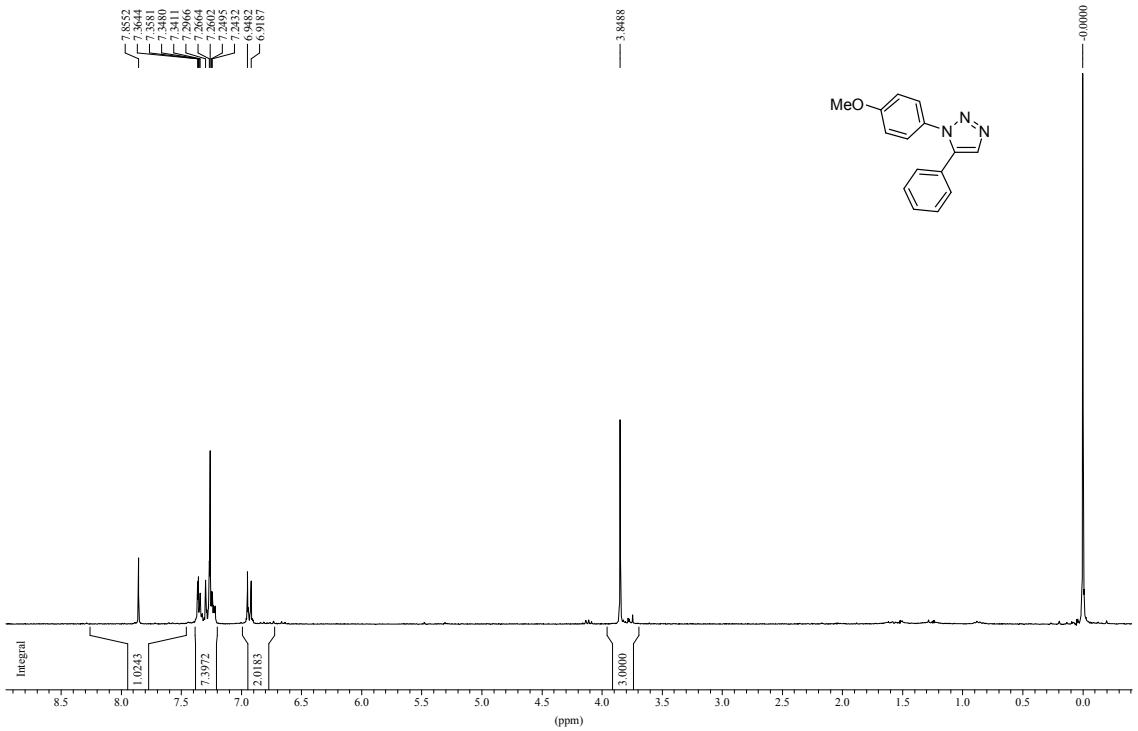
^{1}H NMR Spectra of **4ap** (300 MHz, CDCl3):



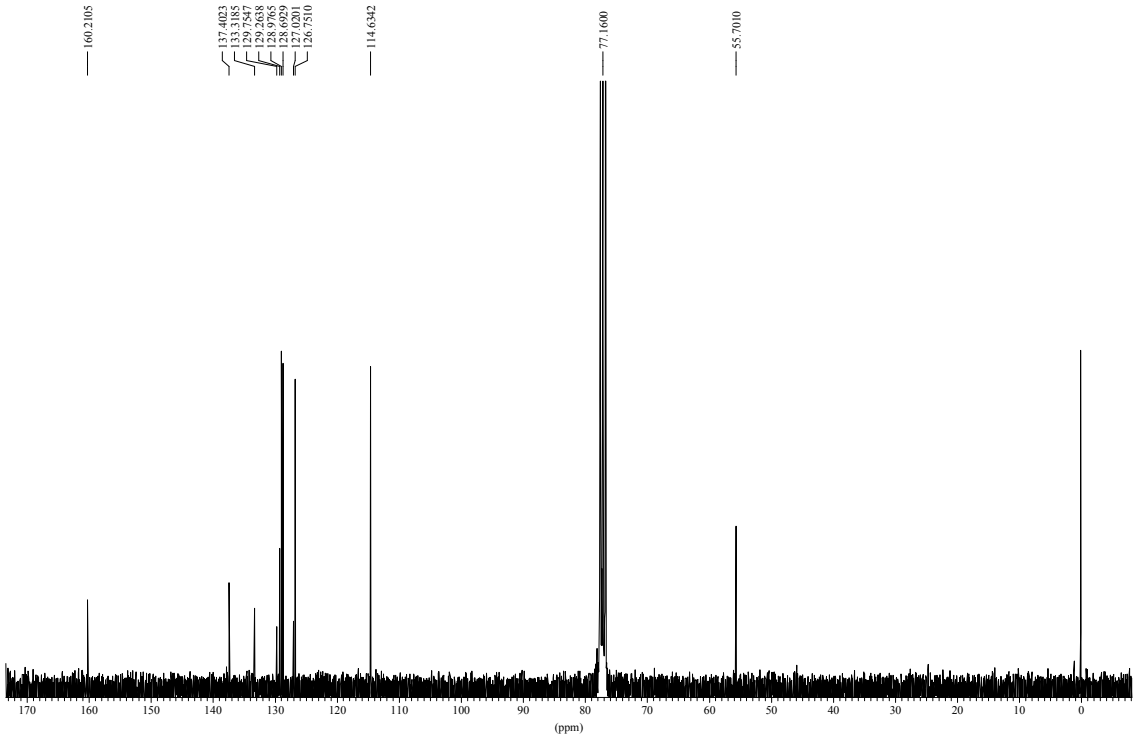
^{13}C NMR Spectra of **4ap** (75 MHz, CDCl3):



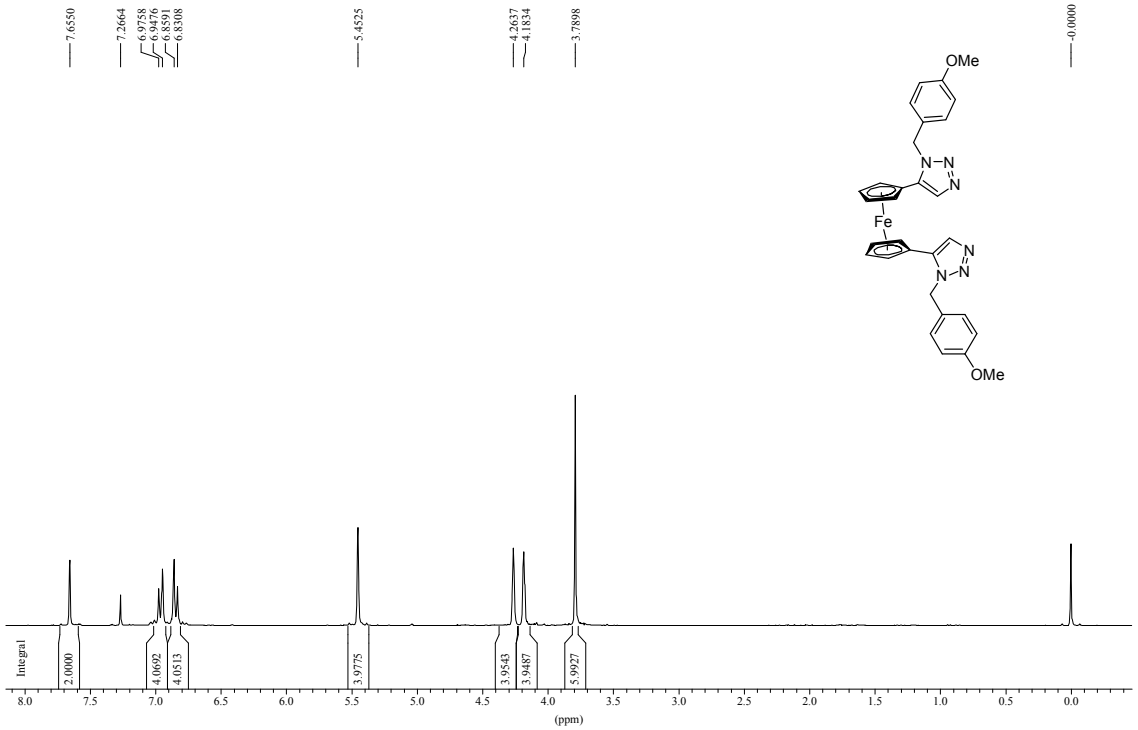
^{1}H NMR Spectra of **4aq** (300 MHz, CDCl3):



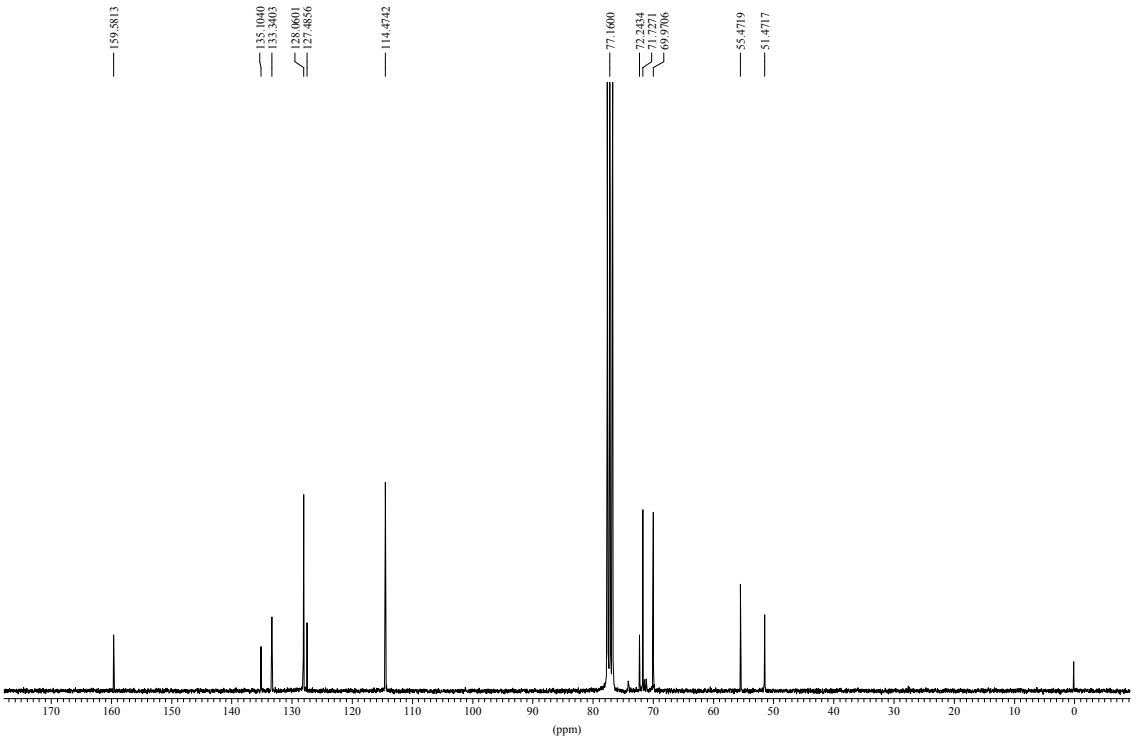
^{13}C NMR Spectra of **4aq** (75 MHz, CDCl3):



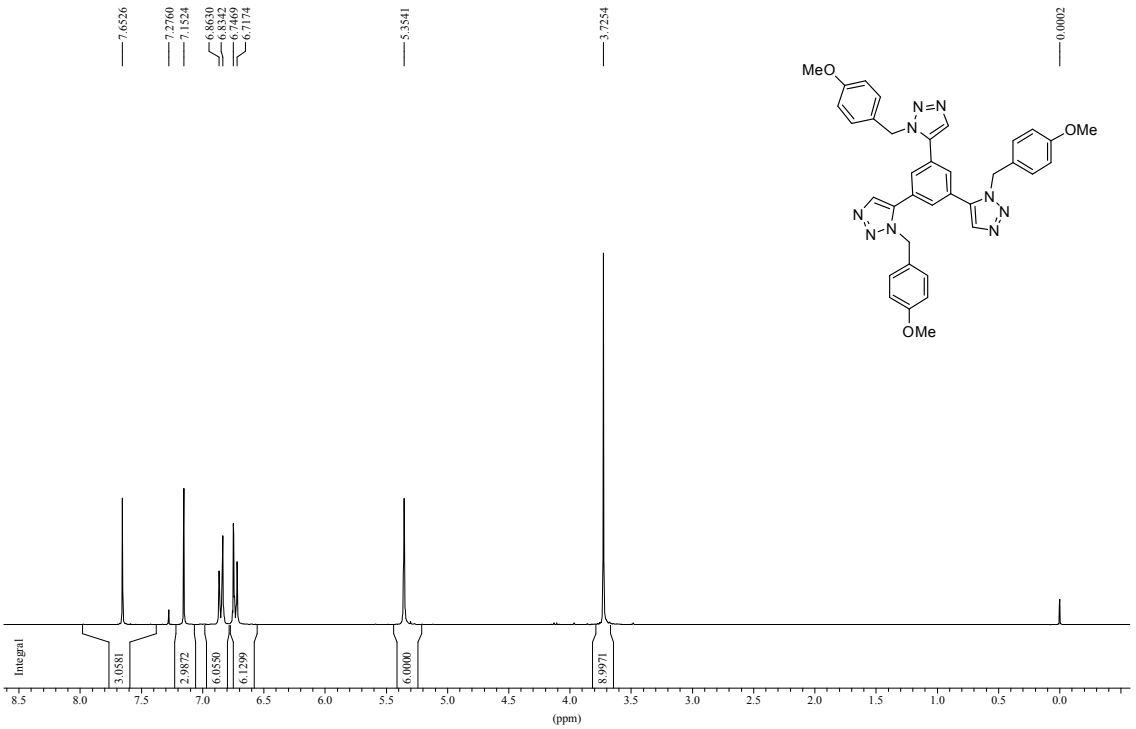
^{1}H NMR Spectra of **7** (300 MHz, CDCl3):



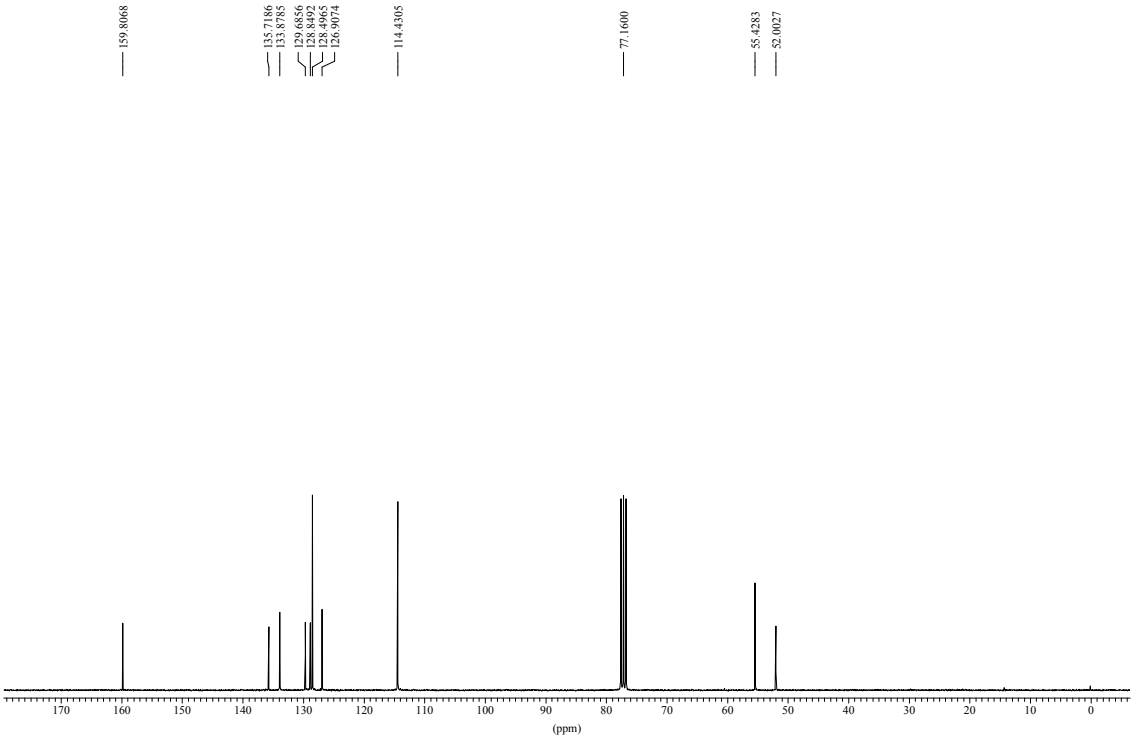
^{13}C NMR Spectra of **7** (75 MHz, CDCl3):



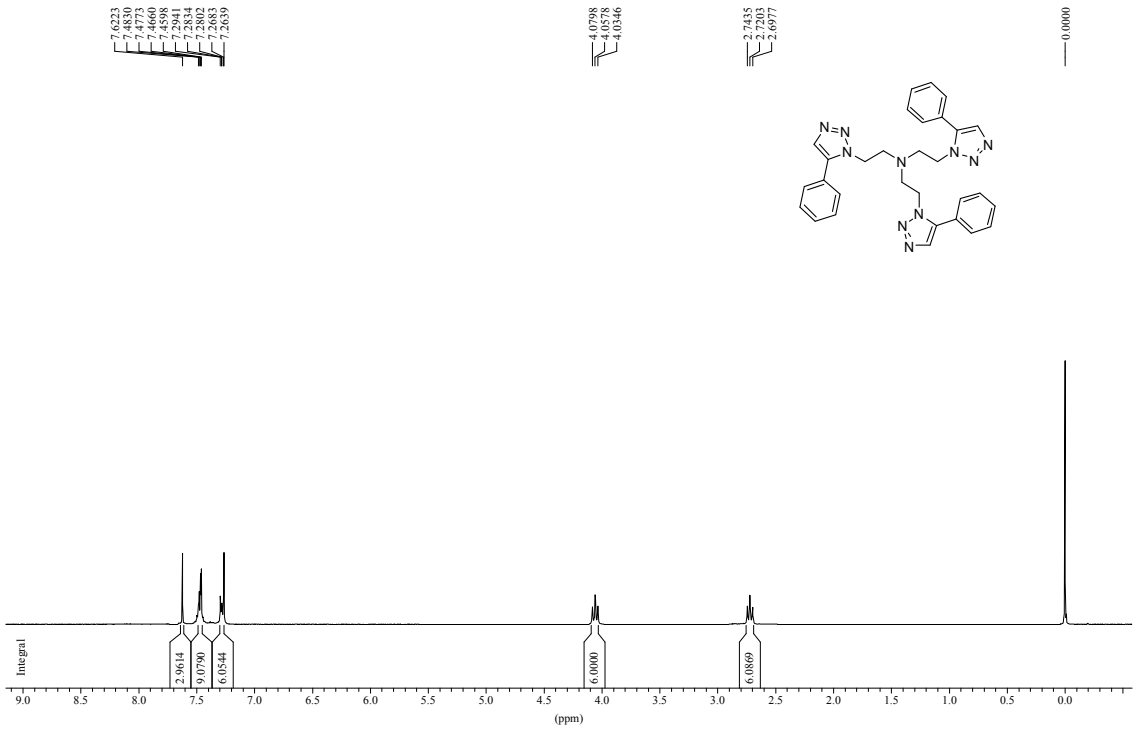
^{1}H NMR Spectra of **8** (300 MHz, CDCl3):



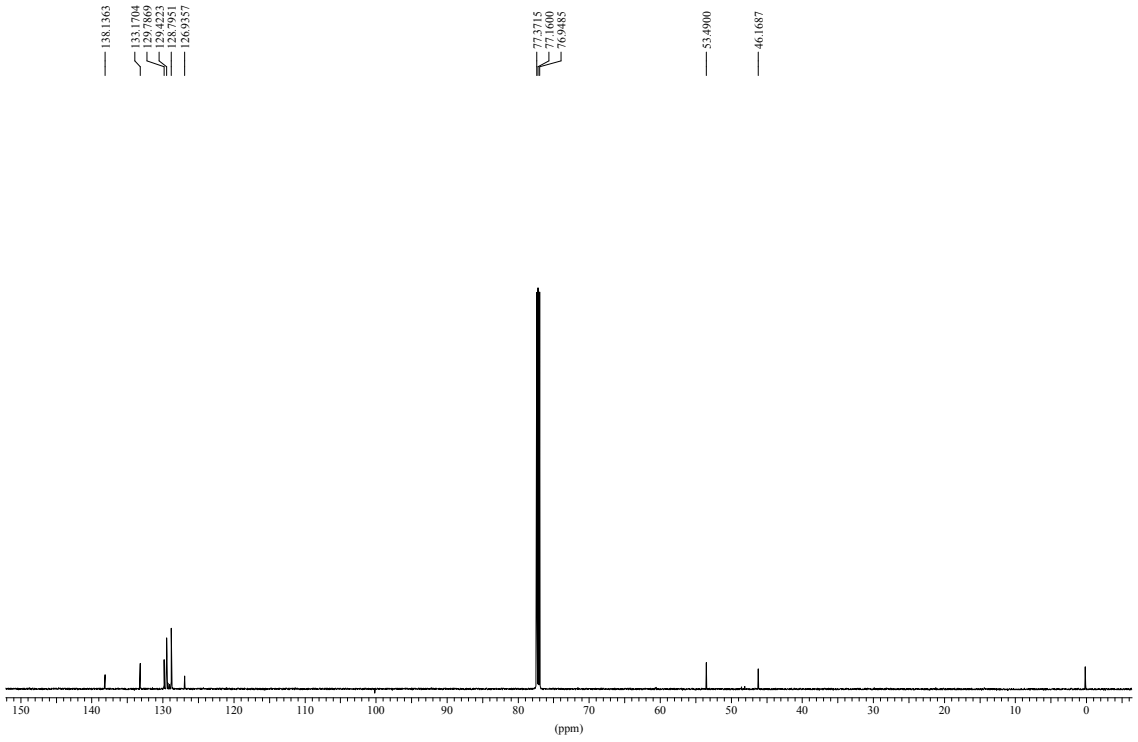
^{13}C NMR Spectra of **8** (75 MHz, CDCl3):



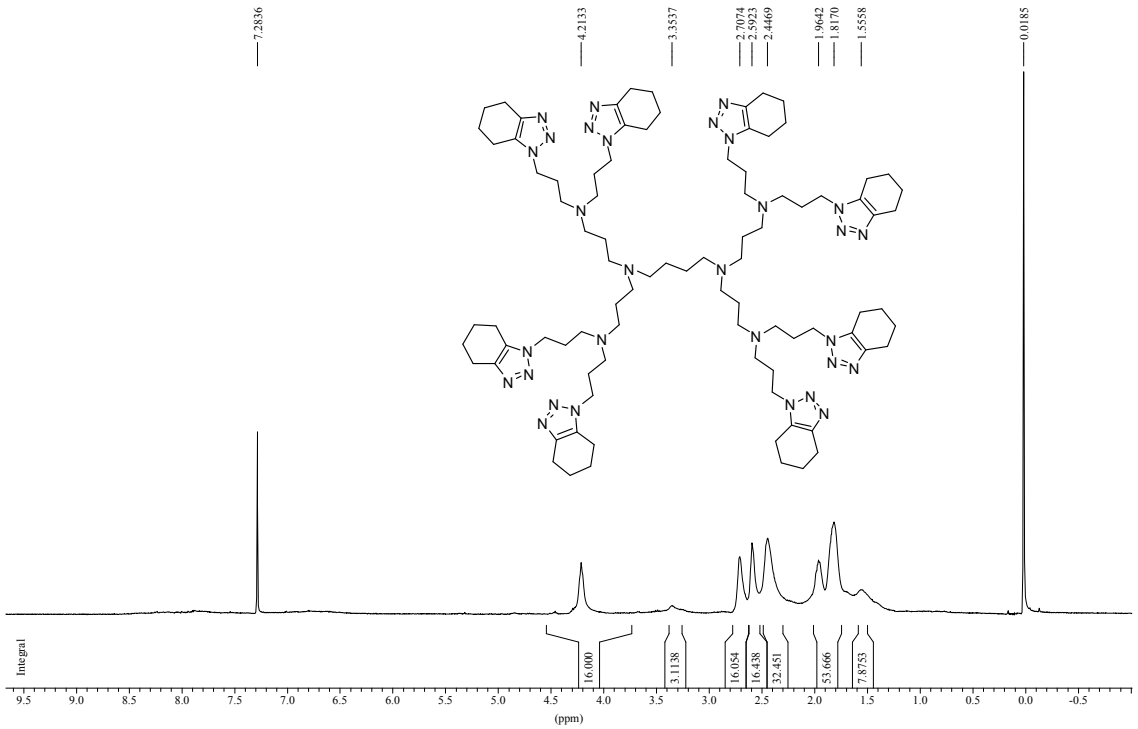
^{1}H NMR Spectra of **9** (300 MHz, CDCl3):



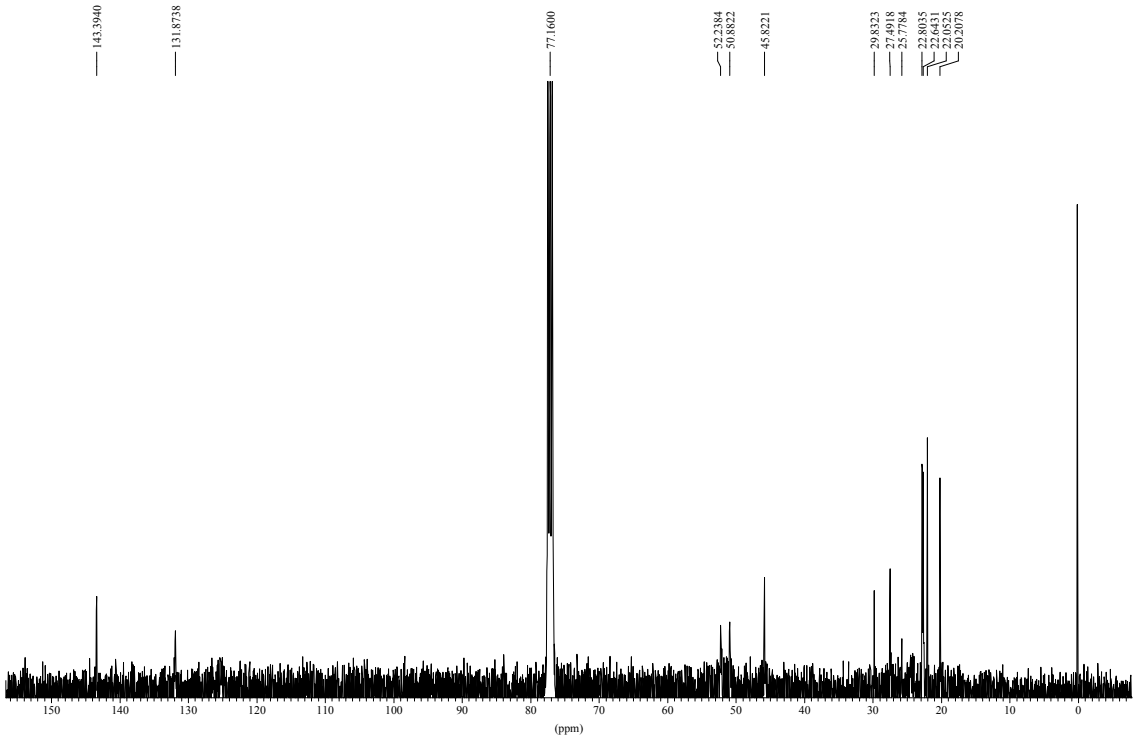
^{13}C NMR Spectra of **9** (75 MHz, CDCl3):



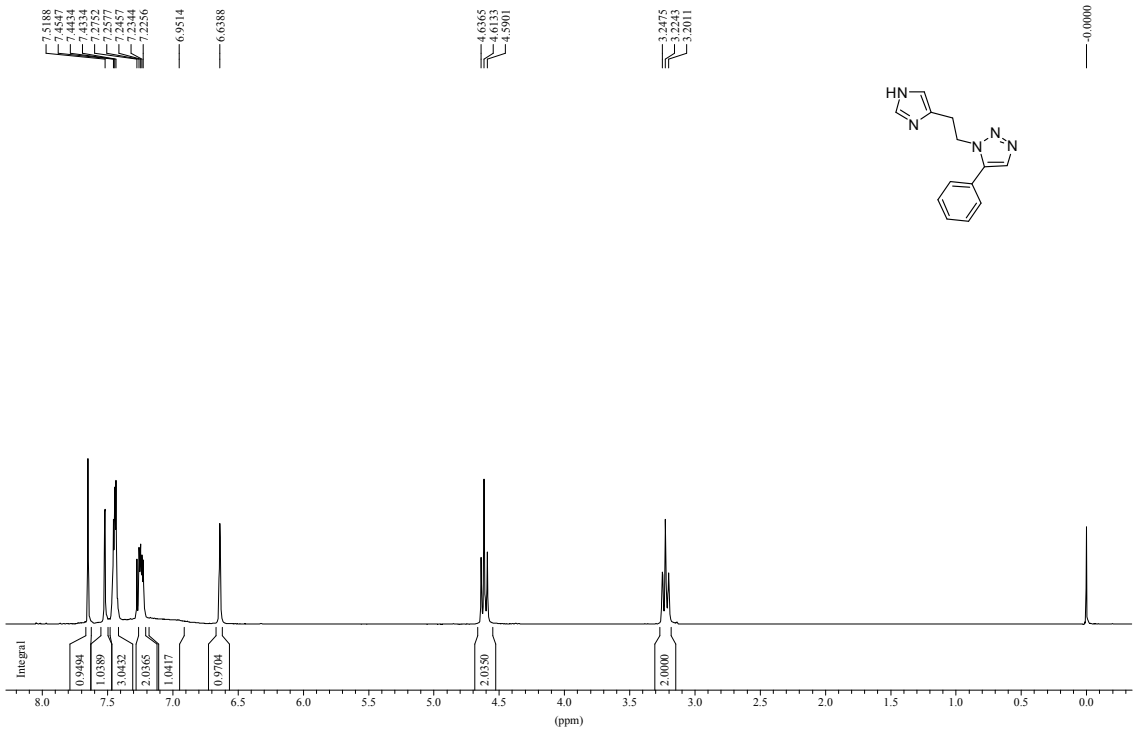
^{1}H NMR Spectra of **11** (300 MHz, CDCl3):



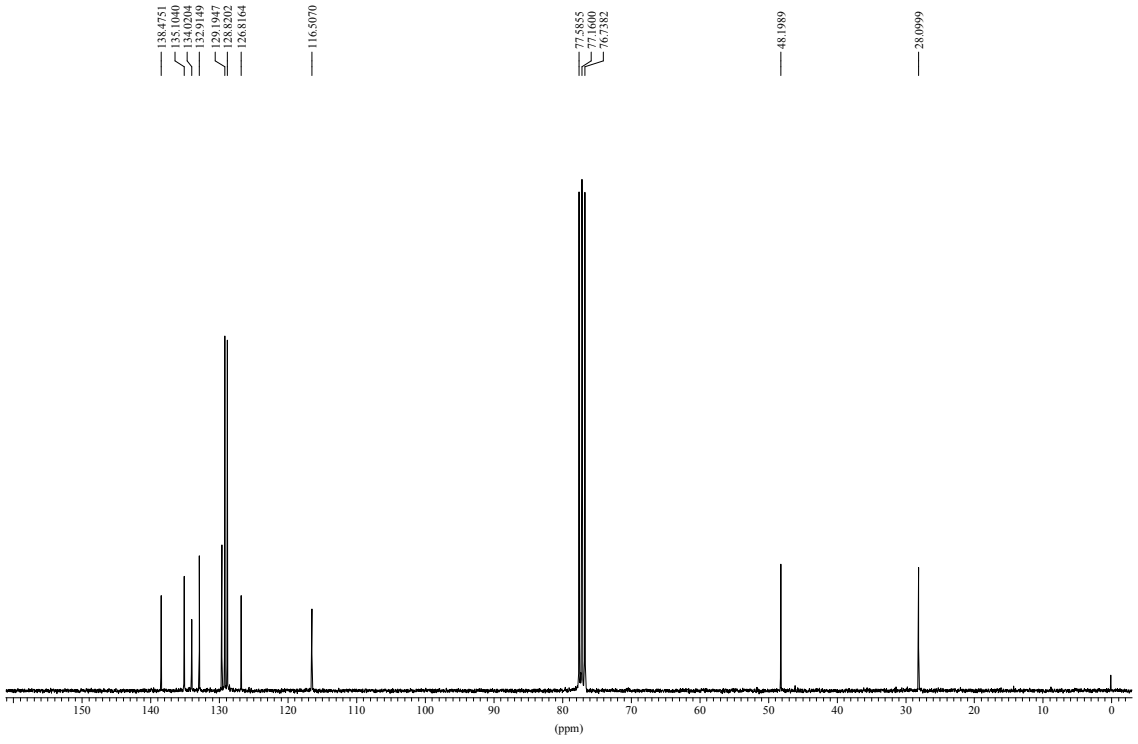
^{13}C NMR Spectra of **11** (75 MHz, CDCl3):



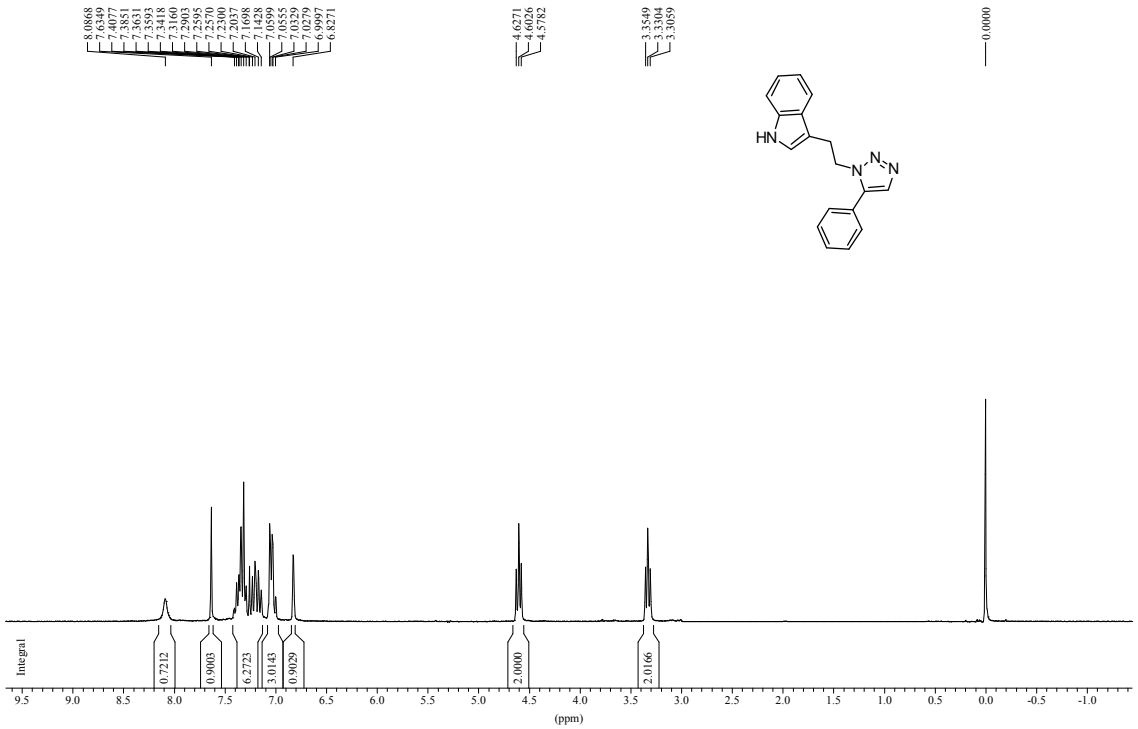
^{1}H NMR Spectra of 1**3a** (300 MHz, CDCl3):



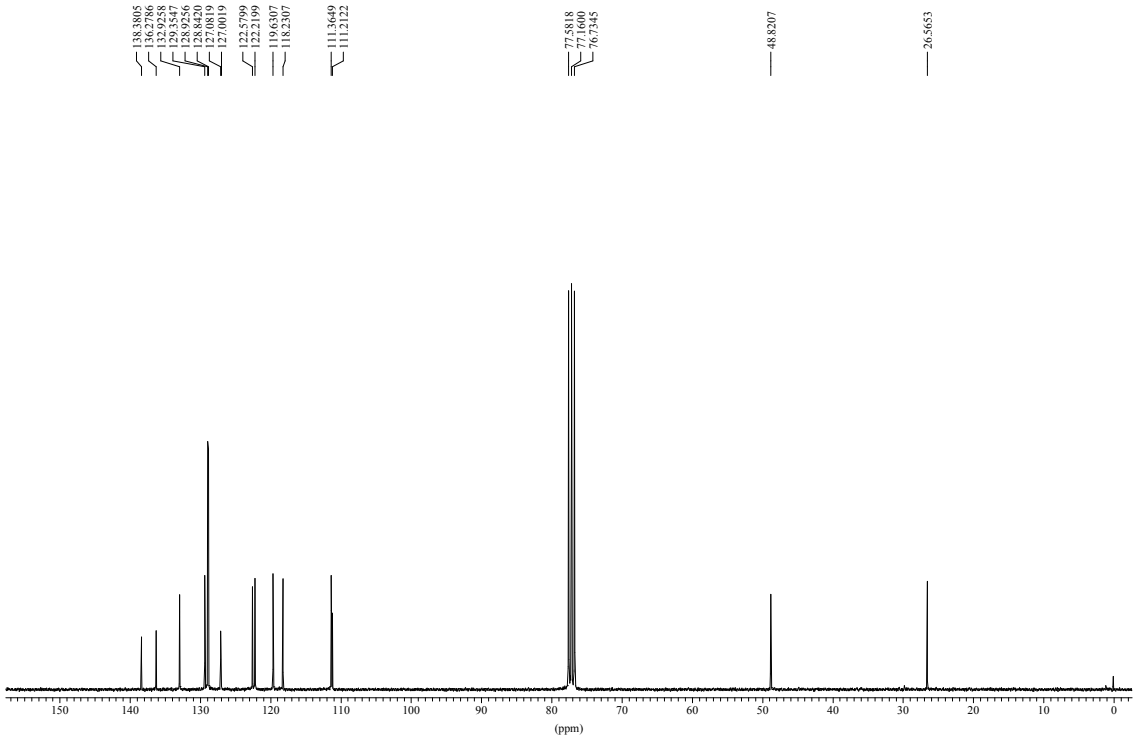
^{13}C NMR Spectra of **13a** (75 MHz, CDCl3):



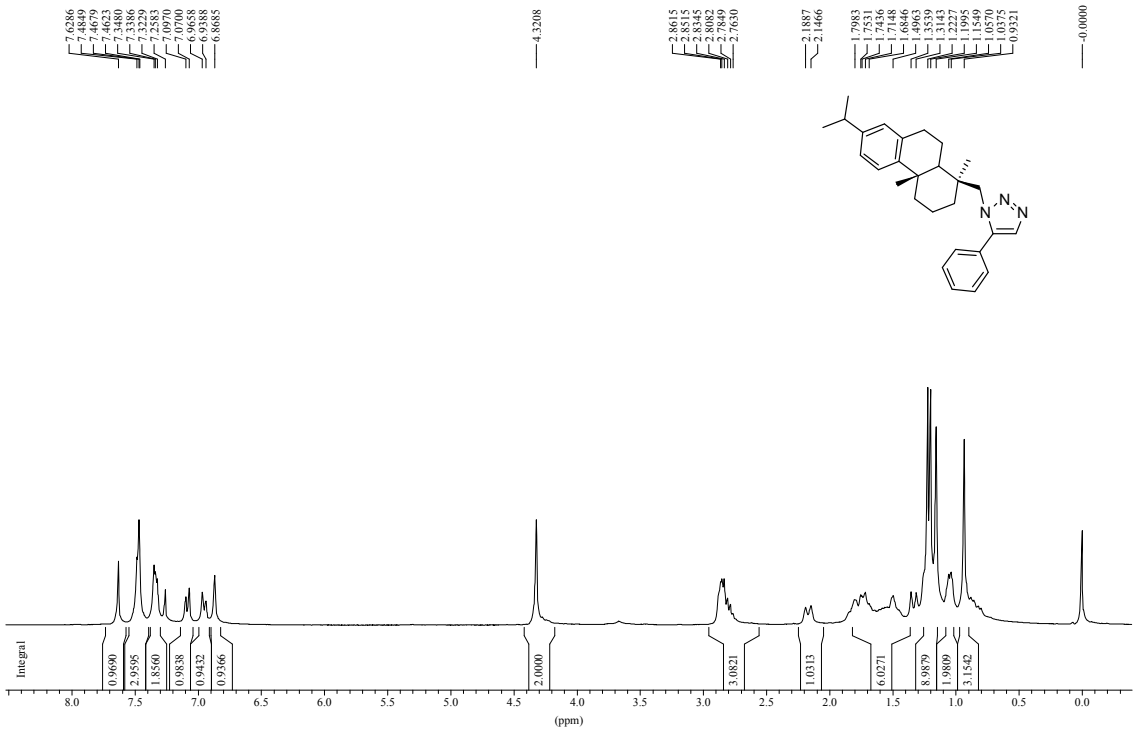
^{1}H NMR Spectra of 1**3b** (300 MHz, CDCl3):



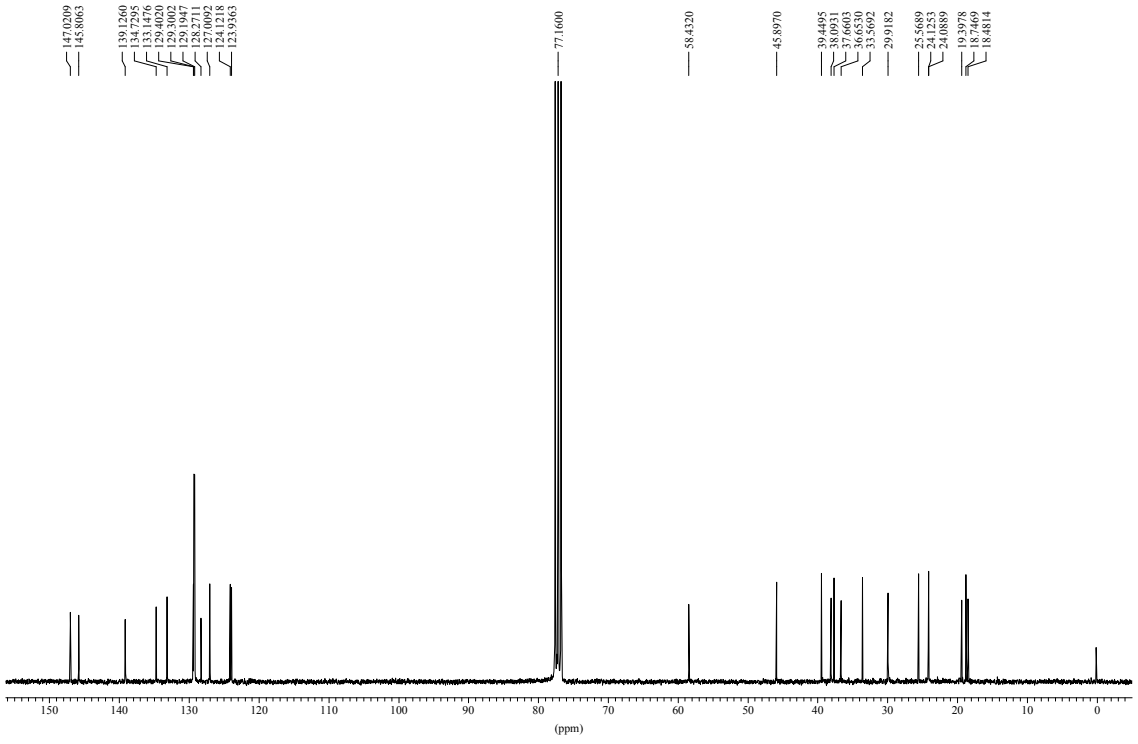
^{13}C NMR Spectra of **13b** (75 MHz, CDCl3):



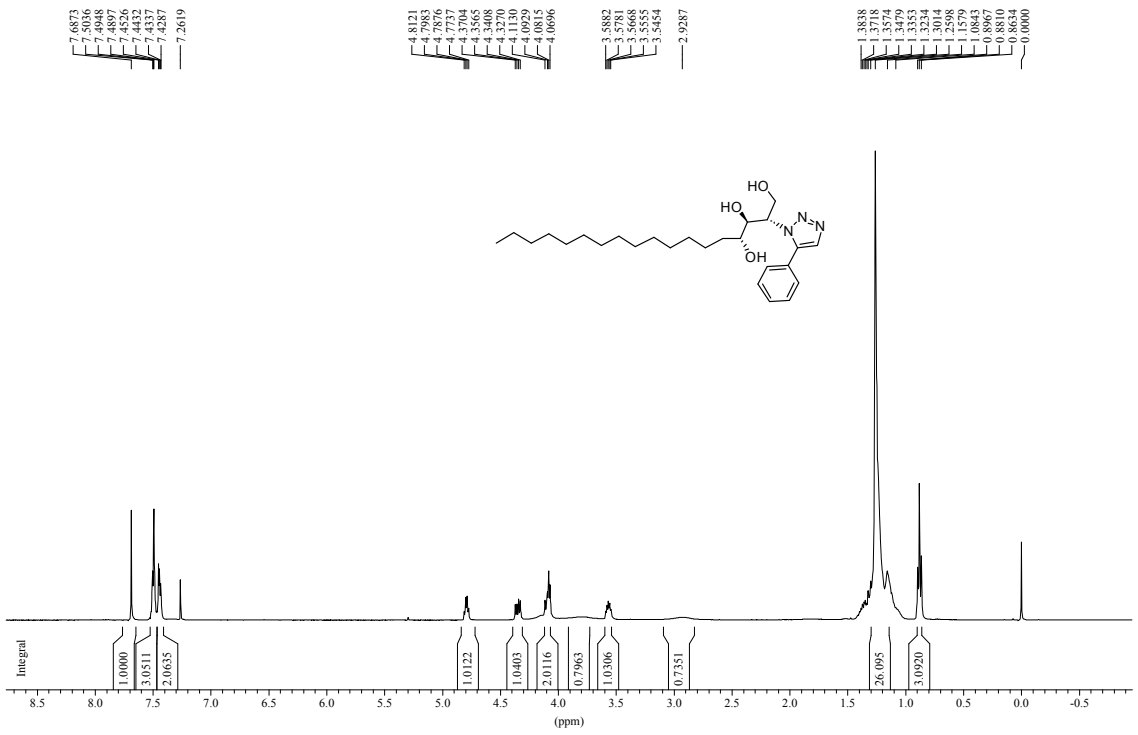
^{1}H NMR Spectra of 1**3c** (300 MHz, CDCl3):



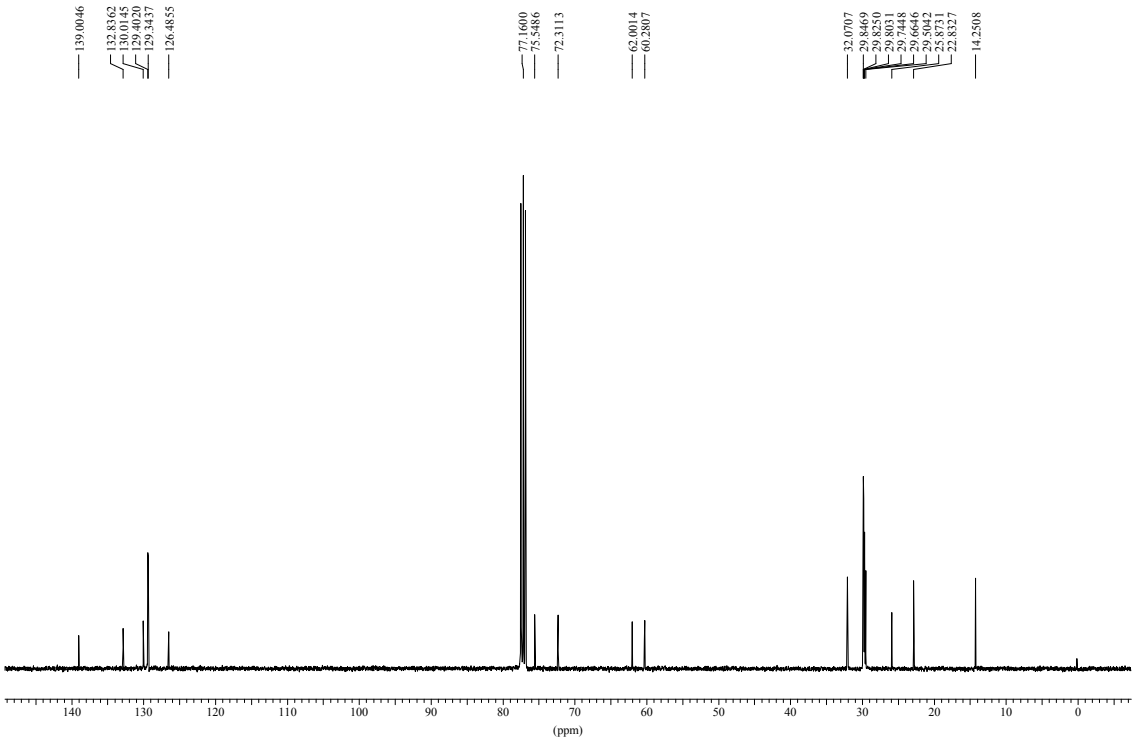
^{13}C NMR Spectra of **13c** (75 MHz, CDCl3):



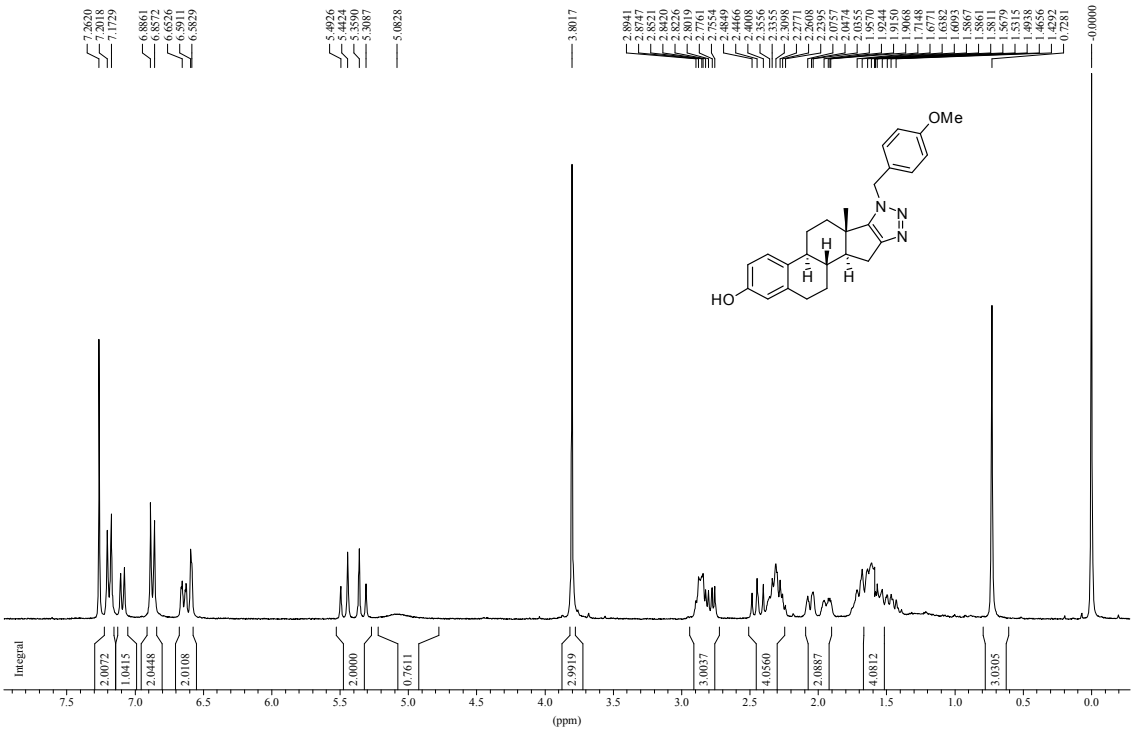
^{1}H NMR Spectra of 1**3d** (300 MHz, CDCl3):



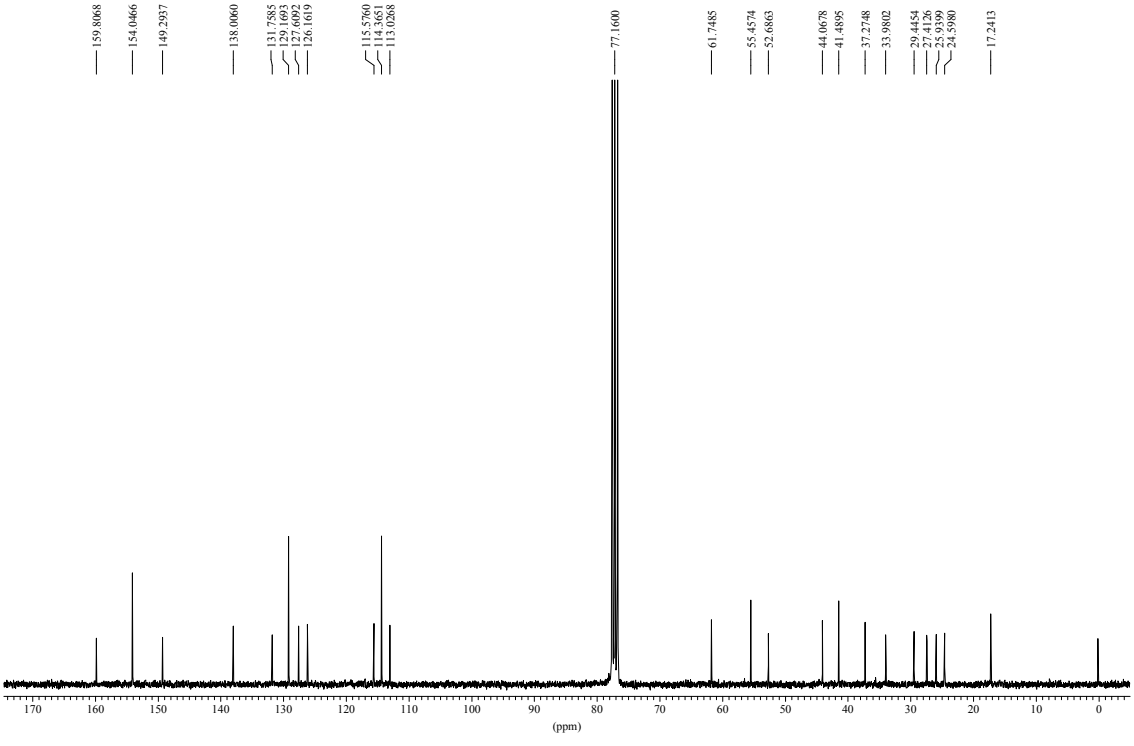
^{13}C NMR Spectra of **13d** (75 MHz, CDCl3):



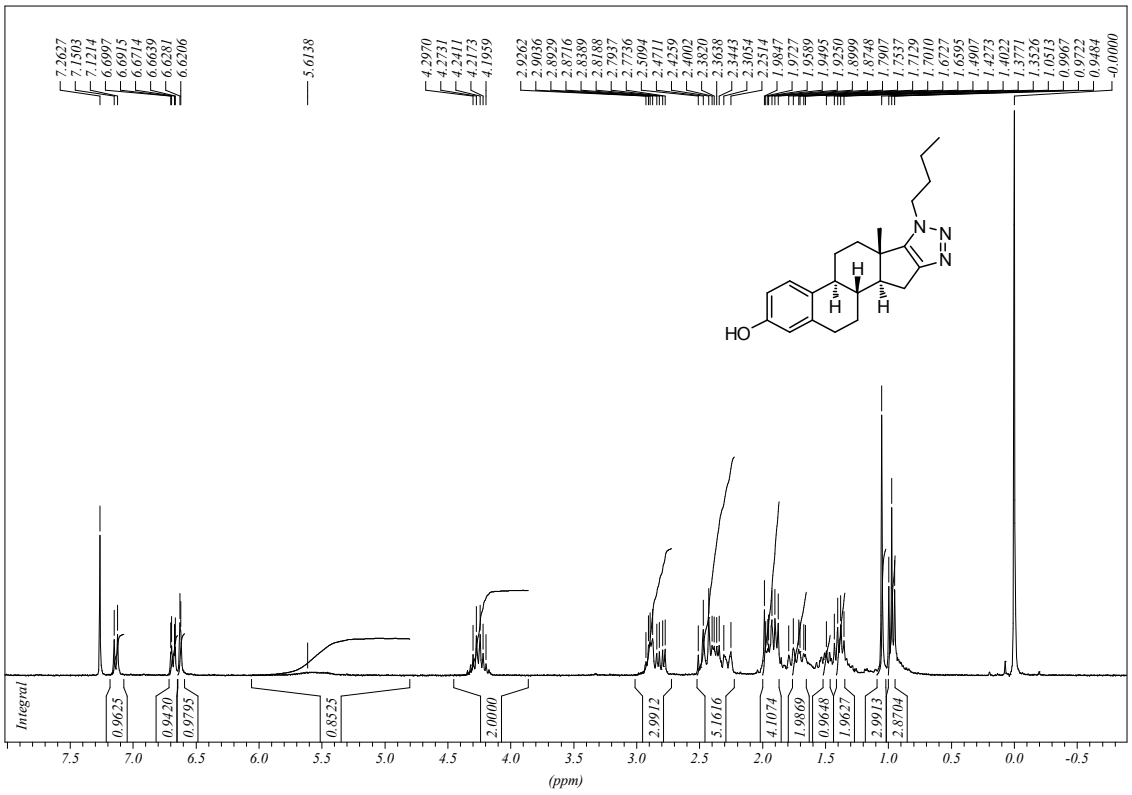
^{1}H NMR Spectra of **13e1** (300 MHz, CDCl3):



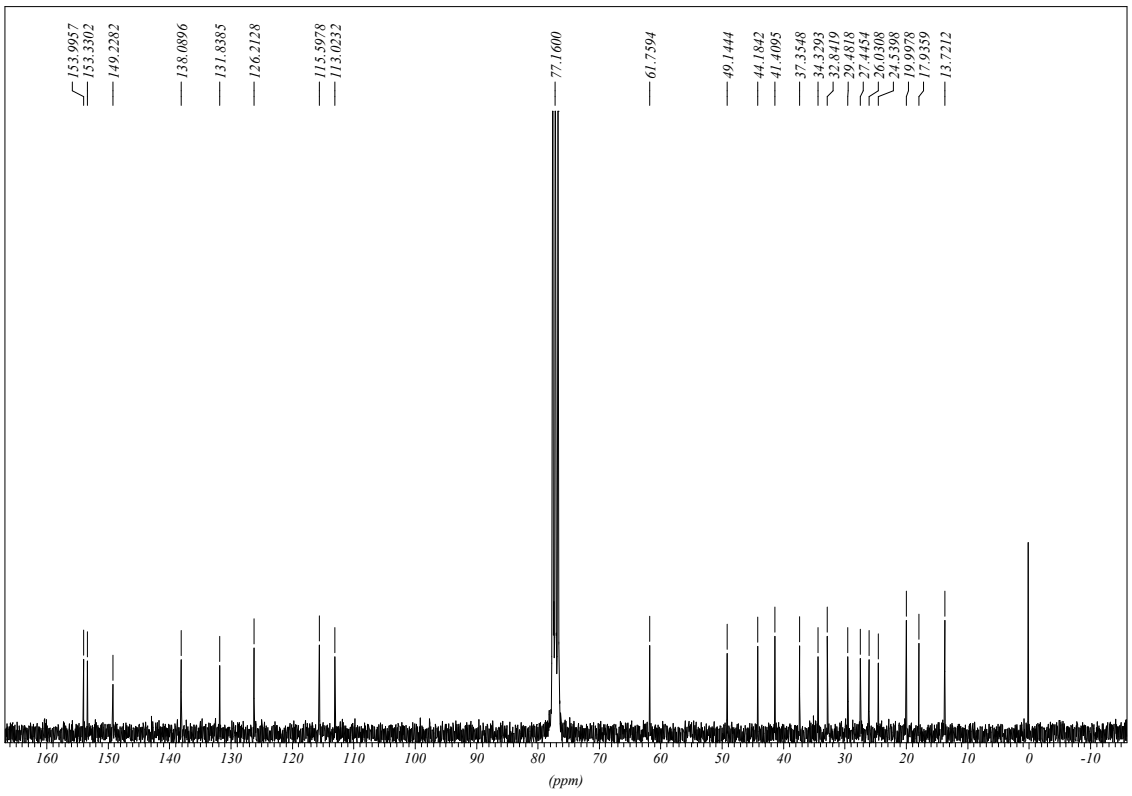
^{13}C NMR Spectra of **13e1** (75 MHz, CDCl3):



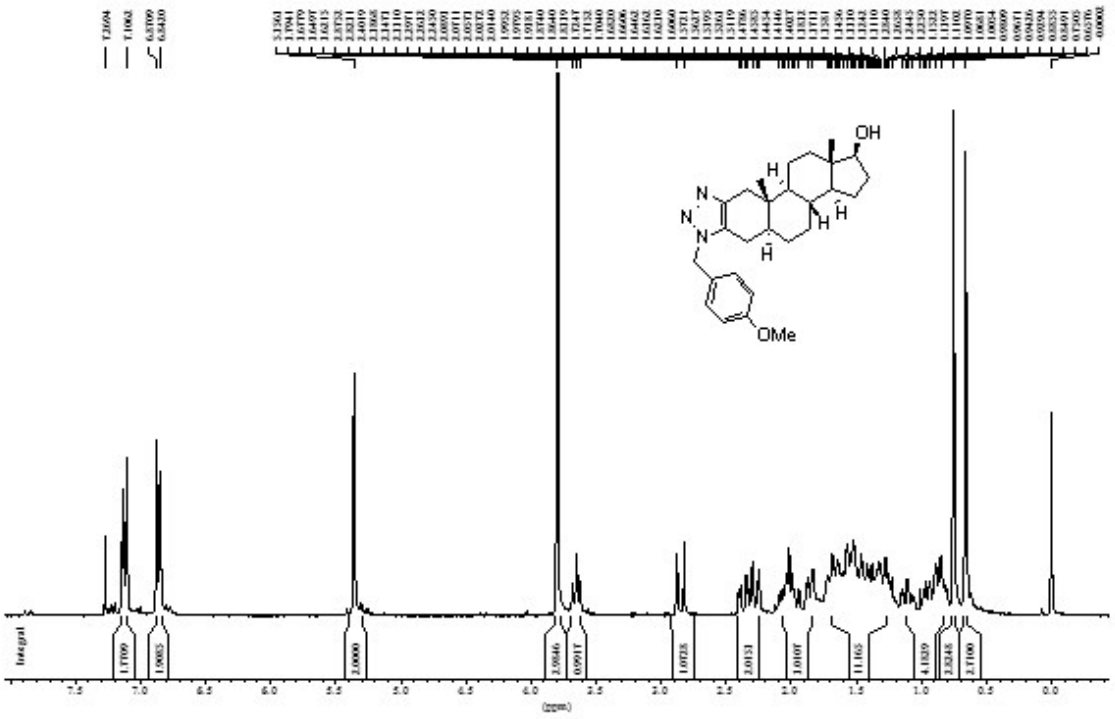
^{1}H NMR Spectra of **13e2** (300 MHz, CDCl3):



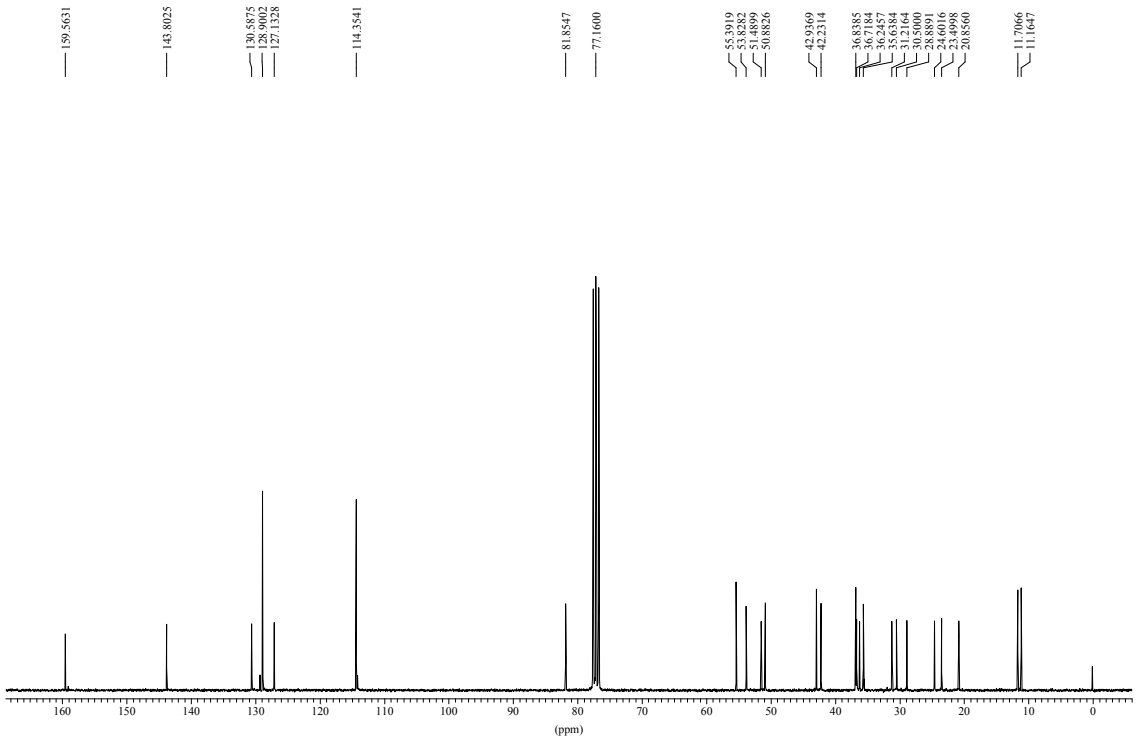
^{13}C NMR Spectra of **13e2** (75 MHz, CDCl3):



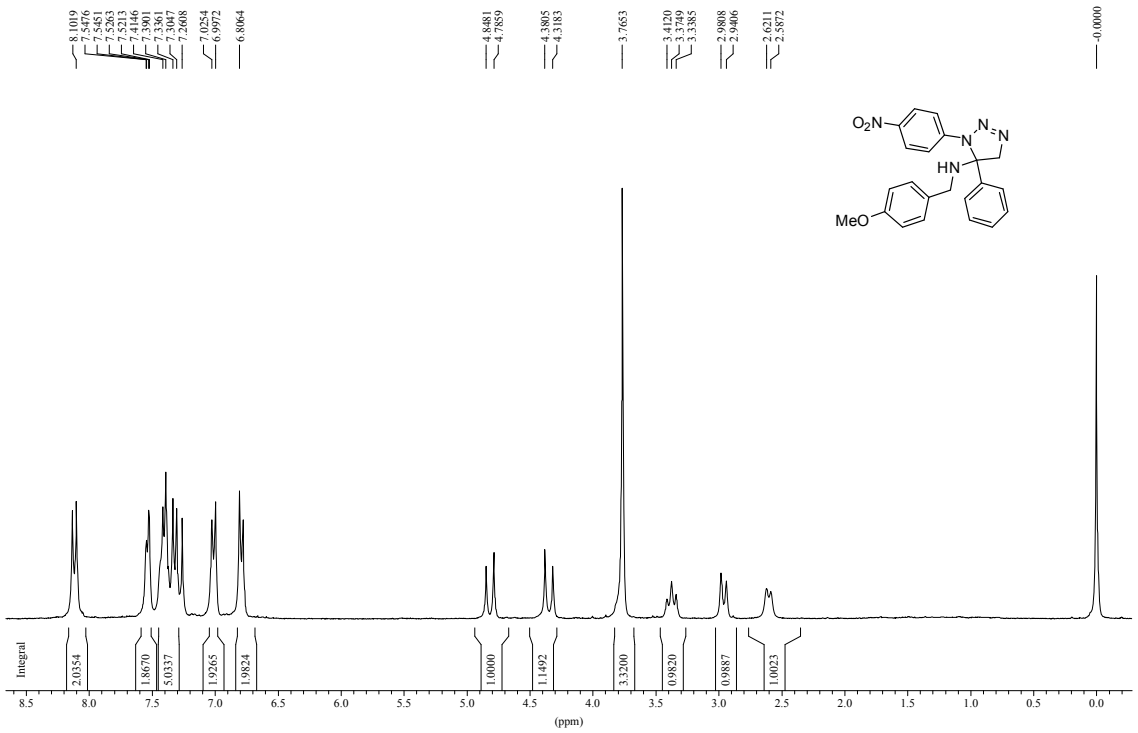
^{1}H NMR Spectra of **13f** (300 MHz, CDCl3):



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



^{1}H NMR Spectra of **6a** (300 MHz, CDCl3):



^{13}C NMR Spectra of **6a** (75 MHz, CDCl3):