Electronic Supplementary Material (ESI) for Green Chemistry.

Cycloaddition of *N*-sulfonyl and *N*-sulfamoyl Azides with Alkynes in Aqueous Media for the Selective Synthesis of 1,2,3-Triazoles

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1.0 General information

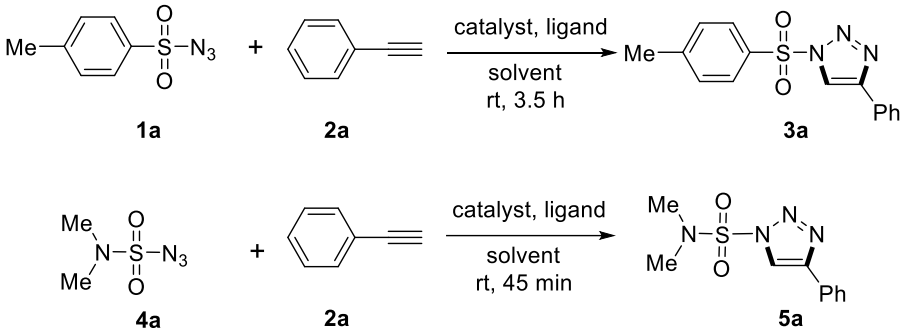
All experiments were carried out in flame-dried reaction vials. Solvents were dried using standard procedures. All starting materials were obtained from commercial suppliers and used as received. Products were purified by flash chromatography on silica gel (100-200 mesh, Merck). Unless otherwise stated, yields refer to analytical pure samples. NMR spectra were recorded in $CDCl_3$ and DMSO-d_6. **^{1}H NMR** spectra were recorded at 500 MHz using Brüker AVANCE 500 MHz and JEOL 400 MHz instruments at 278 K. Signals are quoted as δ values in ppm using residual protonated solvent signals as internal standard ($CDCl_3$: δ 7.26 ppm). Data is reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants and integration (Hz). **^{13}C NMR** spectra were recorded on either a JEOL-400 (100 MHz), or a Brüker AVANCE 500 MHz (125 MHz) with complete proton decoupling. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane with the solvent as the internal reference ($CDCl_3$: δ 77.26 ppm). **HRMS** analyses were performed with Q-TOF YA263 high resolution (Water Corporation) instruments by +ve mode electrospray ionization.

2.0 Optimization of reaction conditions

To optimize the cycloaddition reactions, various conditions were investigated, including the choice of ligand, copper catalyst and solvent. When the reactions were carried out in the absence of either CuI or **Pro-1**, no product was obtained (Table S1, entry 2 and 3), indicating that both CuI and **Pro-1** are necessary for the cycloaddition. Next, we evaluated the effect of different ligands such as DMEDA, phenanthroline, *L*-proline and chiral prolinamide derivatives **Pro-2,** and **Pro-3** on the cycloaddition (entries 4-8). Poor conversion of the starting materials was observed for DMEDA, phenanthroline and *L*-proline (entries 4-6), while among the prolinamide derivatives, **Pro-1** was found to be the best choice for these cycloaddition (entry 1). When the reaction was performed with various copper salts (*i.e* CuBr, $Cu(OAc)_2$, CuO, Cu(0)), it was found that CuI assists the cycloaddition more efficiently as compared to other copper catalysts (Table S1, entries 9-12). Finally, different solvents were used (entries 13-18, Table S1), and the results suggested that water is the optimal solvent for the reactions (entry 1). The cycloadditions did not proceed well in other solvents and the triazole products **3a** and **5a** were obtained in poor yields.

In case of cycloaddition of sulfamoyl azide (**4a**) and phenylacetylene (**2a**), after 3.5 h the triazole product **5a** was obtained in 85% yield (entry 20). Interestingly, the reaction was found to be completed in 45 minutes, providing the desired triazole **5a** in excellent yield (entry 21).

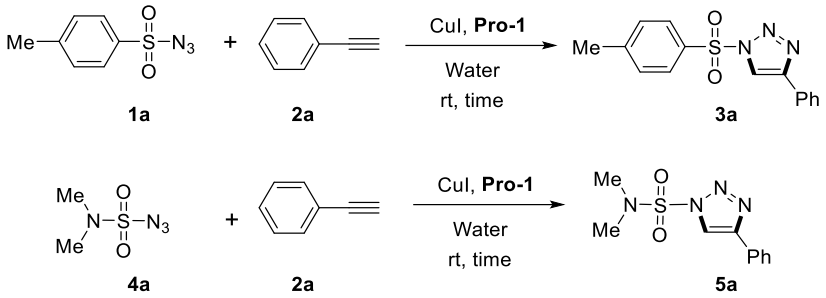
Table S1. Optimization of reaction conditions[a]



entry	ligand	Catalyst	solvent	time (h)	yield (%)[b]
1	**Pro-1**	**CuI**	**H_2O**	**3.5**	**95**
2	-	CuI	H_2O	24	20
3	**Pro-1**	-	H_2O	24	n.r
4	DMEDA	CuI	H_2O	3.5	40
5	Phenanthroline	CuI	H_2O	3.5	51
6	*L*-Proline	CuI	H_2O	3.5	65
7	**Pro-2**	CuI	H_2O	3.5	68
8	**Pro-3**	CuI	H_2O	3.5	40
9	**Pro-1**	$Cu(OAc)_2$	H_2O	3.5	21
10	**Pro-1**	CuO	H_2O	3.5	-
11	**Pro-1**	CuBr	H_2O	3.5	57
12	**Pro-1**	Cu(0)	H_2O	3.5	-
13	**Pro-1**	CuI	*tert*-butanol	3.5	30
14	**Pro-1**	CuI	DMSO	3.5	80
15	**Pro-1**	CuI	EtOH	3.5	55
16	**Pro-1**	CuI	DMF	3.5	60
18	**Pro-1**	CuI	MeCN	3.5	30
20[c]	**Pro-1**	CuI	H_2O	3.5	85
21[c]	**Pro-1**	**CuI**	**H_2O**	**45 min**	**94**

[a]Reaction conditions: **1a / 4a** (1.0 mmol), **2a** (1.50 mmol), CuI (0.05 mmol), **Pro-1** (0.1 mmol), in 2 mL water; [b]yield refers to the isolated yield without chromatographic purification; [c]reaction was performed with **4a** and **2a**.

Table S2. Effect of concentration of ligand, Cu(I) and time on the cycloaddition reactions.[a]



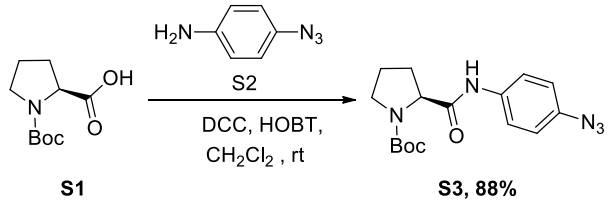
entry	**Pro-1** (mol%)	CuI (mol%)	time (h)	conversion (%)[b]
1	5	2	3.5	55
2	5	4	3.5	60
3	5	5	3.5	75
4	8	5	3.5	85
5	**10**	**5**	**3.5**	**95**
6	10	5	4	95
7	10	5	2	80
8[c]	10	5	30 min	85
9[c]	**10**	**5**	**45 min**	**94**

[a]Reaction conditions: **1a / 4a** (1.0 mmol), **2a** (1.50 mmol), CuI (0.05 mmol), **Pro-1** (0.1 mmol), in 2 mL water; [b]yield refers to the isolated yield without chromatographic purification; [c]reaction was performed with **4a** and **2a**.

The highest conversion was obtained when 10 mol% **Pro-1** and 5 mol% CuI were used in both the reactions. The reaction of **1a** and **2a** was completed after stirring for 3.5 h (entry 5, Table S2), while the cycloaddition of **4a** and **2a** completed in 45 minutes (entry 9, Table S2).

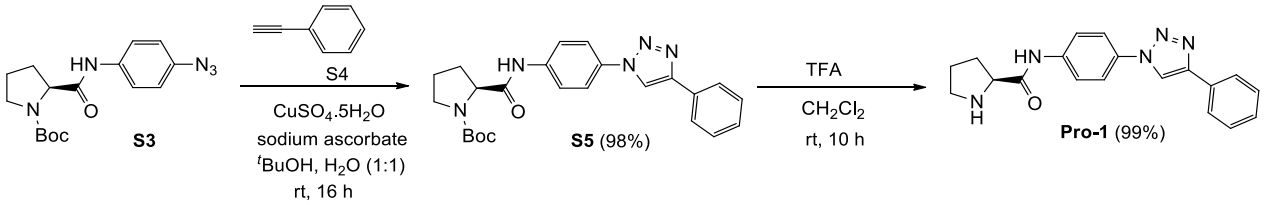
3.0 Preparation of ligands

Preparation of azido prolinamide S3:[1] To an ice-cold suspension of *N*-Boc proline **S1** (1.0 g, 4.65 mmol) in dry CH_2Cl_2 (25 mL), DCC (1.06 g, 5.1 mmol, 1.1 equiv) and HOBT (691 mg, 5.1 mmol, 1.1 equiv) were added and the mixture was allowed to stir for 45 min. Then, a solution of 4-azidoaniline **S2**[2] (624 mg, 4.65 mmol, 1.0 equiv) in dry CH_2Cl_2 (20 mL) was added dropwise to the reaction mixture, and stirred for 12 h. After complete consumption of the azide **S2** (TLC monitoring), the reaction mixture was filtered through celite, washed with dichloromethane (50 mL) and concentrated under vacuum. The product was purified by flash chromatography using hexane-ethylacetate (95:5 to 85:15) as eluent to afford the desired product **S3** as a yellow solid (1.50 g, 88 %) (Scheme S1). ^{1}H NMR (400 MHz, $CDCl_3$): 9.61 (br s, 1H), 7.48 (d, J = 9.4 Hz, 2H), 6.89 (br s, 1H), 4.47 (br s, 1H), 3.45-3.36 (m, 2H), 2.44 (br s, 1H), 1.99-1.90 (m, 3H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): 170.0, 156.5, 135.5, 134.9, 120.8, 119.2, 80.9, 60.4, 47.3, 28.3, 27.5, 24.5; HRMS (ESI) calcd for $C_{16}H_{21}N_5O_3K$ $(M+K)^+$: 370.1281; found: 370.1268.



Scheme S1. Preparation of azido prolinamide **S3**.

Preparation of Pro-1: The Cu(I)-catalyzed cycloaddition of azido prolinamide **S3** and phenyl acetylene **(S4)** afforded triazole derivative **S5**, which upon Boc group removal provided ligand **Pro-1** (Scheme S2).



Scheme S2. Synthesis of ligand **Pro-1**.

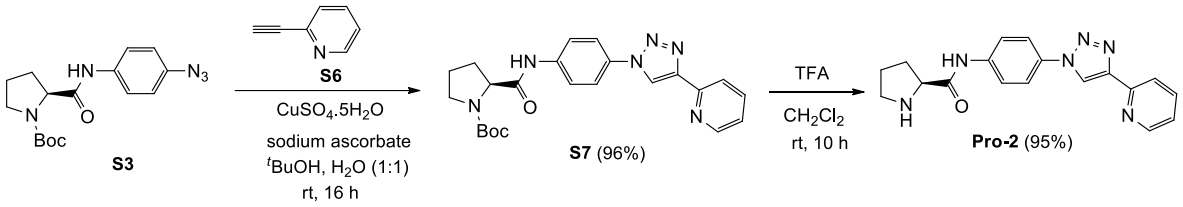
[1]S. Paladhi, J. Das, P K. Mishra and J. Dash, *Adv. Synth. Catal*., 2013, **355**, 274-280.

[2]J. Andersen, U. Madsen, F. Björkling and X. Liang, *Synlett*, 2005, 2209-2213.

Preparation of traizole derivative S5: Phenyl acetylene **(S4)** (1.08 mL, 9.8 mmol), sodium ascorbate (194 mg, 0.98 mmol, 0.1 equiv), $CuSO_4.5H_2O$ (122.4 mg, 0.49 mmol, 0.05 equiv) were dissolved in 10 mL *t*BuOH-H_2O (7:3) mixture. Then the azido prolinamide **S3** (3.3 g, 9.8 mmol, 1.0 equiv) was added and stirred at room temperature for 16 h. After complete consumption of **S3** as monitored by TLC, the reaction mixture was concentrated and the residue was purified by flash chromatography using hexane-ethyl acetate (90:10 to 50:50) mixture to give the pure product **S5** (4.12 g, 98%) as a colorless solid (Scheme S2) . ^{1}H NMR (400 MHz): 9.97 (s, 1H), 8.08 (s, 1H), 7.84 (d, *J* = 9.1 Hz, 2H), 7.57 (d, *J* = 9.6 Hz, 2H), 7.44 (d, *J* = 9.2 Hz, 2H), 7.35 (t, *J* = 8.5 Hz, 2H), 7.36-7.30 (m, 1H), 4.56 (s, 1H), 3.57-3.54 (m, 2H), 2.53 (s, 1H), 2.08-1.91 (m, 3H), 1.51 (s, 9H); ^{13}C NMR (100 MHz): 171.1, 155.7, 148.1, 139.1, 132.0, 130.0, 128.7, 128.1, 125.6, 120.8,119.9, 117.7, 80.7, 60.4, 47.2, 28.9, 28.3, 24.5; HRMS (ESI) calcd for $C_{24}H_{27}N_5O_3K$ (M+K)+: 472.1751; found, 472.1783.

Preparation of ligand Pro-1: To an ice cold solution of compound **S5** (1.0 g, 2.3 mmol) in 30 mL CH_2Cl_2 was added TFA (0.53 mL, 6.9 mmol, 3.0 equiv) and the mixture was stirred for 10 h at room temperature. After consumption of the starting material **S5** (monitored by TLC), the reaction mixture was brought to pH 8-9 by dropwise addition of solution of liquid NH_3 (30%) at 0 °C. Then the reaction mixture was extracted with CH_2Cl_2 (3 x 20 mL), evaporated and dried under vacuum to give **Pro-1** (760 mg, 99%) as a white solid (Scheme S2). ^{1}H NMR (400 MHz): 9.98 (s, 1H), 8.17 (s, 1H), 7.89 (d, *J* = 8.8 Hz, 2H), 7.77 (d, *J* = 11.3 Hz, 2H), 7.72 (d, *J* = 11.1 Hz, 2H), 7.44 (t, *J* = 9.5 Hz, 2H), 7.35 (t, *J* = 9.2 Hz, 1H), 3.89 (dd, *J* = 11.6, 6.5 Hz, 1H), 3.09 (td, *J* = 12.8, 8.5 Hz, 1H), 3.00 (td, *J* = 12.8, 7.9 Hz, 1H), 2.40 (br s, 1H), 2.25-2.20 (m, 1H), 2.04 (dt, *J* = 15.6, 8.3 Hz, 1H), 1.79-1.74 (m, 2H); ^{13}C NMR (100 MHz): 173.7, 148.2, 138.3, 132.6, 130.2, 128.8, 128.3, 125.8, 121.1, 120.0, 117.6, 60.9, 47.3, 30.7, 26.3; HRMS (ESI) calcd for $C_{19}H_{20}N_5O$ (M+H)+:334.1667; found, 334.1693.

Preparation of Pro-2: A Cu(I)-catalyzed cycloaddition of azido prolinamide **S3** and 2-ethynylpyridine **S6** gave triazole derivative **S7,** which uponthe removal of Boc group afforded **Pro-2** (Scheme S3).



Scheme S3. Synthesis of **Pro-2**.

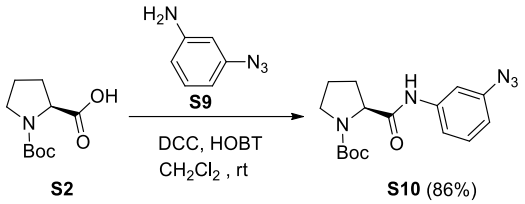
Preparation of traizole derivative S7: 2-Ethynylpyridine **S6** (1.08 mL, 9.8 mmol), sodium ascorbate (194 mg, 0.98 mmol, 0.1 equiv), $CuSO_4.5H_2O$ (122.4 mg, 0.49 mmol, 0.05 equiv) were dissolved in 10 mL *t*BuOH-H_2O (7:3) mixtures. Then the azido prolinamide **S3** (3.3 g, 9.8 mmol, 1.0 equiv) was added and stirred at room temperature for 16 h. After complete consumption of **S3** as monitored by TLC, the reaction mixture was concentrated and the residue was purified by flash chromatography using hexane-ethyl acetate (90:10 to 40:60) mixture to give the pure product **S7** (4.00 g, 96%) as a colorless solid (Scheme S3). ^{1}H NMR (400 MHz, DMSO-d^6): 10.3 (br s, 1H), 9.23 (s, 1H), 8.64 (d, *J* = 3.9 Hz, 1H), 8.11 (d, *J* = 7.8 Hz, 2H), 7. 96 (d, *J* = 8.3 Hz, 3H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.40 (t, *J* = 5.4 Hz, 1H), 4.29-4.21 (m, 1H), 2.27-2.19 (m, 1H), 1.91-1.81 (m, 3H), 1.41 (s, 3H), 1.28 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d^6): 171.9, 153.2, 149.6, 149.5, 147.9, 139.5, 137.4, 131.7, 123.3, 120.9, 120.8, 119.9, 119.8, 78.6, 60.5, 46.7, 30.9, 27.8, 23.3; HRMS (ESI) calcd for $C_{23}H_{27}N_6O_3$ $(M+H)^+$: 435.2145; found, 435.2144.

Preparation of ligand Pro-2: To an ice cold solution of compound **S7** (1.0 g, 2.3 mmol) in 30 mL dry CH_2Cl_2, added TFA (0.53 mL, 6.9 mmol, 3.0 equiv) and the mixture was stirred for 10 h at room temperature. After consumption of the starting material **S7** (monitored by TLC), the reaction mixture was brought to pH 8-9 by dropwise adition of 30 wt% solution of NH_3 in water at 0 °C. Then the reaction mixture was extracted with CH_2Cl_2 (3 x 20 mL), evaporated and dried under vacuum, to give **Pro-2** (730 mg, 95%) as a white solid (Scheme S3). ^{1}H NMR (500 MHz, DMSO-d^6): 10.3 (br s, 1H), 9.24 (s, 1H), 8.64 (d, *J* = 3.4 Hz, 1H), 8.11 (d, *J* = 7.6 Hz, 2H), 7. 96-7.89 (m, 5H), 7.39 (t, *J* = 5.1 Hz, 1H), 3.75 (s, 1H), 2.92 (t, *J* = 6.7 Hz, 2H), 2.11-2.04 (m, 1H), 1.84-1.78 (m, 1H), 1.67 (t, *J* = 5.9 Hz, 1H), 1.34 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d^6): 173.7, 149.6, 149.5, 148.1, 138.9, 137.3, 131.8, 123.3, 120.9, 120.7, 120.0, 119.8, 60.8, 46.7, 30.4, 25.8; HRMS (ESI) calcd for $C_{18}H_{19}N_6O$ $(M+H)^+$: 335.1620; found, 335.1622.

Preparation of 3-azidoaniline S9: Following the literature procedure,[3] to a solution of 3-bromoaniline **S8** (1.0 g, 5.8 mmol, 1.0 equiv) in a mixture of EtOH-H_2O (7:3, 25 mL) and sodium ascorbate (57.6 mg, 0.29 mmol, 0.05 equiv), CuI (115 mg, 0.58 mmol, 0.1 equiv), ligand *N*,*N*′-dimethylethylenediamine (94 μL, 0.87 mmol, 0.15 equiv) were added and stirred for 10 min. Sodium azide (755 mg, 11.62 mmol, 2.0 equiv) was added to the reaction mixture and the mixture was allowed to stir for 3 h at reflux under argon atmosphere. After complete consumption of **S8** (TLC analysis), the reaction was cooled, concentrated under vacuum and the crude product was purified by flash chromatography using hexane-ethyl acetate (95:5) mixture to give the desired azide **S9** (750 mg, 96%) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.10 (t, *J* = 7.9 Hz, 1H), 6.43 (dd, *J* = 6.7, 1.8 Hz, 2H), 6.30 (t, *J* = 1.8 Hz, 1H), 3.73 (br s, 2H); ^{13}C NMR (100 MHz):147.9, 141.1, 130.6, 111.9, 109.1, 105.5; HRMS (ESI) calcd for $C_6H_7N_4(M+H)^+$: 135.0671; found: 135.0670.

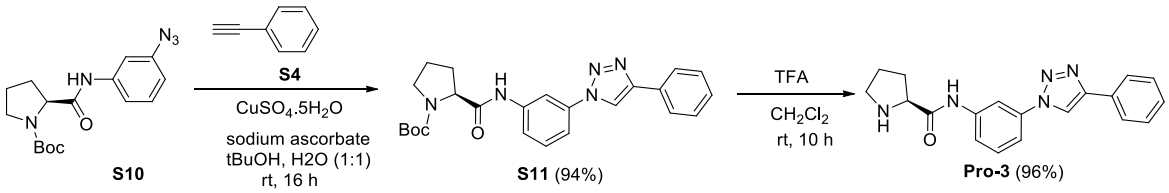
Preparation of 3-azido prolinamide S10: To an ice-cold suspension of *N*-Boc proline **S2** (1.0 g, 4.65 mmol) in dry CH_2Cl_2 (25 mL), DCC (1.06 g, 5.1 mmol, 1.1 equiv) and HOBT (691 mg, 5.1 mmol, 1.1 equiv) were added and the mixture was allowed to stir for 45 min. Then 3-azidoaniline **S9** (624 mg, 4.65 mmol, 1.0 equiv) in 20 mL dry CH_2Cl_2 was added dropwise to the reaction mixture, and stirred for 12 h. After complete consumption of the azide **S9** (TLC monitoring), the reaction mixture was filtered through celite, washed with ethyl acetate (50 mL) and concentrated under vacuum. The product was purified by flash chromatography using hexane-ethylacetate (95:5 to 85:15) as eluent to afford the desired product **S10** as a yellow solid (1.42 g, 86 %) (Scheme S4). ^{1}H NMR (400 MHz, $CDCl_3$): 9.72 (s, 1H), 7.36 (s, 1H), 7.10 (s, 1H), 7.04 (s, 1H), 4.49 (s, 1H), 3.50-3.35 (m, 2H) 2.41-1.89 (m, 4H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$):170.5, 156.0, 140.2, 139.9, 129.6, 115.6, 114.0, 109.8, 80.8, 60.4, 47.1, 28.3, 24.5; HRMS (ESI) calcd for $C_{16}H_{21}N_5O_3K$ $(M+K)^+$: 370.1281; found: 370.1268.

[3](a) J. Andersen, U. Madsen, F. Björkling andX. Liang, *Synlett.* 2005, 2209-2213; (b) S. Paladhi, J. Das, P. K. Mishra and J. Dash, *Adv. Synth. Catal*., 2013, **355**, 274-280.



Scheme S4. Preparation of azido prolinamide **S10.**

Preparation of Pro-3: Pro-3 was prepared by using Cu(I)-catalyzed cycloaddition of azido prolinamide **S10** and phenyl acetylene (**S4**) to give triazole derivative **S11**, which upon subsequent removal of Boc group afforded **Pro-3** (Scheme S5).



Scheme S5. Synthesis of ligand **Pro-3**.

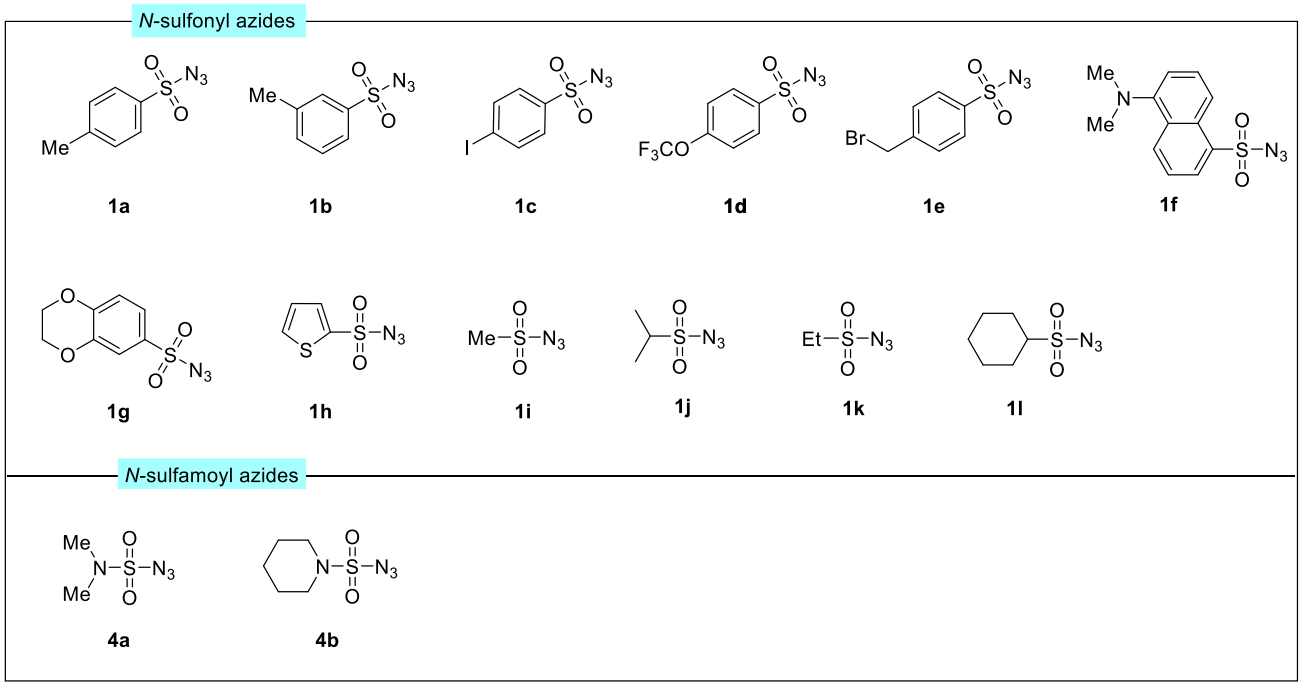
Preparation of traizole derivative S11: Phenyl acetylene (**S4**) (1.08 mL, 9.8 mmol), sodium ascorbate (194 mg, 0.98 mmol, 0.1 equiv), $CuSO_4.5H_2O$ (122.4 mg, 0.49 mmol, 0.05 equiv) were dissolved in 10 mL *t*BuOH-H_2O (7:3) mixture. Then the azido prolinamide **S10** (3.3 g, 9.8 mmol, 1.0 equiv) was added and stirred at room temperature for 16 h. After complete consumption of **S10** as monitored by TLC, the reaction mixture was concentrated and the residue was purified by flash chromatography using hexane-ethyl acetate (90:10 to 50:50) mixture to give the crude product **S11** (4.02 g, 94%) as a colorless solid.

Preparation of Pro-3: To an ice cooled solution of crude compound **S11** (1.0 g, 2.3 mmol) in 30 mL CH_2Cl_2, added TFA (0.53 mL, 6.9 mmol, 3.0 equiv) and the mixture was stirred for 10 h at room temperature. After consumption of the starting material **S11** (monitored by TLC), the reaction mixture was brought to pH 8-9 by dropwise addition of solution of liquid NH_3 (30%) at 0 °C. Then the reaction mixture was extracted with CH_2Cl_2 (3 x 20 mL), dried in vacuum, purified by flash chromatograghy using hexane-ethylacetate (50:50 to 30:70) to give **Pro-3** (746 mg, 96%) as a white solid. ^{1}H NMR (400 MHz, DMSO-d^6): 10.4 (s, 1H), 9.23 (s, 1H), 7.95-7.88 (m, 6H), 7.50 (t, J = 7.8 Hz, 2H), 7.38 (t, J = 7.4 Hz, 1H), 3.91 (q, J = 5.8 Hz, 1H), 3.02 (t, J = 6.8 Hz, 2H), 2.21-2.12 (m, 1H), 1.91-1.83 (m, 1H), 1.79-1.72 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d^6): 172.0,

147.2, 138.7, 132.1, 130.3, 128.9, 128.2, 125.3, 120.6, 120.2, 119.4, 60.6, 46.5, 30.2, 25.2; HRMS (ESI) calcd for $C_{19}H_{20}N_5O$ (M+H)+: 334.1667; found, 334.1693.

4.0 Preparation of Substrates

Preparation of sulfonyl and sulfamoyl azides: Following reported procedures the following *N*-sulfonyl[4] and *N*-sulfamoyl[5] azides were prepared.



5.0 General procedure for cycloaddition of *N*-sulfonyl azides and aromatic alkynes (GP-1)

In a small reaction vial, **Pro-1** (10 mol%), a mixture of *N*-sulfonyl azide (0.2 mmol), aromatic /aliphatic alkyne (0.3 mmol) and water (0.2 M) was taken. Then, copper iodide (5 mol%) was added and the resulting heterogeneous reaction mixture was stirred at rt for 3.5 h. The completion of reaction was monitored by TLC analysis. The reaction mixture was extracted with ethyl acetate (3 x 2 mL), dried over Na_2SO_4, filtered and concentrated under vacuum. The crude product was then purified by flash chromatography on 100-200 mesh silica gel using hexane-ethyl acetate (95:05-80:20) as eluent to remove the residual copper and provide the corresponding products.

[4] C. G. Wang, R. Wu, T. P. Li, T. Jia, Y. Li, D. Fang, X. Chen, Y. Gao, H. L. Ni, P. Hu, B. Q. Wang and P. Cao, *Org. Lett.*, **2020**, *22*, 3234-3238.

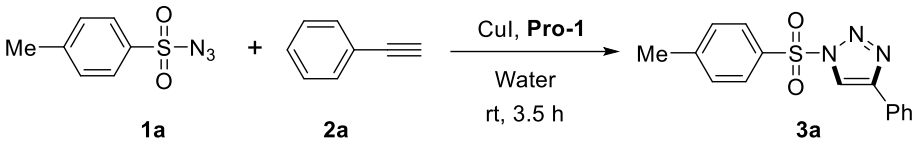
[5] J. C. Culhane and V. V. Fokin, *Org. Lett.*, **2011**, *13*, 4578-4580.

6.0 General procedure for cycloaddition of *N*-sulfamoyl azides and aromatic alkynes (GP-2)

In a small reaction vial, **Pro-1** (10 mol%), *N*-sulfamoyl azide (0.2 mmol), alkyne (0.3 mmol) and water (2.0 mL, 0.2 M) were taken. Then, copper iodide (5 mol%) was added and the resulting heterogeneous reaction mixture was stirred at rt for 45 minutes. The completion of reaction was monitored by TLC analysis. The reaction mixture was extracted with ethyl acetate (3 x 2 mL), dried over Na_2SO_4, filtered and concentrated under vacuum. The crude product was then purified by flash chromatography on 100-200 mesh silica gel using hexane-ethyl acetate (95:05-80:20) as eluent to remove the residual copper and provide the corresponding products.

7.0 Gram scale experiment

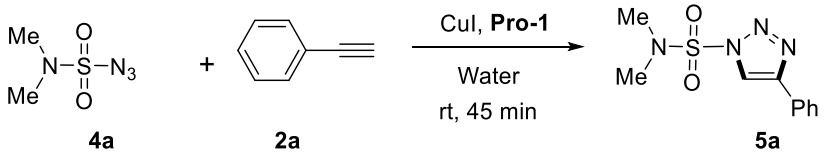
Preparation of 4-phenyl-1-tosyl-1H-1,2,3-triazole (3a):



Scheme S6. Gram scale synthesis of **3a**.

To a suspension of 4-methylbenzenesulfonyl azide **1a** (1.00 g, 5.07 mmol, 1 equiv), phenylacetylene **2a** (776.7 mg, 7.60 mmol, 1.5 equiv) in water (0.2 M), were added copper iodide (48 mg, 0.05 equiv) and **Pro-1** (168 mg, 0.1 equiv). The reaction mixture was stirred at rt for 3.5 h (Scheme S6). After the completion of reaction, the reaction mixture was extracted with ethyl acetate (20 x 3 mL), dried over Na_2SO_4, filtered and concentrated under vacuum. The crude product was then purified by flash chromatography on 100-200 mesh silica gel using hexane-ethyl acetate (95:05-80:20) as eluent to remove the residual copper, providing compound **3a** (1.30 g, 86%) in pure form.

Preparation of N,N-dimethyl-4-phenyl-1H-1,2,3-triazole-1-sulfonamide (5a):



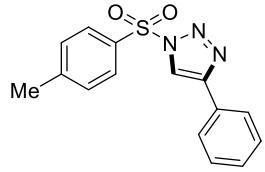
Scheme S7. Gram scale synthesis of **5a**.

To a stirring suspension of ((azidosulfonyl)(methyl)amino)methane **4a** (1.00 g, 6.66 mmol, 1 equiv), phenylacetylene **2a** (1.02 g, 9.99 mmol, 1.5 equiv) in water, copper iodide (64 mg, 0.05

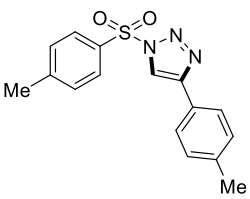
equiv) and **Pro-1** (221 mg, 0.1 equiv) were added and the reaction mixture was stirred at rt for 45 minutes (Scheme S7). After the completion of reaction, as monitored by TLC analysis, the reaction mixture was extracted with ethyl acetate (20 x 3 mL), dried over Na_2SO_4, filtered and concentrated under vacuum. The crude product was then purified by flash chromatography on 100-200 mesh silica gel using hexane-ethyl acetate (95:05-80:20) as eluent to remove the residual copper, providing compound **5a** (1.51 g, 90%) in pure form.

8.0 Analytical data of compounds

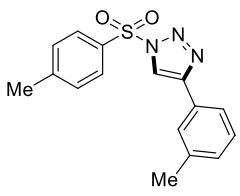
4-Phenyl-1-tosyl-1H-1,2,3-triazole (3a): Following the GP-1, compound **3a** was obtained as a white solid (yield 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.05 (d, *J* = 8.1 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.47-7.39 (m, 5H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 147.46, 133.4, 130.6, 129.2, 129.1, 129.1, 128.9, 126.2, 119.0, 22.0; HRMS (ESI) calcd for $C_{15}H_{13}N_3O_2S$ $[M+H]^+$: 300.0807; found: 300.0818.



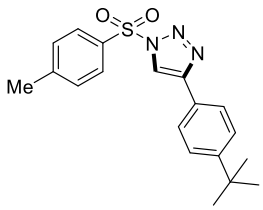
4-(*p*-Tolyl)-1-tosyl-1H-1,2,3-triazole (3b): Following the GP-1, compound **3b** was obtained as a white solid (yield 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 2.44 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 147.4, 139.2, 133.3, 130.5, 130.0, 128.8, 126.2, 126.1, 118.6, 22.0, 21.4. HRMS (ESI) calcd for $C_{16}H_{15}N_3O_2S$ $[M+H]^+$: 314.0963; found: 314.0964.



4-(*m*-Tolyl)-1-tosyl-1H-1,2,3-triazole (3c): Following the GP-1, compound **3c** was obtained as a white solid (yield 88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.02 (d, *J* = 8.3 Hz, 2H), 7.66 (s, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 2.44 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 147.4, 138.9, 133.3, 130.6, 130.0, 129.0, 128.9, 128.8, 126.9, 123.3, 119.0, 22.0, 21.5; HRMS (ESI) calcd for $C_{16}H_{15}N_3O_2S$ $[M+H]^+$: 314.0963; found: 314.0964.

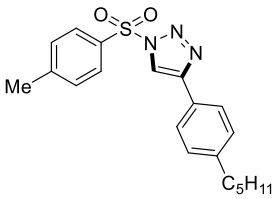


4-(4-(*Tert*-butyl)phenyl)-1-tosyl-1H-1,2,3-triazole (3d): Following the GP-1, compound **3d** was



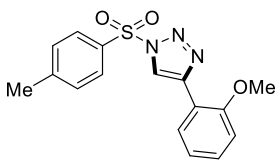
obtained as a white solid (yield 67%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.02 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 147.5, 147.4, 133.3, 130.4, 128.8, 126.1, 126.0, 126.0, 118.7, 34.9, 31.3, 21.9; HRMS (ESI) calcd for $C_{19}H_{21}N_3O_2S$ $[M+H]^+$: 356.1432; found: 356.1434.

4-(4-Pentylphenyl)-1-tosyl-1H-1,2,3-triazole (3e): Following the GP-1, compound **3e** was



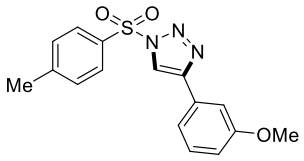
obtained as a white solid (yield 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 2.64-2.60 (m, 2H), 2.44 (s, 3H), 1.66-1.60 (m, 2H), 1.33-1.28 (m, 4H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 147.4, 144.4, 133.4, 130.6, 129.2, 128.9, 126.4, 126.2, 118.6, 35.9, 31.6, 31.1, 22.7, 22.0, 14.1; HRMS (ESI) calcd for $C_{20}H_{23}N_3NaO_2S$ $[M+Na]^+$: 392.1409; found: 392.1408.

4-(2-Methoxyphenyl)-1-tosyl-1H-1,2,3-triazole (3f): Following the GP-1, compound **3f** was



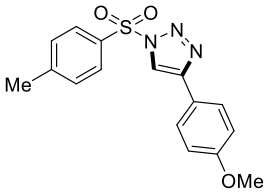
obtained as a yellowish solid (yield 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.31 (dd, *J* = 7.7, 1.6 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.35 (dd, *J* = 15.1, 7.7 Hz, 3H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 3.97 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 147.2, 142.9, 133.6, 130.5, 130.0, 128.8, 128.2, 122.2, 121.2, 117.9, 111.0, 55.6, 22.0; HRMS (ESI) calcd for $C_{16}H_{15}N_3O_3S$ $[M+H]^+$: 330.0912; found: 330.0910.

4-(3-Methoxyphenyl)-1-tosyl-1H-1,2,3-triazole (3g): Following the GP-1, compound **3g** was

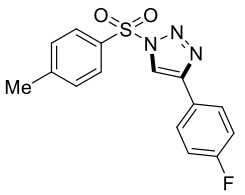


obtained as a white solid (yield 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.41-7.33 (m, 5H), 6.91 (dt, *J* = 7.5, 2.0 Hz, 1H), 3.85 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 147.5, 147.4, 133.3, 130.6, 130.3, 130.2, 128.9, 119.2, 118.6, 115.3, 111.4, 55.5, 22.0; HRMS (ESI) calcd for $C_{16}H_{15}N_3NaO_3S$ $[M+Na]^+$: 352.0732; found: 352.0733.

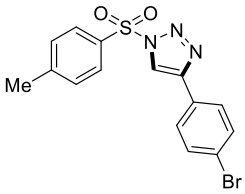
4-(4-Methoxyphenyl)-1-tosyl-1H-1,2,3-triazole (3h): Following the GP-1, compound **3h** was obtained as a white solid (yield 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 147.4, 147.4, 133.4, 130.6, 128.8, 127.6, 121.7, 118.0, 114.6, 55.5, 22.0; HRMS (ESI) calcd for $C_{16}H_{15}N_3O_3S$ $[M+H]^+$: 330.0912; found: 330.0913.



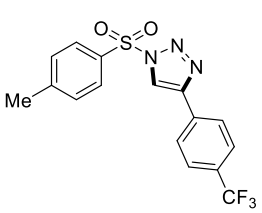
4-(4-Fluorophenyl)-1-tosyl-1H-1,2,3-triazole (3i): Following the GP-1, compound **3i** was obtained as a white solid (yield 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.82-7.78 (m, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.12 (t, *J* = 8.7 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 162.1, 147.6, 146.6, 133.2, 130.6, 128.9, 128.1, 128.1, 125.3, 125.3, 118.8, 116.3, 116.1, 22.0; HRMS (ESI) calcd for $C_{15}H_{14}N_3$$[M+H]^+$: 236.1188; found: 236.1171.



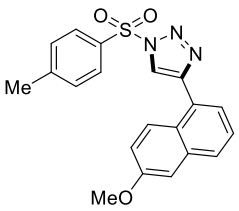
4-(4-Bromophenyl)-1-tosyl-1H-1,2,3-triazole (3j): Following the GP-1, compound **3j** was obtained as a brownish solid (yield 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.02 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 146.4, 133.1, 132.3, 130.6, 129.0, 128.0, 127.7, 123.3, 119.1, 22.0; HRMS (ESI) calcd for $C_{15}H_{12}BrN_3O_2S$ $[M+H]^+$: 377.9911; found: 377.9914.



1-Tosyl-4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (3k): Following the GP-1, compound **3k** was obtained as a greenish solid (yield 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 146.0, 133.0, 132.5, 130.7, 129.0, 126.4, 126.2, 126.1, 126.1, 119.9, 22.0; HRMS (ESI) calcd for $C_{16}H_{12}F_3N_3O_2S$ $[M+H]^+$: 368.0681; found: 368.0697.

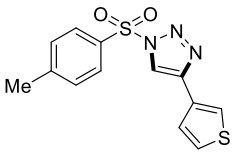


4-(6-Methoxynaphthalen-2-yl)-1-tosyl-1H-1,2,3-triazole (3l): Following the GP-1, compound



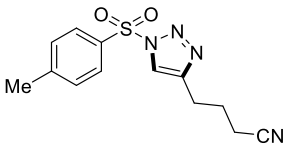
3l was obtained as a white solid (yield 70%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.27 (s, 1H), 8.04 (d, *J* = 8.2 Hz, 2H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.77 (dd, *J* = 8.6, 4.1 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 14.0 Hz, 2H), 3.93 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 147.8, 147.4, 134.9, 133.4, 130.6, 130.0, 128.9, 128.9, 127.7, 125.3, 124.3, 124.2, 119.2, 118.8, 106.0, 55.5, 22.0; HRMS (ESI) calcd for $C_{20}H_{17}N_3O_3S$ $[M+H]^+$: 380.1068; found: 380.1067.

4-(Thiophen-3-yl)-1-tosyl-1H-1,2,3-triazole (3m): Following the GP-1, compound **3m** was



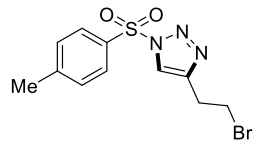
obtained as a white solid (yield 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.77-7.74 (m, 1H), 7.43-7.37 (m, 4H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 143.7, 133.3, 130.6, 130.2, 128.8, 127.0, 125.8, 122.9, 118.7, 22.0; HRMS (ESI) calcd for $C_{15}H_{12}FN_3O_2S$ $[M+H]^+$: 318.0713; found:318.0714.

4-(1-Tosyl-1H-1,2,3-triazol-4-yl)butanenitrile (3n): Following the GP-1, compound **3n** was



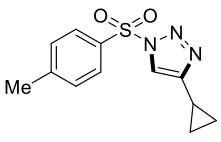
obtained as a white solid (yield 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.93 (s, 1H), 7.39 (d, *J* = 8.2 Hz, 2H), 2.88 (t, *J* = 7.4 Hz, 2H), 2.45 (s, 3H), 2.41 (t, *J* = 7.1 Hz, 2H), 2.06 (p, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 145.6, 133.2, 130.6, 128.8, 121.1, 119.1, 24.6, 24.1, 22.0, 16.7; HRMS (ESI) calcd for $C_{13}H_{14}N_4O_2S$ $[M+H]^+$: 291.0916; found: 291.0901.

4-(2-Bromoethyl)-1-tosyl-1H-1,2,3-triazole (3o): Following the GP-1, compound **3o** was



obtained as a yellowish solid (yield 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 3.61 (t, *J* = 6.8 Hz, 2H), 3.29 (t, *J* = 6.7 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 144.7, 133.3, 130.6, 128.8, 121.6, 30.5, 29.2, 22.0; HRMS (ESI) calcd for $C_{11}H_{12}BrN_3O_2S$ $[M+H]^+$: 329.9912; found: 329.9913.

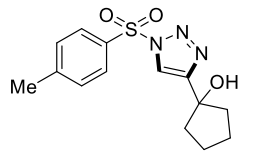
4-Cyclopropyl-1-tosyl-1H-1,2,3-triazole (3p): Following the GP-1, compound **3p** was obtained



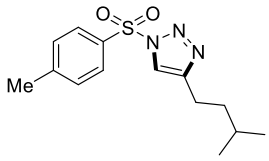
as a greenish solid (yield 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.78 (s, 1H), 7.36 (d, *J* = 8.2 Hz, 2H), 2.43 (s, 3H), 1.92 (m, 1H), 0.99-0.95 (m, 2H), 0.88-0.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 147.2,

133.5, 130.5, 128.7, 119.3, 21.9, 8.1, 6.6; HRMS (ESI) calcd for $C_{12}H_{13}N_3O_2S$ $[M+H]^+$: 264.0806; found: 264.0808.

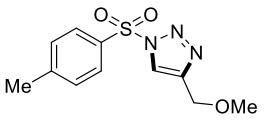
1-(1-Tosyl-1H-1,2,3-triazol-4-yl) cyclopentanol (3q): Following the GP-1, compound **3q** was obtained as a white solid (yield 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 8.00 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 2.45 (s, 3H), 2.13-2.09 (m, 2H), 1.99-1.93 (m, 4H), 1.86-1.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 130.6, 129.9, 128.9, 126.6, 119.7, 79.1, 41.4, 23.8. 21.7; HRMS (ESI) calcd for $C_{14}H_{17}N_3O_3S$ $[M+H]^+$: 308.1069; found: 308.1088.



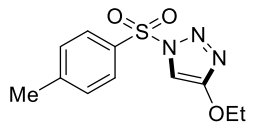
4-Isopentyl-1-tosyl-1H-1,2,3-triazole (3r): Following the GP-1, compound **3r** was obtained as a yellowish solid (yield 78%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.83 (s, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 2.72-2.69 (m, 2H), 2.44 (s, 3H), 1.60-1.54 (m, 3H), 0.92 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 147.2, 133.5, 130.5, 128.7, 120.3, 38.0, 27.7, 23.5, 22.4, 21.9; HRMS (ESI) calcd for $C_{14}H_{19}N_3O_2S$ $[M+H]^+$: 294.1276; found: 294.1277.



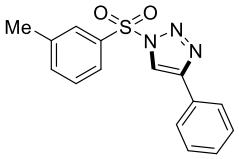
4-(Methoxymethyl)-1-tosyl-1H-1,2,3-triazole (3s): Following the GP-1, compound **3s** was obtained as a white solid (yield 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.98 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 4.56 (s, 2H), 3.41 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 145.2, 133.2, 130.6, 128.9, 122.2, 65.7, 58.8, 22.0; HRMS (ESI) calcd for $C_{11}H_{13}N_3O_3S$ $[M+H]^+$: 268.0765; found: 268.0755.



4-Ethoxy-1-tosyl-1H-1,2,3-triazole (3t): Following the GP-1, compound **3t** was obtained as a greenish solid (yield 76%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.50 (s, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 4.24 (d, *J* = 7.0 Hz, 2H), 2.44 (s, 3H), 1.40 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 147.3, 133.3, 130.5, 130.1, 128.9, 128.7, 105.0, 67.2, 21.9, 14.8; HRMS (ESI) calcd for $C_{11}H_{13}N_3O_3S$ $[M+H]^+$: 268.0756; found: 268.0755.

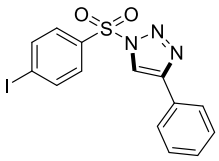


4-Phenyl-1-(m-tolylsulfonyl)-1H-1,2,3-triazole (3u): Following the GP-1, compound **3u** was



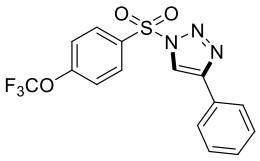
obtained as a white solid (yield 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.94 (d, *J* = 8.6 Hz, 2H), 7.83 (dt, *J* = 8.2, 1.8 Hz, 2H), 7.53-7.39 (m, 5H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 140.6, 136.7, 136.2, 129.8, 129.3, 129.2, 129.1, 129.0, 126.2, 125.9, 119.1, 21.5; HRMS (ESI) calcd for $C_{15}H_{13}N_3O_2S$ $[M+H]^+$:330.0806; found: 300.0808.

1-((4-Iodophenyl)sulfonyl)-4-phenyl-1H-1,2,3-triazole (3v): Following the GP-1, compound **3v**



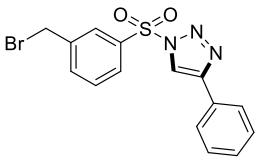
was obtained as a white solid (yield 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.83 (t, *J* = 8.3 Hz, 4H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 139.4, 135.9, 129.8, 129.4, 129.2, 128.8, 126.3, 119.0, 104.6; HRMS (ESI) calcd for $C_{14}H_{10}IN_3O_2S$[$M+H]^+$: 411.9616; found: 411.9615.

4-Phenyl-1-((4-(trifluoromethoxy)phenyl)sulfonyl)-1H-1,2,3-triazole (3w): Following the GP-



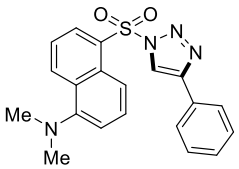
1, compound **3w** was obtained as a white solid (yield 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.22 (dd, *J* = 9.4, 2.3 Hz, 2H), 7.84-7.81 (m, 2H), 7.44-7.38 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 147.8, 134.2, 131.3, 129.5, 129.2, 128.7, 126.3, 121.4, 119.1; HRMS (ESI) calcd for $C_{15}H_{10}F_3N_3O_3S$ $[M+H]^+$: 370.0473; found: 370.0474.

1-((4-(Bromomethyl)phenyl)sulfonyl)-4-phenyl-1H-1,2,3-triazole (3x): Following the GP-1,



compound **3x** was obtained as a white solid (yield 70%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.12 (d, *J* = 7.8 Hz, 2H), 7.83 (d, *J* = 7.5 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.45-7.39 (m, 3H), 4.47 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 146.1, 135.9, 130.5, 129.4, 129.3, 129.3, 129.2, 129.1, 128.9, 128.8, 119.1, 30.8; HRMS (ESI) calcd for $C_{15}H_{12}BrN_3O_2S$ $[M+H]^+$: 377.9912; found: 377.9929.

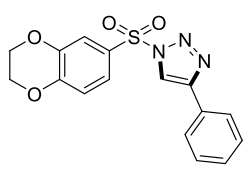
***N,N*-dimethyl-5-((4-phenyl-1H-1,2,3-triazol-1-yl)sulfonyl)naphthalen-1-amine (3y):**



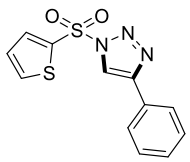
Following the GP-1, compound **3y** was obtained as a greenish solid (yield 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.5 Hz, 1H), 8.64 (d, *J* = 7.5 Hz, 1H), 8.45 (d, *J* = 8.7 Hz, 1H), 8.41 (s, 1H), 7.81 (d, *J* = 7.2 Hz, 2H), 7.66-7.59 (m, 2H), 7.43-7.35 (m, 3H), 7.19 (d, *J* = 7.6 Hz, 1H), 2.86 (s, 6H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 152.5, 147.4, 134.2, 132.5, 131.3, 130.1, 130.0, 129.9, 129.2, 129.1, 126.2, 123.3, 119.2, 118.2, 116.2, 46.0; HRMS (ESI) calcd for $C_{20}H_{18}N_4O_2S$ $[M+H]^+$: 379.1229; found: 379.1228.

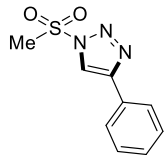
1-((2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)sulfonyl)-4-phenyl-1H-1,2,3-triazole (3z): Following the GP-1, compound **3z** was obtained as a white solid (yield 83%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.83 (d, *J* = 7.2 Hz, 2H), 7.64 (dd, *J* = 7.0, 2.2 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.03-6.99 (m, 1H), 4.33 (dd, *J* = 5.5, 2.1 Hz, 2H), 4.29 (dd, *J* = 5.5, 2.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 147.5, 144.2, 129.2, 129.1, 127.9, 126.2, 122.9, 119.0, 118.7, 118.5, 64.9, 64.2; HRMS (ESI) calcd for $C_{16}H_{13}N_3O_4S$ $[M+H]^+$: 344.0705; found:344.0700.



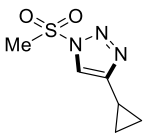
4-Phenyl-1-(thiophen-2-ylsulfonyl)-1H-1,2,3-triazole (3aa): Following the GP-1, compound **3aa** was obtained as a white solid (yield 88%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.03 (dd, *J* = 3.9, 1.3 Hz, 1H), 7.87-7.83 (m, 3H), 7.47-7.38 (m, 3H), 7.20 (dd, *J* = 4.9, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 137.5, 137.4, 135.6, 129.3, 129.2, 128.9, 128.6, 126.3, 118.9; HRMS (ESI) calcd for $C_{12}H_9N_3O_2S_2$ $[M+H]^+$: 292.0214; found: 292.0214.



1-(Methylsulfonyl)-4-phenyl-1H-1,2,3-triazole (3ab) : Following the GP-1, compound **3ab** was obtained as a white solid (yield 85%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.87 (d, *J* = 7.1 Hz, 2H), 7.46 (m, 3H), 3.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 129.4, 129.2, 129.1, 128.8, 126.3, 126.3, 118.9, 42.8; HRMS (ESI) calcd for $C_9H_9N_3O_2S$ $[M+H]^+$: 224.0493; found: 224.0495.



4-Cyclopropyl-1-(methylsulfonyl)-1H-1,2,3-triazole (3ac): Following the GP-1, compound **3ac** was obtained as a brownish solid (yield 72%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.79 (s, 1H), 3.48 (s, 3H), 1.99 (tt, *J* = 8.6, 5.1 Hz, 1H), 1.04-1.01 (m, 2H), 0.93 (t, *J* = 4.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 119.3, 42.7, 8.2, 6.6; HRMS (ESI) calcd for $C_6H_9N_3O_2S$ $[M+H]^+$: 188.0494; found: 188.0495.



1-(Isopropylsulfonyl)-4-phenyl-1H-1,2,3-triazole (3ad): Following the GP-1, compound **3ad** was obtained as a white solid (yield 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.87 (d, *J* = 7.4 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 3.92-3.86 (m, 1H), 1.45 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 129.3, 129.2, 128.8, 126.2, 120.5, 57.5, 16.1; HRMS (ESI) calcd for $C_{11}H_{13}N_3O_2S$ $[M+H]^+$: 252.0807; found: 252.0808.

1-(Ethylsulfonyl)-4-phenyl-1H-1,2,3-triazole (3ae): Following the GP-1, compound **3ae** was obtained as a white solid (yield 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.86 (d, *J* = 7.4 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 3.69 (d, *J* = 7.4 Hz, 2H), 1.38 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 129.4, 129.2, 128.8, 126.2, 119.9, 50.2, 7.8; HRMS (ESI) calcd for $C_{10}H_{11}N_3O_2S$ $[M+H]^+$:238.0650; found: 238.0651.

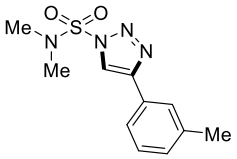
1-(Cyclohexylsulfonyl)-4-phenyl-1H-1,2,3-triazole (3af): Following the GP-1, compound **3af** was obtained as a brownish solid (yield 76%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.88 (d, *J* = 7.4 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 3.62 (ddd, *J* = 12.1, 8.9, 3.3 Hz, 1H), 2.08 (d, *J* = 12.0 Hz, 2H), 1.90 (d, *J* = 13.6 Hz, 2H), 1.60 (td, *J* = 12.4, 3.1 Hz, 2H), 1.33-1.18 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 129.3, 129.1, 128.9, 126.2, 120.5, 64.8, 25.9, 24.8, 24.7; HRMS (ESI) calcd for $C_{10}H_{11}N_3O_2S$ $[M+H]^+$:292.1120; found: 292.1122.

***N,N*-dimethyl-4-phenyl-1H-1,2,3-triazole-1-sulfonamide (5a):** Following the GP-2, compound **5a** was obtained as a white solid (yield 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.0 Hz, 1H), 3.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 129.3, 129.2, 129.1, 126.2, 120.0, 39.0; HRMS (ESI) calcd for $C_{10}H_{12}N_4O_2S$ $[M+H]^+$: 253.0759; found: 253.0782.

***N,N*-dimethyl-4-(p-tolyl)-1H-1,2,3-triazole-1-sulfonamide (5b):** Following the GP-2, compound **5b** was obtained as a white solid (yield 91%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 6.8 Hz, 2H), 3.09 (s, 6H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 139.1, 129.9, 126.5,

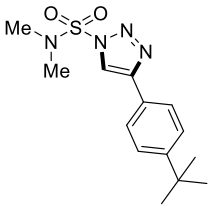
126.1, 119.6, 39.0, 21.5; HRMS (ESI) calcd for $C_{11}H_{14}N_4O_2S$ $[M+H]^+$: 267.0915; found: 267.0912.

***N,N*-dimethyl-4-(m-tolyl)-1H-1, 2, 3-triazole-1-sulfonamide (5c):** Following the GP-2,



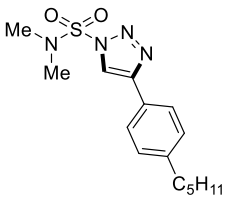
compound **5c** was obtained as a brownish solid (yield 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.70 (s, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 3.08 (s, 6H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 138.9, 129.9, 129.0, 126.9, 123.3, 120.0, 39.0, 21.5 ; HRMS (ESI) calcd for $C_{15}H_{12}FN_3O_2S$ $[M+H]^+$: 267.0915; found: 267.0917.

4-(4-(Tert-butyl)phenyl)-*N,N*-dimethyl-1H-1,2,3-triazole-1-sulfonamide (5d): Following the



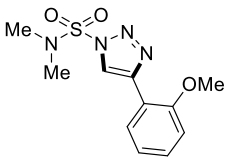
GP-2, compound **5d** was obtained as a green solid (yield 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 3.08 (s, 6H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 146.9, 126.4, 126.1, 125.9, 119.7, 39.0, 34.9, 31.4; HRMS (ESI) calcd for $C_{14}H_{20}N_4O_2S$ $[M+H]^+$: 309.1385; found: 309.1386.

***N,N*-dimethyl-4-(4-pentylphenyl)-1H-1,2,3-triazole-1-sulfonamide (5e):** Following the GP-2,



compound **5e** was obtained as a white solid (yield 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.28 (d, 2H, merged with $CDCl_3$), 3.09 (s, 6H), 2.67-2.63 (m, 2H), 1.68-1.64 (m, 2H), 1.36-1.33 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 144.2, 129.2, 126.7, 126.1, 119.6, 39.0, 35.9, 31.6, 31.1, 22.7, 14.1; HRMS (ESI) calcd for $C_{15}H_{22}N_4O_2S$ $[M+H]^+$: 323.1541; found: 323.1543.

4-(2-Methoxyphenyl)-*N,N*-dimethyl-1H-1,2,3-triazole-1-sulfonamide (5f): Following the GP-



2, compound **5f** was obtained as a white solid (yield 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.36 (d, *J* = 9.0 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 8.3 Hz, 1H), 3.97 (s, 3H), 3.08 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 142.3, 129.9, 128.1, 123.3, 121.2, 118.1, 111.0, 55.6, 39.0; HRMS (ESI) calcd for $C_{11}H_{14}N_4O_3S$ $[M+H]^+$: 283.0864; found: 283.0864.

4-(3-Methoxyphenyl)-*N*,*N*-dimethyl-1H-1,2,3-triazole-1-sulfonamide (5g): Following the GP-2, compound **5g** was obtained as a white solid (yield 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.45 (s, 1H), 7.37 (dd, *J* = 12.3, 7.7 Hz, 2H), 6.93 (d, *J* = 7.9 Hz, 1H), 3.86 (s, 3H), 3.08 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 146.7, 130.5, 130.2, 120.2, 118.5, 115.1, 111.3, 55.5, 39.0; HRMS (ESI) calcd for $C_{11}H_{14}N_4O_3S$ $[M+H]^+$: 283.0864; found: 283.0863.

4-(4-Methoxyphenyl)-*N*,*N*-dimethyl-1H-1,2,3-triazole-1-sulfonamide (5h): Following the GP-2, compound **5h** was obtained as a white solid (yield 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.78 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 3.84 (s, 3H), 3.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 146.7, 127.5, 121.9, 119.1, 114.6, 55.5, 39.0; HRMS (ESI) calcd for $C_{11}H_{14}N_4O_3S$ $[M+H]^+$: 283.0864; found: 283.0866.

4-(4-Methoxy-3-methylphenyl)-*N*,*N*-dimethyl-1H-1,2,3-triazole-1-sulfonamide (5i): Following the GP-2, compound **5i** was obtained as a green solid (yield 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 2H), 3.84 (s, 3H), 3.10 (s, 6H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 146.1, 137.7, 130.6, 121.4, 121.3, 116.7, 111.9, 55.4, 39.1, 21.7; HRMS (ESI) calcd for $C_{12}H_{16}N_4O_3S$ $[M+H]^+$: 297.1021; found: 297.1023.

4-(4-Aminophenyl)-*N*,*N*-dimethyl-1H-1,2,3-triazole-1-sulfonamide (5j): Following the GP-2, compound **5j** was obtained as a yellowish solid (yield 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 2H), 3.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 147.2, 127.5, 119.6, 118.5, 115.4, 39.0; HRMS (ESI) calcd for $C_{10}H_{13}N_5O_2S$ $[M+H]^+$: 268.0868; found: 268.0867.

4-(4-(Dimethylamino)phenyl)-*N*,*N*-dimethyl-1H-1,2,3-triazole-1-sulfonamide (5k): Following the GP-2, compound **5k** was obtained as a brownish solid (yield 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.72 (d, *J* = 8.6 Hz, 2H), 6.77 (d, *J* = 8.7 Hz, 2H), 3.07 (s, 6H), 3.01 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 147.4, 127.1, 118.2, 117.1, 112.5, 40.4, 39.0; HRMS (ESI) calcd for $C_{12}H_{17}N_5O_2S$ $[M+H]^+$: 296.1181; found: 296.1182.

4-(4-Fluorophenyl)-*N,N*-dimethyl-1H-1,2,3-triazole-1-sulfonamide (5l): Following the GP-2, compound **5l** was obtained as a brown solid (yield 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.84 (dd, *J* = 8.8, 5.3 Hz, 2H), 7.16 (dd, *J* = 8.7 Hz, 2H), 3.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 128.1, 128.0, 125.5, 125.5, 119.8, 116.4, 116.2, 39.1; HRMS (ESI) calcd for $C_{10}H_{11}FN_4O_2S$ $[M+H]^+$: 271.0665; found: 271.0664.

4-(4-Bromophenyl)-*N,N*-dimethyl-1H-1,2,3-triazole-1-sulfonamide (5m): Following the GP-2, compound **5m** was obtained as a white solid. (yield 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 3.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 132.4, 128.2, 127.7, 123.2, 120.1, 39.0; HRMS (ESI) calcd for $C_{10}H_{11}BrN_4O_2S$ $[M+H]^+$: 330.9864; found: 352.9684, 354.9684.

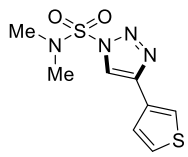
***N,N*-dimethyl-4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazole-1-sulfonamide (5n):** Following the GP-2, compound **5n** was obtained as a colourless solid (yield 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.98 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 3.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 132.8, 126.4, 126.2, 125.4, 120.9, 39.0; HRMS (ESI) calcd for $C_{11}H_{11}F_3N_4O_2S$ $[M+H]^+$: 321.0633; found: 321.0631.

4-(6-Methoxynaphthalen-2-yl)-*N,N*-dimethyl-1H-1,2,3-triazole-1-sulfonamide (5o): Following the GP-2, compound **5o** was obtained as a green solid (yield 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.28 (s, 1H), 7.89 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.81 (dd, *J* = 8.7, 5.3 Hz, 2H), 7.21-7.15 (m, 2H), 3.94 (s, 3H), 3.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 147.1, 135.0, 130.0, 129.06, 127.8, 125.2, 124.4, 124.4, 119.9, 119.7, 106.1, 55.6, 39.1; HRMS (ESI) calcd for $C_{15}H_{16}N_4O_3S$ $[M+H]^+$: 333.1021; found: 333.1013.

***N,N*-dimethyl-4-(phenanthren-9-yl)-1H-1,2,3-triazole-1-sulfonamide (5p):** Following the GP-2, compound **5p** was obtained as a yellow solid (yield 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 8.2 Hz, 1H), 8.73 (d, *J* = 8.3 Hz, 1H), 8.34 (s, 1H), 8.30 (d, *J* = 7.5 Hz, 1H), 8.04 (s, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.72 (tdd, *J* = 8.4, 4.3, 2.1 Hz, 2H), 7.68-7.62 (m, 2H), 3.19 (s, 6H); ^{13}C NMR (100 MHz,

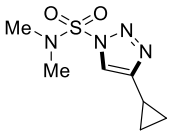
$CDCl_3$) δ 146.0, 131.2, 130.9, 130.9, 129.9, 129.3, 129.2, 127.7, 127.3, 127.2, 127.1, 125.9, 125.4, 123.3, 123.2, 122.8, 39.2; HRMS (ESI) calcd for $C_{18}H_{16}N_4O_2S$ $[M+H]^+$: 353.1072; found: 353.1070.

***N,N*-dimethyl-4-(thiophen-3-yl)-1H-1,2,3-triazole-1-sulfonamide (5q):** Following the GP-2,



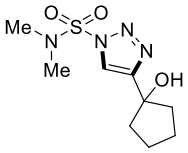
compound **5q** was obtained as a colourless solid (yield 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.78 (d, *J* = 2.8 Hz, 1H), 7.47-7.41 (m, 2H), 3.08 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 130.4, 127.0, 125.8, 122.6, 119.7, 39.0; HRMS (ESI) calcd for $C_8H_{10}N_4O_2S_2$ $[M+H]^+$: 259.0323; found: 259.0311.

4-Cyclopropyl-N,N-dimethyl-1H-1,2,3-triazole-1-sulfonamide (5r): Following the GP-2,



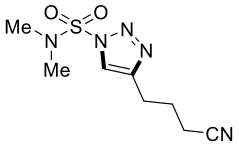
compound **5r** was obtained as a brownish solid (yield 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 1H), 3.02 (s, 6H), 1.97 (tt, *J* = 8.5, 5.0 Hz, 1H), 1.02-0.98 (m, 2H), 0.89 (q, *J* = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 120.3, 38.9, 7.9, 6.6, 6.5; HRMS (ESI) calcd for $C_7H_{12}N_4O_2S$ $[M+H]^+$: 217.0759; found: 217.0759.

4-(1-Hydroxycyclopentyl)-N,N-dimethyl-1H-1,2,3-triazole-1-sulfonamide (5s): Following the



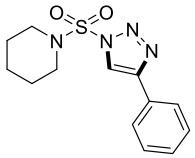
GP-2, compound **5s** was obtained as a brownish solid (yield 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 2.99 (s, 6H), 2.09 (dt, *J* = 11.8, 5.3 Hz, 2H), 1.99-1.91 (m, 4H), 1.80 (dd, *J* = 9.8, 4.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 120.8, 78.8, 41.2, 38.8, 23.6; HRMS (ESI) calcd for $C_9H_{16}N_4O_3S$ $[M+H]^+$: 261.1021; found: 261.1013.

4-(3-Cyanopropyl)-N,N-dimethyl-1H-1,2,3-triazole-1-sulfonamide (5t): Following the GP-2,



compound **5t** was obtained as a white solid (yield 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 3.00 (s, 6H), 2.89 (t, *J* = 7.4 Hz, 2H), 2.43 (t, *J* = 7.0 Hz, 2H), 2.07 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 121.9, 119.1, 38.8, 24.6, 24.1, 16.6; HRMS (ESI) calcd for $C_8H_{13}N_5O_2S$ $[M+H]^+$: 244.0868; found: 244.0866.

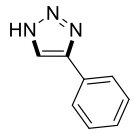
1-((4-Phenyl-1H-1,2,3-triazol-1-yl)sulfonyl)piperidine (5u): Following the GP-1, compound **5u**



was obtained as a white solid (yield 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.86 (d, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 3.47-3.43 (m, 4H), 1.73-1.68 (m, 4H), 1.56 (m, 2H); ^{13}C NMR (100 MHz,

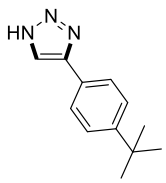
$CDCl_3$) δ 146.8, 129.3, 129.1, 129.1, 126.1, 120.0, 48.3, 24.9, 23.1; HRMS (ESI) calcd for $C_{13}H_{16}N_4O_2S$ $[M+H]^+$: 293.1072; found: 293.1073.

4-Phenyl-1H-1,2,3-triazole (6a): White solid (yield 90% from **3a** and 93% from **5a**). ^1H NMR



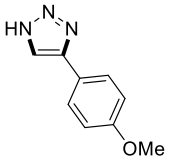
(400 MHz, $CDCl_3$) δ 12.25 (s, 1H), 7.99 (s, 1H), 7.83 (d, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 130.0, 129.9, 129.1, 128.9, 126.3; HRMS (ESI) calcd for C8H7N3 $[M+H]^+$: 146.0718 ; found: 146.0717.

4-(4-(*tert*-Butyl)phenyl)-2H-1,2,3-triazole (6b): White solid (yield 92% from **3d** and 91% from



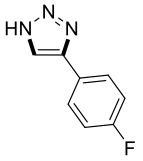
5d). ^1H NMR (500 MHz, $CDCl_3$): 7.97 (s, 1H), 7.75 (d, 2H, *J* = 8.2 Hz), 7.48 (d, 2H, *J* = 8.2 Hz), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): 152.2, 147.2, 129.9, 127.1, 126.0, 34.9, 31.4; HRMS (ESI) calcd for $C_{12}H_{16}N_3$ $[M+H]^+$: 202.1344; found: 202.1338.

4-(4-Methoxyphenyl)-2H-1,2,3-triazole (6c): White solid (yield 94% from **3h** and 92% from **5h**).



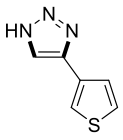
^1H NMR (400 MHz, $CDCl_3$): 7.90 (s, 1H), 7.74 (d, 2H, *J* = 8.8 Hz), 6.98 (d, 2H, *J* = 8.8 Hz), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 160.3, 147.2, 127.6, 122.6, 114.6, 55.5; HRMS (ESI) calcd for $C_9H_{10}N_3O$ $[M+H]^+$: 176.0824; found: 176.0811.

4-(4-Fluorophenyl)-2H-1,2,3-triazole (6d): Pale brown solid (yield 93% from **3i** and 90% from



5l). ^1H NMR (500 MHz, $CDCl_3$): 11.7 (br s, 1H), 7.93 (s, 1H), 7.82-7.79 (m, 2H), 7.17-7.13 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 164.2, 161.8, 147.0, 128.1, 128.0, 126.3, 126.2, 116.3, 116.1; HRMS (ESI) calcd for $C_8H_7FN_3$ [M+H]+: 164.0624; found: 164.0626.

4-(Thiophen-3-yl)-2H-1,2,3-triazole (6e): Colorless solid (yield 93% from **3m** and 94% from



5q). ^1H NMR (400 MHz, $CDCl_3$): 12.4 (br s, 1H), 7.89 (s, 1H), 7.70-7.69 (m, 1H), 7.51-7.49 (m, 1H), 7.44-7.42 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): 143.6, 131.2, 130.2, 126.9, 126.1, 122.3; HRMS (ESI) calcd for $C_6H_5N_3NaS$ $[M+Na]^+$: 174.0102; found: 174.0105.

9.0 X-Ray Crystallography of compounds 3x and 5f

Intensity data was collected on a Bruker's Kappa Apex II CCD Duo diffractometer with graphite monochromated $Mo_{K\alpha}$ radiation (0.71073 Å) at the temperature of 296 K. Scaling and multi-scan absorption correction were employed using SADABS. The structure was solved by direct methods and all the non-hydrogen atoms were refined anisotropically while the hydrogen atoms fixed in the predetermined positions by Shelxs-97 and Shelxl-97 packages respectively.

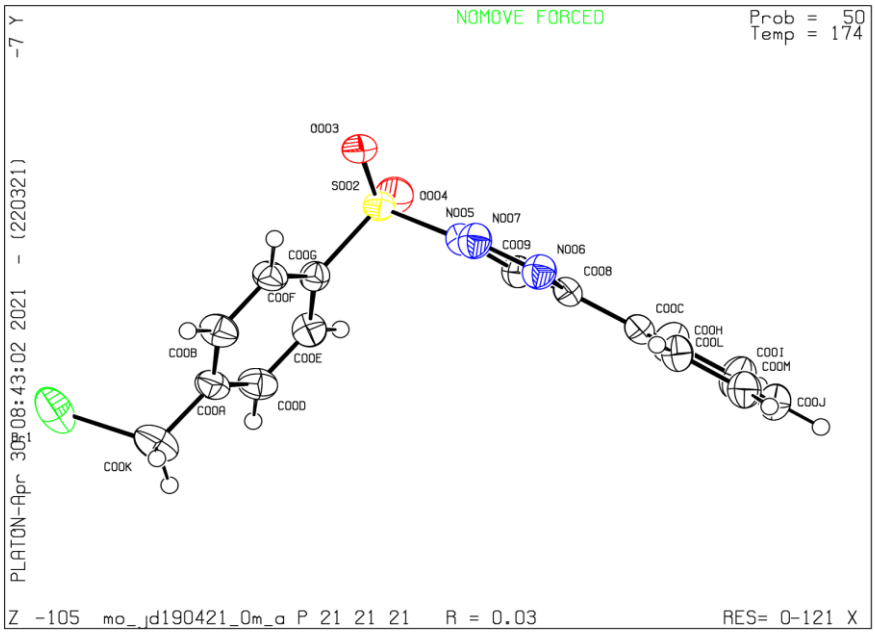


Figure S1. The ORTEP diagram of **3x** showing 50% probability thermal ellipsoid.

Table 1 Crystal data and structure refinement for 3x.	
Identification code	mo_JD190421_0m_a
Empirical formula	$C_{15}H_{12}BrN_3O_2S$
Formula weight	378.25
Temperature/K	174.29
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	4.8673(12)

b/Å	11.348(3)
c/Å	27.751(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1532.8(6)
Z	4
ρ_{calc}g/cm^3	1.639
μ/mm^{-1}	2.828
F(000)	760.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.636 to 50
Index ranges	$-5 \leq h \leq 5$, $-13 \leq k \leq 13$, $-32 \leq l \leq 33$
Reflections collected	15737
Independent reflections	2691 [R_{int} = 0.0500, R_{sigma} = 0.0446]
Data/restraints/parameters	2691/0/200
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0317, wR_2 = 0.0641
Final R indexes [all data]	R_1 = 0.0392, wR_2 = 0.0665
Largest diff. peak/hole / e Å^{-3}	0.22/-0.30
Flack parameter	0.041(14)

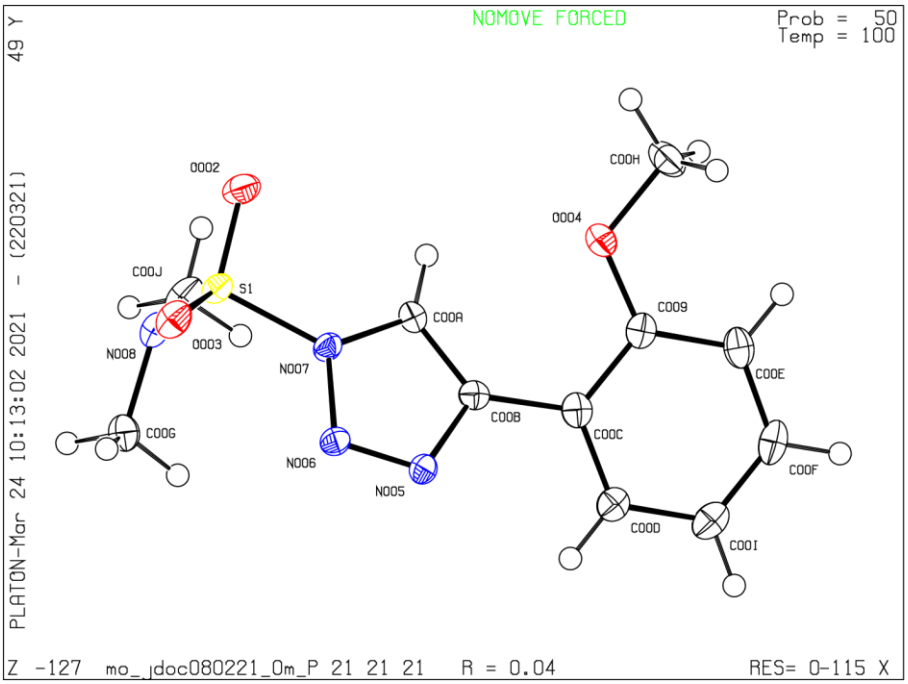


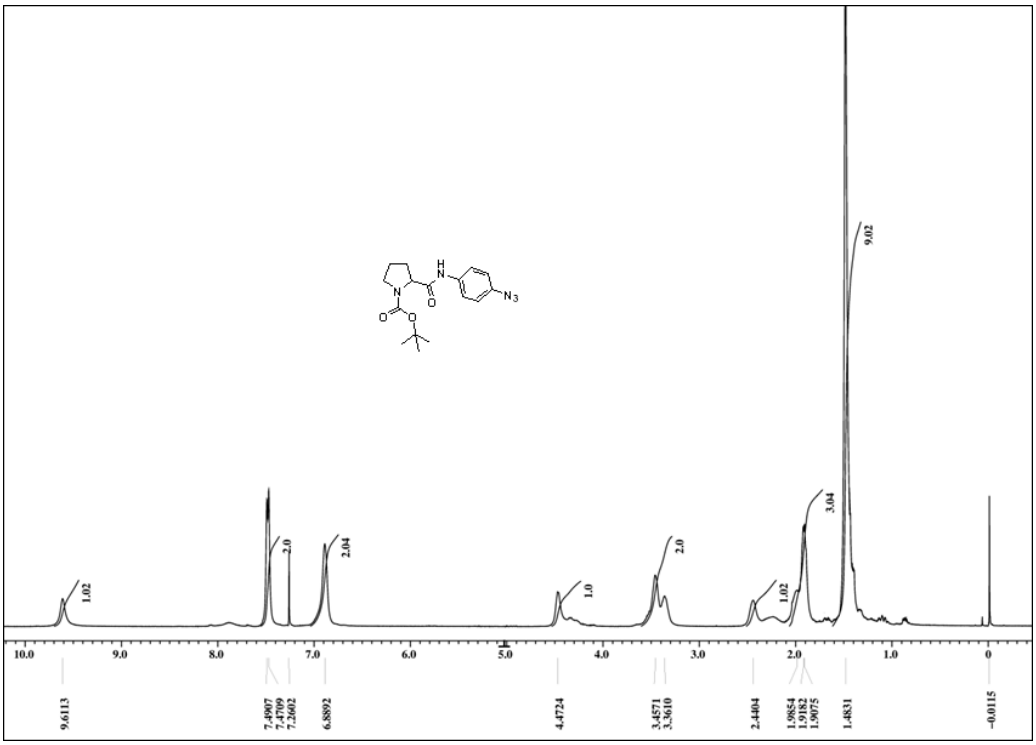
Figure S2. The ORTEP diagram of **5f** showing 50% probability thermal ellipsoid.

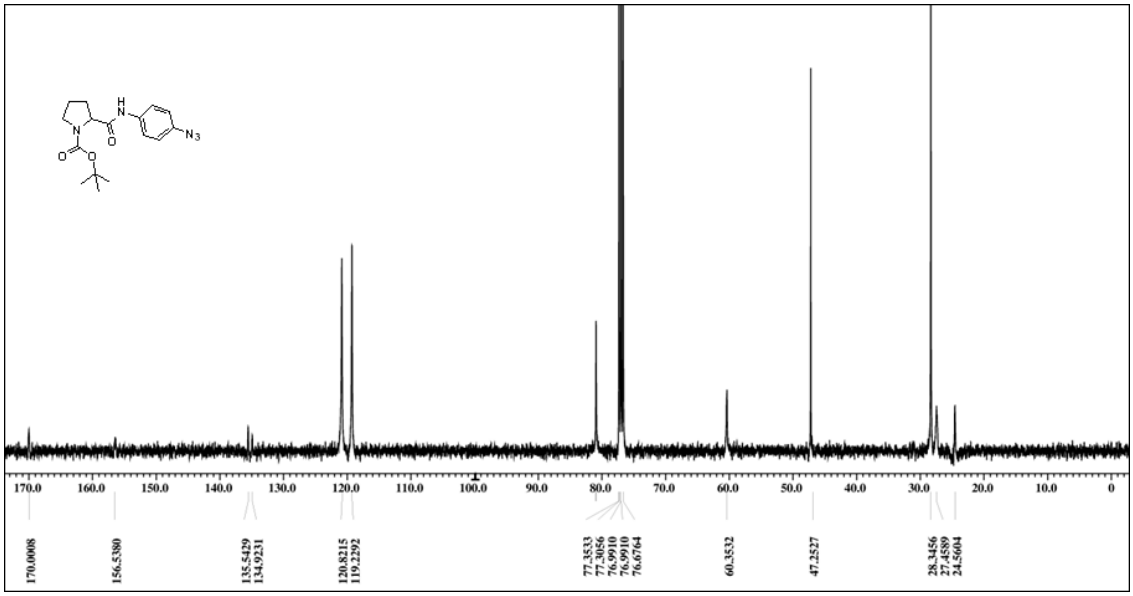
Table 1 Crystal data and structure refinement for 5f.	
Identification code	mo_JDOC080221_0m_a
Empirical formula	$C_{11}H_{14}N_4O_3S$
Formula weight	282.32
Temperature/K	99.83
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.3437(5)
b/Å	14.4207(16)
c/Å	16.6141(16)
α/°	90
β/°	90
γ/°	90

Volume/$Å^3$	1280.3(2)
Z	4
$\rho_{calc}g/cm^3$	1.465
μ/mm^{-1}	0.263
F(000)	592.0
Crystal size/mm^3	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.904 to 49.986
Index ranges	$-6 \leq h \leq 6$, $-17 \leq k \leq 17$, $-19 \leq l \leq 18$
Reflections collected	11636
Independent reflections	2241 [R_{int} = 0.1207, R_{sigma} = 0.0656]
Data/restraints/parameters	2241/0/176
Goodness-of-fit on F^2	1.070
Final R indexes [I>=2σ (I)]	R_1 = 0.0424, wR_2 = 0.0905
Final R indexes [all data]	R_1 = 0.0450, wR_2 = 0.0923
Largest diff. peak/hole / e $Å^{-3}$	0.36/-0.39
Flack parameter	0.39(13)

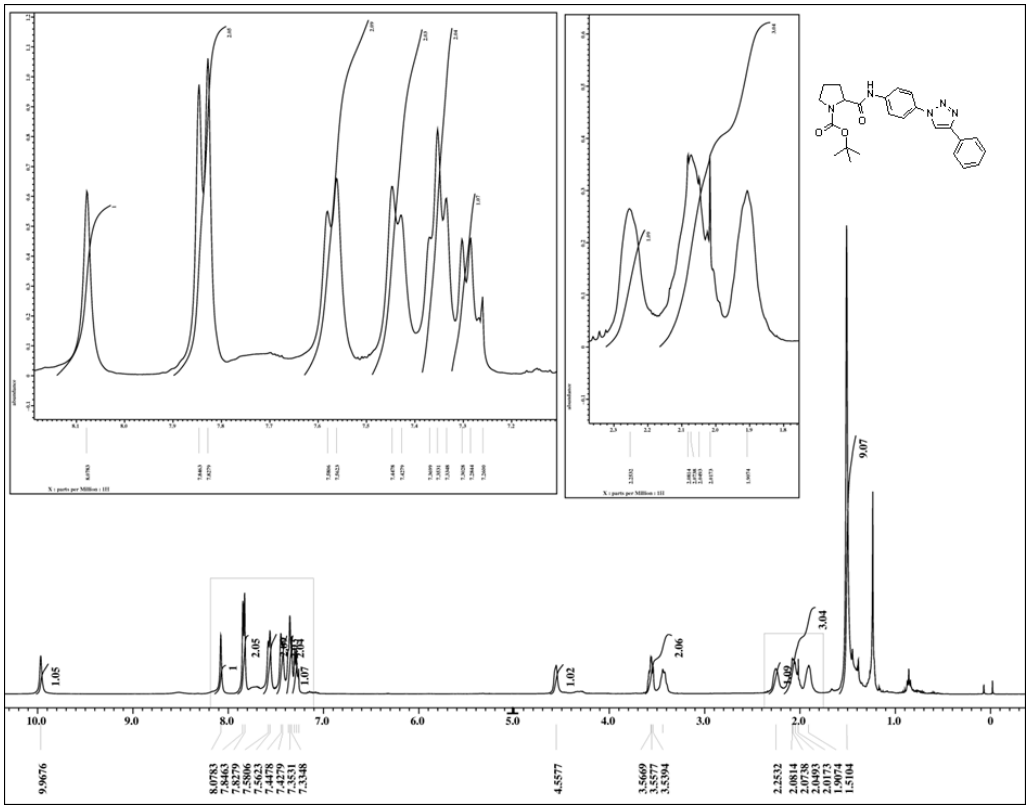
10.0 NMR spectra of all compounds

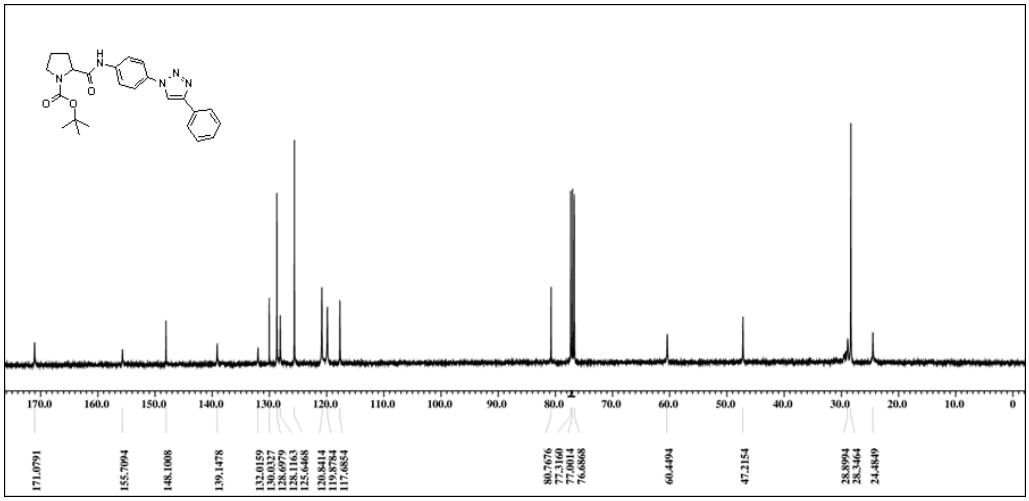
^{1}H and ^{13}C NMR of S3:



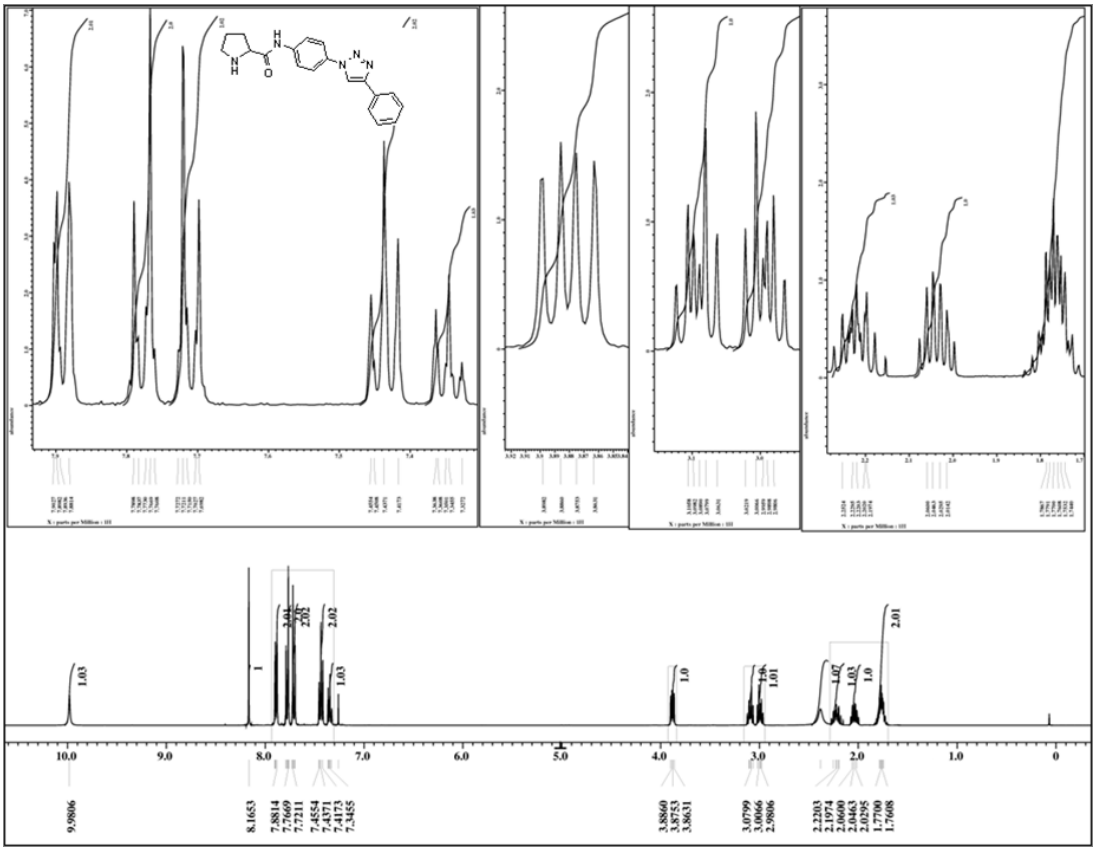


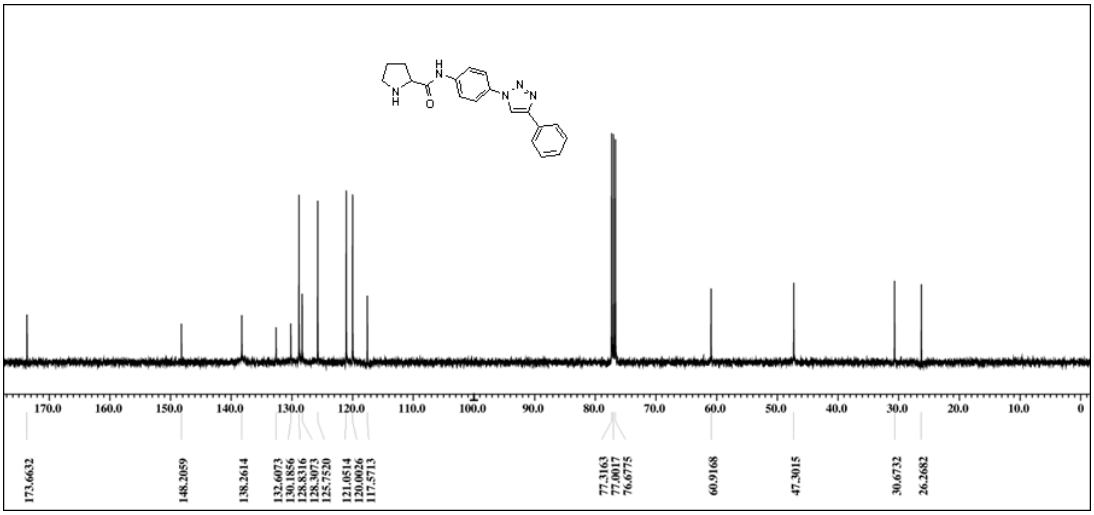
^{1}H and ^{13}C NMR of S5:



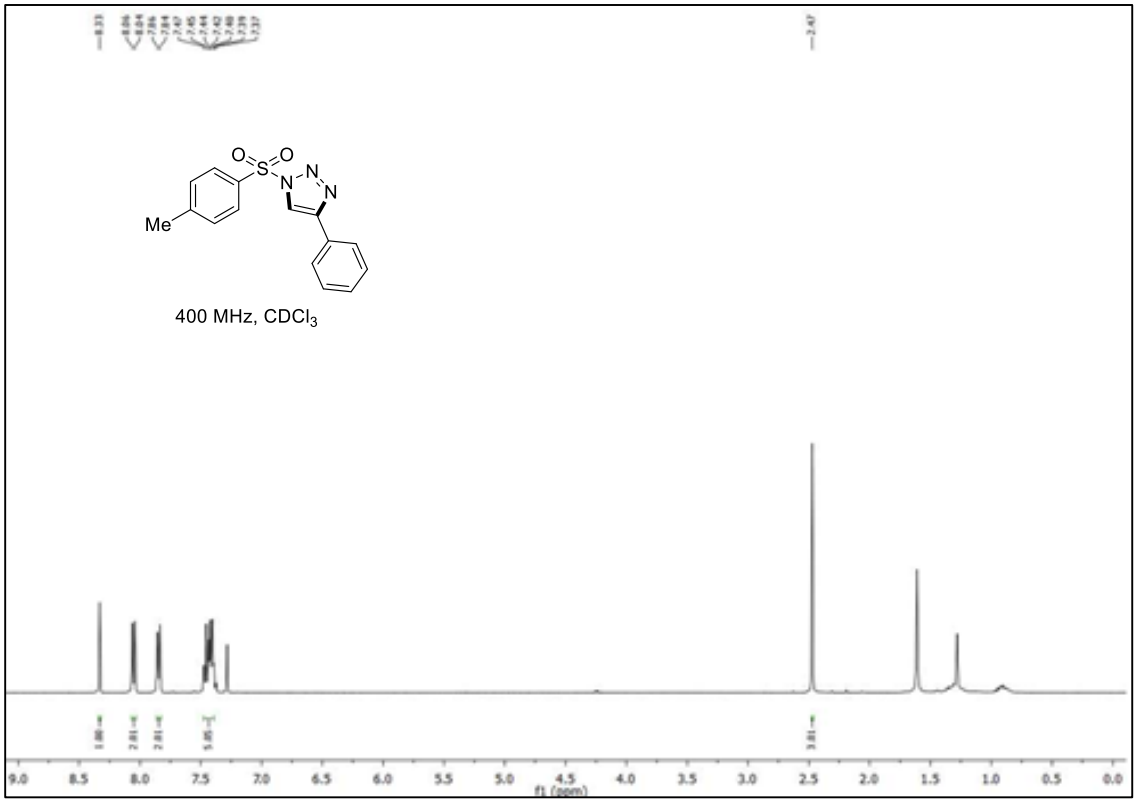


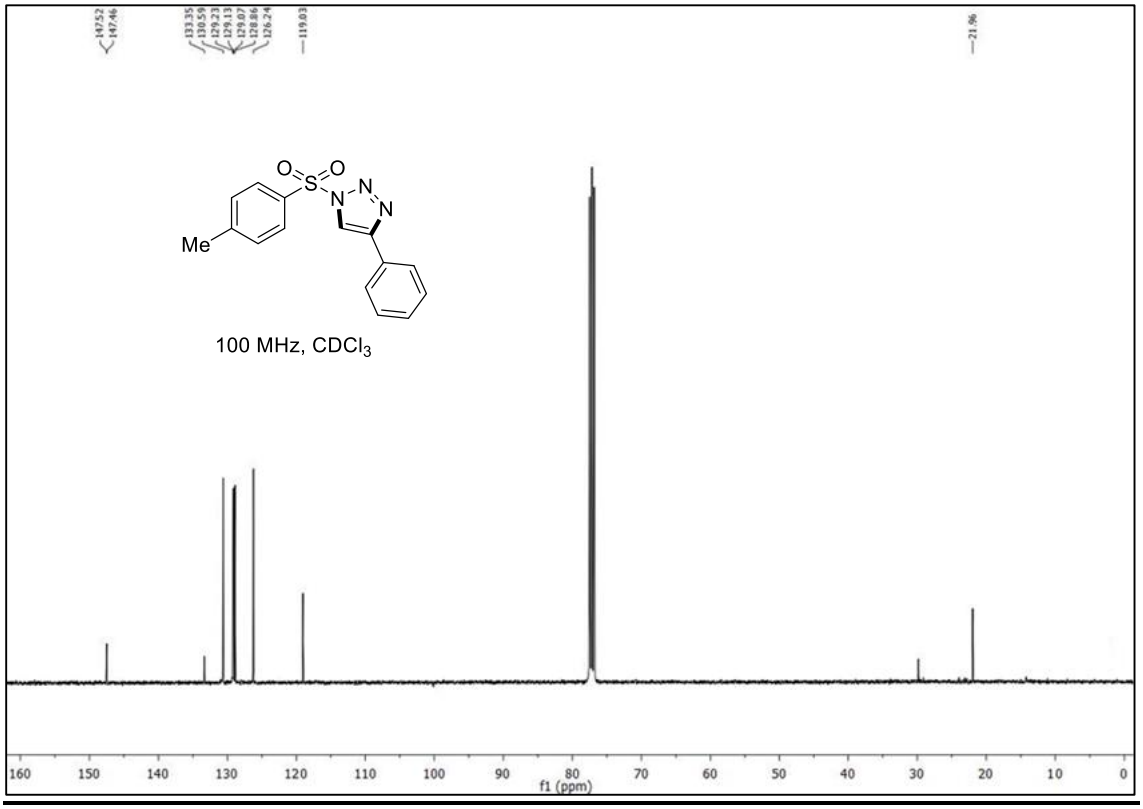
^{1}H and ^{13}C NMR of Pro-1:



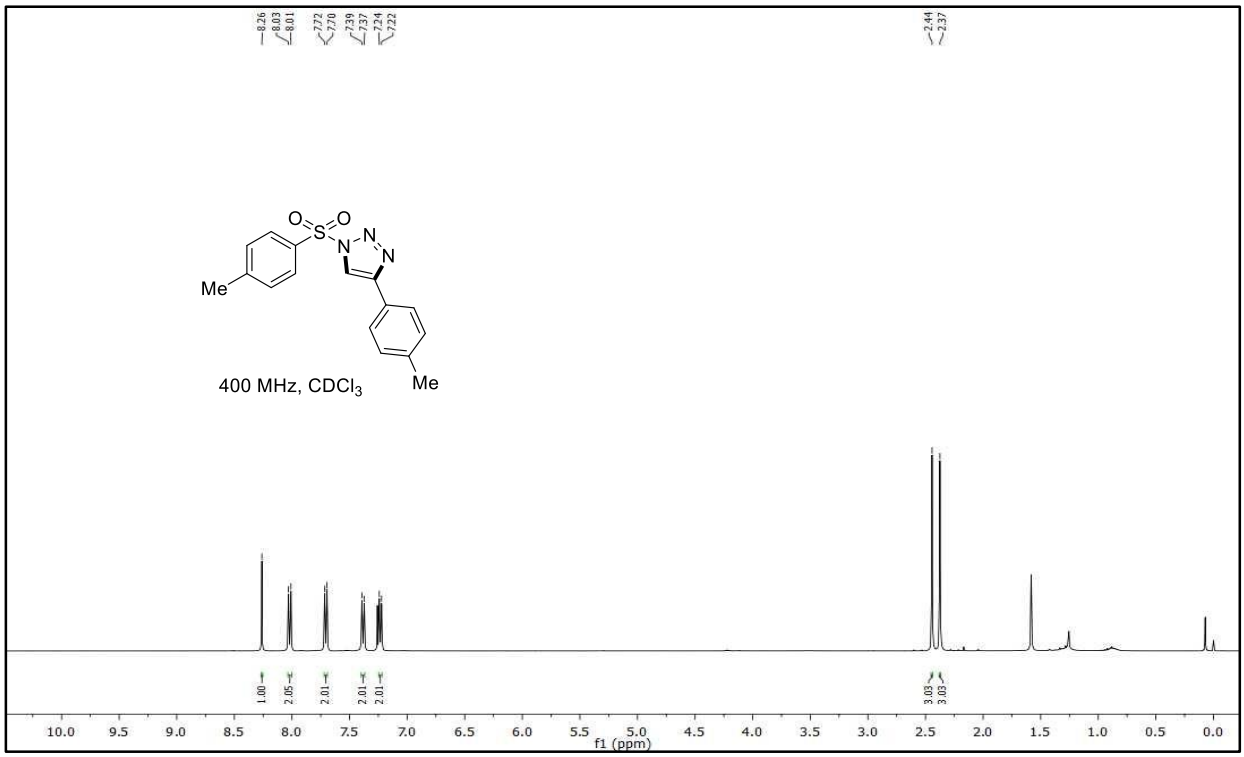


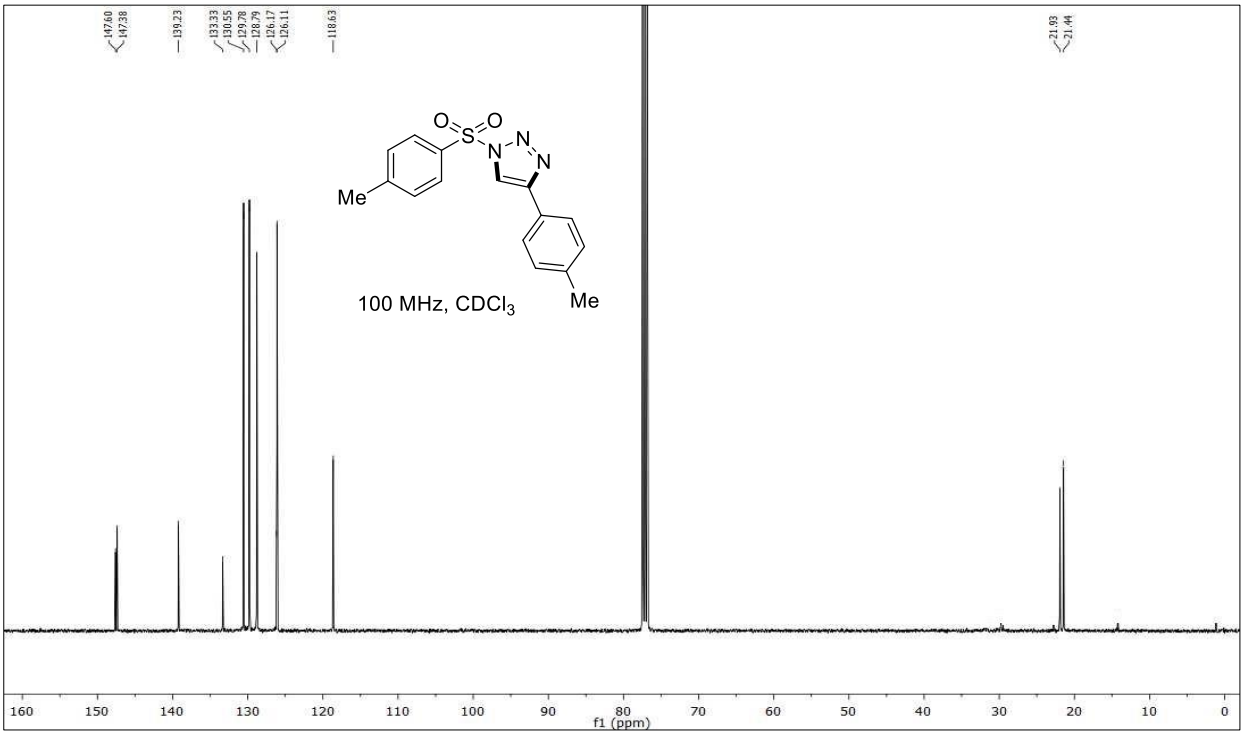
^{1}H and ^{13}C NMR spectra of 3a:



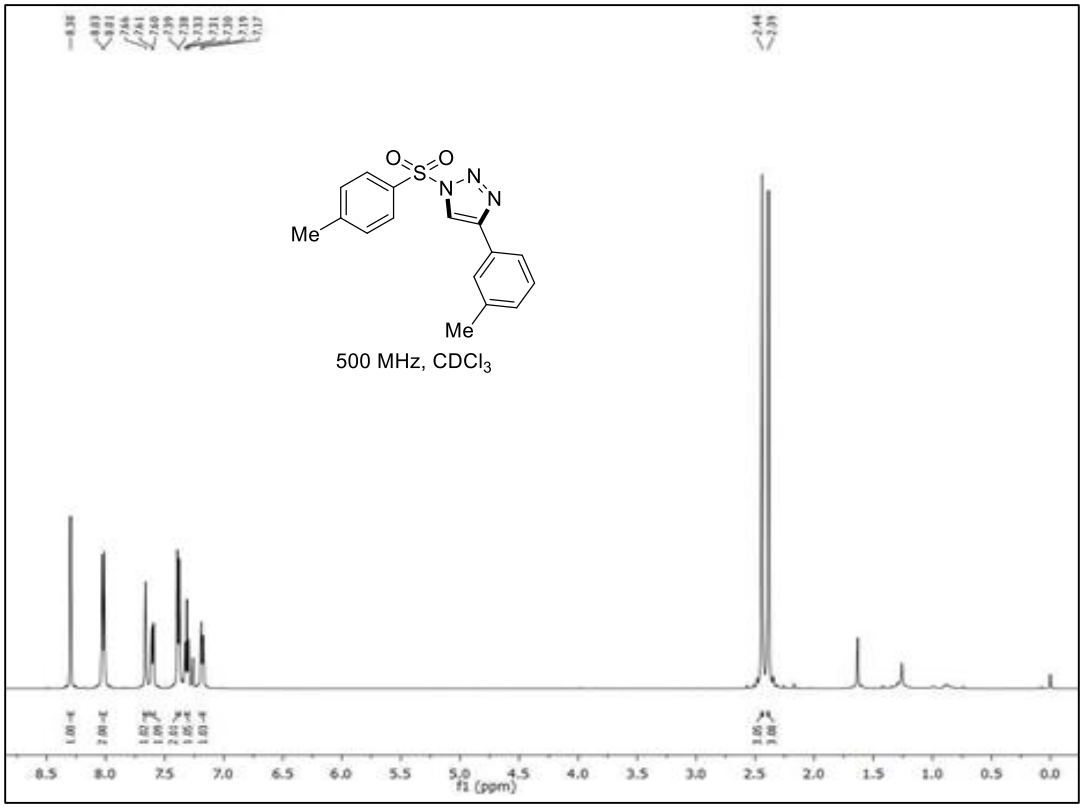


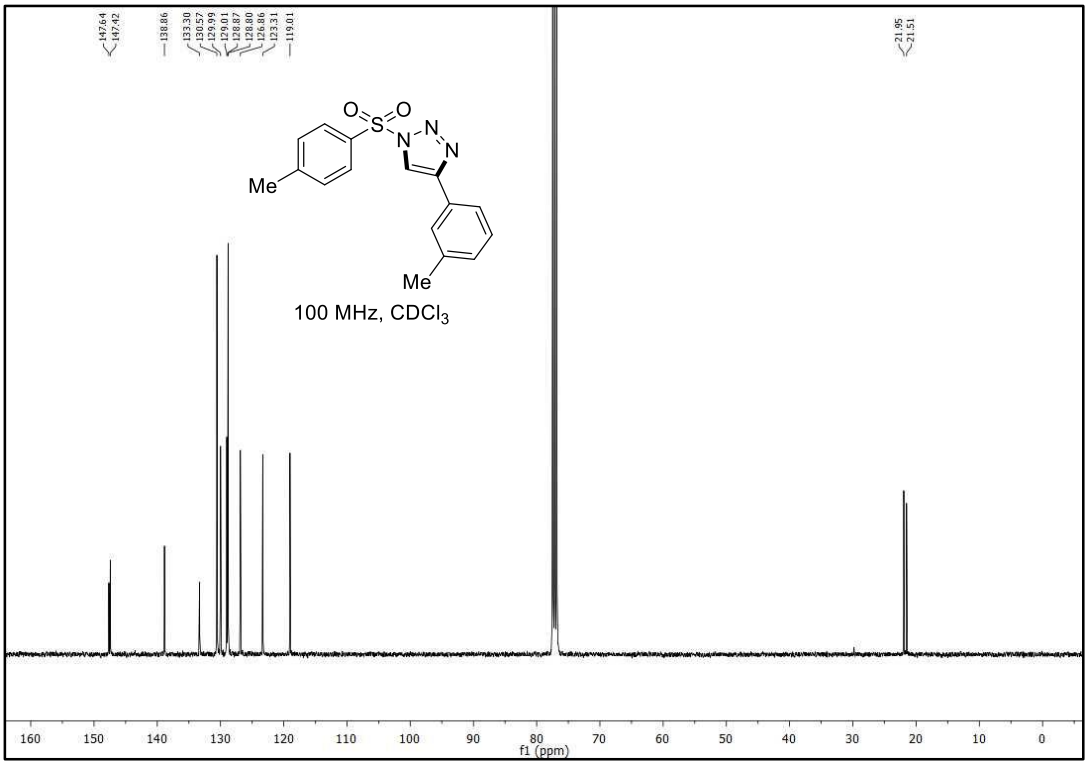
^{1}H and ^{13}C NMR spectra of 3b:



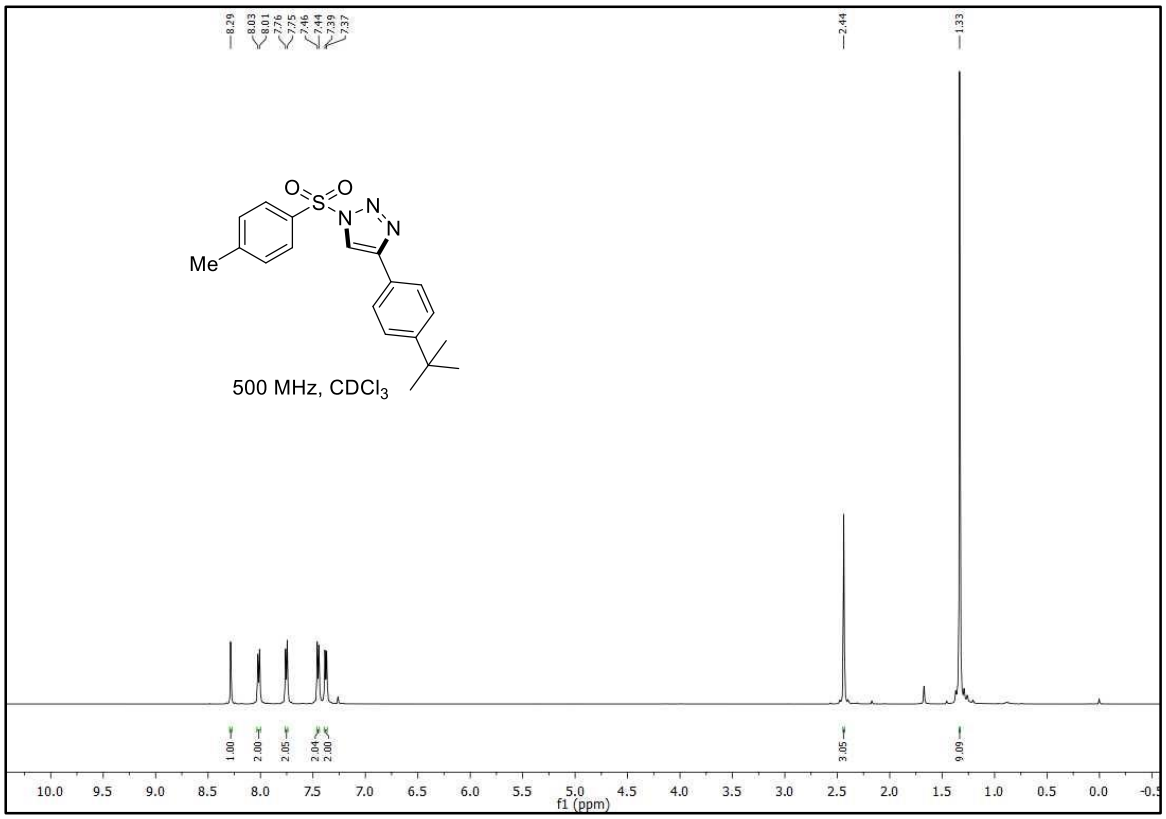


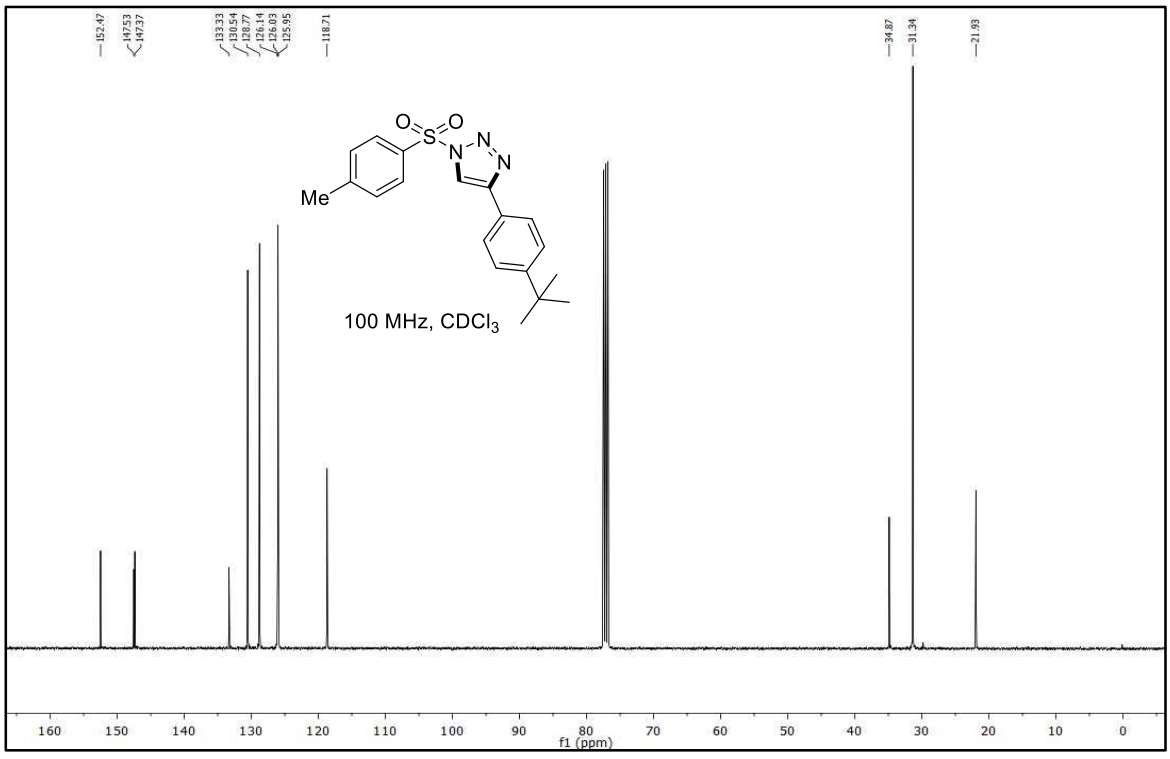
^{1}H and ^{13}C NMR spectra of 3c:



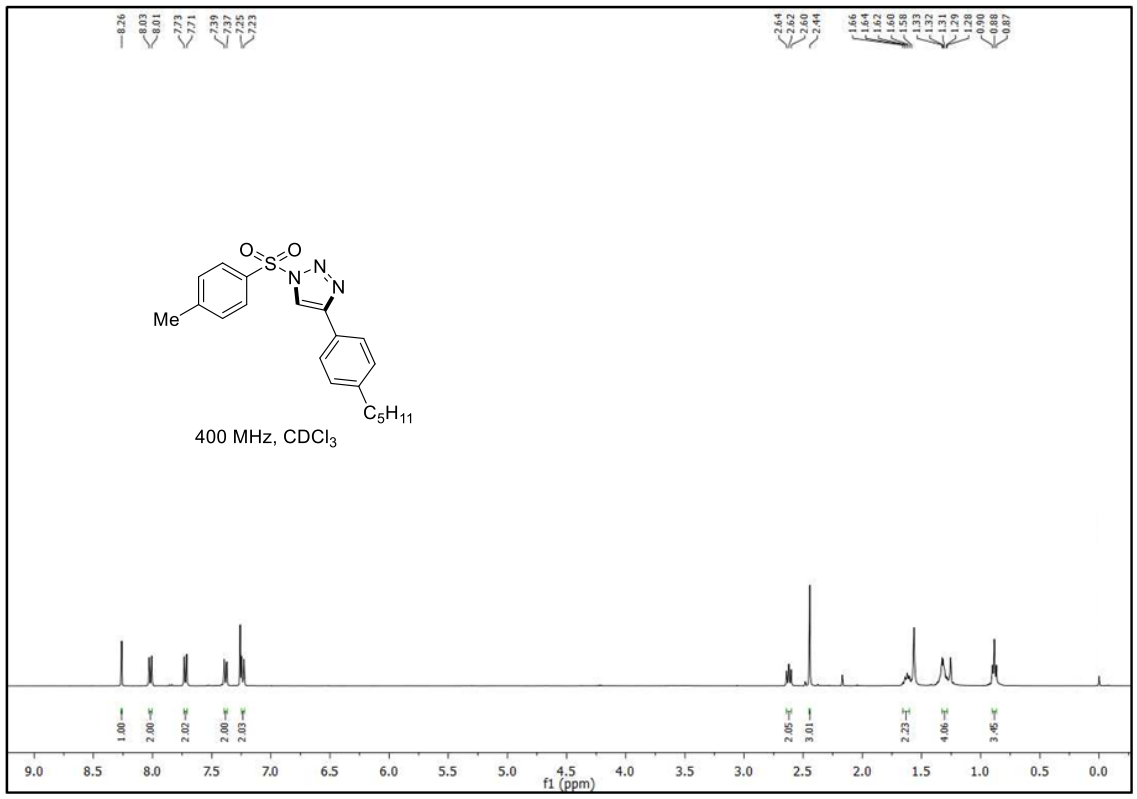


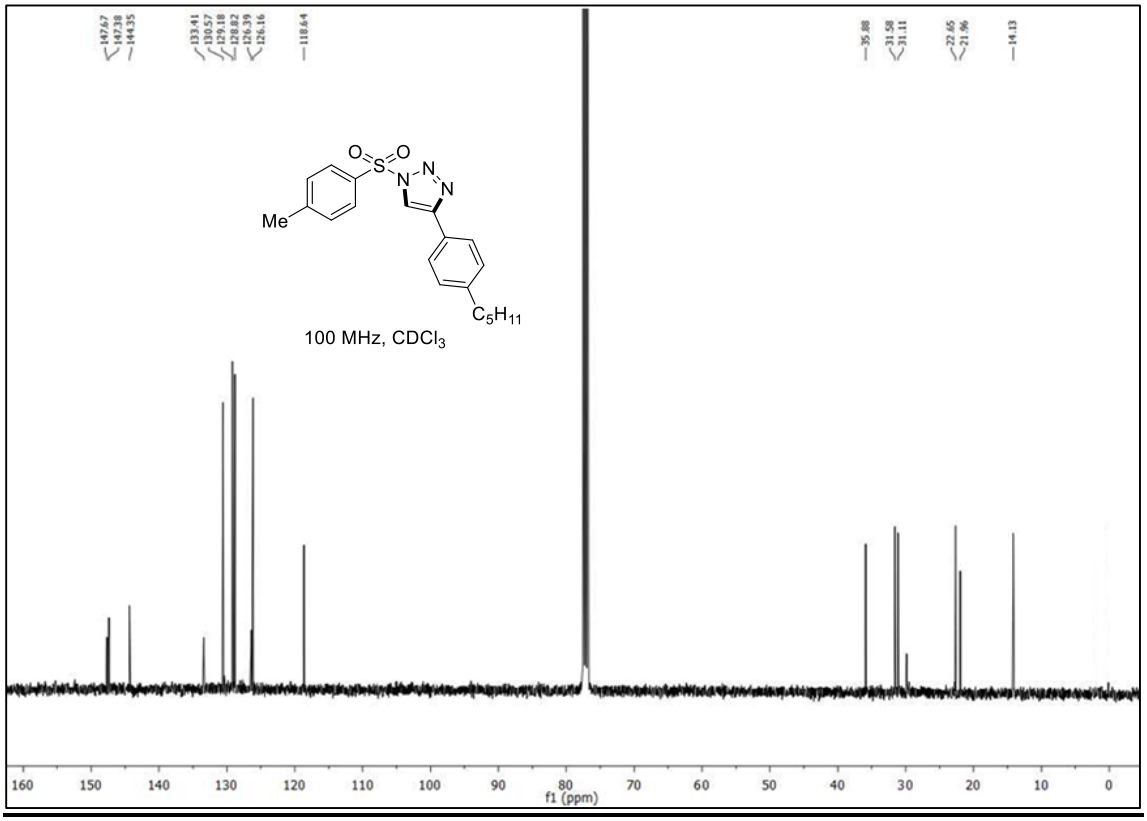
^{1}H and ^{13}C NMR spectra of 3d:



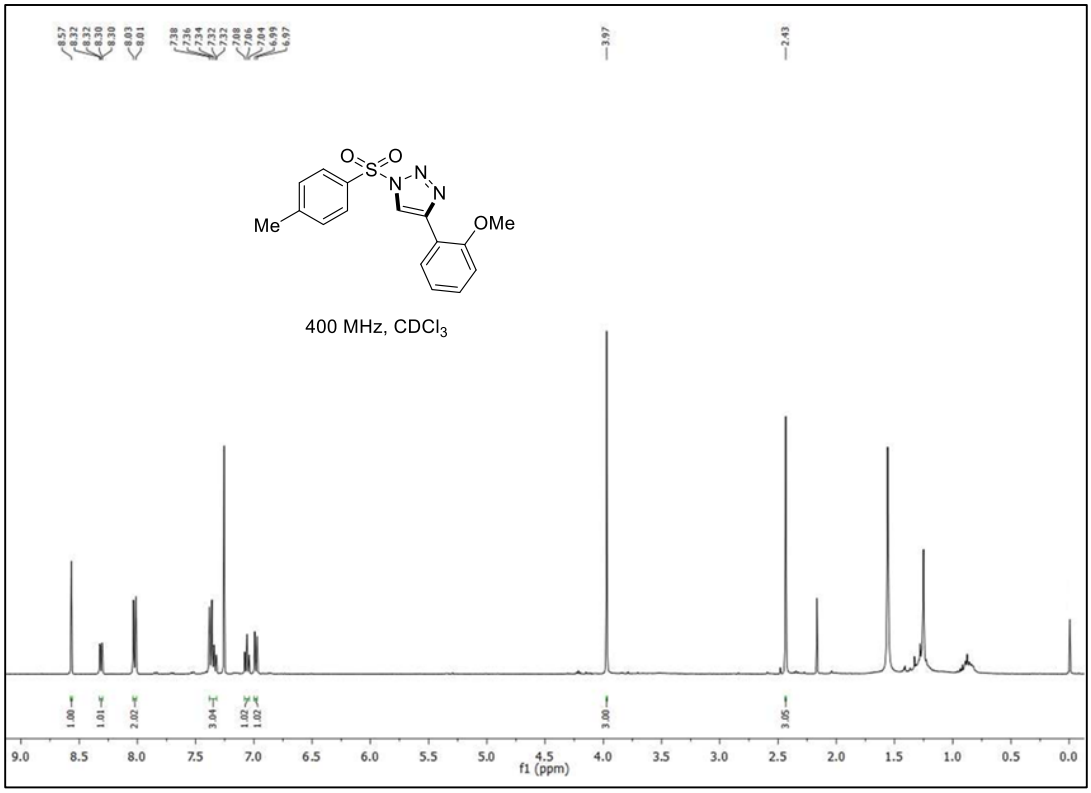


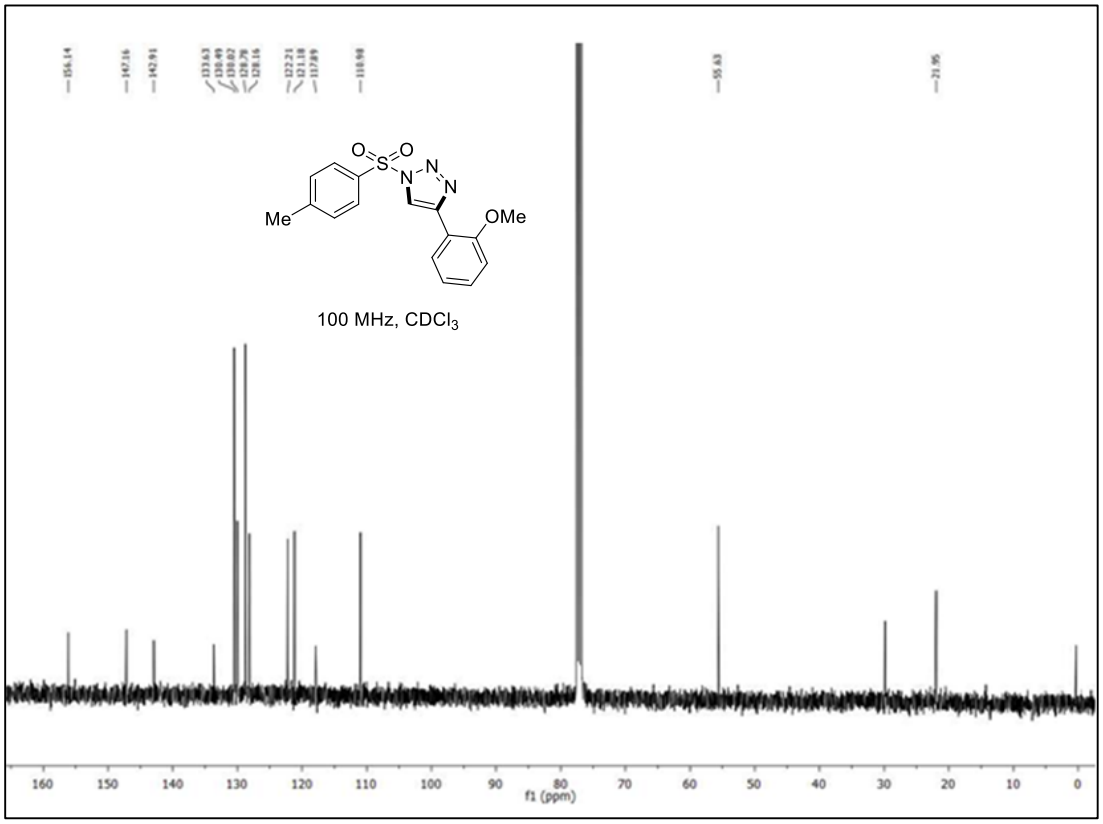
^{1}H and ^{13}C NMR spectra of 3e:



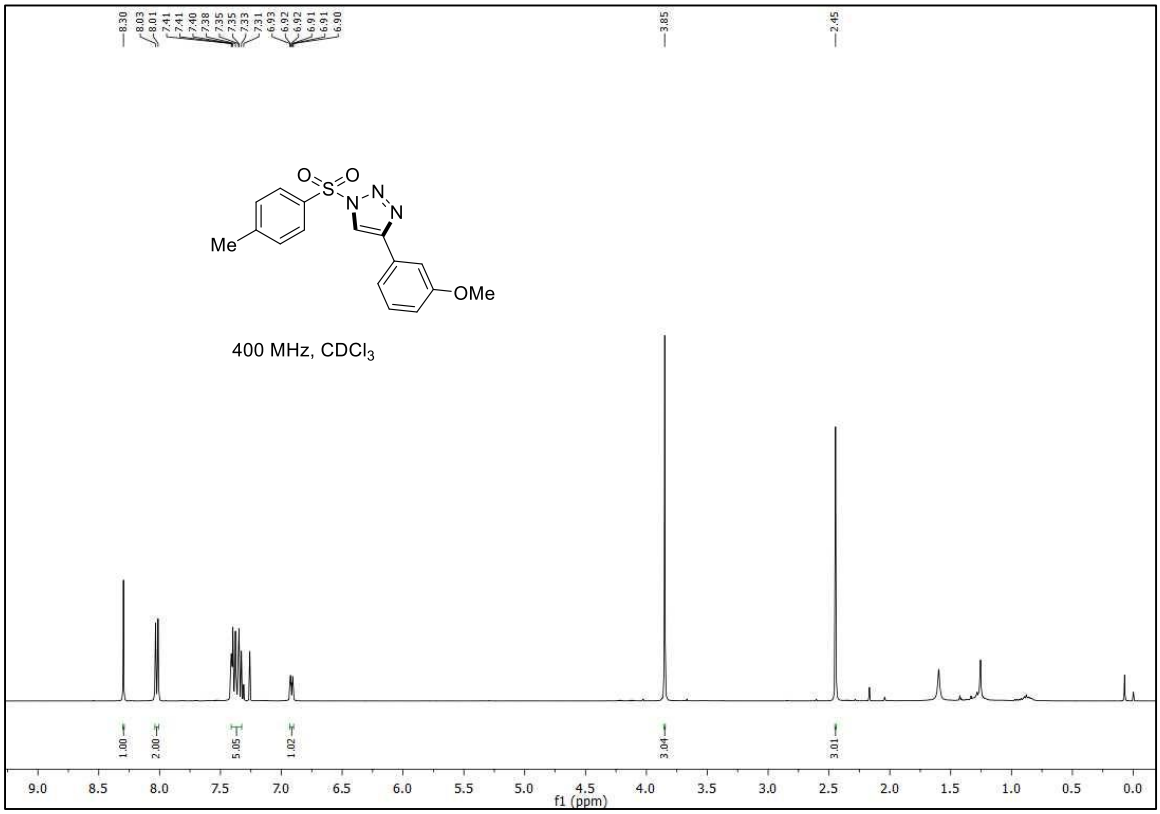


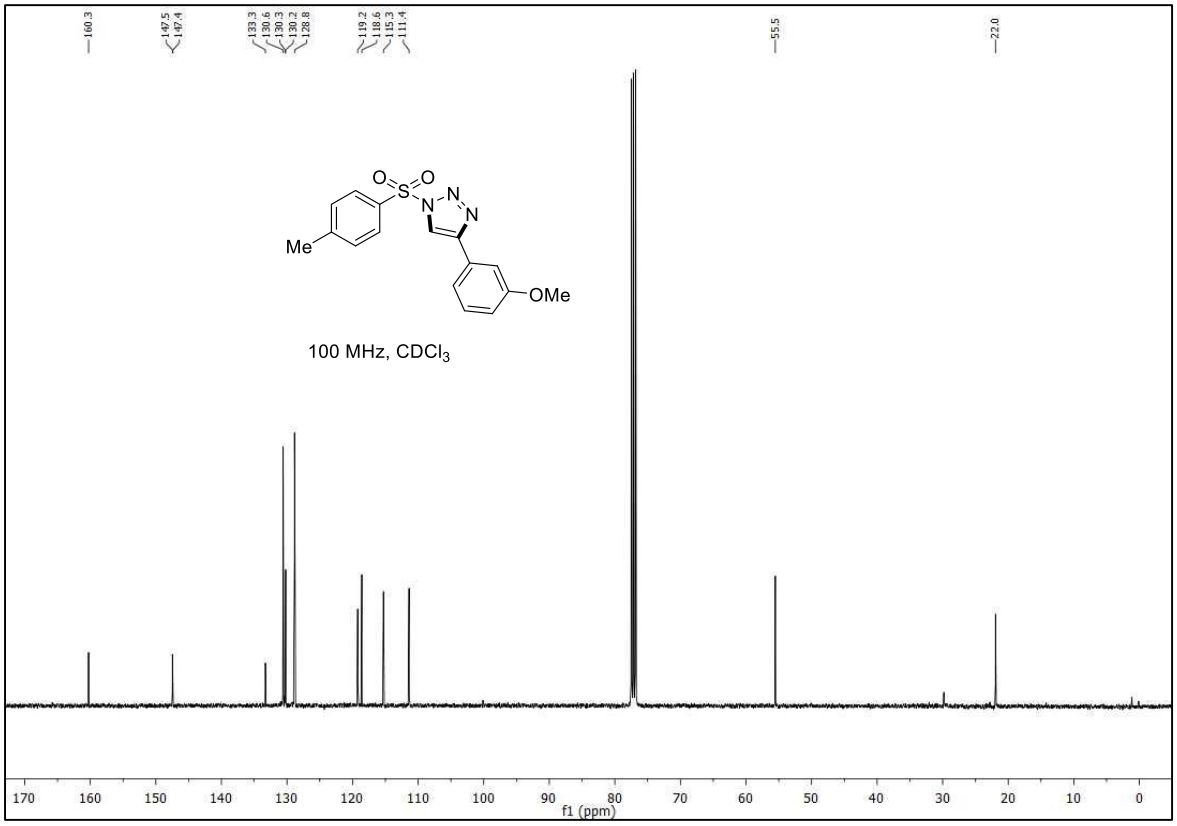
^{1}H and ^{13}C NMR spectra of 3f:



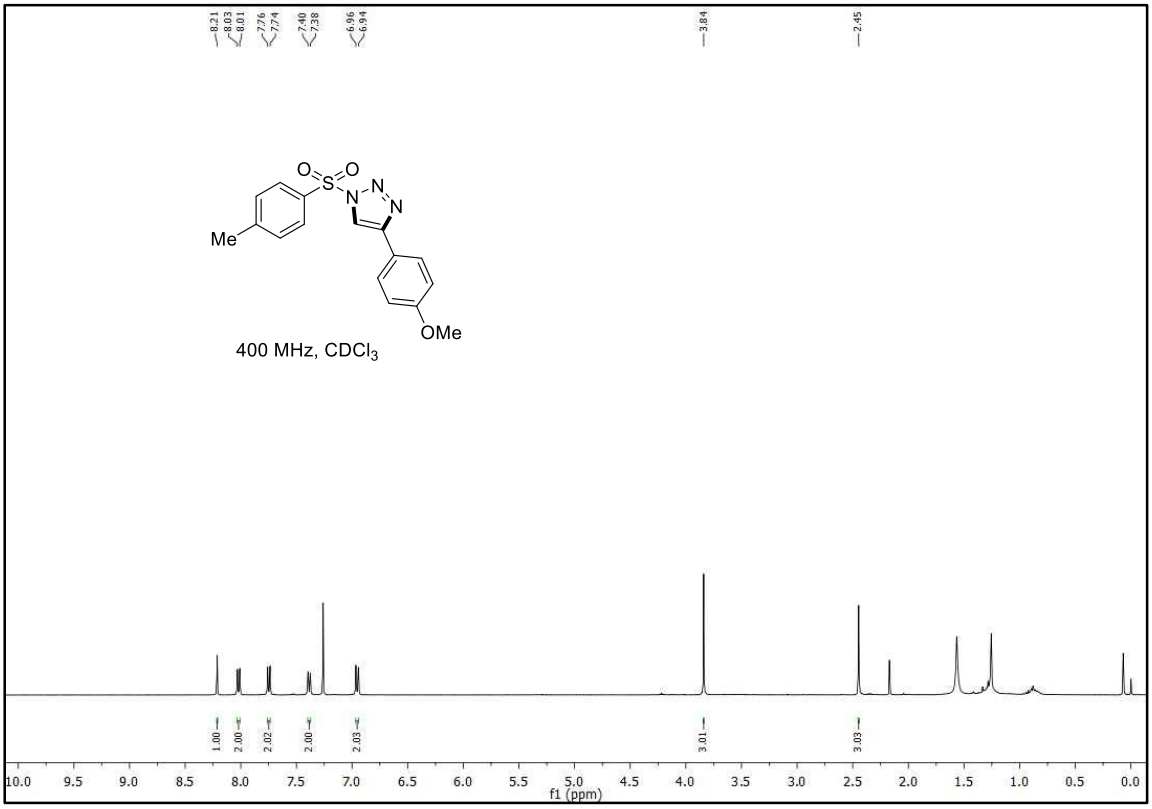


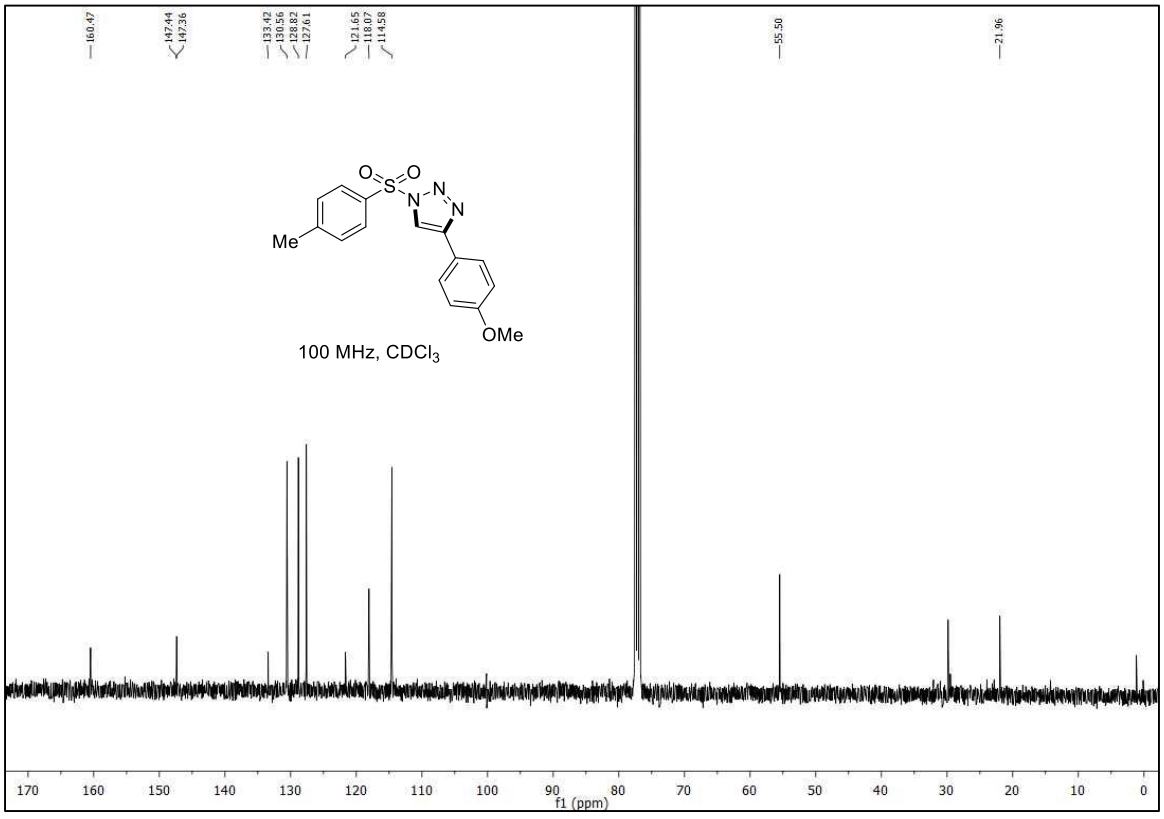
^{1}H and ^{13}C NMR spectra of 3g:



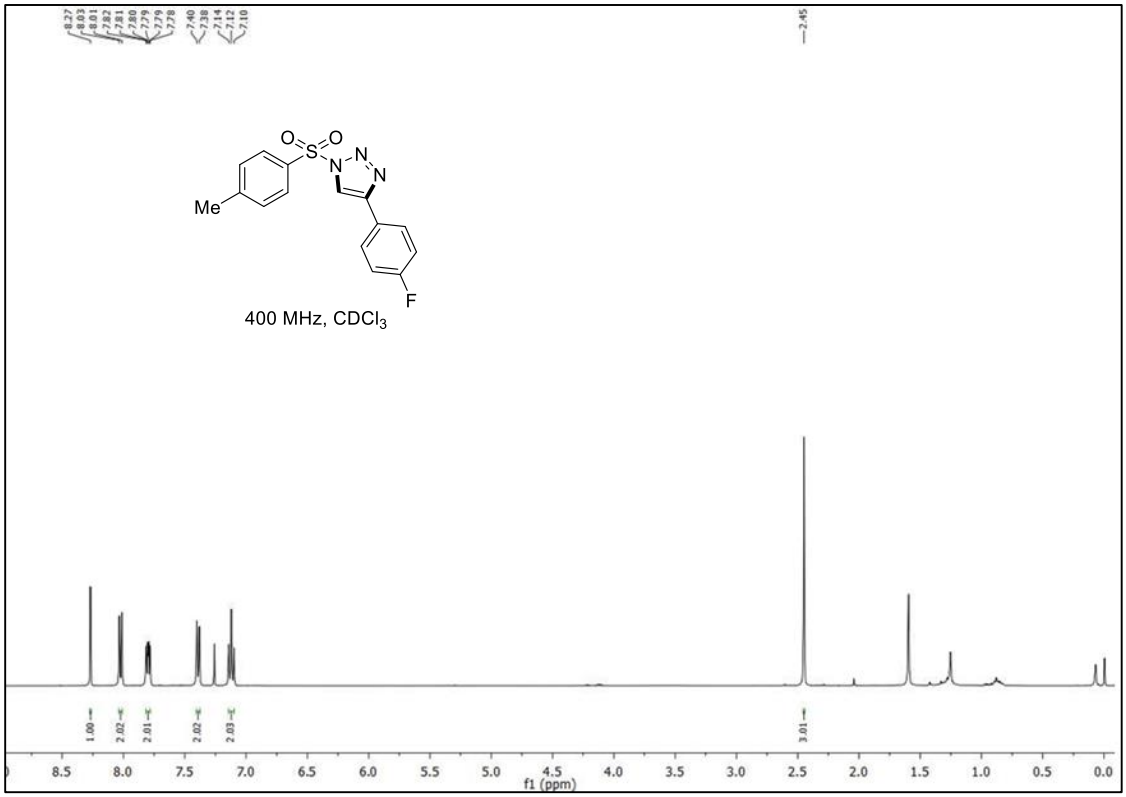


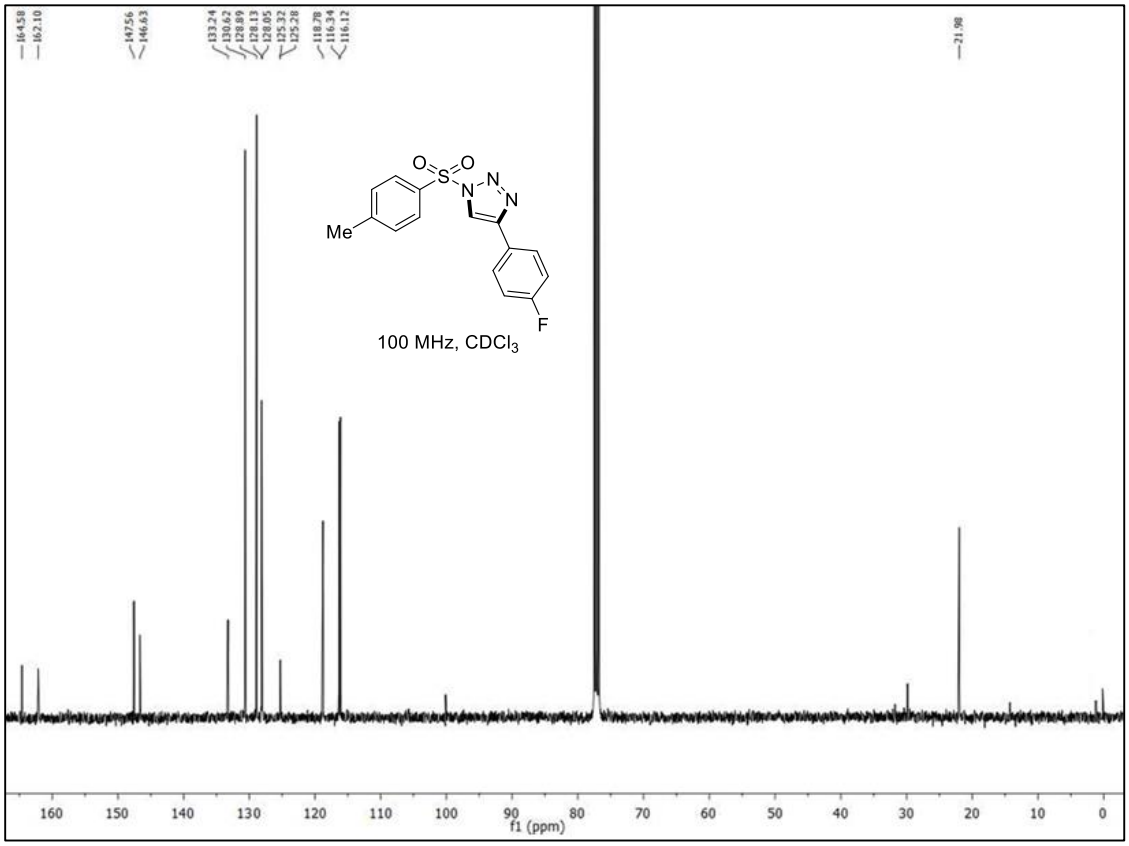
^{1}H and ^{13}C NMR spectra of 3h:



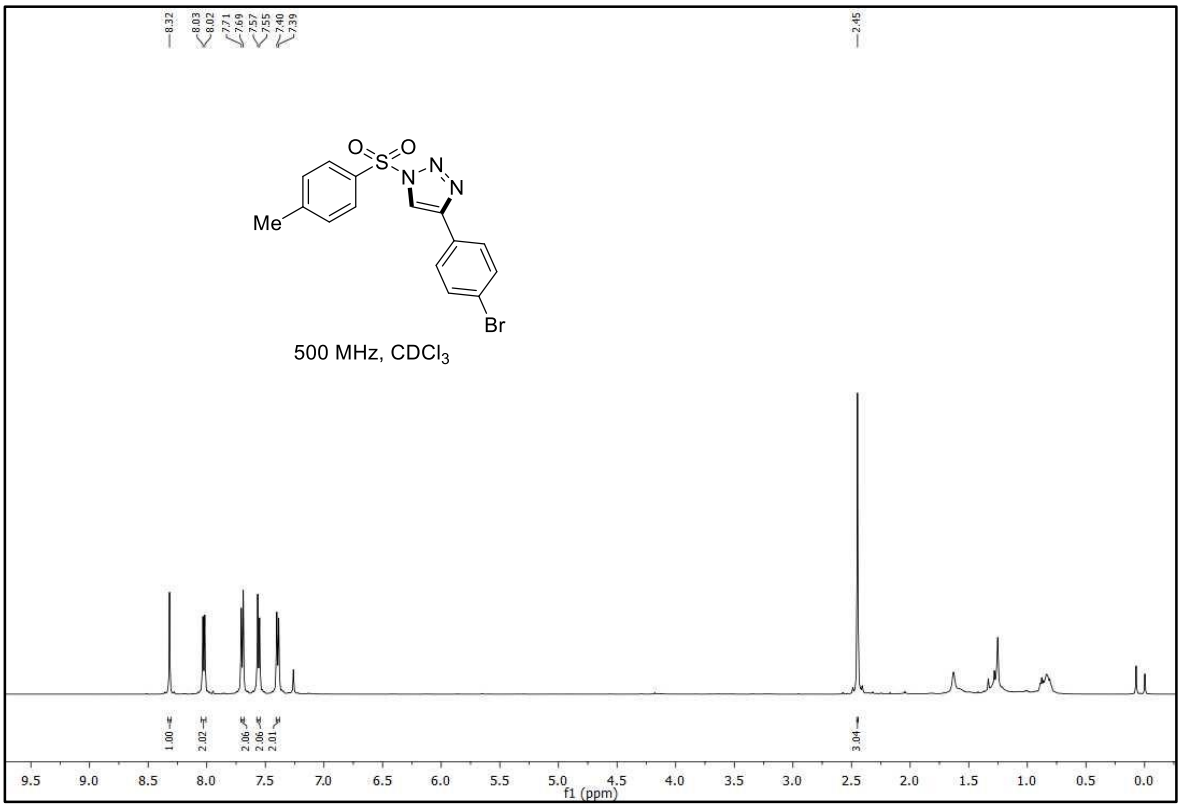


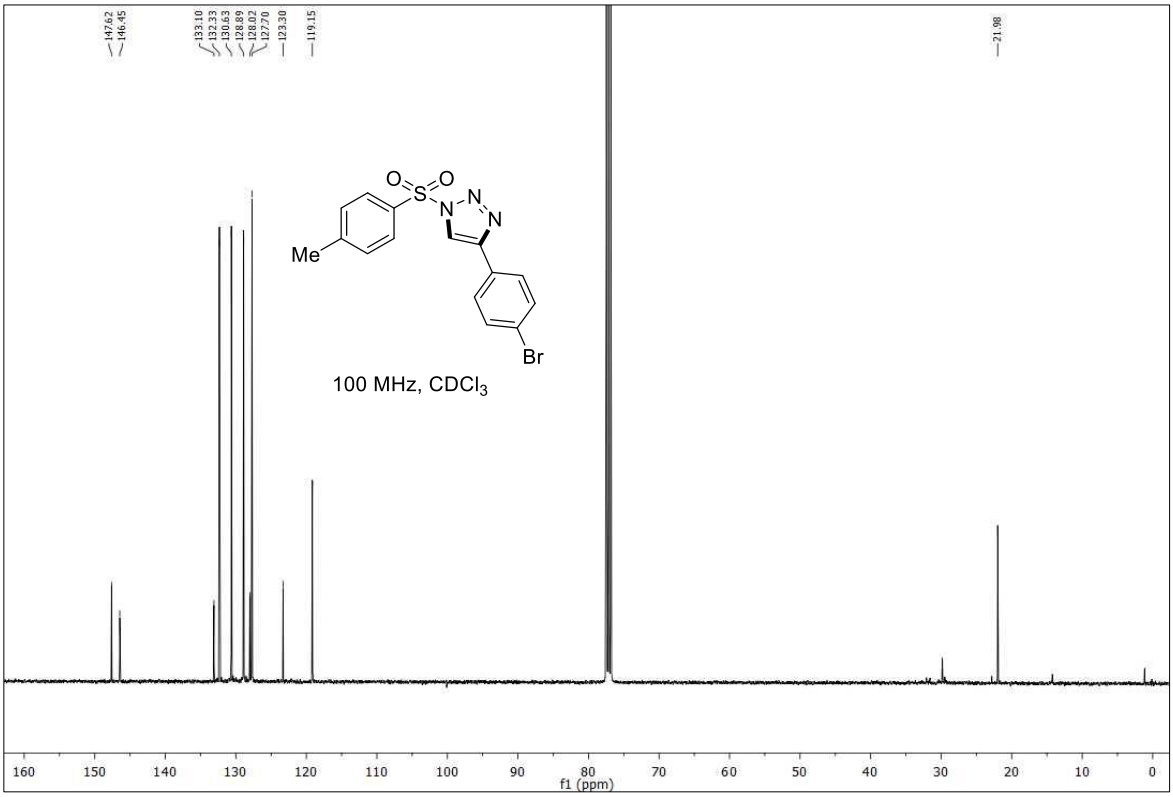
^{1}H and ^{13}C NMR spectra of 3i:



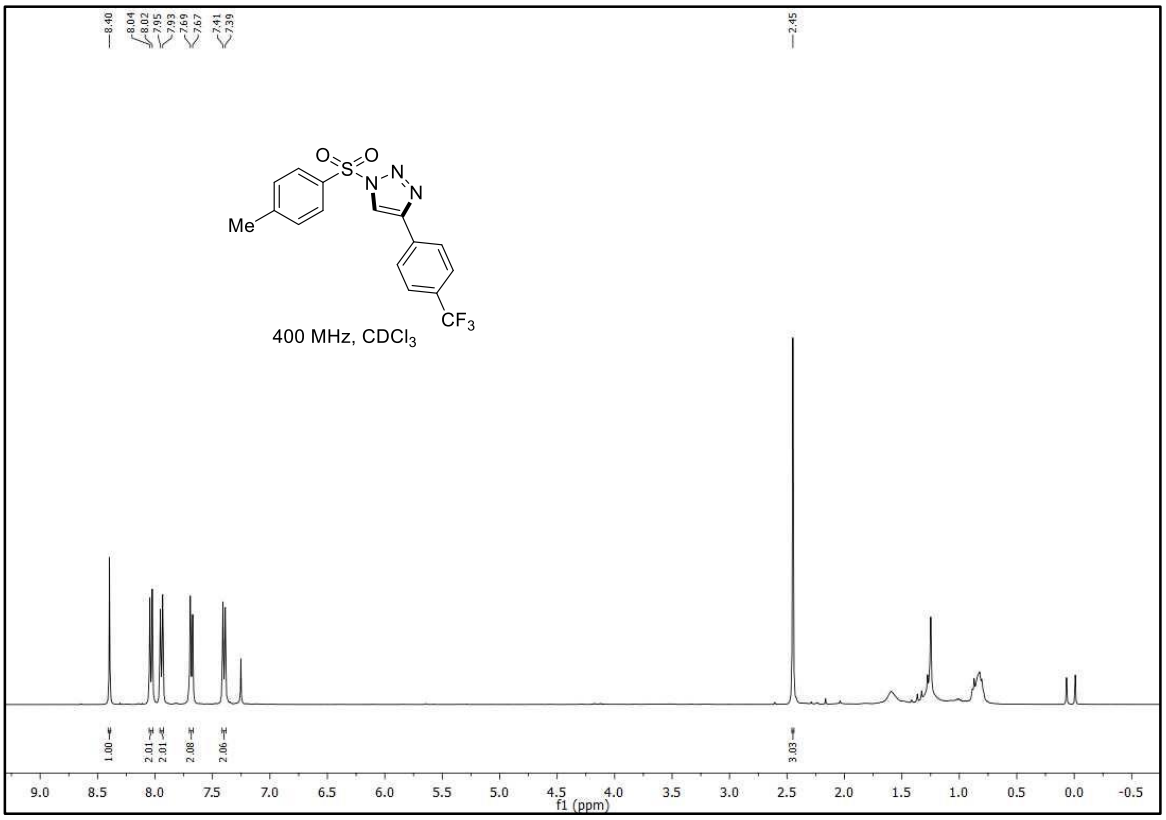


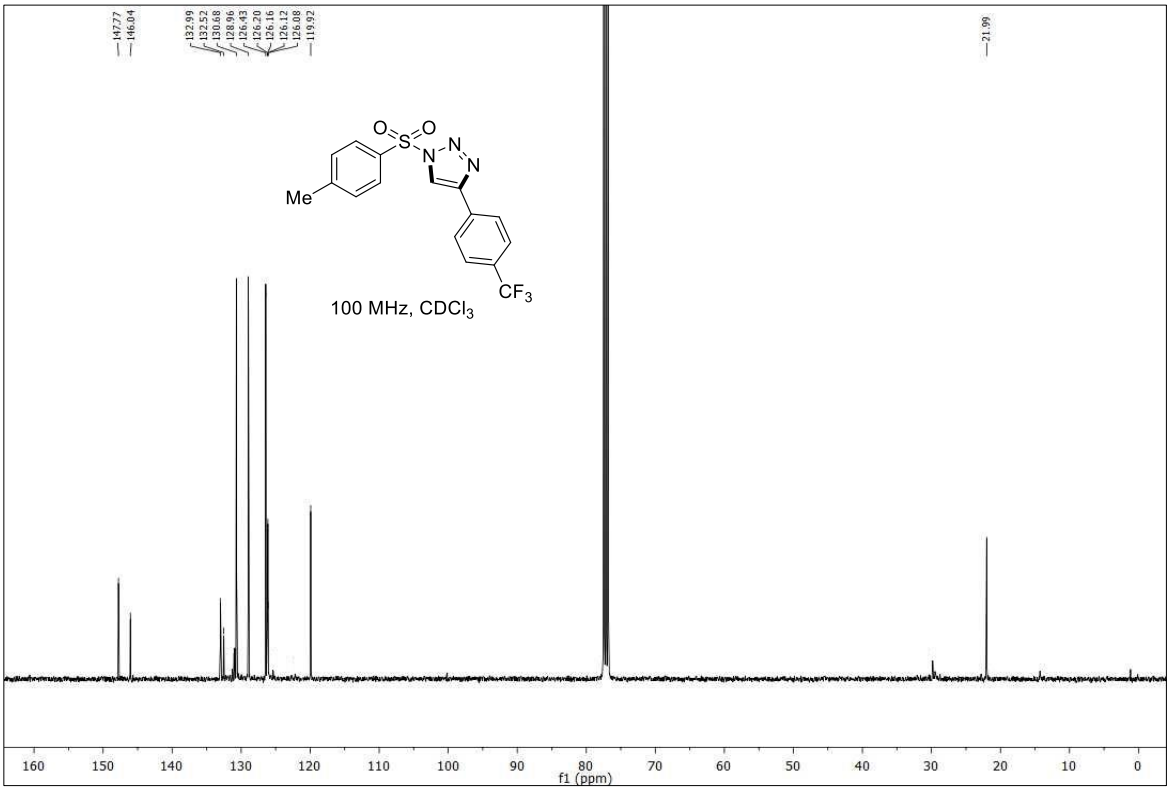
^{1}H and ^{13}C NMR spectra of 3j:



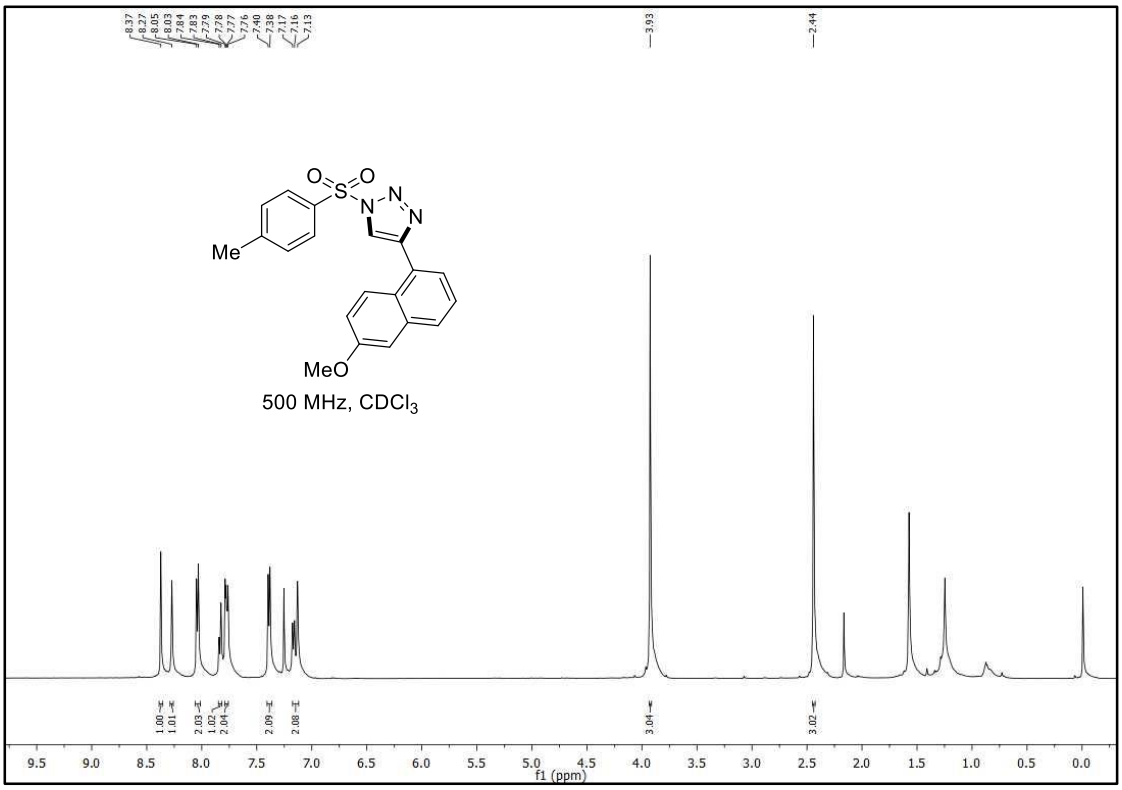


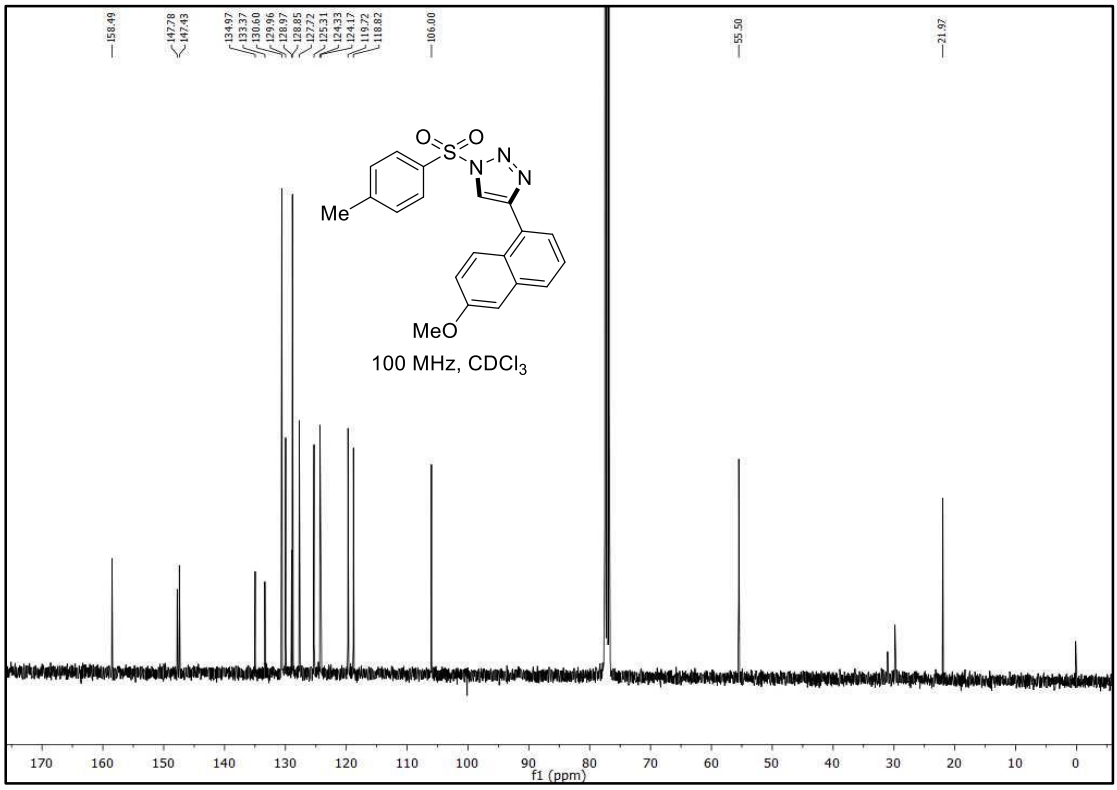
^{1}H and ^{13}C NMR spectra of 3k:



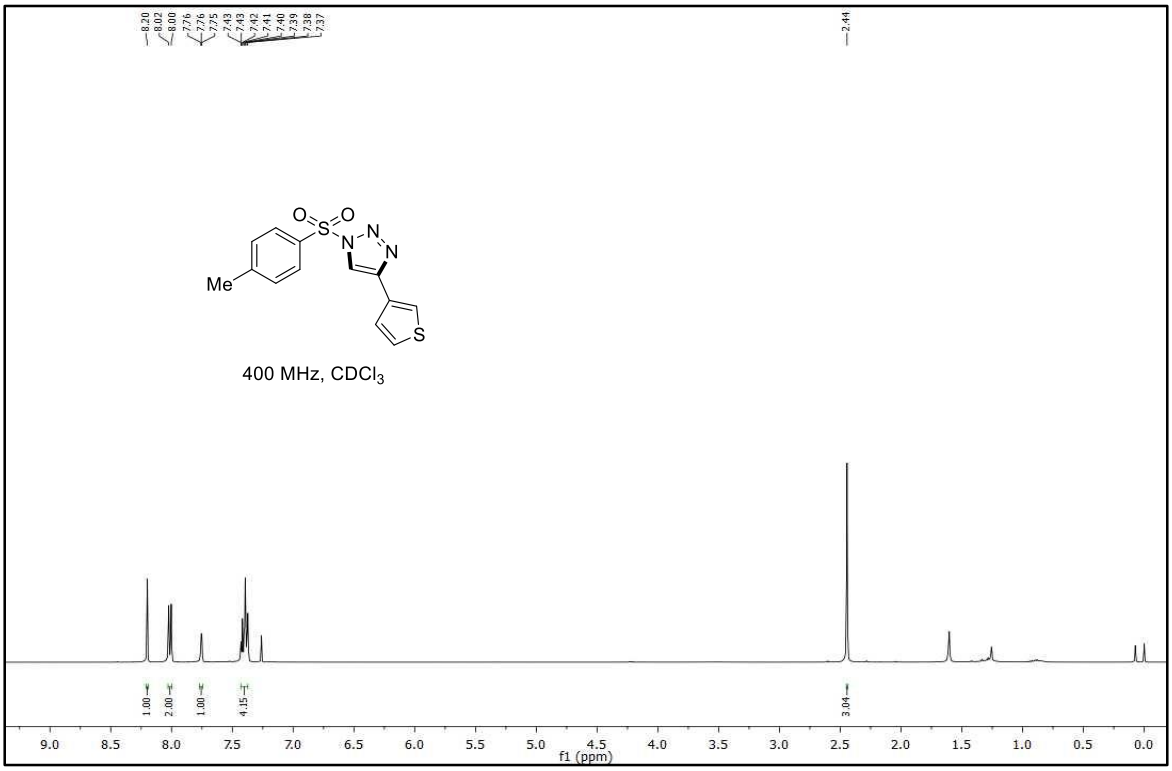


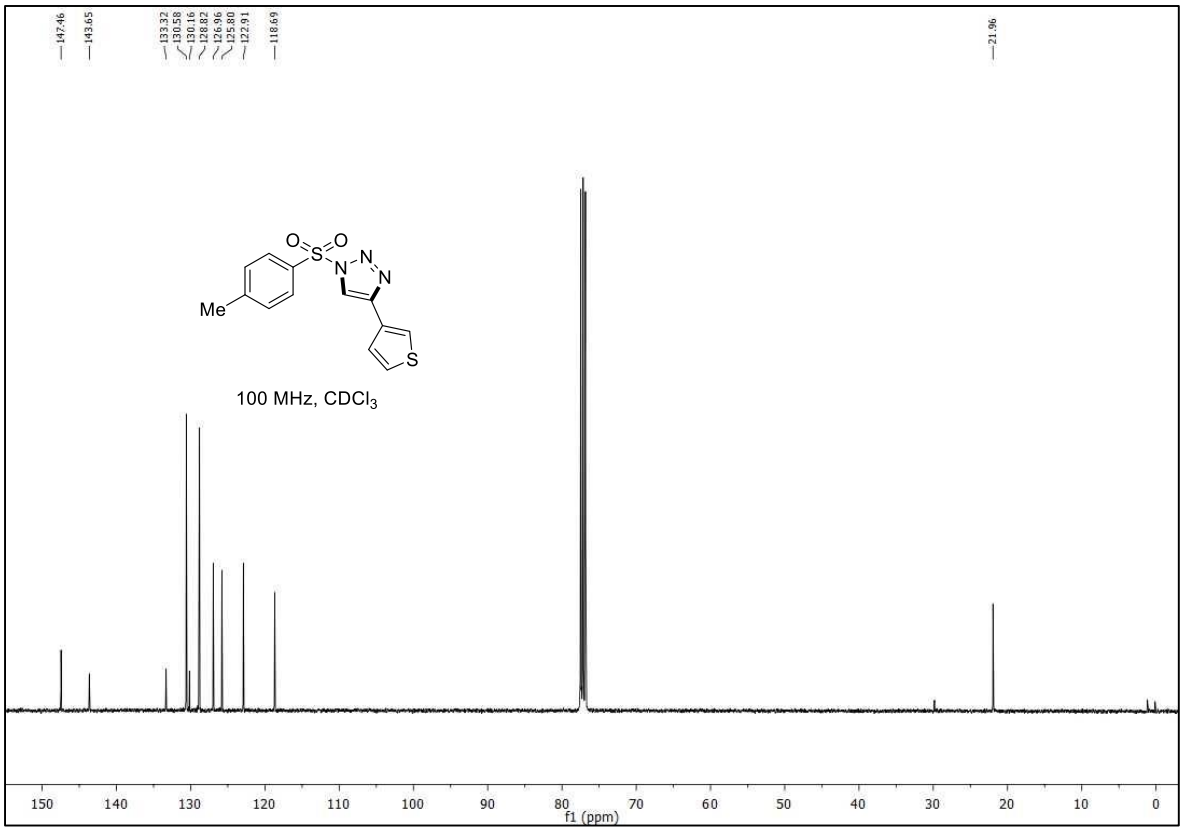
^{1}H and ^{13}C NMR spectra of 3l:



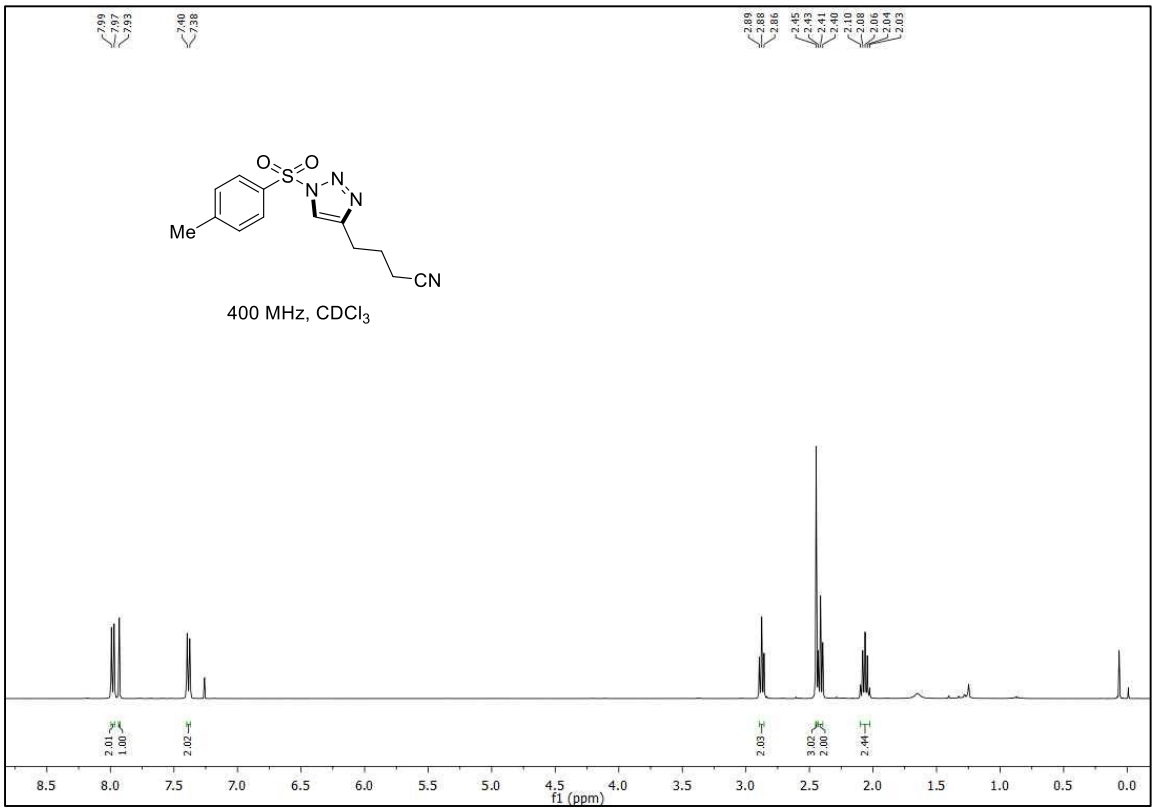


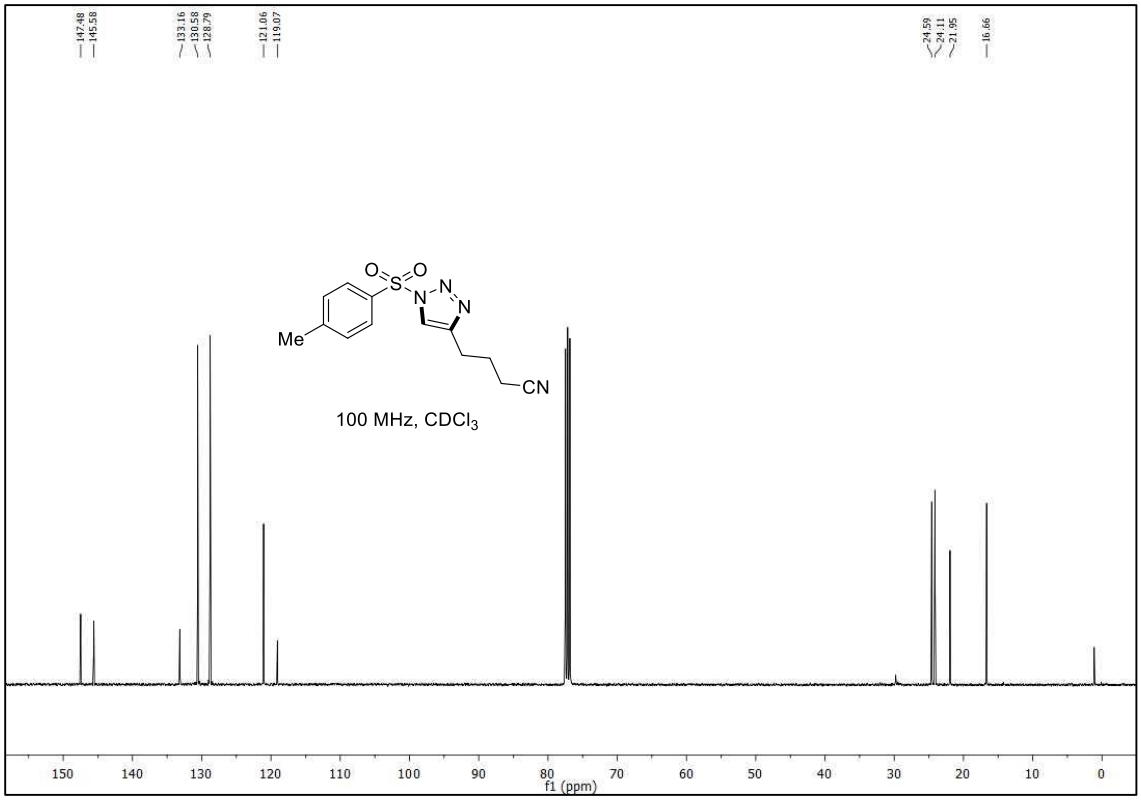
^{1}H and ^{13}C NMR spectra of 3m:



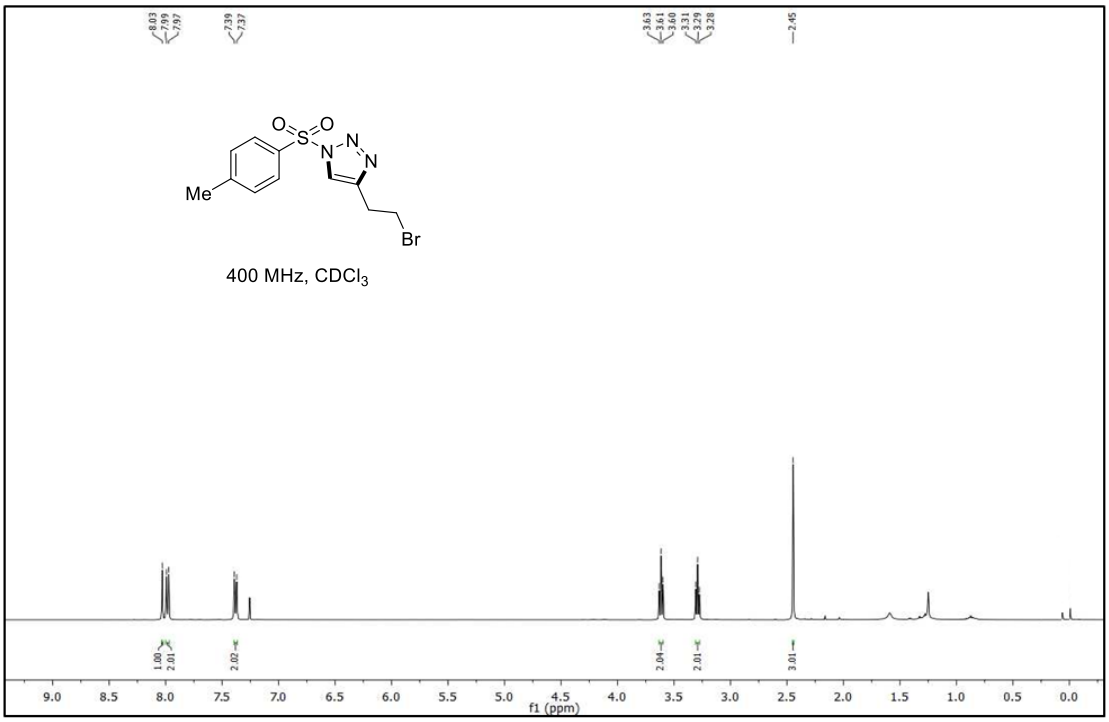


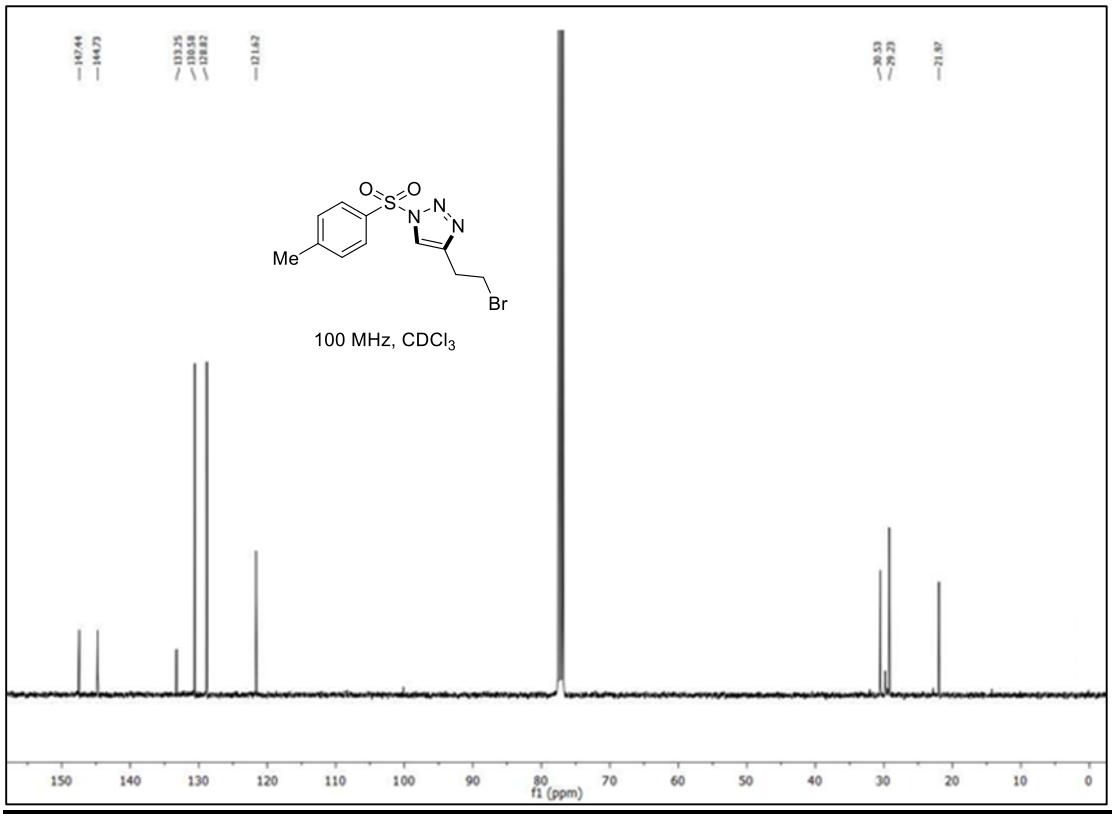
^{1}H and ^{13}C NMR spectra of 3n:



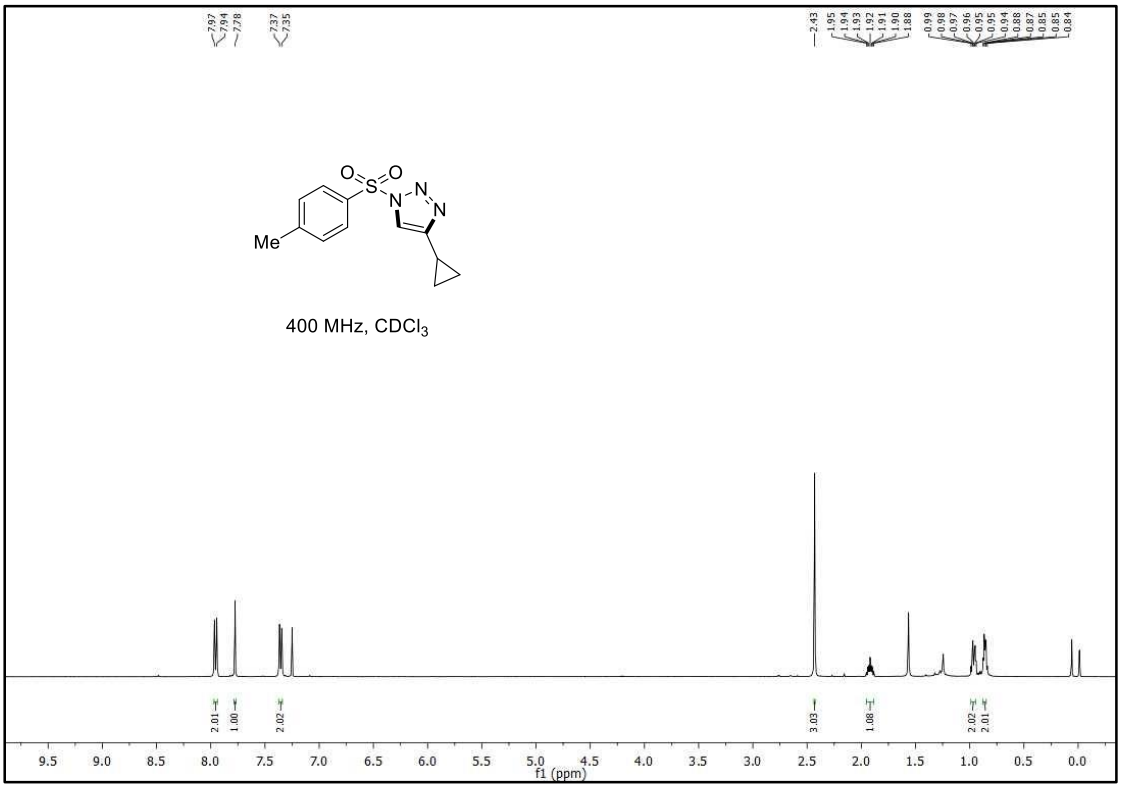


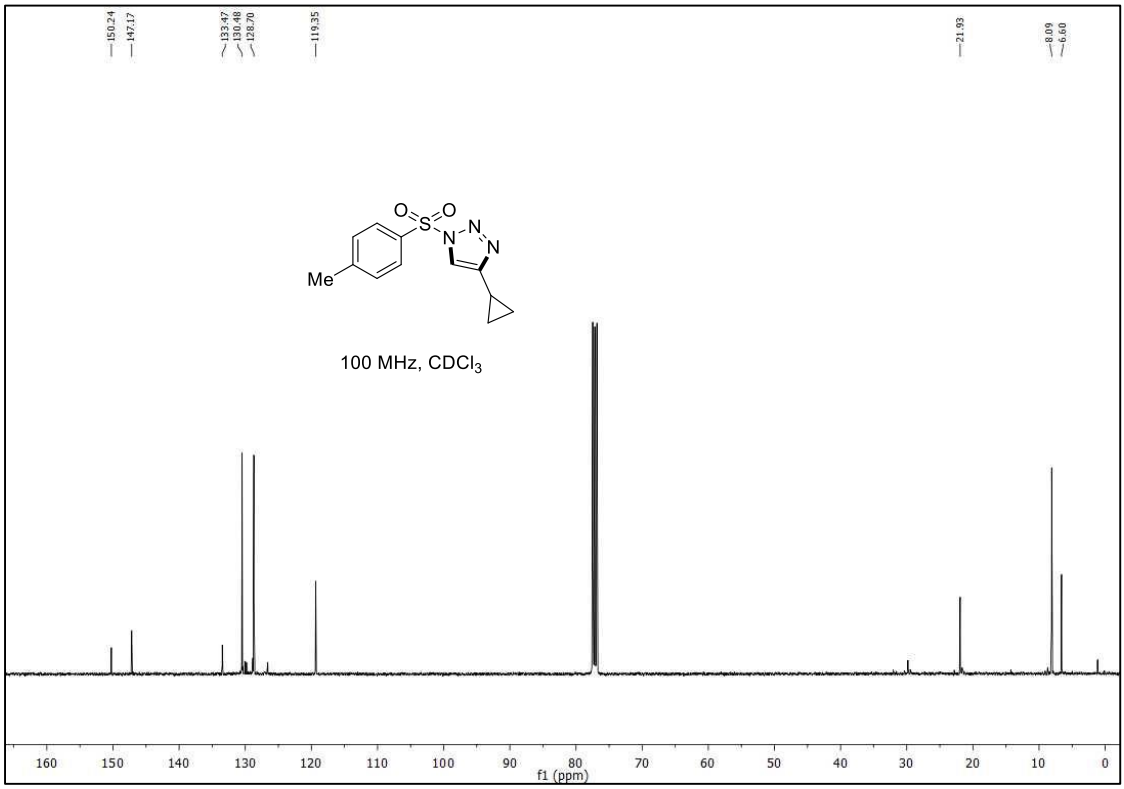
^{1}H and ^{13}C NMR spectra of 3o:



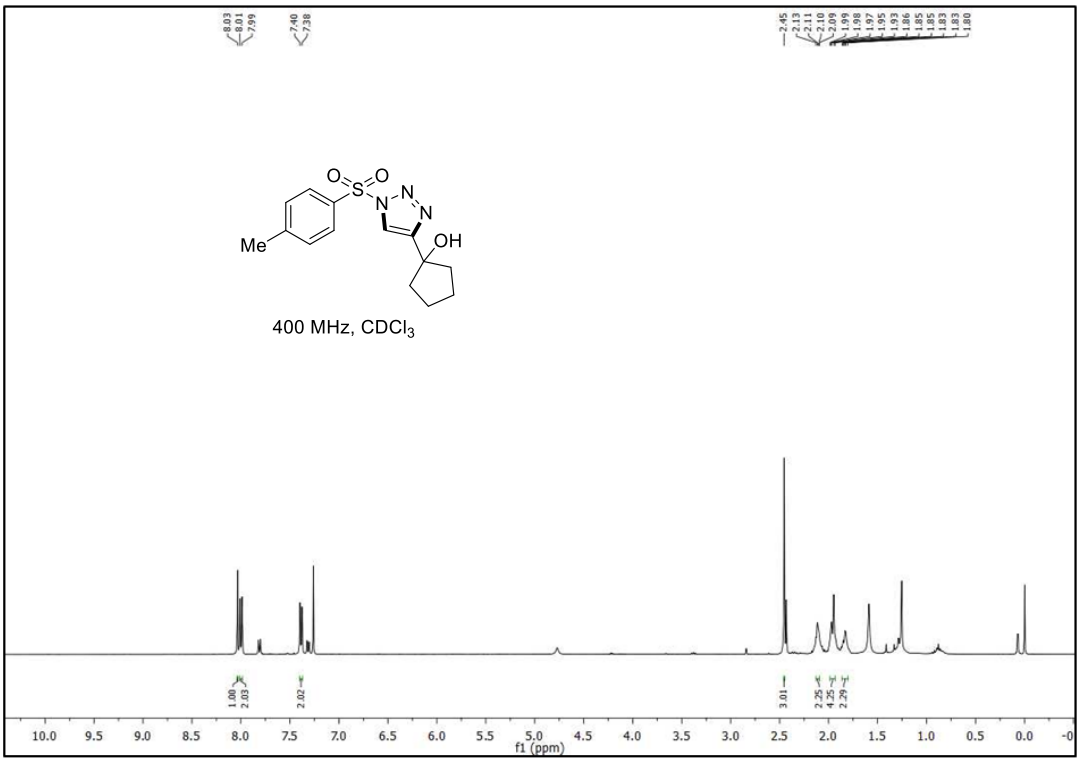


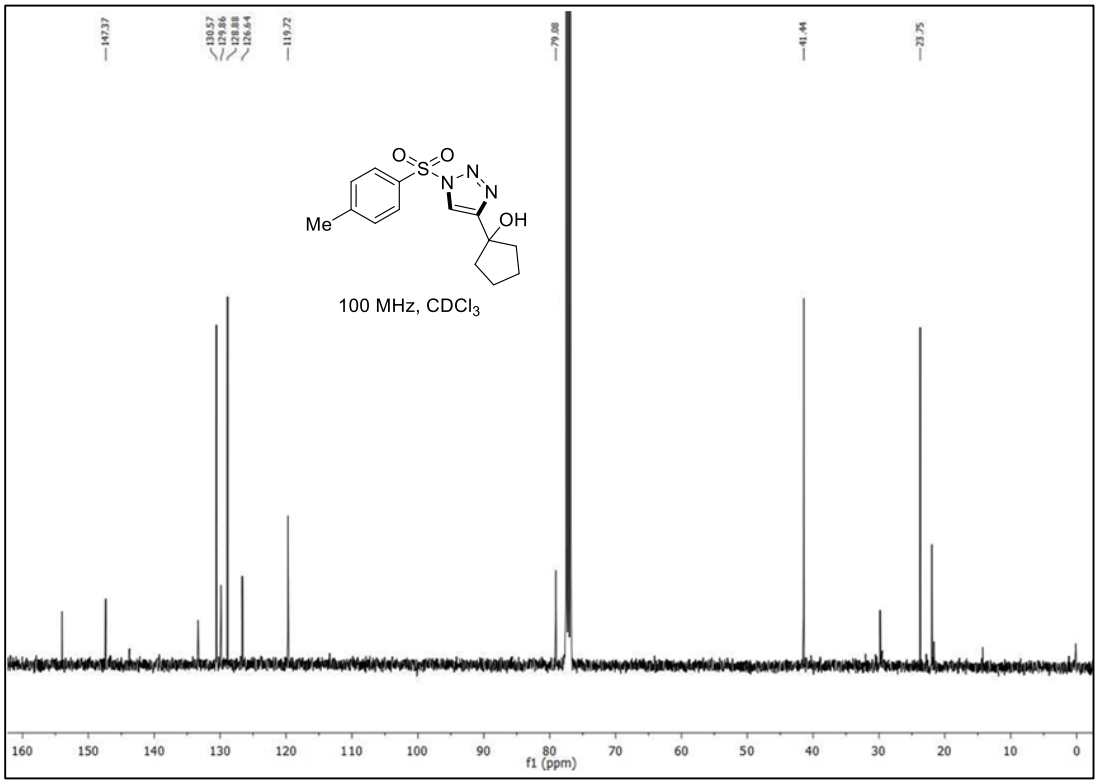
^{1}H and ^{13}C NMR spectra of 3p:



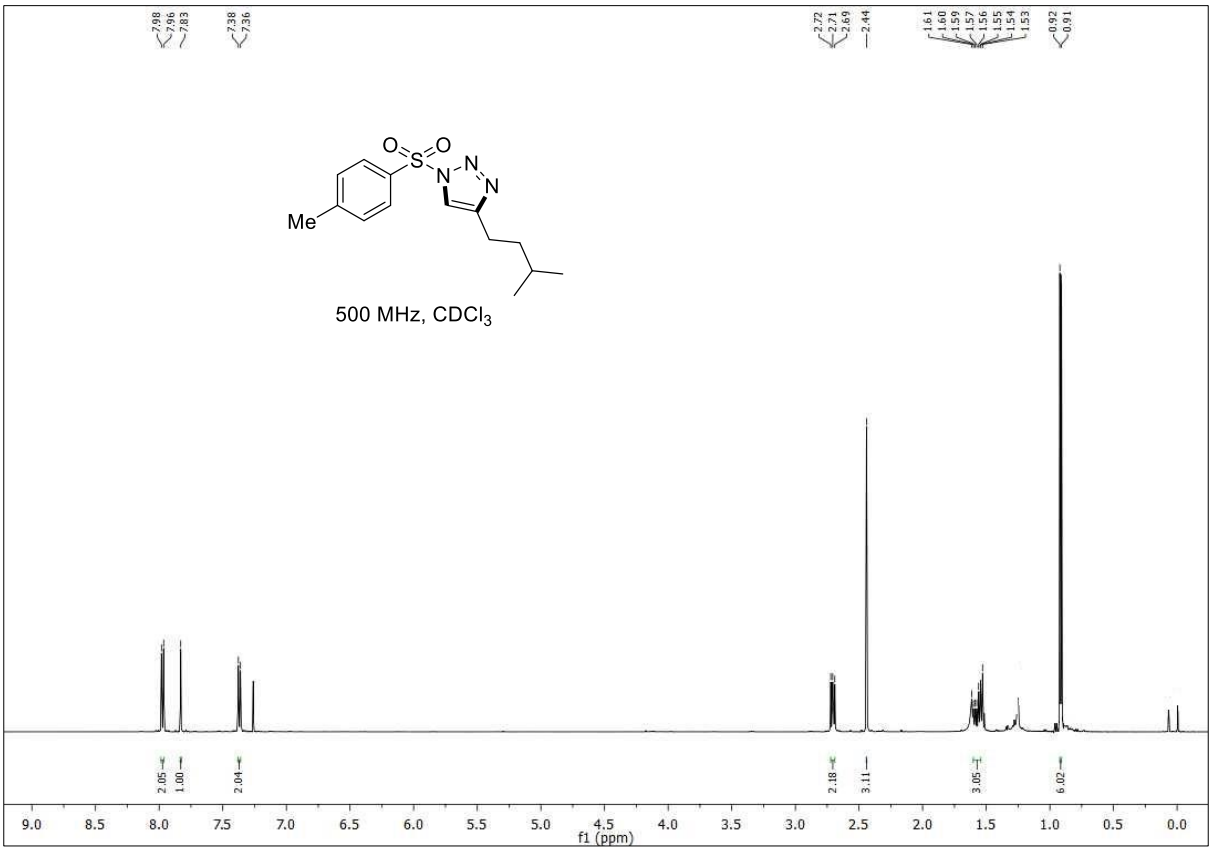


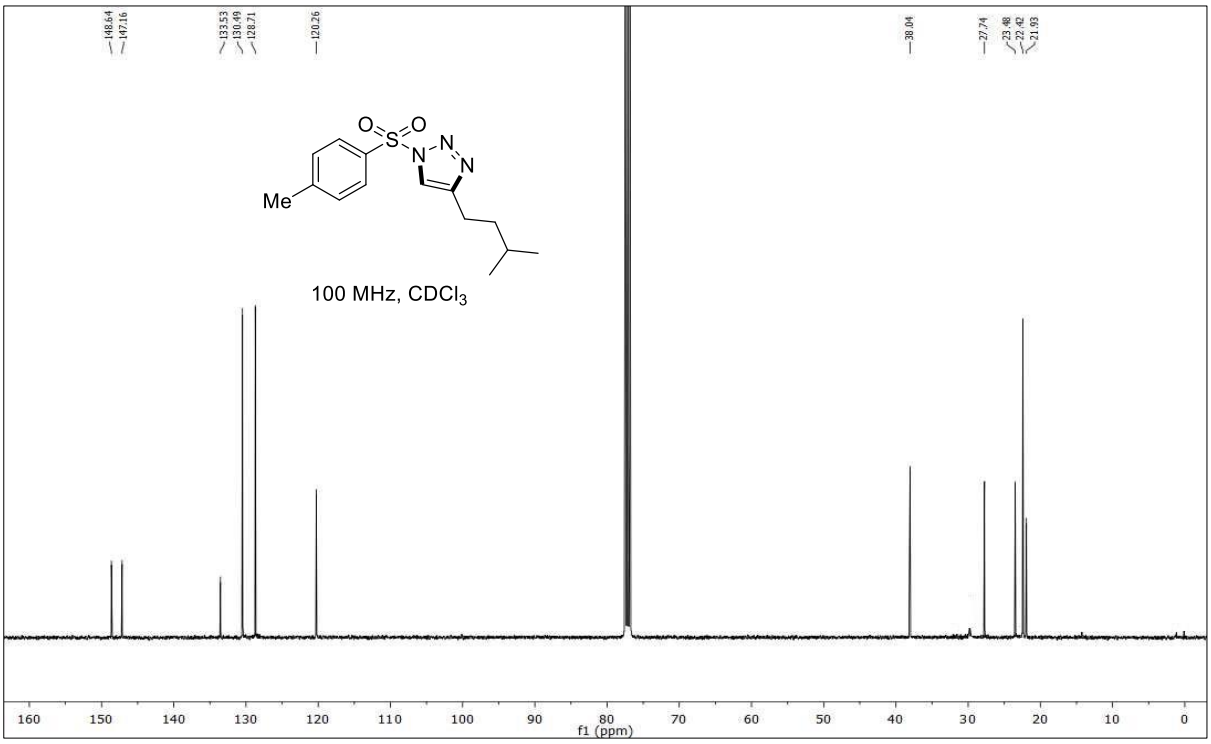
^{1}H and ^{13}C NMR spectra of 3q:



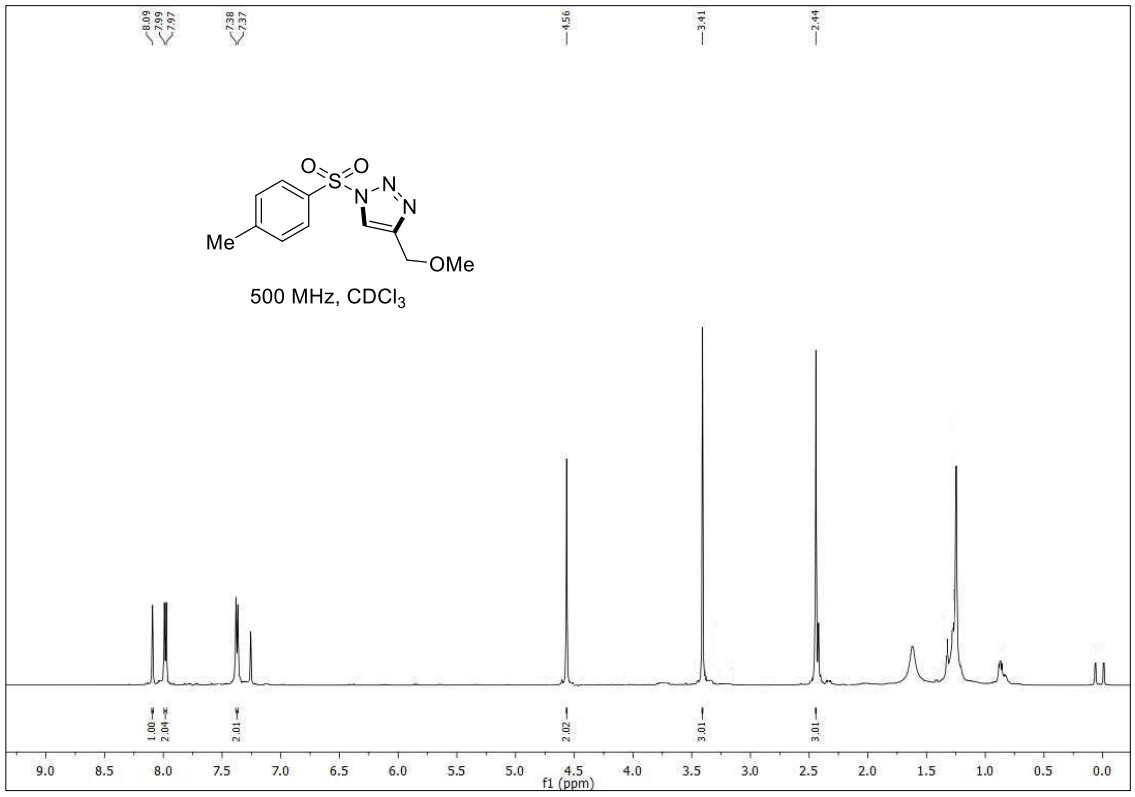


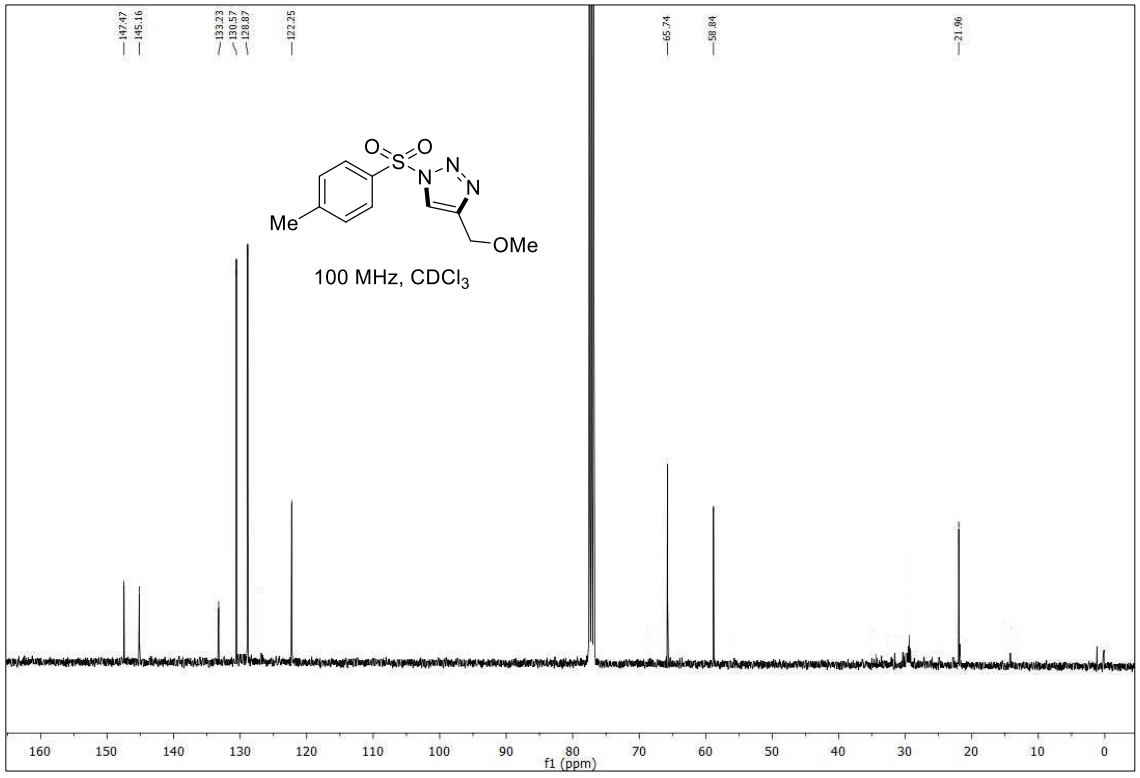
^{1}H and ^{13}C NMR spectra of 3r:



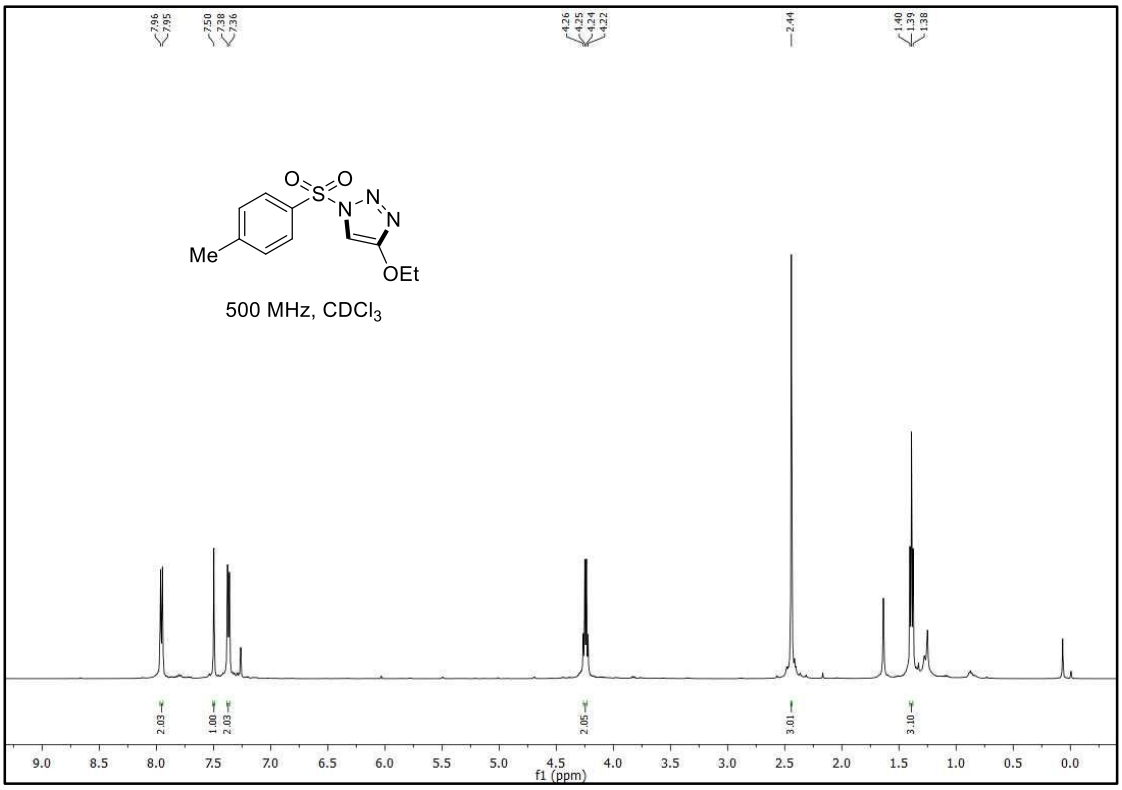


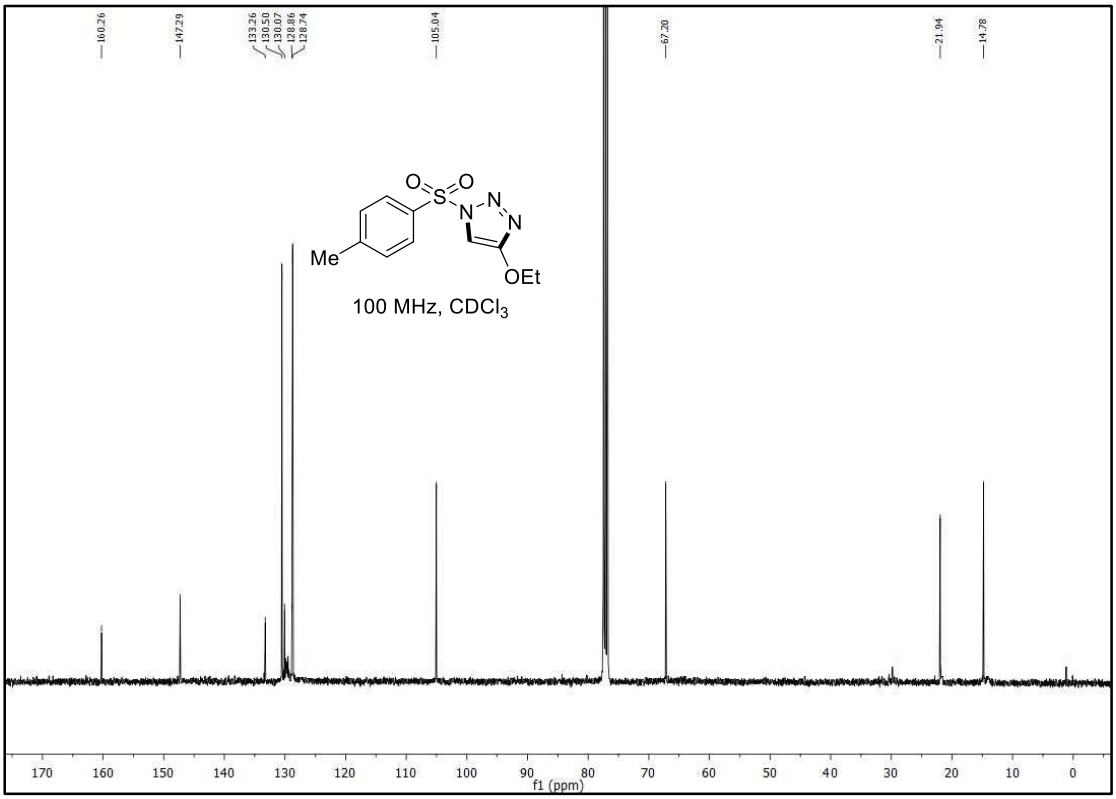
^{1}H and ^{13}C NMR spectra of 3s:



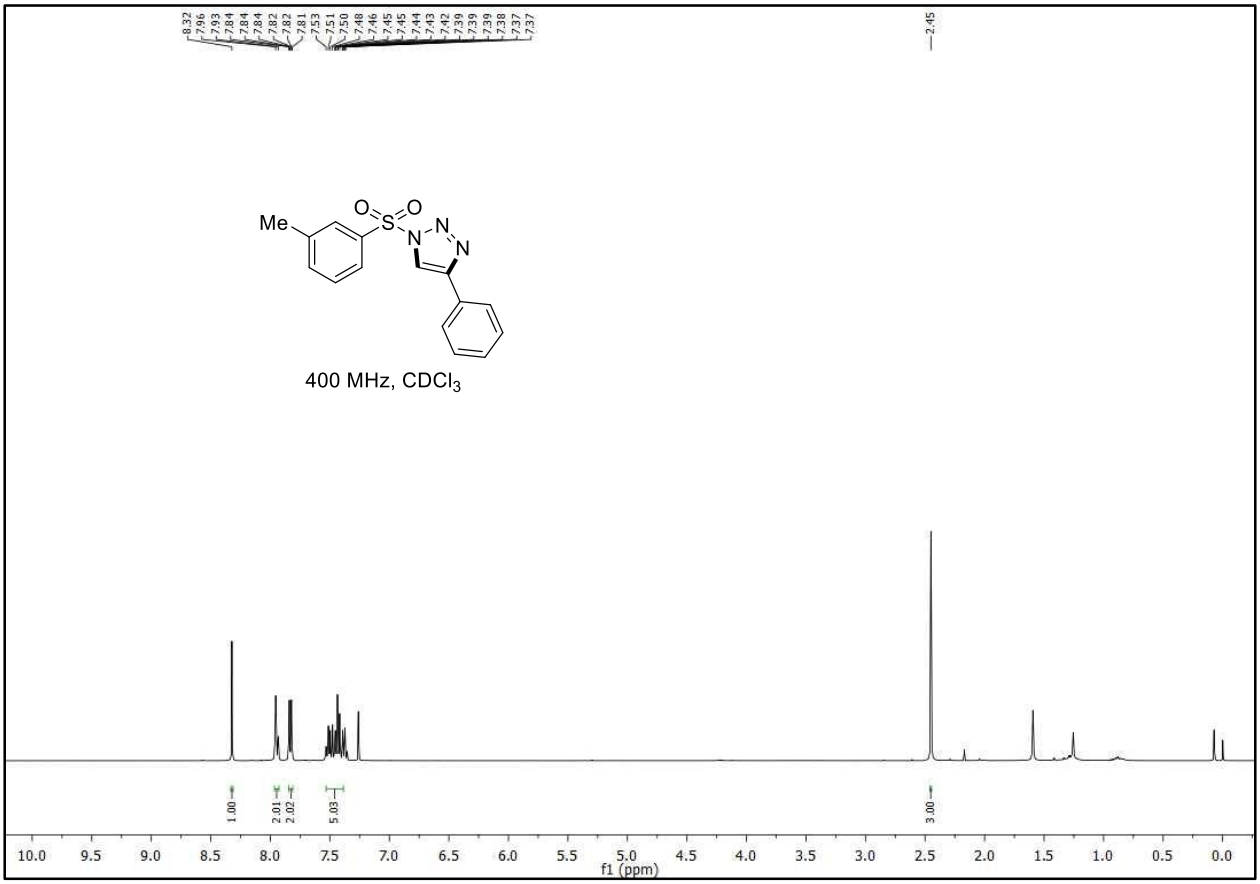


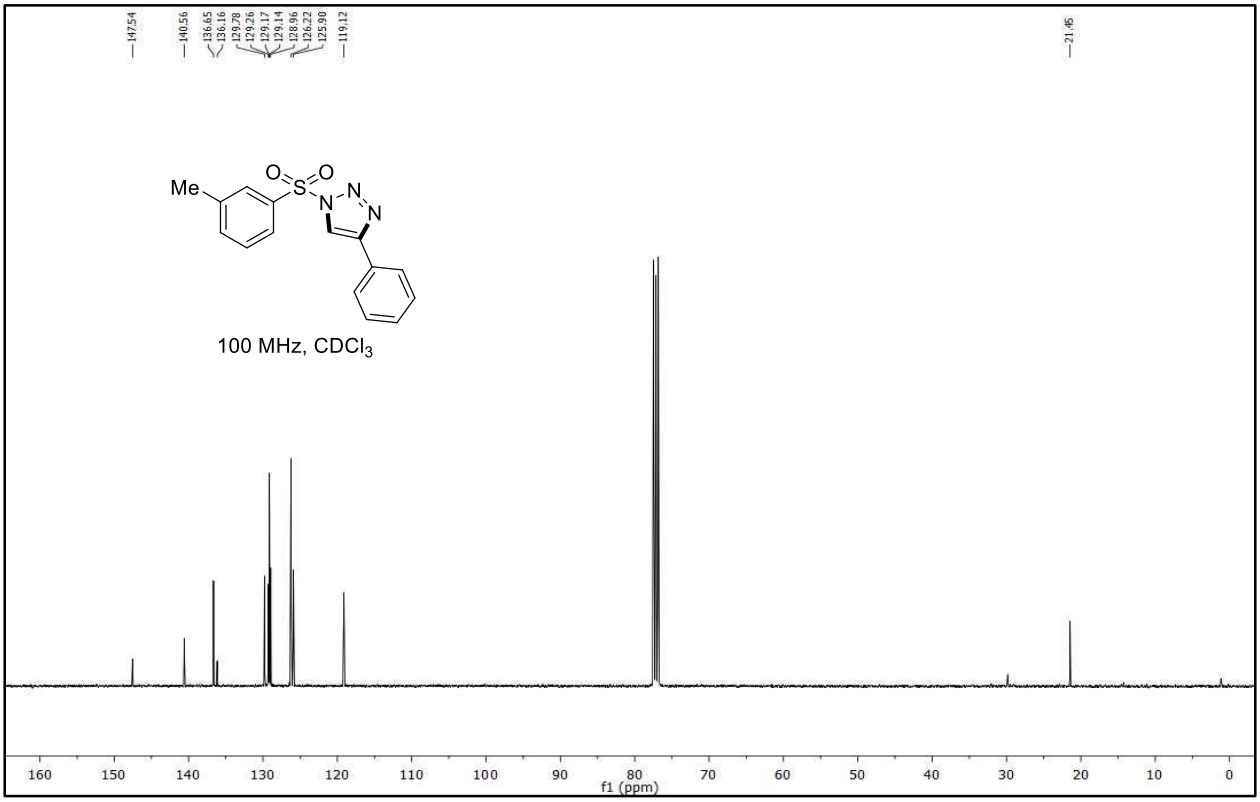
^{1}H and ^{13}C NMR spectra of 3t:



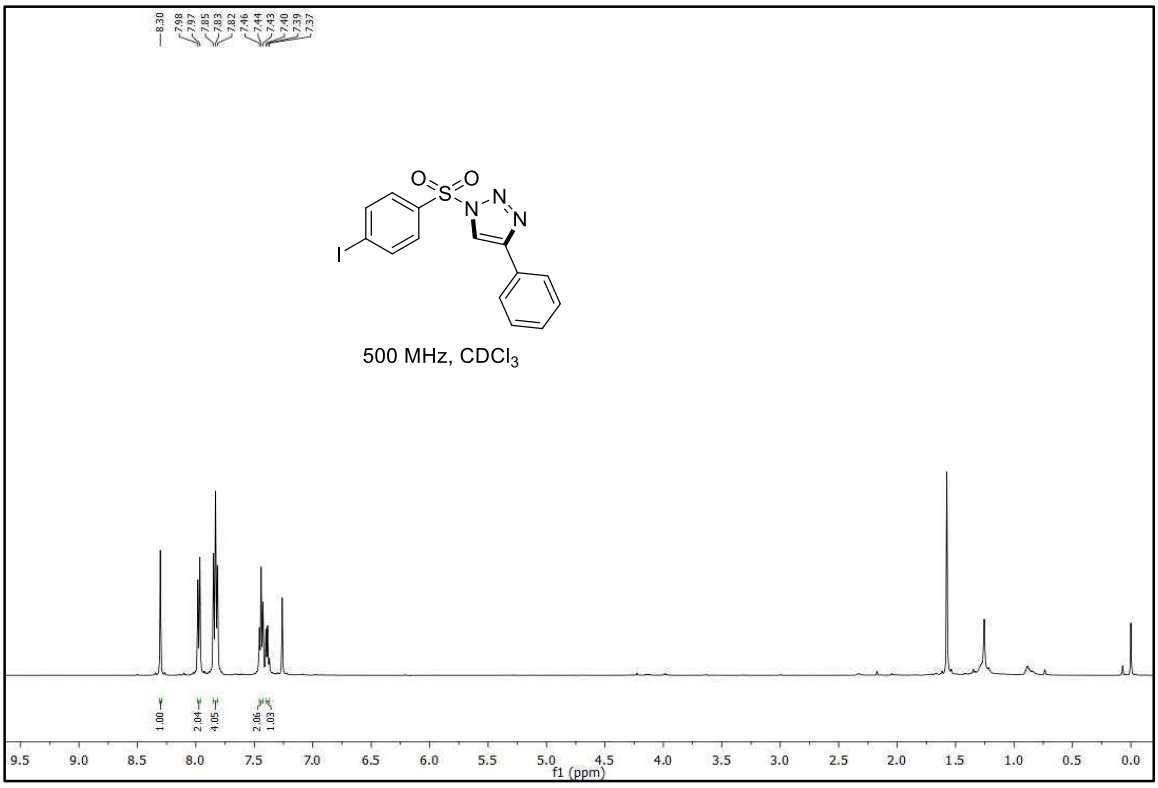


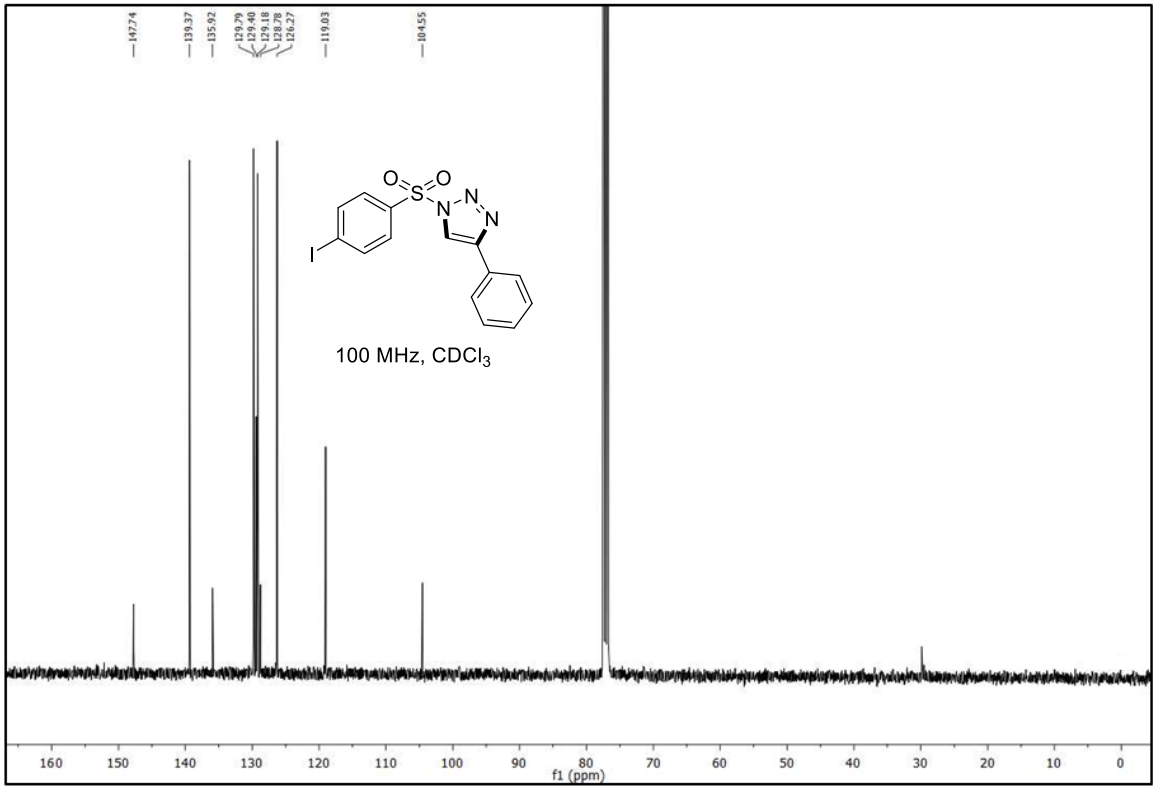
^{1}H and ^{13}C NMR spectra of 3u:



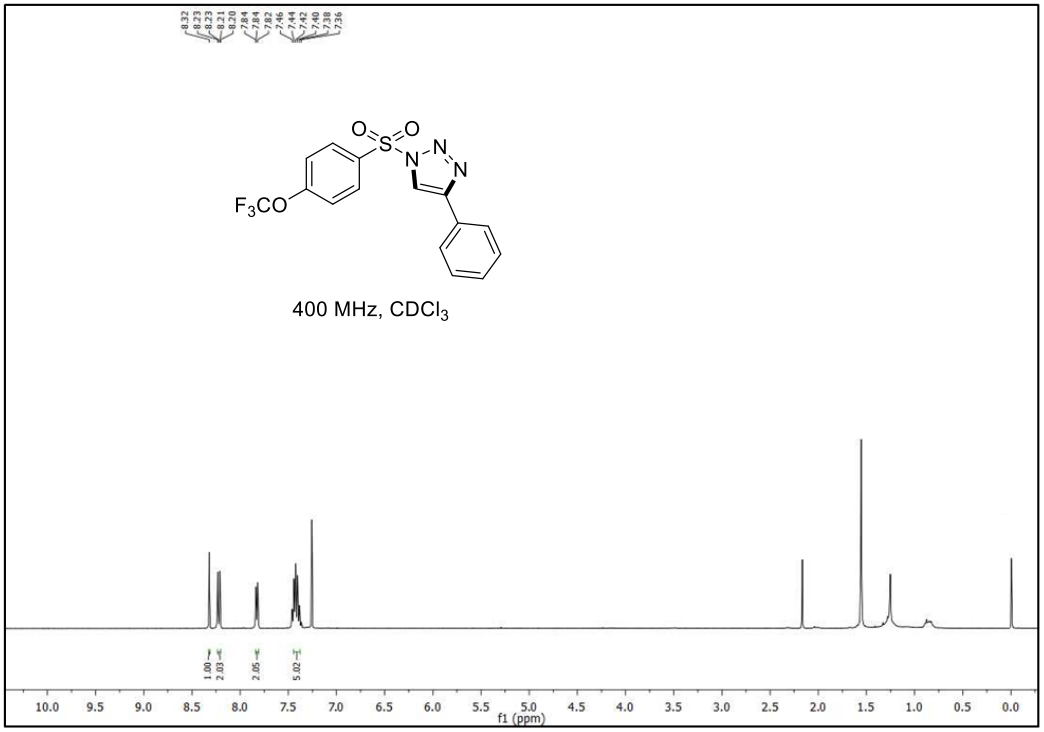


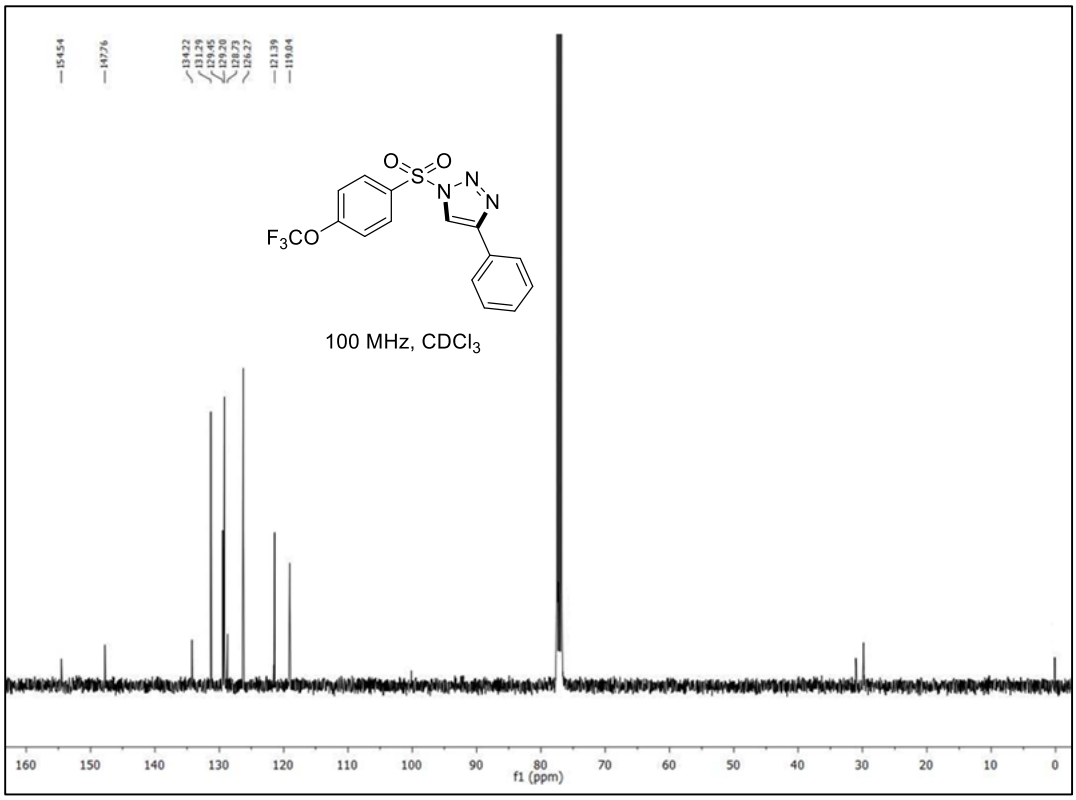
^{1}H and ^{13}C NMR spectra of 3v:



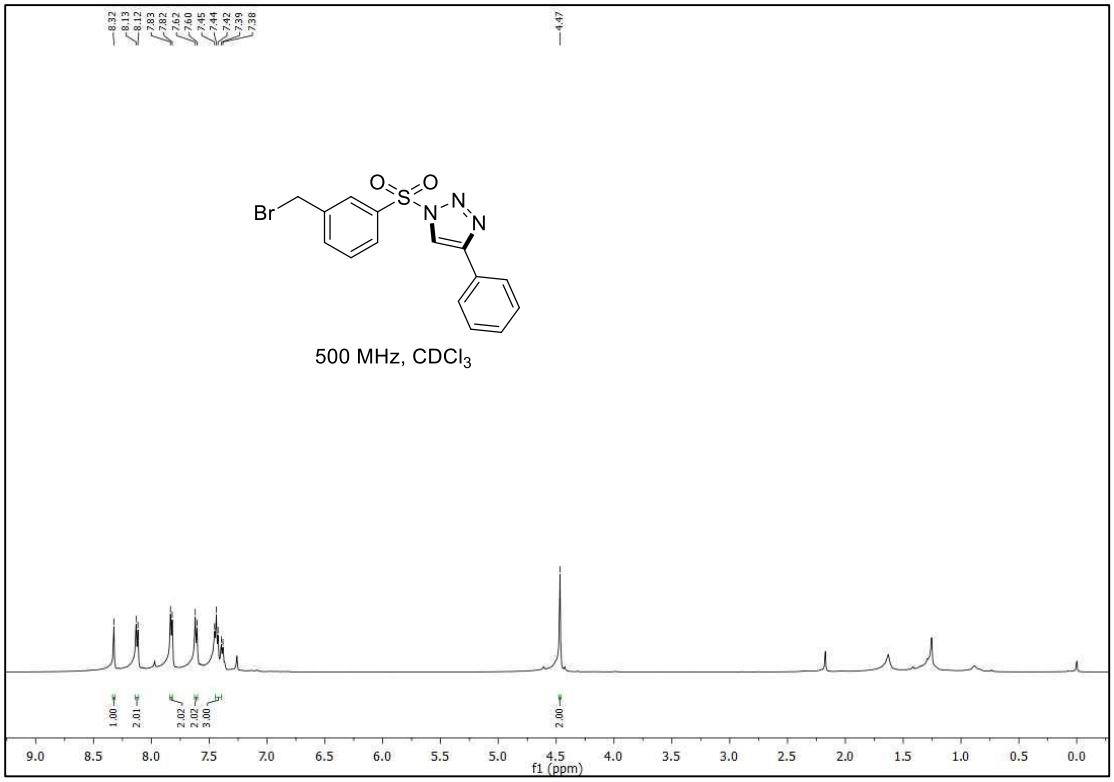


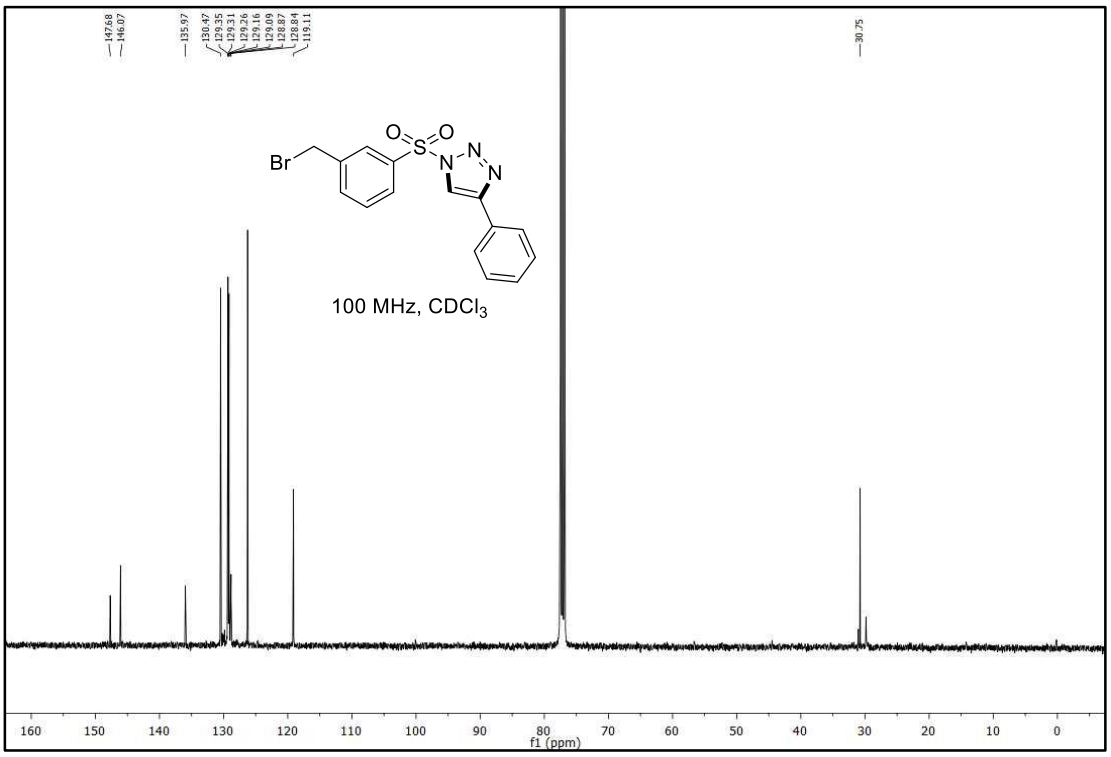
^{1}H and ^{13}C NMR spectra of 3w:



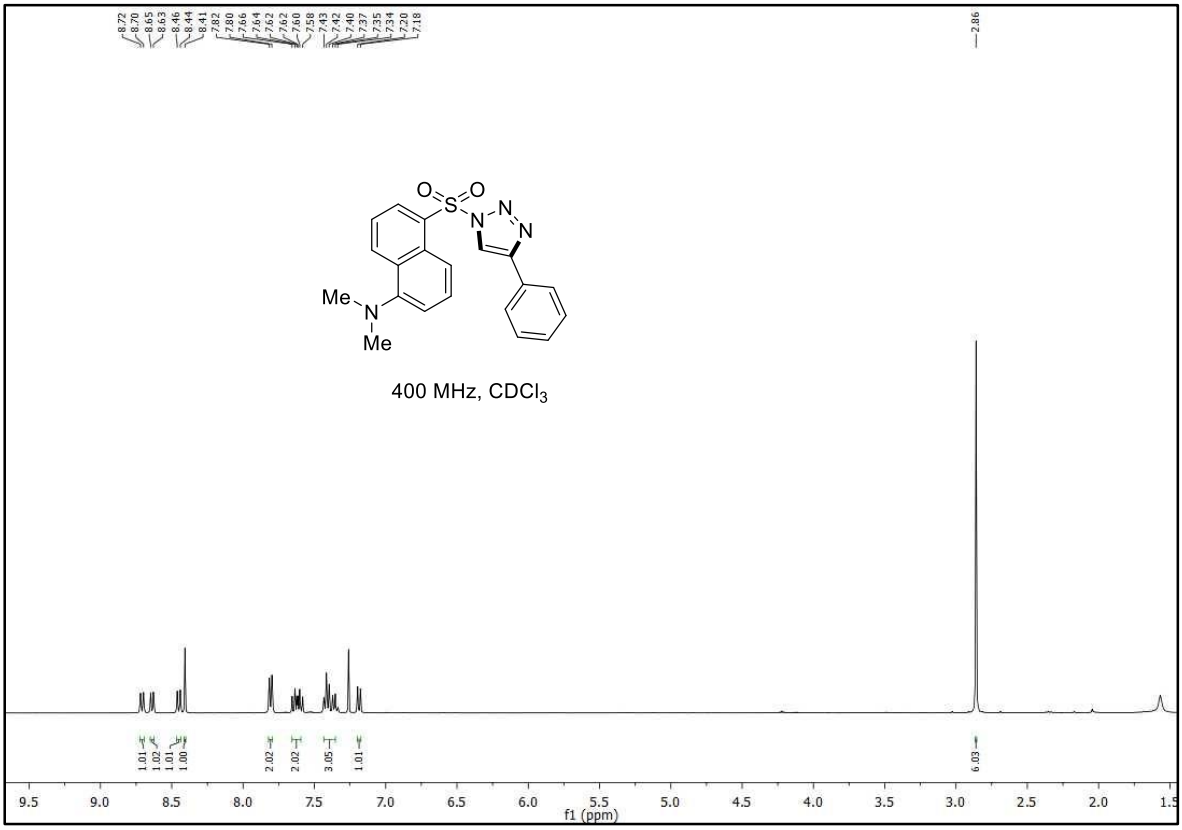


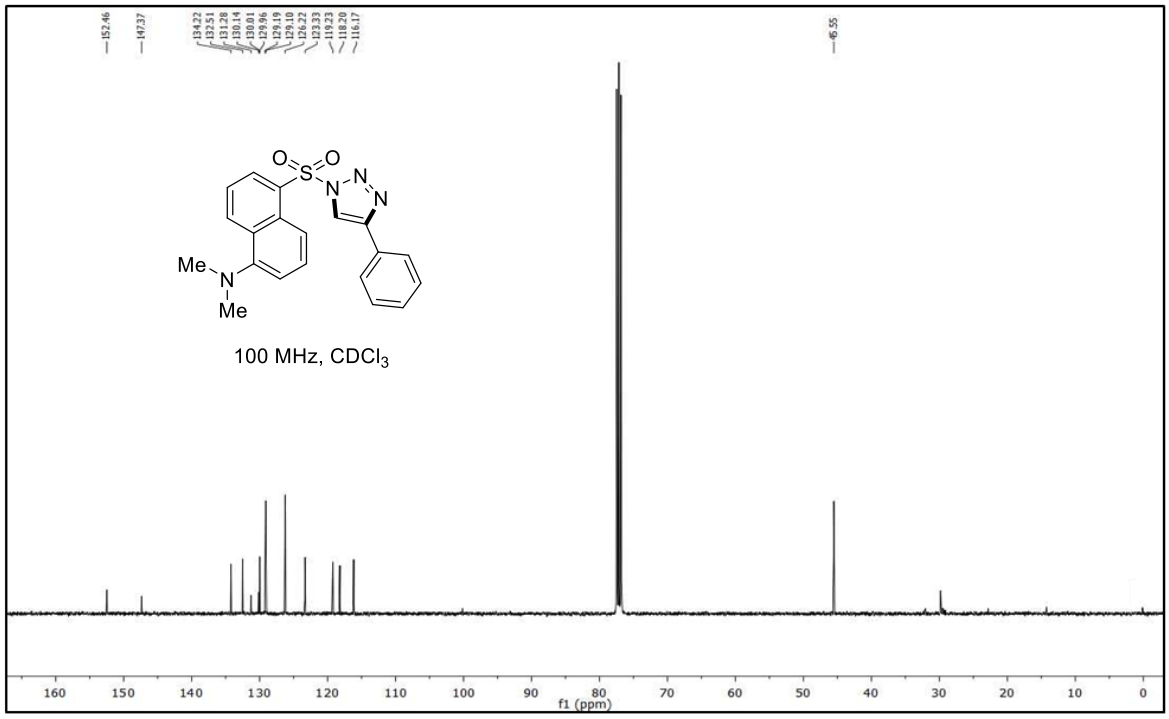
^{1}H and ^{13}C NMR spectra of 3x:



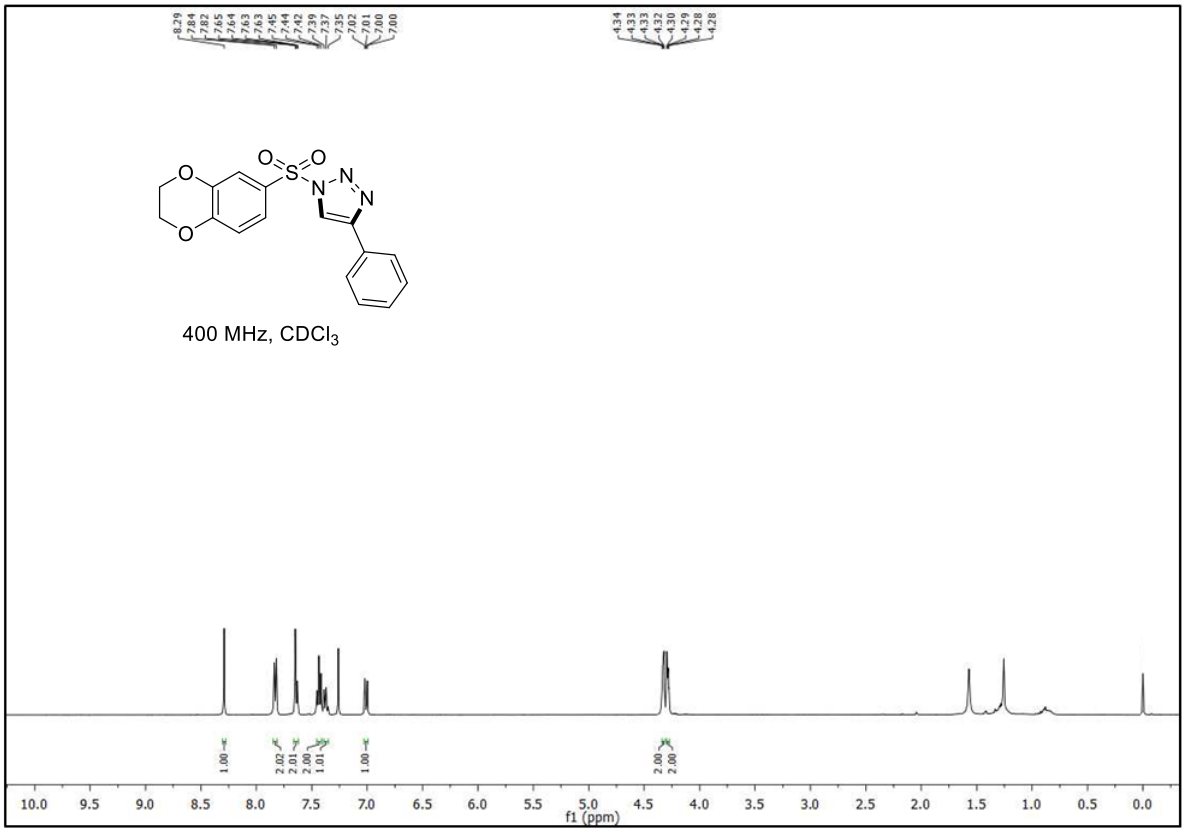


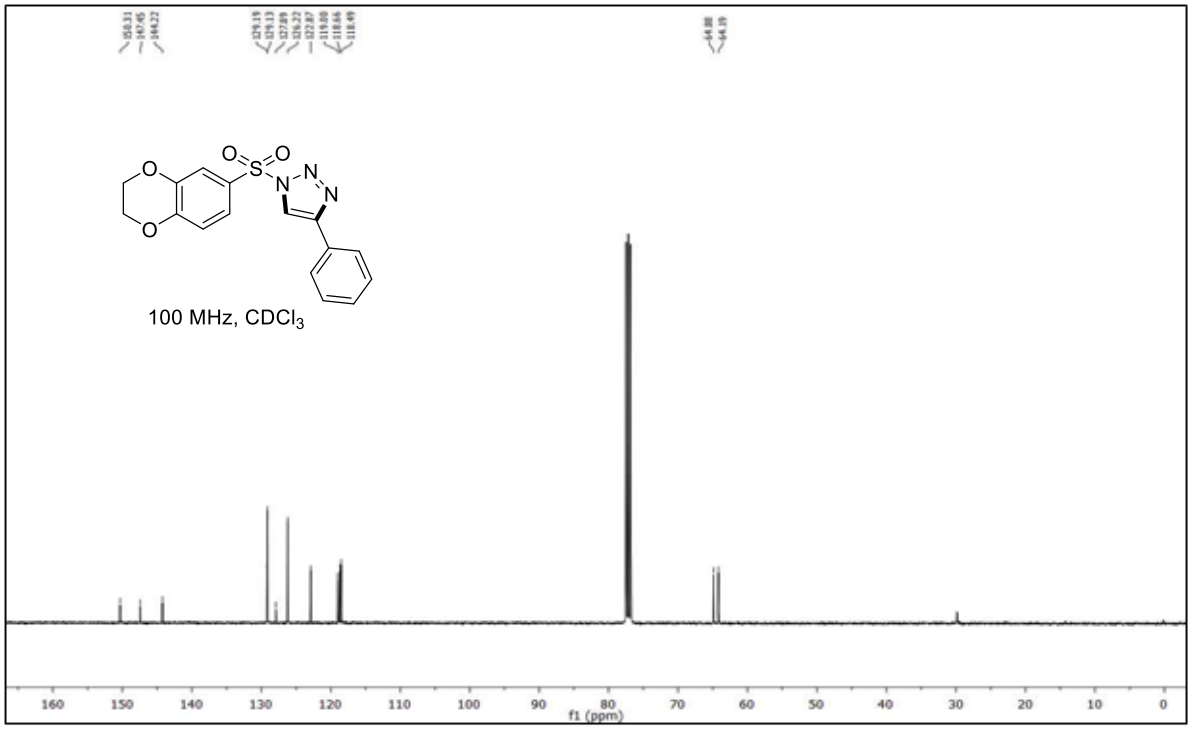
^{1}H and ^{13}C NMR spectra of 3y:



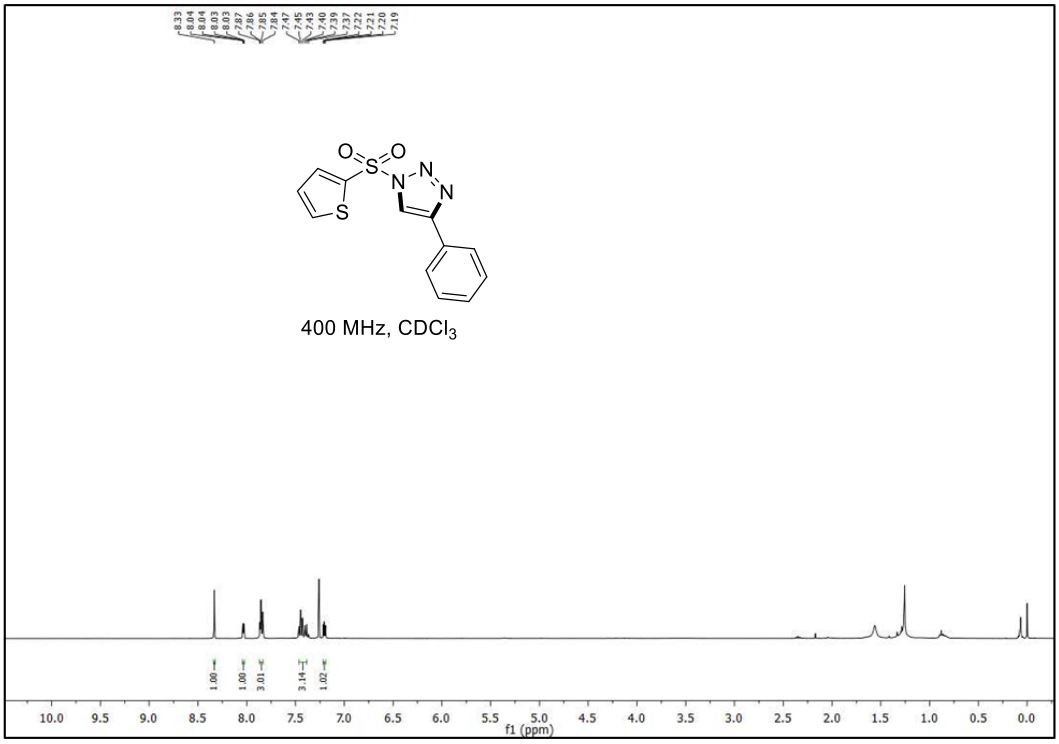


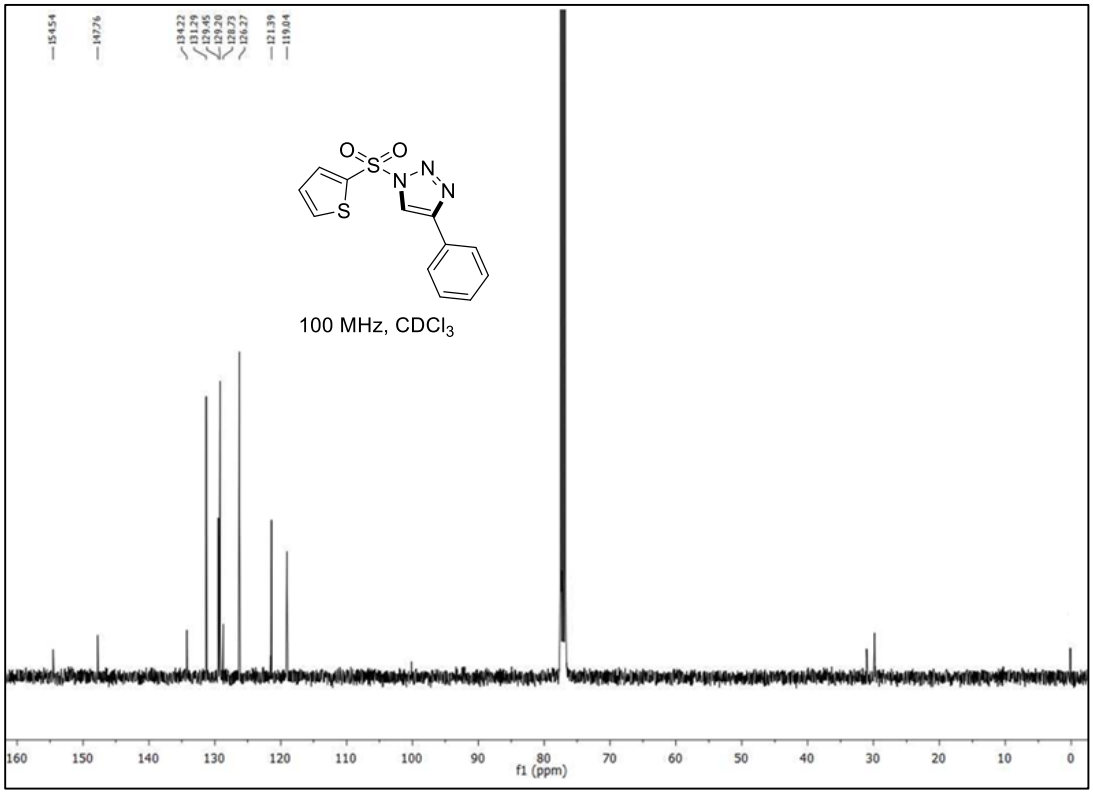
^{1}H and ^{13}C NMR spectra of 3z:



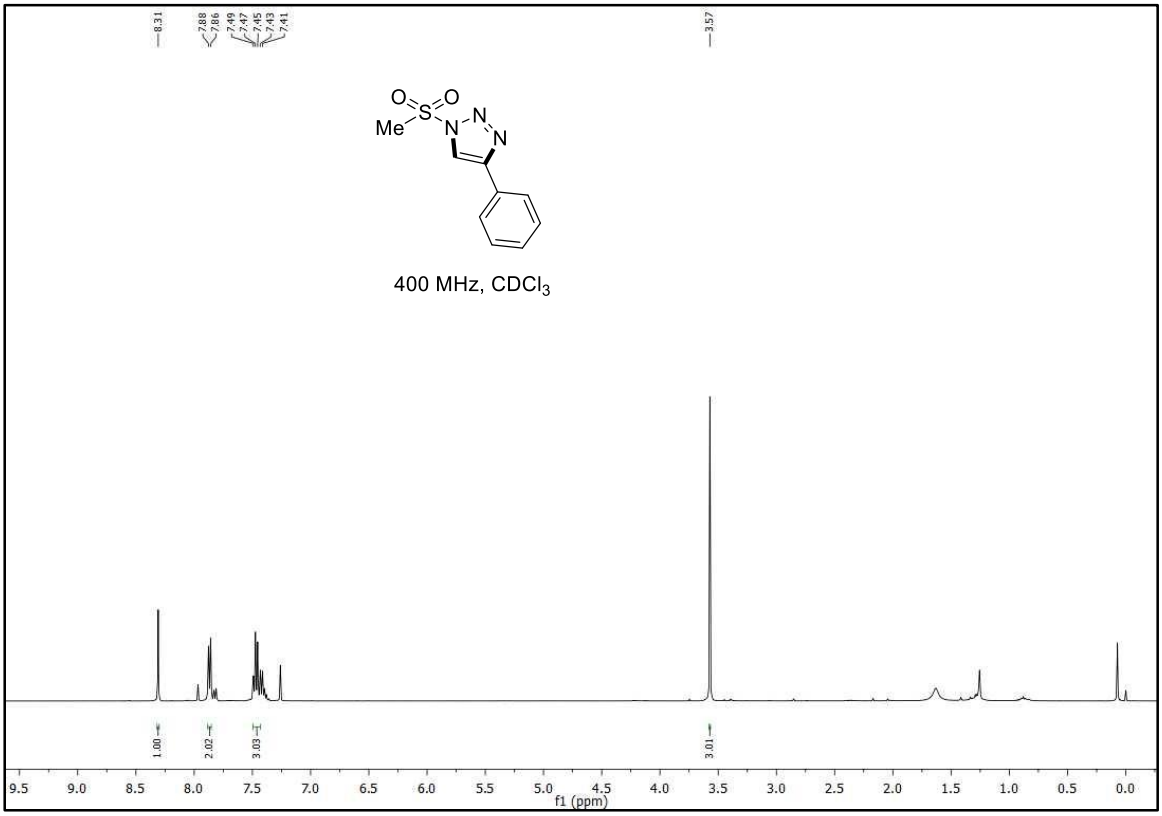


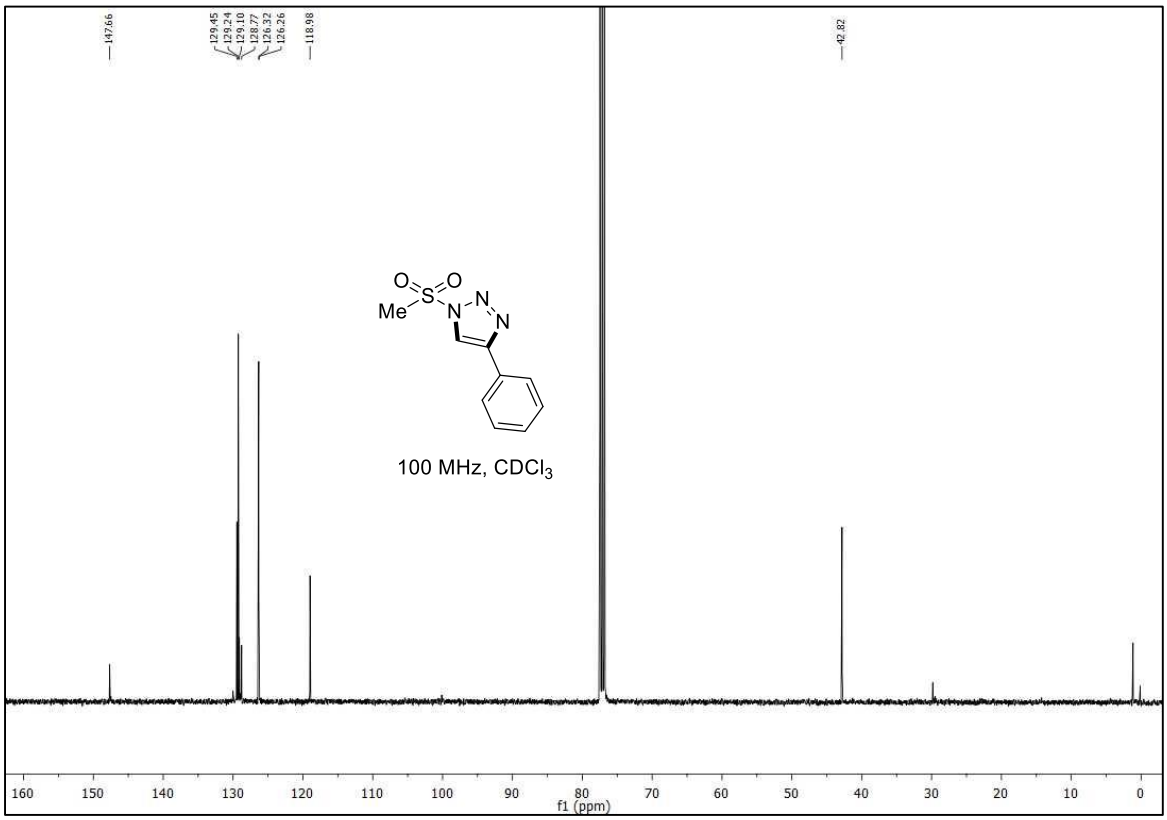
^{1}H and ^{13}C NMR spectra of 3aa:



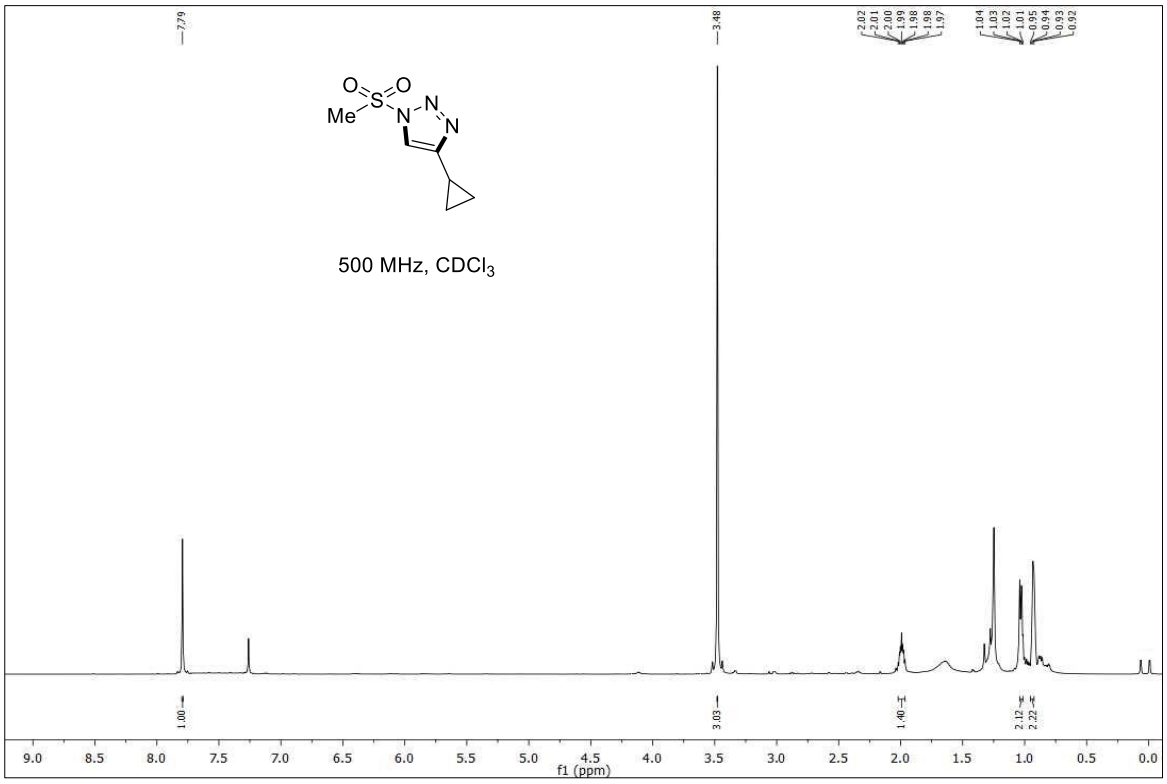


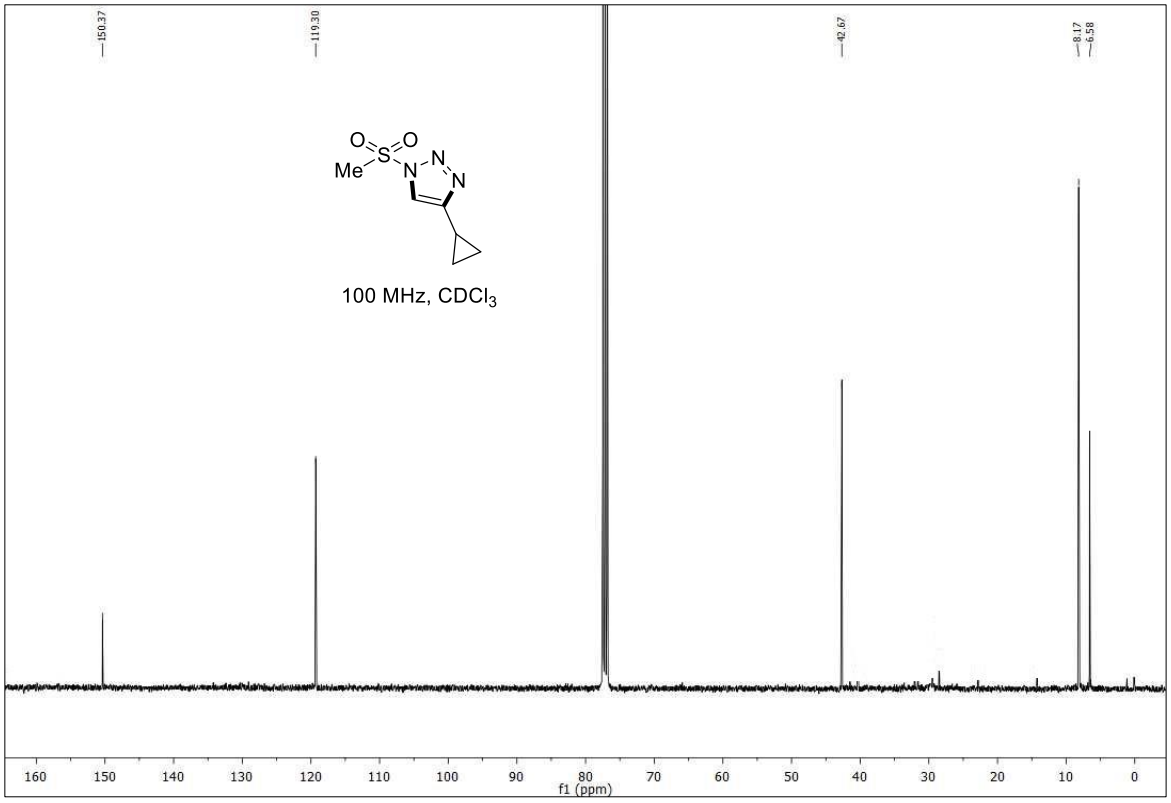
^{1}H and ^{13}C NMR spectra of 3ab:



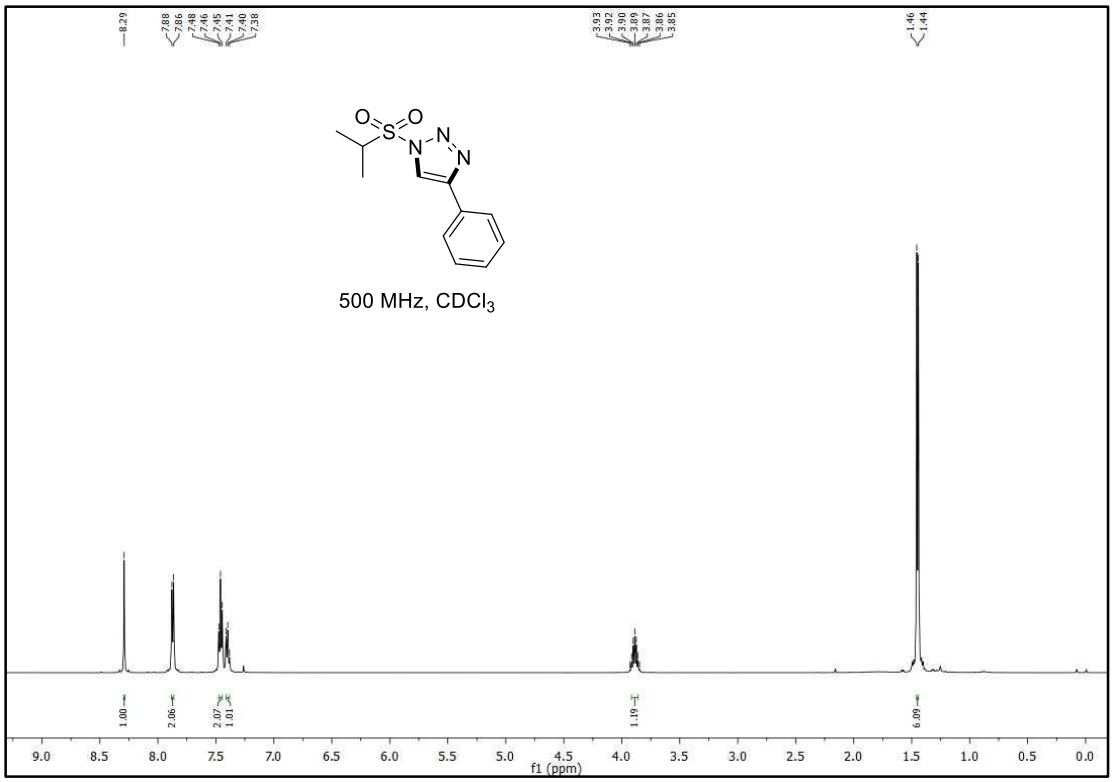


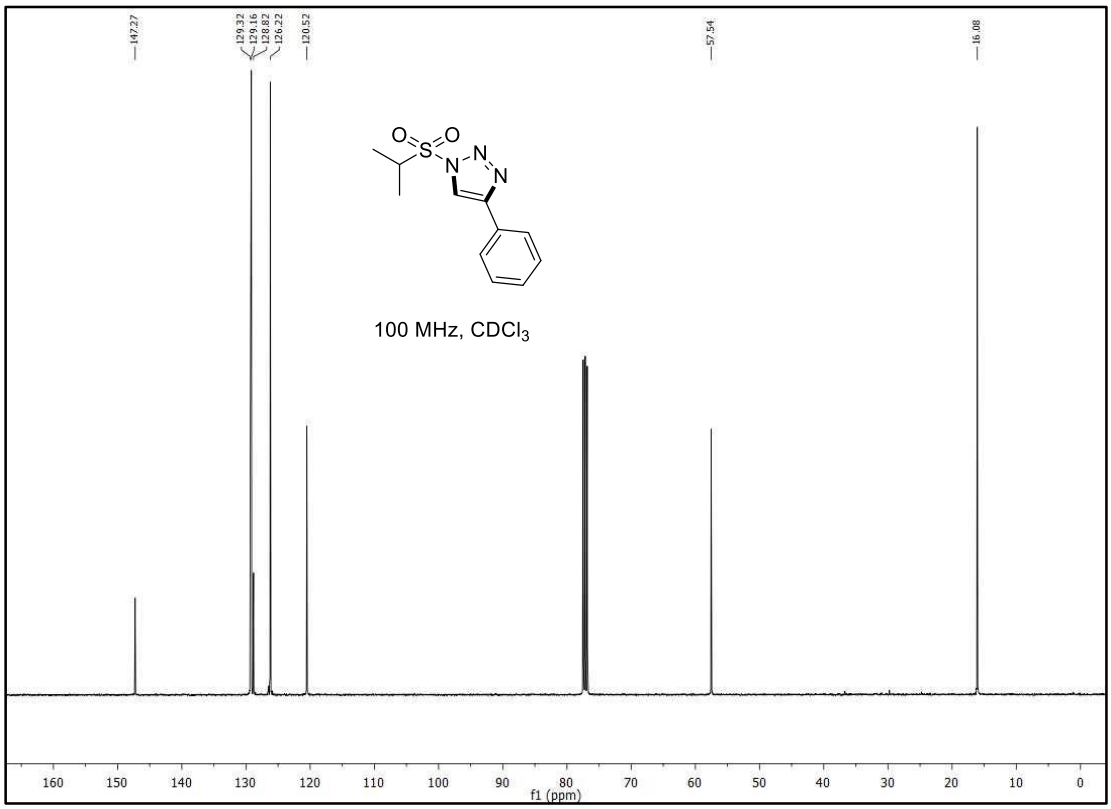
^{1}H and ^{13}C NMR spectra of 3ac:



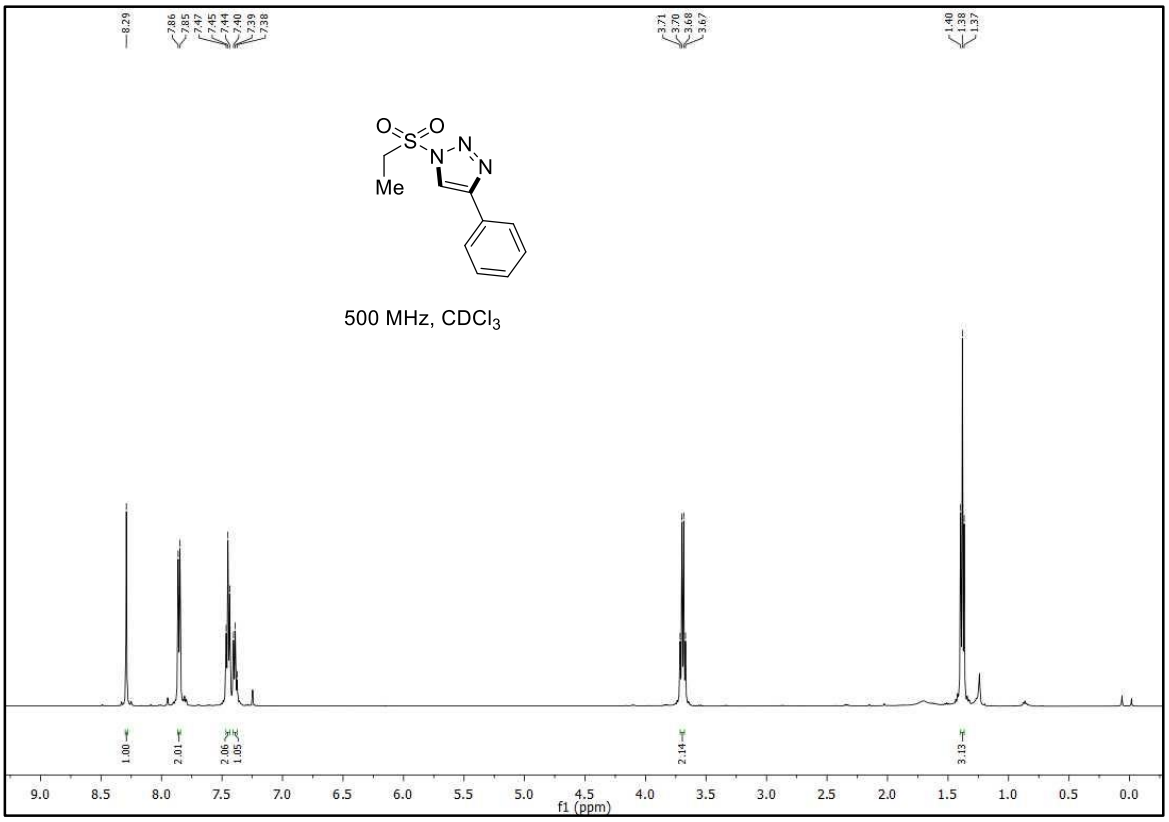


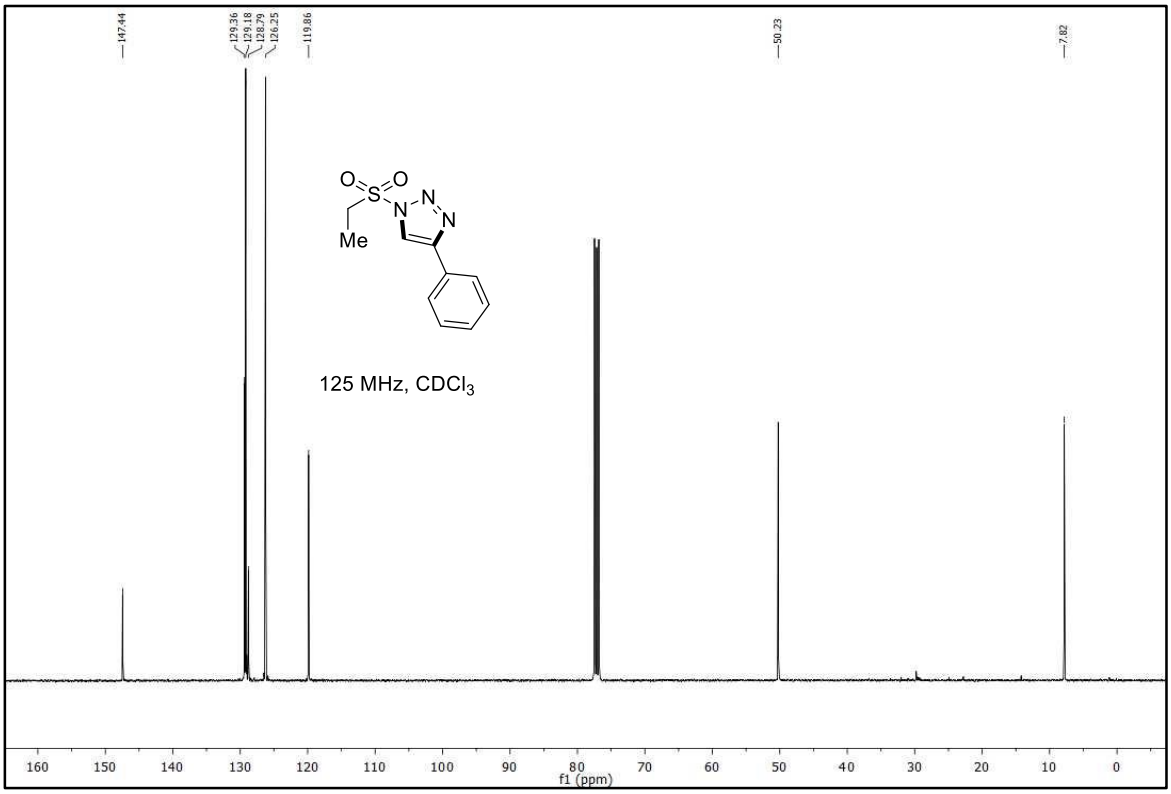
^{1}H and ^{13}C NMR spectra of 3ad:



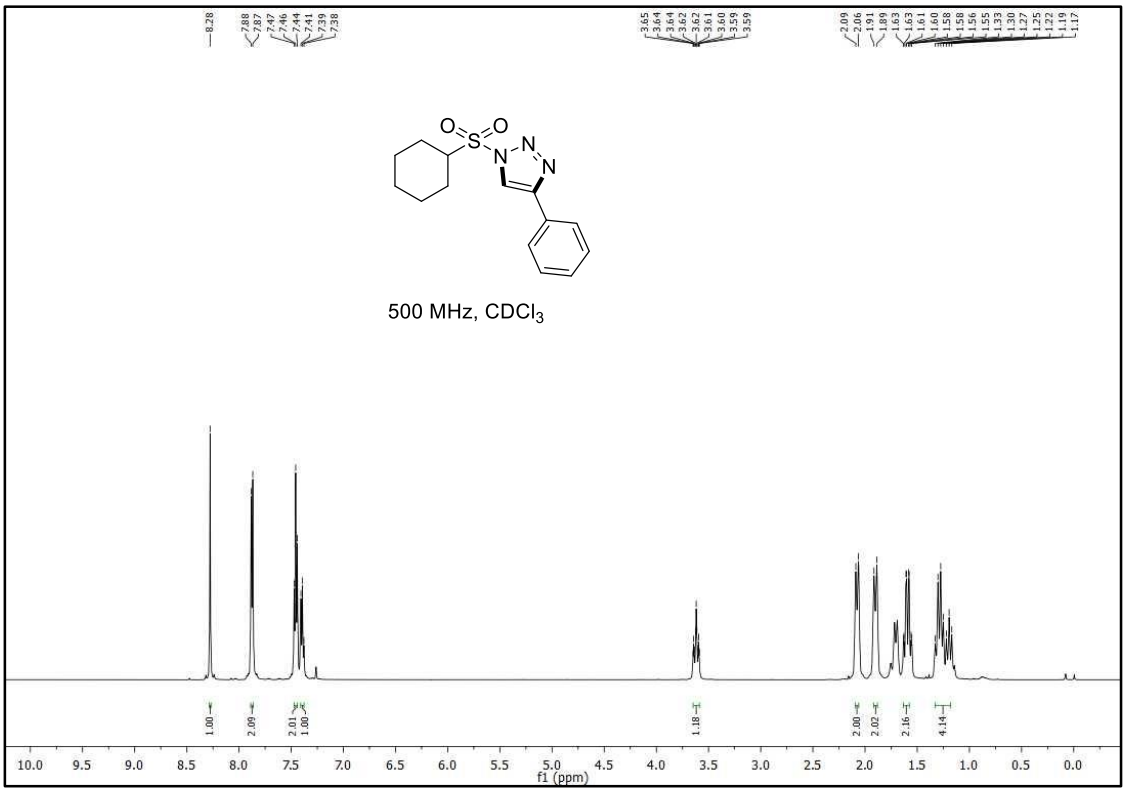


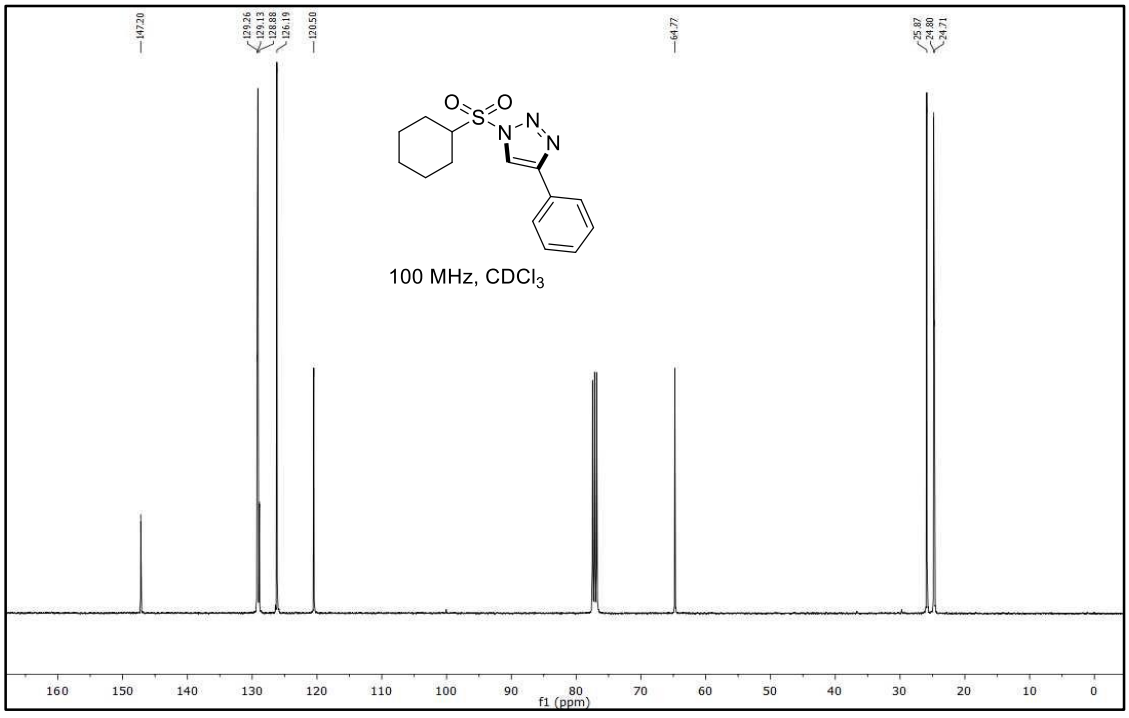
^{1}H and ^{13}C NMR spectra of 3ae:



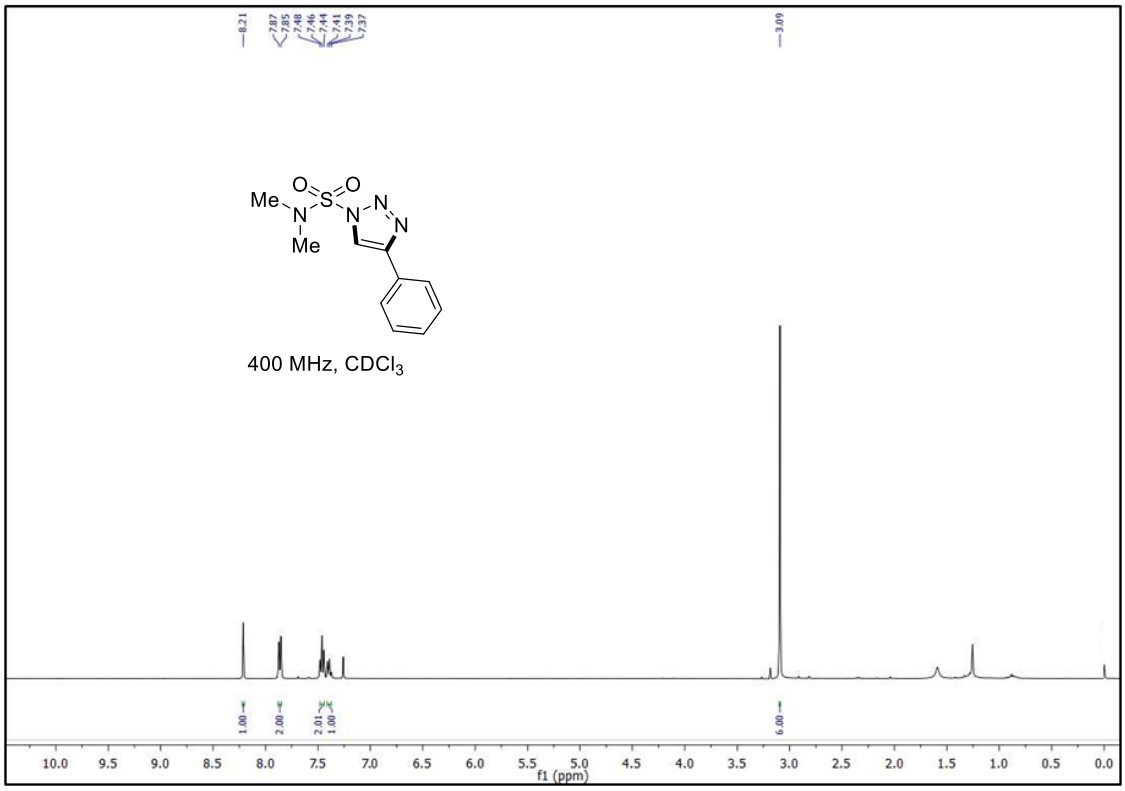


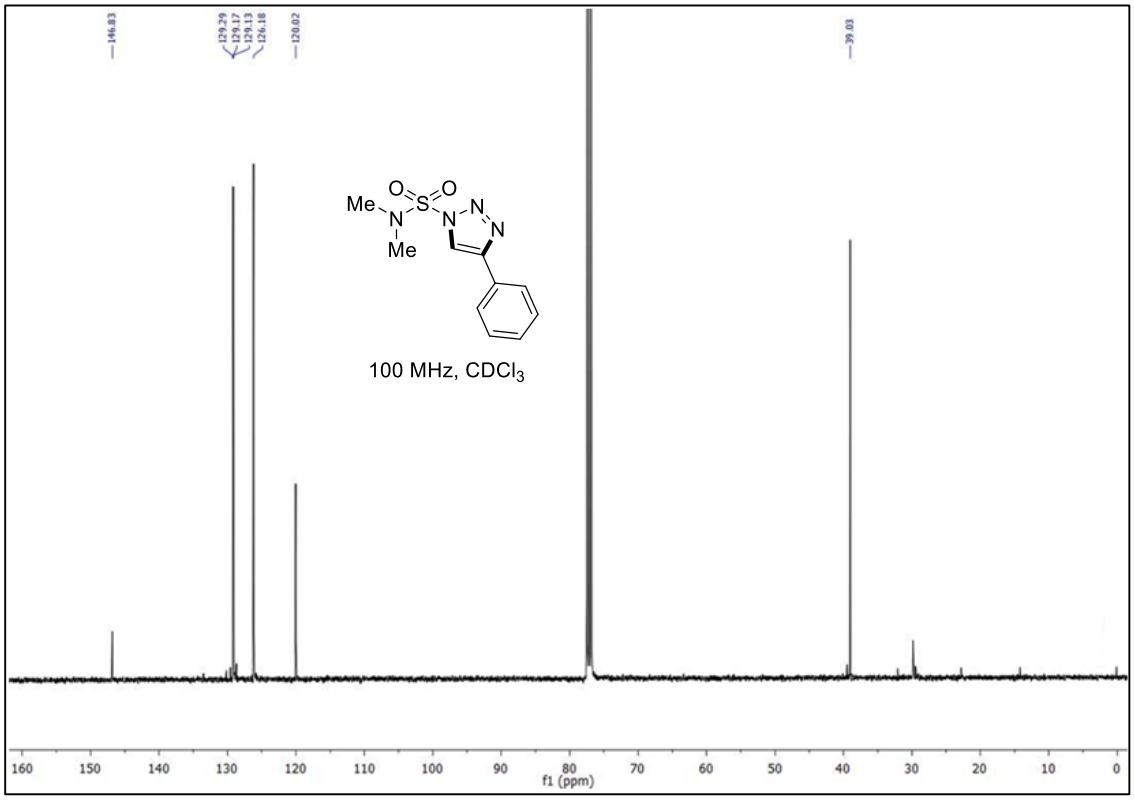
^{1}H and ^{13}C NMR spectra of 3af:



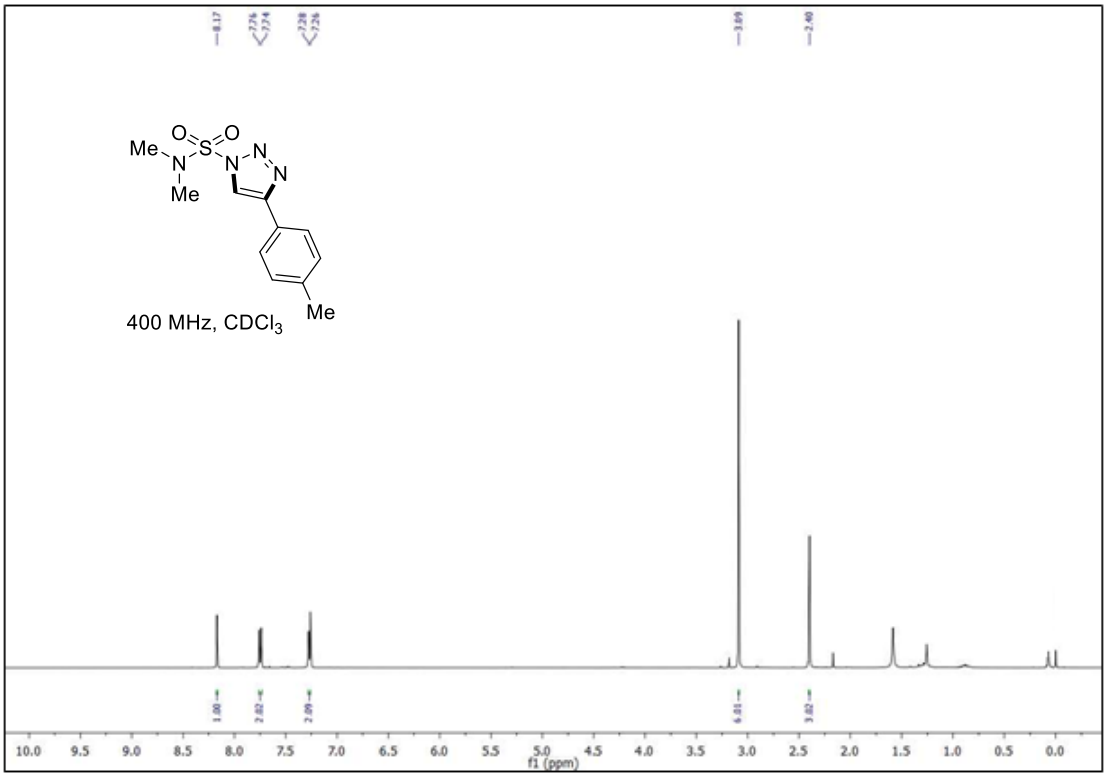


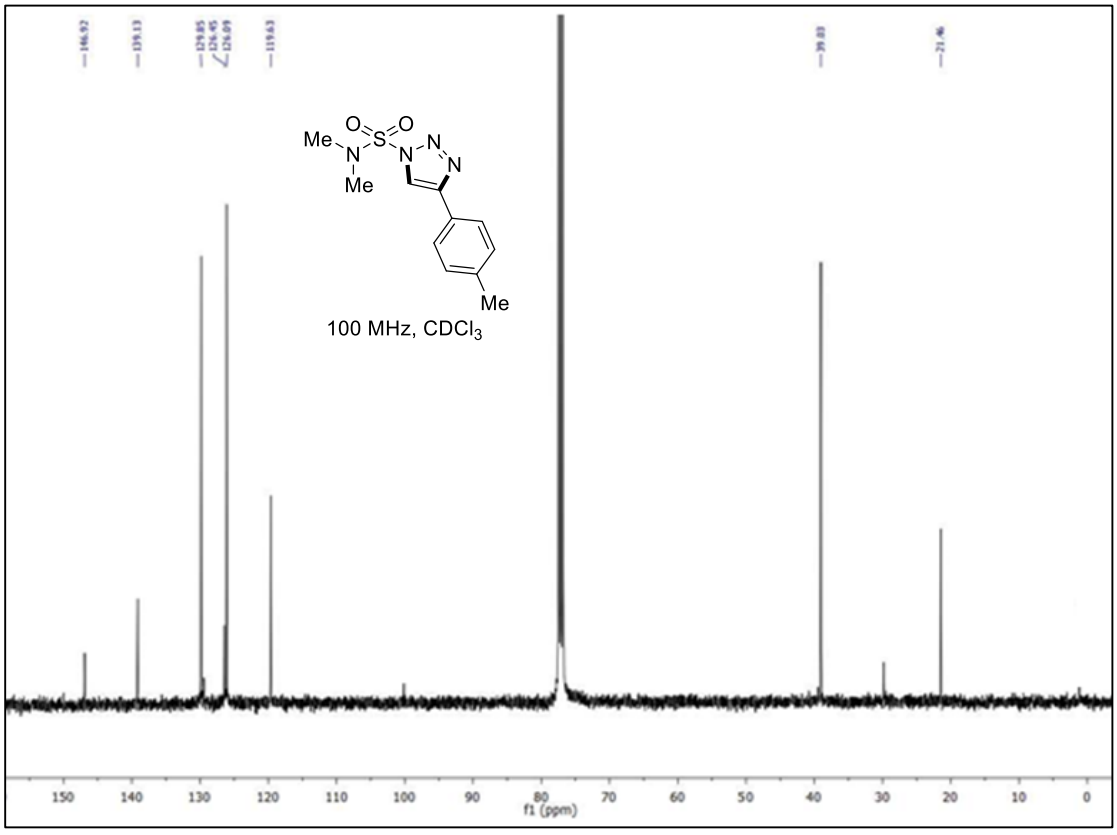
^{1}H and ^{13}C NMR spectra of 5a:



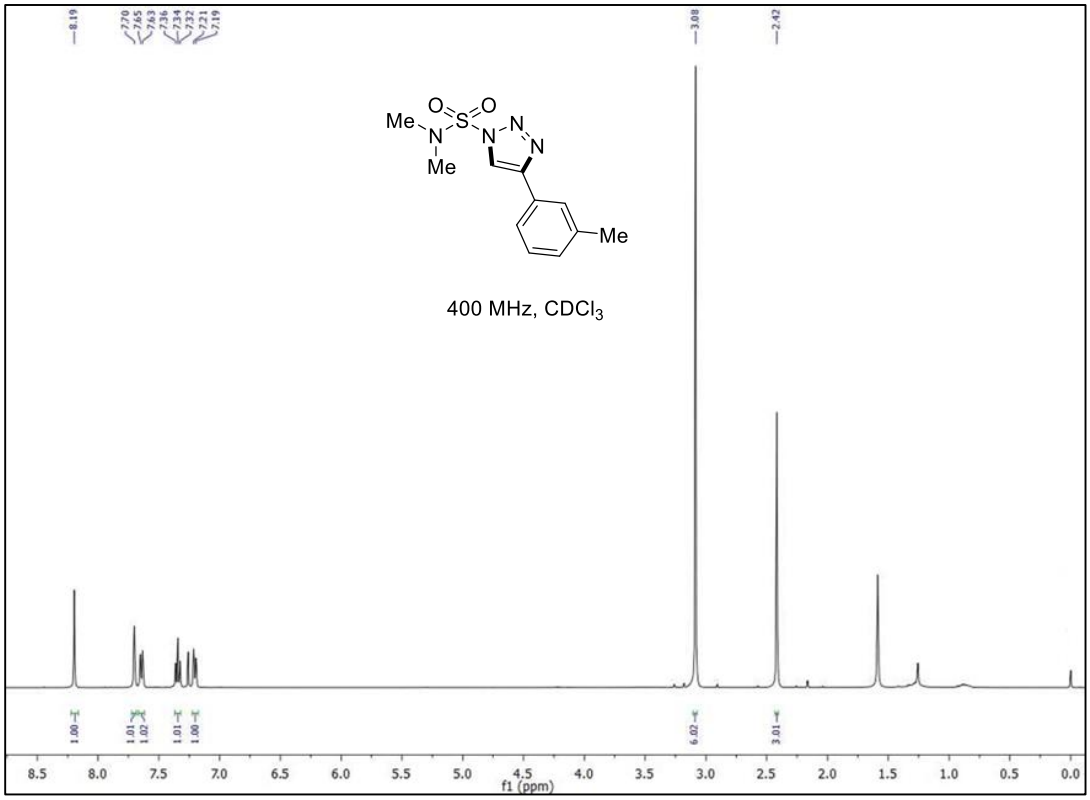


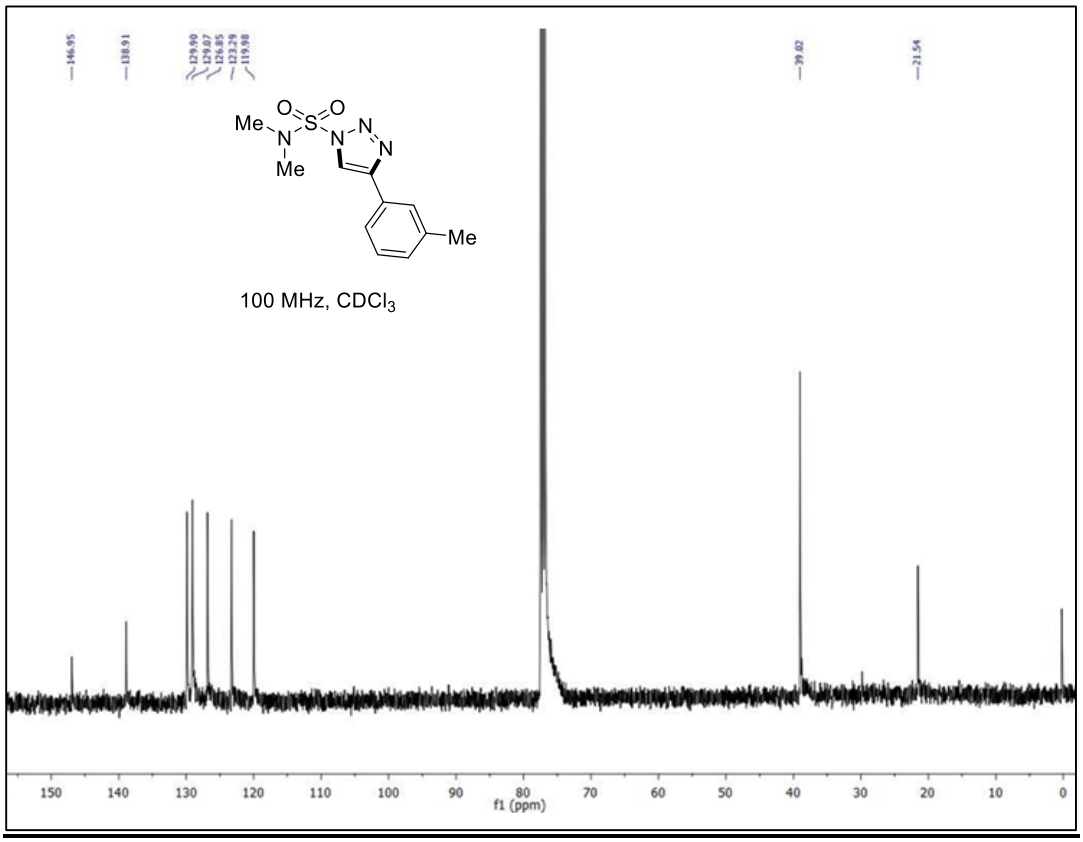
^{1}H and ^{13}C NMR spectra of 5b:



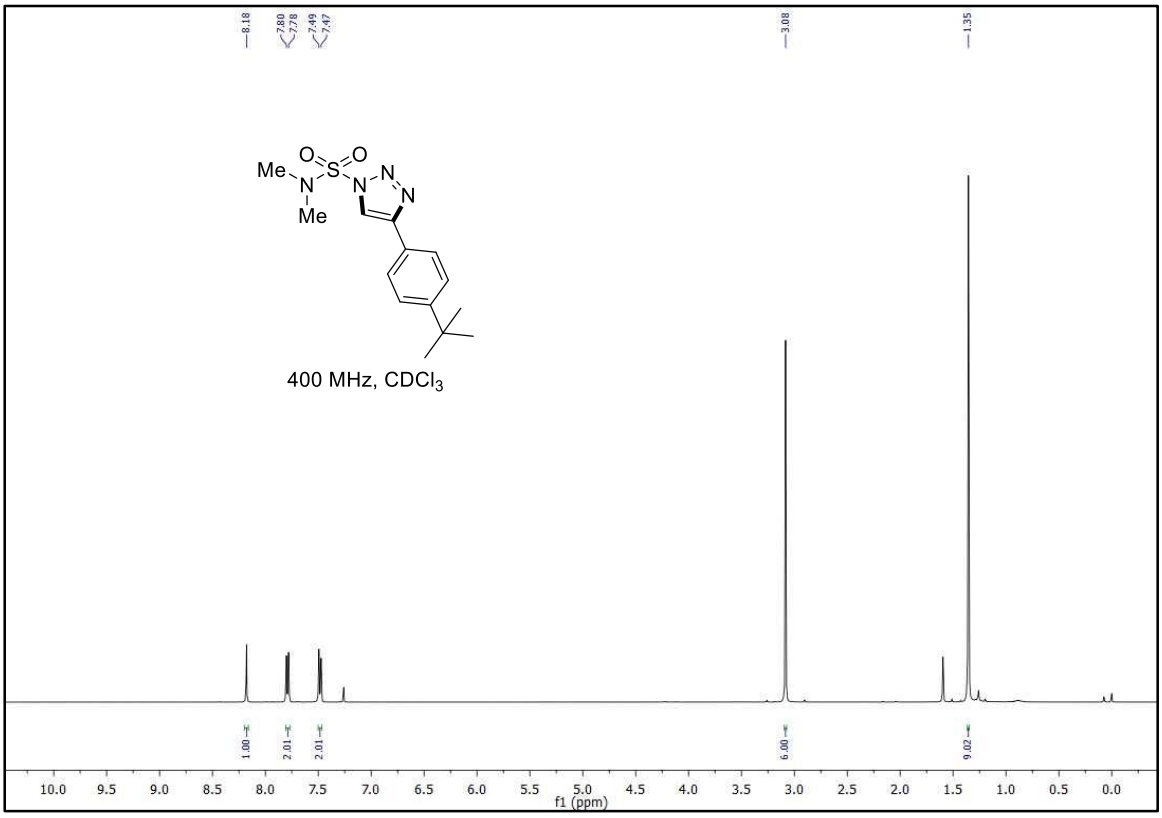


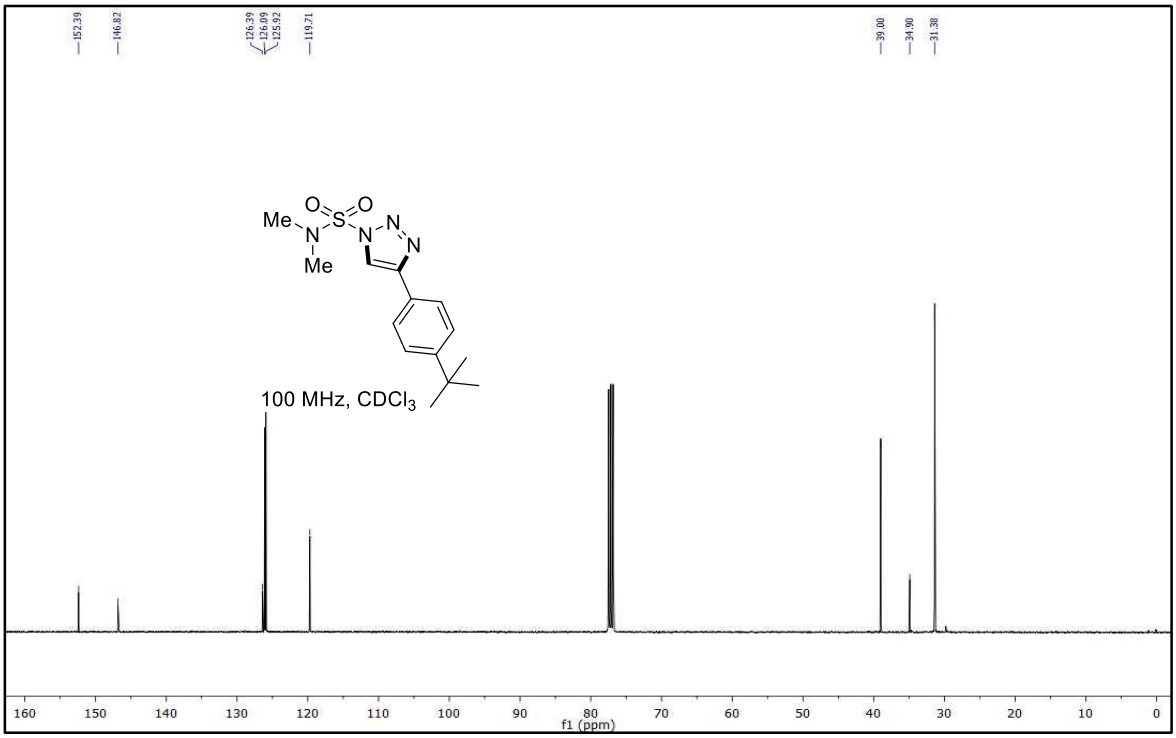
^{1}H and ^{13}C NMR spectra of 5c:



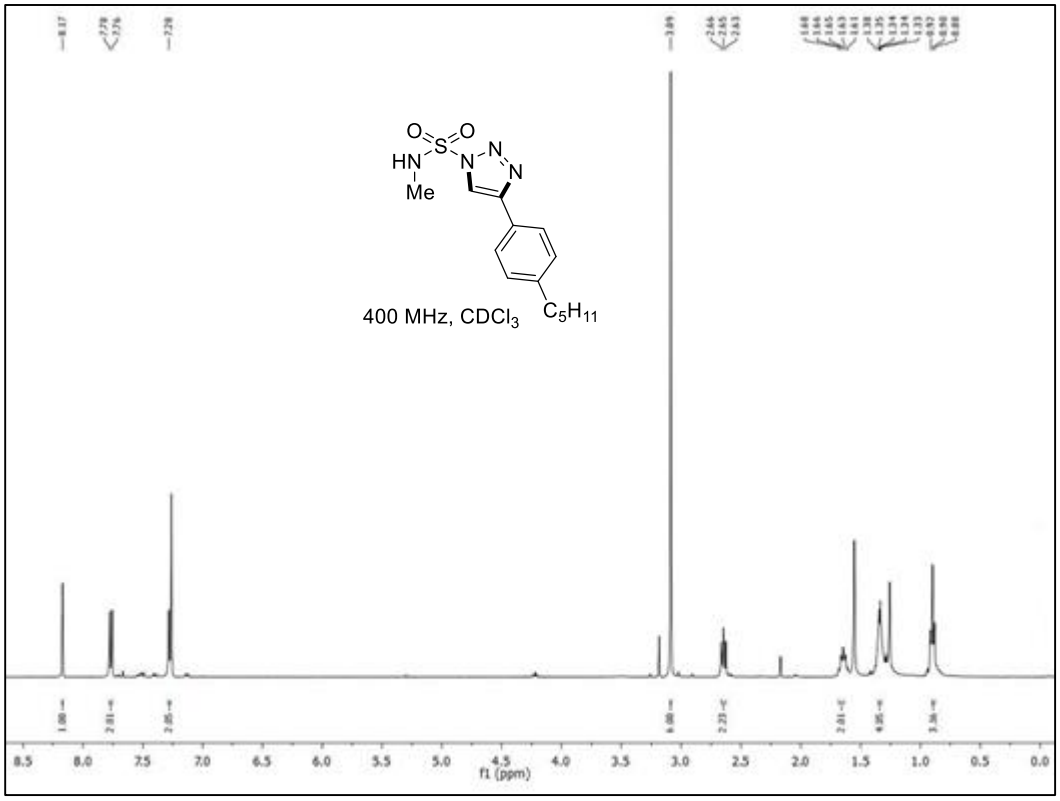


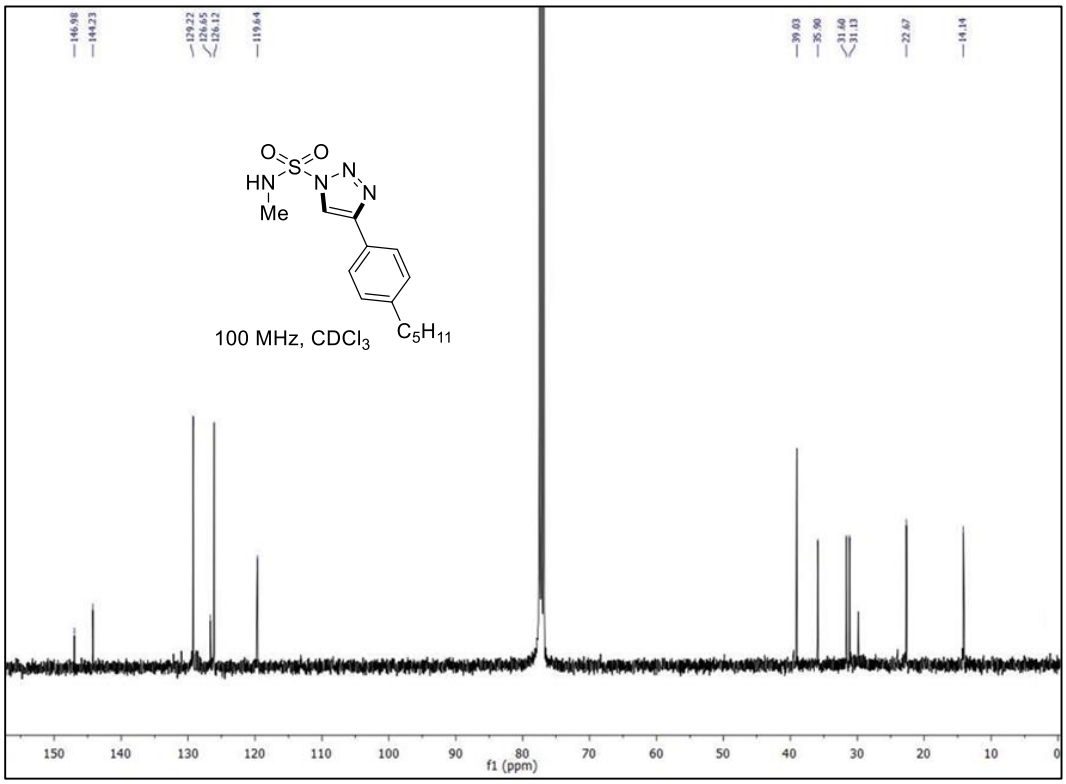
^{1}H and ^{13}C NMR spectra of 5d:



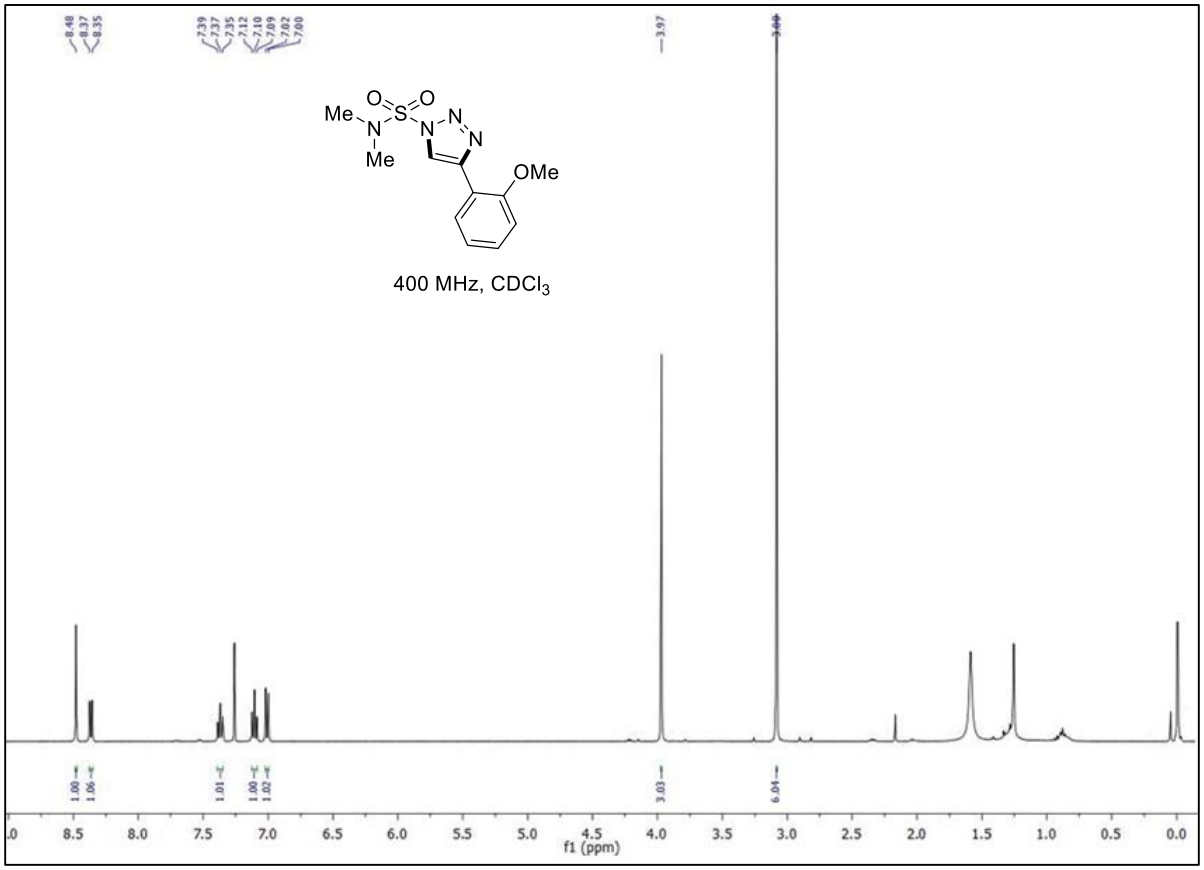


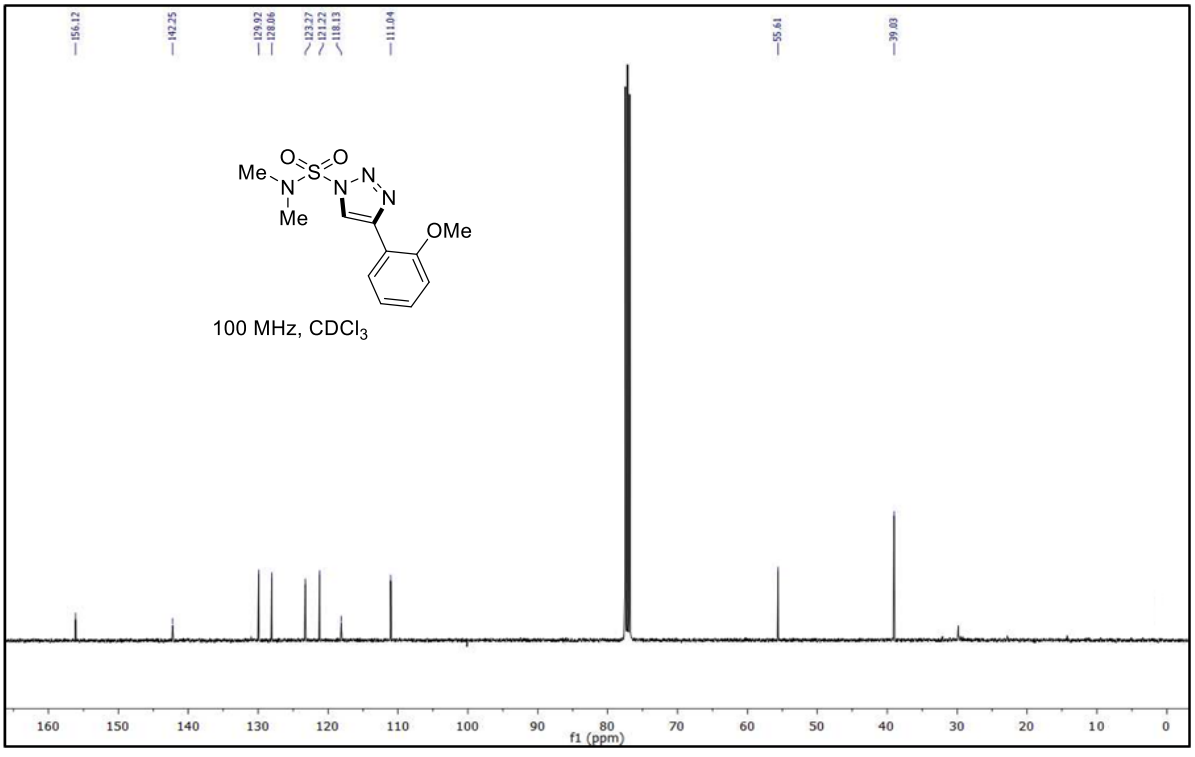
^{1}H and ^{13}C NMR spectra of 5e:



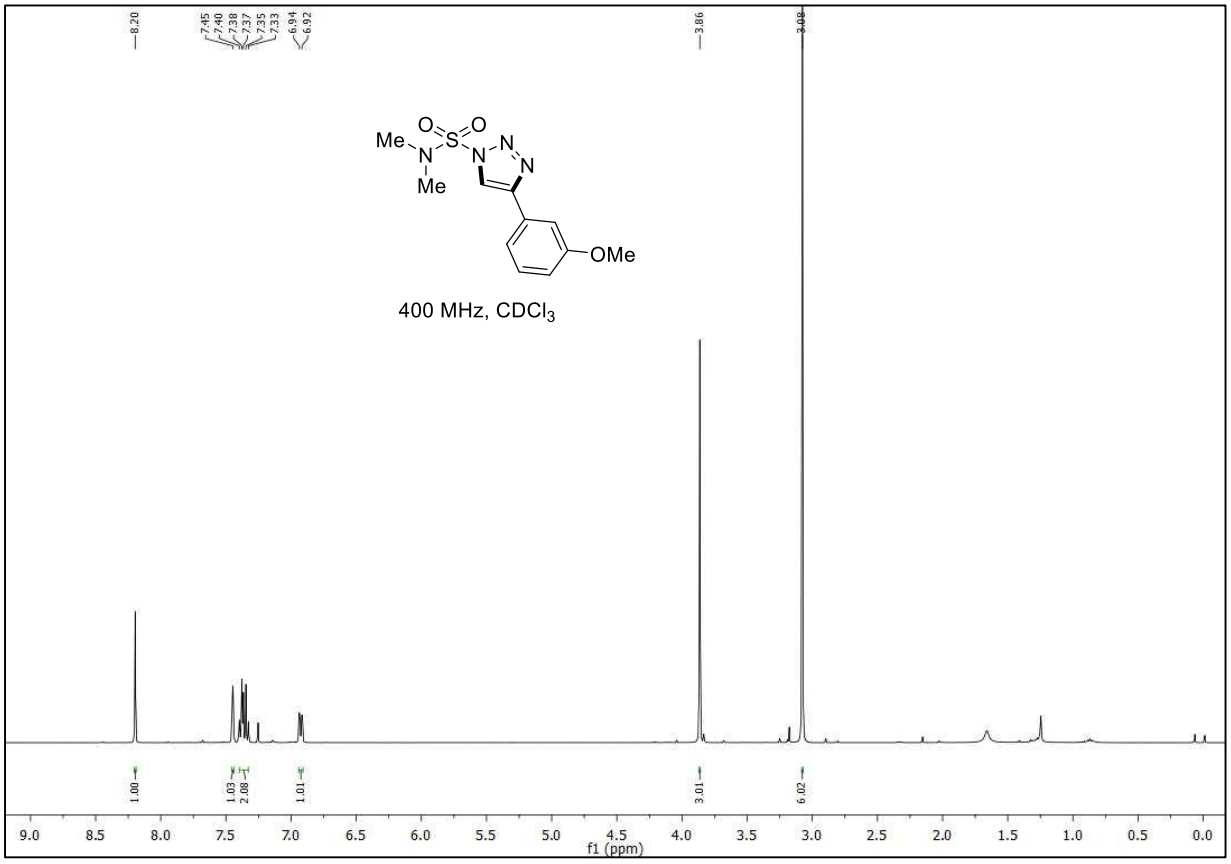


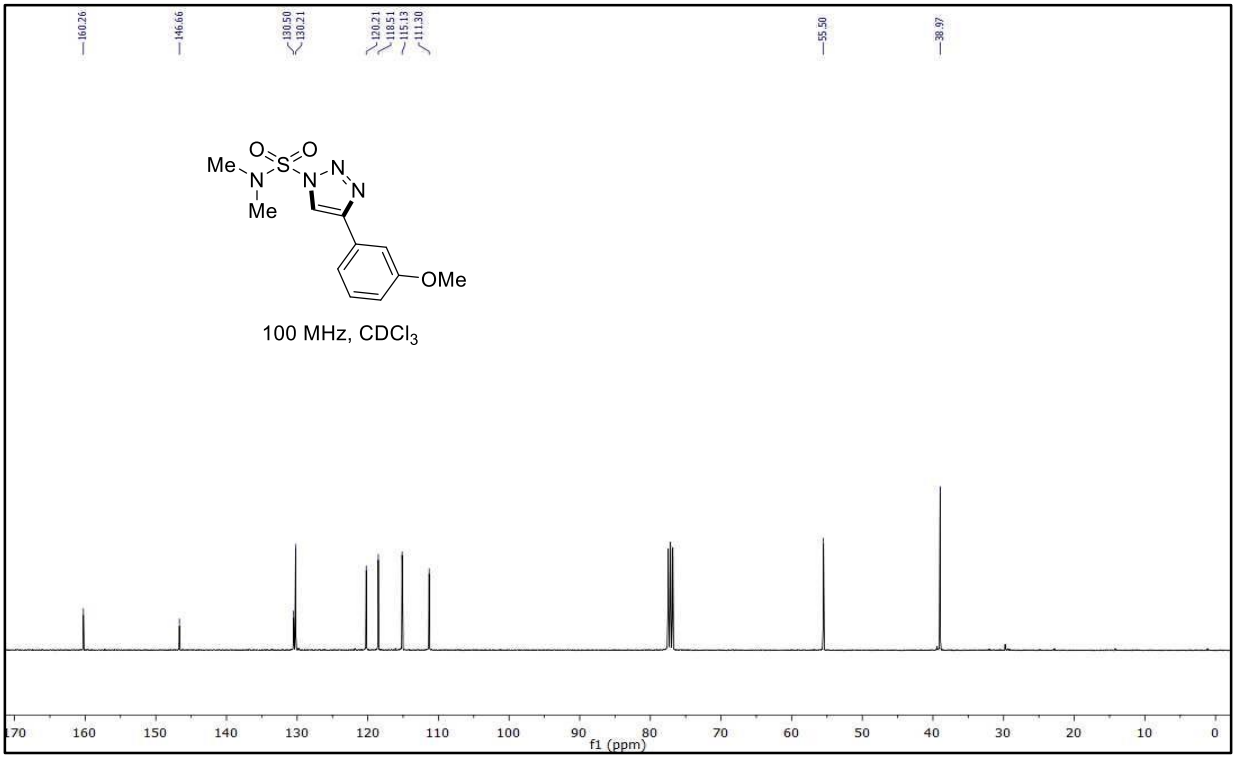
^{1}H and ^{13}C NMR spectra of 5f:



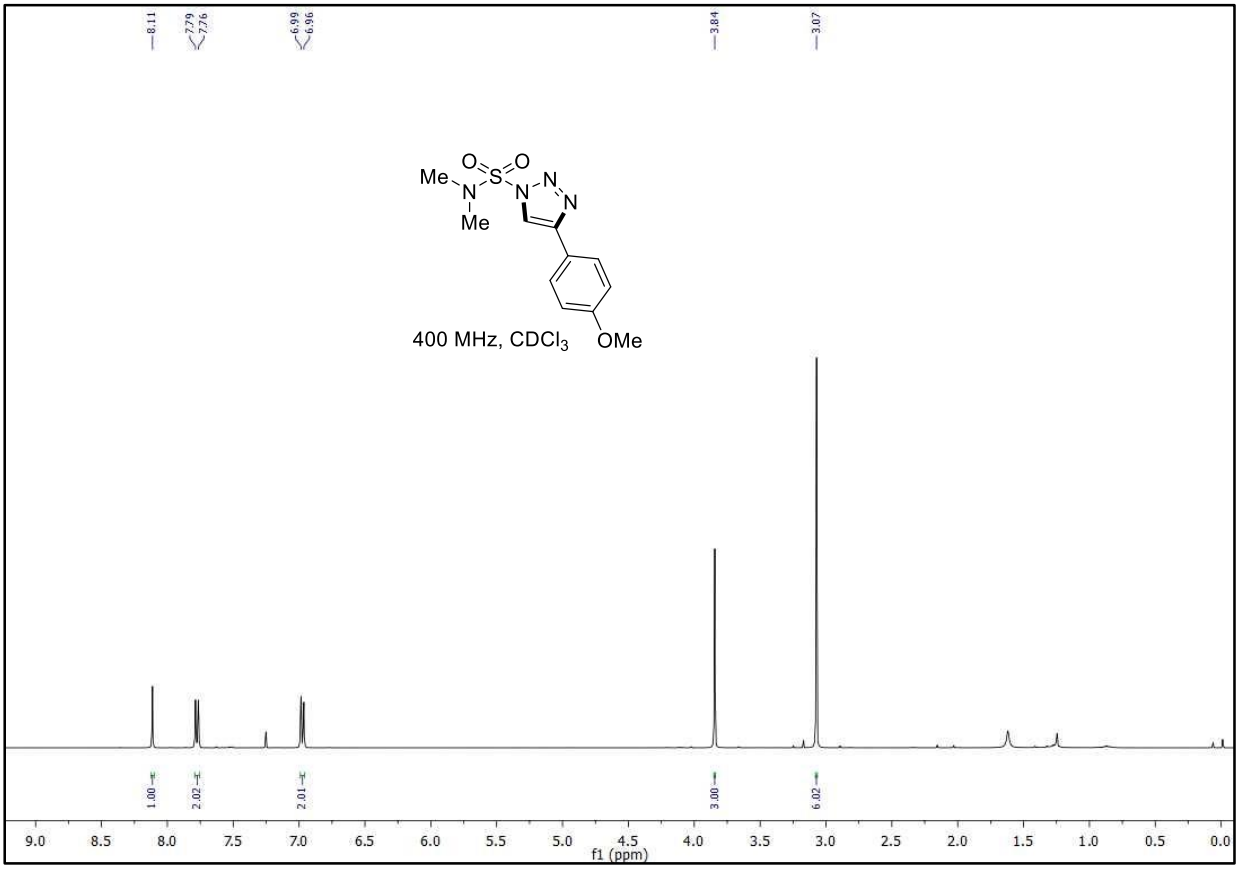


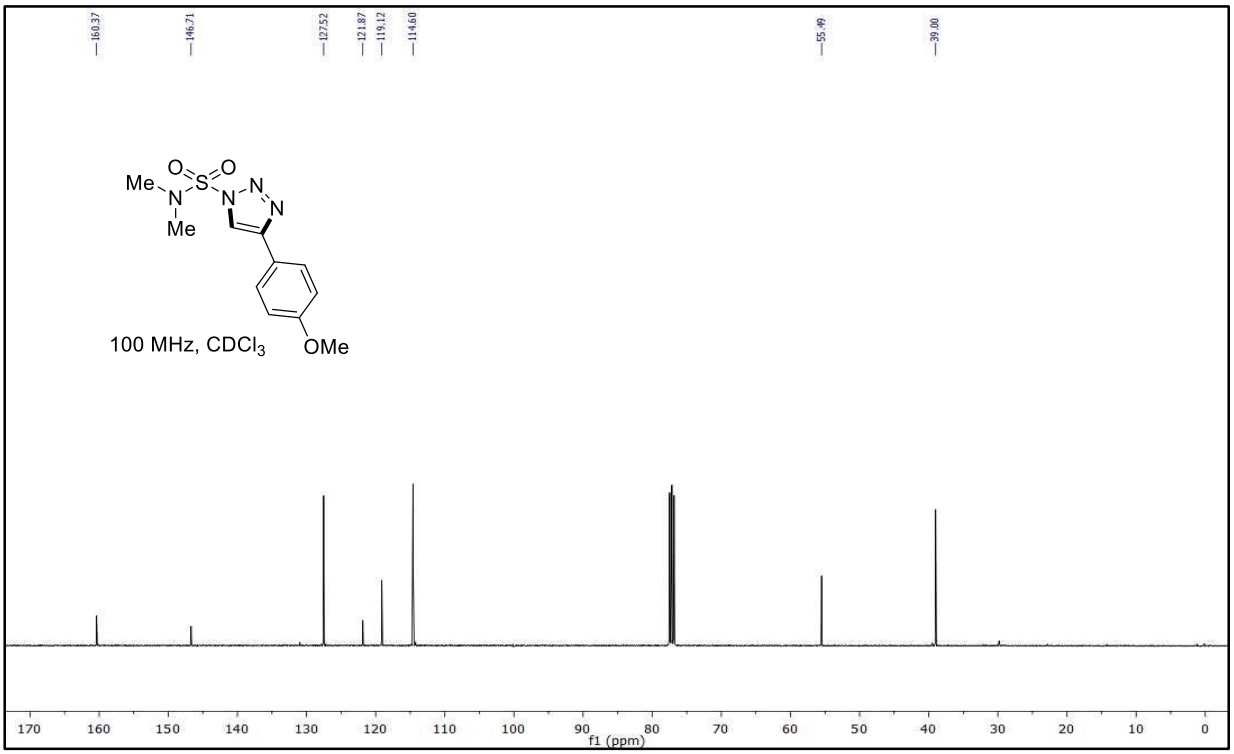
^{1}H and ^{13}C NMR spectra of 5g:



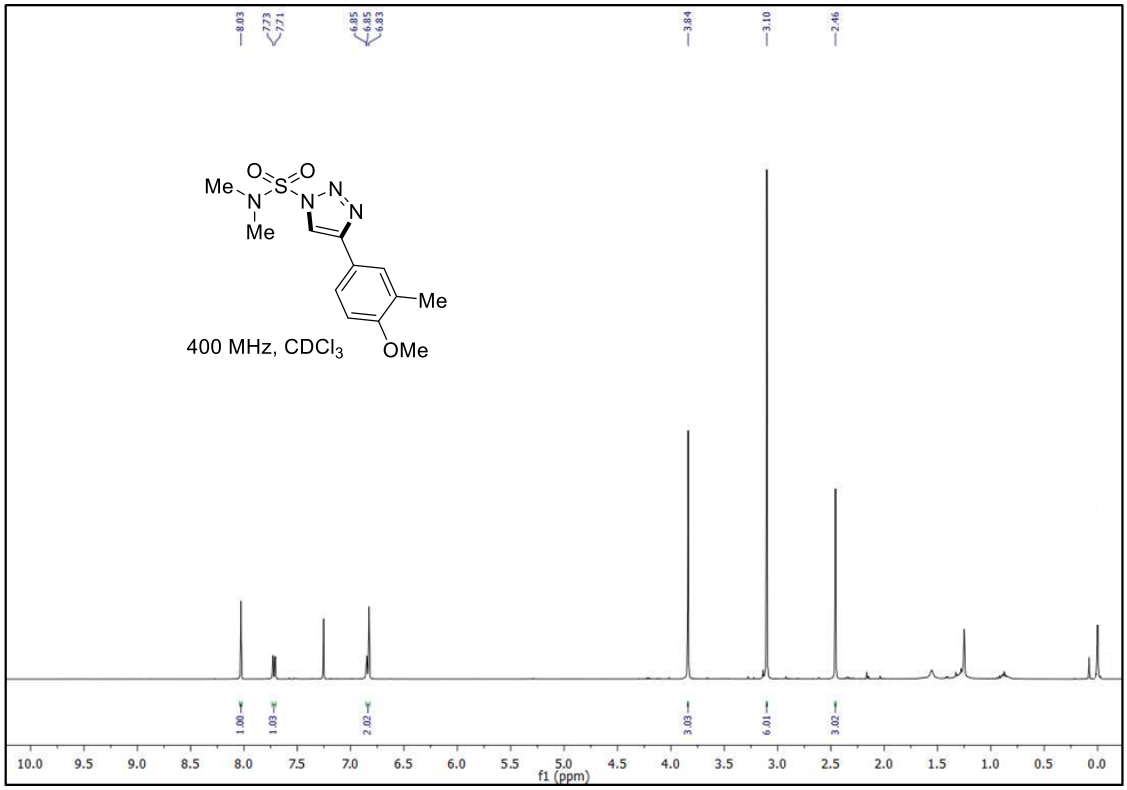


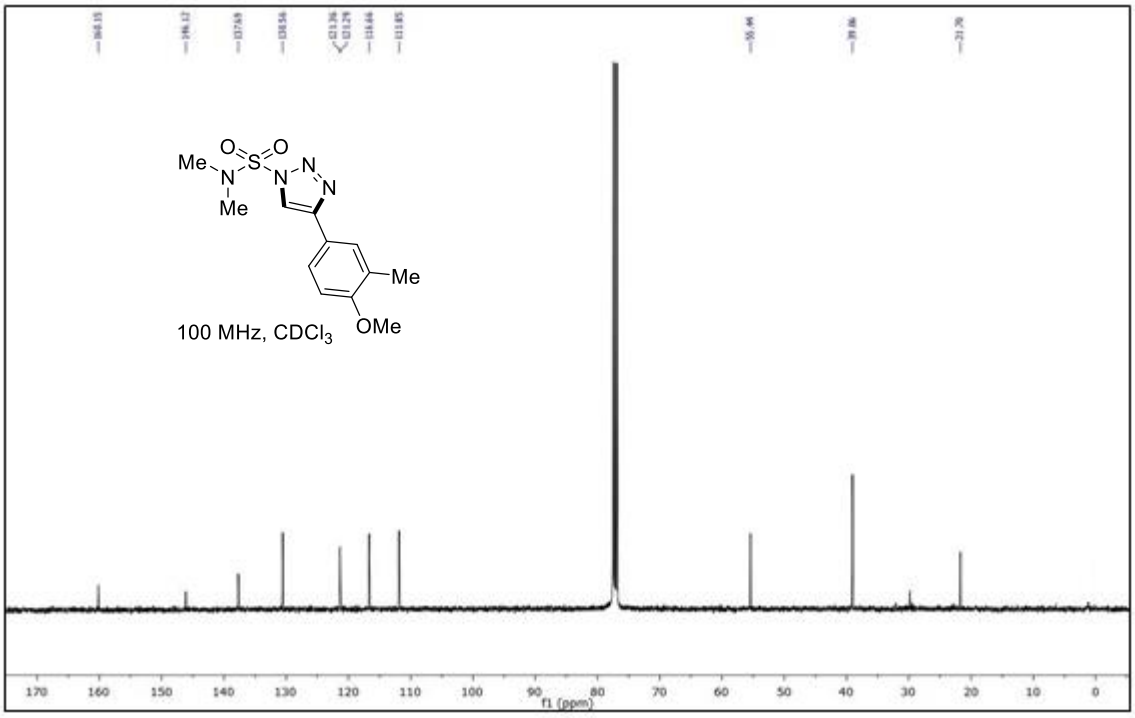
^{1}H and ^{13}C NMR spectra of 5h:



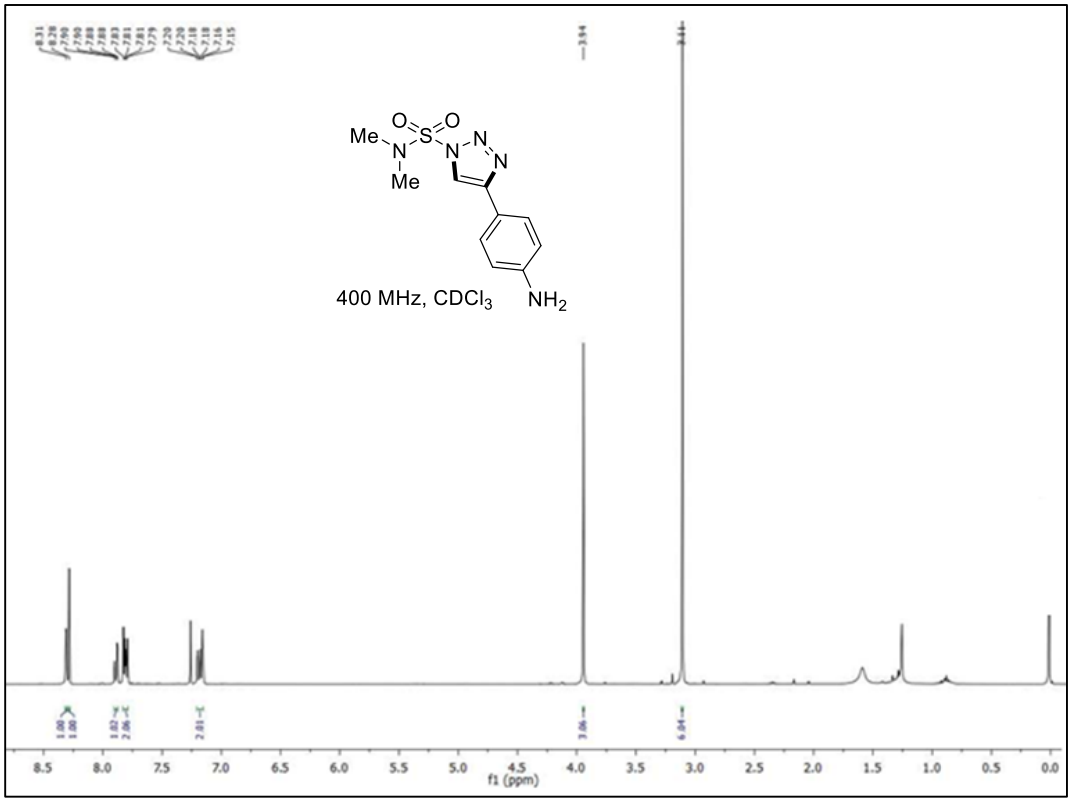


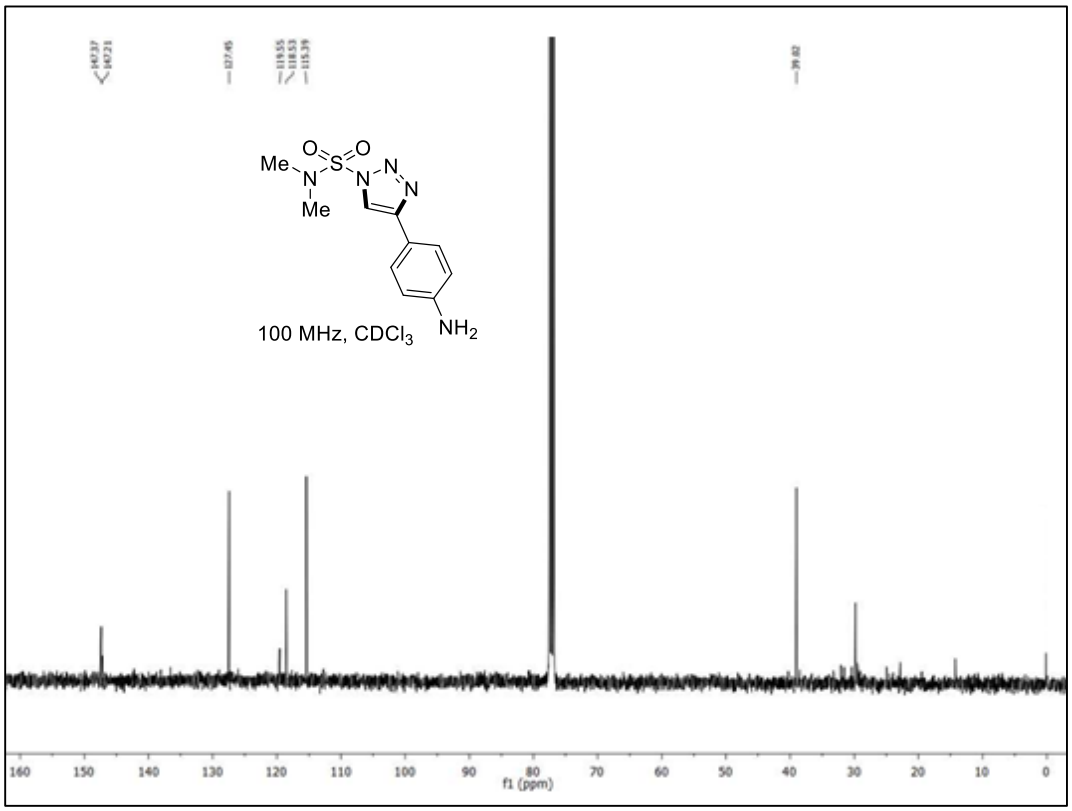
^{1}H and ^{13}C NMR spectra of 5i:



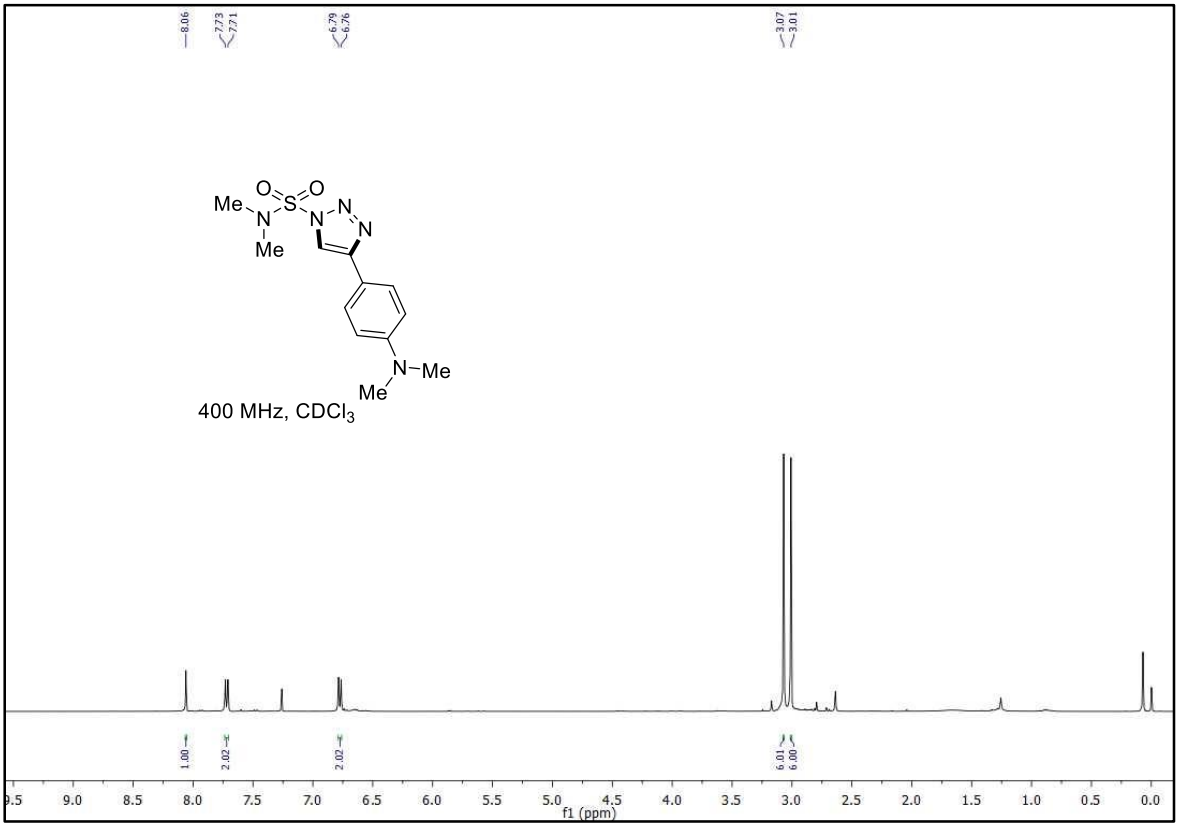


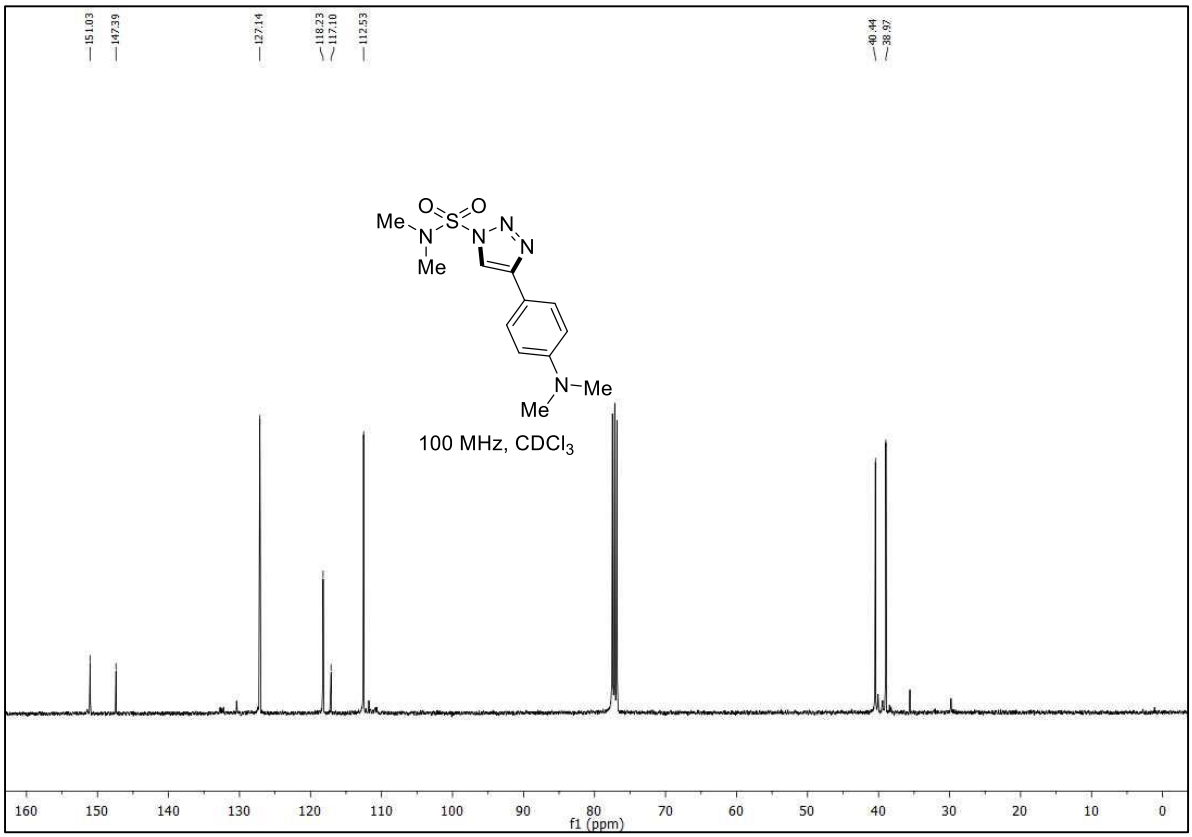
^{1}H and ^{13}C NMR spectra of 5j:



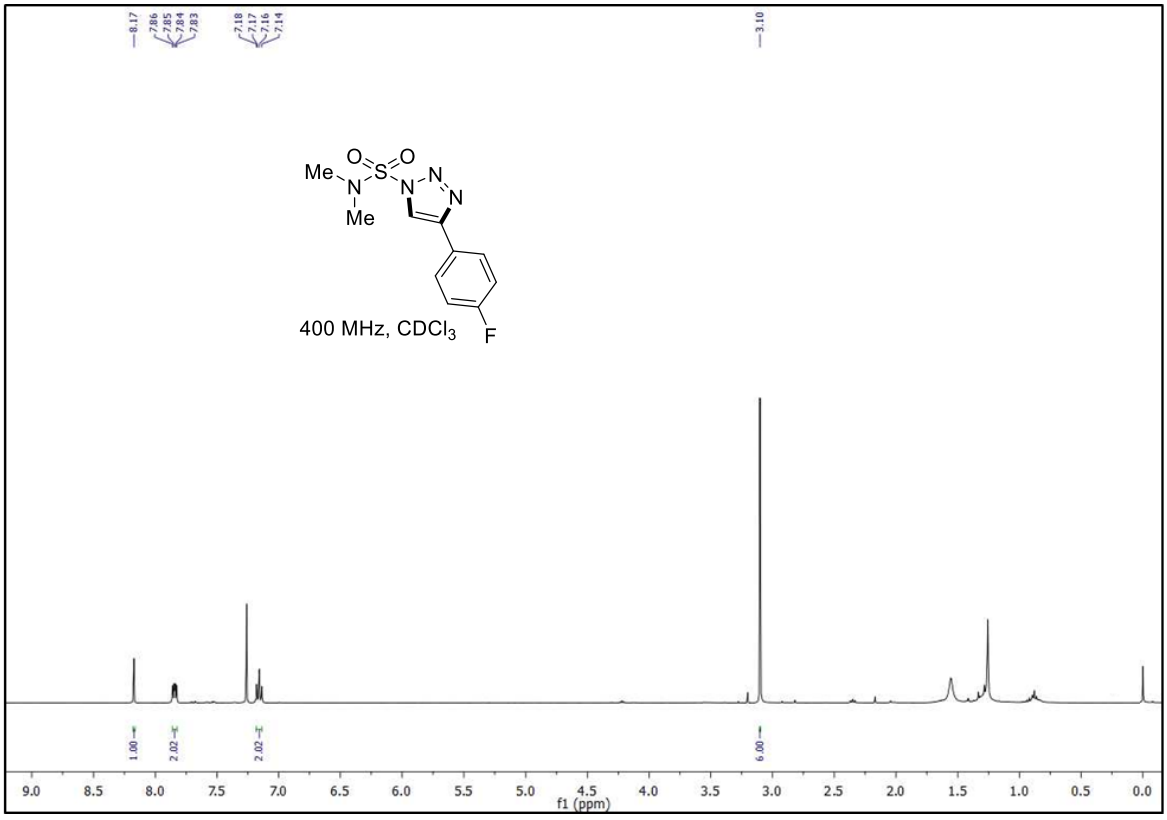


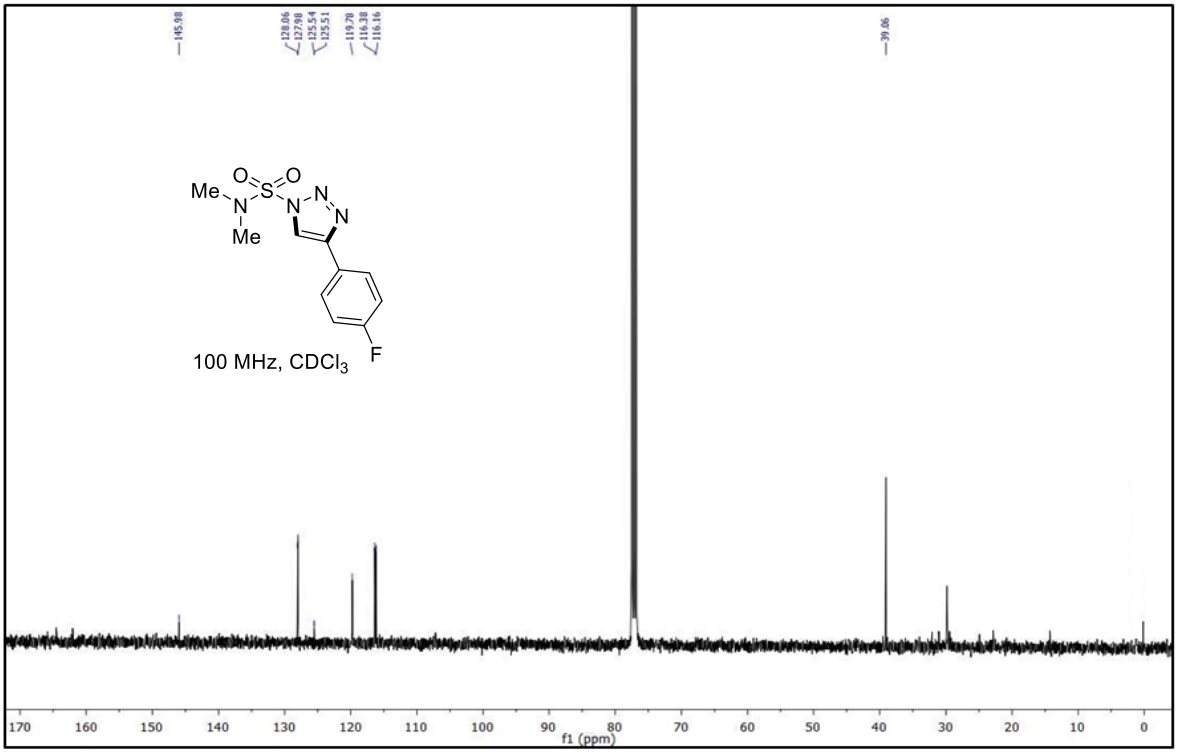
^{1}H and ^{13}C NMR spectra of 5k:



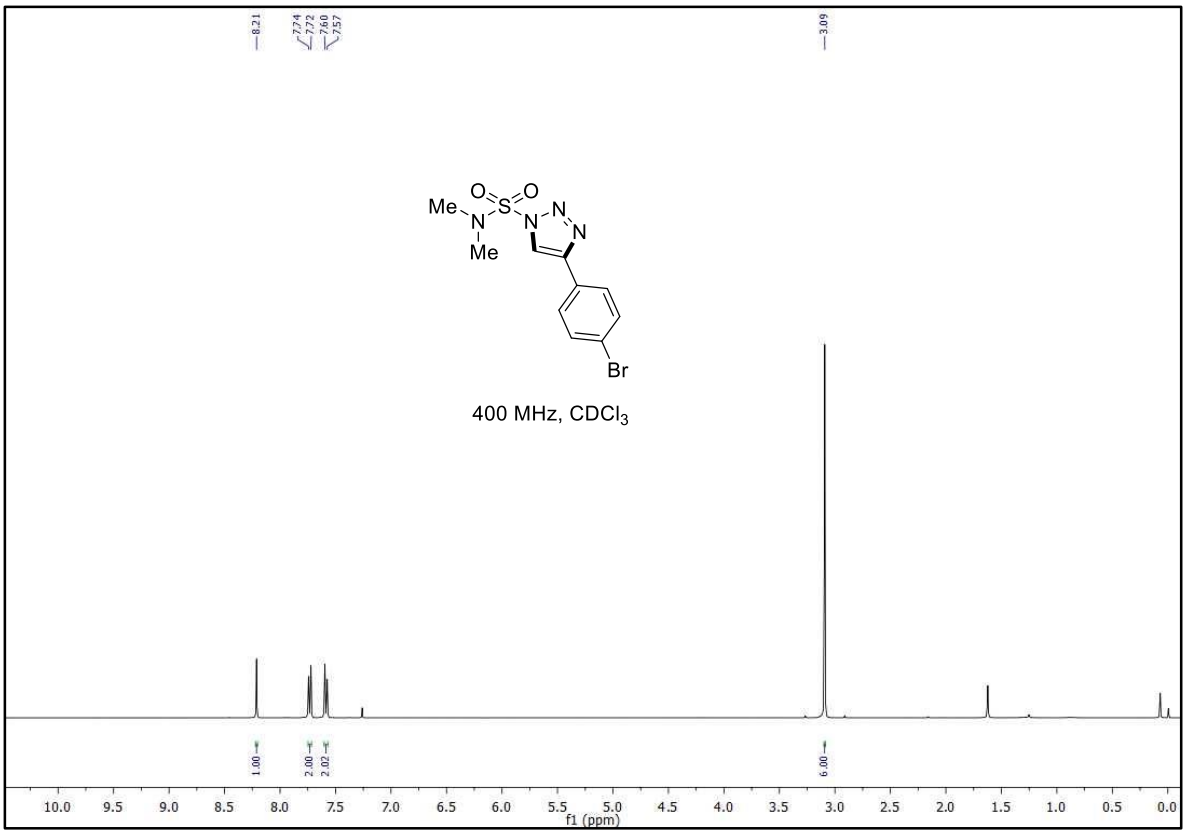


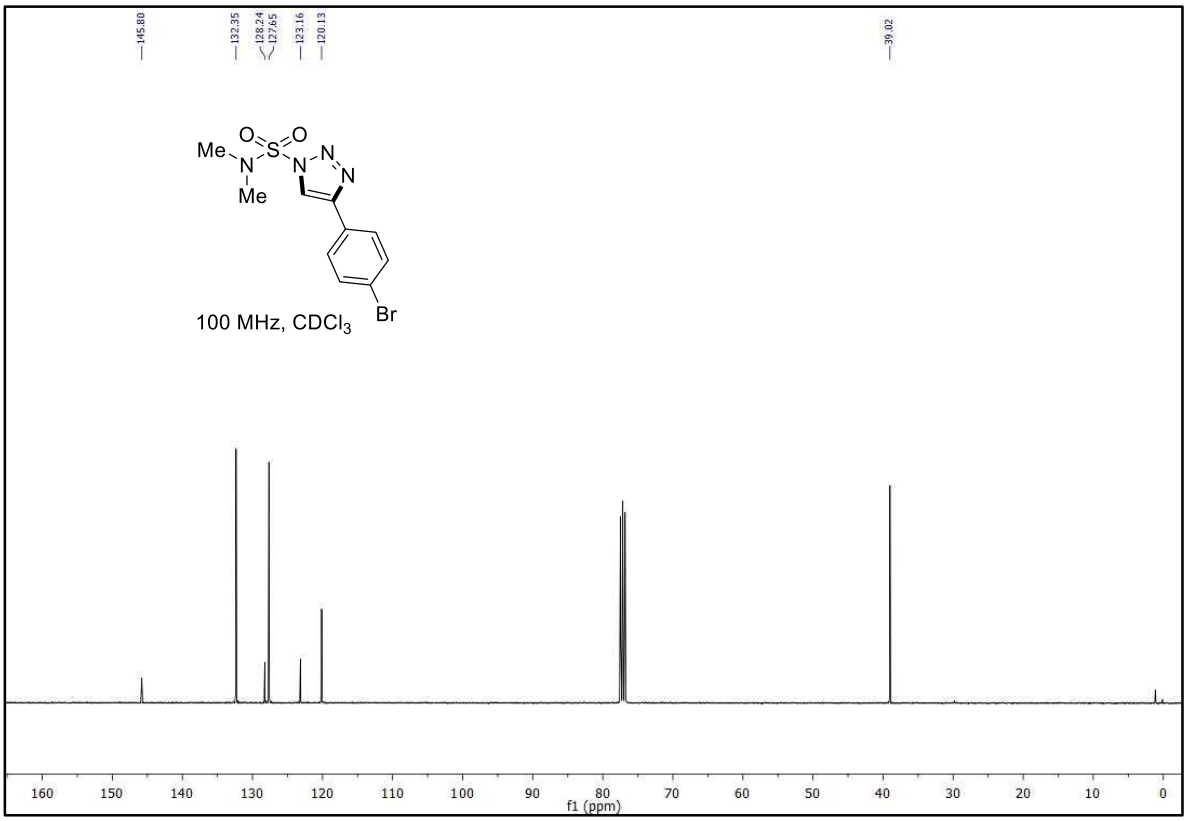
^{1}H and ^{13}C NMR spectra of 5l:



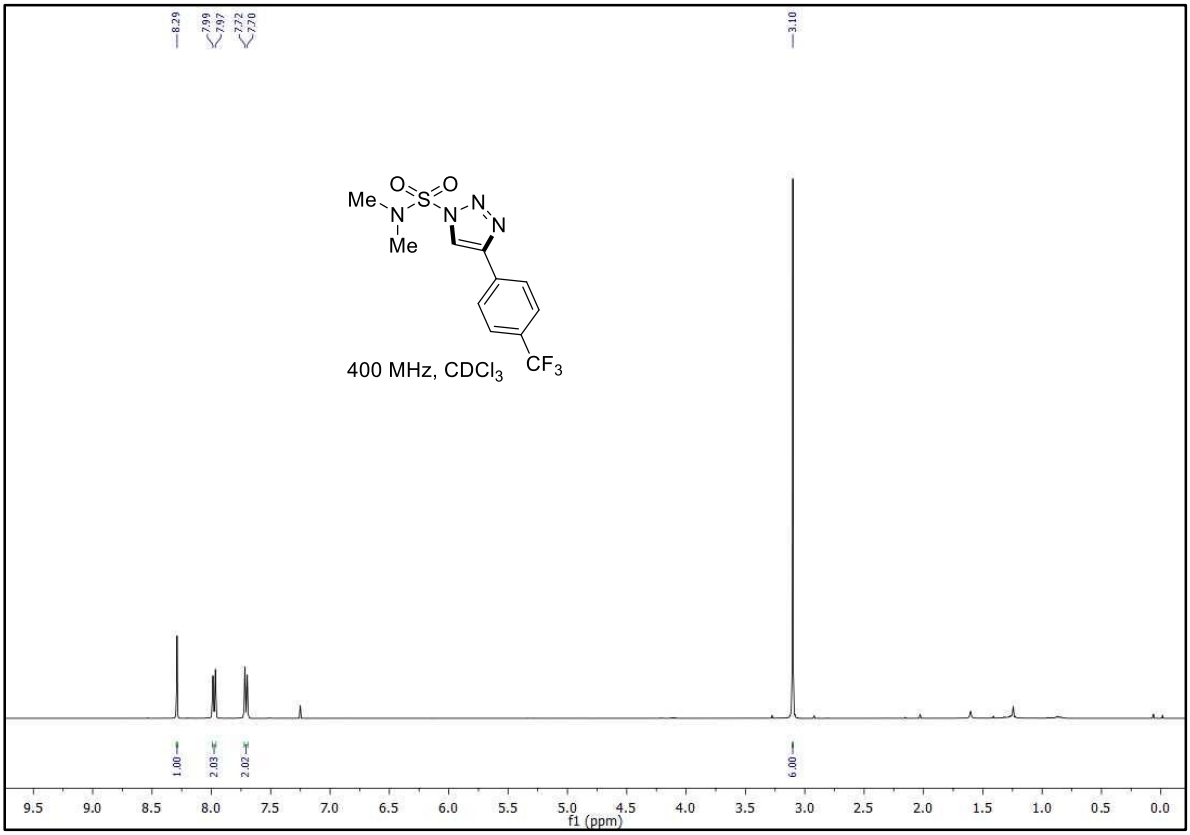


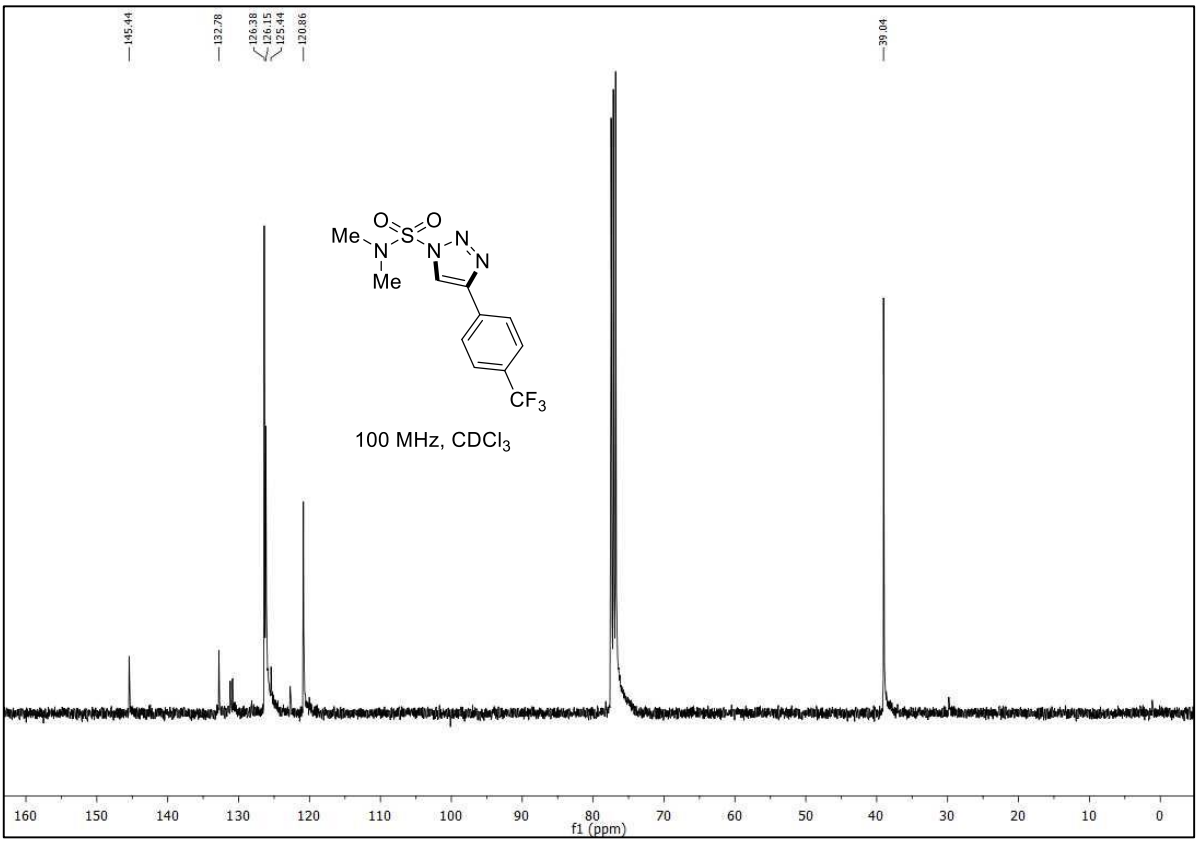
^{1}H and ^{13}C NMR spectra of 5m:



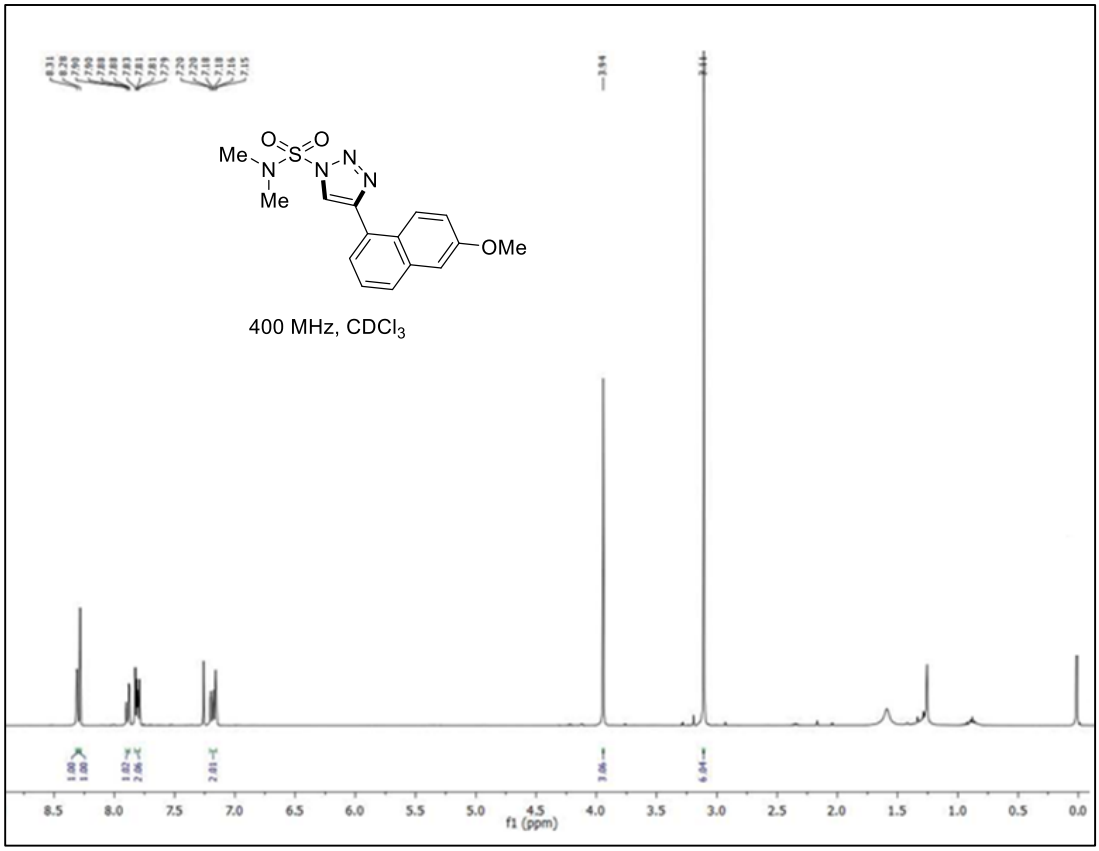


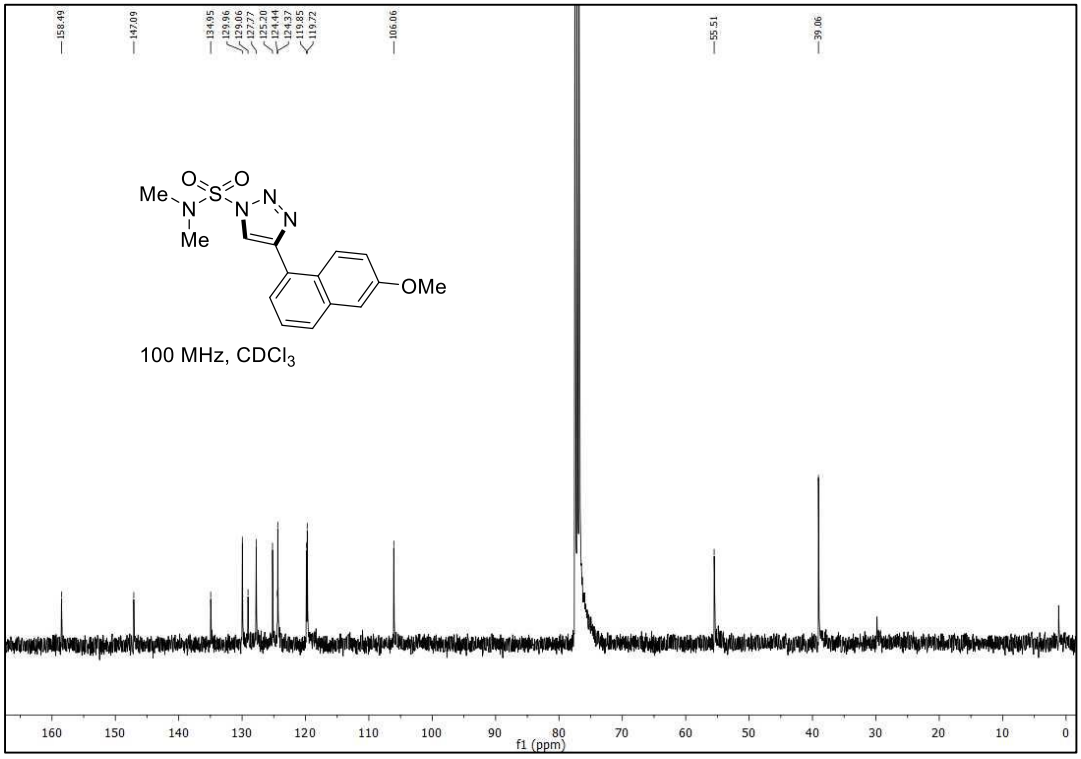
^{1}H and ^{13}C NMR spectra of 5n:



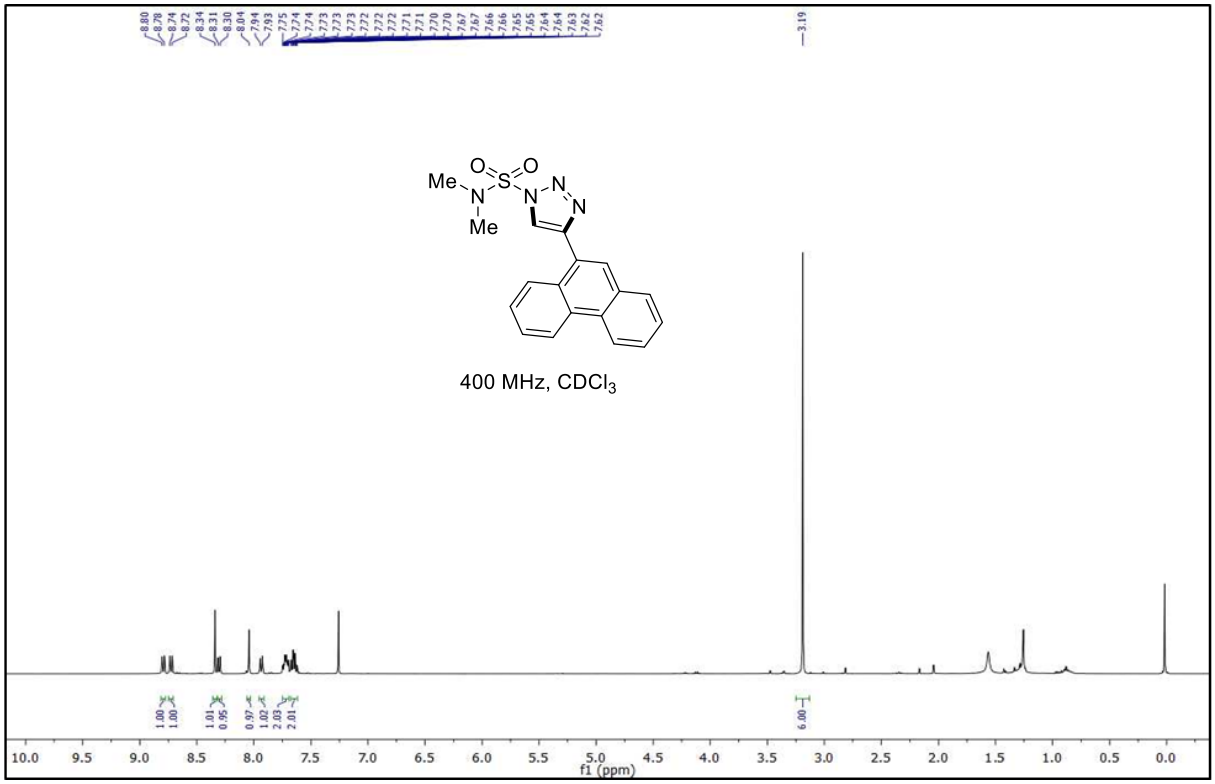


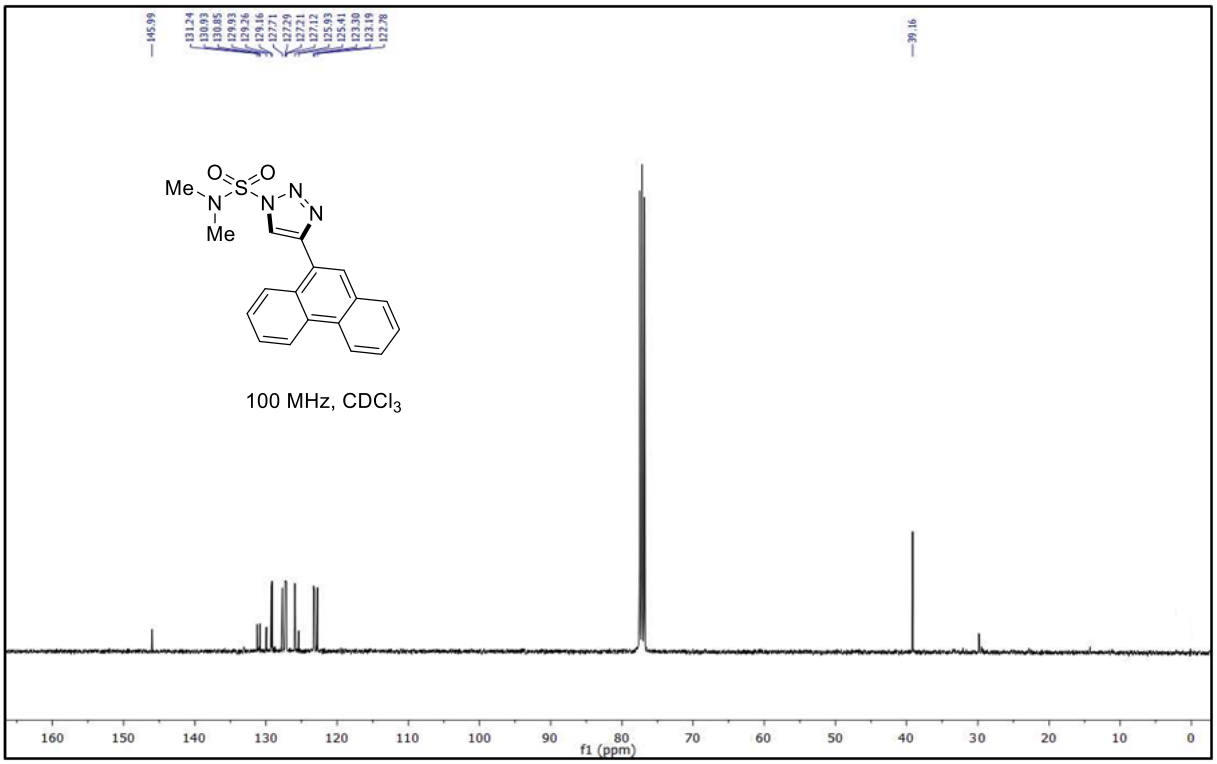
^{1}H and ^{13}C NMR spectra of 5o:



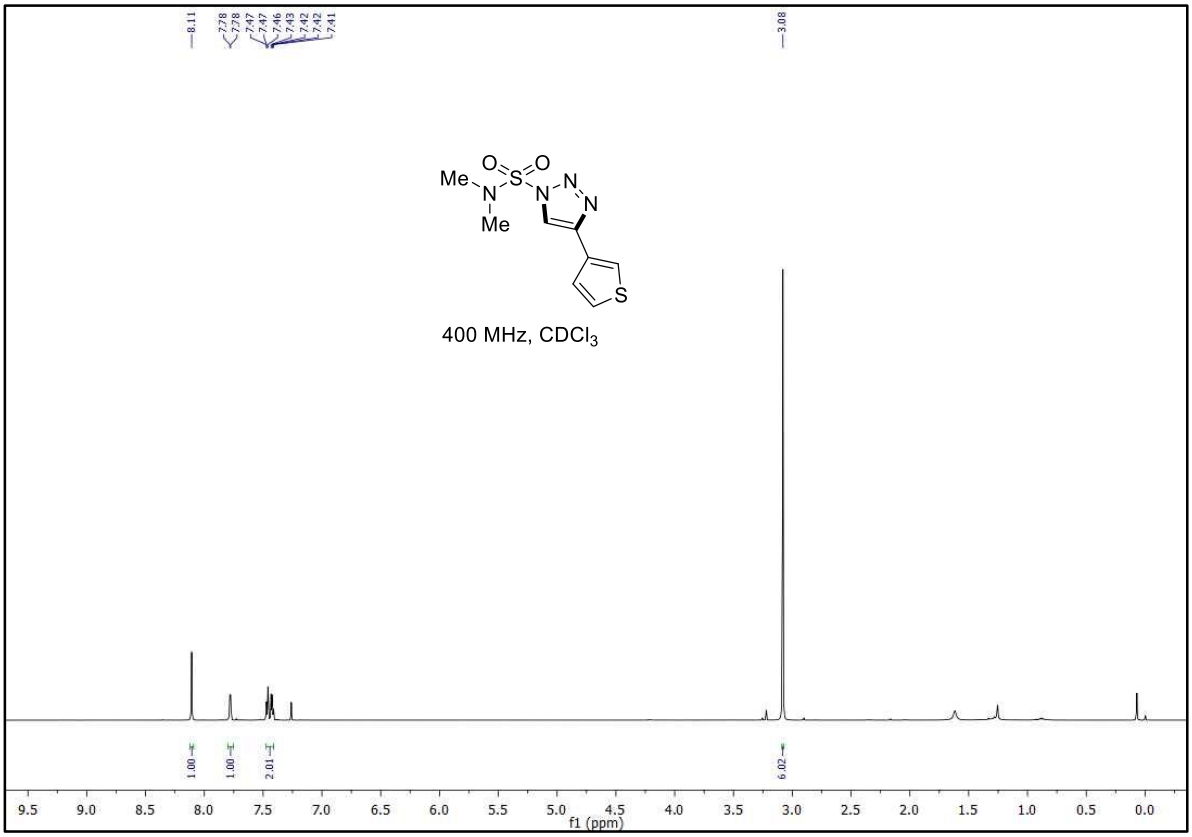


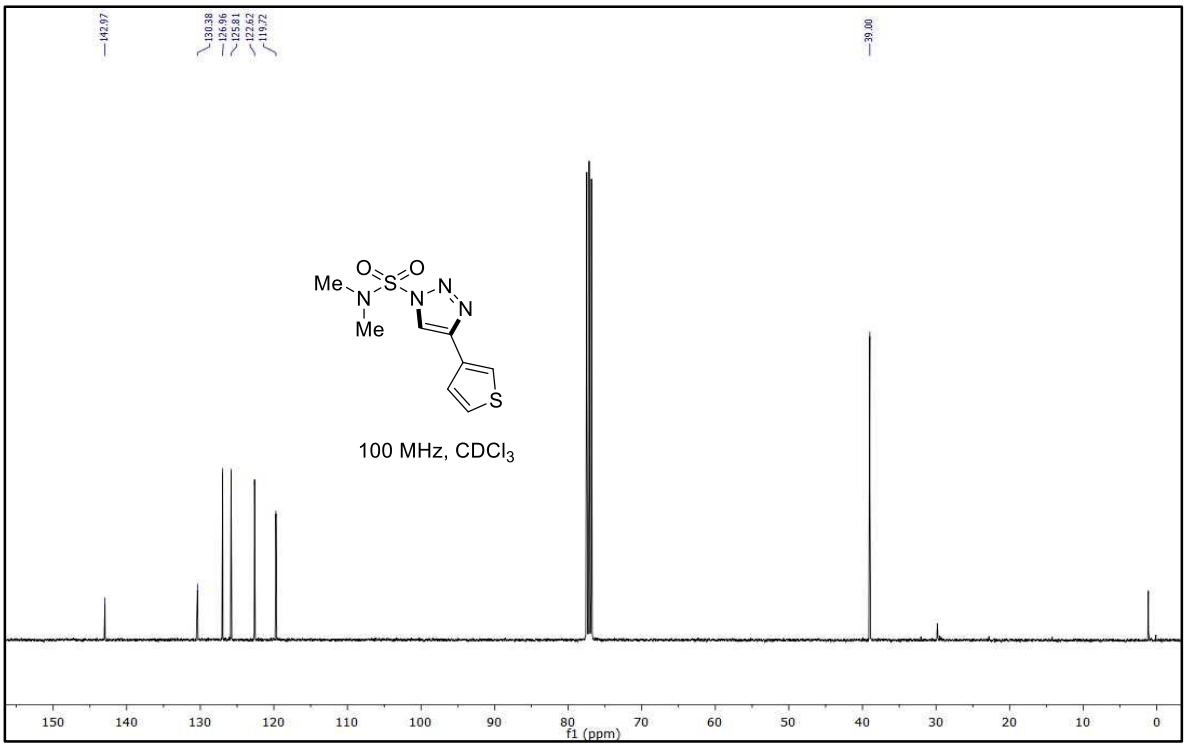
^{1}H and ^{13}C NMR spectra of 5p:



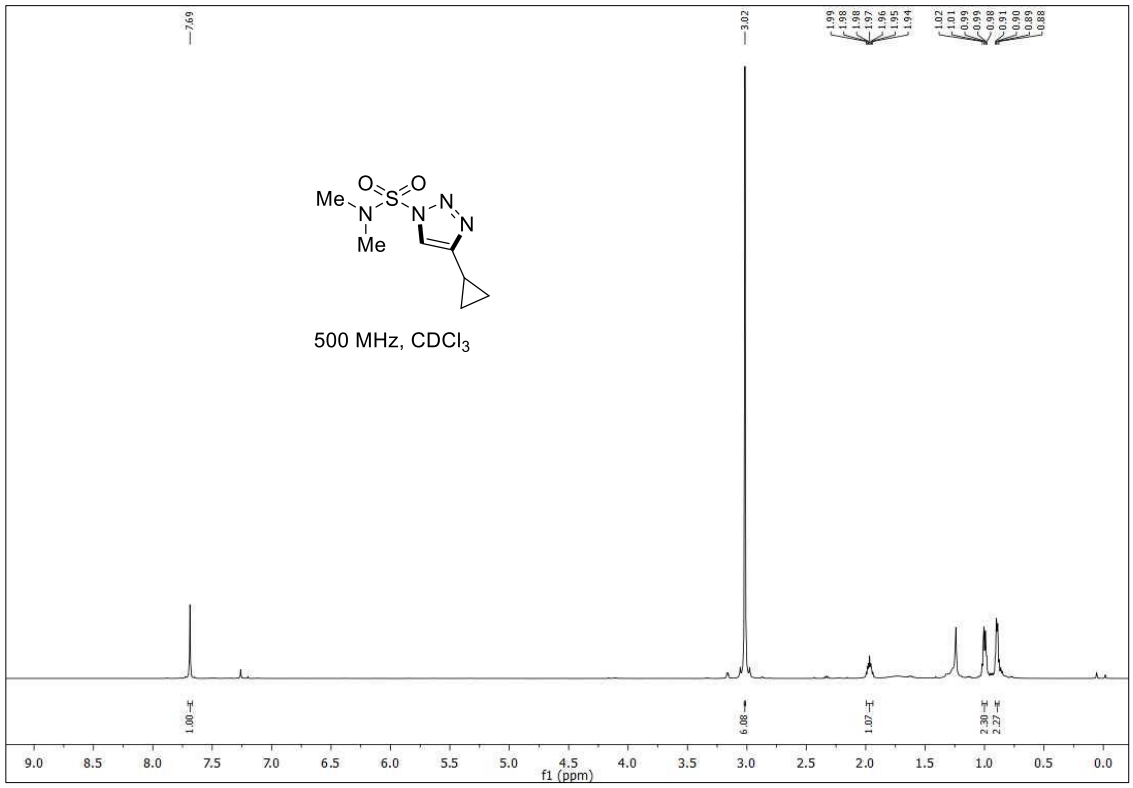


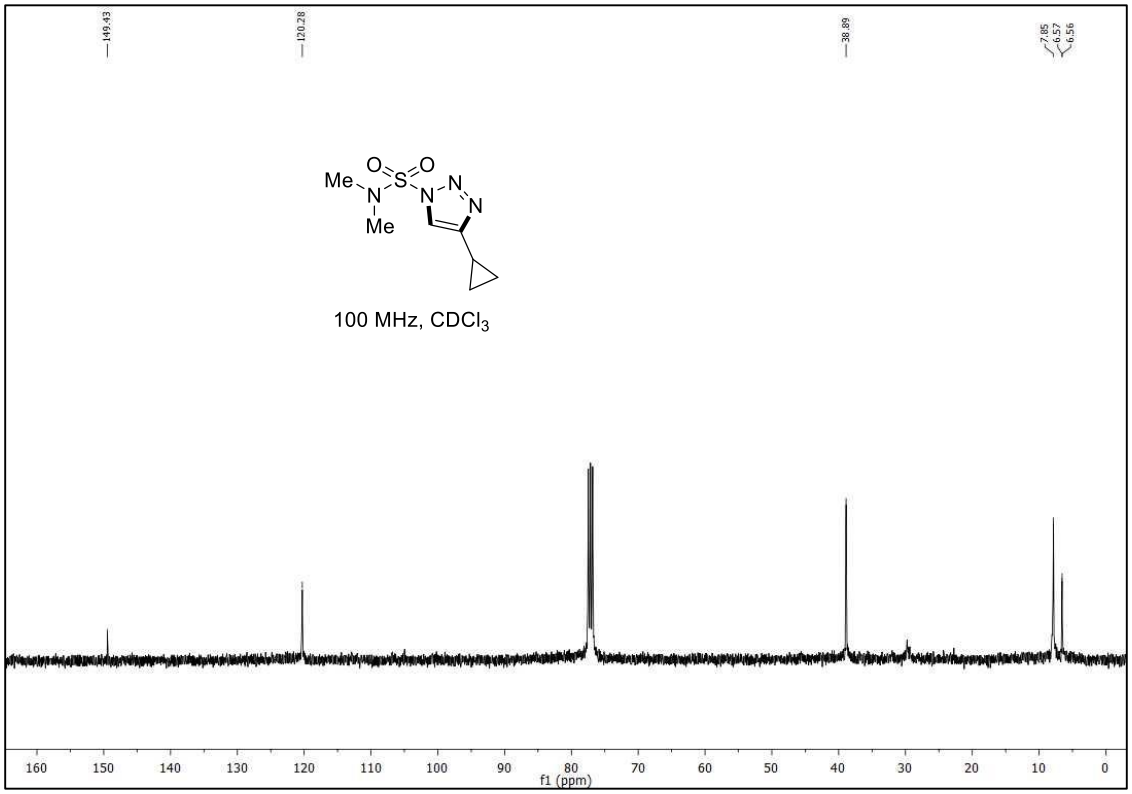
^{1}H and ^{13}C NMR spectra of 5q:



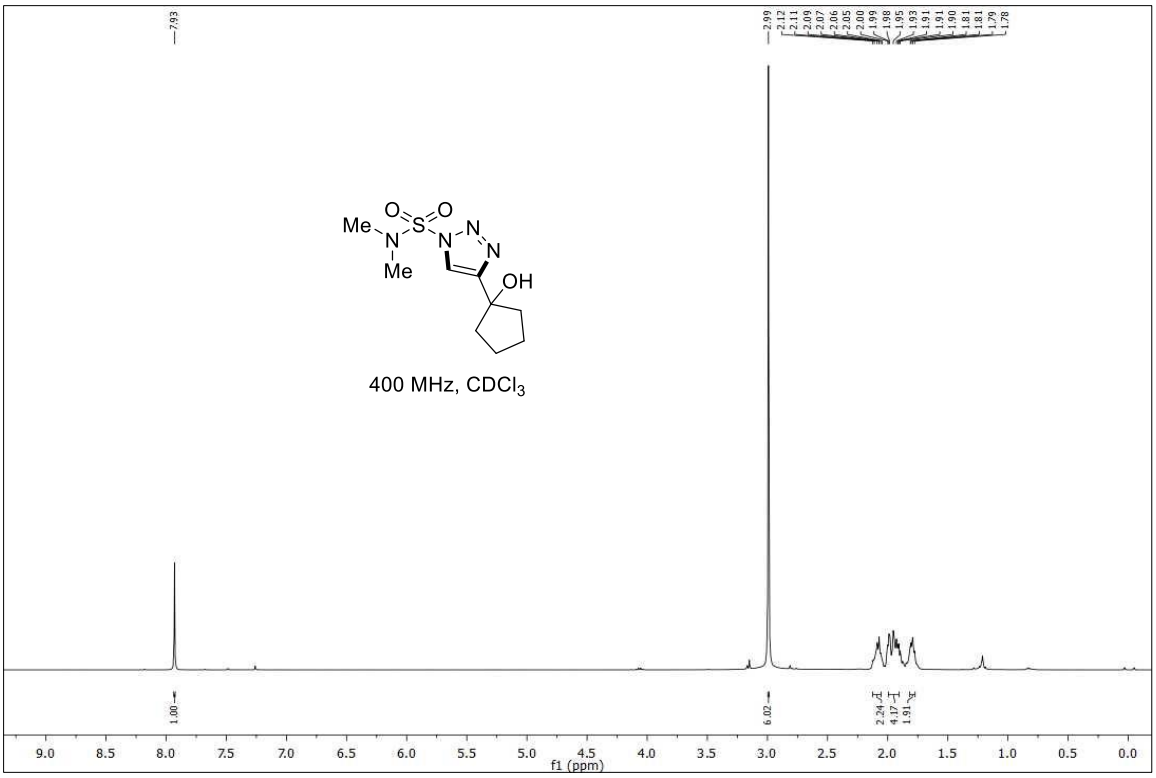


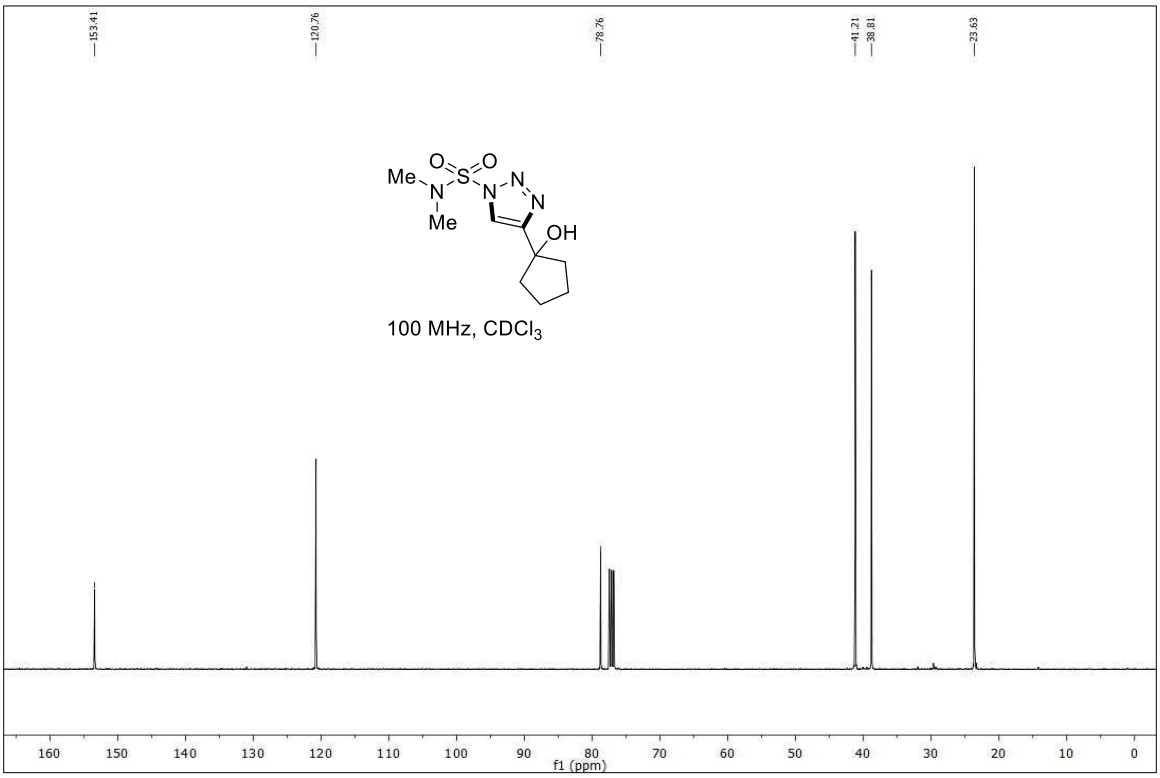
^{1}H and ^{13}C NMR spectra of 5r:



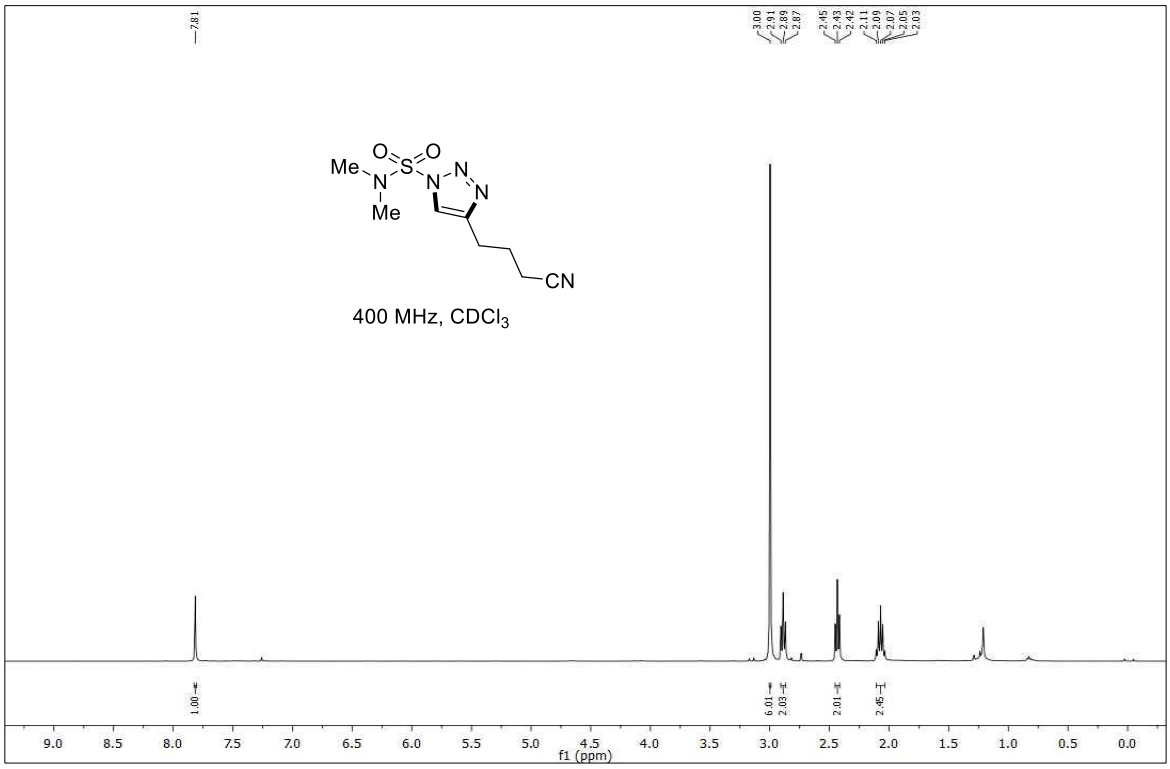


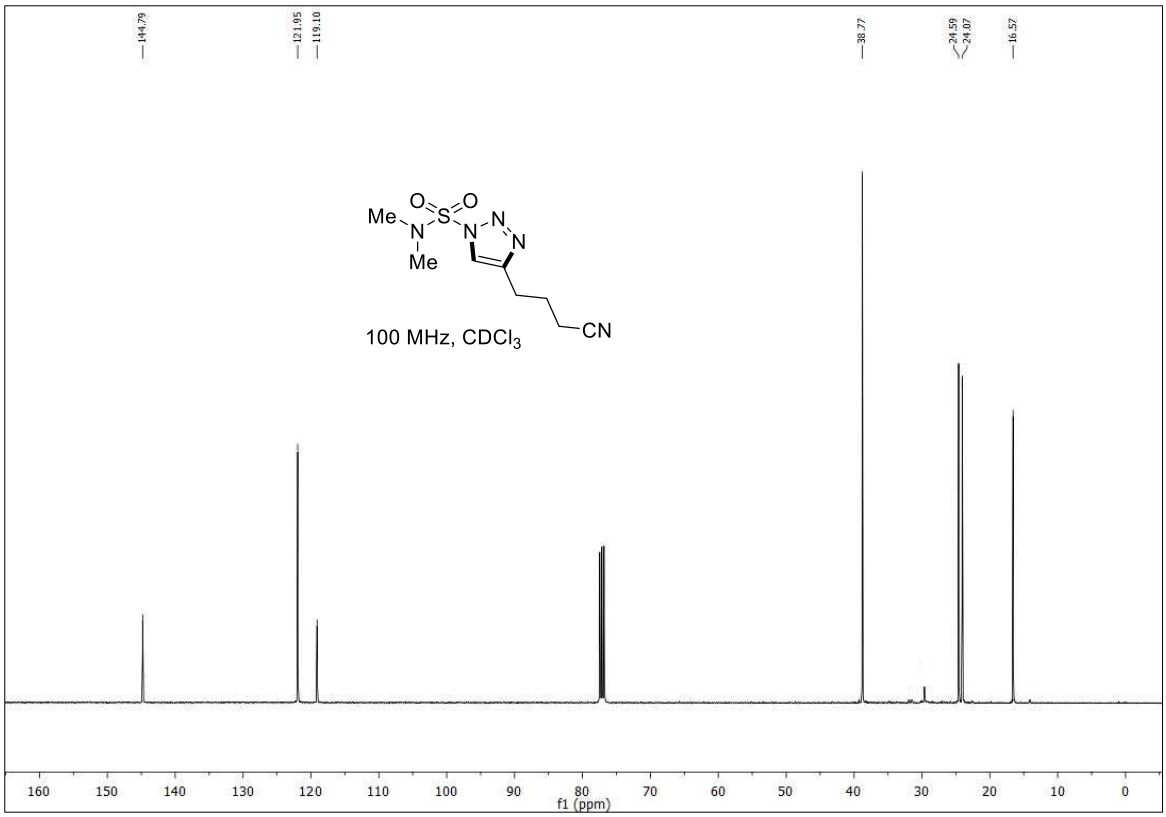
^{1}H and ^{13}C NMR spectra of 5s:



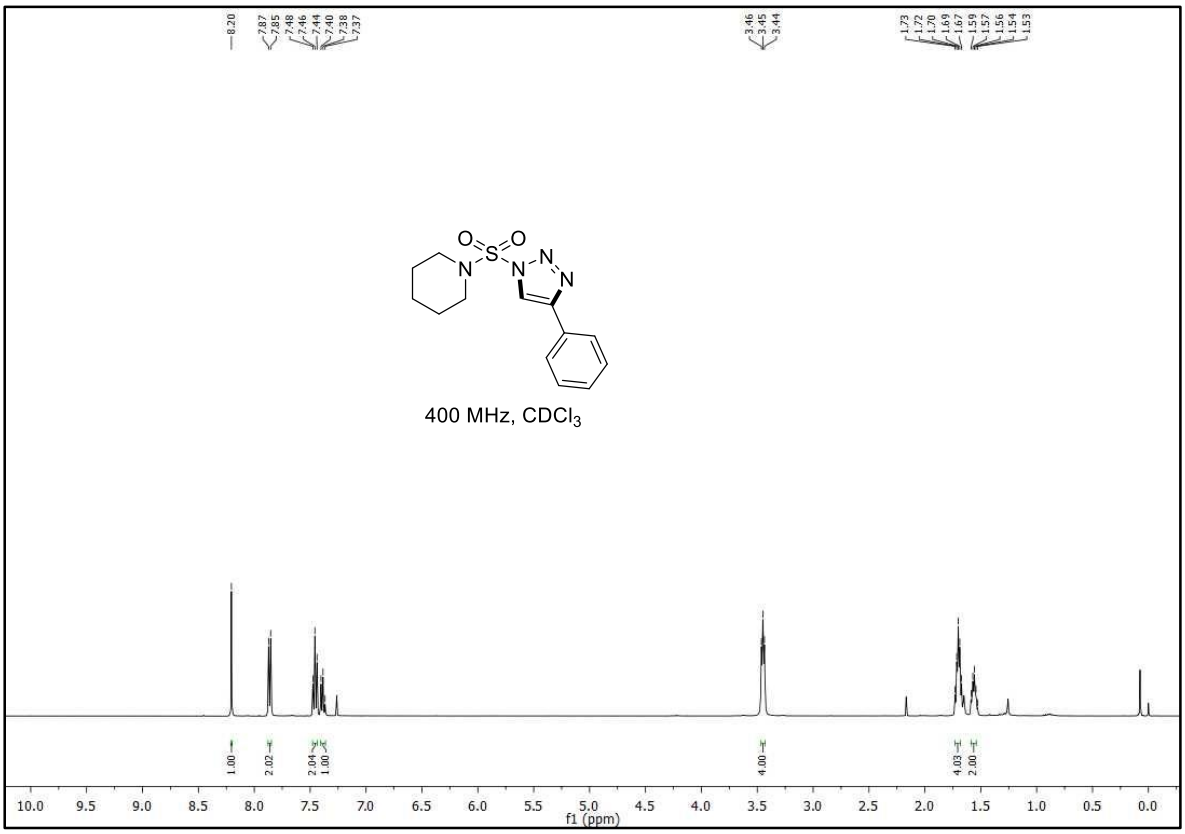


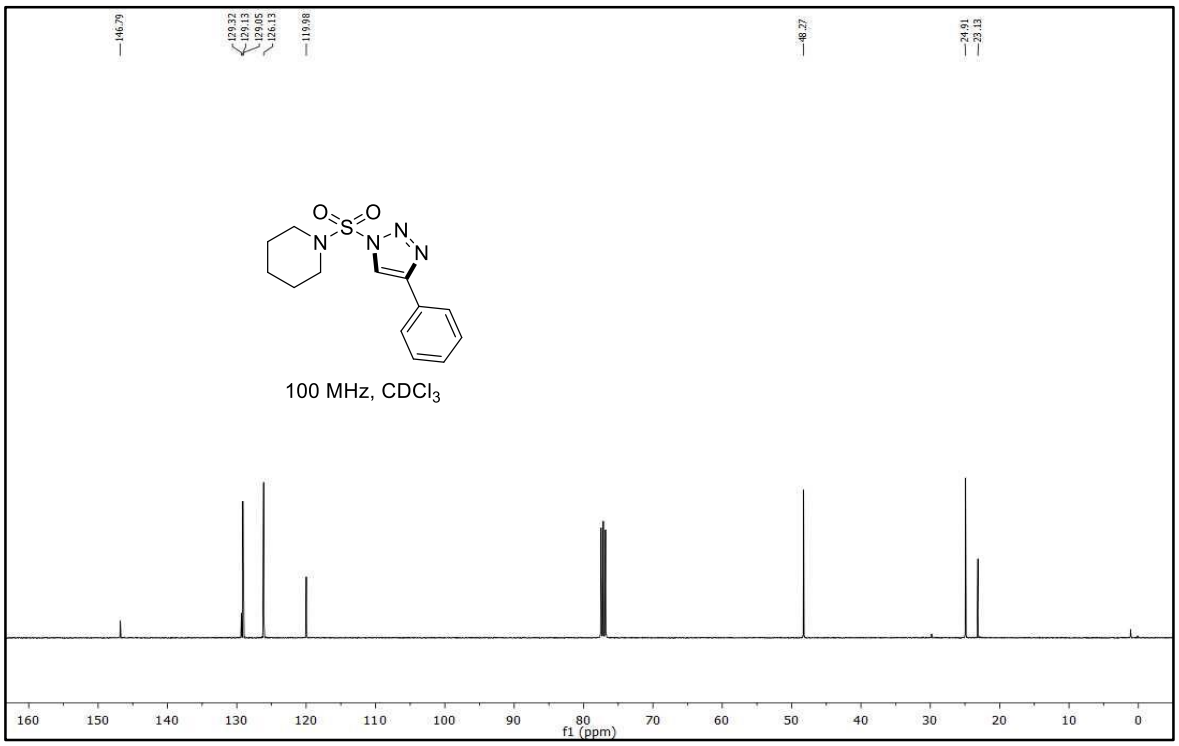
^{1}H and ^{13}C NMR spectra of 5t:



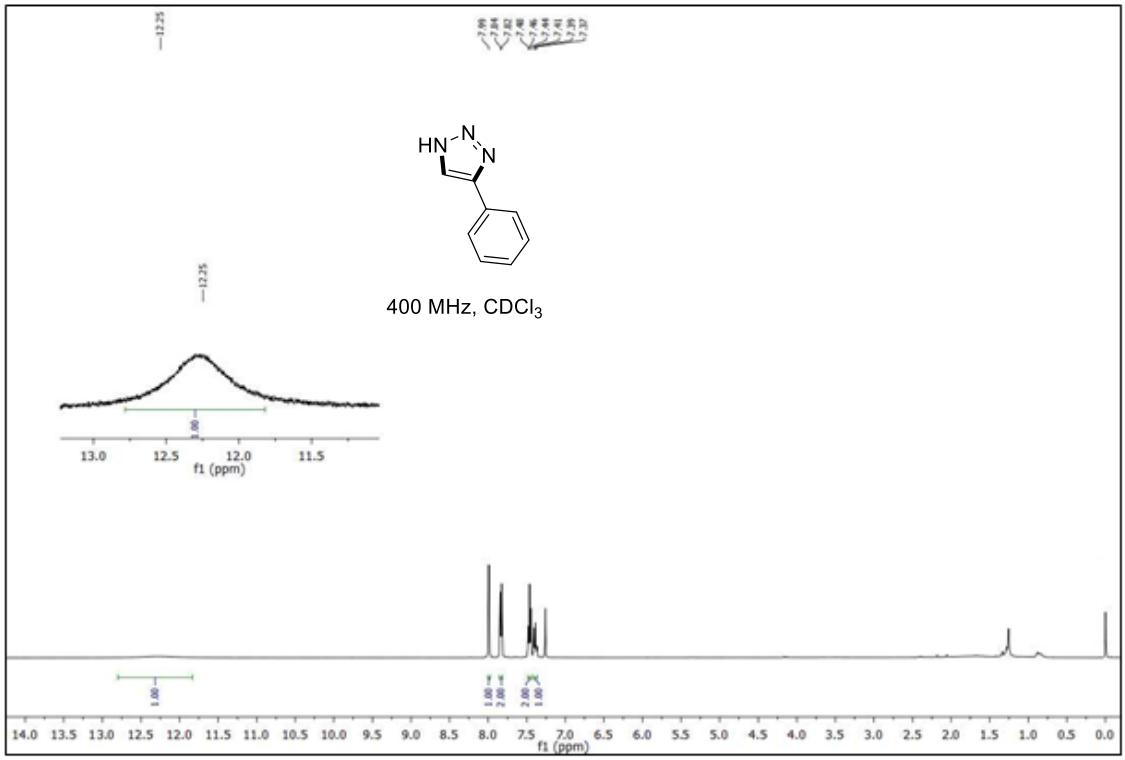


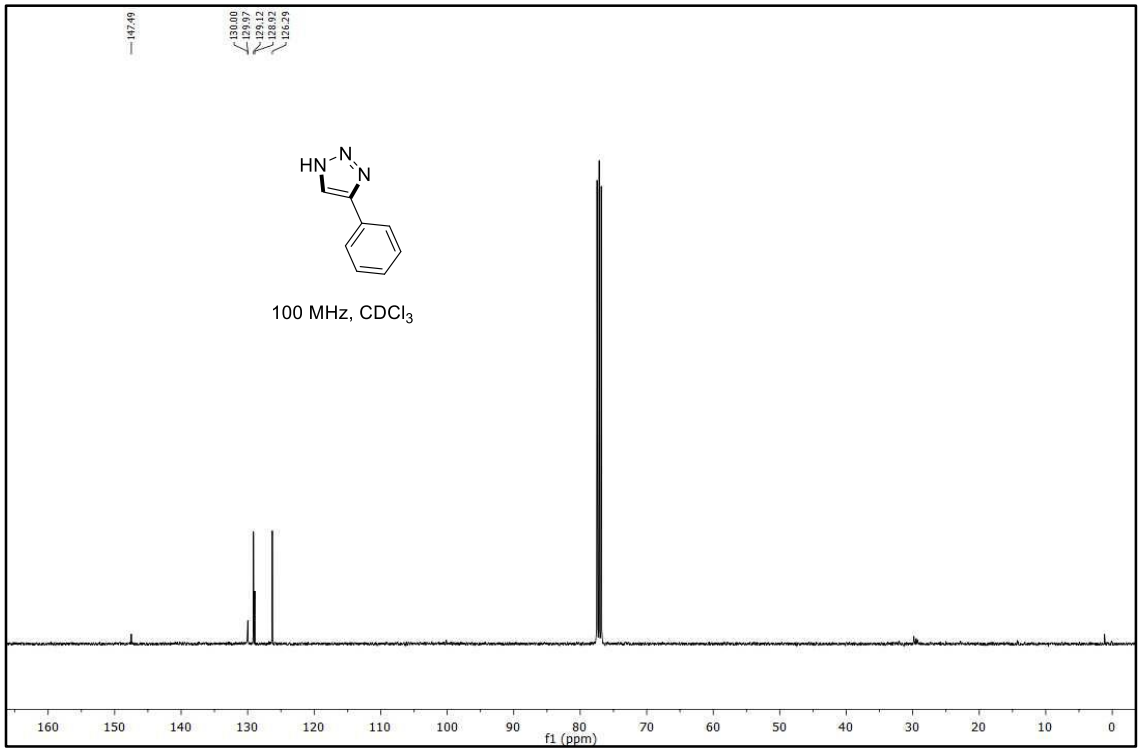
^{1}H and ^{13}C NMR spectra of 5u:



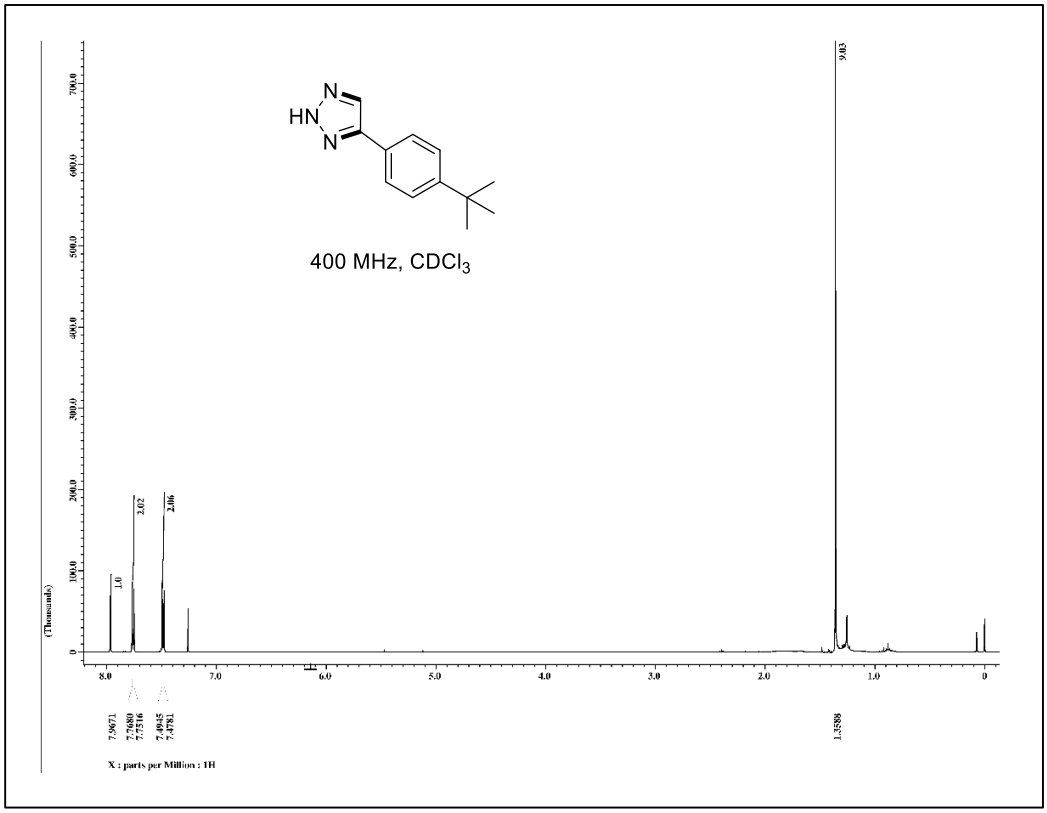


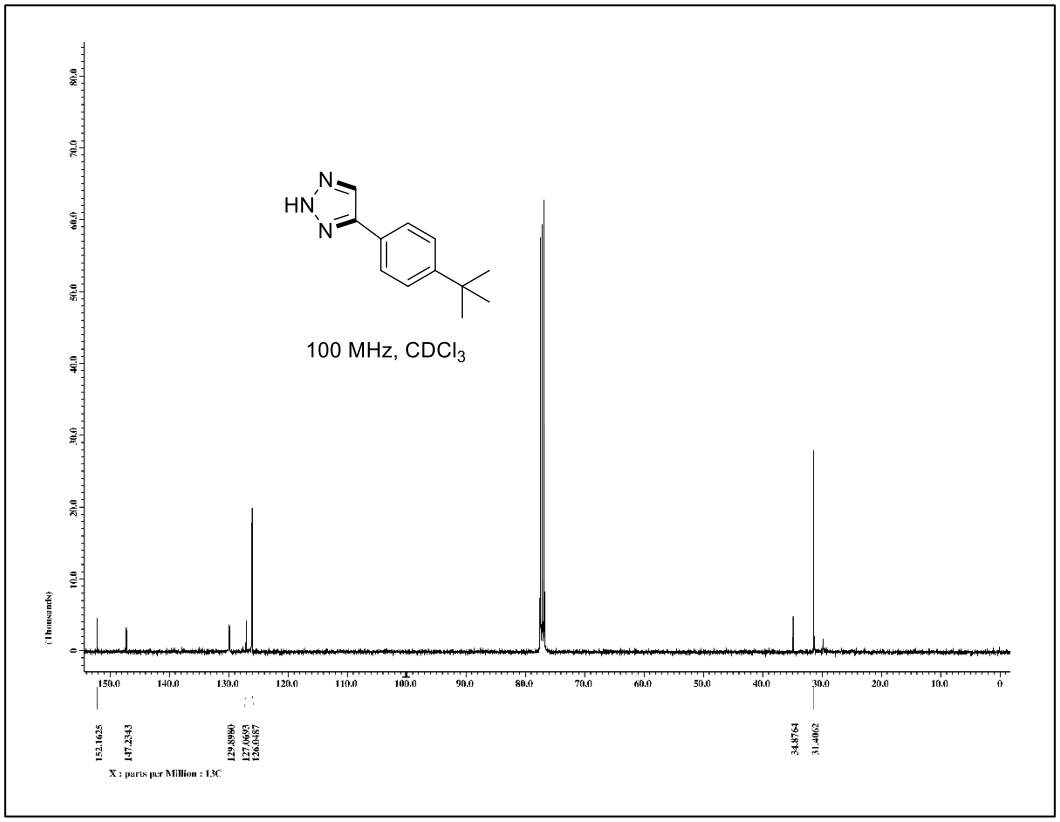
^{1}H and ^{13}C NMR spectra of 6a:



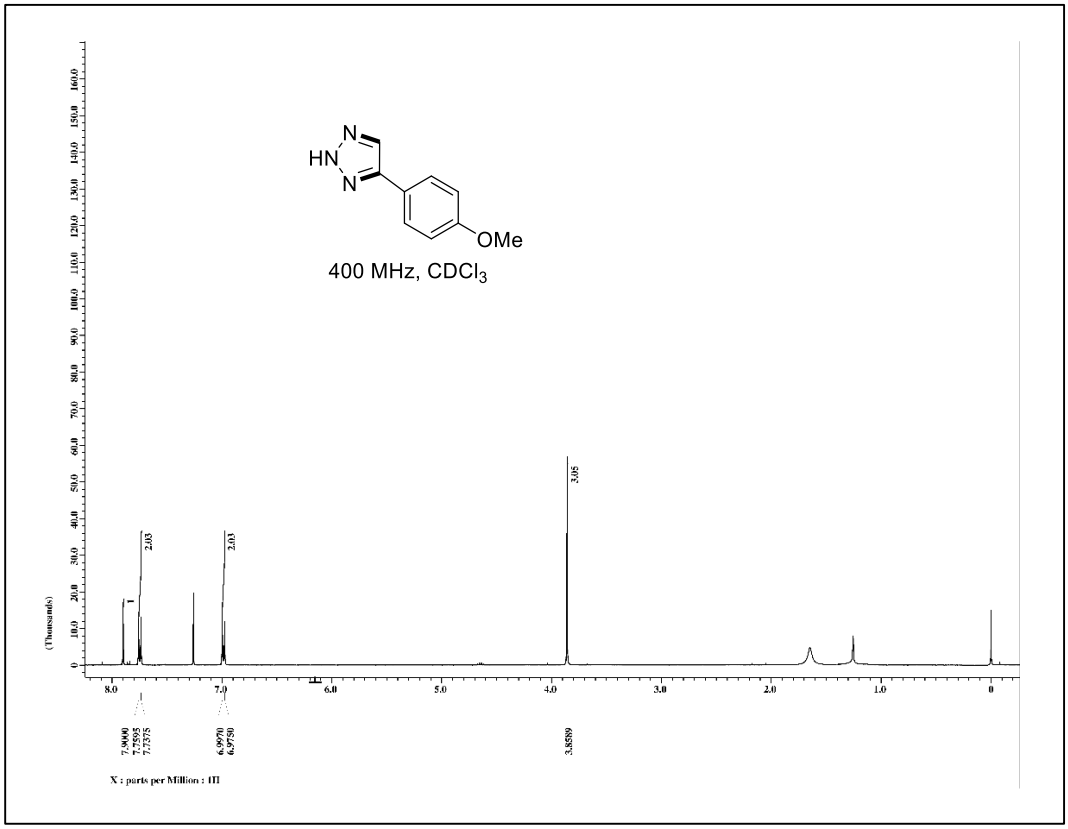


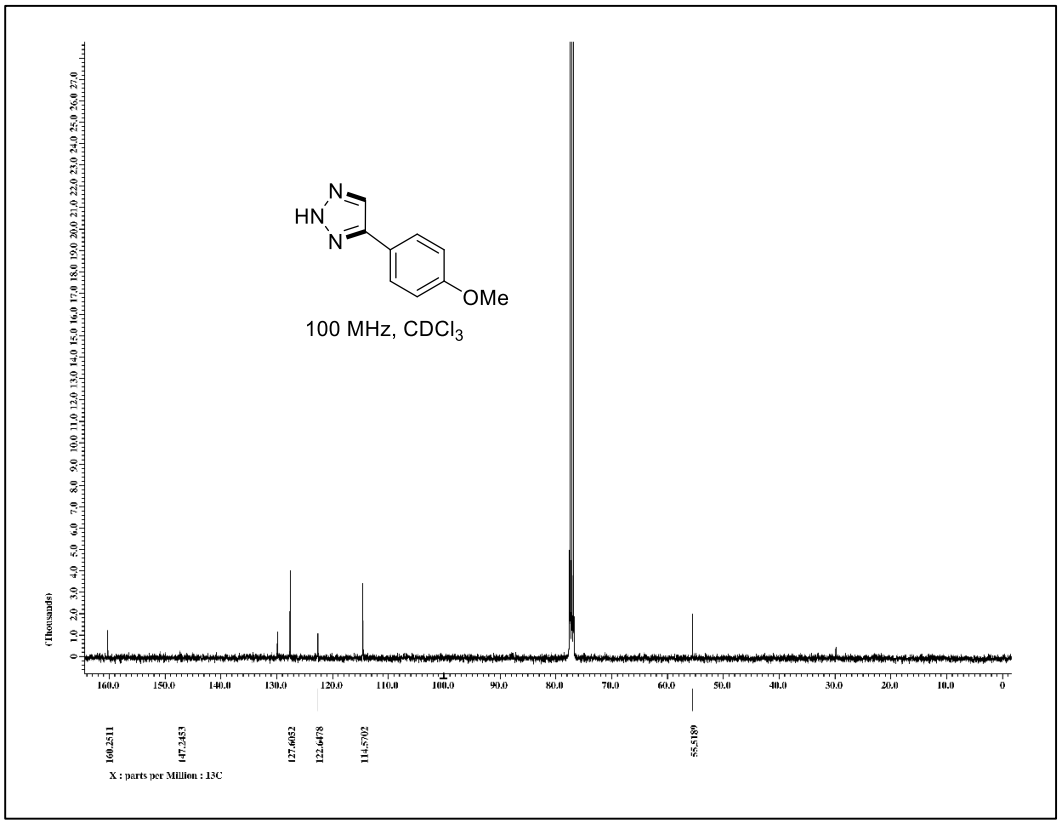
^{1}H and ^{13}C NMR of 6b:



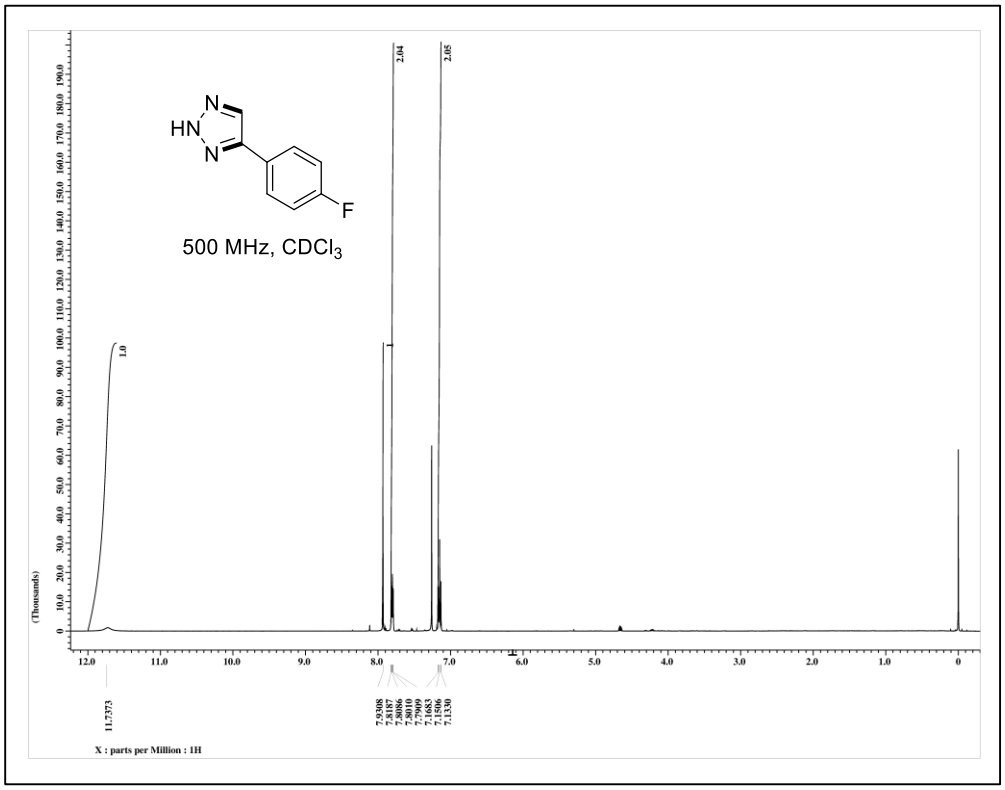


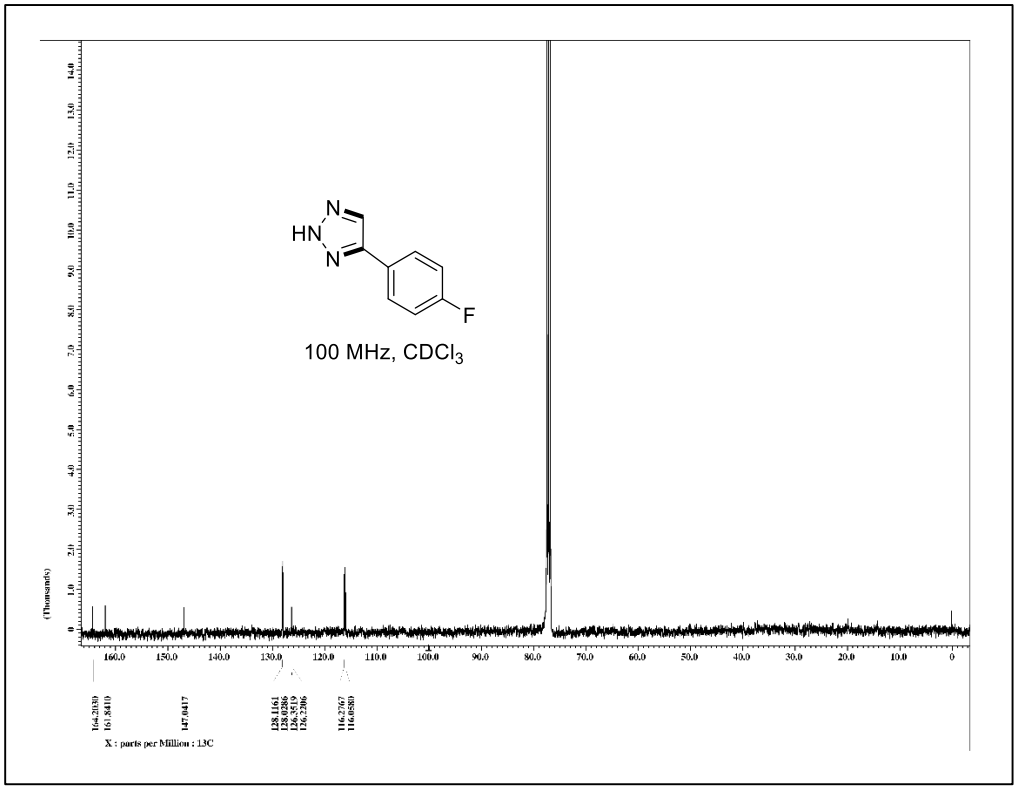
^{1}H and ^{13}C NMR of 6c:





^{1}H and ^{13}C NMR of 6d:





^{1}H and ^{13}C NMR of 6e: