Electronic Supplementary Material (ESI) for ChemComm.

A [3+2] Cycloaddition-1,2-Acyl Migration-Hydrolysis Cascade for Regioselective Synthesis of 1,2,3-Triazoles in Water

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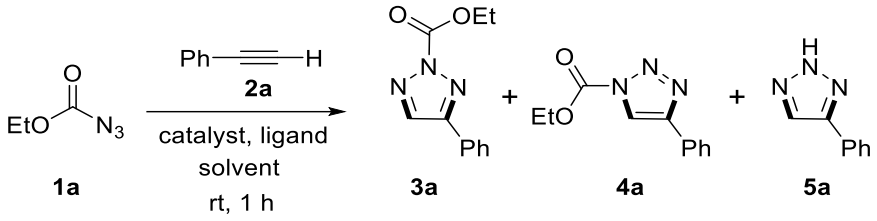
1.0 General information

All experiments were carried out in flame-dried reaction vials. Solvents were dried using standard procedures reported in Perrin, D. D.; Armarego, W. L. F., Purification of Laboratory Chemicals, 3rd edition, Pergamon Press, Oxford, 1988. 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), integration and coupling constants (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

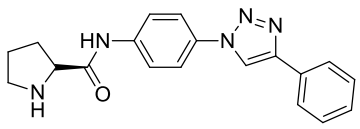
Table S1. Optimization of reaction conditions of the cascade reaction of ethyl azidoformate (1a) with phenylacetylene (2a)[a]



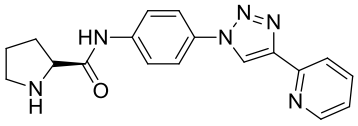
entry	ligand	catalyst	solvent	time	yield (%)[b]		
					3a	**4a**	**5a**
1	**Pro-1**	**CuI**	**H_2O**	**1 h**	**90**	**trace**	**10**
2	**Pro-1**	-	H_2O	1 h	-	-	-
3	-	CuI	H_2O	3 h	-	-	-
4	**Pro-1**	CuI	DMSO	1 h	65	trace	-
5	**Pro-1**	CuI	EtOH	1 h	50	trace	-
6	**Pro-1**	CuI	DMF	1 h	55	trace	-
7	**Pro-1**	CuI	*tert*-butanol	1 h	-	-	-
8	**Pro-1**	CuI	DCM	1 h	-	-	-
9	**Pro-1**	CuI	MeCN	1 h	-	-	-
10	**Pro-1**	CuI	1,4-Dioxane	1 h	10	-	-
11	*L*-Proline	CuI	H_2O	1 h	45	55	-
12	1,4-diphenyl-1H-1,2,3-triazole	CuI	H_2O	1 h	-	-	-
13	*D,L*-Proline	CuI	H_2O	1 h	45	55	-
14	*N*-boc-**Pro-1**	CuI	H_2O	1 h	-	-	-
15	***D,L*-Pro-1**	CuI	H_2O	1 h	90	trace	-
16	**Pro-2**	CuI	H_2O	1 h	85	trace	-
17	**Pro-3**	CuI	H_2O	1 h	70	trace	-
18	**Pro-1**	$Cu(OAc)_2$	H_2O	1 h	-	-	-
19	**Pro-1**	CuO	H_2O	1 h	-	-	-
20	**Pro-1**	CuBr	H_2O	1 h	50	trace	-
21	**Pro-1**	Cu(0)	H_2O	1 h	-	-	-

22[c]	**Pro-1**	CuI	H_2O	1 h	-	-	-
23	**Pro-1**	**CuI**	**H_2O**	**2 h**	**trace**	**-**	**90**

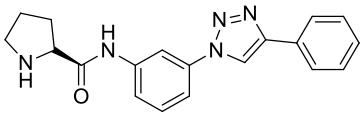
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol) in 2 mL solvent; [b]Yield refers to the isolated yield after chromatographic purification. [c]The reaction was performed at 100 °C.



Pro-1



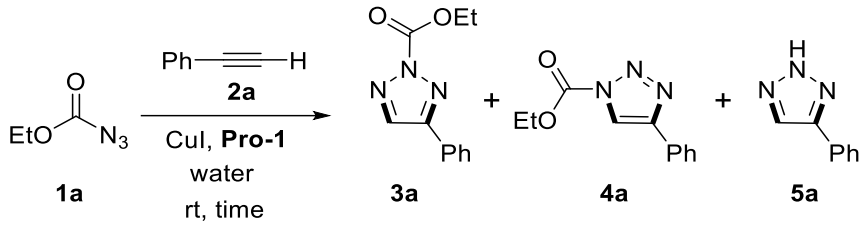
Pro-2



Pro-3

To obtain the optimal reaction conditions a series of solvents, ligands and copper catalysts were screened. Different solvents were used (entries 4-10) and the results suggested that water is the best choice for the reaction (entry 1). The reaction did not proceed well in solvents like DMSO, EtOH and DMF (entries 4-6). In the presence of solvents such as *tert*-butanol, DCM, MeCN and 1,4-Dioxane, no product formation was detected (entries 7-10). Decreased catalytic activity was observed when ligands such as *L*-proline, 1,4-diphenyl-1H-1,2,3-triazole, *D,L*-Proline and *N*-boc-**Pro-1** were used in the place of **Pro-1** (entries 11-14). As a chiral ligand is not necessary, the reactions were carried out using an achiral prolinamide **Pro-1** (prepared from D,L-proline) and results were same as that of **Pro-1** (entry 15). However, chiral **Pro-1**, prepared from L-proline was used in this reaction as L-proline is easily available and commercially cheap compared to D,L-proline. Also, prolinamide analogues **Pro-2** and **Pro-3** provided the desired traizole **3a** in good yield (entries 16-17). Finally, we evaluated the effect of different Cu catalysts on the domino reaction and it was observed that CuI promoted the reaction most effectively compared to other Cu(I), Cu(II) and Cu(0) catalysts (entries 18-21). At elevated temperature (100 °C), no product formation was observed presumably due to the decomposition of azide (entry 22).

Table S2. Effect of ligand, Cu(I) loading and time on the cascade reaction of ethyl azidoformate (1a) with phenylacetylene (2a)[a]



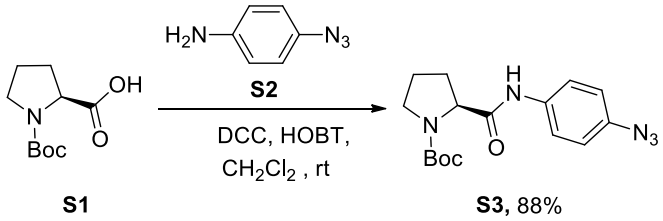
entry	**Pro-1** (mol%)	CuI (mol%)	time	yield (%)[b]		
				3a	**4a**	**5a**
1	1	1	1 h	15	trace	-
2	2	5	1 h	55	trace	-
3	5	5	1 h	60	trace	-
4	8	5	1 h	85	trace	-
5	**10**	**5**	**1 h**	**90**	trace	**10**
6	10	2	1 h	75	trace	-
7	10	1	1 h	55	trace	-
8	15	10	1 h	90	trace	10
9	10	5	5 min	60	trace	2
10	10	5	20 min	70	15	5
11	10	5	50 min	85	trace	8
12	10	5	1.5 h	50	nd	50
13	**10**	**5**	**2 h**	**trace**	**nd**	**90**

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol) in 2 mL water; [b]The yields of **3a, 4a** and **5a** are reffered to isolated yields after chromatographic purofication.

The highest yield of **3a** was obtained when 10 mol% **Pro-1** and 5 mol% CuI were used and the reaction was stirred at room temperature in the presence of water for 1 h (entry 5, Table S2) and the highest yield of **5a** was obtained when 10 mol% **Pro-1** and 5 mol% CuI were used and the reaction was stirred at room temperature in the presence of water for 2 h (entry 13, Table S2).

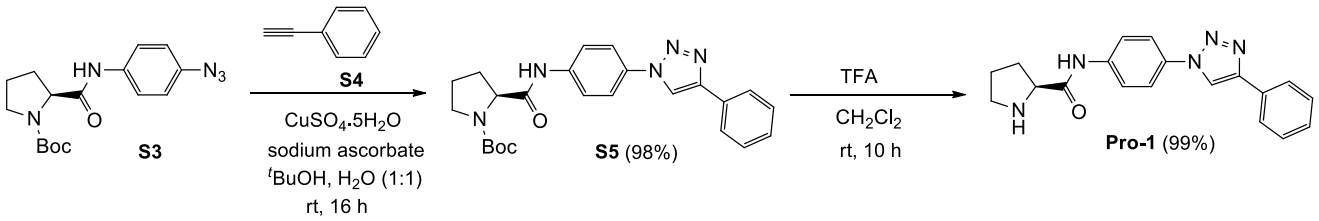
3.0 Preparation of ligands

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, 2H, *J* = 9.4 Hz), 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: A Cu(I)-catalyzed cycloaddition of azido prolinamide **S3** and phenyl acetylene **(S4)** afforded triazole derivative **S5**, which upon removal of Boc group afforded ligand **Pro-1** (Scheme S2).



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

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

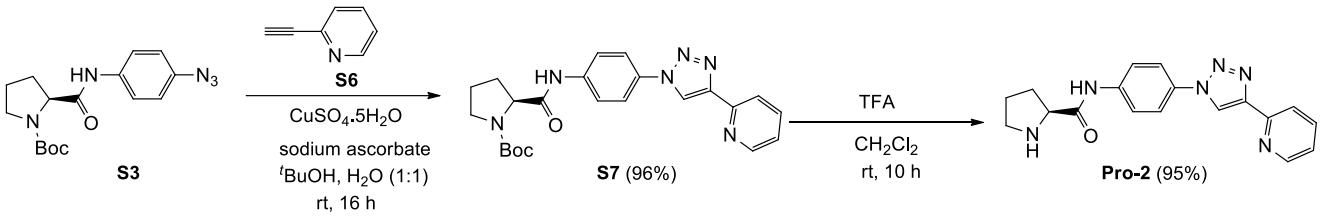
[1]Paladhi, S; Das, J.; Mishra, P. K.; Dash, J. *Adv. Synth. Cat*. **2013**, *355*, 274-280.

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

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, 2H, *J* = 9.1 Hz), 7.57 (d, 2H, *J* = 9.6 Hz), 7.44 (d, 2H, *J* = 9.2 Hz), 7.35 (t, 2H, *J* = 8.5 Hz), 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, 2H, *J* = 8.8 Hz), 7.77 (d, 2H, *J* = 11.3 Hz), 7.72 (d, 2H, *J* = 11.1 Hz), 7.44 (t, 2H, *J* = 9.5 Hz), 7.35 (t, 1H, *J* = 9.2 Hz), 3.89 (dd, 1H, *J* = 11.6, 6.5 Hz), 3.09 (td, 1H, *J* = 12.8, 8.5 Hz), 3.00 (td, 1H, *J* = 12.8, 7.9 Hz), 2.40 (br s, 1H), 2.25-2.20 (m, 1H), 2.04 (dt, 1H, *J* = 15.6, 8.3 Hz), 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, 1H, *J* = 3.9 Hz), 8.11

(d, 2H, *J* = 7.8 Hz), 7. 96 (d, 3H, *J* = 8.3 Hz), 7.83 (d, 2H, *J* = 8.3 Hz), 7.40 (t, 1H, *J* = 5.4 Hz), 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.

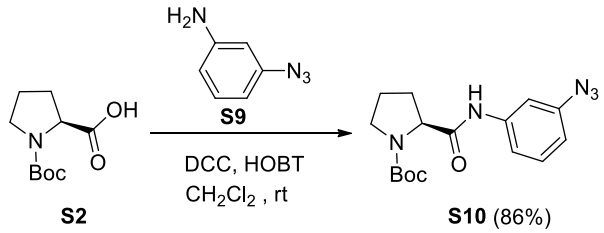
Preparation of ligand Pro-2: To an ice cold solution of compound **S7** (1.0 g, 2.3 mmol) in 30 mL dry CH_2Cl_2, added TFA (0.53 mL, 6.9 mmol, 3.0 equiv) and the mixture was stirred for 10 h at room temperature. After consumption of the starting material **S7** (monitored by TLC), the reaction mixture was brought to pH 8-9 by dropwise adition of 30 wt% solution of NH3 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, 1H, *J* = 3.4 Hz), 8.11 (d, 2H, *J* = 7.6 Hz), 7. 96-7.89 (m, 5H), 7.39 (t, 1H, *J* = 5.1 Hz), 3.75 (s, 1H), 2.92 (t, 2H, *J* = 6.7 Hz), 2.11-2.04 (m, 1H), 1.84-1.78 (m, 1H), 1.67 (t, 1H, *J* = 5.9 Hz), 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, 1H, *J* = 7.9 Hz), 6.43 (dd, 2H, *J* = 6.7Hz, 1.8 Hz), 6.30 (t, 1H, *J* = 1.8 Hz), 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

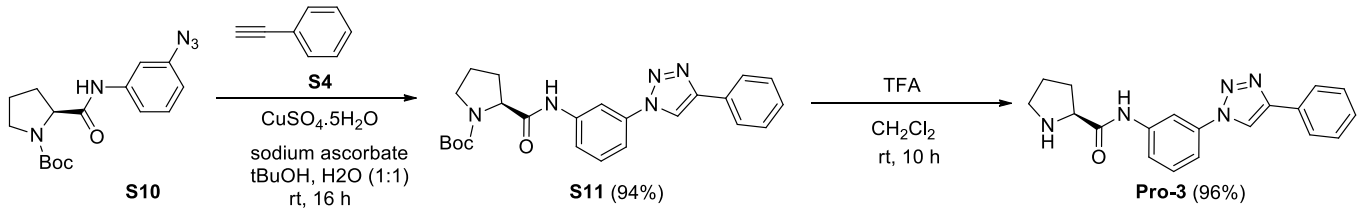
[3](a) Andersen, J.; Madsen, U.; Björkling, F.; Liang, X.*Synlett* **2005**, 2209-2213. (b) Paladhi, S.; Das, J.; Mishra,P. K.; Dash, J. *Adv. Synth. Cat*. **2013**, *355*, 274-280.

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.



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, 2H, *J* = 7.8 Hz), 7.38 (t, 1H, *J* = 7.4 Hz), 3.91 (q, 1H, *J* = 5.8 Hz), 3.02 (t, 2H, *J* = 6.8 Hz), 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 General procedure for the synthesis of N^2-carboxyalkylated-2H-1,2,3-triazoles from azidoformates and alkynes (GP-1)

In a small reaction vial, **Pro-1** (0.02 mmol,), azidoformates (0.2 mmol), aromatic alkyne (0.3 mmol) and water (0. 2 M) were taken. Then, copper iodide (0.01 equiv) was added and the resulting heterogeneous reaction mixture was stirred at rt for 1 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 (95:05-90:10) as eluent to provide the corresponding products.

5.0 General procedure for the synthesis of free 2H-1,2,3-triazoles starting from azidoformates and alkynes (GP-2)

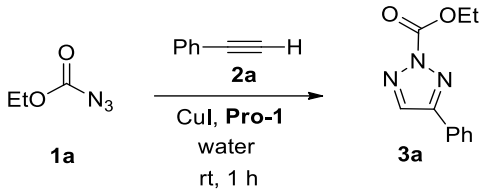
In a small reaction vial, **Pro-1** (0.02 mmol,), azidoformates (0.2 mmol), aromatic alkyne (0.3 mmol) and water (2.0 mL, 0. 2 M) were taken. Then, copper iodide (0.01 equiv) was added and the resulting heterogeneous reaction mixture was stirred at rt for 2 h. The completion of reaction was monitored 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 provide the corresponding products.

6.0 General procedure for the synthesis of free 2H-1,2,3-triazoles starting from N^2-carboxyalkylated-2H-1,2,3-triazoles (GP-3)

In a small reaction vial, N^2-carboxyalkylated-2H-1,2,3-triazoles (0.3 mmol) and water (2.0 mL, 0. 2 M) were taken. Then, **Pro-1** (0.03 equiv) was added and the resulting heterogeneous reaction mixture was stirred at rt for 1 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 provide the corresponding products.

7.0 Gram scale experiments

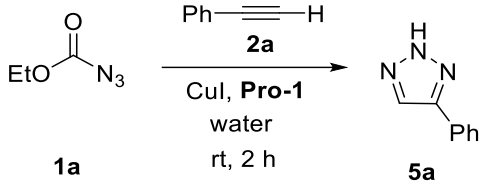
Preparation of ethyl 4-phenyl-2H-1,2,3-triazole-2-carboxylate 3a



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

To a suspension of ethyl carbonazidate **1a** (1.00 g, 8.69 mmol, 1 equiv), phenylacetylene **2a** (1.33 g, 13.03 mmol, 1.5 equiv) in water (0. 2 M), were added copper iodide (82.56 mg, 0.43 mmol, 0.05 equiv) and **Pro-1** (289.4 mg, 0.87 mmol, 0.1 equiv). The reaction mixture was stirred at rt for 1 h (Schme S6). After the completion of reaction, 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 (95:05-90:10) as eluent to provide the corresponding compound **3a** (1.60 g, 85%) in pure form and analyzed by ^{1}H and ^{13}C NMR.

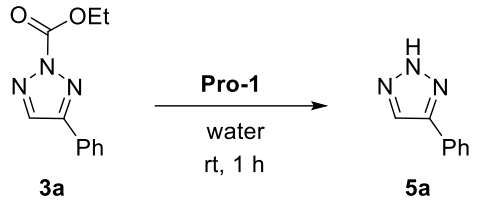
Preparation of 4-phenyl-2H-1,2,3-triazole 5a from 1a



Scheme S7. Gram scale synthesis of **5a** from **1a**.

To a suspension of ethyl carbonazidate **1a** (1.00 g, 8.69 mmol, 1 equiv), phenylacetylene **2a** (1.33 g, 13.03 mmol, 1.5 equiv) in water (0.2 M), were added copper iodide (82.56 mg, 0.43 mmol, 0.05 equiv) and **Pro-1** (289.4 mg, 0.87 mmol, 0.1 equiv). The reaction mixture was stirred at rt for 2 h (Schme S7). After the completion of reaction, 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 provide the corresponding compound **5a** (1.13 g, 92%) in pure form and analyzed by ^{1}H and ^{13}C NMR.

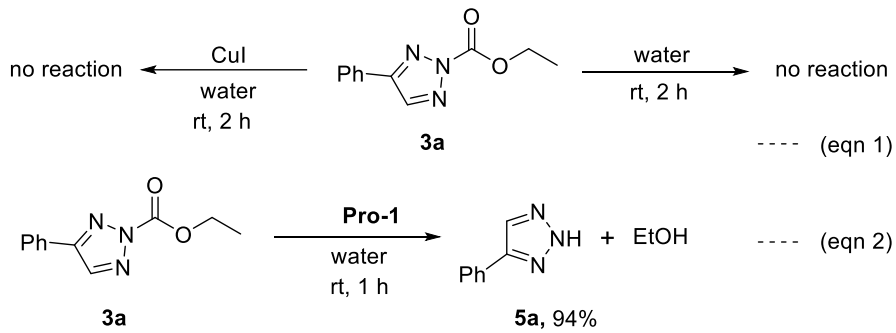
Preparation of 4-phenyl-2H-1,2,3-triazole 5a from 3a



Scheme S8. Gram scale synthesis of **5a** from **3a**.

To a suspension of ethyl 4-phenyl-2H-1,2,3-triazole-2-carboxylate **3a** (1.00 g, 4.60 mmol, 1 equiv) in water (0. 2 M), was added **Pro-1** (153.2 mg, 0.46 mmol, 0.1 equiv). The reaction mixture was stirred at rt for 1 h (Schme S8). After the completion of reaction, 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 provide the corresponding compound **5a** (627 mg, 94%) in pure form and analyzed by ^{1}H and ^{13}C NMR.

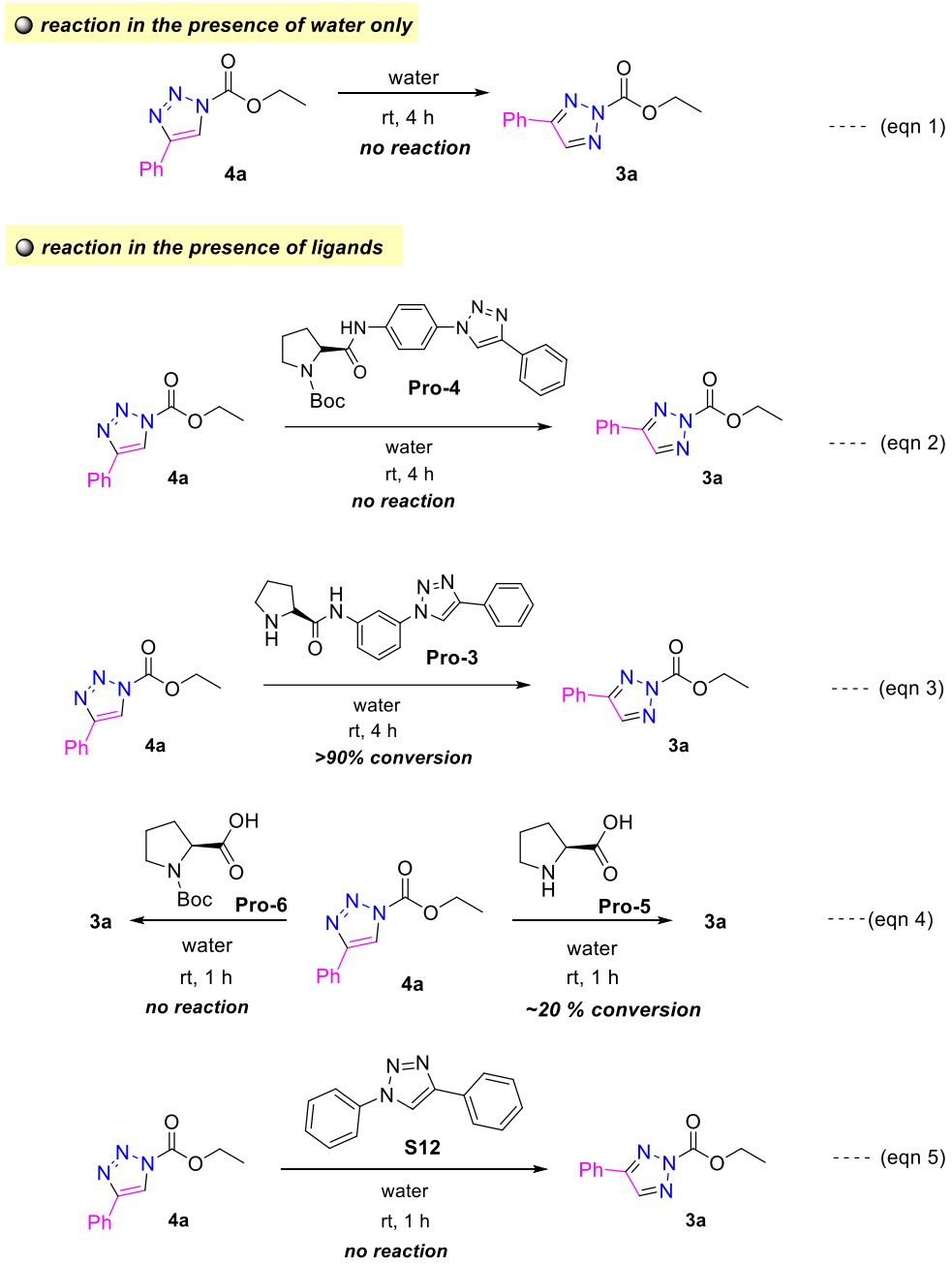
8.0 Control experiments for hydrolysis



Scheme S9. Hydrolysis of N^2-carboxyalkylated-2H-1,2,3-triazole **3a**.

To identify the role of CuI and **Pro-1** in the hydrolysis reaction, control experiments were carried out using **3a** as the model substrate. When **3a** was treated with either water or CuI in the absence of **Pro-1**, no hydrolysis product was detected (eqn 1). In the presence of **Pro-1**, **3a** was completely hydrolyzed to the corresponding product **5a** (eqn 2).

9.0 Factors controlling the 1,2-acyl transfer

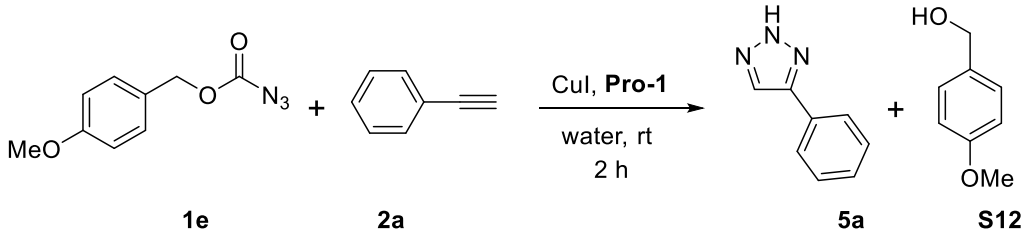


Scheme S10. Acyl migration of **4a** to **3a**.

The 1,2-acyl transfer of **4a** to **3a** was investigated under various reaction conditions. When the acyl migration was carried out only using water, no product formation was observed (eqn 1). Similarly, in the presence of **Pro-4**, no acyl transfer was detected (eqn 2). However, a rapid acyl migration was observed when the reaction was performed using **Pro-3** (eqn 3). In the presence of *L*-proline **Pro-5**, only 20% conversion of **4a** was found (eqn 4). No reaction was observed when *N*-Boc protected *L*-proline **Pro-6** and a triazole derivative **S12** was used as ligand (eqn 4 and 5).

10.0 Detection of side product formed during hydrolysis:

The cascade reaction of *p*-methoxy benzylazidoformate **1e** and phenyl acetylene **2a** provided the free triazole **5a** along with the formation of *p*-methoxy benzylalcohol **S12** as side product after hydrolysis (Scheme S11, S.I.). The 1H NMR of the mixture of **5a** and **S12** is attached herewith and has also been provided in the revised supporting information (Figure S1, S.I.).



Scheme S11. Formation of alcohol as side product during the hydrolysis.

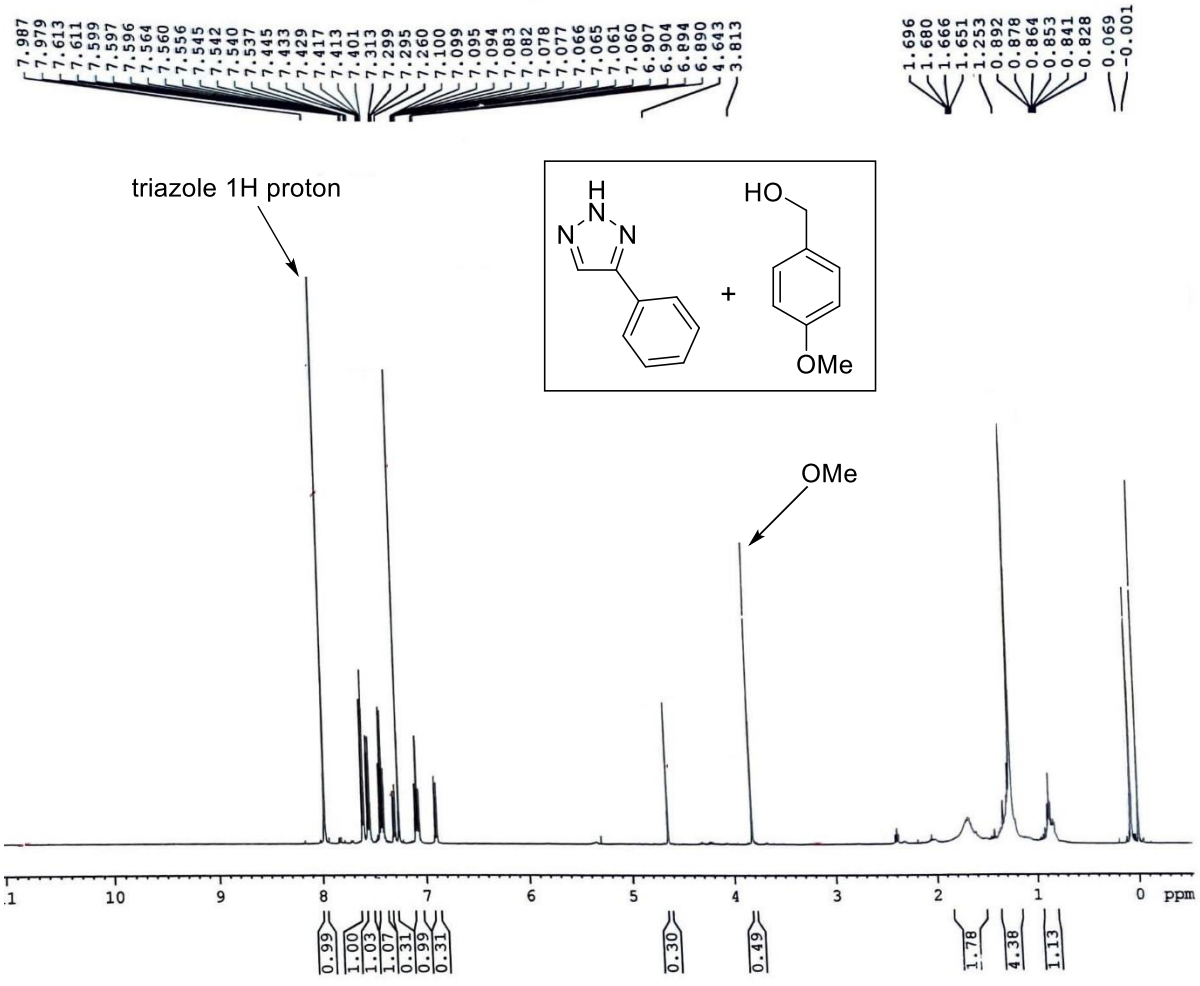
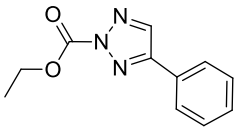


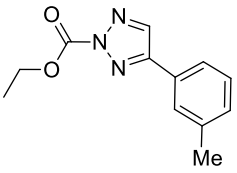
Figure S1. 1H NMR of the free triazole **5a** and *p*-methoxy benzylalcohol **S12**.

11.0 Analytical data of compounds

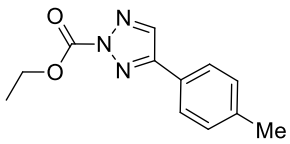
Ethyl 4-phenyl-2H-1,2,3-triazole-2-carboxylate (3a): White solid (90% using **GP-1**). ^{1}H NMR (500 MHz, $CDCl_3$): 8.14 (s, 1H), 7.91-7.89 (m, 2H), 7.49-7.43 (m, 2H), 4.64 (q, 2H, *J* = 7.0 Hz), 1.53 (t, 3H, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 151.6, 147.7, 135.9, 130.2, 129.2, 127.0, 65.9, 14.3; HRMS (ESI) calcd for $C_{11}H_{12}N_3O_2$ $[M+H]^+$: 218.0930; found: 218.0923.



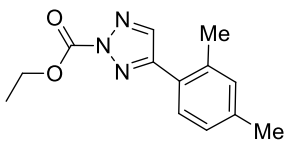
Ethyl 4-(m-tolyl)-2H-1,2,3-triazole-2-carboxylate (3b): White solid (88% using **GP-1**). ^{1}H NMR (500 MHz, $CDCl_3$): 8.13 (s, 1H), 7.76 (s, 1H), 7.67 (d, 1H, *J* = 8.2 Hz), 7.35 (t, 1H, *J* = 7.6 Hz), 7.25 (d, 1H, *J* = 8.2 Hz), 4.64 (q, 2H, *J* = 6.9 Hz), 2.41 (s, 3H), 1.53 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 151.7, 147.7, 139.0, 136.0, 130.9, 129.0, 128.4, 127.5, 124.1, 65.9, 21.4, 14.4; HRMS (ESI) calcd for $C_{12}H_{13}N_3NaO_2$ $[M+Na]^+$: 254.0905; found: 254.0907.



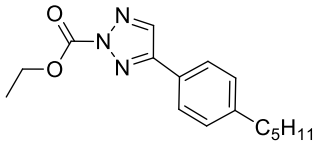
Ethyl 4-(p-tolyl)-2H-1,2,3-triazole-2-carboxylate (3c): White solid (85% using **GP-1**). ^{1}H NMR (300 MHz, $CDCl_3$): 8.11 (s, 1H), 7.80 (d, 2H, *J* = 6.4 Hz), 7.27 (d, 2H, *J* = 8.0 Hz), 4.64 (q, 2H, *J* = 6.8 Hz), 2.40 (s, 3H), 1.53 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): 151.6, 147.7, 140.4, 135.9, 129.9, 126.9, 125.7, 65.9, 21.6, 14.4; HRMS (ESI) calcd for $C_{12}H_{13}N_3NaO_2$ $[M+Na]^+$: 254.0905; found: 254.0904.



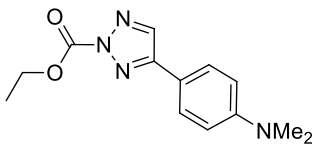
Ethyl 4-(2,4-dimethylphenyl)-2H-1,2,3-triazole-2-carboxylate (3d): White solid (87% using **GP-1**). ^{1}H NMR (400 MHz, $CDCl_3$): 8.02 (s, 1H), 7.46 (s, 1H), 7.20-7.13 (m, 2H), 4.65 (q, 2H, *J* = 7.3 Hz), 2.46 (s, 3H), 2.36 (s, 3H), 1.54 (t, 3H, *J* = 6.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): 151.9, 148.1, 138.1, 135.9, 133.6, 131.3, 131.1, 130.6, 130.2, 127.8, 65.9; HRMS (ESI) calcd for $C_{13}H_{15}N_3NaO_2$ $[M+Na]^+$: 268.1062; found: 268.1049.



Ethyl 4-(4-pentylphenyl)-2H-1,2,3-triazole-2-carboxylate (3e): White solid (86% using **GP-1**). ^{1}H NMR (500 MHz, $CDCl_3$): 8.12 (s, 1H), 7.82 (dd, 2H, *J* = 1.9, 4.4 Hz), 7.28 (d, 2H, *J* = 8.2 Hz), 4.64 (q, 2H, *J* = 7.6 Hz), 2.65 (t, 2H, *J* = 7.6 Hz), 1.67-1.63 (m, 2H), 1.54 (t, 3H, *J* = 7.0 Hz), 1.35-1.31 (m, 4H), 0.89 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 151.7, 147.8, 145.5, 135.9, 129.3, 126.9, 125.9, 65.9, 36.0, 31.6, 31.1, 22.7, 14.3, 14.1; HRMS (ESI) calcd for $C_{16}H_{21}N_3NaO_2$ $[M+Na]^+$: 310.1531; found: 310.1532.



Ethyl 4-(4-(dimethylamino)phenyl)-2H-1,2,3-triazole-2-carboxylate (3f): White solid (85% using **GP-1**). ^{1}H NMR (400 MHz, $CDCl_3$): 8.06 (s, 1H), 7.78 (d, 2H, *J* = 8.8 Hz), 6.75 (d, 2H, *J* = 8.8 Hz), 4.63 (q, 2H, *J* = 7.3 Hz), 3.03 (s, 6H), 1.53 (t, 3H, *J* = 7.4



Hz); ^{13}C NMR (125 MHz, $CDCl_3$): 151.8, 147.9, 135.6, 128.1, 113.1, 111.2, 65.7, 40.9, 14.4; HRMS (ESI) calcd for $C_{13}H_{16}N_4NaO_2$ $[M+Na]^+$: 283.1171; found: 283.1159.

Ethyl 4-(2-methoxyphenyl)-2H-1,2,3-triazole-2-carboxylate (3g): White solid (84% using **GP-1**). ^{1}H NMR (400 MHz, $CDCl_3$): 8.62 (s, 1H), 8.40 (dd, 1H, *J* = 1.5, 6.4 Hz), 7.41-7.35 (m, 1H), 7.12-7.08 (m, 1H), 7.02-6.99 (m, 1H), 4.67-4.62 (m, 2H), 3.97 (s, 3H), 1.56-1.49 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 156.2, 143.4, 131.6, 129.9, 128.4, 122.4, 121.2, 118.2, 110.9, 65.8, 55.6, 14.3; HRMS (ESI) calcd for $C_{12}H_{14}N_3O_3$ $[M+H]^+$: 248.1035; found: 248.1021.

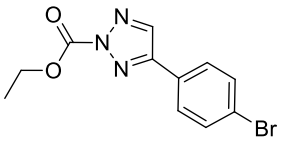
Ethyl 4-(3-methoxyphenyl)-2H-1,2,3-triazole-2-carboxylate (3h): White solid (80% using **GP-1**). ^{1}H NMR (400 MHz, $CDCl_3$): 8.13 (s, 1H), 7.46-7.44 (m, 2H), 7.37 (t, 1H, *J* = 7.8 Hz), 7.00-6.97 (m, 1H), 4.67-4.62 (m, 2H), 3.88 (s, 3H), 1.53 (t, 3H, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 160.3, 151.5, 147.7, 136.1, 130.2, 129.8, 119.4, 116.3, 111.9, 66.0, 55.6, 14.3; HRMS (ESI) calcd for $C_{12}H_{14}N_3O_3$ $[M+H]^+$: 248.1035; found: 248.1031.

Ethyl 4-(4-methoxyphenyl)-2H-1,2,3-triazole-2-carboxylate (3i): White solid (82% using **GP-1**). ^{1}H NMR (400 MHz, $CDCl_3$): 8.08 (s, 1H), 7.85 (d, 2H, *J* = 8.8 Hz), 6.99 (d, 2H, *J* = 8.8 Hz), 4.64 (q, 2H, *J* = 7.3 Hz), 3.86 (s, 3H), 1.53 (t, 3H, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 161.3, 151.1, 147.7, 135.7, 128.4, 127.7, 121.1, 114.7, 65.8, 55.5, 14.4; HRMS (ESI) calcd for $C_{12}H_{14}N_3O_3$ $[M+H]^+$: 248.1035; found: 248.1051.

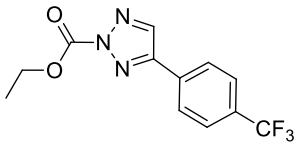
Ethyl 4-(3-fluorophenyl)-2H-1,2,3-triazole-2-carboxylate (3j): White solid (80% using **GP-1**). ^{1}H NMR (500 MHz, $CDCl_3$): 8.13 (s, 1H), 7.68-7.62 (m, 2H), 7.45-7.42 (m, 1H), 7.16-7.12 (m, 1H), 4.64 (q, 2H, *J* = 7.6 Hz), 1.54 (t, 3H, *J* = 6.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 163.3 (d, $^1J_{C-F}$ = 245.0 Hz), 150.3 (d, $^4J_{C-F}$ = 3.0 Hz), 147.5, 135.9, 130.9 (d, $^3J_{C-F}$ = 8.0 Hz), 130.7 (d, $^3J_{C-F}$ = 8.0 Hz), 122.6, 117.1 (d, $^2J_{C-F}$ = 20.0 Hz), 114.0 (d, $^2J_{C-F}$ = 23.0 Hz), 66.1, 14.3; HRMS (ESI) calcd for $C_{11}H_{10}FN_3NaO_2$ $[M+Na]^+$: 258.0655; found: 258.0654.

Ethyl 4-(4-fluorophenyl)-2H-1,2,3-triazole-2-carboxylate (3k): White solid (83% using **GP-1**). ^{1}H NMR (500 MHz, $CDCl_3$): 8.11 (s, 1H), 7.91-7.88 (m, 2H), 7.18-7.15 (m, 2H), 4.64 (q, 2H, *J* = 7.0 Hz), 1.54 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 164.0 (d, $^1J_{C-F}$ = 250.0 Hz), 150.6, 147.6, 135.7, 128.9 (d, $^3J_{C-F}$ = 8.0 Hz), 124.8 (d, $^4J_{C-F}$ = 4.0 Hz), 116.4 (d, $^2J_{C-F}$ = 22.0 Hz), 66.0, 14.4; HRMS (ESI) calcd for $C_{11}H_{10}FN_3NaO_2$ $[M+Na]^+$: 258.0655; found: 258.0668.

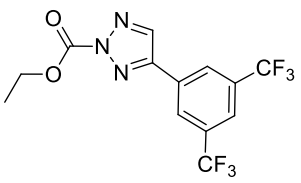
Ethyl 4-(4-bromophenyl)-2H-1,2,3-triazole-2-carboxylate (3l): White solid (81% using **GP-1**). ^{1}H NMR (400 MHz, $CDCl_3$): 8.13 (s, 1H), 7.78 (d, 2H, *J* = 8.3 Hz), 7.62 (d, 2H, *J* = 8.3 Hz), 4.65 (q, 2H, *J* = 7.3 Hz), 1.54 (t, 3H, *J* = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 150.5, 147.7, 135.7, 132.5, 130.9, 128.9, 128.5, 127.5, 124.5, 66.1, 14.2; HRMS (ESI) calcd for $C_{11}H_{10}BrN_3NaO_2$ $[M+Na]^+$: 317.9854; found: 317.9868.



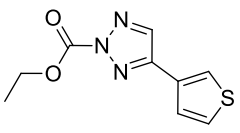
Ethyl 4-(4-(trifluoromethyl)phenyl)-2H-1,2,3-triazole-2-carboxylate (3m): White solid (78% using **GP-1**). ^{1}H NMR (500 MHz, $CDCl_3$): 8.20 (s, 1H), 8.03 (d, 2H, *J* = 7.6 Hz), 7.73 (d, 2H, *J* = 8.2 Hz), 4.66 (q, 2H, *J* = 7.6 Hz), 1.55 (t, 3H, *J* = 6.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): 150.1, 147.5, 136.0, 132.1, 132.0, 131.9, 127.3, 126.3, 126.2, 124.2 (q, $^1J_{C-F}$ = 272.5 Hz), 66.3, 14.4; HRMS (ESI) calcd for $C_{12}H_{10}F_3N_3NaO_2$$[M+Na]^+$: 308.0623; found: 308.0622.



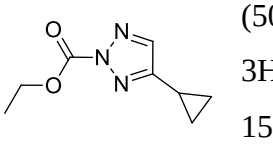
Ethyl 4-(3,5-bis(trifluoromethyl)phenyl)-2H-1,2,3-triazole-2-carboxylate (3n): White solid (76% using **GP-1**). ^{1}H NMR (400 MHz, $CDCl_3$): 8.36 (s, 2H), 8.26 (s, 1H), 7.96 (s, 1H), 4.69 (q, 2H, *J* = 7.4 Hz), 1.57 (t, 3H, *J* = 7.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): 148.8, 135.7, 133.1, 132.7, 130.9, 126.9, 123.5, 123.1 (q, $^1J_{C-F}$ = 270.0 Hz), 66.6, 14.4; HRMS (ESI) calcd for $C_{13}H_9F_6N_3NaO_2$ $[M+Na]^+$: 376.0497; found: 376.0499.



Ethyl 4-(thiophen-3-yl)-2H-1,2,3-triazole-2-carboxylate (3o): Yellowish white solid (75% using **GP-1**). ^{1}H NMR (400 MHz, $CDCl_3$): 8.04 (s, 1H), 7.84-7.83 (m, 1H), 7.59-7.57 (m, 1H), 7.44-7.42 (m, 1H), 4.64 (q, 2H, *J* = 6.8 Hz), 1.53 (t, 3H, *J* = 6.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): 147.6, 147.5, 136.2, 129.9, 127.1, 126.2, 124.7, 65.9, 60.5, 21.1, 14.3; HRMS (ESI) calcd for $C_9H_9N_3NaO_2S$ $[M+Na]^+$: 246.0313; found: 246.0315.



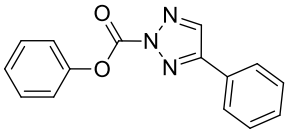
Ethyl 4-cyclopropyl-2H-1,2,3-triazole-2-carboxylate (3p): Colorless solid (68% using **GP-1**). ^{1}H NMR (500 MHz, $CDCl_3$): 7.60 (s, 1H), 4.59 (q, 2H, *J* = 6.9 Hz), 2.07-2.02 (m, 1H), 1.49 (t, 3H, *J* = 6.9 Hz), 1.10-1.06 (m, 2H), 0.94-0.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 155.7, 147.7, 136.4, 65.6, 14.3, 8.9, 7.1; HRMS (ESI) calcd for $C_8H_{12}N_3O_2$ $[M+H]^+$: 182.0930; found: 182.0922.



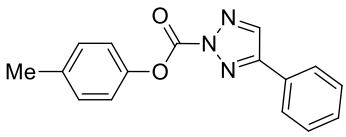
Ethyl 4-(2-bromoethyl)-2H-1,2,3-triazole-2-carboxylate (3q): Pale brown solid (71% using **GP-1**). ^{1}H NMR (500 MHz, $CDCl_3$): 7.82 (s, 1H), 4.61 (q, 2H, *J* = 7.6 Hz), 2.07-2.02 (m, 1H), 3.66 (t, 2H, *J* = 7.0 Hz), 3.37 (t, 2H, *J* = 7.0 Hz), 1.51 (t, 3H, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 150.1, 147.4, 138.2, 66.0, 29.7, 29.4, 14.3; HRMS

(ESI) calcd for $C_7H_{11}BrN_3O_2$ $[M+H]^+$: 248.0035; found: 248.0021.

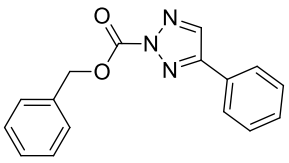
Phenyl 4-phenyl-2H-1,2,3-triazole-2-carboxylate (3r): White solid (71% using **GP-1**). ^{1}H NMR (400 MHz, $CDCl_3$): 8.25 (s, 1H), 7.96 (d, 2H, *J* = 7.3 Hz), 7.51-7.47 (m, 3H), 7.44-7.35 (m, 3H), 7.29-7.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 136.7, 130.4, 130.0, 129.7, 129.3, 127.1, 126.4, 121.3, 121.1; HRMS (ESI) calcd for $C_{15}H_{11}N_3NaO_2$ $[M+Na]^+$: 288.0749; found: 288.0750.



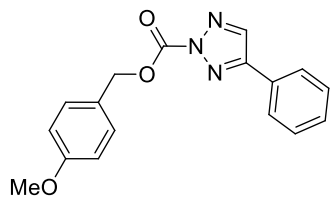
***p*-Tolyl 4-phenyl-2H-1,2,3-triazole-2-carboxylate (3s):** Brown solid (74% using **GP-1**). ^{1}H NMR (400 MHz, $CDCl_3$): 8.24 (s, 1H), 7.95 (d, 2H, *J* = 7.3 Hz), 7.50-7.46 (m, 3H), 7.28-7.23 (m, 1H, merged with $CDCl_3$), 7.20-7.13 (m, 1H), 7.03 (d, 1H, *J* = 7.8 Hz), 6.72 (d, 1H, *J* = 8.3 Hz), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 136.6, 130.5, 130.4, 129.3, 127.1, 120.9, 115.2, 20.8; HRMS (ESI) calcd for $C_{16}H_{13}N_3NaO_2$ $[M+Na]^+$: 302.0905; found: 302.0903.



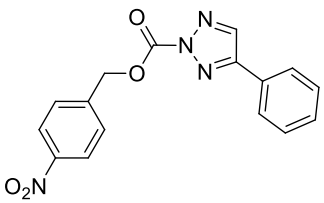
Benzyl 4-phenyl-2H-1,2,3-triazole-2-carboxylate (3t): Brown solid (74% using **GP-1**). ^{1}H NMR (400 MHz, $CDCl_3$): 8.14 (s, 1H), 7.90 (d, 2H, *J* = 7.8 Hz), 7.54 (d, 2H, *J* = 7.8 Hz), 7.47-7.45 (m, 3H), 7.42-7.39 (m, 2H), 5.59 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 144.7, 136.1, 130.2, 129.3, 129.2, 129.1, 127.0, 71.1; HRMS (ESI) calcd for $C_{16}H_{13}N_3NaO_2$ $[M+Na]^+$: 302.0905; found: 302.0921.



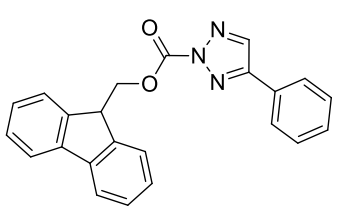
4-Methoxybenzyl 4-phenyl-2H-1,2,3-triazole-2-carboxylate (3u): Brown solid (82% using **GP-1**). ^{1}H NMR (500 MHz, $CDCl_3$): 7.84 (s, 1H), 7.79-7.77 (m, 2H), 7.44-7.40 (m, 2H), 7.34-7.32 (m, 3H), 6.90-6.87 (m, 2H), 5.56 (d, 2H, *J* = 2.5 Hz), 3.79 (d, 3H, *J* = 2.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 159.5, 147.9, 131.5, 130.6, 130.4, 129.7, 128.9, 128.5, 127.6, 126.1, 114.3, 58.4, 55.5; HRMS (ESI) calcd for $C_{17}H_{15}N_3NaO_3$ $[M+Na]^+$: 332.1011; found: 332.1023.



4-Nitrobenzyl 4-phenyl-2H-1,2,3-triazole-2-carboxylate (3v): Deep brown solid (74% using **GP-1**). ^{1}H NMR (400 MHz, $CDCl_3$): 8.24 (d, 2H, *J* = 8.3 Hz), 7.97 (s, 1H), 7.82 (d, 2H, *J* = 7.8 Hz), 7.55 (d, 2H, *J* = 8.3 Hz),. 7.46 (t, 2H, *J* = 7.4 Hz), 7.39 (d, 1H, *J* = 6.8 Hz), 5.29 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 148.3, 147.5, 142.1, 130.4, 129.1, 128.9, 128.7, 127.2, 126.3, 124.1, 123.9, 68.6; HRMS (ESI) calcd for $C_{16}H_{12}N_4NaO_4$ $[M+Na]^+$: 347.0756; found: 347.0741.



(9H-fluoren-9-yl)methyl 4-phenyl-2H-1,2,3-triazole-2-carboxylate (3w): White solid (80% using **GP-1**). ^{1}H NMR (400 MHz, $CDCl_3$): 8.24 (s, 1H), 7.99-7.96 (m, 2H), 7.81-7.78 (m, 4H), 7.54-7.48 (m, 3H), 7.44 (t, 2H, *J* = 7.5 Hz), 7.37-7.33 (m, 2H),. 4.76



(d, 2H, *J* = 8.0 Hz), 4.51 (t, 1H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 151.8, 147.7, 143.0, 141.6, 136.6, 130.3, 129.3, 128.7, 128.3, 127.5, 126.9, 125.6, 120.3, 71.3, 46.7; HRMS (ESI) calcd for $C_{23}H_{17}N_3NaO_2$ $[M+Na]^+$: 390.1218; found: 390.1219.

2-Methoxyethyl 4-phenyl-2H-1,2,3-triazole-2-carboxylate (3x): Colorless gummy liquid (71% using **GP-1**). ^{1}H NMR (500 MHz, $CDCl_3$): 8.15 (s, 1H), 7.92-7.90 (m, 2H), 7.48-7.46 (m, 3H), 4.71 (dd, 2H, *J* = 2.9, 1.4 Hz), 3.83-3.82 (m, 2H),. 3.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 151.8, 136.2, 130.2, 129.2, 128.6, 127.0, 126.3, 69.9, 68.3, 59.3; HRMS (ESI) calcd for $C_{12}H_{14}N_3O_3$ $[M+H]^+$: 248.1035; found: 248.1032.

Isobutyl 4-phenyl-2H-1,2,3-triazole-2-carboxylate (3y): Colorless gummy liquid (65% using **GP-1**). ^{1}H NMR (500 MHz, $CDCl_3$): 8.15 (s, 1H), 7.92-7.90 (m, 2H), 7.47-7.44 (m, 3H), 4.36 (d, 2H, *J* = 7.0 Hz), 2.28-2.20 (m, 1H), 1.07 (d, 6H, *J* = 6.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 151.5, 147.9, 135.9, 130.1, 129.2, 128.7, 127.0, 75.5, 28.0, 19.0; HRMS (ESI) calcd for $C_{13}H_{15}N_3NaO_2$ $[M+Na]^+$: 268.1062; found: 268.1064.

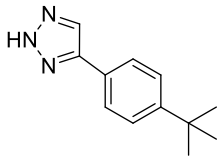
4-Phenyl-2H-1,2,3-triazole (5a): White solid (90% using **GP-2,** 94% using **GP-3**). ^{1}H NMR (500 MHz, $CDCl_3$): 11.9 (br s, 1H), 7.98 (s, 1H), 7.84-7.81 (m, 2H), 7.48-7.45 (m, 2H), 7.41-7.37 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 147.7, 130.0, 129.1, 128.9, 126.3; HRMS (ESI) calcd for $C_8H_8N_3$ $[M+H]^+$: 146.0718; found: 146.0711.

4-(*m*-Tolyl)-2H-1,2,3-triazole (5b): White solid (92% using **GP-2**). ^{1}H NMR (500 MHz, $CDCl_3$): 8.00 (s, 1H), 7.68 (s, 1H), 7.62 (d, 1H, *J* = 7.6 Hz), 7.35 (t, 1H, *J* = 7.6 Hz), 7.20 (d, 1H, *J* = 7.6 Hz), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 147.0, 138.9, 129.7, 129.5, 129.1, 127.0, 123.4, 21.5; HRMS (ESI) calcd for $C_9H_{10}N_3$ $[M+H]^+$: 160.0875; found: 160.0868.

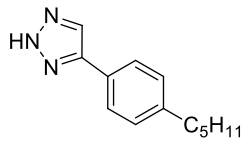
4-(*p*-Tolyl)-2H-1,2,3-triazole (5c): White solid (94% using **GP-2**). ^{1}H NMR (500 MHz, $CDCl_3$): 7.96 (s, 1H), 7.71 (d, 2H, *J* = 7.6 Hz), 7.26 (d, 2H, *J* = 7.0 Hz), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): 147.2, 138.9, 129.8, 127.1, 126.2, 21.5; HRMS (ESI) calcd for $C_9H_{10}N_3$ $[M+H]^+$: 160.0875; found: 160.0863.

4-(2,4-Dimethylphenyl)-2H-1,2,3-triazole (5d): White solid (94% using **GP-2**). ^{1}H NMR (500 MHz, $CDCl_3$): 7.85 (s, 1H), 7.41 (s, 1H), 7.19 (d, 1H, *J* = 7.6 Hz), 7.12 (d, 1H, *J* = 7.6 Hz), 2.43 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 135.8, 133.2, 132.2, 131.1, 129.9, 129.6, 129.0, 21.0, 20.7; HRMS (ESI) calcd for $C_{10}H_{12}N_3$ $[M+H]^+$: 174.1031; found: 174.1024.

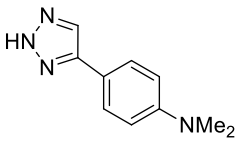
4-(4-(*tert*-Butyl)phenyl)-2H-1,2,3-triazole (5e): White solid (91% using **GP-2**). ^{1}H NMR (500 MHz, $CDCl_3$): 7.97 (s, 1H), 7.75 (d, 2H, *J* = 8.2 Hz), 7.48 (d, 2H, *J* = 8.2 Hz), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): 152.2, 147.2, 129.9, 127.1, 126.0, 34.9, 31.4; HRMS (ESI) calcd for $C_{12}H_{16}N_3$ $[M+H]^+$: 202.1344; found: 202.1338.



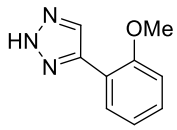
4-(4-Pentylphenyl)-2H-1,2,3-triazole (5f): Colorless solid (88% using **GP-2**). ^{1}H NMR (500 MHz, $CDCl_3$): 7.94 (s, 1H), 7.72 (d, 2H, *J* = 8.2 Hz), 7.27 (d, 2H, *J* = 8.2 Hz), 2.64 (t, 2H, *J* = 7.6 Hz), 1.67-1.61 (m, 2H), 1.35-1.33 (m, 2H), 0.91-0.88 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 147.5, 144.0, 130.1, 129.2, 127.3, 126.2, 35.9, 31.6, 31.2, 22.7, 14.0; HRMS (ESI) calcd for $C_{13}H_{18}N_3$$[M+H]^+$: 216.1501; found: 216.1493.



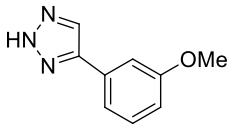
***N,N*-dimethyl-4-(2H-1,2,3-triazol-4-yl)aniline (5g):** Pale brown solid (86% using **GP-2**). ^{1}H NMR (500 MHz, $CDCl_3$): 7.86 (s, 1H), 7.66 (d, 2H, *J* = 8.8 Hz), 6.78 (d, 2H, *J* = 8.8 Hz), 3.01 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): 151.1, 129.4, 127.3, 112.7, 40.5; HRMS (ESI) calcd for $C_{10}H_{13}N_4$ $[M+H]^+$: 189.1140; found: 189.1132.



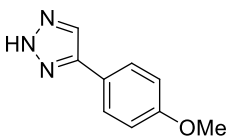
4-(2-Methoxyphenyl)-2H-1,2,3-triazole (5h): Colorless solid (92% using **GP-2**). ^{1}H NMR (500 MHz, $CDCl_3$): 8.13 (s, 1H), 7.87 (dd, 1H, *J* = 6.3, 1.3 Hz), 7.39-7.36 (m, 1H), 7.10-7.04 (m, 2H), 4.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 156.2, 130.3, 128.3, 121.6, 111.7; HRMS (ESI) calcd for $C_9H_{10}N_3O$ $[M+H]^+$: 176.0824; found: 176.0839.



4-(3-Methoxyphenyl)-2H-1,2,3-triazole (5i): White solid (93% using **GP-2**). ^{1}H NMR (400 MHz, $CDCl_3$): 7.99 (s, 1H), 7.41-7.34 (m, 3H), 6.95-6.92 (m, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 160.3, 147.0, 131.2, 130.2, 129.6, 118.8, 114.8, 111.6, 55.5; HRMS (ESI) calcd for $C_9H_{10}N_3O$ $[M+H]^+$: 176.0824; found: 176.0817.

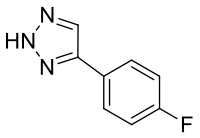


4-(4-Methoxyphenyl)-2H-1,2,3-triazole (5j): White solid (93% using **GP-2,** 95% using **GP-3**). ^{1}H NMR (400 MHz, $CDCl_3$): 7.90 (s, 1H), 7.74 (d, 2H, *J* = 8.8 Hz), 6.98 (d, 2H, *J* = 8.8 Hz), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 160.3, 147.2, 127.6, 122.6, 114.6, 55.5; HRMS (ESI) calcd for $C_9H_{10}N_3O$ $[M+H]^+$: 176.0824; found: 176.0811.

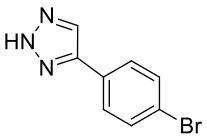


4-(3-Fluorophenyl)-2H-1,2,3-triazole (5k): Brown solid (92% using **GP-2**). ^{1}H NMR (500 MHz, $CDCl_3$): 12.2 (br s, 1H), 7.99 (s, 1H), 7.60 (d, 1H, *J* = 7.6 Hz), 7.55 (d, 1H, *J* = 9.5 Hz), 7.45-7.40 (m, 1H), 7.10-7.06 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 163.4 (d, $^1J_{C-F}$ = 244.0 Hz), 132.2 (d, $^3J_{C-F}$ = 8.0 Hz), 130.7 (d, $^3J_{C-F}$ = 8.0 Hz), 121.9 (d, $^4J_{C-F}$ = 3.0 Hz), 115.7 (d, $^2J_{C-F}$ = 21.0 Hz), 113.2 (d, $^2J_{C-F}$ = 23.0 Hz); HRMS (ESI) calcd for $C_8H_7FN_3$ $[M+H]^+$: 164.0624; found: 164.0618.

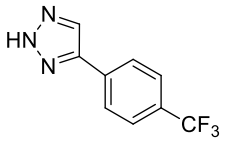
4-(4-Fluorophenyl)-2H-1,2,3-triazole (5l): Pale brown solid (85% using **GP-2**). ^{1}H NMR (500 MHz, $CDCl_3$): 11.7 (br s, 1H), 7.93 (s, 1H), 7.82-7.79 (m, 2H), 7.17-7.13 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 163.0 (d, $^{1}J_{C-F}$ = 240.0 Hz), 147.0, 128.1(d, $^{3}J_{C-F}$ = 10.0 Hz), 126.3 (d, $^{4}J_{C-F}$ = 4.0 Hz), 116.2 (d, $^{2}J_{C-F}$ = 22.0 Hz); HRMS (ESI) calcd for $C_8H_7FN_3$ $[M+H]^+$: 164.0624; found: 164.0626.



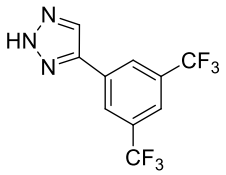
4-(4-Bromophenyl)-2H-1,2,3-triazole (5m): Deep brown solid (89% using **GP-2**). ^{1}H NMR (300 MHz, $CDCl_3$): 7.95 (s, 1H), 7.73-7.68 (m, 2H), 7.61-7.57 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 164.0, 146.6, 132.3, 127.8, 122.8; HRMS (ESI) calcd for $C_8H_7BrN_3$ $[M+H]^+$: 223.9823; found: 223.9815.



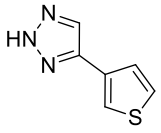
4-(4-(Trifluoromethyl)phenyl)-2H-1,2,3-triazole (5n): Colorless solid (91% using **GP-2**, 94% using **GP-3**). ^{1}H NMR (500 MHz, $CDCl_3$): 8.03 (s, 1H), 7.95 (d, 2H, *J* = 8.2 Hz), 7.71 (d, 2H, *J* = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 146.5, 133.7, 126.5, 126.2, 126.1, 126.0, 121.4 (q, $^{1}J_{C-F}$ = 250.0 Hz); HRMS (ESI) calcd for $C_9H_7F_3N_3$ $[M+H]^+$: 214.0592; found: 214.0586.



4-(3,5-Bis(trifluoromethyl)phenyl)-2H-1,2,3-triazole (5o): Colorless solid (83% using **GP-2**). ^{1}H NMR (400 MHz, $CDCl_3$): 8.28 (s, 2H), 8.09 (s, 1H), 7.88 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 144.9, 132.8, 132.5, 132.4, 126.2, 123.4 (q, $^{1}J_{C-F}$ = 275.0 Hz), 122.2; HRMS (ESI) calcd for $C_{10}H_6F_6N_3$ $[M+H]^+$: 282.0466; found: 282.0463.



4-(Thiophen-3-yl)-2H-1,2,3-triazole (5p): Colorless solid (90% using **GP-2**). ^{1}H 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.



12.0 X-Ray Crystallography of compounds 3b and 5a

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.

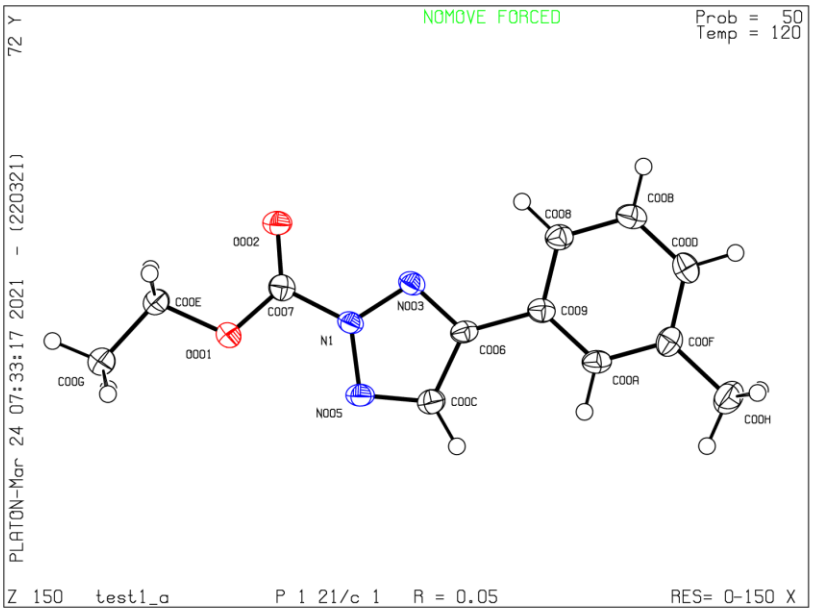


Figure S2. The ORTEP diagram of **3b** showing 50% probability thermal ellipsoid.

Table 1 Crystal data and structure refinement for 3b.	
Identification code	TEST1_a
Empirical formula	$C_{12}H_{13}N_3O_2$
Formula weight	231.25
Temperature/K	119.69
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.539(2)
b/Å	11.834(2)
c/Å	10.092(2)
α/°	90
β/°	114.682(6)
γ/°	90
Volume/Å^3	1143.6(4)
Z	4
ρ_{calc}g/cm^3	1.343
μ/mm^{-1}	0.094
F(000)	488.0
Crystal size/mm^3	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.472 to 49.998
Index ranges	$-12 \le h \le 12$, $-14 \le k \le 14$, $-11 \le l \le 11$
Reflections collected	8965
Independent reflections	2000 [R_{int} = 0.0809, R_{sigma} = 0.0659]
Data/restraints/parameters	2000/0/156

Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0544, wR_2 = 0.1117
Final R indexes [all data]	R_1 = 0.0847, wR_2 = 0.1233
Largest diff. peak/hole / e $Å^{-3}$	0.20/-0.22

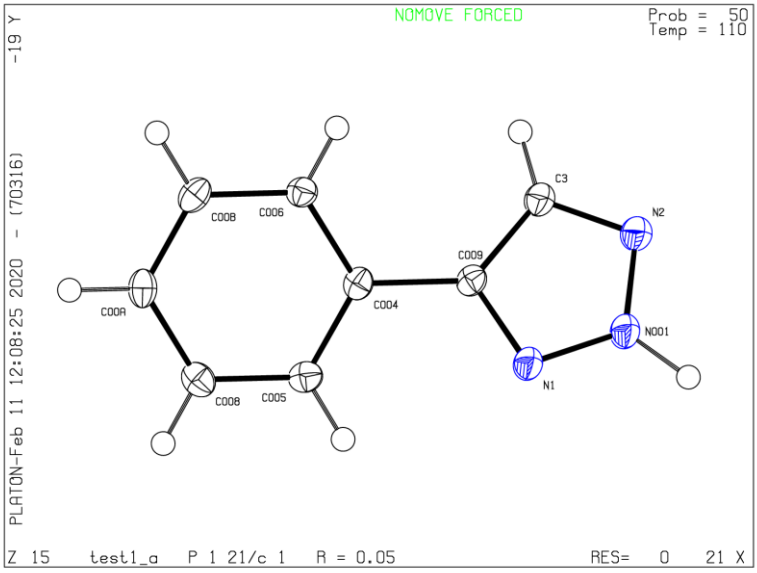


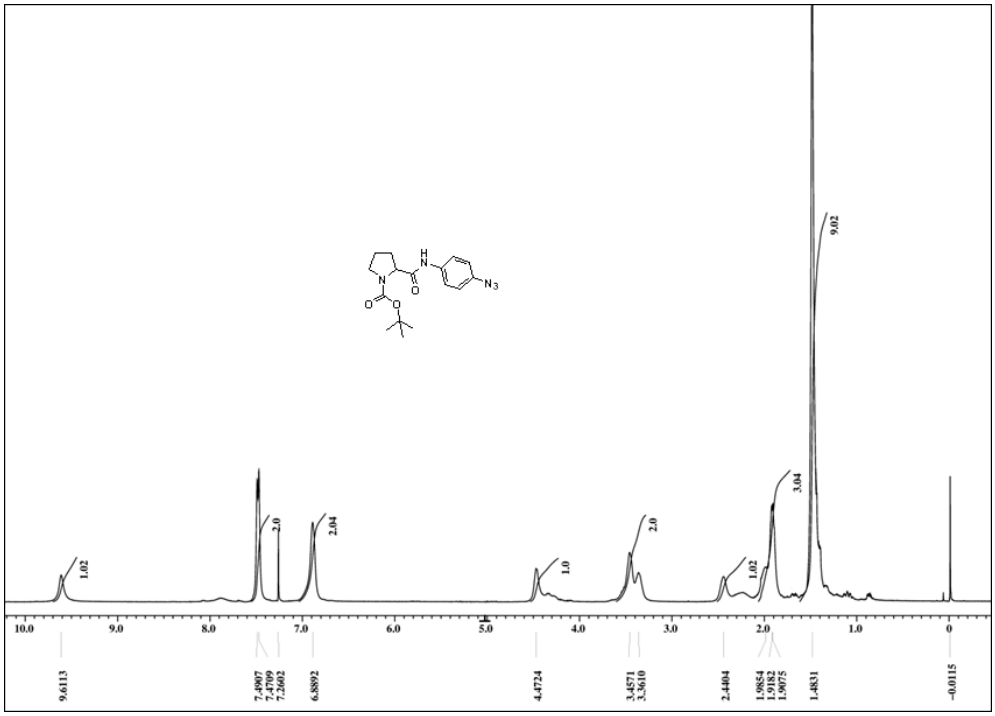
Figure S3. The ORTEP diagram of **5a** showing 50% probability thermal ellipsoid.

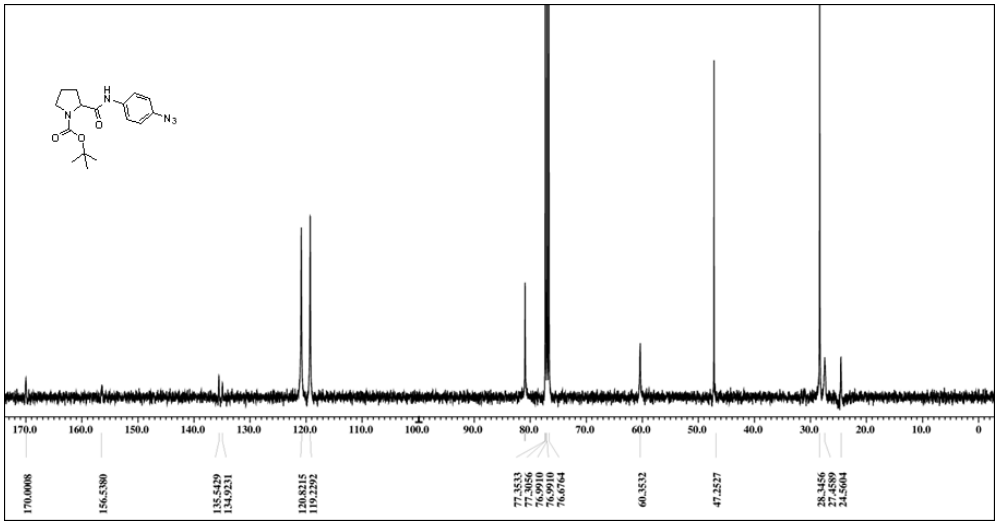
Table 1 Crystal data and structure refinement for 5a.	
Identification code	TEST1_a
Empirical formula	$C_8H_7N_3$
Formula weight	145.17
Temperature/K	110.2
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.9923(16)
b/Å	5.7180(4)
c/Å	7.2858(7)
α/°	90
β/°	94.649(3)
γ/°	90
Volume/$Å^3$	705.57(11)
Z	4
$\rho_{calc}g/cm^3$	1.367
μ/mm^{-1}	0.088
F(000)	304.0
Crystal size/mm^3	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.81 to 52.742

Index ranges	$-21 \leq h \leq 21$, $-7 \leq k \leq 7$, $-9 \leq l \leq 9$
Reflections collected	6650
Independent reflections	1434 [R_{int} = 0.0664, R_{sigma} = 0.0501]
Data/restraints/parameters	1434/0/104
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0512, wR_2 = 0.1349
Final R indexes [all data]	R_1 = 0.0560, wR_2 = 0.1418
Largest diff. peak/hole / e $Å^{-3}$	0.25/-0.40

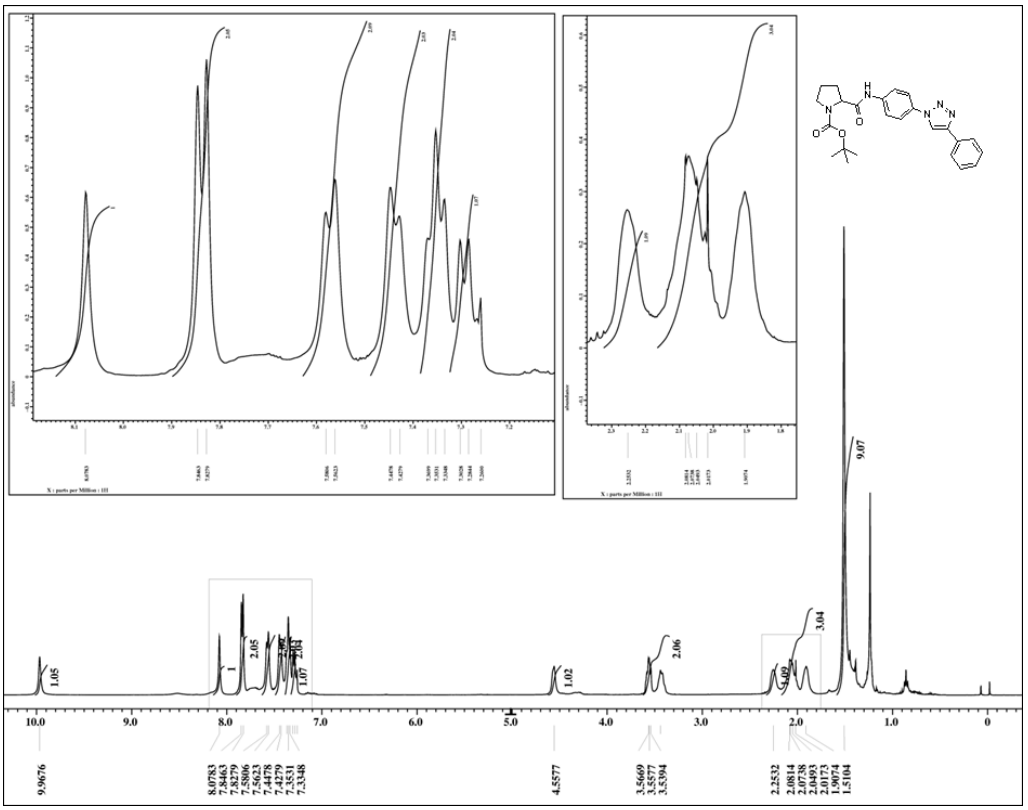
13.0 NMR spectra of all compounds

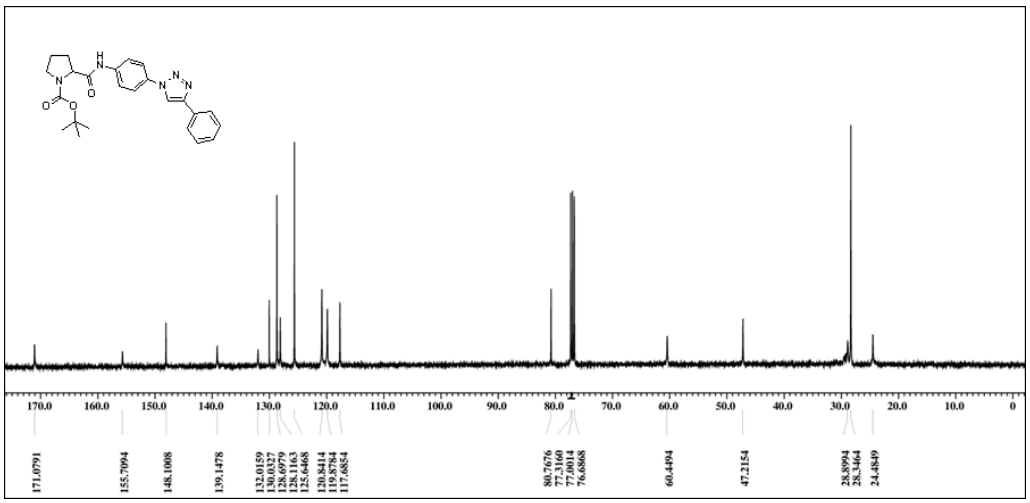
^{1}H and ^{13}C NMR of S3:



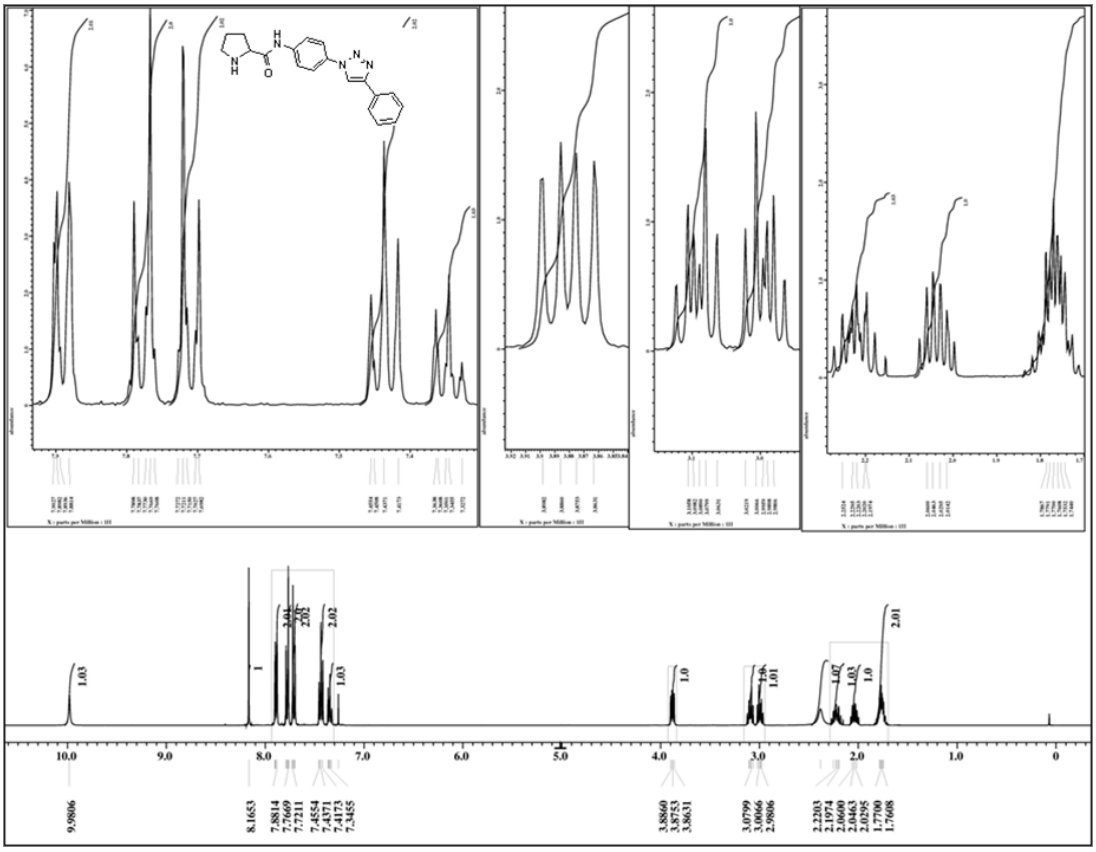


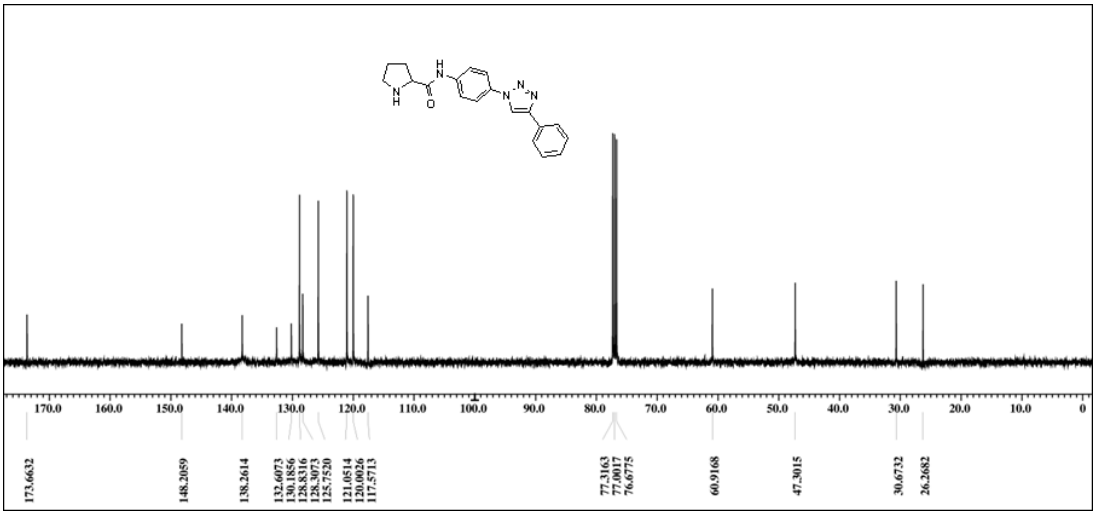
^{1}H and ^{13}C NMR of S5:



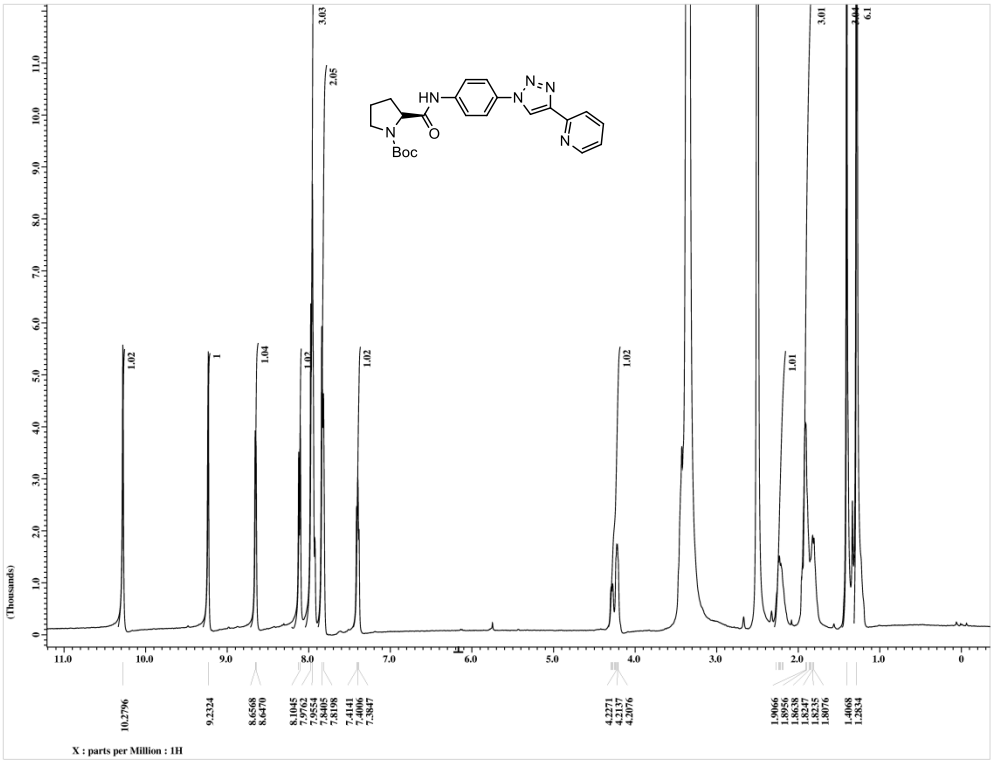


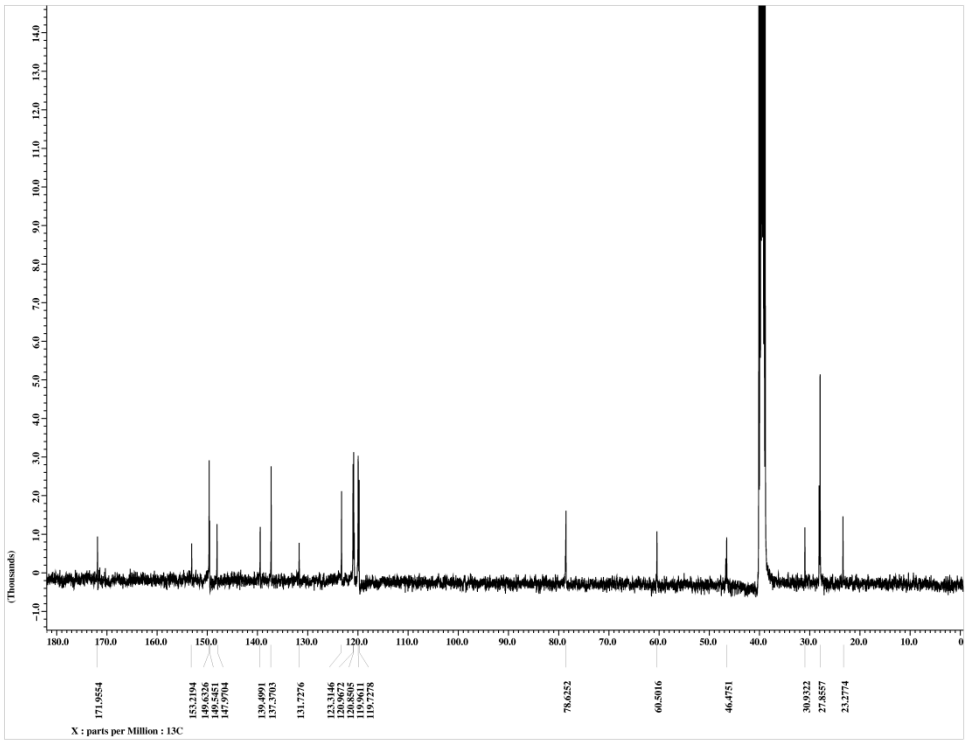
^{1}H and ^{13}C NMR of Pro-1:



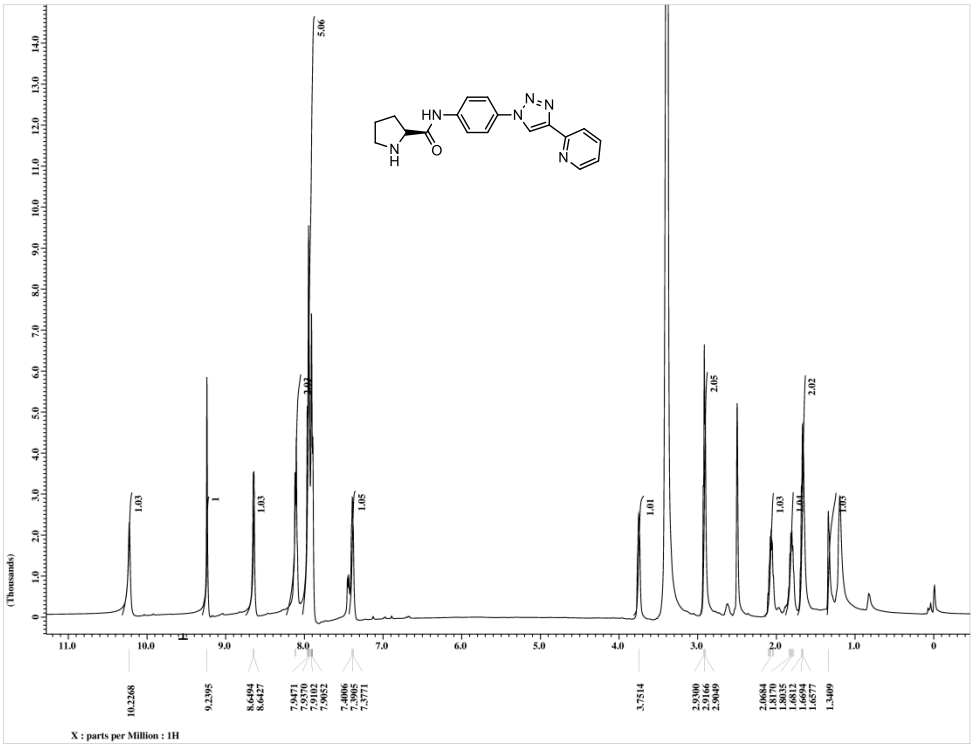


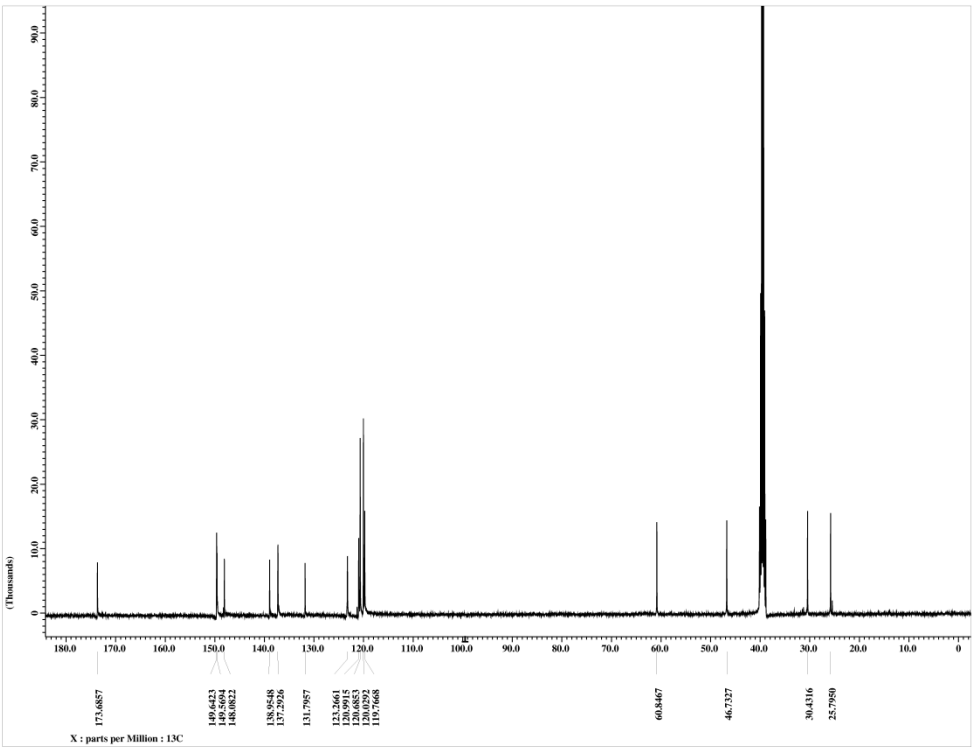
^{1}H and ^{13}C NMR of S7:



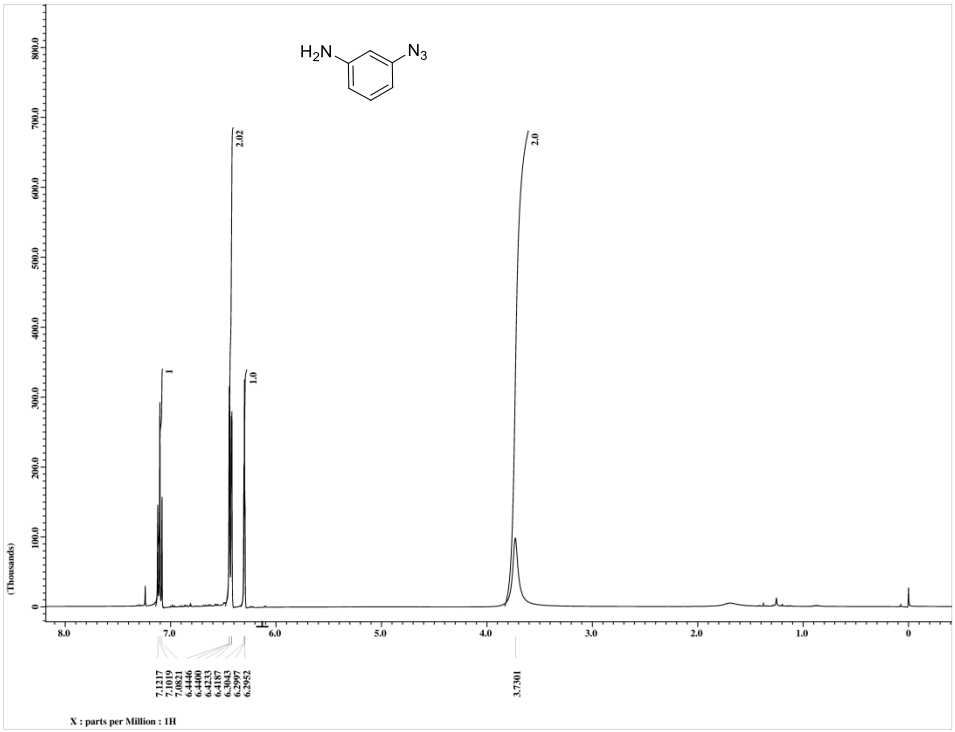


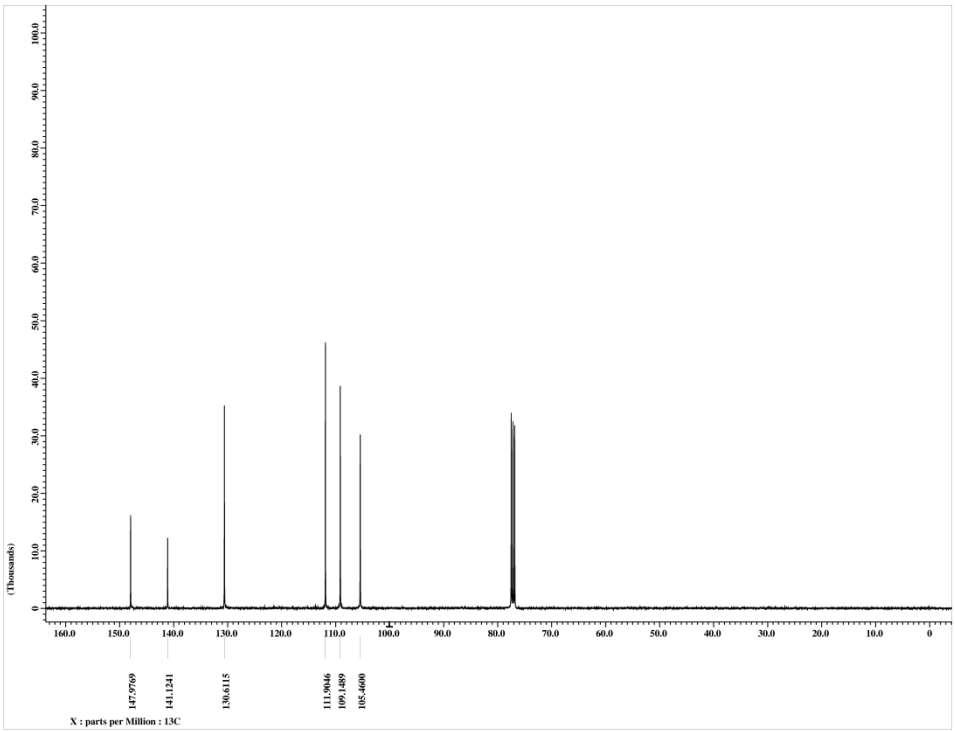
^{1}H and ^{13}C NMR of Pro-2:



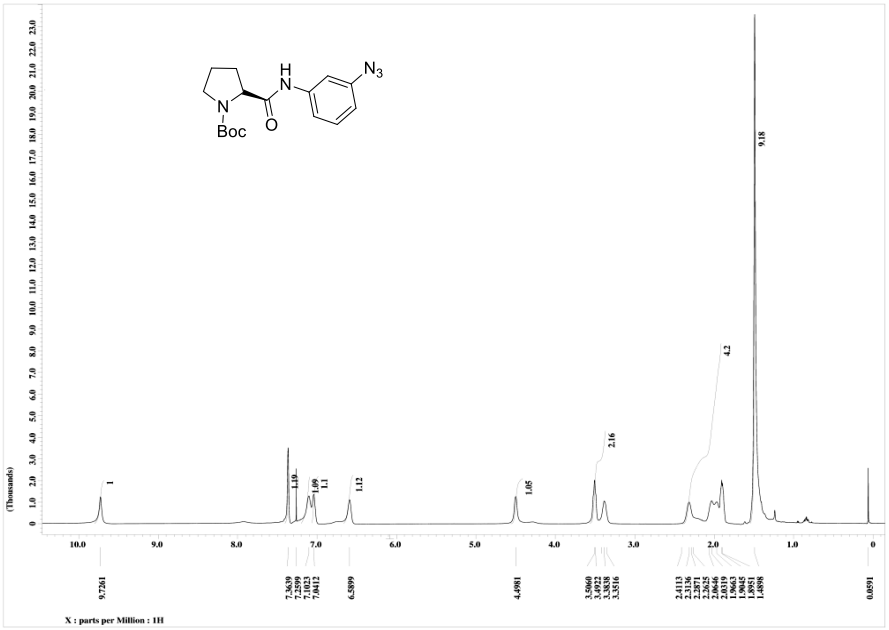


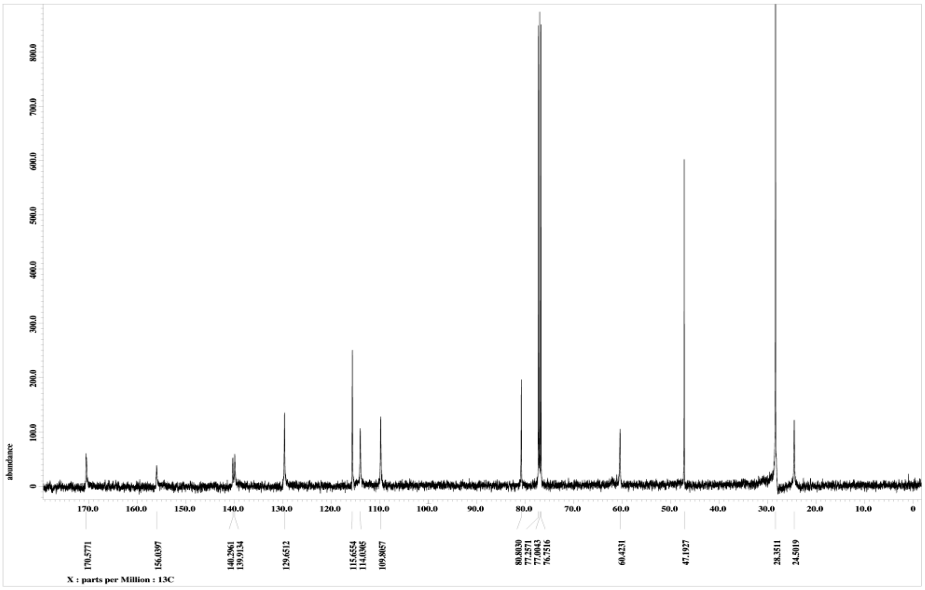
^{1}H and ^{13}C NMR of S9:



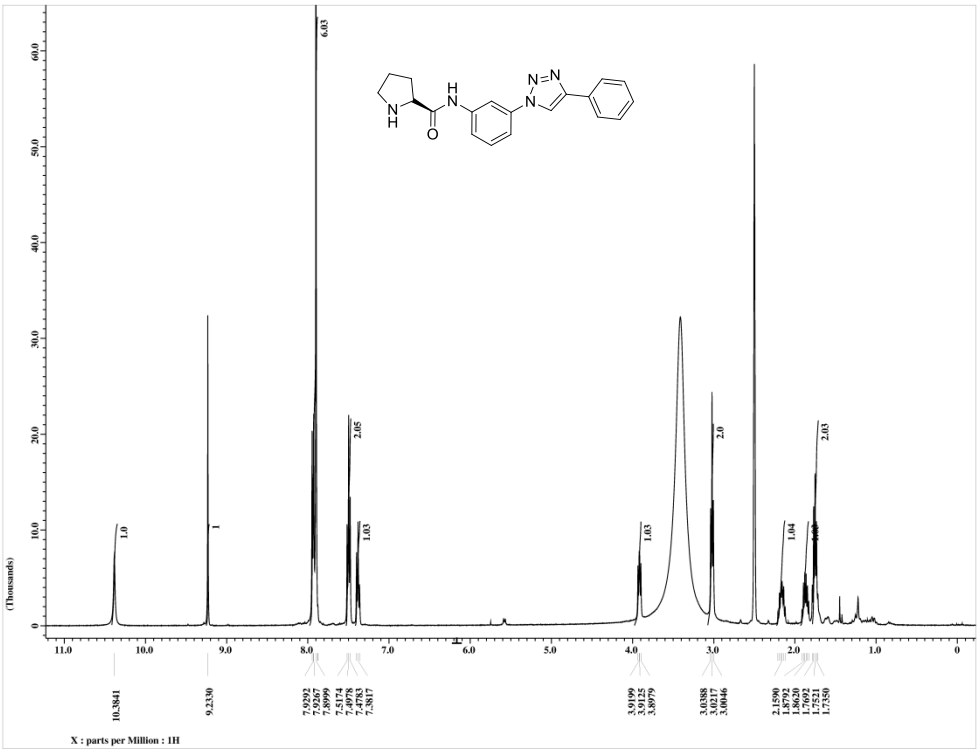


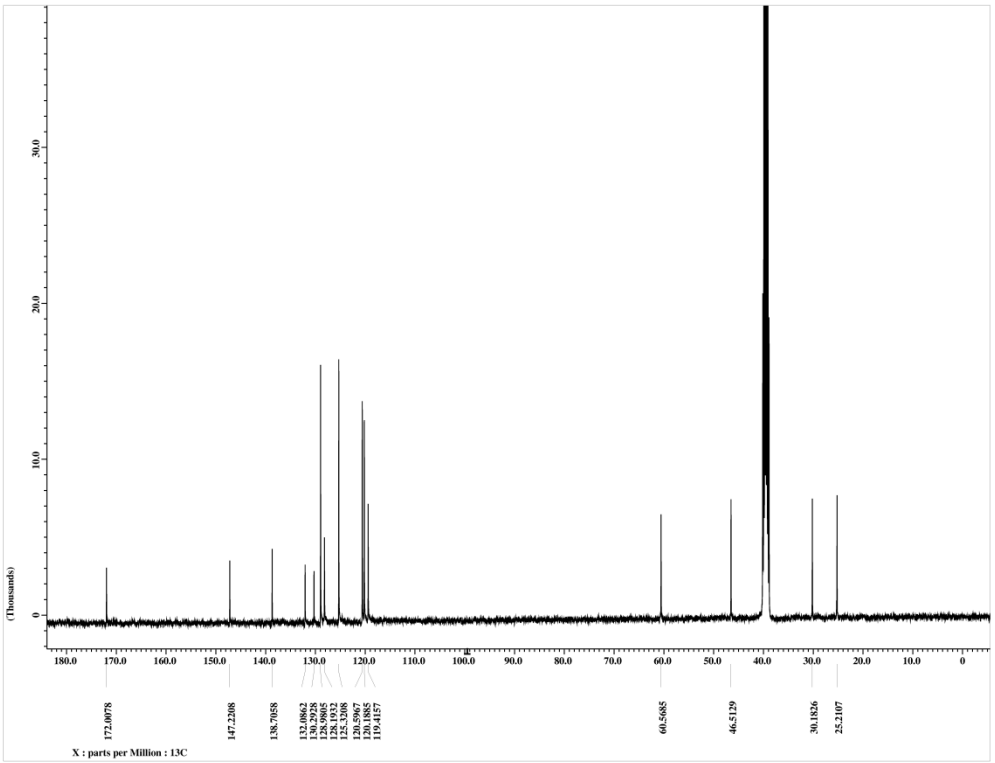
^{1}H and ^{13}C NMR of S10:



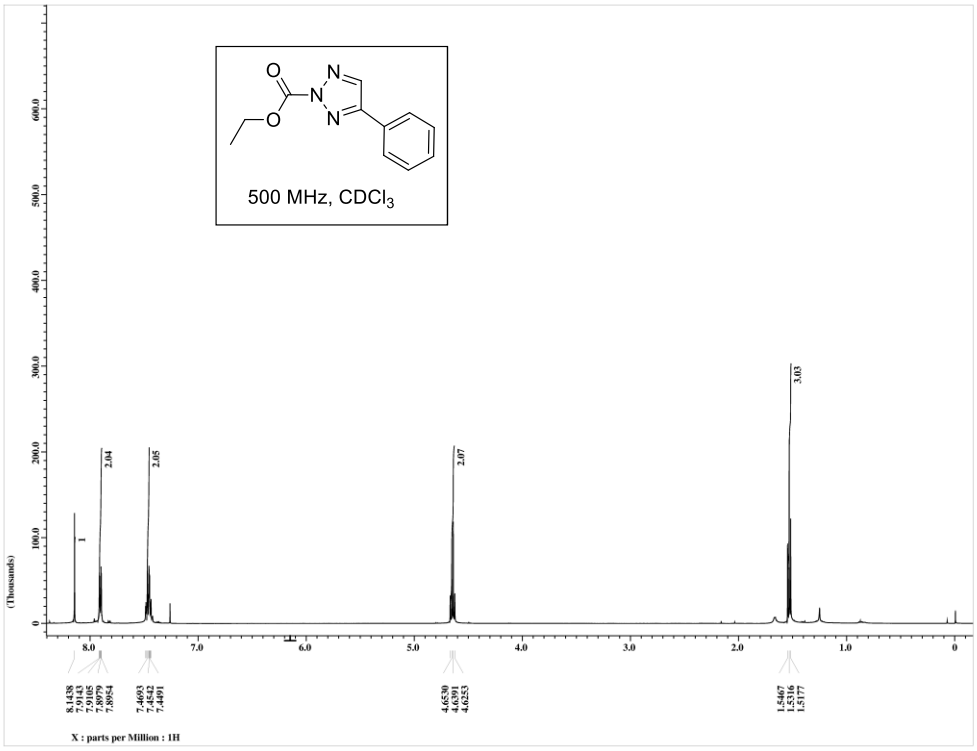


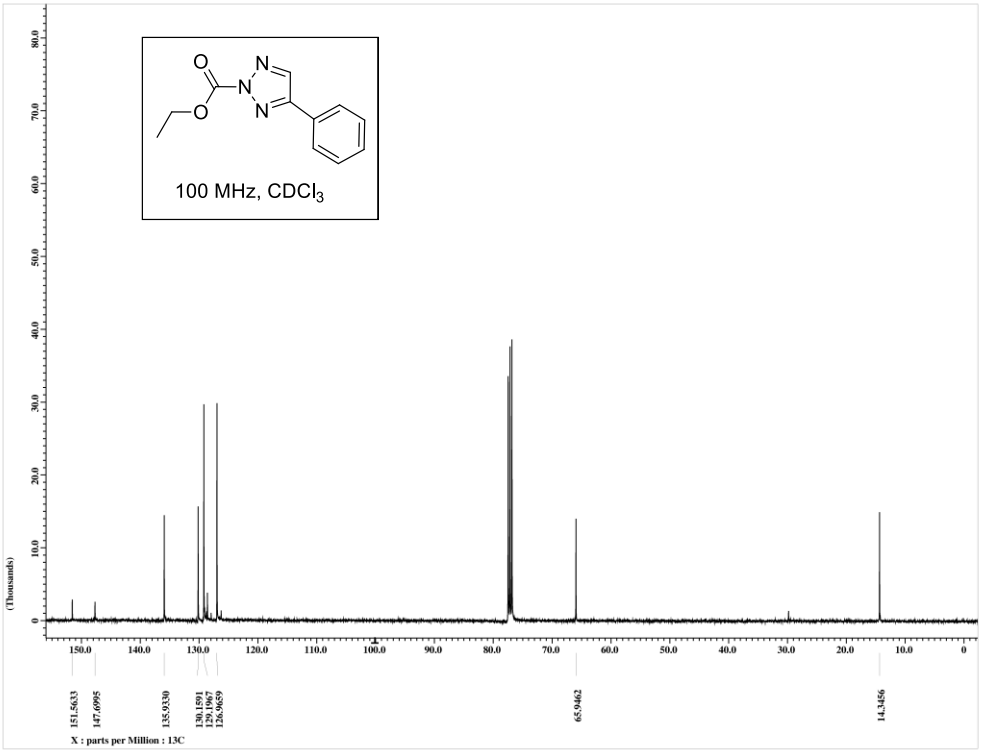
^{1}H and ^{13}C NMR of Pro-3:



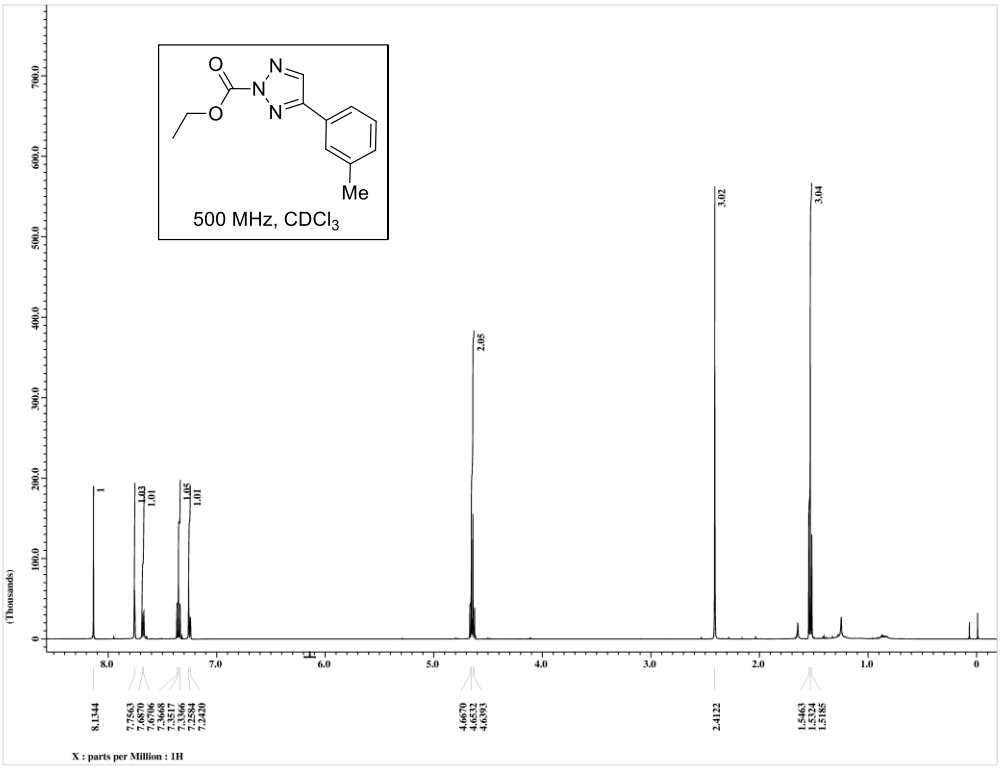


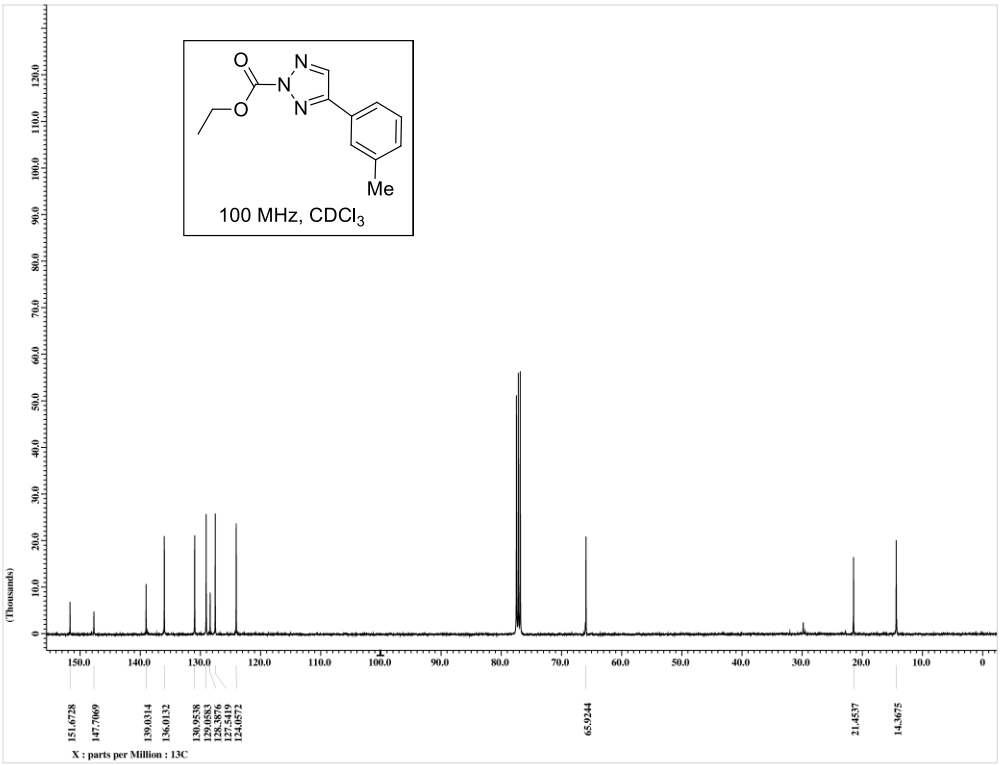
^{1}H and ^{13}C NMR of 3a:



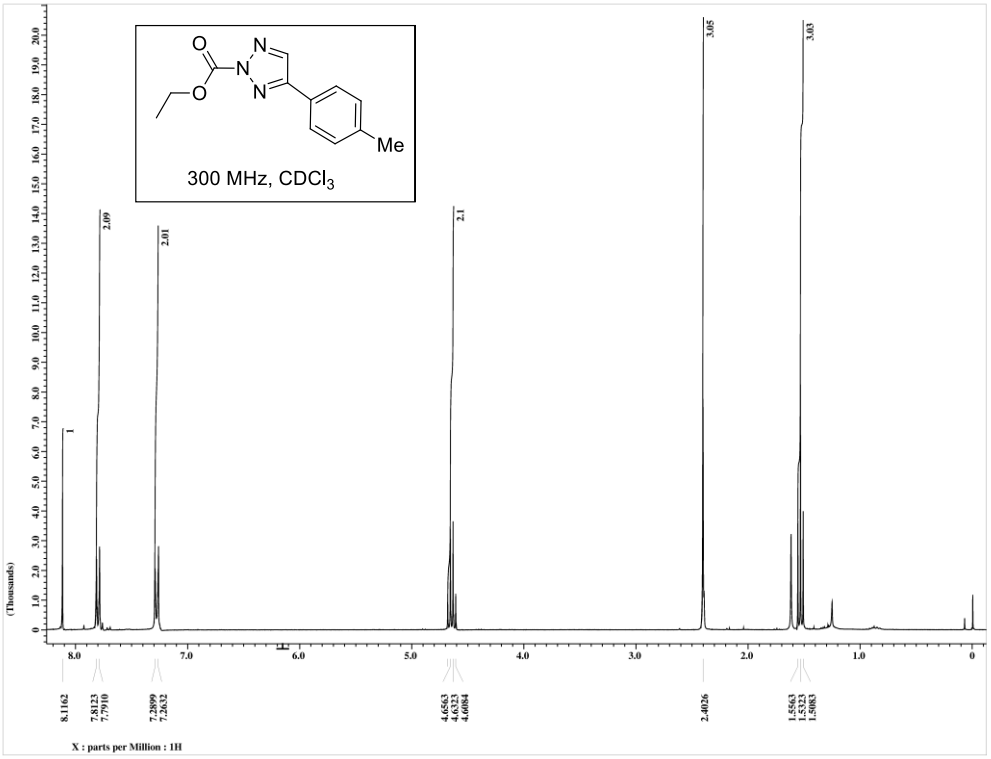


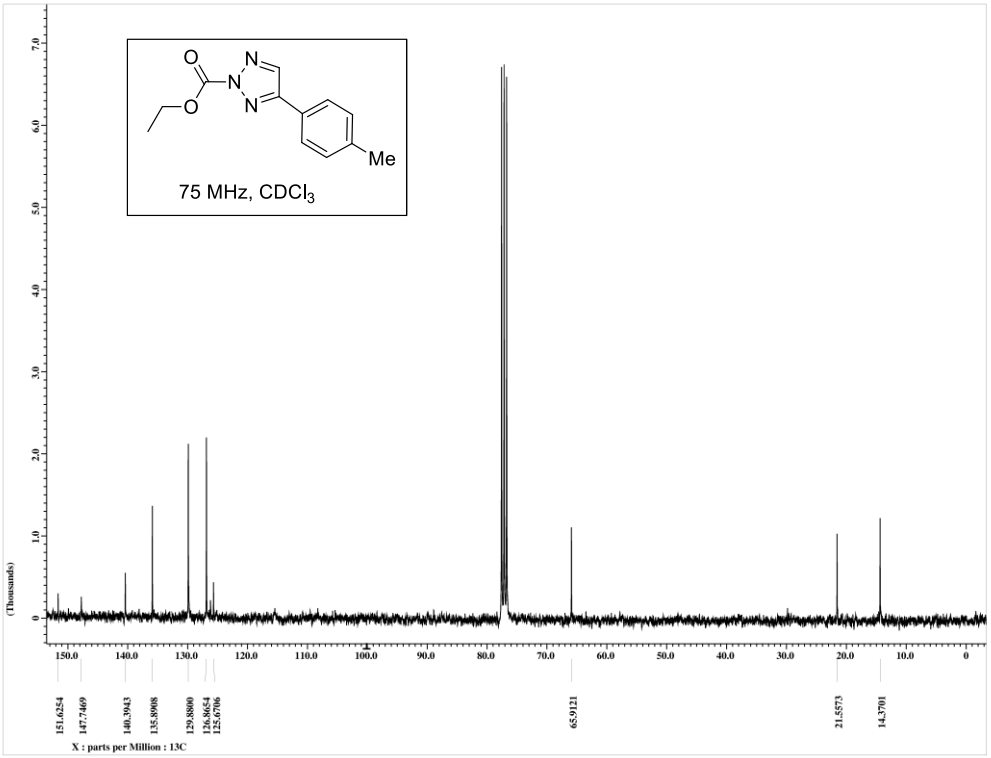
^{1}H and ^{13}C NMR of 3b:



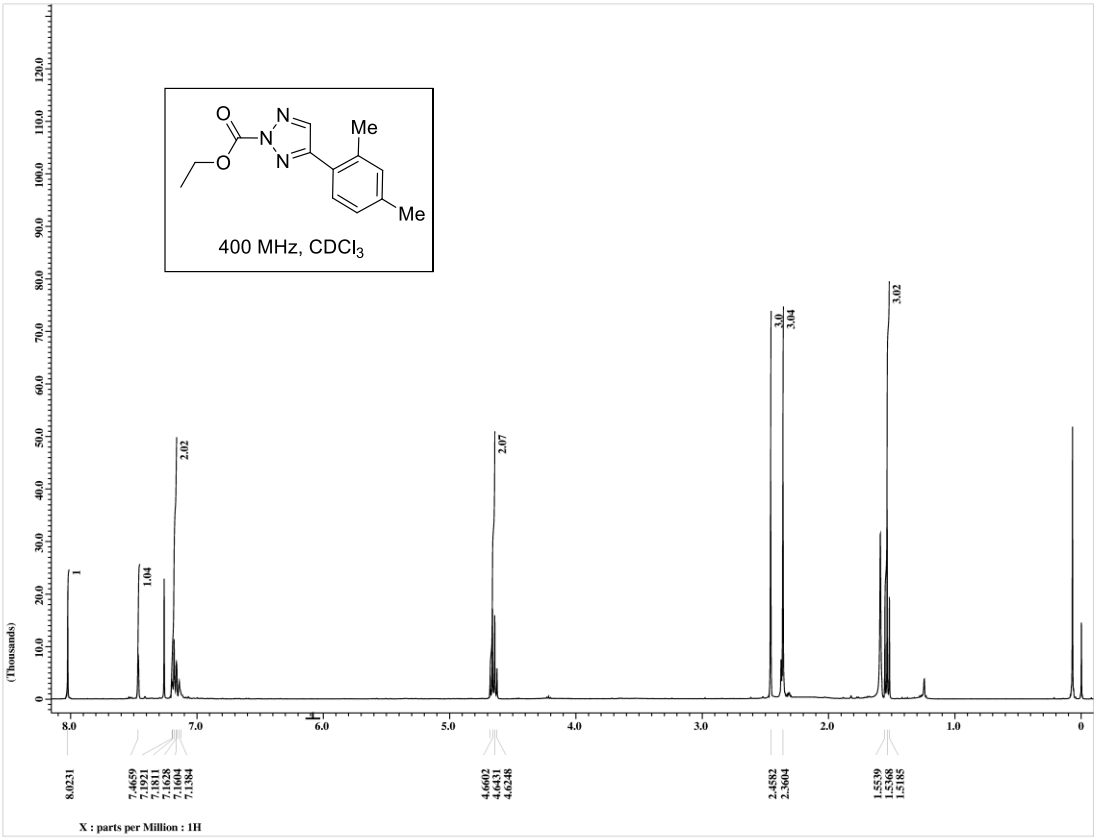


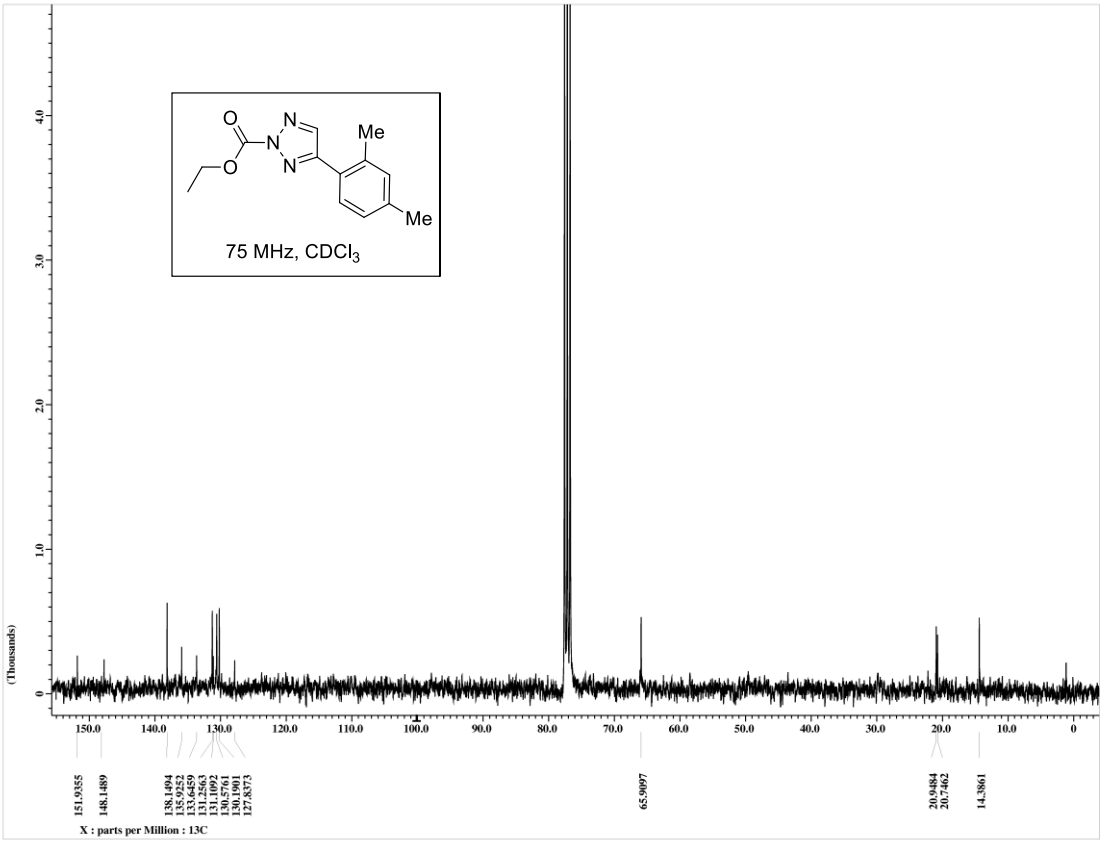
^{1}H and ^{13}C NMR of 3c:



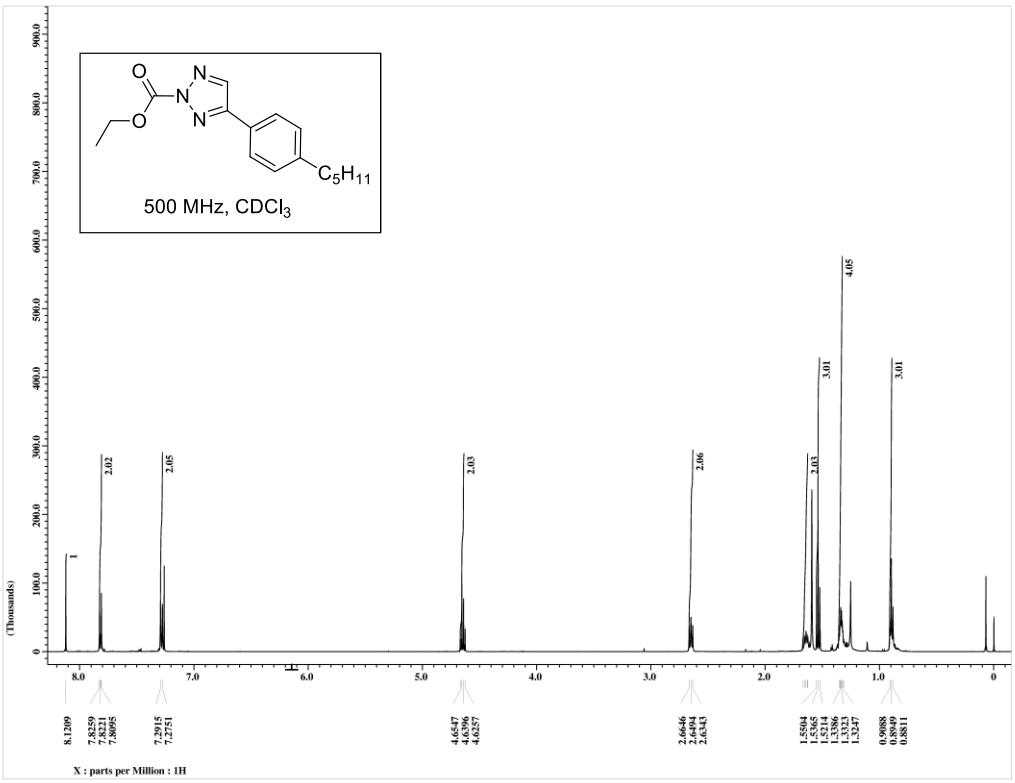


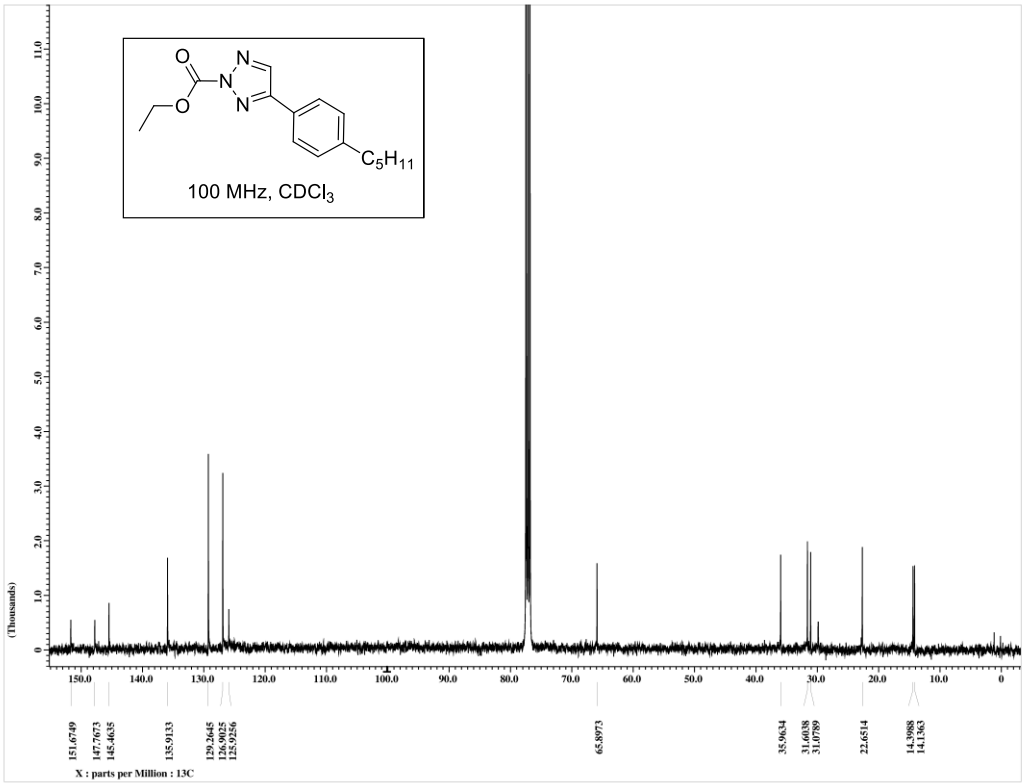
^{1}H and ^{13}C NMR of 3d:



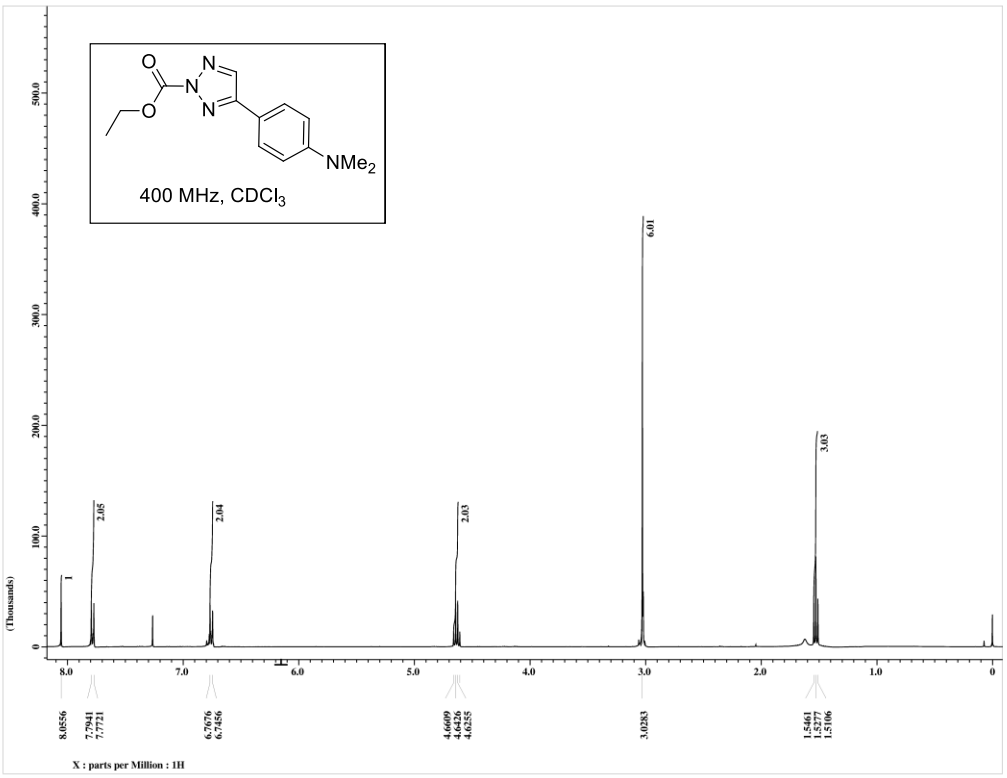


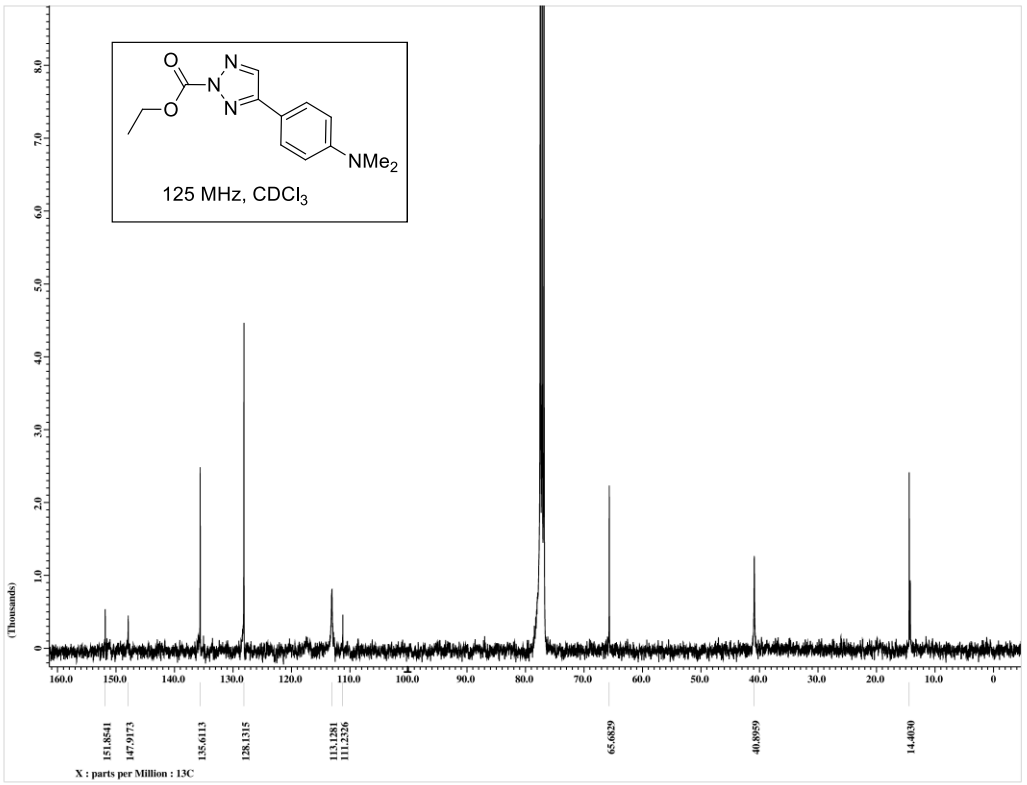
^{1}H and ^{13}C NMR of 3e:



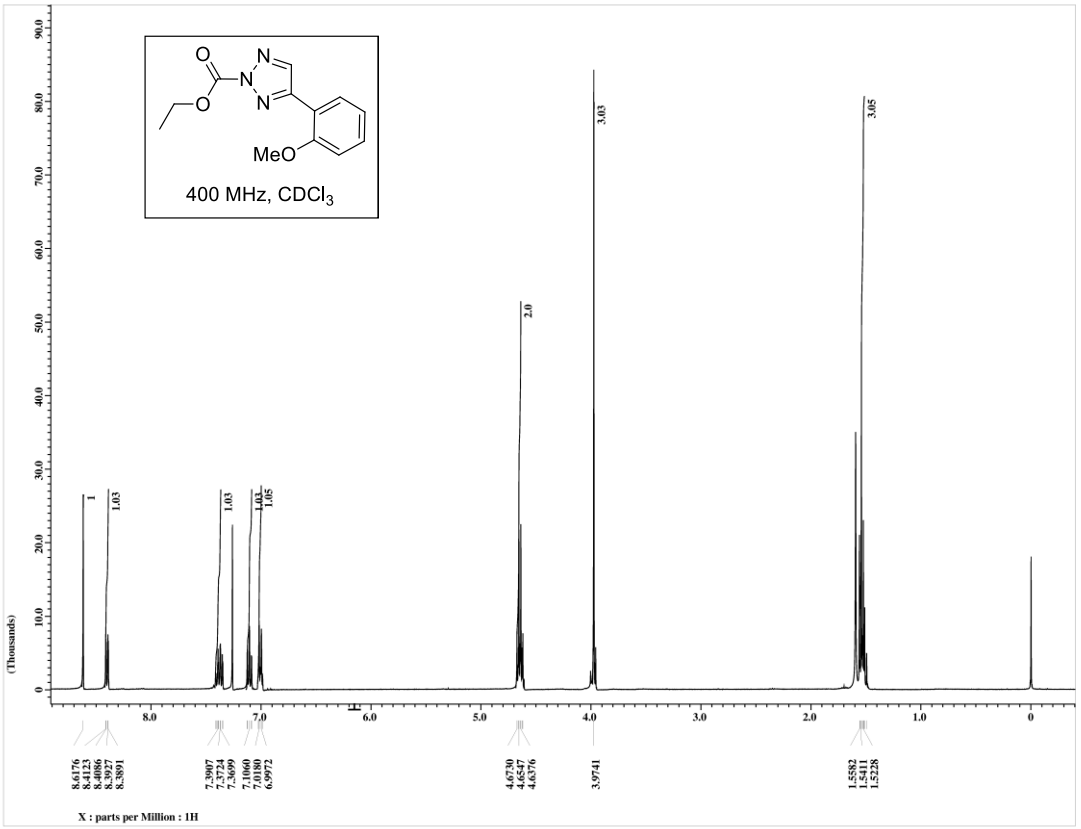


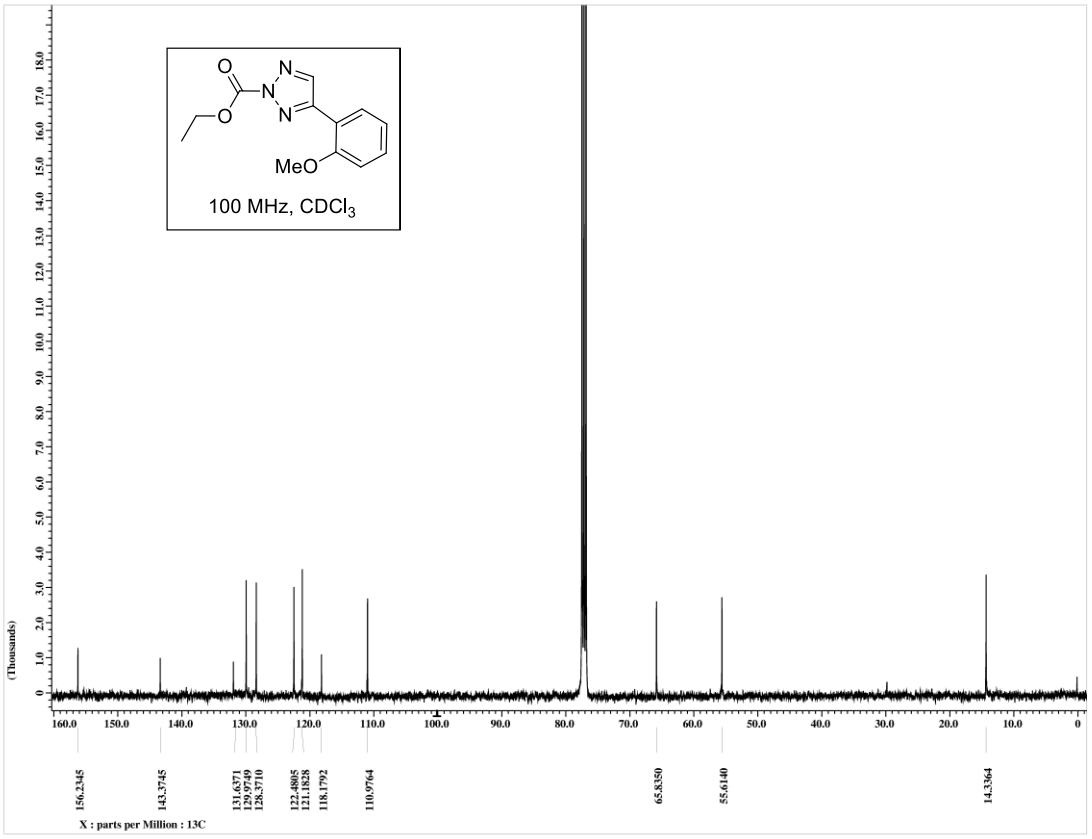
^{1}H and ^{13}C NMR of 3f:



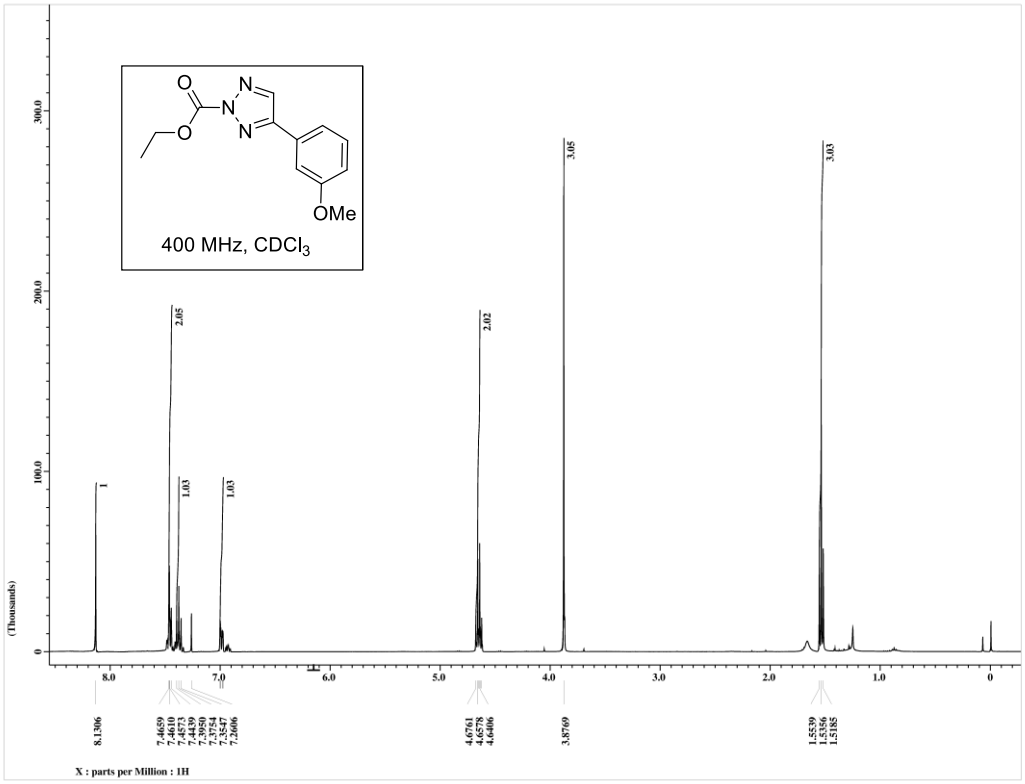


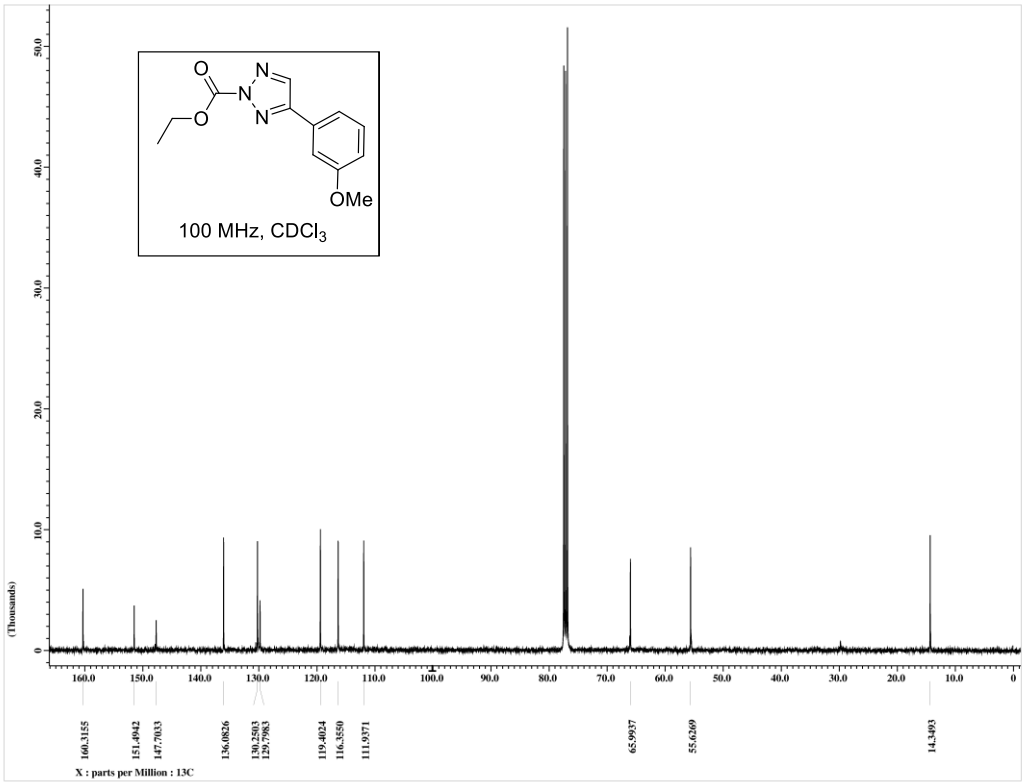
^{1}H and ^{13}C NMR of 3g:



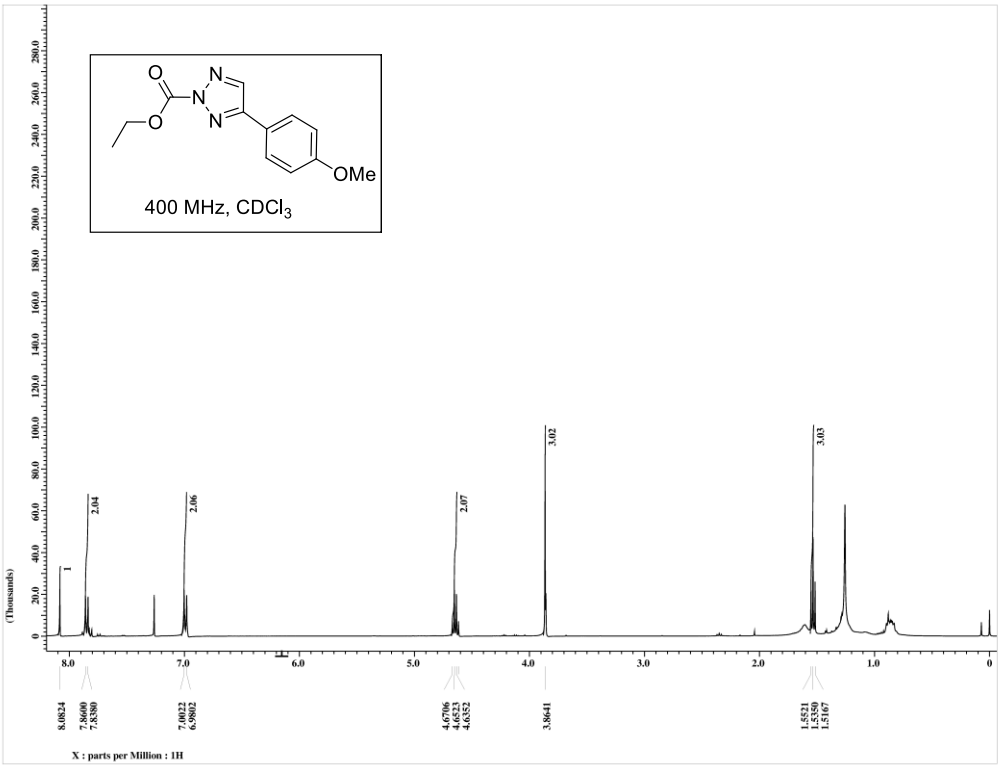


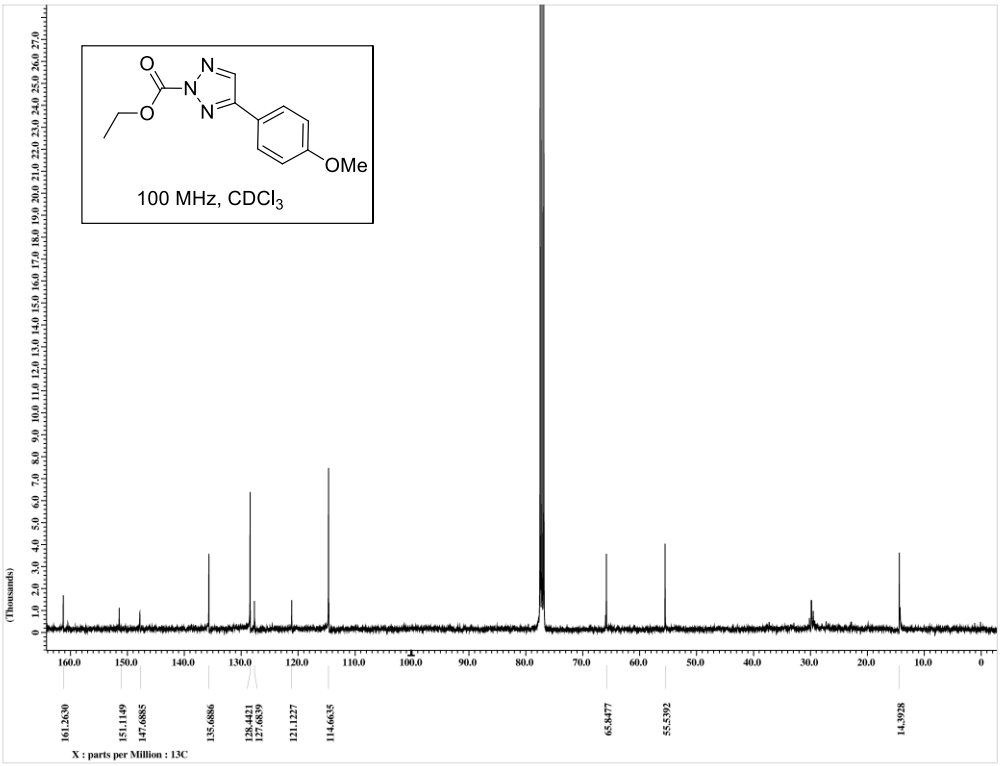
^{1}H and ^{13}C NMR of 3h:



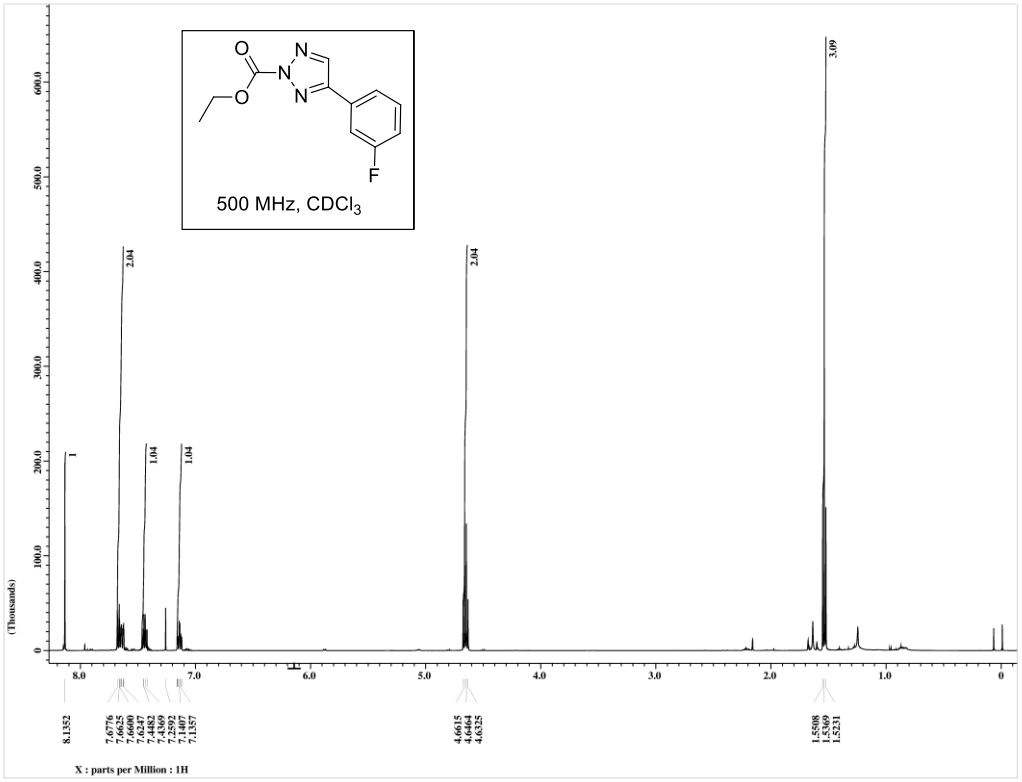


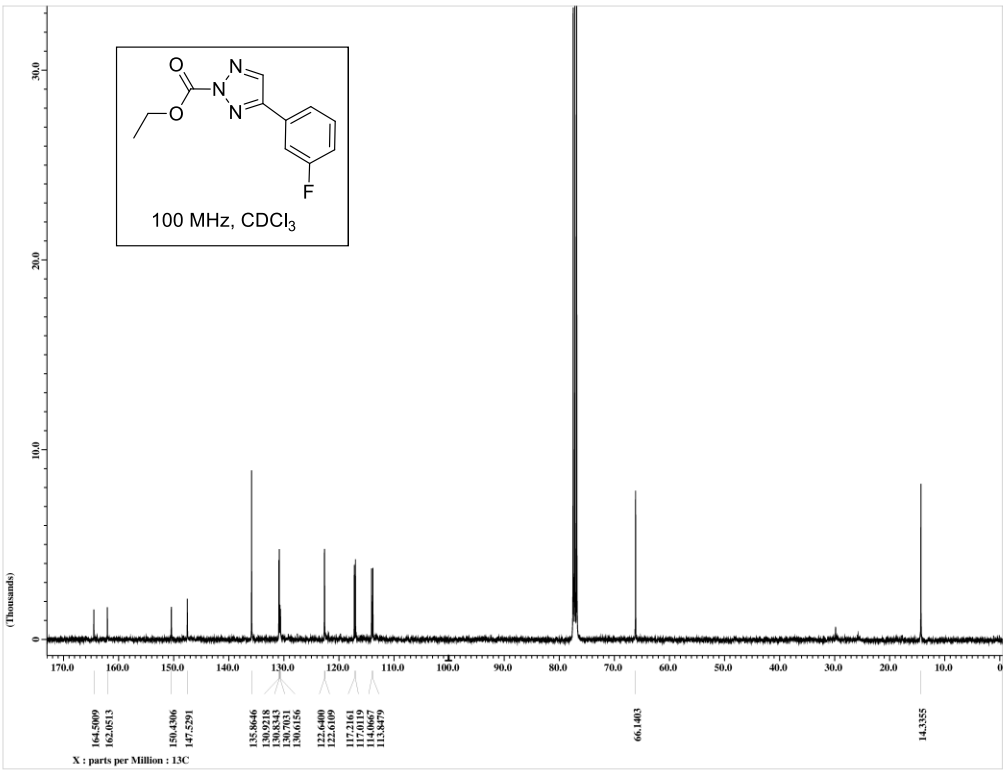
^{1}H and ^{13}C NMR of 3i:



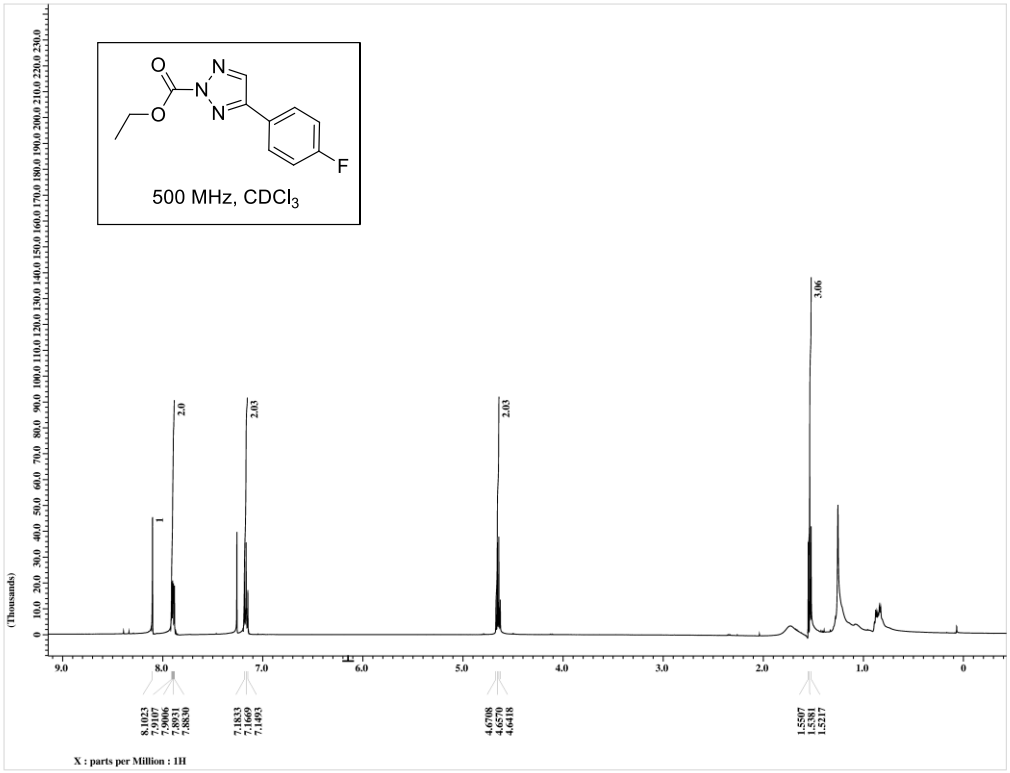


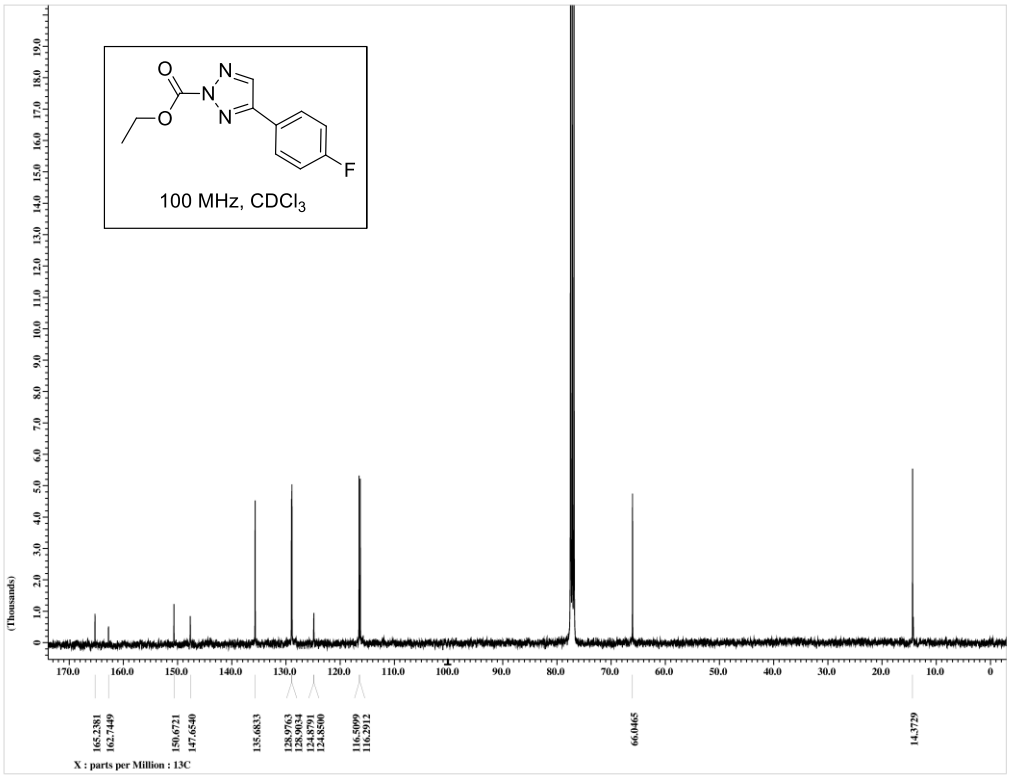
^{1}H and ^{13}C NMR of 3j:



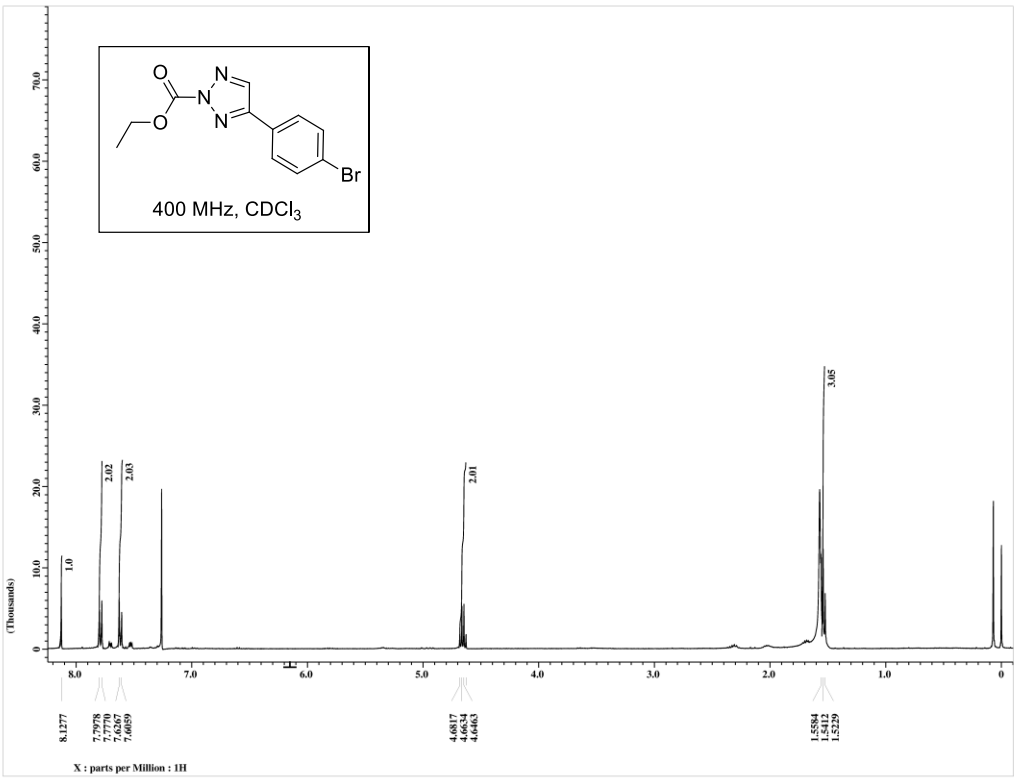


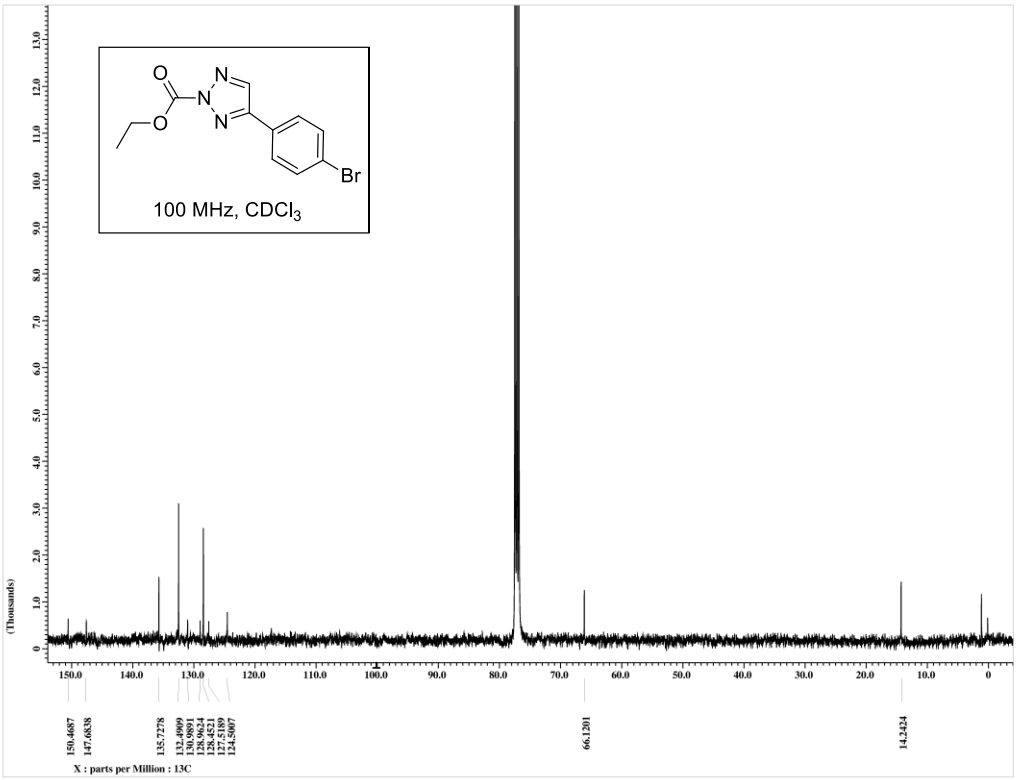
^{1}H and ^{13}C NMR of 3k:



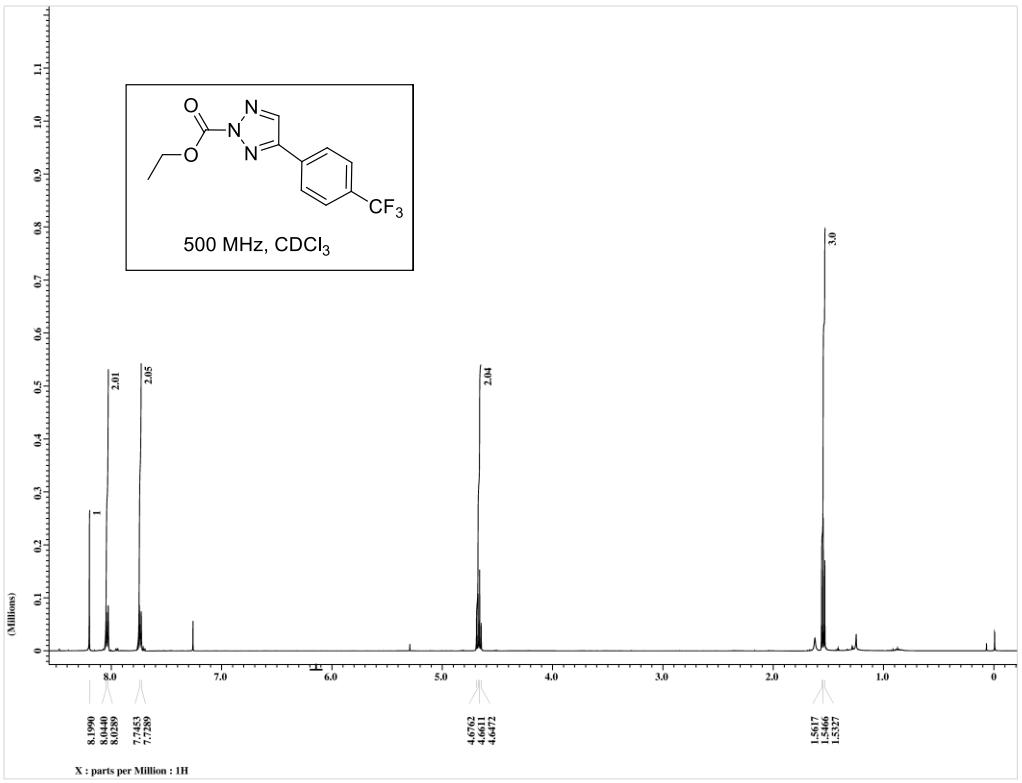


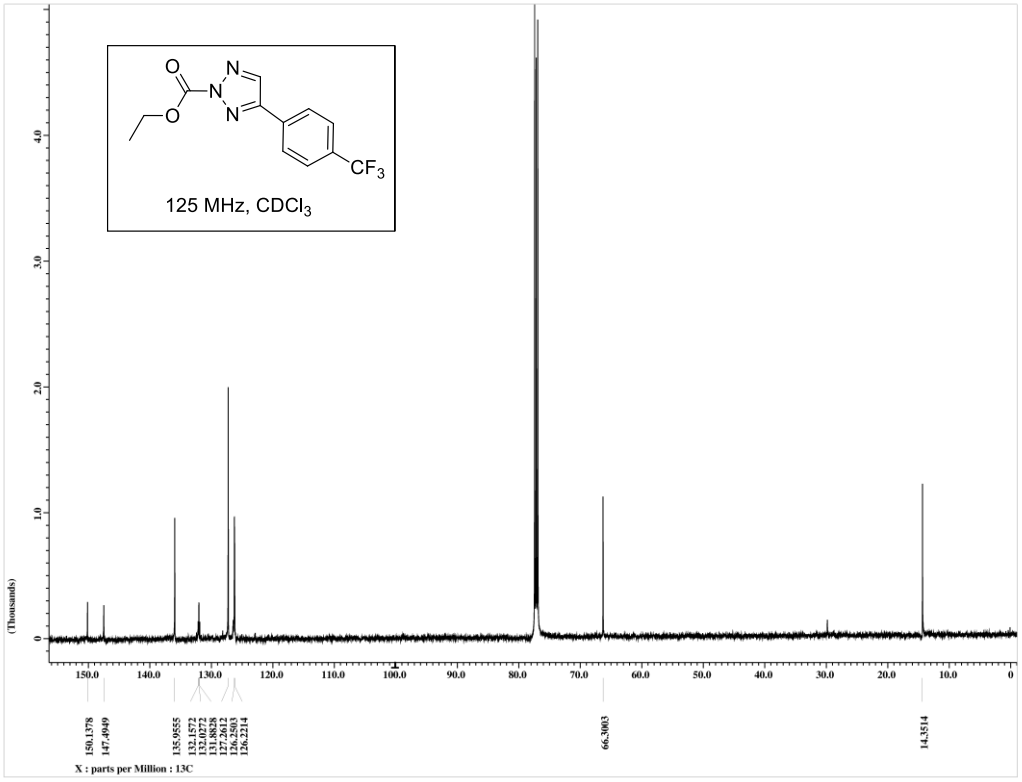
^{1}H and ^{13}C NMR of 3l:



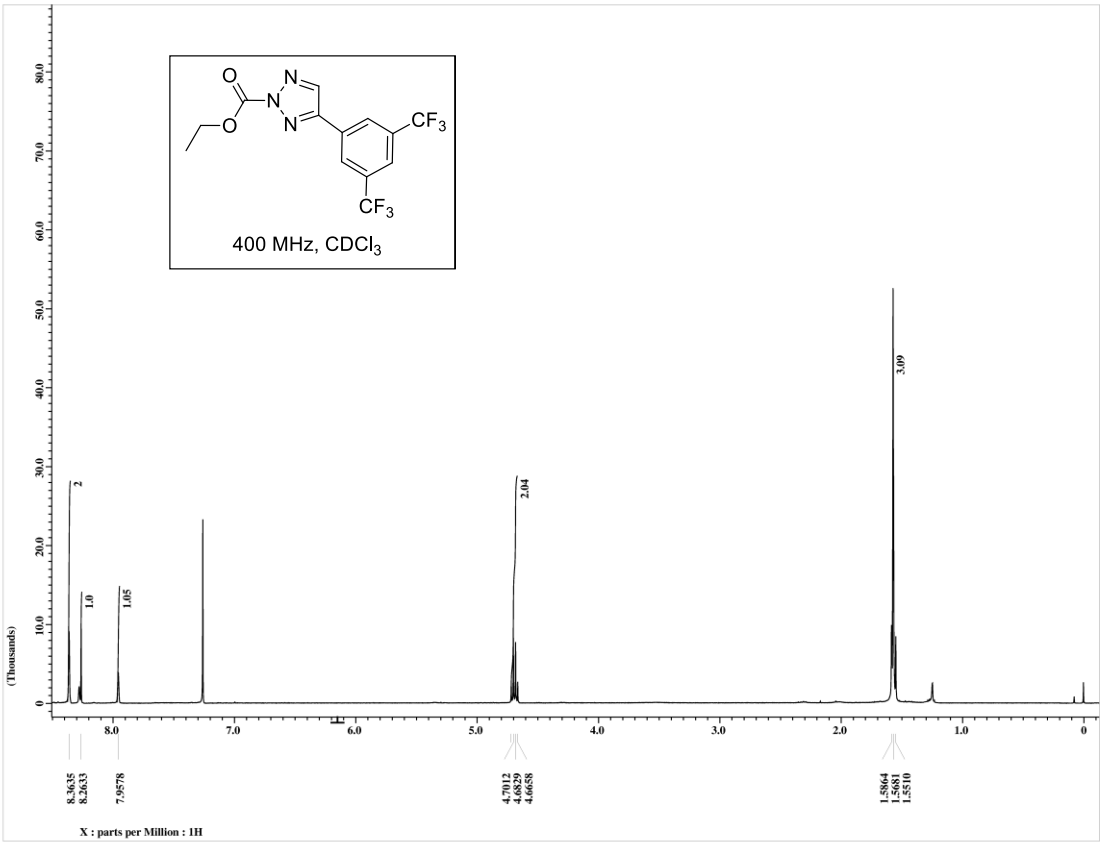


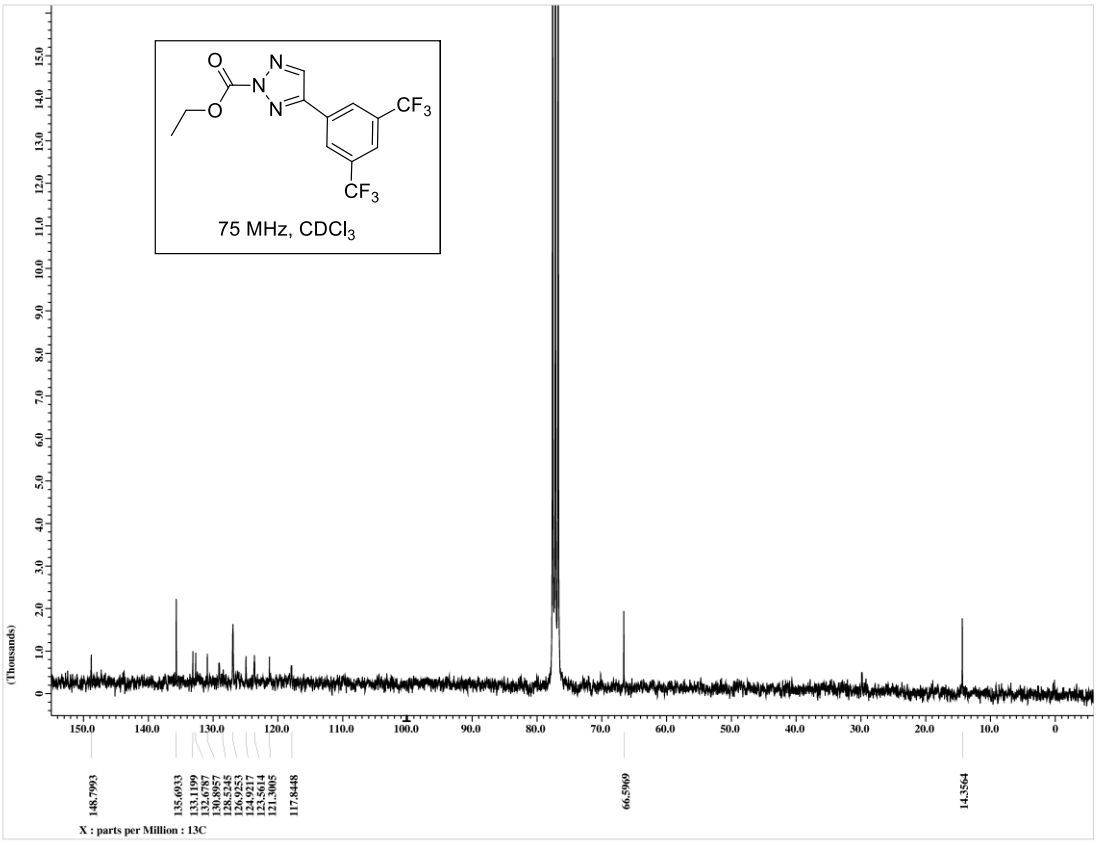
^{1}H and ^{13}C NMR of 3m:



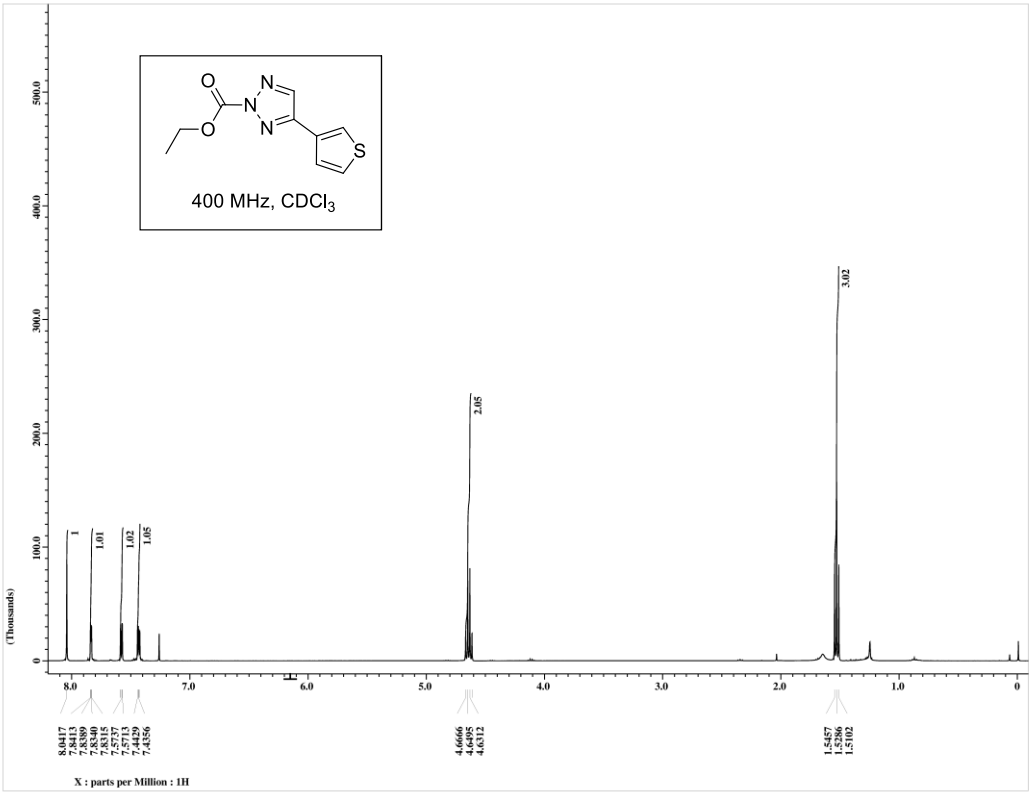


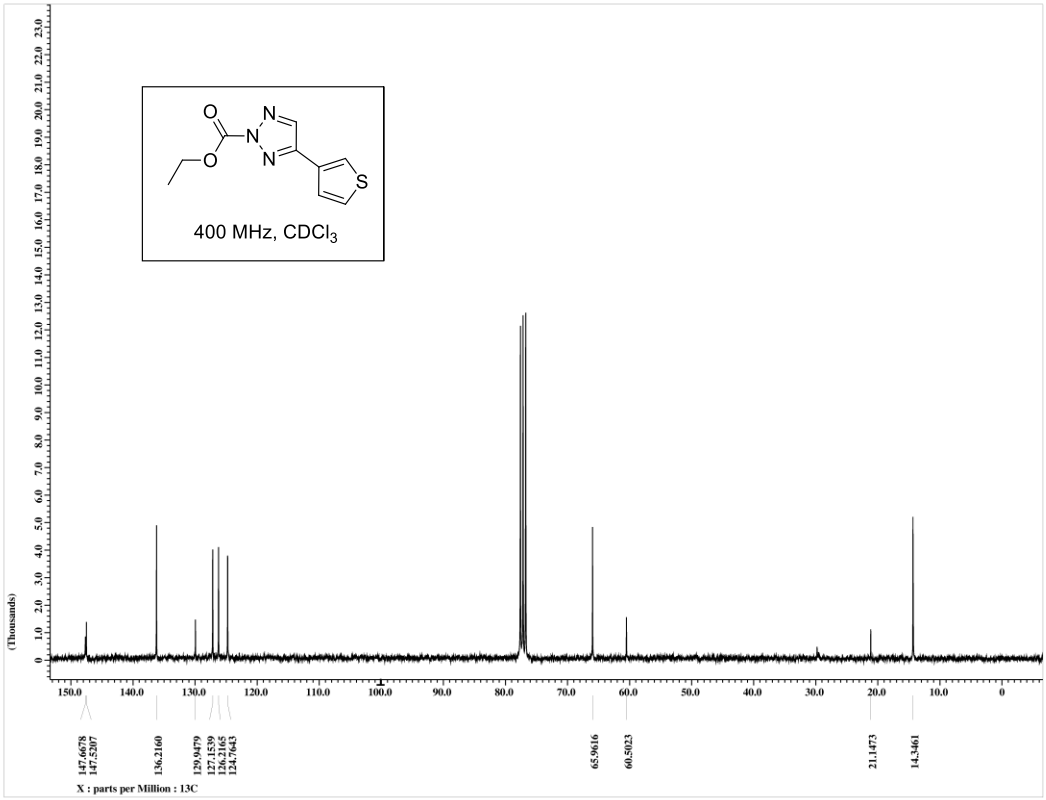
^{1}H and ^{13}C NMR of 3n:



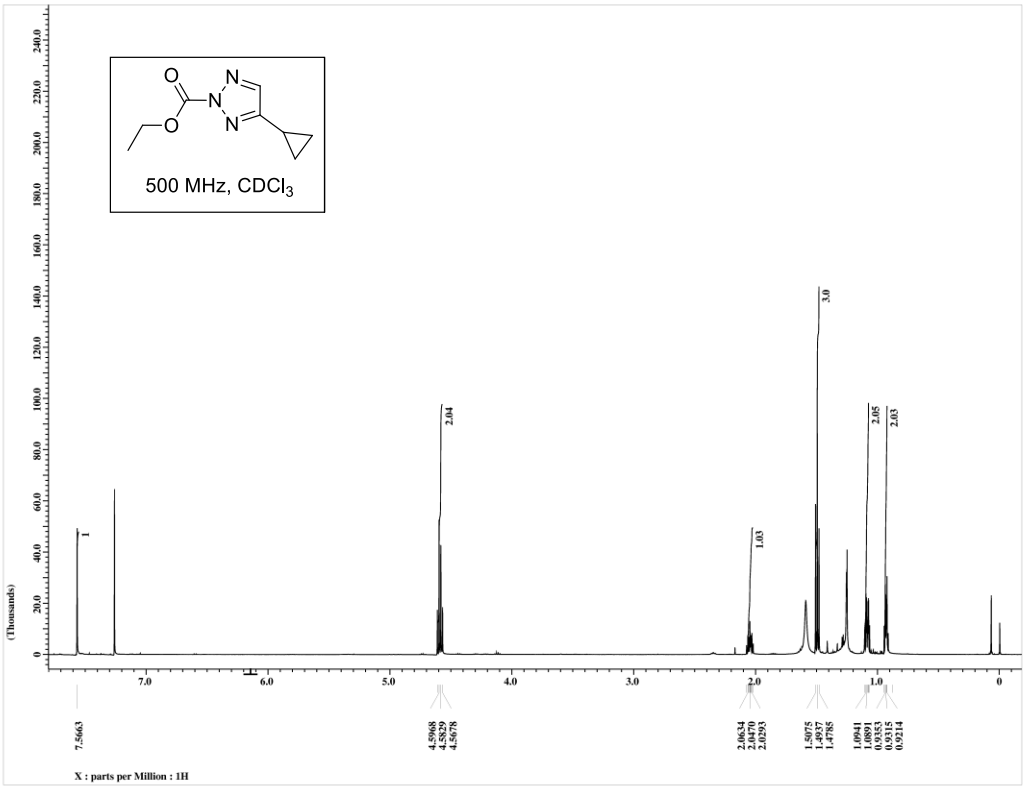


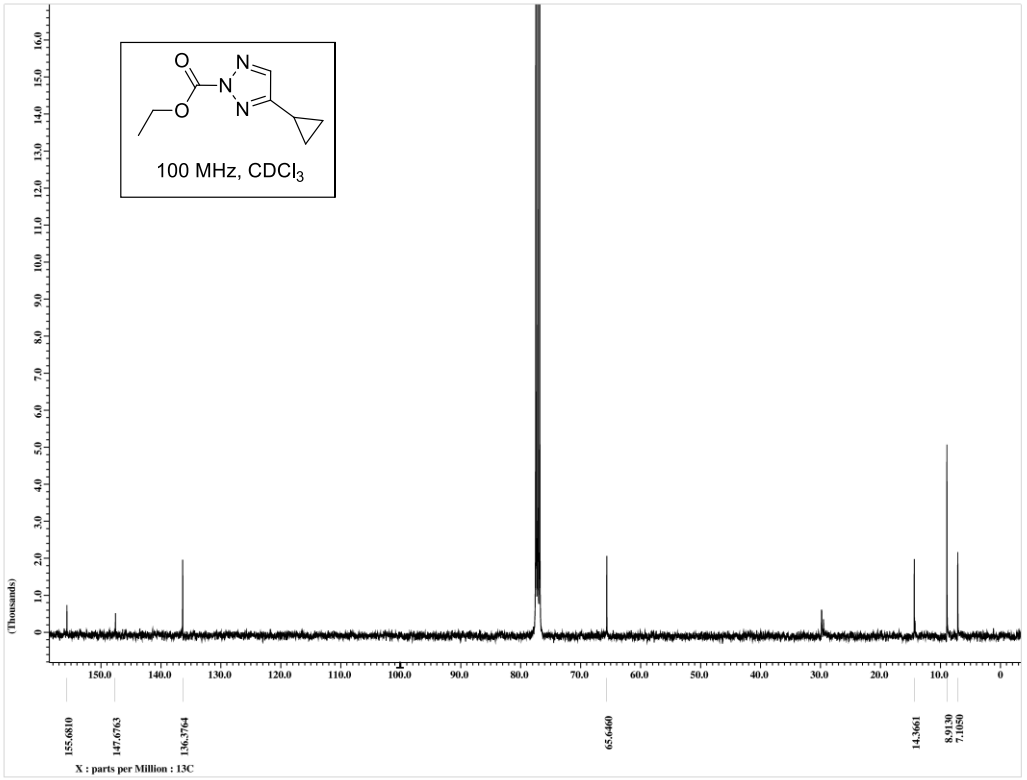
^{1}H and ^{13}C NMR of 3o:



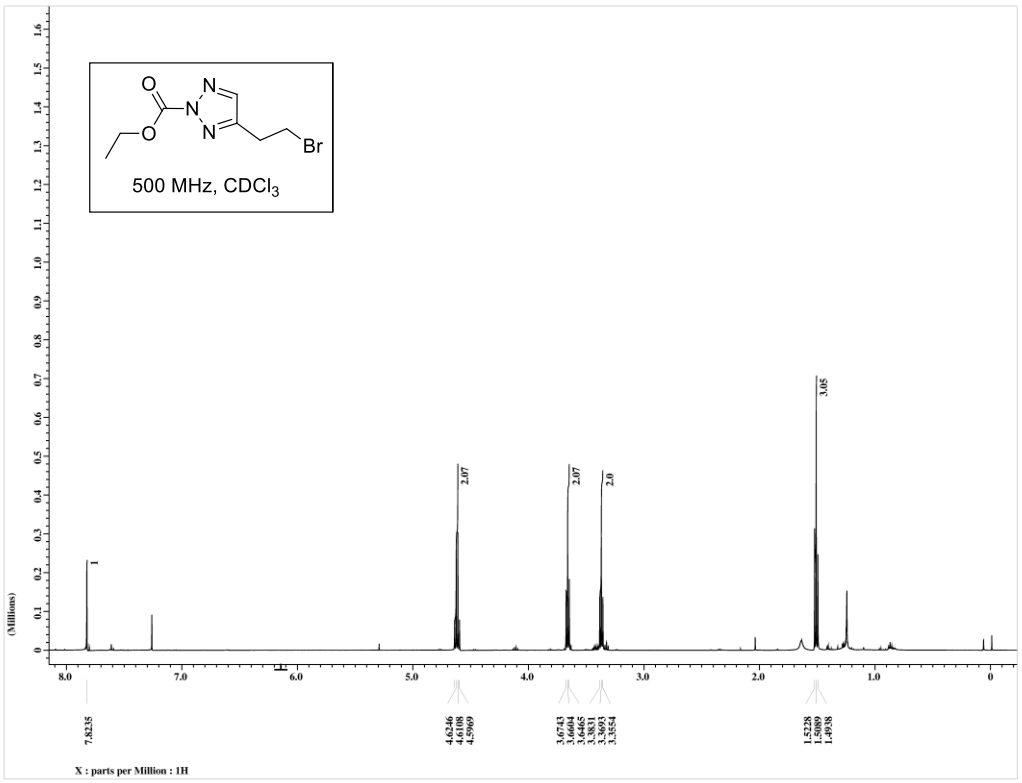


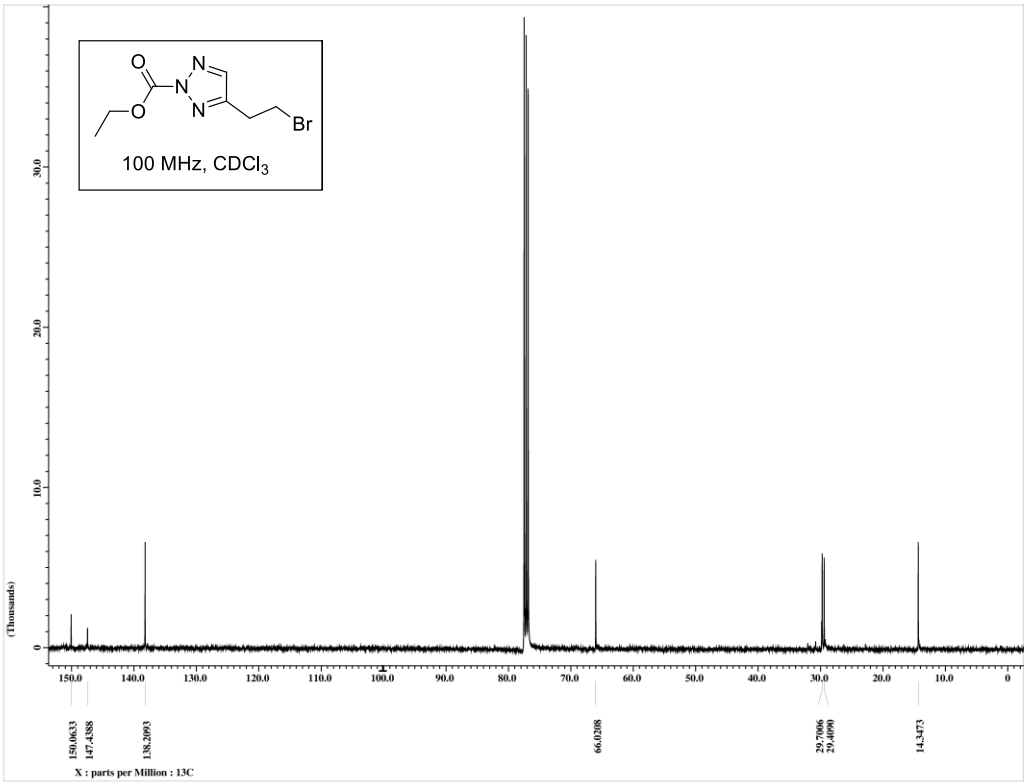
^{1}H and ^{13}C NMR of 3p:



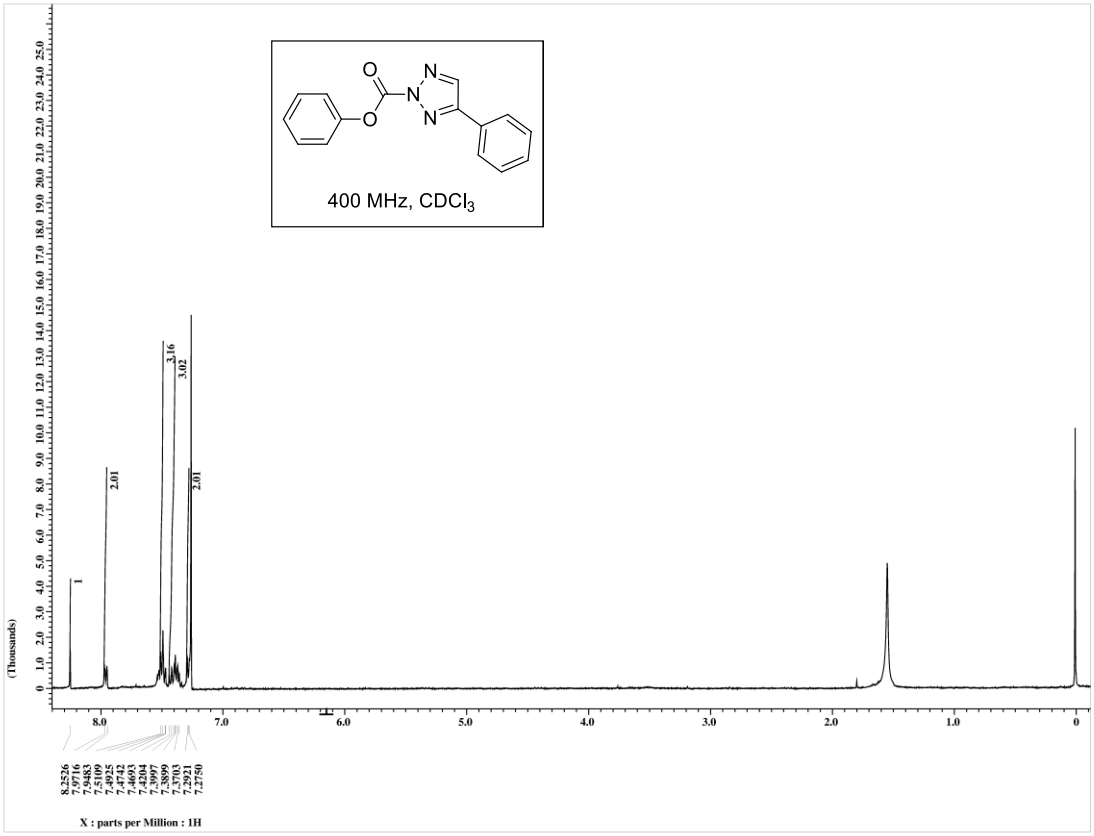


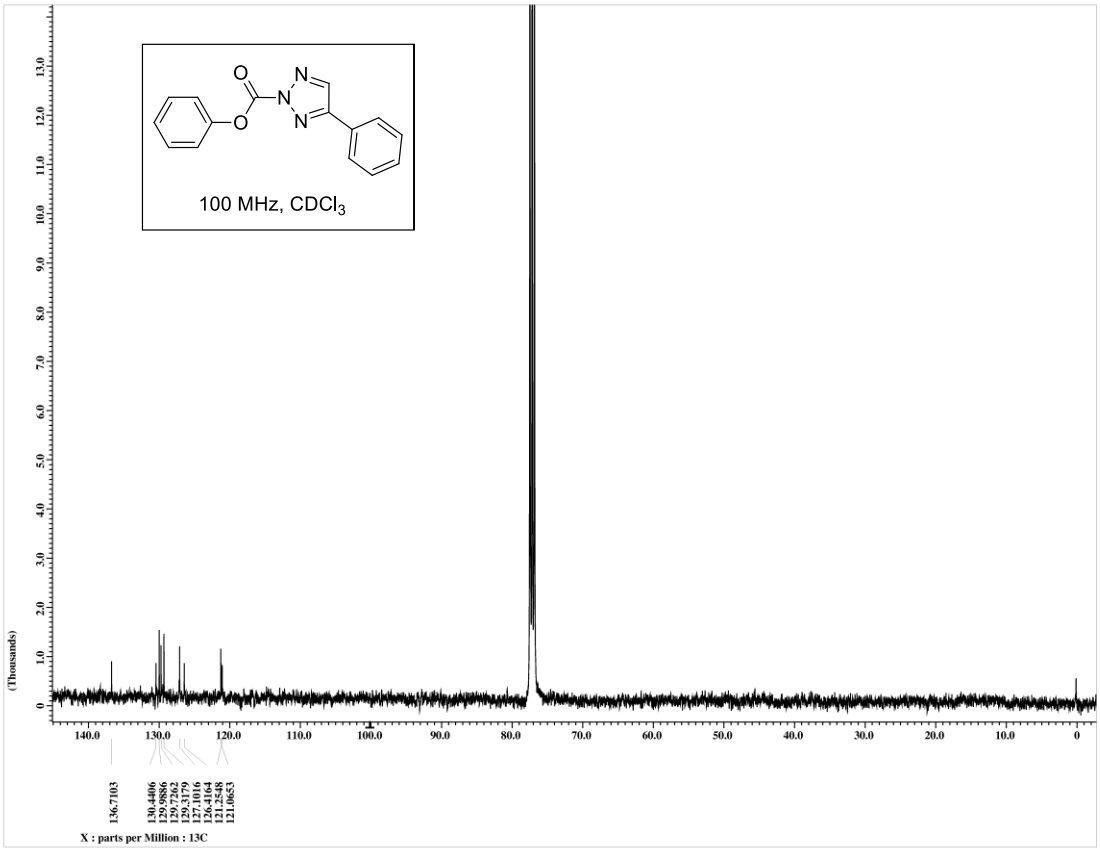
^{1}H and ^{13}C NMR of 3q:



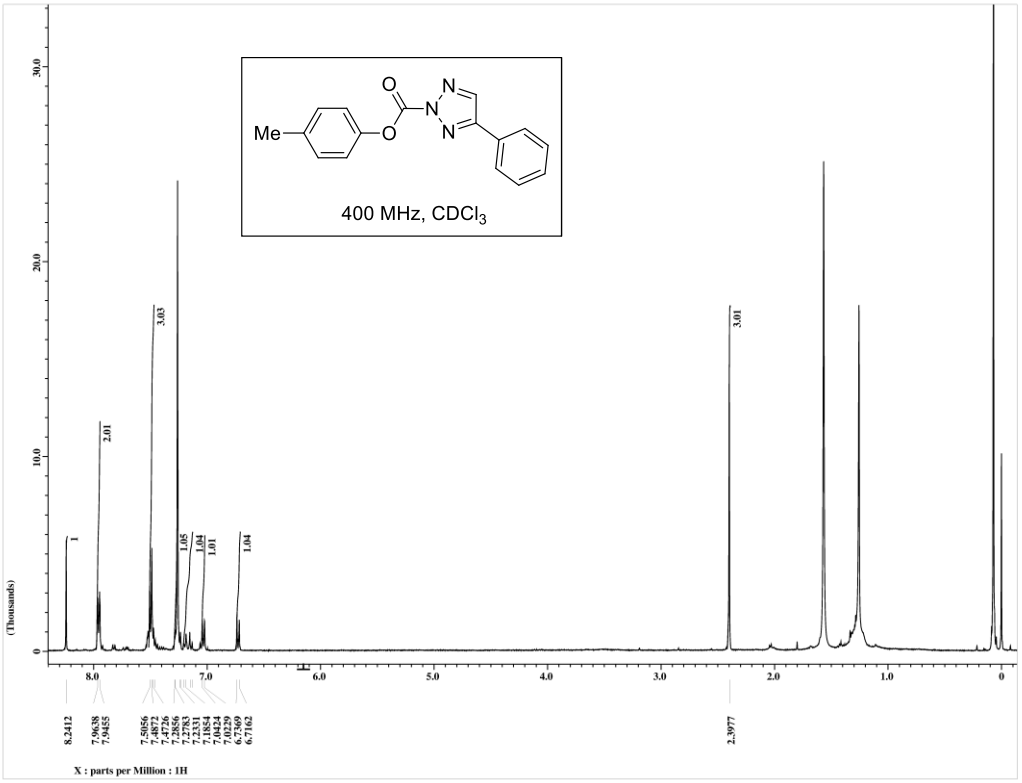


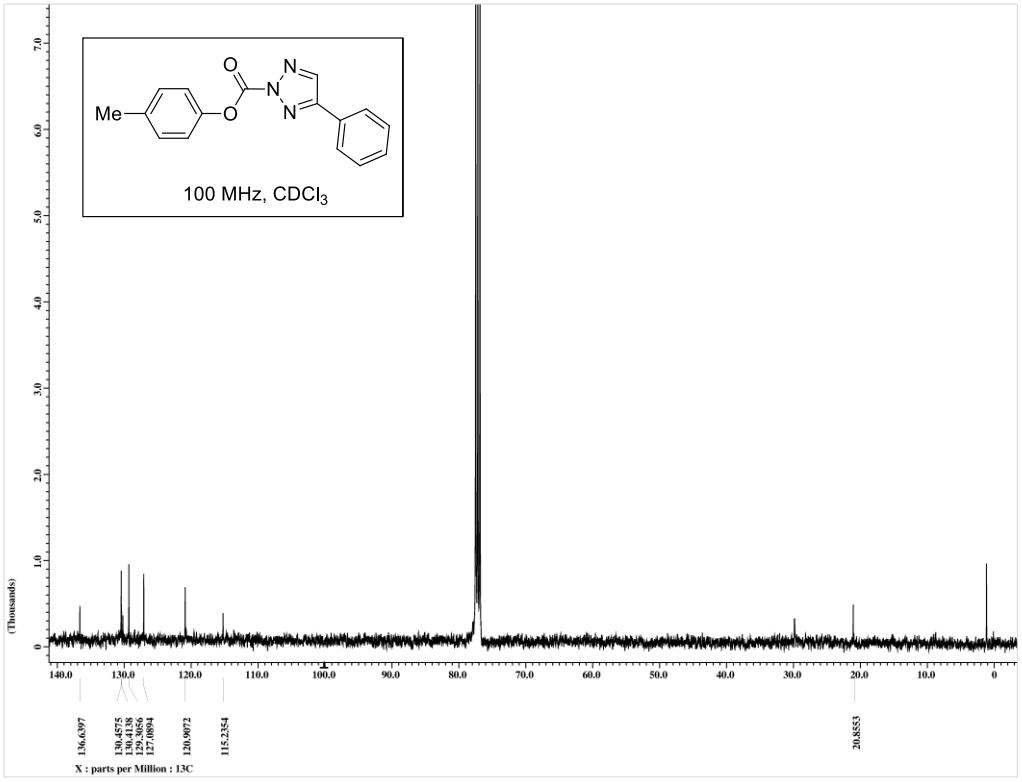
^{1}H and ^{13}C NMR of 3r:



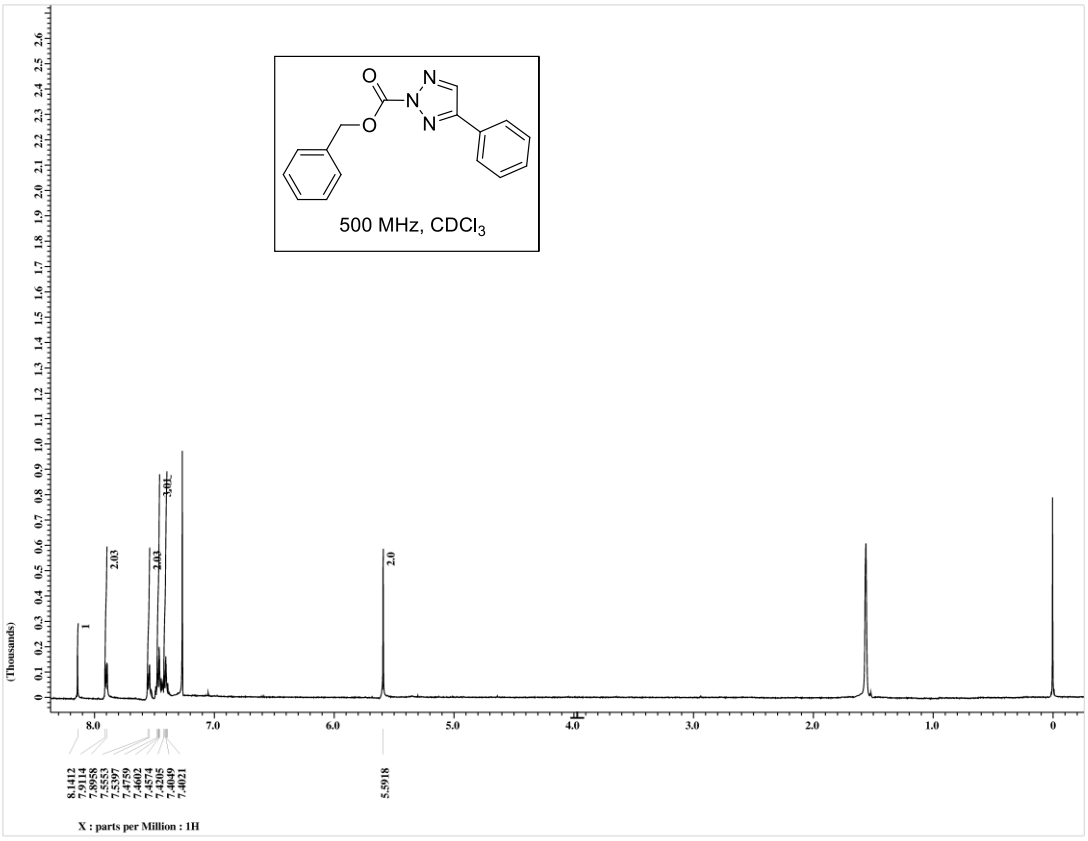


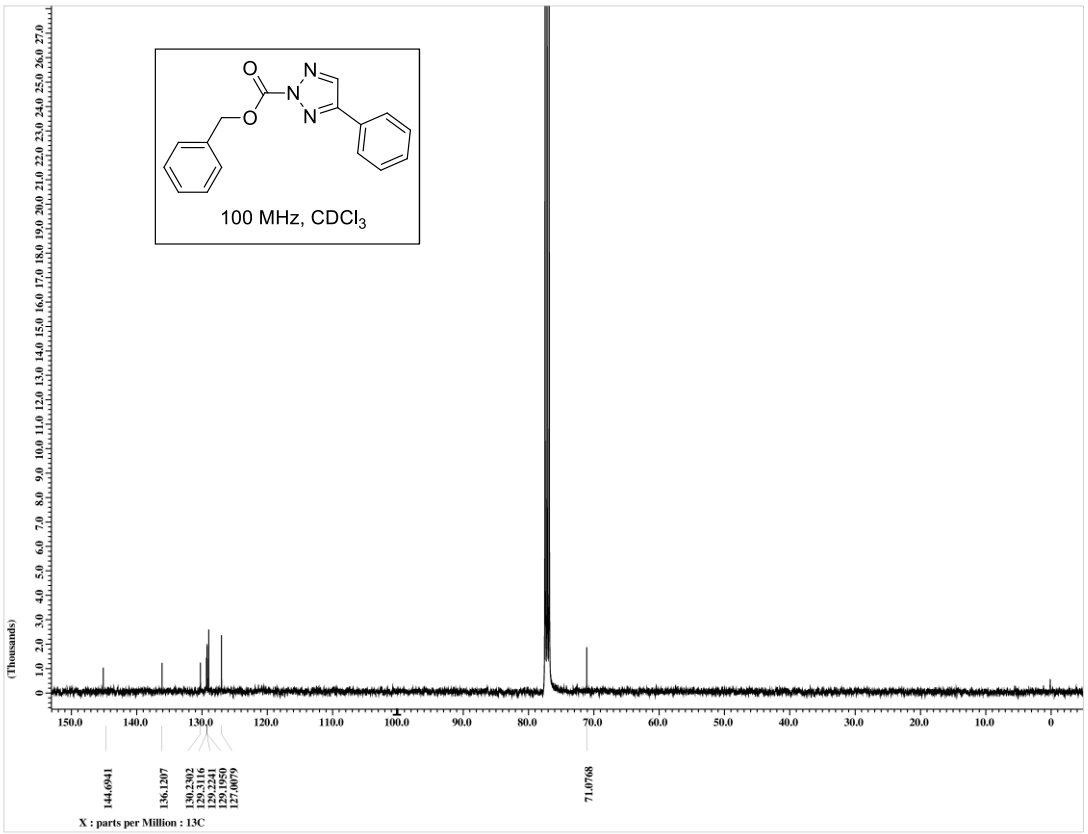
^{1}H and ^{13}C NMR of 3s:



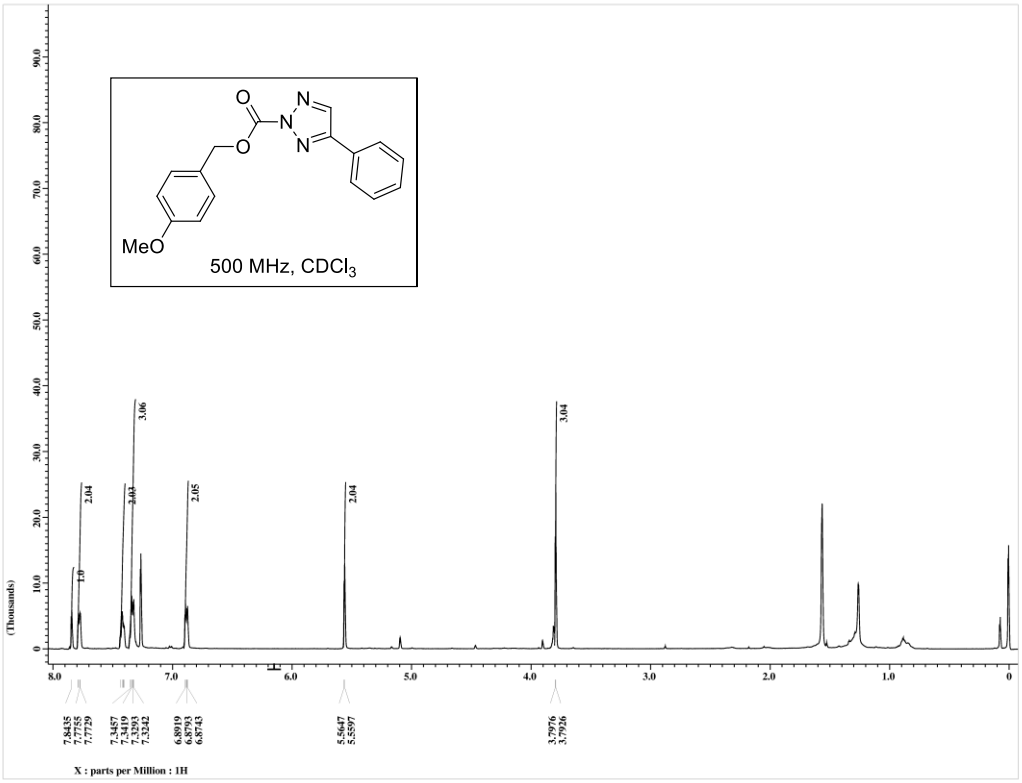


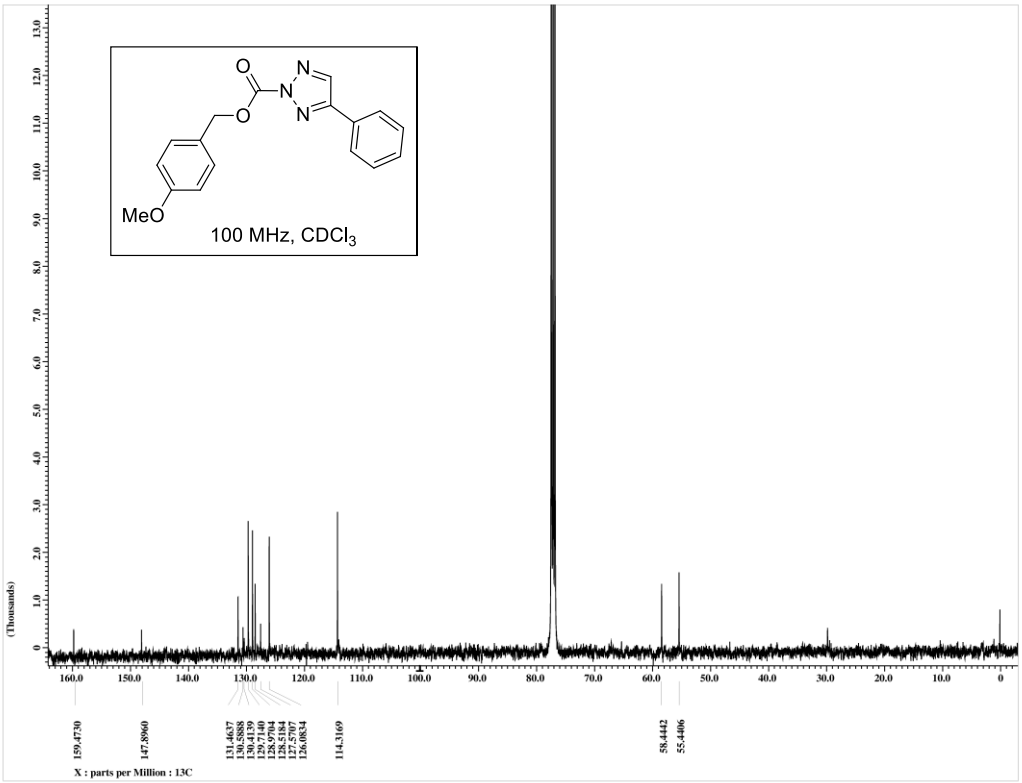
^{1}H and ^{13}C NMR of 3t:



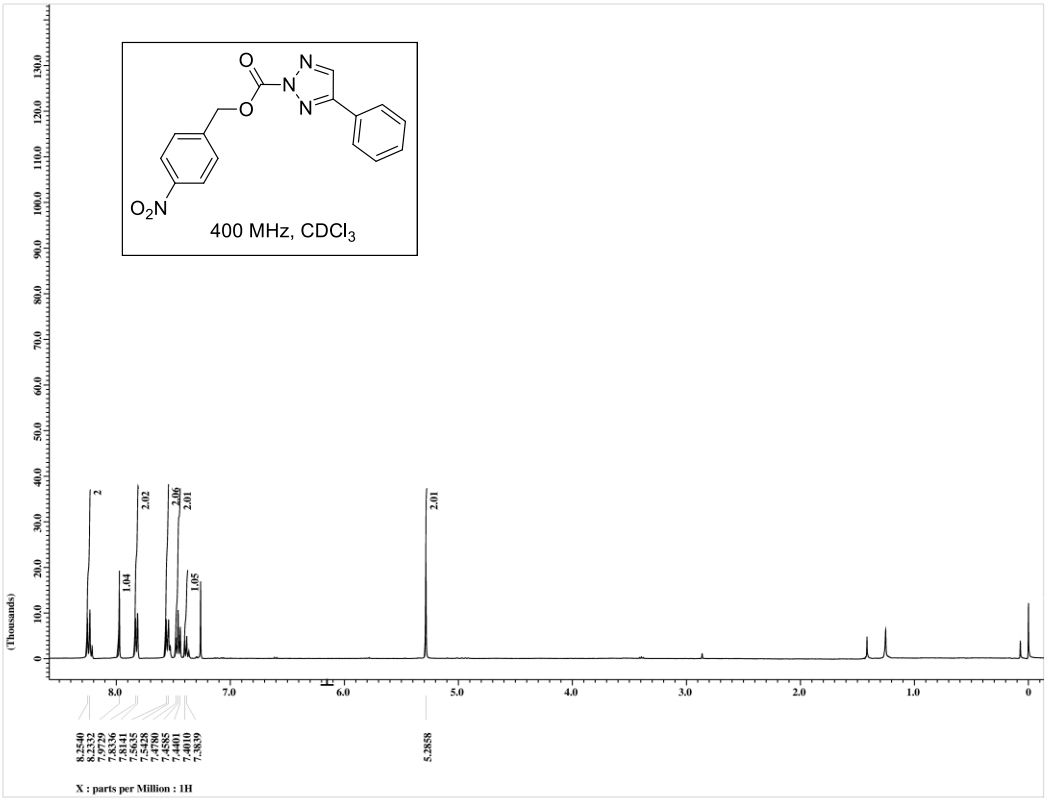


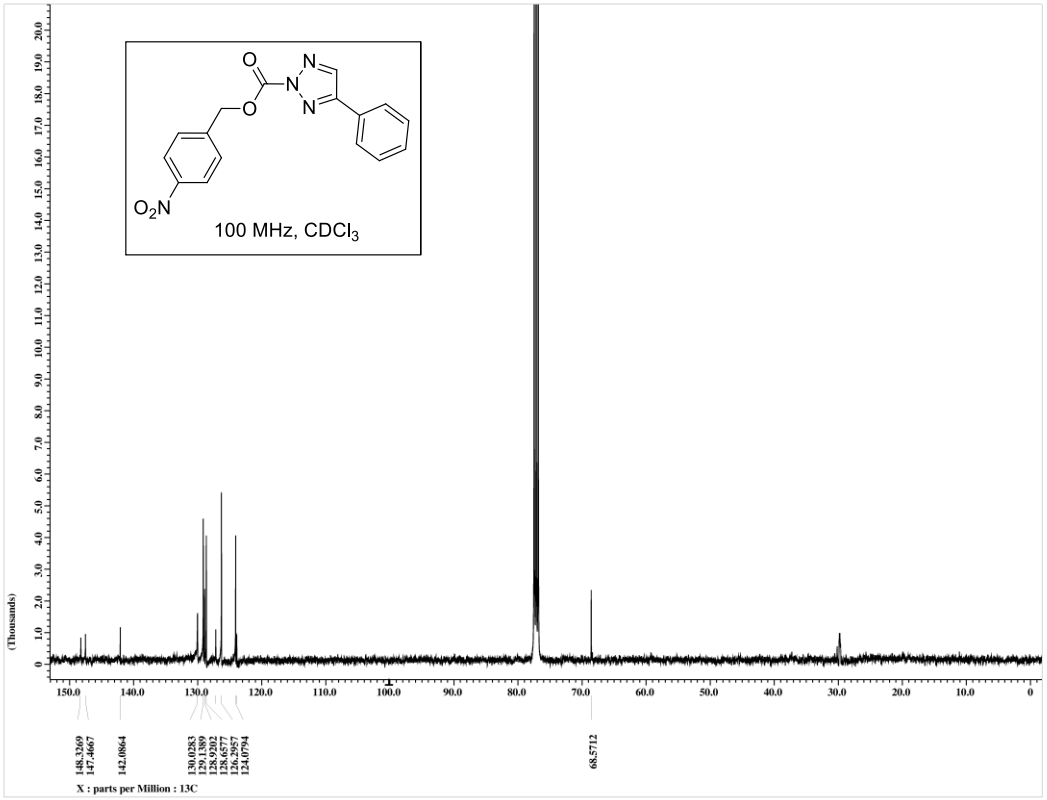
^{1}H and ^{13}C NMR of 3u:



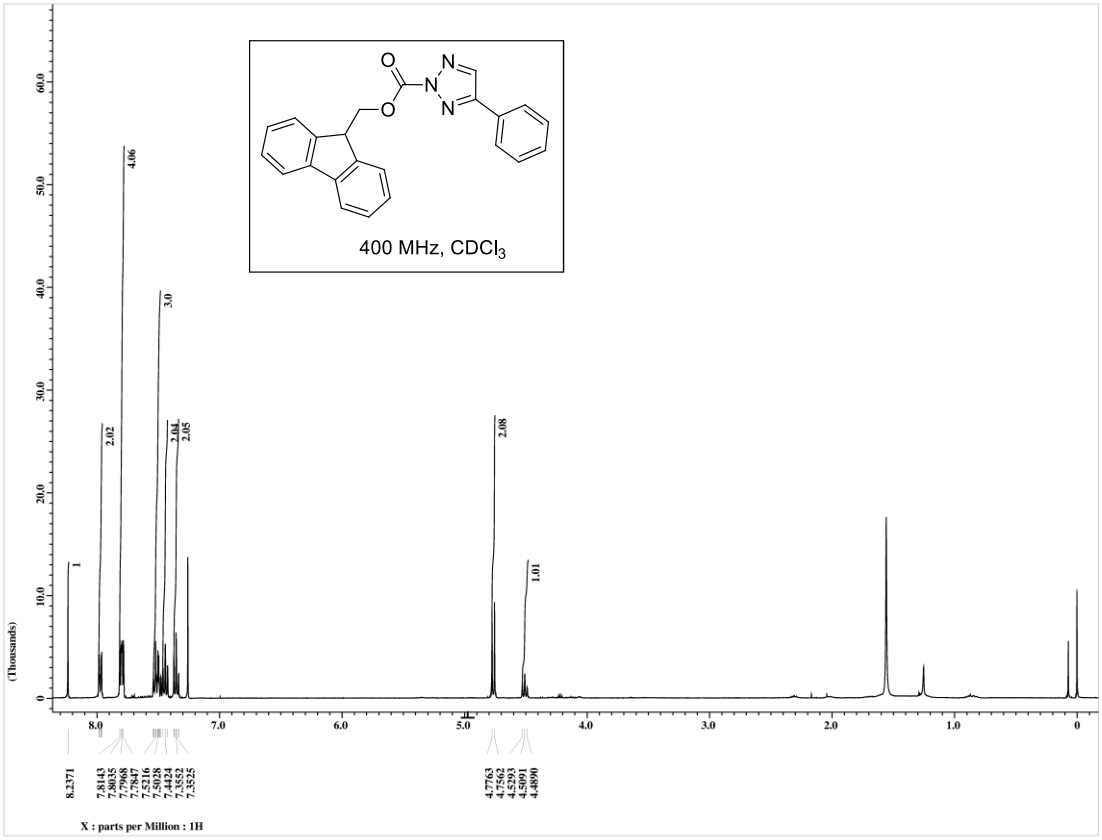


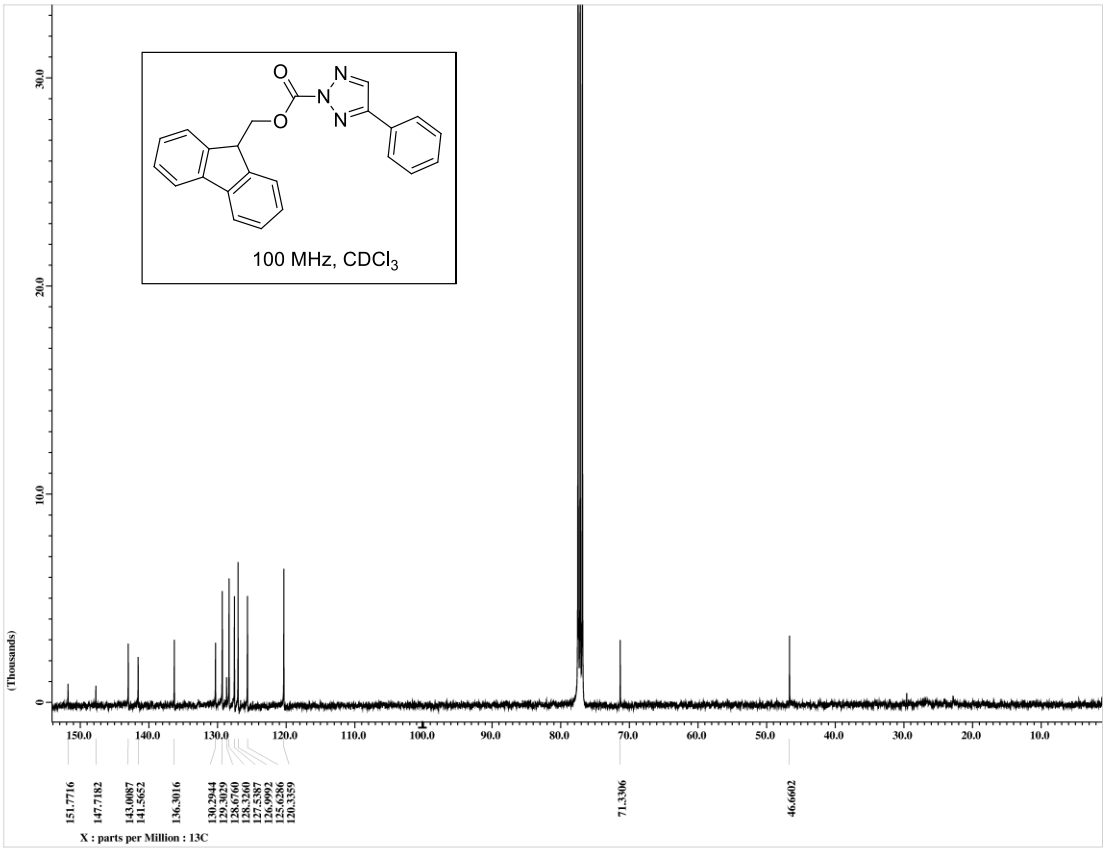
^{1}H and ^{13}C NMR of 3v:



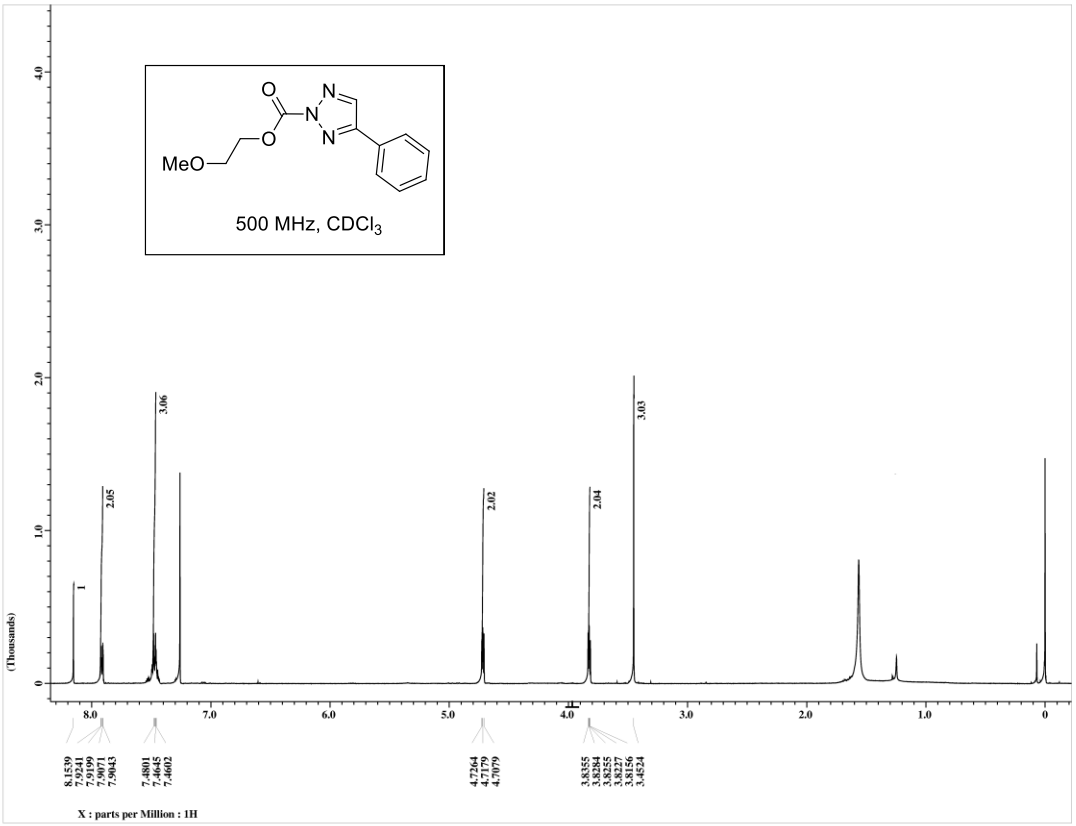


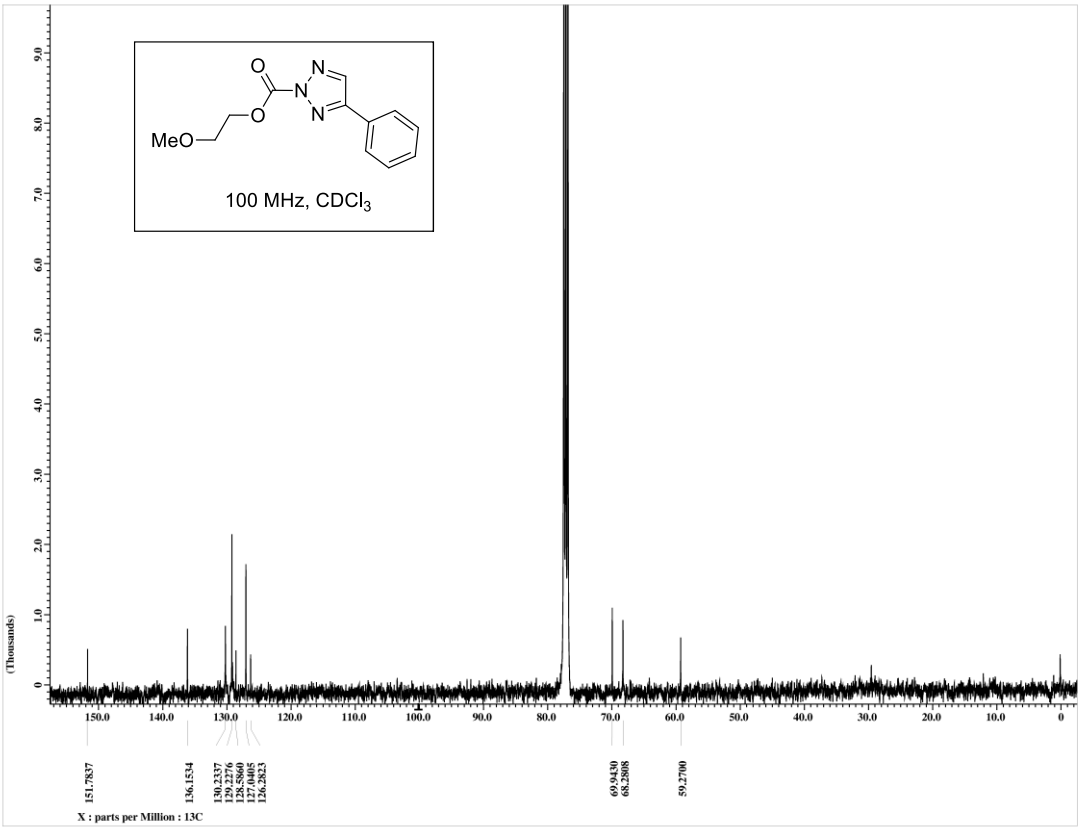
^{1}H and ^{13}C NMR of 3w:



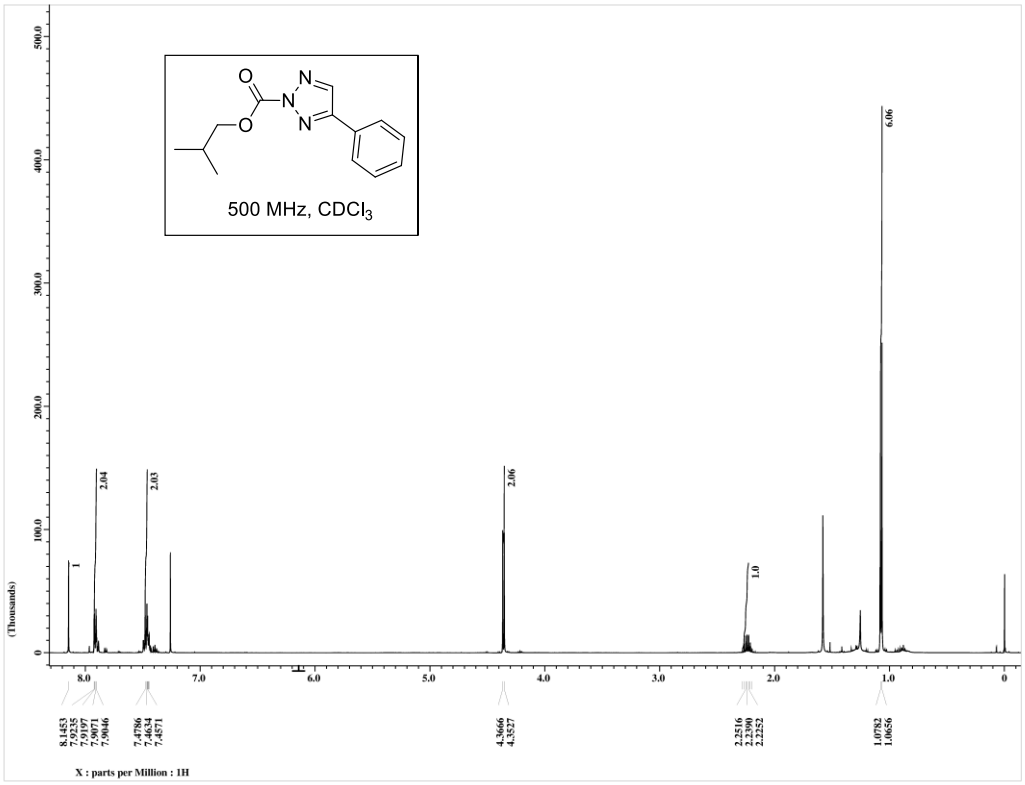


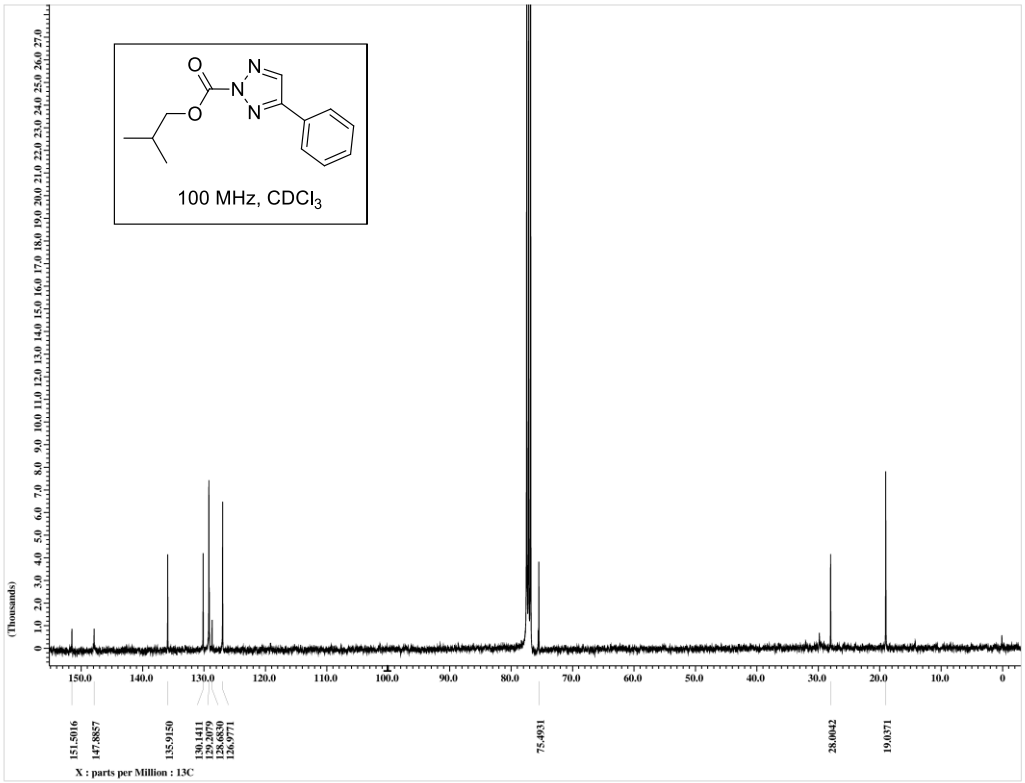
^{1}H and ^{13}C NMR of 3x:



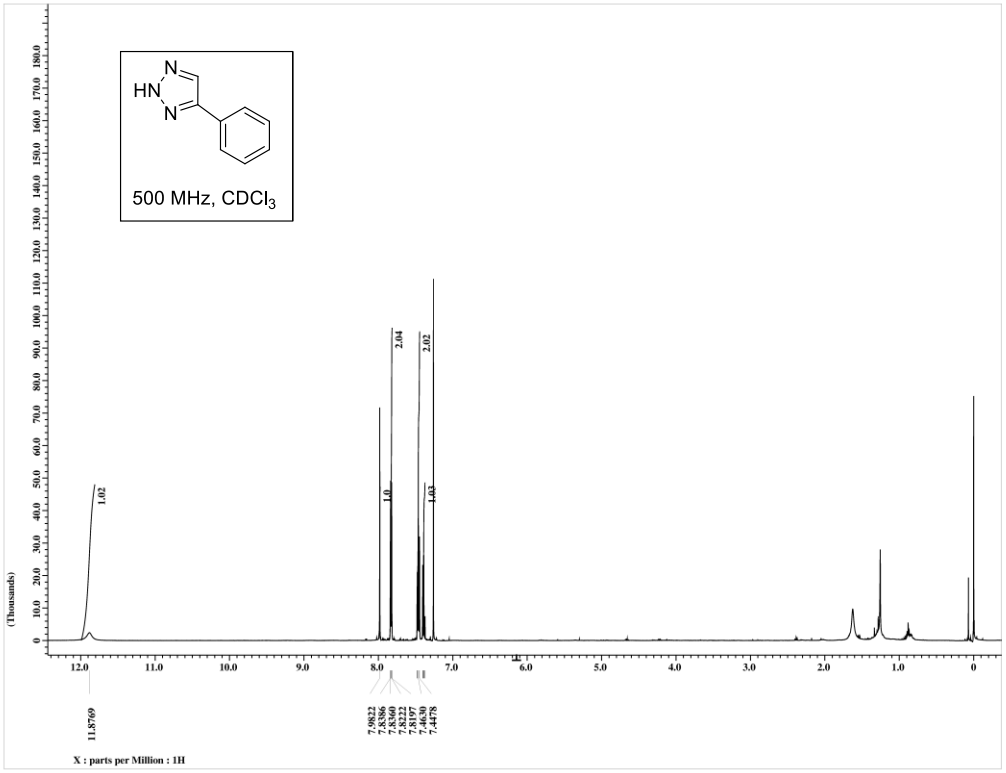


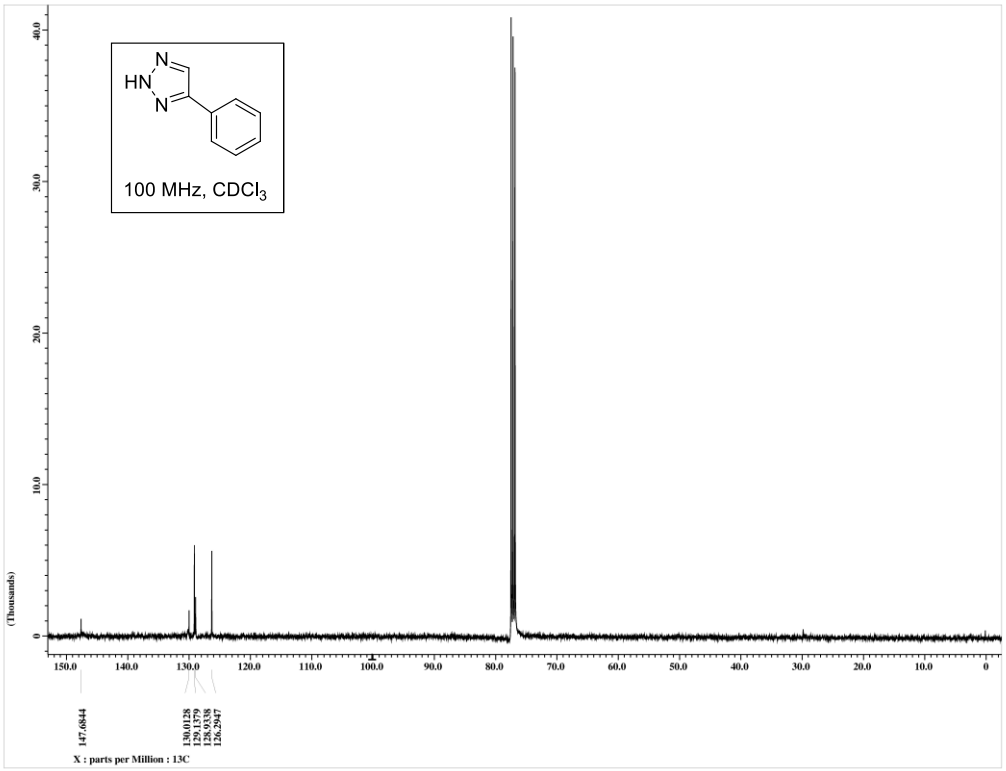
^{1}H and ^{13}C NMR of 3y:



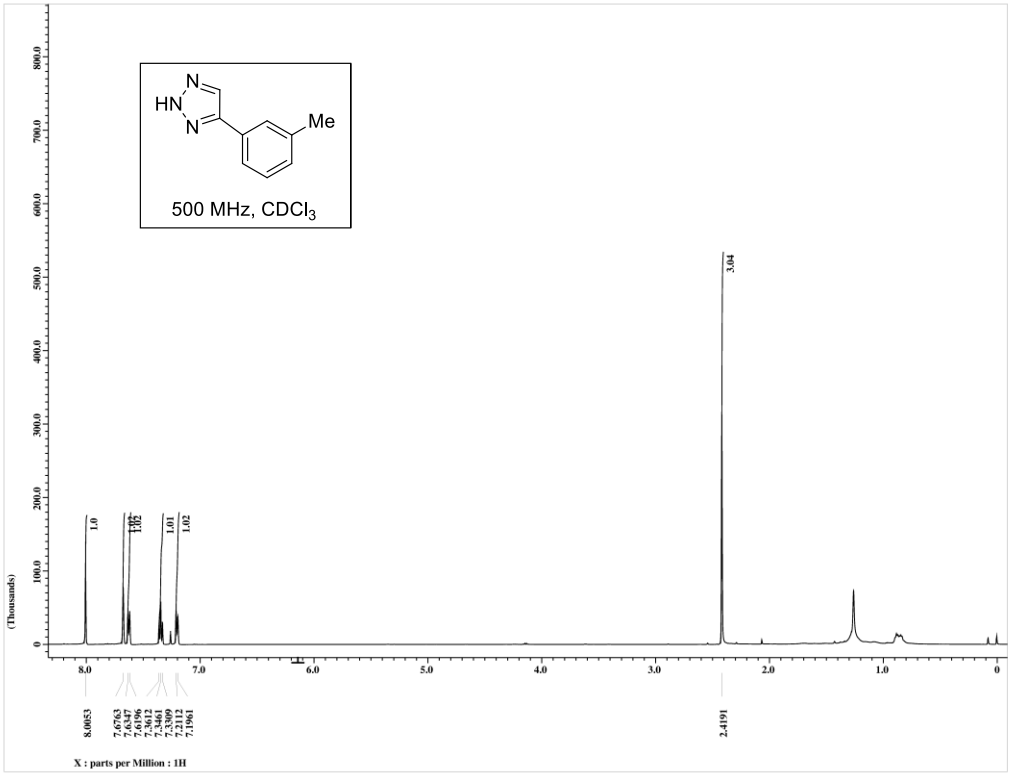


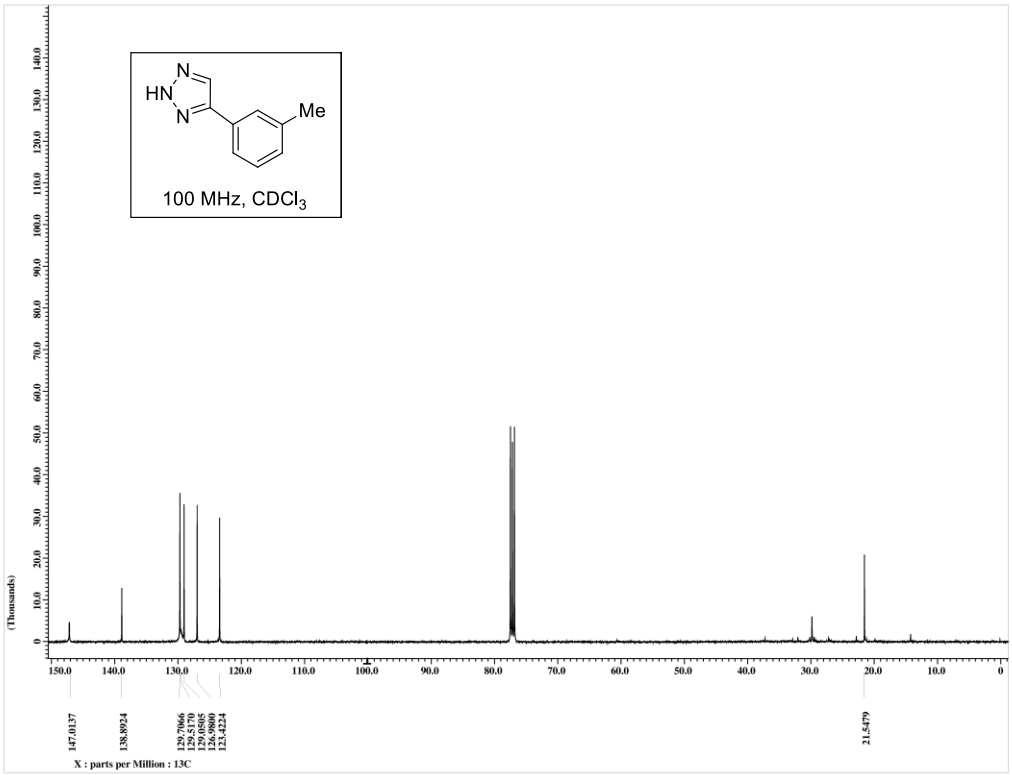
^{1}H and ^{13}C NMR of 5a:



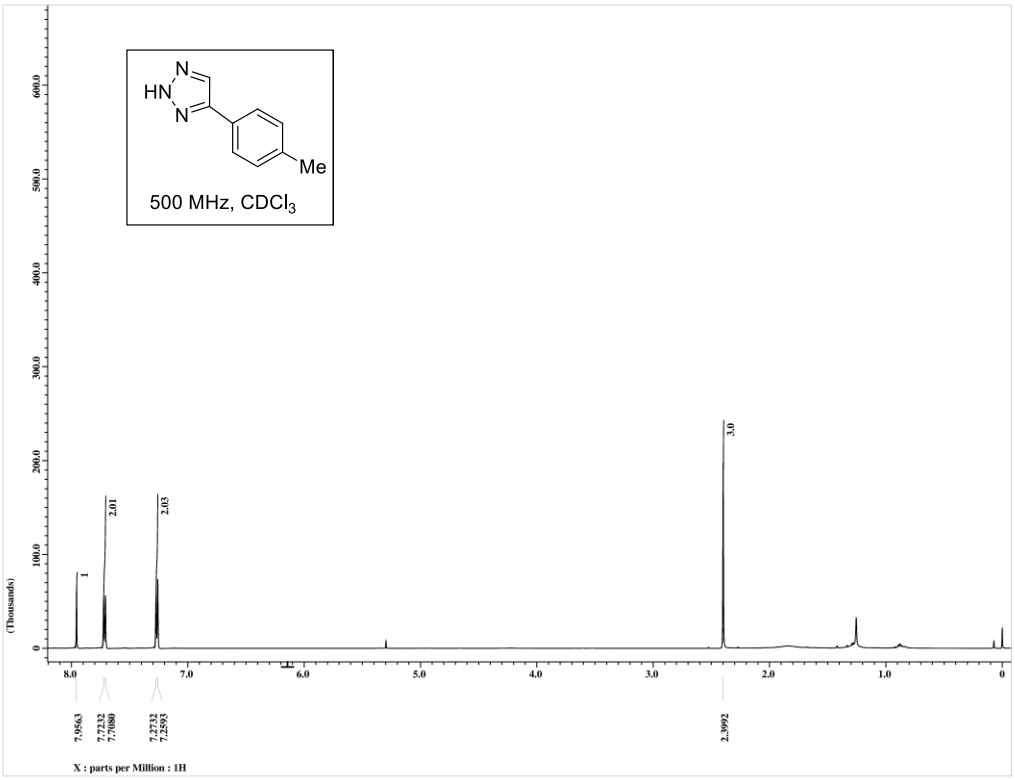


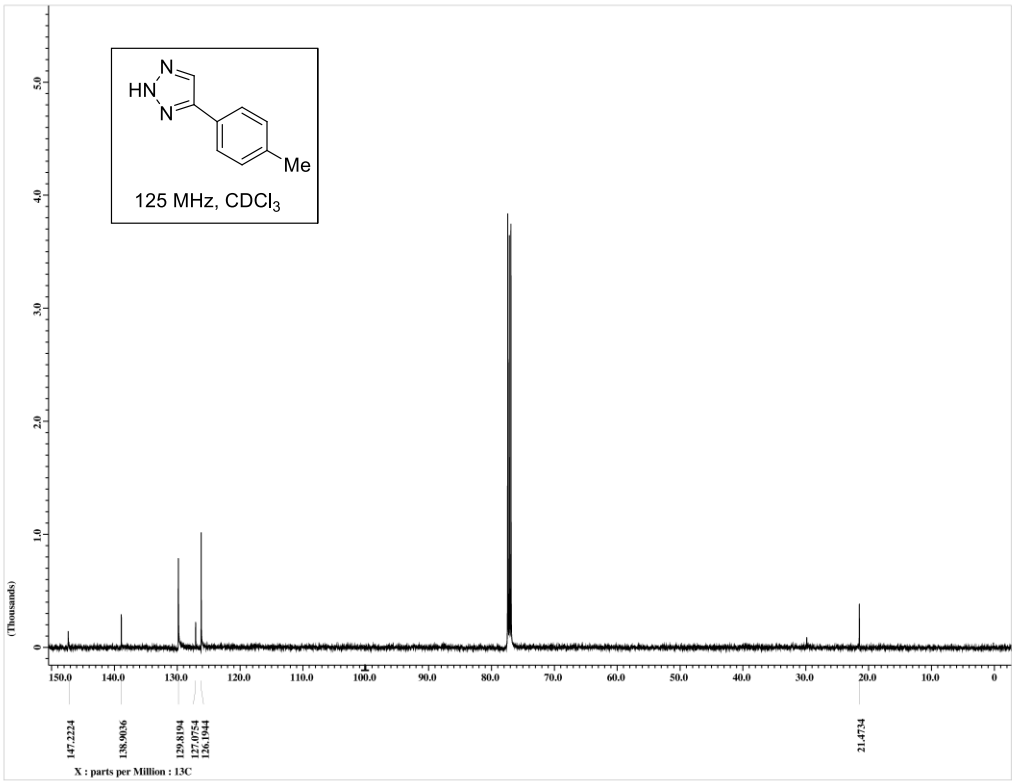
^{1}H and ^{13}C NMR of 5b:



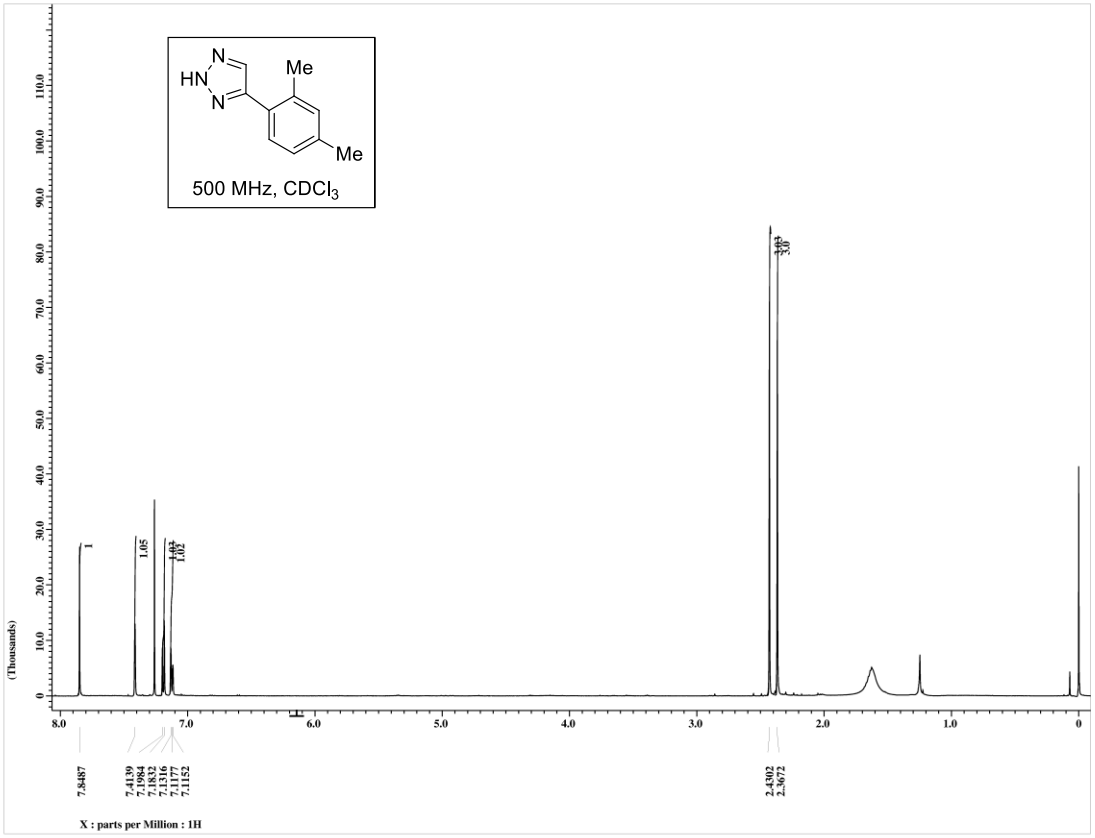


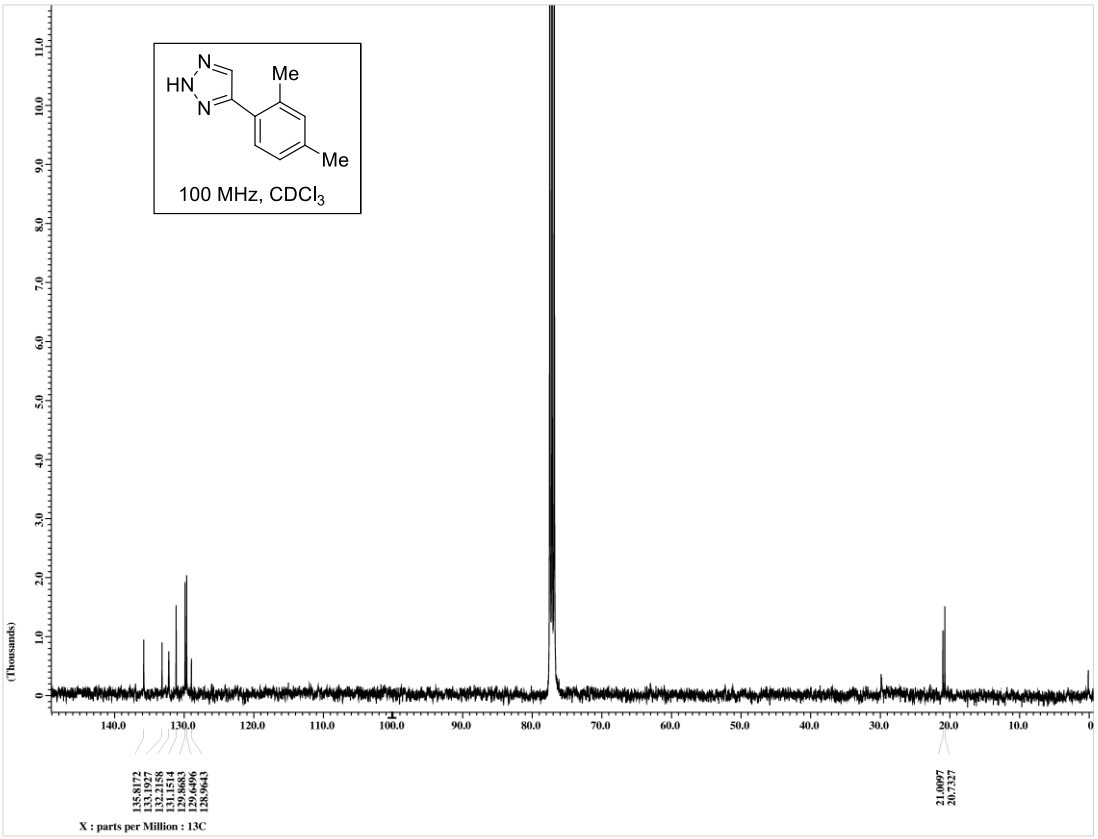
^{1}H and ^{13}C NMR of 5c:



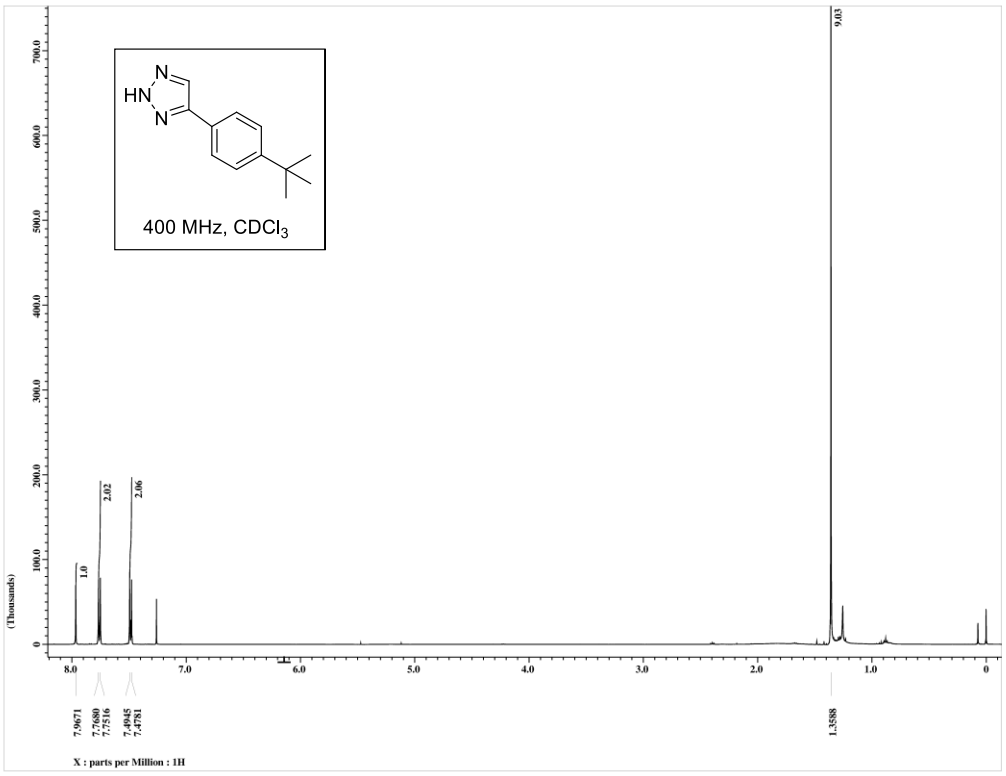


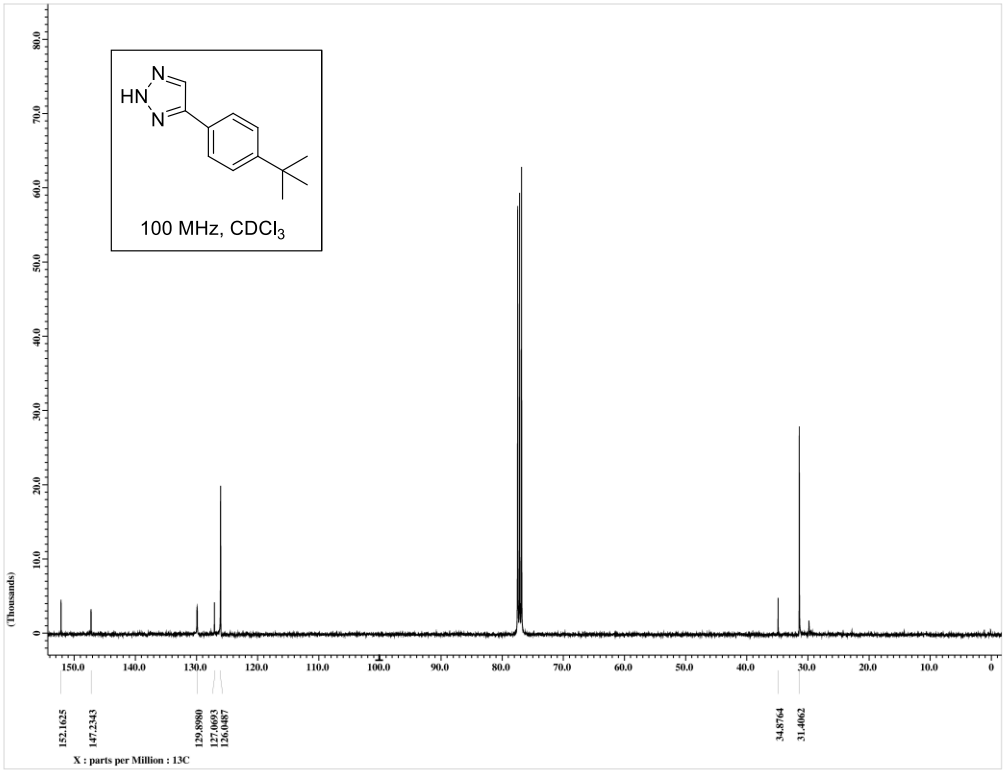
^{1}H and ^{13}C NMR of 5d:



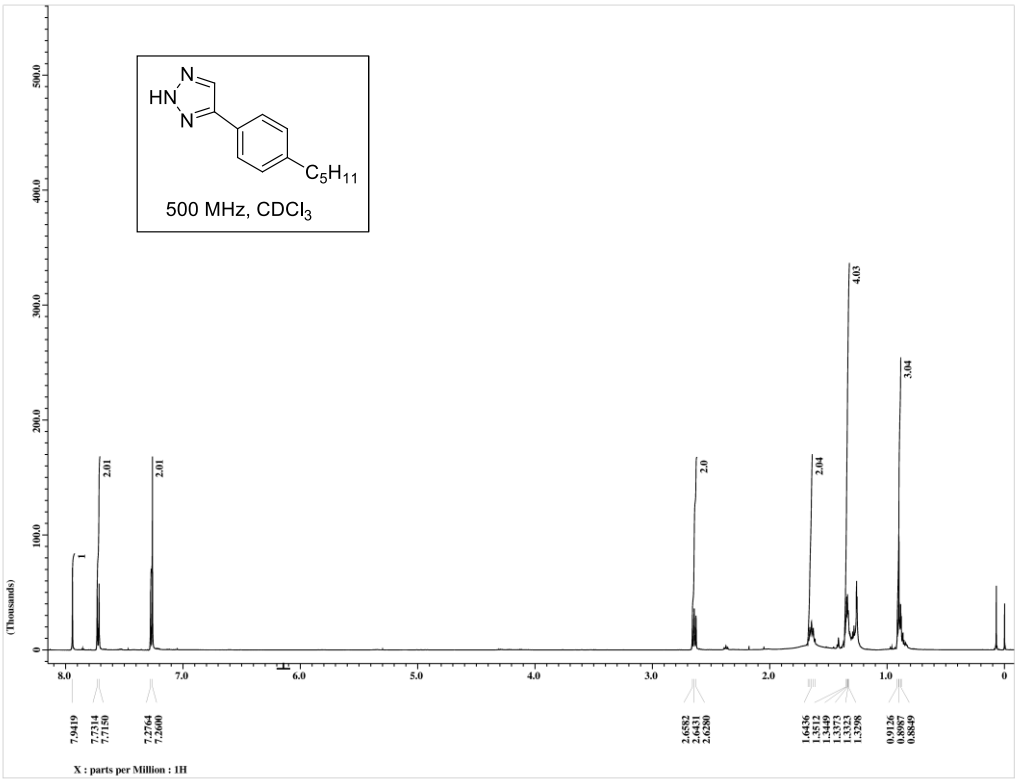


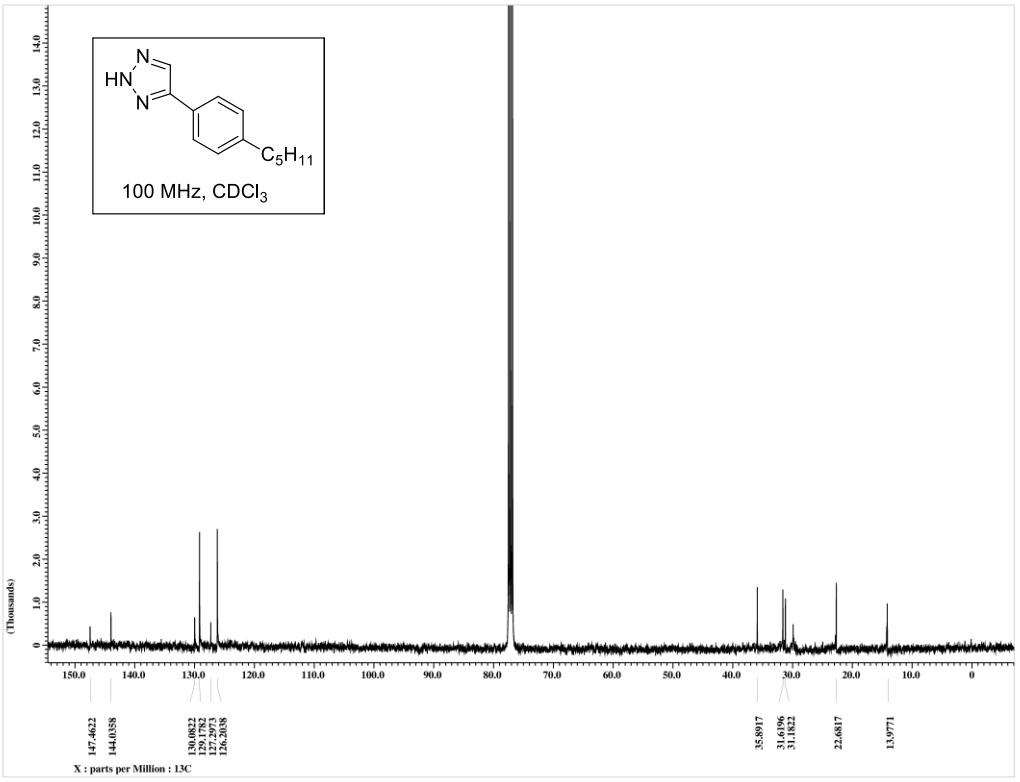
^{1}H and ^{13}C NMR of 5e:



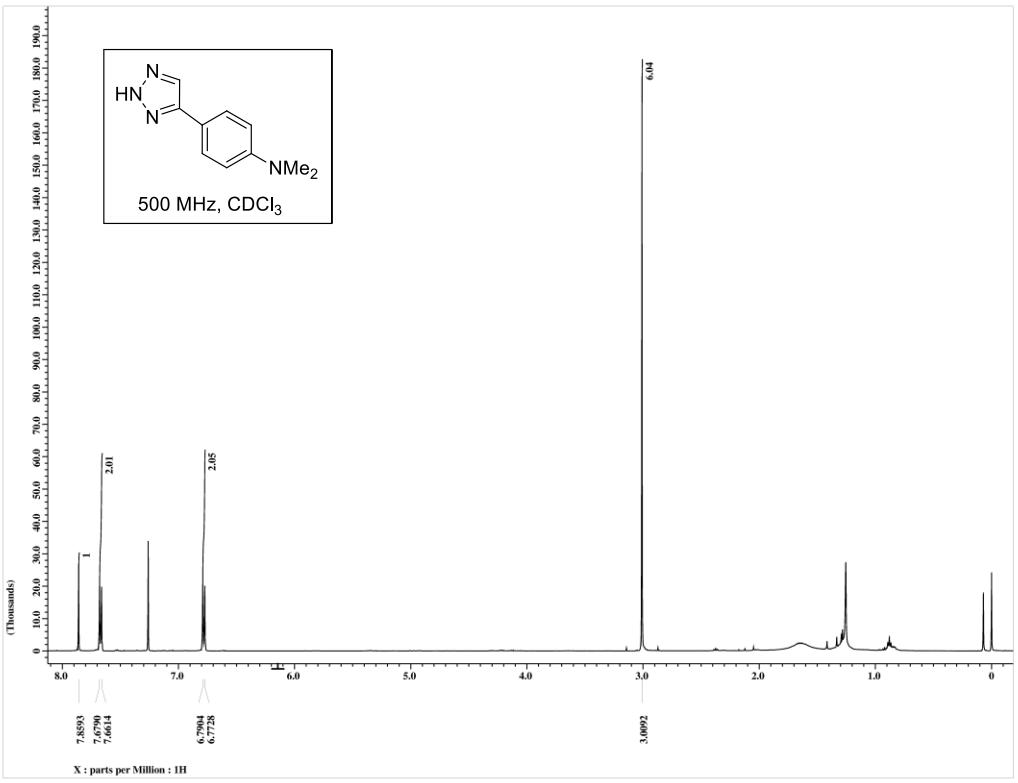


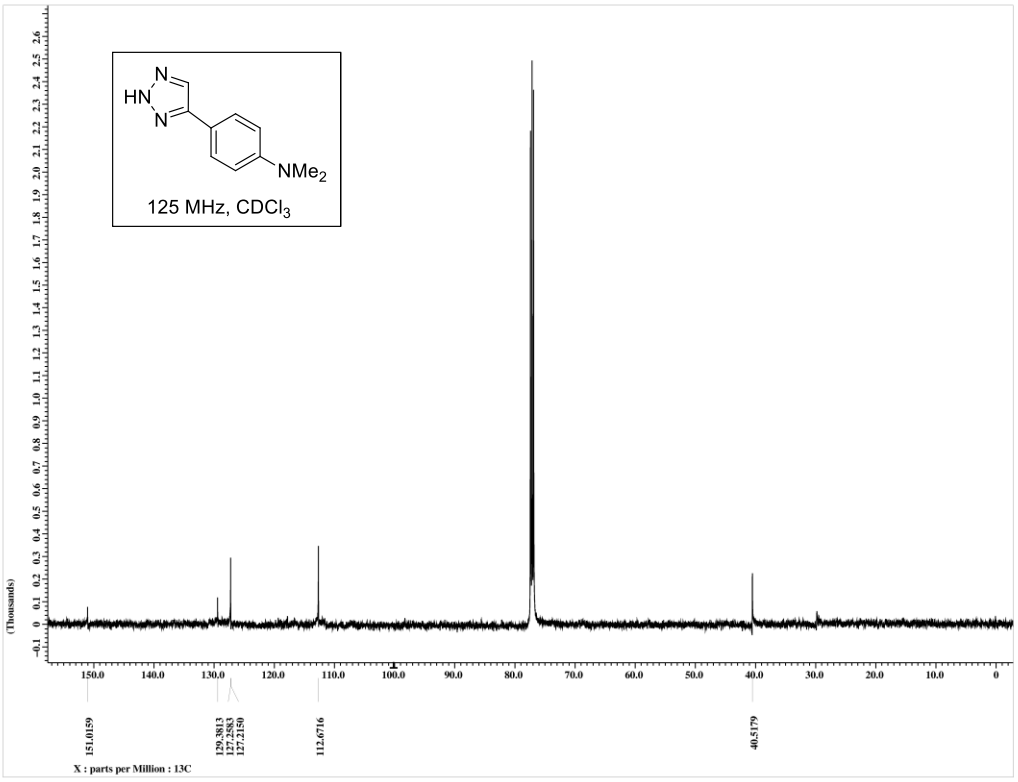
^{1}H and ^{13}C NMR of 5f:



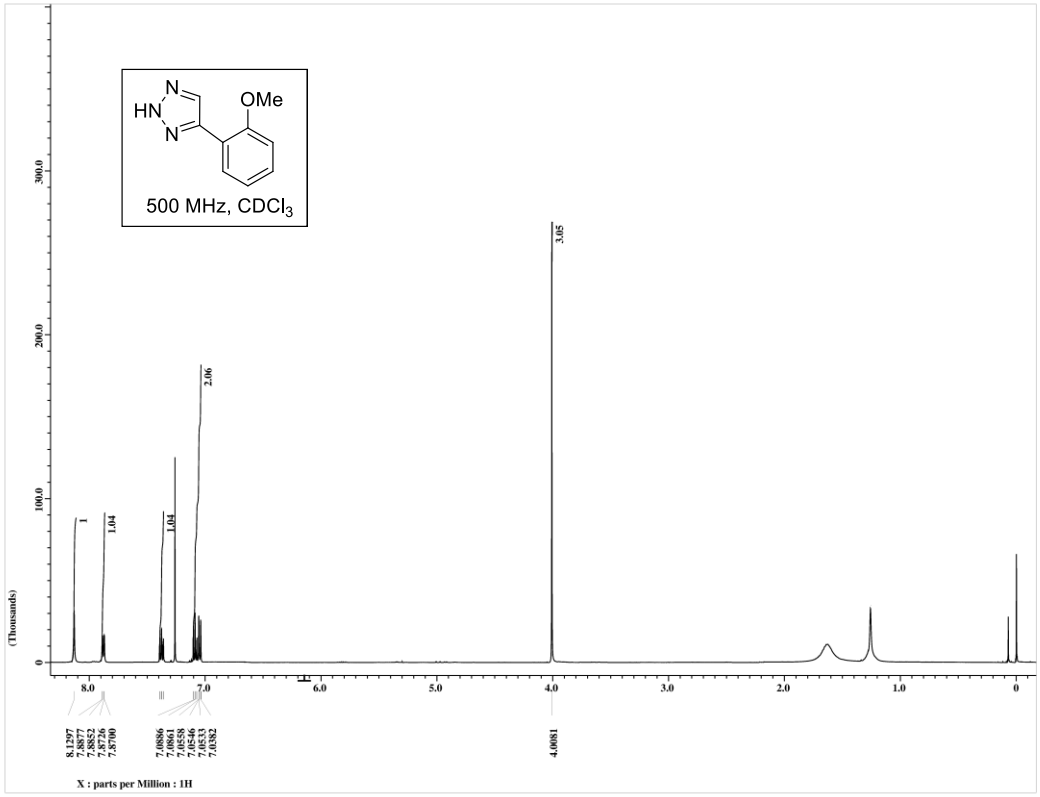


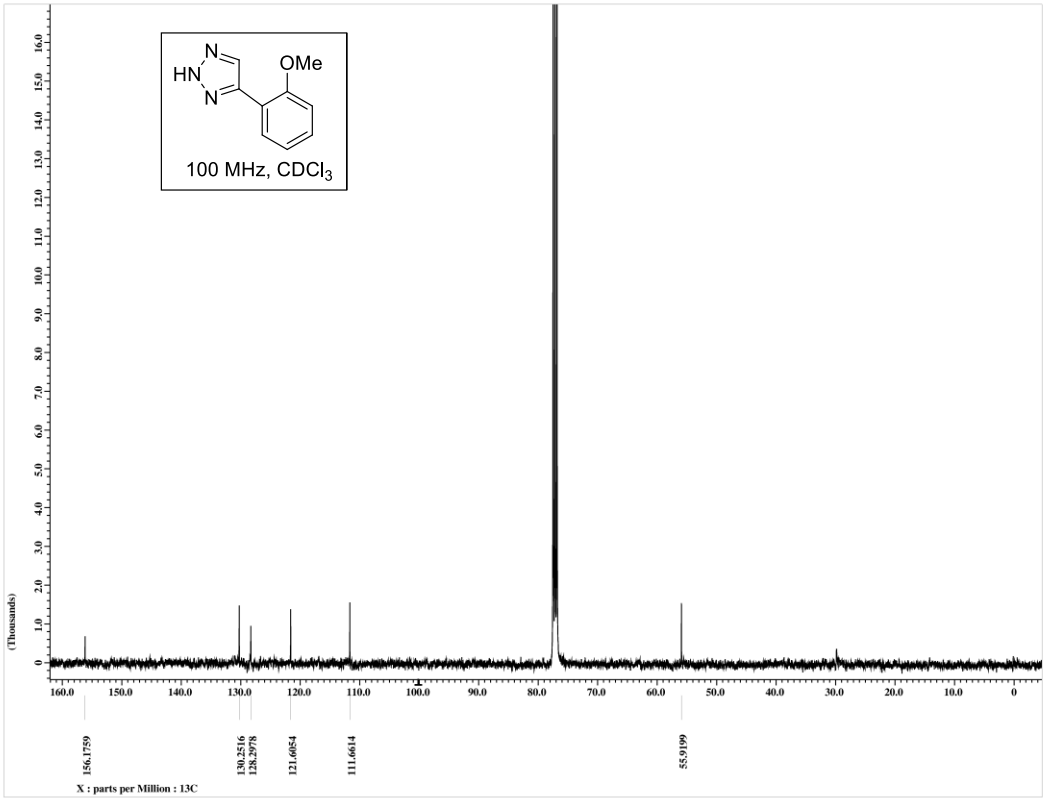
^{1}H and ^{13}C NMR of 5g:



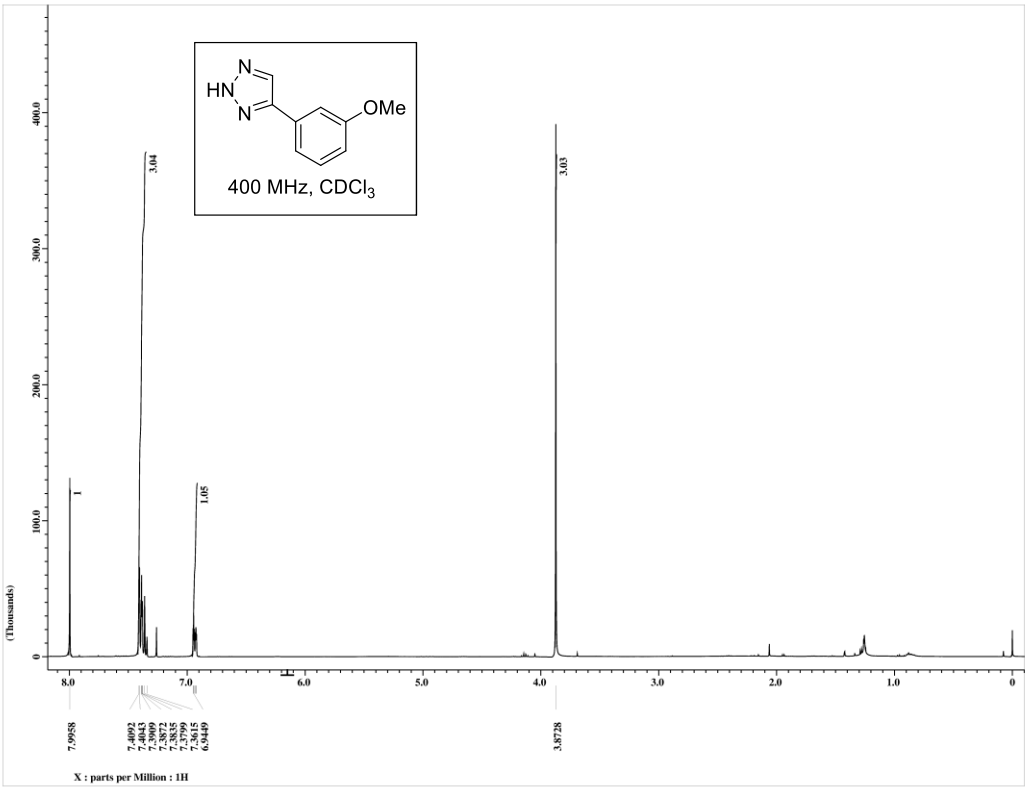


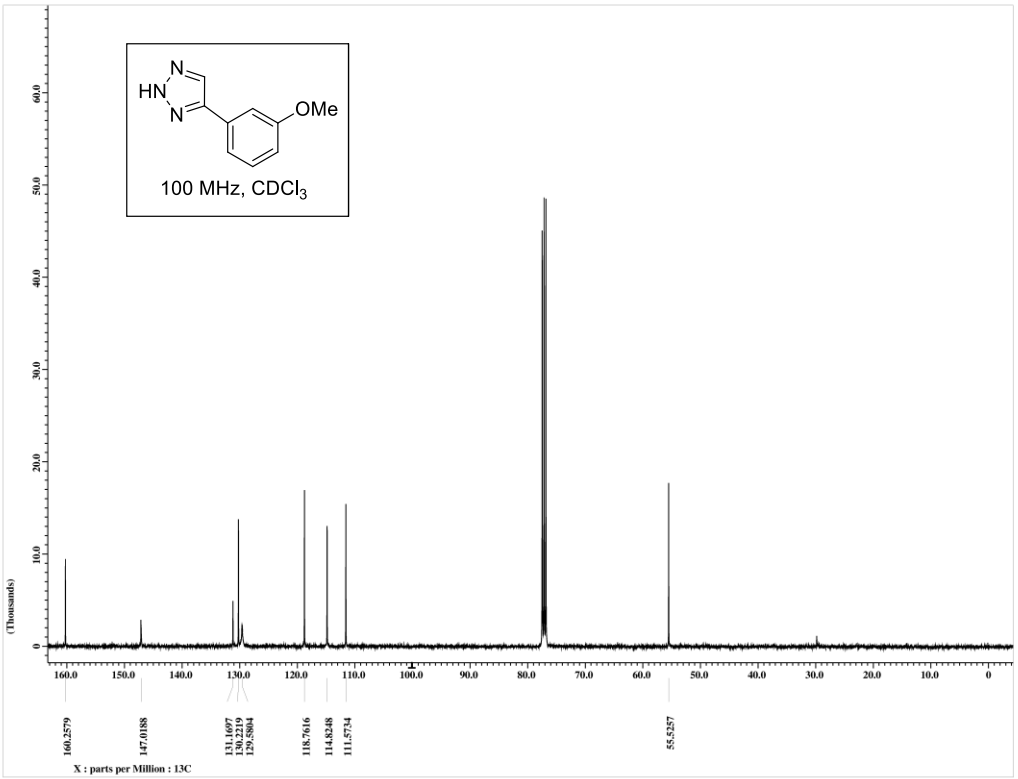
^{1}H and ^{13}C NMR of 5h:



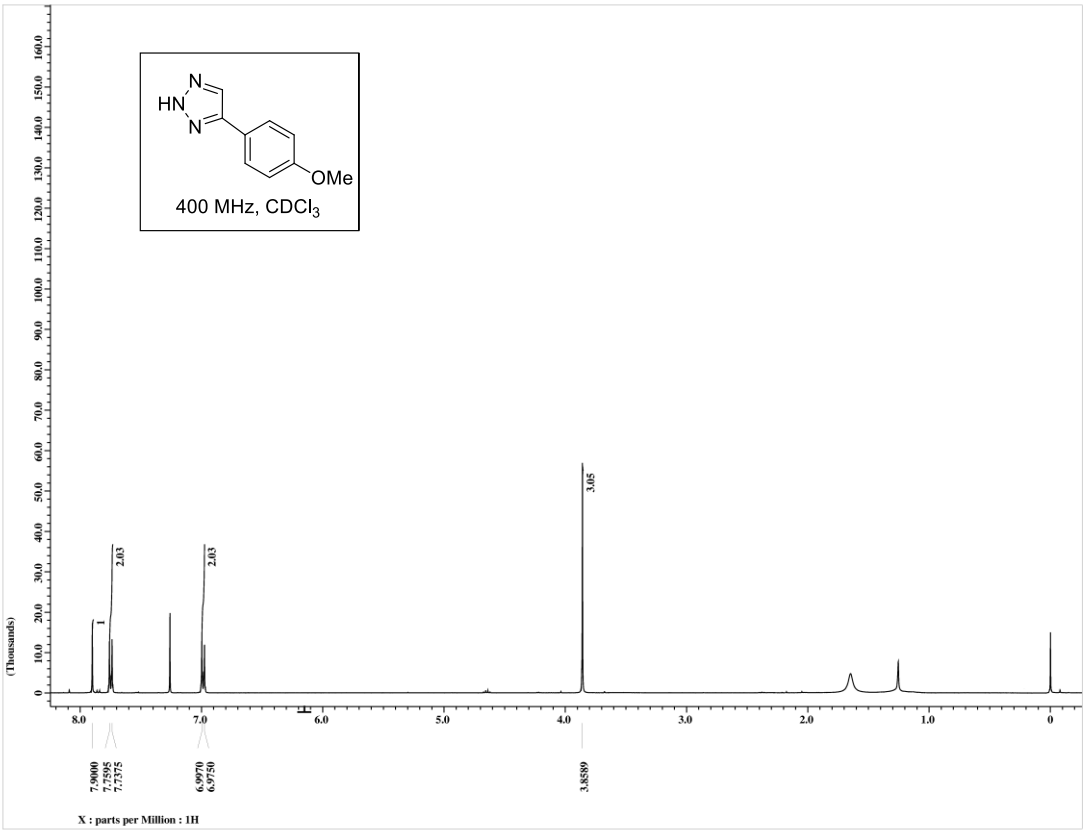


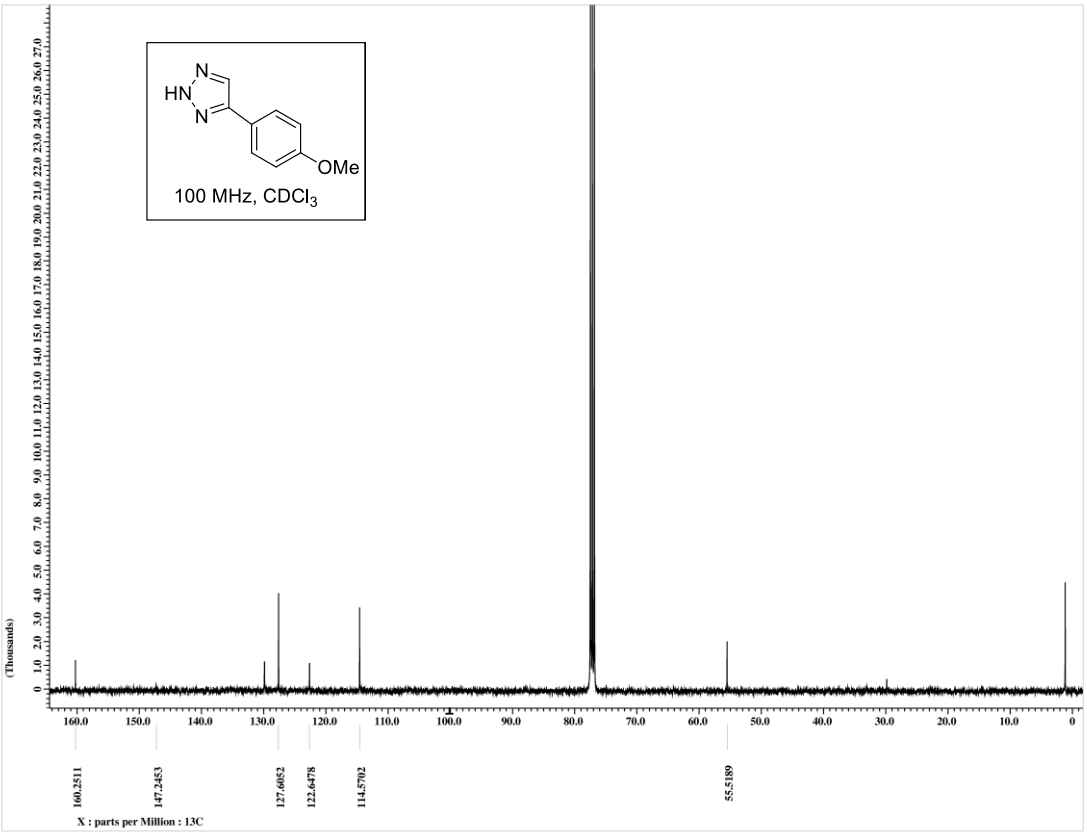
^{1}H and ^{13}C NMR of 5i:



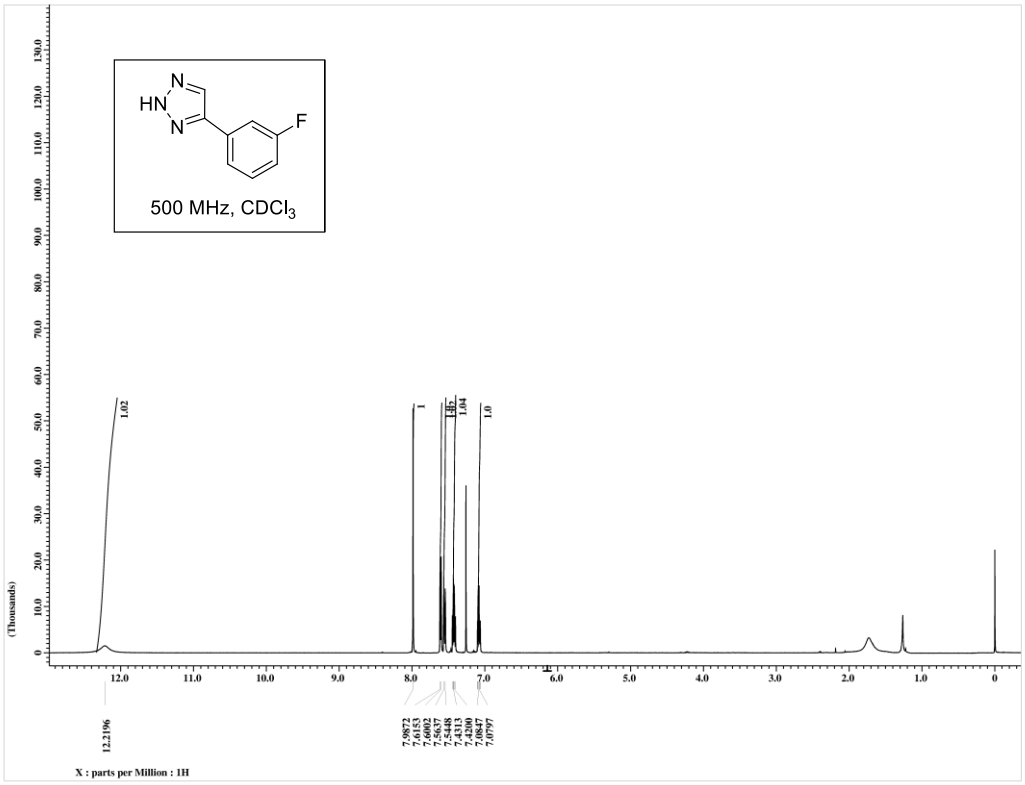


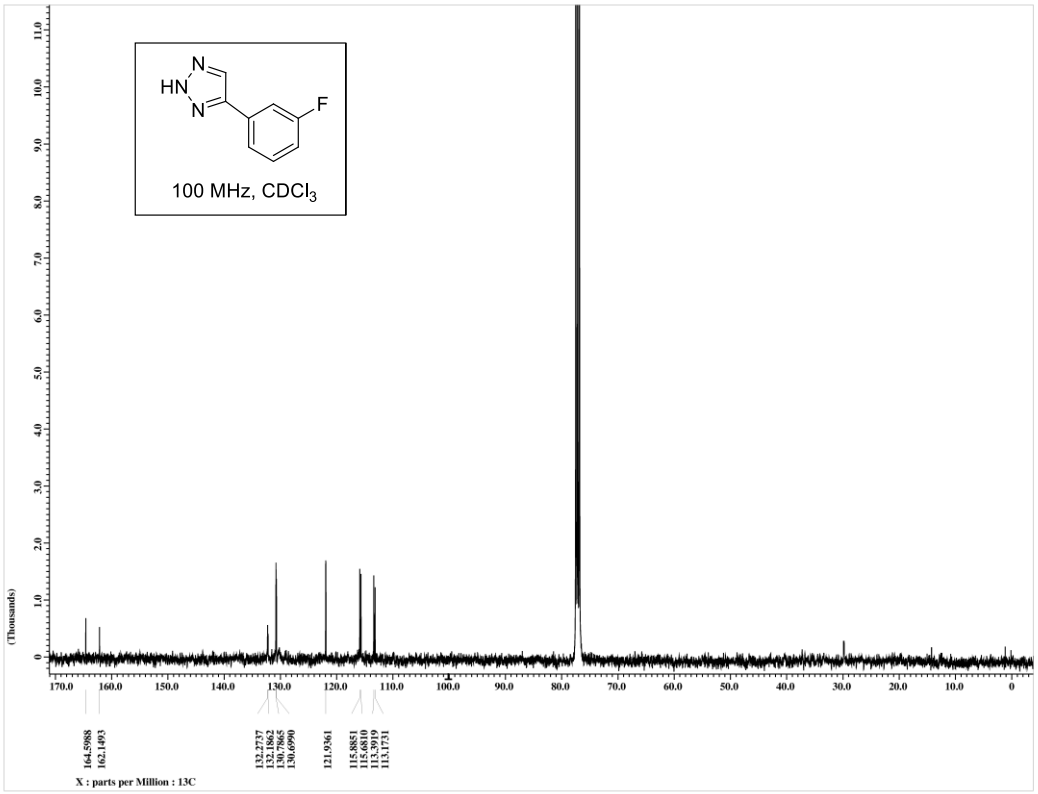
^{1}H and ^{13}C NMR of 5j:



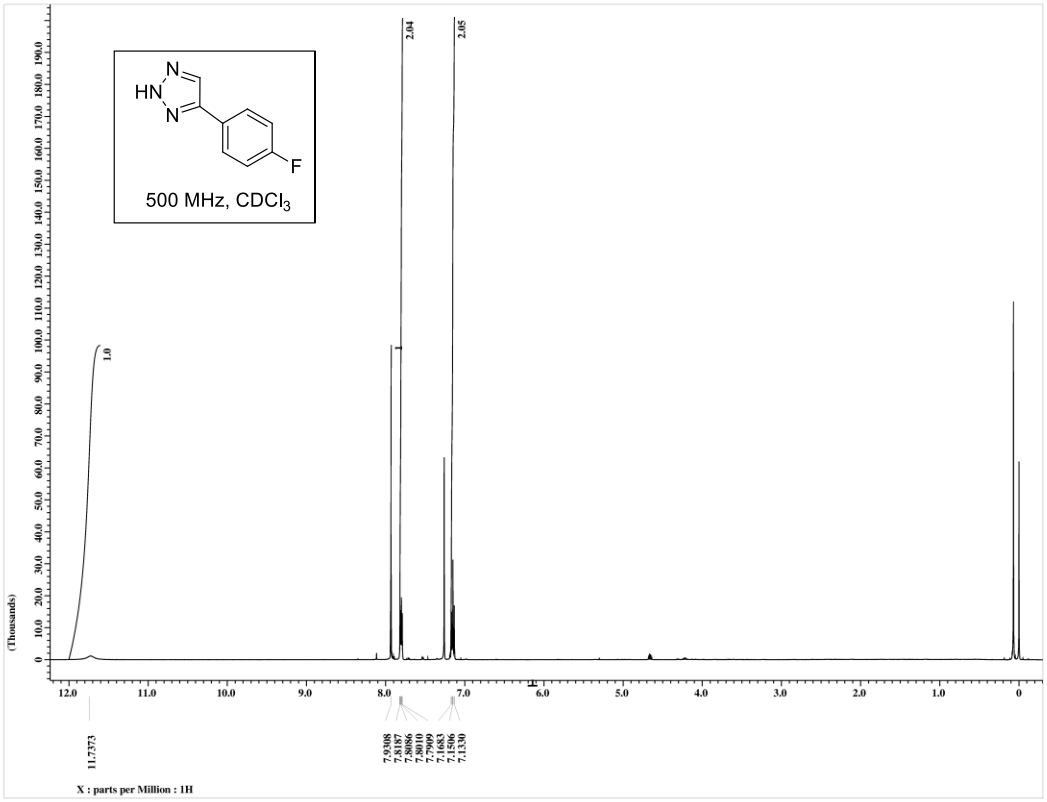


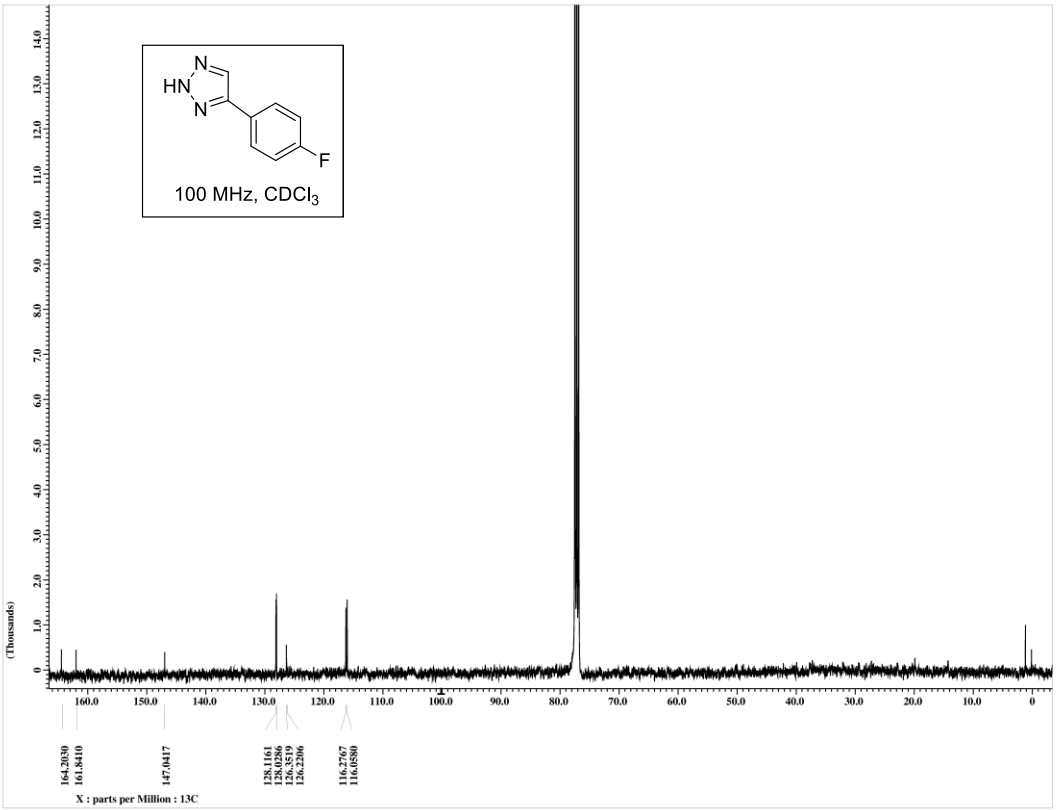
^{1}H and ^{13}C NMR of 5k:



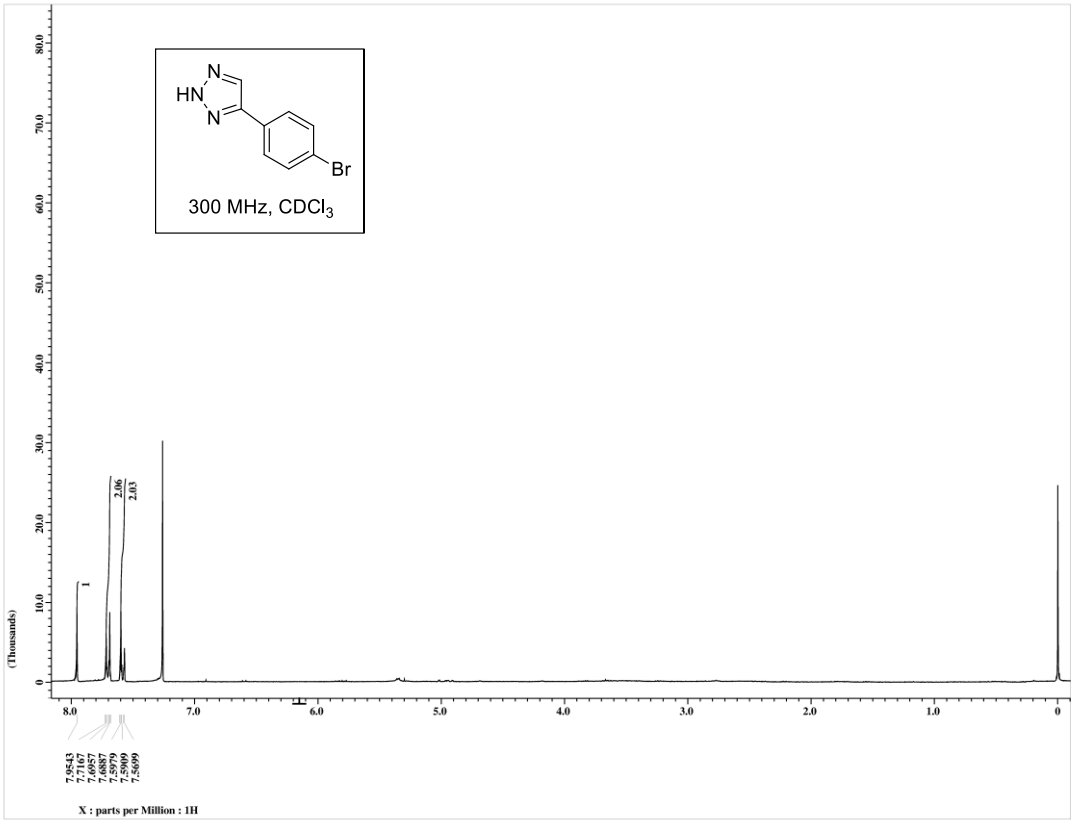


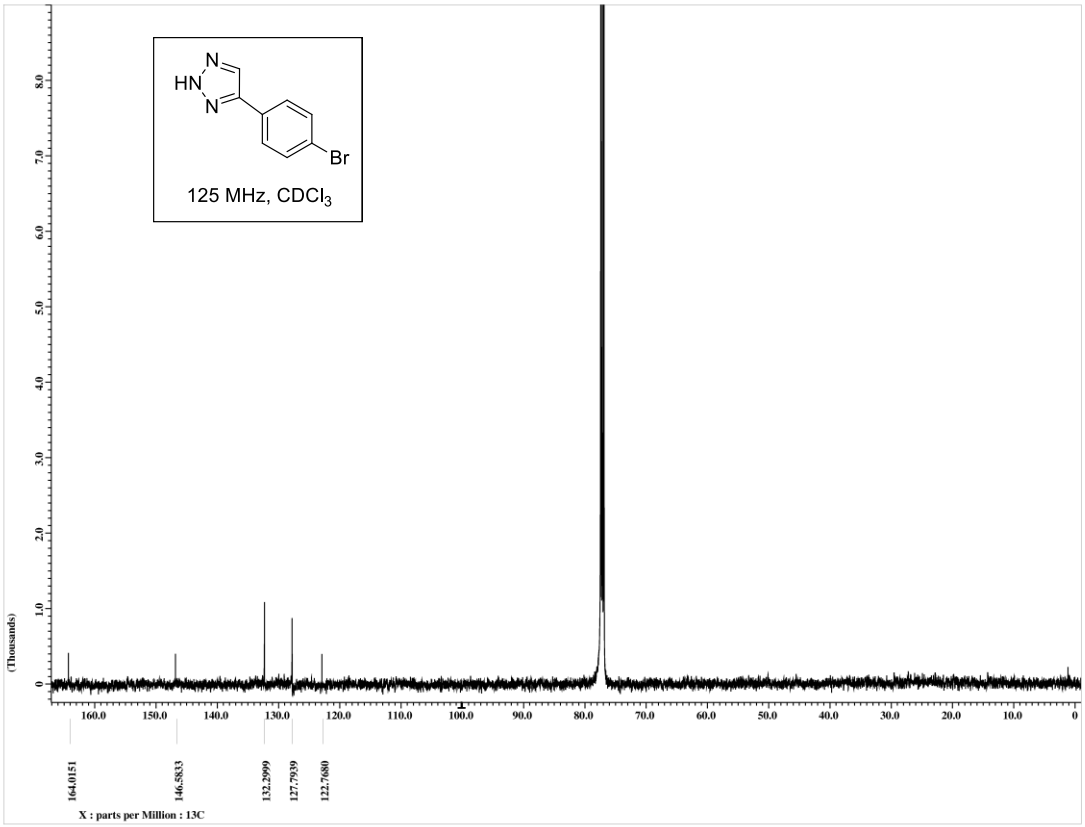
^{1}H and ^{13}C NMR of 5l:



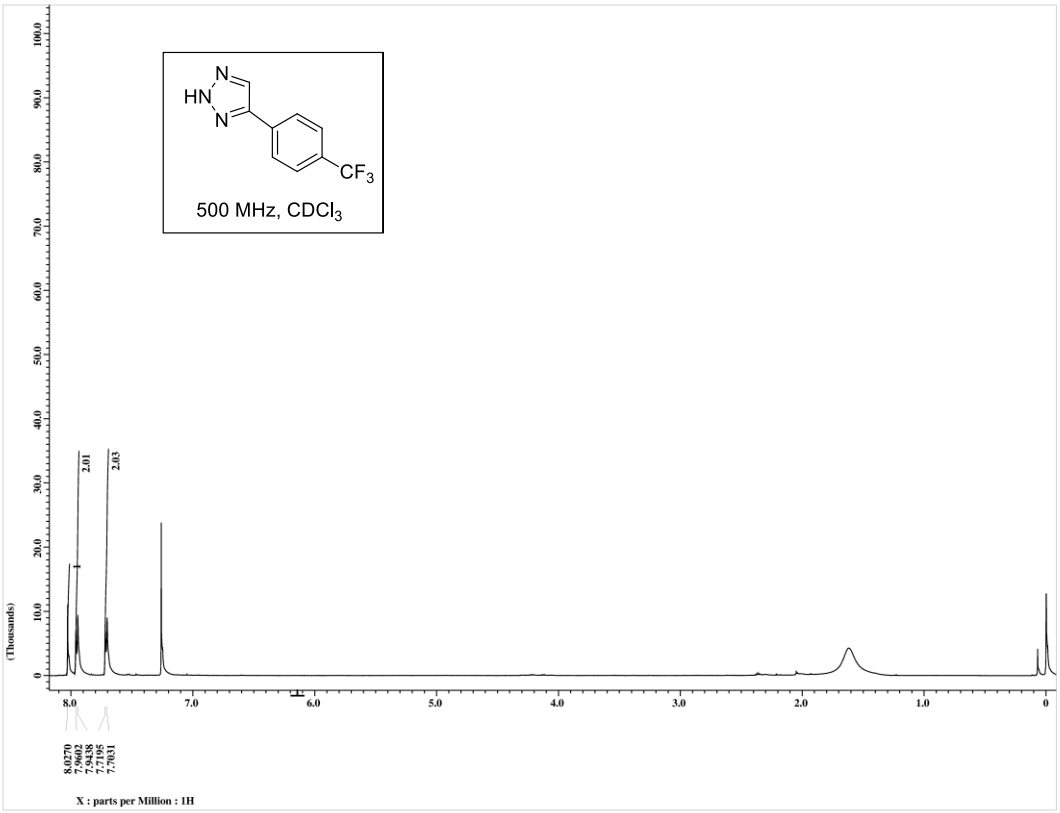


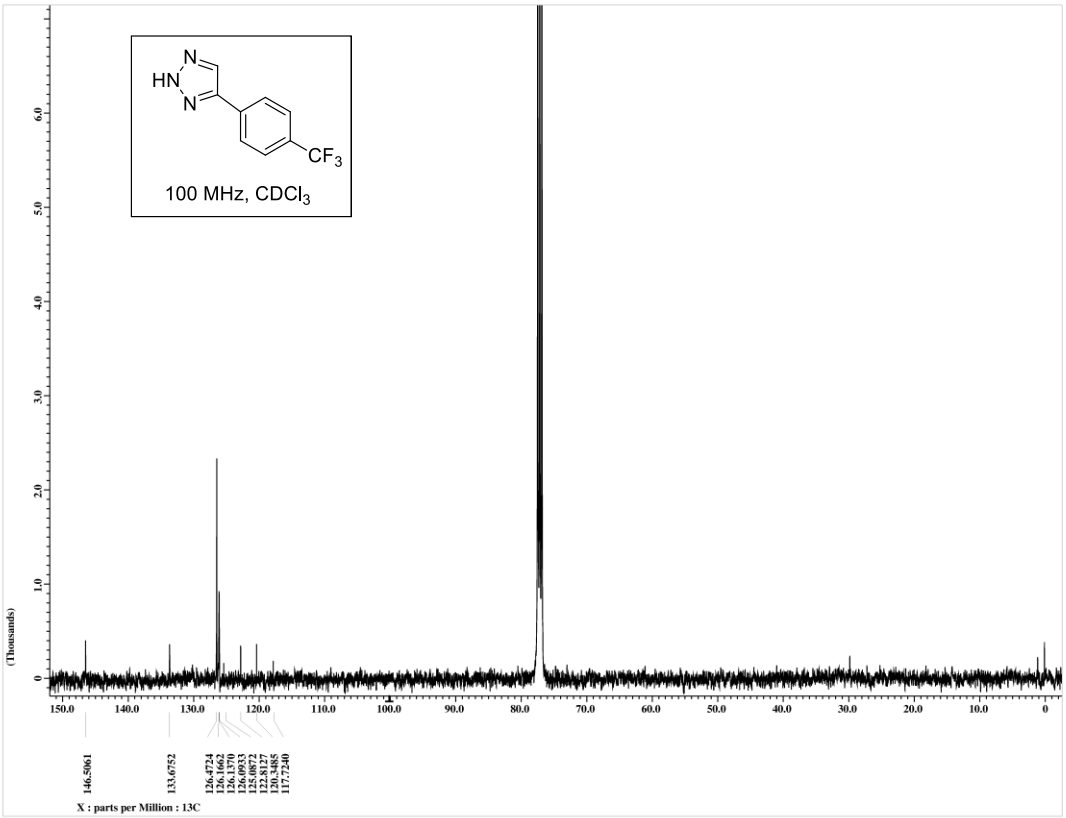
^{1}H and ^{13}C NMR of 5m:



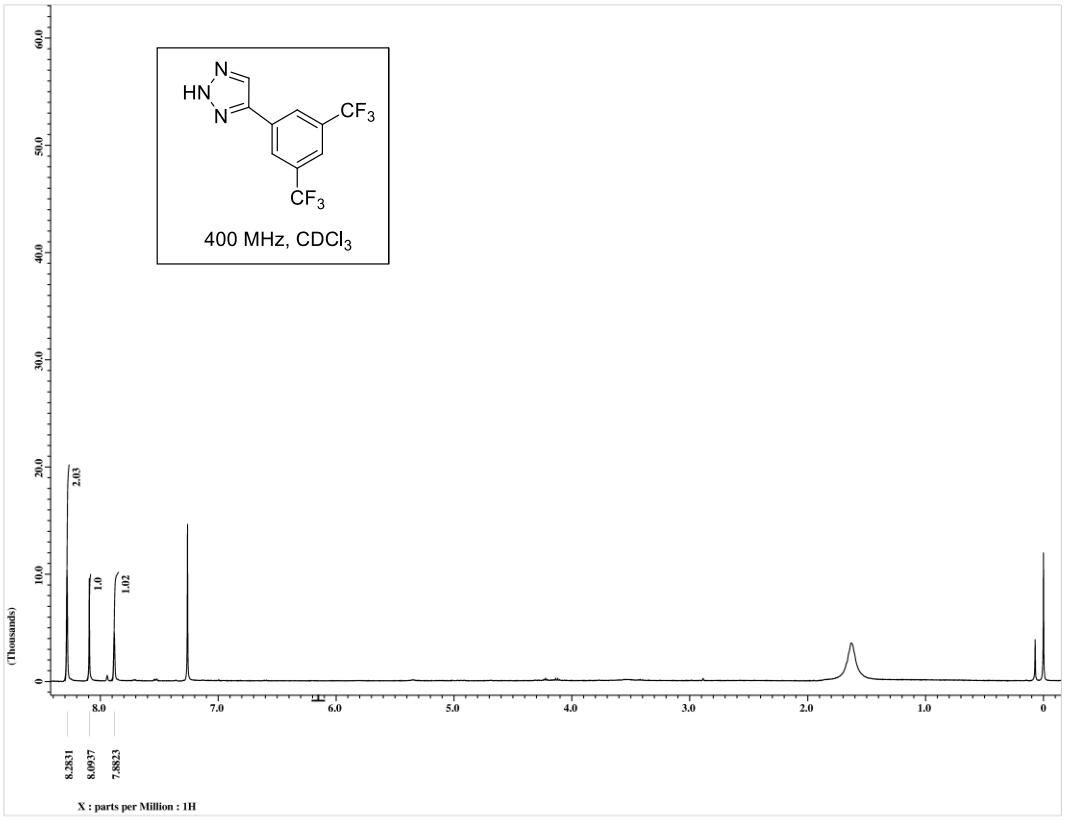


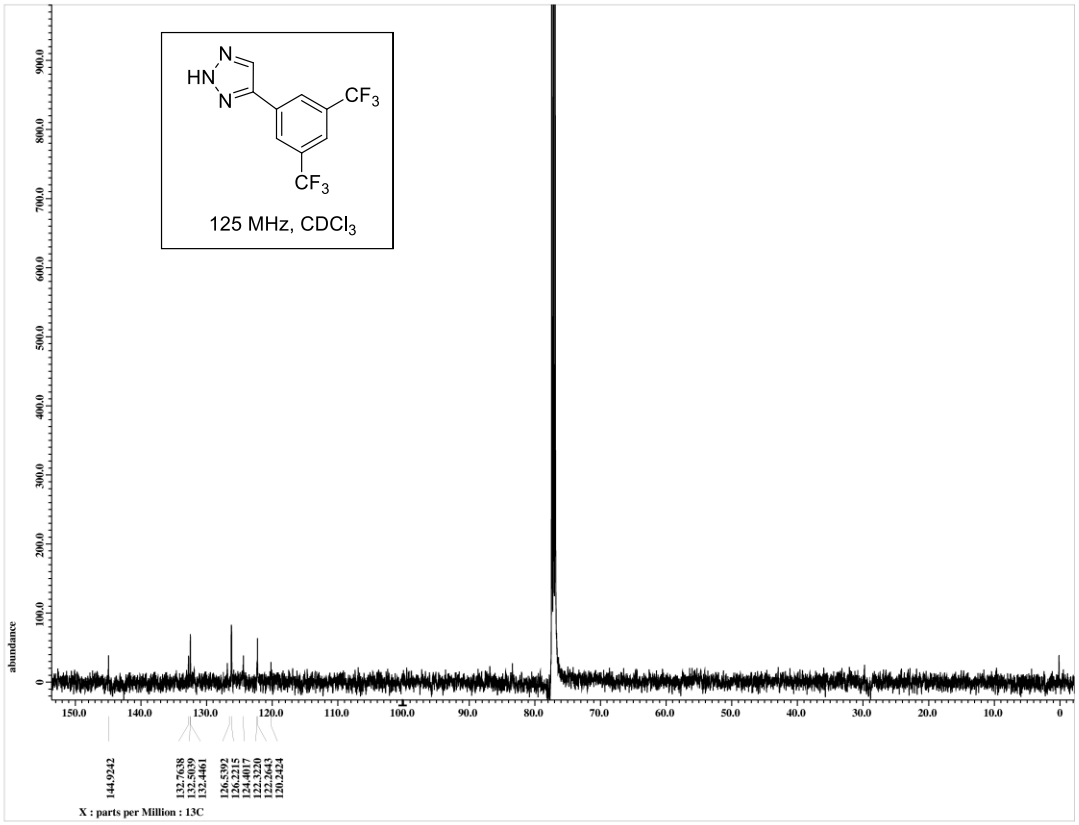
^{1}H and ^{13}C NMR of 5n:





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





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