

Prolinamide plays a key role in promoting copper-catalyzed cycloaddition of azides and alkynes in aqueous media via unprecedented metallacycle intermediates

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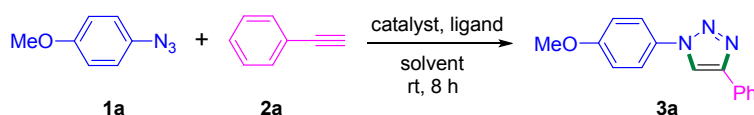
1.0 General information

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 CDCl₃ and DMSO-d₆. **¹H 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 (CDCl₃: 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). **¹³C 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 (CDCl₃: 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, various reaction conditions were investigated, including the choice of solvent, ligand and copper catalyst. Different solvents were screened (entries 3-9, Table S1), and the results suggested that water is the best choice for the reaction (entry 1). When the cycloaddition was performed in the presence of *tert*-butanol, DMSO, EtOH and DMF, the triazole product **3a** was obtained in low yields (entries 3-6). It was observed that the reaction did not proceed well in solvents like benzene, MeCN and 1,4-dioxane (entries 7-9). Next, we evaluated the effect of different ligands such as DMEDA, phenanthroline, *L*-proline and chiral prolinamide derivatives **Pro-1**, **Pro-2**, and **Pro-3** on the cycloaddition (entries 10-16). DMEDA, phenanthroline and *L*-proline resulted in poor conversion of the starting materials (entries 10-12), while among the prolinamide derivatives, **Pro-1** was found to be the optimal ligand for the cycloaddition (entry 1). Finally, screening the reaction with copper catalysts revealed that CuI promotes the reaction more efficiently as compared to other copper salts (CuBr, Cu(OAc)₂, CuO) as well as Cu(0) (Table S1, entries 17-20).

Table S1. Optimization of reaction conditions^a

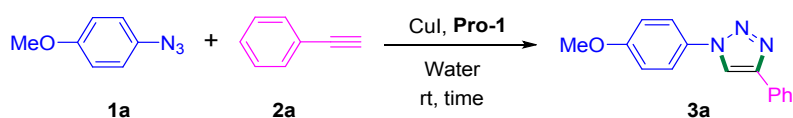


entry	ligand	catalyst	solvent	time	yield (%) ^b
1	Pro-1	CuI	H₂O	8 h	95
2	-	CuI	H ₂ O	48 h	20
3	Pro-1	CuI	<i>tert</i> -butanol	8 h	60
4	Pro-1	CuI	DMSO	8 h	50
5	Pro-1	CuI	EtOH	8 h	57
6	Pro-1	CuI	DMF	8 h	55
7	Pro-1	CuI	Benzene	8 h	25
8	Pro-1	CuI	MeCN	8 h	15
9	Pro-1	CuI	1,4-Dioxane	8 h	18
10	DMEDA	CuI	H ₂ O	8 h	40
11	Phenanthroline	CuI	H ₂ O	8 h	51
12	<i>L</i> -Proline	CuI	H ₂ O	8 h	65
13	<i>D,L</i> -Proline	CuI	H ₂ O	8 h	60

14	<i>D,L</i> -Pro-1	CuI	H ₂ O	8 h	95
15	Pro-2	CuI	H ₂ O	8 h	68
16	Pro-3	CuI	H ₂ O	8 h	40
17	Pro-1	Cu(OAc) ₂	H ₂ O	8 h	21
18	Pro-1	CuO	H ₂ O	8 h	-
19	Pro-1	CuBr	H ₂ O	8 h	57
20	Pro-1	Cu(0)	H ₂ O	8 h	-

^aReaction conditions: **1a** (1.0 mmol), **2a** (1.5 mmol) in 2 mL solvent; ^byield refers to the isolated yield without chromatographic purification.

Table S2. Effect of concentration of ligand, Cu(I) and time on the cycloaddition of *p*-azidoanisole (1a**) with phenylacetylene (**2a**).^a**

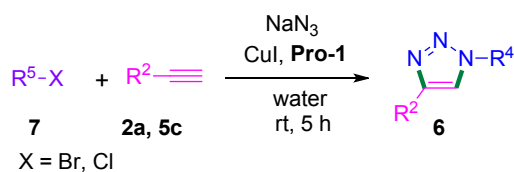


entry	Pro-1 (mol%)	CuI (mol%)	time (h)	conversion (%) ^b
1	2	5	8	50
2	5	5	8	65
3	8	5	8	80
4	10	5	8	98
5	10	2	8	75
6	10	5	2	55
7	10	5	4	70
8	10	5	6	90

^aReaction conditions: **1a** (1.0 mmol), **2a** (1.5 mmol) in 2 mL water; ^bThe conversion of **1a** was determined from ¹H NMR analysis of crude reaction mixture.

The highest conversion 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 8 h (entry 4, Table S2).

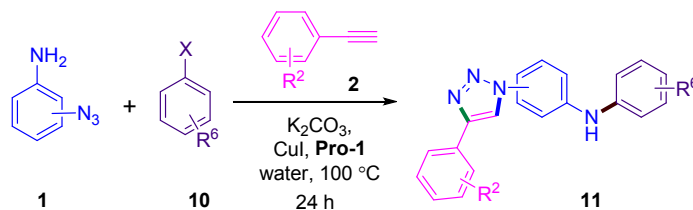
Table S3. Optimization of reaction conditions for one-pot sequential synthesis of triazoles from alkyl halides^a



entry	alkyl halide (equiv)	NaN ₃ (equiv)	time (h)	conversion (%) ^b
1	1	1.2	5	90
2	2	1.2	5	85
3	1	1.0	5	80
4	1	1.1	5	85

^aReaction conditions: **2a, 5c** (1.50 mmol), CuI (0.05 mmol), **Pro-1** (0.1 mmol), in 2 mL water; ^bThe conversion of **7** was determined from ¹H NMR analysis of crude reaction mixture.

Table S4. Optimization of reaction for a relay Ullmann-CuAAC sequence^a



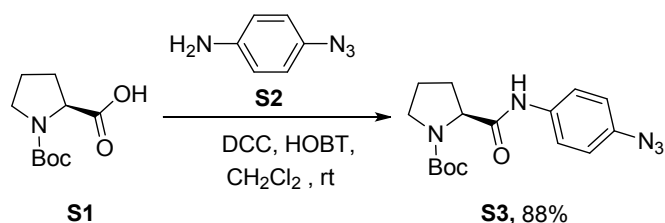
entry	aryl halide (equiv)	Pro-1 (mol%)	CuI (mol%)	K ₂ CO ₃ (equiv)	time (h)	temp (°C)	conversion ^b (%)
1	1.5	30	15	0.5	24	100	55
2	1.5	30	15	1.0	24	100	65
3	1.5	30	15	1.5	24	100	75
5	1.5	10	15	2.0	24	100	30
6	1.5	20	15	2.0	24	100	40
7	1.5	25	15	2.0	24	100	70
8	1.5	30	10	2.0	24	100	55
9	1.5	30	12	2.0	24	100	75
10	1.5	30	15	2.0	12	100	30
11	1.5	30	15	2.0	18	100	65

12	1.5	30	15	2.0	24	100	90
12	1.5	30	15	3.0	24	100	85
13	1.5	30	15	2.0	48	100	85
14	1	30	15	2.0	24	100	60
15	1.2	30	15	2.0	24	100	70
16	1.5	30	15	2.0	24	80	40
17	1.5	30	15	2.0	24	120	90

^aReaction conditions: **1** (1.0 mmol), **2** (1.50 mmol) in 2 mL water; ^bThe conversion of **1** was determined from ¹H NMR analysis after chromatographic purification.

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 CH₂Cl₂ (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 CH₂Cl₂ (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). ¹H NMR (400 MHz, CDCl₃): 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); ¹³C NMR (100 MHz, CDCl₃): 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 C₁₆H₂₁N₅O₃K (M+K)⁺: 370.1281; found: 370.1268.

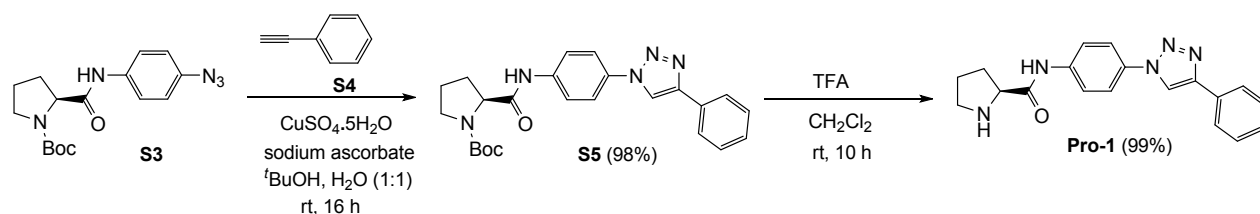


Scheme S1. Preparation of azido prolinamide **S3**.

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).

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

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

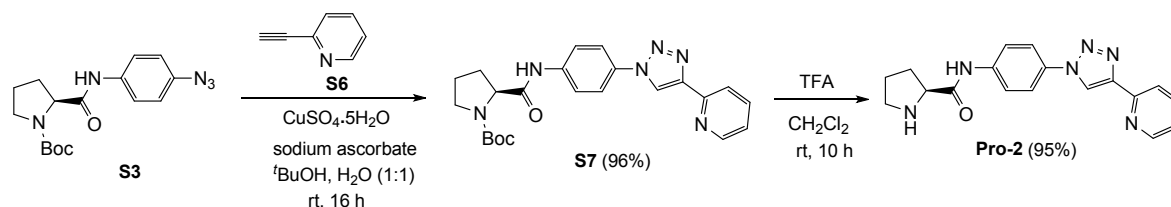


Scheme S2. Synthesis of ligand **Pro-1**.

Preparation of triazole derivative S5: Phenyl acetylene (**S4**) (1.08 mL, 9.8 mmol), sodium ascorbate (194 mg, 0.98 mmol, 0.1 equiv), CuSO₄·5H₂O (122.4 mg, 0.49 mmol, 0.05 equiv) were dissolved in 10 mL *t*BuOH-H₂O (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). ¹H 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); ¹³C 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 C₂₄H₂₇N₅O₃K (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 CH₂Cl₂ 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 NH₃ (30%) at 0 °C. Then the reaction mixture was extracted with CH₂Cl₂ (3 x 20 mL), evaporated and dried under vacuum to give **Pro-1** (760 mg, 99%) as a white solid (Scheme S2). ¹H 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); ¹³C 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 C₁₉H₂₀N₅O (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 upon the removal of Boc group afforded **Pro-2** (Scheme S3).



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

Preparation of triazole derivative S7: 2-Ethynylpyridine **S6** (1.08 mL, 9.8 mmol), sodium ascorbate (194 mg, 0.98 mmol, 0.1 equiv), CuSO₄·5H₂O (122.4 mg, 0.49 mmol, 0.05 equiv) were dissolved in 10 mL *t*BuOH-H₂O (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). ¹H 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); ¹³C 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 C₂₃H₂₇N₆O₃ (M+H)⁺: 435.2145; found, 435.2144.

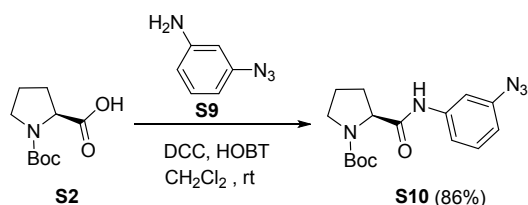
Preparation of ligand Pro-2: To an ice cold solution of compound **S7** (1.0 g, 2.3 mmol) in 30 mL dry CH₂Cl₂, added TFA (0.53 mL, 6.9 mmol, 3.0 equiv) and the mixture was stirred for 10 h at room temperature. After consumption of the starting material **S7** (monitored by TLC), the reaction mixture was brought to pH 8-9 by dropwise addition of 30 wt% solution of NH₃ in water at 0 °C. Then the reaction mixture was extracted with CH₂Cl₂ (3 x 20 mL), evaporated and dried under vacuum, to give **Pro-2** (730 mg, 95%) as a white solid (Scheme S3). ¹H 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); ¹³C 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 C₁₈H₁₉N₆O (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-H₂O (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

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

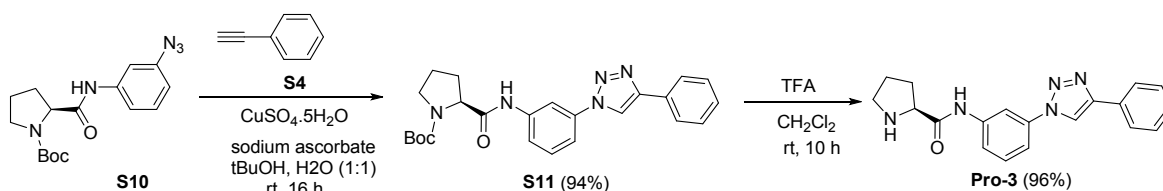
μL , 0.87 mmol, 0.15 equiv) were added and stirred for 10 min. Sodium azide (755 mg, 11.62 mmol, 2.0 equiv) was added to the reaction mixture and the mixture was allowed to stir for 3 h at reflux under argon atmosphere. After complete consumption of **S8** (TLC analysis), the reaction was cooled, concentrated 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. ^1H NMR (400 MHz, CDCl_3): 7.10 (t, 1H, $J = 7.9$ Hz), 6.43 (dd, 2H, $J = 6.7$ Hz, 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 $\text{C}_6\text{H}_7\text{N}_4(\text{M}+\text{H})^+$: 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). ^1H 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 $\text{C}_{16}\text{H}_{21}\text{N}_5\text{O}_3\text{K}(\text{M}+\text{K})^+$: 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 triazole derivative S11: Phenyl acetylene (**S4**) (1.08 mL, 9.8 mmol), sodium ascorbate (194 mg, 0.98 mmol, 0.1 equiv), CuSO₄·5H₂O (122.4 mg, 0.49 mmol, 0.05 equiv) were dissolved in 10 mL *t*BuOH-H₂O (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 CH₂Cl₂, 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 NH₃ (30%) at 0 °C. Then the reaction mixture was extracted with CH₂Cl₂ (3 x 20 mL), dried in vacuum, purified by flash chromatography using hexane-ethylacetate (50:50 to 30:70) to give **Pro-3** (746 mg, 96%) as a white solid. ¹H NMR (400 MHz, DMSO-d₆): 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); ¹³C NMR (100 MHz, DMSO-d₆): 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 C₁₉H₂₀N₅O (M+H)⁺: 334.1667; found, 334.1693.

4.0 General procedure for cycloaddition of aromatic azides and aromatic alkynes (GP-1)

In a small reaction vial, **Pro-1** (0.1 mmol, 0.1 equiv), aromatic azide (1 equiv), aromatic alkyne (1.5 equiv) and water (0.2 M) were taken. Then, copper iodide (0.05 equiv) was added and the resulting heterogeneous reaction mixture was stirred at rt. The completion of reaction was monitored by TLC analysis. The reaction mixture was extracted with ethyl acetate (3 x 2 mL), dried over Na₂SO₄, filtered and concentrated under vacuum. In all examples, the crude products were found to be pure by ¹H and ¹³C NMR.

5.0 General procedure for cycloaddition of aliphatic/heteroaromatic azides and nucleobase derived azides with alkynes (GP-2)

In a small reaction vial, **Pro-1** (0.1 equiv), azide (1 equiv), alkyne (1.5 equiv) and water (2.0 mL, 0.2 M) were taken. Then, copper iodide (0.05 equiv) was added and the resulting heterogeneous reaction mixture was stirred at rt. The completion of reaction was monitored by TLC analysis. The reaction mixture was extracted with ethyl acetate (3 x 2 mL), dried over Na₂SO₄, filtered and concentrated under vacuum. In all examples, the crude products were found to be pure by ¹H and ¹³C NMR.

6.0 General procedure for the synthesis of triazoles from alkyl halides (GP-3)

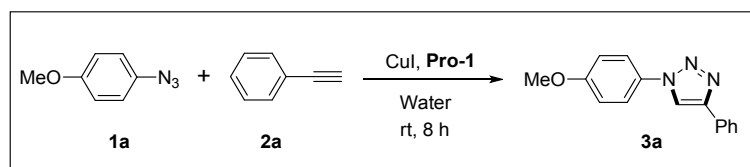
In a small reaction vial, sodium azide (1.2 equiv), alkyl bromide (1.0 equiv), **Pro-1** (0.1 equiv), alkyne (1.5 equiv) and water (2.0 mL, 0.2 M) were taken. Then, copper iodide (0.05 equiv) was added and the resulting heterogeneous reaction mixture was stirred at rt. The completion of reaction was monitored by TLC analysis. The reaction mixture was extracted with ethyl acetate (3 x 2 mL), dried over Na₂SO₄, filtered and concentrated under vacuum. In all examples, the crude products were found to be pure by ¹H and ¹³C NMR.

7.0 General procedure for a relay Ullmann-CuAAC sequence (GP-4)

In a small reaction vial, catalyst **Pro-1** (0.3 equiv), azide (1 equiv), alkyne (1.5 equiv) and water (2.0 mL, 0.2 M) were taken. Then, copper iodide (0.15 equiv), aromatic iodide (1.5 equiv) were added and the reaction mixture was heated in a pre-heated oil bath with stirring at 100 °C for 24 h. The completion of reaction was monitored by TLC analysis. The reaction mixture was extracted with ethyl acetate (3 x 2 mL), dried over Na₂SO₄, 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.

8.0 Gram scale experiment

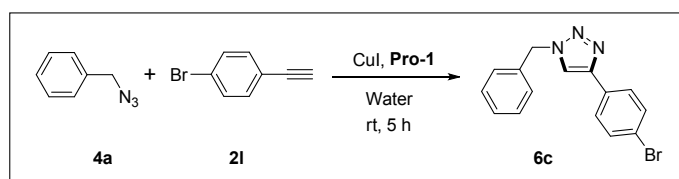
Preparation of 1-(4-methoxyphenyl)-4-phenyl-1H-1,2,3-triazole (3a**):**



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

To a suspension of 1-azido-4-methoxybenzene **1a** (1.00 g, 6.70 mmol, 1 equiv), phenylacetylene **2a** (1.54 g, 10.05 mmol, 1.5 equiv) in water (0.2 M), were added copper iodide (64.30 mg, 0.34 mmol, 0.05 equiv) and **Pro-1** (223 mg, 0.67 mmol, 0.1 equiv). The reaction mixture was stirred at rt (Scheme S6). After the completion of reaction, the reaction mixture was extracted with ethyl acetate (3 x 2 mL), dried over Na₂SO₄, filtered and concentrated under vacuum. The crude compound **3a** (1.48 g, 88%) was obtained in pure form and analyzed by ¹H and ¹³C NMR.

Preparation of 1-benzyl-4-(3-fluorophenyl)-1H-1,2,3-triazole (6c**):**

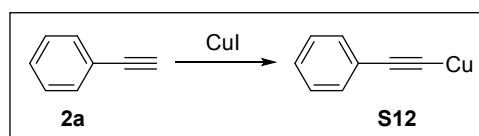


Scheme S7. Gram scale synthesis of **6c.**

To a stirring suspension of benzyl azide **4a** (1.00 g, 7.51 mmol, 1 equiv), 1-ethynyl-4-bromobenzene **2l** (2.06 g, 11.36 mmol, 1.5 equiv) in water, copper iodide (71.3 mg, 0.37 mmol, 0.05 equiv) and **Pro-1** (250 mg, 0.75 mmol, 0.1 equiv) were added and the reaction mixture was stirred at rt (Scheme S7). After the completion of reaction, as monitored by TLC analysis, the reaction mixture was extracted with ethyl acetate (3 x 2 mL), dried over Na₂SO₄, filtered and concentrated under vacuum. The crude compound **6c** (2.12 g, 90%) was obtained in pure form and analysed by ¹H and ¹³C NMR.

9.0 Control experiment using Cu acetylide:

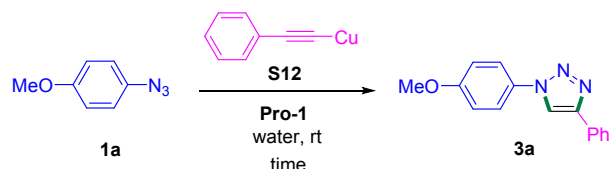
Preparation of copper acetylide **S12**:



Scheme S8. Synthesis of copper acetylide.

Phenylacetylene **2a** was added dropwise to a solution of copper iodide (2.0 mmol) in the mixture of ammonium hydroxide (28% NH₃ solution, 20 mL) and ethanol (12 mL). The reaction mixture was stirred overnight at room temperature under argon atmosphere. The yellow precipitate was filtered and washed with ammonium hydroxide (10% NH₃ solution, 3x10 mL), water (3x10 mL), ethanol (3x10 mL) and diethyl ether (3x10 mL). The yellow solid was dried overnight to provide the desired copper acetylide **S1** which was used without further purification.⁴

Table S5. Control experiment with Cu acetylide.



entry	time (h)	yield of 3a (%) ^a
1	8	50
2	10	65
3	12	70

^ayield refers to the isolated yield

⁴ K. Jouvin, J. Heimburger, G. Evano, *Chem. Sci.*, 2012, **3**, 756-760.

It was observed when the cycloaddition was performed using Cu acetylide **S12** and **Pro-1** for 8h, the yield of **3a** was lower (50%, table S5) compared to the yield of **3a** when the reaction was carried out in the presence of CuI, phenyl acetylene **2a** and **Pro-1**. Even after longer reaction time i.e. 12 h, the yield obtained was 70%. These observations suggest that the binuclear pathway is kinetically more favoured than the mononuclear pathway for our developed CuAAC process.

10.0 General information on computational methods

All the DFT calculations were performed using the Gaussian G16 suit of program.⁵ Geometry optimization and structural properties calculations were carried out using the M06-L functional⁶ (reported to be appropriate for Cu complexes)^{7,8} combined with the relativistic effective core potential (ECP),⁹ LANL2DZ basis set for the Cu atoms,¹⁰ whereas the Pople's split basis, 6-31+G*, was used for the anchoring C, N, O and H atoms.¹¹ Single Point energy calculations with larger and better basis set: SDD and Def2-TZVP for the Cu atoms and 6-31+G** for the anchoring C, N, O, H atoms were also performed (Figure S3). To mimic experimental condition, the conductor-like polarizable continuum model (CPCM) was applied in the calculations with water, DMSO and benzene as solvent for the accurate determination of the activation energy barriers for the transition states (TS). All reported TS structures were confirmed to have only one imaginary frequency which belongs to the reaction coordinate. Intrinsic Reaction Coordinate¹²⁻¹³ (IRC) calculations were performed to determine adjacent intermediates of the TS. Every reported energy in this study are free energies at 298 K.

11.0 Free energy profile for mononuclear and binuclear CuAAC reaction pathway

⁵ M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A., Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian 16, revision C.01; Gaussian, Inc.: Wallingford CT, 2016.

⁶ Y. Zhao and D. G. Truhlar, *J. Chem. Phys.*, 2006, **125**, 194101-194118.

⁷ A. C. Tsipis, *RSC Adv.*, 2014, **4**, 32504-32529.

⁸ Y. Özkılıc and N. Ş. Tüzün, *Organometallics*, 2016, **35**, 2589-2599.

⁹ Y. Zhao and D. G., Truhlar *Theor. Chem. Acc.*, 2008, **120**, 215-241.

¹⁰ C. E. Check, T. O. Faust, J. M. Bailey, B. J. Wright, T. M. Gilbert and L. S. Sunderlin, *J. Phys. Chem. A* 2001, **105**, 8111-8116.

¹¹ A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard III, and W. M. Skiff *J. Am. Chem. Soc.*, 1992, **114**, 10024-10035.

¹² C. Gonzalez, H. B. Schlegel, *J. Chem. Phys.*, 1989, **90**, 2154-216

¹³ C. Gonzalez, H. B. Schlegel, *J. Phys. Chem.*, 1990, **94**, 5523-5527.

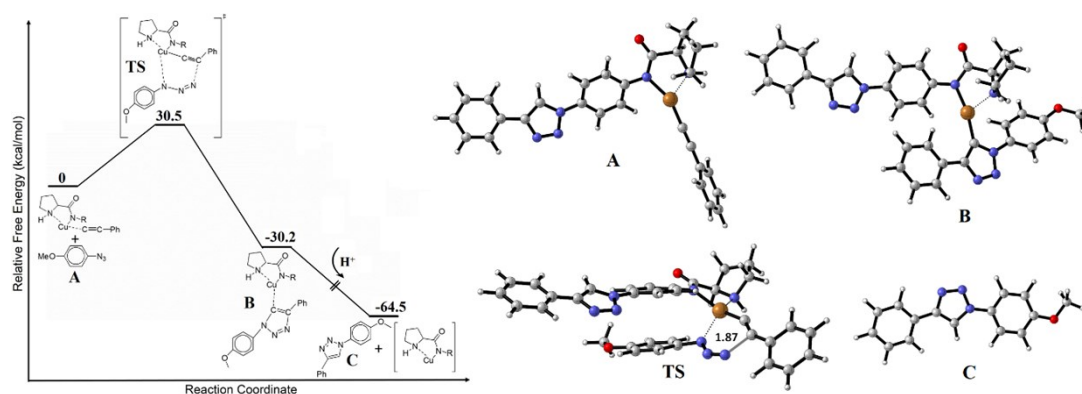


Figure S1: Free energy profile for mononuclear CuAAC reaction pathway and optimized structures of reaction intermediates and transition state.

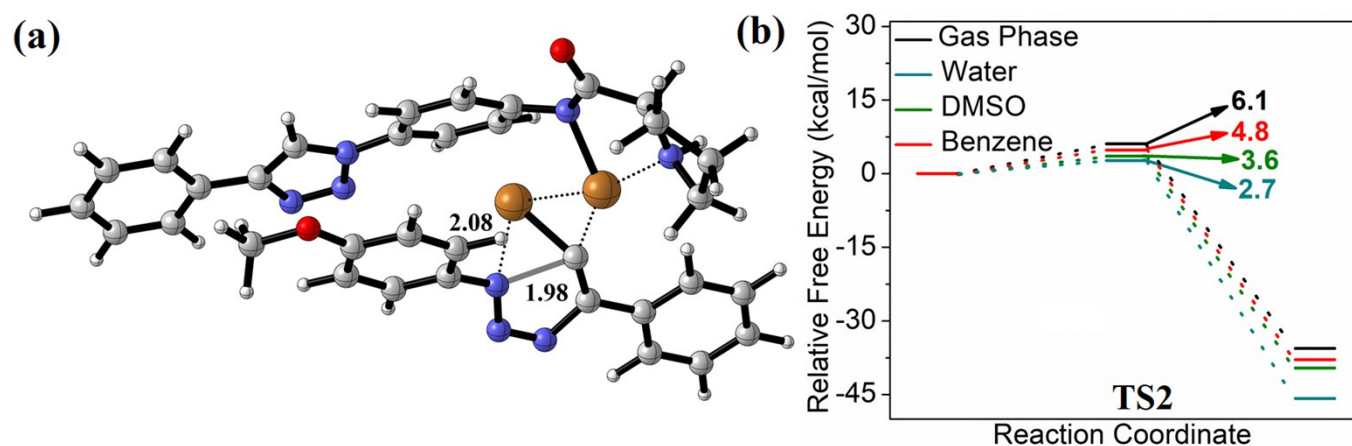


Figure S2: (a) Optimized transition state (TS2) structure of the ring contraction step, (b) Solvent dependent variation of activation energies for TS2.

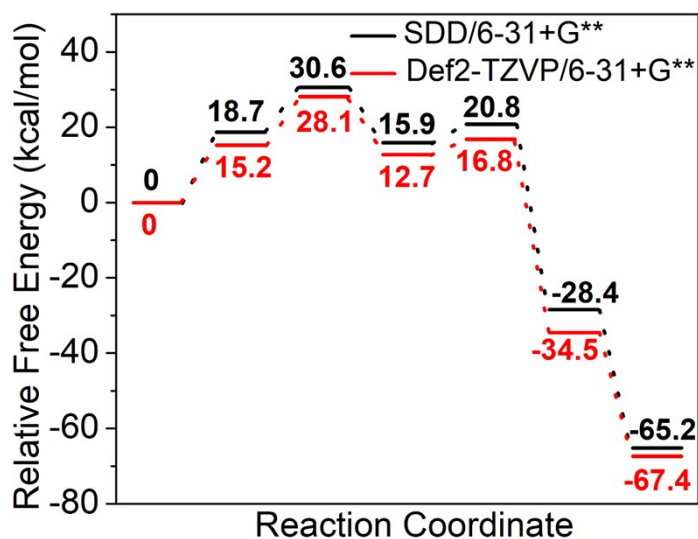


Figure S3. Free energy profile (considering single point energy with better basis sets) for binuclear CuAAC reaction pathway.

12.0 Cartesian coordinates of metallacycle intermediates and transition states

Intermediate-A:

58

Int-A

Cu	2.62896960	0.20364105	-0.49903349
N	1.61542500	1.84745800	-0.76939100
C	2.17364700	2.95100000	-0.20356100
O	1.60087300	3.94098500	0.25427800
C	3.71494300	2.91976600	-0.26876500
C	4.37677800	3.81881900	0.79050400
C	5.21938400	2.87376400	1.65604900
H	3.58509700	4.31346400	1.36339500
H	4.98262800	4.60990200	0.33756700
C	4.59160000	1.51314200	1.39738200
H	6.26782400	2.86486200	1.32582600
H	5.21859600	3.14764700	2.71645200
H	5.22738000	0.64697000	1.60991800
H	3.66021100	1.39387100	1.96823300
N	4.22903300	1.53401400	-0.04078500
C	0.24567300	1.66173800	-0.74183000
C	-0.30030000	0.83337800	-1.77090400
C	-0.63308800	2.07826900	0.27602100
C	-1.59342100	0.28904600	-1.67160100
H	0.29636400	0.68091100	-2.67171500
C	-1.92724900	1.57112000	0.35441900
H	-0.26959100	2.75930100	1.03720900
C	-2.40632300	0.65923200	-0.58397000
H	-2.01650000	-0.30847400	-2.47557700
H	-2.55630700	1.85473700	1.19680800
N	-3.69450100	0.09927800	-0.47074500
C	-4.78888600	0.57191300	0.17563800
C	-5.76228700	-0.38824200	-0.02698700
H	-4.79152500	1.53091200	0.67357600
N	-3.97049300	-1.10768300	-1.04977800
N	-5.21102700	-1.38879900	-0.77985600
C	-7.14796700	-0.43204500	0.42277100
C	-7.96171500	-1.52023000	0.07864900
C	-7.69376700	0.59863800	1.19967600
C	-9.28367500	-1.57213400	0.50233500
H	-7.53618600	-2.31939100	-0.52418900
C	-9.01663200	0.54400100	1.62101800
H	-7.07605500	1.45230300	1.47823800
C	-9.81777000	-0.54206300	1.27430200
H	-9.90306700	-2.42416700	0.22740800
H	-9.42431800	1.35359700	2.22383900
H	-10.85389700	-0.58490300	1.60491300
H	3.98540500	3.20882300	-1.29206900
H	5.09316800	1.42834900	-0.57122200
C	5.62983160	-4.38711790	1.34901252
C	4.45185160	-3.75979990	0.96559852

C	4.48676160	-2.51392490	0.31312952
C	5.73735860	-1.92735890	0.05856052
C	6.91304460	-2.56041190	0.44172652
C	6.86425960	-3.79219490	1.09128352
H	5.58458960	-5.35055590	1.85374652
H	3.48685860	-4.22071790	1.16501452
H	5.76830560	-0.96957490	-0.46156148
H	7.87307760	-2.09275190	0.22977852
H	7.78452560	-4.28814990	1.39346852
C	3.26566860	-1.87152990	-0.07394148
C	2.03737860	-1.71681890	-0.33523748
Cu	0.37848960	-1.00087090	-0.85211248

Intermediate-B:

76

Int-B

Cu	-3.15596375	-1.06237982	-0.74764862
N	-1.87487600	-2.36304300	0.01883000
C	-2.37026500	-2.98998200	1.11688800
O	-1.76043500	-3.58655500	2.00629500
C	-3.90109000	-2.92236600	1.24998600
C	-4.32202700	-2.08084200	2.47989900
C	-5.12162900	-0.91110900	1.90702300
H	-3.45162400	-1.77069400	3.06558200
H	-4.95329200	-2.68135800	3.14510700
C	-5.75541400	-1.52311500	0.67435400
H	-5.85579800	-0.49913900	2.60668100
H	-4.45562600	-0.08860700	1.60149400
H	-6.58158400	-2.19682800	0.95762500
H	-6.13223600	-0.79156900	-0.05056300
N	-4.61837800	-2.27760600	0.10193500
C	-0.52682200	-2.14523800	-0.16625900
C	-0.12937500	-1.73594900	-1.47810700
C	0.47595600	-2.17742200	0.83025200
C	1.18758900	-1.36069900	-1.76428600
H	-0.83656200	-1.89353200	-2.29525300
C	1.77356800	-1.78860700	0.53923400
H	0.20823300	-2.49417300	1.83156300
C	2.13867300	-1.37971600	-0.74734800
H	1.48184000	-1.08140600	-2.77291900
H	2.51002400	-1.75441700	1.34155600
N	3.45194300	-0.93906700	-1.02118400
C	4.60339700	-1.20838000	-0.36236000
C	5.56568900	-0.44662600	-1.00209500
H	4.64453600	-1.91604800	0.45371900
N	3.67767200	-0.04203200	-2.02390800
N	4.94906100	0.24522800	-2.00715000
C	6.98809200	-0.29617300	-0.72059900
C	7.77284000	0.55379100	-1.51214300

C	7.59189200	-0.96662500	0.35242000
C	9.12410700	0.72291700	-1.23671900
H	7.30148100	1.07553900	-2.34219600
C	8.94358100	-0.79462100	0.62519900
H	6.99590500	-1.62751300	0.98229000
C	9.71596800	0.05097500	-0.16866500
H	9.72077800	1.38569300	-1.86104300
H	9.39609000	-1.32353000	1.46211700
H	10.77455900	0.18582500	0.04517900
H	-4.24675800	-3.95782300	1.37532800
H	-4.93362300	-2.98240700	-0.55986000
C	-6.99589300	2.71913800	0.39635100
C	-5.63917700	2.41286400	0.38952700
C	-5.04317300	1.86791500	-0.75690900
C	-5.84070600	1.65383500	-1.89723500
C	-7.19258800	1.96698000	-1.88373600
C	-7.77813300	2.49750200	-0.73417500
H	-7.44472300	3.13792800	1.29532700
H	-5.03203500	2.59027900	1.27201700
H	-5.37656000	1.23602400	-2.78899500
H	-7.79304100	1.79797800	-2.77585700
H	-8.83889200	2.74107500	-0.72292300
C	-3.66125500	1.43745900	-0.80648700
C	-2.81434000	0.76684900	-1.46521700
Cu	-1.02513100	0.25064900	-1.21238200
N	-0.64724018	1.52740859	0.17090520
N	-1.64089218	2.13992459	0.71022820
N	-2.56263667	2.70811471	1.21052207
C	0.61890782	1.68729959	0.79286020
C	1.75556382	1.59149559	-0.00533980
C	0.76500682	1.88353459	2.17240420
C	3.02918882	1.67582259	0.55286220
H	1.65230582	1.44712559	-1.08183880
C	2.02642982	1.98097159	2.73144620
H	-0.12168318	1.95674359	2.79919020
C	3.17015882	1.87298059	1.92843020
H	3.89531382	1.60149459	-0.10002780
H	2.15508982	2.13422659	3.80042920
O	4.36090382	1.97594859	2.57773120
C	5.52595682	1.75279959	1.81004620
H	5.63627782	2.49192959	1.00296120
H	6.36734382	1.84195259	2.50004820
H	5.52118782	0.74862759	1.36358820

Transition state-I (imaginary frequency = -370.40)

76

TS-I

Cu	-3.18977	-1.02806	-0.76787
N	-1.87488	-2.36304	0.01883
C	-2.37026	-2.98998	1.11689

O	-1.76043	-3.58656	2.00630
C	-3.90109	-2.92237	1.24999
C	-4.32203	-2.08084	2.47990
C	-5.12163	-0.91111	1.90702
H	-3.45162	-1.77069	3.06558
H	-4.95329	-2.68136	3.14511
C	-5.75541	-1.52311	0.67435
H	-5.85580	-0.49914	2.60668
H	-4.45563	-0.08861	1.60149
H	-6.58158	-2.19683	0.95762
H	-6.13224	-0.79157	-0.05056
N	-4.61838	-2.27761	0.10193
C	-0.52682	-2.14524	-0.16626
C	-0.12937	-1.73595	-1.47811
C	0.47596	-2.17742	0.83025
C	1.18759	-1.36070	-1.76429
H	-0.83656	-1.89353	-2.29525
C	1.77357	-1.78861	0.53923
H	0.20823	-2.49417	1.83156
C	2.13867	-1.37972	-0.74735
H	1.48184	-1.08141	-2.77292
H	2.51002	-1.75442	1.34156
N	3.45194	-0.93907	-1.02118
C	4.60340	-1.20838	-0.36236
C	5.56569	-0.44663	-1.00209
H	4.64454	-1.91605	0.45372
N	3.67767	-0.04203	-2.02391
N	4.94906	0.24523	-2.00715
C	6.98809	-0.29617	-0.72060
C	7.77284	0.55379	-1.51214
C	7.59189	-0.96662	0.35242
C	9.12411	0.72292	-1.23672
H	7.30148	1.07554	-2.34220
C	8.94358	-0.79462	0.62520
H	6.99590	-1.62751	0.98229
C	9.71597	0.05097	-0.16867
H	9.72078	1.38569	-1.86104
H	9.39609	-1.32353	1.46212
H	10.77456	0.18582	0.04518
H	-4.24676	-3.95782	1.37533
H	-4.93362	-2.98241	-0.55986
C	-6.99589	2.71914	0.39635
C	-5.63918	2.41286	0.38953
C	-5.04317	1.86791	-0.75691
C	-5.84071	1.65383	-1.89724
C	-7.19259	1.96698	-1.88374
C	-7.77813	2.49750	-0.73418
H	-7.44472	3.13793	1.29533
H	-5.03203	2.59028	1.27202
H	-5.37656	1.23602	-2.78899

H	-7.79304	1.79798	-2.77586
H	-8.83889	2.74107	-0.72292
C	-3.66126	1.43746	-0.80649
C	-2.81434	0.76685	-1.46522
Cu	-1.02513	0.25065	-1.21238
N	-0.62433	1.60481	0.25477
N	-1.61798	2.21733	0.79409
N	-2.79575	2.33984	0.65057
C	0.64182	1.76470	0.87672
C	1.77847	1.66890	0.07852
C	0.78792	1.96094	2.25627
C	3.05210	1.75323	0.63673
H	1.67522	1.52453	-0.99797
C	2.04934	2.05838	2.81531
H	-0.09877	2.03415	2.88305
C	3.19307	1.95039	2.01229
H	3.91822	1.67890	-0.01616
H	2.17800	2.21163	3.88429
O	4.38381	2.05335	2.66160
C	5.54887	1.83021	1.89391
H	5.65919	2.56934	1.08682
H	6.39025	1.91936	2.58391
H	5.54410	0.82603	1.44745

Intermediate-C:

76

Int_C

Cu	3.16049262	1.14744799	-0.51234975
N	2.01257000	2.66964200	-0.32528800
C	2.55745200	3.64028900	0.45247000
O	1.98739400	4.55373400	1.04922800
C	4.09865500	3.57739300	0.52600700
C	4.59178900	3.72963200	1.96620900
C	4.83319600	2.29031700	2.40383800
H	3.85598500	4.27381600	2.56418500
H	5.53519700	4.29033200	1.99512500
C	5.48144400	1.69207900	1.17129100
H	5.46068500	2.19826200	3.29531100
H	3.87967700	1.78293200	2.61161000
H	6.53061000	2.01610800	1.09656700
H	5.45525000	0.59780200	1.12535600
N	4.68003300	2.26931000	0.05272900
C	0.65103200	2.47827300	-0.46002000
C	0.24547700	1.58533400	-1.49587600
C	-0.36313400	3.00846600	0.36269900
C	-1.08776100	1.22136400	-1.67819800
H	0.97702600	1.34597800	-2.27357500
C	-1.68358800	2.61450400	0.19538600
H	-0.09566700	3.72333600	1.13202900
C	-2.05651800	1.70876800	-0.80137600

H	-1.38241500	0.58730300	-2.50961900
H	-2.43863300	3.03161800	0.85927100
N	-3.39802300	1.28710400	-0.94605400
C	-4.45639500	1.47401700	-0.12035600
C	-5.50860500	0.82192200	-0.73631700
H	-4.37600500	2.01412300	0.81156800
N	-3.76991900	0.54555300	-2.02910800
N	-5.03560800	0.26926100	-1.89458400
C	-6.88745300	0.63729600	-0.30040200
C	-7.76369900	-0.14402500	-1.06659500
C	-7.34976800	1.18679900	0.90328700
C	-9.06421000	-0.37161200	-0.63378600
H	-7.40163900	-0.57208700	-1.99903600
C	-8.65094900	0.95672700	1.33304800
H	-6.68196300	1.79565300	1.51271500
C	-9.51333700	0.17443400	0.56739700
H	-9.73271500	-0.98212000	-1.23822000
H	-8.99297600	1.38912600	2.27156600
H	-10.53165300	-0.00773000	0.90543200
H	4.47026900	4.39030600	-0.11123300
H	5.27288600	2.42385000	-0.75816900
C	6.73642100	-3.90130700	0.10445100
C	5.37670200	-3.60623700	0.11490600
C	4.91374600	-2.37946900	-0.37462600
C	5.84821000	-1.46321700	-0.88169900
C	7.20487100	-1.75908700	-0.88695300
C	7.65675900	-2.98187100	-0.39187300
H	7.07873300	-4.86047400	0.48948800
H	4.65579200	-4.32170500	0.50081700
H	5.48879200	-0.51698500	-1.28843700
H	7.91406700	-1.03757400	-1.29042900
H	8.71950000	-3.21738100	-0.39925700
C	3.47446700	-2.04192600	-0.34200800
C	2.99982600	-0.81597000	-0.52106900
Cu	1.12790800	-0.37014400	-0.65749300
N	0.60808200	-2.16904700	-0.11221300
N	1.41740200	-3.17925200	0.08982100
N	2.65885800	-3.20066100	-0.04629800
C	-0.71955100	-2.39010400	0.34305800
C	-1.78953800	-1.82758700	-0.35079600
C	-0.98270000	-3.13887500	1.50094100
C	-3.09848400	-1.97798600	0.09870500
H	-1.60461700	-1.28717100	-1.27787900
C	-2.28094800	-3.31066600	1.94338600
H	-0.15079700	-3.58574500	2.03988300
C	-3.35056900	-2.72398400	1.25281000
H	-3.90775800	-1.53933600	-0.47795500
H	-2.49624100	-3.89120300	2.83758600
O	-4.58627300	-2.93878000	1.77579100
C	-5.66113800	-2.25915500	1.15847500

H	-5.79670400	-2.56969800	0.11201300
H	-6.55618400	-2.51308400	1.73065600
H	-5.50761600	-1.17142000	1.18287100

Transition State-II (imaginary frequency = -270.19)

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TS-II

Cu	2.98600100	0.64159400	-0.26654500
N	2.06118300	2.17081100	-1.27148800
C	2.47958600	3.39960800	-0.87027500
O	1.86233700	4.46632400	-0.87830700
C	3.93162700	3.41639400	-0.38089500
C	4.09771800	4.17499000	0.93432200
C	5.39138500	3.61133000	1.50236000
H	3.25414500	3.94597800	1.60197300
H	4.09803100	5.25629400	0.77829300
C	5.24607600	2.12868800	1.19570900
H	6.25752600	4.03180400	0.97185900
H	5.52721000	3.81058500	2.57067900
H	6.18995700	1.57671600	1.13249700
H	4.63062800	1.63514300	1.95888100
N	4.52533300	2.05925800	-0.11108900
C	0.73173900	1.90004000	-1.52492100
C	0.45958300	0.68886300	-2.24414500
C	-0.37541100	2.59342300	-1.00255400
C	-0.81652400	0.10184500	-2.23516700
H	1.24556100	0.28811500	-2.88820500
C	-1.63717700	2.00939300	-0.99864300
H	-0.21460400	3.55022700	-0.51797400
C	-1.85977900	0.75124000	-1.55587300
H	-1.02187800	-0.80697800	-2.79541400
H	-2.44588700	2.51779900	-0.47511200
N	-3.10710300	0.10651600	-1.42405000
C	-4.30254400	0.61238200	-1.03571300
C	-5.14759500	-0.48085500	-0.97464400
H	-4.45343000	1.66826800	-0.86004800
N	-3.19671200	-1.24624700	-1.58731700
N	-4.42341600	-1.58839300	-1.31906600
C	-6.55494100	-0.56057500	-0.60348800
C	-7.19870700	-1.80515400	-0.55715100
C	-7.28719400	0.58936400	-0.27430700
C	-8.53568700	-1.89267900	-0.19003300
H	-6.62985200	-2.69586400	-0.81477700
C	-8.62419400	0.49776500	0.09341100
H	-6.80493900	1.56676200	-0.31058900
C	-9.25433500	-0.74427400	0.13787500
H	-9.02164800	-2.86629700	-0.15926400
H	-9.17781800	1.40111100	0.34339700
H	-10.30159600	-0.81612900	0.42517000
H	4.53154900	3.91424100	-1.15766300

H	5.19649200	1.85148300	-0.84563000
C	5.69014100	-4.84799700	-0.01049100
C	4.42142300	-4.33572000	0.23573700
C	4.19151500	-2.95296900	0.19411900
C	5.27142500	-2.10386500	-0.09598500
C	6.53702400	-2.61942700	-0.34046400
C	6.75321800	-3.99629200	-0.30043800
H	5.84907800	-5.92448600	0.02475000
H	3.59005300	-4.99627400	0.46648000
H	5.10356400	-1.02548900	-0.11741500
H	7.36262100	-1.94400500	-0.56065400
H	7.74521200	-4.40102900	-0.49282000
C	2.85039300	-2.41659300	0.44933700
C	2.48271400	-1.12027500	0.29219100
Cu	0.92195406	-0.60386900	-0.87457509
N	0.67085800	-1.58087200	0.94444000
N	0.78073400	-2.84880100	1.20677000
N	1.88164700	-3.37443200	0.93862700
C	-0.44797200	-0.84727500	1.44003700
C	-1.72872000	-1.40377600	1.45982100
C	-0.26056200	0.48825600	1.81518900
C	-2.81720300	-0.63293400	1.85043300
H	-1.86890700	-2.43458800	1.14525800
C	-1.34689900	1.26021300	2.19240000
H	0.74552100	0.90936900	1.79903200
C	-2.63374500	0.71023000	2.19959900
H	-3.80849900	-1.07889100	1.83843900
H	-1.22268600	2.30364700	2.47315800
O	-3.64035100	1.56147300	2.53478000
C	-4.93883000	1.00926500	2.63652300
H	-4.97824100	0.21634600	3.39654000
H	-5.59303000	1.83124600	2.93387100
H	-5.28350700	0.59730900	1.67716800

Intermediate-D

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Int_D

Cu	-2.48508684	-0.38927897	0.07946583
N	-2.52442300	-2.10538700	-0.89294700
C	-3.09961100	-3.07212100	-0.12709600
O	-2.69444100	-4.21470300	0.09277300
C	-4.42771300	-2.56142100	0.48419700
C	-5.03469800	-3.53654800	1.49935100
C	-4.80557700	-2.88949200	2.87644900
H	-4.51447800	-4.49530700	1.40555600
H	-6.09843400	-3.71109900	1.30868600
C	-3.79424600	-1.78507200	2.59714900
H	-5.73485900	-2.45026700	3.26380100
H	-4.44958900	-3.60082400	3.62891200
H	-3.80239400	-0.95189100	3.30652000

H	-2.77191200	-2.18679900	2.55738600
N	-4.12769300	-1.29881400	1.23690200
C	-1.19855400	-2.17167200	-1.25170200
C	-0.78370900	-1.30255700	-2.31487300
C	-0.17460400	-2.84398400	-0.54641000
C	0.55446400	-0.88686600	-2.43686300
H	-1.53866000	-0.97312200	-3.03004200
C	1.15000400	-2.44656800	-0.68242600
H	-0.44873700	-3.59829800	0.18366500
C	1.51700400	-1.42589500	-1.55985000
H	0.86926500	-0.22259800	-3.23867800
H	1.90324900	-2.88827200	-0.03088200
N	2.80632800	-0.86217600	-1.52243400
C	3.96157700	-1.37833800	-1.03877900
C	4.86800600	-0.33706500	-1.10108800
H	4.05043200	-2.41366600	-0.74149300
N	2.97805200	0.45333300	-1.85753200
N	4.22072500	0.75355900	-1.61029900
C	6.26504000	-0.28743600	-0.69293300
C	7.06303800	0.80888400	-1.04825100
C	6.82688400	-1.30671300	0.08772600
C	8.38618400	0.88158300	-0.62985700
H	6.62199500	1.60100900	-1.65017700
C	8.15273200	-1.23468300	0.49869800
H	6.20966000	-2.15007100	0.39700000
C	8.93782600	-0.13884500	0.14337500
H	8.99362600	1.73981500	-0.91217800
H	8.57328700	-2.03379300	1.10674700
H	9.97494900	-0.08086900	0.46840500
H	-5.10207100	-2.30167600	-0.34066300
H	-4.99024700	-0.75721800	1.30427800
C	-6.24210400	3.31116500	-0.84567400
C	-5.01001800	3.37645700	-0.20476200
C	-3.99126500	2.46695600	-0.52190800
C	-4.24207200	1.50298100	-1.51377500
C	-5.47802600	1.43433900	-2.14664100
C	-6.48630200	2.33762300	-1.81296800
H	-7.02112800	4.02567100	-0.58476600
H	-4.81510900	4.12893700	0.55627500
H	-3.44955200	0.80831800	-1.80700600
H	-5.64866500	0.67925200	-2.91228500
H	-7.45334100	2.28725900	-2.30991400
C	-2.71574100	2.51361900	0.19063000
C	-1.67708700	1.56449400	0.18334500
Cu	-0.18603489	0.41102143	-0.27476486
N	-0.79559400	2.13410900	1.08425800
N	-1.24353000	3.31601200	1.57578700
N	-2.41765400	3.53174200	1.04741600
C	0.51184400	1.68199200	1.39756200
C	1.53201600	2.60570400	1.60831800

C	0.79329000	0.31154300	1.44732600
C	2.83217000	2.17334200	1.84368600
H	1.29932500	3.66626700	1.56793000
C	2.08982700	-0.12037400	1.67604400
H	-0.01068900	-0.41613600	1.31708400
C	3.12395900	0.80539100	1.86295100
H	3.61620500	2.91115200	1.98482400
H	2.32612000	-1.18150200	1.71905100
O	4.36164600	0.28410800	2.05375300
C	5.42972900	1.20433500	2.19060300
H	5.30540000	1.82771100	3.08751800
H	6.33586500	0.60184400	2.28021300
H	5.51395700	1.84945800	1.30482700

Product (E):

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product

C	-5.68235900	-0.70795600	-0.01460900
C	-4.33079700	-1.02247100	-0.07976400
C	-3.36161700	-0.01418500	0.01403300
C	-3.78370400	1.31248200	0.17427300
C	-5.13622200	1.62359300	0.23995900
C	-6.09225500	0.61438300	0.14568200
H	-6.42302700	-1.50242800	-0.08930500
H	-4.00158200	-2.05169400	-0.20448200
H	-3.04475100	2.11050700	0.24651300
H	-5.44567800	2.65992500	0.36453800
H	-7.15190100	0.85800200	0.19661400
C	-1.94590200	-0.35471600	-0.05491700
C	-0.82849200	0.45229500	0.03718700
N	0.22395000	-0.39344800	-0.08882200
N	-0.21603500	-1.67526000	-0.25462600
N	-1.51604400	-1.64211600	-0.23099500
C	1.60873600	-0.10487700	-0.07074000
C	2.51752800	-1.11406200	0.23652200
C	2.06708000	1.18285300	-0.36210800
C	3.88101600	-0.84286200	0.25563600
H	2.14664400	-2.11086600	0.45659700
C	3.42297300	1.45795200	-0.33102800
H	1.36477300	1.96782600	-0.63456200
C	4.34154300	0.44772200	-0.02231400
H	4.57475600	-1.64294400	0.49731400
H	3.79816900	2.45267200	-0.55736800
O	5.64816400	0.81786200	-0.02103200
C	6.59972500	-0.18390300	0.27457900
H	6.56160300	-1.00440500	-0.45598300
H	7.57476100	0.30349900	0.22156600
H	6.45210700	-0.59551900	1.28317600
H	-0.69779000	1.51082600	0.21040400

**Transition state-I with explicit solvent model
(Imaginary frequency = -217.09)**

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TS-I-H₂O

Cu	-2.86774	-1.18485	-0.63247
N	-1.90837	-2.86932	-0.32659
C	-2.50756	-3.67424	0.59124
O	-1.97851	-4.52915	1.30318
C	-4.01727	-3.46577	0.72009
C	-4.42148	-3.09868	2.14578
C	-5.79803	-2.47892	1.95994
H	-3.71742	-2.35313	2.54621
H	-4.39144	-3.96682	2.80858
C	-5.60557	-1.63201	0.70876
H	-6.54485	-3.26616	1.78479
H	-6.13453	-1.88749	2.81799
H	-6.51797	-1.48822	0.11929
H	-5.22354	-0.63398	0.96244
N	-4.56932	-2.34325	-0.09942
C	-0.51831	-2.80186	-0.37002
C	0.12204	-2.72046	-1.62138
C	0.27658	-2.67369	0.78663
C	1.47465	-2.41995	-1.72443
H	-0.47633	-2.87866	-2.51764
C	1.61552	-2.32701	0.69169
H	-0.19269	-2.77875	1.76044
C	2.20926	-2.16817	-0.56208
H	1.96857	-2.35423	-2.69237
H	2.19159	-2.12026	1.59346
N	3.51955	-1.64829	-0.67307
C	4.58082	-1.78658	0.15604
C	5.55816	-0.96482	-0.37856
H	4.56351	-2.46885	0.99450
N	3.80901	-0.76577	-1.67420
N	5.03759	-0.36996	-1.49483
C	6.90954	-0.67792	0.08701
C	7.78840	0.05388	-0.72432
C	7.34476	-1.08976	1.35397
C	9.06468	0.36853	-0.27422
H	7.44910	0.37131	-1.70845
C	8.62351	-0.77682	1.79906
H	6.66975	-1.64822	2.00236
C	9.48791	-0.04410	0.98809
H	9.73588	0.93780	-0.91490
H	8.94468	-1.10129	2.78712
H	10.48779	0.20381	1.33898
H	-4.50963	-4.41086	0.44321
H	-4.98146	-2.71486	-0.94986
C	-6.93341	3.56080	0.90546

C	-5.61179	3.13135	0.87032
C	-5.19663	2.18985	-0.08452
C	-6.14746	1.69910	-1.00170
C	-7.46464	2.13394	-0.96010
C	-7.86481	3.06847	-0.00554
H	-7.23836	4.28929	1.65480
H	-4.88981	3.51971	1.58176
H	-5.82564	0.97227	-1.74657
H	-8.18296	1.74551	-1.68038
H	-8.89724	3.41176	0.02585
C	-3.85970	1.66175	-0.15495
C	-3.11584	0.70082	-0.53296
Cu	-1.25273	0.63293	-0.94264
N	-0.65056	2.18962	0.24126
N	-1.54962	3.00503	0.67010
N	-2.72708	3.13064	0.69916
C	0.70529	2.55842	0.41132
C	1.64981	1.52975	0.46316
C	1.14796	3.88729	0.46911
C	3.01416	1.80751	0.52404
H	1.30609	0.49328	0.47815
C	2.49980	4.16791	0.55769
H	0.41925	4.69510	0.43892
C	3.44848	3.13502	0.56621
H	3.72567	0.98573	0.54889
H	2.85464	5.19512	0.59935
O	4.74789	3.51982	0.61984
C	5.72061	2.49773	0.49311
H	5.58863	1.93610	-0.44277
H	6.68976	3.00029	0.48982
H	5.68415	1.79314	1.33784
O	0.38867	0.45836	-2.09752
H	0.72720	-0.45814	-2.13784
H	1.14160	0.98391	-1.77007

Transition State for mononuclear pathway: (imaginary frequency = -355.28)

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TS

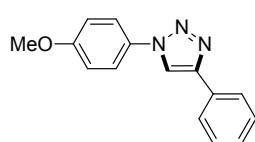
N	1.47335	-1.87015	-0.89130
C	1.71779	-3.20837	-0.89954
O	0.93512	-4.11943	-1.17172
C	3.16208	-3.58419	-0.53996
C	3.76829	-4.58096	-1.55310
C	4.99534	-3.86192	-2.12756
H	3.02219	-4.80818	-2.32172
H	4.03197	-5.53306	-1.08249
C	4.70797	-2.39389	-1.84887
H	5.91048	-4.16651	-1.60147
H	5.15085	-4.06740	-3.19179
H	5.57890	-1.73256	-1.83108

H	3.98644	-1.98684	-2.56989
N	4.04845	-2.39627	-0.52414
C	0.19087	-1.34842	-1.02040
C	0.09053	0.02384	-1.33566
C	-1.00118	-2.05236	-0.75189
C	-1.12244	0.68757	-1.31837
H	1.00532	0.57153	-1.57000
C	-2.21683	-1.39063	-0.73029
H	-0.95197	-3.11120	-0.52700
C	-2.28105	-0.02050	-0.99351
H	-1.18910	1.75019	-1.53398
H	-3.11886	-1.93158	-0.44535
N	-3.50772	0.66801	-0.88877
C	-4.77205	0.20319	-1.03871
C	-5.58381	1.28988	-0.77556
H	-4.97445	-0.81317	-1.34525
N	-3.52667	1.98919	-0.53544
N	-4.77334	2.35160	-0.47408
C	-7.03606	1.40750	-0.79016
C	-7.64074	2.63964	-0.50484
C	-7.85396	0.30860	-1.08643
C	-9.02412	2.76472	-0.51658
H	-7.00386	3.49098	-0.27507
C	-9.23735	0.43738	-1.09822
H	-7.40196	-0.65779	-1.30938
C	-9.82910	1.66633	-0.81323
H	-9.47854	3.72841	-0.29273
H	-9.85725	-0.42677	-1.33102
H	-10.91288	1.76680	-0.82231
H	3.13004	-4.00163	0.47504
H	4.76093	-2.49931	0.19627
C	6.72484	4.52412	-0.97483
C	5.93981	3.38504	-0.87017
C	4.95387	3.28218	0.12873
C	4.78049	4.35413	1.01615
C	5.57105	5.49186	0.90370
C	6.54423	5.58465	-0.08790
H	7.48050	4.58615	-1.75594
H	6.07276	2.55651	-1.56356
H	4.02333	4.28809	1.79100
H	5.42415	6.31477	1.60097
H	7.15928	6.47881	-0.17094
C	4.18428	2.06475	0.19191
C	3.97458	0.88485	-0.23115
Cu	2.88868	-0.66571	-0.20892
N	1.87567	0.22530	1.44265
N	2.02122	1.48484	1.69448
N	2.78018	2.35275	1.38430
C	0.68534	-0.36099	1.93046
C	0.70596	-1.72583	2.22081

C	-0.51930	0.34716	2.05682
C	-0.44985	-2.38998	2.61335
H	1.64429	-2.27154	2.12224
C	-1.67089	-0.30320	2.45597
H	-0.54717	1.40704	1.81066
C	-1.65022	-1.67995	2.71719
H	-0.40940	-3.45623	2.81718
H	-2.61640	0.22994	2.53222
O	-2.84736	-2.23782	3.03715
C	-2.87802	-3.63969	3.19721
H	-2.25345	-3.96620	4.04104
H	-3.91917	-3.89786	3.39868
H	-2.54094	-4.15390	2.28455

13.0 Analytical data of compounds

1-(4-Methoxyphenyl)-4-phenyl-1H-1,2,3-triazole (3a): Following the GP-1, 1-azido-4-methoxybenzene



1a (50 mg, 0.33 mmol, 1 equiv), phenylacetylene **2a** (57 μ L, 0.50 mmol, 1.5 equiv)

afforded **3a** as a white solid (79 mg, 95%). ¹H NMR (500 MHz, DMSO-*d*₆): 9.18 (s,

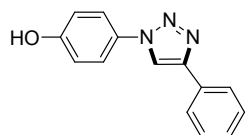
1H), 7.94 (d, 2H, *J* = 7.6 Hz), 7.86 (d, 2H, *J* = 8.9 Hz), 7.50 (t, 2H, *J* = 7.6 Hz),

7.38 (t, 1H, *J* = 6.3 Hz), 7.17 (d, 2H, *J* = 8.9 Hz), 3.85 (s, 3H); ¹³C NMR (100 MHz, DMSO-*d*₆): 159.0,

130.0, 129.7, 128.6, 127.8, 124.9, 121.4, 119.3, 114.6, 55.2; HRMS (ESI) calcd for C₁₅H₁₄N₃O[M+H]⁺:

252.1137; found: 252.1127.

4-(4-Phenyl-1H-1,2,3-triazol-1-yl)phenol (3b): Following the GP-1, 4-azidophenol **1b** (50 mg,



0.37 mmol, 1 equiv) and phenylacetylene **2a** (63 μ L, 0.56 mmol, 1.5 equiv) afforded

3b as a brown solid (79 mg, 90%). ¹H NMR (500 MHz, CDCl₃): 9.97 (s, 1H), 9.11

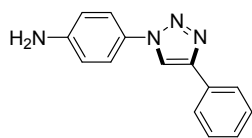
(s, 1H), 7.92 (d, 2H, *J* = 9.8 Hz), 7.72 (d, 2H, *J* = 11.0 Hz), 7.48 (t, 2H, *J* = 9.2 Hz),

7.36 (t, 1H, *J* = 9.2 Hz), 6.96 (d, 2H, *J* = 10.4 Hz); ¹³C NMR (100 MHz, CDCl₃): 157.8, 147.0, 130.4,

128.9, 128.8, 128.1, 125.3, 121.9, 119.5, 116.1; HRMS (ESI) calcd for C₁₄H₁₂N₃O [M+H]⁺: 238.0980;

found: 238.0974.

4-(4-Phenyl-1H-1,2,3-triazol-1-yl)aniline (3c): Following the GP-1, 4-azidoaniline **1c** (50 mg, 0.37



mmol, 1 equiv), phenylacetylene **2a** (63 μ L, 0.56 mmol, 1.5 equiv) afforded **3c** as a

white solid (80 mg, 91%). ¹H NMR (500 MHz, CDCl₃): 7.99 (s, 1H), 7.82 (d, 2H, *J*

= 6.9 Hz), 7.44 (d, 2H, *J* = 8.8 Hz), 7.38 (t, 2H, *J* = 7.6 Hz), 7.28 (t, 1H, *J* = 7.6 Hz),

6.69 (d, 2H, *J* = 8.2 Hz); ¹³C NMR (100 MHz, CDCl₃): 148.1, 147.3, 130.6, 129.0, 128.7, 128.3, 125.9,

122.4, 117.9, 115.4; HRMS (ESI) calcd for C₁₄H₁₃N₄ [M+H]⁺: 237.1140; found: 237.1144.

1-(4-Fluorophenyl)-4-phenyl-1H-1,2,3-triazole (3d): Following the GP-1, 1-azido-4-fluorobenzene **1d** (50 mg, 0.36 mmol, 1 equiv), phenylacetylene **2a** (62 μ L, 0.55 mmol, 1.5 equiv) afforded **3d** as a yellowish white solid (80 mg, 93%). ^1H NMR (500 MHz, DMSO- d_6): 9.28 (s, 1H), 8.02-7.99 (m, 2H), 7.94 (d, 2H, $J = 7.6$ Hz), 7.52-7.49 (m, 4H), 7.40 (t, 1H, $J = 6.9$ Hz); ^{13}C NMR (125 MHz, DMSO- d_6): 147.1, 147.0, 132.9, 128.7, 127.9, 125.0, 122.2, 122.0, 121.0, 119.6, 116.5, 116.3; HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{11}\text{FN}_3$ $[\text{M}+\text{H}]^+$: 240.0937; found: 240.0926.

1-(4-Bromophenyl)-4-phenyl-1H-1,2,3-triazole (3e): Following the GP-1, 1-azido-4-bromobenzene **1e** (50 mg, 0.25 mmol, 1 equiv), phenylacetylene **2a** (43 μ L, 0.38 mmol, 1.5 equiv) afforded **3e** as a brown solid (69 mg, 90%). ^1H NMR (400 MHz, DMSO- d_6): 9.33 (s, 1H), 7.93 (d, 4H, $J = 8.6$ Hz), 7.86-7.84 (m, 2H), 7.51 (t, 2H, $J = 7.3$ Hz), 7.39 (t, 1H, $J = 7.3$ Hz); ^{13}C NMR (100 MHz, DMSO- d_6): 147.5, 135.8, 132.8, 130.1, 128.9, 128.3, 125.3, 121.9, 121.3, 119.6; HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{11}\text{BrN}_3$ $[\text{M}+\text{H}]^+$: 300.0136; found: 300.0132.

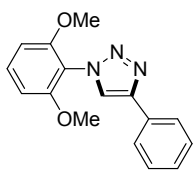
1-(4-Nitrophenyl)-4-phenyl-1H-1,2,3-triazole (3f): Following the GP-1, 1-azido-4-nitrobenzene **1f** (50 mg, 0.30 mmol, 1 equiv), phenylacetylene **2a** (51 μ L, 0.45 mmol, 1.5 equiv) afforded **3f** as a yellow solid (68 mg, 85%). ^1H NMR (400 MHz, DMSO- d_6): 9.53 (s, 1H), 8.51 (d, 2H, $J = 9.2$ Hz), 8.27 (d, 2H, $J = 9.2$ Hz), 7.96 (d, 2H, $J = 7.3$ Hz), 7.53 (t, 2H, $J = 7.3$ Hz), 7.42 (t, 1H, $J = 7.3$ Hz); ^{13}C NMR (100 MHz, DMSO- d_6): 147.5, 146.4, 140.5, 129.4, 128.7, 128.2, 125.3, 125.1, 120.1, 119.6; HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{11}\text{N}_4\text{O}_2$ $[\text{M}+\text{H}]^+$: 267.0882; found: 267.0899.

1-(4-(4-Phenyl-1H-1,2,3-triazol-1-yl)phenyl)ethanone (3g): Following the GP-1, 1-(4-azidophenyl)ethanone **1g** (50 mg, 0.31 mmol, 1 equiv), phenylacetylene **2a** (51 μ L, 0.46 mmol, 1.5 equiv) afforded **3g** as a white solid (73 mg, 92%). ^1H NMR (400 MHz, CDCl_3): 8.27 (s, 1H), 8.15 (d, 2H, $J = 8.6$ Hz), 7.93 (t, 4H, $J = 8.6$ Hz), 7.48 (t, 2H, $J = 7.0$ Hz), 7.40 (d, 1H, $J = 7.5$ Hz), 2.67 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): 196.7, 149.1, 137.1, 130.3, 130.0, 129.2, 128.9, 126.1, 121.4, 120.2, 117.4, 26.8; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{14}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$: 264.1137; found: 264.1149.

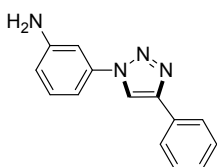
1-(2,6-Dimethylphenyl)-4-phenyl-1H-1,2,3-triazole (3h): Following the GP-1, 2-azido-1,3,5-trimethylbenzene **1h** (50 mg, 0.34 mmol, 1 equiv), phenylacetylene **2a** (58 μ L, 0.51 mmol, 1.5 equiv) afforded **3h** as a white solid (81 mg, 95%). ^1H NMR (400 MHz, CDCl_3): 8.00 (d, 2H, $J = 7.8$ Hz), 7.87 (s, 1H), 7.54 (dd, 2H, $J = 8.3, 8.8$ Hz), 7.44-7.36 (m, 1H), 7.24 (d, 1H, $J = 7.3$ Hz), 6.99 (d, 2H, $J = 7.3$ Hz), 6.70 (t, 1H, $J = 7.4$ Hz), 2.22 (s, 6H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): 147.6, 142.7, 135.9, 135.3, 132.0, 130.4,

129.9, 128.8, 128.4, 128.1, 125.7, 121.5, 121.4, 117.8, 17.4, 17.3; HRMS (ESI) calcd for $C_{17}H_{18}N_3$ $[M+H]^+$: 264.1501; found: 264.1521.

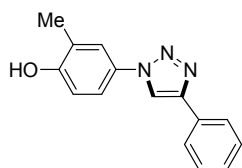
1-(2,6-Dimethoxyphenyl)-4-phenyl-1H-1,2,3-triazole (3i): Following the GP-1, 2-azido-1,3-dimethoxybenzene **1i** (50 mg, 0.28 mmol, 1 equiv), phenylacetylene **2a** (48 μ L, 0.42 mmol, 1.5 equiv) afforded **3i** as a white solid (73 mg, 93%). 1H NMR (400 MHz, $CDCl_3$): 8.16 (s, 1H), 7.89 (d, 2H, $J = 7.8$ Hz), 7.44 (t, 2H, $J = 7.3$ Hz), 7.35 (t, 1H, $J = 7.8$ Hz), 6.94 (d, 2H, $J = 2.0$ Hz), 6.51 (s, 1H), 3.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): 164.7, 148.4, 138.7, 130.3, 129.0, 128.5, 125.9, 117.9, 100.7, 99.1, 55.8; HRMS (ESI) calcd for $C_{16}H_{16}N_3O_2$ $[M+H]^+$: 282.1243; found: 282.1235.



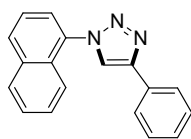
3-(4-Phenyl-1H-1,2,3-triazol-1-yl)aniline (3j): Following the GP-1, 3-azidoaniline **1j** (50 mg, 0.37 mmol, 1 equiv), phenylacetylene **2a** (63 μ L, 0.56 mmol, 1.5 equiv) afford **3j** as a white solid (145 mg, 92%). 1H NMR (400 MHz, $CDCl_3$): 8.15 (s, 1H), 7.90 (d, 2H, $J = 6.8$ Hz), 7.46 (t, 2H, $J = 7.8$ Hz), 7.36 (t, 1H, $J = 7.3$ Hz), 7.29 (d, 1H, $J = 8.3$ Hz), 7.18 (t, 1H, $J = 2.0$ Hz), 7.06 (d, 1H, $J = 7.8$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$): 148.3, 148.0, 138.2, 130.6, 130.5, 129.2, 129.1, 128.5, 126.0, 117.8, 115.3, 110.1, 107.1; HRMS (ESI) calcd for $C_{14}H_{13}N_4$ $[M+H]^+$: 237.1140; found: 237.1145.



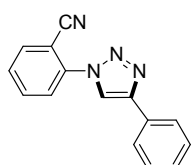
2-Methyl-4-(4-phenyl-1H-1,2,3-triazol-1-yl)phenol (3k): Following the GP-1, 4-azido-2-methylphenol **1k** (50 mg, 0.33 mmol, 1 equiv), phenylacetylene **2a** (56 μ L, 0.50 mmol, 1.5 equiv) afforded **3k** as a white solid (78 mg, 94%). 1H NMR (125 MHz, $CDCl_3$): 9.95 (s, 1H), 9.16 (s, 1H), 7.92 (d, 2H, $J = 8.6$ Hz), 7.48 (t, 2H, $J = 7.9$ Hz), 7.38-7.34 (m, 2H), 7.27 (d, 1H, $J = 7.9$ Hz), 7.21 (dd, 1H, $J = 1.8, 6.1$ Hz), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 156.2, 147.1, 135.3, 131.4, 130.3, 128.9, 128.1, 125.3, 124.9, 119.3, 110.1, 106.3, 15.6; HRMS (ESI) calcd for $C_{15}H_{14}N_3O$ $[M+H]^+$: 252.1137; found: 252.1130.



1-(Naphthalen-1-yl)-4-phenyl-1H-1,2,3-triazole (3l): Following the GP-1, 1-azidonaphthalene **1l** (50 mg, 0.30 mmol, 1 equiv), phenylacetylene **2a** (50 μ L, 0.45 mmol, 1.5 equiv) afforded **3l** as a brownish solid (77 mg, 94%). 1H NMR (400 MHz, $CDCl_3$): 8.14 (s, 1H), 8.02 (d, 1H, $J = 7.5$ Hz), 7.96 (d, 3H, $J = 7.5$ Hz), 7.69 (d, 1H, $J = 8.0$ Hz), 7.63-7.52 (m, 3H), 7.48 (t, 2H, $J = 7.5$ Hz), 7.40-7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 147.8, 134.2, 133.8, 132.2, 130.5, 130.4, 129.1, 128.5, 128.4, 127.9, 127.2, 125.9, 125.1, 123.6, 122.4; HRMS (ESI) calcd for $C_{18}H_{14}N_3$ $[M+H]^+$: 272.1188; found: 272.1180.

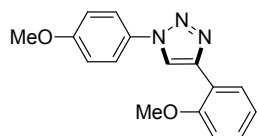


2-(4-phenyl-1H-1,2,3-triazol-1-yl)benzotrile (3m): Following the GP-1, 2-azidobenzotrile **1m** (50 mg, 0.35 mmol, 1 equiv), phenylacetylene **2a** (59 μ L, 0.52 mmol, 1.5 equiv) afforded



3m as a white solid (81 mg, 94%). ¹H NMR (400 MHz, DMSO-d₆): 9.47 (s, 1H), 8.18 (dd, 4H, *J* = 8.6, 12.2 Hz), 7.95 (d, 2H, *J* = 7.8 Hz), 7.52 (t, 2H, *J* = 7.3 Hz), 7.41 (t, 1H, *J* = 7.3 Hz); ¹³C NMR (100 MHz, DMSO-d₆): 147.6, 139.4, 134.2, 129.7, 128.9, 128.4, 125.3, 120.3, 119.7, 110.9; HRMS (ESI) calcd for C₁₅H₁₁N₄[M+H]⁺: 247.0984; found: 247.0977.

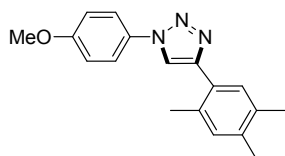
4-(2-methoxyphenyl)-1-(4-methoxyphenyl)-1H-1,2,3-triazole (3n): Following the GP-1, 1-azido-4-



methoxybenzene **1a** (50 mg, 0.33 mmol, 1 equiv), 1-ethynyl-2-methoxybenzene **2b** (66 mg, 0.50 mmol, 1.5 equiv) afforded **3n** as a brownish solid (87 mg, 94%).

¹H NMR (400 MHz, CDCl₃): 8.42-8.38 (m, 2H), 7.70 (dd, 2H, *J* = 1.9, 4.5 Hz), 7.37-7.32 (m, 1H), 7.12 (t, 1H, *J* = 7.8 Hz), 7.06-7.05 (m, 3H), 3.98 (s, 3H), 3.90 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 155.8, 145.8, 137.0, 132.2, 129.2, 128.1, 122.5, 121.4, 121.3, 119.6, 115.0, 111.0, 55.8, 55.6; HRMS (ESI) calcd for C₁₆H₁₆N₃O₂ [M+H]⁺: 282.1243; found: 282.1234.

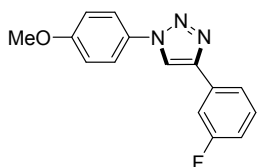
1-(4-Methoxyphenyl)-4-(2,4,5-trimethylphenyl)-1H-1,2,3-triazole (3o): Following the GP-1, 1-azido-4-



methoxybenzene **1a** (50 mg, 0.33 mmol, 1 equiv), 1-ethynyl-2,4,5-trimethylbenzene **2c** (72 mg, 0.50 mmol, 1.5 equiv) afforded **3o** as a white solid

(92 mg, 95%). ¹H NMR (500 MHz, CDCl₃): 7.67 (d, 1H, *J* = 7.6 Hz), 7.45 (d, 1H, *J* = 8.2 Hz), 7.40 (dd, 2H, *J* = 5.7 Hz, 4.0 Hz), 7.27 (d, 1H, *J* = 6.3 Hz), 7.18 (t, 1H, *J* = 6.9 Hz), 7.15 (t, 1H, *J* = 7.0 Hz), 7.03 (dd, 2H, *J* = 8.2 Hz, 7.0 Hz), 6.64 (d, 2H, *J* = 7.6 Hz), 3.87 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 158.4, 136.5, 133.0, 129.1, 128.4, 126.2, 122.3, 121.2, 120.2, 114.9, 110.5, 103.0, 55.7; HRMS (ESI) calcd for C₁₈H₂₀N₃O [M+H]⁺: 294.1606; found: 294.1625.

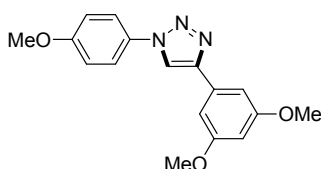
4-(3-Fluorophenyl)-1-(4-methoxyphenyl)-1H-1,2,3-triazole (3p): Following the GP-1, 1-azido-4-



methoxybenzene **1a** (50 mg, 0.33 mmol, 1 equiv), 1-ethynyl-3-fluorobenzene **2d**

(61 mg, 0.50 mmol, 1.5 equiv) afforded **3p** as a white solid (81 mg, 91%). ¹H NMR (500 MHz, CDCl₃): 8.11 (s, 1H), 7.69-7.66 (m, 3H), 7.64-7.62 (m, 1H), 7.44-7.40 (m, 1H), 7.08-7.04 (m, 3H), 3.89 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 164.8, 162.3, 160.2, 147.3, 130.7, 130.6, 122.4, 121.6, 121.5, 118.4, 115.4, 115.2, 115.0, 113.1, 112.8, 55.8; HRMS (ESI) calcd for C₁₅H₁₃FN₃O [M+H]⁺: 270.1043; found: 270.1055.

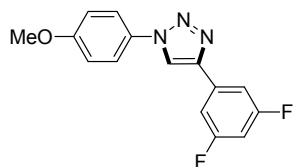
4-(3,5-Dimethoxyphenyl)-1-(4-methoxyphenyl)-1H-1,2,3-triazole (3q): Following the GP-1, 1-azido-4-



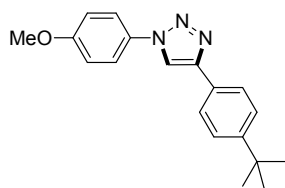
methoxybenzene **1a** (50 mg, 0.33 mmol, 1 equiv), 1-ethynyl-3,5-dimethoxybenzene **2e** (81 mg, 0.50 mmol, 1.5 equiv) afforded **3q** as a white

solid (92 mg, 90%). ¹H NMR (500 MHz, CDCl₃): 8.09 (s, 1H), 7.65 (d, 2H, *J* = 8.2 Hz), 7.06 (s, 2H), 7.01 (d, 2H, *J* = 7.6 Hz), 6.46 (s, 1H), 3.86 (s, 3H), 3.83 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): 161.3, 160.0, 132.3, 130.6, 122.3, 118.3, 114.9, 110.0, 103.9, 100.8, 55.7, 55.6; HRMS (ESI) calcd for C₁₇H₁₈N₃O₃ [M+H]⁺: 312.1348; found: 312.1340.

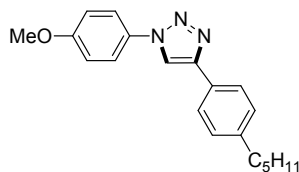
4-(3,5-Difluorophenyl)-1-(4-methoxyphenyl)-1H-1,2,3-triazole (3r): Following the GP-1, 1-azido-4-methoxybenzene **1a** (50 mg, 0.33 mmol, 1 equiv), 1-ethynyl-3,5-difluorobenzene **2f** (69 mg, 0.50 mmol, 1.5 equiv) afforded **3r** as a white solid (87 mg, 92%). ¹H NMR (400 MHz, CDCl₃): 8.12 (s, 1H), 7.67 (d, 2H, *J* = 8.8 Hz), 7.43 (d, 2H, *J* = 6.4 Hz), 7.05 (d, 3H, *J* = 8.8 Hz), 6.83-6.78 (m, 1H), 3.89 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 164.9, 164.8, 162.4, 162.3, 160.3, 133.8, 133.6, 130.4, 122.5, 122.4, 118.7, 115.1, 108.9, 108.8, 108.7, 108.6, 103.9, 103.7, 103.4, 55.8; HRMS (ESI) calcd for C₁₅H₁₂F₂N₃O [M+H]⁺: 288.0948; found: 288.0943.



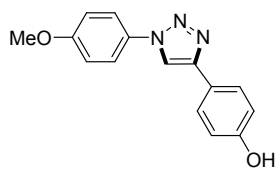
4-(4-(Tert-butyl)phenyl)-1-(4-methoxyphenyl)-1H-1,2,3-triazole (3s): Following the GP-1, 1-azido-4-methoxybenzene **1a** (50 mg, 0.33 mmol, 1 equiv), 1-(*tert*-butyl)-4-ethynylbenzene **2g** (79 mg, 0.50 mmol, 1.5 equiv) afforded **3s** as a white solid (91 mg, 90%). ¹H NMR (400 MHz, CDCl₃): 8.09 (br s, 1H), 7.83 (d, 2H, *J* = 8.3 Hz), 7.69 (d, 2H, *J* = 8.8 Hz), 7.48 (d, 2H, *J* = 7.8 Hz), 7.04 (d, 2H, *J* = 8.8 Hz), 3.88 (s, 3H), 1.36 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): 160.0, 151.6, 127.8, 125.9, 125.7, 122.4, 114.9, 55.8, 34.9, 31.4; HRMS (ESI) calcd for C₁₉H₂₂N₃O [M+H]⁺: 308.1763; found: 308.1776.



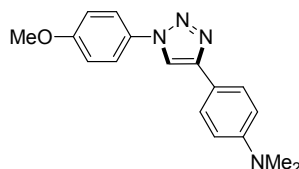
1-(4-Methoxyphenyl)-4-(4-pentylphenyl)-1H-1,2,3-triazole (3t): Following the GP-1, 1-azido-4-methoxybenzene **1a** (50 mg, 0.33 mmol, 1 equiv), 1-ethynyl-4-pentylbenzene **2h** (86 mg, 0.50 mmol, 1.5 equiv) afforded **3t** as a white solid (93 mg, 88%). ¹H NMR (400 MHz, CDCl₃): 8.01 (s, 1H), 7.80 (d, 2H, *J* = 7.8 Hz), 7.67 (d, 2H, *J* = 8.8 Hz), 7.26 (d, 2H, *J* = 7.3 Hz), 7.03 (d, 2H, *J* = 8.3 Hz), 3.87 (s, 3H), 2.64 (t, 2H, *J* = 7.4 Hz), 1.67-1.62 (m, 3H), 1.37-1.31 (m, 3H), 0.92-0.88 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): 160.0, 148.5, 143.4, 130.8, 129.1, 127.9, 125.9, 122.3, 117.6, 114.9, 55.8, 35.9, 31.6, 31.2, 22.7, 14.1; HRMS (ESI) calcd for C₂₀H₂₄N₃O [M+H]⁺: 322.1919; found: 322.1939.



4-(1-(4-Methoxyphenyl)-1H-1,2,3-triazol-4-yl)phenol (3u): Following the GP-1, 1-azido-4-methoxybenzene **1a** (50 mg, 0.33 mmol, 1 equiv), 4-ethynylphenol **2i** (59 mg, 0.50 mmol, 1.5 equiv) afforded **3u** as a brownish solid (83 mg, 94%). ¹H NMR (400 MHz, CDCl₃): 9.63 (s, 1H), 8.97 (s, 1H), 7.81 (d, 2H, *J* = 7.0 Hz), 7.71 (d, 2H, *J* = 7.0 Hz), 7.14 (dd, 2H, *J* = 2.1, 7.0 Hz), 6.84 (d, 2H, *J* = 7.0 Hz), 3.82 (d, 3H, *J* = 2.1 Hz); ¹³C NMR (100 MHz, CDCl₃): 159.2, 157.4, 127.6, 126.7, 121.5, 121.3, 120.1, 118.1, 115.6, 114.8, 55.5; HRMS (ESI) calcd for C₁₅H₁₄N₃O₂ [M+H]⁺: 268.1086; found: 268.1080.



4-(1-(4-Methoxyphenyl)-1H-1,2,3-triazol-4-yl)-N,N-dimethylaniline (3v): Following the GP-1, 1-azido-4-methoxybenzene **1a** (50 mg, 0.33 mmol, 1 equiv), 4-ethynyl-*N,N*-dimethylaniline **2j** (73 mg, 0.50 mmol, 1.5 equiv) afforded **3v** as a brownish



solid (91 mg, 94%). ¹H NMR (500 MHz, CDCl₃): 7.97 (s, 1H), 7.76 (d, 2H, *J* = 9.5 Hz), 7.67 (d, 2H, *J* = 8.9 Hz), 7.02 (d, 2H, *J* = 9.5 Hz), 6.79 (d, 2H, *J* = 8.9 Hz), 3.87 (s, 3H), 3.01 (s, 6H); 1.75-1.70 (m, 4H), 1.57-1.53 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): 159.8, 150.7, 148.9, 130.7, 126.9, 122.2, 118.7, 114.9, 112.7, 110.8, 55.8, 40.6; HRMS (ESI) calcd for C₁₇H₁₉N₄O[M+H]⁺: 295.1559; found: 295.1543.

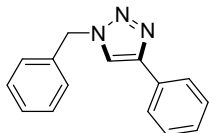
4-(4-Fluorophenyl)-1-(4-methoxyphenyl)-1H-1,2,3-triazole (3w): Following the GP-1, 1-azido-4-methoxybenzene **1a** (50 mg, 0.33 mmol, 1 equiv), 1-ethynyl-4-fluorobenzene **2k** (60 mg, 0.50 mmol, 1.5 equiv) afforded **3w** as a white solid (79 mg, 89%). ¹H NMR (400 MHz, CDCl₃): 8.07 (s, 1H), 7.89-7.86 (m, 2H), 7.68 (d, 2H, *J* = 8.8 Hz), 7.15 (t, 2H, *J* = 8.8 Hz), 7.05 (d, 2H, *J* = 8.8 Hz), 3.89 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 160.1, 147.5, 130.7, 127.8, 127.7, 126.8, 122.4, 117.8, 116.2, 115.9, 115.0, 55.8; HRMS (ESI) calcd for C₁₅H₁₃FN₃O[M+H]⁺: 270.1043; found: 270.1056.

4-(4-Bromophenyl)-1-(4-methoxyphenyl)-1H-1,2,3-triazole (3x): Following the GP-1, 1-azido-4-methoxybenzene **1a** (50 mg, 0.33 mmol, 1 equiv), 1-ethynyl-4-bromobenzene **2l** (91 mg, 0.50 mmol, 1.5 equiv) afforded **3x** as a white solid (99 mg, 91%). ¹H NMR (400 MHz, CDCl₃): 8.10 (s, 1H), 7.78 (d, 2H, *J* = 8.3 Hz), 7.67 (d, 2H, *J* = 8.8 Hz), 7.58 (d, 2H, *J* = 8.3 Hz), 7.04 (d, 2H, *J* = 8.3 Hz), 3.88 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 160.1, 150.5, 146.8, 133.7, 132.3, 129.7, 127.5, 122.4, 118.1, 115.0, 55.8; HRMS (ESI) calcd for C₁₅H₁₃BrN₃O[M+H]⁺: 330.0242; found: 330.0233.

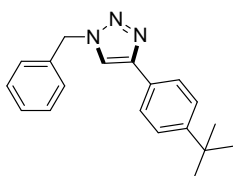
1-(4-Methoxyphenyl)-4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (3y): Following the GP-1, 1-azido-4-methoxybenzene **1a** (50 mg, 0.33 mmol, 1 equiv), 1-ethynyl-4-(trifluoromethyl)benzene **2m** (85 mg, 0.50 mmol, 1.5 equiv) afforded **3y** as a white solid (97 mg, 92%). ¹H NMR (500 MHz, CDCl₃): 8.18 (s, 1H), 8.02 (d, 2H, *J* = 8.2 Hz), 7.73-7.68 (m, 4H), 7.06 (d, 2H, *J* = 8.8 Hz), 3.90 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 158.8, 153.9, 134.0, 133.5, 130.9, 126.2, 126.1, 122.4, 118.7, 115.1, 55.8; HRMS (ESI) calcd for C₁₆H₁₃F₃N₃O[M+H]⁺: 320.1011; found: 320.1030.

4-(4-(1-(4-Methoxyphenyl)-1H-1,2,3-triazol-4-yl)phenyl)butanenitrile (3z): Following the GP-1, 1-azido-4-methoxybenzene **1a** (50 mg, 0.33 mmol, 1 equiv), 4-(4-ethynylphenyl)butanenitrile **2n** (85 mg, 0.50 mmol, 1.5 equiv) afforded **3z** as a white solid (94 mg, 90%). ¹H NMR (400 MHz, CDCl₃): 7.74 (s, 1H), 7.62 (d, 2H, *J* = 9.3 Hz), 7.03 (d, 2H, *J* = 8.8 Hz), 3.88 (s, 3H), 2.97 (t, 2H, *J* = 7.4 Hz), 2.49 (t, 2H, *J* = 7.3 Hz), 2.20-2.13 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): 160.0, 146.3, 130.7, 122.3, 119.9, 119.5, 115.0, 55.8, 25.0, 24.4, 16.7; HRMS (ESI) calcd for C₁₉H₁₉N₄O[M+H]⁺: 319.1559; found: 319.1550.

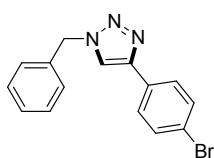
1-Benzyl-4-phenyl-1H-1,2,3-triazole (6a): Following the GP-2, benzyl azide **4a** (50 mg, 0.38 mmol, 1 equiv), phenylacetylene **2a** (65 μ L, 0.57 mmol, 1.5 equiv) afforded **6a** as a white solid (84mg, 94%). ¹H NMR (400 MHz, DMSO-d₆): 8.63 (s, 1H), 7.84 (d, 2H, *J* = 6.7 Hz), 7.45-7.31 (m, 8H), 5.63 (s, 2H); ¹³C NMR (100 MHz, DMSO-d₆): 146.3, 135.6, 130.3, 128.5, 128.4, 127.8, 127.5, 124.8, 121.2, 52.7; HRMS (ESI) calcd for C₁₅H₁₄N₃[M+H]⁺: 236.1188; found: 236.1171.



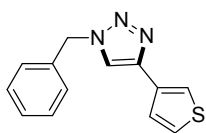
1-Benzyl-4-(3-fluorophenyl)-1H-1,2,3-triazole (6b): Following the GP-2, benzyl azide **4a** (50 mg, 0.38 mmol, 1 equiv), 1-ethynyl-4-bromobenzene **2g** (103 mg, 0.57 mmol, 1.5 equiv) afforded **6b** as a white solid (100 mg, 94%). ¹H NMR (400 MHz, CDCl₃): 7.72 (d, 2H, *J* = 8.2 Hz), 7.62 (s, 1H), 7.42 (d, 2H, *J* = 8.8 Hz), 7.39-7.37 (m, 3H), 7.29 (dd, 2H, *J* = 1.3, 6.3 Hz), 5.58 (s, 2H), 1.33 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): 151.5, 148.4, 134.9, 132.0, 129.3, 128.9, 128.2, 127.9, 125.9, 125.6, 119.4, 54.3, 34.8, 31.4; HRMS (ESI) calcd for C₁₉H₂₂N₃ [M+H]⁺: 292.1814; found: 292.1804.



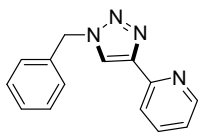
1-Benzyl-4-(3-fluorophenyl)-1H-1,2,3-triazole (6c): Following the GP-2, benzyl azide **4a** (50 mg, 0.38 mmol, 1 equiv), 1-ethynyl-4-bromobenzene **2l** (103 mg, 0.57 mmol, 1.5 equiv) afforded **6c** as a white solid (113 mg, 96%). ¹H NMR (400 MHz, CDCl₃): 7.68 (s, 1H), 7.65 (d, 2H, *J* = 8.3 Hz), 7.52 (d, 2H, *J* = 8.3 Hz), 7.39 (d, 2H, *J* = 6.8 Hz), 7.31 (dd, 2H, *J* = 2.0, 2.4 Hz), 5.58 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): 134.7, 132.1, 129.7, 129.4, 129.1, 128.3, 127.4, 122.3, 119.7, 54.5; HRMS (ESI) calcd for C₁₅H₁₃BrN₃ [M+H]⁺: 314.0293; found: 314.0297.



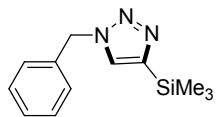
1-Benzyl-4-(thiophen-3-yl)-1H-1,2,3-triazole (6d): Following the GP-2, benzyl azide **4a** (50 mg, 0.38 mmol, 1 equiv), 3-ethynylthiophene **5a** (103 mg, 0.57 mmol, 1.5 equiv) afforded **6d** as a white solid (110 mg, 91%). ¹H NMR (500 MHz, CDCl₃): 7.65 (dd, 1H, *J* = 1.3, 1.9 Hz), 7.56 (s, 1H), 7.41 (dd, 1H, *J* = 1.3, 3.8 Hz), 7.39-7.37 (m, 2H), 7.35 (dd, 2H, *J* = 1.9, 3.1 Hz), 7.30 (dd, 2H, *J* = 1.9, 5.7 Hz), 5.57 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): 144.6, 134.8, 131.9, 129.3, 128.9, 128.2, 126.4, 125.9, 121.3, 119.4, 54.4; HRMS (ESI) calcd for C₁₃H₁₃N₃S [M+H]⁺: 242.0752; found: 242.0748.



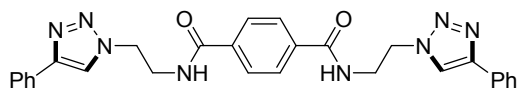
2-(1-Benzyl-1H-1,2,3-triazol-4-yl)pyridine (6e): Following the GP-2, benzyl azide **4a** (50 mg, 0.38 mmol, 1 equiv), 2-ethynylpyridine **5b** (59 mg, 0.57 mmol, 1.5 equiv) afforded **6e** as a white solid (75 mg, 83%). ¹H NMR (400 MHz, DMSO-d₆): 8.63 (s, 1H), 7.84 (d, 2H, *J* = 6.7 Hz), 7.45-7.31 (m, 8H), 5.64 (s, 2H); ¹³C NMR (100 MHz, DMSO-d₆): 146.3, 135.6, 130.3, 128.5, 128.4, 127.8, 127.5, 124.8, 121.2, 52.7; HRMS (ESI) calcd for C₁₄H₁₃N₄[M+H]⁺: 237.1140; found: 237.1156.



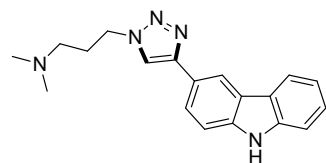
1-Benzyl-4-(trimethylsilyl)-1H-1,2,3-triazole (6f): Following the GP-2, benzyl azide **4a** (50 mg, 0.38 mmol, 1 equiv), trimethylsilylacetylene **5c** (72 mg, 0.57 mmol, 1.5 equiv) afforded **6f** as grey coloured liquid (69 mg, 78%). ¹H NMR (500 MHz, CDCl₃): 7.45 (s, 1H), 7.39-7.35 (m, 3H), 7.29-7.27 (m, 2H), 5.56 (s, 2H), 0.31 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): 135.0, 129.1, 128.7, 128.2, 53.6, -1.02; HRMS (ESI) calcd for C₁₂H₁₈N₃Si[M+H]⁺: 232.1270; found: 232.1277.



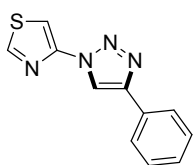
N¹,N⁴-bis(2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethyl)terephthalamide (6g): Following the GP-2, N¹,N⁴-bis(2-azidoethyl)terephthalamide **4b** (50 mg, 0.17 mmol, 1 equiv), phenylacetylene **2a** (28 μL, 0.25 mmol, 1.5 equiv) afforded **6g** as a sticky solid (65 mg, 75%). ¹H NMR (500 MHz, DMSO-d₆): 8.77 (t, 2H, *J* = 5.7 Hz), 8.57 (s, 2H), 7.82-7.81 (m, 8H), 7.43 (t, 4H, *J* = 6.1 Hz), 7.31 (t, 2H, *J* = 6.0 Hz), 4.60 (t, 4H, *J* = 4.6 Hz), 3.37-3.33 (m, 4H); ¹³C NMR (100 MHz, DMSO-d₆): 165.6, 136.1, 130.4, 128.5, 127.4, 126.8, 124.7, 121.3, 48.5, 40.1 (merged with DMSO in ¹³C, found in DEPT); HRMS (ESI) calcd for C₂₈H₂₇N₈O₂[M+H]⁺: 507.2257; found: 507.2241.



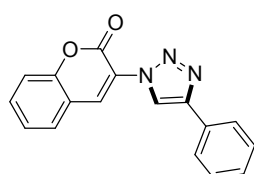
N,N-dimethyl-3-(4-phenyl-1H-1,2,3-triazol-1-yl)propan-1-amine (6h): Following the GP-2, 3-azido-N,N-dimethylpropan-1-amine **4c** (50 mg, 0.39 mmol, 1 equiv), 3-ethynyl-9H-carbazole **5d** (112 mg, 0.58 mmol, 1.5 equiv) afforded **6h** as a white solid (100 mg, 79%). ¹H NMR (500 MHz, DMSO-d₆): 11.35 (s, 1H), 8.85 (s, 1H), 8.15 (d, 1H, *J* = 8.4 Hz), 7.88 (d, 1H, *J* = 8.4 Hz), 7.54 (d, 1H, *J* = 8.4 Hz), 7.50 (d, 1H, *J* = 8.4 Hz), 7.40 (t, 1H, *J* = 6.7 Hz), 7.18 (t, 1H, *J* = 6.7 Hz), 4.44 (t, 2H, *J* = 7.6 Hz), 2.35 (t, 2H, *J* = 7.6 Hz), 2.23 (s, 6H), 2.06 (t, 2H, *J* = 7.6 Hz). ¹³C NMR (100 MHz, DMSO-d₆): 147.5, 140.2, 139.4, 125.7, 123.3, 122.7, 122.3, 121.6, 120.3, 120.2, 118.7, 116.8, 111.2, 111.1, 54.8, 45.5, 44.7, 27.3; HRMS (ESI) calcd for C₁₉H₂₂N₅[M+H]⁺: 320.1875; found: 320.1883.



4-(4-Phenyl-1H-1,2,3-triazol-1-yl)thiazole (6i): Following the GP-2, 4-azidothiazole **4d** (50 mg, 0.40 mmol, 1 equiv), phenylacetylene **2a** (67 μL, 0.59 mmol, 1.5 equiv) afforded **6i** as a white solid (78 mg, 85%). ¹H NMR (500 MHz, DMSO-d₆): 9.42 (s, 1H), 8.03 (d, 2H, *J* = 7.0 Hz), 7.87 (d, 1H, *J* = 3.8 Hz), 7.80 (d, 1H, *J* = 3.8 Hz), 7.50 (t, 2H, *J* = 7.6 Hz), 7.41 (d, 1H, *J* = 7.6 Hz); ¹³C NMR (100 MHz, DMSO-d₆): 156.3, 147.3, 140.3, 129.0, 128.7, 128.4, 125.4, 119.6, 118.5; HRMS (ESI) calcd for C₁₁H₉N₄S [M+H]⁺: 229.0548; found: 229.0531.

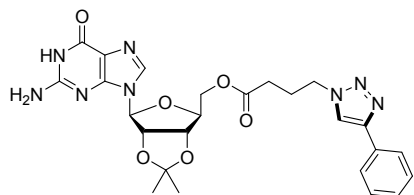


3-(4-Phenyl-1H-1,2,3-triazol-1-yl)-2H-chromen-2-one (6j): Following the GP-2, 3-azido-2H-chromen-2-one **4e** (50 mg, 0.27 mmol, 1 equiv), phenylacetylene **2a** (46 μL, 0.40 mmol, 1.5 equiv) afforded **6j** as a white solid (69 mg, 88%). ¹H NMR (400 MHz, DMSO-d₆): 9.08 (s, 1H), 8.70 (s, 1H), 7.99-7.96 (m, 3H), 7.78-7.73 (m, 1H), 7.57 (d, 1H, *J* =



8.6 Hz), 7.52-7.48 (m, 3H), 7.40 (d, 1H, $J = 7.3$ Hz); ^{13}C NMR (100 MHz, DMSO- d_6): 155.5, 152.2, 146.2, 135.0, 132.7, 130.0, 129.2, 128.7, 127.9, 125.1, 125.0, 122.8, 121.7, 117.8, 116.0; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{12}\text{N}_3\text{O}_2[\text{M}+\text{H}]^+$: 290.0930; found: 290.0911.

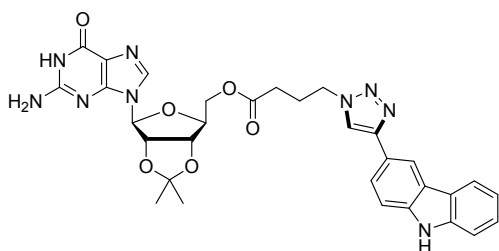
((3aS,4S,6S,6aS)-6-(2-amino-6-oxo-1H-purin-9(6H)-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)methyl-4-(4-phenyl-1H-1,2,3-triazol-1-yl)butanoate (6k): Following the GP-2, ((3aS,4S,6S,6aS)-6-(2-amino-6-oxo-1H-purin-9(6H)-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-



yl)methyl 4-azidobutanoate **4f** (50 mg, 0.12 mmol, 1 equiv), phenylacetylene **2a** (20 μL , 0.17 mmol, 1.5 equiv) afforded **6k** as a sticky solid (50 mg, 77%). ^1H NMR (400 MHz, DMSO- d_6): 10.7 (br s, 1H), 8.46 (s, 1H), 7.74 (d, 2H, $J = 6.1$ Hz), 7.38-7.22 (m, 5H), 6.52 (s, 2H), 5.98 (br s, 1H), 5.14-5.02 (m, 2H), 4.32 (s, 2H), 4.17 (s, 2H),

4.04 (d, 1H, $J = 15.8$ Hz), 2.26 (s, 2H), 1.99 (s, 2H), 1.40 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): 171.4, 131.9, 131.3, 130.4, 128.4, 128.3, 127.4, 124.7, 121.0, 112.9, 83.9, 80.8, 80.3, 63.7, 48.3, 29.8, 26.6, 24.9, 24.6; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{29}\text{N}_8\text{O}_6[\text{M}+\text{H}]^+$: 537.2210; found: 537.2205.

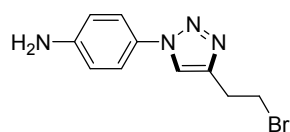
((3aS,4S,6S,6aS)-6-(2-amino-6-oxo-1H-purin-9(6H)-yl)-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)methyl-4-(4-(9H-carbazol-3-yl)-1H-1,2,3-triazol-1-yl)butanoate (6l): Following the GP-2, ((3aS,4S,6S,6aS)-6-(2-amino-6-oxo-1H-purin-9(6H)-yl)-



2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)methyl 4-azidobutanoate **4f** (50 mg, 0.12 mmol, 1 equiv), 3-ethynyl-9H-carbazole **5d** (33 mg, 0.17 mmol, 1.5 equiv) afforded **6l** as a sticky solid (56mg, 74%). ^1H NMR (500 MHz, CDCl_3): 11.32

(s, 1H), 10.77 (s, 1H), 8.58-8.53 (m, 2H), 8.15 (s, 1H), 7.88 (s, 1H), 7.54-7.469 (m, 3H), 7.41-7.38 (m, 1H), 7.19-7.16 (m, 1H), 6.57 (s, 2H), 6.05 (s, 1H), 5.20 (s, 1H), 5.14 (s, 1H), 4.43 (s, 2H), 4.13 (s, 1H), 3.16 (s, 2H), 2.38 (s, 2H), 2.12 (s, 2H), 1.49 (s, 3H), 1.29 (s, 3H), ^{13}C NMR (400 MHz, DMSO- d_6): 171.9, 156.7, 153.7, 150.5, 147.7, 140.1, 139.4, 136.3, 125.8, 123.3, 122.7, 122.4, 121.6, 120.3, 120.2, 118.7, 116.9, 113.3, 11.3, 111.1, 88.4, 84.2, 83.7, 81.1, 64.1, 54.9, 48.6, 30.2, 27.0, 25.3; HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{32}\text{N}_9\text{O}_6[\text{M}+\text{H}]^+$: 626.2476; found: 626.2470.

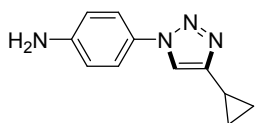
4-(4-(2-Bromoethyl)-1H-1,2,3-triazol-1-yl)aniline (6m): Following the GP-2, 4-azidoaniline **1c** (50 mg, 0.37 mmol, 1 equiv), 4-bromobut-1-yne **5e** (74 mg, 0.56 mmol, 1.5 equiv)



afforded **6m** as a white solid (71 mg, 72%). ^1H NMR (400 MHz, CDCl_3): 7.76 (s, 1H), 7.46 (d, 2H, $J = 8.8$ Hz), 6.76 (d, 2H, $J = 8.8$ Hz), 3.70 (t, 2H, $J = 6.8$ Hz),

3.37 (t, 2H, $J = 6.3$ Hz); ^{13}C NMR (100 MHz, CDCl_3): 147.2, 145.1, 128.9, 122.4, 120.1, 115.4, 31.6, 29.7; HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{12}\text{BrN}_4[\text{M}+\text{H}]^+$: 267.0240; found: 267.0249.

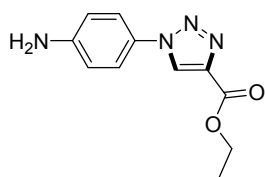
4-(4-Cyclopropyl-1H-1,2,3-triazol-1-yl)aniline (6n): Following the GP-2, 4-azidoaniline **1c** (50 mg, 0.37 mmol, 1 equiv), ethynylcyclopropane **5f** (37 mg, 0.56 mmol, 1.5 equiv)



afforded **6n** as a white solid (51 mg, 70%). ^1H NMR (400 MHz, CDCl_3): 7.53 (s, 1H), 7.42 (d, 2H, $J = 8.8$ Hz), 6.74 (d, 2H, $J = 8.8$ Hz), 2.04-1.98 (m, 1H), 0.99-0.96 (m, 2H), 0.92-0.89 (m, 2H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): 150.7, 146.9,

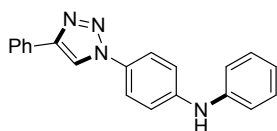
129.2, 122.3, 118.2, 115.4, 7.9, 6.9; HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{13}\text{N}_4[\text{M}+\text{H}]^+$: 201.1135; found: 201.1150.

Ethyl 1-(4-aminophenyl)-1H-1,2,3-triazole-4-carboxylate (6o): Following the GP-2, 4-azidoaniline **1c** (50 mg, 0.37 mmol, 1 equiv), ethyl propiolate **5g** (54 mg, 0.56 mmol, 1.5 equiv) afforded **6o** as a white



solid (64 mg, 75%). ^1H NMR (400 MHz, CDCl_3): 8.36 (s, 1H), 7.47 (d, 2H, $J = 8.3$ Hz), 6.76 (d, 2H, $J = 8.8$ Hz), 4.47-4.44 (m, 2H), 1.44-1.40 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3): 160.9, 147.9, 141.9, 127.7, 125.4, 122.7, 115.4, 61.5, 14.5; HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{13}\text{N}_4\text{O}_2[\text{M}+\text{H}]^+$: 233.1033; found: 233.1025.

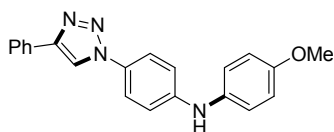
N-phenyl-4-(4-phenyl-1H-1,2,3-triazol-1-yl)aniline (11a): Following the GP-4, 4-azidoaniline **1c** (50



mg, 0.37 mmol, 1 equiv), phenylacetylene **2a** (64 μL , 0.56 mmol, 1.5 equiv), iodobenzene **10a** (63 μL , 0.56 mmol, 1.5 equiv) afforded **11a** as a brown solid (83 mg, 72%). ^1H NMR (500 MHz, CDCl_3): 8.11 (s, 1H), 7.92-7.90 (m, 2H),

7.65-7.63 (m, 2H), 7.48-7.45 (m, 2H), 7.38-7.32 (m, 4H), 7.18-7.14 (m, 3H), 7.05-7.02 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): 148.4, 129.8, 129.1, 128.4, 126.1, 124.1, 122.7, 122.3, 118.6, 117.8, 117.5, 112.0; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{17}\text{N}_4$ $[\text{M}+\text{H}]^+$: 313.1453; found: 313.1447.

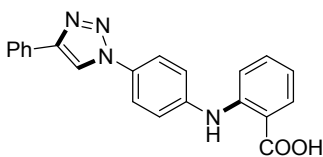
N-phenyl-4-(4-phenyl-1H-1,2,3-triazol-1-yl)aniline (11b): Following the GP-4, 4-azidoaniline **1c** (50



mg, 0.37 mmol, 1 equiv), phenylacetylene **2a** (64 μL , 0.56 mmol, 1.5 equiv), 4-iodoanisole **10b** (132 mg, 0.56 mmol, 1.5 equiv) afforded **11b** as a brown

solid (99 mg, 78%). ^1H NMR (500 MHz, CDCl_3): 8.07 (s, 1H), 7.90 (d, 2H, $J = 7.0$ Hz), 7.56 (d, 2H, $J = 8.9$ Hz), 7.45 (t, 2H, $J = 7.6$ Hz), 7.36 (t, 1H, $J = 7.2$ Hz), 7.13 (d, 2H, $J = 8.8$ Hz), 6.97 (d, 2H, $J = 8.8$ Hz), 6.91 (d, 2H, $J = 8.9$ Hz), 5.72 (br s, 1H), 3.82 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): 156.5, 148.2, 146.5, 134.7, 130.8, 129.3, 129.1, 128.4, 126.4, 123.8, 122.4, 117.8, 115.5, 115.1, 55.8; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{19}\text{N}_4\text{O}$ $[\text{M}+\text{H}]^+$: 343.1559; found: 343.1565.

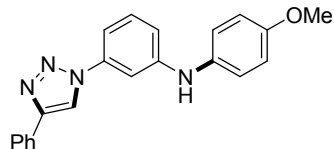
4-((4-(4-Phenyl-1H-1,2,3-triazol-1-yl)phenyl)amino)benzoic acid (11c): Following the GP-4, 4-azidoaniline **1c** (50 mg, 0.37 mmol, 1 equiv), phenylacetylene **2a** (64 μL , 0.56



mmol, 1.5 equiv), 4-iodobenzoic acid **10c** (139 mg, 0.56 mmol, 1.5 equiv) afforded **11c** as a white solid (88 mg, 67%). ^1H NMR (500 MHz, CDCl_3): 8.07 (s, 1H), 8.05-8.04 (m, 1H), 8.01 (dd, 1H, $J = 1.9, 6.3$ Hz), 7.93 (dd, 1H, J

= 1.9, 6.3Hz), 7.90-7.88 (m, 1H), 7.54-7.49 (m, 2H), 7.47-7.43 (m, 3H), 7.22-7.18 (m, 1H), 7.00 (d, 1H, $J = 8.2$ Hz), 6.93 (t, 1H, $J = 7.6$ Hz), 6.79 (d, 1H, $J = 8.9$ Hz); ^{13}C NMR (125 MHz, CDCl_3): 174.3, 170.7, 162.3, 142.1, 136.8, 133.6, 133.5, 131.1, 129.1, 128.5, 128.2, 126.5, 122.5, 119.7, 117.9, 115.6, 111.8, 94.8; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{17}\text{N}_4\text{O}_2$ $[\text{M}+\text{H}]^+$: 357.1352; found: 357.1366.

N-(4-methoxyphenyl)-3-(4-phenyl-1H-1,2,3-triazol-1-yl)aniline (11d): Following the GP-4, 3-

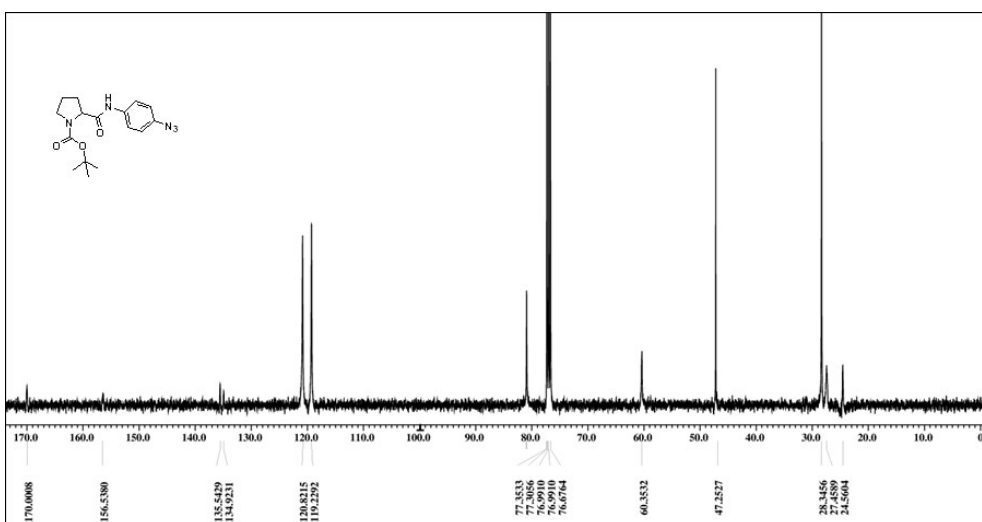
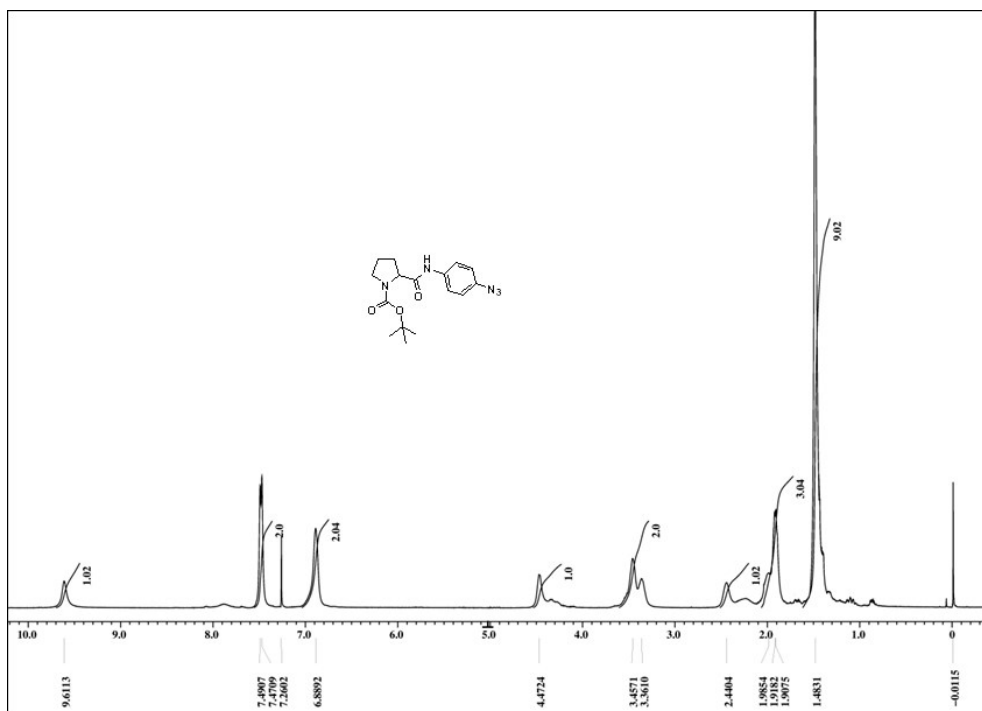


azidoaniline **1k** (50 mg, 0.37 mmol, 1 equiv), phenylacetylene **2a** (64 μL , 0.56 mmol, 1.5 equiv), 4-iodoanisole **10b** (132 mg, 0.56 mmol, 1.5 equiv)

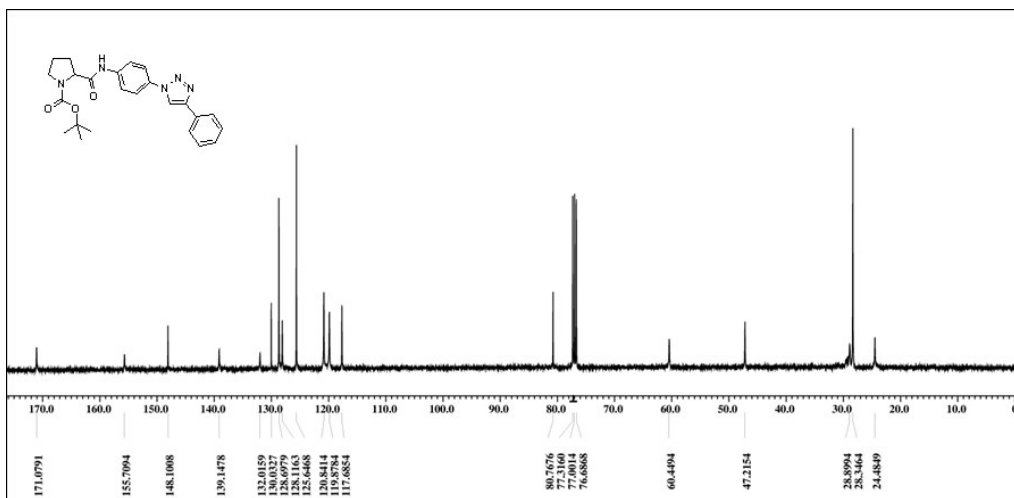
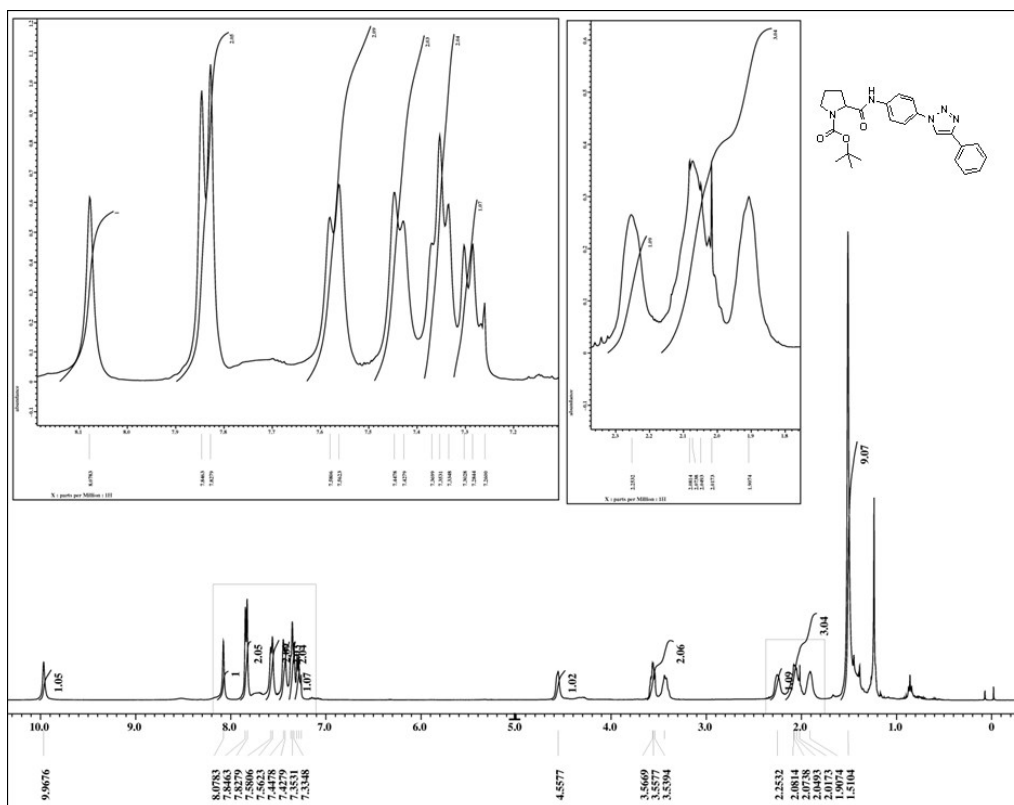
afforded **11d** as a white solid (87 mg, 70%). ^1H NMR (500 MHz, CDCl_3): 8.08 (s, 1H), 7.89 (d, 2H, $J = 7.6$ Hz), 7.57-7.55 (m, 3H), 7.45 (t, 2H, $J = 7.6$ Hz), 7.13 (d, 2H, $J = 8.8$ Hz), 6.97 (d, 2H, $J = 8.2$ Hz), 6.91 (d, 2H, $J = 8.9$ Hz), 3.83 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): 156.4, 134.5, 130.6, 129.0, 128.4, 127.7, 127.6, 126.0, 123.8, 123.7, 122.4, 117.6, 116.1, 115.7, 115.4, 115.3, 115.0, 55.7; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{19}\text{N}_4\text{O}$ $[\text{M}+\text{H}]^+$: 343.1559; found: 343.1567.

13.0 NMR spectra of all compounds

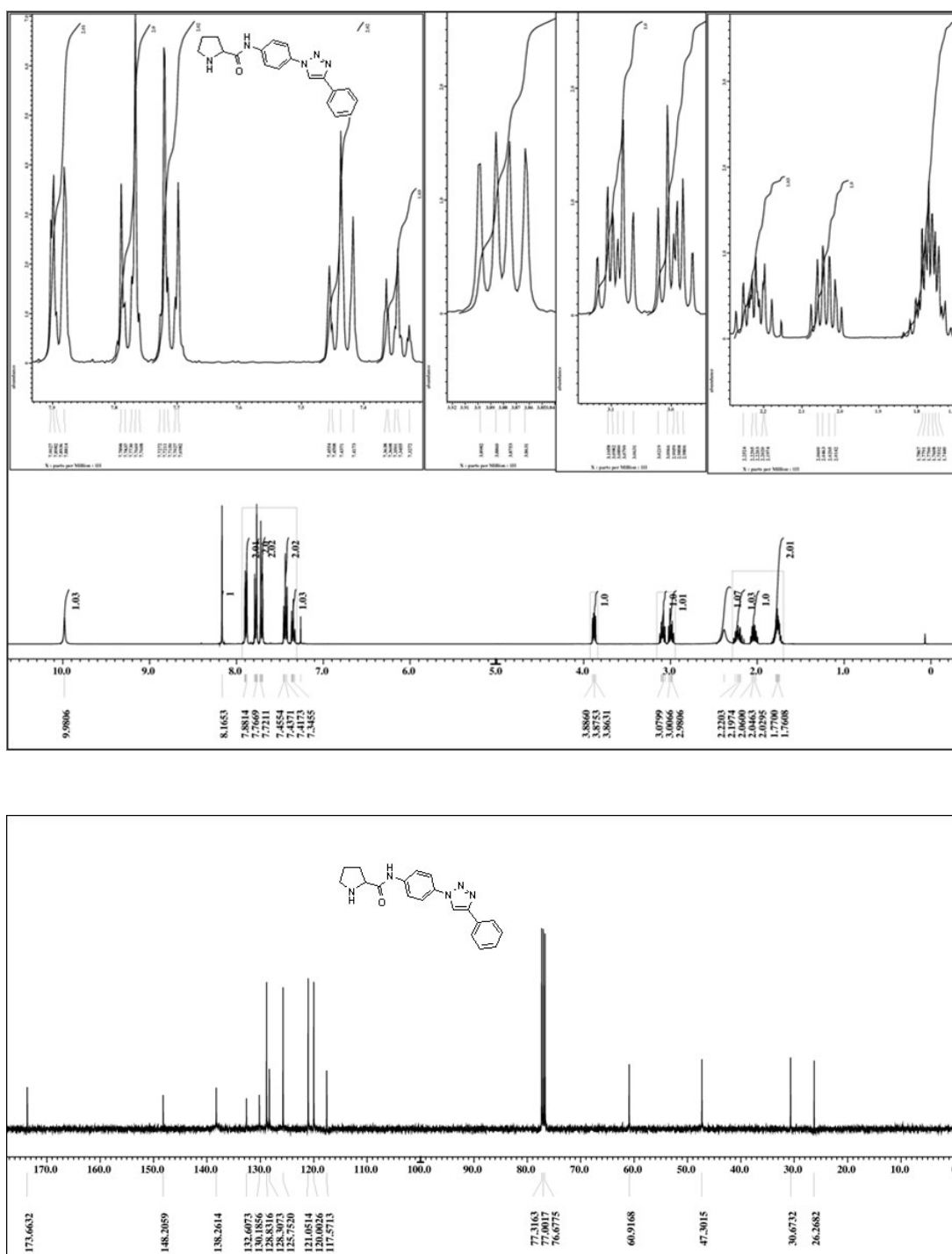
^1H and ^{13}C NMR of S3:



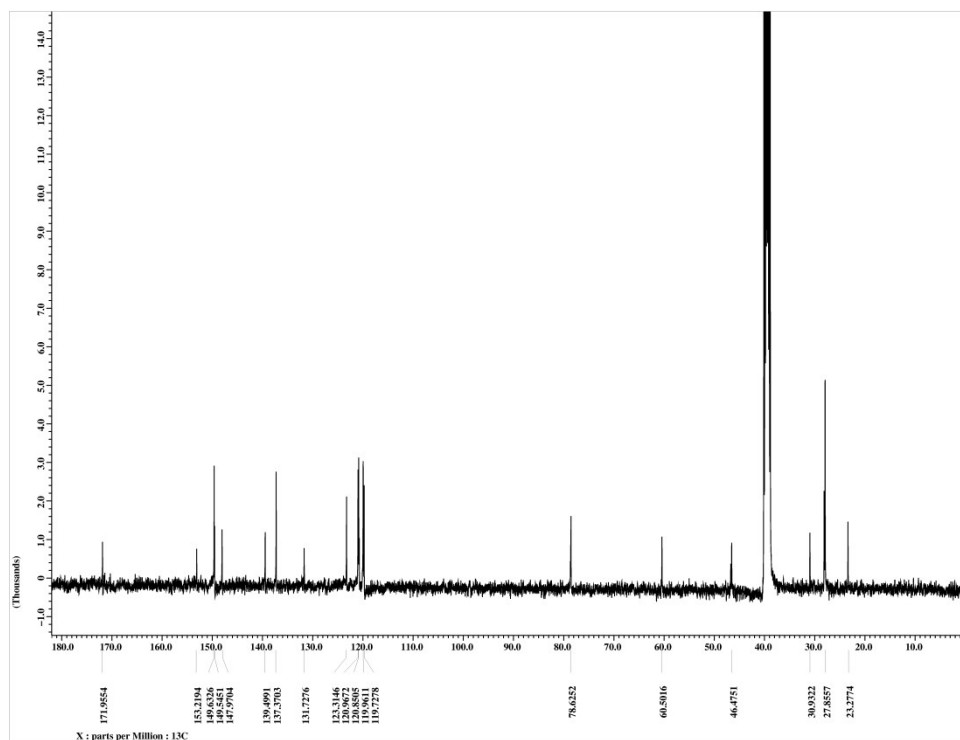
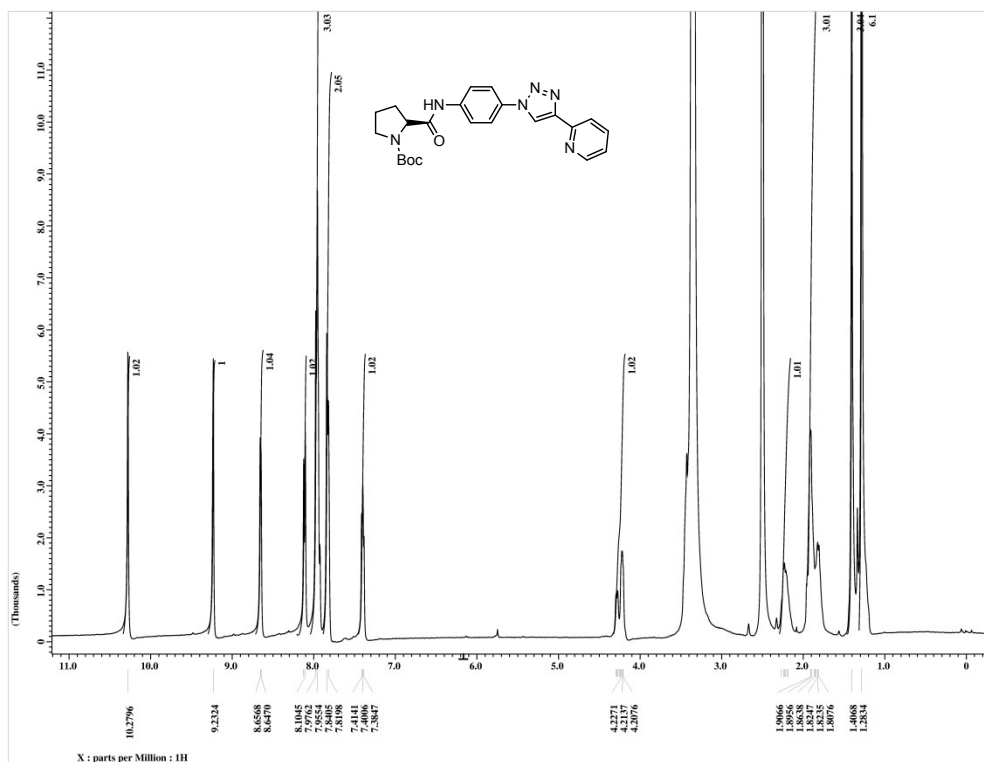
^1H and ^{13}C NMR of S5:



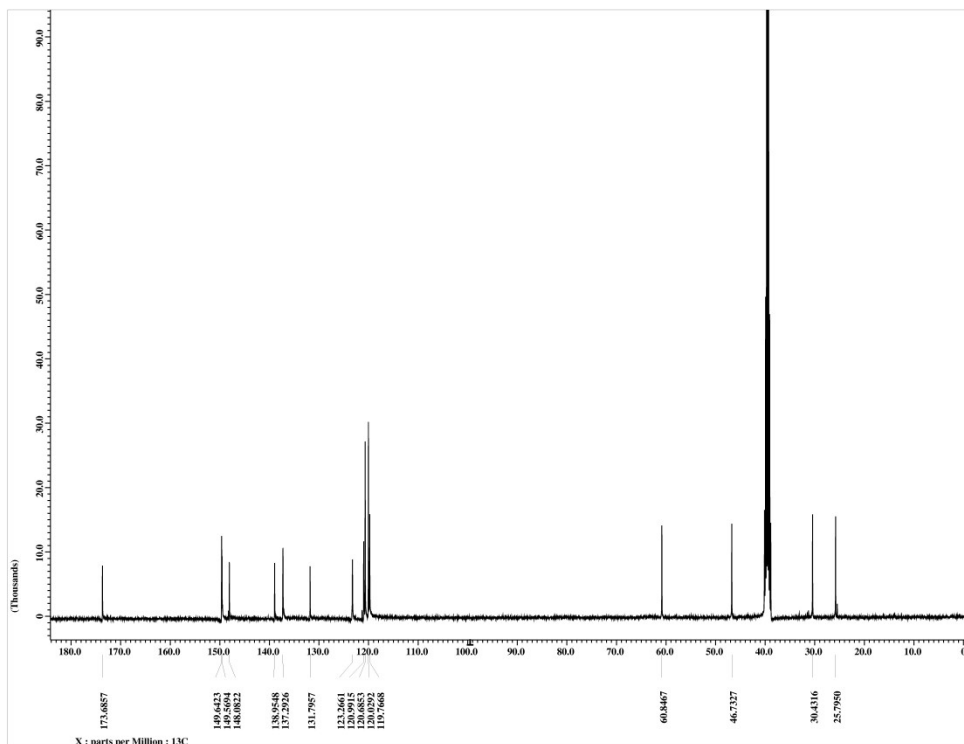
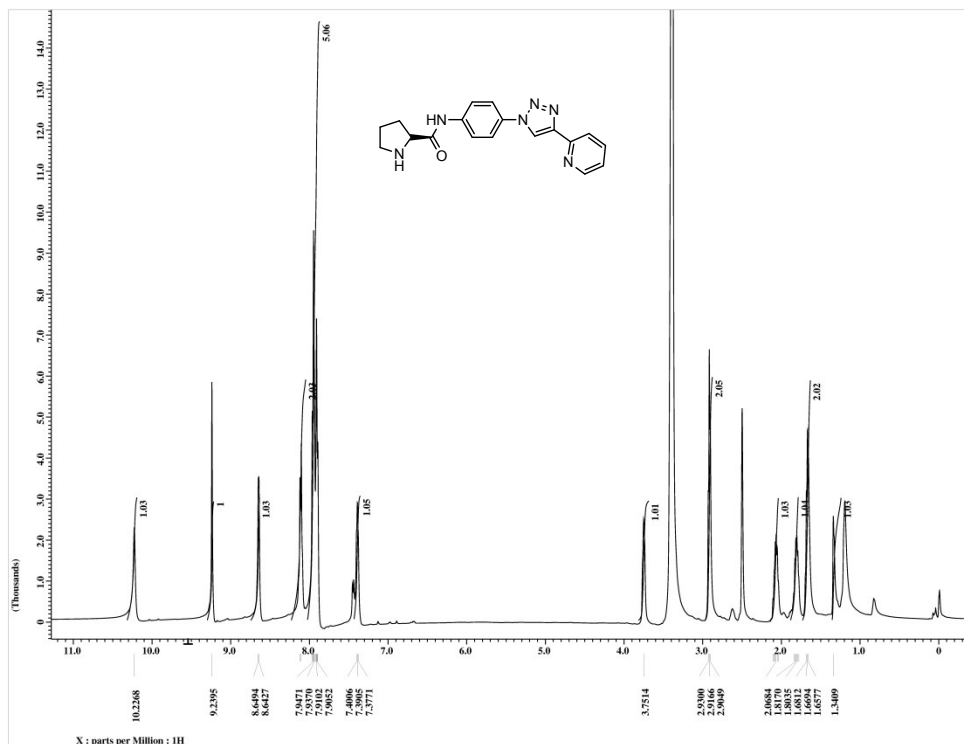
^1H and ^{13}C NMR of Pro-1:



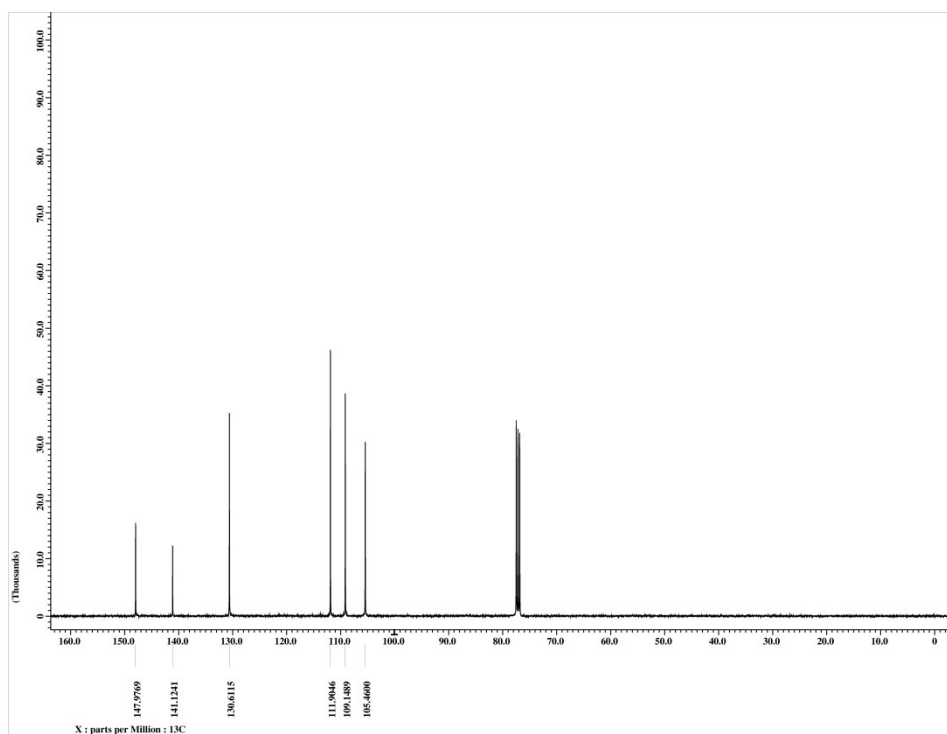
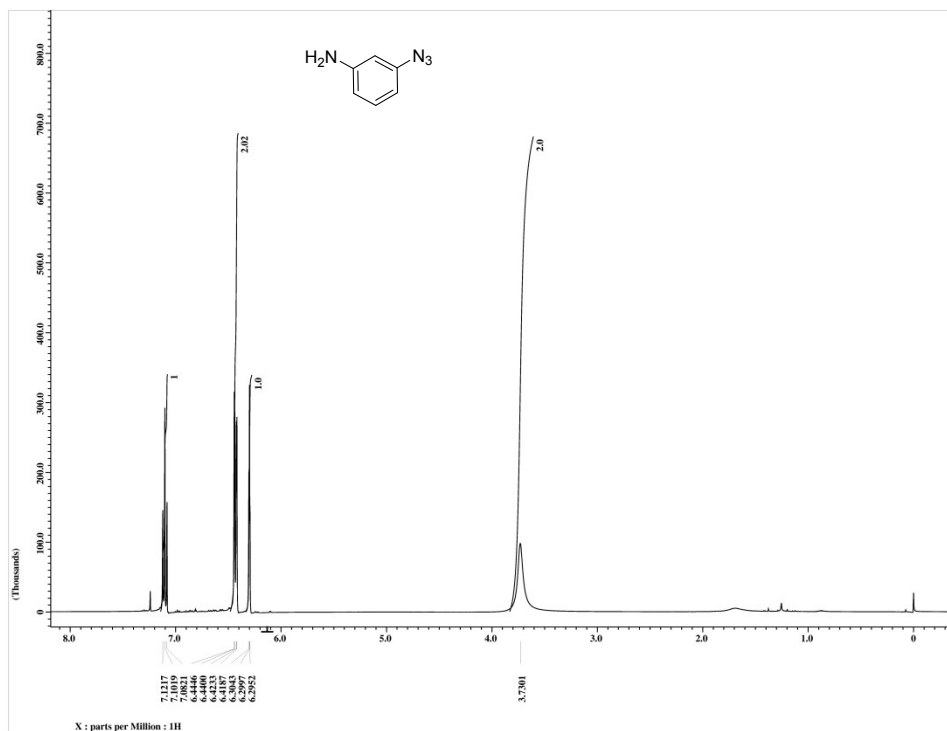
¹H and ¹³C NMR of S7:



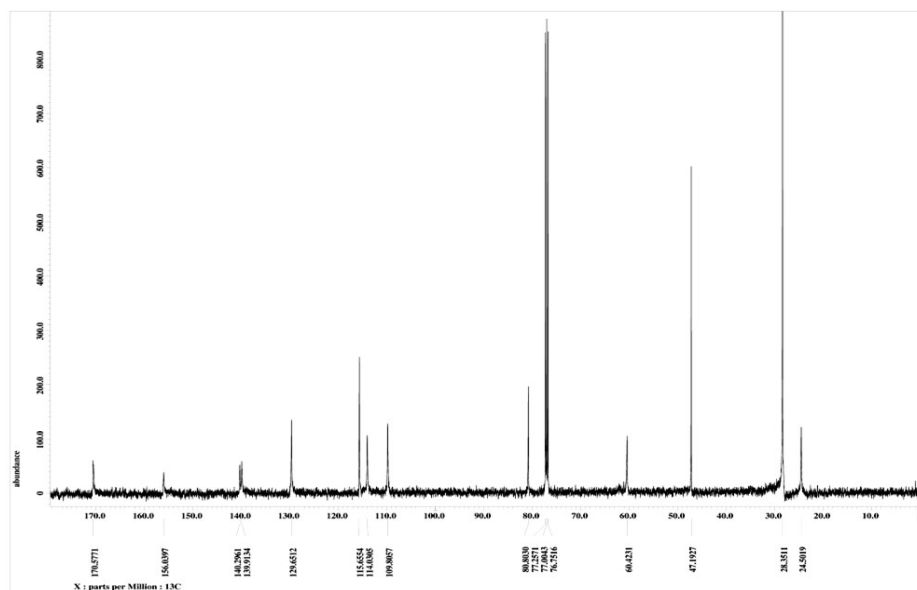
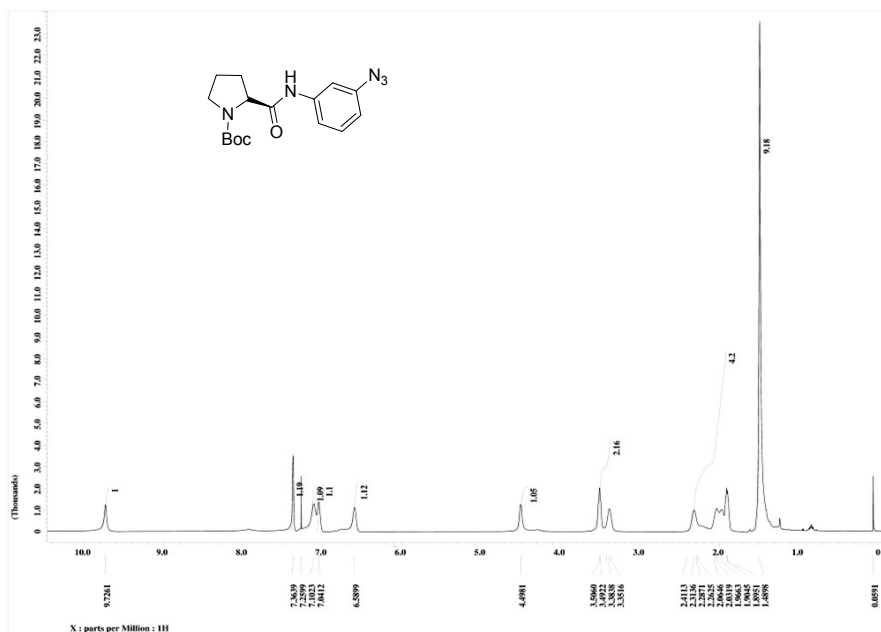
¹H and ¹³C NMR of Pro-2:



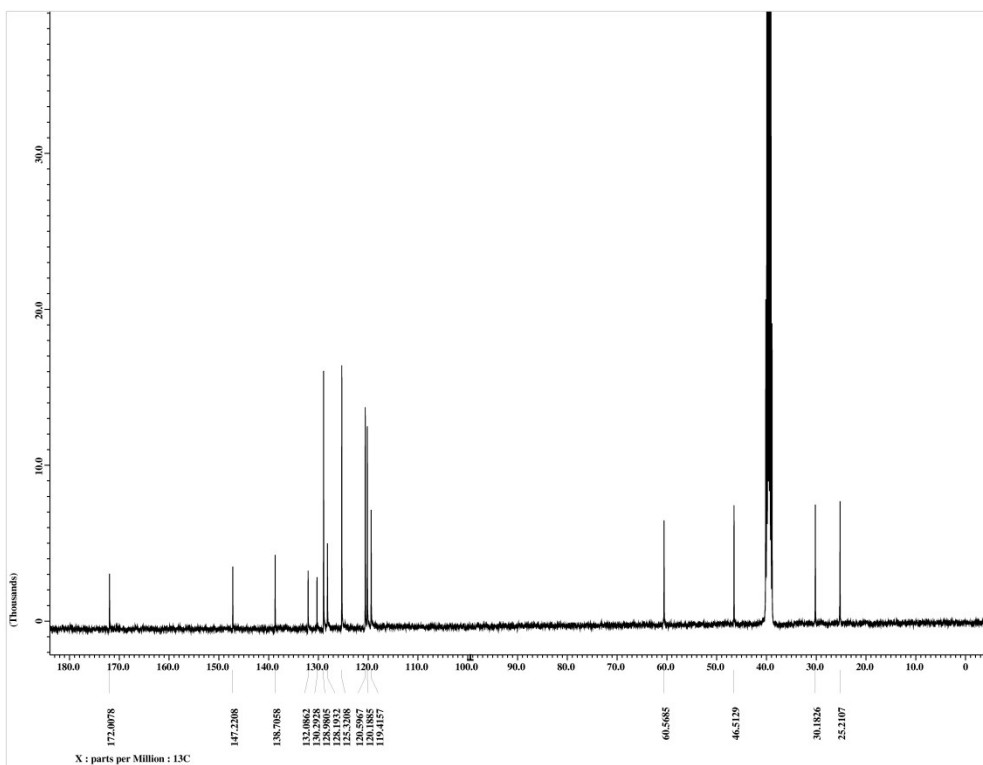
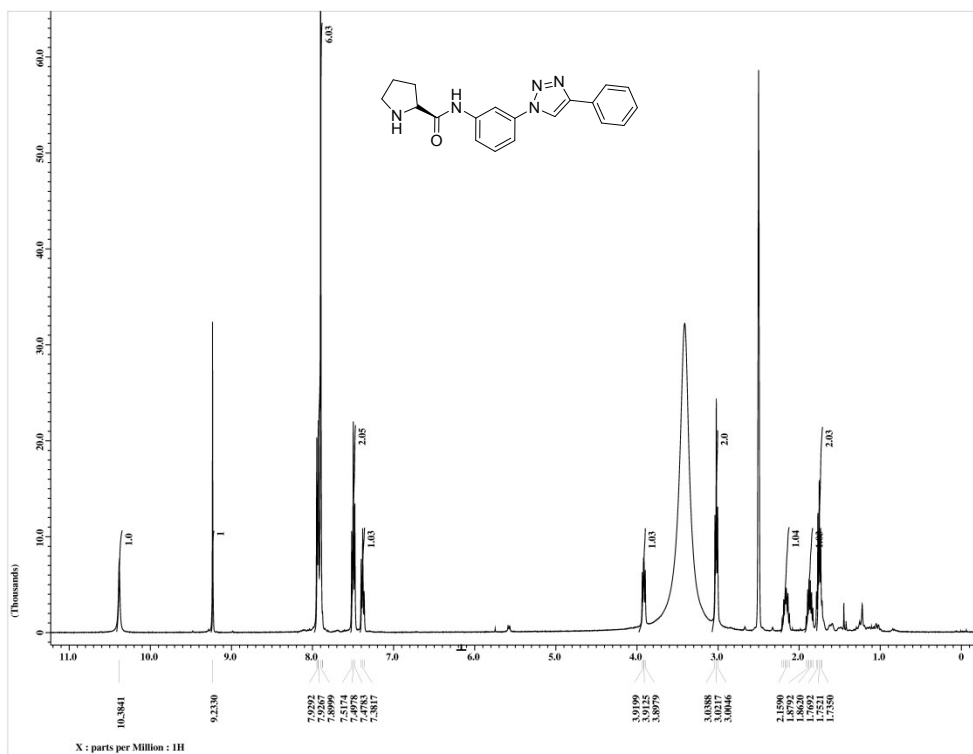
^1H and ^{13}C NMR of S9:



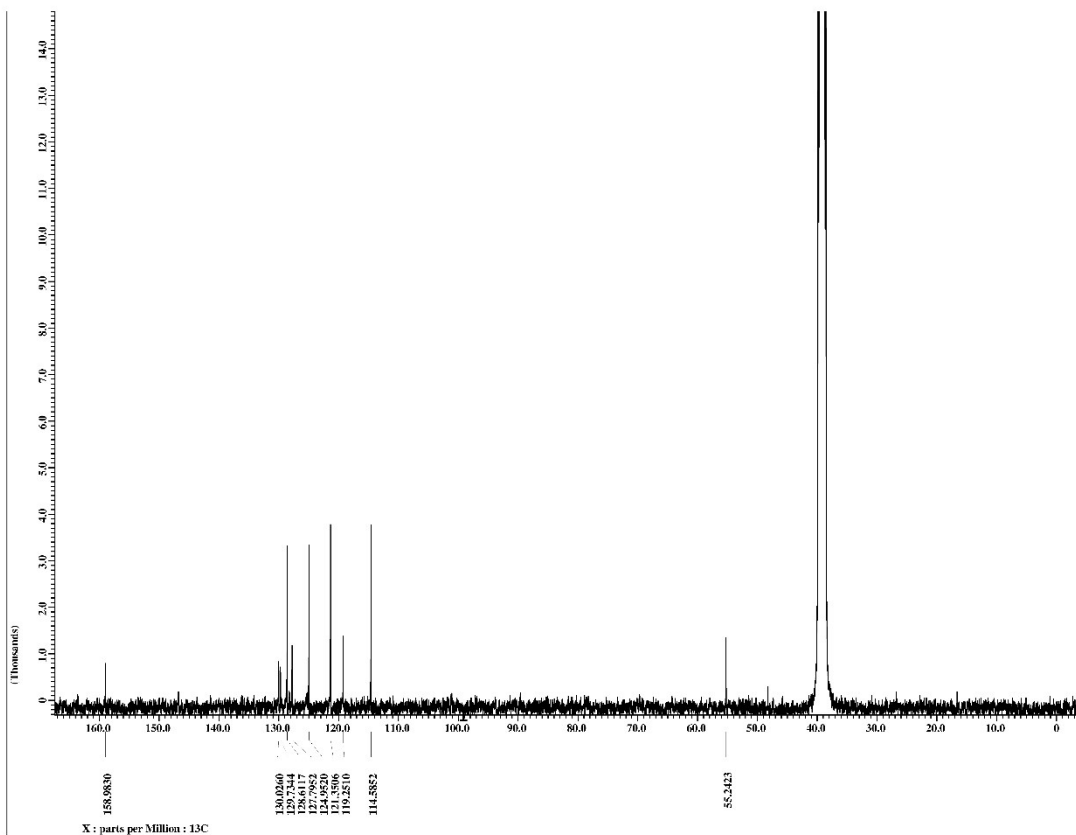
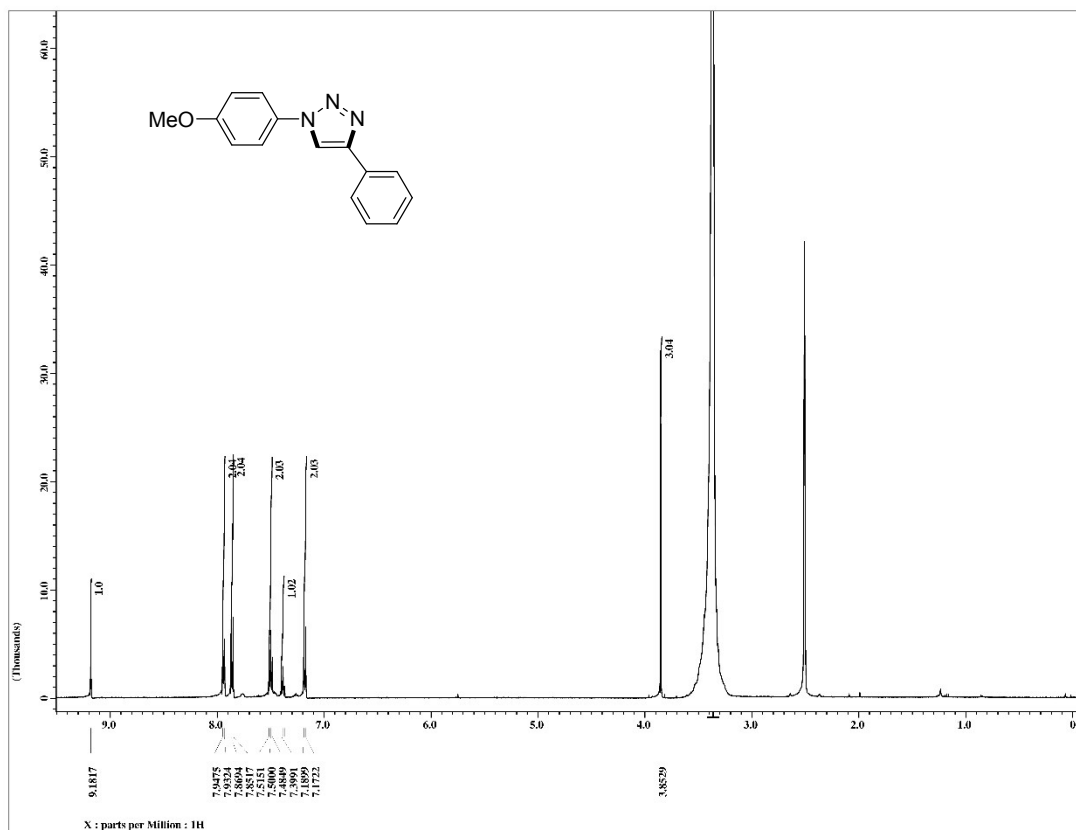
¹H and ¹³C NMR of S10:



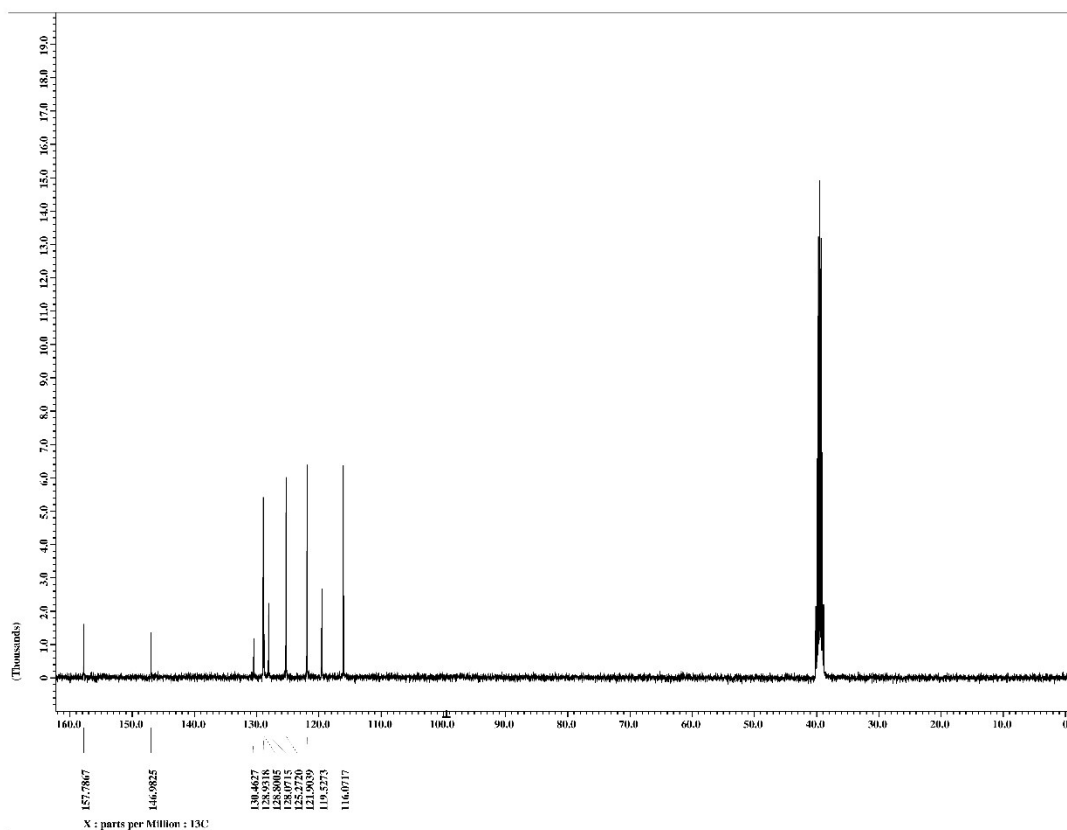
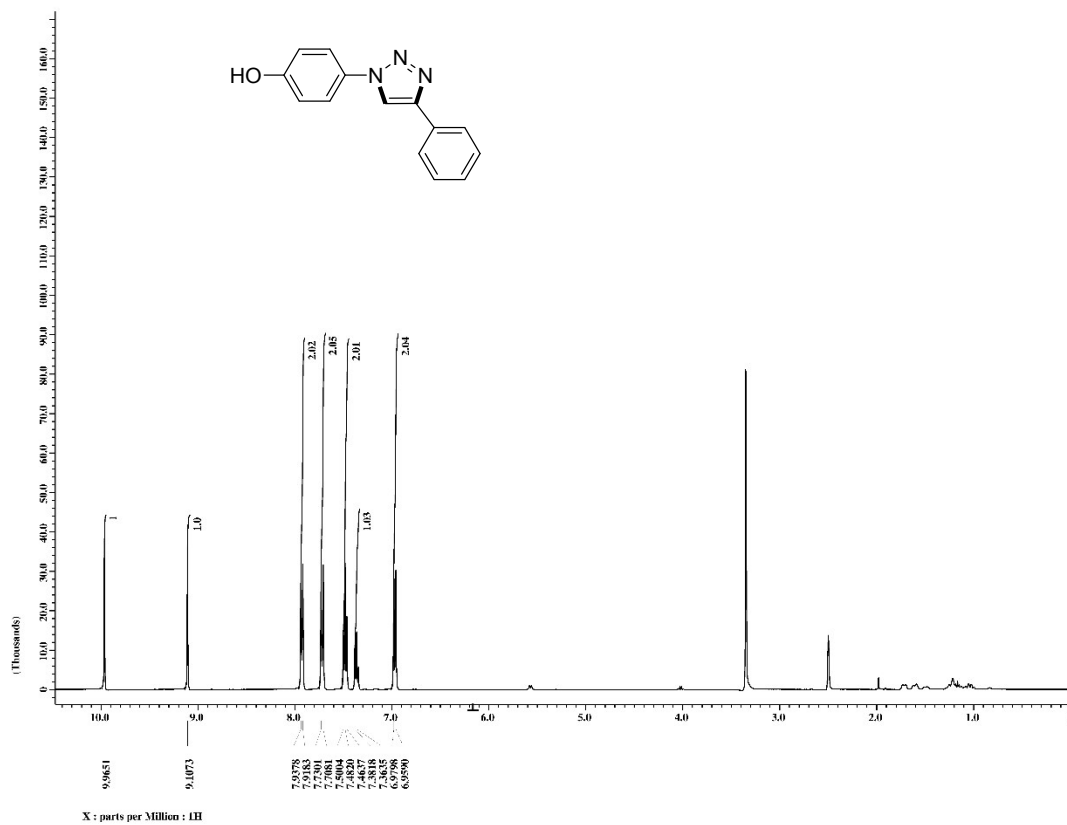
¹H and ¹³C NMR of Pro-3:



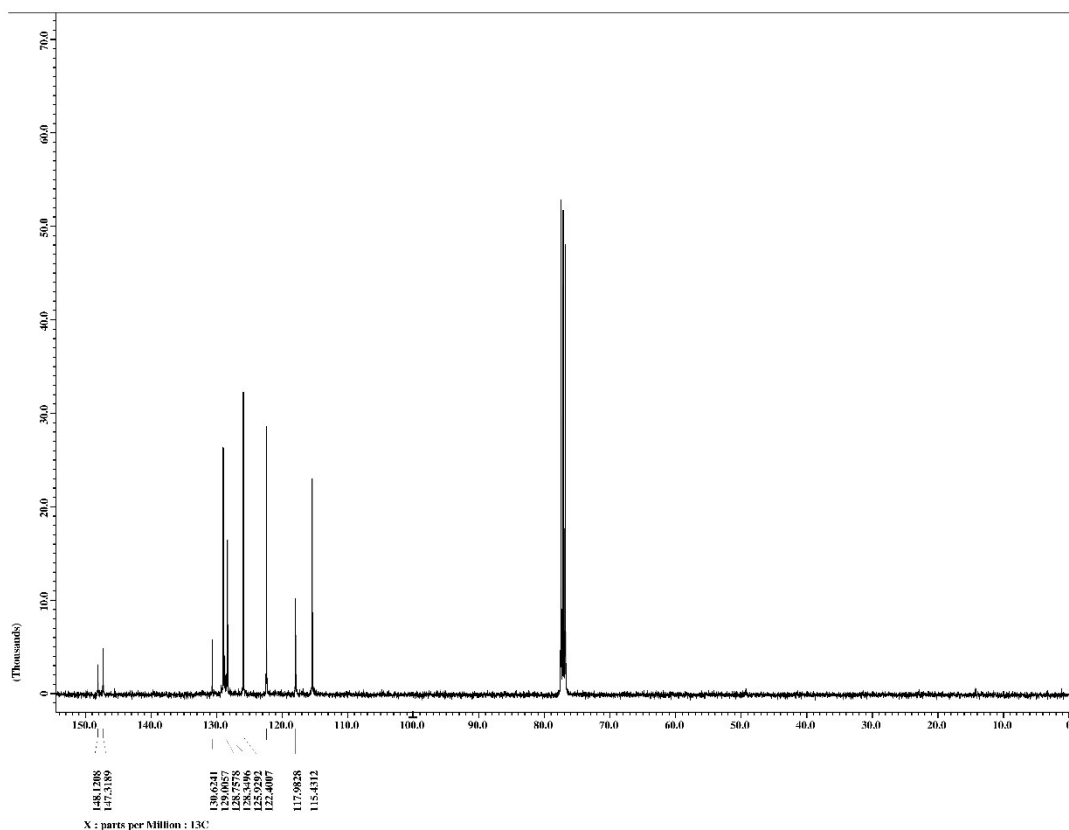
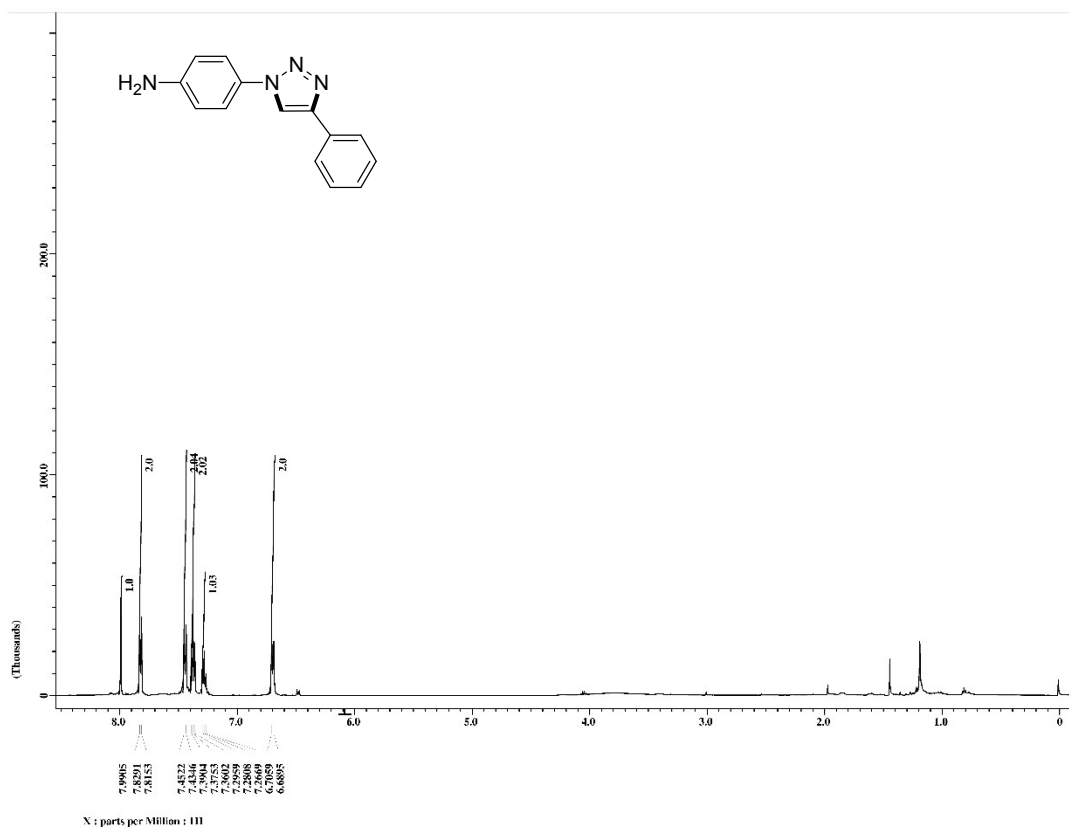
^1H and ^{13}C NMR of 3a:



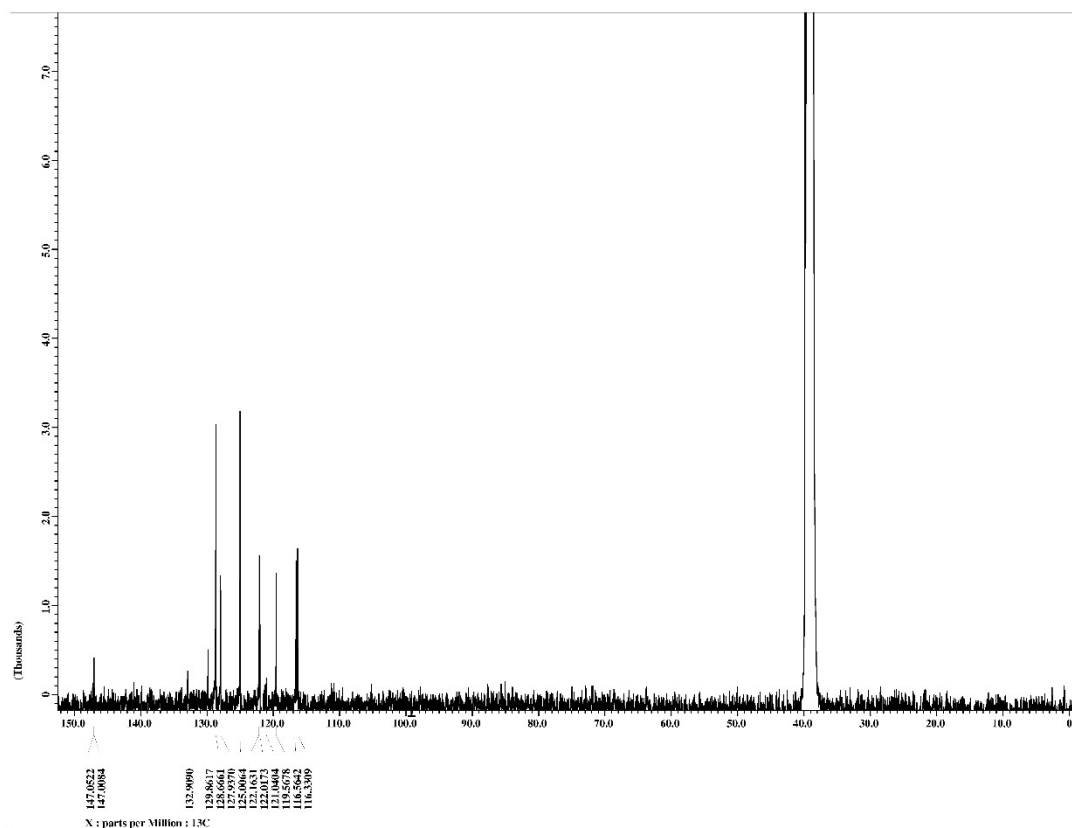
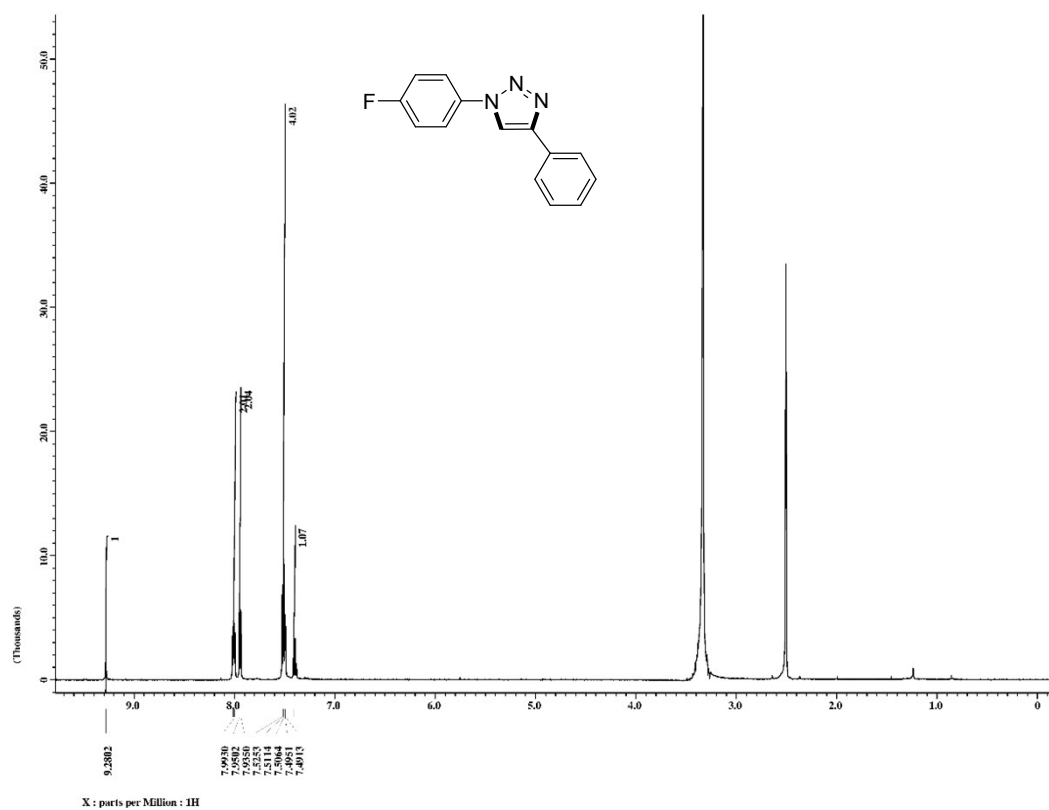
¹H and ¹³C NMR of 3b:



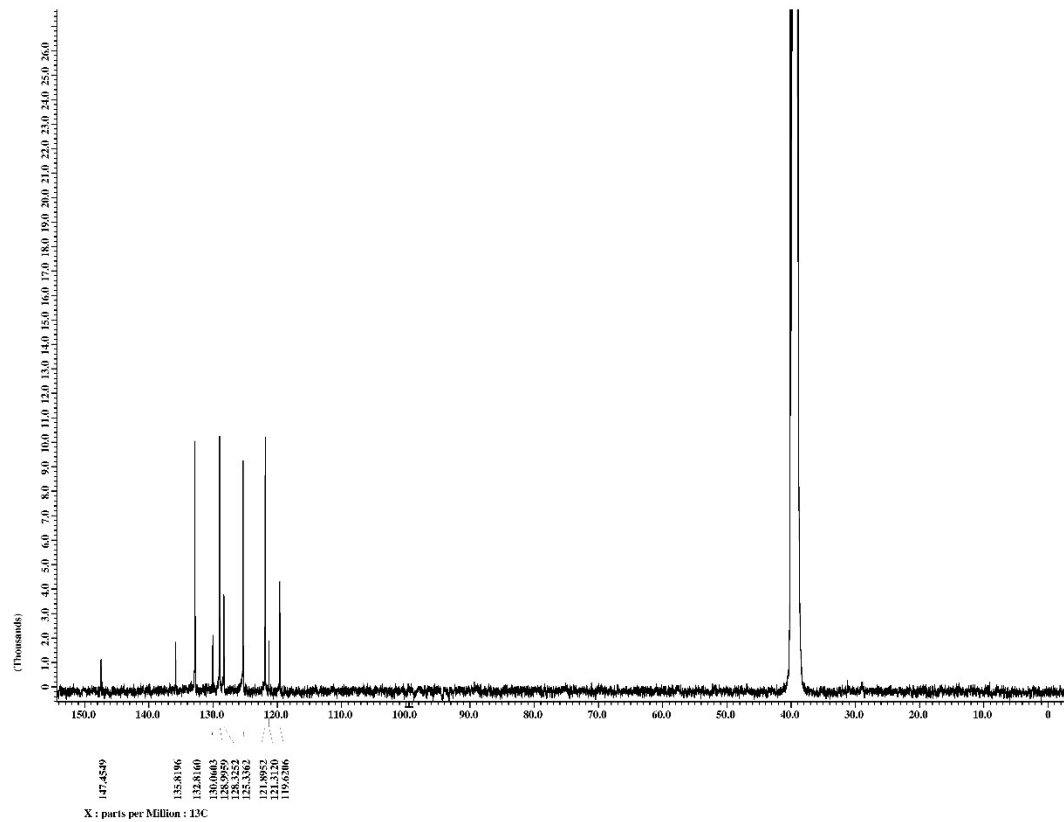
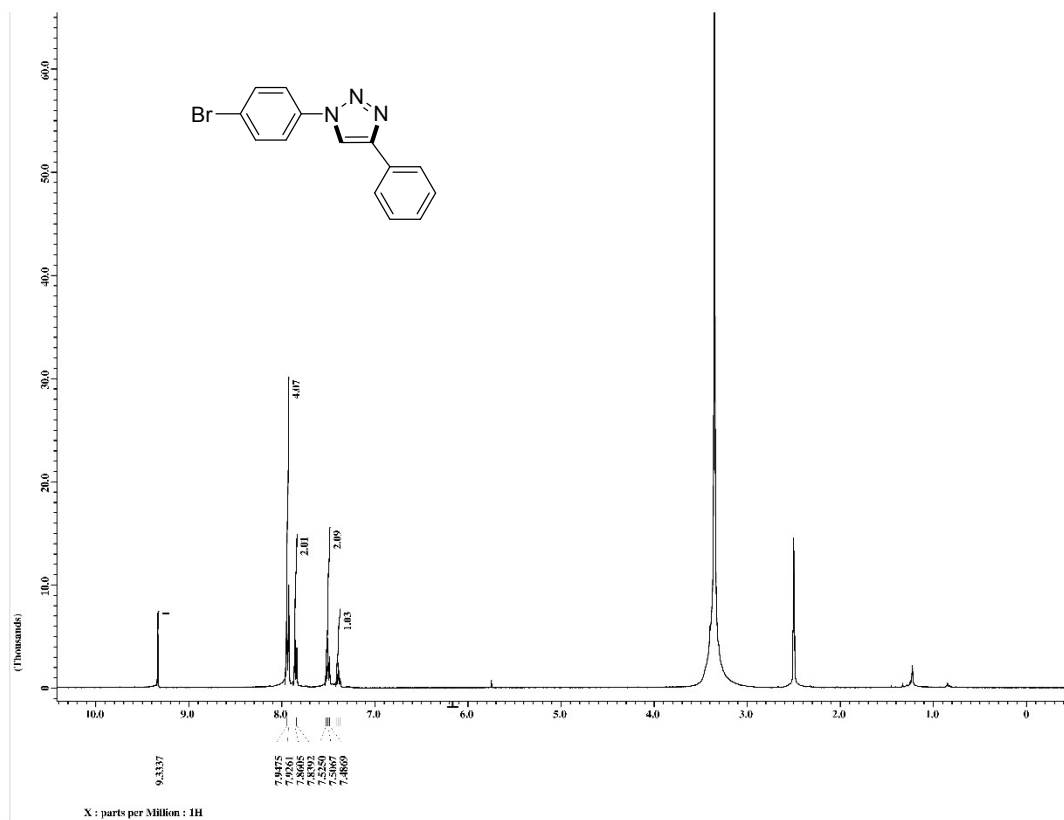
¹H and ¹³C NMR of 3c:



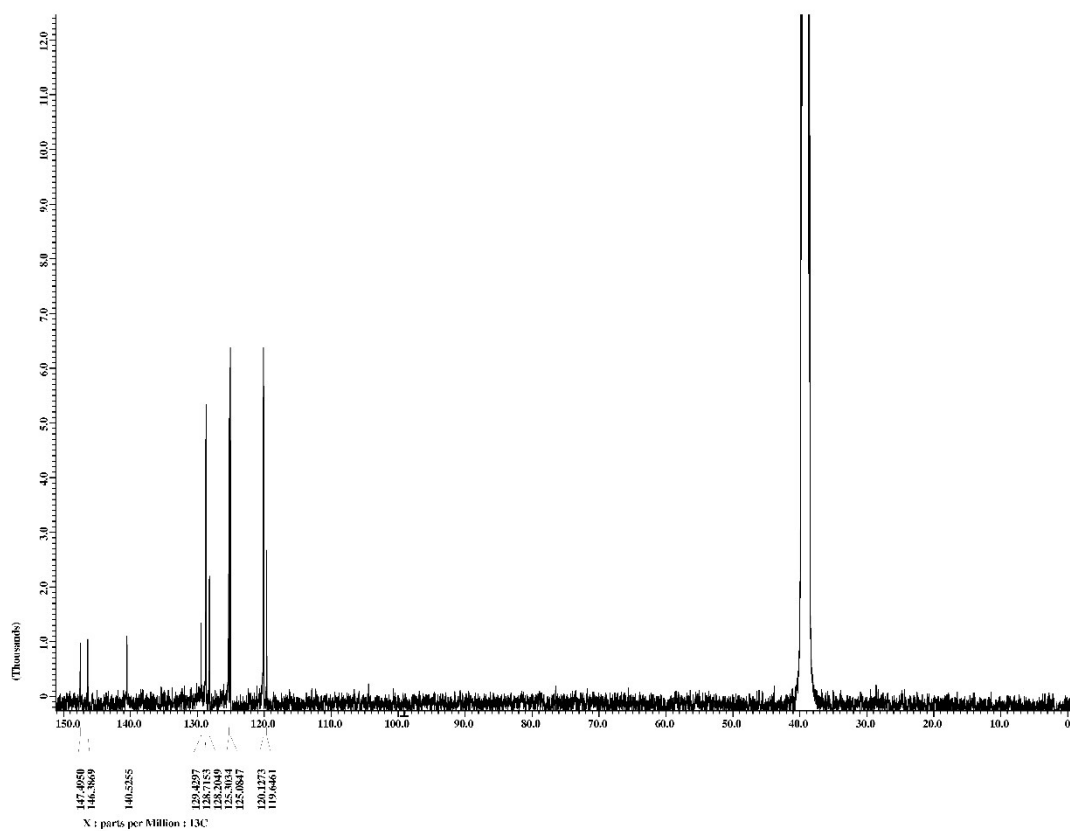
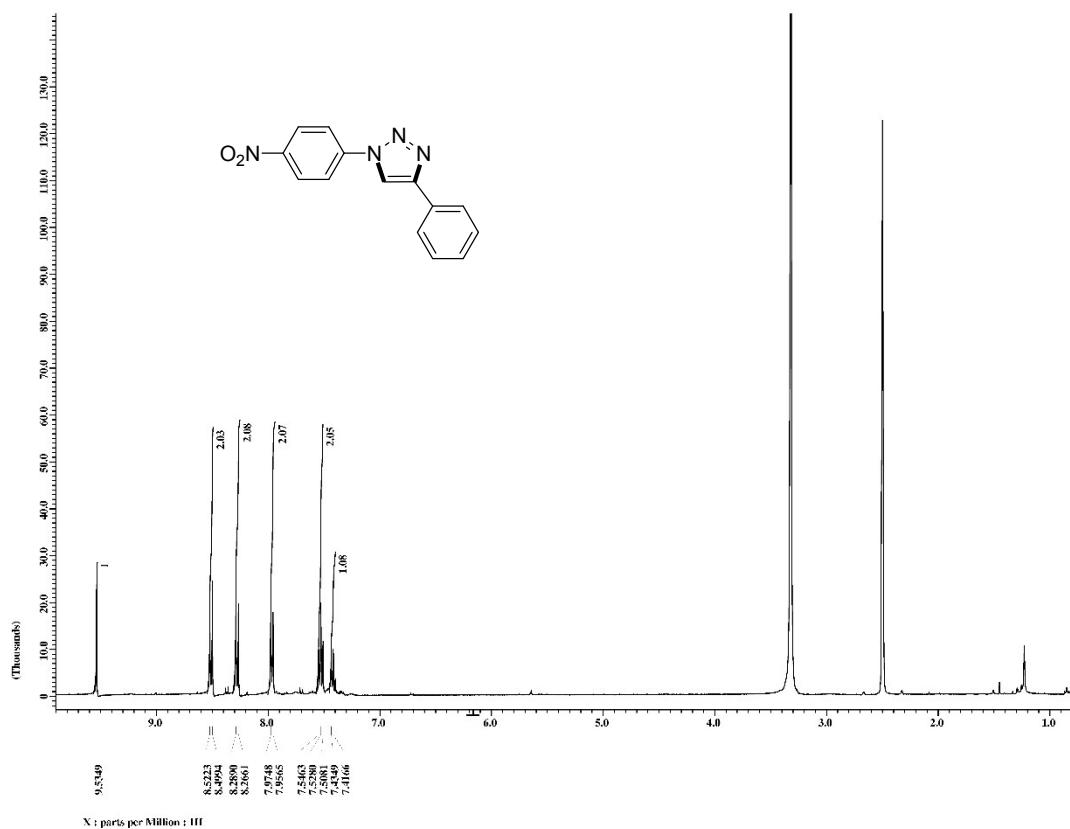
¹H and ¹³C NMR of 3d:



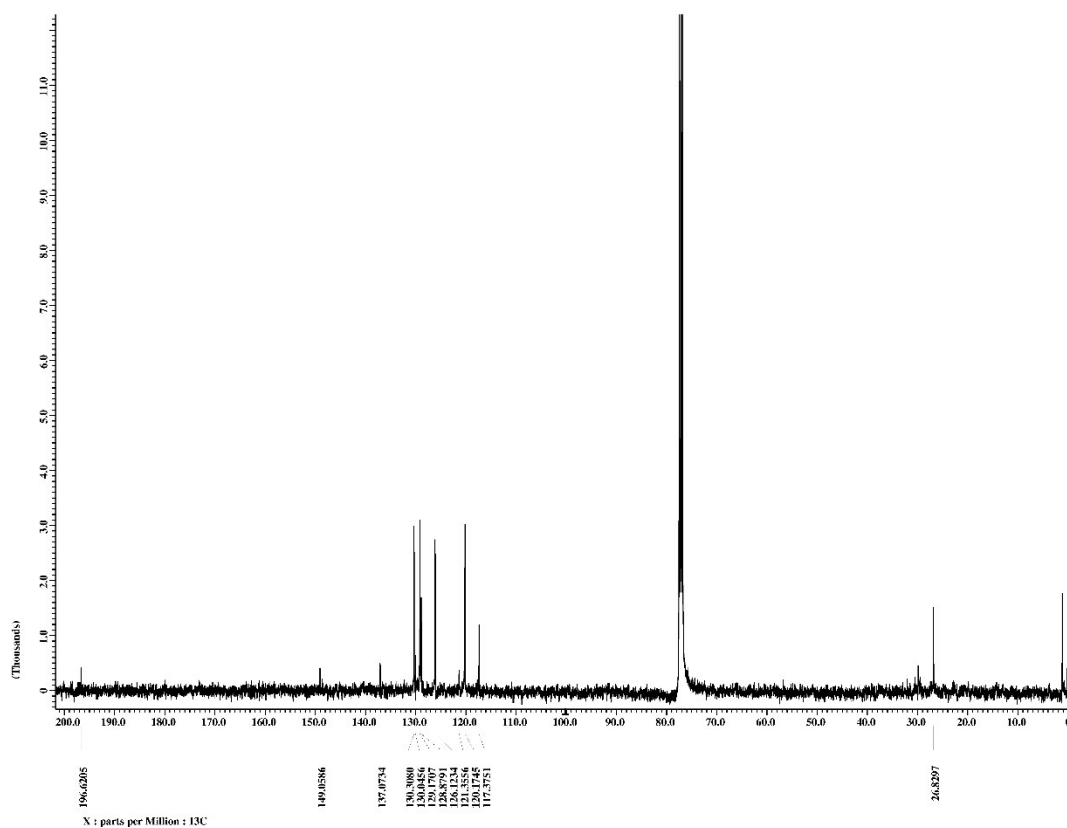
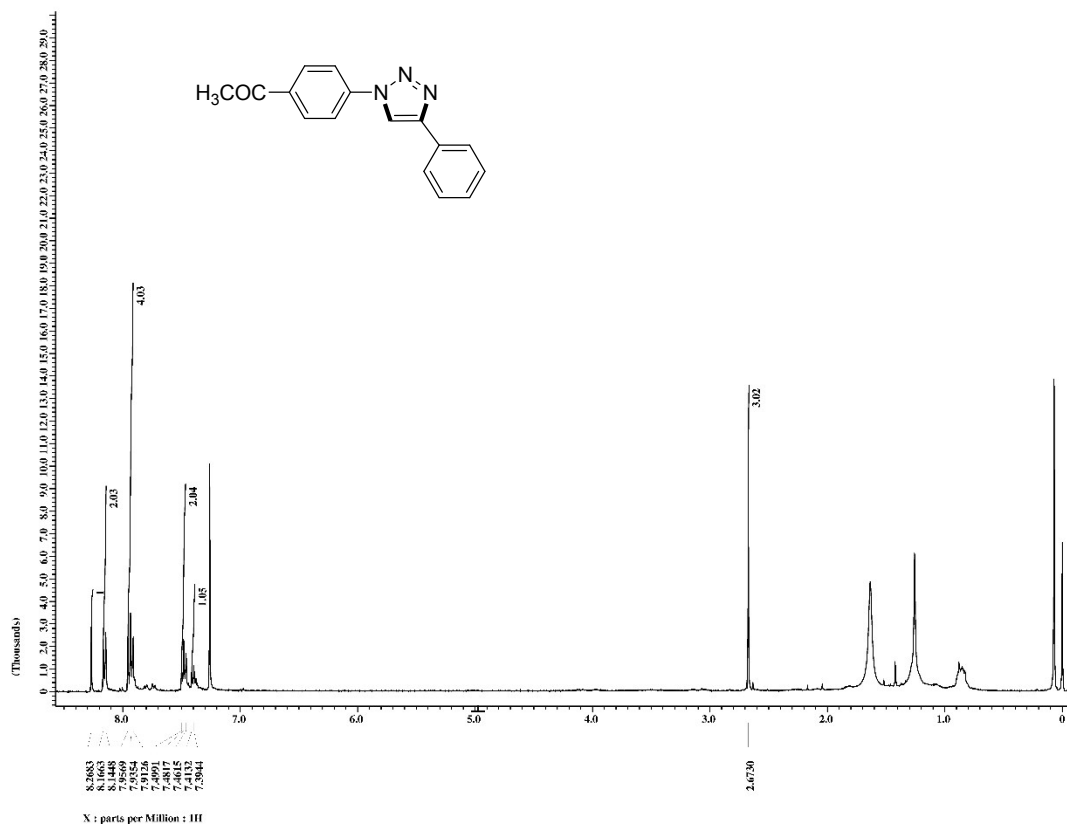
^1H and ^{13}C NMR of 3e:



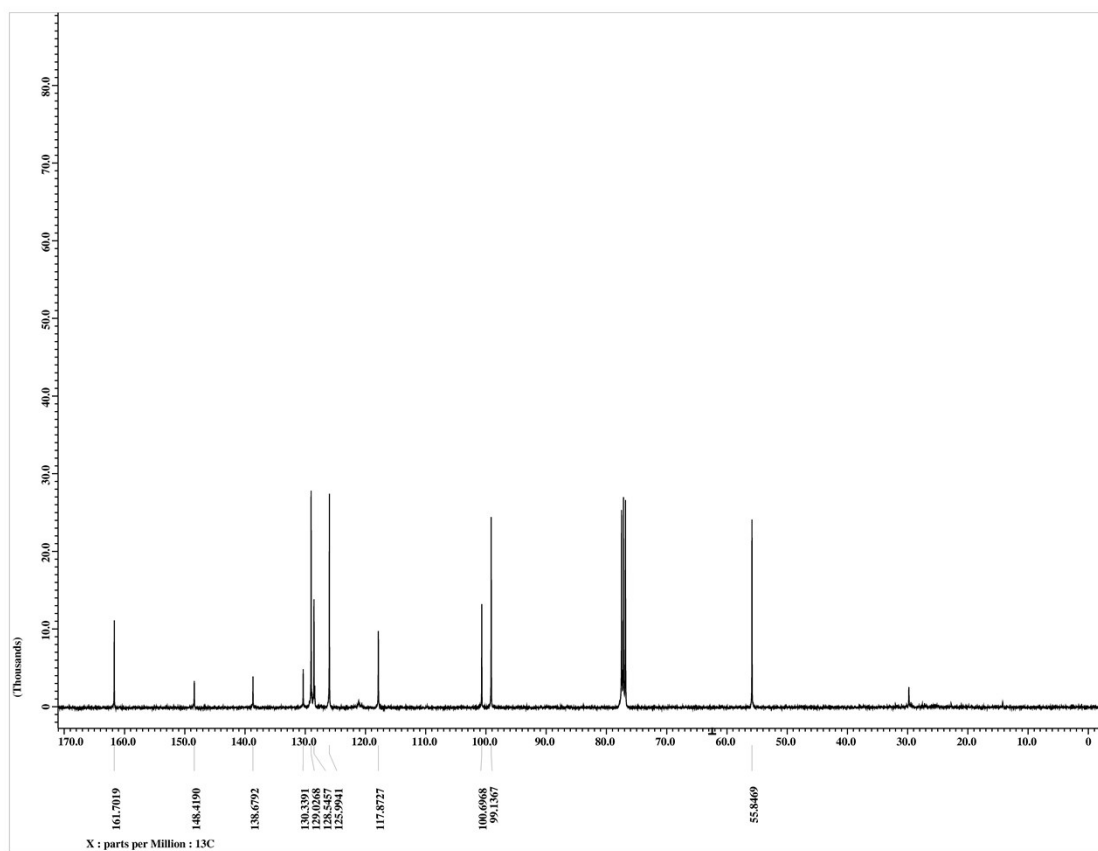
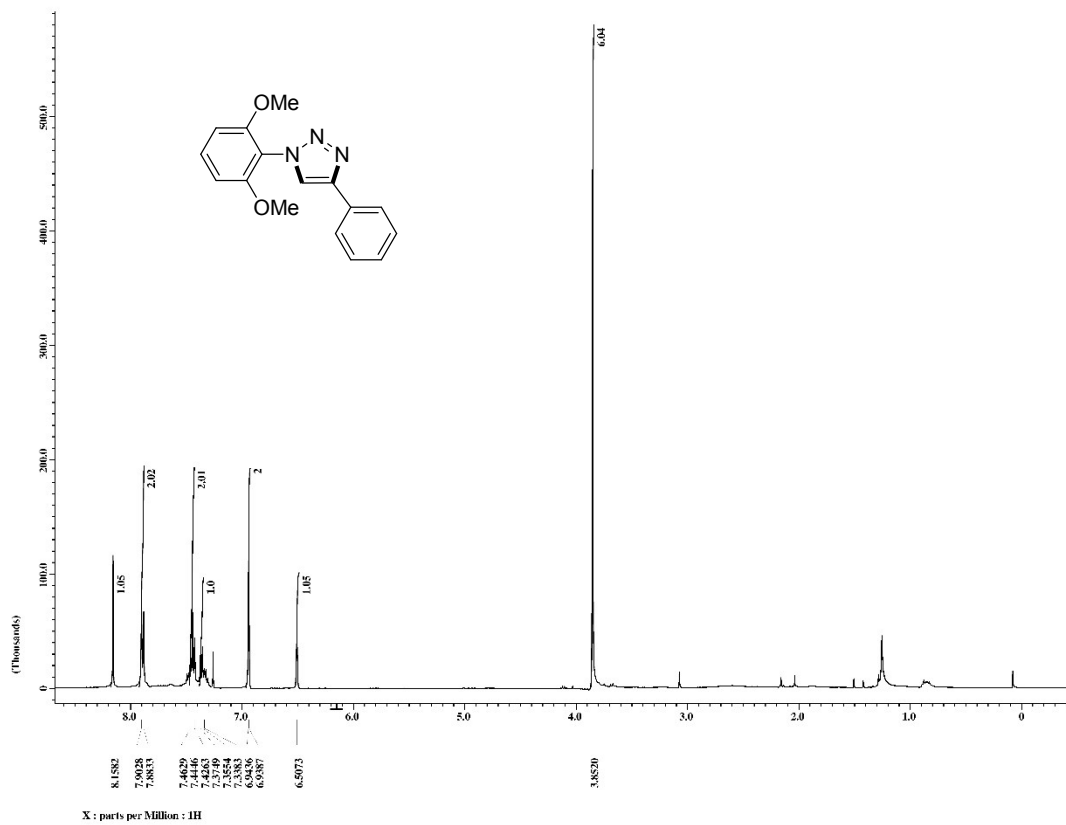
¹H and ¹³C NMR of 3f:



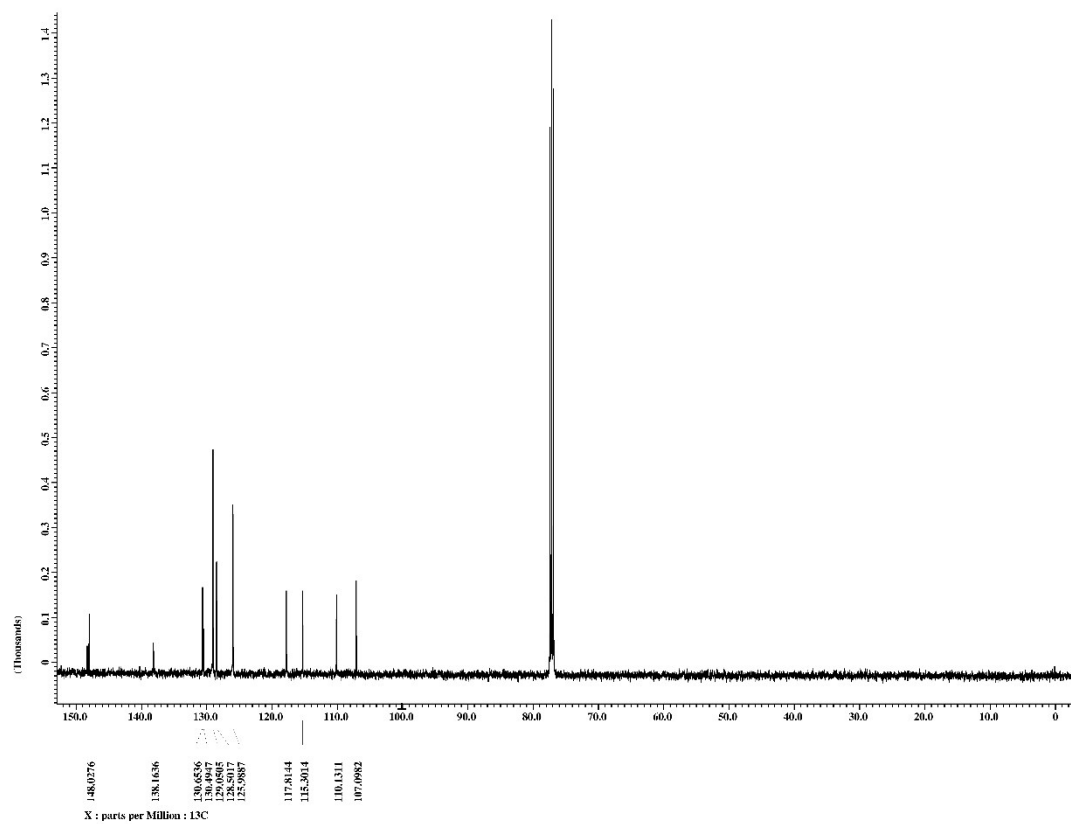
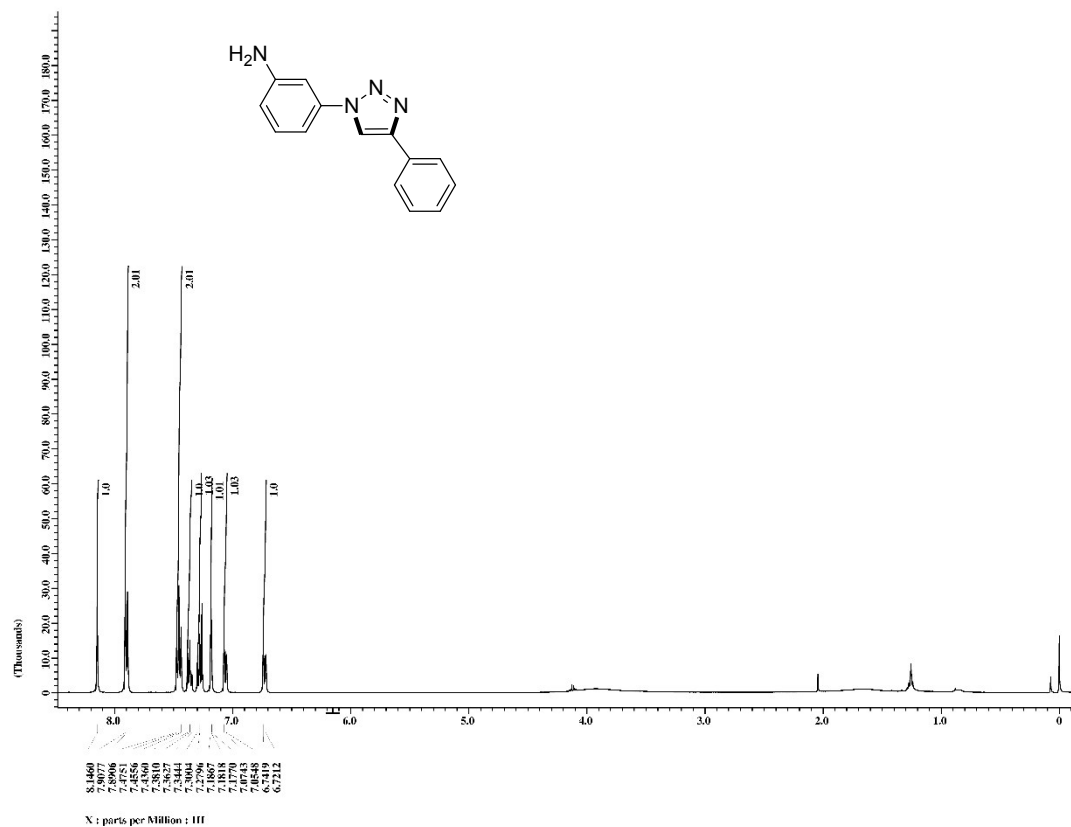
¹H and ¹³C NMR of 3g:



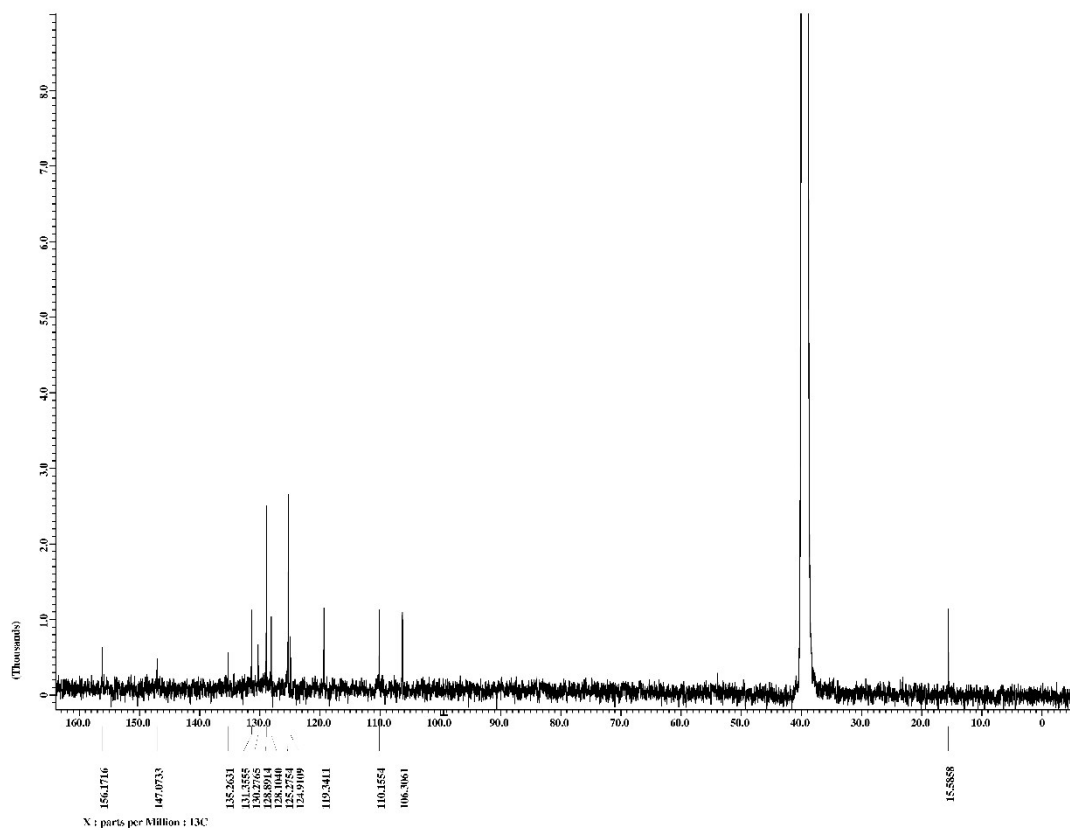
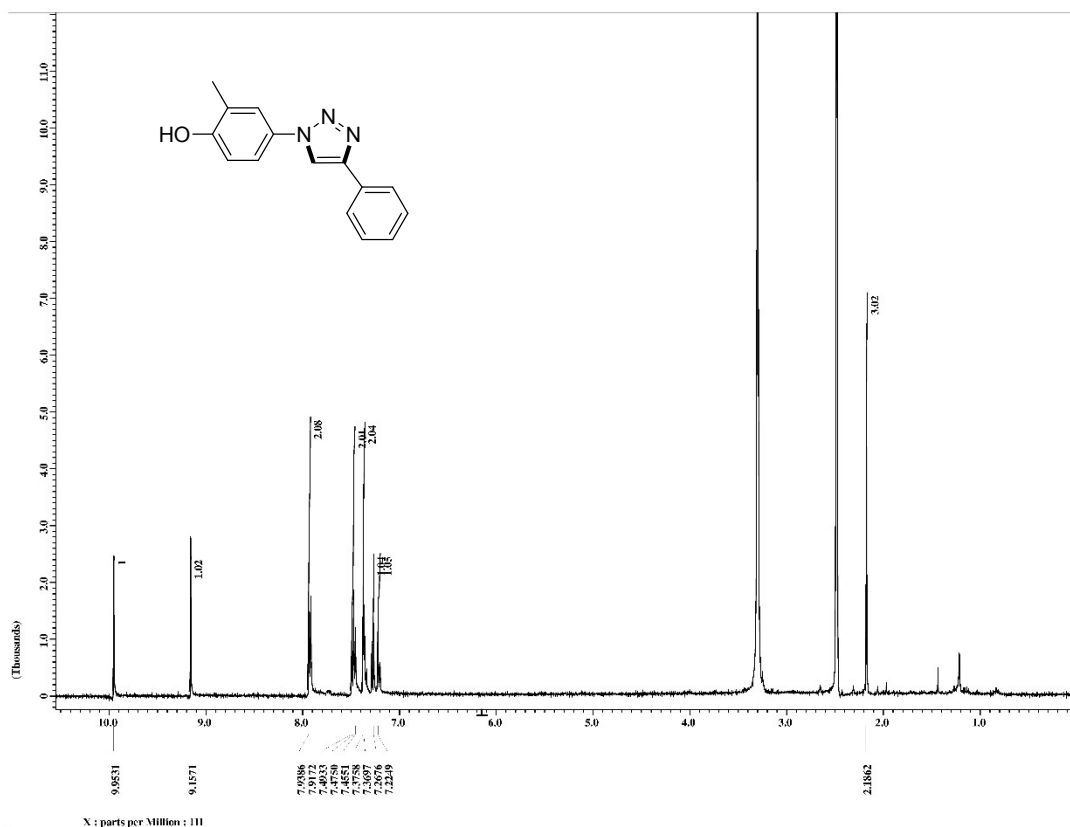
^1H and ^{13}C NMR of 3i:



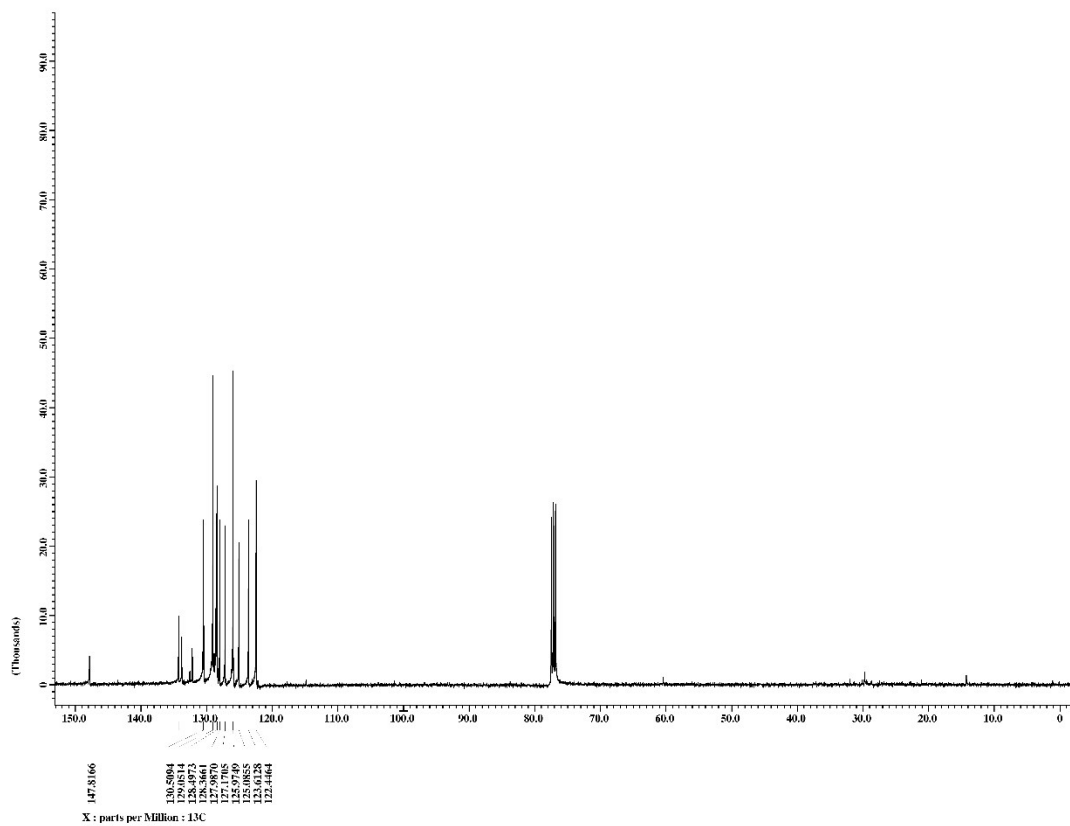
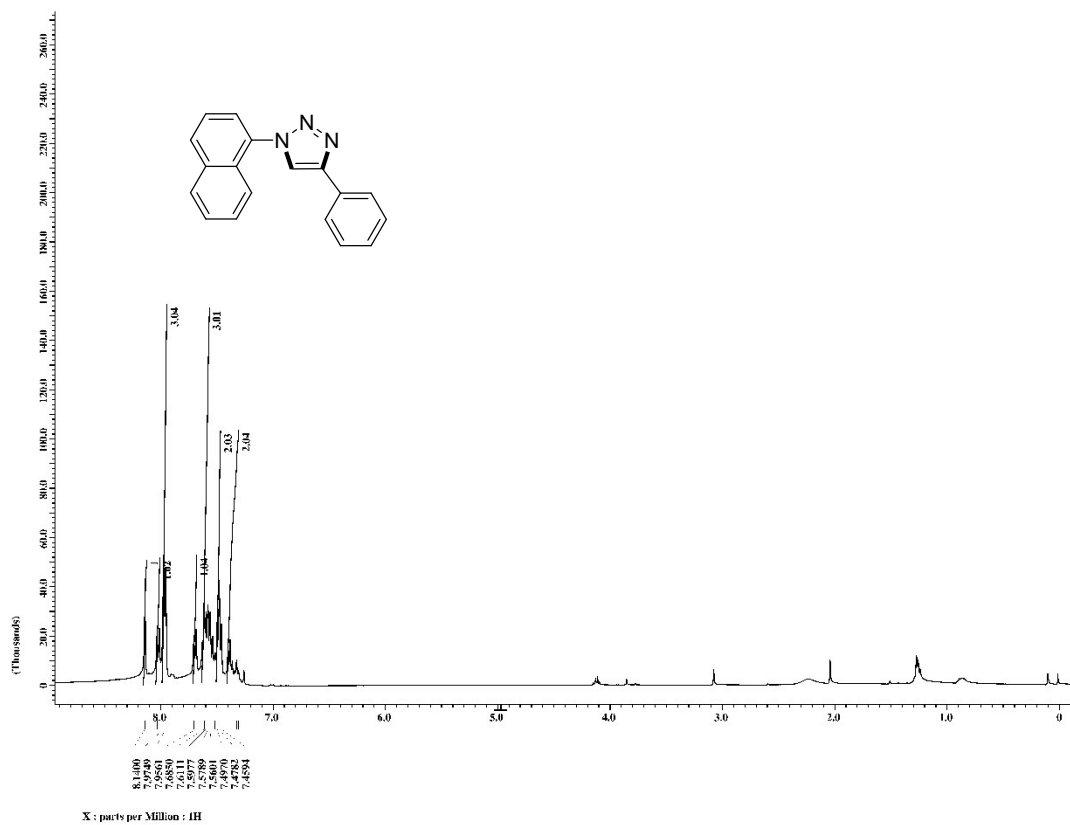
¹H and ¹³C NMR of 3j:



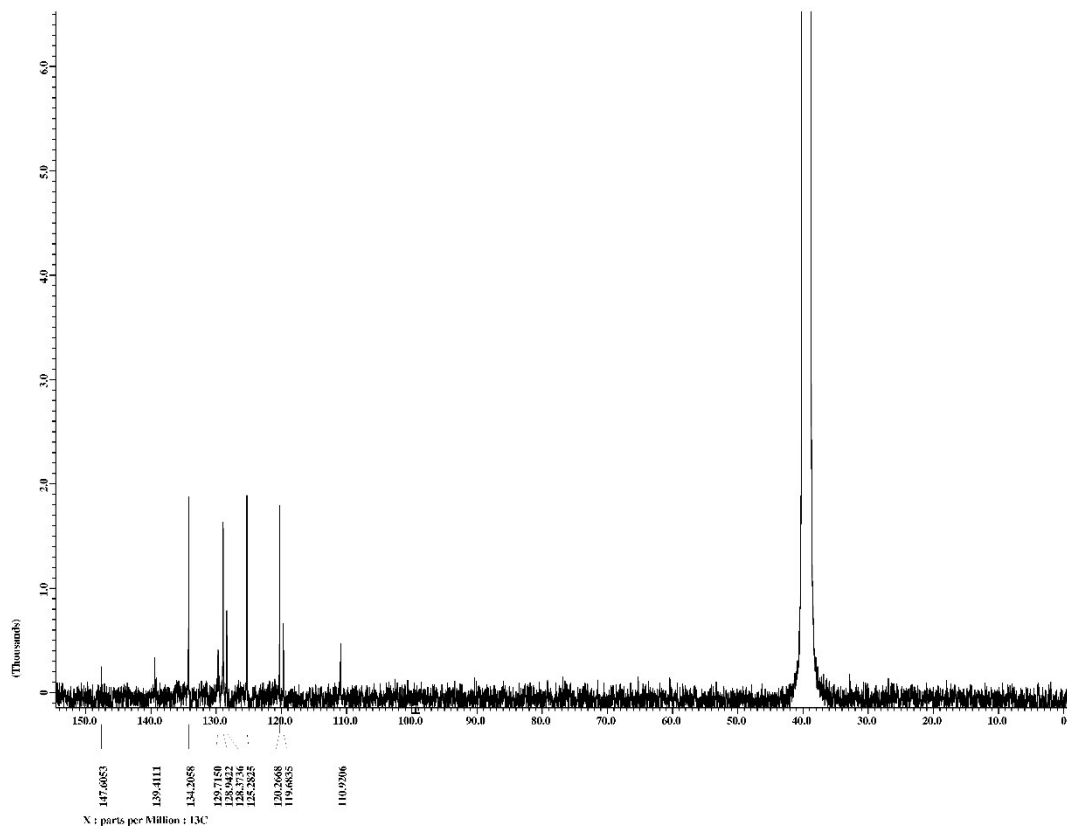
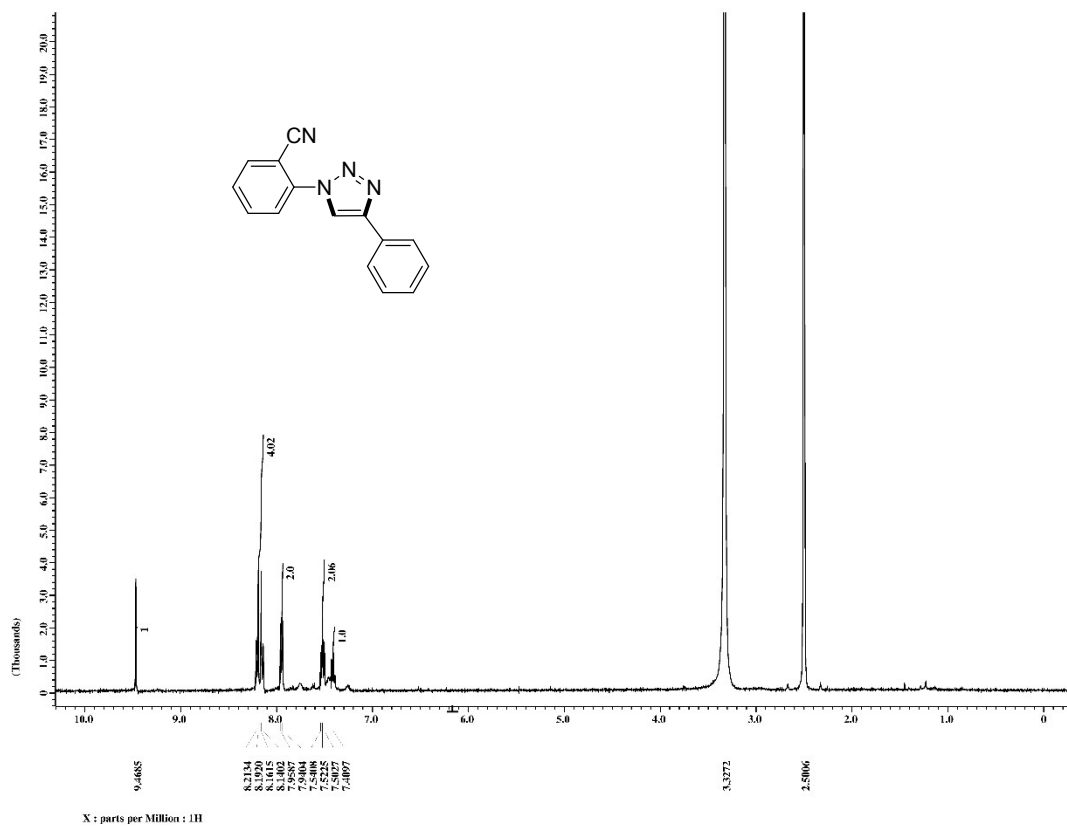
¹H and ¹³C NMR of 3k:



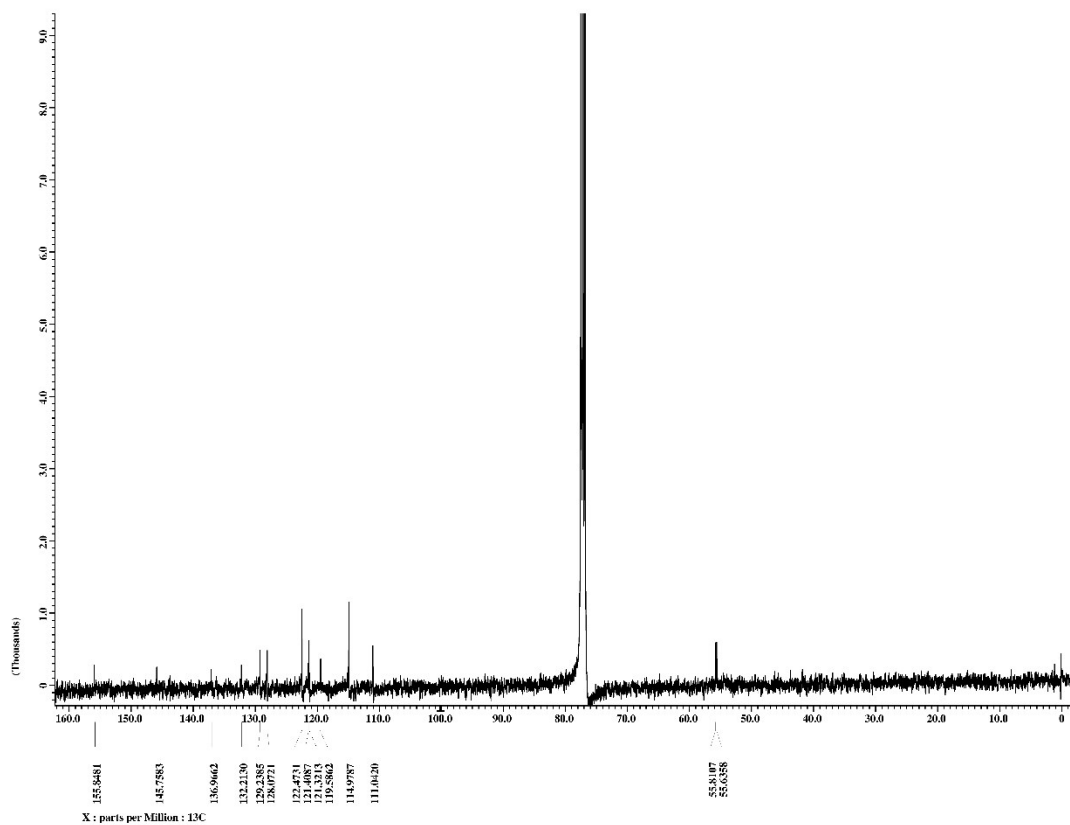
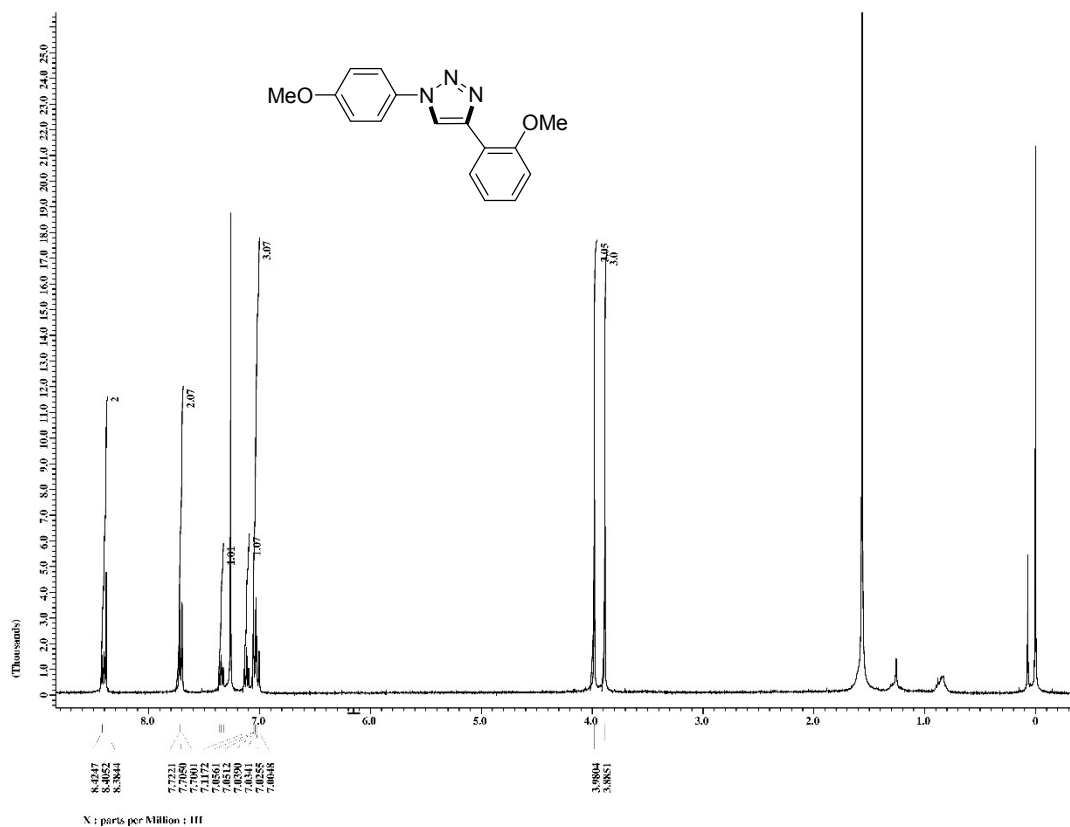
^1H and ^{13}C NMR of 3l:



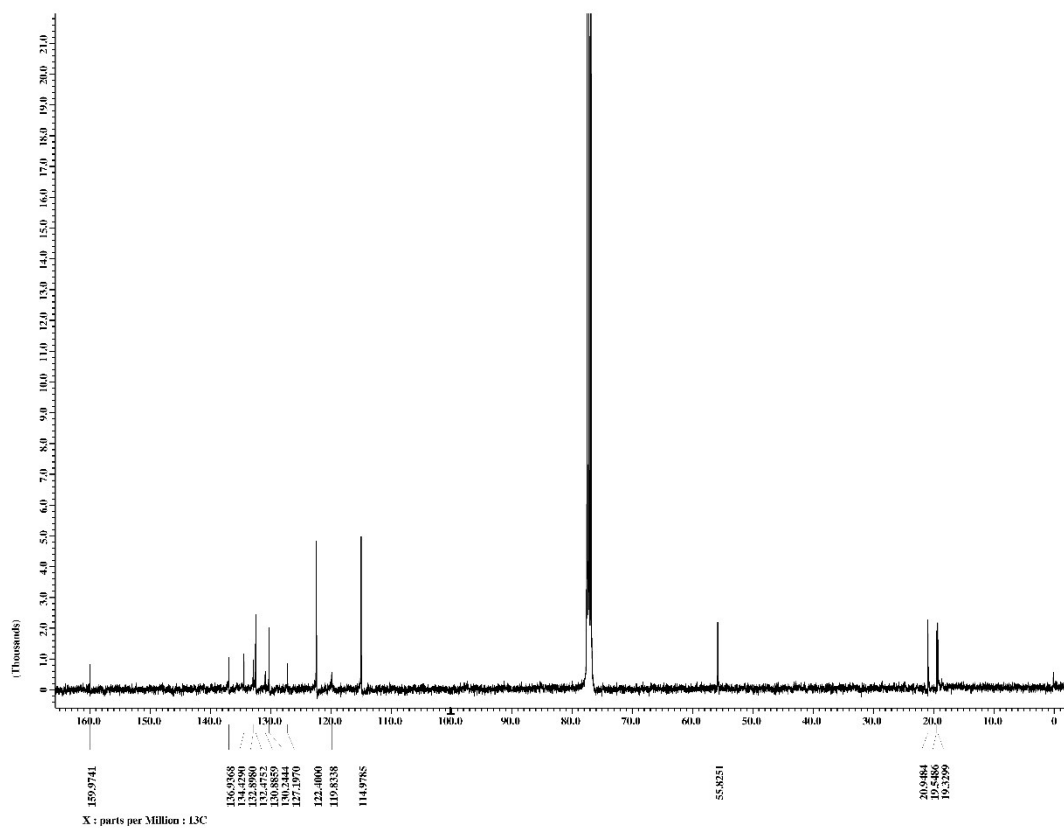
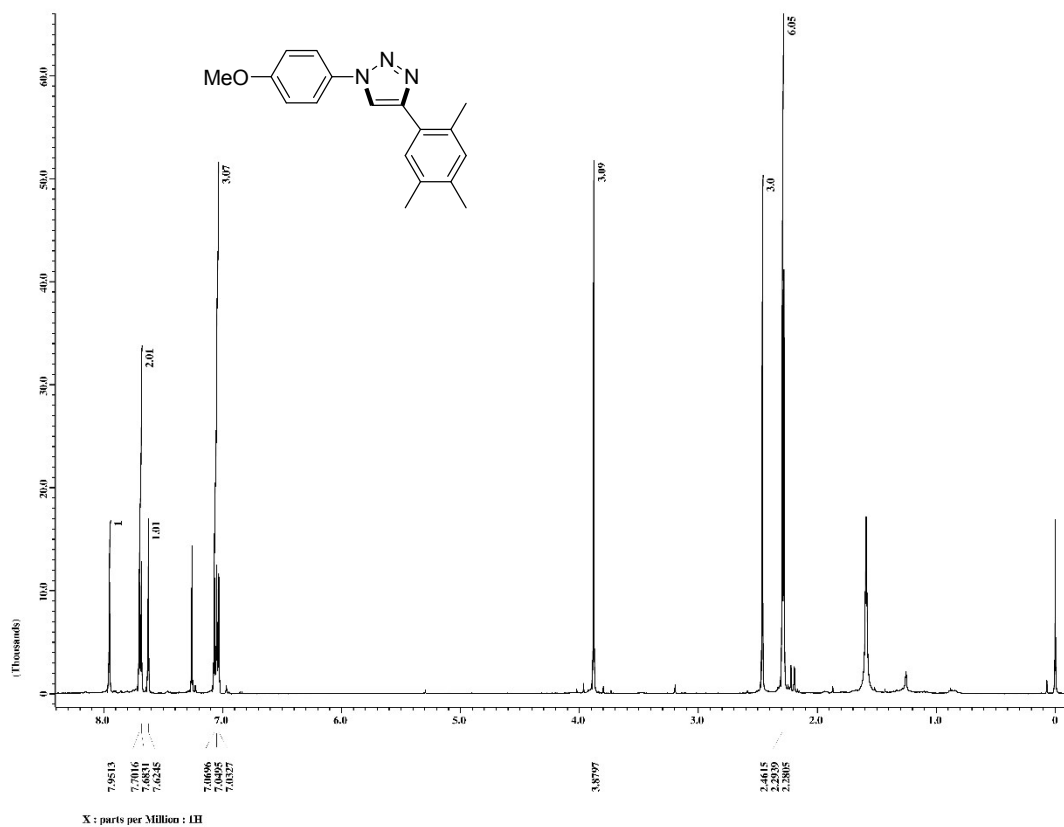
¹H and ¹³C NMR of 3m:



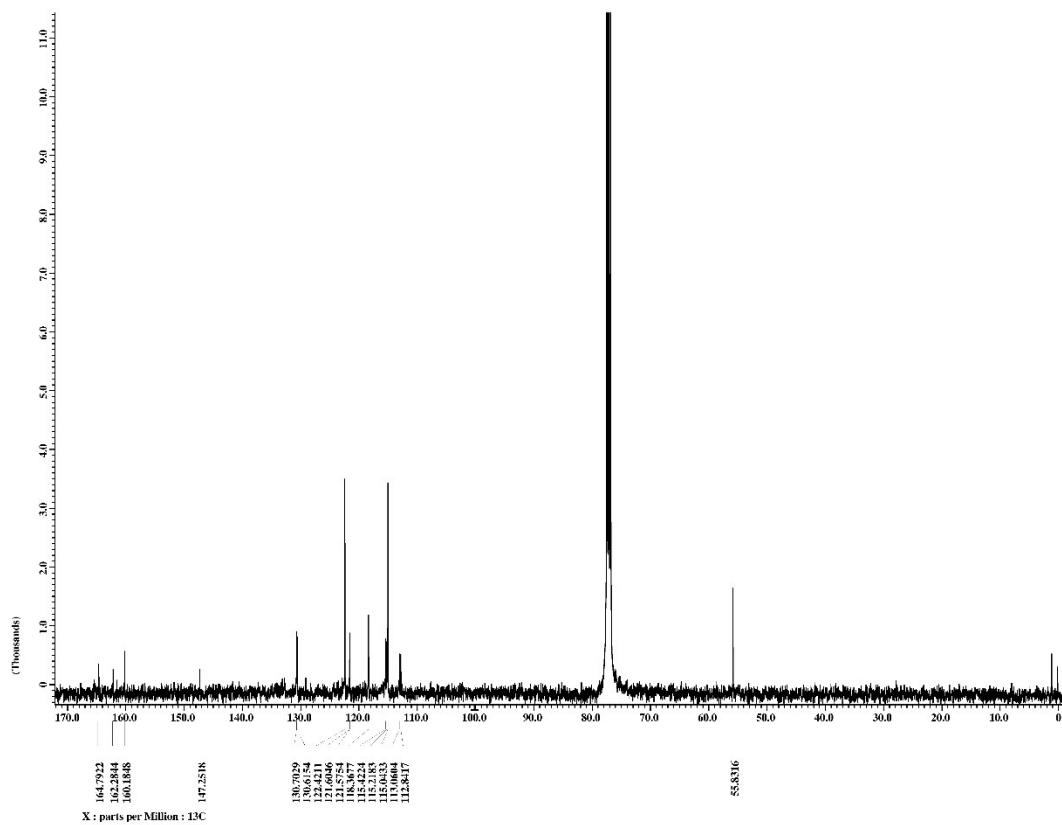
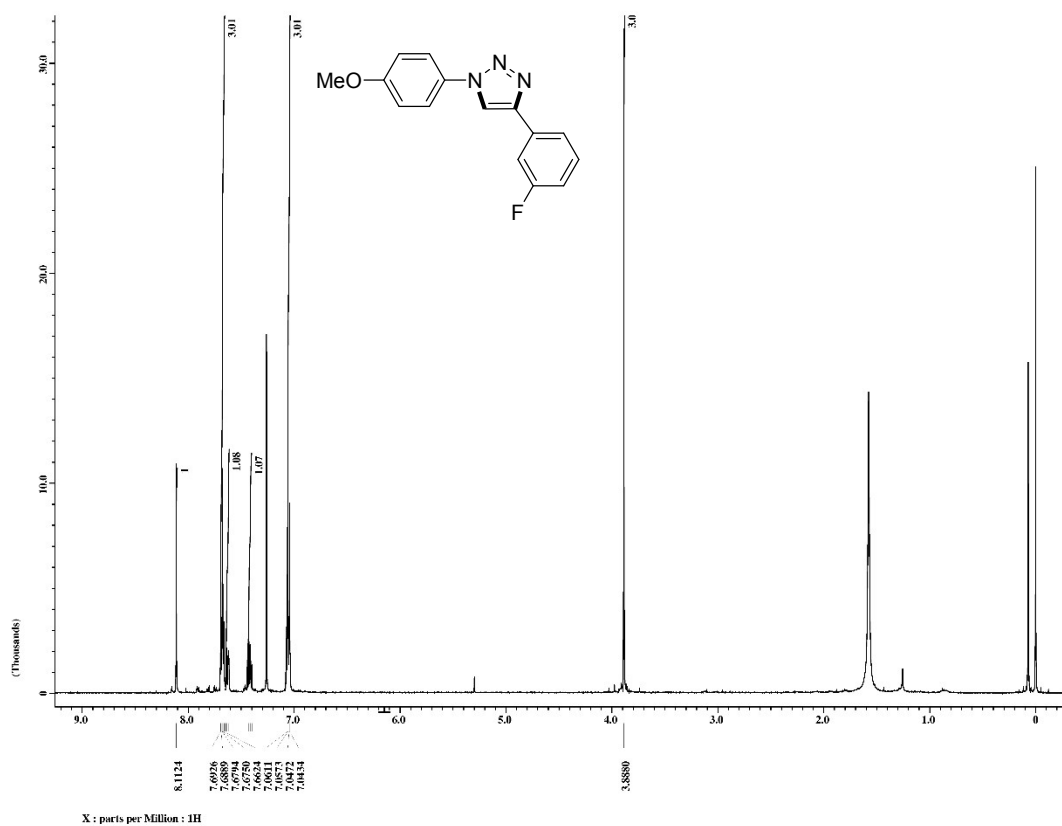
¹H and ¹³C NMR of 3n:



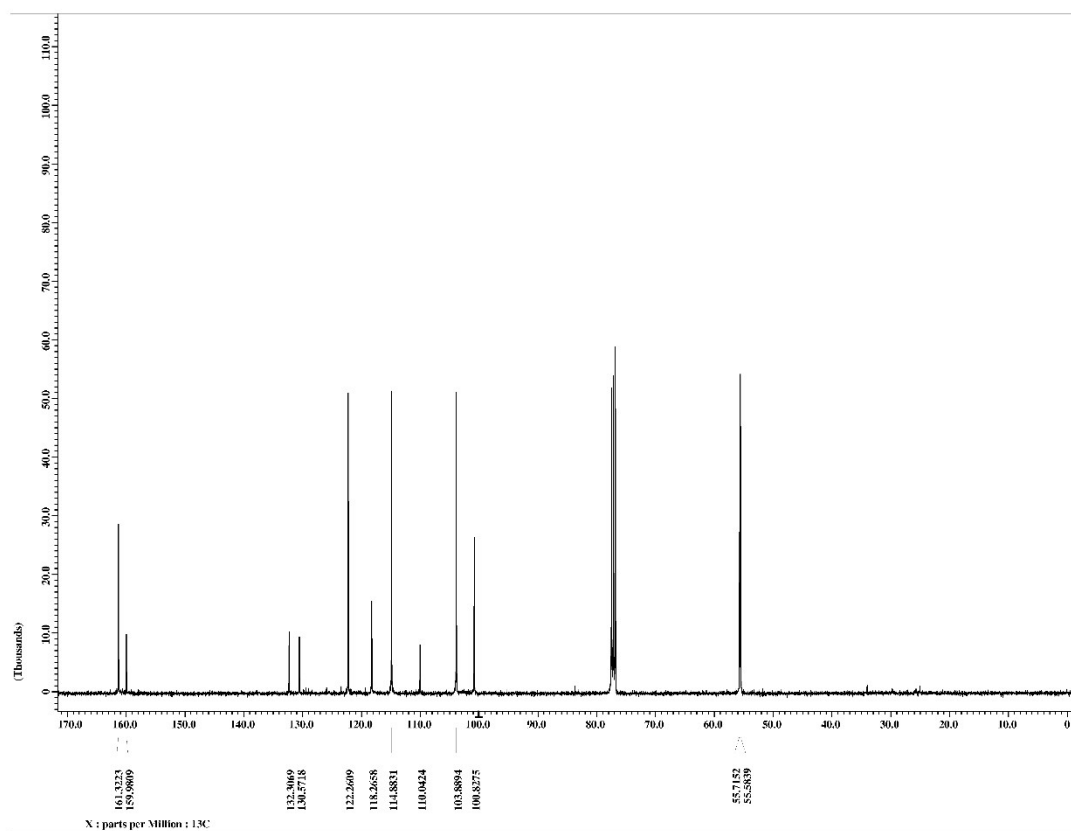
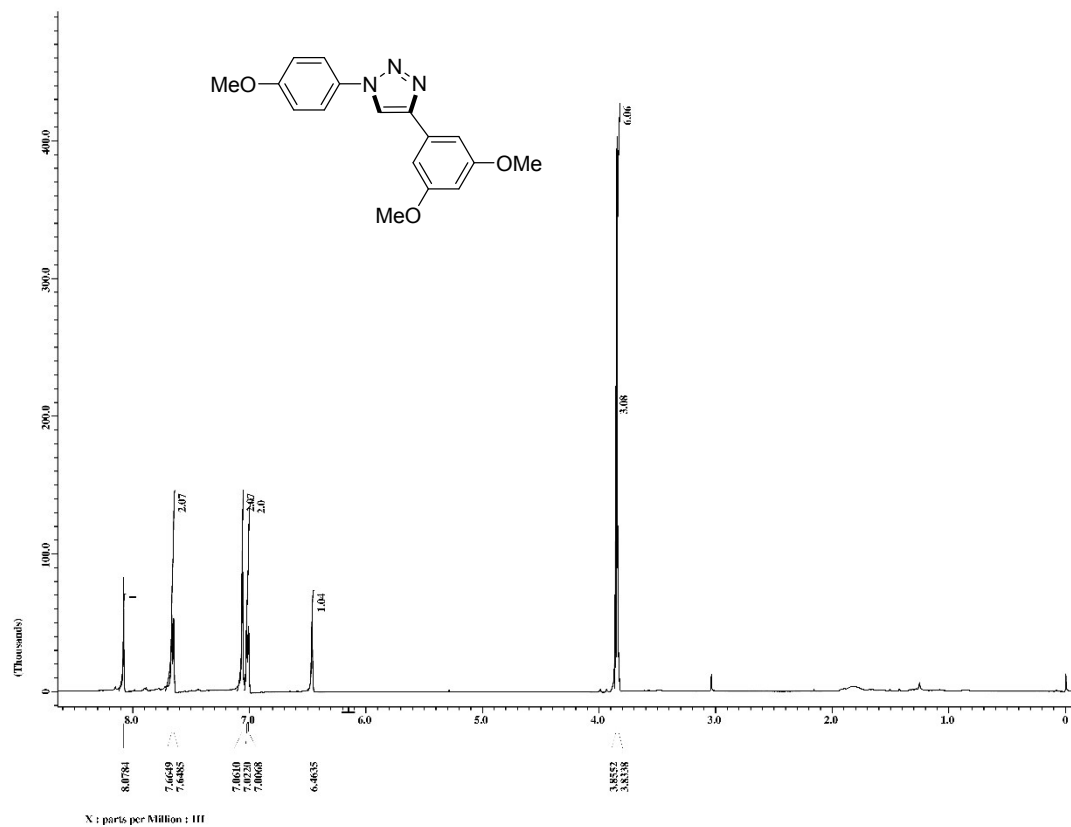
¹H and ¹³C NMR of 3o:



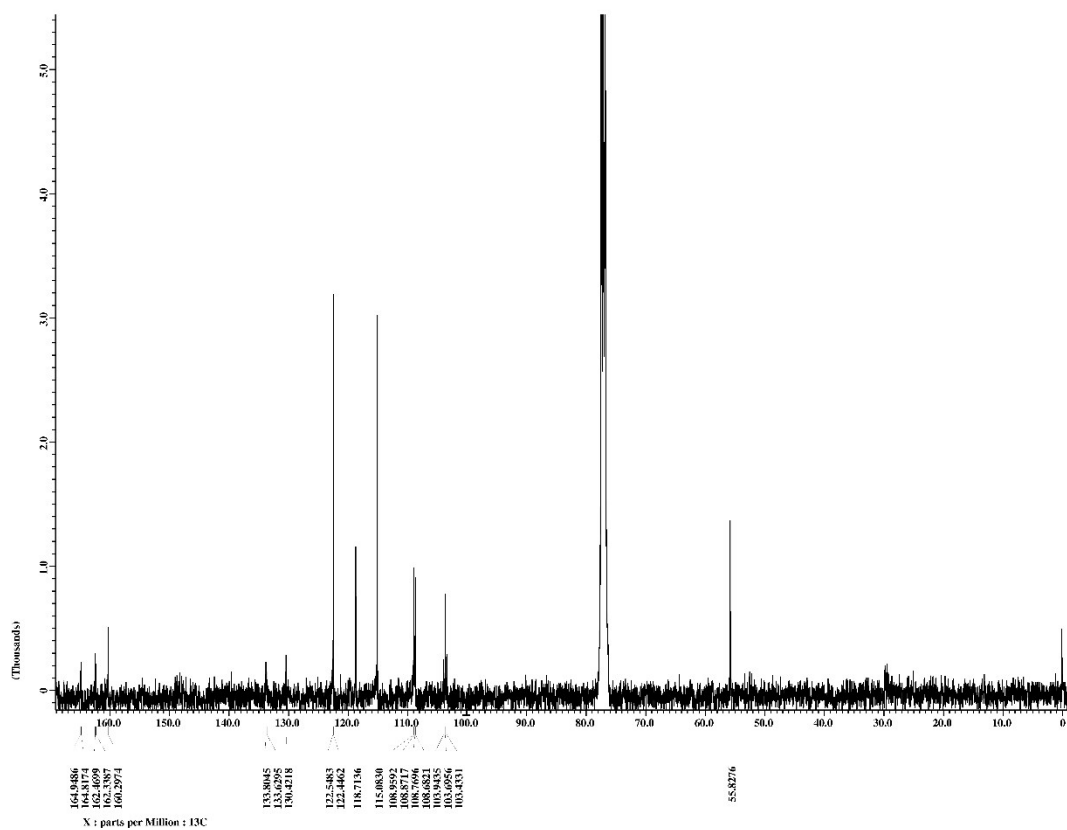
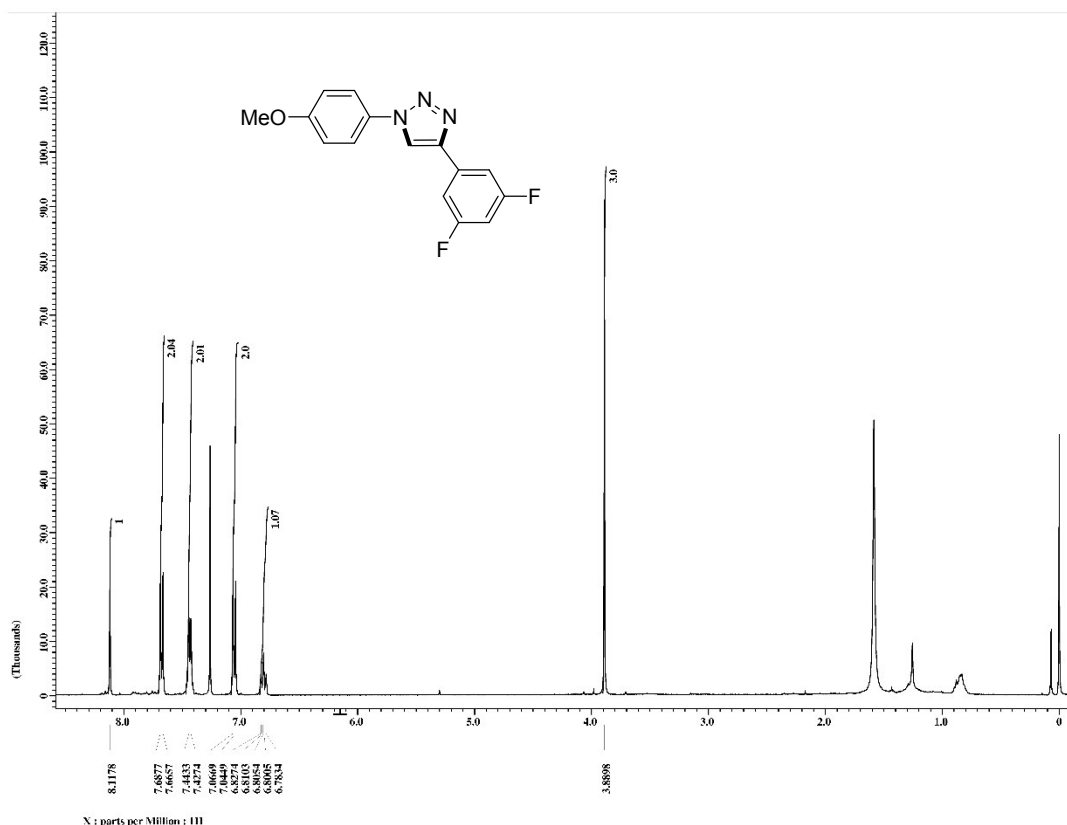
¹H and ¹³C NMR of 3p:



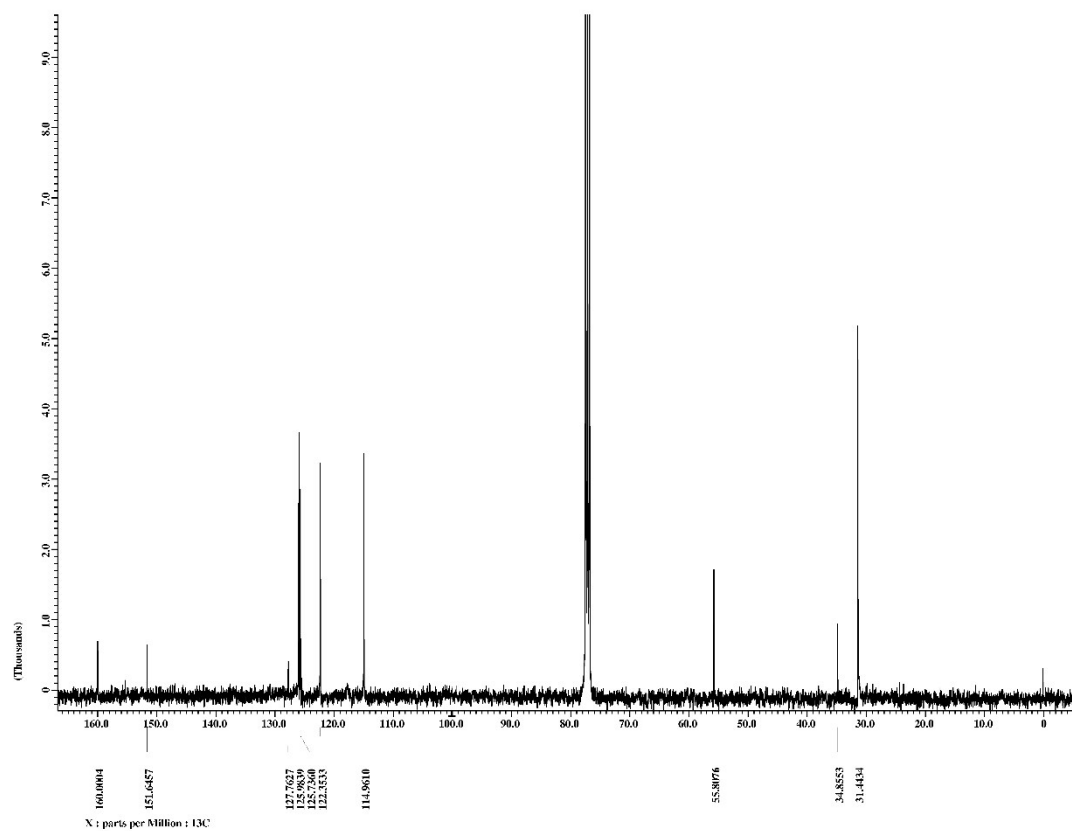
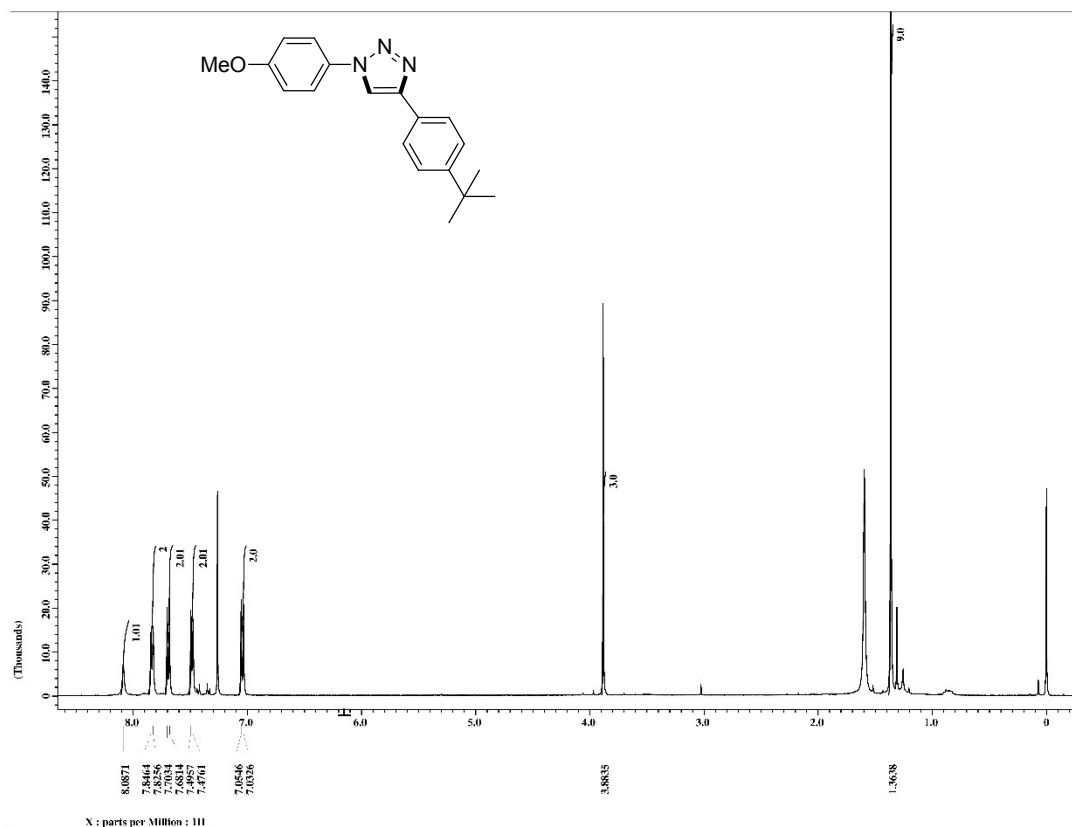
^1H and ^{13}C NMR of 3q:



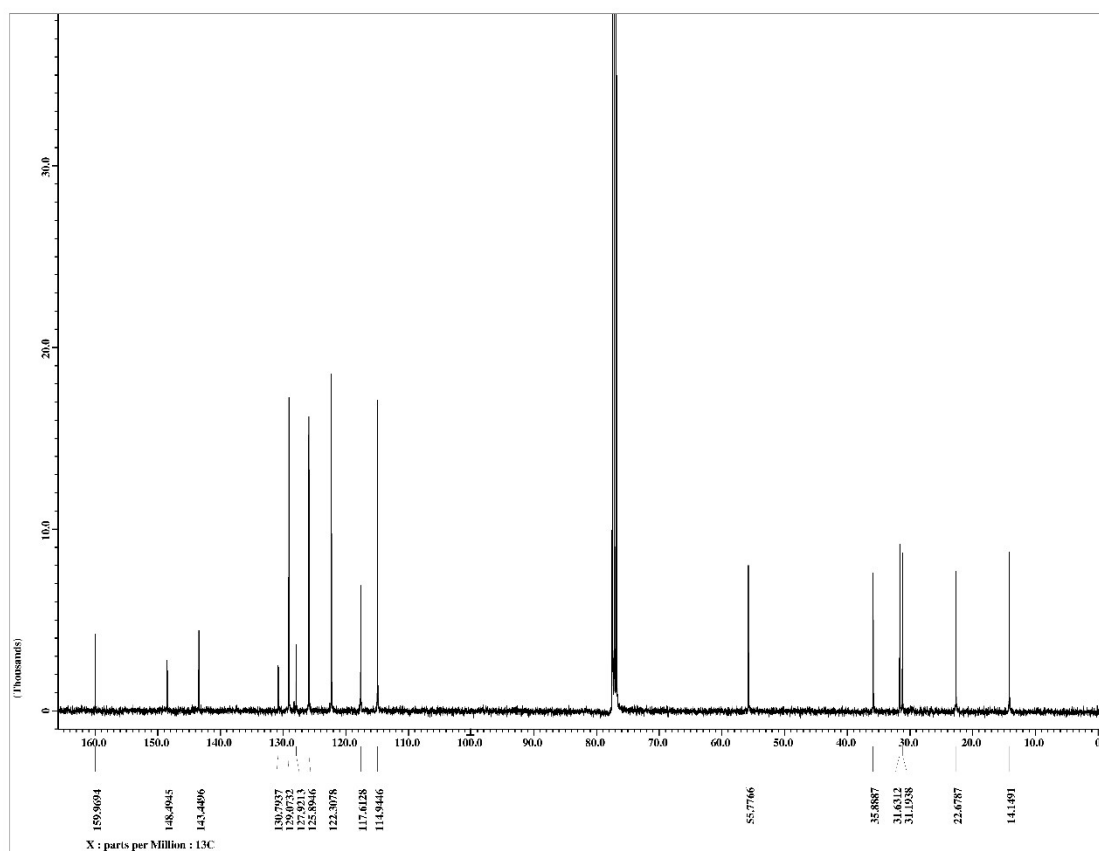
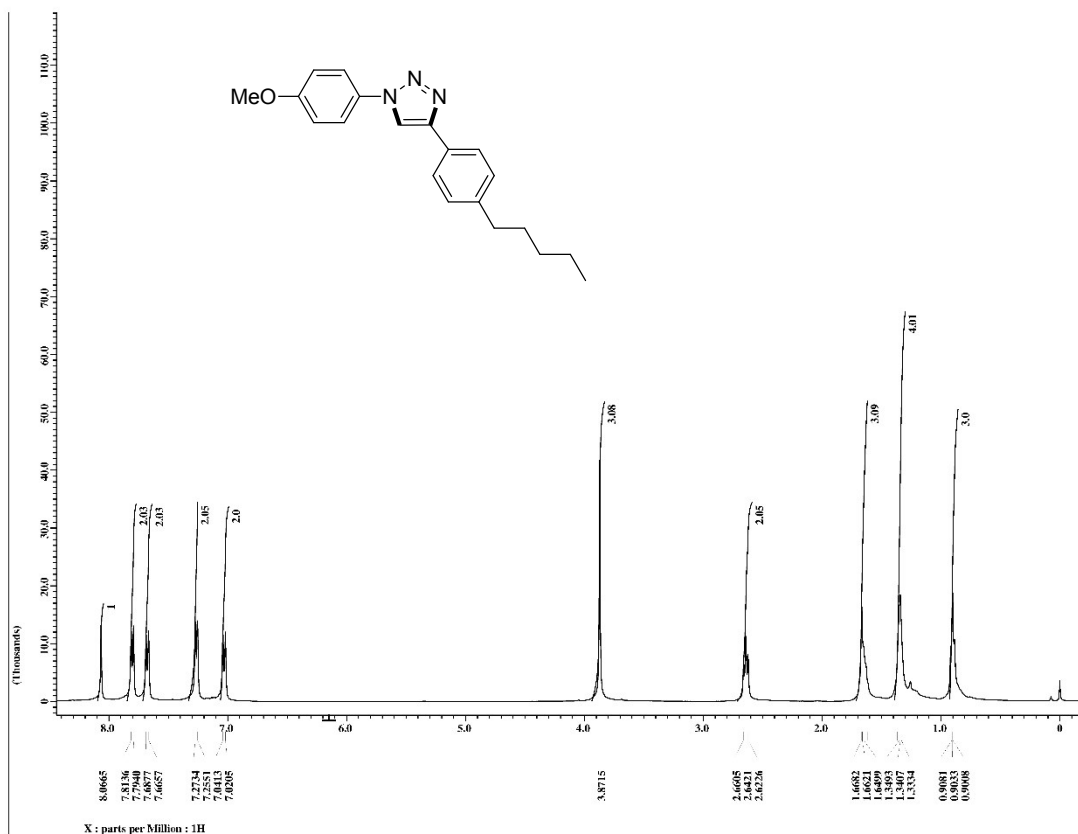
¹H and ¹³C NMR of 3r:



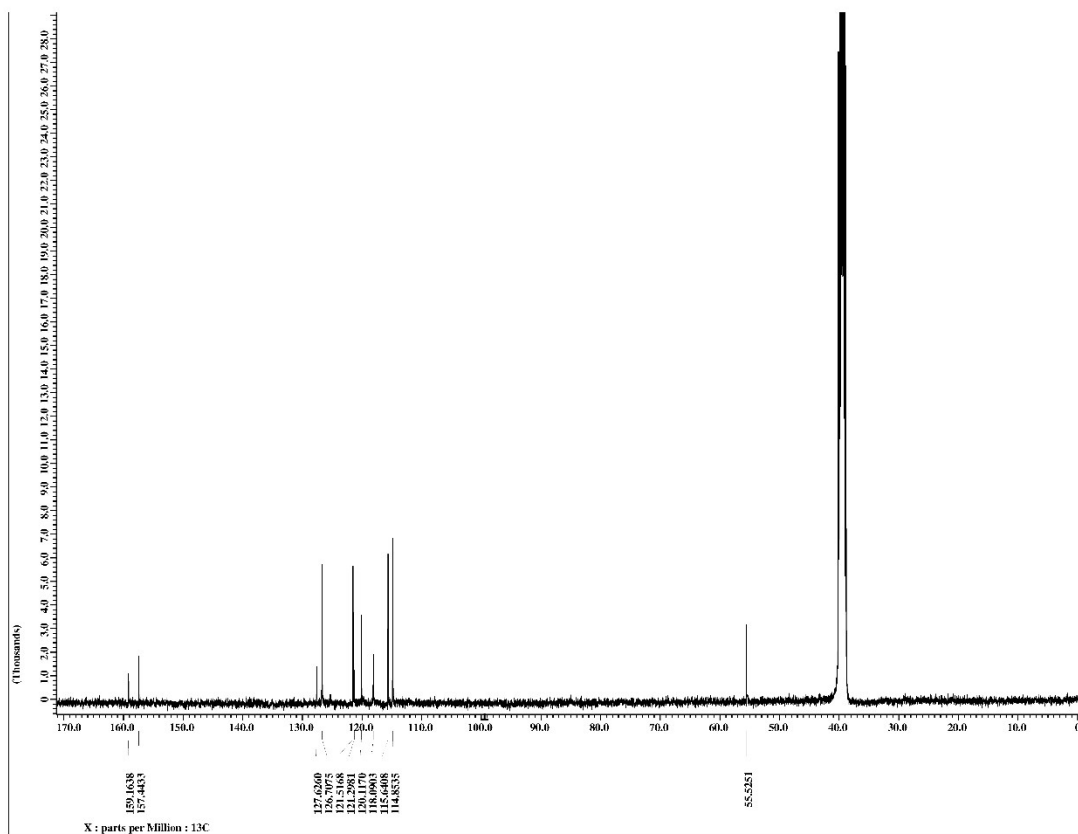
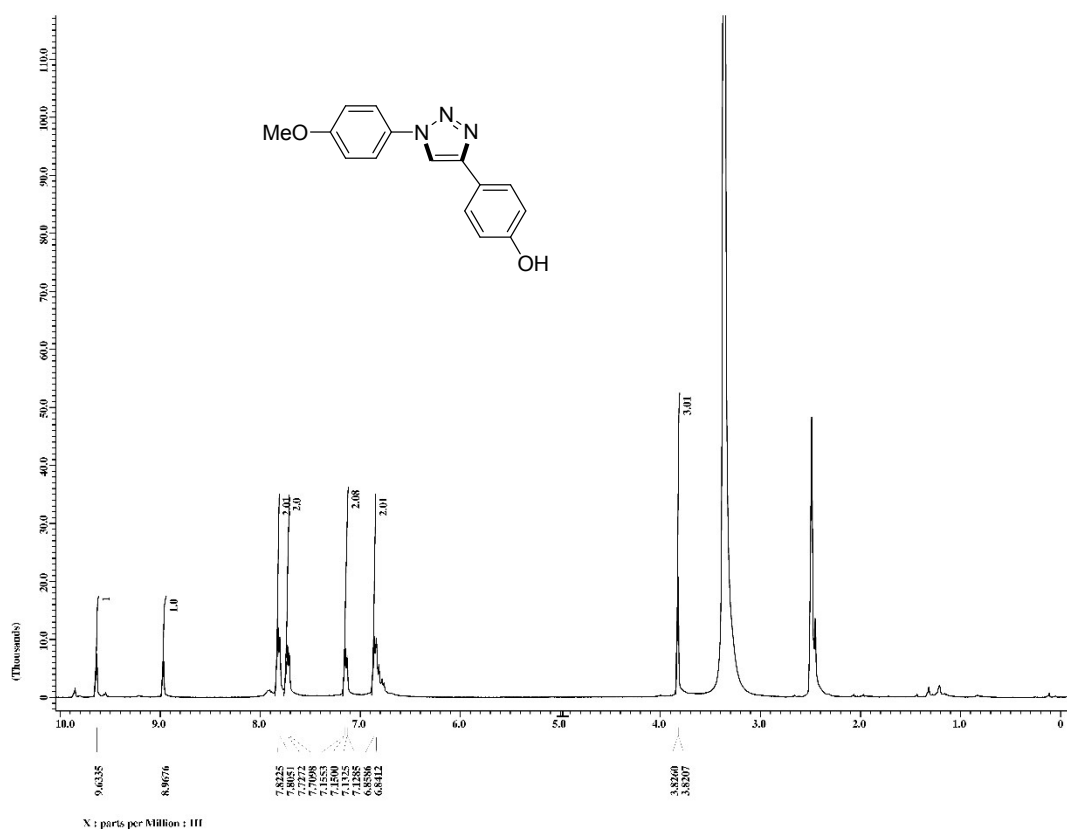
¹H and ¹³C NMR of 3s:



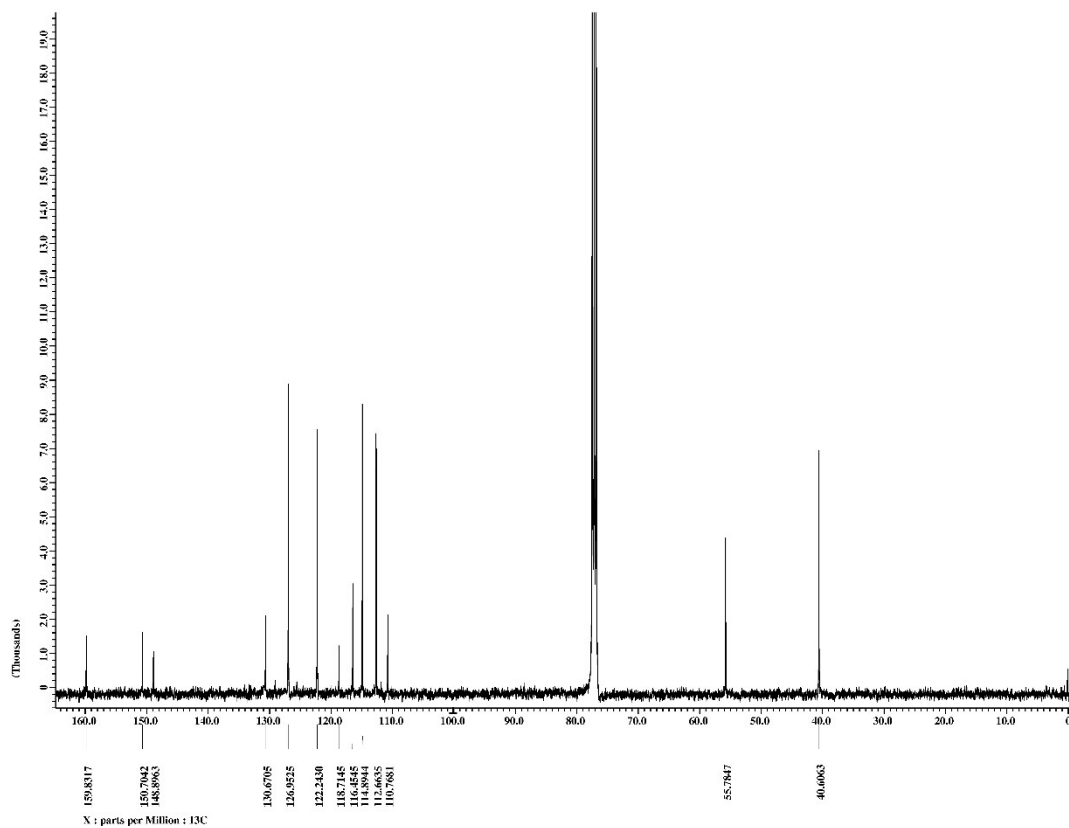
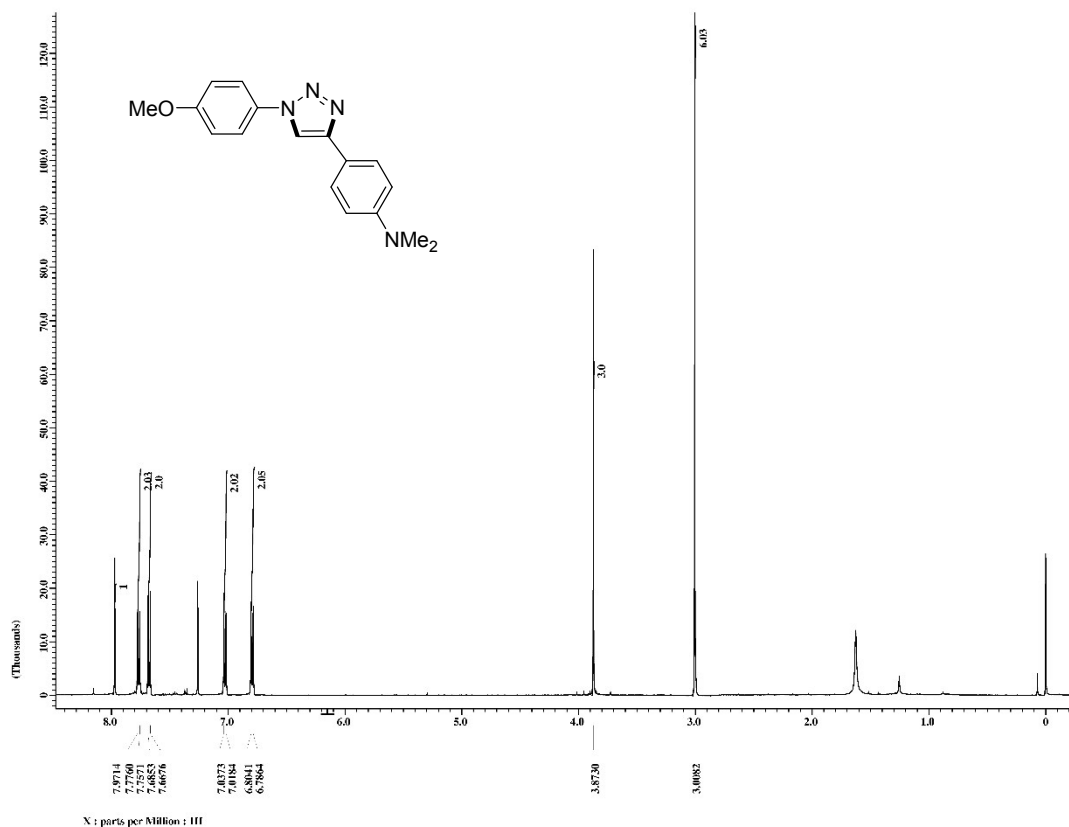
¹H and ¹³C NMR of 3t:



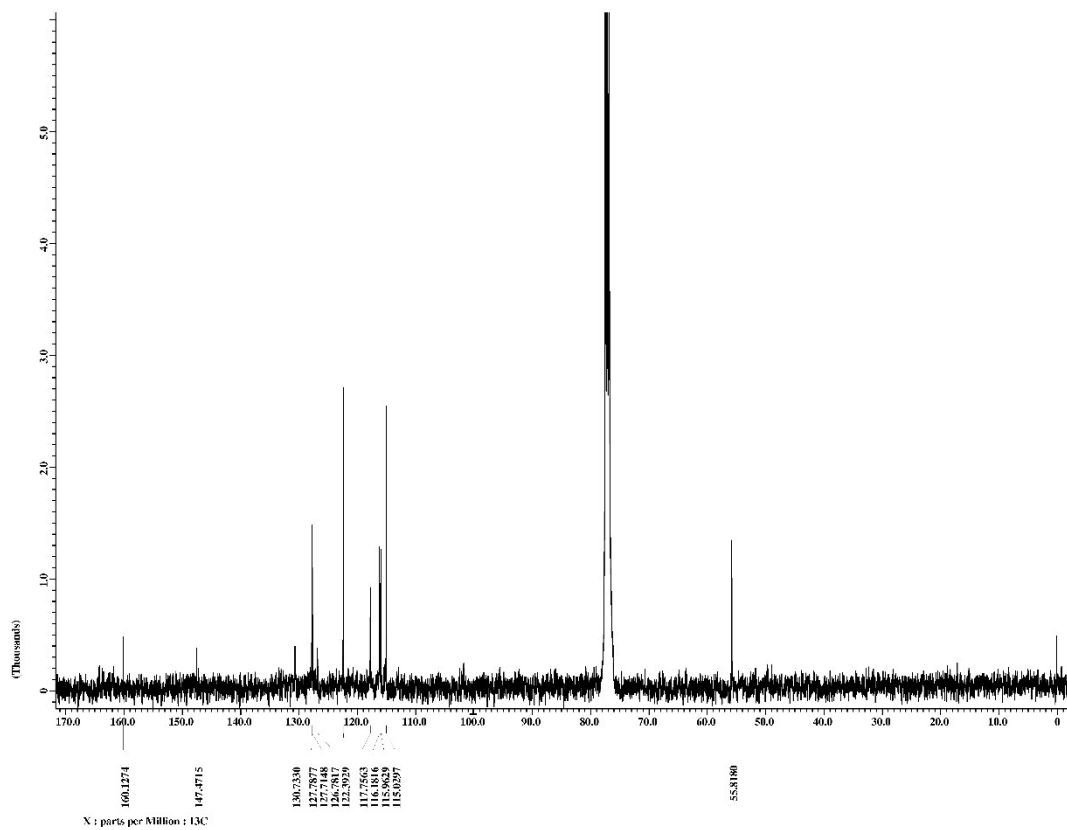
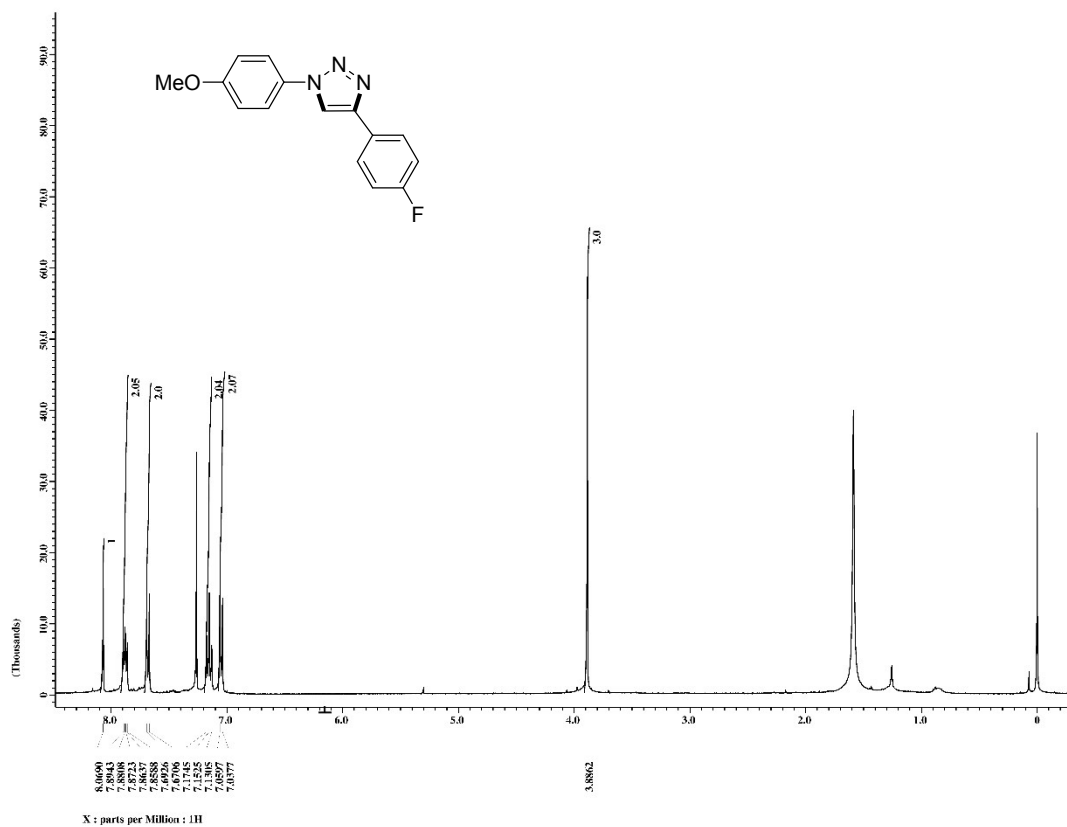
¹H and ¹³C NMR of 3u:



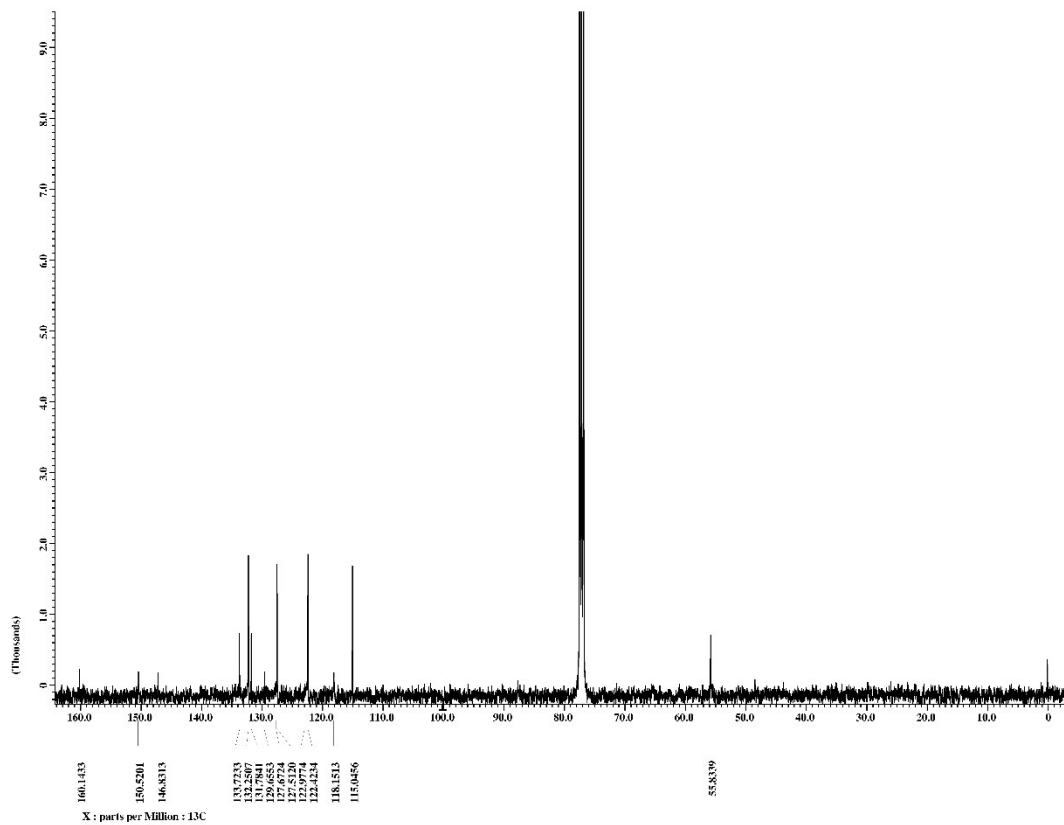
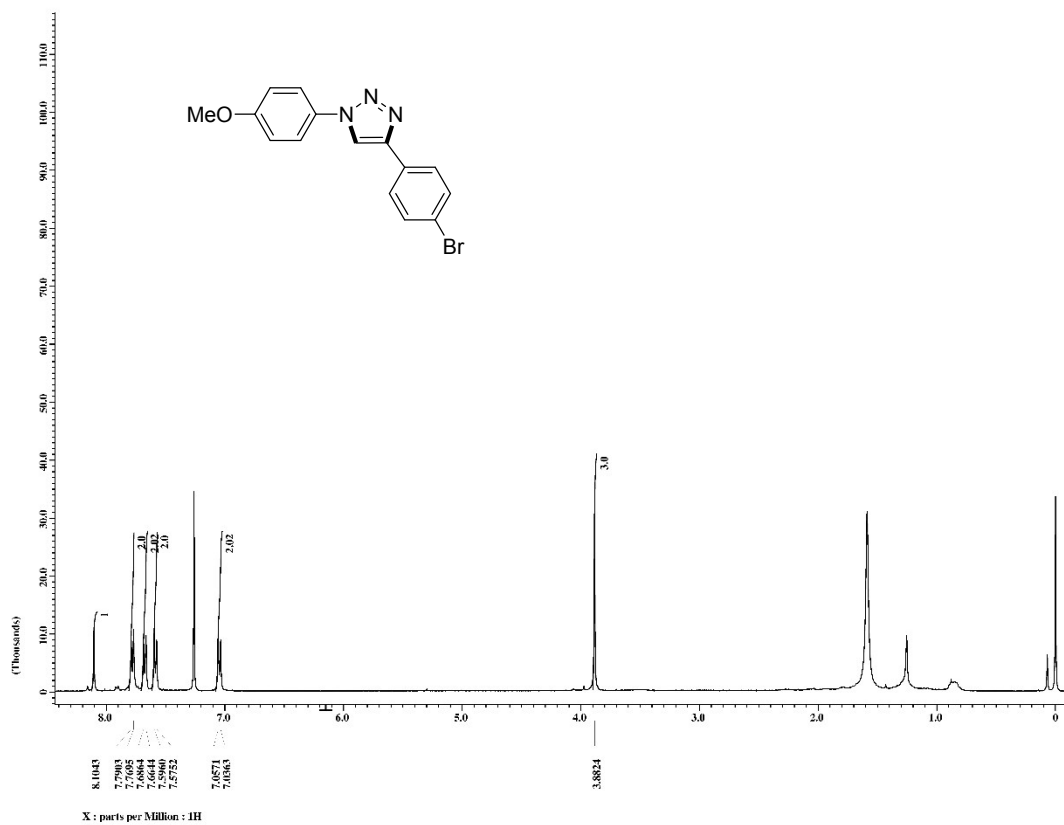
¹H and ¹³C NMR of 3v:



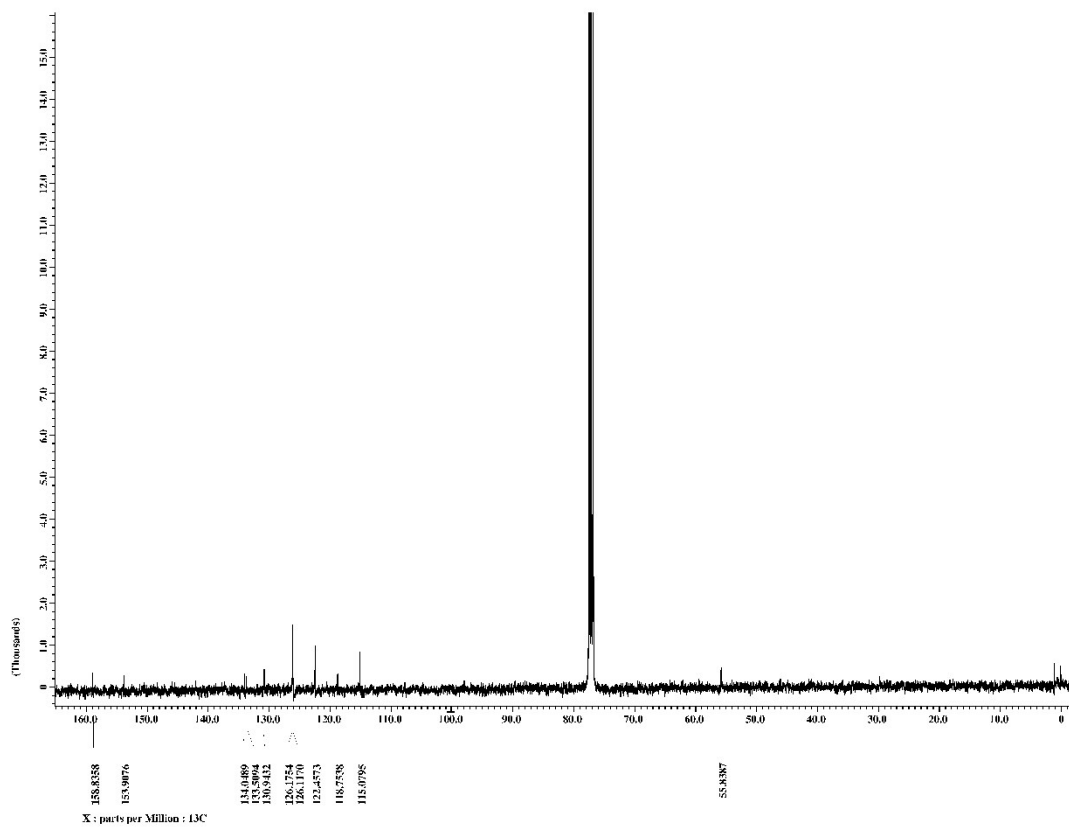
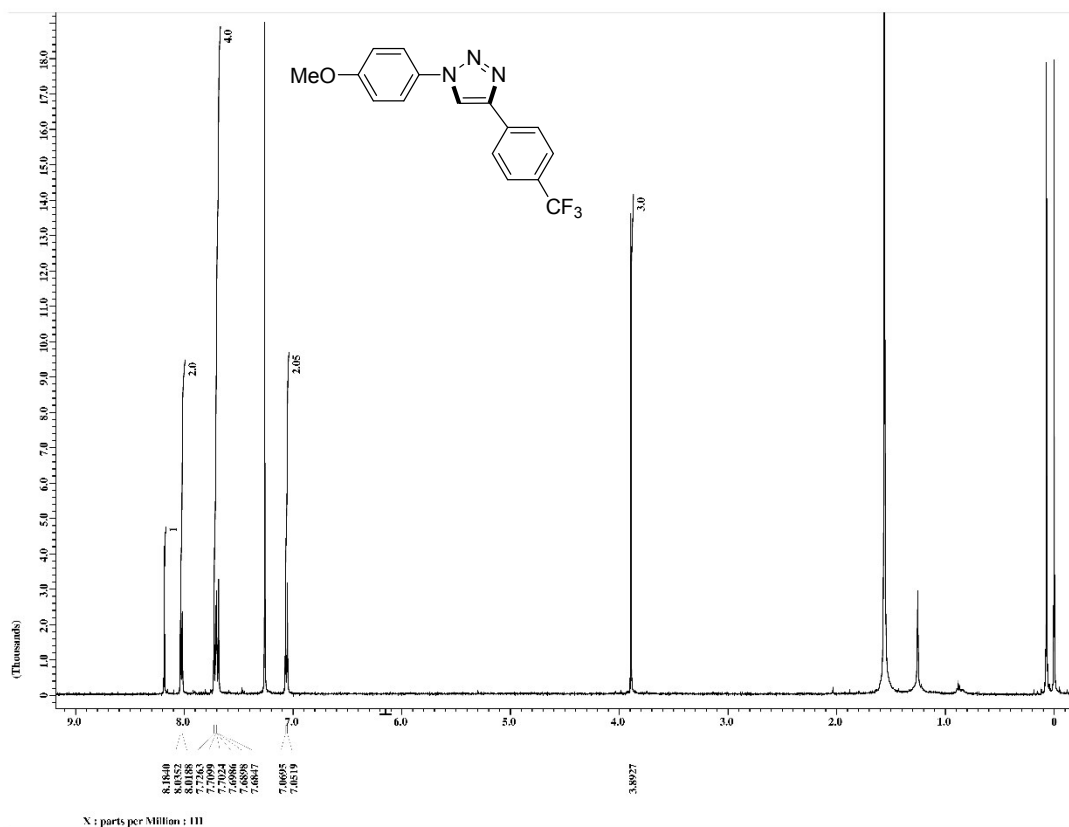
¹H and ¹³C NMR of 3w:



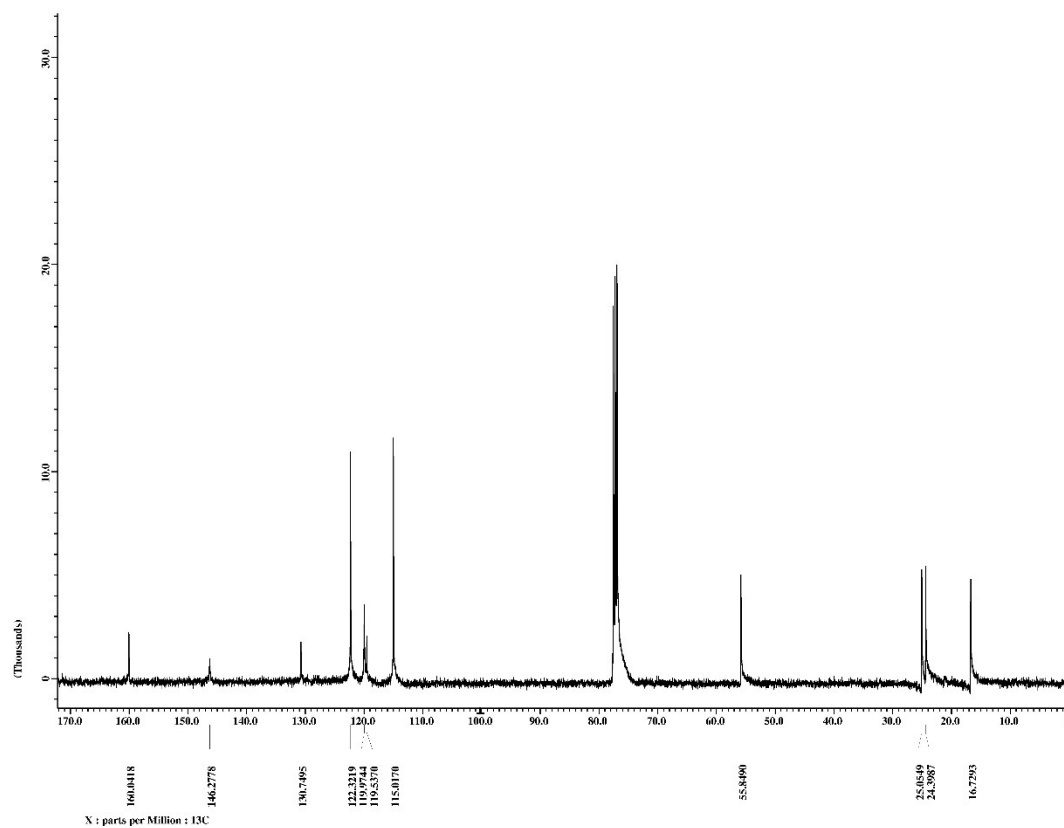
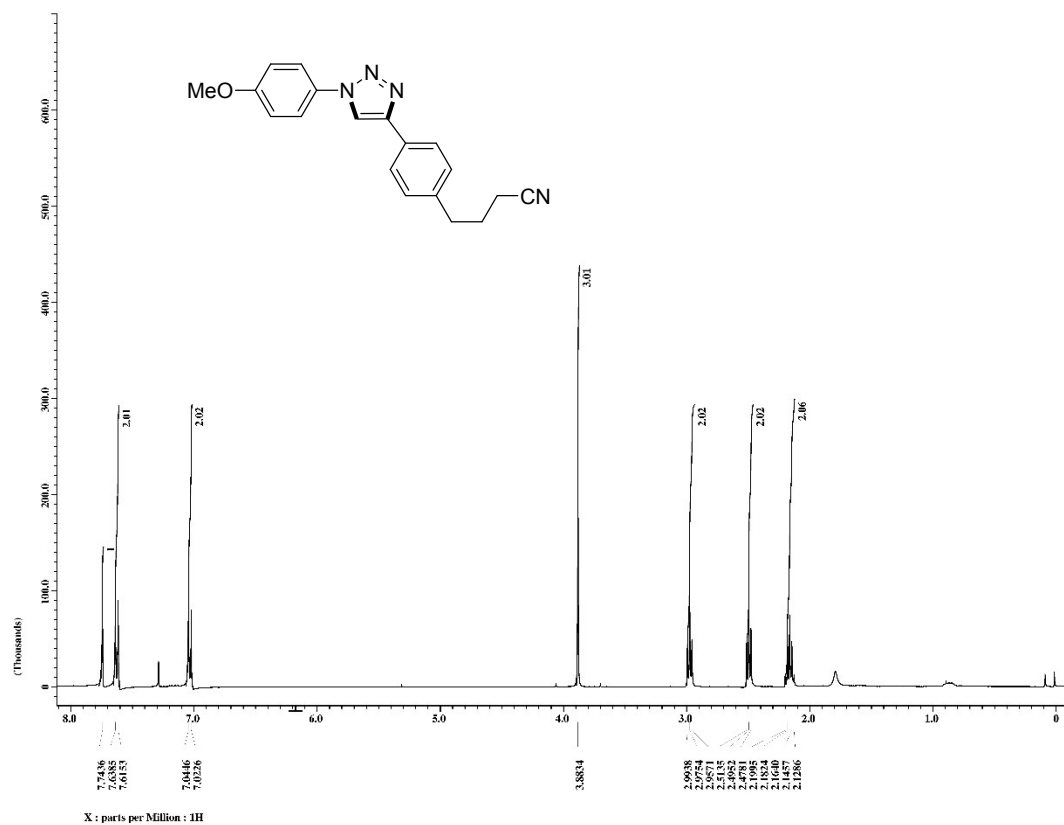
¹H and ¹³C NMR of 3x:



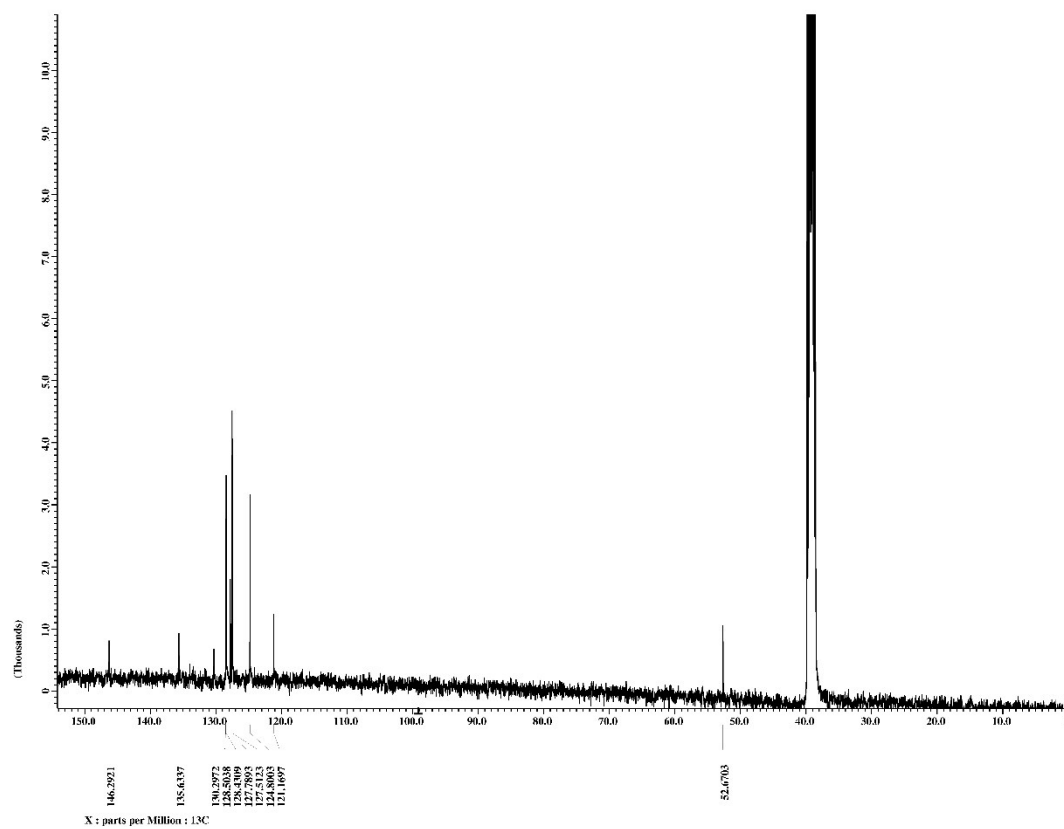
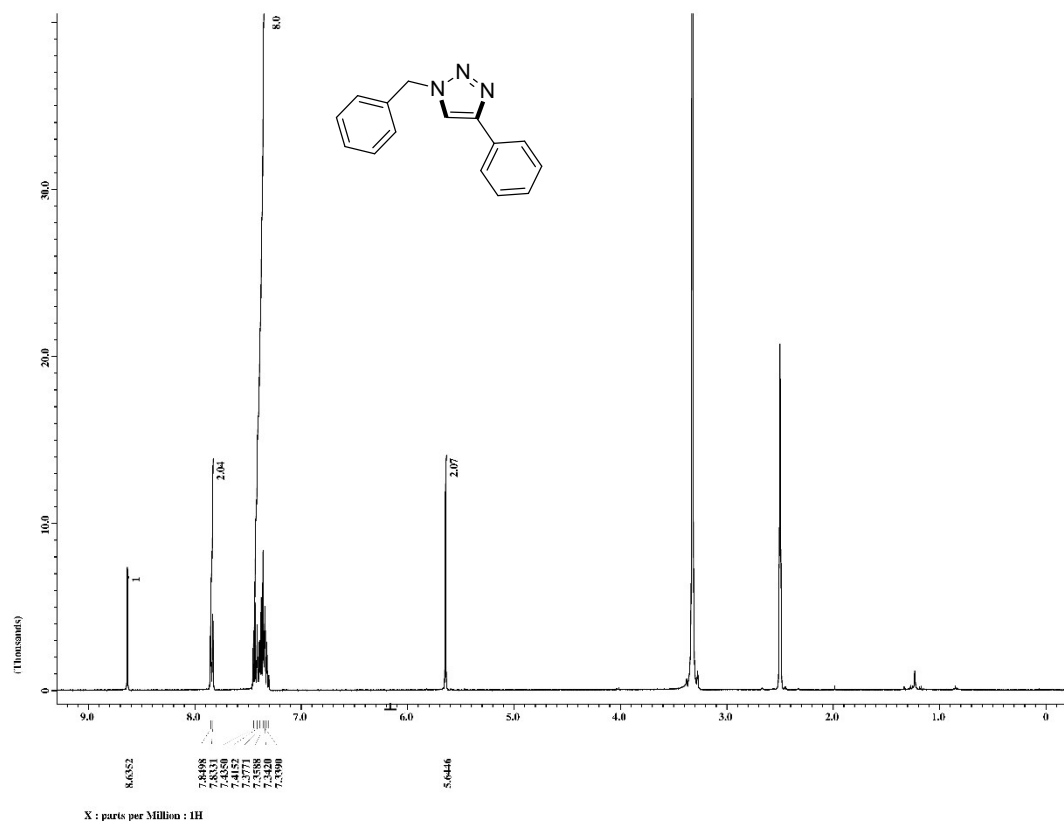
¹H and ¹³C NMR of 3y:



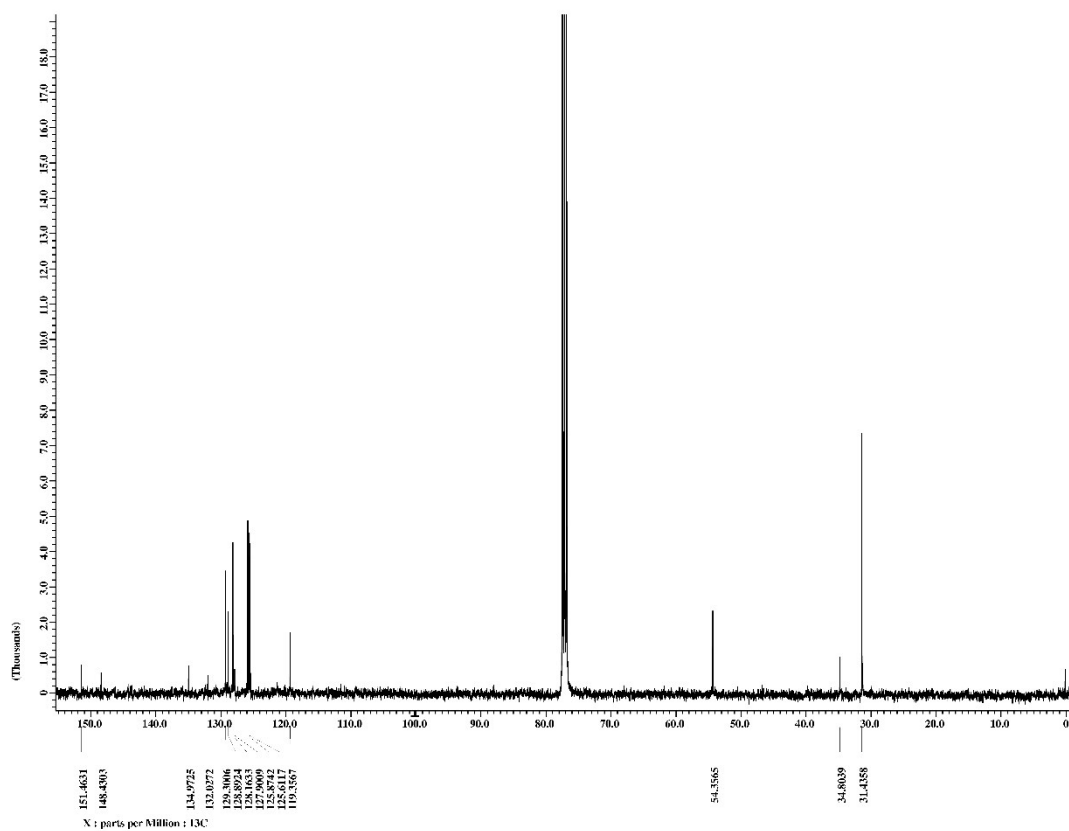
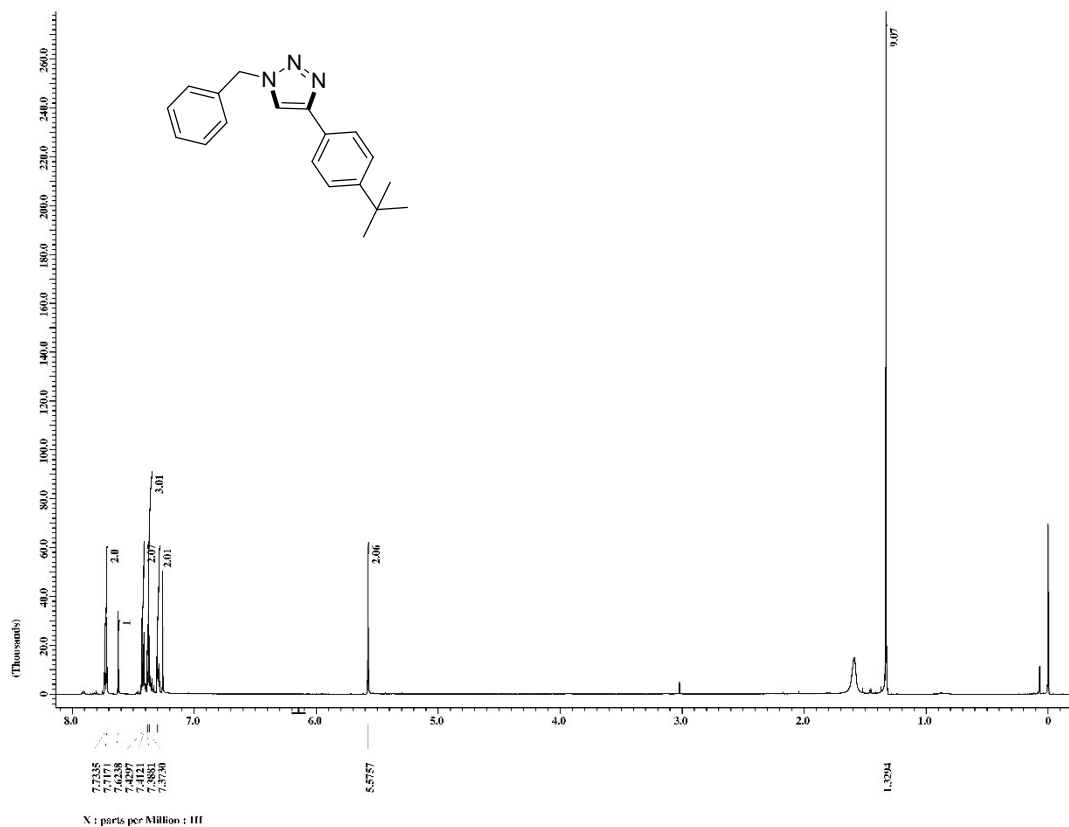
¹H and ¹³C NMR of 3z:



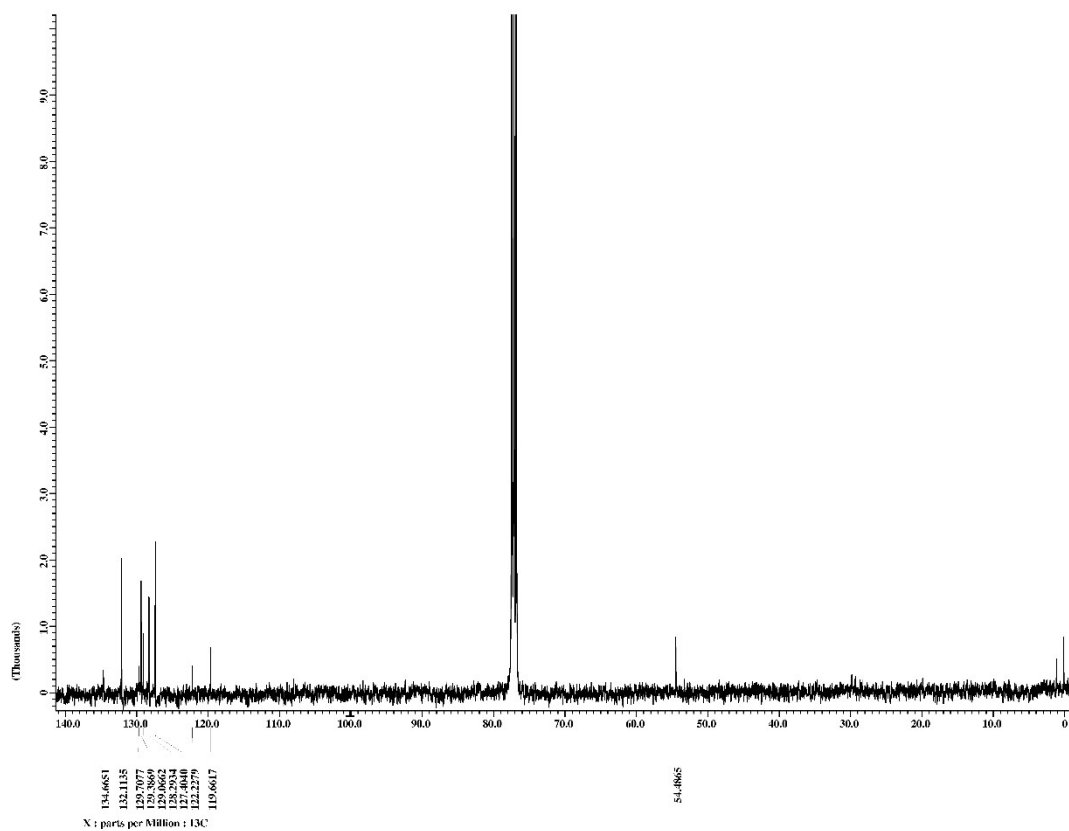
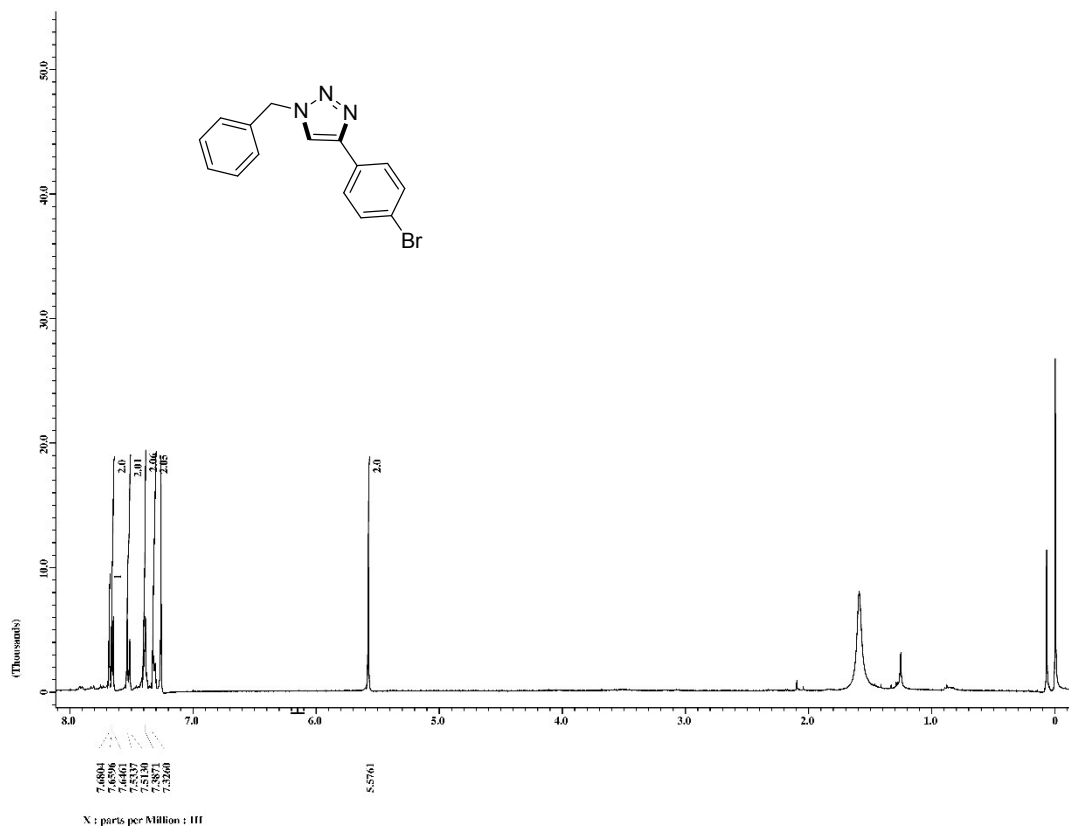
¹H and ¹³C NMR of 6a:



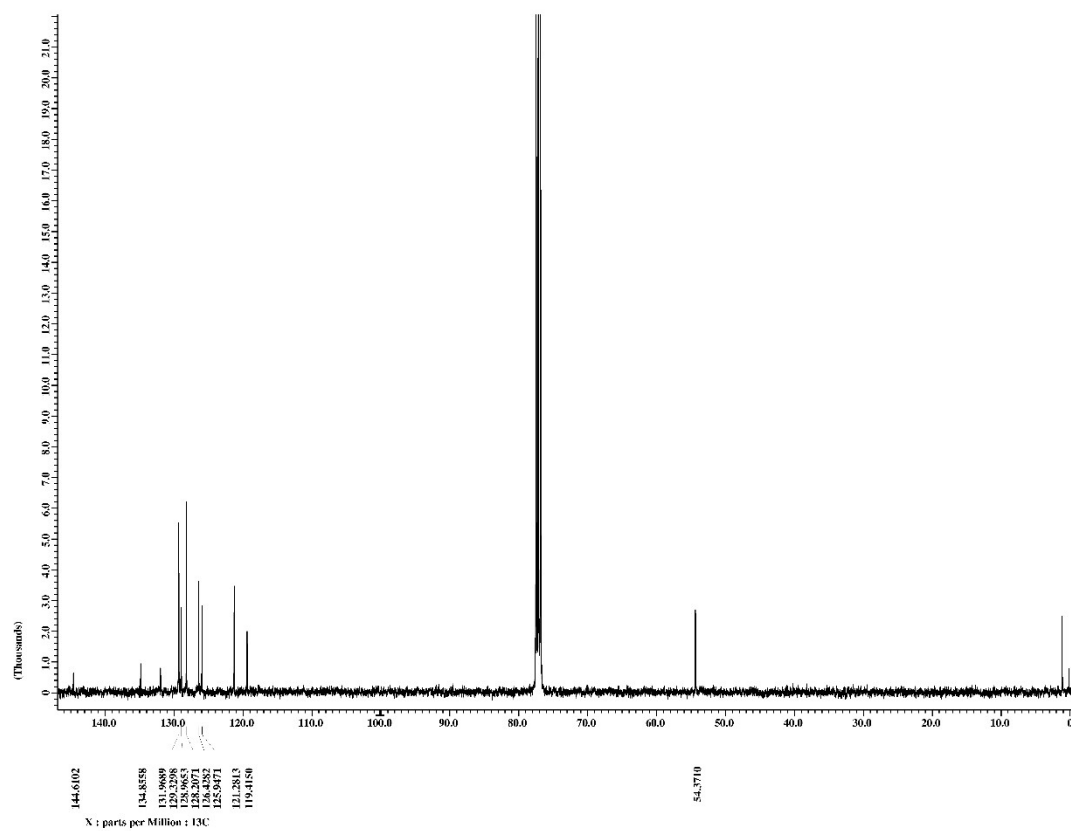
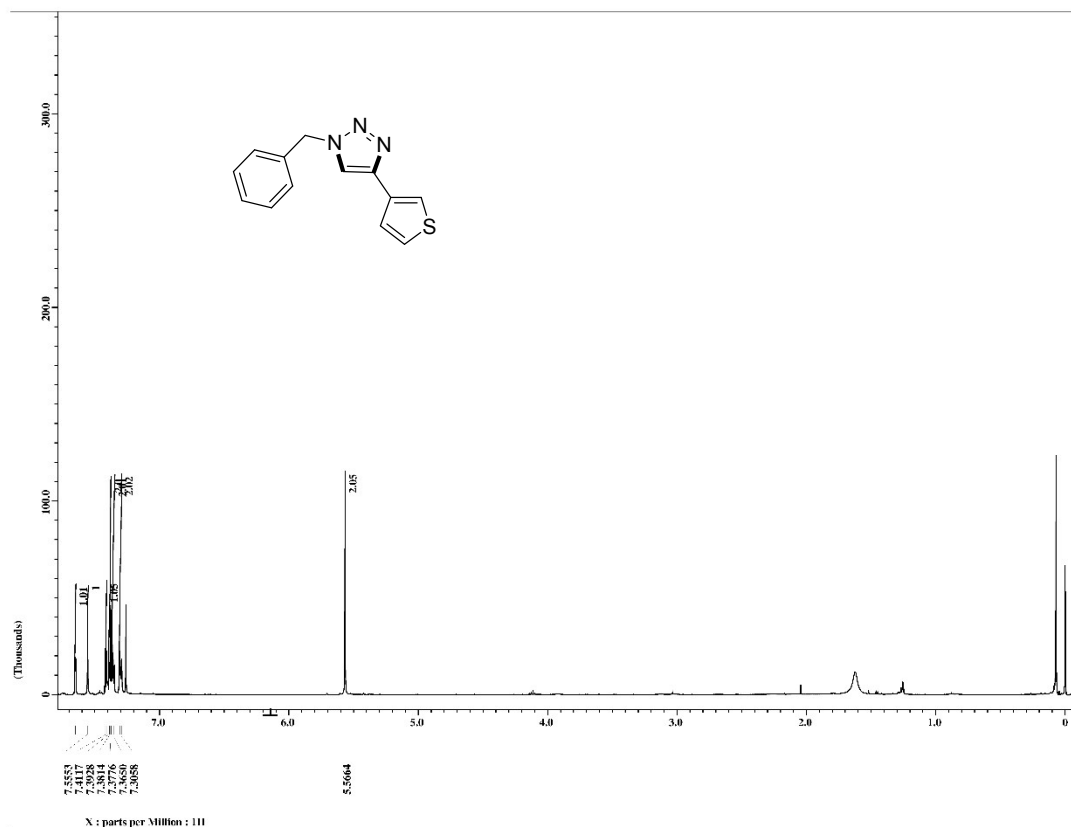
¹H and ¹³C NMR of 6b:



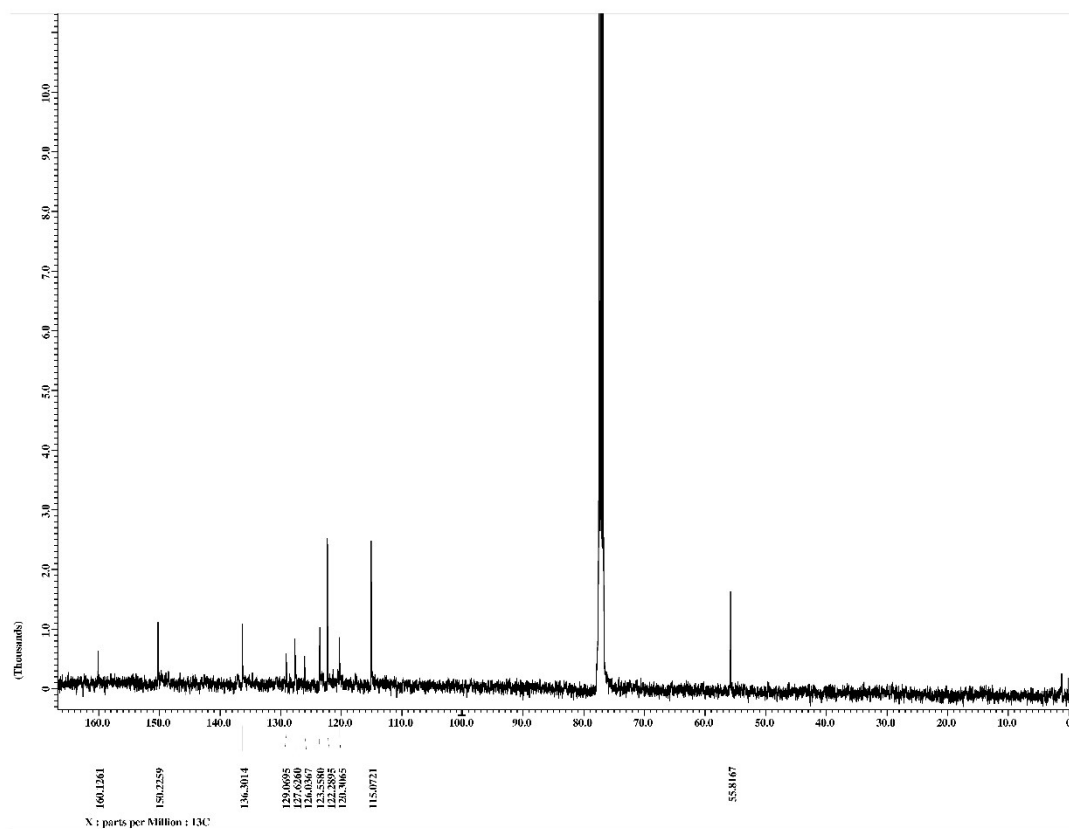
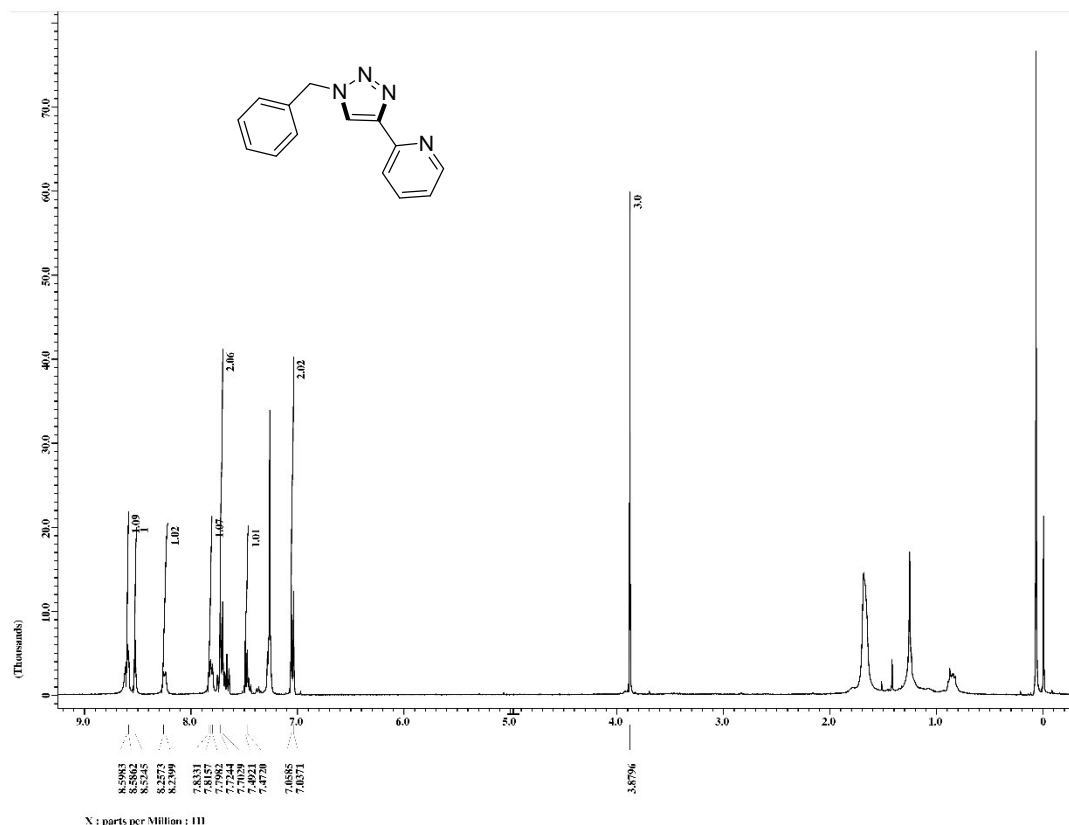
¹H and ¹³C NMR of 6c:



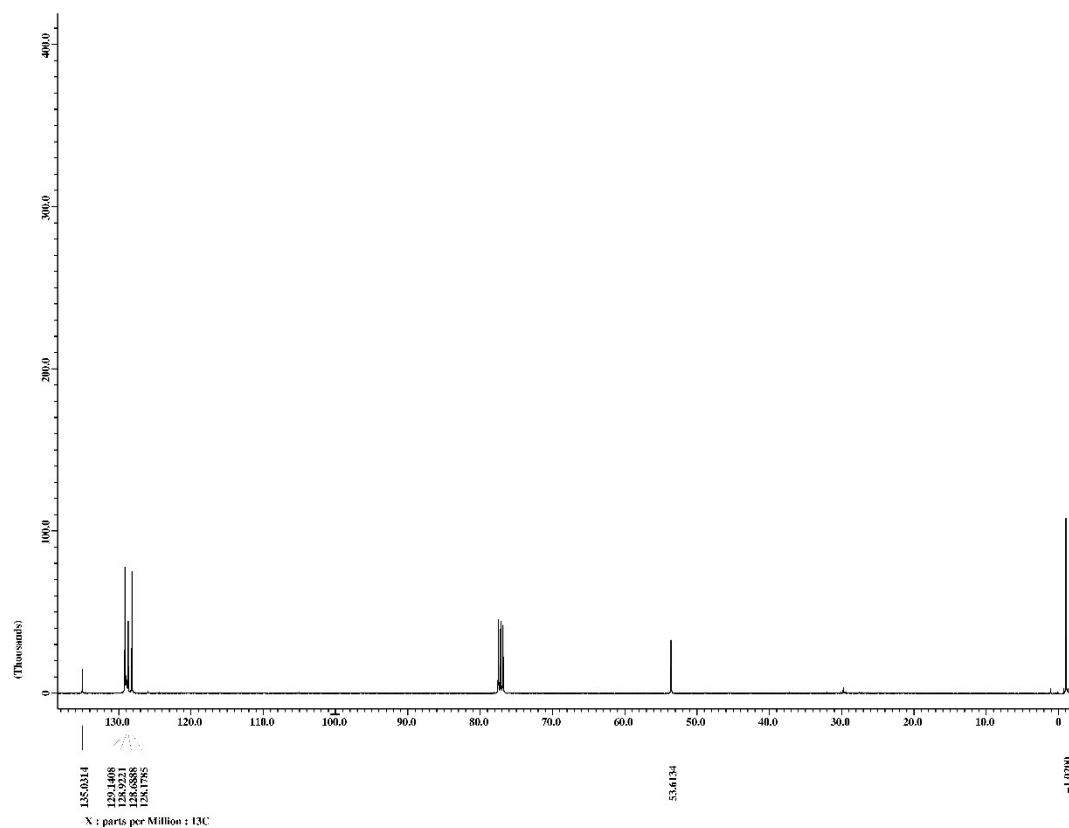
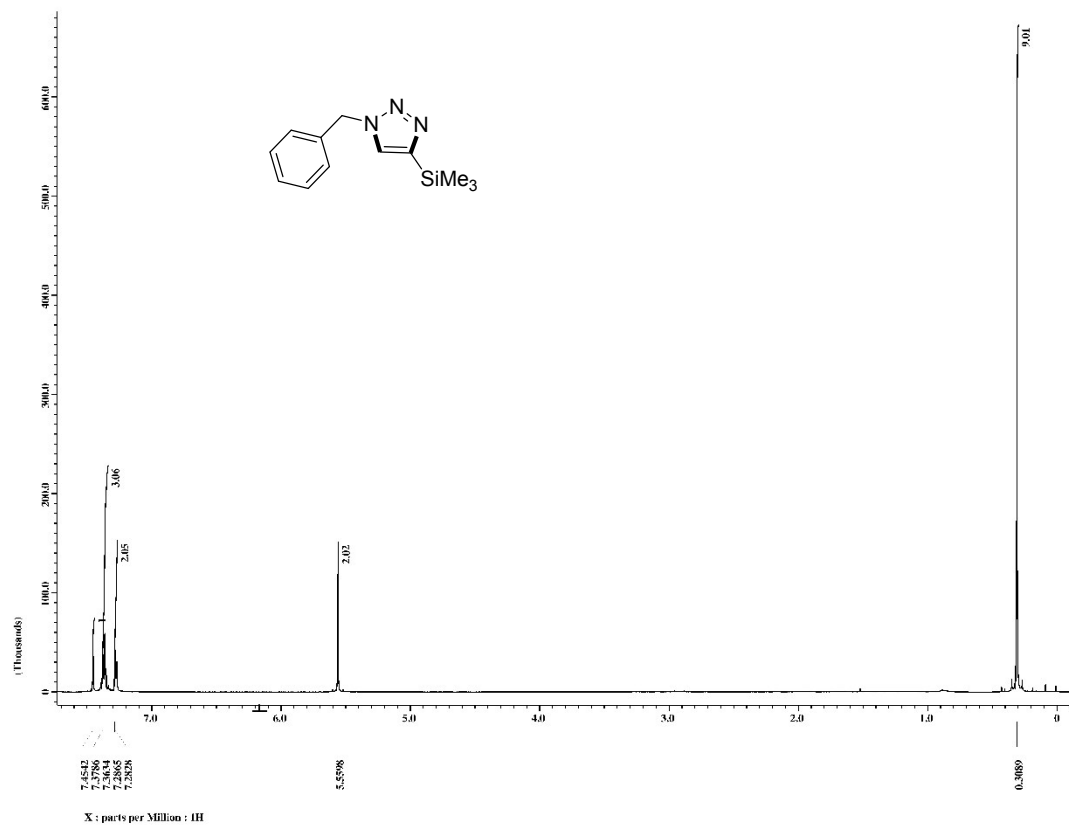
¹H and ¹³C NMR of 6d:



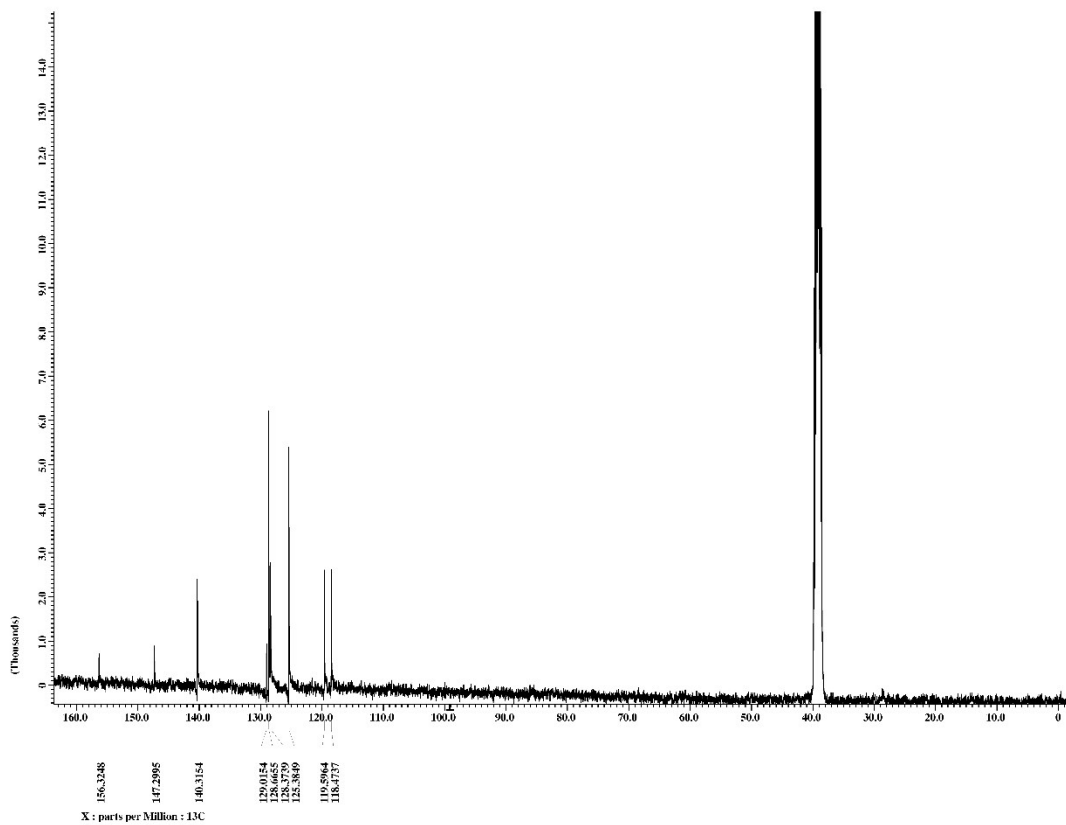
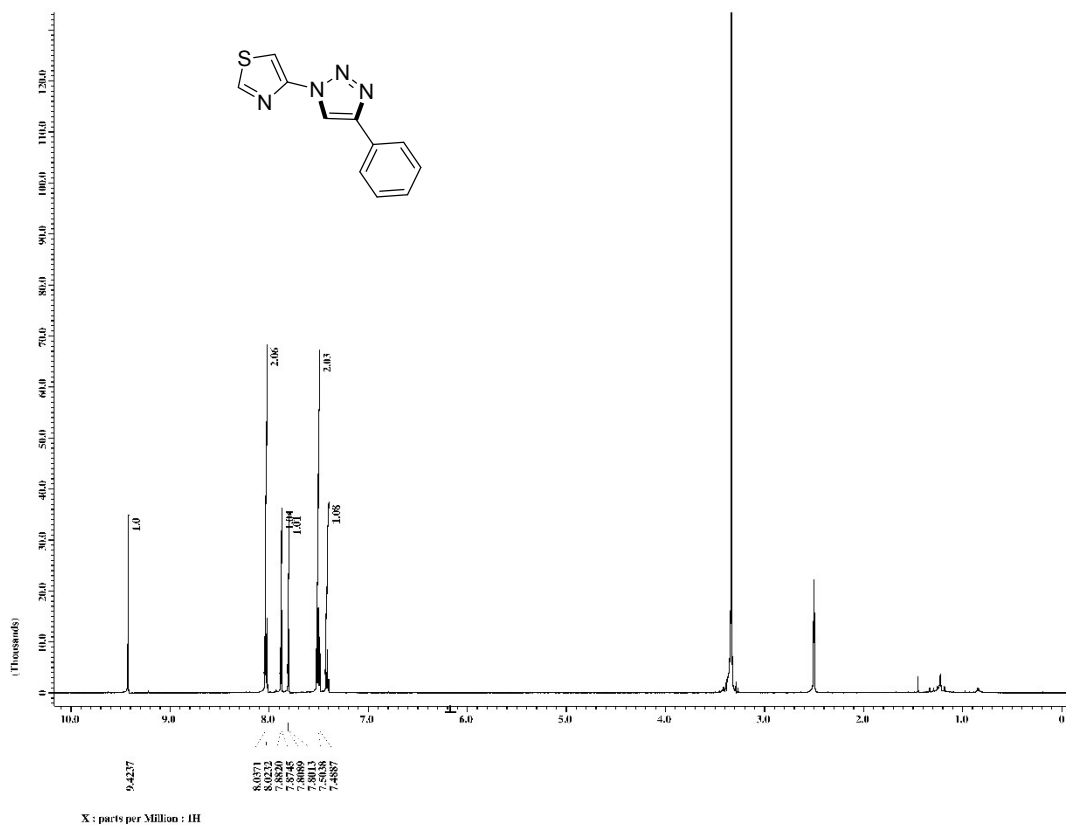
¹H and ¹³C NMR of 6e:



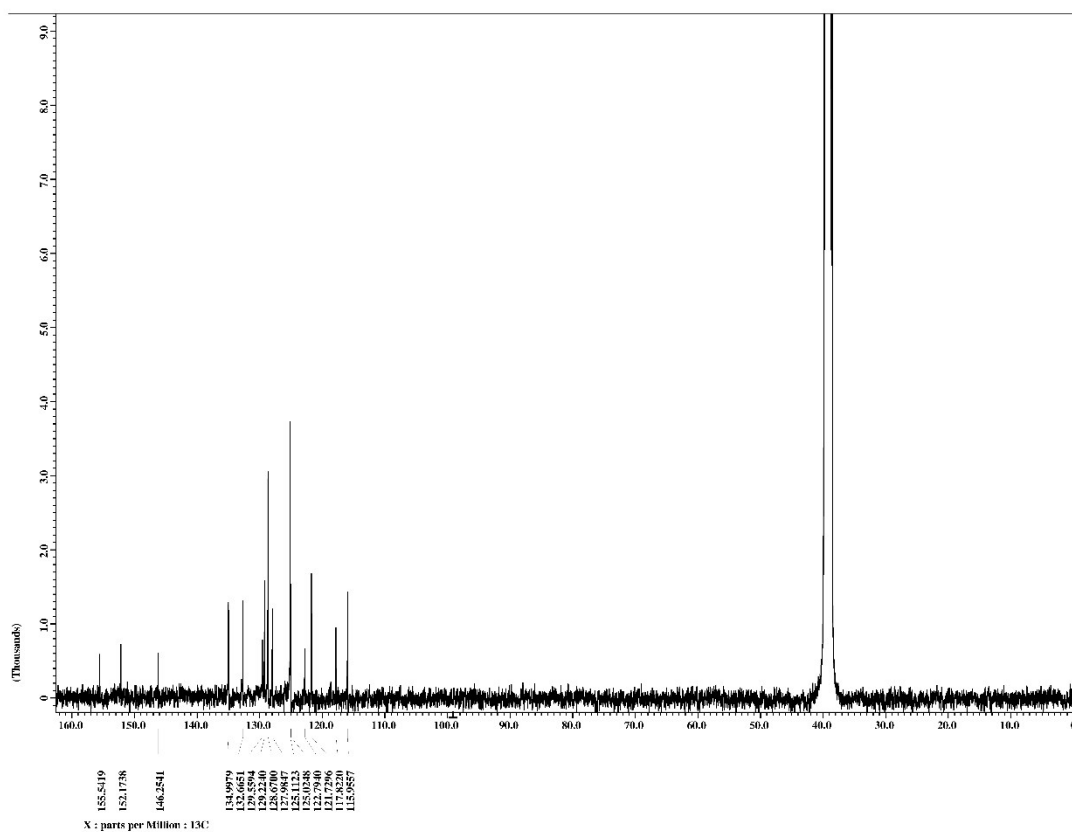
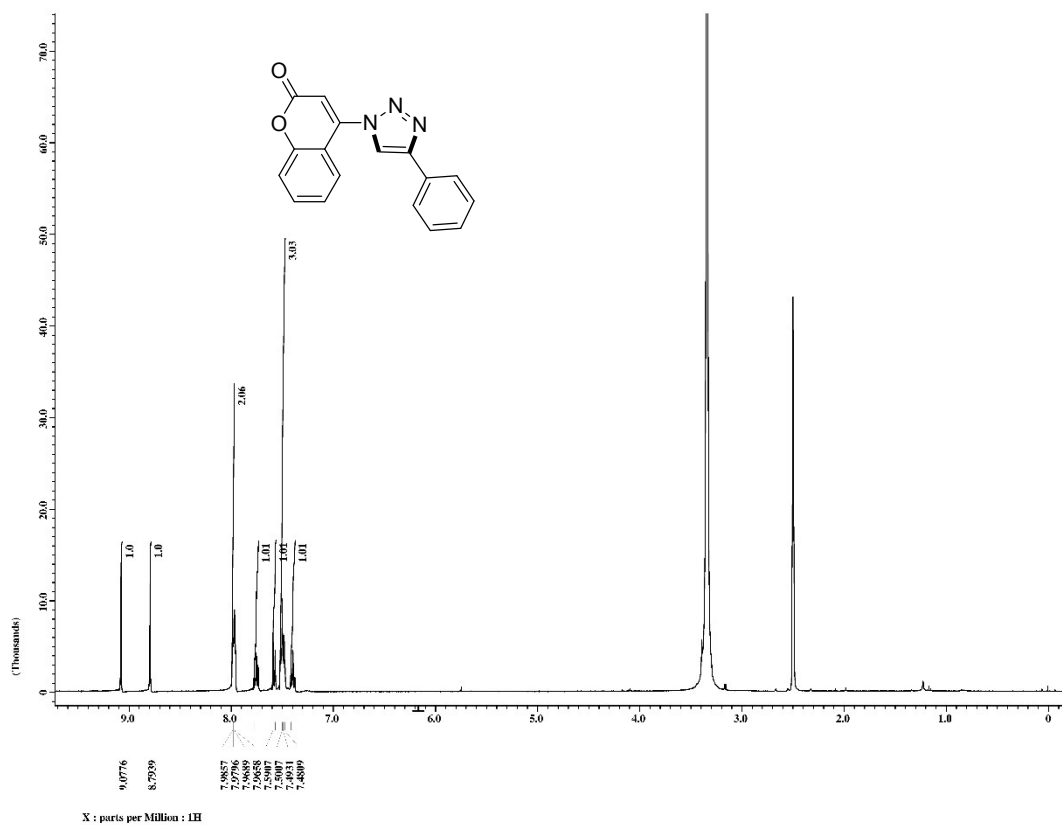
¹H and ¹³C NMR of 6f:



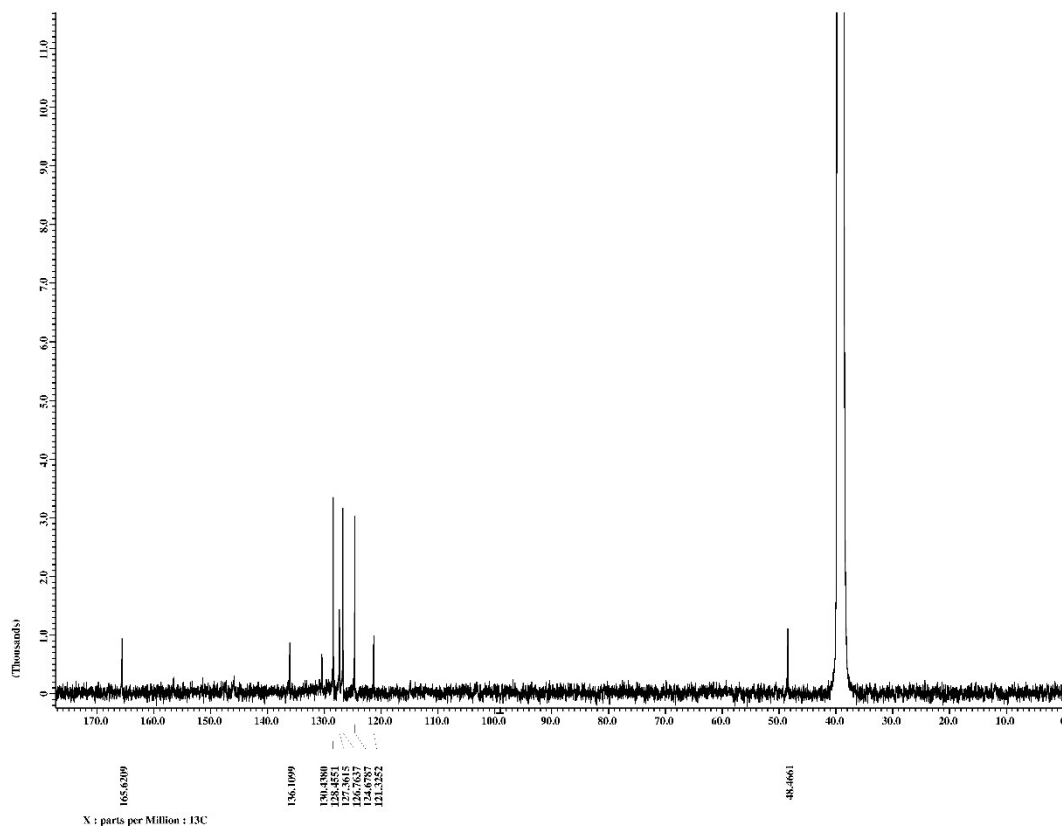
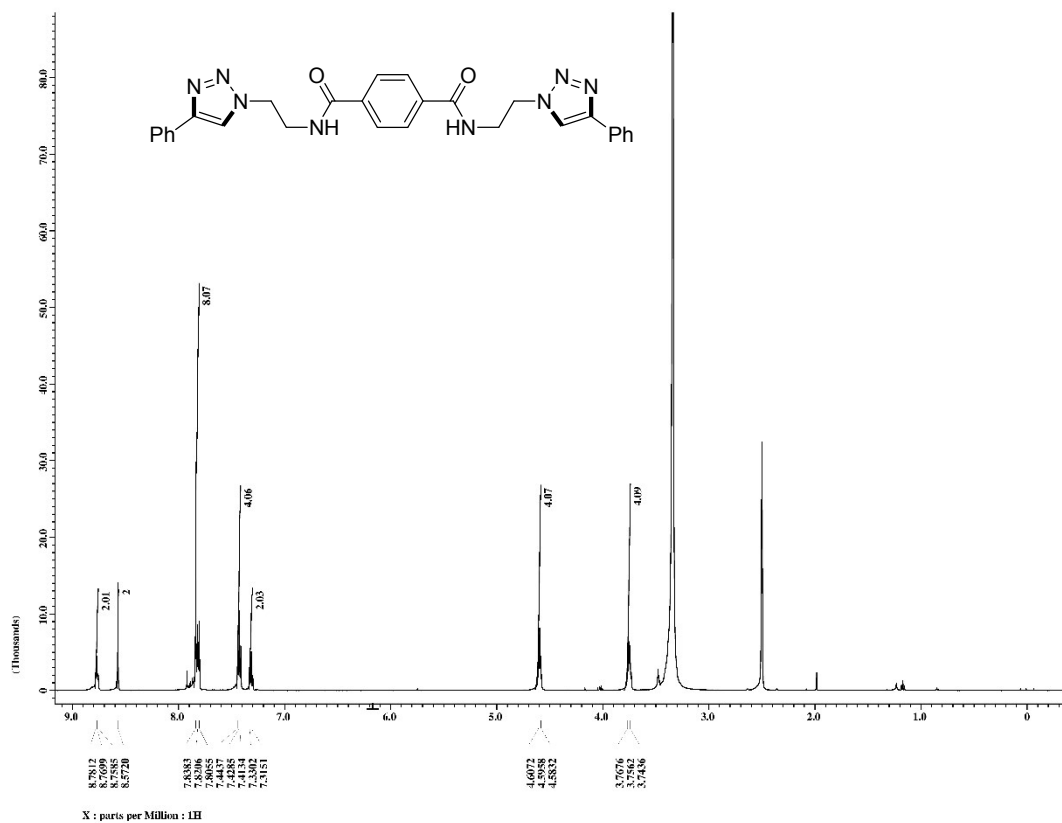
¹H and ¹³C NMR of 6g:



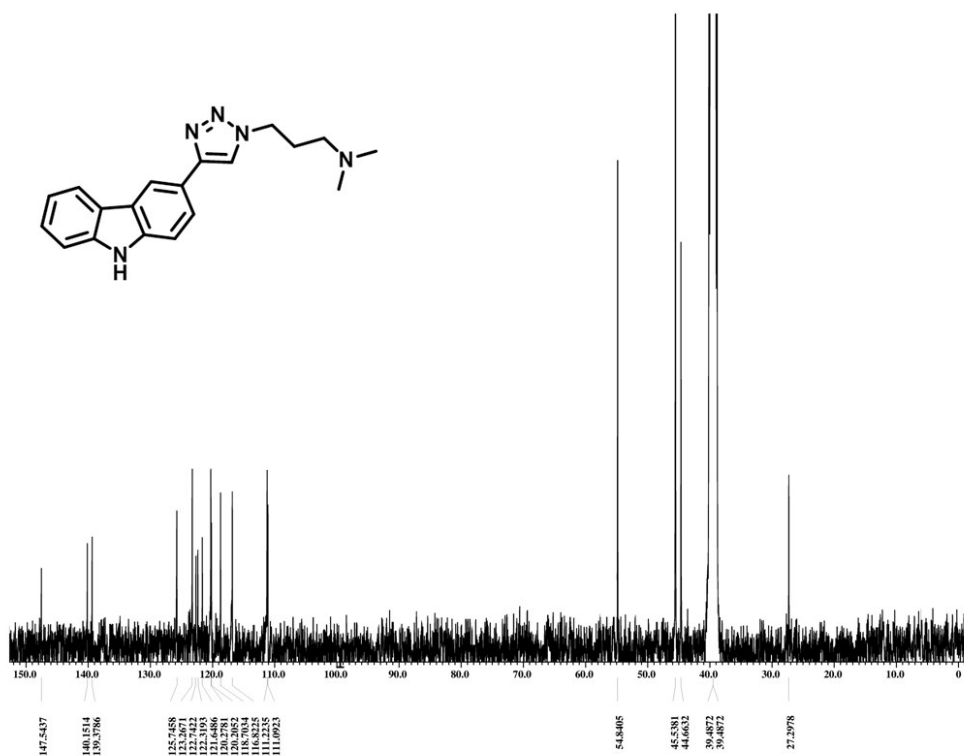
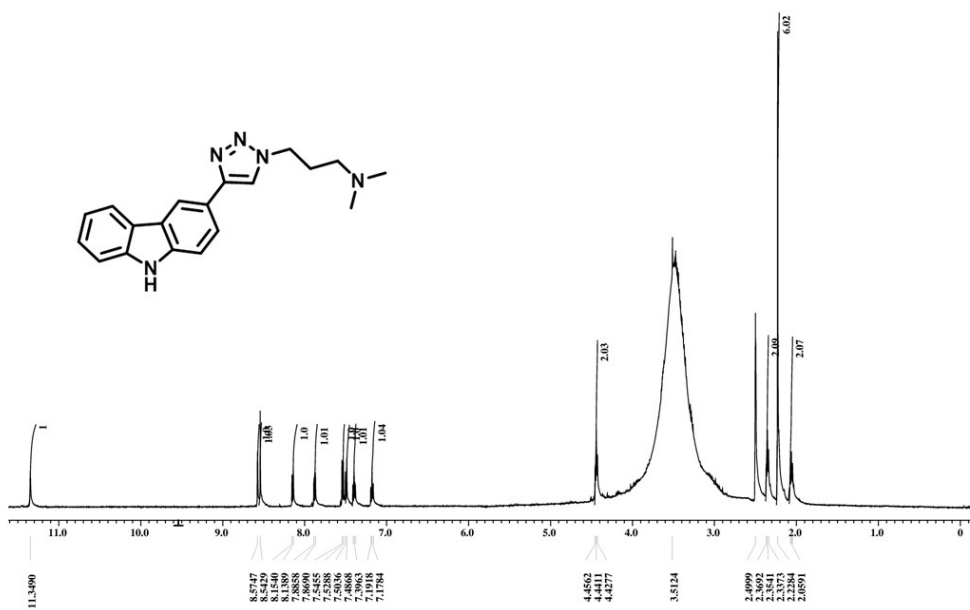
¹H and ¹³C NMR of 6h:



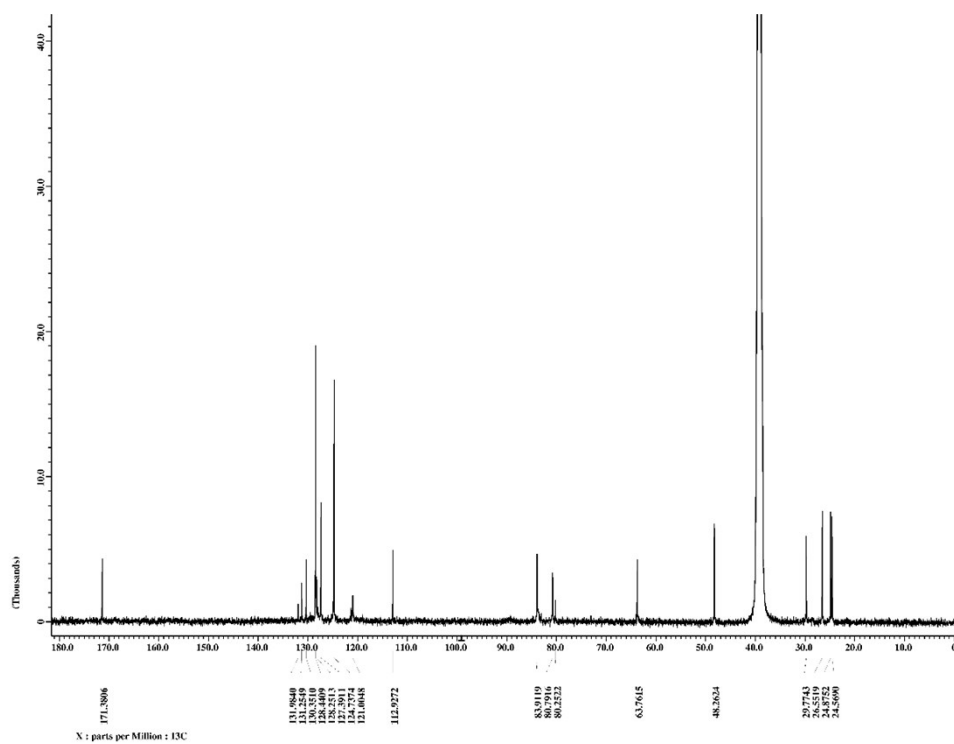
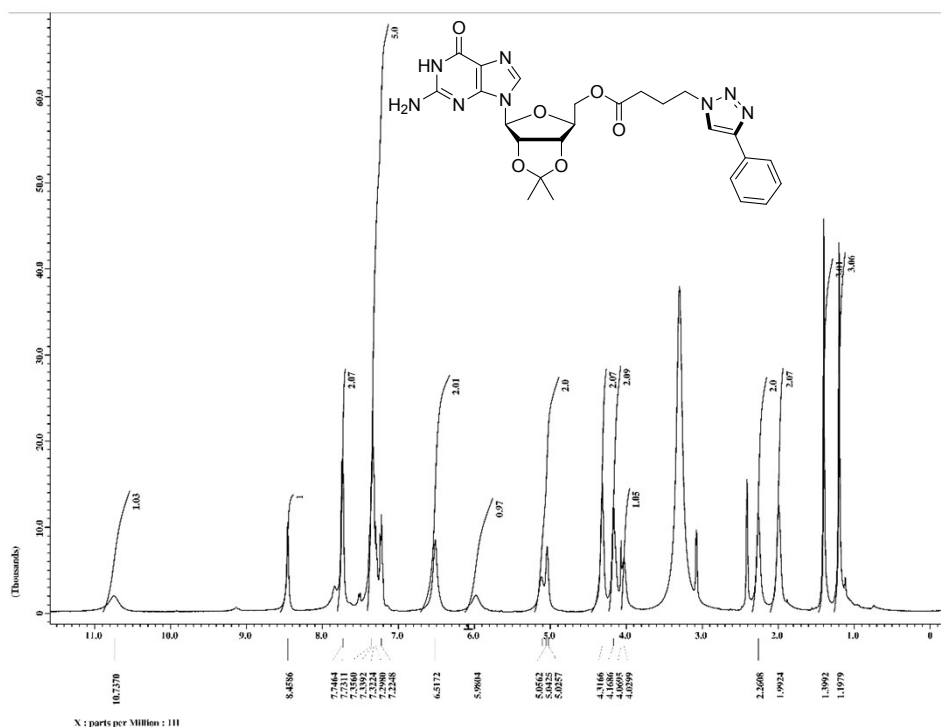
¹H and ¹³C NMR of 6i:



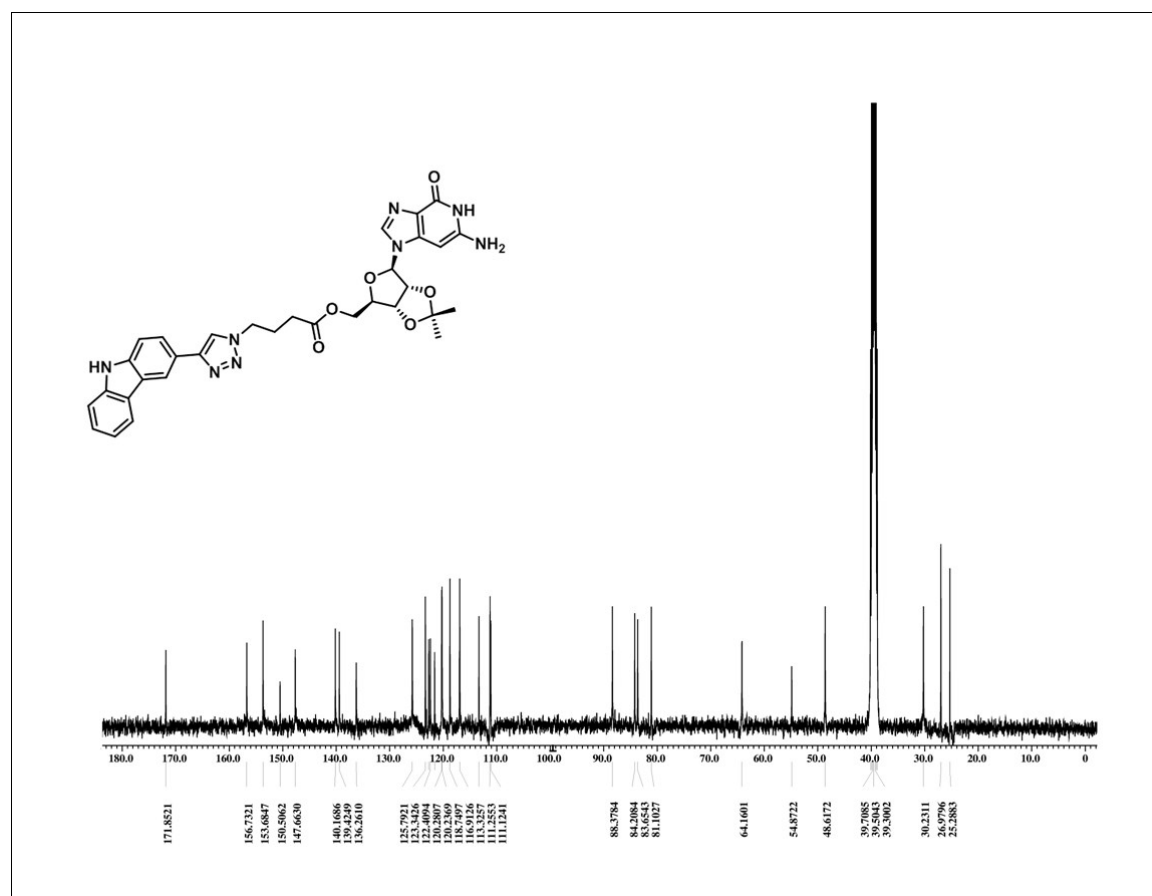
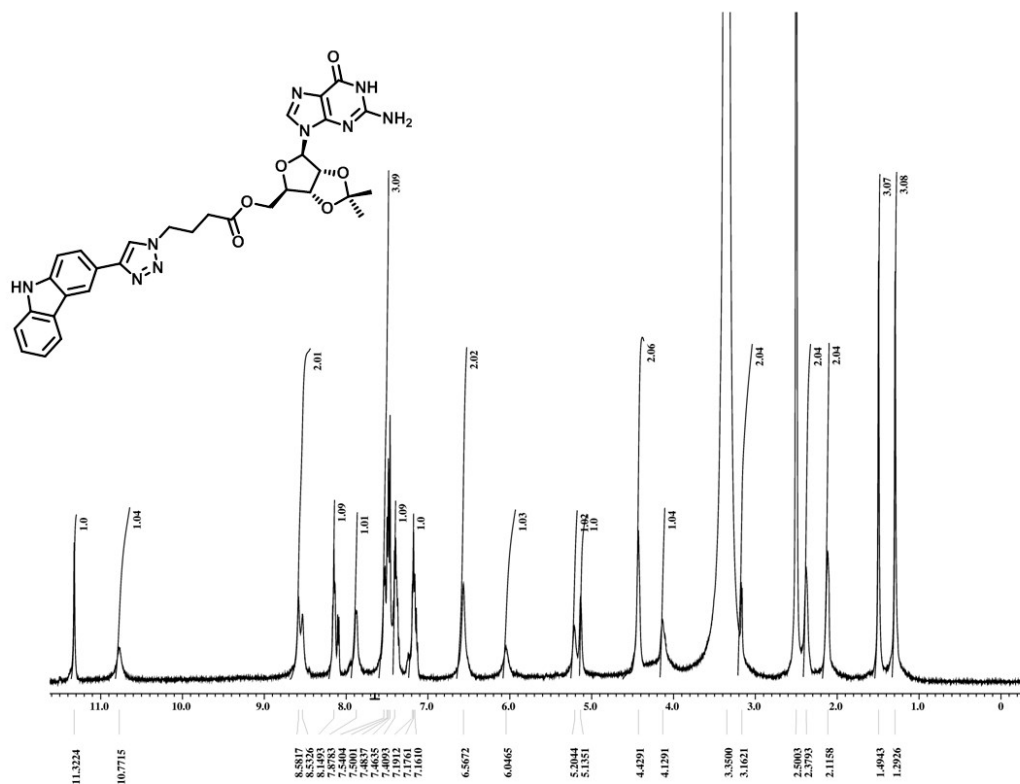
^1H and ^{13}C NMR of 6j:



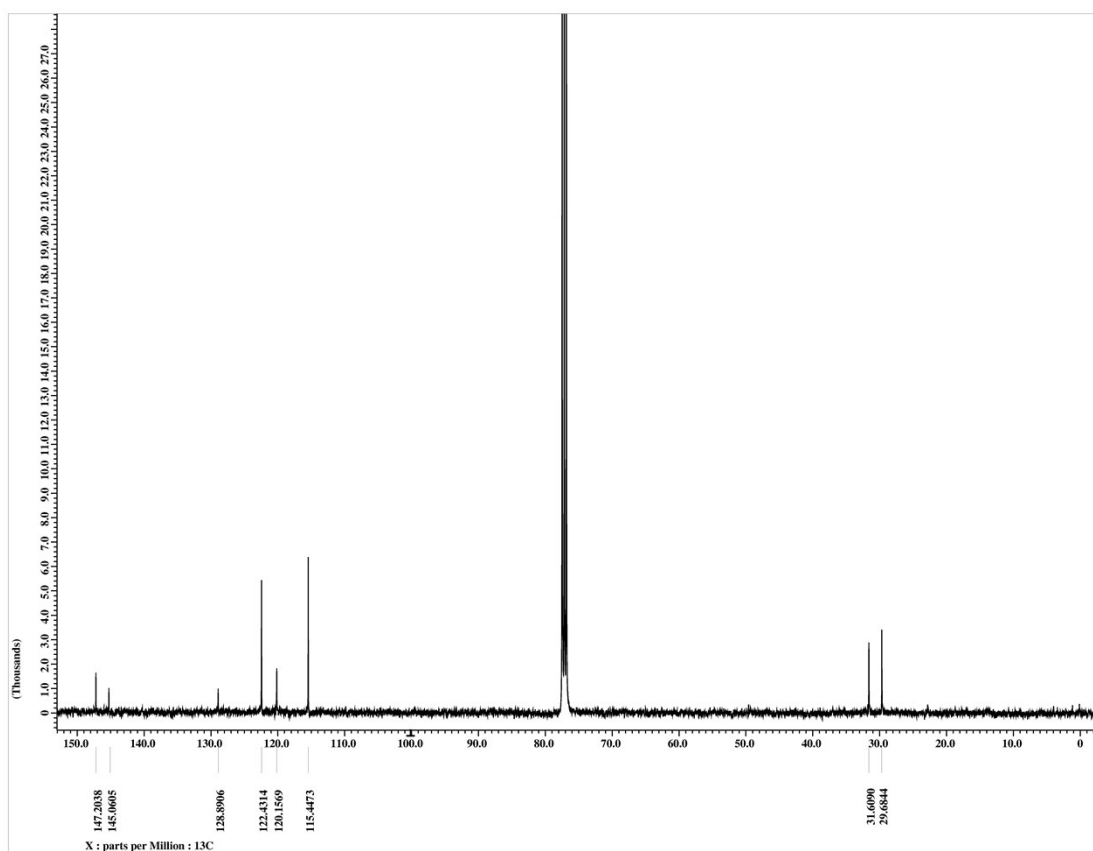
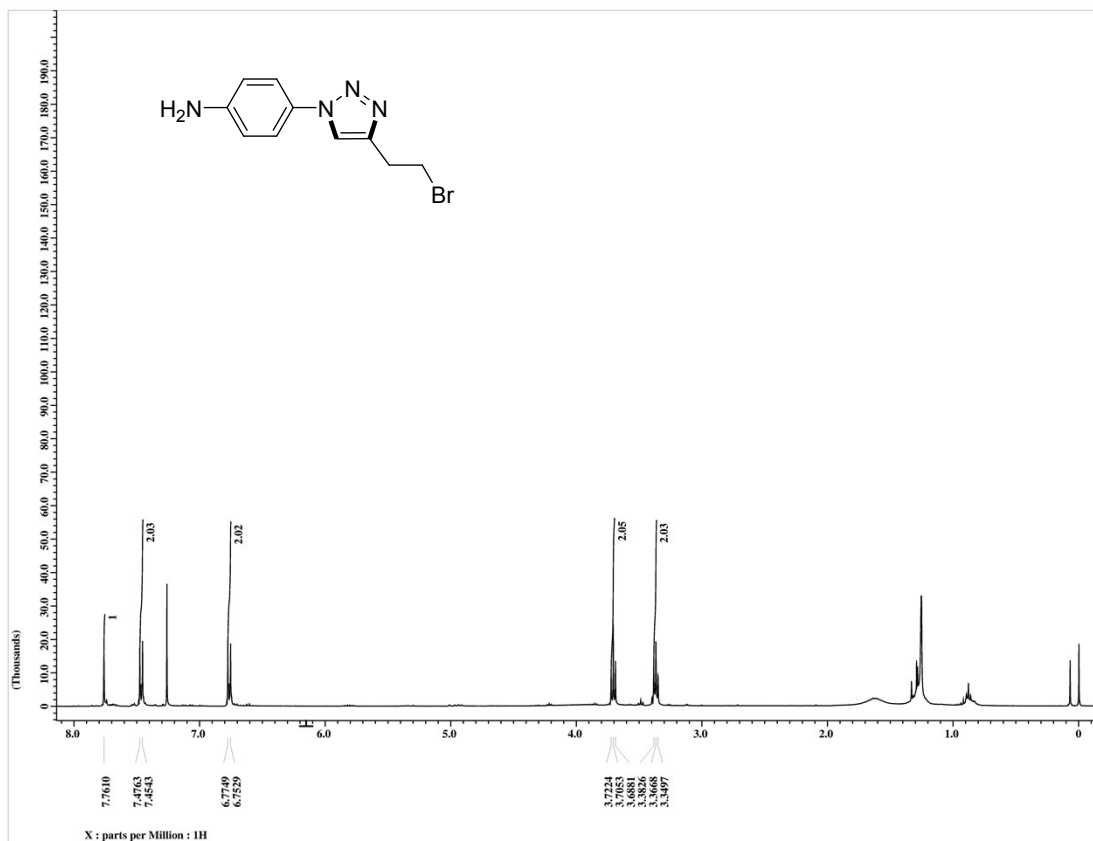
¹H and ¹³C NMR of 6k:



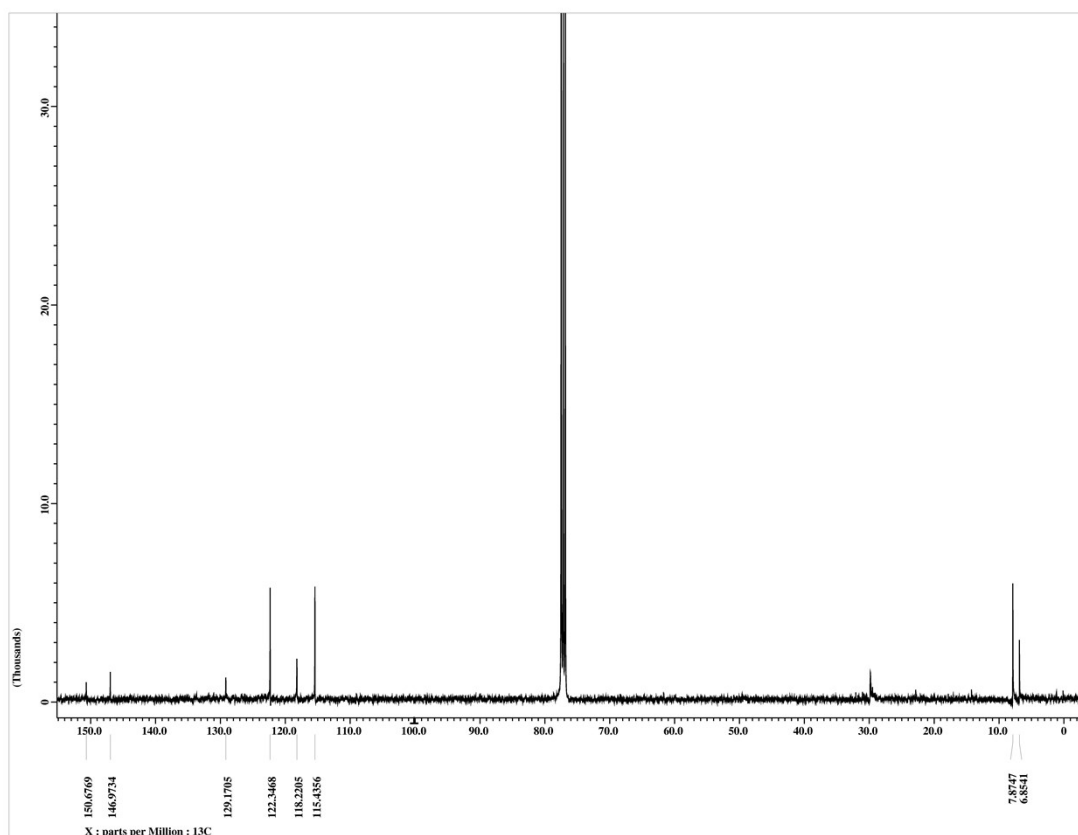
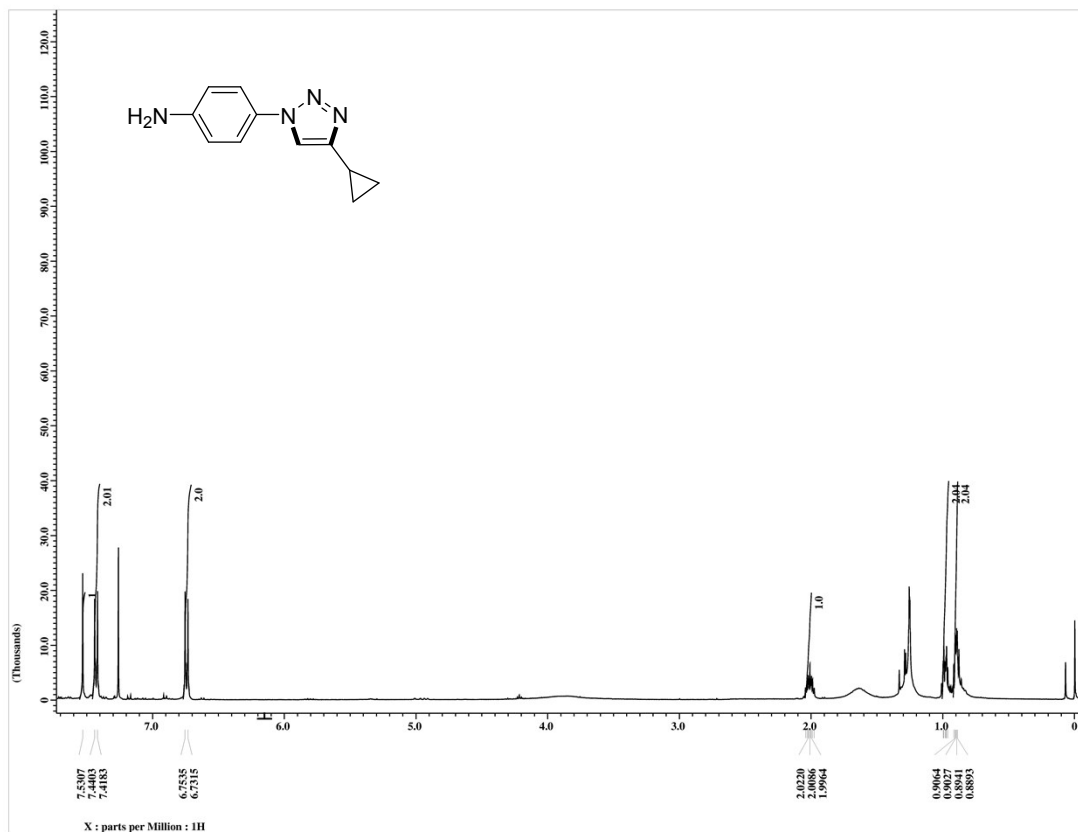
¹H and ¹³C NMR of 6l:



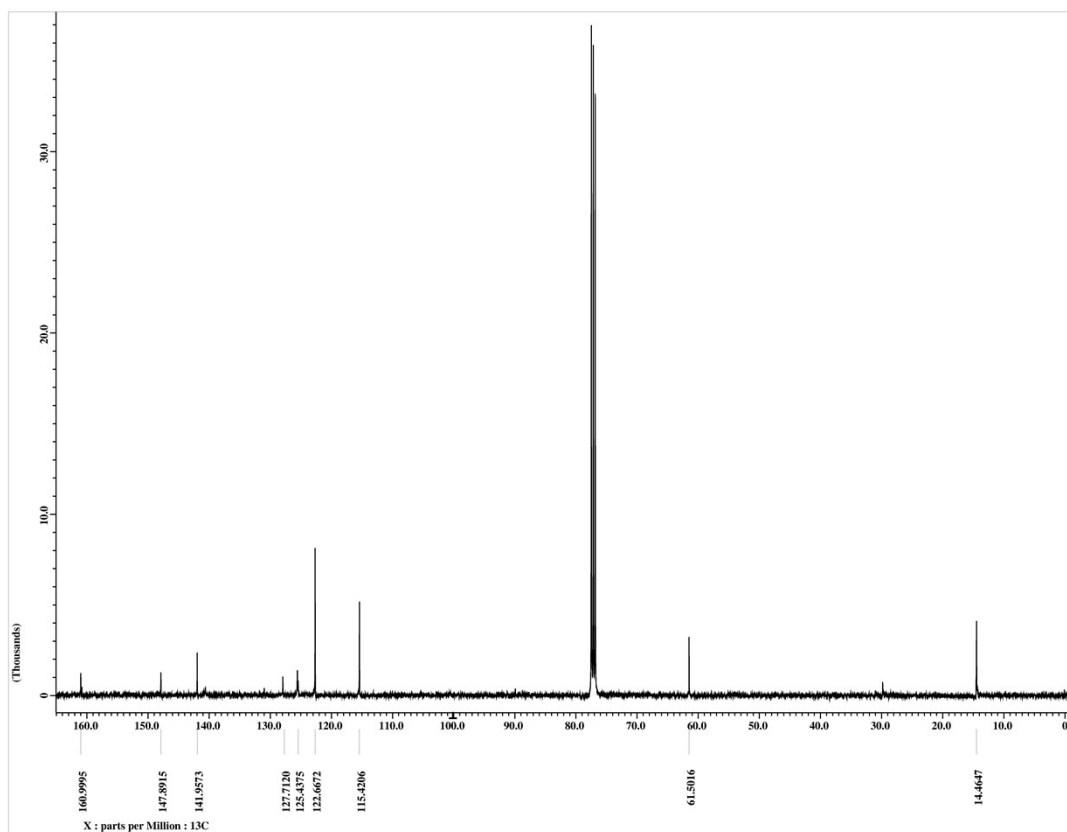
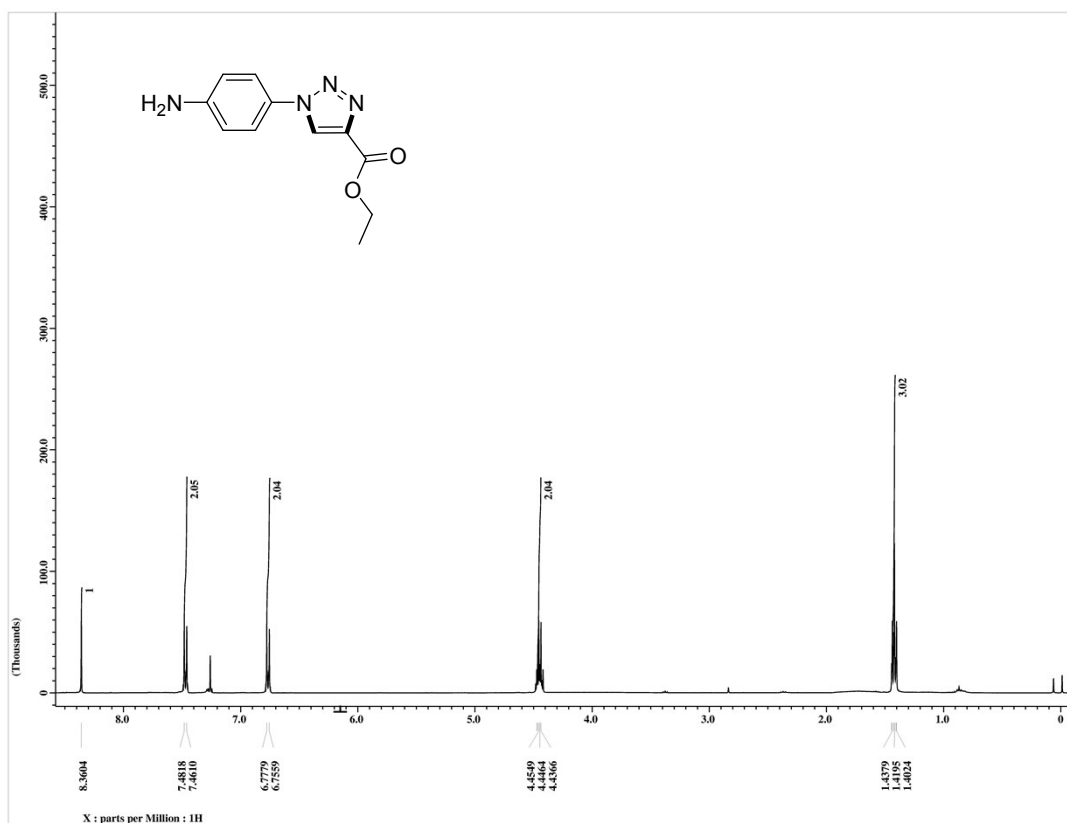
^1H and ^{13}C NMR of 6m:



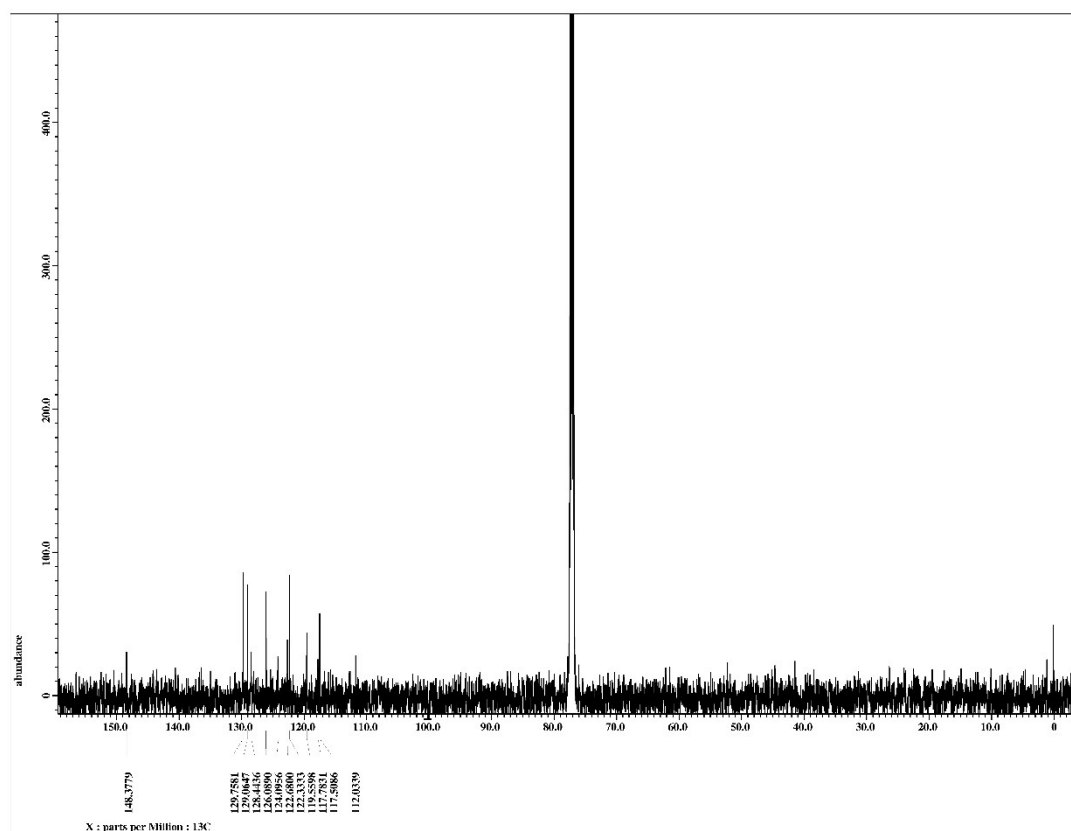
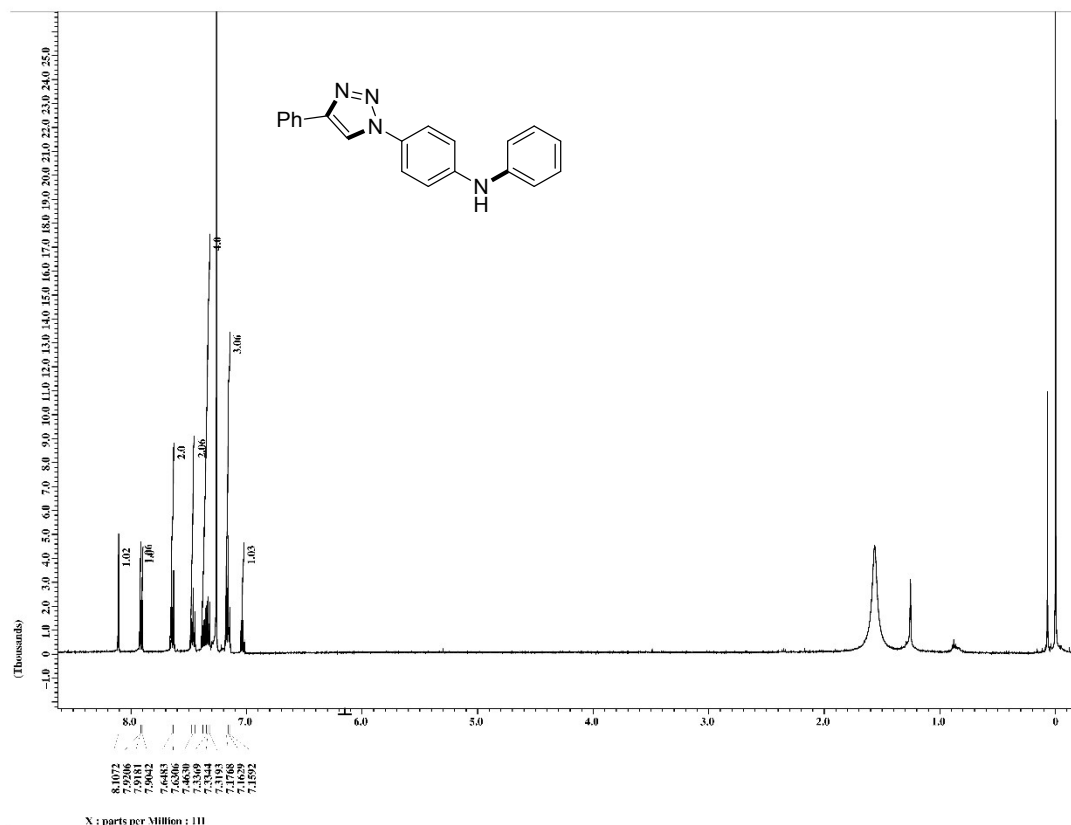
^1H and ^{13}C NMR of 6n:



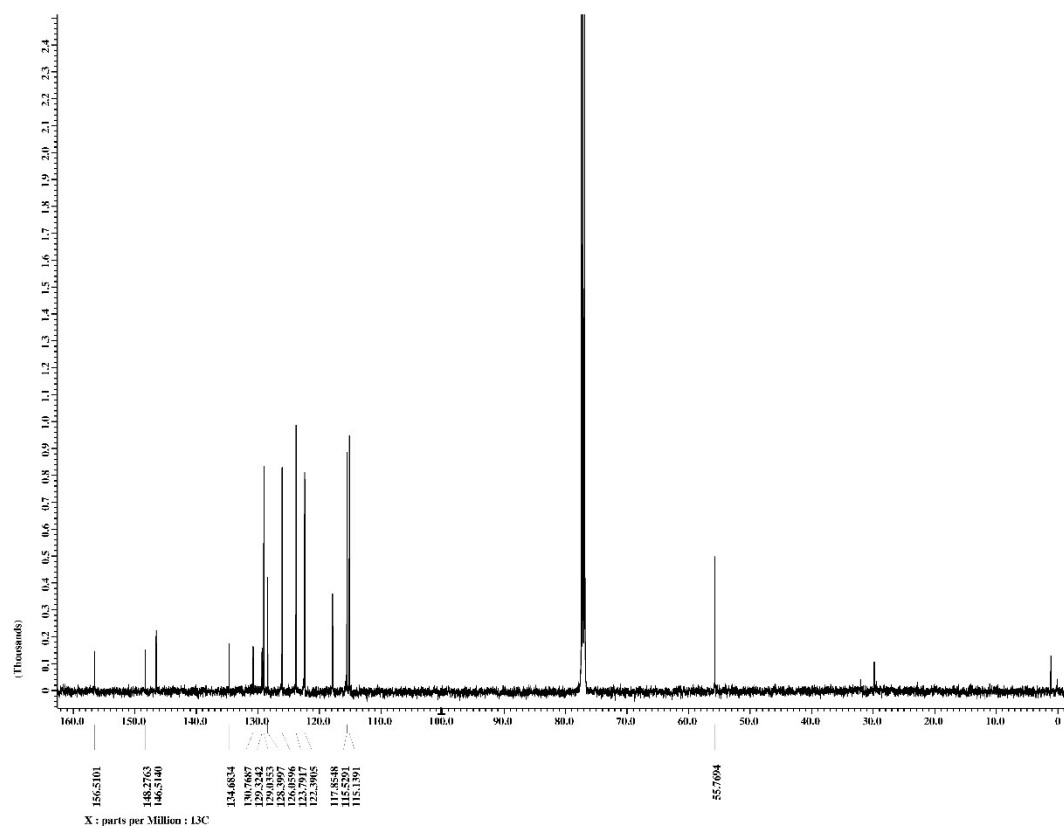
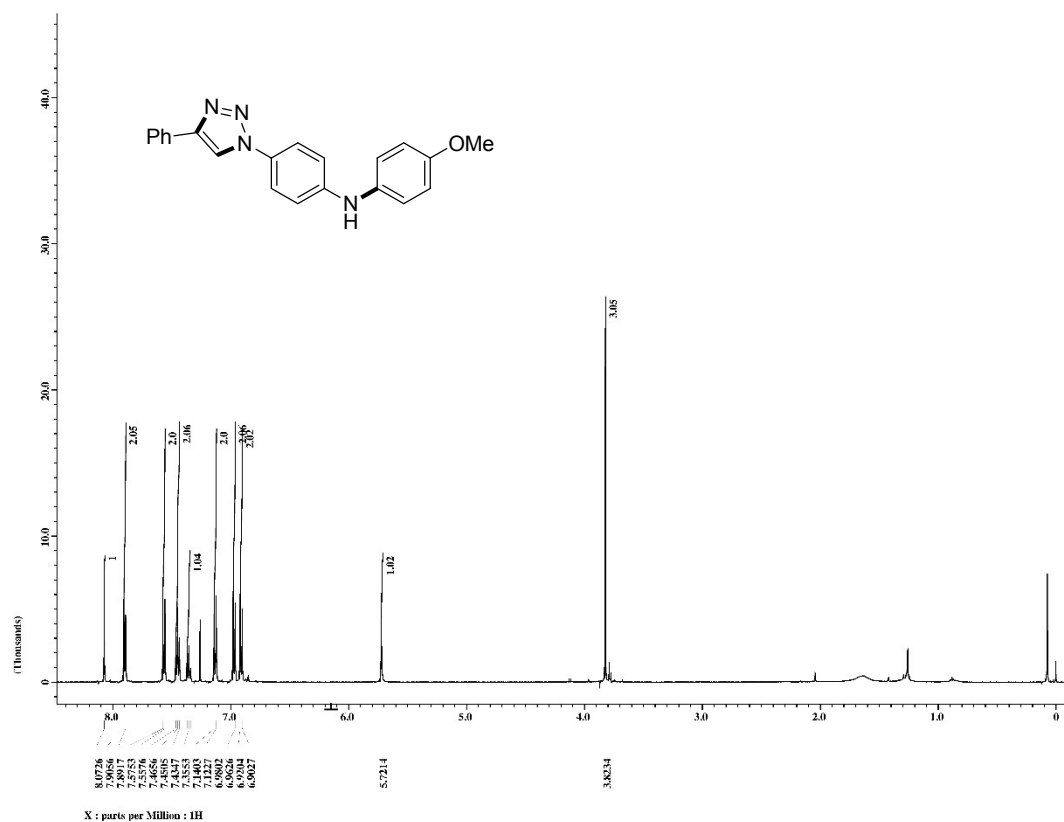
¹H and ¹³C NMR of 6o:



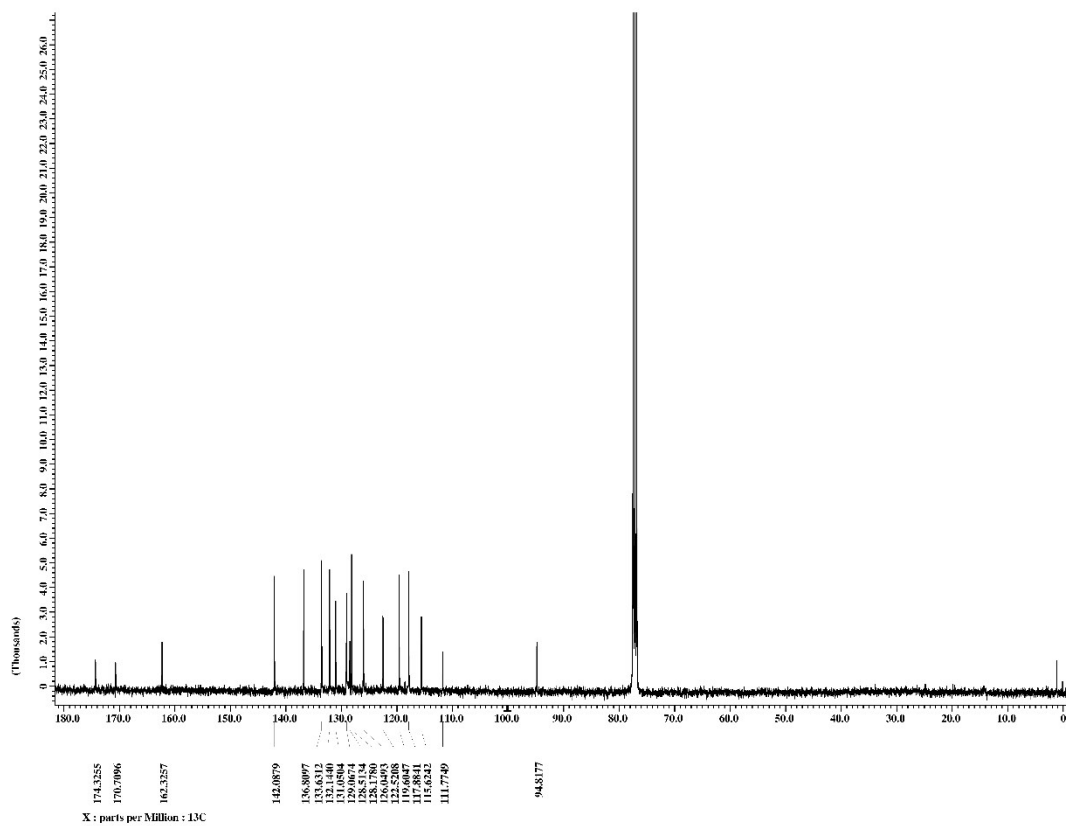
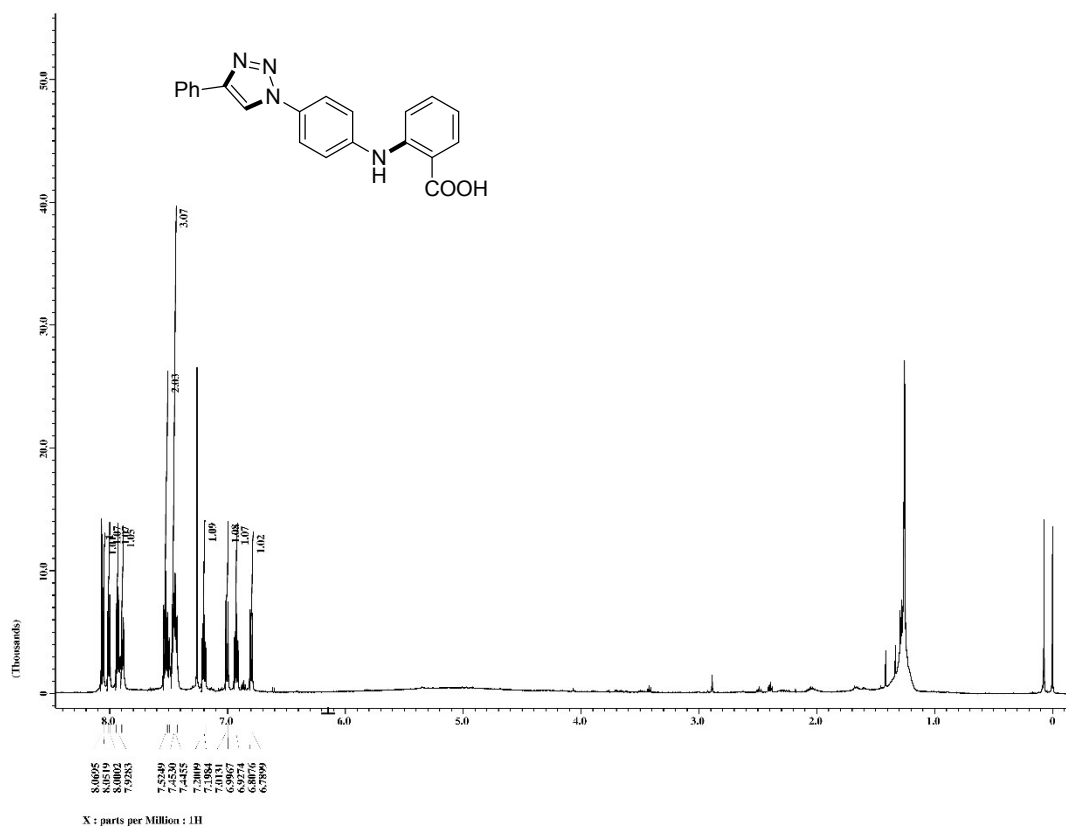
¹H and ¹³C NMR of 11a:



¹H and ¹³C NMR of 11b:



¹H and ¹³C NMR of 11c:



^1H and ^{13}C NMR of 11d:

