Electronic Supplementary Material (ESI) for Materials Advances.

Supporting Information

Nanostructured $Ni(OH)_2$-ZnO mixed crystals as a recyclable catalyst for the synthesis of N-unsubstituted 1,2,3-triazoles

Priyanuj Krishnann Hazarika, Priyanka Gogoi, Roktopol Hazarika, Kalyanjyoti Deori* and Diganta Sarma*

Department of Chemistry, Dibrugarh University, Dibrugarh, Assam 786004, India

Table of Contents

A. Materials and experimental procedures

1. Chemicals

All chemicals namely Zinc acetate ($Zn(OAc)_2 \cdot 2H_2O$, 98.5%), Nickel(II) Acetate tetrahydrate (95.0%) Polyethylene glycol-400 (PEG-400), absolute ethanol (Ethanol, 96%), Sodium Hydroxide (NaOH), Nitromethane (CH_3NO_2), Nitroethane ($C_2H_5NO_2$), Sodium Azide (NaN_3, 99%) and the aldehydes were purchased from commercial suppliers and used without further purification. The products were purified by column chromatography using silica gel (200-300 mesh). The thin-layer chromatography for visualization under UV light was performed using silica gel $60F_{254}$ plates.

2. Instrumentation Details

1H NMR (500 MHz) and 13C NMR (125 MHz) were recorded on a Brucker Avance 500 MHz spectrometer using TMS as an internal standard. The chemical shifts of the analyzed products are informed in parts per million (ppm) and splitting patterns are assigned as: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Thermo Scientific Endura LC/MS mass spectrometer has been used for recording mass spectra. XRD were recorded with Bruker D8 Advance X-Ray Diffractometer. Low resolution transmission electron microscopy (TEM) images, selected area electron diffraction (SAED) and phase-contrast high-resolution TEM (HRTEM) images were recorded using JEOL (JEM-F200) instrument at an accelerating voltage of 200 kV. XPS was done on ESCALAB Xi+ XPS system using an Al Kα source. SEM and EDX analyses are carried out on Jeol JSM-IT300 Scanning electron microscope.

3. Preparation of catalyst

For the synthesis of Nickel-Zinc oxide mixed crystal nanoparticles, CTAB (cetyltrimethyl ammonium bromide) was used as the capping agent. 0.5 g of CTAB was initially dissolved in a solution of 50 mL of deionized water. This was then added to the zinc acetate solution prior to the addition of the nickel acetate. At first, 5.48 g (0.5 M) of zinc acetate was dissolved in 50 mL of deionized water and stirred at room temperature for 30 minutes to obtain a clear solution of zinc acetate. The individually prepared surfactant was then added to the solution of zinc acetate drop wise with continuous stirring. After complete dissolution, 25 mL of nickel acetate solution (0.11g of nickel acetate in 25 mL water) was added to zinc acetate-surfactant solution drop wise and the resultant solution was heated in a magnetic stirrer at 80°C until a homogenous solution was obtained. Then, 0.5 M solution of NaOH was added to the above mixture until precipitation occurs and allowed to agitate at room temperature for 3 hour. The as-obtained

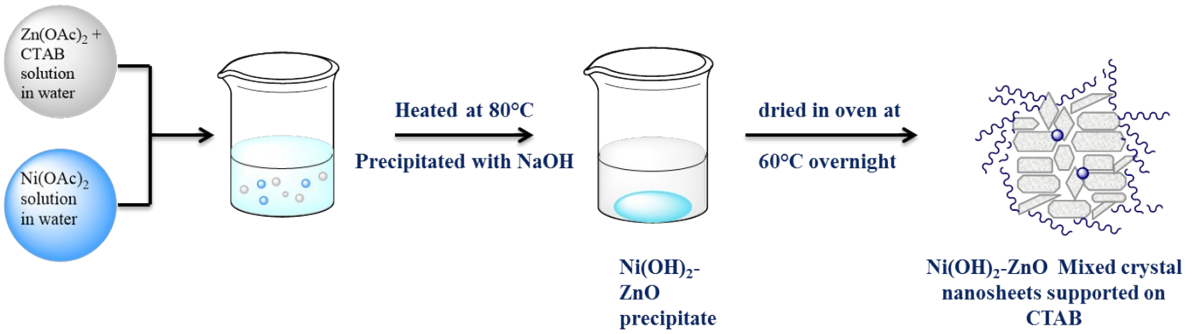
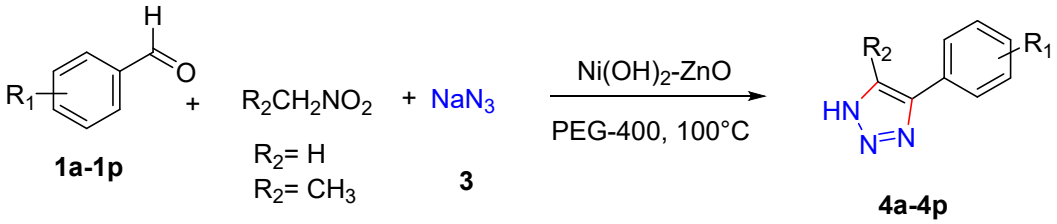


Figure S1 : Schematic representation for the formation of $Ni(OH)_2$-ZnO nanostructured mixed crystals

light blue product was then centrifuged and washed with water and ethanol for several times to remove excess surfactants or any other impurities. The final product was then air dried at 80 °C for 7 h and further characterized by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), XPS and X–Ray Diffraction (XRD) analyses.

ZnO nanoparticles supported on CTAB has been synthesized following the same procedure as above and only the steps involving the addition of nickel acetate was omitted during the reaction.

4. Synthesis of NH-triazoles



The corresponding aromatic aldehyde (1mmol), nitroalkane (2 mmol), sodium azide (3 mmol), and $Ni(OH)_2$-ZnO nanocatalyst (0.025 g) were stirred in a round-bottom flask containing 5 mL of PEG-400 solvent at 100°C . The progress of the reactions was checked by TLC. After completion of the reaction, the mixture was cooled to room temperature and extracted with ethyl acetate (4 × 10 mL). The filtrate was evaporated to dryness under reduced pressure. The final product was purified by column chromatography over silica gel using hexane/ethyl acetate mixture and the products obtained were characterized by NMR and mass spectroscopy. The recovered catalyst was washed with hot ethanol, dried and reused.

B. Characterization of Nanostructured $Ni(OH)_2$-ZnO mixed crystals

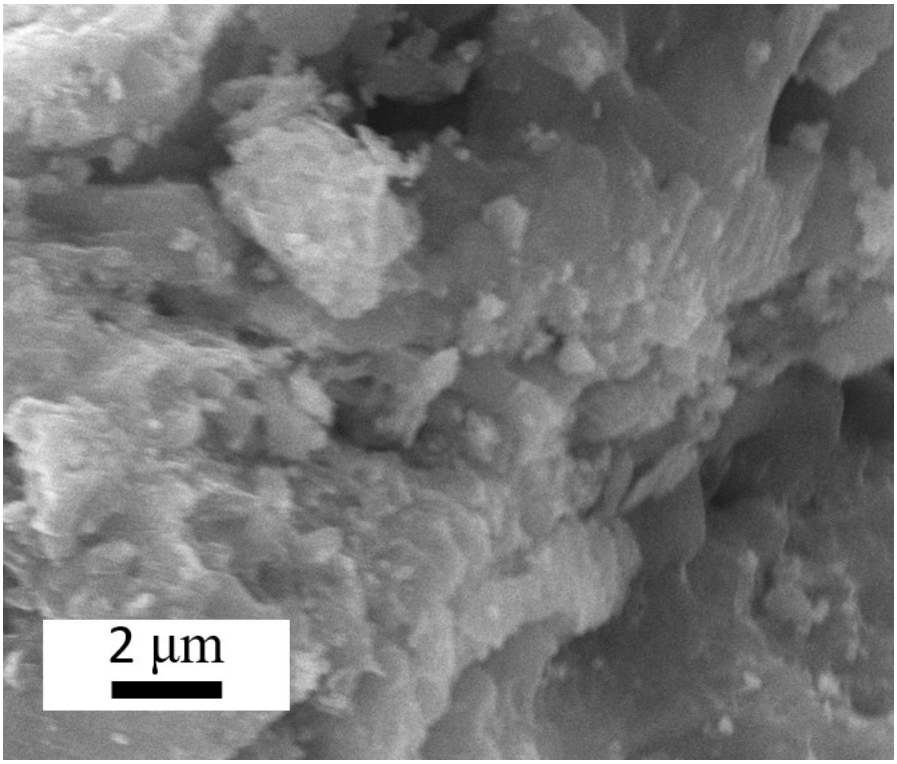
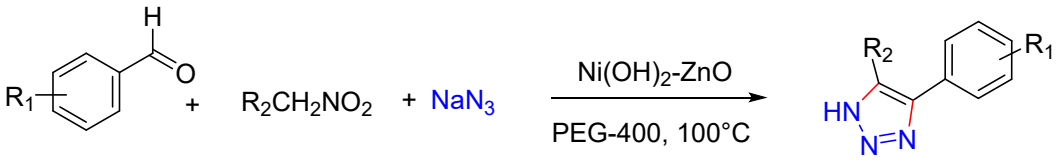


Figure S2: SEM image of the as-synthesized nanostructured $Ni(OH)_2$-ZnO mixed crystals

C. Optimization tables

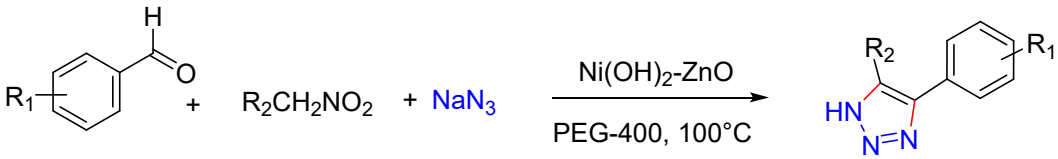
Table S1: Optimization of catalyst loading in the synthesis of 4-aryl-NH-1,2,3-triazoles[a]



Sl. No.	Catalyst (mg)	Time (h)	Yield (%)[b]
1	30	4	96
2	25	4	96
3	20	4	90
4	15	4	85
5	10	4	83
6	5	4	80
7	25	3.5	96
8	25	2	90

[a]Reaction conditions: 4-chloro benzaldehyde (0.140g, 1 mmol), sodium azide (0.195g, 3 mmol) and nitromethane (0.122g, 2 mmol) were refluxed in PEG-400 (4 ml) with different amount of catalysts.
[b]Isolated yield

Table S2: Solvent and temperature optimization[a].

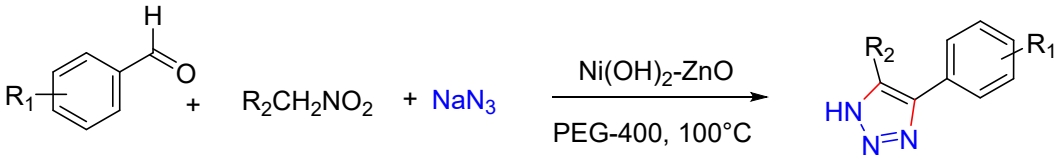


Sl. No.	Solvent	Temperature	Yield (%)[b]
1	Ethylene Glycol	100	50
2	Water	100	trace
3	Ethanol	80	30
4	Toluene	100	50
5	Acetonitrile	80	20
6	DMF	100	60

7	DMSO	100	65
8	PEG-400	100	96
9	PEG-400	80	85
10	PEG-400	60	80
12	PEG-400	r.t.	trace
13	Chloroform	60	-
14	THF	65	-
15	H_2O + PEG (1:1)	100	80
16	H_2O + PEG (1:3)	100	80

[a]*Reaction conditions: 4-chloro benzaldehyde (0.140 g, 1 mmol), sodium azide (0.195 g, 3 mmol) and nitromethane (0.122 g, 2 mmol) were reacted in PEG-400 (4 ml) for 4 h with different solvents.*
[b]*Isolated yield.*

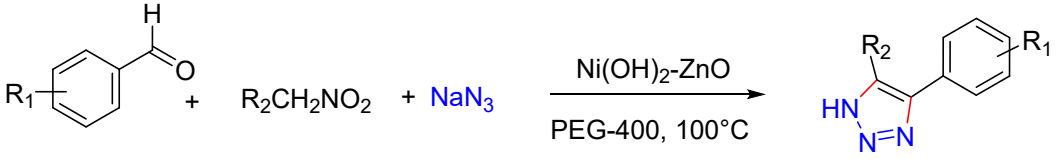
Table 3: Optimization of the catalyst[a]



Sl. No.	catalyst	Amount (mg)	Yield (%)[b]
1	$Zn(OAc)_2$	25	45
2	$Ni(OAc)_2$	25	50
3	ZnO nanoparticles	25	80
4	1% Ni@ ZnO	25	94
5	2% Ni@ZnO	25	96
6	5% Ni@ZnO	25	90
7	Without catalyst	-	45

[a]*Reaction conditions: 4-chloro benzaldehyde (0.140 g, 1 mmol), sodium azide (0.195 g, 3 mmol) and nitromethane (0.122 g, 2 mmol) were reacted in PEG-400 (4 ml) for 4 h with different catalysts.*
[b]*Isolated yield.*

Table S4: Gram Scale Synthesis[a]



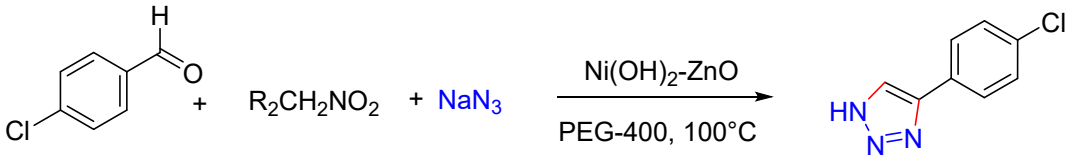
Sl.No.	Aldehyde	Nitroalkane	Sodium Azide	%Yield[b]

1	4-fluorobenzaldehyde (1g, 8.05 mmol)	Nitromethane (0.983g,16.12 mmol)	Sodium Azide (1.6g, 24.15 mmol)	70
2	4-bromobenzaldehyde (1g, 5.40 mmol)	Nitromethane (0.659g, 10.8 mmol)	Sodium Azide (1.05g, 16.2 mmol)	68

[a]*Reaction conditions: aldehyde (1 mmol), sodium azide (3mmol) and nitromethane (2 mmol) were reacted in PEG-400 (4 ml) with* $Ni(OH)_2$–ZnO *catalysts.*
[b]*Isolated yield.*

C. Recyclability of catalyst[a]

We have performed the recyclability test by taking the exact molar ratios of substrates with respect to the amount of the recovered catalyst and found no significant drop of the catalytic activity.



Sl.No.	4-chloro benzaldehyde	Nitromethane	Sodium azide	Catalyst (mg)	Yield (%)[b]
1st Run	**0.140 g, 1 mmol**	**0.122g, 2 mmol**	**0.195g, 3 mmol**	**25***	**96**
2nd Run	**0.123 g, 0.88 mmol**	**0.107 g, 1.76 mmol**	**0.171 g, 2.64 mmol**	**22 ****	**95**
3rd Run	**0.117 g, 0.84 mmol**	**0.102 g, 1.68 mmol**	**0.163 g, 2.52 mmol**	**21 ****	**92**
4th Run	**0.112 g, 0.80 mmol**	**0.070 g, 1.60 mmol**	**0.156 g, 2.40 mmol**	**20****	**90**

*** Initial catalyst amount**

**** Recovered catalyst amount after each successive runs**

[a]Reaction conditions: aldehyde (1 mmol), sodium azide (3mmol) and nitromethane (2 mmol) were reacted in PEG- 400 (4 ml) with $Ni(OH)_2$–ZnO catalysts. [b]Isolated yield.

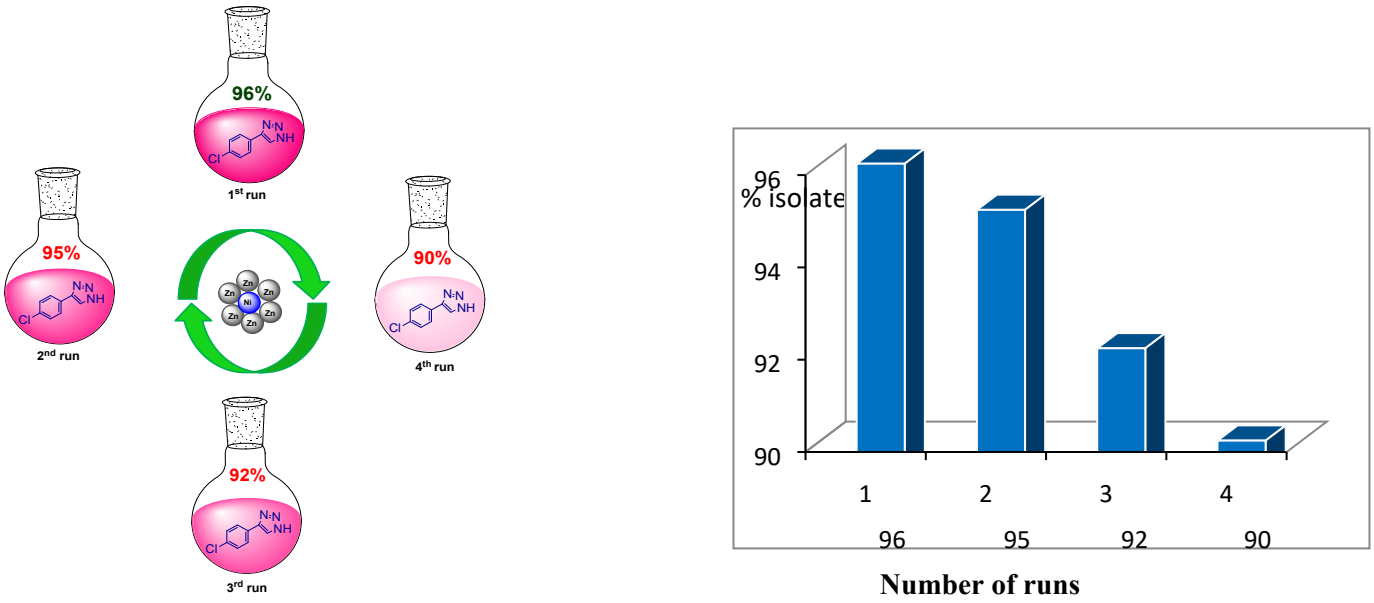


Figure S3: Schematic and graphical representation of the reused catalyst

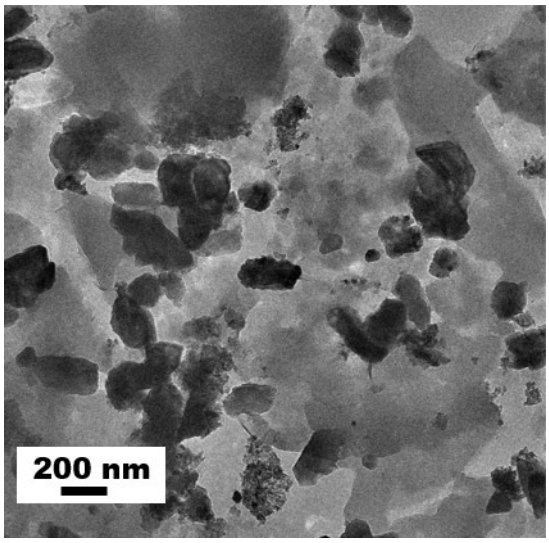
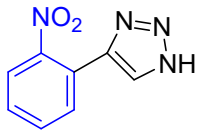


Figure S4: TEM image of the recovered catalyst

D. Characterization data of NH-1,2,3 triazoles derivatives

4-(2-nitrophenyl)-1H-1,2,3-triazole **(Scheme 1 , Entry 4c)**

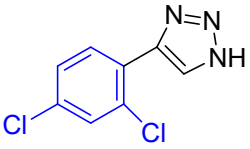


Brown solid; MS (EI) m/z: 191.16 $[M+H]^+$

^{1}H NMR (500 MHz, $CDCl_3$) δ: 12.51(s, 1H), 7.68 (s, 1H), 7.56-7.57(d, 1H), 7.82-7.91 (m, 3H);

^{13}C NMR (126 MHz, $CDCl_3$) δ: 148.73, 132.52, 131.26, 129.51, 124.20.

4-(2,4-dichlorophenyl)-1H-1,2,3-triazole **(Scheme 1 , Entry 4j)**

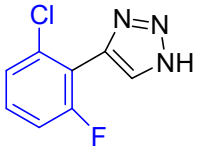


Pale yellow solid; MS (EI) m/z: 213.97 $[M+H]^+$

^{1}H NMR (500 MHz, $CDCl_3$) δ: 10.33 (s, 1H), 8.27 (s, 1H), 7.9-7.95 (d, 1H), 7.53 (s, 1H), 7.27-7.38 (d, 1H),

^{13}C NMR (126 MHz, $CDCl_3$) δ: 131.12, 130.91, 130.21, 129.65, 129.26, 127.64.

4-(2-chloro-6-fluorophenyl)-1H-1,2,3-triazole **(Scheme 1 , Entry 4e)**

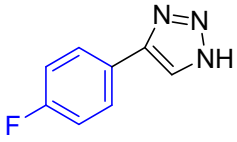


Dark brown solid; MS (EI) m/z: 198.04 $[M+H]^+$

^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.16 (s, 1H), 8.05(s, 1H), 7.33-7.31(t, 1H), 7.10-7.11 (d, 1H), 7.12-7.14 (d, 1H),

^{13}C NMR (126 MHz, $CDCl_3$) δ: 161.74, 137.25, 134.60, 130.50, 126.03, 118.00, 117.87, 114.72.

4-(4-fluorophenyl)-1H-1,2,3-triazole **(Scheme 1 , Entry 4b)**

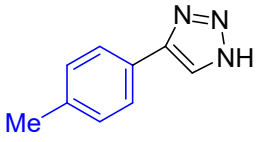


Brick red solid; MS (EI) m/z: 164.08 $[M+H]^+$

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.43 (s, 1H), 7.93 (s, 1H), 7.80-7.82 (d, 2H), 7.15-7.20(d, 2H),

^{13}C NMR (126 MHz, $CDCl_3$) δ: 175.29, 127.91, 127.85, 116.06, 115.89.

4-(p-tolyl)-1H-1,2,3-triazole **(Scheme 1 , Entry 4h)**

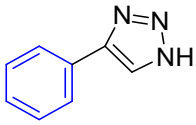


Red Solid, MS (EI) m/z: 160.10 $[M+H]^+$

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.43 (s, 1H), 7.94 (s, 1H), 7.72-7.74 (d, 2H),7.23-7.27 (d, 2H), 2.36 (s, 3H)

^{13}C NMR (126 MHz, $CDCl_3$) δ: 138.69, 129.69, 128.62, 128.42, 126.88, 126.07, 21.34.

4-phenyl-1H-1,2,3-triazole **(Scheme 1 , Entry 4f)**

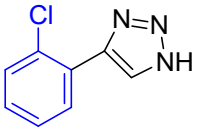


Pale yellow solid; MS (EI) m/z: 146.35 $[M+H]^+$

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.00 (s, 1H), 7.31-7.85 (m, 5H),

^{13}C NMR (126 MHz, $CDCl_3$) δ: 155.57, 129.77, 129.01, 128.78, 126.17.

4-(2-chlorophenyl)-1H-1,2,3-triazole **(Scheme 1 , Entry 4d)**

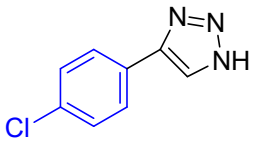


Yellow solid; MS (EI) m/z: 180.15 $[M+H]^+$

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.10 (s, 1H), 8.03 (s, 1H), 7.95-7.97 (d, 1H),7.63-7.74(m,3H),

^{13}C NMR (126 MHz, $CDCl_3$) δ: 175.83, 175.30, 134.78, 132.77, 132.26, 128.82, 127.01, 126.47, 118.68.

4-(4-chlorophenyl)-1H-1,2,3-triazole **(Scheme 1 , Entry 4a)**

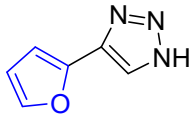


Red solid; MS (EI) m/z: 180.05 $[M+H]^+$

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.46(s, 1H), 7.95 (s, 1H), 7.14-7.45 (m, 4H)

^{13}C NMR (126 MHz, $CDCl_3$) δ: 155.86, 130.00, 129.81, 129.20, 129.03, 128.99, 128.50, 127.37.

4-(furan-2-yl)-1H-1,2,3-triazole **(Scheme 1 , Entry 4i)**

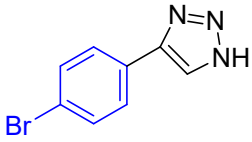


Brown solid; MS (EI) m/z: 136.06 $[M+H]^+$

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.66 (s, 1H), 7.92 (s, 1H), 7.38-7.51 (m, 2H), 6.81-6.83 (d, 1H)

^{13}C NMR (126 MHz, $CDCl_3$) δ: 155.10, 142.99, 139.27, 111.58, 108.04.

4-(4-bromophenyl)-1H-1,2,3-triazole **(Scheme 1 , Entry 4m)**

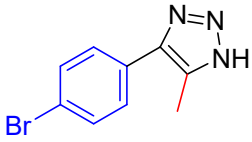


Light yellow; MS (EI) m/z: 223.96 $[M+H]^+$

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.46 (s, 1H), 7.95 (s, 1H), 7.70-7.71 (d, 2H), 7.55-7.59 (d, 2H)

^{13}C NMR (126 MHz, $CDCl_3$) δ: 175.80, 175.27, 132.08, 129.19, 128.82, 127.58.

4-(4-bromophenyl)-5-methyl-1H-1,2,3-triazole **(Scheme 1 , Entry 4n)**

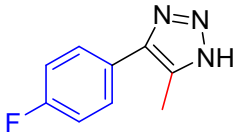


Dark yellow; MS (EI) m/z: 237.99 $[M+H]^+$

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.48-7.50 (d, 2H), 7.53-7.55 (d, 2H), 2.93(s, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ: 173.46, 131.96, 131.75, 129.97, 128.79, 128.52, 121.61, 14.07.

4-(4-fluorophenyl)-5-methyl-1H-1,2,3-triazole **(Scheme 1 , Entry 4l)**

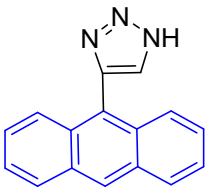


Dark red; MS (EI) m/z: 178.07 $[M+H]^+$

^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.78 (s, 1H), 7.70-7.72 (d, 2H), 7.18-7.21 (d, 2H), 2.51 (s, 3H)

^{13}C NMR (126 MHz, $CDCl_3$) δ: 129.06, 129.00, 128.82, 115.89, 115.72, 14.13.

4-(anthracen-9-yl)-1H-1,2,3-triazole **(Scheme 1 , Entry 4p)**

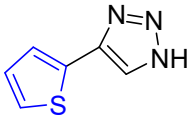


Yellow; MS (EI) m/z: 246.11 $[M+H]^+$

^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.78(s,1H),, 8.58(s,1H), 8.37-8.38(d,1H), , 8.08-8.06(d,1H), 7.98- 7.94(d,1H), 7.50-7.42(m,5H);

^{13}C NMR (126 MHz, $CDCl_3$) δ: 131.21, 128.78, 128.60, 126.46, 126.28, 125.89, 125.76, 125.55, 125.38, 125.28.

4-(thiophen-2-yl)-1H-1,2,3-triazole **(Scheme 1 , Entry 4k)**

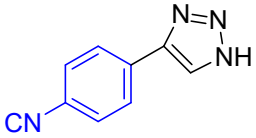


Dark brown solid; MS (EI) m/z: 152.05 $[M+H]^+$

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.53 (s, 1H), 7.91 (s, 1H), 7.45-7.44 (d, 1H), 7.36-7.35 (d, 1H), 7.12- 7.10 (t, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ: 155.90, 142.20, 131.98, 131.01, 128.59, 127.83, 127.75, 126.53, 125.88, 125.38, 77.34, 77.08, 76.83.

4-(4-isocyanophenyl)-1H-1,2,3-triazole **(Scheme 1 , Entry 4o)**



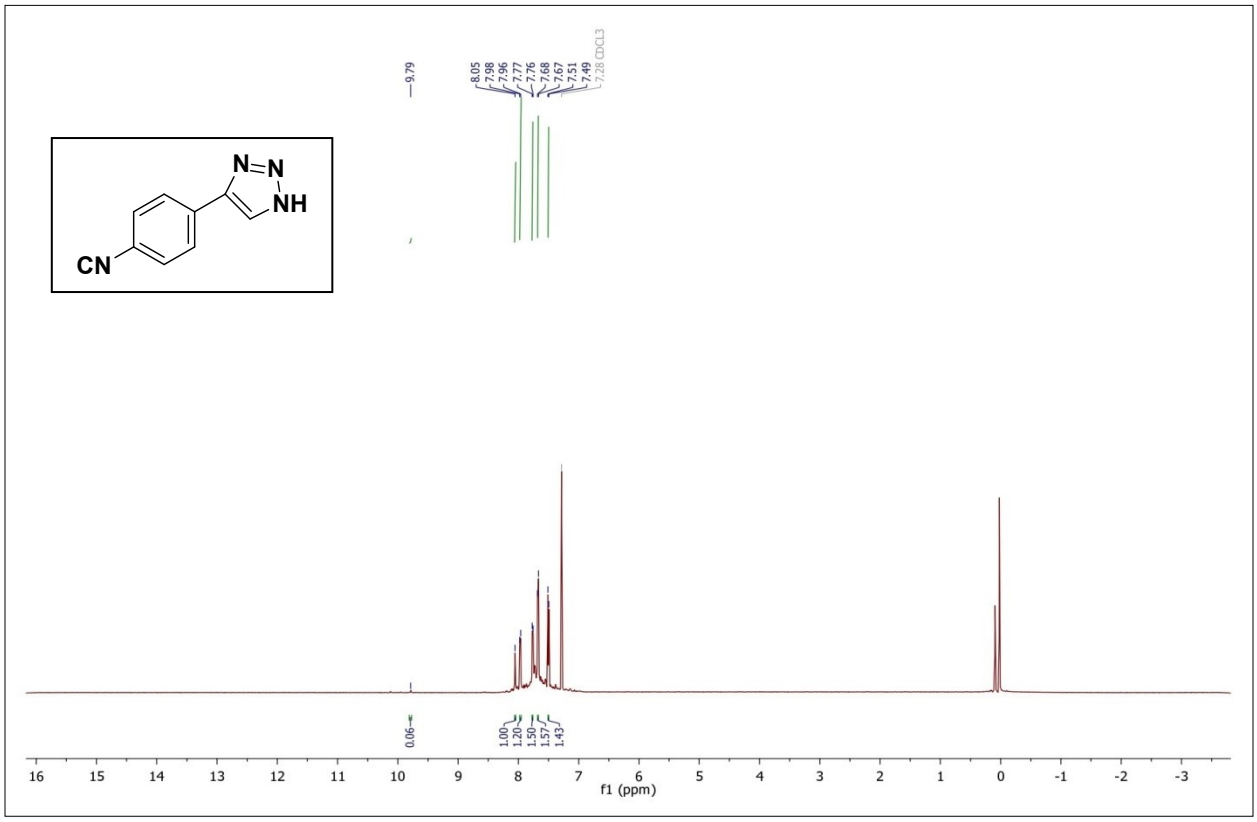
Dark brown solid; MS (EI) m/z: 171.07 [M+H]+

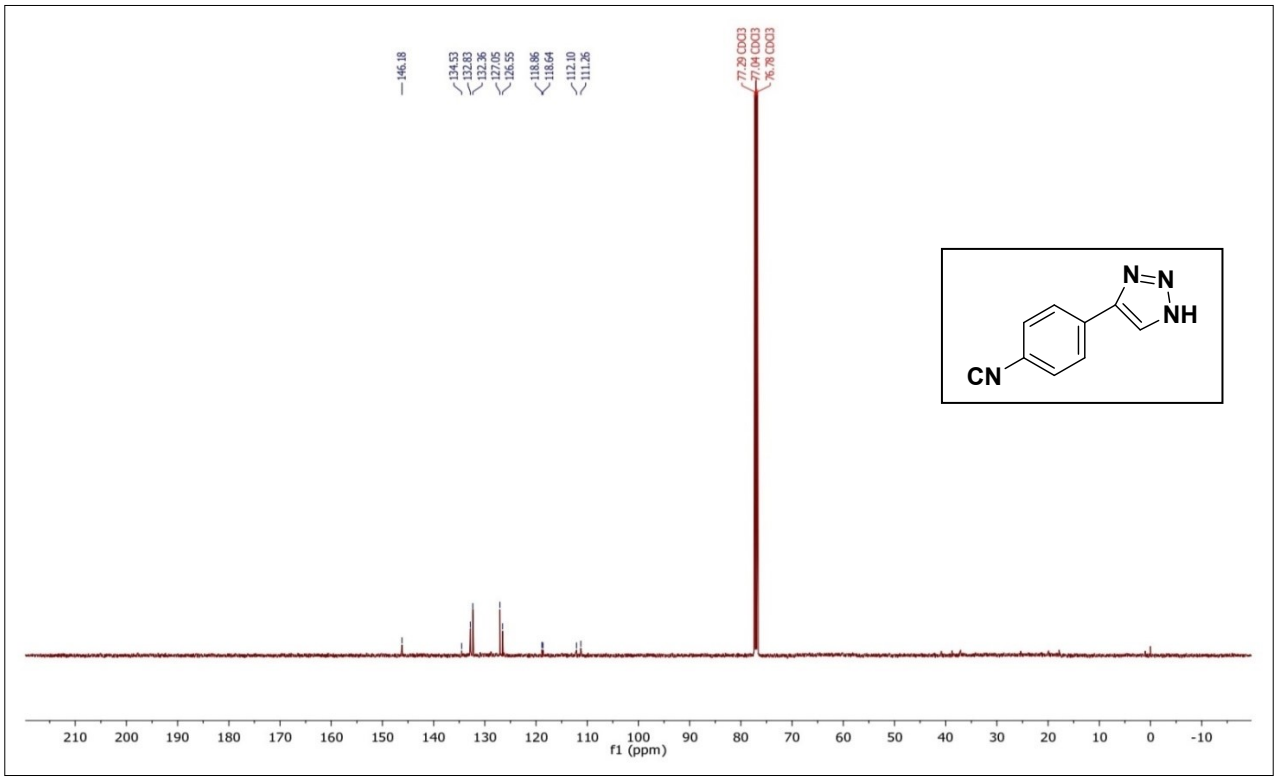
^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.78 (s, 1H), 8.05 (s, 1H), 7.98-7.96 (d, 1H), 7.77- 7.76 (d, 1H), 7.68-7.67 (d, 1H),, 7.51-7.49 (d, 1H);

^{13}C NMR (126 MHz, $CDCl_3$) δ: 146.18, 134.53, 132.83, 132.36, 127.05, 126.55, 118.86, 118.64, 112.10, 111.26, 76.78.

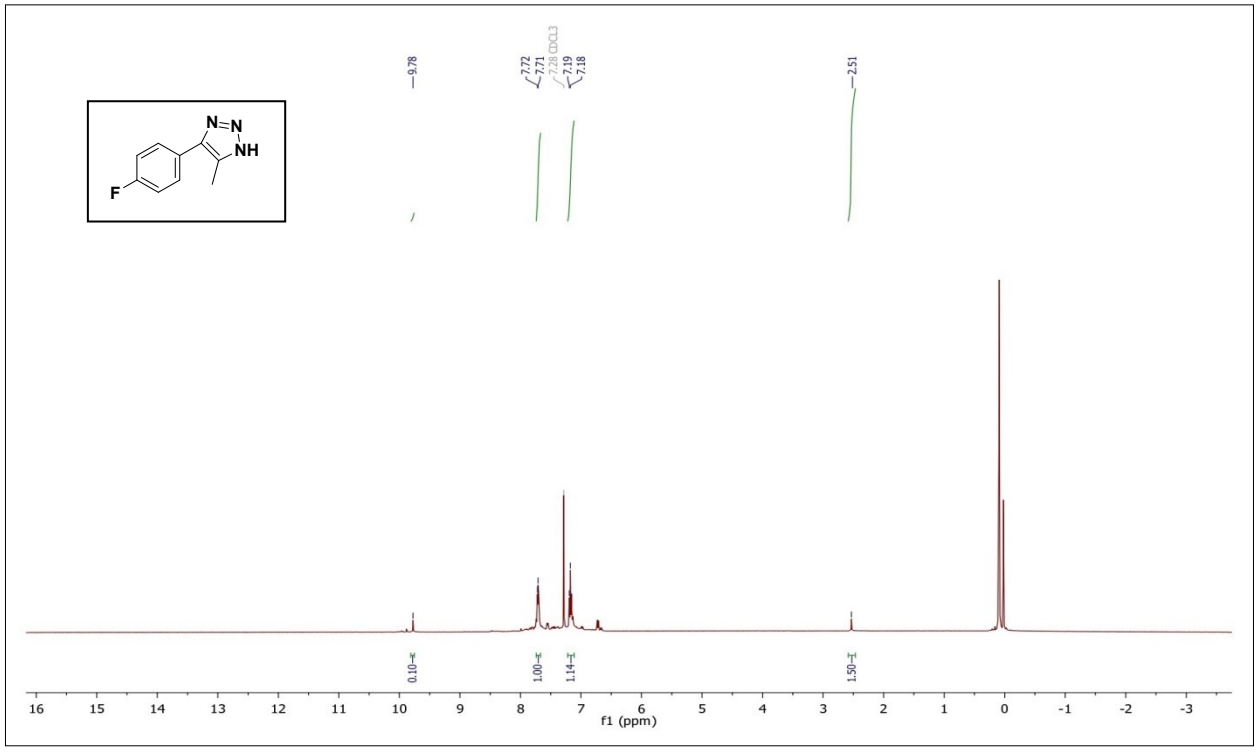
E. ^{1}H NMR and ^{13}C NMR spectra of NH-triazoles derivatives

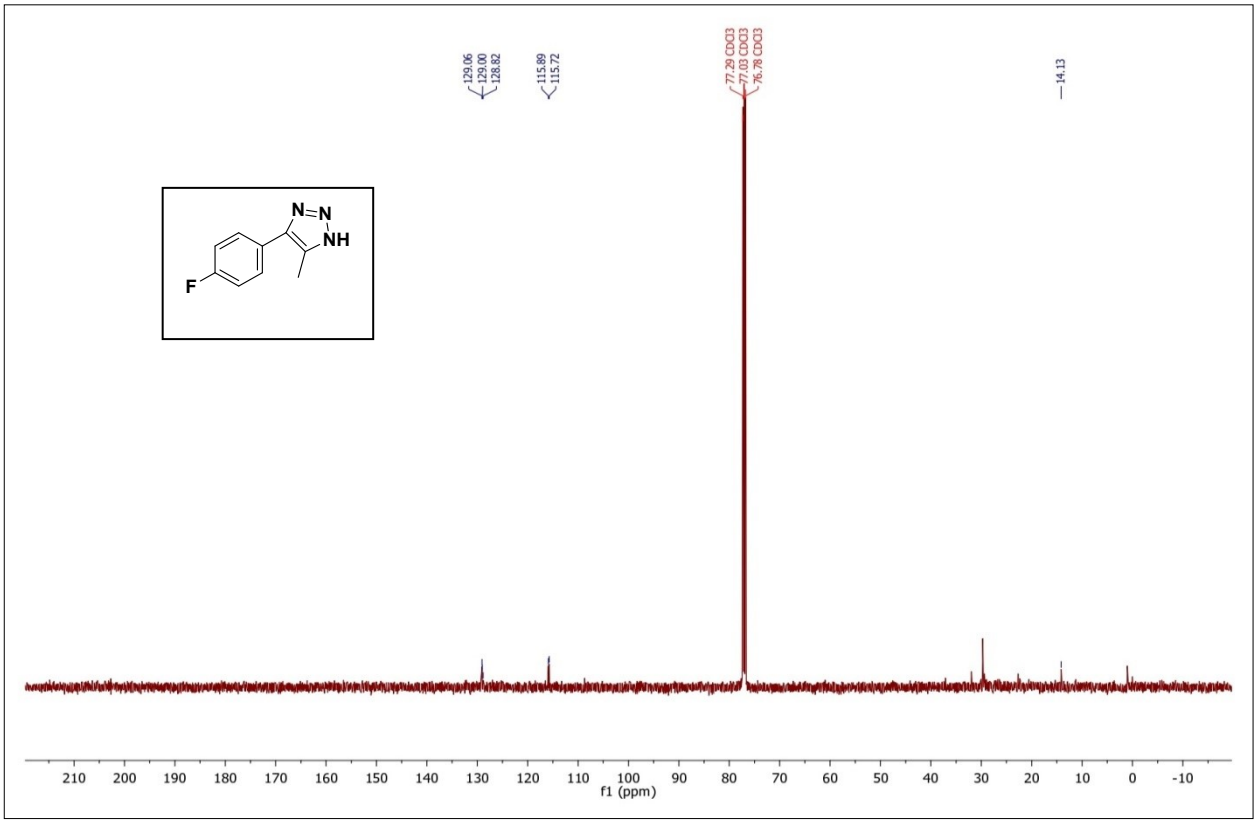
^{1}H NMR and ^{13}C NMR spectra of 4-(4-isocyanophenyl)-1H-1,2,3-triazole **(Scheme 1 , Entry 4o)** respectively.



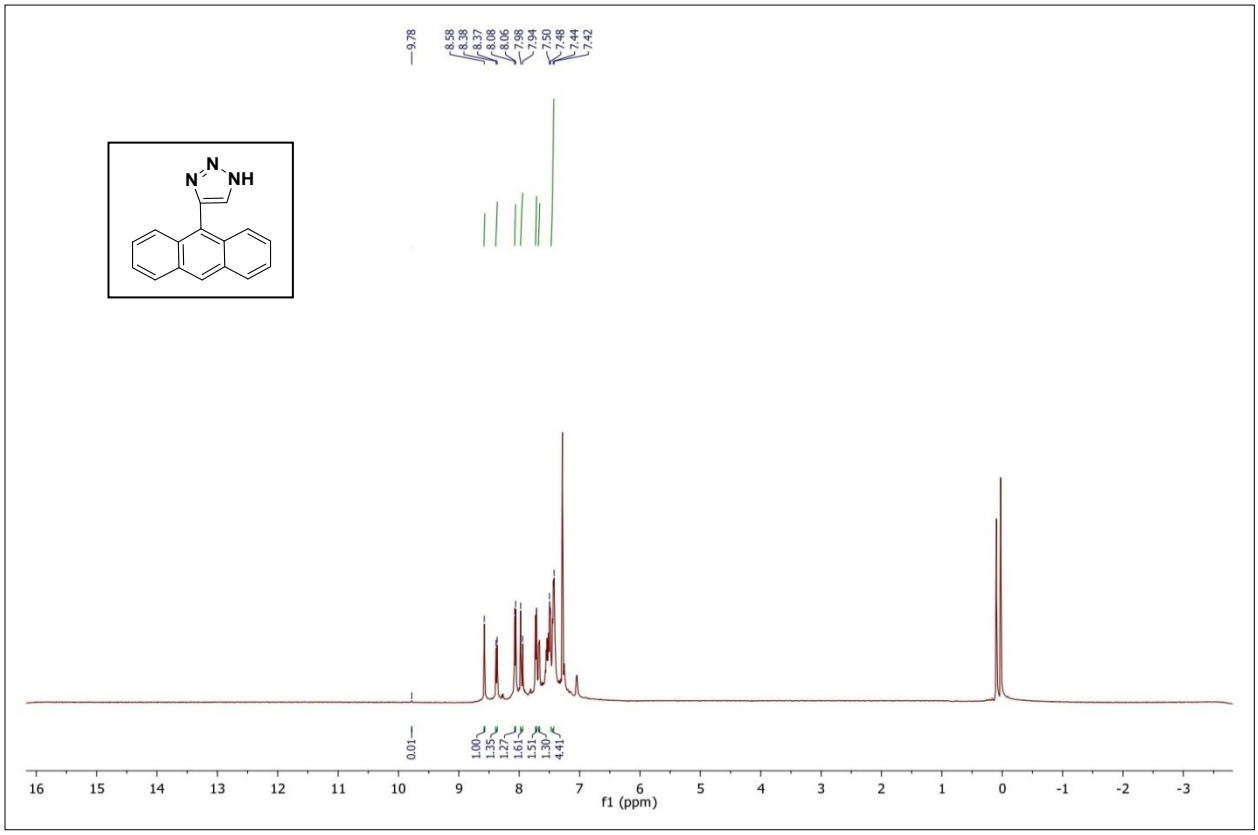


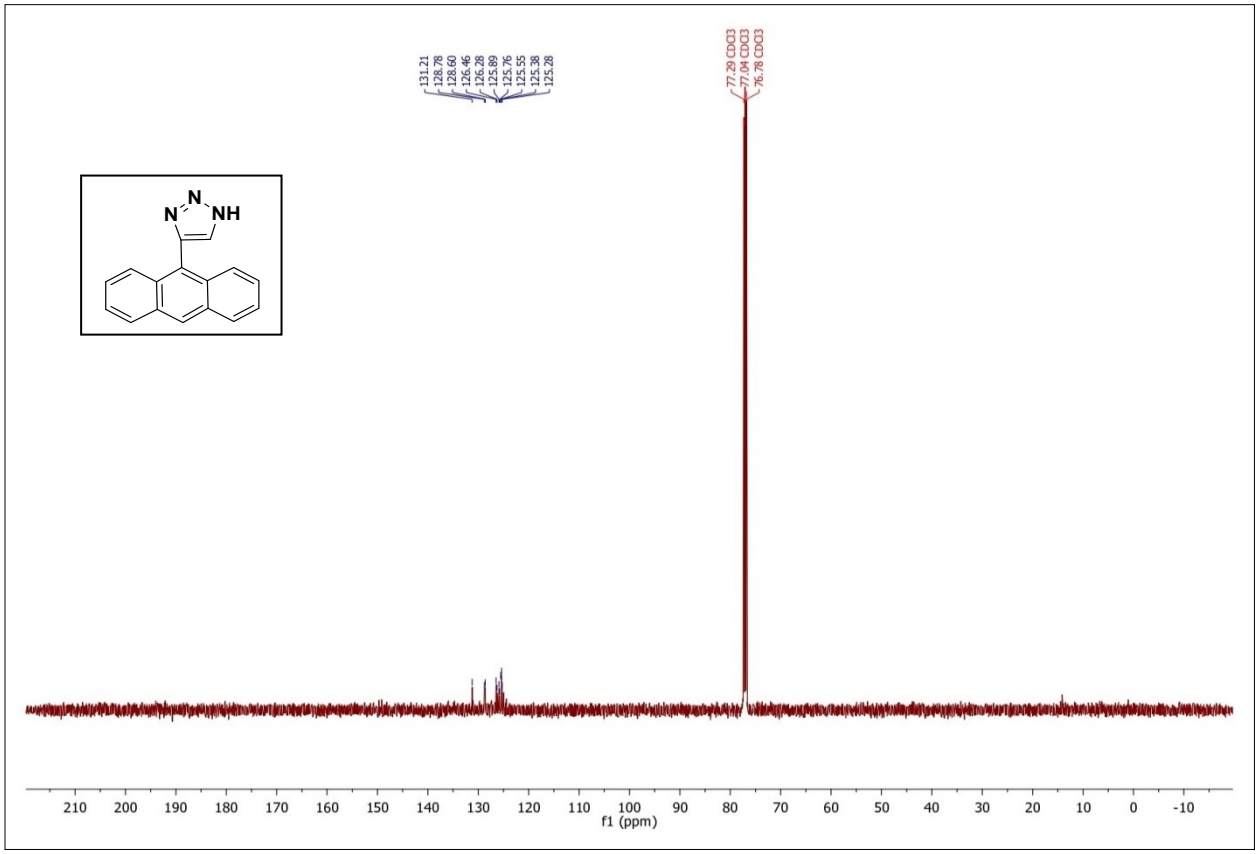
^{1}H NMR and ^{13}C NMR spectra of 4-(4-fluorophenyl)-5-methyl-1H-1,2,3-triazole **(Scheme 1 , Entry 4l)** respectively



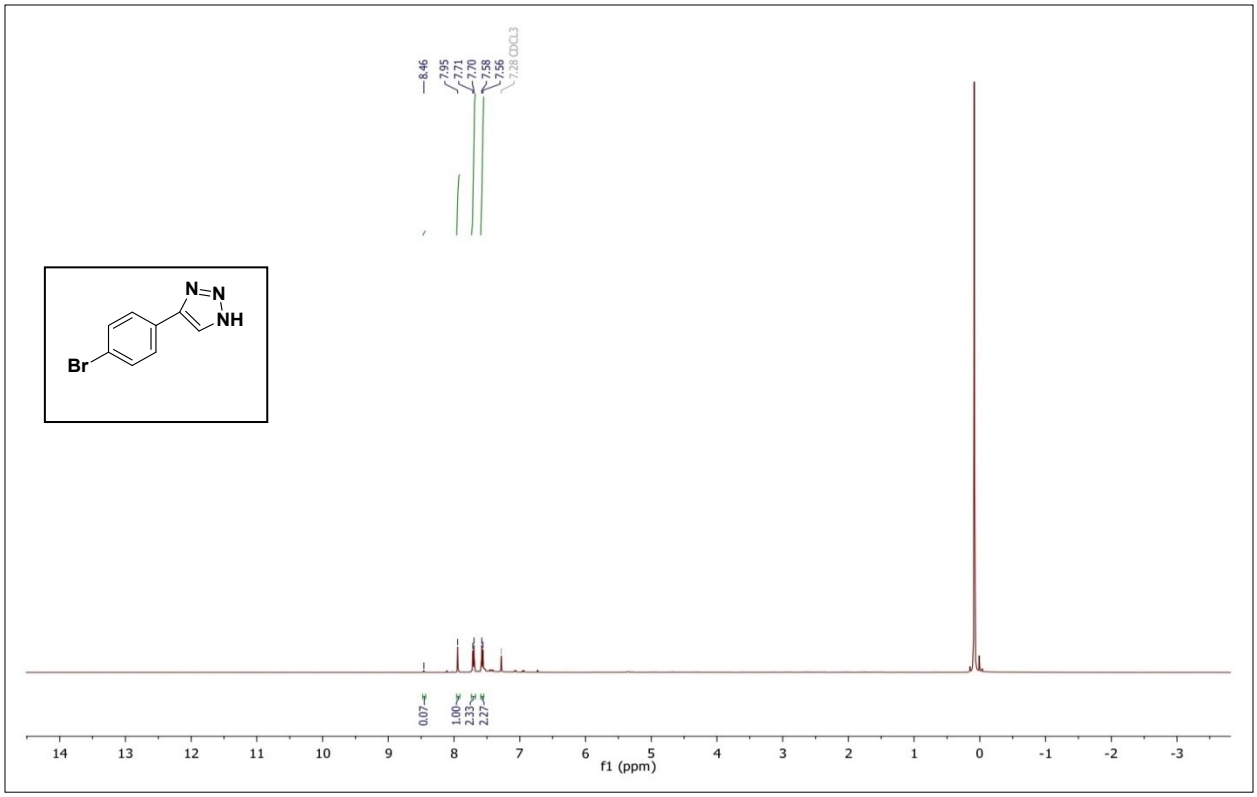


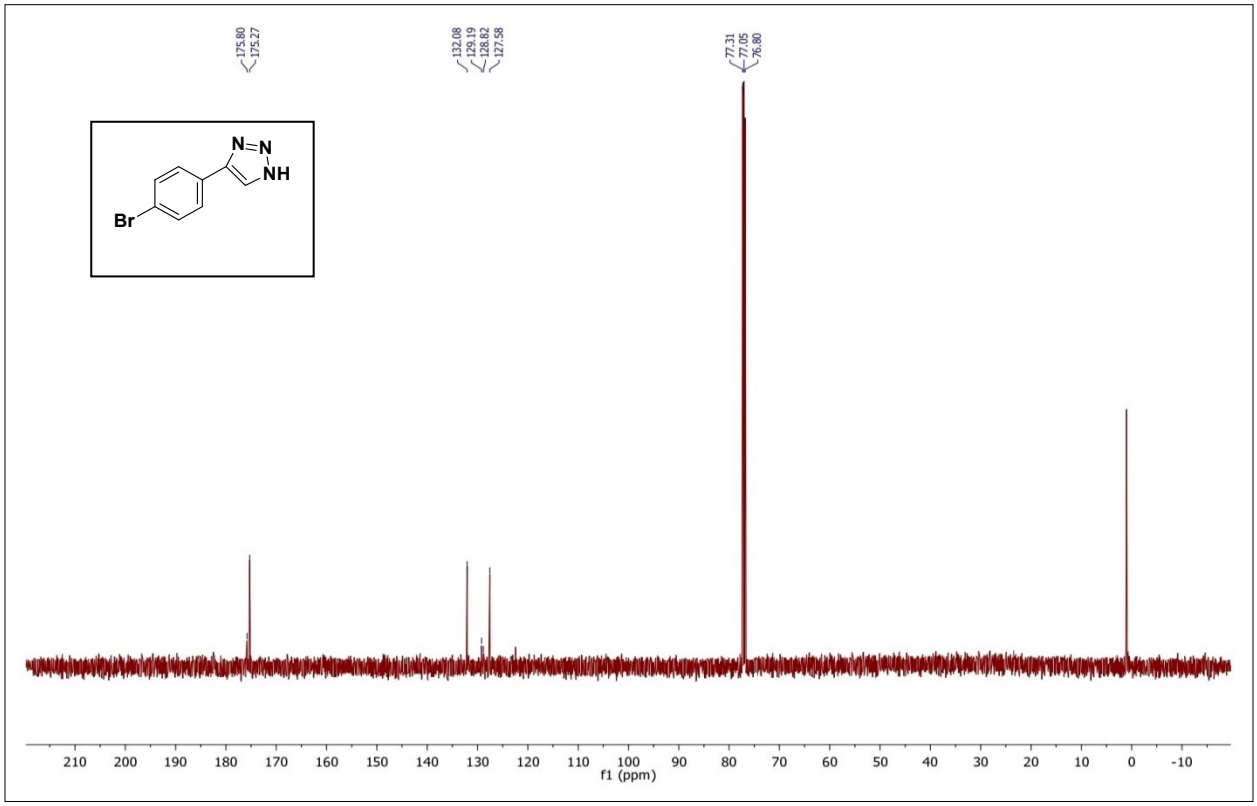
^{1}H NMR and ^{13}C NMR spectra of 4-(anthracen-9-yl)-1H-1,2,3-triazole **(Scheme 1 , Entry 4p)** respectively



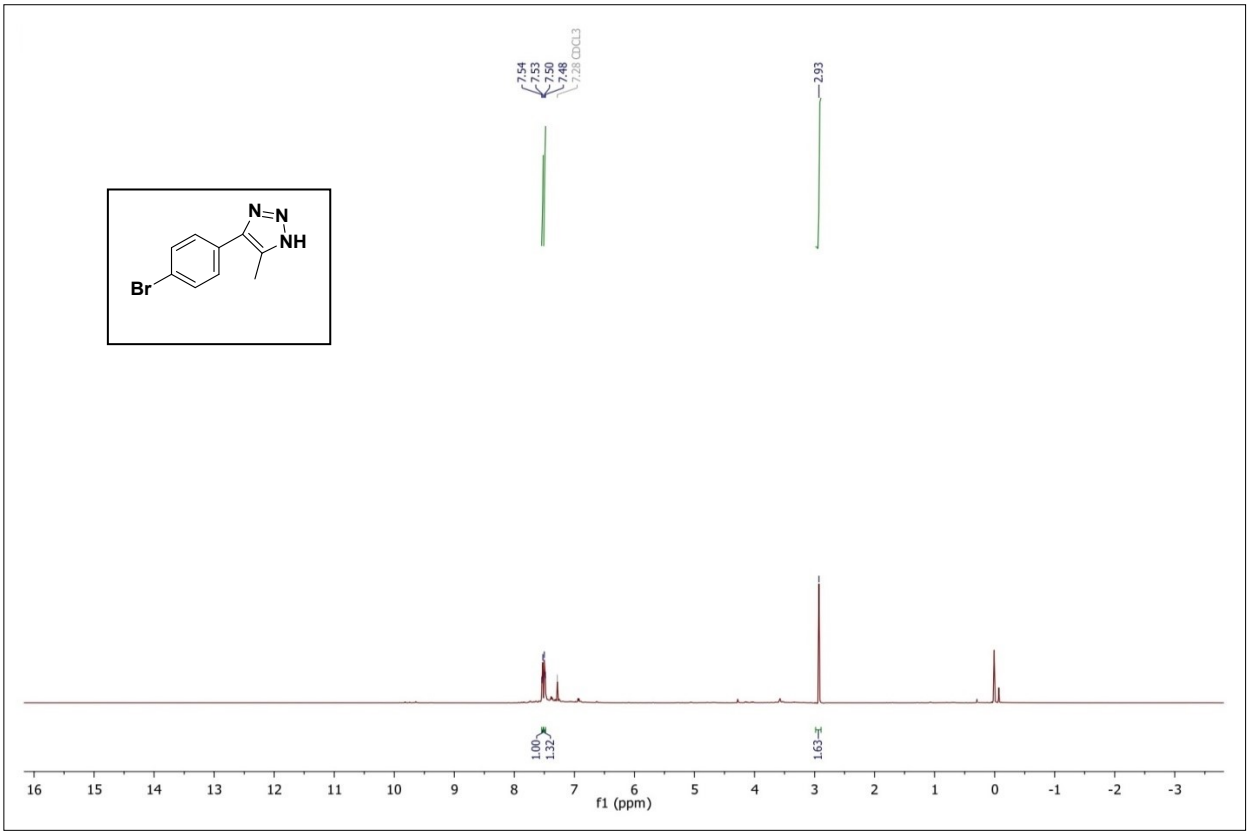


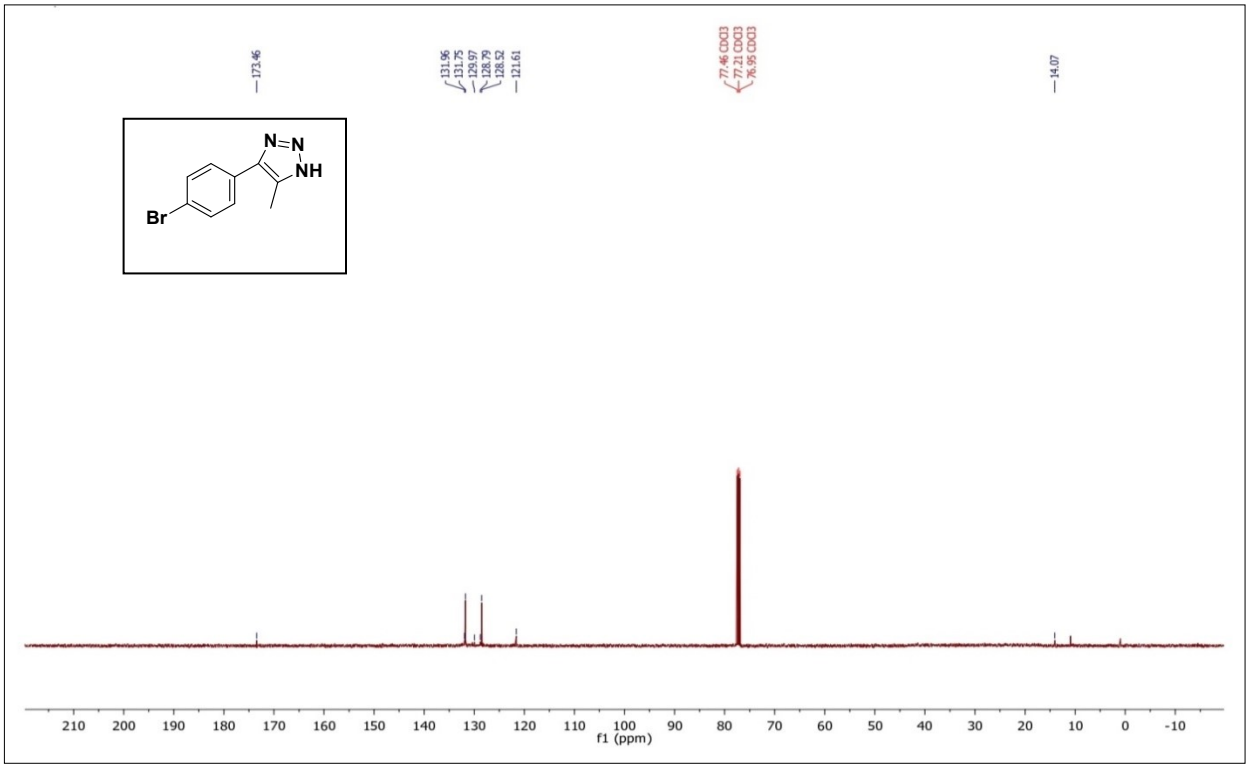
^{1}H NMR and ^{13}C NMR spectra of 4-(4-bromophenyl)-1H-1,2,3-triazole **(Scheme 1 , Entry 4m)** respectively



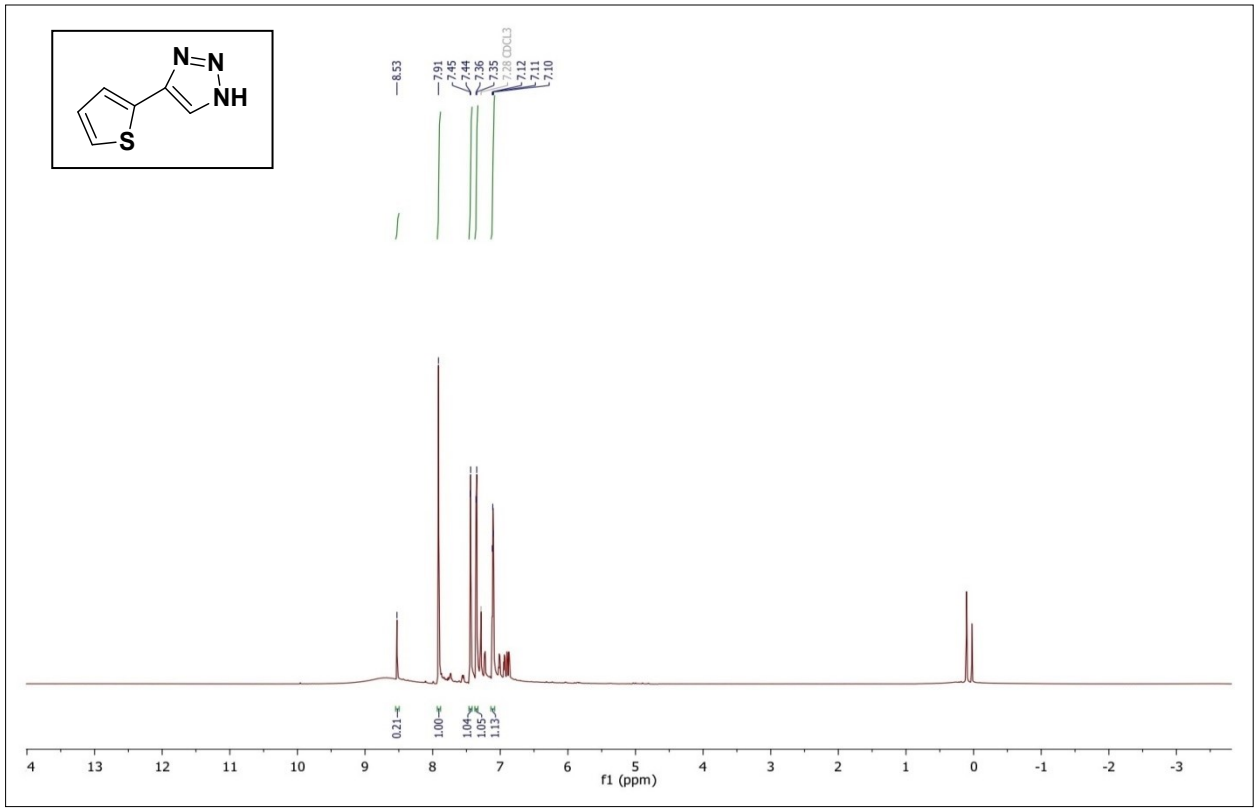


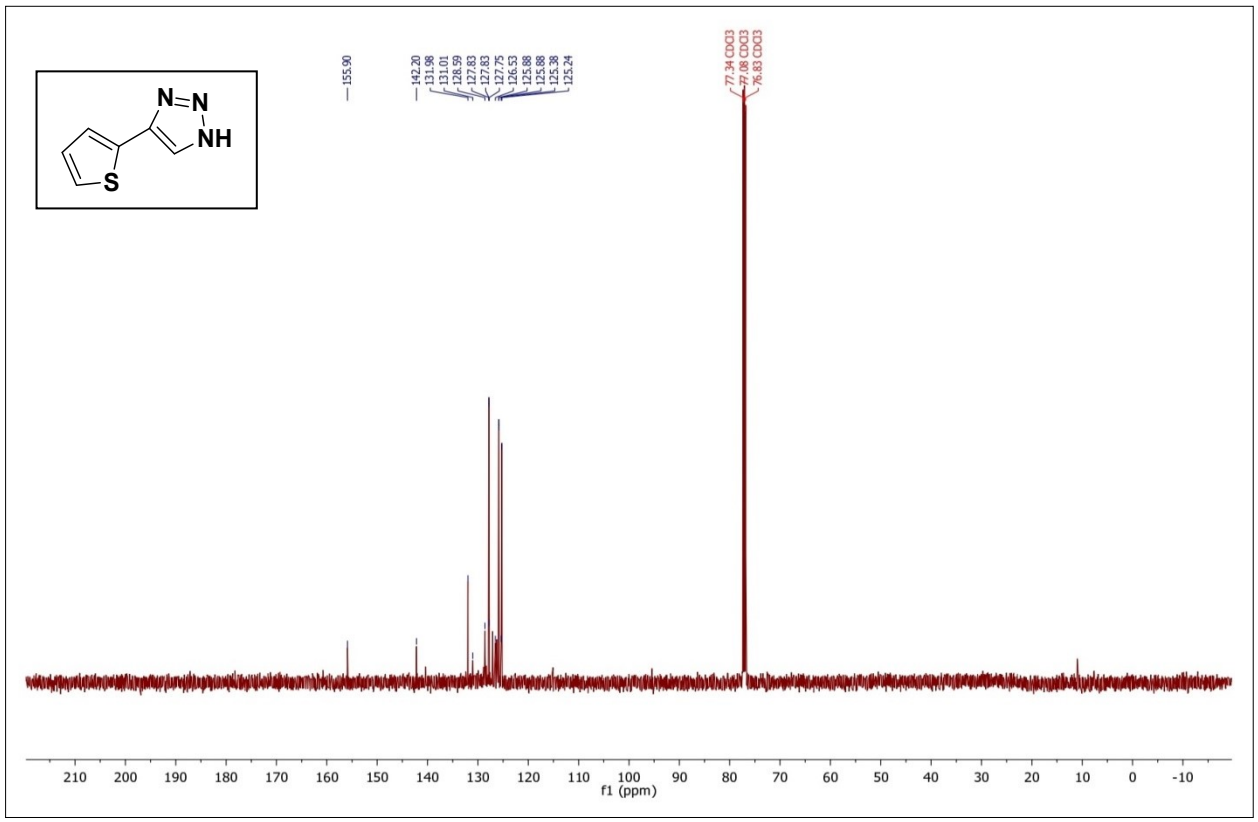
^{1}H NMR and ^{13}C NMR spectra of 4-(4-bromophenyl)-5-methyl-1H-1,2,3-triazole **(Scheme 1 , Entry 4n)** respectively



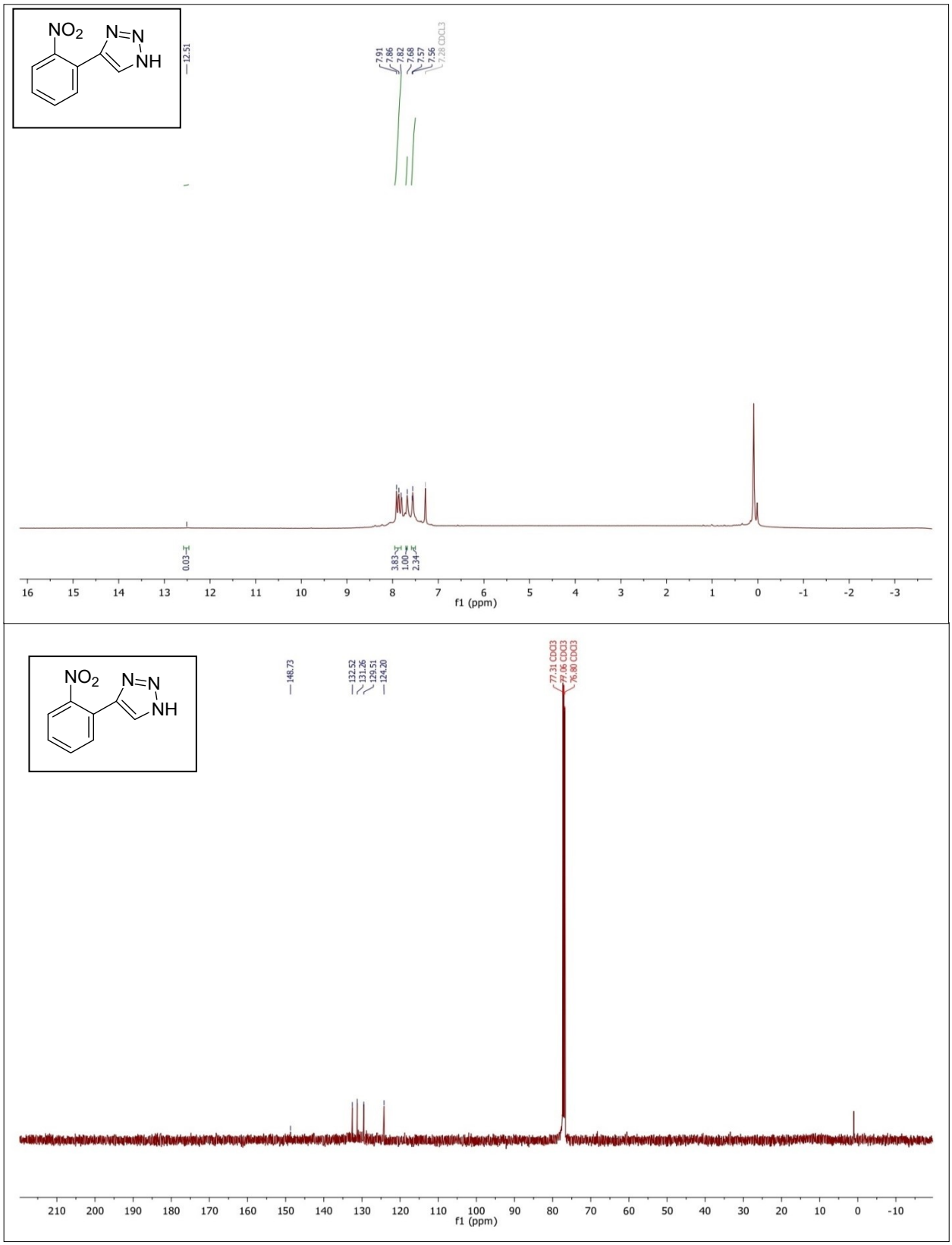


^{1}H NMR and ^{13}C NMR spectra of 4-(thiophen-2-yl)-1H-1,2,3-triazole **(Scheme 1 , Entry 4k)** respectively

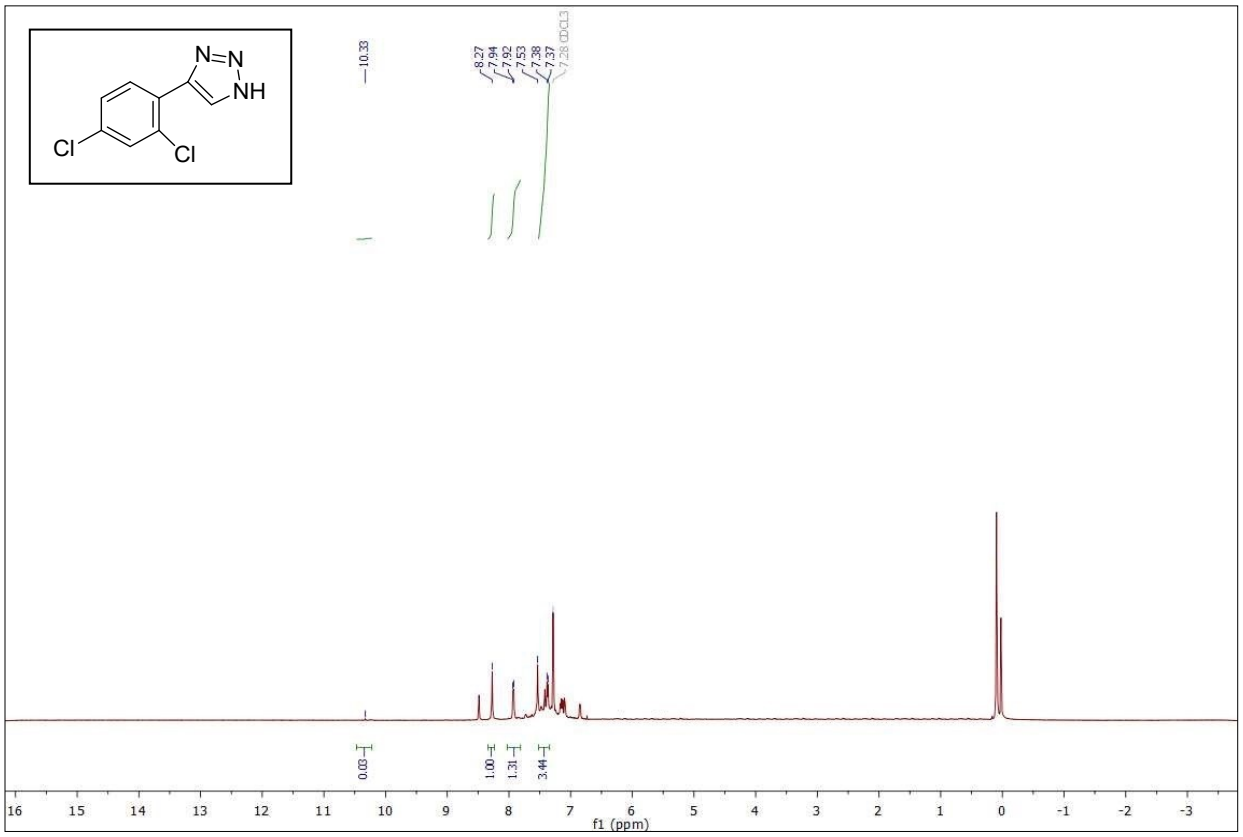


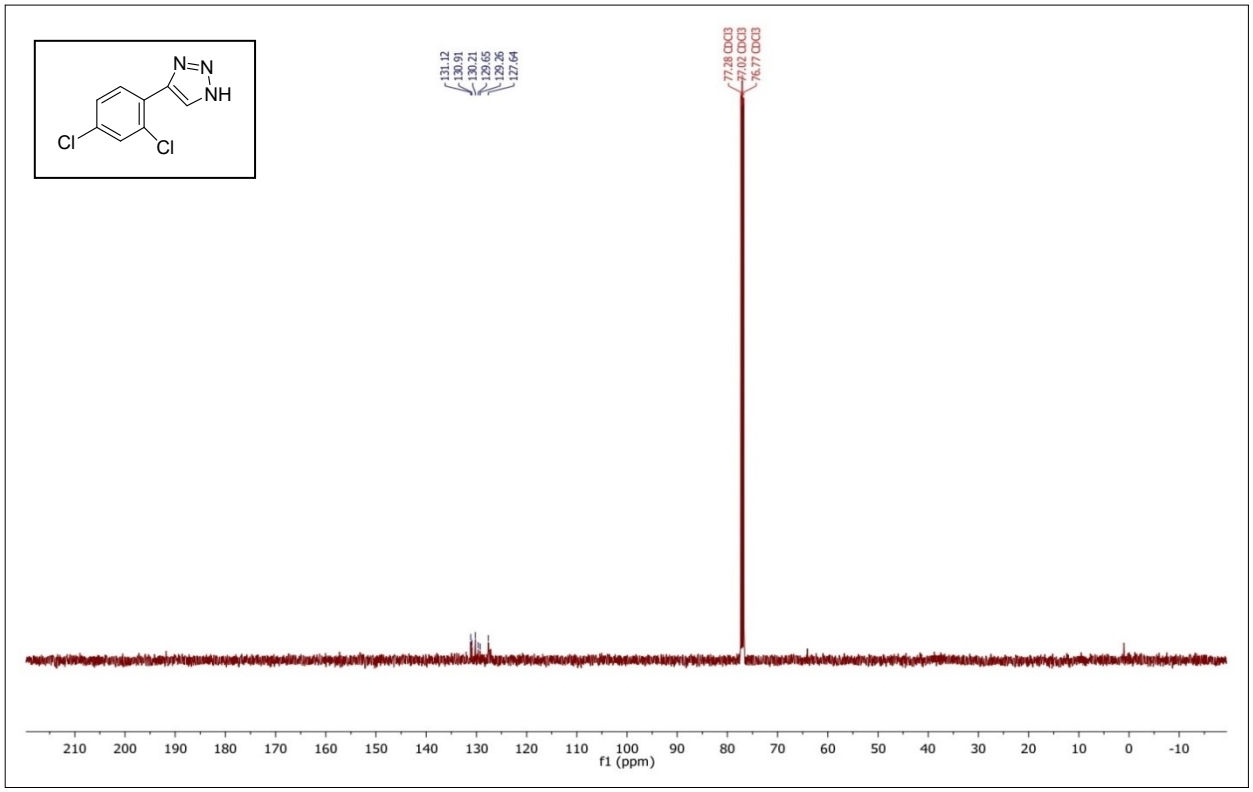


^{1}H NMR and ^{13}C NMR spectra of 4-(2-nitrophenyl)-1H-1,2,3-triazole **(Scheme 1 , Entry 4c)** respectively

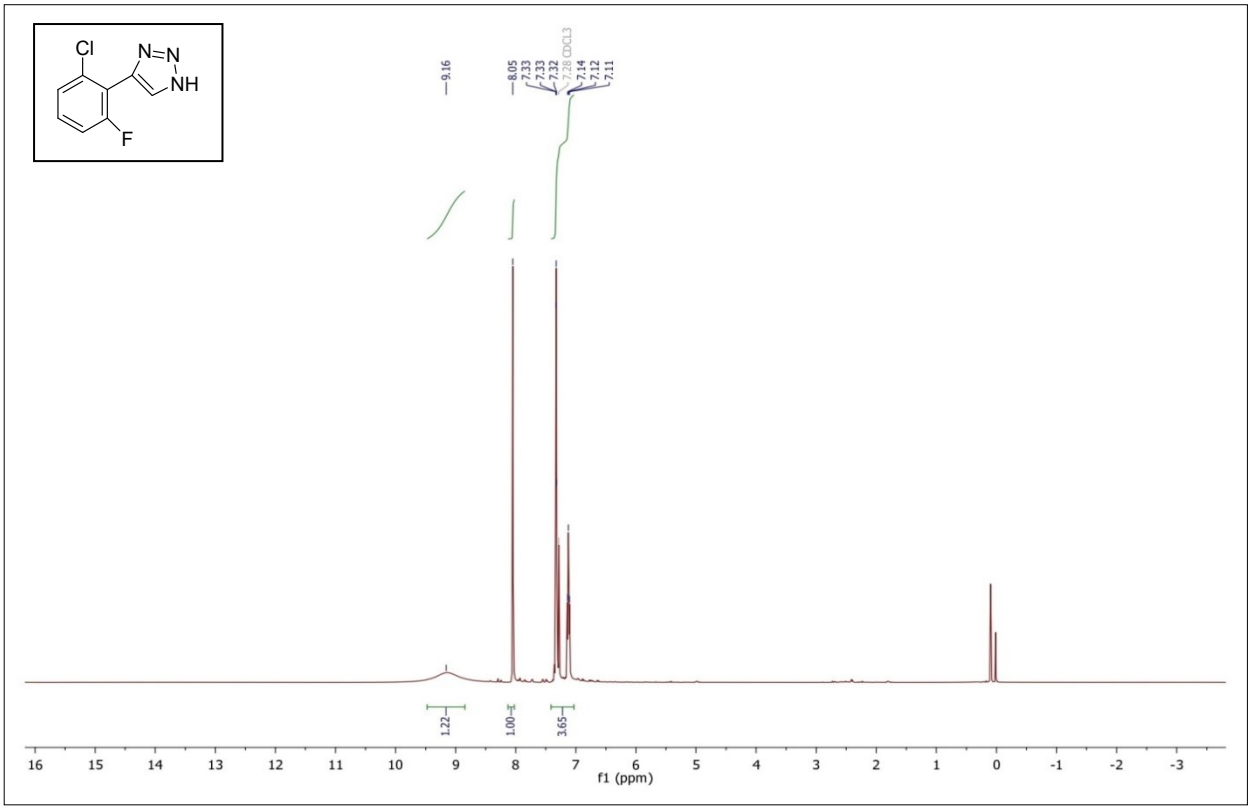


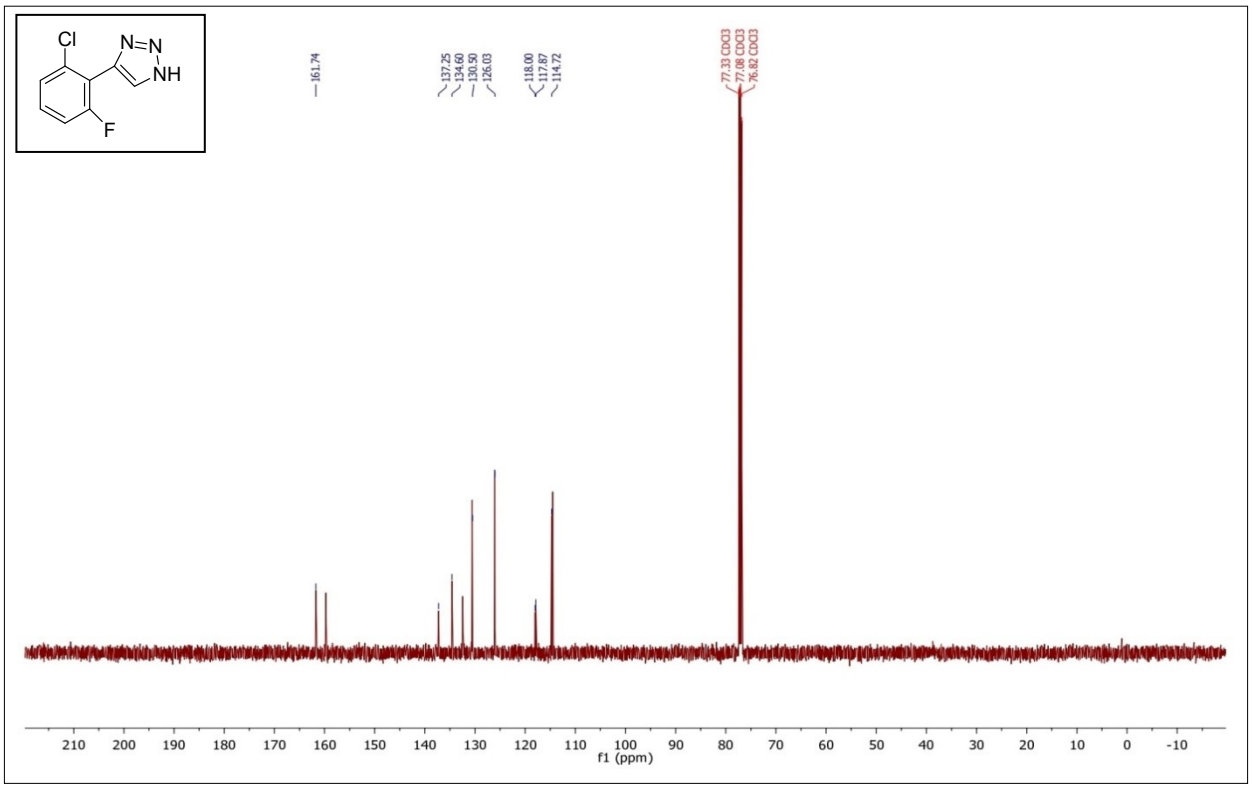
^{1}H NMR and ^{13}C NMR spectra of 4-(2, 4-dichlorophenyl)-1H-1,2,3-triazole **(Scheme 1 , Entry 4j)** respectively



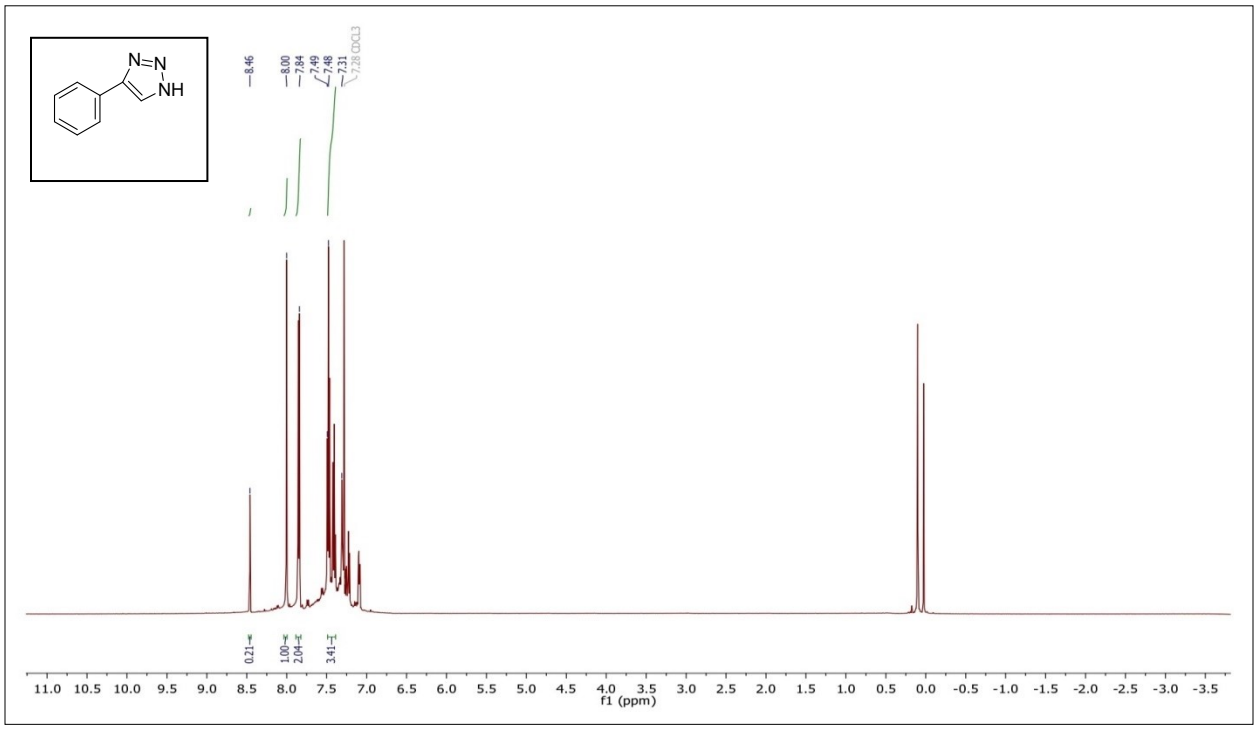


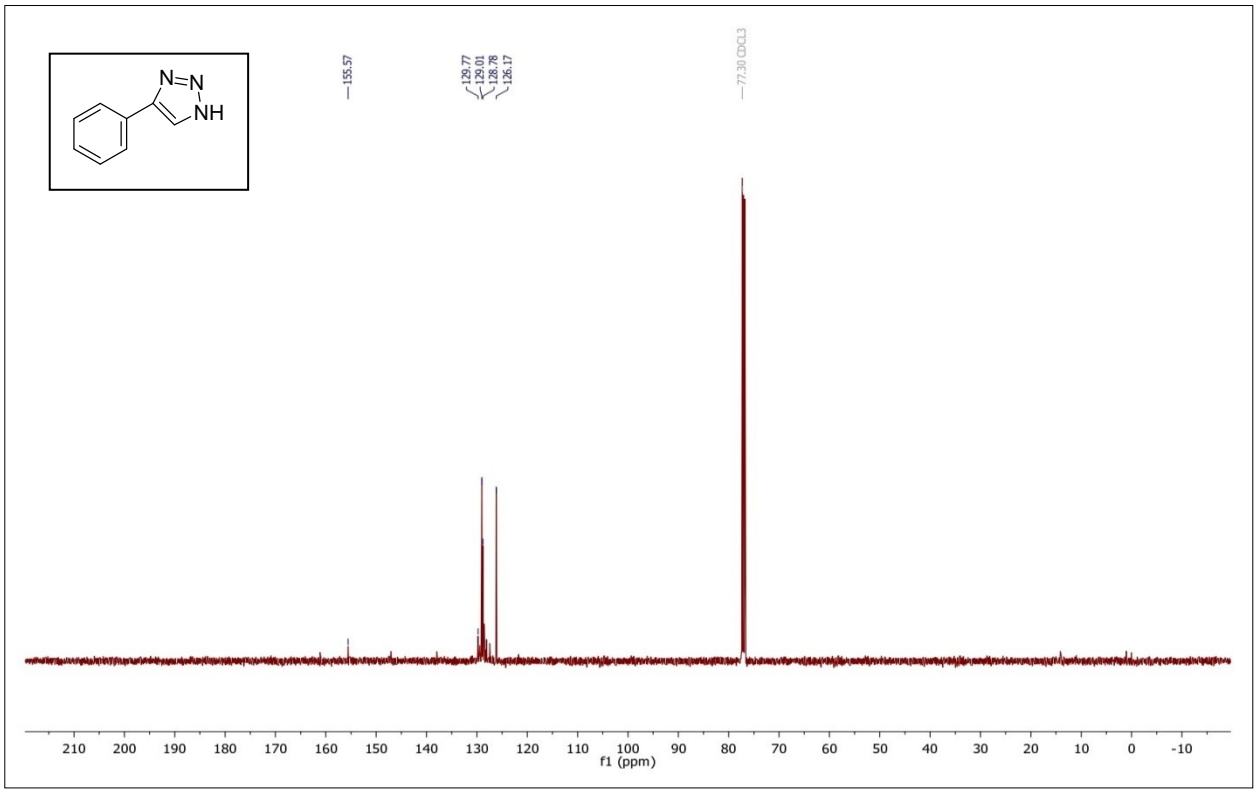
^{1}H NMR and ^{13}C NMR spectra of 4-(2-chloro-6-fluorophenyl)-1H-1,2,3-triazole **(Scheme 1 , Entry 4e)** respectively



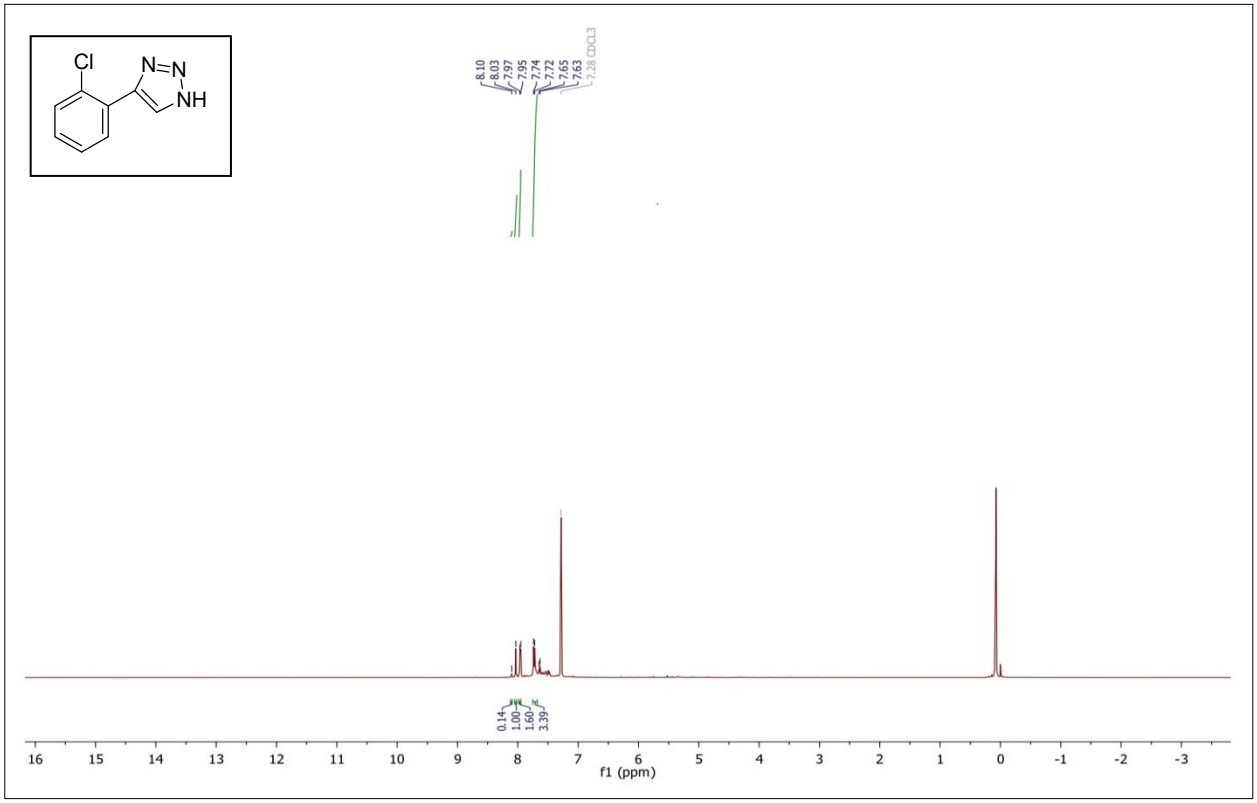


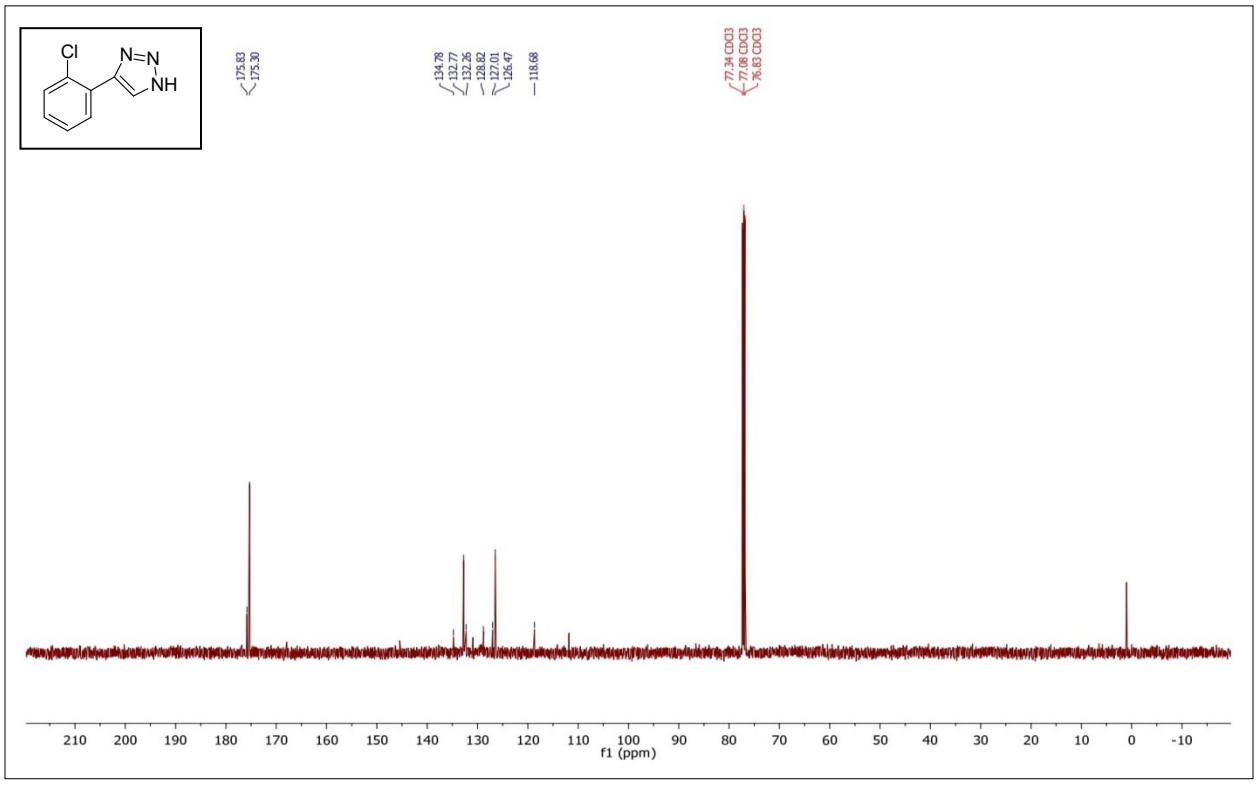
^{1}H NMR and ^{13}C NMR spectra of 4-phenyl-1H-1,2,3-triazole **(Scheme 1 , Entry 4f)** respectively



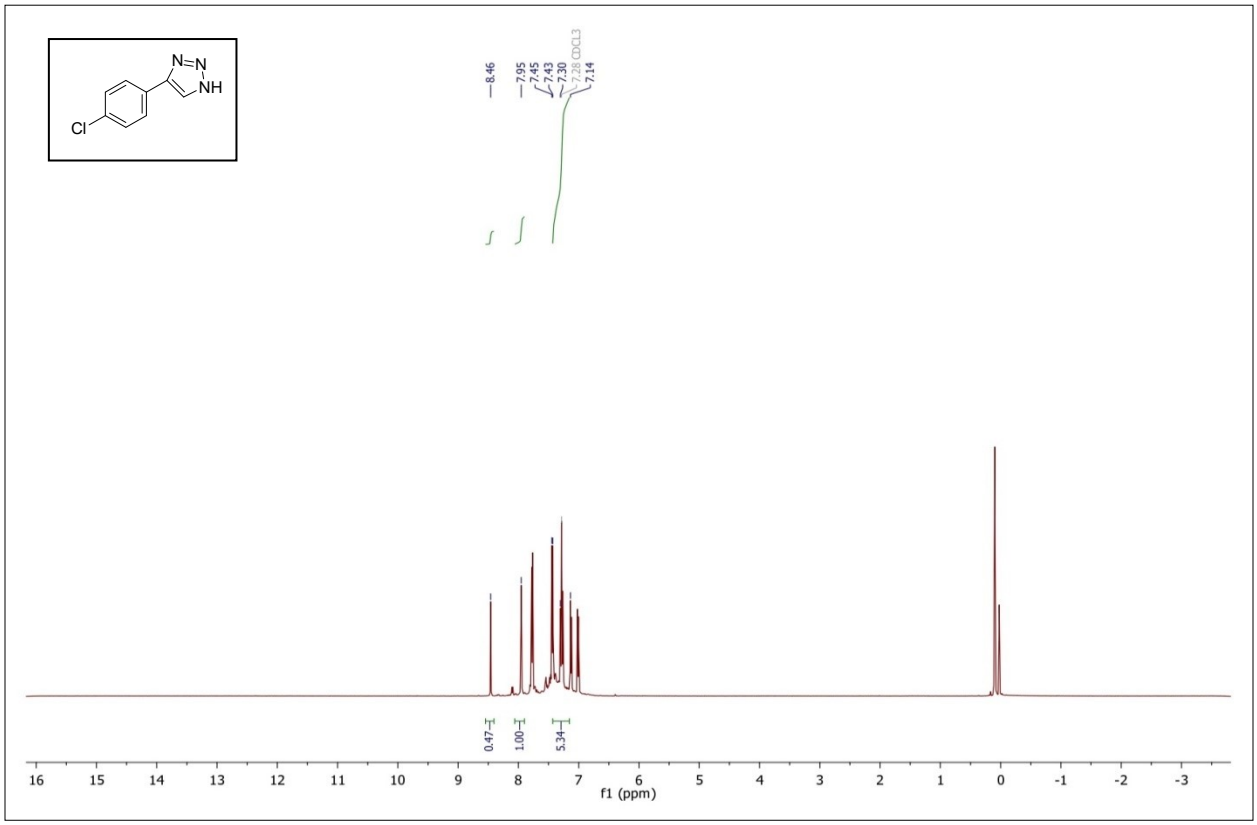


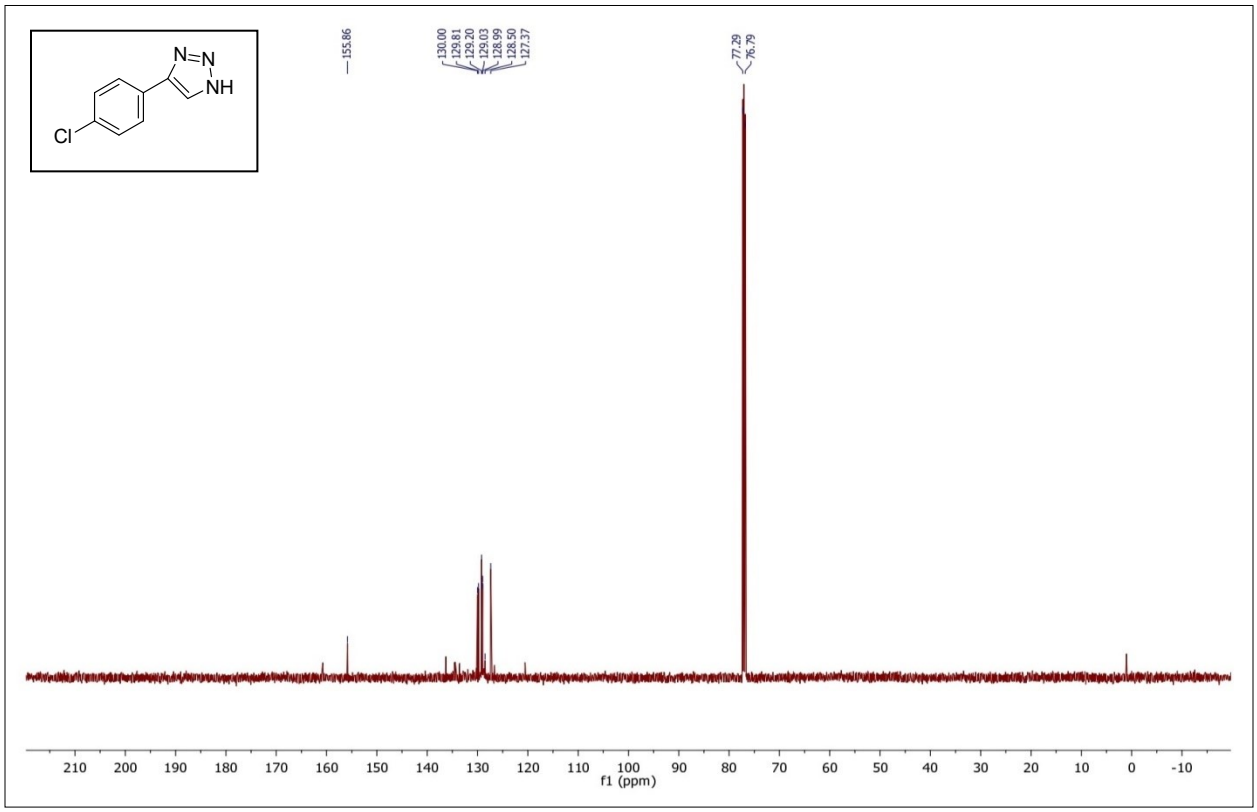
^{1}H NMR and ^{13}C NMR spectra of 4-(2-chlorophenyl)-1H-1,2,3-triazole **(Scheme 1 , Entry 4d)** respectively



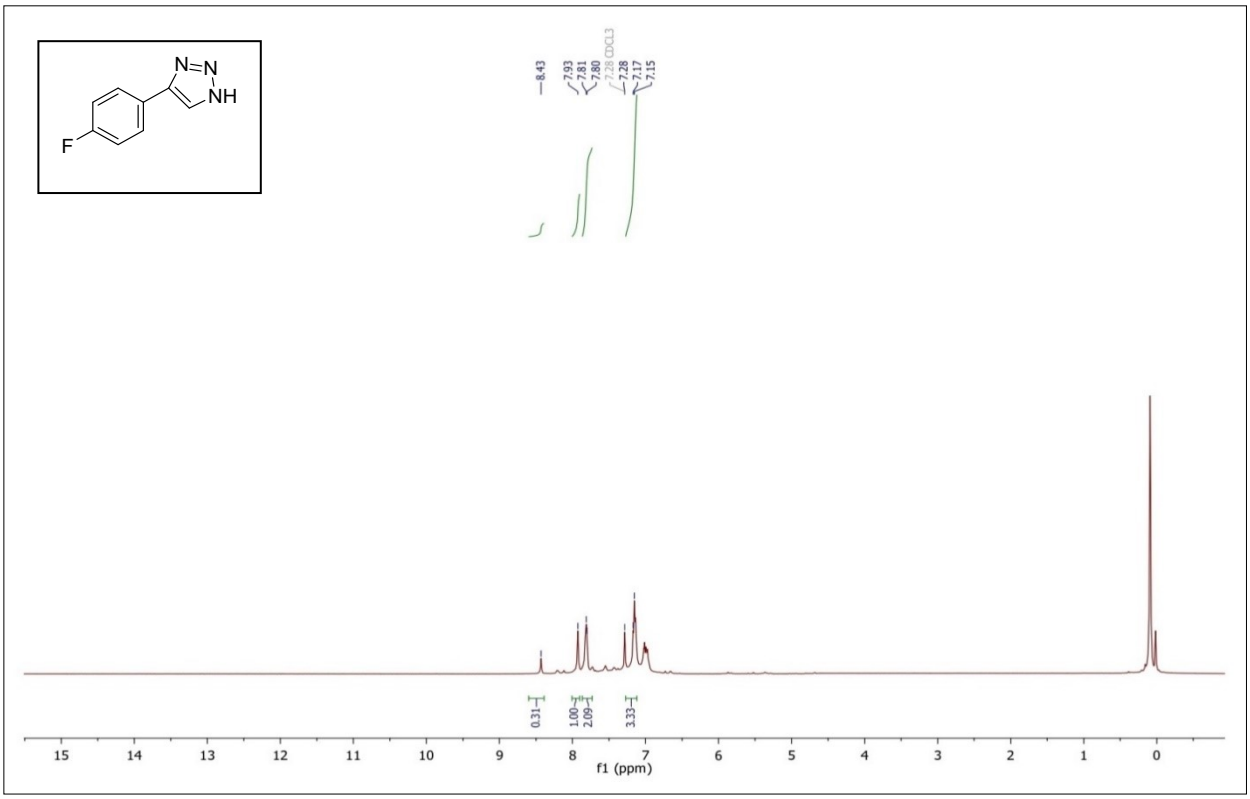


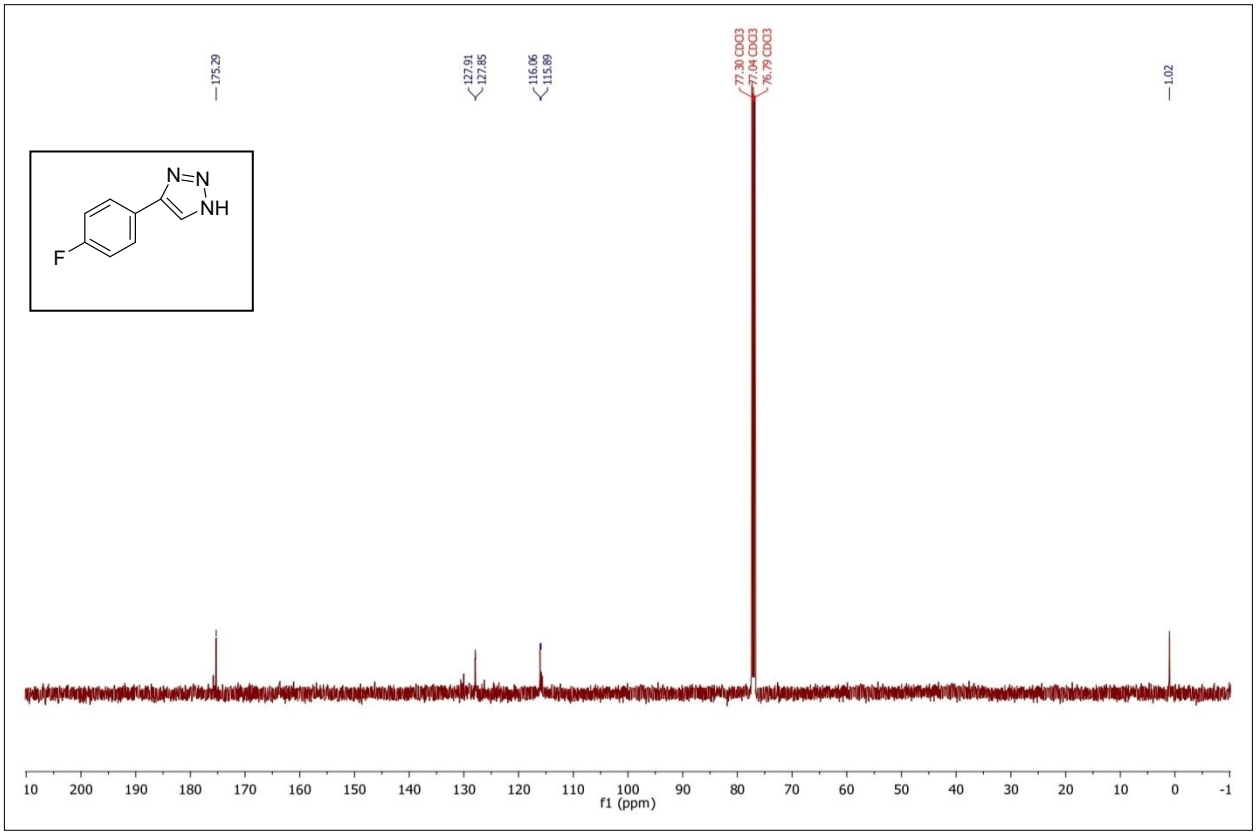
^{1}H NMR and ^{13}C NMR spectra of 4-(4-chlorophenyl)-1H-1,2,3-triazole **(Scheme 1 , Entry 4a)** respectively



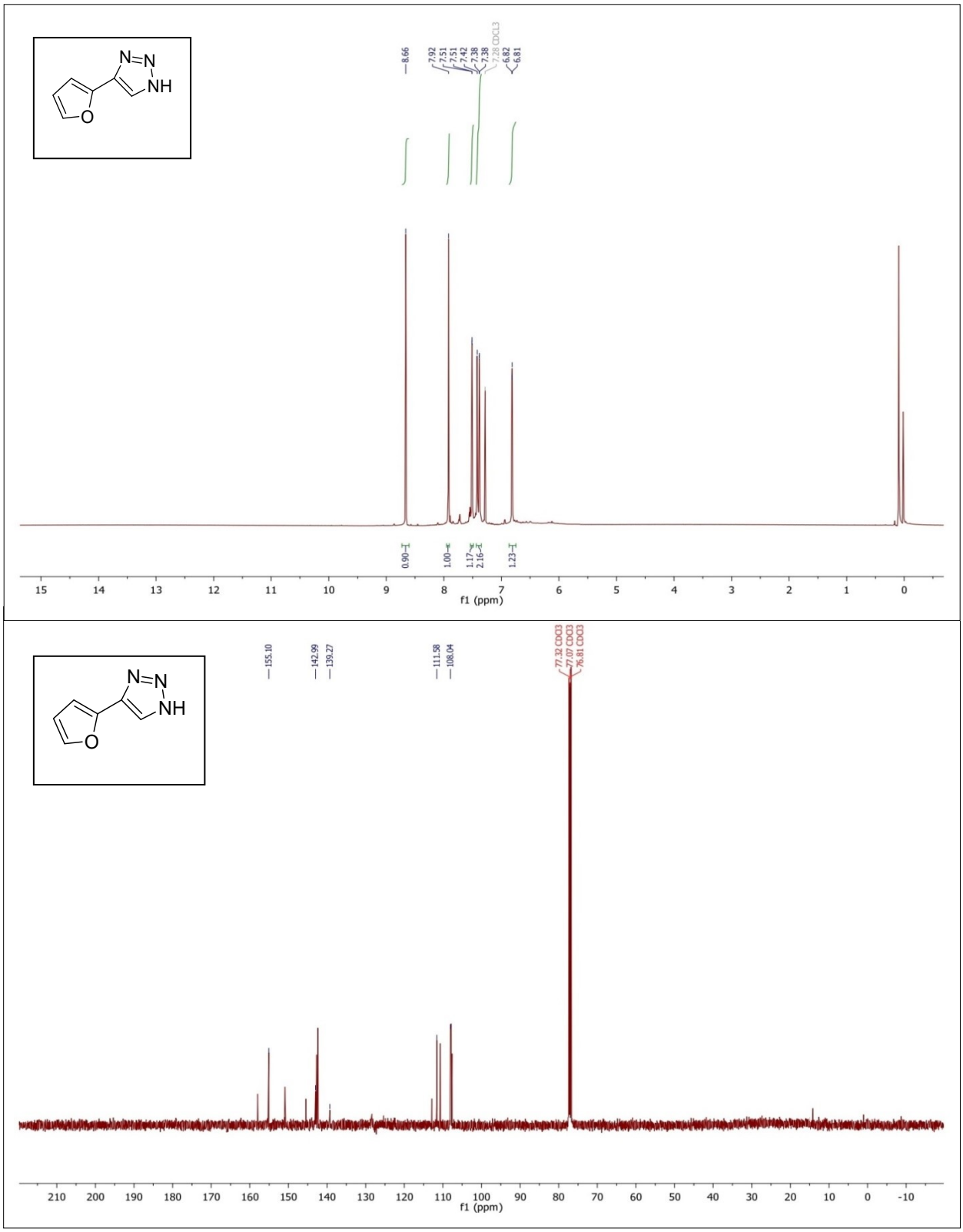


^{1}H NMR and ^{13}C NMR spectra of 4-(4-fluorophenyl)-1H-1,2,3-triazole **(Scheme 1 , Entry 4b)** respectively





^{1}H NMR and ^{13}C NMR spectra of 4-(furan-2-yl)-1H-1,2,3-triazole **(Scheme 1 , Entry 4i)** respectively



^{1}H NMR and ^{13}C NMR spectra of 4-(p-tolyl)-1H-1,2,3-triazole**(Scheme 1 , Entry 4h)** respectively