

Supporting Information

[DDQM][TFSI]: a room temperature ionic liquid as an active electrode material for supercapacitor devices and a catalyst for rapid synthesis of 4-aryl-NH-1,2,3-triazoles under microwave irradiation

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1) General information

All reactions were carried out in oven dried glassware under atmospheric conditions otherwise noted. Starting materials and solvents were obtained from common commercial sources and used without further purification. All reported yields are isolated yields. TLC was carried out using aluminium sheets pre-coated with silica gel 60F₂₅₄ (Merck) and was visualized under 254 nm UV light. Melting points were obtained by an open capillary method and are uncorrected. Infrared spectra were measured using potassium bromide (KBr) pellets on a Perkin-Elmer FT-IR-2000 spectrophotometer and absorptions are reported in cm⁻¹. ¹H NMR (500 MHz) and ¹³C NMR (125 MHz) were recorded on a Bruker Avance 500 MHz spectrometer using TMS as an internal standard. ¹F NMR (471 MHz) was recorded on Bruker Avance 500 MHz FT-NMR spectrometer. Chemical shifts are reported in parts per million (ppm), downfield from residual solvents peaks and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), br (broad) and m (multiplet, for unresolved lines). The mass spectra were recorded on a Q-TOF micromass (YA-105) spectrometer in ESI (electrospray ionization) mode. Thermo gravimetric Analysis (TGA) was performed from 30-800 °C at scanning rate of 10 °C/min with TGA/SDTA851 Mettler Toledo instrument under a nitrogen atmosphere. The reactions under microwave irradiation are carried out in closed glass tube in anton Paar monowave 400 microwave synthesis reactor.

2) General procedure for synthesis of 4-aryl-NH-1,2,3-triazoles derivatives

Aldehyde derivatives (0.216 mmol), nitromethane (0.432 mmol), Sodium Azide (0.648 mmol), [DDQM][TFSI] (25 mol%) and DMSO (100 µL) were subjected to microwave irradiation in 90W (180 °C) for 2 minutes. The progress of the reaction was monitored by TLC under UV light. After completion of the reaction the mixture was extracted with ethyl acetate (3 x 10 mL) and washed

with water (3 x 10 mL). The combined extract was dried over anhydrous Na₂SO₄. The filtrate was concentrated under reduced pressure. The product was purified by column chromatography over silica gel using n-hexane/ethyl acetate (3:1 v/v) as eluent to get the purified product. The products were then characterized by ESI-MS, ¹H NMR, ¹³C NMR spectra.

3) Synthesis and characterization of [DDQM][TFSI]

The acidic ionic liquid [DDQM][TFSI] was prepared following our own developed procedure¹. At first instance, a glass tube charged with quinoline (2 g, 15.48 mmol) and 1-bromododecane (3.76 g, 17.03 mmol) is subjected to microwave irradiation at 150 °C for 10 minutes under continuous stirring and the product was extracted to obtain 1-dodecylquinolin-1-ium bromide ([DDQM][Br]) as dark maroon sticky liquid. The synthesized IL was dried under vacuum until solidified. Thereafter, [DDQM][Br] (3 g, 7.92 mmol) and LiTFSI (2.27 g, 7.92 mmol) in water were stirred for 24 hours at room temperature. The mixture was then centrifuged to remove LiBr. Afterwards, the new ionic liquid 1-dodecylquinolin-1-ium bis(trifluoromethane)sulfonimide was extracted with dichloromethane and labelled as [DDQM][TFSI]. The ionic liquid was characterized by ¹H and ¹³C NMR, HRMS, FT-IR, UV-Visible and TGA analyses.

Characterization of prepared ionic liquid (IL):

NMR Analysis:

¹H NMR (600 MHz, CDCl₃) δ 9.39 (d, *J* = 5.7 Hz, 1H), 9.02 (d, *J* = 8.3 Hz, 1H), 8.34 (d, *J* = 8.2 Hz, 1H), 8.31 (d, *J* = 8.9 Hz, 1H), 8.29 – 8.25 (m, 1H), 8.13 – 8.09 (m, 1H), 8.03 (t, *J* = 7.5 Hz, 1H), 5.06 (t, *J* = 7.7 Hz, 2H), 2.11 (m, 2H), 1.53 – 1.45 (m, 2H), 1.41 – 1.21 (m, 16H), 0.89 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 149.28, 147.44, 136.35, 131.15, 130.47, 130.22, 122.40, 118.05, 58.78, 31.89, 30.16, 29.39, 28.97, 26.44, 22.67, 14.11.

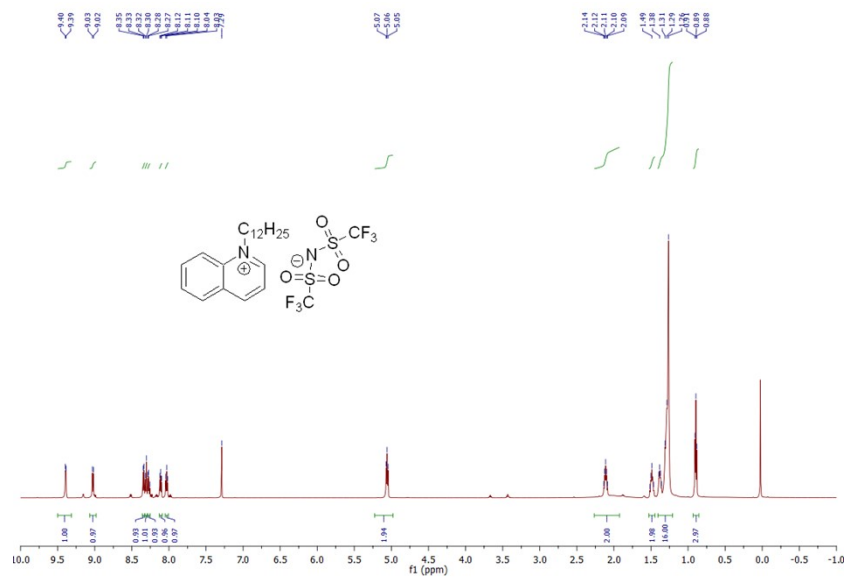


Figure S1: ¹H NMR Spectra of [DDQM][TFSI]

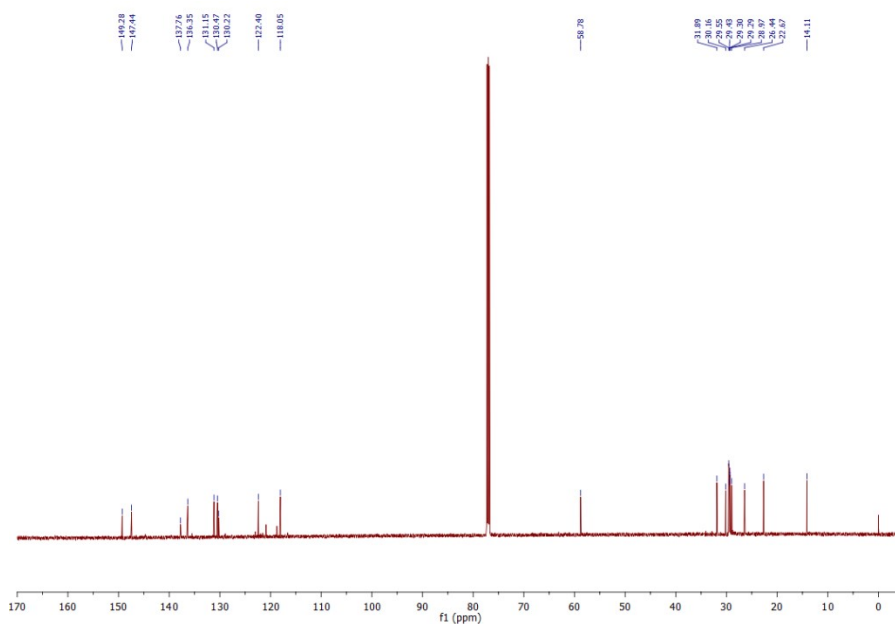


Figure S2: ¹³C NMR Spectra of [DDQM][TFSI]

IR analysis:

For the characterization of prepared ionic liquid, [DDQM][TFSI], FT-IR analysis was carried out as shown in **Figure S3**. The two bands due to the C-H stretching vibration were observed at 2933 cm⁻¹ and 2855 cm⁻¹. The peak at 1185 cm⁻¹ were due to the C-N stretching of cationic counterpart of [DDQM][TFSI]. The band at 1054 cm⁻¹ is for the symmetric SO₂ stretching and antisymmetric

S-N-S stretching vibrations.² The peak at 1348 corresponds to asymmetric SO₂ stretching for trans conformer of TFSI anion.³ The bending modes of SO₂, CF₃ and SNS are most predominant in the region 500-700cm⁻¹. The bands at 740 cm⁻¹ and 766 cm⁻¹ can be attributed to C-F and S-N-S stretches.

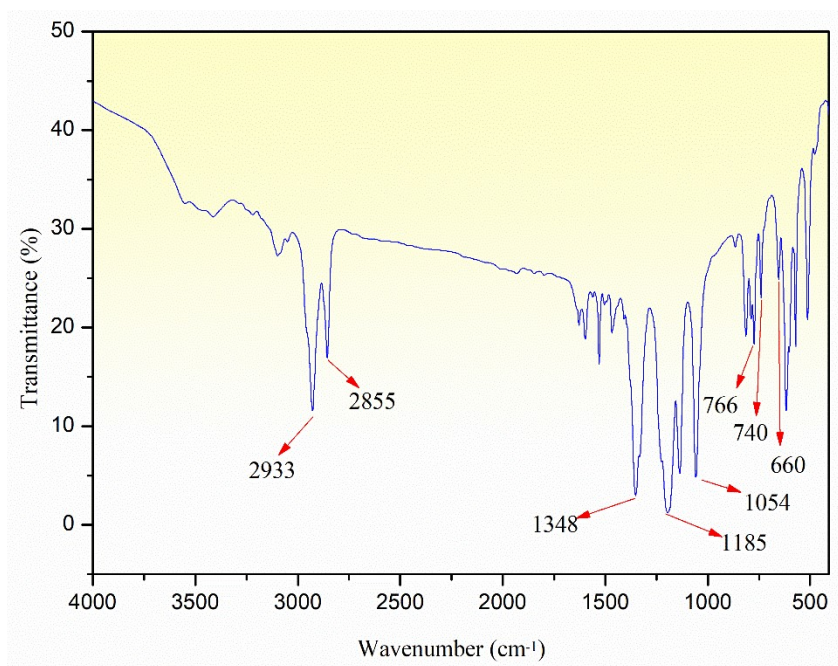
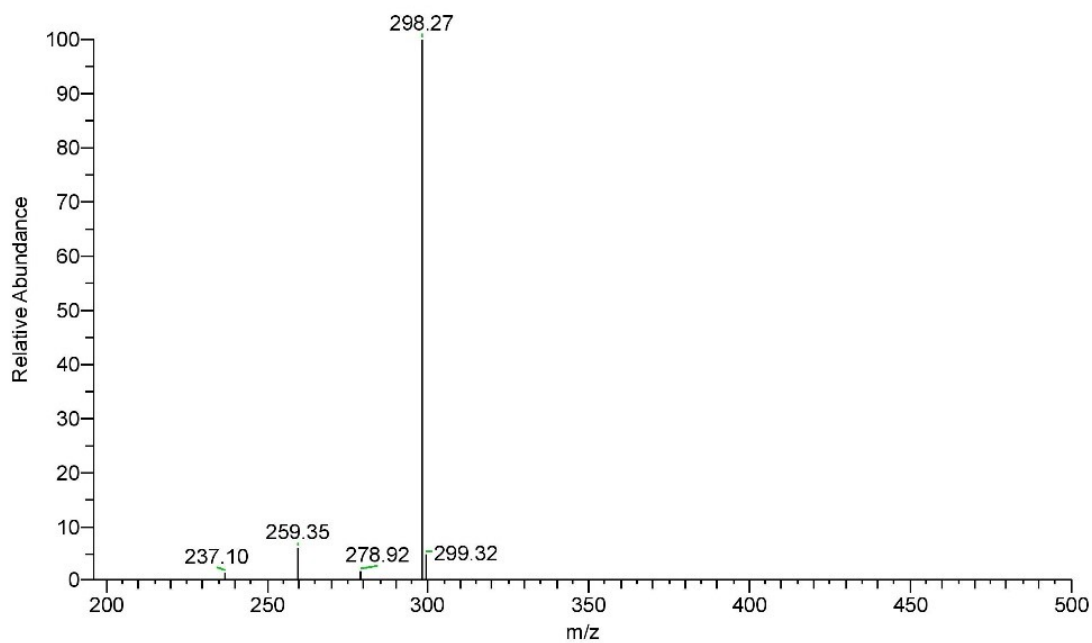


Figure S3: FTIR Spectra of [DDQM][TFSI]

Molecular mass analysis: Mass Spectroscopy of the ionic liquid is done in methanol solvent with MicroMass Q-TOF.

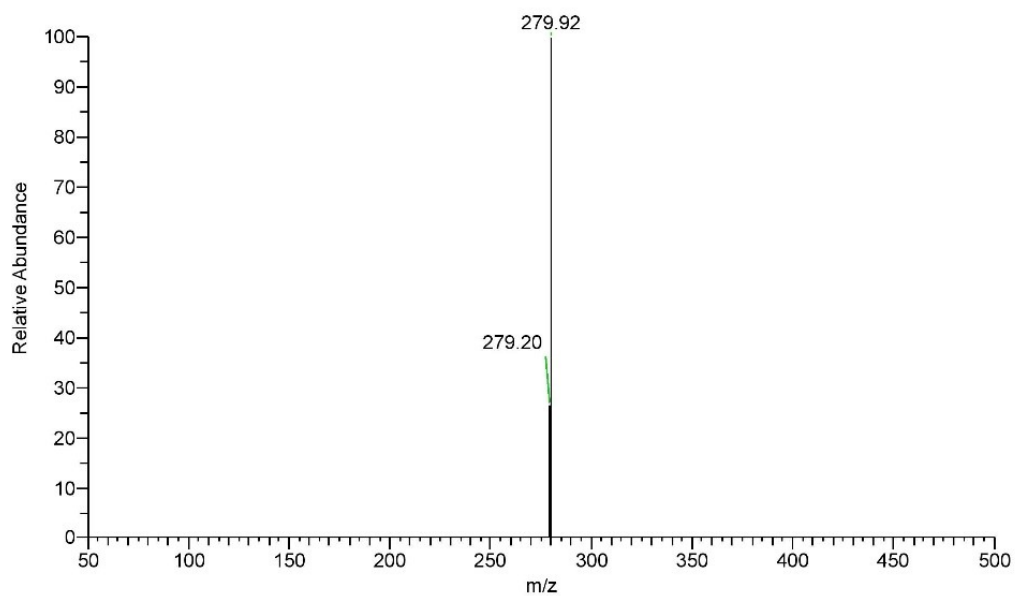
For [DDQM][TFSI]: LC-MS (ESI-Positive) m/z: 298.25 calculated for C₃₅H₂₉N²⁺ and found 298.27. LC-MS (ESI-Negative) m/z: 279.91 calculated for C₃₅H₂₉N²⁺ and found 279.92.

BD-TFS-P_20220425125558 #386 RT: 2.91 AV: 1 NL: 4.58E+004
T: + c ESI Q1MS [50.000-500.000]



(a)

BD-TFS-N #352 RT: 2.65 AV: 1 NL: 5.84E+003
T: - c ESI Q1MS [50.000-500.000]



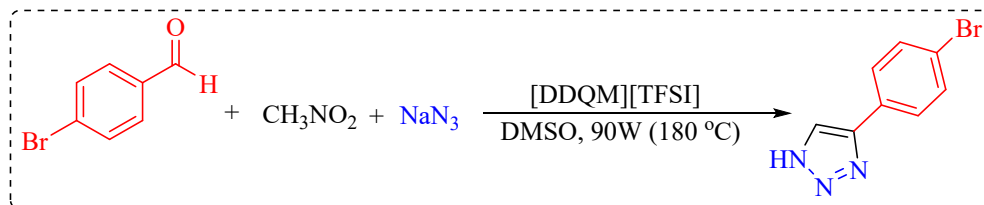
(b)

Figure S4: LC-MS Spectra of [DDQM][TFSI]

4) Table S1: Comparison of [DDQM]/rGO composite with other materials based on capacitive behaviour

Material	electrolyte	Increased Capacitance	References
rGO/Bmim PF ₆	6 M KOH	147.5 Fg ⁻¹	<i>Appl. Surf. Sci.</i> , 2014 , 295, 31-37
rGO/Bmim BF ₄	IL	135 Fg ⁻¹	<i>Electrochim. Acta</i> , 2015 , 176, 1441-1446
rGO- Im-IL	NMP	66 Fg ⁻¹	<i>Int. J. Hydrog. Energy</i> , 2016 , 41, 22134-22143
0.4-Sn doped Co ₃ O ₄ nanowires	6 M KOH	151.8 Fg ⁻¹	<i>Mater. Lett.</i> , 2018 , 216,248–251
[DDQM][TFSI]/rGO composite	NMP	189 Fg ⁻¹	This Work

5) Table S2: Optimization of reaction conditions under microwave in various conditions^a



Entry	Catalyst	Solvent	Power (watt)	Time (minute)	IR Temperature	Yield ^b
1	-	-	100	10	150	-
2	-	DMSO	100	10	150	30%
3	-	DMSO	100	10	180	40%
4	-	DMSO	100	10	200	40%
4 ^c	[DDQM][TFSI] (25 mol%)	DMSO	100	10	200	94%
5	[DDQM][TFSI] (25 mol%)	DMSO	100	10	180	94%

6	[DDQM][TFSI] (25 mol%)	DMSO	90	10	180	94%
7	[DDQM][TFSI] (25 mol%)	DMSO	90	2	180	94%
8	[DDQM][TFSI] (25 mol%)	DMSO	80	2	180	80%
9	[DDQM][TFSI] (25 mol%)	DMSO	90	1.5	180	75%
10	-	DMSO	90	2	180	40%
11	[DDQM][TFSI] (25 mol%)	-	90	2	180	trace
12^d	[DDQM][Br] (25 mol%)	DMSO	90	2	180	40%
13	[DDQM][TFSI] (25 mol%)	DMSO	90	2	170	85%
14	[DDQM][TFSI] (25 mol%)	H ₂ O	90	2	180	-
15	[DDQM][TFSI] (25 mol%)	DMF	90	2	180	10%
16^e	[DDQM][TFSI] (25 mol%)	EG	90	2	180	50%
17	[DDQM][TFSI] (25 mol%)	Toluene	90	2	180	-
18	[DDQM][TFSI] (25 mol%)	Methanol	90	2	180	trace
19	[DDQM][TFSI] (25 mol%)	Ethanol	90	2	180	trace
20	[DDQM][TFSI] (30 mol%)	DMSO	90	2	180	94%
21	[DDQM][TFSI]	DMSO	90	2	180	90%

	(20 mol%)					
22	[DDQM][TFSI]	DMSO	RT	720	-	trace
	(25 mol%)					
23	LiTFSI	DMSO	90	2	180	50%
	(25 mol%)					
24	-	-	90	2	180	-
25^f	[C ₁₂ MIM][TFSI]	DMSO	90	2	180	30%
	(25 mol%)					
26^g	[BMIM][TFSI]	DMSO	90	2	180	30%
	(25 mol%)					
27^h	[DDIM][TFSI]	DMSO	90	2	180	50%
	(25 mol%)					
28ⁱ	[HBDM][TFSI]	DMSO	90	2	180	40%
	(25 mol%)					
29^j	[HBDP][TFSI]	DMSO	90	2	180	35%
	(25 mol%)					

^aReaction conditions: 4-bromobenzaldehyde (0.216 mmol), nitromethane (0.432 mmol), sodium azide (0.648 mmol), Ionic Liquids (20-30 mol%) under microwave irradiation

^b Isolated yield of pure product.

^c [DDQM][TFSI], 1-dodecylquinolin-1-ium bis(trifluoromethane)sulfonimide

^d [DDQM][Br], 1-dodecylquinolin-1-ium bromide

^e EG, Ethelene Glycol

^f [C₁₂MIM][TFSI], 3-dodecyl-1-methyl-*IH*-imidazol-3-ium bis(trifluoromethane)sulfonimide

^g [BMIM][TFSI], 3-butyl-1-methyl-*IH*-imidazol-3-ium bis(trifluoromethane)sulfonimide

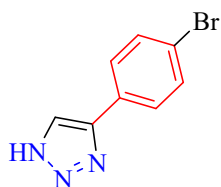
^h [DDIM][TFSI], 1,3-didodecyl-*IH*-imidazol-3-ium bis(trifluoromethane)sulfonimide

^h [HBDM][TFSI], 1,1'-(hexane-1,6-diyl)bis(1-dodecyl-*IH*-indol-1-ium) bis(trifluoromethane)sulfonimide

^h [HBDP][TFSI], 1,1'-(hexane-1,6-diyl)bis(1-dodecyl-4-methylpiperazin-1-ium) bis(trifluoromethane)sulfonimide

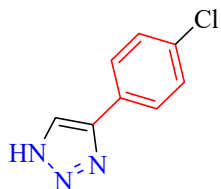
6) Spectral data of products

4-(4-bromophenyl)-1*H*-1,2,3-triazole (Table 3, 4a1)



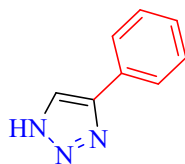
^1H NMR (500 MHz, CDCl_3) δ 8.38 (s, 1H), 7.86 (s, 1H), 7.62 (d, $J = 8.4$ Hz, 2H), 7.49 (d, $J = 8.4$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 175.25, 132.07, 129.18, 128.80, 127.56, 122.45.

4-(4-chlorophenyl)-1*H*-1,2,3-triazole (Table 3, 4a2)



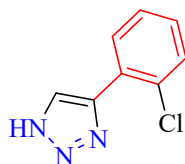
^1H NMR (500 MHz, CDCl_3) δ 8.36 (s, 1H), 7.86 (s, 1H), 7.67 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 154.93, 129.07, 128.88, 128.27, 128.06, 126.44.

4-phenyl-1*H*-1,2,3-triazole (Table 3, 4a3)



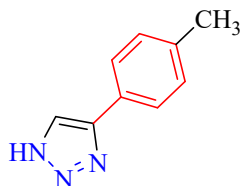
^1H NMR (500 MHz, CDCl_3) δ 8.36 (s, 1H), 7.90 (s, 1H), 7.75 (d, $J = 7.2$ Hz, 2H), 7.38 (m, 2H), 7.30 (t, $J = 7.4$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 155.06, 146.57, 129.26, 128.50, 128.27, 125.65.

4-(2-chlorophenyl)-1*H*-1,2,3-triazole (Table 3, 4a4)



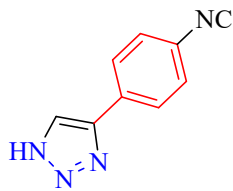
^1H NMR (500 MHz, CDCl_3) δ 8.03 (s, 1H), 7.96 (s, 1H), 7.88 (d, $J = 8.2$ Hz, 1H), 7.65 (d, $J = 8.2$ Hz, 1H), 7.48 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 175.09, 134.58, 132.56, 132.05, 130.73, 128.61, 126.80, 126.26.

4-(*p*-tolyl)-1*H*-1,2,3-triazole (Table 3, 4a5)



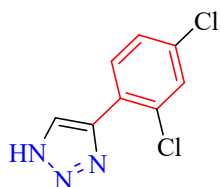
^1H NMR (500 MHz, CDCl_3) δ 8.31 (s, 1H), 7.84 (s, 1H), 7.61 (d, $J = 7.9$ Hz, 2H), 7.16 (d, $J = 7.9$ Hz, 2H), 2.30 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 138.28, 129.28, 128.10, 127.92, 126.46, 125.65, 20.93.

4-(4-isocyanophenyl)-1*H*-1,2,3-triazole (Table 3, 4a6)



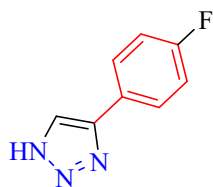
^1H NMR (500 MHz, CDCl_3) δ 8.03 (s, 1H), 7.74 (d, $J = 8.2$ Hz, 2H), 7.48 (d, $J = 8.0$ Hz, 2H).
 ^{13}C NMR (125 MHz, CDCl_3) δ 145.86, 134.21, 132.52, 132.05, 126.73, 126.24, 118.54.

4-(2,4-dichlorophenyl)-1H-1,2,3-triazole (Table 3, 4a7)



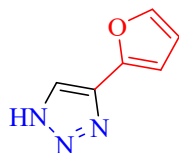
^1H NMR (500 MHz, CDCl_3) δ 8.39 (s, 1H), 8.18 (s, 1H), 7.83 (d, $J = 8.4$ Hz, 1H), 7.44 (s, 1H), 7.28 (d, $J = 8.2$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 155.29, 129.50, 128.73, 128.61, 127.82, 127.17.

4-(4-fluorophenyl)-1H-1,2,3-triazole (Table 3, 4a8)



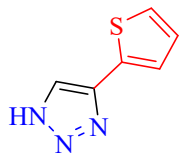
^1H NMR (500 MHz, CDCl_3) δ 8.34 (s, 1H), 7.84 (s, 1H), 7.72 (d, $J = 5.0$ Hz, 2H), 7.10 (m, 2H).
 ^{13}C NMR (125 MHz, CDCl_3) δ 175.50, 174.97, 129.74, 127.53, 115.75.

4-(furan-2-yl)-1H-1,2,3-triazole (Table 3, 4a9)



^1H NMR (500 MHz, CDCl_3) δ 8.57 (s, 1H), 7.82 (s, 1H), 7.42 (d, $J = 1.1$ Hz, 1H), 7.33 (d, $J = 1.4$ Hz, 1H), 6.42 (dd, $J = 3.3, 1.8$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 155.08, 142.70, 142.34, 111.57, 107.83.

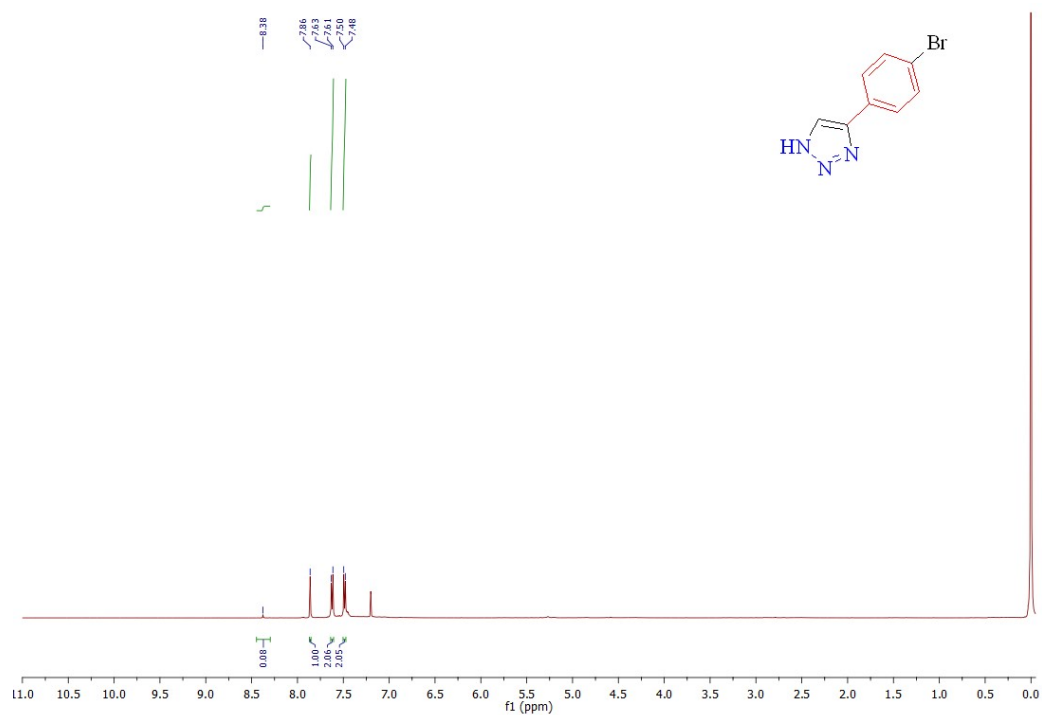
4-(thiophen-2-yl)-1H-1,2,3-triazole (Table 3, 4a10)



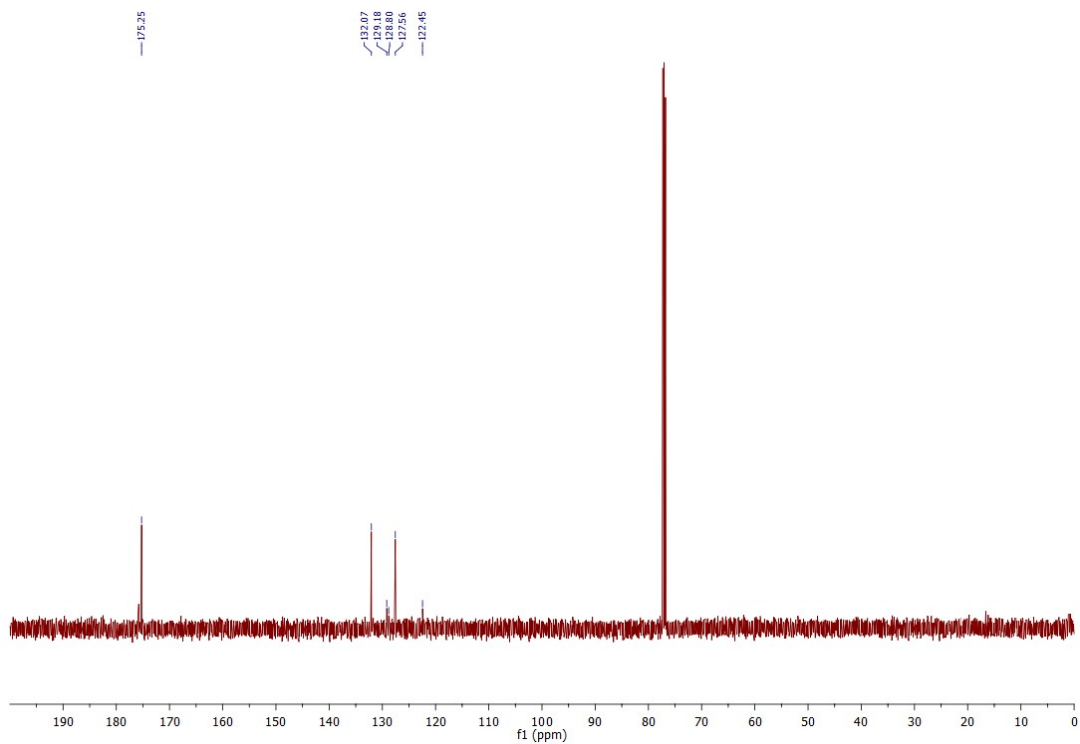
^1H NMR (500 MHz, CDCl_3) δ 8.42 (s, 1H), 7.81 (s, 1H), 7.34 (d, $J = 3.4$ Hz, 1H), 7.25 (d, $J = 5.0$ Hz, 1H), 7.01 (dd, $J = 4.7, 3.8$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 146.33, 132.99, 132.52, 127.20, 126.71.

5) Copies of ^1H NMR and ^{13}C NMR of the products

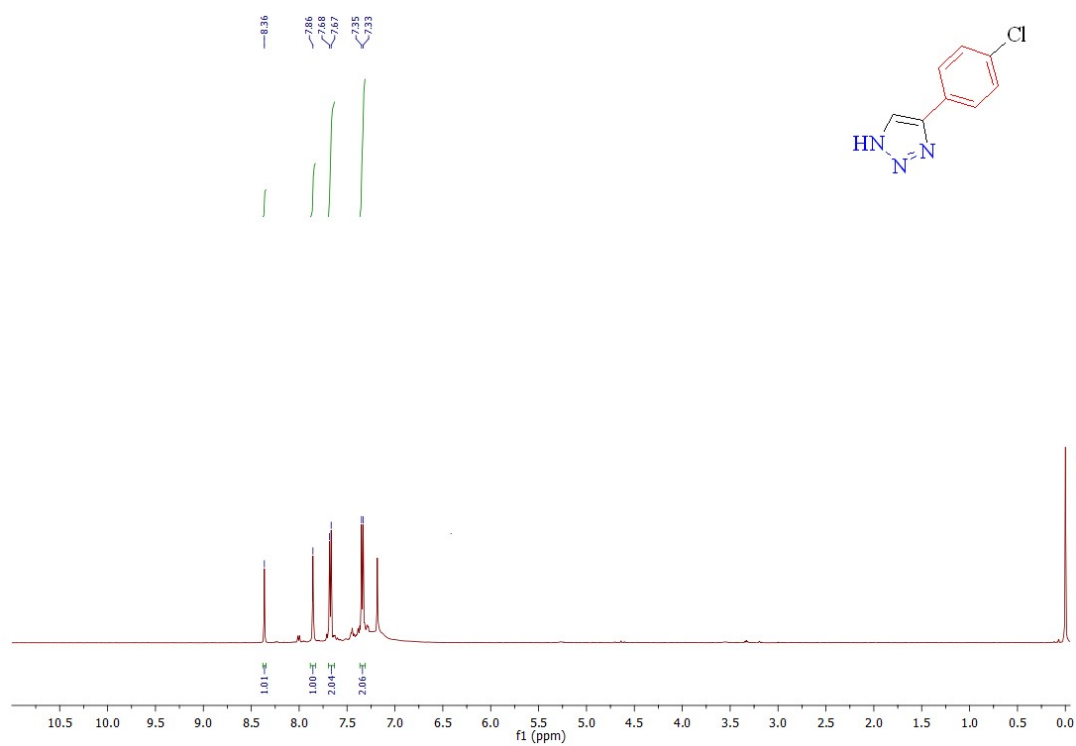
^1H spectrum of 4-(4-bromophenyl)-1*H*-1,2,3-triazole (Table 3, 4a1)



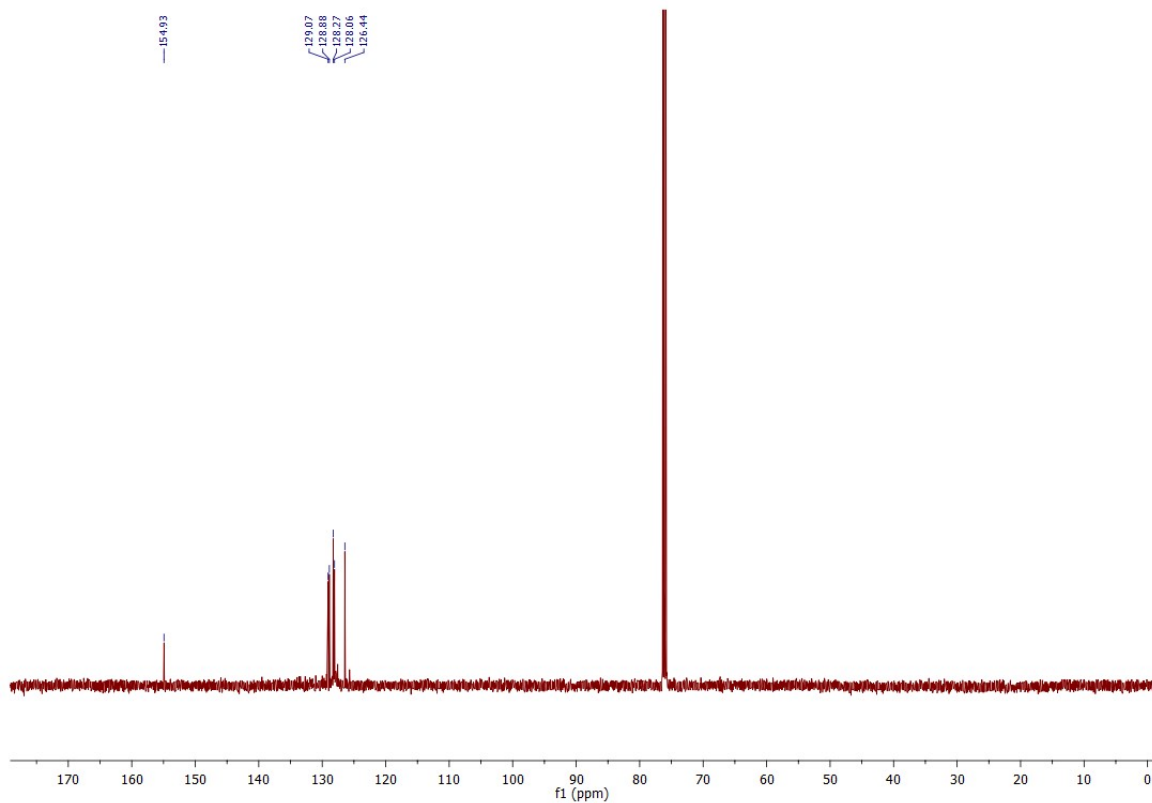
^{13}C spectrum of 4-(4-bromophenyl)-1*H*-1,2,3-triazole (Table 3, 4a1)



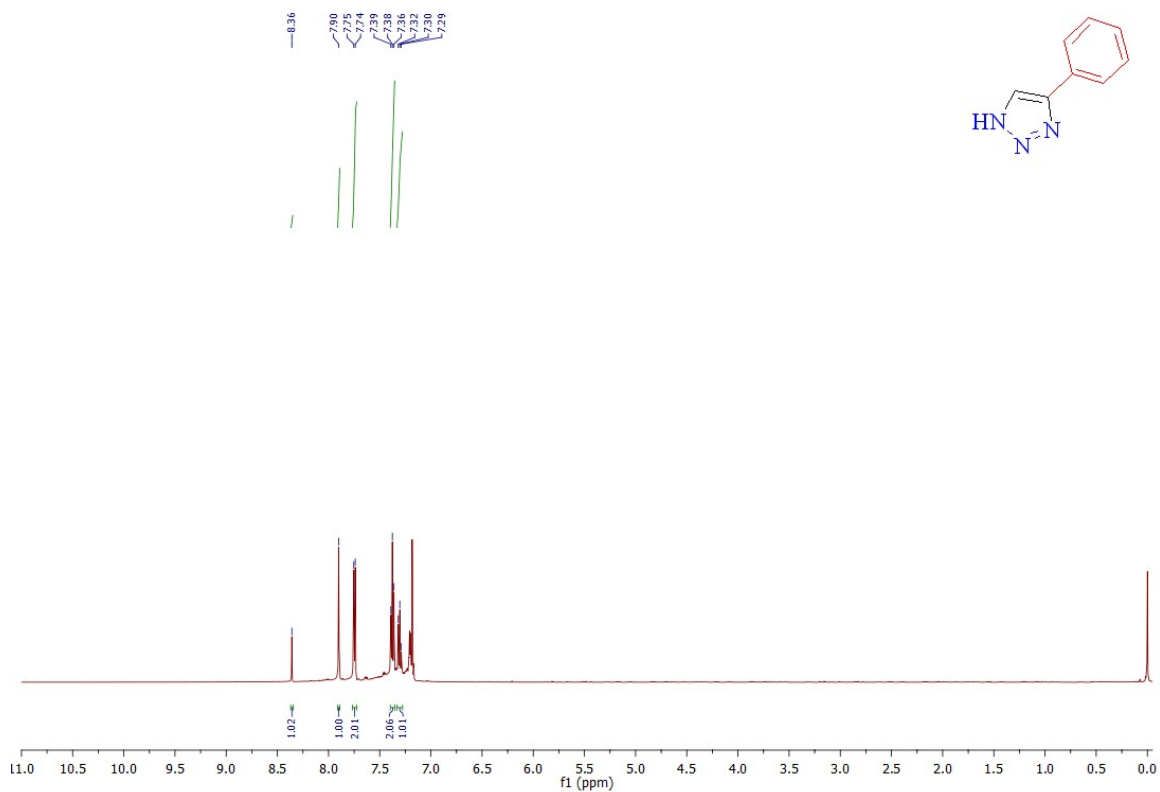
¹H spectrum of 4-(4-chlorophenyl)-1H-1,2,3-triazole (Table 3, 4a2)



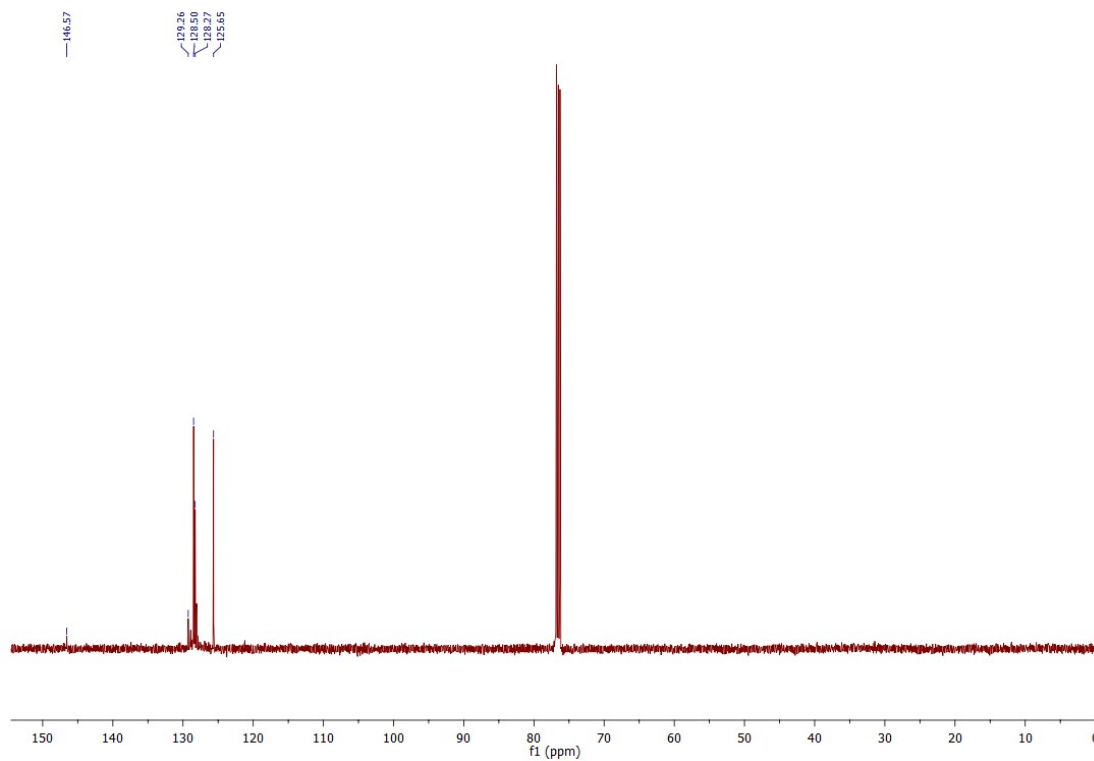
¹³C spectrum of 4-(4-chlorophenyl)-1H-1,2,3-triazole (Table 3, 4a2)



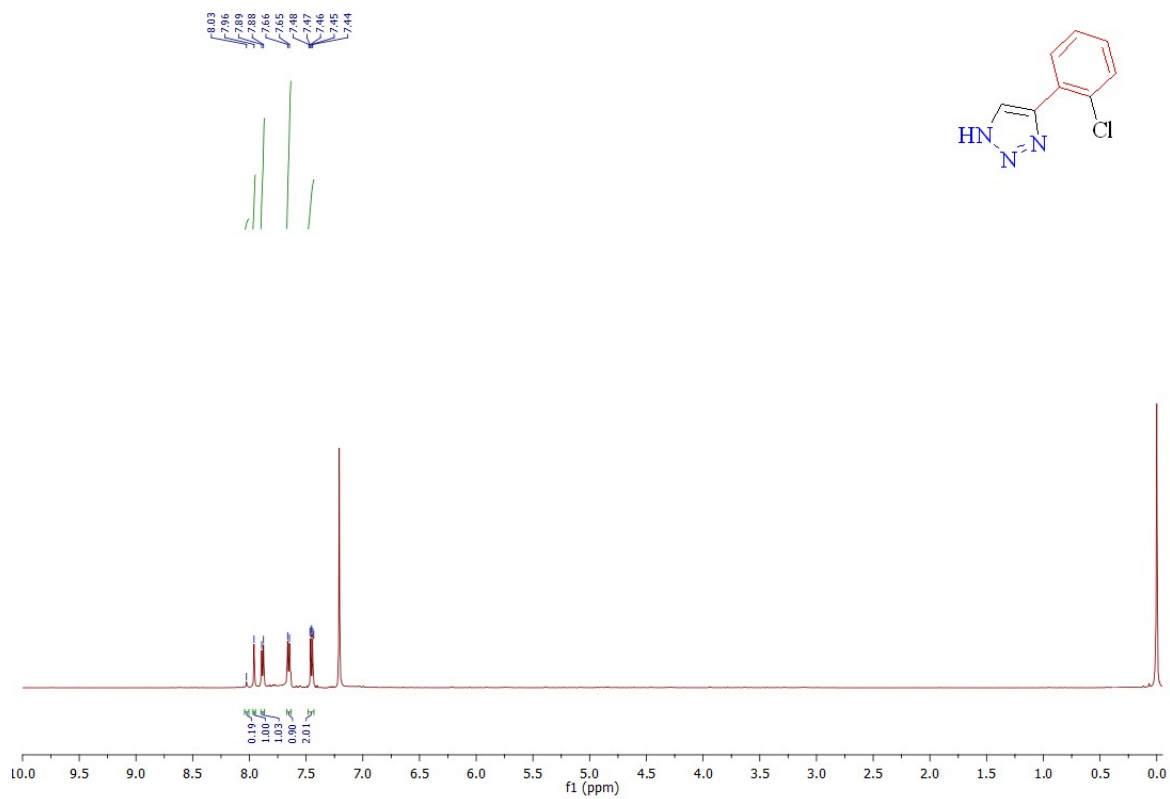
¹H spectrum of 4-phenyl-1*H*-1,2,3-triazole (Table 3, 4a3)



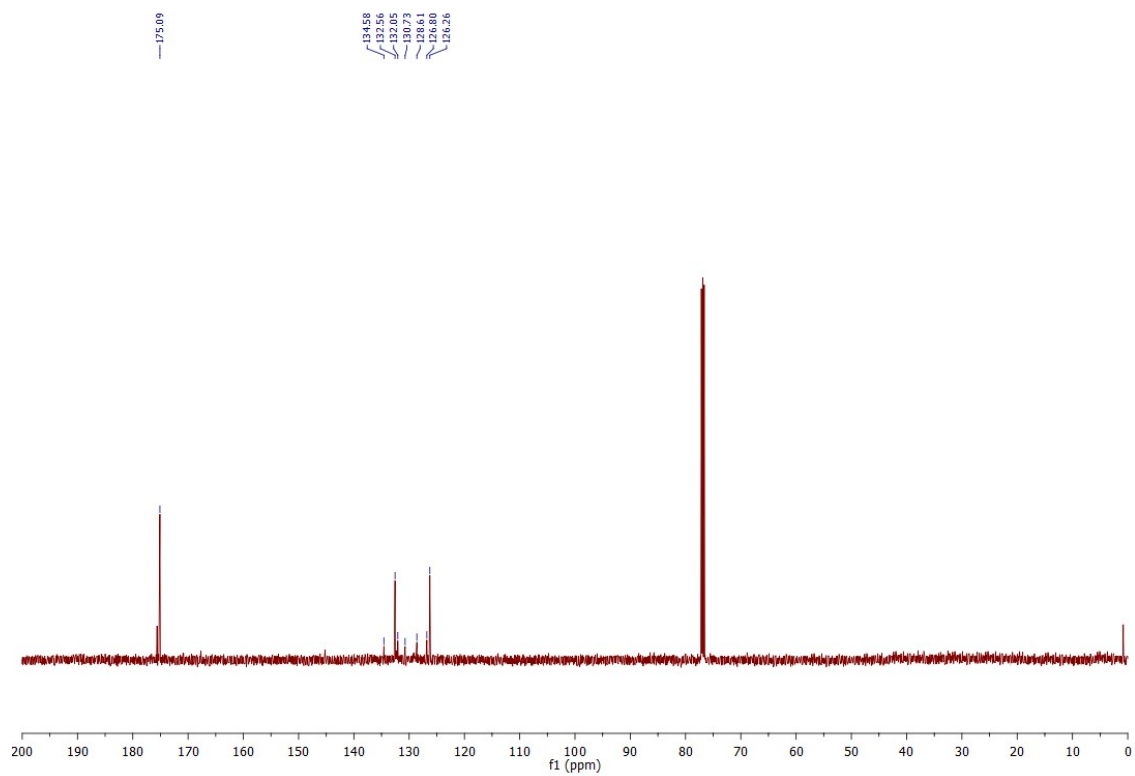
¹³C spectrum of 4-phenyl-1*H*-1,2,3-triazole (Table 3, 4a3)



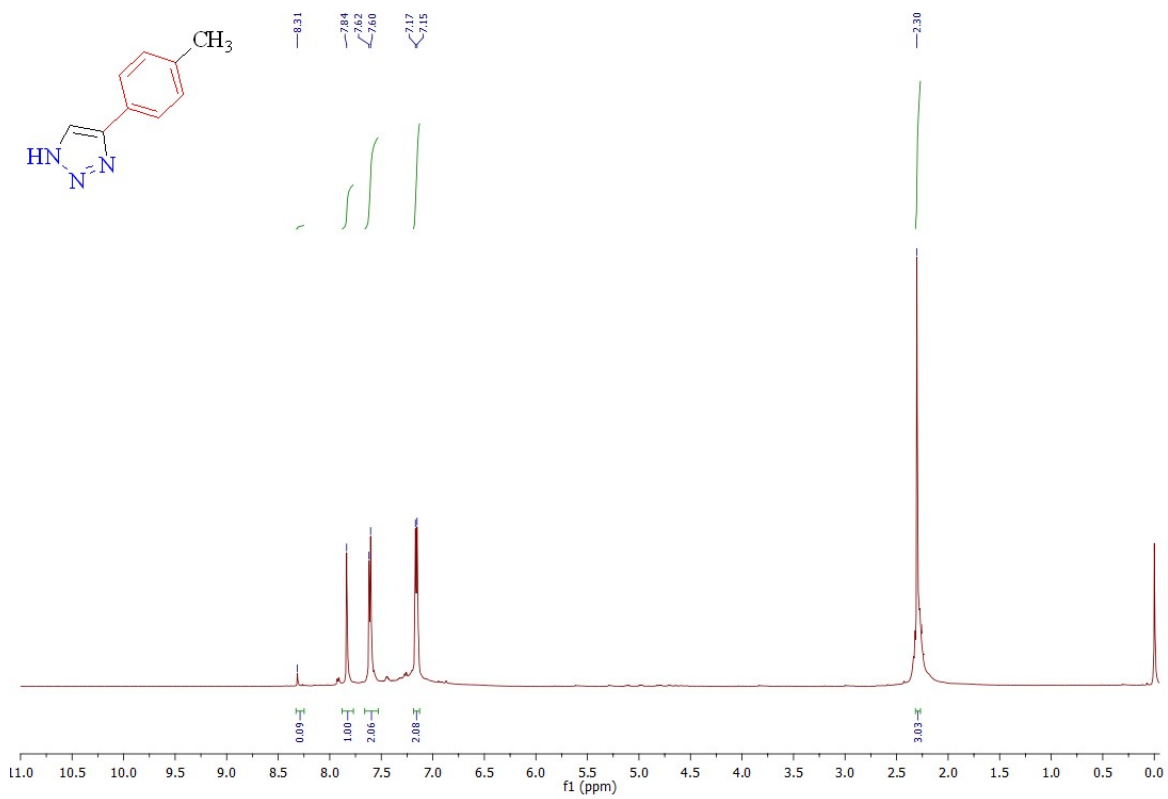
¹H spectrum of 4-(2-chlorophenyl)-1H-1,2,3-triazole (Table 3, 4a4)



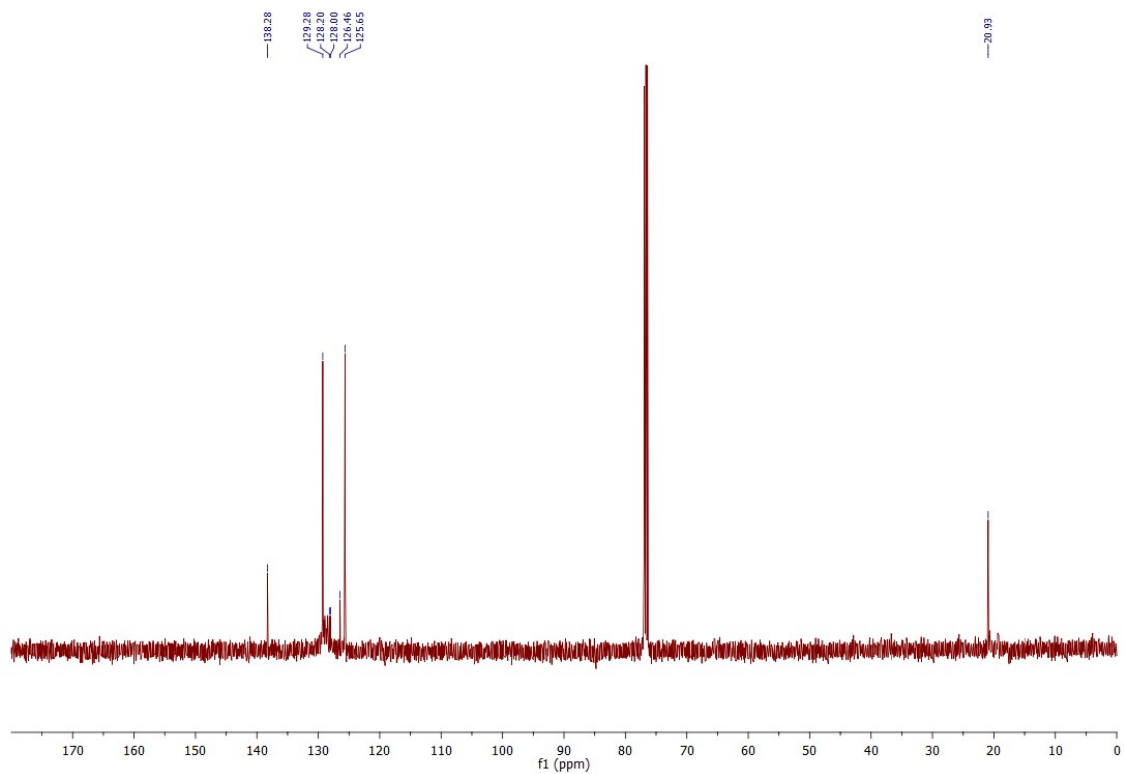
¹³C spectrum of 4-(2-chlorophenyl)-1H-1,2,3-triazole (Table 3, 4a4)



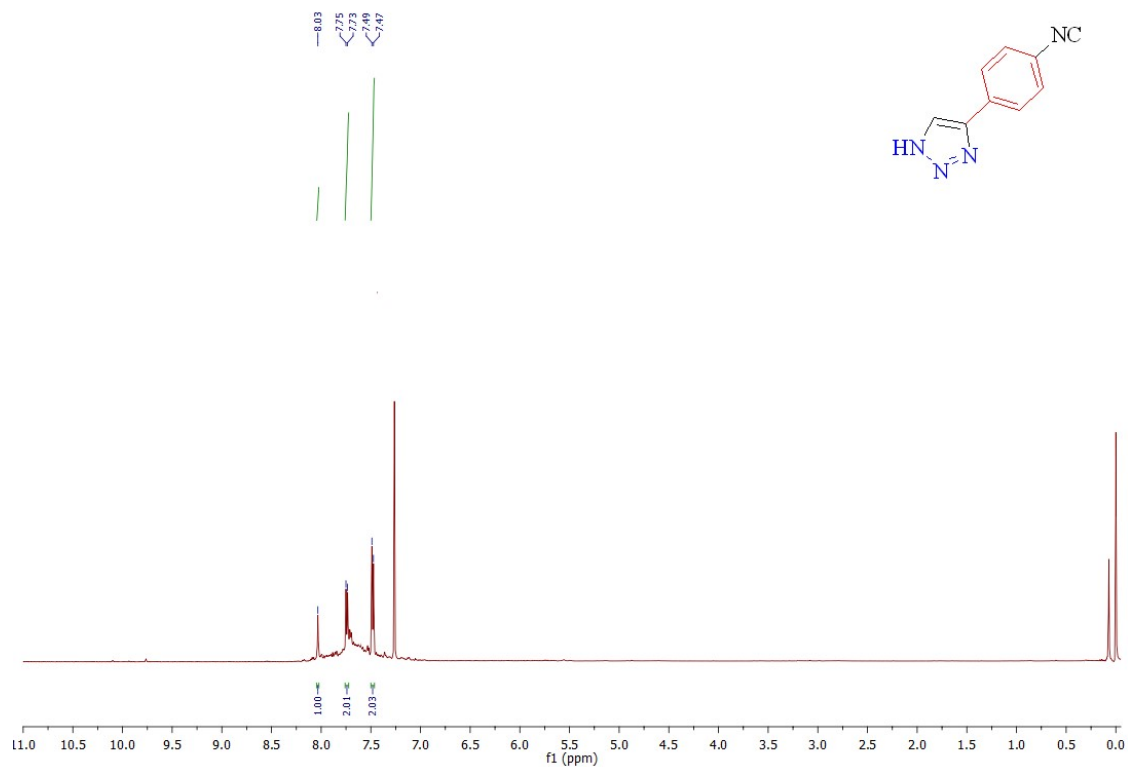
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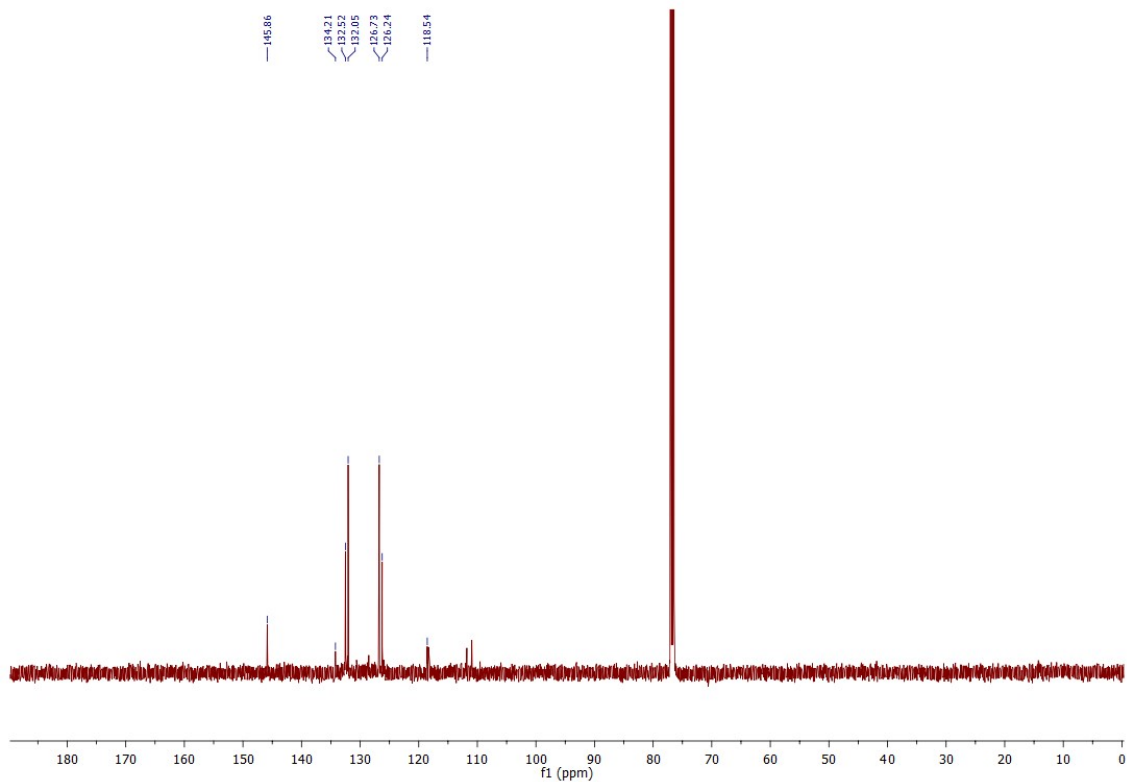
¹³C spectrum of 4-(p-tolyl)-1H-1,2,3-triazole (Table 3, 4a5)



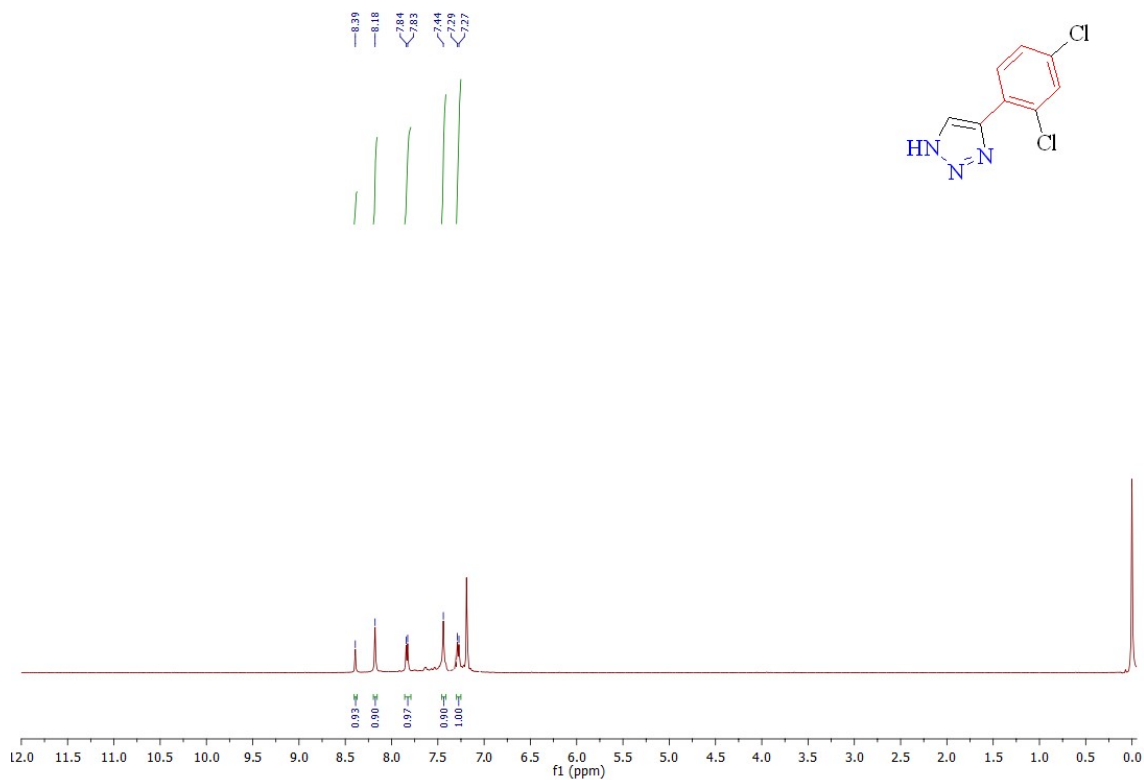
¹H spectrum of 4-(4-isocyanophenyl)-1H-1,2,3-triazole (Table 3, 4a6)



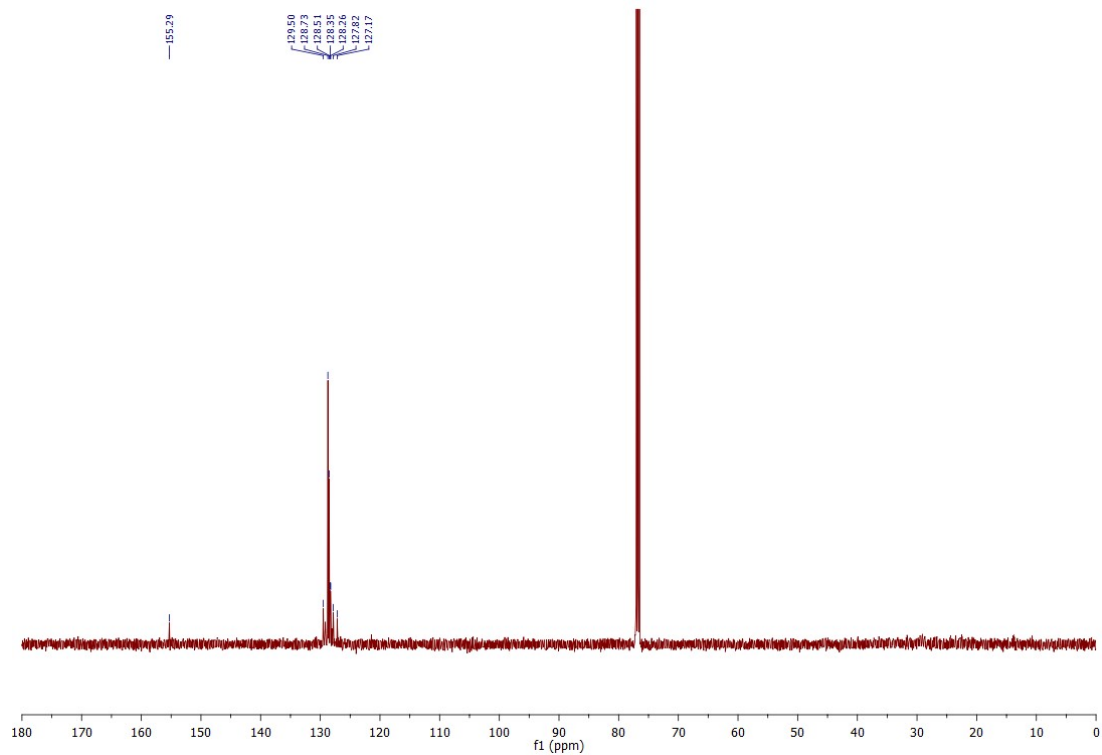
¹³C spectrum of 4-(4-isocyanophenyl)-1H-1,2,3-triazole (Table 3, 4a6)



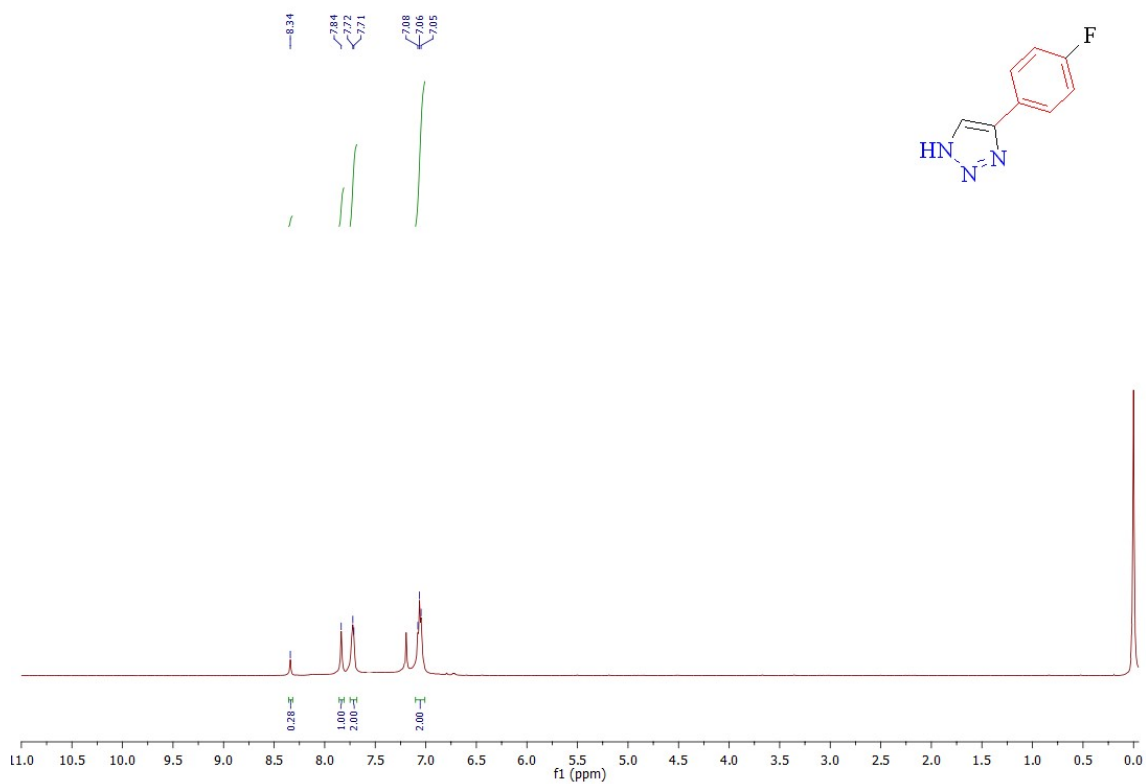
¹H spectrum of 4-(2,4-dichlorophenyl)-1H-1,2,3-triazole (Table 3, 4a7)



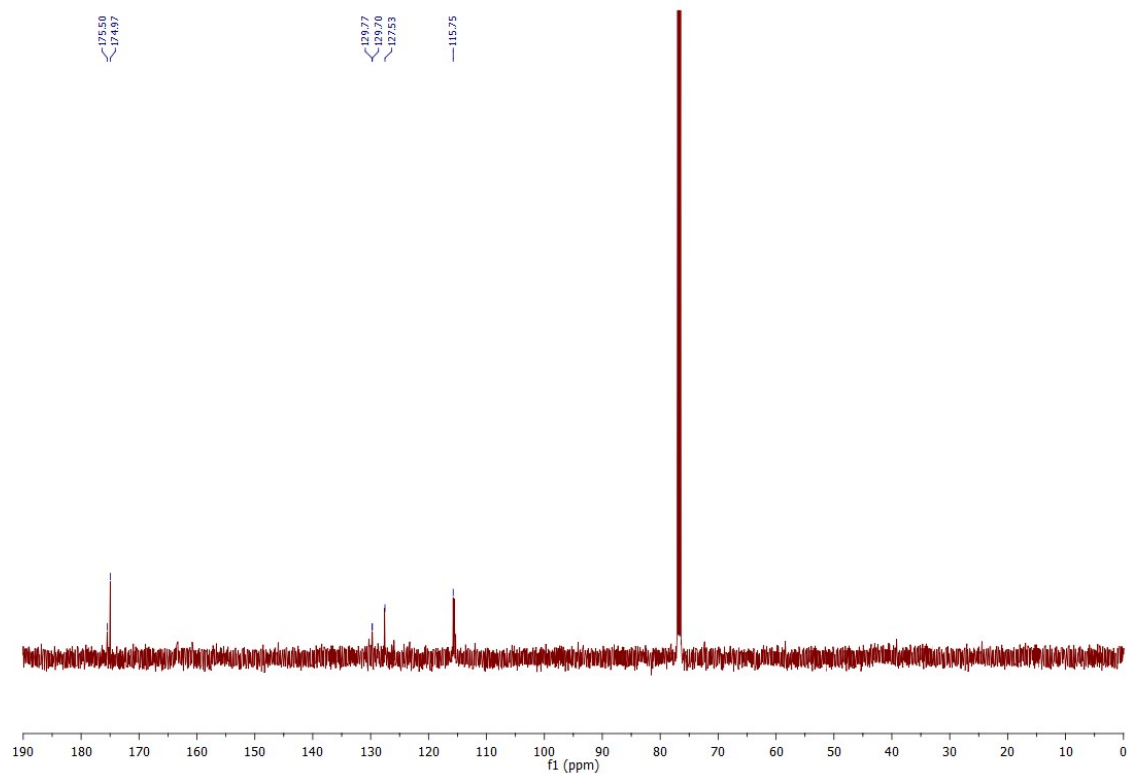
¹³C spectrum of 4-(2,4-dichlorophenyl)-1H-1,2,3-triazole (Table 3, 4a7)



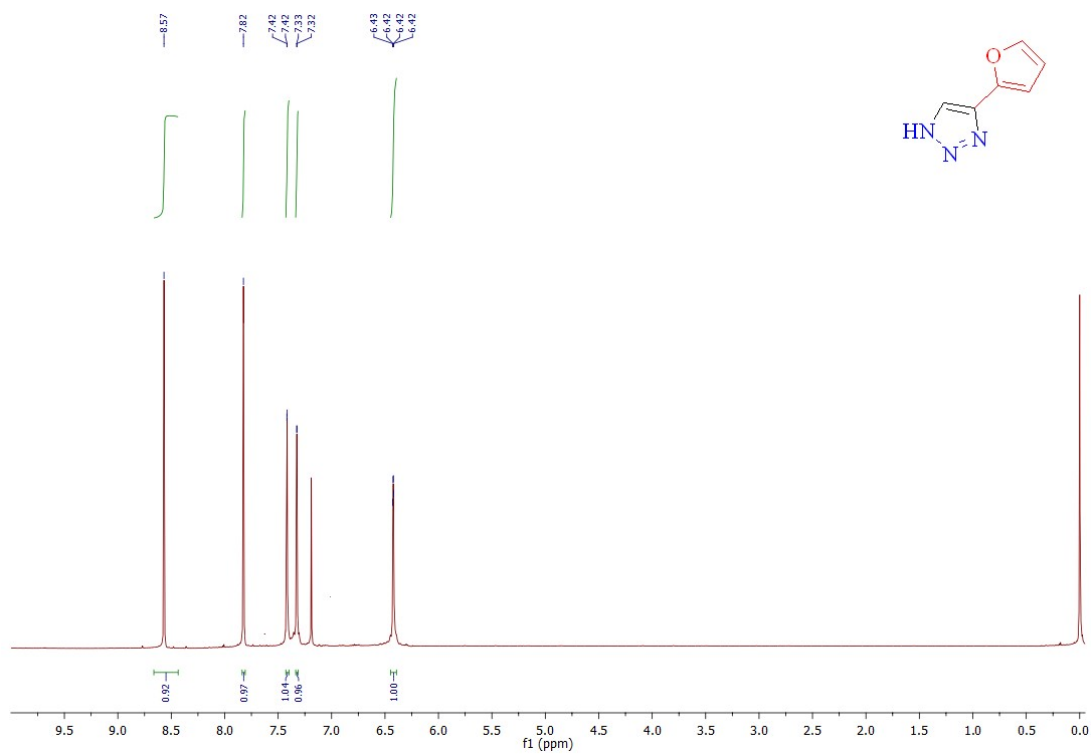
¹H spectrum of 4-(4-fluorophenyl)-1H-1,2,3-triazole (Table 3, 4a8)



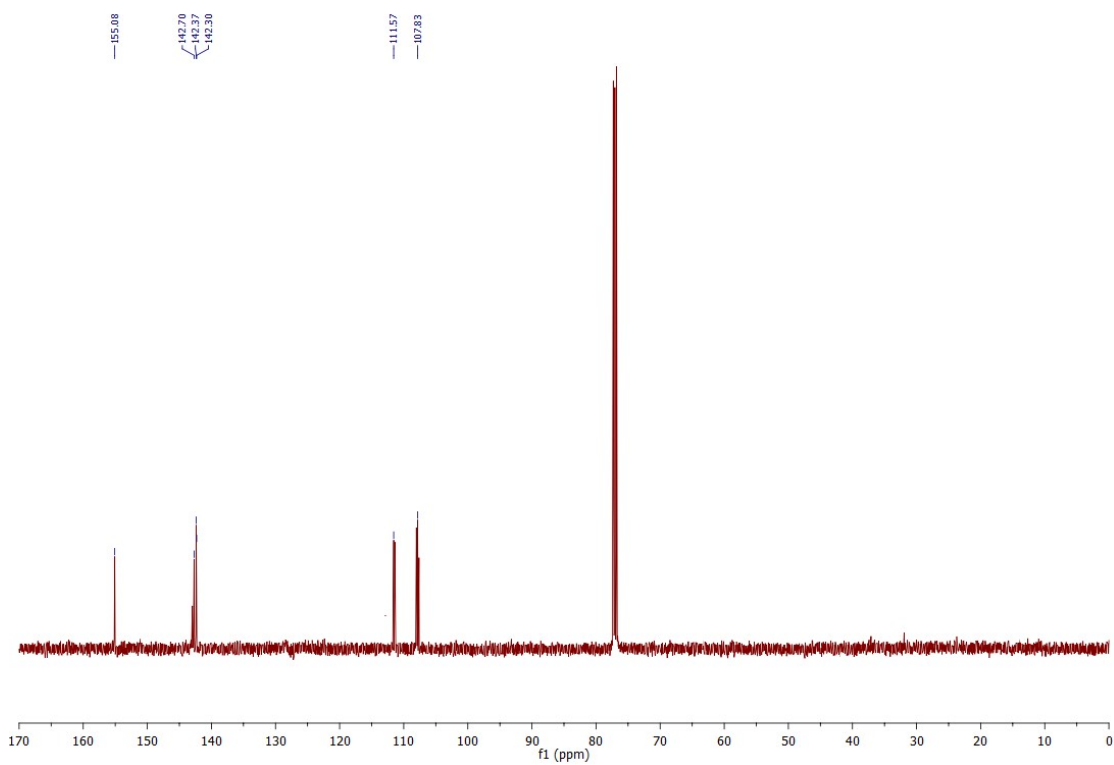
¹³C spectrum of 4-(4-fluorophenyl)-1H-1,2,3-triazole (Table 3, 4a8)



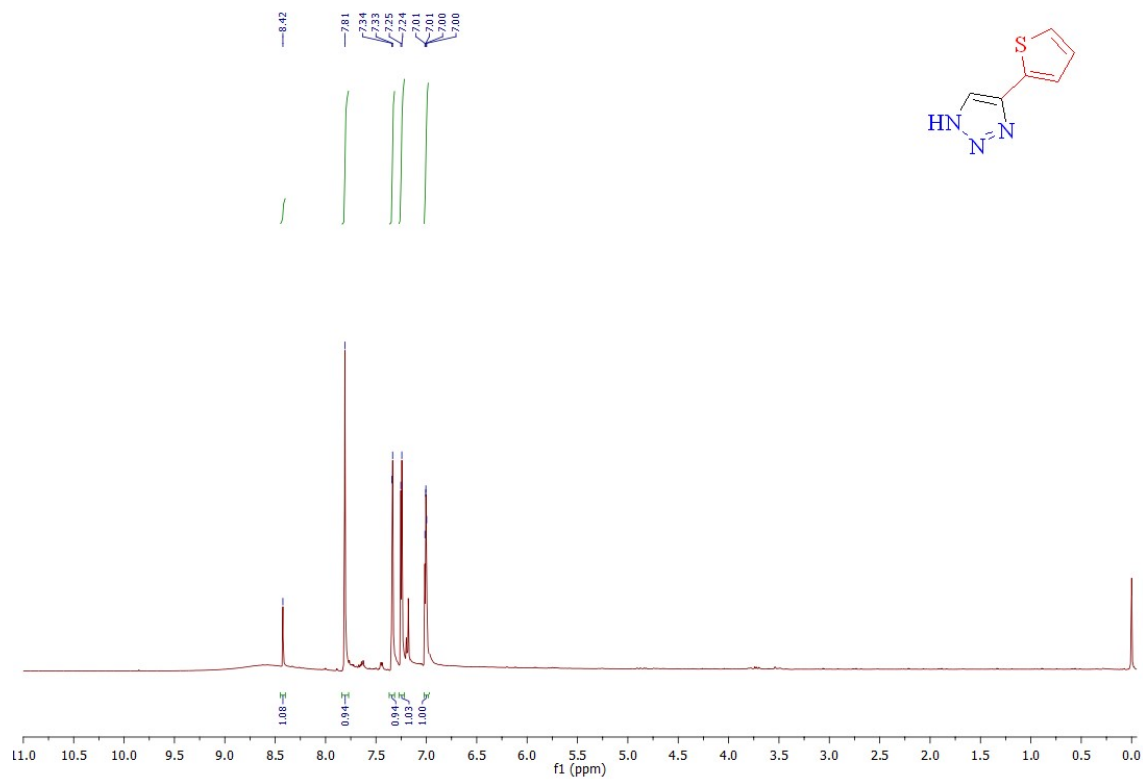
¹H spectrum of 4-(furan-2-yl)-1H-1,2,3-triazole (Table 3, 4a9)



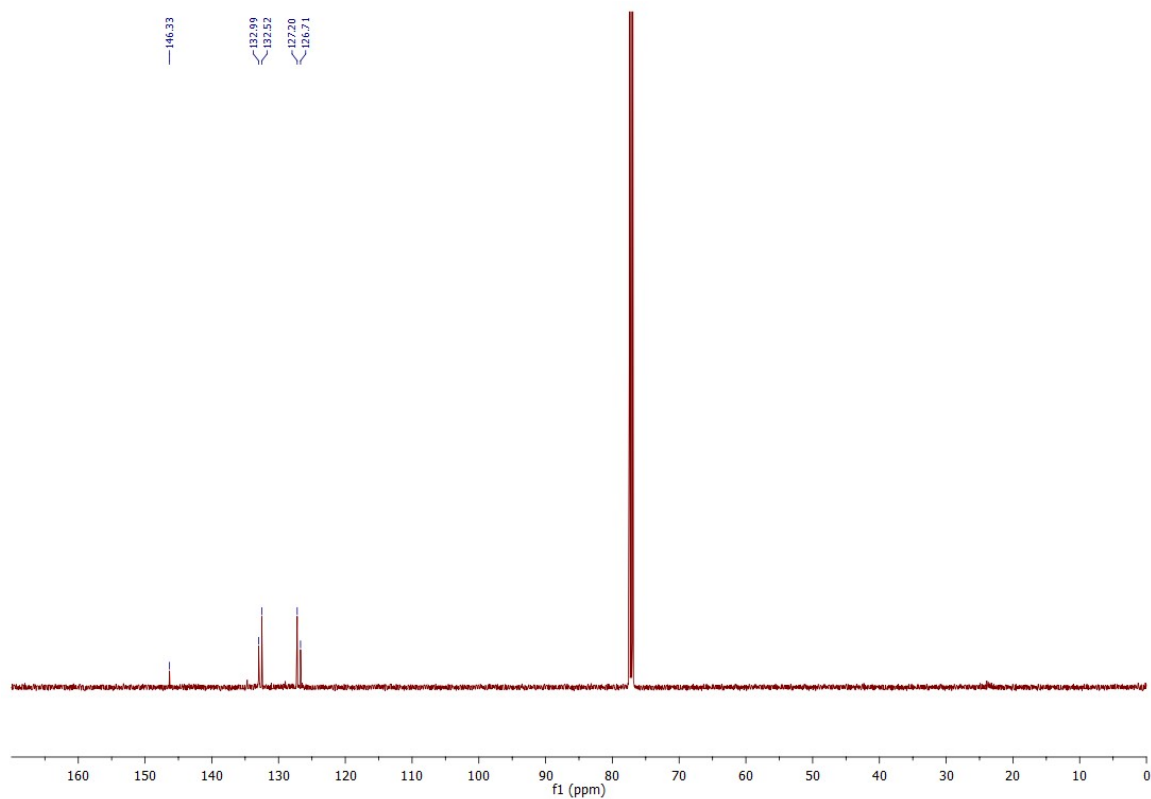
¹³C spectrum of 4-(furan-2-yl)-1H-1,2,3-triazole (Table 3, 4a9)



¹H spectrum of 4-(thiophen-2-yl)-1H-1,2,3-triazole (Table 3, 4a10)



¹³C spectrum of 4-(thiophen-2-yl)-1H-1,2,3-triazole (Table 3, 4a10)



6) References

- 1) B. Dutta, A. Garg, P. Phukan, A. Kulshrestha, A. Kumar, D. Sarma, *New J. Chem.*, 2021, **45**, 12792.
- 2) (a) R. Rey, P. Johansson, J. Lindgren, J.C. Lassègues, J. Grondin, L. Servant, *J. Phys. Chem. A*, 1998, **102**, 3249–3258, (b) H. Abroshan, N.R. Dhumal, Y. Shim, H.J. Kim, *Phys. Chem. Chem. Phys.*, 2016, **18**, 6754–6762.
- 3) J.C. Hannaford, M. Breedon, T. Rüther, P. Johansson, M.J.S. Spencer, *Chem. Eur. J.*, 2021, **27**, 1–10