Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supporting Information

Versatile precursor dependent copper sulfide nanoparticles as multifunctional catalyst for photocatalytic removal of water pollutants and synthesis of aromatic aldehydes and NH-triazoles

Soniya Agarwal, Parmita Phukan, Diganta Sarma* and Kalyanjyoti Deori*

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

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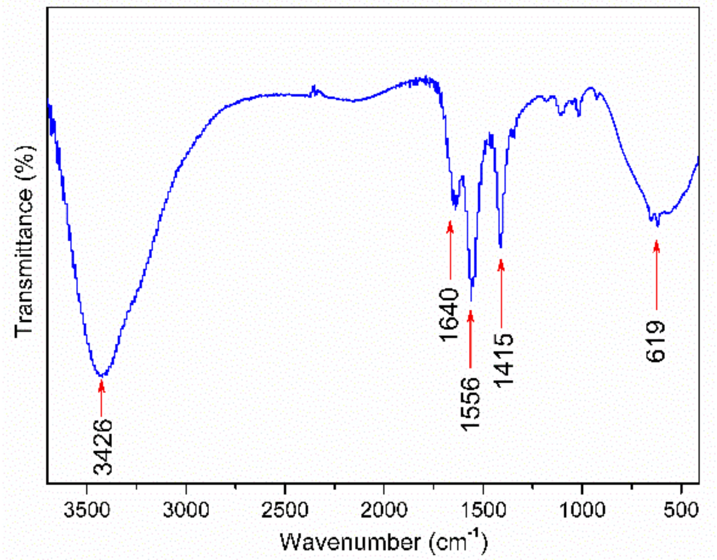


Fig. S1 (a) FT-IR spectrum plot of as synthesized CS2 nanoparticles.

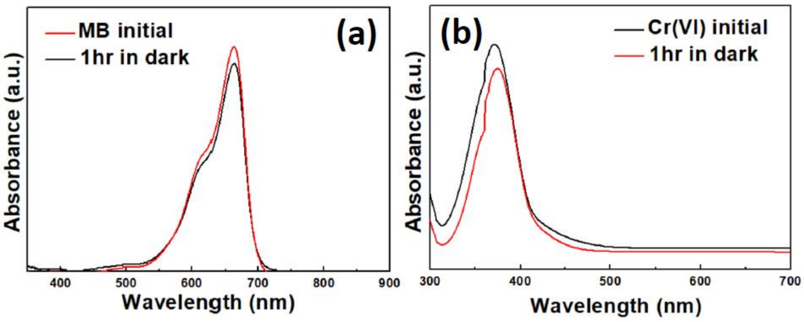


Fig. S2 Time-dependent optical absorption spectra for degradation of (a) Methylene blue (MB) and (b) Cr(VI) for blank and after stirring with photocatalyst for 1 hour under dark condition.

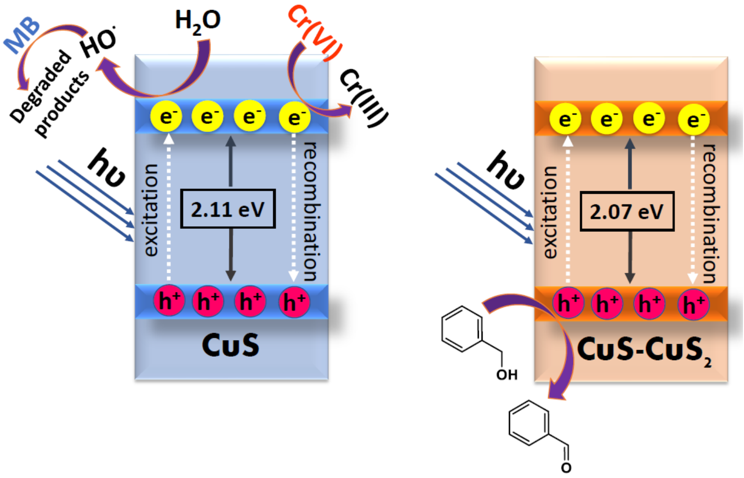


Fig. S3 Band gap structures of CuS (CS2) and CuS-CuS_2 (CS20) photocatalysts.

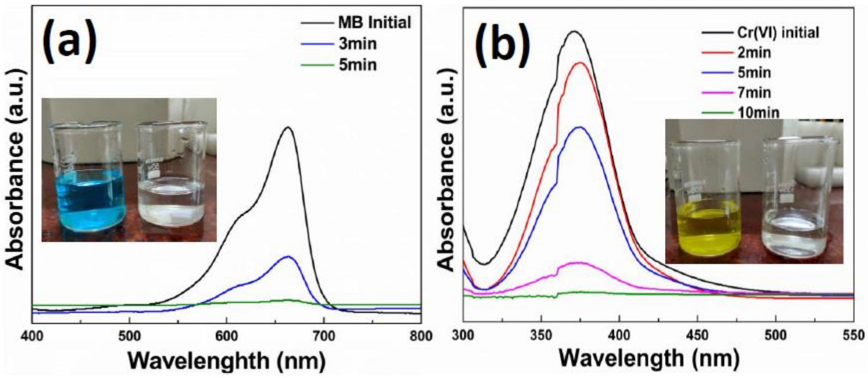


Fig. S4 (a) MB degradation and (b) Cr(VI) reduction conducted with 250 watts high pressure mercury vapour visible lamp (HPMVL).

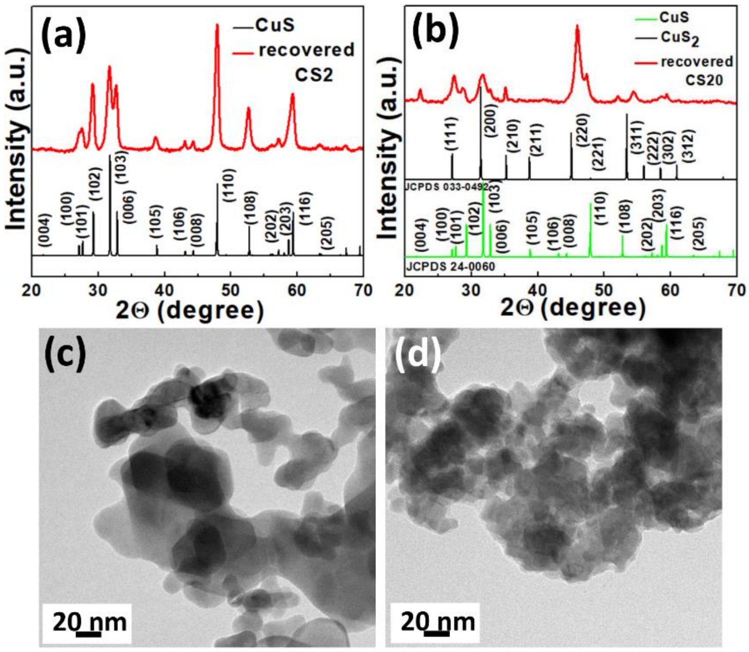
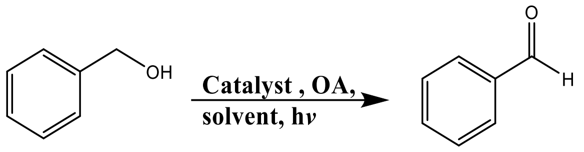


Fig. S5 (a) Powder XRD pattern of recovered CS2 sample after durability test for MB degradation and Cr(VI) reduction reactions along with bulk XRD pattern of covellite CuS. (b) XRD pattern of recovered CS20 sample after recyclability test (5th photocatalytic cycle) for benzyl alcohol oxidation reaction. TEM image of recovered photocatalyst (c) CS2 and (d) CS20.

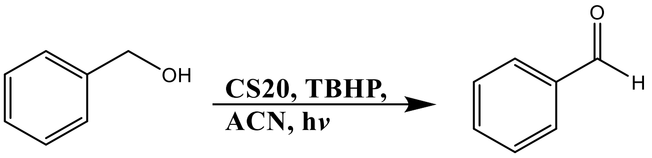
Table S1: Optimization of reaction conditions for photocatalytic selective oxidation of benzyl alcohol to benzaldehyde.

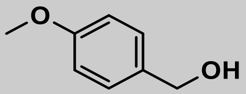
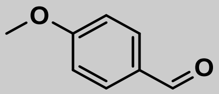
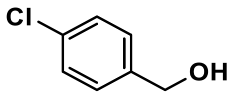
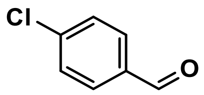
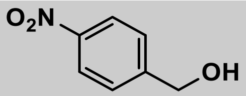
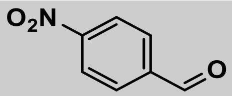
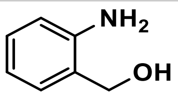
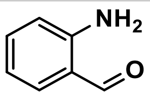
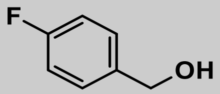
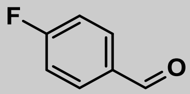
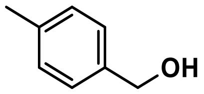
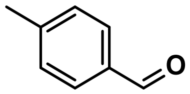
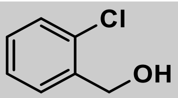
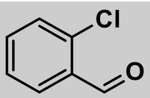


Entry	Oxidant	Solvent	Catalyst	Conversion (%)
1	H_2O_2	ACN	-	-
2	H_2O_2	ACN	CS2	57
3	H_2O_2	ACN	CS20	79
4	O_2	ACN	CS20	-
5	TBHP	ACN	CS20	88
6	TBHP	H_2O	CS20	62
7[a]	TBHP	ACN	CS20	55
8	**TBHP**	**ACN**	**CS20**	**96**

Reaction conditions: All reactions were performed with oxidant = 0.5 mL, catalyst = 20 mg and solvent = 5 mL in the presence of visible light. [a]In the absence of visible light.

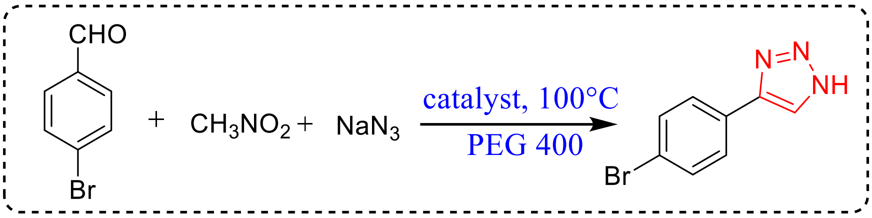
Table S2: Substrate study of various substituted benzyl alcohols to corresponding aldehydes according to the optimised condition obtained from Table S1.



Entry	Substrate	Product	Conversion (%)
1			99
2			97
3			85
4			72
5			93
6			96
7			97

Reaction conditions: All reactions were performed with TBHP = 0.5 mL, CS20 = 20 mg andACN = 5 mL in the presence of visible light.

Table S3: Optimization of catalyst loading in the synthesis of 4-Aryl-NH-1,2,3-Triazoles[a]

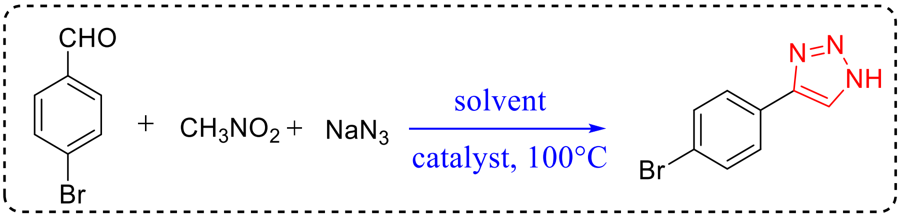


Entry	Catalyst (mg)	Time (h)	Yield[b] (%)
1	20	1	98 %
2	15	1	98 %
3	**10**	**1**	**98 %**
4	5	3	76 %
5	-	3	24 %
6	**10**	**45 mins**	**85 %**
		30 mins	**62 %**

[a] Reaction conditions: 4-bromobenzaldehyde (1 mmol), nitromethane (2mmol), NaN_3 (3 mmol), catalyst, solvent (PEG-400) (3 mL), in air.

[b] Isolated yield.

Table S4: Optimization of reaction conditionsin the synthesis of 4-Aryl-NH-1,2,3-Triazoles[a]



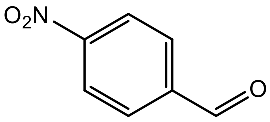
Entry	Solvent	Temperature	Time (h)	Yield[b] (%)
1	H_2O	100°C	1	45 %
2	DMSO	100°C	1	70 %
3	DCM	100°C	1	68 %
4	Toluene	100°C	1	55 %

5	EG	100°C	1	72 %
6	DMF	100°C	1	65 %
7	**PEG-400**	**100°C**	**1**	**98 %**
8	PEG-400	70° C	1	72 %
9	PEG-400	RT	24	Trace

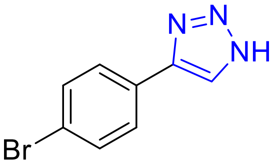
[a] Reaction conditions: 4-bromobenzaldehyde (1 mmol), nitromethane (2 mmol), NaN_3 (3 mmol), and catalyst (10 mg), solvent (3 mL), in air.

[b] Isolated yield.

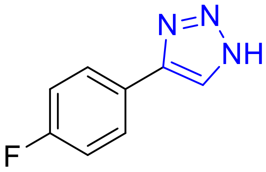
Analytical data of representative compounds:



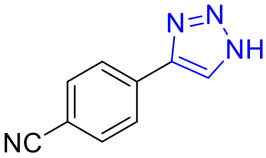
4-nitrobenzaldehyde: light yellow crystalline powder, m.p.= 104-106°C,^{1}H NMR (500 MHz, $CDCl_3$) δ10.16(s, 1H),8.38 (d, *J* = 8.6 Hz, 2H), 8.08 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ=190.28, 150.98, 139.95, 130.38, 124.17.



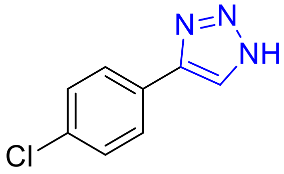
4-(4-bromophenyl)-1H-1,2,3-triazole**:** white solid, m.p.= 177-180°C, ^{1}H NMR (500 MHz, DMSO) δ 9.15 (s, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.78 (s, 1H), 7.66 (d, *J* = 8.5 Hz, 2H).^{13}C NMR (126 MHz, DMSO) δ 141.08, 132.23, 131.01, 130.80, 129.13, 127.87.



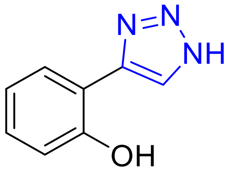
(4-(4-fluorophenyl)-1H-1,2,3-triazole): Yellow solid; mp 148-150°C, ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.08 (s, 1H), 8.25 (s, 1H), 7.86 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.9 Hz, 2H).



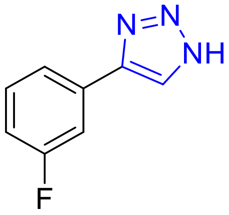
(4-(1H-1,2,3-triazol-4-yl)benzonitrile): Yellow solid; mp 170-172 °C, ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.74 (s, 1H), 8.39 (s, 1H), 8.03 (d, *J* = 8.2 Hz, 2H), 7.89 (d, *J* = 7.6 Hz, 2H).



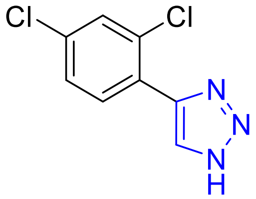
(4-(4-chlorophenyl)-1H-1,2,3-triazole): Yellow solid; mp 160-162°C, ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 9.11 (s, 1H), 8.24 (s, 1H), 7.85 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 7.3 Hz, 2H). ^{13}C NMR (126 MHz, DMSO) δ 157.68, 138.36, 130.48, 129.31, 128.71, 127.58.



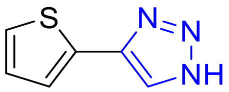
(2-(1H-1,2,3-triazol-4-yl)phenol): Yellow solid; mp 154-156°C, ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 14.92 (s, 1H), 8.19 (s, 1H), 7.82 (s, 1H), 7.20 – 6.89 (m, 4H).^{13}C NMR (126 MHz, DMSO) δ 154.43, 143.94, 133.19, 129.46, 129.00, 127.84, 119.68, 116.50.



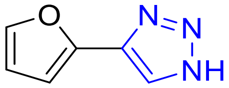
(4-(3-fluorophenyl)-1H-1,2,3-triazole): Yellow solid, ^{1}H NMR (500 MHz, DMSO) δ 11.46 (s, 1H), 8.32 (s, 1H), 7.91 – 7.56 (m, 5H).^{13}C NMR (126 MHz, DMSO) δ 158.46, 146.93, 131.66, 129.87, 128.37, 125.30, 116.54.



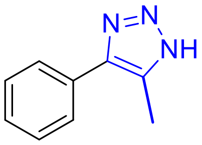
(4-(2,4-dichlorophenyl)-1H-1,2,3-triazole)**:** Yellow solid; mp 168-170°C: ^{1}H NMR (400 MHz, DMSO- d$_6$) δ 9.03 (s, 1H), 8.27 (d, J = 1.3 Hz, 1H), 7.71 (s, 1H), 7.55 (s, 1H), 7.43 (d, J = 13.6 Hz, 1H).^{13}C NMR (126 MHz, DMSO) δ 143.30, 133.75, 131.95, 130.03, 128.14, 127.75.



***(4-(thiophen-2-yl)-1H-1,2,3-triazole)*:** Yellow solid, mp 86-88°C: ^{1}H NMR (400 MHz,) δ 9.19 (s), 8.11 (s), 7.13 – 7.05 (m), 6.91 (t, *J* = 5.1 Hz). ^{13}C NMR (101 MHz,) δ 142.20, 129.11, 128.45, 127.39, 126.44, 125.88.



(4-(furan-2-yl)-1H-1,2,3-triazole): Yellow solid; mp 62-64°C: ^{1}H NMR (600 MHz, DMSO-d_6) δ 15.30 (s, 1H), 9.08 (s, 1H), 8.08 (d, J = 52.2 Hz, 1H), 7.34 (dd, J = 36.0, 28.3 Hz, 2H).^{13}C NMR (151 MHz, DMSO) δ 158.51, 142.53, 116.63, 114.38, 63.93, 38.13.



(5-methyl-4-phenyl-1H-1,2,3-triazole): Yellow solid; mp 124-126 °C; ^{1}H NMR (500 MHz, DMSO) δ 14.36 (s, 1H), 7.94 (d, J = 1.9 Hz, 2H), 7.69 – 7.57 (m, 2H), 7.54 – 7.45 (m, 1H), 2.52(s, 3H).^{13}C NMR (126 MHz, DMSO) δ 167.68, 133.22, 131.07, 129.60, 128.92, 126.02, 11.21.

1H and 13C NMR of the compounds

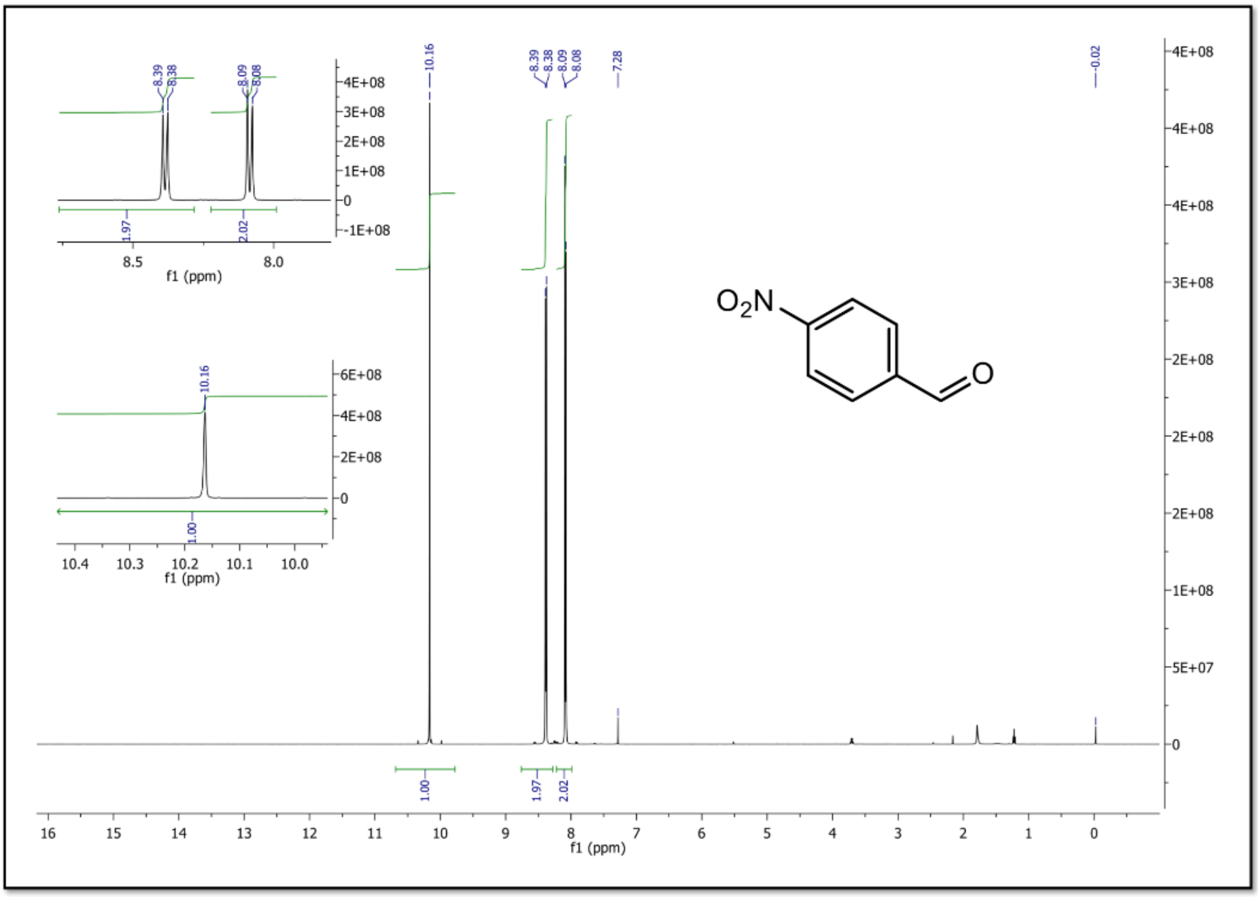


Fig. S6: ^{1}H NMR spectrum of 4-nitrobenzaldehyde.

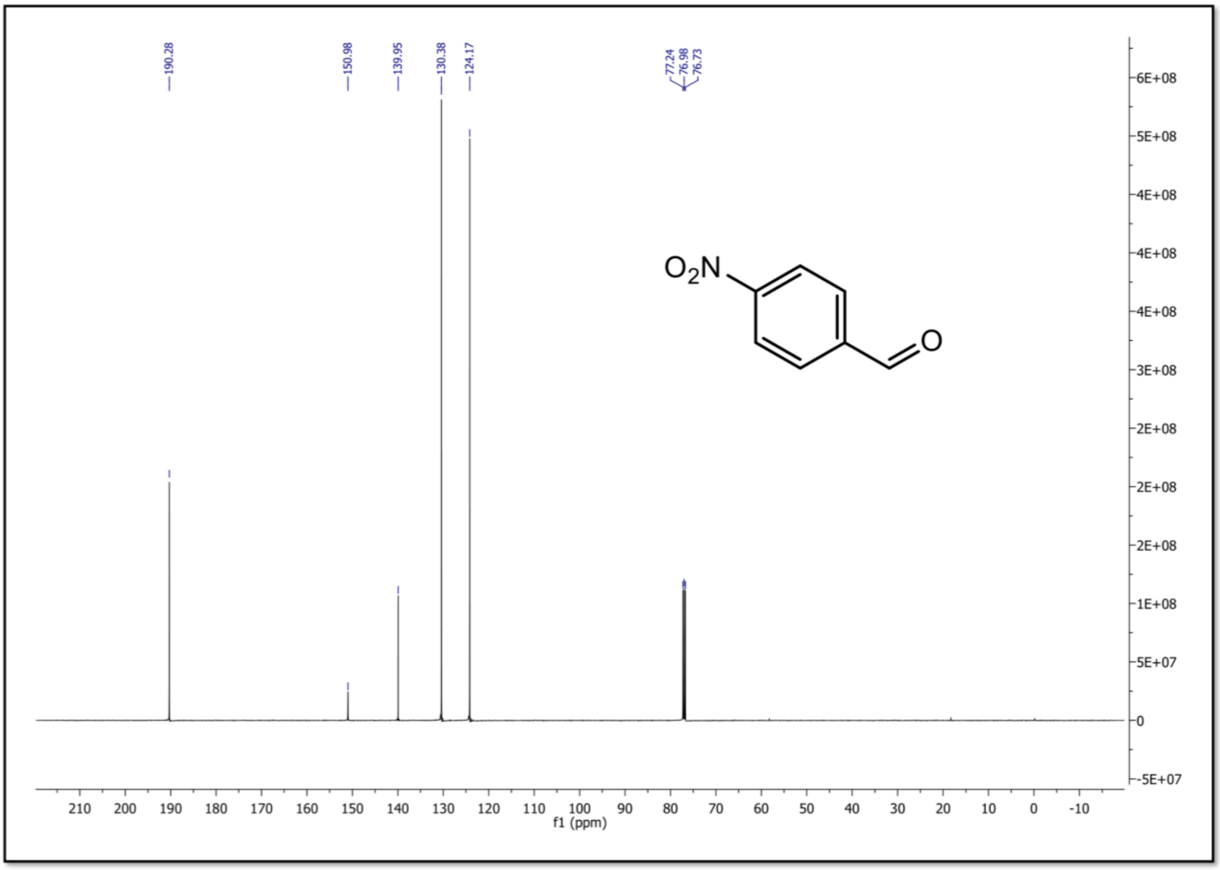


Fig. S7 ^{13}C NMR spectrum of 4-nitrobenzaldehyde.

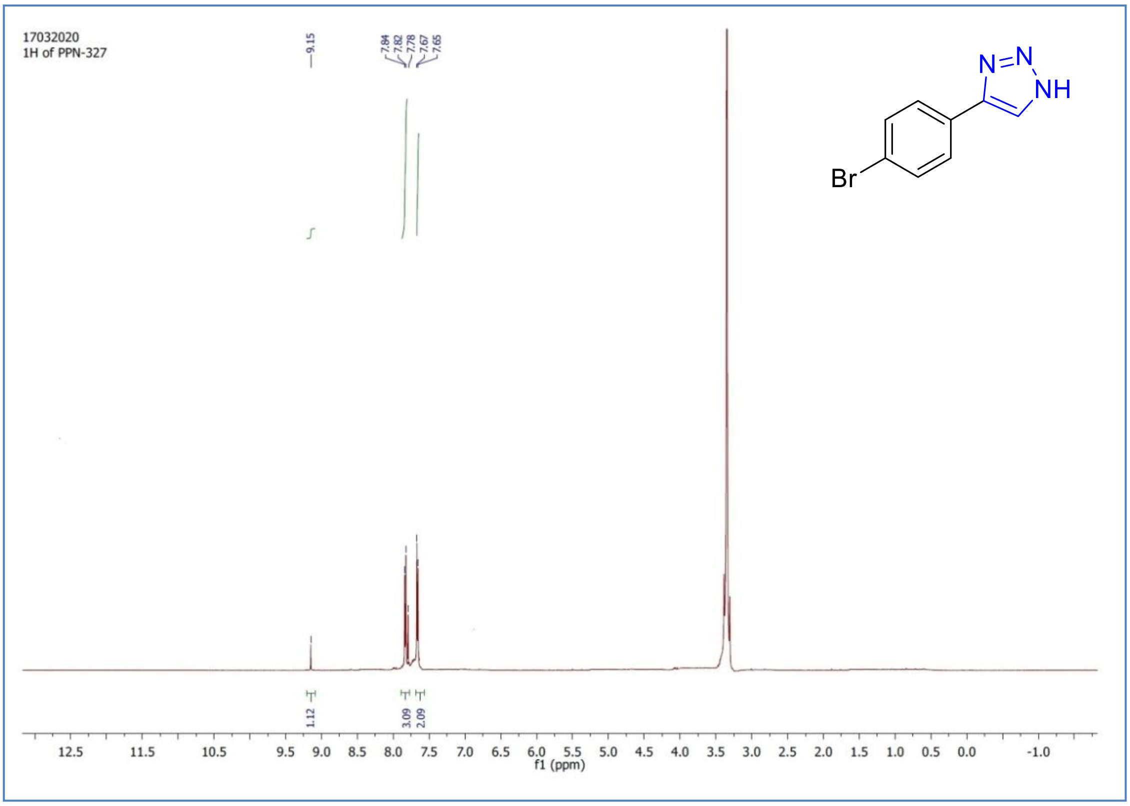


Fig. S8 ^{1}H NMR spectrum of 4-(4-bromophenyl)-1*H*-1,2,3-triazole

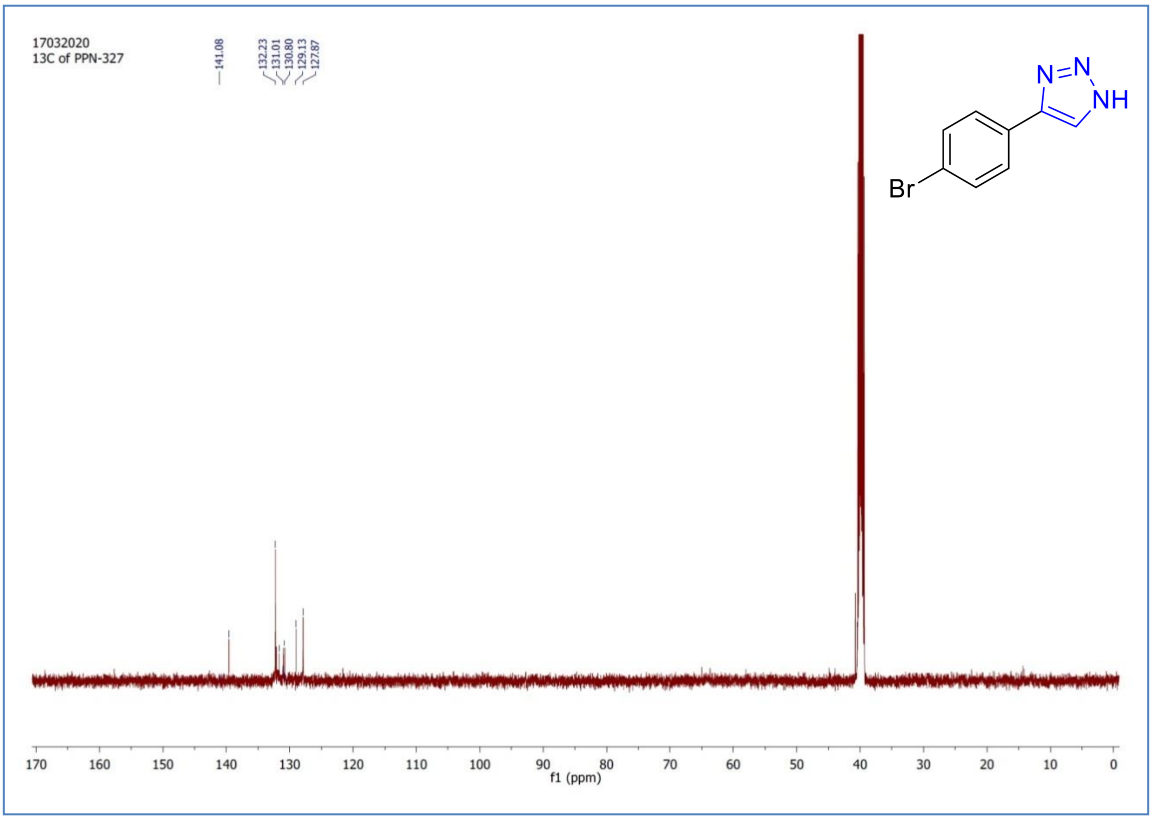


Fig. S9 ^{13}C NMR spectrum of 4-(4-bromophenyl)-1*H*-1,2,3-triazole

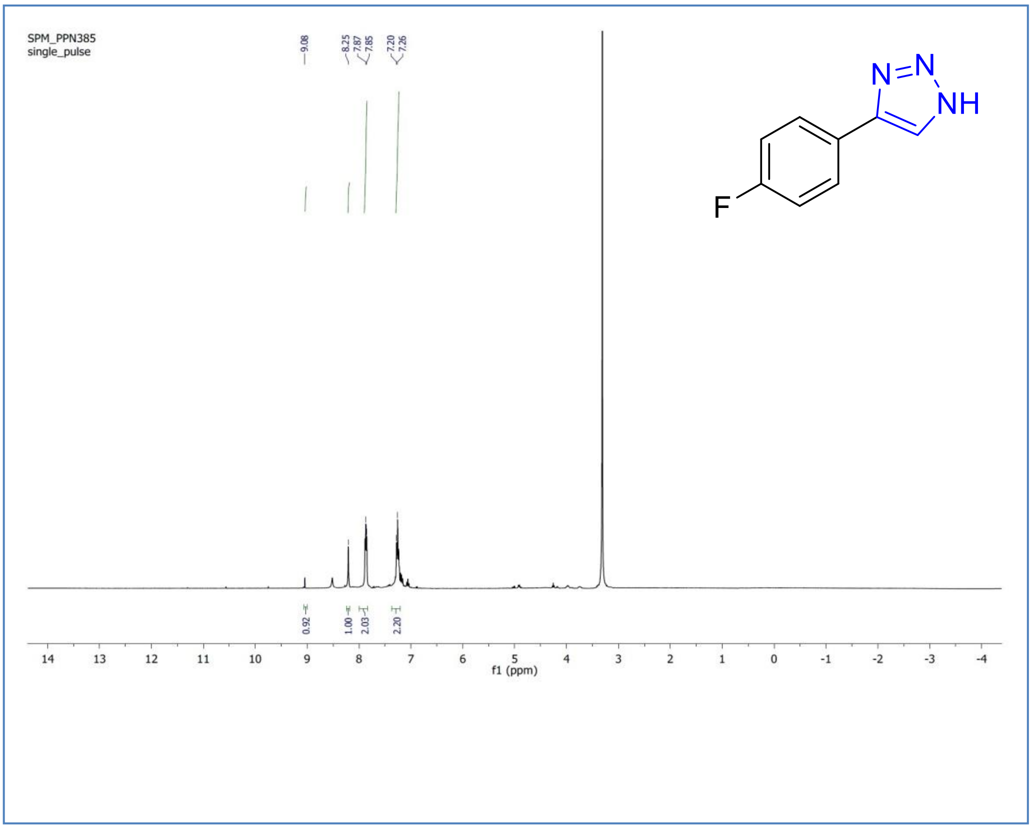


Fig. S10 ^{1}H NMR spectrum of 4-(4-fluorophenyl)-1*H*-1,2,3-triazole

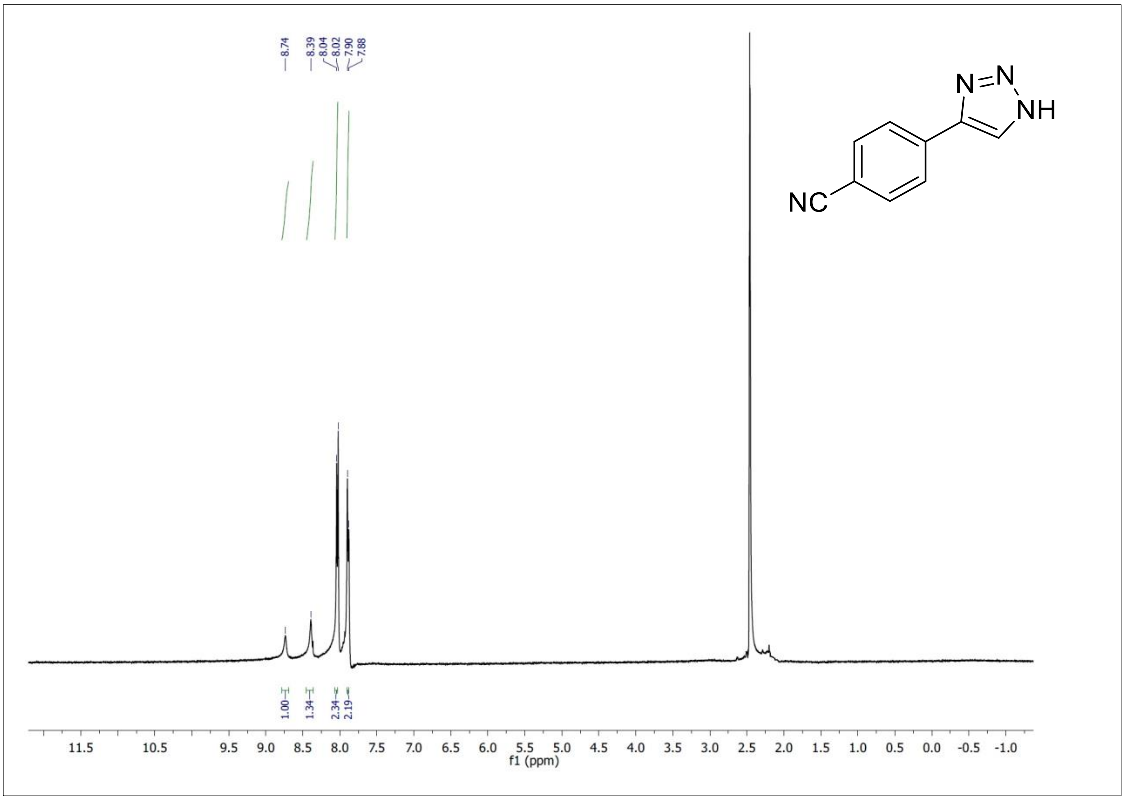


Fig. S11 ^{1}H NMR spectrum of 4-(1*H*-1,2,3-triazol-4-yl)benzonitrile

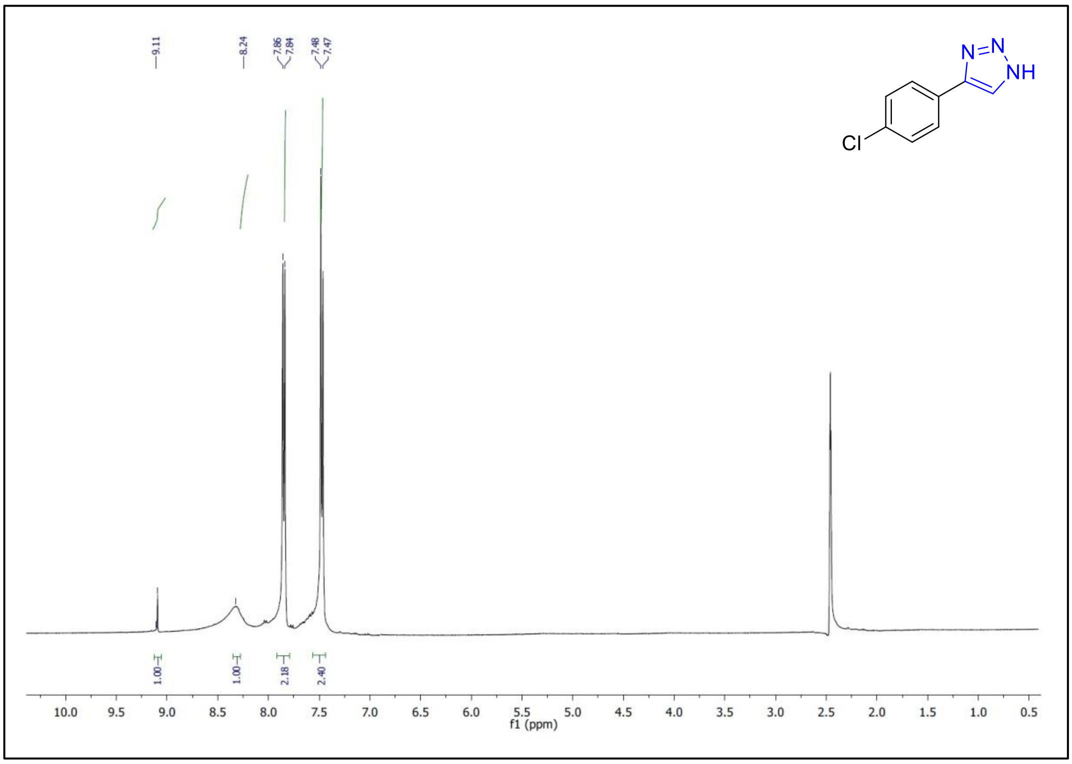


Fig. S12 ^{1}H NMR of (4-(4-chlorophenyl)-1*H*-1, 2, 3-triazole)

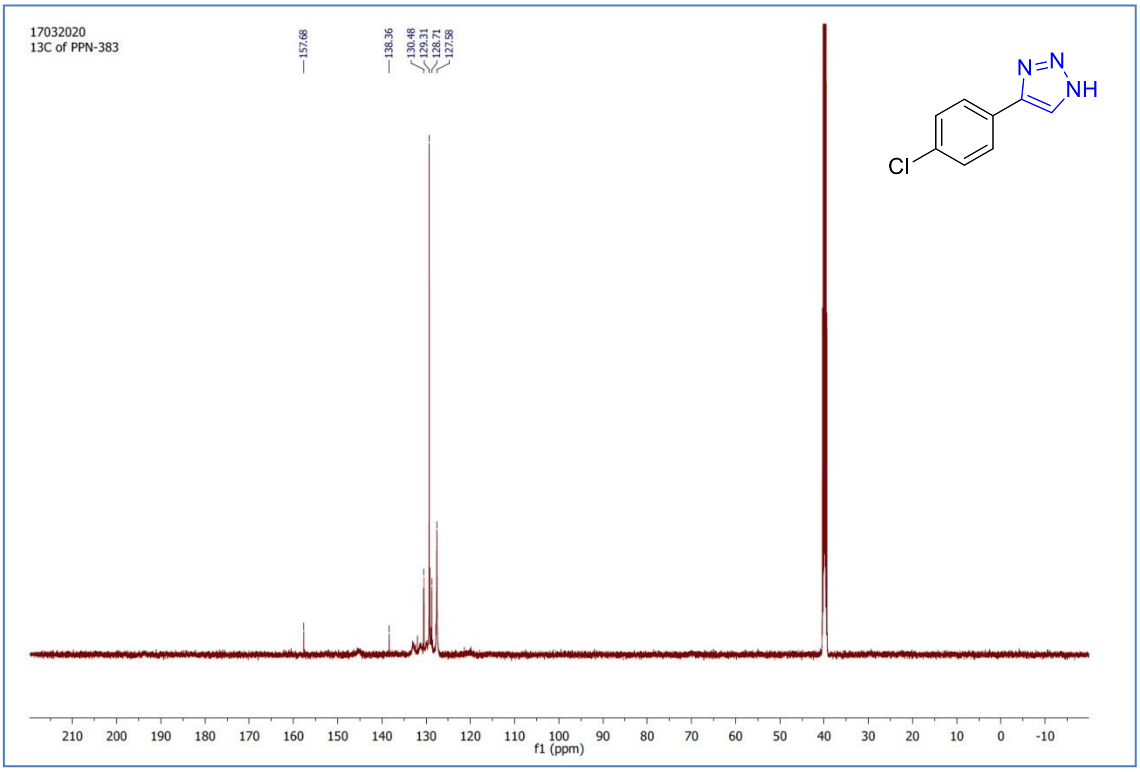


Fig. S13 ^{13}C NMR of (4-(4-chlorophenyl)-1*H*-1, 2, 3-triazole)

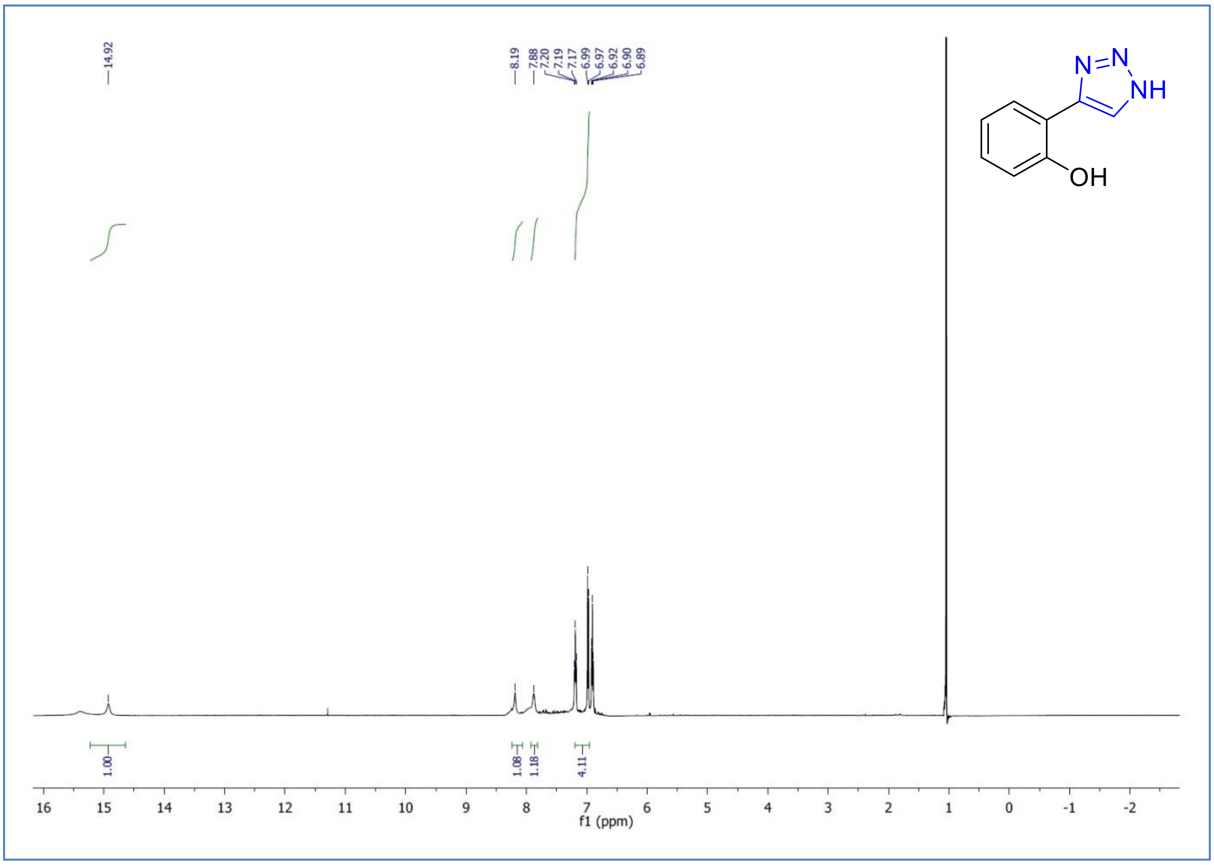


Fig. S14 ^{1}H NMR of 2-(1*H*-1,2,3-triazol-4-yl)phenol

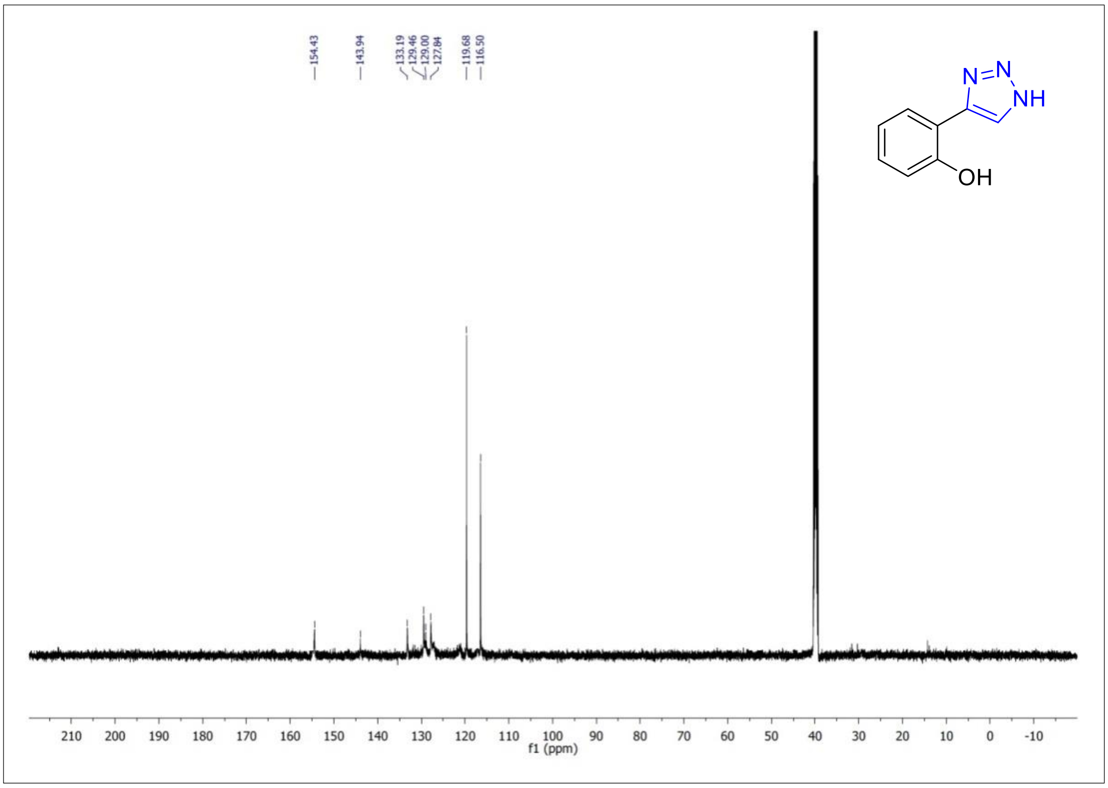


Fig. S15 ^{13}C NMR of 2-(1*H*-1,2,3-triazol-4-yl)phenol

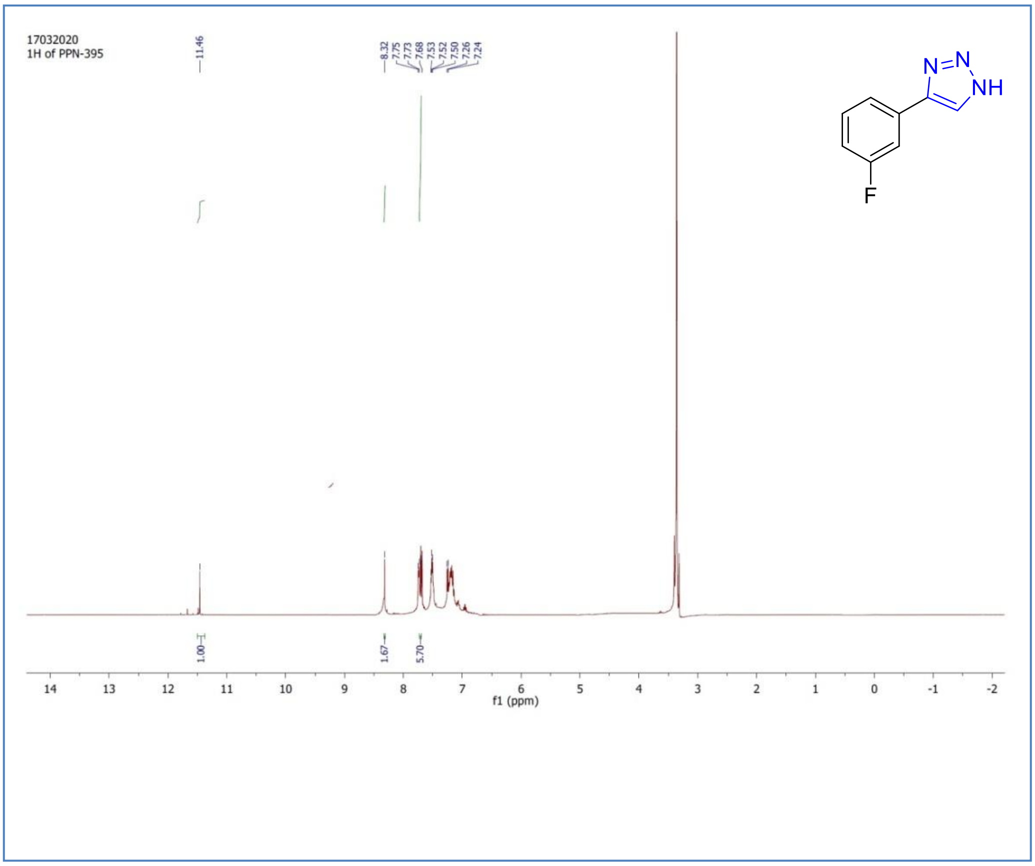


Fig. S16 ^{1}H NMR of 4-(3-fluorophenyl)-1*H*-1,2,3-triazole

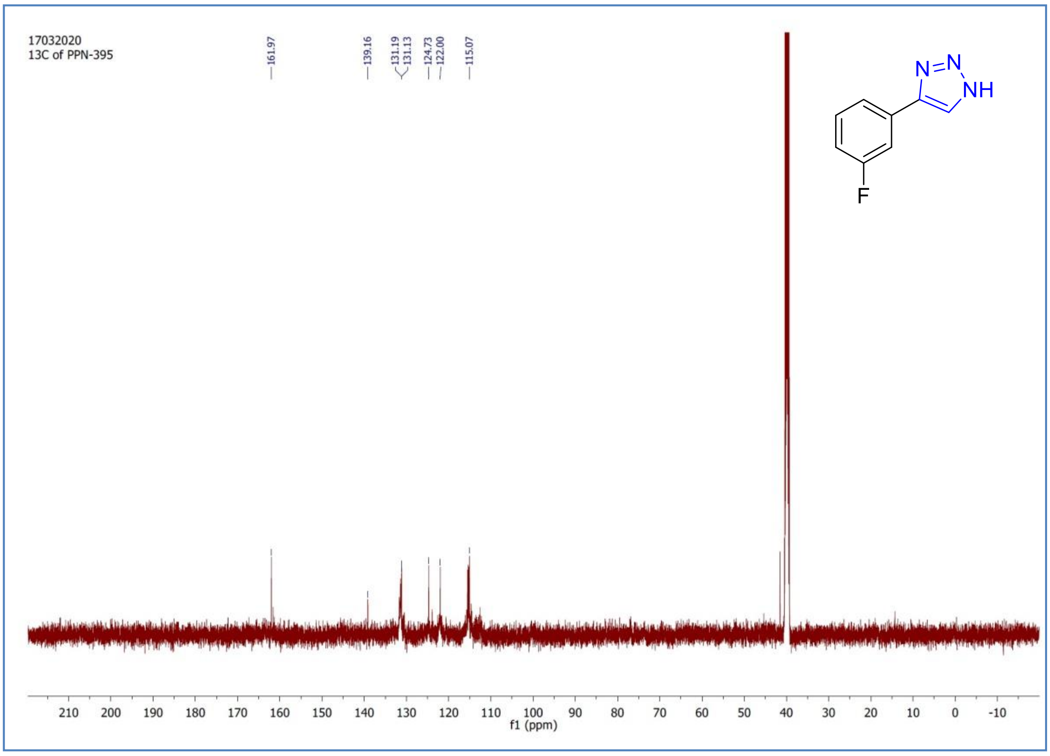


Fig. S17 ^{13}C NMR of 4-(3-fluorophenyl)-1*H*-1,2,3-triazole

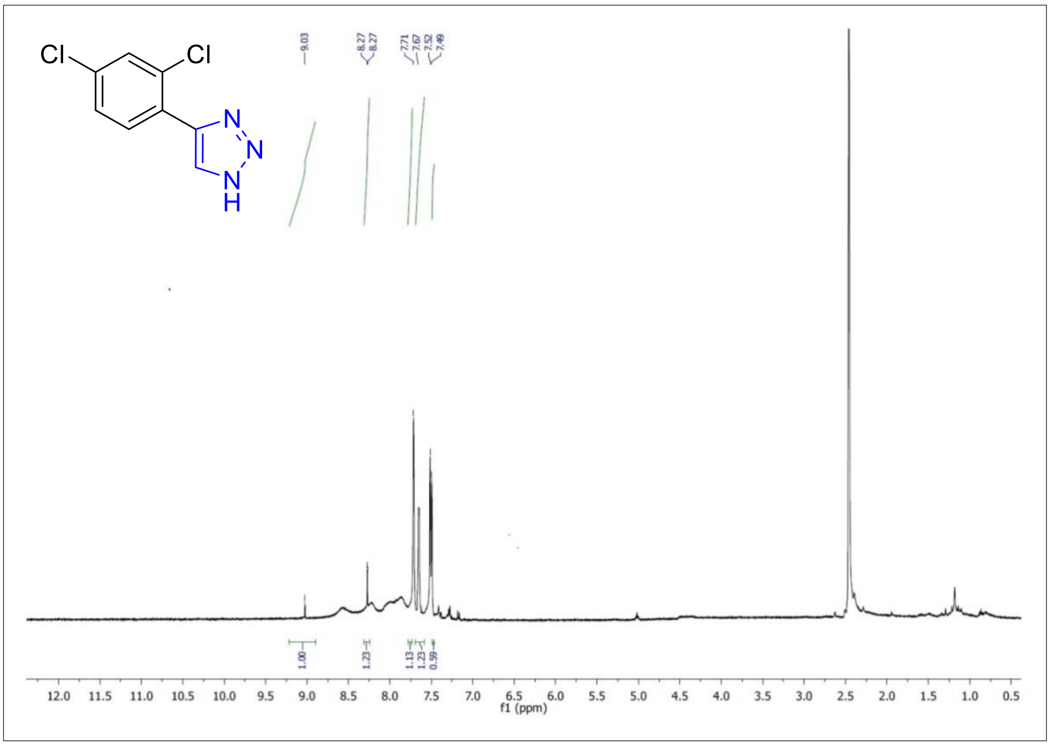


Fig. S18 ^{1}H NMR spectra of (4-(2,4-dichlorophenyl)-1*H*-1, 2, 3-triazole)

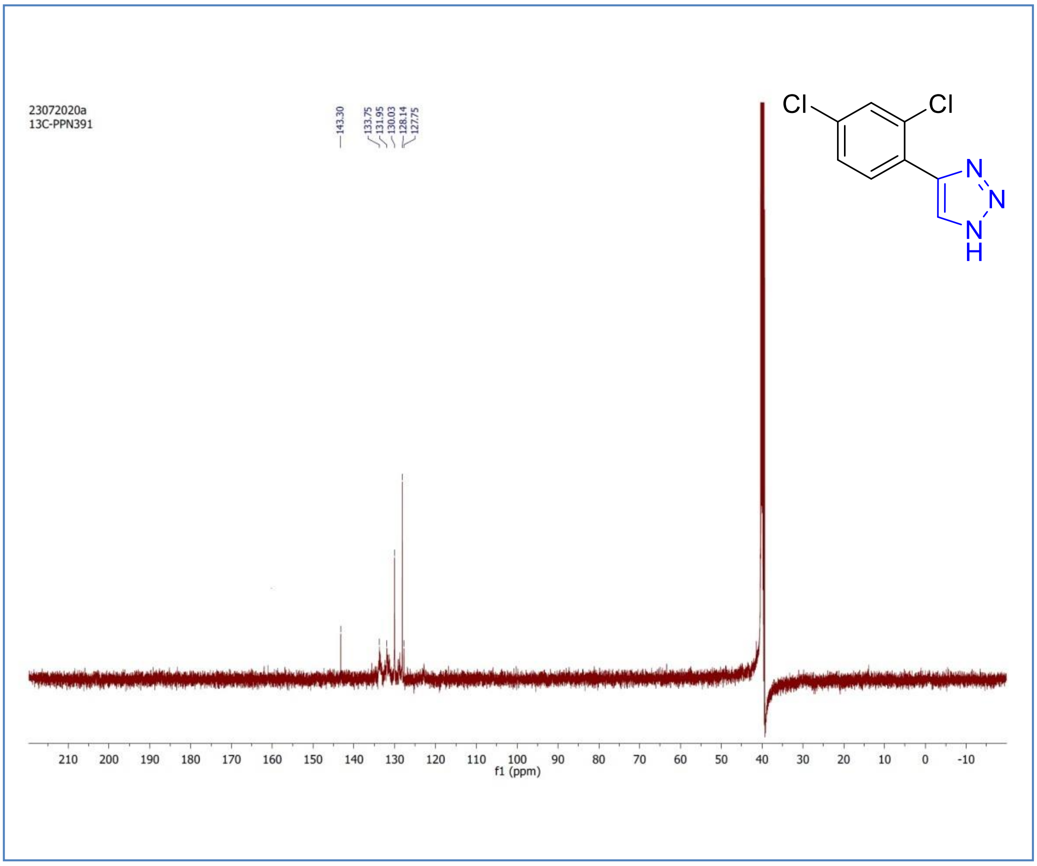


Fig. S19 ^{13}C NMR spectra of (4-(2,4-dichlorophenyl)-1*H*-1, 2, 3-triazole)

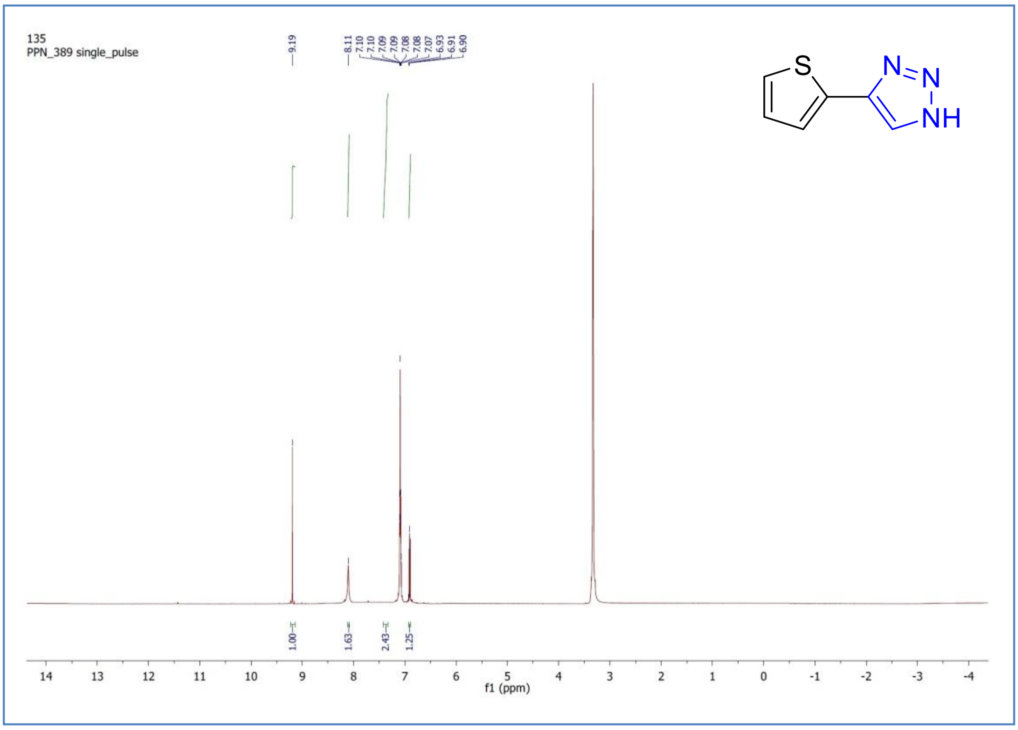


Fig. S20 ^{1}H NMR spectra of (4-(thiophen-2-yl)-1*H*-1,2,3-triazole

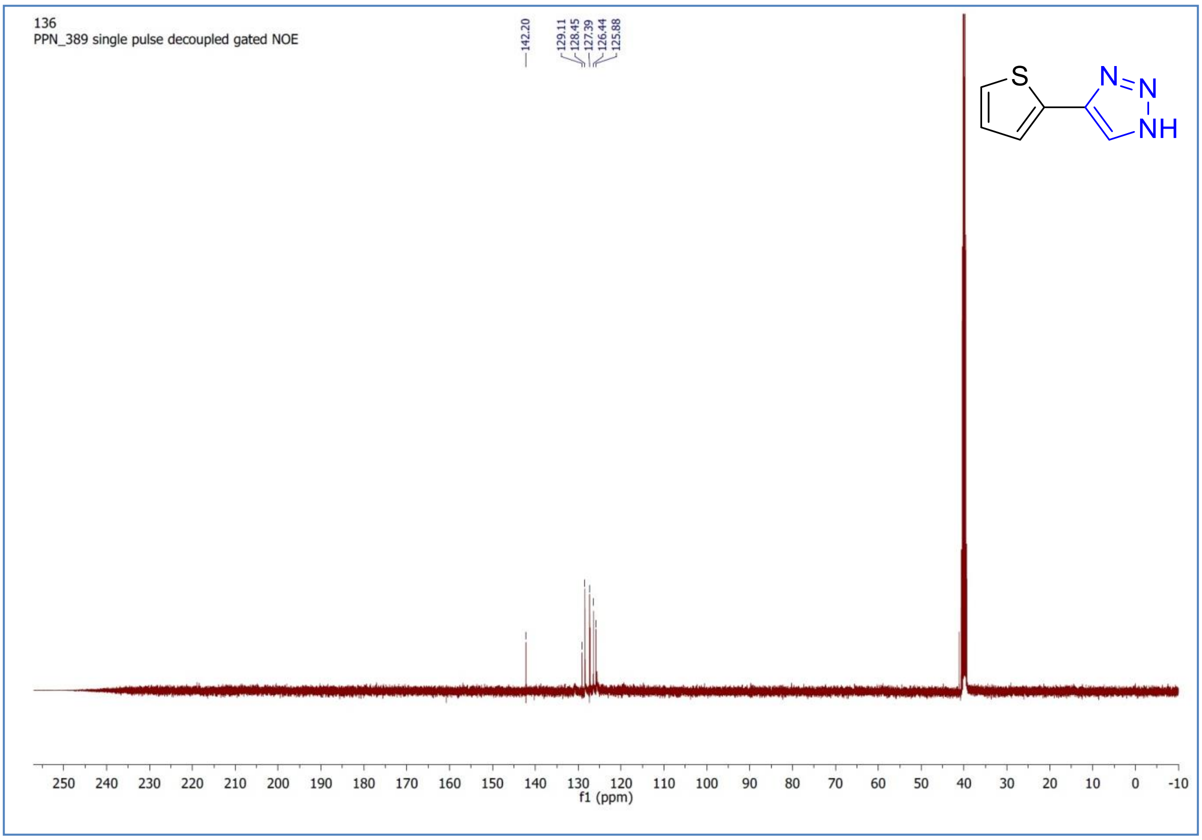


Fig. S21 ^{13}C NMR spectra of ***(***4-(thiophen-2-yl)-1*H*-1,2,3-triazole

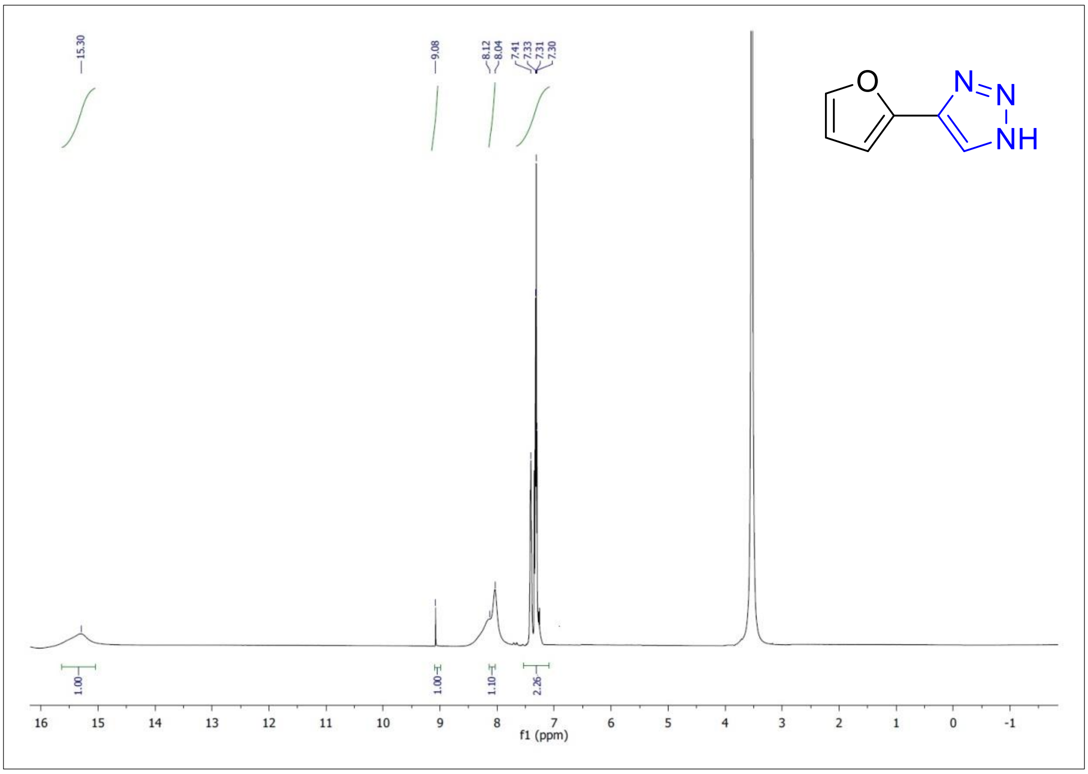


Fig. S22 ^{1}H NMR spectra of (4-(furan-2-yl)-1*H*-1,2,3-triazole)

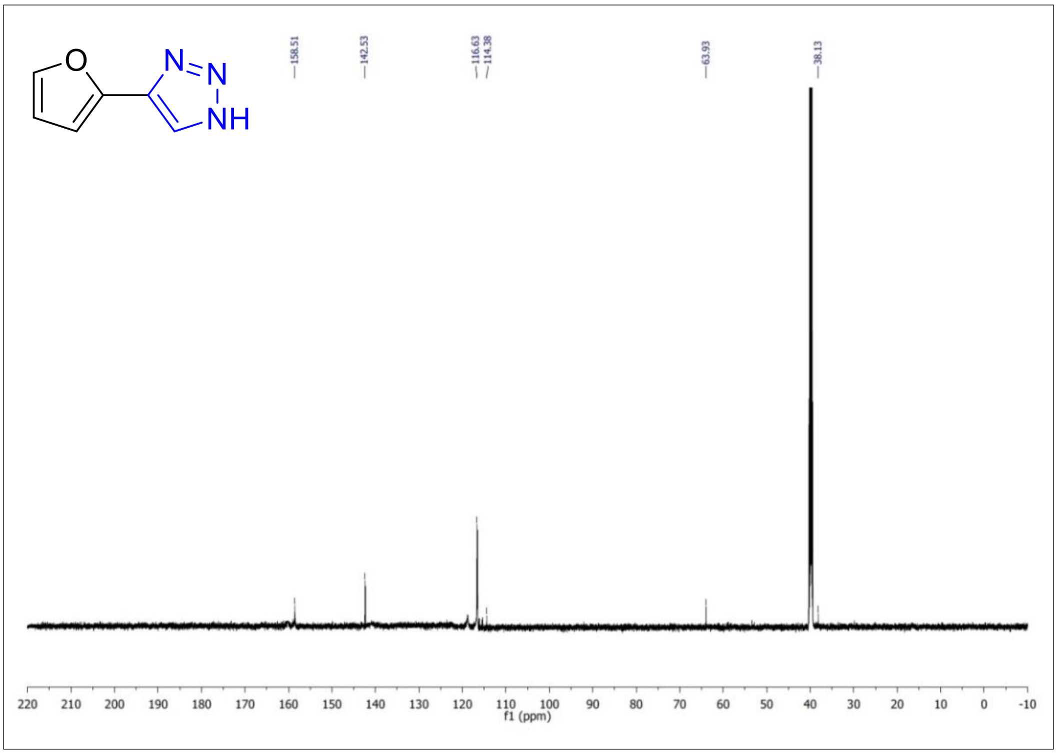


Fig. S23 ^{13}C NMR spectra of (4-(furan-2-yl)-1*H*-1, 2, 3-triazole)

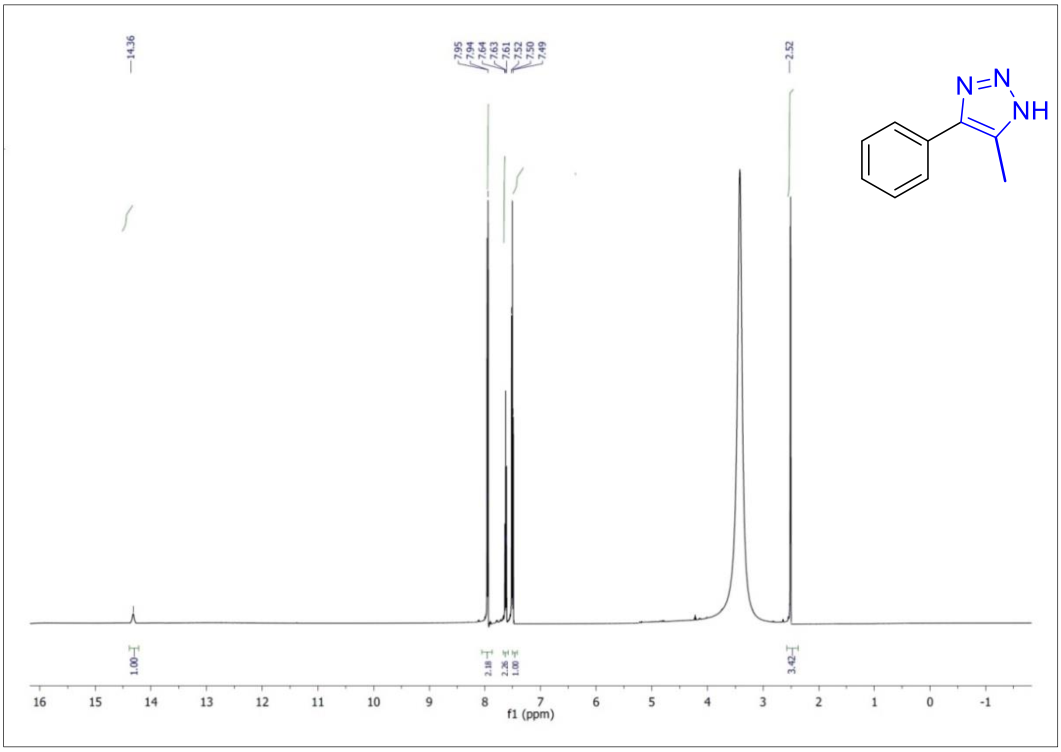


Fig. S24 ^{1}H NMR spectra of (5-methyl-4-phenyl-1*H*-1, 2, 3-triazole)

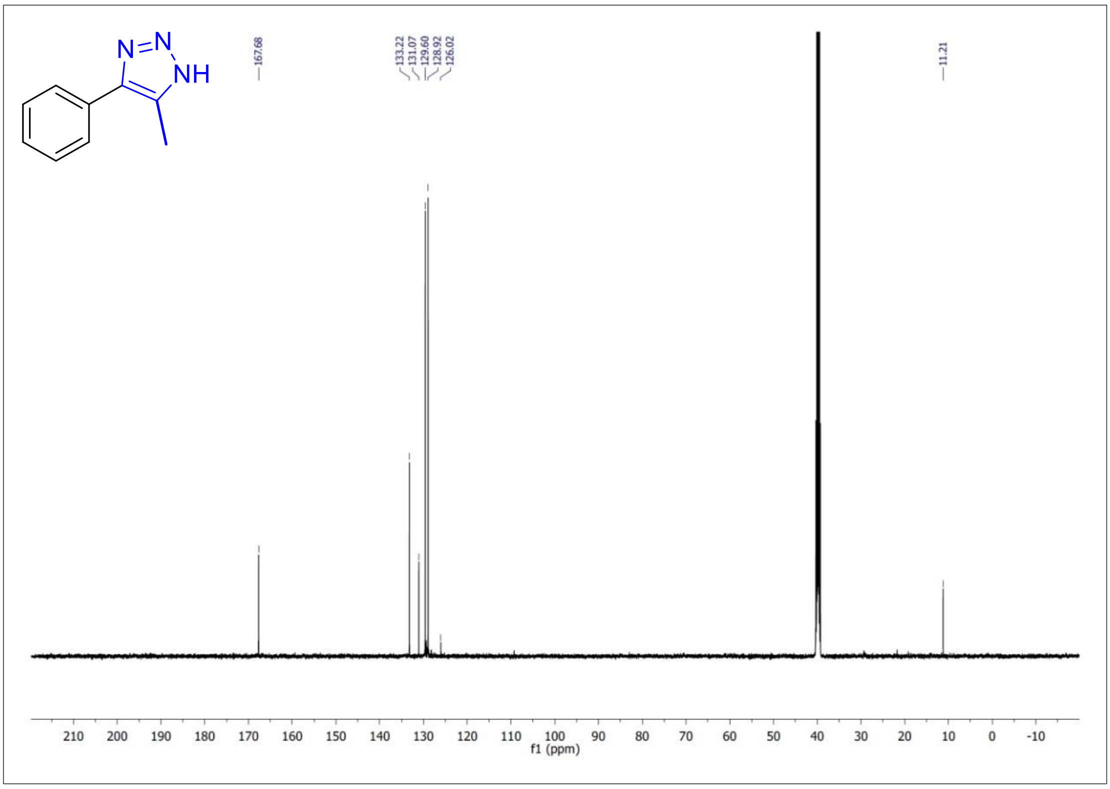


Fig. S25 ^{13}C NMR spectra of (5-methyl-4-phenyl-1*H*-1, 2, 3-triazole)