Supporting Information

Ferrocene Functionalized Schiff Base Containing Cu(II) Complex: Synthesis, Characterization and Parts-per-million Level Catalysis for azide alkyne cycloaddition

Firdaus Rahaman Gayen,[a,b] Abdul Aziz Ali,[a] Debashree Bora,[a,b] Saptarshi Roy,[a] Supriya Saha,[b,c] Lakshi Saikia,[a,b] Rajib Lochan Goswamee,[a,b] Biswajit Saha*[a,b]

[a]Advanced Materials Group, Materials Sciences and Technology Division, CSIR-North East Institute of Science and Technology, Jorhat, Assam – 785006, India

[b]Academy of Scientific and Innovative Research (AcSIR), CSIR-NEIST Campus, Jorhat, Assam – 785006, India

[c]Advanced Computation Data Sciences Division, CSIR-North East Institute of Science and Technology, Jorhat, Assam – 785006, India

Email: bsaha@neist.res.in, bischem@gmail.com

Table of Contents

1. Characterization of Schiff base ligand 1 and Cu(II)-complex 2

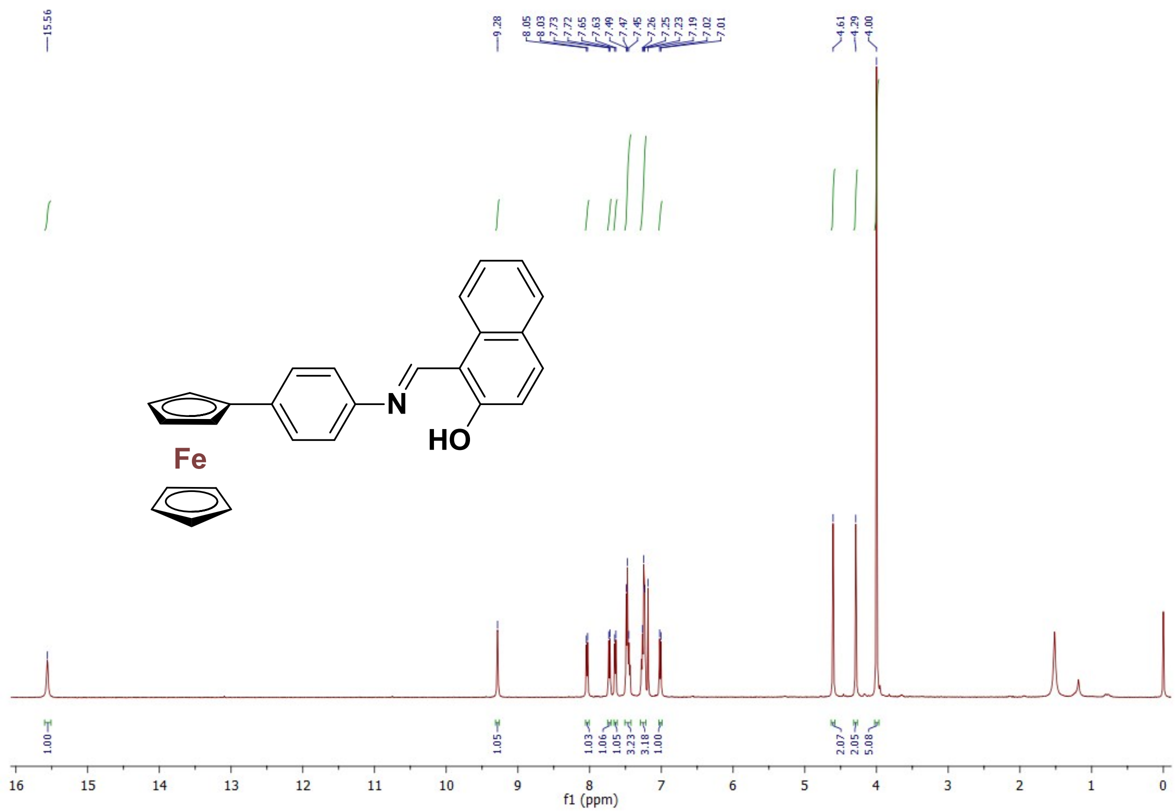


Figure S1 ^{1}H NMR spectrum of **1**.

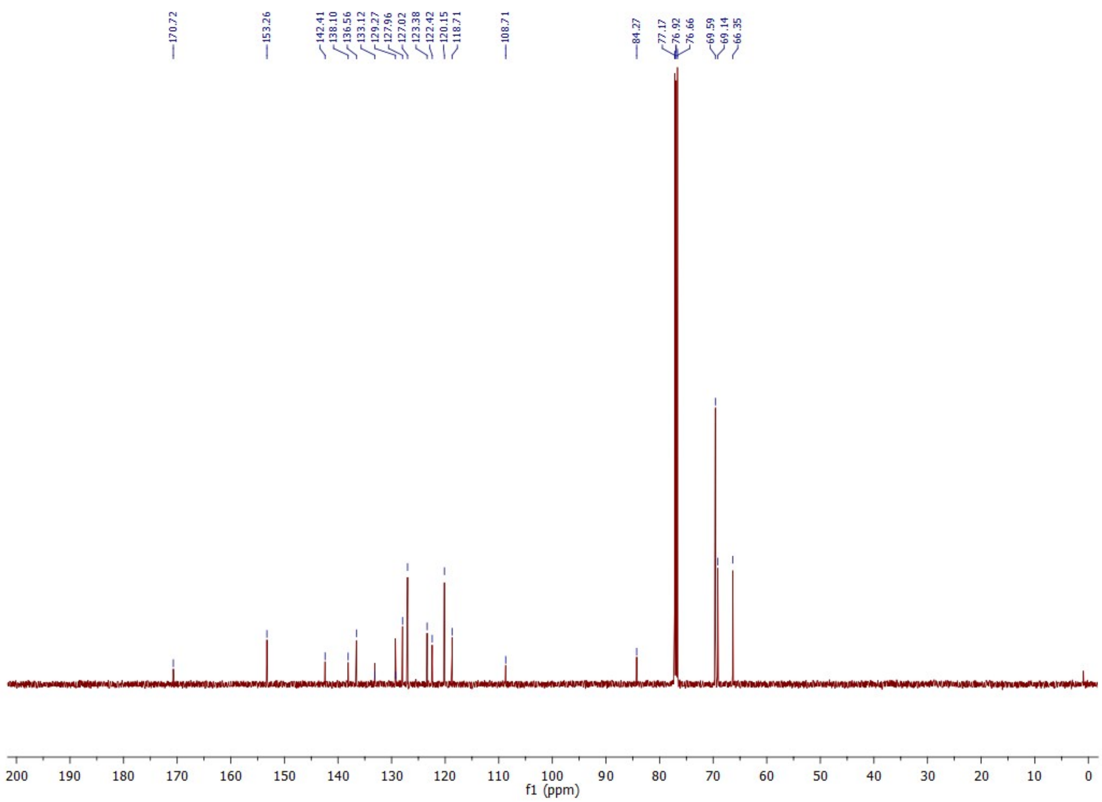


Figure S2 ^{13}C NMR Spectrum of **1**

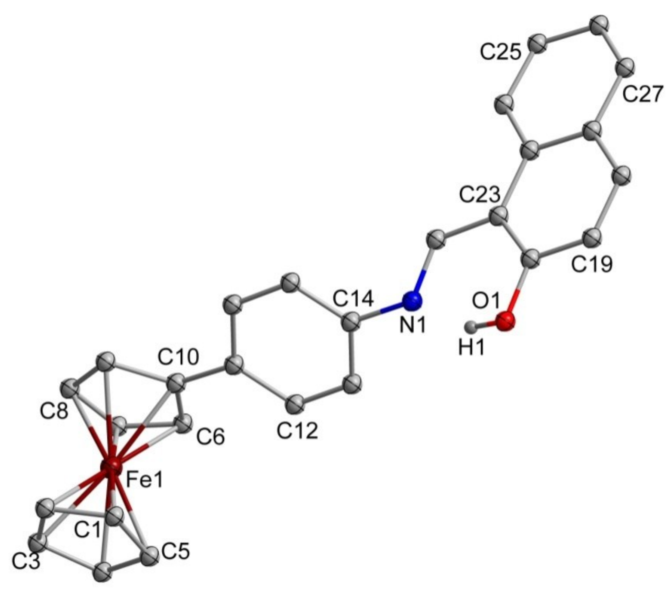


Figure S3 Molecular structure of **1** with important atoms labeled. Hydrogen atoms are omitted (except with oxygen) for clarity

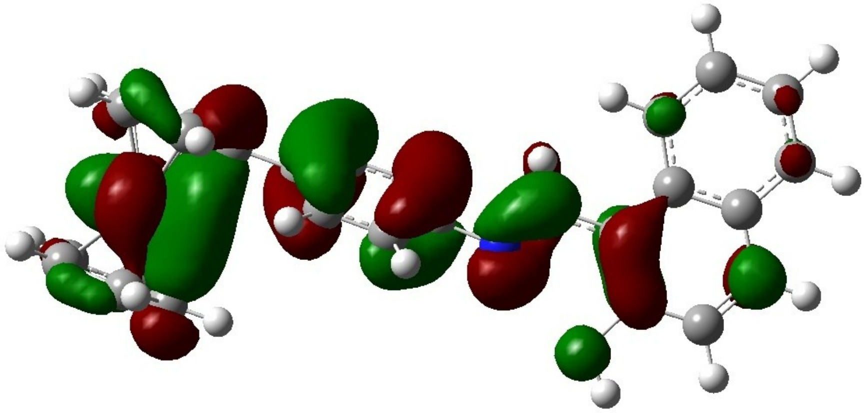


Figure S4 HOMO of **1**

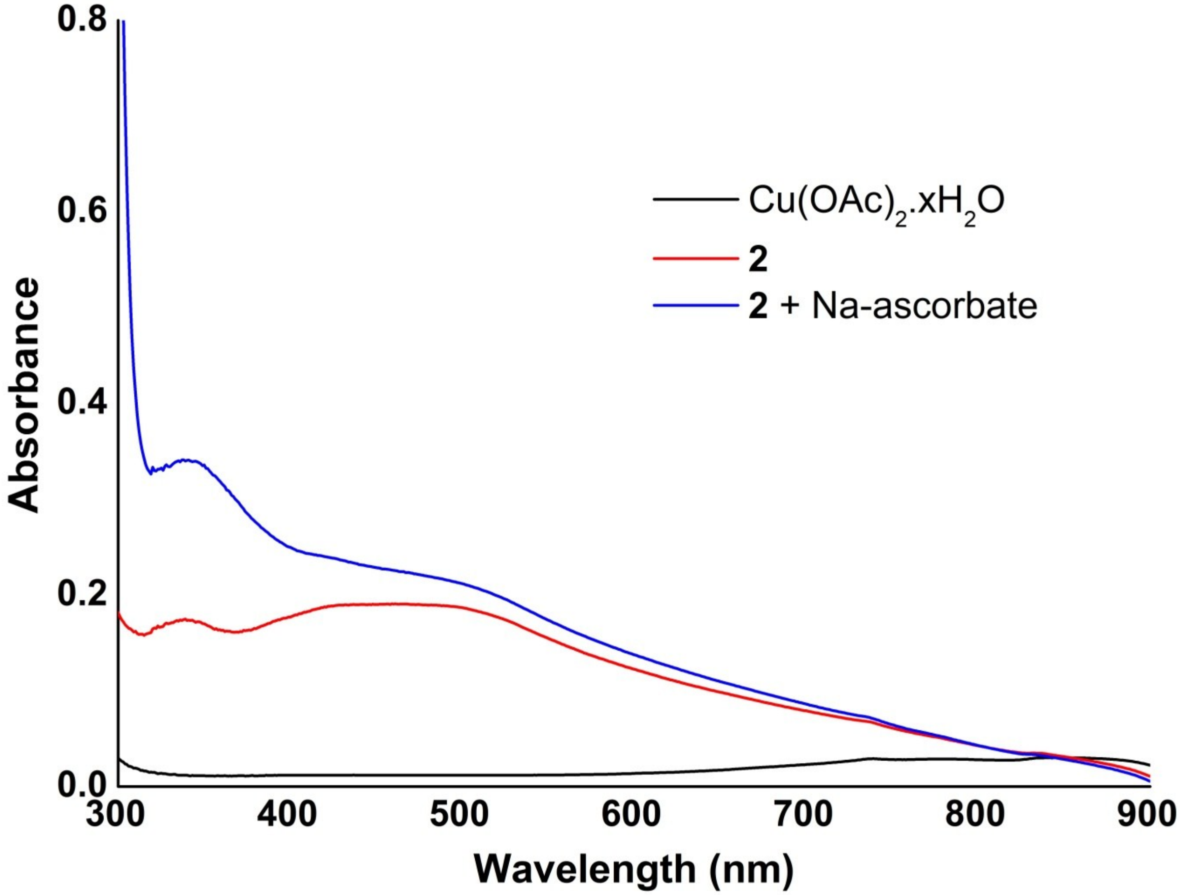


Figure S5 UV-Vis spectra in H_2O/EG

Table S1: Electrochemical parameters of the ferrocene based **1** and **2 (**1 mM each**)** on GCE electrode vs. Ag/AgCl in dichloromethane (100 m Vs^{-1} scan rate) at 30 °C.

Compound	E_{pa} (V)	E_{pc} (V)	E_p (V)	E° (V)
Ligand	0.48	0.38	0.10	0.43
Cu-complex	0.58	0.40	0.18	0.49

E_{pa}: anodic peak potential; E_{pc}: cathodic peak potential; ΔE_p: peak separation; E^o: standard electrode potential.

Table S2. Crystallographic Data and Pertinent Refinement Parameters for **1** and **2**.

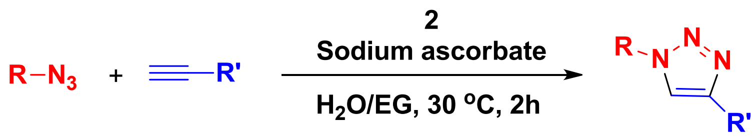
	1	**2**
Empirical formula	$C_{27}H_{21}FeNO$	$C_{54}H_{40}CuFe_2N_2O_2$
Formula Weight	431.30	924.12
Crystal System	Monoclinic	Monoclinic
Space Group	*P21/c*	*P21/n*
a (Å)	9.4133(6)	10.0021(4)
b (Å)	15.4886(9)	12.9594(5)
c (Å)	13.6365(8)	15.1607(5)
α (deg)	90	90
β (deg)	104.721(2)	94.3030(10)
γ (deg)	90	90
V (Å^3)	1922.9(2)	1959.61(13)
Z	4	2
ρ_{calcd} (g cm$^{-3)}$	1.490	1.566
μ (mm^{-1})	0.804	1.318
F(000)	896	950
Reflections		
Collected	31055	30913
Independent	4793	4859
Observed [I >2σ(I)]	4229	3537
No. of variables	275	277
GooF	1.080	1.073
R_{int}	0.0397	0.0515
Final R indices [I > 2σ(I)]^a	R1 = 0.0341 wR2 = 0.0875	R1 = 0.0433 wR2 = 0.1092
R indices (all data)^a	R1 = 0.0407 wR2 = 0.0922	R1 = 0.0684 wR2 = 0.1305

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ with $F_o^2 > 2\sigma(F_o^2)$. $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma|F_o^2|^2]^{1/2}$

Table S3. Comparison of bond distance and angle of **2**.

Bond Distance (Å)		
	Experimental (X-Ray)	Theoretical
Cu1-O1	1.8960(19)	1.91390
Cu1-O1	1.8961(19)	1.91388
Cu1-N1	1.999(2)	2.05114
Cu1-N1	1.999(2)	2.05107
Fe1-C27	2.032(4)	2.08042
Fe1-C18	2.035(3)	2.09812
Fe1-C19	2.037(3)	2.07709
Fe1-C22	2.040(3)	2.07663
Fe1-C26	2.040(3)	2.08087
Fe1-C20	2.043(3)	2.07746
Fe1-C23	2.047(3)	2.07879
Fe1-C24	2.048(3)	2.08040
Fe1-C21	2.050(3)	2.07735
Fe1-C25	2.054(3)	2.08067
Bond Angle (º)		
O1-Cu1-N1	89.41(8)	89.33245
O1-Cu1-N1	90.59(8)	90.66848
O1-Cu1-N1	90.59(8)	90.66501
O1-Cu1-N1	89.41(8)	89.33420
N1-Cu1-N1	180.0	179.90974
C27-Fe1-C18	152.34(15)	156.45484
C27-Fe1-C19	165.98(15)	161.83135
C18-Fe1-C19	41.08(11)	40.24901
C11-O1-Cu1	129.17(18)	132.01636
C1-N1-C12	113.8(2)	115.28388
C1-N1-Cu1	124.42(18)	123.53179
C12-N1-Cu1	121.68(16)	120.81506
O1-C11-C2	125.1(2)	124.53431

2. General procedure for Copper azide-alkyne cycloaddition reaction by 2



Preparation of stock solution of 2

In a 25 mL screw cap vial containing a magnetic stirrer bar, complex **2** (9.24 mg) was dissolved in 10 mL THF and stirred for 10 min at 30 °C. A dark orange stock solution of **2** was obtained for subsequent ppm level click reaction.

General procedure for azide-alkyne cycloaddition reaction by 2

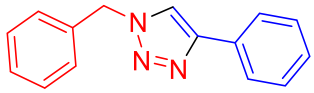
In a 25 mL round-bottomed flask equipped with a magnetic stirring bar, 46 μL (50 ppm) of stock solution of **2** was added and the THF was removed in vacuo. To this, 1 mmol of organic azide, 1.2 mmol of alkyne, 1.9 mg (1 mol%) of sodium ascorbate and 1 mL of EG/H_2O (1:1) were added. The reaction mixture was stirred for 2 h at 30 °C under air. After 2 h, the mixture was extracted using EtOAc (3x10mL). The organic layer was dried over Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified via silica gel column chromatography using a gradient mixture of n-hexanes and ethyl acetate to obtain the corresponding 1,2,3-triazoles.

Gram scale synthesis

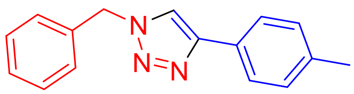
1-benzyl-4-phenyl-1*H*-1,2,3-triazole (**3a**): A 25 mL round bottom flask containing a magnetic stirring bar was charged with 46 μL of stock solution (5 ppm) of **2** was added and the THF was removed in vacuo. To this, benzyl azide (1.33 g, 10 mmol, 1 equiv.), phenylacetylene (1.22 g, 12 mmol, 1.2 equiv.), 1.9 mg (0.01 mmol) of sodium ascorbate and 10 mL of EG/H_2O (1:1) were added. The reaction mixture was stirred for 2 h at 30 °C under air and after completion, the mixture was extracted using EtOAc (3x30 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed in vacuo. The residue was purified on silica gel (hexanes/ethyl acetate) to furnish the 1-benzyl-4-phenyl-1*H*-1,2,3-triazole in 70% yield (1.64 g).

1,4-diphenyl-1*H*-1,2,3-triazole (**3j**): The triazole 3j was synthesized in 72% isolated yield (1.59 g) utilizing phenyl azide (1.19 g, 10 mmol, 1 equiv.), phenylacetylene (1.22 g, 12 mmol, 1.2 equiv.), 1.9 mg (0.01 mmol) of sodium ascorbate, 5 ppm of **2** and 10 mL of EG/H_2O (1:1) according to the procedure described for the gram scale synthesis of **3a**.

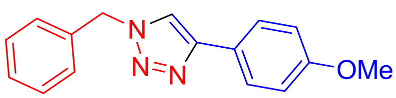
3. Characterization of 1,4-disubstituted 1,2,3-triazoles



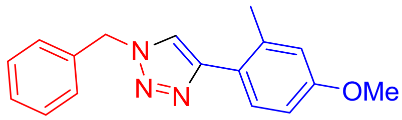
1-benzyl-4-phenyl-1*H*-1,2,3-triazole (**3a**): white solid; yield 92%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.7 Hz, 2H), 7.59 (s, 1H), 7.37 – 7.28 (m, 5H), 7.24 (d, *J* = 5.6 Hz, 3H), 5.51 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.1, 134.5, 130.4, 129.0, 128.7, 128.0, 125.5, 119.3, 54.1.



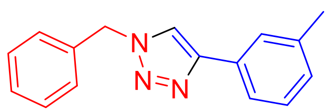
1-benzyl-4-(p-tolyl)-1*H*-1,2,3-triazole (**3b**): off white solid; yield 90%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.62 (s, 1H), 7.41 – 7.35 (m, 3H), 7.32 – 7.28 (m, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 5.56 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.2, 137.9, 134.6, 129.3, 129.0, 128.6, 127.9, 127.5, 125.4, 119.06, 54.0, 21.1.



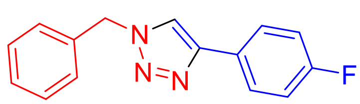
1-benzyl-4-(4-methoxyphenyl)-1*H*-1,2,3-triazole (**3c**): off white solid; yield 90%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.9 Hz, 2H), 7.50 (s, 1H), 7.30 (d, *J* = 7.6 Hz, 3H), 7.24 – 7.21 (m, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 5.48 (s, 2H), 3.74 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 147.9, 134.6, 129.0, 128.6, 127.9, 126.8, 123.1, 118.6, 114.0, 55.2, 54.0.



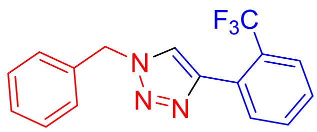
1-benzyl-4-(4-methoxy-2-methylphenyl)-1*H*-1,2,3-triazole (**3d**): off white solid; yield 90%;^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.1 Hz, 1H), 7.42 (s, 1H), 7.34 – 7.26 (m, 3H), 7.25 – 7.20 (m, 2H), 6.74 – 6.70 (m, 2H), 5.51 (s, 2H), 3.74 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 147.3, 136.9, 134.7, 130.0, 129.0, 128.5, 127.8, 122.5, 121.0, 116.0, 111.2, 55.1, 54.0, 21.4.



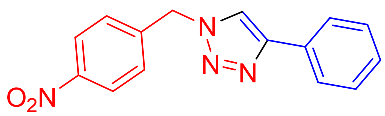
1-benzyl-4-(m-tolyl)-1*H*-1,2,3-triazole (**3e**): off white solid; yield 92%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 4.6 Hz, 2H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.34 – 7.28 (m, 3H), 7.25 – 7.18 (m, 3H), 7.06 (d, *J* = 8.1 Hz, 1H), 5.50 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.2, 138.4, 134.5, 130.2, 129.0, 128.8, 128.6, 127.9, 126.2, 122.6, 119.3, 54.1, 21.3.



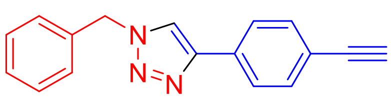
1-benzyl-4-(4-fluorophenyl)-1*H*-1,2,3-triazole (**3f**): off white solid; yield 90%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 8.8, 5.3 Hz, 2H), 7.55 (s, 1H), 7.30 (t, *J* = 6.5 Hz, 3H), 7.23 (d, *J* = 7.7 Hz, 2H), 7.01 (t, *J* = 8.7 Hz, 2H), 5.49 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.5, 161.5, 147.2, 134.4, 129.0 (d, J = 4.0 Hz), 128.7, 128.1, 127.8, 127.3 (d, J = 8.1 Hz), 126.6 (d, J = 3.1 Hz), 119.1, 115.7, 115.6, 54.1.



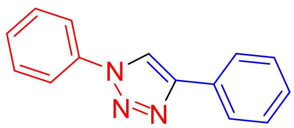
1-benzyl-4-(2-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (**3g**): off white solid; yield 95%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, J = 7.8 Hz, 2H), 7.66 (d, J = 7.9 Hz, 2H), 7.63 (s, 2H), 7.55 (t, J = 7.6 Hz, 2H), 7.40 (t, J = 7.7 Hz, 2H), 7.35 – 7.28 (m, 6H), 7.24 – 7.21 (m, 4H), 7.19 (s, 1H), 5.54 (s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.5, 134.4, 131.8, 131.5, 129.0, 128.6, 128.1, 127.7, 125.9, 122.8, 54.1.



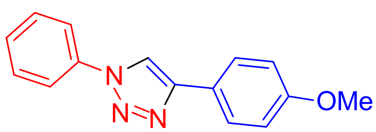
1-(4-nitrobenzyl)-4-phenyl-1H-1,2,3-triazole (**3h**): off white solid; yield 90%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, J = 8.6 Hz, 2H), 7.74 (d, J = 7.5 Hz, 2H), 7.69 (s, 1H), 7.36 (dd, J = 14.6, 8.0 Hz, 4H), 7.28 (t, J = 7.3 Hz, 1H), 5.63 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.6, 147.9, 141.6, 129.9, 128.8, 128.4, 125.6, 124.2, 119.5, 53.0.



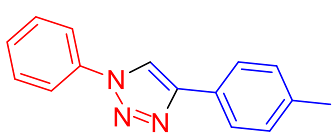
1-benzyl-4-(4-ethynylphenyl)-1H-1,2,3-triazole (**3i**): off white solid; yield 88%;^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 8.5 Hz, 2H), 7.67 (s, 1H), 7.52 (d, J = 8.5 Hz, 2H), 7.43 – 7.34 (m, 3H), 7.31 (dd, J = 7.6, 1.8 Hz, 2H), 5.58 (s, 2H), 3.11 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.3, 134.3, 132.4, 130.7, 129.1, 128.7, 128.0, 125.3, 121.6, 119.6, 83.3, 54.2.



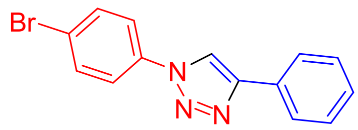
1,4-diphenyl-1*H*-1,2,3-triazole (**3j**): pale yellow solid; yield 94%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.85 (d, J = 7.5 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 7.49 (t, J = 7.9 Hz, 2H), 7.40 (dd, J = 10.3, 5.0 Hz, 3H), 7.31 (t, J = 7.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.3, 136.9, 130.1, 129.6, 128.7, 128.3, 125.7, 120.4, 117.5.



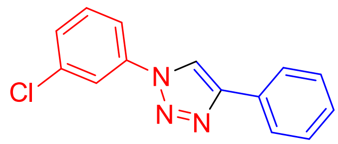
4-(4-methoxyphenyl)-1-phenyl-1*H*-1,2,3-triazole (**3k**): pale yellow solid; yield 90%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.73 (q, J = 4.9 Hz, 2H), 7.70 – 7.64 (m, 2H), 7.44 (s, 2H), 7.34 (d, J = 8.1 Hz, 1H), 6.88 (d, J = 8.8 Hz, 2H), 3.74 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6, 148.1, 136.9, 129.6, 128.5, 127.0, 122.8, 120.3, 116.7, 114.2, 55.2.



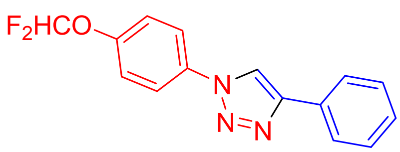
1-phenyl-4-(p-tolyl)-1*H*-1,2,3-triazole (**3l**): off white solid; yield 90%;^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.75 – 7.64 (m, 4H), 7.43 (dd, J = 11.2, 4.5 Hz, 2H), 7.38 – 7.29 (m, 1H), 7.17 (d, J = 7.9 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.3, 138.2, 136.9, 129.5, 128.5, 127.2, 125.6, 120.3, 117.1, 21.2.



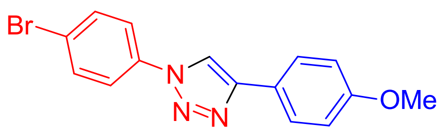
1-(4-bromophenyl)-4-phenyl-1*H*-1,2,3-triazole (**3m**): off white solid; yield 90%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 2H), 7.84 (dd, *J* = 8.3, 1.3 Hz, 4H), 7.65 – 7.60 (m, 8H), 7.40 (t, *J* = 7.6 Hz, 4H), 7.34 – 7.29 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5, 132.8, 128.8, 128.5, 125.7, 121.7, 117.2.



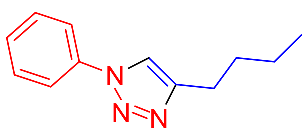
1-(3-chlorophenyl)-4-phenyl-1*H*-1,2,3-triazole (**3n**): pale yellow solid; yield 91%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 2H), 7.84 (d, *J* = 8.2 Hz, 4H), 7.78 (s, 2H), 7.64 (d, *J* = 9.0 Hz, 2H), 7.45 – 7.29 (m, 10H), 7.19 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.5, 137.7, 135.5, 130.7, 129.8, 128.8, 128.5, 125.7, 120.6, 118.3, 117.3.



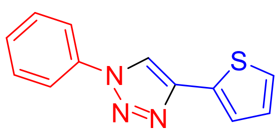
1-(4-(difluoromethoxy)phenyl)-4-phenyl-1*H*-1,2,3-triazole (**3o**): off white solid; yield 94%;^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.84 (d, *J* = 7.3 Hz, 2H), 7.74 (d, *J* = 8.9 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.24 (d, *J* = 8.6 Hz, 2H), 6.52 (t, *J* = 73.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.7, 148.5, 134.2, 129.9, 128.8, 128.4, 125.7, 121.9, 120.8, 117.5, 115.3, 113.3.



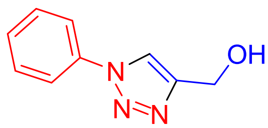
1-(4-bromophenyl)-4-(4-methoxyphenyl)-1*H*-1,2,3-triazole (**3p**): pale yellow solid; yield 88%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.76 (d, *J* = 6.9 Hz, 2H), 7.62 (s, 4H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8, 132.8, 127.1, 121.7, 114.2, 55.2.



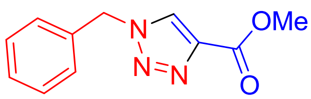
4-butyl-1-phenyl-1*H*-1,2,3-triazole (**3q**): pale yellow solid; yield 75%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (s, 3H), 7.44 (dd, *J* = 8.5, 7.2 Hz, 2H), 7.35 (dt, *J* = 9.2, 4.3 Hz, 1H), 2.77 – 2.70 (m, 2H), 1.69 – 1.61 (m, 4H), 1.36 (dq, *J* = 14.7, 7.4 Hz, 2H), 1.17 (d, *J* = 10.6 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.0, 137.1, 129.5, 128.3, 120.3, 118.6, 31.3, 25.2, 22.2, 13.7.



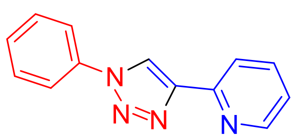
1-phenyl-4-(thiophen-2-yl)-1*H*-1,2,3-triazole (**3r**): off white solid; yield 92%;^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.74 – 7.68 (m, 3H), 7.51 – 7.43 (m, 3H), 7.41 – 7.33 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.4, 136.9, 131.3, 129.6, 128.6, 126.4, 125.7, 121.4, 120.4, 117.2.



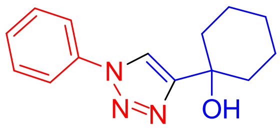
(1-phenyl-1*H*-1,2,3-triazol-4-yl)methanol (**3s**): off white solid; yield 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.74 – 7.67 (m, 2H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.48 – 7.39 (m, 1H), 4.88 (s, 2H), 2.63 (br, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.1, 136.8, 129.6, 129.5, 128.7, 124.5, 120.5, 119.9, 56.4.



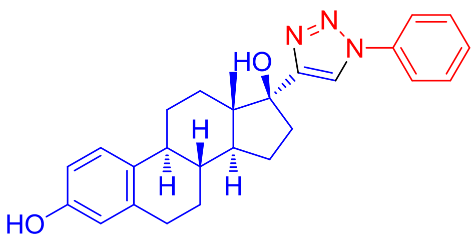
methyl 1-benzyl-1*H*-1,2,3-triazole-4-carboxylate (**3t**): off white solid; yield 90%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.31 (d, *J* = 5.0 Hz, 3H), 7.21 (d, *J* = 8.7 Hz, 2H), 5.50 (s, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.5, 140.5, 133.6, 128.1, 127.2, 61.2, 54.3, 14.1.



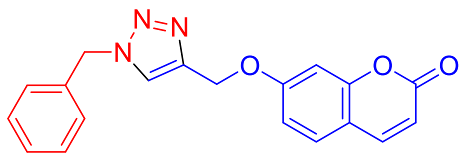
2-(1-phenyl-1*H*-1,2,3-triazol-4-yl)pyridine (**4a**): pale yellow solid; yield 88%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 – 8.54 (m, 2H), 8.25 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 3H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.50 – 7.38 (m, 1H), 7.32 – 7.20 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.7, 149.3, 148.7, 136.9, 129.7, 128.7, 123.0, 120.3, 119.9.



1-(1-phenyl-1*H*-1,2,3-triazol-4-yl)cyclohexanol (**4b**): pale yellow solid; yield 84%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.66 (dd, *J* = 8.6, 1.2 Hz, 2H), 7.44 (dd, *J* = 8.5, 7.1 Hz, 2H), 7.37 (dt, *J* = 9.2, 4.3 Hz, 1H), 2.40 (s, 1H), 2.05 – 1.95 (m, 2H), 1.87 (dd, *J* = 9.1, 4.3 Hz, 2H), 1.71 (tdd, *J* = 14.7, 7.3, 3.6 Hz, 2H), 1.63 – 1.48 (m, 3H), 1.34 (ddt, *J* = 14.0, 10.5, 5.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.1, 137.0, 129.6, 128.5, 120.4, 117.8, 69.6, 37.9, 25.2, 21.8.



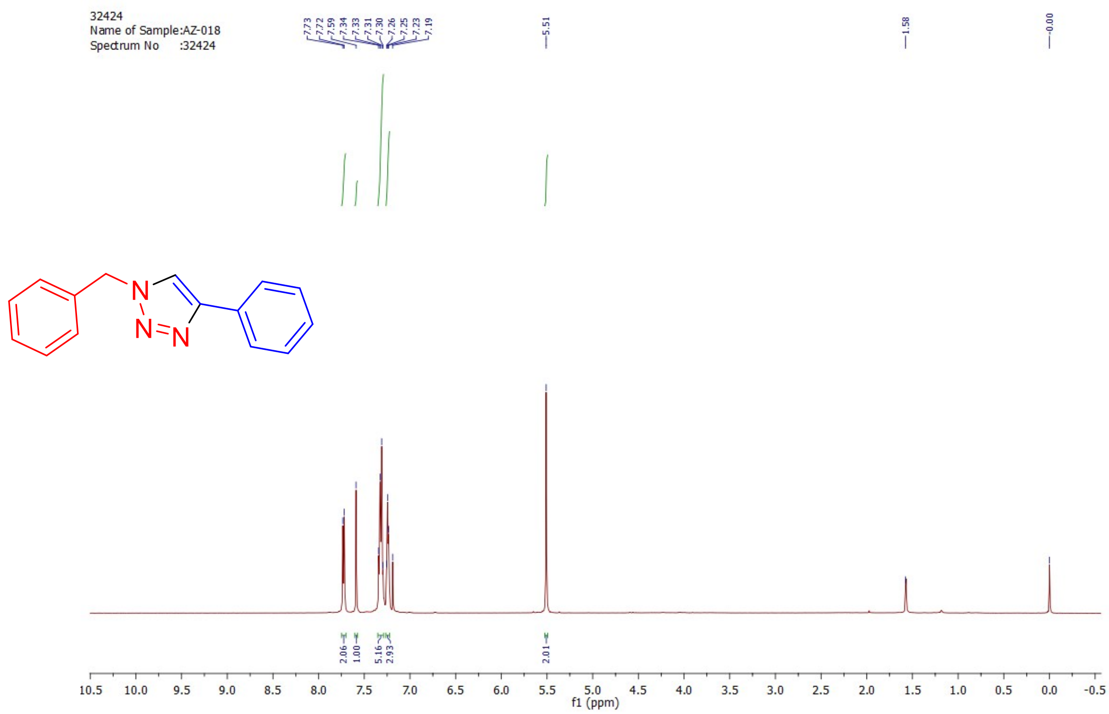
(8R,9S,13S,14S,17S)-13-methyl-17-(1-phenyl-1*H*-1,2,3-triazol-4-yl)7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene-3,17-diol (**4c**): pale yellow gummy; yield 50%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.72 – 7.69 (m, 2H), 7.47 – 7.43 (m, 3H), 7.38 (d, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.5 Hz, 1H), 6.52 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.48 (d, *J* = 2.6 Hz, 1H), 5.23 (s, 1H), 2.79 – 2.66 (m, 4H), 2.48 – 2.38 (m, 1H), 2.13 – 2.05 (m, 3H), 1.98 (s, 1H), 1.33 (s, 1H), 1.19 (d, *J* = 3.1 Hz, 4H), 1.01 (s, 3H), 0.80 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.2, 153.2, 138.1, 132.4, 129.6, 128.5, 127.9, 126.3, 120.3, 119.2, 115.1, 112.5, 82.4, 53.3, 48.3, 47.2, 43.1, 39.3, 37.9, 32.8, 29.5, 27.1, 26.1, 23.3, 14.1, 0.90; HRMS (ESI-TOF-Q) calcd for $C_{26}H_{29}N_3O_2$: 415.2260,found: 416.2411 $[M+H]^+$.

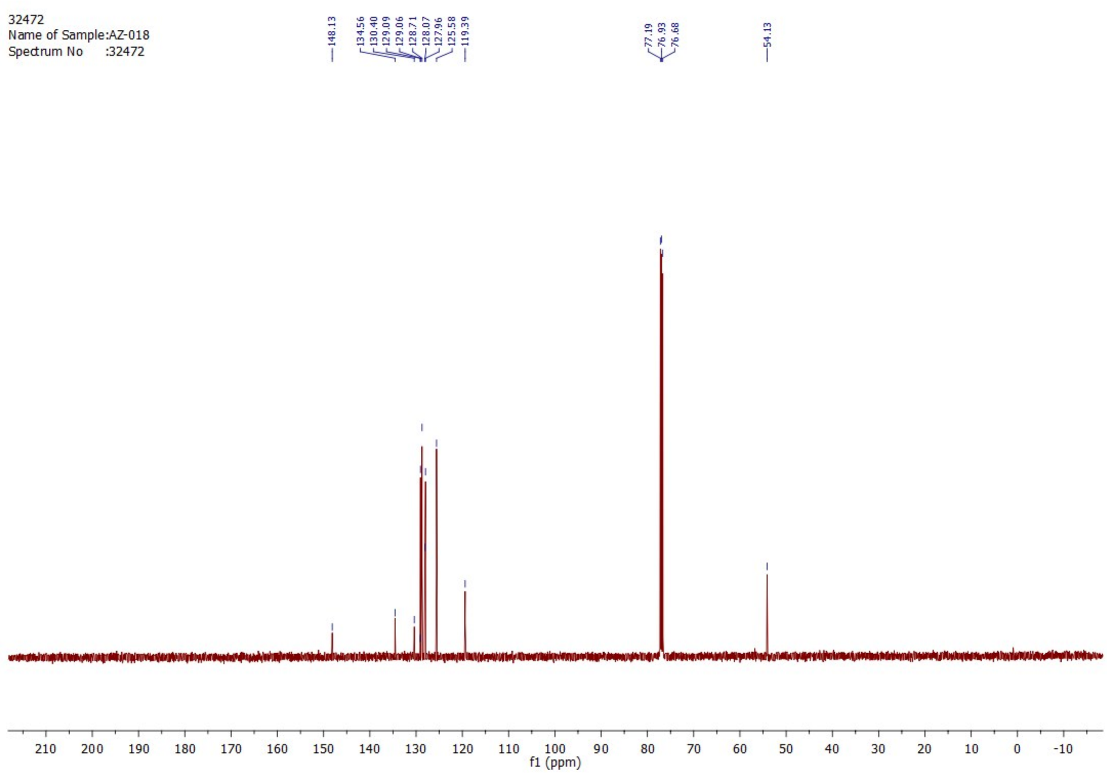


7-((1-benzyl-1*H*-1,2,3-triazol-4-yl)methoxy)-2H-chromen-2-one (**4d**): White solid; yield 60%;[1]H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 9.5 Hz, 1H), 7.58 (s, 1H), 7.42 – 7.33 (m, 4H), 7.28 (dd, *J* = 9.9, 4.1 Hz, 2H), 6.90 (dd, *J* = 11.1, 2.3 Hz, 2H), 6.25 (d, *J* = 9.5 Hz, 1H), 5.55 (s, 2H), 5.22 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.1, 160.9, 155.5, 143.2, 134.1, 129.0, 128.8, 128.0, 122.8, 113.3, 112.8, 112.6, 101.9, 62.2, 54.2.

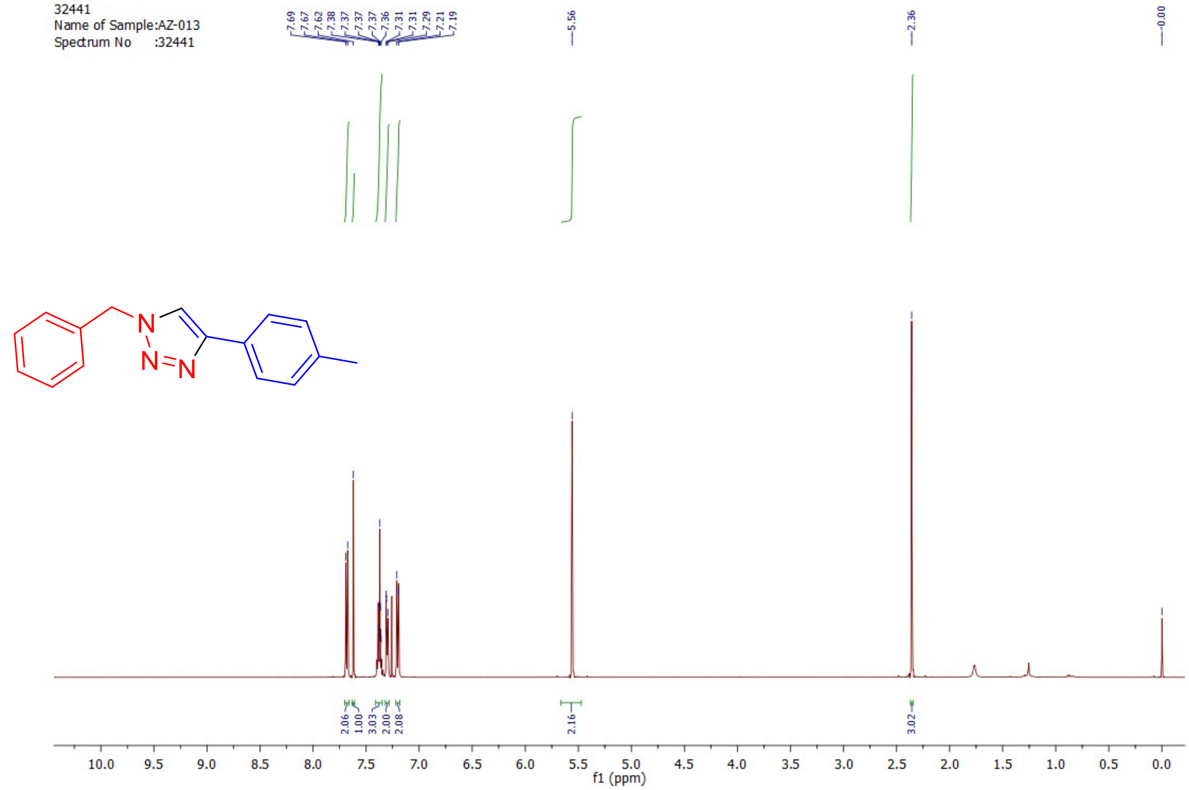
4. ^{1}H NMR and ^{13}C NMR Spectra of 1,4-disubstituted 1,2,3-triazoles

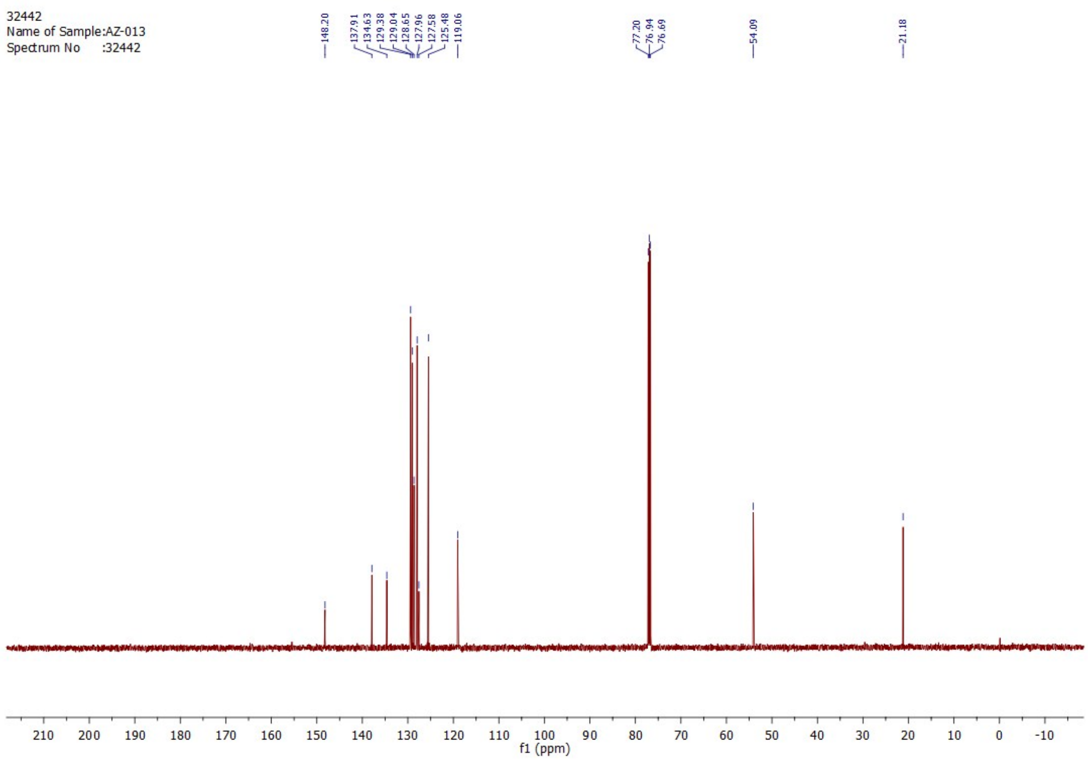
^{1}H and ^{13}C NMR of 1-benzyl-4-phenyl-1*H*-1,2,3-triazole (**3a**)



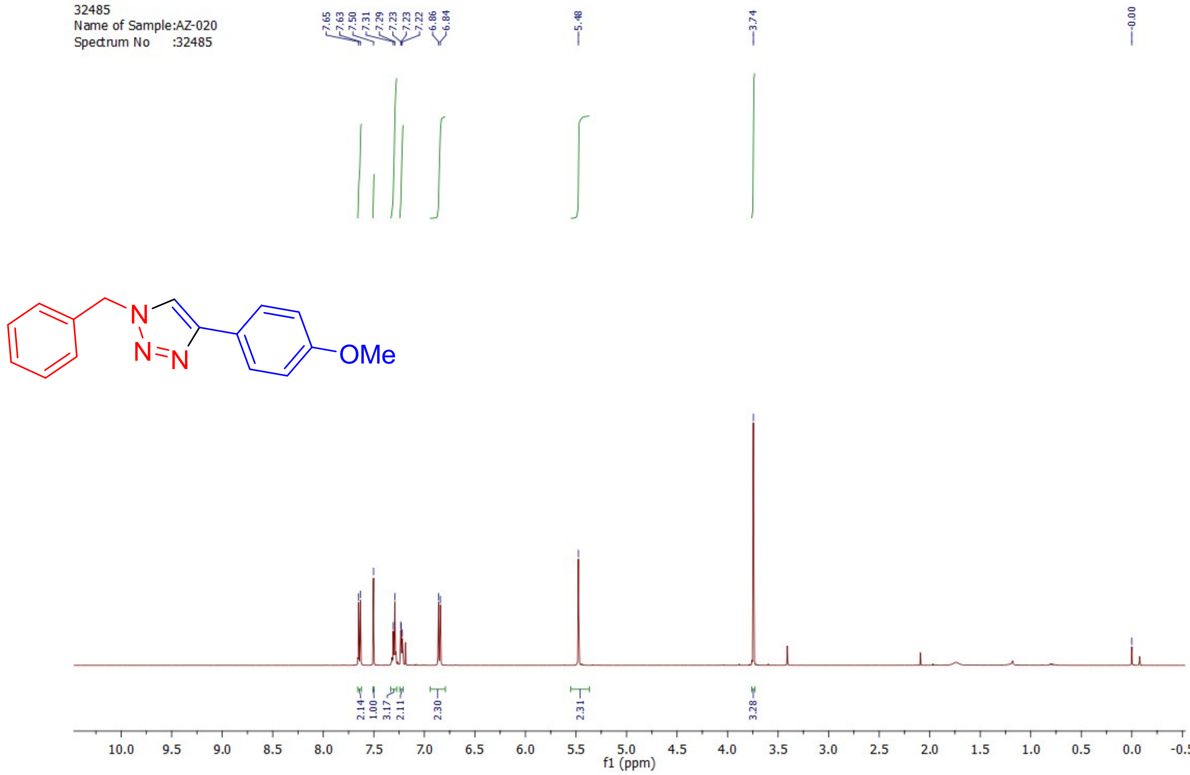


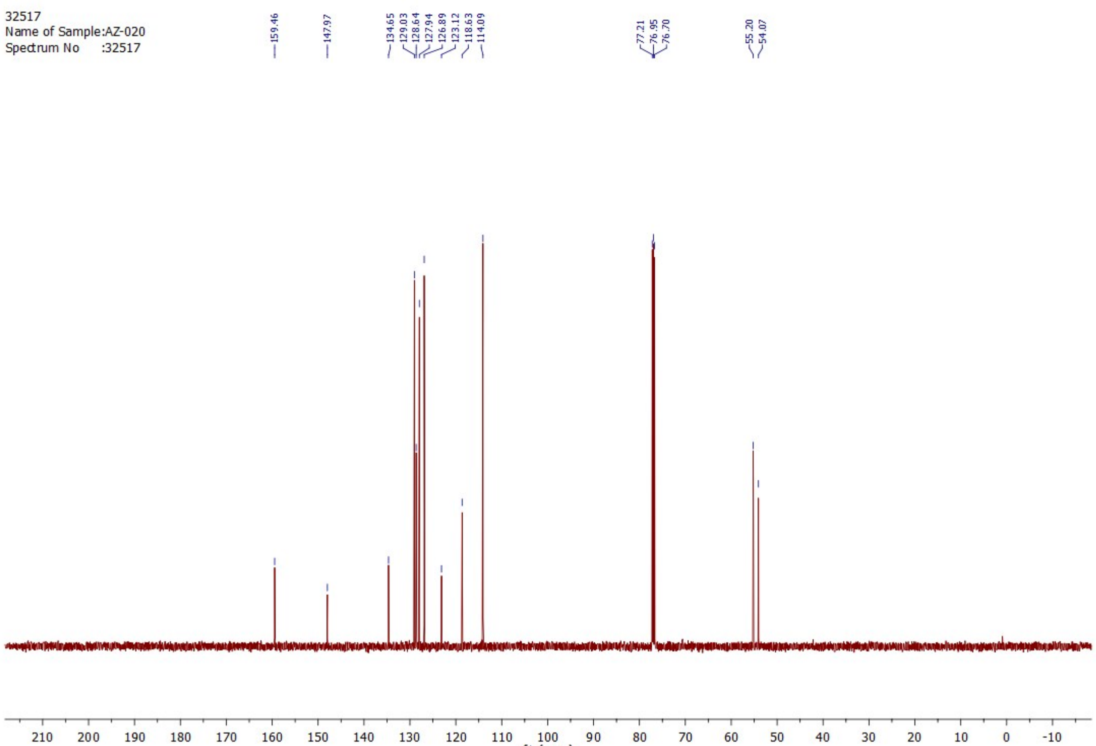
^{1}H and ^{13}C NMR of 1-benzyl-4-(p-tolyl)-1*H*-1,2,3-triazole (**3b**)



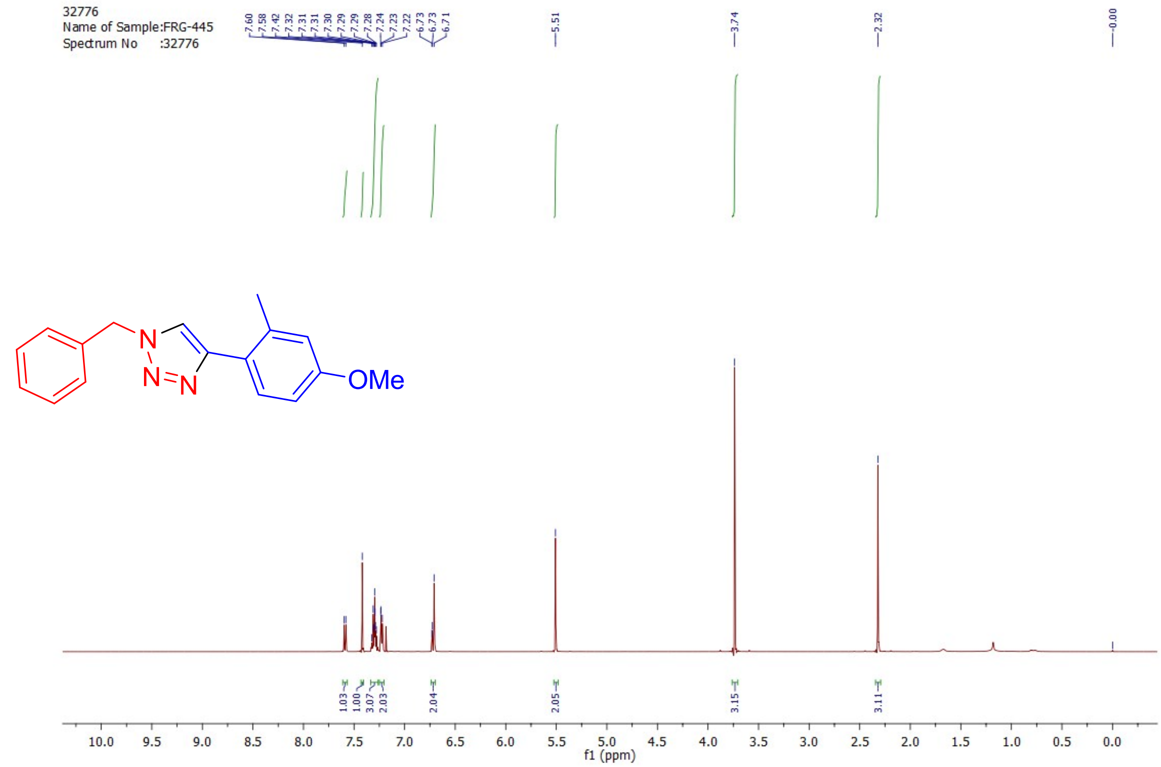


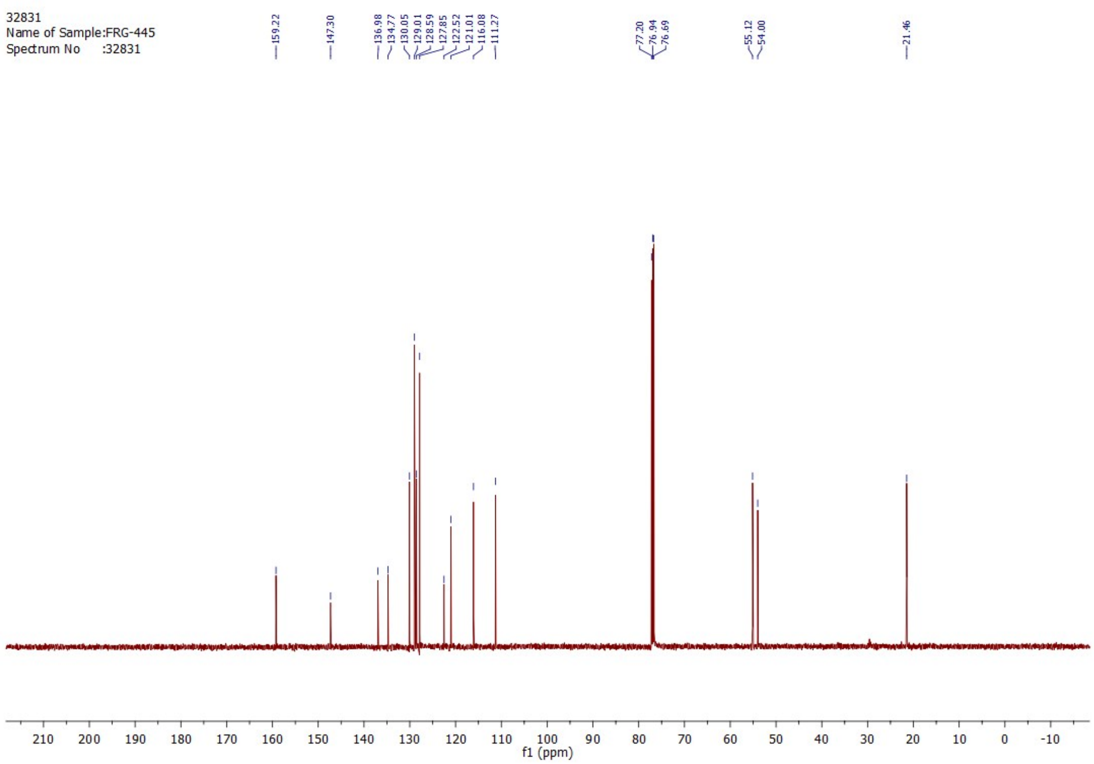
^{1}H and ^{13}C NMR of 1-benzyl-4-(4-methoxyphenyl)-1*H*-1,2,3-triazole (**3c**)



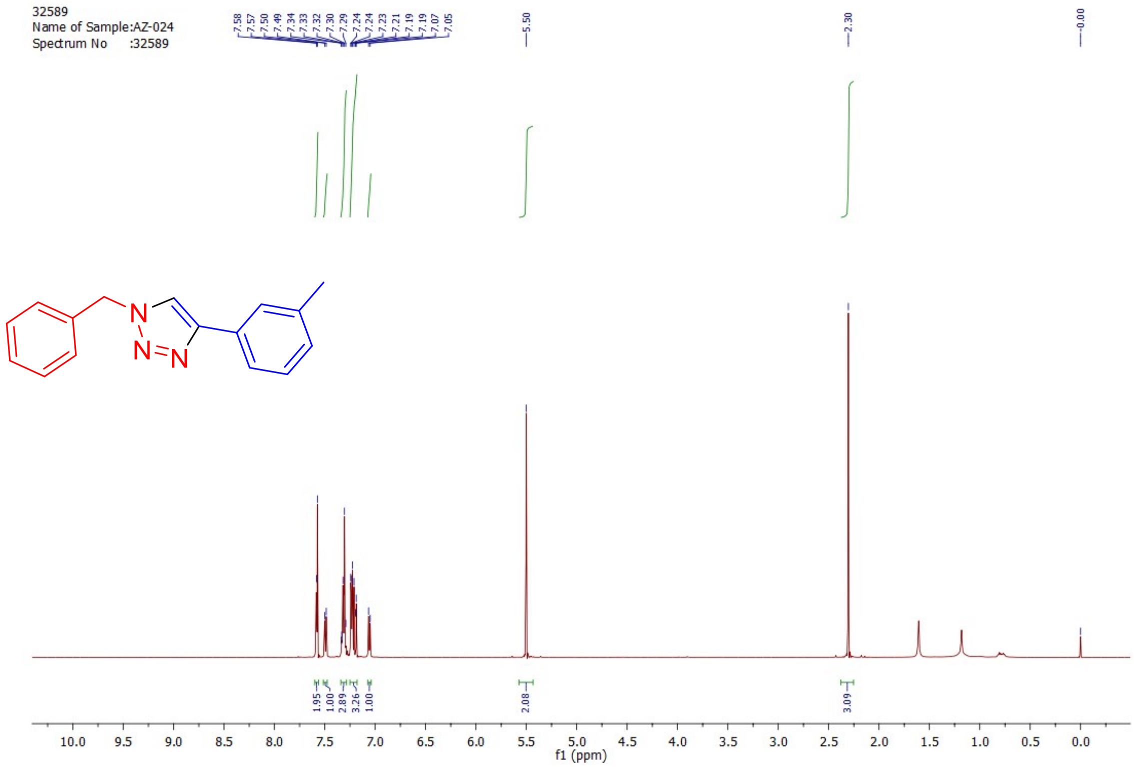


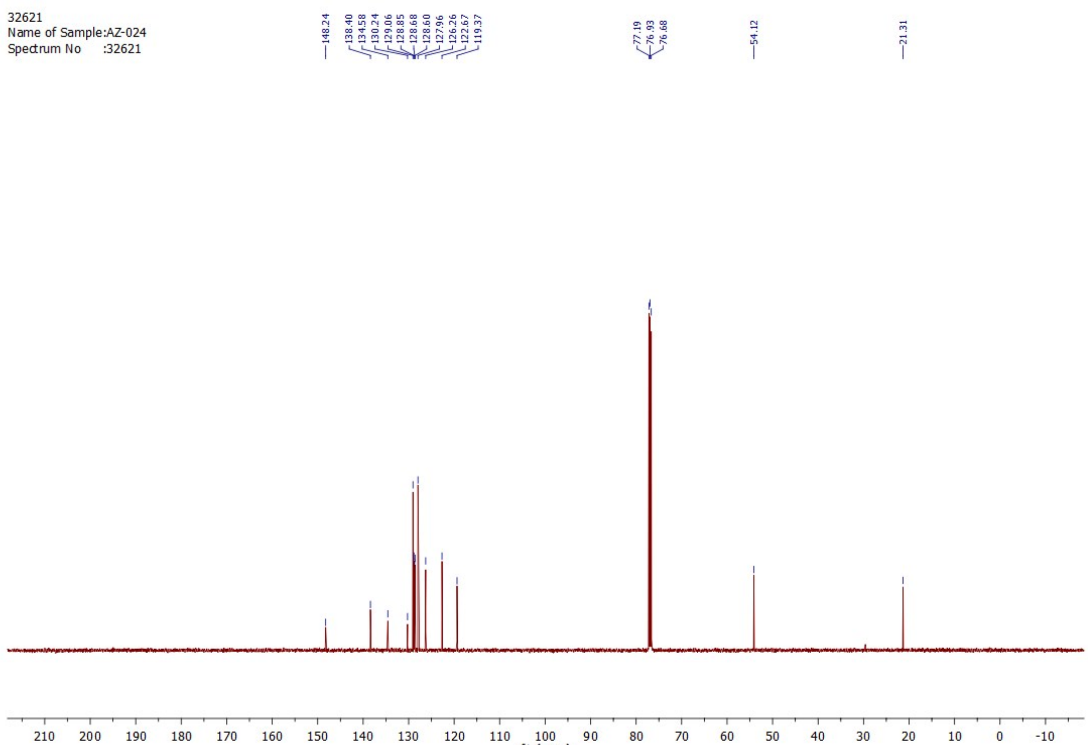
[1]H and [13]C NMR of 1-benzyl-4-(4-methoxy-2-methylphenyl)-1*H*-1,2,3-triazole (**3d**)



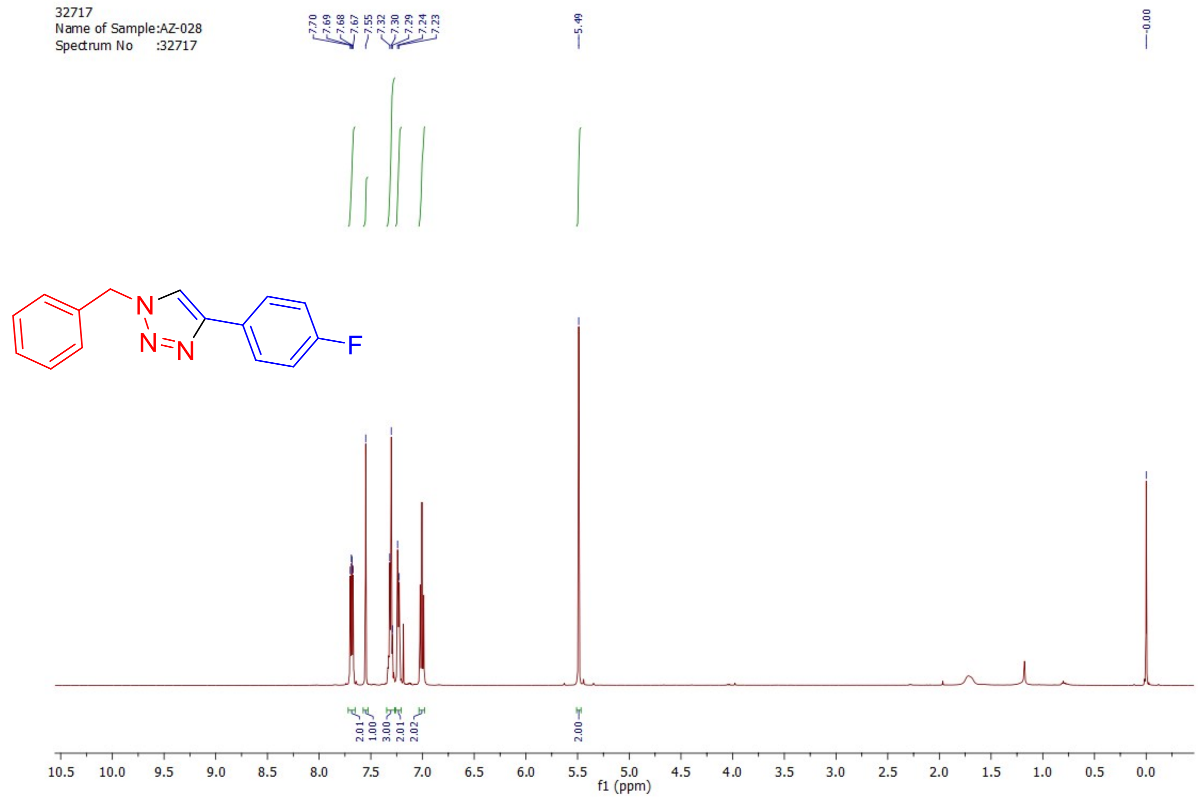


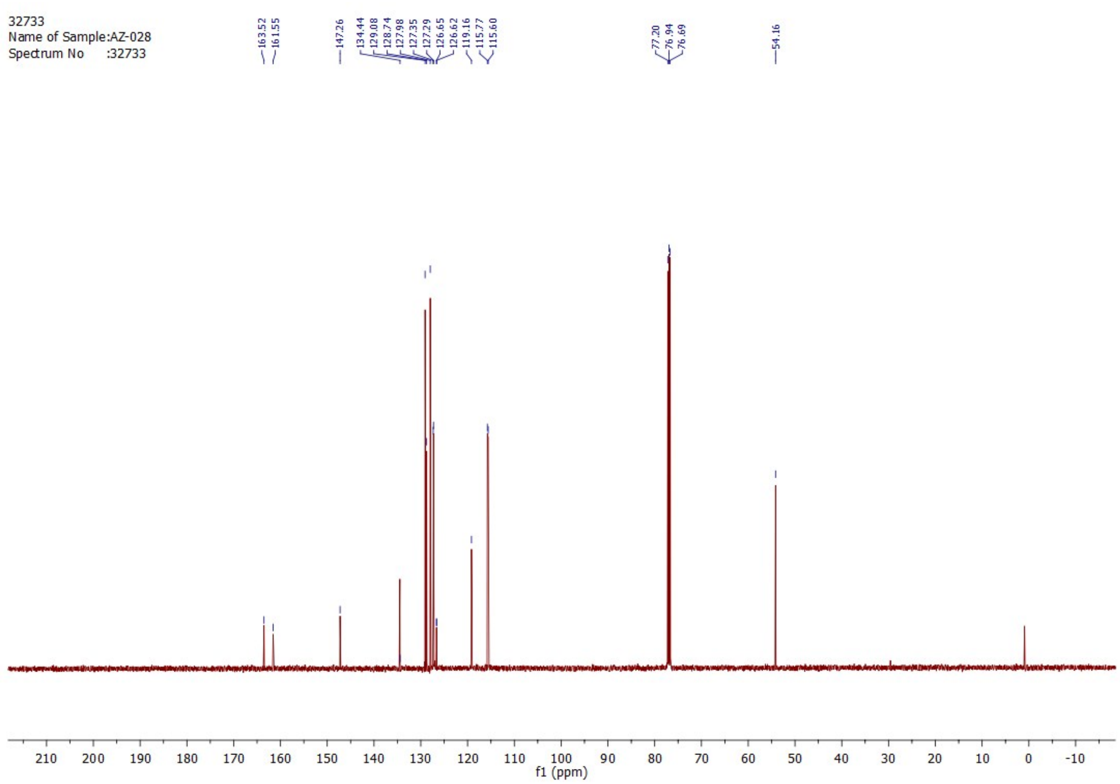
^{1}H and ^{13}C NMR of 1-benzyl-4-(m-tolyl)-1*H*-1,2,3-triazole (**3e**)



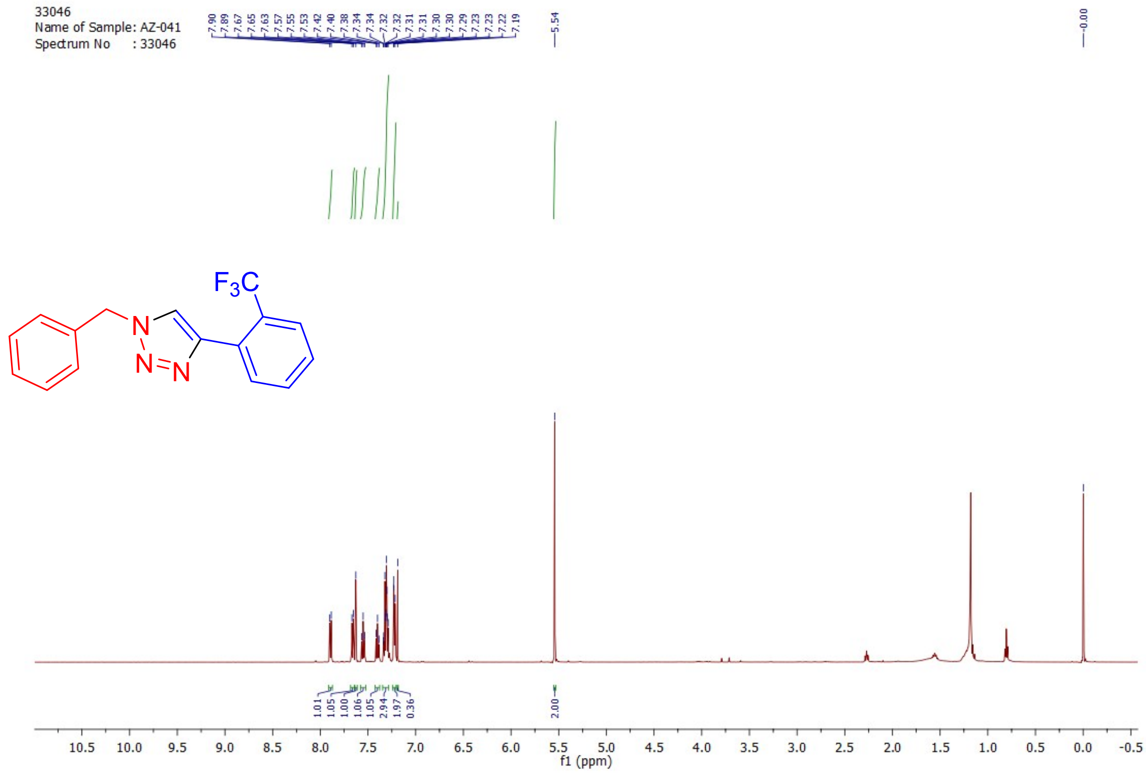


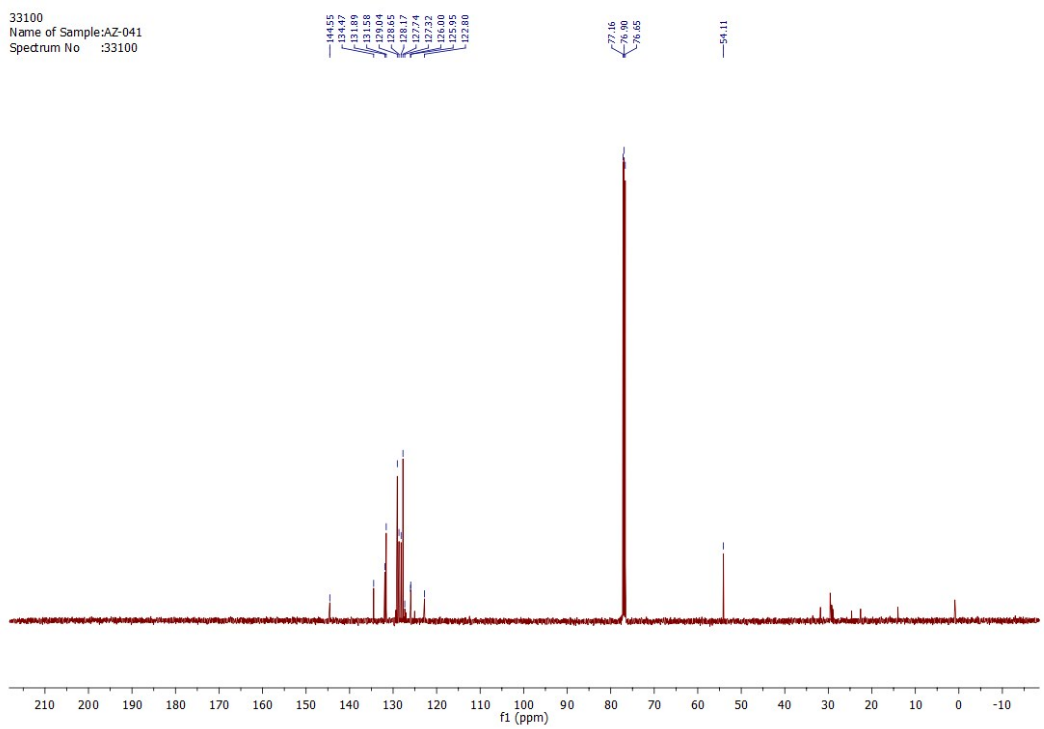
^{1}H and ^{13}C NMR of 1-benzyl-4-(4-fluorophenyl)-1*H*-1,2,3-triazole (**3f**)



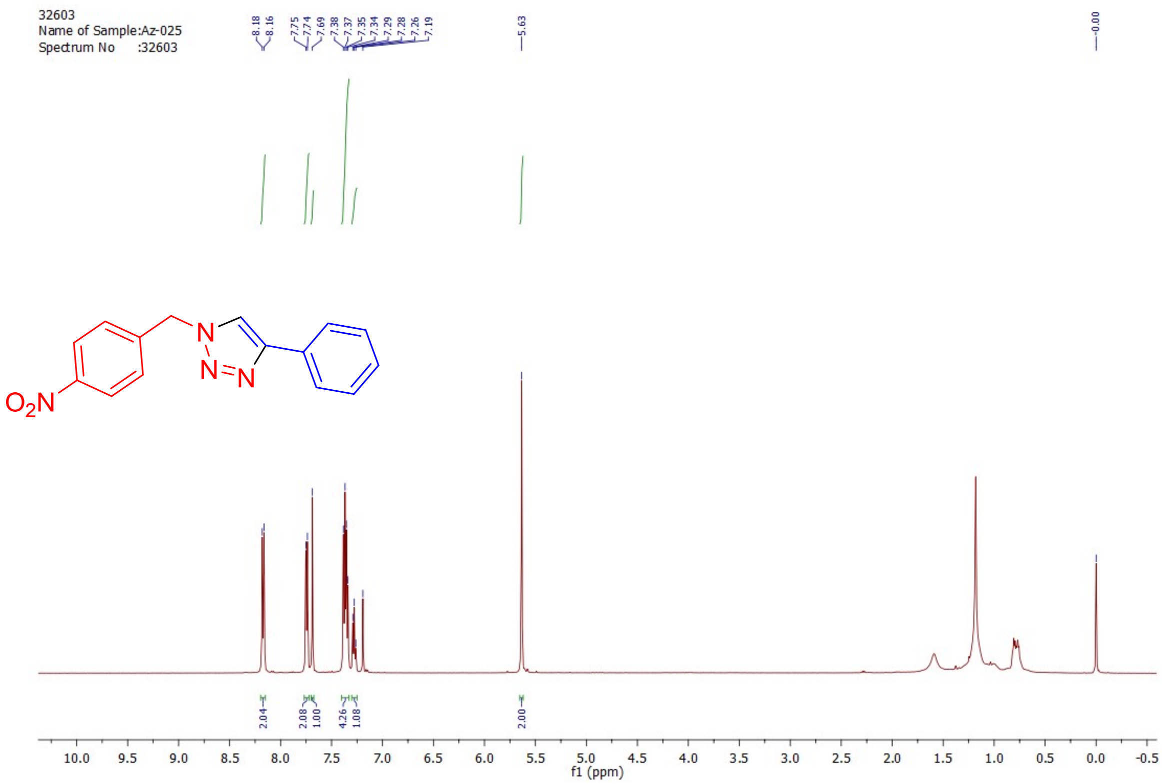


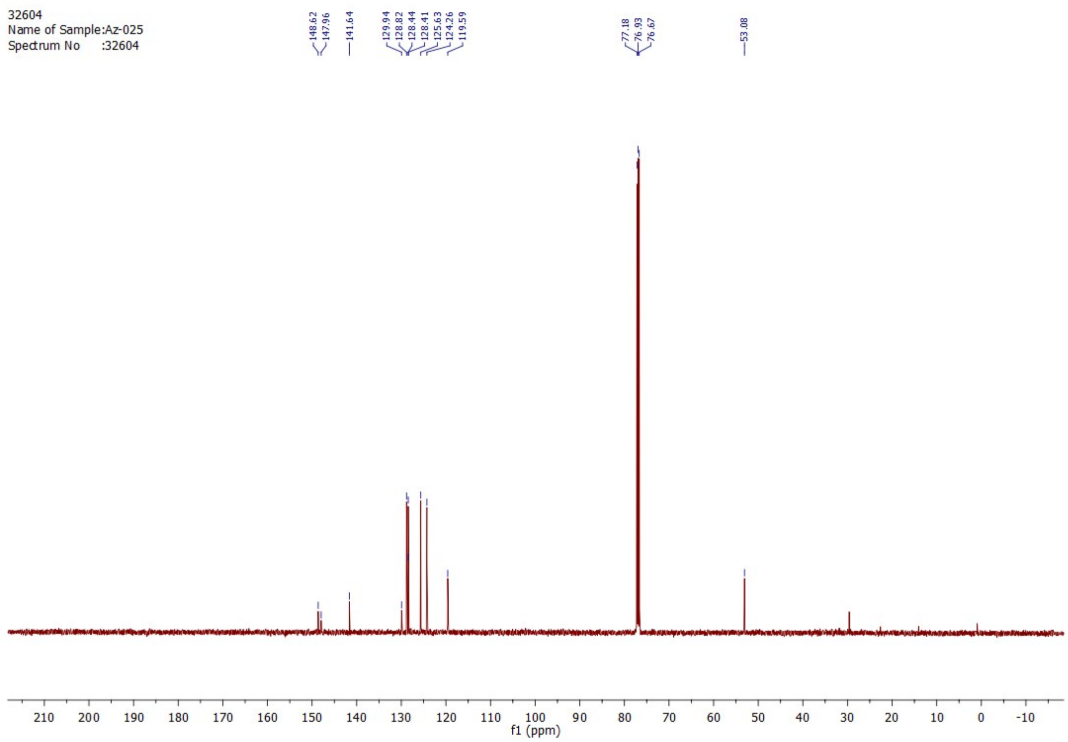
^{1}H and ^{13}C NMR of 1-benzyl-4-(2-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole (**3g**):



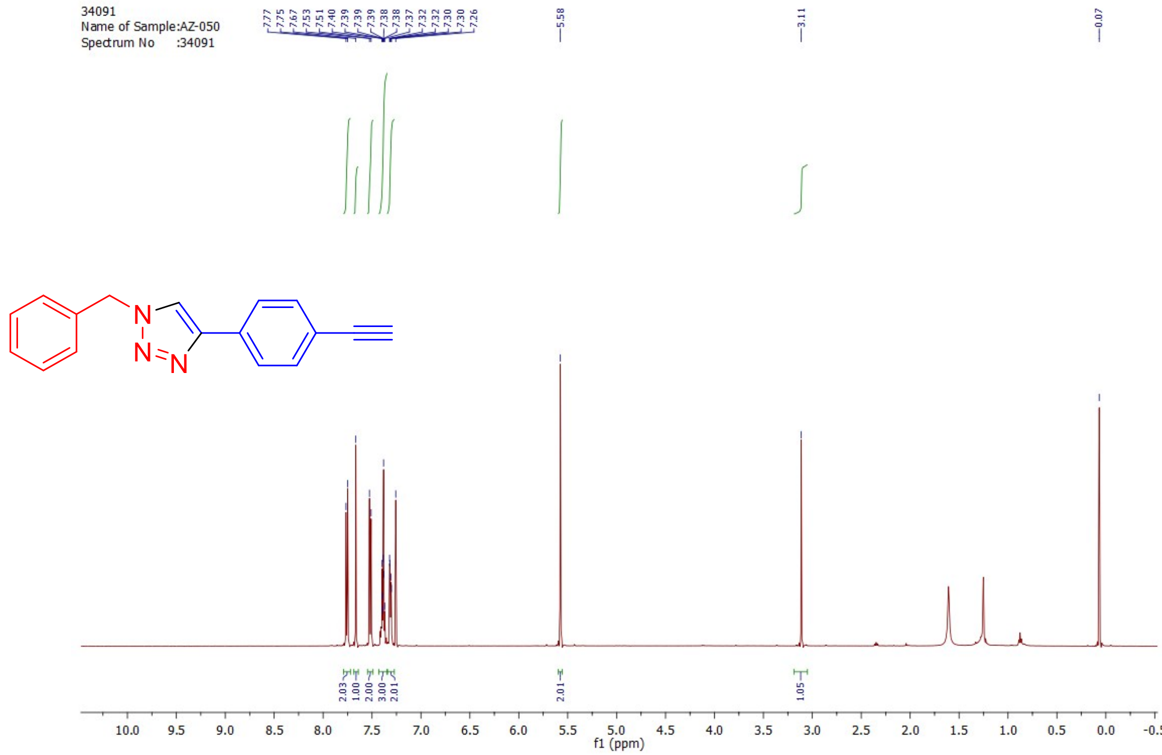


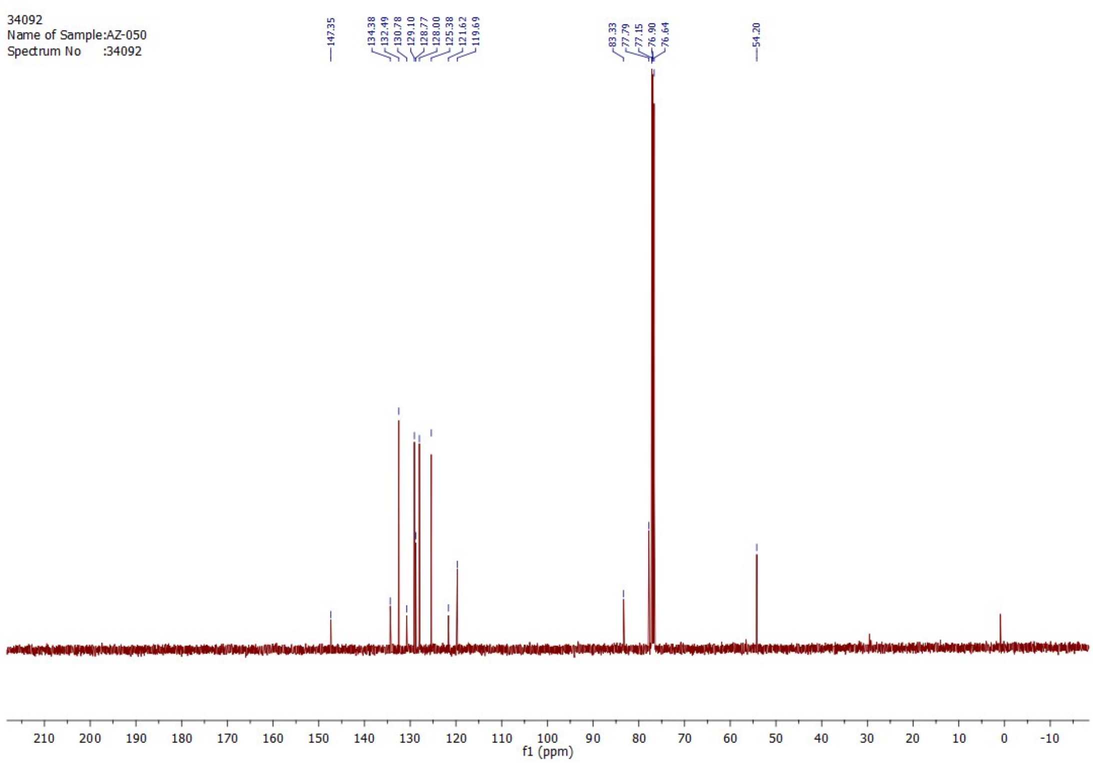
[1]H and [13]C NMR of 1-(4-nitrobenzyl)-4-phenyl-1*H*-1,2,3-triazole (**3h**)



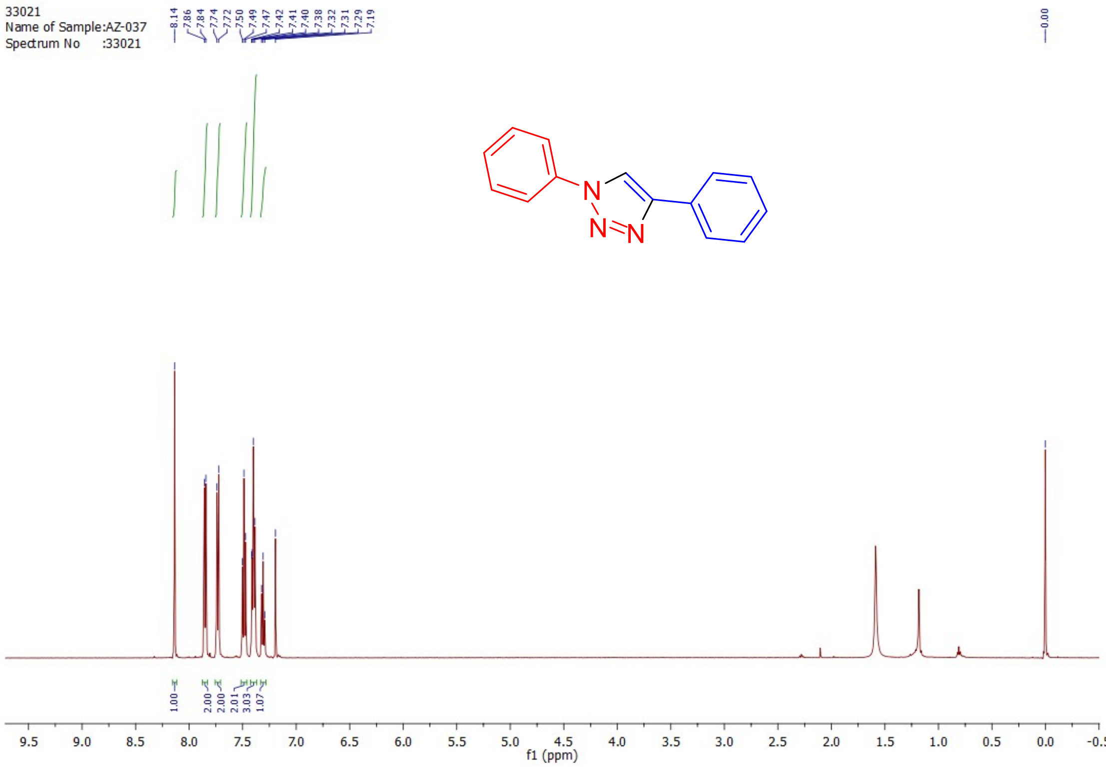


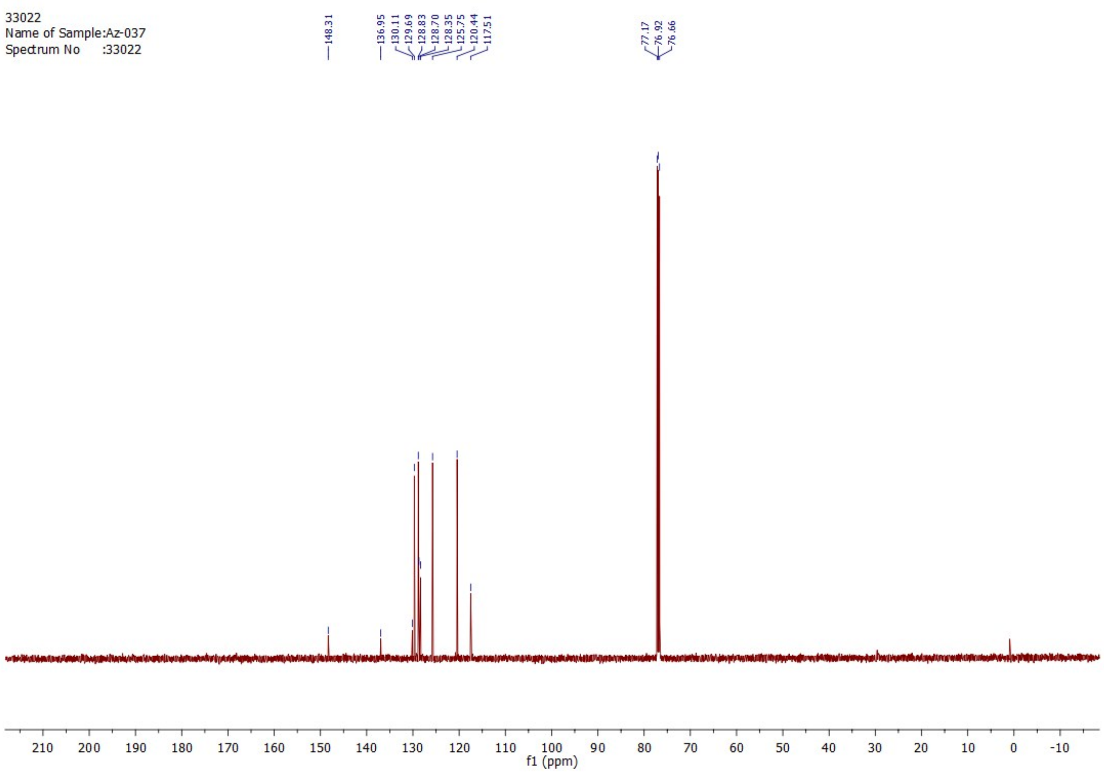
[1]H and [13]C NMR of 1-benzyl-4-(4-ethynylphenyl)-1*H*-1,2,3-triazole (**3i**)



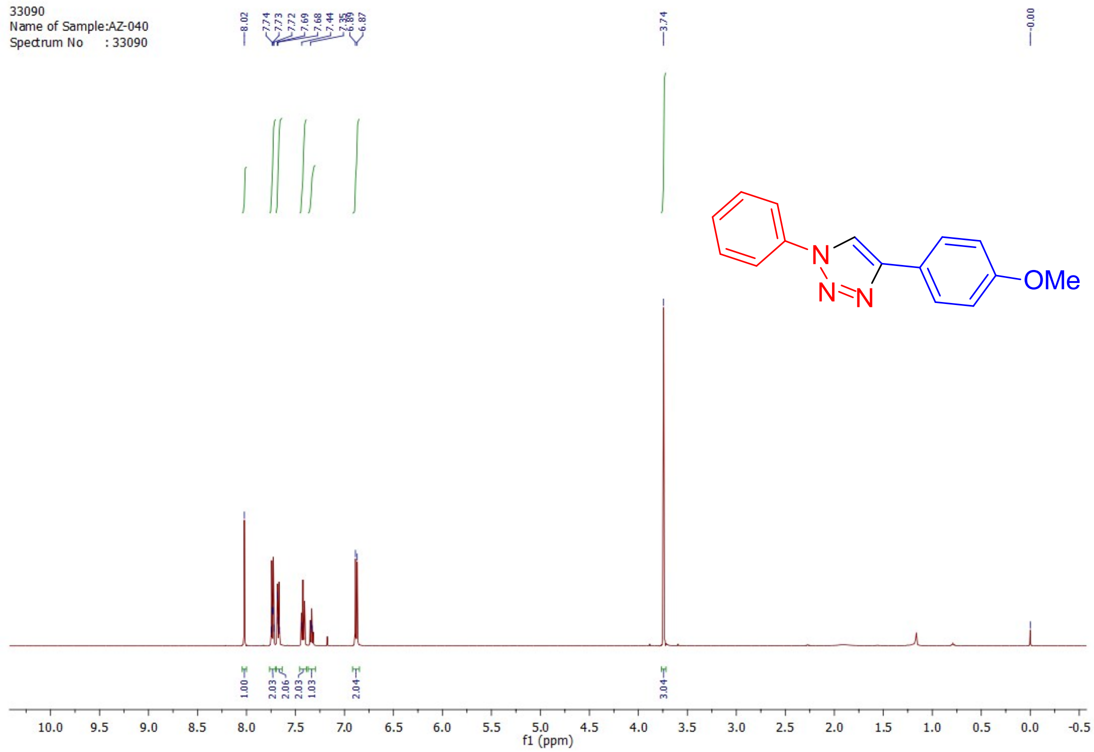


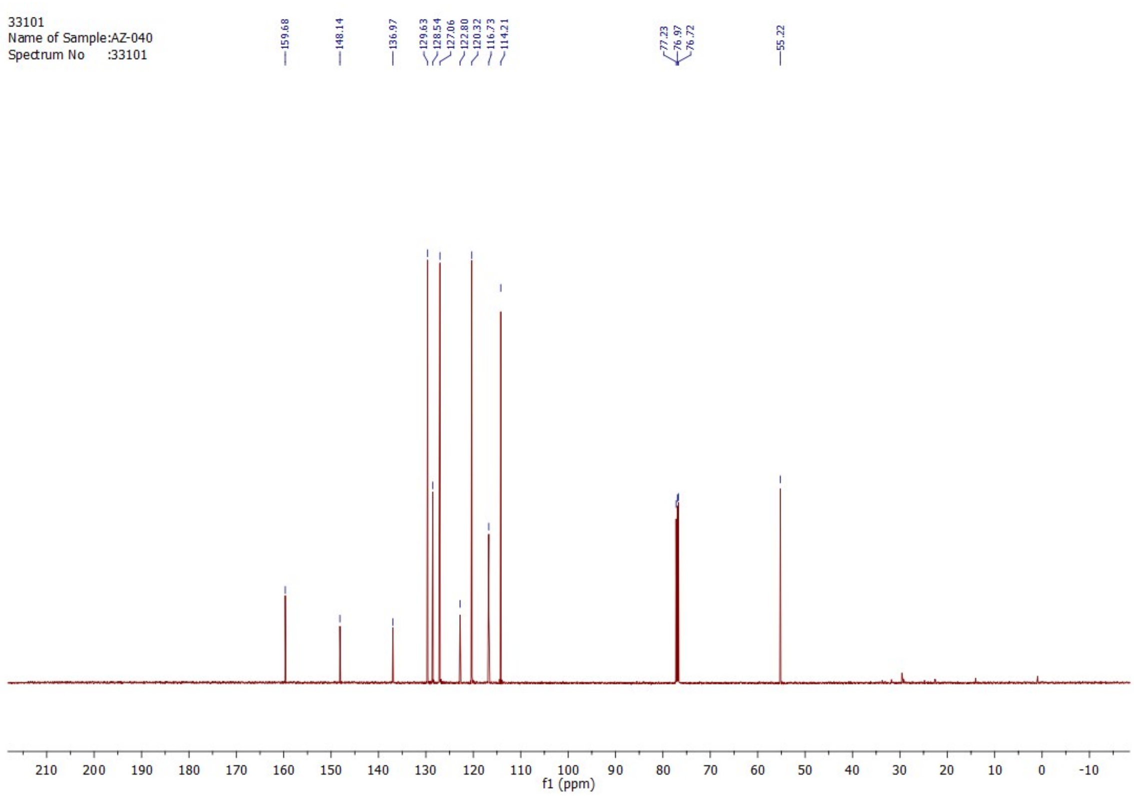
[1]H and [13]C NMR of 1,4-diphenyl-1*H*-1,2,3-triazole (**3j**)



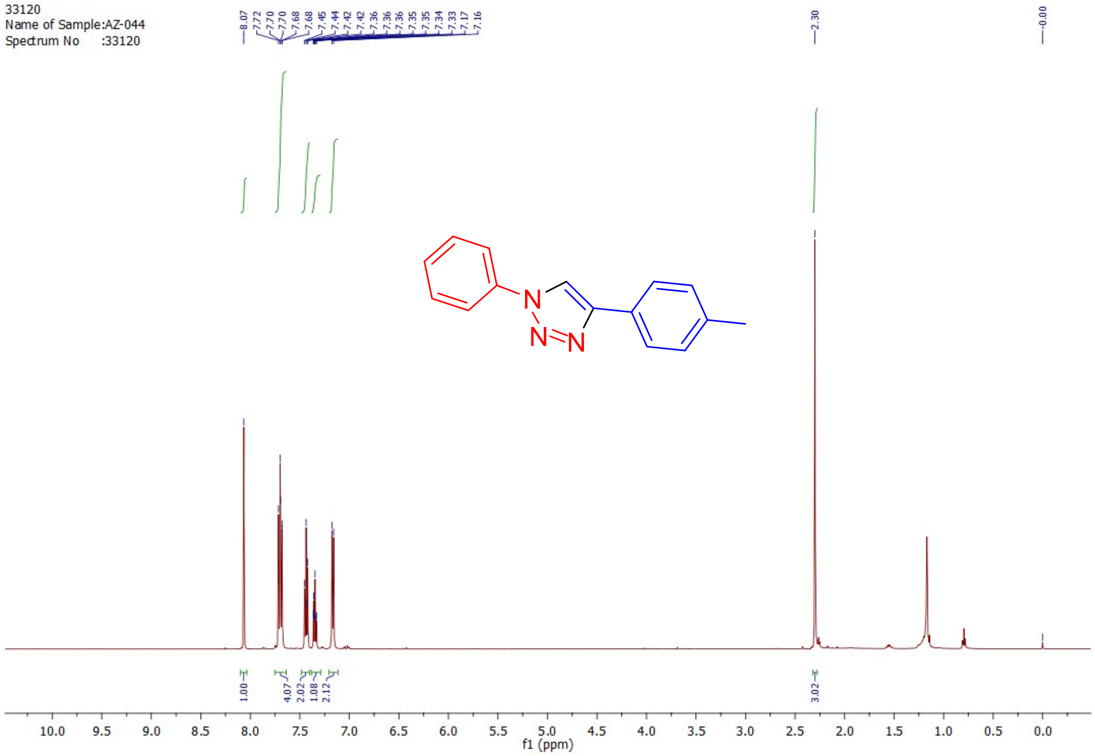


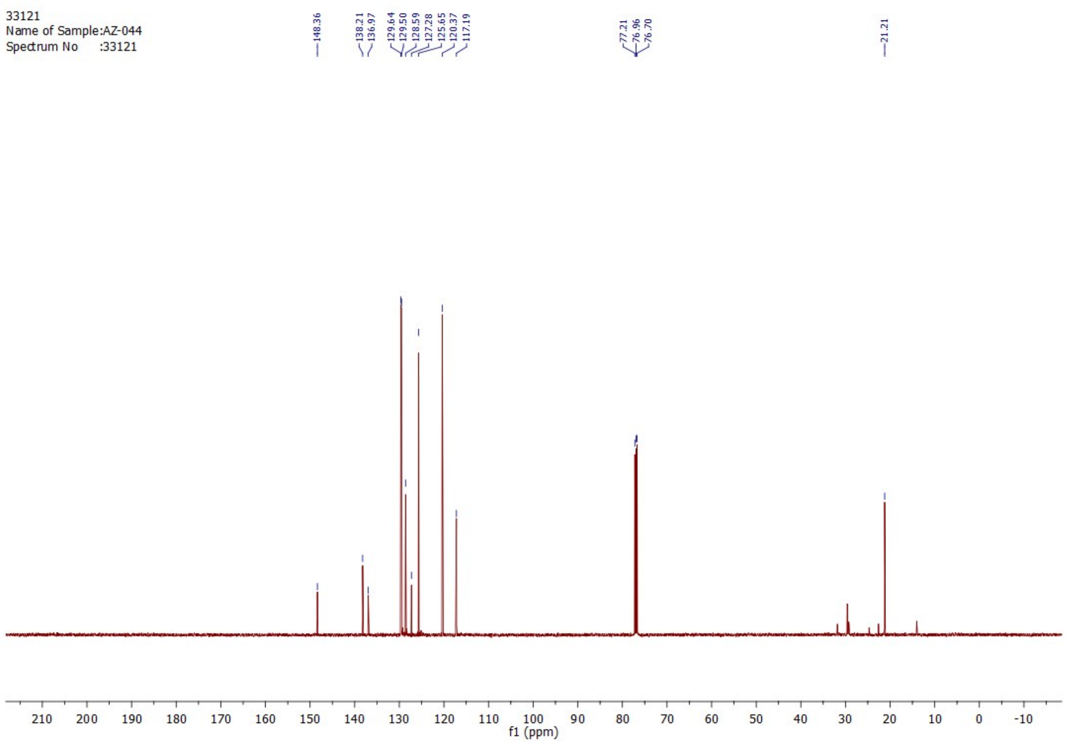
^{1}H and ^{13}C NMR of 4-(4-methoxyphenyl)-1-phenyl-1*H*-1,2,3-triazole (**3k**)



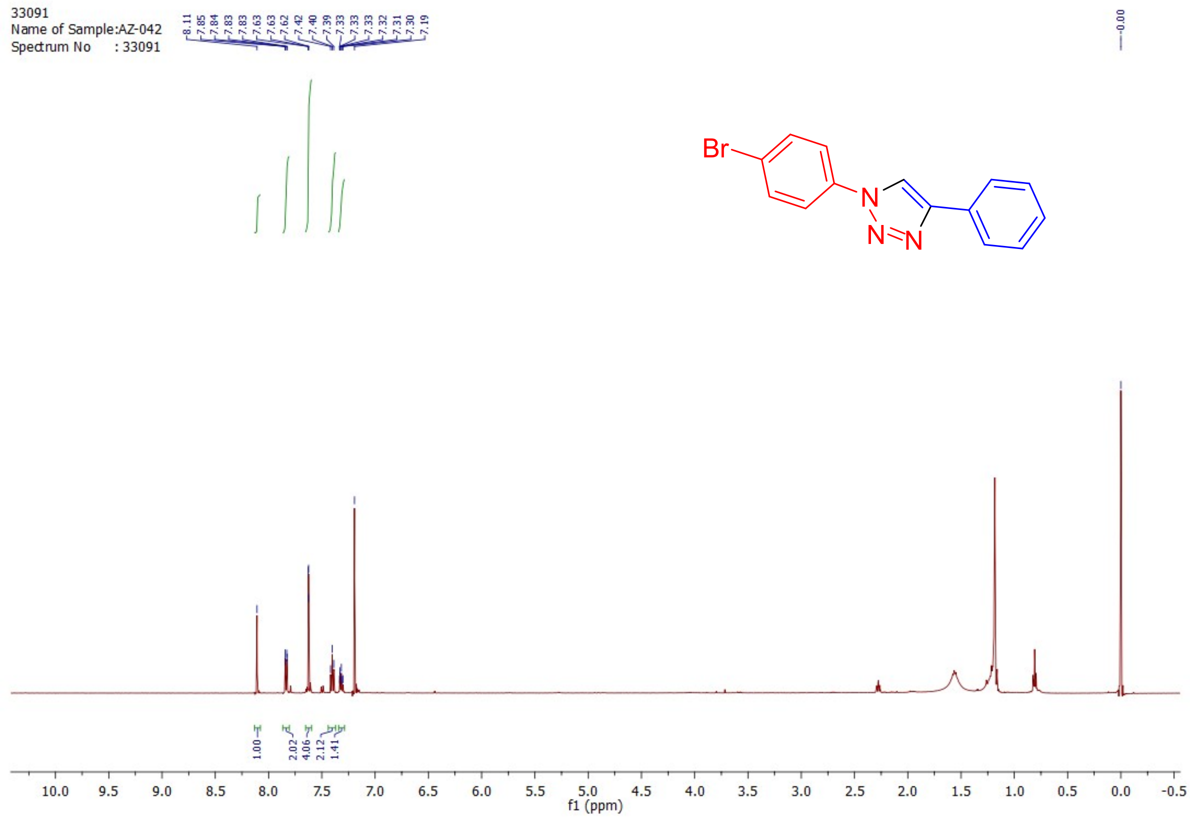


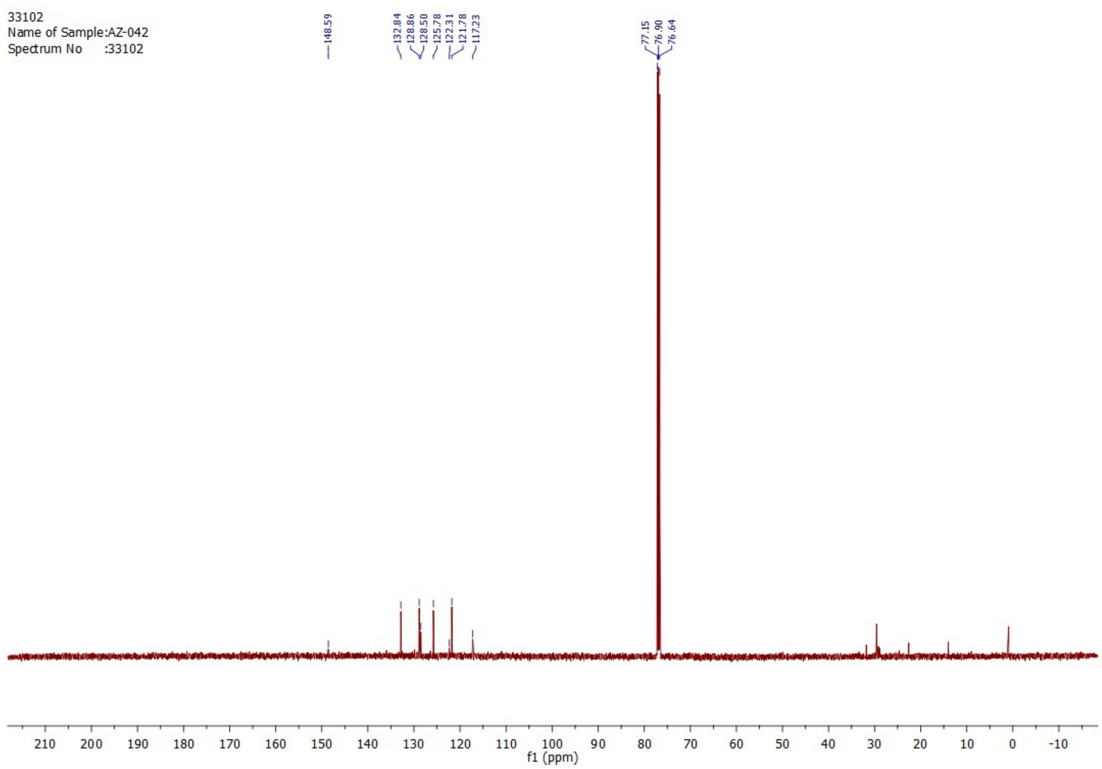
[1]H and [13]C NMR of 1-phenyl-4-(p-tolyl)-1*H*-1,2,3-triazole (**3l**)



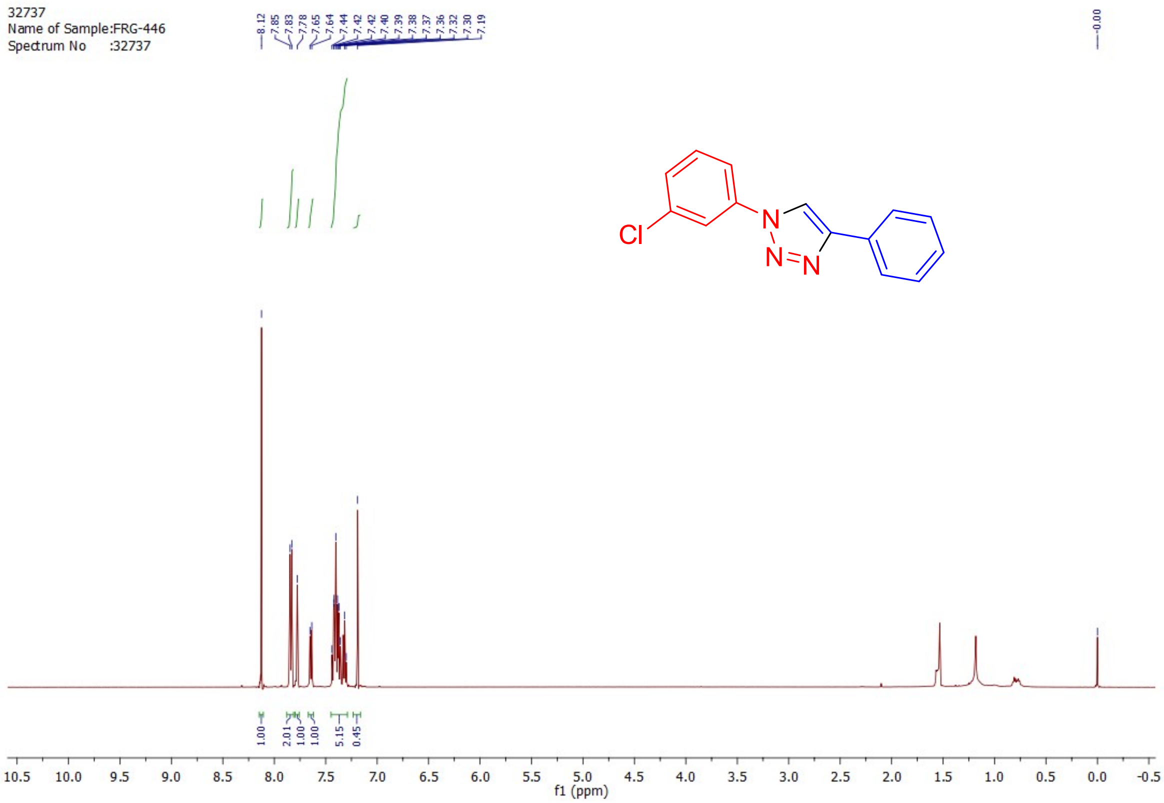


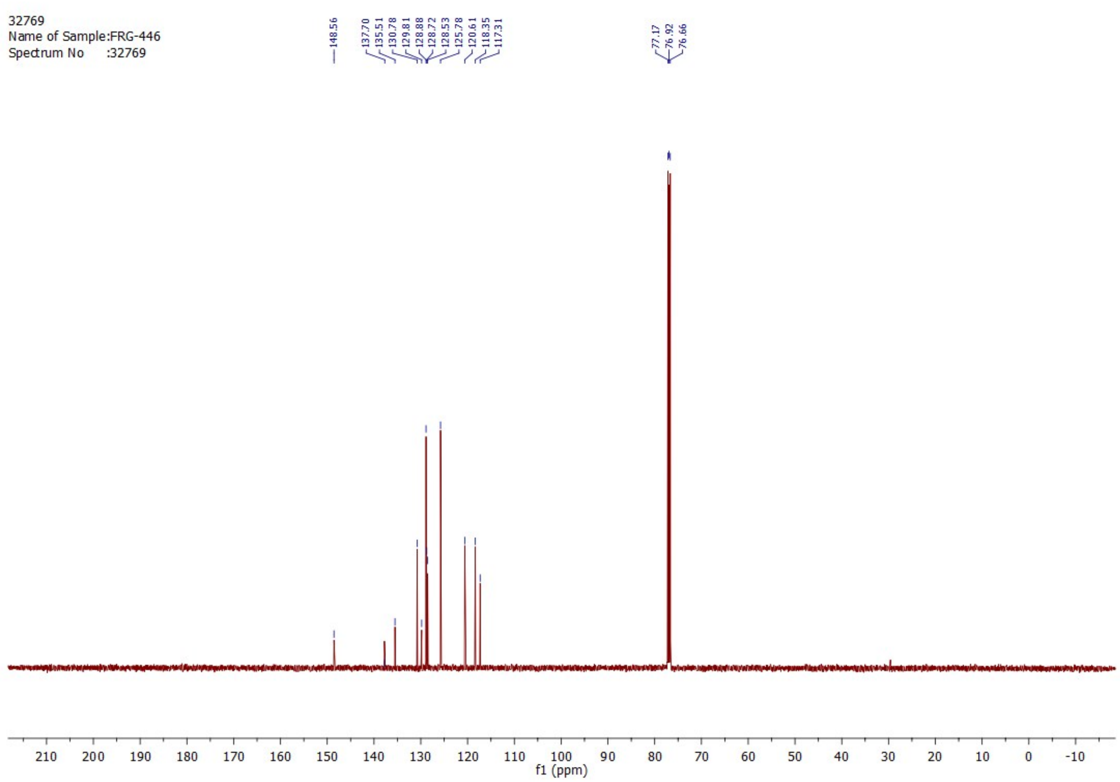
^{1}H and ^{13}C NMR of 1-(4-bromophenyl)-4-phenyl-1*H*-1,2,3-triazole (**3m**):



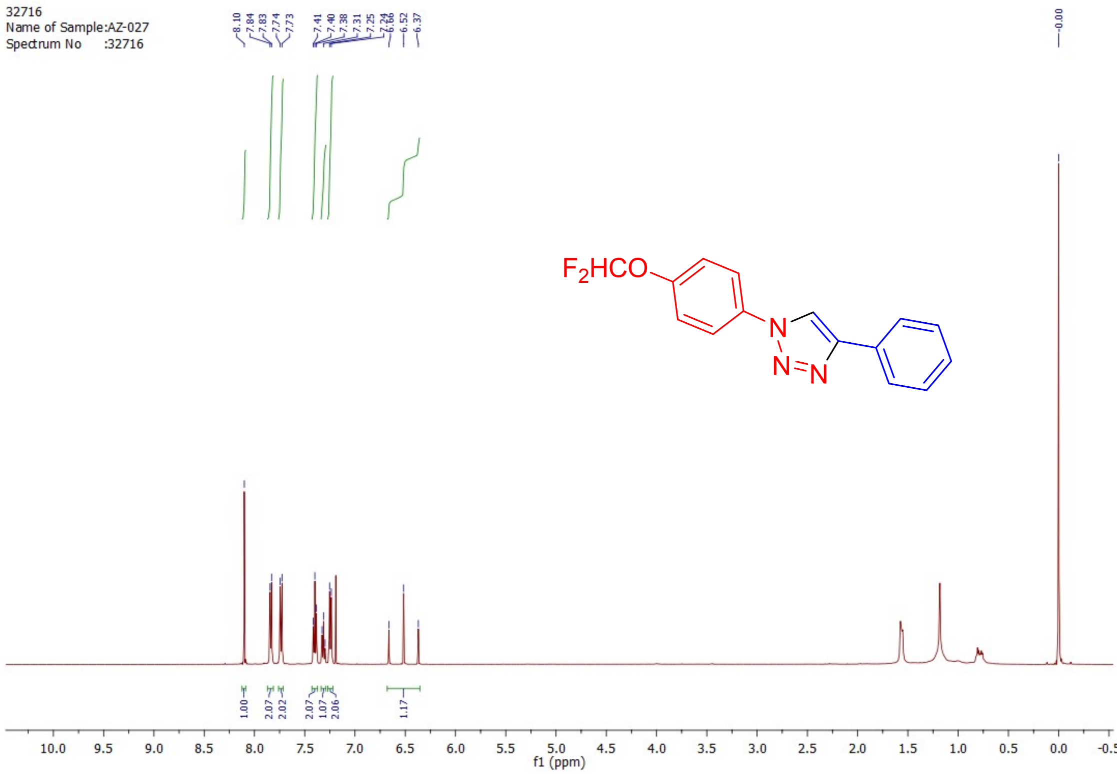


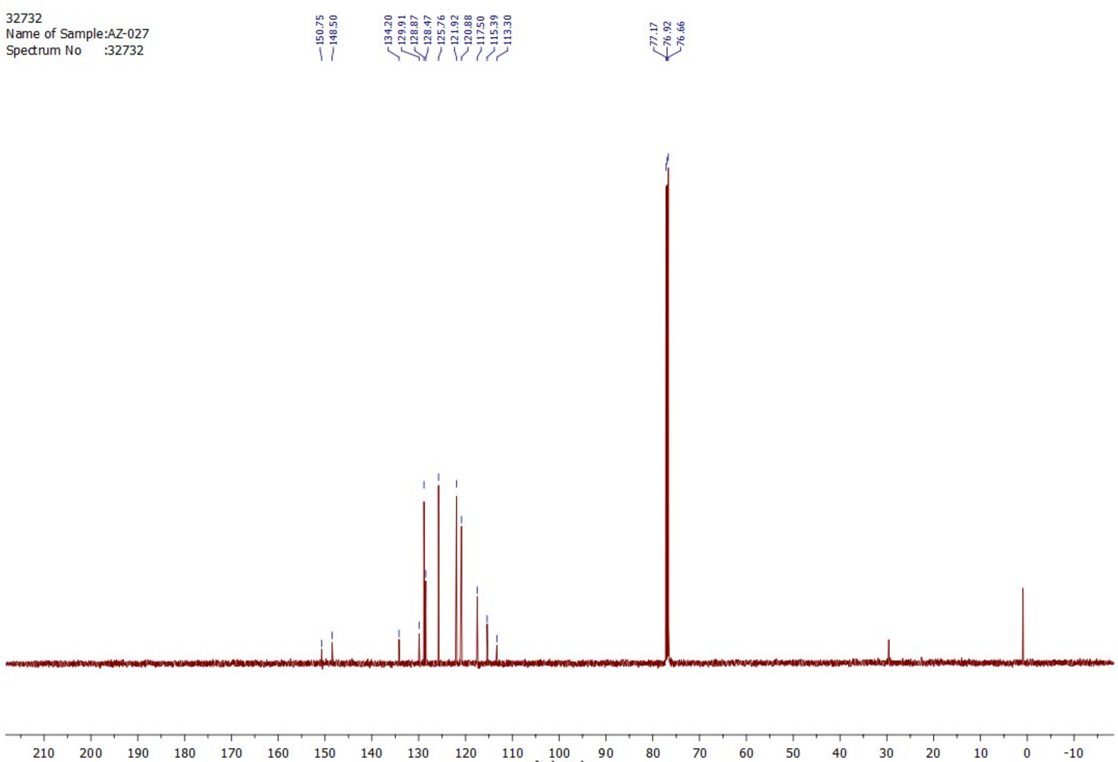
[1]H and [13]C NMR of 1-(3-chlorophenyl)-4-phenyl-1*H*-1,2,3-triazole (**3n**)



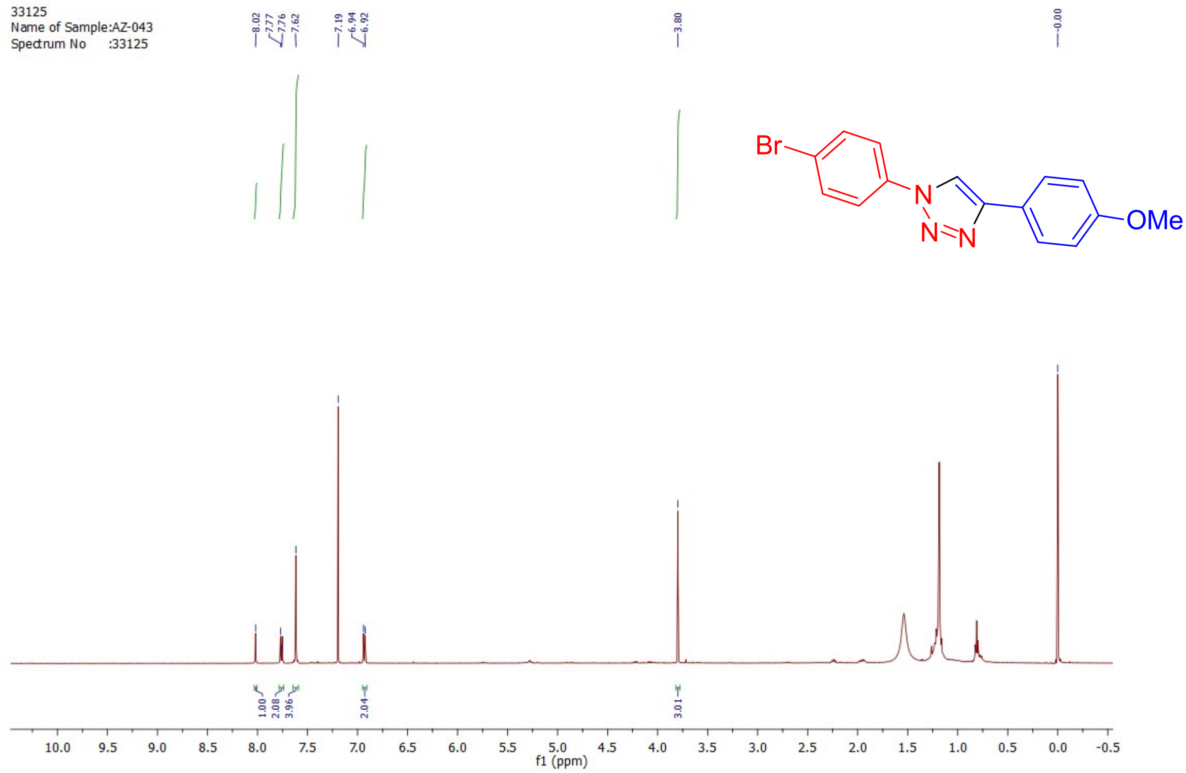


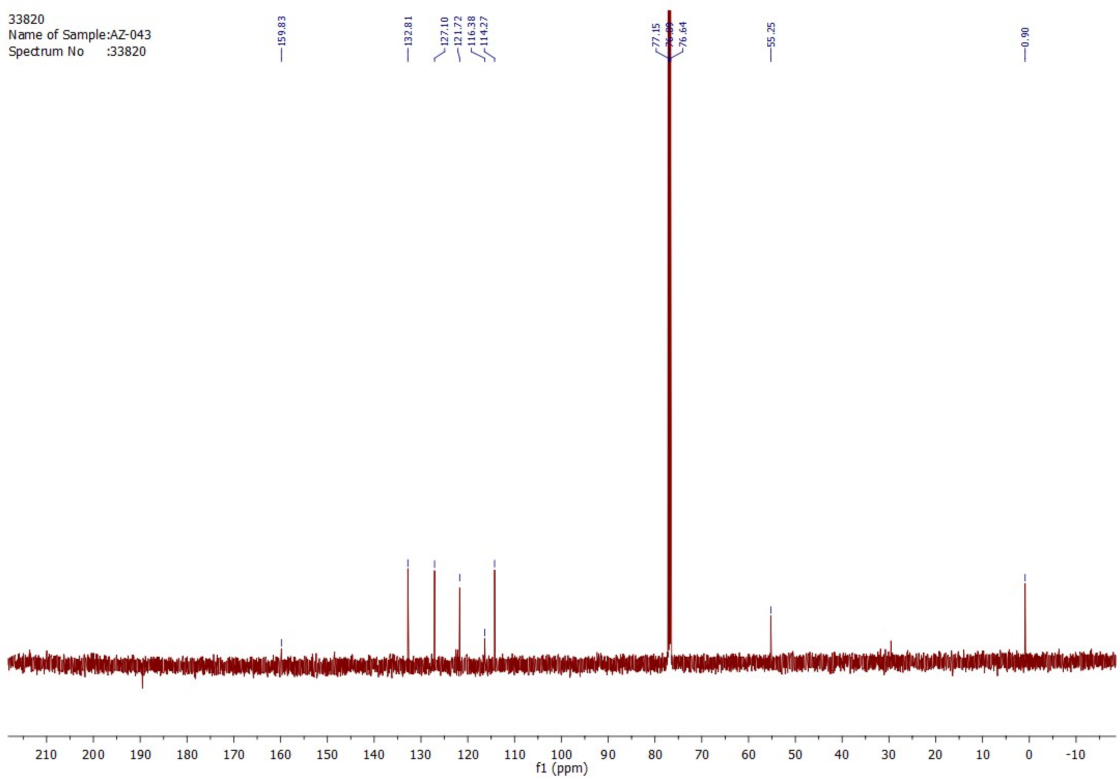
[1]H and [13]C NMR of 1-(4-(difluoromethoxy)phenyl)-4-phenyl-1*H*-1,2,3-triazole (**3o**)



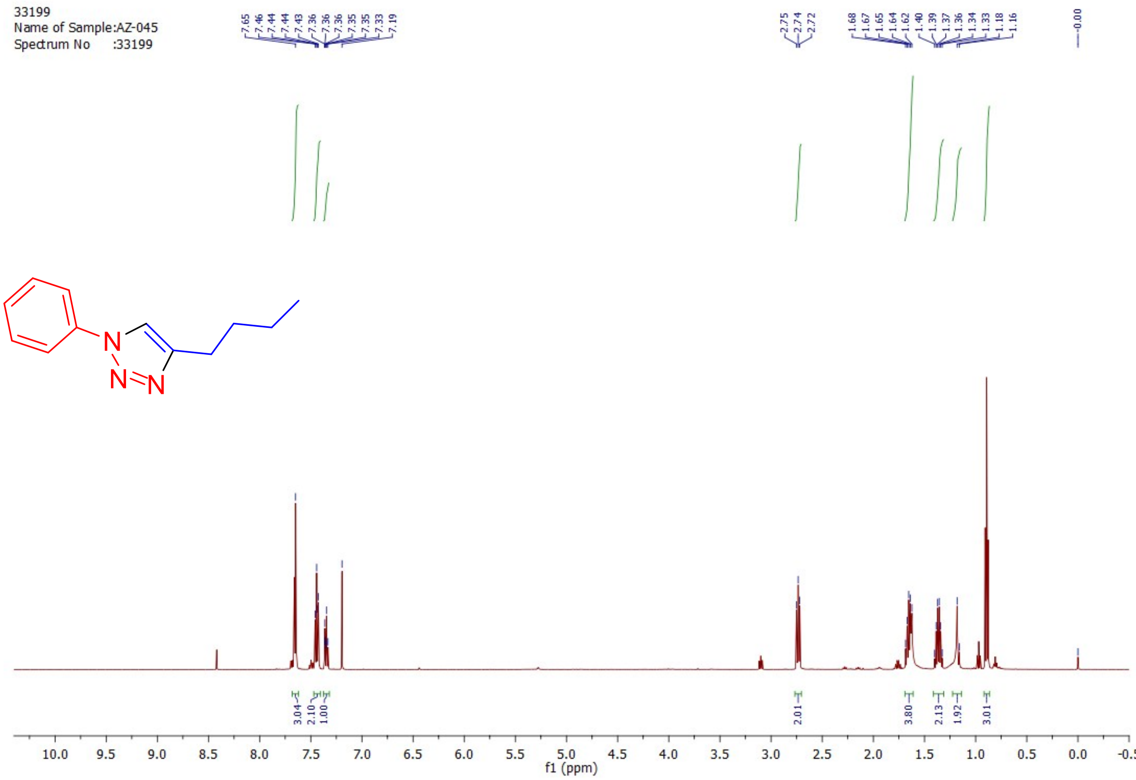


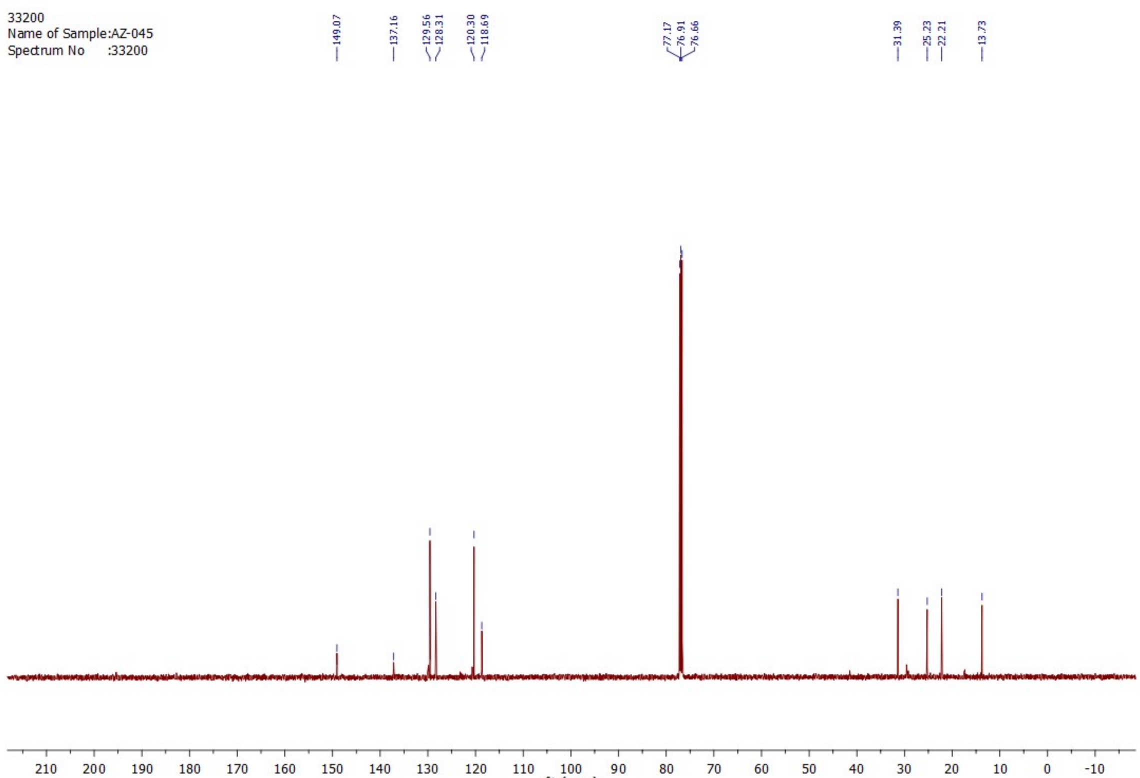
¹H and ¹³C NMR of 1-(4-bromophenyl)-4-(4-methoxyphenyl)-1*H*-1,2,3-triazole (**3p**)



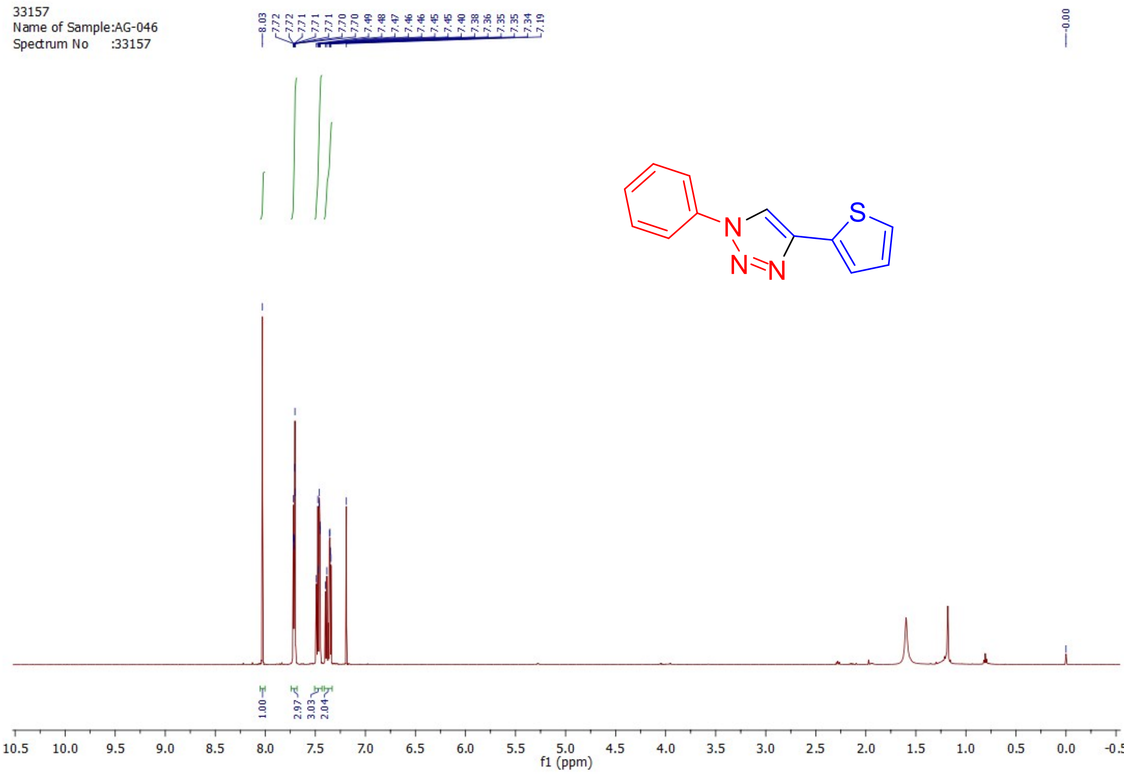


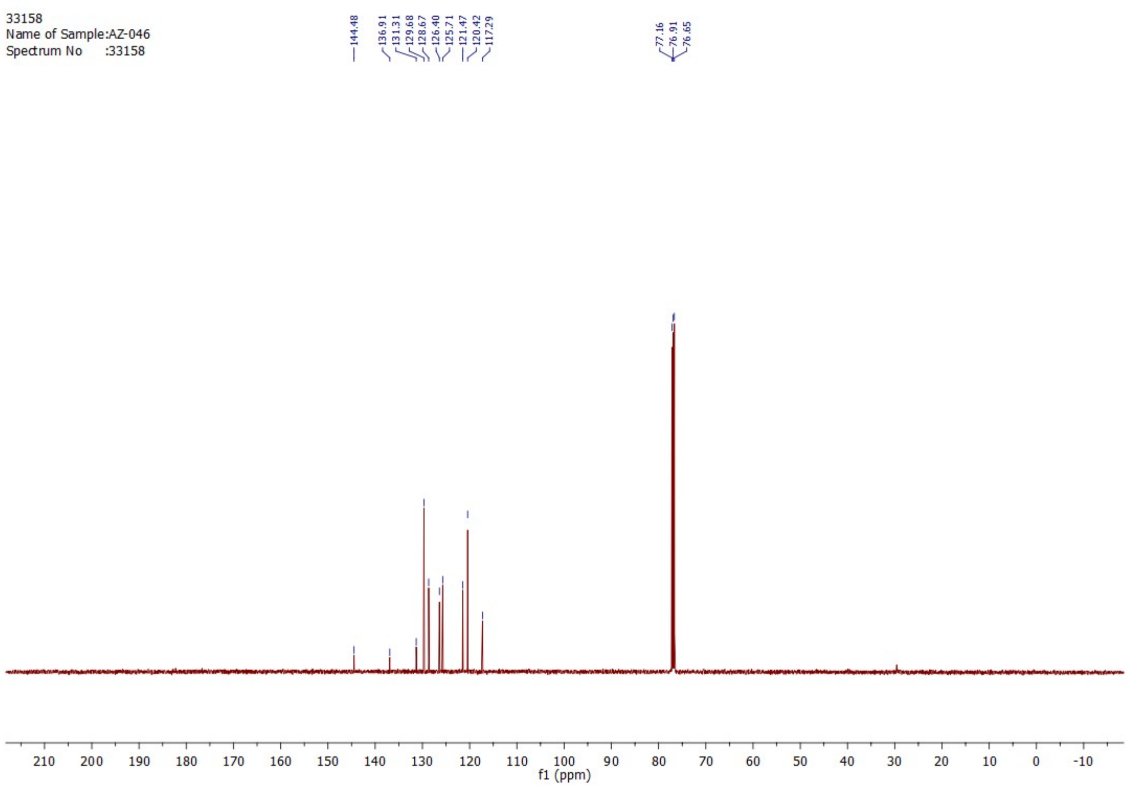
^{1}H and ^{13}C NMR of 4-butyl-1-phenyl-1*H*-1,2,3-triazole (**3q**)



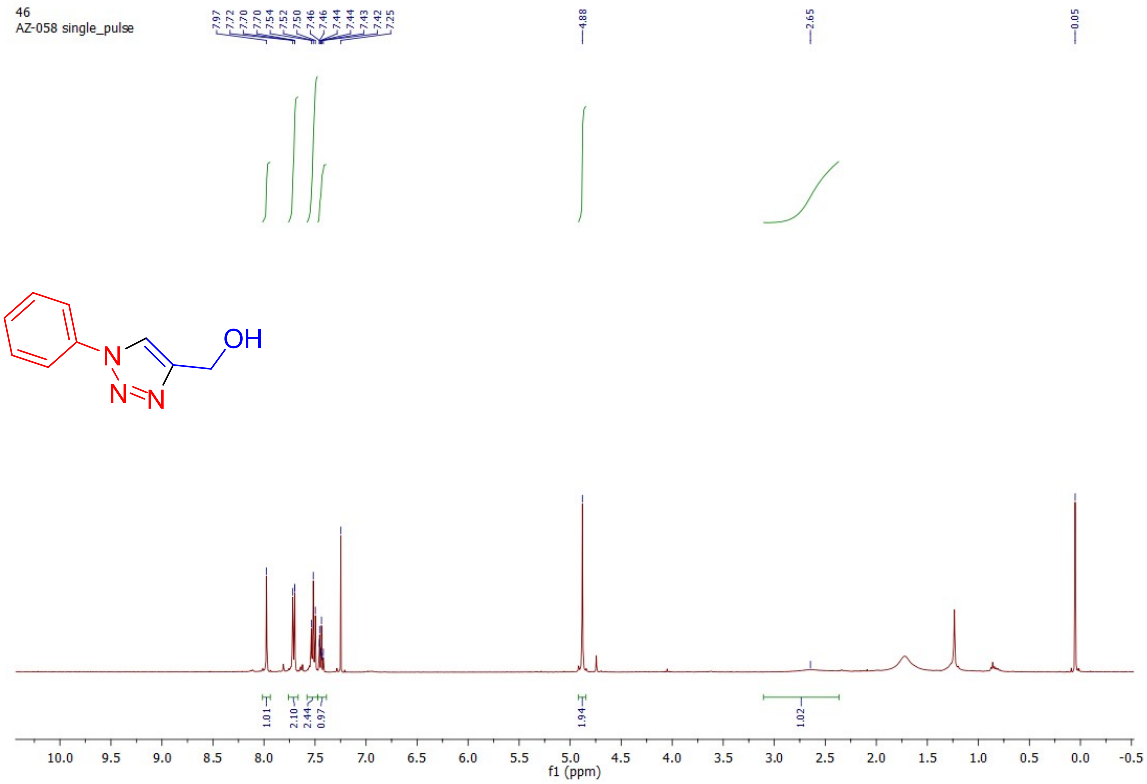


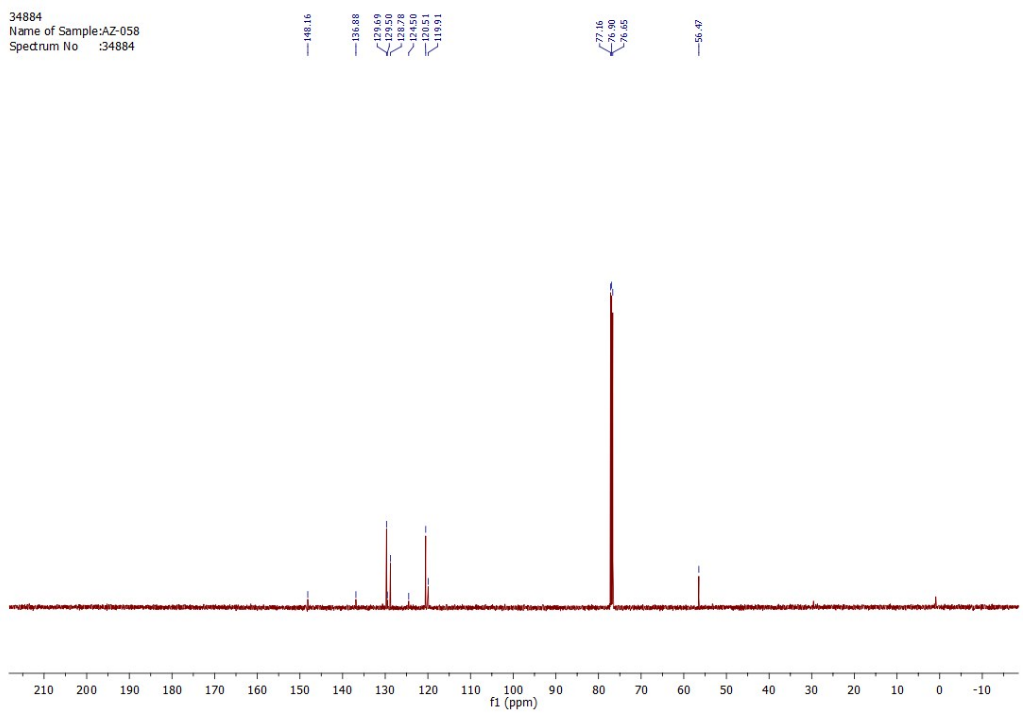
^{1}H and ^{13}C NMR of 1-phenyl-4-(thiophen-2-yl)-1*H*-1,2,3-triazole (**3r**)



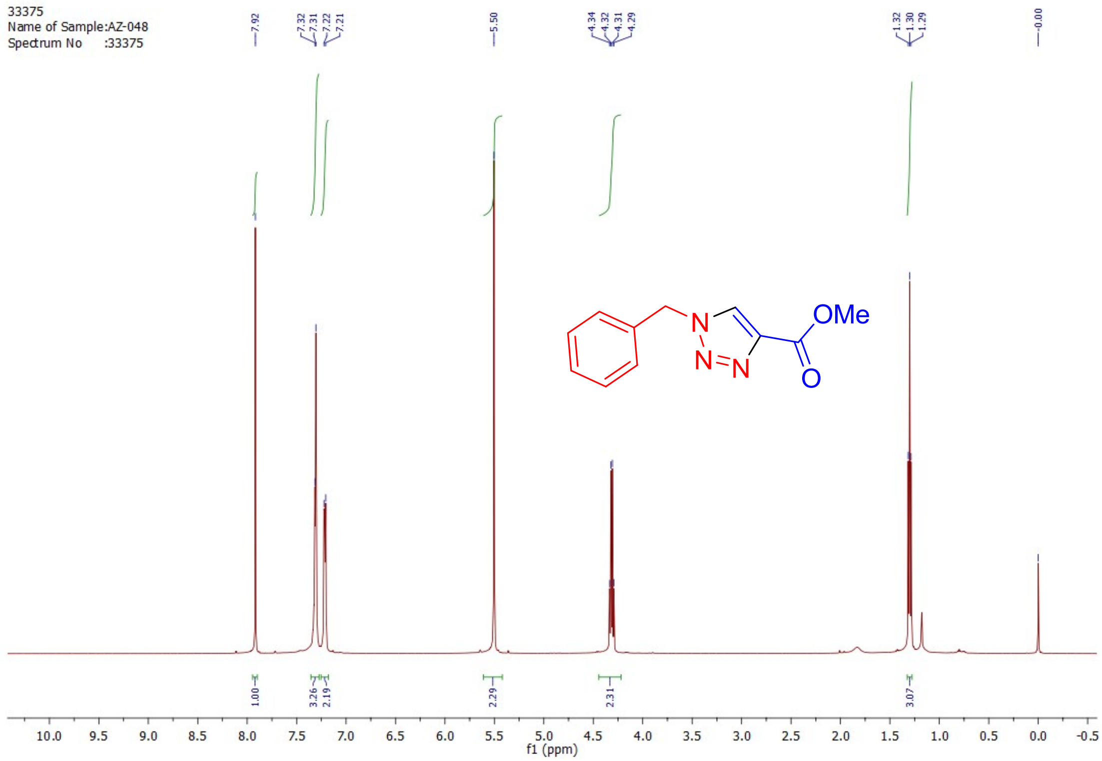


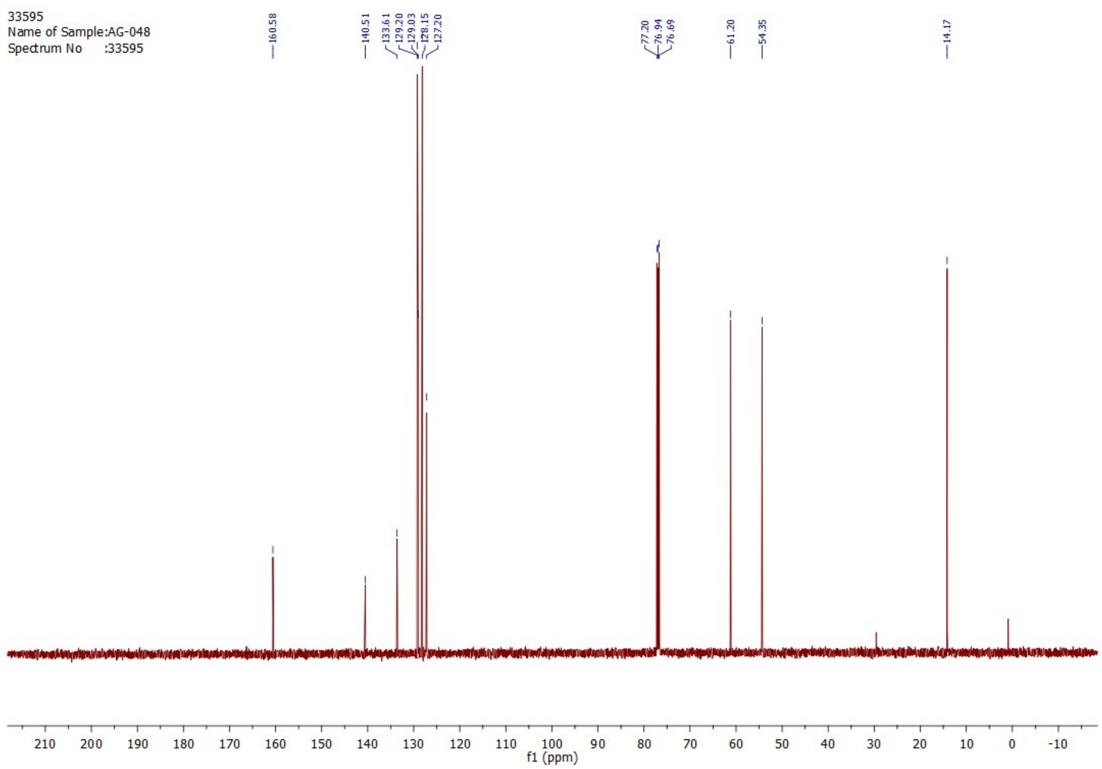
[1]H and [13]C NMR of (1-phenyl-1*H*-1,2,3-triazol-4-yl)methanol (**3s**)



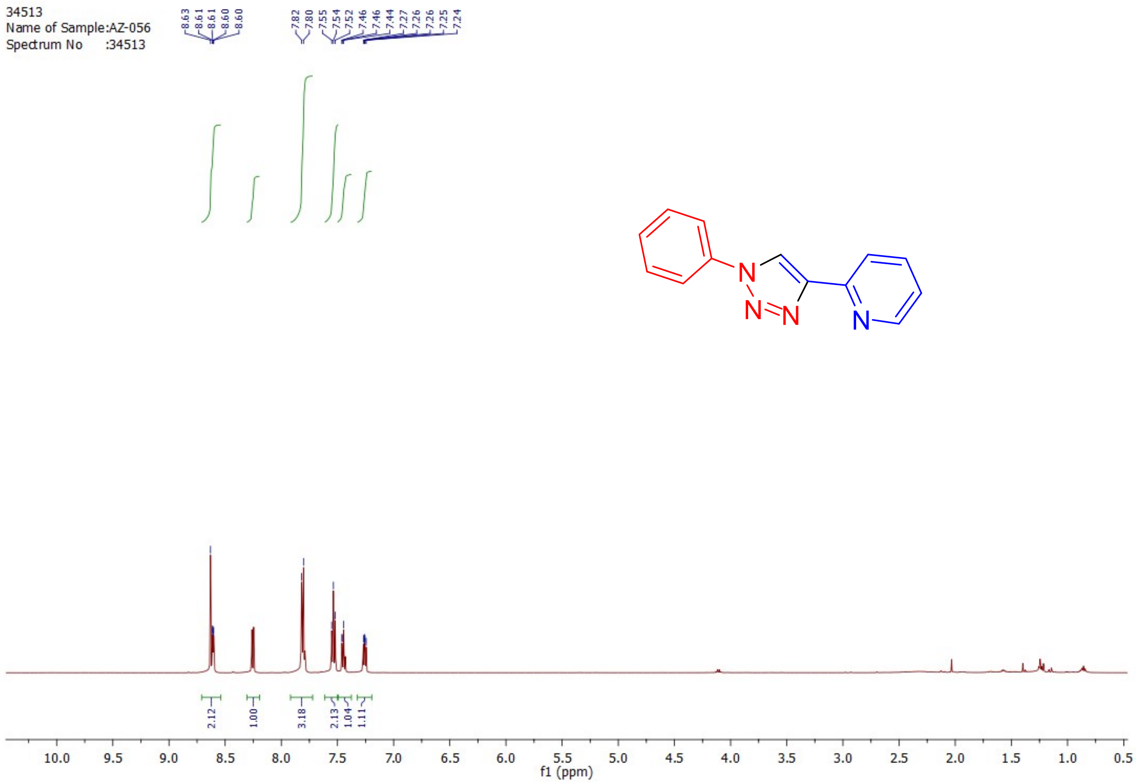


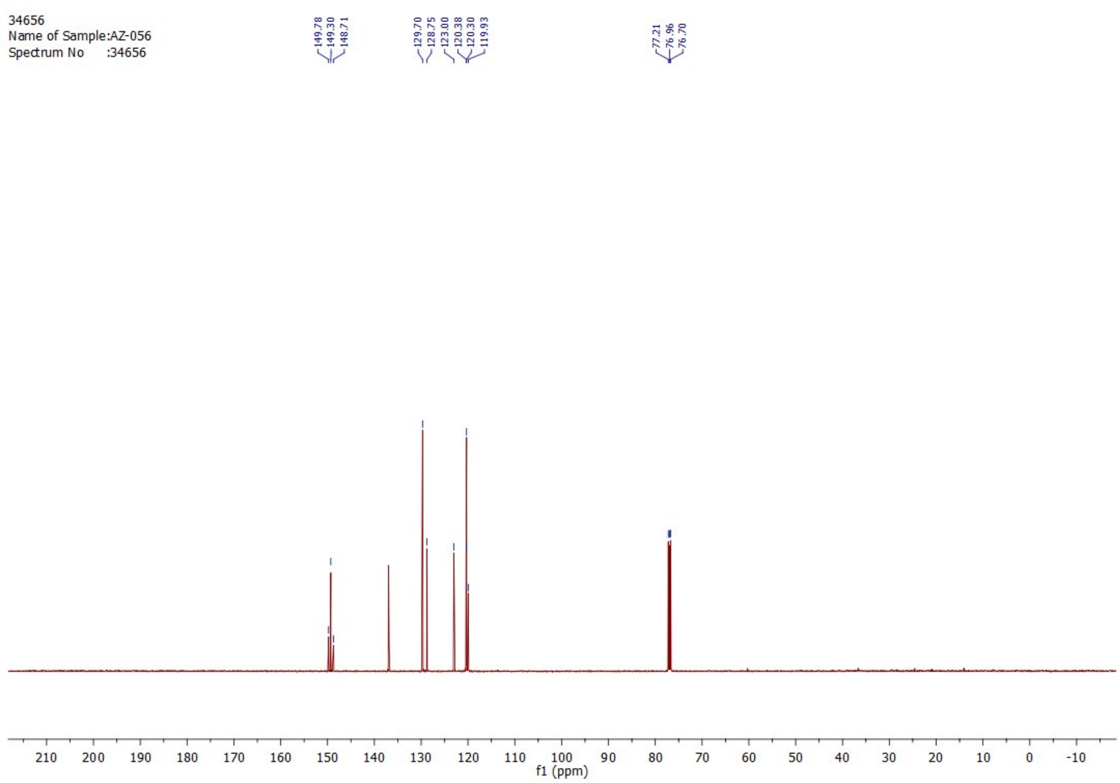
^{1}H and ^{13}C NMR of methyl 1-benzyl-1*H*-1,2,3-triazole-4-carboxylate (**3t**)



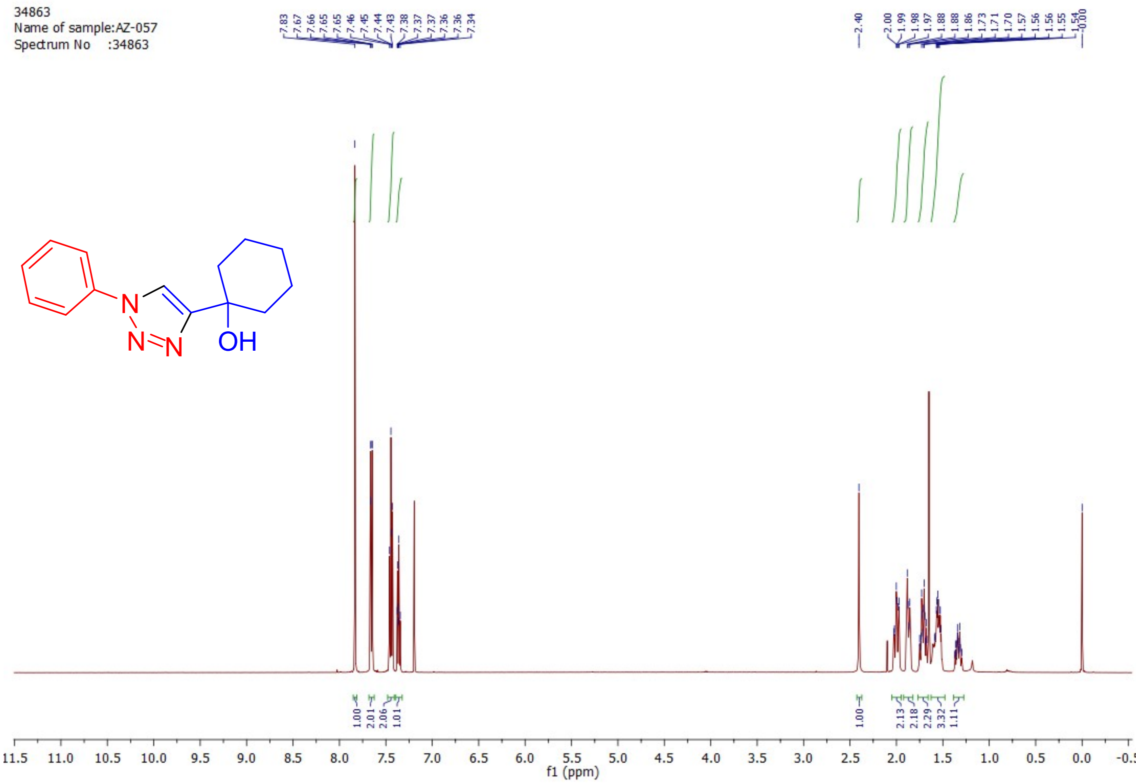


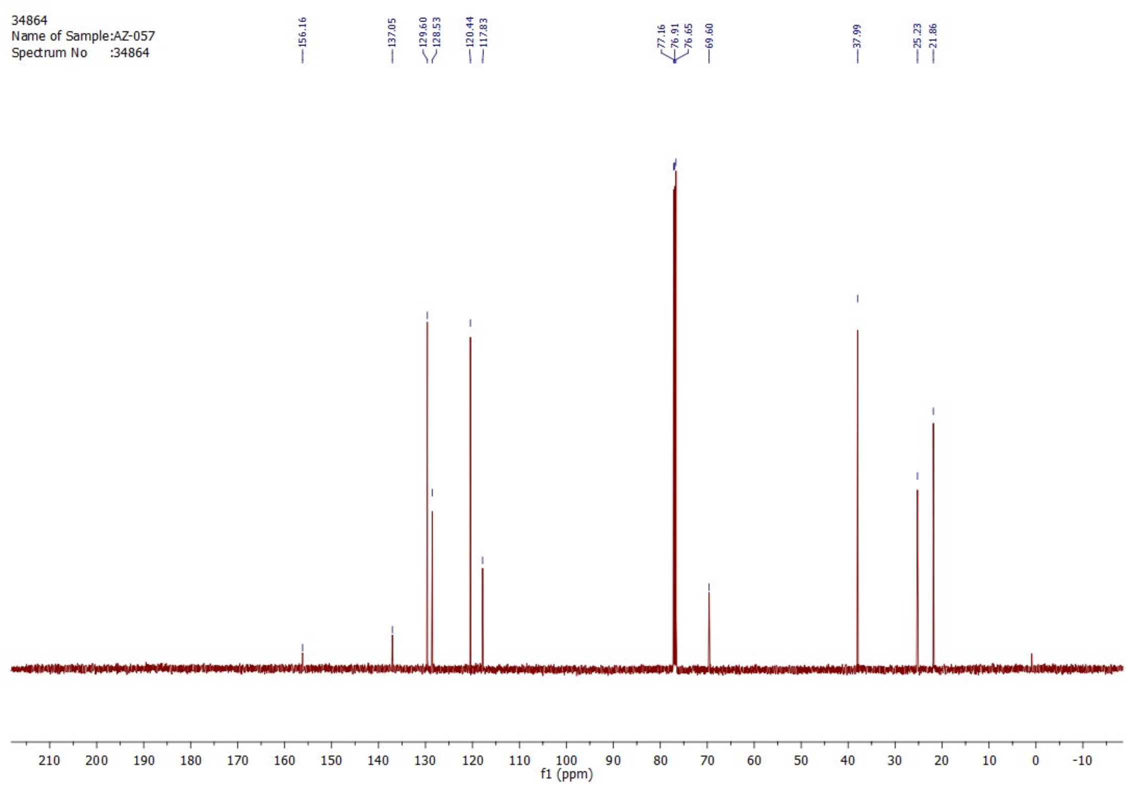
[1]H and [13]C NMR of 2-(1-phenyl-1*H*-1,2,3-triazol-4-yl)pyridine (**4a**)



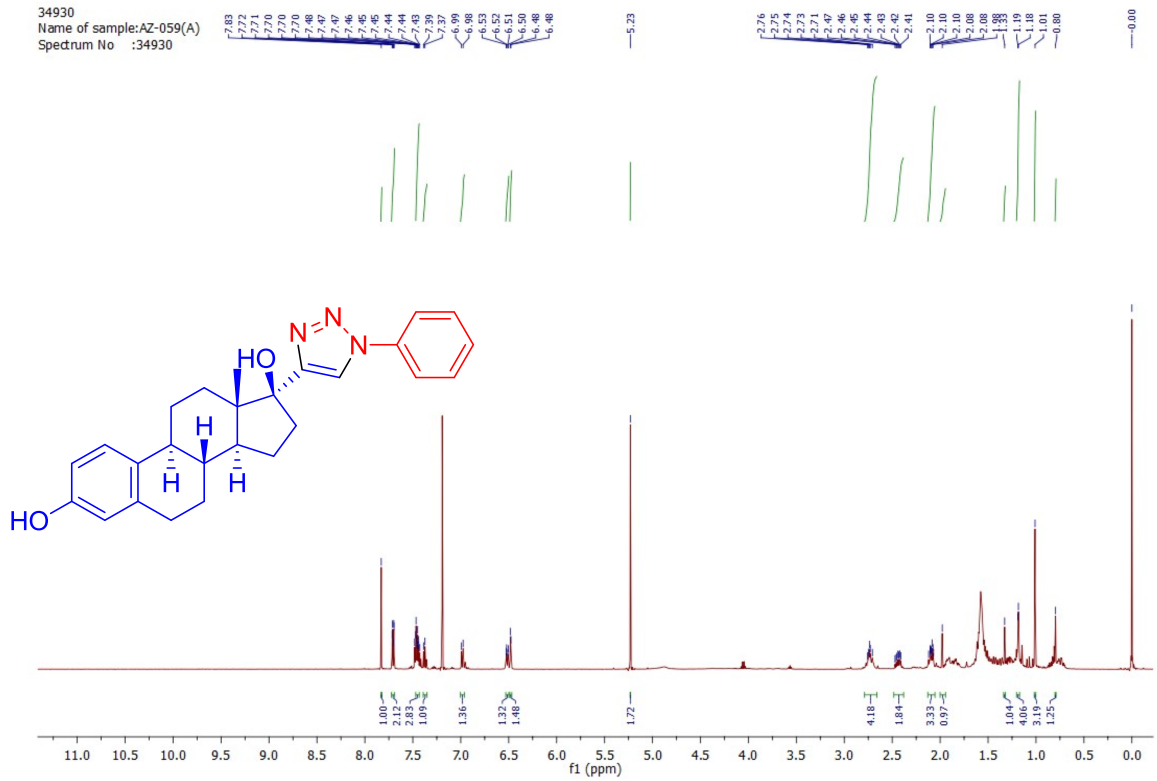


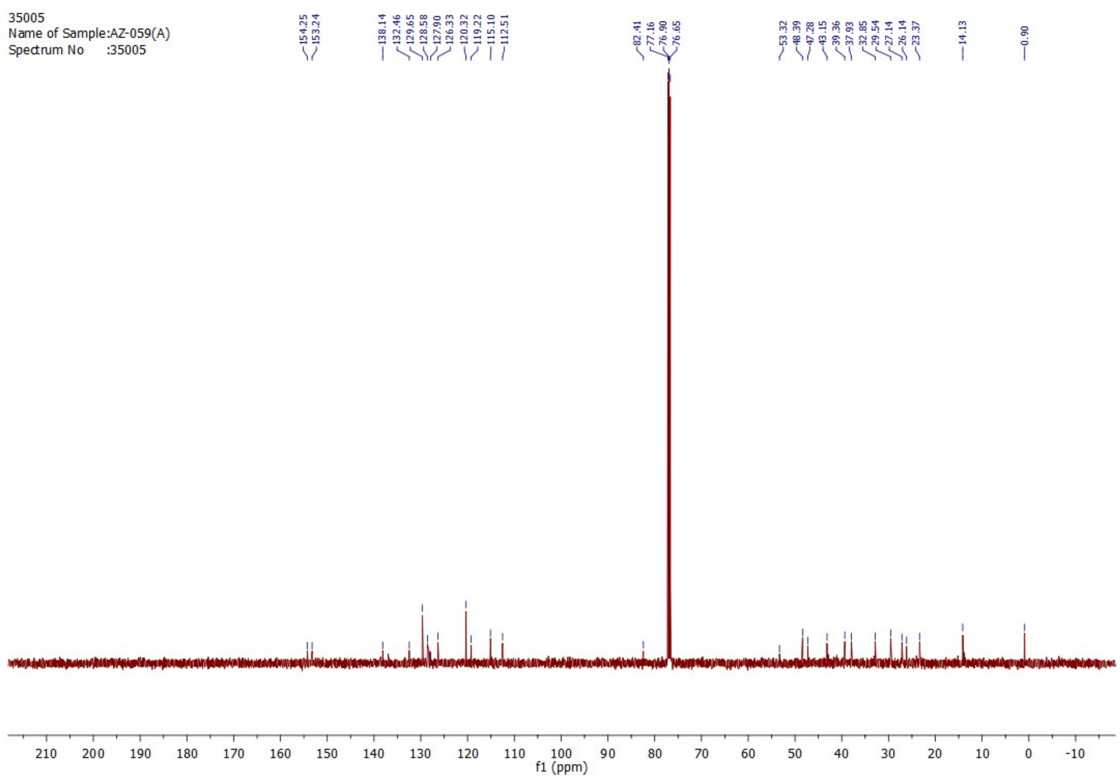
^{1}H and ^{13}C NMR of 1-(1-phenyl-1*H*-1,2,3-triazol-4-yl)cyclohexanol (**4b**)



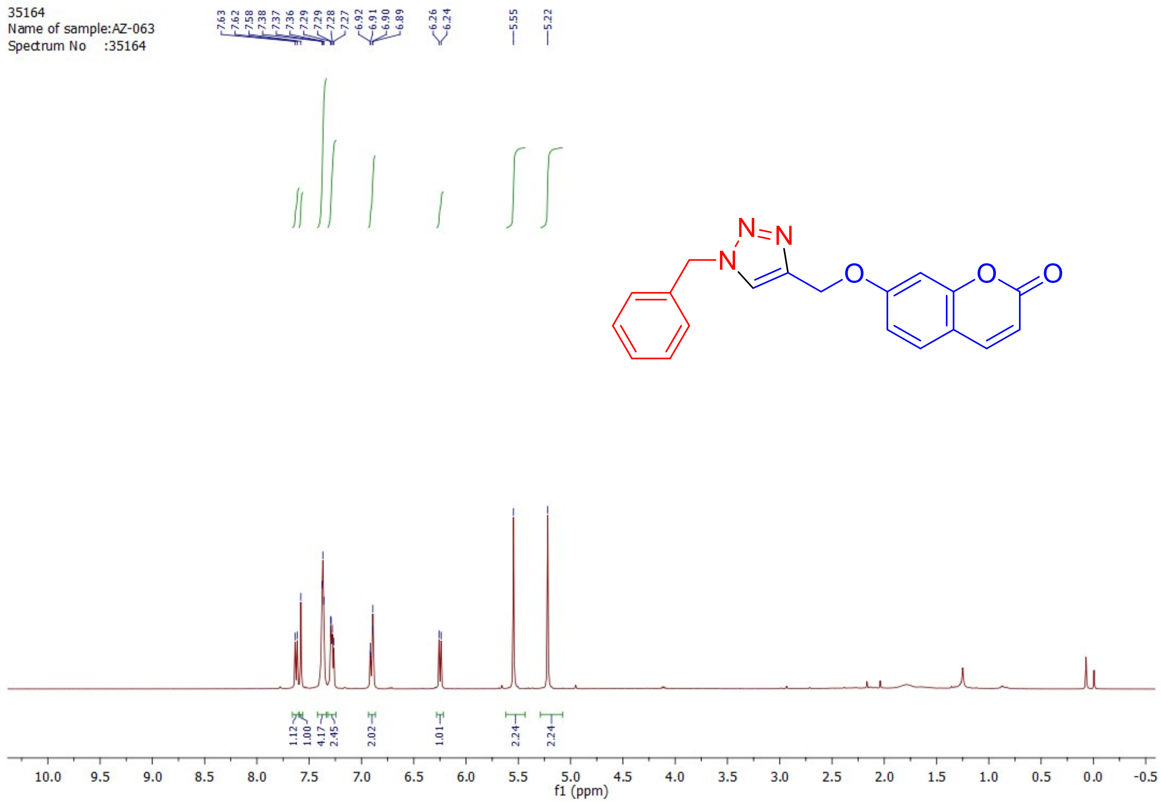


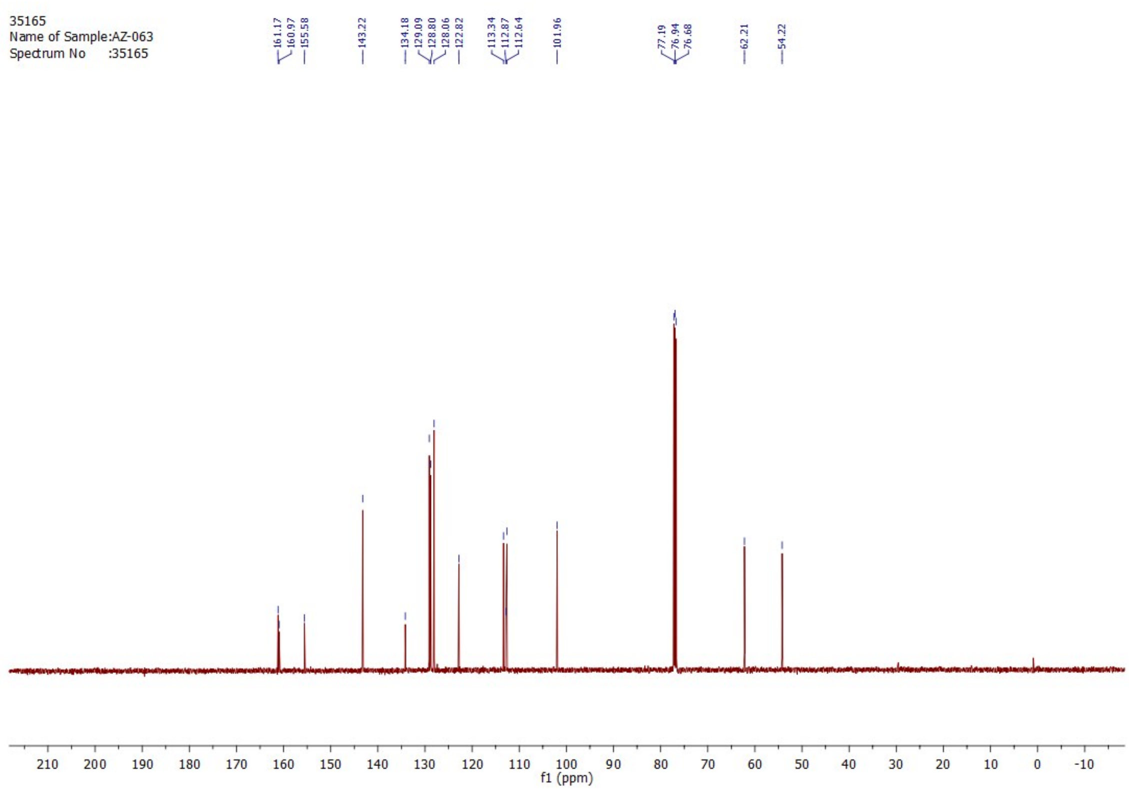
[1]H and [13]C NMR of (8R,9S,13S,14S,17S)-13-methyl-17-(1-phenyl-1*H*-1,2,3-triazol-4-yl)7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene-3,17-diol (**4c**)





^{1}H and ^{13}C NMR of 7-((1-benzyl-1*H*-1,2,3-triazol-4-yl)methoxy)-2H-chromen-2-one (**4d**)





5. References

[1] Y.M. Yamada, S.M. Sarkar, Y. Uozumi, *J. Am. Chem. Soc*. **2012**, *134*, 9285-9290.

[2] C. Deraedt, N. Pinaud, D. Astruc, *J. Am. Chem. Soc*. **2014**, *136*, 12092-12098.

[3] C. Wang, D. Wang, S. Yu, T. Cornilleau, J. Ruiz, L. Salmon, D. Astruc, *ACS Catal.* **2016**, *6*, 5424-5431.