Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic supplementary information

Novel cyano-activated Cu(II) complexes of arylhydrazones of active methylene nitriles and their catalytic application for azide–alkyne cycloaddition in water and glycerol

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1. X-ray data and analysis

Table S1. Crystallographic data and structure refinement details for **1**−**5**.

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{24}H_{24}Cu_2N_8O_8$	$C_{14}H_{12}CuN_6O_3$	$C_{21}H_{20}CuN_6O_5$	$C_{16}H_{13}CuN_5O_3$	$C_{44}H_{34}Cu_3N_{12}O_{10}$
Formula weight	679.59	375.84	499.97	386.85	1081.45
Crystal system	Triclinic	Triclinic	Triclinic	Orthorhombic	Monoclinic
Space group	P-1	P-1	P-1	Pbca	C2/c
a (Å)	9.3312(17)	8.3848(3)	8.6551(13)	7.5563(2)	30.947(5)
b (Å)	9.3618(19)	8.9939(4)	10.2932(18)	19.9231(4)	8.1219(10)
c (Å)	9.4050(15)	11.1413(5)	12.572(2)	19.9344(4)	20.211(2)
α (º)	60.556(6)	102.733(2)	71.796(6)	90	90
β (º)	76.213(6)	90.338(2)	79.500(6)	90	101.999(7)
γ (º)	68.001(7)	113.054(2)	82.626(6)	90	90
V (Å^3)	661.9(2)	750.08(6)	1043.1(3)	3001.02(12)	4969.1(11)
Z	1	2	2	8	4
D_{calc} (g/cm^3)	1.705	1.664	1.592	1.712	1.446
F000	346	382	514	1576	2196
μ (mm^{-1})	1.672	1.483	1.096	1.484	1.338
Rfl. measured	14352	25094	23523	28483	35267
Obs / Unique rfl.	2446 / 2728	2891 / 3032	3498 / 4283	2692 / 3074	2508 / 4626
Nº parameters	192	218	299	227	314
R_{int}	0.0579	0.0316	0.0837	0.0326	0.0993
$R(F)$ ($I \geq 2\sigma$)	0.0274	0.0207	0.0395	0.0249	0.0522
wR (F^2) (all data)	0.0698	0.0580	0.0871	0.0695	0.1590
GOF (F^2)	1.044	1.055	1.020	1.074	0.986

Table S2. Selected bond distances (Å) and angles (º) for **1**-**5**.

1[a]		**2**		**3**	
Cu1−O2	1.932(2)	Cu1−O1	1.911(1)	Cu1−N1	1.951(3)
Cu1−O2^{i}	2.105(2)	Cu1−N1	1.930(1)	Cu1−N3	1.970(2)
Cu1−Cu1^{i}	3.1905(7)	Cu1−N3	1.960(1)	Cu1−N5	2.055(2)
Cu1−O4	2.283(2)	Cu1−N5	1.992(1)	Cu1−O1	1.932(2)
Cu1−N1	1.913(2)	C1−N1	1.280(2)	Cu1−O4	2.343(2)
Cu1−N3	1.963(2)	C1−C2	1.450(2)	C1−N1	1.282(4)
N2−N3	1.310(3)	N2−N3	1.305(2)	C1−C2	1.453(3)
C1−N1	1.281(4)	C2−N2	1.321(2)	C2−N2	1.327(4)
C1−C2	1.449(3)	O1−Cu1−N5	89.32(5)	N2−N3	1.300(4)
C2−N2	1.321(3)	N1−Cu1−N5	91.77(6)	O1−Cu1−O4	106.60(7)
O2−Cu1−O2^{i}	75.65(7)	N1−Cu1−N3	92.21(6)	O1−Cu1−N1	145.83(9)
Cu1−O2−Cu1^{i}	104.35(8)	O1−Cu1−N3	94.19(5)	O1−Cu1−N3	92.56(9)
O2−Cu1−O4	93.57(7)	O1−Cu1−N1	155.20(6)	O1−Cu1−N5	89.16(9)
O2^{i}−Cu1−O4	89.28(6)	N3−Cu1−N5	162.41(6)	N1−Cu1−N5	89.3(1)
O2−Cu1−N3	95.25(7)			N1−Cu1−N3	91.3(1)
N1−Cu1−N3	92.80(8)			O4−Cu1−N1	107.30(9)
N1−Cu1−O2^{i}	94.61(7)			O4−Cu1−N3	90.51(8)
N1−Cu1−O2	165.76(8)			O4−Cu1−N5	85.62(8)
N3−Cu1−O2^{i}	168.02(7)				
4[b]		**5**[c]			
Cu1−O1	1.889(1)	Cu1−O1	1.888(4)		
Cu1−N1	1.938(1)	Cu1−N1	1.947(4)		
Cu1−N3	1.966(1)	Cu1−N3	1.929(4)		
Cu1−N4^{i}	2.597(2)	Cu1−N5	2.041(5)		
Cu1−N5	2.031(1)	N1−N2	1.314(5)		
C1−N1	1.279(2)	C13−N2	1.309(6)		
C1−C2	1.457(2)	C14−N3	1.280(7)		
C2−N2	1.327(2)	C13−N14	1.439(8)		
N2−N3	1.308(2)	Cu2−O3	2.411		
N1−Cu1−N3	92.78(6)	Cu2−O4	2.045		
N1−Cu1−N4^{i}	92.28(5)	Cu2−N6	1.998		
N1−Cu1−N5	89.36(6)	Cu1−Cu2	9.186		
N1−Cu1−O1	162.20(6)	N1−Cu1−O1	92.6(2)		
N3−Cu1−O1	93.44(6)	N3−Cu1−O1	164.9(2)		
N4^{i}−Cu1−O1	105.00(5)	N5−Cu1−O1	84.1(2)		
N5−Cu1−O1	86.00(6)	N1−Cu1−N3	93.7(2)		
N3−Cu1−N5	174.48(6)	N1−Cu1−N5	169.0(2)		
		N3−Cu1−N5	92.0(2)		
		N6−Cu2−O4	91.0		
		N6−Cu2−O3	93.7		
		N6−Cu2−N6^{i}	180.0		
		O3−Cu2−O4	59.1		
		O3−Cu2−O4^{i}	120.9		
		N6−Cu2−O3^{i}	86.3		
		N6−Cu2−O4^{i}	89.0		

[a] (*i*) -x,1-y,1-z. [b] (*i*) -1/2x,y,1/2-z. [c] (*i*) 1-x,2-y,1-z.

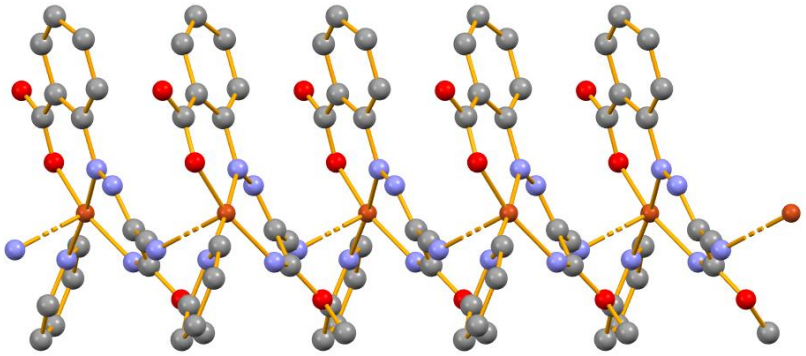

Figure S1. A structural fragment showing the 1D polymeric nature of **4**. Hydrogens in the bottom figure are omitted for clarity.

Table S3. Hydrogen bonding distances (Å) and angles (°) for for **1** - **5**.[a]

D–H···A	D–H	H···A	D···A	D–H···A
1				
O4–H4O···N4^{i}	0.850	1.959	2.805(4)	173.5
N1–H1N···O1^{ii}	0.900	1.914	2.707(2)	146.0
2				
N6–H6N···O2^{i}	0.882	1.937	2.812(2)	171.6
N1–H1N···O2^{ii}	0.882	2.093	2.927(2)	157.5
3				
O4–H4B···O5^{i}	0.850	2.014	2.853(3)	168.9
O4–H4A···O5^{ii}	0.850	2.043	2.869(3)	164.0
O5–H5A···N6^{iii}	0.850	1.961	2.808(3)	174.4
N5–H5B···O2	0.850	1.971	2.770(3)	156.3
N1–H1N···O2^{iv}	0.875	2.169	2.997(3)	157.9
4				
N1–H1N···O2^{i}	0.918	2.062	2.967(2)	168.49
5				
N3–H3N···O2^{i}	0.860	2.141	2.996(6)	172.7

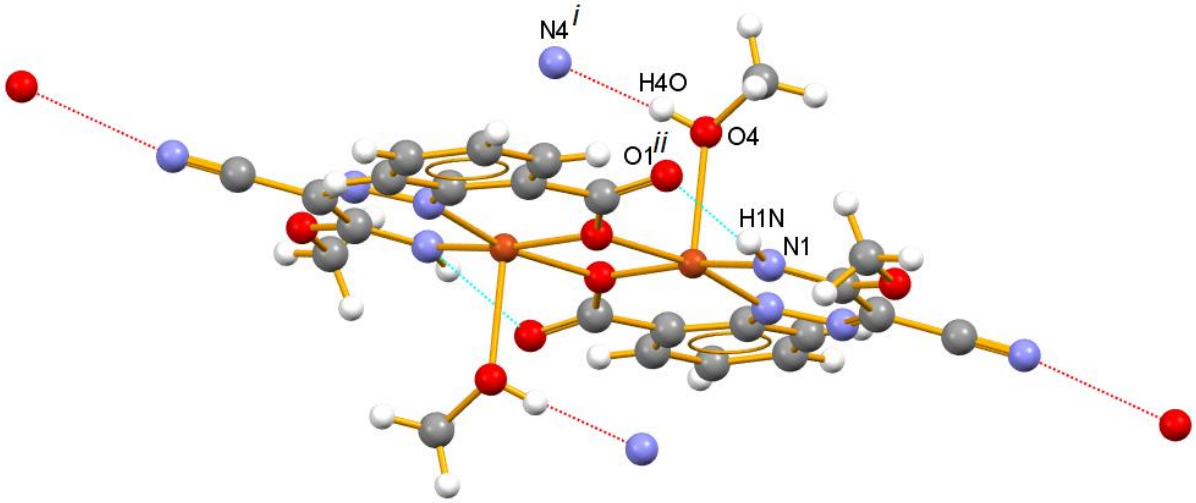

Figure S2. Hydrogen bond interactions in the structure of **1**.Symmetry operations to generate equivalent atoms: (*i*) -1+x,y,z. (*ii*) -x,1-y,1-z.

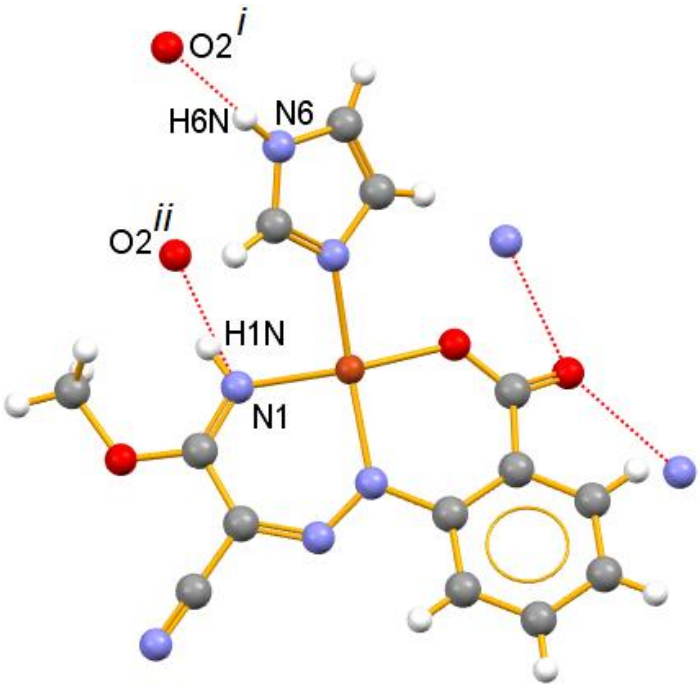

Figure S3. Hydrogen bond interactions in the structure of **2**. Symmetry operations to generate equivalent atoms: (*i*) 1+x,1+y,z. (*ii*) 1-x,1-y,2-z.

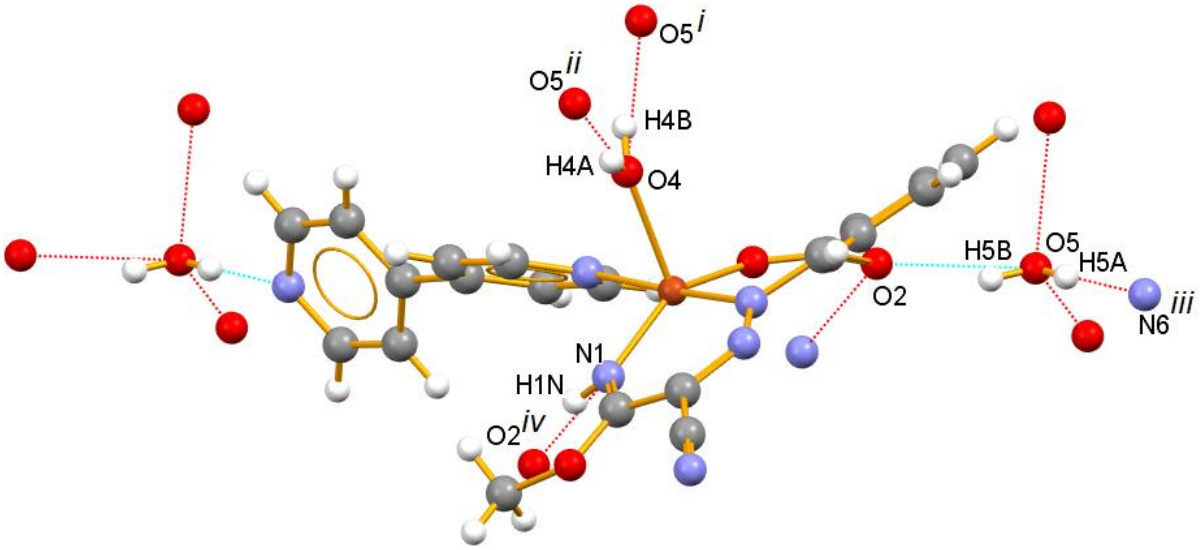

Figure S4. Hydrogen bond interactions in the structure of **3**. Symmetry operations to generate equivalent atoms: (*i*) 2-x,1-y,1-z. (*ii*) x,-1+y,z. (*iii*) 1+x,1+y,-1+z. (*iv*) 1-x,1-y,1-z.

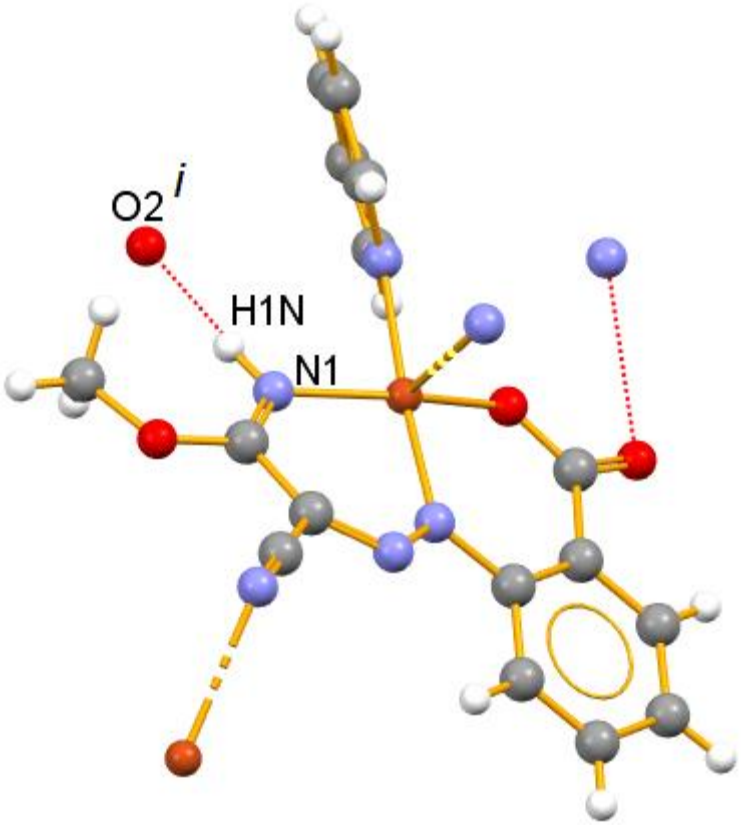

Figure S5. Hydrogen bond interactions in the structure of **4**. Symmetry operations to generate equivalent atoms: (*i*) 1/2+x,1.5-y,1-z.

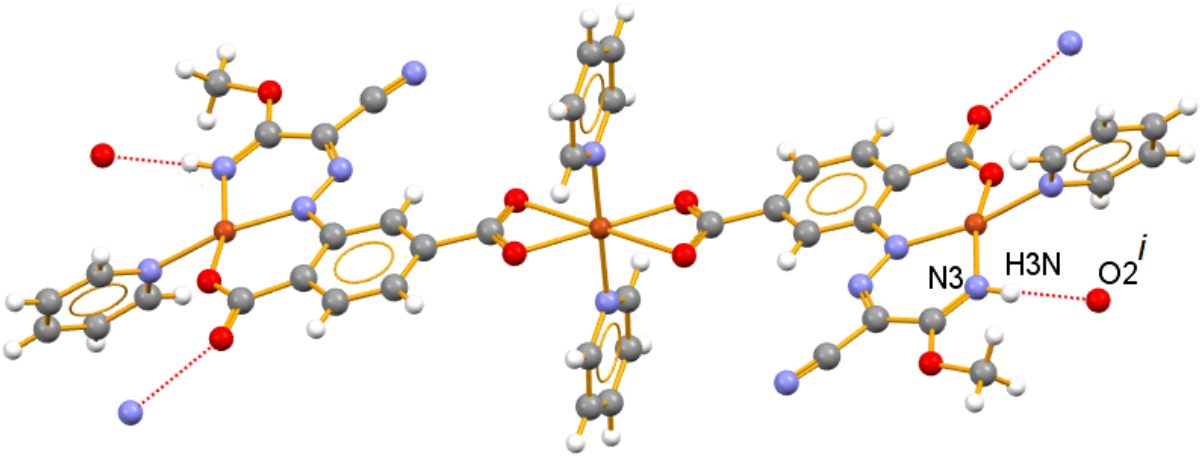

Figure S6. Hydrogen bond interactions in the structure of **5**. Symmetry operations to generate equivalent atoms: (*i*) 1.5-x,-1/2+y,1/2-z.

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

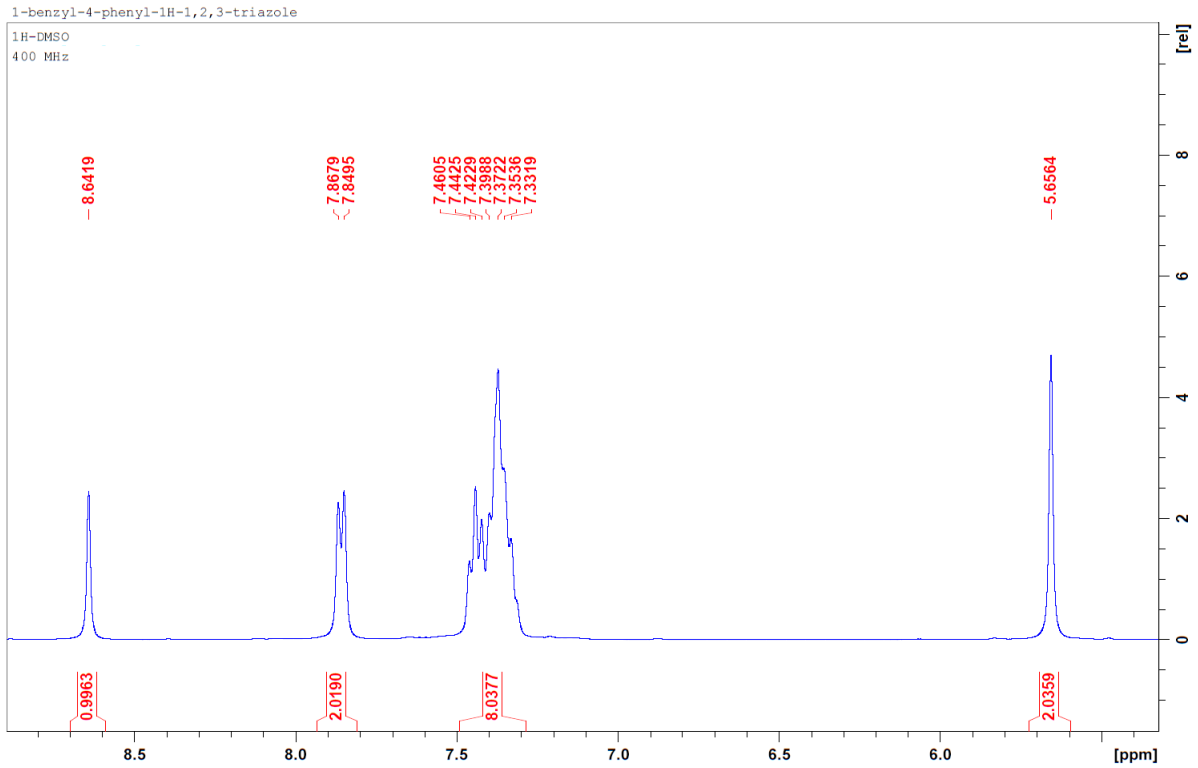

Figure S7. ^{1}H-NMR of 1-benzyl-4-phenyl-1*H*-1,2,3-triazole (Table 2, entry 1) obtained in $(CD_3)_2SO$.

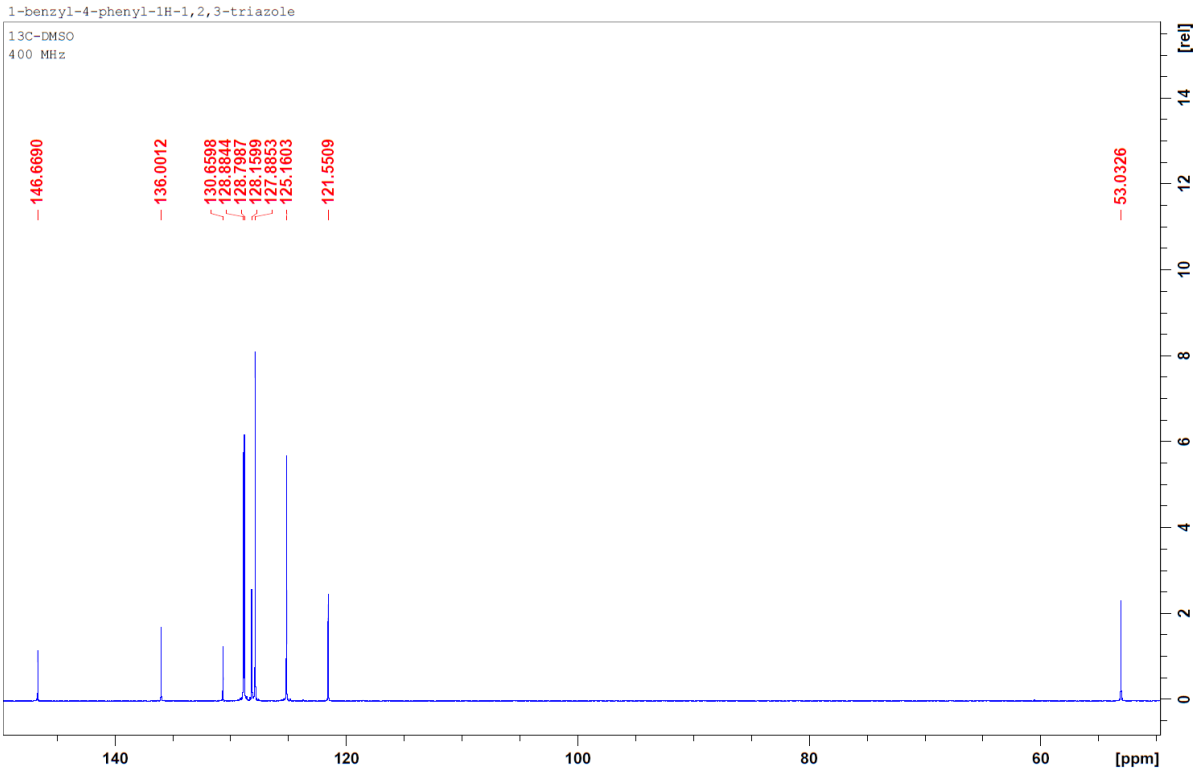

Figure S8. ^{13}C-NMR of 1-benzyl-4-phenyl-1*H*-1,2,3-triazole (Table 2, entry 1) obtained in $(CD_3)_2SO$.

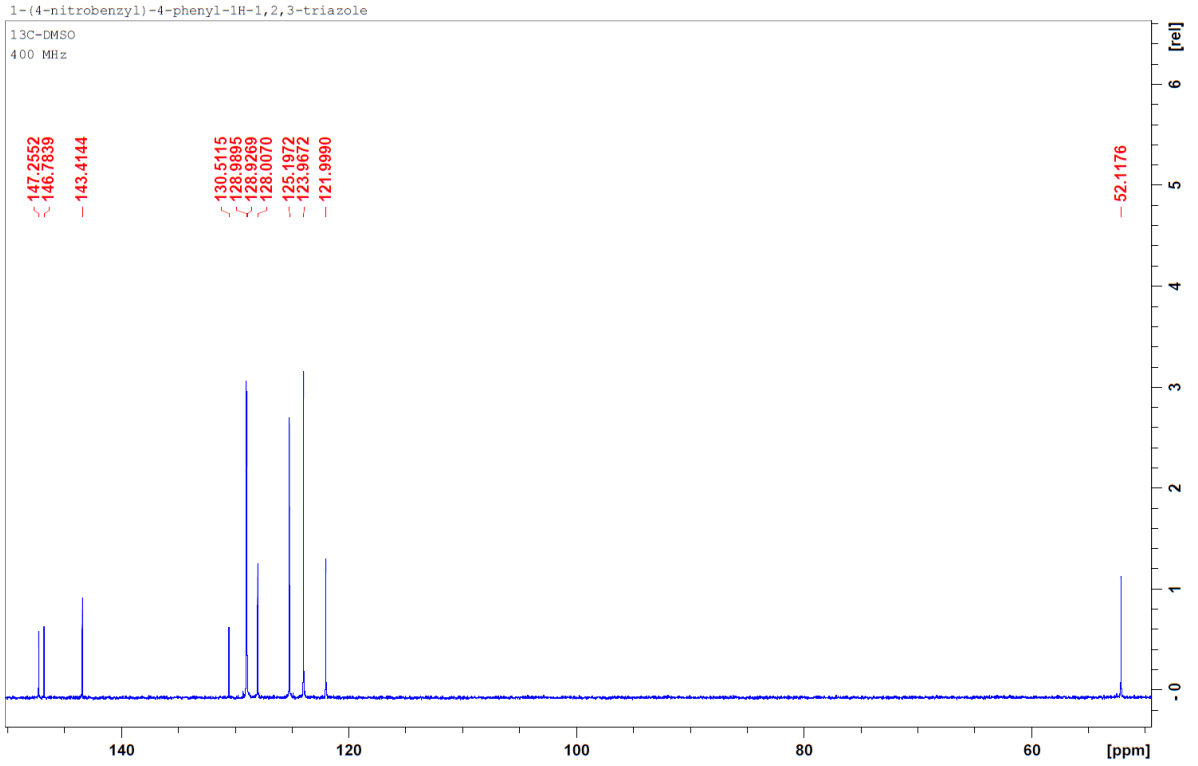

Figure S9. ^{1}H-NMR of 1-(4-nitrobenzyl)-4-phenyl-1*H*-1,2,3-triazole (Table 2, entry 2) obtained in $(CD_3)_2SO$.

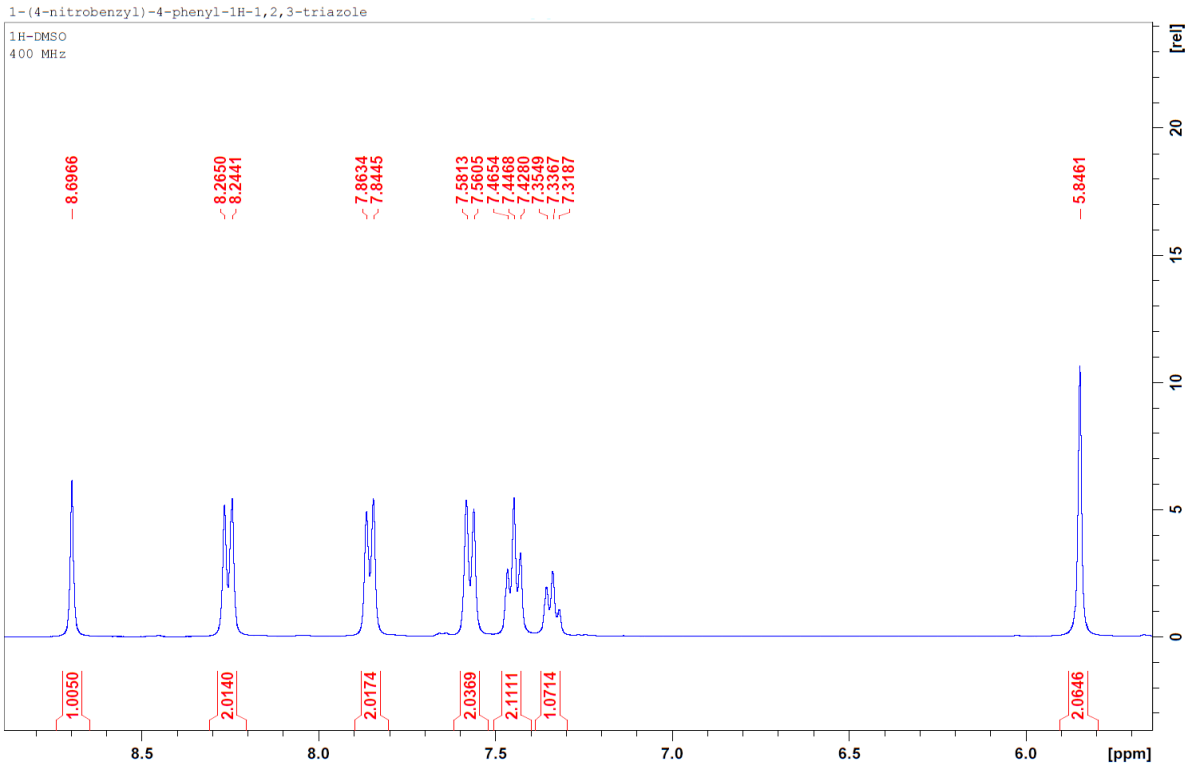

Figure S10. ^{13}C-NMR of 1-(4-nitrobenzyl)-4-phenyl-1*H*-1,2,3-triazole (Table 2, entry 2) obtained in $(CD_3)_2SO$.

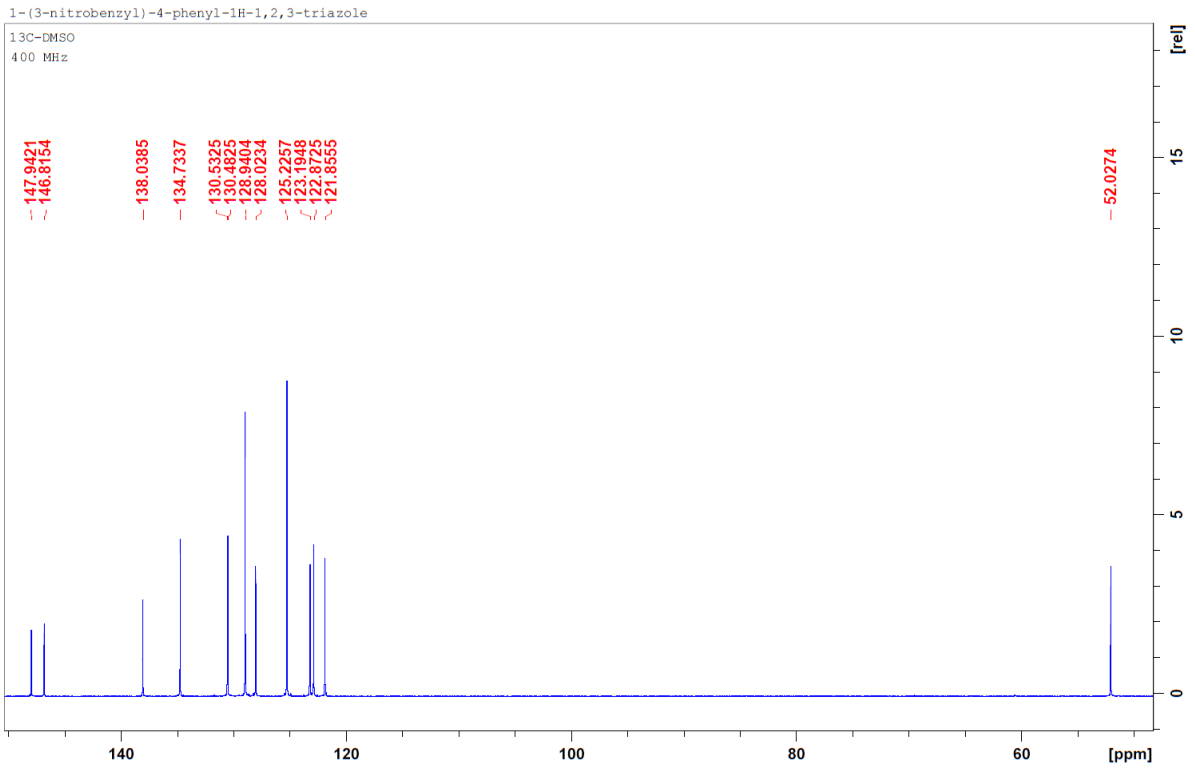

Figure S11. ^{1}H-NMR of 1-(3-nitrobenzyl)-4-phenyl-1*H*-1,2,3-triazole (Table 2, entry 3) obtained in $(CD_3)_2SO$.

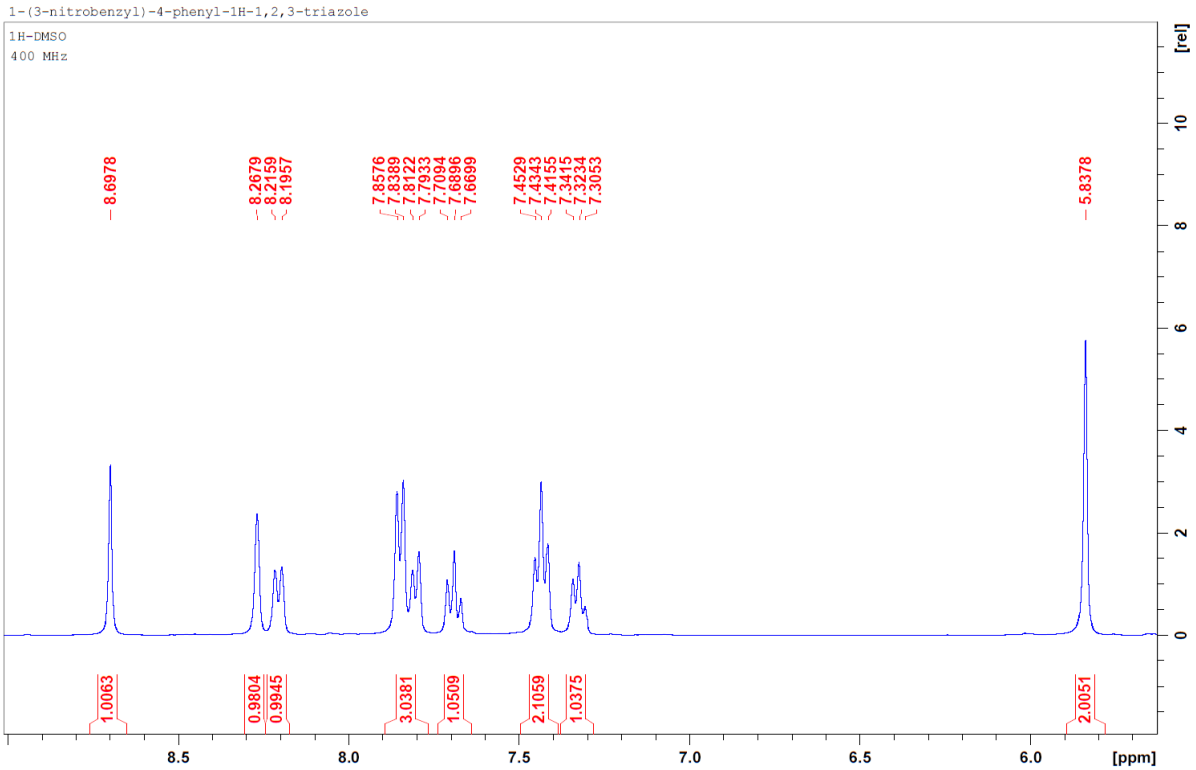

Figure S12. ^{13}C-NMR of 1-(3-nitrobenzyl)-4-phenyl-1*H*-1,2,3-triazole (Table 2, entry 3) obtained in $(CD_3)_2SO$.

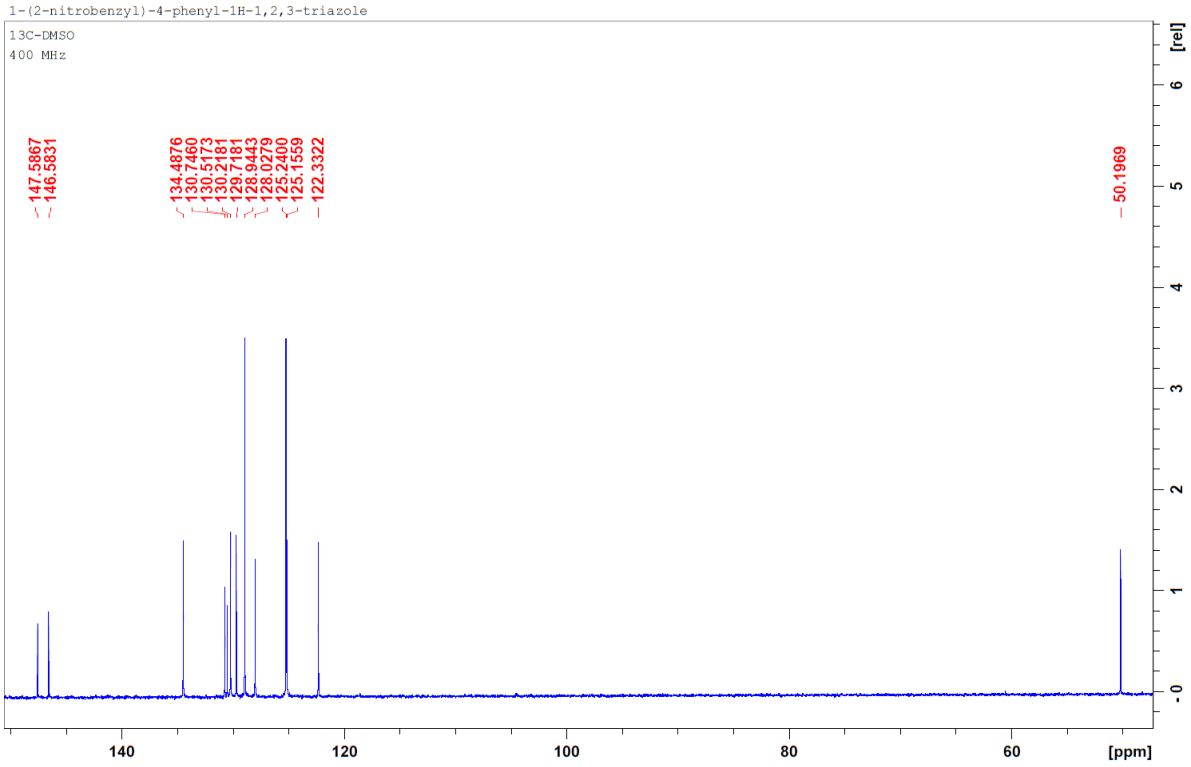

Figure S13. ^{1}H-NMR of 1-(2-nitrobenzyl)-4-phenyl-1*H*-1,2,3-triazole (Table 2, entry 4) obtained in $(CD_3)_2SO$.

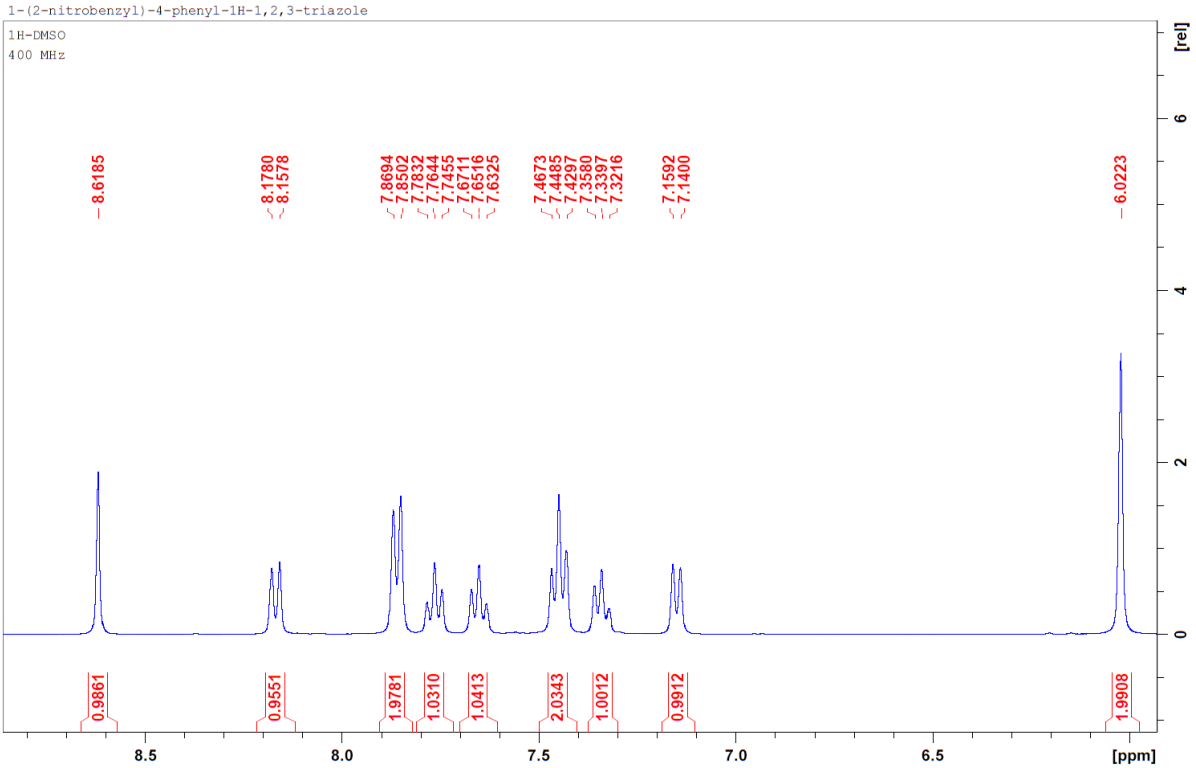

Figure S14. ^{13}C-NMR of 1-(2-nitrobenzyl)-4-phenyl-1*H*-1,2,3-triazole (Table 2, entry 4) obtained in $(CD_3)_2SO$.

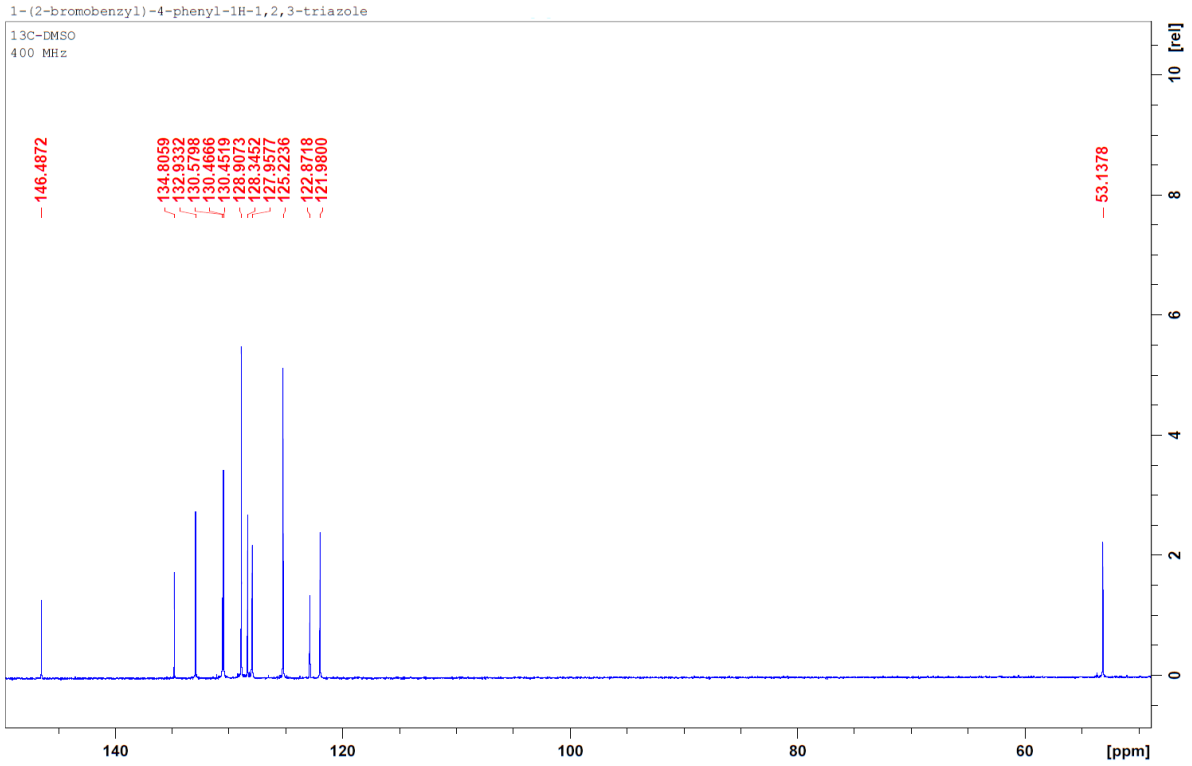

Figure S15. ^{1}H-NMR of 1-(2-bromobenzyl)-4-phenyl-1*H*-1,2,3-triazole (Table 2, entry 6) obtained in $(CD_3)_2SO$.

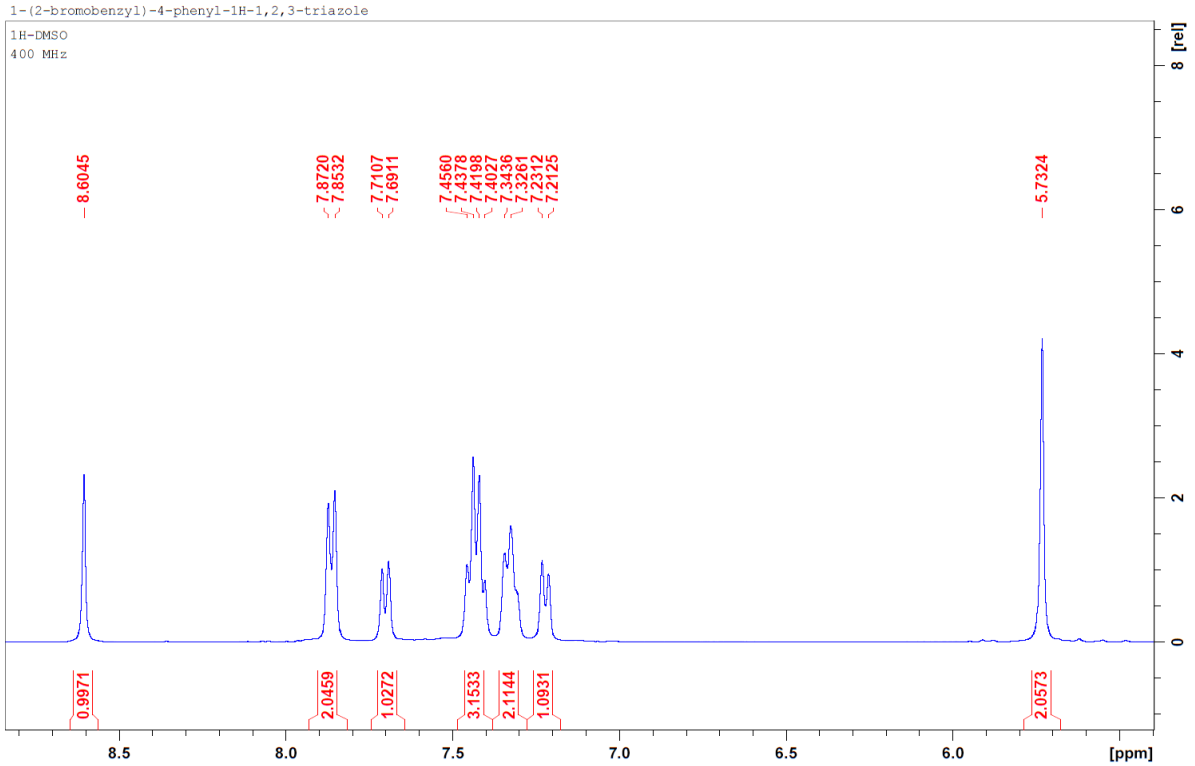

Figure S16. ^{13}C-NMR of 1-(2-bromobenzyl)-4-phenyl-1*H*-1,2,3-triazole (Table 2, entry 6) obtained in $(CD_3)_2SO$.

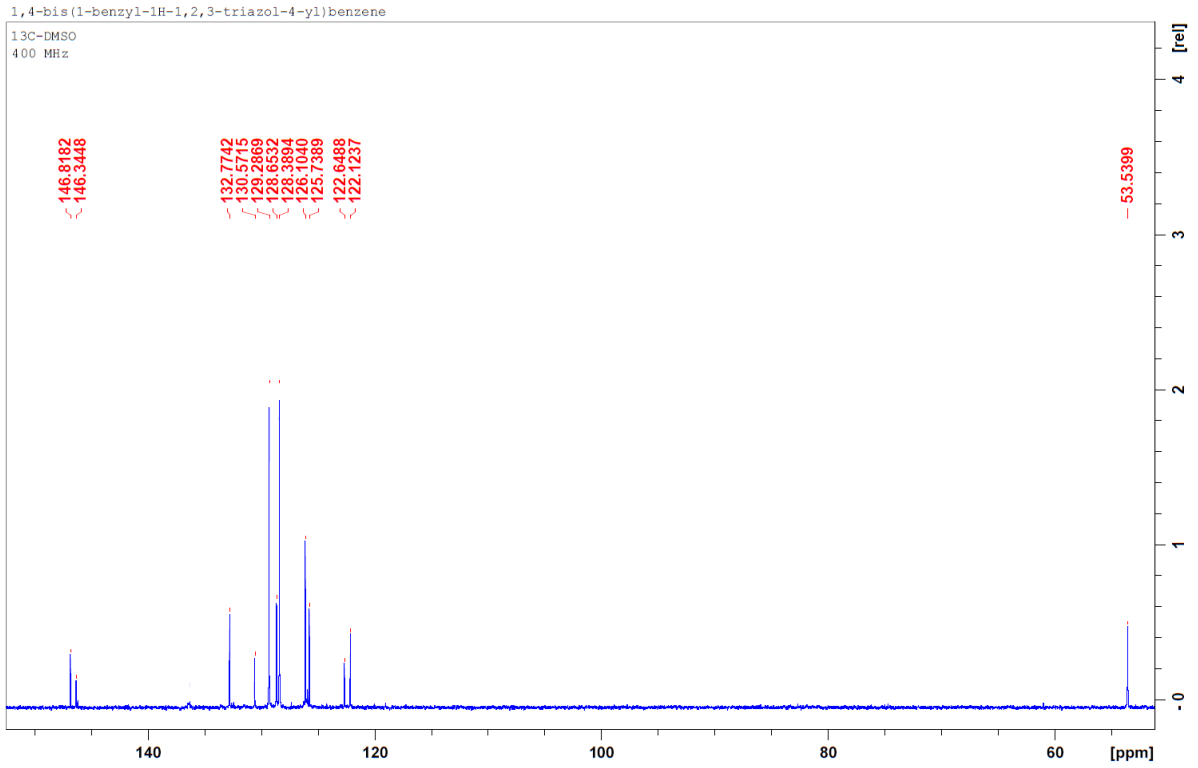

Figure S17. ^{1}H-NMR of 1,4-bis(1-benzyl-1*H*-1,2,3-triazol-4-yl)benzene (Table 2, entry 7) obtained in $(CD_3)_2SO$.

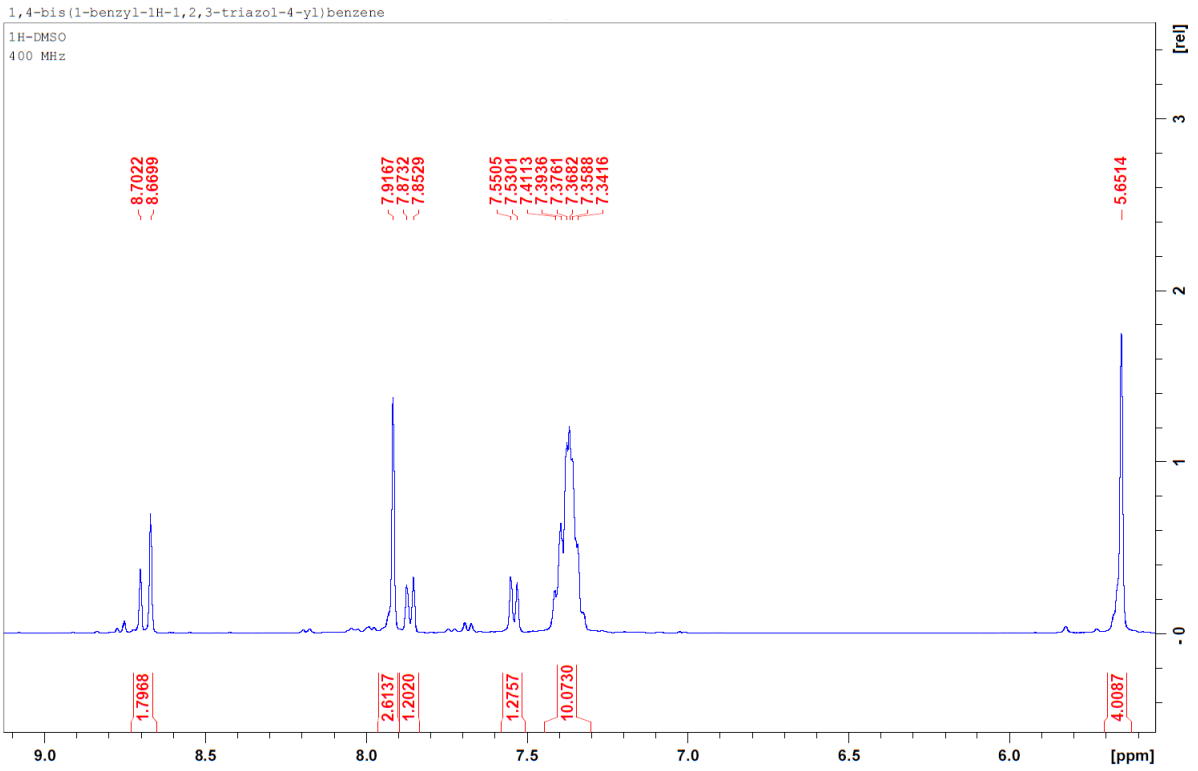

Figure S18. ^{13}C-NMR of 1,4-bis(1-benzyl-1*H*-1,2,3-triazol-4-yl)benzene (Table 2, entry 7) obtained in $(CD_3)_2SO$.

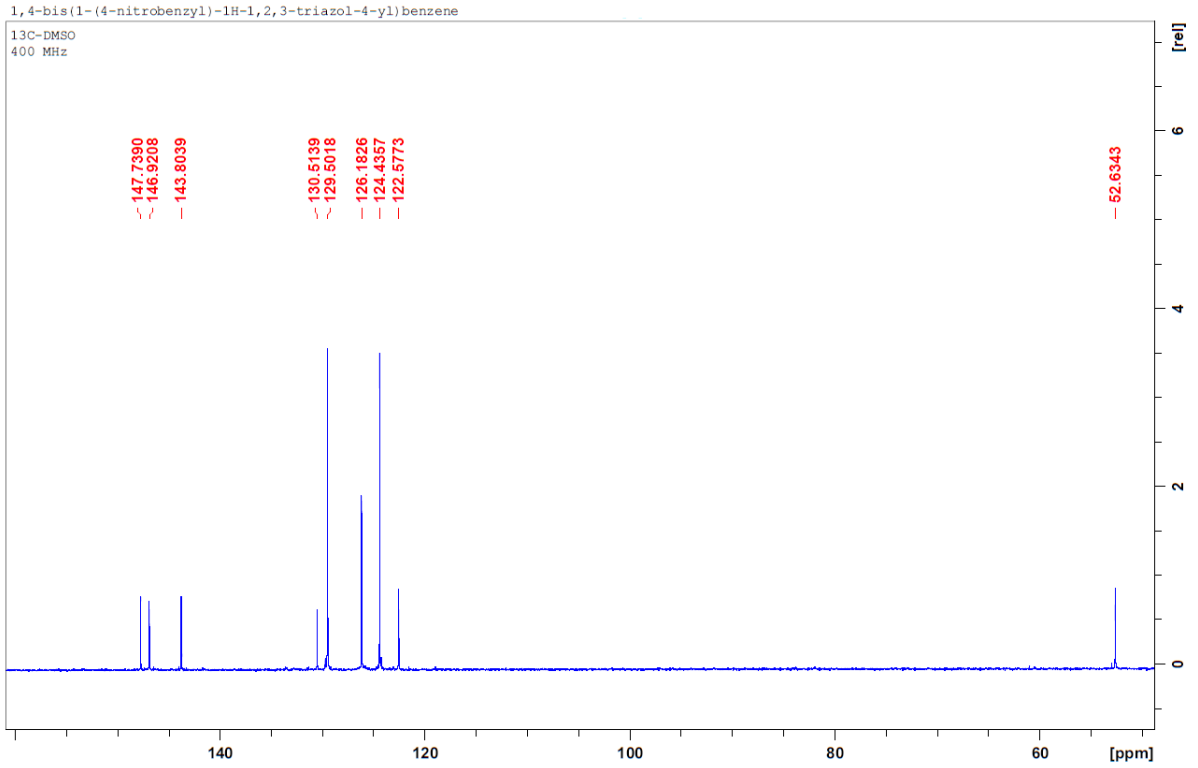

Figure S19. ^{1}H-NMR of 1,4-bis(1-(4-nitrobenzyl)-1*H*-1,2,3-triazol-4-yl)benzene (Table 2, entry 8) obtained in $(CD_3)_2SO$.

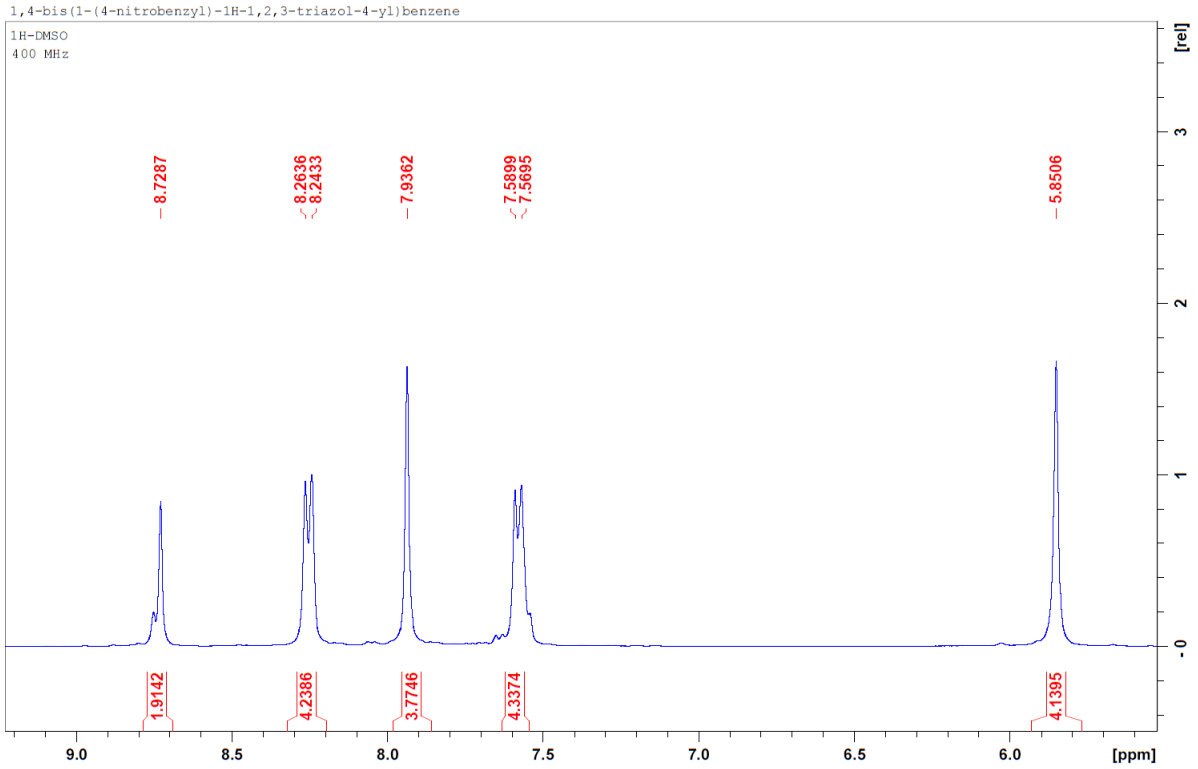

Figure S20. ^{13}C-NMR of 1,4-bis(1-(4-nitrobenzyl)-1*H*-1,2,3-triazol-4-yl)benzene (Table 2, entry 8) obtained in $(CD_3)_2SO$.

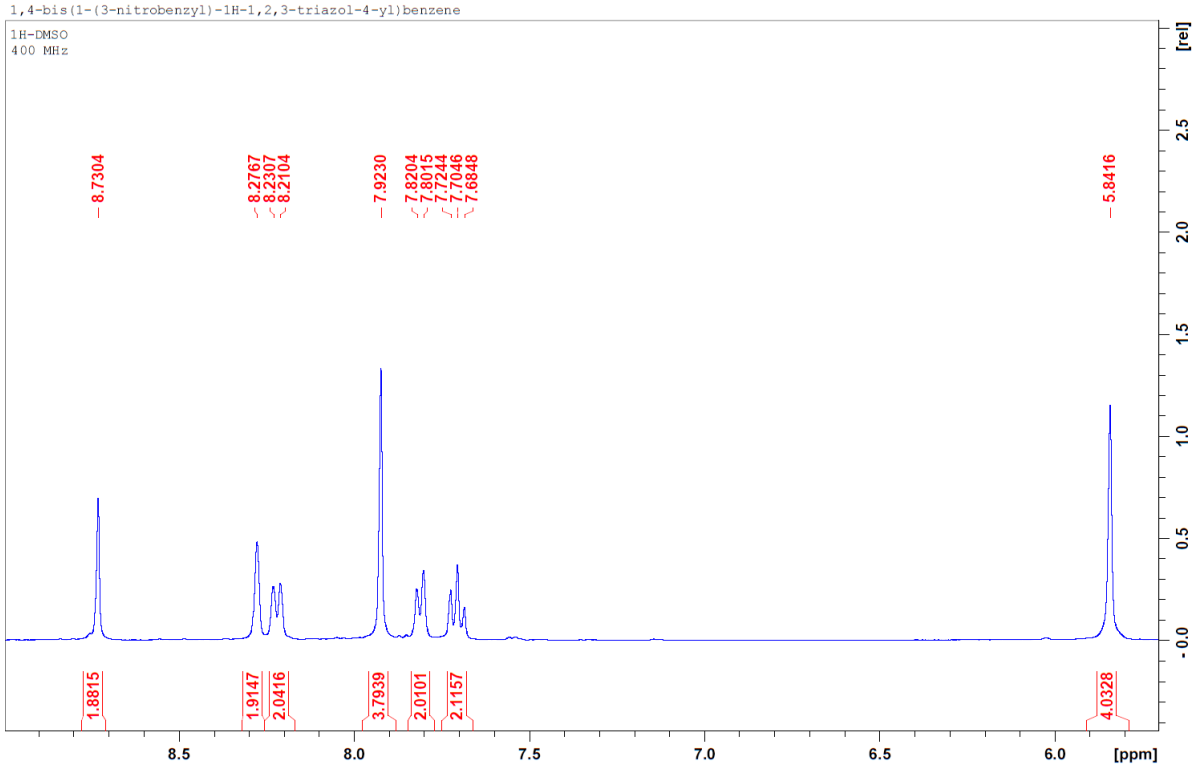

Figure S21. ^{1}H-NMR of 1,4-bis(1-(3-nitrobenzyl)-1*H*-1,2,3-triazol-4-yl)benzene (Table 2, entry 9) obtained in $(CD_3)_2SO$.

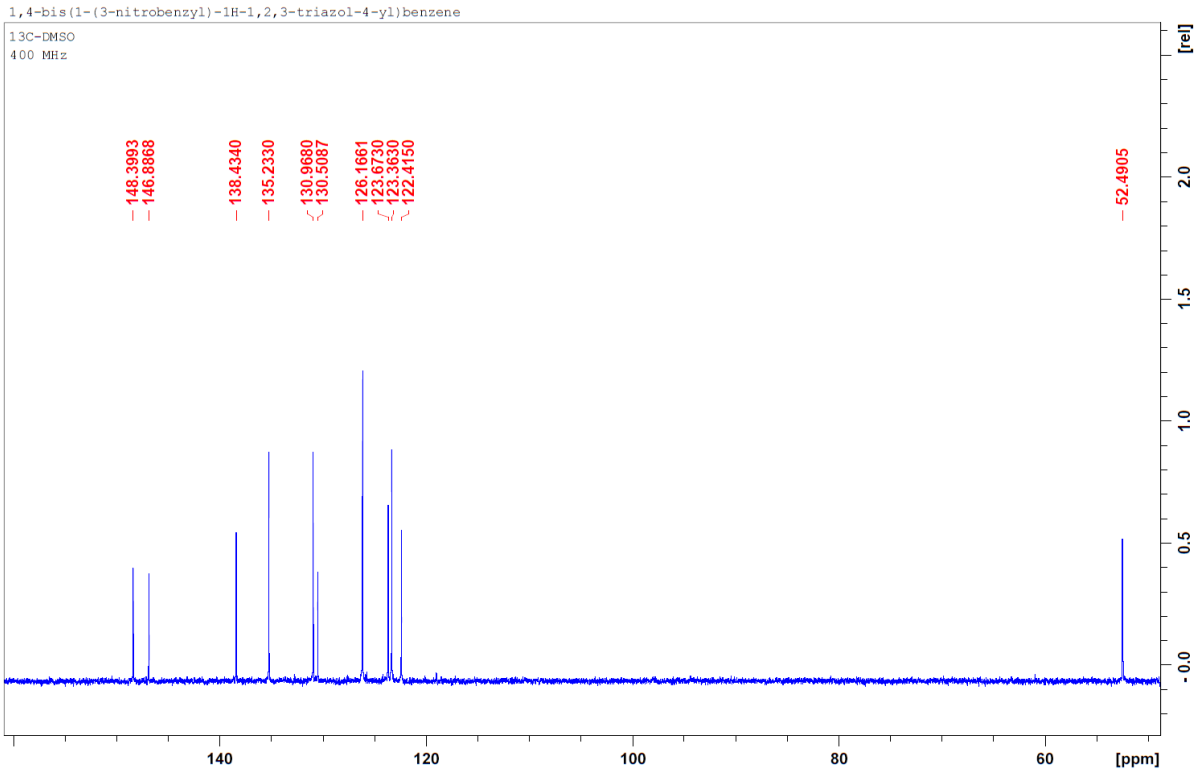

Figure S22. ^{13}C-NMR of 1,4-bis(1-(3-nitrobenzyl)-1*H*-1,2,3-triazol-4-yl)benzene (Table 2, entry 9) obtained in $(CD_3)_2SO$.

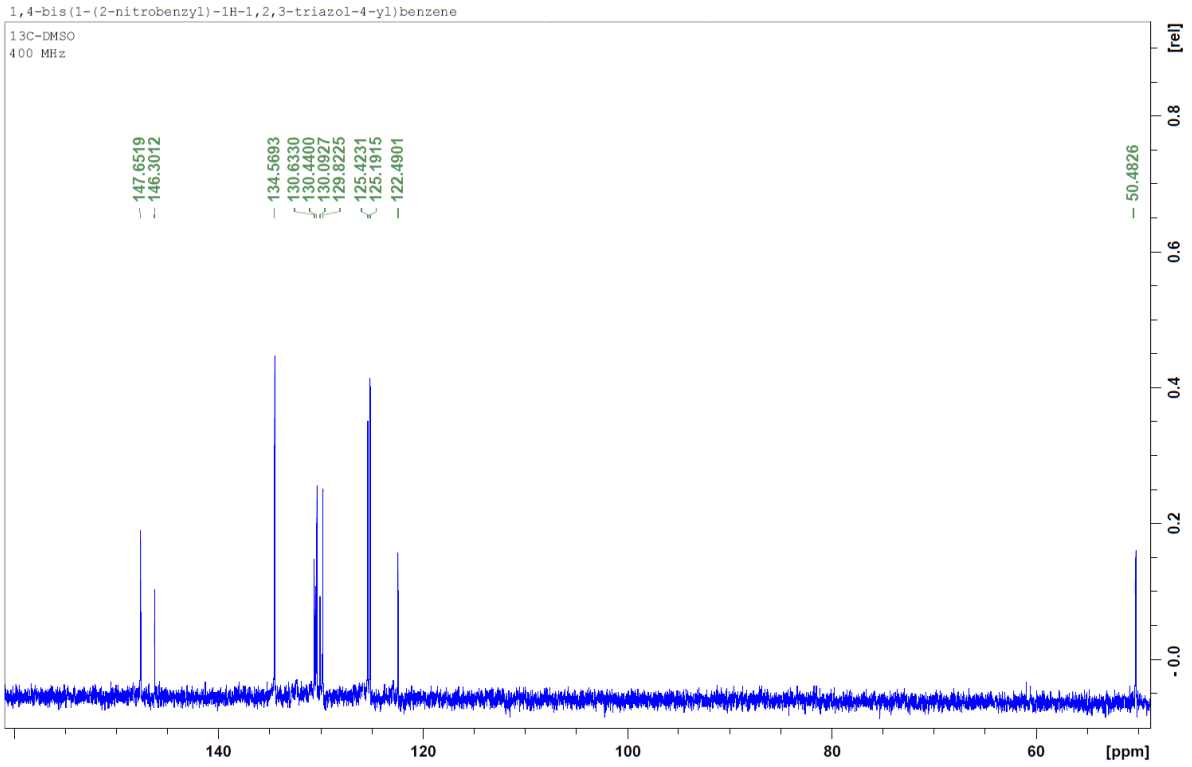

Figure S23. ^{1}H-NMR of 1,4-bis(1-(2-nitrobenzyl)-1*H*-1,2,3-triazol-4-yl)benzene (Table 2, entry 10) obtained in $(CD_3)_2SO$.

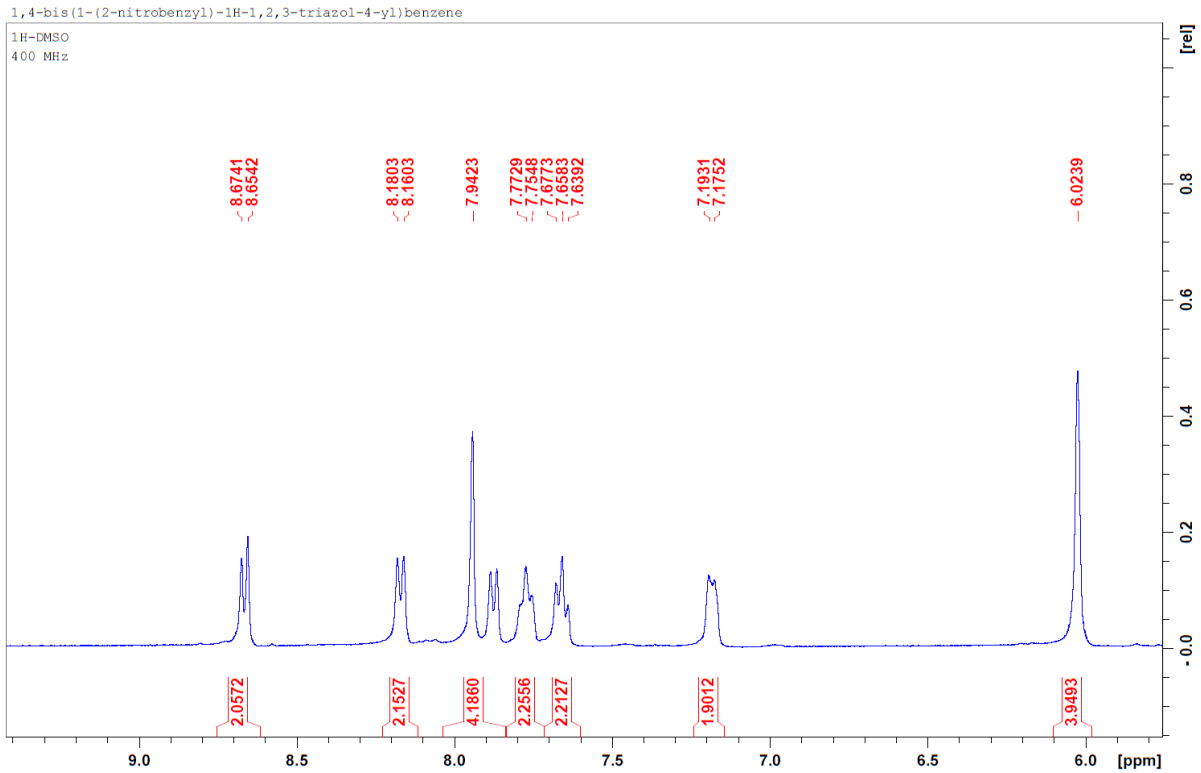

Figure S24. ^{13}C-NMR of 1,4-bis(1-(2-nitrobenzyl)-1*H*-1,2,3-triazol-4-yl)benzene (Table 2, entry 10) obtained in $(CD_3)_2SO$.

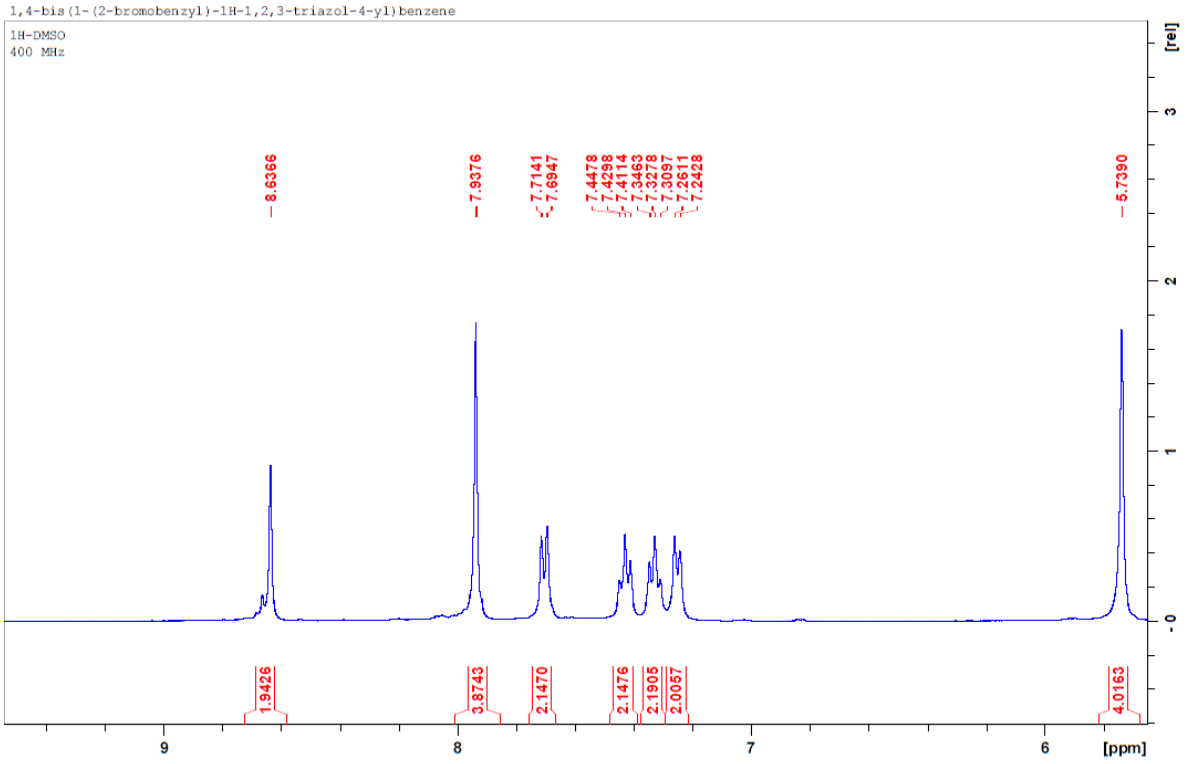

Figure S25. ^{1}H-NMR of 1,4-bis(1-(2-bromobenzyl)-1*H*-1,2,3-triazol-4-yl)benzene (Table 2, entry 12) obtained in $(CD_3)_2SO$.

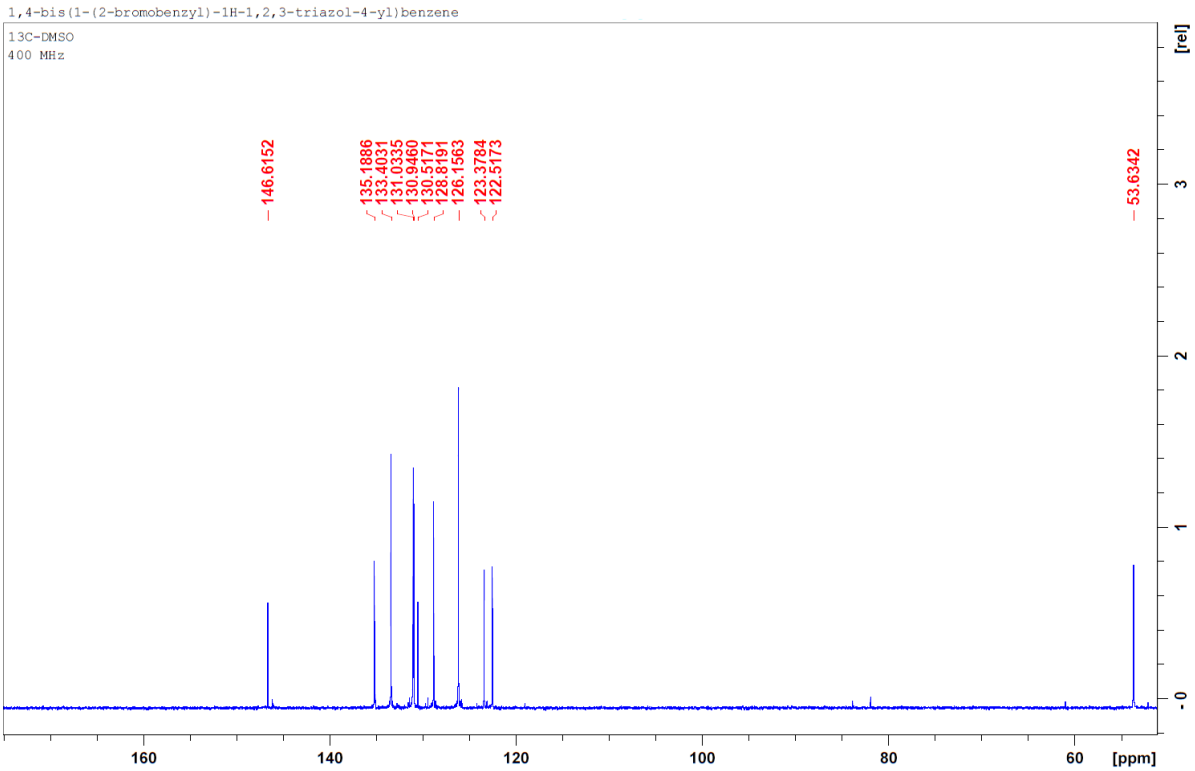

Figure S26. ^{13}C-NMR of 1,4-bis(1-(2-bromobenzyl)-1*H*-1,2,3-triazol-4-yl)benzene (Table 2, entry 12) obtained in $(CD_3)_2SO$.