Electronic supplementary information

Arylhydrazone ligand as Cu-protector and -catalysis promoter in the azide–alkyne cycloaddition reaction

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1. X-ray data and analysis

Table S1. Crystallographic data and structure refinement details for **1**−**7**.

	1	**2**	**3**	**4**	**5**	**6**	**7**
Empirical formula	$C_{10}H_{10}N_3NaO_5S$	$C_{10}H_{17}CuN_3O_9S$	$C_{20}H_{28}CuN_6O_{14}S_2$	$C_{20}H_{32}N_6Na_2O_{18}S_2$	$C_{20}H_{28}CuN_6O_{16}S_2$	$C_{44}H_{48}N_6Na_2O_{14}S_2$	$C_{46}H_{58}CuN_8O_{18}S_2$
Formula weight	307.26	418.86	704.14	754.61	736.14	994.98	1138.66
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	P 21/c	P b c a	P 21/n	P 21/c	P 21/c	P -1	P -1
a (Å)	5.9967(9)	21.9238(18)	9.589(2)	6.9078(3)	7.0948(7)	7.3204(13)	7.4839(11)
b (Å)	28.244(5)	6.6867(5)	13.188(3)	27.7995(12)	13.2858(11)	12.411(2)	11.1918(15)
c (Å)	7.6942(12)	22.2697(17)	11.558(2)	8.5286(4)	16.1728(15)	13.597(2)	16.739(3)
α (º)	90	90	90	90	90	86.394(9)	106.232(10)
β (º)	111.292(5)	90	108.545(4)	101.458(2)	100.556(3)	75.139(9)	102.070(10)
γ (º)	90	90	90	90	90	75.607(10)	97.821(10)
V (Å^3)	1214.2(3)	3264.7(4)	1385.7(5)	1605.14(12)	1498.7(2)	1156.6(4)	1287.8(3)
Z	4	8	2	2	2	1	1
D_{calc} (g/cm^3)	1.681	1.704	1.688	1.561	1.631	1.429	1.468
F000	632	1720	726	784	758	520	595
μ (mm^{-1})	0.326	1.517	1.020	0.280	0.951	0.208	0.586
Rfl. measured	16006	41628	37290	20235	25305	32097	26077
Obs / Unique rfl.	2273 / 1882	3003 / 2142	7122 / 5063	2943 / 2329	2782 / 2095	4257 / 3262	4621 / 1878
Nº parameters	191	248	218	276	230	322	367
R_{int}	0.0389	0.0916	0.0800	0.0788	0.0895	0.0880	0.3122
$R(F)$ ($I \geq 2\sigma$)	0.0381	0.0420	0.0419	0.0453	0.0497	0.0432	0.0916
wR (F^2) (all data)	0.0830	0.1036	0.0911	0.1142	0.1075	0.1038	0.1987
GOF (F^2)	1.090	1.087	1.020	1.019	1.047	1.012	0.984

Table S2. Selected bond distances (**Å**) for **1 – 7.**

	1	**2**	**3**	**4**	**5**	**6**	**7**
NN	1.313(3)	1.294(4)	1.3071(17)	1.309(3)	1.299(5)	1.307(2)	1.303(9)
M–N	-	1.963(3)	-	-	-	-	-
$M–O_{sulfonate}$	2.3084(18) to 2.3343(18)	1.971(3)	-	2.45(2)	2.363(3)	2.3304(18) 2.3913(17)	-
$M–O_{amide}$	2.3471(18) 2.3963(19)	1.913(3)	2.3102(11)	-	-	2.3203(18)	-
$M–O_{water(methanol)}$	-	1.952(3) 2.305(3)	1.9601(11) 1.9879(12)	2.352(3) to 2.475(3)	1.932(3) to 2.363(3)	2.350(2) 2.357(2)	1.989(6) to 2.214(7)
$l.s.plane_{hydrazone}\cdots M$	0.748	1.025	0.00	0.308	3.130	0.568	-
*Intra*molecular M···M	4.359	-	-	10.664	-	5.079	-
*Inter*molecular M···M	3.599	4.629	9.069	6.186	7.0948	6.208	7.484

Table S3. Hydrogen bonding distances (Å) and angles (°) for for **1** - **7**.[(a)]

D–H···A	D–H	H···A	D···A	D–H···A
		1		
N1–H1···O3	0.88(3)	2.20(3)	2.823(3)	128(2)
N1–H1···O4	0.88(3)	1.93(3)	2.602(3)	132(3)
N3–H2A···O2^{i}	0.86(3)	2.14(3)	2.986(3)	169(3)
N3–H2B···O5	0.88(3)	2.01(3)	2.694(3)	134(3)
		2		
N1–H1···O3^{v}	0.84(9)	2.04(9)	2.881(5)	177(10)
N1–H2···O1	0.92(9)	1.88(8)	2.616(5)	136(6)
O7–H10···O8	0.94(5)	1.85(6)	2.751(5)	160(7)
O7–H11···O3^{vii}	0.96(5)	2.00(6)	2.918(4)	160(5)
O6–H12···O9^{vi}	0.95(7)	1.74(6)	2.694(6)	177(10)
O6–H13···O7^{ii}	0.94(5)	1.85(4)	2.795(4)	178(8)
O8–H14···O4^{i}	0.94(5)	2.11(6)	2.856(5)	136(5)
O8–H15···O4^{vii}	0.93(5)	2.13(6)	2.956(5)	146(5)
O9–H16···O8	0.95(6)	2.16(6)	3.098(7)	172(5)
O9–H17···O1^{iii}	0.99(7)	1.82(7)	2.790(5)	167(6)
		3		
N1–H1N···O1	0.81(2)	2.55(2)	3.037(2)	119.5(17)
N1–H1N···O2	0.81(2)	2.48(2)	2.9832(19)	121.7(18)
N1–H1N···O5	0.81(2)	1.97(2)	2.6031(17)	134.9(19)
N3–H3A···O4	0.85(2)	2.06(2)	2.728(2)	134.8(17)
N3–H3B···O6	0.83(2)	2.39(2)	3.090(2)	143.3(18)
O6–H6A···O3^{iv}	0.75(2)	1.97(2)	2.704(2)	171(2)
O6–H6B···O1	0.85(2)	1.81(2)	2.6547(17)	176.7(15)
O7–H7D···O2	0.82(2)	1.85(2)	2.6710(17)	178(2)
O7–H7E···O4^{ix}	0.79(2)	1.99(2)	2.7652(18)	170(2)
		4		
N1–H1N···O2	0.90(3)	1.87(3)	2.570(3)	133(4)
N1–H1N···O3	0.90(3)	2.28(3)	2.624(2)	103(2)
N3–H3A···O6^{viii}	0.89(9)	2.38(4)	3.17(2)	148(3)
N3–H3A···O1	0.89(3)	2.00(3)	2.684(3)	133(3)
N3–H3B···O8^{ix}	0.89(3)	2.49(3)	3.248(3)	144(3)
O3–H3O···O7^{iii}	0.90(3)	1.77(3)	2.673(2)	176(3)
O7–H7A···O2^{viii}	0.90(3)	1.83(3)	2.729(2)	177(3)
O7–H7B···O4^{vii}	0.88(3)	1.95(3)	2.813(14)	166(3)
O8–H8A···O5	0.90(3)	2.52(3)	3.387(5)	161(4)
O8–H8A···O6^{xi}	0.88(3)	1.81(4)	2.67(2)	165(3)
O8–H8B···O9^{xi}	0.90(3)	2.07(3)	2.933(3)	162(3)
O9–H9A···O5^{v}	0.88(3)	1.98(3)	2.861(14)	175(3)
		5		
N3–H3N1···O4^{vii}	0.87(5)	2.25(6)	3.064(5)	156(5)
N1–H1N···O1	0.95(3)	2.22(5)	2.641(4)	106(3)

N1–H1N···O3	0.95(3)	1.92(4)	2.577(4)	124(4)
O1–H1O···O6^{iv}	0.896(17)	1.779(19)	2.672(4)	174(5)
N3–H3N2···O2	0.90(6)	1.95(6)	2.674(6)	137(5)
O7–H71···O6^{iii}	0.88(3)	1.89(4)	2.756(5)	166(5)
O7–H72···O2^{x}	0.88(4)	1.83(3)	2.697(5)	168(5)
O8–H81···O5^{v}	0.88(3)	1.87(3)	2.730(5)	165(5)
O8–H72···O3^{ix}	0.90(3)	1.84(3)	2.702(4)	160(5)
		6		
O6–H6A···O4^{ii}	0.88(3)	1.96(3)	2.827(3)	171(3)
N7–H7A···O2	0.88(2)	1.96(3)	2.640(2)	132(3)
N7–H7A···O3	0.88(2)	1.96(3)	2.639(2)	132(3)
O7–H7B···O2	0.88(2)	1.98(3)	2.843(3)	165(3)
N10–H10A···O1	0.88(3)	1.91(2)	2.678(3)	143(2)
		7		
N1–H1N···O1	0.91(10)	1.80(11)	2.657(12)	156(9)
N3–H3N···O2	0.86(10)	1.88(10)	2.603(10)	141(9)
N3–H3N···O4	0.86(10)	2.09(10)	2.668(10)	124(8)
O6–H6A···O3	0.94(8)	1.92(9)	2.813(9)	158(8)
O6–H6C···O5^{iii}	0.86(9)	1.86(8)	2.706(10)	168(9)
O7–H7A···O4	0.96(9)	2.12(8)	3.014(9)	155(7)
O7–H7B···O9	0.95(8)	1.68(8)	2.627(10)	172(9)
O8–H8B···O4^{iii}	0.95(7)	2.08(8)	2.841(8)	135(7)
O8–H8C···O3^{iv}	0.94(4)	2.33(9)	2.850(9)	115(5)

[(a)] For symmetry transformations see legend of figures S1-S7. In **4**, only the interactions involving the main component of the disordered sulfonate group is indicated.

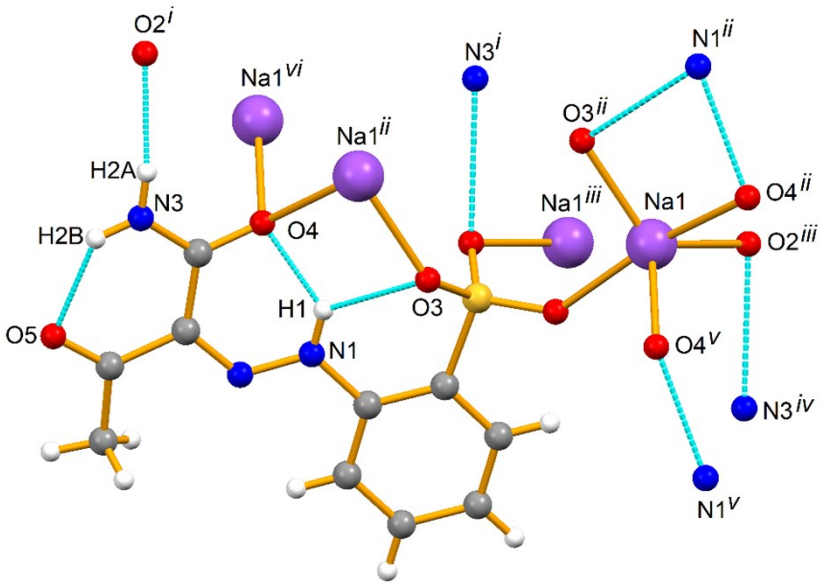


Figure S1. Hydrogen bond interactions in the structure of **1**. Symmetry operations to generate equivalent atoms: i) 2-x,-y,1-z; ii) 2-x,-y,2-z; iii) 1-x,-y,2-z; iv) -1+x,y,1+z; v) x,y,1+z ; vi) x,y,-1+z.

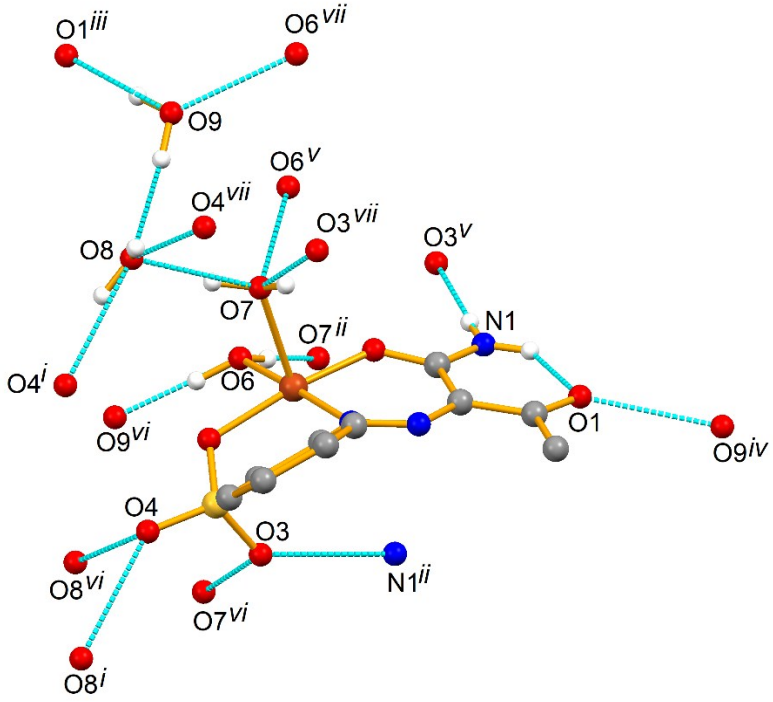


Figure S2. Hydrogen bond interactions in the structure of **2**. Hydrogen atoms not involved in the contacts were omitted for clarity. Symmetry operations to generate equivalent atoms: i) 1-x,-y,1-z; ii) 1.5-x,-1/2+y,z; iii) 1.5-x,1-y,-1/2+z; iv) 1.5-x,1-y,1/2+z; v) 1.5-x,1/2+y,z; vi) x,-1+y,z; vii) x,1+y,z.

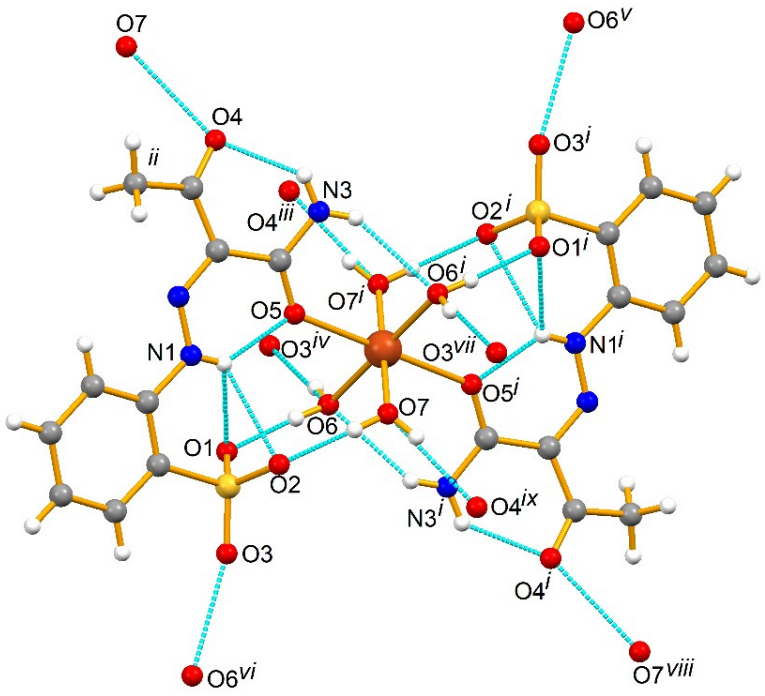


Figure S3. Hydrogen bond interactions in the structure of **3**. Symmetry operations to generate equivalent atoms: i) -x,1-y,1-z; ii) -1+x,y,z; iii) -1-x,1-y,1-z; iv) -1/2+x,1/2-y,-1/2+z; v) -1/2-x,1/2+y,1/2-z; vi) 1/2+x,1/2-y,1/2+z; vii) 1/2-x,1/2+y,1.5-z; viii) 1-x,1-y,1-z; ix) 1+x,y,z.

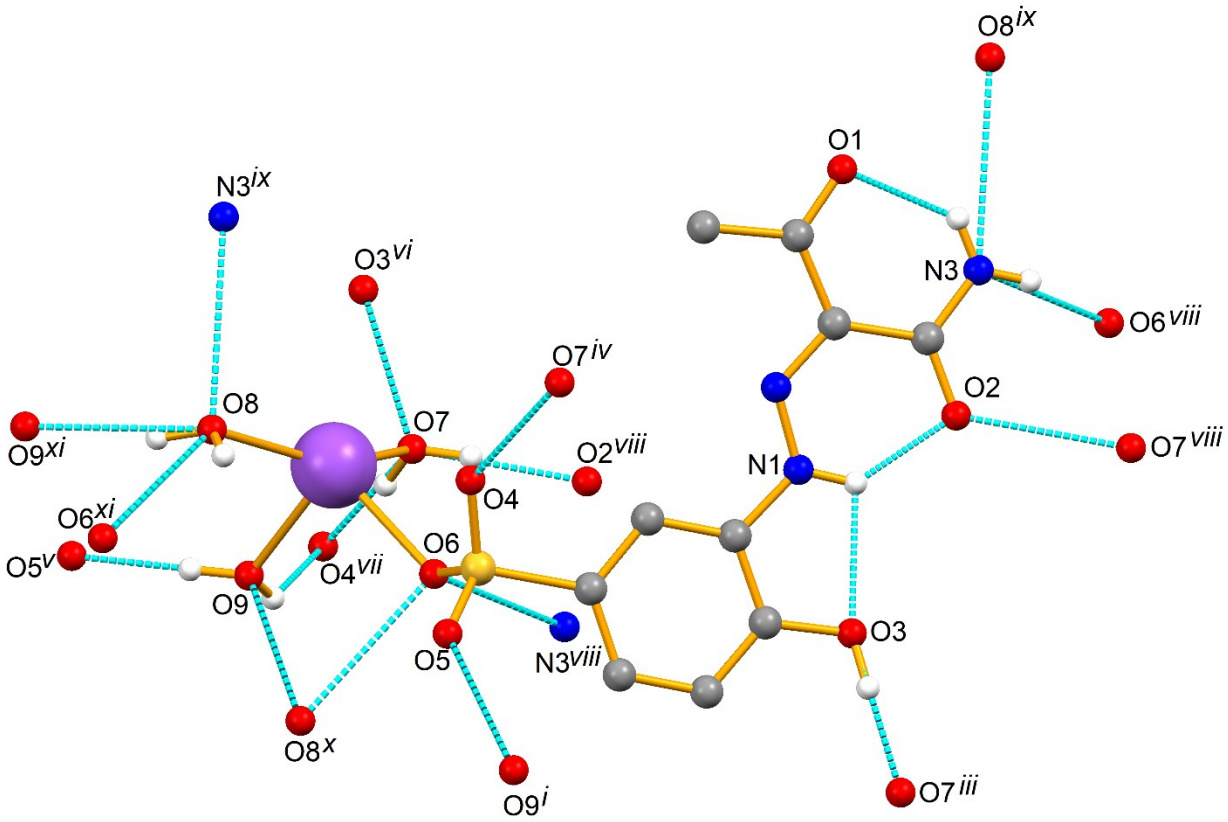


Figure S4. Hydrogen bond interactions in the structure (asymmetric unit) of **4**. Hydrogen atoms not involved in the contacts were omitted for clarity. Symmetry operations to generate equivalent atoms: ii) -1+x,1/2-y,-1/2+z: iii) -1+x,y,-1+z; iv) -1+x,y,z; v) 1+x,1/2-y,1/2+z; vi) 1+x,y,1+z; vii) 1+x,y,z; viii) 1-x,-y,1-z; ix) 1-x,-y,2-z; x) x,1/2-y,-1/2+z; xi) x,1/2-y,1/2+z.
Operation i) was assigned to generate the symmetry related counter part of the molecule (see manuscript).

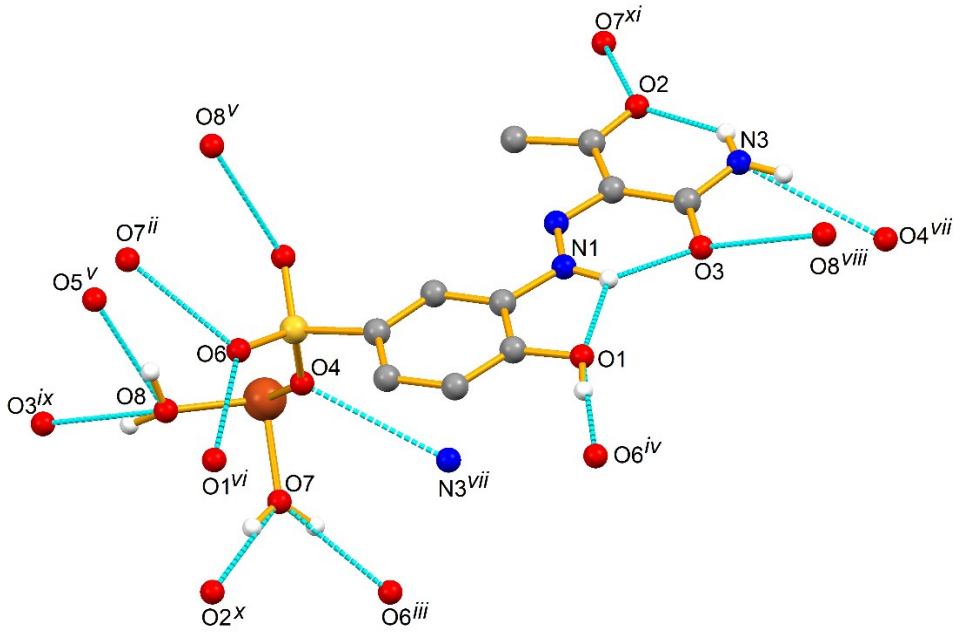


Figure S5. Hydrogen bond interactions in the structure (asymmetric unit) of **5**. Hydrogen atoms not involved in the contacts were omitted for clarity. Symmetry operations to generate equivalent atoms: ii) -1+x,y,z; iii) 1+x,y,z; iv) 1-x,-1/2+y,1/2-z; v) 1-x,1-y,1-z; vi) 1-x,1/2+y,1/2-z; vii) 2-x,-y,1-z; viii) x,-1+y,z; ix) x,-1+y,z; x) x,1/2-y,-1/2+z; xi) x,1/2-y,1/2+z.
Operation i) was assigned to generate the symmetry related counter part of the molecule (see manuscript).

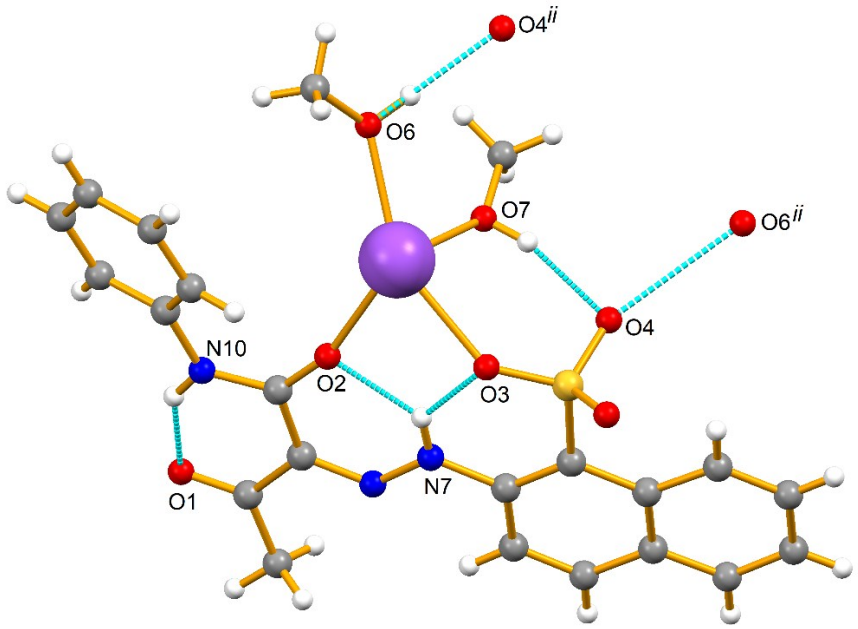


Figure S6. Hydrogen bond interactions in the structure (asymmetric unit) of **6**. Symmetry operations to generate equivalent atoms: ii) 2-x,-y,1-z.
Operation i) was assigned to generate the symmetry related counter part of the molecule (see manuscript).

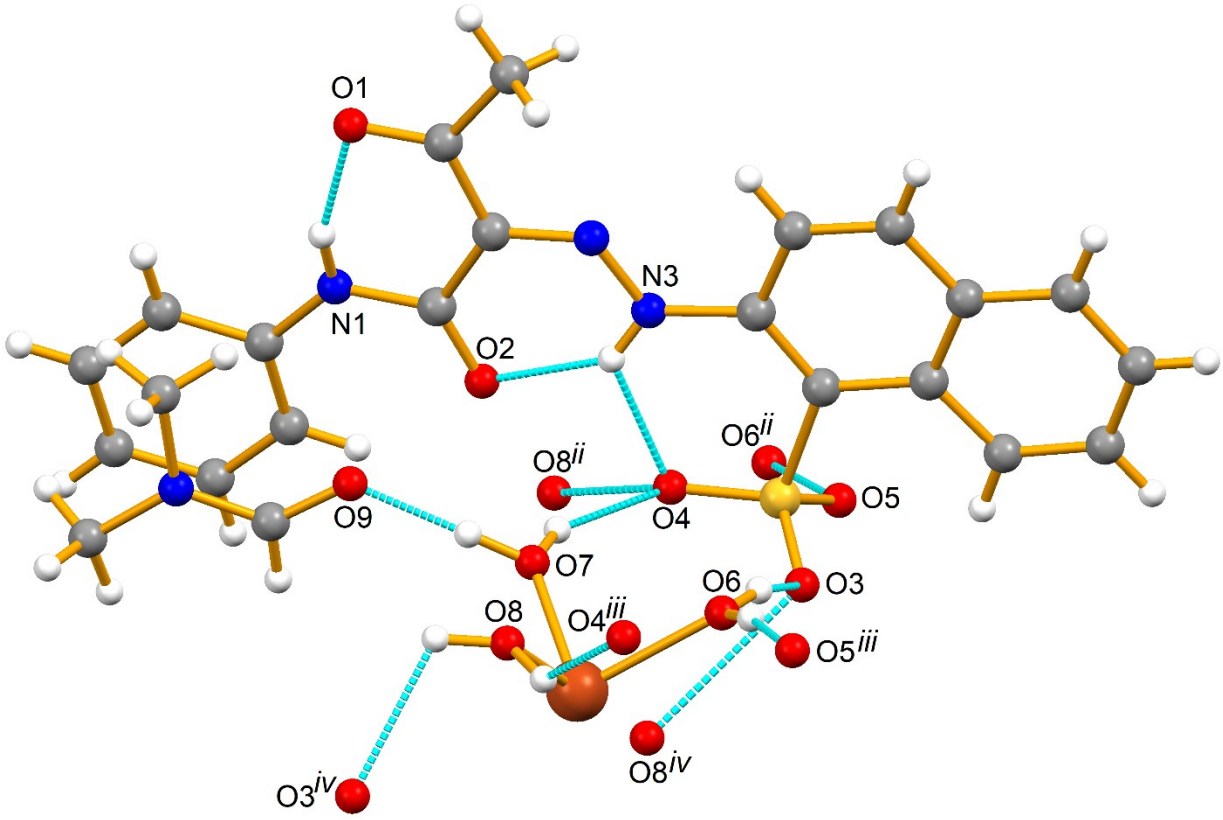
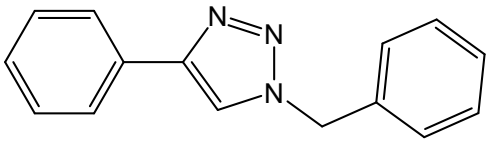


Figure S7. Hydrogen bond interactions in the structure (asymmetric unit) of **7**. Symmetry operations to generate equivalent atoms: ii) -1+x,y,z; iii) 1+x,y,z; iv) 2-x,-y,1-z.
Operation i) was assigned to generate the symmetry related counter part of the molecule (see manuscript).

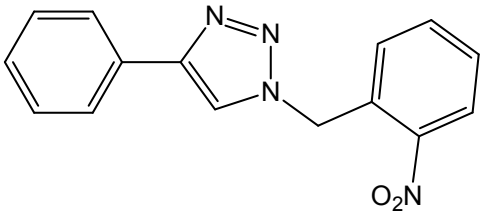
2. Characterization of 1,4-disubstituted-1,2,3-triazole products:

1-benzyl-4-phenyl-1H-1,2,3-triazole



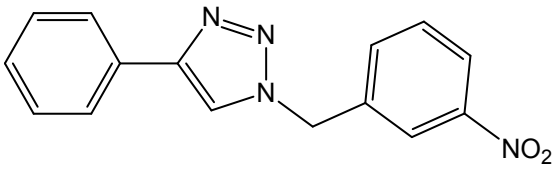
^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.63 (s, 1H), 7.85 (d, J = 7.6 Hz, 2H), 7.45-7.32 (m, 8H), 5.65 (s, 2H). ^{13}C NMR (400 MHz, DMSO-d_6, δ): 146.67, 136.01, 130.66, 128.89, 128.80, 128.16, 127.89, 125.16, 121.56, 53.03. DEPT (400 MHz, DMSO-d_6, δ): 128.63, 128.55, 127.91, 127.63, 124.91, 121.30, -52.78. Elemental analysis calcd (%) for $C_{15}H_{13}N_3$: C 76.57, H 5.57, N 17.86; found: C 77.21, H 5.69, N 18.32.

1-(2-nitrobenzyl)-4-phenyl-1H-1,2,3-triazole



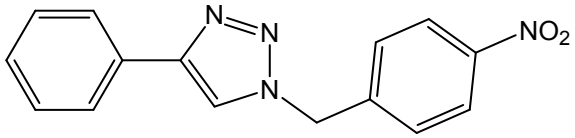
^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.62 (s, 1H), 8.17 (d, J = 8 Hz, 1H), 7.86 (d, J = 7.6 Hz, 2H), 7.77 (t, J = 7.6 Hz, 1H), 7.65 (t, J = 8 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.34 (m, 1H), 7.15 (d, J = 7.6 Hz, 1H), 6.02 (s, 2H). ^{13}C NMR (400 MHz, DMSO-d_6, δ): 147.59, 146.59, 134.49, 130.75, 130.52, 130.22, 129.72, 128.95, 128.03, 125.24, 125.16, 122.34, 50.20. DEPT (400 MHz, DMSO-d_6, δ): 134.25, 129.97, 129.47, 128.70, 127.78, 124.99, 124.91, 122.09, -49.95. Elemental analysis calcd (%) for $C_{15}H_{12}N_4O_2$: C 64.28, H 4.32, N 19.99; found: C 65.02, H 4.58, N 20.53.

1-(3-nitrobenzyl)-4-phenyl-1H-1,2,3-triazole



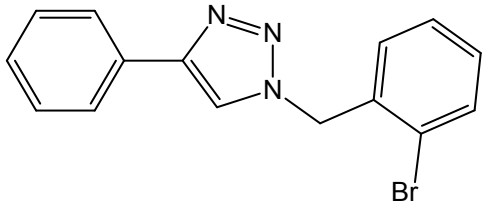
^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.70 (s, 1H), 8.27 (s, 1H), 8.21 (d, J = 8 Hz, 1H), 7.79-7.86 (m, 3H), 7.69 (t, J = 8 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.32 (m, 1H), 5.84 (s, 2H). ^{13}C NMR (400 MHz, DMSO-d_6, δ): 147.95, 146.82, 138.04, 134.74, 130.54, 130.49, 128.94, 128.03, 125.23, 123.20, 122.88, 121.86, 52.03. DEPT (400 MHz, DMSO-d_6, δ): 134.49, 130.24, 128.70, 127.78, 124.98, 122.95, 122.63, 121.61, -51.77. Elemental analysis calcd (%) for $C_{15}H_{12}N_4O_2$: C 64.28, H 4.32, N 19.99; found: C 64.81, H 4.67, N 20.70.

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



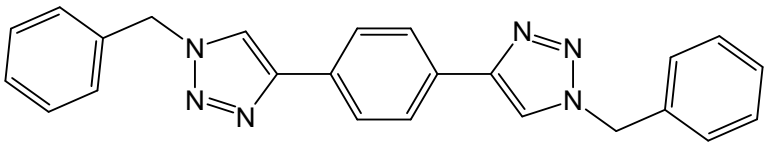
^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.70 (s, 1H), 8.25 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 7.6 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.34 (m, 1H), 5.85 (s, 2H). ^{13}C NMR (400 MHz, DMSO-d_6, δ): 147.26, 146.79, 143.42, 130.52, 129.00, 128.93, 128.01, 125.20, 123.97, 122.00, 52.12. DEPT (400 MHz, DMSO-d_6, δ): 128.74, 128.68, 127.76, 124.95, 123.72, 121.75, -51.87. Elemental analysis calcd (%) for $C_{15}H_{12}N_4O_2$: C 64.28, H 4.32, N 19.99; found: C 64.87, H 4.41, N 20.65.

1-(2-bromobenzyl)-4-phenyl-1H-1,2,3-triazole



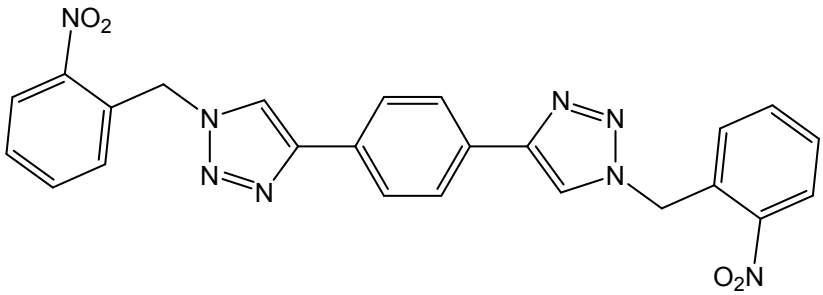
^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.61 (s, 1H), 7.86 (d, J = 7.6 Hz, 2H), 7.70 (d, J = 8 Hz, 1H), 7.46-7.33 (m, 5H), 7.22 (d, J = 7.6 Hz, 1H), 5.73 (s, 2H). ^{13}C NMR (400 MHz, DMSO-d_6, δ): 146.49, 134.81, 132.94, 130.59, 130.47, 130.46, 128.91, 128.35, 127.96, 125.23, 122.88, 121.99, 53.14. DEPT (400 MHz, DMSO-d_6, δ): 132.69, 130.22, 130.21, 128.66, 128.1, 127.71, 124.98, 121.74, -52.89. Elemental analysis calcd (%) for $C_{15}H_{12}BrN_3$: C 57.34, H 3.85, N 13.37; found: C 58.12, H 4.08, N 13.98.

1,4-bis(1-benzyl-1*H*-1,2,3-triazol-4-yl)benzene



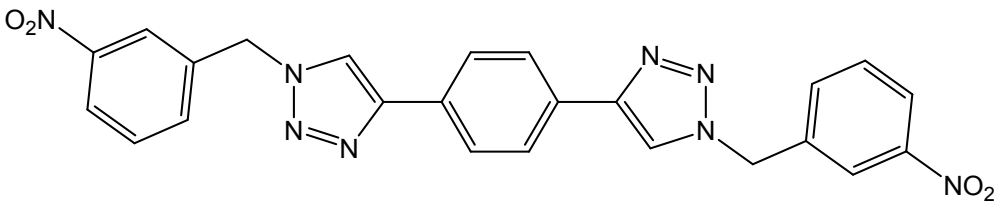
^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.70 (s, 1H), 8.67 (s, 1H), 7.92 (s, 2H), 7.86 (d, J = 8 Hz, 1H), 7.54 (d, J = 8 Hz, 4H), 7.41-7.32 (m, 10H), 5.65 (s, 4H). ^{13}C NMR (400 MHz, DMSO-d_6, δ): 146.35, 145.88, 132.31, 130.11, 128.82, 128.19, 127.93, 125.64, 125.27, 122.18, 121.66, 53.07. DEPT (400 MHz, DMSO-d_6, δ): 132.06, 128.57, 127.94, 127.67, 125.39, 125.02, 121.94, 121.41, 52.82. Elemental analysis calcd (%) for $C_{24}H_{20}N_6$: C 73.45, H 5.14, N 21.41; found: C 74.31, H 5.27, N 21.80.

1,4-bis(1-(2-nitrobenzyl)-1H-1,2,3-triazol-4-yl)benzene



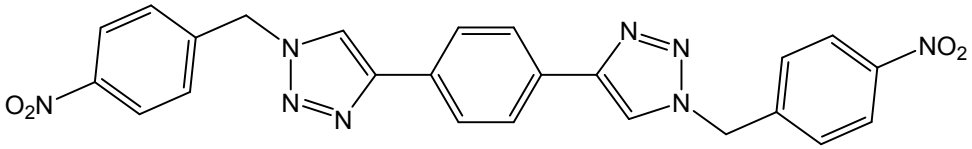
^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.67 (d, J = 8 Hz, 2H), 8.17 (d, J = 8 Hz, 2H), 7.94 (s, 4H), 7.79-7.75 (m, 2H), 7.67-7.64 (m, 2H), 7.18 (d, J = 7.2 Hz, 2H), 6.02 (s, 4H). ^{13}C NMR (400 MHz, DMSO-d_6, δ): 147.64, 146.25,134.52, 130.64, 130.55, 130.38, 129.79, 125.38, 125.18, 122.45, 50.25. DEPT (400 MHz, DMSO-d_6, δ): 134.27, 130.12, 129.53, 125.12, 124.93, 122.19, -50.00. Elemental analysis calcd (%) for $C_{24}H_{18}N_8O_4$: C 59.75, H 3.76, N 23.23; found: C 60.72, H 4.22, N 24.14.

1,4-bis(1-(3-nitrobenzyl)-1H-1,2,3-triazol-4-yl)benzene



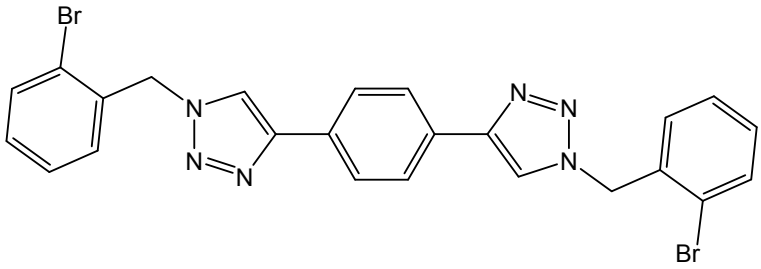
^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.73 (s, 2H), 8.28 (s, 2H), 8.22 (d, J = 7.6 Hz, 2H), 7.92 (s, 4H), 7.81 (d, J = 7.6 Hz, 2H), 7.70 (t, J = 7.6 Hz, 2H), 5.84 (s, 4H). ^{13}C NMR (400 MHz, DMSO-d_6, δ): 147.96, 146.45, 138.00, 134.80, 130.53, 130.07, 125.73, 123.23, 122.92, 121.98, 52.05. DEPT (400 MHz, DMSO-d_6, δ): 134.54, 130.28, 125.47, 122.98, 122.67, 121.72, -51.79. Elemental analysis calcd (%) for $C_{24}H_{18}N_8O_4$: C 59.75, H 3.76, N 23.23; found: C 60.21, H 3.88, N 23.72.

1,4-bis(1-(4-nitrobenzyl)-1H-1,2,3-triazol-4-yl)benzene



^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.73 (s, 2H), 8.25 (d, J = 8.4 Hz, 4H), 7.94 (s, 4H), 7.58 (d, J = 8.4 Hz, 4H), 5.85 (s, 4H). ^{13}C NMR (400 MHz, DMSO-d_6, δ): 147.32, 146.50, 143.38, 130.09, 129.08, 125.76, 124.01, 122.15, 52.21. DEPT (400 MHz, DMSO-d_6, δ): 128.83, 125.51, 123.76, 121.90, -51.95. Elemental analysis calcd (%) for $C_{24}H_{18}N_8O_4$: C 59.75, H 3.76, N 23.23; found: C 60.53, H 3.93, N 23.90.

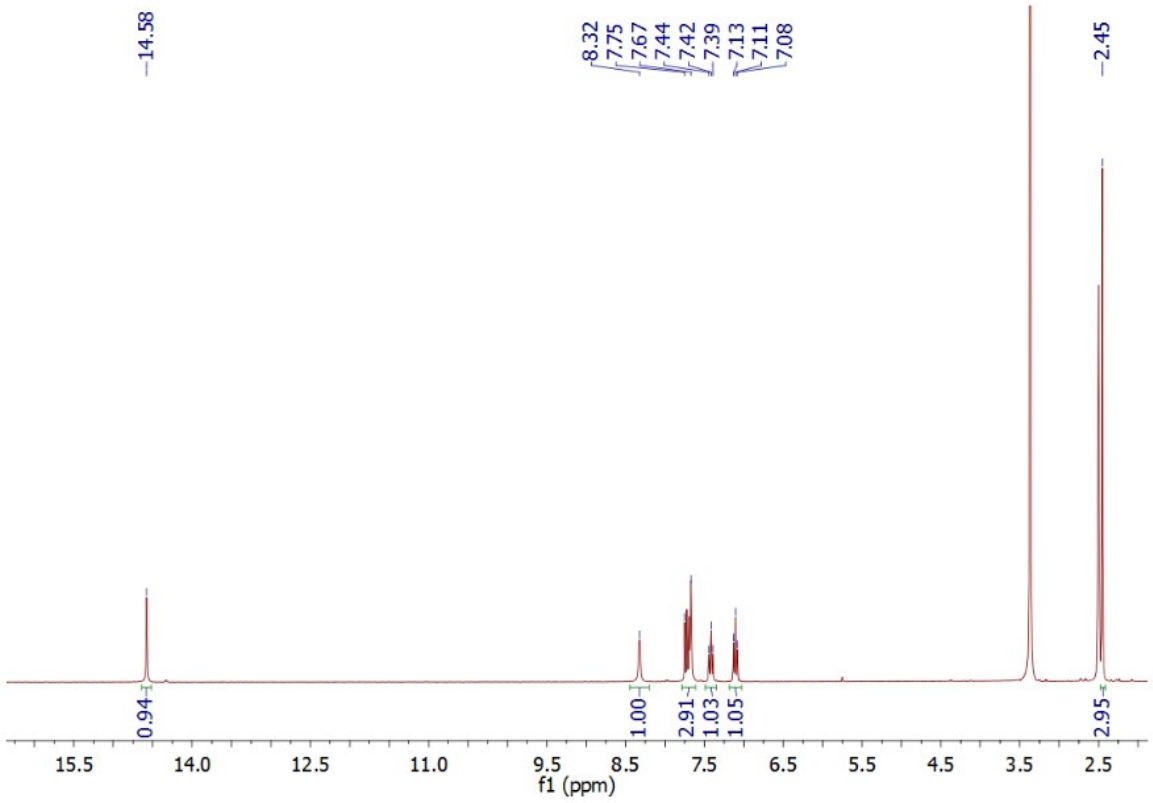
1,4-bis(1-(2-bromobenzyl)-1H-1,2,3-triazol-4-yl)benzene



^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.64 (s, 2H), 7.94 (s, 4H), 7.70 (d, J = 7.6 Hz, 2H), 7.45-7.41 (m, 2H), 7.35-7.31 (m, 2H), 7.25 (d, J = 7.2 Hz, 2H), 5.74 (s, 4H). ^{13}C NMR (400 MHz, DMSO-d_6, δ): 146.18, 134.76, 132.97, 130.60, 130.51, 130.08, 128.39, 125.72, 122.95, 122.08, 53.20. DEPT (400 MHz, DMSO-d_6, δ): 132.72, 130.35, 130.26, 128.14, 125.47, 121.83, -52.94. Elemental analysis calcd (%) for $C_{24}H_{18}Br_2N_6$: C 52.39, H 3.30, N 15.27; found: C 53.41, H 3.47, N 15.82.

3. NMR Spectra

3.1 ^{1}H, ^{13}C and DEPT NMR specta of compounds 1, 4 and 6



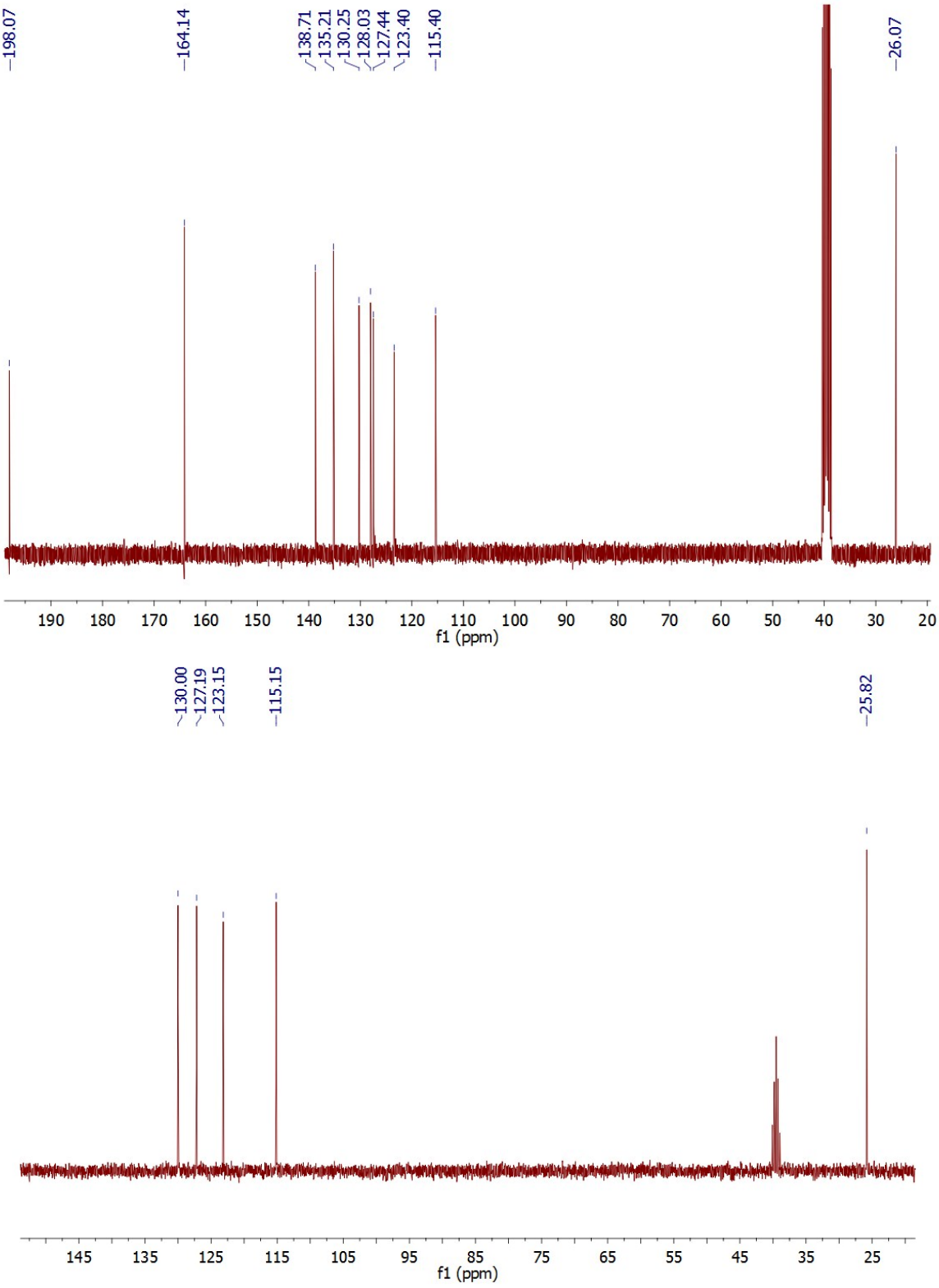
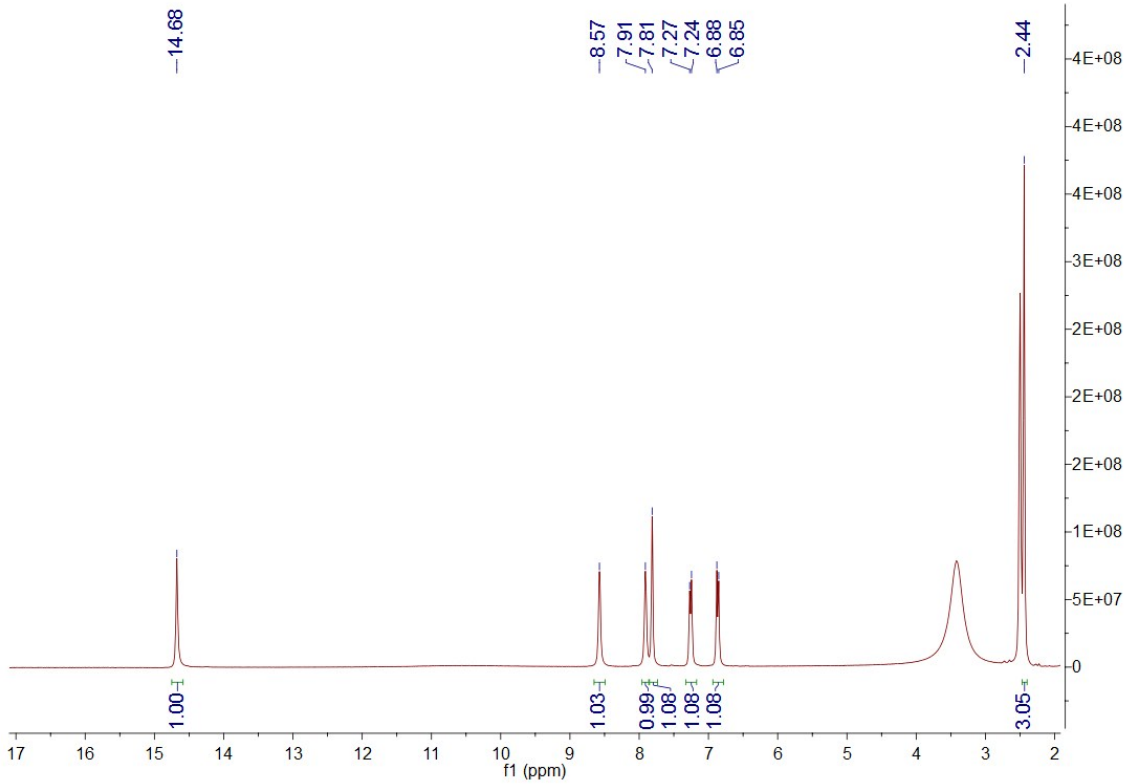
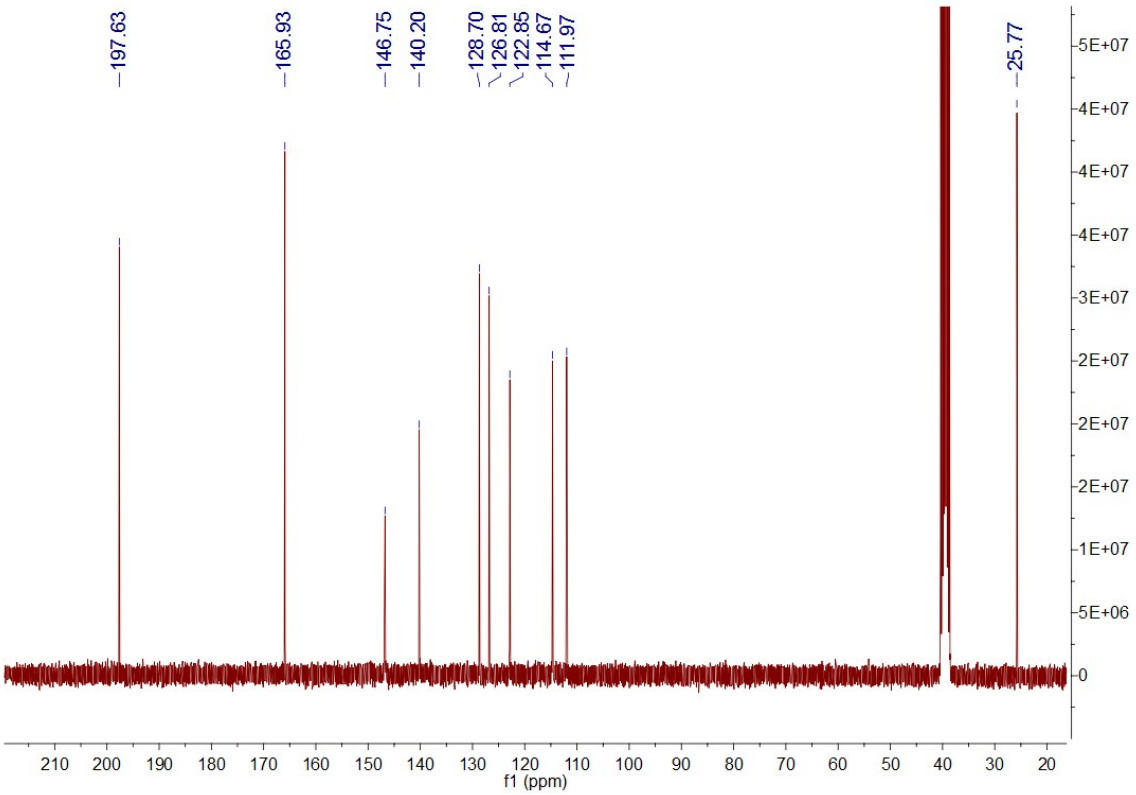


Figure S8. ^{1}H, ^{13}C and DEPT NMR specta of **1**.


14.68
8.57
7.91
7.81
7.27
7.24
6.88
6.85
2.44
1.00
1.03
0.99
1.08
1.08
1.08
3.05
f1 (ppm)


197.63
165.93
146.75
140.20
128.70
126.81
122.85
114.67
111.97
25.77
f1 (ppm)

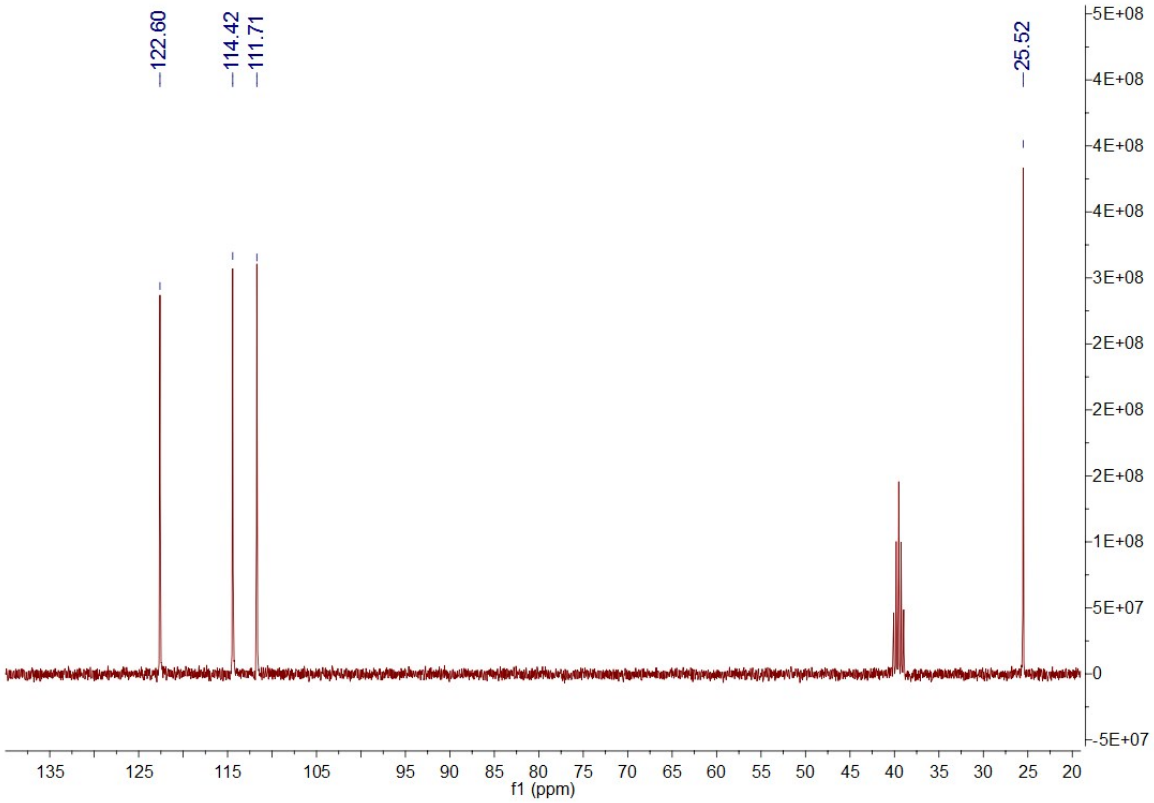
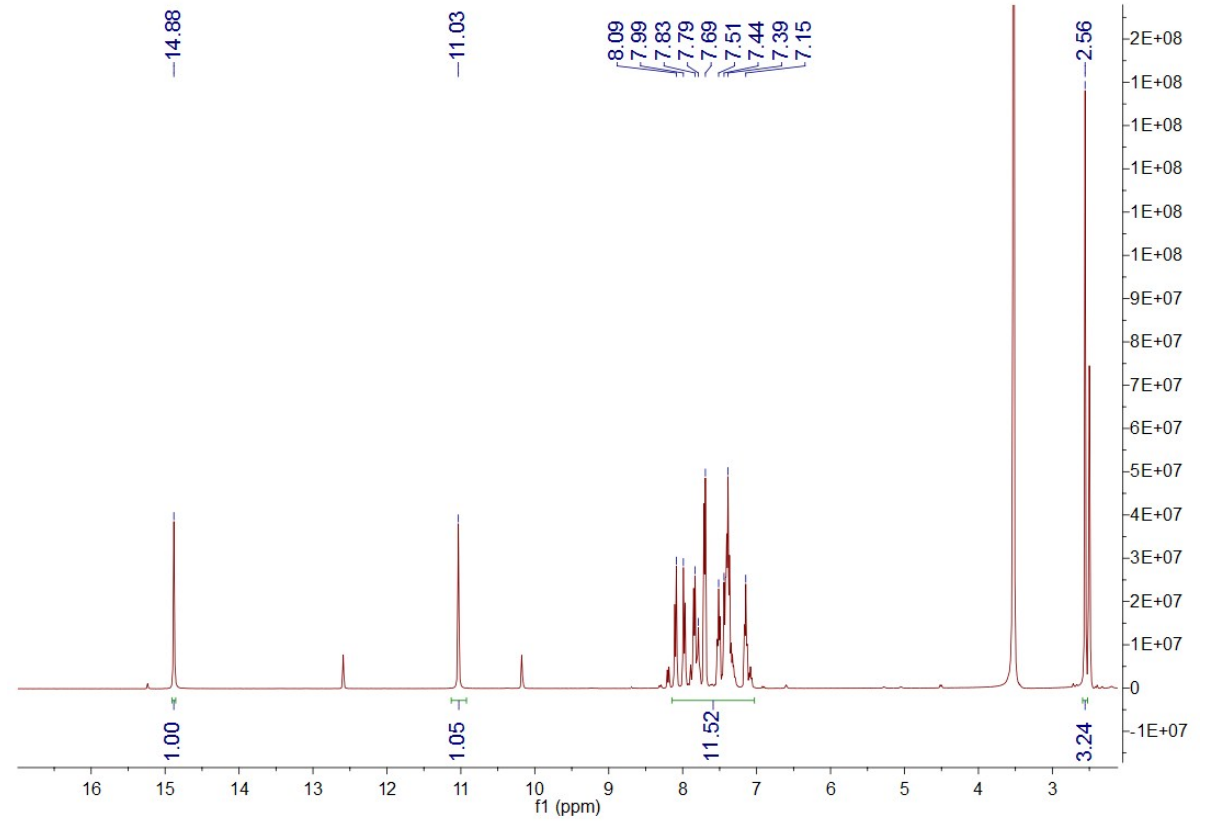
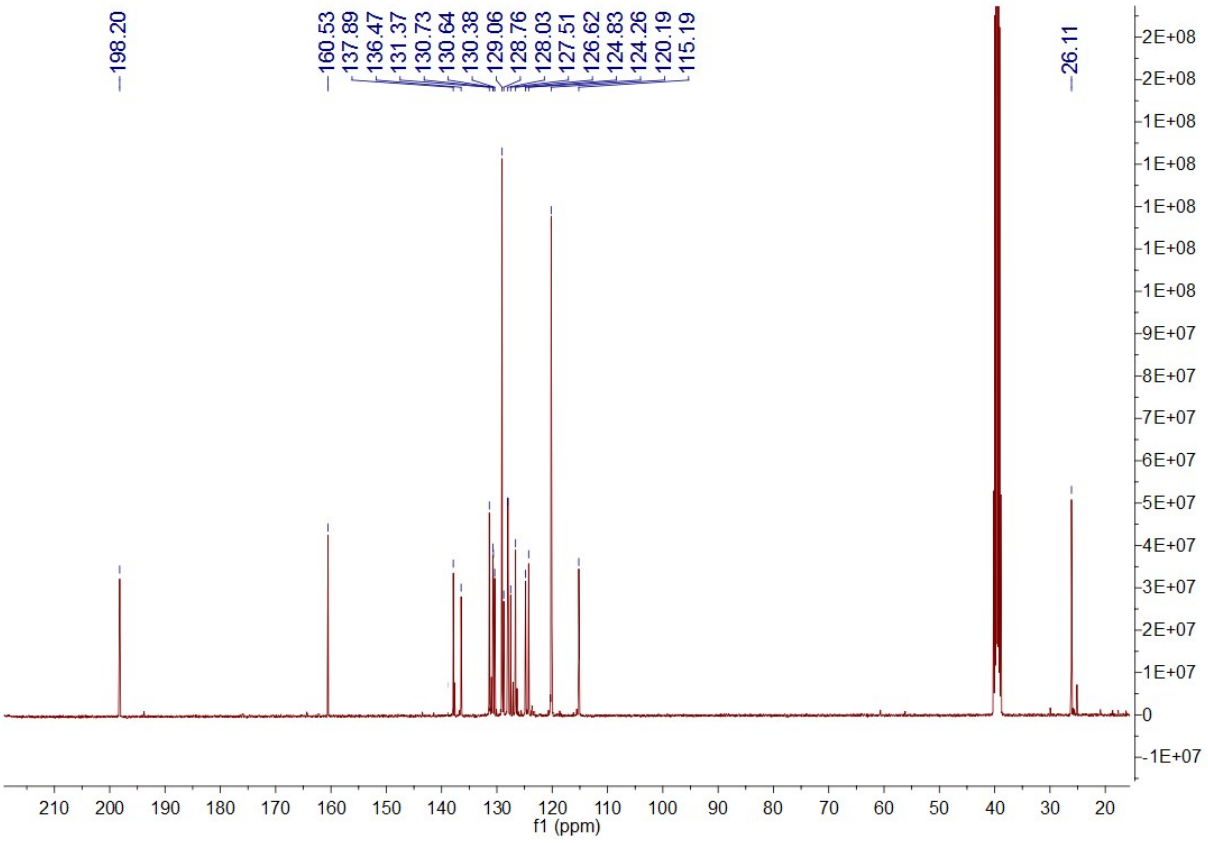


Figure S9. ^{1}H, ^{13}C and DEPT NMR specta of **4**.


14.88
11.03
8.09
7.99
7.83
7.79
7.69
7.51
7.44
7.39
7.15
2.56
1.00
1.05
11.52
3.24
f1 (ppm)


198.20
160.53
137.89
136.47
131.37
130.73
130.64
130.38
129.06
128.76
128.03
127.51
126.62
124.83
124.26
120.19
115.19
26.11
f1 (ppm)

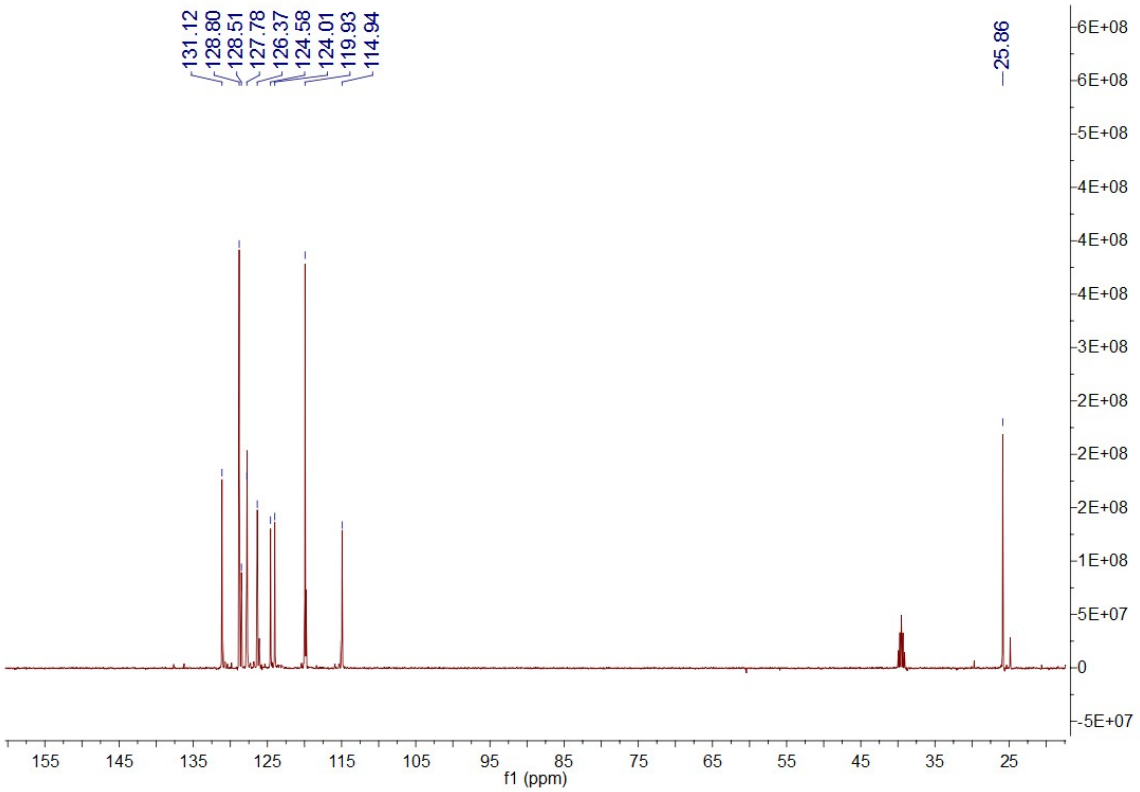
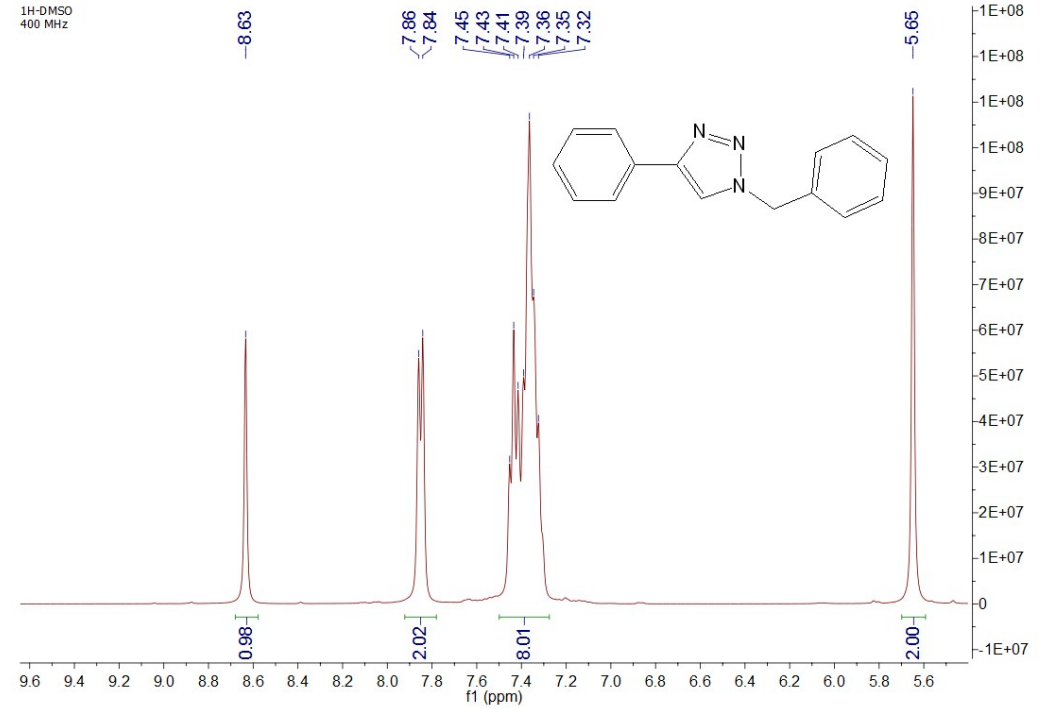
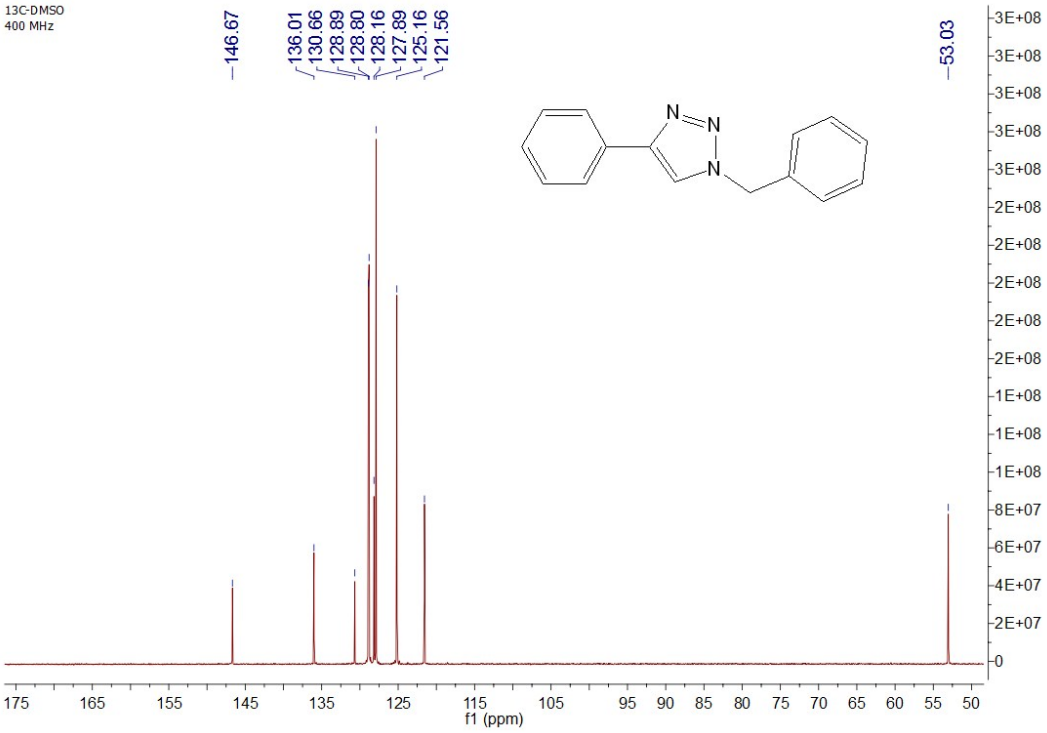


Figure S10. ^{1}H, ^{13}C and DEPT NMR specta of **6**.

3.2. ^{1}H, ^{13}C and DEPT NMR specta of 1,4-disubstituted 1,2,3-triazoles





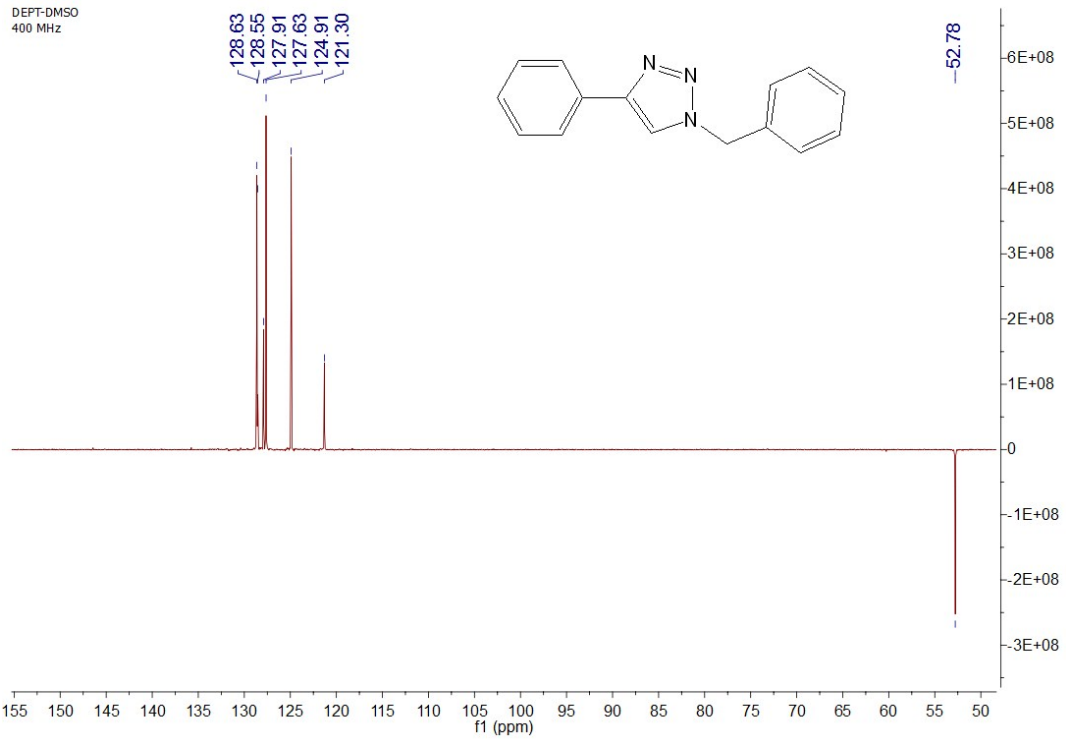
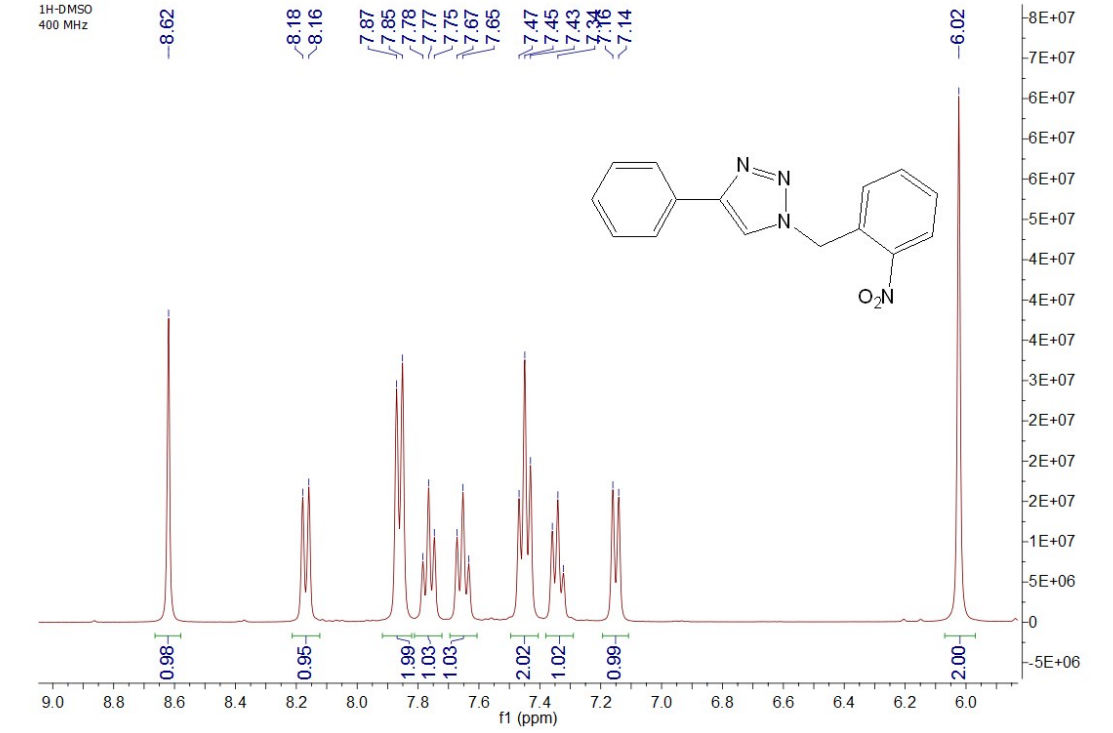
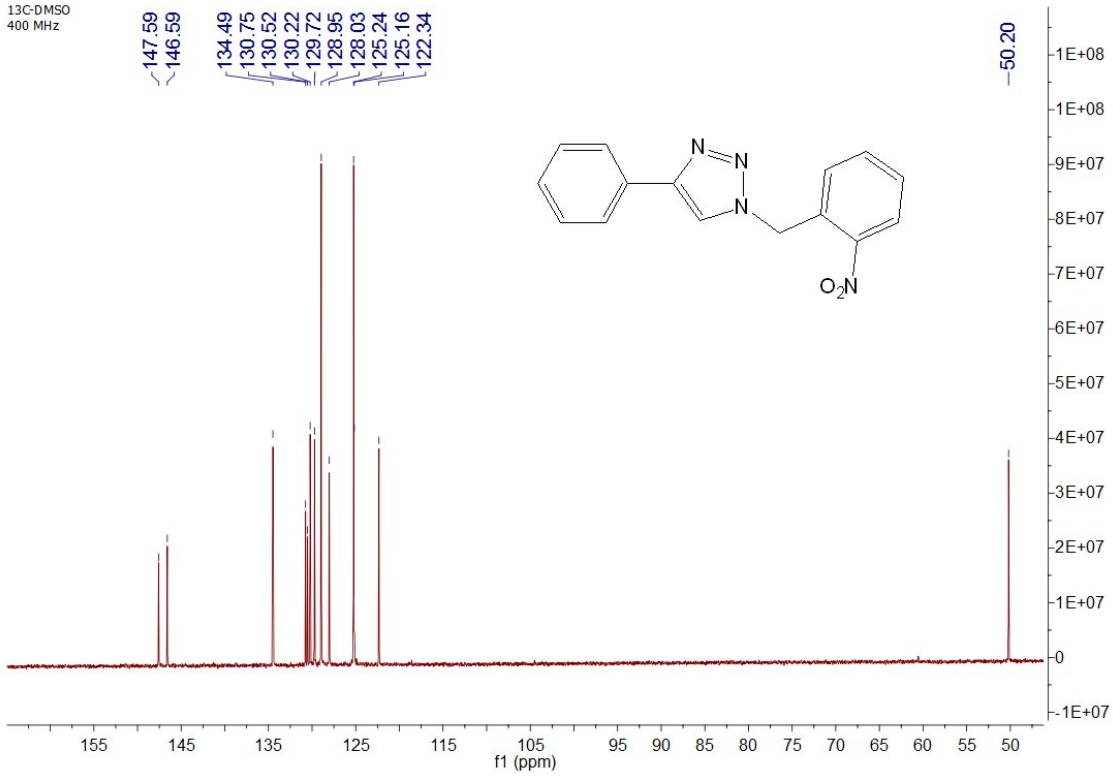


Figure S11. ^{1}H, ^{13}C and DEPT NMR specta of 1-benzyl-4-phenyl-1H-1,2,3-triazole.


1H-DMSO
400 MHz
8.62
8.18
8.16
7.87
7.85
7.78
7.77
7.75
7.67
7.65
7.47
7.45
7.43
7.14
6.02
0.98
0.95
1.99
1.03
1.03
2.02
1.02
0.99
2.00
f1 (ppm)


13C-DMSO
400 MHz
147.59
146.59
134.49
130.75
130.52
130.22
129.72
128.95
128.03
125.24
125.16
122.34
50.20
f1 (ppm)

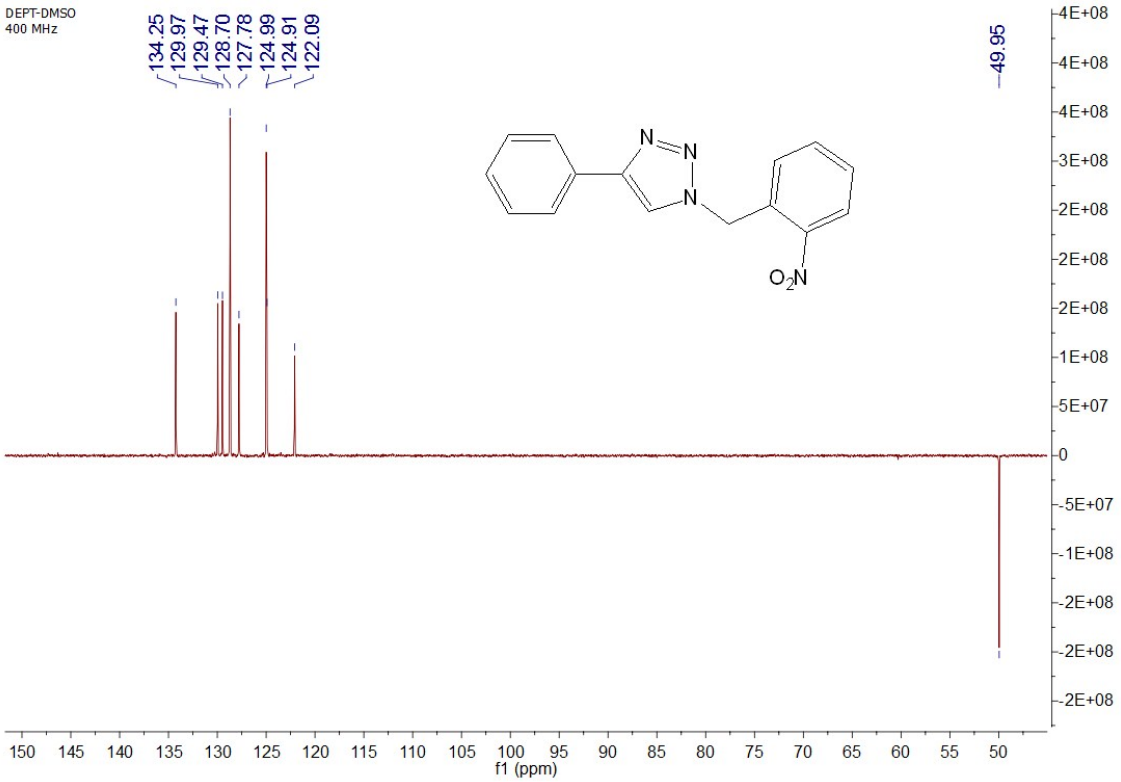
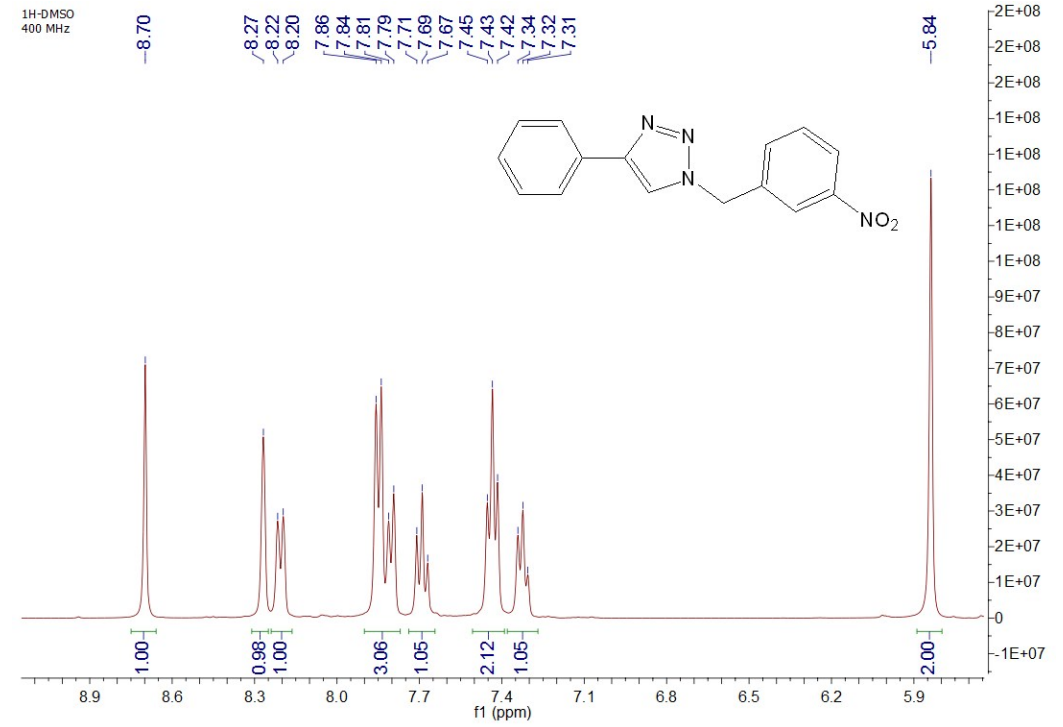
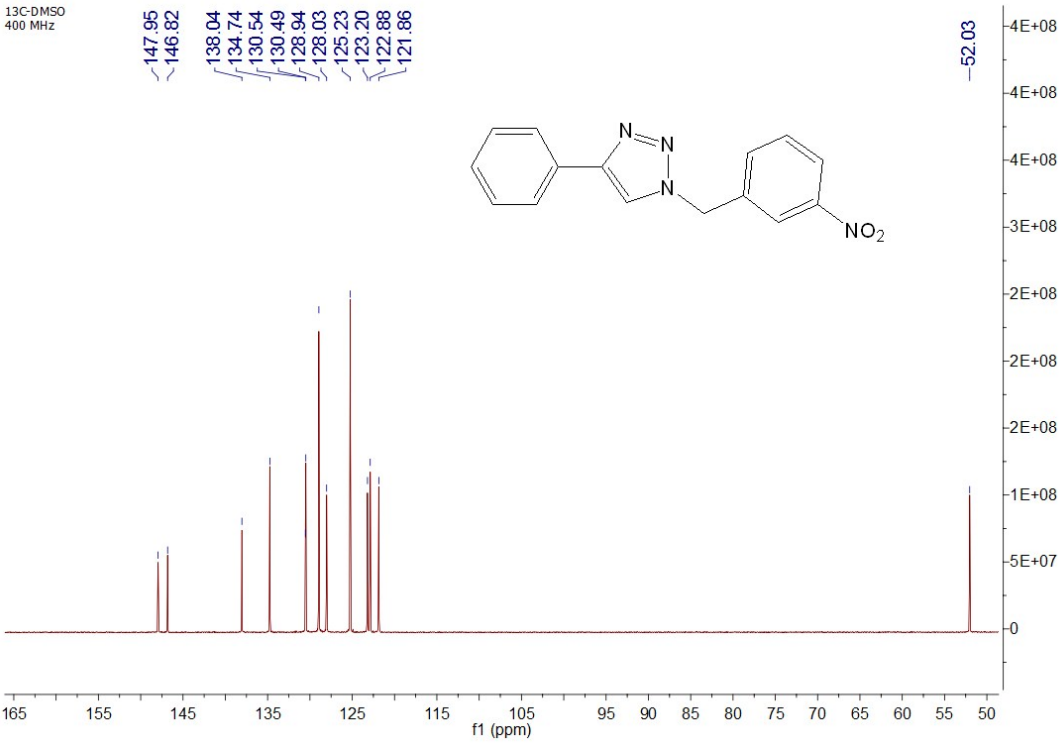


Figure S12. ^{1}H, ^{13}C and DEPT NMR specta of 1-(2-nitrobenzyl)-4-phenyl-1H-1,2,3-triazole.


1H-DMSO
400 MHz
8.70
8.27
8.22
8.20
7.86
7.84
7.81
7.79
7.71
7.69
7.67
7.45
7.43
7.42
7.34
7.32
7.31
5.84
N
N
N
NO2
1.00
0.98
1.00
3.06
1.05
2.12
1.05
2.00
f1 (ppm)


13C-DMSO
400 MHz
147.95
146.82
138.04
134.74
130.54
130.49
128.94
128.03
125.23
123.20
122.88
121.86
52.03
N
N
N
NO2
f1 (ppm)

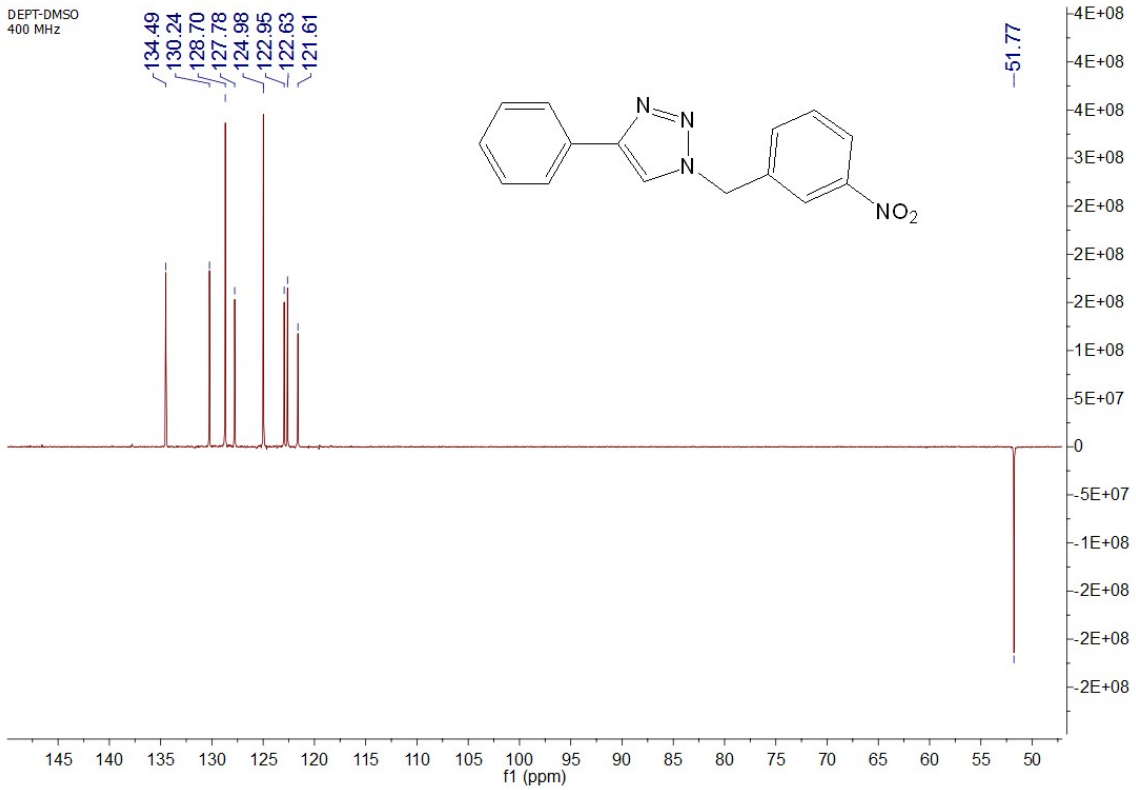
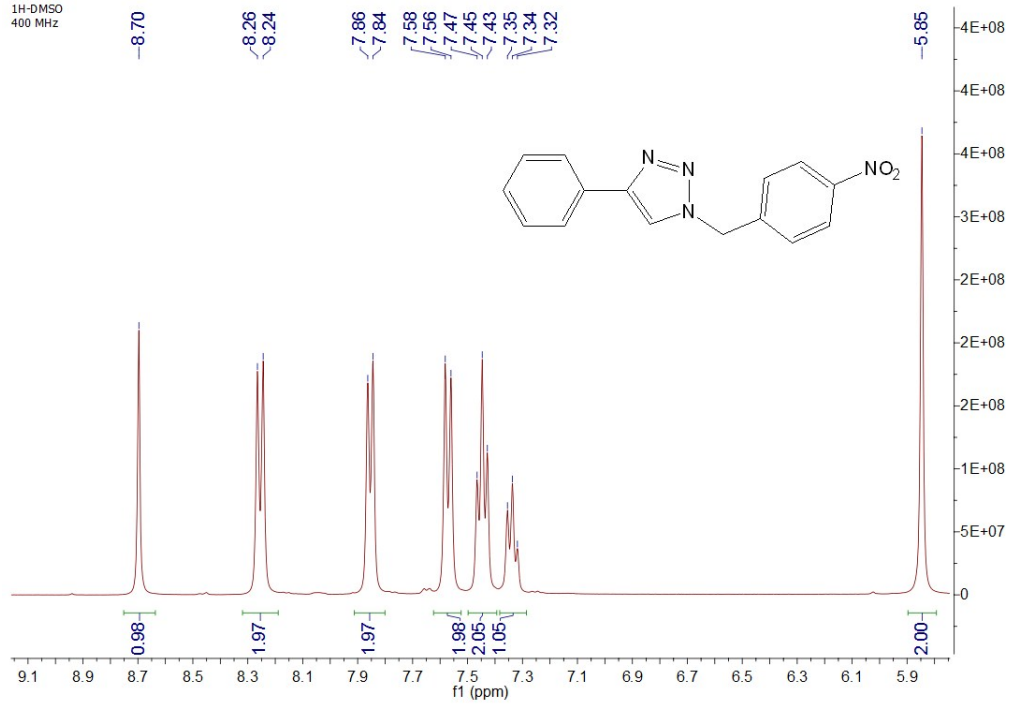
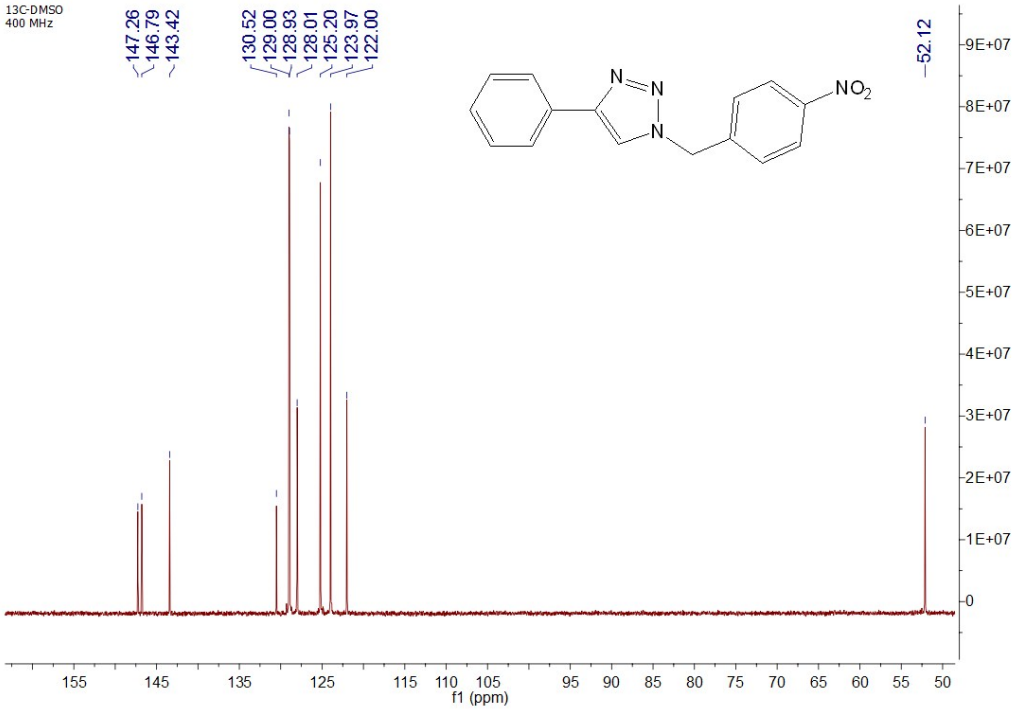


Figure S13. ^{1}H, ^{13}C and DEPT NMR specta of 1-(3-nitrobenzyl)-4-phenyl-1H-1,2,3-triazole.


1H-DMSO
400 MHz
8.70
8.26
8.24
7.86
7.84
7.58
7.56
7.47
7.45
7.43
7.35
7.34
7.32
5.85
N
N
N
NO2
0.98
1.97
1.97
1.98
2.05
1.05
2.00
f1 (ppm)


13C-DMSO
400 MHz
147.26
146.79
143.42
130.52
129.00
128.93
128.01
125.20
123.97
122.00
52.12
N
N
N
NO2
f1 (ppm)

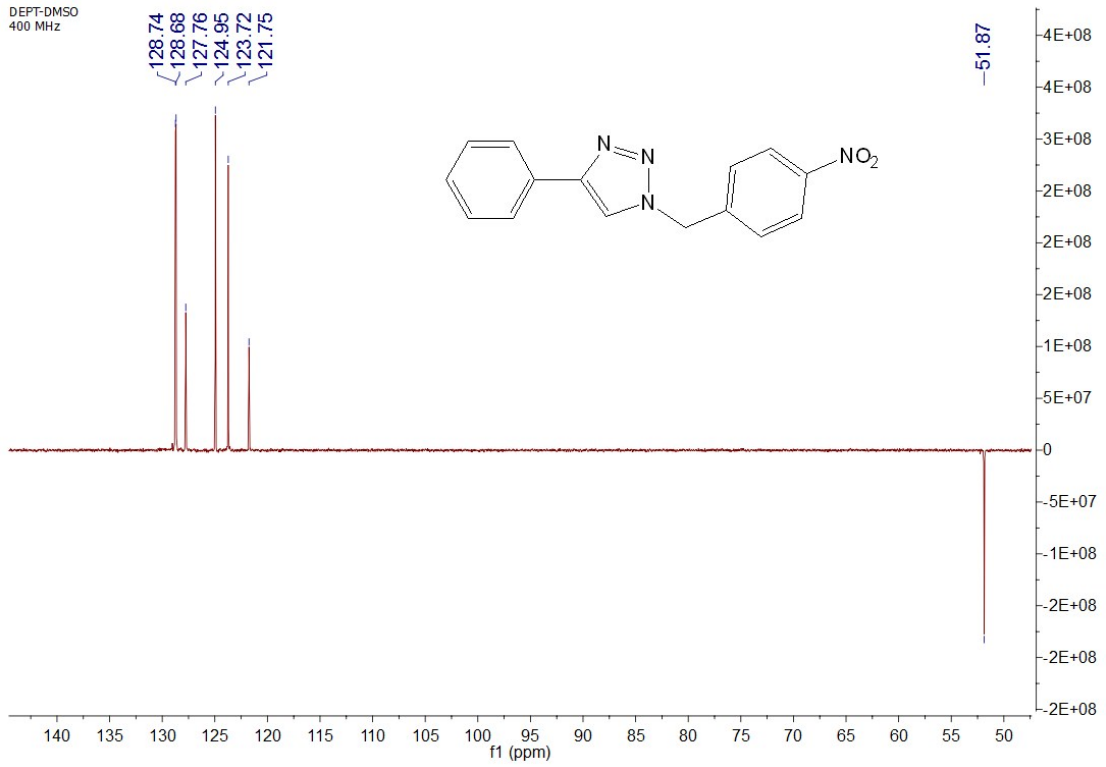
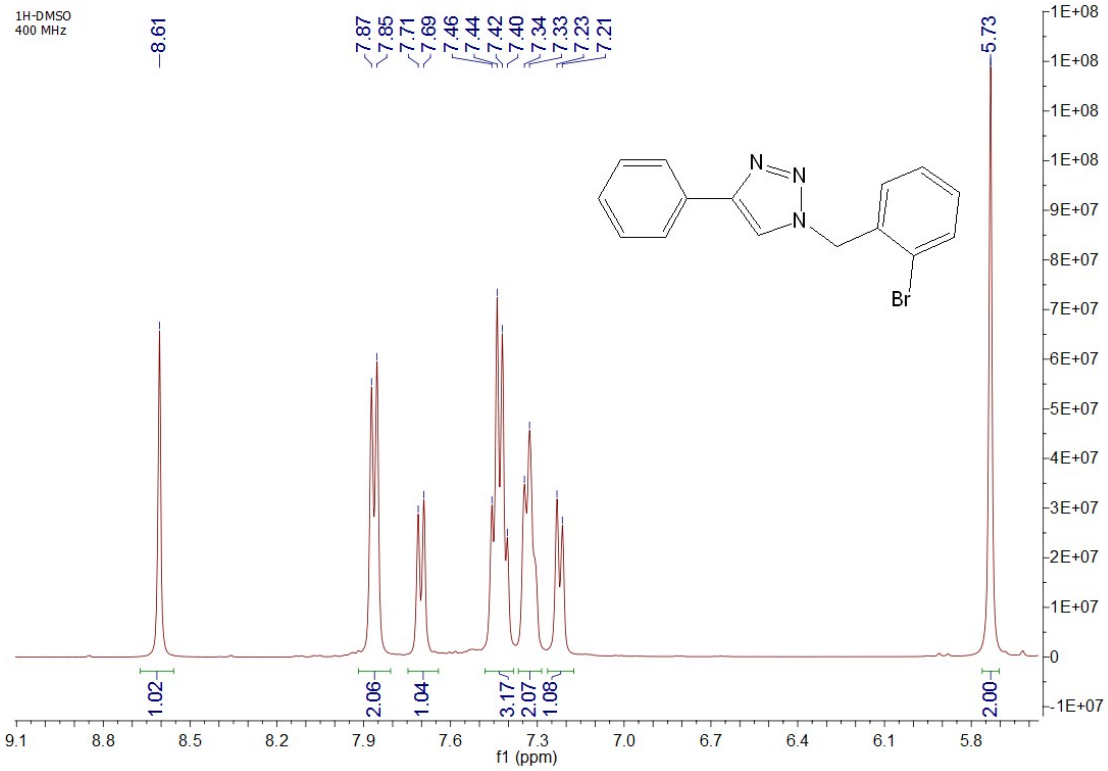
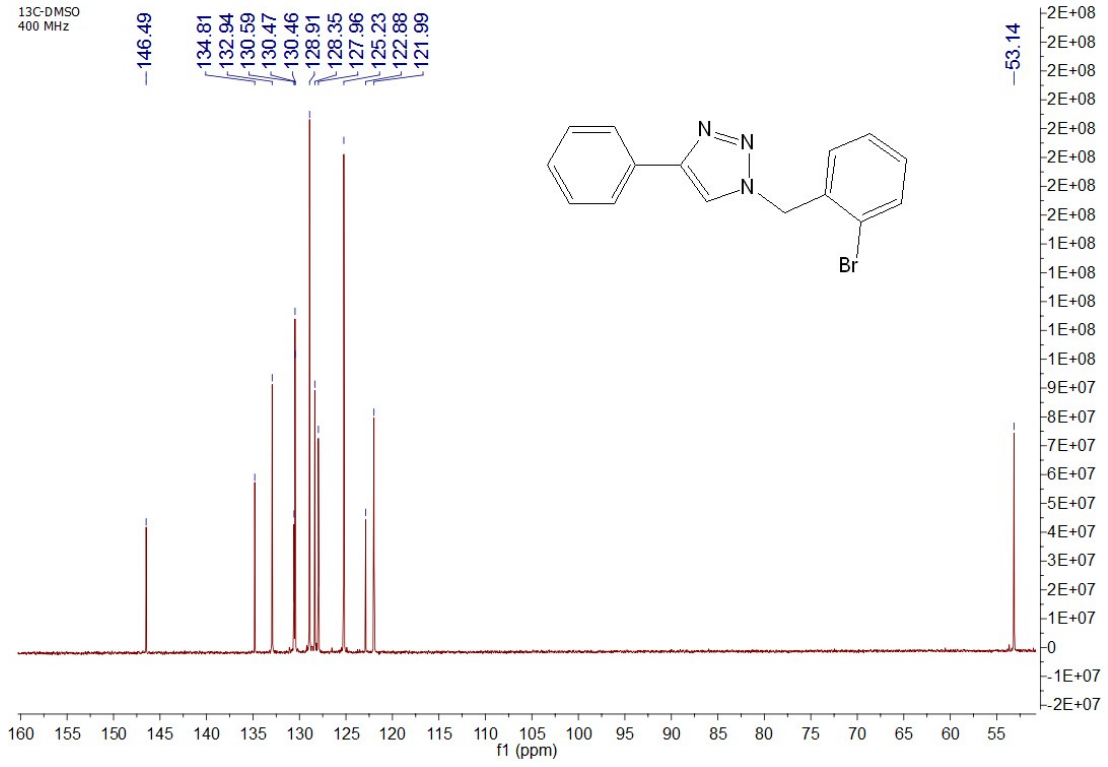


Figure S14. ^{1}H, ^{13}C and DEPT NMR specta of 1-(4-nitrobenzyl)-4-phenyl-1H-1,2,3-triazole.


1H-DMSO
400 MHz
8.61
7.87
7.85
7.71
7.69
7.46
7.44
7.42
7.40
7.34
7.33
7.23
7.21
5.73
1.02
2.06
1.04
3.17
2.07
1.08
2.00
N
N
N
Br
f1 (ppm)


13C-DMSO
400 MHz
146.49
134.81
132.94
130.59
130.47
130.46
128.91
128.35
127.96
125.23
122.88
121.99
53.14
N
N
N
Br
f1 (ppm)

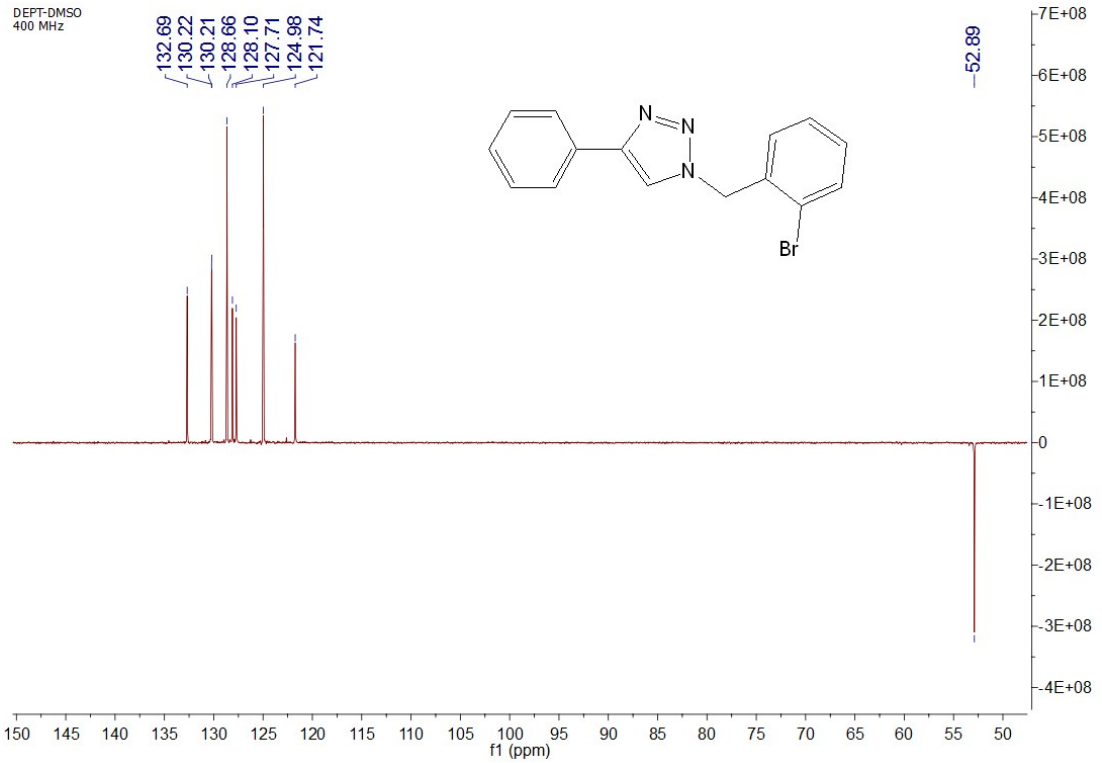
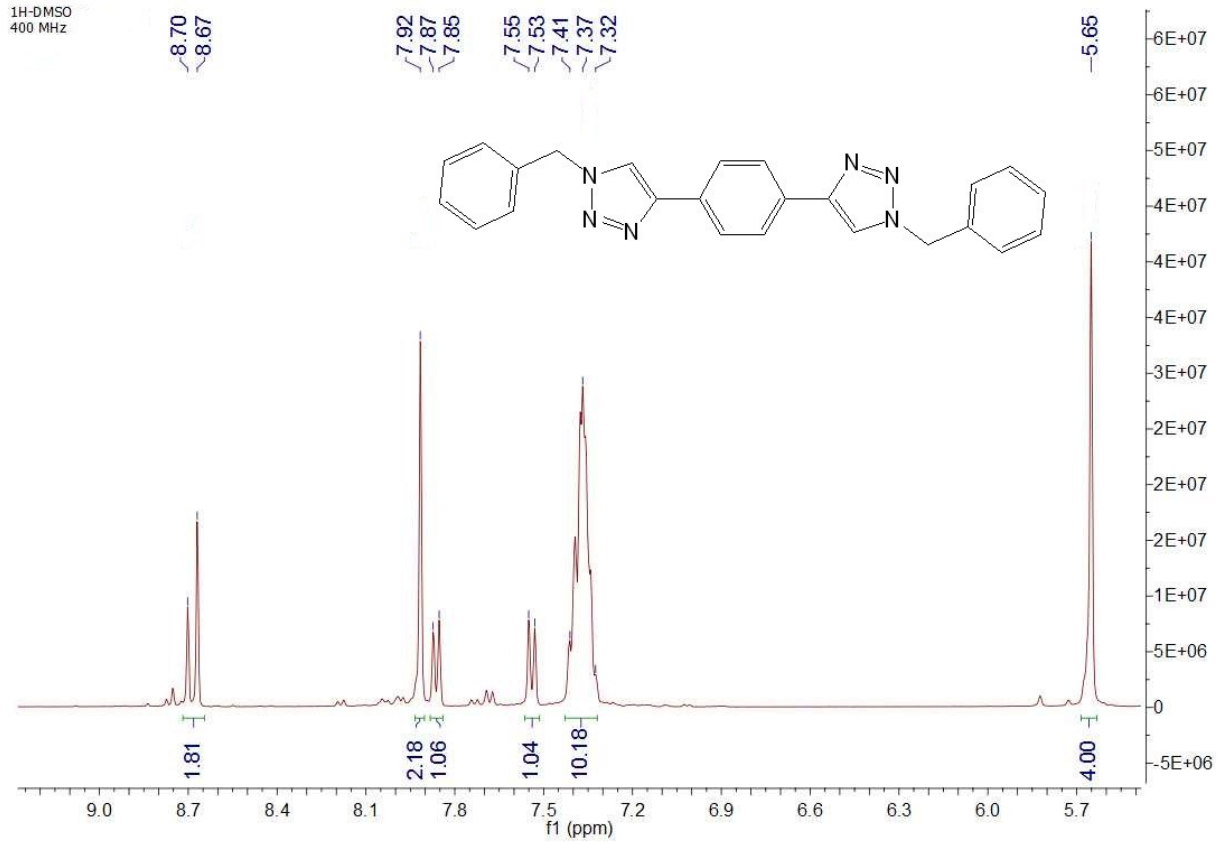
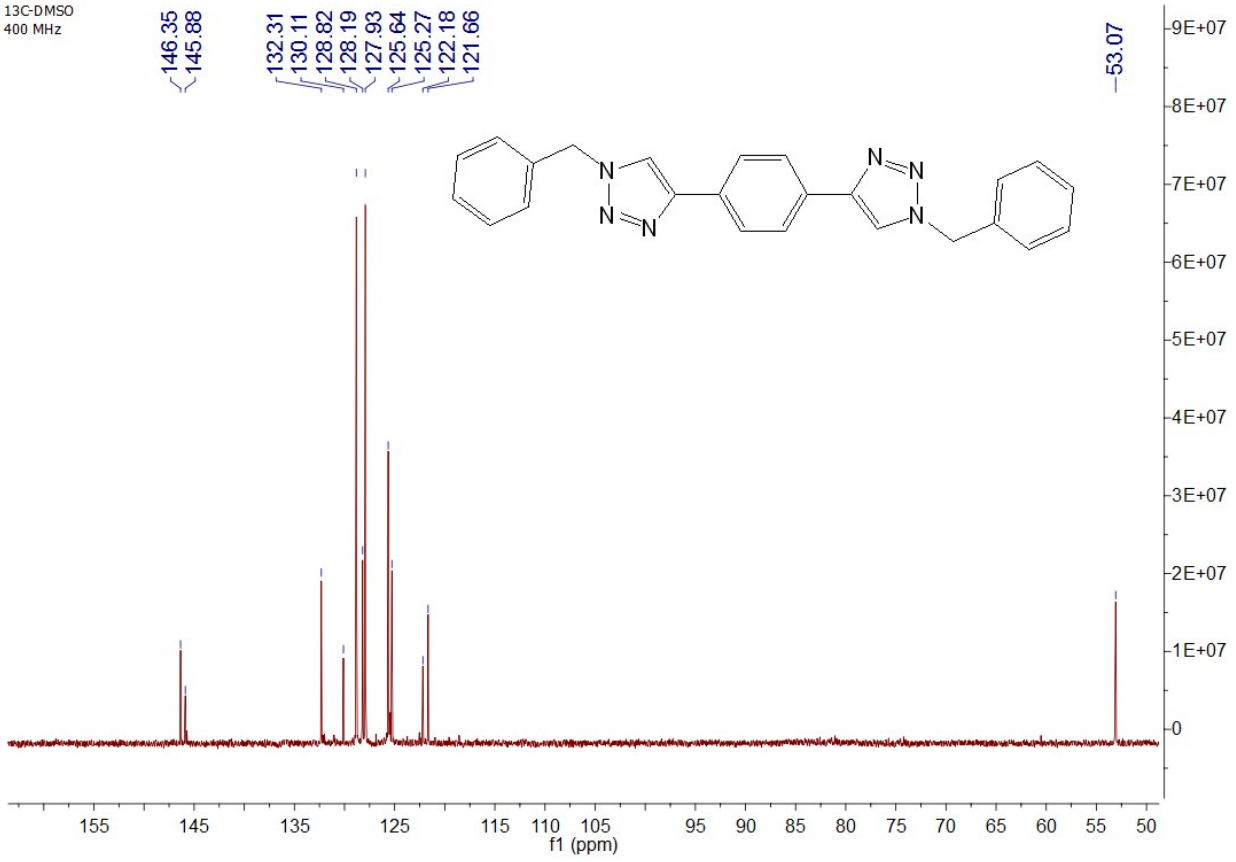


Figure S15. ^{1}H, ^{13}C and DEPT NMR specta of 1-(2-bromobenzyl)-4-phenyl-1H-1,2,3-triazole.


1H-DMSO
400 MHz
8.70
8.67
7.92
7.87
7.85
7.55
7.53
7.41
7.37
7.32
5.65
1.81
2.18
1.06
1.04
10.18
4.00
f1 (ppm)


13C-DMSO
400 MHz
146.35
145.88
132.31
130.11
128.82
128.19
127.93
125.64
125.27
122.18
121.66
53.07
f1 (ppm)

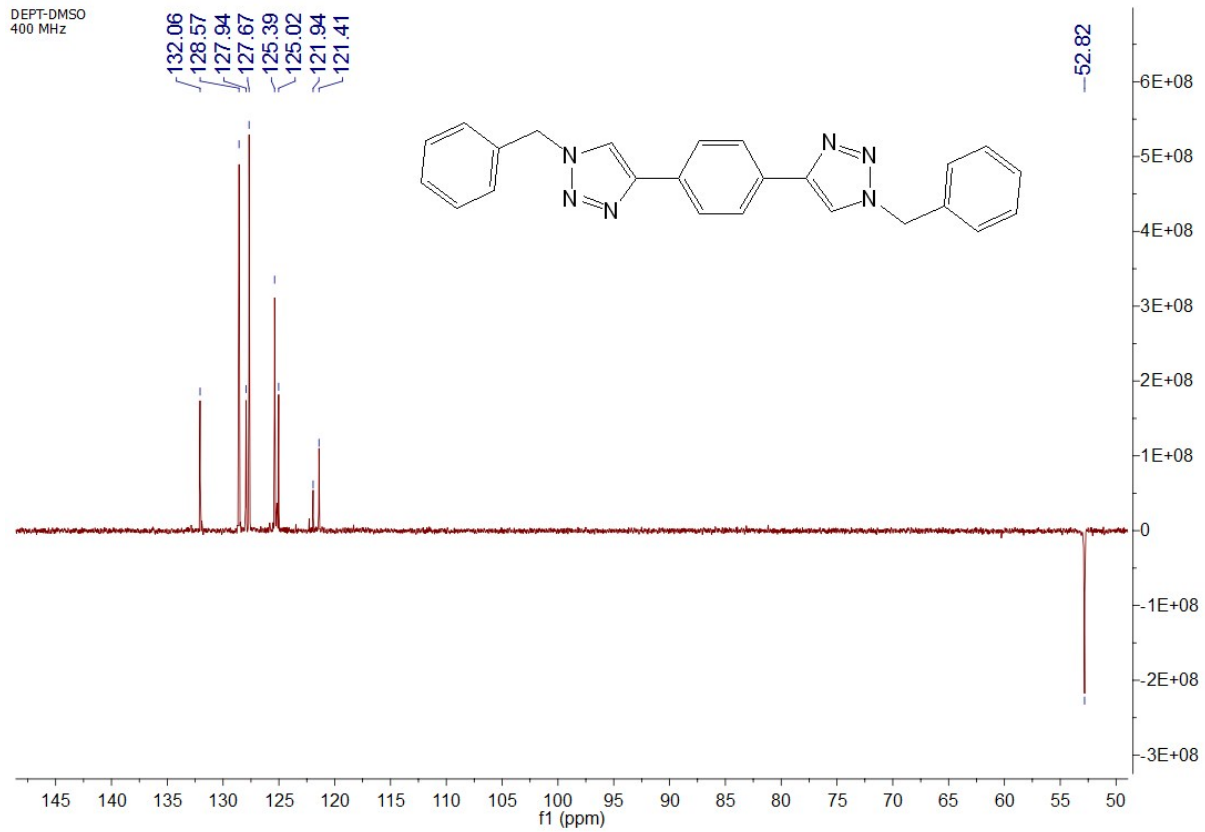
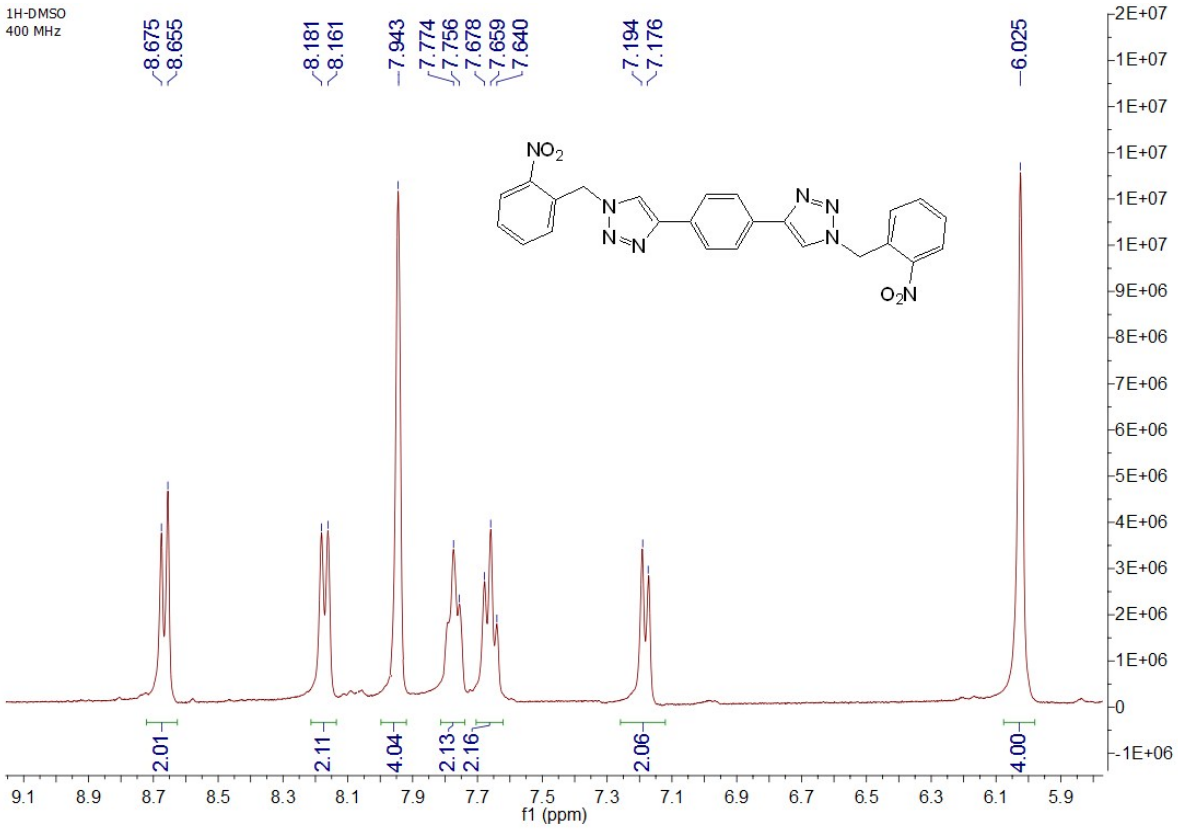
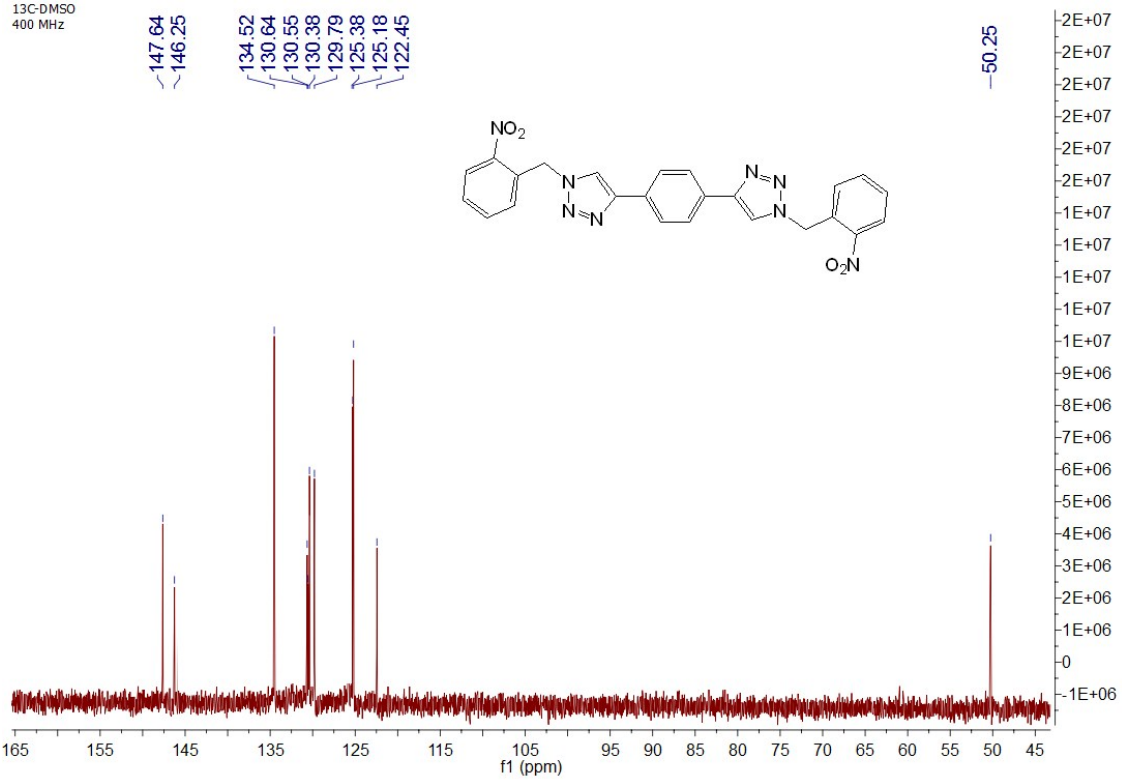


Figure S16. ^{1}H, ^{13}C and DEPT NMR specta of 1,4-bis(1-benzyl-1H-1,2,3-triazol-4-yl)benzene.


1H-DMSO
400 MHz
8.675
8.655
8.181
8.161
7.943
7.774
7.756
7.678
7.659
7.640
7.194
7.176
6.025
NO2
O2N
2.01
2.11
4.04
2.13
2.16
2.06
4.00
f1 (ppm)


13C-DMSO
400 MHz
147.64
146.25
134.52
130.64
130.55
130.38
129.79
125.38
125.18
122.45
50.25
NO2
O2N
f1 (ppm)

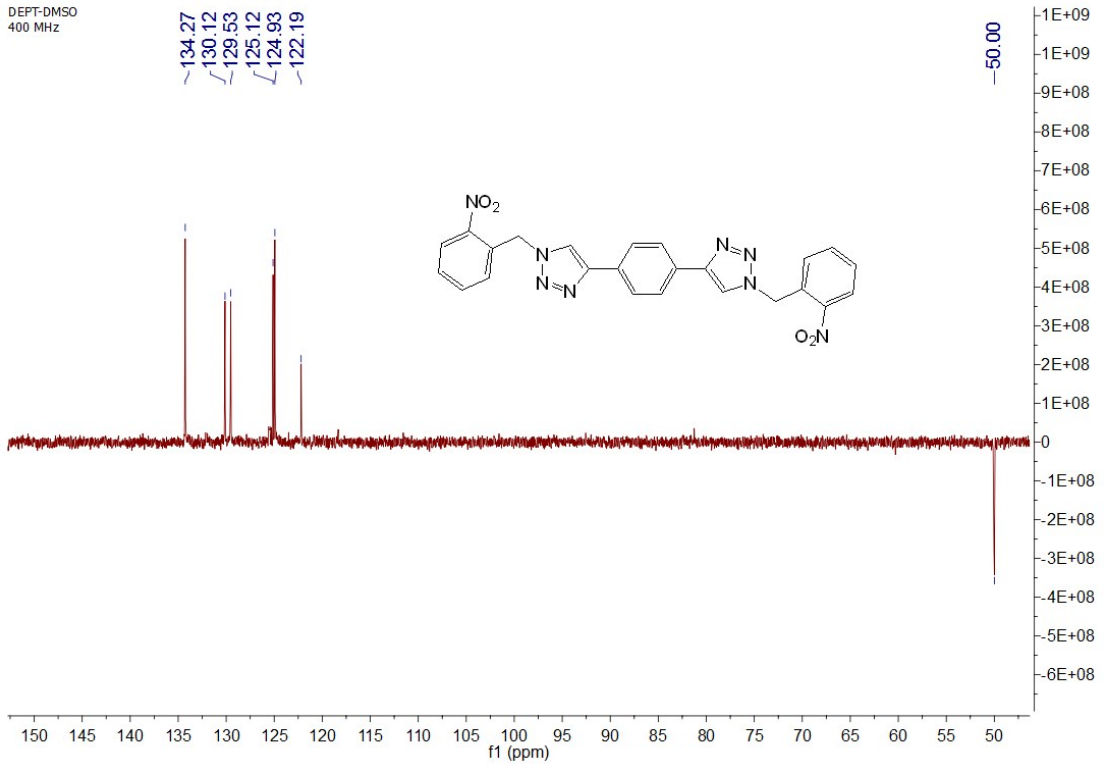
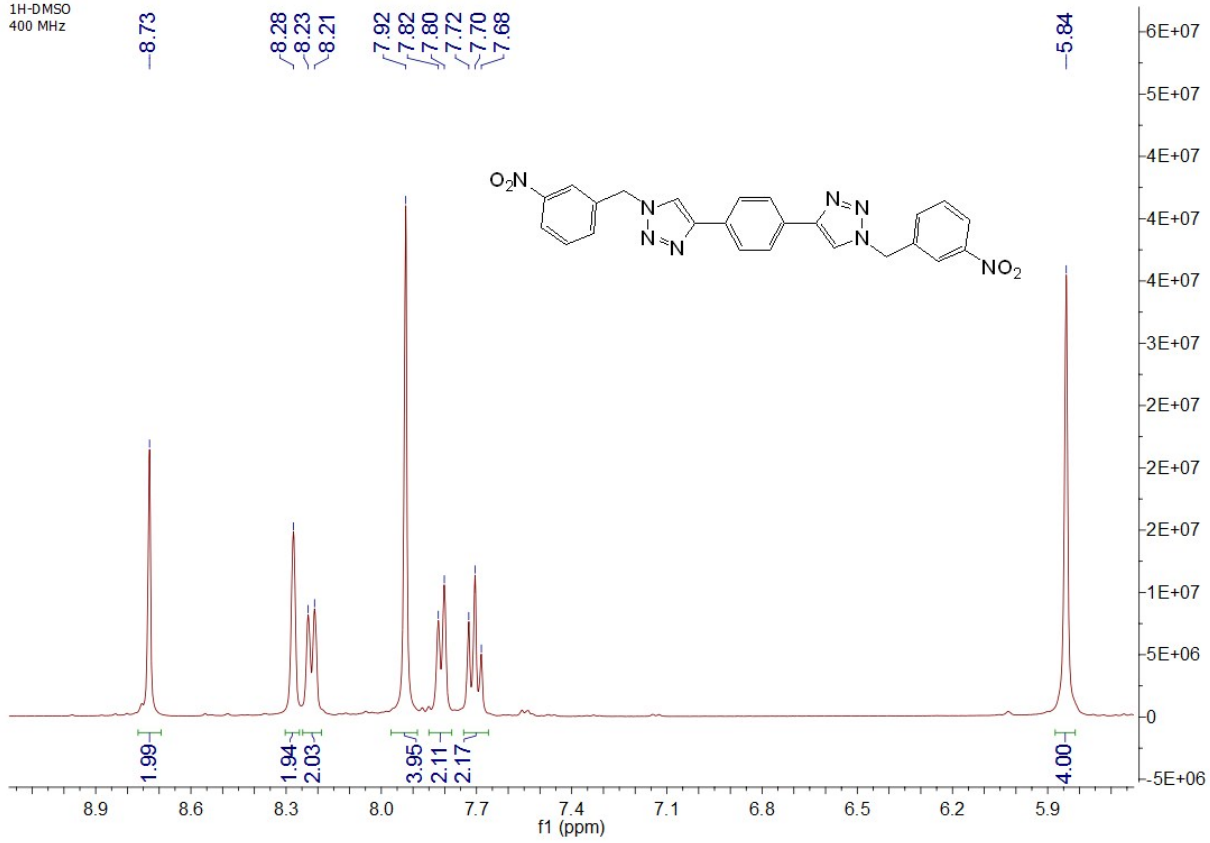
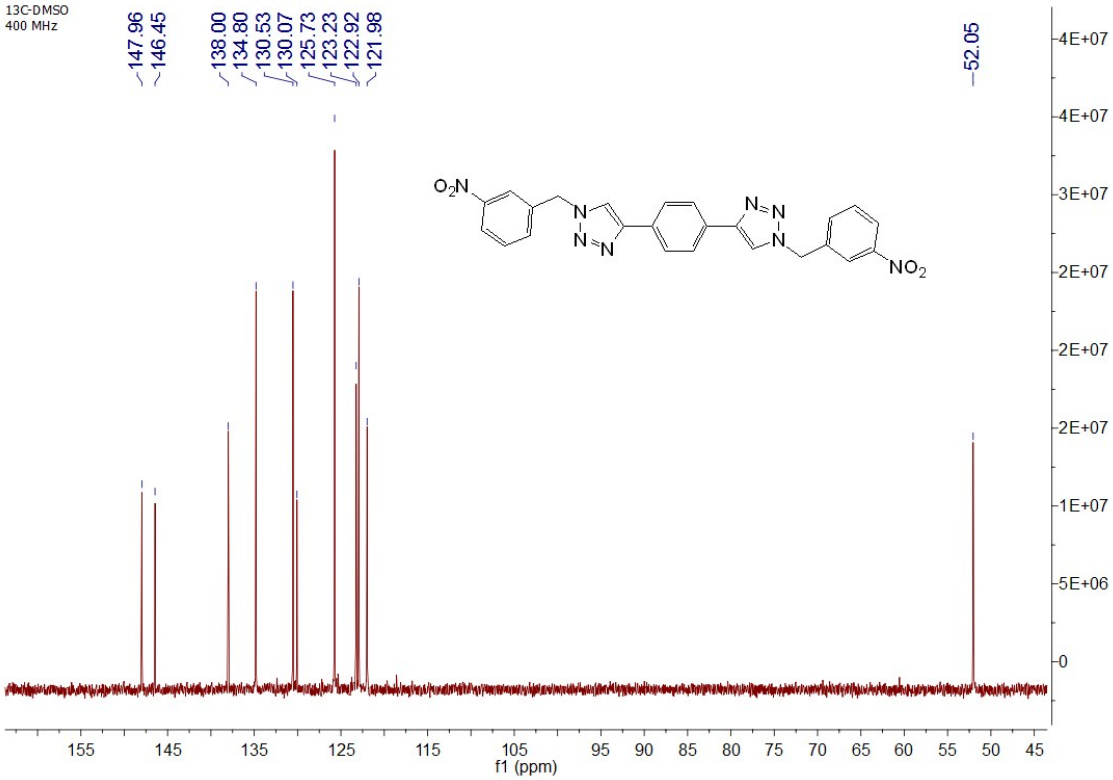


Figure S17. ^{1}H, ^{13}C and DEPT NMR specta of 1,4-bis(1-(2-nitrobenzyl)-1H-1,2,3-triazol-4-yl)benzene.


1H-DMSO
400 MHz
8.73
8.28
8.23
8.21
7.92
7.82
7.80
7.72
7.70
7.68
5.84
1.99
1.94
2.03
3.95
2.11
2.17
4.00
f1 (ppm)


13C-DMSO
400 MHz
147.96
146.45
138.00
134.80
130.53
130.07
125.73
123.23
122.92
121.98
52.05
f1 (ppm)

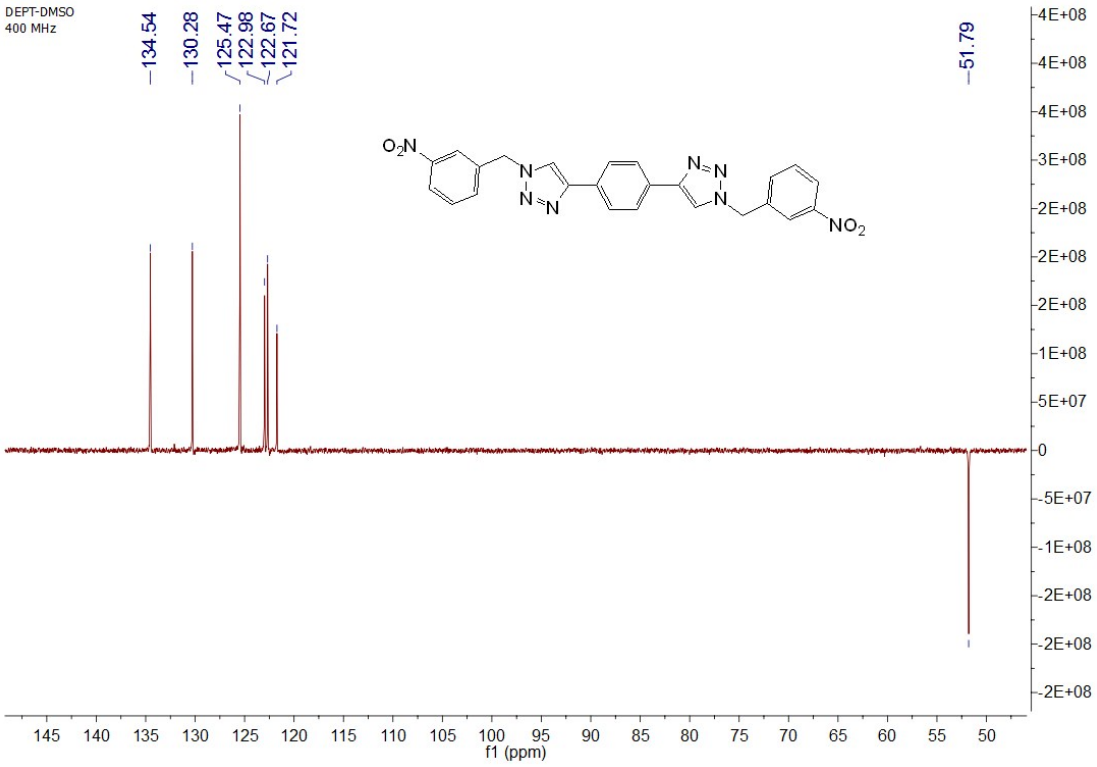
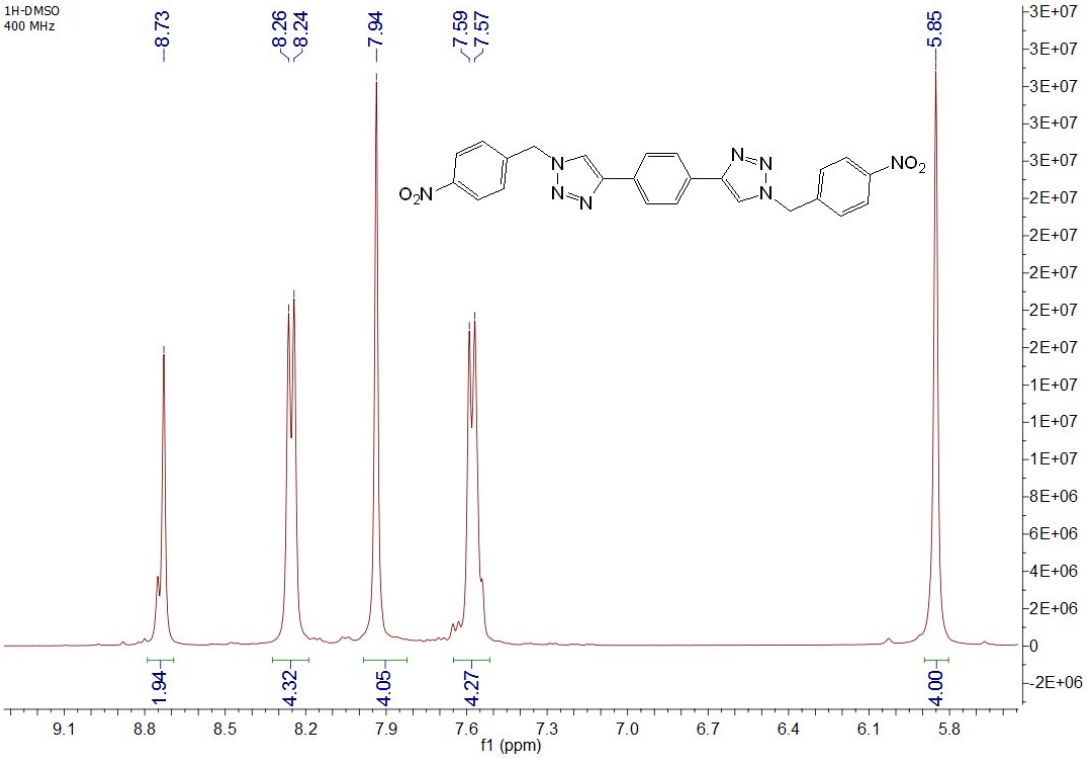
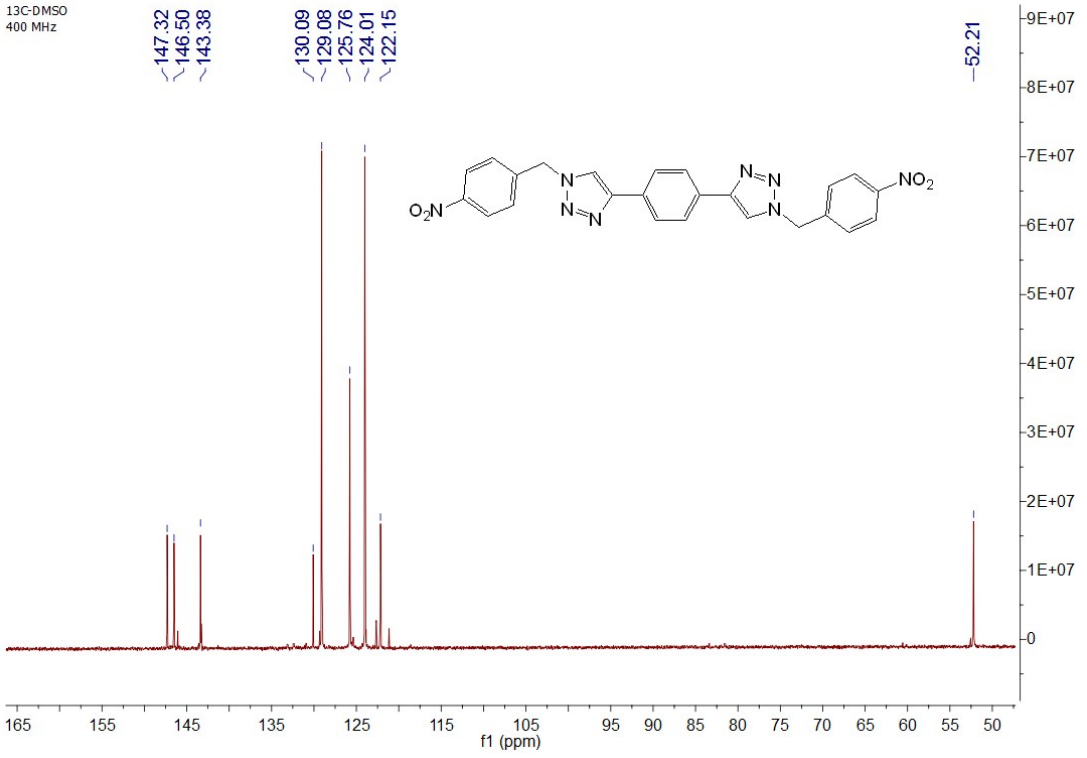


Figure S18. ^{1}H, ^{13}C and DEPT NMR specta of 1,4-bis(1-(3-nitrobenzyl)-1H-1,2,3-triazol-4-yl)benzene.


1H-DMSO
400 MHz
8.73
8.26
8.24
7.94
7.59
7.57
5.85
1.94
4.32
4.05
4.27
4.00
f1 (ppm)


13C-DMSO
400 MHz
147.32
146.50
143.38
130.09
129.08
125.76
124.01
122.15
52.21
f1 (ppm)

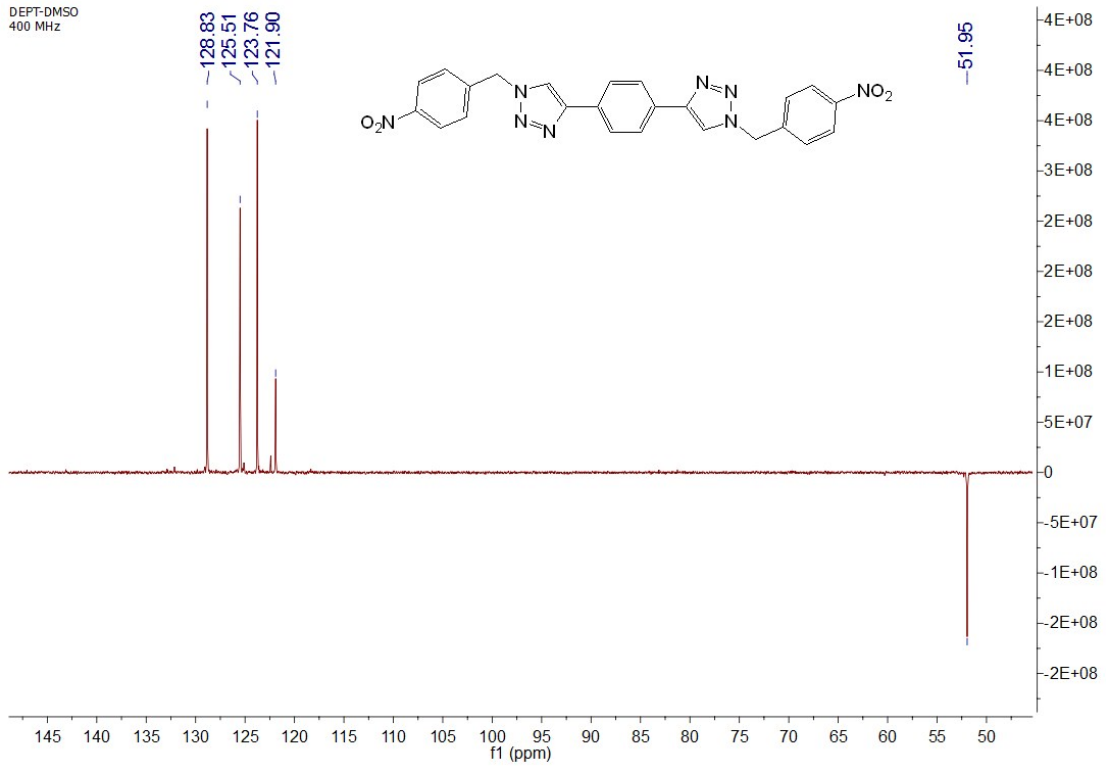
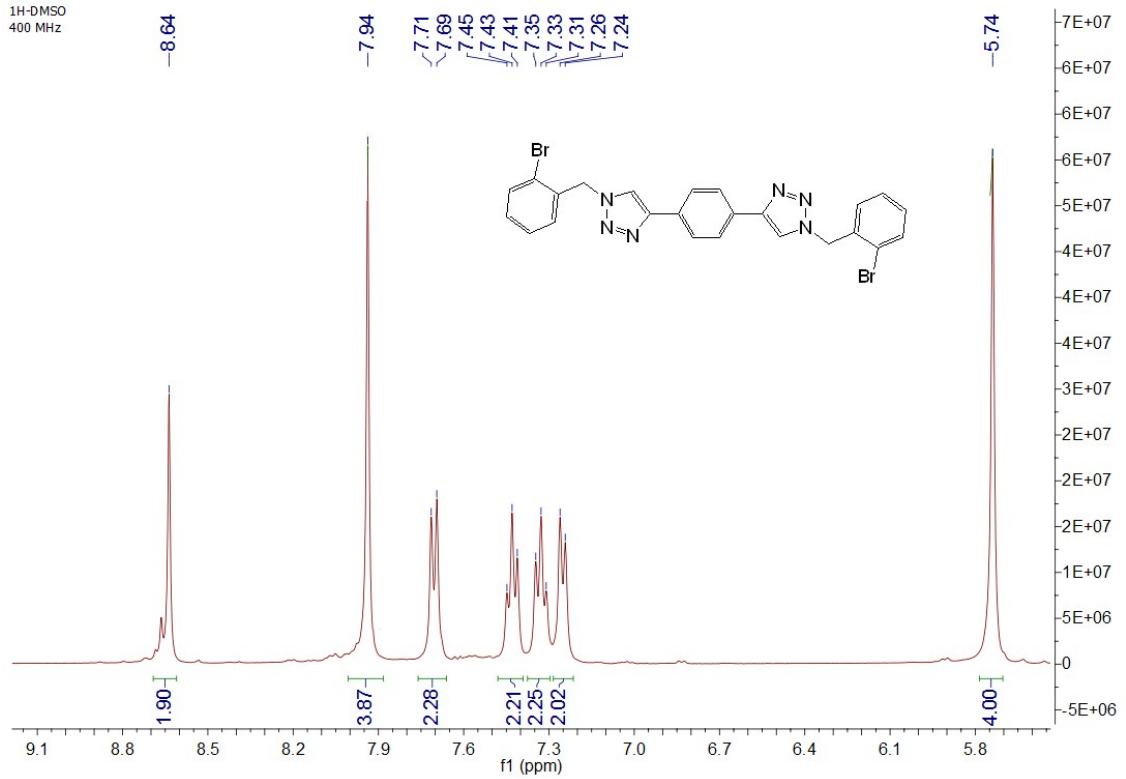
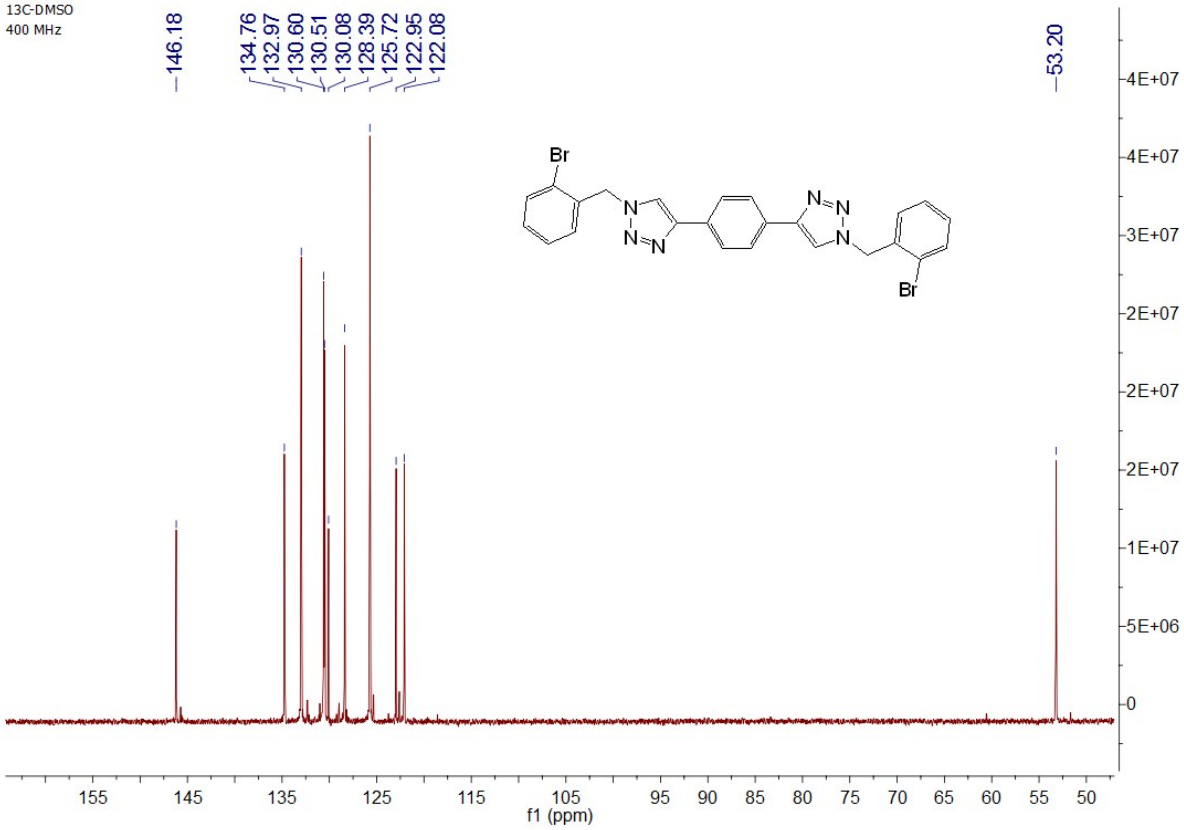


Figure S19. ^{1}H, ^{13}C and DEPT NMR specta of 1,4-bis(1-(4-nitrobenzyl)-1H-1,2,3-triazol-4-yl)benzene.


1H-DMSO
400 MHz
8.64
7.94
7.71
7.69
7.45
7.43
7.41
7.35
7.33
7.31
7.26
7.24
5.74
Br
Br
1.90
3.87
2.28
2.21
2.25
2.02
4.00
f1 (ppm)


13C-DMSO
400 MHz
146.18
134.76
132.97
130.60
130.51
130.08
128.39
125.72
122.95
122.08
53.20
Br
Br
f1 (ppm)

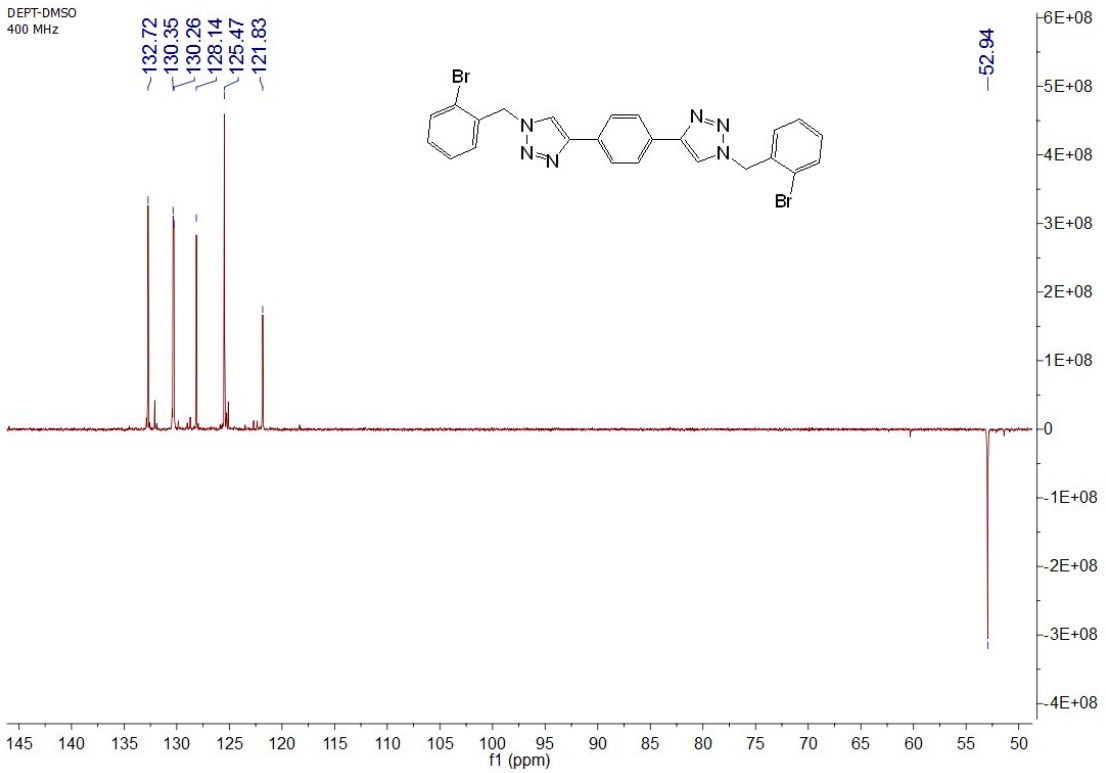


Figure S20. ^{1}H, ^{13}C and DEPT NMR specta of 1,4-bis(1-(2-bromobenzyl)-1H-1,2,3-triazol-4-yl)benzene.

4. ESI(+)-Ms spectra of catalytic mixtures

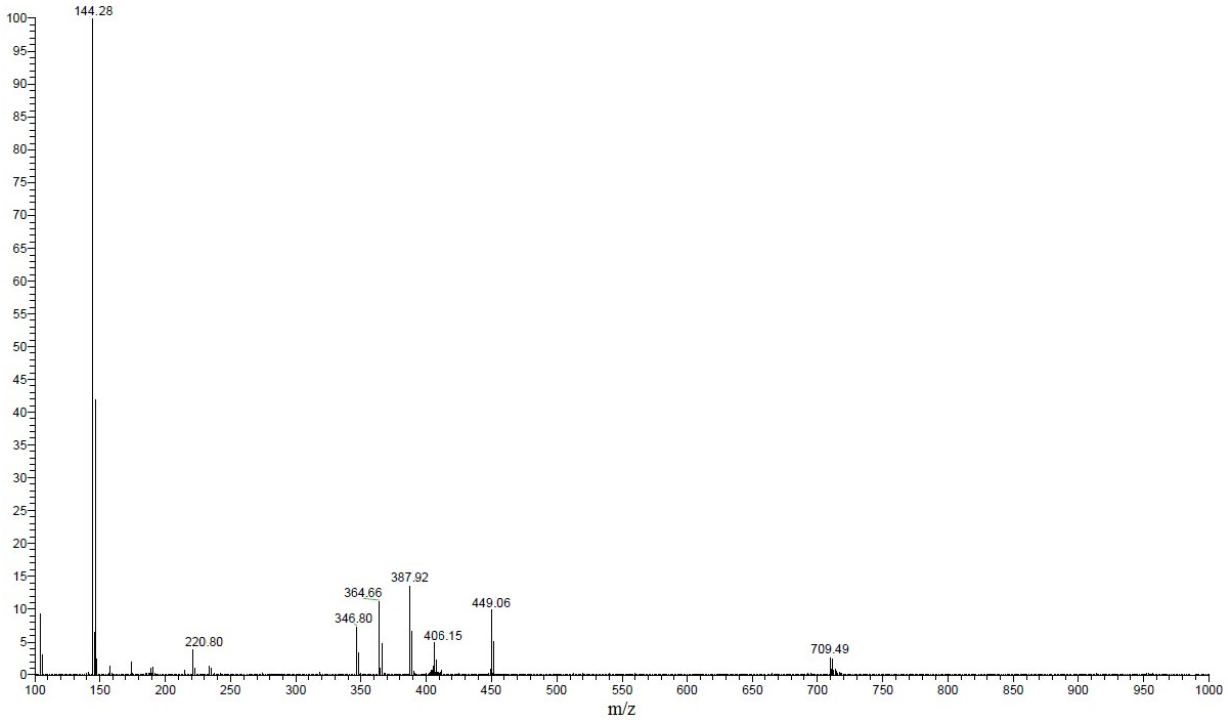


Figure S21. ESI-MS$^+$ spectrum of a mixture of complex **2** and ethynylbenzene.

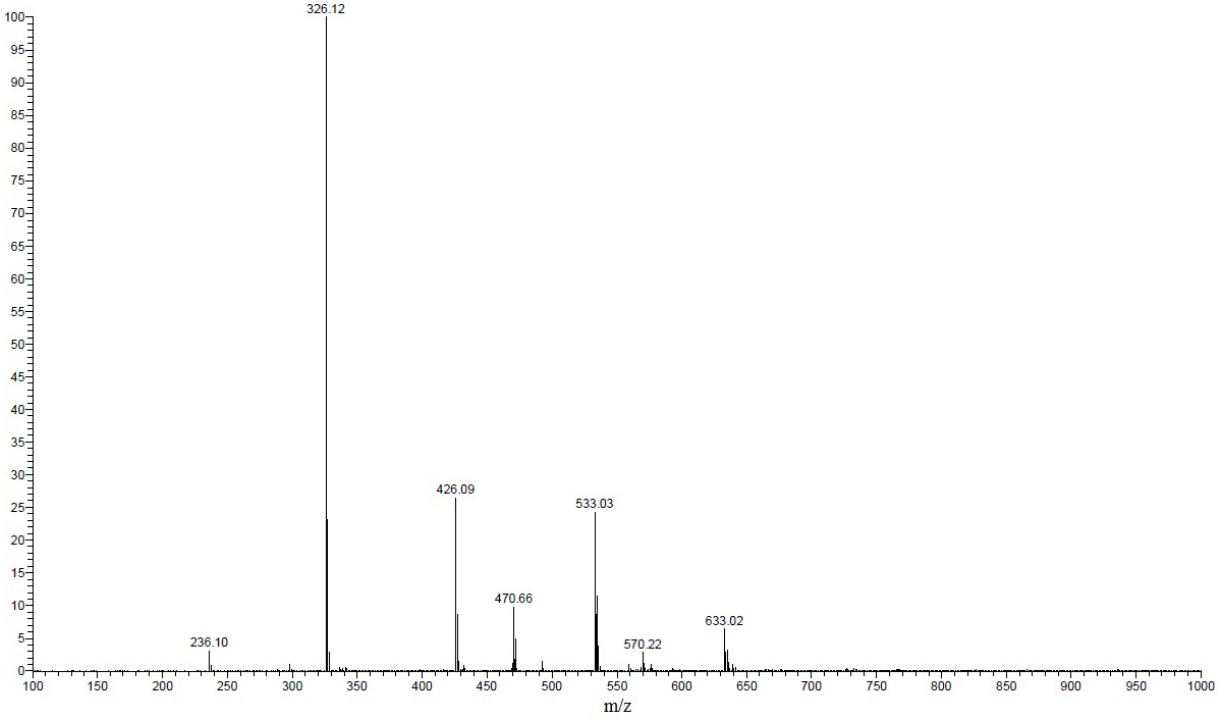


Figure S22. ESI-MS$^+$ spectrum of mixture 2 (Complex **2** + ethynylbenzene + NaN_3 + Benzyl bromide).