Supplementary Materials: Expanding the Scope of Cu(I) Catalyzed "Click Chemistry" with Abnormal-NHCs: Threefold Click to Tris-triazoles

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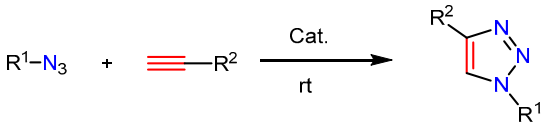
Contents:

Materials and Methods

Catalytic Activity of 2, 3, and 4: Two methods (**A** and **B**) were used to elucidate the catalytic activity of compounds **2**, **3**, and **4**.

Table S1. Scope of the [3+2] cycloaddition of alkynes and azides promoted by complexes 2, 3, and 4.



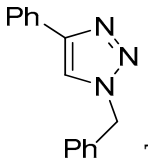
Entry	Time	R^1	R^2	Cat (mol%)	Method	TZ	Yield (%)[a]
1	5 min.	$PhCH_2$	Ph	(aIPr^{Ph})CuI (**2**) (1)	**A**	**TZ-1**	99 (87)
2	5 min	$PhCH_2$	Ph	(aIPr^{Ph})CuI (**2**) (0.5)	**A**	**TZ-1**	100 (70)
3	1h	$PhCH_2$	Ph	(aIPr^{Ph})CuI (**2**) (0.1)	**A**	**TZ-1**	99 (74)
4	3h	$PhCH_2$	Ph	(aIPr^{Ph})CuI (**2**) (0.05)	**B**	**TZ-1**	100 (87)
5	1h	$PhCH_2$	Ph	[(aIPr^{Ph})Cu(IPr)]I (**3**) (1)	**A**	**TZ-1**	-
6	1h	$PhCH_2$	Ph	[(aIPr^{Ph})$_2$Cu]I (**4**) (1)	**A**	**TZ-1**	-
7	5h	$PhCH_2$	Ph	[(aIPr^{Ph})Cu(IPr)]I (**3**) (1)	**A**	**TZ-1**	99 (70)
8	15h	$PhCH_2$	Ph	[(aIPr^{Ph})$_2$Cu]I (**4**) (1)	**A**	**TZ-1**	80 (62)
9	6h	$PhCH_2$	Ph	[(aIPr^{Ph})Cu(IPr)]I (**3**) (1)	**B**	**TZ-1**	99 (69)
10	48h	$PhCH_2$	Ph	[(aIPr^{Ph})$_2$Cu]I (**4**) (1)	**B**	**TZ-1**	55 (40)

11	0.5 h	$PhCH_2$	C_2H_4OH	(aIPr^{Ph})CuI (**2**) (0.5)	**A**	**TZ-2**	99 (78)
12	6h	$PhCH_2$	C_2H_4OH	(aIPr^{Ph})CuI (**2**) (1)	**B**	**TZ-2**	100 (58)
13	6h	$PhCH_2$	C_2H_4OH	[(aIPr^{Ph})Cu(IPr)]I (**3**) (1)	**B**	**TZ-2**	100 (46)
14	15h	$PhCH_2$	C_2H_4OH	[(aIPr^{Ph})$_2$Cu]I (**4**) (1)	**B**	**TZ-2**	80 (40)
15	0.5 h	$PhCH_2$	Bu	(aIPr^{Ph})CuI (**2**) (0.5)	**A**	**TZ-3**	99 (85)
16	6h	$PhCH_2$	Bu	(aIPr^{Ph})CuI (**2**) (1)	**B**	**TZ-3**	100 (85)
17	15h	$PhCH_2$	Bu	[(aIPr^{Ph})Cu(IPr)]I (**3**) (1)	**B**	**TZ-3**	26
18	15h	$PhCH_2$	Bu	[(aIPr^{Ph})$_2$Cu]I (**4**) (1)	**B**	**TZ-3**	8
19	0.5 h	$PhCH_2$	C_3H_6OH	(aIPr^{Ph})CuI (**2**) (0.15)	**A**	**TZ-4**	100 (92)
20	6h	$PhCH_2$	C_3H_6OH	(aIPr^{Ph})CuI (**2**) (1)	**B**	**TZ-4**	99 (92)
21	15h	$PhCH_2$	C_3H_6OH	[(aIPr^{Ph})Cu(IPr)]I (**3**) (1)	**B**	**TZ-4**	99 (76)
22	48h	$PhCH_2$	C_3H_6OH	[(aIPr^{Ph})$_2$Cu]I (**4**) (1)	**B**	**TZ-4**	3
23	0.5 h	$PhCH_2$	C_5H_4N	(aIPr^{Ph})CuI (**2**) (0.5)	**B**	**TZ-5**	100 (80)
24	6 h	$PhCH_2$	C_5H_4N	(aIPr^{Ph})CuI (**2**) (0.5)	**B**	**TZ-5**	99 (80)
25	15h	$PhCH_2$	C_5H_4N	[(aIPr^{Ph})Cu(IPr)]I (**3**) (1)	**B**	**TZ-5**	99 (78)
26	15h	$PhCH_2$	C_5H_4N	[(aIPr^{Ph})$_2$Cu]I (**4**) (1)	**B**	**TZ-5**	83 (68)
27	4h	$PhCH_2$	Me_2NCH_2	(aIPr^{Ph})CuI (**2**) (0.05)	**A**	**TZ-6**	99 (76)
28	4h	$PhCH_2$	$PhOCH_2$	(aIPr^{Ph})CuI (**2**) (0.05)	**B**	**TZ-7**	100 (98)
29	4h	Ph	Ph	(aIPr^{Ph})CuI (**2**) (0.05)	**A**	**TZ-8**	99 (57)
30	4h	4-tolyl	Ph	(aIPr^{Ph})CuI (**2**) (0.05)	**A**	**TZ-9**	98 (44)
31	1h	4-Br-$C_6H_4CH_2$	Ph	(aIPr^{Ph})CuI (**2**) (0.05)	**A**	**TZ-10**	99 (55)

[a]Conversion by ^{1}H NMR analysis (Isolated yield).

I. Synthesis of Triazoles

***Synthesis of 1-benzyl-4-phenyl-1H-1,2,3-triazol* (TZ-1).**



TZ-1

Method A. To a neat solution of phenyl acetylene (0.41 mL, 3.75 mmol) and benzyl azide (0.50 g, 3.75 mmol) was added compound **2** (25 mg, 1 mol%). The reaction mixture was stirred at room temperature (23 °C), which turned into an off-white solid after 5 minutes. The ^{1}H NMR analysis of the crude product indicated 100% conversion. The residue was washed with pentane and dried under vacuum to obtain the triazole **TZ-1**.

Catalyst loading:	Conversion	Time (h)	Isolated yield:
(aIPr^{Ph})CuI (**2**), 25 mg, 1 mol%	100 %	0.08	87%.
(aIPr^{Ph})Cu(IPr)I (**3**), 39 mg, 1 mol%	0 %	1	-
(aIPr^{Ph})$_2$CuI (**4**), 42 mg, 1 mol%	0 %	1	-
(aIPr^{Ph})Cu(IPr)I (**3**), 39 mg, 1 mol%	99 %	5	70%
(aIPr^{Ph})$_2$CuI (**4**), 42 mg, 1 mol%	0 %	5	-

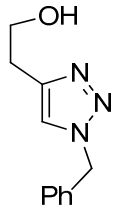
Method B. Phenylacetylene (0.41 mL, 3.75 mmol) and benzyl azide (0.5 g, 3.75 mmol) was added to a solution of the appropriate catalyst in DCM (10 mL). The reaction mixture was stirred for 3 or 48 h. The conversion of the reactants was monitored by ^{1}H-NMR spectroscopy. The reaction mixture was filtered and all volatiles were removed under vacuum to obtain the product. Catalyst loadings, ^{1}H-NMR conversion, and isolated yields are shown in the tables below.

Catalyst loading:	Conversion after 3 h	Isolated yield:
(aIPr^{Ph})CuI (**2**), 25 mg, 1 mol%	83 %	570 mg, 2.42 mmol, 65%.
(aIPr^{Ph})Cu(IPr)I (**3**), 39 mg, 1 mol%	0 %	-
(aIPr^{Ph})$_2$CuI(**4**), 42 mg, 1 mol%	0 %	-

Catalyst loading:	Conversion after 48 h	Isolated yield:
(aIPr^{Ph})CuI (**2**), 25 mg, 1 mol%	100 %	758 mg, 3.33 mmol, 89%.
(aIPr^{Ph})Cu(IPr)I (**3**), 39 mg, 1 mol%	100 %	610 mg, 2.59 mmol, 69%
(aIPr^{Ph})$_2$CuI(**4**), 42 mg, 1 mol%	55 %	350 mg, 1.48 mmol, 40%

^{1}H NMR (300.13 MHz, 298 K, $CDCl_3$): δ 5.57 (s, 2H, $CH_2C_6H_5$), 7.28-7.42 (m, 8H, $CH_2C_6H_5$, *m*-C_6H_5, *p*-C_6H_5), 7.67 (s, 1H, CN_3CH), 7.80 (dd, J = 8.3 Hz, 2H, *o*-C_6H_5) ppm.
^{13}C NMR (75.47 MHz, 298 K, $CDCl_3$): δ 54.32 ($CH_2C_6H_5$), 119.61 (CN_3CH), 125.80, 128.15, 128.25, 128.87, 128.90, 129.25, 130.66, 134.81 ($CH_2C_6H_5$, C_6H_5), 148.32 (CN_3CH) ppm.
Reference[1]

***Synthesis of 2-(1-benzyl-1H-1,2,3-triazol-4-yl)ethanol* (TZ-2).**



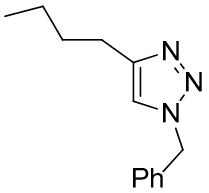
Method B. 3-Butyne-1-ol (0.29 mL, 3.75 mmol) and benzyl azide (0.5 g, 3.75 mmol):

Catalyst loading:	Conversion after 15 h	Isolated yield:
(aIPr^{Ph})CuI (**2**), 25 mg, 1 mol%	100 %	445 mg, 2.19 mmol, 58%
(aIPr^{Ph})Cu(IPr)I (**3**), 39 mg, 1 mol%	100 %	350 mg, 1.73 mmol, 46%.
(aIPr^{Ph})$_2$CuI (**4**), 42 mg, 1 mol%	80 %	304 mg, 1.50 mmol, 40%

^{1}H NMR (300.13 MHz, 298 K, $CDCl_3$): δ 3.37 (dt, 4H, J = 11.5, 6.0 Hz C_2H_4OH), 5.46 (s, 2H, $CH_2C_6H_5$), 7.22–7.26 (m, 2H, *o*-C_6H_5), 7.31–7.36 (m, 4H, *p*-C_6H_5, *m-p*-C_6H_5, CN_3CH) ppm.

^{13}C NMR (75.47 MHz, 298 K, $CDCl_3$): δ 28.84 (C_2H_4OH), 53.95 ($CH_2C_6H_5$), 61.22 (C_2H_4OH), 121.88 (CN_3CH), 127.97, 128.57, 128.98 ($CH_2C_6H_5$), 134.73 (CN_3CH) ppm.
Reference:[2]

***Synthesis of 1-benzyl-4-butyl-1H-1,2,3-triazol* (TZ-3).**

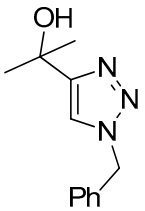


Method B. 1-Hexyne (0.43 mL, 3.75 mmol) and benzyl azide (0.5 g, 3.75 mmol):

Catalyst loading:	Conversion after 15 h	Isolated yield:
(aIPr^{Ph})CuI (**2**), 25 mg, 1 mol%	100 %	690 mg, 3.21 mmol, 85%.
(aIPr^{Ph})Cu(IPr)I (**3**), 39 mg, 1 mol%	26 %	96 mg, 0.45 mmol, 12%
(aIPr^{Ph})$_2$CuI (**4**), 42 mg, 1 mol%	8 %	-

^{1}H NMR (300.13 MHz, 298 K, $CDCl_3$): δ 0.90 (t, J = 7.3 Hz, 3H, C_4H_6Me), 1.35 (sext, 2H, J = 7.3 Hz, C_4H_6Me), 1.61 (pent, 2H, J = 7.3 Hz, C_4H_6Me), 2.67 (t, J = 8.1 Hz, 2H, C_4H_6Me), 5.47 (s, 2H, $CH_2C_6H_5$), 7.17 (s, 1H, CN_3CH), 7.22–7.26 (m, 2H, *o*-$CH_2C_6H_5$), 7.32–7.39 (m, 3H, *m-p*-$CH_2C_6H_5$) ppm.
^{13}C NMR (75.47 MHz, 298 K, $CDCl_3$): δ 13.84 (C_4H_6Me), 22.35 (C_4H_6Me), 25.45 (C_4H_6Me), 31.55 (C_4H_6Me), 53.98 ($CH_2C_6H_5$), 120.57 (CN_3CH), 127.97 (*m*-C_6H_5), 128.59 (*p*-C_6H_5), 129.05 (*o*-C_6H_5), 135.09 (*ipso*-C_6H_5), 148.98 (CN_3CH) ppm.
Reference: [2]

***Synthesis of 2-(1-benzyl-1H-1,2,3-triazol-4-yl)propan-2-ol*(TZ-4).**



Method B. 2-Methyl-3-butyne-2-ol (0.37 mL, 3.75 mmol) and benzyl azide (0.5 g, 3.75 mmol):

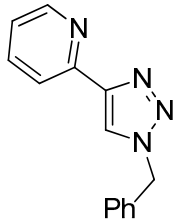
Catalyst loading:	Conversion after 15 h	Isolated yield:
(aIPr^{Ph})CuI (**2**), 25 mg, 1 mol%	100 %	740 mg, 3.48 mmol, 92 %.

(aIPr^{Ph})Cu(IPr)I (**3**), 39 mg, 1 mol%	100 %	620 mg, 2.85 mmol, 76 %.

Catalyst loading:	Conversion after 48 h	Isolated yield:
(aIPr^{Ph})$_2$CuI (**4**), 42 mg, 1 mol%	3 %	-

^{1}H NMR (300.13 MHz, 298 K, $CDCl_3$): δ 1.60 (s, 6H, C(OH)*Me*$_2$), 2.73 (s, 1H, O*H*), 5.48 (s, 2H, C*H*$_2$C$_6$H$_5$), 7.24–7.30 (m, 2H, *o*-CH$_2$C$_6$*H*$_5$), 7.34–7.39 (m, 4H, *m*-*p*- CH$_2$C$_6$*H*$_5$, CN$_3$*CH*) ppm.
^{13}C NMR (75.47 MHz, 298 K, $CDCl_3$): δ 30.51 (C*Me*$_2$OH), 54.16 (*C*H$_2$C$_6$H$_5$), 68.55 (*C*Me$_2$OH), 119.22 (N*C*HC), 128.19 (*o*-*C*$_6$H$_5$), 128.76 (*p*-*C*$_6$H$_5$), 129.15 (*m*-*C*$_6$H$_5$), 134.74 (NCH*C*) ppm.
Reference: [3]

***Synthesis of 2-(1-benzyl-1H-1,2,3-triazol-4-yn)pyridine* (TZ-5).**

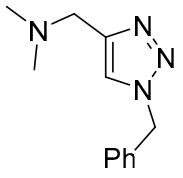


Method B. 2-Ethynylpyridine (0.41 mL, 3.75 mmol) and (azidomethyl)benzene (0.5 g, 3.75 mmol):

Catalyst loading:	Conversion after 15 h	Isolated yield:
(aIPr^{Ph})CuI (**2**), 25 mg, 1 mol%	100%	710 mg, 3.00 mmol, 80%.
(aIPr^{Ph})Cu(IPr)I (**3**), 39 mg, 1 mol%	100%	690 mg, 2.92 mmol, 78%
(aIPr^{Ph})$_2$CuI (**4**), 42 mg, 1 mol%	83 %	600 mg, 2.54 mmol, 68%

^{1}H NMR (300.13 MHz, 298 K, $CDCl_3$): δ 5.50 (s, 2H, C*H*$_2$C$_6$H$_5$), 7.13 (m, 1H, *J* = 7.4, 4.9, 1.1 Hz, *p*-C$_5$*H*$_4$N), 7.23–7.34 (m, 5H, CH$_2$C$_6$*H*$_5$), 7.68 (dt, *J* = 7.7, 1.7 Hz, 1H, *m*- NC$_5$*H*$_4$), 7.98 (s, 1H, CN$_3$C*H*), 8.08 (d, 1H, *J* = 8.0 Hz, *o*-NC$_5$*H*$_4$), 8.45 (d, *J* = 4.9 Hz, 1H, *m*-NC$_5$*H*$_4$) ppm.
^{13}C NMR (75.47 MHz, 298 K, $CDCl_3$): δ 54.46 (CH$_2$C$_6$H$_5$), 120.30 (*p*-*C*$_5$NH$_4$), 122.01 (NCHC), 122.92 (*p*-C$_5$NH$_4$), 128.39 (*o*-*C*$_6$H$_5$), 128.92 (*p*-*C*$_6$H$_5$), 129.25 (*m*-*C*$_6$H$_5$), 134.45 (NCH*C*), 136.95 (*m*-*C*$_5$NH$_4$), 148.83 (*ipso*-*C*$_6$H$_5$), 149.42 (*m*-NC$_5$H$_4$), 150.34 (*ipso*-NC$_5$H$_4$) ppm.
Reference: [4]

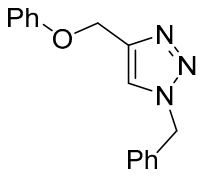
***Synthesis of 1-(1-benzyl-1H-1,2,3-triazol-4-yl)-N,N-dimethylmethanamine* (TZ-6).**



1-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-*N*,*N*-dimethylmethanamine

Method A.
^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ 2.20 (s, 6H, C*H*3), 3.53 (s, 2H, NC*H*$_2$) 5.47 (s, 2H, PhC*H*$_2$), 7.21 (m, 2H, C$_6$*H*$_5$), 7.30 (m, 3H, C$_6$*H*$_5$), 7.36 (s, 1H NC*H*) ppm.
^{13}C NMR (125 MHz, 298 K, $CDCl_3$): δ 44.73 (*C*H$_3$), 54.13 (NCH$_2$), 54.31 (PhCH$_2$), 123.24 (*C*$_6$H$_5$), 128.18 (*C*$_6$H$_5$), 128.84 (*C*$_6$H$_5$), 129.20, 134.65, 144.23.

***Synthesis of 1-benzyl-4-(phenoxymethyl)-1H-1,2,3-triazole* (TZ-7).**



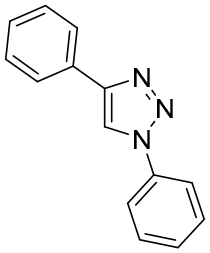
1-benzyl-4-(phenoxymethyl)-1*H*-1,2,3-triazole

Method A.

^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ 5.24 (s, 2H, CH_2), 5.55 (s, 2H, CH_2), 7.29 (m, 5H, C_6H_5), 7.39 (m, 5H, C_6H_5), 7.59 (s, 1H NC*H*) ppm.

^{13}C NMR (125 MHz, 298 K, $CDCl_3$): δ 54.27 (*C*H_2), 62.09 (*C*H_2), 114.78 (*C*$_6$H$_5$), 121.25 (*C*$_6$H$_5$), 122.53 (NCH), 128.12, 128.82, 129.15, 129.52, 134.47, 144.74, 158.20 (*C*$_6$H$_5$) ppm.

Synthesis of 1,4-diphenyl-1H-1,2,3-triazole (**TZ-8**).



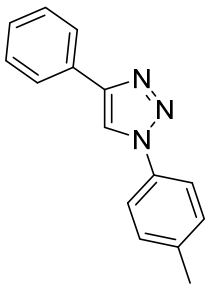
1,4-diphenyl-1*H*-1,2,3-triazole

Method A.

^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ 7.38 (t, *J* = 7.41 Hz, 1H, C_6H_5), 7.47 (t, *J* = 7.61 Hz, 3H, C_6H_5), 7.56 (t, *J* = 7.85 Hz, 2H, C_6H_5), 7.80 (d, *J* = 8.45 Hz, 2H, C_6H_5), 7.92 (d, *J* = 8.30 Hz, 2H, C_6H_5), 8.20 (s, 1H, NC*H*) ppm.

^{13}C NMR (125 MHz, 298 K, $CDCl_3$): δ 117.72 (NCH), 120.70 (*C*$_6$H$_5$), 126.01 (*C*$_6$H$_5$), 128.58 (*C*$_6$H$_5$), 128.93 (*C*$_6$H$_5$), 129.08, 129.94 (*C*$_6$H$_5$), 130.41, 137.25, 148.58 ppm.

Synthesis of 4-phenyl-1-(p-tolyl)-1H-1,2,3-triazole (**TZ-9**).



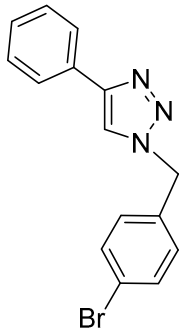
4-phenyl-1-(*p*-tolyl)-1*H*-1,2,3-triazole

Method A.

^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ 2.44 (s, 3H, CH_3), 7.36 (m, 3H, C_6H_5), 7.46 (t, *J* = 7.63 Hz, 2H, C_6H_5), 7.67 (d, *J* = 8.42 Hz, 2H, C_6H_4), 7.91 (d, *J* = 7.88 Hz, 2H, C_6H_4), 8.15 (s, 1H, NC*H*) ppm.

^{13}C NMR (125 MHz, 298 K, $CDCl_3$): δ 21.28 (*C*H_3), 117.75 (NCH), 120.62 (*C*$_6$H$_4$), 126.00 (*C*$_6$H$_4$), 128.51 (*C*$_6$H$_5$), 129.06 (*C*$_6$H$_5$), 130.42 (*C*$_6$H$_5$), 130.52, 139.05, 148.44 ppm.

Synthesis of 1-(4-bromobenzyl)-4-phenyl-1H-1,2,3-triazole (**TZ-10**).



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

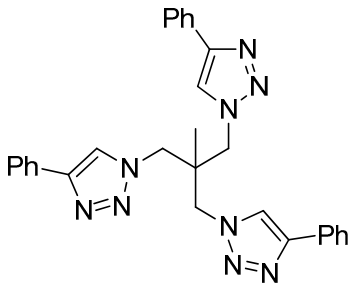
Method A.

^{1}H NMR (500 MHz, 298 K, $CDCl_3$): δ 5.54 (s, 2H, CH_2), 7.19 (d, J = 8.55 Hz, 3H, *o*-C$_6H_5$), 7.33 (t, J = 7.40 Hz, 1H, *p*-C$_6H_5$), 7.41 (t, J = 7.40 Hz, 2H, *m*-C$_6H_5$),7.52 (d, J = 8.48 Hz, 2H, C$_6H_4$), 7.66 (s, 1H, NC*H*),7.80 (d, J = 7.08 Hz, 2H, C$_6H_4$) ppm.

^{13}C NMR (125 MHz, 298 K, $CDCl_3$): δ 53.70 (*C*H$_2$), 119.52 (N*C*H), 123.13, 125.87 (*C*$_6$H$_4$), 128.44 (*C*$_6$H$_5$), 128.99, 129.79 (*C*$_6$H$_5$), 130.52, 132.50 (*C*$_6$H$_4$), 133.85, 148.59 (*C*$_6$H$_5$, *C*$_6$H$_4$) ppm.

II. Synthesis of Tris-triazoles

Synthesis of 1,1′-(2-methyl-2-((4-phenyl-1H-1,2,3-triazol-1-yl)methyl)propane-1,3-diyl)bis(4-phenyl-1H-1,2,3-triazole) **(TT-1)**

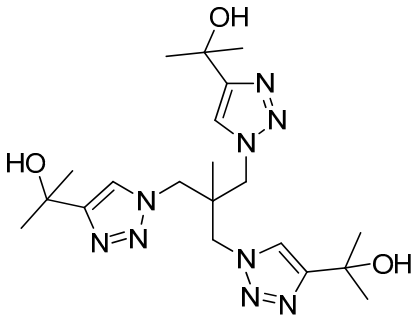


Method B. Phenylacetylene (0.84 mL, 7.68 mmol) and 1,3-diazido-2-(azidomethyl)-2-methylpropane (0.5 g, 2.54 mmol) was added to a solution of the appropriate catalyst in DCM (10 mL). The reaction mixture was stirred for 5 h. The solution was halved under vacuum and cold pentane was added. The product precipitates as a white solid. The solution was filtered and dried under vacuum to yield the pure product.

Catalyst loading:	Isolated yield:
(aIPr^{Ph})CuI (**2**),, 17 mg, 1 mol%	1,27 g, 2.53 mmol, 99%.
aIPr^{Ph})Cu(IPr)I (**3**), 26 mg, 1 mol%	1,28 g, 2.55 mmol, 99.7%
(aIPr^{Ph})$_2$CuI (**4**), 29 mg, 1 mol%	1.02 g, 2.03 mmol, 79 %

^{1}H NMR (300 MHz, 298 K, THF-*d*$_8$): *δ* 0.96 (s, 3 H, C*H*$_3$), 4.64 (s, 6 H, (C*H*$_2$)$_3$), 7.27 (t, *J* = 7.4 Hz, 3H, *p*-C$_6$*H*$_5$), 7.38 (t, *J* = 7.4 Hz, 6H, *m*-C$_6$*H*$_5$), 7.91 (d, *J* = 7.0 Hz, 6H, *o*-C$_6$*H*$_3$), 8.54 (s, 3 H, C$_2$*H*N$_3$) ppm.
^{13}C NMR (75.47 MHz, 298 K, THF-*d*$_8$): *δ* 19.43 (CH$_2$)$_3$C*Me*), 42.21 ((CH$_2$)$_3$CMe), 54.46 ((CH$_2$)$_3$CMe), 123.76 (*ipso*-C$_6$H$_5$), 126.37 (*o*-C$_6$H$_5$), 128.65 (*p*-C$_6$H$_5$) 129.56 (*m*-C$_6$H$_5$), 132.23 (NC*H*C), 147.92 (NCH*C*) ppm.
ESI–MS m/z [%]: 524.2 [M+Na]$^+$.

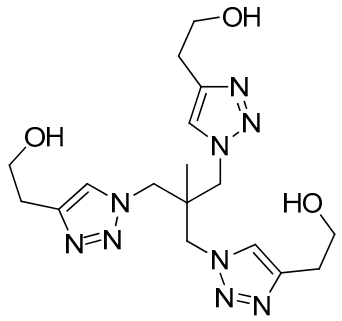
Synthesis of 2,2′-(1,1′-(2-((4-(2-hydroxypropan-2-yl)-1H-1,2,3-triazol-1-yl)methyl)-2-methylpropane-1,3-diyl)bis(1H-1,2,3-triazole-4,1-diyl))bis(propan-2-ol) **(TT-2)**



Method B. 2-Methyl-3-butyne-2-ol (0.86 mL, 7.68 mmol) and 1,3-diazido-2-(azidomethyl)-2-methylpropane (0.5 g, 2.56 mmol) was added to a solution of the catalyst **2** (17 mg, 1 mol%) in DCM (20 mL). The reaction mixture was stirred for 5 h. The solution was halved under vacuum and cold pentane was added. The product precipitates as a white solid. The solution was filtered and dried under vacuum to yield the pure product.

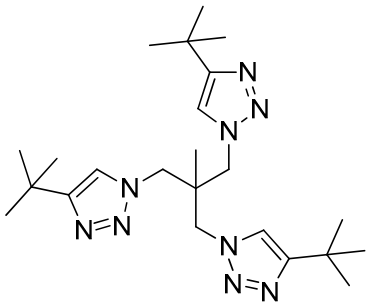
Yield: 850 mg, 1.89 mmol, 74%.
^{1}H NMR (300 MHz, 298 K, THF-d_8): δ 7.97 (s, 3 H, C_2HN_3), 4.39 (s, 6H, $(CH_2)_3$), 4.30(s, 3H, OH), 1.53 (s, 18H,C_3H_6OH), 0.79 (s, 3 H, CH_3) ppm.
^{13}C NMR (75.47 MHz, 298 K, THF-d_8): δ 19.49 $(CH_2)_3CMe$), 31.29 ($(CH_3)_2COH$), 42.07 ($(CH_2)_3CMe_3$), 54.16 ($CH_2)_3CMe_3$), 68.46 ($(CH_3)_2COH$), 123.15 (NCHC), 157.21 (NCHC) ppm.
ESI–MS m/z [%]: 470.3 $[M+Na]^+$.

Synthesis of 2,2′-(1,1′-(2-((4-(2-hydroxyethyl)-1H-1,2,3-triazol-1-yl)methyl)-2-methylpropane-1,3-diyl)bis(1H-1,2,3-triazole-4,1-diyl))diethanol **(TT-3).**



Method B. 3-Butyne-1-ol (0.58 mL, 7.68 mmol) and 1,3-diazido-2-(azidomethyl)-2-methylpropane (0.5 g, 2.56 mmol) was added to a solution of the catalyst **2** (17 mg, 1 mol%) in DCM (20 mL). The reaction mixture was stirred for 5 h. The solution was halved under vacuum and cold pentane was added. The product precipitates as a white solid. The solution was filtered and dried under vacuum to yield the pure product.
Yield: 680 mg, 1.68 mmol, 65%.
^{1}H NMR (300 MHz, 298 K, DMSO-d_6): δ 7.93 (s, 3 H, NC*H*C), 4.56 (br, 3H, OH), 4.36 (br, 6H, $(CH_2)_3CCH_3$), 3.76 (br, 6H, $(CH_2CH_2OH)_3$), 2.90 (br, 6H, $(CH_2CH_2OH)_3$), 0.79 (s, 3H,$(CH_2)_3CCH_3$) ppm.
^{13}C NMR (75.47 MHz, 298 K, DMSO-d_6): δ 18.66 $(CH_2)_3CMe$), 28.83 ($(CH_2CH_2OH)_3$), 40.58 (CMe_3), 52.75($(CH_2)_3CCH_3$), 60.36 ($(CH_2CH_2OH)_3$), 124.38 (NCHC), 144.61 (NCHC) ppm.
ESI–MS m/z [%]: 428.2 $[M+Na]^+$.

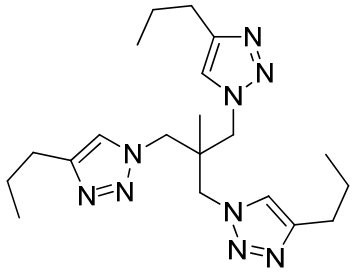
Synthesis of 1,1′-(2-methyl-2-((4-neopentyl-1H-1,2,3-triazol-1-yl)methyl)propane-1,3-diyl)bis(4-(tert-butyl)-1H-1,2,3-triazole) **(TT-4).**



Method B. 3,3-Dimethyl-1-butyne (0.95 mL, 7.68 mmol) and 1,3-diazido-2-(azidomethyl)-2-methylpropane (0.5 g, 2.56 mmol) was added to a solution of the catalyst **2** (17 mg, 1 mol%) in DCM (20 mL). The reaction mixture was stirred for 5 h. The solution was halved under vacuum and cold

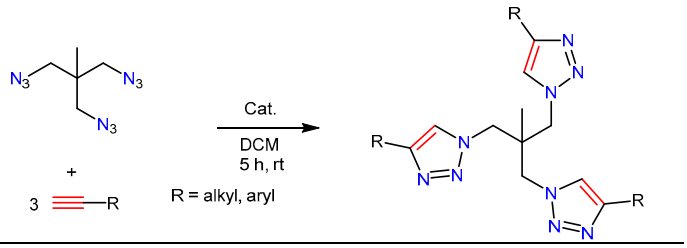
pentane was added. The product precipitates as a white solid. The solution was filtered and dried under vacuum to yield the pure product.
Yield: 830 mg, 1.82 mmol, 71%.
^{1}H NMR (300 MHz, 298 K, THF-d_8): δ 7.91 (s, 3 H, C_2HN_3), 4.38 (s, 6H, $(CH_2)_3$), 1.35(s, 27H, CMe_3), 0.77 (s, 3H, CH_3) ppm.
^{13}C NMR (75.47 MHz, 298 K, THF-d_8): δ 19.33 $(CH_2)_3CMe$), 30.88 (CMe_3), 31.52 (CMe_3), 42.12 $(CH_2)_3CMe$), 54.09 ($(CH_2)_3CMe$), 122.46 (NCHC), 157.34 (NCHC) ppm.
ESI–MS m/z [%]: 464.3 $[M+Na]^+$.

***Synthesis of 1,1′-(2-methyl-2-((4-propyl-1H-1,2,3-triazol-1-yl)methyl)propane-1,3-diyl)bis(4-propyl-1H-1,2,3-triazole)* (TT-5).**



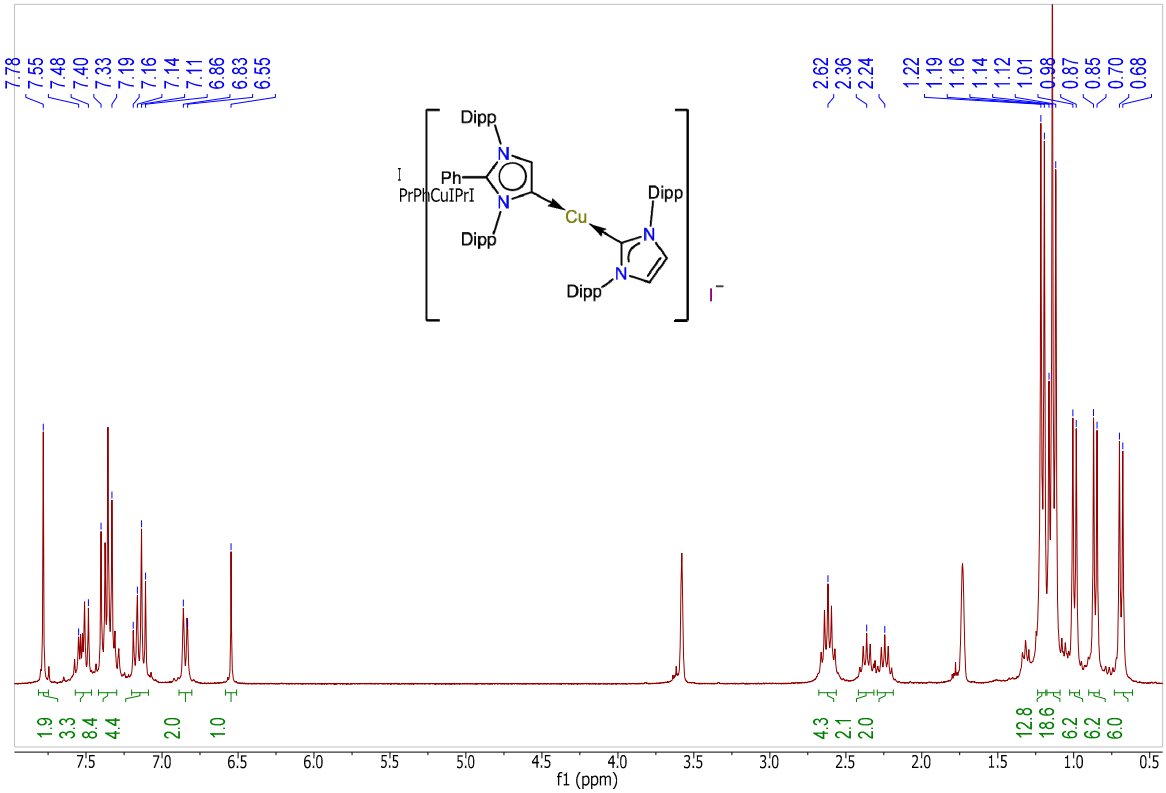
Method B. 1-Pentyne (0.76 mL, 7.68 mmol) and 1,3-diazido-2-(azidomethyl)-2-methylpropane (0.5 g, 2.56 mmol) was added to a solution of the catalyst **2** (17 mg, 1 mol%) in DCM (20 mL). The reaction mixture was stirred for 5 h. The solution was halved under vacuum and cold pentane was added. The product precipitates as a white solid. The solution was filtered and dried under vacuum to yield the pure product.
Yield: 886 mg, 2.21 mmol, 87%.
^{1}H NMR (300 MHz, 298 K, THF-d_8): δ 7.93 (s, 3 H, C_2HN_3), 4.39 (s, 6H, $(CH_2)_3$), 2.67(t, J =7.5 Hz, 6H, C_2H_4Me), 1.76–1.64 (m, 6H, C_2H_4Me), 0.97 (t, 9H, C_2H_4Me), 0.77 (s, 3H, Me) ppm.
^{13}C NMR (75.47 MHz, 298 K, THF-d_8): δ 14.17 (C_2H_4Me), 19.36 ($(CH_2)_3CMe$), 23.63 (C_2H_4Me), 28.50 (C_2H_4Me), 42.16 ($(CH_2)_3CMe$), 53.98 ($(CH_2)_3CMe$), 124.58 (NCHC), 147.95 (NCHC) ppm.
ESI–MS m/z [%]: 422.3 $[M+Na]^+$.

Table S2. Scope of the [3+2] cycloaddition of alkynes and a tris-azide promoted by complexes 2, 3, and 4.

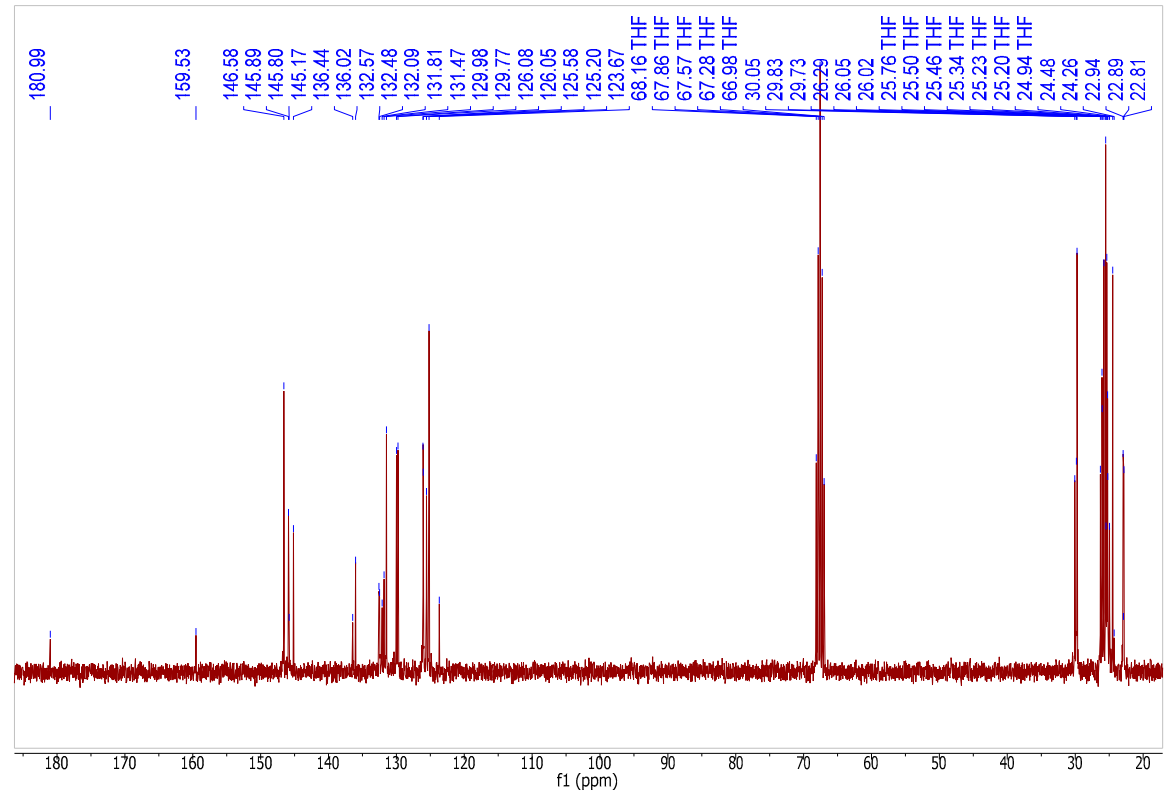


Entry	Cat.	Loading	Alkyne	Yield
1	**2**	1	Phenylacetylene	99
2	**2**	0.5	Phenylacetylene	91
3	**3**	1	Phenylacetylene	79
4	**4**	1	Phenylacetylene	76
5	**2**	1	3-Butyne-1-ol	65
6	**2**	1	2-Methyl-3-butyne-2-ol	74
7	**2**	1	3,3-Dimethyl-1-butyne	71
8	**2**	1	1-Pentyne	87

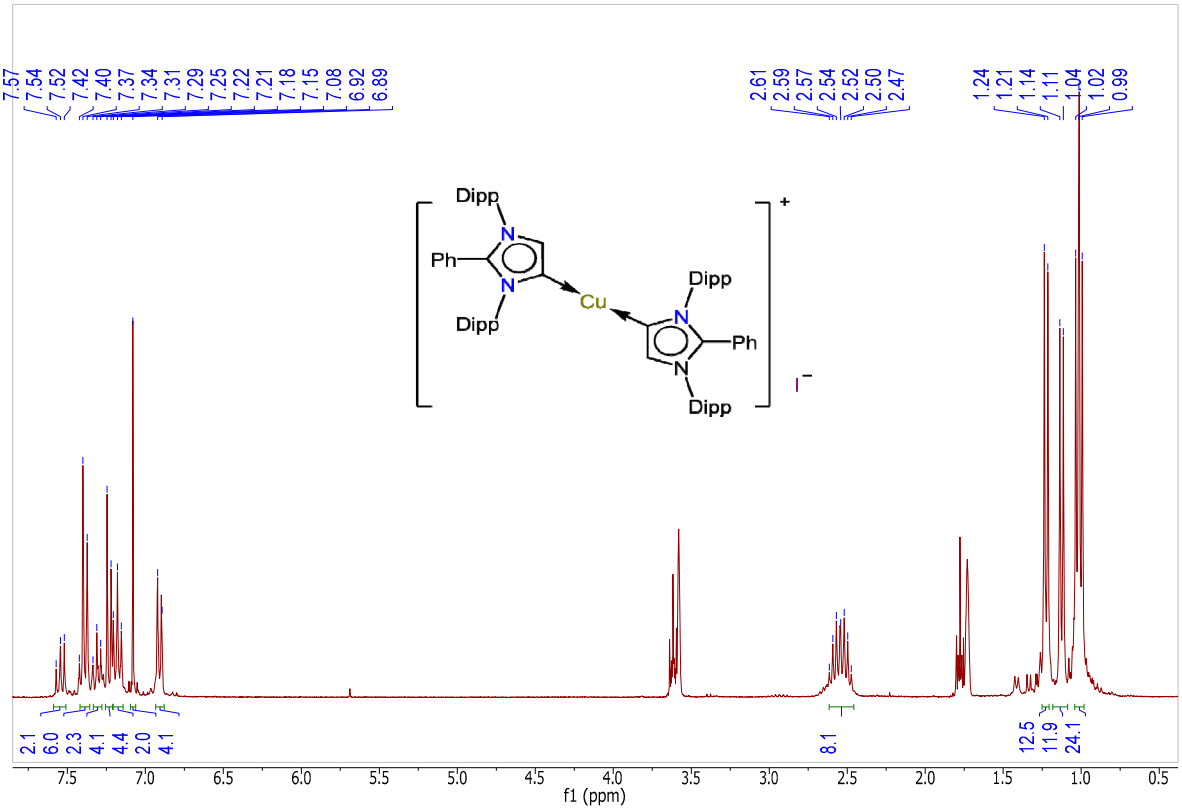
NMR Plots



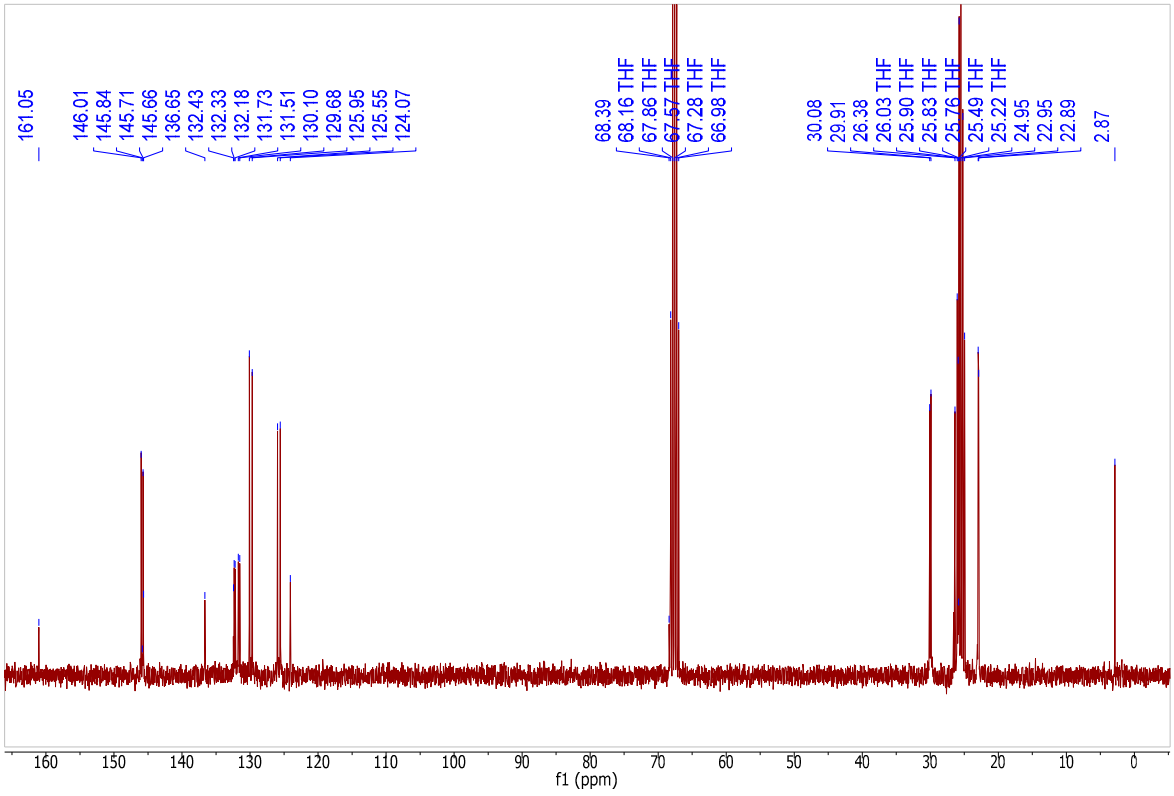
Plot P1: ^{1}H NMR (in THF-d$_8$) spectrum of compound **3**



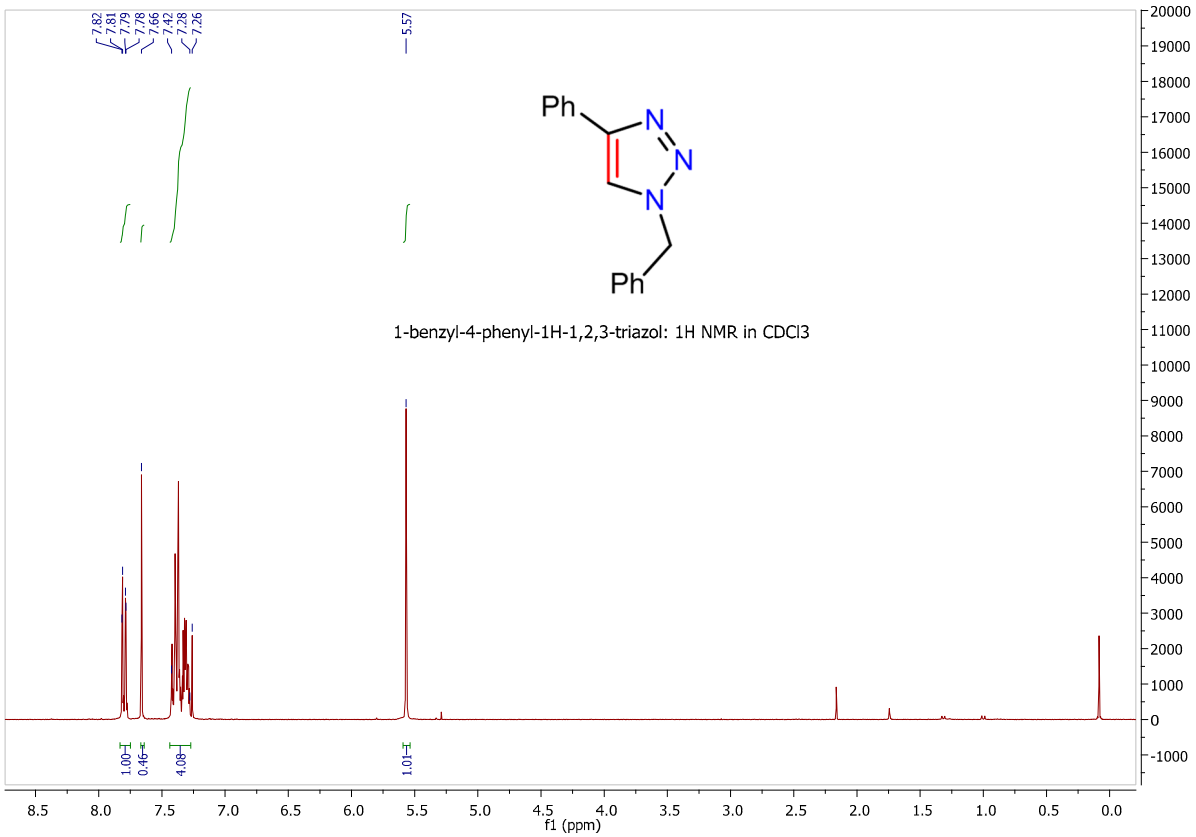
Plot P2: ^{13}C NMR (in THF-d$_8$) spectrum of compound **3**.



Plot P3: ^{1}H NMR (in THF-d$_8$) spectrum of compound **4**.

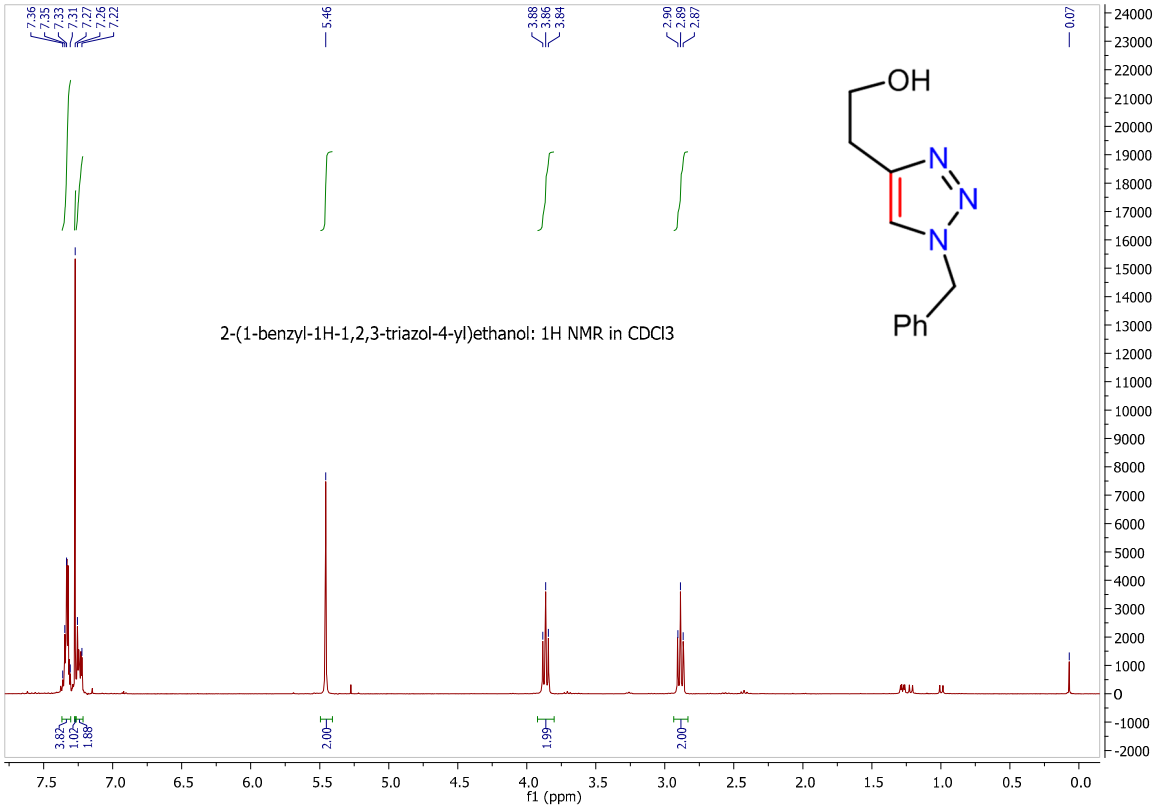


Plot P4: ^{13}C NMR (in THF-d$_8$) spectrum of compound **4**.



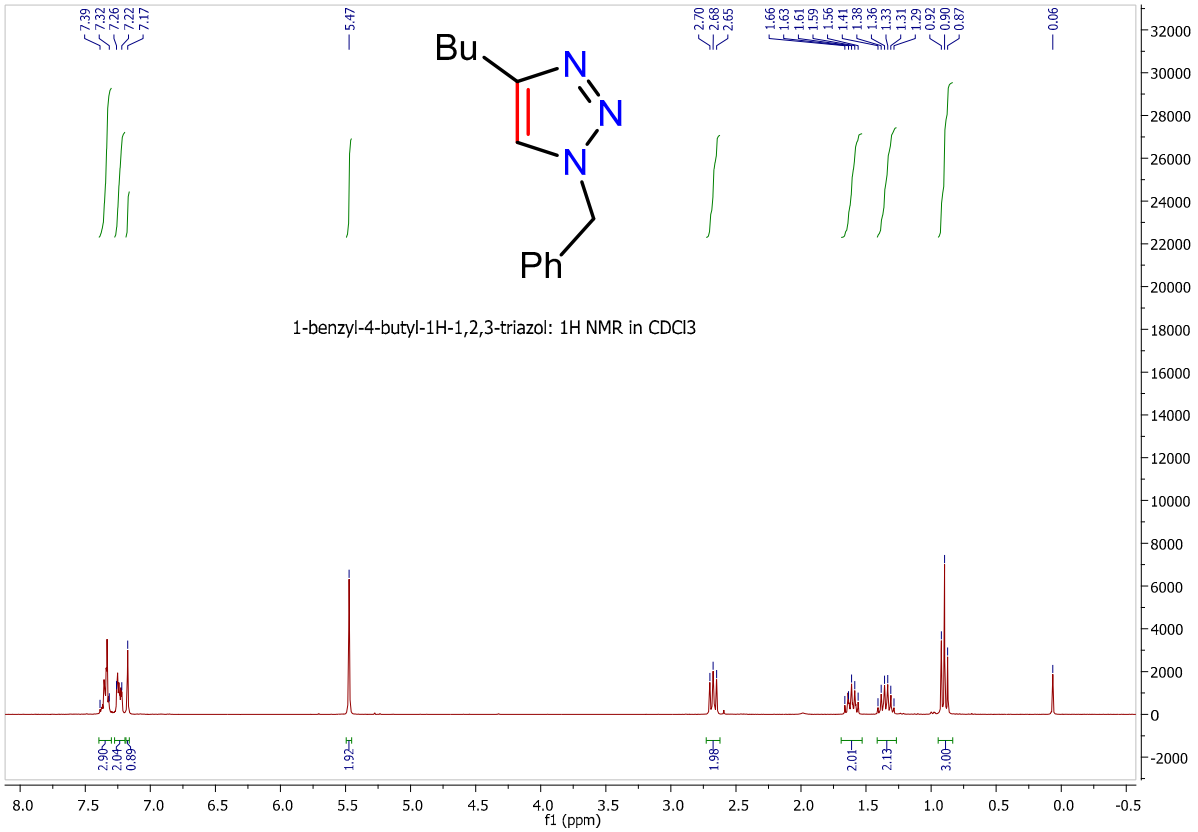
Plot P1: ^{1}H NMR (in $CDCl_3$) spectrum of 1-benzyl-4-phenyl-1H-1,2,3-triazole (**TZ-1**).

Plot P2: ^{13}C NMR (in $CDCl_3$) spectrum of 1-benzyl-4-phenyl-1H-1,2,3-triazole (**TZ-1**)..

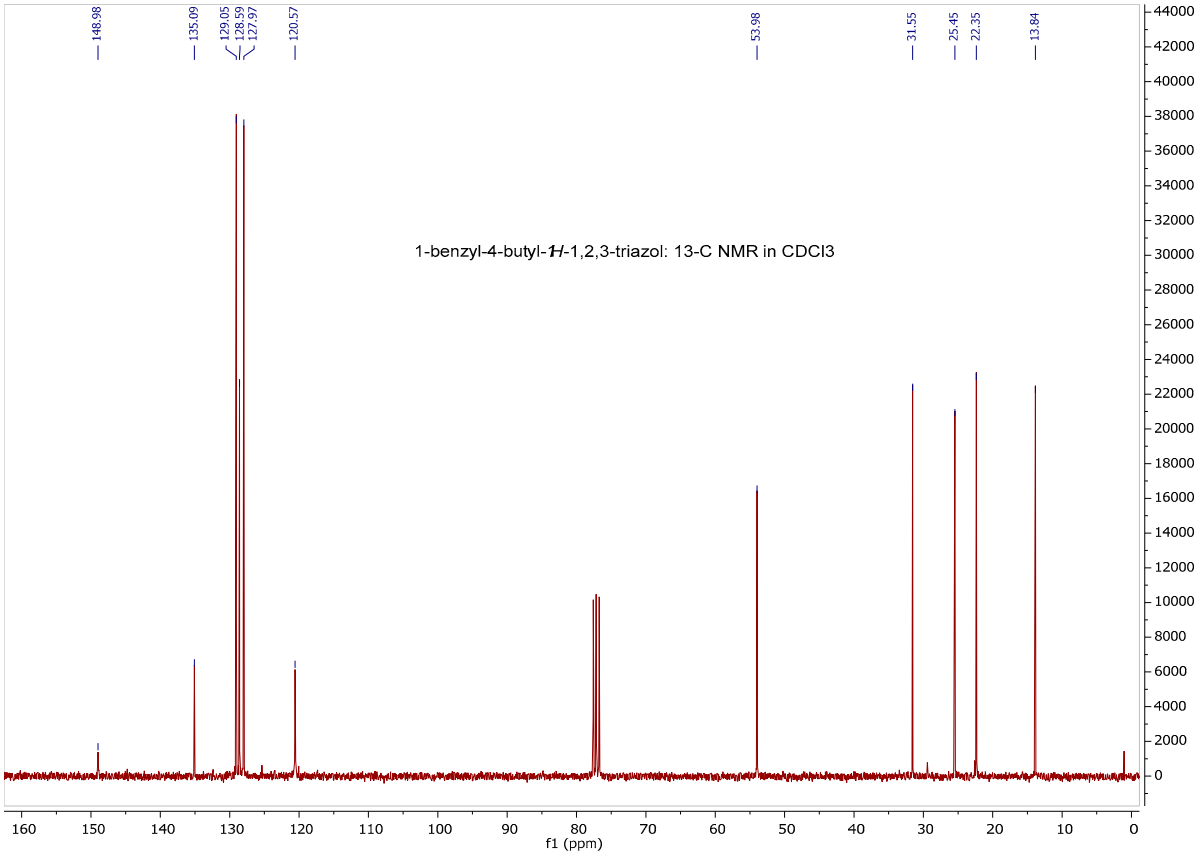


Plot P3: ^{1}H NMR (in $CDCl_3$) spectrum of 2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)ethanol (**TZ-2**).

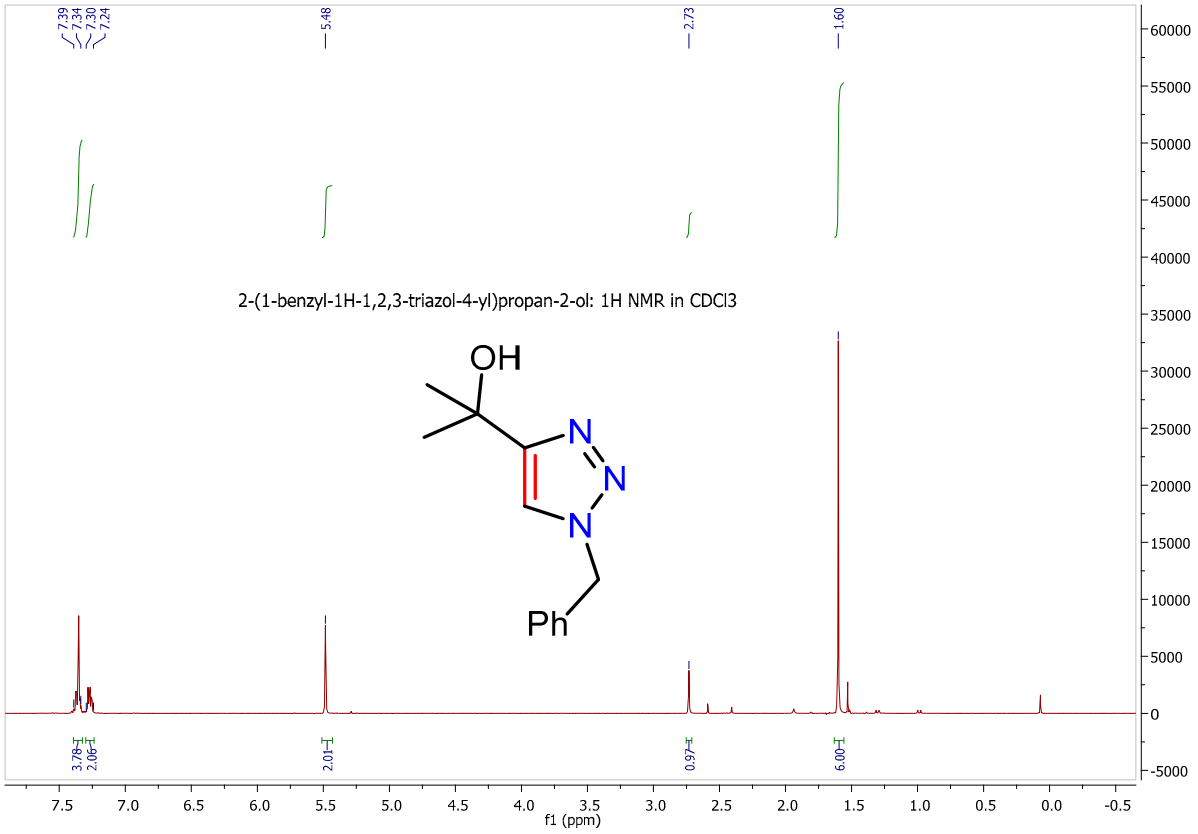
Plot P4: ^{13}C NMR (in $CDCl_3$) spectrum of 2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)ethanol (**TZ-2**).



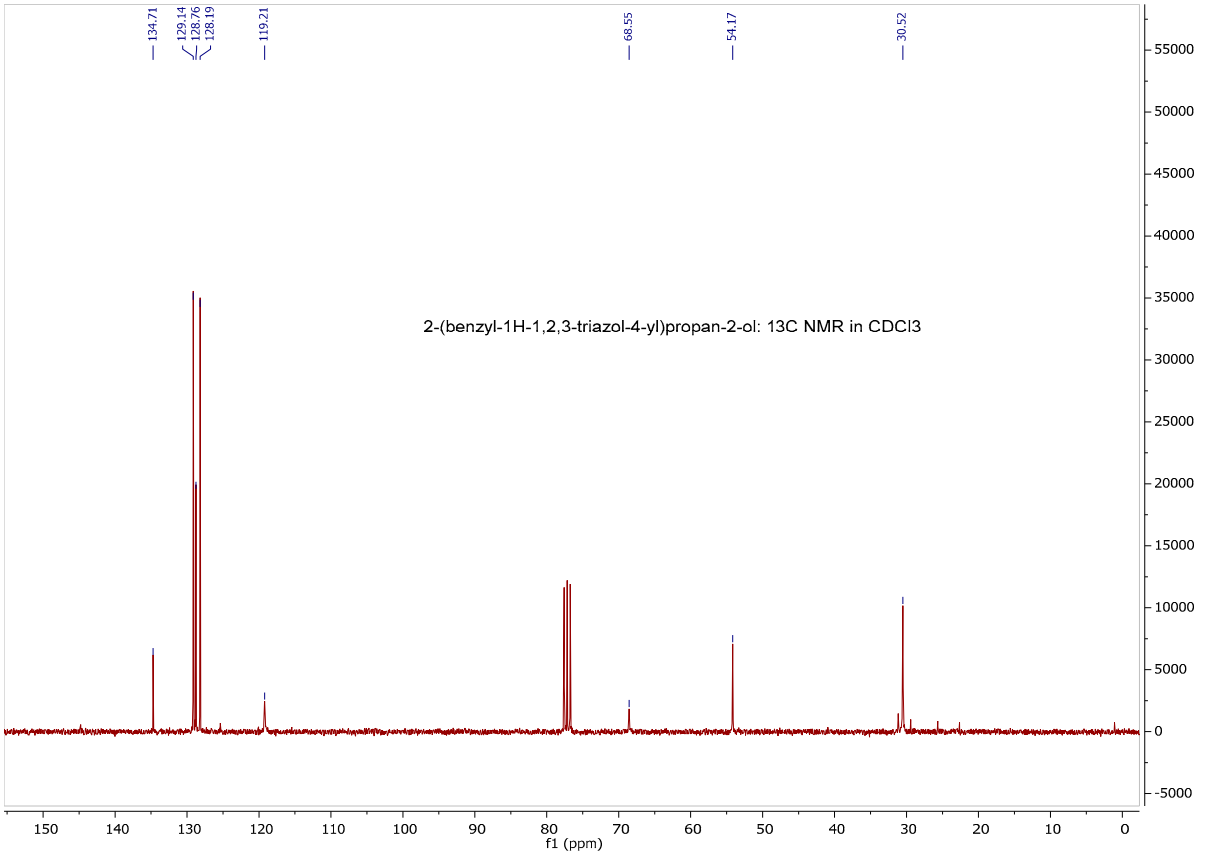
Plot P9: ^{1}H NMR (in $CDCl_3$) spectrum of 1-benzyl-4-butyl-1*H*-1,2,3-triazole (**TZ-3**).



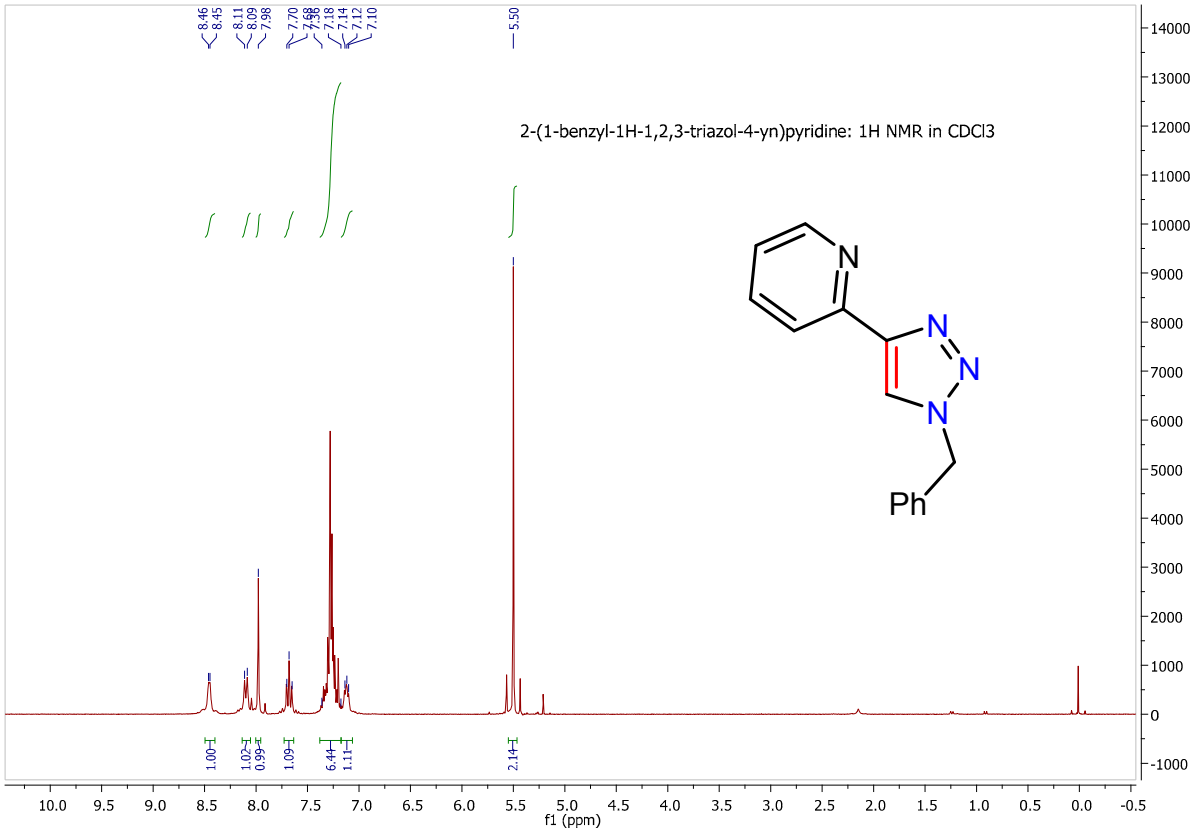
Plot P5: ^{13}C NMR (in $CDCl_3$) spectrum of 1-benzyl-4-butyl-1*H*- triazole (**TZ-3**).



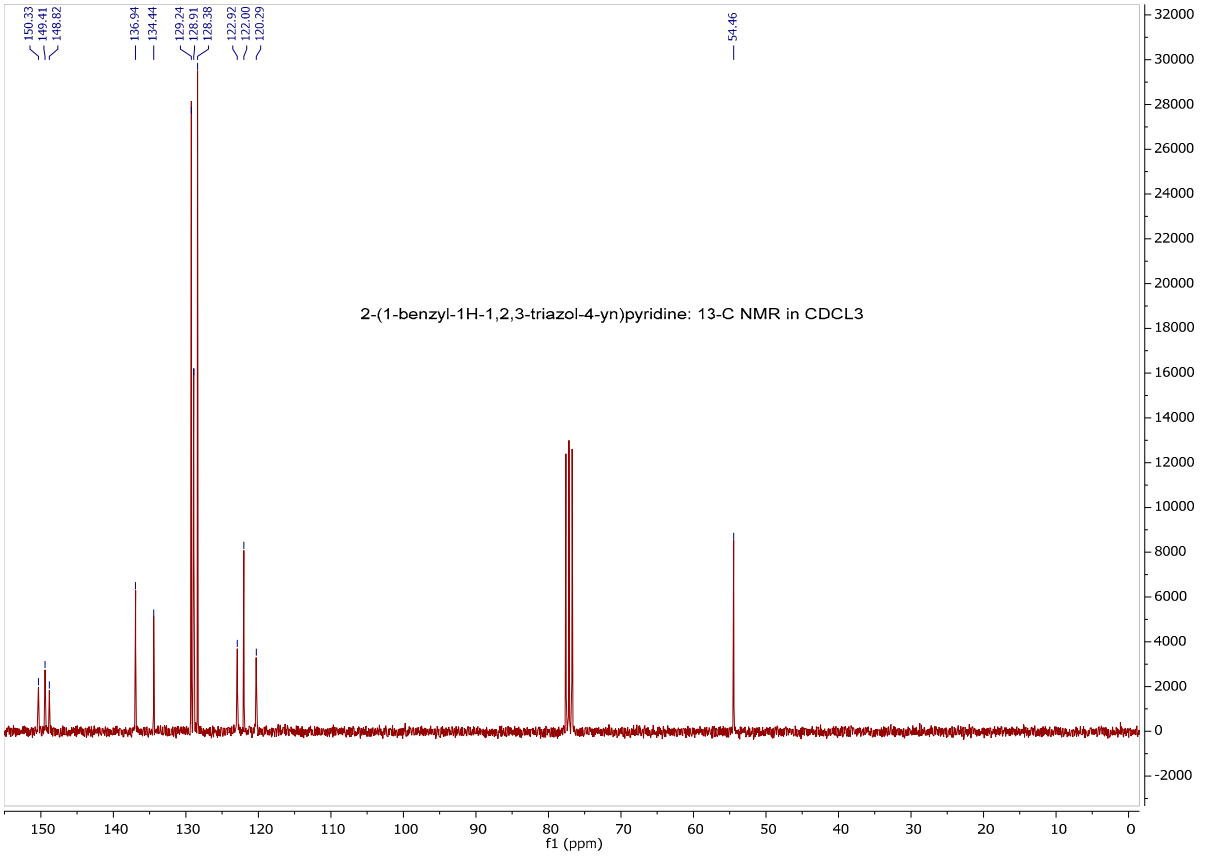
Plot P11: ^{1}H NMR (in $CDCl_3$) spectrum of 2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-ol (**TZ-4**).



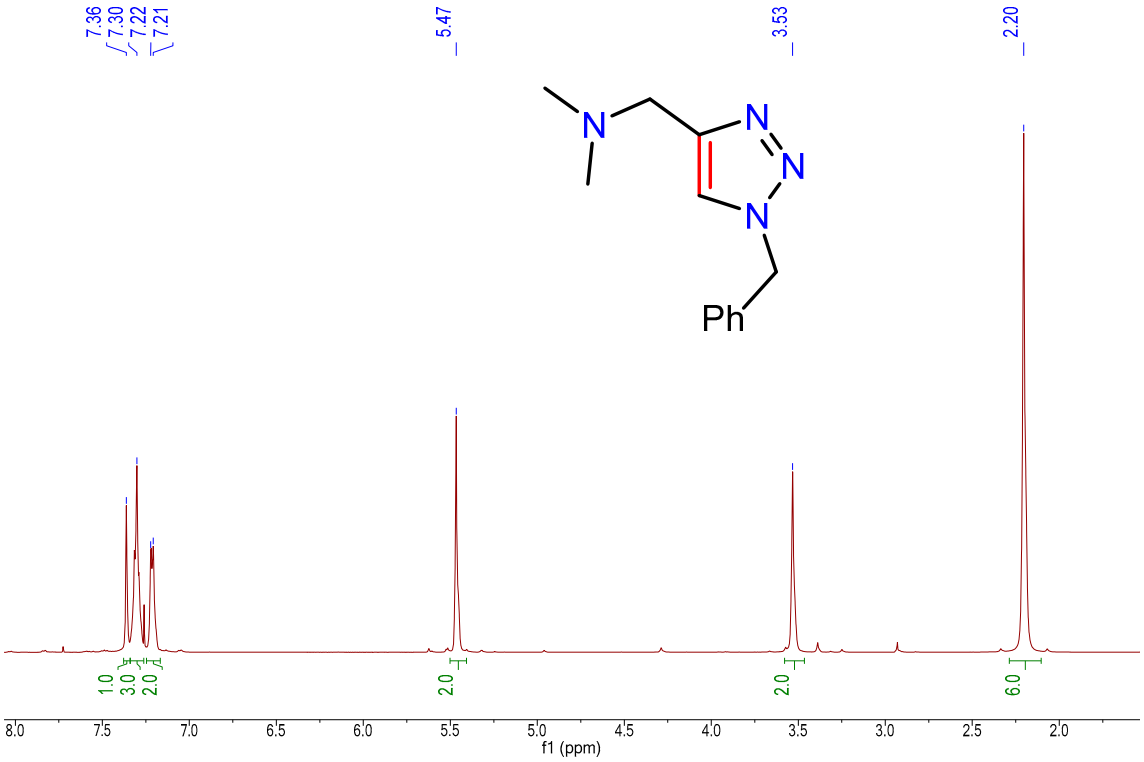
Plot P12: ^{13}C NMR (in $CDCl_3$) spectrum of 2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-ol (**TZ-4**).



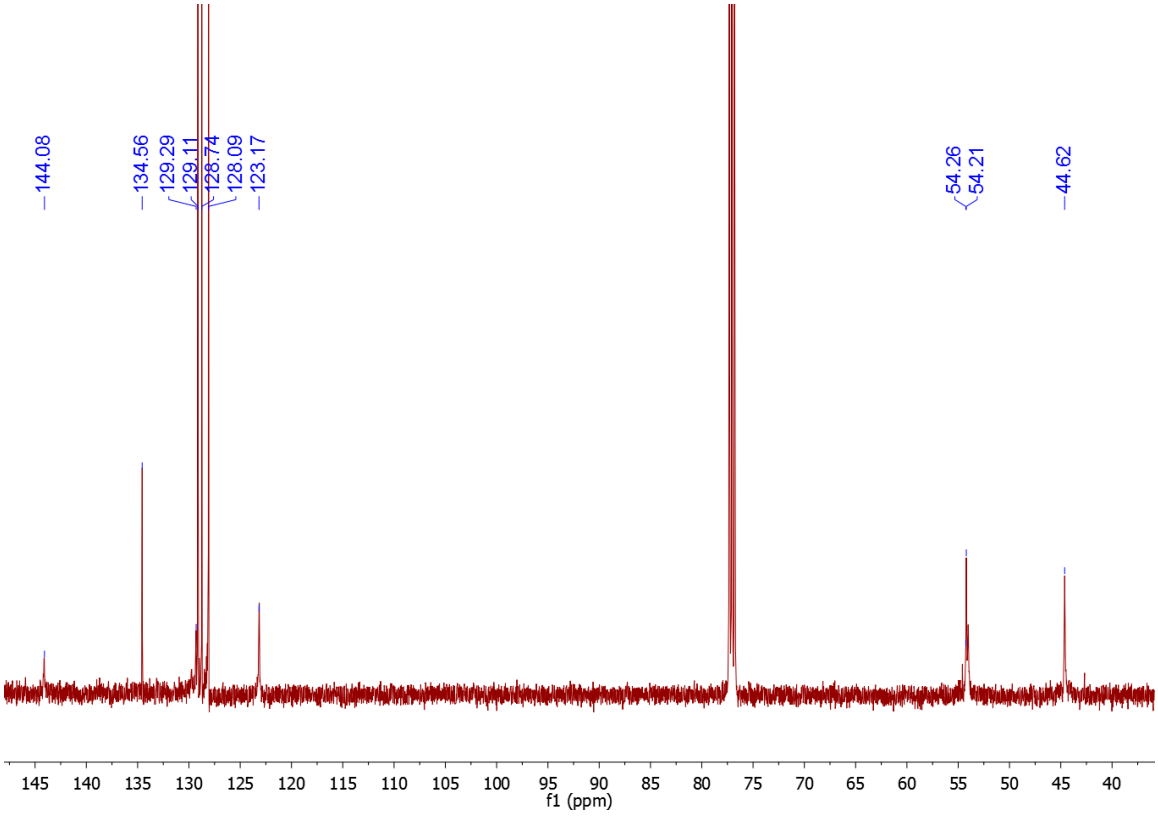
Plot P13: ^{1}H NMR (in $CDCl_3$) spectrum of 2-(1-benzyl-1*H*-1,2,3-triazol-4-yn)pyridine (**TZ-5**).



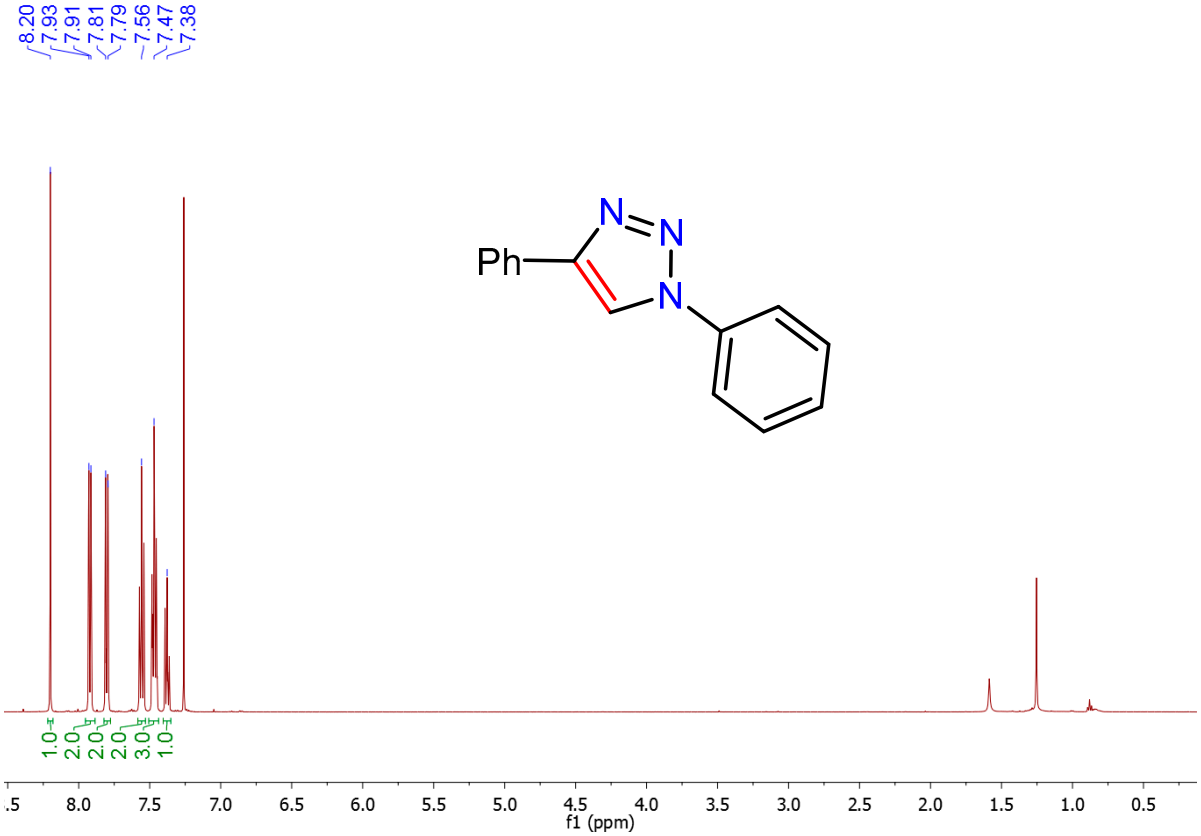
Plot P14: ^{13}C NMR (in $CDCl_3$) spectrum of 2-(1-benzyl-1*H*-1,2,3-triazol-4-yn)pyridine (**TZ-5**).



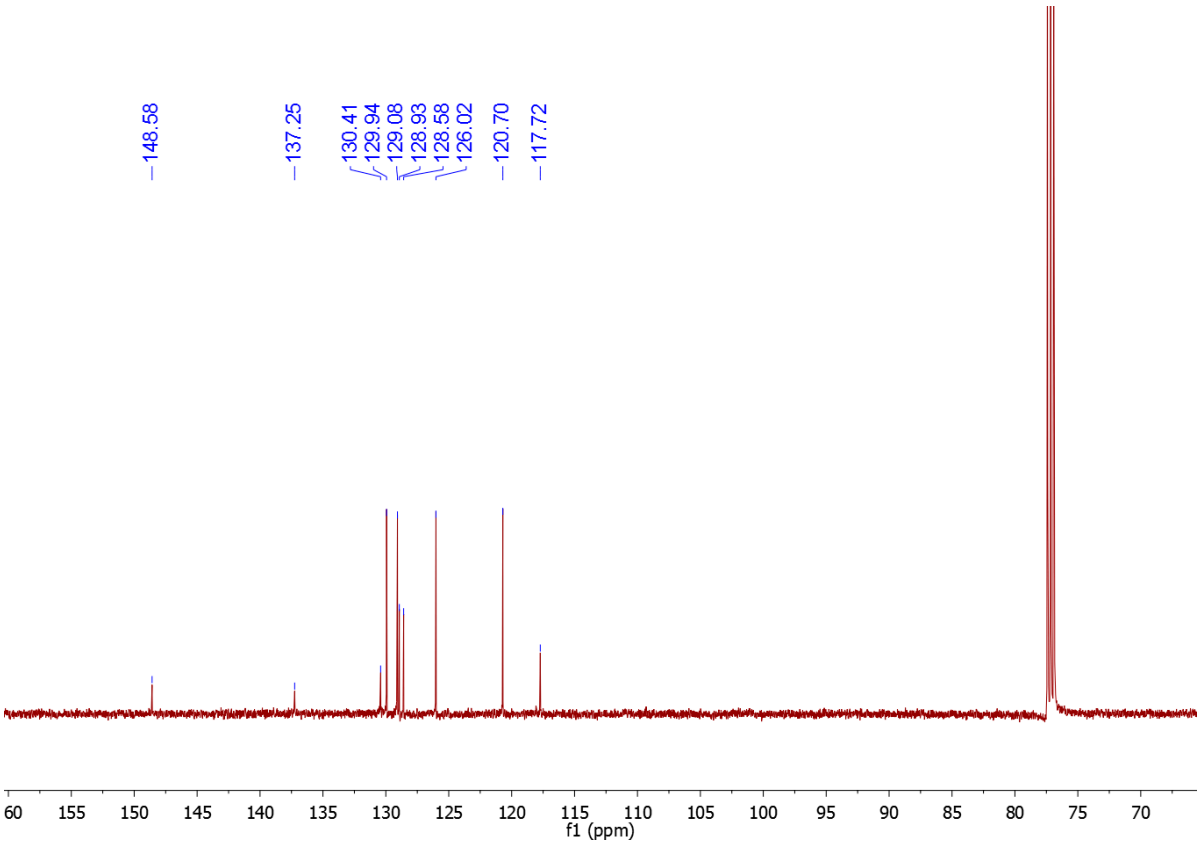
Plot P6: ^{1}H NMR (in $CDCl_3$) spectrum of **TZ-6**.



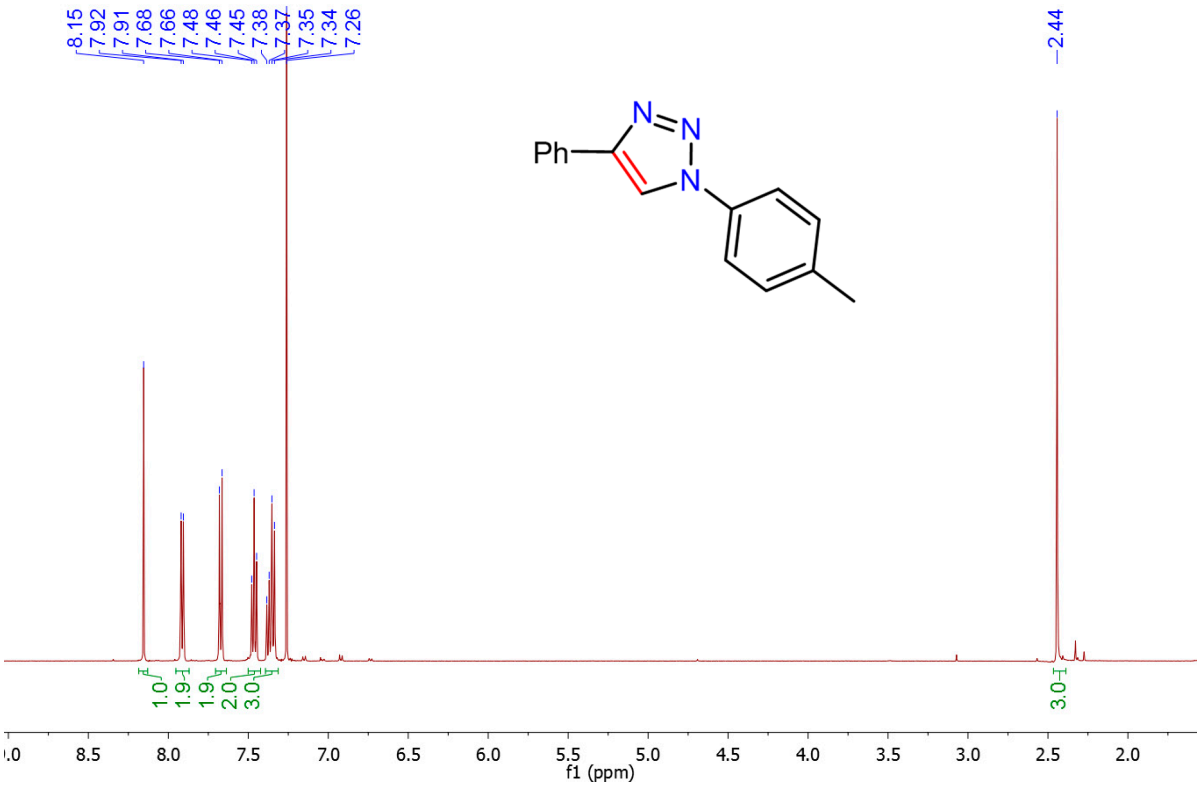
Plot P76: ^{13}C NMR (in $CDCl_3$) spectrum of **TZ-6**.



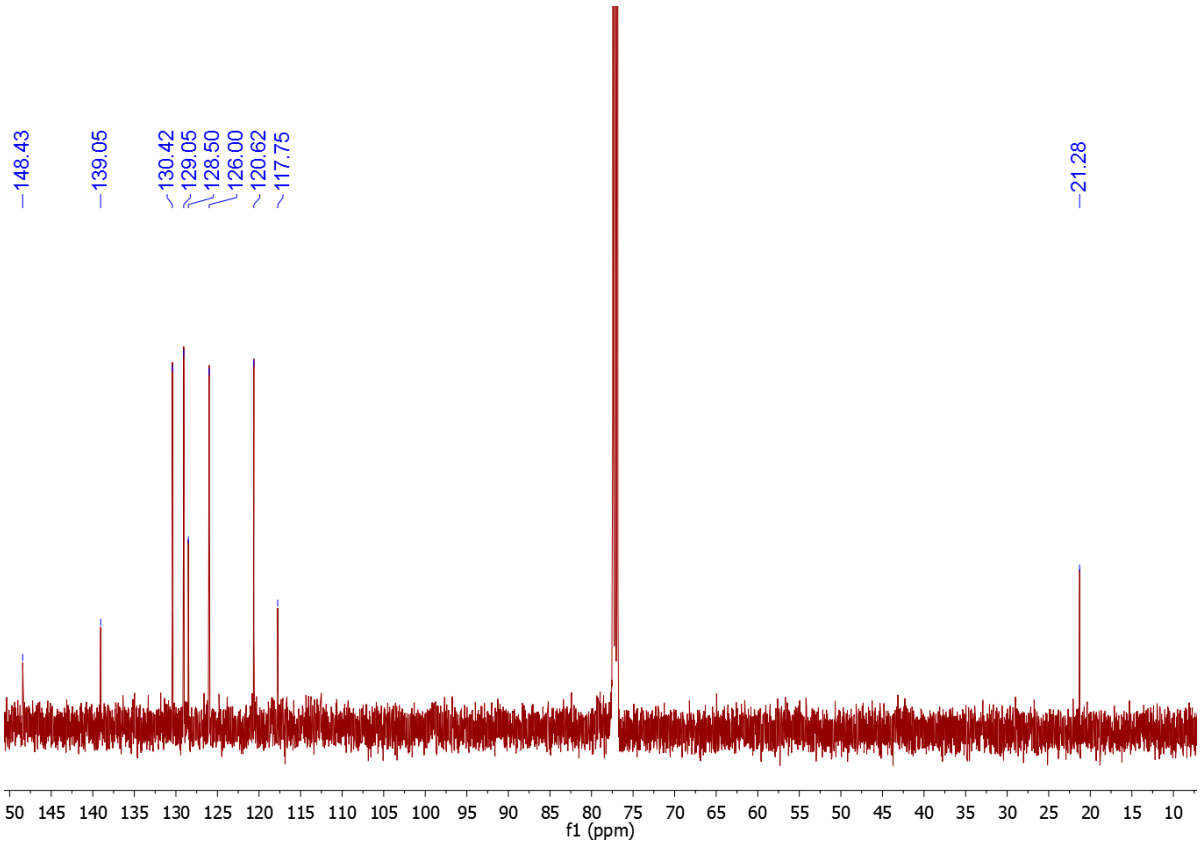
Plot P8: ^{1}H NMR (in $CDCl_3$) spectrum of **TZ-8**.



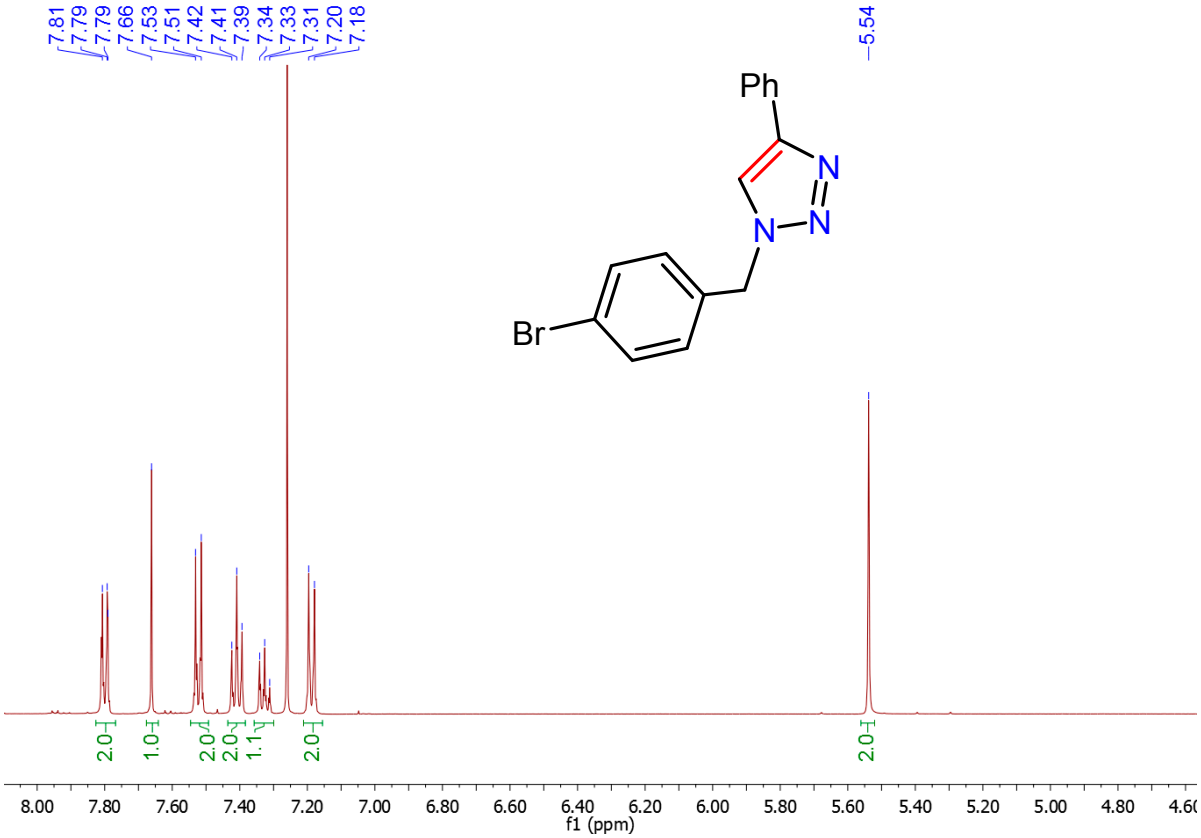
Plot P98: ^{13}C NMR (in $CDCl_3$) spectrum of **TZ-8**.



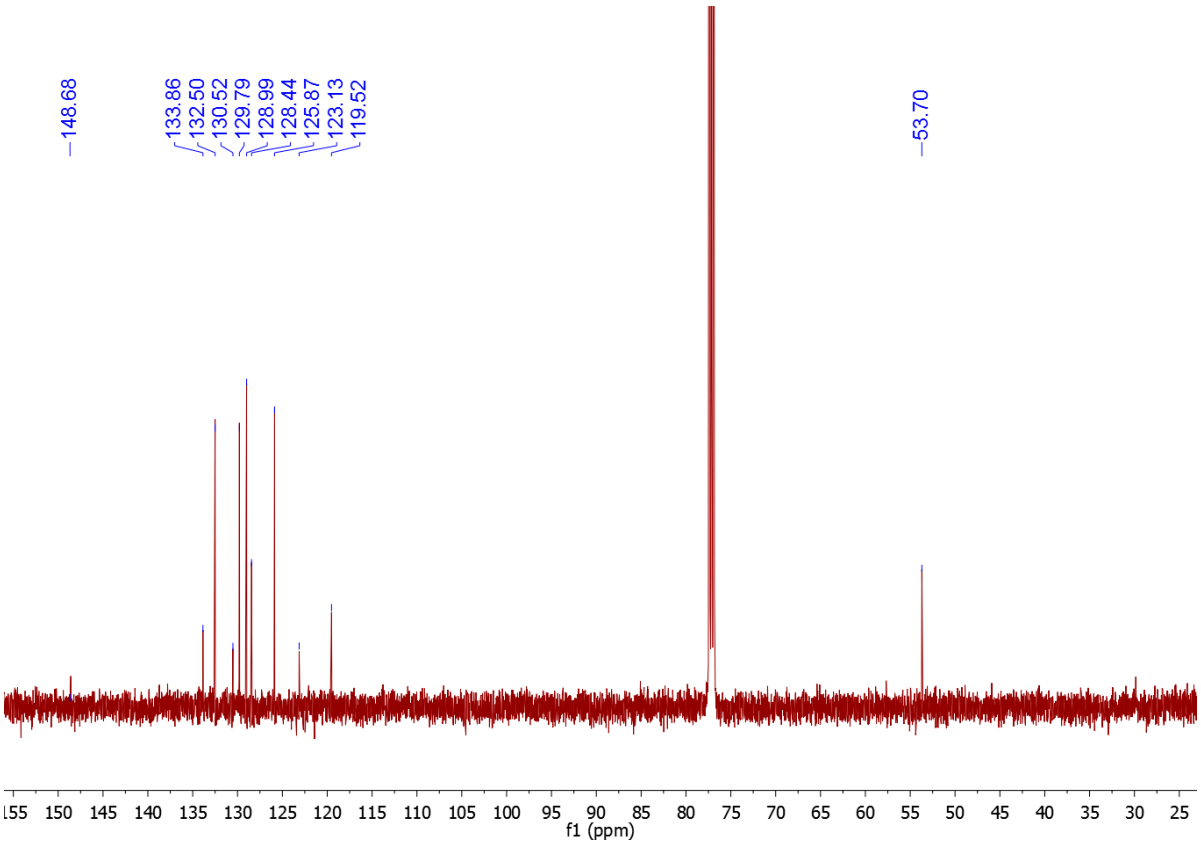
Plot P19: ^{1}H NMR (in $CDCl_3$) spectrum of **TZ-9**.



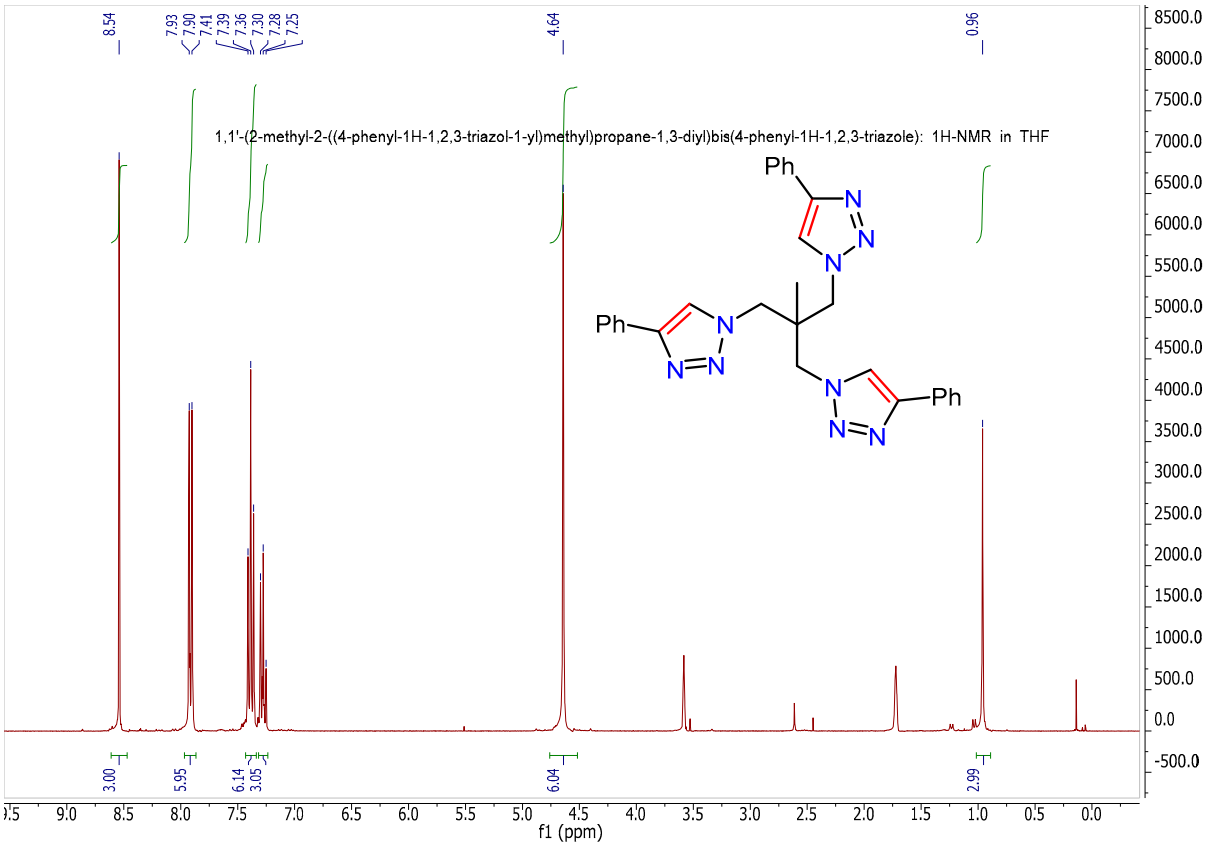
Plot P20: ^{13}C NMR (in $CDCl_3$) spectrum of **TZ-9**.



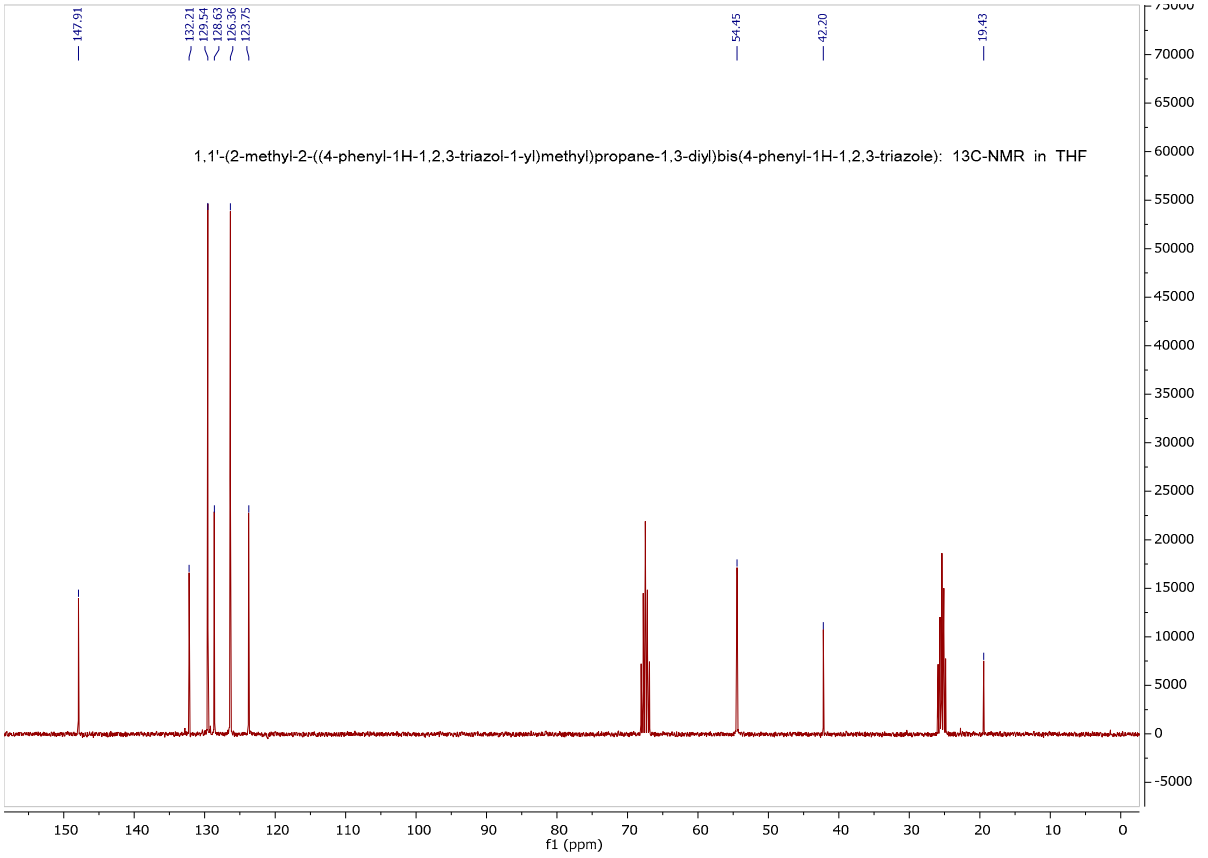
Plot P21: ^{1}H NMR (in $CDCl_3$) spectrum of **TZ-10**.



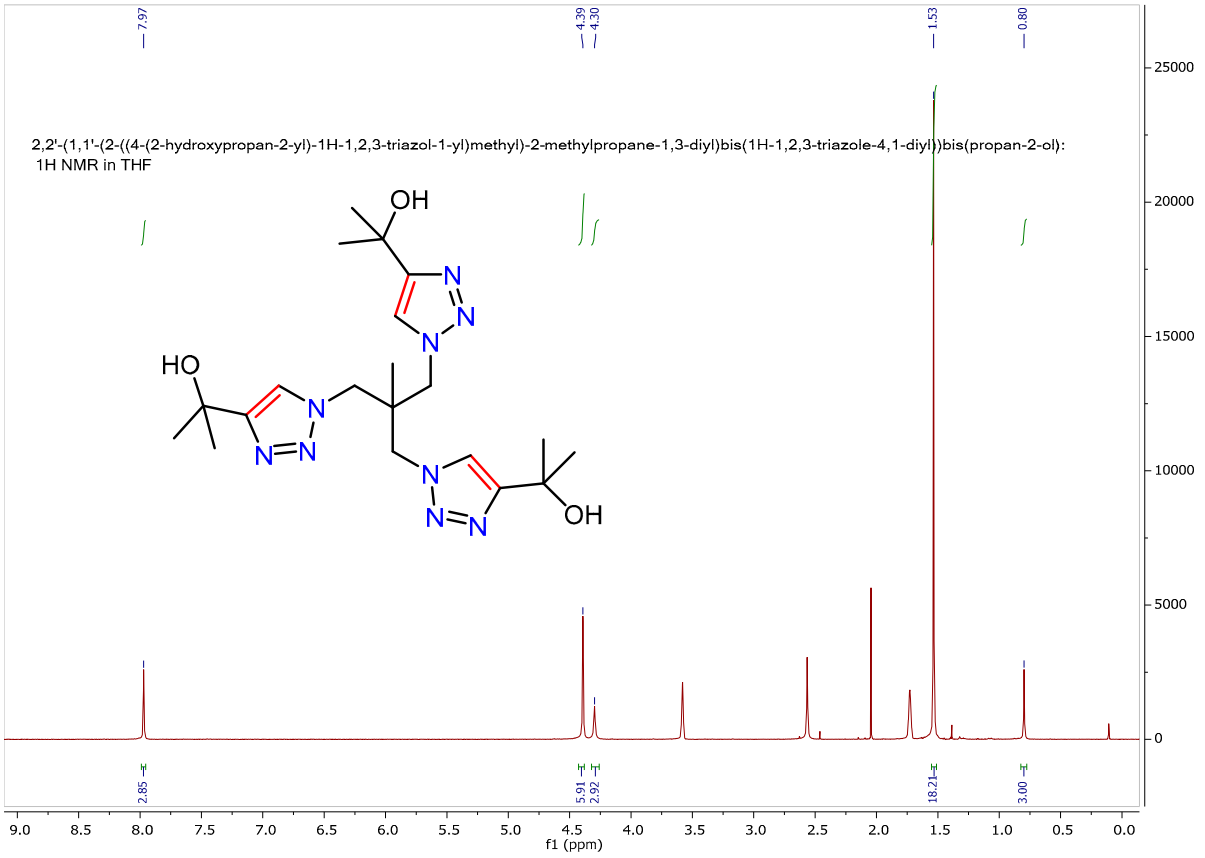
Plot P22: ^{13}C NMR (in $CDCl_3$) spectrum of **TZ-10**.



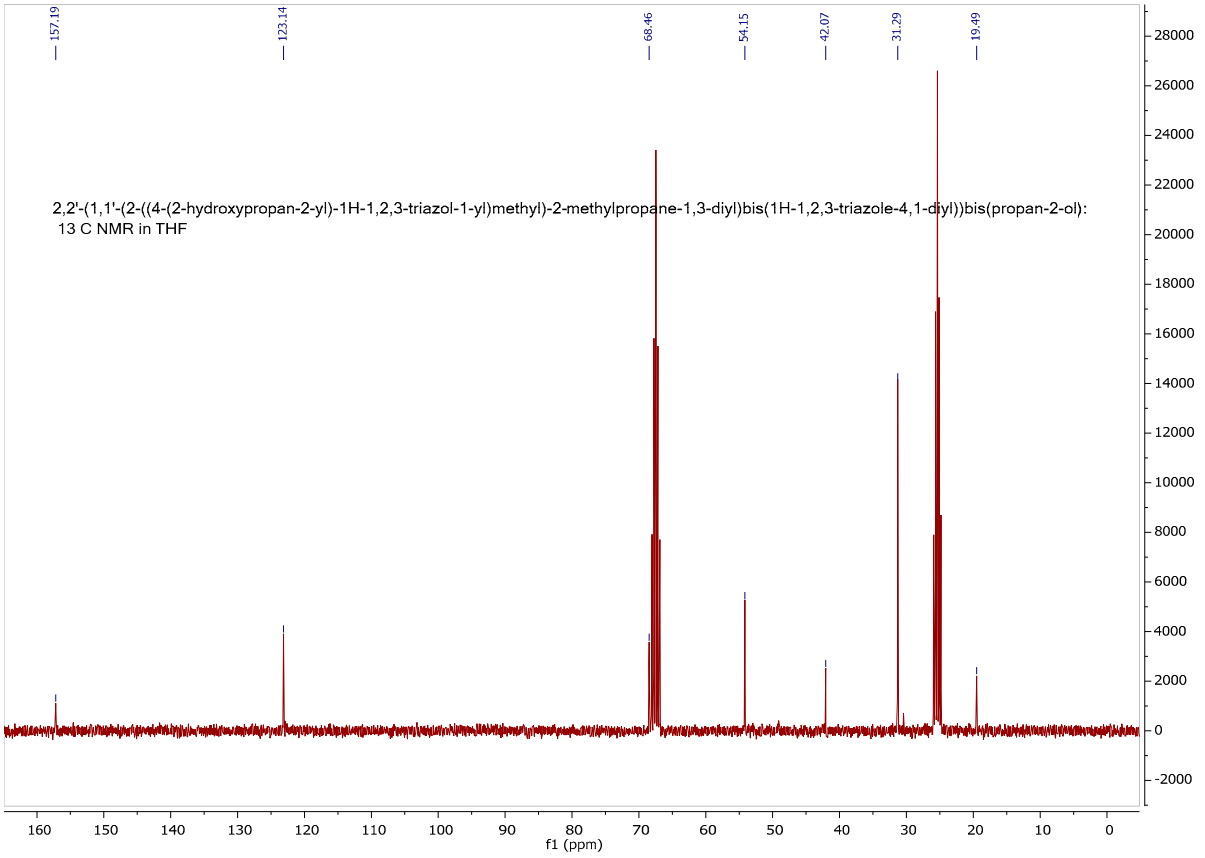
Plot P10: ^{1}H NMR (in THF) spectrum of (**TT-1**).



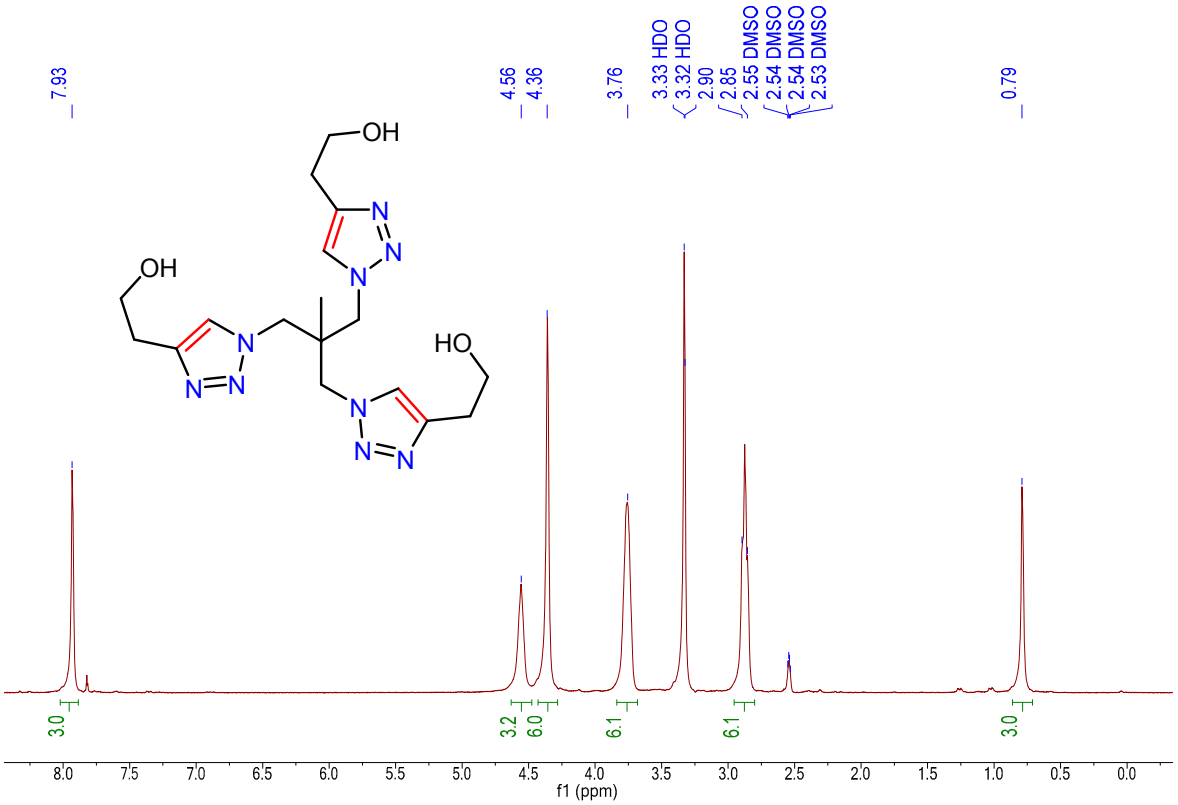
Plot P24: ^{13}C NMR (in THF) spectrum of (**TT-1**).



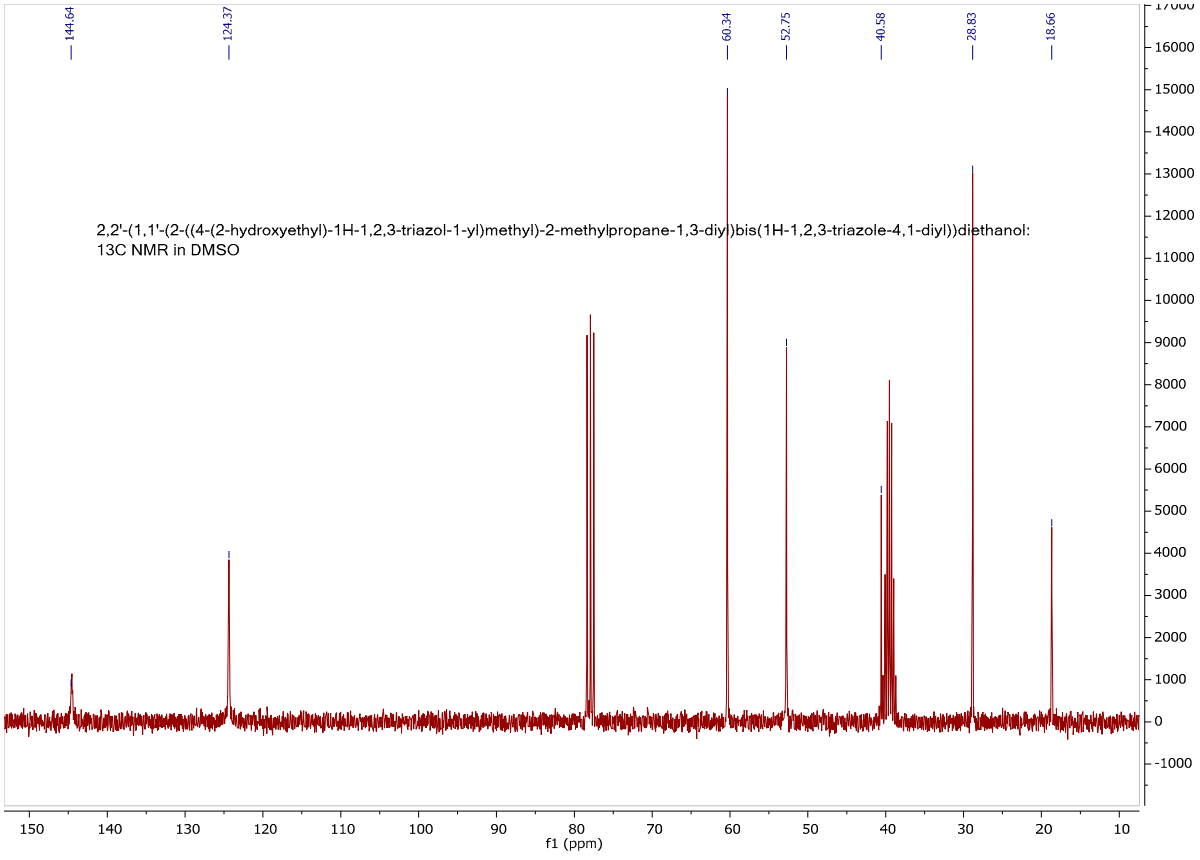
Plot 25: ^{1}H NMR (in THF) spectrum of (**TT-2**).



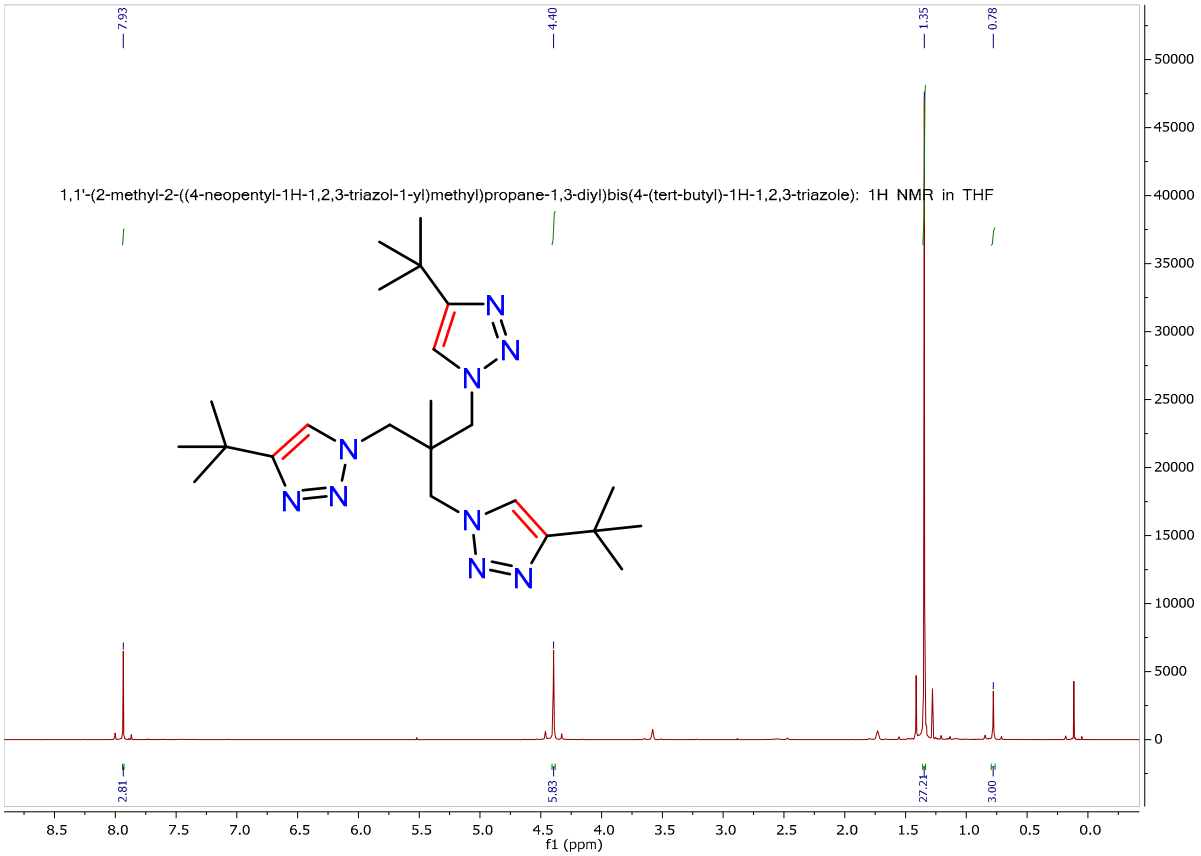
Plot 26: ^{13}C NMR (in THF) spectrum of (**TT-2**).



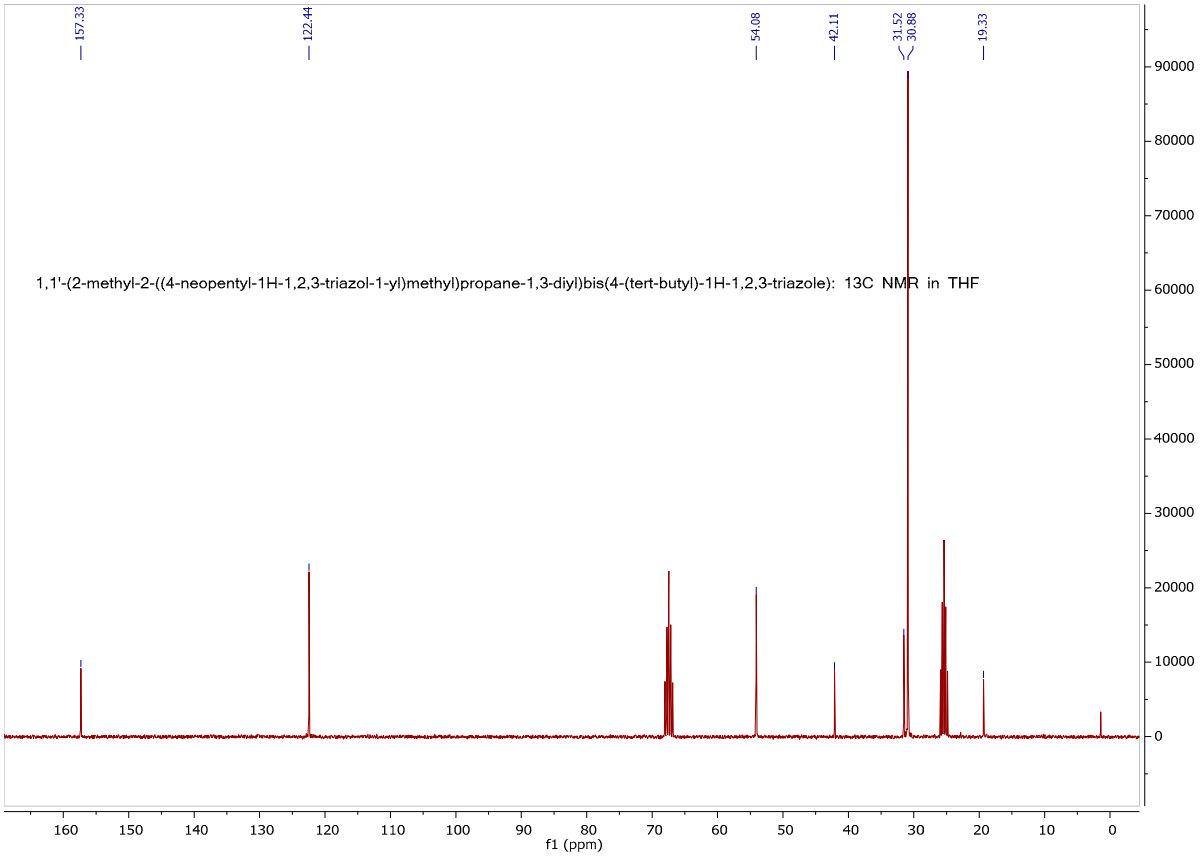
Plot 27: ^{1}H NMR (in DMSO) spectrum of (**TT-3**).



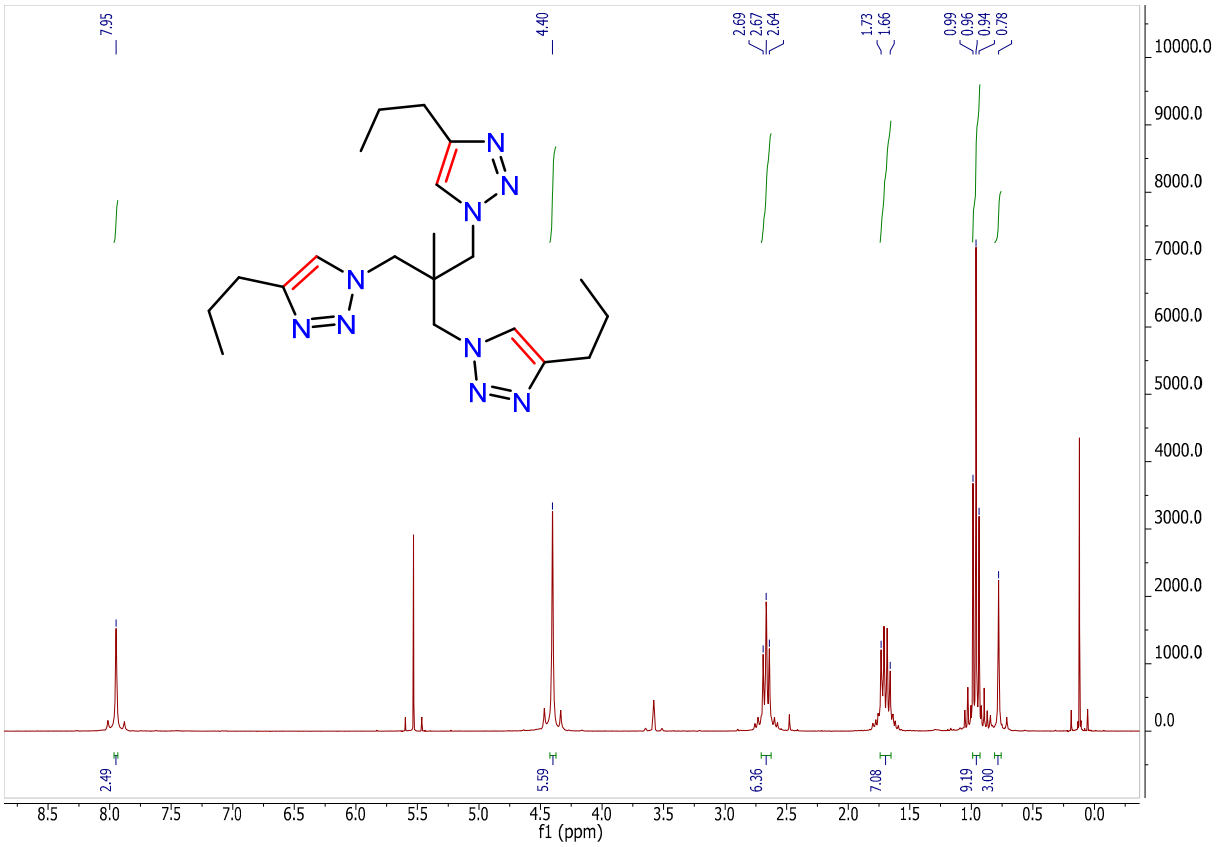
Plot 11: ^{13}C NMR (in DMSO) spectrum of (**TT-3**).



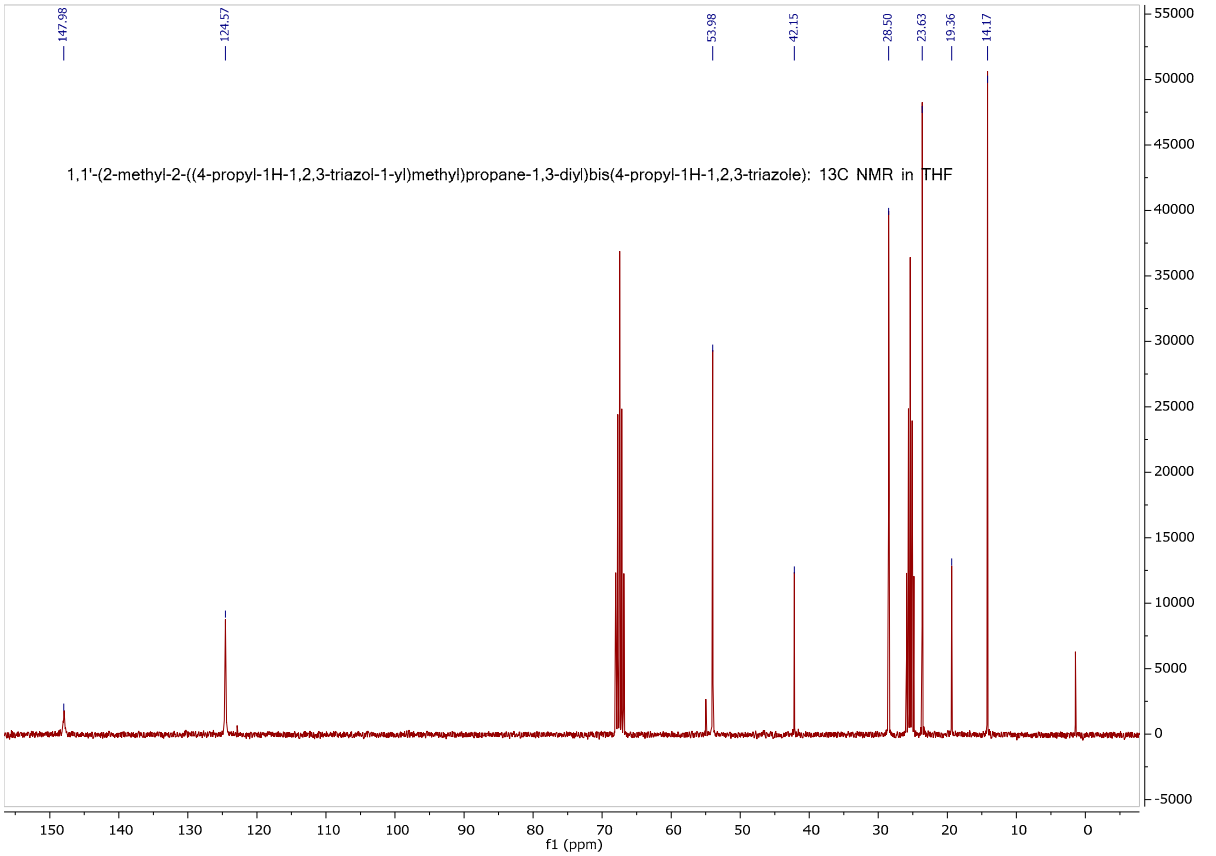
Plot 12: ^{1}H NMR (in THF) spectrum of (**TT-4**).



Plot 30: ^{13}C NMR (in THF) spectrum of (**TT-4**).



Plot 31: ^{1}H NMR (in THF) spectrum of (**TT-5**).



Plot 32: ^{13}C-NMR (in THF) spectrum of (**TT-5**).

Crystallographic Details

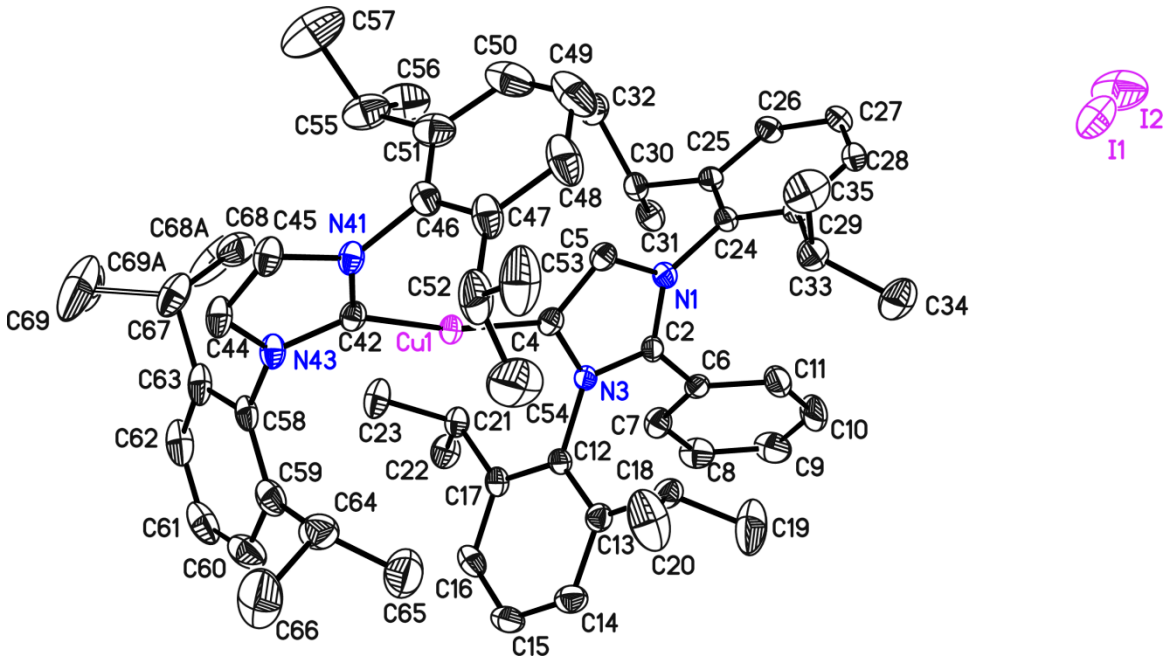
Single Crystal X-ray Diffraction Study: Suitable single crystals were selected from the mother liquor and covered with perfluorinated polyether oil on a microscope slide. The diffraction data of compound **3**, **4**, **TZ-4**, and **TZ-2** (Table S3, S4) were collected at 100 K on a Bruker D8 three circle diffractometer equipped with a SMART APEX II CCD detector and a microfocus source[4] with INCOATEC Quazar mirror optics (λ = 0.71073 Å). The diffraction data of compound **TZ-3** were collected at 100 K on a Bruker D8 TXS-Mo-rotating anode with mirror optics and a Smart Apex II Ultra detector. The data were integrated with SAINT.[5] A multi-scan absorption correction for all structures and a 3λ correction[6] for structures **3**, **4**, **TZ-2** and **TZ-4** were applied using SADABS.[7] The structures were solved by direct methods (SHELXT)[8] and refined against all data by full-matrix least-squares methods on F^2 (SHELXL)[9] within the shelXle GUI.[10] The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Hydrogens bound to oxygen were refined freely with a distance restraint (DFIX). All non-hydrogen-atoms were refined with anisotropic displacement parameters. Disordered moieties were refined using distance restraints (SAME) and anisotropic displacement parameter restraints (SIMU and RIGU).[11]

Table S3. Crystal data and structure refinement for 3 and 4.

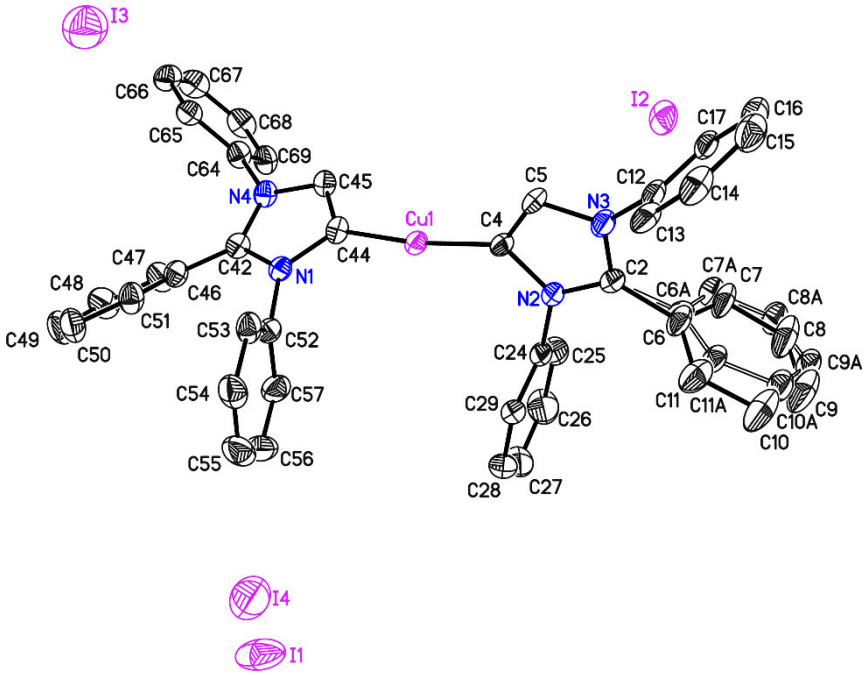
	[(aIPr^{Ph})Cu(IPr)]I (**3**)	[(aIPr^{Ph})$_2$Cu]I (**4**)
Empirical formula	$C_{60}H_{76}CuIN_4$	$C_{66}H_{80}N_4I$
CCDC no.	1560171	1560172
Molecular weight	1043.68	1119.78
Crystal size [mm]	0.14 x 0.11 x 0.08	0.18 x 0.19 x 0.90
Crystal system	Monoclinic	Hexagonal
Space group	$P2_1/c$	$P6_322$
a [Å]	14.199(2)	24.661(2)
b [Å]	20.651(3)	24.661(2)
c [Å]	19.460(2)	42.161(3)
α [°]	90	90
β [°]	97.46(2)	90
γ[°]	90	120
V [Å^3]	5657.8(13)	22206(4)
Z	4	12
ρ [Mgm^{-3}]	1.225	1.005
μ [mm^{-1}]	0.970	0.746
F (000)	2184	7032
θ-range [°]	1.444-25.681	1.069-26.398
Reflections collected.	72914	337920
Independent reflections	10760	15201
R(int)	0.0564	0.0509
Number of restraints	67	412
Parameters	642	737
$R1$ [$I>2\sigma(I)$]	0.0296	0.0317
$wR2$ [$I>2\sigma(I)$]	0.0681	0.0846
$R1$ [all data]	0.0399	0.0364
$wR2$ [all data]	0.0732	0.0873
GooF	1.022	1.081
Absolute structure parameter	-	0.000(3)
Extinction coefficient	-	0.00012(3)
Largest diff. peak / hole [e· Å^{-3}]	0.465/-0.303	0.985/-0.404

Table S4. Crystal data and structure refinement for TZ-3, TZ-4, and TZ-2.

	Triazole **TZ-3**	Triazole **TZ-4**	Triazole **TZ-2**
Empirical formula	$C_{13}H_{17}N_3$	$C_{12}H_{15}N_3O$	$C_{11}H_{13}N_3O$
CCDC no.	1560174	1560175	1560173
Molecular weight	215.29	217.27	203.24
Crystal size [mm]	0.11 x 0.15 x 0.16	0.127 x 0.134 x 0.368	0.10 x 0.12 x 0.15
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a [Å]	13.061(3)	11.515(3)	22.580(3)
b [Å]	5.473(2)	10.493(3)	5.375(2)
c [Å]	17.510(3)	9.342(2)	8.599(2)
β [°]	108.84(2)	94.62(2)	100.86(2)
V [Å ^{3}]	1184.6(6)	1125.1(5)	1024.9(5)
Z	4	4	4
ρ [Mgm^{-3}]	1.207	1.283	1.317
μ [mm^{-1}]	0.074	0.085	0.088
F (000)	464	464	432
θ-area [°]	1.647- 26.560	1.774-26.353	1.837-25.347
Reflections collected.	30375	33082	16590
Independent reflections	2462	2300	1886
R(int)	0.0387	0.0241	0.0265
Number of restraints	0	1	1
Parameters	146	152	141
$R1$ [$I>2\sigma(I)$]	0.0364	0.0325	0.0325
$wR2$ [$I>2\sigma(I)$]	0.0945	0.0746	0.0776
$R1$ [all data]	0.0405	0.0353	0.0394
$wR2$ [all data]	0.0980	0.0765	0.0813
GooF	1.065	1.061	1.071
Extinction coefficient	-	0.0075(12)	0.0042(13)
Largest diff. peak / hole [e· Å^{-3}]	0.186/ -0.235	0.283/-0.193	0.235/-0.194



Asymmetric unit of compound 3. The anisotropic displacement parameters are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.
The iodine shows a positional disorder with a side occupation factor of the main component of 0.945(4) and a vibrational disorder of an isopropyl group with a side occupation factor of the main component of 0.74(3).



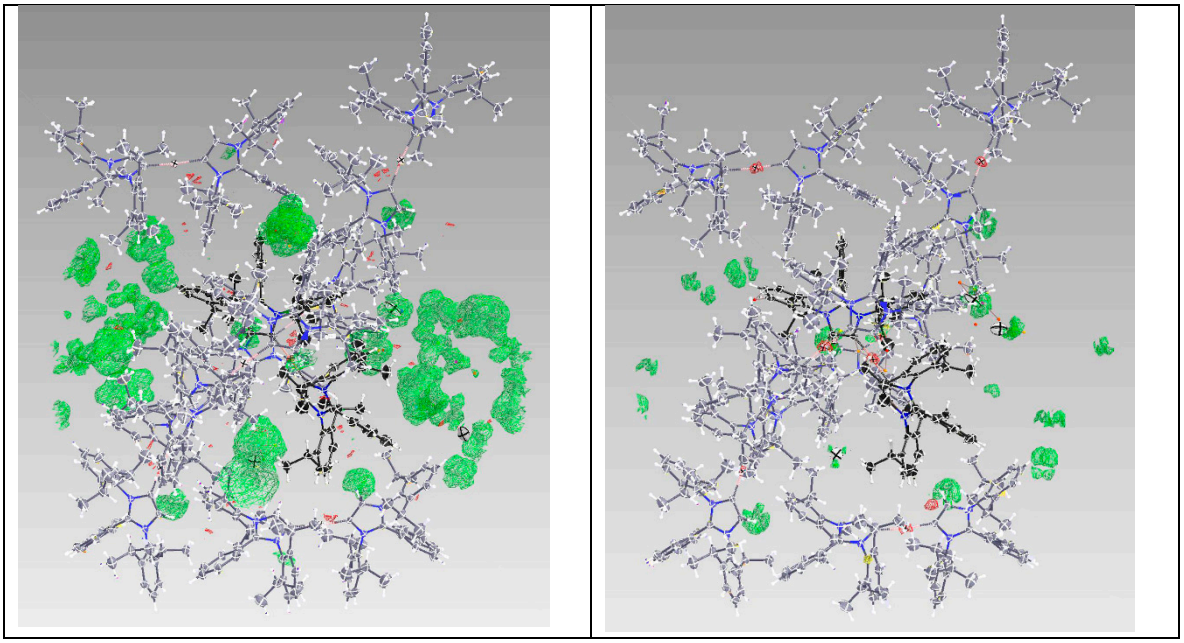
Asymmetric unit of compound 4. The anisotropic displacement parameters are shown at the 50% probability level. Hydrogen atoms and isopropyl groups are omitted for clarity.
One phenyl ring is vibrationally disordered with a side occupation factor of the main component of 0.513(19). Furthermore, the counterion iodine is positionally disordered on four positions with side occupation factors of 0.0350(6), 0.044(1), 0.4407(8), and 0.4810(8).

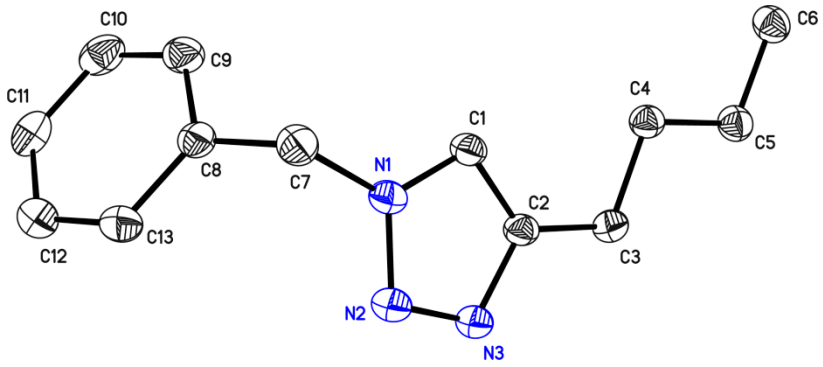
Diffuse residual electron density was observed in the crystal voids. The pictures show the residual electron density in the solvent channels. Heavily disordered lattice solvent (THF) could hardly be modelled into these voids. However, the refined model with solvent molecules was not satisfying. Therefore, the SQUEEZE routine of PLATON[12] program package was used, which allows for the

mathematical compensation of the electron distribution of disordered solvent contained in the voids to the calculated diffraction intensities.

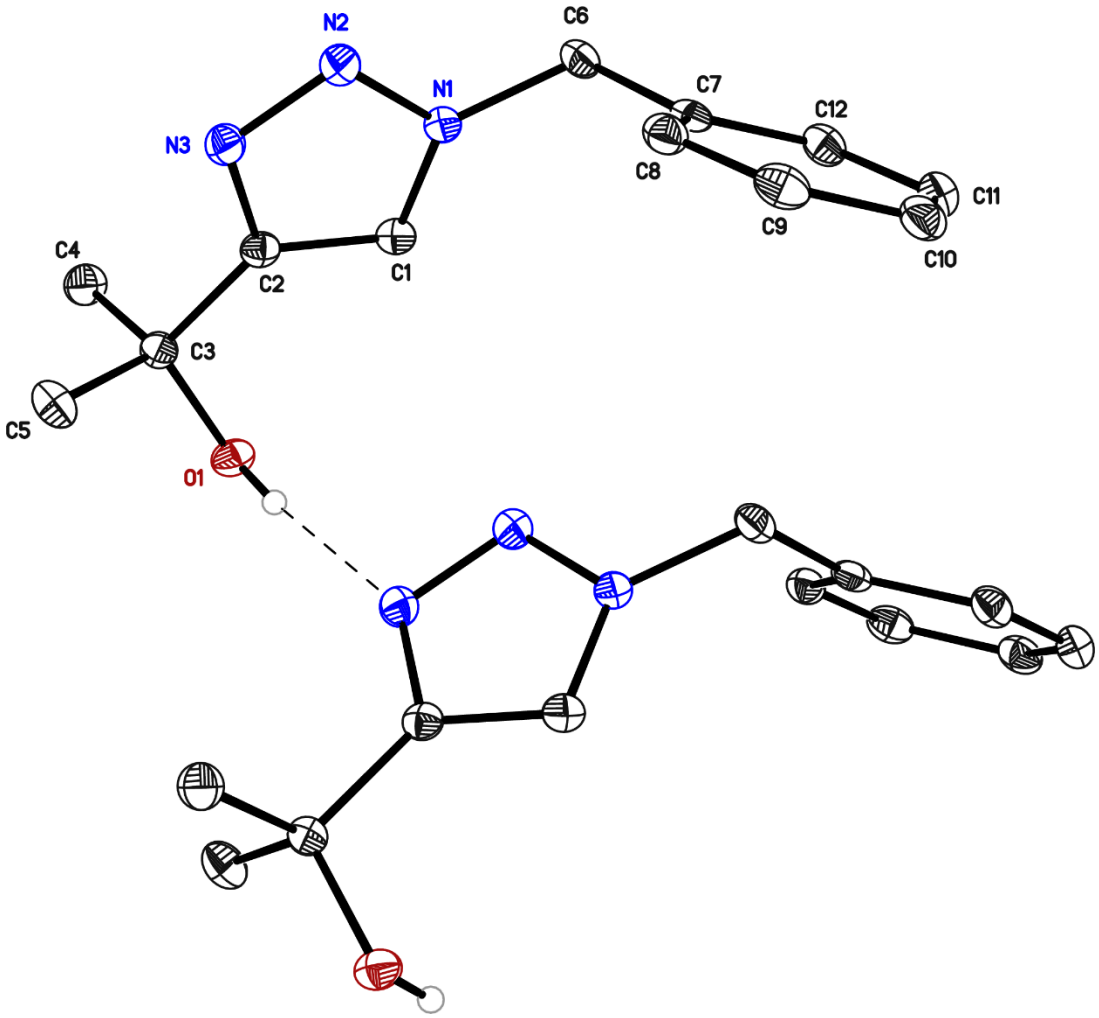
	without solvent	with solvent	squeeze
R1*	0.3399	0.0497	0.0378
wR2*	0.6779	0.1398	0.0956

*indices for all data





Asymmetric unit of compound 1-benzyl-4-butyl-1H-1,2,3-triazole (TZ-3). The anisotropic displacement parameters are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.



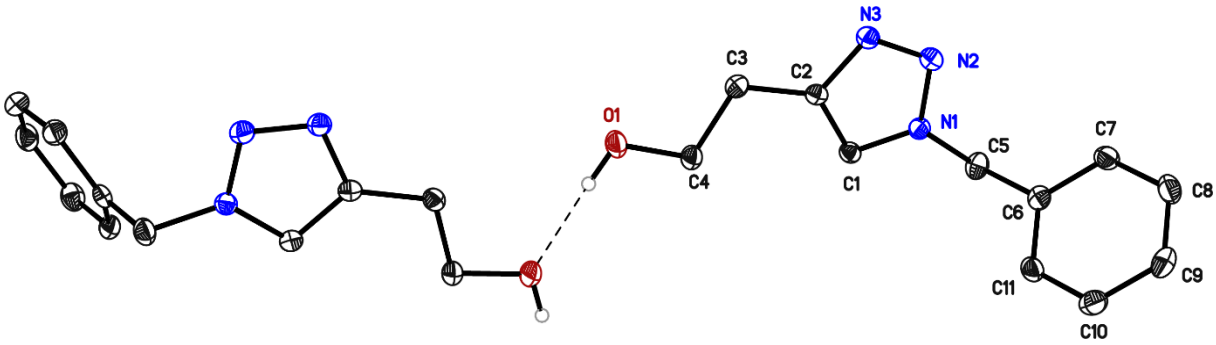
Structure of 2-(1-benzyl-1-1,2,3-triazol-4-yl)propan-2-ol (TZ-4). The anisotropic displacement parameters are shown at the 50% probability level. Not freely refined hydrogen atoms are omitted for clarity.

Hydrogen bonds for **tz_4** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1O)...N(3)#1	0.858(14)	2.012(14)	2.8621(13)	170.8(16)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1/2,z+1/2



Structure of unit of 2-(1-benzyl-1H-1,2,3-triazol-4-yl)ethanol (TZ-2). The anisotropic displacement parameters are shown at the 50% probability level. Not freely refined hydrogen atoms are omitted for clarity.

Hydrogen bonds for **tz_2** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1O)...O(1)#1	0.870(15)	2.024(15)	2.8933(12)	178.1(19)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y+1/2,-z+3/2

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