Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Exploring potential cooperative effects in dicopper(I)-di-mesoionic carbene complexes: Applications in click catalysis

Supporting information

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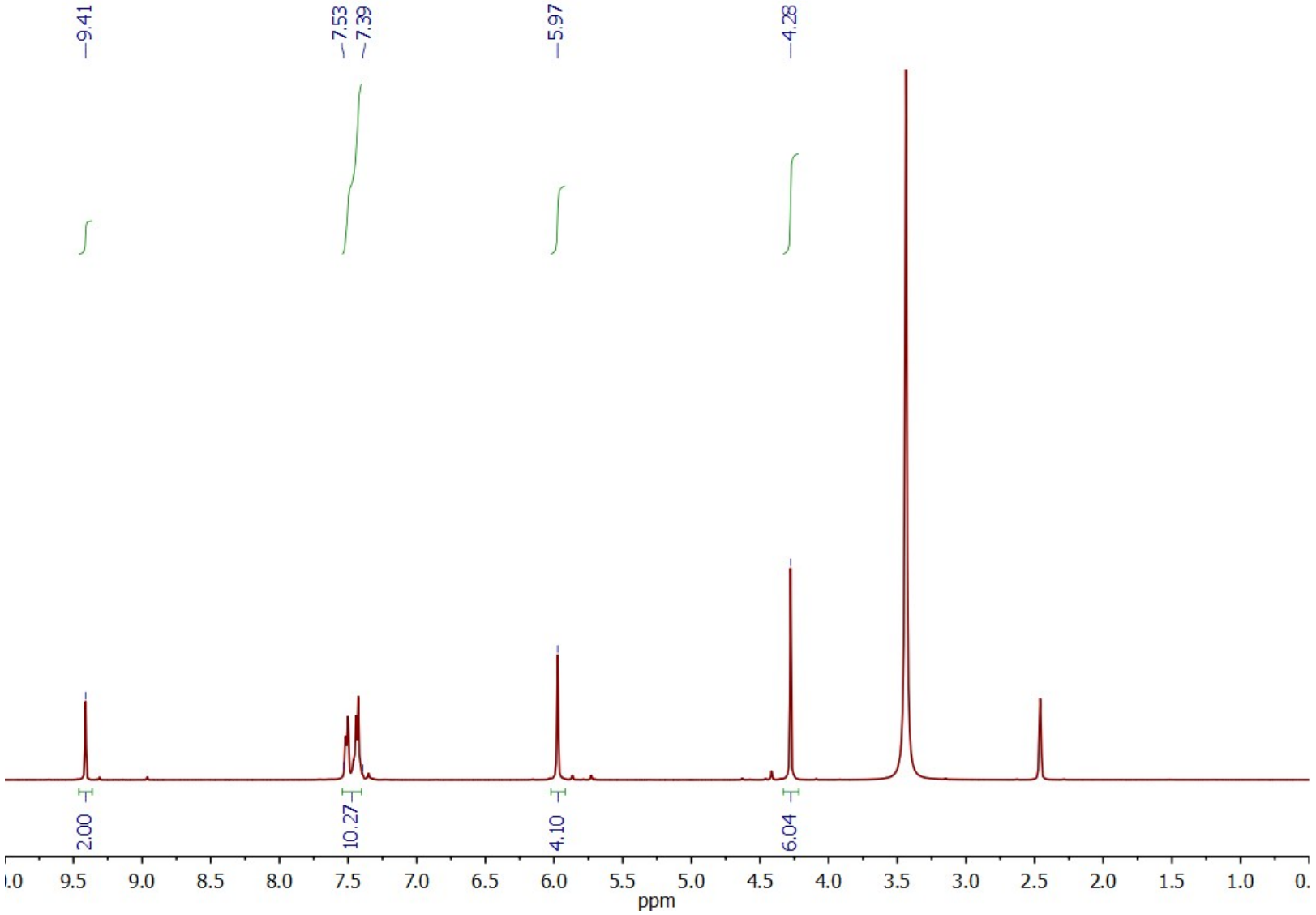
^{1}H and ^{13}C spectra of ligands and complexes



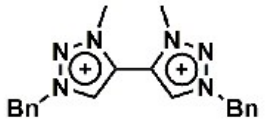


Fig. S 1 ^{1}H NMR spectrum of **$[H_2L^1](BF4)_2$** in DMSO-d_6.

^{1}H and ^{13}C spectra of ligands and complexes

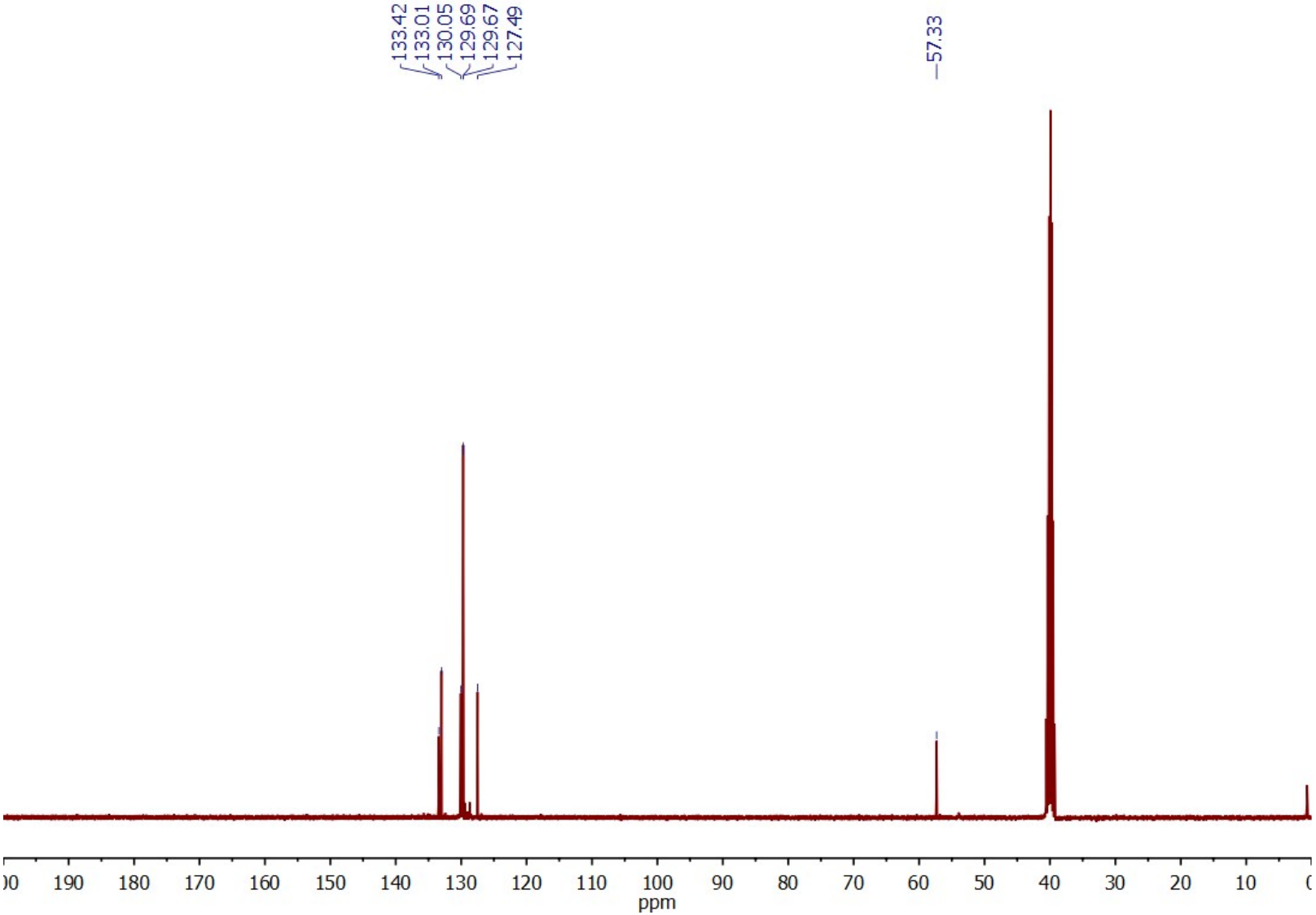


Fig. S 2 ^{13}C NMR spectrum of **$[H_2L^1](BF4)_2$** in DMSO-d_6.

^{1}H and ^{13}C spectra of ligands and complexes

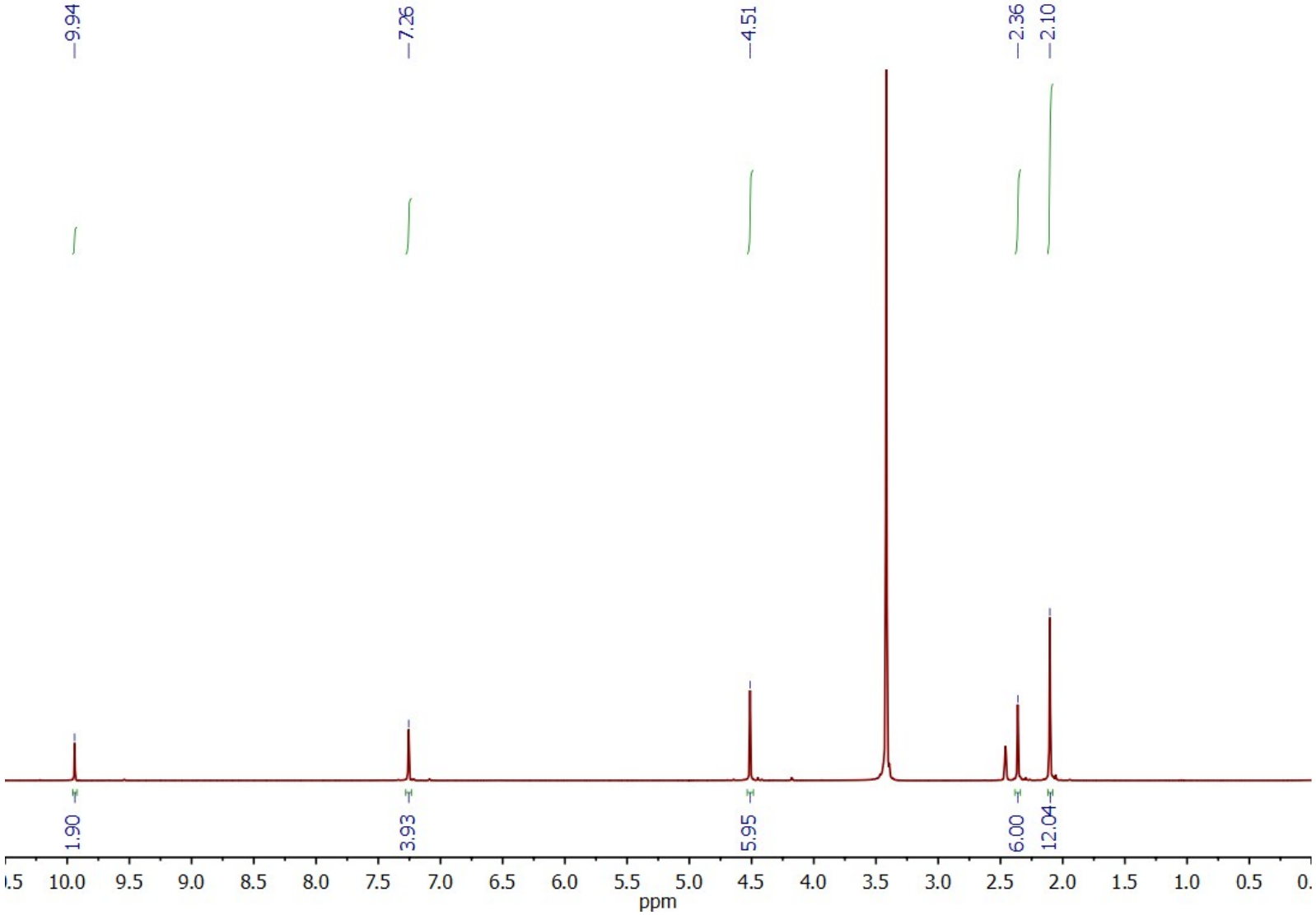


Fig. S 3 ^{1}H NMR spectrum of **$[H_2L^2](BF4)_2$** in DMSO-d_6.

^{1}H and ^{13}C spectra of ligands and complexes

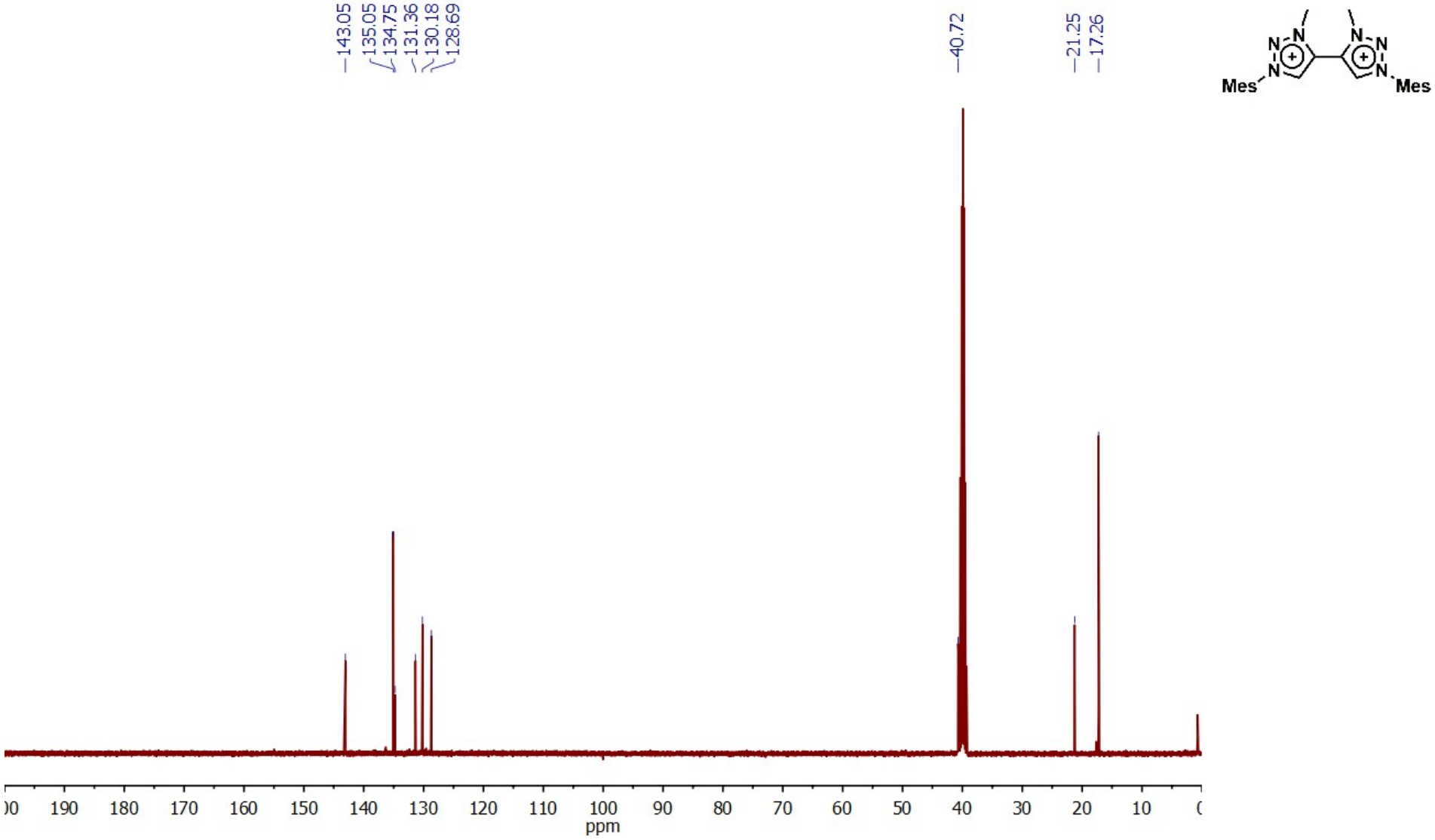


Fig. S 4 ^{13}C NMR spectrum of **$[H_2L^2](BF4)_2$** in DMSO-d_6.

^{1}H and ^{13}C spectra of ligands and complexes

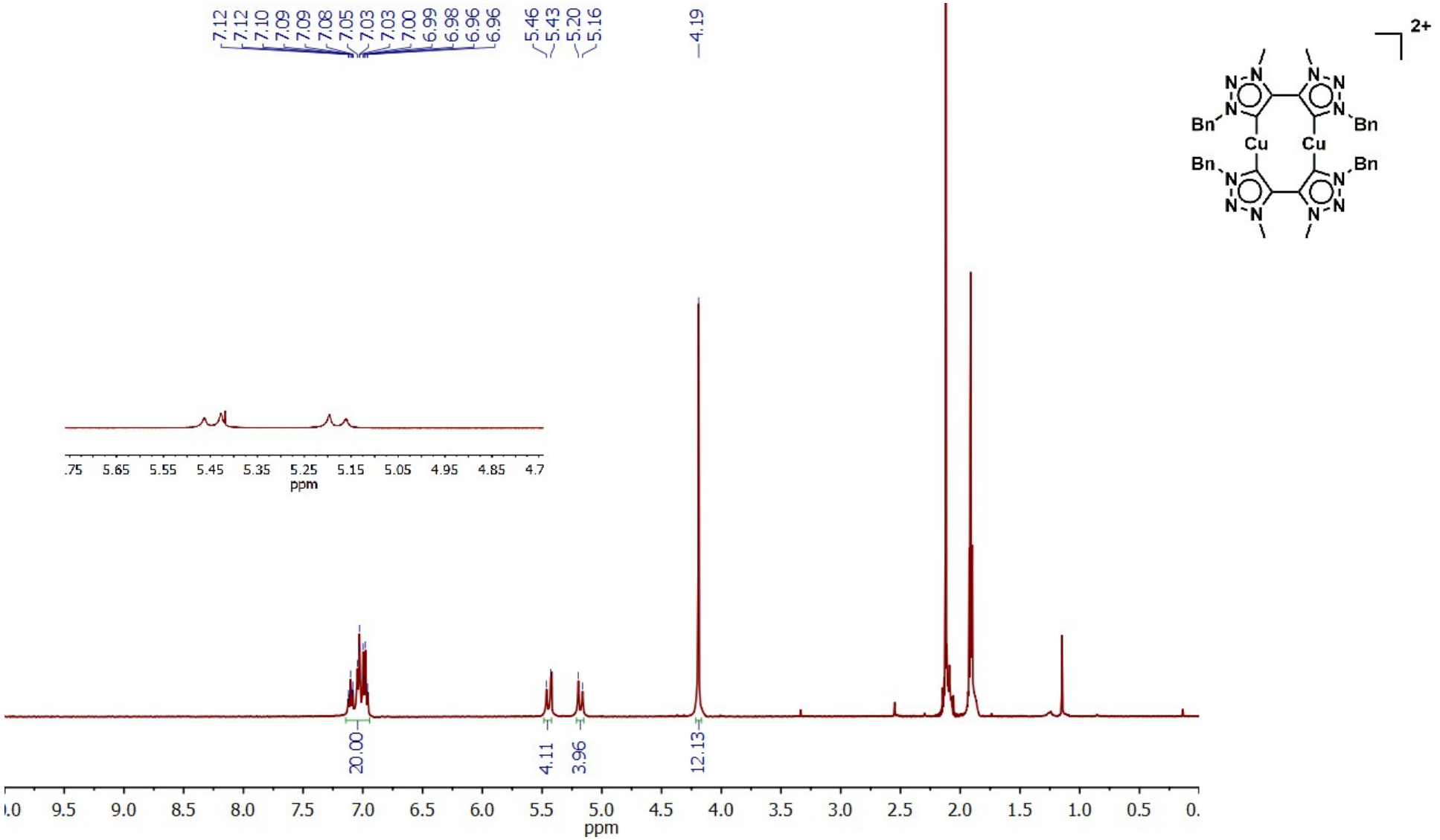


Fig. S 5 ^{1}H NMR spectrum of **1** in CD_3CN (inlet shows benzyl splitting, impurity of dichloromethane).

^{1}H and ^{13}C spectra of ligands and complexes

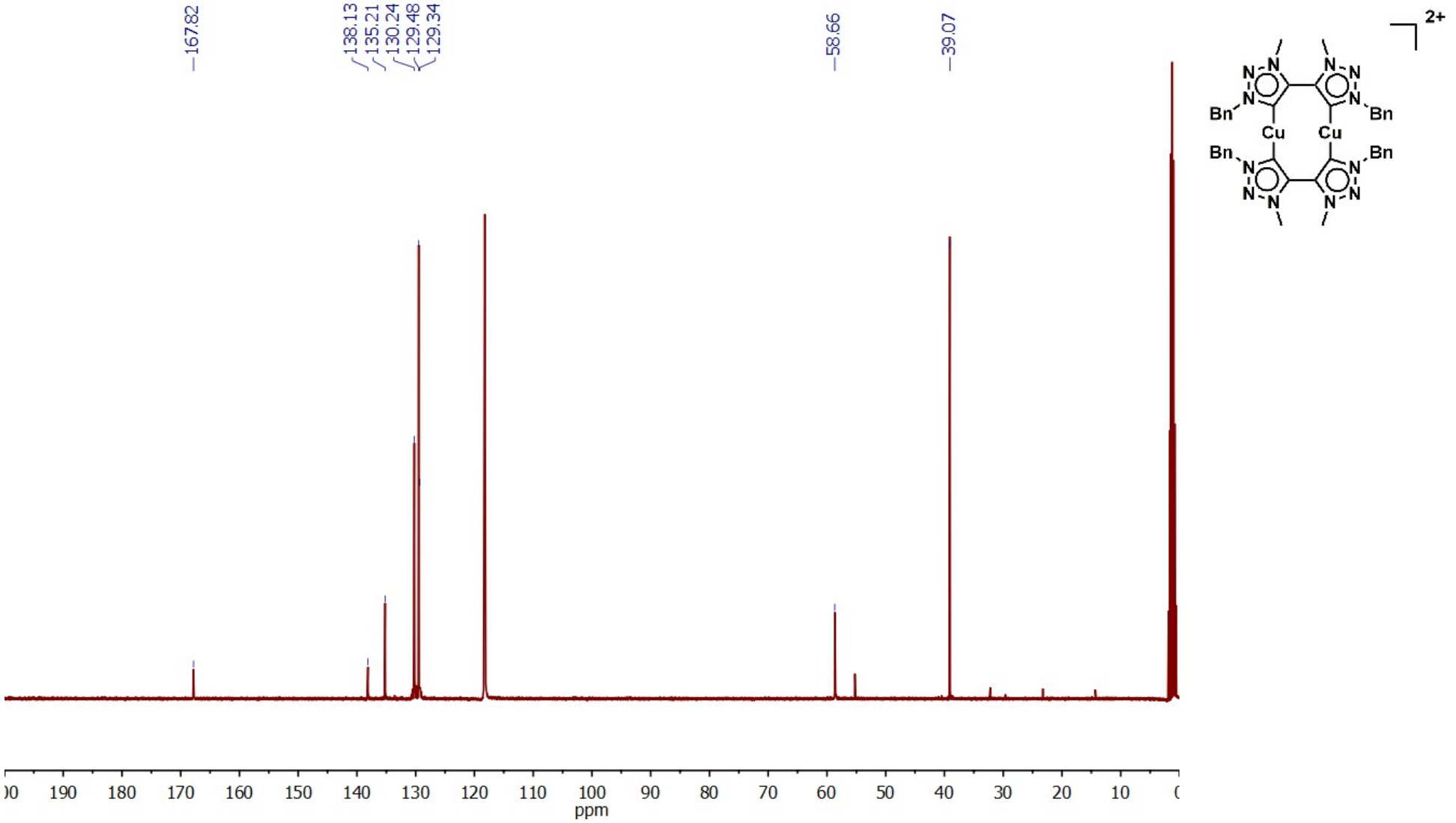


Fig. S 6 ^{13}C NMR spectrum of **1** in CD_3CN (small impurities of hexane and dichloromethane).

^{1}H and ^{13}C spectra of ligands and complexes

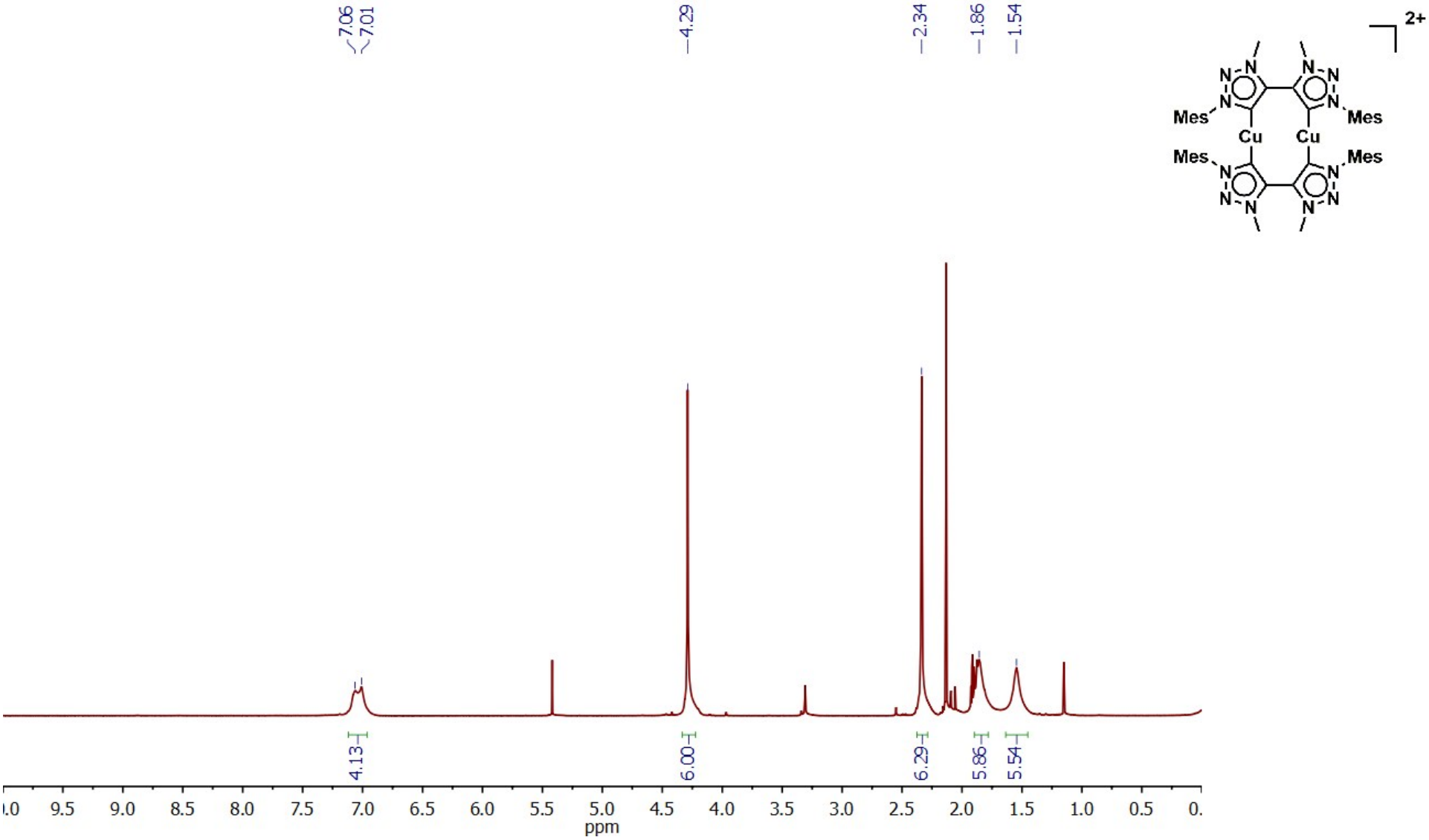


Fig. S 7 ^{1}H NMR spectrum of **2** in CD_3CN.

^{1}H and ^{13}C spectra of ligands and complexes

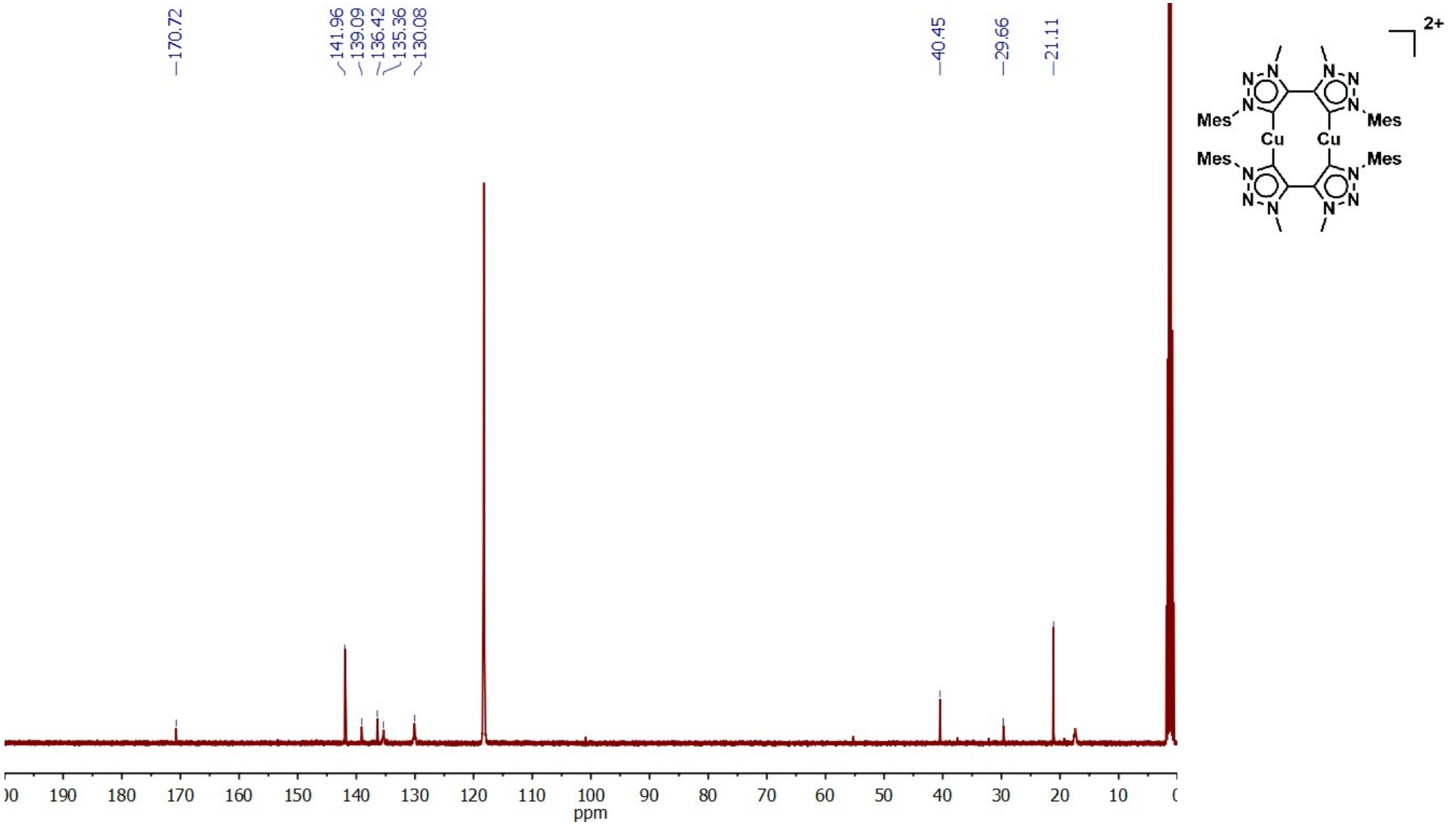


Fig. S 8 ^{13}C NMR spectrum of **2** in CD_3CN.

^{1}H and ^{13}C spectra of ligands and complexes

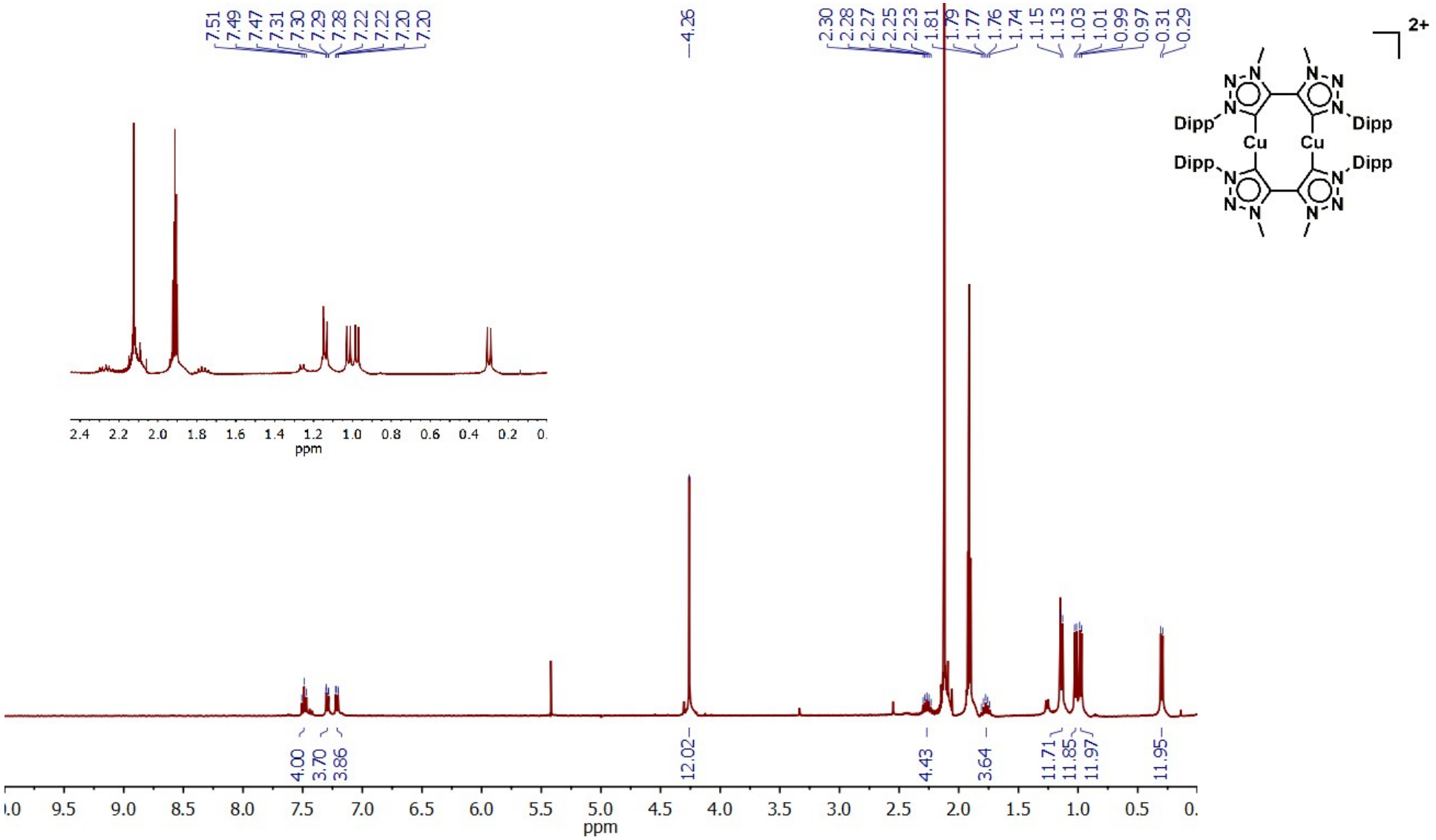


Fig. S 9 ^{1}H NMR spectrum of **3** in CD_3CN (inlet shows dipp-splitting, 2x $CH(CH_3)_2$ and 4x $CH(CH_3)_2$ signals, small grease impurities).

^{1}H and ^{13}C spectra of ligands and complexes

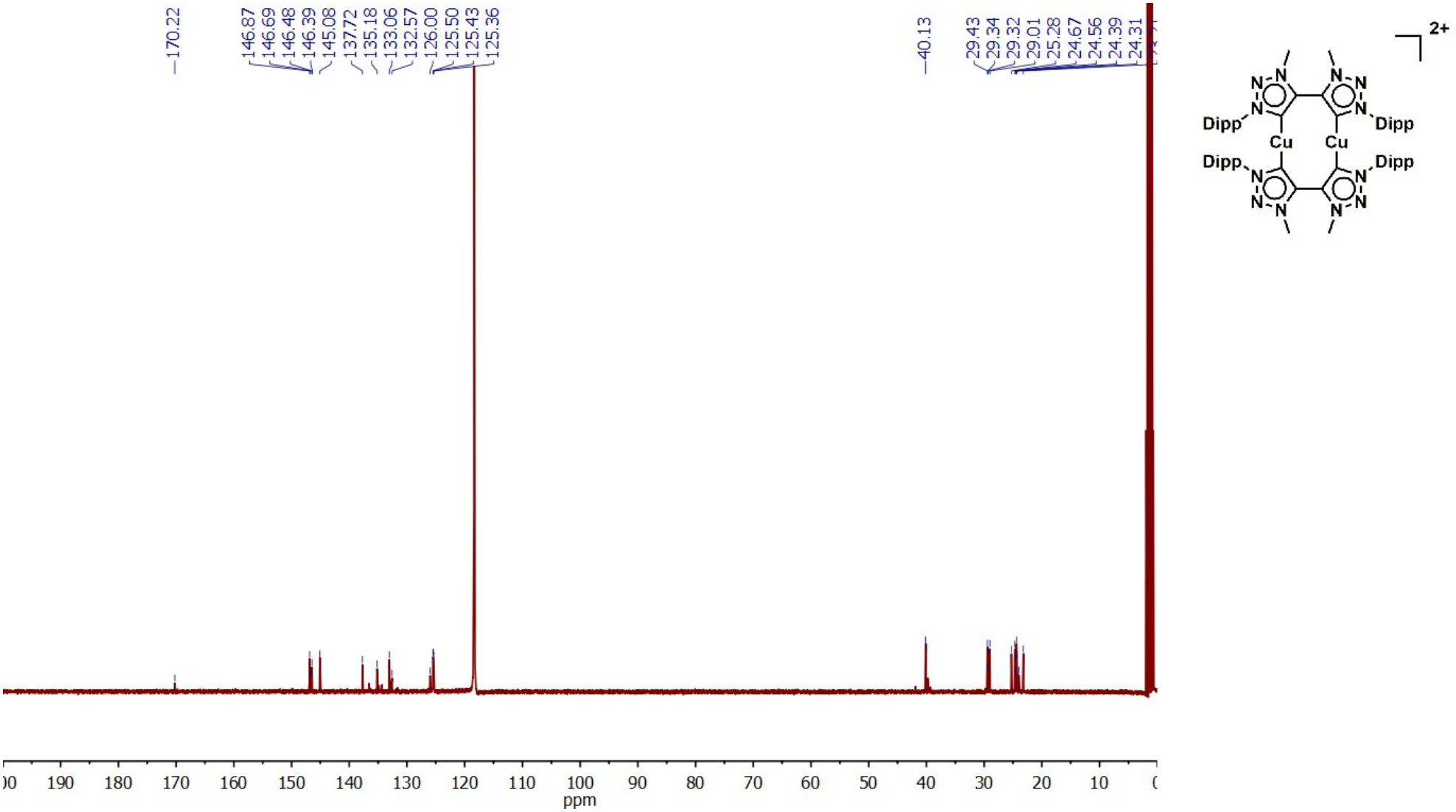


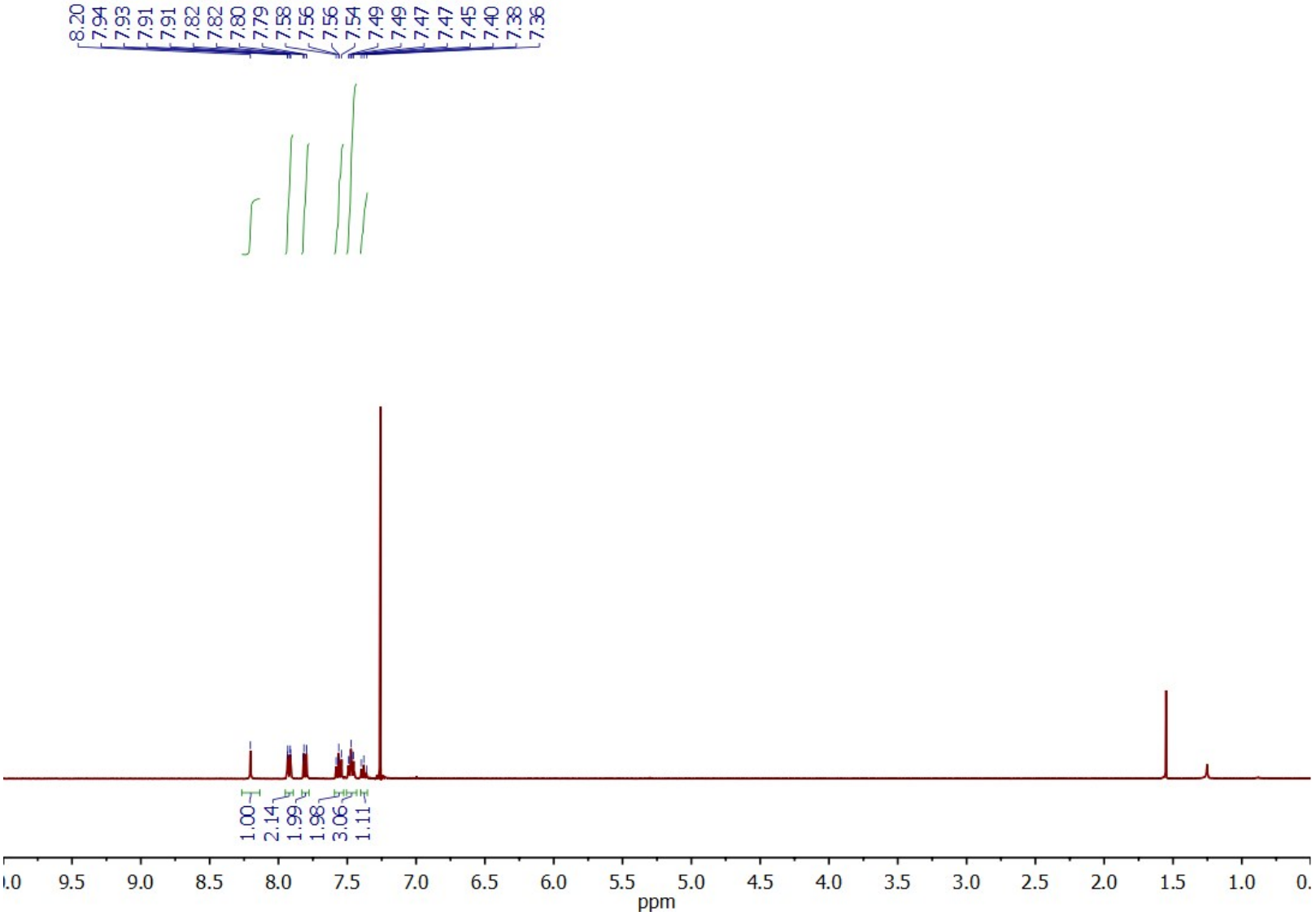
Fig. S 10 ^{13}C NMR spectrum of **3** in CD_3CN.

^{1}H spectra of triazole reactions

General Remarks to the NMR spectra:

NMR spectra of **T3**, **T5** – **T8**, **T10** - **T12**, **T14** and **T18** were recorded without purifications of the reaction to determine the conversion of the reaction. Reactions from DCM were just evaporated and the crude mixture was subjected to NMR measurements. Additionally, for **T6**, **T8** and **T11** the conversions were also determined by the use of an internal standard (1,2-dibromoethane, 0.25 mmol). **T1**, **T2**, **T4**, **T9**, **T13**, **T15** – **T17** and **T19** - **T22** are isolated products.

^{1}H spectra of triazole reactions



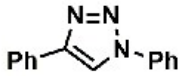
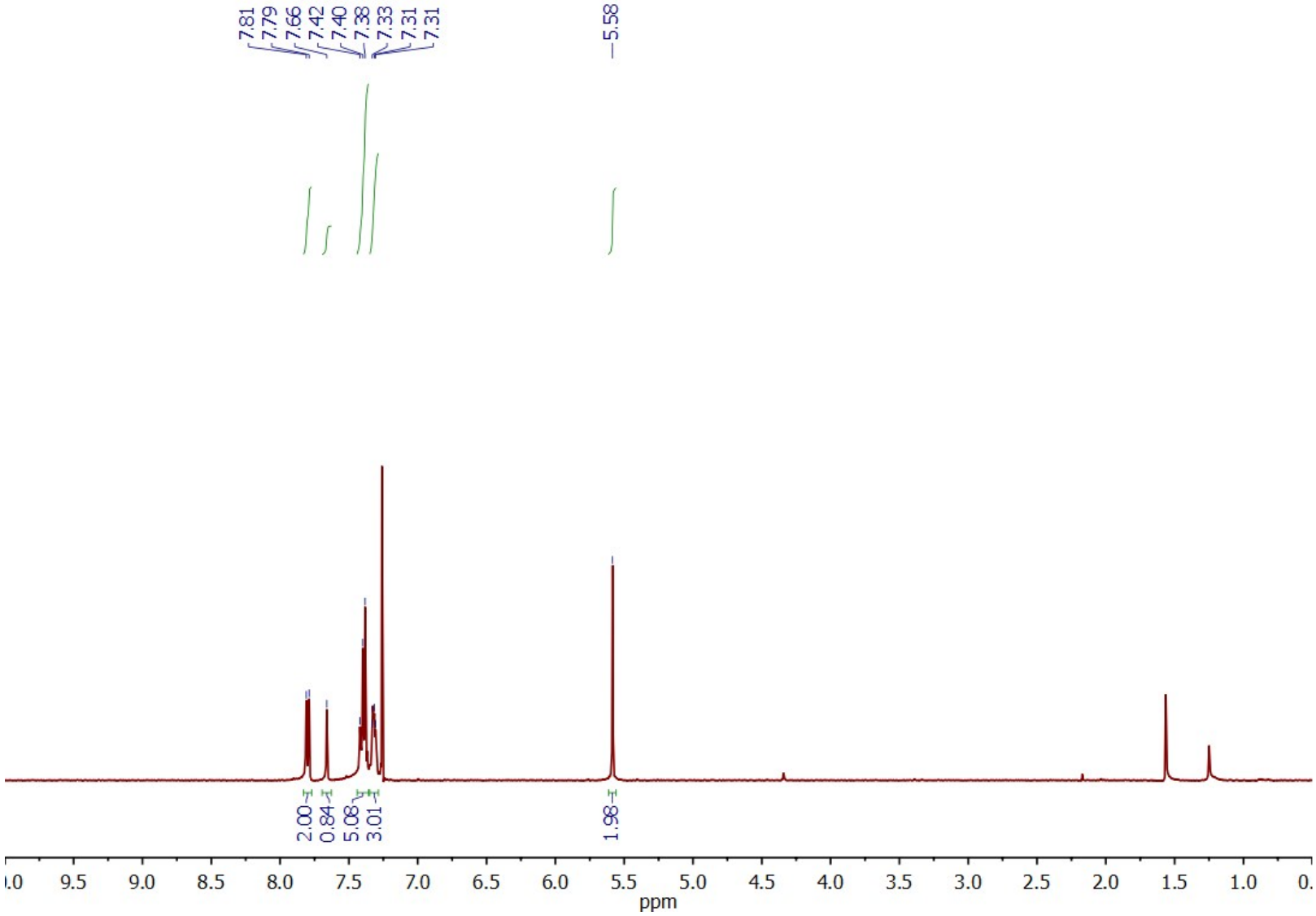


Fig. S 11 ^{1}H NMR spectrum of isolated **T1** in $CDCl_3$.

[1]H spectra of triazole reactions



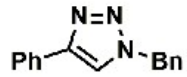


Fig. S 12 [1]H NMR spectrum of isolated **T2** in $CDCl_3$.

[1]H spectra of triazole reactions

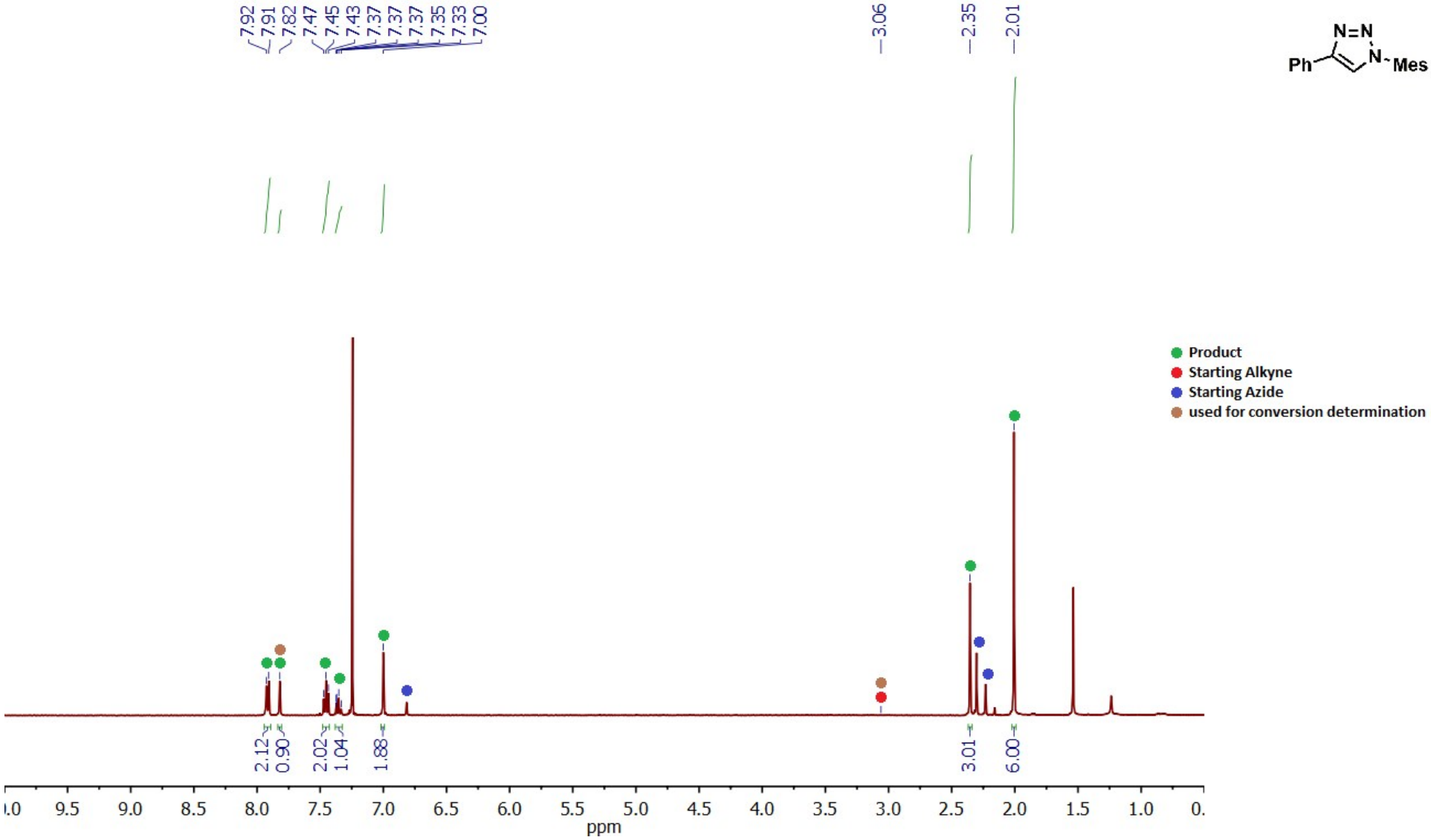
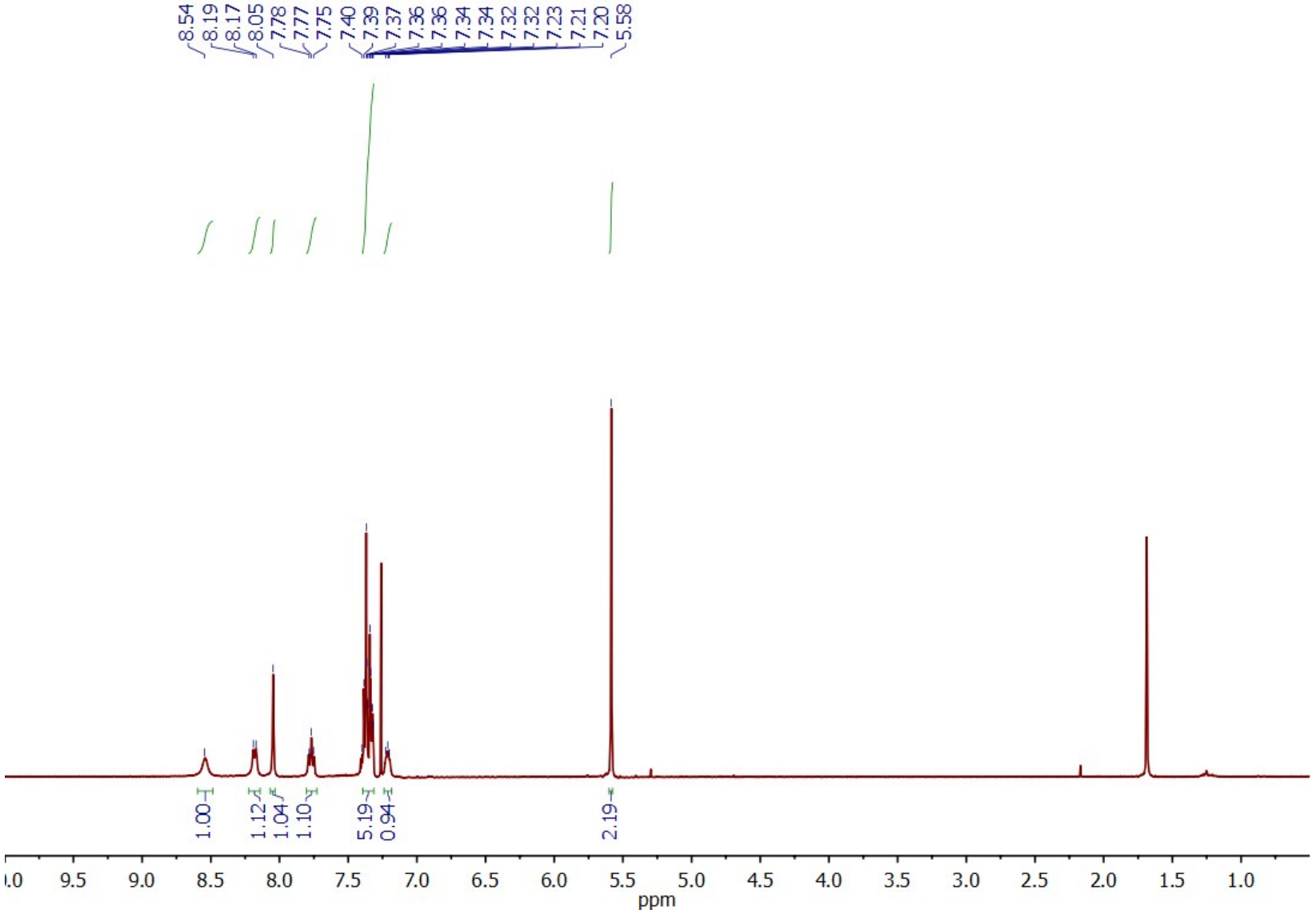


Fig. S 13 [1]H NMR spectrum of crude **T3** in $CDCl_3$.

[1]H spectra of triazole reactions



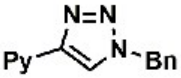


Fig. S 14 [1]H NMR spectrum of isolated **T4** in $CDCl_3$.

[1]H spectra of triazole reactions

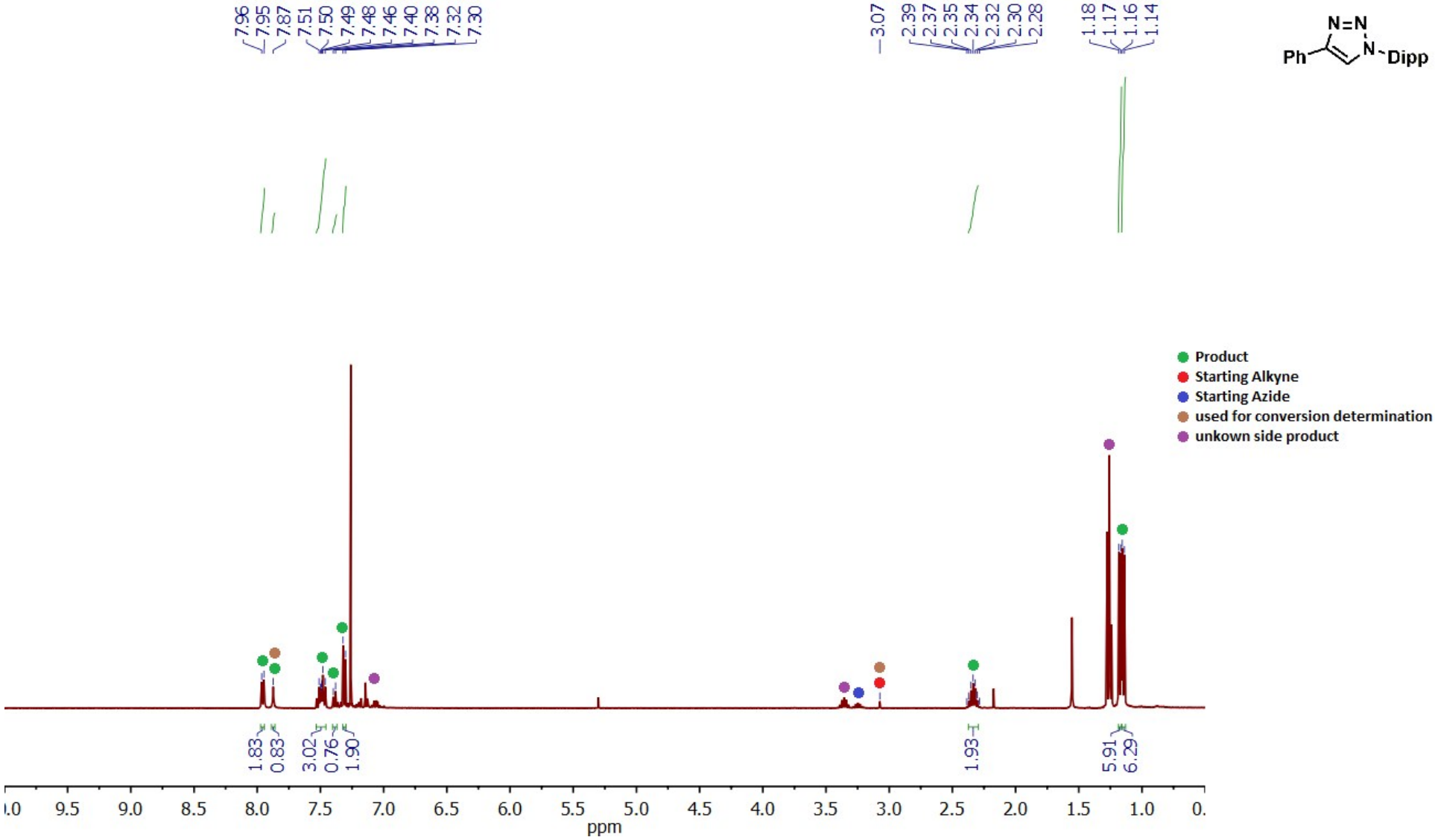


Fig. S 15 [1]H NMR spectrum of crude **T5** in $CDCl_3$.

^{1}H spectra of triazole reactions

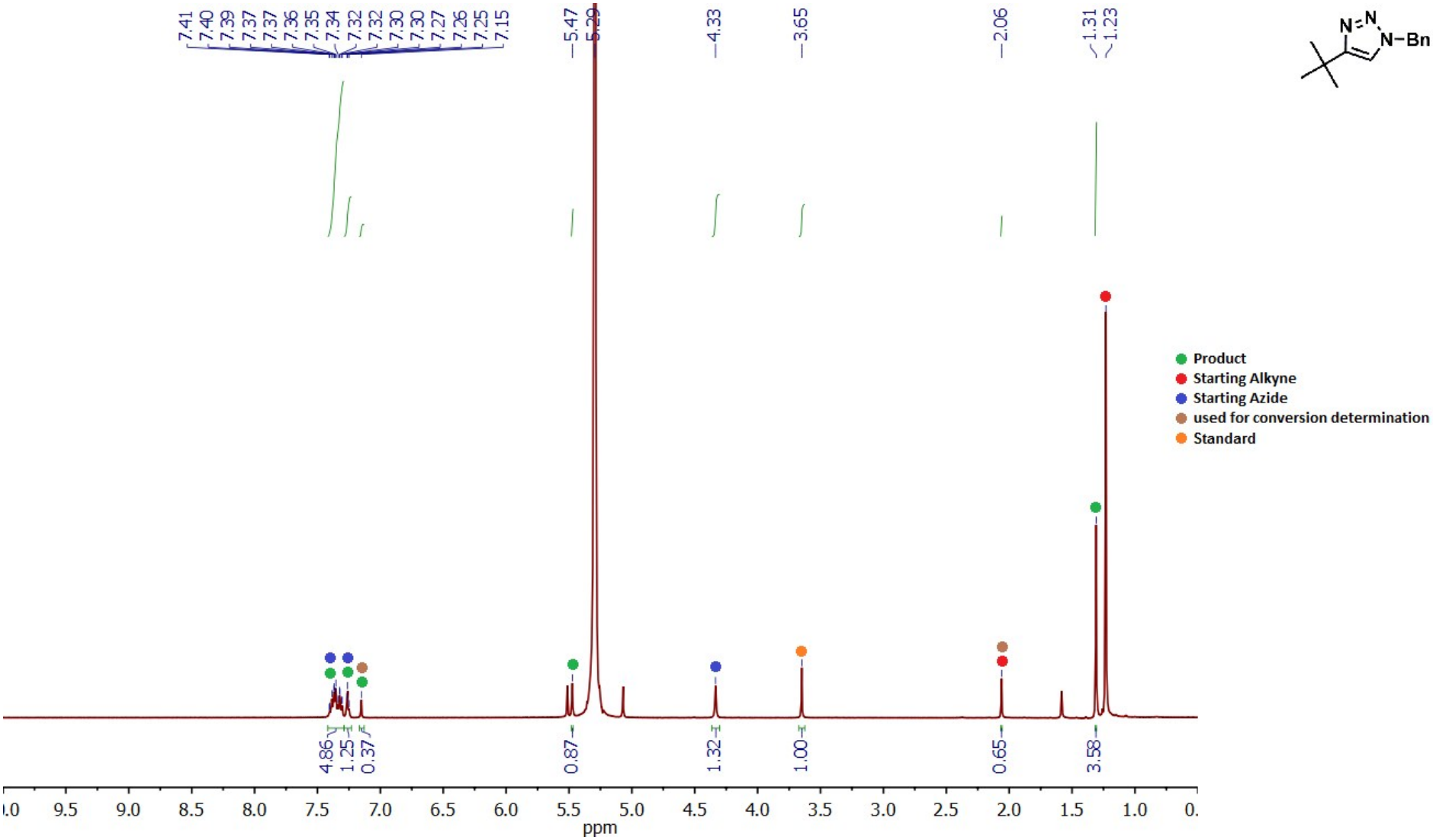


Fig. S 16 ^{1}H NMR spectrum of crude **T6** in $CDCl_3$ with 1,2-dibromoethane as an internal standard. Peak at 5.3 ppm is DCM since the spectra was taken directly from the reaction mixture without any purifications.

[1]H spectra of triazole reactions

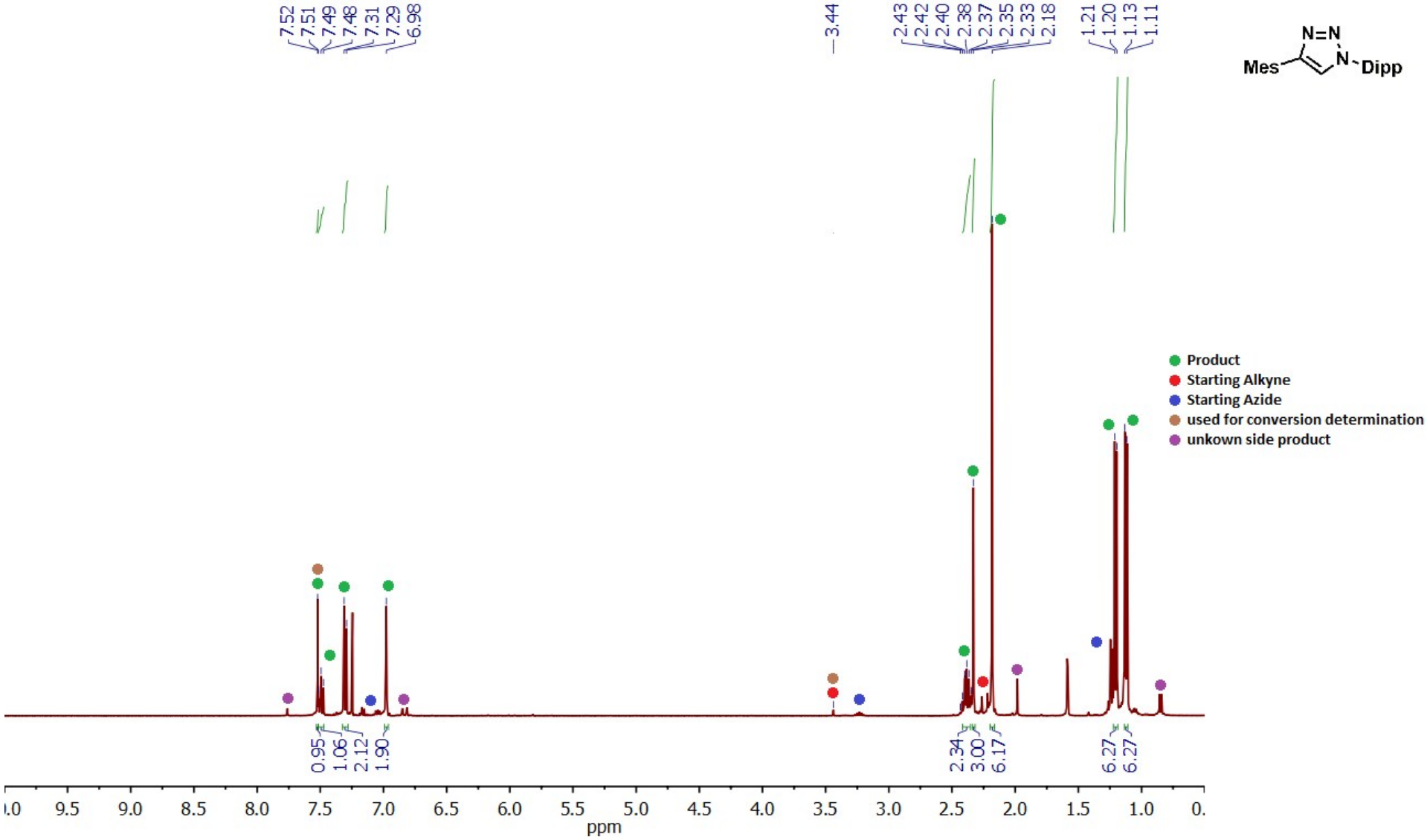


Fig. S 17 [1]H NMR spectrum of crude **T7** in $CDCl_3$.

[1]H spectra of triazole reactions

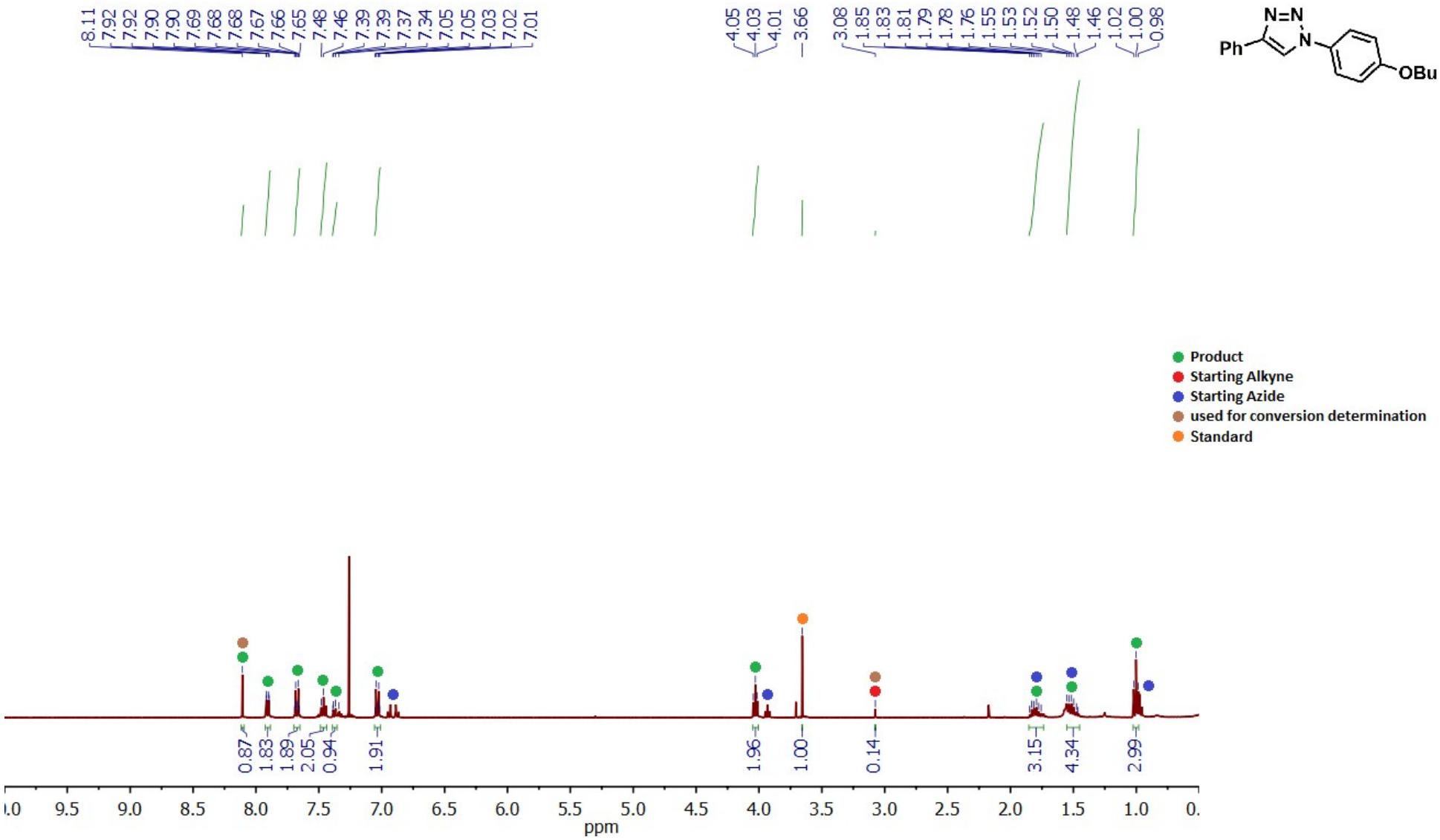
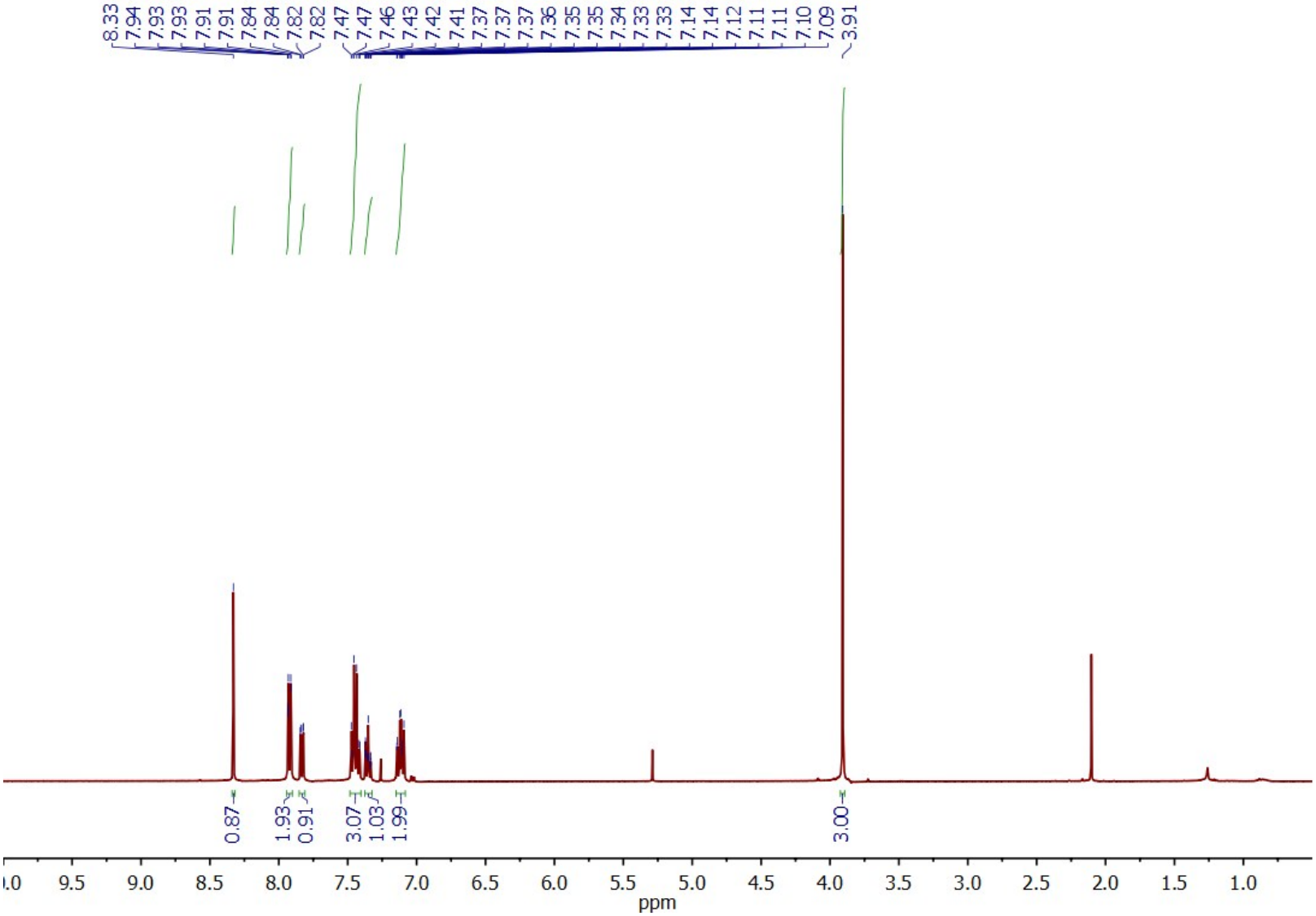


Fig. S 18 [1]H NMR spectrum of crude **T8** in $CDCl_3$ with 1,2-dibromoethane as internal standard.

[1]H spectra of triazole reactions



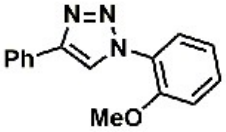


Fig. S 19 [1]H NMR spectrum of isolated **T9** in $CDCl_3$.

[1]H spectra of triazole reactions

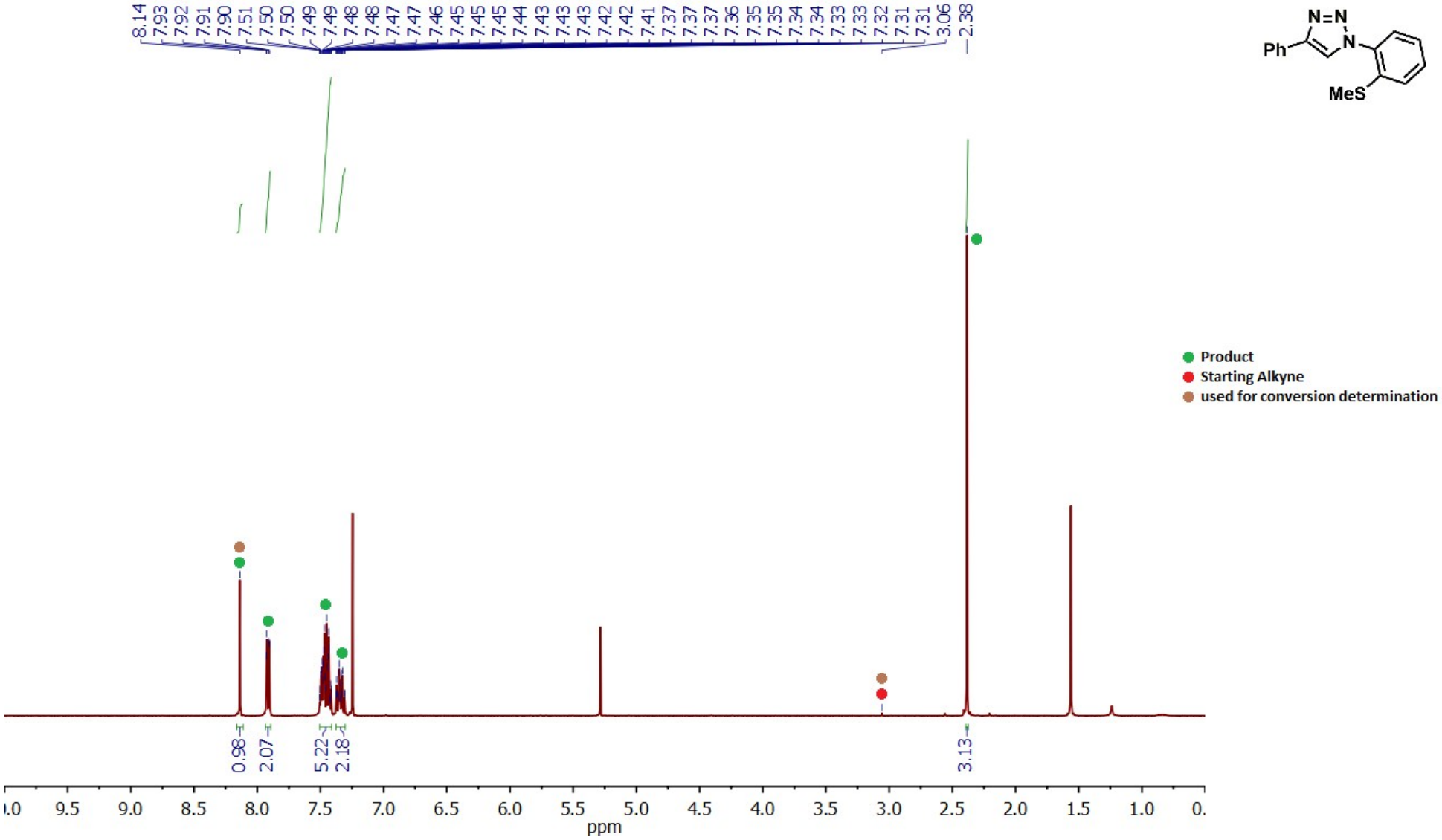


Fig. S 20 [1]H NMR spectrum of crude **T10** in $CDCl_3$.

^{1}H spectra of triazole reactions

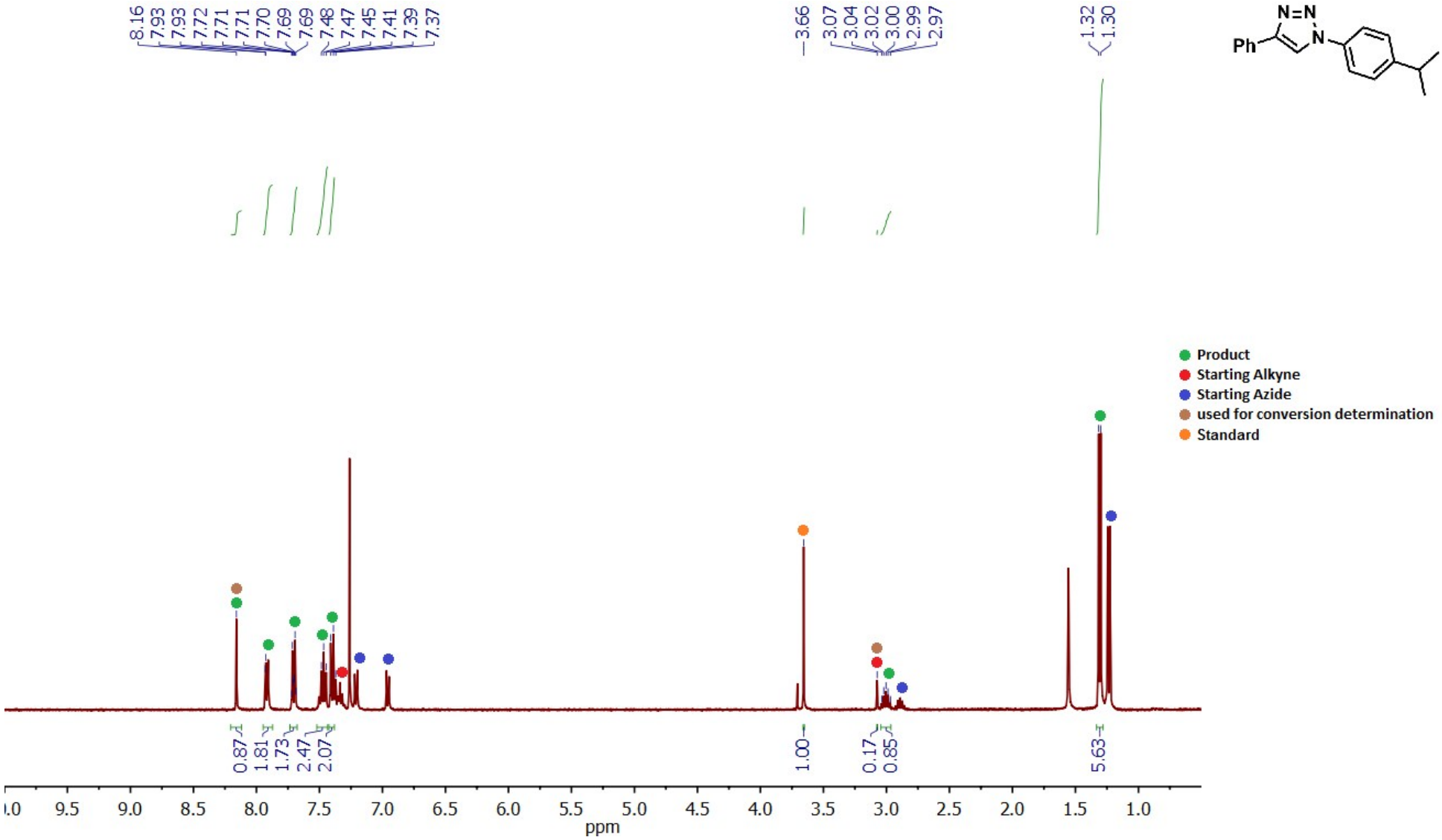


Fig. S 21 ^{1}H NMR spectrum of crude **T11** in $CDCl_3$ with 1,2-dibromoethane as internal standard.

^{1}H spectra of triazole reactions

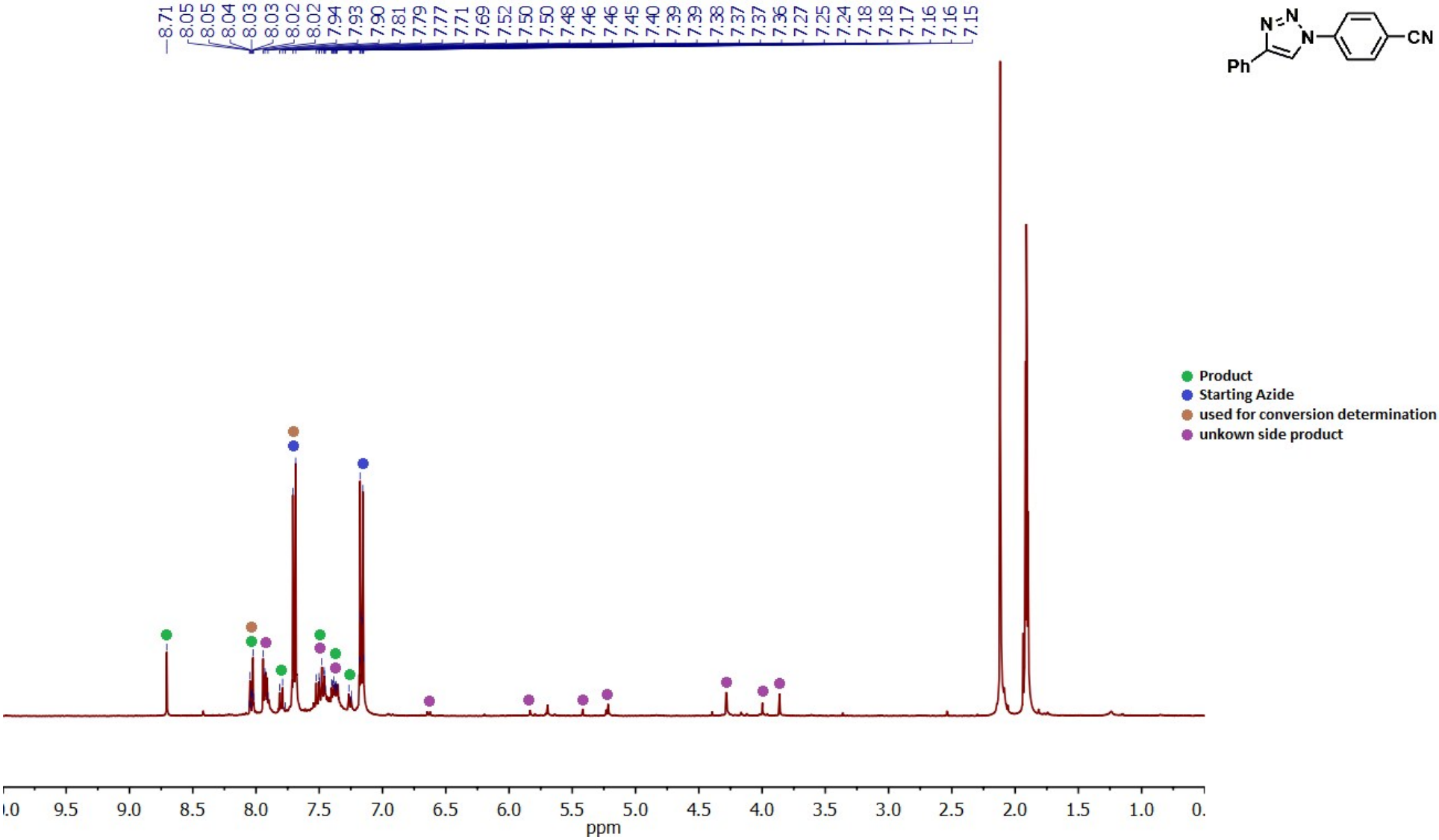


Fig. S 22 ^{1}H NMR spectrum of crude **T12** in MeCN-d_3.

[1]H spectra of triazole reactions

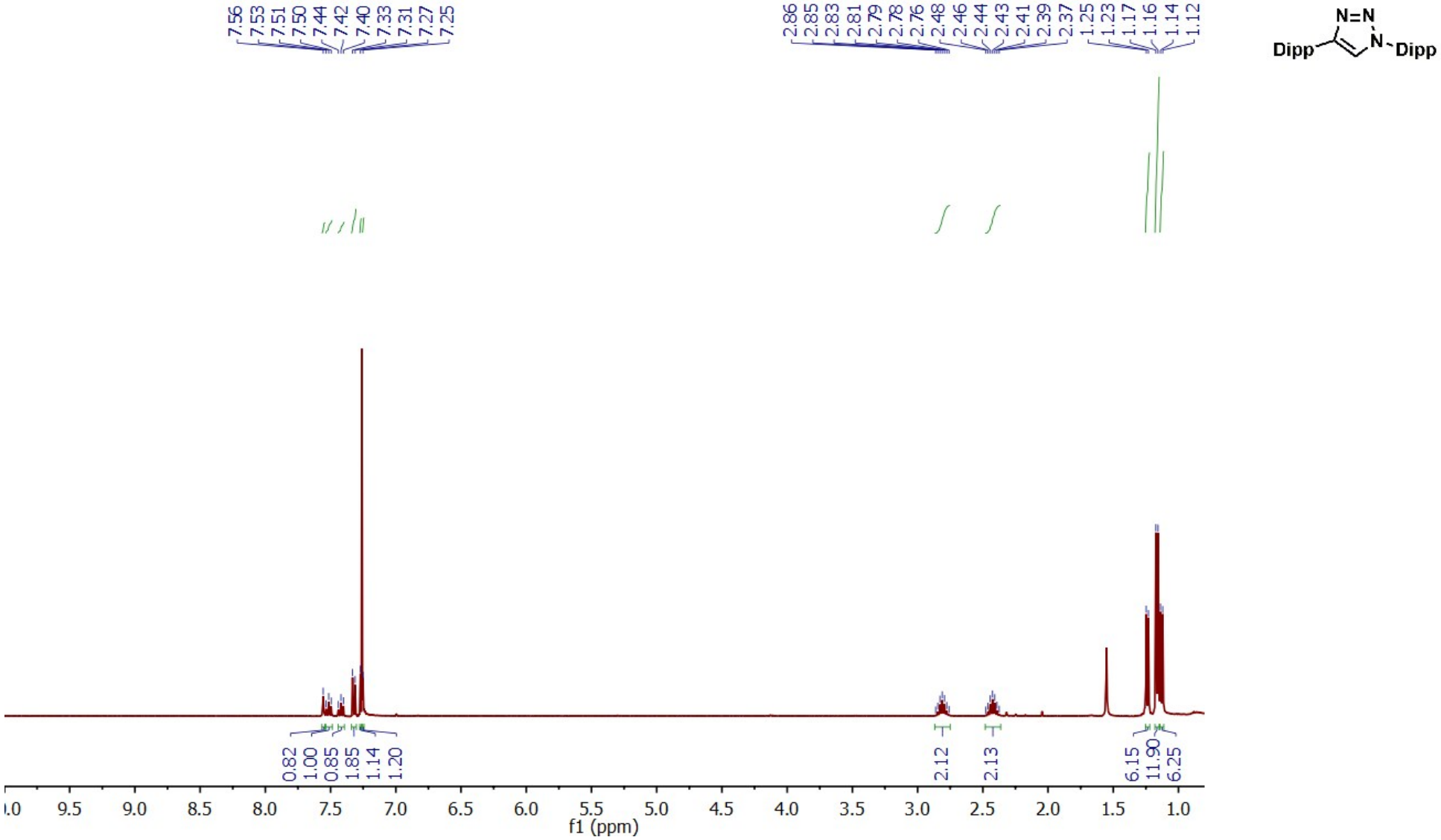


Fig. S 23 [1]H NMR spectrum of isolated **T13** in $CDCl_3$.

[1]H spectra of triazole reactions

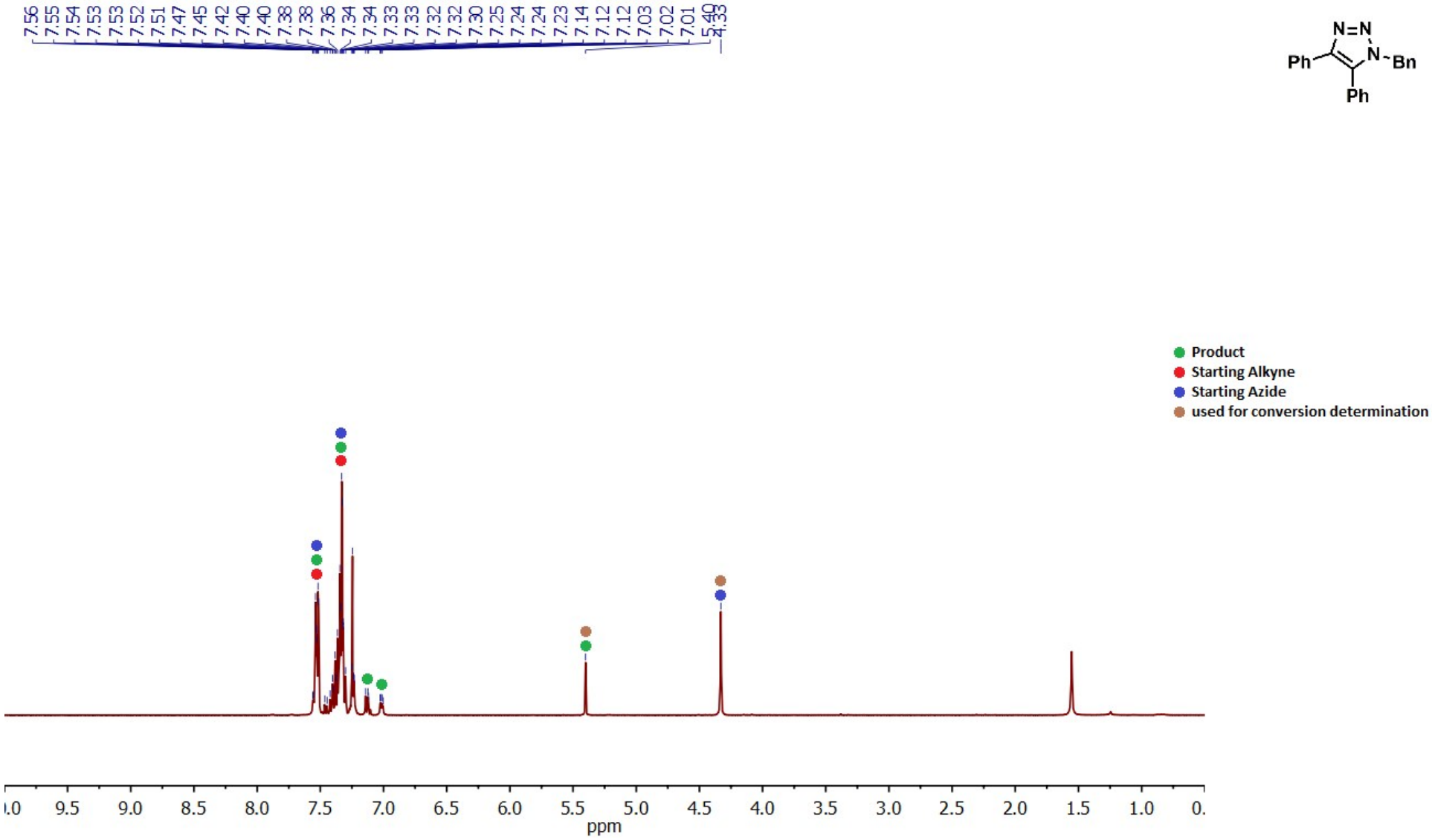
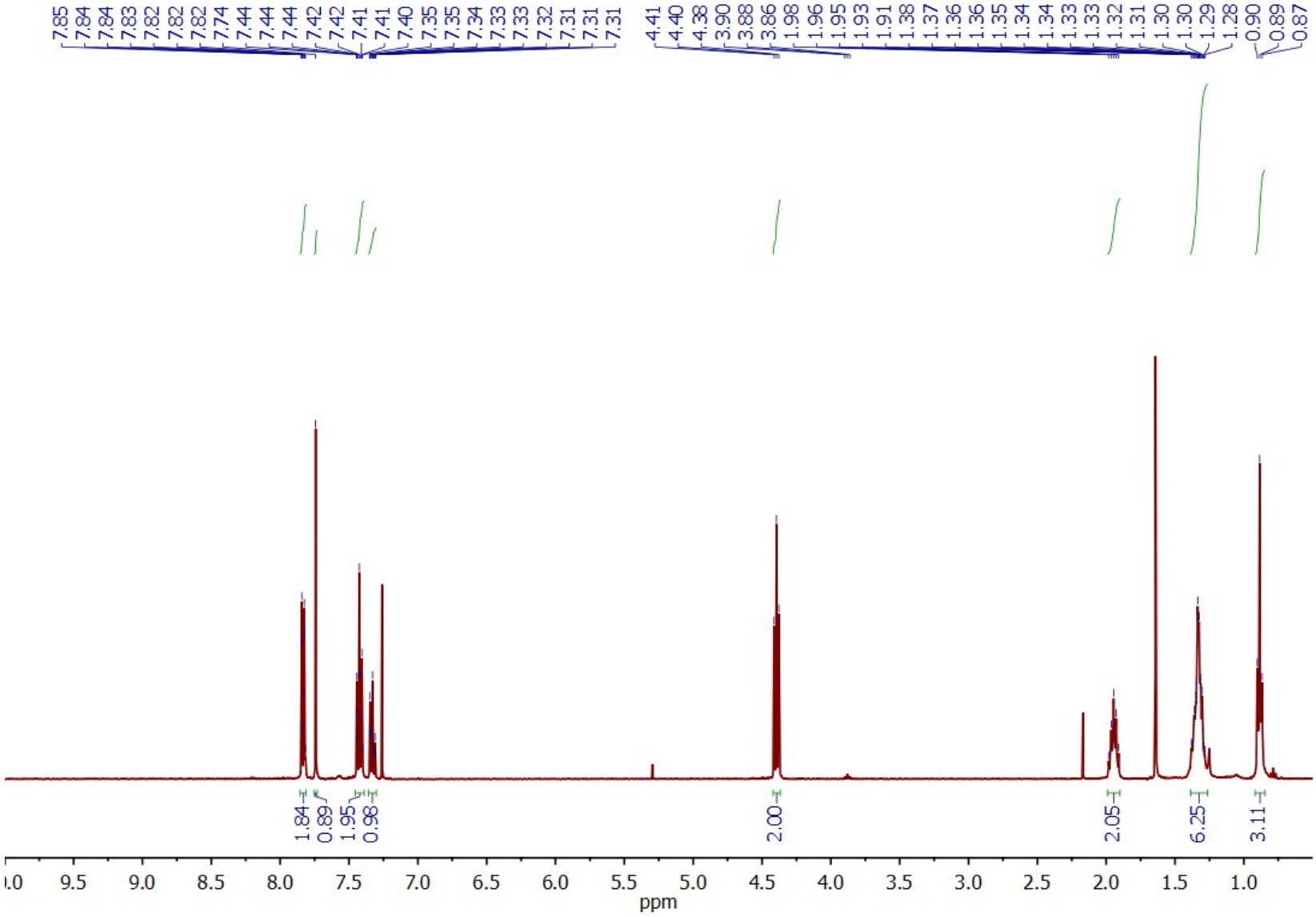


Fig. S 24 [1]H NMR spectrum of crude **T14** in $CDCl_3$.

^{1}H spectra of triazole reactions



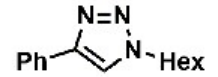
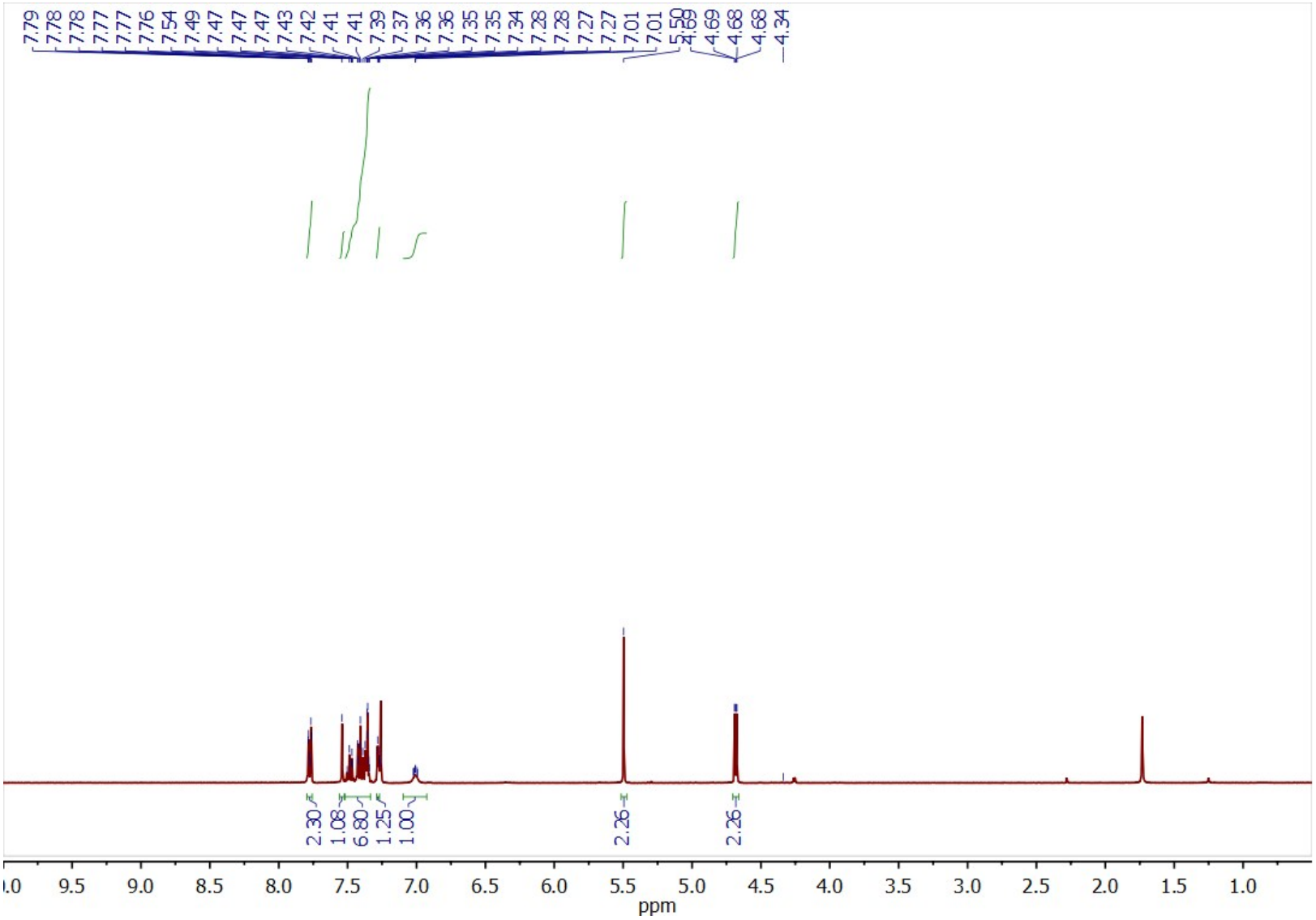


Fig. S 25 ^{1}H NMR spectrum of isolated **T15** in $CDCl_3$.

^{1}H spectra of triazole reactions



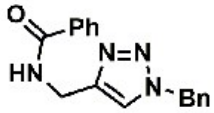


Fig. S 26 ^{1}H NMR spectrum of isolated **T16** in $CDCl_3$.

[1]H spectra of triazole reactions

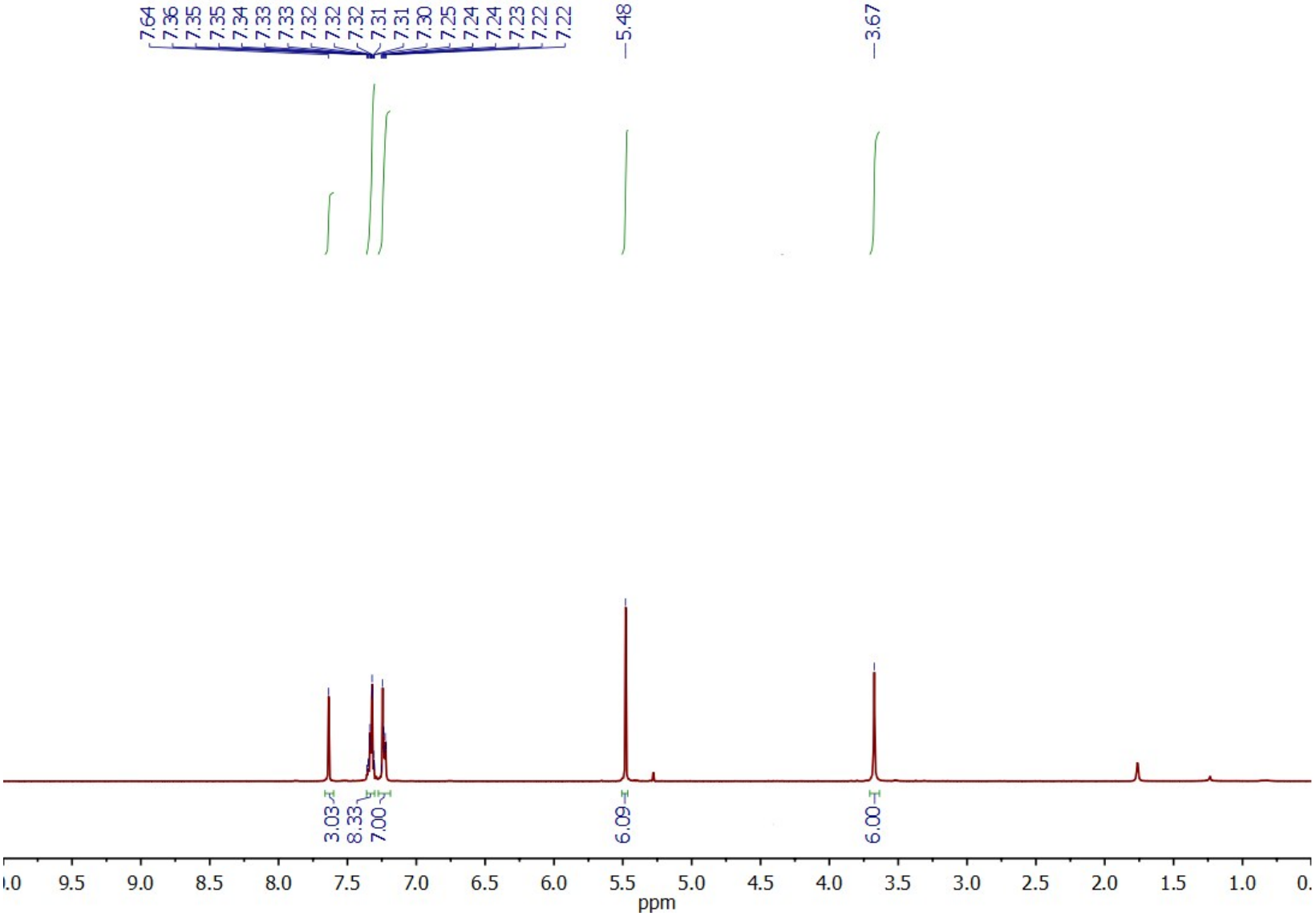


Fig. S 27 [1]H NMR spectrum of isolated **T17** in $CDCl_3$.

[1]H spectra of triazole reactions

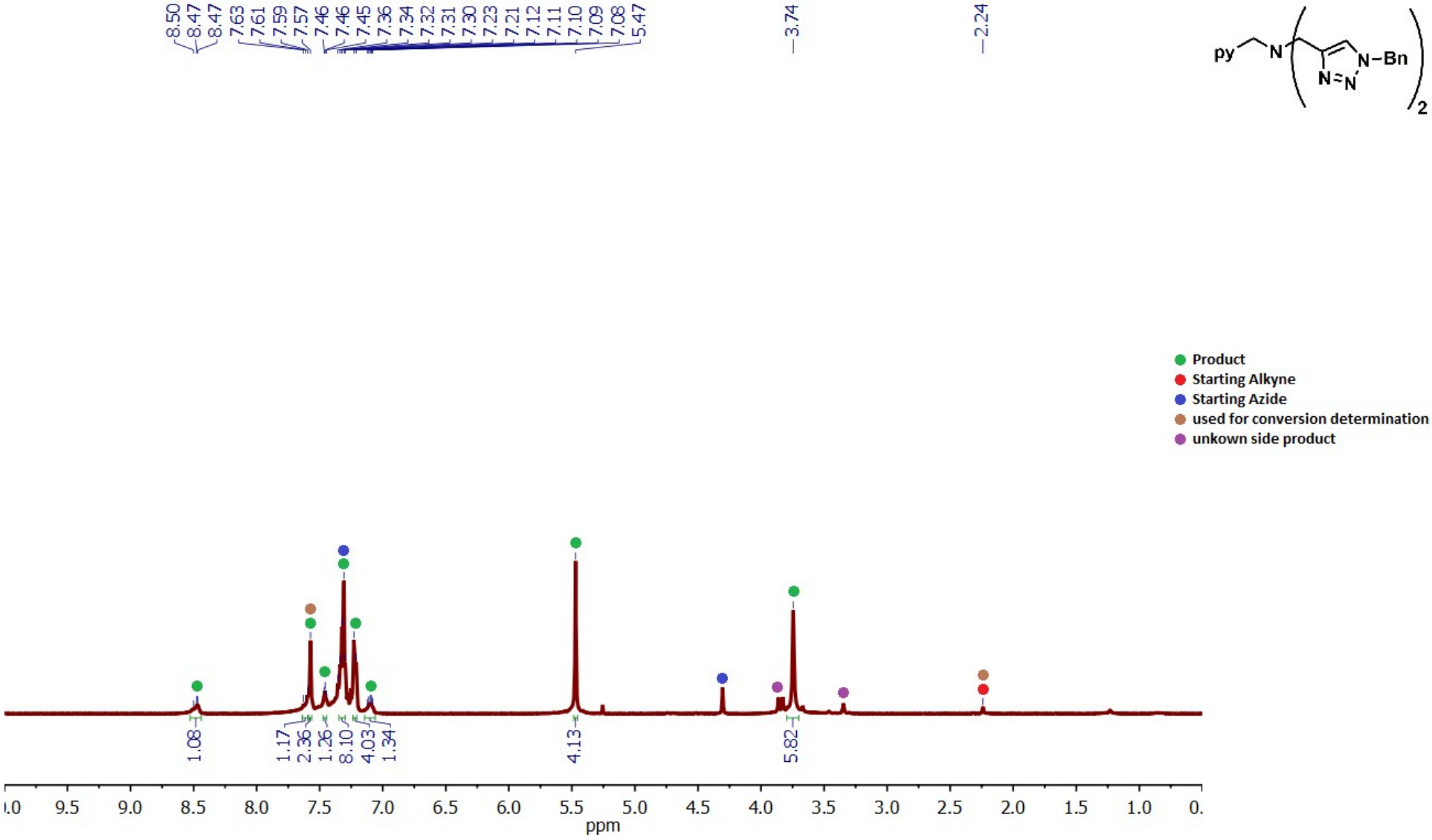


Fig. S 28 [1]H NMR spectrum of crude **T18** in $CDCl_3$.

^{1}H spectra of triazole reactions

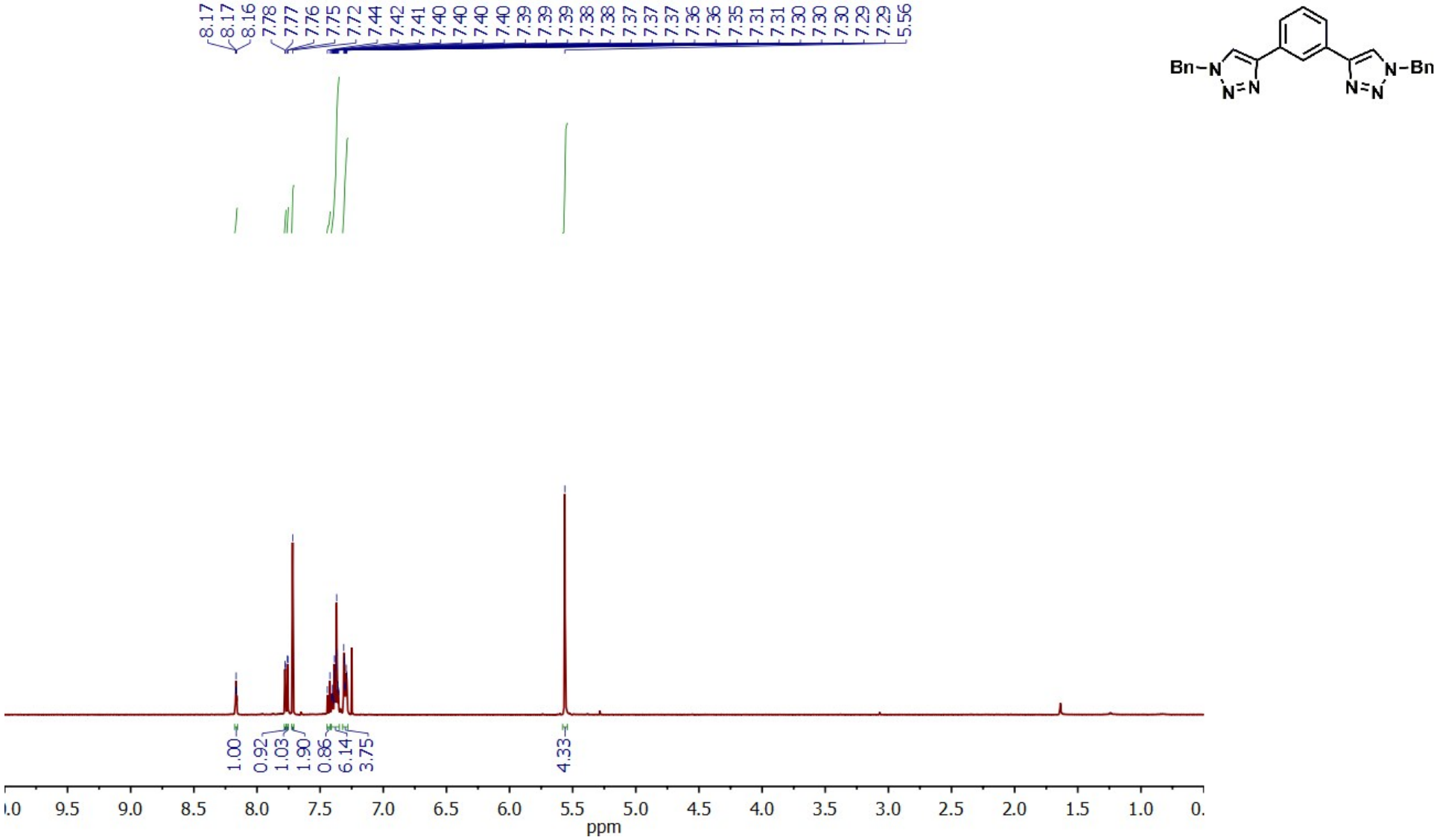


Fig. S 29 ^{1}H NMR spectrum of isolated **T19** in $CDCl_3$.

[1]H spectra of triazole reactions

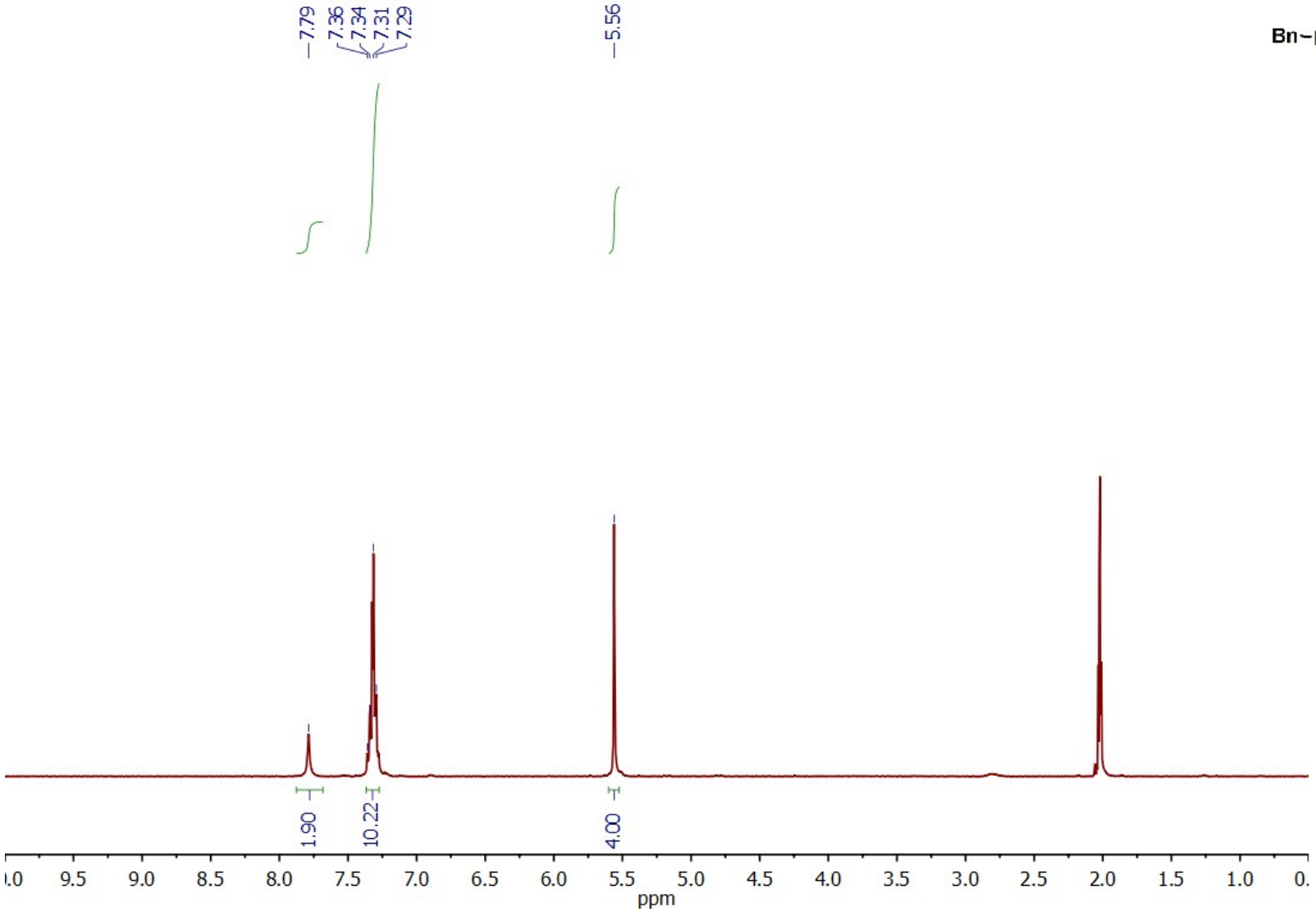


Fig. S 30 [1]H NMR spectrum of isolated **T20** in acetone-d_6 (NH-Peak not observed).

^{1}H spectra of triazole reactions

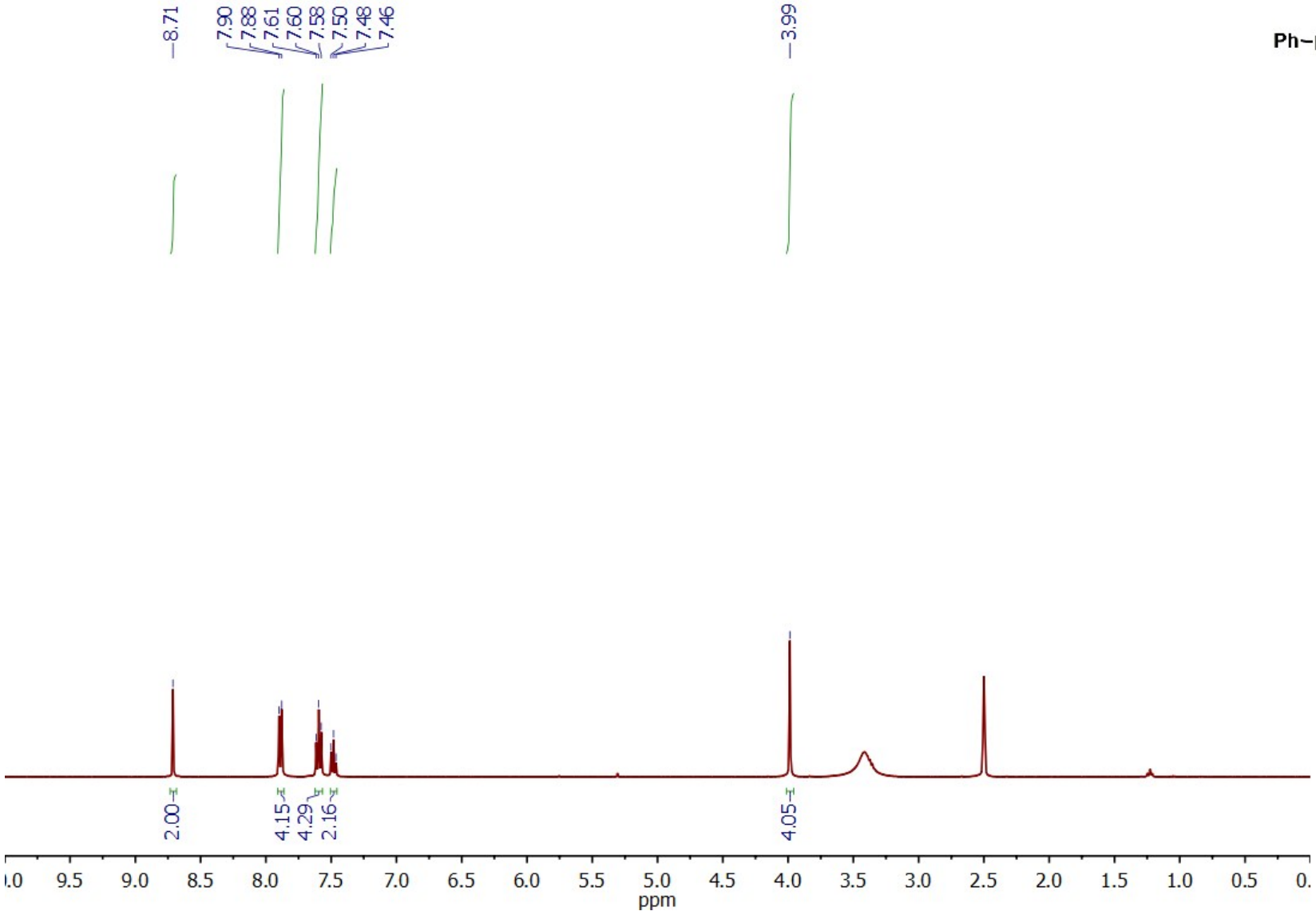


Fig. S 31 ^{1}H NMR spectrum of isolated **T21** in DMSO-d_6.

^{1}H spectra of triazole reactions

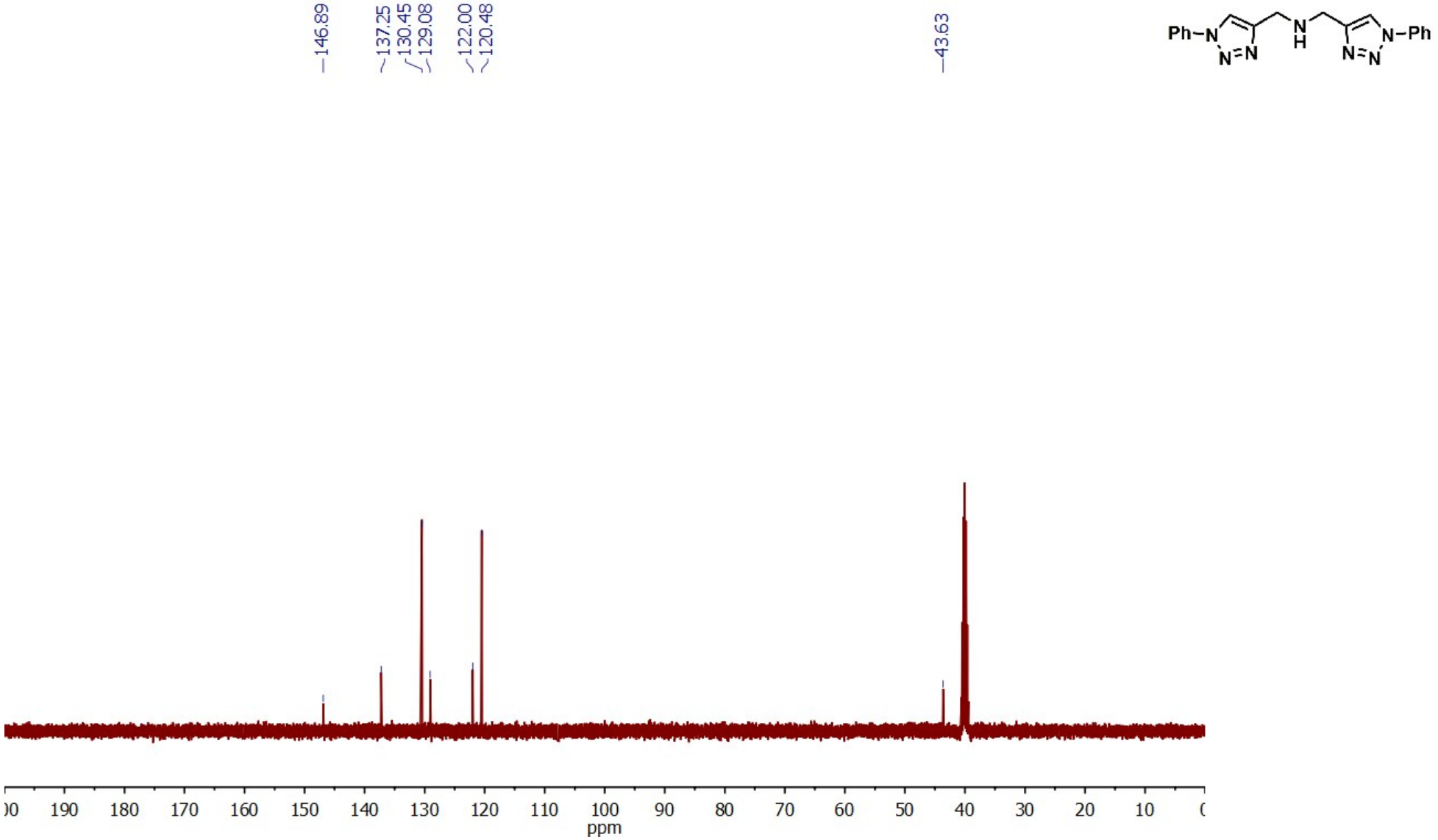


Fig. S 32 ^{13}C NMR spectrum of isolated **T21** in DMSO-d_6.

[1]H spectra of triazole reactions

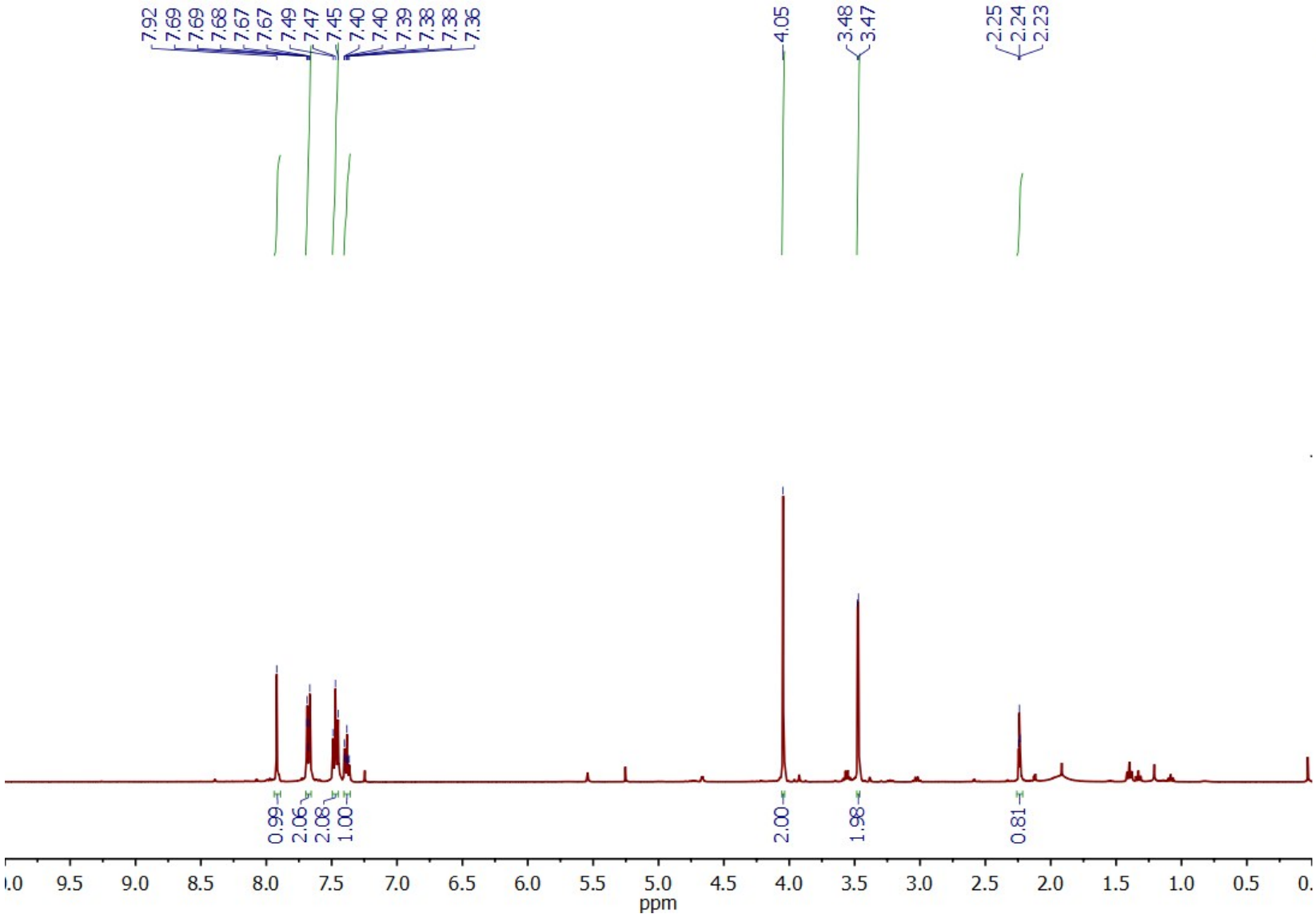


Fig. S 33 [1]H NMR spectrum of isolated **T22** in $CDCl_3$.

Crystallographic Details

Table S1 Crystallographic details for the structures of **$[H_2L^2](BF_4)_2$**, **1** and **3**

	$[H_2L^2](BF_4)_2$	**1 • 2 DCM**	**3 • 1.5 DCM**
Chemical formula	$C_{24}H_{30}N_6\ B_2F_8$	$C_{40}H_{40}N_{12}Cu_2\ 2(BF_4)\ 2(CH_2Cl_2)$	$C_{120}H_{160}N_{24}Cu_4\ 4(BF_4)\ 3(CH_2Cl_2)$
M_r	576.16	1159.39	2794.90
Crystal system	Monoclinic	Monoclinic	Tetragonal
Space group	P2(1)/c	C2/c	P4(3)2(1)2
a (Å)	12.995(4)	21.220(4)	13.543(1)
b (Å)	8.874(3)	13.993(3)	13.543(1)
c (Å)	11.389(3)	17.774(3)	41.646(9)
α (°)	90	90	90
β (°)	91.646(7)	111.151(4)	90
γ (°)	90	90	90
V (Å^3)	1312.8(6)	4922(2)	7639(2)
Z	2	4	2
Densitiy (g cm^{-3})	1.458	1.565	1.215
F(000)	596	2352	2908
Radiation Type	MoK_α	MoK_α	MoK_α
μ (mm^{-1})	0.128	1.158	0.723
Crystal size	0.20 x 0.19 x 0.04	0.41 x 0.19 x 0.12	0.35 x 0.32 x 0.27
Meas. Refl.	9409	24229	61580
Indep. Refl.	2301	5627	6766
Obsvd. [$I > 2\sigma(I)$] refl.	1633	4796	5893
R_{int}	0.0462	0.0215	0.489
R [$F^2 > 2\sigma(F^2)$], wR(F^2), S	0.0556, 0.1892, 1.071	0.0264, 0.0673, 1.034	0.0900, 0.2475, 1.084
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.733, -0.426	0.450, -0.297	1.289, -0.583

Crystallographic Details

Table S2 Selected bond lengths (Å) and angles (°) and tilt angles (°) for **$[H_2L^2](BF_4)_2$**, **1** and **3**

Atoms	$[H_2L^2](BF_4)_2$	1 • 2 DCM	3 • 1.5 DCM
Bond lengths			
Cu1-Cu1 (or Cu1-Cu2)	-	2.796(1)	2.882(2)
Cu1-C1	-	1.902(2)	1.900(9)
Cu1-C2	-	1.904(2)	-
Cu2-C2	-	-	1.859(9)
C1-C3	1.369(5)	1.396(2)	1.38(1)
C2-C4	-	1.388(2)	1.41(1)
C3-C4, (or C3-C3; C4-C4)	1.452(6)	1.458(3)	1.47(1)
		1.461(3)	
C3-N1	1.362(4)	1.366(2)	1.37(1)
N1-N3	1.313(4)	1.324(2)	1.32(1)
N3-N5	1.324(4)	1.333(2)	1.31(1)
N2-N4	-	1.320(2)	1.31(1)
N4-N6	-	1.330(2)	1.34(1)
N1-C29	1.459(4)	1.464(2)	1.46(2)
N2-C30	-	1.467(2)	1.45(2)
Angles			
C1-Cu-C2	-	175.2(1)	178.8(4)
(or C1-Cu-C1; C2-Cu-C2)			179.0(5)
N5-C1-C3	105.8(3)	101.5(1)	102.7(8)
N6-C2-C4	-	101.5(1)	102.3(8)
Dihedral Angles			
Triazole	0.0	48.0(1) / 44.5(1)	43.5(4)
Triazole-R_1	67.1(1)	-	81.4(4)
Triazole-R_2	-	-	84.3(3)

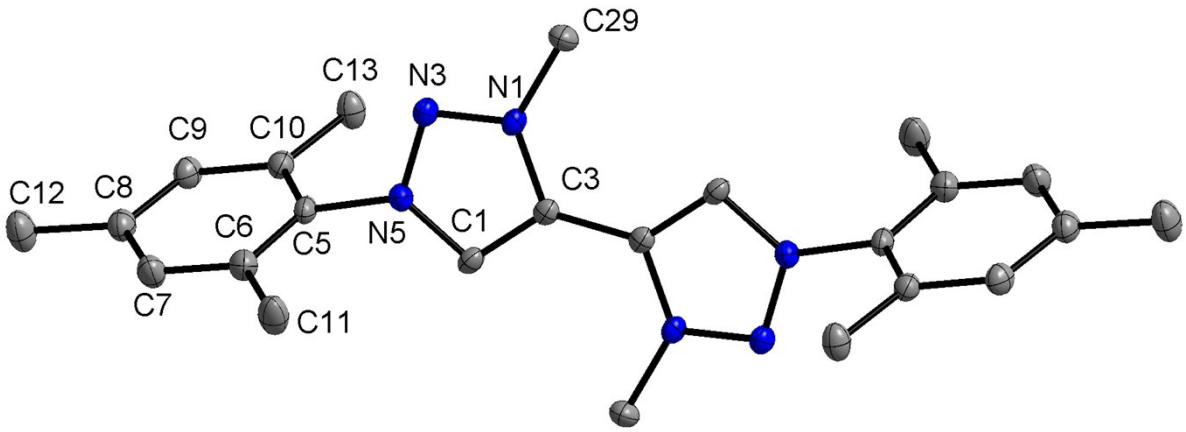


Fig. S 34 ORTEP plot of **$[H_2L^2](BF4)_2$.** Hydrogen atoms and counter ions are omitted for clarity. Thermal ellipsoids are shown at a probability level of 50%.

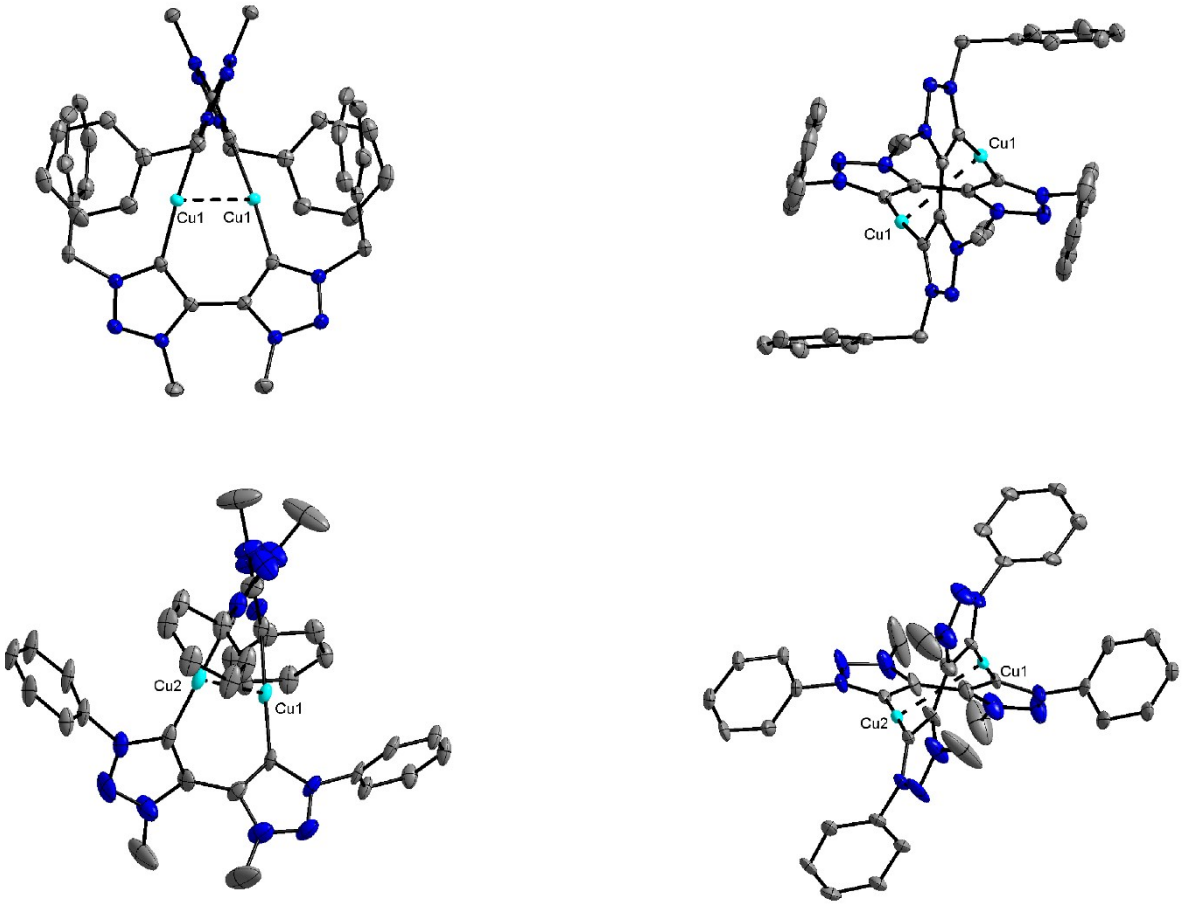


Fig. S 35 ORTEP plots of **1** (top) and **3** (bottom) from different points of view. Hydrogen atoms, solvent molecules and counter ions are omitted for clarity. In **3** the ^{i}Pr groups are also omitted for clarity.

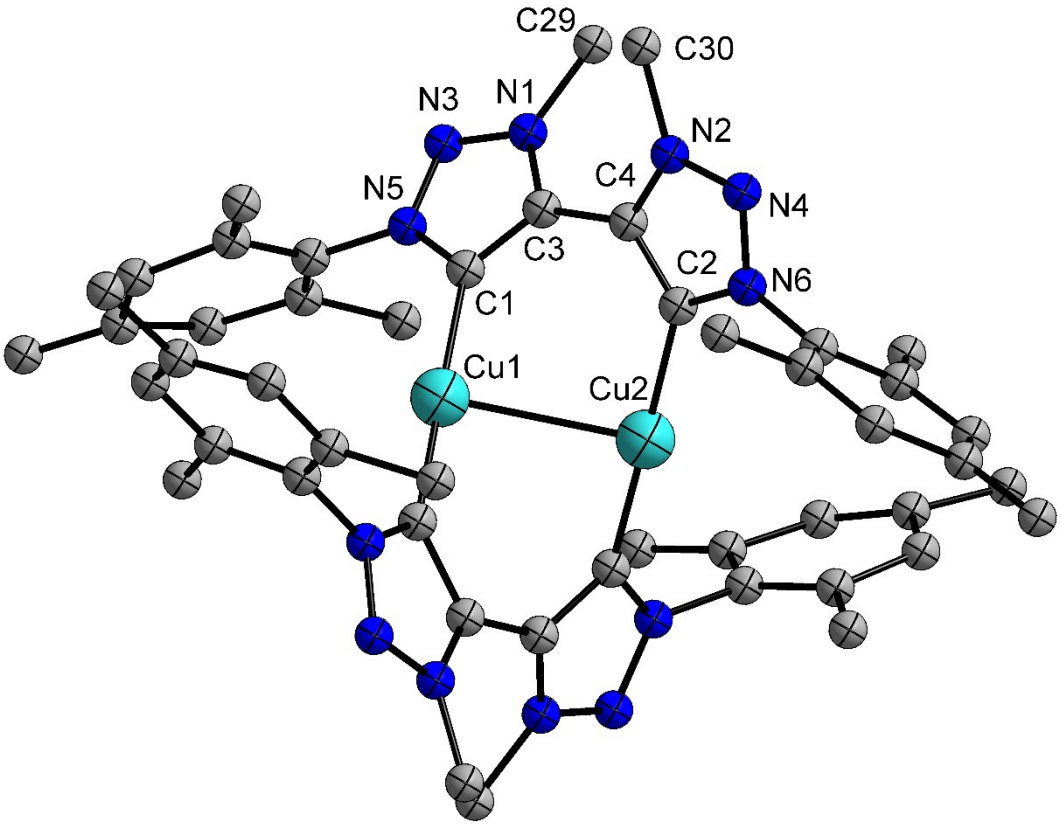


Fig. S 36 Ball and stick model of **2**. Hydrogen atoms, solvent molecules and counter ions are omitted for clarity.

Catalysis

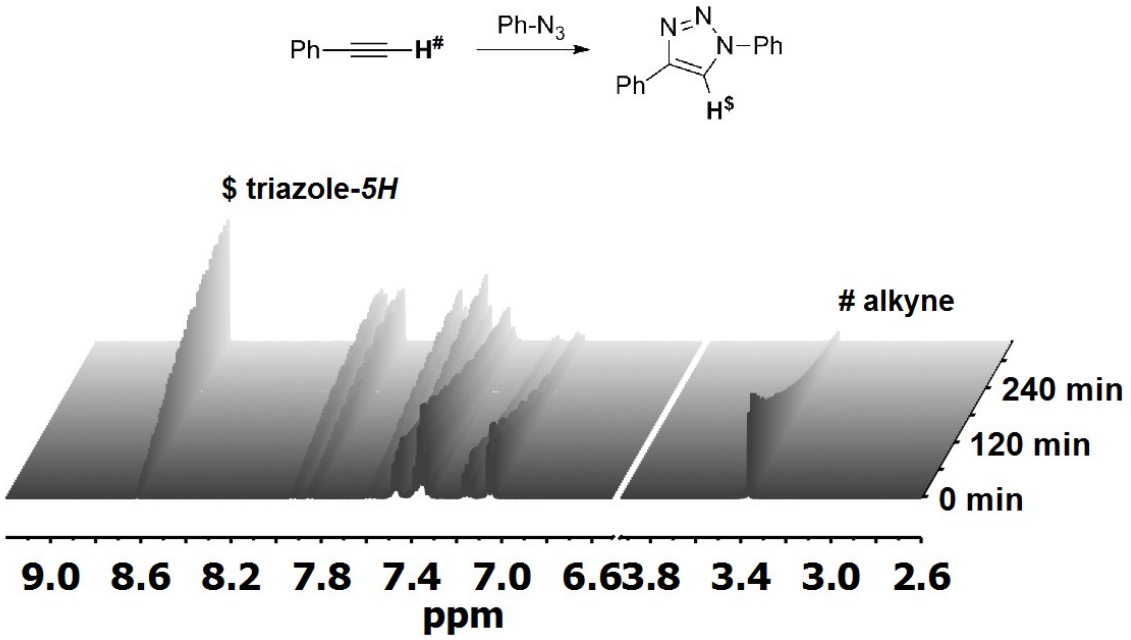


Fig. S 37 Stacked time-dependent ^{1}H NMR spectra of the reaction between phenyl azide and phenylacetylene from one of the kinetic experiments in CD_3CN.

Catalysis

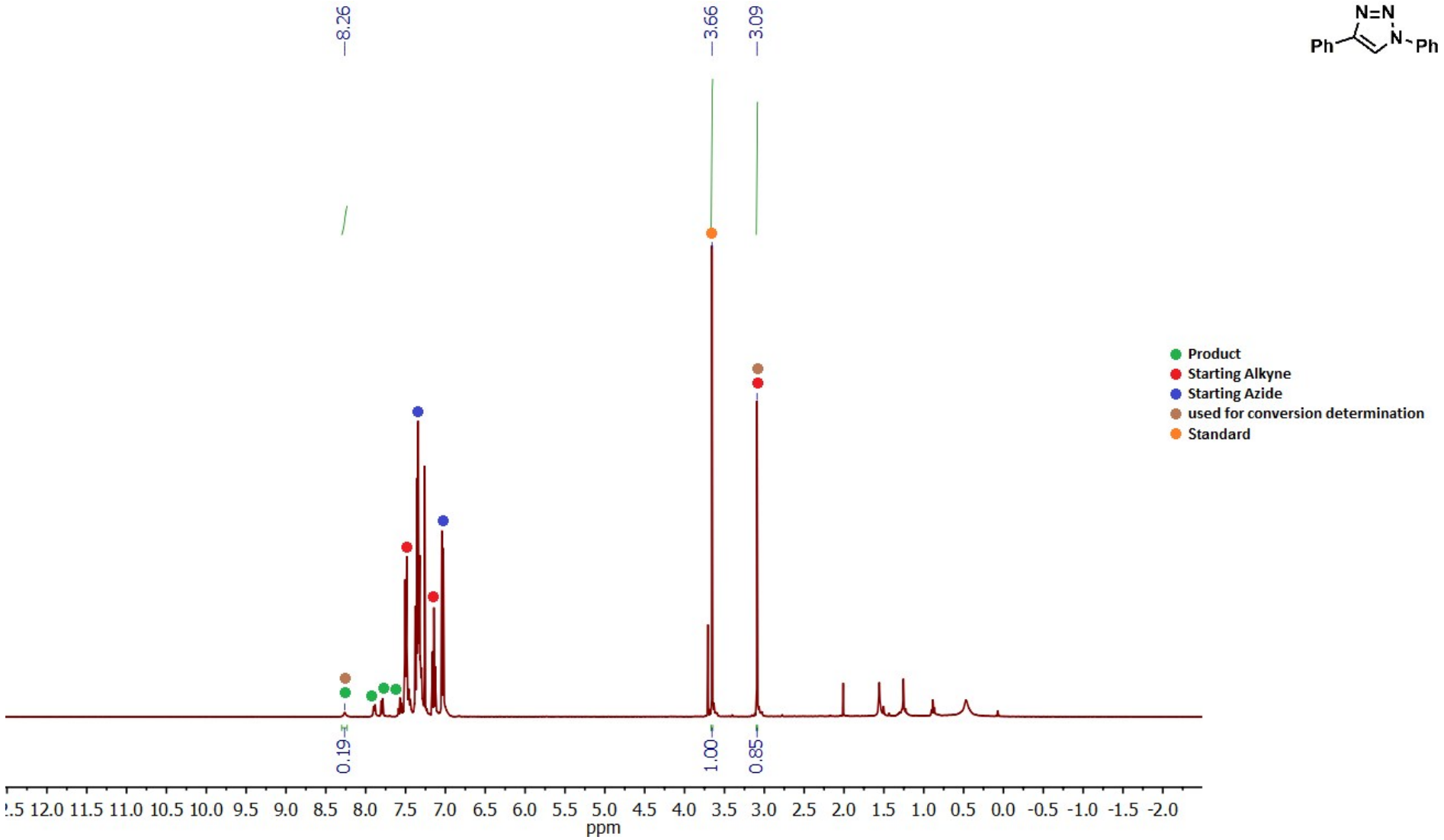


Fig. S 38 Crude NMR spectrum of the reaction between phenylacetylene and phenyl azide to give **T1** after 135 min. Catalyst: $[Cu(MeCN)_4][BF_4]$ 0.5 mol%.

Catalysis

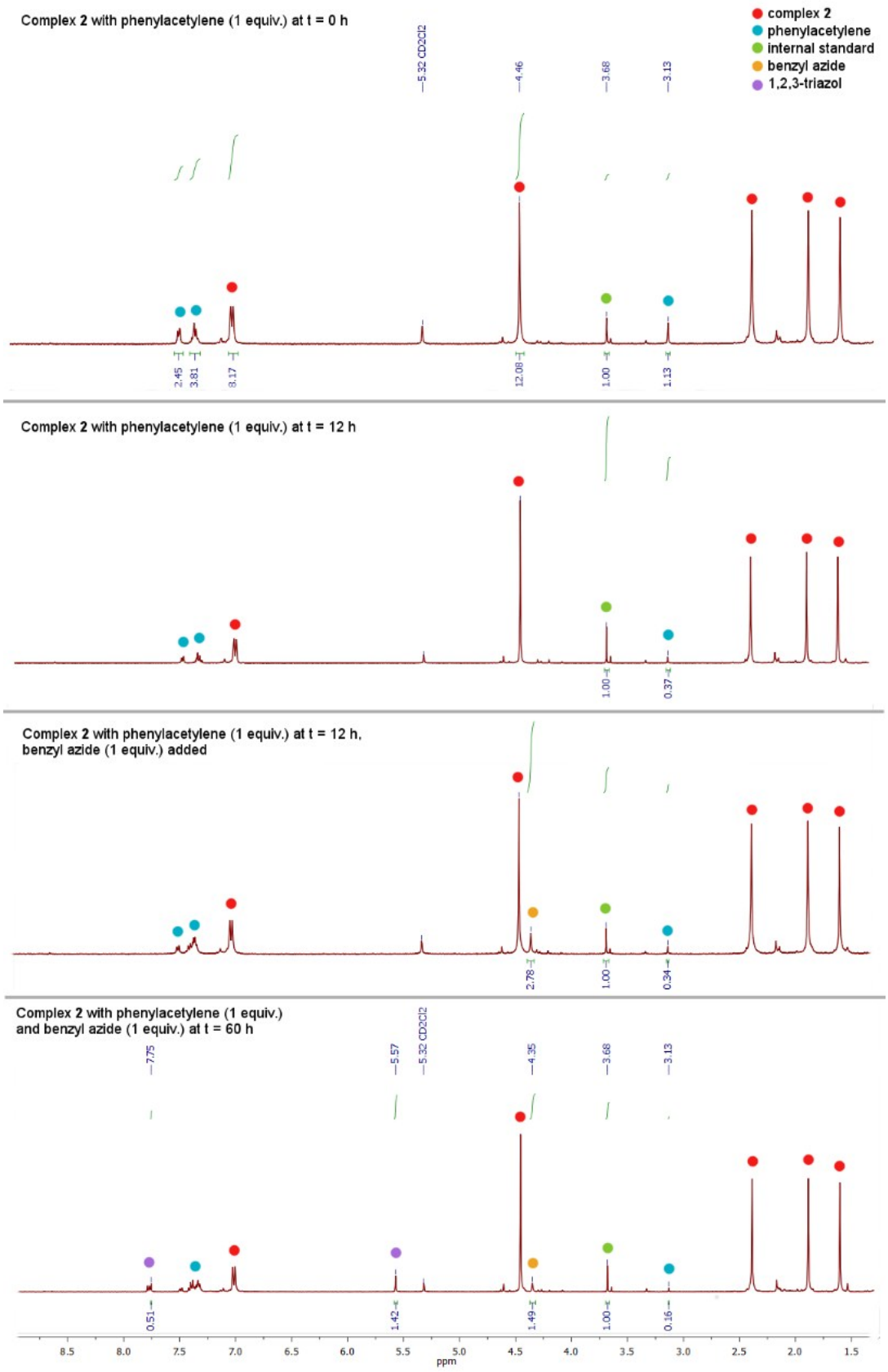


Fig. S 39 ^{1}H NMR spectra of reaction monitoring of complex **2**, phenylacetylene and benzyl azide in DCM-d_2 with 1,2-dibromoethane as internal standard.

Catalysis

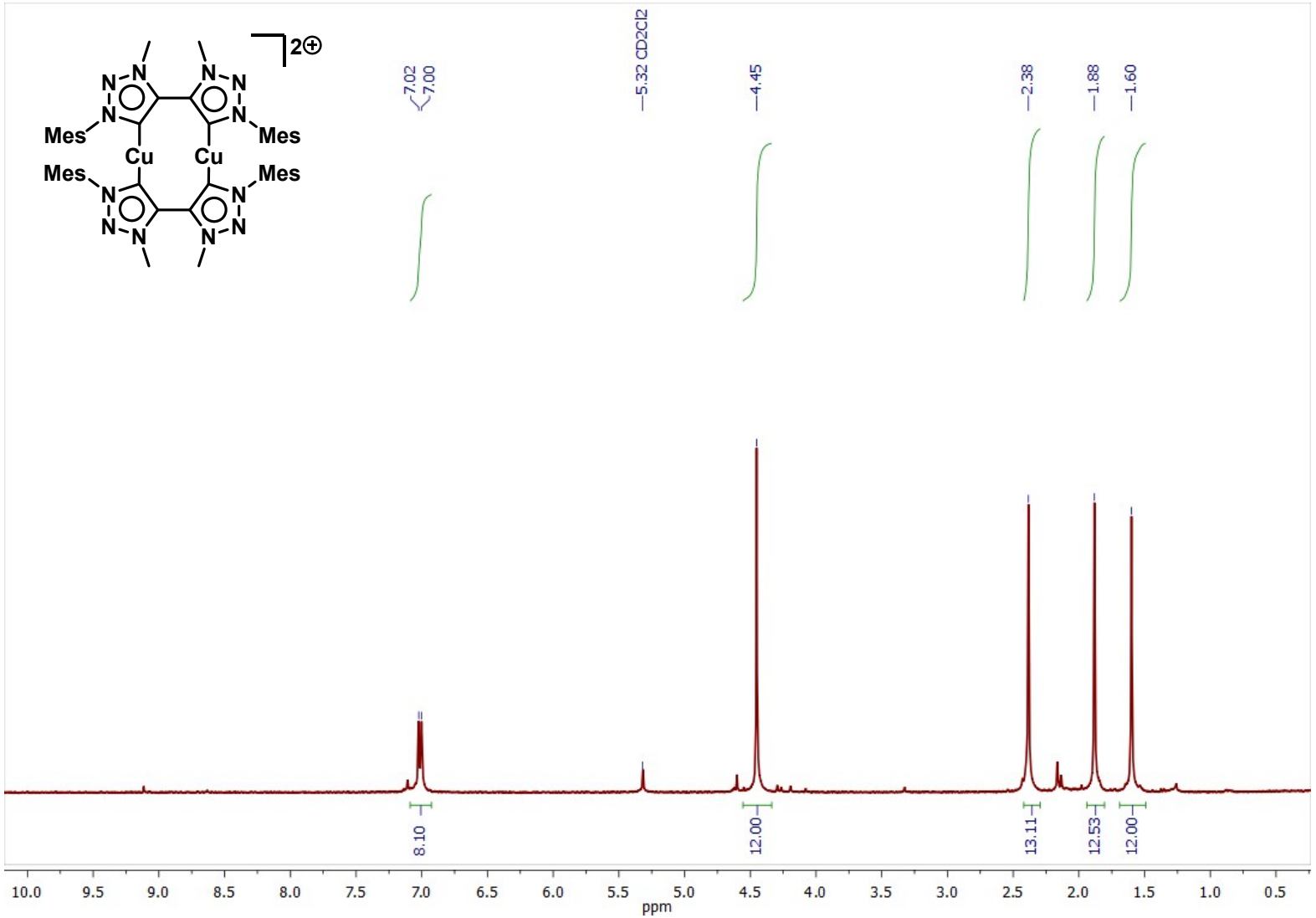


Fig. S 40 ^{1}H NMR spectrum of **2** in DCM-d_2 for comparison in NMR experiment.