Supporting Information

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Investigation of the copper(I) catalysed azide-alkyne cycloaddition reactions (CuAAC) in molten PEG_{2000}

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Results of the CuAAC between azides **1** and **2** and alkynes **3b-d**

The reactions involving **3c** required more diluted conditions since using 0.3 g PEG_{2000} per mmol of substrate gave a very viscous reacting mixture and, under these conditions, the conversion did not exceed 90%, even after a prolonged reaction time (12 h), either with 3-azidopropanol (**1**) or its acetate derivatives **2**. Using 0.4 g PEG_{2000} per mmol allowed complete conversions with all catalysts and the isolated yields were between 91 and 97% (Table).

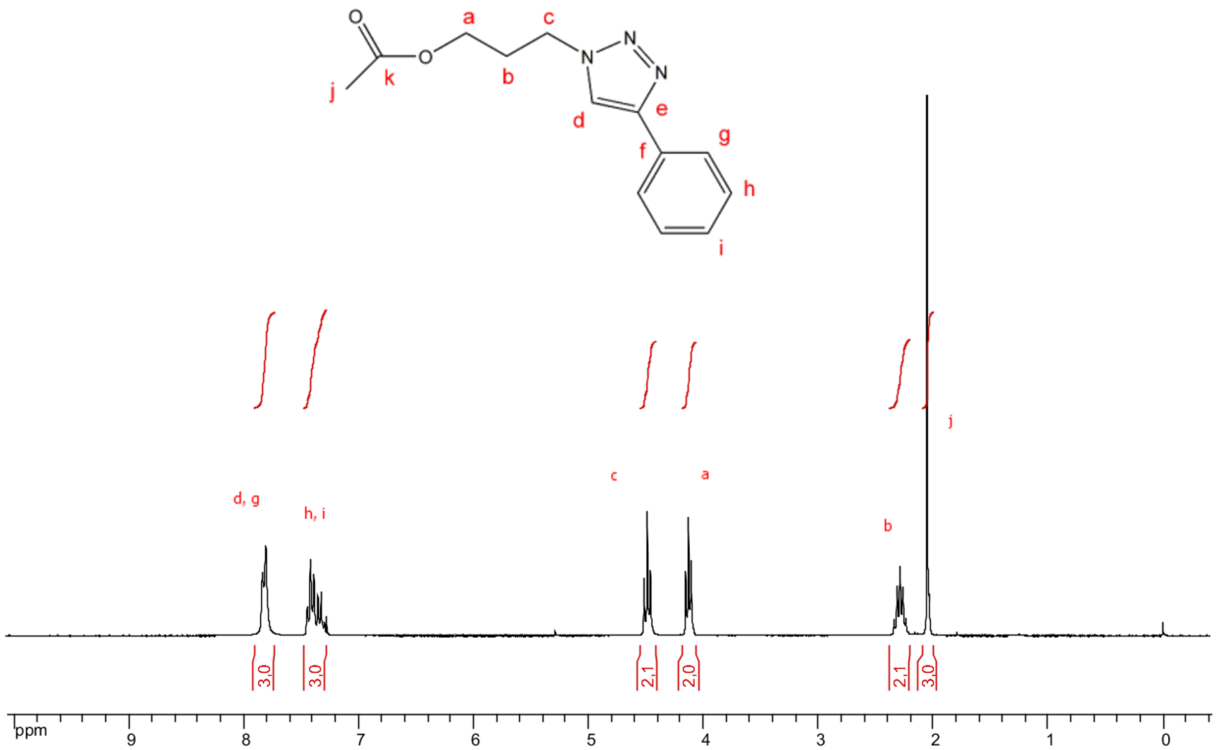
Yields[a] for the CuAAC between azides **1** and **2** and alkynes **3b-d** using CuI, Cu nanopowder (CuNP), or Cu turnings (CuT) in PEG_{2000} at 70 °C.

Entry	Azide	Acetylene	Catalyst (wt %)	Time (h)	Product	Yield (%)
1	**1**	**3b**	CuI (1%)	2	**4b**	96
2			CuNP (1%)	2		97
3			CuT (40%)	8		94
4	**2**		CuI (1%)	4	**5b**	100
5			CuNP (1%)	4		100
6			CuT (40%)	4		100
7	**1**	**3c**[a]	CuI (1%)	2	**4c**[b]	91
8			CuNP (1%)	2		92
9			CuT (40%)	4		93
10	**2**		CuI (1%)	2	**5c**[b]	96
11			CuNP (1%)	6		97
12			CuT (40%)	17		96
13	**1**	**3d**	CuI (1%)	0.5	**4d**	98
14			CuNP (1%)	0.5		97
15			CuT (40%)	6		96
16	**2**		CuI (1%)	0.5	**5d**	97
17			CuNP (1%)	2		96
18			CuT (40%)	4		94

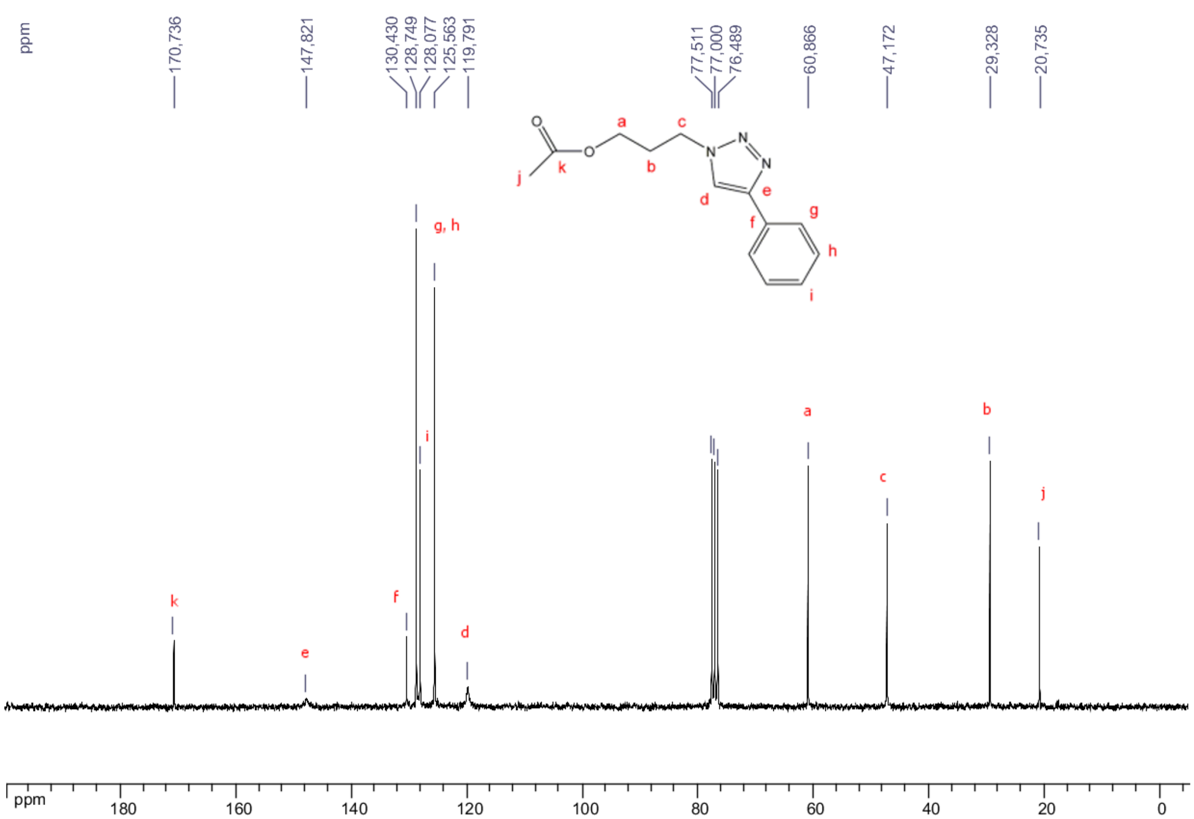
[a] 0.4 g PEG_{2000} per mmol of substrate; [b] EtOH was used instead of CH_2Cl_2 for the workup.

1-(3-Acetoxypropyl)-4-phenyl-1,2,3-triazole (5a)

^{1}H NMR (250 MHz, $CDCl_3$)

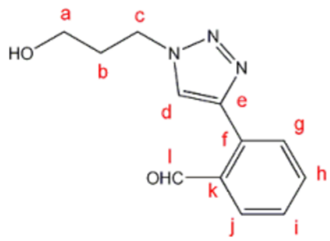


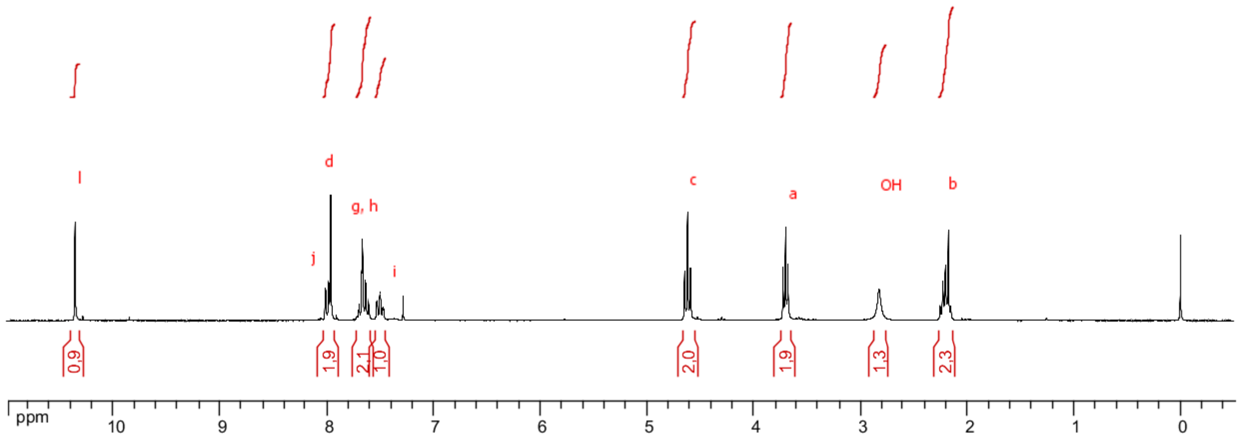
^{13}C NMR (62.9 MHz, $CDCl_3$)



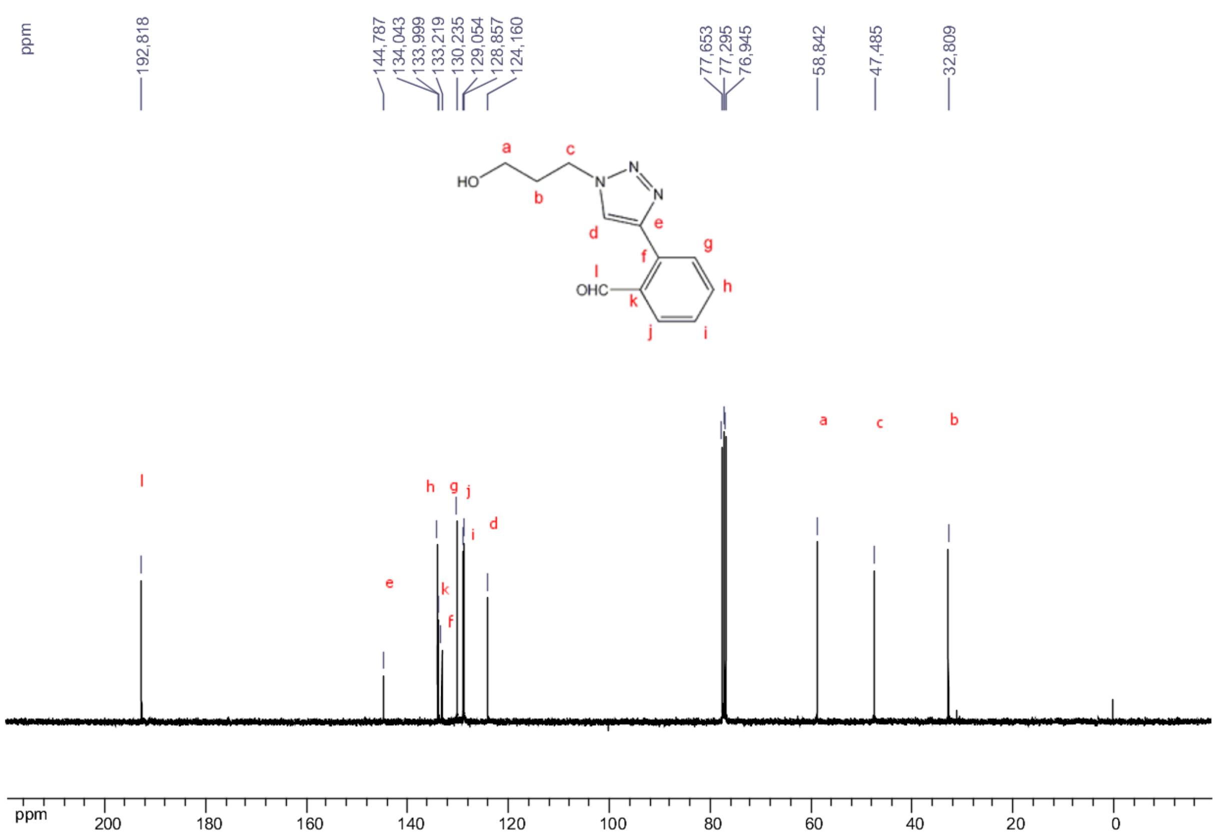
4-(2-Formylphenyl)-1-(3-hydroxypropyl)-1,2,3-triazole (4b)

^{1}H NMR (250 MHz, $CDCl_3$)



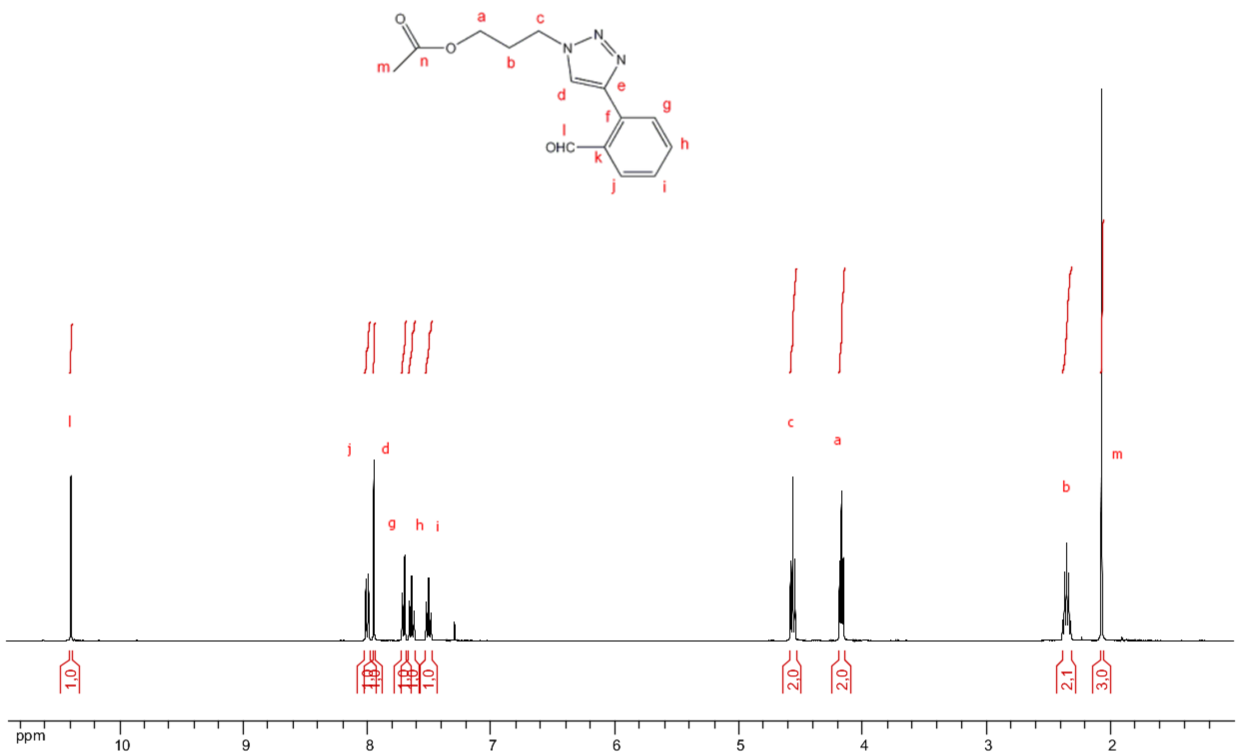


^{13}C NMR (90.6 MHz, $CDCl_3$)

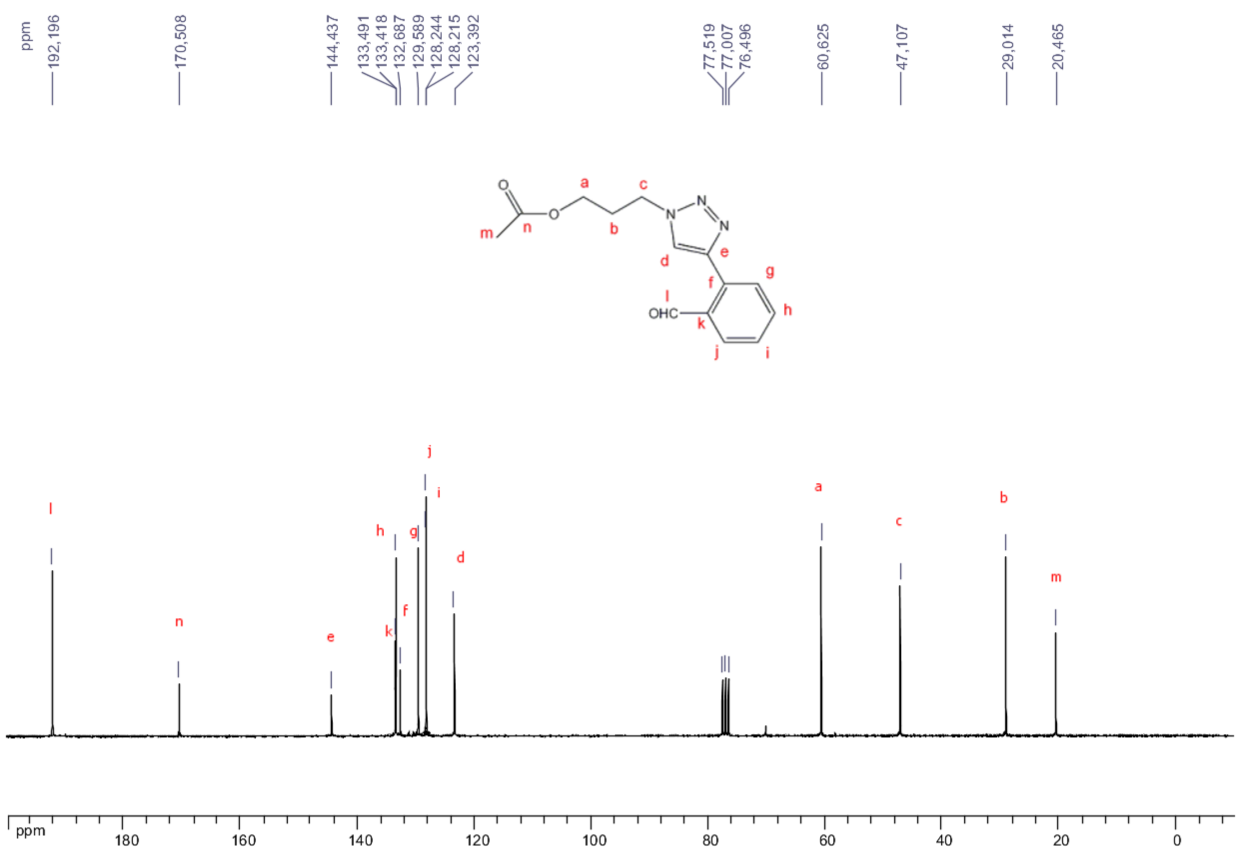


1-(3-Acetoxypropyl)-4-(2-formylphenyl)-1,2,3-triazole (5b)

^{1}H NMR (400 MHz, $CDCl_3$)

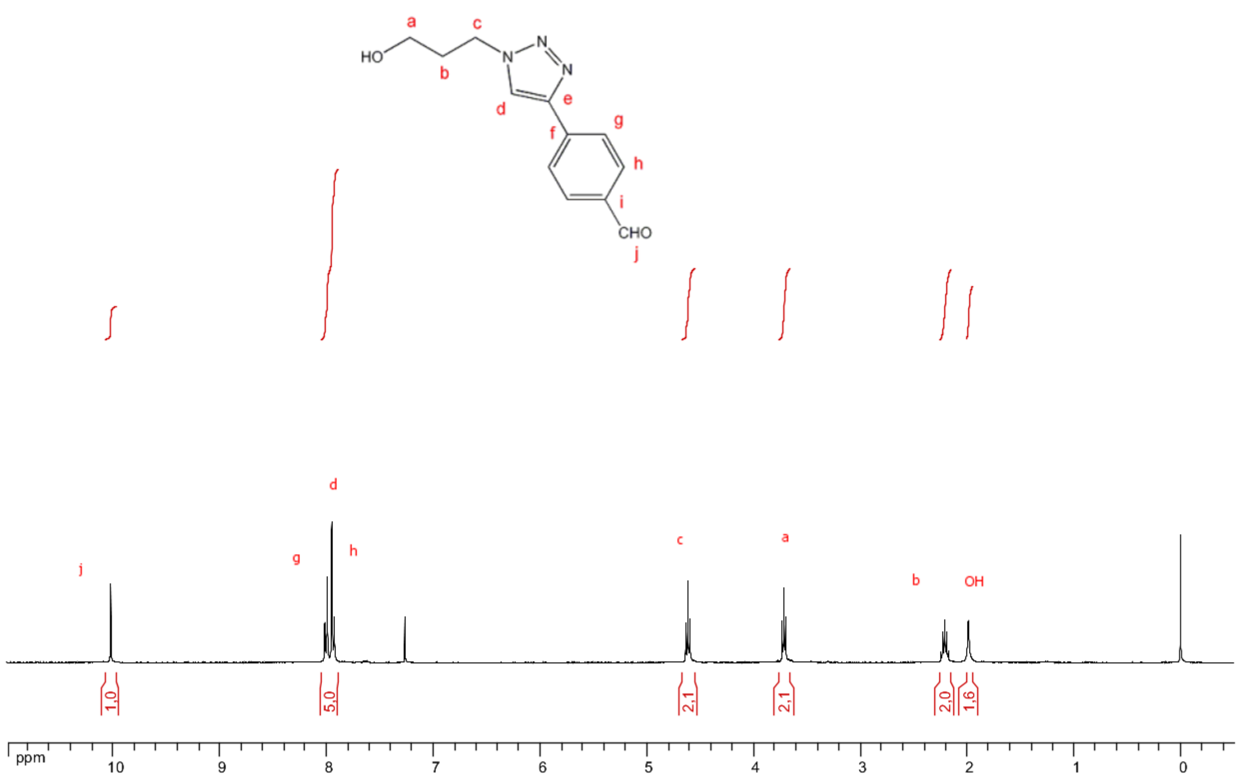


^{13}C NMR (62.9 MHz, $CDCl_3$)

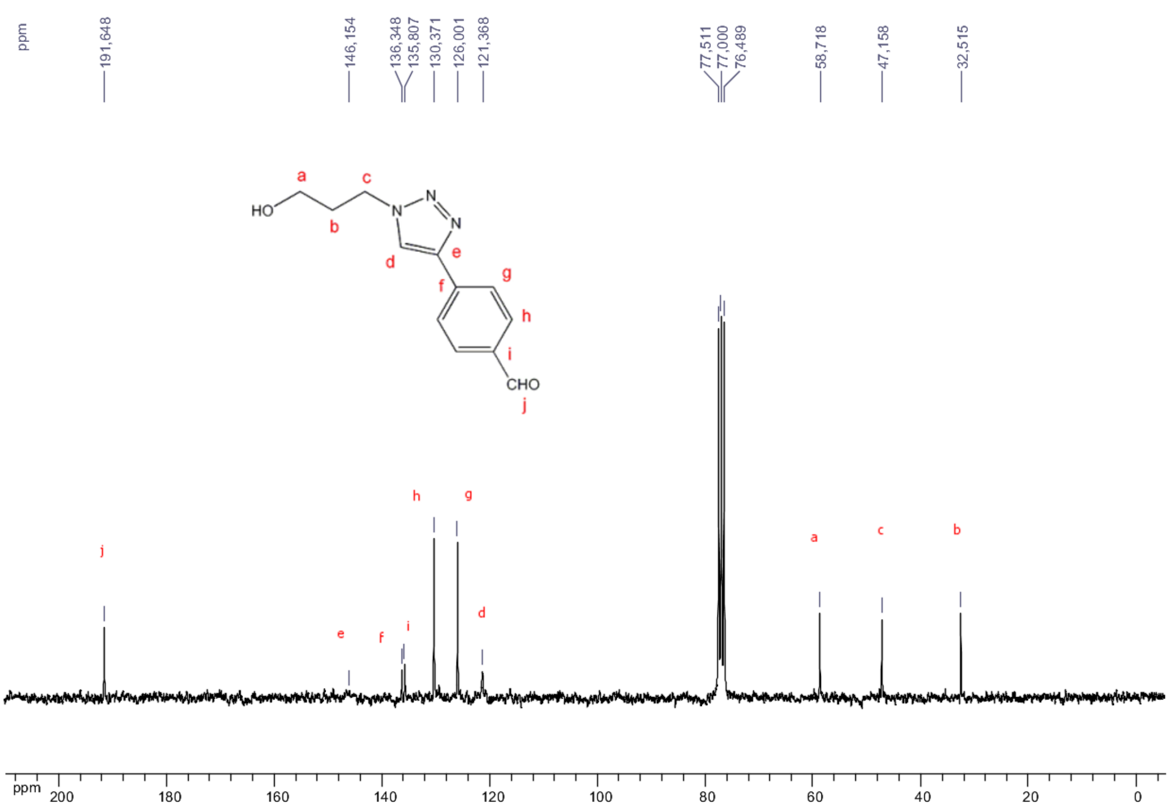


4-(4-Formylphenyl)-1-(3-hydroxypropyl)-1,2,3-triazole (4c)

^{1}H NMR (360 MHz, $CDCl_3$)

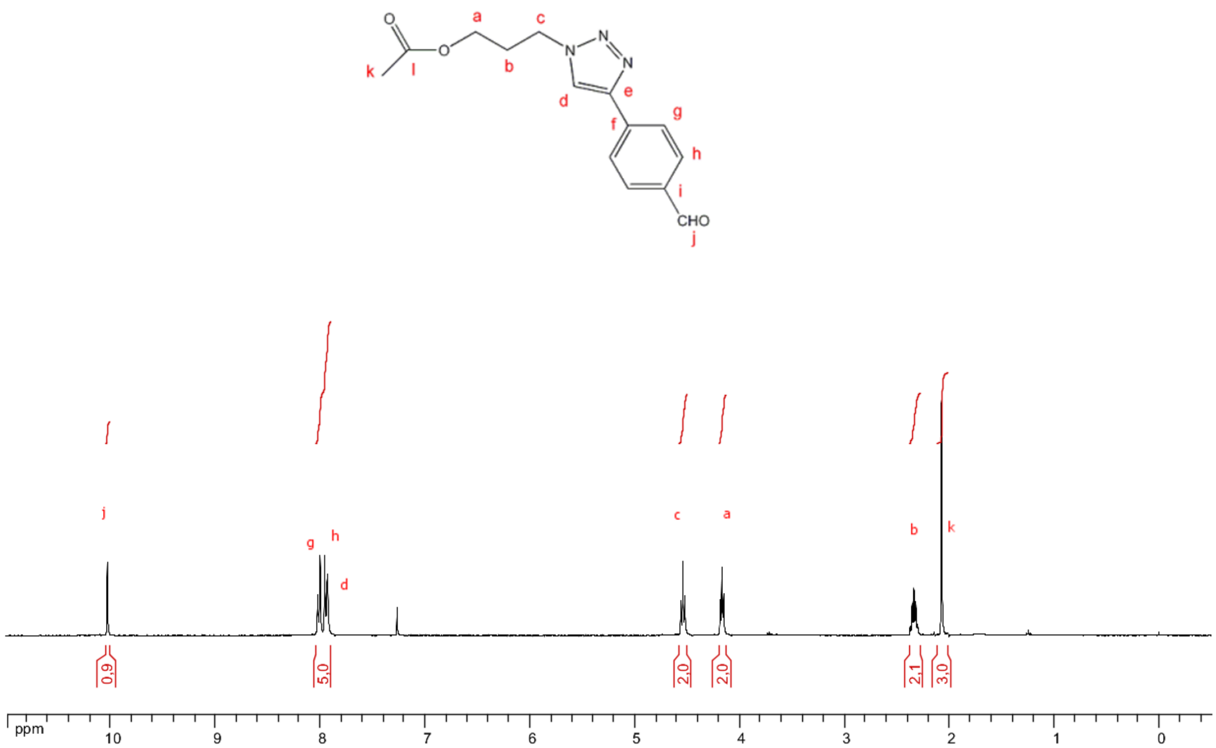


^{13}C NMR (62.9 MHz, $CDCl_3$)

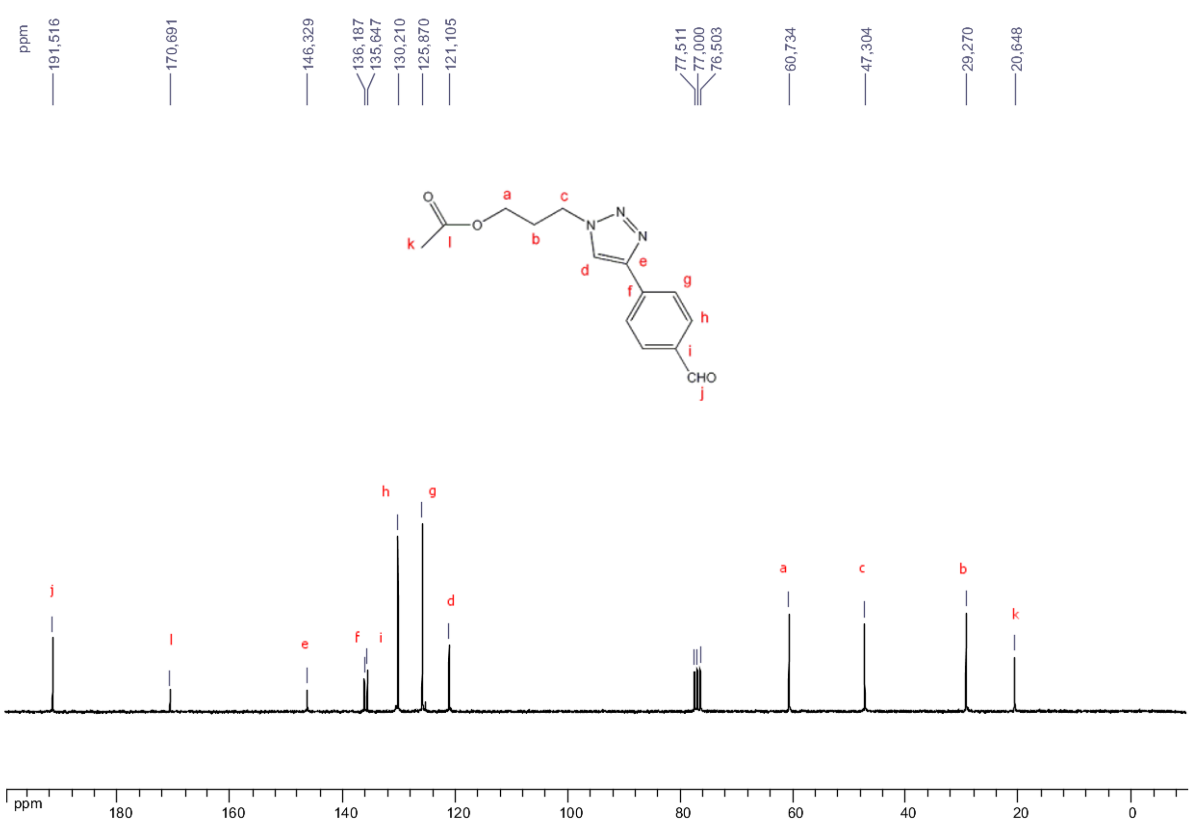


1-(3-Acetoxypropyl)-4-(4-formylphenyl)-1,2,3-triazole (5c)

^{1}H NMR (360 MHz, $CDCl_3$)

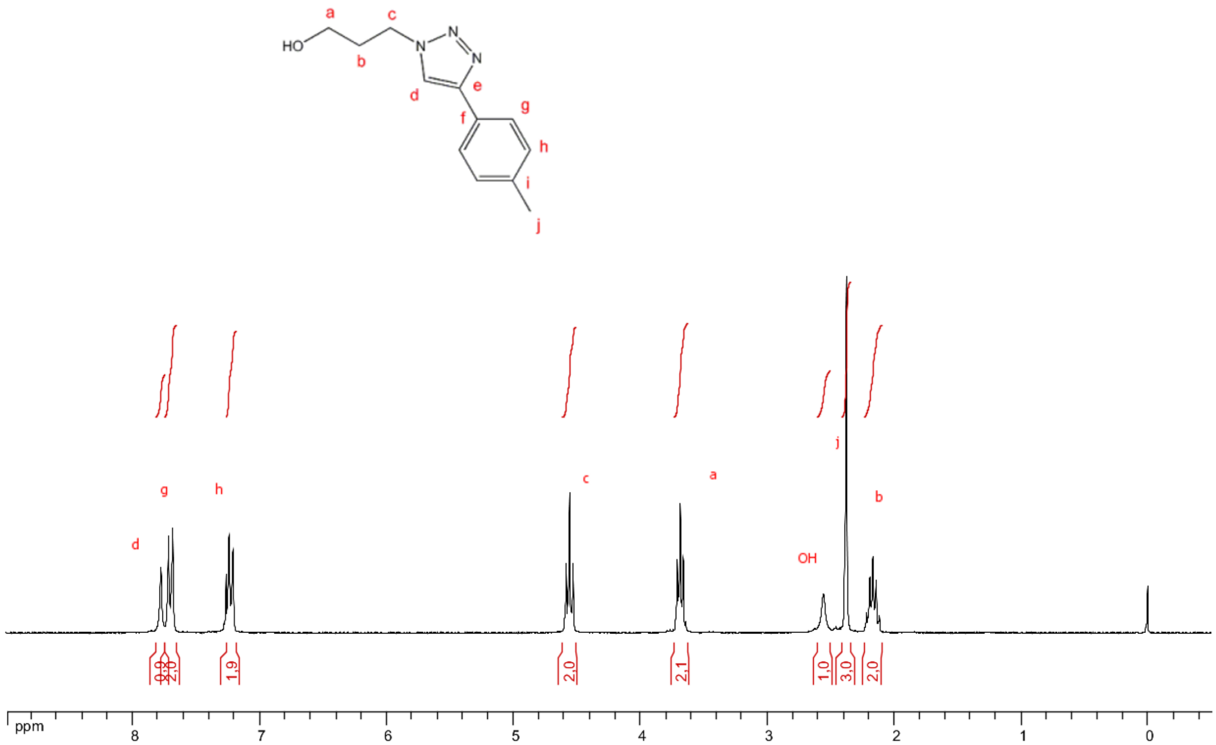


^{13}C NMR (62.9 MHz, $CDCl_3$)

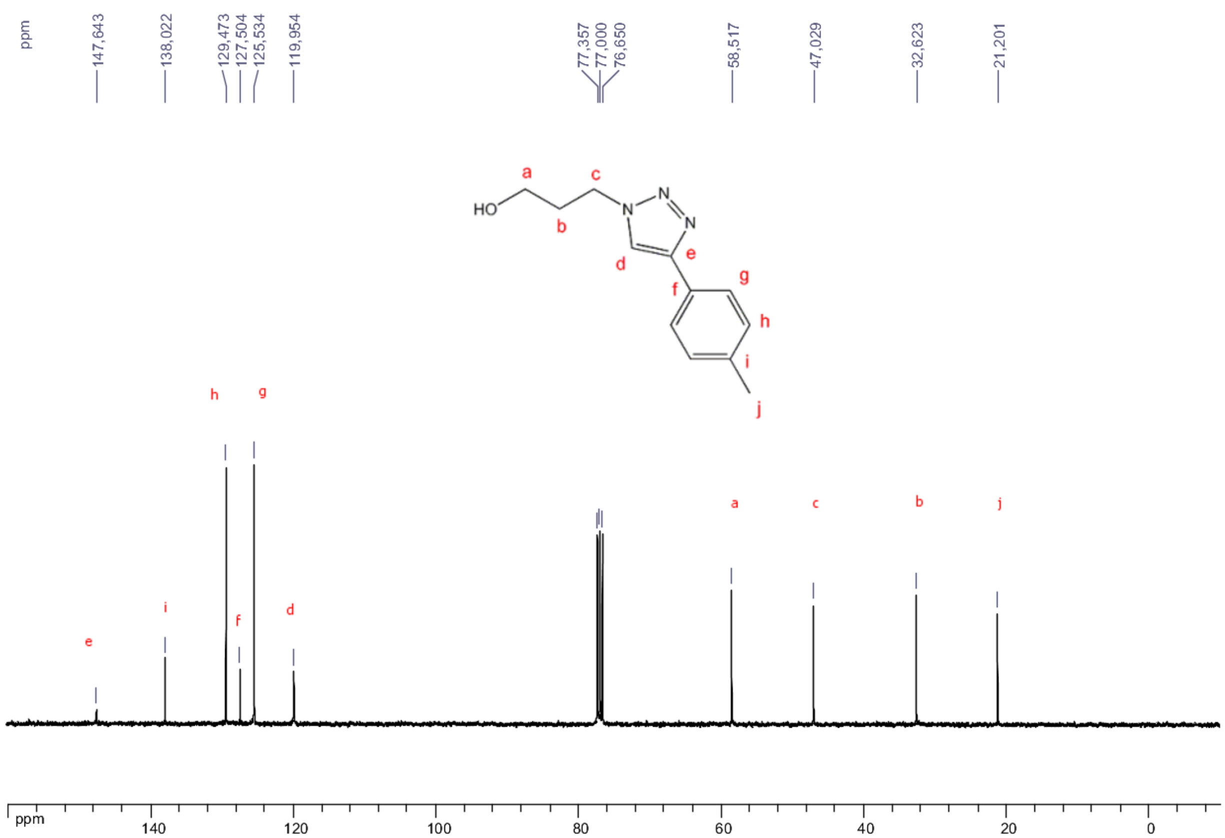


1-(3-Hydroxypropyl)-4-(4-methylphenyl)-1,2,3-triazole (4d)

^{1}H NMR (250 MHz, $CDCl_3$)

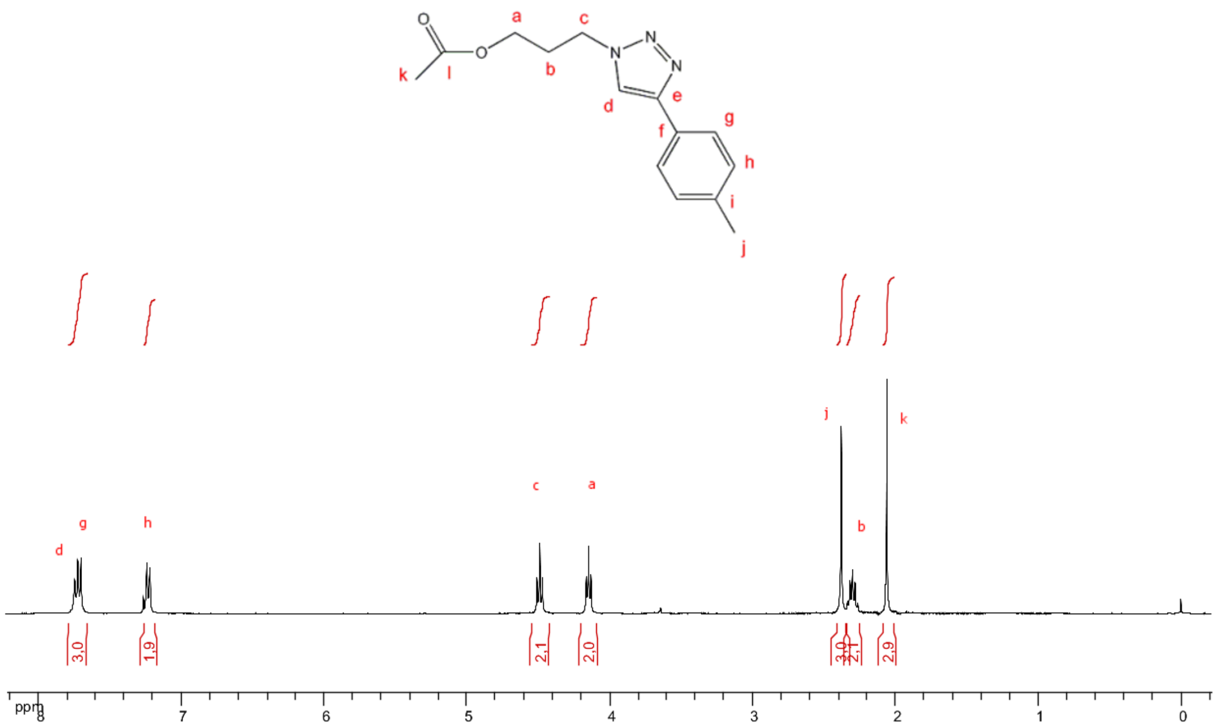


^{13}C NMR (90.6 MHz, $CDCl_3$)

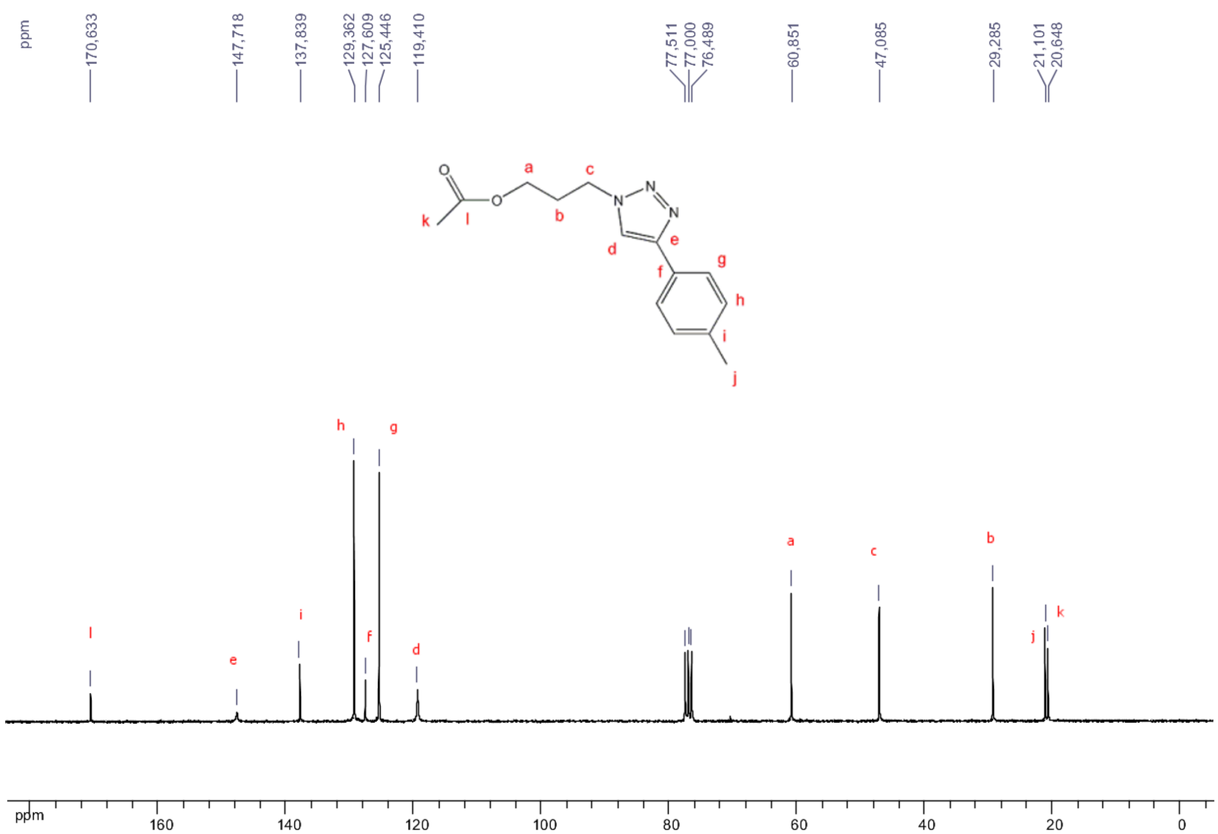


1-(3-Acetoxypropyl)-4-(4-methylphenyl)-1,2,3-triazole (5d)

^{1}H NMR (360 MHz, $CDCl_3$)

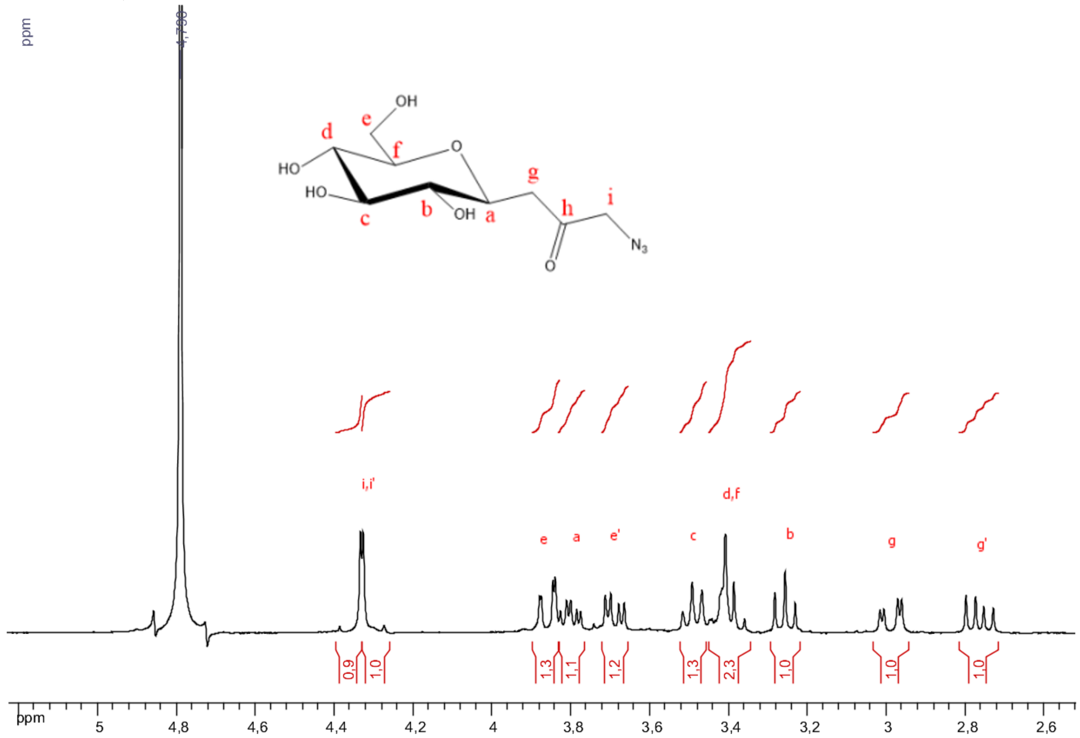


^{13}C NMR (62.9 MHz, $CDCl_3$)

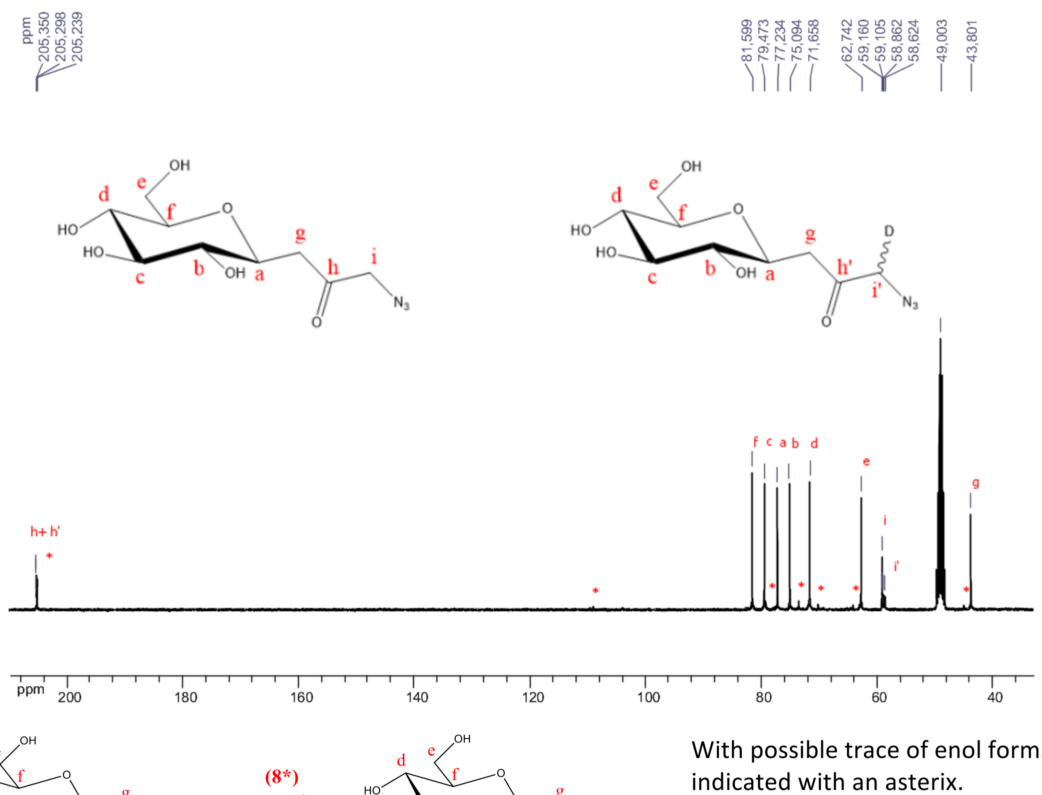


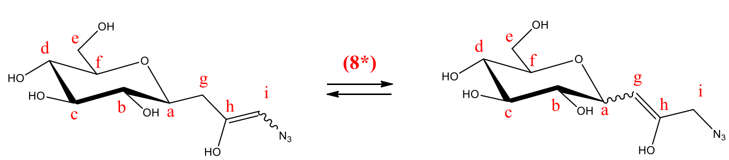
3-Azido-1-(*C*-β-D-glucopyranosyl)-propan-2-one (8)

^{1}H NMR (360 MHz, D_2O)



^{13}C NMR (90.6 MHz, CD_3OD)

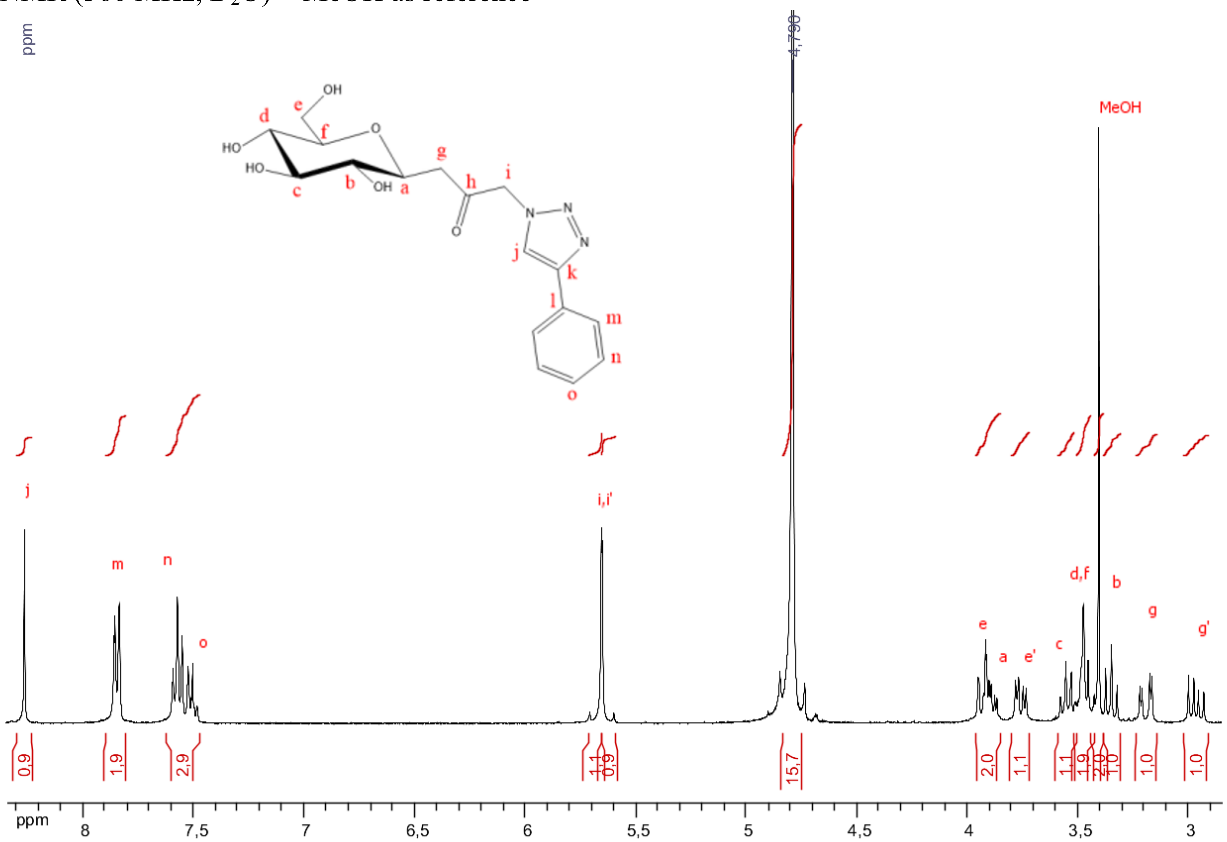




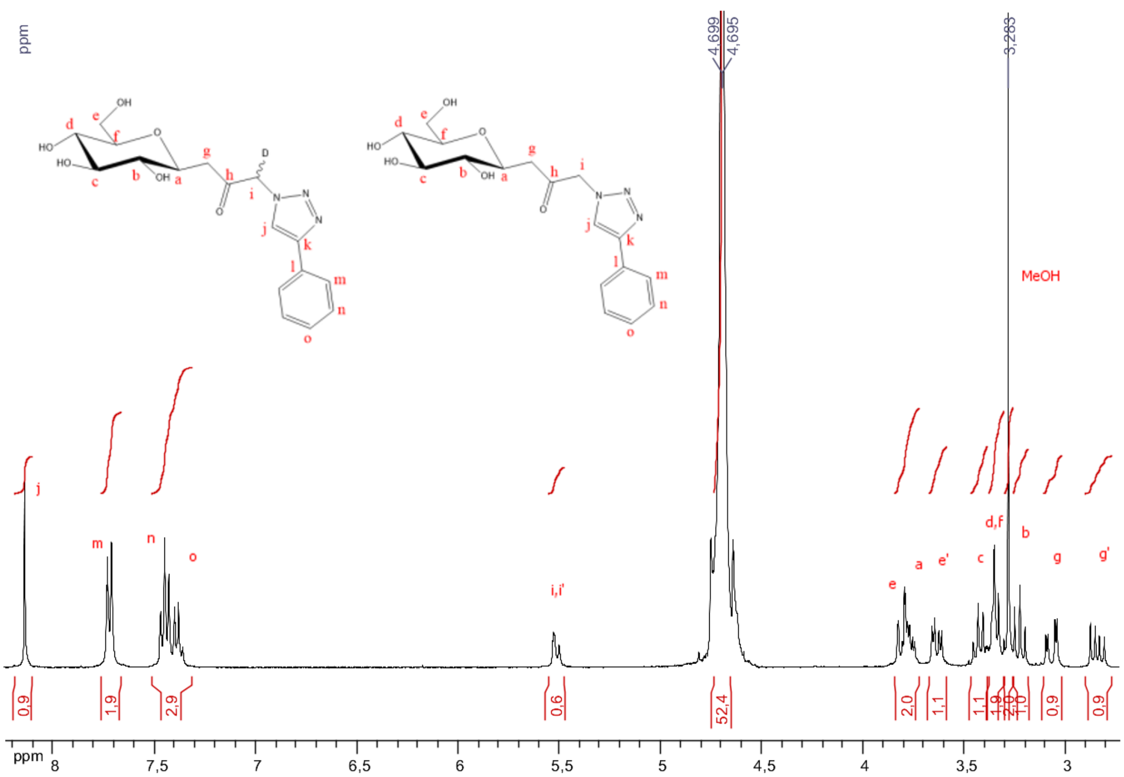
With possible trace of enol forms, indicated with an asterix.

1-(1-(*C*-β-D-glucopyranosyl)-2-oxo-propyl)-4-phenyl-1,2,3-triazole (9)

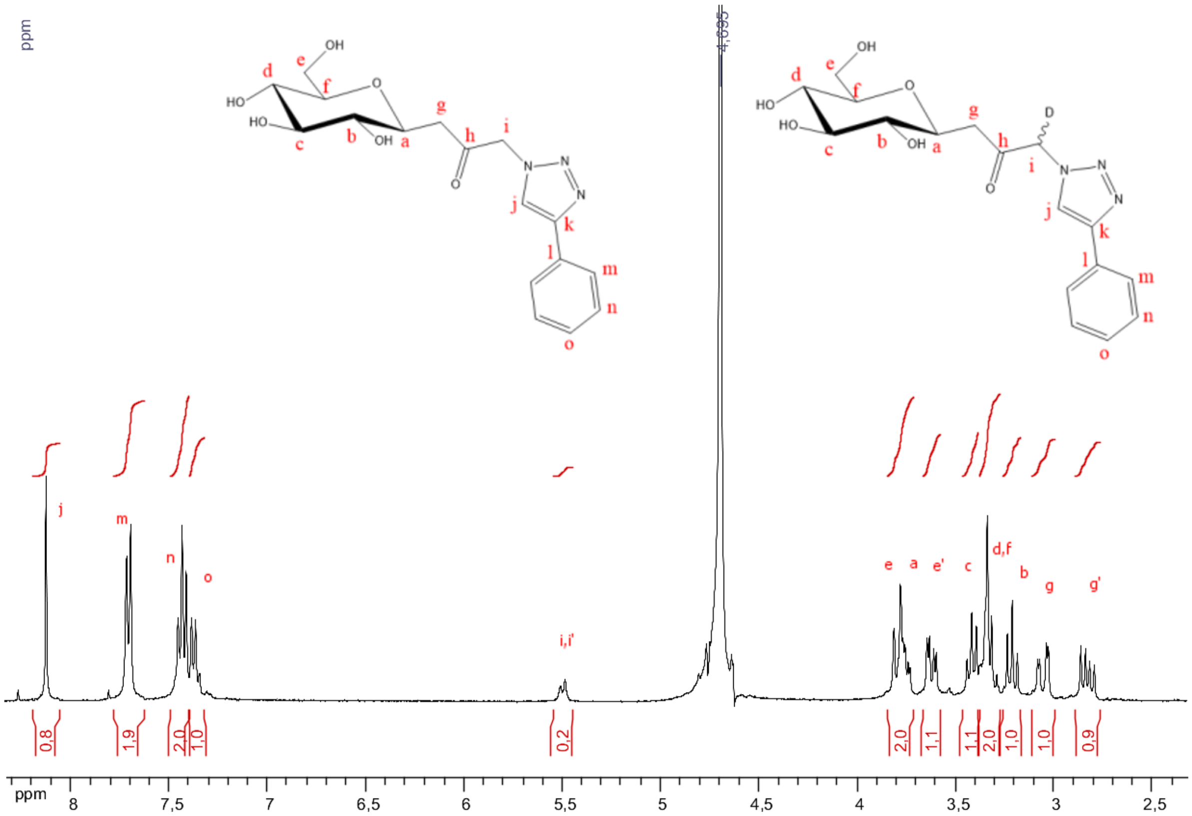
^{1}H NMR (360 MHz, D_2O) + MeOH as reference



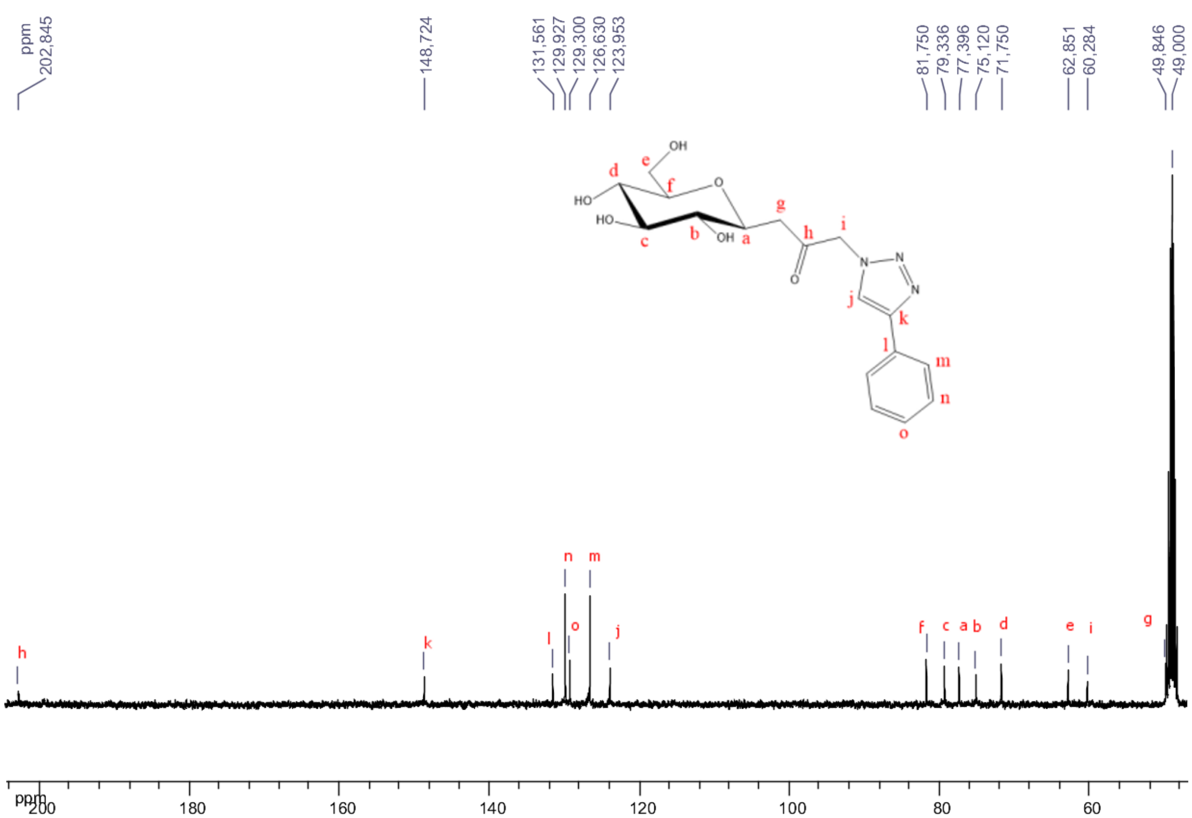
^{1}H NMR (360 MHz, D_2O), with exchange H/D at position i,i' (MeOH as reference)



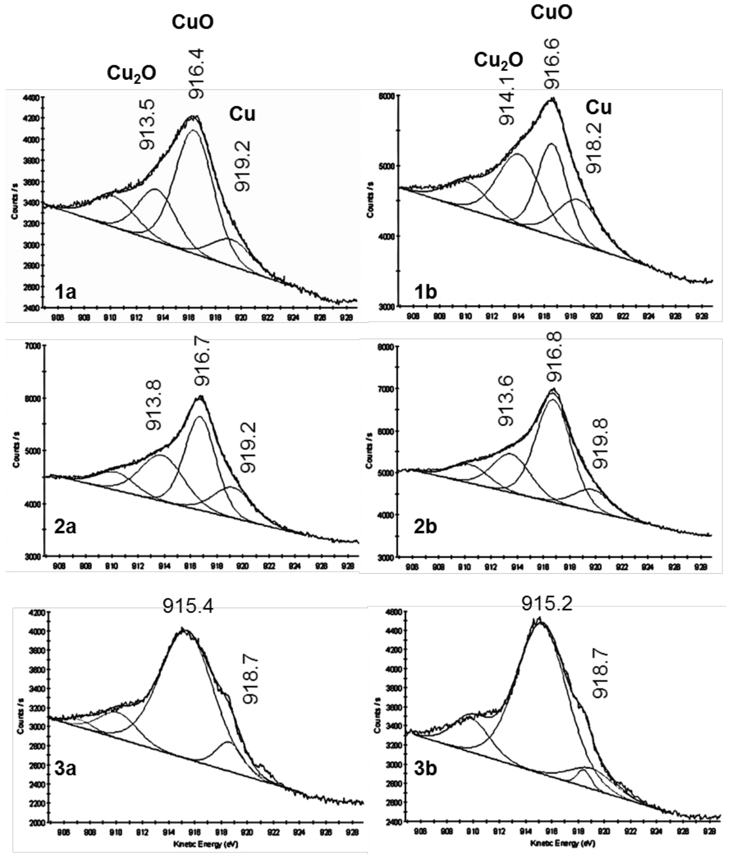
^{1}H NMR (360 MHz, D_2O) with exchange H/D at position i,i'



^{13}C NMR (90.6 MHz, CD_3OD)

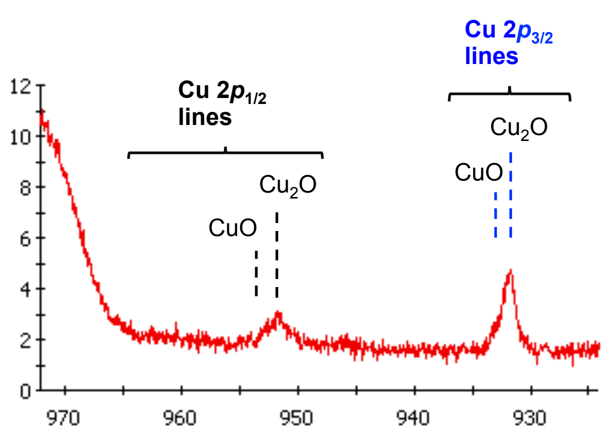


Auger kinetic energies (Cu $L_3M_{45}M_{45}$)



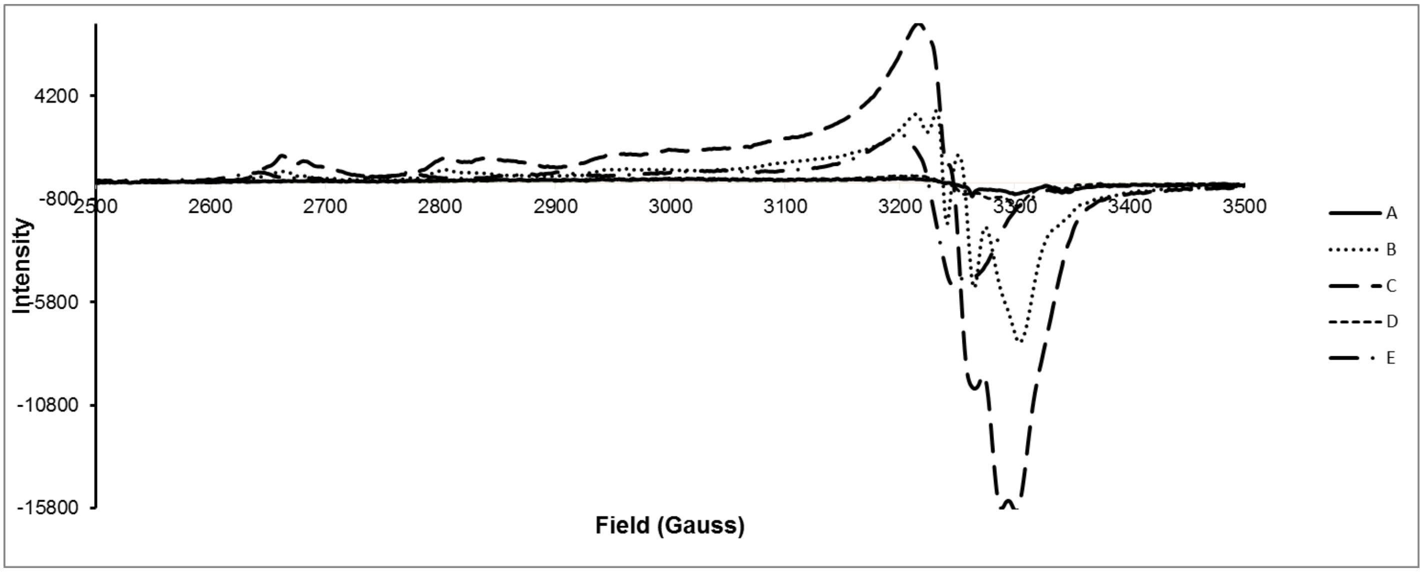
1 a and **b**: Matte and glossy surfaces of copper turnings before reaction ; **2 a** and **b**: Matte and glossy surfaces after reaction in the presence of azide **1** ; **3 a** and **b**: Matte and glossy surfaces after reaction in the presence of azide **8**.

XPS spectra (Cu $2p_{3/2}$ lines) for PEG sample after 5 recycling of PEG and CuT, [Cu] = 4502 ppm.



The ratio of CuO/Cu_2O in the reaction mixture could be approximate by the XP spectra of a PEG sample after CuAAC reaction using CuT. The PEG sample with a high copper concentration (4502 ppm) gave a ratio signal/noise acceptable to identify copper species in PEG. Comparison of both signal areas shown that the ratio CuO/Cu_2O was approximately 9:90, which is in agreement with the weight percentage of the Cu(II) determined by EPR spectroscopy at 5% for the same sample.

EPR spectra of PEG samples with catalysts recovered by precipitation.



(A) PEG + CuNP after the first run, [Cu] = 1989 ppm
(B) PEG + Cu T after 6 recycling in new PEG, [Cu] = 962 ppm
(C) PEG + Cu T after 6 recycling of PEG and Cu T, [Cu] = 4502 ppm
(D) PEG + Cu T, 6 days at 70 °C no use for CuAAC, [Cu] = 114 ppm
(E) PEG + CuI after the first run, [Cu] = 1879 ppm.