Supporting Information for

“Click Chemistry” in Cu^I-Zeolites: The Huisgen [3+2]-Cycloaddition

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All prepared triazoles **3a-j** are known compounds and exhibit spectroscopic data identical to the previously reported ones in the literature.¹ ¹³C NMR spectra are nevertheless provided. They were recorded on a Bruker AMX-300 in CDCl₃, in (CD₃)₂CO or in a 1:1 mixture of CDCl₃ and CD₃OD (for solubility reasons). Reagents and solvents were purchased from Aldrich or Acros and used without further purification. Cu^I-exchanged zeolites were prepared according to a well-established procedure.² Aromatic azides **2b**, **2c** and **2d** were prepared using conventional methods.³

Main characteristics of H-Zeolites used in the study:

H-Zeolite	Source	Topology	Pore diameter (Å)	Si/Al ratio	Acidic sites number (mmol / g)
H-Y	Aldrich (334413)	Cage-type	7.4 × 7.4	1.5	6.67
H-USY	Zeolyst International (CBV500)	Cage-type	7.4 × 7.4	2.8	4.39
H-MOR	Zeolyst International (CBV20A)	Channel-type	6.5 × 7.0 3.4 × 3.8	10.3	1.48
H-ZSM5	Zeolyst International (CBV5020)	Channel-type	5.1 × 5.5 5.3 × 5.6	15	1.04
H-β	Zeochem International (ZEOCAT PB/H)	Channel-type	7.6 × 6.4 5.5 × 5.5	12.5-17.5	0.90 - 1.23

General procedure for the cycloaddition: To a suspension of Cu^I-USY (50 mg) in 1.5 mL of toluene were added azides **2** (1.3 mmol, 1.0 equiv) and then alkynes **1** (1.6 mmol, 1.2 equiv). After 15 hours stirring at room temperature, the mixture was extracted overnight with dichloromethane (15 mL). The catalyst was removed by filtration and the resulting organic phase was successively washed with NaHCO₃ (10 %) solution, water and brine and then dried over sodium sulfate. Filtration and solvent evaporation provided the resulting crude product usually at > 95 % purity as judged by NMR. Column chromatography was performed when necessary (adducts **3b**, **3h** and **3i**).

References:

- (1) For compounds **3a** and **3i**, see: Appukkuttan, P.; Dehaen, W.; Fokin, V. V.; Van der Eycken, E. *Org. Lett.* **2004**, *6*, 4223-4225; for compound **3b**, see: Feldman, A. K.; Colasson, B.; Fokin, V. V. *Org. Lett.* **2004**, *6*, 3897-3899; for compounds **3c** and **3d**, see: Zhao, Y.-B.; Yan, Z.-Y.; Liang, Y.-M. *Tetrahedron Lett.* **2006**, *47*, 1545-1549; for compound **3e**, see: Gerard, B.; Ryan, J.; Beeler, B. B.; Porco Jr., J. A. *Tetrahedron* **2006**, *62*, 6405-6411; for compounds **3f** and **3g**, see: Pachon, L. D.; van Maarseveen, J. H.; Rothenberg, G. *Adv. Synth. Catal.* **2005**, *347*, 811-815; for compound **3h**, see: L'abbé, G.; Verbeke, M.; Dehaen, W.; Toppet, S. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1719-1725.
- (2) Li, Z.; Xie, K.; Slade, R. C. T. *Appl. Catal. A: Gen.* **2001**, *209*, 107-115.
- (3) (a) Sun, C.; Bittmann, R. *J. Org. Chem.* **2006**, *71*, 2200-2202; (b) Pagliai, F.; Piraly, T.; Del Grosso, E.; Di Brisco, R.; Tron, G. S.; Sorba, G.; Genazzani, A. A. *J. Med. Chem.* **2006**, *49*, 467-470.