

Supporting information

S Table S-1: Reaction conditions and results for a model click reaction of benzyl azide and phenylacetylene catalyzed by a heterogeneous copper catalyst.

Solid support	<i>T</i> / °C	Solvent	Excess	Time / h	Conv. / %	Cu-loading / mmol·g ⁻¹	Ref.
Amberlyst ^a	25	CH ₂ Cl ₂	1.1 (azide)	12	92	1.23	14,15
Amberlyst	25	-	1.1 (azide)	< 0.5	99	1.35	17
Amberlyst ^b	N ^c	CH ₂ Cl ₂	1.5 (azide)	N ^c	85	1.33	18
Cryogel	25	Acetone	1.1 (alkyne)	5.5	95	0.12	21
Merrifield	25	tBuOH/H ₂ O	1.1 (alkyne)	2.5	99	0.25	22
Merrifield ^e	25	H ₂ O	1.2 (alkyne)	48	98	1.25	23
TentaGel	25	tBuOH/H ₂ O	-	24	99	0.19	24
TentaGel	40	H ₂ O	1.5 (azide)	6	87	0.26	25
HP20 ^d	25	H ₂ O	1.1 (alkyne)	6	100	0.16	26
PS-bead	40	DMF	1.1 (azide)	8	90	0.04	27
PMEI network	25	EtOAc	2.2 (alkyne)	0.7	99	0.41	28
Polymeric ionic liquid ^e	25	H ₂ O	1.2 (alkyne)	48	98	1.00	23
PVP	37	H ₂ O	-	24	87	N ^c	29
phenylethynylCu(I) ladder polymer	100 ^e	H ₂ O	2 (alkyne)	0.16	91	6.15	31
Isonitrile complex	25	H ₂ O	1.05 (alkyne)	0.08	94	N ^c	32
Metal organic framework	70	Ethanol	1.2 (alkyne)	4	99	4.16	33
Alginate	25	H ₂ O	1.1 (alkyne)	18	98.2	0.21 ^f	34
Chitosan	25	EtOH	1.1 (alkyne)	18	95	0.6	36
Chitosan	70	H ₂ O/dioxane (8/2)	-	0.5	86	0.17	37
Silica	25	-	-	0.5	93	0.87	38
Silica	40	DMF	1.1 (azide)	8	84	0.05	27
Silica ^e	25	H ₂ O	1.2 (alkyne)	48	98	1.25	23
Silica ^e	78	EtOH	-	24	91	0.43	39
Silica ^e	25	H ₂ O	-	0.25	92	0.55	40
Silica ^h	25	-	-	3	96	0.38	41
Silica	25	CH ₃ CN	1.1 (azide)	12	81	0.45	42
Fe ₃ O ₄ /SiO ₂ ^h	25	-	-	15	99	1.29	41
Silica	25	EtOH/H ₂ O	1.35 (alkyne)	1.5	98	0.15	43
Al ₂ O ₃	25	Toluene	-	7	98	0.151	44
TiO ₂	25	Toluene	-	0.7	99	0.25	45
Cu-Mn spinel oxide ⁱ	25	CH ₃ CN	-	8	99	N ^c	46
Montmorillonite	25	CH ₂ Cl ₂	1.1 (azide)	18	99	0.72	47

Hydrotalcite	25	CH ₃ CN	1.2 (alkyne)	6	86	N ^c	49
Zeolite	25	Toluene	1.2 (alkyne)	15	83	4.39	52
Zeolite ^g	90	H ₂ O	-	15	90	N ^c	54
Charcoal	25	Dioxane	-	10	99	1.01	59
Charcoal ^b	170 ^c	Acetone	1.08 (alkyne)	1	99	1.38	20
Charcoal ^g	100	H ₂ O	-	0.6	91	1.57	62
Charcoal ^g	25	CH ₂ Cl ₂	2 (azide)	18	95	1.83	63
Charcoal	60	Dioxane	1.1 (alkyne)	0.3	99	0.56	64
Activated carbon ^g	70	H ₂ O	-	3	98	0.25	65
Acetylene black	50	tBuOH/H ₂ O	1.4 (alkyne)	5	100	N ^c	66
Carbon nanotubes ^g	25	H ₂ O	1.1 (alkyne)	0.8	95	0.55	67
- ^{g, j}	115	DMF/ H ₂ O	2 (azide)	0.7	64	N ^c	70
-	25	H ₂ O/tBuOH	2 (alkyne)	18	80	N ^c	71
- ^h	25	H ₂ O/tBuOH	-	2	92	N ^c	72
-	65	THF	-	0.17	98	N ^c	73-74
PVP	25	Formamide	-	0.33	91	N ^c	77
PVP	25	H ₂ O/ionic liquid	-	0.3	89	N ^c	78
Al ₂ O ₃	25	H ₂ O	-	3	92	10.9	79
AlO(OH)	25	Hexane	1.1 (azide)	6	94	0.62	80
Cu flow reactor ^{b, g, k}	150	DMF	2 (azide)	0.08	72	N ^c	83

a. Propargyl phenol ether is used as an alkyne.

b. Continuous reaction.

c. Not available.

d. 3-Methyl-1-butyn-3-ol is used as an alkyne.

5 e. Microwave-assisted reaction.

f. Mmol Cu per 50 beads.

g. *In situ* generation of organic azide.

h. Propargyl alcohol is used as an alkyne.

i. Methyl propiolate is used as an alkyne.

10 j. 2-Bromoethanol is used as organic halide.

k. 4-Ethynyltoluene is used as an alkyne; ethyl iodide is used as organic halide.

Note on the table: This table presents only the reaction conditions and results for the model click reaction of benzylazide and phenylacetylene. The reader should be careful not only to look to this model reaction when comparing different solid supports, since the result can vary drastically in case that another type of azide or alkyne is used. Even in the case of the model click reaction, it is already difficult to compare the results because the experimental conditions can differ a lot.