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Copper Nanoparticles on Charcoal for Multicomponent Catalytic Synthesis of 1,2,3-Triazole Derivatives from Benzyl Halides or Alkyl Halides, Terminal Alkynes and Sodium Azide in Water as a "Green" Solvent

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Abstract: A one-pot procedure for synthesis of 1,2,3-triazole derivatives *via* the three-component coupling (TCC) reaction between terminal alkynes, benzyl or alkyl halides, and sodium azide in the presences of 1 mol% nanoparticles copper/carbon (Cu/C) catalyst has been developed. The catalyst showed high catalytic activity and 1,4-regioselectivity for the [3+2] Huisgen cycloaddition in water as a "green" solvent and good to excellent yields were obtained in all cases. This procedure eliminates the need to handle organic azides, and they are generated *in situ*. The reaction has a broad scope and is especially practical for the synthesis of new azacrown ether and anthraquinone derivatives of triazole. The heterogeneous catalysts were fully characterized by scanning electron microscopy (SEM), atomic forced microscopy (AFM), X-ray diffraction (XRD), inductively coupled plasma (ICP) analysis and FT-IR experimental techniques. The catalyst was recycled ten times without significant loss of activity.

Keywords: activated carbon; anthraquinone derivatives; aza crown ethers; heterogeneous catalysts; 1,2,3-triazoles; water

Introduction

1,2,3-Triazoles are an important class of heterocyclic compounds due to their wide range of applications including use as pharmaceutical agents, agrochemicals, industrial applications such as dyes, corrosion inhibition (of copper and copper alloys), photostabilizers, and photographic materials.[1]

The most popular method for the construction of the 1,2,3-triazole framework is the 1,3-dipolar Huisgen cycloaddition reaction of azides with alkynes.[2] The Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC),[3] one of the most reliable "click reactions",[4] has enabled the practical and efficient preparation of 1,4-disubstituted-1,2,3-triazoles, from a wide range of substrates with excellent selectivity, which cannot be prepared *via* traditional Huisgen uncatalyzed thermal approaches.[5] Active copper(I) catalytic species can be prepared *in situ* by reduction of copper(II) salts,[3a] oxidation of copper(0) metal,[6] or copper(II)/copper(0) comproportionation.[7] Copper(I) salts have been less used[3b,8] because of their thermodynamic instability and the formation of undesired alkyne-alkyne coupling products is sometimes observed in their presence.[9] Nevertheless, nitrogen- or phosphorus-based ligands have been shown to protect the metal center from oxidation and disproportionation, while enhancing its catalytic activity.[10] To improve the recovery and reuse, copper species have been immobilized onto various supports such as activated carbon,[11] amine-functionalized polymers,[12] zeolites[13] , amine-functionalized silica[14] and aluminum oxyhydroxide fiber.[15] Although organic azides are generally stable against most reaction conditions such as water and oxygen,[16] isolation or purification of lower organic azides or polyazides can be problematic. Therefore, a procedure that avoids the isolation of organic azides is desirable. Recently some examples were reported for the *in situ* generation of organic azides using a one-pot procedure to prepare 1,2,3-triazole derivatives based on the three-component coupling reaction.[14,17] As a part of our continued efforts to utilize heterogeneous catalysts for developing organic reactions,[18] herein we report on a new and

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reused catalyst system based on Cu(I) on charcoal (Cu/C). This heterogeneous catalyst system exhibits an excellent catalytic performance for 1,3-dipolar Huisgen cycloaddition reaction for the construction of the 1,2,3-triazole framework. Moreover, Cu/C can be repeatedly used for this transformation and subsequently recovered after the reaction.

Results and Discussion

The copper catalyst immobilized on activated carbon was readily prepared in a two-step procedure. In a general procedure, the activated carbon was refluxed with a nitric acid solution for several hours and washed with deionized water until pH 6–7 and then dried in an oven at 110 °C overnight under vacuum.[19] The oxidized activated carbon was refluxed with a solution of CuI under an N_2 atmosphere in absolute EtOH for the synthesis of CuI/Cu nanostructures. This method was developed for the effective synthesis of copper nanoparticles incorporated heterogeneously as catalyst in some organic reactions. The CuI/Cu nanostructures were then chemically incorporated into activated carbon *via* π-bonds. This interaction is the result of the back-donation of *d* electrons from the occupied 4*d* orbital of the copper ion to the unoccupied π*-2*p* antibonding orbitals of the carbon-carbon double bond.[20] Scanning electron microscopy (SEM), atomic forced microscopy (AFM), X-ray diffraction (XRD) analysis and FT-IR experimental techniques were used to characterize the CuI/Cu nanostructures. According to the conditions of the reaction, the following equations are proposed for CuI in ethanol:[27]

$$CuI\,(S) \rightleftharpoons Cu^{+} + I^{-}$$

$$CuI\,(S) + I^{-} \rightleftharpoons CuI_2^{-}$$

Because of the low solubility of CuI in ethanol (K_{sp} in water = 5.1 E 12), most of the copper iodide crystals tend to deposit on to the activated carbon. The CuI crystals are graphically observed using SEM (Figure 1). Based on the SEM image, CuI crystals are estimated to around several micrometers in size.

Anyway, the poor solubility of the CuI under the condition of the reaction causes the formation of a dilute solution of Cu^{+}. Then, *via* a disproportionation reaction, Cu^{+} is changed to Cu nanoparticles and Cu^{2+} species according to the following equation:

$$Cu^{+} \rightleftharpoons Cu + Cu^{2+}$$

Then Cu^{2+} as the product of the disproportionation reaction of Cu^{+}, reacts with iodide ion or micro crystals of CuI to form nanocrystals of deposited CuI. The yellowness of the solution during the reflux is good evidence for the formation of I_3^{-} based on following equation:

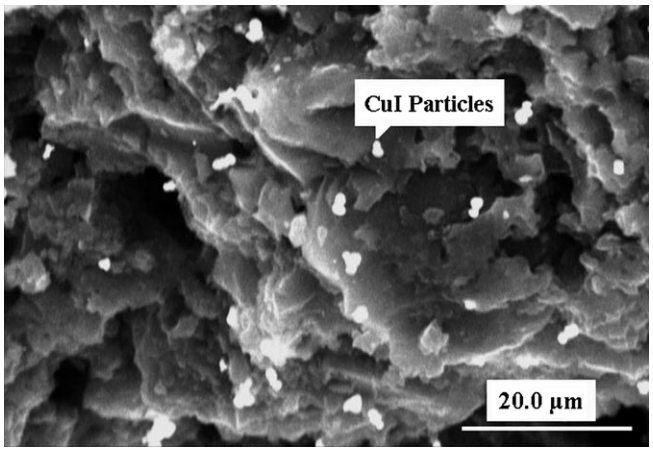

Figure 1. SEM image of copper particles on activated carbon as substrate.

$$2\,CuI_2 + CuI_{(micro\ scale)}\,(S) \rightleftharpoons 2\,CuI_{(nano\ scale)} + CuI_3\,(S)$$

The above reactions are repeated continuously during several steps of the use of Cu/C that make it active in playing the catalytic role of Cu/CuI (the nature of the copper catalyst) in organic reactions.

The size and morphology of the copper nanoparticles are clearly observed based on two-dimensional (2-D), three-dimensional (3-D) AFM images (Figure 2). The AFM images of copper nanoparticles reveal the spherical copper nanoparticles and CuI nanocrystals which are normally distributed on activated carbon. The average size of the copper nanostructures is estimated to 80–300 nm according to the voltage profile of AFM image (Figure 2c). According to the histogram based on the AFM image (Figure 2d), the maximum frequency percent of copper nanoparticles has been estimated to by around 250 nm.

Figure 3 shows the XRD patterns of capped copper nanoparticles on activated carbon. The peak positions are consistent with metallic copper and copper iodide nanocrystals. Sharp peaks of copper are observed which indicate the crystalline nature of the products. Planes of charcoal, CuI nanocrystals and Cu nanoparticles are reported in Table 1. The diffraction features were consistent with the "fcc" crystal structures of copper and copper iodide.[22] The size of the copper nanoparticle was also determined from X-ray line broading using the Debye–Scherrer formula[23] given as $D = 0.9\,l/\beta\cos\theta$, where D is the average crystalline size, l the X-ray wavelength used, β the angular line

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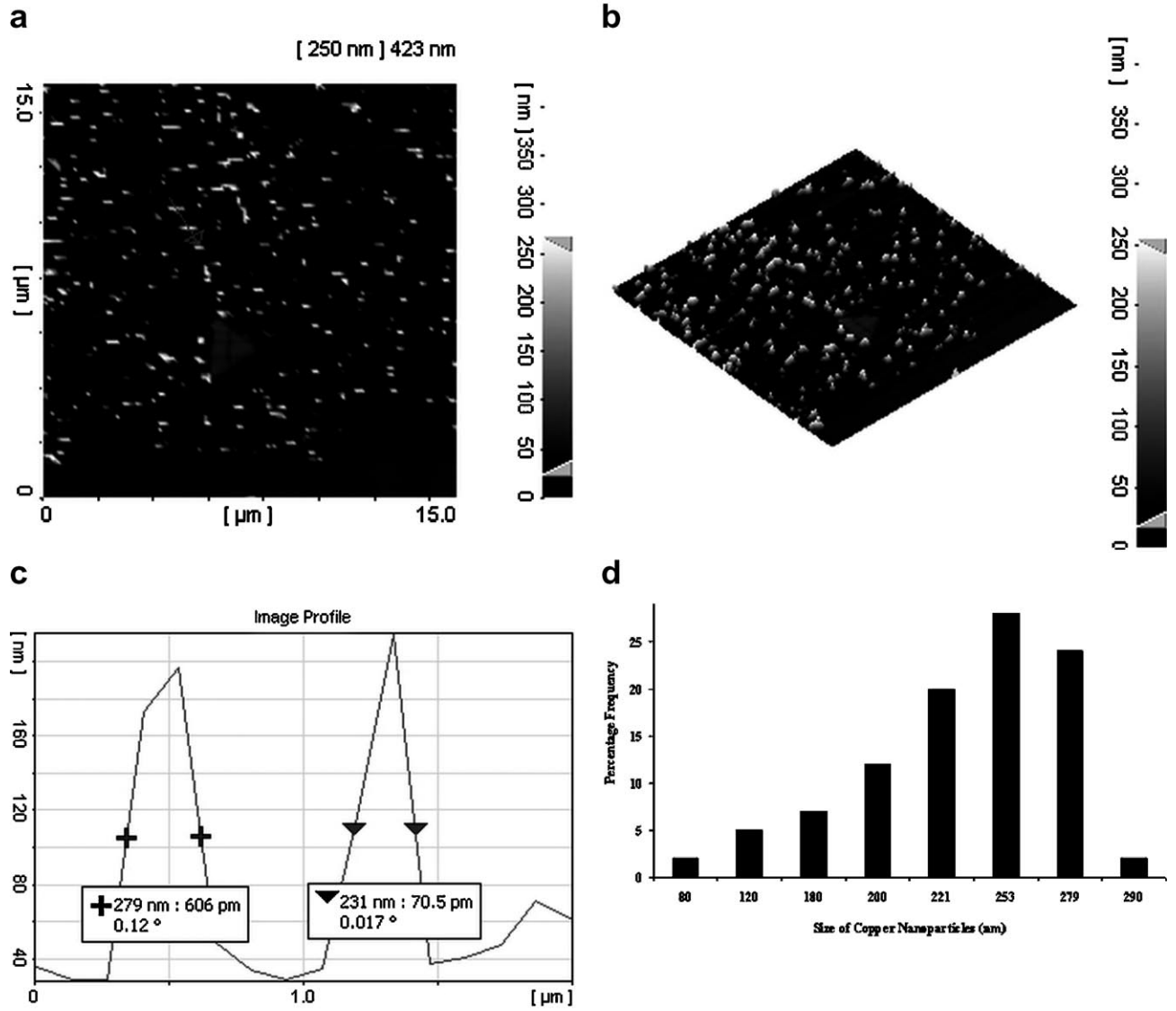

Figure 2. AFM images of copper nanoparticles, **a**: 2-D, **b**: 3-D, **c**: voltage profile and **d**: the histogram representing the average size of copper nanoparticles.

width at half maximum intensity and θ the Bragg's angle. For $\theta = 20°$, $l = 1.056$ Å and $\beta = 0.36$ mm, the average size of the copper nanoparticles on activated carbon is estimated to be around 283.3 nm.

Comparison between the FT-IR spectra of the copper nanoparticles on activated carbon with that of activated carbon, reveals weak absorption band at around 667 cm^{-1} (Figure 4). This is related to the immobilization of copper nanoparticles on activated carbon. Also the shift observed in the peak absorption of the carbonyl group from 1635.5 to 1612 cm^{-1} is related to the chemical bond formed between the carboxylic group and Cu^{+}.[24c] This decrease in the electron density at the carbonyl group is probably due to the donation of electrons from the carbonyl group into Cu^{+}.

To evaluate the Cu content, the supported catalyst was treated with concentrated HCl and concentrated nitric acid to digest the copper species and then analyzed by inductively coupled plasma (ICP) analysis. The Cu content was determined to be 9.97% w/w (See Experimental Section for details).

The principle advantages of this immobilization technique include the absence of any complexity in the immobilization process, the widespread availability of activated carbon, the lack of any laborious need to alter the catalyst to facilitate the immobilization, the rapidity and experimental simplicity of the procedure by which the immobilization can be completed.

To exploit a method for the preparation of new 1,2,3-triazole derivatives, the reaction of benzyl bromide, phenylacetylene and sodium azide in the pres-

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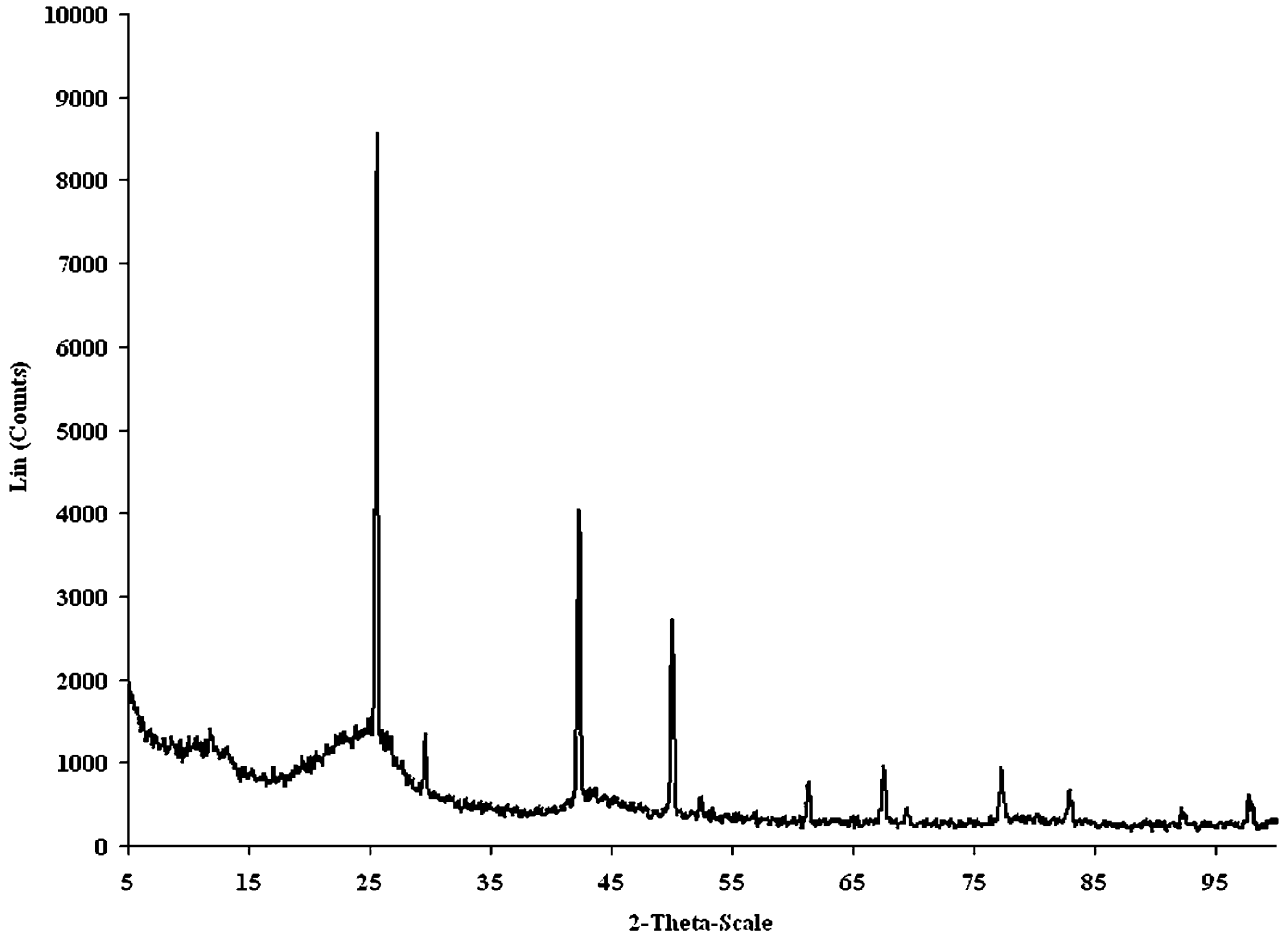

Figure 3. XRD pattern of copper nanoparticles on activated carbon as substrate.

ence of Cu/C *via* a 1,3-dipolar Huisgen cycloaddition reaction was chosen as a model and its behavior was studied under a variety of conditions *via* TLC and NMR spectroscopy (Table 2).

During our optimization studies, various solvents were examined and it was found that the solvent plays a significant role in terms of reaction rate, isolated yield, and selectivity. Water clearly stands out as the solvent of choice with its fast reaction rate, high yield, selectivity, cheapness, "green" solvent nature and environmental acceptability. The reaction between, benzyl bromide, phenylacetylene and sodium azide in the presence of 1 mol% of Cu/C in the water, furnished the 1,4-disubstituted triazole product in 91% yield after stirring for 45 min at 100 °C in a uncapped vial (Scheme 1). The product was isolated by simple washing of the solid mass by acetone followed by the usual work-up. An increase in the amount of Cu/C had negligible effects on the efficiency of the reaction.

Table 1. Analysis of XRD patterns related to CuI/Cu on activated carbon.

2-Theta-Scale (2θ)	Matrix and Morphology			Reference
	C	Cu	CuI/CuI_3	
25.5	(002)	–	(111)	[24a,24b]
29.5	(422)	–	(200)	[24a]
40	–	(111)	(220)	[24a]
50.2	(008)	(200)	(311)	[22,24]
52.1	–	–	(222)	[22]
61.2	–	–	(400)	[24a]
67.2	–	–	(331)	[22]
69.2	–	–	(420)	[22]
77	–	(220)	–	[22,24c]

Structural assignments of triazole **1** were made by comparison of the ^{1}H- and ^{13}C NMR spectra with those reported previously. In particular, the ^{1}H NMR spectra show resonances of the proton in the 5-position of the 1,2,3-triazole ring that perfectly agree with literature data.[17c]

To investigate the generality and versatility of this method, the reaction was extended to various structurally diverse terminal alkynes and alkyl halides. In all cases, [3+2] cycloadditions were complete in a rea-

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Table 2. 1,3-Dipolar Huisgen cycloaddition reaction of benzyl bromide, phenylacetylene and sodium azide under various conditions.

Entry	Catalyst	Conditions	Temperature [°C]	Time	Yield [%]
1	Cu/C (1 mol%)	neat	100	2 h	0
2	Cu/C (1 mol%)	Dioxane	100	6 h	15
3	Cu/C (1 mol%)	THF	65	6 h	20
4	Cu/C (1 mol%)	*t*-BuOH	80	2 h	35
5	Cu/C (1 mol%)	EtOH (96%)	reflux	1 h	58
6	Cu/C (1 mol%)	CH_3CN	reflux	1.5 h	45
7	Cu/C (1 mol%)	DMF	100	2 h	40
8	Cu/C (1 mol%)	H_2O/dioxane	100	2 h	65
9	Cu/C (1 mol%)	H_2O/THF	65	2 h	40
10	Cu/C (1 mol%)	H_2O/DMF	100	2 h	50
11	Cu/C (1 mol%)	H_2O	25	24 h	40
12	Cu/C (1 mol%)	H_2O	100	45 min	91
13	Cu/C (5 mol%)	H_2O	100	40 min	92

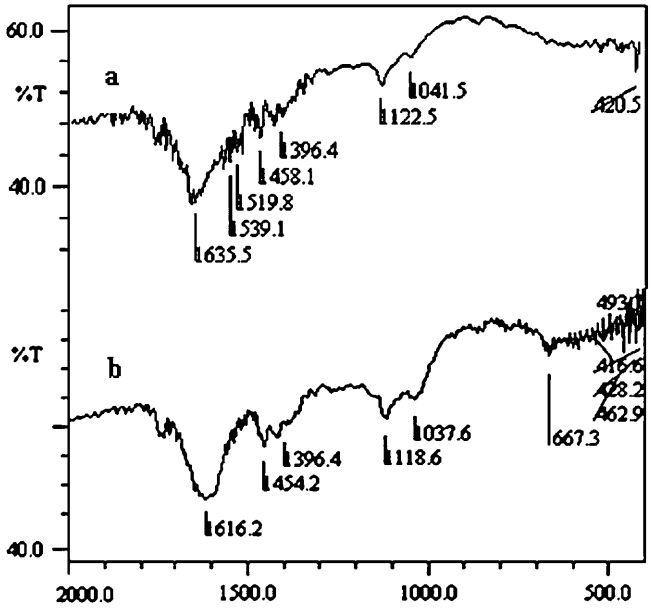


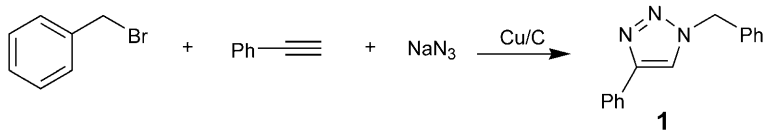
Figure 4. FT-IR spectra of **a**: activated carbon, **b**: activated carbon supported with Cu nanoparticles.

sonable time and 1,2,3-triazole derivatives were isolated in good to high yields.

The use of this methodology in the reaction of the sodium azide, alkyl or benzyl halides with different terminal alkynes produced only one of the possible regioisomers, as expected (Table 3). Various benzyl halides with both electron-donating and -withdrawing substituents were subjected to the same reaction conditions as **3** to furnish the corresponding 1,2,3-triazole derivatives. However the rate drops as electron-withdrawing substituents are added, as in **4** (Table 3, entry 5).

We envisaged that the reaction of anthraquinone derivatives[25] (**5** and **7**) containing a single bromomethyl group with sodium azide would lead to the quantitative formation of the desired azidomethyl group, which could then be coupled with phenylacetylene to give the next-generation 1,2,3-triazole derivatives in good yields.(Table 3, entries 6 and 7). We felt that this methodology could then be extended to synthesize azacrown ether-containing triazoles. The azacrown ether, which has a chloroacetylated substituent at the nitrogen position (**9**), gave the corresponding triazole **10** in good yield (Table 3, entry 8). Azacrown ether propargylamine **11** also reacted without any problems to give the corresponding triazole **12** in high yield (Table 3, entry 9). We decided to extend the scope of this methodology to the anthraquinone dipropargyl ether **13** as starting material; the reaction proceeded smoothly in good yield.

The reaction of an alkylacetylene such as 1-hexyne and aliphatic terminal alkynes bearing functional groups afforded the desired triazoles (**15**, **16** and **17**) in high yields, although prolonged reaction times were required (Table 3, entries 11–13). When methyl iodide and allyl bromide were used as substrate, the reaction was performed in a sealed tube to afford the desired product in good yield. The use of methylene



Scheme 1.

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Table 3. The reaction of alkyl and benzyl halide (1 mmol), terminal alkyne (1 mmol) and sodium azide (1.1 mmol) catalyzed by Cu/C (1 mol%) in water at 100 °C.

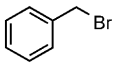
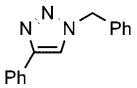
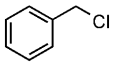
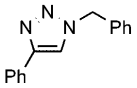
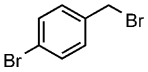
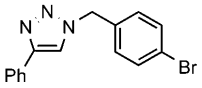
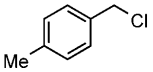
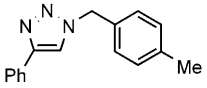
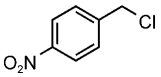
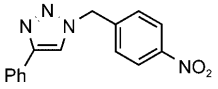
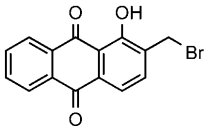
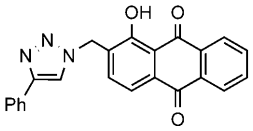
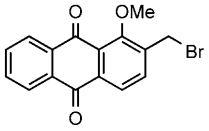
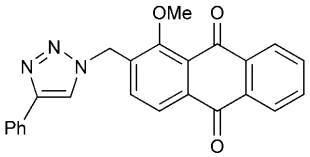
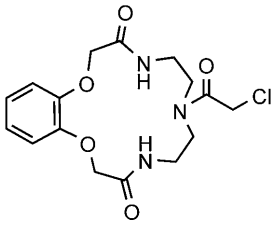
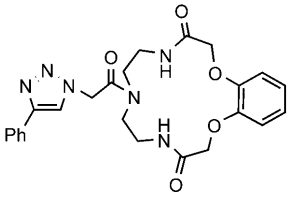
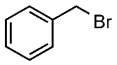
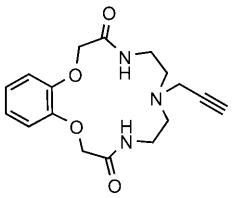
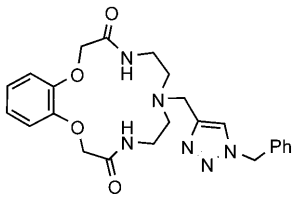
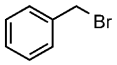
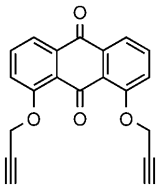
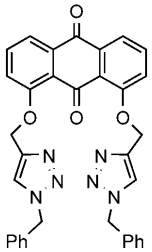
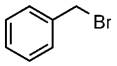
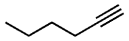
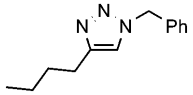
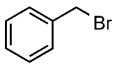
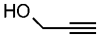
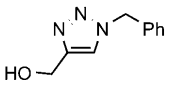
Entry	Halide	Alkyne	Product	Time [h]	Yield [%]
1			**1** 	0.6	91
2				1	90
3			**2** 	1.5	87
4			**3** 	0.5	88
5			**4** 	2.5	84
6	**5** 		**6** 	5	78
7	**7** 		**8** 	6	75
8	**9** 		**10** 	6	79
9		**11** 	**12** 	4	75
10		**13** 	**14** 	8	72
11			**15** 	2.5	76
12			**16** 	3	81

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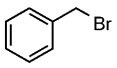
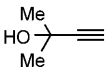
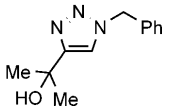
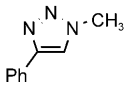
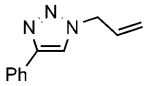
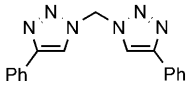
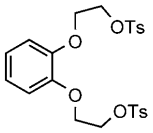
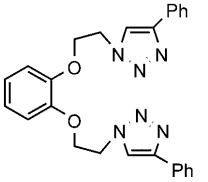
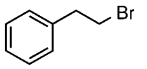
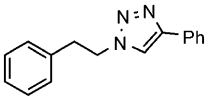
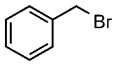
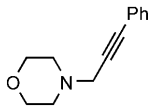
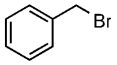
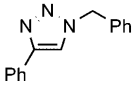
Table 3. (Continued)

Entry	Halide	Alkyne	Product	Time [h]	Yield [%]
13			**17** 	3	84
14	CH_3I		**18** 	10	86
15			**19** 	8	83
16	CH_2I_2		**20** 	12	71
17	**21** 		**22** 	20	69
18			**23** 	18	85
19		**24** 	no reaction	24	–
20				1	89

iodide as an alkyl halide afforded the bridged 1,2,3-triazole **20** in 71% yield (Table 3, entry 16). Next, we explored the synthesis of symmetrical bis-triazoles starting from the bis-OTs derivative **22**, by the successive 1,3-dipolar cycloaddition reactions with phenylacetylene and obtained the product in good yield (Table 3, entry 17).

In an attempt to broaden the scope of our methodology, the possibility of performing the reaction with an alkyl halide instead of benzyl halide was also investigated. In this way, 2-phenylethyl bromide was reacted with phenylacetylene and sodium azide in the presence of Cu/C at 100 °C for 18 h to afford the expected product in 85% yield.

No competitive formation of N–H triazoles, resulting from the addition of an inorganic azide to the alkyne, was detected with this catalytic system.

As expected, internal alkynes gave no reaction. The reactive behavior is in agreement with a mechanism involving the formation of a CuI acetylide species, probably on the Cu/C surface (Table 3, entry 19).

To access the feasibility of applying this method in a preparative scale, we carried out the reaction of benzyl bromide, phenylacetylene and sodium azide on a 100-mmol scale in the presence of the heterogeneous catalyst (Table 3, entry 20). As expected, the reaction proceeded similar to the case on a smaller scale (Table 3, entry 1), and the desired 1,2,3-triazole was obtained in 89% isolated yield in 1 h.

The recyclability of Cu/C was tested in the cycloaddition of phenylacetylene, benzyl bromide and sodium azide. The charcoal-supported CuI was recovered simply by filtration after each experiment, after washing with acetone and drying in the air it could be reused directly without further purification for the 1,2,3-triazole synthesis in more than 10 successive reactions. After 10 consecutive reactions, the recovered Cu/C was found to contain 9.83% (w/w) of Cu based on ICP analysis, which is comparable to the initial value of 9.97% (w/w), indicative of less than 1.40% leaching during the reaction cycles (see Experimental Section for details). The stability of copper species on activated carbon is so high that, no leaching was observed even in the presence of copper complexing agents such as azacrown ethers.[27a]

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Also, the FT-IR spectrum and the XRD pattern of the copper catalyst supported on activated carbon, analyzed after its use as catalyst in organic reactions for at least 10 times, were similar to those obtained before the first cycle.[26]

In conclusion, we have developed a simple and reproducible synthetic method for a recyclable heterogeneous copper catalyst (Cu/C). We have determined the morphology, the surface and total composition of the mixed Cu/C by SEM, AFM, XRD, IR and ICP analyses. The Cu/C surface is mostly composed of both CuI and Cu nanoparticles. With this catalyst, a safe and efficient three-component reaction for the regioselective generation of 1,4-disubstituted 1,2,3-triazoles has been developed. The method avoids isolation and handling of potentially unstable small organic azides and provides the triazole products in pure form. The scope of the cycloaddition using our catalyst is quite broad; various terminal alkynes react readily with benzyl and alkyl halides at 100 °C in water. Furthermore, the Cu/C can be recovered and recycled by simple filtration of the reaction solution and reused for at least ten consecutive trials without decrease in the activity.

Experimental Section

Instrumentation, Analyses and Starting Material

NMR spectra were recorded on a Bruker Avance DPX-250 (^{1}H NMR at 250 MHz and ^{13}C NMR at 62.9 MHz) spectrometer in pure deuterated solvents with tetramethylsilane as an internal standard. IR spectra were obtained using a Shimadzu FT-IR 8300 spectrophotometer. Scanning electron micrographs were obtained with the SEM instrumentation XL-30 FEG SEM (Philips, at 20 KV). An atomic forced microscope (AFM, DME-SPM, version 2.0.0.9) was also used for AFM images. Mass spectra were determined on a Shimadzu GCMS-QP 1000 EX instruments at 70 or 20 eV. Melting points determined in open capillary tubes in a Büchi-535 circulating oil melting point apparatus. X-ray diffraction (XRD, D8, Advance, Bruker, axs) patterns were obtained for characterization of the heterogeneous catalyst. The ICP analysis data were obtained using a Varian Vistapro analyzer. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica gel PolyGram SILG/UV 254 plates. Column chromatography was carried out on short columns of silica gel 60 (70–230 mesh) in glass columns (2–3 cm diameter) using 15–30 g of silica gel per g crude mixture. Chemical materials were purchased from Fluka, Aldrich and Merck. The used activated carbon was also purchased from Merck (Atr. No. 9631, 0.3–0.05 mm).

Activated Charcoal Oxidation

The activated carbon was refluxed with a 5.0 M nitric acid solution for 6 h (1.0 g/30 mL), washed with deionized water until pH 6–7 and then dried in an oven at 110 °C overnight under vacuum.[19]

Deposition of Copper on Purified Activated Carbon using CuI as Copper Source

CuI (100 mg) was dissolved in 30 mL absolute ethanol, and magnetically stirred in a pre-heated oil bath at reflux temperature for 4 h under a nitrogen atmosphere in the presence of 1.0 g of purified activated carbon. The resulting materials were washed with ethanol (4 × 30 mL); no leaching of the copper was observed. Finally, the copper in charcoal was dried under vacuum in an oven overnight at 110 °C. To evaluate the copper content, the supported copper was treated with concentrated HCl and HNO_3 (1:1) followed by ICP analysis. The copper content was determined to be 9.97% w/w.

Determination of the Copper Content in Cu/C Catalyst

The Cu/C (100 mg) was extracted with concentrated HCl (5 × 2 mL) in a screw-capped vessel, followed by treatment with concentrated nitric acid (2 mL) to digest the metal complex. The mixture was then transferred into a volumetric flask (100 mL), diluted 1:50 for the second time and was analyzed by the ICP analysis. The copper concentration was determined from the atomic emissions (324.754 nm) by reference to a linear (R = 0.99) calibration curve of (1–4 ppm) of CuI prepared in a manner identical to the sample preparation.

General Procedure

The Cu/C catalyst was subjected to 10 successive reuses under the reaction conditions: For each reaction, alkyl halide (1 mmol), alkyne (1 mmol) and sodium azide (1.1 mmol) were stirred in water (1 mL) in the presence of the heterogeneous catalyst (1 mol%, 0.021 g) at 100 °C in a uncapped vial. According to the ICP analysis, the copper content in the heterogeneous catalyst was determined to be 9.97% (w/w). Therefore, each gram of heterogeneous catalyst includes 0.525 mmol of copper. For 1 mmol of reactants, 0.01 mmol of catalyst is needed, which is equal to 0.021 g of the heterogeneous catalyst. The reaction was complete after appropriate time (Table 3) as monitored by TLC analysis. After the reaction was complete the whole reaction mixture was directly passed through celite and rinsed with acetone (3 × 15 mL). The recovered catalyst was dried and stored for another consecutive reaction run. The acetone was removed by rotation evaporator under vacuum and the residue was precipitated in water. The precipitate was collected by filtration. After washing with water three times, the precipitate was dried under vacuum for 24 h at room temperature, which resulted in a 91% yield as white solid. For further purification the solid was recrystallized with ethanol/water (3:1).

1-Benzyl-4-phenyl-1*H*-1,2,3-triazole (1): Recrystallization from EtOH/H_2O (3:1) gave compound **1** as colorless crystals in 91% yield; mp 129–129.5 °C; IR (KBr): ν = 694 (s), 729 (s), 768 (s), 1049 (m), 1076 (m), 1223 (m), 1358 (w), 1466 (m), 3121 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 5.53 (s, 2H), 7.26–7.41 (m, 6H), 7.69 (s, 1H), 7.79–7.82 (m, 4H);

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^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 54.1, 119.7, 125.7, 128.0, 128.2, 128.7, 128.8, 129.1, 130.6, 134.7, 148.1; MS: *m/z* (%) = 237 (M^++2, 0.2), 236 (M^++1, 7.3), 235 (M^+, 7.7), 207 (24.7), 206 (30.8), 179 (9.7), 149 (23.1), 116 (94.8), 91 (100), 57 (56.0); anal. calcd. for $C_{15}H_{13}N_3$ (235.284): C 76.57, H 5.57: found: C 76.40, H 5.69.

1-(4-Bromobenzyl)-4-phenyl-1*H*-1,2,3-triazole (2): Recrystallization from EtOH/H_2O (3:1) gave compound **2** as colorless crystals in 87% yield; mp 152–152.5 °C; IR (KBr): ν = 690 (s), 764 (s), 798 (s), 1049 (m), 1076 (s), 1219 (s), 1350 (w), 1435 (m), 1462 (m), 1485 (s), 3082 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 5.52 (s, 2H), 7.17 (d, 2H, *J* = 8.4 Hz), 7.24–7.44 (m, 3H), 7.51 (d, 2H, *J* = 8.4 Hz), 7.67 (s, 1H), 7.80 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 53.4, 119.7, 122.8, 125.7, 127.6, 128.3, 128.7, 129.1, 129.6, 132.2, 133.8, 148.3; MS: *m/z* (%) = 316 (M^++2, 1.8), 315 (M^++1, 1.8), 314 (M^+, 2.4), 312 (0.8), 284 (4.7), 286 (5.3), 207 (8.6), 180 (2.5), 178 (2.7), 171 (15.1), 169 (16.3), 116 (100), 89 (37.3); anal. calcd. for $C_{15}H_{12}BrN_3$ (314.180): C 57.34, H 3.85; found: C 57.17, H 3.98.

1-(4-Methylbenzyl)-4-phenyl-1*H*-1,2,3-triazole (3): Recrystallization from EtOH/H_2O (3:1) gave compound **3** as colorless crystals in 88% yield; mp 110 °C; IR (KBr): ν = 694 (s), 764 (s), 1045 (m), 1076 (m), 1223 (s), 1350 (m), 1462 (m), 1516 (m), 3117 (w), 3445 (br) cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.36 (s, 3H), 5.52 (s, 2H), 7.30–7.43 (m, 7H), 7.64 (s, 1H), 7.79 (dd, 2H, J_1 = 8.1, J_2 = 1.5 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 21.2, 53.9, 119.6, 126.0, 128.1, 128.8, 130.2, 130.6, 131.7, 138.6, 148.1; MS: *m/z* (%) = 251 (M^++2, 3.0), 25 0(M^++1, 15.9), 249 (M^+, 16.2), 220 (41.4), 206 (14.2), 179 (16.3), 130 (7.0), 116 (100), 89 (25.9), 77 (27.4); anal. calcd for $C_{16}H_{15}N_3$ (249.311): C 77.08, H 6.06; found: C 76.92, H 5.94.

1-(4-Nitrobenzyl)-4-phenyl-1*H*-1,2,3-triazole (4): Recrystallization from EtOH/H_2O (3:1) gave compound **4** as pale yellow crystals in 84% yield; mp 156–157 °C; IR (KBr): ν = 690 (s), 733 (s), 764 (s), 1045 (m), 1076 (m), 1223 (m), 1350 (s), 1520 (s), 1605 (m), 3082 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 5.68 (s, 2H), 7.32–7.38 (m, 3H), 7.42 (d, 2H, *J* = 8.5 Hz), 7.78 (s, 1H), 7.79 (d, 2H, *J* = 7.9 Hz), 8.19 (dd, 2H, J_1 = 9.1, J_2 = 2.2 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 53.1, 119.8, 124.3, 125.7, 128.5, 128.9, 130.1, 141.8, 148.6; MS: *m/z* (%) = 281 (M^++1, 4.1), 280 (M^+, 5.6), 252 (3.3), 206 (7.0), 136 (5.0), 116 (100.0), 89 (41.0), 63 (18.8); anal. calcd. for $C_{15}H_{12}N_4O_2$ (280.282): C 64.28, H 4.32; found: C 64.09, H, 4.45.

1-Hydroxy-2-[(4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl]anthra-9,10-quinone (6): Recrystallization from EtOH/H_2O (3:1) gave compound **6** as an orange powder in 78% yield; mp 209 °C; IR (KBr): ν = 694 (s), 714 (s), 764 (s), 999 (s), 1045 (w), 1284 (s), 1257 (s), 1350 (s), 1427 (s), 1589 (s), 1632 (s), 1670 (s), 3086 (m) cm^{-1}; ^{1}H NMR (DMSO-d_6, 250 MHz): δ = 5.72 (s, 2H), 7.29 (d, 1H, *J* = 7.0 Hz), 7.40 (t, 1H, *J* = 7.3 Hz), 7.64 (d, 1H, *J* = 7.9 Hz), 7.81–7.85 (m, 5H), 7.90–8.21 (m, 2H), 8.62 (s, 1H), 12.84 (s, 1H); ^{13}C NMR (DMSO-d_6, 62.9 MHz): δ = 47.6, 115.7, 118.7, 122.0, 125.1, 126.5, 126.8, 127.8, 128.8, 130.3, 130.5, 132.5, 132.8, 134.6, 135.2, 136.6, 146.4, 159.1, 181.3, 188.3; MS: *m/z* (%) = 382 (M^++1, 5.7), 381 (M^+, 5.9), 368 (7.0), 366 (5.6), 314 (17.5), 300 (3.6), 282 (9.4), 263 (3.5), 251 (7.5), 238 (18.8), 209 (9.2), 181 (7.1), 164 (5.0), 145 (21.3), 116 (10.5), 97 (29.1), 71 (54.2), 55 (100); anal. calcd. for $C_{23}H_{15}N_3O_3$ (381.384): C 72.43, H 3.96; found: C 72.58, H 4.12.

1-Methoxy-2-[(4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl]anthra-9,10-quinone (8): Recrystallization from EtOH/H_2O (3:1) gave compound **8** as a yellow powder in 75% yield; mp 211–212 °C; IR (KBr): ν = 694 (m), 714 (s), 764 (m), 964 (m), 1014 (s), 1045 (s), 1265 (s), 1323 (s), 1574 (m), 1670 (vs), 3078 (m) cm^{-1}; ^{1}H NMR (DMSO-d_6, 250 MHz): δ = 3.85 (s, 3H), 5.80 (s, 2H), 7.29 (d, 1H, *J* = 7.1 Hz), 7.41 (t, 1H, *J* = 7.3 Hz), 7.64 (d, 1H, *J* = 7.9 Hz), 7.83–7.90 (m, 5H), 7.98 (d, 1H, *J* = 7.9 Hz), 8.10 (t, 1H, *J* = 7.3 Hz), 8.65 (s, 1H); ^{13}C NMR (DMSO-d_6, 62.9 MHz): δ = 48.7, 62.4, 122.6, 123.4, 125.6, 126.3, 127.2, 128.4, 129.3, 131.0, 132.4, 134.4, 134.7, 135.0, 135.5, 135.6, 137.6, 147.0, 158.7, 181.8, 182.5; MS: *m/z* (%) = 397 (M^++2, 1.6), 396 (M^++1, 6.7), 395 (M^+, 2.9), 369 (7.9), 353 (6.2), 337 (13.3), 264 (11.9), 252 (24.2), 221 (10.6), 165 (16.2), 116 (100), 83 (24.9), 57 (48.5); anal. calcd. for $C_{24}H_{17}N_3O_3$ (395.410): C 72.90, H 4.33; found: C 72.79, H 4.17.

7-[(4-Phenyl-1*H*-1,2,3-triazol-1-yl)acetyl]-5,6,7,8,9,10-hexahydro-2*H*-1,13,4,7,10-benzodioxatriazacyclopentadecine-3,11(4*H*,12*H*)-dione(10): Recrystallization from EtOH/H_2O (3:1) gave compound **10** as a white powder in 79% yield; mp 207 °C; IR (KBr): ν = 768 (w), 1045 (w), 1122 (w), 1238 (m), 1500 (s), 1539 (s), 1666 (vs), 2928 (w), 3302 (m), 3391 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.46–3.86 (m, 8H), 4.52 (s, 2H), 4.75 (s, 2H), 5.21 (s, 2H), 6.95–7.06 (m, 4H), 7.30–7.41 (m, 3H), 7.71–7.76 (m, 2H), 7.87 (s, 1H), 7.23 (s, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 48.6, 51.0, 115.4, 118.3, 121.7, 124.0, 125.7, 128.1, 128.7, 130.4, 147.9, 167.5129.1, 136.1, 143.5, 146.3, 167.5; MS: *m/z* (%) = 479 (M^++1, 2.5), 478 (M^+, 4.2), 451 (3.2), 450 (2.6), 332 (0.2), 304 (0.4), 293 (0.4), 292 (0.5), 277 (2.5), 225 (2.1), 206 (6.3), 194 (3.7), 167 (4.2), 130 (24.3), 103 (34.7), 85 (51.1), 56 (100); anal. calcd. for $C_{24}H_{26}N_6O_5$ (478.501): C 60.24, H 5.48; found: C 60.07, H 5.62.

7-(2-Propynyl)-5,6,7,8,9,10-hexahydro-2*H*-1,13,4,7,10-benzodioxatriazacyclopentadecine-3,11(4*H*,12*H*)-dione (11)

A mixture of azacrown ether[27] (5 mmol), propargyl bromide (10 mmol), and K_2CO_3 (12 mmol) in DMF (50 mL) was stirred at room temperature for 24 h and then poured into ice/water (500 mL). The mixture was filtered under vacuue and the residue was air-dried to constant weight to give **11** in 95% yield; mp 110 °C; IR (KBr): ν = 744 (s), 818 (m), 1057 (s), 1134 (s), 1223 (s), 1261 (s), 1439 (m), 1462 (m), 1512 (s), 1682 (vs), 2847 (m), 3229 (m), 3406(s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.26 (s, 1H), 2.85 (t, 4H, *J* = 5.3 Hz), 3.32 (s, 2H), 3.37 (t, 4H, *J* = 5.3 Hz), 4.46 (s, 4H), 6.82–7.01 (m, 4H), 7.42 (s, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 35.0, 37.1, 51.3, 66.8, 74.6, 75.4, 112.3, 121.9, 146.5, 167.1; MS: *m/z* (%) = 333 (M^++2, 6.6), 332 (M^++1, 35.2), 331 (M^+, 23.4), 293 (1.4), 292 (2.2), 207 (14.4), 165 (33.6), 123 (33.2), 94 (78.9), 69 (82.3), 55 (100); anal. calcd. for $C_{17}H_{21}N_3O_4$ (331.366): C 61.62, H 6.39; found: C 61.47, H 6.54.

7-[(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl]-5,6,7,8,9,10-hexahydro-2*H*-1,13,4,7,10-benzodioxatriazacyclopentadecine-3,11(4*H*,12*H*)-dione (12): Recrystallization from EtOH/H_2O (3:1) gave compound 12 as a colorless powder in 75% yield;

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mp 195–196 °C; IR (KBr): ν = 752 (m), 818 (m), 1049 (s), 1130 (s), 1219 (s), 1257 (s), 1504 (s), 1527 (s), 1682 (vs), 2858 (w), 3229 (m), 3406 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.77 (t, 4H, J = 5.3 Hz), 3.52 (t, 4H, J = 5.3 Hz), 3.95 (s, 2H), 4.41 (s, 4H), 5.44 (s, 2H), 6.84–7.05 (m, 4H), 7.13–7.14 (m, 2H), 7.26 (s, 1H), 7.30–7.36 (m, 3H), 7.56 (s, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 35.3, 44.3, 52.0, 54.1, 67.1, 112.8, 122.2, 127.8, 128.7, 129.1, 134.5, 143.4, 146.3, 167.2; MS: m/z (%) = 466 (M^+ + 2, 0.9), 465 (M^+ + 1, 8.2), 464 (M^+, 7.6), 392 (3.7), 293 (6.5), 292 (14.1), 227 (11.1), 215 (12.6), 173 (16.0), 144 (25.7), 121 (10.5), 91 (100), 56 (33.8); anal. calcd. for $C_{24}H_{28}N_6O_4$ (464.517): C 62.06, H 6.08; found: C 61.95, H 6.19.

1,8-Bis(2-propynyloxy)anthra-9,10-quinone (13)

A mixture of 1,8-dihydroxyanthraquinone (5 mmol), propargyl bromide (20 mmol), and K_2CO_3 (24 mmol) in DMF (50 mL) was stirred at room temperature for 24 h and then poured into ice/water (500 mL). The mixture was filtered under vacuum and the residue was air-dried. The crude product was purified by column chromatography on silica gel using *n*-hexane as eluent. Compound **13** was obtained as yellow crystals in 89% yield; mp 190–192 °C; IR (KBr): ν = 741 (s), 814 (w), 903 (m), 968 (s), 1041 (s), 1238 (s), 1292 (s), 1443 (m), 1585 (s), 1659 (vs), 2341 (w), 3252 (s), 3298 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.55 (s, 2H), 4.93 (s, 4H), 7.49 (dd, 2H, J_1 = 8.4, J_2 = 1.1 Hz), 7.66 (t, 2H, J = 8.2 Hz), 7.91 (dd, 2H, J_1 = 7.7, J_2 = 1.1 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 57.2, 77.9, 80.5, 120.3, 120.9, 124.9, 133.7, 134.8, 157.1, 183.6; MS: m/z (%) = 314 (M^+ − 2, 8.4), 313 (1.5), 236 (9.6), 173 (6.3), 149 (10.5), 129 (15.9), 111 (19.2), 83 (51.5), 57 (100); anal. calcd. for $C_{20}H_{12}O_4$ (316.307): C 75.94, H 3.82; found: C 76.12, H 4.01.

1,8-Bis[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methoxy]anthra-9,10-quinone (14): Recrystallization from EtOH/H_2O (3:1) gave compound **14** as a yellow powder in 72% yield; mp 195–196 °C; IR (KBr): ν = 744 (s), 980 (s), 1049 (s), 1242 (s), 1281 (s), 1315 (s), 1458 (m), 1585 (s), 1670 (vs), 3445 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ = 5.31 (s, 4H), 5.43 (s, 4H), 7.13–7.25 (m, 10H), 7.39 (dd, 2H, J_1 = 8.3, J_2 = 0.9 Hz), 7.53 (t, 2H, J = 7.6 Hz), 7.71 (s, 2H), 7.78 (dd, 2H, J_1 = 7.6, J_2 = 0.9 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 54.1, 64.0, 120.1, 121.1, 123.4, 124.9, 128.4, 128.7, 129.0, 133.9, 134.6, 134.7, 144.2, 157.7, 182.4, 183.5; MS: m/z (%) = 584 (M^+ + 2, 1.4), 583 (M^+ + 1, 4.9), 582 (M^+, 5.3), 411 (3.5), 250 (3.0), 240 (12.0), 144 (27.4), 91 (100); anal. calcd. for $C_{34}H_{26}N_6O_4$ (582.608): C 70.09, H 4.50; found: C 70.21, H 4.66.

1-Benzyl-4-butyl-1*H*-1,2,3-triazole (15): Purification by plate chromatography, eluting with n-*h*exane/ethyl acetate (10/2), gave compound **15** in 76% yield; IR (neat): ν = 698 (s), 737 (s), 1018 (s), 1207 (m), 1454 (s), 1497 (m), 2338 (w), 2816 (m), 2874 (m), 3028 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.81 (t, 3H, J = 7.0 Hz), 1.17–1.56 (m, 4H), 2.35–2.62 (m, 2H), 5.38 (s, 2H), 7.03–7.26 (m, 5H), 7.38 (s, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 13.8, 22.7, 25.3, 31.5, 53.9, 120.5, 126.8, 127.9, 128.9, 134.6, 149.1; anal. calcd. for $C_{13}H_{17}N_3$ (215.294): C 72.52, H 7.96; found: C 72.37, H 7.79.

(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methanol (16): Recrystallization from EtOH/H_2O (3:1) gave compound **16** as colorless crystals in 81% yield; mp 78–78.5 °C; IR (KBr): ν = 690 (s), 721 (s), 769 (m), 841 (s), 1014 (s), 1038 (s), 1130 (m), 1223 (m), 1458 (m), 3263 (br) cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ = 4.65 (s, 2H), 5.40 (s, 2H), 7.17–7.29 (m, 5H), 7.45 (s, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 4.0, 55.8, 122.0, 128.1, 128.7, 129.0, 134.6, 148.3; MS: m/z (%) = 191 (M^+ + 2, 0.1), 190 (M^+ + 1, 0.8), 189 (M^+, 1.1), 160 (3.3), 149 (3.4), 143 (5.2), 130 (6.6), 91 (100), 65 (21.5); anal. calcd. for $C_{10}H_{11}N_3O$ (189.214): C 63.48, H 5.86; found: C 63.62, H 5.73.

2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)-2-propanol (17): Recrystallization from EtOH/H_2O (3:1) gave compound **17** as colorless crystals in 84% yield; mp 77 °C; IR (KBr): ν = 698 (w), 733 (s), 795 (m), 960 (m), 1057 (m), 1173 (s), 1219 (m), 1369 (m), 1458 (m), 1500 (w), 2978 (s), 3310 (br) cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.57 (s, 6H), 3.18 (s, 1H), 5.42 (s, 2H), 7.21–7.36 (m, 5H), 7.39 (s, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 30.4, 54.1, 68.4, 119.2, 128.1, 128.7, 129.1, 134.6, 152.1; MS: m/z (%) = 217 (M^+, 0.5), 204 (0.4), 203 (2.3), 202 (16.0), 201 (3.2), 130 (1.6), 91 (100), 90 (30.3), 65 (18.5); anal. calcd. for $C_{12}H_{15}N_3O$ (217.267): C 66.34, H 6.96; found: C 66.49, H 7.11.

1-Methyl-4-phenyl-1*H*-1,2,3-triazole (18): Recrystallization from EtOH/H_2O (3:1) gave compound **18** as colorless crystals in 86% yield; mp 125 °C; IR (KBr): ν = 698 (s), 768 (s), 976 (w), 1076 (m), 1192 (m), 1219 (m), 1454 (m), 1724 (w), 2932 (m), 3124 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ = 4.15 (s, 3H), 7.30–7.46 (m, 3H), 7.40 (s,1H), 7.82 (dd, 2H, J_1 = 7.1, J_2 = 1.0 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 36.7, 120.6, 125.7, 128.1, 128.8, 130.5; MS: m/z (%) = 160 (M^+ + 1, 4.1), 159 (M^+, 22.5), 130 (44.5), 116 (100), 89 (46.0), 63 (25.0); anal. calcd. for $C_9H_9N_3$ (159.188): C 67.90, H 5.70; found: C 67.79, H 5.57.

1-Allyl-4-phenyl-1*H*-1,2,3-triazole (19): Purification by plate chromatography, eluting with *n*-hexane/ethyl acetate (10/1), gave compound **19** in 83% yield; IR (neat): ν = 698 (s), 764 (s), 933 (w), 991 (w), 1045 (w), 1076 (w), 1443 (m), 1608 (w), 1720 (m), 2928 (m), 3074 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ = 4.96 (d, 2H, J = 6.1 Hz), 5.29 (dd, 2H, J_1 = 16.9, J_2 = 10.2 Hz), 5.86–6.08 (m, 1H), 7.23–7.42 (m, 3H), 7.69 (s, 1H), 7.76 (dd, 2H, J_1 = 8.5, J_2 = 1.1 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 52.8, 118.7, 119.4, 120.2, 125.7, 128.2, 128.8, 129.0, 129.5, 131.3; anal. calcd. for $C_{11}H_{11}N_3$ (185.225): C 71.33, H 5.99; found: C 71.19, H 5.79.

4-Phenyl-1-[(4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl]-1*H*-1,2,3-triazole (20): Recrystallization from EtOH/H_2O (3:1) gave compound **20** as colorless crystals in 71% yield; mp 243 °C; IR (KBr): ν = 521 (w), 690 (s), 760 (s), 914 (w), 984 (m), 1041 (m), 1080 (s), 1188 (s), 1230 (m), 1427 (m), 1458 (m), 3016 (w), 3082 (s) cm^{-1}; ^1H NMR (DMSO-d_6, 250 MHz): δ = 7.12 (s, 2H), 7.30–7.51 (m, 6H), 7.84 (d, 2H, J = 7.2 Hz); ^{13}C NMR (DMSO-d_6, 62.9 MHz): δ = 35.1, 37.5, 47.4, 51.6, 52.3, 66.7, 77.6, 80.9, 112.3, 122.0, 146.0, 167.2; MS: m/z (%) = 304 (M^+ + 2, 0.9), 303 (M^+ + 1, 4.6), 302 (M^+, 7.0), 262 (9.1), 245 (9.6), 231 (0.9), 194 (4.5), 171 (8.2), 129 (94.0), 103 (41.5), 83 (47.5), 69 (62.6), 55 (100); anal. calcd. for $C_{17}H_{14}N_6$ (302.333): C 67.54, H 4.67; found: C 67.66, H 4.78.

4-Phenyl-1-(2-{2-[2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)ethoxy]phenoxy}ethyl)-1*H*-1,2,3-triazole (22): Recrystallization from EtOH gave compound **22** as colorless crystals in 69% yield; mp 107–108 °C; IR (KBr): ν = 690 (s), 744 (s), 764 (s), 1049 (s), 1126 (s), 1219 (s), 1257 (s), 1450 (m), 1508 (s), 1593 (m), 2098 (w), 2874 (w), 3128 (m), 3445 (m) cm^{-1}; ^1H NMR

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($CDCl_3$, 250 MHz): δ = 4.27 (t, 4H, *J* = 5.1 Hz), 4.64 (t, 4H, *J* = 5.1 Hz), 6.74–6.88 (m, 4H), 7.19–7.36 (m, 6H), 7.71–7.76 (m, 4H), 7.89 (s, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 49.9, 67.9, 115.5, 121.1, 122.8, 125.6; MS: *m*/*z* (%) = 424 (M^+-N_2, 5.0), 423 (3.3), 245 (15.0), 144 (39.2), 121 (100.0), 91 (91.7), 83 (94.2), 57 (65.8); anal. calcd. for $C_{26}H_{24}N_6O_2$ (452.508): C 69.01, H 5.35; found: C 68.87, H 5.51.

4-Phenyl-1-(2-phenylethyl)-1*H*-1,2,3-triazole (23): Recrystallization from EtOH/H_2O (3:1) gave compound **23** as colorless crystals in 85% yield; mp 139 °C; IR (KBr): ν = 694 (s), 734 (m), 764 (s), 845 (w), 976 (w), 1084 (m), 1223 (m), 1454 (m), 3086 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.25 (t, 2H, *J* = 7.2 Hz), 4.63 (t, 8H, *J* = 7.2 Hz), 7.14 (d, 2, *J* = 7.6 Hz), 7.25–7.44 (m, 6H), 7.47 (s, 1H), 7.77 (d, 2H, *J* = 7.1 Hz), 7.66 (t, 2H, *J* = 8.1 Hz), 7.89 (d, 2H, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 36.7, 51.7, 120.1, 125.7, 127.1, 128.1, 128.8, 130.8, 137.1, 147.4; MS: *m*/*z* (%) = 251 (M^++2, 1.4), 250 (M^++1, 6.1), 249 (M^+, 14.6), 220 (12.1), 193 (7.9), 179 (4.7), 130 (26.4), 118 (53.0), 105 (100), 77 (51.3), 51 (25.6); anal. calcd. for $C_{16}H_{15}N_3$ (249.311): C 77.08, H 6.06; found: C 76.93, H 5.91.

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