

An Efficient Synthesis of 1,4-Disubstituted Triazoles in Water via CuCl₂/Zn-Catalyzed Huisgen Cycloaddition

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An efficient method for the synthesis of 1,4-disubstituted triazoles in water at room temperature has been developed using CuCl₂/Zn as a catalyst system. Under the optimized conditions, a novel series of 1,4-disubstituted 1,2,3-triazoles were synthesized.

Key words: Huisgen Cycloaddition, CuCl₂/Zn, 1,4-Disubstituted Triazole

Introduction

Triazoles are an important class of heterocyclic compounds. In recent years 1,2,3-triazoles gained more and more interest due to their diverse biological activities and synthetic methodology [1–3]. An efficient approach for constructing the 1,2,3-triazole unit is the copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) reaction, which was discovered independently by the groups of Sharpless and Meldal [4, 5].

The sources of the copper(I) catalyst for a CuAAC reaction usually are Cu(I) salts, or Cu(II) salts together with a reducing agent (often sodium ascorbate or metallic copper). Furthermore, it was reported that metallic copper can be an alternative source for the CuAAC reaction. Using metallic copper as the catalyst was attractive because of a much easier work-up and purification. Unfortunately, the reaction times are usually long when using metallic copper as the catalyst [6, 7], except when physical techniques such as ultrasound irradiation are used [8]. In order to shorten the reaction time, nanosized copper was used as the catalyst. Orgueira successfully performed a CuAAC reaction utilizing an activated nanosized copper powder as the source of the catalytic species in the presence of amine hydrochloride salts [9]. A CuAAC reaction reported by Pachón was carried out in *t*-BuOH/H₂O catalyzed by copper nanoclusters, and it took 18 h to complete the reaction [10]. In comparison with the nanosized copper mentioned above, copper nanoparticles prepared by mixing copper(II) chloride, lithium metal and a catalytic amount of 4,4'-di-*tert*-butyl-biphenyl (DTBB) in THF at r. t., showed a better catalytic effi-

ciency. The CuAAC reaction catalyzed by these copper nanoparticles was completed within 30 min [11]. Some supported catalysts [12, 13] were also successfully applied. It is worth to mention that alumina-supported copper nanoparticles, prepared by Kantam from copper(II) acetylacetonate and aluminum isopropoxide precursors using an aerogel protocol, were successfully applied in a three-component CuAAC reaction among terminal alkynes, sodium azide and alkyl/allyl halides [12]. The application of solution-state copper nanoparticles is a useful way to avoid the aggregation of nanoparticles. For instance, Sarka used PVP-stabilized copper nanoparticles in DMF or formamide as a catalyst for the CuAAC reaction [14]. However, the nanosized copper has limited application due to its complicated and costly preparation.

Metallic copper could also be generated *in situ* in a redox reaction between CuSO₄ and Zn. The catalytic activity effect of the CuSO₄/Zn powder in the CuAAC reaction led to a further study of this catalyst system. In the work described in this paper, an efficient method for 1,3-dipolar cycloadditions at relatively mild and environmentally friendly conditions is established. The *in situ* generated copper from CuCl₂/Zn powder in water was directly used as a catalyst without a stabilizing agent.

Results and Discussion

The CuAAC reaction between propargyl phenyl ether and benzyl azide was selected as a model reaction to optimize the reaction conditions (Scheme 1). For screening the suitable solvent, the model reaction cat-



Scheme 1. Model reaction of cycloaddition for optimizing the reaction conditions.

Table 1. Screening of solvents for the model reaction using CuSO₄ (10 mol-%)/Fe powder (10 mol-%) as the catalyst system.^a

Entry	Solvent	Time (min)	Yield (%) ^b
1	H ₂ O	150	82
2	H ₂ O/DMF	150	21
3	H ₂ O/DMSO	150	60
4	H ₂ O/ <i>t</i> -BuOH	150	10
5	H ₂ O/EtOH	150	57
6	H ₂ O/CHCl ₃	150	38
7	H ₂ O/THF	150	11
8	H ₂ O/CH ₃ CN	150	30
9	DMF	150	15

^a Model reaction conditions: propargyl phenyl ether (1 mmol), benzyl azide (1 mmol), solvent 6 mL, the equal volume mixed for co-solvent; ^b isolated yield.

alyzed by the CuSO₄ (10 mol-%)/Fe powder (10 mol-%) system was carried out in different solvents (including water, pure organic solvents or their co-mixtures) with vigorous magnetic stirring at r. t. for 150 min as shown in Table 1. Among the tested solvents, the highest yield was obtained in water (82%). The moderate yield obtained in H₂O-DMSO or H₂O-EtOH at a ratio of 1:1 (v/v) is 60 and 57%, respectively. Although propargyl phenyl ether and benzyl azide have a good solubility in the tested organic solvents (such as DMF, DMSO and *t*-BuOH), the yield was not more than 15%. The poor yield might be attributed to the poor solubility of CuSO₄ and Fe powder in organic solvents, which hampered the generation of metallic copper. The yield increases in the order: organic solvent, co-solvent, water. Thus water was selected as the reaction solvent.

Different copper(II) salts (10 mol-%) together with Zn or Fe powder (10 mol-%) shown in Table 2 were screened for the catalytic efficiency of the model reaction. All the reactions were performed in water with vigorous stirring for 60 min. Among the tested catalytic systems, the best catalytic efficiency was observed for the CuCl₂/Zn powder. The 1,3-dipolar cycloaddition reaction catalyzed by this system was completed within 60 min in 90% yield (Table 2). In comparison to CuCl₂/Zn powder, lower catalytic efficiencies were observed for other copper(II) salt/metallic powder catalysts, among which Cu(OAc)₂/Fe powder showed the lowest (9%) and CuCl₂/Zn powder the highest (90%) yield. The catalytic efficiency of the

Table 2. Screening of catalysts for the model reaction in water for 60 min.^a

Entry	Catalyst system (10 mol-%)	Time (min)	Yield (%) ^b
1	CuSO ₄ /Fe	60	42
2	CuSO ₄ /Zn	60	75
3	CuCl ₂ /Fe	60	29
4	CuCl ₂ /Zn	60	90
5	Cu(OAc) ₂ /Fe	60	9
6	Cu(OAc) ₂ /Zn	60	34
7	CuBr ₂ /Fe	60	17
8	CuBr ₂ /Zn	60	70

^a Model reaction conditions: propargyl phenyl ether (1 mmol), benzyl azide (1 mmol), solvent 6 mL, the equal volume mixed for co-solvent; ^b isolated yield.

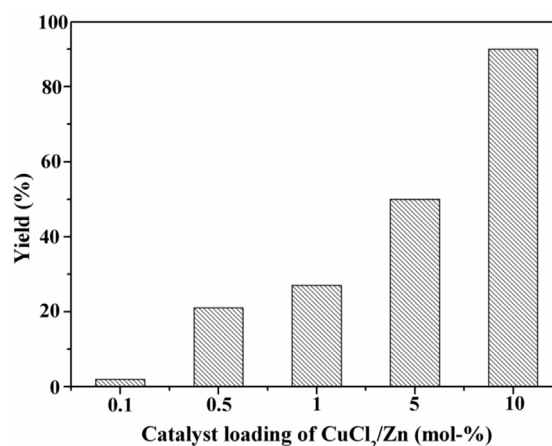


Fig. 1. Screening of catalyst loading for the model reaction in water for 60 min.

copper(II) salt/Zn powder is better than that of the copper(II) salt/Fe powder, because Zn is more active than Fe in the redox reaction.

In order to investigate the influence of smaller amounts of the copper(II) salt/Zn powder on the model reaction, the amounts of the CuCl₂/Zn powder were reduced to 5, 1, 0.5, and 0.1 mol-%. As shown in Fig. 1, the yield decreased from 90 to 2% indicating that the catalytic efficiency of the catalyst system CuCl₂/Zn powder decreased when lower catalyst loading was used, and the reaction takes more time to be finished. When CuCl₂ (5 mol-%)/Zn powder (5 mol-%) was used as the catalyst, 2.5 h were needed to complete the model reaction. Considering the catalytic efficiency, CuCl₂ (10 mol-%)/Zn powder (10 mol-%) was selected as the optimized catalyst.

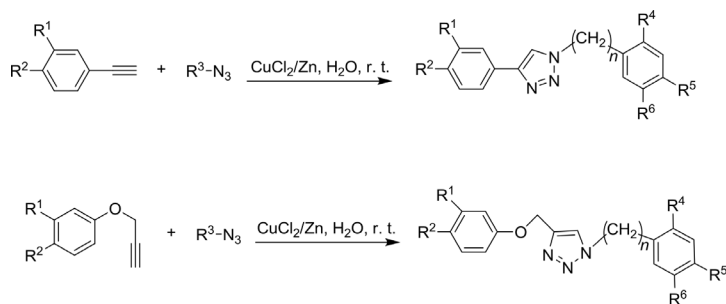
Scheme 2. Synthesis of compounds **1–8**.

Table 3. Synthesis of 1,4-disubstituted 1,2,3-triazoles (Scheme 2).

Compd.	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶	<i>n</i>	Time (min)	Yield (%)
1	H	CH ₃	benzyl	H	NO ₂	H	1	90	83
2	H	CH ₃	phenyl	CH ₃	H	NO ₂	0	80	80
3	H	C ₃ H ₇	phenyl	CF ₃	H	H	0	50	90
4	H	C ₃ H ₇	phenyl	CH ₃	H	NO ₂	0	75	87
5	NH ₂	H	phenyl	CF ₃	H	H	0	80	84
6	H	NO ₂	phenyl	CH ₃	H	NO ₂	0	75	82
7	H	Cl	benzyl	H	NO ₂	H	1	85	85
8	OCH ₃	H	phenyl	CH ₃	H	NO ₂	0	60	88

The optimized relative quantities of reactants, catalyst and solvent are: organic azide (1.0 mmol), terminal alkyne (1.0 mmol), CuCl₂ (10 mol-%)/Zn powder (10 mol-%) and water (6 mL).

A series of 1,4-disubstituted 1,2,3-triazole derivatives were synthesized based on the optimized conditions (Scheme 2, Table 3). As shown in Table 3, reactions between substituted terminal alkynes and organic azides, including benzyl azide and phenyl azide gave 1,4-disubstituted 1,2,3-triazoles in good yields.

In summary, an efficient protocol for the synthesis of a series of 1,2,3-triazole derivatives was established using CuCl₂ (10 mol-%)/Zn powder (10 mol-%) as the catalyst and water as the solvent.

Experimental Section

General

All the chemicals were obtained from Tianjin Kermel Chemical Reagent Co., Ltd. and were used as received. All melting points were determined on a YUHUA X-3 melting point apparatus and are uncorrected. IR spectra were recorded on a Bio-rad FTS-40 spectrometer. ¹H and ¹³C spectra were recorded on a Bruker Avance 400 MHz spectrometer operating at 400.13 and 100.61 MHz, respectively. NMR spectra were recorded in CDCl₃ or [D₆]DMSO at r. t. (20 ± 2 °C). ¹H and ¹³C chemical shifts are quoted in parts per million downfield from TMS. ESI MS were recorded on a Bruker Esquire 3000 instrument. High-resolution mass spec-

tra (HRMS) were performed on a MicrOTOF-Q II mass spectrometer with an ESI source (Waters, Manchester, UK). Substituted terminal alkynes were synthesized according to the literature [15–19]. Benzyl azide [20] was also synthesized according to previous reports.

General procedure for the synthesis of triazoles

A mixture of the organic azide (1.0 mmol), the terminal alkyne (1.0 mmol) and CuCl₂ (10 mol-%)/Zn powder (10 mol-%) in water (6 mL) was vigorously stirred at r. t. After completion of the reaction as indicated by TLC, the reaction mixture was diluted with saturated aq. NH₄Cl (20 mL) and extracted with CH₂Cl₂ (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous Na₂SO₄ and filtered. The solvent of the filtrate was removed *in vacuo* to give the pure product.

1-(4-Nitrobenzyl)-4-(*p*-tolyl)-1,2,3-triazole (**1**)

M. p. 145–147 °C. – IR (KBr): ν (cm⁻¹) = 3097, 3047, 2921, 2851, 1670, 1605, 1556, 1515, 1456, 1427, 1350, 820, 731. – ¹H NMR (400 MHz, CDCl₃): δ = 8.21 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.74 (s, 1H, CH-H), 7.69 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.43 (d, *J* = 12.0 Hz, 2H, Ar-H), 7.22 (d, *J* = 8.0 Hz, 2H, Ar-H), 5.68 (s, 2H, CH₂-H), 2.37 (s, 3H, CH₃-H). – ¹³C NMR (100 MHz, CDCl₃): δ = 148.6, 147.8, 142.0, 138.3, 129.6, 128.5, 127.3, 125.6, 124.2, 119.8, 53.0, 21.3. – MS (ESI): *m/z* (%) = 295 (100) [M+H]⁺. – HRMS ((+)-ESI): *m/z* = 295.1197 (calcd. 295.1195 for C₁₆H₁₅N₄O₂, [M+H]⁺).

1-(2-Methyl-5-nitrophenyl)-4-(*p*-tolyl)-1,2,3-triazole (**2**)

M. p. 102–103 °C. – IR (KBr): ν (cm⁻¹) = 3135, 3117, 3065, 3030, 2980, 2921, 2859, 1633, 1600, 1521, 1440, 1380, 1350, 810, 797, 739, 706. – ¹H NMR (400 MHz, CDCl₃): δ = 8.30 (s, 1H, Ar-H), 8.28 (d, *J* = 4.0 Hz, 1H, Ar-H), 8.02 (s, 1H, CH-H), 7.80 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.60 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.28 (d, *J* = 8.0 Hz, 2H, Ar-H), 2.43 (s, 3H, CH₃-H), 2.41 (s, 3H, CH₃-H). – ¹³C NMR (100 MHz, CDCl₃): δ = 148.2, 146.4, 141.6, 138.6, 136.8, 132.6, 129.7, 126.9, 125.7, 124.2, 121.1, 120.7, 21.3, 18.6. – MS (ESI):

m/z (%) = 295 (100) $[M+H]^+$. – HRMS ((+)-ESI): m/z = 295.1197 (calcd. 295.1195 for $C_{16}H_{15}N_4O_2$, $[M+H]^+$).

1-[2-(Trifluoromethyl)phenyl]-4-(4-propylphenyl)-1,2,3-triazole (3)

M.p. 87–89 °C. – IR (KBr): ν (cm^{-1}) = 3125, 3103, 2964, 2932, 2860, 1643, 1609, 1591, 1513, 1495, 1460, 1377, 1319, 835, 806, 767, 704. – 1H NMR (400 MHz, $CDCl_3$): δ = 8.02 (s, 1H, CH-H), 7.88 (d, J = 8.0 Hz, 1H, Ar-H), 7.82 (d, J = 8.0 Hz, Ar-H), 7.76 (t, J = 8.0 Hz, 16.0 Hz, 1H, Ar-H), 7.69 (t, J = 8.0 Hz, 16.0 Hz, Ar-H), 7.61 (d, J = 8.0 Hz, 1H, Ar-H), 7.28 (d, J = 8.0 Hz, 2H, Ar-H), 2.63 (t, J = 4.0 Hz, 12.0 Hz, 2H, CH_2 -H), 1.63–1.72 (m, 2H, CH_2 -H), 0.96 (t, J = 4.0 Hz, 12.0 Hz, 3H, CH_3 -H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.9, 143.2, 135.1, 134.9, 133.1, 130.4, 129.0, 128.9, 127.4, 127.3, 126.3, 125.8, 121.9, 37.8, 24.5, 13.8. – MS (ESI): m/z (%) = 332 (100) $[M+H]^+$. – HRMS ((+)-ESI): m/z = 332.1378 (calcd. 332.1375 for $C_{18}H_{17}N_3O_3$, $[M+H]^+$).

1-(2-Methyl-5-nitrophenyl)-4-(4-propylphenyl)-1,2,3-triazole (4)

M.p. 93–95 °C. – IR (KBr): ν (cm^{-1}) = 3111, 2957, 2930, 2868, 1600, 1539, 1523, 1498, 1450, 1434, 1379, 1350, 837, 797, 710. – 1H NMR (400 MHz, $[D_6]DMSO$): δ = 9.07 (s, 1H, CH-H), 8.42 (d, J = 4.0 Hz, 1H, Ar-H), 8.37 (dd, J = 4.0 Hz, 12.0 Hz, 1H, Ar-H), 7.85 (dd, J = 8.0 Hz, 32.0 Hz, 3H, Ar-H), 7.32 (d, J = 8.0 Hz, 2H, Ar-H), 2.60 (t, J = 8.0 Hz, 16.0 Hz, 2H, CH_2 -H), 2.40 (s, 3H, CH_3 -H), 1.58–1.68 (m, 2H, CH_2 -H), 0.92 (t, J = 8.0 Hz, 16.0 Hz, 3H, CH_3 -H). – ^{13}C NMR (100 MHz, $[D_6]DMSO$): δ = 147.3, 146.5, 142.7, 141.6, 137.0, 133.3, 129.3, 128.0, 125.8, 124.5, 123.2, 121.2, 37.4, 24.4, 18.6, 14.0. – MS (ESI): m/z (%) = 323 (100) $[M+H]^+$. – HRMS ((+)-ESI): m/z = 323.1511 (calcd. 323.1508 for $C_{18}H_{19}N_4O_2$, $[M+H]^+$).

3-(1-(2-(Trifluoromethyl)phenyl)-1,2,3-triazol-4-yl)benz-enamine (5)

M.p. 146–147 °C. – IR (KBr): ν (cm^{-1}) = 3396, 3120, 3090, 3074, 3050, 2925, 2854, 1627, 1607, 1590, 1512, 1491, 1462, 1450, 1350, 1313, 1279, 1178, 793, 772, 696. – 1H NMR (400 MHz, $[D_6]DMSO$): δ = 8.85 (s, 1H, CH-H), 8.06 (d, J = 8.0 Hz, 1H, Ar-H), 7.96 (t, J = 8.0 Hz, 16.0 Hz, 1H, Ar-H), 7.88 (t, J = 8.0 Hz, 16.0 Hz, 1H, Ar-H), 7.81 (d, J = 8.0 Hz, 1H, Ar-H), 7.20 (s, 1H, Ar-H), 7.11 (t, J = 8.0 Hz, 16.0 Hz, 1H, Ar-H), 7.02 (d, J = 8.0 Hz, 1H, Ar-H), 6.57 (d, J = 8.0 Hz, 1H, Ar-H), 5.25 (s, 2H, NH_2). – ^{13}C NMR (100 MHz, $[D_6]DMSO$): δ = 149.6, 147.6, 134.8, 134.4, 131.6, 130.9, 129.9, 129.8, 127.9, 127.9, 124.1, 121.9, 114.4, 113.6, 111.0. – MS (ESI): m/z (%) = 305 (100) $[M+H]^+$. – HRMS ((+)-ESI): m/z = 305.1011 (calcd. 305.1014 for $C_{15}H_{12}N_4F_3$, $[M+H]^+$).

4-[(4-Nitrophenoxy)methyl]-1-(2-methyl-5-nitrophenyl)-1,2,3-triazole (6)

M.p. 183–185 °C. – IR (KBr): ν (cm^{-1}) = 3156, 3120, 3085, 2927, 1610, 1594, 1530, 1510, 1498, 1470, 1383, 1345, 1112, 844, 819, 798, 750. – 1H NMR (400 MHz, $[D_6]DMSO$): δ = 8.85 (s, 1H, CH-H), 8.37 (d, J = 8.0 Hz, 2H, Ar-H), 8.26 (d, J = 12.0 Hz, 2H, Ar-H), 7.82 (d, J = 8.0 Hz, 1H, Ar-H), 7.34 (d, J = 12.0 Hz, 2H, Ar-H), 5.46 (s, 2H, CH_2 -H), 2.32 (s, 3H, CH_3 -H). – ^{13}C NMR (100 MHz, $[D_6]DMSO$): δ = 163.6, 146.5, 142.7, 141.8, 141.5, 136.8, 133.3, 127.3, 126.3, 124.8, 121.5, 115.8, 62.2, 18.4. – MS (ESI): m/z (%) = 356 (100) $[M+H]^+$. – HRMS ((+)-ESI): m/z = 356.0997 (calcd. 356.0995 for $C_{16}H_{14}N_5O_5$, $[M+H]^+$).

4-[(4-Chlorophenoxy)methyl]-1-(4-nitrobenzyl)-1,2,3-triazole (7)

M.p. 90–91 °C. – IR (KBr): ν (cm^{-1}) = 3112, 3062, 2960, 2897, 2870, 1624, 1609, 1594, 1580, 1532, 1490, 1462, 1433, 1350, 822, 723. – 1H NMR (400 MHz, $[D_6]DMSO$): δ = 8.37 (s, 1H, CH-H), 8.25 (d, J = 8.0 Hz, 2H, Ar-H), 7.53 (d, J = 8.0 Hz, 2H, Ar-H), 7.34 (d, J = 8.0 Hz, 2H, Ar-H), 7.07 (d, J = 12.0 Hz, 2H, Ar-H), 5.81 (s, 2H, CH_2 -H), 5.16 (s, 2H, CH_2 -H). – ^{13}C NMR (100 MHz, $[D_6]DMSO$): δ = 157.2, 147.6, 134.8, 143.3, 129.7, 129.4, 125.7, 125.1, 124.3, 116.9, 61.8, 52.4. – MS (ESI): m/z (%) = 345 (100) $[M+H]^+$. – HRMS ((+)-ESI): m/z = 345.0752 (calcd. 345.0754 for $C_{16}H_{14}ClN_4O_3$, $[M+H]^+$).

5-[(3-Methoxyphenoxy)methyl]-1-(2-methyl-5-nitrophenyl)-1,2,3-triazole (8)

M.p. 93–95 °C. – IR (KBr): ν (cm^{-1}) = 3157, 3086, 2966, 2943, 2875, 2838, 1670, 1610, 1596, 1526, 1494, 1456, 1439, 1376, 1351, 1153, 758, 741. – 1H NMR (400 MHz, $[D_6]DMSO$): δ = 8.78 (s, 1H, CH-H), 8.36 (d, J = 8.0 Hz, 2H, Ar-H), 7.81 (d, J = 8.0 Hz, 1H, Ar-H), 7.22 (t, J = 8.0 Hz, 16.0 Hz, 1H, Ar-H), 6.66–6.69 (m, 2H, Ar-H), 6.57 (d, J = 8.0 Hz, 1H, Ar-H), 5.25 (s, 2H, CH_2 -H), 3.75 (s, 3H, CH_3 -H), 2.32 (s, 3H, CH_3 -H). – ^{13}C NMR (100 MHz, $[D_6]DMSO$): δ = 160.9, 159.7, 146.5, 143.6, 141.7, 136.9, 133.2, 130.4, 126.8, 124.6, 121.4, 107.3, 107.1, 101.4, 61.4, 55.5, 18.4. – MS (ESI): m/z (%) = 341 (100) $[M+H]^+$. – HRMS ((+)-ESI): m/z = 341.1253 (calcd. 341.1250 for $C_{17}H_{17}N_4O_4$, $[M+H]^+$).

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