EurJOC European Journal of Organic Chemistry

FULL PAPER

DOI: 10.1002/ejoc.201201696

CuI-Catalyzed Synthesis of Functionalized Terminal Allenes from 1-Alkynes

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Keywords: Synthetic methods / Heterogeneous catalysis / Copper / Alkynes / Allenes

Relative to our original protocol that uses CuI (0.5 equiv.), paraformaldehyde (2.5 equiv.), and dicyclohexylamine (1.8 equiv.), a facile and efficient protocol for the gram-scale synthesis of functionalized terminal allenes by using CuI (7.5–10 mol-%), paraformaldehyde (1.6 equiv.), and diisopropylamine (1.4 equiv.) has been developed. This method accommodates different functional groups such as hydroxy or carbonyl, and it also performed well in the synthesis of allenylamides and 2,3-butadien-1-ol.

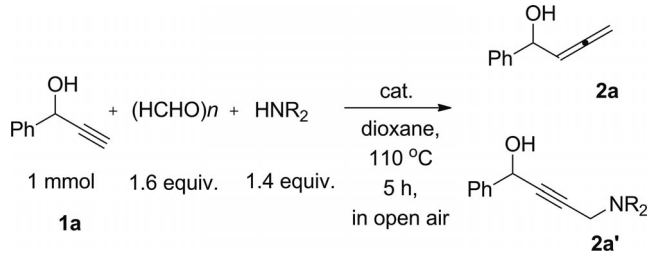
Introduction

As a useful class of compounds, allenes not only act as versatile intermediates in organic synthesis,[1,2] but also exist in many natural products and pharmaceuticals.[3] Thus, efficient synthetic methods for allenes from readily available materials are highly desirable.[2h,4] So far, several one-step syntheses of terminal allenes from 1-alkynes with paraformaldehyde in the presence of amines and Cu^I salts have been developed.[5,6a] Recently, this group developed several methods for constructing terminal or 1,3-disubstituted allenes from 1-alkynes, aldehydes and amines.[6] However, each of them needs substoichiometric metal salts and an excess of paraformaldehyde, which is the obvious shortcoming for any large-scale synthesis. Herein, we wish to report a facile and efficient CuI-catalyzed gram-scale synthesis of functionalized terminal allenes from 1-alkynes, paraformaldehyde, and diisopropylamine.

Results and Discussion

In our previous work to prepare 1,3-disubstituted allenes with CuI as the catalyst, we carried out one example synthesis of a terminal allene. The reaction of CuI (10 mol-%), 1-(4-chlorophenyl)-2-propyn-1-ol (**1d**), paraformaldehyde (1.6 equiv.) and di(*n*-butyl)amine (1.4 equiv.) in dioxane at 130 °C afforded 1-(4-chlorophenyl)buta-2,3-dien-1-ol (**2d**) in 67% yield.[7] To develop a general catalytic version to synthesize terminal allenes, we started the initial study by using 1-phenyl-2-propyn-1-ol (**1a**), paraformaldehyde, diisopropylamine, and CuI (10%) in dioxane at 110 °C. This experiment afforded allenol **2a** in 88% yield according to NMR spectroscopic data (Table 1, Entry 1). To improve the yield, the effect of the amine, which was an important parameter in the CuI-catalyzed synthesis of 1,3-disubstituted allenes,[7] was investigated. Dicyclohexylamine also performed well to give **2a** in 84% yield according to NMR spectroscopic data (Table 1, Entry 2).[6a] However, morpholine, which was used in the ZnI_2-mediated synthesis of 1,3-disubstituted allenes,[6b] failed to give any allene product (Table 1, Entry 3).

Table 1. Optimization of conditions for the reaction of 1-phenyl-2-propyn-1-ol (**1a**) with paraformaldehyde, amine, and metal catalyst.



Entry	Amine	Catalyst [mol-%]	Conc. [M]	Yield of **2a**/**2a**′ [%][a]
1	iPr_2NH	CuI (10)	0.67	88:9
2	Cy_2NH	CuI (10)	0.67	84:11
3	morpholine	CuI (10)	0.67	–/92
4	iPr_2NH	CuBr (10)	0.67	66:23
5	iPr_2NH	ZnI_2 (10)	0.67	25:60
6	iPr_2NH	CuI (10)	0.4	84:14
7	iPr_2NH	CuI (10)	0.5	85:12
8	iPr_2NH	CuI (10)	1	86:7
9[b]	iPr_2NH	CuI (7.5)	0.67	88[c]/–

[a] The yield was determined by ^1H NMR spectroscopic analysis with 1,3,5-trimethylbenzene as the internal standard. [b] The reaction was conducted with on a 10 mmol scale of **1a** for 10 h. [c] Isolated yield.

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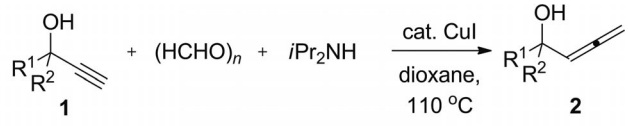
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201201696.

By using diisopropylamine as the amine, a further study on different metal catalysts was investigated. It was noted that CuI was a better catalyst than CuBr and ZnI_2 (Table 1, Entries 4 and 5). Subsequent study on reagent concentration revealed that the amount of solvent has limited influence in the yield (Table 1, Entries 6–8). When the reaction was carried out on a 10 mmol scale, it proceeded smoothly to afford **2a** in 88% isolated yield with CuI (7.5 mol-%) without any intermediate product **2a′** (Table 1, Entry 9). Relative to the reports of Crabbé, which used a mixture of 1-alkyne, paraformaldehyde, diisopropylamine and CuBr in a ratio 1.0:2.5:2.0:0.5,[5c] and our previous work,[6a] which improved the yield of allene products by using paraformaldehyde (2.5 equiv.), dicyclohexylamine (1.8 equiv.) and CuI (0.5 equiv.), and the work of Nakamura,[5d] which decreased the amount of CuBr catalyst to 0.3 equiv., but required high temperatures and microwave irradiation, this protocol has the obvious advantage with respect of the amount of catalyst and paraformaldehyde. It should be noted that all reactions in this study were carried out without the protection of an inert atmosphere. Thus, we defined the reaction of 1-alkynes (10 mmol) with paraformaldehyde (1.6 equiv.), diisopropylamine (1.4 equiv.), and CuI (7.5 mol-%) in dioxane at 110 °C as the standard for the study on the scope of this procedure.

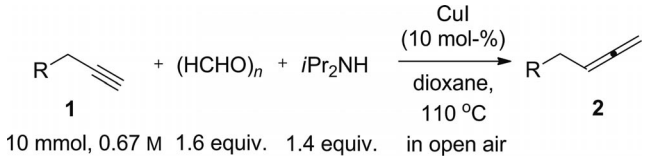
With the standard conditions in hand, the substrate scope and generality of the reaction was investigated and the results summarized in Table 2. The reaction of secondary alcohols **1b**–**1f** bearing electron-donating or electron-withdrawing substituents, such as *o*/*p*-OMe, *p*-Cl, or *m*-NO_2 on the phenyl group afforded the corresponding allenols **2b**–**2f** in good yields (Table 2, Entries 2–6). It should be noted that under this set of reaction conditions, allenol **2d** can be synthesized in 88% yield, an improvement of 21%.[7] For alkyl- or heterocyclic-substituted substrates, the reaction also proceeded smoothly to afford α-allenols in moderate to good yields (Table 2, Entries 7–12). When tertiary propargylic alcohols were applied (R^1, $R^2 \neq H$), a longer reaction time and a slightly higher catalyst loading were needed to obtain satisfactory results (Table 2, Entries 13–15). To our delight, this protocol is also suitable for the synthesis of allenes with ether or thioether functionality (Table 3).

Table 2. The CuI-catalyzed reaction of substituted propargylic alcohols, paraformaldehyde, and *i*-Pr_2NH in dioxane.



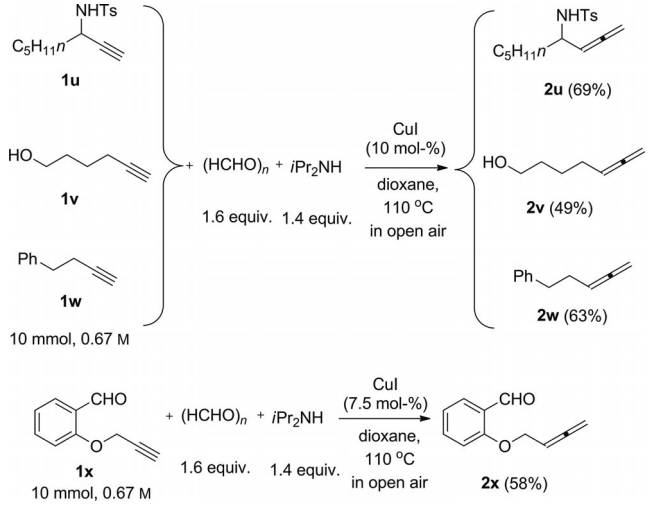
Entry	R^1/R^2	CuI [mol-%]	Time [h]	Isolated yield of **2** [%]
1	Ph/H (**1a**)	7.5	10	88 (**2a**)
2	4-$MeOC_6H_4$/H (**1b**)	7.5	10	79 (**2b**)
3	2-$MeOC_6H_4$/H (**1c**)	7.5	10	87 (**2c**)
4	4-ClC_6H_4/H (**1d**)	7.5	10	88 (**2d**)
5	2,4-$Cl_2C_6H_3$/H (**1e**)	7.5	10	84 (**2e**)
6	3-$O_2NC_6H_4$/H (**1f**)	7.5	10.5	81 (**2f**)
7	2-thienyl/H (**1g**)	7.5	10	86 (**2g**)
8	2-furyl/H (**1h**)	7.5	10	76 (**2h**)
9	nC_5H_{11}/H (**1i**)	7.5	12	77 (**2i**)
10	nC_7H_{15}/H (**1j**)	7.5	12	59 (**2j**)
11	Bn/H (**1k**)	7.5	14	79 (**2k**)
12	*c*Cy/H (**1l**)	10	17	82 (**2l**)
13	Ph/Me (**1m**)	10	23	84 (**2m**)
14	nC_6H_{13}/Me (**1n**)	10	17	74 (**2n**)
15	$-(CH_2)_5-$ (**1o**)	10	21	80 (**2o**)

Table 3. Synthesis of allenes with ether and thioether functionality.



Entry	R	Time [h]	Isolated yield of **2** [%]
1	4-$O_2NC_6H_4O$ (**1p**)	11	76 (**2p**)
2	BnO (**1q**)	12.5	75 (**2q**)
3	TBDMSO (**1r**)	12.5	60 (**2r**)
4	THPO (**1s**)	12.5	66 (**2s**)
5	BnS (**1t**)	16	79 (**2t**)

Moreover, amide, carbonyl, or ω-hydroxy functionality in the substrates is also tolerated on a 10 mmol-scale reaction, affording the products in moderate yields (Scheme 1). The example in Scheme 1 with simple 1-alkyne **1w** as the substrate demonstrates this non-functionalized alkyne is also compatible with this method.

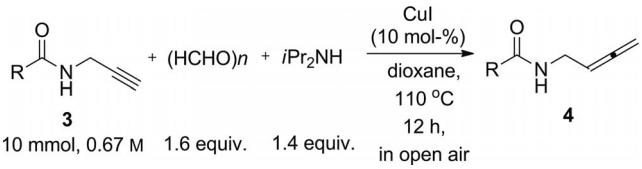


Scheme 1. Synthesis of allenes from functionalized or non-functionalized 1-alkynes.

In 2011, Hashmi et al. synthesized allenylamides **4** by the method of Crabbé[5a,8] with very low yields.[9] To prove the potential of this protocol, a series of experiments were carried out to synthesize this type of product. The substrate

scope and generality of the reaction have been investigated and the results are summarized in Table 4. In all cases this method afforded allenylamides **4** in much higher yield than previously reported. It should be noted that the thiophene-base substrate also gave a good yield of 80%, which means any interaction between the sulfur atom and the copper catalyst does not seriously inhibit the reaction (Table 4, Entry 6).

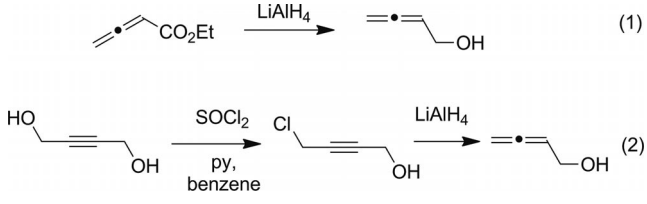
Table 4. The synthesis of allenylamides from propargylic amide, paraformaldehyde, and iPr_2NH in dioxane.



Entry	R	Isolated yield of **4** [%]	Reported yield of **4** [%][a]
1	Ph (**3a**)	78 (**4a**)	34 (**4a**)
2	(*E*)-PhCH=CH (**3b**)	82 (**4b**)	28 (**4b**)
3	2-furyl (**3c**)	84 (**4c**)	55 (**4c**)
4[b]	2,5-dimethylfuran-3-yl (**3d**)	84 (**4d**)	48 (**4d**)
5[c]	5-nitrofuran-2-yl (**3e**)	53 (**4e**)	24 (**4e**)
6	2-thienyl (**3f**)	80 (**4f**)	9 (**4f**)
7	adamantyl (**3g**)	64 (**4g**)	15 (**4g**)
8	EtO_2C (**3h**)	48 (**4h**)	4 (**4h**)
9	EtO_2CCH_2 (**3i**)	28 (**4i**)	8 (**4i**)
10	$EtO_2CCH_2CH_2$ (**3j**)	64 (**4j**)	8 (4j)

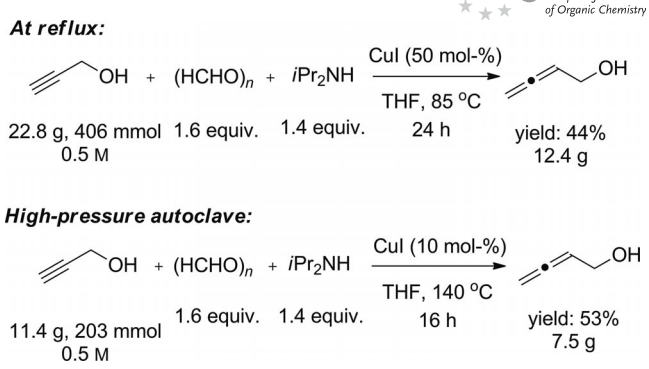
[a] Conditions in ref.[9a]: Propargylic amide (1 equiv.) with paraformaldehyde (2 equiv.), diisopropylamine (2 equiv.), and CuBr (0.3 equiv.) in dioxane at 100 °C. [b] 1-alkyne (7 mmol) was used. [c] Reaction time of 24 h.

Buta-2,3-dien-1-ol is a very simple but useful reagent in organic synthesis.[3d,10] Traditional methods to synthesize this compound often require a multistep manipulation from but-2-yn-1,4-diol, and $LiAlH_4$ as the reducing reagent in the last step (Scheme 2).[3d,10a–10c]



Scheme 2. Typical method for the synthesis of buta-2,3-dien-1-ol.

After extensive screening, tetrahydrofuran (THF) was used instead of dioxane for the purpose of easy separation, and we established two procedures to afford buta-2,3-dien-1-ol (Scheme 3): (1) with heating to reflux, propargyl alcohol (0.4 mol) reacts smoothly to afford 40–45% yield of the product with CuI (0.5 equiv.). Here a catalytic amount of CuI is not effective; and (2) interestingly, under high-pressure autoclave conditions, CuI (10 mol-%) is sufficient to get a better result of 50–53% yield (see Scheme 3).



Scheme 3. Gram-scale synthesis of buta-2,3-dien-1-ol.

Conclusions

In conclusion, we have developed an efficient catalytic synthesis of functionalized terminal allenes from readily available terminal alkynes, paraformaldehyde and diisopropylamine. The high compatibility of functional groups indicates the high potential of this protocol. Based on this protocol, we developed two practical procedures to obtain useful reagent 2,3-butadien-1-ol on a 12 g or 7 g scale. Owing to the easy availability of all the reagents, high potential of the functionalized allenes, and simple operation as well as its catalytic nature, this method will be of interest to organic and medicinal chemists although it is still somewhat lower-yielding relative to the reaction using CuI (0.5 equiv.) and Cy_2NH (1.8 equiv.).[6a] Further studies in this area are being actively pursued in our laboratory.

Experimental Section

General Information: All reactions were carried out in oven-dried three-neck round-bottom flasks. Paraformaldehyde (≥ 94.0%) and CuI (≥ 99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. and used without further treatment. Dioxane was distilled from sodium wire with diphenyl ketone as the indicator. THF was dried with sodium wire. Diisopropylamine was dried with anhydrous barium oxide and distilled. All the temperatures stated refer to the oil baths used.

Typical Procedure: Cu(I)-Catalyzed Gram-Scale Synthesis of 1-Phenyl-2,3-butadien-1-ol (2a): To a 50 mL three-neck round-bottom flask equipped with a magnetic stirring bar were added CuI (143.2 mg, 0.75 mmol), paraformaldehyde (481.2 mg, 16.02 mmol), and dioxane (10 mL). The resulting mixture was stirred at room temperature before subsequent addition of iPr_2NH (1.98 mL, d = 0.716 g mL^{-1}, 1.4177 g, 14.01 mmol), **1a** (1.3207 g, 10.00 mmol), and dioxane (5 mL). The mixture was stirred at 110 °C without protection with an inert atmosphere. After 10 h, the reaction mixture was cooled to room temperature and filtered through a short column of silica gel (Et_2O). The solvent was evaporated, and the residue was diluted with Et_2O. After filtration again to remove the precipitate, evaporation of the solvent and chromatography on silica gel (petroleum ether/ethyl acetate, 5:1 to 2:1) afforded **2a**[11a] (1.2915 g, 88%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.21 (m, 5 H, ArH), 5.41 (q, J = 6.6 Hz, 1 H, C=CH), 5.26–5.19 (m, 1 H, OCH), 4.96–4.83 (m, 2 H, C=CH_2), 2.50 (br. s, 1 H, OH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 207.0, 142.7, 128.4, 127.7, 126.0, 95.1, 78.0, 71.9 ppm. IR (neat): $\tilde{\nu}$ = 3334, 1955, 1493,

1452, 1022 cm^{-1}. MS (70 eV, EI): *m/z* (%) = 146 (4.13) [M^+], 107 (100).

1-(4-Methoxyphenyl)-2,3-butadien-1-ol (2b): The reaction of CuI (142.6 mg, 0.75 mmol), paraformaldehyde (480.2 mg, 15.99 mmol), **1b** (1.6246 g, 10.02 mmol), and *i*Pr_2NH (2.0 mL, *d* = 0.716 gmL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **2b**[11a] (1.3876 g, 79%) after purification (eluent for chromatography: petroleum ether/ethyl acetate, 10:1 to 5:1) as a liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.27 (m, 2 H, ArH), 6.94–6.82 (m, 2 H, ArH), 5.43 (q, *J* = 6.6 Hz, 1 H, C=CH), 5.25–5.16 (m, 1 H, OCH), 4.97–4.85 (m, 2 H, $C=CH_2$), 3.80 (s, 3 H, OCH_3), 2.43 (br. s, 1 H, OH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 207.0, 159.1, 135.0, 127.4, 113.7, 95.2, 78.0, 71.4, 55.2 ppm. IR (neat): $\tilde{\nu}$ = 3397, 1955, 1611, 1585, 1511, 1246, 1173, 1032 cm^{-1}. MS (70 eV, EI): *m/z* (%) = 176 (9.32) [M^+], 137 (100).

1-(2-Methoxyphenyl)-2,3-butadien-1-ol (2c): The reaction of CuI (142.6 mg, 0.75 mmol), paraformaldehyde (481.6 mg, 16.04 mmol), **1c** (1.6128 g, 9.94 mmol), and *i*Pr_2NH (2.0 mL, *d* = 0.716 gmL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **2c**[10i] (1.5255 g, 87%) after purification (eluent for chromatography: petroleum ether/ethyl acetate, 15:1 to 10:1 to 5:1) as a liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 7.5 Hz, 1 H, ArH), 7.26 (t, *J* = 7.8 Hz, 1 H, ArH), 6.95 (t, *J* = 7.5 Hz, 1 H, ArH), 6.89 (d, *J* = 8.4 Hz, 1 H, ArH), 5.54 (q, *J* = 6.3 Hz, 1 H, C=CH), 5.47–5.38 (m, 1 H, OCH), 4.92–4.78 (m, 2 H, $C=CH_2$), 3.85 (s, 3 H, OCH_3), 3.01–2.93 (m, 1 H, OH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 207.1, 156.6, 130.8, 128.7, 127.1, 120.8, 110.6, 94.1, 77.7, 68.8, 55.3 ppm. IR (neat): $\tilde{\nu}$ = 3405, 1955, 1601, 1588, 1490, 1463, 1439, 1240, 1048, 1026 cm^{-1}. MS (70 eV, EI): *m/z* (%) = 176 (3.57) [M^+], 137 (100).

1-(4-Chlorophenyl)-2,3-butadien-1-ol (2d): The reaction of CuI (142.7 mg, 0.75 mmol), paraformaldehyde (481.4 mg, 16.03 mmol), **1d** (1.6655 g, 10.00 mmol), and *i*Pr_2NH (2.0 mL, *d* = 0.716 gmL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **2d**[7] (1.5817 g, 88%) after purification (eluent for chromatography: petroleum ether/ethyl acetate, 10:1 to 5:1) as a liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.29 (s, 4 H, ArH), 5.37 (q, *J* = 6.3 Hz, 1 H, C=CH), 5.24–5.16 (m, 1 H, OCH), 4.90 (d, *J* = 6.3 Hz, 2 H, $C=CH_2$), 2.65–2.43 (m, 1 H, OH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 207.1, 141.2, 133.3, 128.5, 127.4, 94.8, 78.3, 71.2 ppm. IR (neat): $\tilde{\nu}$ = 3357, 2888, 1955, 1597, 1491, 1406, 1091, 1013 cm^{-1}. MS (70 eV, EI): *m/z* (%) = 182 (0.86) [M^+ (^{37}Cl)], 180 (2.61) [M^+ (^{35}Cl)], 141 (100).

1-(2,4-Dichlorophenyl)-2,3-butadien-1-ol (2e): The reaction of CuI (142.9 mg, 0.75 mmol), paraformaldehyde (480.4 mg, 16.00 mmol), **1e** (2.0153 g, 10.02 mmol), and *i*Pr_2NH (2.0 mL, *d* = 0.716 gmL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **2e** (1.8157 g, 84%) after purification (eluent for chromatography: petroleum ether/ethyl acetate, 10:1 to 5:1) as a solid, m.p. 56–58 °C (petroleum ether/ethyl acetate). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.1 Hz, 1 H, ArH), 7.34 (d, *J* = 2.1 Hz, 1 H, ArH), 7.25 (dd, *J* = 8.1, 2.1 Hz, 1 H, ArH), 5.62–5.54 (m, 1 H, OCH), 5.40 (q, *J* = 6.6 Hz, 1 H, C=CH), 4.91 (dd, *J* = 6.3, 2.3 Hz, 2 H, $C=CH_2$), 2.59–2.49 (m, 1 H, OH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 207.2, 136.4, 130.6, 130.3, 128.5, 127.8, 126.5, 93.8, 78.1, 70.4 ppm. IR (neat): $\tilde{\nu}$ = 3333, 1957, 1632, 1590, 1543, 1511, 1468, 1247, 1037 cm^{-1}. MS (70 eV, EI): *m/z* (%) = 218 (0.17) [M^+ ($^{37,37}Cl$)], 216 (1.00) [M^+ ($^{37,35}Cl$)], 214 (1.58) [M^+ ($^{35,35}Cl$)], 175 (100). HRMS: calcd. for $C_{10}H_8{}^{35,35}Cl_2O$ [M^+] 213.9952; found 213.9954.

1-(3-Nitrophenyl)-2,3-butadien-1-ol (2f): The reaction of CuI (142.5 mg, 0.75 mmol), paraformaldehyde (480.5 mg, 16.00 mmol), **1f** (1.7732 g, 10.00 mmol), and *i*Pr_2NH (2.0 mL, *d* = 0.716 gmL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **2f**[11b] (1.5460 g, 81%) after purification (eluent for chromatography: petroleum ether/ethyl acetate, 5:1) as a liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.24 (s, 1 H, ArH), 8.10 (d, *J* = 7.8 Hz, 1 H, ArH), 7.72 (d, *J* = 7.8 Hz, 1 H, ArH), 7.50 (t, *J* = 7.6 Hz, 1 H, ArH), 5.46–5.32 (m, 2 H, C=CH and OCH), 5.00–4.86 (m, 2 H, $C=CH_2$), 2.84–2.55 (m, 1 H, OH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 207.4, 148.2, 144.8, 132.2, 129.3, 122.5, 121.0, 94.4, 78.7, 71.0 ppm. IR (neat): $\tilde{\nu}$ = 3405, 1955, 1526, 1347 cm^{-1}. MS (70 eV, EI): *m/z* (%) = 191 (0.58) [M^+], 152 (100) [$M^+ - C_3H_3$].

1-(Thiophen-2-yl)-2,3-butadien-1-ol (2g): The reaction of CuI (143.5 mg, 0.75 mmol), paraformaldehyde (480.5 mg, 16.00 mmol), **1g** (1.3824 g, 10.00 mmol), and *i*Pr_2NH (2.0 mL, *d* = 0.716 gmL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **2g**[11c] (1.3053 g, 86%) after purification (eluent for chromatography: petroleum ether/ethyl acetate, 10:1 to 5:1) as a liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.25 (d, *J* = 4.8 Hz, 1 H of thienyl group), 7.04–6.98 (m, 1 H of thienyl group), 6.98–6.90 (m, 1 H of thienyl group), 5.56–5.41 (m, 2 H, C=CH and OCH), 5.01–4.88 (m, 2 H, $C=CH_2$), 2.60 (br. s, 1 H, OH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 207.1, 146.8, 126.6, 125.1, 124.2, 94.7, 78.6, 68.0 ppm. IR (neat): $\tilde{\nu}$ = 3378, 1954, 1227, 1077 cm^{-1}. MS (70 eV, EI): *m/z* (%) = 152 (8.97) [M^+], 113 (100).

1-(Furan-2-yl)-2,3-butadien-1-ol (2h): The reaction of CuI (142.5 mg, 0.75 mmol), paraformaldehyde (481.1 mg, 16.02 mmol), **1h** (1.2161 g, 9.96 mmol), and *i*Pr_2NH (2.0 mL, *d* = 0.716 gmL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **2h**[11c] (1.0307 g, 76%) after purification (eluent for chromatography: petroleum ether/ethyl acetate, 10:1 to 5:1) as a liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.35 (m, 1 H of furan group), 6.36–6.31 (m, 1 H of furan group), 6.31–6.25 (m, 1 H of furan group), 5.51 (q, *J* = 6.6 Hz, 1 H, C=CH), 5.30–5.20 (m, 1 H, OCH), 5.01–4.89 (m, 2 H, $C=CH_2$), 2.54–2.44 (m, 1 H, OH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 207.6, 154.9, 142.3, 110.2, 106.5, 92.1, 78.5, 65.6 ppm. IR (neat): $\tilde{\nu}$ = 3558, 1957, 1503, 1146, 1008 cm^{-1}. MS (70 eV, EI): *m/z* (%) = 136 (9.08) [M^+], 97 (100).

1,2-Nonadien-4-ol (2i): The reaction of CuI (143.0 mg, 0.75 mmol), paraformaldehyde (480.6 mg, 16.00 mmol), **1i** (1.2625 g, 10.00 mmol), and *i*Pr_2NH (2.0 mL, *d* = 0.716 gmL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **2i**[11a] (1.0788 g, 77%) after purification (eluent for chromatography: petroleum ether/ethyl acetate, 10:1 to 5:1) as a liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.19 (q, *J* = 6.6 Hz, 1 H, C=CH), 4.86–4.74 (m, 2 H, $C=CH_2$), 4.18–4.07 (m, 1 H, OCH), 2.20 (br. s, 1 H, OH), 1.63–1.17 (m, 8 H, 4 × CH_2), 0.86 (t, *J* = 6.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 206.9, 94.7, 77.1, 69.7, 37.3, 31.6, 25.0, 22.5, 13.9 ppm. IR (neat): $\tilde{\nu}$ = 3317, 2957, 2930, 2859, 1956, 1464, 1020 cm^{-1}. MS (70 eV, EI): *m/z* (%) = 111 (4.32) [$M^+ - C_2H_5$], 83 (100).

1,2-Undecadien-4-ol (2j): The reaction of CuI (142.5 mg, 0.75 mmol), paraformaldehyde (480.8 mg, 16.01 mmol), **1j** (1.5484 g, 10.04 mmol), and *i*Pr_2NH (2.0 mL, *d* = 0.716 gmL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **2j**[11d] (0.9972 g, 59%) after purification (eluent for chromatography: petroleum ether/ethyl acetate, 10:1 to 5:1) as a liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.23 (q, *J* = 6.5 Hz, 1 H, C=CH), 4.90–4.78 (m, 2 H, $C=CH_2$), 4.22–4.10 (m, 1 H, OCH), 1.73–1.18 (m, 13 H, OH and 6 × CH_2), 0.87 (t, *J* = 5.9 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 207.0, 94.9, 77.3, 69.7, 37.5, 31.8, 29.4, 29.2, 25.4, 22.6, 14.0 ppm. IR (neat): $\tilde{\nu}$ = 3333, 2926, 2856, 1957, 1466 cm^{-1}. MS (70 eV, EI): *m/z* (%) = 129 (10.57) [$M^+ - C_3H_3$], 69 (100).

1-Phenyl-3,4-pentadien-2-ol (2k): The reaction of CuI (142.6 mg, 0.75 mmol), paraformaldehyde (481.2 mg, 16.02 mmol), **1k**

(1.4583 g, 9.98 mmol), and *i*Pr_2NH (2.0 mL, d = 0.716 g mL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **2k**[11e] (1.2690 g, 79%) after purification (eluent for chromatography: petroleum ether/ethyl acetate, 10:1 to 5:1) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.16 (m, 5 H, ArH), 5.28 (q, J = 6.3 Hz, 1 H, C=CH), 4.90–4.77 (m, 2 H, C=CH_2), 4.46–4.33 (m, 1 H, OCH), 2.95–2.78 (m, 2 H, CH_2), 1.89 (br. s, 1 H, OH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 206.9, 137.6, 129.5, 128.3, 126.4, 94.0, 77.7, 70.1, 43.8 ppm. IR (neat): $\tilde{\nu}$ = 3377, 1955, 1603, 1496, 1453, 1049, 1028 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 160 (0.62) [M$^+$], 159 (1.80) [M$^+$ – H], 92 (100).

1-Cyclohexyl-2,3-butadien-1-ol (2l): The reaction of CuI (190.6 mg, 1.00 mmol), paraformaldehyde (480.7 mg, 16.01 mmol), **1l** (1.3827 g, 10.00 mmol), and *i*Pr_2NH (2.0 mL, d = 0.716 g mL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **2l**[11d] (1.2546 g, 82%) after purification (eluent for chromatography: petroleum ether/ethyl acetate, 5:1) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.21 (q, J = 6.6 Hz, 1 H, C=CH), 4.82 (dd, J = 6.8, 2.2 Hz, 2 H, C=CH_2), 3.97–3.86 (m, 1 H, OCH), 1.90–1.58 (m, 6 H, Cy), 1.49–1.34 (m, 1 H, OH), 1.31–0.91 (m, 5 H, Cy) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 207.2, 93.2, 77.1, 74.0, 44.1, 28.6, 28.3, 26.4, 26.03. 25.97 ppm. IR (neat): $\tilde{\nu}$ = 3354, 2923, 2852, 1955, 1449, 1083, 1014 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 152 (0.51) [M$^+$], 134 (1.22) [M$^+$ – H_2O], 69 (100).

2-Phenyl-3,4-pentadien-2-ol (2m): The reaction of CuI (191.2 mg, 1.00 mmol), paraformaldehyde (481.4 mg, 16.03 mmol), **1m** (1.4657 g, 10.03 mmol), and *i*Pr_2NH (2.0 mL, d = 0.716 g mL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **2m**[11f] (1.3540 g, 84%) after purification (eluent for chromatography: petroleum ether/ethyl acetate, 10:1) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49 (d, J = 7.8 Hz, 2 H, ArH), 7.33 (t, J = 7.2 Hz, 2 H, ArH), 7.23 (t, J = 6.9 Hz, 1 H, ArH), 5.54 (t, J = 6.4 Hz, 1 H, C=CH), 5.00–4.85 (m, 2 H, C=CH_2), 2.30 (s, 1 H, OH), 1.64 (s, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 205.8, 147.1, 128.1, 126.9, 124.9, 100.1, 79.0, 72.9, 30.3 ppm. IR (neat): $\tilde{\nu}$ = 3363, 3028, 1956, 1492, 1446, 1217, 1178, 1102, 1067, 1028 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 160 (1.79) [M$^+$], 121 (100).

4-Methyl-1,2-decadien-4-ol (2n): The reaction of CuI (190.6 mg, 1.00 mmol), paraformaldehyde (480.7 mg, 16.01 mmol), **1n** (1.5403 g, 9.98 mmol), and *i*Pr_2NH (1.98 mL, d = 0.716 g mL^{-1}, 1.4177 g, 14.01 mmol) in dioxane (15 mL) afforded **2n**[11g] (1.2535 g, 74%) after purification (eluent for chromatography: petroleum ether/ethyl acetate, 5:1) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.24 (t, J = 6.6 Hz, 1 H, C=CH), 4.84 (d, J = 6.6 Hz, 2 H, C=CH_2), 1.87 (s, 1 H, OH), 1.59–1.45 (m, 2 H, CH_2), 1.39–1.18 (m, 11 H, CH_3 and 4 × CH_2), 0.85 (t, J = 6.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 205.5, 99.3, 78.2, 71.3, 42.8, 31.8, 29.6, 27.7, 24.0, 22.5, 14.0 ppm. IR (neat): $\tilde{\nu}$ = 3368, 2958, 2932, 2860, 1957, 1464, 1375, 1128, 1061 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 168 (0.14) [M$^+$], 153 (2.39) [M$^+$ – CH_3], 83 (100).

1-(Propa-1,2-dienyl)cyclohexanol (2o): The reaction of CuI (190.1 mg, 1.00 mmol), paraformaldehyde (480.0 mg, 15.98 mmol), **1o** (97% purity, 1.2838 g, 10.03 mmol), and *i*Pr_2NH (2.0 mL, d = 0.716 g mL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **2o**[11a] (1.1056 g, 80%) after purification (eluent for chromatography: petroleum ether/ethyl acetate, 10:1 to 5:1) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.28 (t, J = 6.6 Hz, 1 H, C=CH), 4.86 (d, J = 6.6 Hz, 2 H, C=CH_2), 1.74–1.18 (m, 11 H, OH and 5 × CH_2) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 206.2, 99.4, 78.1, 70.4, 38.3, 25.5, 22.5 ppm. IR (neat): $\tilde{\nu}$ = 3354, 2931, 2854, 1955, 1448, 1147, 1056 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 138 (0.85) [M$^+$], 120 (3.40) [M$^+$ – H_2O], 99 (100).

1-(Buta-2,3-dien-1-yloxy)-4-nitrobenzene (2p): The reaction of CuI (190.3 mg, 1.00 mmol), paraformaldehyde (480.3 mg, 15.99 mmol), **1p** (1.7789 g, 10.04 mmol), and *i*Pr_2NH (2.0 mL, d = 0.716 g mL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **2p** (1.4635 g, 76%) after purification (eluent for chromatography: petroleum ether/ethyl acetate, 20:1 to 10:1) as a solid, m.p. 60–62 °C (petroleum ether/ethyl acetate): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.22–8.13 (m, 2 H, ArH), 7.00–6.75 (m, 2 H, ArH), 5.37 (quint, J = 6.8 Hz, 1 H, C=CH), 4.90 (dt, J = 6.6, 2.1 Hz, 2 H, C=CH_2), 4.65 (dt, J = 6.9, 2.4 Hz, 2 H, OCH_2) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 209.6, 163.2, 141.5, 125.8, 114.8, 86.1, 77.1, 66.4 ppm. IR (neat): $\tilde{\nu}$ = 2930, 1958, 1606, 1592, 1509, 1342, 1256, 1112 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 191 (1.26) [M$^+$], 53 (100). HRMS: calcd. for $C_{10}H_9NO_3$ [M$^+$] 191.0582; found 191.0583.

Benzyl 2,3-Butadienyl Ether (2q): The reaction of CuI (190.5 mg, 1.00 mmol), paraformaldehyde (480.5 mg, 16.00 mmol), **1q** (1.4666 g, 10.03 mmol), and *i*Pr_2NH (2.0 mL, d = 0.716 g mL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **2q**[6a] (1.2001 g, 75%) after purification (eluent for chromatography: petroleum ether/ethyl acetate, 40:1) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.22 (m, 5 H, ArH), 5.28 (quint, J = 6.6 Hz, 1 H, C=CH), 4.83–4.75 (m, 2 H, C=CH_2), 4.53 (s, 2 H, $ArCH_2$), 4.06 (d, J = 6.9 Hz, 2 H, OCH_2) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 209.3, 138.1, 128.3, 127.8, 127.6, 87.7, 75.6, 71.8, 67.8 ppm. IR (neat): $\tilde{\nu}$ = 3094, 3031, 2858, 1955, 1496, 1453, 1360, 1074, 1051, 1029, 1003 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 130 (27.21) [M$^+$ – CH_2O], 91 (100).

(Buta-2,3-dien-1-yloxy)(*tert*-butyl)dimethylsilane (2r): The reaction of CuI (191.3 mg, 1.00 mmol), paraformaldehyde (481.6 mg, 16.04 mmol), **1r** (1.7113 g, 10.05 mmol), and *i*Pr_2NH (2.0 mL, d = 0.716 g mL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **2r**[11h] (1.1115 g, 60%) after purification (eluent for chromatography: 30–60 °C petroleum ether) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.23 (quint, J = 6.5 Hz, 1 H, C=CH), 4.81–4.70 (m, 2 H, C=CH_2), 4.24–4.14 (m, 2 H, OCH_2), 0.90 (s, 9 H, *t*Bu), 0.08 (s, 6 H, 2 × $SiCH_3$) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 208.1, 90.9, 76.0, 61.4, 25.9, 18.4, –5.1 ppm. IR (neat): $\tilde{\nu}$ = 2858, 1958, 1471, 1255, 1085 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 127 (51.00) [M$^+$ – ^{t}Bu], 75 (100). Please note that the dioxane should be evaporated < 40 °C/4.8 kPa to ensure the yield.

2-(Buta-2,3-dien-1-yloxy)tetrahydro-2*H*-pyran (2s): The reaction of CuI (191.1 mg, 1.00 mmol), paraformaldehyde (481.0 mg, 16.02 mmol), **1s** (1.4010 g, 9.99 mmol), and *i*Pr_2NH (2.0 mL, d = 0.716 g mL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **2s**[11i] (1.0234 g, 66%) after purification (eluent for chromatography: petroleum ether/ethyl acetate = 20:1) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.26 (quint, J = 6.5 Hz, 1 H, C=CH), 4.82–4.72 (m, 2 H, C=CH_2), 4.72–4.64 (m, 1 H, OCHO), 4.28–4.15 (m, 1 H of OCH_2), 4.09–3.98 (m, 1 H of OCH_2), 3.93–3.80 (m, 1 H of OCH_2), 3.56–3.45 (m, 1 H of OCH_2), 1.92–1.43 (m, 6 H, 3 × CH_2) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 209.3, 97.6, 87.8, 75.6, 64.8, 62.2, 30.5, 25.4, 19.4 ppm. IR (neat): $\tilde{\nu}$ = 2943, 1957, 1056, 1023 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 115 (2.80) [M$^+$ – C_3H_3], 85 (100).

4-Benzylthio-1,2-butadiene (2t): The reaction of CuI (190.9 mg, 1.00 mmol), paraformaldehyde (481.3 mg, 16.03 mmol), **1t** (1.6255 g, 1.00 mmol), and *i*Pr_2NH (2.0 mL, d = 0.716 g mL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **2t**[11j] (1.4032 g, 79%) after purification (eluent for chromatography: petroleum ether) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34–7.17 (m,

5 H, ArH), 5.16 (quint, J = 7.1 Hz, 1 H, C=CH), 4.85–4.76 (dd, J = 6.2, 2.0 Hz, 2 H, C=CH_2), 3.72 (s, 2 H, ArCH_2), 3.07–2.96 (m, 2 H, SCH_2) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 209.6, 138.2, 128.9, 128.4, 126.9, 87.8, 76.1, 35.0, 29.8 ppm. IR (neat): $\tilde{\nu}$ = 1949, 1494, 1453, 1416, 1322, 1224 cm^{-1}. MS (70 eV, EI): m/z (%) = 176 (3.72) [M$^+$], 91 (100).

4-Methyl-*N*-(nona-1,2-dien-4-yl)benzenesulfonamide (2u): The reaction of CuI (191.0 mg, 1.00 mmol), paraformaldehyde (481.6 mg, 16.04 mmol), **1u** (2.7886 g, 9.98 mmol), and *i*Pr$_2$NH (2.0 mL, d = 0.716 g mL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **2u** (2.0181 g, 69%) after purification (eluent for chromatography: petroleum ether/ethyl acetate, 10:1 to 5:1) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75 (d, J = 7.8 Hz, 2 H, ArH), 7.28 (d, J = 7.8 Hz, 2 H, ArH), 4.95 (q, J = 6.3 Hz, 1 H, C=CH), 4.75–4.54 (m, 3 H, NH and C=CH_2), 3.87–3.72 (m, 1 H, NCH), 2.42 (s, 3 H, ArCH_3), 1.60–1.39 (m, 2 H, CH_2), 1.39–1.10 (m, 6 H, 3 × CH_2), 0.85 (t, J = 6.3 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 206.8, 143.2, 138.1, 129.4, 127.2, 92.4, 78.3, 52.1, 36.1, 31.3, 24.9, 22.4, 21.5, 13.9 ppm. IR (neat): $\tilde{\nu}$ = 3271, 2930, 1957, 1598, 1426, 1324, 1158 cm^{-1}. MS (70 eV, EI): m/z (%) = 293 (2.26) [M$^+$], 91 (100). HRMS: calcd. for $C_{16}H_{23}NO_2S$ [M$^+$] 293.1450; found 293.1451.

Hepta-5,6-dien-1-ol (2v): The reaction of CuI (190.9 mg, 1.00 mmol), paraformaldehyde (480.7 mg, 16.01 mmol), **1v** (0.9850 g, 10.04 mmol), and *i*Pr$_2$NH (2.0 mL, d = 0.716 g mL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **2v**[11k] (0.5541 g, 49%) after purification (eluent for chromatography: petroleum ether/ethyl acetate, 5:1) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.08 (quint, J = 6.6 Hz, 1 H, C=CH), 4.69–4.57 (m, 2 H, C=CH_2), 3.62 (t, J = 6.2 Hz, 2 H, OCH_2), 2.08–1.95 (m, 2 H, CH_2C=C), 1.87 (br. s, 1 H, OH), 1.65–1.38 [m, 4 H, C(CH_2)$_2$C] ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 208.5, 89.7, 74.7, 62.6, 32.1, 27.9, 25.2 ppm. IR (neat): $\tilde{\nu}$ = 3324, 2935, 2861, 1956, 1437, 1057 cm^{-1}. MS (70 eV, EI): m/z (%) = 94 (2.20) [M$^+$ – H_2O], 79 (100).

Penta-3,4-dienylbenzene (2w): The reaction of CuI (190.9 mg, 1.00 mmol), paraformaldehyde (481.0 mg, 16.02 mmol), **1w** (1.3104 g, 10.06 mmol), and *i*Pr$_2$NH (2.0 mL, d = 0.716 g mL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **2w**[11l] (0.9123 g, 63%) after purification (eluent for chromatography: petroleum ether) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32–7.13 (m, 5 H, ArH), 5.14 (quint, J = 6.6 Hz, 1 H, C=CH), 4.71–4.62 (m, 2 H, C=CH_2), 2.72 (t, J = 8.0 Hz, 2 H, ArCH_2), 2.37–2.24 (m, 2 H, CH_2C=C) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 208.5, 141.7, 128.5, 128.3, 125.8, 89.4, 75.1, 35.4, 30.0 ppm. IR (neat): $\tilde{\nu}$ = 3027, 2922, 2855, 1955, 1603, 1496, 1453 cm^{-1}. MS (70 eV, EI): m/z (%) = 144 (9.27) [M$^+$], 91 (100).

2-(Buta-2,3-dienyloxy)benzaldehyde (2x): The reaction of CuI (143.4 mg, 0.75 mmol), paraformaldehyde (480.9 mg, 16.01 mmol), **1x** (1.6028 g, 10.01 mmol), and *i*Pr$_2$NH (2.0 mL, d = 0.716 g mL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **2x**[11m] (1.0189 g, 58%) by double chromatography on silica gel (first round: petroleum ether/ethyl acetate, 20:1; second round: petroleum ether/ethyl acetate, 30:1) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.50 (s, 1 H, CHO), 7.82 (d, J = 8.1 Hz, 1 H, ArH), 7.52 (t, J = 7.8 Hz, 1 H, ArH), 7.07–6.93 (m, 2 H, ArH), 5.41 (quint, J = 6.6 Hz, 1 H, C=CH), 4.95–4.81 (m, 2 H, C=CH_2), 4.72–4.60 (m, 2 H, OCH_2) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 209.5, 189.7, 160.7, 135.7, 128.3, 125.2, 120.9, 113.0, 86.5, 77.0, 66.2 ppm. IR (neat): $\tilde{\nu}$ = 1957, 1685, 1597, 1481, 1456, 1397, 1377, 1283, 1236, 1217, 1189, 1161, 1120 cm^{-1}. MS (70 eV, EI): m/z (%) = 174 (3.28) [M$^+$], 121 (100).

***N*-(Buta-2,3-dien-1-yl)benzamide (4a):** The reaction of CuI (190.7 mg, 1.00 mmol), paraformaldehyde (480.8 mg, 16.01 mmol), **3a** (1.5918 g, 10.00 mmol), and *i*Pr$_2$NH (2.0 mL, d = 0.716 g mL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **4a**[9a] (1.3601 g, 78%) after purification (eluent for chromatography: petroleum ether/ethyl acetate, 5:1 to 2:1) as a solid, m.p. 51–53 °C (petroleum ether/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.77 (d, J = 7.8 Hz, 2 H, ArH), 7.53–7.33 (m, 3 H, ArH), 6.57 (br. s, 1 H, NH), 5.31 (quint, J = 6.2 Hz, 1 H, C=CH), 4.92–4.80 (m, 2 H, C=CH_2), 4.09–3.96 (m, 2 H, NCH_2) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 207.9, 167.3, 134.4, 131.4, 128.4, 126.9, 88.0, 77.7, 37.8 ppm. IR (neat): $\tilde{\nu}$ = 3316, 1955, 1641, 1537, 1489, 1293 cm^{-1}. MS (70 eV, EI): m/z (%) = 173 (12.93) [M$^+$], 105 (100).

(E)-*N*-(Buta-2,3-dien-1-yl)-3-phenylacrylamide (4b): The reaction of CuI (190.6 mg, 1.00 mmol), paraformaldehyde (480.0 mg, 15.98 mmol), **3b** (1.8525 g, 10.00 mmol), and *i*Pr$_2$NH (2.0 mL, d = 0.716 g mL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **4b**[9a] (1.6313 g, 82%) after purification (eluent for chromatography: petroleum ether/ethyl acetate, 5:1 to 2:1) as a solid, m.p. 72–74 °C (petroleum ether/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64 (d, J = 15.9 Hz, 1 H, C=CH), 7.52–7.43 (m, 2 H, ArH), 7.37–7.27 (m, 3 H, ArH), 6.47 (d, J = 15.6 Hz, 1 H, C=CH), 6.30 (br. s, 1 H, NH), 5.27 (quint, J = 6.3 Hz, 1 H, C=CH), 4.90–4.79 (m, 2 H, C=C=CH_2), 4.04–3.94 (m, 2 H, CH_2) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 208.0, 165.8, 141.0, 134.7, 129.6, 128.7, 127.7, 120.5, 87.8, 77.5, 37.8 ppm. IR (neat): $\tilde{\nu}$ = 3243, 3063, 1952, 1654, 1609, 1553, 1344, 1222 cm^{-1}. MS (70 eV, EI): m/z (%) = 199 (45.81) [M$^+$], 131 (100).

***N*-(Buta-2,3-dien-1-yl)-2-furamide (4c):** The reaction of CuI (190.5 mg, 1.00 mmol), paraformaldehyde (480.0 mg, 15.98 mmol), **3c** (1.4875 g, 9.97 mmol), and *i*Pr$_2$NH (2.0 mL, d = 0.716 g mL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **4c**[9a] (1.3740 g, 84%) after purification (eluent for chromatography: petroleum ether/ethyl acetate, 4:1 to 2:1) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.36 (m, 1 H of furan group), 7.10–7.03 (m, 1 H of furan group), 6.64 (br. s, 1 H, NH), 6.44–6.40 (m, 1 H of furan group), 5.25 (quint, J = 6.3 Hz, 1 H, C=CH), 4.82 (dt, J = 6.6, 3.3 Hz, 2 H, C=CH_2), 4.03–3.93 (m, 2 H, CH_2) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 208.0, 158.1, 147.8, 143.8, 114.1, 111.9, 87.6, 77.5, 37.1 ppm. IR (neat): $\tilde{\nu}$ = 3305, 1958, 1645, 1593, 1572, 1523, 1474, 1294, 1184, 1013 cm^{-1}. MS (70 eV, EI): m/z (%) = 163 (15.91) [M$^+$], 95 (100).

***N*-(Buta-2,3-dien-1-yl)-2,5-dimethyl-3-furamide (4d):** The reaction of CuI (133.2 mg, 0.70 mmol), paraformaldehyde (336.7 mg, 11.21 mmol), **3d** (1.2404 g, 7.00 mmol), and *i*Pr$_2$NH (1.4 mL, d = 0.716 g mL^{-1}, 1.0024 g, 9.91 mmol) in dioxane (10.5 mL) afforded **4d**[9a] (1.1191 g, 84%) after purification (eluent for chromatography: petroleum ether/ethyl acetate, 5:1 to 3:1) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.99 (s, 1 H of furan group), 5.93 (br. s, 1 H, NH), 5.32–5.20 (m, 1 H, C=CH), 4.88–4.78 (m, 2 H, C=CH_2), 3.98–3.89 (m, 2 H, CH_2), 2.51 (s, 3 H, CH_3), 2.21 (s, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 207.9, 163.9, 155.0, 149.8, 115.8, 103.9, 88.1, 77.6, 37.1, 13.3, 13.2 ppm. IR (neat): $\tilde{\nu}$ = 3324, 2922, 1957, 1637, 1586, 1523, 1227, 1125 cm^{-1}. MS (70 eV, EI): m/z (%) = 191 (39.56) [M$^+$], 123 (100).

***N*-(Buta-2,3-dien-1-yl)-5-nitro-2-furamide (4e):** The reaction of CuI (191.2 mg, 1.00 mmol), paraformaldehyde (481.6 mg, 16.04 mmol), **3e** (1.9434 g, 10.01 mmol), and *i*Pr$_2$NH (2.0 mL, d = 0.716 g mL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **4e**[9a] (1.0950 g, 53%) after purification (eluent for chromatography: petroleum ether/ethyl acetate, 5:1 to 3:1) as a solid, m.p. 94–95 °C (petroleum ether/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37 (d, J =

3.6 Hz, 1 H of furan group), 7.27 (d, J = 3.9 Hz, 1 H of furan group), 6.80 (br. s, 1 H, NH), 5.30 (quint, J = 6.3 Hz, 1 H, C=CH), 4.92 (dt, J = 6.6, 3.3 Hz, 2 H, C=CH_2), 4.11–4.02 (m, 2 H, CH_2) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 208.3, 156.0, 151.1, 147.9, 116.0, 112.4, 87.0, 78.1, 37.7 ppm. IR (neat): $\tilde{\nu}$ = 3312, 1953, 1650, 1551, 1484, 1350, 1268, 1058, 1016 cm^{-1}. MS (70 eV, EI): m/z (%) = 208 (44.46) [M$^+$], 140 (100).

***N*-(Buta-2,3-dien-1-yl)thiophene-2-carboxamide (4f):** The reaction of CuI (191.0 mg, 1.00 mmol), paraformaldehyde (481.4 mg, 16.03 mmol), **3f** (1.6679 g, 10.09 mmol), and iPr$_2$NH (2.0 mL, d = 0.716 g mL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **4f**[9a] (1.4457 g, 80%) after purification (eluent for chromatography: petroleum ether/ethyl acetate, 5:1 to 3:1) as a liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (dd, J = 4.0, 1.2 Hz, 1 H of thienyl group), 7.46 (dd, J = 5.0, 1.0 Hz, 1 H of thienyl group), 7.06 (dd, J = 4.8, 3.6 Hz, 1 H of thienyl group), 6.35 (br. s, 1 H, NH), 5.30 (quint, J = 6.4 Hz, 1 H, C=CH), 4.87 (dt, J = 6.84, 3.2 Hz, 2 H, C=CH_2), 4.06–3.98 (m, 2 H, CH_2) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 208.0, 161.8, 138.8, 129.9, 128.0, 127.5, 87.8, 77.5, 37.9 ppm. IR (neat): $\tilde{\nu}$ = 3306, 1957, 1625, 1539, 1510, 1420, 1352, 1293 cm^{-1}. MS (70 eV, EI): m/z (%) = 179 (24.17) [M$^+$], 111 (100).

***N*-(Buta-2,3-dien-1-yl)adamantane-1-carboxamide (4g):** The reaction of CuI (190.8 mg, 1.00 mmol), paraformaldehyde (481.2 mg, 16.02 mmol), **3g** (2.1697 g, 9.98 mmol), and iPr$_2$NH (2.0 mL, d = 0.716 g mL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **4g**[9a] (1.4671 g, 64%) after purification (eluent for chromatography: petroleum ether/ethyl acetate, 8:1 to 5:1) as a solid, m.p. 111–113 °C (petroleum ether/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.77 (br. s, 1 H, NH), 5.27–5.16 (m, 1 H, C=CH), 4.84 (dt, J = 6.9, 3.5 Hz, 2 H, C=CH_2), 3.85–3.77 (m, 2 H, NCH_2), 2.07–1.98 (m, 3 H, 3 × CH), 1.84 (d, J = 2.7 Hz, 6 H, 3 × CH_2), 1.78–1.61 (m, 6 H, 3 × CH_2) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 207.7, 177.7, 88.3, 77.7, 40.6, 39.2, 36.9, 36.5, 28.1 ppm. IR (neat): $\tilde{\nu}$ = 3361, 2908, 2848, 1954, 1632, 1517, 1268 cm^{-1}. MS (70 eV, EI): m/z (%) = 231 (48.40) [M$^+$], 135 (100).

Ethyl 2-(Buta-2,3-dien-1-ylamino)-2-oxoacetate (4h): The reaction of CuI (190.9 mg, 1.00 mmol), paraformaldehyde (480.7 mg, 16.01 mmol), **3h** (1.5517 g, 10.00 mmol), and iPr$_2$NH (2.0 mL, d = 0.716 g mL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **4h**[9a] (0.8105 g, 48%) after purification (eluent for chromatography: petroleum ether/ethyl acetate, 4:1) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33 (br. s, 1 H, NH), 5.25 (quint, J = 6.3 Hz, 1 H, C=CH), 4.90 (dt, J = 6.6, 3.3 Hz, 2 H, C=CH_2), 4.36 (q, J = 7.2 Hz, 2 H, OCH_2), 3.99–3.90 (m, 2 H, NCH_2), 1.39 (t, J = 7.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 208.1, 160.4, 156.2, 86.7, 77.9, 63.1, 37.8, 13.9 ppm. IR (neat): $\tilde{\nu}$ = 3321, 1958, 1735, 1685, 1527, 1299, 1202 cm^{-1}. MS (70 eV, EI): m/z (%) = 169 (28.72) [M$^+$], 53 (100).

Ethyl 3-(Buta-2,3-dien-1-ylamino)-3-oxopropanoate (4i): The reaction of CuI (190.0 mg, 1.00 mmol), paraformaldehyde (480.5 mg, 16.00 mmol), **3i** (1.7074 g, 10.09 mmol), and iPr$_2$NH (2.0 mL, d = 0.716 g mL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **4i**[9a] (0.5183 g, 28%) after purification (eluent for chromatography: petroleum ether/ethyl acetate, 4:1 to 2:1) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28 (br. s, 1 H, NH), 5.23 (quint, J = 6.3 Hz, 1 H, C=CH), 4.86 (dt, J = 6.6, 3.3 Hz, 2 H, C=CH_2), 4.20 (q, J = 7.1 Hz, 2 H, OCH_2), 3.94–3.85 (m, 2 H, NCH_2), 3.32 (s, 2 H, CH_2CO), 1.30 (t, J = 7.1 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 208.0, 169.4, 164.8, 87.5, 77.6, 61.5, 41.0, 37.6, 14.0 ppm. IR (neat): $\tilde{\nu}$ = 3305, 1958, 1739, 1652, 1546, 1156, 1028 cm^{-1}. MS (70 eV, EI): m/z (%) = 183 (35.75) [M$^+$], 70 (100).

Ethyl 4-(Buta-2,3-dien-1-ylamino)-4-oxobutanoate (4j): The reaction of CuI (190.6 mg, 1.00 mmol), paraformaldehyde (480.9 mg, 16.01 mmol), **3j** (1.8388 g, 10.04 mmol), and iPr$_2$NH (2.0 mL, d = 0.716 g mL^{-1}, 1.432 g, 14.15 mmol) in dioxane (15 mL) afforded **4j**[9a] (1.2747 g, 64%) after purification (eluent for chromatography: petroleum ether/ethyl acetate, 2:1 to 1:1) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.11 (br. s, 1 H, NH), 5.15 (quint, J = 6.3 Hz, 1 H, C=CH), 4.78 (dt, J = 6.6, 3.3 Hz, 2 H, C=CH_2), 4.09 (q, J = 7.2 Hz, 2 H, OCH_2), 3.83–3.75 (m, 2 H, NCH_2), 2.61 (t, J = 6.8 Hz, 2 H, CCH_2C), 2.45 (t, J = 6.9 Hz, 2 H, CCH_2C), 1.21 (t, J = 7.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 207.9, 172.9, 171.3, 87.8, 77.3, 60.6, 37.5, 30.8, 29.5, 14.0 ppm. IR (neat): $\tilde{\nu}$ = 3305, 1958, 1733, 1650, 1542, 1165, 1037 cm^{-1}. MS (70 eV, EI): m/z (%) = 197 (6.51) [M$^+$], 101 (100).

Procedure for the Synthesis of Buta-2,3-dien-1-ol. Method 1: To a 2 L oven-dried three-neck round-bottom flask equipped with a magnetic stirring bar, a reflux condenser, and a thermometer were added CuI (38.1 g, 0.200 mol), paraformaldehyde (19.2 g, 0.639 mol), THF (800 mL), iPr$_2$NH (80.0 mL, d = 0.716 g mL^{-1}, 57.3 g, 0.566 mol), and propargyl alcohol (24.0 mL, d = 0.949 g mL^{-1}, 22.8 g, 0.406 mol) in open air. After the addition, the resulting mixture was heated for 24 h in an oil bath at 85 °C without protection under an inert atmosphere. After cooling to room temperature, the dark-brown solution was concentrated by rotary evaporation (< 20 °C/4.8 kPa). The mixture was diluted with diethyl ether (300 mL) followed by filtration through a short column of silica gel [height = 5.0 cm, ø = 9.0 cm, diethyl ether (5 × 50 mL)]. Then the residue was transferred to a 1 L Erlenmeyer flask equipped with a magnetic stirring bar and a saturated NaCl aqueous (300 mL). Hydrochloric acid (12 N) was added slowly until pH 2–3 (about 20 mL). The mixture was filtered through a short column of quartz sand [hight = 5.0 cm, diameter = 10.0 cm, diethyl ether (3 × 100 mL)], and transferred to a separatory funnel. The aqueous layer was separated and extracted with diethyl ether (4 × 150 mL). The combined organic layer was dried with anhydrous $MgSO_4$ (50 g). After filtration and concentration through evaporation (< 20 °C/4.8 kPa), the product was carefully distilled under vacuum. The main fraction was collected at 54–56 °C (3.8 kPa) to afford buta-2,3-dien-1-ol[10d] (12.4 g, 44%) as a light yellow liquid, with additional fractions of less pure material. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.24 (quint, J = 6.5 Hz, 1 H, C=CH), 4.75 (dt, J = 6.6, 3.3 Hz, 2 H, C=CH_2), 4.05 (dt, J = 6.0, 3.0 Hz, 2 H, CH_2), 3.35 (br. s, 1 H, OH) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 207.8, 90.5, 76.4, 59.9 ppm. IR (neat): $\tilde{\nu}$ = 3331, 1955, 1009 cm^{-1}. MS (70 eV, EI): m/z (%) = 70 (13.41) [M$^+$], 55 (100).

Method 2: To an oven-dried high-pressure autoclave (500 mL) equipped with a magnetic stirring bar were added CuI (3.8 g, 0.020 mol), paraformaldehyde (9.6 g, 0.320 mol), THF (400 mL), iPr$_2$NH (40.0 mL, d = 0.716 g mL^{-1}, 28.6 g, 0.283 mol), and propargyl alcohol (12.0 mL, d = 0.949 g mL^{-1}, 11.4 g, 0.203 mol). After the addition, the resulting mixture was sealed and heated for 16 h in an oil bath at 140 °C. After cooling to room temperature, and purified following the workup procedure as for Method 1, buta-2,3-dien-1-ol[10d] (7.484 g, 53%) was afforded as a light yellow liquid upon vacuum distillation [b.p.48–51 °C (2.7–3.2 kPa)].

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra for the products.

Acknowledgments

Financial support from the National Basic Research Program of China (grant number 2009CB825300) and National Natural Sci-

ence Foundation of China (NSFC) (grant number 21232006) are greatly appreciated. The authors thank Li Qiankun for reproducing the results of Table 2 (Entry 9), Table 3 (Entry 3), and Table 4 (Entry 7).

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Received: December 16, 2012
Published Online: ■

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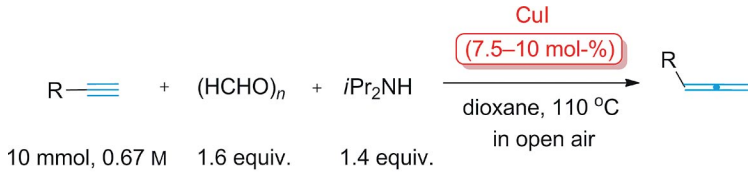
Copper Catalysis



R = alkyl with hydroxyl, ether, thioether, amide, or carbonyl functionality

A practical reaction for the CuI-catalyzed synthesis of terminal allenes from terminal alkynes, paraformaldehyde, and iPr$_2$NH was developed.

Keywords: Synthetic methods / Heterogeneous catalysis / Copper / Alkynes / Allenes

