JOC The Journal of Organic Chemistry

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CuI-Catalyzed Cross-Coupling of *N*-Tosylhydrazones with Terminal Alkynes: Synthesis of 1,3-Disubstituted Allenes

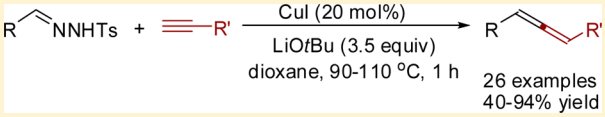
Mohammad Lokman Hossain,[†,§] Fei Ye,[†,§] Yan Zhang,[†] and Jianbo Wang*[,†,‡]

[†]Beijing National Laboratory of Molecular Sciences (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China

[‡]State Key Laboratory of Organometallic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

Supporting Information

ABSTRACT: A CuI-catalyzed synthesis of 1,3-disubstituted allenes from 1-alkynes by the reaction with various *N*-tosylhydrazones has been developed. This method, which uses readily available starting materials and is operationally simple, offers 1,3-disubstituted allenes in moderate to good yields. The reaction also tolerates various functional groups.

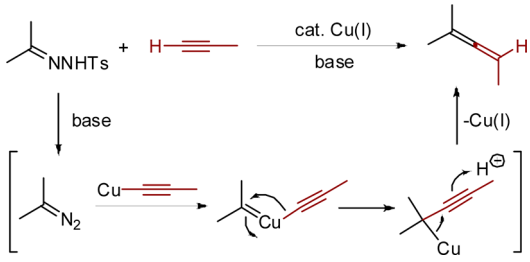


Owing to the unique structural feature related to the presence of two perpendicular π bonds, allenes are particularly prone to undergo various transformations. Because of their rich reactivity, allenes have been recognized as versatile substrates or intermediates in modern organic synthesis.[1,2] Allene moieties are also structural units of many natural products and pharmacologically interesting compounds.[3] It is thus not surprising that numerous synthetic methodologies to access such compounds have been explored in the past decades.[4] Among the various methods, the most general one is based on an S_N2'-type displacement of propargyl alcohol derivatives with organocopper species.[4,5]

However, an allene synthesis based on a coupling reaction is relatively less developed, and up to now, there are only a few catalytic methods reported in the literature. Barrett and co-workers demonstrated a cross-metathesis by employing the Grubbs catalysts and observed that the terminal carbon of allenes could be exchanged to afford symmetrically substituted allenes, but with a considerable amount of polymeric side products.[6] Bertrand and co-workers employed a cationic Au(I) complex for the catalytic coupling of enamines and terminal alkynes to afford allenes in good yields.[7] In 1979, Crabbé and co-workers reported the CuBr-mediated reaction to form terminal allenes from 1-alkynes and formaldehyde in the presence of diisopropylamine.[8] This reaction only works with formaldehyde, thus it can only be applied to the synthesis of monosubstituted allenes. Recently, Ma and co-workers significantly improved this reaction.[9] The same group also expanded the reaction to aldehydes, morpholine, and terminal alkynes by using ZnI_2, which led to an efficient synthesis of 1,3-disubstituted allenes.[9b]

Our group has recently developed a different approach toward allenes by Cu(I)/bisoxazoline-catalyzed cross-coupling reaction of *N*-tosylhydrazones with terminal alkynes.[10,11] Mechanistically, it has been proposed that the reaction involves a Cu-carbene migratory insertion process (Scheme 1).[12] This reaction provides a straightforward access to trisubstituted allenes using *N*-tosylhydrazones derived from ketones. However, the previously reported reaction is not suitable for the synthesis of disubstituted allenes because the reaction did not proceed well when *N*-tosylhydrazones derived from aldehydes were employed as the substrates.

Scheme 1. Allene Synthesis through Cu-Carbene Migratory Insertion



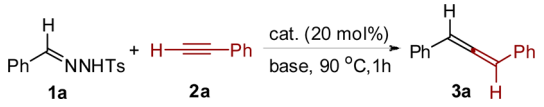
In this note, we report a modification of the previous reaction conditions for the reaction of *N*-tosylhydrazones derived from aldehydes. The reaction is now significantly simplified by only using CuI as the catalyst, while in the previous reaction, a complex bisoxazoline ligand is needed. The new reaction conditions can be successfully applied to the cross-coupling of *N*-tosylhydrazones derived from various aldehydes and terminal alkynes, affording 1,3-disubstituted allenes in moderate to good yields.

The study began with an evaluation of the reaction between *N*-tosylhydrazone **1a** with phenylacetylene **2a** by surveying different potential Cu(I) catalysts without using any ligand (Table 1). With LiO*t*Bu as the base and dioxane as the solvent, $(CuOTf)_2{\cdot}C_6H_6$ proved to be ineffective, giving **3a** only in trace amounts (Table 1, entry 1). Both CuCl and CuBr showed catalytic activity, affording the desired allene product **3a** in 10 and 40% yield, respectively (Table 1, entries 2 and 3). To our

Received: November 10, 2012
Published: January 9, 2013

   dx.doi.org/10.1021/jo3024686 | *J. Org. Chem.* 2013, 78, 1236−1241

Table 1. Optimization of Reaction Conditions[a]



entry	catalyst (20 mol %)	base	solvent	yield (%)[b]
1	$(CuOTf)_2{\cdot}C_6H_6$	LiO*t*Bu	dioxane	trace
2	CuCl	LiO*t*Bu	dioxane	10
3	CuBr	LiO*t*Bu	dioxane	40
4	**CuI**	**LiO*t*Bu**	**dioxane**	**78**
5	CuI	NaOH	dioxane	50
6	CuI	Cs_2CO_3	dioxane	15
7	CuI	KOH	dioxane	8
8	CuI	K_2CO_3	dioxane	trace
9	CuI	Na_2CO_3	dioxane	trace
10	CuI	LiO*t*Bu	DCE	72
11	CuI	LiO*t*Bu	MeCN	33

[a]Reaction conditions: **1a** (0.88 mmol), **2a** (0.4 mmol), base (3.5 equiv), solvent (5 mL). [b]Isolated yields.

delight, with CuI as the catalyst, the yield of **3a** could be improved to 78% (Table 1, entry 4). Next, we examined the effect of base on the reaction and observed that other commonly used bases all gave inferior results (Table 1, entries 5−9). It was noted that Cs_2CO_3, which was the base used in our previous study,[10] afforded **3a** in only 15% yield under the current reaction conditions (Table 1, entry 6). Finally, two other polar solvents, 1,2-dichloroethane (DCE) and MeCN, were examined. The reaction with DCE afforded comparable results, while in MeCN, the yield was diminished (Table 1, entries 10 and 11). On the basis of the above experiments, the optimized reaction conditions can be summarized as follows: substrate ratio of **1a** to **2a** is 2.2:1, CuI (20 mol %), LiO*t*Bu (3.5 equiv), 1,4-dioxane (5 mL), 90 °C, 1 h (Table 1, entry 4).

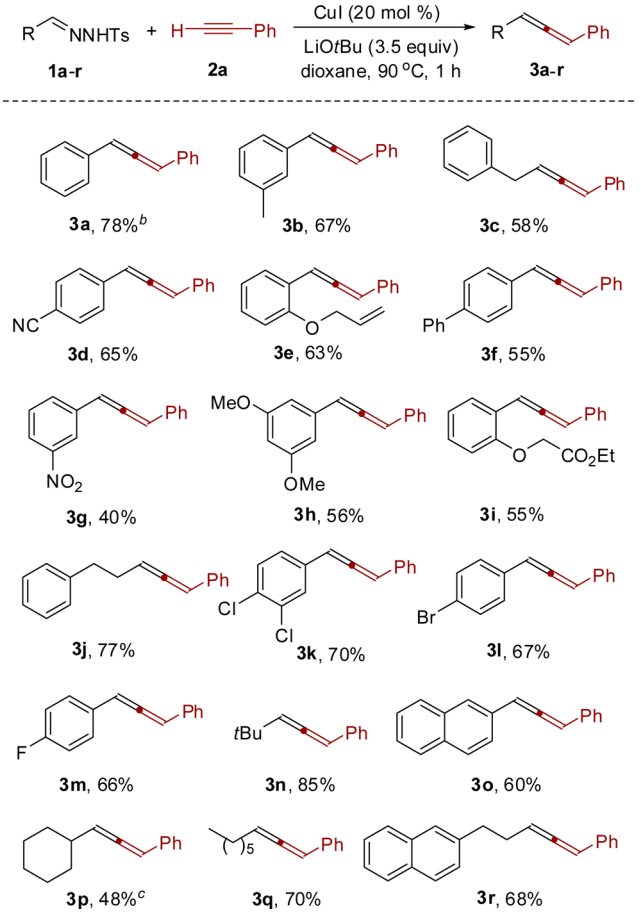
With the optimized reaction conditions in hand, we next explored the scope of this reaction with various *N*-tosylhydrazones and terminal alkynes. First, we examined the scope of *N*-tosylhydrazones by the reaction with **2a** (Scheme 2). The reactions of *N*-tosylhydrazones derived from a variety of aldehydes proceeded smoothly, affording the corresponding products **3a**−**r** in moderate to good yields.

For the *N*-tosylhydrazones derived from aromatic aldehydes, it is noted that the reactions were not significantly affected by the substituents on the aromatic ring, although a slightly lower yield was observed with *m*-nitrobenzaldehyde tosylhydrazone (Scheme 2, **3g**). Functional groups, such as allyloxy, methoxy, acetoxy, and $-OCH_2CO_2Et$, are all tolerated in this reaction. Moreover, the reaction with aliphatic tosylhydrazones also proceeded well (Scheme 2, **3n**, **3p**, **3q**, and **3r**).

Next, the reaction scope was investigated for a variety of terminal alkynes under the optimized reaction conditions (Scheme 3). The reactions examined under the identical reaction conditions afforded the corresponding allene products in moderate to good yields.

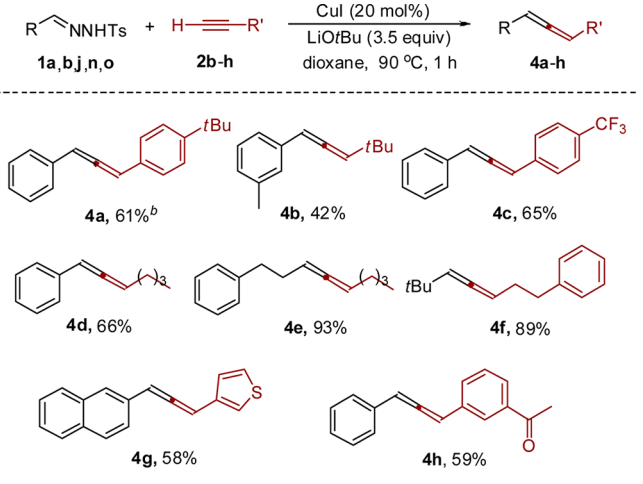
To validate whether this allene synthesis can be practiced in organic synthesis, scale-up experiments were carried out for several substrates. To our delight, the reactions all proceeded well and the corresponding allenes could be isolated on a gram-scale (Scheme 4). Notably, the diazo intermediate is generated in situ at a slow rate from the corresponding *N*-tosylhydrazone, so the evolution of N_2 gas is gentle even in scale-up experiments.

Scheme 2. Substrate Scope of *N*-Tosylhydrazones[a]



[a]Reaction conditions: *N*-tosylhydrazone (2.2 equiv), **2a** (0.4 mmol), CuI (20 mol %), LiO*t*Bu (3.5 equiv), dioxane (5 mL), 90 °C, 1 h. [b]Isolated yield by column chromatography. [c]CuI (40 mol %) was used.

Scheme 3. Substrate Scope of Terminal Alkynes[a]

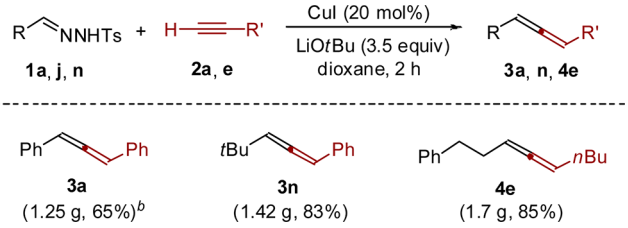


[a]Reaction condition: *N*-tosylhydrazone (2.2 equiv), alkyne (0.4 mmol), CuI (20 mol %), LiO*t*Bu (3.5 equiv), dioxane (5 mL), 90 °C, 1 h. [b]Isolated yield by column chromatography.

Finally, we have carried out experiments in a one-pot reaction mode directly starting from the aldehydes. To our delight, the one-pot procedure afforded similar results as

dx.doi.org/10.1021/jo3024686 | J. Org. Chem. 2013, 78, 1236−1241

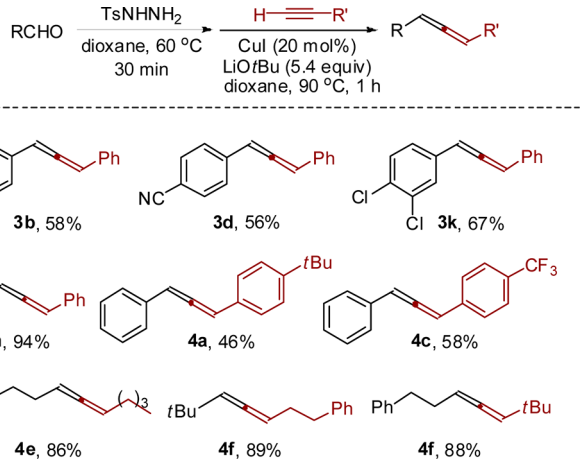
Scheme 4. Gram-Scale Experiments[a]



[a]Reaction conditions: *N*-tosylhydrazone (2.2 equiv), alkyne (10 mmol), CuI (20 mol %), LiO*t*Bu (3.5 equiv), dioxane (125 mL for **3a**; 100 mL for **3n** and **4e**), 90 °C (for **3a**) or 110 °C (for **3n** and **4e**), 2 h. [b]Isolated yield by column chromatography.

compared to the stepwise transformations (Scheme 5). This appreciably simplifies the allene preparation.

Scheme 5. One-Pot Preparation of Allenes[a]



[a]Reaction conditions: Aldehyde (2.2 equiv), $TsNHNH_2$ (2.2 equiv), 1-alkyne (0.4 mmol), CuI (20 mol %), LiO*t*Bu (5.4 equiv), dioxane (5 mL), 90 °C, 1 h. [b]Isolated yield by column chromatography.

In conclusion, we have developed a straightforward synthesis of 1,3-disubstituted allenes from terminal alkynes and *N*-tosylhydrazones by a CuI-catalyzed migratory insertion reaction. The prominent features of this method include the following: (1) *N*-tosylhydrazones are easily available from the corresponding aldehydes; (2) the CuI catalyst is inexpensive, and no ligand is required; (3) the reaction is simple to operate and tolerates various functional groups. It is thus expected that this method will be useful in organic synthesis.

EXPERIMENTAL SECTION

General Experimental Methods. Except for the gram-scale experiments, all reactions were performed under a nitrogen atmosphere in a 20 mL Schlenk tube. For the gram-scale experiments, the reactions were carried out in round-bottomed flasks. Dioxane was dried over Na before use. For chromatographic purifications, 200−300 mesh silica gel was employed. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in parts per million using tetramethylsilane (TMS) as the internal standard. IR spectra are reported in wavenumbers (cm^{-1}). For HRMS measurements, the mass analyzer is FT-ICR. *N*-Tosylhydrazones were prepared according to a literature procedure.[10] Unless noted otherwise, materials obtained from commercial suppliers were used without further purifications.

Typical Procedure for the CuI-Catalyzed Cross-Coupling of *N*-Tosylhydrazones and Terminal Alkynes. Under a nitrogen atmosphere, ethynylbenzene **2a** (40.8 mg, 0.4 mmol) was added to a mixture of CuI (15.3 mg, 0.08 mmol), Li*t*OBu (112 mg, 1.4 mmol), and the *N*-tosylhydrazone **1a** (241 mg, 0.88 mmol) in 1,4-dioxane (5 mL). The solution was stirred at 90 °C for 1 h, and the progress of the reaction was monitored by TLC. Upon completion of the reaction, the mixture was cooled to room temperature and was filtered through a short silica gel column eluting with EtOAc. The solvent was removed in vacuum to leave a crude mixture, which was purified by column chromatography on silica gel (eluting with petroleum ether) to afford pure 1,3-diphenylpropa-1,2-diene **3a**[13] as a colorless oil (60 mg, 78%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.50 (s, 2H), 7.11−7.14 (m, 2H), 7.20−7.27 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 98.4, 127.0, 127.3, 128.7, 133.6, 207.8.

*1-Methyl-3-(3-phenylpropa-1,2-dienyl)benzene (**3b**).* Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether) to afford pure **3b** as a light yellow oil (55 mg, 67%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 (s, 3H), 6.45−6.50 (m, 2H), 6.94−6.98 (m, 1H), 7.05−7.14 (m, 4H), 7.20−7.28 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 98.3, 98.4, 124.2, 127.0, 127.2, 127.6, 128.2, 128.6, 128.7, 133.4, 133.7, 138.4, 207.7; IR (film, cm^{-1}) 3027, 1937, 1603, 1410, 1261, 798, 695, 667; EI-MS (*m*/*z*, relative intensity) 206 (M$^+$, 100), 191 (90), 178 (15), 165 (20), 89 (10); HRMS (EI) calcd for $C_{16}H_{15}$ [(M + H)$^+$] 207.1168, found 207.1166.

*Buta-1,2-diene-1,4-diyldibenzene (**3c**).*[14] Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether) to afford pure **3c** as a colorless oil (48 mg, 58%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.40 (dd, *J* = 2.4, 7.2 Hz, 2H), 5.65 (dd, *J* = 7.2, 13.9 Hz, 1H), 6.09−6.12 (m, 1H), 7.10−7.16 (m, 2H), 7.19−7.26 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.6, 94.4, 94.9, 126.3, 126.7, 126.8, 128.5, 128.6, 134.6, 140.0, 205.7.

*4-(3-Phenylpropa-1,2-dienyl)benzonitrile (**3d**).*[15] Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether/EtOAc = 30:1) to afford pure **3d** as a light yellow oil (56 mg, 65%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.52 (d, *J* = 6.4 Hz, 1H), 6.60 (d, *J* = 6.4 Hz, 1H), 7.17−7.19 (m, 1H), 7.25 (d, *J* = 4.4 Hz, 4H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 97.6, 99.3, 110.5, 118.9, 127.1, 127.4, 127.8, 128.9, 132.4, 132.5, 138.8, 209.2.

*1-(Allyloxy)-2-(3-phenylpropa-1,2-dienyl)benzene (**3e**).* Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether/EtOAc = 60:1) to afford pure **3e** as a light yellow oil (62 mg, 63%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.48 (d, *J* = 5.2 Hz, 2H), 5.18 (dd, *J* = 1.2, 10.8 Hz, 1H), 5.34 (dd, *J* = 1.6, 17.2 Hz, 1H), 5.92−6.02 (m, 1H), 6.47 (d, *J* = 6.8 Hz, 1H), 6.77−6.82 (m, 2H), 6.96 (d, *J* = 6.8 Hz, 1H), 7.06−7.13 (m, 2H), 7.19−7.33 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 69.3, 92.5, 97.8, 112.5, 117.4, 121.0, 122.3, 126.9, 127.0, 128.0, 128.3, 128.6, 133.3, 134.0, 155.2, 208.3; IR (film, cm^{-1}) 2923, 1935, 1596, 1492, 1451, 1243, 1020, 792, 749, 690; EI-MS (*m*/*z*, relative intensity) 248 (M$^+$, 15), 207 (100), 178 (60), 152 (12), 115 (10); HRMS (EI) calcd for $C_{18}H_{17}O$ [(M + H)$^+$] 249.1274, found 249.1270.

*4-(3-Phenylpropa-1,2-dienyl)biphenyl (**3f**).*[5d] Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether) to afford pure **3f** as a white powder (59 mg, 55%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.52 (s, 2H), 7.19−7.34 (m, 10H), 7.44−7.49 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 98.1, 98.5, 126.9, 127.0, 127.2, 127.3, 127.40, 127.44, 128.8, 132.6, 133.5, 140.2, 140.7, 208.1.

*1-Nitro-3-(3-phenylpropa-1,2-dienyl)benzene (**3g**).* Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether/EtOAc = 60:1) to afford pure **3g** as a reddish oil (38 mg, 40%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57 (d, *J* = 6.4 Hz, 1H), 6.62 (d, *J* = 6.4 Hz, 1H), 7.17−7.20 (m, 1H), 7.24−7.27 (m, 4H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 8.09 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 97.0, 99.5, 121.5, 122.0, 127.2, 127.8, 128.9, 129.5, 132.5, 132.6, 135.9, 148.7, 208.4; IR (film, cm^{-1}) 2962, 1938,

dx.doi.org/10.1021/jo3024686 | J. Org. Chem. 2013, 78, 1236−1241

1527, 1350, 1260, 1018, 799, 729, 693, 672; EI-MS (*m*/*z*, relative intensity) 237 (M^+, 50), 220 (15), 207 (72), 189 (100), 178 (15), 165 (35), 115 (25); HRMS (EI) calcd for $C_{15}H_{12}NO_2$ [$(M + H)^+$] 238.0863, found 238.0858.

1,3-Dimethoxy-5-(3-phenylpropa-1,2-dienyl)benzene (**3h**). Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether/EtOAc = 30:1) to afford pure **3h** as a light yellow oil (56 mg, 56%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.69 (s, 6H), 6.28 (t, J = 2.0 Hz, 1H), 6.44−6.46 (m, 3H), 6.51 (d, J = 6.4 Hz, 1H), 7.16 (d, J = 9.1 Hz, 1H), 7.22−7.28 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 98.5, 98.6, 99.7, 105.0, 127.0, 127.3, 128.7, 133.5, 135.7, 161.0, 207.9; IR (film, cm^{-1}) 2962, 1943, 1593, 1455, 1260, 1204, 1154, 1018, 798, 694; EI-MS (*m*/*z*, relative intensity) 252 (M^+, 100), 237 (35), 221 (30), 207 (40), 178 (30), 165 (65), 115 (25); HRMS (EI) calcd for $C_{17}H_{17}O_2$ [$(M + H)^+$] 253.1223, found 253.1220.

Ethyl-2-(2-(3-phenylpropa-1,2-dienyl)phenoxy)acetate (**3i**). Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether/EtOAc = 40:1) to afford pure **3i** as a light yellow oil (65 mg, 55%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (t, J = 7.2 Hz, 3H), 4.18 (q, J = 7.2 Hz, 2H), 4.58 (s, 2H), 6.49 (d, J = 6.8 Hz, 1H), 6.70 (d, J = 8.4 Hz, 1H), 6.85 (t, J = 7.2 Hz, 1H), 7.02 (d, J = 6.8 Hz, 1H), 7.06−7.15 (m, 2H), 7.20−7.28 (m, 4H), 7.35 (dd, J = 1.2 and J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 61.3, 66.1, 92.4, 97.9, 112.5, 122.0, 122.8, 126.9, 127.1, 128.2, 128.3, 128.6, 133.8, 154.5, 168.8, 208.3; IR (film, cm^{-1}) 2963, 1936, 1758, 1493, 1454, 1260, 1200, 1115, 1024, 795, 750, 692; EI-MS (*m*/*z*, relative intensity) 294 (M^+, 5), 279 (15), 207 (45), 167 (35), 149 (100), 57 (30); HRMS (EI) calcd for $C_{19}H_{19}O_3$ [$(M + H)^+$] 295.1329, found 295.1328.

Penta-1,2-diene-1,5-diyldibenzene (**3j**).[16] Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether) to afford pure **3j** as a light yellow oil (68 mg, 77%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31−2.40 (m, 2H), 2.67−2.73 (m, 2H), 5.48 (q, J = 8.8 Hz, 1H), 6.02 (td, J = 4.0, 8.0 Hz, 1H), 7.05−7.21 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.5, 35.3, 94.3, 94.9, 125.9, 126.6, 126.7, 128.3, 128.4, 128.5, 134.8, 141.5, 205.2.

1,2-Dichloro-4-(3-phenylpropa-1,2-dienyl)benzene (**3k**). Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether) to afford pure **3k** as a light yellow oil (73 mg, 70%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.41 (d, J = 6.4 Hz, 1H), 6.54 (d, J = 6.4 Hz, 1H), (dd, J = 1.6, 8.4 Hz, 1H), 7.15−7.18 (m, 1H), 7.24−7.28 (m, 5H), 7.32 (d, J = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 96.8, 99.2, 126.1, 127.1, 127.7, 128.5, 128.8, 130.6, 130.9, 132.7, 132.8, 133.9, 208.1; IR (film, cm^{-1}) 2917, 1938, 1589, 1473, 1260, 1131, 1029, 887, 823, 696; EI-MS (*m*/*z*, relative intensity) 260 (M^+, 35), 225 (100), 189 (55), 94 (20); HRMS (EI) calcd for $C_{15}H_{11}Cl_2$ [$(M + H)^+$] 261.0232, found 261.0231.

1-Bromo-4-(3-phenylpropa-1,2-dienyl)benzene (**3l**).[17] Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether) to afford pure **3l** as a colorless oil (72 mg, 67%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.46 (d, J = 6.4 Hz, 1H), 6.51 (d, J = 6.4 Hz, 1H), 7.12−7.17 (m, 3H), 7.22−7.29 (m, 4H), 7.35 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 97.6, 98.8, 121.0, 127.0, 127.5, 128.5, 128.8, 131.8, 132.6, 133.1, 207.9.

1-Fluoro-4-(3-phenylpropa-1,2-dienyl)benzene (**3m**).[18] Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether) to afford pure **3m** as a colorless oil (55 mg, 66%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.50 (q, J = 6.5 Hz, 2H), 6.92 (t, J = 8.0 Hz, 2H), 7.13−7.16 (m, 1H), 7.21−7.27 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 97.4, 98.6, 115.7 (d, J = 21.6 Hz), 127.0, 127.4, 128.6 (d, J = 37.3 Hz), 129.1, 129.5 (d, J = 3.4 Hz), 133.4, 162.1 (d, J = 245.1 Hz), 207.5.

(4,4-Dimethylpenta-1,2-dienyl)benzene (**3n**).[19] Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether) to afford pure **3n** as a colorless oil (59 mg, 85%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (s, 9H), 5.49 (d, J = 6.4 Hz, 1H), 6.10 (d, J = 6.4 Hz, 1H), 7.08−7.11 (m, 1H), 7.21 (d, J = 4.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.3, 32.7, 96.2, 106.9, 126.4, 126.6, 128.5, 135.3, 202.4.

2-(3-Phenylpropa-1,2-dienyl)naphthalene (**3o**).[20] Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether) to afford pure **3o** as a white powder (58 mg, 60%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.58 (d, J = 6.4 Hz, 1H), 6.68 (d, J = 6.4 Hz, 1H), 7.13−7.44 (m, 8H), 7.65−7.71 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 98.6, 98.8, 124.8, 125.8, 125.9, 126.3, 127.0, 127.4, 127.7, 128.4, 128.8 (one carbon was missed because of overlap), 131.1, 132.8, 133.6, 133.7, 208.4.

(3-Cyclohexylpropa-1,2-dienyl)benzene (**3p**).[21] Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether) to afford pure **3p** as a colorless oil (38 mg, 48%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11−1.27 (m, 5H), 1.55−1.78 (m, 5H), 2.05 (s, 1H), 5.49 (t, J = 6.0 Hz, 1H), 6.06−6.08 (m, 1H), 7.09−7.22 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.0, 26.1, 33.1, 33.2, 37.6, 95.4, 101.0, 126.4, 126.6, 128.5, 135.2, 204.1.

Nona-1,2-dienylbenzene (**3q**).[19] Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether) to afford pure **3q** as a colorless oil (56 mg, 70%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (t, J = 6.8 Hz, 3H), 1.18−1.32 (m, 6H), 1.35−1.44 (m, 2H), 2.04 (dq, J = 3.0, 7.1 Hz, 2H), 5.48 (q, J = 6.8 Hz,1H), 6.04 (td, J = 2.9, 6.1 Hz, 1H), 7.07−7.12 (m, 1H), 7.21 (d, J = 4.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 28.8, 28.9, 29.1, 31.6, 94.5, 95.1, 126.6, 128.5 (one carbon was missed because of overlap), 135.2, 205.1.

2-(5-Phenylpenta-3,4-dienyl)naphthalene (**3r**). Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether) to afford pure **3s** as a light yellow oil (73 mg, 68%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44−2.51 (m, 2H), 3.15 (t, J = 7.7 Hz, 2H), 5.55 (dd, J = 6.6, 13.1 Hz, 1H), 6.05 (td, J = 2.8, 6.0 Hz, 1H), 7.04−7.38 (m, 9H), 7.61 (d, J = 7.6 Hz, 1H), 7.73 (d, J = 7.6 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.8, 32.5, 94.5, 95.2, 123.7, 125.4, 125.5, 125.8, 126.2, 126.6, 126.7, 126.8, 128.5, 128.7, 131.8, 133.9, 134.8, 137.6, 205.2; IR (film, cm^{-1}) 3060, 2960, 2926, 2852, 1948, 1596, 1494, 1458, 1395, 1260, 1024, 875, 796, 776, 961; EI-MS (*m*/*z*, relative intensity) 270 (M^+, 90), 242 (40), 179 (88), 141 (100), 128 (35), 115 (60); HRMS (EI) calcd for $C_{21}H_{19}$ [$(M + H)^+$] 271.1481, found 271.1480.

1-tert-Butyl-4-(3-phenylpropa-1,2-dienyl)benzene (**4a**).[5d] Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether) to afford pure **4a** as a colorless oil (60 mg, 61%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (s, 9H), 6.50 (s, 2H), 7.16−7.26 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.3, 34.6, 98.1, 98.3, 125.7, 126.7, 127.0, 127.2, 128.7, 130.6, 133.8, 150.5, 207.8.

1-(4,4-Dimethylpenta-1,2-dienyl)-3-methylbenzene (**4b**). Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether) to afford pure **4b** as a colorless oil (31 mg, 42%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (s, 9H), 2.25 (s, 3H), 5.48 (d, J = 6.4 Hz, 1H), 6.08 (d, J = 6.4 Hz, 1H), 6.92 (d, J = 7.6 Hz, 1H), 7.02 (d, J = 6.0 Hz, 2H), 7.09−7.16 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 30.3, 32.7, 96.2, 106.8, 123.5, 127.1, 127.4, 128.4, 135.2, 138.1, 202.4; IR (film, cm^{-1}) 2960, 2865, 1948, 1604, 1459, 1362, 1251, 1190, 903, 880, 792, 690; EI-MS (*m*/*z*, relative intensity) 186 (M^+, 65), 171 (35), 156 (20), 130 (70), 57 (100); HRMS (EI) calcd for $C_{14}H_{19}$ [$(M + H)^+$] 187.1481, found 187.1482.

1-(3-Phenylpropa-1,2-dienyl)-4-(trifluoromethyl)benzene (**4c**).[5d,22] Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether) to afford pure **4c** as a colorless oil (68 mg, 65%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.54 (dd, J = 7.4, 17.5 Hz, 2H), 7.09−7.18 (m, 4H), 7.23−7.25 (m, 3H), 7.34 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 97.6, 99.0, 124.2 (q, J =

dx.doi.org/10.1021/jo3024686 | J. Org. Chem. 2013, 78, 1236−1241

270.1 Hz), 125.6 (q, J = 3.8 Hz), 127.7, 128.2, 128.8, 129.2 (q, J = 32.2 Hz), 130.2, 132.8, 137.6 (d, J = 1.2 Hz), 208.7.

*Hepta-1,2-dienylbenzene (**4d**).*[19] Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether) to afford pure **4d** as a colorless oil (45 mg, 66%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (t, J = 7.2 Hz, 3H), 1.29−1.46 (m, 4H), 2.06 (dq, J = 3.0, 7.2 Hz, 2H), 5.49 (q, J = 6.8 Hz, 1H), 6.04 (td, J = 3.0, 6.2 Hz, 1H), 7.09−7.12 (m, 1H), 7.21 (d, J = 4.4, Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 22.2, 28.4, 31.3, 94.5, 95.1, 126.5, 126.6, 128.5, 135.1, 205.1.

*Nona-3,4-dienylbenzene (**4e**).*[20] Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether) to afford pure **4e** as a colorless oil (74 mg, 93%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 (t, J = 6.8 Hz, 3H), 1.23−1.28 (m, 4H), 1.84−1.90 (m, 2H), 2.19−2.25 (m, 2H), 2.64 (t, J = 7.8 Hz, 2H), 4.97−5.07 (m, 2H), 7.07−7.21 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 22.1, 28.6, 30.7, 31.3, 35.5, 90.2, 91.5, 125.7, 128.2, 128.5, 141.9, 204.0.

*(6,6-Dimethylhepta-3,4-dienyl)benzene (**4f**).*[21] Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether) to afford pure **4f** as a colorless oil (71 mg, 89%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (s, 9H), 2.20−2.26 (m, 2H), 2.63 (t, J = 8.0 Hz, 2H), 5.03 (td, J = 3.0, 6.3 Hz, 1H), 5.12 (q, J = 6.3 Hz, 1H), 7.07−7.21 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.2, 30.9, 31.7, 35.5, 92.1, 103.5, 125.8, 128.3, 128.5, 142.0, 201.1.

*3-(3-(Naphthalen-2-yl)propa-1,2-dienyl)thiophene (**4g**).* Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether/EtOAc = 100:1) to afford pure **4g** as a colorless oil (57 mg, 58%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.61 (dd, J = 6.4, 14.4 Hz, 1H), 6.74 (s, 1H), 7.02−7.16 (m, 2H), 7.27−7.33 (m, 3H), 7.47 (dd, J = 8.5, 41.1 Hz, 1H), 7.60−7.68 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 93.1, 98.0, 121.5, 124.8, 125.8, 125.9, 126.0, 126.4, 127.0, 127.5, 127.6, 127.7, 128.0, 128.1, 128.4, 130.5, 208.6; IR (film, cm^{-1}) 3054, 2959, 2925, 1936, 1597, 1505, 1377, 1260, 1018, 650, 905, 794, 731; EI-MS (m/z, relative intensity) 248 (M^+, 35), 207 (100), 133 (8), 96 (10), 59 (12); HRMS (EI) calcd for $C_{17}H_{13}S$ [$(M + H)^+$] 249.0732, found 249.0731.

*1-(3-(3-Phenylpropa-1,2-dien-1-yl)phenyl)ethanone (**4h**).* Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether/EtOAc = 20:1) to afford pure **4h** as a colorless oil (55 mg, 59%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.59 (s, 3H), 6.64 (s, 2H), 7.22−7.24 (m, 1H), 7.30−7.37 (m, 4H), 7.40−7.42 (m, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.90 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.7, 97.9, 99.0, 126.8, 127.1, 127.2, 127.6, 128.8, 129.0, 131.4, 133.2, 134.4, 137.7, 198.0, 208.0; IR (film, cm^{-1}) 2957, 2924, 1937, 1737, 1686, 1240, 1046, 735, 693; EI-MS (m/z, relative intensity) 234 (M^+, 48), 219 (45), 207 (48), 191 (100), 165 (30), 115 (12), 89 (10), 63 (10); HRMS (EI) calcd for $C_{17}H_{15}O$ [$(M + H)^+$] 235.1117, found 235.1116.

Typical Procedure for Gram-Scale Experiments. Under a nitrogen atmosphere, 1-hexyne **2e** (820 mg, 10 mmol) was added to a mixture of CuI (382 mg, 2.0 mmol), *Li*tOBu (2.8 g, 35 mmol), and *N*-tosylhydrazones **1j** (6.65 g, 22 mmol) in dioxane (100 mL). The solution was stirred at 90 °C for 1 h. Upon the completion of the reaction, the reaction mixture was cooled to room temperature and filtered through a short silica gel column eluting with EtOAc. The solvent was removed in vacuum to leave a crude mixture, which was purified by silica gel column chromatography using petroleum ether as an eluting solvent to afford pure nona-3,4-dienylbenzene **4e** as colorless oil (1.7 g, 85%).

Typical Procedure for One-Pot Preparation of Allenes. Pivalaldehyde (*t*BuCHO, 76 mg, 0.88 mmol) and 4-methylbenzenesulfonohydrazide ($TsNHNH_2$, 164 mg, 0.88 mmol) were suspended in dioxane (1 mL) in a 25 mL Schlenk tube, and the resulting solution was stirred at 60 °C for 30 min. Upon completion of the reaction (as monitored by TLC), a solution of CuI (15.3 mg, 0.08 mmol) and *Li*tOBu (176 mg, 2.2 mmol) in dioxane (4 mL) was added under nitrogen. Then phenylacetylene **2a** (40.8 mg, 0.4 mmol) was added. The resulting mixture was stirred at 90 °C for 1 h. After cooling to room temperature, the mixture was filtered through a short silica gel column eluting with EtOAc. The solvent was removed under vacuum, and the crude residue was purified by column chromatography on silica gel eluting with petroleum ether to afford pure (4,4-dimethylpenta-1,2-dienyl)benzene **3n** as a colorless oil (70 mg, 94%).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H and ^{13}C spectra for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: wangjb@pku.edu.cn.

Author Contributions

[§]These authors contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The project is supported by National Basic Research Program (973 Program, No. 2009CB825300), Natural Science Foundation of China (21272010).

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