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Note

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Synthesis of Terminal Allenes through Copper-mediated Cross-Coupling of Ethyne with *N*-Tosylhydrazones or *α*-Diazoesters

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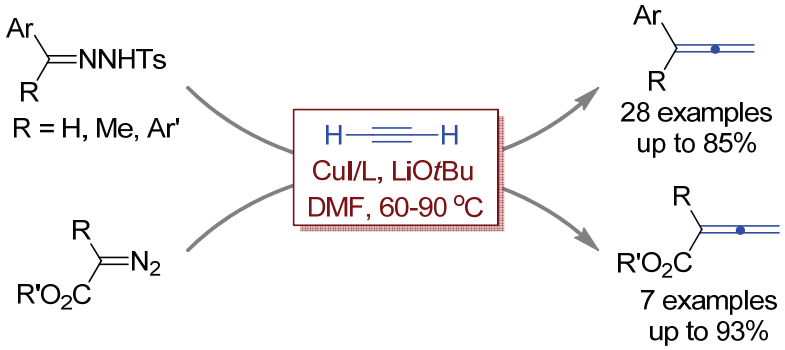
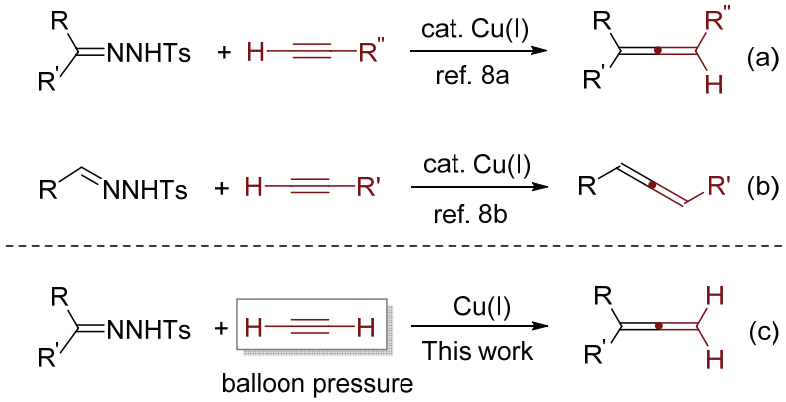


ABSTRACT: Ethyne is employed as coupling partner in copper-mediated cross-coupling reactions with *N*-tosylhydrazones and *α*-diazoacetate, leading to the development of a new synthetic method for terminal allenes. With this novel coupling method, the terminal allenes were obtained in good yields and

with excellent functional group tolerance. Copper carbene migratory insertion is proposed as the key step in these transformations.

Allenes have found increasing applications in organic synthesis.[1] Consequently, various synthetic methods to access allenes have been developed over the past decades.[2] In general, S_N2'-type displacement of propargyl alcohol derivatives with organocopper species is the most widely practiced method.[3] On the contrary, there are only few reports in the literature on the allene synthesis based on coupling reactions.[4] Crabbé and co-workers in 1979 reported the terminal allene synthesis through CuBr-mediated reaction of 1-alkynes and formaldehyde in the presence of diisopropylamine.[5] Recently, this reaction has been significantly improved and expanded by Ma and coworkers.[6,7] In 1980, a reaction of ethyl diazoacetate with acetylene to generate terminal allene mediated by CuO was reported by Shapiro and co-workers.[8]

Scheme 1. Allene Synthesis through Cu Carbene Migratory Insertion

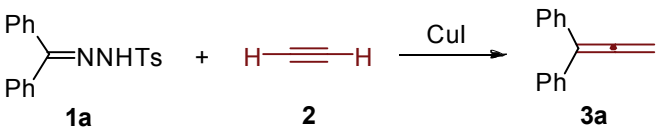


We have recently reported an alternative allene synthesis by Cu(I)-catalyzed cross-coupling reaction of *N*-tosylhydrazones with terminal alkynes.[9] The reaction is proposed to follow Cu(I) carbene migratory insertion process.[10] However, our previous method by using terminal alkynes as coupling partner is only applicable to the synthesis of di- and tri-substituted allenes (Scheme 1, a and b). On the

other hand, the copper-catalyzed coupling reactions between terminal alkynes and diazoacetates were studied by Jones and Vidal.[11] More recently this type of coupling reactions have been developed into the methods for the synthesis of allenoates and 3-alkynoates by Fox and Fu, respectively.[12,13] Herein we report the copper-mediated synthesis of terminal allenes by the application of ethyne as the cross-coupling partner under atmospheric pressure conditions. The cross-coupling reaction of *N*-tosylhydrazones with a balloon of ethyne is highly efficient and operationally simple, leading to the straightforward synthesis of mono- and 1,1-disubstituted allenes. The reaction can also be applied to *α*-diazoacetates.[12,14]

At the outset of this study, *N*-tosylhydrazone **1a** and acetylene **2** were subjected to the coupling reaction under the similar reaction conditions as we previously reported for the synthesis of 1,3-disubstituted allene (20 mol% CuI, 2.0 equiv of LiO*t*Bu and 2.0 mL dioxane).[9b] The desired allene product **3a** could be isolated in 5% yield (Table 1, entry 1). Further study of the solvent effect indicated that the reaction in DMF afforded improved yield (enter 4), while the reaction in toluene or MeCN gave poor results (entries 2 and 3). Screening the reaction concentration and the loading of catalyst led to the conclusion that more concentrated solution and higher loading of CuI were favorable for the reaction (entries 5-9). Thus, in the presence of 1.0 equiv of CuI, 2.0 equiv of LiO*t*Bu and 1.0 mL DMF, the allene **3a** could be isolated with an optimized yield of 76% (entry 9). Finally, other bases such as KO*t*Bu and KOMe were examined, but the corresponding reactions only gave trace amount of the allene product (entries 10 and 11).

Table 1. Optimization of Reaction Conditions[a]



entry	cat. (equiv)	base (equiv)	solvent (mL)	yield (%)[b]

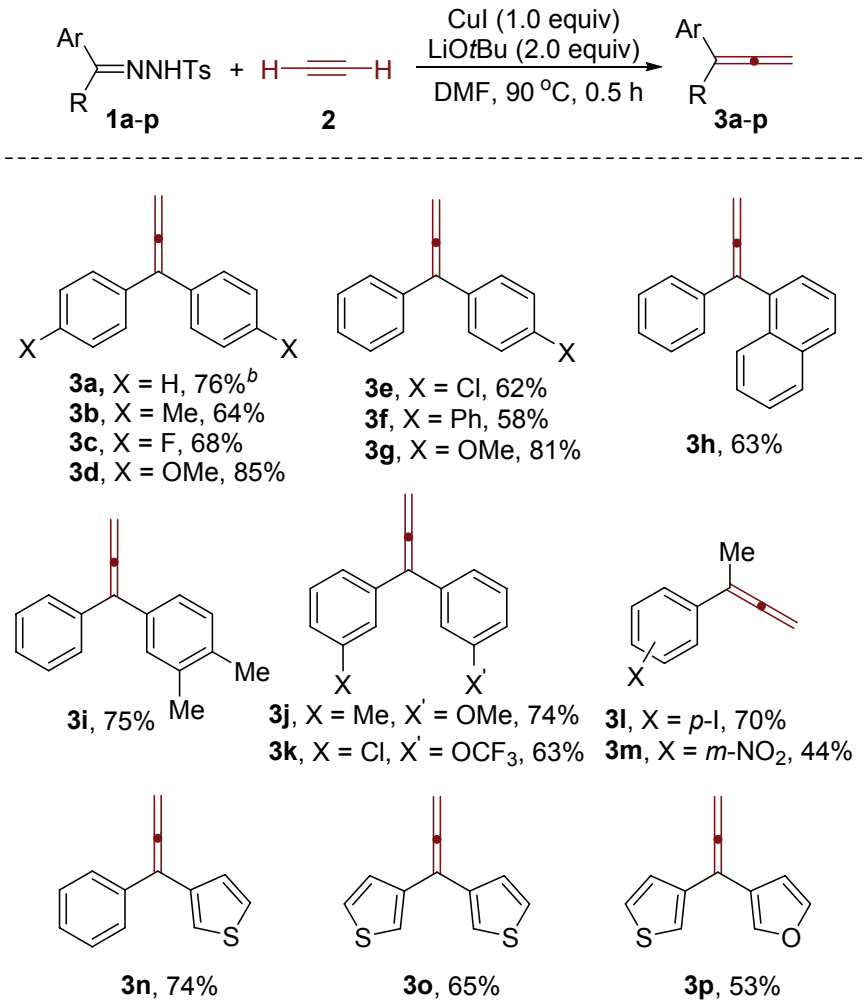
1	CuI (0.2)	LiO*t*Bu (2)	dioxane (2)	5
2	CuI (0.2)	LiO*t*Bu (2)	MeCN (2)	*trace*
3	CuI (0.2)	LiO*t*Bu (2)	toluene (2)	*trace*
4	CuI (0.2)	LiO*t*Bu (2)	DMF (2)	12
5	CuI (0.2)	LiO*t*Bu (2)	DMF (1.5)	14
6	CuI (0.4)	LiO*t*Bu (2)	DMF (1.5)	32
7	CuI (0.6)	LiO*t*Bu (2)	DMF (1.5)	46
8	CuI (0.6)	LiO*t*Bu (2)	DMF (1)	52
9	CuI (1)	LiO*t*Bu (2)	DMF (1)	76
10	CuI (1)	KO*t*Bu (2)	DMF (1)	*trace*
11	CuI (1)	KOMe (2)	DMF (1)	*trace*

[a]The reaction was carried out with **1a** (0.4 mmol) at 90 ^{o}C under an atmosphere of acetylene (balloon) for 0.5 h. [b]Isolated yields. DMF: *N,N*-dimethylformamide.

With the optimized reaction conditions, we proceeded to explore the substrate scope, firstly by using a series of *N*-tosylhydrazones **1a-p** derived from aryl ketones (Scheme 2). In all the cases, the corresponding 1,1-disubstituted allene products **3a**-**p** could be isolated in moderate yields. The reaction is not significantly affected by the electronic effects of the substituents on the aromatic ring of the *N*-tosylhydrazones which were derived from diaryl ketones. Both electron-withdrawing groups (such as fluoro, chloro, and phenyl group), and electron-donating group (such as methyl and alkoxyl group), show little influence on the reaction (**3a-g**, **3i-k**). Besides, the reactions with the *N*-tosylhydrazones

derived from aryl methyl ketones also afforded the desired products (**3l** and **3m**). Notably, the reaction proceeded well with the *N*-tosylhydrazones bearing naphthyl, thiophenyl and furanyl groups (**3h**, **3n** and **3p**). However, the *N*-tosylhydrazones derived from other aliphatic ketones, such as cyclohexanone, 1,2-diphenylethanone and 4-phenylbutan-2-one, are not suitable substrates for this reaction because 1,2-hydrogen shift becomes competitive and the side products are difficult to separate from the allenes. It was noted that there were two major side reactions in these transformations: the dimerization of the carbene intermediates that generated olefins, and the reaction of Ts anion with carbene or diazo intermediates that gave sulfonyl compounds.

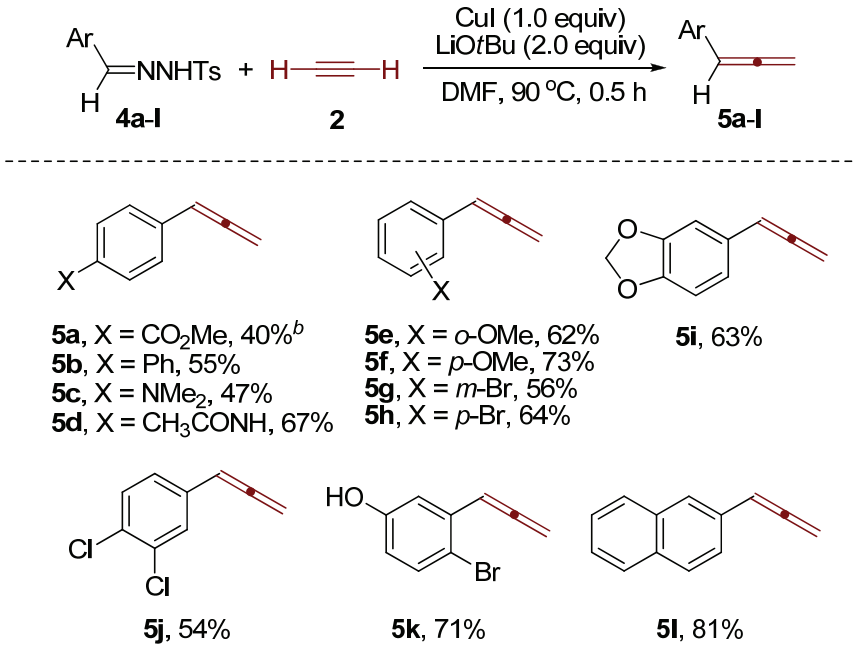
Scheme 2. The Substrate Scope of *N*-Tosylhydrazones Derived from Aromatic Ketones[a]



[a]The reaction conditions are as following: *N*-tosylhydrazones **1a**-**p** (0.4 mmol), acetylene **2** (1 atm), CuI (1.0 equiv), LiO*t*Bu (0.8 mmol), DMF (1.0 mL), 90 °C, 0.5 h. [b]Isolated yield.

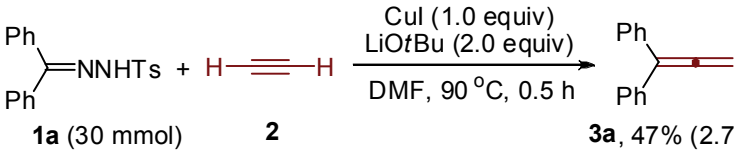
Next, we explored the reaction scope with *N*-tosylhydrazones derived from aromatic aldehydes, which would afford mono-substituted allenes as the products. As shown in Scheme 3, a series of *N*-tosylhydrazones derived from benzaldehydes bearing *para*, *ortho* and *meta* substituents all reacted smoothly with acetylene **2** under the optimized reaction conditions (Scheme 3, **5a**-**h**). Moreover, the *N*-tosylhydrazones derived from benzaldehydes bearing multiple substituents also worked well (**5i**-**k**). Finally, the reaction with *N*-tosylhydrazone derived from naphthaldehyde gave the corresponding allene product **5l** in 81% yield.

Scheme 3. The Substrate Scope of *N*-Tosylhydrazones Derived from Aromatic Aldehydes[a]

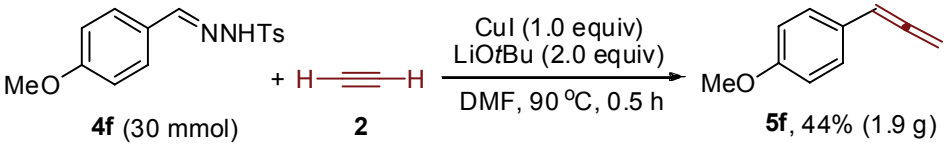


[a]The reaction conditions are as following: *N*-tosylhydrazones **4a**-**l** (0.4 mmol), acetylene **2** (1 atm), CuI (1.0 equiv), LiO*t*Bu (0.8 mmol), DMF (1.0 mL), 90 °C, 0.5 h. [b]Isolated yield.

To validate whether this strategy can be practically useful, scale-up experiments were carried out for *N*-tosylhydrazones **1a** and **4f**. The reactions afforded the corresponding allene products **3a** and **5f** in gram-scale, albeit in diminished yields as compared with the small scale experiments (eq 1 and 2).



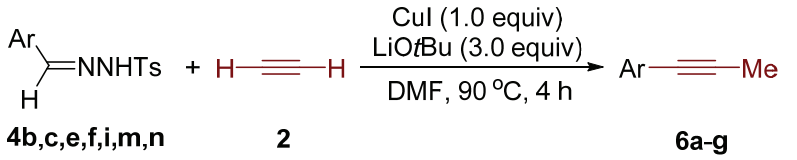
(1)

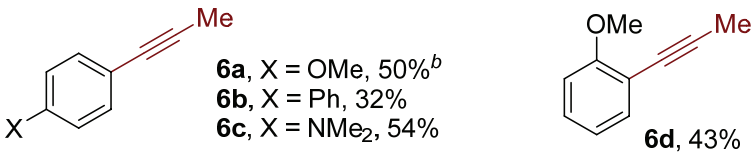


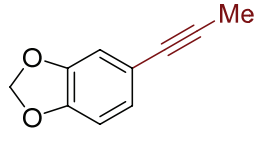
(2)

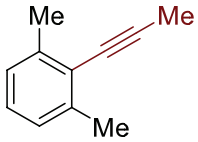
During the substrate scope study shown in Scheme 3, we noticed that in some cases 1-methyl-2-aryl acetylene derivatives could be isolated as side products, in particular for the reactions with aromatic *N*-tosylhydrazones bearing electron-donating substituents. We reasoned that the formation of 1-methyl-2-aryl acetylene side products were attributed to the base-promoted rearrangement of the primary allene products. Thus, by extending the reaction time and increasing the amount of base, the 1-methyl-2-aryl acetylene derivatives might turn to be the major products. This was proved to be the case. As summarized in Scheme 4, carrying out the coupling reaction for 4 h with increased base (LiO*t*Bu, 3 equiv) could afford the 1-methyl-2-aryl acetylene products in moderate yields.

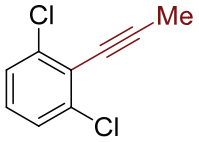
Scheme 4. Formation of 1-Methyl-2-aryl Acetylene Derivatives [a]







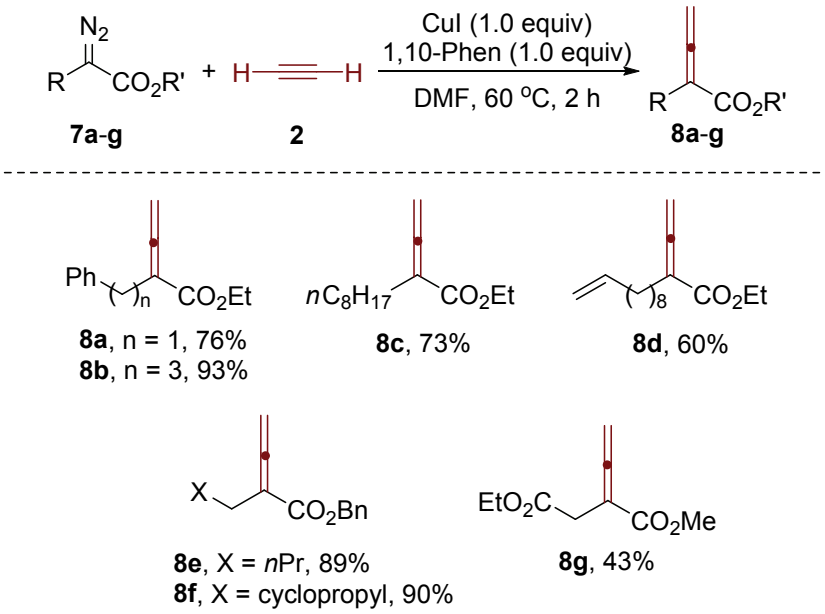




[a]All the reaction conditions are as following: *N*-tosylhydrazones **4b-c**, **4e-f**, **4i**, **4m-n** (0.4 mmol), acetylene **2** (1 atm), CuI (1.0 equiv), LiO*t*Bu (1.2 mmol), DMF (1.0 mL), 90 °C, 4.0 h. [b]Isolated yield.

Encouraged by the successful coupling of acetylene gas with *N*-tosylhydrazones, we then proceeded to extend this transformation to α-diazo esters.[10] To our delight, under modified reaction conditions [CuI (1.0 equiv), 1,10-phenanthrene (1.0 equiv), DMF, 60 °C, 2 h], the expected allene products could be isolated in moderate yields (Scheme 5). Notably, the side products due to 1,2-hydrogen shift, which is a common reaction for metal carbene species, were not observed in most cases.[15]

Scheme 5. Cross-coupling with α-Diazo Acetates[a]



[a] The reaction conditions are as following: α-diazo ester **7a-h** (0.4 mmol), acetylene **2** (1 atm), CuI (1.0 equiv), 1,10-phenanthrene (1.0 equiv), DMF (1.5 mL), 60 °C, 2.0 h. [b]Isolated yield.

In conclusion, we have developed a novel strategy for the synthesis of mono- and 1,1-disubstituted terminal allenes. This transformation has the following features: 1) the reaction is

operationally simple by using a balloon of acetylene gas; 2) cheap copper catalyst is used; 3) the *N*-tosylhydrazones are easily prepared from the corresponding ketones or aldehydes and they are stable and easy to purify; 4) the reaction is efficient and tolerates various functional groups. With those advantages, we expect that this method will find wide applications for the synthesis of terminal allenes.

EXPERIMENTAL SECTION

General Experimental Methods. Except the gram-scale experiments, all reactions were performed under acetylene gas atmosphere in a 10 mL microwave tube (Note: the reactions are not carried out under microwave conditions). DMF and acetylene gas obtained from commercial suppliers were used without further purifications. For the gram-scale experiments, the reaction was carried out in round-bottle flask. For chromatographic purification, 200-300 mesh silica gel (Qingdao, China) was employed. Chemical shifts for ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra are reported relative to the chemical shift of tetramethylsilane (TMS). IR spectra are reported in wave numbers, cm^{-1}. For HRMS measurements, the mass analyzer is FT-ICR.

N-Tosylhydrazones **1a**-**p** and **4a**-**l** were prepared according to the literature procedure.[9] α-Diazo esters **7a**-**h** were prepared by a two-step procedure as reported in the literature.[16] Unless otherwise noted, materials obtained from commercial suppliers were used without further purifications.

General procedure for the preparation of *N*-tosylhydrazones 1a-p, 4a-l. A solution of $TsNHNH_2$ (5 mmol) in methanol (5 mL) was stirred and heated to 60 ^{o}C until the $TsNHNH_2$ was completely dissolved. Then the ketone or aldehydes was dropped to the mixture slowly. After approximately 5-30 min the crude products was obtained as precipitates. The precipitates were washed by petroleum ether, then they were dried *in vacuo* to afford the corresponding *N*-tosylhydrazone which was used for the coupling without further purification.

General procedure for Cu(I)-mediated coupling of 1a-p and 4a-l with acetylene. CuI (76.2 mg, 100 mol%), Li*O*t*Bu* (0.80 mmol, 64.0 mg) and *N*-tosylhydrazone (0.40 mmol) were suspended in DMF

(1.0 mL) in a 10 mL microwave tube under an atmosphere of acetylene gas (a balloon equipped with a needle was inserted through a rubber plug to the reaction system). The reaction solution was stirred at 90 ^{o}C for 20 min. After cooling to room temperature, the resulting mixture was filtered through a short path of silica gel, eluting with ethyl acetate and diethyl ether. The filtrate was washed by brine twice to remove DMF. Then the aqueous phase was extracted by ethyl acetate and diethyl ether. The organic phases were combined and the volatile compounds were removed in *vacuo* with rotvap. The crude residue was purified by column chromatography (SiO_2, hexane) to afford the pure allene product.

*Propa-1,2-diene-1,1-diyldibenzene (**3a**).*[17] yield 76% (58 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.30 (m, 8H), 7.26-7.24 (m, 2H), 5.24 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.9, 136.2, 128.4, 128.3, 127.2, 109.1, 78.0.

*4,4'-(Propa-1,2-diene-1,1-diyl)bis(methylbenzene) (**3b**).*[18] yield 64% (56 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 8.0 Hz, 4H), 7.14 (d, J = 8.0 Hz, 4H), 5.22 (s, 2H), 2.35 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.6, 136.9, 133.4, 129.1, 128.3, 108.8, 77.7, 21.1.

*4,4'-(Propa-1,2-diene-1,1-diyl)bis(fluorobenzene) (**3c**).*[19] yield 68% (62 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.27 (m, 4H), 7.05-7.00 (m, 4H), 5.25 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 162.1 (d, J = 247.0 Hz), 132.1 (d, J = 3.2 Hz), 129.9 (d, J = 8.0 Hz), 115.4 (d, J = 21.7 Hz), 107.5, 78.4.

*4,4'-(Propa-1,2-diene-1,1-diyl)bis(methoxybenzene) (**3d**).*[18] yield 85% (86 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 8.8 Hz, 4H), 6.87 (d, J = 8.8 Hz, 4H), 5.20 (s, 2H), 3.80 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.4, 158.8, 129.4, 128.7, 113.8, 108.2, 77.7, 55.2.

*1-Chloro-4-(1-phenylpropa-1,2-dien-1-yl)benzene (**3e**).*[20] yield 62% (56 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.31 (m, 4H), 7.29-7.26 (m, 5H), 5.27 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 135.8, 134.8, 133.0, 129.6, 128.6, 128.5, 128.3, 127.4, 108.3, 78.4.

*4-(1-Phenylpropa-1,2-dien-1-yl)-1,1'-biphenyl (**3f**).* yield 58% (62 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.56 (m, 4H), 7.45-7.33 (m, 9H), 7.31-7.27 (m, 1H), 5.29 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.0, 140.7, 140.0, 136.2, 135.2, 128.8, 128.7, 128.5, 128.4, 127.3, 127.1, 127.0, 108.9, 78.2; IR

(film) 1932, 1486, 842, 766, 732, 696 cm^{-1}; EI-MS (*m/z*, relative intensity) 268 (M^+, 100), 253 (21), 244 (24), 207 (73), 191 (26), 165 (22); HRMS (ESI) calcd for $C_{21}H_{17}$ [$(M+H)^+$] 269.1325, found: 269.1322.

*1-Methoxy-4-(1-phenylpropa-1,2-dien-1-yl)benzene (**3g**).*[18] yield 81% (72 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.31 (m, 4H), 7.29-7.26 (m, 3H), 6.88 (d, J = 8.8 Hz, 2H), 5.23 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 158.9, 136.5, 129.5, 128.4, 128.3, 127.1, 113.9, 108.7, 77.9, 55.3.

*1-(1-Phenylpropa-1,2-dien-1-yl)naphthalene (**3h**).*[21] yield 63% (61 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.90-7.85 (m, 3H), 7.51-7.50 (m, 2H), 7.47-7.44 (m, 1H), 7.40-7.36 (m, 1H), 7.25-7.24 (m, 4H), 7.20-7.18 (m, 1H), 5.24 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.1, 136.7, 133.9, 133.8, 132.0, 128.7, 128.4, 128.3, 128.2, 127.8, 126.8, 126.1, 126.0, 125.8, 125.6, 106.4, 77.7.

*1,2-Dimethyl-4-(1-phenylpropa-1,2-dien-1-yl)benzene (**3i**).* yield 75% (66 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.30 (m, 4H), 7.27-7.23 (m, 1H), 7.14 (s, 1H), 7.12-7.07 (m, 2H), 5.22 (s, 2H), 2.26 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 136.6, 136.5, 135.7, 133.6, 129.7, 129.6, 128.4, 128.3, 127.1, 125.9, 109.0, 77.8, 19.8, 19.4; IR (film) 2920, 1934, 1492, 1449, 854, 764, 697 cm^{-1}; EI-MS (*m/z*, relative intensity) 220 (M^+, 90), 205 (100), 189 (21), 178 (12), 165 (11), 115 (6), 89 (6); HRMS (ESI) calcd for $C_{17}H_{17}$ [$(M+H)^+$] 221.1325, found: 221.1326.

*1-Methoxy-3-(1-(m-tolyl)propa-1,2-dien-1-yl)benzene (**3j**).* yield 74% (70 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.27-7.14 (m, 4H), 7.08 (d, J = 7.6 Hz, 1H), 6.95-6.92 (m, 2H), 6.82 (dd, J = 2.2, 8.2 Hz, 1H), 5.24 (s, 2H), 3.78 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 159.6, 138.0, 137.8, 136.0, 129.3, 129.1, 128.2, 128.0, 125.5, 120.9, 114.0, 112.7, 109.1, 78.0, 55.2, 21.4; IR (film) 2961, 1931, 1597, 1486, 1260, 1089, 856, 794 cm^{-1}; EI-MS (*m/z*, relative intensity) 236 (M^+, 100), 221 (53), 205 (22), 193 (19), 178 (39), 165 (14), 152 (9); HRMS (ESI) calcd. for $C_{17}H_{17}O$ [$(M+H)^+$] 237.1274, found: 237.1277.

*1-Chloro-3-(1-(3-(trifluoromethoxy)phenyl)propa-1,2-dien-1-yl)benzene (**3k**).* yield 63% (78 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.34 (m, 2H), 7.29-7.24 (m, 3H), 7.22-7.20 (m, 2H), 7.16-7.14 (m, 1H), 5.35 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.9, 149.4, 137.9, 137.5, 134.5, 129.8, 129.7,

128.4, 127.6, 126.6, 126.4, 120.9, 120.5 (q, J = 257.5 Hz), 119.8, 107.5, 79.3; IR (film) 1934, 1255, 1217, 1164, 789, 694 cm^{-1}; EI-MS (*m/z*, relative intensity) 310 (M^+, 97), 286 (16), 275 (100), 251 (23), 225 (28), 189 (34), 178 (25); HRMS (ESI) calcd for $C_{16}H_{11}ClF_3O$ [$(M+H)^+$] 311.0445, found: 311.0451.

*1-(Buta-2,3-dien-2-yl)-4-iodobenzene (**3l**)*. yield 70% (72 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 5.02 (q, J = 3.0 Hz, 2H), 2.05 (t, J = 3.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.9, 137.6, 137.3, 136.4, 127.6, 99.2, 91.7, 16.5; IR (film) 2923, 1942, 1483, 1071, 1004, 854, 820, 799 cm^{-1}; EI-MS (*m/z*, relative intensity) 256 (M^+, 100), 241 (8), 128 (97), 114 (10), 102 (12), 77 (13); HRMS (ESI) calcd for $C_{10}H_{10}I$ [$(M+H)^+$] 256.9822, found: 256.9823.

*1-(Buta-2,3-dien-2-yl)-3-nitrobenzene (**3m**)*. yield 44% (31 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 7.2 Hz, 1H), 7.48 (dt, J = 1.2, 8.0 Hz, 1H), 5.15 (br, 2H), 2.14 (br, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2, 148.6, 139.0, 131.5, 129.0, 121.3, 120.3, 98.7, 78.2, 16.5; IR (film) 2962, 1943, 1528, 1345, 1260, 1089, 799 cm^{-1}; EI-MS (*m/z*, relative intensity) 175 (M^+, 62), 128 (100), 102 (16), 77 (10), 63 (10), 51 (14); HRMS (ESI) calcd for $C_{10}H_{10}NO_2$ [$(M+H)^+$] 176.0706, found: 176.0701.

*3-(1-Phenylpropa-1,2-dien-1-yl)thiophene (**3n**)*. yield 74% (59 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.43-7.41 (m, 2H), 7.37-7.33 (m, 2H), 7.32-7.28 (m, 2H), 7.14-7.11 (m, 2H), 5.24 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.0, 136.8, 136.2, 128.4, 128.1, 127.9, 127.4, 125.5, 122.3, 104.8, 78.0; IR (film) 1932, 1260, 1078, 1028, 850, 787, 698 cm^{-1}; EI-MS (*m/z*, relative intensity) 198 (M^+, 100), 173 (17), 165 (36), 152 (13), 113 (6); HRMS (ESI) calcd for $C_{13}H_{11}S$ [$(M+H)^+$] 199.0576, found: 199.0575.

*3,3'-(Propa-1,2-diene-1,1-diyl)dithiophene (**3o**)*. ^1H NMR (400 MHz, $CDCl_3$) yield 65% (53 mg). δ 7.33-7.31 (m, 2H), 7.25-7.23 (m, 2H), 7.17-7.16 (m, 2H), 5.24 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.1, 136.7, 127.8, 125.5, 122.1, 100.4, 78.1; IR (film) 2961, 2924, 1260, 1080, 1018, 790, 665 cm^{-1}; EI-MS (*m/z*, relative intensity) 204 (M^+, 100), 188 (15), 180 (40), 171 (45), 165 (59), 115 (18); HRMS (ESI) calcd for $C_{11}H_9S_2$ [$(M+H)^+$] 205.0140, found: 205.0141.

*3-(1-(Thiophen-3-yl)propa-1,2-dien-1-yl)furan (**3p**)*. yield 53% (40 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.43 (t, J = 1.6 Hz, 1H), 7.31 (m, 1H), 7.25 (s, 1H), 7.17 (dd, J = 1.0, 5.0 Hz, 1H), 6.49

(d, J = 1.0 Hz, 1H), 5.23 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.6, 143.1, 140.1, 136.3, 127.5, 125.6, 121.6, 121.3, 110.3, 96.8, 78.2; IR (film) 2960, 2924, 1260, 1085, 1023, 873, 792, 670 cm^{-1}; EI-MS (*m/z*, relative intensity) 188 (M^+, 11), 165 (100), 152 (5), 115 (12); HRMS (ESI) calcd for $C_{11}H_9OS$ [$(M+H)^+$] 189.0369, found: 189.0365.

*Methyl 4-(propa-1,2-dien-1-yl)benzoate (**5a**).*[22] yield 40% (28 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 6.20 (t, J = 6.8 Hz, 1H), 5.21 (d, J = 6.8 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.6, 166.9, 139.0, 131.4, 129.9, 126.5, 93.6, 79.2, 52.0.

*4-(Propa-1,2-dien-1-yl)-1,1'-biphenyl (**5b**).*[23] yield 55% (42 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.53 (m, 4H), 7.42 (t, J = 7.6 Hz, 2H), 7.37-7.30 (m, 3H), 6.20 (t, J = 6.8 Hz, 1H), 5.17 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.0, 140.8, 139.7, 133.0, 128.7, 127.3, 127.2, 127.1, 126.9, 93.6, 78.9.

N,N-Dimethyl-4-(propa-1,2-dien-1-yl)aniline (**5c**). yield 47% (30 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, J = 8.8 Hz, 2H), 6.69 (d, J = 8.8 Hz, 2H), 6.11 (t, J = 6.8 Hz, 1H), 5.10 (d, J = 6.8 Hz, 2H), 2.94 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2, 149.7, 127.5, 121.5, 112.8, 93.6, 78.5, 40.6; IR (film) 2927, 1611, 1520, 908, 859, 817, 731 cm^{-1}; EI-MS (*m/z*, relative intensity) 159 (M^+, 60), 129 (85), 103 (61), 77 (100); HRMS (ESI) calcd for $C_{11}H_{14}N$ [$(M+H)^+$] 160.1121, found: 160.1123.

*N-(4-(Propa-1,2-dien-1-yl)phenyl)acetamide (**5d**).*[24] yield 67% (46 mg). ^{1}H NMR (400 MHz, CD_3COCD_3) δ 9.20 (s, 1H), 7.61 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 6.23 (t, J = 6.8 Hz, 1H), 5.16 (d, J = 6.8 Hz, 2H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 210.4, 168.8, 139.5, 129.4, 127.8, 120.2, 94.0, 79.0, 24.3.

*1-Methoxy-2-(propa-1,2-dien-1-yl)benzene (**5e**).*[7] yield 62% (36 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, J = 1.2, 7.6 Hz, 1H), 7.17 (dt, J = 1.2, 8.4 Hz, 1H), 6.92 (t, J = 7.6 Hz, 1H), 6.85 (d, J = 8.4 Hz, 1H), 6.57 (t, J = 6.8 Hz, 1H), 5.10 (d, J = 6.8 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.2, 155.8, 127.9, 127.7, 122.3, 120.8, 110.9, 87.8, 78.0, 55.5.

*1-Methoxy-4-(propa-1,2-dien-1-yl)benzene (**5f**)*.[24] yield 73% (43 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.12 (t, *J* = 6.8 Hz, 1H), 5.11 (d, *J* = 6.8 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 158.7, 127.7, 126.1, 114.1, 93.3, 78.7, 55.3.

*1-Bromo-3-(propa-1,2-dien-1-yl)benzene (**5g**)*.[25] yield 56% (44 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.21-7.14 (m, 2H), 6.09 (t, *J* = 6.8 Hz, 1H), 5.19 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.9, 136.3, 130.0, 129.8, 129.5, 125.3, 122.8, 93.0, 79.4.

*1-Bromo-4-(propa-1,2-dien-1-yl)benzene (**5h**)*.[22] yield 64% (50 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 6.10 (t, *J* = 6.8 Hz, 1H), 5.14 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 133.0, 131.7, 128.2, 120.5, 93.2, 79.3.

*5-(Propa-1,2-dien-1-yl)benzo[d][1,3]dioxole (**5i**)*.[26] yield 63% (40 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84-6.83 (m, 1H), 6.76-6.71 (m, 2H), 6.09 (t, *J* = 6.8 Hz, 1H), 5.94 (s, 2H), 5.13 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 148.0, 146.7, 127.9, 120.3, 108.3, 106.6, 101.0, 93.8, 79.1.

*1,2-Dichloro-4-(propa-1,2-dien-1-yl)benzene (**5j**)*. yield 54% (40 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.34 (m, 2H), 7.11-7.09 (m, 1H), 6.07 (t, *J* = 6.8 Hz, 1H), 5.19 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.0, 134.3, 132.7, 130.4, 128.2, 125.9, 92.4, 79.7; IR (film) 1941, 1473, 1133, 1031, 884, 854, 802 cm^{-1}; EI-MS (*m*/*z*, relative intensity) 184 (41), 149 (100), 113 (17), 87 (6), 63 (8); HRMS (EI) calcd for $C_9H_6Cl_2$ [M^+] 183.9847, found: 183.9855.

*4-Bromo-3-(propa-1,2-dien-1-yl)phenol (**5k**)*. yield 71% (60 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.8 Hz, 1H), 6.95 (d, *J* = 3.2 Hz, 1H), 6.59-6.54 (m, 2H), 5.17 (d, *J* = 6.8 Hz, 2H), 5.08 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.5, 154.8, 134.6, 133.7, 116.1, 114.6, 113.2, 93.0, 79.1; IR (film) 3298, 1942, 1571, 1430, 1289, 1023, 870, 804 cm^{-1}; EI-MS (*m*/*z*, relative intensity) 207 (90), 149 (57), 131 (100), 102 (46), 77 (53), 63 (15), 51 (27); HRMS (ESI) calcd for C_9H_6BrO [$(M-H)^-$] 208.9608, found: 208.9605.

*2-(Propa-1,2-dien-1-yl)naphthalene (**5l**)*.[27] yield 81% (54 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.75 (m, 3H), 7.64 (s, 1H), 7.51-7.48 (m, 1H), 7.46-7.39 (m, 2H), 6.33 (t, *J* = 6.8 Hz, 1H), 5.21 (d, *J* =

6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.3, 133.6, 132.6, 131.4, 128.2, 127.7, 127.6, 126.2, 125.6, 125.4, 124.6, 94.3, 79.1.

General procedure for the formation of 1-methyl-2-aryl acetylene derivatives 6a-g. CuI (76.2 mg, 100 mol%), Li*O*t*Bu (1.20 mmol, 96.0 mg) and *N*-tosylhydrazone (0.40 mmol) were suspended in DMF (1.0 mL) in a 10 mL microwave tube under an atmosphere of acetylene gas (a balloon equipped with a needle was inserted through a rubber plug to the reaction system). The resulting solution was stirred at 90 ^{o}C for 4 h. After cooling down to room temperature, the reaction mixture was filtered through a short path of silica gel, eluting with ethyl acetate and diethyl ether. The filtrate was washed by brine twice to remove DMF. Then the aqueous phase was extracted by ethyl acetate and diethyl ether. The organic phases were combined and the volatile compounds were removed in *vacuo* with rotvap. The crude residue was purified by column chromatography (SiO_2, hexane) to afford the pure 1-methyl-2-aryl acetylene derivative products.

*1-Methoxy-4-(prop-1-yn-1-yl)benzene (**6a**).*[28] yield 50% (29 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 132.8, 116.1, 113.8, 84.0, 79.4, 55.2, 4.2.

*4-(Prop-1-yn-1-yl)-1,1'-biphenyl (**6b**).*[29] yield 32% (25 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.46-7.42 (m, 4H), 7.34 (t, *J* = 6.8 Hz, 1H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 140.2, 131.9, 128.8, 127.4, 127.0, 126.9, 123.0, 86.5, 79.6, 4.4.

*N,N-dimethyl-4-(prop-1-yn-1-yl)aniline (**6c**).*[28] yield 54% (34 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.8 Hz, 2H), 6.60 (d, *J* = 8.8 Hz, 2H), 2.93 (s, 6H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 132.4, 112.7, 111.9, 82.9, 80.2, 40.2, 4.3.

*1-Methoxy-2-(prop-1-yn-1-yl)benzene (**6d**).*[30] yield 43% (25 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.36 (m, 1H), 7.26-7.22 (m, 1H), 6.90-6.84 (m, 2H), 3.87 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 133.6, 128.9, 120.4, 113.0, 110.4, 90.0, 75.7, 55.7, 4.7.

*5-(Prop-1-yn-1-yl)benzo[d][1,3]dioxole (**6e**).*[31] yield 49% (31 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (dd, *J* = 1.4, 8.0 Hz, 1H), 6.84 (d, *J* = 1.4 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 5.93 (s, 2H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 147.2, 125.7, 117.3, 111.5, 108.3, 101.1, 83.9, 79.4, 4.2.

*1,3-Dimethyl-2-(prop-1-yn-1-yl)benzene (**6f**).* yield 74% (43 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05-6.99 (m, 3H), 2.41 (s, 6H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 126.8, 126.5, 123.7, 94.0, 77.3, 21.1, 4.5; IR (film) 2918, 1648, 1592, 1467, 1377, 769, 734 cm^{-1}; EI-MS (*m/z*, relative intensity) 144 (M^+, 94), 128 (100), 115 (20), 102 (6), 77 (8), 63 (10); HRMS (ESI) calcd for $C_{11}H_{12}NO$ [$(M+NO)^+$] 174.0913, found: 174.0912.

*1,3-Dichloro-2-(prop-1-yn-1-yl)benzene (**6g**).* yield 62% (46 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.10 (t, *J* = 8.0 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 128.2, 127.4, 123.7, 97.5, 74.0, 4.8; IR (film) 2919, 2256, 1556, 1429, 1195, 790, 774, 723 cm^{-1}; EI-MS (*m/z*, relative intensity) 184 (M^+, 48), 149 (100), 113 (24), 87 (10), 74 (11), 63 (9); HRMS (EI) calcd for $C_9H_6Cl_2$ (M^+) 183.9847, found: 183.9855.

General procedure for Cu(I)-mediated coupling of α-diazo acetate 7a-g. CuI (76.2 mg, 100 mol%), 1,10-phenanthroline (72 mg, 100 mol%) and diazo compound **7a**-**g** (0.4 mmol) were suspended in DMF (1.5 mL) in a 10 mL microwave tube under a atmosphere of acetylene gas (a balloon equipped with a needle was inserted through a rubber plug to the reaction system). The resulting solution was stirred at 60 ^{o}C for 2 hours. After cooling down to room temperature, the reaction mixture was filtered through a short path of silica gel, eluting with ethyl acetate and diethyl ether. The filtrate was washed by brine twice to remove DMF. Then the aqueous phase was extracted by ethyl acetate and diethyl ether. The organic phases were combined and the volatile compounds were removed in *vacuo* with rotvap. The crude residue was purified by column chromatography (SiO_2, hexane:ethyl acetate = 30:1). The combined products were further purified *via* productive thin-layer chromatography (SiO_2, hexane:ethyl acetate = 30:1).

*Ethyl 2-benzylbuta-2,3-dienoate (**8a**).*[32] yield 76% (61 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.20 (m, 5H), 5.09 (t, *J* = 2.6 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.57 (t, *J* = 2.4 Hz, 2H), 1.25 (t, *J* = 7.2 Hz,

3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.4, 166.8, 139.1, 128.8, 128.2, 126.3, 100.3, 79.2, 61.1, 34.9, 14.2.

*Ethyl 5-phenyl-2-vinylidenepentanoate (**8b**)*. yield 93% (86 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.24 (m, 2H), 7.18-7.14 (m, 3H), 5.12 (t, J = 3.2 Hz, 2H), 4.19 (q, J = 7.2 Hz, 2H), 2.65 (t, J = 7.6 Hz, 2H), 2.30-2.25 (m, 2H), 1.83-1.75 (m, 2H), 1.26 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.7, 167.1, 142.1, 128.3, 128.2, 125.7, 100.1, 79.0, 60.8, 35.2, 29.6, 27.5, 14.2; IR (film) 2935, 1940, 1710, 1603, 1496, 1454, 1367, 1258, 1214, 1152, 1097, 1029, 849, 797, 746, 699 cm^{-1}; EI-MS (*m/z*, relative intensity) 229 (4), 215 (14), 201 (7), 157 (100), 141 (19), 129 (32), 115 (8), 104 (44), 91 (53), 77 (13), 65 (12), 51 (8); HRMS (ESI) calcd for $C_{15}H_{19}O_2$ [$(M+H)^+$]: 231.1380, found: 231.1383.

*Ethyl 2-vinylidenedecanoate (**8c**)*. yield 73% (65 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.11 (t, J = 3.0 Hz, 2H), 4.20 (q, J = 7.2 Hz, 2H), 2.24-2.19 (m, 2H), 1.46-1.41 (m, 2H), 1.30-1.26 (m, 13H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.7, 167.3, 100.4, 78.7, 60.9, 31.8, 29.3, 29.2, 29.1, 28.0, 27.9, 22.6, 14.2, 14.1; IR (film) 2926, 2856, 1942, 1714, 1465, 1367, 1212, 1173, 1129, 1081, 1040, 844, 784 cm^{-1}; EI-MS (*m/z*, relative intensity) 224 (M^+, 13), 206 (13), 167 (13), 153 (22), 140 (21), 127 (100), 112 (30), 99 (84), 91 (24), 81 (84), 67 (61), 55 (73); HRMS (ESI) calcd for $C_{14}H_{25}O_2$ [$(M+H)^+$]: 225.1849, found: 225.1853.

*Ethyl 2-vinylidenedodec-11-enoate (**8d**)*. yield 60% (60 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85-5.75 (m, 1H), 5.10 (t, J = 3.0 Hz, 2H), 5.10-4.91 (m, 2H), 4.20 (t, J = 7.1 Hz, 2H), 2.24-2.19 (m, 2H), 2.06-2.01 (m, 2H), 1.45-1.26 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.7, 167.2, 139.1, 114.1, 100.4, 78.7, 60.8, 33.7, 29.6, 26.3, 29.3, 29.0, 28.9, 27.9, 27.8, 14.2; IR (film) 2927, 2855, 1841, 1714, 1641, 1464, 1367, 1258, 1213, 1173, 1096, 1020, 910, 844, 806 cm^{-1}; EI-MS (*m/z*, relative intensity) 250 (M^+, 2), 235 (2), 221 (2), 205 (4), 189 (4), 177 (10), 169 (9), 161 (10), 154 (4), 135 (19), 127 (90), 114 (25), 107 (32), 99 (64), 81 (100), 67 (85), 51 (87); HRMS (ESI) calcd for $C_{16}H_{27}O_2$ [$(M+H)^+$]: 251.2006, found: 251.2008.

*Benzyl 2-vinylidenehexanoate (**8e**)*.[33] yield 89% (82 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.24 (m, 5H), 5.18 (s, 2H), 5.12 (t, J = 3.0 Hz, 2H), 2.27-2.22 (m, 2H), 1.49-1.39 (m, 2H), 1.37-1.32 (m, 2H),

0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.0, 167.1, 136.2, 128.4, 127.9, 127.7, 100.2, 78.9, 66.3, 30.0, 27.7, 22.1, 13.8.

*Benzyl 2-(cyclopropylmethyl)buta-2,3-dienoate (**8f**)*. yield 90% (82 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.24 (m, 5H), 5.19 (s, 2H), 5.15 (t, J = 3.0 Hz, 2H), 2.18-2.15 (m, 2H), 0.92-0.83 (m, 1H), 0.47-0.43 (m, 2H), 0.14-0.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.4, 167.1, 136.1, 128.4, 127.9, 127.7, 100.1, 78.9, 66.4, 33.2, 9.6, 4.5; IR (film) 2960, 1966, 1710, 1498, 1456, 1376, 1258, 1212, 1135, 1069, 1018, 799, 687 cm^{-1}; EI-MS (*m/z*, relative intensity) 183 (4), 169 (15), 155 (5), 104 (10), 91 (100), 77 (8), 65 (12); HRMS (ESI) calcd for $C_{15}H_{17}O_2$ [$(M+H)^+$]: 229.1223, found: 229.1226.

*4-Ethyl 1-methyl 2-vinylidenesuccinate (**8g**)*. yield 43% (32 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.24 (t, J = 2.2 Hz, 2H), 4.17 (q, J = 7.2 Hz, 2H)，3.77 (s, 3H), 3.27 (t, J = 2.2 Hz, 2H), 1.26 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.6, 170.3, 166.7, 94.3, 79.5, 60.9, 52.4, 34.7, 14.1; IR (film) 2959, 2926, 2852, 1971, 1739, 1720, 1439, 1369, 1260, 1179, 1099, 1028, 863, 797 cm^{-1}; EI-MS (*m/z*, relative intensity) 156 (100), 141 (60), 124 (21), 111 (27), 97 (29), 83 (27), 79 (8), 69 (6), 59 (32), 51 (47); HRMS (ESI) calcd for $C_9H_{13}O_4$[$(M+H)^+$]: 185.0808, found: 185.0807.

ASSOCIATED CONTENTS

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.

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