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Graphical Abstract

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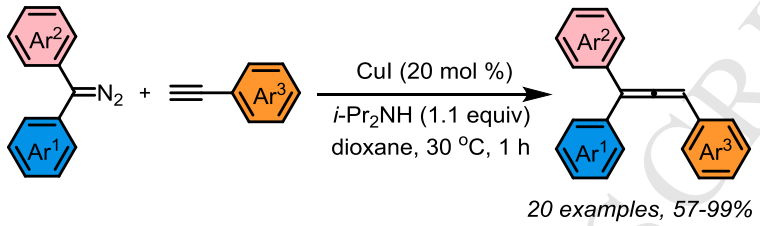

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Cu(I)-Catalyzed Coupling of Diaryldiazomethanes with Terminal Alkynes: An Efficient Synthesis of Tri-Aryl-Substituted Allenes

Chenggui Wu,[a,b] Fangdong Hu,[b] Zhenxing Liu,[b] Guisheng Deng,[a,*] Fei Ye,[b] Yan Zhang[b] and Jianbo Wang[b,*]

[a]*College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, People's Republic of China*
[b]*Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, People's Republic of China*

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ABSTRACT

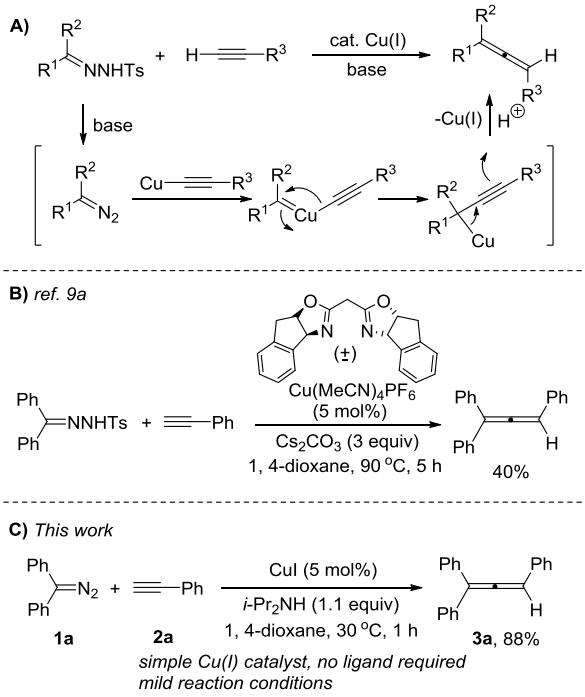
A highly efficient method for the synthesis of tri-aryl-substituted allenes has been developed through Cu(I)-catalyzed coupling of diaryldiazomethanes with terminal alkynes. The reaction is under mild conditions and uses simple and inexpensive CuI as the catalyst. Mechanistically, the reaction follows a pathway involving Cu(I) carbene migratory insertion.

1. Introduction

In recent years, the study of allenes has attracted considerable attention due to their unique structural features and chemical properties attributed to the presence of two perpendicular π bonds.[1] On one hand, allenes have been recognized as versatile substrates or intermediates in modern organic synthesis,[2] on the other hand many natural products and pharmaceutically related compounds bear allene structural units.[3] Accordingly, the methods for the synthesis of allenes have been studied extensively over the past decades.[4] One of the typical methods to access allenes is the S_N2'-type displacement of propargyl alcohol derivatives with organocopper species.[4,5] Up to now, the allene synthesis by means of direct coupling has remained much less developed with only few examples reported in the literature.[6] Among the previously reported methods, the Crabbé homologation is quite attractive.[7] While the scope of the original the Crabbé homologation is limited, recent extensive studies by Ma and co-workers have significantly expanded this methodology for allene synthesis.[8]

We have recently developed a method for allene synthesis through Cu(I)-catalyzed cross-coupling reaction of *N*-tosylhydrazones and terminal alkynes.[9,10] This method is based on a Cu(I) carbene migratory insertion process, which has been extensively explored in our research group (Scheme 1A).[11] Our method can be applied to the synthesis of allenes of various substitution patterns, however, its application to the synthesis of tri-aryl-substituted allenes is less efficient. In our previous

Scheme 1. Allene Synthesis through Cu(I) Carbene Migratory Insertion

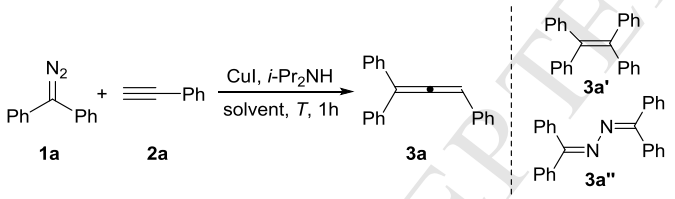


communication, we have only examined one example of the Cu(I)-catalyzed coupling for the synthesis of tri-phenyl-substituted allene.[9a] The reaction is carried out under harsh conditions and requires expensive ligand and the allene product could only be obtained in 40% yield (Scheme 1B). To further improve the allene synthesis based on the Cu(I) carbene migratory insertions, we herein report an efficient method towards the synthesis of tri-substituted aromatic allenes based on copper(I)-catalyzed cross-coupling of diaryldiazomethanes with terminal alkynes under mild conditions (Scheme 1C).

2. Results and discussion

At the beginning of this investigation, Cu(I)-catalyzed reaction of (diazomethylene)dibenzene **1a** and phenylacetylene **2a** was examined with copper(I) iodide as the catalyst, 1,4-dioxane as the solvent and *i*-Pr_2NH as the base at 30 °C (Table 1). The characteristic violet color of diazo compound **1a** of the reaction system turned to a pale yellow solution in an hour, which indicated the completion of the reaction. Upon work-up and isolation by column chromatography, the desired allene product **3a** was obtained in 88% yield (entry 1). We have also examined the effect of temperature and solvent, and found that the yield was diminished with the raise of the temperature. Under elevated temperature, significant amount of by-products **3a′** and **3a″** were observed (entries 2-3). In terms of the solvent, 1,4-dioxane was found better than other solvents, such as THF, toluene, MeCN, DCE, as it led to a clean reaction system (entry 4-7). Furthermore, we founded that the CuI and *i*-Pr_2NH were indispensable for the reaction (entries 8-9). However, the yield of the product **3a** could not be improved with the increase of the *i*-Pr_2NH. Instead, significant amount of the products derived from the addition of *i*-Pr_2NH to allene was observed in GC-MS (entry 10). The optimized reaction condition is summarized as follows: under a nitrogen atmosphere, substrate ratio of **1a** to **2a** is 1 : 1, CuI (20 mol%), *i*-Pr_2NH (1.1 equiv), 1,4-dioxane (1 mL), 30 °C, 1 h.

Table 1. Optimization of the Reaction Conditions[a]

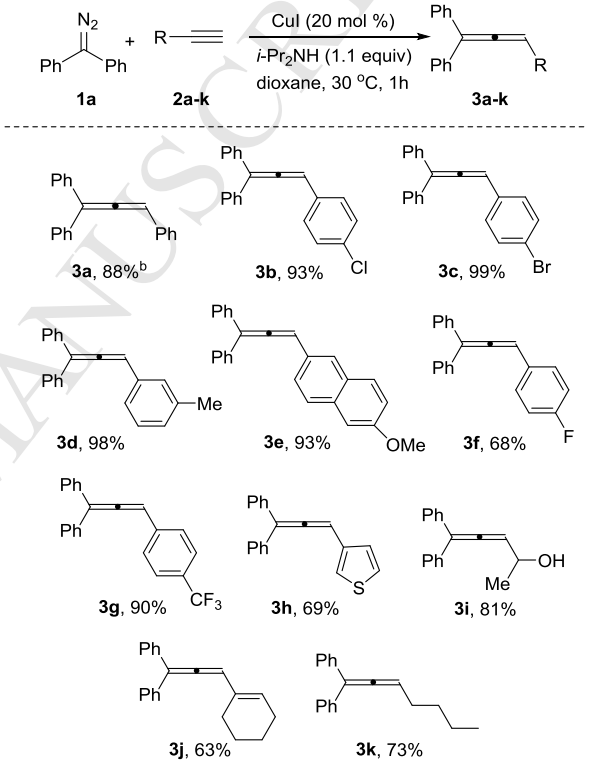


Entry	CuI (mol%)	$^{i}Pr_2NH$ (equiv)	solvent	T(°C)	Yield(%)[a]
1	20	1.1	dioxane	30	88
2	20	1.1	dioxane	50	--[c]
3	20	1.1	dioxane	70	--[c]
4	20	1.1	THF	30	70
5	20	1.1	toluene	30	80
6	20	1.1	DCE	30	75
7	20	1.1	MeCN	30	*trace*
8	--	1.1	dioxane	30	0
9	20	--	dioxane	30	0
10	20	2.2	dioxane	30	70

[a]All the reactions were carried out with (diazomethylene)dibenzene **1a** (0.2 mmol), phenylacetylene **2a** (0.2 mmol), CuI and *i*-Pr_2NH in solvent (1 mL) under nitrogen atmosphere at the indicated tenperature for 1 h. [b]Isolated yield by column chromatography. [c]The product was a mixture of **3a**, **3a′** and **3a″**. It was difficult to separate.

With the optimized reaction conditions in hand, we then explored the scope of this reaction with (diazomethylene)dibenzene **1a** and various terminal alkynes **2a-k** (Scheme 2). The reactions afforded the corresponding products in good yields under the optimized reaction conditions. It is noteworthy that the reactions are not significantly affected by the substituents on the aromatic moiety of the terminal alkynes (**3b-g**). Heterocycle such as thiophene (**3h**) is also tolerated in the reaction system. In addition, the reaction with alkyl terminal alkynes also afforded the allene product in good yield. In particular, the alkyl-substituted terminal alkyne bearing free hydroxyl group (**3i**) can also be employed in this reaction.

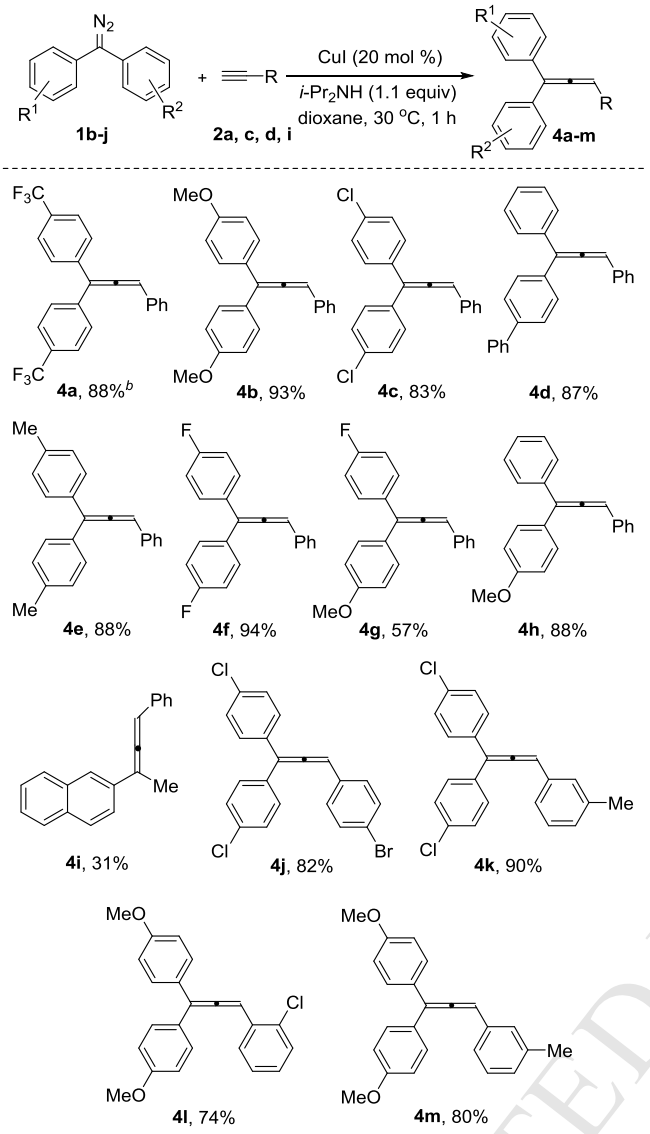
Scheme 2. The Substrate Scope of Terminal Alkynes[a]



[a]All the reactions were set with (diazomethylene)dibenzene **1a** (0.2 mmol), alkyne **2a-k** (1 equiv), CuI (20 mol%) and *i*-Pr_2NH (1.1 equiv) in dioxane (1 mL) under nitrogen atmosphere at 30 °C for 1 h, [b]Isolated yield by column chromatography.

Next, the reaction scope was examined for a variety of diaryldiazomethanes under the optimized reaction conditions (Scheme 3). The reactions of a series of diaryldiazomethanes with phenylacetylene **2a** under the identical reaction conditions afforded the corresponding allene products **4a-j** in moderate to good yields, except the case of the 2-(1-diazoethyl)naphthalene (**4i**), in which the dimished yield is attributed to the instability of the allene product at room temperature. For the diaryldiazomethanes derived from the corresponding ketones, it is noteworthy that the reactions were marginally affected by the substituents on the aromatic ring (**4a-h**). Furthermore, we have tried the reaction of substituted terminal alkynes and diaryldiazomethanes **2c**, **d**, **i** under the optimized reaction conditions. The corresponding allene products (**4j-m**) were obtained in good yields.

Scheme 3. The Substrate Scope of Diaryldiazomethanes[a]



[a]All the reactions were set with diaryldiazomethane **1** (0.2 mmol), alkyne **2** (1 equiv), CuI (20 mol%) and *i*-Pr_2NH (1.1 equiv) in dioxane (1 mL) under nitrogen atmosphere at 30 °C for 1 h, [b] Isolated yield by column chromatography.

Finally, a scale-up experiment was carried out with 3 mmol of **1d** under the optimized reaction conditions, affording 0.89 gram of **4c** (88%). The results demonstrate the practical usefulness of this preparative method.

3. Summary

In summary, we have developed an efficient approach towards the synthesis of tri-aryl-substituted allenes from terminal alkynes and diaryldiazomethanes *via* CuI-catalyzed cross-coupling. The advantages of the method are: 1) the CuI catalyst is cheap, and no ligand is necessary; 2) the reaction is easy to operate with wide substrate scope at relatively low temperature; 3) the reactions are carried out with 1:1 ratio of the starting materials. With these advantages, it is expected that this method will find wide applications in organic synthesis.

4. Experimental section

4.1 General

Except the gram-scale experiments, all the reactions were performed under nitrogen atmosphere in a 20 mL Schlenk tube. For the gram-scale experiments, the reaction was carried out in round-bottle flask. Dioxane was dried over Na before use. For chromatographic purification, 200-300 mesh silica gel (Qingdao, China) was employed. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian 300 MHz and Brucker ARX 400 MHz spectrometer in $CDCl_3$ solution and the chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0 ppm). Diaryldiazomethanes were prepared according to the literature procedure.[12] Unless otherwise noted, the materials received from commercial suppliers were used without further purifications.

General Procedure for the Preparation of Diaryldiazomethanes

Step 1. Preparation of Diarylmethanone Hydrazone. Hydrazine monohydrate (85% purity, 18.2 mL, 30 mmol) was added to a solution of diarylmethanone (20 mmol) in ethanol (20 mL). Then, aqueous HCl (36.0-38.0%, 0.5 mL) was added and the mixture was heated to reflux for 12 hours. After cooling to room temperature, the diarylmethanone hydrazone was precipitated as white needle-shaped crystal. Filtration of the crude mixture gave pure diarylmethanone hydrazone (82-94% yield) as white solid.

Step 2. Preparation of Diaryldiazomethane. A mixture of diarylmethanone hydrazone (10 mmol, 1.0 equiv), anhydrous $MgSO_4$ (1 g) and 30 mL CH_2Cl_2 was cooled to 0 °C. To this rapidly stirring mixture was added activated MnO_2 (3.04 g, 35 mmol, 3.5 equiv) in one portion. The reaction mixture was warmed to room temperature and kept stirring for 8 hours, and then the solid was filtered off with a *Celite* pad and washed with CH_2Cl_2. After removal of the solvent under reduced pressure, the residual was purified by silica gel (pretreated with petroleum ether : Et_3N = 10 : 1) with petroleum ether : Et_3N = 20 : 1 as the eluent to afford diaryldiazomethane as purple solid (72-85% yield). The diaryldiazomethanes can be kept at -20 °C for weeks without evident decomposition.

General Procedure for the CuI-Catalyzed Cross-Coupling of Diaryldiazomethanes and Terminal Alkynes

Under nitrogen atmosphere, terminal alkyne (0.2 mmol) was added to a mixture of CuI (8 mg, 0.04 mmol), *i*-Pr_2NH (22 mg, 0.22 mmol) and diaryldiazomethane (0.2 mmol) in 1,4-dioxane (1 mL). The solution was stirred at 30 °C for 1 hour and the progress of the reaction was monitored by TLC. Upon completion of the reaction, the reaction mixture was cooled down to room temperature and filtered through a short path of silica gel by using EtOAc as the eluent. The solvent was removed *in vacuo* to leave a crude mixture, which was purified by column chromatography with silica gel to afford the pure allene product.

*Propa-1,2-diene-1,1,3-triyltribenzene (**3a**).*[9a] Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford pure **3a** as a yellow oil (47 mg, 88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.35 (m, 6H), 7.16-7.26 (m, 8H), 7.09-7.14 (m, 1H), 6.61(s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.27, 136.13, 133.84, 128.78, 128.47, 128.44, 127.56, 127.36, 126.96, 113.71, 97.70.

*(3-(4-Chlorophenyl)propa-1,2-diene-1,1-diyl)dibenzene (**3b**).* Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford pure **3b** as a yellow oil (56 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.41 (m, 3H), 7.25-7.36 (m, 11H), 6.65 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.30, 135.85, 132.94, 132.41, 128.95, 128.53, 128.42, 128.10, 127.72,

114.11, 96.82; IR (film, cm^{-1}) 1929, 1596, 1489, 1442, 1094, 1013; EI-MS (*m/z*, relative intensity) 302 (M^+, 22), 267 (100), 252 (18), 207 (45), 165(39), 126 (20), 91(19); HRMS (ESI) calcd for $C_{21}H_{16}Cl$ [$(M+H)^+$] 303.0935, found: 303.0935.

(3-(4-Bromophenyl)propa-1,2-diene-1,1-diyl)dibenzene ***(3c)***. Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford pure **3c** as a yellow oil (69 mg, 99%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.29-7.33 (m, 6H), 7.23-7.35 (m, 8H), 6.65 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.33, 135.80, 132.92, 131.90, 128.54, 128.43, 127.74, 121.03, 114.17, 96.90 (one peak was missed because of overlap); IR (film, cm^{-1}) 1930, 1597, 1458, 1442, 1070, 1009; EI-MS (*m/z*, relative intensity) 346 (M^+, 21), 281 (18), 267 (25), 253 (12), 207 (100), 191 (29), 168 (72), 147 (29), 91 (45); HRMS (ESI) calcd for $C_{21}H_{16}Br$ [$(M+H)^+$] 347.0430, found: 347.0430.

(3-(m-Tolyl)propa-1,2-diene-1,1-diyl)dibenzene ***(3d)***. Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford pure **3d** as a yellow oil (55 mg, 98%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.36 (m, 4H), 7.17-7.27 (m, 6H), 7.10-7.13 (m, 3H), 6.94-6.96 (m, 1H), 6.59 (s, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.31, 138.43, 136.22, 133.73, 128.69, 128.46, 128.23, 127.60, 127.52, 124.15, 113.56, 97.25, 21.39 (one peak was missed because of overlap); IR (film, cm^{-1}) 1931, 1597, 1490, 1442, 906; EI-MS (*m/z*, relative intensity) 282 (M^+, 100), 267 (81), 252 (11), 239 (5), 207 (9), 189 (10), 178 (5), 165 (6), 138 (5), 125 (9); HRMS (ESI) calcd for $C_{22}H_{19}$ [$(M+H)^+$] 283.1481, found: 283.1481.

2-(3,3-Diphenylpropa-1,2-dien-1-yl)-6-methoxynaphthalene ***(3e)***. Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 30 : 1) to afford pure **3e** as a yellow solid (38 mg, 88%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.64-7.67 (m, 3H), 7.54-7.56 (m, 1H), 7.45-7.47 (m, 4H), 7.26-7.36 (m, 6H), 7.08-7.13 (m, 2H), 6.84 (s, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.58, 157,69, 136.29, 134.01, 129.26, 129.17, 129.04, 128.48, 127.54, 127.33, 125.81, 125.24, 118.97, 113.80, 105.95, 98.07, 55.25 (one peak was missed because of overlap); IR (film, cm^{-1}) 1923, 1629, 1604, 1491, 1389, 1266, 1234, 1172, 1030; HRMS (ESI) calcd for $C_{26}H_{21}O$ [$(M+H)^+$] 349.1587, found: 349.1588.

(3-(4-Fluorophenyl)propa-1,2-diene-1,1-diyl)dibenzene ***(3f)***. Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford pure **3f** as a yellow oil (39 mg, 68%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.42 (m, 4H), 7.27-7.37 (m, 8H), 6.98-7.00 (m, 2H), 6.67 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.94，162.17 (d, J = 245.0 Hz), 136.06, 129.83 (d, J = 31.0 Hz), 128.51, 128.43, 128.36, 127.65, 115.76 (d, J = 17.0 Hz), 113.93, 96.73; IR (film, cm^{-1}) 1930, 1600, 1506, 1490, 1225, 1155; EI-MS (*m/z*, relative intensity) 286 (M^+, 100), 270 (12), 209 (27), 190 (5), 183 (11), 134 (15); RMS (ESI) calcd for $C_{21}H_{16}F$ [$(M+H)^+$] 287.1230, found: 287.1230.

(3-(4-(Trifluoromethyl)phenyl)propa-1,2-diene-1,1-diyl)dibenzene ***(3g)***. Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford pure **3g** as a yellow oil (61 mg, 90%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.40-7.42 (m, 4H), 7.29-7.38 (m, 6H), 6.72 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.03, 137.89, 135.56, 129.23 (q, J = 32.2 Hz), 128.61, 128.46, 127.90, 127.05, 125.75 (q, J = 4.0 Hz), 124.18 (q, J = 270.4 Hz), 114.37, 96.85; IR (film, cm^{-1}) 1928, 1616, 1492, 1322, 1164, 1122, 1064; EI-MS (*m/z*, relative intensity) 336 (M^+, 100), 321 (11), 267 (57), 252 (12), 207 (20), 189 (23), 165 (17), 126 (13); HRMS (ESI) calcd for $C_{22}H_{16}F_3$ [$(M+H)^+$] 337.1199, found 337.1197.

3-(3,3-Diphenylpropa-1,2-dien-1-yl)thiophene ***(3h)***. Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford pure **3h** as a yellow oil (38 mg, 69%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34-7.42 (m, 4H), 7.32-7.36 (m, 4H), 7.24-7.30 (m, 3H), 7.17-7.18 (m, 2H), 6.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.42, 136.26, 135.08, 128.49, 128.46, 127.51, 126.29, 126.15, 127.50, 112.83, 92.17; IR (film, cm^{-1}) 1935, 1957, 1491, 1442, 1073, 907; EI-MS (*m/z*, relative intensity) 274 (M^+, 15), 256 (100), 241 (32), 226 (10), 207 (98), 191 (12), 178 (11), 165 (12), 152 (11), 141 (40), 128 (51), 113 (15), 102 (10); HRMS (ESI) calcd for $C_{19}H_{15}S$ [$(M+H)^+$] 275.0889, found: 275.0889.

5,5-Diphenylpenta-3,4-dien-2-ol ***(3i)***. Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 10 : 1) to afford pure **3i** as a yellow oil (38 mg, 88%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.17-7.29 (m, 10H), 5.74 (d, J = 5.6 Hz, 1H), 4.39-4.45 (m, 1H), 1.31 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.22, 136.37, 128.40, 128.36, 127.42, 112.59, 100.01, 66.33, 23.52; IR (film, cm^{-1}) 3373, 1944, 1597, 1492, 1451, 1073, 908; EI-MS (*m/z*, relative intensity) 236 (M^+, 12), 218 (5), 207 (5), 193 (100), 178 (17), 165 (10), 152 (5), 115 (85), 91 (16); HRMS (ESI) calcd for $C_{17}H_{17}O$ [$(M+H)^+$] 237.1274, found: 237.1273.

(3-(Cyclohex-1-en-1-yl)propa-1,2-diene-1,1-diyl)dibenzene ***(3j)***. Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford pure **3j** as a yellow oil (34 mg, 63%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.23-7.20 (m, 8H), 7.15-7.20 (m, 2 H), 6.29 (s, 1H), 5.70 (m, 1H), 2.05-2.06 (m, 4H), 1.52-1.59 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.29, 136.95, 132.07, 128.35, 128.32, 127.29, 127.11, 112.37, 100.87, 26.04, 25.94, 22.48, 22.36; IR (film, cm^{-1}) 1924, 1597, 1491, 1450, 1075, 1029; EI-MS (*m/z*, relative intensity) 272 (M^+, 100), 243 (12), 229 (13), 215 (14), 191 (17), 165 (20), 115 (17); HRMS (ESI) calcd for $C_{21}H_{21}$ [$(M+H)^+$] 273.1638, found: 273.1638.

*Hepta-1,2-diene-1,1-diyldibenzene(****3k****)*. Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford pure **3k** as a colorless oil (36 mg, 73%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.22-7.29 (m, 8H), 7.13-7.19 (m, 2H), 5.61 (t, J = 6.8 Hz, 1H), 2.08-2.14 (m, 2H), 1.39-1.46 (m, 2H), 1.24-1.33 (m, 2H), 0.81 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.40, 137.31, 128.35, 128.27, 126.90, 109.61, 94.36, 31.37, 28.73, 22.30, 13.88; IR (film, cm^{-1}) 1942, 1597, 1491, 1452, 1442, 1074, 1058; EI-MS (*m/z*, relative intensity) 248 (M^+, 5), 219 (4), 206 (100), 191 (32), 178 (8), 165 (10), 128 (12), 115 (11), 91 (50); HRMS (ESI) calcd for $C_{19}H_{21}$ [$(M+H)^+$] 249.1638, found 249.1637.

3,3'-(3-Phenylpropa-1,2-diene-1,1-diyl)bis((trifluoromethyl)benzene) ***(4a)***. Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford pure **4a** as a yellow oil (71 mg, 88%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 2H), 7.48 (d, J = 7.2 Hz, 4H), 7.38 (t, J = 8.0

Hz, 2H), 7.30-7.33 (m, 2H), 7.24-7.28 (m, 2H), 7.13-7.20 (m, 1H), 6.73 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.64, 136.62, 132.67, 131.56, 131.25 (q, J = 37.2 Hz), 129.24, 129.03, 128.05, 127.18, 124.94 (q, J = 37.2 Hz), 124.68 (q, J = 3.8 Hz), 123.97 (q, J = 270.9 Hz), 112.01, 99.11; IR (film, cm^{-1}) 1939, 1599, 1489, 1443, 1330, 1250, 1166, 1124, 1093, 1073; EI-MS (*m/z*, relative intensity) 404 (M^+, 100), 385 (5), 335 (52), 320 (4), 265 (11), 189 (10), 157 (2), 131 (4); HRMS (ESI) calcd for $C_{23}H_{15}F_6$ [$(M+H)^+$] 405.1073, found: 405.1073.

*4,4'-(3-Phenylpropa-1,2-diene-1,1-diyl)bis(methoxybenzene) (**4b**)*. Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 30 : 1) to afford pure **4b** as a yellow oil (61 mg, 93%); 1H NMR (400 MHz, $CDCl_3$) δ 7.21-7.32 (m, 8H), 7.10-7.15 (m, 1H), 6.78-6.81 (m, 4H), 6.57 (s, 1H), 3.72 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.69, 159.61, 134.37, 129.54, 128.73, 128.59, 127.15, 126.87, 113.90, 112.82, 97.34, 55.28; IR (film, cm^{-1}) 1924, 1605, 1508, 1462, 1247, 1172, 1032; EI-MS (*m/z*, relative intensity) 328 (M^+, 100), 313 (15), 297 (12), 281 (87),253 (19), 207 (98), 191 (13), 164 (15), 147 (13), 126 (17); HRMS (ESI) calcd for $C_{23}H_{21}O_2$ [$(M+H)^+$] 329.1536, found: 329.1535.

*4,4'-(3-Phenylpropa-1,2-diene-1,1-diyl)bis(chlorobenzene) (**4c**)*. Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford pure **4c** as a yellow oil (56 mg, 83%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.39 (m, 13H), 6.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.16, 134.28, 133.60, 133.18, 129.60, 128.92, 128.78, 127.74, 127.02, 112.04, 98.36; IR (film, cm^{-1}) 1928, 1589, 1488, 1395, 1090, 1014; EI-MS (*m/z*, relative intensity) 336 (M^+, 23), 301 (52), 281 (11), 265 (40), 224 (10), 207 (100), 191 (15), 178 (11), 147 (9), 133 (16), 91 (17); HRMS (ESI) calcd for $C_{21}H_{15}Cl_2$ [$(M+H)^+$] 337.0545, found: 337.0547.

*4-(1,3-Diphenylpropa-1,2-dien-1-yl)-1,1'-biphenyl (**4d**)*. Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford pure **4d** as a yellow oil (60 mg, 87%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.60 (m, 4H), 7.40-7.46 (m, 8H), 7.28-7.38 (m, 6H), 7.20-7.24 (m, 1H), 6.73 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.43, 140.67, 140.40, 136.09, 135.07, 133.80, 128.81, 128.79, 128.78, 128.52, 127.64, 127.41, 127.32, 127.20, 126.99, 113.45, 97.82 (two peaks ware missed because of overlap); IR (film, cm^{-1}) 1928, 1598, 1486, 1446, 1073, 1007; HRMS (ESI) calcd for $C_{27}H_{21}$ [$(M+H)^+$] 345.1638, found: 345.1629.

*4,4'-(3-Phenylpropa-1,2-diene-1,1-diyl)bis(methylbenzene) (**4e**)*. Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford pure **4e** as a yellow oil (57 mg, 94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.41 (m, 2H), 7.29-7.33 (m, 6H), 7.19-7.23 (m, 1H), 7.15 (d, J = 8.0 Hz, 4H), 6.67 (s, 1H), 2.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.98, 137.32, 134.18, 133.28, 129.15, 128.73, 128.32, 127.19, 126.92, 113.39, 97.42, 21.17; IR (film, cm^{-1}) 1926, 1599, 1509, 1406, 1259, 1066; EI-MS (*m/z*, relative intensity) 296 (M^+, 72), 281 (61), 253 (10), 236 (11), 222 (12), 207 (85), 191 (100), 178 (12), 165 (21), 126 (13), 115 (52); HRMS (ESI) calcd for $C_{23}H_{21}$ [$(M+H)^+$] 297.1638, found: 297.1635.

*4,4'-(3-Phenylpropa-1,2-diene-1,1-diyl)bis(fluorobenzene) (**4f**)*. Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford pure **4f** as a yellow oil (57 mg, 94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.31 (m, 8H), 7.14-7.17 (m, 1H), 6.92-6.98 (m, 4H), 6.60 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.85, 162.37 (d, J = 245.6 Hz), 133.55, 132.00 (d, J = 3.2 Hz), 129.94 (d, J = 8.0 Hz), 128.88, 127.59, 126.96, 115.51 (d, J = 21.4 Hz), 112.02, 97.99; IR (film, cm^{-1}) 1930, 1600, 1504, 1224, 1156, 1067; EI-MS (*m/z*, relative intensity) 304 (M^+, 100), 283 (11), 270 (5), 227 (7), 209 (15), 183 (9), 141 (7), 131 (5), 107 (4); HRMS (ESI) calcd for $C_{21}H_{15}F_2$ [$(M+H)^+$] 305.1136, found: 305.1136.

*1-Fluoro-4-(1-(4-methoxyphenyl)-3-phenylpropa-1,2-dien-1-yl)benzene (**4g**)*. Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 30 : 1) to afford pure **4g** as a yellow oil (36 mg, 57%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.39 (m, 8H), 7.20-7.24 (m, 1H), 7.00-7.04 (m, 2 H), 6.86-6.90 (m, 2H), 6.67 (s, 1H), 3.8 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.75, 162.27 (d, J = 245.2 Hz), 159.26, 133.94, 132.38 (d, J = 3.2 Hz), 129.99 (d, J = 8.0 Hz), 129.47, 128.80, 128.13, 127.36, 115.35 (d, J = 21.4 Hz), 113.99, 112.42, 97.85, 55.28; IR (film, cm^{-1}) 1930, 1604, 1506, 1248, 1175, 1034; HRMS (ESI) calcd for $C_{22}H_{18}FO$ [$(M+H)^+$] 317.1336, found: 317.1336.

*(1-(4-Methoxyphenyl)propa-1,2-diene-1,3-diyl)dibenzene (**4h**)*. Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 30 : 1) to afford pure **4h** as a yellow oil (52 mg, 88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.44 (m, 4H), 7.25-7.36 (m, 7H), 7.18-7.22 (m, 1H), 6.86-6.89 (m, 2H), 6.67 (s, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.97, 159.17, 136.42, 134.09, 129.57, 128.75, 128.43, 128.40, 128.27, 127.50, 127.25, 126.91, 113.91, 113.27, 97.52, 55.27; IR (film, cm^{-1}) 1927, 1064, 1508, 1248, 1174, 1035; EI-MS (*m/z*, relative intensity) 298 (M^+, 90), 283 (100), 252 (10), 220 (12), 207 (90), 191 (81), 178 (52), 165 (50), 132 (11), 115 (52), 105 (20); HRMS (ESI) calcd for $C_{22}H_{19}O$ [$(M+H)^+$] 299.1431, found: 299.1431.

*2-(4-Phenylbuta-2,3-dien-2-yl)naphthalene (**4i**)*. Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford pure **4i** as a yellow oil (16 mg, 31%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.88 (m, 4H), 7.59-7.64 (m, 1H), 7.41-7.50 (m, 4H), 7.29-7.38 (m, 2H), 7.19-7.23 (m, 1H), 6.55 (q, J = 2.8 Hz, 1H), 2.34 (d, J = 2.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.55, 134.47, 133.75, 133.63, 132.56, 128.73, 128.03, 127.83, 127.57, 127.07, 126.95, 126.15, 125.78, 124.98, 123.65, 104.82, 96.83, 16.81; IR (film, cm^{-1}) 1922, 1681, 1629, 1597, 1503, 1393, 1230, 1065; EI-MS (*m/z*, relative intensity) 256 (M^+, 100), 241 (50), 216 (32), 207 (98), 191 (23), 178 (30), 165 (43), 141 (72), 128 (73), 115 (33), 91 (17); HRMS (ESI) calcd for $C_{20}H_{17}$ [$(M+H)^+$] 257.1325, found 257.1325.

*4,4'-(3-(4-Bromophenyl)propa-1,2-diene-1,1-diyl)bis(chlorobenzene) (**4j**)*. Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford pure **4j** as a yellow oil (68 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.45 (m, 2H), 7.21-7.33 (m, 8H), 7.21-7.24 (m, 2H), 6.66 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.19, 133.91, 133.79, 132.19, 132.03, 129.58, 128.84, 128.46, 121.44, 122.49, 97.55; IR (film, cm^{-1}) 1928, 1950, 1486, 1400, 1090, 1012; HRMS (ESI) calcd for $C_{21}H_{14}BrCl_2$ [$(M+H)^+$] 414.9650, found: 414.9645.

*4,4'-(3-(m-Tolyl)propa-1,2-diene-1,1-diyl)bis(chlorobenzene) (**4k**)*. Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford pure **4k** as a yellow oil (63 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.33 (m, 8H), 7.17-7.22 (m, 3H), 7.06 (d, J = 7.2 Hz, 1H), 6.68 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.21, 138.60, 134.32, 133.54, 133.03, 129.59, 128.81, 128.75, 128.58, 127.65, 124.17, 111.87, 98.40, 21.39; IR (film, cm^{-1}) 1929, 1604, 1488, 1397, 1090, 1013; EI-MS (*m*/*z*, relative intensity) 350 (M^+, 10), 315 (9), 225 (8), 207 (100), 191 (13), 132 (10), 95 (12), 73 (30); HRMS (ESI) calcd for $C_{22}H_{17}Cl_2$ [$(M^+H)^+$] 351.0702, found: 351.0699.

*4,4'-(3-(2-Chlorophenyl)propa-1,2-diene-1,1-diyl)bis(methoxybenzene) (**4l**)*. Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 30 : 1) to afford pure **4l** as a yellow oil (52 mg, 74%);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.56 (m, 1 H), 7.32-7.36 (m, 5H), 7.10-7.19 (m, 3H), 6.87-6.90 (m, 4 H), 3.81 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.61, 159.22, 132.24, 131.97, 129.89, 129.54, 128.20, 128.11, 126.73, 113.93, 113.02, 93.68, 55.28 (one peak was missed because of overlap); IR (film, cm^{-1}) 1928, 1606, 1509, 1247, 1173, 1034; EI-MS (*m*/*z*, relative intensity) 362 (M^+, 20), 342 (35), 332 (9), 281 (12), 267 (8), 207 (100), 191 (7), 165 (7), 147 (11), 96 (10), 73 (21); HRMS (ESI) calcd for $C_{23}H_{20}ClO_2$ [$(M+H)^+$] 363.1146, found 363.1148.

*4,4'-(3-(m-Tolyl)propa-1,2-diene-1,1-diyl)bis(methoxybenzene) (**4m**)*. Following the typical procedure above, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 30 : 1) to afford pure **4m** as a yellow oil (54 mg, 79%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.36 (m, 4H), 7.20 (d, J = 3.6 Hz, 3H), 7.00-7.04 (m, 1H), 6.66-6.89 (m, 4H), 3.80 (s, 6H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.69, 159.09, 138.34, 134.19, 129.52, 128.61, 128.00, 127.48, 124.03, 113.85, 112.63, 97.37, 55.27, 21.38; IR (film, cm^{-1}) 2928, 1605, 1508, 1247, 1173, 1033; EI-MS (*m*/*z*, relative intensity) 342 (M^+, 15), 253 (12), 207 (100), 165 (10), 135 (10), 96 (13), 73 (9); HRMS (ESI) calcd for $C_{24}H_{23}O_2$ [$(M+H)^+$] 343.1692, found 343.1692.

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Supplementary data

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