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Synthesis of Allenes via Gold-Catalyzed Intermolecular Reaction of Propargylic Alcohols and Aromatic Compounds

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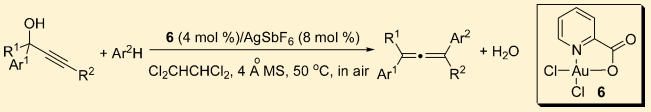
Supporting Information

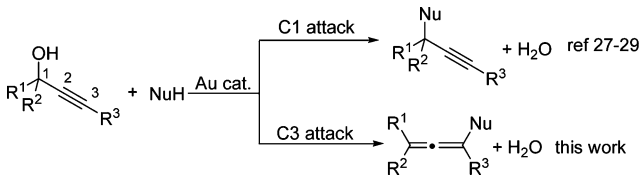
ABSTRACT: Functionalized allenes are efficiently synthesized in moderate to high yield from gold-catalyzed intermolecular reaction of propargylic alcohols and aromatic compounds. The user-friendly process could be conducted under mild reaction conditions with easily accessible starting materials.



Allenes are versatile synthons in synthetic organic chemistry because of their unique cumulene structure and axis-to-center chirality transfer ability.[1,2] Additionally, allenes are important subunits in a variety of natural products and pharmaceutically related compounds.[3] As a result, efficient and simple approaches for synthesizing allenes are hot topics of organic chemists.[4,5] Among all the methods developed, the S_N2' displacement of propargylic compounds with organometallic reagents is the most commonly used one.[6] Moreover, methods based on the construction of 1,2-diene skeleton have also been developed.[7−12] Despite this, considering the importance of allenes, new efficient and versatile catalytic processes to access allenes are still of great interest.

In the past decade, gold salts have emerged as powerful catalysts in the carbon−carbon multibonds related reactions.[13−15] Because of the good functional group tolerance and low air and moisture sensitivity, gold catalysts have been used to construct some complicated compounds. Allenes are normally used as substrates or intermediates in gold-catalyzed cascade reactions.[16] On the other hand, synthesis of allenes in the presence of gold catalysts has also been reported in recent years.[9,17−26] However, most of these reactions are intramolecular versions, and very bulky phosphine or NHC ligands were used to achieve high chemoselectivity. In 2005, Campagne reported an S_N1 reaction of propargylic alcohol (Scheme 1)[27,28] where various C-, O-, and S-nucleophiles were used. Since only racemic product could be obtained from enantiomerically enriched propargylic alcohol, the author proposed an S_N1 mechanism. Direct substitution of propargylic alcohols is attractive because water is the only byproduct and the alkyne moiety allows many further synthetic modifications; many research works have been reported in this area.[29−32] Considering the resonance between propargyl carbocation and allene cation, we envisioned that by tuning the properties of nucleophiles, C3 attack reaction may be realized and thus allenes can be prepared in a simple manner. Here, we report an intermolecular reaction of propargylic alcohol and aromatic compounds leading to allenes.

Scheme 1. Initial Hypothesis



Initially, *m*-xylene **2a** was selected and reacted with propargylic alcohol **1a** in the presence of various gold catalysts at room temperature. All of the gold catalysts we screened gave some allene products in several hours (Table 1, entries 1−5), and catalyst **6** proved to be the best (entry 5). Reaction temperature, silver salts, and solvents were investigated next, and the yield could be improved to 58% when the reaction conducted in $Cl_2CHCHCl_2$ with 4 mol % of **6** and 8 mol % of $AgSbF_6$ (entry 8). Control experiments demonstrated that $AgSbF_6$ was necessary (entry 9). $AgSbF_6$ and $HSbF_6$ could also catalyze the reaction but with an enormously diminished rate (entries 10 and 11). When the reaction conducted in an open flask, a slightly higher yield was obtained (entry 12). Molecular sieves were necessary for high yield (entry 13). Finally, when 5 equiv of **2a** was used, allene products could be obtained in 47% yield (entry 14).

Using the conditions from entry 12 of Table 1 and mesitylene as the nucleophile, we were pleased to find that functionalized allenes could be regioselectively synthesized in moderate to high yields (Table 2). Propargyl alcohols bearing electron-rich (entries 2 and 3) and electron-deficient (entries 4−7) aromatic rings were effective, although a slightly lower yield was observed when the substituent was *p*-$MeOC_6H_4$ (entry 3). Notably, *p*-BrC_6H_4 and *p*-IC_6H_4 were well tolerated in this reaction, which provides a handle for further functionalization (entries 6 and 7). Trisubstituted allenes could be obtained in high yield (entries 7−9) when tertiary propargylic alcohols were used. Additionally, internal alkynyl

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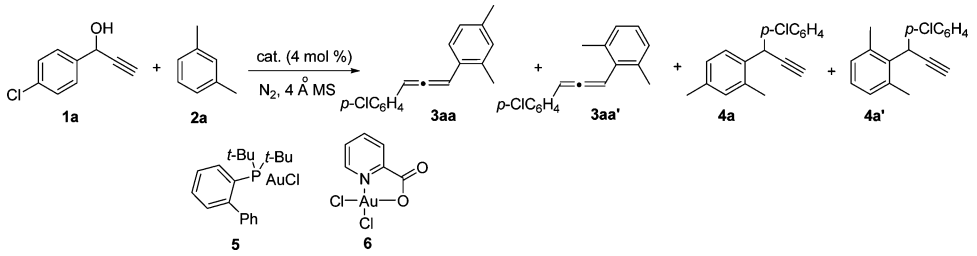
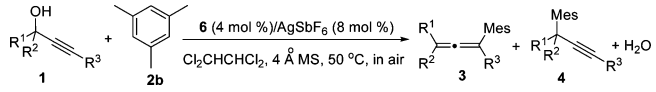
Table 1. Optimization of Reaction Conditions[a]



entry	catalyst (4 mol %)	solvent	temp (°C)	time (h)	yield[b] (%) (3aa:3aa′:4a + 4a′)[c]
1	AuCl	$ClCH_2CH_2Cl$	rt	4.0	10
2	$AuCl_3$	$ClCH_2CH_2Cl$	rt	4.0	15
3	$Ph_3PAuCl/AgSbF_6$	$ClCH_2CH_2Cl$	rt	5.0	36 (1.0:0.4:0.5)
4	**5**/$AgSbF_6$	$ClCH_2CH_2Cl$	rt	5.0	20 (1.0:0.5:0.8)
5	**6**/$AgSbF_6$[d]	$ClCH_2CH_2Cl$	rt	4.5	46 (1.0:0.25:0.5)
6	**6**/$AgSbF_6$[d]	$ClCH_2CH_2Cl$	50	1.0	52 (1.0:0.3:0.56)
7	**6**/AgOTf[d]	$ClCH_2CH_2Cl$	50	1.1	25 (1.0:0.62:0.5)
8	**6**/$AgSbF_6$[d]	$Cl_2CHCHCl_2$	50	1.5	58 (1.0:0.32:0.3)
9	**6**	$Cl_2CHCHCl_2$	50	24	no reaction
10	$AgSbF_6$[d]	$Cl_2CHCHCl_2$	50	24	29 (1.0:0.4:0.51)
11	$HSbF_6$[h]	$Cl_2CHCHCl_2$	50	24	22 (0.78:1.0:0.36)
12[e]	**6**/$AgSbF_6$[d]	$Cl_2CHCHCl_2$	50	1.1	60 (1.0:0.31:0.3)
13[e,f]	**6**/$AgSbF_6$[d]	$Cl_2CHCHCl_2$	50	2.0	50 (1.0:0.52:0.3)
14[e,g]	**6**/$AgSbF_6$[d]	$Cl_2CHCHCl_2$	50	2.5	47 (1.0:0.4:0.5)

[a]0.2 mmol of propargylic alcohol and 2.0 mmol of *m*-xylene. The reactions were carried out under an atmosphere of nitrogen in 2 mL of dry solvent. [b]Yield of **3aa** and **3aa′**. [c]Molar ratio of products based on ^{1}H NMR analysis of the crude reaction mixture. [d]8 mol % of $AgSbF_6$. [e]The reaction was conducted in the air with solvent of technical grade. [f]No molecular sieves. [g]0.2 mmol of propargylic alcohol and 1.0 mmol of *m*-xylene. [h]8 mol % of $HSbF_6$.

Table 2. Reaction Scope[a]



entry	substrate (R^1, R^2, R^3)	time (min)	product	yield[b] (%) (3:4)[c]
1	**1b** (Ph, H, H)	20	**3bb**	69 (1.0:0.23)
2	**1c** (*p*-$CH_3C_6H_4$, H, H)	15	**3cb**	75 (1.0:0.25)
3	**1d** (*p*-$CH_3OC_6H_4$, H, H)	10	**3db**	49 (1.0:0.23)
4	**1e** (*p*-FC_6H_4, H, H)	20	**3eb**	69 (1.0:0.14)
5	**1a** (*p*-ClC_6H_4, H, H)	30	**3ab**	73 (1.0:0.26)
6	**1f** (*p*-BrC_6H_4, H, H)	60	**3fb**	51 (1.0:0.30)
7	**1g** (*p*-IC_6H_4, CH_3, H)	15	**3gb**	82 (1.0:0)
8	**1h** (Ph, CH_3, H)	10	**3hb**	90 (1.0:0)
9	**1i** (Ph, Ph, H)	5	**3ib**	90 (1.0:0)
10	**1j** (Ph, H, Ph)	17	**3jb**	87 (1.0:0.08)
11	**1k** (Ph, H, *n*-C_8H_{17})	20	**3kb**	87 (1.0:0.09)
12	**1l** (Ph, H, cyclopropyl)	12	**3 lb**	82 (1.0:0)
13	**1m** (Ph, CH_3, cyclopropyl)	25	**3mb**	73 (1.0:0)
14	**1n** ($PhCH_2$, H, H)	600	**3nb**	NR[d]
15	**1o** (*n*-C_7H_{15}, H, H)	600	**3ob**	NR[d]

[a]0.2 mmol of propargylic alcohol and 2 mmol of mesitylene. The reactions were carried out in an open flask in 2 mL of $Cl_2CHCHCl_2$ of technical grade. [b]Yield of allene product. [c]Molar ratio of products based on ^{1}H NMR analysis of the crude reaction mixture. [d]No reaction.

substrates also worked well (entries 10−13), both aryl group and alkyl group were tolerated and the regioselectivities were better than terminal propargylic alcohols. Tetrasubstituted allene could also be easily obtained (entry 13). Unfortunately, the reaction did not work when neither R^1 nor R^2 was an aromatic ring (entries 14 and 15).

To further demonstrate the effectiveness of this gold-catalyzed allene synthesis procedure, a variety of aromatic compounds were investigated. *p*-Xylene, *m*-xylene, 1,2,4,5-tetramethylbenzene, and pentamethylbenzene are all effective nucleophiles for this reaction (Table 3, entries 1−5). When *m*-xylene was used, an inseparable mixture with a *p*-, *o*- ratio of 1.0:0.53 could be obtained (entry 1). Aromatic compounds with a substituent other than a methyl group were also investigated. Ketone and cyano groups are well tolerated in the reaction (entries 6−8), and functionalized allenes could be

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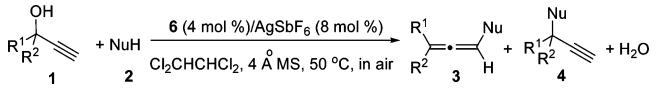
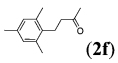
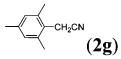
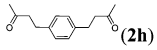
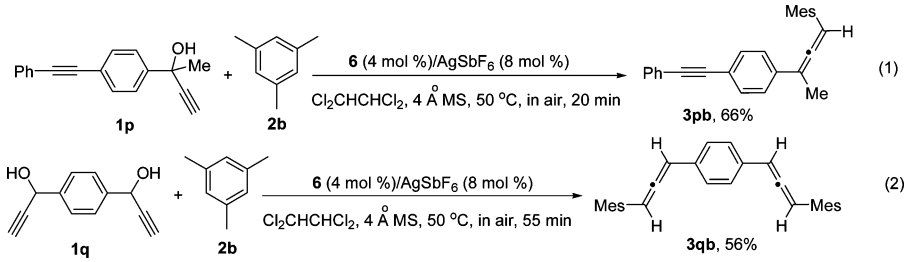
Table 3. Substrate Scope[a]



entry	substrate (R^1, R^2)	NuH	time (min)	product	yield[b] (%)	3:4[c]
1	**1f** (*p*-BrC_6H_4, H)	*m*-xylene(**2a**)	90	**3fa**+**3fa'**	53 (1.0:0.53)[d]	1.0:0.23
2	**1f** (*p*-BrC_6H_4, H)	*p*-xylene(**2c**)	25	**3fc**	60	1.0:0.07
3	**1a** (*p*-ClC_6H_4, H)	*p*-xylene(**2c**)	60	**3ac**	65	1.0:0.17
4	**1h** (Ph, CH_3)	1,2,4,5-tetramethylbenzene(**2d**)	15	**3hd**	80	1.0:0.09
5	**1h** (Ph, CH_3)	pentamethylbenzene(**2e**)	15	**3he**	83	1.0:0.05
6	**1f** (*p*-BrC_6H_4, H)	 (**2f**)	60	**3ff**	58	1.0:0.25
7	**1f** (*p*-BrC_6H_4, H)	 (**2g**)	150	**3fg**	33	1.0:0.27
8	**1f** (*p*-BrC_6H_4, H)	 (**2h**)	30	**3fh**	59	1.0:0.22
9[e]	**1b** (Ph, H)	toluene (**2i**)	40	**3bi** + **3bi'**	51 (1.0:1.0)[d]	1.0:0.14
10	**1a** (*p*-ClC_6H_4, H)	1,3-dimethoxybenzene (**2j**)	180	**4b**+**4b'**	42 (1.0:0.1)[f]	0:1.0
11	**1b** (Ph, H)	anisole (**2k**)	20	**4c**+**4c'**	56 (1.0:0.36)[f]	0:1.0

[a]0.2 mmol of propargylic alcohol and 2 mmol of NuH. The reactions were carried out in an open flask in 2 mL of $Cl_2CHCHCl_2$ of technical grade. [b]Yield of allene product. [c]Molar ratio of allene and alkyne products based on ^{1}H NMR analysis of the crude reaction mixture. [d]*Para*-attack product **3**:*ortho*-attack product **3'**. [e]Toluene as solvent. [f]No allene product, ratio of alkyne isomers.

Scheme 2. Reaction Scope



obtained in moderate yield. To gain more information about the relationship of regioselectivity and arene nucleophiles, toluene, anisole, and 1,3-dimethoxybenzene were tested in this reaction. When 10 equiv of toluene was used, only very poor yield was achieved. However, when toluene was used as solvent, allene products **3bi** and **3bi'** could be obtained in 51% yield (entry 9). When anisole or 1,3-dimethoxybenzene were used as nucleophile, only alkyne products could be isolated (entries 10 and 11).

Impressively, when compound **1p** was prepared, which has two carbon carbon triple bonds, and employed for the synthesis of allene (Scheme 2, eq 1), **3pb** could be obtained smoothly in 66% yield in only 20 min. Additionally, the reaction of substrate **1q** led to the formation of bisallene **3qb** in 55 min (Scheme 2, eq 2).

In Campagne's report,[27,28] the author observed the lack of reactivity when the aryl ring at the C1 or C3 position (Scheme 1) was substituted by strong electron-withdrawing groups or when the propargylic position is only substituted by one alkyl group. In light of these facts, the author proposed an S_N1 carbocation mechanism with gold catalyst acting as a Lewis acid. This mechanism was further confirmed when enantiomerically enriched substrate led to racemic product. Under our reaction conditions, only benzylic propargylic alcohols gave rise to the substitution reaction (Table 2, entries 14 and 15), which indicated a similar carbocation mechanism. Further experiments showed that the conversion of substrates with *p*-$NO_2C_6H_4$ or *p*-$CF_3C_6H_4$ substituents at the propargylic position was very low (Scheme 3). Additionally, **3bb** was obtained with only 6% ee when enantiomerically enriched propargylic alcohol **1b** and mesitylene were used. All these results suggest an S_N1-type reaction mechanism (Scheme 3).

The next issue needs to be addressed is the different regioselectivity. On the basis of the data we obtained, a simple steric effect is not a key factor for the regioselectivity (Table 2, entries 1−9 vs 10−13). We proposed loose ion pair was formed as a key intermediate in the reaction (Scheme 3), and the interaction between nucleophile and gold catalyst resulted in different products. Thus, coordination of cationic $[AuL]^{2+}$ to the triple bond and OH group leads to intermediate **I**, which eliminates $[HOAuL]^+$ to afford loose ion pair **II**. When nucleophiles bearing OMe group were used, $[HOAuL]^+$ coordinated to the oxygen atom, and then the nucleophile would attack the propargylic position, which led to product **4**, water, and regenerated $[AuL]^{2+}$. On the contrary, when a nucleophile such as mesitylene was used, no coordination could be expected, and then mesitylene attacked the C3 position because of steric bias, which led to allene **3**.

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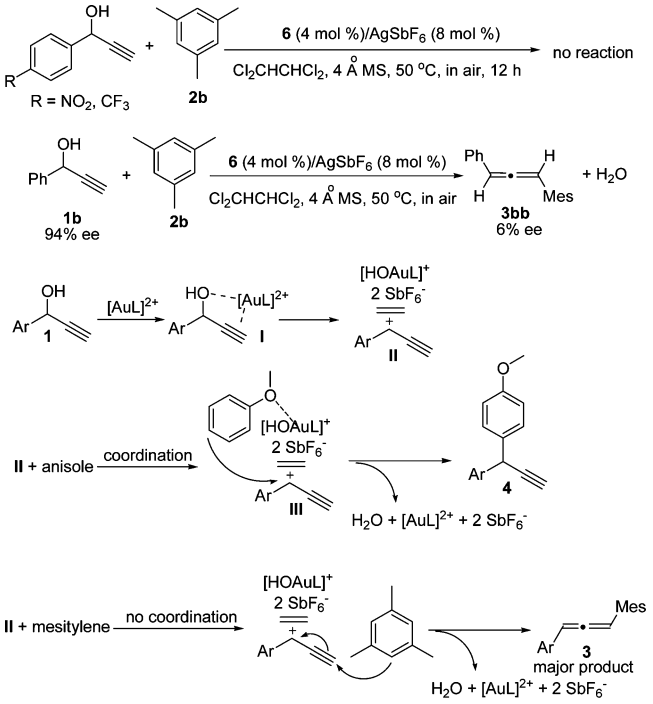
Scheme 3. Proposed Reaction Mechanism



In summary, we have presented the first example that allenes can be synthesized via an intermolecular reaction of benzylic propargylic alcohols and alkyl-substituted aromatic compounds, which catalyzed by a commercially available gold catalyst. Di-, tri-, and tetrasubstituted allenes could be obtained very easily. Among the reasons for its appeal are easily accessible reagents, a user-friendly procedure, mild reaction conditions, short reaction time, and water as the only byproduct.

EXPERIMENTAL SECTION

General Procedure for Synthesis of Propargylic Alcohol. To a solution of trimethylsilylacetylene (1.1 g, 11 mmol) in THF (10 mL) at −70 °C was added *n*-BuLi (4.4 mL, 11 mmol, 2.5 M in hexane) dropwise under N_2 atmosphere. The mixture was stirred for 1 h at −70 °C, the corresponding aldehyde (10 mmol) was added, and the reaction was stirred for an additional 30 min at −70 °C and warmed to room temperature over 30 min. The mixture was quenched with saturated NH_4Cl solution and extracted with diethyl ether. The organic layers were combined, washed with brine, and dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. K_2CO_3 (4.1 g, 30 mmol) was added to the crude mixture in MeOH (10 mL), and stirring was continued at room temperature for 2 h. The mixture was filtered through a short plug of silica gel. After evaporation of the solvent, the residue was purified by column chromatography on silica gel to afford the corresponding propargylic alcohol.

*1-(4-Chlorophenyl)prop-2-yn-1-ol (**1a**)*:[33] yellow oil (1.6 g, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (d, J = 7.9 Hz, 2H), 7.36 (d, J = 7.9 Hz, 2H), 5.45 (d, J = 5.1 Hz, 1H), 2.68 (s, 1H), 2.30 (t, J = 5.1 Hz, 1H).

*1-Phenylprop-2-yn-1-ol (**1b**)*:[34] yellow oil (1.2 g, 89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54−7.47 (m, 2H), 7.39−7.27 (m, 3H), 5.39 (dd, J = 6.0, 2.2 Hz, 1H), 2.91 (br s, 1H), 2.62 (d, J = 2.2 Hz, 1H).

*1-p-Tolylprop-2-yn-1-ol (**1c**)*:[35] yellow oil (1.2 g, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (d, J = 7.8 Hz, 2H), 7.20 (d, J = 7.8 Hz, 2H), 5.43 (d, J = 6.2 Hz, 1H), 2.65 (s, 1H), 2.36 (s, 3H), 2.15 (d, J = 6.2 Hz, 1H).

*1-(4-Methoxyphenyl)prop-2-yn-1-ol (**1d**)*:[35] yellow oil (1.4 g, 86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47 (d, J = 8.6 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 5.41 (d, J = 2.1 Hz, 1H), 3.81 (s, 3H), 2.65 (d, J = 2.1 Hz, 1H), 2.31 (s, 1H).

*1-(4-Fluorophenyl)prop-2-yn-1-ol (**1e**)*:[35] yellow oil (1.2 g, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (dd, J = 8.2, 5.4 Hz, 2H), 7.07 (t, J = 8.6 Hz, 2H), 5.45 (dd, J = 5.7, 2.1 Hz, 1H), 2.68 (d, J = 2.1 Hz, 1H), 2.27 (d, J = 5.7 Hz, 1H).

*1-(4-Bromophenyl)prop-2-yn-1-ol (**1f**)*:[36] pale yellow solid (1.8 g, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 5.43 (dd, J = 5.9, 1.7 Hz, 1H), 2.68 (d, J = 1.7 Hz, 1H), 2.23 (d, J = 5.9 Hz, 1H).

*2-(4-Iodophenyl)but-3-yn-2-ol (**1g**)*: orange solid (1.8 g, 65%); mp 67−69 °C; IR (film) 3391, 3293, 2985, 2928, 2115, 1584, 1482 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.6 Hz, 2H), 7.40 (d, J = 8.6 Hz, 2H), 2.68 (s, 1H), 2.37 (s, 1H), 1.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 137.4, 127.0, 93.5, 86.6, 73.4, 69.5, 33.1; HRMS (EI) calcd for $C_{10}H_9IO$ M$^+$ 271.9698, found 271.9691.

*2-Phenylbut-3-yn-2-ol (**1h**)*:[37] pale yellow solid (1.1 g, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (d, J = 8.2 Hz, 2H), 7.37 (t, J = 7.4 Hz, 2H), 7.30 (t, J = 7.0 Hz, 1H), 2.67 (s, 1H), 2.33 (s, 1H), 1.79 (s, 3H).

*1,1-Diphenylprop-2-yn-1-ol (**1i**)*:[38] colorless solid (1.8 g, 88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (d, J = 7.2 Hz, 4H), 7.34 (t, J = 7.3 Hz, 4H), 7.30−7.24 (m, 2H), 2.88 (s, 1H), 2.78 (s, 1H).

*1,3-Diphenylprop-2-yn-1-ol (**1j**)*:[39] colorless solid (1.8 g, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (d, J = 7.3 Hz, 2H), 7.50−7.42 (m, 2H), 7.42 (t, J = 7.3 Hz, 2H), 7.40−7.27 (m, 4H), 5.70 (d, J = 6.2 Hz, 1H), 2.31 (d, J = 6.2 Hz, 1H).

*1-Phenylundec-2-yn-1-ol (**1k**)*:[40] pale yellow oil (2.3 g, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.0 Hz, 2H), 7.41−7.35 (m, 2H), 7.35−7.29 (m, 1H), 5.45 (d, J = 6.1 Hz, 1H), 2.27 (dt, J = 7.1, 2.0 Hz, 2H), 2.11 (d, J = 6.1 Hz, 1H), 1.57−1.50 (m, 2H), 1.45−1.34 (m, 2H), 1.34−1.20 (m, 8H), 0.88 (t, J = 6.8 Hz, 3H).

*3-Cyclopropyl-1-phenylprop-2-yn-1-ol (**1l**)*:[41] colorless oil (1.7 g, 99%); ^{1}H NMR (400 MHz, $CDCl_3$) δ:7.50 (d, J = 7.5 Hz, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.30 (t, J = 7.5 Hz, 1H), 5.39 (d, J = 5.6 Hz, 1H), 2.30 (t, J = 6.2 Hz, 1H), 1.35−1.24 (m, 1H), 0.82−0.74 (m, 2H), 0.74−0.66 (m, 2H).

*4-Cyclopropyl-2-phenylbut-3-yn-2-ol (**1m**)*:[42] pale yellow oil (1.5 g, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.60 (m, 2H), 7.35 (t, J = 7.4 Hz, 2H), 7.29 (t, J = 7.4 Hz,1H), 2.25 (s, 1H), 1.73 (s, 3H), 1.35−1.29 (m, 1H), 0.85−0.77 (m, 2H), 0.75−0.70 (m, 2H).

*1-Phenylbut-3-yn-2-ol (**1n**)*:[43] pale yellow oil (1.0 g, 70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.23 (m, 5H), 4.61−4.59 (m, 1H), 3.07−2.97 (m, 2H), 2.49 (d, J = 2.0 Hz, 1H), 1.93 (d, J = 5.9 Hz, 1H).

*Dec-1-yn-3-ol (**1o**)*:[34] clear oil (1.5 g, 95%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.30 (q, J = 5.2 Hz, 1H), 2.39 (d, J = 1.9 Hz, 1H), 1.81−1.60 (m, 3H), 1.56−1.09 (m, 10H), 0.81 (t, J = 6.2 Hz, 3H).

*2-(4-(Phenylethynyl)phenyl)but-3-yn-2-ol (**1p**)*: yellow solid (1.5 g, 62%); mp 78−80 °C; IR (film) 3399, 3288, 2984, 2930, 2213, 2104, 1593, 1505 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.1 Hz, 2H), 7.53 (d, J = 7.1 Hz, 4H), 7.34 (s, 3H), 2.69 (s, 1H), 2.46 (s, 1H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 131.61, 131.58, 128.33, 128.30, 125.0, 123.2, 122.8, 89.7, 89.0, 86.8, 73.4, 69.7, 33.0; HRMS (EI) calcd for $C_{18}H_{14}O$ M$^+$ 246.1045, found 246.1042.

*1,1′-(1,4-Phenylene)diprop-2-yn-1-ol (**1q**)*:[44] yellow solid (1.2 g, 67%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 4H), 5.49 (s, 2H), 2.68 (s, 2H), 2.21 (br s, 2H).

General Procedure for Synthesis of 4-Aryl-2-butaone. Anhydrous ethanol (8 mL) was placed in a three-necked flask (50 mL) fitted with reflux condenser. Small pieces of sodium (0.3 g, 12 mmol) were added and dissolved to form sodium ethoxide. Ethyl acetoacetate (1.6 g, 12 mmol) was added and the mixture stirred for 2 h. After the addition of benzyl chloride (1.3 g, 10 mmol), the reaction mixture was heated under reflux on oil bath for 4−5 h and kept at room temperature for 4 h. Ethanol was distilled off under reduced pressure, and the reaction mixture was quenched with saturated aqueous ammonium chloride (8 mL) and extracted with ether. The extract was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by flash chromatography to afford ethyl α-benzylacetoacetate.

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NaOH solution (40%, 3.9 g, 39 mmol) was added to the flask charged with ethyl α-benzylacetoacetate and the mixture stirred for several minutes. Water was added to the mixture to dissolve the solid. The solution was heated to 70 °C and stirred for about 2.5 h. The mixture was cooled to room temperature and acidified with concentrated hydrochloric acid. The mixture was reheated to 70 °C and stirred for another 3 h. The obtained mixture was extracted with ether and wash with brine. The organic solution was dried and filtered. Solvent was removed under reduced pressure, and the residue was purified by flash chromatography to afford product.

*4-Mesitylbutan-2-one (**2f**)*:.[45] white solid (1.3 g, 70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 2H), 2.86 (t, *J* = 8.0 Hz, 2H), 2.56 (t, *J* = 8.0 Hz, 2H), 2.26 (s, 6H), 2.24 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.3, 135.9, 135.4, 134.4, 129.0, 42.8, 29.8, 23.3, 20.7, 19.6.

*4, 4′-(1,4-Phenylene)dibutan-2-one (**2h**)*:.[46] white solid (0.9 g, 40%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.09 (s, 4H), 2.86 (t, *J* = 7.6 Hz, 4H), 2.74 (t, *J* = 7.6 Hz, 4H), 2.13 (s, 6H).

General Procedure for Synthesis of Allenes. $Cl_2CHCHCl_2$ (0.5 mL) was added to reaction flask charged with dichloro(2-pyridinecarboxylato)gold (4.2 mg, 4 mmol %), $AgSbF_6$ (5.4 mg, 8 mmol %), and 4 Å molecular sieves (17 mg). The reaction mixture was heated to 50 °C and stirred for 5 min. After 2 mmol of mesitylene was added, a solution of propargylic alcohols (0.2 mmol) in $Cl_2CHCHCl_2$ (1.5 mL) was added dropwise in 5 min. The reaction was stirred until TLC analysis showed that propargylic alcohol was completely consumed. The reaction mixture was cooled to room temperature and filtered through a short plug of silica gel. The solution of mixture was concentrated and then purified by flash chromatography to give the product.

*1-(3-(4-Chlorophenyl)propa-1,2-dienyl)-2,4-dimethylbenzene (**3aa**) and 2-(3-(4-Chlorophenyl)propa-1,2-dienyl)-1,3-dimethylbenzene (**3aa′**)*. The crude product was purified by flash chromatography (petroleum ether) to give the product with ratio about 1.0:0.31 according to ^{1}H NMR (colorless oil, 30.6 mg, 60%): IR (film) 3013, 2920, 2851, 1932, 1499, 1378, 835 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.22 (m, 5.6H), 7.07−6.91 (m, 3.5H), 6.75 (d, *J* = 6.6 Hz, 1.31H), 6.47 (d, *J* = 6.6 Hz, 1H of **3aa**), 6.31 (d, *J* = 6.6 Hz, 0.31H of **3aa′**), 2.37 (s, 1.86H of **3aa′**), 2.35 (s, 3H of **3aa**), 2.29 (s, 3H of **3aa**); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.3, 208.1, 137.2, 136.7, 135.3, 132.9, 132.67, 132.65, 132.56, 131.5, 130.7, 128.83, 128.78, 128.5, 128.4, 128.1, 128.0, 127.6, 127.0, 96.6, 96.1, 94.6, 94.2, 21.4, 21.0, 19.9; HRMS (EI) calcd for $C_{17}H_{15}Cl$ M$^+$ 254.0862, found 254.0868.

*2-(3-(4-Chlorophenyl)propa-1,2-dienyl)-1,3,5-trimethylbenzene (**3ab**)*: pale yellow oil (39.2 mg, 73%); IR (film) 2980, 2926, 2857, 1938, 1599, 1375, 833 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25 (s, 4H), 6.86 (s, 2H), 6.74 (d, *J* = 6.8 Hz, 1H), 6.30 (d, *J* = 6.8 Hz, 1H), 2.34 (s, 6H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.1, 136.7, 136.6, 133.1, 132.4, 129.2, 128.7, 128.1, 127.6, 94.5, 94.1, 21.3, 20.9; HRMS (EI) calcd for $C_{18}H_{17}Cl$ M$^+$ 268.1019, found 268.1013.

*2-(3-(4-Chlorophenyl)propa-1,2-dienyl)-1,4-dimethylbenzene (**3ac**)*: pale yellow oil (33.1 mg, 65%); IR (film) 3023, 2921, 2856, 1933, 1592, 1494, 812 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28 (s, 4H), 7.16 (s, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 6.6 Hz,1H), 6.50 (d, *J* = 6.6 Hz, 1H), 2.36 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4, 135.7, 132.7, 132.5, 132.4, 131.2, 130.6, 128.9, 128.3, 128.1, 128.0, 96.6, 96.3, 20.9, 19.5; HRMS (EI) calcd for $C_{17}H_{15}Cl$ M$^+$ 254.0862, found 254.0859.

*1,3,5-Trimethyl-2-(3-phenylpropa-1,2-dienyl)benzene (**3bb**)*: pale yellow oil (32.3 mg, 69%); IR (film) 3028, 2968, 2916, 2857, 1934, 1600, 1495, 1376 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26−7.37 (m, 4H), 7.20 (t, *J* = 7.0 Hz, 1H), 6.87 (s, 2H), 6.74 (d, *J* = 6.8 Hz, 1H), 6.35 (d, *J* = 6.8 Hz, 1H), 2.36 (s, 6H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.0, 136.6, 136.5, 134.5, 129.2, 128.6, 127.9, 127.0, 126.9, 95.4, 93.7, 21.3, 20.9; HRMS (EI) calcd for $C_{18}H_{18}$ M$^+$ 234.1409, found 234.1411.

*1-Methyl-4-(3-phenylpropa-1,2-dienyl)benzene (**3bi**)*[47] *and 1-Methyl-2-(3-phenylpropa-1,2-dienyl)benzene (**3bi′**)*:.[48] colorless oil (21.0 mg, 51%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.27 (m, 10.00H), 7.28−7.20 (m, 5.29H), 7.18−7.10 (m, 5.72H), 6.78 (d, *J* = 6.6 Hz, 1.1H), 6.56 (d, *J* = 9.2 Hz, 3.01H), 2.42 (s, 3H), 2.33 (s, 3.18H).

*1,3,5-Trimethyl-2-(3-p-tolylpropa-1,2-dienyl)benzene (**3cb**)*: pale yellow oil (37.3 mg, 75%); IR (film) 3011, 2964, 2918, 2857, 1932, 1610, 1511, 1376, 832 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 7.6 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 2H), 6.85 (s, 2H), 6.71 (d, *J* = 6.8 Hz, 1H), 6.32 (d, *J* = 6.8 Hz, 1H), 2.35 (s, 6H), 2.32 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.8, 136.63, 136.59, 136.4, 131.5, 129.3, 129.1, 128.1, 126.9, 95.2, 93.7, 21.3, 21.2, 20.9; HRMS (EI) calcd for $C_{19}H_{20}$ M$^+$ 248.1565, found 248.1561.

*2-(3-(4-Methoxyphenyl)propa-1,2-dienyl)-1,3,5-trimethylbenzene (**3db**)*: pale yellow oil (25.9 mg, 49%); IR (film) 2956, 2922, 2853, 1932, 1607, 1509, 1376, 834 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.7 Hz, 2H), 6.94−6.89 (m, 4H), 6.76 (d, *J* = 6.8 Hz, 1H), 6.36 (d, *J* = 6.8 Hz, 1H), 3.85 (s, 3H), 2.41 (s, 6H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 158.7, 136.6, 136.4, 129.1, 128.2, 128.0, 126.8, 114.1, 94.8, 93.7, 55.3, 21.3, 20.9; HRMS (EI) calcd for $C_{19}H_{20}O$ M$^+$ 264.1514, found 264.1513.

*2-(3-(4-Fluorophenyl)propa-1,2-dienyl)-1,3,5-trimethylbenzene (**3eb**)*: pale yellow oil (34.8 mg, 69%); IR (film) 2969, 2916, 2857, 1933, 1603, 1498, 1376, 837 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.2, 5.7 Hz, 2H), 7.00 (t, *J* = 8.6 Hz, 2H), 6.87 (s, 2H), 6.73 (d, *J* = 6.8 Hz, 1H), 6.32 (d, *J* = 6.8 Hz, 1H), 2.35 (s, 6H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.8, 163.2, 160.7, 136.7, 130.53, 130.50, 129.2, 128.4, 128.3, 127.9, 115.7, 115.5, 94.5, 94.0, 21.3, 20.9; HRMS (EI) calcd for $C_{18}H_{17}F$ M$^+$ 252.1314, found 252.1313.

*1-(3-(4-Bromophenyl)propa-1,2-dienyl)-2,4-dimethylbenzene (**3fa**) and 2-(3-(4-Bromophenyl)propa-1,2-dienyl)-1,3-dimethylbenzene (**3fa′**)*. The crude product was purified by flash chromatography (petroleum ether) to give the product in a ratio of approximately 1.0:0.53 according to ^{1}H NMR: pale yellow oil, 31.7 mg, 53%; IR(film) 3015, 2976, 2919, 2851, 1933, 1621, 1496, 1378, 833 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.38 (m, 3.06H), 7.23 (s, 1.06H), 7.22−7.14 (m, 3H), 7.04 (s, 1.53H), 6.98 (s, 1H), 6.94 (d, *J* = 7.8 Hz, 1.06H), 6.74 (d, *J* = 6.6 Hz, 1.53H), 6.46 (d, *J* = 6.6 Hz, 1H of **3fa**), 6.29 (d, *J* = 6.8 Hz, 0.53H of **3fa′**), 2.37 (s, 3.18H of **3fa′**), 2.35 (s, 3H of **3fa**), 2.29 (s, 3H of **3fa**); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.3, 208.1, 137.2, 136.7, 135.3, 133.4, 133.1, 131.8, 131.7, 131.5, 130.6, 128.5, 128.4, 127.6, 127.0, 120.8, 120.6, 96.7, 96.2, 94.6, 94.2, 21.4, 21.1, 19.9; HRMS (EI) calcd for $C_{17}H_{15}Br$ M$^+$ 298.0357, found 298.0359.

*2-(3-(4-Bromophenyl)propa-1,2-dienyl)-1,3,5-trimethylbenzene (**3fb**)*: pale yellow oil (31.9 mg, 51%); IR (film) 2970, 2917, 2854, 1933, 1610, 1496, 1377, 831 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 6.87 (s, 2H), 6.73 (d, *J* = 6.8 Hz, 1H), 6.29 (d, *J* = 6.8 Hz, 1H), 2.34 (s, 6H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.1, 136.7, 136.6, 133.6, 131.7, 129.2, 128.4, 127.5, 120.5, 94.6, 94.1, 21.3, 20.9; HRMS (EI) calcd for $C_{18}H_{17}Br$ M$^+$ 312.0514, found 312.0514.

*2-(3-(4-Bromophenyl)propa-1,2-dienyl)-1,4-dimethylbenzene (**3fc**)*: pale yellow oil (35.9 mg, 60%); IR (film) 3019, 2922, 2857, 1934, 1589, 1502, 1380, 814 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.16 (s, 1H), 7.06 (d, *J* = 7.7 Hz, 1H), 6.95 (d, *J* = 7.7 Hz, 1H), 6.75 (d, *J* = 6.6 Hz, 1H), 6.48 (d, *J* = 6.6 Hz, 1H), 2.36 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4, 135.7, 133.0, 132.4, 131.8, 131.1, 130.6, 128.4, 128.3, 128.0, 120.8, 96.7, 96.3, 20.9, 19.5; HRMS (EI) calcd for $C_{17}H_{15}Br$ M$^+$ 298.0357, found 298.0360.

*4-(3-(3-(4-Bromophenyl)propa-1,2-dienyl)-2,4,6-trimethylphenyl)butan-2-one (**3ff**)*: pale yellow oil (44.5 mg, 58%); IR (film) 2970, 2920, 1940, 1694, 1486, 1360, 833 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.4 Hz, 2H), 7.19 (d, *J* = 7.4 Hz, 2H), 6.88 (s, 1H), 6.67 (d, *J* = 6.7 Hz, 1H), 6.26 (d, *J* = 6.7 Hz, 1H), 2.91 (t, *J* = 8.0 Hz, 2H), 2.55 (t, *J* = 8.0 Hz, 2H), 2.33 (s, 3H), 2.31 (s, 3H), 2.27 (s, 3H), 2.16 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.1, 207.5, 135.6, 135.1, 134.5, 134.4, 133.3, 131.7, 130.3, 129.3, 128.5, 120.6, 94.7, 94.3, 43.0, 29.8, 23.9, 21.2, 19.9, 16.9; HRMS (EI) calcd for $C_{22}H_{23}BrO$ M$^+$ 382.0932, found 382.0926.

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*2-(3-(3-(4-Bromophenyl)propa-1,2-dienyl)-2,4,6-trimethylphenyl)acetonitrile (**3fg**):* pale yellow oil (23.3 mg, 33%); IR (film) 2922, 2853, 2247, 1940, 1587, 1497, 1378, 833 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 6.95 (s, 1H), 6.66 (d, J = 6.8 Hz, 1H), 6.29 (d, J = 6.8 Hz, 1H), 3.64 (s, 2H), 2.43 (s, 3H), 2.35 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 207.5, 136.7, 135.4, 135.1, 132.9, 131.7, 130.6, 130.0, 128.5, 125.7, 120.8, 117.4, 94.6, 94.3, 21.3, 20.1, 18.2, 17.4; HRMS (EI) calcd for $C_{20}H_{18}BrN$ M^+ 351.0623, found 351.0618.

*4,4′-(2-(3-(4-Bromophenyl)propa-1,2-dienyl)-1,4-phenylene)-dibutan-2-one (**3fh**):* pale yellow oil (48.4 mg, 59%); IR (film) 3004, 2924, 2848, 1935, 1707, 1609, 1486, 1363, 834 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 7.16 (s, 1H), 7.09 (d, J = 7.8 Hz, 1H), 7.00 (d, J = 7.8 Hz, 1H), 6.75 (d, J = 6.6 Hz, 1H), 6.50 (d, J = 6.6 Hz, 1H), 3.06−2.89 (m, 2H), 2.85−2.78 (m, 2H), 2.74−2.67 (m, 4H), 2.11 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.5, 207.7, 207.5, 139.5, 136.2, 132.7, 131.9, 130.9, 130.1, 128.4, 128.0, 127.8, 121.0, 96.9, 95.9, 45.0, 44.6, 30.0, 29.9, 29.1, 26.9; HRMS (EI) calcd for $C_{23}H_{23}BrO_2$ M^+ 410.0881, found 410.0865.

*2-(3-(4-Iodophenyl)buta-1,2-dienyl)-1,3,5-trimethylbenzene (**3gb**):* pale yellow oil (61.3 mg, 82%); IR (film) 2944, 2917, 2854, 1935, 1610, 1489, 1375, 812 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 6.87 (s, 2H), 6.64 (q, J = 3.1 Hz, 1H), 2.33 (s, 6H), 2.26 (s, 3H), 2.14 (d, J = 3.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.2, 137.3, 136.9, 136.42, 136.37, 129.2, 128.2, 127.7, 100.0, 92.3, 91.8, 21.3, 20.9, 17.0; HRMS (EI) calcd for $C_{19}H_{19}I$ M^+ 374.0531, found 374.0529.

*1,3,5-Trimethyl-2-(3-phenylbuta-1,2-dienyl)benzene (**3hb**):* pale yellow oil (44.6 mg, 90%); IR (film) 2920, 2856, 1934, 1609, 1375, 852 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.7 Hz, 2H), 7.30 (t, J = 7.7 Hz, 2H), 7.18 (t, J = 7.3 Hz, 1H), 6.85 (s, 2H), 6.63 (q, J = 3.1 Hz, 1H), 2.34 (s, 6H), 2.25 (s, 3H), 2.18 (d, J = 3.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.3, 137.1, 136.4, 136.2, 129.2, 128.6, 128.3, 126.5, 125.9, 100.6, 91.9, 21.3, 20.9, 17.2; HRMS (EI) calcd for $C_{19}H_{20}$ M^+ 248.1565, found 248.1560.

*1,2,4,5-Tetramethyl-3-(3-phenylbuta-1,2-dienyl)benzene (**3hd**):* pale yellow oil (41.9 mg, 80%); IR (film) 2921, 2862, 1940, 1597, 1493, 1463, 1380 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.6 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.18 (t, J = 7.3 Hz, 1H), 6.89 (s, 1H), 6.57 (q, J = 3.1 Hz, 1H), 2.29 (s, 6H), 2.23 (s, 6H), 2.18 (d, J = 3.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.3, 137.1, 133.7, 132.6, 132.3, 130.3, 128.2, 126.5, 125.9, 100.1, 92.9, 20.4, 16.9, 16.6; HRMS (EI) calcd for $C_{20}H_{22}$ M^+ 262.1722, found 262.1716.

*1,2,3,4,5-Pentamethyl-6-(3-phenylbuta-1,2-dienyl)benzene (**3he**):* pale yellow oil (45.8 mg, 83%); IR (film) 3032, 2982, 2922, 1943, 1597, 1493, 1378 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.6 Hz, 2H), 7.29 (t, J = 7.6 Hz, 2H), 7.17 (t, J = 7.3 Hz, 1H), 6.56 (q, J = 3.1 Hz, 1H), 2.36 (s, 6H), 2.23 (s, 3H), 2.22 (s, 6H), 2.16 (d, J = 3.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.0, 137.2, 133.7, 132.5, 131.9, 130.4, 128.2, 126.4, 125.9, 100.0, 93.5, 18.1, 16.8, 16.7, 16.5; HRMS (EI) calcd for $C_{21}H_{24}$ M^+ 276.1878, found 276.1868.

*2-(3,3-Diphenylpropa-1,2-dienyl)-1,3,5-trimethylbenzene (**3ib**):* pale yellow oil (55.8 mg, 90%); IR (film) 3022, 2916, 2856, 1931, 1597, 1490, 1376, 853 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 7.2 Hz, 4H), 7.32 (t, J = 7.5 Hz, 4H), 7.25 (t, J = 7.1 Hz,2H), 6.90 (s, 1H), 6.85 (s, 2H), 2.28 (s, 6H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.6, 136.9, 136.8, 136.5, 129.2, 128.5, 128.4, 128.2, 127.1, 110.0, 93.0, 21.3, 20.9; HRMS (EI) calcd for $C_{24}H_{22}$ M^+ 310.1722, found 310.1727.

*2-(1,3-Diphenylpropa-1,2-dienyl)-1,3,5-trimethylbenzene (**3jb**):* pale yellow oil (53.9 mg, 87%); IR (film) 3080, 3059, 3026, 2918, 2855, 1933, 1609, 1596, 1489, 1446, 1376, 850, 766, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 7.2 Hz, 2H), 7.33−7.16 (m, 8H), 6.94 (s, 2H), 6.58 (s, 1H), 2.31 (s, 3H), 2.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.0, 137.2, 137.0, 135.6, 134.2, 131.7, 128.8, 128.7, 128.5, 127.22, 127.20, 126.2, 109.5, 97.1, 21.1, 20.6; HRMS (EI) calcd for $C_{24}H_{22}$ M^+ 310.1722, found 310.1720.

*1,3,5-Trimethyl-2-(1-phenylundeca-1,2-dien-3-yl)benzene (**3kb**):* colorless oil (60.2 mg, 87%); IR (film) 3030, 2950, 2924, 2854, 1946, 1610, 1599, 1496, 1458, 816, 745, 693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34−7.29 (m, 2H), 7.26 (t, J = 7.6 Hz, 2H), 7.14 (t, J = 7.6 Hz, 1H), 6.86 (s, 2H), 6.18 (t, J = 3.5 Hz, 1H), 2.35 (s, 6H), 2.31−2.26 (m, 1H), 2.24 (s, 3H), 2.22−2.14 (m, 1H), 1.62−1.54 (m, 2H), 1.41−1.34 (m, 2H), 1.28−1.20 (m, 8H), 0.85 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.6, 136.4, 135.5, 134.7, 128.6, 128.4, 126.9, 126.6, 107.9, 95.0, 33.8, 31.9, 29.7, 29.6, 29.4, 27.8, 22.7, 21.0, 20.4, 14.2; HRMS (EI) calcd for $C_{26}H_{34}$ M^+ 346.2661, found 346.2667.

*2-(1-Cyclopropyl-3-phenylpropa-1,2-dienyl)-1,3,5-trimethylbenzene (**3lb**):* pale yellow oil (44.9 mg, 82%); IR (film) 3082, 3005, 2917, 2856, 1942, 1610, 1594, 1495, 1457, 816, 746, 693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32−7.23 (m, 4H), 7.18−7.12 (m, 1H), 6.87 (s, 2H), 6.22 (s, 1H), 2.38 (s, 6H), 2.25 (s, 3H), 1.41−1.37 (m, 1H), 0.85−0.70 (m, 2H), 0.59−0.45 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.8, 136.7, 136.1, 135.3, 133.3, 128.6, 128.4, 126.9, 126.7, 100.3, 95.9, 21.0, 20.7, 13.4, 7.5, 7.4; HRMS (EI) calcd for $C_{21}H_{22}$ M^+ 274.1722, found 274.1718.

*2-(1-Cyclopropyl-3-phenylbuta-1,2-dienyl)-1,3,5-trimethylbenzene (**3mb**):* colorless oil (42.0 mg, 73%); IR (film) 3081, 3000, 2972, 2946, 2917, 2857, 1941, 1610, 1958, 1493, 1443, 1373, 848, 760, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43−7.37 (m, 2H), 7.29 (t, J = 7.7 Hz, 2H), 7.16 (t, J = 7.7 Hz, 1H), 6.87 (s, 2H), 2.38 (s, 6H), 2.25 (s, 3H), 2.10 (s, 3H), 1.39−1.35 (m, 1H), 0.81−0.71 (m, 2H), 0.58−0.41(m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.7, 138.0, 136.4, 136.2, 134.0, 128.3, 128.2, 126.4, 125.9, 108.1, 102.1, 21.0, 20.9, 17.0, 13.7, 7.6, 7.1; HRMS (EI) calcd for $C_{22}H_{24}$ M^+ 288.1878, found 288.1874.

*1,3,5-Trimethyl-2-(3-(4-(phenylethynyl)phenyl)buta-1,2-dienyl)-benzene (**3pb**):* pale yellow oil (45.9 mg, 66%); IR (film) 3032, 2968, 2857, 2214, 1934, 1595, 1507, 1374, 840 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 5.6 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 7.40 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 5.4 Hz, 3H), 6.86 (s, 2H), 6.67 (s, 1H), 2.34 (s, 6H), 2.26 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.8, 137.2, 136.5, 136.4, 131.6, 129.2, 128.3, 128.1, 125.8, 123.4, 121.2, 100.5, 92.2, 89.7, 89.6, 21.3, 20.9, 17.1; HRMS (EI) calcd for $C_{27}H_{24}$ M^+ 348.1878, found 348.1876.

*1,4-Bis(3-mesitylpropa-1,2-dienyl)benzene (**3qb**):* white solid (43.7 mg, 56%); mp 59−61 °C; IR (film) 3011, 2967, 2917, 2854, 1932, 1610, 1508, 1497, 1376, 850 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 4H), 6.86 (s, 4H), 6.73 (d, J = 6.7 Hz, 2H), 6.33 (d, J = 6.7 Hz, 2H), 2.35 (s, 12H), 2.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.3, 136.6, 136.5, 133.1, 129.2, 127.9, 127.2, 95.2, 93.8, 21.3, 20.9; HRMS (EI) calcd for $C_{30}H_{30}$ M^+ 390.2348, found 390.2351.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra for propargylic alcohols and allenes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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