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Note

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Synthesis of Terminal Allenes via a Copper-Catalyzed Decarboxylative Coupling Reaction of Alkynyl Carboxylic Acids

Jeongah Lim,† *Jinseop Choi,*† *Han-Sung Kim,*† *In Seon Kim,*‡ *Kye Chun Nam,*†
Jimin Kim,†* *Sunwoo Lee*†*

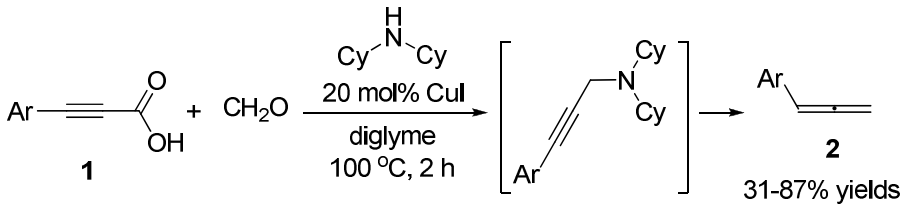
†Department of Chemistry, Chonnam National University, Gwangju, 61186, Republic of Korea
‡Department of Agricultural Chemistry, College of Agriculture and Life Sciences, Chonnam National University, Gwangju, 61186, Republic of Korea

Corresponding Author: J. Kim (jiminkim@chonnam.ac.kr), S. Lee (sunwoo@chonnam.ac.kr)

Keywords: allene, copper, propargyl amine, decarboxylative coupling, propiolic acids

Abstract

Synthesis of terminal allenes via a copper-catalyzed decarboxylative coupling reaction was developed. Aryl alkynyl carboxylic acid, paraformaldehyde, and dicyclohexylamine were reacted with CuI (20 mol%) in diglyme at 100 °C for 2 h to produce the terminal allene in moderate to good yields. The method showed good functional group tolerance.



Allene is one of the most versatile compounds and intermediates in organic synthesis because it has high reactivity and a unique structural feature in which one carbon atom has two double bonds.[1] Allene structures are also found in nature, as shown in Figure 1.[2]

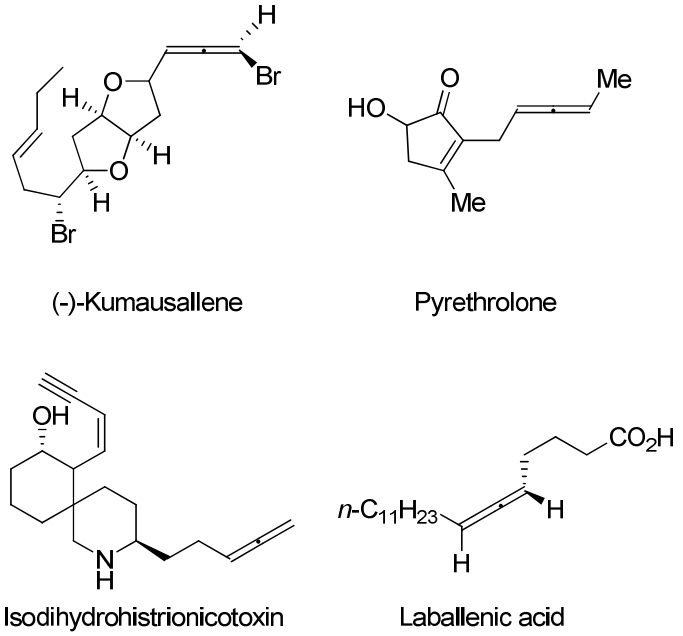
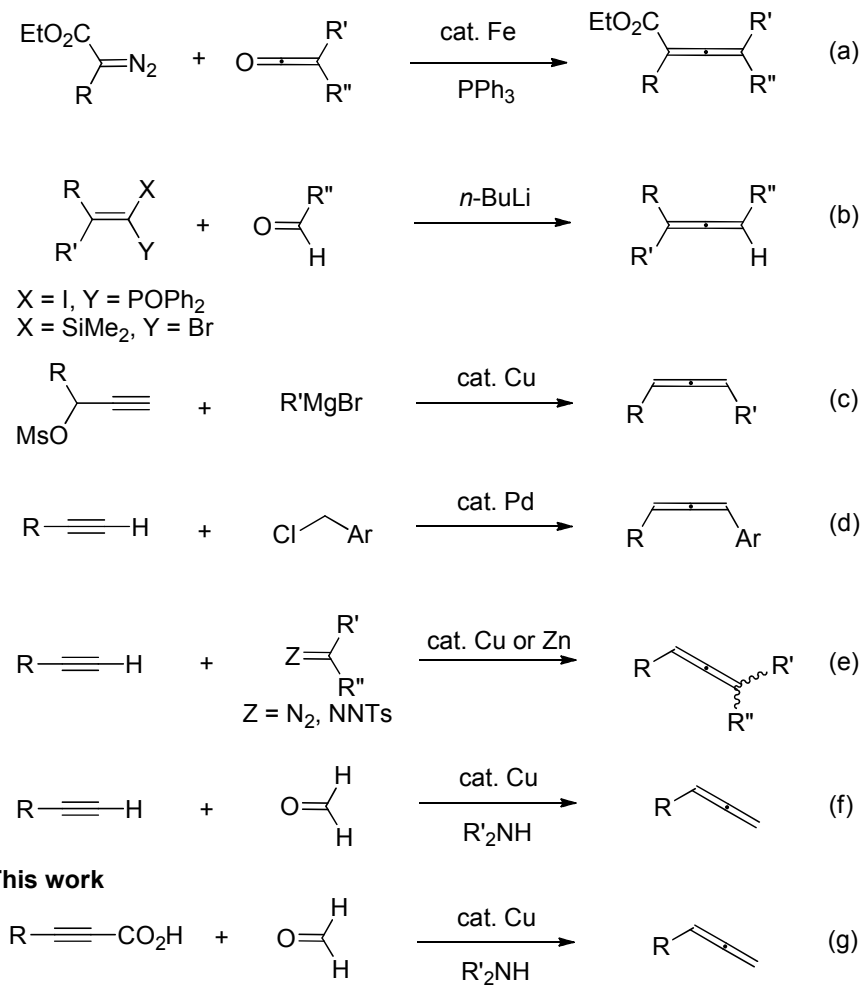


Figure 1. Natural compounds bearing an allene group.

In addition, an allene can be converted to many useful building blocks for the synthesis of pharmaceutical compounds.[3] A number of synthetic methods have been developed.[4] Both classic and recently developed methods are shown in Scheme 1. Tang and Zhou reported that the iron-catalyzed reaction of an α-diazoester and a ketene afforded the allene in the presence of PPh_3 under neutral conditions (Scheme 1a).[5] Also, the reaction of an aldehyde with an activated vinyl halide in the presence of BuLi to afford the corresponding allene has been reported (Scheme 1b).[6] Copper-mediated S_N2'-substitution of propargyl electrophile has been developed (Scheme 1c).[7] Buchwald reported the palladium-catalyzed coupling of a terminal alkyne and benzyl chloride to afford the allene in good yield (Scheme 1d).[8] In the presence of a copper or zinc catalyst, the terminal alkyne was reacted with a diazoester or an *N*-

tosylhydrazone to form 1,3-disubstituted allene (Scheme 1e).[9] In 1979, Crabbé reported that the coupling of a terminal alkyne and paraformaldehyde in the presence of a copper catalyst and a secondary amine afforded the terminal allene(Scheme 1f).[10]. This process was named the Crabbé homologation reaction, has been regarded as a useful synthetic tool along a Cu(I) catalyzed SN_2' substitution of propargylic electrophiles with Grignard reagents in the construction of allenyl functionalities. Also, this reaction method has been employed for the synthesis of chiral allenes.[11]

A variety of transition metal-catalyzed decarboxylative coupling reaction of propiolic acids have been developed since our first report in 2008.[12] Recently, we reported that propargyl amine can be obtained from the coupling of propiolic acid derivatives, paraformaldehyde, and amines under metal-free conditions.[13] Moreover, the employment of a copper catalyst enabled the application of this methodology to the synthesis of propargyl amines via coupling with aryl or alkyl aldehydes.[14] During this study, we found that the allene was formed as a side-product in some cases. This result inspired us to develop a synthetic method for the allene via decarboxylative coupling of propiolic acids, because aryl propiolic acid derivatives are readily prepared from the coupling reaction of aryl halides and propiolic acid.[15] Herein, we report a copper-catalyzed decarboxylative coupling reaction for the synthesis of terminal allenes (Scheme 1g).

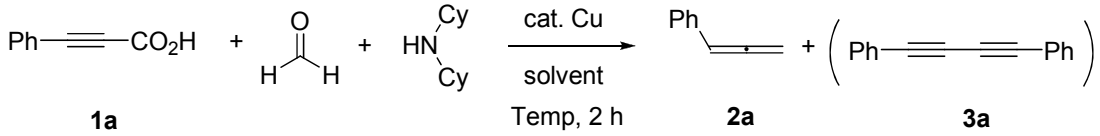


Scheme 1. Synthesis of allenes.

We chose phenyl propiolic acid as a standard substrate to optimize the reaction, and allowed it to react with paraformaldehyde and cyclohexylamine under a variety of conditions. The results are summarized in Table 1. First, we investigated the ratio of substrates. Increasing the amount of paraformaldehyde and cyclohexylamine increases the yield of the allene. However, the yield of the undesired homocoupled product remains unchanged. We found that a **1** to paraformaldehyde to dicyclohexylamine ratio of 1:3:3 is optimal (entry 3). Employing this ratio, the source of copper catalyst was investigated. CuBr decreases the yield of side-product;

however, the yield of **2a** is lower than that obtained with CuI (entry 4). Unfortunately, other copper catalysts such as Cu_2O, $Cu(OAc)_2$, and $Cu(OTf)_2$ afford the homocoupled species as the major product (entries 5-7). Instead of toluene, different solvents were investigated. Xylene affords **3a** in 30% yield (entry 8). However, DMSO and DMF give poor yields (entries 9 and 10). Reaction under monoglyme and diglyme affords **2a** in 57% and 77% yields, respectively (entries 11 and 12). The formation of the side-product is especially low in diglyme. Temperatures higher or lower than 100 °C do not give satisfactory results (entries 13 and 14). The employment of diisopropyl amine, which is most commonly used amine in the Crabbé reaction, affords **3a** in 45% yield (entry 15). Decreasing the amount of CuI to 5 mol% decreased the yield of **3a** to 32% (entry 16). When 20 mol% CuI is employed, **2a** is formed in 82% yield (entry 17). Consequently, the following are the optimized conditions: aryl alkynyl carboxylic acid (1.0 equiv), paraformaldehyde (3.0 equiv), and dicyclohexylamine (3.0 equiv) reacted with CuI (20 mol%) in diglyme at 100 °C for 2 h.

Table 1. Optimization of the synthesis of a terminal allene via a copper-catalyzed decarboxylative three-component reaction.[a]



1a **2a** **3a**

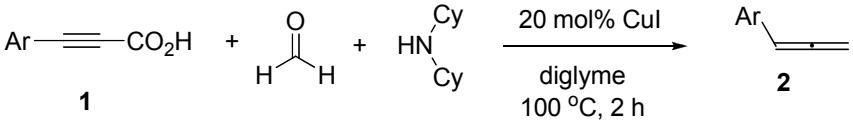
Entry	Ratio[b]	Cu/(mol%)	Solvent	Temperature (°C)	Yield (%)[c] **2a** (**3a**)
1	1/1.2/1.2	CuI (10)	toluene	100	27 (42)
2	1/1.5/1.5	CuI (10)	toluene	100	33 (39)
3	1/3/3	CuI (10)	toluene	100	40 (41)
4	1/3/3	CuBr (10)	toluene	100	32 (12)
5	1/3/3	Cu_2O (10)	toluene	100	5 (90)
6	1/3/3	$Cu(OAc)_2$ (10)	toluene	100	9 (63)
7	1/3/3	$Cu(OTf)_2$ (10)	toluene	100	15 (65)
8	1/3/3	CuI (10)	xylene	80	30 (51)
9	1/3/3	CuI (10)	DMSO	100	9 (3)
10	1/3/3	CuI (10)	DMF	100	9 (5)
11	1/3/3	CuI (10)	monoglyme	100	57 (12)

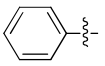
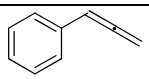
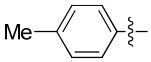
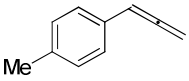
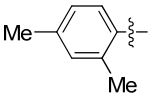
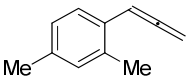
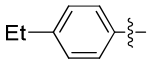
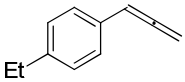
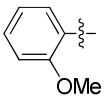
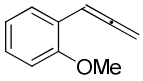
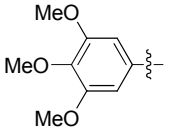
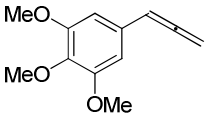
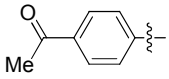
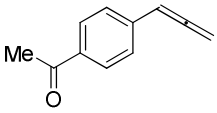
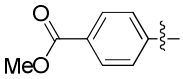
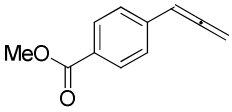
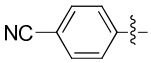
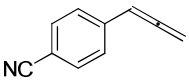
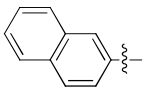
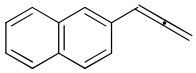
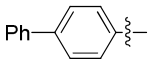
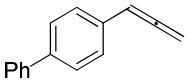
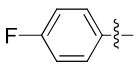
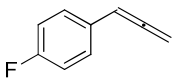
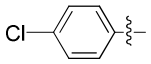
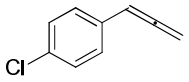
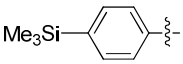
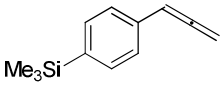
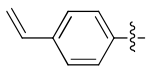
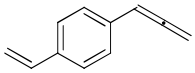
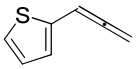
12	1/3/3	CuI (10)	diglyme	100	77 (6)
13	1/3/3	CuI (10)	diglyme	130	25 (2)
14	1/3/3	CuI (10)	diglyme	80	45 (36)
15[d]	1/3/3	CuI (10)	diglyme	100	45 (25)
16	1/3/3	CuI (5)	diglyme	100	32 (14)
17	1/3/3	CuI (20)	diglyme	100	82 (5)

[a]Reaction conditions: **1a** (0.3 mmol), paraformaldehyde (0.36, 0.45, 0.9 mmol), dicyclohexylamine (0.36, 0.45, 0.9 mmol), and Cu (0.015, 0.03, 0.06 mmol) were reacted for 2 h. [b]Ratio of **1a**/paraformaldehyde/dicyclohexylamine. [c]Yield obtained from GC analysis with standard substrate. [d]Instead of dicyclohexylamine, diisopropylamine was used.

To demonstrate the general applicability of this method for the synthesis of terminal allenes, various substituted aryl alkynyl carboxylic acids were investigated (Table 2). As expected, phenyl propiolic acid is smoothly converted into propa-1,2-dienylbenzene (**1a**) in 82% yield (entry 1).[16] Methyl or ethyl-substituted phenyl propiolic acids **1b**, **1c**, and **1d** afford corresponding terminal allenes in 77%, 65%, and 75% yields, respectively (entries 2-4). 2-Methoxy- and 3,4,5-trimethoxy-substituted phenyl propiolic acids are transformed to the corresponding allenes **2e** and **2f** in 62% and 87% yields, respectively (entries 5 and 6). Aryl alkynyl carboxylic acids bearing a ketone, an ester, or a cyano group show moderate yields (entries 7-9). 2-Naphthyl and 4-biphenyl propiolic acids afford corresponding allenes **2j** and **2k** in 62% and 84% yields, respectively (entries 10 and 11). 4-Fluoro and 4-chloro phenyl propiolic acids also give desired products **2l** and **2m**, respectively (entries 12 and 13). 4-(Trimethylsilyl)phenyl propiolic acid (**1n**) shows 51% yield of product (entry 14). Vinyl substituted phenyl and thiophenyl propiolic acid give the corresponding product **2o** and **2p**, with 32% and 31% yields, respectively (entries 15 and 16). However, the alkyl substituted propiolic acid such as 2-octynoic acid does not give the desired allene (entry 17).

Table 2. Synthesis of terminal allenes from aryl alkynyl carboxylic acids.

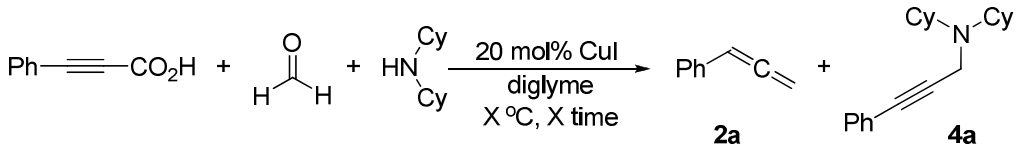


Entry	**1** (Ar =)		Product		Yield (%)
1		**1a**		**2a**	82
2		**1b**		**2b**	77
3		**1c**		**2c**	65
4		**1d**		**2d**	75
5		**1e**		**2e**	62
6		**1f**		**2f**	87
7		**1g**		**2g**	53
8		**1h**		**2h**	59
9		**1i**		**2i**	62
10		**1j**		**2j**	84
11		**1k**		**2k**	65
12		**1l**		**2l**	72
13		**1m**		**2m**	79
14		**1n**		**2n**	52
15		**1o**		**2o**	32
16		**1p**		**2p**	31

17	n-C_6H_{11}-	**1q**	n-C_6H_{11}	**2q**	0

[a]Reaction conditions: **1** (3.0 mmol), $(H_2CO)_n$ (9.0 mmol), Cy_2NH (9.0 mmol), and CuI (0.06 mmol) were reacted in diglyme at 100 °C for 2 h.

To investigate the reaction pathway, we monitored a reaction mixture of phenyl propiolic acid, paraformaldehyde, and dicyclohexylamine in the presence of CuI by gas chromatography using an internal standard. As shown in Figure 2, the terminal allene and three-component coupled propargyl amine are found in the reaction mixture. As the reaction proceeded, the yield of the allene increases. Propargyl amine **4a** (*N*-cyclohexyl-*N*-(3-phenylprop-2-ynyl)cyclohexanamine) is found in 24% yield at 30 min. The amount of propargyl amine slowly decreases proportionally as the amount of allene increases. We found that **3a** is formed in 81% yield in 30 min at 130 °C and slowly decomposes with time.



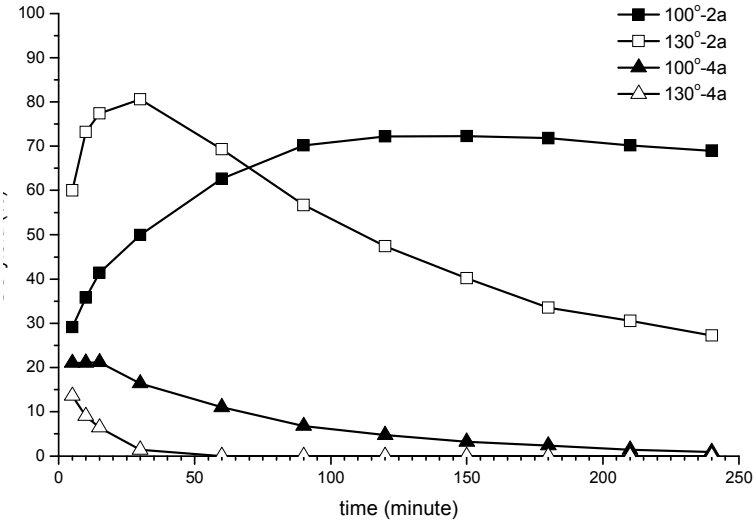
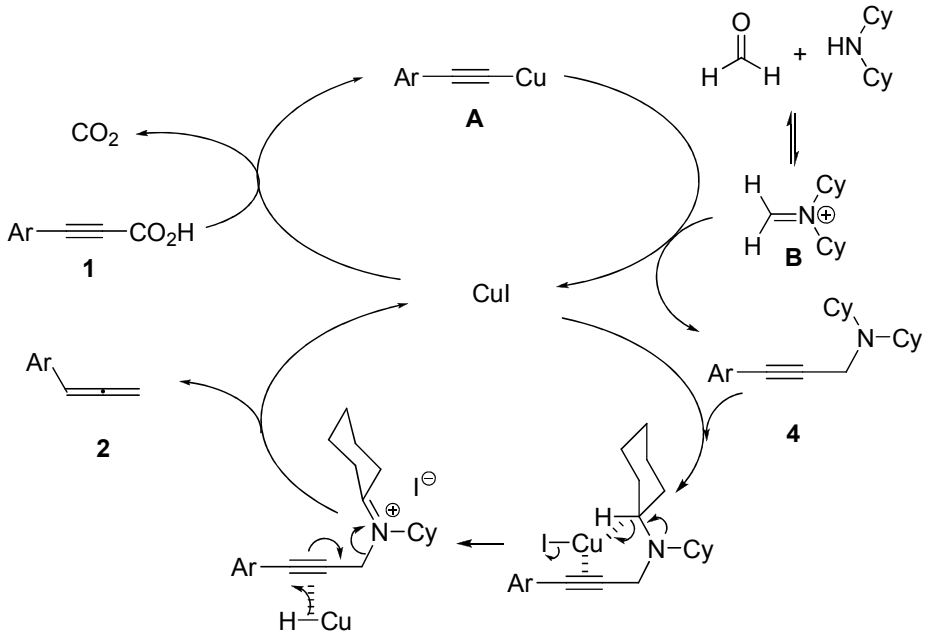


Figure 2. Reaction profile for the formation of terminal allene **2a** and intermediate **4a**.

It has been reported that the three-component reaction of aryl alkynyl carboxyl acid,

paraformaldehyde, and a secondary amine produced the corresponding propargyl amine via a copper-free decarboxylative coupling reaction. However, when the standard reaction is carried out in the absence of copper catalyst, neither propargyl amine nor allene is formed. In addition, it was found that propargyl amine is not converted to the allene in the absence of a copper catalyst. From these results, we infer that propargyl amine is an intermediate and is formed by the copper catalyst, and that the allene is also formed by the copper catalyst and is unstable over 130 °C. We propose the reaction pathway shown in Scheme 2. Aryl alkynyl carboxylic acid reacts with CuI to afford copper alkynide **A**. This copper complex reacts with imine intermediate **B**, which was formed by the reaction between paraformaldehyde and dicyclohexylamine, to form propargyl amine **4**. Propargyl amine is activated by the copper catalyst to give allene **2**.



Scheme 2. Proposed reaction pathway.

In summary, we have developed a synthesis of terminal allenes via decarboxylative coupling with aryl alkynyl carboxylic acid, paraformaldehyde, and dicyclohexylamine in the presence

of a copper catalyst. The optimized conditions converted the alkynyl carboxylic acid to the terminal allene in moderate to good yields. These reactions were completed in 2 h, and exhibited good functional group tolerance. We found that copper was vital for the formation of both propargylamine and terminal allene.

Experimental

All commercially available reagents were used without further purification unless otherwise stated. Thin layer chromatography was conducted on silica gel. Column chromatography was performed with silica gel (60-120 mesh). NMR spectra were recorded on a ^{1}H NMR (300, 500 MHz) and ^{13}C NMR (75, 126 MHz) spectra were recorded in DMSO-d_6 or $CDCl_3$. Chemical shifts are reported in ppm. Coupling constants (*J* values) are reported in Hertz.

General procedure for the preparation of aryl alkynyl carboxylic acids

Propiolic acid (3.6 mmol, 252 mg) was diluted with DMSO (3.0 mL). The solution was added to a mixture of $Pd(PPh_3)_4$ (0.25 mmol, 288.9 mg), aryl bromide (5.0 mmol), DBU (11.0 mmol, 1.67 g), and DMSO (7.0 mL) in a small round-bottom flask. The resulting mixture was stirred at 35 or 25 °C for 24 h, poured into ethyl acetate (25.0 mL), and extracted with saturated aqueous $NaHCO_3$ solution. The aqueous layer was separated, acidified to pH 2.0 by adding cold HCl (1 M), and extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, filtered, and the solvent was removed under reduced pressure.

3-(4-Vinylphenyl)propiolic acid (1o)

1-Bromo-4-vinylbenzene (915 mg, 5.0 mmol) provided **1o** (251 mg, 1.15 mmol, 32% yield, colorless oil); ^{1}H NMR (500 MHz, DMSO) δ 7.64–7.53 (m, 4H), 6.79 (dd, *J* = 17.7, 11.0 Hz, 1H), 5.97 (dd, *J* = 17.7, 0.8 Hz, 1H), 5.41 (dd, *J* = 10.9, 0.7 Hz, 1H); ^{13}C NMR (126 MHz, DMSO) δ 154.7, 139.9, 136.1, 133.4, 127.1, 118.5, 117.5, 84.9, 82.7; HRMS (ESI, TOF) calcd. for $C_{11}H_9O_2$ $[M+H]^+$ 173.0603 found, 173.0601.

General methods for the synthesis of allenes from aryl propiolic acids and aryl aldehydes with amines

Aryl alkynyl carboxylic acids (3.0 mmol), paraformaldehydes (9.0 mmol), dicyclohexylamines (9.0 mmol), CuI (0.06 mmol, 114 mg) and diglyme (10 mL) was charged in a 20 mL reaction vial. The mixture was stirred at 100 °C for 2 h. The reaction mixture was poured into water and extracted with Et_2O (3 × 20 mL). The combined extracts were dried over $MgSO_4$, and passed through a filter paper. The solvent was removed under vacuum, and the resulting crude product was purified by flash chromatography on silica gel. The product was eluted with pentane or Et_2O.

Propa-1,2-dienylbenzene (2a)[17]

Phenyl propiolic acid (438 mg, 3.0 mmol) was reacted with dicyclohexylamine (1.63 g, 9.0 mmol) and paraformaldehyde (270 mg, 9.0 mmol) to give (**2a**) (290 mg, 2.5 mmol, 82% yield, colorless oil); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29–7.28 (d, J = 4.5 Hz, 4H), 7.19 (m, 1H), 6.15 (t, J = 6.8 Hz, 1H), 5.12 (d, J = 6.9 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 209.7, 133.9, 128.6, 126.8, 126.6, 93.9, 78.7; EIMS (70 eV) m/z M^+ 116.

1-Methyl-4-(propa-1,2-dienyl)benzene(2b)[17]

3-*p*-Tolylpropiolic acid (481 mg, 3.0 mmol) was reacted with dicyclohexylamine (1.63 g, 9.0 mmol) and paraformaldehyde (270 mg, 9.0 mmol) to give (**2b**) (301 mg, 2.31 mmol) 77% yield, colorless oil); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19 (d, J = 7.8 Hz, 2H), 7.11 (d, J = 7.8 Hz, 2H), 6.13 (t, J = 6.6 Hz, 1H), 5.12 (d, J = 7.2 Hz, 2H), 2.32 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 209.5, 136.6, 130.8, 129.3, 126.5, 93.7, 78.7, 21.2; EIMS (70 eV) m/z M^+ 130.

2,4-Dimethyl-1-(propa-1,2-dienyl)benzene(2c)

3-(2,4-Dimethylphenyl)propiolic acid (523mg, 3.0 mmol) was reacted with dicyclohexylamine (1.63 g, 9.0 mmol) and paraformaldehyde 270 mg, 9.0 mmol) to give (**2c**) (281 mg, 1.95 mmol, 65% yield, colorless oil); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, J = 8.4 Hz, 1H), 6.98–6.96 (m, 2H), 6.31 (t, J = 6.9 Hz, 1H), 5.09 (d, J = 6.9 Hz, 2H), 2.31 (s, 3H), 2.29 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 210.2, 136.5, 134.7, 131.2, 129.0, 127.1, 126.9, 91.0, 77.9, 21.0, 19.7; HRMS (ESI, TOF) calcd. for $C_{11}H_{13}$ $[M+H]^+$ 145.1017, found 145.1017 HRMS (ESI, TOF) calcd. for $C_{11}H_{13}$ $[M+H]^+$ 145.1017, found 145.1015.

1-Ethyl-4-(propa-1,2-dienyl)benzene(2d)

3-(4-Ethylphenyl)propiolic acid (523 mg, 3.0 mmol) was reacted with dicyclohexylamine (1.63 g, 9.0 mmol) and paraformaldehyde (270 mg, 9.0 mmol) to give (**2d**) (324.5 mg, 2.25 mmol 75% yield, colorless oil); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (m, 2H), 7.13 (m, 2H), 6.14 (t, J = 6.9 Hz, 1H), 5.12 (d, J = 6.9 Hz, 2H), 2.62 (q, J = 7.5 Hz, 2H), 1.22 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 209.6, 143.1, 131.1, 128.1, 126.6, 93.7, 78.6, 28.6, 15.6; HRMS (ESI, TOF) calcd. for $C_{11}H_{13}$ $[M+H]^+$ 145.1017, found 145.1016.

1-Methoxy-2-(propa-1,2-dienyl)benzene(2e)[17]

3-(2-Methoxyphenyl)propiolic acid (529 mg, 3.0 mmol) was reacted with dicyclohexylamine (1.63 g, 9.0 mmol) and paraformaldehyde (270 mg, 9.0 mmol) to give (**2e**) (272 mg, 1.86 mmol, 62% yield, colorless oil); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (dd, J = 7.8, 1.5 Hz, 1H), 7.19 (td, J = 7.8, 1.5 Hz, 1H), 6.93 (td, J = 7.5, 0.8 Hz, 1H), 6.87 (d, J = 8.4 Hz, 1H), 6.59 (t, J = 6.9 Hz, 1H), 5.12 (d, J = 6.9 Hz, 2H), 3.85 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 210.1, 155.8, 127.9, 127.7, 122.3, 120.7, 110.9, 87.8, 78.0, 55.5; EIMS (70 eV) m/z M^+ 146.

1,2,3-Trimethoxy-5-(propa-1,2-dienyl)benzene(2f)[18]

3-(3,4,5-Trimethoxyphenyl)propiolic acid (709.7 mg, 3.0 mmol) was reacted with dicyclohexylamine (1.63 g, 9.0 mmol) and paraformaldehyde (270 mg, 9.0 mmol) to give (**2f**) (538.3 mg, 2.61 mmol, 87% yield, colorless oil); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.52 (s, 2H),

6.09 (t, J = 6.8 Hz, 1H), 5.16 (d, J = 6.6 Hz, 2H), 3.86 (s, 6H), 3.83 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 209.5, 153.4, 137.0, 129.4, 103.6, 94.1, 79.2, 60.9, 56.0; EIMS (70 eV) m/z M^+ 206.

1-(4-(Propa-1,2-dienyl)phenyl)ethanone(2g)[19]

3-(4-Acetylphenyl)propiolic acid (564.5 mg, 3.0 mmol) was reacted with dicyclohexylamine (1.63 g, 9.0 mmol) and paraformaldehyde (270 mg, 9.0 mmol) to give (**2g**) (252 mg, 1.6 mmol, 53% yield, colorless oil); ^1H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 6.21 (t, J = 6.8 Hz, 1H), 5.22 (d, J = 6.8 Hz, 2H), 2.59 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 210.7, 197.5, 139.2, 135.5, 128.7, 126.7, 93.6, 79.3, 26.6; EIMS (70 eV) m/z M^+ 158.

Methyl 4-(propa-1,2-dienyl)benzoate(2h)[9a]

3-(4-(Methoxycarbonyl)phenyl)propiolic acid (613 mg, 3.0 mmol) was reacted with dicyclohexylamine (1.63 g, 9.0 mmol) and paraformaldehyde (270 mg, 9.0 mmol) to give (**2h**) (308.3 mg, 1.77 mmol, 59% yield, colorless oil); ^1H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 6.21 (t, J = 6.8 Hz, 1H), 5.22 (d, J = 6.8 Hz, 2H), 2.59 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 210.6, 166.9, 138.9, 129.9, 128.4, 126.5, 93.6, 79.3, 52.1; EIMS (70 eV) m/z M^+ 174.

4-(Propa-1,2-dienyl)benzonitrile(2i)

3-(4-Cyanophenyl)propiolic acid (513.5 mg, 3.0 mmol) was reacted with dicyclohexylamine (1.63 g, 9.0 mmol) and paraformaldehyde (270 mg, 9.0 mmol) to give (**2i**) (262.6 mg, 1.86 mmol, 62% yield, colorless oil); ^1H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 6.18 (t, J = 6.8 Hz, 1H), 5.25 (d, J = 6.7 Hz, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 210.8, 139.2, 132.4, 127.1, 119.0, 110.1, 93.3, 79.8; HRMS (ESI, TOF) calcd. for $C_{10}H_8N$ $[M+H]^+$ 142.0657, found 142.0652.

2-(Propa-1,2-dienyl)naphthalene(2j)[9a]

3-(Naphthalen-2-yl)propiolic acid (588.6 mg, 3.0 mmol) was reacted with dicyclohexylamine (1.63 g, 9.0 mmol) and paraformaldehyde (270 mg, 9.0 mmol) to give (**2j**) (419 mg, 2.52 mmol, 84% yield, colorless oil); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (m, 1H), 7.85 (m, 1H), 7.74 (d, J = 8.1 Hz, 1H), 7.59 (d, J = 7.2 Hz, 1H), 7.55–7.39 (m, 3H), 6.86 (t, J = 6.9 Hz, 1H), 5.20 (d, J = 6.9 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 211.0, 133.9, 130.8, 130.1, 128.6, 127.4, 126.0, 125.7, 125.6, 125.3, 123.5, 90.4, 77.8; EIMS (70 eV) m/z M^+ 166.

4-(Propa-1,2-dienyl)biphenyl(2k)[9a]

3-(Biphenyl-4-yl)propiolic acid (666.7 mg, 3.0 mmol) was reacted with dicyclohexylamine (1.63 g, 9.0 mmol) and paraformaldehyde (270 mg, 9.0 mmol) to give (**2k**) (375 mg, 1.95 mmol, 65% yield, white solid); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64–7.53 (m, 4H), 7.49–7.31 (m, 5H), 6.23 (t, J = 6.8 Hz, 1H), 5.20 (d, J = 6.8 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 210.0, 140.8, 139.7, 132.9, 128.7, 127.3, 127.2, 127.1, 126.9, 93.6, 78.9; EIMS (70 eV) m/z M^+ 192.

1-Fluoro-4-(propa-1,2-dienyl)benzene(2l)[20]

3-(4-Fluorophenyl)propiolic acid (492.4 mg, 3.0 mmol) was reacted with dicyclohexylamine (1.63 g, 9.0 mmol) and paraformaldehyde (270.0 mg, 9.0 mmol) to give (**2l**) (185mg, 1.38 mmol, 46% yield, colorless oil); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (m, 2H), 6.98 (m, 2H), 6.13 (t, J = 6.9 Hz, 1H), 5.14 (d, J = 6.9 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 209.5 (d, $J_{C\text{-}F}$ = 2.3 Hz), 161.8 (d, $J_{C\text{-}F}$ = 245.9 Hz), 129.8 (d, $J_{C\text{-}F}$ = 3.3 Hz), 128.0 (d, $J_{C\text{-}F}$ = 8.0 Hz), 115.5 (d, $J_{C\text{-}F}$ = 21.7 Hz), 93.0 , 79.0; EIMS (70 eV) m/z M^+ 134.

1-Chloro-4-(propa-1,2-dienyl)benzene(2m)[20]

3-(4-Chlorophenyl)propiolic acid (541.8 mg, 3.0 mmol) was reacted with dicyclohexylamine (1.63 g, 9.0 mmol) and paraformaldehyde (270 mg, 9.0 mmol) to give (**2m**) (357 mg, 2.37 mmol, 79% yield, colorless oil); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.12 (m, 4H), 6.11 (t, J = 6.8 Hz, 1H), 5.15 (d, J = 6.8 Hz, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 209.8, 132.4,

132.40, 128.7, 127.8, 93.1, 79.2; EIMS (70 eV) m/z M^+ 150.

Trimethyl(4-(propa-1,2-dienyl)phenyl)silane (2n)

3-(4-(Trimethylsilyl)phenyl)propiolic acid (655 mg, 3.0 mmol) was reacted with dicyclohexylamine (1.63 g, 9.0 mmol) and paraformaldehyde (270mg, 9.0 mmol) to give (**2n**) (287 mg, 1.53 mmol, 51% yield, colorless oil); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 6.19 (t, *J* = 6.8 Hz, 1H), 5.17 (d, *J* = 6.8 Hz, 2H), 0.29 (s, 9H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 210.0, 139.0, 134.4, 133.6, 126.0, 94.0, 78.8, -1.1; HRMS (ESI, TOF) calcd. for $C_{12}H_{17}Si$ $[M+H]^+$ 189.1100, found 189.1130.

1-(Propa-1,2-dienyl)-4-vinylbenzene (2o)

3-(4-Vinylphenyl)propiolic acid (516 mg, 3.0 mmol) was reacted with dicyclohexylamine (1.63 g, 9.0 mmol) and paraformaldehyde (270 mg, 9.0 mmol) to give (**2o**) (171 mg, 1.2 mmol, 32% yield, colorless oil); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 6.69 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.15 (t, *J* = 6.8 Hz, 1H), 5.73 (d, *J* = 17.6 Hz, 1H), 5.21 (d, *J* = 10.9 Hz, 1H), 5.15 (d, *J* = 6.8 Hz, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 210.1, 136.6, 136.4, 133.6, 127.0, 126.6, 113.6, 93.9, 79.0; HRMS (ESI, TOF) calcd. for $C_{11}H_{11}$ $[M+H]^+$ 143.0861, found 143.0858.

2-(Propa-1,2-dienyl)thiophene (2p)

3-(Thiophen-2-yl)propiolic acid (456 mg, 3.0 mmol) was reacted with dicyclohexylamine (1.63 g, 9.0 mmol) and paraformaldehyde (270mg, 9.0 mmol) to give (**2p**) (113 mg, 0.93 mmol, 31% yield, colorless oil); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (d, *J* = 5.1 Hz, 1H), 6.94 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.90 (m, 1H), 6.39 (t, *J* = 6.8 Hz, 1H), 5.16 (d, *J* = 6.8 Hz, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 209.4, 137.9, 127.4, 124.7, 124.5, 88.5, 79.2; HRMS (ESI, TOF) calcd. for C_7H_7 $[M+H]^+$ 123.0268, found 123.0264.

***N*-cyclohexyl-*N*-(3-phenylprop-2-ynyl)cyclohexanamine (4a)**[21]

Phenyl propiolic acid (438 mg, 3.0 mmol) was reacted with dicyclohexylamine (1.63 g, 9.0

mmol) and paraformaldehyde (270 mg, 9.0 mmol) at 100 °C for 30 min to give (**4a**) (212 mg, 0.7 mmol 24% yield, colorless oil, 90% purity);^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (m, 2H), 7.33–7.23 (m, 3H), 3.70 (s, 2H), 2.82 (tt, *J* = 10.9, 3.2 Hz, 2H), 1.90 (d, *J* = 10.9 Hz, 4H), 1.79 (d, *J* = 12.3 Hz, 4H), 1.62 (m, 2H), 1.46–1.03 (m, 10H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 131.4, 128.2, 127.8, 123.7, 88.3, 84.0, 57.7, 35.6, 30.8, 26.9; EIMS (70 eV) m/z M^+ 295.

Author Information

Corresponding Author

E-mail : jiminkim@chonnam.ac.kr(J. Kim); sunwoo@chonnam.ac.kr (S. Lee).

Notes

The authors declare no competing financial interest.

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Copies of ^{1}H and ^{13}C{^{1}H} NMR spectra of products (**1n**, **1o**, **2a**-**2p** and **4a**)

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