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Synthesis of Allenes by Catalytic Coupling of Propargyl Carbonates with Aryl Iodides in the Presence of Diboron Species

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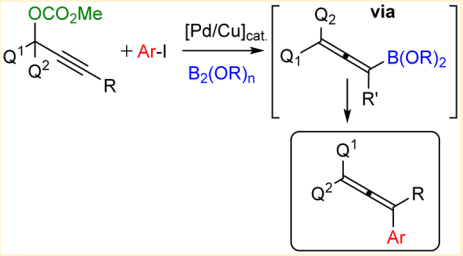
Supporting Information

ABSTRACT: Bimetallic copper-/palladium-catalyzed multicomponent reaction of propargyl carbonates, aryl iodides, and diboron species was studied. This procedure can be used for synthesis of di-, tri-, and tetra-substituted allenes. Using diboronic acid, the reaction is supposed to proceed via allenylboronic acid intermediate.



Allenes are important substrates in advanced organic synthesis[1−6] and in natural product synthesis.[7] Therefore, development of new methodology for allene synthesis from simple starting materials is an important area. Most of the reported synthetic methodology is based on transformation of propargyl alcohol derivatives or allenyl halides.[1−6] The groups of Sawamura,[8] Lalik,[9] and Molander[10] presented useful Suzuki−Miyaura type transformations of propargyl phosphates and carbonates with aryl and vinyl boronates.[11] Many of these processes are suitable for synthesis of enantioenriched allenes from chiral propargyl alcohol derivatives.[8] Burke and co-workers[12] employed Suzuki−Miyaura coupling of allenyl iodides with aryl boronates for synthesis of functionalized allenes. Many of these reactions also proceed with useful levels of chirality transfer, which could be exploited for natural product synthesis.[6]

In addition, many excellent catalytic transformations have been presented for allene synthesis.[13−21] These transformations are usually based on coupling reactions of propargyl substrates with organometallic reagents and reduction or rearrangement of the propargyl or allenyl substrates. Organoboron reagents, which are often used for synthesis of functionalized allenes,[8−10,12,15,21−24] are usually air-stable and fairly easy to purify. However, the synthesis of the organoboron reagents often requires a couple of additional synthetic steps involving reactive organometallic reagents.[25] Therefore, it would be desirable to develop multicomponent reactions, in which the in situ formed organoboronates would directly react forming allenyl products.

Recently, we have reported a new Pd/Cu bimetallic catalytic reaction for synthesis of allenyl boronates from propargyl carbonates and acetates.[21] We have now found that this reaction can easily be combined with the Suzuki−Miyaura coupling.[11,26] After optimization we have found that propargyl carbonate **1a** undergoes cross-coupling reaction with phenyl iodide **2a** with good yield in the presence of catalytic amounts of palladium (**3**) and copper (**4**) catalysts and base (**5**). An essential component of the coupling reaction is (commercially available) diboronic acid **6a** (Table 1, entry 1). When **6a** was replaced with the widely used B_2pin_2 **6b**, the yield was significantly dropped from 68% to 21% (entry 2). Without any diboron reagent (**6a**−**b**), product formation was not observed (entry 3). When palladium catalyst **3** was replaced by $Pd_2(dba)_3$ the yield was dropped to 39% (entry 4), while $Pd(PPh_3)_4$ was not efficient (entry 5). We could not observe any reaction without palladium catalyst **3** (entry 6). Replacement of CuCl with CuI slightly reduced the yield (entry 7). Again, we could not observe any reaction without copper catalyst (entry 8), indicating that both palladium and copper catalysts are necessary for the successful cross-coupling reaction affording **7**. We have also varied the applied base (**5**). However, changing of Na_2CO_3 to NaOMe, Cs_2CO_3, or Li_2CO_3 led to lowering of the yield by 20−30% (entries 9−11).

Change of the methyl-carbonate to ethyl-carbonate leaving group led to a slight decrease of the yield (entry 12). Phosphonate leaving group could also be used in the propargyl substrate, but the reaction proceeds with lower yield than with methyl carbonate (entry 13). However, propargyl acetate or alcohol could not be used as substrates (entry 14). We have found that the highest yield can be obtained when MeOH/toluene 4:1 mixture was used as solvent. Increase or descrease of the amount of MeOH led to decrease of the yield (entries 15−17). Under the applied conditions Ph-I substrate could not be replaced by Ph-Br.

With the optimized conditions in hand, we studied the synthetic scope of the reaction. First we studied the cross-coupling reactions of disubstiuted alkynes **1a**−**d**, which gave trisubstituted allenes **7a**−**j** (Table 2). The coupling reaction can easily be performed with propargyl carbonate **1a** and various aryl iodides **2a**−**d**. Aryl iodide with electron-withdrawing fluoro-substitutient **2b** (entry 2) gave higher yield than

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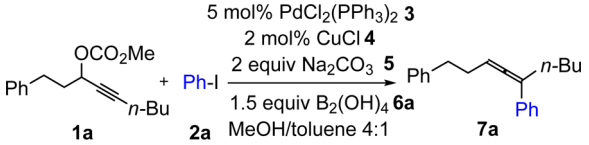
Table 1. Cross-Coupling of Propargyl Carbonate 1a with Phenyl Iodide 2a[a]



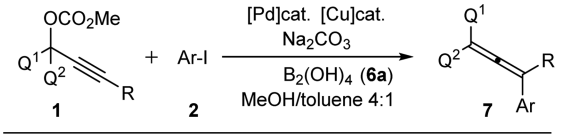
entry	deviation from the standard conditions	yield (%)
1	no change	68
2	$B_2(pin)_2$ instead of $B_2(OH)_4$	21
3	without $B_2(OH)_4$	NR
4	$Pd_2(dba)_3CHCl_3$&PPh_3 instead of $PdCl_2(PPh_3)_2$	39
5	$Pd(PPh_3)_4$ instead of $PdCl_2(PPh_3)_2$	0
6	without $PdCl_2(PPh_3)_2$	NR
7	CuI instead of CuCl	54
8	without CuCl	NR
9	NaOMe instead of Na_2CO_3	42
10	Cs_2CO_3 instead of Na_2CO_3	35
11	Li_2CO_3 instead of Na_2CO_3	47
12	$-OCO_2Et$ as LG instead of $-OCO_2Me$	52
13	$-OPO(OEt)_2$ as LG instead of $-OCO_2Me$	27
14	−OAc or −OH as LG instead of $-OCO_2Me$	<5
15	MeOH as solvent	42
16	MeOH/toluene 2:1 as solvent	39
17	MeOH/toluene 9:1 as solvent	58
18	Ph-Br instead of Ph-I	0

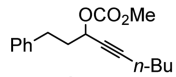
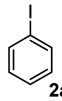
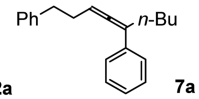
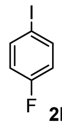
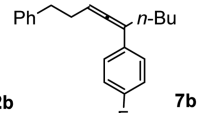
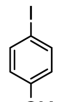
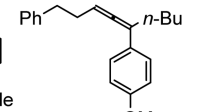
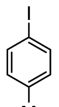
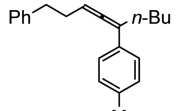
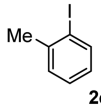
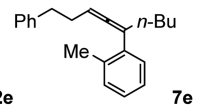
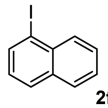
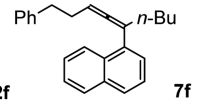
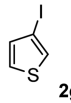
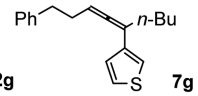
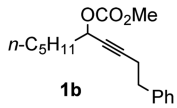
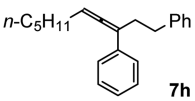
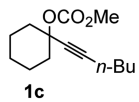
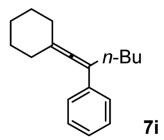
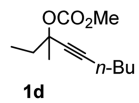
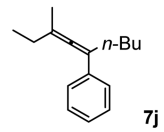
[a]Standard conditions (entry 1): **1a** (0.2 mmol), **2a** (0.3 mmol), **3** (0.01 mmol), **4** (0.004 mmol), **5** (0.4 mmol), and **6a** (0.3 mmol) were stirred in a mixture of MeOH (0.8 mL) and toluene (0.2 mL) under Ar at room temperature for 16 h.

methoxy-substituted substrate **2c** (entry 3). A slight decrease of the yield was observed, when *para*-methyl-substituted aryl iodide **2d** (entry 4) was replaced by the *ortho*-methyl-substituted **2e** (entry 5). Naphthyl- and thiophenyl-substituted (**2f**−**g**) substrates also reacted smoothly (entries 6−7) albeit with lower yield than the parent phenyl iodide **2a** (entry 1). Subsequently, we varied the propargyl carbonate substrate. Pentyl analogue of **1a** reacted with **2a** in a clean reaction resulting in **7h** (entry 8) with good yield. Trisubstitued propargyl substrates **1c**−**d** also underwent cross-coupling reaction with phenyl iodide resulting in tetrasubstituted allenes **7i**−**j** (entries 9−10).

In a previous study,[21] we have pointed out that catalytic borylation of terminal alkynes (such as **1e**-**h**) is much more challenging than the borylation of disubstituted alkynes (such as **1a**−**d**). The main reason is that the boronated product from terminal alkynes is highly instable,[21] and it may undergo various side reactions, in particular in the presence of palladium and coper catalysts. When we attempted the cross-coupling of **1e** with phenyl iodide (**2a**) under the same conditions as for disubstituted alkynes (**1a**-**d**, Table 2), a very complex mixture of products was obtained. We reasoned that the intermediate allenyl boronic acid (see below) can be unstable under the reactions conditions. Therefore, we replaced diboronic acid **6a** with B_2pin_2 **6b** to obtain a less reactive but more stable allenyl-Bpin derivative as reaction intermediate. Gratifyingly, the cross-coupling reaction of **1e** and **2a** in the presence of B_2pin_2 **6b** proceeded smoothly affording disubstituted allene **7k** (Table 3, entry 1).

Table 2. Tandem Borylation and Suzuki−Miyaura Coupling of Propargyl Carbonates with Aryl Iodides[a]



Entry	Propargyl substrates	Ar-I	Product	Yield(%)[b]
1				68
2	**1a**			77
3	**1a**			46
4	**1a**			66
5	**1a**			51
6	**1a**			45
7	**1a**			42
8		**2a**		54
9		**2a**		75
10		**2a**		62

[a]Conditions: **1** (0.2 mmol), **2** (0.3 mmol), **3** (0.01 mmol, 5 mol %), **4** (0.004 mmol, 2 mol %), **5** (0.4 mmol), and **6a** (0.3 mmol) were stirred in a mixture of MeOH (0.8 mL) and toluene (0.2 mL) at room temperature for 16 h. [b]Isolated yield.

Fluoro derivative **2b** was also readily reacted with **1e** (entry 2) similarly to propargyl substrate **1a** (Table 2, entry 2). The reaction could be extended to further terminal propargyl compounds as well. Compound **1f** reacted readily with **2a** affording **7m** (entry 3). Disubstituted terminal alkynes **1g** and **1h** also reacted with **2a** affording trisubstituted allenes **7n** and

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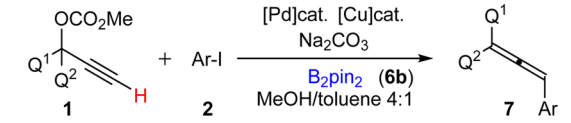
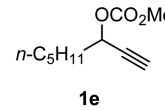
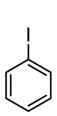
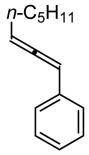
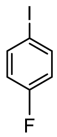
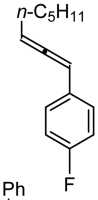
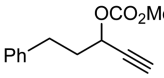
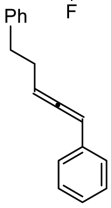
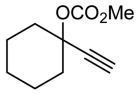
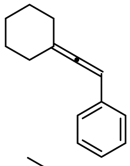
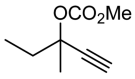
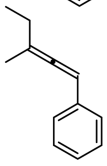
Table 3. Cross-Coupling Reactions with Terminal Alkyne Derivatives[a]



Entry	Propargyl substrates	Ar-I	Product	Yield(%)[b]
1	 **1e**	 **2a**	 **7k**	65
2	**1e**	 **2b**	 **7l**	55
3	 **1f**	**2a**	 **7m**	58
4	 **1g**	**2a**	 **7n**	43
5	 **1h**	**2a**	 **7o**	57

[a]Conditions: **1** (0.2 mmol), **2** (0.3 mmol), **3** (0.01 mmol, 5 mol %), **4** (0.004 mmol, 2 mol %), **5** (0.4 mmol), and **6b** (0.3 mmol) were stirred in a mixture of MeOH (1.6 mL) and toluene (0.4 mL) at 50 °C for 6 h. [b]Isolated yield.

7o (entries 4–5). Accordingly, by variation of the propargyl substrate, two different types of trisubstituted allenes can be synthesized. Using **1g–h** as substrates the aryl group is introduced to the C–H terminus of the allene in **7n–o**, while using **1a–b** the aryl group can be attached at the alkylated terminus, such as in **7a–h** (Table 2, entries 1–7).

Exploration of the exact mechanism of the cross-coupling reaction requires further studies. However, considering the previous papers on borylation of propargyl alcohol derivatives and the results of the above studies, at least a presumed mechansitic scheme can be given (Figure 1). We suggest that the first reaction is a copper-catalyzed borylation of the propargyl carbonate substrate **1**.[21,24] Sawamura and co-workers[24] have shown that this reaction can be performed using CuO^{t}Bu as catalyst. The active copper catalyst is probably formed in situ from CuCl, base, and MeOH under the above reaction conditions. After transmetalation with diboronate[27] **6** copper–boronate complex **8** is formed, which reacts with **1** to give the intermediate allenyl boron species **9**. The next step is a Suzuki–Miyaura coupling of **9** and **2**. In this process **2**

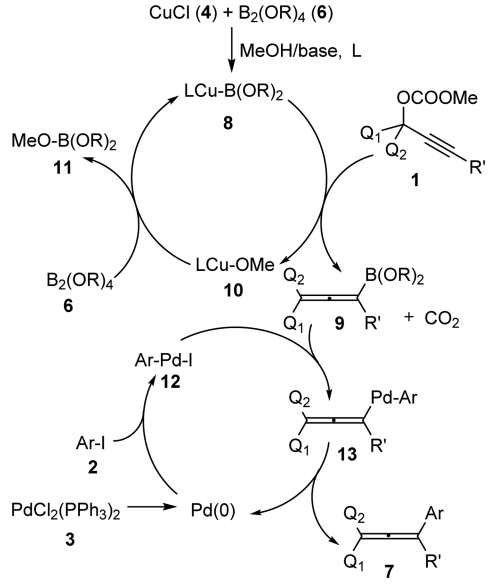


Figure 1. Suggested mechanism for the cross-coupling reaction.

undergoes oxidative addition with palladium (**12**) and then transmetalation with **9** to give **13**, which after reductive ellimination gives product **7**. Recent studies on synthesis of allenyl boron species[21,24] (such as **9**) from enantiomerically pure propargyl alcohol derivatives indicate that chirality transfer can be performed in these processes. This suggests that the above reaction can be used for synthesis of chiral allenes (such as **7**) from suitable propargyl alcohol derivatves.

Another alternative could be that the aryl halide undergoes to palladium-catalyzed formation of arylboronic acid, which subsequently react with **1**. However, according to our experiments under the applied reaction conditions, Ph-I **2a** failed to undergo borylation with diboronic acid **6a**.[28,29] In addition, the reaction did not proceed without copper catalysis (Table 1, entry 8). These findings indicate that palladium itself is not able to catalyze both the borylation and the Suzuki–Miyaura step of the reaction.

In case of using diboronic acid **6a** as reagent (Table 2), the allenyl boron species **9** is probably allenyl boronic acid (**9**, R = H). These species are supposed to be very instable and have not been reported in the literature yet. Our attempts to isolate allylboronic acids have also failed. An important consequence of the intermediary formation of allylboronic acids (**9**, R = H) is their (expectedly) higher reactivity[26] in Suzuki–Miyaura coupling than the corresponding allyl-Bpin compounds. In particular for tetrasubstituted allenyl boron species, such as **9**, the transmetalation of the Bpin functionality is expected to be much slower than the corresponding $B(OH)_2$ group. This would explain our finding that the overall reaction for these type of intermediates proceeded with higher yield using $B_2(OH)_4$ (**6a**) than with B_2pin_2 (**6b**) (cf. entries 1 and 2 in Table 1). For example, when **9a**[21] was reacted with **2a** under the reaction condition of one-pot reaction, a very poor (18%) yield of **7a** was obtained (Figure 2). The higher yield (68%) in case of the one-pot reaction (Table 2, entry 1) is probably due to intermediary formation of the allenyl boronic acid analog of **9a**.

In summary, we have shown that propargyl carbonates, aryl iodides and diboron species undergo a multicomponent coupling reaction to allenes. We suggest that the reaction

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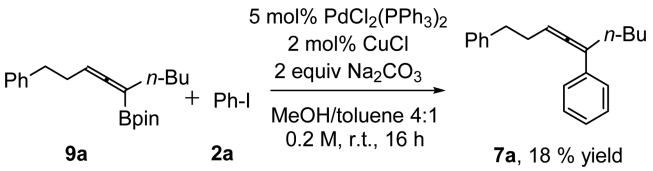

Figure 2. Reaction of **9a** with **2a** under the reaction conditions identical to the one-pot borylation-cross-coupling sequence (cf. entry 1, Table 1).

proceeds via allenyl boronic acid or allenyl-Bpin intermediates depending on the applied diboron reagent. The presented method extends the scope of allene synthesis using simple starting materials in the coupling reaction.

EXPERIMENTAL SECTION

All reactions were performed under argon unless otherwise stated. The solvents were dried before use by standard procedures. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a 400 MHz instrument. All ^{1}H NMR spectra are measured relative to the signals for residual $CHCl_3$ (7.26 ppm), and all ^{13}C NMR spectral data are reported relative to $CDCl_3$ (77.16 ppm). HRMS data were recorded on a micrOTOF instrument using ESI or APCI technique. All column chromatography was performed using silica gel (35−70 μm). Unless otherwise noted, commercially available chemicals were used as received.

General Procedure for Synthesis of Arylated allenes from Nonterminal Propargylic Carbonates 1a−d (General Method I). Inside a glovebox, a 8 mL screw top vial equipped with a Teflon-coated stirring bar was charged with CuCl (0.004 mmol), $PdCl_2(PPh_3)_2$ (0.01 mmol), Na_2CO_3 (0.4 mmol), $B_2(OH)_4$ (0.3 mmol), aromatic iodide (0.3 mmol), MeOH (0.8 mL), and toluene (0.2 mL). The mixture was prestirred for 10−15 s after which the nonterminal propargylic carbonate (0.2 mmol) was added to the mixture. The vial was then closed and stirred at room temperature for 16 h. After the reaction was finished, the content of the vial was washed out with pentane and concentrated under reduced pressure. The remaining content was purified by flash column chromatography.

*Nona-3,4-diene-1,5-diyldibenzene (**7a**).* Following general method I, **7a** was purified by flash column chromatography using pentane as eluent. The product was isolated as colorless oil (37.6 mg) in 68% yield. The spectral data are in agreement with the corresponding literature values:[8] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35−7.24 (m, 6H), 7.23−7.14 (m, 4H), 5.52 (ddt, J = 10.4, 3.2, 3.2 Hz, 1H), 2.80 (t, J = 7.4 Hz, 2H), 2.50−2.41 (m, 2H), 2.37 (dt, J = 7.3, 3.1 Hz, 2H), 1.52−1.34 (m, 4H), 0.93 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.1, 141.9, 137.5, 128.7, 128.5, 128.4, 126.4, 126.0, 125.9, 106.1, 93.7, 35.7, 31.1, 30.3, 29.8, 22.7, 14.6. HRMS (ESI): m/z calcd for $[C_{21}H_{24}Na]^+$ 299.1770, found 299.1769.

*1-Fluoro-4-(1-phenylnona-3,4-dien-5-yl)benzene (**7b**).* Following general method I, **7b** was purified by flash column chromatography using pentane as eluent. The product was isolated as colorless oil (45.2 mg) in 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31−7.27 (m, 2H), 7.25−7.18 (m, 5H), 6.99−6.91 (m, 2H), 5.51 (ddt, J = 10.4, 3.2, 2.8 Hz, 1H), 2.88−2.72 (m, 2H), 2.54−2.40 (m, 2H), 2.34 (dt, J = 7.2, 3.1 Hz, 2H), 1.50−1.34 (m, 4H), 0.93 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.8 (d, J = 1.9 Hz), 161.7 (d, J = 245.3 Hz), 141.8, 133.4 (d, J = 3.1 Hz), 128.6 (d, J = 24.2 Hz), 127.5, 127.4, 126.0, 115.1 (d, J = 21.4 Hz), 105.3, 93.9, 35.7, 31.1, 30.2, 29.9, 22.6, 14.1. HRMS (ESI): m/z calcd for $[C_{21}H_{23}FNa]^+$ 317.1676, found 317.1668.

*1-Methoxy-4-(1-phenylnona-3,4-dien-5-yl)benzene (**7c**).* Following general method I, **7c** was purified by flash column chromatography using pentane as eluent. The product was isolated as colorless oil (28.2 mg) in 46% yield. The spectral data are in agreement with the corresponding literature values:[8] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.27 (m, 2H), 7.25−7.20 (m, 5H), 6.86−6.80 (m, 2H), 5.51 (ddt, J = 10.4, 3.2, 3.0 Hz, 1H), 3.81 (s, 3H), 2.81 (dt, J = 7.4, 2.0 Hz, 2H), 2.51−2.40 (m, 2H), 2.35 (dt, J = 7.3, 3.0 Hz, 2H), 1.55−1.35 (m, 4H), 0.94 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.5, 158.4, 142.0, 129.8, 128.7, 128.4, 127.1, 126.0, 113.9, 105.6, 93.6, 55.4, 35.8, 31.2, 30.3, 29.9, 22.7, 14.2. HRMS (ESI): m/z calcd for $[C_{22}H_{26}ONa]^+$ 329.1876, found 329.1884.

*1-Methyl-4-(1-phenylnona-3,4-dien-5-yl)benzene (**7d**).* Following general method I, **7d** was purified by flash column chromatography using pentane as eluent. The product was isolated as colorless oil (38.3 mg) in 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33−7.27 (m, 2H), 7.25−7.17 (m, 5H), 7.13−7.07 (m, 2H), 5.51 (ddt, J = 10.0, 3.4, 2.8 Hz, 1H), 2.80 (t, J = 7.8 Hz, 2H), 2.49−2.41 (m, 2H), 2.36 (dt, J = 7.2, 2.8 Hz, 2H), 2.34 (s, 3H), 1.53−1.33 (m, 4H), 0.93 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.8, 141.9, 136.1, 134.5, 129.1, 128.7, 128.4, 126.0, 125.9, 105.9, 93.6, 35.8, 31.2, 30.3, 29.9, 22.7, 21.2, 14.2. HRMS (ESI): m/z calcd for $[C_{22}H_{26}Na]^+$ 313.1927, found 313.1922.

*1-Methyl-2-(1-phenylnona-3,4-dien-5-yl)benzene (**7e**).* Following general method I, **7e** was purified by flash column chromatography using pentane as eluent. The product was isolated as colorless oil (29.6 mg) in 51% yield. The spectral data are in agreement with the corresponding literature values:[8] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31−7.25 (m, 2H), 7.22−7.11 (m, 7H), 5.24 (ddt, J = 10.3, 3.4, 2.8 Hz, 1H), 2.80−2.70 (m, 2H), 2.42−2.34 (m, 2H), 2.33 (s, 3H), 2.30−2.22 (m, 2H), 1.45−1.30 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.6, 142.0, 138.6, 135.9, 130.5, 128.6, 128.4, 128.2, 126.7, 126.0, 125.8, 105.1, 90.9, 35.8, 33.9, 31.0, 30.1, 22.5, 20.5, 14.1. HRMS (ESI): m/z calcd for $[C_{22}H_{26}Na]^+$ 313.1927, found 313.1918.

*1-(1-Phenylnona-3,4-dien-5-yl)naphthalene (**7f**).* Following general method I, **7f** was purified by flash column chromatography using pentane as eluent. The product was isolated as a yellow oil (29.2 mg) in 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20−8.14 (m, 1H), 7.90−7.82 (m, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.51−7.42 (m, 3H), 7.37 (dd, J = 7.2, 1.2 Hz, 1H), 7.30−7.23 (m, 2H), 7.22−7.15 (m, 3H), 5.34 (ddt, J = 10.4, 3.4, 3.0 Hz, 1H), 2.83−2.70 (m, 2H), 2.46−2.37 (m, 4H), 1.50−1.34 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.3, 142.0, 137.3, 134.1, 131.5, 128.6, 128.5, 128.4, 127.3, 126.0, 125.8, 125.7, 125.5, 125.4, 104.4, 90.9, 35.8, 34.7, 31.0, 30.4, 22.6, 14.1. HRMS (ESI): m/z calcd for $[C_{25}H_{26}Na]^+$ 349.1927, found 349.1922.

*3-(1-Phenylnona-3,4-dien-5-yl)thiophene (**7g**).* Following general method I, **7g** was purified by flash column chromatography using pentane as eluent. The product was isolated as a pale yellow oil (23.6 mg) in 42% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.27 (m, 2H), 7.24−7.18 (m, 4H), 7.00−6.98 (m, 1H), 6.94 (dd, J = 5.0, 1.3 Hz, 1H), 5.49 (ddt, J = 10.2, 3.2, 2.8 Hz, 1H), 2.80 (dt, J = 7.1, 2.5 Hz, 2H), 2.50−2.40 (m, 2H), 2.34 (dt, J = 7.3, 3.1 Hz, 2H), 1.53−1.44 (m, 2H), 1.44−1.35 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.0, 141.9, 139.5, 128.7, 128.5, 127.1, 126.0, 125.1, 118.5, 102.6, 93.4, 35.7, 31.2, 30.5, 30.1, 22.7, 14.2. HRMS (ESI): m/z calcd for $[C_{19}H_{22}SNa]^+$ 305.1334, found 305.1344.

*Deca-3,4-diene-1,3-diyldibenzene (**7h**).* Following general method I, **7h** was purified by flash column chromatography using pentane as eluent. The product was isolated as colorless oil (31.3 mg) in 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47−7.45 (m, 2H), 7.37−7.28 (m, 4H), 7.28−7.19 (m, 4H), 5.54 (ddt, J = 10.4, 3.4, 3.0 Hz, 1H), 2.91−2.85 (m, 2H), 2.79−2.68 (m, 2H), 2.12−2.05 (m, 2H), 1.51−1.41 (m, 2H), 1.40−1.30 (m, 6H), 0.92 (t, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 204.0, 142.4, 137.5, 128.6, 128.5, 128.4, 126.5, 126.0, 126.0, 105.2, 95.3, 34.5, 32.0, 31.6, 29.2, 22.6, 14.2. HRMS (ESI): m/z calcd for $[C_{22}H_{26}Na]^+$ 313.1927, found 313.1930.

*(1-Cyclohexylidenehex-1-en-2-yl)benzene (**7i**).* Following general method I, **7i** was purified by flash column chromatography using pentane as eluent. The product was isolated as colorless oil (36.1 mg) in 75% yield. The spectral data are in agreement with the corresponding literature values:[30] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43−7.38 (m, 2H), 7.32−7.27 (m, 2H), 7.19−7.13 (m, 1H), 2.40 (t, J = 7.0 Hz, 2H), 2.26−2.18 (m, 4H), 1.74−1.64 (m, 4H), 1.64−1.55 (m, 2H), 1.55−1.48 (m, 2H), 1.47−1.35 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.3, 138.8, 128.3, 126.1, 126.0,

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105.8, 103.2, 31.7, 30.3, 29.9, 28.0, 26.4, 22.5, 14.2. HRMS (APCI/TOF-Q) m/z: $[M + H]^+$ calcd for $C_{18}H_{25}$ 241.1951, found 241.1958.

*(3-Methylnona-3,4-dien-5-yl)benzene (**7j**).* Following general method I, **7j** was purified by flash column chromatography using pentane as eluent. The product was isolated as colorless oil (26.5 mg) in 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43−7.38 (m, 2H), 7.34−7.27 (m, 2H), 7.20−7.15 (m, 1H), 2.42 (t, J = 7.3 Hz, 2H), 2.15−2.05 (m, 2H), 1.81 (s, 3H), 1.55−1.40 (m, 4H), 1.07 (t, J = 7.4 Hz, 3H), 0.95 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.1, 138.8, 128.3, 126.1, 126.0, 105.4, 104.6, 30.4, 30.1, 27.6, 22.7, 19.0, 14.2, 12.6. HRMS (APCI/TOF-Q) m/z: $[M + H]^+$ calcd for $C_{16}H_{23}$ 215.1794, found 215.1801.

General Method for Synthesis of Arylated allenes from terminal Propargylic Carbonates 1f−h (General Method II). Inside a glovebox, a 8 mL screw top vial equipped with a Teflon-coated stirring bar was charged with CuCl (0.004 mmol), $PdCl_2(PPh_3)_2$ (0.01 mmol), Na_2CO_3 (0.4 mmol), B_2pin_2 (0.3 mmol), armomatic iodide (0.3 mmol), MeOH (1.6 mL), and toluene (0.4 mL). The mixture was prestirred for 10−15 s after which the terminal propargylic carbonate (0.2 mmol) was added to the mixture. The vial was then closed, taken out of glovebox, and stirred at 50 °C for 6 h. After the reaction was finished, the content of the vial was washed out with pentane and concentrated under reduced pressure. The remaining content was purified by flash column chromatography.

*Octa-1,2-dien-1-ylbenzene (**7k**).* Following general method II, **7k** was purified by flash column chromatography using pentane as eluent. The product was isolated as colorless oil (24.2 mg) in 65% yield. The spectral data are in agreement with the corresponding literature values:[12] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.27 (m, 4H), 7.22−7.15 (m, 1H), 6.12 (dt, J = 6.4, 3.0 Hz, 1H), 5.57 (dd, J = 13.2, 6.6 Hz, 1H), 2.17−2.08 (m, 2H), 1.55−1.44 (m, 2H), 1.40−1.20 (m, 4H), 0.89 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.3, 135.3, 128.7, 126.7, 126.6, 95.3, 94.7, 31.5, 29.0, 28.9, 22.6, 14.2. HRMS (APCI/TOF-Q) m/z: $[M + H]^+$ calcd for $C_{14}H_{19}$ 187.1481, found 187.1490.

*Octa-1,2-dien-1-ylbenzene (**7l**).* Following general method II, **7l** was purified by flash column chromatography using pentane as eluent. The product was isolated as colorless oil (22.4 mg) in 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26−7.21 (m, 2H), 7.02−6.95 (m, 2H), 6.09 (dt, J = 6.4, 3.0 Hz, 1H), 5.56 (dd, J = 13.3, 6.6 Hz, 1H), 2.16−2.08 (m, 2H), 1.53−1.40 (m, 2H), 1.38−1.340 (m, 4H), 0.89 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.0 (d, J = 2.3 Hz), 161.9 (d, J = 245.2 Hz), 131.2 (d, J = 3.3 Hz), 128.1 (d, J = 8.0 Hz), 115.6 (d, J = 21.7 Hz), 95.5, 93.7, 31.5, 29.0, 28.9, 22.6, 14.2. HRMS (APCI/TOF-Q) m/z: $[M + H]^+$ calcd for $C_{14}H_{18}F$ 205.1387, found 205.1385.

*Penta-1,2-diene-1,5-diyldibenzene (**7m**).* Following general method II, **7m** was purified by flash column chromatography using pentane as eluent. The product was isolated as colorless oil (25.5 mg) in 58% yield. The spectral data are in agreement with the corresponding literature values:[14] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31−7.27 (m, 3H), 7.25−7.20 (m, 4H), 7.20−7.15 (m, 3H), 6.13 (dt, J = 6.4, 3.0 Hz, 1H), 5.60 (dd, J = 13.2, 6.6 Hz, 1H), 2.90−2.78 (m, 2H), 2.54−2.40 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.4, 141.7, 135.0, 128.7, 128.6, 128.5, 126.8, 126.7, 126.1, 95.1, 94.5, 35.5, 30.7. HRMS (APCI/TOF-Q) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}$ 221.1325, found 221.1314.

*(2-Cyclohexylidenevinyl)benzene (**7n**).* Following general method II, **7n** was purified by flash column chromatography using pentane as eluent. The product was isolated as colorless oil (15.8 mg) in 43% yield. The spectral data are in agreement with the corresponding literature values:[30] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30−7.26 (m, 4H), 7.19−7.12 (m, 1H), 5.99 (ddt, J = 7.2, 2.0, 2.0 Hz, 1H), 2.32−2.24 (m, 2H), 2.22−2.15 (m, 2H), 1.77−1.54 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.8, 136.3, 128.6, 126.6, 126.4, 106.6, 92.5, 31.5, 27.9, 26.3. HRMS (APCI/TOF-Q) m/z: $[M + H]^+$ calcd for $C_{14}H_{17}$ 185.1325, found 185.1333.

*(3-Methylpenta-1,2-dien-1-yl)benzene (**7o**).* Following general method II, **7o** was purified by flash column chromatography using pentane as eluent. The product was isolated as colorless oil (18.0 mg) in 57% yield. The spectral data are in agreement with the corresponding literature values:[31] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (dd, J = 8.3, 1.3 Hz, 1H), 7.32−7.27 (m, 2H), 7.17−7.07 (m, 2H), 6.07 (dq, J = 6.0, 3.0 Hz, 1H), 2.12−2.04 (m, 2H), 1.80 (d, J = 3.0 Hz, 3H), 1.05 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.5, 137.5, 136.2, 130.2, 128.5, 127.5, 126.5, 126.4, 105.5, 94.4, 27.2, 18.8, 12.3. HRMS (APCI/TOF-Q) m/z: $[M + H]^+$ calcd for $C_{12}H_{15}$ 159.1168, found 159.1167.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01842.

Copies of ^{1}H NMR and ^{13}C NMR spectra for **7a−o** (PDF)

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Notes

The authors declare no competing financial interest.

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