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Synthesis of 1,4-Diarylbuta-1,3-dienes through Palladium-Catalyzed Decarboxylative Coupling of Unsaturated Carboxylic Acids

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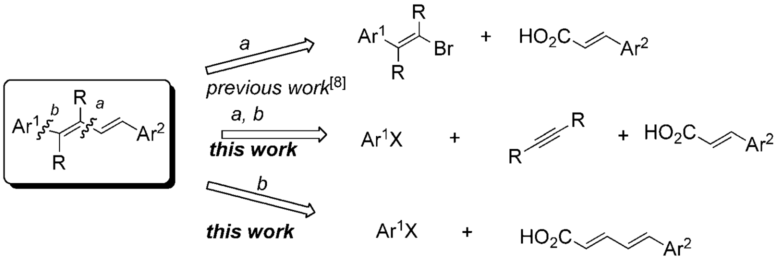
Abstract: It has been found that readily available hydroxylated cinnamic acids such as ferulic acid undergo palladium-catalyzed decarboxylative coupling with aryl iodides and internal alkynes in a 1:1:1 manner to produce 1,4-diarylbuta-1,3-dienes. The butadiene synthesis has also been achieved through the coupling of aryl halides with dienoic acids. Some of the products exhibit solid-state fluorescence.

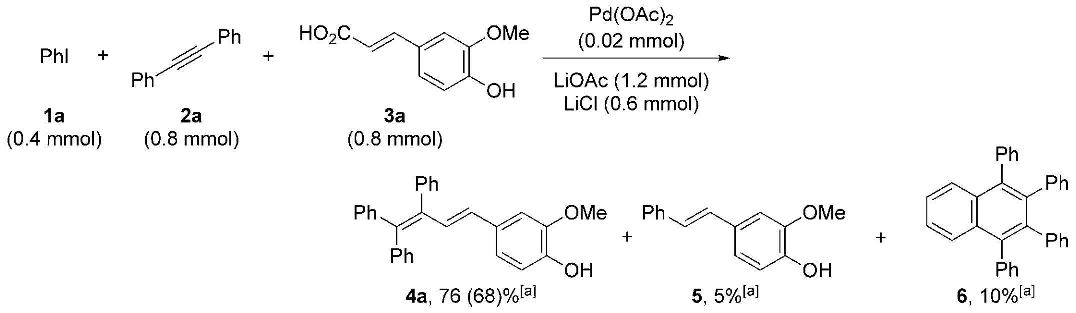
Keywords: alkynes; C–C coupling; decarboxylation; multicomponent reactions; palladium

Unsymmetrically substituted 1,4-diarylbuta-1,3-dienes are of substantial importance for their application in liquid crystals, illuminants, and non-linear optical materials.[1] Their syntheses have been conventionally conducted by Wittig-type or transition metal-catalyzed cross-coupling reactions.[2] These reactions usually need activated substrates, prepared through complicated multistep reactions, and are essentially accompanied by formation of stoichiometric amounts of phosphorus- or metal-containing by-products.

Meanwhile, the decarboxylative coupling of arene- and vinylcarboxylic acids with organic halides has attracted much attention as a new, atom-economical cross-coupling, because air- and water-stable, widely available carboxylic acids can be employed as carbon nucleophiles in place of organometallic reagents.[3,4] Actually, a variety of alkenoic and dienoic acids such as ferulic acid[5] and cinnamylidene acetic acid[6] are widely present in biomass and readily available. They appear to be promising building blocks for constructing π-conjugated molecules. Recently, we have found that hydroxylated cinnamic acids including ferulic acid readily undergo decarboxylative arylation[7] and vinylation[8] under relatively mild conditions compared to those needed for the parent cinnamic acid. Particularly, the vinylation using β-bromostyrenes as coupling partners provides a simple method for 1,4-arylbuta-1,3-diene synthesis (Scheme 1, *via* bond *a* formation). In the context of our study on catalytic decarboxylative coupling,[9] we have found that the desired butadiene molecules can also be constructed from more simple substrates, aryl iodides, internal alkynes, and the cinnamic acids *via* two carbon-carbon bond formations *a*, *b* shown in Scheme 1.[10] In addition, another approach to the target through the coupling of aryl halides with dienoic acids has also been



Scheme 1. Synthetic strategies for 1,4-diarylbuta-1,3-dienes.



[a] GC yield based on the amount of **1a** used. Value in parentheses indicates isolated yield.

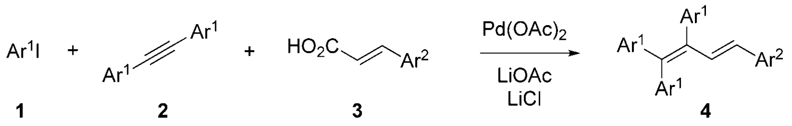
Scheme 2. Reaction of iodobenzene (**1a**), diphenylacetylene (**2a**), and ferulic acid (**3a**).

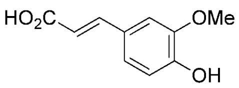
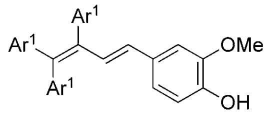
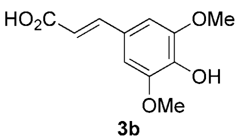
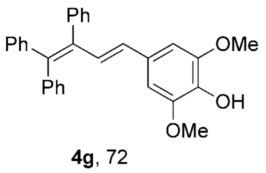
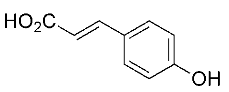
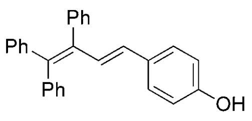
investigated (*via* bond *b* formation). The results obtained for these reactions are described herein.

First, the reaction of iodobenzene (**1a**), diphenylacetylene (**2a**) (2 equiv.), and ferulic acid (**3a**) (2 equiv.) was conducted under similar conditions to those for the coupling of β-bromostyrenes with **3a**. Thus, in the presence of $Pd(OAc)_2$ (5 mol%), LiOAc (3 equiv.), and LiCl (1.5 equiv.) as catalyst, base, and additive, respectively, in DMF at 100 °C for 6 h under N_2, the corresponding three-component coupling product **4a** was obtained in 76% yield (Scheme 2). Minor amounts of stilbene **5** and naphthalene **6** were also detected by GC and GC-MS.

Although treatment of 4-iodotoluene (**1b**) with **2a** and **3a** under similar conditions gave the three-component coupling product in 70% yield, its NMR spectra indicated that it consists of (1*E*,3*E*)- and (1*Z*,3*E*)-4-(4-hydroxy-3-methoxyphenyl)-1-(4-methylphenyl)-

Table 1. Reaction of aryl iodides **1**, diarylacetylenes **2**, and cinnamic acids **3**.[a]



Entry	1, 2	3	4, yield [%][b]
			
1	**1c**, **2b**: Ar^1 = 4-*t*-BuC_6H_4	**3a**	**4b**: Ar^1 = 4-*t*-BuC_6H_4, 64
2	**1d**, **2c**: Ar^1 = 4-$MeOC_6H_4$		**4c**: Ar^1 = 4-$MeOC_6H_4$, 55
3	**1e**, **2d**: Ar^1 = 4-ClC_6H_4		**4d**: Ar^1 = 4-ClC_6H_4, 60
4	**1f**, **2e**: Ar^1 = 4-$CF_3C_6H_4$		**4e**: Ar^1 = 4-$CF_3C_6H_4$, 45
5	**1g**, **2f**: Ar^1 = 4-$EtO_2CC_6H_4$		**4f**: Ar^1 = 4-$EtO_2CC_6H_4$, 51
6	**1a**, **2a**: Ar^1 = Ph	 **3b**	 **4g**, 72
7	**1a**, **2a**: Ar^1 = Ph	 **3c**	 **4h**, 57

[a] *Reaction conditions:* [**1**]:[**2**]:[**3**]:[$Pd(OAc)_2$]:[LiOAc]:[LiCl] = 0.4:0.8:0.8:0.02:1.2:0.6 (in mmol), DMF (2.5 mL) at 100 °C for 6 h under N_2.

[b] Isolated yield based on the amount of **1** used.

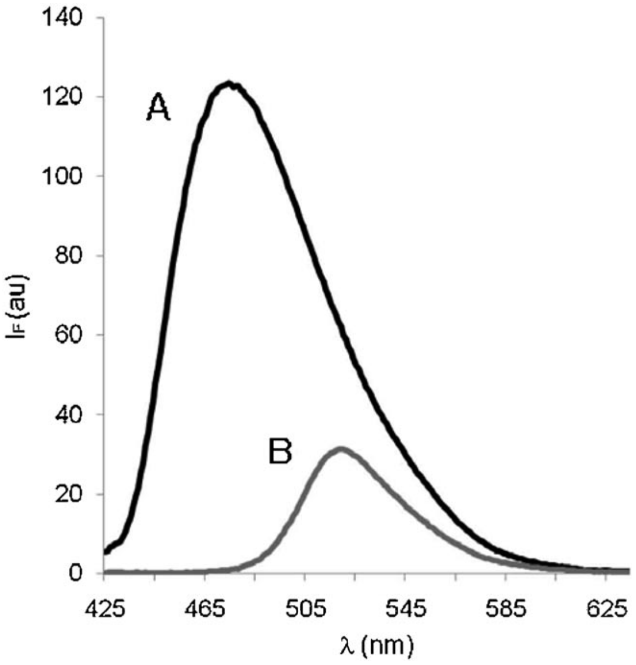


Figure 1. Fluorescence spectra of **4e** (A) and coumarin 153 (B) in the solid-state upon excitation at 422 nm.

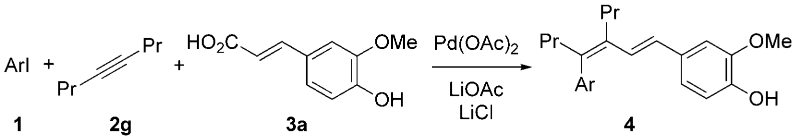
1,2-diphenylbuta-1,3-dienes.[11] As expected, the reaction using the substrate combination of an aryl iodide and a diarylacetylene, in which the same aryl groups are contained, with **3a** gave the corresponding (3*E*)-1,1,2,4-tetraarylbuta-1,3-dienes **4** as single major product. Thus, as shown in Table 1, dienes **4b–f** were obtained from **1c–g** and **2b–f** (entries 1–5). Sinapinic acid (**3b**) and coumaric acid (**3c**), which are also present in plants as well as ferulic acid, underwent the coupling with **1a** and **2a** to produce dienes **4g** and **4h** (entries 6 and 7).

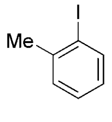
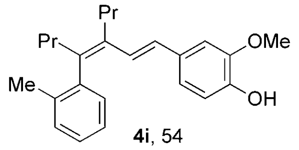
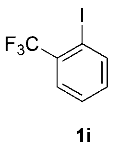
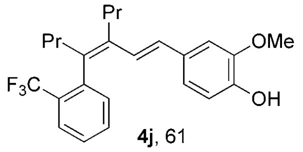
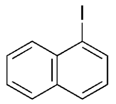
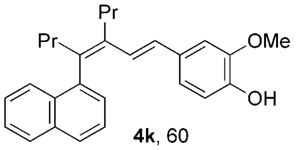
Some of 1,1,2,4-tetraarylbuta-1,3-dienes **4** obtained above showed solid-state fluorescence in a range of 440–540 nm (see the Supporting Information). Notably, **4e** exhibited a relatively strong emission compared to a typical emitter, coumarin 153, by a factor of 5.8 (λ_{emis} = 478 nm, A versus B in Figure 1).

Interestingly, the reactions of sterically hindered aryl iodides **1h–j** with 4-octyne (**2g**) and **3a** afforded only (1*E*,3*Z*)-1,4-diaryl-3-propylhepta-1,3-dienes **4i–k** without any other isomers (Table 2). In these cases, the yields of **4** significantly decreased at 100 °C. In contrast, the reaction of **1a**, **2g** and **3a** gave a mixture of (1*E*,3*Z*)- and (1*E*,3*E*)-isomers. At the present stage, the origin of the difference remains obscure.

A plausible mechanism for the present three-component coupling is illustrated in Scheme 3. Oxidative addition of aryl iodide **1** toward Pd(0) species generated *in situ* followed by alkyne insertion and ligand

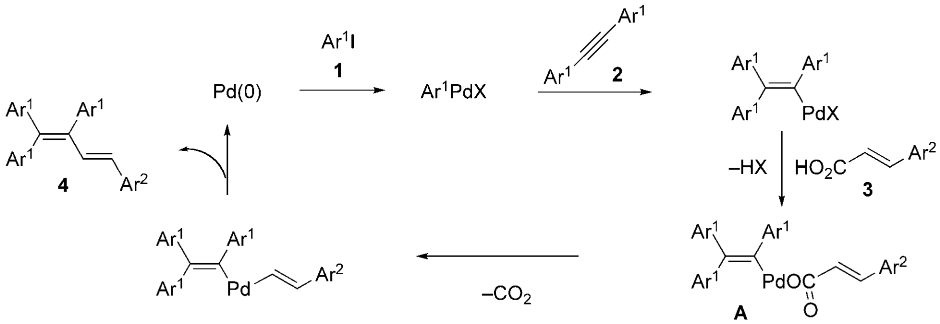
Table 2. Reaction of aryl iodides **1**, 4-octyne (**2g**), and ferulic acid (**3a**).[a]



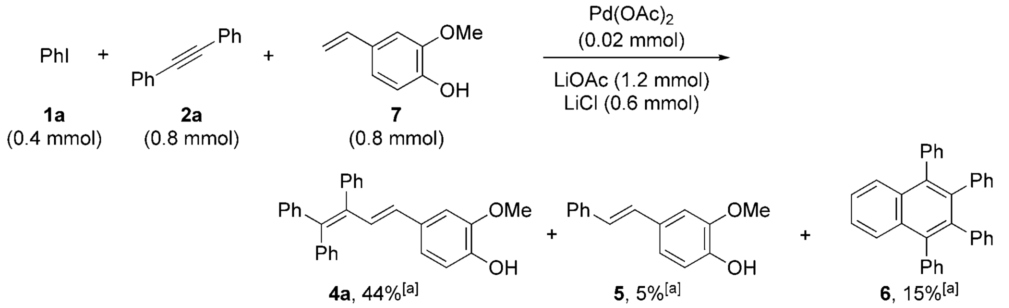
Entry	1	4, yield [%][b]
1	 **1h**	 **4i**, 54
2	 **1i**	 **4j**, 61
3	 **1j**	 **4k**, 60

[a] *Reaction conditions:* [**1**]:[**2g**]:[**3a**]:[Pd(OAc)$_2$]:[LiOAc]:[LiCl] = 0.4:0.8:0.8:0.02:1.2:0.6 (in mmol), DMF (2.5 mL) at 140 °C for 4 h under N$_2$.

[b] Isolated yield based on the amount of **1** used.



Scheme 3. A plausible mechanism for the reaction of **1** with **2** and **3**.



[a] GC yield based on the amount of **1a** used.

Scheme 4. Reaction of iodobenzene (**1a**), diphenylacetylene (**2a**), and 4-hydroxy-3-methoxystyrene (**7**).

exchange with cinnamic acid **3** gives a vinylpalladium carboxylate intermediate **A**. The subsequent decarboxylation and reductive elimination afford butadiene **4**.

Another possible sequence may involve the initial decarboxylation of **3** to the corresponding styrenes which then couple with **1** and **2**. During the three-component coupling reactions, small amounts of such styrenes were actually detected by GC-MS.[7] However, treatment of 4-hydroxy-3-methoxystyrene (**7**) with **1a** and **2a** gave **4a** in a meaningfully lower yield (44%, Scheme 4) than that from **1a**, **2a**, and **3a** (Scheme 2). The fact indicates that the latter sequence may partly participate, while the catalytic cycle in Scheme 3 may occur as the significant route. Whichever sequence is involved, the direct use of cinnamic acids **3** rather than the corresponding styrenes seems to be advantageous due to their availabilities.

As described above, the syntheses of 1,4-diarylbuta-1,3-dienes could also be achieved by the decarboxylative coupling of **1** with dienoic acids. Thus, treatment of **1a** with cinnamylidene acetic acid (**3d**) (2 equiv.) in the presence of $Pd(OAc)_2$ (5 mol%), AgOAc (2 equiv.), LiOAc (3 equiv.), and LiCl (1.5 equiv.) in DMF at 120 °C for 6 h gave (1*E*,3*E*)-1,4-diphenylbuta-1,3-diene (**4l**) in 73% yield (entry 1 in Table 3). The addition of AgOAc was essential to conduct the reaction efficiently. Without it, the reaction was sluggish to afford only a trace amount of **4l**. Diene **4l** could also be produced through the coupling using bromobenzene in place of **1a** with **3d** in the presence of PPh_3 (10 mol%), in spite of a moderate yield (52%). Other iodides **1b**, **d–f** also coupled with **3d** smoothly to afford the corresponding substituted dienes **4m–p** (entries 2–5). In addition, sorbic acid (**3e**) underwent the decarboxylative coupling with **1a** to give 1-phenylpenta-1,3-diene (**4q**) as a mixture of geometric isomers (entry 6).

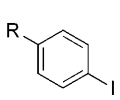
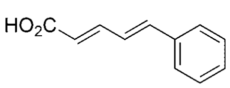
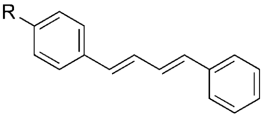
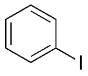
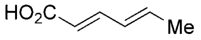
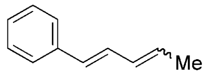
In summary, we have demonstrated that 1,4-diarylbuta-1,3-dienes can be prepared through the palladium-catalyzed decarboxylative coupling of ω-arylalkenoic and -dienoic acids with aryl halides in the presence or absence of internal alkynes, respectively. Such unsaturated acids are apparently useful building blocks because of their wide and ready availability.

Experimental Section

General Remarks

^1H and ^{13}C NMR spectra were recorded at 400 or 600 and 100 or 150 MHz, respectively, for $CDCl_3$ solutions. MS data were obtained by EI. GC analysis was carried out using a silicon OV-17 column (i. d. 2.6 mm × 1.5 m) or a CBP-1 capillary column (i. d. 0.5 mm × 25 m). GC-MS analysis was carried out using a CBP-1 capillary column (i. d. 0.25 mm × 25 m). The structures of all products were unambiguously

Table 3. Reaction of aryl iodides **1** and dienoic acids **3**.[a]

Entry	1	3	4, yield [%][b]
			
1	**1a**: R = H	**3d**	**4l**: R = H, 73
2	**1b**: R = Me		**4m**: R = Me, 76
3	**1d**: R = OMe		**4n**: R = OMe, 57
4	**1e**: R = Cl		**4o**: R = Cl, 61
5	**1f**: R = CF_3		**4p**: R = CF_3, 62
			
6[c]	**1a**	**3e**	**4q**, 51 (*E*:*Z* = 5:1)[d]

[a] *Reaction conditions:* [**1**]:[**3**]:[$Pd(OAc)_2$]:[AgOAc]:[LiOAc]:[LiCl] = 0.4:0.8:0.02:0.8:1.2:0.6 (in mmol), DMF (2.5 mL) at 120 °C for 6 h under N_2.

[b] Isolated yield based on the amount of **1** used.

[c] At 140 °C.

[d] Determined by NMR.

determined by ^{1}H and ^{13}C NMR with the aid of NOE, COSY, HMQC, and HMBC experiments.

Diarylacetylenes **2b–f** were prepared according to published procedures.[12] Other starting materials were commercially available. Characterization data of all products are reported in the Supporting Information.

The fluorescence analysis of some products was carried out with the samples recrystallized from hexane.[13]

The following experimental procedures may be regarded as typical in methodology and scale.

Decarboxylative Coupling of Aryl Iodides, Alkynes, and Cinnamic Acids

To a 20-mL two-necked flask were added halide **1** (0.4 mmol), internal alkyne **2** (0.8 mmol), cinnamic acid **3** (0.8 mmol), $Pd(OAc)_2$ (0.02 mmol, 4 mg), LiOAc (1.2 mmol, 79 mg), LiCl (0.6 mmol, 25 mg), 1,2-diphenylethane (ca. 40 mg) as internal standard, and DMF (2.5 mL). The resulting mixture was stirred under N_2 at 100–140 °C for 4–6 h. GC and GC-MS analyses of the mixture confirmed formation of **4**. After cooling, the reaction mixture was poured into dilute aqueous HCl (50 mL), extracted with ethyl acetate (50 mL, three times), washed with saturated aqueous NaCl (50 mL), and dried over Na_2SO_4. The product was isolated by column chromatography on silica gel using hexane-ethyl acetate as eluant.

(3*E*)-1,1,2-Tris(4-*tert*-butylphenyl)-4-(4-hydroxy-3-methoxyphenyl)buta-1,3-diene (4b) (entry 1 in Table 1): mp 182–184 °C; ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 1.20$ (s, 9H), 1.29 (s, 9H), 1.36 (s, 9H), 3.78 (s, 3H), 5.56 (s, 1H), 6.25 (d, $J = 16.1$ Hz, 1H), 6.72 (d, $J = 1.8$ Hz, 1H), 6.75 (dd, $J = 1.8$, 8.5 Hz, 1H), 6.77 (d, $J = 8.5$ Hz, 2H), 6.79 (d, $J = 16.2$ Hz, 1H), 6.99 (d, $J = 8.5$ Hz, 2H), 7.06–7.08 (m, 3H), 7.20 (d, $J = 8.2$ Hz, 2H), 7.25 (d, $J = 8.2$ Hz, 2H), 7.37 (d, $J = 8.2$ Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 31.1$, 31.3, 31.4, 34.3, 34.4, 34.6, 55.6, 108.2, 114.3, 120.2, 123.8. 124.5, 124.6, 129.8, 130.7, 130.9, 131.0, 131.1, 131.3, 137.8, 138.5, 139.8, 140.1, 141.8, 145.0, 146.5, 148.6, 149.2, 149.9; HR-MS: $m/z = 572.3651$, calcd. for $C_{41}H_{48}O_2$ (M^+): 572.3654.

Acknowledgements

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