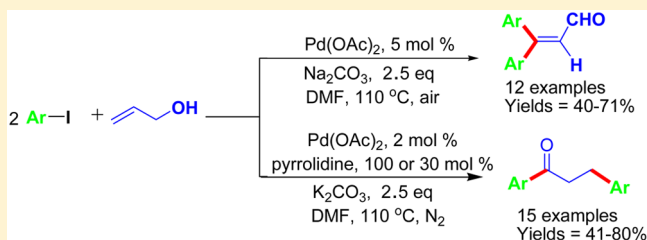


Domino Reactions Containing Different Types of Heck Reactions for Selective 3,3- and 1,3-Diarylations of Propenol with Aryl Halides by Triple Catalysis

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Supporting Information

ABSTRACT: A new domino Heck-isomerization/Saegusa/Heck reaction of propenol with aryl iodides has been developed for the synthesis of 3,3-diaryl propenals by triple transition-metal catalysis. Moreover, we also developed the domino Heck-isomerization/Heck-type reaction of propenol with aryl iodides for the synthesis of 1,3-diaryl propanones by double transition-metal catalysis and the mediation of secondary amine or triple transition metal catalysis and aminocatalysis.



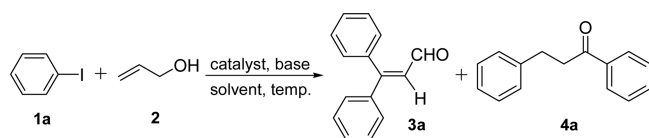
A domino reaction can form two or more bonds in one reaction and need not isolate intermediates, change reaction conditions, or add reagents or catalysts during the reaction. Moreover, domino reactions can decrease the amount of solvents, reagents, energy, labor, and so forth dramatically, and have great potential to be used in the synthesis of natural products and pharmaceuticals, especially in the chemical industry.¹ It is well-known that Heck reactions are very important and classic transition metal-catalyzed coupling reactions for the formation of carbon–carbon bonds mainly through arylation of alkenes.² Among them, there are some reports on the synthesis of 3,3-diaryl propenals through Heck reactions from 3-aryl propenals.³ In 2001, Strauss and co-workers revealed that when they performed the reaction of propenol with excess phenyl iodide under palladium catalysis, complex mixtures of 3-phenylpropanal, 3-phenylpropenal, 3,3-diphenylpropenal, 3,3-diphenylpropanal, 2,3-diphenylpropenol, and 2,3-diphenylpropanal were observed.⁴ In 2010, Li et al. developed a domino Heck-isomerization/Saegusa reaction of aryl iodides with propenol for the synthesis of 3-aryl propenals via 3-aryl propanal intermediates.⁵ Because 3-aryl propenal retains a 3-olefinic hydrogen, it may continue to perform Heck reactions in a domino pathway, giving 3,3-diaryl propenals, which have been widely applied in the synthesis of biologically active compounds.⁶ Thus, we carried out the investigation on the domino Heck-isomerization/Saegusa/Heck reaction of allyl alcohol with aryl halides for the synthesis of 3,3-diaryl propenals by triple transition-metal catalysis.

When exploring the domino Heck-isomerization/Saegusa/Heck reaction of propenol with phenyl iodide in the presence of palladium catalyst and secondary amine, we once

unexpectedly obtained 1,3-diphenyl propanone. In 2011, Xiao and co-workers reported that under the catalysis of palladium complex and using Cy₂NMe and K₂CO₃ as a base and additive, respectively, the Heck-isomerization reaction of propenol with aryl bromides was performed to generate 3-aryl propanals in situ.⁷ Then, a second molecule of aryl bromides and equivalent pyrrolidine were added to perform a Heck-type arylation of the formed 3-aryl propanals to give 1,3-diaryl propanones under palladium catalysis via enamine intermediates. 1,3-Diaryl propanones have many biological activities, such as antibacterial, anticancer, and antioxidant activities,⁸ and have been widely applied in natural product synthesis and drug discovery.⁹ Considering that this is a two-step reaction, and as the continuation of our investigation on a domino reaction based on Heck reactions by a combination of transition metal catalysis and aminocatalysis,¹⁰ we embarked on an investigation about a domino Heck-isomerization/Heck-type reaction for the synthesis of 1,3-diaryl propanones by triple transition-metal catalysis and aminocatalysis.

Initially, iodobenzene **1a** and propenol **2** were chosen as model substrates to explore and optimize the domino Heck-isomerization/Saegusa/Heck reaction. When the reaction was performed in the presence of 5 mol % Pd(OAc)₂ and 2.5 equiv of Cy₂NMe in DMF at 110 °C, we found that desired 3,3-diphenyl propenal **3a** was formed in ~7% yield (entry 1, Table 1). After various bases were examined in the reaction, Na₂CO₃ was found to be most efficient for the reaction, increasing the yield of **3a** to 64% (compare entries 1–4 with entry 5, Table 1;

Received: July 26, 2015

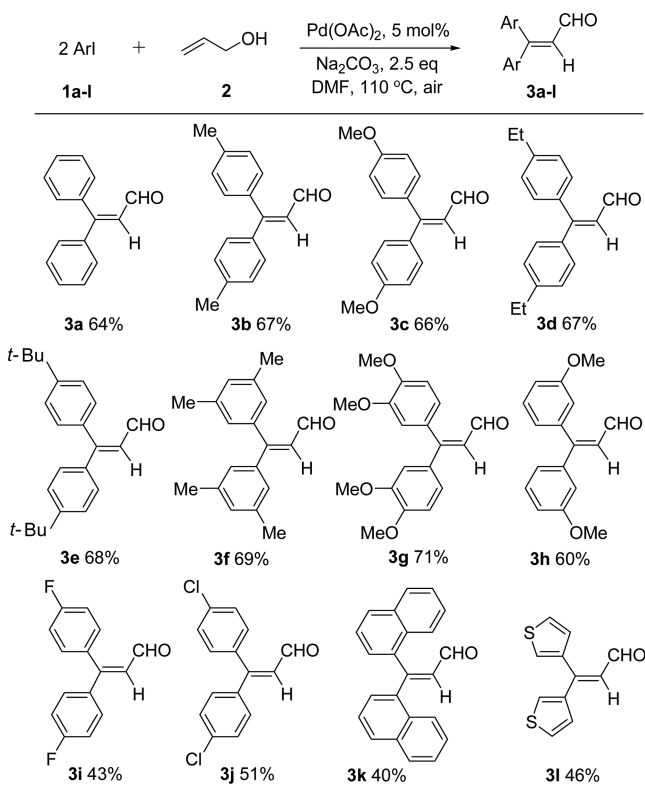
Table 1. Optimization of the Domino Reaction Conditions for the Synthesis of 3,3-Diphenyl Propenal 3a^a

entry	catalyst	base	solvent	T (°C)	yield (%)
1	Pd(OAc) ₂	Cy ₂ NMe	DMF	110	7
2	Pd(OAc) ₂	Et ₃ N	DMF	110	trace
3	Pd(OAc) ₂	K ₂ CO ₃	DMF	110	42
4	Pd(OAc) ₂	NaHCO ₃	DMF	110	47
5	Pd(OAc) ₂	Na ₂ CO ₃	DMF	110	64
6 ^b	Pd(OAc) ₂	Et ₂ NH	DMF	110	0
7	PdCl ₂	Na ₂ CO ₃	DMF	110	37
8	Pd(PPh ₃) ₄	Na ₂ CO ₃	DMF	110	35
9	Pd(dba) ₃	Na ₂ CO ₃	DMF	110	43
10	Rh(PPh ₃) ₃ Cl	Na ₂ CO ₃	DMF	110	trace
11		Na ₂ CO ₃	DMF	110	0
12	Pd(OAc) ₂	Na ₂ CO ₃	NMP	110	56
13	Pd(OAc) ₂	Na ₂ CO ₃	DMSO	110	10
14	Pd(OAc) ₂	Na ₂ CO ₃	DMF	100	59
15	Pd(OAc) ₂	Na ₂ CO ₃	DMF	120	61

^a1a (1.25 mmol), 2a (0.5 mmol), catalyst (5 mol %), base (1.25 mmol), solvent (2 mL), at 110 °C under air for 24 h. ^bYield of 4a was 11%.

also see the Supporting Information (SI)). Interestingly, when Et₂NH was used instead of the above bases, 1,3-diphenyl propanone 4a was obtained in an 11% yield without observation of expected 3a (entry 6, Table 1). Then, various transition-metal catalysts were screened for 3a, and the experiment indicated that Pd(OAc)₂ was the best transition-metal catalyst among them (compare entries 7–10 with entry 5, Table 1; also see SI). In the absence of a palladium catalyst, no reaction occurred (entry 11, Table 1). Various solvents in this reaction were also examined. DMF was proved to be best in the yield of 3a as compared to DMA, NMP, and DMSO (compare entries 12–13 with entry 5, Table 1). No desired product 3a was observed in other solvents, such as toluene, MeCN, THF, and DCE (see SI). The effect of temperature on this reaction was also studied, and lower yields of 3a were obtained no matter whether the temperature was elevated or reduced (entries 14–15 with entry 5, Table 1; also see SI).

After the reaction conditions were screened, it could be concluded that the optimized reaction should be performed under the catalysis of 5 mol % Pd(OAc)₂ using 2.5 equiv of Na₂CO₃ as a base in DMF at 110 °C. As shown in Table 2, various aryl iodides 1a–l were able to undergo the domino Heck-isomerization/Saegusa/Heck reaction smoothly with propenol 2 to give desired 3,3-diaryl propenals 3a–l in the yields of 40–71% under the optimized conditions. The experimental results also demonstrated that the functional groups connected to the benzene rings in substituted phenyl iodides 1b–j had an effect on the yields of desired products 3b–j. The electron-donating groups on the benzene rings of phenyl iodides 1b–h were more beneficial to the domino reaction as compared to the electron-withdrawing groups on the benzene rings of phenyl iodides 1i–j. Furthermore, the aryl iodides, other than substituted phenyl iodides, 1-naphthalenyl iodide 1k, or 3-thienyl iodide 1l, could also undergo the domino reaction to give the corresponding 3,3-diaryl propenals

Table 2. Domino Heck-Isomerization/Saegusa/Heck Reaction for the Synthesis of 3,3-Diaryl Propenals 3a–l^a

^aReaction conditions: the mixture of 1 (1.25 mmol), 2 (0.5 mmol), Pd(OAc)₂ (5 mol %), and Na₂CO₃ (1.25 mmol) was stirred in DMF (2 mL) at 110 °C under air for 24 h.

3k–l expediently. It is noteworthy that the domino reaction tolerates a range of functional groups, such as fluoro, chloro, methoxy, *tert*-butyl, ethyl, and methyl groups. When but-3-en-2-ol was employed instead of propenol 2, its domino reaction with phenyl iodide 1a was able to occur as well, but only 23% yield of desired product 3m, 4,4-diphenylbut-3-en-2-one, was achieved (see SI).

The possible mechanism for the domino Heck-isomerization/Saegusa/Heck reaction is depicted in Scheme 1. Initially, under the catalysis of palladium(0), which is reduced from Pd(OAc)₂ by propenol, and so forth, aryl iodide 1, and propenol 2 perform a Heck-isomerization reaction in the first catalytic cycle to give the tautomer 7a of 3-aryl propanal.¹¹ Then, 7a undergoes the Saegusa oxidative reaction to afford 3-aryl propenal 9 by the catalysis of Pd(OAc)₂ using air as an oxidant in the second catalytic cycle.¹² Finally, 9 undergoes a Heck reaction with another molecular aryl iodide 1 by palladium catalysis in the third catalytic cycle, giving desired 3,3-diaryl propenals 3.^{2d}

As mentioned above, when we employed Et₂NH instead of Na₂CO₃ in the reaction of phenyl iodide with propenol 2 under the catalysis of Pd(OAc)₂, 1,3-diphenyl propanone 4a instead of 3a was obtained (entry 6, Table 1). Then, iodobenzene 1a and propenol 2 were chosen as model substrates to optimize the domino Heck-isomerization/Heck-type reaction under the catalysis of transition-metal and the mediation of secondary amine (see SI). After optimization, it can be concluded that the domino reaction should be performed under the catalysis of Pd(OAc)₂ (2 mol %) and the mediation of pyrrolidine (1.0

Scheme 1. Possible Mechanism for the Domino Heck-Isomerization/Saegusa/Heck Reaction

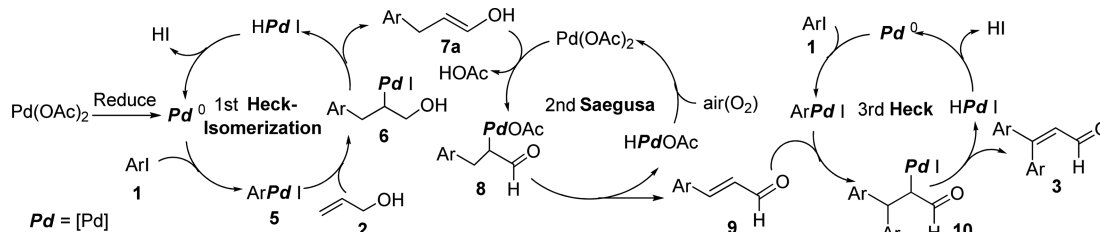
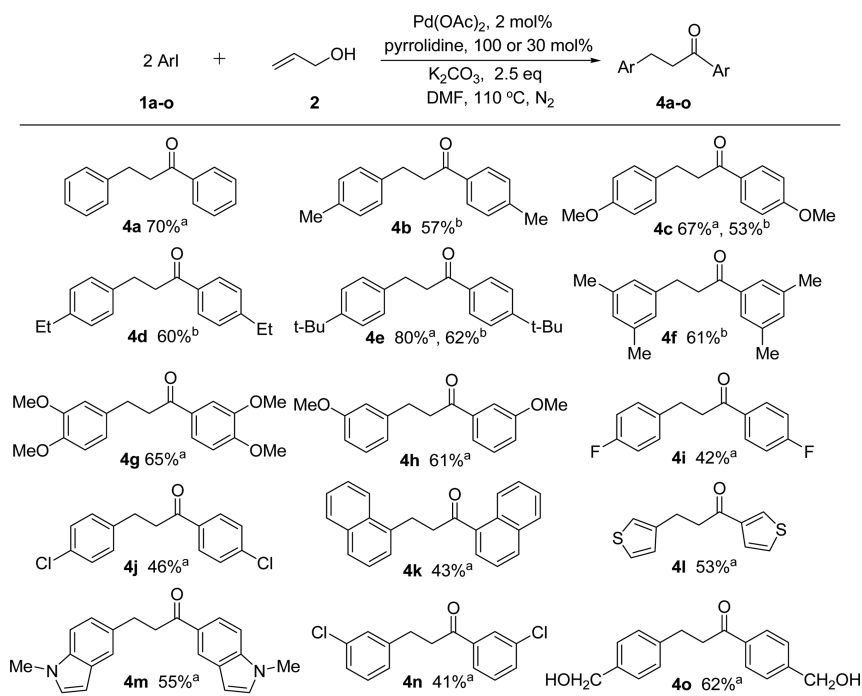
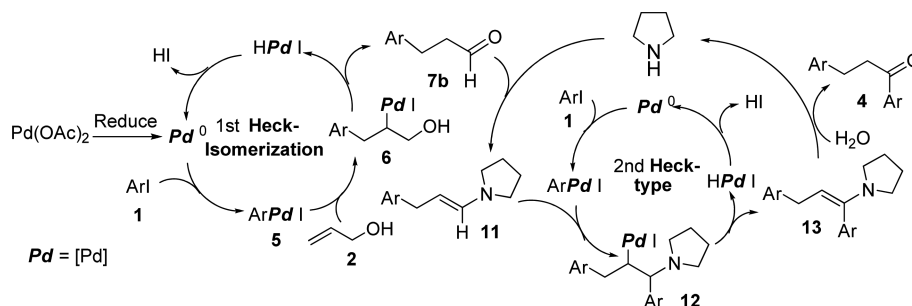


Table 3. Domino Heck-Isomerization/Heck-Type Reaction for the Synthesis of 1,3-Diaryl Propanones 4a–o



^aReaction conditions A: **1** (1.05 mmol), **2** (0.5 mmol), Pd(OAc)₂ (2 mol %), K₂CO₃ (1.25 mmol), and pyrrolidine (0.5 mmol) was stirred in DMF (2 mL) at 110 °C under nitrogen for 24 h. ^bReaction conditions B are the same as A except pyrrolidine is at 0.15 mmol.

Scheme 2. Possible Mechanism for the Domino Heck-Isomerization/Heck-Type Reaction



equiv) using K₂CO₃ (2.5 equiv) as a base in DMF at 110 °C, leading to the desired 1,3-diphenyl propanone **4a** in 70% yield. As shown in Table 3, a series of aryl iodides **1a–o** were able to undergo the domino Heck-isomerization/Heck-type reaction smoothly with propenol **2** to give desired 1,3-diaryl propanones **4a–o** in yields of 41–80% under the optimized conditions. Our experiment also indicated that the domino reaction was sensitive to the functional groups connected to the benzene rings in substituted phenyl iodides **1b–j** and **1n–o**. The electron-donating groups on benzene rings of aryl iodides **1b–h** and **1o** were more beneficial to the domino reaction as

compared to the electron-withdrawing groups on benzene rings of aryl iodides **1i–j** and **1n**. In addition, the aryl iodides bearing other aromatic rings than benzene, 1-naphthalenyl iodide **1k**, 3-thienyl iodide **1l**, and 1-methyl-1H-indol-5-yl iodide **1m** could also undergo the domino reaction readily to furnish desired 1,3-diaryl propanones **4k–m**. The domino reaction for 1,3-diaryl propanones **4** under the palladium catalysis and mediated by pyrrolidine also tolerates a variety of functional groups, such as fluoro, chloro, methoxy, hydroxymethyl, *tert*-butyl, ethyl, and methyl groups. Furthermore, when the amount of pyrrolidine was decreased to 30 mol %, the domino reaction of propenol **2**

with aryl iodides **1b–f** also performed smoothly to give desired 1,3-diaryl propanones **4b–f** under optimized conditions, albeit in slightly lower yields.¹³ Compared with the literature method by Xiao,⁷ this is a domino reaction and only uses K₂CO₃ and an equivalent or catalytic amount of pyrrolidine rather than a two-step reaction and using Cy₂NMe, K₂CO₃, and an equivalent amount of pyrrolidine, respectively.

Therefore, the domino Heck-isomerization/Heck-type reaction for 1,3-diaryl propanone **4** may be performed by triple catalysis, which is the relay catalysis of palladium and pyrrolidine, and another palladium catalysis inserted into the aminocatalysis (Scheme 2). The possible mechanism of the domino reaction for **4** is as follows. Initially, aryl iodide **1** and propenol **2** undergo a Heck-isomerization reaction in the first catalytic cycle to give 3-aryl propanal **7b**.¹¹ Then, enamine **11** resulted from the reaction of 3-aryl propanal **7b** with pyrrolidine undergoes the Heck-type reaction with another molecular aryl iodide **1** to generate the corresponding 1-arylated enamine **13** under palladium catalysis.¹⁴ Finally, hydrolysis of **13** led to the desired 1,3-diaryl propanone **4** with regenerating pyrrolidine as an organocatalyst.

In conclusion, a new domino Heck-isomerization/Saegusa/Heck reaction of propenol with aryl iodides has been developed for the synthesis of 3,3-diaryl propenals by triple transition-metal catalysis. Moreover, we also developed the domino Heck-isomerization/Heck-type reaction of propenol with aryl iodides for the synthesis of 1,3-diaryl propanones by double transition-metal catalysis and the mediation of secondary amine or triple transition metal catalysis and aminocatalysis. These domino reactions tolerate a range of functional groups, such as fluoro, chloro, methoxy, *tert*-butyl, ethyl, and methyl groups to afford 3,3-diaryl propenals or 1,3-diaryl propanones in satisfactory yields. The novel domino reactions may have potential applications in natural product synthesis and drug discovery in the future.

EXPERIMENTAL SECTION

General Procedure for the Domino Heck-Isomerization/Saegusa/Heck Reaction between Aryl Iodides **1 and Propenol **2**.** The reaction mixture of Pd(OAc)₂ (5.6 mg, 0.025 mmol), Na₂CO₃ (132.5 mg, 1.25 mmol), aryl iodide **1** (1.25 mmol), and propenol **2** (29.04 mg, 0.5 mmol) in DMF (2 mL) was stirred at 110 °C under air for 24 h. After cooling to room temperature, the mixture was diluted with EtOAc (15 mL) and washed with water and brine, respectively. The organic layer was dried over Na₂SO₄ and then concentrated in vacuo. The residue was subjected to flash column chromatography (silica gel, petroleum ether/ethyl acetate as an eluent) to give desired 3,3-diaryl propenals **3**.

3,3-Diphenylpropenal (3a).^{6a} Yield 64% (66.5 mg); light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 9.53 (d, *J* = 8.0 Hz, 1H), 7.47–7.40 (m, 4H), 7.38–7.29 (m, 6H), 6.60 (d, *J* = 8.0 Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 193.5, 162.2, 139.8, 136.7, 130.8, 130.5, 129.5, 128.7, 128.6, 128.4, 127.3; MS (EI) *m/z* 208 (M⁺), 178, 165, 102, 77.

3,3-Bis(4-methylphenyl)propenal (3b). Yield 67% (79.1 mg); light yellow solid; mp 93–94 °C (lit.^{6a} 93–94 °C); ¹H NMR (400 MHz, CDCl₃) δ 9.52 (d, *J* = 8.0 Hz, 1H), 7.26–7.23 (m, 4H), 7.19–7.16 (m, 4H), 6.55 (d, *J* = 8.0 Hz, 1H), 2.42 (s, 3H), 2.37 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 193.6, 162.5, 140.9, 139.6, 137.2, 134.0, 130.8, 129.3, 129.0, 128.8, 126.5, 21.4; MS (EI) *m/z* 236 (M⁺), 178, 165, 115, 91.

3,3-Bis(4-methoxyphenyl)propenal (3c). Yield 66% (88.4 mg); light yellow solid; mp 56–57 °C (lit.^{6a} 56–57 °C); ¹H NMR (400 MHz, CDCl₃) δ 9.27 (d, *J* = 8.4 Hz, 1H), 7.11 (d, *J* = 8.8 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 6.28 (d, *J* = 8.0 Hz, 1H), 3.66 (s, 3H), 3.63 (s, 3H); ¹³C{¹H}

NMR (100 MHz, CDCl₃) δ 193.6, 162.0, 161.7, 160.8, 132.5, 130.5, 129.2, 125.5, 114.0, 113.7, 55.4, 55.4; MS (EI) *m/z* 268 (M⁺), 237, 165, 132, 77.

3,3-Bis(4-ethylphenyl)propenal (3d). Yield 67% (88.5 mg); light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 9.52 (d, *J* = 7.6 Hz, 1H), 7.30–7.19 (m, 8H), 6.56 (d, *J* = 8.0 Hz, 1H), 2.73 (q, *J* = 7.6 Hz, 2H), 2.68 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H), 1.25 (t, *J* = 7.6 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 193.8, 162.6, 147.2, 145.9, 137.4, 134.2, 130.9, 128.9, 128.1, 127.8, 126.5, 28.7, 15.4, 15.3; HRMS (EI-TOF) *m/z* calcd for C₁₉H₂₀O 264.1514, found 264.1516.

3,3-Bis(4-*tert*-butylphenyl)propenal (3e). Yield 68% (108.8 mg); light yellow solid; mp 111–112 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.52 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.58 (d, *J* = 8.4 Hz, 1H), 1.37 (s, 9H), 1.33 (s, 9H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 193.9, 162.4, 154.0, 152.7, 137.0, 133.8, 130.7, 128.6, 126.6, 125.6, 125.2, 34.9, 34.8, 31.3, 31.2; HRMS (EI-TOF) *m/z* calcd for C₂₃H₂₈O 320.2140, found 320.2141.

3,3-Bis(3,5-dimethylphenyl)propenal (3f). Yield 69% (91.1 mg); light yellow solid; mp 112–113 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.50 (d, *J* = 8.0 Hz, 1H), 7.09 (s, 1H), 7.06 (s, 1H), 6.97 (s, 2H), 6.90 (s, 2H), 6.51 (d, *J* = 8.4 Hz, 1H), 2.35 (s, 6H), 2.30 (s, 6H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 193.9, 163.3, 140.0, 138.1, 137.8, 136.8, 132.2, 131.0, 128.5, 127.1, 126.6, 21.3; HRMS (EI-TOF) *m/z* calcd for C₁₉H₂₀O 264.1514, found 264.1516.

3,3-Bis(3,4-dimethoxyphenyl)propenal (3g). Yield 71% (116.4 mg); light yellow solid; mp 129–131 °C (lit.^{6a} 129–130 °C); ¹H NMR (400 MHz, CDCl₃) δ 9.51 (d, *J* = 8.0 Hz, 1H), 6.95–6.92 (m, 4H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.79 (s, 1H), 6.52 (d, *J* = 8.0 Hz, 1H), 3.96 (s, 3H), 3.92 (s, 3H), 3.85 (s, 6H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 193.5, 162.0, 151.3, 150.3, 148.9, 148.6, 132.4, 129.3, 125.7, 124.4, 122.9, 113.7, 111.2, 110.7, 110.5, 56.0, 56.0, 56.0; MS (EI) *m/z* 328 (M⁺), 285, 165, 139, 77.

3,3-Bis(3-methoxyphenyl)propenal (3h).^{6a} Yield 60% (80.4 mg); light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 9.55 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.01 (dd, *J* = 8.4 Hz, *J* = 2.0 Hz, 1H), 6.98–6.90 (m, 4H), 6.82 (s, 1H), 3.81 (s, 3H), 3.79 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 193.6, 161.8, 159.7, 159.4, 140.9, 137.9, 129.6, 129.4, 127.4, 123.2, 121.2, 116.1, 116.0, 115.0, 114.1, 55.4, 55.4; MS (EI) *m/z* 268 (M⁺), 237, 165, 132, 77.

3,3-Bis(4-fluorophenyl)propenal (3i). Yield 43% (52.4 mg); light yellow solid; mp 58–60 °C (lit.^{6a} 58–59.5 °C); ¹H NMR (400 MHz, CDCl₃) δ 9.50 (d, *J* = 8.0 Hz, 1H), 7.36–7.27 (m, 4H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 2H), 6.54 (d, *J* = 8.0 Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 192.9, 165.2 (d, *J*_{C–F} = 69.3 Hz), 162.7 (d, *J*_{C–F} = 67.6 Hz), 159.8, 135.7 (d, *J*_{C–F} = 2.6 Hz), 132.6 (d, *J*_{C–F} = 9.1 Hz), 132.5 (d, *J*_{C–F} = 3.5 Hz), 130.7 (d, *J*_{C–F} = 8.3 Hz), 127.4, 115.9 (d, *J*_{C–F} = 16.1 Hz), 115.7 (d, *J*_{C–F} = 16.5 Hz); MS (EI) *m/z* 244 (M⁺), 214, 149, 120, 96.

3,3-Bis(4-chlorophenyl)propenal (3j).^{6a} Yield 41% (77.0 mg); light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 9.52 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.56 (d, *J* = 8.0 Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 192.6, 159.3, 137.8, 137.0, 136.1, 134.6, 132.0, 129.8, 129.1, 128.9, 127.7; MS (EI) *m/z* 276 (M⁺), 178, 165, 136, 111.

3,3-Di(naphthalen-1-yl)propenal (3k). Yield 40% (61.6 mg); light yellow solid; mp 110–112 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.53 (d, *J* = 8.0 Hz, 1H), 8.47 (d, *J* = 7.6 Hz, 1H), 7.96–7.83 (m, 5H), 7.59–7.53 (m, 4H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.36–7.30 (m, 2H), 7.25–7.23 (m, 1H), 6.78 (d, *J* = 8.0 Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 193.0, 159.9, 138.5, 135.5, 134.3, 134.2, 133.8, 132.1, 130.4, 130.2, 129.9, 129.5, 129.0, 128.6, 127.6, 127.3, 127.2, 126.4, 126.3, 125.6, 125.0, 124.9; HRMS (EI-TOF) *m/z* calcd for C₂₃H₁₆O 308.1201, found 308.1206.

3,3-Di(thiophen-3-yl)propenal (3l). Yield 46% (50.6 mg); light yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 9.64 (d, *J* = 8.0 Hz, 1H), 7.45–7.43 (m, 2H), 7.40–7.38 (m, 1H), 7.34–7.33 (m, 1H), 7.29 (dd, *J* = 5.2 Hz, *J* = 1.2 Hz, 1H), 7.14 (dd, *J* = 4.8 Hz, *J* = 1.2 Hz, 1H), 6.55 (d, *J* = 8.0 Hz, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 193.5, 150.4,

141.6, 136.8, 129.4, 128.8, 127.7, 126.9, 126.5, 126.2, 126.2; HRMS (EI-TOF) m/z calcd for $C_{11}H_8OS_2$ 220.0017, found 220.0013.

4,4-Diphenylbut-3-en-2-on (3m).¹⁵ Yield 23% (25.5 mg); yellow oil; 1H NMR (400 MHz, $CDCl_3$) δ 7.42–7.41 (m, 3H), 7.36–7.27 (m, 5H), 7.23–7.21 (m, 2H), 6.58 (s, 1H), 1.88 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 200.2, 154.0, 140.8, 139.0, 129.6, 129.5, 128.8, 128.5, 128.4, 127.7, 30.4; MS (EI) m/z 222 (M^+), 207, 179, 149, 77.

General Procedure for the Domino Heck-Isomerization/Heck-Type Reaction between Aryl Iodides 1 and Propenol 2. The mixture of $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), K_2CO_3 (172.8 mg, 1.25 mmol), aryl iodide 1 (1.05 mmol), and propenol 2 (29.04 mg, 0.5 mmol) in DMF (2 mL) was stirred at 110 °C under nitrogen for 5 min, and then pyrrolidine (0.5 mmol, method A; 0.15 mmol, method B) was added. The reaction mixture was stirred at 110 °C for 24 h. After the reaction was finished, a similar workup to that for 3 led to desired 1,3-diaryl propanones 4.

1,3-Diphenylpropan-1-one (4a). Yield 70% (73.5 mg, method A); white solid; mp 69–71 °C (lit.¹⁶ 70–70.5 °C); 1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.0 Hz, 2H), 7.55 (t, J = 7.0 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.41–7.24 (m, 4H), 7.20 (t, J = 6.8 Hz, 1H), 3.30 (t, J = 7.6 Hz, 2H), 3.07 (t, J = 7.6 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 199.2, 141.3, 136.9, 133.0, 128.6, 128.5, 128.4, 128.0, 126.1, 40.4, 30.1; MS (EI) m/z 210 (M^+), 131, 105, 91, 77.

1,3-Bis(4-methylphenyl)propan-1-one (4b). Yield 57% (67.8 mg, method B); white solid; mp 59–61 °C (lit.¹⁶ 65–65.5 °C); 1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 7.6 Hz, 2H), 7.14 (d, J = 7.6 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 3.24 (t, J = 7.8 Hz, 2H), 3.01 (t, J = 7.8 Hz, 2H), 2.39 (s, 3H), 2.31 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 199.0, 143.7, 138.3, 135.6, 134.5, 129.3, 129.2, 128.3, 128.2, 40.5, 29.8, 21.6, 21.0; MS (EI) m/z 238 (M^+), 223, 105, 91, 77.

1,3-Bis(4-methoxyphenyl)propan-1-one (4c).¹⁷ Yield 67% (90.5 mg, method A); yield 53% (71.4 mg, method B); colorless liquid; 1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.8 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 9.2 Hz, 2H), 6.74 (d, J = 8.4 Hz, 2H), 3.75 (s, 3H), 3.68 (s, 3H), 3.11 (t, J = 7.6 Hz, 2H), 2.90 (t, J = 7.6 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.0, 163.4, 158.0, 133.5, 130.3, 130.1, 129.4, 113.9, 113.7, 55.5, 55.3, 40.4, 29.5; MS (EI) m/z 270 (M^+), 239, 135, 107, 77.

1,3-Bis(4-ethylphenyl)propan-1-one (4d). Yield 60% (79.8 mg, method B); colorless liquid; 1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 3.25 (t, J = 7.6 Hz, 2H), 3.02 (t, J = 7.8 Hz, 2H), 2.68 (q, J = 7.6 Hz, 2H), 2.61 (q, J = 7.6 Hz, 2H), 1.24 (t, J = 7.6 Hz, 3H), 1.22 (t, J = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 199.0, 150.0, 142.0, 138.6, 134.7, 128.4, 128.3, 128.0, 40.5, 29.9, 29.0, 28.5, 15.7, 15.2; HRMS (EI-TOF) m/z calcd for $C_{19}H_{22}O$ 266.1671, found 266.1674.

1,3-Bis(4-tert-butylphenyl)propan-1-one (4e).¹⁸ Yield 80% (128.8 mg, method A); yield 62% (99.8 mg, method B); white solid; mp 57–58 °C; 1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 3.19 (t, J = 7.6 Hz, 2H), 2.94 (t, J = 7.6 Hz, 2H), 1.24 (s, 9H), 1.22 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 199.1, 156.8, 148.9, 138.4, 134.4, 128.1, 128.0, 125.6, 125.4, 40.4, 35.1, 34.4, 31.5, 31.2, 29.7; MS (EI) m/z 322 (M^+), 265, 161, 91, 77.

1,3-Bis(3,5-dimethylphenyl)propan-1-one (4f).¹⁹ Yield 61% (81.2 mg, method B); white solid; mp 63–65 °C; 1H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 2H), 7.18 (s, 1H), 6.87 (s, 2H), 6.85 (s, 1H), 3.24 (t, J = 7.6 Hz, 2H), 2.97 (t, J = 7.6 Hz, 2H), 2.35 (s, 6H), 2.29 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 199.8, 141.4, 138.2, 138.0, 137.1, 134.6, 127.8, 126.3, 125.9, 40.8, 30.1, 21.3, 21.2; MS (EI) m/z 266 (M^+), 133, 105, 91, 77.

1,3-Bis(3,4-dimethoxyphenyl)propan-1-one (4g). Yield 65% (107.3 mg, method A); white solid; mp 87–89 °C (lit.²⁰ 88–90 °C); 1H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, J = 8.8 Hz, J = 1.6 Hz, 1H), 7.53 (s, 1H), 6.87 (d, J = 8.4 Hz, 1H), 6.80 (d, J = 8.8 Hz, 2H), 6.79 (s, 1H), 3.94 (s, 3H), 3.93 (s, 3H), 3.87 (s, 3H), 3.85 (s, 3H), 3.24 (t, J = 7.6 Hz, 2H), 3.01 (t, J = 7.6 Hz, 2H); $^{13}C\{^1H\}$ NMR (100

MHz, $CDCl_3$) δ 198.0, 153.3, 149.0, 148.9, 147.4, 134.1, 130.2, 122.7, 120.2, 111.9, 111.4, 110.2, 110.0, 56.1, 56.0, 55.9, 55.8, 40.2, 30.2; MS (EI) m/z 330 (M^+), 239, 165, 137, 97.

1,3-Bis(3-methoxyphenyl)propan-1-one (4h).²¹ Yield 61% (82.4 mg, method A); colorless liquid; 1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.6 Hz, 1H), 7.48 (s, 1H), 7.34 (t, J = 8.0 Hz, 1H), 7.21 (d, J = 7.6 Hz, 1H), 7.09 (dd, J = 8.4 Hz, J = 2.8 Hz, 1H), 6.83 (d, J = 7.6 Hz, 1H), 6.80 (s, 1H), 6.75 (d, J = 8.0 Hz, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 3.27 (t, J = 7.8 Hz, 2H), 3.03 (t, J = 7.6 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 199.0, 159.9, 159.8, 142.9, 138.3, 129.6, 129.5, 120.8, 120.7, 119.6, 114.3, 112.3, 111.4, 55.4, 55.2, 40.5, 30.3; MS (EI) m/z 270 (M^+), 239, 135, 107, 77.

1,3-Bis(4-fluorophenyl)propan-1-one (4i).²² Yield 42% (51.6 mg, method A); colorless liquid; 1H NMR (400 MHz, $CDCl_3$) δ 7.99–7.96 (m, 2H), 7.22–7.18 (m, 2H), 7.12 (t, J = 8.6 Hz, 2H), 6.97 (t, J = 8.8 Hz, 2H), 3.25 (t, J = 7.6 Hz, 2H), 3.04 (t, J = 7.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 197.4, 165.8 (d, J_{C-F} = 253.0 Hz), 161.4 (d, J_{C-F} = 242.5 Hz), 136.7 (d, J_{C-F} = 2.7 Hz), 133.2 (d, J_{C-F} = 2.2 Hz), 130.7 (d, J_{C-F} = 9.7 Hz), 129.8 (d, J_{C-F} = 7.5 Hz), 115.7 (d, J_{C-F} = 20.9 Hz), 115.3 (d, J_{C-F} = 20.2 Hz), 40.4, 29.2; MS (EI) m/z 246 (M^+), 228, 123, 109, 95.

1,3-Bis(4-chlorophenyl)propan-1-one (4j).²³ Yield 46% (63.59 mg, method A); white solid; mp 70–72 °C; 1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 3.24 (t, J = 7.6 Hz, 2H), 3.03 (t, J = 7.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 197.6, 139.6, 139.5, 135.1, 132.0, 129.8, 129.4, 129.0, 128.7, 40.1, 29.3; MS (EI) m/z 278 (M^+), 243, 139, 111, 75.

1,3-Di(naphthalen-1-yl)propan-1-one (4k). Yield 43% (66.7 mg, method A); white solid; mp 76–78 °C (lit.²⁴ 76–77 °C); 1H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J = 8.8 Hz, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.86–7.83 (m, 2H), 7.77 (d, J = 7.6 Hz, 1H), 7.71 (dd, J = 6.4 Hz, J = 2.4 Hz, 1H), 7.57 (td, J = 6.8 Hz, J = 1.2 Hz, 1H), 7.53–7.45 (m, 3H), 7.41–7.35 (m, 3H), 3.59 (t, J = 7.4 Hz, 2H), 3.48 (t, J = 7.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 203.5, 137.2, 135.8, 134.0, 134.0, 132.7, 131.7, 130.2, 129.0, 128.5, 128.0, 127.6, 127.1, 126.5, 126.2, 126.1, 125.9, 125.7, 125.6, 124.4, 123.6, 43.0, 27.8; MS (EI) m/z 310 (M^+), 182, 155, 127, 77.

1,3-Di(thiophen-3-yl)propan-1-one (4l).²⁵ Yield 53% (58.8 mg, method A); colorless liquid; 1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 1.6 Hz, 1H), 7.53 (dd, J = 5.2 Hz, J = 0.8 Hz, 1H), 7.29–7.22 (m, 2H), 6.99–6.96 (m, 2H), 3.19 (t, J = 7.2 Hz, 2H), 3.06 (t, J = 7.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 193.5, 142.2, 141.4, 131.9, 128.2, 126.9, 126.5, 125.7, 120.6, 40.7, 24.6; MS (EI) m/z 222 (M^+), 111, 97, 83, 39.

1,3-Bis(1-methyl-1H-indol-5-yl)propan-1-one (4m). Yield 55% (86.9 mg, method A); white solid; mp 120–122 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 0.8 Hz, 1H), 7.91 (dd, J = 8.4 Hz, J = 1.2 Hz, 1H), 7.51 (s, 1H), 7.29 (d, J = 8.4 Hz, 1H), 7.24 (d, J = 8.4 Hz, 1H), 7.15 (d, J = 8.4 Hz, 1H), 7.06 (d, J = 3.2 Hz, 1H), 7.00 (d, J = 3.2 Hz, 1H), 6.56 (d, J = 3.2 Hz, 1H), 6.41 (d, J = 2.8 Hz, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 3.41 (t, J = 7.8 Hz, 2H), 3.19 (t, J = 7.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 199.9, 139.1, 135.5, 132.5, 130.4, 129.2, 129.1, 128.8, 128.0, 122.8, 122.5, 121.8, 120.1, 109.2, 109.1, 103.0, 100.6, 41.5, 33.0, 32.9, 31.0; HRMS (EI-TOF) m/z calcd for $C_{21}H_{20}N_2O$ 316.1576, found 316.1573.

1,3-Bis(3-chlorophenyl)propan-1-one (4n).²⁶ Yield 41% (57.0 mg, method A); light yellow liquid; 1H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 5.2 Hz, 1H), 7.39 (t, J = 8.0 Hz, 1H), 7.23–7.16 (m, 3H), 7.12 (d, J = 5.2 Hz, 1H), 3.26 (t, J = 7.4 Hz, 2H), 3.03 (t, J = 7.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 197.3, 143.0, 138.2, 135.0, 134.3, 133.1, 130.0, 129.8, 128.6, 128.2, 126.7, 126.5, 126.1, 40.1, 29.5; MS (EI) m/z 278 (M^+), 243, 139, 111, 75.

1,3-Bis(4-(hydroxymethyl)phenyl)propan-1-one (4o). Yield 62% (83.7 mg, method A); white solid; mp 102–104 °C; 1H NMR (400 MHz, $DMSO-d_6$) δ 7.94 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.24–7.20 (m, 4H), 5.35 (br s, 1H), 5.08 (br s, 1H), 4.57 (s, 2H), 4.44 (s, 2H), 3.33 (t, J = 7.4 Hz, 2H), 2.92 (t, J = 7.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 199.3, 148.5, 140.5, 140.0, 135.6, 128.5,

128.4, 127.0, 126.7, 63.2, 62.9, 40.4, 29.8; HRMS (EI-TOF) m/z calcd for $C_{17}H_{18}O_3$, 270.1256, found 270.1262.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01650.

Optimization of reaction conditions and spectra of 1H NMR, ^{13}C NMR, MS, and HRMS for products (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from MOST of China (973 program 2011CB808600) and National Natural Science Foundation of China (No. 21372195) are gratefully acknowledged.

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