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Rhodium- and Iridium-Catalyzed Oxidative Coupling of Benzoic Acids with Alkynes via Regioselective C−H Bond Cleavage

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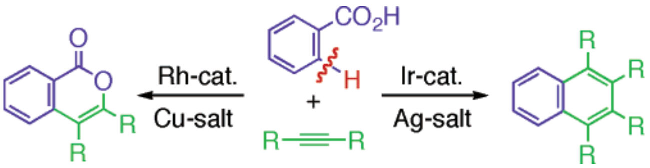

The oxidative coupling of benzoic acids with internal alkynes effectively proceeds in the presence of $[Cp^*RhCl_2]_2$ and $Cu(OAc)_2{\cdot}H_2O$ as catalyst and oxidant, respectively, to produce the corresponding isocoumarin derivatives. The copper salt can be reduced to a catalytic quantity under air. Interestingly, by using $[Cp^*IrCl_2]_2$ in place of $[Cp^*RhCl_2]_2$, the substrates undergo 1:2 coupling accompanied by decarboxylation to afford naphthalene derivatives exclusively. In this case, Ag_2CO_3 acts as an effective oxidant.

Introduction

Transition-metal-catalyzed organic reactions via C−H bond cleavage have attracted much attention from the atom-economic point of view, and various catalytic processes involving different modes to activate the ubiquitously available bond have been developed.[1] Among the most promising activation strategies is to utilize the proximate effect by coordination of a functional group in a given substrate to the metal center of a catalyst that brings about regioselective C−H bond activation and functionalization. Several catalytic coupling reactions of aromatic compounds bearing carbonyl or nitrogen-containing groups with alkenes or alkynes via such directed C−H bond cleavage have successfully been developed.[1] Besides the functional groups containing a neutral heteroatom, hydroxyl,[2] carboxyl,[3] and amide groups[2a,3a,4] can also act as good anionic anchors to exhibit the proximate effect.

As such examples, we demonstrated that 2-phenylphenols,[2e] *N*-(arylsulfonyl)-2-phenylanilines,[3a] and benzoic acids[3a] undergo direct oxidative coupling with alkenes under air in the presence of a Pd/Cu catalyst as depicted in Scheme 1 as a general sequence (−LH = 2-hydroxyphenyl, 2-(aminosulfonyl)phenyl, CO_2H). The reaction of the third substrates, benzoic acids, seems to be of particular interest because of their wide availability as aryl sources.[5] The reactions of benzoic acid with styrene and an acrylate afford isocoumarin and phthalide derivatives, respectively, via *ortho*-vinylation and subsequent oxidative or nonoxidative cyclization.[3a]

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SCHEME 1. Transition-Metal-Catalyzed Oxidative Coupling of Functionalized Aromatic Substrates with Unsaturated Compounds

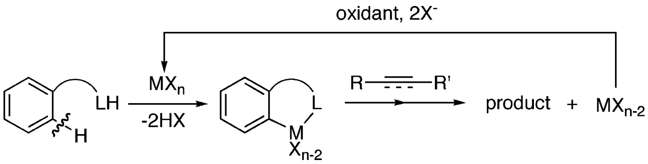
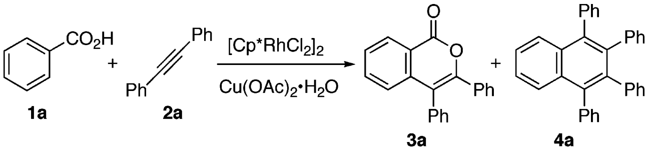


TABLE 1. Dehydrogenative Coupling of Benzoic Acid (1a) with Diphenylacetylene (2a)[a]



entry	$Cu(OAc)_2{\cdot}H_2O$ (mmol)	solvent	temp (°C)	time (h)	% yield[b] 3a	4a
1[c]	4	*o*-xylene	120	6	95	5
2[c]	4	*o*-xylene	100	9	94	2
3[c]	2	*o*-xylene	100	10	90 (81)	3
4[d]	0.025	*o*-xylene	120	5	25	32
5[d]	0.025	DMF	120	2	96 (93)	3
6[d]	0.025	DMSO	120	5	2	<1
7[d]	0.025	diglyme	120	5	0	4
8[d]	0.025	*n*-nonane	120	5	0	<1
9[d]	0.025	DMF	100	5	41	17

[a] Reaction conditions: [**1a**]/[**2a**]/[[$Cp^*RhCl_2]_2$] = 0.5:0.6:0.005 (in mmol), under N_2. [b] GC yield based on the amount of **1a** used. Value in parentheses indicates yield after purification. [c] [**1a**]/[**2a**] = 1:1.2 (in mmol). [d] Under air.

Isocoumarin and phthalide nuclei are found in various natural products that exhibit a broad range of interesting biological properties.[6] Although these reactions have high potential to provide atom-economic routes to such heterocycles,[7,8] their efficiency is moderate to low: decomposition of the homogeneous palladium-based catalyst into inactive bulk metal seems to be involved. During palladium-catalyzed oxidation, in general, the regeneration of Pd(II) from Pd(0) is considered to be the crucial step to determine catalyst efficiency.[9] Moreover, the coupling partners are so far limited to some alkenes, and the reactions with other unsaturated substrates including alkynes are unexplored. In the context of our study of catalytic coupling of benzoic acid derivatives,[10] we have succeeded in finding that the direct oxidative coupling of benzoic acids with internal alkynes can be realized by using Rh[11,12] in place of Pd as the principal catalyst component to afford isocoumarin derivatives in good to excellent yields.[13] Furthermore, by using an iridium catalyst, the corresponding naphthalene derivatives can be produced selectively from the same combination of substrates accompanied by decarboxylation. This represents a new example of aromatic homologation by the coupling of ArX and two alkyne molecules.[14] The results obtained with respect to the scope and limitations for these reactions are described herein.

Results and Discussion

When benzoic acid (**1a**) was treated with diphenylacetylene (**2a**, 1.2 equiv) in the presence of $[Cp^*RhCl_2]_2$ (1 mol %) and $Cu(OAc)_2{\cdot}H_2O$ (4 equiv) in *o*-xylene at 120 °C for 6 h under N_2, 3,4-diphenylisocoumarin (**3a**) was formed in 95% yield, along with a small amount of 1,2,3,4-tetraphenylnaphthalene (**4a**, 5%) (entry 1 in Table 1, Cp* = η^5-pentamethylcyclopentadienyl). No amount of **3a** or trace amounts of **3a** were obtained in the case using $RhCl_3{\cdot}H_2O$, $Rh(acac)_3$, $[RhCl(cod)]_2$, or $[RhCl(C_2H_4)_2]_2$ in place of $[Cp^*RhCl_2]_2$ (acac = acetylacetonate, cod = cyclooctadiene). Although the reaction was somewhat retarded, **3a** was obtained in 90% yield even using a reduced amount of $Cu(OAc)_2{\cdot}H_2O$ (2 equiv) at 100 °C (entry 3). The amount of the copper salt could be reduced to 5 mol % when the reaction was conducted under air. Thus, the aerobic oxidative coupling of **1a** with **2a** using a catalyst system of $[Cp^*RhCl_2]_2$/$Cu(OAc)_2{\cdot}H_2O$ proceeded efficiently in DMF at 120 °C to afford **3a** in 96% yield (entry 5). DMF was found to be the solvent of choice. Thus, a significant amount of **4a** (32%) was formed accompanied by a decrease of the yield of **3a** in *o*-xylene (entry 4). The reaction did not proceed catalytically in other solvents

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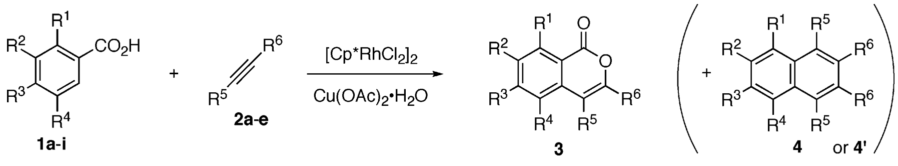
TABLE 2. Dehydrogenative Coupling of Benzoic Acids 1a−i with Alkynes 2a−e[a]



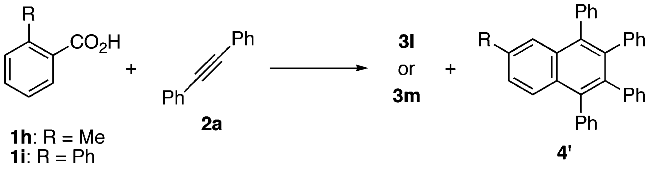
entry	**1**	R^1	R^2	R^3	R^4	**2**	R^5	R^6	conditions	time (h)	products, % yield[b]
1	**1a**	H	H	H	H	**2b**	Pr^n	Pr^n	A	9	**3b**, 96 (86)
2									B	2	**3b**, 83 (77)
3	**1a**	H	H	H	H	2c	$C_7H_{15}^n$	$C_7H_{15}^n$	A	9	**3c**, 96 (90)
4									B	2	**3c**, 97 (94)
5	**1a**	H	H	H	H	**2d**	Me	Ph	A	6	**3d**, 89 (86)[c]
6									B	2	**3d**, 84 (79)[c]
7	**1a**	H	H	H	H	**2e**	Bu^n	Ph	A	6	**3e**, 86 (81)[c]
8									**B**	**2**	**3e**, 88 (84)[c]
9	**1b**	H	H	Me	H	**2a**	Ph	Ph	A	8	**3f**, 92 (82); **4b**, 6 (6)
10									B	2	**3f**, 94 (84); **4b**, 6 (6)
11	**1c**	H	H	OH	H	**2a**	Ph	Ph	A	10	**3g**, (63)
12	**1d**	H	H	Cl	H	**2a**	Ph	Ph	A	8	**3h**, 82 (74); **4c**, 16 (12)
13									B[d]	2	**3h**, 84 (76); **4c**, 16 (13)
14	**1e**	H	H	CF_3	H	**2a**	Ph	Ph	A	10	**3i**, 73 (65); **4d**, 12 (10)
15									B[d]	2	**3i**, 59; **4d**, 16
16	**1f**	H	Me	H	H	**2a**	Ph	Ph	A	9	**3j**, 97 (92); **4b**, 3 (3)
17									B[d]	2	**3j**, 81 (75); **4b**, 2 (2)
18	**1g**	H	OMe	H	OMe	**2a**	Ph	Ph	A	5	**3k**, 99 (89)
19									B[d]	2	**3k**, 97 (92)
20	**1h**	Me	H	H	H	**2a**	Ph	Ph	A	10	**3l**, 67 (57); **4′e** (=**4b**), 17 (14)[e]
21									B[d]	2	**3l**, 91 (83); **4′e** (=**4b**), 7 (7)[e]
22	**1i**	Ph	H	H	H	**2a**	Ph	Ph	A[f]	4	**3m**, 42 (30); **4′f**, 53 (43)[g]

[a] Reaction conditions A: [**1**]/[**2**]/[[Cp*$RhCl_2$]$_2$]/[$Cu(OAc)_2\cdot H_2O$] = 1:1.2:0.005:2 (in mmol), in *o*-xylene at 120 °C under N_2; B: [**1**]/[**2**]/[[Cp*$RhCl_2$]$_2$]/$Cu(OAc)_2\cdot H_2O$) = 0.5:0.6:0.005:0.025 (in mmol), in DMF at 120 °C under air. [b] GC yield based on the amount of **1** used. Value in parentheses indicates yield after purification. [c] A minor amount of 3-alkyl-4-phenyl isomer was formed (see text). [d] At 140 °C. [e] 6-Methyl-1,2,3,4-tetraphenylnaphthalene **(4′e** = **4b**) was formed in place of 5-methyl-1,2,3,4-tetrahenylnaphthalene (**4**: R^1 = Me, $R^2 = R^3 = R^4$ = H, $R^5 = R^6$ = Ph). [f] With **2a** (2 mmol) at 160 °C. [g] 1,2,3,4,6-Pentaphenylnaphthalene **(4′f)** was formed in place of 1,2,3,4,5-pentaphenylnaphthalene (**4**: $R^1 = R^5 = R^6$ = Ph, $R^2 = R^3 = R^4$ = H).

such as DMSO, diglyme, and *n*-nonane (entries 6−8). Even in DMF, the reaction efficiency was low at 100 °C (entry 9). Again, $RhCl_3\cdot H_2O$, Rh(acac)$_3$, [RhCl(cod)]$_2$, and [RhCl(C_2H_4)$_2$]$_2$ showed no catalytic activity, as they showed none in the reaction using a stoichiometric amount of $Cu(OAc)_2\cdot H_2O$. The addition of the copper cocatalyst was crucial for the reaction. Thus, the reaction did not proceed without it.

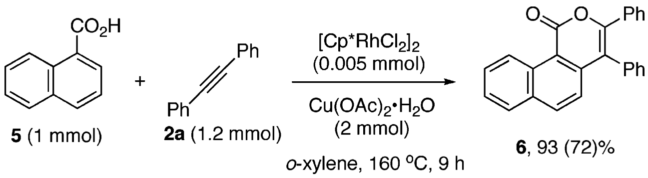
Table 2 summarizes the results for the coupling employing a series of benzoic acids and alkynes in the presence of a stoichiometric (conditions A) or catalytic amount of $Cu(OAc)_2\cdot H_2O$ (conditions B). The reaction of **1a** with dialkylacetylenes **2b** and **2c** proceeded efficiently, as that with diphenylacetylene, to produce 3,4-dialkylisocoumarins **3b** and **3c** in good yields under both conditions A and B (entries 1−4). From unsymmetrical alkylphenylacetylenes, **2d** and **2e**, 4-alkyl-3-phenylisocoumarins **3d** and **3e** were predominantly formed in 84−89% yields, along with minor amounts of their regioisomers, 3-alkyl-4-phenylisocoumarins (9, 5, 14, and 10% for entries 5, 6, 7, and 8, respectively). In these reactions of **1a** with **2b**−**e**, in contrast to the case using **1a** with **2a**, naphthalene derivatives as byproducts were not detected by gas chromatography−mass spectrometry (GC-MS). 1-Phenyl-2-(trimethylsilyl)acetylene and phenylacetylene did not couple with **1a** at all, and only a desilylative or dehydrogenative homocoupling product, diphenylbutadiyne, was detected by GC-MS. Bis(trimethylsilyl)acetylene and diethyl acetylenedicarboxylate could not be used for the reaction; they were consumed by unidentified reactions other than the desired coupling in treatment with **1a** under conditions A. Electron-rich (**1b**, **c**, **f**, **g**) and -deficient (**1d**, **e**) benzoic acids were found to react with **2a** smoothly under conditions A to give the corresponding substituted isocoumarins **3f**−**k** in 63−99% yields (entries 9, 11, 12, 14, 16, and 18). On the other hand, the oxidative coupling under conditions B also proceeded similarly (entries 10, 13, 15, 17, and 19), except that the reaction of 4-hydroxybenzoic acid (**1c**) with **2a** did not give **3g** at all under air. The reaction of 3-toluic acid (**1f**) exclusively gave a single regioisomer, 7-methyl-3,4-diphenylisocoumarin (**3j**) (entries 16 and 17). This indicates that the C−H bond cleavage only occurs at the sterically less hindered 6-position regioselectively. In most cases, minor amounts of **4** were also formed as separable byproducts. Although the reactions of sterically hindered benzoic acids **1h** and **1i** with **2a** proceeded under conditions A, considerable amounts of naphthalenes **4′** were formed with decrease of yields of **3** (entries 20 and 22). They were identified to be 6-substituted naphthalenes, 6-methyl-1,2,3,4-tetraphenylnaphthalene (**4′e** = **4b**) and 1,2,3,4,6-pentaphenylnaphthalene (**4′f**), and not the expected 5-substituted naphthalenes (Scheme 2). The 6-substituted naphthalenes were obtained similarly under iridium catalysis (vide infra).

SCHEME 2. Dehydrogenative Coupling of Benzoic Acids 1h, i with Diphenylacetylene (2a)

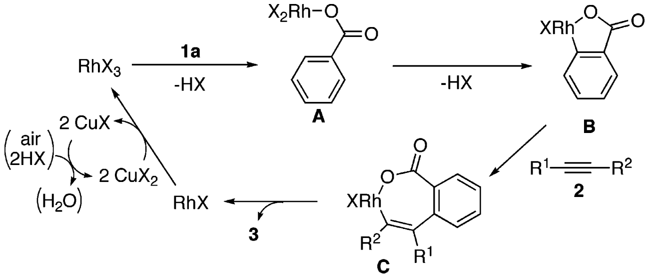


Under similar conditions to those for the reaction of **1i** with **2a** (Table 2, entry 22), 1-naphthoic acid (**5**) efficiently underwent

SCHEME 3. Dehydrogenative Coupling of 1-Naphthoic Acid (5) with Diphenylacetylene (2a)



SCHEME 4. A Plausible Mechanism for the Rhodium-Catalyzed Reaction of 1a with 2



coupling with **2a** to give **6** exclusively in 93% yield (Scheme 3).

A plausible mechanism for the reaction of benzoic acid (**1a**) with alkyne **2** is illustrated in Scheme 4, in which neutral ligands are omitted. Coordination of the carboxylate oxygen to Cp^*RhX_2(III) gives a rhodium(III) benzoate **A**. Subsequent *ortho*-rhodation to form a rhodacycle intermediate **B**,[15] alkyne insertion, and reductive elimination occur to produce isocoumarin **3**. The resulting Cp*Rh(I) species may be oxidized in the presence of a copper(II) salt to regenerate Cp^*RhX_2(III). Under air (conditions B), Cu(I) formed in the last step may also be reoxidized to Cu(II). No deposition of deactivated bulk metal is observed during the reaction, while this often occurs in Pd/Cu-catalyzed reactions.[9] The minor products, naphthalene **4** and **4′**, may be produced via decarboxylation of **C**, the second insertion of **2**, and reductive elimination, as proposed for the iridium catalysis (vide infra, Scheme 8).

Benzoic acid (**1a**) also reacted with *n*-butyl acrylate (**9a**) smoothly under conditions B using a less polar solvent such as *o*-xylene (Scheme 5). Interestingly, disubstitution at both the ortho-positions occurred to afford 7-vinylphthalide **8a** as a 1:2 coupling product in 66% isolated yield along with a minor amount of its dehydrogenated separable derivative **9a**. In DMF, which is the solvent of choice for the isocoumarin synthesis (Table 1), the reaction was sluggish to give **8a** in a poor yield (ca. 10%). The reaction of **1a** with ethyl acrylate (**7b**) also proceeded efficiently in *o*-xylene to give the corresponding phthalide **8b** in 76% yield.

In this reaction, a rhodacycle intermediate, generated in a similar manner to that in the reaction with alkynes (**B** in Scheme 4), may undergo alkene insertion and successive β-hydride elimination to form the *ortho*-monovinylated benzoic acid. Prior to the nucleophilic cyclization, the second vinylation takes place to lead to the divinylated product **8** along with **9**.

In contrast to the acrylates, *N*,*N*-dimethylacrylamide (**7c**) and acrylonitrile (**7d**) reacted with **1a** in a 1:1 ratio under similar conditions to afford **10c** and **10d** (Scheme 6). In these cases, the cyclization exclusively occurs after the first vinylation (see Scheme 5), as occurs in the palladium-catalyzed reaction.[3a]

The synthesis of naphthalene derivatives by the 1:2 coupling of benzoic acids **1** with alkynes **2** was next examined aiming at developing a new method for aromatic homologation. Treatment of **1a** with **2a** (2 equiv) in the presence of $[Cp^*RhCl_2]_2$ (1 mol %) and $Cu(OAc)_2{\cdot}H_2O$ (4 equiv) in mesitylene at 180 °C for 2 h gave a mixture of **3a** and **4a** in 81% and 19% yields, respectively (Table 3, entry 1). The naphthalene **4a** became a predominant product (**3a**:**4a** = 40:60) when the reaction was conducted using AgOAc (4 equiv) in place of the copper salt as an oxidant (entry 2). Ag_2CO_3 (2 equiv) could be used as well as AgOAc (entry 4). Interestingly, it was found that **4a** can be obtained exclusively under iridium catalysis. Thus, the reaction in the presence of $[Cp^*IrCl_2]_2$ (2 mol %) and AgOAc (2 equiv) in *o*-xylene at 160 °C for 6 h afforded **4a** in 73% yield and did not give **3a** (entry 6). Ag_2CO_3 (1 equiv) was as effective as AgOAc (entry 7). The reactions in polar solvents such as DMAc, DMSO, and diglyme were sluggish (entries 8−10). When $[IrCl(cod)]_2$, $[IrCl(coe)_2]_2$, and $IrCl(CO)(PPh_3)_2$ were used in place of $[Cp^*IrCl_2]_2$, the reaction did not proceed catalytically (entries 11−13). Increasing the amount of Ag_2CO_3 to 2 equiv enhanced the yield of **4a** up to 88% (entry 15). Decreasing the amount of catalyst to 1 mol % still gave 60% yield of **4a** (entry 16).

Table 4 summarizes the results for the reactions of substituted benzoic acids **1** with 2 equiv of diarylacetylenes **2** in the presence of $[Cp^*IrCl_2]_2$ and Ag_2CO_3. Bis(4-methoxyphenyl)-(**2f**) and bis(4-chlorophenyl)acetylene (**2g**) reacted with **1a** efficiently to give the corresponding 1,2,3,4-tetraarylnaphthalenes **4g** and **4h** in 64% and 91% yields, respectively (entries 1 and 2). In contrast to the rhodium-catalyzed reactions (Table 2), the iridium-catalyzed reactions with dialkylacetylenes were found to be sluggish. Thus, treatment of **1a** with **2b** and **2c**

SCHEME 5. Dehydrogenative Coupling of Benzoic Acid (1a) with Acrylates 7a, b

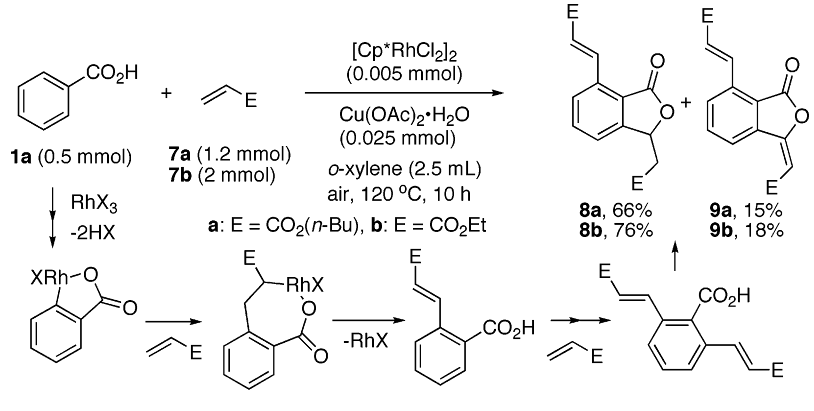
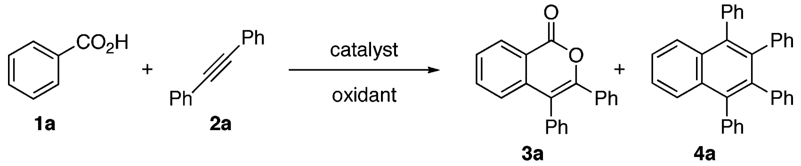


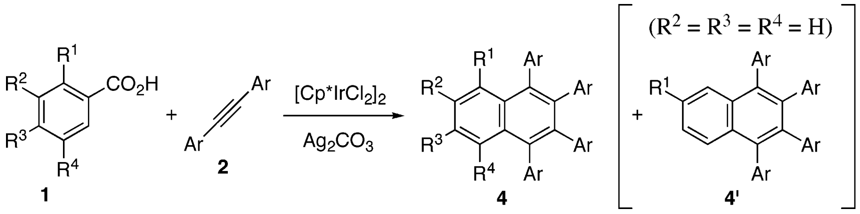
TABLE 3. Dehydrogenative, Decarboxylative Coupling of Benzoic Acid (1a) with Diphenylacetylene (2a)[a]



entry	catalyst	oxidant (mmol)	solvent	temp (°C)	time (h)	% yield[b]	
						3a	4a
1[c]	[Cp*RhCl$_2$]$_2$	Cu(OAc)$_2$·H$_2$O (1)	mesitylene	180	2	81	19
2[c]	[Cp*RhCl$_2$]$_2$	AgOAc (1)	mesitylene	180	2	40 (43)	60 (57)
3	[Cp*RhCl$_2$]$_2$	AgOAc (1)	mesitylene	180	2	39	61
4[c]	[Cp*RhCl$_2$]$_2$	Ag$_2$CO$_3$ (0.5)	mesitylene	180	2	41	59
5	[Cp*IrCl$_2$]$_2$	Cu(OAc)$_2$·H$_2$O (0.5)	*o*-xylene	160	6		18
6	[Cp*IrCl$_2$]$_2$	AgOAc (0.5)	*o*-xylene	160	6		73
7	[Cp*IrCl$_2$]$_2$	Ag$_2$CO$_3$ (0.25)	*o*-xylene	160	6		75
8	[Cp*IrCl$_2$]$_2$	Ag$_2$CO$_3$ (0.25)	DMAc	160	6		12
9	[Cp*IrCl$_2$]$_2$	Ag$_2$CO$_3$ (0.25)	DMSO	160	6		2
10	[Cp*IrCl$_2$]$_2$	Ag$_2$CO$_3$ (0.25)	diglyme	160	6		31
11	[IrCl(cod)]$_2$	Ag$_2$CO$_3$ (0.25)	*o*-xylene	160	6		2
12	[IrCl(coe)$_2$]$_2$	Ag$_2$CO$_3$ (0.25)	*o*-xylene	160	6		<1
13	IrCl(CO)(PPh$_3$)$_2$	Ag$_2$CO$_3$ (0.25)	*o*-xylene	160	6		<1
14	[Cp*IrCl$_2$]$_2$	Ag$_2$CO$_3$ (0.25)	*o*-xylene	120	10		70
15	[Cp*IrCl$_2$]$_2$	Ag$_2$CO$_3$ (0.5)	*o*-xylene	160	6		88 (79)
16[c]	[Cp*IrCl$_2$]$_2$	Ag$_2$CO$_3$ (0.5)	*o*-xylene	160	6		60

[a] Reaction conditions: [**1a**]/[**2a**]/[catalyst] = 0.25:0.5:0.005 (in mmol), under N$_2$. [b] GC yield based on the amount of **1a** used. Value in parentheses indicates yield after purification. [c] [catalyst] = 0.0025 (in mmol).

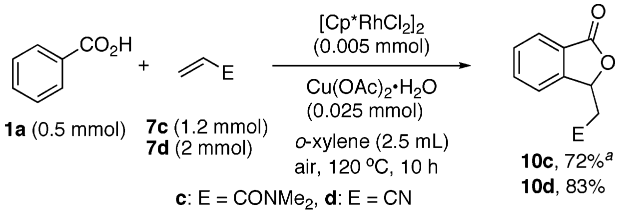
TABLE 4. Reaction of Benzoic Acids 1 with Diarylacetylenes 2 Accompanied by Dehydrogenation and Decarboxylation[a]



entry	1	R^1	R^2	R^3	R^4	2	Ar	time (h)	products, % yield[b]
1	**1a**	H	H	H	H	**2f**	4-MeOC$_6$H$_4$	3	**4g**, 64 (53)
2	**1a**	H	H	H	H	**2g**	4-ClC$_6$H$_4$	2	**4h**, 91 (89)
3	**1b**	H	H	Me	H	**2a**	Ph	2	**4b**, 95 (86)
4	**1j**	H	Me	H	Me	**2a**	Ph	2	**4i**, 93 (85)
5	**1k**	Cl	H	H	H	**2a**	Ph	10	**4j** and **4′k** (=**4c**) (3:1), 63 (63)
6	**1h**	Me	H	H	H	**2a**	Ph	6	**4′e** (= **4b**), 88(81)
7[c]	**1l**	Cy	H	H	H	**2a**	Ph	10	**4′l**, 60 (60)
8	**1m**	O(*i*-Pr)	H	H	H	**2a**	Ph	2	**4′m**, 80 (76)

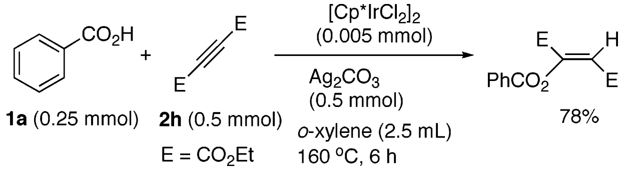
[a] Reaction conditions: [**1**]/[**2**]/[[Cp*IrCl$_2$]$_2$]/[Ag$_2$CO$_3$] = 0.25:0.5:0.005:0.5 (in mmol), in *o*-xylene at 160 °C under N$_2$. [b] GC yield based on the amount of **1** used. Value in parentheses indicates yield after purification. [c] R^1 = Cy = cyclohexyl.

SCHEME 6. Dehydrogenative Coupling of Benzoic Acid (1a) with Alkenes 7c, d



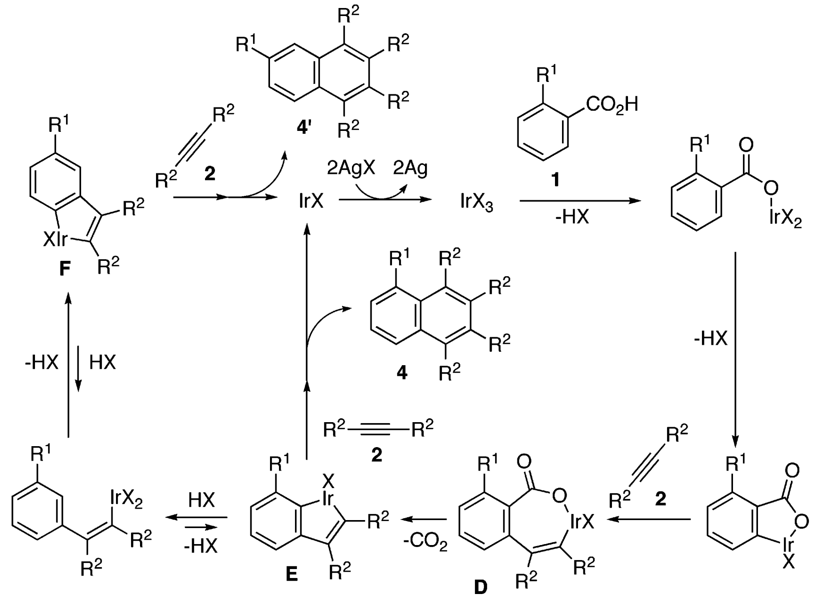
[a] The reaction was conducted at 160 °C.

SCHEME 7. Reaction of Benzoic Acid (1a) with Diethyl Acetylenedicarboxylate (2h)



gave the corresponding tetraalkylnaphthalenes in low yields (10−20%, by GC-MS). Diethyl acetylenedicarboxylate (**2h**) reacted with **1a** to afford not the desired naphthalene but an O−H adduct, diethyl (*Z*)-(benzoyloxy)fumarate, in 78% yield (Scheme 7). The reactions of **1b** and 3,5-dimethylbenzoic acid (**1j**) with **2a** proceeded smoothly to give naphthalenes **4b** and **4i** in 95 and 93% yields, respectively (entries 3 and 4). The reaction of 2-chlorobenzoic acid (**1k**) with **2a** gave not only an expected naphthalene, 5-chloro-1,2,3,4-tetraphenylnaphthalene

SCHEME 8. A Plausible Mechanism for the Iridium-Catalyzed Reaction of 1 with 2



(**4j**), but also its isomer, 6-chloro-1,2,3,4-tetraphenylnaphthalene (**4′k** = **4c**). The possible pathway toward the latter unexpected naphthalene via isomerization will be discussed below (Scheme 8). Furthermore, the reactions of other 2-substituted benzoic acids **1h**−**m** with **2a** proceeded involving the isomerization to exclusively form 6-substituted 1,2,3,4-tetraphenylnaphthalenes **4′e** (=**4b**), **4′l**, and **4′m** in 60−88% yields (entries 6−8).

A plausible mechanism for the reaction of benzoic acids **1** with diarylacetylenes **2** by the iridium catalysis is illustrated in Scheme 8, in which neutral ligands are omitted. A seven-membered iridacycle intermediate **D** appears to be generated in a manner similar to that to a rhodacycle **C** in Scheme 4. Then, **D** undergoes decarboxylation to form a key, five-membered iridacycle intermediate **E** rather than reductive elimination that is a preferable pathway in the rhodium catalysis. Subsequently, the second alkyne insertion and reductive elimination occur to produce naphthalene **4**. The resulting Ir(I)X species may be oxidized in the presence of the silver salt to regenerate Ir(III)X_3. In the cases with 2-substituted benzoic acids, the key intermediate **E** may undergo rearrangement driven by steric reasons through protonation and cycloiridation to form an isomeric iridacycle **F**, which reacts with alkyne to afford 6-substituted naphthalene **4′**.

In summary, we have demonstrated that the oxidative coupling reaction of benzoic acids with internal alkynes can be performed in the presence of a rhodium catalyst and a copper oxidant to selectively give the corresponding 1:1 coupling products, isocoumarin derivatives. The reaction proceeds catalytically with respect to both metals under air. Under the aerobic conditions, the coupling of benzoic acids with acrylates takes place efficiently. On the other hand, the acids and alkynes have been found to react in a ratio of 1:2 under iridium catalysis to produce naphthalene derivatives exclusively accompanied by decarboxylation. Rh− and Ir−catalyst systems for oxidative C−C coupling reactions have been less explored than those with Pd. The present catalyst systems and related ones are expected to be applicable to other coupling reactions. Work is underway toward further development of the catalysis.

Experimental Section

Rh/Cu-Catalyzed Reaction of Benzoic Acid (1a) with Diphenylacetylene (2a) (Entry 5 in Table 1). To a 20 mL two-necked flask were added benzoic acid (**1a**) (0.5 mmol, 61 mg), diphenylacetylene (**2a**) (0.6 mmol, 107 mg), $[Cp^*RhCl_2]_2$ (0.005 mmol, 3.1 mg), $Cu(OAc)_2\cdot H_2O$ (0.025 mmol, 5 mg), 1-methylnaphthalene (ca. 50 mg) as internal standard, and DMF (2.5 mL). The resulting mixture was stirred under air (with a calcium chloride tube) at 120 °C (bath temperature) for 2 h. After cooling, analysis of the mixture by GC confirmed formation of compounds **3a** and **4a** in 96 and 3% yields, respectively. The product **3a** (139 mg, 93%) was also isolated by evaporation of DMF in vacuo and chromatography on silica gel using hexane-ethyl acetate (98:2, v/v). Compound **3a**: mp 172−174 °C (lit.[16] 170 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16−7.27 (m, 6H), 7.33 (d, $J = 8.3$ Hz, 2H), 7.39−7.44 (m, 3H), 7.52 (dd, $J = 7.6, 7.6$ Hz, 1H), 7.64 (ddd, $J = 7.6, 7.6, 1.5$ Hz, 1H), 8.41 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 116.9, 120.4, 125.3, 127.8 (2C), 128.06, 128.09, 128.9, 129.0 (2C), 129.2 (2C), 129.5, 131.2 (2C), 132.9, 134.3, 134.6, 138.8, 150.9, 162.2; HRMS m/z (M^+) calcd for $C_{21}H_{14}O_2$: 298.0994. Found 298.0998.

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Supporting Information Available: Standard experimental procedure and characterization data of products. This material is available free of charge via the Internet at http://www.pubs.acs.org.

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(16) Delaunay, J.; Simonet, J. *Tetrahedron Lett.* **1988**, *29*, 543.