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Rhodium-Catalyzed Oxidative Coupling between Salicylaldehydes and Internal Alkynes with C–H Bond Cleavage To Produce 2,3-Disubstituted Chromones

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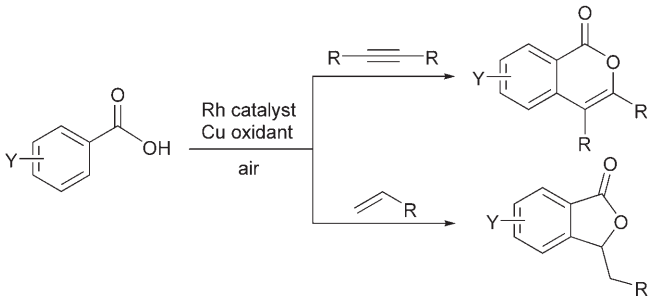
Abstract: A direct oxidative coupling of salicylaldehydes with internal alkynes proceeds efficiently with cleavage of the aldehyde C–H bond to produce the corresponding chromone derivatives. A rhodium catalyst in combination with a cyclopentadiene ligand and a copper oxidant promote this straightforward annulation reaction. Solid-state luminescence was observed for certain chromone products.

Keywords: C–C coupling · C–H activation · homogeneous catalysis · oxidation · rhodium

Introduction

Transition-metal-catalyzed organic reactions involving C–H bond cleavage have attracted much attention from the point of view of atom economy, and various catalytic processes have been developed on the basis of different modes of activation of the ubiquitously available bond.[1] Among the most promising activation strategies is the use of a metal-directing group in an appropriate substrate to bring about regioselective C–H functionalization. We demonstrated previously that some functionalized arenes undergo oxidative coupling with alkenes in the presence of a Pd catalyst and a Cu/air oxidant.[2] For example, benzoic acids react with styrene and an acrylate to afford isocoumarin and phthalide derivatives, respectively, through *ortho* vinylation directed by the carboxy functionality and subsequent oxidative or nonoxidative cyclization.[2a] Furthermore, we discovered recently a more efficient atom-economical synthesis of such O-containing heterocycles through the oxidative coupling of benzoic acids with alkynes and alkenes in the presence of a Rh catalyst system (Scheme 1).[3] Rh-based systems for oxidative C–C coupling reactions[4] have been explored less than those with Pd.[1q,5] In the course of our studies on Rh-catalyzed C–H functionalization,[3,6] we discovered that salicylaldehydes also react with internal alkynes under similar conditions in the presence of a Rh catalyst to produce 2,3-disubstituted chromone derivatives through vinylation at the aldehyde C–H bond[6a,b,7] and subsequent oxidative cyclization. Chromone structures are found in a wide variety of naturally occurring compounds that exhibit a broad range of interesting biological activities.[8] They are also of interest for their fluorescence properties.[9] We describe herein a method for the synthesis of 2,3-disubstituted chromones through the rhodium-catalyzed oxidative coupling of salicylaldehydes with internal alkenes.



Scheme 1. Reactions of benzoic acids with alkynes and alkenes.

Results and Discussion

In an initial attempt to carry out the desired coupling reaction, salicylaldehyde (**1a**; 0.5 mmol) was treated with diphenylacetylene (**2a**; 0.5 mmol) under conditions similar to those employed for the coupling of benzoic acids with **2a**.[3a]

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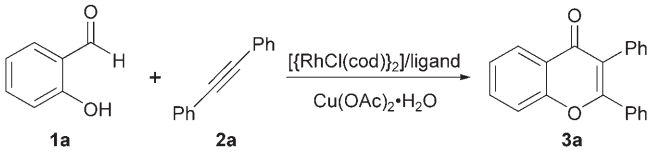
In the presence of $[\{Cp^*RhCl_2\}_2]$ (0.005 mmol) and $Cu(OAc)_2{\cdot}H_2O$ (1 mmol) in *o*-xylene at 150 °C (bath temperature) under N_2, 2,3-diphenylchromone (**3a**) formed in only 6% yield in 4 h (Table 1, entry 1; $Cp^* = \eta^5$-pentamethylcyclopentadienyl). A similar poor result was obtained when $[\{RhCl(cod)\}_2]$ was used in place of $[\{Cp^*RhCl_2\}_2]$ (Table 1, entry 2; cod = 1,5-cyclooctadiene). Interestingly, the addition of 1,2,3,4-tetraphenyl-1,3-cyclopentadiene ($C_5H_2Ph_4$; 0.02 mmol) as a ligand in combination with $[\{RhCl(cod)\}_2]$ led to a significant improvement in the yield of **3a** to 88% (Table 1, entry 3).[10] The phenylated cyclopentadiene ligands $C_5H_3Ph_3$ and C_5HPh_5 were less effective than $C_5H_2Ph_4$ (Table 1, entries 4 and 5). The replacement of $Cu(OAc)_2{\cdot}H_2O$ with other oxidants, such as $Cu(OCOCF_3)_2$ and AgOAc, led to a significant decrease in the yield (Table 1, entries 6 and 7). The reaction did not proceed catalytically in the presence of a catalytic amount of $Cu(OAc)_2{\cdot}H_2O$ in air. Finally, the best result was obtained with the catalyst system $[\{RhCl(cod)\}_2]/C_5H_2Ph_4/Cu(OAc)_2{\cdot}H_2O$ at 140 °C, under which conditions **3a** was produced in 92% yield (Table 1, entry 8). A further decrease in the reaction temperature to 120 °C led to a decrease in the efficiency of the reaction (Table 1, entry 9).

Table 1. Oxidative coupling of salicylaldehyde (**1a**) with diphenylacetylene (**2a**).[a]



1a 2a 3a

Entry	Ligand	T [°C]	t [h]	Yield [%][b]
1[c]	–	150	4	6
2	–	150	2	2
3	$C_5H_2Ph_4$	150	2	88
4	$C_5H_3Ph_3$	150	7	43
5	C_5HPh_5	150	2	0
6[d]	$C_5H_2Ph_4$	150	2	0
7[e]	$C_5H_2Ph_4$	150	4	31
8	$C_5H_2Ph_4$	140	2	92 (86)
9	$C_5H_2Ph_4$	120	12	73

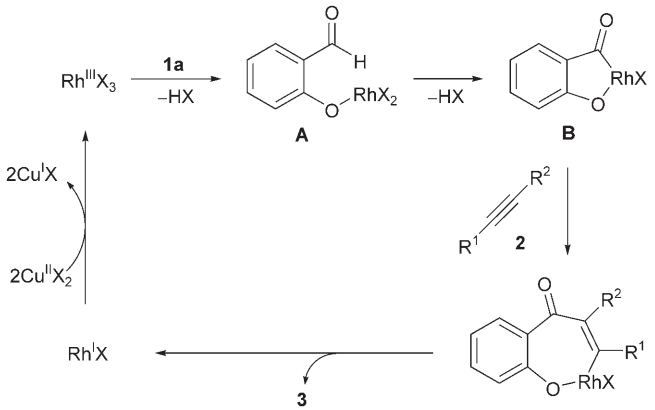
[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), $[\{RhCl(cod)\}_2]$ (0.005 mmol), ligand (0.02 mmol), $Cu(OAc)_2{\cdot}H_2O$ (1 mmol), *o*-xylene (2.5 mL), N_2 atmosphere. [b] The yield of **3a** was determined by GC. The value in parentheses indicates the yield after purification. [c] $[\{Cp^*RhCl_2\}_2]$ was used in place of $[\{RhCl(cod)\}_2]$. [d] $Cu(OCOCF_3)_2$ was used in place of $Cu(OAc)_2{\cdot}H_2O$. [e] AgOAc (2 mmol) was used in place of $Cu(OAc)_2{\cdot}H_2O$.

Under the optimized conditions (Table 1, entry 8), 2-hydroxy-4-methoxybenzaldehyde (**1b**) reacted effectively with **2a** to produce 7-methoxy-2,3-diphenylchromone (**3b**; Table 2, entry 1). This protocol provides a simple and useful route to 7-alkoxy- and 7-hydroxy-2,3-diphenylchromone derivatives, which are of particular interest because of their biological activities.[8a–d] The 3-methoxy-, 5-chloro-, and 5-nitro-2-hydroxybenzaldehydes **1c–e** underwent oxidative coupling with **2a** to afford the corresponding chromones **3c–e** (Table 2, entries 2–4). The reaction of 2-hydroxy-1-naphthaldehyde (**1f**) with **2a** also proceeded smoothly, although a separable mixture of the expected product 2,3-diphenyl-5,6-benzochromone (**3f**) and a decarbonylative coupling product, 2,3-diphenylnaphtho[2,1-*b*]furan (**4**), was obtained in this case (Table 2, entry 5).

Table 3 summarizes the results for the coupling of **1a** with several internal alkynes **2b–f**. The methyl-, methoxy-, and chloro-substituted diphenylacetylenes **2b–d** and bis(2-thienyl)acetylene (**2e**) were used in place of **2a** to form the 2,3-diaryl chromones **3g–j** in good yields (Table 3, entries 1–4). 1-Phenylpropyne (**2f**) reacted with **1a** to afford 3-methyl-2-phenylchromone (**3k**) in moderate yield, along with a minor amount of an isomer of **3k** (Table 3, entry 5). Diphenylacetylene (**1a**) also reacted with 8-hexadecyne (**2g**) to give 2,3-diheptylchromone (**3l**; Table 3, entry 6). In contrast to these internal alkynes, phenylacetylene underwent oxidative dimerization rather than cross-coupling with **1a** under similar conditions to form 1,4-diphenyl-1,3-butadiyne in 72% yield.

Preliminary fluorescence analysis of the chromones indicated that **3h** and **3i** show solid-state luminescence ($\lambda_{max,em}$(**3h**) = 439 nm; $\lambda_{max,em}$(**3i**) = 485 nm). In particular, the emission of compound **3h** was of a comparable strength to that of tris(8-hydroxyquinolino)aluminum (Alq_3), which is a well-known green emitter. In contrast, **3a**, **3g**, and **3j** were not fluorescent.

A plausible mechanism for the reaction of salicylaldehyde (**1a**) with alkynes **2** is illustrated in Scheme 2, in which neutral ligands are omitted for clarity. The coordination of the phenolic oxygen atom to an $Rh^{III}X_3$ species gives a rhodium(III) phenolate **A**. Directed C–H rhodation to form a rhodacycle intermediate **B**[11] is then followed by alkyne insertion and reductive elimination to form a chromone **3**. The resulting Rh^IX species is oxidized by the copper(II) salt to



Scheme 2. Plausible mechanism for the reaction of **1a** with alkynes **2**.

Abstract in Japanese:

サリチルアルデヒド類と内部アルキンとの酸化的カップリングが、アルデヒドC–H結合切断を伴って効率よく進行し、クロモン誘導体が生成することを見出した。この直接的な環化反応は、ロジウム触媒をシクロペンタジエン配位子および銅酸化剤とともに用いることにより効果的に促進される。ここで得られたいくつかのクロモン類は、固体蛍光を示した。

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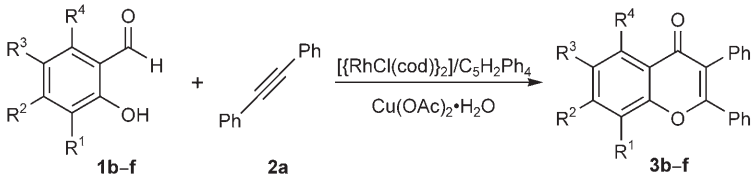
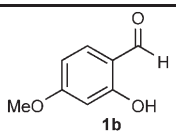
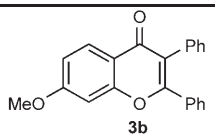
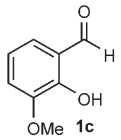
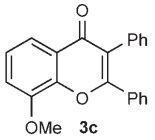
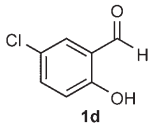
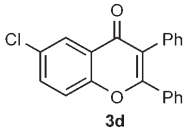
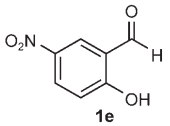
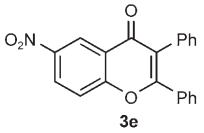
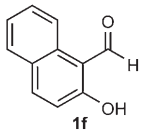
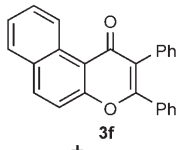
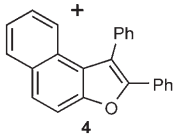
Table 2. Oxidative coupling of salicylaldehydes **1b–f** with **2a**.[a]



Entry	**1**	*t* [h]	Product	Yield [%][b]
1	 **1b**	2	 **3b**	90 (84)
2	 **1c**	2	 **3c**	86 (70)
3	 **1d**	2	 **3d**	93 (78)
4[c]	 **1e**	8	 **3e**	52 (46)
5	 **1f**	4	 **3f** +  **4**	49 (45) 37 (34)

[a] Reaction conditions: **1** (0.5 mmol), **2a** (0.5 mmol), [{RhCl(cod)}$_2$] (0.005 mmol), $C_5H_2Ph_4$ (0.02 mmol), $Cu(OAc)_2{\cdot}H_2O$ (1 mmol), *o*-xylene (2.5 mL), 140 °C, N_2 atmosphere. [b] The yield of **3** was determined by GC. The value in parentheses indicates the yield after purification. [c] The reaction was carried out at 150 °C.

regenerate $Rh^{III}X_3$.[12] Although the exact role of the $C_5H_2Ph_4$ ligand is not clear at the present stage, it may support the unstable Rh^I species during the reoxidation step to prolong the lifetime of the catalyst. The C–H bond-cleavage step from **A** to **B** may be promoted effectively by the metal-directing hydroxy oxygen atom. We confirmed that an *O*-protected salicylaldehyde, 2-methoxybenzaldehyde, did not react with **2a** at all. In the reaction of **1f** with **2a** (Table 2, entry 5), partial decarbonylation occurred to form **4**. Although the specific details of the decarbonylation step are not identifiable at present, steric *peri* repulsion appears to promote the side reaction.

Conclusions

In summary, we have demonstrated that salicylaldehydes undergo oxidative coupling with internal alkynes in the presence of a rhodium catalyst, a cyclopentadiene ligand, and a copper oxidant to give selectively the corresponding 2,3-disubstituted chromone derivatives with cleavage of the aldehyde C–H bond. Rh-based catalyst systems are less common than Pd catalysts for oxidative C–C coupling reactions. We expect this and related catalyst systems to be applicable to other coupling reactions. Studies are under way toward the further development of this catalysis.

Experimental Section

General

GC analysis was carried out with 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 with a CBP-1 capillary column (i.d. 0.25 mm × 25 m). The structures of all products were determined unambiguously by ^1H and ^{13}C NMR spectroscopy with the aid of NOE, COSY, HMQC, and HMBC experiments.

Diaryl acetylenes **2b–e**[13] and 1,2,4-triphenyl-1,3-cyclopentadiene[14] were prepared according to published procedures. Other starting materials and reagents were purchased. Copies of the ^{13}C NMR spectra of **3j** and **3l** are provided in the Supporting Information.

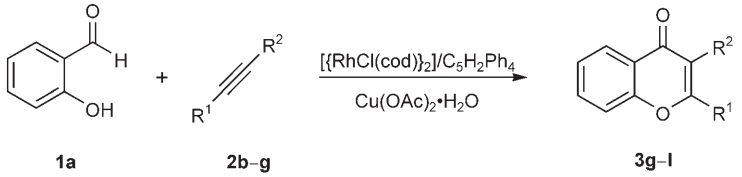
Syntheses

General procedure for the oxidative coupling of salicylaldehydes with internal alkynes: The salicylaldehyde **1** (0.5 mmol), the internal alkyne **2** (0.5 mmol), [{RhCl(cod)}$_2$] (2.5 mg, 0.005 mmol), $C_5H_2Ph_4$ (7.4 mg, 0.02 mmol), $Cu(OAc)_2{\cdot}H_2O$ (199 mg, 1 mmol), 1-methylnaphthalene (≈50 mg, as an internal standard), and *o*-xylene (2.5 mL) were placed in a 20-mL two-necked flask. The resulting mixture was stirred under N_2 at 140 °C (bath temperature) for 2–8 h. GC and GC–MS analysis of the mixture confirmed the formation of **3** (and **4**). The product was isolated by chromatography on silica gel with hexane/ethyl acetate. Solid products were recrystallized from hexane/ethyl acetate.

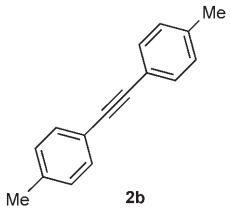
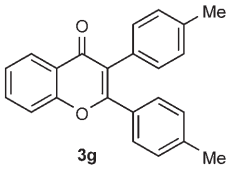
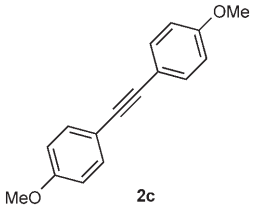
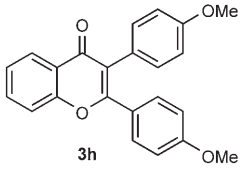
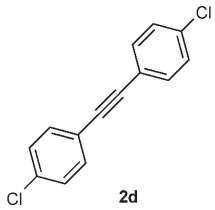
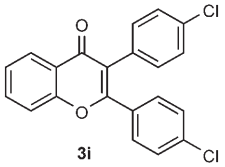
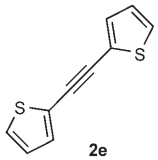
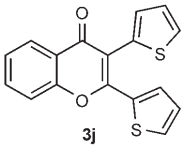
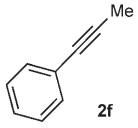
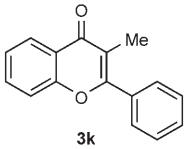
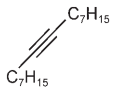
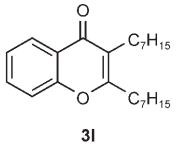
3a: 2,3-Diphenylchromone: m.p.: 151–153 °C (lit.:[15] 152 °C); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.21$–7.45 (m, 11H), 7.54 (d, $J = 8.0$ Hz, 1H), 7.71 (ddd, $J = 8.8$, 7.3, 1.4 Hz, 1H), 8.30 ppm (dd, $J = 8.0$, 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 118.0$, 123.0, 123.5, 125.1, 126.4, 127.6, 128.1, 128.2, 129.6, 130.0, 131.2, 132.8, 133.3, 133.7, 156.1, 161.5, 177.3 ppm; HRMS (EI): *m*/*z* calcd for $C_{21}H_{14}O_2$: 298.0994; found: 298.0987.

3b: 7-Methoxy-2,3-diphenylchromone: m.p.: 222–223 °C (lit.:[16] 215 °C); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.92$ (s, 3H), 6.93 (d, $J = 2.2$ Hz, 1H), 7.00 (dd, $J = 8.8$, 2.2 Hz, 1H), 7.20–7.39 (m, 10H), 8.19 ppm (d, $J = 8.8$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 55.8$, 100.0, 114.5, 117.4, 122.8, 127.5, 127.8, 128.0, 128.2, 129.5, 129.9, 131.2, 132.9, 133.4, 157.8,

Table 3. Oxidative coupling of **1a** with alkynes **2b–g**.[a]



1a **2b–g** **3g–l**

Entry	**2**	*t* [h]	Product	Yield [%][b]
1	 **2b**	2	 **3g**	98 (88)
2	 **2c**	2	 **3h**	92 (90)
3[c]	 **2d**	6	 **3i**	83 (75)
4	 **2e**	4	 **3j**	78 (73)
5	 **2f**	4	 **3k**	40 (36)[d]
6		2	 **3l**	27 (23)

[a] Reaction conditions: **1a** (0.5 mmol), **2** (0.5 mmol), [{RhCl(cod)}$_2$] (0.005 mmol), $C_5H_2Ph_4$ (0.02 mmol), Cu(OAc)$_2$·H$_2$O (1 mmol), *o*-xylene (2.5 mL), 140 °C, N_2 atmosphere. [b] The yield of **3** was determined by GC. The value in parentheses indicates the yield after purification. [c] The reaction was carried out at 150 °C. [d] An isomer of **3k** was also formed in 15% yield.

3c: 8-Methoxy-2,3-diphenylchromone: m.p.: 173–178 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.01 (s, 3H), 7.18–7.36 (m, 10H), 7.42–7.45 (m, 2H), 7.84 ppm (dd, J = 8.0, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.4, 114.2, 117.1, 122.8, 124.5, 124.7, 127.6, 128.1, 128.2, 129.7, 130.0, 131.2, 132.9, 133.2, 146.5, 148.9, 161.1, 177.3 ppm; MS (EI): m/z = 328 $[M]^+$; elemental analysis: calcd (%) for $C_{22}H_{16}O_3$: C 80.47, H 4.91; found: C 80.35, H 4.89.

3d: 6-Chloro-2,3-diphenylchromone: m.p.: 175–180 °C (lit.:[17] 178–179 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19–7.39 (m, 10H), 7.50 (d, J = 8.8 Hz, 1H), 7.65 (dd, J = 8.8, 2.6 Hz, 1H), 8.25 (d, J = 2.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 119.7, 123.0, 124.5, 125.7, 127.8, 128.1, 128.3, 129.5, 130.3, 131.0, 131.1, 132.4, 132.9, 133.9, 154.4, 161.7, 176.2 ppm; HRMS (EI): m/z calcd for $C_{21}H_{13}ClO_2$: 332.0604; found: 332.0608.

3e: 6-Nitro-2,3-diphenylchromone: m.p.: 214–216 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21–7.42 (m, 10H), 7.69 (d, J = 9.2 Hz, 1H), 8.54 (dd, J = 9.2, 2.6 Hz, 1H), 9.16 (d, J = 3.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 119.7, 123.2, 123.5, 123.6, 128.0, 128.2, 128.3, 128.5, 129.6, 130.7, 131.0, 131.7, 132.3, 144.8, 158.9, 162.0, 176.0 ppm; MS (EI): m/z = 343 $[M]^+$; elemental analysis: calcd (%) for $C_{21}H_{13}NO_4$: C 73.46, H 3.82, N 4.08; found: C 73.29, H 3.82, N 4.12.

3f: 2,3-Diphenyl-5,6-benzochromone: m.p.: 192–194 °C (lit.:[15] 188 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.38 (m, 8H), 7.44–7.47 (m, 2H), 7.59–7.64 (m, 2H), 7.73 (ddd, J = 8.4, 7.0, 1.5 Hz, 1H), 7.92 (d, J = 7.7 Hz, 1H), 8.12 (d, J = 9.2 Hz, 1H), 10.10 ppm (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 116.7, 117.6, 125.3, 126.5, 127.2, 127.7, 128.1, 128.2, 128.3, 129.3, 129.5, 130.0, 130.7, 130.8, 131.2, 132.9, 133.1, 135.6, 157.3, 159.0, 179.0 ppm; HRMS (EI): m/z calcd for $C_{25}H_{16}O_2$: 348.1150; found: 348.1135.

4: 2,3-Diphenylnaphtho[2,1-*b*]furan[18] was obtained as an oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22–7.29 (m, 4H), 7.36–7.40 (m, 1H), 7.52–7.56 (m, 8H), 7.73 (dd, J = 12.8, 8.8 Hz, 2H), 7.90 ppm (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 112.2, 119.5, 123.1, 123.6, 124.2, 125.9, 126.0, 126.2, 127.8, 128.2, 128.3, 128.4, 128.9, 129.4, 130.5, 130.9, 130.9, 134.7, 150.1, 151.4 ppm; HRMS (EI): m/z calcd for $C_{24}H_{16}O$: 320.1201; found: 320.1205.

3g: 2,3-Bis(4-methylphenyl)chromone: m.p.: 145–146 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3H), 2.34 (s, 3H), 7.07–7.12 (m, 6H), 7.31 (d, J = 8.1 Hz, 2H), 7.39–7.43 (m, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.68 (ddd, J = 7.4, 7.0, 1.5 Hz, 1H), 8.28 ppm (dd, J = 8.0, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3, 21.4, 117.9, 122.5, 123.5, 124.9, 126.4, 128.8, 129.0, 129.5, 130.0, 130.5, 131.0, 133.5, 137.2, 140.3, 156.0, 161.3, 177.5 ppm; MS (EI): m/z = 326 $[M]^+$; elemental analysis: calcd (%) for $C_{23}H_{18}O_2$: C 84.64, H 5.56; found: C 84.44, H 5.51.

3h: 2,3-Bis(4-methoxyphenyl)chromone: m.p.: 158–161 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.80 (s, 3H), 3.81 (s, 3H), 6.78–6.88 (m, 4H), 7.14–7.17 (m, 2H), 7.37–7.42 (m, 3H), 7.52 (d, J = 8.4 Hz, 1H), 7.68 (ddd, J = 8.4, 7.0, 1.5 Hz, 1H), 8.28 ppm (dd, J = 8.0, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.2, 55.3, 113.5, 113.9, 117.8, 121.6, 123.5, 124.8,

125.4, 125.6, 126.3, 131.2, 132.3, 133.4, 155.9, 158.9, 160.8, 161.1, 177.6 ppm; MS (EI): $m/z = 358$ $[M]^+$; elemental analysis: calcd (%) for $C_{23}H_{18}O_4$: C 77.08, H 5.06; found: C 76.87, H 5.02.

3i: 2,3-Bis(4-chlorophenyl)chromone: m.p.: 175–180 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.14$–7.17 (m, 2H), 7.26–7.35 (m, 6H), 7.41–7.47 (m, 1H), 7.53 (d, $J = 8.4$ Hz, 1H), 7.70–7.74 (m, 1H), 8.28 ppm (dd, $J = 7.5$, 1.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 117.9$, 121.9, 123.3, 125.4, 126.4, 128.6, 128.7, 130.8, 131.0, 131.4, 132.5, 133.9, 134.0, 136.6, 155.9, 160.4, 176.9 ppm; HRMS (EI): m/z calcd for $C_{21}H_{12}Cl_2O_2$: 366.0214; found: 366.0210; elemental analysis: calcd (%) for $C_{21}H_{12}Cl_2O_2$: C 68.68, H 3.29, Cl 19.31; found: C 68.58, H 3.27, Cl 19.47.

3j: 2,3-Bis(2-thienyl)chromone: m.p.: 147–148 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.02$–7.07 (m, 2H), 7.18 (dd, $J = 5.1$, 3.7 Hz, 1H), 7.40–7.57 (m, 5H), 7.68–7.73 (m, 1H), 8.24 ppm (dd, $J = 8.0$, 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 114.2$, 117.7, 122.9, 125.2, 126.3, 127.4, 127.7, 128.4, 129.9, 131.6, 131.8, 132.8, 133.9, 134.6, 155.5, 157.1, 177.1 ppm; HRMS (EI): m/z calcd for $C_{17}H_{10}O_2S_2$: 310.0122; found: 310.0117.

3k: 3-Methyl-2-phenylchromone[19] was obtained as an oil: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.17$ (s, 3H), 7.37–7.41 (m, 1H), 7.45 (d, $J = 8.0$ Hz, 1H), 7.50–7.54 (m, 3H), 7.62–7.67 (m, 3H), 8.26 ppm (dd, $J = 8.1$, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 11.7$, 117.5, 117.8, 122.5, 124.7, 125.8, 128.4, 128.9, 130.2, 133.3, 133.4, 156.1, 161.0, 178.8 ppm; HRMS (EI): m/z calcd for $C_{16}H_{12}O_2$: 236.0837; found: 236.0817.

3l: 2,3-Diheptylchromone was obtained as an oil: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.82$–0.92 (m, 6H), 1.29–1.58 (m, 18H), 1.71–1.79 (m, 2H), 2.52 (t, $J = 7.8$ Hz, 2H), 2.69 (t, $J = 7.8$ Hz, 2H), 7.31–7.39 (m, 2H), 7.60 (ddd, $J = 8.4$, 7.5, 1.7 Hz, 1H), 8.19 ppm (dd, $J = 7.7$, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.1$, 14.1, 22.6, 22.7, 24.7, 27.6, 29.0, 29.2, 29.4 (overlapped), 29.8, 31.7, 31.8 (overlapped), 117.5, 121.4, 122.9, 124.3, 125.9, 132.8, 155.9, 165.6, 177.9 ppm; HRMS (EI): m/z calcd for $C_{23}H_{34}O_2$: 342.2559; found: 342.2555.

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[1] For reviews concerning the functionalization of C–H bonds, see: a) F. Kakiuchi, *Top Organomet. Chem.* **2007**, *24*, 1; b) L. Ackermann, *Top Organomet. Chem.* **2007**, *24*, 35; c) T. Satoh, M. Miura, *Top Organomet. Chem.* **2007**, *24*, 61; d) D. Kalyani, M. S. Sanford, *Top Organomet. Chem.* **2007**, *24*, 85; e) D. Alberico, M. E. Scott, M. Lautens, *Chem. Rev.* **2007**, *107*, 174; f) C.-H. Jun, E.-A. Jo, J.-W. Park, *Eur. J. Org. Chem.* **2007**, 1869; g) T. Satoh, M. Miura, *Chem. Lett.* **2007**, *36*, 200; h) T. Satoh, M. Miura, *J. Synth. Org. Chem. Jpn.* **2006**, *64*, 1199; i) B. L. Conley, W. J. Tenn III, K. J. H. Young, S. K. Ganesh, S. K. Meier, V. R. Ziatdinov, O. Mironov, J. Oxgaard, J. Gonzales, W. A. Goddard III, R. A. Periana, *J. Mol. Catal. A* **2006**, *251*, 8; j) M. Miura, T. Satoh in *Handbook of C–H Transformations*, *Vol. 1* (Ed.: G. Dyker), Wiley-VCH, Weinheim, **2005**, p. 223; k) M. Miura, T. Satoh, *Top Organomet. Chem.* **2005**, *14*, 55; l) M. S. Sigman, M. Schults, *Org. Biomol. Chem.* **2004**, *2*, 2551; m) F. Kakiuchi, N. Chatani, *Adv. Synth. Catal.* **2003**, *345*, 1077; n) V. Ritleng, C. Sirlin, M. Pfeffer, *Chem. Rev.* **2002**, *102*, 1731; o) M. Miura, M. Nomura, *Top. Curr. Chem.* **2002**, *219*, 211; p) F. Kakiuchi, S. Murai, *Acc. Chem. Res.* **2002**, *35*, 826; q) C. Jia, T. Kitamura, Y. Fujiwara, *Acc. Chem. Res.* **2001**, *34*, 633; r) F. Kakiuchi, S. Murai, *Top. Organomet. Chem.* **1999**, *3*, 47; s) G. Dyker, *Angew. Chem.* **1999**, *111*, 1808; *Angew. Chem. Int. Ed.* **1999**, *38*, 1698; t) A. E. Shilov, G. B. Shul'pin, *Chem. Rev.* **1997**, *97*, 2879.

[2] a) M. Miura, T. Tsuda, T. Satoh, S. Pivsa-Art, M. Nomura, *J. Org. Chem.* **1998**, *63*, 5211; b) M. Miura, T. Tsuda, T. Satoh, M. Nomura, *Chem. Lett.* **1997**, 1103.

[3] a) K. Ueura, T. Satoh, M. Miura, *J. Org. Chem.* **2007**, *72*, 5362; b) K. Ueura, T. Satoh, M. Miura, *Org. Lett.* **2007**, *9*, 1407.

[4] For the Rh-catalyzed oxidative coupling of benzene with ethylene, see: a) T. Matsumoto, R. A. Periana, D. J. Taube, H. Yoshida, *J. Catal.* **2002**, *206*, 272; b) T. Matsumoto, H. Yoshida, *Chem. Lett.* **2000**, 1064; for the Rh-catalyzed oxidative arylation of 2-aryl pyridines and an imine, see: c) T. Vogler, A. Studer, *Org. Lett.* **2008**, *10*, 129; for examples of rhodium-catalyzed aerobic oxidation, see: d) A. K. Fazlur-Rahman, J.-C. Tsai, K. M. Nicholas, *J. Chem. Soc. Chem. Commun.* **1992**, 1334; e) M. Bressan, A. Morvillo, *Inorg. Chim. Acta* **1989**, *166*, 177; f) H. Mimoun, *Angew. Chem.* **1982**, *94*, 750; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 734; g) H. Mimoun, M. M. Perez-Machirant, I. Sérée de Roch, *J. Am. Chem. Soc.* **1978**, *100*, 5437.

[5] J. Tsuji, *Palladium Reagents and Catalysts*, *2nd ed.*, John Wiley & Sons, Chichester, **2004**.

[6] a) K. Kokubo, K. Matsumasa, M. Miura, M. Nomura, *J. Org. Chem.* **1997**, *62*, 4564; b) K. Kokubo, K. Matsumasa, Y. Nishinaka, M. Miura, M. Nomura, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 303; c) K. Oguma, M. Miura, T. Satoh, M. Nomura, *J. Am. Chem. Soc.* **2000**, *122*, 10464; d) T. Sugihara, T. Satoh, M. Miura, M. Nomura, *Adv. Synth. Catal.* **2004**, *346*, 1765; e) K. Ueura, T. Satoh, M. Miura, *Org. Lett.* **2005**, *7*, 2229; f) T. Katagiri, H. Tsurugi, A. Funayama, T. Satoh, M. Miura, *Chem. Lett.* **2007**, *36*, 830; g) T. Uto, M. Shimizu, K. Ueura, H. Tsurugi, T. Satoh, M. Miura, *J. Org. Chem.* **2008**, *73*, 298.

[7] For a Pd-catalyzed arylation, see: a) T. Satoh, T. Itaya, M. Miura, M. Nomura, *Chem. Lett.* **1996**, 823; for an Ir-catalyzed arylation, see: b) Y. Nishinaka, T. Satoh, M. Miura, H. Morisaka, M. Nomura, H. Matsui, C. Yamaguchi, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1727; for Rh-catalyzed alkylation, see: c) M. Imai, M. Tanaka, S. Nagumo, N. Kawahara, H. Suemune, *J. Org. Chem.* **2007**, *72*, 2543, and references therein; d) R. T. Stemmler, C. Bolm, *Adv. Synth. Catal.* **2007**, *349*, 1185.

[8] See, for example: a) A. K. Soni, G. L. D. Krupadanam, G. Srimannarayana, *Synth. Commun.* **2007**, *37*, 795; b) P. Valenti, A. Bisi, A. Rampa, F. Belluti, S. Gobbi, A. Zampiron, M. Carrara, *Bioorg. Med. Chem.* **2000**, *8*, 239; c) A. Lévai, T. Patonay, *Monatsh. Chem.* **1995**, *126*, 219; d) A. Saeed, A. P. Sharma, N. Durani, R. Jain, S. Durani, R. S. Kapil, *J. Med. Chem.* **1990**, *33*, 3210; e) E. S. C. Wu, J. T. Loch III, B. H. Toder, A. R. Borrelli, D. Gawlak, L. A. Radov, N. P. Gensmantel, *J. Med. Chem.* **1992**, *35*, 3519.

[9] a) M. I. Lvovskaya, A. D. Roshal, A. O. Doroshenko, A. V. Kyrychenko, V. P. Khilya, *Spectrochim. Acta Part A* **2006**, *65*, 397; b) W. Sato, T. Nakai, T. Yoneyama, Mitsubishi Chemical Copr., Japan Japanese Patent JP 2004155665, **2004**; c) R. Schipfer, O. S. Wolfbeis, A. Knierzinger, *J. Chem. Soc. Perkin Trans. 2* **1981**, 1443.

[10] A similar promotional effect of this ligand was observed in the reaction of triaryl methanol compounds with alkynes; see reference [6g].

[11] For the preparation and characterization of a similar rhodacycle, $[Cp^*Rh(C(O)C_6F_4O)(PMe_3)]$, see: R. P. Hughes, D. C. Lindner, L. M. Liable-Sands, A. L. Rheingold, *Organometallics* **2001**, *20*, 3519.

[12] The participation of another sequence, in which the Rh^I-catalyzed hydroacylation of the alkyne (see reference [6a,b]) is followed by oxidative cyclization, cannot be excluded. However, it is known that dialkyl acetylenes, such as **2g**, undergo hydroacylation smoothly under Rh^I catalysis. Under the present oxidative conditions, **2g** underwent sluggish coupling with **1a**, and no hydroacylation product was formed in a detectable amount. Thus, the predominant active species in the present reaction seems to be different from that in the hydroacylation.

[13] Z. Novák, P. Nemes, A. Kotschy, *Org. Lett.* **2004**, *6*, 4917.

[14] S. S. Hirsch, W. J. Bailey, *J. Org. Chem.* **1978**, *43*, 4090.

[15] T. C. Chadha, H. S. Mahal, K. Venkataraman, *J. Chem. Soc.* **1933**, 1459.

[16] A. Saeed, A. P. Sharma, N. Durani, R. Jain, S. Durani, R. S. Kapil, *J. Med. Chem.* **1990**, *33*, 3210.

[17] G. Wittig, F. Bangert, H. E. Richter, *Justus Liebigs Ann. Chem.* **1925**, *446*, 155.
[18] C. Pan, J. Yu, Y. Zhou, Z. Wang, M.-M. Zhou, *Synlett* **2006**, 1657.
[19] S. Gobbi, A. Cavalli, A. Rampa, F. Belluti, L. Piazzi, A. Paluszcak, R. W. Hartmann, M. Recanatini, A. Bisi, *J. Med. Chem.* **2006**, *49*, 4777.

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