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Reaction of 2-Hydroxybenzaldehydes with Alkynes, Alkenes, or Allenes via Cleavage of the Aldehyde C–H Bond Using a Rhodium Catalyst System

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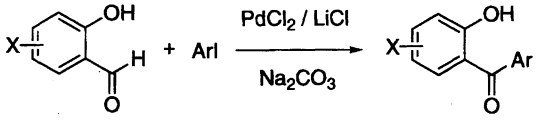
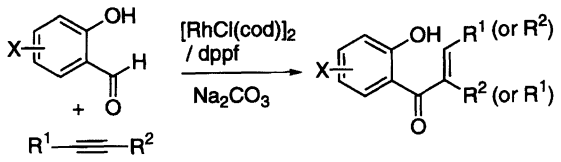
2-Hydroxybenzaldehydes smoothly and efficiently react with various internal and terminal alkynes accompanied by cleavage of the aldehyde C–H bond by using a rhodium-based catalyst system of $[RhCl(cod)]_2$/dppf/Na_2CO_3 [cod = 1,5-cyclooctadiene; dppf = 1,1′-bis(diphenylphosphino)ferrocene] to give the corresponding 2-alkenoylphenols in good to excellent yields. The regioselectivity of the reaction depends on the substituents of acetylene; an oxygen function on the propargylic position shows a considerable directing effect. The aldehydes can also react with some alkenes or allenes, such as triethylvinylsilane and 2-norbornene or 3-methyl-1,2-butadiene and 1,2-nonadienes, in place of alkynes.

The activation of C–H bonds in organic compounds by transition-metal complexes is currently one of the most significant subjects in both organic and organometallic chemistry. An effective strategy to regioselectively activate a C–H bond in a given molecule has been known to introduce a functional group having ligating ability at an appropriate position of it.[1] Recently, a number of catalytic coupling reactions of aromatic or vinylic compounds bearing carbonyl,[2—6] nitrogen-containing,[7—11a] or phenolic hydroxy group[11b] with alkenes and/or alkynes involving such a C–H bond activation mode as the key step have been developed, especially by using ruthenium, rhodium, and palladium complexes.

Meanwhile, we have recently reported that 2-hydroxybenzaldehydes, i.e. salicylaldehydes, smoothly react with aryl iodides in the presence of a palladium catalyst and a base to give 2-aroylphenols, demonstrating that the phenolic function can act as a good anchor for catalytic intermolecular C–C coupling via cleavage of the aldehyde C–H bond (Scheme 1).[12] It was expected that, if vinyl halides could be used in place of aryl iodides, 2-alkenoylphenols could also be obtained in one step. The phenolic compounds are valuable precursors of chromones and chromanones,[13,14] whose skeletons are widely found in naturally occurring compounds, and a number of them exhibit interesting biological activities.[13] However, the reaction using vinyl halides was less efficient. One of the other possible routes to prepare 2-alkenoylphenols using 2-hydroxybenzaldehydes via the C–H cleavage is their coupling with alkynes. Indeed, the latter route was found to be realized with high efficiency by using a rhodium-based catalyst system (Scheme 2).[15] The reaction may be regarded as being a hydroacylation reaction. While the rhodium-catalyzed hydroacylation of alkenes with aldehydes has been well studied,[16—23] only the intramolecular reaction is generally effective, and its intermolecular version is less common.[20—27] Furthermore, the reaction with alkynes has been little explored.[23,26,28] Consequently, we carried out a detailed study of the aldehyde-alkyne coupling reaction. The results as well as those with some alkenes and allenes in place of alkynes are described herein.



Scheme 1.



Scheme 2.

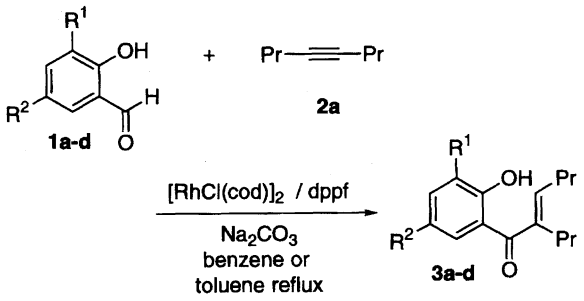
Results and Discussion

Reaction of 2-Hydroxybenzaldehyde with 4-Octyne. Table 1 summarizes the results for the reaction of 2-hydroxybenzaldehyde (**1a**) (2 mmol) with 4-octyne (**2a**) (2 mmol) in the presence of catalytic amounts of $[RhCl(cod)]_2$ (0.01 mmol, 1 mol%) and Na_2CO_3 (0.1 mmol) using a variety of phosphorus ligands (P/Rh = 2) in refluxing toluene under nitrogen (Scheme 3, $R^1 = R^2 = H$). The expected product, (*E*)-1-(2-hydroxyphenyl)-2-propyl-2-hexen-1-one (**3a**) was produced in 21—56% yields in reactions with monodentate ligands (PPh_3, PBu_3, PCy_3 (Cy = cyclohexyl), $P(OPh)_3$, and $P(OEt)_3$) for 20 h, no isomeric product being accompanied (Entries 1—5). While using common bidentate ligands, such as dppe, dppp, and dppb, the reaction efficiency was not improved (Entries 6—8), it was very interesting that the product was formed in a quantitative yield within 0.5 h by using dppf (Entry 9). Although the reaction using dppf proceeded in the

Table 1. Reaction of 2-Hydroxybenzaldehyde (**1a**) with 4-Octyne (**2a**)[a]

Entry	Ligand (mol amt.)[b]	Time/h	Yield of **3a**[c]/%
1	PPh_3 (2)	20	33
2	PBu_3 (2)	20	49
3	PCy_3 (2)	20	56
4	$P(OPh)_3$ (2)	20	21
5	$P(OEt)_3$ (2)	20	32
6	dppe (1)	20	46
7	dppp (1)	21	52
8	dppb (1)	21	49
9	dppf (1)	0.5	100
10[d]	dppf (1)	0.5	5
11[d]	dppf (1)	24	99
12[e]	dppf (1)	20	17

a) The reaction was carried out in refluxing toluene under N_2 unless otherwise noted. $[[RhCl(cod)]_2] : [Na_2CO_3] : \mathbf{1a} : \mathbf{2a} = 0.01 : 0.1 : 2 : 2$ (in mmol). b) Relative to rhodium metal; dppe = 1,2-bis(diphenylphosphino)ethane, dppp = 1,3-bis(diphenylphosphino)propane, dppb = 1,4-bis(diphenylphosphino)butane, dppf = 1,1′-bis(diphenylphosphino)ferrocene. c) Determined by GLC analysis. d) Without Na_2CO_3. e) Reaction at 100 °C.



a: $R^1=R^2=H$; **b**: $R^1=OMe$, $R^2=H$; **c**: $R^1=H$, $R^2=OH$; **d**: $R^1=H$, $R^2=Cl$

Scheme 3.

absence of Na_2CO_3 (Entries 10 and 11), a rather longer time was required for the reaction to be completed. In contrast to Na_2CO_3, an organic base, $NEt(i\text{-}Pr)_2$, which is effective for the rhodium-catalyzed hydroacylation of alkenes with acid anhydrides and molecular hydrogen,[29] showed no promoting effect on the reaction. The reaction at 100 °C was sluggish (Entry 12), whereas that in refluxing benzene at a bath temperature of 100 °C was completed within 2.5 h (Entry 1 in Table 2), suggesting that solvent reflux is an essential factor for the reaction to proceed smoothly.[2]

Reaction of 2-Hydroxybenzaldehyde with Various Alkynes. The results for the reaction of **1a** with alkynes **2a**—**i** using the catalyst system of $[RhCl(cod)]_2$/dppf/Na_2CO_3 in refluxing benzene or toluene are recorded in Table 2. The reaction of **1a** with an aromatic alkyne, 1,2-diphenylacetylene (**2b**), also gave product **4** in good yield (Entry 2), though the reaction was somewhat slower than that with **2a**. In contrast to the previously reported catalytic C–H/alkyne coupling reactions,[2d,3,10] terminal alkynes, 1-octyne (**2c**) and phenylacetylene (**2d**), could smoothly react with **1a**, giving pairs of regioisomers **5**/**5′** and

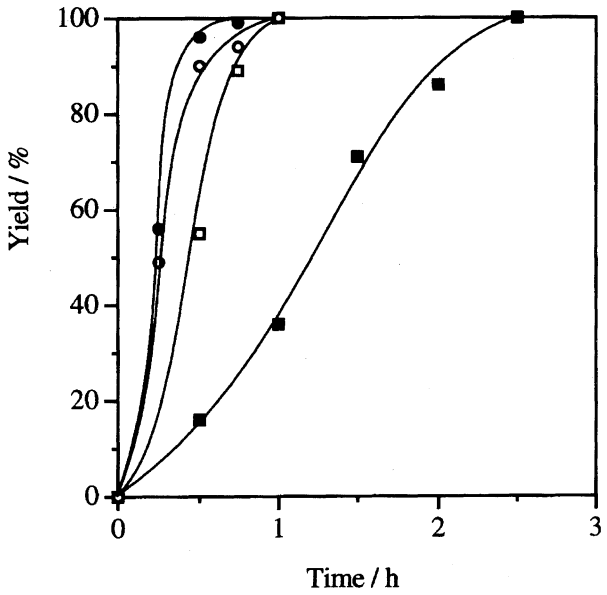
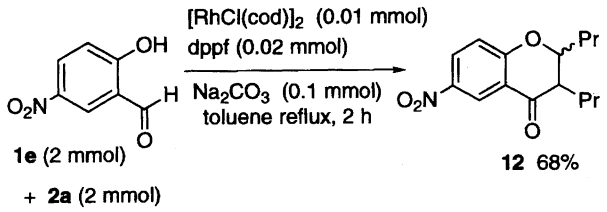


Fig. 1. Time course of the reaction of **1a**—**d** with **2a** showing yield of **3a** (○), **3b** (●), **3c** (□), and **3d** (■). Reaction conditions: $[[RhCl(cod)]_2] : [dppf] : [Na_2CO_3] : [\mathbf{1}] : [\mathbf{2a}] = 0.01 : 0.02 : 0.1 : 2 : 2$ (in mmol), in refluxing benzene under N_2.

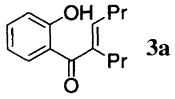
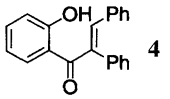
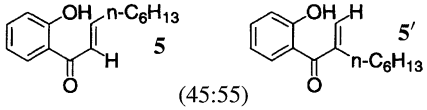
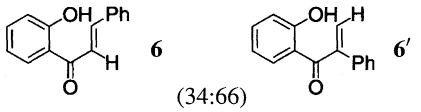
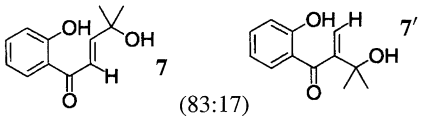
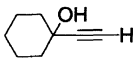
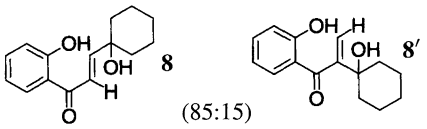
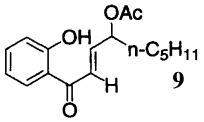
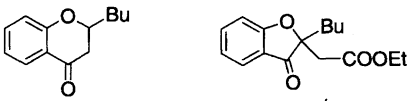
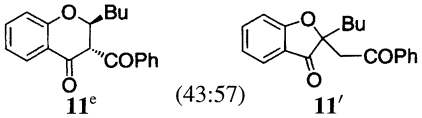


Scheme 4.

6/**6′** in comparable amounts (Entries 3 and 4). Good regioselectivities were observed in the reactions with propargyl alcohols **2e** and **2f**, product pairs of **7**/**7′** and **8**/**8′** being obtained in ratios of 83 : 17 and 85 : 15, respectively (Entries 5 and 6). The reaction of **1a** with 3-acetoxy-1-octyne (**2g**) predominantly afforded compound **9** along with minor amounts of some unidentified products (Entry 7). From reactions with **2h** and **2i** were obtained pairs of cyclized compounds **10**/**10′** and **11**/**11′** (Entries 8 and 9). The cyclization leading to the products seems to have occurred via a Michael-type reaction after formation of the corresponding 2-alkenoylphenols; this may have been due to the electron-withdrawing nature of the ethoxycarbonyl and benzoyl groups. Note that compound **10** had no ethoxycarbonyl group; it is considered to be eliminated under the reaction conditions.

Substituent Electronic Effect. In order to examine the effect of introducing a substituent onto 2-hydroxybenzaldehyde upon its reaction with an alkyne, the reactions of 3-methoxy-, 5-hydroxy-, and 5-chlorobenzaldehydes (**1b**—**d**) with **2a** were carried out in refluxing benzene as well as that of **1a** (Scheme 3). The yield of products **3a**—**d** against the reaction time (monitored by GLC) is shown in Fig. 1. It can be seen that (a) the products are quantitatively formed irrespective of the aldehydes used, and (b) the reactions of **1a**—**c**

Table 2. Reaction of 2-Hydroxybenzaldehyde (**1a**) with Various Alkynes (**2a—i**)[a]

Entry	Alkyne	Solvent[b]	Time / h	Product(s)(Ratio)[c]	Yield[c,d] / %
1	Pr—≡—Pr **2a**	B	2	 **3a**	99 (99)
2	Ph—≡—Ph **2b**	B	7	 **4**	99 (86)
3	n-C_6H_{13}—≡—H **2c**	B	2	 **5** (45:55) **5′**	99 (99)
4	Ph—≡—H **2d**	B	4	 **6** (34:66) **6′**	93 (75)
5	HO(Me)$_2$C—≡—H **2e**	T	5.5	 **7** (83:17) **7′**	75 (72)
6	 **2f**	T	4	 **8** (85:15) **8′**	86 (83)
7	n-C_5H_{11}(AcO)CH—≡—H **2g**	T	2	 **9**	70 (68)
8	Bu—≡—COOEt **2h**	T	30	 **10** (44:56) **10′**	70 (63)
9	Bu—≡—COPh **2i**	T	5	 **11**[e] (43:57) **11′**	99 (90)

a) The reaction was carried out in refluxing benzene or toluene under N_2. [[RhCl(cod)]$_2$] : [dppf] : [Na_2CO_3] : [**1a**] : [**2**] = 0.01 : 0.02 : 0.1 : 2 : 2 (in mmol). b) B = Benzene, T = Toulene. c) Determined by GLC analysis. d) Value in parentheses indicates yield (or total yield in the case of a mixture of isomers) after isolation by chromatography (see also Experimental). e) A part of this compound (ca. 30%) exists as an enol form in $CDCl_3$.

were completed within 1 h, whereas **1d** required a longer time of 2.5 h to come to its quantitative conversion. It should be noted that the reaction using 20 mmol of each of **1b** and **2a** in refluxing toluene was quantitatively proceeded within 2 h, the turnover rate being approximately estimated to be as high as 500 h^{-1}. The reaction of 2-hydroxy-5-nitrobenzaldehyde (**1e**) with **2a** in refluxing benzene was significantly slower than that of **1d**, the conversion of **1e** being ca. 10% at 3 h.

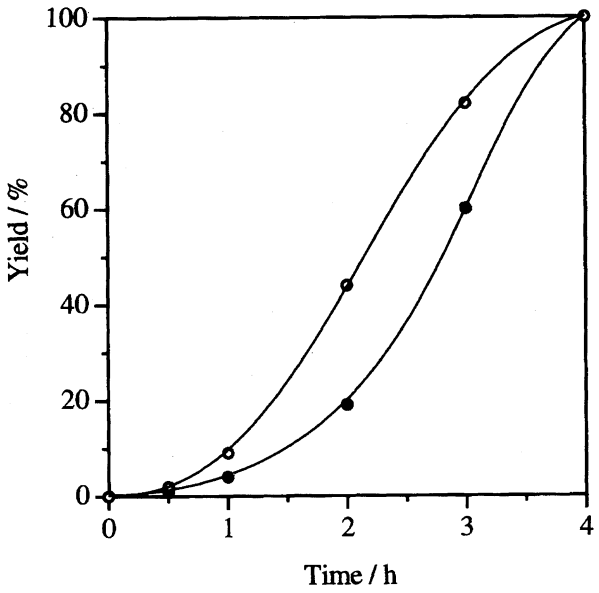


Fig. 2. Time course of the competitive reaction of **1b** and **1d** with **2a** showing yield of **3b** (●) and **3d** (○). Reaction conditions: [[RhCl(cod)]$_2$] : [dppf] : [Na_2CO_3] : [**1b**] : [**1d**] : [**2a**] = 0.01 : 0.02 : 0.1 : 2 : 2 : 2 (in mmol), in refluxing benzene under N_2.

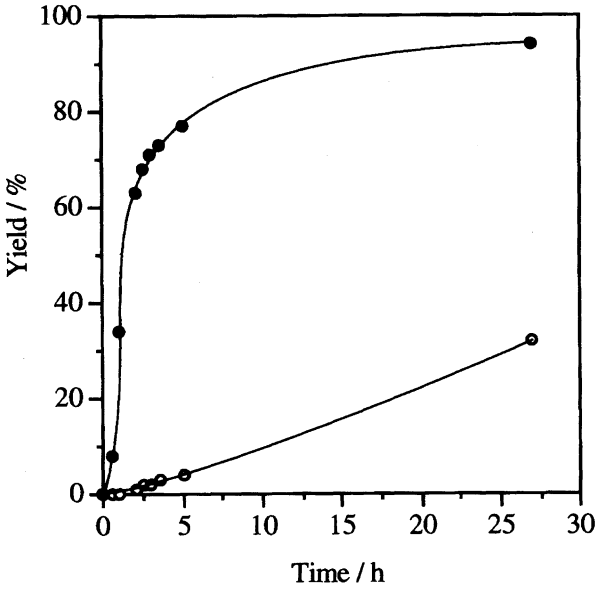
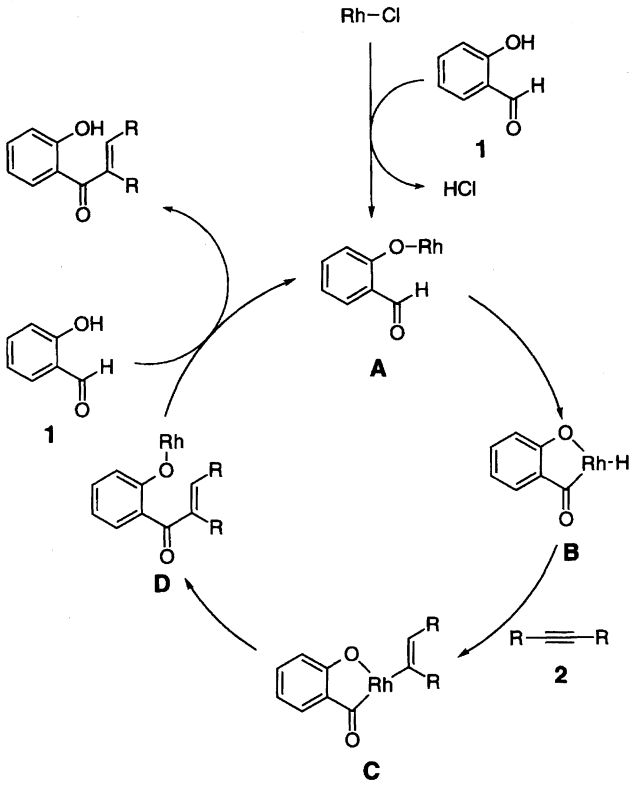
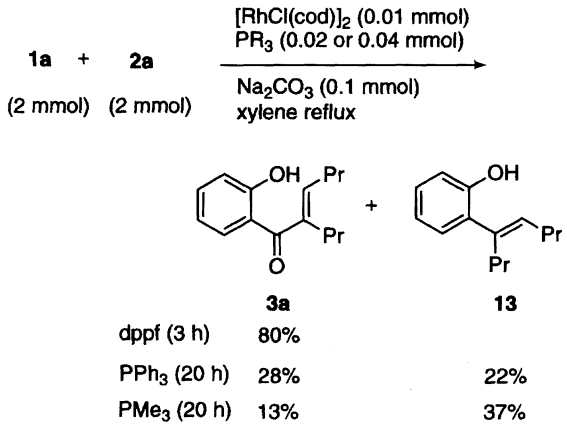


Fig. 3. Time course of the competitive reaction of **1a** and **1e** with **2a** showing yield of **3b** (○) and **12** (●). Reaction conditions: [[RhCl(cod)]$_2$] : [dppf] : [Na_2CO_3] : [**1a**] : [**1e**] : [**2a**] = 0.01 : 0.02 : 0.1 : 2 : 2 : 2 (in mmol), in refluxing toluene under N_2.

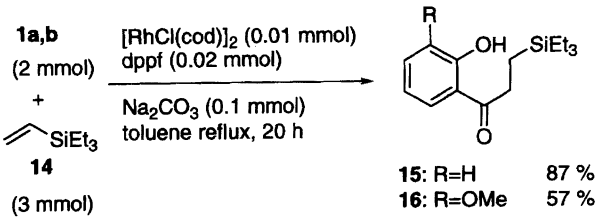
Therefore, it was carried out in refluxing toluene (Scheme 4); in this case, a cyclized product **12** (*cis/trans* = 36 : 64) was formed in a yield of 68% at 2 h; the formation of **12** may be attributed to the electron-withdrawing nature of the nitro group, this being similar to the reactions of **1a** with **2h,i**. The results using **1d,e** may indicate that the electron-withdrawing groups apparently retard the reaction. The fact that the rate of the reaction of **1c** was somewhat slower than those of **1a, b**, however, suggests that another factor other than electronic effect (probably ligation of the oxygen at the 5 position to rhodium) also intervenes.



Scheme 5.

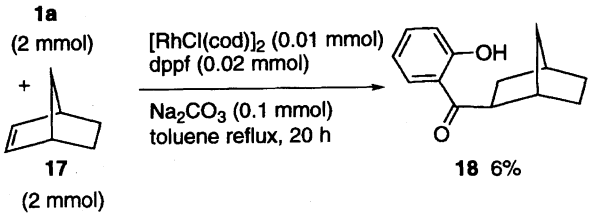


Scheme 6.

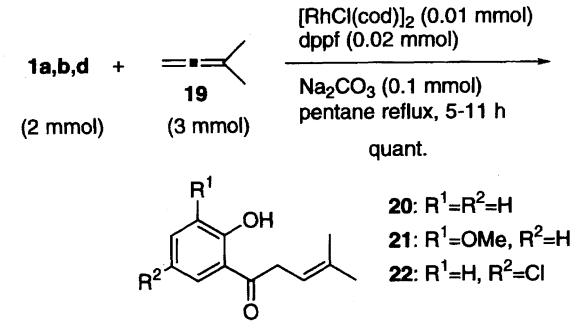


Scheme 7.

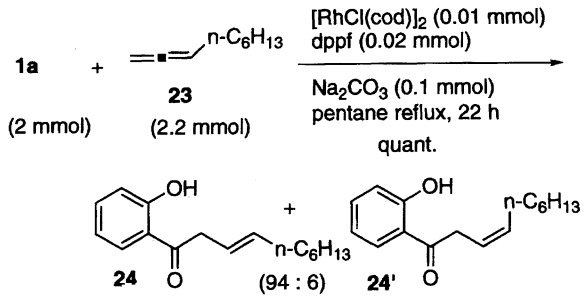
Figure 2 shows the time course of the reaction of an equimolar mixture of **1b** and **1d** with **2a** in refluxing benzene, showing the yield of products **3b** and **3d** against the reaction



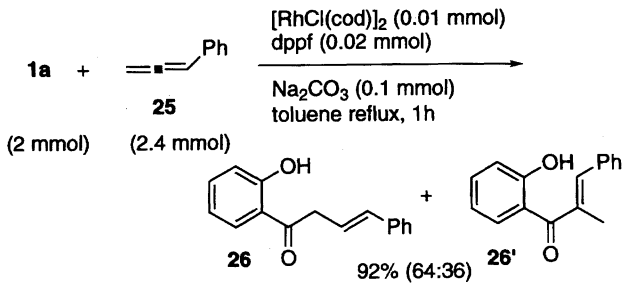
Scheme 8.



Scheme 9.



Scheme 10.



Scheme 11.

time. It should be noted that, while both compounds were produced quantitatively within 4 h, **3d** was formed faster than **3b**, this being not consistent with the reactivity order observed in Fig. 1. Moreover, in the competitive reaction of **1a** and **1e** in refluxing toluene (Fig. 3), **12** was the predominant product and the yield of **3a** was less than 40%, even after 27 h. These results indicate that the reactivity order of 2-hydroxybenzaldehydes is completely different between the independent and competitive reactions.

Reaction Scheme for the Formation of 2-Alkenoylphenols. A plausible reaction mechanism for the reaction of **1** with **2** is illustrated in Scheme 5 in which neutral ligands on rhodium as well as substituents on **1** are omitted for clarity. The reaction may involve initial coordination of **1** to a chlororhodium(I) species to form phenolate complex **A**, accompanied by the liberation of HCl; then, oxidative addition of the aldehyde C–H bond to the metal center occurs to give aroylhydridorhodium(III) complex **B** as the key steps.[12,30] After insertion of **2** to the Rh–H bond in **B** to produce complex **C**,[31] reductive elimination of the alkenoyl moiety takes place to give complex **D**. Complex **A** is then reproduced by ligand exchange with **1** accompanied by liberation of the product alkenoylphenol.

It should be noted that 4-hydroxybenzaldehyde and 2-methoxybenzaldehyde as well as benzaldehyde, itself, could not be used in place of **1a**, supporting the above consideration that the coordination of the phenolic oxygen to the metal center plays a significant role. It was confirmed that the addition of AgOTf or $AgClO_4$ in place of Na_2CO_3 to the reaction of **1a** with **2a**, which may generate a cationic rhodium(I) species, could not enhance the reaction. Thus, the insoluble solid base Na_2CO_3 seems to effectively remove initially formed HCl which could be a poison for the catalysis.

One of the crucial factors showing good efficiency of the present reaction may also be the formation of the relatively stable intermediary five-membered metalacycle **B** in which decarbonylation leading to catalytically less active or inactive rhodiumcarbonyl species hardly occurs. It was found that from the reaction of **1a** with **2a** using PPh_3 or PMe_3 as ligand in refluxing xylene, a decarbonylated product **13** was formed together with **3a**, whereas **13** was not detected in the reaction using dppf (Scheme 6). This suggests that under forced conditions catalytic coupling accompanied by decarbonylation takes place to some extent, while it is prevented by the bidentate ligand dppf.[17]

The observed substituent electronic effects in the competitive reactions that **1d** and **1e** reacted faster than **1b** and **1a**, respectively, could be interpreted as follows. Substrates **1**, having an electron-withdrawing group, coordinate to the metal center relatively faster than those having an electron-donating group; electron-withdrawing groups may promote deprotonation from **1**, so that complex **A** may form more easily.[32] In the catalytic step of **D** to **A**, **1d** and **1e** may preferably react with **D** compared with **1b** and **1a**, and thus, **3d** and **12** were produced more rapidly than **3b** and **3a**, respectively. In contrast, in the independent reactions, **1a** and **1b** reacted faster than **1d** and **1e**. This could imply that the rate of step **D** to **A** in the case using **1a** or **1b** alone is relatively faster than that using **1d** or **1e**. Thus, the relative ease of the final catalytic step (probably reversible) in the independent reactions, which seems to depend on the difference of acidity as well as steric bulkiness between the starting materials and the products, may significantly affect the overall reaction rate. It should be noted that the rate also depends on the substituents on acetylene (Table 2) and that the coupling reaction of **1** with an allene, 3-methyl-1,2-propadiene, proceeds under much milder conditions, as described below. These facts imply that the rate can also be significantly affected by the structure of unsaturated compounds as coupling partners of **1**. Therefore, a further investigation is required for more detailed discussion about the factors determining

the overall reaction rate.

The product regiochemistry may be determined in the step **B** to **C**. The insertion of propargyl alcohol derivatives **2e—g** appears to be especially regioselective. This may be attributed to the interaction of the oxygen functions in the alkynes with the metal center before insertion, although the details are not definitive.

Reaction of 2-Hydroxybenzaldehydes with Alkenes and Allenes. In order to see the applicability of alkenes and dienes in place of alkynes in the present coupling, **1a** was treated with a number of them. While styrene, 1-octene, butyl vinyl ether, butyl acrylate, allyl alcohol were unreactive, triethylvinylsilane (**14**) was observed to efficiently react in refluxing toluene, giving the corresponding ketone **15** (87%), as depicted in Scheme 7. No regio-isomer was detected.[27] Similarly, ketone **16** (57%) was obtained from **1b** and **14**. 2-Norbornene (**17**) reacted with **1a** to stereoselectively give compound **18**, though the yield (6%) was low (Scheme 8). It was found that the addition of $AgClO_4$ (1 mol%) to the reaction increased the yield of **18** to 39%. However, the role of the silver salt is not definitive, since no meaningful effect of its addition was observed in the reaction with **14**.

Some 1,2-dienes, i.e. allenes, were also found to efficiently react with **1** to give the corresponding acylphenols, although 1,3-dienes such as isoprene, 2,4-hexadien-1-ol, and myrcene, could not be used. It was of considerable interest that the reactions of **1a,b,d** with 3-methyl-1,2-butadiene (**19**) could proceed even in refluxing pentane to afford compounds **20—22** in quantitative yield (Scheme 9). Similarly, **1a** quantitatively reacted with 1,2-nonadiene (**23**) to give a mixture of two stereoisomers, **24** and **24′**, in a ratio of 94 : 6 (Scheme 10). The reaction of **1a** with 3-phenyl-1,2-propadiene (**25**) needed a higher temperature; it proceeded effectively in refluxing toluene to produce a mixture of two regioisomers, **26** and **26′** (64 : 36), in a total yield of 92% (Scheme 11).

The above reactions with alkenes and allenes may proceed via their insertion to complex **B** in Scheme 5, as may do those with alkynes.

Experimental

^{1}H and ^{13}C NMR spectra were recorded at 400 or 270 MHz and 100 or 68 MHz, respectively, for $CDCl_3$ solutions. MS data were obtained by EI. GC analysis was carried out using a silicone OV-17 glass column (ϕ 2.6 mm×1.5 m) or a CBP-1capillary column (ϕ 0.5 mm × 25 m). Alkyne **2g** was prepared by the reaction of 1-octyn-3-ol with acetic anhydride in pyridine. Compounds **2h**,[33] **2i**,[34] **23**,[35] and **25**[35] were prepared by previously reported methods. Other starting materials were commercially available. The following experimental details given below may be regarded as typical in methodology and scale.

Reaction of 2-Hydroxybenzaldehyde (1a) with 4-Octyne (2a): A mixture of **1a** (244 mg, 2 mmol), **2a** (220 mg, 2 mmol), $[RhCl(cod)]_2$ (4.9 mg, 0.01 mmol,), dppf (11.1 mg, 0.02 mmol), and Na_2CO_3 (10.6 mg, 0.1 mmol) in refluxing benzene (5 cm^3) was stirred under nitrogen for 2 h. After evaporation of the solvent, product **3a** (460 mg, 99%) was isolated by column chromatography on silica gel using hexane–ethyl acetate (98 : 2, v/v) as eluent. Compound **3a** was an oil: ^{1}H NMR (400 MHz) δ = 0.94 (t, 3H, J = 7.3 Hz), 0.98 (t, 3H, J = 7.3 Hz), 1.43—1.53 (m, 4H), 2.27 (q, 2H, J = 7.3 Hz), 2.47 (t, 2H, J = 7.3 Hz), 5.97 (t, 1H, J = 7.3 Hz), 6.86 (t, 1H, J = 7.8 Hz), 7.00 (d, 1H, J = 7.8 Hz), 7.45 (t, 1H, J = 7.8 Hz), 7.67 (d, 1H, J = 7.8 Hz), 11.95 (s, 1H); ^{13}C NMR δ = 13.96, 14.10, 22.04, 22.32, 29.71, 30.49, 118.22, 118.27, 119.54, 132.77, 135.70, 139.66, 141.25, 162.93, 204.21; MS *m/z* 232 (M^+). IR ν 1624 cm^{-1}. Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68%. Found: C, 77.44; H, 8.72%.

Products. Compounds **4**[14c] and **6**[14b] are known and were compared with those authentic specimens. Characterization data of other products were as follows. Note that product pairs of **7/7′**, **8/8′**, **10/10′**, and **11/11′** could be completely separated by column chromatography on silica gel using hexane/ethyl acetate as eluent in each single run (60/12, 70/13, 28/35, and 40/50, respectively, in isolated yields). The pairs of **5/5′** and **6/6′**, and **26/26′** were separated by repeating the process two or three times to obtain each compound for the characterization. *cis/trans* Mixtures of **12** and **24/24′** were characterized without separation. The observed NOE peak enhancements in the measurement of ^{1}H NMR of **24** and **26′** as well as **3a** are shown in Chart 1.

(*E*)-1-(2-Hydroxy-3-methoxyphenyl)-2-propyl-2-hexen-1-one (3b): Oil; ^{1}H NMR (400 MHz) δ = 0.93 (t, 3H, J = 7.3 Hz), 0.97 (t, 3H, J = 7.3 Hz), 1.43—1.53 (m, 4H), 2.27 (q, 2H, J = 7.3 Hz), 2.46 (t, 2H, J = 7.3 Hz), 3.92 (s, 3H), 5.99 (t, 1H, J = 7.3 Hz), 6.80 (t, 1H, J = 7.8 Hz), 7.05 (d, 1H, J = 7.8 Hz), 7.26 (d, 1H, J = 7.8 Hz), 12.10 (s, 1H); ^{13}C NMR δ = 13.95, 14.08, 22.05, 22.28, 29.63, 30.50, 56.23, 116.55, 117.55, 119.82, 124.10, 139.79, 141.67, 148.88, 152.98, 204.26; MS *m/z* 262 (M^+). Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45%. Found: C, 73.13; H, 8.53%.

(*E*)-1-(2,5-Dihydroxyphenyl)-2-propyl-2-hexen-1-one (3c): Oil; ^{1}H NMR (400 MHz) δ = 0.92 (t, 3H, J = 7.3 Hz), 0.96 (t, 3H, J = 7.3 Hz), 1.41—1.51 (m, 4H), 2.25 (q, 2H, J = 7.3 Hz), 2.45 (t, 2H, J = 7.3 Hz), 5.22 (s, 1H), 5.99 (t, 1H, J = 7.3 Hz), 6.89 (d, 1H, J = 8.8 Hz), 7.02 (dd, 1H, J = 8.8, 2.9 Hz), 7.15 (d, 1H, J = 3.4 Hz), 11.49 (s, 1H); ^{13}C NMR δ = 13.96, 14.09, 22.04, 22.27, 29.69, 30.48, 117.91, 118.96, 119.35, 124.00, 139.64, 141.32, 147.08, 156.77, 203.73; MS *m/z* 248 (M^+). Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12%. Found: C, 72.30; H, 8.11%.

(*E*)-1-(5-Chloro-2-hydroxyphenyl)-2-propyl-2-hexen-1-one (3d): Oil; ^{1}H NMR (400 MHz) δ = 0.94 (t, 3H, J = 7.3 Hz), 1.00 (t, 3H, J = 7.3 Hz), 1.41—1.57 (m, 4H), 2.29 (q, 2H, J = 7.3 Hz), 2.45 (t, 2H, J = 7.3 Hz), 6.00 (t, 1H, J = 7.3 Hz), 6.96 (d, 1H, J = 8.8

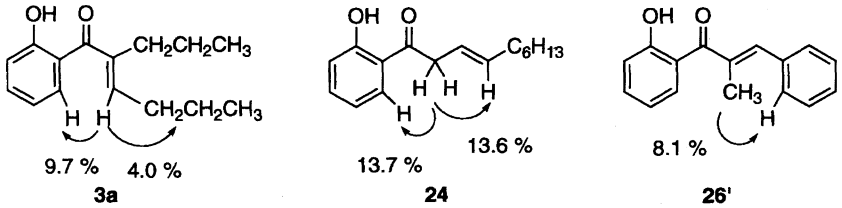


Chart 1. NOE Peak Enhancement in the Measurement of ^{1}H NMR of **3a**, **24**, and **26′**.

Hz), 7.40 (dd, 1H, J = 8.8, 2.4 Hz), 7.61 (d, 1H, J = 2.4 Hz), 11.79 (s, 1H); ^{13}C NMR δ = 13.92, 14.14, 22.08, 22.26, 29.63, 30.56, 119.87, 120.17, 123.01, 131.80, 135.47, 139.50, 142.41, 161.33, 202.97; MS m/z 266, 268 (M^+). Anal. Calcd for $C_{15}H_{19}ClO_2$: C, 67.54; H, 7.18; Cl, 13.29%. Found: C, 67.30; H, 7.22; Cl, 13.21%.

(*E*)-1-(2-Hydroxyphenyl)-2-nonen-1-one (5): Oil; ^{1}H NMR (270 MHz) δ = 0.90 (t, 3H, J = 6.8 Hz), 1.28—1.59 (m, 8H), 2.35 (q, 2H, J = 6.8 Hz), 6.90 (t, 1H, J = 7.8 Hz), 6.98—7.05 (m, 2H), 7.21 (dt, 1H, J = 15.6, 6.8 Hz), 7.47 (t, 1H, J = 7.8 Hz), 7.81 (d, 1H, J = 7.8 Hz), 12.75 (s, 1H); ^{13}C NMR δ = 14.04, 22.53, 28.09, 28.91, 31.59, 32.97, 118.49, 118.71, 119.59, 123.82, 129.81, 136.18, 151.01, 163.55, 194.17; HRMS m/z (M^+). Calcd for $C_{15}H_{20}O_2$: M, 232.1463. Found: m/z 232.1456.

1-(2-Hydroxyphenyl)-2-methylene-1-octanone (5′): Oil; ^{1}H NMR (270 MHz) δ = 0.87 (t, 3H, J = 6.8 Hz), 1.28—1.51 (m, 8H), 2.46 (t, 2H, J = 6.8 Hz), 5.38 (s, 1H), 5.65 (s, 1H), 6.87 (t, 1H, J = 7.8 Hz), 7.01 (d, 1H, J = 7.8 Hz), 7.48 (t, 1H, J = 7.8 Hz), 7.75 (d, 1H, J = 7.8 Hz), 12.00 (s, 1H); ^{13}C NMR δ = 14.01, 22.52, 27.88, 28.92, 31.54, 33.40, 118.30, 118.51, 118.96, 121.16, 132.85, 136.34, 147.41, 163.14, 204.00; MS m/z 232 (M^+). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68%. Found: C, 77.19; H, 8.74%.

1-(2-Hydroxyphenyl)-2-phenyl-2-propen-1-one (6′): Oil; ^{1}H NMR (270 MHz) δ = 5.54 (s, 1H), 6.03 (s, 1H), 6.82 (t, 1H, J = 7.8 Hz), 7.04 (d, 1H, J = 7.8 Hz), 7.27—7.52 (m, 6H), 7.66 (d, 1H, J = 7.8 Hz), 12.11 (s, 1H); ^{13}C NMR δ = 118.33, 118.36, 118.86, 119.20, 126.47, 128.72, 128.83, 133.30, 136.41, 136.88, 147.07, 163.36, 203.33; HRMS m/z (M^+). Calcd for $C_{15}H_{12}O_2$: M, 224.0837. Found: m/z 224.0849.

(*E*)-4-Hydroxy-1-(2-hydroxyphenyl)-4-methyl-2-penten-1-one (7): Oil; ^{1}HNMR (270 MHz) δ = 1.45 (s, 6H), 1.71 (s, 1H), 6.91 (t, 1H, J = 7.8 Hz), 7.01 (d, 1H, J = 7.8 Hz), 7.19 (d, 1H, J = 15.6 Hz), 7.30 (d, 1H, J = 15.6 Hz), 7.49 (t, 1H, J = 7.8 Hz), 7.87 (d, 1H, J = 7.8 Hz), 12.65 (s, 1H); ^{13}C NMR δ = 29.54, 71.47, 118.50, 118.85, 119.72, 120.06, 130.02, 136.50, 155.34, 163.50, 194.53; HRMS m/z (M^+). Calcd for $C_{12}H_{14}O_3$: M, 206.0943. Found: m/z 206.0942.

3-Hydroxy-1-(2-hydroxyphenyl)-3-methyl-2-methylene-1-butanone (7′): Oil; ^{1}H NMR (270 MHz) δ = 1.26 (s, 1H), 1.52 (s, 6H), 5.36 (s, 1H), 5.93 (s, 6H), 6.89 (t, 1H, J = 7.8 Hz), 7.02 (d, 1H, J = 7.8 Hz), 7.51 (t, 1H, J = 7.8 Hz), 7.70 (d, 1H, J = 7.8 Hz), 11.91 (s, 1H); ^{13}C NMR δ = 29.37, 72.37, 118.48, 118.76, 119.34, 119.48, 133.38, 136.99, 151.79, 163.43, 205.12; HRMS m/z (M^+). Calcd for $C_{12}H_{14}O_3$: M, 206.0943. Found: m/z 206.0941.

(*E*)-3-(1-Hydroxycyclohexyl)-1-(2-hydroxyphenyl)-2-propen-1-one (8): Oil; ^{1}H NMR (270 MHz) δ = 1.61—1.71 (m, 11H), 6.91 (t, 1H, J = 7.8 Hz), 7.01 (d, 1H, J = 7.8 Hz), 7.23 (d, 1H, J = 15.6 Hz), 7.34 (d, 1H, J = 15.6 Hz), 7.49 (t, 1H, J = 7.8 Hz), 7.87 (d, 1H, J = 7.8 Hz), 12.68 (s, 1H); ^{13}C NMR δ = 21.49, 25.14, 37.18, 72.46, 118.50, 118.82, 119.78, 120.52, 130.03, 136.45, 155.50, 163.53, 194.62; MS m/z 246 (M^+). Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37%. Found: C, 72.88; H, 7.40%.

2-(1-Hydroxycyclohexyl)-1-(2-hydroxyphenyl)-2-propen-1-one (8′): Oil; ^{1}H NMR (270 MHz) δ = 1.25—1.82 (m, 10H), 2.99 (s, 1H), 5.37 (s, 1H), 5.90 (s, 1H), 6.88 (t, 1H, J = 7.8 Hz), 7.01 (d, 1H, J = 7.8 Hz), 7.51 (t, 1H, J = 7.8 Hz), 7.71 (d, 1H, J = 7.8 Hz), 11.96 (s, 1H); ^{13}C NMR δ = 21.83, 25.43, 36.66, 73.26, 118.47, 118.73, 119.43, 119.60, 133.55, 136.99, 152.10, 163.48, 205.59; MS m/z 246 (M^+). Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37%. Found: C, 73.43; H, 7.15%.

(*E*)-4-Acetoxy-1-(2-hydroxyphenyl)-2-nonen-1-one (9): Oil; ^{1}H NMR (270 MHz) δ = 0.89 (t, 3H, J = 6.8 Hz), 1.25—1.40 (m, 6H), 1.70—1.78 (m, 2H), 2.15 (s, 3H), 5.52 (q, 1H, J = 5.9 Hz), 6.93 (t, 1H, J = 7.8 Hz), 6.98—7.06 (m, 2H), 7.15 (d, 1H, J = 15.6 Hz), 7.50 (t, 1H, J = 7.8 Hz), 7.79 (d, 1H, J = 7.8 Hz), 12.54 (s, 1H); ^{13}C NMR δ = 13.94, 21.09, 22.44, 24.65, 31.47, 33.91, 73.11, 118.59, 118.91, 119.54, 123.75, 129.93, 136.66, 146.12, 163.56, 170.16, 193.69; MS m/z 290 (M^+). Anal. Calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64%. Found: C, 70.21; H, 7.63%.

2-Butyl-2,3-dihydro-4*H*-1-benzopyran-4-one (10): Oil; ^{1}H NMR (270 MHz) δ = 0.98 (t, 3H, J = 6.8 Hz), 1.23—1.89 (m, 8H), 2.69 (d, 2H, J = 7.8 Hz), 4.42—4.46 (m, 1H), 6.96— 7.02 (m, 2H), 7.44—7.50 (m, 1H), 7.86—7.89 (m, 1H); ^{13}C NMR δ = 13.94, 22.47, 27.02, 34.63, 42.99, 77.92, 117.90, 121.02, 121.10, 126.92, 135.90, 161.69, 192.66: HRMS m/z (M^+). Calcd for $C_{13}H_{16}O_2$: M, 204.1150. Found: m/z 204.1144.

2-Butyl-2-ethoxycarbonylmethyl-1-benzofuran-3(2*H*)-one (10′): Oil; ^{1}H NMR (270 MHz) δ = 0.82 (t, 3H, J = 7.3 Hz), 0.96 (t, 3H, J = 7.3 Hz), 1.07—1.34 (m, 4H), 1.79—1.85 (m, 2H), 2.93 (d, 2H, J = 15.6 Hz), 3.03 (d, 2H, J = 15.6 Hz), 3.87—4.00 (m, 2H), 7.05—7.10 (m, 2H), 7.60 (t, 1H, J = 7.8 Hz), 7.69 (d, 1H, J = 7.8 Hz); ^{13}C NMR δ = 13.65, 13.70, 22.68, 24.78, 36.49, 40.99, 60.76, 88.87, 112.92, 121.71, 121.89, 124.12, 137.63, 168.51, 171.59, 202.82; MS m/z 276 (M^+). Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.55; H, 7.29%. Found: C, 69.62; H, 7.22%.

***trans*-3-Benzoyl-2-butyl-2,3-dihydro-4*H*-1-benzopyran-4-one (11):** Mp 71.5—72.5 °C; ^{1}H NMR (400 MHz) (ca. 30% of this compound was found to exist as an enol form in $CDCl_3$) δ = 0.73 (t, 3H, J = 7.3 Hz; enol), 0.88 (t, 3H, J = 7.3 Hz), 1.04—1.93 (m, 6H), 4.69 (d, 1H, J = 11.0 Hz), 4.97 (ddd, 1H, J = 11.0, 8.3, 3.3 Hz), 5.28 (dd, 1H, J = 9.6, 4.7 Hz; enol), 6.91—7.07 (m, 2H), 7.44—7.64 (m, 5H), 7.86—8.04 (m, 2H), 16.24 (s, 1H; enol); ^{13}C NMR δ = 13.79, 13.87, 21.83, 22.33, 27.11, 27.51, 33.20, 35.34, 58.44, 75.77, 79.67, 117.97, 120.65, 121.39, 121.44, 126.40, 127.25, 128.63, 128.79, 128.89, 130.75, 133.72, 135.02, 135.48, 136.44, 137.61, 157.53, 161.18, 190.29, 196.63; MS m/z 308 (M^+). Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54%. Found: C, 77.61; H, 6.54%.

2-Benzoylmethyl-2-butyl-1-benzofuran-3(2*H*)-one (11′): Mp 119.5 °C; ^{1}H NMR (400 MHz) δ = 0.85 (t, 3H, J = 7.3 Hz), 1.16—1.39 (m, 4H), 1.83—1.97 (m, 2H), 3.58 (d, 1H, J = 17.3 Hz), 3.84 (d, 1H, J = 17.3 Hz), 7.03 (d, 1H, J = 8.3 Hz), 7.10 (t, 1H, J = 7.8 Hz), 7.42 (t, 2H, J = 7.8, 1.5 Hz), 7.53—7.61 (m, 2H), 7.74 (dd, 1H, J = 7.8, 1.5 Hz), 7.85—7.87 (m, 2H); ^{13}C NMR δ = 13.75, 22.78, 24.84, 36.81, 44.90, 88.80, 112.79, 121.62, 122.33, 124.02, 128.20, 128.56, 133.38, 136.32, 137.33, 171.33, 194.78, 203.45; MS m/z 296 (M^+). Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54%. Found: C, 77.60; H, 6.57%.

6-Nitro-2,3-dipropyl-2,3-dihydro-4*H*-1-benzopyran-4-one (12): Oil (*cis*/*trans* = 36 : 64); ^{1}H NMR (270 MHz) δ = 0.90—1.03 (m, 6H), 1.26—1.90 (m, 8H), 2.58 (dd, 1H, J = 12.7, 5.9 Hz; *trans*), 2.68—2.74 (m, 1H; *cis*), 4.53—4.63 (m, 1H), 7.05—7.09 (m, 1H), 8.30—8.36 (m, 1H), 8.75—8.77 (m, 1H); ^{13}C NMR δ = 13.63, 13.72, 13.92, 14.00, 18.47, 18.76, 19.79, 20.05, 25.72, 30.02, 31.90, 34.23, 48.96, 49.78, 81.49, 81.75, 118.90, 119.14, 119.67, 119.80, 123.72, 123.91, 130.05, 130.23, 141.85, 141.96, 163.68, 164.61, 192.78, 193.39; MS m/z 277 (M^+). Anal. Calcd for $C_{15}H_{19}NO_4$: C, 64.96; H, 6.91; N, 5.05%. Found: C, 65.20; H, 6.93; N, 5.04%.

(*E*)-4-(2-Hydroxyphenyl)-4-octene (13): Oil; ^{1}H NMR (400 MHz) δ = 0.82 (t, 3H, J = 7.3 Hz), 0.89 (t, 3H, J = 7.3 Hz), 1.31—1.39 (m, 4H), 1.81 (q, 2H, J = 7.3 Hz), 2.26 (t, 2H, J = 7.3 Hz), 5.16 (s, 1H), 5.71 (t, 1H, J = 7.3 Hz), 6.87—6.93 (m, 2H), 6.99 (dd, 1H, J = 7.3, 2.0 Hz), 7.17 (td, 1H, J = 7.3, 2.0 Hz);

^{13}C NMR δ = 13.66, 13.82, 21.30, 22.68, 30.98, 41.26, 114.57, 120.17, 126.96, 128.32, 128.69, 131.29, 135.79, 151.99; HRMS *m/z* (M^+). Calcd for $C_{14}H_{20}O$: M, 204.1521. Found: *m/z* 204.1527.

3-(Triethylsilyl)-1-(2-hydroxyphenyl)-1-propanone (15): Oil; ^{1}H NMR (400 MHz) δ = 0.59 (q, 6H, *J* = 7.8 Hz), 0.92—0.99 (m, 11H), 2.93—2.97 (m, 2H), 6.90 (td, 1H, *J* = 7.8, 1.0 Hz), 6.99 (d, 1H, *J* = 7.8 Hz), 7.46 (td, 1H, *J* = 7.8, 1.5 Hz), 7.74 (dd, 1H, *J* = 7.8, 1.5 Hz), 12.39 (s, 1H); ^{13}C NMR δ = 3.18, 6.22, 7.39, 32.87, 118.59, 118.81, 118.91, 129.79, 136.12, 162.56, 207.78; MS *m/z* 264 (M^+). Anal. Calcd for $C_{15}H_{24}O_2Si$: C, 68.13; H, 9.15%. Found: C, 68.41; H, 8.97%.

3-(Triethylsilyl)-1-(2-hydroxy-3-methoxyphenyl)-1-propanone (16): Oil; ^{1}H NMR (400 MHz) δ = 0.59 (q, 6H, *J* = 7.8 Hz), 0.92—0.99 (m, 11H), 2.93—2.97 (m, 2H), 3.90 (s, 3H), 6.84 (t, 1H, *J* = 7.8 Hz), 7.05 (d, 1H, *J* = 7.8 Hz), 7.35 (dd, 1H, *J* = 8.3, 1.5 Hz), 12.72 (s, 1H); ^{13}C NMR δ = 3.09, 6.07, 7.29, 33.16, 56.05, 116.60, 118.06, 118.86, 120.90, 148.99, 152.94, 208.07; MS *m/z* 294 (M^+). Anal. Calcd for $C_{16}H_{26}O_3Si$: C, 65.26; H, 8.90%. Found: C, 65.54; H, 8.80%.

***exo*-2-(2-Hydroxybenzoyl)bicyclo[2.2.1]heptane (18):** Oil; ^{1}H NMR (400 MHz) δ = 1.18—1.65 (m, 7H), 2.01—2.07 (m, 1H), 2.37 (s, 1H), 2.55 (s, 1H), 3.25 (dd, 1H, *J* = 8.8, 5.4 Hz), 6.89 (td, 1H, *J* = 7.8, 1.0 Hz), 6.98 (dd, 1H, *J* = 7.8, 1.0 Hz), 7.44 (td, 1H, *J* = 7.8, 1.5 Hz), 7.78 (dd, 1H, *J* = 7.8, 1.5 Hz), 12.48 (s, 1H); ^{13}C NMR δ = 28.92, 29.70, 33.84, 36.24, 36.33, 41.48, 49.22, 118.58, 118.67, 130.05, 135.82, 162.95, 207.88; HRMS *m/z* (M^+). Calcd for $C_{12}H_{14}O_2$: M, 216.1150. Found: *m/z* 216.1143.

1-(2-Hydroxyphenyl)-4-methyl-3-penten-1-one (20): Oil; ^{1}H NMR (400 MHz) δ = 1.72 (s, 3H), 1.78 (d, 3H, *J* = 1.0 Hz), 3.70 (d, 2H, *J* = 6.8 Hz), 5.38—5.42 (m, 1H), 6.90 (td, 1H, *J* = 7.8, 1.0 Hz), 6.98 (dd, 1H, *J* = 7.8, 1.0 Hz), 7.46 (td, 1H, *J* = 7.8, 1.5 Hz), 7.78 (dd, 1H, *J* = 7.8, 1.5 Hz), 12.27 (s, 1H); ^{13}C NMR δ = 18.18, 25.79, 38.27, 115.60, 118.55, 118.85, 119.13, 130.14, 136.25, 136.31, 162.68, 204.97; HRMS *m/z* (M^+). Calcd for $C_{12}H_{14}O_2$: M, 190.0994. Found: *m/z* 190.0993.

1-(2-Hydroxy-3-methoxyphenyl)-4-methyl-3-penten-1-one (21): Oil; ^{1}H NMR (400 MHz) δ = 1.71 (s, 3H), 1.78 (s, 3H), 3.71 (d, 2H, *J* = 6.8 Hz), 3.90 (s, 3H), 5.40 (t, 1H, *J* = 6.8 Hz), 6.85 (t, 1H, *J* = 7.8 Hz), 7.05 (d, 1H, *J* = 7.8 Hz), 7.38 (d, 1H, *J* = 7.8 Hz), 12.60 (s, 1H); ^{13}C NMR δ = 18.16, 25.77, 38.56, 56.18, 115.50, 116.81, 118.17, 119.17, 121.29, 136.34, 149.04, 153.14, 205.34; MS *m/z* 220 (M^+). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32%. Found: C, 70.78; H, 7.36%.

1-(5-Chloro-2-Hydroxyphenyl)-4-methyl-3-penten-1-one (22): Oil; ^{1}H NMR (400 MHz) δ = 1.72 (s, 3H), 1.79 (d, 3H, *J* = 1.5 Hz), 3.67 (d, 2H, *J* = 6.8 Hz), 5.36—5.40 (m, 1H), 6.94 (d, 1H, *J* = 8.8 Hz), 7.41 (dd, 1H, *J* = 8.8, 2.9 Hz), 7.72 (d, 1H, *J* = 2.9 Hz), 12.16 (s, 1H); ^{13}C NMR δ = 18.21, 25.79, 38.34, 114.97, 119.67, 120.20, 123.51, 129.34, 136.12, 136.86, 161.13, 204.06; HRMS *m/z* (M^+), Calcd for $C_{12}H_{13}ClO_2$: M, 224.0604. Found: *m/z* 224.0597.

1-(2-Hydroxyphenyl)-3-decen-1-one (24/24′): Oil [(*E*) : (*Z*) = 94 : 6]; ^{1}H NMR (400 MHz) δ = 0.85—0.89 (m, 3H), 1.26—1.39 (m, 8H), 2.03—2.14 (m, 2H), 3.70 (d, 2H, *J* = 5.4 Hz; **24**), 3.76 (d, 2H, *J* = 4.9 Hz; **24′**), 5.63—5.67 (m, 2H), 6.87—6.93 (m, 1H), 6.97—7.00 (m, 1H), 7.44—7.49 (m, 1H), 7.77 (dd, 1H, *J* = 7.8, 1.5 Hz; **24**), 7.78 (d, 1H, *J* = 7.8 Hz; **24′**), 12.23 (s, 1H; **24′**), 12.25 (s, 1H; **24**); ^{13}C NMR δ = 14.05, 22.58, 27.66, 28.78, 28.96, 29.10, 29.25, 31.66, 31.71, 32.62, 37.30, 42.34, 118.55, 118.59, 118.85, 119.03, 120.42, 121.43, 130.10, 130.23, 134.26, 135.84, 136.33, 136.34, 162.65, 162.69, 204.55, 204.93; HRMS *m/z* (M^+) Calcd for $C_{12}H_{14}O_2$: M, 246.1620. Found: **24**; *m/z* 246.1628, **24′**; *m/z* 246.1631.

(*E*)-1-(2-Hydroxyphenyl)-4-phenyl-3-buten-1-one (26): Mp 81—82 °C; ^{1}H NMR (400 MHz) δ = 3.93 (dd, 2H, *J* = 6.8, 1.0 Hz), 6.43 (dt, 1H, *J* = 16.1, 6.8 Hz), 6.57 (d, 1H, *J* = 16.1 Hz), 6.93 (td, 1H, *J* = 7.8, 1.0 Hz), 7.00 (dd, 1H, *J* = 7.8, 1.0 Hz), 7.21—7.25 (m, 1H), 7.31 (t, 2H, *J* = 7.3 Hz), 7.39 (d, 2H, *J* = 7.3 Hz), 7.49 (td, 1H, *J* = 7.8, 1.5 Hz), 7.82 (dd, 1H, *J* = 7.8, 1.5 Hz), 12.20 (s, 1H); ^{13}C NMR δ = 42.41, 118.66, 119.02, 119.04, 121.67, 126.30, 127.68, 128.56, 130.11, 134.15, 136.54, 136.71, 162.72, 204.12; MS *m/z* 238 (M^+). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92%. Found: C, 80.16; H, 5.98%.

(*E*)-1-(2-Hydroxyphenyl)-2-methyl-3-phenyl-2-propen-1-one (26′): Oil; ^{1}H NMR (400 MHz) δ = 2.27 (d, 3H, *J* = 1.5 Hz), 6.89 (td, 1H, *J* = 7.8, 1.0 Hz), 6.96 (d, 1H, *J* = 1.5 Hz), 7.05 (dd, 1H, *J* = 7.8, 1.0 Hz), 7.30—7.43 (m, 5H), 7.49 (td, 1H, *J* = 7.8, 2.0 Hz), 7.77 (dd, 1H, *J* = 7.8, 2.0 Hz), 11.85 (s, 1H); ^{13}C NMR δ = 15.36, 118.42, 118.51, 118.93, 128.46, 128.53, 129.52, 132.80, 135.47, 135.60, 136.01, 138.40, 163.04, 203.96; MS *m/z* 238 (M^+). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92%. Found: C, 80.57; H, 6.03%.

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