Rhodium-catalysed cyclic carbonylation of 2-alkynylphenols: synthesis of benzofuranones and coumarins

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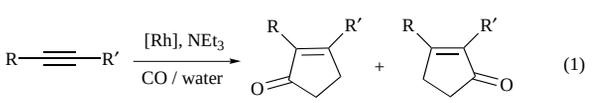
Rhodium-catalysed carbonylation of 2-alkynylphenols 1 under water-gas shift reaction conditions gives benzofuranone derivatives 2 and coumarin derivatives 3 in high yield (up to 96%, 2 : 3 = 65 : 35), in which the hydroxy group adjacent to the carbon–carbon triple bond participitates in the cyclic carbonylation.

Introduction

Carbonylations of alkenes and alkynes with transition metal catalysts have been extensively investigated for a long time by many chemists because of their industrial importance.[1–3] Even in recent years the development of new types of carbonylations is still the subject of both academic and industrial research.[4–8] Of special interest is cyclic carbonylation giving heterocyclic products, which are often employed as important intermediates leading to bioactive substances.[9–13] Such examples include cyclic carbonylation of acetylenes (alkynes) to give furanones.[14,15] We previously showed that carbonylation of acetylenes under water-gas shift reaction conditions ($CO + H_2O$)[16–19] selectively gives furan-2(3*H*)-ones in the presence of a rhodium catalyst [eqn. (1)].[20] This carbonylation may be characteristic of water-gas shift reaction conditions, since the carbonylation under oxo reaction conditions ($CO + H_2$) resulted in formation of normal hydroxymethylation products. The furanones formed under water-gas shift reaction conditions are derived from the incorporation of one molecule of acetylene, two molecules of carbon monoxide and one molecule of hydrogen, of which the latter comes from water.

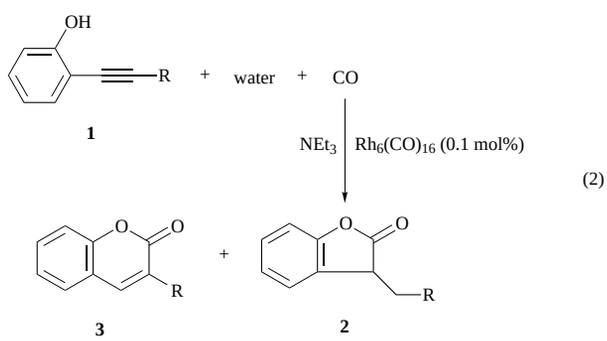


(1)

The reaction has wide applications and a variety of aromatic and aliphatic acetylenes give the corresponding furanone derivatives. We also paid attention to the carbonylation of acetylenes having a neighbouring functional group and found a novel cyclic carbonylation which afforded indolone[21] and tricyclic lactone products,[22] in which the neighbouring functional groups such as amino and formyl groups participate in the carbonylation of acetylenes. Here we report a new cyclic carbonylation of acetylenes having a hydroxy group which gives 3-substituted benzofuranone and 3-substituted coumarin under water-gas shift reaction conditions by using a $Rh_6(CO)_{16}$ catalyst.

Results and discussion

2-Alkynylphenols having a hydroxy group at an *ortho* position were prepared by a coupling reaction between terminal acetylenes and aryl halides which we previously developed by using CuI–$Pd(PPh_3)_2Cl_2$ catalyst.[23] First the carbonylation of 2-(phenylethynyl)phenol **1a** was attempted at 80 °C under 100 atm of CO in the presence of a $Rh_6(CO)_{16}$ catalyst, water and triethylamine, which are the same reaction conditions as successfully employed for the synthesis of diarylfuranones from diarylacetylenes,[19] but a complex mixture which could not be identified was formed. However, when the reaction temperature was raised from 80 to 175 °C, the reaction gave benzofuranone and coumarin derivatives in a total yield of up to 96% [eqn. (2)].



(2)

(**a**: R = Ph; **b**: C_6H_4OMe-4; **c**: C_6H_4CN-4; **d**: Bu^t; **e**: Bu^n; **f**: Me)

A representative reaction procedure is as follows. A mixture of 2-(phenylethynyl)phenol **1a** (5 mmol), $Rh_6(CO)_{16}$ (0.005 mmol), triethylamine (5 mmol) and water (20 mmol) in 1,4-dioxane (60 ml) was stirred at 175 °C for 3 h under 100 atm of carbon monoxide. After the usual work-up, isolation by column chromatography gave 3-benzylbenzofuran-2-one **2a** and 3-phenylcoumarin **3a** in 61 and 33% high-performance liquid chromatography (HPLC) yield, and in 52 and 25% isolated yield, respectively. Products **2a** and **3a** were identified by ^1H NMR, IR and mass spectra and elemental analyses. The benzofuranone **2a** was identified by its mass spectrum which showed a peak with *m*/*z* 224 (M^+) corresponding to the sum of the mass number of substrate **1a** + 30 amu ($CO + H_2$). In the IR spectrum, a characteristic absorption appeared at 1802 cm^{-1} due to typical $\nu_{C=O}$ of unsaturated five-membered lactones, and the ^1H NMR spectrum is consistent with 3-benzylbenzofuran-2-one.[24] Similarly, its mass spectrum [*m*/*z*, 222 (M^+)] suggested compound **3a** to be the product derived from substrate **1a** (M = 194) with CO (M = 28). An absorption at 1716 cm^{-1} attributable to typical $\nu_{C=O}$ of unsaturated six-membered lactones was observed. The ^1H NMR spectrum is consistent with 3-phenylcoumarin.[25] Small amounts (<2%) of (*E*)-1-(2-hydroxyphenyl)-2-phenylethylene were also detected as a hydrogenated ion by-product from substrate **1a**.

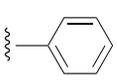
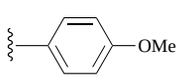
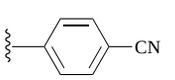
Product **2a** is constructed from reagents **1a**, CO and H_2, while product **3a** comes from one molecule each of reagents **1a** and CO. Formation of product **3a** does not apparently require hydrogen; however, the reaction in the absence of water gave

Table 1 Synthesis of compounds **2** and **3** from 2-(phenylethynyl)-phenol **1a**[a]

Entry	Solvent	NEt_3 (mmol)	Water (mmol)	Conv. (%)	Yield (%)[b] **2**	**3**
1	1,4-dioxane	5	20	100	61	33
2	THF	5	20	100	44	5
3	toluene	5	20	100	48	15
4	1,4-dioxane	10	20	100	63	36
1	1,4-dioxane	5	20	100	61	33
5	1,4-dioxane	0	20	10	0	0
6	1,4-dioxane	5	80	100	60	32
1	1,4-dioxane	5	20	100	61	33
7	1,4-dioxane	5	0	8	0	0

[a] Conditions: substrate, 5 mmol; $Rh_6(CO)_{16}$, 0.1 mol%; 1,4-dioxane, 60 ml; 175 °C; 3 h. [b] Yields are based on 2-alkynylphenol and determined by HPLC.

Table 2 Synthesis of compounds **2** and **3** from 2-alkynylphenols **1**

Entry	Substituent R	Yield of products (%)[a] **2**	**3**
1	 **1a**	61(52)	33(25)
2	 **1b**	55(48)	31(22)
3	 **1c**	57(47)	32(25)
4	Bu^t **1d**	58(51)	24(20)
5	Bu^n **1e**	42(25)	39(23)
6	Me **1f**	45(11)	51(47)

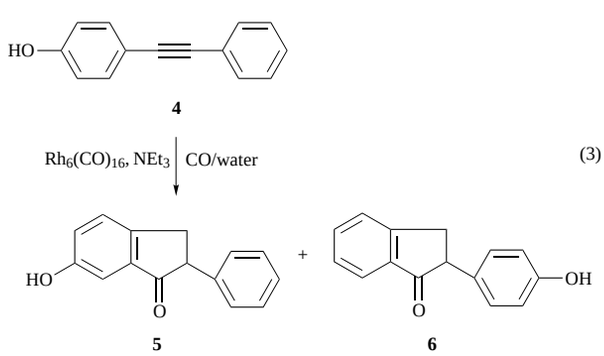
[a] Yields were determined by HPLC; parentheses indicate isolated yields.

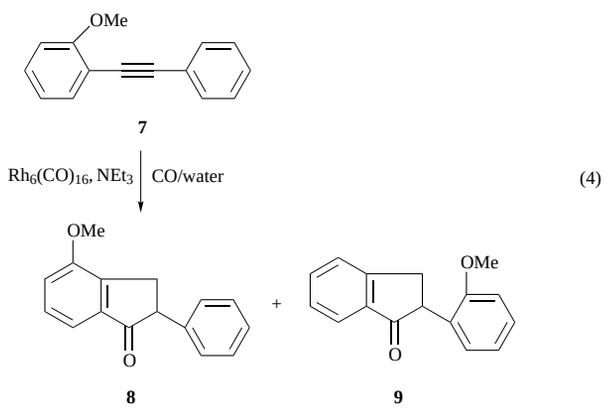
neither compound **2a** nor compound **3a**. Thus, the present reaction seems to proceed only under the water-gas shift reaction conditions.

The effects of solvents and additives such as water and amine are summarized in Table 1. 1,4-Dioxane is the best choice as a solvent for the product selectivity although the reaction also proceeds in solvents such as tetrahydrofuran (THF) and toluene. In the absence of either triethylamine or water, the reaction did not occur and the starting material was recovered. This suggests that both water and amine are requisite for the present reaction system. Although rhodium complexes such as $[Rh(CO)_2Cl]_2$ and $RhCl_3$ showed almost the same catalytic activity as $Rh_6(CO)_{16}$, no catalytic activity was recognized for metal carbonyls such as $Ru_3(CO)_{12}$, $Fe_2(CO)_{10}$ or $Co_2(CO)_8$ under the same reaction conditions.

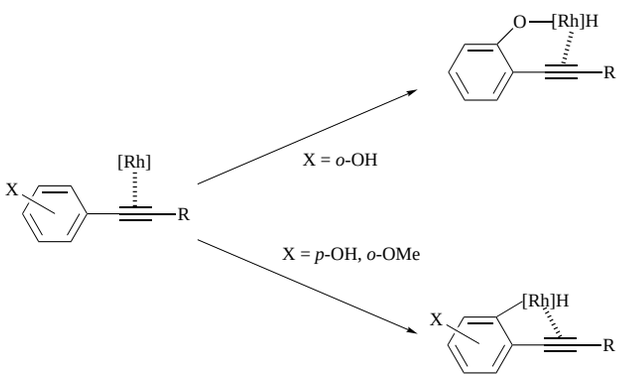
In order to explore the scope of the present reaction, the carbonylation of substrates bearing several kinds of substituent R on the ethynyl group of 2-alkynylphenol derivatives **1** was carried out and the results are summarized in Table 2. The Table shows wide applications of the present carbonylation to 2-alkynylphenols including 2-alkyl- and 2-aryl-ethynylphenols, and all the reactions proceeded smoothly to give products **2** and **3** in good yield. The reaction of 2-alkynylphenol **1b** (R = 4-$CH_3OC_6H_4$) gave products **2b** and **3b** in a total yield of 86% in the ratio 64:36, and substrate **1c** (R = 4-NCC_6H_4) produced compounds **2c** and **3c** in the ratio 64:36, indicating that the electron-releasing and -withdrawing substituents on the phenyl group have almost no effect on the product distribution. Alkyl substituents, however, significantly affect the distribution; **1d** (R = Bu^t) afforded products **2d** and **3d** in the ratio 71:29, while ratios of 52:48 for an *n*-butyl group (**1e**) and 47:53 for a methyl group (**1f**) were observed. These results suggest that the substituent R on the ethynyl group is likely to affect the product selectivity by steric factors rather than electronic ones. Thus among substrates **1a**–**1f**, the largest substituent, Bu^t, gave the lowest selectivity for the coumarins **3**, while the smallest one, CH_3, results in the highest selectivity.

On the other hand, 4-alkynylphenol **4** and 2-(phenylethynyl)-anisole **7** did not undergo a similar cyclic carbonylation under the same reaction conditions, and instead gave indanone derivatives in good yields which were formed by accompanying C–H bond activation of a phenyl ring. Thus, the phenol **4** gave an isomeric mixture of indanones **5** and **6** in 43 and 40% HPLC yield, respectively [eqn. (3)]. This reaction may be understood by considering the fact that the hydroxy group in substrate **4** is located at the *para*-position to the acetylenic group and is unable to participate in the intramolecular carbonylation. The carbonylation of compound **7** also produced an isomeric mixture of indanones **8** and **9** in 38 and 45% HPLC yield, respectively [eqn. (4)], because of inactivity of the methoxy group, although it is at the neighbouring position to the acetylenic group.





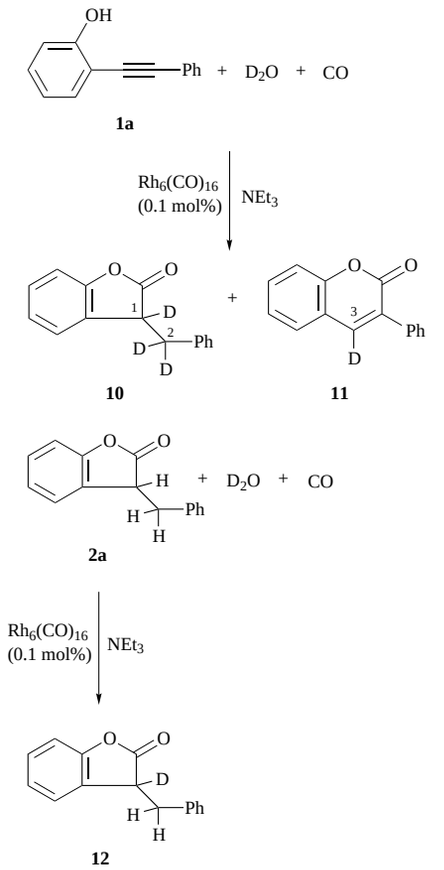
The formation of indanones (**5**, **6**, **8** and **9**) must involve *ortho* C–H bond activation of a phenyl group (Scheme 1). If a



Scheme 1

hydroxy group exists at a position adjacent to the C≡C group, the oxidative addition of the OH to the Rh centre would be preferred to the *ortho* C–H bond activation of a phenyl group.

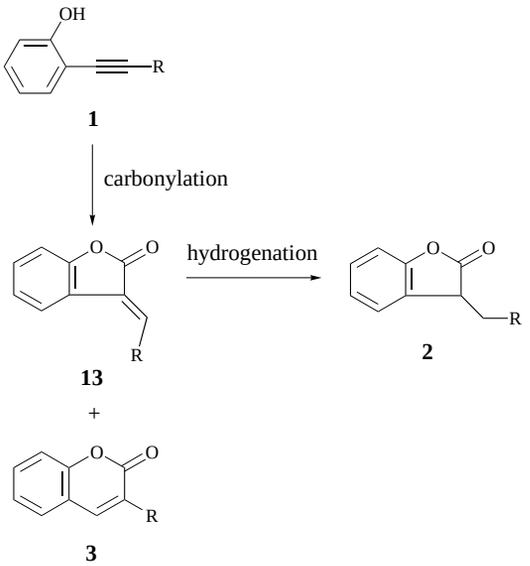
In order to investigate the mechanism of the present reaction, the carbonylation of compound **1a** was carried out by use of D_2O (10.0 mol equiv.) instead of water. The ^1H NMR spectrum indicated the products to be compounds **10** and **11** (Scheme 2).



Scheme 2

An H–D exchange may be expected to occur at the C-1 position after formation of the indanone **10** since C-1–H must be activated by the neighbouring carbonyl group. In fact, treatment of compound **2a** with an excess of D_2O under the same reaction conditions afforded compound **12** in which only C-1 was deuteriated, while no H–D exchange was observed at C-2. These facts suggest that compounds **2** were produced *via* an initial formation of compounds **13**, followed by hydrogenation with hydrogen which came from water by catalysis of the Rh species (Scheme 3). The hydrogenation of *exo*-methylene lactones **13** to products **2** may be understood on the basis of the fact that the present catalytic system is also effective for hydrogenation of some olefins.[18] In a separate experiment no H–D exchange was observed at all in the reaction between compounds **3** and D_2O, indicating, as combined with the above experimental results, that the hydrogen at C-3 in compounds **3** as well as one of the two hydrogen atoms at C-2 in compounds **2** may derive from the hydrogen of the phenol.

The carbonylation of compound **1a** in the presence of excess of phenol (50 mmol) was carried out and we confirmed that the same reaction as that in the absence of phenol took place according to eqn. (2) and the additive phenol was recovered intact. This fact may imply the first step of the present carbonylation to be a coordination of the C≡C, but not OH, to the Rh catalyst. A possible mechanism for the formation of benzofuranone and coumarin products is proposed in Scheme 4. The initial step may involve coordination[26] of the acetylene to the Rh catalyst giving complex **14** of a (π-acetylene) Rh species and



Scheme 3

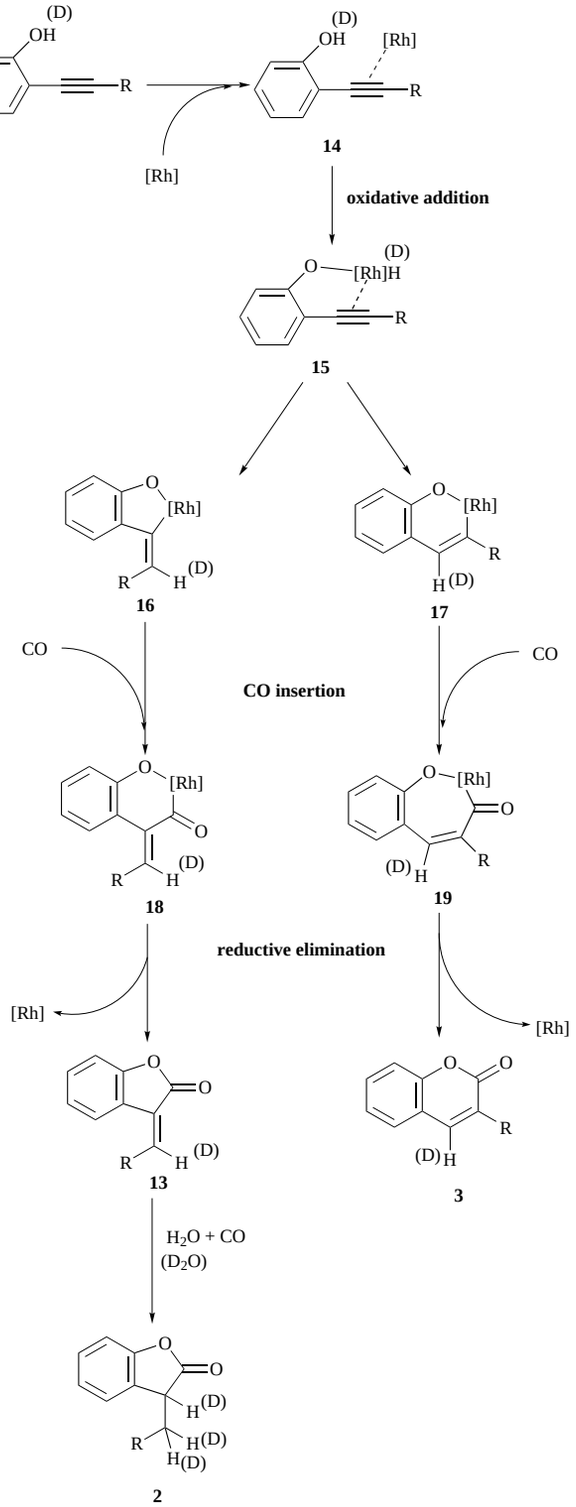
then oxidative addition[27] of the adjacent hydroxy group to the central Rh atom may form cyclic intermediate **15**. Insertion of the acetylene to the M–H bond gives complex **16** or **17**, which depends on the steric effect of substituent R. Successive insertion of carbon monoxide into the M–C bond[28] gives complex **18** or **19**, followed by reductive elimination of the Rh species to give cyclic product **2** or **3**. An alternative mechanism as shown in Scheme 5 may be considered. This involves an addition of a rhodium hydride to an acetylenic bond prior to that of phenol, followed by carbonyl insertion to give acyl intermediates **20** and **21**. The intramolecular nucleophilic attack of phenol to the acyl-Rh species gives rise to intermediates **22** and **23** which correspond to intermediates **18** and **19** in Scheme 4, respectively. Both mechanisms can explain the configuration of the products as well as the result of labelling experiments, but there may be drawbacks in the pathways leading to the formation of product **3**. The pathway from intermediates **15** to **17** in Scheme 4 requires *E* addition of Rh–H which is unprecedented, and the one from intermediates **21** to **23** in Scheme 5 involves an attack of the phenolic OH group to the Rh centre which is located far from the OH. Further study on the mechanism is required and is now in progress.

Conclusions

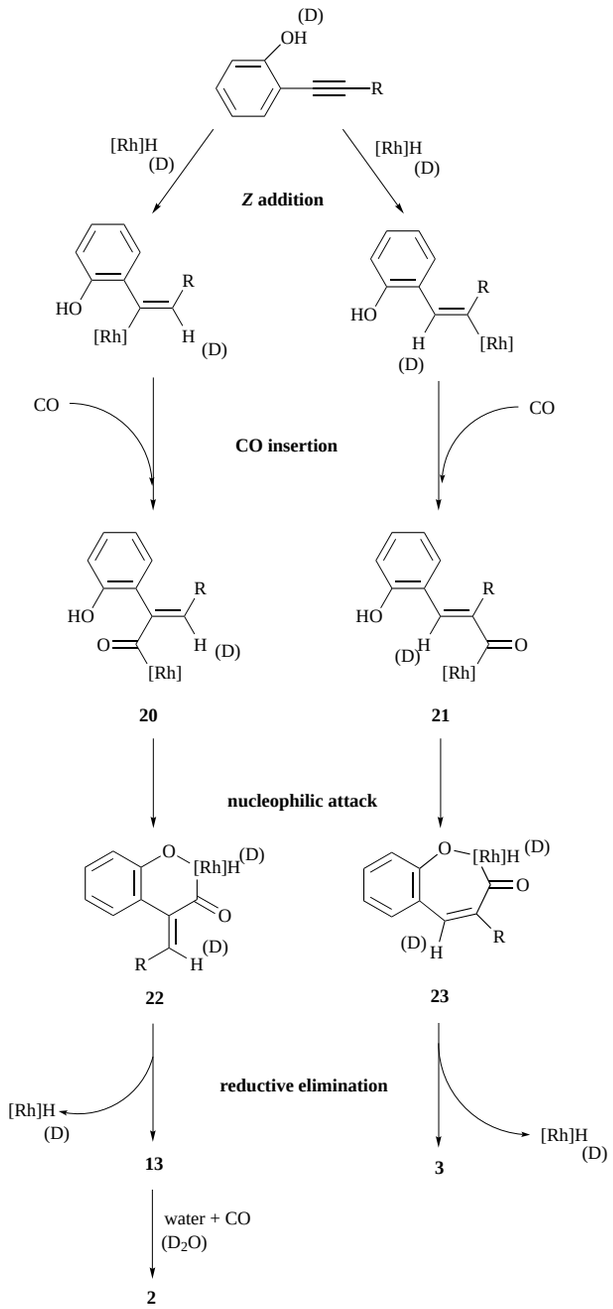
Cyclic carbonylations of 2-alkynylphenols **1** (R = Ph, Bu^t, Bu^n, Me, *p*-methoxyphenyl, *p*-cyanophenyl) catalysed by a rhodium complex under water-gas shift reaction conditions give benzofuranone **2** and coumarin **3** derivatives in high yield, in which the hydroxy group adjacent to the triple bond is incorporated in the cyclization. This reaction may provide a useful method for the synthesis of a variety of benzofuranone and coumarin derivatives directly from 2-alkynylphenols which are easily prepared from commercially available substances by a Pd–Cu-catalysed C(sp)–C(sp^2) coupling reaction. On the other hand, the carbonylation of 4-(phenylethynyl)phenol **4** and 2-(phenylethynyl)anisole **7** gives indanone derivatives *via ortho* C–H bond activation of a phenyl group adjacent to the triple bond.

Experimental

^1H NMR spectra were recorded on a JEOL JNM-LA 400 (400 MHz) spectrometer for solutions in $CDCl_3$ using $SiMe_4$ as internal standard. *J*-Values are given in Hz. IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrophotometer. Mass spectra were obtained using a Shimadzu GCMS-QP2000 spectrometer. Elemental analyses were per-



Scheme 4



Scheme 5

formed using a Perkin-Elmer 240c instrument. Analytical HPLC was performed on a Nakarai 5SL (4.6 × 250 mm) chromatograph. Mps were determined using a Yamato Melting Point Apparatus Model MP-21 and are uncorrected. Solvents and reagents were dried and purified prior to use according to standard procedures. TLC was carried out with Merck precoated silica gel plates (Kieselgel G 60 F_{254}). Spots were visualized with UV light. The following compounds were known and have spectral data in accord with the literature data: **1a**,[29] **1e**,[29] **1f**,[30] **2a**,[24] **3a**,[25] **3b**,[31] **3e**,[32] **4**[33] and **7**.[34]

Preparation of 2-(phenylethynyl)phenol 1a

A mixture of 2-iodophenol (25.0 g, 113 mmol) and NaH (3.9 g, 186 mmol) in 1,2-dimethoxyethane (120 ml) was stirred for 0.5 h on an ice-bath, then at room temp. for 5 h. After filtration, the filtrate was evaporated under reduced pressure. The residue was extracted with diethyl ether, the extract was dried over Na_2SO_4, and the diethyl ether was removed to give 2-iodophenyl methoxymethyl ether.

A mixture of 2-iodophenyl methoxymethyl ether (7.44 g, 30 mmol) and phenylacetylene (4.60 g, 45 mmol) in the presence of $PdCl_2(PPh_3)_2$ (0.21 g, 0.3 mmol) and CuI (0.23 g, 0.60 mmol) in Et_2NH (150 ml) was stirred for 12 h at room temp. After removal of the solvent under reduced pressure, the residue was passed through a silica gel column successively with benzene–hexane (1 : 5) and then benzene. The benzene eluate was evaporated to give methoxymethyl 2-(phenylethynyl)phenol ether (5.37 g, 75%).[23]

A mixture of methoxymethyl 2-(phenylethyl)phenyl ether (1.91 g, 8.0 mmol) and conc. HCl (1.5 ml) in MeOH (40 ml) was stirred for 24 h at room temp. After removal of the solvent, water was added to the residue. The resulting mixture was extracted with CH_2Cl_2, and the extract was dried over Na_2SO_4.

The solvent was removed under reduced pressure and recrystallization of the residue from hexane gave 2-(phenylethynyl)-phenol **1a** as needles (0.95 g, 68%), mp 67 °C; ν_{max}(KBr)/cm^{-1} 3494 (O–H), 2214 (C≡C) and 1198 (C–O); δ_H(400 MHz; $CDCl_3$) 5.83 (1 H, s, OH) and 6.88–7.57 (9 H, m, ArH); *m*/*z* (EI) 194 (M^+, 100%), 165 (47), 92 (10) and 82 (16).

2-[(4-Methoxyphenyl)ethynyl]phenol 1b

According to the preparation of compound **1a**, 2-iodophenyl methoxymethyl ether was treated with 4-methoxyphenylacetylene to give *title compound* **1b** as crystals (2.47 g, 77%), mp 48 °C (Found: C, 80.2; H, 5.2. $C_{15}H_{12}O_2$ requires C, 80.3; H, 5.3%); ν_{max}(KBr)/cm^{-1} 3518 (O–H), 1248 (C–O), 1175 (C–O) and 1027 (C–O); δ_H(400 MHz; $CDCl_3$) 3.84 (3 H, s, OCH_3), 5.84 (1 H, s, OH), 6.87–6.99 (4 H, m, ArH), 7.38–7.42 (2 H, m, ArH) and 7.47 (2 H, d, *J* 8.9, ArH); *m*/*z* (EI) 224 (M^+, 100%), 209 (100), 181 (67), 152 (33), 112 (20) and 82 (8).

2-[(4-Cyanophenyl)ethynyl]phenol 1c

According to the preparation of compound **1a**, 2-iodophenyl methoxymethyl ether was treated with 4-cyanophenylacetylene to give *title compound* **1c** as crystals (3.51 g, 62%), mp 149 °C (Found: C, 82.1; H, 4.1; N, 6.4. $C_{15}H_9NO$ requires C, 82.1; H, 4.1; N, 6.3%); ν_{max}(KBr)/cm^{-1} 3403 (O–H), 2233 (C≡N), 2215 (C≡C) and 1200 (C–O); δ_H(400 MHz; $CDCl_3$) 5.69 (1 H, s, OH), 6.94 (1 H, t, *J* 7.5, ArH), 6.99 (1 H, d, *J* 7.5, ArH), 7.32 (1 H, t, *J* 7.3, ArH), 7.44 (1 H, d, *J* 7.5, ArH) and 7.61–7.68 (4 H, m, ArH); *m*/*z* (EI) 219 (M^+, 100%), 190 (43), 164 (9), 109 (15), 82 (26) and 63 (18).

2-(3,3-Dimethylbut-1-ynyl)phenol 1d

According to the preparation of compound **1a**, 2-iodophenyl methoxymethyl ether was treated with 3,3-dimethylbut-1-yne to give *title compound* **1d** as a pale yellow oil (1.73 g, 67%) (Found: C, 82.9; H, 7.8. $C_{12}H_{14}O$ requires C, 82.7; H, 8.0%); ν_{max}(KBr)/cm^{-1} 3508 (O–H), 2231 (C≡C) and 1152 (C–O); δ_H(400 MHz; $CDCl_3$) 1.55 [9 H, s, $C(CH_3)$], 5.82 (1 H, s, OH) and 7.00–7.49 (4 H, m, ArH); *m*/*z* (EI) 174 (M^+, 36%), 159 (100), 131 (18), 115 (31), 91 (32) and 77 (19).

2-(Hex-1-ynyl)phenol 1e

According to the preparation of compound **1a**, 2-iodophenyl methoxymethyl ether was treated with hex-1-yne to give *title compound* **1e** as a pale yellow oil (6.20 g, 89%); ν_{max}(KBr)/cm^{-1} 3504 (O–H); δ_H(400 MHz; $CDCl_3$) 0.95 (3 H, t, *J* 7.3, CH_3), 1.40–1.66 (4 H, m, CH_2CH_2), 2.47 (2 H, t, *J* 6.9, CH_2), 5.82 (1 H, s, OH), 6.80–6.94 (2 H, m, ArH) and 7.15–7.30 (2 H, m, ArH); *m*/*z* (EI) 174 (M^+, 20%), 131 (100), 77 (21) and 51 (12).

2-(Prop-1-ynyl)phenol 1f

According to the preparation of compound **1a**, 2-iodophenyl methoxymethyl ether was treated with propyne to give *title compound* **1f** as needles (2.95 g, 81%), mp 56 °C; ν_{max}(KBr)/cm^{-1} 3501 (O–H), 2254 (C≡C) and 181 (C–O); δ_H(400 MHz; $CDCl_3$) 2.13 (3 H, s, CH_3), 5.80 (1 H, s, OH), 6.80–6.93 (2 H, m, ArH), 7.16–7.30 (2 H, m, ArH); *m*/*z* (EI) 132 (M^+, 77%), 131 (100), 103 (25), 86 (48), 84 (66) and 77 (29).

4-(Phenylethynyl)phenol 4

According to the preparation of compound **1a**, 4-iodophenyl methoxymethyl ether was treated with propyne to give title compound **4** as crystals (4.27 g, 58%); mp 124 °C; ν_{max}(KBr)/cm^{-1} 3272 (O–H) and 1236 (C–O); δ_H(400 MHz; $CDCl_3$) 4.83 (1 H, s, OH), 6.85 (2 H, d, *J* 8.8, ArH), 6.96 (1 H, s, ArH), 7.39 (2 H, t, *J* 7.6, ArH), 7.59 (2 H, d, *J* 8.8, ArH) and 7.71 (2 H, d, *J* 7.8, ArH); *m*/*z* (EI) 194 (M^+, 100%) and 165 (38).

1-Methoxy-2-(phenylethynyl)benzene 7

A mixture of iodo-2-methoxybenzene and hex-1-yne in the presence of $PdCl_2(PPh_3)_2$ and CuI in Et_2NH was stirred for 12 h at room temp. After removal of the solvent under reduced pressure, the residue was passed through a silica gel column with benzene and then with benzene–ethyl acetate (1 : 3). The benzene–ethyl acetate (1 : 3) eluent was evaporated to give 1-methoxy-2-(phenylethynyl)benzene **7** as a pale yellow oil (5.04 g, 81%); δ_H(400 MHz; $CDCl_3$) 3.83 (3 H, s, OCH_3), 6.83 (1 H, d, *J* 8.3, ArH), 6.88 (1 H, t, *J* 7.6, ArH), 7.21–7.30 (4 H, m, ArH), 7.45 (1 H, d, *J* 7.6, ArH) and 7.52 (2 H, d, *J* 5.1, ArH); *m*/*z* (EI) 208 (M^+, 100%), 178 (13), 165 (22) and 131 (28).

General procedure for carbonylation

A mixture of 2-(phenylethynyl)phenol **1a** (970 mg, 5 mmol), $Rh_6(CO)_{16}$ (5 mg, 0.005 mmol), Et_3N (505 mg, 5 mmol) and water (360 mg, 20 mmol) in 1,4-dioxane (60 ml) was placed in a 100 ml stainless steel autoclave and stirred under 100 atm of carbon monoxide at 175 °C for 3 h. After removal of the solvent from the reaction mixture under reduced pressure, TLC analysis of the residue showed formation of two kinds of products, which were separated by column chromatography on silica gel using benzene as an eluent. Recrystallization from ethanol gave 3-benzylbenzofuran-2-(3*H*)-one **2a** in 52% yield and 3-phenyl-2*H*-chromen-2-one **3a** in 25% yield.

3-Benzylbenzofuran-2-(3*H*)-one 2a. This was obtained as crystals (578 mg, 52%); mp 57 °C; ν_{max}(KBr)/cm^{-1} 1802 (C=O), 1231 (C–O) and 1062 (C–O); δ_H(400 MHz, $CDCl_3$) 3.03 (1 H, dd, *J* 9.2 and 13.9, CH_2), 3.50 (1 H, dd, *J* 4.8 and 13.7, CH_2), 4.01 (1 H, dd, *J* 4.8 and 8.7, CH) and 6.75–7.31 (9 H, m, ArH); *m*/*z* (EI) 224 (M^+, 68%), 165 (49) and 91 (100).

3-Phenyl-2*H*-chromen-2-one 3a. This was obtained as pale yellow needles (280 mg, 25%), mp 140 °C (Found: C, 80.8; H, 4.2. Calc. for $C_{15}H_{10}O_2$: C, 81.0; H, 4.5%); ν_{max}(KBr)/cm^{-1} 1716 (C=O), 1610 (C=C) and 1119 (C–O); δ_H(400 MHz, $CDCl_3$) 7.20–7.79 (9 H, m, ArH) and 7.83 (1 H, s, CH); *m*/*z* (EI) 222 (M^+, 100%), 194 (92), 165 (84), 139 (15), 111 (7), 97 (13), 83 (73) and 63 (21).

Carbonylation of compound 1b

According to the carbonylation of compound **1a**, the carbonylation of compound **1b** was carried out at 175 °C for 3 h to give products **2b** and **3b**.

3-[(4-*Methoxyphenyl*)*methyl*]*benzofuran*-2-(3H)-*one* **2b** was obtained as crystals (610 mg, 48%), mp 175 °C (Found: C, 75.5; H, 5.3. $C_{16}H_{14}O_3$ requires C, 75.5; H, 5.5%); ν_{max}(KBr)/cm^{-1} 1802 (C=O), 1250 (C–O), 1179 (C–O), 1124 (C–O) and 1061 (C–O); δ_H(400 MHz; $CDCl_3$) 3.01 (1 H, dd, *J* 8.9 and 13.9, CH), 3.42 (1 H, dd, *J* 4.7 and 13.7, CH), 3.78 (3 H, s, OCH_3), 3.96 (1 H, dd, *J* 4.7 and 8.6, CH), 6.78–6.85 (3 H, m, ArH), 7.03 (4 H, t, *J* 7.9, ArH) and 7.25–7.36 (1 H, m, ArH); *m*/*z* (EI) 254 (M^+, 36%), 237 (8), 224 (35), 209 (35), 202 (11), 121 (100) and 97 (7).

3-(4-Methoxyphenyl)-2*H*-chromen-2-one **3b** was obtained as crystals (277 mg, 22%); ν_{max}(KBr)/cm^{-1} 1715 (C=O), 1608 (C=C), 1253 (C–O), 1175 (C–O), 1127 (C–O) and 1032 (C–O); δ_H(400 MHz; $CDCl_3$) 3.86 (3 H, s, OCH_3), 6.99 (2 H, d, *J* 8.9, ArH), 7.28–7.38 (2 H, m, ArH), 7.51 (4 H, q, *J* 7.9, ArH) and 7.77 (1 H, s, CH); *m*/*z* (EI) 252 (M^+, 100%), 209 (59), 181 (34), 152 (26) and 63 (10).

Carbonylation of compound 1c

According to the carbonylation of compound **1a**, the carbonylation of compound **1c** was carried out at 175 °C for 3 h to give products **2c** and **3c**.

3-[(4-*Cyanophenyl*)*methyl*]*benzofuran*-2-(3H)-*one* **2c** was obtained as pale yellow crystals (585 mg, 47%), mp 156 °C (Found: C, 76.8; H, 4.2; N, 5.4. $C_{16}H_{11}NO_2$ requires C, 77.1; H, 4.4; N, 5.6%); ν_{max}(KBr)/cm^{-1} 2224 (C≡N), 1796 (C=O), 1123 (C–O) and 1064 (C–O); δ_H(400 MHz; $CDCl_3$) 3.22 (1 H, dd, *J* 7.8 and 13.9, CH_2), 3.48 (1 H, dd, *J* 5.1 and 13.9, CH_2), 4.05 (1 H, dd, *J* 5.3 and 7.8, CH), 6.92 (1 H, d, *J* 7.3, ArH), 7.03 (1 H, d, *J* 8.0, ArH), 7.08 (1 H, t, *J* 7.5, ArH), 7.23–7.30 (3 H,

m, ArH) and 7.55 (2 H, d, *J* 6.5, ArH); *m*/*z* (EI) 249 (M^+, 58%), 247 (38), 219 (37), 190 (40), 133 (97), 116 (100), 89 (17) and 77 (25).

3-(4-*Cyanophenyl*)-2H-*chromen*-2-*one* **3c** was obtained as crystals (309 mg, 25%), mp 238 °C (Found: C, 77.8; H, 3.3; N, 5.4. $C_{16}H_9NO_2$ requires C, 77.7; H, 3.6; N, 5.6%); ν_{max}(KBr)/cm^{-1} 2229 (C≡N), 1711 (C=O), 1609 (C=C), 1175 (C–O) and 1153 (C–O); δ_H(400 MHz; $CDCl_3$) 7.34 (1 H, t, *J* 7.0, ArH), 7.40 (1 H, d, *J* 8.5, ArH), 7.59 (2 H, d, *J* 7.3, ArH), 7.74 (2 H, d, *J* 8.3, ArH), 7.85 (2 H, d, *J* 8.1, Ph) and 7.90 (1 H, s, CH); *m*/*z* (EI) 247 (M^+, 88%), 219 (100), 190 (62), 164 (26), 123 (12), 110 (7), 95 (6) and 82 (41).

Carbonylation of compound 1d

According to the carbonylation of compound **1a**, the carbonylation of compound **1d** was carried out at 175 °C for 3 h to give products **2d** and **3d**.

3-(2,2-*Dimethylpropyl*)*benzofuran*-2(3H)-*one* **2d** was obtained as an oil (520 mg, 51%) (Found: C, 76.1; H, 7.6. $C_{13}H_{16}O_2$ requires C, 76.4; H, 7.9%); ν_{max}(KBr)/cm^{-1} 1805 (C=O), 1618 (C=C), 1233 (C–O) and 1064 (C–O); δ_H(400 MHz; $CDCl_3$) 1.07 [9 H, s, $C(CH_3)$], 1.75 (1 H, dd, *J* 4.5 and 14.3, CH), 2.05 (1 H, dd, *J* 4.7 and 14.3, CH), 3.61 (1 H, t, *J* 4.6, CH) and 7.06–7.30 (4 H, m, ArH); *m*/*z* (EI) 204 (M^+, 51%), 161 (19), 147 (38), 134 (42), 120 (56), 119 (46) and 57 (100).

3-(tert-*Butyl*)-2H-*chromen*-2-*one* **3d** was obtained as needles (202 mg, 20%), mp 83 °C (Found: C, 77.4; H, 6.8. $C_{13}H_{14}O_2$ requires C, 77.2; H, 6.9%); ν_{max}(KBr)/cm^{-1} 1718 (C=O), 1621 (C=C), 1136 (C–O) and 1036 (C–O); δ_H(400 MHz; $CDCl_3$) 1.40 [9 H, s, $C(CH_3)$], 7.20 (4 H, m, ArH) and 7.54 (1 H, s, CH); *m*/*z* (EI) 202 (M^+, 46%), 187 (100), 160 (82), 144 (10), 121 (19), 115 (31) and 78 (19).

Carbonylation of compound 1e

According to the carbonylation of compound **1a**, the carbonylation of compound **1e** was carried out at 175 °C for 3 h to give products **2e** and **3e**.

3-*Phenylbenzofuran*-2(3H)-*one* **2e** was obtained as an oil (253 mg, 25%) (Found: C, 76.2; H, 7.6. $C_{13}H_{16}O_2$ requires C, 76.4; H, 7.9%); ν_{max}(KBr)/cm^{-1} 1803 (C=O), 1231 (C–O) and 1054 (C–O); δ_H(400 MHz; $CDCl_3$) 0.86 (3 H, t, *J* 3.6, CH_3), 1.40–1.42 (6 H, m, $CH_2CH_2CH_2$), 2.47 (2 H, m, CH_2), 3.71 (1 H, t, *J* 5.9, CH) and 7.07–7.32 (4 H, m, ArH); *m*/*z* (EI) 204 (M^+, 55%), 175 (9), 147 (19), 133 (100), 120 (71), 107 (91), 91 (34) and 77 (34).

3-Butyl-2*H*-chromen-2-one **3e** was obtained as crystals (232 mg, 23%), mp 64 °C; ν_{max}(KBr)/cm^{-1} 1718 (C=O), 1610 (C=C), 1235 (C–O) and 1055 (C–O); δ_H(400 MHz; $CDCl_3$) 0.96 (3 H, t, *J* 7.2, CH_3), 1.35–1.69 (6 H, m, $CH_2CH_2CH_2$), 2.57 (2 H, t, *J* 7.2 CH_2) and 7.21–7.49 (4 H, m, ArH); *m*/*z* (EI) 202 (M^+, 22%), 173 (29), 160 (100), 131 (28), 115 (33) and 77 (9).

Carbonylation of compound 1f

According to the carbonylation of compound **1a**, the carbonylation of compound **1f** was carried out at 175 °C for 3 h to give products **2f** and **3f**.

3-*Ethylbenzofuran*-2-(3H)-*one* **2f** was obtained as an oil (96 mg, 11%) (Found: C, 73.8; H, 6.0. $C_{10}H_{10}O_2$ requires C, 74.0; H, 6.2%); ν_{max}(KBr)/cm^{-1} 1806 (C=O), 1127 (C–O) and 1051 (C–O); δ_H(400 MHz; $CDCl_3$) 0.97 (3 H, t, *J* 7.6, CH_3), 2.01–2.11 (2 H, m, CH_2), 3.70 (1 H, t, *J* 5.6, CH) and 7.08–7.33 (4 H, m, ArH); *m*/*z* (EI) 162 (M^+, 100%), 134 (76), 119 (92), 105 (28), 91 (70) and 77 (51).

3-*Methyl*-2H-*chromen*-2-*one* **3f** was obtained as crystals (396 mg, 45%), mp 91 °C (Found: C, 74.9; H, 4.7. $C_{10}H_8O_2$ requires C, 74.9; H, 5.0%); ν_{max}(KBr)/cm^{-1} 1717 (C=O), 1612 (C=C), 1185 (C–O) and 1072 (C–O); δ_H(400 MHz; $CDCl_3$) 2.22 (3 H, s, CH_3), 7.22–7.49 (4 H, m, ArH) and 7.52 (1 H, s, CH); *m*/*z* (EI) 160 (M^+, 100%), 145 (8), 131 (96), 115 (13), 103 (10) and 77 (29).

Carbonylation of compound 4

According to the carbonylation of compound **1a**, the carbonylation of compound **4** was carried out at 175 °C for 3 h to give products **5** and **6**.

6-*Hydroxy*-2-*phenylindan*-1-*one* **5** was obtained as crystals (414 mg, 37 %), mp 172 °C (Found: C, 80.0; H, 5.3. $C_{15}H_{12}O_2$ requires C, 80.3; H, 5.3%); δ_H(400 MHz; $CDCl_3$) 3.13 (1 H, dd, *J* 3.9 and 17.3, CH_2), 3.62 (1 H, dd, *J* 8.2 and 17.0, CH_2), 3.93 (1 H, dd, *J* 3.9 and 8.0, CH), 7.08 (1 H, s, ArH), 7.16–7.24 (4 H, m, ArH), 7.27–7.31 (2 H, m, ArH), 7.46 (1 H, d, *J* 8.3, ArH) and 8.75 (1 H, s, OH); *m*/*z* (EI) 208 (M^+, 100%).

2-(4-*Hydroxyphenyl*)*indan*-1-*one* **6** was obtained as crystals (347 mg, 31%), mp 168 °C (Found: C, 80.1; H, 5.3%); δ_H(400 MHz, $CDCl_3$) 3.23 (1 H, dd, *J* 3.9 and 16.8, CH_2), 3.67 (1 H, dd, *J* 8.7 and 17.9, CH_2), 3.84 (1 H, dd, *J* 3.9 and 8.2, CH), 6.76 (2 H, d, *J* 8.7, ArH), 7.04 (2 H, d, *J* 8.7, ArH), 7.16–7.44 (3 H, m, ArH), 7.65 (1 H, t, *J* 7.3, ArH) and 7.81 (1 H, d, *J* 7.5, ArH).

Carbonylation of compound 7

According to the carbonylation of compound **1a**, the carbonylation of compound **7** was carried out at 175 °C for 3 h to give products **8** and **9**.

4-*Methoxy*-2-*phenylindan*-1-*one* **8** was obtained as crystals (369 mg, 31%), mp 94 °C (Found: C, 80.8; H, 5.7. $C_{16}H_{14}O_2$ requires C, 80.6; H, 5.9%); ν_{max}(KBr)/cm^{-1} 1714 (C=O), 1244 (C–O) and 1051 (C–O); δ_H(400 MHz; $CDCl_3$) 3.16 (1 H, dd, *J* 4.9 and 17.1, CH), 3.55 (1 H, dd, *J* 8.3 and 17.1, CH), 3.58 (3 H, s, OCH_3), 3.91 (1 H, dd, *J* 4.9 and 8.3, CH) and 6.80–7.82 (8 H, m, ArH); *m*/*z* (EI) 238 (M^+, 100%), 165 (63), 108 (37) and 89 (40).

2-(2-*Methoxyphenyl*)*indan*-1-*one* **9** was obtained as crystals (416 mg, 35%), mp 92 °C (Found: C, 80.3; H, 5.8%); ν_{max}(KBr)/cm^{-1} 1705 (C=O), 1251 (C–O) and 1071 (C–O); δ_H(400 MHz; $CDCl_3$) 3.14 (1 H, dd, *J* 3.8 and 17.9, CH), 3.57 (1 H, dd, *J* 8.3 and 17.9, CH), 3.84 (1 H, dd, *J* 3.8 and 8.2, CH), 3.85 (3 H, s, OCH_3) and 7.04–7.39 (8 H, m, Ph).

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