EurJOC
European Journal of Organic Chemistry

A Journal of
ChemPubSoc Europe

Accepted Article

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To be cited as: Eur. J. Org. Chem. 10.1002/ejoc.201601042

Link to VoR: http://dx.doi.org/10.1002/ejoc.201601042

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Catalytic Availabilities of Lewis Acidic $SnCl_2$: Ph_3PAuCl-$SnCl_2$ Composite-Catalyzed Successive *ortho*-Alkenylation/*O*-Alkenylation of Phenols Followed by Cyclization to 1-Benzopyrans

Atsushi Tochigi,[a] Kadzuoki Tsukamoto,[a] Noriyuki Suzuki,*[a] and Yoshiro Masuyama*[a]

Abstract: Ph_3PAuCl-$SnCl_2$ composite, prepared beforehand in situ from Ph_3PAuCl and $SnCl_2$, catalyzed the preparation of 1-benzopyrans from phenols and phenylacetylene. The Ph_3PAuCl-$SnCl_2$ composite-catalyzed reaction was presumed to proceed via the successive *ortho*-alkenylation and *O*-alkenylation of phenols with phenylacetylene followed by the cyclization of prepared *ortho*- and *O*-dialkenylated phenol derivatives. Conveniently, all reactions with Ph_3PAuCl-$SnCl_2$ composite were established without much attention to air and water.

Introduction

Tin(II) chloride, which is insensitive to air and water, can be applied as a Lewis acid catalyst into various organic syntheses.[1] During the development of $SnCl_2$-mediated carbonyl allylations by allylic alcohols, acetates or carbonates with a catalytic amount of $PdCl_2(PhCN)_2$,[2] $[RhCl(cod)]_2$,[3] or $[IrCl(cod)]_2$,[4] we had perceived that the coordination of $SnCl_2$ to chloride in chlorometal (M-Cl) complexes would reduce the electron density on metals such as Pd(II), Rh(I) or Ir(I). Therefore, the formation of metal stannate (M-$SnCl_3$) complexes from chlorometal complexes and $SnCl_2$ might induce each of the catalyst activations.[5] Our idea of activating the chlorometal complexes with $SnCl_2$ was realized for phosphine-free $[IrCl(cod)]_2$-catalyzed cyclotrimerization of terminal alkynes.[6] We planned to apply this idea to the activation of various chlorometal complexes. A kind of chlorometal complex, Ph_3PAuCl, is usually converted with Ag(I) salts such as AgOTf, $AgPF_6$, or $AgSbF_6$ into the corresponding active cationic Au(I) complexes that can be applied as π-Lewis acids into various organic reactions.[7] If $SnCl_2$ can be used instead of Ag(I) salts for preparing an active π-Lewis acidic Au(I) complex from Ph_3PAuCl,[8] π-Lewis acidic Au(I)-catalyzed organic reactions will attract much further attention, because $SnCl_2$ is relatively inexpensive and is easy to handle. Herein, we describe Ph_3PAuCl-catalyzed nucleophilic additions of phenols to phenylacetylene with $SnCl_2$ as a Lewis acidic auxiliary agent; Ph_3PAuCl-$SnCl_2$ composite-catalyzed successive *ortho*-alkenylation[9, 10] and *O*-alkenylation[11, 12] of phenols followed by cyclization to 1-benzopyrans.[13, 14] In addition, the *ortho*-alkenylation catalyzed by $SnCl_2$ itself is described, which has been found in the course of the study of Ph_3PAuCl-$SnCl_2$ composite catalysis.

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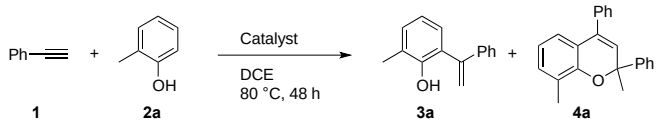
Results and Discussion

Preparation of 1-benzopyran derivatives

The nucleophilic addition of 2-methylphenol **2a** to phenylacetylene **1** was investigated using some catalysts such as $AlCl_3$, $FeCl_3$, $SnCl_2$, Ph_3PAuCl, $Ph_3PAuCl/AgSbF_6$ (1:1) composite, and $Ph_3PAuCl/SnCl_2$ (1:1) composite, prepared beforehand in situ by stirring a mixture of Ph_3PAuCl and $SnCl_2$ in dichloroethane (DCE) at room temperature for 10 min (Table 1). The nucleophilic addition scarcely proceeded with traditional Lewis acids such as $AlCl_3$ or $FeCl_3$, and Ph_3PAuCl, and starting materials were almost entirely recovered (Entries 1, 2 and 5). A weak Lewis acidic $SnCl_2$ caused slight *ortho*-alkenylation of **2a** to afford only 2-methyl-6-(1-phenylethenyl)phenol **3a** in an 11% yield (Entry 3). While the reaction of **2a** (0.5 mmol) and **1** (1.0 mmol) with Ph_3PAuCl-$SnCl_2$ composite produced the mixture of **3a** (35%) and 2,8-dimethyl-2,4-diphenyl-1-benzopyran **4a** (40%) (Entry 7), the use of **1** increased to 2.0 mmol afforded only **4a** in 62% yield (Entry 8). The reaction with $SnCl_2$ in CH_3NO_2 (Entry 4) or that with a cationic Au(I) complex that was prepared in situ from Ph_3PAuCl with $AgSbF_6$ (Entry 6) also afforded only **4a** in 31% or 9% yield respectively, but structurally unconfirmed complex mixtures of high molecular weights were concurrently produced. Some 1-benzopyran derivatives **4** were selectively prepared from **1** and phenols **2** under the same conditions as those of entry 8 in Table 1 (Table 2). Neither 2,6-bis(1-phenylethenyl)phenols nor the corresponding 8-(1-phenylethenyl)-1-benzopyrans were detected in the reaction of phenol **2b** and 4-substituted phenols **2e–h** (Entries 1 and 4–7). Under the same conditions as those of Entry 8 in Table 1, an electron-deficient phenol, 2,4-dichlorophenol was scarcely consumed, and salicylaldehyde was gradually consumed with producing neither the corresponding *ortho*-(1-phenylethenyl)phenol derivative nor 1-benzopyran derivative. The reactivity of other alkynes was also investigated under the same conditions as those of Entry 8 in Table 1; a terminal aliphatic alkyne, 1-octyne resulted in a structurally unconfirmed

complex mixture, and an internal alkyne, 1-phenylpropyne did not seem to react.

Table 1. Nucleophilic addition of 2-methylphenol **2a** to phenylacetylene **1**.[a]

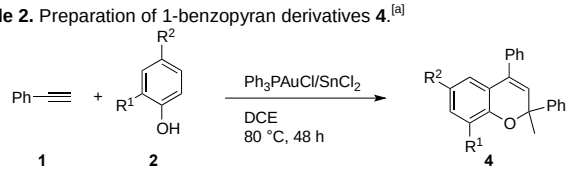


1 2a 3a 4a

Entry	Catalyst	**3a**, Yield [%][b]	**4a**, Yield [%][b]
1	$AlCl_3$	0	0
2	$FeCl_3$	0	0
3	$SnCl_2$	11	0
4[c]	$SnCl_2$	0	31
5	Ph_3PAuCl	0	0
6	$Ph_3PAuCl/AgSbF_6$	0	9
7[d]	$Ph_3PAuCl/SnCl_2$	35	40
8	$Ph_3PAuCl/SnCl_2$	0	62
9[e]	$Ph_3PAuCl/SnCl_2$	27	36

[a] Reaction conditions: **1** (2.0 mmol), **2a** (0.5 mmol), catalyst (0.05 mmol), DCE (0.25 mL). [b] Isolated yields. [c] CH_3NO_2 was used as a solvent. [d] 1.0 mmol of **1** was used. [e] Toluene was used as a solvent.

Table 2. Preparation of 1-benzopyran derivatives **4**.[a]

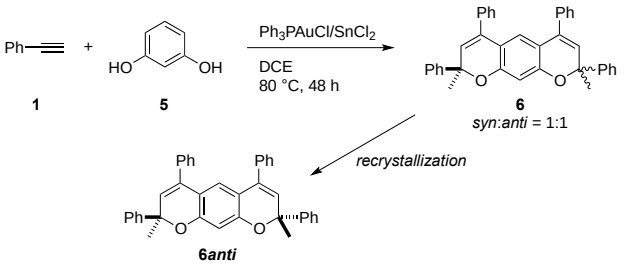


1 2 4

Entry	Phenol	R^1	R^2	Product	Yield [%][b]
1	**2b**	H	H	**4b**	67
2	**2c**	CH_3O	H	**4c**	73
3	**2d**	Ph	H	**4d**	23
4	**2e**	H	CH_3O	**4e**	81
5	**2f**	H	CH_3	**4f**	80
6	**2g**	H	*t*-Bu	**4g**	84
7	**2h**	H	Ph	**4h**	71
8	**2i**	CH_3	CH_3	**4i**	62

[a] Reaction conditions: **1** (2.0 mmol), **2** (0.5 mmol), $Ph_3PAuCl/SnCl_2$ (0.05 mmol), DCE (0.25 mL). [b] Isolated yields.

To confirm the structure of 1-benzopyrans **4** independently, an X-ray diffraction study was performed on colorless crystals of **6*anti*** (mp 177–178 ºC) obtained by the slow diffusion of hexane into a DCE solution of **6** (*syn*:*anti* = 1:1) that was produced in 73% yield by the reaction of **1** (4.0 mmol) and 1,3-dihydroxybenzene (**5**, 0.5 mmol) with Ph_3PAuCl-$SnCl_2$ (0.05 mmol) in DCE (0.5 mL) at 80 ºC for 48 h (Scheme 1). The ORTEP drawing of the molecular structure of **6*anti*** is shown in Figure 1. This result supported the structure of 1-benzopyrans **4** shown in Tables 1 and 2.



1 5 6

Scheme 1. Preparation of a crystallized 1-benzopyran derivative **6*anti*** from **1** and **5**.

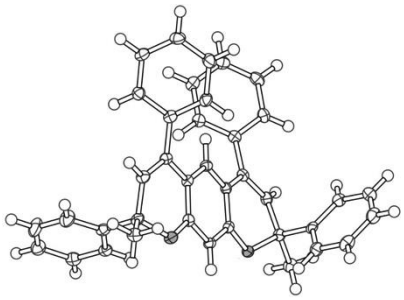


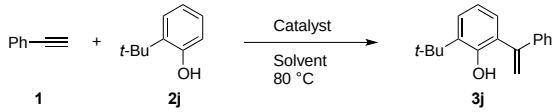
Figure 1. ORTEP drawing of the molecular structure of **6*anti***.

ortho-Alkenylation of Phenols

Because an *ortho*-alkenylated product **3a** was obtained from the reaction of **1** and **2a** (Entries 3, 8, and 9 in Table 1), the selective *ortho*-alkenylation of phenols **2** with **1** was investigated. The reaction of 2-*t*-butylphenol **2j** (1.0 mmol) bearing a bulky substituent on the 2-position with **1** (0.5 mmol) was conducted under various conditions (Table 3). The *ortho*-alkenylation proceeded smoothly with a catalytic amount of $SnCl_2$ in CH_3NO_2 at 80 ºC for 3 h to afford **3j** selectively (Entry 4), while no reaction proceeded in solvents such as THF, dioxane, DMF, or DMSO at 80 ºC for 24 h. Ph_3PAuCl-$SnCl_2$ composite catalyst also served for the selective *ortho*-alkenylation in CH_3NO_2 (Entry 12). Even if excess **1** was used with prolonged stirring at 80 ºC (Entry 9), the corresponding 1-benzopyran was not detected by GC, similarly to any other conditions in Table 3. The bulky 2-*t*-butyl substituent would hinder the formation of 1-benzopyran.

Next, the *ortho*-alkenylation of various phenols **2** bearing smaller substituents than *t*-butyl on 2-position was conducted with $SnCl_2$ catalyst in CH_3NO_2 at 60 ºC in Table 4. The reaction of **1** (0.5 mmol) and **2a** (1.0 mmol) produced not only the *ortho*-alkenylated product **3a** (22%), but also the corresponding 1-benzopyran **4a** (35%) (Entry 1). Consequently, using 10 equimolar amounts of **2** to **1** made selective *ortho*-alkenylation possible to afford only **3** without preparing 1-benzopyrans **4** (Entries 2-7). 2,6-Bis(1-phenylethenyl)phenol derivatives were not detected in the reaction of 4-substituted phenols **2e–g** (Entries 4–6).

Table 3. *ortho*-Alkenylation of 2-*t*-butylphenol **2b** with phenylacetylene **1**.[a]

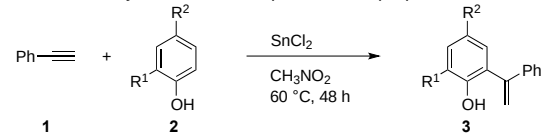


1 2j 3j

Entry	Catalyst	Solvent	Time [h]	Yield [%][b]
1	$SnCl_2$	DCE	24	trace
2	$SnCl_2$	toluene	24	trace
3	$SnCl_2$	CH_3CN	24	28
4	$SnCl_2$	CH_3NO_2	3	70
5[c]	$SnCl_2$	CH_3NO_2	8	74
6[d]	$SnCl_2$	CH_3NO_2	72	28
7[e]	$SnCl_2$	CH_3NO_2	3	65
8[f]	$SnCl_2$	CH_3NO_2	3	70
9[g]	$SnCl_2$	CH_3NO_2	24	58
10	$AlCl_3$	CH_3NO_2	8	0
11	$FeCl_3$	CH_3NO_2	8	26
12	$Ph_3PAuCl/SnCl_2$	CH_3NO_2	3	58

[a] Reaction conditions: **1** (0.5 mmol), **2j** (1.0 mmol), catalyst (0.05 mmol), solvent (0.5 mL). [b] Isolated yields. [c] The reaction was carried out at 60 ºC. [d] The reaction was carried out at 40 ºC. [e] 0.5 mmol of **2j** was used. [f] 1.5 mmol of **2j** was used. [g] 1.0 mmol of **1** and 0.5 mmol of **2j** were used.

Table 4. *ortho*-Alkenylation of various phenols **2** to prepare **3**.[a]



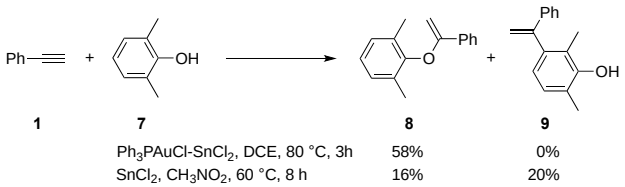
1 2 3

Entry	Phenol	R^1	R^2	Product	Yield [%][b]
1[c]	**2a**	CH_3	H	**3a**	22
2	**2a**	CH_3	H	**3a**	65
3	**2d**	Ph	H	**3d**	45
4	**2e**	H	CH_3O	**3e**	74
5	**2f**	H	CH_3	**3f**	68
6	**2g**	H	*t*-Bu	**3g**	57
7	**2i**	CH_3	CH_3	**3i**	52
8[d]	**2k**	*t*-Bu	*t*-Bu	**3k**	70
9[d]	**2l**	*t*-Bu	CH_3O	**3l**	76

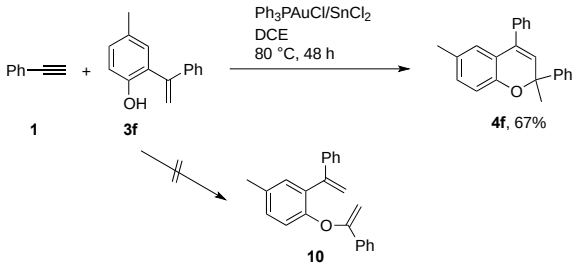
[a] Reaction conditions: **1** (0.5 mmol), **2** (5.0 mmol), $SnCl_2$ (0.05 mmol), CH_3NO_2 (1.5 mL). [b] Isolated yields. [c] 1.0 mmol of **2** was used. **4a** was also obtained in 35% yield. [d] The reaction of **1** (0.5 mmol) and **2** (1.0 mmol) was carried out with $SnCl_2$ (0.05 mmol) in CH_3NO_2 (0.5 mL) at 60 ºC for 4 h.

Mechanism for Preparing 1-Benzopyrans

While 2,6-dimethylphenol **7** (1.0 mmol) reacted with **1** (0.5 mmol) in the presence of $SnCl_2$ (0.05 mmol) in CH_3NO_2 (0.25 mL) at 60 ºC for 8 h to afford 2,6-dimethylphenyl 1-phenylethenyl ether **8** (16%) and 2,6-dimethyl-3-(1-phenylethenyl)phenol **9** (20%), using Ph_3PAuCl-$SnCl_2$ composite (0.05 mmol) in DCE (0.25 mL) at 80 ºC for 3 h selectively caused the *O*-alkenylation of **7** (1.0 mmol) with **1** (0.5 mmol); in other words, it caused the hydrophenoxylation of **1** with **7**, to afford **8** in 58% yield (Scheme 2).[15] Ph_3PAuCl-$AgSbF_6$ did not function as a catalyst for preparing **8** or **9** under the same conditions as those of the reaction with the Ph_3PAuCl-$SnCl_2$ composite.[16] No reaction of 2,6-di-*t*-butylphenol (1.0 mmol) and **1** (0.5 mmol) with Ph_3PAuCl-$SnCl_2$ composite catalyst (0.05 mmol) occurred even in DCE (0.25 mL) at 80 ºC for 72 h. An *ortho*-alkenylated phenol, **3f** (1.0 mmol) reacted with **1** (4.0 mmol) in the presence of Ph_3PAuCl-$SnCl_2$ composite (0.1 mmol) in DCE (0.5 mL) at 80 ºC for 48 h to produce **4f** in 67% yield, although no intermediate, such as *O*-alkenylated derivative of **3f**, namely 4-methyl-2-(1-phenylethenyl)phenyl 1-phenylethenyl ether **10**, or any others was detected (Scheme 3).



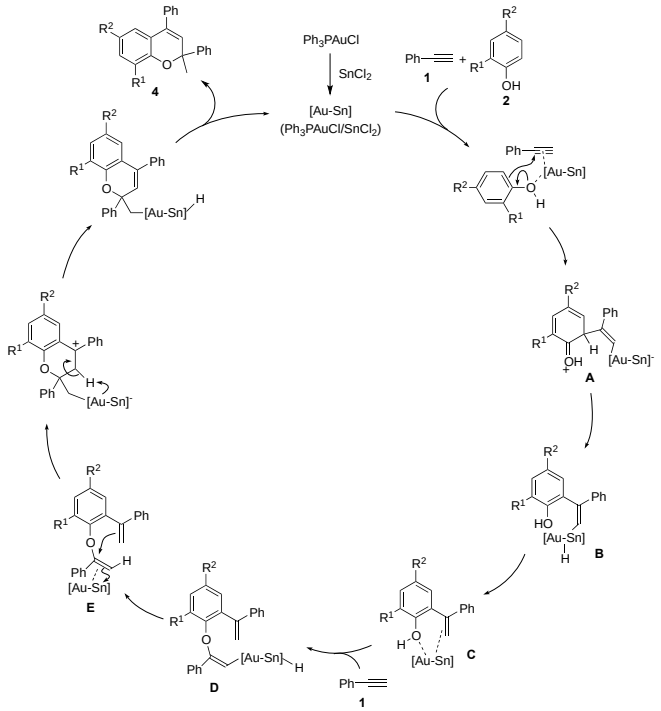
Scheme 2. *O*-Alkenylation of 2,6-dimethylphenol **7**.



Scheme 3. Preparation of **4f** from **1** and **3f** with Ph_3PAuCl-$SnCl_2$ composite catalyst.

On the basis of the *ortho*-alkenylation of **2**, the *O*-alkenylation of **7** and the preparation of 1-benzopyran derivative **4f** from **3f**, we propose a plausible mechanism for the preparation of **3** and **4** with Ph_3PAuCl-$SnCl_2$ composite catalyst in Scheme 4, although no isolation of Ph_3PAuCl-$SnCl_2$ composite has been successfully carried out and consequently its structure has not been determined. Ph_3PAuCl-$SnCl_2$ composite catalyst, abbreviated to [Au–Sn], was presumed to serve for the coordination of Au moiety to alkyne and that of Sn moiety to phenolic OH. Phenols **2** would be coordinated to [Au–Sn] together with phenylacetylene **1** to cause the nucleophilic addition to **1** at the *ortho*-position (intermediates **A**) followed by proton transfer from the *ortho*-position onto Au (intermediates **B**). *Ortho*-alkenylated products **3** would be prepared by the reductive elimination of **B**, and at that time the chelated complex (intermediates **C**) of **3** with regenerated [Au–Sn] species would be formed to allow the nucleophilic addition to another molecule of **1** at the phenolic *O*-position followed by a proton transfer from the *O*-position onto Au (intermediates **D**). 1-Phenylethenyl 2-(1-phenylethenyl)phenyl ethers, prepared by the reductive elimination of intermediates **D**, might rather be coordinated to

[Au–Sn] at the more electron-rich *O*-ethenyl moiety than at the *ortho*-ethenyl moiety to form intermediates **E** that would rapidly undergo cyclization, proton transfer, and then reductive elimination to produce 1-benzopyran derivatives **4** while reproducing an active [Au–Sn] species. In cases of R^1 = H, the coordination (intermediates **C**) of *ortho*-alkenyl group to [Au–Sn] might not lead to second *ortho*-alkenylation, but to *O*-alkenylation.



Scheme 4. Plausible mechanism for *ortho*-alkenylation followed by cyclization to 1-benzopyrans **4**.

Conclusions

We developed a Ph_3PAuCl-$SnCl_2$ composite catalyst system for the preparation of 1-benzopyran derivatives from phenols and phenylacethylene, which would proceed via the successive *ortho*-alkenylation and *O*-alkenylation of phenols with excess phenylacetylene followed by the cyclization of prepared *ortho*- and *O*-dialkenylated phenol derivatives. In cases of phenol and 4-substituted phenols bearing no *ortho*-substituent, the corresponding 1-benzopyrans were obtained selectively without leading to dialkenylation at two *ortho*-positions. In the course of the application of Ph_3PAuCl-$SnCl_2$ composite catalyst for preparing 1-benzopyrans, such as the Ph_3PAuCl-$SnCl_2$ composite, $SnCl_2$ itself was found to be an efficient catalyst for the *ortho*-alkenylation in CH_3NO_2. This Ph_3PAuCl-$SnCl_2$ composite would be more effective than $SnCl_2$ itself for the *O*-alkenylation of a key step in the preparation of 1-benzopyrans. Conveniently, like those with $SnCl_2$, all reactions with Ph_3PAuCl-$SnCl_2$ composite were established without much attention to air and water. Further applications of the Ph_3PAuCl-$SnCl_2$ composite catalyst system to synthetic methodologies are in progress.

Experimental Section

General methods: Tin (II) chloride (Wako first-grade, over 97%) was purchased from Wako Pure Chemical Industries, Ltd. and was used after being dried at 120 °C for 5 h under vacuum. Ph_3PAuCl was prepared from Ph_3P and $HAuCl_4$ $3.6H_2O$ by the conventional method. $HAuCl_4$ $3.6H_2O$ was purchased from Kojima Chemical Co., Ltd. and was used as received.
GC analyses were carried out with InertCap 1 (0.25 mm x 30 m) as a GC column on a GL Sciences GC-4000. TLC analyses were carried out with silica gel plates (Merck 105735). Column chromatography was carried out with silica gel (Kanto Chemical Co., Inc. Cat. No.37564). GPC purification was carried out on a Japan Analysis Industry Co. Ltd. LC-908 or LC-9201 (JAIGEL-2H; $CHCl_3$). ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECX300 spectrometer. IR spectra were recorded on a JASCO FT/IR-4600typeA. GC/MS spectra were recorded on a JEOL JMS-700 instrument.

Typical procedure for *ortho*-alkenylation: To a solution of tin(II) chloride (19 mg, 0.1 mmol) in CH_3NO_2 (1.5 mL) were successively added phenylacetylene (**1**, 51 mg, 0.5 mmol) and 2-methylphenol (**2a**, 0.54 g, 5.0 mmol). The mixture was stirred at 60 ºC for 48 h (discontinued times); the disappearance of phenylacetylene mostly confirmed after 6~12 hours by being monitored by GC. The mixture was extracted with diethyl ether (150 mL). The extracted mixture was washed with water and saturated aqueous NaCl solution, and then was dried over anhydrous $MgSO_4$. After evaporation of volatiles, purification by column chromatography (Kanto Chemical Co., silica gel 60, 37564; hexane/EtOAc = 10/1) and GPC (Japan Analytical Industry Co. Ltd., LC-908, JAIGEL-2H; $CHCl_3$) afforded 68 mg (65%) of 2-methyl-6-(1-phenylethenyl)phenol (**3a**).

Typical procedure for the preparation of 1-benzopyrans 4: After stirring the mixture of Ph_3PAuCl (25 mg, 0.05 mmol) and $SnCl_2$ (10 mg, 0.05 mmol) in DCE (0.25 mL) at room temperature for 20 min, phenylacetylene (**1**, 0.20 g, 2.0 mmol) and 2-methylphenol (**2a**, 54 mg, 0.5 mmol) were successively added, and the mixture was stirred at 80 ºC for 48 h (discontinued times); the disappearance of **2** and **3** mostly confirmed after 24~36 hours by being monitored by TLC and GC. The mixture was extracted with diethyl ether (150 mL). The extracted mixture was washed with water and saturated aqueous NaCl solution, and then was dried over anhydrous $MgSO_4$. After evaporation of volatiles, purification by column chromatography (Kanto Chemical Co., silica gel 60, 37564; hexane/EtOAc = 10/1) and GPC (Japan Analytical Industry Co. Ltd., LC-908, JAIGEL-2H; $CHCl_3$) afforded 0.19 g (62%) of 2,8-dimethyl-2,4-diphenyl-1-benzopyran (**4a**).

2-Methyl-6-(1-phenylethenyl)phenol (3a):[10a, 10b] Pale yellow oil. R_f = 0.57 (hexane : ethyl acetate = 10 : 1). ^1H NMR (300 MHz, $CDCl_3$): δ 2.27 (s, 3H), 5.25 (s, 1H), 5.41 (d, *J* = 1.0 Hz, 1H), 5.87 (d, *J* = 1.0 Hz, 1H), 6.83 (t, *J* = 7.6 Hz, 1H), 6.96 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.12 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.27-7.39 (m, 5H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ 16.2, 116.6, 119.9, 124.7, 127.1, 127.9, 128.56, 128.64, 130.7, 139.5, 145.5, 151.2 ppm. IR: 3510, 3082, 3058, 2920, 2854, 1682, 1598, 1494, 1463, 1446, 1359, 1325, 1266, 1223, 1173, 1119, 1079, 1026, 1000, 957, 908, 837, 779, 746, 690, 588 cm^{-1}. HRMS (FAB): *m/z* calcd for $C_{15}H_{14}O$ 210.1045; found 210.1041.

2-Phenyl-6-(1-phenylethenyl)phenol (3d): Pale yellow oil. R_f = 0.27 (hexane : ethyl acetate = 10 : 1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.37 (s, 1H), 5.46 (d, *J* = 1.0 Hz, 1H), 5.87 (d, *J* = 1.0 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 7.17 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.28-7.37 (m, 5H), 7.39-7.45 (m, 4H), 7.53~7.56 (m, 2H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ 116.8, 120.4, 126.9, 127.4, 128.33, 128.36, 128.48, 128.55, 128.63, 129.3, 130.0, 130.4, 137.7, 139.8, 145.7, 149.9 ppm. IR: 3522, 3082, 3057, 3030, 1814, 1598, 1494, 1454, 1426, 1326, 1227, 1175, 1075, 1054, 1026, 957, 913, 851, 827, 805, 780, 752, 691, 636, 602, 564 cm^{-1}. HRMS (FAB): *m/z* calcd for $C_{20}H_{16}O$ 272.1201; found 272.1179.

4-Methoxy-2-(1-phenylethenyl)phenol (3e):[10a] Pale yellow solid. R_f = 0.27 (hexane : ethyl acetate = 10 : 1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.73 (s, 3H), 4.83 (s, 1H), 5.41 (d, *J* = 1.0 Hz, 1H), 5.85 (d, *J* = 1.0 Hz, 1H), 6.69 (d, *J* = 3.1 Hz, 1H), 6.81 (dd, *J* = 8.9, 2.8 Hz, 1H), 6.87 (d, *J* = 8.9 Hz, 1H), 7.28-7.39 (m, 5H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ 55.7, 115.0, 115.3, 116.5, 116.7, 127.0, 128.1, 128.6, 128.7, 139.1, 145.3, 147.1, 153.3 ppm. IR: 3518, 3081, 3056, 3000, 2952, 2935, 2832, 1589, 1491, 1446, 1422, 1320, 1275, 1173, 1145, 1038, 899, 807, 782, 764, 690 cm^{-1}. HRMS (FAB): *m/z* calcd for $C_{15}H_{14}O_2$ 226.0994; found 226.0979.

4-Methyl-2-(1-phenylethenyl)phenol (3f):[10b] Pale yellow oil. R_f = 0.23 (hexane : ethyl acetate = 10 : 1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.26 (s, 3H), 5.02 (s, 1H), 5.39 (d, *J* = 1.0 Hz, 1H), 5.84 (d, *J* = 1.0 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 6.93 (d, *J* = 1.7 Hz, 1H), 7.05 (d, *J* = 8.3, 1.7 Hz, 1H), 7.30-7.39 (m, 5H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): □ = 20.4, 115.6, 116.5, 127.0, 127.3, 128.5, 128.6, 129.6, 130.0, 130.7, 139.5, 145.4, 150.8 ppm. IR: 3509, 3085, 3058, 3026, 2921, 2857, 1815, 1672, 1598, 1493, 1446, 1332, 1269, 1241, 1178, 1118, 1069, 1027, 959, 903, 816, 780, 758, 698, 657, 610, 589 cm^{-1}. HRMS (FAB): *m/z* calcd for $C_{15}H_{14}O$ 210.1045; found 210.1033.

4-*t*-Butyl-2-(1-phenylethenyl)phenol (3g):[10b] Pale yellow oil. R_f = 0.37 (hexane : ethyl acetate = 10 : 1). ^{1}H NMR (300 MHz, $CDCl_3$): □ = 1.29 (s, 9H), 4.99 (s, 1H), 5.41 (d, *J* = 1.4 Hz, 1H), 5.87 (d, *J* = 1.4 Hz, 1H), 6.88 (d, *J* = 8.6 Hz, 1H), 7.14 (d, *J* = 2.4 Hz, 1H), 7.28 (d, *J* = 8.6, 2.4 Hz, 1H), 7.32-7.40 (m, 5H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ 31.5, 34.1, 115.2, 116.5, 126.3, 126.8, 127.0, 127.2, 128.5, 128.7, 139.4, 143.1, 145.7, 150.7 ppm. IR: 3522, 3084, 3058, 3030, 2958, 2904, 2867, 1680, 1606, 1494, 1446, 1412, 1363, 1335, 1259, 1209, 1178, 1123, 1027, 897, 824, 780, 757, 707, 691, 652, 620, 588 cm^{-1}. HRMS (FAB): *m/z* calcd for $C_{18}H_{20}O$ 252.1514; found 252.1516.

2,4-Dimethyl-6-(1-phenylethenyl)phenol (3i): Pale yellow oil. R_f = 0.53 (hexane : ethyl acetate = 10 : 1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.22 (s, 3H), 2.23 (s, 3H), 5.09 (s, 1H), 5.38 (d, *J* = 1.0 Hz, 1H), 5.83 (d, *J* = 1.0 Hz, 1H), 6.76 (d, *J* = 1.4 Hz, 1H), 6.93 (d, *J* = 1.4 Hz, 1H), 7.27-7.38 (m, 5H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ 16.1, 20.4, 116.4, 124.4, 126.8, 127.1, 128.1, 128.5, 128.6, 128.9, 131.4, 139.6, 145.7, 149.0 ppm. IR: 3520, 3059, 3025, 2976, 2947, 2919, 2859, 1799, 1729, 1680, 1600, 1477, 1446, 1381, 1338, 1290, 1226, 1194, 1143, 1092, 1024, 972, 911, 861, 785, 758, 697, 666, 564 cm^{-1}. HRMS (EI): *m/z* calcd for $C_{16}H_{16}O$ 224.1201; found 224.1163.

2-*t*-Butyl-6-(1-phenylethenyl)phenol (3j): Pale yellow oil. R_f = 0.70 (hexane : ethyl acetate = 10 : 1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 (s, 9H), 5.43 (d, *J* = 1.0 Hz, 1H), 5.50 (s, 1H), 5.94 (d, *J* = 1.0 Hz, 1H), 6.85 (t, *J* = 7.5 Hz, 1H), 6.97 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.28 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.31-7.38 (m, 5H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ 29.6, 34.9, 117.1, 119.5, 126.6, 127.0, 128.06, 128.13, 128.58, 128.62, 136.3, 139.3, 145.4, 151.6 ppm. IR: 3510, 3084, 3058, 3027, 3004, 2956, 2908, 2871, 1739, 1610, 1483, 1430, 1391, 1362, 1329, 1267, 1230, 1189, 1134, 1084, 911, 844, 799, 779, 748, 712, 695, 568 cm^{-1}. HRMS (FAB): *m/z* calcd for $C_{18}H_{20}O$ 252.1514; found 252.1505.

2,4-Di-*t*-butyl-6-(1-phenylethenyl)phenol (3k):[17] Pale yellow solid. R_f = 0.73 (hexane : ethyl acetate = 10 : 1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.28 (s, 9H), 1.42 (s, 9H), 5.31 (s, 1H), 5.43 (d, *J* = 1.0 Hz, 1H), 5.93 (d, *J* = 1.0 Hz, 1H), 6.97 (d, *J* = 2.4 Hz, 1H), 7.29-7.40 (m, 6H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ 29.7, 31.6, 34.2, 35.1, 116.8, 123.7, 124.7, 127.0, 127.3, 128.5, 128.6, 135.3, 139.4, 141.7, 145.9, 149.2 ppm. IR: 3503, 3077, 3054, 3025, 2956, 2904, 2874, 1802, 1598, 1443, 1389, 1361, 1326, 1266, 1237, 1201, 1167, 1146, 1119, 1087, 1027, 914, 879, 833, 806, 781, 739, 707, 684, 649, 603 cm^{-1}. HRMS (EI): *m/z* calcd for $C_{22}H_{28}O$ 308.2140; found 308.2137.

2-*t*-Butyl-4-methoxy-6-(1-phenylethenyl)phenol (3l): Pale yellow solid. R_f = 0.50 (hexane : ethyl acetate = 10 : 1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.41 (s, 9H), 3.71 (s, 3H), 5.12 (s, 1H), 5.42 (d, *J* = 1.0 Hz, 1H), 5.93 (d, *J* = 1.0 Hz, 1H), 6.51 (d, *J* = 3.1 Hz, 1H), 6.89 (d, *J* = 3.1 Hz, 1H), 7.30-7.39 (m, 5H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ 29.5, 35.0, 55.6, 111.4, 114.1, 117.0, 126.9, 128.2, 128.60, 128.64, 137.7, 139.1, 145.6, 145.7, 152.4 ppm. IR: 3524, 3080, 3058, 2999, 2951, 2869, 2832, 1739, 1596, 1448, 1429, 1363, 1210, 1123, 1055, 1027, 911, 874, 850, 784, 693, 603 cm^{-1}. HRMS (EI): *m/z* calcd for $C_{19}H_{22}O_2$ 282.1620; found 282.1616.

2,8-Dimethyl-2,4-diphenyl-1-benzopyran (4a): Pale yellow oil. R_f = 0.67 (hexane : ethyl acetate = 10 : 1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.81 (s, 3H), 2.34 (s, 3H), 5.94 (s, 1H), 6.67 (t, *J* = 7.5 Hz, 1H), 6.80 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.00 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.16-7.25 (m, 1H), 7.28-7.40 (m, 7H), 7.56 (bd, *J* = 7.2 Hz, 2H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ 16.0, 29.9, 78.2, 120.1, 121.9, 123.5, 125.0, 125.6, 127.2, 127.5, 127.7, 128.1, 128.3, 128.8, 130.8, 136.0, 138.6, 146.1, 151.3 ppm. IR: 3058, 3027, 2977, 2958, 2924, 2853, 1635, 1598, 1493, 1444, 1372, 1353, 1258, 1240, 1178, 1108, 1074, 1028, 953, 921, 846, 784, 756, 744, 699, 647, 585 cm^{-1}. HRMS (EI): *m/z* calcd for $C_{23}H_{20}O$ 312.1514; found 312.1504.

2-Methyl-2,4-diphenyl-1-benzopyran (4b): Pale yellow oil. R_f = 0.67 (hexane : ethyl acetate = 10 : 1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.82 (s, 3H), 5.96 (s, 1H), 6.78 (dt, *J* = 7.5, 1.4 Hz, 1H), 6.95~7.00 (m, 2H), 7.11-7.24 (m, 2H), 7.28~7.40 (m, 7H), 7.54~7.58 (m, 2H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ 29.7, 78.3, 116.9, 120.8, 122.4, 125.2, 125.7, 127.2, 127.8, 127.9, 128.2, 128.3, 128.8, 129.4, 135.5, 138.2, 145.9, 153.4 ppm. IR: 3057, 3027, 2978, 2926, 2859, 1627, 1600, 1573, 1481, 1446, 1371, 1352, 1305, 1263, 1243, 1179, 1117, 1091, 1072, 1053, 1028, 965, 922, 843, 813, 756, 745, 724, 695, 635, 605, 589, 575 cm^{-1}. HRMS (EI): *m/z* calcd for $C_{22}H_{18}O$ 298.1358; found 298.1354.

8-Methoxy-2-methyl-2,4-diphenyl-1-benzopyran (4c): Pale yellow solid. R_f = 0.40 (hexane : ethyl acetate = 10 : 1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.85 (s, 3H), 3.90 (s, 3H), 6.05 (s, 1H), 6.56 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.70 (t, *J* = 7.6 Hz, 1H), 6.78 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.15-7.21 (m, 1H), 7.24-7.30 (m, 2H), 7.31~7.40 (m, 5H), 7.56~7.60 (m, 2H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ 30.5, 56.2, 78.3, 112.2, 118.1, 120.3, 123.5, 124.9, 127.1, 127.8, 128.0, 128.15, 128.23, 128.7, 135.8, 138.4, 142.6, 145.9, 148.5 ppm. IR: 3082, 3055, 3026, 2981, 2958, 2925, 2851, 1625, 1598, 1572, 1490, 1476, 1458, 1442, 1371, 1353, 1261, 1209, 1176, 1113, 1066, 981, 907, 830, 811, 787, 768, 753, 735, 698, 661, 580 cm^{-1}. HRMS (EI): *m/z* calcd for $C_{23}H_{20}O_2$ 328.1463; found 328.1464.

2-Methyl-2,4,8-triphenyl-1-benzopyran (4d): Pale yellow solid. R_f = 0.53 (hexane : ethyl acetate = 10 : 1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.76 (s, 3H), 6.03 (s, 1H), 6.85 (t, *J* = 7.6 Hz, 1H), 6.97 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.15-7.24 (m, 4H), 7.30-7.47 (m, 10H), 7.58-7.62 (m, 2H) ppm. ^{13}C

NMR (75.6 MHz, $CDCl_3$): δ 29.8, 78.5, 120.6, 123.1, 125.2, 126.7, 126.8, 127.1, 127.8, 128.03, 128.07, 128.36, 128.46, 128.9, 129.6, 130.3, 130.7, 136.0, 138.2, 138.5, 145.5, 150.1 ppm. IR: 3081, 3057, 3027, 2978, 2960, 2925, 2851, 1632, 1600, 1492, 1446, 1423, 1371, 1355, 1263, 1243, 1213, 1178, 1113, 1071, 1027, 917, 804, 756, 695, 590 cm^{-1}. HRMS (FAB): *m/z* calcd for $C_{28}H_{22}O$ 374.1671; found 374.1662.

6-Methoxy-2-methyl-2,4-diphenyl-1-benzopyran (4e): Pale yellow solid. R_f = 0.47 (hexane : ethyl acetate = 10 : 1). ^1H NMR (300 MHz, $CDCl_3$): δ 1.80 (s, 3H), 3.61 (s, 3H), 6.02 (s, 1H), 6.54 (d, *J* = 3.1 Hz, 1H), 6.70 (dd, *J* = 8.6, 3.1 Hz, 1H), 6.92 (d, *J* = 8.6 Hz, 1H), 7.18-7.24 (m, 1H), 7.28-7.41 (m, 7H), 7.54~7.57 (m, 2H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ 29.6, 55.6, 78.0, 111.4, 114.3, 117.4, 123.1, 125.3, 127.2, 127.9, 128.1, 128.4, 128.7, 128.8, 135.7, 138.1, 145.8, 147.3, 153.6 ppm. IR: 3084, 3056, 3025, 2979, 2927, 2859, 1631, 1600, 1573, 1486, 1444, 1248, 1189, 1125, 1070, 1029, 940, 815, 789, 772, 754, 696, 589, 571 cm^{-1}. HRMS (FAB): *m/z* calcd for $C_{23}H_{20}O_2$ 328.1463; found 328.1465.

2,6-Dimethyl-2,4-diphenyl-1-benzopyran (4f): Pale yellow solid. R_f = 0.50 (hexane : ethyl acetate = 10 : 1). ^1H NMR (300 MHz, $CDCl_3$): δ 1.80 (s, 3H), 2.12 (s, 3H), 5.95 (s, 1H), 6.76 (br, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.93 (brd, *J* = 8.3 Hz, 1H), 7.15-7.21 (m, 1H), 7.27-7.40 (m, 7H), 7.53-7.57 (m, 2H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ 20.7, 29.7, 78.0, 116.7, 122.1, 125.2, 126.1, 127.1, 127.7, 128.07, 128.12, 128.3, 128.8, 129.87, 129.91, 135.6, 138.4, 145.9, 151.1 ppm. IR: 3061, 3019, 2978, 1633, 1604, 1486, 1443, 1247, 1125, 1069, 818, 753, 695, 589, 572 cm^{-1}. HRMS (FAB): *m/z* calcd for $C_{23}H_{20}O$ 312.1514; found 312.1513.

6-*t*-Butyl-2-methyl-2,4-diphenyl-1-benzopyran (4g): Pale yellow solid. R_f = 0.50 (hexane : ethyl acetate = 10 : 1). ^1H NMR (300 MHz, $CDCl_3$): δ 1.17 (s, 9H), 1.81 (s, 3H), 5.94 (s, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 7.02 (d, *J* = 2.4 Hz, 1H), 7.15-7.24 (m, 2H), 7.29-7.41 (m, 7H), 7.55-7.59 (m, 2H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ 29.8, 31.4, 34.1, 78.1, 116.1, 121.4, 122.8, 125.2, 126.2, 127.1, 127.8, 128.2, 128.3, 128.7, 135.7, 138.4, 143.3, 146.2, 151.0 ppm. IR: 3054, 3027, 2959, 2924, 2864, 1627, 1597, 1490, 1443, 1366, 1257, 1177, 1130, 1050, 1029, 896, 823, 775, 762, 749, 699, 672, 602, 567 cm^{-1}. HRMS (FAB): *m/z* calcd for $C_{26}H_{26}O$ 354.1984; found 354.2001.

2-Methyl-2,4,6-triphenyl-1-benzopyran (4h): Pale yellow solid. R_f = 0.63 (hexane : ethyl acetate = 10 : 1). ^1H NMR (300 MHz, $CDCl_3$): δ 1.85 (s, 3H), 6.01 (s, 1H), 7.06 (d, *J* = 8.3 Hz, 1H), 7.19-7.46 (m, 15H), 7.56-7.61 (m, 2H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ 29.7, 78.5, 117.2, 122.5, 124.4, 125.3, 126.6, 126.7, 127.3, 127.9, 128.1, 128.2, 128.3, 128.5, 128.6, 128.8, 133.9, 135.5, 138.1, 140.8, 145.8, 153.0 ppm. IR: 3058, 3029, 2981, 2927, 1600, 1477, 1445, 1409, 1371, 1257, 1180, 1124, 1093, 1072, 1045, 1028, 967, 897, 828, 756, 691, 608, 592, 579, 560 cm^{-1}. HRMS (FAB): *m/z* calcd for $C_{28}H_{22}O$ 374.1671; found 374.1642.

2,6,8-Triimethyl-2,4-diphenyl-1-benzopyran (4i): Pale yellow solid. R_f = 0.70 (hexane : ethyl acetate = 10 : 1). ^1H NMR (300 MHz, $CDCl_3$): δ 1.80 (s, 3H), 2.10 (s, 3H), 2.31 (s, 3H), 5.94 (s, 1H), 6.60 (d, *J* = 1.4 Hz, 1H), 6.82 (d, *J* = 1.4 Hz, 1H), 7.18-7.23 (m, 1H), 7.28-7.40 (m, 7H), 7.54-7.58 (m, 2H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ 15.9, 20.6, 29.9, 78.0, 121.8, 123.8, 125.0, 125.3, 127.1, 127.7, 128.1, 128.3, 128.4, 128.8, 129.1, 131.5, 136.1, 138.8, 146.2, 149.1 ppm. IR: 3084, 3056, 3030, 2958, 2923, 2855, 1632, 1598, 1492, 1469, 1261, 1224, 1069, 1025, 859, 795, 744, 697 cm^{-1}. HRMS (EI): *m/z* calcd for $C_{24}H_{22}O$ 326.1671; found 326.1664.

2,8-Dimethyl-2,4,6,8-tetraphenylbenzo[1,2-*b*:5,4-*b'*]bispyran (6) (syn:anti = 1:1): R_f = 0.53, 0.56 (hexane : ethyl acetate = 10 : 1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.79, 1.81 (2s, 6H), 5.80, 5.81 (2s, 2H), 6.676, 6.681, 6.689 (3s, 2H), 7.15-7.40 (m, 16H), 7.47-7.60 (m, 4H) ppm. IR: 3057, 3025, 2979, 1611, 1488, 1443, 1279, 1155, 1113, 1073, 1027, 904, 878, 755, 696 cm^{-1}. HRMS (FAB): *m/z* calcd for $C_{38}H_{30}O_2$ 518.2246; found 518.2234.

2,8-Dimethyl-2,4,6,8-tetraphenylbenzo[1,2-*b*:5,4-*b'*]bispyran (6*anti*): Colorless crystals. Mp 177-178 ºC. R_f = 0.53 (hexane : ethyl acetate = 10 : 1). ^1H NMR (300 MHz, $CDCl_3$): δ 1.79 (s, 6H), 5.80 (s, 2H), 6.68 (s, 1H), 6.69 (s, 1H), 7.22-7.27 (m, 12H), 7.30-7.36 (m, 4H), 7.53-7.57 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 29.9, 78.9, 105.5, 115.5, 123.2, 125.2, 125.3, 127.2, 127.7, 128.1, 128.2, 128.5, 135.2, 138.1, 146.1, 154.9 ppm. IR: 3052, 3026, 2989, 2931, 1612, 1563, 1490, 1444, 1360, 1308, 1280, 1222, 1160, 1118, 1073, 1029, 945, 899, 878, 860, 769, 755, 725, 695, 667, 586, 577 cm^{-1}. HRMS (FAB): *m/z* calcd for $C_{38}H_{30}O_2$ 518.2246; found 518.2251.

2,6-Dimethylphenyl 1-phenylethenyl ether (8): Colorless oil. R_f = 0.80 (hexane : ethyl acetate = 10 : 1). ^1H NMR (300 MHz, $CDCl_3$): δ 2.21 (s, 6H), 3.83 (d, *J* = 2.4 Hz, 1H), 4.70 (d, *J* = 2.4 Hz, 1H), 7.00-7.10 (m, 3H), 7.34-7.46 (m, 3H), 7.80-7.86 (m, 2H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ 16.0, 84.7, 124.9, 125.4, 128.3, 128.71, 128.75, 131.1, 135.3, 151.1, 157.6 ppm. IR: 3084, 3056, 3025, 2952, 2923, 2854, 1649, 1617, 1576, 1494, 1474, 1444, 1377, 1314, 1276, 1191, 1106, 1074, 1028, 953, 919, 816, 764, 706, 689, 606 cm^{-1}. HRMS (EI): *m/z* calcd for $C_{16}H_{16}O$ 224.1201; found 224.1186.

2,6-Dimethyl-3-(1-phenylethenyl)phenol (9): Pale yellow solid. R_f = 0.30 (hexane : ethyl acetate = 10 : 1). ^1H NMR (300 MHz, $CDCl_3$): δ 1.96 (s, 3H), 2.28 (s, 3H), 4.66 (s, 1H), 5.18 (d, *J* = 1.7 Hz, 1H), 5.76 (d, *J* = 1.7 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 7.20-7.36 (m, 5H) ppm. ^{13}C NMR (75.6 MHz, $CDCl_3$): δ 12.9, 16.0, 114.7, 121.2, 122.1, 122.2, 126.4, 127.5, 127.8, 128.3, 140.7, 140.9, 149.1, 152.1 ppm. IR: 3499, 3084, 3054, 3022, 2923, 2859, 1611, 1596, 1571, 1493, 1444, 1414, 1309, 1232, 1195, 1095, 1021, 943, 912, 825, 800, 780, 746, 725, 701, 690, 651, 633 cm^{-1}. HRMS (FAB): *m/z* calcd for $C_{16}H_{16}O$ 224.1201; found 224.1202.

Acknowledgements

Ms. E. Okano and Ms. S. Machishima (Sophia University) are acknowledged for their assistance in NMR, mass spectrometry and elemental analysis.

Keywords: Homogeneous catalysis • Gold • Tin • Phenols • Alkynes • Alkenylation • Cyclization

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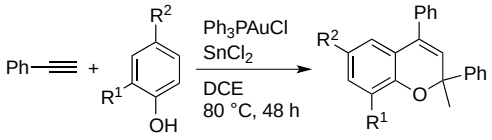

Ph_3PAuCl-$SnCl_2$ composite, prepared beforehand in situ from Ph_3PAuCl and $SnCl_2$, catalyzed the preparation of 1-benzopyrans from phenols and phenylacetylene.

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Phenols to 1-Benzpyranes

Atsushi Tochigi, Kadzuoki Tsukamoto, Noriyuki Suzuki, and Yoshiro Masuyama**

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Catalytic Availabilities of Lewis Acidic $SnCl_2$: Ph_3PAuCl-$SnCl_2$ Composite-Catalyzed Successive *ortho*-Alkenylation/*O*-Alkenylation of Phenols Followed by Cyclization to 1-Benzopyrans