Microwave-Accelerated Alkylation of Arenes/Heteroarenes with Benzylic Alcohols Using Antimony(III) Chloride as Catalyst: Synthesis of O-Heterocycles

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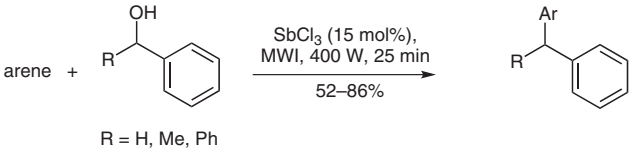
Abstract: An efficient protocol for alkylation of electron-rich arenes/heteroarenes with benzylic alcohols under microwave irradiation using antimony(III) chloride as catalyst has been developed. The mild reaction conditions, high yields, operational simplicity, and applicability to various substrates render the approach a useful route for the synthesis of diaryl/triarylalkane. In addition, a new route for the conversion of *ortho*-alkenylated phenols into functionalized O-heterocycles has been accomplished.

Key words: antimony(III) chloride, alkylation, arenes, microwave, oxygen heterocycles

The alkylation and acylation of arenes are of prime importance in organic synthesis as they can be elaborated further to the synthesis of various useful organic molecules including the synthesis of pharmaceuticals, agrochemicals, and fine chemicals.[1] To this end, several procedures for aromatic alkylation/acylation have been reported.[2] Friedel–Crafts (FC) reaction is one of the most studied methods for the alkylation and acylation of arenes, and several procedures have been reported for this purpose.[3] However, classical FC alkylation reaction involves the use of alkyl halide as electrophile and drastic reaction conditions with regard to temperature and acidity. In addition, significant amounts of inorganic salts are formed as byproducts. Furthermore, during the synthesis of alkyl halides, hydrogen halides were formed causing environmental pollution. Due to the increasing demand for the development of efficient, economic, and environmentally benign protocols, the direct catalytic alkylation of aromatics without using the organic halides is an important task. From the synthetic point of view, alcohols are an attractive source of electrophile for alkylation as compared to organic halides as water will be formed as a byproduct. However, activation of alcohol is needed as it is a poor leaving group. Activation of alcohols is generally achieved in the presence of various Lewis acids including $IrCl_3$,[4] H_2PdCl_4,[4] H_2PtCl_6,[4] $HAuCl_4$,[5a] $AuCl_3$,[5b] $Bi(OTf)_3$,[6] $Fe/CuBr_2$,[7] lanthanide-triflates,[8] $NbCl_5$,[9] I_2.[10] However, many of these procedures require expensive catalysts, elevated temperatures, long reaction times, and anhydrous conditions. Thus, development of direct nucleophilic substitution of alcohols with more convenient and general reaction conditions will be welcome. In continuation of our work on the use of $SbCl_3$ as a catalyst in synthetically useful organic transformations, we hereby disclose its use as an efficient catalyst for nucleophilic substitution reaction of benzylic alcohols with arenes (Scheme 1).



Scheme 1

Recently, we have reported the activation of imines with $SbCl_3$ in Mannich-type reaction.[11] To explore its catalytic potential further, the alkylation of 1,3-dimethoxybenzene (**1**) with 1-phenylethanol (**2a**, 1.1 equiv) in acetonitrile using $SbCl_3$ (0.1 equiv, 10 mol%) as catalyst was carried out at ambient temperature. The reaction was found to be very sluggish, and after stirring at ambient temperature for 16 hours about 30% conversion was observed (as monitored by TLC). The products were found to have very close R_f to **1** in TLC and they could not be separated by column chromatography. To overcome this problem, the crude compound was dried and demethylated with BBr_3. The demethylated products were conveniently purified by column chromatography to afford 4-(1-phenylethyl)benzene-1,3-diol (**3a**) and 4,6-bis(1-phenylethyl)benzene-1,3-diol (**3b**) in 14% and 8%, respectively. The compounds **3a** and **3b** were characterized by IR, ^{1}H NMR, and ^{13}C NMR data. Increase in catalyst loading (15 mol%) did not accelerate the reaction at ambient temperature. Even under refluxing conditions, there was no substantial improvement in the reaction rate and took very long reaction time (72 h) to get a moderate yield of the products.

Microwave-assisted organic synthesis (MAOS) has become an important tool in organic synthesis to improve the selectivity, rate enhancement, and reduction of thermal degradative byproducts.[12] Keeping this in view, the above $SbCl_3$-catalyzed alkylation of **1** with **2a** was carried out in a microwave reactor (400 W) with $SbCl_3$ (10 mol%) when the reaction got completed in 40 minutes (**2a** completely consumed). As before, demethylation of the crude product with BBr_3 afforded a mixture of **3a** and **3b** in 71%

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total yield. With a higher catalyst loading (15 mol%), the reaction got completed in 25 minutes, and demethylation of the crude product afforded a mixture of **3a** and **3b** in 79% overall yield[23] (Table 1, entry 1). Thus, the same reaction conditions (400 W, 25 min) were used for all subsequent reactions. To establish the mechanism of the alkylation, **1** was reacted with enantiomerically pure (*S*)-1-phenylethanol when **3a** was obtained as a racemic mixture. This clearly indicates the formation of the benzylic carbonium ion in the transition state which was subsequently attacked by the arene to afford the alkylated products.

As expected, reactions of 1,2-dimethoxybenzene (**4**) and 1,4-dimethoxybenzene (**6**) with **2a** also yielded a mixture of corresponding mono- and dialkylated products which were purified after demethylation (Table 1, entries 2 and 3). Similarly, the reaction of anisole (**8**) with **2a** yielded a mixture of both *ortho*- and *para*-alkylated products in good yields (Table 1, entry 4).

Table 1 $SbCl_3$-Catalyzed Alkylation of Electron-Rich Arenes/Heteroarenes with Alcohols under Microwave Irradiation[a]

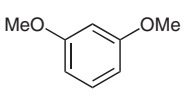
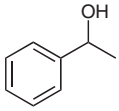
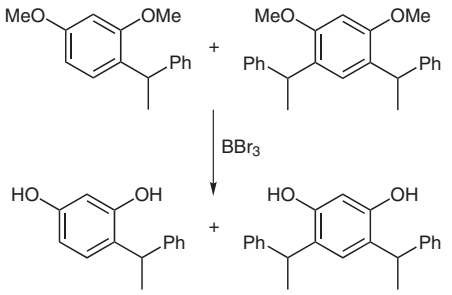
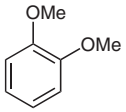
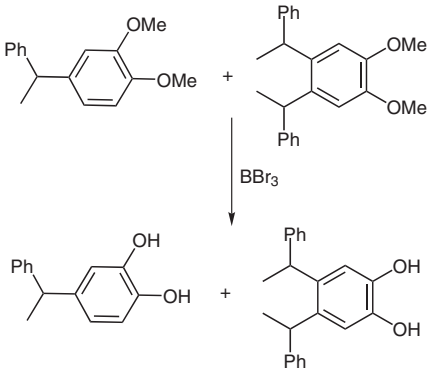
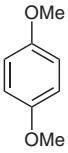
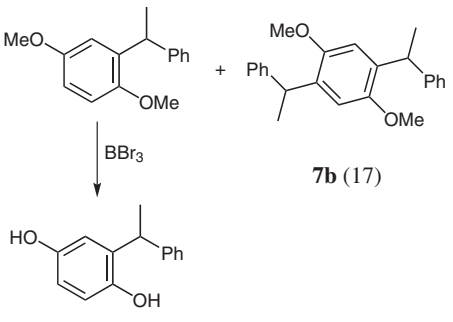
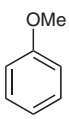
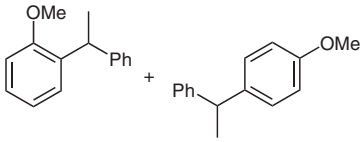
Entry	Arenes/heteroarenes	Alcohols	Product, yield (%)[b,c]
1	 **1**	 **2a**	 **3a** (65) **3b** (14)
2	 **4**	**2a**	 **5a** (62) **5b** (10)
3	 **6**	**2a**	 **7b** (17) **7a**[13] (63)
4	 **8**	**2a**	 **9a**[14] (14) **9b**[14] (65)

Table 1 $SbCl_3$-Catalyzed Alkylation of Electron-Rich Arenes/Heteroarenes with Alcohols under Microwave Irradiation[a] (continued)

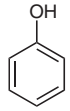
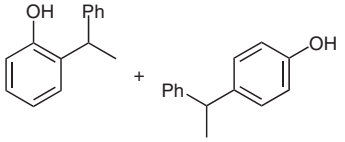
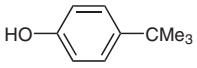
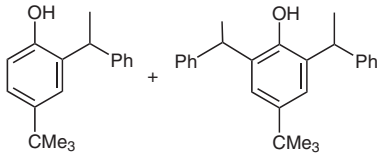
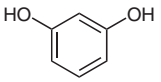
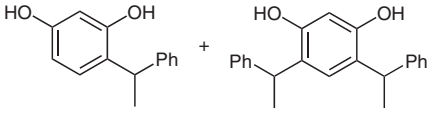
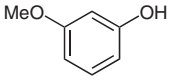
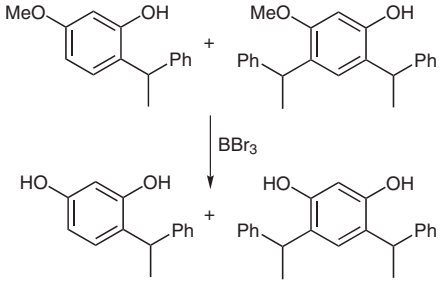
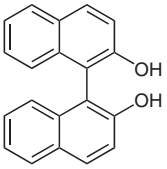
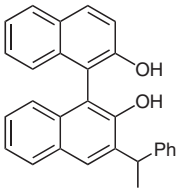
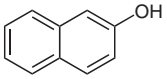
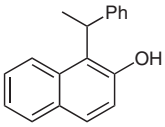
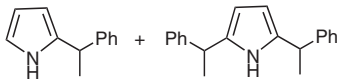
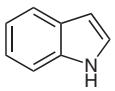
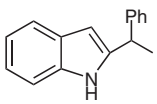
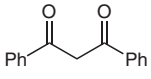
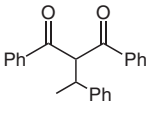
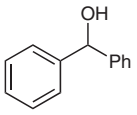
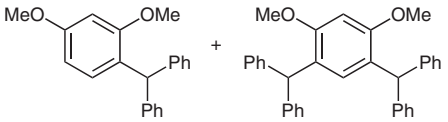
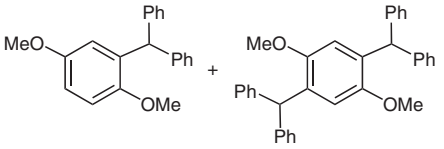
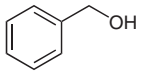
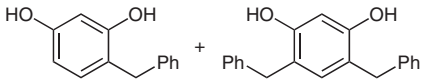
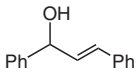
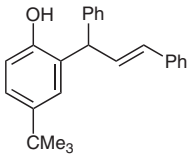
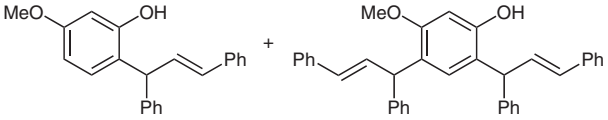
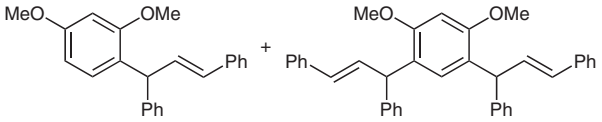
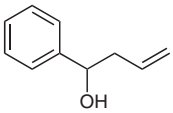
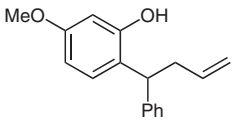
Entry	Arenes/heteroarenes	Alcohols	Product, yield (%)[b,c]
5	 **10**	**2a**	 **11a**[15] (22) **11b**[15] (53)
6	 **12**	**2a**	 **13a** (68) **13b** (11)
7	 **14**	**2a**	 **3a** (61) **3b** (23)
8	 **15**	**2a**	 **3a** (62) **3b** (18)
9	 **16**	**2a**	 **17** (64)
10	 **18**	**2a**	 **19**[16] (72)
11[d]	 **20**	**2a**	 **21a**[17] (51) **21b** (13)
12[d]	 **22**	**2a**	 **23**[18] (52)
13	 **24**	**2a**	 **25**[19] (55)

Table 1 $SbCl_3$-Catalyzed Alkylation of Electron-Rich Arenes/Heteroarenes with Alcohols under Microwave Irradiation[a] (continued)

Entry	Arenes/heteroarenes	Alcohols	Product, yield (%)[b,c]
14	**1**	 **2b**	 **26a** (61) **26b** (13)
15	**6**	**2b**	 **27a** (57) **27b** (21)
16	**14**	 **2c**	 **28a** (72) **28b**[20] (14)
17	**12**	 **2d**	 **29** (67)
18	**15**	**2d**	 **30a** (61) **30b** (18)
19	**1**	**2d**	 **31a**[21] (51) **31b** (23)
20	**15**	 **2e**	 **32** (68)

[a] Reaction conditions: arene/heteroarene/1,3-diketone (2 mmol), benzylic alcohol (2.2 mmol), $SbCl_3$ (15 mol%), in dry MeCN (4 mL) under 400 W microwave power at 65 °C for 25 min.
[b] 6–11% of the unreacted nucleophiles were recovered.
[c] Isolated yield; yields are based on the amounts of consumed nucleophiles.
[d] 200 W power was used for 5 min.

To see the generality of the above reaction, alkylation of various phenolics was explored. Thus reaction of phenol (**10**) with **2a** yielded a mixture of both *ortho*- and *para*-alkylated products (**11a** and **11b**, Table 1, entry 5). Similarly, alkylations of 4-*tert*-butylphenol (**12**), resorcinol (**14**), 3-methoxyphenol (**15**) with **2a** proceeded smoothly to yield a mixture of the corresponding mono- and dialkylated products (Table 1, entries 6–8). However, 1,1′-bi(2-naphthol) (**16**) and 2-naphthol (**18**) yielded only the monoalkylated products **17** and **19**, respectively (Table 1, entries 9 and 10).

At this point, it became necessary to compare the efficiency of $SbCl_3$ with some of the reported catalysts. For this, alkylation of **12** with **2a** was chosen as a model reaction, and the results are summarized in Table 2. As evident from Table 2, the reactions in acetonitrile with both I_2 (15 mol%) and Fe (30 mol%)/$CuBr_2$ (15 mol%) as catalysts were sluggish at 65 °C (Table 2, entries 1 and 3) which could be improved under microwave irradiation (Table 2,

entries 2 and 4). In all the cases a mixture of monoalkylated product **13a** and dialkylated product **13b** was obtained along with unreacted **12** and **2a**. The $Yb(OTf)_3$-catalyzed reaction in MeCN at 65 °C was also equally sluggish as in the cases with I_2 and Fe/$CuBr_2$, and both **13a** and **13b** were obtained in 8% and 4% yields, respectively, after heating at 65 °C for 1 hour with a large amount of unreacted starting materials (Table 2, entry 5). However, the same reaction under microwave irradiation at 65 °C improved the yields of **13a** and **13b** (Table 2, entry 6). Thus, the catalytic efficiency of $Yb(OTf)_3$ was found to be superior to both I_2 and Fe/$CuBr_2$ in the alkylation of arene. Although the $SbCl_3$-catalyzed reaction in MeCN at 65 °C was sluggish (Table 2, entry 7), the same under microwave irradiation was much faster (400 W, 65 °C) when **2a** was totally consumed in 1 hour to afford a mixture of **13a** and **13b** in 68% and 12% yields, respectively, and only 7% of **12** was recovered (Table 2, entry 8). Thus it was concluded that the catalytic alkylation of arenes can be accelerated under microwave irradiation over conventional heating, and, among them, $SbCl_3$ afforded the highest yields of the products. On the basis of the above results, $SbCl_3$ emphasizes its superiority over the reported catalysts in microwave-assisted FC alkylation of arenes.

Beside phenols and alkyl aryl ethers, alkylation of other substrates such as heteroarenes and 1,3-diketones was also investigated. Thus, alkylation of pyrrole (**20**) and indole (**22**) was very fast and completed at a lower power (200 W, 5 min, Table 1, entries 11 and 12). Although indole underwent monoalkylation (**23**), pyrrole afforded a mixture of both mono- and dialkylated products (**21a** and **21b**). Dibenzoyl methane (**24**) also underwent smooth alkylation with **2a** to yield the expected 2-alkylated product **25** in moderate yield (Table 1, entry 13).

To show that alkylation of electron-rich substrates are not restricted to only **2a**, few other benzylic alcohols such as diphenyl methanol (**2b**), benzyl alcohol (**2c**), 1,3-diphenyl-2-propen-1-ol (**2d**), and 1-phenyl-3-buten-1-ol (**2e**) were also used as alkylating agents. In all the cases, alkylation went smoothly to furnish the expected product/s in high yields (Table 1, entries 14–20).

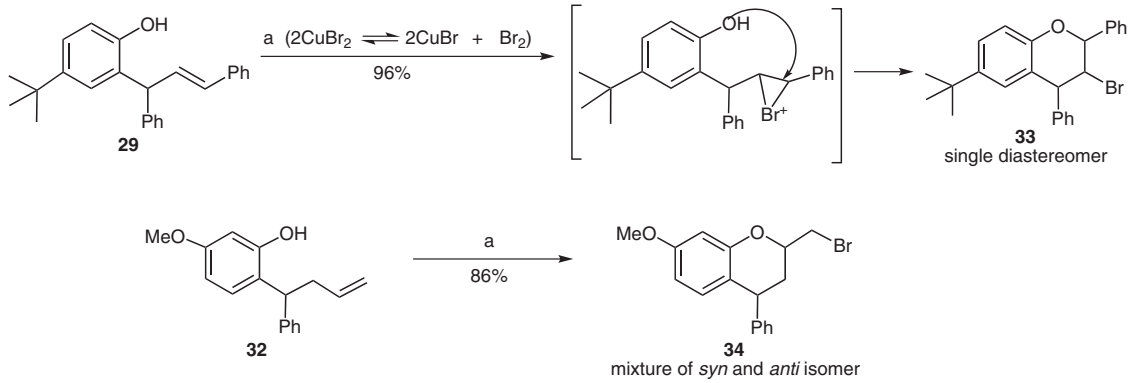
Application of the above reaction was further extended to the synthesis of O-heterocycles. Recently, we have developed a $CuBr_2$-mediated protocol for the conversion of 2-styryl phenols to benzo[*b*]furans involving both intramolecular cyclization of phenol with sterically close alkene as well as dehydrobromination in situ.[22] Keeping this in view, it was of interest to investigate the possibility of intramolecular cyclization in 4-*tert*-butyl-2-(1,3-diphenylallyl)phenol (**29**) with $CuBr_2$. To our satisfaction, the cyclization occurred instantaneously with $CuBr_2$ to yield 3-bromo-6-*tert*-butyl-2,4-diphenyl chroman (**33**) in quantitative yield[23] (Scheme 2). More interestingly, only one of the two possible diastereomers of **33** was formed as the sole product as evidenced by ^1H NMR and ^{13}C NMR data. However, relative stereochemistry at C-2, C-3, and C-4 could not be assigned. Similarly, 5-methoxy-2-(1-phenylbut-3-enyl) phenol (**32**) underwent intramolecular cyclization to afford 2-(bromomethyl)-7-methoxy-4-phenyl-chroman (**34**) in 86% yield.[23] The ^1H NMR and ^{13}C NMR data of **34** showed the formation of both *syn* and *anti* isomers but the diastereomeric ratio could not be estimated. Although we have no evidence about the reaction mechanism, the above intramolecular cyclizations can be explained by the disproportionation of $CuBr_2$ to CuBr and Br_2 in acetonitrile solution.[24] The generated bromine reacted with the alkene function to form the unstable bromonium cation intermediates which were attacked by sterically close phenolic group. Incidentally, this is an unprecedented route to the synthesis of chroman skeleton.

In summary an easy and convenient protocol involving microwave-accelerated alkylation of arenes and heteroarenes with benzylic alcohols catalyzed by $SbCl_3$ has been developed. The present protocol has several advantages including mild reaction conditions, short reaction time, simple workup, no need of anhydrous reaction conditions, and applicability to various substrates. Antimony chloride is known to undergo facile decomposition with

Table 2 Screening of Various Catalysts for the Alkylation of 4-*tert*-Butylphenol (**12**, 2 mmol) with 1-Phenyl Ethanol (**2a**, 2.2 mmol)

Entry	Catalyst (mol%)	Reaction conditions[a]	Reaction time (h)	Yield of **13a** (%)[b]	Yield of **13b** (%)[b]	Recovered **12** and **2a** (%)
1	I_2 (15.0)	MeCN, 65 °C	1.0	8.0	3.0	**46** (72) **2a** (64)
2	I_2 (15.0)	MeCN, MWI (400 W, 65 °C)	1.0	28.0	11.0	**12** (51) **2a** (38)
3	Fe (30.0), $CuBr_2$ (15.0)	MeCN, 65 °C	1.0	5.0	2.0	**12** (78) **2a** (65)
4	Fe (30.0), $CuBr_2$ (15.0)	MeCN, MWI (400 W, 65 °C)	1.0	26.0	9.0	**12** (51) **2a** (46)
5	$Yb(OTf)_3$ (15.0)	MeCN, 65 °C	1.0	8.0	4.0	**12** (69) **2a** (62)
6	$Yb(OTf)_3$ (15.0)	MeCN, MWI (400 W, 65 °C)	1.0	38.0	12.0	**12** (41) **2a** (36)
7	$SbCl_3$ (15.0)	MeCN, 65 °C	1.0	11.0	3.0	**12** (57) **2a** (41)
8	$SbCl_3$ (15.0)	MeCN, MWI (400 W, 65 °C)	1.0	68.0	12.0	**12** (7) **2a** (0)

[a] Reaction conditions: **12** (2 mmol), **2a** (2.2 mmol), catalyst (0.3 mmol, 15 mol%), in dry MeCN (4 mL).
[b] Isolated yields and the yields are based on the amount of **12** consumed.



Scheme 2 Intramolecular cyclization of *ortho*-alkenyl phenols with $CuBr_2$. *Reagents and conditions*: (a) $CuBr_2$ (2.4 equiv), MeCN, r.t.

water and is therefore likely to get deactivated by the stoichiometric amount of water produced during the alkylation. Nevertheless, the reaction proceeded to completion with substoichiometric amount of the catalyst. As an extension of the work, conversion of a few synthesized 2-alkenylated phenols to functionalized oxygen heterocycles via intramolecular cyclization was accomplished.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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(23) **Typical Procedure for the Alkylation of 1,3-Dimethoxybenzene (1) with 1-Phenylethanol (2a) Followed by Demethylation**
1,3-Dimethoxybenzene (**1**, 0.276 g, 2 mmol), 1-phenylethanol (**2a**, 0.268 g, 2.2 mmol), and $SbCl_3$ (0.068 g, 0.30 mmol) were mixed with dry MeCN (2 mL) in an Anton Paar microwave vessel and sealed with a cap. The resulting mixture was irradiated with microwave (400 W) for 25 min when **2a** was fully consumed (checked by TLC). The reaction mixture was quenched with sat. aq $NaHCO_3$ solution (1 mL), and the viscous mass thus obtained was dissolved in EtOAc and passed through Celite to remove metal salts. The Celite bed was thoroughly washed with EtOAc, and the filtrate was washed with H_2O, brine, and dried ($MgSO_4$). Removal of solvent yielded the crude product which was dried under vacuo and then dissolved in dry CH_2Cl_2 (5 mL). The solution was cooled (–20 °C), and BBr_3 (0.5 mL, 5 mmol) was added. The solution was slowly brought to 0 °C. The dark brown reaction mixture was stirred at 0 °C for 2 h when TLC showed complete disappearance of the starting compound. The reaction mixture was quenched with ice-water, and the product was extracted with CH_2Cl_2. The organic layer was washed with brine and dried (Na_2SO_4). The solvent was removed under vacuo, and the residue was purified by chromatography (silica, eluant: $CHCl_3$–MeOH) to get pure monoalkylated and dialkylated products **3a** and **3b**, respectively.

4-(1-Phenylethyl)benzene-1,3-diol (3a)
Yield 65%; thick oil. IR (neat): ν = 3400, 3025, 2968, 2932, 1605, 1517, 1451, 1215, 1113, 972, 909, 758, 735, 701 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.11–7.25 (m, 5 H), 6.98 (d, 1 H, *J* = 8.3 Hz), 6.32 (dd, 1 H, *J* = 8.3, 2.4 Hz), 6.17 (d, 1 H, *J* = 2.4 Hz), 4.61 (br s, 2 H), 4.20 (q, 1 H, *J* = 7.1 Hz), 1.50 (d, 3 H, *J* = 7.1 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 154.7, 154.0, 145.8, 128.7, 128.6, 127.4, 126.3, 124.8, 107.8, 103.5, 38.0, 21.1. Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: 78.11; H, 6.38.

4,6-Bis(1-phenylethyl)benzene-1,3-diol (3b)
Yield 14%; thick oil. IR (neat): ν = 3522, 3025, 2968, 2932, 1605, 1517, 1506, 1451, 1215, 1113, 972, 909, 759, 735, 703 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.10–7.28 (m, 10 H), 7.05 (s, 1 H), 6.11 (s, 1 H), 4.20 (q, 2 H, *J* = 7.2 Hz), 1.54 (d, 6 H, *J* = 7.2 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 152.4, 145.7, 128.6, 127.4, 127.2, 127.0, 126.3, 124.1, 104.3, 38.5, 21.2. Anal. Calcd for $C_{22}H_{22}O_2$: C, 82.99; H, 6.96. Found: 82.64; H, 6.68.

4-*tert*-Butyl-2-(1,3-diphenylallyl)phenol (29)
Yield 67%; thick oil. IR (neat): ν = 3447, 2963, 2928, 1491, 1261, 752, 698 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.10–7.37 (m, 12 H), 6.64–6.75 (m, 2 H), 6.35 (d, 1 H, *J* = 16.0 Hz), 5.07 (d, 1 H, *J* = 7.1 Hz), 1.23 (s, 9 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 151.2, 143.7, 142.2, 137.2, 131.8, 131.5, 128.7, 127.4, 126.7, 126.4, 124.7, 115.9, 114.8, 49.1, 34.2, 31.5. Anal. Calcd for $C_{25}H_{26}O$: C, 87.68; H, 7.65. Found: 87.31; H, 7.41.

5-Methoxy-2-(1-phenylbut-3-enyl)phenol (32)
Yield 68%; thick oil. IR (neat): ν = 3420, 3026, 1614, 1597, 1200, 1150, 698 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.19–7.37 (m, 5 H), 7.16 (d, 1 H, *J* = 8.5 Hz), 6.50 (dd, 1 H, *J* = 8.5, 2.5 Hz), 6.34 (d, 1 H, *J* = 2.5 Hz), 5.70–5.78 (m, 1 H), 4.95–5.09 (m, 2 H), 4.21 (t, 1 H, *J* = 7.8 Hz), 3.76 (s, 3 H), 2.74–2.84 (m, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 158.9, 154.2, 144.1, 136.9, 128.7, 128.4, 127.9, 126.2, 123.2, 116.1, 105.9, 102.3, 55.1, 43.7, 39.1. Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: 79.91; H, 6.87.

Typical Procedure for the Intramolecular Cyclization of 4-*tert*-Butyl-2-(1,3-diphenylallyl)phenol (29) with Copper(II) Bromide
To a solution of **29** (0.342 g, 1 mmol) in dry MeCN (5 mL), was added $CuBr_2$ (0.536 g, 2.4 mmol) and stirred at ambient temperature. After completion of the reaction (5 min, checked by TLC) MeCN was removed under vacuo, and the crude product was quenched with H_2O, dissolved in EtOAc, and the suspension was passed through Celite. The organic layer was washed with brine and dried (Na_2SO_4). The solvent was removed under vacuo, and the residue was purified by chromatography (silica, eluant: hexane–EtOAc) to get pure **33**.

6-*tert*-Butyl-3-bromo-2,4-diphenyl chroman (33)
Single diastereomer; yield 96%; colorless solid; mp 240–241 °C. IR (neat): ν = 2955, 1497, 1238, 1005, 696 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.26–7.49 (m, 11 H), 6.86 (d, 1 H, *J* = 8.6 Hz), 6.67 (d, 1 H, *J* = 1.8 Hz), 5.17 (d, 1 H, *J* = 9.8 Hz), 4.44–4.63 (m, 2 H), 1.14 (s, 9 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 152.4, 144.4, 141.9, 138.7, 129.3, 128.9, 128.5, 128.4, 127.9, 127.4, 126.7, 125.2, 124.1, 116.2, 82.6, 57.4, 53.9, 34.1, 31.3. ESI-MS: *m/z* = 421 [M^+]. Anal. Calcd for $C_{25}H_{25}BrO$: C, 71.26; H, 5.98. Found: 70.98; H, 5.73.

2-(Bromomethyl)-3,4-dihydro-7-methoxy-4-phenyl-2*H*-chromene (34)
Mixture of *syn* and *anti* isomers; yield 86%; thick oil. IR (neat): ν = 2930, 1609, 1504, 1491, 1206, 1051, 752 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.13–7.34 (m, 7 H), 6.31 and 6.28 (2 s, 1 H), 4.36–4.48 (m, 1 H), 3.53–3.83 (m, 6 H), 2.85–2.98 (m, 1 H), 2.16–2.26 (m, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 155.3, 155.1, 154.0, 153.4, 142.8, 141.0, 132.6, 131.4, 128.9, 128.7, 128.1, 127.5, 127.2, 126.8, 124.1, 121.7, 102.5, 102.3, 101.7, 101.3, 56.3, 56.2, 50.9, 42.1, 41.8, 41.2, 41.1, 36.6, 36.5, 29.6. ESI-MS: *m/z* = 333 [M^+]. Anal. Calcd for $C_{17}H_{17}BrO_2$: C, 61.28; H, 5.14. Found: 60.91; H, 4.87.

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