# Reusable Scandium/Ionic Liquid Catalyst System for Sequential C–C and C–O Bond Formations between Phenols and Dienes with Atom Economy

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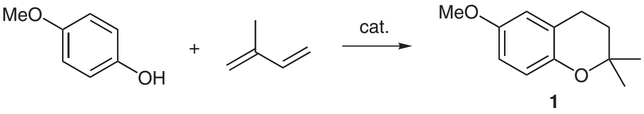
**Abstract:** Mild, efficient, and atom economical sequential C–C/C–O bond formations between phenols and dienes using the reusable catalyst system, $Sc(OTf)_3$–[bmim][$PF_6$], have been developed to afford in good yields a variety of dihydrobenzopyran and dihydrobenzofuran ring systems, which are important motifs in both naturally occurring and biologically active compounds. In these reactions the ionic liquid acts as not only an efficient additive but also an immobilizing agent for facilitating catalyst recycling.

**Key words:** heterocycles, bicyclic compounds, annulations, scandium, ionic liquids

Dihydrobenzopyrans and dihydrobenzofurans are pervasive motifs in biologically active natural products and pharmaceutical drug targets.[1] The dihydrobenzofurans are generally prepared in two steps from allyl aryl ethers by the Claisen rearrangement followed by cyclization of the resulting 2-allylphenols with strong acid.[2,3] The dihydrobenzopyrans are constructed typically by intramolecular hydroarylation from arene-ene substrates[4] or by cycloaddition of *o*-quinonemethides generated from salicylaldehydes and alcohols with alkenes using a protic acid or Lewis acid.[5] Recently, we reported mild, efficient, and economical Ag(I)-catalyzed sequential C–C/C–O bond formations between phenols and dienes (Scheme 1).[6] In view of green chemistry, atom-economical one-pot syntheses and the reuse of catalysts are preferable. Although Ag(I)-catalyzed reaction is an atom-economical one-pot reaction for the synthesis of dihydrobenzopyrans and dihydrobenzofurans, recovery and reuse of catalysts are not yet possible. Therefore, we were interested in exploring the possibility of the reuse of catalyst, and we reasoned that the use of ionic liquids as reaction media might offer a convenient solution to the catalyst recycling problem, obviating the need for structural modification of catalysts.[7]

In particular, air- and moisture-stable room temperature ionic liquids (RTILs) consisting of 1,3-dialkylimidazolium cations and various anions have attracted considerable attention as eco-friendly reaction media for organic synthesis in the last few years.[8] They are immiscible with some organic solvents, such as alkanes and ethers, and, hence, can be used as nonaqueous, polar alternatives in biphasic systems. In biphasic systems, catalysts having polar or ionic character can reside in ionic liquids, and thus catalysts can easily be recovered from the reaction mixture and then be reused. Herein we report the discovery of a recyclable catalytic system, $Sc(OTf)_3$–[bmim][$PF_6$], for the sequential addition/cyclization of phenols with dienes in an atom-economical manner.



**Scheme 1** Sequential C–C/C–O bond-formation reaction of *p*-methoxyphenol and isoprene

In light of our recent success in Ag(I)-catalyzed sequential C–C/C–O bond formations,[6] we chose this catalyst system in preliminary studies of annulation of phenols with dienes in ionic liquid as a solvent. Disappointingly, treatment of *p*-methoxyphenol and isoprene with 10 mol% of AgOTf in a range of RTILs, [bmim][X] ([bmim] = 1-butyl-3-methylimidazolium, X = $PF_6$, $BF_4$, OTf) and [emim][$BF_4$] ([emim] = 1-ethyl-3-methylimidazolium), afforded no desired products (Table 1, entries 1–4). Therefore, we made a conscious effort to develop a catalytic system that would work in RTILs. Several metal salts and complexes that were included in the screen in our previous works[6] were examined in this reaction, and most of them did not show the ability to produce the desired product **1** (Table 1, entries 9–13). In contrast, when the reaction was carried out in the presence of $Sc(OTf)_3$ in [bmim][$PF_6$],[9,10] **1** was produced in 30% yield (Table 1, entry 5). Since $Sc(OTf)_3$ is only slightly soluble in the hydrophobic ionic liquid, [bmim][$PF_6$], the hydrophilic ionic liquid, [bmim][$BF_4$], in which $Sc(OTf)_3$ is highly soluble,[9b,11] was used as a solvent. However, lower conversion was obtained (Table 1, entry 6). Interestingly, no reaction occurred in other hydrophilic ionic liquids, such as [bmim][OTf] and [emim][$BF_4$] (Table 1, entries 7 and 8). These results suggest that the catalytic activity of $Sc(OTf)_3$ was influenced by both the anions and the cations of ionic liquids in this reaction.[12]

The low conversion in [bmim][$PF_6$] as a sole solvent can be attributed to the low solubilities of phenols and dienes in [bmim][$PF_6$].[13] To provide biphasic systems in which catalyst recycling and separation of the products would be easy, toluene was then introduced into the system. Surprisingly, the use of toluene as a co-solvent increased the

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**Table 1** Optimization Studies for the Reaction of *p*-Methoxyphenol and Isoprene Using RTILs[a]

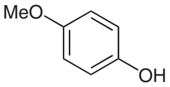
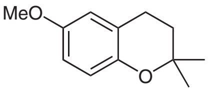
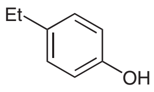
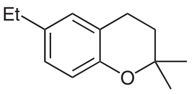
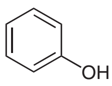
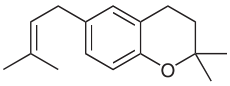
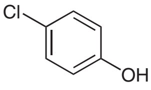
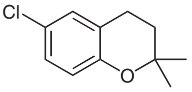
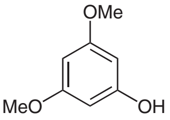
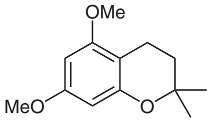
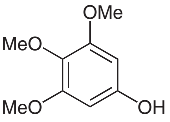
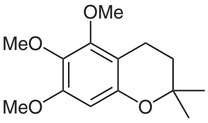
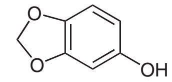
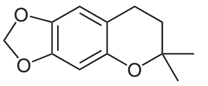
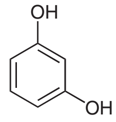
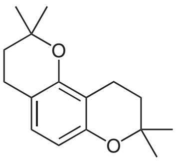
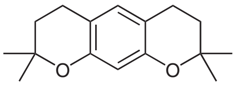
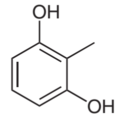
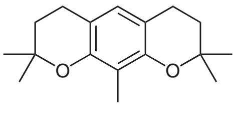
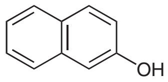
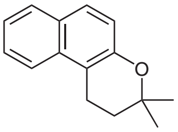
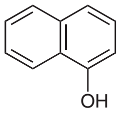
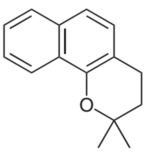
| Entry | Catalyst | Solvent (ratio) | Yield (%)[b] |
|---|---|---|---|
| 1 | AgOTf | [bmim][$PF_6$] | – |
| 2 | AgOTf | [bmim][$BF_4$] | – |
| 3 | AgOTf | [bmim][OTf] | – |
| 4 | AgOTf | [emim][$BF_4$] | – |
| 5 | $Sc(OTf)_3$ | [bmim][$PF_6$] | 30 |
| 6 | $Sc(OTf)_3$ | [bmim][$BF_4$] | 20 |
| 7 | $Sc(OTf)_3$ | [bmim][OTf] | trace |
| 8 | $Sc(OTf)_3$ | [emim][$BF_4$] | – |
| 9 | $Cu(OTf)_2$ | [bmim][$PF_6$] | – |
| 10 | AgOTf–$PPh_3$[c] | [bmim][$PF_6$] | – |
| 11 | AuCl–AgOTf–$PPh_3$[d] | [bmim][$PF_6$] | – |
| 12 | $RuCl_3$–AgOTf[e] | [bmim][$PF_6$] | – |
| 13 | $AgNO_3$ | [bmim][$PF_6$] | – |
| 14 | $Sc(OTf)_3$ | [bmim][$PF_6$]–toluene (1:1) | 50 |
| 15 | $Sc(OTf)_3$ | [bmim][$PF_6$]–toluene (1:4) | 55 |
| 16 | $Sc(OTf)_3$ | [bmim][$PF_6$]–THF (1:4) | – |
| 17 | $Sc(OTf)_3$ | [bmim][$PF_6$]–1,4-dioxane (1:4) | 7 |
| 18 | $Sc(OTf)_3$ | [bmim][$PF_6$]–MeCN (1:4) | 25 |
| 19 | $Sc(OTf)_3$ | [bmim][$PF_6$]–$CH_2Cl_2$ (1:4) | 20 |
| 20 | $Sc(OTf)_3$ | [bmim][$PF_6$]–DCE (1:4) | 30 |
| 21 | $Sc(OTf)_3$ | [bmim][$PF_6$]–toluene (1:10)[f] | 60 |
| 22 | $Sc(OTf)_3$ | [bmim][$PF_6$]–toluene (1:20)[g] | 60 |
| 23 | $Sc(OTf)_3$ | [bmim][$PF_6$]–toluene (1:50)[h] | 63 |
| 24 | $Sc(OTf)_3$ | [bmim][$PF_6$]–toluene (1:100)[i] | 67 |
| 25 | – | [bmim][$PF_6$]–toluene (1:100)[i] | – |
| 26 | $Sc(OTf)_3$ | toluene | 40 |
| 27[j] | $Sc(OTf)_3$ | [bmim][$PF_6$]–toluene (1:100)[i] | 70 |

[a] Reaction conditions: *p*-$MeOC_6H_4OH$ (1 equiv), isoprene (1 equiv), catalyst (10 mol%), solvent (0.1 M), 60 °C, 24 h.
[b] Determined by $^1H$ NMR using trichloroethylene as internal standard.
[c] Performed with AgOTf (10 mol%) and $PPh_3$ (10 mol%).
[d] Performed with AuCl (10 mol%), AgOTf (10 mol%), and $PPh_3$ (10 mol%).
[e] Performed with $RuCl_3$ (10 mol%) and AgOTf (20 mol%).
[f] The amount of [bmim][$PF_6$] was about 400 mol% of the amount of *p*-$MeOC_6H_4OH$.
[g] The amount of [bmim][$PF_6$] was about 200 mol% of the amount of *p*-$MeOC_6H_4OH$.
[h] The amount of [bmim][$PF_6$] was about 100 mol% of the amount of *p*-$MeOC_6H_4OH$.
[i] The amount of [bmim][$PF_6$] was about 50 mol% of the amount of *p*-$MeOC_6H_4OH$.
[j] Performed with isoprene (2 equiv) in the presence of $Sc(OTf)_3$ (20 mol%).

yields of **1**. Various organic solvents were examined, and toluene appeared preferable (Table 1, entries 15–20). It was also found that decreasing the amounts of [bmim][$PF_6$] led to gradually better yields of annulated products (Table 1, entries 14, 15 and 21–24). The most dramatic improvement was observed when the ratio of [bmim][$PF_6$] and toluene was 1:100, in which case the amount of [bmim][$PF_6$] was less than 50 mol% of the amount of *p*-methoxyphenol (Table 1, entry 24). Control experiments employing only either Sc(OTf)$_3$ or [bmim][PF$_6$] as the sole catalyst in toluene gave lower or no conversions, respectively (Table 1, entries 25 and 26). These results mean that [bmim][PF$_6$] plays a role as an additive to enhance either the catalytic activity of Sc(OTf)$_3$ or the nucleophilicity of phenol[14] and itself is not responsible for the product formation.

With the optimized conditions in hand, we set out to explore the scope of this coupling process.[15] As shown in Table 2, a variety of phenols underwent tandem addition/cyclization in the presence of Sc(OTf)$_3$ and [bmim][PF$_6$] to form the corresponding dihydrobenzopyrans in comparable or better yields than in the previously reported method.[6] The yields remained moderate to high with both electron-donating and electron-withdrawing substituents on the phenol ring. However, it is likely that the more electron-rich substrates work better in this reaction system than in the Ag(I)-catalyzed reaction system because highly electron-rich substrates, such as di- or trimethoxyphenol and resorcinol derivatives, did not react in the latter system (Table 2, entries 5–10). Our attention then turned to the synthesis of bicyclic compounds. To examine the possibility of double cyclization, we used resorcinol derivatives as substrates in this coupling process. We were delighted to find that the reactions using four equivalents of isoprene in the presence of Sc(OTf)$_3$ and [bmim][PF$_6$] proceeded smoothly to afford the corresponding bicyclic products **8**–**10** in good yields (Table 2, entries 8 and 9).

**Table 2** Sc–IL-Catalyzed Reaction of ROH with Isoprene[a]

| Entry | ROH | Product | | Yield (%)[b] |
|---|---|---|---|---|
| 1 |  | **1** |  | 55 |
| 2 |  | **2** |  | 65 |
| 3[c] |  | **3** |  | 60 |
| 4[d] |  | **4** |  | 53 |
| 5 |  | **5** |  | 73 |
| 6 |  | **6** |  | 85 |
| 7 |  | **7** |  | 92 |
| 8[c] |  | **8** |  | 88 (**8/9** = 3:2)[e] |
| | | **9** |  | |
| 9[c] |  | **10** |  | 91 |
| 10 |  | **11** |  | 99<br>(100)[f,g]<br>(100)[f,h] |
| 11[d] |  | **12** |  | 52 |

[a] Reaction conditions: ROH (1 equiv), isoprene (2 equiv), Sc(OTf)$_3$ (20 mol%), [bmim][PF$_6$] (0.5 equiv), toluene (0.1 M), 60 °C, 24 h, unless otherwise noted.

[b] Isolated yields.

[c] Performed with isoprene (4 equiv).

[d] Reaction time: 48 h.

[e] The ratio of two isomers was determined by $^1$H NMR.

[f] Determined by $^1$H NMR using trichloroethylene as internal standard.

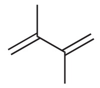
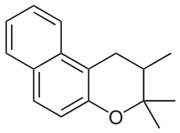
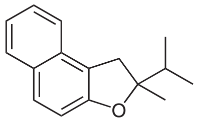
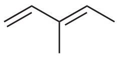
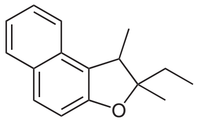
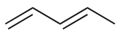
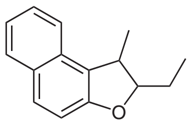
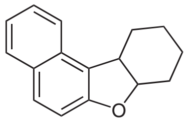
[g] Second cycle.

[h] Third cycle.

Finally, this reaction system allowed easy recovery and recycling of the catalyst, with three consecutive runs providing similar results. After completion of the reaction, the ionic liquid phase containing Sc(OTf)$_3$ was recovered by simple decantation of the toluene phase containing products/substrates, and then reused. Second and third runs using recovered Sc(OTf)$_3$-containing [bmim][PF$_6$] in the same reaction of 2-naphthol with isoprene yielded amounts of **11** as high as in the first cycle (Table 2, entry 10).

Subsequently, the reaction was examined on a range of dienes (Table 3). Both cyclic and acyclic dienes participated in the Sc–IL-catalyzed C–C/C–O bond formations, allowing the preparation of dihydrobenzopyrans and dihydrobenzofurans. Good yields were obtained for all cases. With the exception of 2,3-dimethyl-1,3-butadiene, all 1-substituted 1,3-dienes gave the corresponding dihydrobenzofurans as the sole products. Both **16** and **17** could be obtained in better yields than in Ag(I)-catalyzed reaction (Table 3, entries 3 and 4).[6] Regioselectivity of Sc–IL-catalyzed reaction presented herein parallels the regioselectivity observed for Ag(I)-catalyzed reaction of phenols with dienes, which suggests that C–C/C–O bond formation occurs by a similar mechanism in those reactions.

**Table 3** Sc–IL-Catalyzed Reaction of 2-Naphthol with Dienes[a]

| Entry | Diene | Product | Yield (%)[b] |
|---|---|---|---|
| 1[c] |  | **13**  | 98 (**13**/**14** = 40:60)[d] |
| | | **14**  | |
| 2[c] |  | **15**  | 95 (*syn*/*anti* = 83:17)[d] |
| 3[e] |  | **16**  | 92 (*syn*/*anti* = 64:36)[d] |
| 4[e] |  | **17**  | 91 (only *syn*) |

[a] Reaction conditions: 2-naphthol (1 equiv), diene (2 equiv), $Sc(OTf)_3$ (20 mol%), [bmim][$PF_6$] (0.5 equiv), toluene (0.1 M), 18–24 h.

[b] Isolated yields.

[c] Performed at 60 °C.

[d] The ratio of two isomers was determined by $^1H$ NMR.

[e] Performed at 100 °C.

In summary, we have developed mild and efficient Sc–IL-catalyzed sequential C–C/C–O bond formations between phenols and dienes. In these reactions, an ionic liquid plays an important role as not only an efficient additive but also an immobilizing agent for facilitating catalyst recycling. Electron-rich substrates are more beneficial than electron-deficient substrates, and both cyclic and acyclic dienes could be applied. Because of the simple procedure, easy recovery and reuse of this new catalytic system, $Sc(OTf)_3$–[bmim][$PF_6$], this one-pot reaction represents a greener and more attractive means for the facile and atom economical construction of dihydrobenzopyran and dihydrobenzofuran ring systems, which are important motifs in both naturally occurring and biologically active compounds.

## Acknowledgment

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(15) **General Procedure for the Sc–IL-Catalyzed Reaction of Phenols and Dienes and Catalyst Recycling**: To a solution of phenol and diene (2 equiv) in toluene (0.1 M) and [bmim][$PF_6$] (0.5 equiv) was added $Sc(OTf)_3$ (20 mol%). The resulting mixture was stirred at the reported temperature for 18–48 h. The organic(toluene) layer was decanted to leave the ionic liquid phase containing $Sc(OTf)_3$ which was washed with $Et_2O$ (3 ×) for extraction of the product. The combined organic layer was concentrated and the residue was purified by column chromatography on silica gel (EtOAc–*n*-hexanes, 1:20–1:100) to give the corresponding product.

The recovered ionic liquid layer remaining in the vessel was reused without any pre-treatment. For the second cycle, more reactants (phenol and diene) and toluene were added to the recovered ionic liquid layer.

**5,7-Dimethoxy-2,2-dimethylchroman (5)**:
Colorless oil (EtOAc–*n*-hexane, 1:20). $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.32 (s, 6 H), 1.75 (t, $J$ = 6.8 Hz, 2 H), 2.57 (t, $J$ = 6.8 Hz, 2 H), 3.75 (s, 3 H), 3.78 (s, 3 H), 6.01 (d, $J$ = 2.4 Hz, 1 H), 6.03 (d, $J$ = 2.4 Hz, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 16.6, 26.6, 32.4, 55.2, 55.3, 74.2, 90.8, 93.5, 102.4, 155.0, 158.5, 159.3. HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{13}H_{18}O_3$: 222.1256; found: 222.1255.

**5,6,7-Trimethoxy-2,2-dimethylchroman (6)**:
Colorless oil (EtOAc–*n*-hexane, 1:20). $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.31 (s, 6 H), 1.74 (t, $J$ = 6.8 Hz, 2 H), 2.63 (t, $J$ = 6.8 Hz, 2 H), 3.78 (s, 3 H), 3.80 (s, 3 H), 3.88 (s, 3 H), 6.16 (s, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 17.0, 26.6, 32.3, 55.7, 60.5, 61.0, 74.0, 96.5, 106.6, 135.3, 149.9, 151.3, 152.3. HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{14}H_{20}O_4$: 252.1362; found: 252.1364.

**2,2,8,8-Tetramethyl-3,4,9,10-tetrahydro-2*H*,8*H*-pyrano[2,3-*f*]chromene (8) and 2,2,8,8-Tetramethyl-3,4,7,8-tetrahydro-2*H*,6*H*-pyrano[3,2-*g*]chromene (9)**:
The mixture of isomers was obtained as a colorless oil (**8**/**9** = 3:2, EtOAc–*n*-hexane, 1:50). Signals corresponding to **8**: $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.32 (s, 3 H), 1.33 (s, 3 H), 1.77 (m, 4 H), 2.62 (t, $J$ = 6.8 Hz, 2 H), 2.70 (t, $J$ = 6.8 Hz, 2 H), 6.34 (d, $J$ = 8.5 Hz, 1 H), 6.80 (d, $J$ = 8.2 Hz, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 17.1, 22.0, 26.7, 27.1, 32.4, 32.9, 73.5, 73.9, 108.4, 109.5, 111.3, 127.0, 151.7, 152.8. Signals corresponding to **9**: $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.32 (s, 6 H), 1.77 (m, 4 H), 2.69 (t, $J$ = 6.8 Hz, 4 H), 6.24 (s, 1 H), 6.74 (s, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 21.8, 26.8, 33.1, 73.8, 104.7, 112.6, 129.3, 153.1. HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{22}O_2$: 246.1620; found: 246.1618.

**2,2,8,8,10-Pentamethyl-3,4,7,8-tetrahydro-2*H*,6*H*-pyrano[3,2-*g*]chromene (10)**:
White solid (EtOAc–*n*-hexane, 1:50). $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.33 (s, 12 H), 1.76 (t, $J$ = 6.8 Hz, 4 H), 2.03 (s, 3 H), 2.70 (t, $J$ = 6.8 Hz, 4 H), 6.62 (s, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 8.0, 22.1, 27.1, 33.1, 73.5, 111.8, 113.0, 125.8, 150.7. HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{24}O_2$: 260.1776; found: 260.1776.

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