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# Ionic Liquids with Multi-Active Sites Synergistically Catalyzed Metal-Free Transformation of Alcohols Using Dimethyl Carbonate as an Environmental Solvent

Zengmin Li[+],[a] Yating Wen[+],[a] Ning Wang,[a] Feng Han,*[a] Ying Li,[a] Hongfeng Zhuang,[a] and Chengxia Miao*[a]

One of the ultimate goals in organic synthesis is to develop metal-free, efficient and easily separable catalytic system for atom economic organic reactions in an environmental solvent. Direct substitution reaction of alcohols and hydrocarbon compounds is a significant and atom economic method for C–C bond formation. Herein, a metal-free and efficient catalytic system including recyclable pyridine-based ionic liquids with multiple active sites as the catalyst and dimethyl carbonate as the environmentally friendly solvent was developed for atom economic C3 substitution of 4-hydroxycoumarins with alcohols. Primary aromatic alcohols, secondary aliphatic and aromatic alcohols were suitable for the reaction, providing up to 99% yield. The catalytic system could be easily scaled up to gram-scale with nearly quantitative yield. Coumatetralyl as commercial rodenticide could be prepared directly from commercially available 4-hydroxycoumarin and 1,2,3,4-tetrahydronaphthalen-1-ol. Racemic product derived from the reaction of (*R*)-1-phenylethanol and 4-hydroxycoumarin indicated the reaction was achieved through an $S_N1$ pathway. The comparison of the activities and acidities of the ionic liquids demonstrated that there was no directly relationship between them. Control experiments showed that the reaction probably proceeded via carbocation, ether intermediate and synergistically promoted effect of hydrogen bonding between the ionic liquid with multi-active sites and substrates.

## Introduction

Developing metal-free, efficient and easily separable catalytic system for atom economic organic reactions in an environmental solvent is one of the ultimate goals in organic synthesis from the view-point of green chemistry. The direct substitution reaction of alcohols is an attractive process for water as the sole by-product, which is recognized as one of ten key Green Chemistry research areas.[1–2] Direct substitution of hydrocarbon compounds with alcohols is a significant C–C bond forming method for petrochemical processing, the synthesis of pharmaceutical agents and so on.[3–5] 4-Hydroxycoumarins as important precursors in the realm of organic synthesis can be transformed by different methods into a series of 4-hydroxycoumarin derivatives, especially 3-(benzyl)-substituted 4-hydroxycoumarins, which exhibit a wide range of biological activities such as anti-HIV, antimalarial, antibacterial, cytotoxic and so on.[6–10] At present, there are several methods for the synthesis of 3-substituted 4-hydroxycoumarin derivatives through C3 substitution. One strategy was achieved with olefins as the alkylation reagent using $FeCl_3 \cdot 6H_2O$ as the catalyst or Pd-catalyzed oxidative Heck reactions *via* simultaneous C–H functionalization at the C3 position of coumarins under aerobic conditions.[11–12] Besides, Pd-catalyzed C–C bond formation reaction for the synthesis of 4-hydroxycoumarins with C3-alkylation could be realized with organic halides and boronic acid as the substrates.[13] And the C3 substitution of 4-hydroxycoumarins with alcohols catalyzed by $Fe(ClO_4)_3 \cdot H_2O$,[14] $Al(OTf)_3$,[15] $Bi(NO_3)_3 \cdot 5H_2O$ in ionic liquid,[16] $Yb(OTf)_3$,[17] $I_2$,[18] TMSOTf (TMS, trimethylsilyl),[19] Amberlite IR-120,[20] palladium complexes,[21] $RuCl_2[PPh_3]_3$[22] or *p*-toluenesulfonic acid[23] was also reported. However, metals were usually used as catalysts in the reported methods. And carbocation was usually recognized as the key intermediate derived from alcohols especially in Lewis or Brønsted acid-catalyzed systems among the third developed systems. Previously, we have developed several efficient and mild systems catalyzed by acidic ionic liquids to generate carbocations from alcohols, which can react with sulfonamide, amide, carbamate, aromatic amine, olefins, thiols et al. to produce corresponding products.[24–28] Ionic liquids exhibit high thermal and chemical stability, negligible vapor pressure, easy recyclability, tunable properties and could be used as environmental catalysts for the reaction by introducing different functionalized groups.[29–33] On the other hand, dimethyl carbonate (DMC) is recognized as a green solvent for fast biodegradability, low toxicity, mild odor, low evaporation rate, low density and good environmental compatibility[34,35] and it has been used in several reactions, such as rearrangement reaction,[36] Diels-Alder reaction,[37] insertion reaction,[38] olefin metathesis transformations,[39] asymmetric hydrogenation,[40] oxidation.[41]

[a] *Z. Li,[+] Y. Wen,[+] N. Wang, Prof. F. Han, Prof. Y. Li, H. Zhuang, Prof. C. Miao*
*College of Chemistry and Material Science*
*Shandong Agricultural University*
*Daizong Road No. 61, Tai'an 271018, China*
*E-mail: chxmiao@sdau.edu.cn*
*fenghan@sdau.edu.cn*

[+] *These authors contributed equally to this work.*

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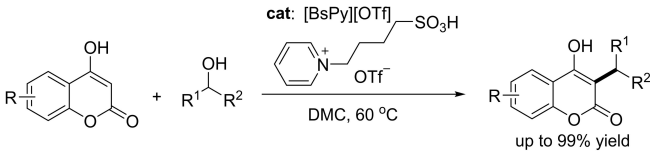
As a continuation of our efforts to develop reactions involving generated carbocation as the intermediate,[24–28] we wanted to exploit more efficient, mild and environmental system to catalyze the atom economic C3 substitution of 4-hydroxycoumarins with carbocations derived from alcohols. The reaction was synergistically catalyzed by metal-free pyridine-based ionic liquids with multiple active sites using DMC as the green solvent, providing up to 99% yield (Scheme 1 and Figure 1). The developed catalytic system could be easily separated from the product and be suitable for one-step synthesis of coumatetralyl as commercial rodenticide. And a mechanism involving the synergistically promoted effect of hydrogen bonding, carbocation and ether intermediate was proposed.




**Scheme 1.** C3 substitution of 4-hydroxycoumarins with alcohols catalyzed by [BsPy][OTf].

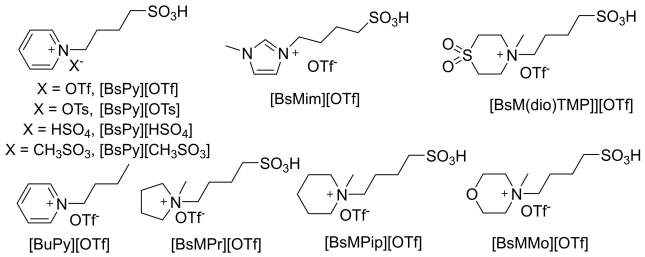
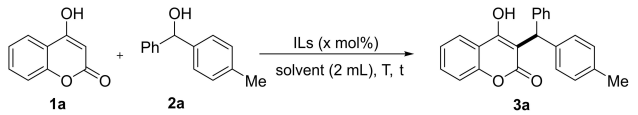



**Figure 1.** Ionic liquids used in the work.

**Table 1.** Screening the reaction conditions for the substitution of 4-hydroxycoumarin with phenyl(*p*-tolyl)methanol catalyzed by ionic liquids.[a]




| Entry | Cat. [mol%] | Solvent | T [°C] | Yield [%][b] |
|---|---|---|---|---|
| 1 | – | $CH_3CN$ | 80 | NR[c] |
| 2 | [BsPy][OTf] (1) | $CH_3CN$ | 80 | 52 |
| 3 | [BsPy][OTf] (2) | $CH_3CN$ | 80 | 84 |
| 4 | [BsPy][OTf] (5) | $CH_3CN$ | 80 | 94 |
| 5 | [BsPy][OTf] (10) | $CH_3CN$ | 80 | 96 |
| 6 | [BsPy][OTf] (5) | DMF | 80 | NR[c] |
| 7 | [BsPy][OTf] (5) | DMSO | 80 | NR[c] |
| 8 | [BsPy][OTf] (5) | $H_2O$ | 80 | NR[c] |
| 9 | [BsPy][OTf] (5) | THF[d] | 80 | 86 |
| 10 | [BsPy][OTf] (5) | *n*-hexane | 80 | 79 |
| 11 | [BsPy][OTf] (5) | 1,4-dioxane | 80 | 99 |
| 12 | [BsPy][OTf] (5) | DMC | 80 | 98 |
| 13 | [BsPy][OTf] (5) | DCE[d] | 80 | 98 |
| 14 | [BsPy][OTf] (5) | toluene | 80 | 96 |
| 15 | [BsPy][OTf] (5) | CYH[d] | 80 | 96 |
| 16 | [BsPy][OTf] (5) | DMC | 60 | 96 |
| 17 | [BsPy][OTf] (5) | DMC | 40 | 27 |
| 18 | [BsPy][OTf] (5) | DMC | 25 | trace |
| 19 | [BsPy][OTf] (5) | DMC | 60 | 47[e] |
| 20 | [BsMim][OTf] (5) | DMC | 60 | 32 |
| 21 | [BsMPr][OTf] (5) | DMC | 60 | 11 |
| 22 | [BsMPip][OTf] (5) | DMC | 60 | 47 |
| 23 | [BsMMo][OTf] (5) | DMC | 60 | NR[c] |
| 24 | [BsM(dio)TMP][OTf] (5) | DMC | 60 | 16 |
| 25 | [BuPy][OTf] (5) | DMC | 60 | NR[c] |
| 26 | [BsPy][$HSO_4$] (5) | DMC | 60 | trace |
| 27 | [BsPy][OTs] (5) | DMC | 60 | 31 |
| 28 | [BsPy][$CH_3SO_3$] (5) | DMC | 60 | 33 |

[a] Reaction conditions: 4-hydroxycoumarin **1a** (0.5 mmol), phenyl(*p*-tolyl) methanol **2a** (0.6 mmol), catalyst (catalytic amount refers to 4-hydroxycoumarin), solvent (2 mL), at a certain temperature for 2 h. [b] Isolated yield. [c] NR = no reaction. [d] THF: tetrahydrofuran; DCE: dichloroethane; CYH: cyclohexane; [e] t = 1 h.

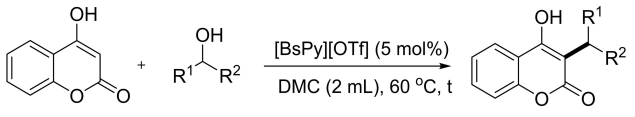
## Results and Discussion

The initial examination was performed by using 4-hydroxycoumarin and phenyl(*p*-tolyl)methanol as the substrates (Table 1). Obviously, the reaction did not occur without any catalyst (Table 1, entry 1). Interestingly, 52% yield could be provided with 1 mol% of [BsPy][OTf] as the catalyst and $CH_3CN$ as the solvent at 80 °C (Table 1, entry 2). Using 5 mol% of [BsPy][OTf] as the catalyst for the transformation led to 94% yield, and there was no significant change by further increasing the catalyst loading to 10 mol% (Table 1, entries 3–5). Then we examined the influence of solvents on the reaction. Most solvents gave moderate to excellent yields, except DMF (*N,N*-dimethylformamide), DMSO (dimethyl sulfoxide) and $H_2O$ (Table 1, entries 4, 6–15). DMC was chosen as the best solvent for availability in large amounts and at low prices, providing a suitable liquid temperature range, low (eco)toxicity, and complete biodegradability (Table 1, entry 12).[34,35,42] Besides, the reaction was sensitive to the temperature and would become poorer when the temperature was lower than 60 °C (Table 1, entries 12 and 16–18). Moreover, shorten the reaction time would also decrease the yield (Table 1, entry 16 vs 19). Subsequently, the effects of the cations derived from pyridine, imidazole, pyrrolidine, piperidine, morpholine and thiomorpholine 1,1-dioxide were investigated (Figure 1 and Table 1, entries 16 and 20–25). The results indicated that the cation had significant influence on the reaction. Excellent yield could be obtained only by employing pyridine-based ionic liquids as the catalyst (Table 1, entry 16). Moreover, the sulfonic acid in the side chain of ionic liquids was also necessary for the reaction (Table 1, entry 16 vs 25). Utilizing other anions such as $HSO_4^-$, $OTs^-$ or $CH_3SO_3^-$ instead of $OTf^-$ also resulted in lower yields (Table 1, entries 16 vs 26–28). The phenomena indicated that the reaction needed the synergistic action of multiple active sites belonging to pyridine-based ionic liquids to display excellent activity. Additionally, the optimum ratios of 4-hydroxycoumarin and phenyl(*p*-tolyl)methanol were compared and 1:1.2 gave the best result (Table S1). Also, the recyclability of [BsPy][OTf] was tested. The results indicated that the ionic liquids could be recycled and reused, and there was some change in yield after the fourth run under the optimized reaction conditions, providing yield from 96% to 86% (Table 1, entry 16 and Figure S1).

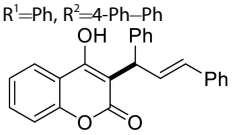
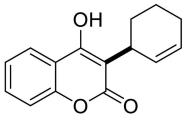
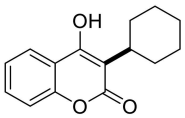
The generality of the reaction was studied under the optimized reaction conditions (Table 2). The activities of a series of secondary aromatic alcohols were tested. The results demonstrated that most secondary aromatic alcohols bearing either electron-donating or electron-withdrawing substituents on the phenyl ring proved reactive with certain variation in the isolated yields (Table 2, entries 1–12). Diphenylmethanol without any substituent just gave 64% yield under optimized reaction conditions (Table 2, entry 5). However, 96% yield could be obtained by prolonging the reaction time to 8 h (Table 2, entry 6). In order to prove the structure of the desired products, the x-ray structure of **3e** was obtained from *n*-hexane/ethyl acetate (Figure 2 and Table S2). An electron-donating substituent in the 4-position of the phenyl ring was well tolerated, generating 96% or 98% yield for Me or OMe respectively (Table 2, entries 1 and 3). Substrate with two electron-donating substituents in 4, 4′-position on the phenyl ring exhibited better activity, furnishing 99% yield of **3d** with 2 h (Table 2, entry 4). There is some relationship between the activity and the steric hindrance and moving the Me to the 2-position of the phenyl ring was detrimental for the transformation (Table 2, entry 1 vs 2). Besides, substrates with halogen substituents in the 4-position on the phenyl group were also tolerated by prolonging the reaction time (Table 2, entries 7–11). The more the electron-withdrawing substituents had, the poorer the activity was (Table 2, entry 11). And 81% yield could be obtained with phenyl as the substituent to disperse the positive charge and make it more stable (Table 2, entry 12). Other activated secondary aromatic alcohol such as 1,3-diphenylprop-2-en-1-ol also exhibited a good yield under optimized reaction conditions (Table 2, entry 13). 1-Phenylethan-1-ol and primary aromatic alcohols such as (4-methoxyphenyl)methanol could provide moderate yields when the reaction time was extended to 8 or 24 h (Table 2, entries 14 and 15). In addition, the reaction of secondary aliphatic alcohols such as 2-cyclohexen-1-ol and cyclohexanol could also occur, providing 45% and 35% yield respectively by prolong the reaction time to 24 h (Table 2, entries 16 and 17).

Additionally, application of the catalytic system to 4-hydroxycoumarin derivatives showed that excellent yields could be obtained with substrates bearing both electron-withdrawing and electron-donating groups in the 6 or 7-position (Table 3). 4-Hydroxycoumarins with electron-donating groups such as Me,

**Table 2.** Substrate scope of C3 substitution of 4-hydroxycoumarin with different alcohols catalyzed by [BsPy][OTf].[a]




1a 2 3

| Entry | Product | Yield [%][b] |
|---|---|---|
| 1 | **3a**, $R^1$=Ph, $R^2$=4-Me–Ph | 96 |
| 2 | **3b**, $R^1$=Ph, $R^2$=2-Me–Ph | 78[c] |
| 3 | **3c**, $R^1$=Ph, $R^2$=4-OMe–Ph | 98 |
| 4 | **3d**, $R^1$=$R^2$=4-OMe–Ph | 99 |
| 5 | **3e**, $R^1$=$R^2$=Ph | 64 |
| 6 | | 96[c] |
| 7 | **3f**, $R^1$=Ph, $R^2$=4-F–Ph | 92[d] |
| 8 | **3g**, $R^1$=Ph, $R^2$=4-Cl–Ph | 81[d] |
| 9 | **3h**, $R^1$=Ph, $R^2$=4-Br–Ph | 66[d] |
| 10 | **3i**, $R^1$=Ph, $R^2$=4-$CF_3$–Ph | 81[e] |
| 11 | **3j**, $R^1$=$R^2$=4-Cl–Ph | 62[d] |
| 12 | **3k**, $R^1$=Ph, $R^2$=4-Ph–Ph | 81 |
| 13 |  **3l** | 90 |
| 14 | **3m**, $R^1$=Me, $R^2$=Ph | 68[c] |
| 15 | **3n**, $R^1$=H, $R^2$ = 4-OMe–Ph | 67[f] |
| 16 |  **3o** | 45[g] |
| 17 |  **3p** | 35[f] |

[a] Reaction conditions: 4-hydroxycoumarin **1a** (0.5 mmol), alcohol **2** (0.6 mmol), [BsPy][OTf] (5 mol% refers to 4-hydroxycoumarin), DMC (2 mL), at 60 °C for 2 h. [b] Isolated yield. [c] t = 8 h. [d] t = 12 h. [e] 80 °C, 4 h. [f] [BsPy][OTf] (10 mol%), at 80 °C for 24 h. [g] t = 24 h.

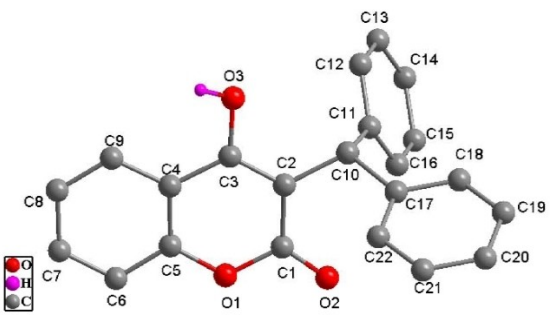
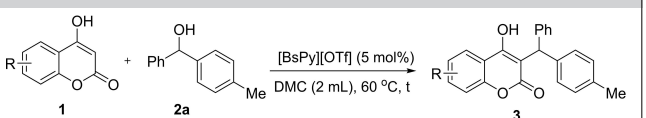



**Figure 2.** X-ray structure of **3e** (hydrogen atoms linked to carbons are omitted for clarity, CCDC-2092740).

**Table 3.** C3 substitution of 4-hydroxycoumarins with phenyl(*p*-tolyl) methanol catalyzed by [BsPy][OTf].[a]




1 2a 3

| Entry | Product | Yield [%][b] |
|---|---|---|
| 1 | **3a**, R=H | 96 |
| 2 | **3q**, R=7-Me | 96 |
| 3 | **3r**, R=7-OMe | 99 |
| 4 | **3s**, R=6-Me | 97 |
| 5 | **3t**, R=6-F | 63[c] |
| 6 | **3u**, R=6-Cl | 92[c] |
| 7 | **3v**, R=6-Br | 92[c] |

[a] Reaction conditions: 4-hydroxycoumarin derivative **1** (0.5 mmol), phenyl(*p*-tolyl)methanol **2a** (0.6 mmol), [BsPy][OTf] (5 mol% refers to 4-hydroxycoumarin derivative), DMC (2 mL) at 60 °C for 2 h. [b] Isolated yield. [c] 12 h.

OMe in the 6 or 7-position displayed good activities, giving nearly quantitative yields (Table 3, entries 2–4). Good yields were also observed by employing halogen-substituted substrates by prolonging the reaction time to 12 h, except 6-fluoro-4-hydroxycoumarin (Table 3, entries 4, 6, 7 vs 5).

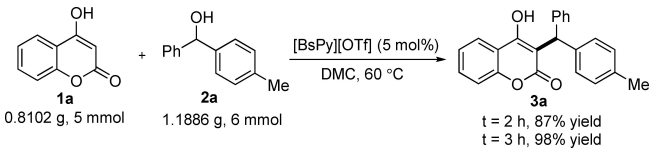
After demonstrating the substrate scope of the catalytic system, we examined the scalability of our catalytic system for the C3 substitution of 4-hydroxycoumarin with phenyl(*p*-tolyl) methanol (Scheme 2). Delightedly, the reaction could be carried out smoothly to provide 87% yield of the desired product under the optimized reaction conditions, and up to 98% yield could be acquired by prolonging the reaction time from 2 to 3 h.

Coumatetralyl (**3w**) is a common agricultural chemical and the first anticoagulant rodenticides since mid-1950s. Now it is still widely used for pest control in many aeras.[43] As a further demonstration of the utility of our developed system, the C3 substitution of 4-hydroxycoumarin with 1,2,3,4-tetrahydronaphthalen-1-ol to generate coumatetralyl was performed under certain reaction conditions with [BsPy][OTf] as the catalyst (Scheme 3). Interestingly, 71% yield could be provided without any by-product under optimized reaction conditions by prolonging the reaction time to 24 h. And 69% yield could be obtained with 20 mol% [BsPy][OTf] as the catalyst at 80 °C for 2 h. That's to say, the catalytic system was available for one step synthesis of coumatetralyl.

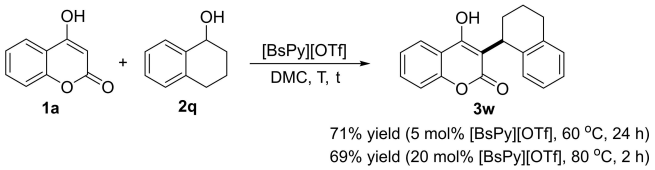
According to the previous reports, the reaction in our developed acidic system seems to proceed by a carbocation intermediate,[14] which was attacked by 4-hydroxycoumarin as the nucleophile. Some control experiment was performed in order to test the reaction mechanism. (*R*)-1-phenylethanol was tested to react with 4-hydroxycoumarin under the optimized reaction conditions for 8 h, providing racemic product **3m** (Scheme 4). The result indicated that the reaction was achieved through an $S_N1$ pathway and not an $S_N2$ pathway.

Ethers also usually recognized as the reaction intermediates could be detected by GC-MS compared with the standard sample during the reactions. And the corresponding ethers could be isolated under the optimized reaction conditions when 4-hydroxycoumarin was not added into the catalytic system (Scheme 5, (1)). Nearly quantitative yield could be obtained when 0.5 mmol 4-hydroxycoumarin was reacted with 0.3 mmol 4,4′-(oxybis(phenylmethylene))bis(methylbenzene) under optimized reaction conditions (Scheme 5, (2)). The phenomena demonstrated that aromatic ether may be involved in the reaction.

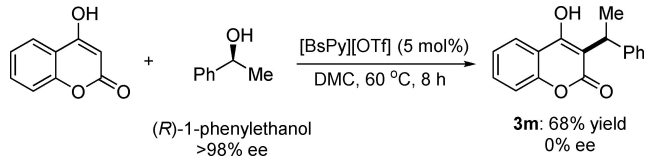
According to our results and the previous report,[24–28,44] we proposed a possible mechanism involving carbocation and ethers as the intermediates and synergistically promoted effect of hydrogen bonding (Scheme 6). Initially, we thought that the activities may be significantly influenced by the acidities of the ionic liquids. So, the acidities of the ionic liquids were tested in order to demonstrate the effect of the ionic liquids (Table S3),[45–48] which indicated that the order of the acidities was as follows: $[BsPy][CH_3SO_3] > [BsPy][OTf] > [BuPy][OTf] > [BsPy][OTs] > [BsPy][HSO_4]$. Compared with the data in Table 1 (entries 16, 25–28), the results showed that there was no obvious relationship between the activity and acidity. Also, the screening of the cations and the side chain in Table 1 (entries 16, 20–25) indicated that both cations and the sulfonic acid group were important for the reaction. And trifluoromethylsulfonate was also essential for the reaction after testing several anions. Moreover, Liu et al. proved the hydrogen bonding effect between ionic liquids and ethers using NMR analysis and DFT calculation.[44] Therefore, we proposed cation and anion of the ionic liquids would synergistically catalyze the reaction in our developed system through the effect of hydrogen bonding based on the phenomena. Sulfonic acid group of the cation and trifluoromethanesulfonate as the anion would activate the hydrogen of alcohols and the hydrogen of 4-hydroxycoumarin respectively under the effect of hydrogen bonding. Electron-donating group in the phenyl ring of aromatic alcohols was beneficial for the reaction, possibly advantageous to stabilization of the carbocation (Table 2,



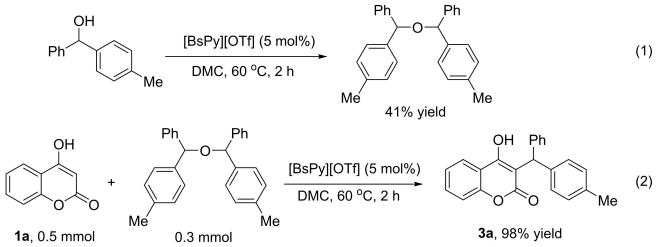

**Scheme 2.** Scale-up experiments.



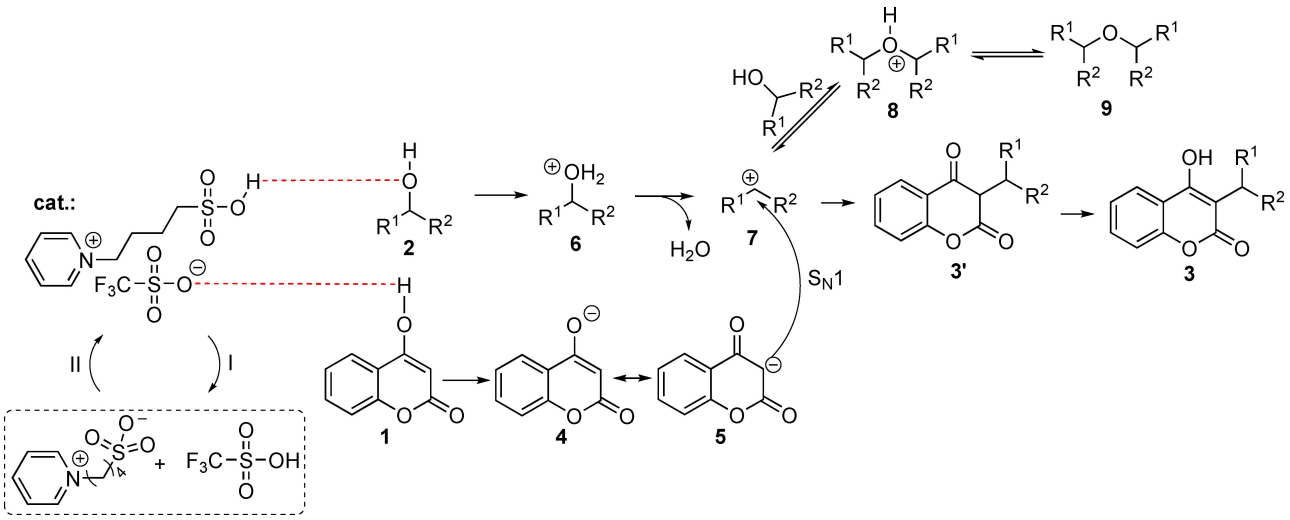

**Scheme 3.** Application of the catalytic system for one step synthesis of coumatetralyl.




**Scheme 4.** The reaction of 4-hydroxycoumarin with (*R*)-1-phenylethanol.




**Scheme 5.** Control experiments for the substitution of 4-hydroxycoumarin with phenyl(*p*-tolyl)methanol.




**Scheme 6.** Proposed mechanism for the substitution under the reaction conditions.

entries 1, 3 and 4). 4-(Pyridin-1-ium-1-yl)butane-1-sulfonate and trifluoromethanesulfonic acid would be formed during the reaction (I), which could be in-situ transformed to [BsPy][OTf] acting as the catalyst again (II). On the other hand, formed carbocation would be attacked by carbanion **5** derived from **1** through $S_N1$ pathway to generate compound **3'**, which could exist in tautomeric keto-enol forms with desired product **3**. Meanwhile, carbocation **7** would react with another alcohol immediately to providing intermediate **8**, which would generate **9** by losing the proton. Intermediates **7**, **8** and **9** could exist in balance.

## Conclusion

We have developed an efficient, economic and environmental system for C3 substitution of 4-hydroxycoumarin with alcohols. The system was catalyzed by pyridine-based ionic liquids with multi-active sites in dimethyl carbonate as the environmental solvent, providing a series of 4-hydroxycoumarin derivatives with up to 99% yield. Nearly quantitively yield could be obtained when the scalability of our catalytic system was applied for the C3 substitution of 4-hydroxycoumarin with phenyl(*p*-tolyl)methanol. Interestingly, coumatetralyl as commercial rodenticide could be smoothly synthesized in one step with the developed system. An $S_N1$ pathway was deduced from the racemic product derived from the reaction of (*R*)-1-phenylethanol and 4-hydroxycoumarin. The comparison between the activities and acidities of the ionic liquids demonstrated that there was no directly relationship for them. And a mechanism involving effects of hydrogen bonding between the ionic liquids and substrates, carbocation and ether was proposed. Developing new strategies for the transformation of alcohols are in progress in our lab.

## Experimental Section

### General

NMR spectra were recorded on BRUKER AVANCETM III 400, BRUKER AVANCE III HD 600 spectrometers. $^1$H NMR (400 or 600 MHz) and $^{13}$C NMR (101 or 151 MHz) spectra were obtained as solutions in $CDCl_3$ or $(CD_3)_2SO$. Chemical shifts were reported in parts per million (ppm, δ) and referenced to TMS (trimethylsilane). The high-resolution mass spectra (HRMS) were recorded on an Agilent Technologies 1260-G6530B LC-MS. Optical rotation was recorded with a WZZ-3 automatic polarimeter (sodium lamp, 1-dm cuvette, c in g/100 mL, 20 °C). All reagents and solvents were obtained from commercial suppliers without further purification unless noted otherwise. All reactions were monitored by TLC (Thin Layer Chromatography) with silica gel coated plates. Silica gel (200–300 microns) was used for all chromatographic separations, providing isolated yields.

### Representative experimental procedure for the substitution of 4-hydroxycoumarin with alcohols

To a mixture of 4-hydroxycoumarin (81 mg, 0.5 mmol) and phenyl (*p*-tolyl)methanol (118.9 mg, 0.6 mmol) in DMC (2 mL), a certain amount of catalyst was added, and the reaction mixture was stirred for several hours at a definite temperature. The progress of the reaction mixture was monitored by TLC. After completion of the reaction, the mixture was extracted with ethyl acetate and concentrated under vacuum. The crude product was purified by silica gel column (200–300 mesh) with petroleum ether/ethyl acetate (6:1) as eluent to afford the corresponding product. Finally, the pure product can be obtained after vacuum drying and oil pump to remove the remaining solvent.

### The procedure for the reuse of [BsPy][OTf] in the substitution of 4-hydroxycoumarin with phenyl(*p*-tolyl)methanol

To test the catalyst reusability, the reaction was carried out in the presence of [BsPy][OTf] under the optimal reaction conditions with 4-hydroxycoumarin and phenyl(*p*-tolyl)methanol as the substrates for 2 h detected by TLC. After each cycle, DMC was removed with oil pump, and the residue was dissolved with petroleum ether:eth-

hyl acetate (3:1, 10 mL) and heated under 60 °C, so the product and ionic liquids were extracted and separated. The Schlenk tube containing ionic liquids was then dried and used directly for the next cycle.

## Characterization of the products[14–22]

### *4-Hydroxy-3-(phenyl(p-tolyl)methyl)-2H-chromen-2-one (3 a)*

White solid, 164.3 mg, 96% yield; Melting point: 146–147 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.76–7.69 (m, 1H), 7.53 (ddd, *J* = 8.7, 7.4, 1.6 Hz, 1H), 7.41–7.34 (m, 2H), 7.33–7.23 (m, 5H), 7.17 (q, *J* = 8.2 Hz, 4H), 6.33 (dd, *J* = 7.4, 2.8 Hz, 1H), 5.93 (s, 1H), 2.35 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 163.2, 160.7, 152.8, 140.1, 137.7, 137.0, 132.1, 130.3, 129.4, 128.8, 128.7, 127.7, 123.9, 123.2, 116.5, 116.0, 107.9, 47.0, 21.1. HRMS-ESI: Calcd. For $C_{23}H_{18}O_3$: 342.1256. Found $[M+Na]^+$: 365.1148.

### *4-Hydroxy-3-(phenyl(o-tolyl)methyl)-2H-chromen-2-one (3 b)*

White solid, 133.5 mg, 78% yield; Melting point: 161–162 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.9 Hz, 1H), 7.54 (dd, *J* = 11.4, 4.2 Hz, 1H), 7.34 (ddd, *J* = 21.2, 15.9, 7.0 Hz, 6H), 7.20 (dd, *J* = 17.4, 9.5 Hz, 3H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.37 (s, 1H), 6.01 (s, 1H), 2.32 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 163.0, 161.0, 152.7, 139.8, 138.6, 138.1, 132.1, 131.7, 129.5, 128.8, 128.0, 127.8, 127.4, 127.0, 123.9, 123.2, 116.5, 115.8, 106.5, 45.2, 19.7. HRMS-ESI: Calcd. For $C_{23}H_{18}O_3$: 342.1244. Found $[M+Na]^+$: 365.1136.

### *4-Hydroxy-3-((4-methoxyphenyl)(phenyl) methyl)-2H-chromen-2-one (3 c)*

Orange solid, 175.3 mg, 98% yield; Melting point: 87–88 °C; $^1$H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.9 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.34–7.30 (m, 2H), 7.28 (d, *J* = 8.1 Hz, 3H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.31 (s, 1H), 5.91 (s, 1H), 3.81 (s, 3H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 163.3, 160.6, 159.2, 152.7, 140.2, 132.1, 131.7, 129.9, 129.4, 128.7, 127.7, 123.9, 123.2, 116.5, 116.0, 114.9, 107.9, 55.3, 46.6. HRMS-ESI: Calcd. For $C_{23}H_{18}O_4$: 358.1205. Found $[M+Na]^+$: 381.1099.

### *3-(Bis(4-methoxyphenyl)methyl)-4-hydroxy-2H-chromen-2-one (3 d)*

Reddish orange solid, 191.5 mg, 99% yield; Melting point: 148–149 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.33–7.15 (m, 6H), 6.90 (d, *J* = 8.5 Hz, 4H), 6.39 (s, 1H), 5.84 (s, 1H), 3.81 (s, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 163.2, 160.5, 159.1, 152.7, 132.01, 132.0, 129.8, 123.9, 123.1, 116.4, 116.0, 114.8, 113.4, 108.0, 55.3, 45.8. HRMS-ESI: Calcd. For $C_{24}H_{20}O_5$: 388.1311, Found $[M+Na]^+$: 411.1200.

### *3-Benzhydryl-4-hydroxy-2H-chromen-2-one (3 e)*

White solid, 157.8 mg, 96% yield; Melting point: 154–156 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.54 (ddd, *J* = 8.8, 7.4, 1.6 Hz, 1H), 7.42–7.36 (m, 4H), 7.36–7.30 (m, 3H), 7.30–7.26 (m, 5H), 6.22 (s, 1H), 5.99 (s, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 163.2, 152.7, 139.9, 132.2, 129.5, 128.8, 127.9, 123.9, 123.2, 116.5, 115.9, 107.7, 107.1, 47.4. HRMS-ESI: Calcd. For $C_{22}H_{15}FO_3$: 328.1099, Found $[M+Na]^+$: 351.0994.

### *3-((4-Fluorophenyl)(phenyl) methyl)-4-hydroxy-2H-chromen-2-one (3 f)*

White solid, 159.8 mg, 92% yield; Melting point: 164–165 °C; $^1$H NMR (600 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.57–7.52 (m, 1H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.34 (dd, *J* = 13.1, 7.6 Hz, 2H), 7.25 (s, 5H), 7.07 (t, *J* = 8.6 Hz, 2H), 6.19 (s, 1H), 5.95 (s, 1H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 163.1, 161.3, 160.6, 152.7, 140.0, 135.3, 132.3, 130.5, 130.4, 129.7, 128.6, 128.1, 124.0, 123.2, 116.3 (t, *J* = 21.2 Hz), 115.8, 107.6, 46.6. HRMS-ESI: Calcd. For $C_{22}H_{16}O_3$: 346.1005, Found $[M+Na]^+$: 369.0893.

### *3-((4-Chlorophenyl)(phenyl) methyl)-4-hydroxy-2H-chromen-2-one (3 g)*

White solid, 147.1 mg, 81% yield; Melting point: 151–152 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.9 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.36 (dt, *J* = 15.5, 7.4 Hz, 6H), 7.28–7.20 (m, 5H), 6.30 (s, 1H), 5.94 (s, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 163.1, 160.8, 152.7, 139.8, 138.2, 133.5, 132.3, 130.2, 129.7, 129.4, 128.6, 128.2, 124.0, 123.2, 116.5, 115.8, 107.3, 46.7. HRMS-ESI: Calcd. For $C_{22}H_{15}ClO_3$: 362.0710, Found $[M+Na]^+$: 385.0598.

### *3-((4-Bromophenyl)(phenyl) methyl)-4-hydroxy-2H-chromen-2-one (3 h)*

White solid, 135.2 mg, 66% yield; Melting point: 176–177 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.9 Hz, 1H), 7.58–7.47 (m, 3H), 7.37 (dt, *J* = 19.2, 7.9 Hz, 4H), 7.25 (d, *J* = 8.7 Hz, 3H), 7.17 (d, *J* = 7.6 Hz, 2H), 6.19 (s, 1H), 5.93 (s, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 163.1, 160.7, 152.7, 139.7, 138.7, 132.4, 132.3, 130.5, 129.8, 128.6, 128.2, 124.0, 123.2, 121.7, 116.5, 115.8, 107.3, 46.8. HRMS-ESI: Calcd. For $C_{22}H_{15}BrO_3$: 406.0205, Found $[M+Na]^+$: 429.0088.

### *4-Hydroxy-3-(phenyl(4-(trifluoromethyl)phenyl) methyl)-2H-chromen-2-one (3 i)*

White solid, 159.6 mg, 81% yield; Melting point: 158–159 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.9 Hz, 1H), 7.63 (d, *J* = 7.9 Hz, 2H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.37 (ddd, *J* = 27.9, 16.9, 8.8 Hz, 6H), 7.27–7.21 (m, 3H), 6.30 (s, 1H), 6.03 (s, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 163.1, 161.0, 152.7, 143.8, 139.5, 132.5, 129.9, 129.3, 128.7, 128.4, 126.1 (q, *J* = 7.41 Hz), 125.4, 124.1, 123.2, 122.7, 116.6, 115.7, 107.0, 47.2. HRMS-ESI: Calcd. For $C_{23}H_{15}F_3O_3$: 396.0973, Found $[M+Na]^+$: 419.0861.

### *3-(Bis(4-chlorophenyl)methyl)-4-hydroxy-2H-chromen-2-one (3 j)*

White solid, 123.5 mg, 62% yield; Melting point: 177–178 °C; $^1$H NMR (600 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.58–7.52 (m, 1H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.34 (dt, *J* = 16.5, 5.9 Hz, 4H), 7.26–7.19 (m, 4H), 6.21 (s, 1H), 5.94 (s, 1H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 163.1, 160.7, 152.7, 139.80, 138.2, 133.6, 132.3, 130.2, 129.8, 129.5, 128.7, 128.2, 124.0, 123.2, 116.5, 115.8, 107.4, 46.8. HRMS-ESI: Calcd. For $C_{22}H_{14}Cl_2O_3$: 396.0320, Found $[M+Na]^+$: 419.0208.

### *3-([1,1′-Biphenyl]-4-yl(phenyl) methyl)-4-hydroxy-2H-chromen-2-one (3 k)*

White solid, 163.2 mg, 81% yield; Melting point: 181–182 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.9 Hz, 1H), 7.66–7.51 (m, 5H), 7.47–7.25 (m, 12H), 6.35 (s, 1H), 6.02 (s, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 163.2, 160.7, 152.7, 140.7, 140.3, 140.0, 138.8, 132.2, 129.5, 129.2, 128.83, 128.77, 128.1, 127.9, 127.5, 127.0, 124.0, 123.2, 116.5,

115.9, 107.7, 47.0. HRMS-ESI: Calcd. For $C_{28}H_{20}O_3$: 404.1412, Found $[M+Na]^+$: 427.1301.

### *3-(1,3-Diphenylallyl)-4-hydroxy-2H-chromen-2-one (3 l)*

White solid, 161.3 mg, 90% yield; Melting point: 85–86 °C; $^1$H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, $J$ = 7.9 Hz, 1H), 7.55 (t, $J$ = 7.2 Hz, 1H), 7.41 (dd, $J$ = 17.2, 9.0 Hz, 6H), 7.36–7.31 (m, 4H), 7.29 (d, $J$ = 8.0 Hz, 2H), 6.85 (s, 1H), 6.74 (dd, $J$ = 16.1, 6.1 Hz, 1H), 6.52 (d, $J$ = 16.0 Hz, 1H), 5.48 (d, $J$ = 5.9 Hz, 1H). $^{13}$C NMR (151 MHz, $CDCl_3$) δ 163.1, 162.4, 160.9, 152.8, 139.4, 136.0, 134.1, 132.2, 129.5, 128.7, 128.2, 128.1, 127.9, 126.6, 124.0, 123.1, 116.5, 115.9, 106.3, 44.0. HRMS-ESI: Calcd. For $C_{24}H_{18}O_3$: 354.1256, Found $[M+Na]^+$: 377.1146.

### *4-Hydroxy-3-(1-phenylethyl)-2H-chromen-2-one (3 m)*

White solid, 91.1 mg, 68% yield; Melting point: 159–161 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, $J$ = 7.8 Hz, 1H), 7.48 (dt, $J$ = 14.9, 7.2 Hz, 4H), 7.34 (dd, $J$ = 19.9, 7.7 Hz, 2H), 7.23 (dd, $J$ = 15.0, 7.5 Hz, 1H), 6.10 (s, 1H), 4.74 (q, $J$ = 7.0 Hz, 1H), 1.67 (d, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 163.5, 159.7, 152.5, 141.5, 131.9, 129.8, 127.9, 127.3, 123.9, 122.9, 116.4, 116.1, 110.1, 34.5, 16.5. HRMS-ESI: Calcd. For $C_{17}H_{14}O_3$: 266.0943, Found $[M+Na]^+$: 289.0837.

### *4-Hydroxy-3-(4-methoxybenzyl)-2H-chromen-2-one (3 n)*

White solid, 94.9 mg, 67% yield; Melting point: 128–129 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, $J$ = 7.9 Hz, 1H), 7.53 (t, $J$ = 7.7 Hz, 1H), 7.30 (dd, $J$ = 19.2, 8.7 Hz, 4H), 6.87 (d, $J$ = 8.3 Hz, 2H), 6.52 (s, 1H), 3.98 (s, 2H), 3.78 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 163.9, 160.4, 158.9, 152.5, 131.9, 129.6, 129.0, 124.0, 122.8, 116.6, 115.7, 114.8, 104.5, 55.3, 29.3. HRMS-ESI: Calcd. For $C_{17}H_{14}O_4$: 282.0892, Found $[M+Na]^+$: 305.0783.

### *3-(Cyclohex-2-en-1-yl)-4-hydroxy-2H-chromen-2-one (3 o)*

White solid, 54.5 mg, 45% yield; Melting point: 115–116 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, $J$ = 10.2 Hz, 2H), 7.52 (t, $J$ = 7.7 Hz, 1H), 7.30 (d, $J$ = 7.5 Hz, 1H), 6.32 (d, $J$ = 9.7 Hz, 1H), 6.06 (d, $J$ = 9.9 Hz, 1H), 3.87 (s, 1H), 2.22 (s, 2H), 2.17–2.00 (m, 1H), 1.90–1.56 (m, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 163.3, 161.0, 152.4, 135.0, 131.7, 128.8, 123.8, 122.8, 116.3, 116.0, 107.4, 77.3, 77.0, 76.7, 33.0, 28.1, 25.2, 21.0. HRMS-ESI: Calcd. For $C_{15}H_{14}O_3$: 242.0943, Found $[M+H]^+$: 243.0885.

### *3-Cyclohexyl-4-hydroxy-2H-chromen-2-one (3 p)*

White solid, 42.7 mg, 35% yield; Melting point: 108–110 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, $J$ = 7.5 Hz, 1H), 7.54 (t, $J$ = 7.3 Hz, 1H), 7.36–7.26 (m, 2H), 5.67 (s, 1H), 4.48 (s, 1H), 2.07–1.34 (m, 10H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 164.4, 163.4, 153.5, 132.3, 123.8, 123.2, 116.7, 116.3, 90.7, 77.4, 77.1, 76.8, 30.9, 25.3, 23.3. HRMS-ESI: Calcd. For $C_{15}H_{16}O_3$: 244.1099, Found $[M+Na]^+$: 267.0997.

### *4-Hydroxy-7-methyl-3-(phenyl(p-tolyl) methyl)-2H-chromen-2-one (3 q)*

White solid, 171.1 mg, 96% yield; Melting point: 139–140 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, $J$ = 8.1 Hz, 1H), 7.44–7.22 (m, 5H), 7.19–7.03 (m, 6H), 6.30 (s, 1H), 5.92 (s, 1H), 2.43 (s, 3H), 2.34 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 163.5, 161.0, 152.9, 143.3, 140.2, 137.6, 137.2, 130.2, 129.3, 128.8, 128.7, 127.6, 125.2, 122.9, 116.6, 113.5, 106.9, 47.0, 21.8, 21.1. HRMS-ESI: Calcd. For $C_{24}H_{20}O_3$: 356.1412, Found $[M+Na]^+$: 379.1306.

### *4-Hydroxy-7-methoxy-3-(phenyl(p-tolyl) methyl)-2H-chromen-2-one (3 r)*

White solid, 183.6 mg, 99% yield; Melting point: 133–135 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.40–7.26 (m, 6H), 7.18 (dt, $J$ = 24.8, 8.3 Hz, 5H), 6.26 (s, 1H), 5.93 (s, 1H), 2.36 (d, $J$ = 9.5 Hz, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 163.4, 160.7, 150.9, 140.1, 137.7, 137.0, 133.6, 133.1, 130.2, 129.3, 128.8, 128.6, 127.7, 122.8, 116.2, 115.6, 107.8, 47.0, 21.1, 20.9. HRMS-ESI: Calcd. For $C_{24}H_{20}O_3$: 356.1412, Found $[M+Na]^+$: 379.1303.

### *4-Hydroxy-6-methyl-3-(phenyl(p-tolyl) methyl)-2H-chromen-2-one (3 s)*

White solid, 172.7 mg, 97% yield; Melting point: 128–129 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, $J$ = 8.6 Hz, 1H), 7.42–7.23 (m, 5H), 7.16 (q, $J$ = 8.0 Hz, 4H), 6.81 (d, $J$ = 10.6 Hz, 2H), 6.25 (s, 1H), 5.90 (s, 1H), 3.86 (s, 3H), 2.35 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 163.7, 163.0, 161.1, 154.5, 140.3, 137.6, 137.2, 130.2, 129.3, 128.8, 128.6, 127.6, 124.2, 112.2, 109.1, 105.2, 100.2, 55.8, 46.9, 21.1. HRMS-ESI: Calcd. For $C_{24}H_{20}O_4$: 372.1362, Found $[M+Na]^+$: 395.1252.

### *6-Fluoro-4-hydroxy-3-(phenyl(p-tolyl) methyl)-2H-chromen-2-one (3 t)*

White solid, 113.9 mg, 63% yield; Melting point: 167–168 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.42–7.34 (m, 3H), 7.34–7.21 (m, 5H), 7.21–7.11 (m, 4H), 6.40 (s, 1H), 5.91 (s, 1H), 2.35 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 162.9, 159.8 (t, $J$ = 2.5 Hz), 157.5, 148.8 (d, $J$ = 1.5 Hz), 139.8, 137.8, 136.7, 130.3, 129.4, 128.0 (d, $J$ = 10.9 Hz), 127.8, 119.6, 119.5, 118.0 (d, $J$ = 8.1 Hz), 117.0 (d, $J$ = 8.8 Hz), 109.1, 108.7 (d, $J$ = 18.2 Hz), 47.1, 21.1. HRMS-ESI: Calcd. For $C_{23}H_{17}FO_3$: 360.1162, Found $[M+Na]^+$: 383.1053.

### *6-Chloro-4-hydroxy-3-(phenyl(p-tolyl) methyl)-2H-chromen-2-one (3 u)*

White solid, 173.5 mg, 92% yield; Melting point: 157–158 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.47 (d, $J$ = 8.7 Hz, 1H), 7.36 (dt, $J$ = 22.4, 7.2 Hz, 3H), 7.26 (s, 3H), 7.16 (dd, $J$ = 25.7, 7.8 Hz, 4H), 6.31 (s, 1H), 5.90 (s, 1H), 2.36 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 162.7, 159.5, 151.0, 139.7, 137.9, 136.6, 132.0, 130.3, 129.5, 128.7, 128.6, 127.9, 122.8, 117.9, 117.2, 108.7, 47.1, 21.1. HRMS-ESI: Calcd. For $C_{23}H_{17}ClO_3$: 376.0866, Found $[M+Na]^+$: 399.0754.

### *6-Bromo-4-hydroxy-3-(phenyl(p-tolyl) methyl)-2H-chromen-2-one (3 v)*

White solid, 194.2 mg, 92% yield; Melting point: 148–149 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.61 (d, $J$ = 8.8 Hz, 1H), 7.43–7.30 (m, 3H), 7.26–7.25 (m, 2H), 7.20 (d, $J$ = 8.8 Hz, 3H), 7.13 (d, $J$ = 7.6 Hz, 2H), 6.31 (s, 1H), 5.90 (s, 1H), 2.36 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 162.6, 159.4, 151.5, 139.7, 137.9, 136.6, 134.8, 130.3, 129.5, 128.7, 128.6, 127.9, 125.9, 118.2, 117.6, 116.7, 108.7, 47.1, 21.1. HRMS-ESI: Calcd. For $C_{23}H_{17}BrO_3$: 420.0361, Found $[M+H]^+$: 421.0433.

***4-Hydroxy-3-(1,2,3,4-tetrahydronaphthalen-1-yl)-2H-chromen-2-one (3 w)***

White solid, 103.6 mg, 71% yield; Melting point: 120–121 °C; $^1$H NMR (400 MHz, $(CD_3)_2SO$) δ 11.47 (s, 1H), 8.00 (d, $J$ = 7.6 Hz, 1H), 7.60 (t, $J$ = 7.7 Hz, 1H), 7.48–7.28 (m, 2H), 7.20–6.65 (m, 4H), 4.49 (dd, $J$ = 10.5, 5.8 Hz, 1H), 2.82 (ddd, $J$ = 32.0, 22.0, 9.8 Hz, 2H), 2.26–1.56 (m, 4H). $^{13}$C NMR (101 MHz, DMSO) δ 160.7, 152.2, 138.7, 136.8, 131.7, 128.7, 126.4, 125.7, 125.1, 123.8, 123.4, 116.3, 116.1, 109.0, 35.3, 29.5, 27.1, 23.1. HRMS-ESI: Calcd. For $C_{19}H_{16}O_3$: 292.1099, Found $[M+Na]^+$: 315.0991.

Deposition Number 2092740 (for **3 e**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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## Conflict of Interest

The authors declare no conflict of interest.

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