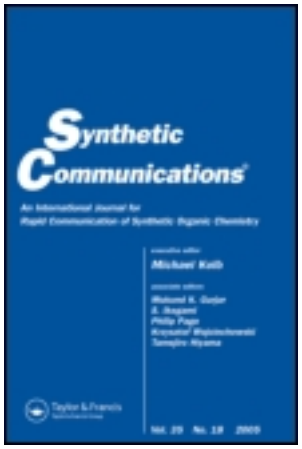


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Divergent Products Obtained from the Reactions of Salicylaldehyde and 4-Hydroxycoumarin in TEBAC-H_2O, KF-Al_2O_3-EtOH, and Ionic Liquid

Xiang-Shan Wang [a b], Jie Zhou [a], Ke Yang [a] & Mei-Mei Zhang [b]

[a] School of Chemistry and Chemical Engineering, Xuzhou Normal University, Xuzhou, Jiangsu, China

[b] Key Laboratory of Biotechnology for Medical Plants, Xuzhou, Jiangsu, China

Version of record first published: 15 Oct 2010.

To cite this article: Xiang-Shan Wang , Jie Zhou , Ke Yang & Mei-Mei Zhang (2010): Divergent Products Obtained from the Reactions of Salicylaldehyde and 4-Hydroxycoumarin in TEBAC-H_2O, KF-Al_2O_3-EtOH, and Ionic Liquid, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 40:22, 3332-3345

To link to this article: http://dx.doi.org/10.1080/00397910903419837

Synthetic Communications®, 40: 3332–3345, 2010

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910903419837

Taylor & Francis
Taylor & Francis Group

DIVERGENT PRODUCTS OBTAINED FROM THE REACTIONS OF SALICYLALDEHYDE AND 4-HYDROXYCOUMARIN IN TEBAC-H_2O, KF-Al_2O_3-EtOH, AND IONIC LIQUID

Xiang-Shan Wang,[1,2] Jie Zhou,[1] Ke Yang,[1] and Mei-Mei Zhang[2]

[1]*School of Chemistry and Chemical Engineering, Xuzhou Normal University, Xuzhou, Jiangsu, China*

[2]*Key Laboratory of Biotechnology for Medical Plants, Xuzhou, Jiangsu, China*

Controlling selectivity of the reactions of salicylaldehydes and 4-hydroxycoumarin in triethylbenzylammonium chloride–H_2O, ionic liquid, or KF-Al_2O_3-EtOH systems, respectively, resulted in the syntheses of three series of different coumarin derivatives.

Keywords: Aqueous media; coumarin; ionic liquid; KF-Al_2O_3

INTRODUCTION

Control of selectivity, for example, chemo- and regioselectivity, is among the most important objectives in organic chemistry. Many different process parameters such as temperature, pressure, solvent, catalyst type, and other factors can be utilized to modulate the selectivity of synthetic transformations.[1] Multicomponent reactions (MCRs) can be distinguished from classical, sequential two-component chemistry synthetic processes in that they use three or more chemical starting materials as the input for product formation. Up to seven starting components have been used, and MCRs have often been shown to produce greater product yields than classical chemistry.[2] For multicomponent reactions involving the simultaneous molecular interaction of three or more components, the issue of selectivity is of particular significance because of the high probability of several potential parallel reaction pathways leading to different product classes.[3] They also provide a powerful tool for the one-pot synthesis of diverse and complex compounds as well as small and druglike heterocycles.[4]

Compounds containing coumarin moieties are ubiquitous to a variety of important compounds and potent drugs, including a number of HIV protease inhibitors.[5] Besides, they are known to display a wide range of biological activities,

Received April 15, 2009.

Address correspondence to Xiang-Shan Wang, School of Chemistry and Chemical Engineering, Xuzhou Normal University, Xuzhou, Jiangsu, 221116, China. E-mail: xswang1974@yahoo.com

including anti-angiogenesis activity,[6] antimicrobial activity,[7] anticoagulant activity,[8] antibacterial activity,[9] and anti-inflammatory activity.[10] As part of our ongoing research about the synthesis of bioactive compounds,[11] herein we report the reactions of aromatic aldehyde and 4-hydroxycoumarin by controlling selectivity of MCRs in triethylbenzylammonium chloride (TEBAC)–H_2O, ionic liquid, or KF-Al_2O_3-EtOH systems, respectively, resulting in five series of different coumarin derivatives.

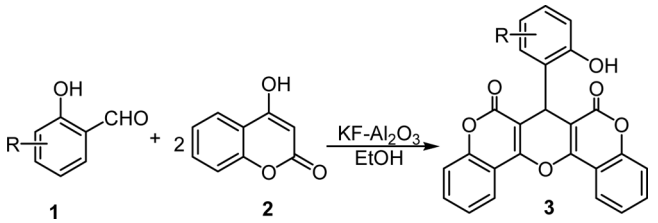
RESULTS AND DISCUSSION

In our initial study, we tested the reaction of salicylaldehyde **1** with 2 equiv. of 4-hydroxycoumarin **2** in EtOH at 80 °C (Scheme 1). A small amount of piperidine was added to enhance the rate of conversion. The interesting 2,7,10-trioxaanthracene-1-,8-dione derivatives **3** were isolated. Obviously, this structure, **3**, was different from the simple dehydrated aldol product **4** reported by Sullivan et al.[12] in 1943 for the reaction carried out in refluxing EtOH without added base. The structure of **3d** is further confirmed by x-ray diffraction and is shown in Fig. 1.

Using the conversion of salicylaldehyde and 4-hydroxycoumarin as a model reaction; different solvents such as CH_3CN, CH_3OH, and dimethylformamide (DMF) and various bases such as NaOH, KOH, K_2CO_3, Et_3N, piperidine and KF-Al_2O_3 were used to optimize the conditions. This resulted in 2,7,10-trioxaanthracene-1,8-dione compound **3**a as the only product in good yields (Table 1). An optimized yield of 84% was obtained in the presence of 100 mol% of KF-Al_2O_3 in EtOH (Table 1, entry 6). Subsequently, these optimized conditions were applied for the conversion of various substituted salicylaldehydes **1** into the corresponding fused biscoumarine analogs **3b–g** (Table 2).

To obtain the products by a green method, we performed the same reaction in water in the presence of 5 mol% TEBAC at room temperature. To our disappointment, only the simple Knoevenagel condensation products **4** were obtained, which failed to react with another molecule of 4-hydroxycoumarin (Scheme 2). Noticeably, the reaction of various substituted salicylaldehydes **1** selectively furnished (*E*)-3--(2-hydroxybenzylidene)-3*H*-chromene-2,4-dione derivatives **4a–h** in good yields (Table 3). These results are in accordance with those reported by Sullivan et al.[12] and are listed in Table 3.

As a comparison experiment, we also tested the same reactants using the ionic liquid [BMIM]Br as another green solvent. Interestingly, under these conditions,



Scheme 1. Reaction of salicylaldehyde and 4-hydroxycoumarin in KF-Al_2O_3-EtOH.

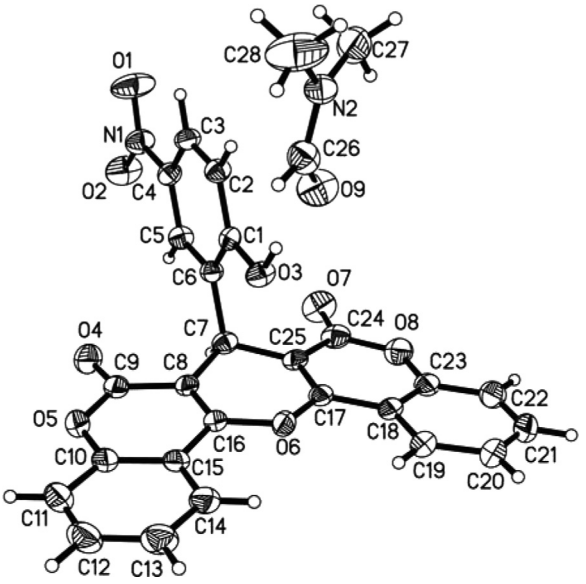


Figure 1. Crystal structure of **3d** with DMF solvate.

salicylaldehyde did react with two molecules of 4-hydroxycoumarin, affording the 6*H*,7*H*-7-(4-hydroxy-3-coumaranyl)[1]benzopyrano[4,3-*b*][1]benzopyran-6-one derivative **5a** in excellent yield (Scheme 3). This result also accords with that reported by Sullivan et al. in refluxing EtOH.[12]

Various substituted salicylaldehydes **1** were then subjected to reaction with 4-hydroxycoumarin to generate a series of benzopyrano[4,3-*b*][1]benzopyran-6-one derivatives **5** (Table 4). For aldehyde **1**, the yields of **5** were not sensitive to the electronic properties of the aromatic ring in the presence of electron-withdrawing

Table 1. Synthesis of **3a** under different reaction conditions[a]

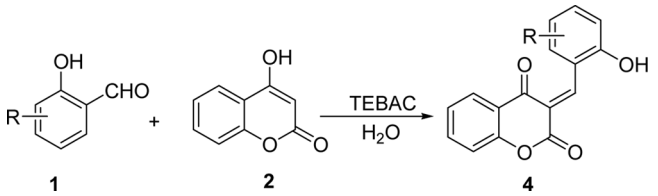
Entry	Solvents	Catalysts	Mol %	Yields/(%)[b]
1	EtOH	Piperidine	100	68
2	EtOH	Et_3N	100	72
3	EtOH	NaOH	100	54
4	EtOH	KOH	100	62
5	EtOH	K_2CO_3	100	74
6	EtOH	KF-Al_2O_3	100	84
7	EtOH	KF-Al_2O_3	50	70
8	EtOH	KF-Al_2O_3	200	84
9	CH_3CN	KF-Al_2O_3	100	79
10	CH_3OH	KF-Al_2O_3	100	82
11	DMF	KF-Al_2O_3	100	82

[a]Reagents and conditions: salicylaldehyde **1** (0.122 g, 1 mmol), 4-hydroxycoumarin **2** (0.324 g, 2 mmol), solvent (10 mL).
[b]Isolated yields.

Table 2. Reaction of salicylaldehyde **1** and 4-hydroxycoumarin **2** in EtOH catalyzed by KF-Al_2O_3[a]

Entry	R	Products	Time (h)	Yields (%)[b]
1	H	**3a**	14	84
2	5-Cl	**3b**	12	82
3	5-Br	**3c**	14	86
4	5-NO_2	**3d**	10	82
5	3,5-Cl_2	**3e**	10	78
6	3,5-Br_2	**3f**	12	88
7	4-OCH_3	**3g**	16	79

[a]Reagents and conditions: **1** (1 mmol), **2** (0.324 g, 2 mmol), KF-Al_2O_3 (0.102 g, 1 mmol), and EtOH (10 mL).
[b]Isolated yields.



Scheme 2. Reaction of salicylaldehyde and 4-hydroxycoumarin in water.

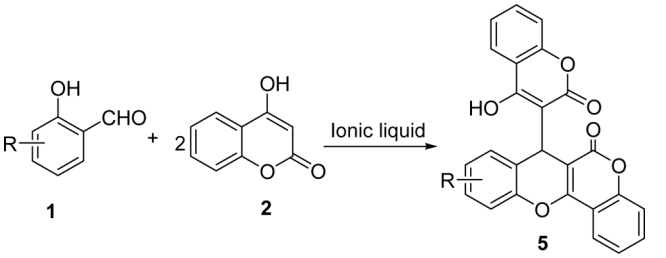
groups (such as halide, nitro) or electron-donating groups (such as alkyl group, or alkoxyl group) (Table 4). The structure of **5a** was further confirmed by x-ray diffraction (Fig. 2).

Although the detailed mechanisms of these reactions have not been clarified, the formation of coumarin derivatives **3**, **4**, and **5** could be explained by a possible mechanism as presented in Scheme 4. The Knoevenagel condensation of salicylaldehyde and 4-hydroxycoumarin may occur to generate (*E*)-3-(2-hydroxy benzylidene)-3*H*-chromene-2,4-dione **4** first, and then another 4-hydroxycoumarin attacks **4** to produce bis-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-(2-hydrophenyl) methane **I**. In the ionic liquid, the intramolecular nucleophilic addition between the hydroxyl

Table 3. Reaction of salicylaldehyde **1** and 4-hydroxycoumarin **2** in water catalyzed by TEBAC[a]

Entry	R	Products	Time (h)	Yields (%)[b]
1	H	**4a**	12	76
2	5-Cl	**4b**	10	78
3	5-Br	**4c**	14	87
4	5-Me	**4d**	18	74
5	4-OMe	**4e**	18	73
6	5,6-$(CH{=}CH)_2$-	**4f**	16	80
7	3,5-Cl_2	**4g**	12	78
8	3,5-$(CMe_3)_2$	**4h**	18	75

[a]Reagents and conditions: **1** (1 mmol), **2** (0.162 g, 1 mmol), TEBAC (0.023 g, 0.1 mmol), water (10 mL).
[b]Isolated yields.



Scheme 3. Reaction of salicylaldehyde and 4-hydroxycoumarin in ionic liquid.

Table 4. Reaction of salicylaldehyde **1** and 4-hydroxycoumarin **2** in ionic liquid[a][17]

Entry	R	Products	Time/h	Yields/%[b]
1	H	**5a**	8	86
2	5-Cl	**5b**	6	84
3	5-Br	**5c**	10	89
4	5-NO_2	**5d**	6	78
5	3,5-Cl_2	**5e**	6	92
6	3,5-Br_2	**5f**	6	90
7	5-Me	**5g**	12	82
8	4-OMe	**5h**	10	85
9	5,6-(CH=CH)$_2$-	**5i**	10	81

[a]Reagents and conditions: salicylaldehyde **1** (1 mmol), **2** (0.324 g, 2 mmol), and [BMIM]Br (2 mL).
[b]Isolated yields.

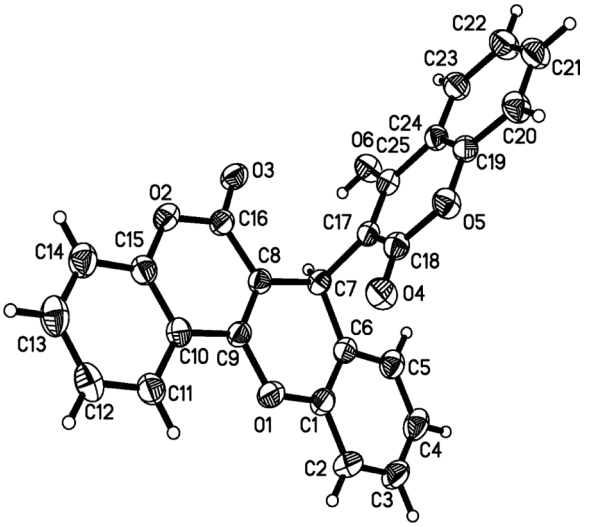
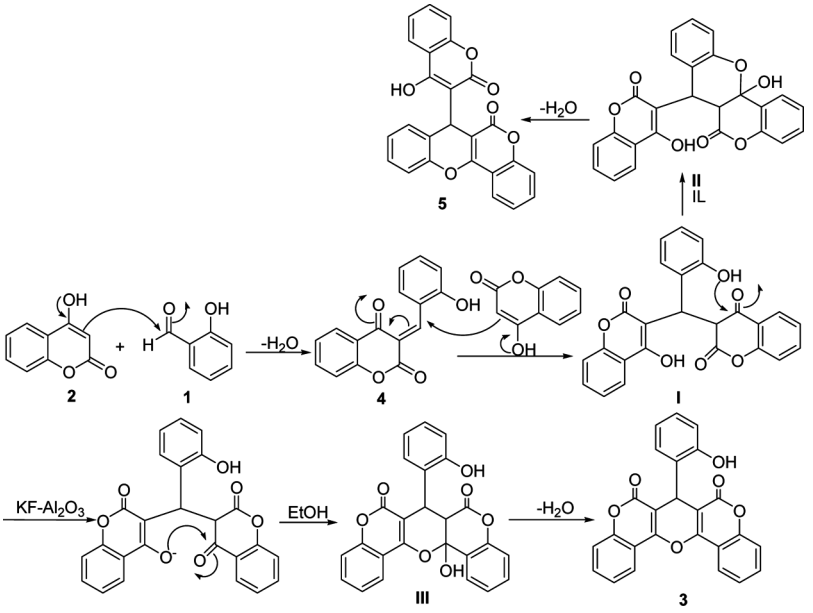


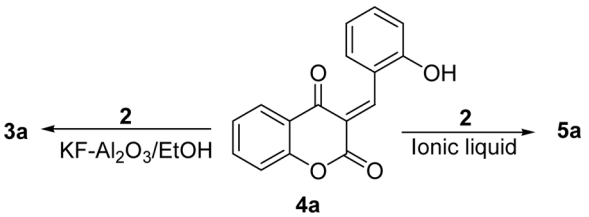
Figure 2. Crystal structure of the product **5a** with another molecule and two molecules of EtOH, with monohydration deleted for clarity.



Scheme 4. Possible mechanism of the formation of coumarin derivatives **3**, **4**, and **5**.

group of phenol and the carbonyl group in coumarin takes place to give **II**, which is followed by dehydration to yield the final product **5**. While in the KF-Al_2O_3-EtOH system, the enol of coumarin in the Michael addition product of **I** is changed into anion rather than the hydroxyl group of phenol, which then attacks another carbonyl group to give **III**, which finally loses one molecule of water to result in **3**.

To gain more insight into the reaction mechanism, we performed the reaction of (*E*)-3-(2-hydroxybenzylidene)-3*H*-chromene-2,4-dione **4a** and 4-hydroxycoumarin **2** in ionic liquid and KF-Al_2O_3-EtOH, respectively. To our delight, the designed reaction proceeded smoothly to give 9-(2-hydroxylphenyl)-9*H*-dibenzo[*c,h*]-2,7,10-tioxanthene-1,8-dione **3a** and 6*H*,7*H*-7-(4-hydroxy-3-coumaranyl)[1]benzopyrano [4,3-*b*] [1]benzopyran-6-one **5a** in good yields (Scheme 5). This result may indicate that the Michael addition takes place in these reactions.



Scheme 5. Reaction of (*E*)-3-(2-hydroxybenzylidene)-3*H*-chromene-2,4-dione, 4-hydroxycoumarin in KF-Al_2O_3-EtOH and ionic liquid.

CONCLUSION

In conclusion, we controlled the selectivity of the interesting reactions of salicylaldehydes and 4-hydroxycoumarin in TEBAC-H_2O, ionic liquid, or KF-Al_2O_3-EtOH systems, respectively, resulting in (*E*)-3-arylidene-3H-chromene-2,4-dione derivatives, 6*H*,7*H*-7-(4-hydroxy-3-coumaranyl)[1]benzopyrano[4,3-*b*][1] benzopyran-6-one derivatives, and 2,7,10-trioxaanthracene-1,8-dione derivatives, respectively. The features of this procedure are mild reaction conditions, good to excellent yields, and operational simplicity.

EXPERIMENTAL

Melting points were determined in open capillaries and are uncorrected. Infrared (IR) spectra were recorded on a Tensor 27 spectrometer in KBr pellets. ^{1}H NMR spectra were obtained from a solution in dimethylsulfoxide (DMSO-d_6) or $CDCl_3$ with Me_4Si as internal standard using a Bruker 400 spectrometer. High-resolution mass spectrometry (HRMS) was carried out using a Bruker MicroTOF-Q-MS analyzer.

General Procedure for the Syntheses of 2,7,10-Trioxaanthracene-1,8-dione Derivatives

A dry 100-mL flask was charged with salicylaldehyde **1** (1 mmol), 4-hydroxycoumarin **2** (0.324 g, 2 mmol), KF/Al_2O_3 (0.102 g), and EtOH (10 mL). The mixture was stirred at 80 °C for 10–16 h. After being cooled to room temperature, the solid material was filtered off, and the crude product was purified by recrystallization from dimethylformamide (DMF) and water to give **3**.

Selected Data

9-(2-Hydroxylphenyl)-9*H*-dibenzo[*c,h*]-2,7,10-tioxanthene-1,8-dione 3a. Mp 230–232 °C. IR (KBr): 3418, 1661, 1608, 1556, 1453, 1404, 1278, 1244, 1184, 1109, 1048, 948, 905, 862, 817, 758 cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): 6.15 (s, 1H, CH), 6.58–6.62 (m, 2H, ArH), 6.88–6.91 (m, 1H, ArH), 7.13 (d, $J = 7.6$ Hz, 1H, ArH), 7.20–7.23 (m, 4H, ArH), 7.45–7.49 (m, 2H, ArH), 7.79–7.81 (m, 2H, ArH). HRMS (ESI, m/z): calcd for $C_{25}H_{14}NaO_6$ ($M + Na^+$) 433.0688; found 433.0688.

9-(2-Hydroxyl-5-chlorophenyl)-9*H*-dibenzo[*c,h*]-2,7,10-tioxanthene-1,8-dione 3b. Mp 228–230 °C. IR (KBr): 3077, 1662, 1608, 1557, 1410, 1273, 1184, 1113, 1044, 913, 818, 761 cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): 6.13 (s, 1H, CH), 6.60 (d, $J = 8.4$ Hz, 1H, ArH), 6.95 (dd, $J = 8.4$ Hz, $J' = 2.4$ Hz 1H, ArH), 7.06 (d, $J = 2.4$ Hz, 1H, ArH), 7.21–7.24 (m, 4H, ArH), 7.47–7.50 (m, 2H, ArH), 7.81–7.83 (m, 2H, ArH). HRMS (ESI, m/z): calcd. for $C_{25}H_{13}ClO_6Na$ ($M + Na^+$) 467.0298; found 467.0262.

9-(2-Hydroxyl-5-bromophenyl)-9*H*-dibenzo[*c,h*]-2,7,10-tioxanthene-1,8-dione 3c. Mp 228–230 °C. IR (KBr): 3463, 1670, 1607, 1559, 1475, 1407, 1273, 1184, 1111, 1042, 909, 817, 762 cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): 6.13

(s, 1H, CH), 6.57 (d, $J = 8.4$ Hz, 1H, ArH), 7.07 (dd, $J = 8.4$ Hz, $J' = 2.0$ Hz, 1H, ArH), 7.19–7.24 (m, 5H, ArH), 7.47–7.51 (m, 2H, ArH), 7.82 (d, $J = 8.0$ Hz, 2H, ArH). ^{13}C NMR (DMSO-d_6, 100 MHz): 33.0, 103.1, 109.3, 115.3, 116.7, 120.1, 122.8, 124.0, 128.6, 130.6, 131.4, 132.0, 152.4, 154.5, 164.0, 167.2. HRMS (ESI, m/z): calcd. for $C_{25}H_{13}BrO_6Na$ ($M + Na^+$) 510.9793; found 510.9764.

9-(2-Hydroxyl-5-nitrophenyl)-9*H*-dibenzo[*c,h*]-2,7,10-tioxanthene-1,8-dione 3d. Mp 251–253 °C. IR (KBr): 3567, 1670, 1607, 1558, 1497, 1431, 1405, 1338, 1284, 1240, 1184, 1109, 1085, 1043, 931, 898, 763 cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): 6.20 (s, 1H, CH), 6.79 (d, $J = 8.8$ Hz, 1H, ArH) 7.22–7.26 (m, 4H, ArH), 7.48–7.52 (m, 2H, ArH), 7.82 (d, $J = 7.2$ Hz, 2H, ArH), 7.93 (dd, $J = 8.8$ Hz, $J' = 2.8$ Hz, 1H, ArH), 8.04 (d, $J = 2.0$ Hz, 1H, ArH). HRMS (ESI, m/z): calcd. for $C_{25}H_{13}NO_6Na$ ($M + Na^+$) 478.0539; found 478.0523.

9-(2-Hydroxyl-3,5-dichlorophenyl)-9*H*-dibenzo[*c,h*]-2,7,10-tioxanthene-1,8-dione 3e. Mp 238–240 °C. IR (KBr): 3410, 1664, 1607, 1541, 1458, 1407, 1330, 1274, 1182, 1110, 1047, 917, 853, 800, 762 cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): 6.23 (s, 1H, CH), 7.08 (s, 1H, ArH), 7.22–7.25 (m, 5H, ArH), 7.48–7.52 (m, 2H, ArH), 7.82 (d, $J = 8.0$ Hz, 2H, ArH). HRMS (ESI, m/z): calcd. for $C_{25}H_{12}Cl_2O_6Na$ ($M + Na^+$) 500.9909; found 500.9890.

9-(2-Hydroxyl-3,5-dibromophenyl)-9*H*-dibenzo[*c,h*]-2,7,10-tioxanthene-1,8-dione 3f. Mp 250–252 °C. IR (KBr): 3205, 1656, 1604, 1540, 1453, 1402, 1332, 1274, 1250, 1232, 1181, 1137, 1111, 1045, 913, 856, 798, 767 cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): 6.25 (s, 1H, CH), 7.22–7.25 (m, 5H, ArH), 7.46–7.52 (m, 3H, ArH), 7.83 (d, $J = 8.0$ Hz, 2H, ArH). HRMS (ESI, m/z): calcd. for $C_{25}H_{12}Br_2O_6Na$ ($M + Na^+$) 588.8898; found 590.8866.

9-(2-Hydroxyl-4-methoxxyphenyl)-9*H*-dibenzo[*c,h*]-2,7,10-tioxanthene-1,8-dione 3g. Mp 194–196 °C. IR (KBr): 3446, 1669, 1607, 1558, 1428, 1404, 1374, 1289, 1202, 1110, 1040, 950, 904, 839, 762 cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): 3.62 (s, 3H, CH_3O), 6.09 (s, 1H, CH), 6.19–6.21 (m, 2H, ArH), 7.02 (d, $J = 8.0$ Hz, 1H, ArH), 7.19–7.22 (m, 4H, ArH), 7.44–7.48 (m, 2H, ArH), 7.80 (d, $J = 7.6$ Hz, 2H, ArH). HRMS (ESI, m/z): calcd. for $C_{26}H_{16}O_7Na$ ($M + Na^+$) 463.0794; found 463.0774.

General Procedure for the Syntheses of (E)-3-(2-Hydroxybenzylidene)-3H-chromene-2,4-dione Derivatives 4

A 50-mL flask was charged with salicylaldehyde **1** (1.0 mmol), 4-hydroxycoumarin 2 (0.162 g, 1.0 mmol), TEBAC (0.1 mmol, 0.023 g), and water (10 mL). The reaction mixture was stirred at 90 °C for 10–18 h; the solid was isolated by filtration. The filtrate, together with TEBAC, could be used directly for the same reaction. The crude products were washed with water and purified by recrystallization from EtOH to give **4**.

Selected Data

(*E*)-3-(2-Hydroxybenzylidene)-3*H*-chromene-2,4-dione 4a. Mp 176–177 °C (lit.[12] 174–175 °C). IR (KBr): 3463, 1718, 1628, 1607, 1592, 1568, 1456, 1440, 1346, 1313, 1277, 1243, 1215, 1173, 1123, 1039, 941, 810, 767, 745 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz): 6.90–6.97 (m, 2H, ArH), 7.40–7.50 (m, 3H, ArH), 7.67–7.74 (m, 2H, ArH), 7.87 (d, $J = 7.6$ Hz, 1H, ArH), 8.32 (s, 1H, CH), 10.77 (s, 1H, OH). HRMS (ESI, m/z): calcd. for $C_{16}H_{10}O_4Na$ ($M + Na^+$) 289.0477; found 289.0477.

(*E*)-3-(2-Hydroxy-5-chlorobenzylidene)-3*H*-chromene-2,4-dione 4b. Mp 188–190 °C. IR (KBr): 3449, 1719, 1627, 1608, 1568, 1479, 1456, 1354, 1340, 1307, 1239, 1211, 1168, 1151, 1046, 946, 930, 817, 733, 707. ^1H NMR (DMSO-d_6, 400 MHz): 6.91–6.97 (m, 2H, ArH), 7.41–7.54 (m, 2H, ArH), 7.69–7.76 (m, 2H, ArH), 7.80 (s, 1H, ArH), 8.28 (s, 1H, ArH), 10.73 (s, 1H, OH). HRMS (ESI, m/z): calcd. for $C_{16}H_9ClO_4Na$ ($M + Na^+$) 323.0087; found 323.0083.

(*E*)-3-(2-Hydroxy-5-bromobenzylidene)-3*H*-chromene-2,4-dione 4c. Mp 186–188 °C. IR (KBr): 3423, 3041, 1680, 1719, 1628, 1606, 1562, 1484, 1474, 1450, 1411, 1354, 1340, 1308, 1269, 1239, 1211, 1173, 1152, 1045, 1032, 944, 928, 815, 772, 751, 705 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz): 6.90–6.97 (m, 2H, ArH), 7.47–7.53 (m, 2H, ArH), 7.69 (d, $J = 7.6$ Hz, 1H, ArH), 7.75 (d, $J = 9.2$ Hz, 1H, ArH), 7.99 (s, 1H, ArH), 8.27 (s, 1H, CH), 10.80 (s, 1H, OH). HRMS (ESI, m/z): calcd. for $C_{16}H_9BrO_4Na$ ($M + Na^+$) 366.9582; found 366.9582.

(*E*)-3-(2-Hydroxy-5-methylbenzylidene)-3*Hh*-chromene-2,4-dione 4d. Mp 186–188 °C. IR (KBr): 3066, 1718, 1625, 1597, 1573, 1542, 1479, 1457, 1360, 1330, 1306, 1277, 1242, 1186, 932, 831, 819, 768, 722 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz): 2.38 (s, 3H, CH_3), 6.89–6.96 (m, 2H, ArH), 7.37 (d, $J = 8.4$ Hz, 1H, ArH), 7.46–7.54 (m, 2H, ArH), 7.65–7.67 (m, 2H, ArH), 8.25 (s, 1H, CH), 10.76 (s, 1H, OH). HRMS (ESI, m/z): calcd. for $C_{17}H_{12}O_4Na$ ($M + Na^+$) 303.0633; found 303.0633.

(*E*)-3-(2-Hydroxy-4-methoxybenzylidene)-3*H*-chromene-2,4-dione 4e. Mp 198–200 °C. IR (KBr): 3463, 1717, 1620, 1599, 1560, 1508, 1489, 1446, 1376, 1340, 1311, 1283, 1238, 1206, 1160, 1122, 1027, 857, 822, 757 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz): 3.89 (s, 3H, CH_3O), 6.89–6.95 (m, 2H, ArH), 7.02 (dd, $J = 8.8$ Hz, $J' = 2.0$ Hz, 1H, ArH), 7.06 (s, 1H, ArH), 7.44–7.47 (m, 1H, ArH), 7.61 (d, $J = 7.6$ Hz, 1H, ArH), 7.80 (d, $J = 8.4$ Hz, 1H, ArH), 8.31 (s, 1H, ArH), 10.66 (s, 1H, OH). HRMS (ESI, m/z): calcd. for $C_{17}H_{12}O_5Na$ ($M + Na^+$) 319.0582; found 319.0582.

(*E*)-3-(2-Hydroxy-1-naphthalenylidene)-3*H*-chromene-2,4-dione 4f. Mp 252–254 °C. IR (KBr): 3403, 2062, 1708, 1625, 1620, 1569, 1519, 1488, 1439, 1396, 1341, 1327, 1307, 1288, 1252, 1216, 1181, 1094, 995, 951, 929, 819, 783, 748 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz): 6.93–6.99 (m, 2H, ArH), 7.48–7.52 (m, 1H, ArH), 7.64–7.68 (m, 2H, ArH), 7.74–7.77 (m, 2H, ArH), 8.10 (d, $J = 8.0$ Hz, 1H, ArH), 8.31 (d, $J = 9.2$ Hz, 1H, ArH), 8.62 (d, $J = 8.4$ Hz, 1H, ArH), 9.11 (s, 1H, CH), 10.83 (s, 1H, OH). HRMS (ESI, m/z): calcd. for $C_{20}H_{12}O_4Na$ ($M + Na^+$) 339.0633; found 339.0632.

(*E*)-3-(2-Hydroxy-3,5-dichlorobenzylidene)-3*H*-chromene-2,4-dione 4g. Mp 192–194 °C. IR (KBr): 3435, 3074, 1727, 1627, 1604, 1561, 1483, 1454, 1362, 1336, 1307, 1242, 1216, 1149, 1033, 988, 944, 926, 869, 841, 816, 766, 719 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz): 6.91–6.98 (m, 2H, ArH), 7.48–7.52 (m, 1H, ArH), 7.72 (dd, J = 8.0 Hz, J' = 1.6 Hz, 1H ArH), 7.99 (d, J = 2.4 Hz, 1H, ArH), 8.05 (d, J = 2.4 Hz, 1H, ArH), 8.30 (s, 1H, ArH), 10.79 (s, 1H, OH). HRMS (ESI, m/z): calcd. for $C_{16}H_9Cl_2O_4$ ($M + H^+$) 334.9878; found 334.9878.

(*E*)-3-(2-Hydroxy-3,5-di-*t*-butylbenzylidene)-3*H*-chromene-2,4-dione 4h. Mp 225–227 °C. ^1H NMR (DMSO-d_6, 400 MHz): 1.33 (s, 9H, $3CH_3$), 1.48 (s, 9H, $3CH_3$) 6.93–6.95(m, 2H, ArH), 7.47–7.51 (m, 1H, ArH), 7.64–7.69 (m, 2H, ArH), 7.76 (s, 1H, ArH), 8.32 (s, 1H, CH), 10.68 (s, 1H., OH). IR (KBr): 3012, 2964, 2871, 1714, 1632, 1603, 1580, 1444, 1398, 1370, 1341, 1306, 1272, 1217, 1172, 1058, 1032, 999, 960, 935, 907, 898, 873, 815, 762, 739 cm^{-1}. HRMS (ESI, m/z): calcd. for $C_{24}H_{27}O_4$ ($M + H^+$) 379.1909; found 379.1890.

General Procedure for the Syntheses of 6H,7H-7-(4-Hydroxy-3-coumaranyl)[1]benzopyrano[4,3-b][1]benzopyran-6-one Derivatives 5

A dry 50-mL flask was charged with salicylaldehyde (2.0 mmol), 4-hydroxycoumarin (0.324 g, 2.0 mmol), and ionic liquid of [$bmim^+$][Br^-] (2 mL). The reaction mixture was stirred at 90 °C for 6–12 h. Five mL water were then added to the mixture, and the solid was isolated by filtration. The water in the filtrate was removed by evaporation at reduced pressure, and the ionic liquid in could be recovered easily at 80 °C in a vacuum for 4 h. The crude yellow products were washed with water and purified by recrystallization from DMF to give **5**.

Selected Data

6*H*,7*H*-7-(4-Hydroxy-3-coumaranyl)[1]benzopyrano[4,3-*b*][1]benzopyran-6-one 5a. Mp 240–242 °C. IR (KBr): 2972, 1699, 1645, 1610, 1567, 1488, 1455, 1390, 1276, 1242, 1221, 1106, 1044, 979, 905, 866, 757 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz): 5.75 (s, 1H, CH), 7.13–7.17 (m, 1H, ArH), 7.21 (d, J = 7.2 Hz, 1H, ArH), 7.31–7.36 (m, 4H, ArH), 7.46 (d, J = 8.0 Hz, 1H, ArH), 7.49 (t, J = 8.0 Hz, 1H, ArH), 7.58–7.62 (m, 1H, ArH), 7.68–7.73 (m, 1H, ArH), 8.03–8.12 (m, 2H, ArH). HRMS (ESI, m/z): calcd. for $C_{25}H_{14}NaO_6$ ($M + Na^+$) 433.0688; found 433.0659.

9-Chloro-6*H*,7*H*-7-(4-hydroxy-3-coumaranyl)[1]benzopyrano[4,3-*b*][1]-benzopyran-6-one 5b. Mp > 300 °C. IR (KBr): 3269, 3051, 1709, 1671, 1643, 1631, 1608, 1572, 1496, 1479, 1454, 1393, 1303, 1244, 1220, 1183, 1166, 1110, 1070, 1058, 881, 833, 796, 760, 748 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz): 5.72 (s, 1H, CH), 7.18 (s, 1H, ArH), 7.32–7.51 (m, 6H, ArH), 7.60–7.64 (m, 1H, ArH), 7.69–7.73 (m, 1H, ArH), 8.03–8.11 (m, 2H, ArH). HRMS (ESI, m/z): calcd. for $C_{25}H_{13}ClO_6Na$ ($M + Na^+$) 467.0298; found 467.0293.

9-Bromo-6*H*,7*H*-7-(4-hydroxy-3-coumaranyl)[1]benzopyrano[4,3-*b*][1]-benzopyran-6-one 5c. Mp > 300 °C. IR (KBr): 3273, 3057, 1700, 1672, 1643, 1569, 1496, 1478, 1455, 1334, 1303, 1284, 1220, 1167, 1152, 1109, 1068, 985, 906, 879, 832, 797, 766, 748 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz): 5.72 (s, 1H, CH), 7.31–7.38 (m, 4H, ArH), 7.44–7.53 (m, 3H, ArH), 7.60–7.648 (m, 1H, ArH), 7.69–7.73 (m, 1H, ArH), 8.05–8.10 (m, 2H, ArH). HRMS (ESI, m/z): calcd. for $C_{25}H_{13}BrO_6Na$ ($M + Na^+$) 510.9793; found 510.9725.

9-Nitro-6*H*,7*H*-7-(4-hydroxy-3-coumaranyl)[1]benzopyrano[4,3-*b*][1]-benzopyran-6-one 5d. Mp > 300 °C. IR (KBr): 3309, 3072, 1703, 1670, 1646, 1629, 1609, 1523, 1496, 1455, 1392, 1337, 1286, 1243, 1218, 1185, 1111, 1090, 1059, 904, 848, 754 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz): 5.82 (s, 1H, CH), 7.22–7.26 (m, 4H, ArH), 7.32–7.57 (m, 4H, ArH), 7.60–7.64 (m, 2H, ArH), 7.71–7.28 (m, 1H, ArH), 8.02–8.08 (m, 2H, ArH), 8.14 (d, $J = 7.6$ Hz, 1H, ArH), 8.24 (dd, $J = 8.8$ Hz, $J' = 1.2$ Hz, 1H, ArH). HRMS (ESI, m/z): calcd. for $C_{25}H_{13}NO_8Na$ ($M + Na^+$) 478.0539; found 478.0514.

9,11-Dichloro-6*H*,7*H*-7-(4-hydroxy-3-coumaranyl)[1]benzopyrano[4,3-*b*]-[1]benzopyran-6-one 5e. Mp > 300 °C. IR (KBr): 3077, 1697, 1662, 1639, 1610, 1570, 1494, 1456, 1396, 1341, 1315, 1216, 1188, 1108, 1079, 1050, 953, 913, 860, 806, 759 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz): 5.71 (s, 1H, CH), 7.15 (s, 1H, ArH), 7.32–7.39 (m, 2H, ArH), 7.43–7.51 (m, 2H, ArH), 7.59–7.62 (m, 2H, ArH), 7.68–7.72 (m, 1H, ArH), 7.96–8.04 (m, 2H, ArH). HRMS (ESI, m/z): calcd. for $C_{25}H_{12}Cl_2O_6$ ($M + H^+$) 500.9909; found 500.9895.

11-Dibromo-6*H*,7*H*-7-(4-hydroxy-3-coumaranyl)[1]benzopyrano[4,3-*b*][1]-benzopyran-6-one 5f. Mp > 300 °C. IR (KBr): 3073, 1698, 1661, 1639, 1611, 1568, 1494, 1452, 1393, 1341, 1315, 1271, 1238, 1219, 1166, 1108, 1076, 1047, 941, 913, 914, 860, 804, 760, 731 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz): 5.72 (s, 1H, CH), 7.30–7.37 (m, 3H, ArH), 7.46 (d, $J = 8.0$ Hz, 1H, ArH), 7.50–7.54 (m, 1H, ArH), 7.60–7.63 (m, 1H, ArH), 7.70–7.74 (m, 1H, ArH), 7.86 (s, 1H, ArH), 8.01 (d, $J = 8.0$ Hz, 1H, ArH). ^{13}C NMR (DMSO-d_6, 100 MHz): 29.1, 111.1, 113.3, 116.1, 116.3, 116.6, 116.8, 122.2, 123.9, 124.0, 124.1, 124.8, 126.3, 130.4, 132.4, 132.8, 133.7, 145.5, 151.9, 152.3, 155.6, 159.9, 161.47, 161.52, 161.54. HRMS (ESI, m/z): calcd. for $C_{25}H_{12}Br_2O_6Na$ ($M + Na^+$) 588.8898; found 588.8854.

9-Methyl-6*H*,7*H*-7-(4-hydroxy-3-coumaranyl)[1]benzopyrano[4,3-*b*][1]-benzopyran-6-one 5g. Mp 291–293 °C. ^1H NMR (DMSO-d_6, 400 MHz): 2.21 (s, 3H, CH_3), 5.71 (s, 1H, CH), 7.10 (d, $J = 8.0$ Hz, 1H, ArH), 7.22 (d, $J = 8.0$ Hz, 1H, ArH), 7.31–7.37 (m, 2H, ArH), 7.43–7.49 (m, 2H, ArH), 7.58–7.62 (m, 1H, ArH), 7.66–7.70 (m, 1H, ArH), 8.07 (d, $J = 8.0$ Hz, 1H, ArH). IR (KBr): 1715, 1667, 1632, 1608, 1574, 1490, 1454, 1394, 1304, 1215, 1174, 1149, 1108, 1074, 1055, 905, 883, 832, 798, 766, 747 cm^{-1}. HRMS (ESI, m/z): calcd. for $C_{26}H_{16}O_6Na$ ($M + Na^+$) 447.0845; found 447.0826.

10-Methoxy-6*H*,7*H*-7-(4-hydroxy-3-coumaranyl)[1]benzopyrano[4,3-*b*][1]-benzopyran-6-one 5h. Mp > 300 °C (lit.[12]: 310–304 °C). IR (KBr): 3068, 1717, 1673, 1650, 1624, 1586, 1568, 1494, 1455, 1387, 1330, 1277, 1201, 1166, 1145, 1108, 1068, 1032, 976, 947, 902, 829, 789, 755 cm^{-1}. ^1H NMR (DMSO-d_6,

400 MHz): 3.79 (s, 3H, CH_3O), 5.66 (s, 1H, CH), 6.74 (dd, $J = 8.4$ Hz, $J' = 1.6$ Hz, 1H, ArH), 6.95 (d, $J = 1.6$ Hz, 1H, ArH), 7.09 (d, $J = 8.4$ Hz, 1H, ArH), 7.04–7.37 (m, 2H, ArH), 7.44–7.51 (m, 2H, ArH), 7.58–7.62 (m, 1H, ArH), 7.68–7.72 (m, 1H, ArH), 8.06–8.12 (m, 2H, ArH). HRMS (ESI, m/z): calcd. for $C_{26}H_{16}O_7Na$ ($M + Na^+$) 463.0794; found 463.0796.

6*h*,7*H*-7-(4-hydroxy-3-coumaranyl)[1]-benzo[*f*]benzopyrano[4,3-*b*][1]-benzopyran-6-one 5i. Mp > 300 °C. IR (KBr): 2930, 1719, 1694, 1653, 1607, 1568, 1490, 1455, 1385, 1311, 1289, 1229, 1213, 1106, 1051, 1030, 929, 859, 819, 753 cm^{-1}. ^1H NMR (DMSO-d_6, 400 MHz): 6.20 (s, 1H, CH), 7.25–7.61 (m, 8H, ArH), 7.68–7.72 (m, 1H, ArH), 7.92–7.98 (m, 3H, ArH), 8.12–8.17 (m, 2H, ArH). HRMS (ESI, m/z): calcd. for $C_{29}H_{16}O_6Na$ ($M + Na^+$) 483.0845. found 483.0860.

Crystal Data for 3d

$C_{28}H_{20}N_2O_9$; $M = 528.46$, pale yellow block crystals, $0.26 \times 0.22 \times 0.20$ mm, triclinic, space group P-1, $a = 10.210$ (3), $b = 10.698$ (4), $c = 12.522$ (4) Å, $\alpha = 92.214$ (6), $\beta = 113.751$ (5), $\gamma = 105.040$ (5)°, $V = 1193.0$ (7) Å^3, $Z = 2$, $Dc = 1.471$ gcm^{-3}. F (000) = 548, μ (MoKα) = 0.112 mm^{-1}. Intensity data were collected on a charge coupled device (CCD) area detector with graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å) using phi and omega scan modes with $1.80° < \theta < 25.02°$; 4178 unique reflections were measured and 2667 reflections with $I > 2\sigma$ (I) were used in the refinement. Structure was solved by direct methods and expanded using Fourier techniques. The final cycle of full-matrix least squares technique was to $R = 0.0444$ and $wR = 0.1373$.

Crystal Data for 5a

$C_{54}H_{42}O_{15}$; $M = 930.88$, pale yellow block crystals, $0.259 \times 0.184 \times 0.101$ mm, monoclinic, space group P2(1)/c, $a = 18.6254$ (3), $b = 15.2692$ (2), $c = 17.7026$ (2) Å, $\beta = 115.534$ (1)°, $V = 4542.80$ (11) Å^3, $Z = 2$, $Dc = 1.361$ gcm^{-3}. F (000) = 1944, μ (MoKα) = 0.100 mm^{-1}. Intensity data were collected on a CCD area detector with graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å) using phi and omega scans mode with $1.21° < \theta < 27.56°$; 10426 unique reflections were measured and 4775 reflections with $I > 2\sigma$ (I) were used in the refinement. Structure was solved by direct methods and expanded using Fourier techniques. The final cycle of full-matrix least squares technique was to $R = 0.0568$ and $wR = 0.1406$.

ACKNOWLEDGMENTS

We are grateful to the National Natural Science Foundation of China (20802061), the Natural Science Foundation (08KJD150019), and the Qing Lan Project (08QLT001) of the Jiangsu Education Committee for financial support.

REFERENCES

1. (a) Erkkila, A.; Majander, I.; Pihko, P. M. Iminium catalysis. *Chem. Rev.* **2007**, *107*, 5416–5470; (b) Laschat, S.; Becheanu, A.; Bell, T.; Baro, A. Regioselectivity, stereoselectivity, and catalysis in intermolecular Pauson–Khand reactions: Teaching an old dog new tricks.

Synlett **2005**, 2547–2570; (c) Dirwald, F. Z. Solvent-controlled selectivity in the synthesis of five-membered carbocycles from carbene complexes. *Angew. Chem. Int. Ed.* **2003**, *42*, 1332–1334; (d) Beak, P.; Anderson, D. R.; Curtis, M. D.; Laumer, J. M.; Pippel, D. J.; Weisenburger, G. A. Dynamic thermodynamic resolution: Control of enantioselectivity through diastereomeric equilibration. *Acc. Chem. Res.* **2000**, *33*, 715–727; (e) Beckwith, A. L. J. Regio-selectivity and stereo-selectivity in radical reactions. *Tetrahedron* **1981**, *37*, 3073–3100.

2. (a) Vijjay, N. C.; Rajesh, A. U.; Vinod, S.; Bindu, A. R.; Sreekanth, J. S.; Lakshmi, B. Strategies for heterocyclic construction via novel multicomponent reactions based on isocyanides and nucleophilic carbenes. *Acc. Chem. Res.* **2003**, *36*, 899–907; (b) Tietze, L. F. Domino reactions in organic synthesis. *Chem. Rev.* **1996**, *96*, 115–136; (c) Wang, X. S.; Li, Q.; Yao, C. S.; Tu, S. J. An efficient method for the synthesis of benzo[*f*]quinoline and benzo[*a*]phenanthridine derivatives catalyzed by iodine by a three-component reaction of arenecarbaldehyde, naphthalen-2-amine, and cyclic ketone. *Eur. J. Org. Chem.* **2008**, 3513–3518; (d) Padwa, A.; Bur, S. K. The domino way to heterocycles. *Tetrahedron* **2007**, *63*, 5341–5378; (e) Nicolaou, K. C.; Edmonds, D. J.; Bulger, P. G. Cascade reactions in total synthesis. *Angew. Chem. Int. Ed.* **2006**, *45*, 7134–7186; (f) Weber, L.; Illgen, K.; Almstetter, M. Discovery of new multi component reactions with combinatorial methods. *Synlett* **1999**, 366–374.
3. (a) Heravi, M. M.; Baghernejad, B.; Oskooie, H. A.; Hekmatshoar, R. A novel and facile synthesis of 2-(cyclohexylamino)-6,7-dihydro-3-aryl-1*H*-indole-4(5*H*)-ones via a one-pot multi-component reaction. *Tetrahedron Lett.* **2008**, *49*, 6101–6103; (b) Willy, B.; Müller, T. J. J. Regioselective three-component synthesis of highly fluorescent 1,3,5-trisubstituted pyrazoles. *Eur. J. Org. Chem.* **2008**, 4157–4168; (c) Umkehrer, M.; Kolb, J.; Burdack, C.; Hiller, W. 2,4,5-Trisubstituted thiazole building blocks by a novel multi-component reaction. *Synlett* **2005**, 79–82.
4. (a) Domling, A.; Ugi, I. Multicomponent reactions with isocyanides. *Angew. Chem. Int. Ed.* **2000**, *39*, 3168–3210; (b) Simon, C.; Constantieux, T.; Rodriguez, J. Utilisation of 1,3-dicarbonyl derivatives in multicomponent reactions. *Eur. J. Org. Chem.* **2004**, 4957–4980.
5. (a) Kostova, I.; Mojzis, J. Biologically active coumarins as inhibitors of HIV-1. *Future HIV Therapy* **2007**, *1*, 315–329; (b) Chiang, C.-C.; Mouscadet, J.-F.; Tsai, H.-J.; Liu, C.-T.; Hsu, L.-Y. Synthesis and HIV-1 integrase inhibition of novel bis- or tetra-coumarin analogues. *Chem. Pharm. Bull.* **2007**, *55*, 1740–1743; (c) Al-Soud, Y. A.; Al-Masoudi, I. A.; Saeed, B.; Beifuss, U.; Al-Masoudi, N. A. Synthesis of new 1*H*-1,2,4-triazolylcoumarins and their antitumor and anti-HIV activities. *Chem. Heterocycl. Comp.* **2006**, *42*, 583–590; (d) Al-Masoudi, N. A.; Al-Masoudi, I. A.; Ali, I. A. I.; Al-Soud, Y. A.; Saeed, B.; La Colla, P. Amino acid derivarives, part I: Synthesis, antiviral, and antitumor evaluation of new α-amino acid esters bearing coumarin side chain. *Acta Pharm.* **2006**, *56*, 175–188.
6. Lee, S.; Sivakumar, K.; Shin, W.-S.; Xie, F.; Wang, Q. Synthesis and anti-angiogenesis activity of coumarin derivatives. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 4596–4599.
7. Creaven, B. S.; Egan, D. A.; Kavanagh, K.; McCann, M.; Noble, A.; Thati, B.; Walsh, M. Synthesis, characterization, and antimicrobial activity of a series of substituted coumarin-3-carboxylato silver(I) complexes. *Inorgan. Chim. Acta* **2006**, *359*, 3976–3984.
8. Garazd, Y. L.; Kornienko, E. M.; Maloshtan, L. N.; Garazd, M. M.; Khilya, V. P. Modified coumarins, 17: Synthesis and anticoagulant activity of 3,4-cycloannelated coumarin D-glycopyranosides. *Chem. Nat. Comp.* **2005**, *41*, 508–512.
9. Figueroa, M.; Rivero-Cruz, I.; Rivero-Cruz, B.; Bye, R.; Navarrete, A.; Mata, R. Constituents, biological activities, and quality control parameters of the crude extract and essential oil from *Arracacia tolucensis* var. multifida. *J. Ethnopharm.* **2007**, *113*, 125–131; (b) Nawrot-Modranka, J.; Nawrot, E.; Graczyk, J. In vivo antitumor, in vitro

antibacterial activity, and alkylating properties of phosphorohydrazine derivatives of coumarin and chromone. *Eur. J. Med. Chem.* **2006**, *41*, 1301–1309.

10. Kontogiorgis, C. A.; Hadjipavlou-Litina, D. J. Synthesis and anti-inflammatory activity of coumarin derivatives. *J. Med. Chem.* **2005**, *48*, 6400–6408.
11. (a) Wang, X. S.; Wu, J. R.; Li, Q.; Yao, C. S.; Tu, S. J. A novel and green method for the synthesis of indeno[2,1-c]pyridine derivatives in ionic liquid catalyzed by malononitrile. *Synlett* **2008**, 1185–1188; (b) Wang, X. S.; Li, Q.; Wu, J. R.; Li, Y. L.; Yao, C. S.; Tu, S. J. An efficient and highly selective method for the synthesis of 3-arylbenzoquinoline derivatives catalyzed by iodine via three-component reactions. *Synthesis* **2008**, 1902–1910; (c) Wang, X. S.; Zhang, M. M.; Li, Q.; Yao, C. S.; Tu, S. J. An unexpected ring-opening of 2-pyrone ring in the synthesis of 1-arylbenzo[*f*]quinoline-2-carboxmide derivatives in aqueous media catalyzed by TEBAC. *Synlett* **2007**, 3141–3144; (d) Wang, X. S.; Zhang, M. M.; Jiang, H.; Shi, D. Q.; Tu, S. J.; Wei, X. Y.; Zong, Z. M. An improved and benign synthesis of 9,10-diarylacridin-1,8-dione and indenoquinoline derivatives from 3-arylamino-5,5-dimethylcyclohex-2-enone, arylaldehyde, and 1,3-dicarbonyl compound in ionic liquid medium. *Synthesis* **2006**, 4187–4199.
12. Sullivan, W. R.; Huebner, C. F.; Stahmann, M. A.; Link, K. P. Studies on 4-hydroxycoumarins, ii: the condensation of aldehydes with 4-hydroxycoumarins. *J. Am. Chem. Soc.* **1943**, *65*, 2288–2291.