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Regioselective Bismuth-Catalyzed Synthesis of Pyranocoumarins and Furocoumarins from 4-Hydroxycoumarins and Propargyl Alcohols

Jaehyun Kim,[†] Kooyeon Lee,[†,*] and Phil Ho Lee[‡,*]

[†]*Department of Bio-Health Technology, Kangwon National University, Chuncheon 24341, Republic of Korea*
[‡]*Department of Chemistry, Kangwon National University, Chuncheon 24341, Republic of Korea.*
**E-mails: lky@kangwon.ac.kr, phlee@kangwon.ac.kr*
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An efficient method for the bismuth-catalyzed regioselective synthesis of pyranocoumarins and furocoumarins has been developed from the reaction of 4-hydroxycoumarins with propargyl alcohols. The reaction proceeds through sequential propargylation and intramolecular cyclization reactions catalyzed by bismuth(III) triflate.

Keywords: Bismuth, Catalysis, Pyranocoumarin, Furocoumarin, Regioselectivity

Introduction

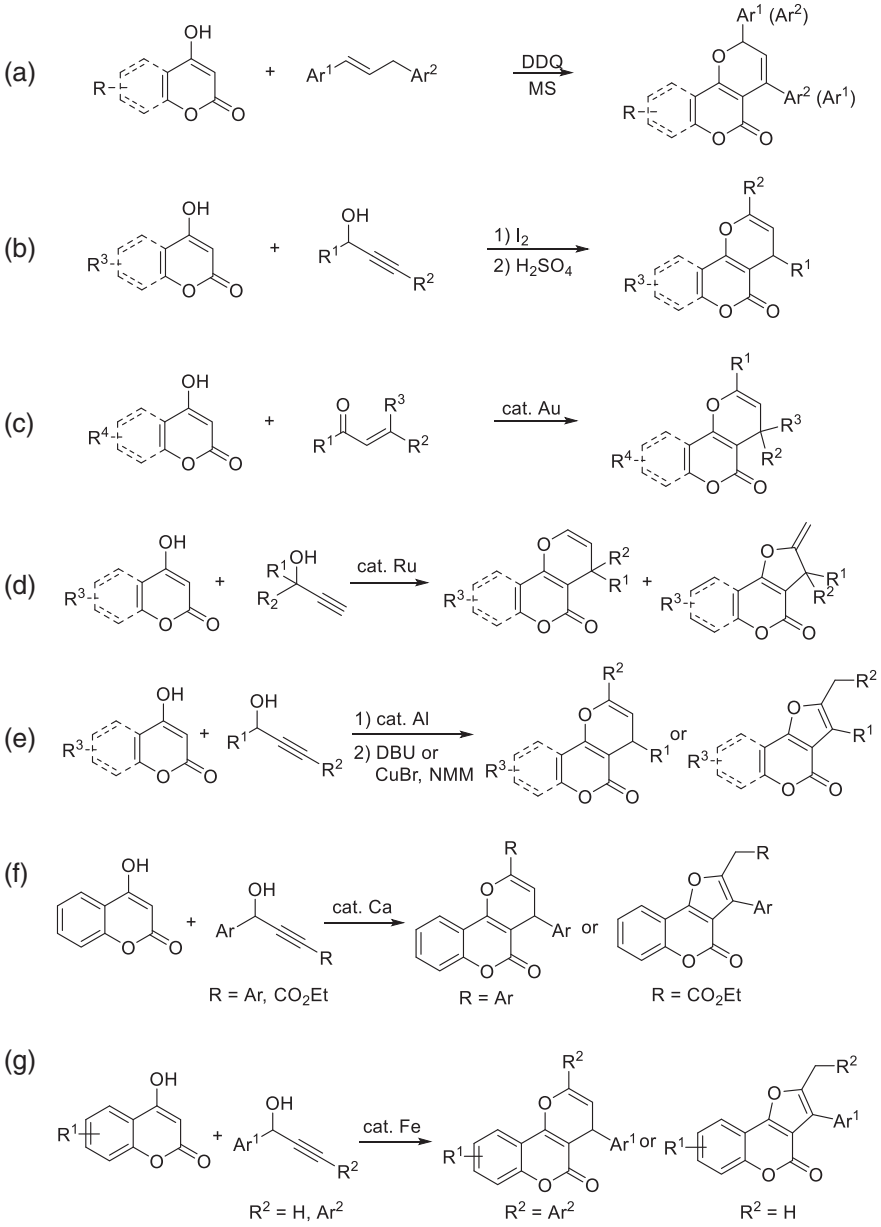
Pyranocoumarins and furocoumarins are important privileged scaffolds among naturally occurring oxygen-containing cyclic compounds and have been shown to have a wide range of bioactivities such as antifungal, anticancer, anti-HIV, anti-inflammatory, antioxidant, antiproliferative, antibacterial, and insecticidal activities.[1] Recently, these compounds have received considerable attention in medicinal chemistry for the treatment of skin disorders.[2] For example, neo-tanshinlactone is a kind of furocoumarin that was isolated from the rhizome of Salvia miltiorrhiza Bunge. The agent has shown potent and selective activity against breast cancer.[3] For this reason, many chemists are interested in the development of synthetic methods for pyranocoumarins and furocoumarins (Scheme 1).[4,5] Typically, pyranocoumarins are prepared from the reaction of 4-hydroxycoumarins with various electrophiles including 1,3-diarylallylic compounds (*a*),[6a] propargyl alcohols (*b*),[6b] and α,β-unsaturated aldehydes or ketones (*c*),[6c] as well as multicomponent reactions.[7] Additionally, Ru-catalyzed reaction of 4-hydroxycoumarins with propargyl alcohols has been shown to produce pyranocoumarins (*d*).[6d] In 2015, Bezuidenhoudt and co-workers reported a catalytic system involving $Al(OTf)_3$ and organocatalysts (DBU, NMM) that could promote coupling of 4-hydroxycoumarins with activated propargyl alcohols for the synthesis of either pyranocoumarins or furocoumarins (*e*).[6e] Recently, Yaragorla and co-workers reported an efficient regioselective synthesis of fused and substituted furans using $Ca(OTf)_2$ as the catalyst (*f*).[6f] More recently, Ren and Wang developed regioselective access to structurally diverse coumarin derivatives through iron-catalyzed annulation reactions (*g*).[6g] Although the previously reported methods are effective and have many advantages, these reactions occasionally suffer from introduction of the same aryl group on the substrate and formation of a mixture of pyranocoumarins and furocoumarins. Thus, the development of new and convenient methods to regioselectively prepare pyranocoumarins and furocoumarins is continuously required.

Bismuth catalysts have received considerable attention due to their low toxicity and cost, ease of handling, high catalytic efficiency, and stability.[8] Moreover, bismuth is a well-known catalyst for the dual activation of alkynes and hydroxyl groups through σ,π-chelation, as reported by Shibasaki *et al.*[9] Because of these characteristics, bismuth is an efficient catalyst for propargylation through σ,π-dual activation of propargyl alcohols. In addition, sequential processes that involve multiple chemical transformations in one-pot, with minimal work-up steps and less waste generation, have improved synthetic chemistry in recent years.

In continuation with our investigations directed toward the synthesis of coumarin, phosphacoumarin, and phosphaisocoumarin derivatives,[10] we report herein a regioselective Bi-catalyzed synthesis of pyranocoumarins and furocoumarins through sequential propargylation and cyclization reactions (Scheme 2).

Results and Discussion

The initial cyclization was carried out with 4-hydroxycoumarin (**1a**) and 1,3-diphenylprop-2-yn-1-ol (**2a**) in the presence of a variety of metal triflates in chlorobenzene (Table 1). When $Yb(OTf)_3$ (10 mol %) was used as a catalyst, a propargylated coumarin **3a** was selectively produced in 59% yield (entry 1). Although $In(OTf)_3$ and $Fe(OTf)_3$ gave **3a** as the major product, $Cu(OTf)_2$ and AgOTf selectively provided the desired pyranocoumarin **4a** even at low yields (entries 4 and 5). Gratifyingly, $Bi(OTf)_3$

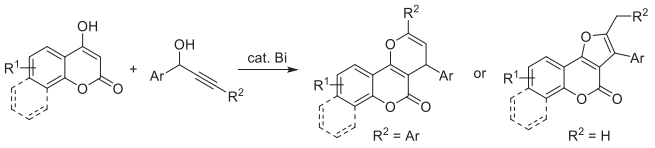


Scheme 1. Previously reported synthetic methods of pyranocoumarins and furocoumarins.

increased the yield of **3a** up to 56%, maintaining high selectivity (entry 6). These results indicate that $Bi(OTf)_3$ efficiently catalyzes propargylation followed by cyclization in one-pot. Next, a wide range of solvents, including chlorobenzene, dichloroethane, tetrahydrofuran, diglyme, toluene, and nitromethane (CH_3NO_2), were screened, and CH_3NO_2 gave the best result (entry 11). When the amount of $Bi(OTf)_3$ was decreased to 5 mol%, the yield of **4a** decreased to 65%, maintaining the selectivity (entry 12). Next, $BiCl_3$ and $Bi(NO_3)_3{\cdot}5H_2O$ were examined to determine the optimum catalyst. In contrast to $Bi(OTf)_3$, $BiCl_3$ afforded propargylated coumarin **3a** as the major product (entry 13). However, $Bi(NO_3)_3{\cdot}5H_2O$ was inefficient as a catalyst (entry 14). When AgOTf (30 mol%) was used in the presence of $BiCl_3$ (10 mol%), **4a** was obtained in 61% yield (entry 15). To check the possibility of catalysis by a protic acid, we attempted the sequential propargylation and cyclization reaction in the presence of trifluoromethanesulfonic acid (10 mol%) in CH_3NO_2 at 100 °C, which produced **3a** in 13% yield (entry 16). These results indicate that $Bi(OTf)_3$ is essential for the selective synthesis of pyranocoumarin **4a**. The optimum conditions were obtained from the reaction of **1a** (1.2 equiv) with **2a** (0.2 mmol, 1.0 equiv) using $Bi(OTf)_3$ (10 mol%) in CH_3NO_2 at 100 °C for 8 h, providing **4a** in 83% yield (entry 11).

Stimulated by these results, the scope of propargyl alcohols and coumarins was examined (Table 2). First, many

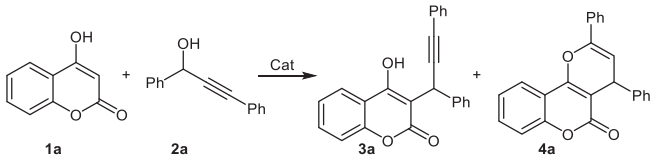
substituents were examined as the R^2 group on the aryl ring of the propargyl alcohol (**2**). Substrates bearing electron-donating 2-methyl and 3-methoxy groups were cyclized to afford **4b** and **4c** in 53% and 40%, respectively. Moreover, 3-Cl- and 2-Br-substituted propargyl alcohols provided the desired pyranocoumarins **4d** (79%) and **4e** (70%). Electron-withdrawing groups including 4-CF_3 and 3-NO_2 gave the corresponding pyranocoumarins (**4f** and **4g**) in 90% and 66% yields, respectively. As a result, it was determined that substrates with electron-withdrawing groups were more reactive than those with electron-donating groups, and the positional characteristics were not significant in these reactions. We also investigated the effects of substituents at the R^3 position. Propargyl alcohols substituted with 2-methyl- and 3-chlorophenyl groups on R^3 gave the desired pyranocoumarins **4h** and **4j** in 77% and 65% yields, respectively. However, the propargyl alcohol substituted with the strong electron-donating 3-methoxyphenyl group was less reactive. Next, some substituents such as methyl, *tert*-butyl, methoxy, and benzo groups were introduced into the R^1 position of 4-hydroxycoumarin to investigate the reactivity of the substrate. When the 4-hydroxycoumarins bore methyl groups at positions 6 and 8, the desired pyranocoumarins **4k** and **4l** were produced in 65% and 72% yields, respectively. In the case of 6,8-di(*tert*-butyl)- and 7-methoxy-substituted 4-hydroxycoumarins, the corresponding pyranocoumarins (**4m** and **4n**) were obtained in moderate yields. When 4-hydroxy-2*H*-benzo[*h*]chromen-2-one was used, pyranocoumarin **4o** was produced in 30% yield. Unfortunately, the reaction did not proceed when R^2 was replaced with aliphatic groups.



Scheme 2. Selective Bi-catalyzed synthesis of pyranocoumarins and furocoumarins.

To broaden the scope of the reaction, we applied 1-phenylprop-2-yn-1-ol (**5a**), which is a terminal propargyl alcohol, in the reaction with 4-hydroxycoumarin **1a** under the optimum reaction conditions (Table 3). Surprisingly, furocoumarin (**6a**) and furochromone (**7a**) instead of pyranocoumarin were obtained in 51% and 27% yields,

Table 1. Reaction optimization for the regioselective synthesis of pyranocoumarins.[a]



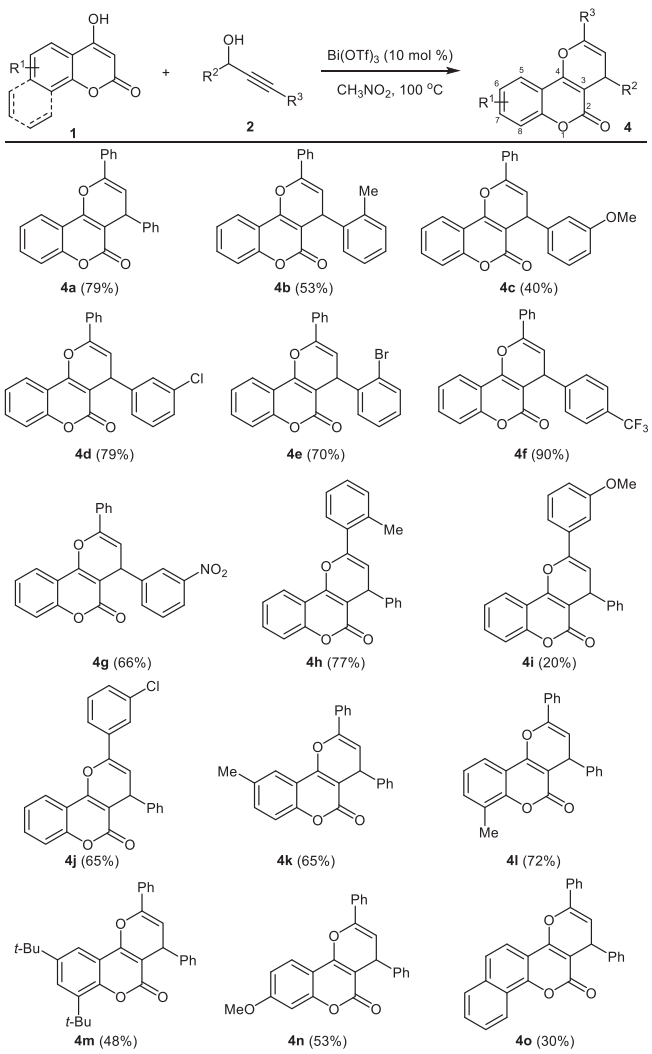
Entry	Cat (mol %)	Solvent	Temp (°C)	Time (h)	Yield (%)[b] (3a:4a)
1	$Yb(OTf)_3$ (10)	PhCl	100	24	59:0
2	$In(OTf)_3$ (10)	PhCl	100	24	43:16
3	$Fe(OTf)_3$ (10)	PhCl	100	24	43:16
4	$Cu(OTf)_2$ (10)	PhCl	100	24	0:28
5	AgOTf (10)	PhCl	100	10	0:32
6	$Bi(OTf)_3$ (10)	PhCl	100	24	0:56 (51)[c]
7	$Bi(OTf)_3$ (10)	DCE	84	24	23:25
8	$Bi(OTf)_3$ (10)	THF	66	24	42:25
9	$Bi(OTf)_3$ (10)	diglyme	100	24	3:52
10	$Bi(OTf)_3$ (10)	toluene	100	24	0:65
11	$Bi(OTf)_3$ (10)	CH_3NO_2	100	8	0:83 (79)[c]
12	$Bi(OTf)_3$ (5)	CH_3NO_2	100	8	0:65
13	$BiCl_3$ (10)	CH_3NO_2	100	24	64:4
14	$Bi(NO_3)_3{\cdot}5H_2O$	CH_3NO_2	100	24	0:0
15	$BiCl_3$ (10)/AgOTf (30)	CH_3NO_2	100	24	0:61
16	TfOH (10)	CH_3NO_2	100	8	0:13

[a] Reaction conditions: 4-Hydroxycoumarin (**1a**, 1.2 equiv) and 1,3-diphenylprop-2-yn-1-ol (**2a**, 0.2 mmol, 1 equiv) were used in solvent (1.0 mL) under air.

[b] NMR yields using dibromomethane as the internal standard.

[c] Isolated yield.

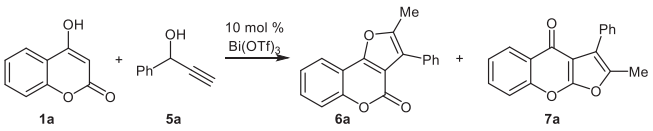
Table 2. Regioselective synthesis of pyranocoumarins.[a]



[a] Reaction was carried out with 4-hydroxycoumarin (**1**, 1.2 equiv), propargyl alcohol (**2**, 0.3 mmol, 1.0 equiv), and $Bi(OTf)_3$ (10 mol %) in CH_3NO_2 (1.5 mL) at 100 °C for 8–12 h under air.

respectively (entry 1). Regarding the synthesis of furocoumarins (**6a**), the selectivity depended on the solvent. High selectivity was not observed with PhCl and DCE (entries 2 and 3). In the case of 1,4-dioxane, the ratio of **6a** and **7a** increased to 63:10 (entry 4). When diglyme was used as a solvent, the highest selectivity was obtained in 76% yield (**6a**:**7a** = 14.2:1) (entry 5). To check the possibility of catalysis by a protic acid, we attempted the sequential propargylation and cyclization reaction in the presence of trifluoromethanesulfonic acid (10 mol %) in diglyme at 100 °C, which produced furochromone (**7a**) in 70% yield (entry 6). These results indicate that $Bi(OTf)_3$ is essential for the selective synthesis of furocoumarin **6a**.

Table 3. Reaction optimization for the synthesis of furocoumarins.[a]



Entry	Solvent	Temp (°C)	Time (h)	Yield (%)[b] (**6a**:**7a**)
1	CH_3NO_2	100	3.5	51:27
2	PhCl	100	3.5	34:22
3	DCE	84	3.5	42:39
4	1,4-dioxane	100	3	63:10
5	diglyme	100	3	71:5
6[c]	diglyme	100	14	10:70

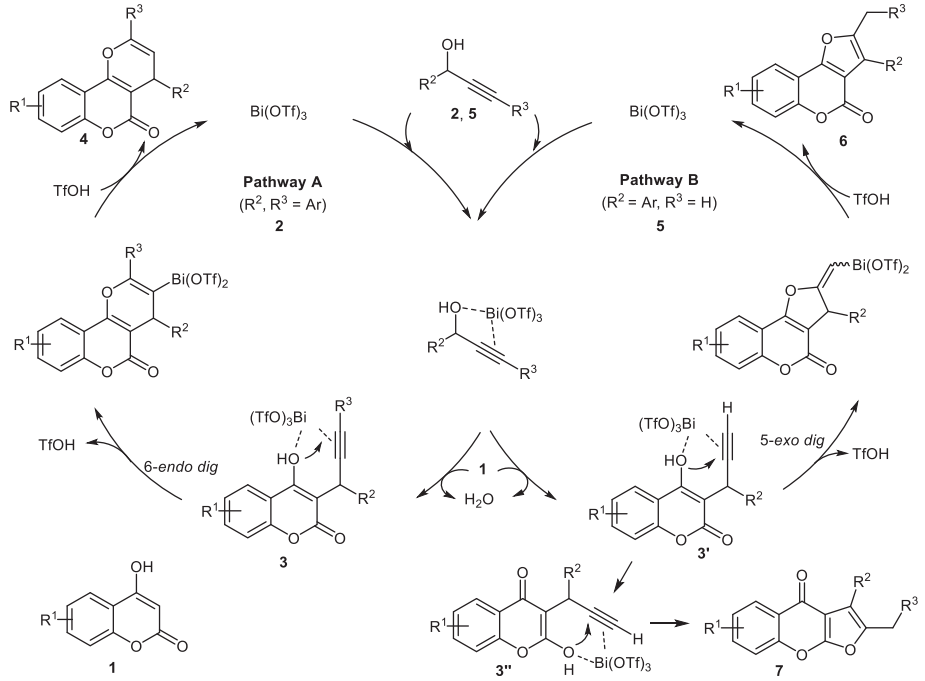
[a] Reaction conditions: 4-Hydroxycoumarin (**1a**, 1.2 equiv) and 1,3-diphenylprop-2-yn-1-ol (**5a**, 0.2 mmol, 1 equiv) were used in solvent (1.0 mL) under air.

[b] NMR yields using dibromomethane as an internal standard.

[c] TfOH (10 mol %) was used instead of $Bi(OTf)_3$.

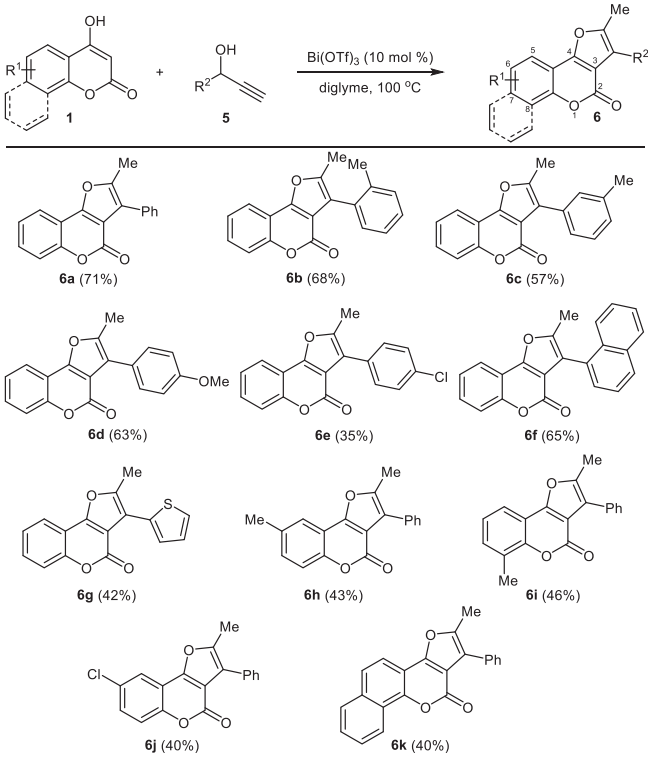
With these results in hand, a wide range of substrates were applied in the regioselective synthesis of furocoumarins (**6**) (Table 4). When R^2 was 2- and 3-tolyl groups, **6b** and **6c** were obtained in 68% and 57% yields, respectively. In the case of a propargyl alcohol with a 4-methoxyphenyl group, the corresponding furocoumarin **6d** was produced in 63% yield. The reactivity of 4-chlorophenyl-substituted propargyl alcohol was poor. 1-Naphthyl-substituted propargyl alcohol was applied to the present transformation, providing the corresponding furocoumarin **6f** in 65% yield. When a propargyl alcohol bearing a thiophen-2-yl group was used, **6g** was produced in 42% yield. Methyl and chloro-substituted 4-hydroxycoumarins were converted to furocoumarins **6h**, **6i**, and **6j**, respectively, in acceptable yields. Additionally, benzene-ring-fused 4-hydroxycoumarin was subjected to sequential propargylation and cyclization, producing the desired furocoumarin **6k** in 40% yield. It is noteworthy that **6k** is the skeleton of neotanshinlactone, which is an important natural product.[3] In all cases, a trace amount (5% <) of the furochromone derivatives **7** was detected.

Although the detailed mechanism remains to be clarified, a plausible reaction mechanism is shown in Scheme 3. $Bi(OTf)_3$ is a particularly interesting Lewis acid, with both oxophilic and carbophilic character, thus presenting broad catalytic activity and activating carbonyl and hydroxyl groups as well as isolated C─C multiple bonds.[8d,11] Thus, the proposed mechanism of the present reaction involves activation of the propargyl alcohol (**2** and **5**) through σ,π-dual activation by the bismuth catalyst, which shows hard/soft borderline characteristics, and the formation of a propargylation intermediate **3** through attack of the 4-hydroxycoumarin (**1**). The resulting intermediate (**3**) is



Scheme 3. A proposed mechanism.

Table 4. Regioselective synthesis of furocoumarins.[a]



[a] Reactions were carried out with **1** (1.2 equiv), **5** (0.3 mmol, 1 equiv), and $Bi(OTf)_3$ (10 mol %) in diglyme (1.5 mL) at 100 °C for 3 h under air.

again σ,π-dual activated by the bismuth catalyst, and when an aryl group is present in the R^2 position, pyranocoumarins (**4**) are obtained through 6-*endo*-dig cyclization. When no substituents are present in the R^2 position, furocoumarins (**6**) are obtained through 5-*exo*-dig cyclization. The isomerization of the propargylation intermediate (**3′**) to **3″** followed by 5-*exo*-dig cyclization provides furochromones (**7**). Notably, $Bi(OTf)_3$ acts as a bifunctional catalyst and efficiently catalyzes propargylation as well as cyclization in one-pot.

Conclusion

In conclusion, a regioselective Bi-catalyzed synthetic method for pyranocoumarin derivatives has been developed through sequential propargylation and cyclization reactions (6-*endo* mode) of 4-hydroxycoumarins with propargyl alcohols. When terminal propargyl alcohols were used, furocoumarins and furochromones were obtained through the 5-*exo* mode, and the best selectivity for furocoumarins was observed with diglyme as the solvent. Elucidation of the exact reason behind the observed regioselectivity is underway in our laboratory.

Experimental

General. The starting 1,3-diphenylprop-2-yn-1-ol[12] and 1-phenylprop-2-yn-1-ol[13] derivatives were prepared according to the reported literature procedure. Commercial available reagents were used without purification. All reaction mixtures were stirred magnetically and were monitored

by thin-layer chromatography using silica gel precoated glass plates, which were visualized with UV light and then, developed using either iodine or a solution of anisaldehyde. Flash column chromatography was carried out using silica gel (230–400 mesh). ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on NMR spectrometer. Deuterated chloroform was used as the solvents, and chemical shift values (δ) are reported in parts per million relative to the residual signals of these solvent [7.26 for ^{1}H (chloroform-*d*) and δ 77.16 for ^{13}C (chloroform-*d*)]. Infrared spectra were recorded on FTIR spectrometer. High-resolution mass spectra (HRMS) were obtained electron impact (EI) ionization technique (magnetic sector—electric sector double focusing mass analyzer) from the Kangwon National University Central Laboratory and KBSI (Korea Basic Science Institute Daegu Center). Melting points were determined in open capillary tube.

General Procedure for Pyrano[3,2-*c*]coumarins. To a test tube were added 4-hydroxycoumarin (**1**, 0.36 mmol), internal propargyl alcohol (**2**, 0.3 mmol), and $Bi(OTf)_3$ (10 mol %) in nitromethane (1.5 mL). The resulting mixture was stirred at 100 °C for 8–12 h. After completion of the reaction, the mixture was concentrated and directly purified by column chromatography on silica gel using EtOAc:hexane = 1:10.

2,4-Diphenyl-4*H*-pyrano[3,2-*c*]chromen-5-one (4a)**.** Yield: 83 mg (79%); R_f = 0.3 (EtOAc:Hexane = 1:10); White solid; Melting point: 176–178 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.02 (dd, J_1 = 1.52 Hz, J_2 = 7.92 Hz, 1H), 7.74–7.71 (m, 2H), 7.59–7.54 (m, 1H), 7.47–7.29 (m, 9H), 7.25–7.21 (m, 1H), 5.85–5.84 (d, J = 4.92 Hz, 1H), 4.72–4.70 (d, J = 4.92 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 155.8, 152.8, 146.9, 143.6, 132.6, 132.0, 129.3, 128.7, 127.3, 124.7, 124.2, 122.7, 116.9, 114.6, 103.8, 103.7, 36.6.[6c]

2-Phenyl-4-*o*-tolylpyrano[3,2-*c*]chromen-5(4H)-one (4b)**.** Yield: 58 mg (53%); R_f = 0.3 (EtOAc: Hexane = 1:10); Pale yellow powder; Melting point: 184–186 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.04 (dd, J_1 = 1.50 Hz, J_2 = 7.90 Hz, 1H), 7.72–7.69 (m, 2H), 7.61–7.57 (m, 1H), 7.46–7.35 (m, 5H), 7.20–7.16 (m, 2H), 7.13–7.10 (m,,2H), 5.78 (d, J = 4.68 Hz, 1H), 4.95 (d, J = 4.68 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 156.2, 152.7, 146.4, 142.3, 135.6, 132.7, 132.0, 130.6, 129.2, 128.8, 128.6, 126.9, 126.6, 124.6, 124.2, 122.6, 116.8, 114.5, 103.7, 103.4, 32.6, 19.6.[6e]

4-(3-Methoxyphenyl)-2-phenylpyrano[3,2-*c*]chromen-5(*4H*)-one (4c)**.** Yield: 46 mg (40%); R_f = 0.15 (EtOAc: Hexane = 1:10); White solid; Melting point: 144–146 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.01 (dd, J_1 = 1.46 Hz, J_2 = 7.90 Hz, 1H), 7.74–7.59 (m, 2H), 7.57–7.55 (m, 1H), 7.47–7.33 (m, 5H), 7.25–7.22 (m, 1H), 7.02–6.96 (m, 2H), 6.79–6.76 (m, 1H), 5.84 (d, J = 4.96 Hz, 1H), 4.70 (d, J = 4.92 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 159.8, 155.8, 152.7, 146.9, 145.2, 132.6, 132.0, 129.6, 129.2, 128.7, 124.7, 124.2, 122.7, 120.8, 116.8, 114.6, 114.5, 112.3, 103.7, 103.5, 55.2, 36.6.[6]

4-(3-Chlorophenyl)-2-phenylpyrano[3,2-*c*]chromen-5(*4H*)-one (4d)**.** Yield: 91 mg (79%); R_f = 0.3 (EtOAc:Hexane = 1:10); White solid; Melting point: 132–133 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.03 (dd, J_1 = 1.52 Hz, J_2 = 7.92 Hz, 1H), 7.74–7.72 (m, 2H), 7.60–7.56 (m, 1H), 7.48–7.31 (m, 7H), 7.25–7.19 (m, 2H), 5.79 (d, J = 4.84 Hz, 1H), 4.69 (d, J = 4.84 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 156.0, 152.8, 147.2, 145.6, 134.6, 132.4, 132.3, 129.9, 129.5, 128.8, 128.6, 127.5, 124.7, 124.3, 122.8, 116.9, 114.4, 103.1, 103.0, 36.5.[1h]

4-(2-Bromophenyl)-2-phenylpyrano[3,2-*c*]chromen-5(*4H*)-one (4e)**.** Yield: 90 mg (70%); R_f = 0.3 (EtOAc:Hexane = 1:10); White power; Melting point: 238–239 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.05–8.03 (m, 1H), 7.71–7.68 (m, 2H), 7.63–7.58 (m, 2H), 7.45–7.38 (m, 5H), 7.25–7.17 (m, 2H), 7.11–7.06 (m, 1H), 5.89 (d, J = 4.64 Hz, 1H), 5.22 (d, J = 4.60 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 157.2, 152.9, 146.7, 142.4, 133.2, 132.5, 132.3, 129.6, 129.3, 128.7, 128.6, 128.1, 124.7, 124.3, 123.3, 122.8, 116.9, 114.3, 102.2, 102.1, 36.4.[14]

4-(4-(Trifluoromethyl)phenyl)-2-phenylpyrano[3,2-*c*]chromen-5(*4H*)-one (4f)**.** Yield: 113 mg (90%); R_f = 0.3 (EtOAc:Hexane = 1:10); Light yellow solid; Melting point: 180–182 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.04 (dd, J_1 = 1.52 Hz, J_2 = 7.92 Hz, 1H), 7.75–7.72 (m, 2H), 7.62–7.53 (m, 5H), 7.49–7.35 (m, 5H), 5.81 (d, J = 4.84 Hz, 1H), 4.80 (d, J = 4.84 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 156.1, 152.8, 147.4, 132.4, 132.3, 129.6, 129.3, 128.9, 128.8, 125.7, 125.6, 125.6, 124.7, 124.4, 122.7, 116.9, 114.3, 102.9, 102.8, 36.6; FTIR (ATR): 3056, 2924, 1928, 1720, 1610, 1322, 1159, 1010, 853, 840, 761, 639, 527, 425 cm^{-1}; HRMS (EI) *m/z*: M^+ Calcd. for $C_{25}H_{15}F_3O_3$ 420.0973; found 420.0975.[15]

4-(3-Nitrophenyl)-2-phenylpyrano[3,2-*c*]chromen-5(*4H*)-one (4g)**.** Yield: 78 mg (66%); R_f = 0.3 (EtOAc:Hexane = 1:10); Light yellow solid; Melting point: 185–186 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.25 (t, J = 2.0 Hz, 1H), 8.12–8.09 (m, 1H), 8.05 (dd, J_1 = 1.52 Hz, J_2 = 7.92 Hz, 1H), 7.81–7.79 (m, 1H), 7.76–7.73 (m, 2H), 7.63–7.59 (m, 1H), 7.52–7.40 (m,5H), 7.37–7.35 (m, 1H), 5.80 (d, J = 4.72 Hz, 1H), 4.86 (d, J = 4.72 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 156.3, 152.8, 148.6, 147.7, 145.6, 134.8, 132.5, 132.1, 129.7, 129.5, 128.8, 124.8, 124.4, 123.4, 122.9, 122.4, 116.9, 114.2, 102.4, 102.3, 36.6.[15]

4-Phenyl-2-(*o*-tolyl)pyrano[3,2-*c*]chromen-5(*4H*)-one (4h)**.** Yield: 85 mg (77%); R_f = 0.3 (EtOAc: Hexane = 1:10); White powder; Melting point: 128–130 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.87–7.85 (m, 1H), 7.53–7.41 (m, 4H), 7.35–7.21 (m, 8H), 5.44 (d, J = 4.92 Hz, 1H), 4.71 (d, J = 4.92 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 155.9, 152.7, 148.6, 143.7, 136.8, 133.4, 131.9, 130.7, 129.5, 129.3, 128.7,

128.5, 127.2, 126.0, 124.1, 122.7, 116.8, 114.5, 107.7, 103.5, 36.8, 20.5; FTIR (ATR): 3026, 1714, 1628, 1454, 1385, 1243, 1009, 752, 696, 666, 459 cm^{-1}; HRMS (EI) *m/z*: M^+ Calcd. for $C_{25}H_{18}O_3$ 366.1256; found 366.1258.

2-(3-Methoxyphenyl)-4-phenylpyrano[3,2-*c*]chromen-5 (*4H*)-one (4i)**.** Yield: 23 mg (20%); R_f = 0.2 (EtOAc:Hexane = 1:10); Pale red powder; Melting point: 141–143 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.01 (dd, J_1 = 1.44 Hz, J_2 = 7.92 Hz, 1H), 7.59–7.55 (m, 1H), 7.43–7.21 (m, 10H), 6.97–6.94 (m, 1H), 5.84 (d, J = 4.92 Hz, 1H), 4.71 (d, J = 4.92 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 159.8, 155.7, 152.7, 146.7, 143.5, 134.92, 132.0, 129.7, 128.6, 128.5, 127.2, 124.2, 122.7, 117.2, 116.0, 114.5, 114.4, 110.7, 104.92, 103.6, 55.4, 36.6; FT-IR (ATR): 3081, 3028, 1712, 1627, 1490, 1392, 1305, 1046, 752, 701, 663, 551, 440 cm^{-1}; HRMS (EI) *m/z*: M^+ Calcd. for $C_{25}H_{18}O_4$ 382.1205; found 382.1205.

2-(3-Chlorophenyl)-4-phenylpyrano[3,2-*c*]chromen-5 (*4H*)-one (4j)**.** Yield: 75 mg (65%); R_f = 0.3 (EtOAc:Hexane = 1:10); Pale yellow solid; Melting point: 200–202 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.00 (dd, J_1 = 1.44 Hz, J_2 = 7.92 Hz, 1H), 7.71–7.70 (m, 1H), 7.62–7.56 (m, 2H), 7.41–7.31 (m, 8H), 7.25–7.22 (m, 1H), 5.86 (d, J = 4.92 Hz, 1H), 4.71 (d, J = 4.92 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 155.6, 152.7, 145.7, 143.2, 134.8, 134.4, 132.1, 129.9, 129.2, 128.7, 128.4, 127.4, 124.8, 124.3, 122.8, 122.6, 116.9, 114.3, 104.9, 103.6, 36.6; FT-IR (ATR): 3083, 3027, 1711, 1628, 1391, 1270, 1022, 759, 747, 680, 549, 421 cm^{-1}; HRMS (EI) *m/z*: M^+ Calcd. for $C_{24}H_{15}ClO_3$ 386.0710; found 386.0713.

9-Methyl-2,4-diphenylpyrano[3,2-*c*]chromen-5(*4H*)-one (4k)**.** Yield: 71 mg (65%); R_f = 0.3 (EtOAc: Hexane = 1:10); White solid; Melting point: 216–218 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.77–7.73 (m, 3H), 7.47–7.30 (m, 8H), 7.25–7.22 (m, 2H), 5.84 (d, J = 4.96 Hz, 1H), 4.71 (d, J = 4.92 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 155.8, 151.0, 146.9, 143.7, 134.92, 133.1, 132.7, 129.3, 128.9, 128.7, 128.5, 127.2, 124.7, 122.3, 116.6, 114.2, 103.8, 103.6, 103.4, 36.6, 21.1.[6c]

7-Methyl-2,4-diphenylpyrano[3,2-*c*]chromen-5(*4H*)-one (4l)**.** Yield: 79 mg (72%); R_f = 0.3 (EtOAc: Hexane = 1:10); Yellow powder; Melting point: 162–163 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.86 (dd, J_1 = 1.0 Hz, J_2 = 7.92 Hz, 1H),), 7.74–7.71 (m, 2H), 7.46–7.37 (m, 6H), 7.34–7.19 (m, 4H), 5.84 (d, J = 4.92 Hz, 1H), 4.71 (d, J = 4.96 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 161.5, 155.9, 151.1, 147.0, 143.7, 133.2, 132.7, 129.2, 128.7, 128.6, 128.5, 127.2, 126.3, 124.7, 123.7, 120.3, 114.3, 103.7, 103.4, 36.6, 15.7; FT-IR (ATR): 3062, 3026, 1713, 1630, 1467, 1386, 1216, 1012, 757, 701, 606, 548, 447 cm^{-1}; HRMS (EI) *m/z*: M^+ Calcd. for $C_{25}H_{18}O_3$ 366.1256; found 366.1254.

7,9-Di-tert-butyl-2,4-diphenylpyrano[3,2-*c*]chromen-5 (*4H*)-one (4m)**.** Yield: 67 mg (48%); R_f = 0.6 (EtOAc: Hexane = 1:10); Yellow solid; Melting point: 116–118 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.89 (d, J = 2.32 Hz, 1H), 7.75–7.72 (m, 2H), 7.61 (d, J = 2.36 Hz, 1H), 7.49–7.40 (m, 5H), 7.34–7.29 (m, 2H), 7.25–7.20 (m, 1H), 5.84 (d, J = 4.96 Hz, 1H), 4.71 (d, J = 4.96 Hz, 1H), 1.49 (s, 9H), 1.42 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 156.4, 149.6, 147.1, 146.3, 143.8, 137.4, 133.0, 129.2, 128.7, 128.6, 128.5, 127.2, 124.7, 116.7, 114.2, 103.8, 102.9, 36.56, 35.2, 34.9, 31.5, 29.9, 29.7; FT-IR (ATR): 2964, 1708, 1611, 1364, 1264, 1045, 732, 699, 609, 509 cm^{-1}; HRMS (EI) *m/z*: M^+ Calcd. for $C_{32}H_{32}O_3$ 464.2351; found 464.2353.

8-Methoxy-2,4-diphenylpyrano[3,2-*c*]chromen-5(*4H*)-one (4n)**.** Yield: 61 mg (53%); R_f = 0.2 (EtOAc: Hexane = 1:10); Pale yellow solid; Melting point: 205–207 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.89 (d, J = 8.84 Hz, 1H), 7.72–7.70 (m, 2H), 7.46–7.40 (m, 5H), 7.33–7.29 (m, 2H), 7.25–7.20 (m, 1H), 6.94–6.92 (m, 1H), 6.80 (d, J = 2.36 Hz, 1H), 5.83 (d, J = 4.92 Hz, 1H), 4.66 (d, J = 4.92 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 161.9, 156.1, 154.5, 146.7, 143.8, 132.7, 129.2, 128.6, 128.5, 128.4, 127.1, 124.6, 123.7, 112.6, 107.7, 103.8, 100.9, 100.5, 55.8, 36.5; FT-IR (ATR): 3074, 3025, 2851, 1711, 1616, 1398, 1254, 1174, 1029, 694, 553, 459 cm^{-1}; HRMS (EI) *m/z*: M^+ Calcd. for $C_{25}H_{18}O_4$ 382.1205; found 382.1206.

General Procedure for Furo[3,2-*c*]coumarins. To a test tube were added 4-hydroxycoumarin (**1**, 0.36 mmol), terminal propargyl alcohol (**5**, 0.3 mmol), and $Bi(OTf)_3$ (10 mol %) in diglyme (1.5 mL). The resulting mixture was stirred at 100 °C for 3 h. After completion of the reaction, the mixture was concentrated and directly purified by column chromatography on silica gel using EtOAc:hexane = 1:7.

1,3-Diphenylbenzo[*h*]pyrano[3,2-*c*]chromen-12(1*H*)-one (4o)**.** Yield: 36 mg (30%); R_f = 0.3 (EtOAc: Hexane = 1:10); Yellow powder; Melting point: 222–224 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.51–8.49 (m, 1H), 8.00 (d, J = 8.72 Hz, 1H), 7.91–7.88 (m, 1H), 7.78–7.76 (m, 3H), 7.64–7.61 (m, 2H), 7.49–7.42 (m, 5H), 7.34–7.31 (m, 2H), 7.25–7.23 (m, 1H), 5.88 (d, J = 4.92 Hz, 1H), 4.76 (d, J = 4.92 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 157.1, 150.6, 147.4, 144.1, 135.3, 133.2, 129.7, 129.5, 129.4, 129.2, 128.7, 128.3, 127.7, 127.6, 125.2, 124.7, 123.4, 123.0, 118.7, 110.2, 104.2, 103.6, 37.1; FT-IR (ATR): 3058, 3024, 2921, 1710, 1617, 1376, 1021, 811, 756, 695, 567, 422 cm^{-1}; HRMS (EI) *m/z*: M^+ Calcd. for $C_{28}H_{18}O_3$ 402.1256; found 402.1254.

2-Methyl-3-phenyl-*4H*-furo[3,2-*c*]chromen-4-one (6a)**.** Yield: 59 mg (71%); R_f = 0.3 (EtOAc:Hexane = 1:7); Pale yellow powder; Melting point: 195–197 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.84 (dd, 1H, J_1 = 1.36 Hz, J_2 = 7.8 Hz), 7.52–7.30 (m, 8H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 156.3, 152.3, 151.7, 130.3, 130.0, 129.9, 128.2, 127.8, 124.3, 120.6, 120.5, 117.1, 112.8, 109.6, 12.6; FTIR (ATR): 3069, 2918,

1722, 1628, 1591, 1083, 747, 692, 514 cm^{-1}; HRMS (EI) *m/z*: M^+ Calcd. for $C_{18}H_{12}O_3$ 276.0786; found 276.0786.[16]

2-Methyl-3-(*o*-tolyl)-*4H*-furo[3,2-*c*]chromen-4-one (6b). Yield: 59 mg (68%); R_f = 0.3 (EtOAc:Hexane = 1:7); Pale yellow solid; Melting point: 146–147 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.88 (dd, 1H, J_1 = 1.5 Hz, J_2 = 7.8 Hz), 7.49–7.46 (m, 1H), 7.43–7.40 (m, 1H), 7.36–7.31 (m, 3H), 7.25–7.22 (m, 2H), 2.35 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 156.1, 152.4, 151.9, 137.8, 130.5, 130.2, 130.1, 129.7, 128.4, 125.7, 124.3, 120.6, 119.5, 117.2, 112.9, 111.0, 19.9, 12.2; FT-IR (ATR): 2923, 1726, 1629, 1500, 1074, 943, 897, 746, 735, 446 cm^{-1}; HRMS (EI) *m/z*: M^+ Calcd. for $C_{19}H_{14}O_3$ 290.0943; found 290.0943.

2-Methyl-3-(*m*-tolyl)-*4H*-furo[3,2-*c*]chromen-4-one (6c). Yield: 50 mg (57%); R_f = 0.3 (EtOAc: Hexane = 1:7); Pale yellow solid; Melting point: 128–130 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.83 (dd, 1H, J_1 = 1.3 Hz, J_2 = 7.8 Hz), 7.48–7.44 (m, 1H), 7.40–7.24 (m, 5H), 7.19–7.17 (m, 1H), 2.50 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 156.2, 152.3, 151.7, 137.7, 130.6, 130.2, 129.9, 128.6, 128.1, 127.0, 124.3, 120.6, 117.1, 112.8, 109.7, 21.5, 12.6; FT-IR (ATR): 3043, 2920, 1722, 1680, 1500, 1063, 953, 749, 703, 697, 434 cm^{-1}; HRMS (EI) *m/z*: M^+ Calcd. for for $C_{19}H_{14}O_3$ 290.0943; found 290.0943.[5f]

3-(4-Methoxyphenyl)-2-methyl-*4H*-furo[3,2-*c*]chromen-4-one (6d). Yield: 58 mg (63%); R_f = 0.2 (EtOAc:Hexane = 1:7); Pale brown solid; Melting point: 165–167 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.83 (dd, 1H, J_1 = 1.4 Hz, J_2 = 7.8 Hz), 7.49–7.39 (m, 4H), 7.33–7.29 (m, 1H), 7.01–6.97 (m, 2H), 3.85 (s, 1H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 157.8, 156.1, 152.2, 151.2, 131.1, 130.2, 124.3, 122.2, 120.5, 120.1, 117.0, 113.7, 112.8, 109.7, 55.3, 12.6; FT-IR (ATR): 2922, 2843, 1737, 1596, 1515, 1251, 945, 837, 753, 548 cm^{-1}; HRMS (EI) *m/z*: M^+ Calcd. for $C_{19}H_{14}O_4$ 306.0892; found 306.0892.[5f]

3-(4-Chlorophenyl)-2-methyl-*4H*-furo[3,2-*c*]chromen-4-one (6e). Yield: 33 mg (35%); R_f = 0.3 (EtOAc:Hexane = 1:7); Pale yellow solid; Melting point: 176–177 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.86 (dd, 1H, J_1 = 1.4 Hz, J_2 = 7.8 Hz), 7.50–7.48 (m, 1H), 7.43–7.41 (m, 5H), 7.29–7.25 (m, 1H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 156.5, 152.4, 151.8, 131.8, 131.2, 130.5, 129.2, 128.5, 124.4, 120.7, 119.5, 117.1, 112.7, 109.4, 12.6; FT-IR (ATR): 3076, 2919, 1743, 1631, 1492, 1382, 1069, 966, 748, 692, 528 cm^{-1}; HRMS (EI) *m/z*: M^+ Calcd. for $C_{18}H_{11}ClO_3$ 310.0397; found 310.0397.

2-Methyl-3-(naphthalen-1-yl)-*4H*-furo[3,2-*c*]chromen-4-one (6f). Yield: 64 mg (65%); R_f = 0.3 (EtOAc:Hexane = 1:7); Pale yellow solid; Melting point: 140–141 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.94–7.90 (m, 3H), 7.69–7.67 (m, 1H), 7.57–7.53 (m, 1H), 7.50–7.47 (m, 3H), 7.45–7.41 (m, 2H), 7.35–7.33 (m, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 156.4, 152.9, 152.5, 133.7, 132.3, 130.3, 128.9, 128.6, 128.5, 127.7, 126.3, 125.9, 125.5, 125.3, 124.4, 120.7, 118.3, 117.2, 113.0, 111.4, 12.6; FT-IR (ATR) 3050, 2927, 1736, 1660, 1065, 959, 775, 754, 424 cm^{-1}; HRMS (EI) *m/z*: M^+ Calcd. for $C_{22}H_{14}O_3$ 326.0943; found 326.0943.[16]

2-Methyl-3-(thiophen-2-yl)-*4H*-furo[3,2-*c*]chromen-4-one (6g). Yield: 35 mg (42%); R_f = 0.3 (EtOAc: Hexane = 1:7); Brown solid; Melting point: 137–138 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.82 (dd, 1H, J_1 = 1.4 Hz, J_2 = 7.8 Hz), 7.59–7.58 (m, 1H), 7.49–7.46 (m, 1H), 7.39–7.38 (m, 2H), 7.32–7.30 (m, 1H), 7.16–7.13 (m, 1H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 156.3, 152.4, 152.0, 130.5, 129.1, 127.4, 125.8, 124.4, 120.7, 117.0, 114.4, 112.5, 109.3, 13.4; FT-IR (ATR): 3104, 3062, 2921, 1724, 1627, 1072, 751, 718, 695, 455 cm^{-1}; HRMS (EI) *m/z*: M^+ Calcd. for $C_{16}H_{10}O_3S$ 282.0351; found 282.0351.[5f]

2,8-Dimethyl-3-phenyl-*4H*-furo[3,2-*c*]chromen-4-one (6h). Yield: 37 mg (43%); R_f = 0.3 (EtOAc: Hexane = 1:7); Pale yellow solid; Melting point: 128–130 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.61 (s, 1H), 7.51–7.42 (m, 4H), 7.38–7.34 (m, 1H), 7.29–7.24 (m, 2H), 2.49 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 156.4, 151.5, 150.5, 134.1, 131.3, 130.1, 129.9, 128.2, 127.7, 120.5, 120.3, 116.8, 112.4, 109.5, 20.9, 12.6; FT-IR (ATR): 3051, 2924, 1727, 1568, 1381, 1062, 753, 705, 543, 508 cm^{-1}; HRMS (EI) *m/z*: M^+ Calcd. for $C_{19}H_{14}O_3$ 290.0943; found 290.0943.[16]

2,6-Dimethyl-3-phenyl-*4H*-furo[3,2-*c*]chromen-4-one (6i). Yield: 40 mg (46%); R_f = 0.3 (EtOAc: Hexane = 1:7); Pale yellow solid; Melting point: 142–144 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.68 (dd, 1H, J_1 = 0.9 Hz, J_2 = 7.7 Hz), 7.50–7.43 (m, 4H), 7.38–7.36 (m, 1H), 7.31–7.29 (m, 1H), 7.21–7.19 (m, 1H), 2.50 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 156.7, 151.5, 150.8, 131.6, 130.2, 129.9, 128.2, 127.7, 126.6, 123.8, 120.4, 118.2, 112.4, 109.4, 16.1, 12.7; FT-IR (ATR): 3047, 2921, 1739, 1566, 1021, 766, 747, 696, 505 cm^{-1}; HRMS (EI) *m/z*: M^+ Calcd. for $C_{19}H_{14}O_3$ 290.0943; found 290.0943.

8-Chloro-2-methyl-3-phenyl-*4H*-furo[3,2-*c*]chromen-4-one (6j). Yield: 37 mg (40%); R_f = 0.3 (EtOAc:Hexane = 1:7); Pale yellow solid; Melting point: 149–150 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.80 (d, 1H, J = 2.4 Hz), 7.50–7.32 (m, 8H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 154.9, 152.5, 150.6, 130.2, 129.9, 129.8, 129.7, 128.3, 128.0, 120.7, 120.1, 118.5, 113.8, 110.4, 12.7; FT-IR (ATR): 3082, 2916, 1744, 1502, 1055, 966, 943, 757, 697, 559, 504 cm^{-1}; HRMS (EI) *m/z*: M^+ Calcd. for $C_{18}H_{11}ClO_3$ 310.0397; found 310.0397.[16]

2-Methyl-1-phenyl-*11H*-benzo[*h*]furo[3,2-*c*]chromen-11-one (6k). Yield: 39 mg (40%); R_f = 0.3 (EtOAc:Hexane = 1:7); Pale yellow solid; Melting point: 212–214 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.58–8.55 (m, 1H), 7.86–7.83 (m, 2H), 7.73–7.71 (m, 1H), 7.64–7.54 (m, 4H), 7.50–7.46 (m, 2H), 7.41–7.37 (m, 1H) 2.54 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 157.3, 151.5, 149.0, 134.0, 130.1, 129.9, 128.2, 128.0, 127.9, 127.7, 127.2, 124.5, 123.3, 122.6, 120.4, 116.9, 109.2, 107.9, 12.7; FTIR (ATR): 2920, 1724, 1485, 1095, 1002, 808, 700, 563, 421 cm^{-1}; HRMS (EI) *m/z*: M^+ Calcd. for $C_{22}H_{14}O_3$ 326.0943; found 326.0943.[16]

2-Methyl-3-phenyl-*4H*-furo[2,3-*b*]chromen-4-one (7a)**.** Yield: 22 mg (27%); R_f = 0.27 (EtOAc: Hexane = 1:7); Pale yellow solid; Melting point: 164–166 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.30 (dd, 1H, J_1 = 1.3 Hz, J_2 = 7.9 Hz), 7.69–7.64 (m, 1H), 7.59–7.53 (m, 3H), 7.47–7.42 (m, 3H), 7.38–7.34 (m, 1H), 2.46 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 161.8, 152.7, 142.9, 133.1, 130.6, 129.9, 128.1, 127.6, 126.7, 125.2, 124.0, 119.2, 117.5, 102.4, 12.1; FT-IR (ATR): 3054, 2921, 1655, 1606, 1475, 1175, 871, 754, 732, 524 cm^{-1}; HRMS (EI) *m/z*: M^+ Calcd. for $C_{18}H_{12}O_3$ 276.0786; found 276.0786.

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Supporting Information. Additional supporting information (^{1}H and ^{13}C NMR spectra for new compounds) is available in the online version of this article.

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