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Palladium-Catalyzed Synthesis of 4-Arylcoumarins Using Triarylbismuth Compounds as Atom-Efficient Multicoupling Organometallic Nucleophiles

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Triarylbismuth compounds have been cross-coupled as atom-efficient multicoupling organometallic nucleophiles with 4-bromo- and 4-(trifluoromethylsulfonyloxy)coumarins under palladium catalysis conditions. These reactions afforded an array of 4-arylcoumarins in high yields. The general palladium protocol has been demonstrated to be efficient for the coupling of both bromide and triflate derivatives of coumarins with triarylbismuth reagents.

Introduction

Coumarin and its analogues exhibit several important biological activities such as anticancer, antiviral, anti-inflammatory, anticoagulant, antioxidant, anti-HIV, and central nervous system activities.[1a–1g] In addition, these compounds are also known for their various photophysical applications.[1h–1j] Several procedures have been published in the literature for the synthesis of various substituted coumarins.[2]

Transition-metal-catalyzed cross-coupling reactions of organometallic reagents are well known for the formation of carbon–carbon bonds. Reactions involving a variety of organometallic nucleophiles are routinely used to synthesize a plethora of molecules in synthetic organic chemistry[3,4] and various functionalized 4-arylcoumarins are easily accessible under metal-catalyzed coupling conditions.[5] Organic electrophiles such as triflate,[5a–5f] bromo,[5d,5f] tosylate,[5d,5g–5q] and phosphonate[5r] derivatives of coumarins have been successfully coupled with, for example, organoboron, -tin, -zinc, and -indium organometallic reagents to synthesize 4-arylcoumarins under metal-catalyzed conditions. The coupling reactions of 4-trimethylstannylcoumarins with aryl iodides or triflates under palladium-catalyzed conditions have also been reported for the preparation of 4-arylcoumarins.[5s] A few other methods involving ring-closing metathesis or metal-catalyzed cyclization reactions are also useful for the synthesis of coumarin scaffolds.[6] In particular, various organometallic reagents exhibit varied reactivity in these cross-coupling reactions. Moreover, these reactions provide only 1 equiv. of 4-arylcoumarin product with 1 equiv. of organometallic nucleophile under metal-catalyzed conditions.

However, we favor coupling reactions with triarylbismuth organometallic nucleophiles as these reagents can efficiently couple with 3 equiv. of organic electrophiles.[7] Recent interest in organobismuth reagents is due to their potential nontoxicity and novel reactivity in various applications.[8,9] As a continuation of our efforts to develop triarylbismuth compounds as atom-efficient multicoupling organometallic nucleophiles,[10] we have studied the cross-coupling reactions of 4-bromo- and 4-(trifluoromethylsulfonyloxy)coumarins with triarylbismuth compounds. Herein, we report a general and efficient palladium-catalyzed protocol for the facile synthesis of an array of 4-arylcoumarins using triarylbismuth compounds as atom-efficient multicoupling nucleophiles.

Results and Discussion

First, the bromo (**1a**–**5a**) and triflate (**1b**–**4b**) derivatives of coumarin required for the coupling reactions were prepared following literature procedures starting from the corresponding 4-hydroxycoumarins (Figure 1).[5a,11] To establish efficient cross-coupling conditions, initial experiments were carried out with 4-bromocoumarin (**1a**) and triphenylbismuth under different coupling conditions (Table 1). The reaction in the presence of $[PdCl_2(PPh_3)_2]$ as catalyst and K_3PO_4 as base in *N*,*N*-dimethylacetamide (DMA) at room temperature furnished cross-coupling product 4-phenyl-2*H*-1-benzopyran-2-one (**1c**) in 39% yield (Table 1, entry 1) along with biphenyl and unreacted 4-bromocoumarin. The formation of homocoupling product biphenyl from triphenylbismuth is well known under palladium-catalyzed conditions.[9e] At elevated temperatures, improved conversions to **1c** were obtained (Table 1, entries 2 and 3).

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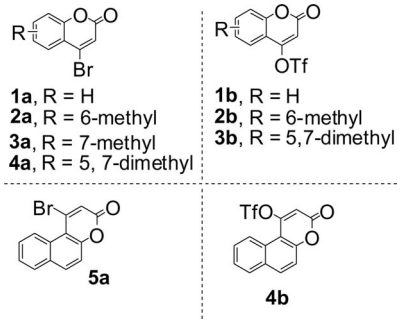
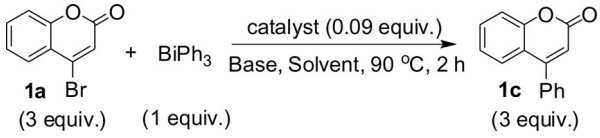


Figure 1. 4-Bromo and triflate derivatives of coumarins.

Table 1. Screening conditions.[a]



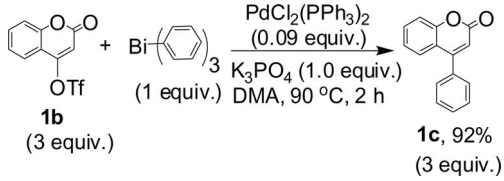
Entry	Catalyst	Base [equiv.]	Solvent	Temp. [°C]	Yield[b,c,d] [%]
1	$[PdCl_2(PPh_3)_2]$	K_3PO_4	DMA	r.t.	39
2	$[PdCl_2(PPh_3)_2]$	K_3PO_4	DMA	60	67
3	$[PdCl_2(PPh_3)_2]$	K_3PO_4	DMA	80	81
4	$[PdCl_2(PPh_3)_2]$	K_3PO_4	NMP	90	69
5	$[PdCl_2(PPh_3)_2]$	K_3PO_4	CH_3CN	90	(47)
6	$[PdCl_2(PPh_3)_2]$	K_3PO_4	1,4-dioxane	90	(19)
7	$[PdCl_2(PPh_3)_2]$	K_3PO_4	DME	90	(26)
8	$[PdCl_2(PPh_3)_2]$	K_3PO_4	DMA	90	98
9	$[PdCl_2(PPh_3)_2]$	Na_2CO_3	DMA	90	84
10	$[PdCl_2(PPh_3)_2]$	K_2CO_3	DMA	90	88
11	$[PdCl_2(PPh_3)_2]$	Cs_2CO_3	DMA	90	97
12	$[PdCl_2(PPh_3)_2]$	CsF	DMA	90	83
13	$[PdCl_2(PhCN)_2]$	K_3PO_4	DMA	90	(43)
14	$[PdCl_2(PPh_3)_2]$	K_3PO_4	DMA	90	74[e]
15	$[PdCl_2(PPh_3)_2]$	No base	DMA	90	69
16	no catalyst	K_3PO_4	DMA	90	(4)

[a] Reagents and conditions: 4-bromocoumarin (185.6 mg, 0.825 mmol, 3.3 equiv.), $BiPh_3$ (110 mg, 0.25 mmol, 1.0 equiv.), catalyst (0.0225 mmol, 0.09 equiv.), base (1 equiv.), and solvent (3 mL). [b] Isolated yields. [c] GC conversion given in parentheses. [d] Homocoupling biphenyl from triphenylbismuth was formed in all the reactions in minor amounts. The amount is more in the absence of the cross-coupling product. [e] Reaction time 1 h.

In an effort to further increase product formation, the reaction was screened in different solvents (Table 1, entries 4–8): DMA was found to be an effective solvent for obtaining a high yield of the product **1c** (Table 1, entry 8). Other solvents such as *N*-methyl-2-pyrrolidinone (NMP) and acetonitrile provided moderate conversions, whereas 1,4-dioxane and 1,2-dimethoxyethane (DME) afforded poor conversions. Encouraged by the high coupling conversion obtained in DMA with K_3PO_4 as base (Table 1, entry 8), we next screened different bases. Interestingly, bases such as Na_2CO_3, K_2CO_3, Cs_2CO_3, and CsF also furnished high yields of the product in DMA (Table 1, entries 9–12). Additional screening with different catalytic precursors did not result in good conversions under similar conditions (Table 1, entry 13).

The coupling reaction performed over 1 h provided a relatively low yield of the product (Table 1, entry 14). A few control reactions were next carried out to gain an understanding of the effective role of the catalyst and base. The reaction without base afforded only a moderate yield of the product (Table 1, entry 15), whereas the reaction performed without the catalyst led to only 4% conversion to the product (Table 1, entry 16). From the above screening it is clear that the cross-coupling reaction is dependent on the nature of the solvent, base, and catalyst precursor as well as temperature. In all these screening reactions biphenyl was formed as a side-product, the amount varying with respect to the yield of the product. Overall, the catalytic protocol using $[PdCl_2(PPh_3)_2]$ as catalyst with K_3PO_4 as base in DMA at 90 °C was found to be the most effective combination for obtaining an excellent yield of cross-coupled product (Table 1, entry 8). Although other carbonate bases were found to be equally efficient, we continued our studies with K_3PO_4 as base.

Having established an efficient palladium protocol for the coupling of 4-bromocoumarin, it was of interest to study the reactivity of 4-(trifluoromethylsulfonyloxy)coumarin derivatives as these compounds are also potential substrates for coupling reactions and can easily be prepared from the corresponding 4-hydroxycoumarin compounds. Thus, 4-(trifluoromethylsulfonyloxy)coumarin (**1b**) was subjected to cross-coupling with triphenylbismuth under the optimized protocol developed for 4-bromocoumarin (Scheme 1). The coupling reaction of **1b** with triphenylbismuth proceeded smoothly to deliver the desired product **1c** in 92% isolated yield. This is interesting from the point of view that both 4-bromo- and 4-(trifluoromethylsulfonyloxy)-coumarins can be cross-coupled with triphenylbismuth under the same conditions to furnish excellent yields of 4-phenyl-2*H*-1-benzopyran-2-one (**1c**) in an efficient manner.

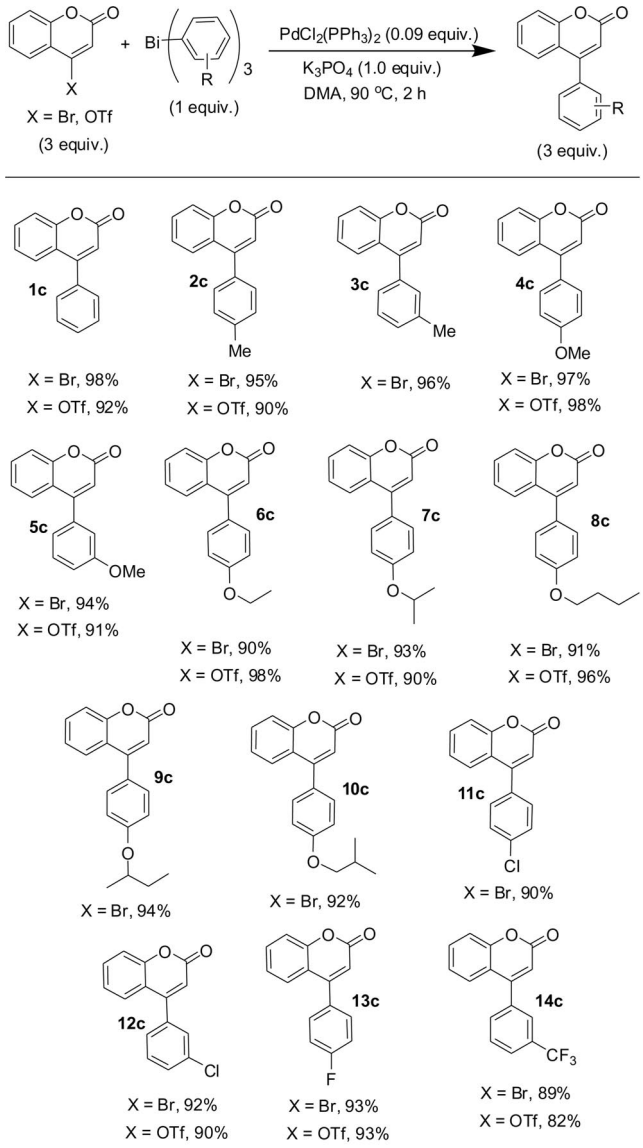


Scheme 1. Cross-coupling reaction of **1b** with triphenylbismuth.

Encouraged by the observed facile reactivity of both the bromo and triflate derivatives of coumarin under the optimized protocol it was of interest to expand the scope of this method. The coupling reactions of electronically divergent triarylbismuth compounds were investigated with 4-bromo- and 4-(trifluoromethylsulfonyloxy)coumarins and the results are summarized in Table 2. The reactivity of the triarylbismuth compounds was generally found to be excellent giving the substituted 4-arylcoumarins in high yields. Both electron-rich and -deficient triarylbismuth compounds participated efficiently in multicoupling reactions with 3 equiv. of both 4-bromo- and 4-(trifluoromethylsulfonyloxy)cou-

marins under the optimized conditions. Note that the coupling reactions of triarylbismuth compounds are equally fast with both 4-bromo- and 4-(trifluoromethylsulfonyloxy)coumarins furnishing three aryl couplings in a short reaction time.

Table 2. Cross-coupling reactions with different triarylbismuth compounds[a–c].



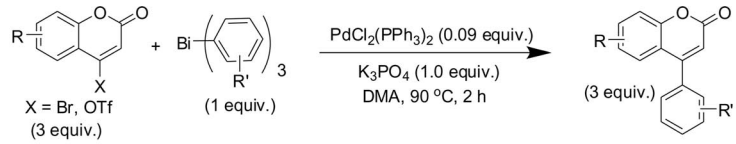
[a] Reagents and conditions: 4-bromo- or 4-(trifluoromethylsulfonyloxy)coumarin (0.825 mmol, 3.3 equiv.), $BiAr_3$ (0.25 mmol, 1.0 equiv.), $[PdCl_2(PPh_3)_2]$ (0.0225 mmol, 0.09 equiv.), K_3PO_4 (0.25 mmol, 1.0 equiv.), and DMA (3 mL), 90 °C, 2 h. [b] Isolated yields were calculated on the basis of all three aryl groups of the triarylbismuth compounds participating in the coupling reactions. Thus, 0.75 mmol of product corresponds to a 100% yield. [c] Homocoupling biaryls were formed in all the reactions in minor amounts.

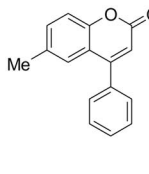
Furthermore, we also studied the reactivity of various substituted 4-bromo- and 4-(trifluoromethylsulfonyloxy)-coumarins with different triarylbismuth compounds under the established conditions (Table 3). All these coumarins smoothly underwent cross-coupling reactions to furnish variously functionalized 4-arylcoumarins in excellent yields. These reactions demonstrate the generality and versatility of the coupling protocol with both bromo and triflate derivatives of coumarins. This study has also revealed the high coupling reactivity of triarylbismuth compounds with 3 equiv. of 4-bromo- and 4-(trifluoromethylsulfonyloxy)-coumarins. Notably, the bromide and triflate derivatives of coumarins were found to be similarly reactive, furnishing excellent yields of the products with different triarylbismuth compounds under the established protocol. Thus, this method is a general protocol for the efficient coupling of both bromo and triflate derivatives of coumarins with triarylbismuth reagents.

The reactions of 4-bromo- and 4-(trifluoromethylsulfonyloxy)coumarins with triarylbismuth compounds under the established conditions are completed in 2 h giving high yields of 4-arylcoumarins through three C–C coupling reactions. However, the majority of coupling reactions reported in the literature for the synthesis of 4-arylcoumarins using triflate, bromide, tosylate, and phosphonate derivatives of coumarins involve longer reaction times at a variety of temperatures even for the formation of 1 equiv. of product.[5] Although the coupling reactivity of triarylindiums with 4-(tosyloxy)coumarins was reported to be fast at room temperature under palladium-catalyzed conditions, the triarylindiums are involved in only one C–C coupling reaction.[5o] Our initial study of the reaction of 4-tosyloxycoumarin with triphenylbismuth under the present coupling conditions provided only 9% of 4-phenylcoumarin. Thus, the protocol in hand is not appropriate for the coupling of 4-tosyloxycoumarin with triarylbismuth compounds and thus further study is required to find suitable conditions.

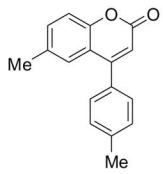
The catalytic cycle of these coupling reactions is expected to follow the general pathway known[3e] for this type of coupling reaction (Scheme 2). The initial oxidative addition of 4-Br- or 4-OTf-substituted coumarin to Pd^0 forms intermediate **A**. This intermediate then undergoes transmetalation with triarylbismuth to give Pd^{II} intermediate **B**, which upon reductive elimination delivers 4-arylcoumarin, regenerating Pd^0 and enabling the catalytic cycle to continue. The added base is expected to activate the Ar–Bi bond during the transmetalation step for transfer of the aryl group. Furthermore, successive involvement of di- or monoarylbismuth in the transmetalation step is likely for the atom-efficient utilization of all three aryl groups from the bismuth reagent. Alternatively, regeneration of triarylbismuth compounds in situ by disproportionation of mono- or diarylbismuth compounds is another possibility for the effective participation of the three aryl groups from the triarylbismuth compounds during the transmetalation step.[9e] The efficient coupling of 3 equiv. of both bromide and triflate derivatives of coumarins with triarylbismuth compounds furnishing very high yields of 4-arylcoumarins proves the effective transfer of all three groups from triarylbismuth compounds under the coupling conditions.

Table 3. Coupling reactions of functionalized 4-bromo- and 4-(trifluoromethylsulfonyloxy)coumarins with triarylbismuth compounds.[a–c]

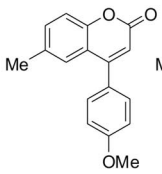




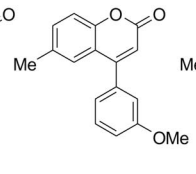
15c
X = Br, 97%
X = OTf, 81%



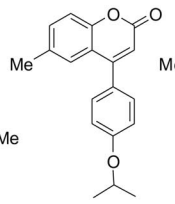
16c
X = Br, 98%
X = OTf, 85%



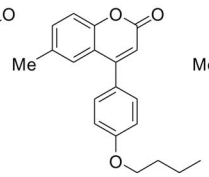
17c
X = Br, 92%
X = OTf, 86%



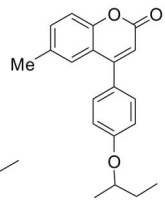
18c
X = Br, 94%
X = OTf, 84%



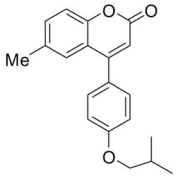
19c
X = Br, 90%
X = OTf, 95%



20c
X = Br, 92%
X = OTf, 92%



21c
X = Br, 85%
X = OTf, 93%



22c
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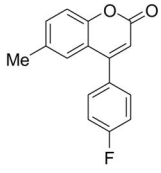
X = OTf, 91%



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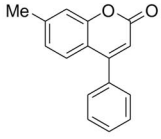

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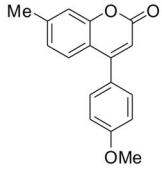
X = Br, 86%



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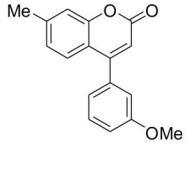

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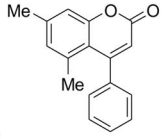

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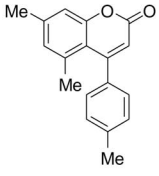
X = OTf, 87%



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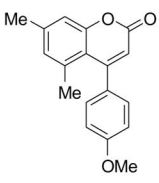

29c
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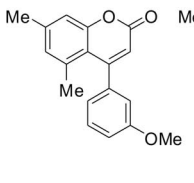

30c
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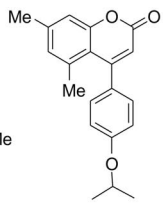

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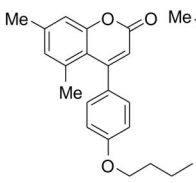
X = OTf, 83%



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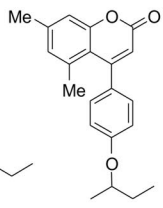

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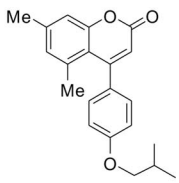

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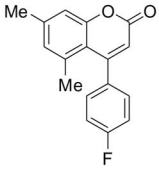

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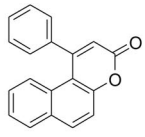
X = OTf, 78%



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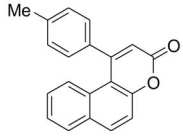
X = OTf, 84%



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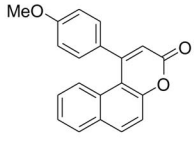
X = OTf, 86%



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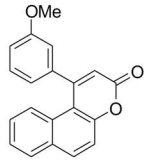
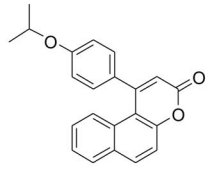
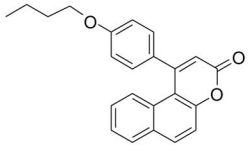
X = OTf, 88%



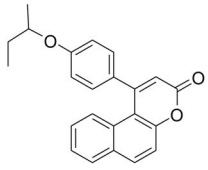
39c
X = Br, 79%
X = OTf, 83%



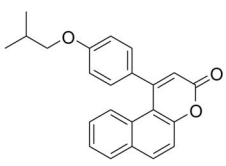
40c
X = Br, 80%
X = OTf, 86%



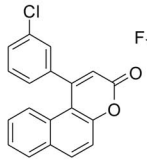
41c
X = Br, 82%
X = OTf, 84%



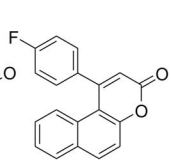
42c
X = Br, 82%
X = OTf, 86%



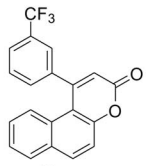
43c
X = Br, 83%
X = OTf, 85%



44c
X = Br, 82%

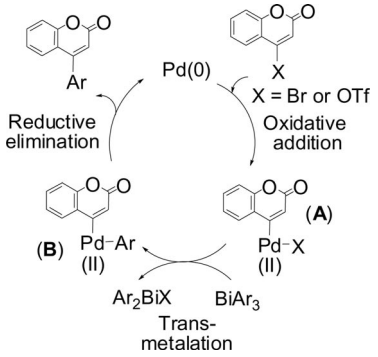


45c
X = Br, 81%
X = OTf, 89%



46c
X = Br, 80%

[a] Reagents and conditions: functionalized 4-bromo- or 4-(trifluoromethylsulfonyloxy)coumarin (0.825 mmol, 3.3 equiv.), $BiAr_3$ (0.25 mmol, 1.0 equiv.), $[PdCl_2(PPh_3)_2]$ (0.0225 mmol, 0.09 equiv.), K_3PO_4 (0.25 mmol, 1.0 equiv.), and DMA (3 mL), 90 °C, 2 h. [b] Isolated yields were calculated on the basis on the basis of all three aryl groups of the triarylbismuth compounds participating in the coupling reactions. Thus, 0.75 mmol of the product corresponds to a 100% yield. [c] Homocoupling biaryls were formed in all the reactions in minor amounts.



Scheme 2. Proposed catalytic cycle for the coupling reactions.

Conclusions

The palladium-catalyzed cross-coupling reactions of 4-bromo- and 4-(trifluoromethylsulfonyloxy)coumarins with triarylbismuth compounds have been investigated. The reactions demonstrate excellent reactivity under the established general catalytic conditions furnishing 4-arylcoumarins in excellent yields. Triarylbismuth compounds serve as atom-efficient multicoupling organometallic nucleophiles reacting efficiently with 3 equiv. of either 4-bromo- or 4-(trifluoromethylsulfonyloxy)coumarins to furnish 3 equiv. of 4-arylcoumarins. The reactions with triarylbismuth compounds as multicoupling organometallic nucleophiles proceeded smoothly in short reaction times to afford excellent yields of an array of functionalized 4-arylcoumarins.

Experimental Section

General: All reactions were carried out under nitrogen in oven-dried apparatus. All solvents were distilled following standard drying procedures. Commercially obtained materials were used without further purification. The bromo (**1a**–**5a**) and triflate (**1b**–**4b**) derivatives of coumarin were prepared following literature procedures starting from the corresponding 4-hydroxycoumarins.[5a,11] Triarylbismuth compounds were synthesized following literature procedures.[8a] GC analysis was carried out with a Perkin–Elmer Clarus-500 gas chromatograph. Analytical thin layer chromatography was performed on glass plates precoated with silica gel GF254 (Spectrochem, Mumbai) and the product spots were visualized with ultraviolet light. Column chromatography was performed with 60–120 silica gel (Acme, Mumbai) using ethyl acetate/petroleum ether as the eluent. Product purity was analyzed with a Waters-2996 HPLC chromatograph using 2-propanol/hexane as eluent and a Chiralcel OD-H column. The ^{1}H and ^{13}C NMR spectra were recorded with JEOL Lambda (400 MHz) and Delta (500 MHz) NMR spectrometers in $CDCl_3$. The chemical shifts (δ) for protons and carbon atoms are quoted in parts per million (ppm). The coupling constants (J) are expressed in hertz (Hz). The IR spectra were recorded with a Bruker Vector 22 FT-IR spectrometer and are reported in wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were recorded with Waters HAB213 and CAB155 micromass spectrometers using the electrospray (ES) and electroionization (EI) techniques.

Spectral Data for Coumarins 1a–5a and 1b–4b

4-Bromo-2*H*-chromen-2-one[11a] **(1a):** Colorless solid (76%, 2.11 g); m.p. 75–77 °C. ^{1}H NMR (500 MHz, $CDC1_3$): δ = 6.84 (s, 1 H, $CH_{alkenyl}$), 7.30–7.35 (m, 2 H, CH_{ar}), 7.57 (t, J = 7.4 Hz, 1 H, CH_{ar}), 7.82 (d, J = 8.0 Hz, 1 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDC1_3$): δ = 117.0, 119.0, 119.6, 125.0, 128.1, 133.2, 141.5, 152.5, 158.7 ppm. IR: $\tilde{\nu}_{max}$ = 1717, 1599, 1172, 915, 841, 766 cm^{-1}. HRMS (ES^+): calcd. for $C_9H_6BrO_2$ $[M + H]^+$ 224.9551, 226.9531; found 224.9556, 226.9534.

4-Bromo-6-methyl-2*H*-chromen-2-one (2a): Colorless solid (72%, 1.93 g); m.p. 78–80 °C. ^{1}H NMR (500 MHz, $CDC1_3$): δ = 2.42 (s, 3 H, CH_3), 6.81 (s, 1 H, $CH_{alkenyl}$), 7.18–7.21 (m, 1 H, CH_{ar}), 7.36 (d, J = 8.0 Hz, 1 H, CH_{ar}), 7.58 (s, 1 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDC1_3$): δ = 20.9, 116.8, 118.6, 119.5, 127.7, 134.2, 134.9, 141.5, 150.7, 159.0 ppm. IR: $\tilde{\nu}_{max}$ = 3073, 2919, 1715, 1562, 1341, 1173, 930, 851, 602 cm^{-1}. HRMS (ES^+): calcd. for $C_{10}H_8BrO_2$ $[M + H]^+$ 238.9708, 240.9687; found 238.9709, 240.9687.

4-Bromo-7-methyl-2*H*-chromen-2-one (3a): Pale-yellow solid (75%, 2.01 g); m.p. 124–126 °C. ^{1}H NMR (500 MHz, $CDC1_3$): δ = 2.44 (s, 3 H, CH_3), 6.50 (s, 1 H, $CH_{alkenyl}$), 7.14 (d, J = 9.1 Hz, 2 H, CH_{ar}), 7.69 (d, J = 8.0 Hz, 1 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDC1_3$): δ = 21.8, 114.3, 115.7, 117.1, 125.2, 126.0, 144.9, 149.8, 153.1, 159.4 ppm. IR: $\tilde{\nu}_{max}$ = 3064, 1739, 1351, 1137, 859, 786 cm^{-1}. HRMS (EI^+): calcd. for $C_{10}H_7BrO_2$ $[M]^+$ 237.9629, 239.9609; found 237.9629, 239.9611.

4-Bromo-5,7-dimethyl-2*H*-chromen-2-one (4a): Pale-yellow solid (67%, 1.78 g); m.p. 125–127 °C. ^{1}H NMR (500 MHz, $CDC1_3$): δ = 2.36 (s, 3 H, CH_3), 2.84 (s, 3 H, CH_3), 6.46 (s, 1 H, $CH_{alkenyl}$), 6.78 (s, 1 H, CH_{ar}), 7.01 (s, 1 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDC1_3$): δ = 21.3, 24.5, 115.7, 116.3, 120.4, 130.5, 137.4, 139.7, 143.4, 150.5, 154.1, 158.6 ppm. IR: $\tilde{\nu}_{max}$ = 2921, 1722, 1586, 1381, 882, 844 cm^{-1}. HRMS (ES^+): calcd. for $C_{11}H_{10}BrO_2$ $[M + H]^+$ 252.9864, 254.9844; found 252.9866, 254.9838.

1-Bromo-3*H*-benzo[*f*]chromen-3-one (5a): Pale-yellow solid (70%, 1.81 g); m.p. 126–128 °C. ^{1}H NMR (500 MHz, $CDC1_3$): δ = 6.91 (s, 1 H, $CH_{alkenyl}$), 7.34–7.38 (m, 1 H, CH_{ar}), 7.51 (t, J = 7.4 Hz, 1 H, CH_{ar}), 7.59–7.62 (m, 1 H, CH_{ar}), 7.82 (d, J = 8.0 Hz, 1 H, CH_{ar}), 7.94 (d, J = 8.5 Hz, 1 H, CH_{ar}), 9.47 (d, J = 8.6 Hz, 1 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDC1_3$): δ = 117.2, 117.3, 121.2, 124.6, 126.2, 127.8, 129.1, 129.4, 131.2, 135.2, 135.3, 138.6, 153.9, 158.2 ppm. IR: $\tilde{\nu}_{max}$ = 1721, 1537, 848, 819, 754 cm^{-1}. HRMS (ES^+): calcd. for $C_{13}H_8BrO_2$ $[M + H]^+$ 274.9708, 276.9687; found 274.9708, 276.9663.

2-Oxo-2*H*-chromen-4-yl Trifluoromethanesulfonate[5a] **(1b):** Pale-yellow solid (81%, 2.94 g) m.p. 54–56 °C. ^{1}H NMR (500 MHz, $CDC1_3$): δ = 6.49 (s, 1 H, $CH_{alkenyl}$), 7.38–7.44 (m, 2 H, CH_{ar}), 7.66–7.69 (m, 2 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDC1_3$): δ = 105.9, 113.9, 117.4, 122.6, 125.3, 134.2, 153.5, 157.2, 159.6 ppm. IR: $\tilde{\nu}_{max}$ = 3085, 1738, 1634, 1430, 1374, 1215, 1046, 874, 765 cm^{-1}. HRMS (ES^+): calcd. for $C_{10}H_6F_3O_5S$ $[M + H]^+$ 294.9888; found 294.9885.

6-Methyl-2-oxo-2*H*-chromen-4-yl Trifluoromethanesulfonate[11b] **(2b):** Pale-yellow solid (78%, 2.73 g); m.p. 84–87 °C. ^{1}H NMR (500 MHz, $CDC1_3$): δ = 2.40 (s, 3 H, CH_3), 6.41 (s, 1 H, $CH_{alkenyl}$), 7.20–7.26 (m, 1 H, CH_{ar}), 7.39–7.43 (m, 2 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDC1_3$): δ = 21.0, 105.7, 113.6, 117.2, 122.1, 135.3, 151.7, 157.2, 159.8 ppm. IR: $\tilde{\nu}_{max}$ = 3080, 2928, 1739, 1637, 1574, 1417, 1212, 1135, 840 cm^{-1}. HRMS (ES^+): calcd. for $C_{11}H_8F_3O_5S$ $[M + H]^+$ 309.0045; found 309.0045.

5,7-Dimethyl-2-oxo-2*H*-chromen-4-yl Trifluoromethanesulfonate (3b): Pale-yellow solid (75%, 2.55 g); m.p. 115–117 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.37 (s, 3 H, CH_3), 2.78 (s, 3 H, CH_3), 6.46 (s, 1 H, $CH_{alkenyl}$), 6.91 (s, 1 H, CH_{ar}), 7.01 (s, 1 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.3, 24.1, 114.1, 114.2, 115.7, 116.2, 117.5, 125.4, 130.3, 137.1, 143.6, 150.4, 154.7, 159.0 ppm. IR: $\tilde{\nu}_{max}$ = 3064, 2918, 1722, 1547, 1148, 874 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{12}H_{10}F_3O_5S$ [M + H]$^+$ 323.0201; found 323.0206.

3-Oxo-3*H*-benzo[*f*]chromen-1-yl Trifluoromethanesulfonate (4b): Pale-yellow solid (79%, 2.56 g); m.p. 113–115 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.66 (s, 1 H, $CH_{alkenyl}$), 7.42 (d, J = 8.8 Hz, 1 H, CH_{ar}), 7.56–7.59 (m, 1 H, CH_{ar}), 7.65–7.68 (m, 1 H, CH_{ar}), 7.88 (d, J = 8.0 Hz, 1 H, CH_{ar}), 8.00 (d, J = 8.8 Hz, 1 H, CH_{ar}), 9.38 (d, J = 9.2 Hz, 1 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 111.5, 116.7, 117.3, 124.8, 126.2, 128.4, 128.9, 129.5, 131.2, 135.3, 150.0, 154.6, 158.6 ppm. IR: $\tilde{\nu}_{max}$ = 3077, 1724, 1543, 1515, 782, 749 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{14}H_8F_3O_5S$ [M + H]$^+$ 345.0045; found 345.0049.

Representative Procedure for the Cross-Coupling Reactions of 4-Bromocoumarins with Triarylbismuth Compounds: An oven-dried Schlenk tube under nitrogen was charged with 4-bromocoumarin (185.6 mg, 0.825 mmol, 3.3 equiv.), $BiPh_3$ (110 mg, 0.25 mmol, 1 equiv.), K_3PO_4 (53.1 mg, 0.25 mmol, 1 equiv.), $[PdCl_2(PPh_3)_2]$ (15.8 mg, 0.0225 mmol, 0.09 equiv.), and dry DMA and the mixture was stirred at 90 °C for 2 h. Then the contents were cooled to room temperature and extracted with ethyl acetate, washed with dilute HCl (5 mL), water (5 mL), and brine (5 mL × 2), and dried with anhydrous $MgSO_4$. The solvent was concentrated on a rotary evaporator to give the crude product which by column chromatography afforded the desired product **1c** as a colorless solid (98%, 163.3 mg). The isolated yield was calculated on the basis that all three aryl groups of triphenylbismuth participate in the coupling reactions. Thus, 0.75 mmol of the product corresponds to a 100% yield.

Representative Procedure for the Cross-Coupling Reactions of 4-(Trifluoromethanesulfonyloxy)coumarins with Triarylbismuth Compounds: An oven-dried Schlenk tube under nitrogen was charged with 4-(trifluoromethylsulfonyloxy)coumarin (242.7 mg, 0.825 mmol, 3.3 equiv.), $BiPh_3$ (110 mg, 0.25 mmol, 1 equiv.), K_3PO_4 (53.1 mg, 0.25 mmol, 1 equiv.), $[PdCl_2(PPh_3)_2]$ (15.8 mg, 0.0225 mmol, 0.09 equiv.), and dry DMA and the mixture was stirred at 90 °C for 2 h. Then the contents were cooled to room temperature and extracted with ethyl acetate, washed with dilute HCl (5 mL), water (5 mL), and brine (5 mL × 2), and dried with anhydrous $MgSO_4$. Then the solvent was concentrated on a rotary evaporator to give the crude product, which, on column chromatography, afforded the desired product **1c** as a colorless solid (92%, 153.2 mg). The isolated yield was calculated on the basis that all three aryl groups of triphenylbismuth participate in the coupling reactions. Thus, 0.75 mmol of the product corresponds to a 100% yield.

4-Phenyl-2*H*-chromen-2-one[5g] (1c): Colorless solid (98%, 163.3 mg); m.p. 74–76 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.37 (s, 1 H, $CH_{alkenyl}$), 7.20–7.25 (m, 1 H, CH_{ar}), 7.39–7.56 (m, 8 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 115.2, 117.4, 119.0, 124.2, 127.1, 128.5, 129.7, 132.0, 135.2, 154.2, 155.7, 160.8 ppm. IR: $\tilde{\nu}_{max}$ = 1723, 1605, 1447, 1369, 1181, 937, 867, 816, 777 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{15}H_{11}O_2$ [M + H]$^+$ 223.0759; found 223.0759.

4-(*p*-Tolyl)-2*H*-chromen-2-one[12a] (2c): Colorless solid (95%, 168.3 mg); m.p. 94–96 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.44 (s, 3 H, CH_3), 6.35 (s, 1 H, $CH_{alkenyl}$), 7.20–7.25 (m, 1 H, CH_{ar}), 7.31–7.40 (m, 5 H, CH_{ar}), 7.52–7.55 (m, 2 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.4, 114.9, 117.4, 119.1, 124.2, 127.1, 128.5, 129.6, 131.9, 132.3, 140.0, 154.2, 155.8, 161.0 ppm. IR: $\tilde{\nu}_{max}$ = 2920, 1728, 1605, 1448, 1367, 1183, 930, 819, 708 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{16}H_{13}O_2$ [M + H]$^+$ 237.0916; found 237.0919.

4-(*m*-Tolyl)-2*H*-chromen-2-one[12a] (3c): Colorless solid (96%, 170.1 mg); m.p. 69–71 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.45 (s, 3 H, CH_3), 6.37 (s, 1 H, $CH_{alkenyl}$), 7.24 (t, J = 8.2 Hz, 3 H, CH_{ar}), 7.33 (d, J = 7.3 Hz, 1 H, CH_{ar}), 7.40 (d, J = 7.8 Hz, 2 H, CH_{ar}), 7.50–7.57 (m, 2 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.4, 115.0, 117.2, 119.0, 124.0, 125.5, 127.0, 128.6, 128.9, 130.3, 131.8, 135.1, 138.7, 154.1, 155.8, 160.7 ppm. IR: $\tilde{\nu}_{max}$ = 2919, 1728, 1604, 1448, 1367, 1251, 1179, 935, 868, 751 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{16}H_{13}O_3$ [M + H]$^+$ 237.0916; found 237.0916.

4-(4-Methoxyphenyl)-2*H*-chromen-2-one[12a] (4c): Colorless solid (97%, 183.5 mg); m.p. 116–118 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.87 (s, 3 H, OCH_3), 6.33 (s, 1 H, $CH_{alkenyl}$), 7.03 (d, J = 8.6 Hz, 1 H, CH_{ar}), 7.20–7.25 (m, 2 H, CH_{ar}), 7.39 (t, J = 8.4 Hz, 3 H, CH_{ar}), 7.51–7.55 (m, 2 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.5, 114.4, 114.6, 117.4, 119.2, 124.1, 127.1, 127.5, 130.0, 131.9, 154.3, 155.4, 160.9, 161.0 ppm. IR: $\tilde{\nu}_{max}$ = 2932, 2838, 1726, 1605, 1510, 1368, 1247, 1180, 1030, 930, 867, 772 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{16}H_{13}O_3$ [M + H]$^+$ 253.0865; found 253.0866.

4-(3-Methoxyphenyl)-2*H*-chromen-2-one[12b] (5c): Pale-yellow solid (94%, 177.8 mg); m.p. 134–136 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.85 (s, 3 H, OCH_3), 6.37 (s, 1 H, $CH_{alkenyl}$), 7.01–7.05 (m, 2 H, CH_{ar}), 7.21–7.25 (m, 1 H, CH_{ar}), 7.37–7.44 (m, 2 H, CH_{ar}), 7.51–7.56 (m, 2 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.5, 114.1, 115.1, 115.2, 117.4, 119.0, 120.8, 124.2, 127.1, 130.1, 132.0, 136.5, 154.2, 155.6, 159.8, 160.8 ppm. IR: $\tilde{\nu}_{max}$ = 3070, 2938, 2837, 1728, 1603, 1449, 1181, 1037, 935, 862, 752, 716 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{16}H_{13}O_3$ [M + H]$^+$ 253.0865; found 253.0867.

4-(4-Ethoxyphenyl)-2*H*-chromen-2-one (6c): Colorless solid (90%, 179.7 mg); m.p. 94–96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.47 (t, J = 7.0 Hz, 3 H, CH_3), 4.12 (q, J = 7.0 Hz, 2 H, OCH_2), 6.35 (s, 1 H, $CH_{alkenyl}$), 7.03 (d, J = 8.5 Hz, 2 H, CH_{ar}), 7.22–7.26 (m, 1 H, CH_{ar}), 7.36 (s, 1 H, CH_{ar}), 7.40 (d, J = 8.5 Hz, 2 H, CH_{ar}), 7.52–7.58 (m, 2 H, CH_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.7, 63.6, 114.5, 114.7, 117.3, 119.1, 124.0, 127.0, 127.2, 128.2, 129.9, 131.7, 154.2, 155.3, 160.2, 160.9 ppm. IR: $\tilde{\nu}_{max}$ = 3071, 2979, 2930, 1727, 1607, 1510, 1368, 1245, 1180, 1117, 1044, 929, 839, 752 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{17}H_{15}O_3$ [M + H]$^+$ 267.1021; found 267.1020.

4-(4-Isopropoxyphenyl)-2*H*-chromen-2-one (7c): Colorless solid (93%, 195.5 mg); m.p. 123–125 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.40 [d, J = 5.8 Hz, 6 H, $C(CH_3)_2$], 4.61–4.67 (m, 1 H, OCH), 6.35 (s, 1 H, $CH_{alkenyl}$), 7.02 (d, J = 8.8 Hz, 2 H, CH_{ar}), 7.22–7.26 (m, 1 H, CH_{ar}), 7.35–7.41 (m, 3 H, CH_{ar}), 7.52–7.60 (m, 2 H, CH_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.9, 70.0, 114.4, 115.8, 117.3, 119.1, 124.0, 127.0, 129.9, 131.7, 154.2, 155.3, 159.2, 160.9 ppm. IR: $\tilde{\nu}_{max}$ = 2976, 2923, 1725, 1605, 1368, 1244, 1182, 1118, 930, 814 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{19}H_{17}O_3$ [M + H]$^+$ 281.1178; found 281.1175.

4-(4-Butoxyphenyl)-2*H*-chromen-2-one[12c] (8c): Pale-yellow solid (91%, 200.8 mg); m.p. 52–54 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.01 (t, J = 7.3 Hz, 3 H, CH_3), 1.49–1.62 (m, 2 H, CH_2), 1.79–1.86 (m, 2 H, CH_2), 4.05 (t, J = 6.6 Hz, 2 H, OCH_2), 6.35 (s, 1 H, $CH_{alkenyl}$), 7.03 (d, J = 8.7 Hz, 2 H, CH_{ar}), 7.21–7.26 (m, 1 H,

CH_{ar}), 7.39–7.41 (d, J = 8.5 Hz, 3 H, CH_{ar}), 7.52–7.58 (m, 2 H, CH_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 19.2, 31.2, 67.8, 114.5, 114.7, 117.3, 119.1, 124.0, 127.0, 127.1, 129.8, 131.7, 154.2, 155.3, 160.4 ppm. IR: $\tilde{\nu}_{max}$ = 2958, 2933, 2872, 1727, 1606, 1510, 1368, 1245, 1179, 1117, 929, 837, 753 cm^{-1}. HRMS (ES^+): calcd. for $C_{19}H_{19}O_3$ $[M + H]^+$ 295.1334; found 295.1333.

4-(4-*sec*-Butoxyphenyl)-2*H*-chromen-2-one (9c): Pale-yellow solid (94%, 207.5 mg); m.p. 92–94 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.02 (t, J = 7.3 Hz, 3 H, CH_3), 1.35 (d, J = 5.6 Hz, 3 H, CH_3), 1.64–1.85 (m, 2 H, CH_2), 4.36–4.43 (m, 1 H, OCH), 6.35 (s, 1 H, $CH_{alkenyl}$), 7.01 (d, J = 8.5 Hz, 2 H, CH_{ar}), 7.22–7.26 (m, 1 H, CH_{ar}), 7.39 (dd, J = 1.9, 8.6 Hz, 3 H, CH_{ar}), 7.52–7.60 (m, 2 H, CH_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.7, 19.1, 29.1, 75.1, 114.4, 114.5, 115.8, 117.2, 119.1, 124.0, 126.9, 127.0, 129.9, 131.7, 154.2, 155.3, 159.5, 160.9 ppm. IR: $\tilde{\nu}_{max}$ = 2959, 2872, 1725, 1606, 1469, 1368, 1245, 1141, 1117, 867, 835, 752 cm^{-1}. HRMS (ES^+): calcd. for $C_{19}H_{19}O_3$ $[M + H]^+$ 295.1334; found 295.1333.

4-(4-Isobutoxyphenyl)-2*H*-chromen-2-one (10c): Yellow oil (92%, 203.1 mg). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.06 [d, J = 6.7 Hz, 6 H, $C(CH_3)_2$], 2.11–2.17 (m, 1 H, CH), 3.80 (d, J = 6.5 Hz, 2 H, OCH_2), 6.35 (s, 1 H, $CH_{alkenyl}$), 7.04 (d, J = 8.4 Hz, 2 H, CH_{ar}), 7.22–7.26 (m, 1 H, CH_{ar}), 7.40 (d, J = 8.4 Hz, 3 H, CH_{ar}), 7.53–7.58 (m, 2 H, CH_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.2, 28.2, 74.5, 114.5, 114.8, 117.3, 119.1, 124.0, 127.0, 127.1, 129.8, 131.7, 154.2, 155.4, 160.5, 160.9 ppm. IR: $\tilde{\nu}_{max}$ = 2971, 2932, 1725, 1605, 1507, 1368, 1245, 1180, 1117, 928, 837, 752 cm^{-1}. HRMS (ES^+): calcd. for $C_{19}H_{19}O_3$ $[M + H]^+$ 295.1334; found 295.1334.

4-(4-Chlorophenyl)-2*H*-chromen-2-one[12a] **(11c):** Pale-yellow solid (90%, 173.2 mg); m.p. 164–166 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 6.35 (s, 1 H, $CH_{alkenyl}$), 7.21–7.25 (m, 1 H, CH_{ar}), 7.34–7.44 (m, 4 H, CH_{ar}), 7.49–7.51 (m, 2 H, CH_{ar}), 7.53–7.57 (m, 1 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 115.3, 117.4, 118.6, 124.2, 126.6, 129.2, 129.7, 132.1, 133.5, 135.9, 154.1, 154.4, 160.4 ppm. IR: $\tilde{\nu}_{max}$ = 3070, 2922, 2853, 1720, 1604, 1363, 1181, 1104, 940, 836, 750 cm^{-1}. HRMS (ES^+): calcd. for $C_{15}H_{10}ClO_2$ $[M + H]^+$ 257.0369; found 257.0365.

4-(3-Chlorophenyl)-2*H*-chromen-2-one (12c): Pale-yellow solid (92%, 176.9 mg); m.p.122–124 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.29 (s, 1 H, $CH_{alkenyl}$), 7.16–7.20 (m, 1 H, CH_{ar}), 7.26 (d, J = 7.0 Hz, 1 H, CH_{ar}), 7.33–7.53 (m, 6 H, CH_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 115.5, 117.4, 118.5, 124.3, 126.5, 126.6, 128.4, 129.7, 130.2, 132.1, 134.9, 136.8, 154.0, 160.3 ppm. IR: $\tilde{\nu}_{max}$ = 2919, 1728, 1605, 1559, 1367, 1181, 936, 868, 751 cm^{-1}. HRMS (ES^+): calcd. for $C_{15}H_{10}ClO_2$ $[M + H]^+$ 257.0369; found 257.0369.

4-(4-Fluorophenyl)-2*H*-chromen-2-one[5q] **(13c):** Pale-yellow solid (93%, 167.6 mg); m.p. 140–142 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 6.34 (s, 1 H, $CH_{alkenyl}$), 7.19–7.25 (m, 3 H, CH_{ar}), 7.38–7.46 (m, 4 H, CH_{ar}), 7.53–7.56 (m, 1 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 115.3, 116.0 (d, J = 21.4 Hz) 117.3, 118.8, 124.2, 126.7, 130.3 (d, J = 8.3 Hz), 131.1, 132.0, 154.1, 154.5, 160.5, 163.5 (d, J = 249.1 Hz) ppm. IR: $\tilde{\nu}_{max}$ = 2919, 2850, 1741, 1606, 1018, 943, 841, 752 cm^{-1}. HRMS (ES^+): calcd. for $C_{15}H_{10}FO_2$ $[M + H]^+$ 241.0665; found 241.0688.

4-[3-(Trifluoromethyl)phenyl]-2*H*-chromen-2-one[12b] **(14c):** Pale-yellow solid (89%, 193.7 mg); m.p. 112–114 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 6.33 (s, 1 H, $CH_{alkenyl}$), 7.17–7.20 (m, 1 H, CH_{ar}), 7.30 (dd, J = 1.5, 8.0 Hz, 1 H, CH_{ar}), 7.36 (d, J = 8.4 Hz, 1 H, CH_{ar}), 7.49–7.53 (m, 1 H, CH_{ar}), 7.57–7.65 (m, 3 H, CH_{ar}), 7.73 (d, J = 7.6 Hz, 1 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 116.0, 117.6, 118.6, 124.5, 125.3, 126.5, 129.6, 131.4, 131.7, 131.8, 132.4, 136.0, 154.1, 154.2, 160.3 ppm. IR: $\tilde{\nu}_{max}$ = 3074, 1729, 1607, 1331, 1163, 1114, 944, 810 cm^{-1}. HRMS (ES^+): calcd. for $C_{16}H_{10}F_3O_2$ $[M + H]^+$ 291.0633; found 291.0636.

6-Methyl-4-phenyl-2*H*-chromen-2-one[6h] **(15c):** Colorless solid (97%, 171.9 mg); m.p. 114–116 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.32 (s, 3 H, CH_3), 6.34 (s, 1 H, $CH_{alkenyl}$), 7.24–7.35 (m, 3 H, CH_{ar}), 7.42–7.45 (m, 2 H, CH_{ar}), 7.52 (t, J = 3.8 Hz, 3 H, CH_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9, 115.1, 117.0, 118.6, 126.6, 128.3, 128.8, 129.5, 132.8, 133.8, 135.3, 152.3, 155.5, 160.9 ppm. IR: $\tilde{\nu}_{max}$ = 3061, 2922, 1725, 1615, 1565, 1310, 1180, 941, 815, 774, 702 cm^{-1}. HRMS (ES^+): calcd. for $C_{16}H_{13}O_2$ $[M + H]^+$ 237.0916; found 237.0916.

6-Methyl-4-(*p*-tolyl)-2*H*-chromen-2-one (16c): Colorless solid (98%, 184.0 mg); m.p. 74–76 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.31 (s, 3 H, CH_3), 2.44 (s, 3 H, CH_3), 6.30 (s, 1 H, $CH_{alkenyl}$), 7.27 (d, J = 8.2 Hz, 2 H, CH_{ar}), 7.32 (s, 5 H, CH_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9, 21.3, 114.8, 116.9, 118.7, 126.7, 128.3, 129.5, 132.4, 132.7, 139.7, 152.3, 155.6, 161.0 ppm. IR: $\tilde{\nu}_{max}$ = 2921, 1726, 1615, 1566, 1419, 1362, 1255, 1181, 932, 818 cm^{-1}. HRMS (ES^+): calcd. for $C_{17}H_{15}O_2$ $[M + H]^+$ 251.1072; found 251.1073.

4-(4-Methoxyphenyl)-6-methyl-2*H*-chromen-2-one[5q] **(17c):** Colorless solid (92%, 183.7 mg); m.p. 90–92 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.32 (s, 3 H, CH_3), 3.87 (s, 3 H, OCH_3), 6.29 (s, 1 H, $CH_{alkenyl}$), 7.03 (dd, J = 1.9, 6.7 Hz, 2 H, CH_{ar}), 7.24–7.33 (m, 3 H, CH_{ar}), 7.38 (dd, J = 1.9, 6.5 Hz, 2 H, CH_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9, 55.3, 114.2, 114.5, 117.0, 118.8, 126.7, 127.5, 129.8, 132.7, 133.7, 152.3, 155.2, 160.7, 161.1 ppm. IR: $\tilde{\nu}_{max}$ = 2929, 2838, 1724, 1609, 1511, 1362, 1249, 1029, 933, 817 cm^{-1}. HRMS (ES^+): calcd. for $C_{17}H_{15}O_3$ $[M + H]^+$ 267.1021; found 267.1021.

4-(3-Methoxyphenyl)-6-methyl-2*H*-chromen-2-one (18c): Pale-yellow solid (94%, 187.7 mg); m.p. 97–99 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.31 (s, 3 H, CH_3), 3.84 (s, 3 H, OCH_3), 6.32 (s, 1 H, $CH_{alkenyl}$), 6.93–7.05 (m, 3 H, CH_{ar}), 7.24–7.34 (m, 3 H, CH_{ar}), 7.42 (t, J = 7.7 Hz, 1 H, CH_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9, 55.4, 114.0, 114.9, 115.0, 116.9, 118.6, 120.7, 126.6, 129.9, 132.8, 133.8, 136.6, 152.2, 155.4, 159.7, 160.9 ppm. IR: $\tilde{\nu}_{max}$ = 2922, 1729, 1568, 1485, 1430, 1288, 1227, 1174, 1045, 937, 819 cm^{-1}. HRMS (ES^+): calcd. for $C_{17}H_{15}O_3$ $[M + H]^+$ 267.1021; found 267.1024.

4-(4-Isopropoxyphenyl)-6-methyl-2*H*-chromen-2-one (19c): Colorless solid (90%, 198.7 mg); m.p. 85–87 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.38 [d, J = 5.8 Hz, 6 H, $C(CH_3)_2$], 2.32 (s, 3 H, CH_3), 4.59–4.65 (m, 1 H, OCH), 6.29 (s, 1 H, $CH_{alkenyl}$), 7.00 (d, J = 8.8 Hz, 2 H, CH_{ar}), 7.24–7.37 (m, 5 H, CH_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.0, 70.0, 114.4, 115.7, 117.0, 118.8, 126.7, 129.9, 132.7, 133.6, 152.3, 155.3, 159.1 ppm. IR: $\tilde{\nu}_{max}$ = 2978, 2921, 1727, 1614, 1568, 1506, 1245, 1174, 1114, 937, 818 cm^{-1}. HRMS (ES^+): calcd. for $C_{19}H_{19}O_3$ $[M + H]^+$ 295.1334; found 295.1333.

4-(4-*n*-Butoxyphenyl)-6-methyl-2*H*-chromen-2-one (20c): Pale-yellow solid (92%, 212.8 mg); m.p. 62–64 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.98 (t, J = 7.3 Hz, 3 H, CH_3), 1.48–1.54 (m, 2 H, CH_2), 1.76–1.82 (m, 2 H, CH_2), 2.32 (s, 3 H, CH_3), 4.02 (t, J = 6.6 Hz, 2 H, OCH_2), 6.29 (s, 1 H, $CH_{alkenyl}$), 7.01 (d, J = 8.5 Hz, 2 H, CH_{ar}), 7.24–7.33 (m, 3 H, CH_{ar}), 7.36 (d, J = 8.5 Hz, 2 H, CH_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 19.2, 20.9, 31.2, 67.8, 114.5, 114.7, 117.0, 118.8, 126.7, 127.3, 129.8, 132.7, 133.6, 152.3, 155.3, 160.3, 161.1 ppm. IR: $\tilde{\nu}_{max}$ = 2957, 2871, 1725, 1608, 1510, 1248, 1179, 933, 819 cm^{-1}. HRMS (ES^+): calcd. for $C_{20}H_{21}O_3$ $[M + H]^+$ 309.1491; found 309.1491.

4-(4-*sec*-Butoxyphenyl)-6-methyl-2*H*-chromen-2-one (21c): Yellow oil (85%, 196.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.99 (t, J = 7.4 Hz, 3 H, CH_3), 1.32 (d, J = 6.1 Hz, 3 H, CH_3), 1.61–1.80 (m, 2 H, CH_2), 2.31 (s, 3 H, CH_3), 4.35–4.39 (m, 1 H, OCH), 6.28 (s, 1 H, $CH_{alkenyl}$), 6.97–7.00 (m, 2 H, CH_{ar}), 7.25 (s, 1 H, CH_{ar}), 7.29–7.31 (m, 2 H, CH_{ar}), 7.33–7.36 (m, 2 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 9.7, 19.1, 20.8, 29.0, 75.1, 114.3, 115.7, 116.9, 118.7, 126.7, 129.8, 132.6, 133.6, 152.2, 155.3, 159.4, 161.1 ppm. IR: $\tilde{\nu}_{max}$ = 2969, 2923, 1723, 1604, 1246, 1121, 1020, 818 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{20}H_{21}O_3$ [M + H]$^+$ 309.1491; found 309.1491.

4-(4-Isobutoxyphenyl)-6-methyl-2*H*-chromen-2-one (22c): Pale-yellow solid (82%, 189.6 mg); m.p. 88–90 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.03 [d, J = 6.9 Hz, 6 H, $C(CH_3)_2$], 2.07–2.15 (m, 1 H, CH), 2.31 (s, 3 H, CH_3), 3.77 (d, J = 6.5 Hz, 2 H, OCH_2), 6.29 (s, 1 H, $CH_{alkenyl}$), 7.02 (dd, J = 1.9, 6.8 Hz, 2 H, CH_{ar}), 7.26 (d, J = 8.0 Hz, 1 H, CH_{ar}), 7.30 (s, 1 H, CH_{ar}), 7.32 (s, 1 H, CH_{ar}), 7.36 (dd, J = 1.9, 6.5 Hz, 2 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.2, 20.9, 28.2, 74.5, 114.4, 114.7, 117.0, 118.8, 126.7, 127.2, 129.8, 132.7, 133.6, 152.3, 155.3, 160.4, 161.1 ppm. IR: $\tilde{\nu}_{max}$ = 2959, 2924, 2871, 1724, 1608, 1569, 1510, 1363, 1247, 1177, 1028, 933, 819 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{20}H_{21}O_3$ [M + H]$^+$ 309.1491; found 309.1493.

4-(4-Fluorophenyl)-6-methyl-2*H*-chromen-2-one[5q] **(23c):** Pale-yellow solid (95%, 181.2 mg); m.p. 158–160 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.27 (s, 3 H, CH_3), 6.25 (s, 1 H, $CH_{alkenyl}$), 7.12–7.18 (m, 3 H, CH_{ar}), 7.22 (d, J = 8.4 Hz, 1 H, CH_{ar}), 7.29 (dd, J = 1.9, 8.4 Hz, 1 H, CH_{ar}), 7.35–7.38 (m, 2 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.9, 115.2, 115.3, 116.0 (d, J = 21.5 Hz), 117.1, 118.5, 126.4 (d, J = 4.7 Hz), 130.3 (d, J = 8.3 Hz), 131.2, 133.0, 133.9, 152.2, 154.5, 160.7, 163.4 (d, J = 249.1 Hz) ppm. IR: $\tilde{\nu}_{max}$ = 2922, 2852, 1721, 1603, 1507, 1316, 1225, 1183, 938, 819 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{16}H_{12}FO_2$ [M + H]$^+$ 255.0821; found 255.0821.

7-Methyl-4-phenyl-2*H*-chromen-2-one[6h] **(24c):** Colorless solid (86%, 152.3 mg); m.p. 59–61 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.47 (s, 3 H, CH_3), 6.29 (s, 1 H, $CH_{alkenyl}$), 7.01 (d, J = 8.0 Hz, 1 H, CH_{ar}), 7.19 (s, 1 H, CH_{ar}), 7.34 (d, J = 8.0 Hz, 1 H, CH_{ar}), 7.41–7.43 (m, 2 H, CH_{ar}), 7.49 (t, J = 3.1 Hz, 3 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.5, 114.0, 116.5, 117.4, 125.3, 126.6, 128.4, 128.8, 129.5, 135.4, 143.1, 154.2, 155.6, 161.0 ppm. IR: $\tilde{\nu}_{max}$ = 2920, 1728, 1614, 1371, 860, 819, 707 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{16}H_{13}O_2$ [M + H]$^+$ 237.0916; found 237.0918.

4-(4-Methoxyphenyl)-7-methyl-2*H*-chromen-2-one (25c): Colorless solid (88%, 175.7 mg); m.p. 133–135 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.49 (s, 3 H, CH_3), 3.92 (s, 3 H, OCH_3), 6.31 (s, 1 H, $CH_{alkenyl}$), 7.07 (d, J = 8.7 Hz, 3 H, CH_{ar}), 7.24 (s, 1 H, CH_{ar}), 7.42–7.47 (m, 3 H, CH_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5, 55.3, 113.4, 114.2, 116.6, 117.4, 125.2, 126.6, 127.6, 129.8, 143.0, 150.7, 154.3, 155.3, 160.7, 161.1 ppm. IR: $\tilde{\nu}_{max}$ = 2922, 2850, 1729, 1608, 1512, 1373, 1255, 1026, 823 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{17}H_{15}O_3$ [M + H]$^+$ 267.1021; found 267.1021.

4-(3-Methoxyphenyl)-7-methyl-2*H*-chromen-2-one (26c): Pale-yellow solid (91%, 181.7 mg); m.p. 83–85 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.49 (s, 3 H, CH_3), 3.89 (s, 3 H, OCH_3), 6.34 (s, 1 H, $CH_{alkenyl}$), 6.99–7.08 (m, 4 H, CH_{ar}), 7.24 (s, 1 H, CH_{ar}), 7.42–7.47 (m, 2 H, CH_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5, 55.3, 113.9, 114.9, 116.4, 117.3, 120.6, 125.3, 126.6, 129.8, 136.6, 143.1, 154.2, 155.4, 159.7, 161.0 ppm. IR: $\tilde{\nu}_{max}$ = 2922, 1729, 1592, 1372, 1221, 1039, 877, 812 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{17}H_{15}O_3$ [M + H]$^+$ 267.1021; found 267.1021.

5,7-Dimethyl-4-phenyl-2*H*-chromen-2-one[6h] **(27c):** Yellow oil (88%, 165.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.76 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 6.14 (s, 1 H, $CH_{alkenyl}$), 6.80 (s, 1 H, CH_{ar}), 7.05 (s, 1 H, CH_{ar}), 7.24–7.26 (m, 2 H, CH_{ar}), 7.41–7.42 (m, 3 H, CH_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 23.2, 115.5, 115.8, 116.1, 127.3, 128.5, 128.6, 129.4, 137.0, 139.6, 142.3, 155.2, 156.7, 160.4 ppm. IR: $\tilde{\nu}_{max}$ = 2924, 1730, 1617, 1445, 1317, 1203, 1159, 1069, 851, 775, 707 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{17}H_{15}O_2$ [M + H]$^+$ 251.1072; found 251.1071.

5,7-Dimethyl-4-(*p*-tolyl)-2*H*-chromen-2-one (28c): Colorless solid (91%, 180.4 mg); m.p. 122–124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.81 (s, 3 H, CH_3), 2.38 (s, 3 H, CH_3), 2.42 (s, 3 H, CH_3), 6.15 (s, 1 H, $CH_{alkenyl}$), 6.83 (s, 1 H, CH_{ar}), 7.07 (s, 1 H, CH_{ar}), 7.15 (d, J = 7.9 Hz, 2 H, CH_{ar}), 7.24 (d, J = 7.8 Hz, 2 H, CH_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 23.3, 115.7, 116.0, 127.2, 129.1, 129.3, 136.6, 137.0, 138.6, 142.1, 155.1, 156.9, 160.5 ppm. IR: $\tilde{\nu}_{max}$ = 2923, 1724, 1598, 1444, 1317, 1203, 1129, 1033, 937, 849, 821 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{18}H_{17}O_2$ [M + H]$^+$ 265.1229; found 265.1229.

4-(4-Methoxyphenyl)-5,7-dimethyl-2*H*-chromen-2-one (29c): Colorless solid (86%, 180.8 mg); m.p. 126–128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.84 (s, 3 H, CH_3), 2.38 (s, 3 H, CH_3), 3.87 (s, 3 H, OCH_3), 6.16 (s, 1 H, $CH_{alkenyl}$), 6.83 (s, 1 H, CH_{ar}), 6.95–6.97 (m, 2 H, CH_{ar}), 7.07 (s, 1 H, CH_{ar}), 7.18–7.26 (m, 2 H, CH_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 23.4, 55.3, 113.9, 115.7, 115.8, 116.1, 128.6, 129.4, 131.8, 137.0, 142.1, 155.2, 156.6, 160.0, 160.6 ppm. IR: $\tilde{\nu}_{max}$ = 2923, 1721, 1611, 1510, 1443, 1247, 1030, 836 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{18}H_{17}O_3$ [M + H]$^+$ 281.1178; found 281.1177.

4-(3-Methoxyphenyl)-5,7-dimethyl-2*H*-chromen-2-one (30c): Yellow oil (89%, 187.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.75 (s, 3 H, CH_3), 2.29 (s, 3 H, CH_3), 3.74 (s, 3 H, OCH_3), 6.09 (s, 1 H, $CH_{alkenyl}$), 6.71–6.78 (m, 3 H, CH_{ar}), 6.87–6.90 (m, 1 H, CH_{ar}), 6.98 (s, 1 H, CH_{ar}), 7.24–7.27 (m, 1 H, CH_{ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 22.9, 55.3, 113.1, 114.1, 115.4, 115.8, 115.9, 119.7, 129.4, 129.7, 137.0, 140.8, 142.2, 155.1, 156.4, 159.6, 160.4 ppm. IR: $\tilde{\nu}_{max}$ = 2925, 1726, 1595, 1445, 1286, 1158, 1042, 851, 797, 721 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{18}H_{17}O_3$ [M + H]$^+$ 281.1178; found 281.1178.

4-(4-Isopropoxyphenyl)-5,7-dimethyl-2*H*-chromen-2-one (31c): Pale-yellow solid (91%, 210.5 mg); m.p. 102–104 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.35 [d, J = 6.1 Hz, 6 H, $C(CH_3)_2$], 1.82 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 4.55–4.62 (m, 1 H, OCH), 6.14 (s, 1 H, $CH_{alkenyl}$), 6.81 (s, 1 H, CH_{ar}), 6.90–6.93 (m, 2 H, CH_{ar}), 7.04 (s, 1 H, CH_{ar}), 7.13–7.16 (m, 2 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.2, 21.9, 23.4, 70.03, 115.6, 115.8, 116.0, 128.6, 129.4, 131.5, 137.1, 142.1, 155.1, 156.7, 158.3, 160.7 ppm. IR: $\tilde{\nu}_{max}$ = 2975, 2925, 1724, 1611, 1507, 1444, 1355, 1244, 1119, 951, 839 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{20}H_{21}O_3$ [M + H]$^+$ 309.1491; found 309.1491.

4-(4-Butoxyphenyl)-5,7-dimethyl-2*H*-chromen-2-one (32c): Colorless solid (88%, 212.7 mg); m.p. 86–88 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.97 (t, J = 7.2 Hz, 3 H, CH_3), 1.48–1.52 (m, 2 H, CH_2), 1.76–1.81 (m, 2 H, CH_2), 1.82 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 3.99 (t, J = 6.5 Hz, 2 H, OCH_2), 6.14 (s, 1 H, $CH_{alkenyl}$), 6.81 (s, 1 H, CH_{ar}), 6.93 (dd, J = 2.3, 6.5 Hz, 2 H, CH_{ar}), 7.04 (s, 1 H, CH_{ar}), 7.15 (dd, J = 2.3, 6.4 Hz, 2 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8, 19.2, 21.2, 23.4, 31.2, 67.8, 114.4, 115.7, 115.8, 116.0, 116.1, 128.6, 129.4, 131.6, 137.1, 142.1, 155.2, 156.7, 159.6, 160.7 ppm. IR: $\tilde{\nu}_{max}$ = 2957, 2929, 2870, 1723, 1611, 1509, 1444, 1245, 1028, 836 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{21}H_{23}O_3$ [M + H]$^+$ 323.1647; found 323.1646.

4-(4-*sec*-Butoxyphenyl)-5,7-dimethyl-2*H*-chromen-2-one (33c): Pale-yellow solid (82%, 198.3 mg); m.p. 62–64 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.99 (t, J = 7.4 Hz, 3 H, CH_3), 1.31 (d, J = 6.1 Hz, 3 H, CH_3), 1.60–1.80 (m, 2 H, CH_2), 1.84 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 4.33–4.36 (m, 1 H, OCH), 6.15 (s, 1 H, $CH_{alkenyl}$), 6.82 (s, 1 H, CH_{ar}), 6.93 (dd, J = 1.9, 6.5 Hz, 2 H, CH_{ar}), 7.05 (s, 1 H, CH_{ar}), 7.15 (dd, J = 2.3, 6.6 Hz, 2 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 9.7, 19.1, 21.2, 23.4, 29.0, 75.1, 115.6, 115.8, 115.9, 128.6, 129.4, 131.4, 137.1, 142.1, 155.1, 156.7, 158.6, 160.7 ppm. IR: $\tilde{\nu}_{max}$ = 2971, 2930, 1723, 1610, 1444, 1243, 844 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{21}H_{23}O_3$ [M + H]$^+$ 323.1647; found 323.1646.

4-(4-Isobutoxyphenyl)-5,7-dimethyl-2*H*-chromen-2-one (34c): Pale-yellow solid (84%, 203.1 mg); m.p. 108–110 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.03 [d, J = 6.8 Hz, 6 H, $C(CH_3)_2$], 1.83 (s, 3 H, CH_3), 2.06–2.14 (m, 1 H, CH), 2.36 (s, 3 H, CH_3), 3.75 (d, J = 6.3 Hz, 2 H, OCH_2), 6.14 (s, 1 H, $CH_{alkenyl}$), 6.82 (s, 1 H, CH_{ar}), 6.94 (dd, J = 2.0, 6.8 Hz, 2 H, CH_{ar}), 7.05 (s, 1 H, CH_{ar}), 7.16 (dd, J = 2.2, 6.7 Hz, 2 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.3, 21.3, 23.5, 28.3, 74.6, 114.6, 115.8, 115.9, 116.1, 128.7, 129.5, 131.7, 137.2, 142.2, 155.3, 156.8, 159.8, 160.8 ppm. IR: $\tilde{\nu}_{max}$ = 2959, 1722, 1610, 1508, 1244, 1028, 835 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{21}H_{23}O_3$ [M + H]$^+$ 323.1647; found 323.1647.

4-(4-Fluorophenyl)-5,7-dimethyl-2*H*-chromen-2-one (35c): Pale-yellow solid (91%, 183.1 mg); m.p. 96–98 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.78 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 6.14 (s, 1 H, $CH_{alkenyl}$), 6.82 (s, 1 H, CH_{ar}), 7.06 (s, 1 H, CH_{ar}), 7.13 (t, J = 8.4 Hz, 2 H, CH_{ar}), 7.24–7.26 (m, 2 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.3, 23.4, 115.4, 115.7 (d, J = 21.4 Hz), 115.8, 116.4, 116.4, 129.2 (d, J = 7.1 Hz), 129.5, 135.5, 136.7, 142.5, 155.1, 155.6, 160.3, 162.9 (d, J = 246.8 Hz) ppm. IR: $\tilde{\nu}_{max}$ = 2957, 2928, 2868, 1723, 1612, 1508, 1407, 1355, 1242, 1159, 1068, 841 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{17}H_{14}FO_2$ [M + H]$^+$ 269.0978; found 269.0979.

1-Phenyl-3*H*-benzo[*f*]chromen-3-one[12d] (36c): Pale-yellow solid (86%, 175.6 mg); m.p. 135–137 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.38 (s, 1 H, $CH_{alkenyl}$), 7.12–7.16 (m, 1 H, CH_{ar}), 7.23 (d, J = 6.9 Hz, 1 H, CH_{ar}), 7.35–7.41 (m, 3 H, CH_{ar}), 7.48–7.53 (m, 4 H, CH_{ar}), 7.83 (d, J = 8.0 Hz, 1 H, CH_{ar}), 7.99 (d, J = 8.7 Hz, 1 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 112.9, 116.7, 116.7, 117.3, 125.3, 125.8, 126.6, 127.3, 128.9, 129.0, 129.1, 129.2, 131.2, 133.9, 139.4, 154.6, 156.4, 160.3 ppm. IR: $\tilde{\nu}_{max}$ = 1730, 1546, 1513, 996, 819, 700 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{19}H_{13}O_2$ [M + H]$^+$ 273.0916; found 273.0915.

1-(*p*-Tolyl)-3*H*-benzo[*f*]chromen-3-one (37c): Pale-yellow solid (80%, 171.8 mg); m.p. 95–97 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.46 (s, 3 H, CH_3), 6.35 (s, 1 H, $CH_{alkenyl}$), 7.14–7.18 (m, 2 H, CH_{ar}), 7.22–7.24 (m, 2 H, CH_{ar}), 7.28 (d, J = 8.0 Hz, 1 H, CH_{ar}), 7.33 (d, J = 8.8 Hz, 1 H, CH_{ar}), 7.37–7.40 (m, 1 H, CH_{ar}), 7.50 (d, J = 9.2 Hz, 1 H, CH_{ar}), 7.82 (d, J = 8.0 Hz, 1 H, CH_{ar}), 7.98 (d, J = 9.1 Hz, 1 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.4, 113.1, 116.6, 117.4, 125.3, 125.9, 126.5, 127.3, 128.9, 129.4, 129.7, 131.2, 133.8, 136.6, 139.2, 154.6, 156.6, 160.4 ppm. IR: $\tilde{\nu}_{max}$ = 2921, 1730, 1546, 1512, 1182, 996, 817 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{20}H_{15}O_2$ [M + H]$^+$ 287.1072; found 287.1075.

1-(4-Methoxyphenyl)-3*H*-benzo[*f*]chromen-3-one (38c): Pale-brown solid (89%, 201.8 mg); m.p. 102–104 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.90 (s, 3 H, OCH_3), 6.35 (s, 1 H, $CH_{alkenyl}$), 7.01 (dd, J = 1.9, 6.7 Hz, 2 H, CH_{ar}), 7.17–7.20 (m, 1 H, CH_{ar}), 7.28 (dd, J = 1.9, 6.6 Hz, 2 H, CH_{ar}), 7.37–7.41 (m, 2 H, CH_{ar}), 7.50 (d, J = 8.8 Hz, 1 H, CH_{ar}), 7.83 (d, J = 8.0 Hz, 1 H, CH_{ar}), 7.98 (d, J = 8.8 Hz, 1 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.4, 113.2, 114.4, 116.5, 117.4, 125.3, 126.0, 126.5, 128.9, 129.4, 131.2, 131.7, 133.8, 154.7, 156.2, 160.4, 160.5 ppm. IR: $\tilde{\nu}_{max}$ = 2922, 2849, 1727, 1605, 1511, 1248, 1179, 996, 819 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{20}H_{15}O_3$ [M + H]$^+$ 303.1021; found 303.1022.

1-(3-Methoxyphenyl)-3*H*-benzo[*f*]chromen-3-one (39c): Yellow oil (79%, 179.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.79 (s, 3 H, OCH_3), 6.36 (s, 1 H, $CH_{alkenyl}$), 6.87–6.90 (m, 2 H, CH_{ar}), 7.03–7.05 (m, 1 H, CH_{ar}), 7.14–7.18 (m, 1 H, CH_{ar}), 7.28 (d, J = 8.8 Hz, 1 H, CH_{ar}), 7.36–7.40 (m, 2 H, CH_{ar}), 7.49 (d, J = 8.8 Hz, 1 H, CH_{ar}), 7.81 (d, J = 8.0 Hz, 1 H, CH_{ar}), 7.97 (d, J = 9.1 Hz, 1 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.3, 112.8, 112.9, 114.8, 116.6, 117.3, 119.7, 125.3, 125.8, 126.7, 128.9, 129.2, 130.2, 131.2, 133.9, 140.7, 154.6, 156.2, 160.0, 160.3 ppm. IR: $\tilde{\nu}_{max}$ = 2923, 1729, 1589, 1546, 1430, 1213, 1042, 957, 819 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{20}H_{15}O_3$ [M + H]$^+$ 303.1021; found 303.1021.

1-(4-Isopropoxyphenyl)-3*H*-benzo[*f*]chromen-3-one (40c): Pale-yellow solid (80%, 198.2 mg); m.p. 72–74 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.40 [d, J = 6.1 Hz, 6 H, $C(CH_3)_2$], 4.62–4.67 (m, 1 H, OCH), 6.34 (s, 1 H, $CH_{alkenyl}$), 6.96–6.98 (m, 2 H, CH_{ar}), 7.16–7.25 (m, 3 H, CH_{ar}), 7.37–7.40 (m, 2 H, CH_{ar}), 7.48 (dd, J = 1.5, 8.9 Hz, 1 H, CH_{ar}), 7.81 (d, J = 8.4 Hz, 1 H, CH_{ar}), 7.96 (d, J = 9.1 Hz, 1 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.9, 70.0, 113.1, 116.1, 116.3, 117.3, 125.2, 126.0, 126.4, 128.8, 128.8, 129.3, 131.2, 131.3, 133.7, 154.6, 156.2, 158.7, 160.4 ppm. IR: $\tilde{\nu}_{max}$ = 2976, 2927, 1729, 1604, 1508, 1245, 1182, 1116, 819 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{22}H_{19}O_3$ [M + H]$^+$ 331.1334; found 331.1333.

1-(4-Butoxyphenyl)-3*H*-benzo[*f*]chromen-3-one (41c): Pale-brown solid (82%, 211.7 mg); m.p. 74–76 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.01 (t, J = 7.6 Hz, 3 H, CH_3), 1.50–1.56 (m, 2 H, CH_2), 1.79–1.84 (m, 2 H, CH_2), 4.05 (t, J = 6.1 Hz, 2 H, OCH_2), 6.35 (s, 1 H, $CH_{alkenyl}$), 6.97–7.00 (m, 2 H, CH_{ar}), 7.17–7.26 (m, 3 H, CH_{ar}), 7.37–7.51 (m, 3 H, CH_{ar}), 7.82 (t, J = 8.0 Hz, 1 H, CH_{ar}), 7.97 (t, J = 8.7 Hz, 1 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8, 19.2, 31.2, 67.8, 113.1, 114.9, 116.3, 116.3, 117.3, 125.2, 126.0, 126.5, 128.8, 129.3, 131.2, 131.4, 133.7, 154.6, 156.3, 159.9, 160.5 ppm. IR: $\tilde{\nu}_{max}$ = 2957, 2870, 1728, 1605, 1511, 1246, 1178, 819, 751 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{23}H_{21}O_3$ [M + H]$^+$ 345.1491; found 345.1491.

1-(4-*sec*-Butoxyphenyl)-3*H*-benzo[*f*]chromen-3-one (42c): Pale-brown solid (82%, 211.8 mg); m.p. 87–89 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.01 (t, J = 7.4 Hz, 3 H, CH_3), 1.36 (d, J = 6.0 Hz, 3 H, CH_3), 1.64–1.84 (m, 2 H, CH_2), 4.38–4.42 (m, 1 H, OCH), 6.36 (s, 1 H, $CH_{alkenyl}$), 6.98 (dd, J = 2, 6.8 Hz, 2 H, CH_{ar}), 7.17–7.20 (m, 1 H, CH_{ar}), 7.24–7.27 (m, 2 H, CH_{ar}), 7.38–7.42 (m, 2 H, CH_{ar}), 7.50 (d, J = 9.1 Hz, 1 H, CH_{ar}), 7.83 (d, J = 7.7 Hz, 1 H, CH_{ar}), 7.98 (d, J = 8.8 Hz, 1 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 9.86, 19.2, 29.2, 75.4, 113.3, 116.3, 116.5, 117.5, 125.4, 126.2, 126.6, 129.0, 129.5, 131.4, 133.8, 154.8, 156.5, 159.2, 160.7 ppm. IR: $\tilde{\nu}_{max}$ = 2970, 1729, 1604, 1454, 1244, 1181, 995, 819 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{23}H_{21}O_3$ [M + H]$^+$ 345.1491; found 345.1490.

1-(4-Isobutoxyphenyl)-3*H*-benzo[*f*]chromen-3-one (43c): Pale-brown solid (83%, 214.4 mg); m.p. 92–94 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.06 [d, J = 6.8 Hz, 6 H, $C(CH_3)_2$], 2.11–2.17 (m, 1 H, CH), 3.80 (d, J = 6.5 Hz, 2 H, OCH_2), 6.34 (s, 1 H, $CH_{alkenyl}$), 6.99 (d, J = 8.4 Hz, 2 H, CH_{ar}), 7.17–7.20 (m, 1 H, CH_{ar}), 7.25 (d, J = 8.4 Hz, 2 H, CH_{ar}), 7.39 (t, J = 7.2 Hz, 2 H, CH_{ar}), 7.49 (d, J = 9.2 Hz, 1 H, CH_{ar}), 7.82 (d, J = 7.6 Hz, 1 H, CH_{ar}), 7.97 (d, J = 9.2 Hz, 1 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.2, 28.2, 74.4, 113.1, 114.9, 116.3, 116.4, 117.3, 125.2, 126.0, 126.5, 128.8, 129.3, 131.2, 131.3, 133.7, 154.6, 156.3, 160.0, 160.5 ppm. IR: $\tilde{\nu}_{max}$ = 2959, 1729, 1605, 1510, 1245, 1176, 1027, 996, 818 cm^{-1}.

HRMS (ES$^+$): calcd. for $C_{23}H_{21}O_3$ $[M + H]^+$ 345.1491; found 345.1494.

1-(3-Chlorophenyl)-3*H*-benzo[*f*]chromen-3-one (44c): Pale-yellow solid (82%, 188.6 mg); m.p. 117–119 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.35 (s, 1 H, $CH_{alkenyl}$), 7.18–7.25 (m, 3 H, CH_{ar}), 7.38–7.52 (m, 5 H, CH_{ar}), 7.85 (d, J = 8.0 Hz, 1 H, CH_{ar}), 8.01 (d, J = 8.9 Hz, 1 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 112.6, 117.1, 117.5, 125.6, 125.7, 125.8, 127.1, 129.1, 129.2, 129.5, 130.5, 131.4, 134.3, 135.3, 141.2, 154.8, 154.9, 160.1 ppm. IR: $\tilde{\nu}_{max}$ = 1730, 1514, 1454, 997, 948, 819 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{19}H_{12}ClO_2$ $[M + H]^+$ 307.0526; found 307.0523.

1-(4-Fluorophenyl)-3*H*-benzo[*f*]chromen-3-one (45c): Pale-yellow solid (81%, 176.3 mg); m.p. 103–105 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.35 (s, 1 H, $CH_{alkenyl}$), 7.17–7.25 (m, 4 H, CH_{ar}), 7.33–7.35 (m, 2 H, CH_{ar}), 7.41 (t, J = 7.7 Hz, 1 H, CH_{ar}), 7.51 (d, J = 9.1 Hz, 1 H, CH_{ar}), 7.84 (d, J = 8.0 Hz, 1 H, CH_{ar}), 8.00 (d, J = 9.1 Hz, 1 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 112.9, 116.4 (d, J = 21.7 Hz), 117.0, 117.5, 125.5, 125.8, 126.9, 129.2, 129.3, 129.4, 129.5, 131.4, 134.2, 135.6, 154.9, 155.4, 160.2, 163.4 (d, J = 249.1 Hz) ppm. IR: $\tilde{\nu}_{max}$ = 1729, 1509, 1182, 997, 819, 751 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{19}H_{12}FO_2$ $[M + H]^+$ 291.0821; found 291.0822.

1-[3-(Trifluoromethyl)phenyl]-3*H*-benzo[*f*]chromen-3-one (46c): Yellow oil (80%, 204.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.37 (s, 1 H, $CH_{alkenyl}$), 7.11 (d, J = 8.8 Hz, 1 H, CH_{ar}), 7.15–7.18 (m, 1 H, CH_{ar}), 7.40–7.45 (m, 2 H, CH_{ar}), 7.53 (d, J = 9.1 Hz, 1 H, CH_{ar}), 7.56 (d, J = 7.3 Hz, 1 H, CH_{ar}), 7.65 (d, J = 6.9 Hz, 1 H, CH_{ar}), 7.80 (d, J = 7.6 Hz, 1 H, CH_{ar}), 7.86 (d, J = 8.0 Hz, 1 H, CH_{ar}), 8.02 (d, J = 8.8 Hz, 1 H, CH_{ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 112.3, 117.2, 117.4, 124.4, 125.3, 125.5, 126.0, 126.9, 128.8, 128.9, 129.2, 129.7, 130.9, 131.2, 134.3, 140.2, 154.6, 154.8, 159.8 ppm. IR: $\tilde{\nu}_{max}$ = 2918, 1732, 1547, 1314, 1168, 1126, 1071, 815 cm^{-1}. HRMS (ES$^+$): calcd. for $C_{20}H_{12}F_3O_2$ $[M + H]^+$ 341.0789; found 341.0788.

Supporting Information (see also the footnote on the first page of this article): Spectroscopic data and HPLC traces of all the compounds.

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