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Note

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Synthesis of 4*H*-Chromen-4-one Derivatives by Intramolecular Palladium-Catalyzed Acylation of Alkenyl Bromides with Aldehydes

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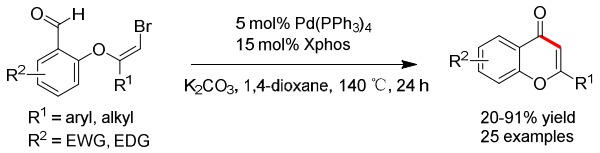
ABSTRACT



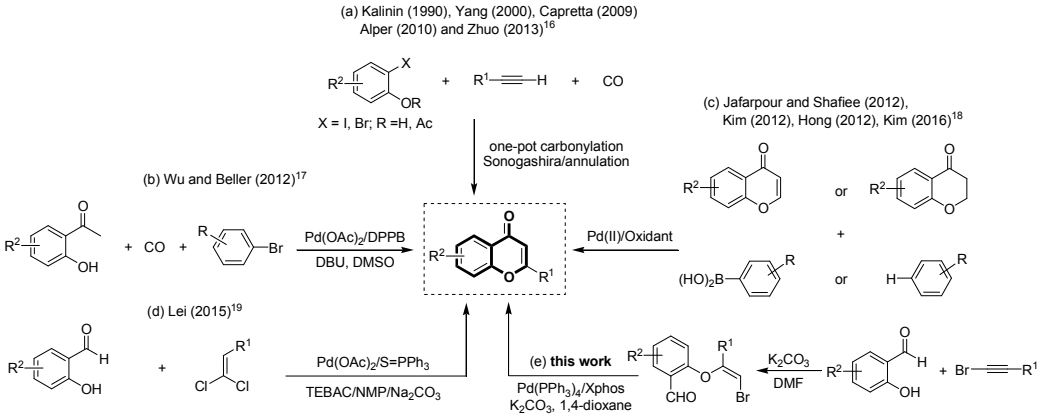
The palladium-catalyzed intramolecular acylation of alkenyl bromides and aldehydes has been developed for an efficient synthesis of 4*H*-chromen-4-ones. With $Pd(PPh_3)_4$/Xphos as the catalyst and K_2CO_3 as the base, this protocol was applied to synthesize a small library of diversely functionalized flavonoids in moderate to good yields in 1,4-dioxane.

Chromone frameworks are frequently found in a diverse array of compounds, including natural flavone and isoflavone products, biologically and therapeutically active drugs such as anti-inflammatory, antiplatelet, antimicrobial, antiobesity and anticancer agents, and drug candidates for neurodegenerative diseases and adenosine receptors.[1] Chromones as a privileged scaffold in drug discovery have received considerable attention over the past years; consequently, much effort has been focused on the development of new synthetic methods.

The main classical synthetic routes enclose the following approaches: (a) Claisen condensation (classic Claisen condensation,[2] Baker-Venkatamaran,[3] and Kostanecki−Robinson reaction[4]), benzopyrylium salts[5] and Vilsmeier−Haack reaction[6] from *ortho*-hydroxyarylalkylketones; (b) Simonis[7] and Ruhemann reaction[8] from phenols; (c) synthesis of chromones from salicylic acid and derivatives.[9] Although these processes are widely used, there remain many drawbacks to overcome such as the use of strong acids or bases, high temperature, long reaction time, unexpected

side-products and unsatisfactory yields.[10] The design and development of mild, novel, and efficient methods for the assembly of the chromone ring is still highly imperative. Organo-catalyzed,[11] base-mediated,[12] hypervalent iodine or iodine-promoted,[13] and one-pot cascade syntheses[14] have been recently developed. During the last decades, transition-metal-catalyzed reactions provide one of the most attractive methodologies for C–C and C-heteroatom formation. The application of these reactions in the construction of polycyclic structures nowadays has increased tremendously.[15] Following this tendency, several attractive palladium-catalyzed protocols have been discovered for the synthesis of chromones (Scheme 1, paths a-d). Despite the significant progress made in the Pd-catalyzed synthesis of chromones, novel synthetic approaches, with enhanced reaction efficiency, milder reaction conditions as well as improved availability of starting materials, are still desirable.

Scheme 1. Pathways for the Synthesis of Chromones *via* Palladium-Catalyzed Reactions



Among various Pd-catalyzed cross-coupling processes, the nucleophilic additions of σ-arylpalladium intermediates to unsaturated carbon–heteroatom bonds have been emerging as powerful synthetic methodologies for the construction of ring systems in recent years.[20] In a continuation of our efforts to develop Pd-catalyzed new synthetic protocols for building valuable heterocyclic frameworks,[21] herein we report on a new and efficient entry to 4*H*-chromen-4-ones through Pd-catalyzed intramolecular acylation of ether-tethered alkenyl bromides and aldehydes, readily accessible starting material from regio- and stereoselective nucleophilic addition of

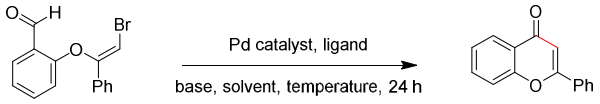
salicylaldehydes to alkynyl bromides (Scheme 1, path e).[22]

(Z)-Alkenyl bromide **1a** was selected as a model substrate for a palladium-catalyzed intramolecular acylation. We first tested the reaction conditions previously used for cross-coupling of aryliodides with aldehydes.[23] However, a combination of $Pd_2(dba)_3$, dtpf, and Cs_2CO_3/Et_3N (1:2) can not efficiently promote the reaction in toluene, and **2a** was obtained in low yields. Benzofuran by-product, formed through Pd-catalyzed direct aromatic C-H vinylation,[22] can be isolated in 24% yield. To suppress this competitive reaction, a judicious choice of catalysts, ligands, bases, solvents and temperatures is needed. The data from that study are summarized in Table 1. Investigation of the effect of temperature on reaction yields showed that with the reaction temperature increasing, higher yields were obtained (entries 1-3). A survey of reaction media showed that 1,4-dioxane provided better results (34% yield, entry 8) than toluene, DMF, DMA, DMSO, and THF (entries 3-7). The effect of palladium sources on the reaction was next investigated, $Pd(PPh_3)_4$ was found to give the best result (entries 9-12). To increase the yield of **2a**, different bases such as Cs_2CO_3, K_2CO_3, K_3PO_4, Na_2CO_3, NaO^tBu, and NaOH were then tested (entries 12-17). Compared to other bases, K_2CO_3 provided a better result, and the acylation product **2a** can be obtained in 61% yield (entry 13). Finally, the effect of different ligands, including bulky monodentate phosphines, biaryl monodentate phosphines, and bidentate phosphines, was investigated (entries 13, and 18-24). Sterically hindered biaryl phosphine Xphos proved to be a highly efficient ligand for the acylation, providing **2a** in 72% yield (entry 21). A higher ratio of ligand to Pd is preferable to afford a better result [58% (1:1), 72% (2:1), and 80% (3:1), entry 12]. It is worth noting that Et_3N as the additive led to an inferior result (51% vs 72%, entries 21 and 22). In addition, the reaction can be carried out on a 1.0 mmol scale without compromising the yield (entries 21 and 25).

With the optimized reaction conditions in hand, the scope of this acylation process was then examined. A variety of diversely substituted chromone derivatives was obtained in moderate to good yields (schemes 2 and 3). As shown in scheme 2, for the olefin-linked aryl moiety, a variety of substituents (Me, OMe, F, Cl, and Br) were

applicable, affording products **2b-2i** in 31-80% yields. The electronic nature of the aromatic motifs did not seem to affect the efficiency, both electron-donating (**2b-2e**) and electron-withdrawing (**2f**-**2i**) substituents can be incorporated at either the *para*- or *meta*-position. In addition, a wide array of alkenyl bromides with simple linear alkyl substitutions (**1j**-**1l**) was amenable to the protocol, delivering chromen-4-ones **2j**-**2l** in 60-78% yields. Alkenyl bromide **1m** that contained a protected alcohol functionality is also tolerated, and provide the corresponding product **2m** in 41% yield.

Table 1. Optimization of Intramolecular Acylation Reaction Conditions[a]

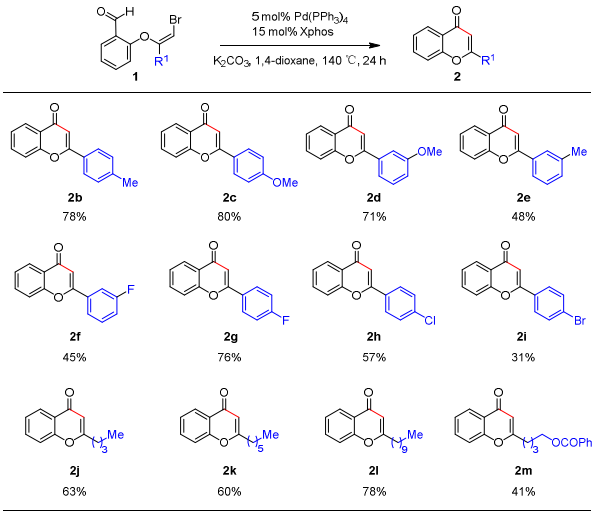


1a **2a**

entry	catalyst	ligand	base/additive[b]	solvent	temp(℃)	yield[c]
1	$Pd_2(dba)_3$	dtpf	Cs_2CO_3/Et_3N	Toluene	80	16
2[d]	$Pd_2(dba)_3$	dtpf	Cs_2CO_3/Et_3N	Toluene	110	21
3	$Pd_2(dba)_3$	dtpf	Cs_2CO_3/Et_3N	Toluene	140	27
4	$Pd_2(dba)_3$	dtpf	Cs_2CO_3/Et_3N	DMF	140	15
5	$Pd_2(dba)_3$	dtpf	Cs_2CO_3/Et_3N	DMA	140	20
6	$Pd_2(dba)_3$	dtpf	Cs_2CO_3/Et_3N	DMSO	140	25
7	$Pd_2(dba)_3$	dtpf	Cs_2CO_3/Et_3N	THF	140	30
8	$Pd_2(dba)_3$	dtpf	Cs_2CO_3/Et_3N	1,4-dioxane	140	34
9	$Pd_2(dba)_3$	dtpf	Cs_2CO_3	1,4-dioxane	140	21
10	$Pd(OAc)_2$	dtpf	Cs_2CO_3	1,4-dioxane	140	23
11	$PdCl_2$	dtpf	Cs_2CO_3	1,4-dioxane	140	22
12	$Pd(PPh_3)_4$	dtpf	Cs_2CO_3	1,4-dioxane	140	27
13[d]	$Pd(PPh_3)_4$	dtpf	K_2CO_3	1,4-dioxane	140	61
14[d]	$Pd(PPh_3)_4$	dtpf	K_3PO_4	1,4-dioxane	140	22
15[d]	$Pd(PPh_3)_4$	dtpf	Na_2CO_3	1,4-dioxane	140	48
16[d]	$Pd(PPh_3)_4$	dtpf	NaO^tBu	1,4-dioxane	140	49
17[d]	$Pd(PPh_3)_4$	dtpf	NaOH	1,4-dioxane	140	trace
18[d]	$Pd(PPh_3)_4$	$(^tBu)_3P{\cdot}HBF_4$	K_2CO_3	1,4-dioxane	140	44
19[d]	$Pd(PPh_3)_4$	$Cy_3P{\cdot}HBF_4$	K_2CO_3	1,4-dioxane	140	66
20[d]	$Pd(PPh_3)_4$	Davephos	K_2CO_3	1,4-dioxane	140	49
21[d]	$Pd(PPh_3)_4$	Xphos	K_2CO_3	1,4-dioxane	140	72/58[e]/80[f]
22	$Pd(PPh_3)_4$	Xphos	K_2CO_3/ Et_3N	1,4-dioxane	140	51
23[d]	$Pd(PPh_3)_4$	DPEphos	K_2CO_3	1,4-dioxane	140	50
24[d]	$Pd(PPh_3)_4$	Xantphos	K_2CO_3	1,4-dioxane	140	61
25	$Pd(PPh_3)_4$	Xphos	K_2CO_3	1,4-dioxane	140	77[g]

[a] Reaction conditions: **1a** (0.2 mmol), base (0.4 mmol), Pd (5 mol %), ligand (10 mol %), solvent (2 mL), 24 h. [b] Et_3N (1.2 mmol). [c] Isolated yield. [d] base (0.6 mmol). [e] ligand (5 mol%). [f] ligand (15 mol%). [g] 1.0 mmol scale.

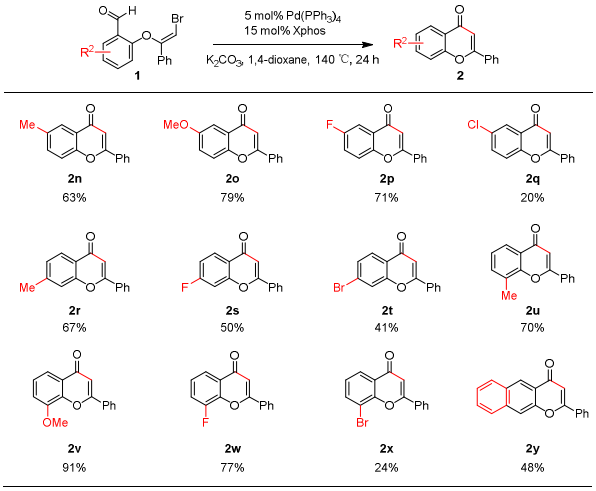
Scheme 2. Variation of the Alkenyl Bromides[a,b]



[a] Reaction conditions: 1 (0.2 mmol), K_2CO_3 (0.6 mmol), 5 mol % of $Pd(PPh_3)_4$, 15 mol % of Xphos, 1,4-dioxane (2 mL), 140 ℃, 24 h. [c] Isolated yield after chromatography.

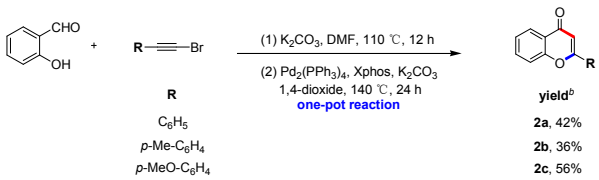
The generality of the aryl aldehydes **1** were then examined (Scheme 3). A variety of substituents (Me, OMe, F, Cl, and Br) were tolerated, affording the corresponding products in 20-91% yields. The electronic nature of the aryl aldehyde motifs affected the outcome to some extent. The incorporation of electron-donating substituents (Me and OMe) at either the *para*- or *meta*-position did not seem to hamper the reaction, and the flavonoids **2n**, **2o**, **2r**, **2u**, and **2v** could be obtained in good yields (61-91%). When electron-withdrawing substituents (Cl and Br) are introduced to the aryl aldehyde moiety, the corresponding products **2q**, **2t**, and **2x** were obtained in low yields (20-41%). However, when fluoro-substituted aryl aldehydes **1p**, **1s**, and **1w** were used, the corresponding chromones can be obtained in good yields (50-77%). In addition, β-naphthyl aldehyde substrate **1y** can also be efficiently transformed into **2y** in 48% yield. The capacity to perform nucleophilic addition and Pd-catalyzed acylation together in one pot potentially makes this method more versatile and valuable. Consequently, one-pot approach was finally explored. As shown in scheme 4, the reaction of salicylaldehyde and arylethynyl bromides can smoothly proceed to generate the corresponding products **2a-c** in 42%, 36% and 56% yield, respectively.

Scheme 3. Variation of the Aromatic Aldehydes[a, b]



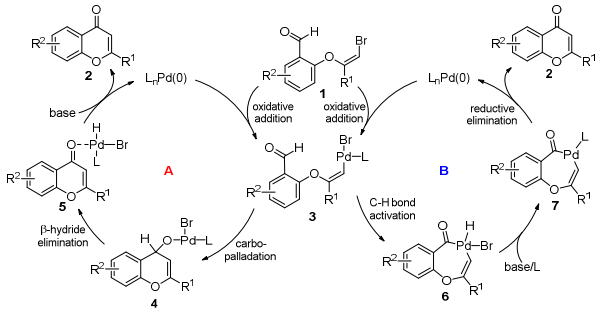
[a] Reaction conditions: **1** (0.2 mmol), K_2CO_3 (0.6 mmol), 5 mol % of $Pd(PPh_3)_4$, 15 mol % of Xphos, 1,4-dioxane (2 mL), 140 ℃, 24 h. [c] Isolated yield after chromatography.

Scheme 4. One-Pot synthesis of 4*H*-chromen-4-ones[a]



[a] Conditions: salicylaldehyde (0.5 mmol), alkynyl bromides (0.6 mmol), K_2CO_3 (2.5 mmol), DMF (1 mL), 110 ℃, 12 h; then $Pd(PPh_3)_4$ (5 mol%), Xphos (15 mol%), 1,4-dioxane (2 mL), 140 ℃, 24 h. [b] Isolated yield.

Scheme 5. Proposed catalytic mechanism



On the basis of the results obtained by Miura,[24] and Solé,[23,25] two competitive catalytic cycles have been proposed. The first one (Scheme 5A), describes the nucleophilic addition of the alkenyl-Pd(II) intermediate to the carbonyl group, while the second one (Scheme 5B), shows direct C-H vinylation at the formyl group of aryl

aldehyde. The initial step involved the oxidative addition of alkenyl bromide **1** by Pd(0) to generate **3**. Carbopalladation of the alkenyl-Pd(II) intermediate **3** across the C=O bond[26] provided nucleophilic addition intermediate **4**, which was followed by β-hydride elimination would afford the ketone **2** and regenerate the Pd(0) catalyst (mechanism A). Alternatively, the alkenyl-Pd(II) **3** underwent C-H activation of the aldehyde to provide intermediate **6**. After loss of HX from the resulting Pd(IV) intermediate **6** by the base and reductive elimination from the acyl-Pd complex **7** would also form the ketone **2** and regenerate the catalyst (mechanism B).[27]

In summary, we have developed a practical protocol for the synthesis of flavonoids through Pd-catalyzed intramolecular acylation of alkenyl bromides and aldehydes. The success of the reaction heavily relies on the careful selection of proper base and solvent. K_2CO_3 as the base in 1,4-dioxane was found to be essential for the efficient formation of chromenones. The result presented here should be of considerable interest for valuable synthetic targets for medicinal chemistry.

EXPERIMENTAL SECTION

General Experimental Methods. Chemicals were all purchased from commercial supplies and used without further purification unless otherwise stated. Solvents were dried and purified according to the standard procedures before use. Reactions were monitored by analytical thin-layer chromatography (TLC). All reactions were conducted in dried glassware. Purification of reaction products was done by flash chromatography with 230-400 mesh silica gel. Alkenyl bromide substrates were prepared according to the literature methods.[22] Melting points were determined on a melting point apparatus in open capillaries and are uncorrected. ^{1}H NMR spectra were recorded on a 400 or 600 MHz spectrometer, and ^{13}C NMR spectra were recorded at 100 or 150 MHz. Unless otherwise stated, deuterochloroform ($CDCl_3$) was used as a solvent. Chemical shifts (δ) are given in parts per million downfield relative to residual $CHCl_3$ (δ = 7.26 ppm). Chemical shifts for carbon resonances are reported in parts per million and are referenced to the carbon resonance of the solvent $CHCl_3$ (δ = 77.16 ppm). The splitting patterns are reported as s (singlet), d (doublet), dd (double doublet), t (triplet), and m (multiplet). Coupling constants are

given in hertz. High-resolution mass spectra were recorded on a BIO TOF Q mass spectrometer.

General Procedures for Synthesis of Chromenone derivatives.

A 10 mL Schlenk tube equipped with a magnetic stirring bar was charged with alkenyl bromides (0.2 mmol, 1.0 equiv), K_2CO_3 (82.5 mg, 0.6 mmol, 3.0 equiv), and then $Pd(PPh_3)_4$ (0.01 mmol, 12 mg) and Xphos (0.03 mmol, 14 mg) were added. Finally, 1,4-Dioxane (2.0 mL) was added to the mixture via syringe at room temperature under air. The tube was sealed and put into a preheated oil bath at 140 ℃ for 24 h. The mixture was cooled to room temperature, quenched with water (5 mL), and diluted with ethyl acetate (8 mL). The layers were separated, and the aqueous layer was extracted with 2 × 8 mL of ethyl acetate. The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The crude product was then purified by flash chromatography on silica gel (H), eluting with 5−10% ethyl acetate/petroleum ether.

2-Phenyl-4*H*-chromen-4-one (**2a**). Yield, 80% (35.5 mg). Yellow solid, Mp: 94-97 ℃ (Lit.[14b] mp 97 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, *J* = 7.9 Hz, 1H), 7.93 (d, *J* = 5.8 Hz, 2H), 7.70 (t, *J* = 7.7 Hz, 1H), 7.58-7.53 (m, 4H), 7.42 (t, *J* = 7.5 Hz, 1H), 6.83 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.5, 163.4, 156.3, 133.8, 131.8, 131.6, 129.1, 126.3, 125.7, 125.3, 124.0, 118.1, 107.6.

2-(*p*-Tolyl)-4*H*-chromen-4-one (**2b**). Yield, 78% (36.8 mg). Yellow solid, Mp: 100-102 ℃(Lit.[14b,28a] mp 100-102 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 2H), 6.80 (s, 1H), 2.45 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.5, 163.7, 156.3, 142.3, 133.7, 129.8, 129.0, 126.3, 125.7, 125.2, 124.0, 118.1, 107.0, 21.6.

2-(4-Methoxyphenyl)-4*H*-chromen-4-one (**2c**). Yield, 80% (40.3 mg). Yellow solid. Mp: 157-158 ℃ (Lit.[14b,28a] mp 155-156 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.5 Hz, 2H), 7.69 (t, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 2H), 6.75 (s, 1H), 3.90 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.4, 163.4, 162.4, 156.2, 133.6, 128.0, 125.7, 125.1, 124.0, 123.9, 118.0,

114.5, 106.2, 55.5.

2-(3-Methoxyphenyl)-4*H*-chromen-4-one (**2d**). Yield, 71% (35.8 mg). Yellow solid. Mp: 132-134 ℃ (Lit.[28a] mp 128-129 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 8.0, 1.2 Hz 1H), 7.74-7.66 (m, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.45-7.40 (m, 3H), 7.08 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.82 (s, 1H), 3.90 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.5, 163.2, 160.0, 156.2, 133.8, 133.1, 130.1, 125.7, 125.3, 124.0, 118.7, 118.1, 117.2, 111.7, 107.8, 55.5.

2-(*m*-Tolyl)-4*H*-chromen-4-one (**2e**). Yield, 48% (31.0 mg). Yellow solid. Mp: 105-107 ℃ (Lit.[17] mp 128-129 ℃). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.67 (m, 3H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.38 (m, 2H), 7.31 (d, *J* = 7.4 Hz, 1H), 6.78 (s, 1H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.4, 163.6, 156.2, 138.8, 133.7, 132.4, 131.6, 128.9, 126.8, 125.6, 125.2, 123.9, 123.5, 118.1, 107.5, 21.5.

2-(3-Fluorophenyl)-4*H*-chromen-4-one (**2f**). Yield, 45% (21.6 mg). Yellow solid. Mp: 97-99 ℃ (Lit.[18b] mp 96-98 ℃). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.8 Hz, 1H), 7.74-7.71 (m, 2H), 7.65 (d, *J* = 9.6 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 1H), 7.53-7.49 (m, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.27-7.24 (m, 1H), 6.82 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.4, 163.1 (d, *J* = 246 Hz), 161.92, 161.91, 156.2, 134.0, 133.9, 130.8 (d, *J* = 9 Hz), 125.6 (d, *J* = 48 Hz), 123.9, 122.0 (d, *J* = 3 Hz), 118.6 (d, *J* = 21 Hz), 118.1, 113.4 (d, *J* = 24 Hz), 108.2.

2-(4-Fluorophenyl)-4*H*-chromen-4-one (**2g**). Yield, 80% (55.5 mg). Yellow solid. Mp: 143-145 ℃ (Lit.[28d] mp 148-150 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.9 Hz, 1H), 7.94 (m, 2H), 7.71 (t, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.22 (m, 2H), 6.77 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.4, 164.8 (d, *J* = 246 Hz), 162.4, 156.2, 133.9, 128.5 (d, *J* = 9 Hz), 128.0 (d, *J* = 3 Hz), 125.8, 125.4, 123.9, 118.1, 116.3 (d, *J* = 21 Hz), 107.4.

2-(4-Chlorophenyl)-4*H*-chromen-4-one (**2h**). Yield, 57% (29.2 mg). Yellow solid. Mp: 188-189 ℃ (Lit.[28a] mp 185-187 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, *J* = 7.8 Hz, 1H), 7.96-7.87 (m, 2H), 7.72 (t, *J* = 7.9 Hz, 1H), 7.60-7.50 (m, 3H), 7.44 (t, *J* = 7.6 Hz, 1H), 6.80 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.3, 162.3, 156.2, 133.9, 131.7, 130.3, 129.4, 127.6, 125.8, 125.4, 123.9, 118.1, 107.7.

2-(4-Bromophenyl)-4*H*-chromen-4-one (**2i**). Yield, 31% (18.6 mg). Yellow solid. Mp 163-165 ℃ (Lit.[28d] mp 164-166 ℃). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.95 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.73-7.70 (m, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.57-7.52 (m, 3H), 7.44 (t, *J* = 7.5 Hz, 1H), 6.85 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.5, 163.4, 156.3, 133.8, 131.8, 131.6, 129.1, 126.3, 125.7, 125.3, 123.9, 118.1, 107.6.

2-Butyl-4*H*-chromen-4-one (**2j**).[16c,28b] Yield, 63% (63.7 mg). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.9 Hz, 1H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 6.17 (s, 1H), 2.62 (t, *J* = 7.6 Hz, 2H), 1.73 (m, 2H), 1.43 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.5, 169.9, 156.5, 133.4, 125.6, 124.9, 123.7, 117.9, 109.8, 34.0, 28.9, 22.1, 13.8.

2-Hexyl-4*H*-chromen-4-one (**2k**).[16c] Yield, 60% (55.2 mg). Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.9 Hz, 1H), 7.62 (t, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 6.17 (s, 1H), 2.60 (t, *J* = 7.7 Hz, 2H), 1.76-1.68 (m, 2H), 1.38 (m, 2H), 1.31 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.3, 169.8, 156.4, 133.4, 125.5, 124.8, 123.6, 117.8, 109.6, 34.2, 31.4, 28.6, 26.7, 22.4, 14.0.

2-Decyl-4*H*-chromen-4-one (**2l**).[28c] Yield, 78% (89.3mg). Yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.9 Hz, 1H), 7.66-7.58 (m, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 6.17 (s, 1H), 2.61 (t, *J* = 7.6 Hz, 2H), 1.76-1.71 (m, 2H), 1.41-1.37 (m, 2H), 1.35-1.31 (m, 2H), 1.31-1.24 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.3, 169.8, 156.5, 133.4, 125.6, 124.8, 123.7, 117.8, 109.8, 34.3, 31.9, 29.5, 29.4, 29.3, 29.2, 29.0, 26.8, 22.7, 14.1.

4-(4-Oxo-4*H*-chromen-2-yl)butyl benzoate (**2m**). Yield, 41% (27.7 mg). Yellow solid. Mp: 122-124 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.8 Hz, 1H), 8.01 (d, *J* = 7.2 Hz, 2H), 7.61-7.51 (m, 2H), 7.42-7.32 (m, 4H), 6.17 (s, 1H), 4.36 (br, 2H), 2.68 (br, 2H), 1.88 (br, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.2, 168.9, 166.5, 156.4, 133.5, 133.0, 130.1, 129.5, 128.4, 125.6, 125.0, 123.7, 117.8, 110.0, 64.2, 33.9, 28.1, 23.4. HRMS-ESI: $[M + Na]^+$ calcd for $C_{20}H_{18}NaO_4$ m/z 345.1103, found m/z 345.1112.

6-Methyl-2-phenyl-4*H*-chromen-4-one (**2n**). Yield, 63% (59.5 mg). Yellow solid. Mp:

119-121 ℃ (Lit.[14b,17] mp 112-114 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.93-7.91 (m, 2H), 7.53-7.45 (m, 5H), 6.81 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.6, 163.2, 154.5, 135.2, 135.0, 131.9, 131.5, 129.0, 126.3, 125.0, 123.6, 117.8, 107.4, 20.9.

6-Methoxy-2-phenyl-4*H*-chromen-4-one (**2o**). Yield, 80% (79.7 mg). Yellow solid. Mp: 163-165 ℃ (Lit.[14b,17] mp 165-167 ℃). ^{1}H NMR (600 Hz, $CDCl_3$) δ 7.95-7.89 (m, 2H), 7.59 (d, *J* = 3.1 Hz, 1H), 7.56-7.47 (m, 4H), 7.29 (dd, *J* = 9.1, 3.1 Hz, 1H), 6.82 (s, 1H), 3.91 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.3, 163.2, 157.0, 151.1, 131.9, 131.5, 129.0, 126.2, 124.6, 123.8, 119.5, 106.8, 104.8, 55.9.

6-Fluoro-2-phenyl-4*H*-chromen-4-one (**2p**). Yield, 71% (68.2 mg). Yellow solid. Mp: 100-102 ℃ (Lit.[28c] mp 99-103 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.83 (m, 3H), 7.60-7.50 (m, 4H), 7.44-7.39 (m, 1H), 6.80 (d, *J* = 2.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.6 (d, *J* = 1.5 Hz), 163.7, 159.6 (d, *J* = 246 Hz), 152.4, 131.8, 131.5, 129.1, 126.3, 125.1 (d, *J* = 7.5 Hz), 121.9 (d, *J* = 24 Hz), 120.2 (d, *J* = 9 Hz), 110.6 (d, *J* = 22.5 Hz), 106.9.

6-Chloro-2-phenyl-4*H*-chromen-4-one (**2q**). Yield, 20% (20.5 mg). Yellow solid. Mp: 183-184 ℃ (Lit.[14b,17] mp 184-186 ℃). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 4.0 Hz, 1H), 7.92 (d, *J* = 7.9 Hz, 2H), 7.64 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.58-7.51 (m, 4H), 6.83 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.2, 163.7, 154.6, 134.0, 131.9, 131.4, 131.2, 129.2, 126.4, 125.2, 124.9, 119.9, 107.5.

7-Methyl-2-phenyl-4*H*-chromen-4-one (**2r**). Yield, 67% (31.6 mg). Yellow solid. Mp: 126-128 ℃ (Lit.[17,28g] mp 122-124 ℃). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.1 Hz, 1H), 7.89 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.54–7.48 (m, 3H), 7.34 (s, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 6.77 (s, 1H), 2.49 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.4, 163.0, 156.3, 145.1, 131.8, 131.5, 129.0, 126.7, 126.2, 125.4, 121.7, 117.8, 107.5, 21.8.

7-Fluoro-2-phenyl-4*H*-chromen-4-one (**2s**). Yield, 50% (36 mg). Yellow solid. Mp: 100-102 ℃ (Lit.[28b,g] mp 100-101 ℃). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 8.8, 6.3 Hz, 1H), 7.91 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.58-7.53 (m, 3H), 7.28-7.26 (m, 1H), 7.18-7.15 (m, 1H), 6.81 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.5, 165.7 (d, *J* = 254 Hz), 163.8, 157.3 (d, *J* = 13.5 Hz), 131.8, 131.4, 129.1, 128.3 (d, *J* = 10.5 Hz), 126.3,

120.8, 114.0 (d, *J* = 22.5 Hz), 107.7, 104.8 (d, *J* = 25.5 Hz).

7-Bromo-2-phenyl-4*H*-chromen-4-one (**2t**). Yield, 80% (49.2 mg). White solid. Mp: 163-165 ℃ (Lit.[28b,g] mp 164-165 ℃). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.95 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.73-7.70 (m, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.58-7.52 (m, 3H), 7.44 (t, *J* = 7.5 Hz, 1H), 6.85 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.5, 163.4, 156.3, 133.8, 131.8, 131.6, 129.1, 126.3, 125.7, 125.3, 124.0, 118.1, 107.6.

8-Methyl-2-phenyl-4*H*-chromen-4-one (**2u**). Yield, 80% (66.1 mg). White solid. Mp: 168-170 ℃ (Lit.[28d] mp 170 °C). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.9 Hz, 1H), 7.94 (d, *J* = 7.5 Hz, 2H), 7.57-7.52 (m, 4H), 7.31 (t, *J* = 7.5 Hz, 1H), 6.84 (s, 1H), 2.61 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.9, 162.9, 154.7, 134.7, 132.0, 131.6, 129.1, 127.5, 126.2, 124.8, 123.8, 123.3, 107.3, 15.9.

8-Methoxy-2-phenyl-4*H*-chromen-4-one (**2v**). Yield, 80% (45.9 mg). Yellow solid. Mp: 199-200 ℃ (Lit.[28e] mp 199-200 ℃). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00-7.96 (m, 2H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.54-7.51 (m, 3H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 7.9 Hz, 1H), 6.85 (s, 1H), 4.03 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.5, 163.0, 149.1, 146.7, 131.8, 131.6, 129.1, 126.4, 125.0, 124.8, 116.4, 114.4, 107.4, 56.4.

8-Fluoro-2-phenyl-4*H*-chromen-4-one (**2w**). Yield, 77% (73.9 mg). White solid. Mp: 125-126 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.96 (m, 3H), 7.59-7.52 (m, 3H), 7.51-7.45 (m, 1H), 7.38-7.33 (m, 1H), 6.86 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.5, 163.1, 151.4 (d, *J* = 252 Hz), 145.0 (d, *J* = 12 Hz), 131.9, 131.2, 129.2, 126.4, 125.9, 124.8 (d, *J* = 7.5 Hz), 120.7 (d, *J* = 3 Hz), 119.6 (d, *J* = 16.5 Hz), 107.6.

8-Bromo-2-phenyl-4H-chromen-4-one (**2x**). Yield, 24% (14.4 mg). Yellow solid. Mp: 173-175 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.8 Hz, 1H), 8.10-7.99 (m, 2H), 7.93 (d, *J* = 7.7 Hz, 1H), 7.61-7.52 (m, 3H), 7.31 (t, *J* = 7.8 Hz, 1H), 6.88 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.9, 163.4, 152.8, 137.2, 132.0, 131.3, 129.2, 126.5, 125.9, 125.3, 125.1, 112.0, 107.2.

2-Phenyl-4*H*-benzo[g]chromen-4-one (**2y**). Yield, 48% (52.2 mg). Yellow solid. Mp: 129-131 ℃ (Lit.[28f] mp 129−130 ℃). ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.06 (d, *J* = 7.9 Hz, 1H), 8.09-8.05 (m, 1H), 7.95-7.89 (m, 2H), 7.88-7.86 (m, 1H), 7.75-7.73 (m, 1H),

7.60-7.56 (m, 2H), 7.52 (br, 3H), 6.96-6.94 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 180.3, 160.8, 157.3, 135.5, 131.4, 131.3, 130.6, 130.4, 129.2, 129.0, 128.1, 127.1, 126.6, 126.0, 117.5, 117.2, 110.3.

ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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