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Rhodium(III)-catalyzed one-pot synthesis of flavonoids from salicylaldehydes and sulfoxonium ylides

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Abstract

Rh(III)-catalyzed C–H activation of salicylaldehyde followed by an insertion reaction with sulfoxonium ylides and cyclization is applied to the synthesis of flavonoids. This one-pot strategy exhibits good functional group tolerance and gives flavones in moderate-to-good yields.

Keywords

C–H functionalization, rhodium, salicylaldehyde, sulfoxonium ylide

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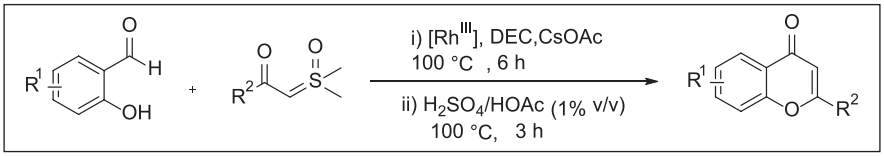

Introduction

Flavonoids are a class of natural products with various biological activities[1–7] and are widely used in medicines,[8,9] such as nobiletin,[10,11] luteolin,[12–15] and flavone-8-acetic acid.[16] Therefore, the development of efficient methods to synthesize flavonoid scaffolds remains a topic of interest.[17–24] In recent years, transition metal catalyzed C–C bond and C–hetero bond formation are effective methods for the synthesis of flavonoids.[25,26] Baruah et al.[27] developed Ru(II)-catalyzed C–H activation and annulations of salicylaldehydes and alkynes to afford flavonoids (Scheme 1(a)). Sun et al.[28] prepared flavonoids via Rh(III)-catalyzed selective cyclization of salicylaldehyde and diazo compounds (Scheme 1(b)). These reactions showed significant advances in building the flavonoid scaffold, but these methods demonstrated some limitations, such as moderate yields and the employment of potentially dangerous diazo compounds. Recently, sulfoxonium ylides have received wide attention[29] as safer carbene precursor.[30–35] Based on our previous research on C–H bond activation[36,37] and heterocyclic chemistry, herein we report an efficient one-pot synthesis of flavonoids via Rh(III)-catalyzed C–H bond activation and annulation of salicylaldehydes[23,27] with sulfoxonium ylides (Scheme 1(c)).

Results and discussion

We envisaged that Rh(III)-catalyzed C–H activation of salicylaldehyde followed by the insertion reaction with the sulfoxonium ylide and cyclization might afford 2-phenyl-4*H*-chromen-4-one (**3aa**).[38–41] A preliminary attempt with 2.5 mol% of $[Cp^*RhCl_2]_2$ and 1 equiv. of NaOAc in dichloroethane (DCE) was demonstrated to be effective, giving the desired product **3aa** in 56% yield after the acid-promoted

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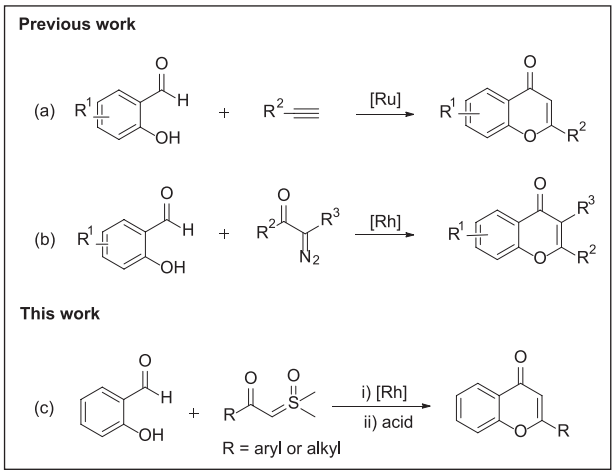
cyclization (Table 1, entry 1). Among a set of representative additives including NaOAc and AgOAc, CsOAc was optimal, promoting the yield of **3aa** to 86% (entries 1–5). Furthermore, decreasing the additive loading to 0.5 equiv. did not diminish the yield (entry 6). Different solvents, such as MeOH, dioxane, toluene, acetonitrile, and acetic acid, were also screened; however, none of them gave higher yields compared to DCE (entries 7–11). After optimizing the reaction time and temperature, the highest yield (89%) was obtained (entries 12–14). Finally, a control experiment revealed that omission of $[Cp^*RhCl_2]_2$ completely inhibited the reaction (entry 15).

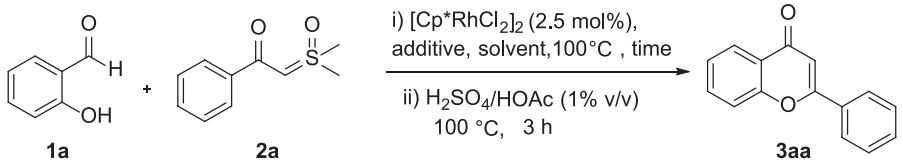


Scheme 1. Synthesis of flavonoids from salicylaldehydes.

With optimized reaction conditions in hand, we sought to evaluate the scope and generality of the salicylaldehydes in this reaction (Table 2). Salicylaldehydes bearing electron-donating substituents such as methyl and methoxy groups at 5-position gave the corresponding products **3ea** and **3ga** in 81% and 93% yields, respectively. Halides were also tolerated under the standard conditions, which provided the desired products **3ba**–**3da** in 92%–94% yields. In contrast, a substrate with a strongly electron-withdrawing nitro groups gave a lower yield in this reaction, delivering the corresponding product **3fa** in 36% yield. Steric effects were also investigated in this reaction; when the C3 position and C4 position of the salicylaldehydes contained Cl, Br, Me, or methoxy groups, the reactions proceeded well to provide **3ha–3la** in 73%–93% yields. To our delight, a hydroxy group substituted piperonal also provided the desired product **3ma** in 64% yield.

Subsequently, the scope of the sulfoxonium ylides was explored (Table 3). Sulfoxonium ylides bearing various electron-donating (Me and OMe) and electron-withdrawing groups (F, Cl, Br, and CF_3) on the phenyl ring reacted smoothly with **1a** to afford corresponding products **3ab–3al** in 73%–95% yields. It is worth noting that not only aryl-substituted sulfoxonium ylides, but also alkyl-substituted substrates could be transformed into the desired products, for example, **3am** and **3ap** in high yields (91% and 95%). Furthermore, thiophene- and naphthalene-substituted sulfoxonium ylides afford electron-donating products **3an** and **3ao** in 87% and 93% yield, respectively.

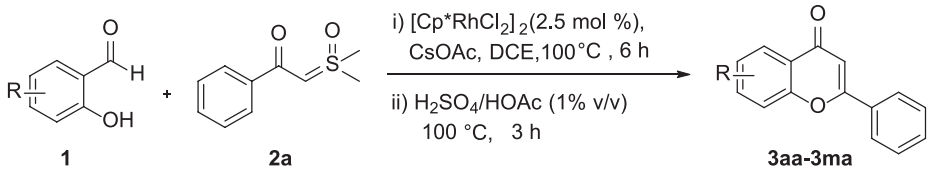
Table 1. Optimization of the reaction conditions[a].



Entry	Additive (equiv.)	Solvent	Time (h)	Yield[b] (%)
1	NaOAc (1)	DCE	12	56
2	HOAc (1)	DCE	12	12
3	AgOAc (1)	DCE	12	80
4	CsOAc (1)	DCE	12	86
5	–	DCE	12	<5
6	CsOAc (0.5)	DCE	12	87
7	CsOAc (0.5)	MeOH	12	Trace
8	CsOAc (0.5)	Dioxane	12	67
9	CsOAc (0.5)	Toluene	12	26
10	CsOAc (0.5)	CH_3CN	12	71
11	CsOAc (0.5)	HOAc	12	<5
12	**CsOAc (0.5)**	**DCE**	**6**	**89**
13[c]	CsOAc (0.5)	DCE	6	71
14[d]	CsOAc (0.5)	DCE	6	87
15[e]	CsOAc (0.5)	DCE	6	–

[a]Reaction conditions: (1) **1a** (0.2 mmol), **2a** (0.3 mmol, 1.5 equiv.), base (0.5 equiv.), $[Cp^*RhCl_2]_2$ (2.5 mol%) solvent (2.0 mL), 100 °C, Ar. (2) H_2SO_4/HOAc (1% v/v, 1 mL), 100 °C, 3 h.
[b]Isolated yields.
[c]At 80 °C.
[d]At 120 °C.
[e]In the absence of $[Cp^*RhCl_2]_2$.
The bold-faced values indicated the optimized conditions in this table.

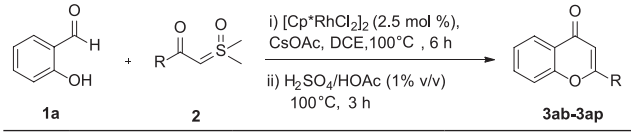
Table 2. Substrate scope of salicylaldehydes[a].



Entry	Product	R	Yield[b] (%)
1	**3aa**	H	89
2	**3ba**	5-F	93
3	**3ca**	5-Cl	94
4	**3da**	5-Br	92
5	**3ea**	5-Me	81
6	**3fa**	5-NO_2	36
7	**3ga**	5-MeO	93
8	**3ha**	4-Cl	88
9	**3ia**	4-Me	81
10	**3ja**	3-Br	73
11	**3ka**	3-Me	89
12	**3la**	3-MeO	93
13	**3ma**	1,3-Benzodioxole	64

[a]Reaction conditions: (1) **1a** (0.2 mmol), **2a** (0.3 mmol, 1.5 equiv.), CsOAc (0.5 equiv.), $[Cp^*RhCl_2]_2$ (2.5 mol%), DCE (2.0 mL), 100 °C, Ar. (2) H_2SO_4/HOAc (1% v/v, 1 mL), 100 °C, 3 h.
[b]Isolated yields.

Table 3. Substrate scope of the sulfoxonium ylides[a].



Entry	Product	R	Yield[b] (%)
1	**3ab**	4-F-C_6H_4	88
2	**3ac**	4-Cl-C_6H_4	87
3	**3ad**	4-Br-C_6H_4	89
4	**3ae**	4-Me-C_6H_4	92
5	**3af**	4-F_3C-C_6H_4	88
6	**3ag**	4-MeO-C_6H_4	75
7	**3ah**	2-Cl-C_6H_4	74
8	**3ai**	2-Me-C_6H_4	83
9	**3aj**	2-MeO-C_6H_4	95
10	**3ak**	3-Me-C_6H_4	77
11	**3al**	3-Br-C_6H_4	73
12	**3am**	$C(CH_3)_3$	91
13	**3an**	2-Thienyl	87
14	**3ao**	2-Naphthyl	93
15	**3ap**	1-Adamantyl	95

[a]Reaction conditions: (1) **1a** (0.2 mmol), **2a** (0.3 mmol, 1.5 equiv.), CsOAc (0.5 equiv.), $[Cp^*RhCl_2]_2$ (2.5 mol%), DCE (2.0 mL), 100 °C, Ar. (2) H_2SO_4/HOAc (1% v/v, 1 mL), 100 °C, 3 h.
[b]Isolated yields.

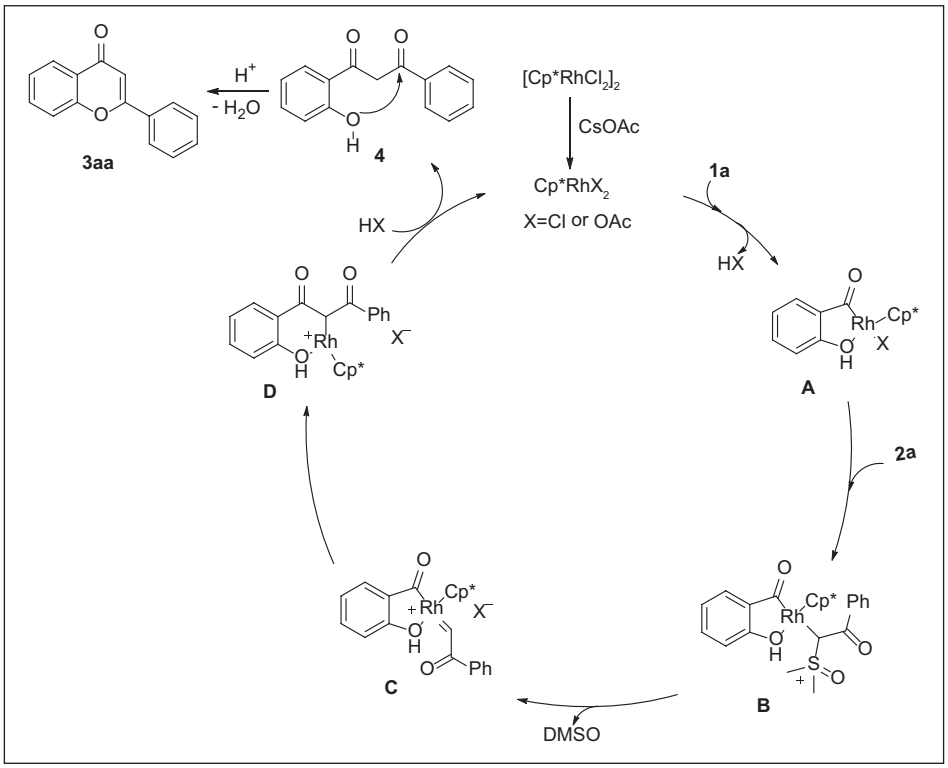
Based on previous literature reports on related systems,[28,31,34,42,43] a plausible reaction mechanism is proposed in Scheme 2. Initially, salicylaldehyde **1a** was activated by the Rh(III) catalyst to produce a rhodacyclic intermediate **A**. Next sulfoxonium ylide **2a** reacted with **A** to afford intermediate **B**, which transformed into intermediate **C** by elimination of dimethyl sulfoxide (DMSO). Next, a six-membered rhodacyclic intermediate **D** formed by migratory insertion of the Rh–C bond into the activated carbene. Protonation of **D** would release the catalyst and afford **4**, which is transformed into product **3aa** via an acid-promoted cyclization.

Conclusion

In summary, we have described a Rh(III)-catalyzed one-pot synthesis of flavones via the reaction of salicylaldehydes and sulfoxonium ylides. The reaction exhibits good functional group tolerance with a broad range of substrates, affording with moderate-to-good yields of the products under optimized conditions. Further investigations on the synthetic applications of this method are currently underway in our laboratory.

Experimental section

All commercially available reagents were used as received unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) and visualized under UV light (254 nm). Melting points were determined using a Büchi B-540 capillary melting point apparatus. Nuclear magnetic resonance (NMR) spectra were recorded on Varian spectrometer (400 MHz) with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an internal standard. High-resolution mass spectra (HRMS) were recorded on an electrospray ionization quadrupole time-of-flight (ESI-Q-TOF) System ESI spectrometer.



Scheme 2. Proposed reaction mechanism.

General procedure for the synthesis of **3**

A sealed tube was charged with **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.3 mmol, 1.5 equiv.), $[Cp^*RhCl_2]_2$ (0.005 mmol, 2.5 mol%), and CsOAc (0.1 mmol, 0.5 equiv.) in DCE (2 mL). After the reaction mixture had been stirred at 100 °C under Ar for 6 h, 1 mL of H_2SO_4/HOAc (10 μL of H_2SO_4 dissolved in 0.99 mL of HOAc) was added at room temperature. After completion of the addition, the reaction mixture was then stirred at 100 °C for 3 h before being cooled to room temperature. The mixture was diluted with EtOAc (20 mL), washed with brine, and dried over anhydrous Na_2SO_4. After removal of the EtOAc, the residue was purified by chromatography on basic silica gel (PE/EtOAc = 8/1) to afford **3aa** (40 mg, 89%) as a white solid.

*2-Phenyl-4*H-*chromen-4-one* (**3aa**): Product **3aa** was obtained as a white solid (40 mg, 89%); m.p.: 96–98 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (1H, d, *J* = 8.0 Hz, CH), 7.97–7.89 (2H, m, 2CH), 7.71 (1H, t, *J* = 7.8 Hz, CH), 7.61–7.49 (4H, m, 4CH), 7.43 (1H, t, *J* = 7.6 Hz, CH), 6.84 (1H, s, CH). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.48 (C_q), 163.40 (C_q), 156.24 (C_q), 133.77 (CH), 131.75 (C_q), 131.59 (CH), 129.03 (CH), 126.28 (CH), 125.69 (CH), 125.22 (CH), 123.95 (C_q), 118.07 (CH), 107.58 (CH). HRMS (ESI): *m*/*z* calcd for $C_{15}H_{11}O_2$ $[M + H]^+$: 223.0754; found: 223.0743.

*6-Fluoro-2-phenyl-4*H-*chromen-4-one* (**3ba**): Product **3ba** was obtained as a yellow solid (45 mg, 93%); m.p.: 105–107 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96–7.83 (3H, m, 3CH), 7.63–7.50 (4H, m, 4CH), 7.43 (1H, t, *J* = 8.0 Hz, CH), 6.82 (1H, s, CH). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.63 (C_q), 163.69 (C_q), 160.81 (C_q), 158.35 (C_q), 152.45 (CH), 131.65 (d, $^2J_{C-F}$ = 28.2 Hz, C_q), 129.09 (CH), 126.31 (CH), 125.16 (d, $^3J_{C-F}$ = 7.2 Hz, C_q), 121.91 (d, $^2J_{C-F}$ = 25.6 Hz, CH), 120.16 (d, $^3J_{C-F}$ = 8.0 Hz, CH), 110.64 (d, $^2J_{C-F}$ = 23.8 Hz, CH), 106.90 (CH). HRMS (ESI): *m*/*z* calcd for $C_{15}H_9FNaO_2$ $[M + Na]^+$: 263.0479; found: 263.0473.

*6-Chloro-2-phenyl-4*H-*chromen-4-one* (**3ca**): Product **3ca** was obtained as a yellow solid (48 mg, 94%); m.p.: 178–180 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (1H, d, *J* = 2.4 Hz, CH), 7.97–7.84 (2H, m, 2CH), 7.64 (1H, dd, *J* = 9.0, 2.4 Hz, CH), 7.58–7.50 (4H, m, 4CH), 6.83 (1H, s, CH). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.19 (C_q), 163.65 (C_q), 154.53 (C_q), 133.93 (CH), 131.84 (C_q), 131.36 (CH), 131.17 (C_q), 129.09 (CH), 126.29 (CH), 125.15 (C_q), 124.91 (CH), 119.79 (CH), 107.46 (CH). HRMS (ESI): *m*/*z* calcd for $C_{15}H_9ClNaO_2$ $[M + Na]^+$: 279.0183; found: 279.0175.

*6-Bromo-2-phenyl-4*H-*chromen-4-one* (**3da**): Product **3da** was obtained as a yellow solid (55 mg, 92%); m.p.: 192 –194 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 8.35 (1H, d, *J* = 2.4 Hz, CH), 7.91 (2H, dd, *J* = 8.0, 1.8 Hz, 2CH), 7.78 (1H, dd, *J* = 9.0, 2.6 Hz, CH), 7.58–7.50 (3H, m, 3CH), 7.47 (1H, d, *J* = 9.0 Hz, CH), 6.83 (1H, s, CH). ^{13}C NMR (101 MHz, $CDCl_3$): δ= 177.04 (Cq), 163.65 (Cq), 154.96 (Cq), 136.69 (CH), 131.85 (CH), 131.32 (Cq), 129.08 (CH), 128.33 (CH), 126.29 (CH), 125.27 (Cq), 120.01 (CH), 118.64 (Cq), 107.52 (CH). HRMS (ESI): m/z calcd for $C_{15}H_9BrNaO_2$ $[M + Na]^+$: 322.9678; found: 322.9686.

*6-Methyl-2-phenyl-4*H-*chromen-4-one* (**3ea**): Product **3ea** was obtained as a yellow solid (38 mg, 81%); m.p.: 124–126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (1H, s, CH), 7.97–7.89 (2H, m, 2CH), 7.59–7.43 (5H, m, 5CH), 6.82 (1H, s, CH), 2.47 (3H, s, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.62 (C_q), 163.24 (C_q), 154.53 (C_q), 135.19 (CH),

134.98 (C_q), 131.88 (CH), 131.48 (C_q), 128.99 (CH), 126.25 (CH), 125.03 (CH), 123.62 (C_q), 117.82 (CH), 107.44 (CH), 20.94 (CH_3). HRMS (ESI): *m/z* calcd for $C_{16}H_{12}O_2$ $[M + H]^+$: 237.0910; found: 237.0903.

*6-Nitro-2-phenyl-4*H-*chromen-4-one* (**3fa**): Product **3fa** was obtained as a yellow solid (19 mg, 36%); m.p.: 195–197 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.11 (1H, d, *J* = 2.8 Hz, CH), 8.55 (1H, dd, *J* = 9.0, 2.8 Hz, CH), 7.94 (2H, dd, *J* = 8.0, 1.4 Hz, 2CH), 7.74 (1H, d, *J* = 9.0 Hz, CH), 7.67–7.51 (3H, m, 3CH), 6.90 (1H, s, CH). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 176.64 (C_q), 164.10 (C_q), 159.03 (C_q), 144.80 (C_q), 132.35 (CH), 130.72 (C_q), 129.26 (CH), 128.11 (CH), 126.41 (CH), 124.05 (CH), 122.48 (C_q), 119.81 (CH), 107.83 (CH). HRMS (ESI): *m/z* calcd for $C_{15}H_{10}NO_4$ $[M + H]^+$: 268.0604; found: 268.0608.

*6-Methoxy-2-phenyl-4*H-*chromen-4-one* (**3ga**): Product **3ga** was obtained as a yellow solid (47 mg, 93%); m.p.: 161–163 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97–7.85 (2H, m, 2CH), 7.60 (1H, d, *J* = 3.0 Hz, CH), 7.55–7.48 (4H, m, 4CH), 7.30 (1H, dd, *J* = 9.0, 3.0 Hz, CH), 6.83 (1H, s, CH), 3.91 (3H, s, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.41 (C_q), 163.12 (C_q), 156.97 (C_q), 151.06 (C_q), 131.84 (C_q), 131.46 (CH), 128.99 (CH), 126.21 (CH), 124.64 (C_q), 123.80 (CH), 119.49 (CH), 106.86 (CH), 104.78 (CH), 55.92 (CH_3). HRMS (ESI): *m/z* calcd for $C_{16}H_{13}O_3$ $[M + H]^+$: 253.0859; found: 253.0849.

*7-Chloro-2-phenyl-4*H-*chromen-4-one* (**3ha**): Product **3ha** was obtained as a yellow solid (45 mg, 88%); m.p.: 159–161 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (1H, d, *J* = 8.6 Hz, CH), 7.90 (2H, d, *J* = 6.6 Hz, 2CH), 7.61 (1H, s, CH), 7.54 (3H, d, *J* = 6.8 Hz, 3CH), 7.39 (1H, d, *J* = 8.2 Hz, CH), 6.82 (1H, s, CH).^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.94 (C_q), 163.51 (C_q), 156.34 (C_q), 139.75 (C_q), 131.82 (C_q), 131.32 (CH), 129.09 (CH), 127.06 (CH), 126.26 (CH), 126.06 (CH), 122.83 (C_q), 118.17 (CH), 107.87 (CH). HRMS (ESI): *m/z* calcd for $C_{15}H_9ClNaO_2$ $[M + Na]^+$: 279.0183; found: 279.0174.

*7-Methyl-2-phenyl-4*H-*chromen-4-one* (**3ia**): Product **3ia** was obtained as a yellow solid (38 mg, 81%); m.p.: 124–126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (1H, d, *J* = 8.0 Hz, CH), 7.96–7.87 (2H, m, 2CH), 7.52 (3H, d, *J* = 4.0 Hz, 3CH), 7.38 (1H, s, CH), 7.23 (1H, d, *J* = 8.0 Hz, CH), 6.80 (1H, s, CH), 2.51 (3H, s, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.42 (C_q), 163.10 (C_q), 156.37 (C_q), 145.10 (C_q), 131.87 (C_q), 131.46 (CH), 128.99 (CH), 126.70 (CH), 126.21 (CH), 125.41 (CH), 121.68 (CH), 117.83 (C_q), 107.50 (CH), 21.84 (CH_3). HRMS (ESI): *m/z* calcd for $C_{16}H_{12}NaO_2$ $[M + Na]^+$: 259.0730; found: 259.0724.

*8-Bromo-2-phenyl-4*H-*chromen-4-one* (**3ja**): Product **3ja** was obtained as a yellow solid (44 mg, 73%); m.p.: 174–176 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (1H, d, *J* = 8.8 Hz, CH), 8.05–8.00 (2H, m, 2CH), 7.92 (1H, d, *J* = 8.4 Hz, CH), 7.60–7.51 (3H, m, 3CH), 7.30 (1H, t, *J* = 7.8 Hz, CH), 6.88 (1H, s, CH). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.84 (C_q), 163.34 (C_q), 152.73 (C_q), 137.14 (CH), 131.95 (C_q), 131.20 (CH), 129.16 (CH), 126.46 (CH), 125.82 (CH), 125.32 (CH), 125.07 (C_q), 111.98 (C_q), 107.19 (CH). HRMS (ESI): *m/z* calcd for $C_{15}H_9BrNaO_2$ $[M + Na]^+$: 322.9678; found: 322.9669.

*8-Methyl-2-phenyl-4*H-*chromen-4-one* (**3ka**): Product **3ka** was obtained as a yellow solid (42 mg, 89%); m.p.: 164–166 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (1H, d, *J* = 7.8 Hz, CH), 7.98–7.90 (2H, m, 2CH), 7.57–7.49 (4H, m, 4CH), 7.30 (1H, t, *J* = 7.6 Hz, CH), 6.84 (1H, s, CH), 2.61 (3H, s, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.85 (C_q), 162.86 (C_q), 154.66 (C_q), 134.69 (C_q), 132.01 (C_q), 131.53 (CH), 129.07 (CH), 127.49 (CH), 126.16 (CH), 124.73 (CH), 123.82 (CH), 123.28 (C_q), 107.29 (CH), 15.83 (CH_3). HRMS (ESI): *m/z* calcd for $C_{16}H_{12}NaO_2$ $[M + Na]^+$: 259.0730; found: 259.0720.

*8-Methoxy-2-phenyl-4*H-*chromen-4-one* (**3la**): Product **3la** was obtained as a yellow solid (46 mg, 93%); m.p.: 197–199 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99–7.95 (2H, m, 2CH), 7.78 (1H, dd, *J* = 8.0, 1.0 Hz, CH), 7.54–7.50 (3H, m, 3CH), 7.33 (1H, t, *J* = 8.0 Hz, CH), 7.22–7.15 (1H, m, CH), 6.85 (1H, s, CH), 4.03 (3H, s, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.46 (C_q), 163.01 (C_q), 149.09 (C_q), 146.62 (C_q), 131.79 (C_q), 131.54 (CH), 129.00 (CH), 126.33 (CH), 124.91 (CH), 124.81 (C_q), 116.39 (CH), 114.40 (CH), 107.31 (CH), 56.35 (CH_3). HRMS (ESI): *m/z* calcd for $C_{16}H_{12}NaO_3$ $[M + Na]^+$: 275.0679; found: 275.0672.

*6-Phenyl-8*H-*[1,3]dioxolo[4,5-g]chromen-8-one* (**3ma**): Product **3ma** was obtained as a yellow solid (34 mg, 64%); m.p.: 207–209 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90–7.86 (2H, m, 2CH), 7.60–7.46 (4H, m, 4CH), 6.97 (1H, s, CH), 6.77 (1H, s, CH), 6.12 (2H, s, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.41 (C_q), 162.70 (C_q), 153.49 (C_q), 152.76 (C_q), 146.18 (C_q), 131.71 (C_q), 131.34 (CH), 128.99 (CH), 126.04 (CH), 118.98 (C_q), 106.98 (CH), 102.42 (CH), 102.31 (CH_2), 98.04 (CH). HRMS (ESI): *m/z* calcd for $C_{16}H_{11}O_4$ $[M + H]^+$: 267.0652; found: 267.0655.

*2-(4-Fluorophenyl)-4*H-*chromen-4-one* (**3ab**): Product **3ab** was obtained as a yellow solid (42 mg, 88%); m.p.: 145–147 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31–8.16 (1H, m, CH), 7.97–7.91 (2H, m, 2CH), 7.78–7.67 (1H, m, CH), 7.57 (1H, d, *J* = 8.4 Hz, CH), 7.43 (1H, t, *J* = 7.6 Hz, CH), 7.22 (2H, t, *J* = 8.6 Hz, 2CH), 6.78 (1H, s, CH).^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.30 (C_q), 164.73 (d, $^1J_{C-F}$ = 253.2 Hz, C_q), 162.37 (C_q), 156.15 (C_q), 133.82 (CH), 128.48 (d, $^3J_{C-F}$ = 9.0 Hz, CH), 127.96 (d, $^4J_{C-F}$ = 3.2 Hz, C_q), 125.72 (CH), 125.30 (CH), 123.87 (C_q), 117.99 (CH), 116.28 (d, $^2J_{C-F}$ = 22.0 Hz, CH), 107.36 (CH). HRMS (ESI): *m/z* calcd for $C_{15}H_{10}FO_2$ $[M + H]^+$: 241.0659; found: 241.0662.

*2-(4-Chlorophenyl)-4*H-*chromen-4-one* (**3ac**): Product **3ac** was obtained as a yellow solid (45 mg, 87%); m.p.: 185–187 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (1H, dd, *J* = 8.0, 1.4 Hz, CH), 7.87 (2H, d, *J* = 8.6 Hz, 2CH), 7.75–7.67 (1H, m, CH), 7.56 (1H, d, *J* = 8.4 Hz, CH), 7.50 (2H, d, *J* = 8.6 Hz, 2CH), 7.43 (1H, t, *J* = 7.6 Hz, CH), 6.80 (1H, s, CH). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.23 (C_q), 162.17 (C_q), 156.12 (C_q), 137.85 (C_q), 133.89 (CH), 130.20 (CH), 129.35 (CH), 127.51 (C_q), 125.71 (CH), 125.35 (CH), 123.87 (C_q), 118.01 (CH), 107.66 (CH). HRMS (ESI): *m/z* calcd for $C_{15}H_{10}ClO_2$ $[M + H]^+$: 257.0364; found: 257.0368.

*2-(4-Bromophenyl)-4*H-*chromen-4-one* (**3ad**): Product **3ad** was obtained as a yellow solid (54 mg, 89%); m.p.: 176–178 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29–8.18 (1H, m, CH), 7.80 (2H, d, *J* = 8.6 Hz, 2CH), 7.74–7.69 (1H, m, CH), 7.67 (2H, d, *J* = 8.6 Hz, 2CH), 7.57 (1H, d,

J = 8.2 Hz, CH), 7.43 (1H, t, *J* = 7.6 Hz, CH), 6.81 (1H, s, CH). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.28 (C_q), 162.25 (C_q), 156.13 (C_q), 133.91 (CH), 132.33 (CH), 130.67 (CH), 127.68 (C_q), 126.29 (C_q), 125.72 (CH), 125.37 (CH), 123.94 (C_q), 118.03 (CH), 107.70 (CH). HRMS (ESI): *m*/*z* calcd for $C_{15}H_{10}BrO_2$ $[M + H]^+$: 300.9859; found: 300.9867.

*2-(p-Tolyl)-4*H*-chromen-4-one* (**3ae**): Product **3ae** was obtained as a yellow solid (43 mg, 92%); m.p.: 109–111 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (1H, d, *J* = 8.0 Hz, CH), 7.82 (2H, d, *J* = 8.0 Hz, 2CH), 7.69 (1H, t, *J* = 7.8 Hz, CH), 7.56 (1H, d, *J* = 8.4 Hz, CH), 7.41 (1H, t, *J* = 7.6 Hz, CH), 7.32 (2H, d, *J* = 8.0 Hz, 2CH), 6.80 (1H, s, CH), 2.43 (3H, s, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.44 (C_q), 163.57 (C_q), 156.20 (C_q), 142.22 (C_q), 133.62 (CH), 129.73 (CH), 128.90 (CH), 126.19 (C_q), 125.63 (CH), 125.09 (CH), 123.94 (C_q), 118.02 (CH), 106.93 (CH), 21.52 (CH_3). HRMS (ESI): *m*/*z* calcd for $C_{16}H_{13}O_2$ $[M + H]^+$: 237.0910; found: 237.0914.

*2-[4-(Trifluoromethyl)phenyl]-4*H*-chromen-4-one* (**3af**): Product **3af** was obtained as a yellow solid (51 mg, 88%); m.p.: 139–141 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (1H, d, *J* = 8.0 Hz, CH), 8.05 (2H, d, *J* = 8.2 Hz, 2CH), 7.80 (2H, d, *J* = 8.2 Hz, 2CH), 7.74 (1H, t, *J* = 7.8 Hz, CH), 7.60 (1H, d, *J* = 8.4 Hz, CH), 7.45 (1H, t, *J* = 7.6 Hz, CH), 6.88 (1H, s, CH). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.17 (C_q), 161.58 (C_q), 156.17 (C_q), 135.16 (d, $^4J_{C–F}$ = 1.0 Hz, C_q), 134.10 (C_q), 133.12 (d, $^2J_{C–F}$ = 33.0 Hz, CH), 126.62 (CH), 126.03 (q, $^3J_{C–F}$ = 3.8 Hz, CH), 125.78 (CH), 125.54 (CH), 123.92 (C_q), 123.58 (d, $^1J_{C–F}$ = 272.6 Hz, C_q), 118.10 (CH), 108.73 (CH). HRMS (ESI): *m*/*z* calcd for $C_{16}H_{10}F_3O_2$ $[M + H]^+$: 291.0627; found: 291.0632. The NMR data agree with those in a literature report.[44]

*2-(4-Methoxyphenyl)-4*H*-chromen-4-one* (**3ag**): Product **3ag** was obtained as a yellow solid (38 mg, 75%); m.p.: 151–153 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (1H, d, *J* = 8.0 Hz, CH), 7.89 (2H, d, *J* = 8.8 Hz, 2CH), 7.69 (1H, t, *J* = 7.8 Hz, CH), 7.55 (1H, d, *J* = 8.4 Hz, CH), 7.41 (1H, t, *J* = 7.6 Hz, CH), 7.03 (2H, d, *J* = 8.8 Hz, 2CH), 6.76 (1H, s, CH), 3.89 (3H, s, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.34 (C_q), 163.40 (C_q), 162.38 (C_q), 156.15 (C_q), 133.54 (CH), 127.98 (CH), 125.63 (CH), 125.05 (CH), 123.98 (C_q), 123.88 (C_q), 117.93 (CH), 114.43 (CH), 106.14 (CH), 55.48 (CH_3). HRMS (ESI): *m*/*z* calcd for $C_{16}H_{12}NaO_3$ $[M + Na]^+$: 275.0679; found: 275.0685.

*2-(2-Chlorophenyl)-4*H*-chromen-4-one* (**3ah**): Product **3ah** was obtained as a yellow solid (38 mg, 74%); m.p.: 113–115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 (1H, d, *J* = 7.8 Hz, CH), 7.71 (1H, t, *J* = 7.6 Hz, CH), 7.64 (1H, d, *J* = 7.0 Hz, CH), 7.53 (2H, t, *J* = 8.2 Hz, 2CH), 7.49–7.38 (3H, m, 3CH), 6.66 (1H, s, CH). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.13 (C_q), 162.63 (C_q), 156.57 (C_q), 133.91 (CH), 132.91 (C_q), 131.90 (C_q), 131.76 (CH), 130.79 (CH), 130.63 (CH), 127.07 (CH), 125.74 (CH), 125.33 (CH), 123.83 (C_q), 118.18 (CH), 112.99 (CH). HRMS (ESI): *m*/*z* calcd for $C_{15}H_9ClNaO_2$ $[M + Na]^+$: 279.0183; found: 279.0184.

*2-(o-Tolyl)-4*H*-chromen-4-one* (**3ai**): Product **3ai** was obtained as a yellow oil (39 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 (1H, d, *J* = 8.0 Hz, CH), 7.70 (1H, t, *J* = 7.8 Hz, CH), 7.51 (2H, dd, *J* = 13.8, 8.0 Hz, 2CH), 7.46–7.39 (2H, m, 2CH), 7.33 (2H, d, *J* = 7.2 Hz, 2CH), 6.50 (1H, s, CH), 2.49 (3H, s, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.29 (C_q), 166.08 (C_q), 156.42 (C_q), 136.75 (C_q), 133.74 (C_q), 132.56 (CH), 131.22 (CH), 130.68 (CH), 129.16 (CH), 126.17 (CH), 125.70 (CH), 125.20 (CH), 123.74 (C_q), 118.01 (CH), 111.90 (CH), 20.52 (CH_3). HRMS (ESI): *m*/*z* calcd for $C_{16}H_{12}NaO_2$ $[M + Na]^+$: 259.0730; found: 259.0720.

*2-(2-Methoxyphenyl)-4*H*-chromen-4-one* (**3aj**): Product **3aj** was obtained as a yellow solid (48 mg, 95%); m.p.: 101–102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (1H, dd, *J* = 8.0, 1.6 Hz, CH), 7.91 (1H, dd, *J* = 7.8, 1.6 Hz, CH), 7.70–7.65 (1H, m, CH), 7.53 (1H, d, *J* = 8.2 Hz, CH), 7.51–7.45 (1H, m, CH), 7.40 (1H, t, *J* = 7.6 Hz, CH), 7.15 (1H, s, CH), 7.11 (1H, t, *J* = 7.2 Hz, CH), 7.05 (1H, d, *J* = 8.4 Hz, CH), 3.94 (3H, s, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.89 (C_q), 160.84 (C_q), 157.96 (C_q), 156.46 (C_q), 133.50 (CH), 132.38 (CH), 129.25 (CH), 125.58 (CH), 124.87 (CH), 123.79 (C_q), 120.80 (C_q), 120.69 (CH), 118.00 (CH), 112.63 (CH), 111.72 (CH), 55.65 (CH_3). HRMS (ESI): *m*/*z* calcd for $C_{16}H_{12}NaO_3$ $[M + Na]^+$: 275.0679; found: 275.0668.

*2-(m-Tolyl)-4*H*-chromen-4-one* (**3ak**): Product **3ak** was obtained as a yellow solid (36 mg, 77%); m.p.: 108–110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (1H, d, *J* = 8.0 Hz, CH), 7.76–7.66 (3H, m, 3CH), 7.58 (1H, d, *J* = 8.4 Hz, CH), 7.45–7.38 (2H, m, 2CH), 7.35 (1H, d, *J* = 7.6 Hz, CH), 6.82 (1H, s, CH), 2.46 (3H, s, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.50 (C_q), 163.60 (C_q), 156.25 (C_q), 138.81 (C_q), 133.69 (CH), 132.38 (CH), 131.70 (CH), 128.91 (C_q), 126.82 (CH), 125.66 (CH), 125.15 (CH), 124.00 (C_q), 123.48 (CH), 118.06 (CH), 107.54 (CH), 21.49 (CH_3). HRMS (ESI): *m*/*z* calcd for $C_{16}H_{12}NaO_2$ $[M + Na]^+$: 259.0730; found: 259.0719.

*2-(3-Bromophenyl)-4*H*-chromen-4-one* (**3al**): Product **3al** was obtained as a yellow solid (44 mg, 73%); m.p.: 90–92 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (1H, d, *J* = 7.0 Hz, CH), 8.08 (1H, s, CH), 7.83 (1H, d, *J* = 8.0 Hz, CH), 7.75–7.69 (1H, m, CH), 7.67 (1H, d, *J* = 8.0 Hz, CH), 7.59 (1H, d, *J* = 8.4 Hz, CH), 7.47–7.36 (2H, m, 2CH), 6.80 (1H, s, CH). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.17 (C_q), 161.64 (C_q), 156.13 (C_q), 134.41 (CH), 133.98 (CH), 133.77 (CH), 130.53 (CH), 129.22 (C_q), 125.73 (CH), 125.42 (CH), 124.81 (C_q), 123.89 (C_q), 123.22 (CH), 118.08 (CH), 108.16 (CH). HRMS (ESI): *m*/*z* calcd for $C_{15}H_{10}BrO_2$ $[M + H]^+$: 300.9859; found: 300.9869.

*2-(tert-Butyl)-4*H*-chromen-4-one* (**3am**): Product **3am** was obtained as a yellow solid (37 mg, 91%); m.p.: 72–74 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (1H, d, *J* = 8.0 Hz, CH), 7.66 (1H, t, *J* = 7.8 Hz, CH), 7.46 (1H, d, *J* = 8.4 Hz, CH), 7.38 (1H, t, *J* = 7.6 Hz, CH), 6.29 (1H, s, CH), 1.36 (9H, s, $3CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.94 (C_q), 176.04 (C_q), 156.44 (C_q), 133.43 (CH), 125.52 (CH), 124.78 (CH), 123.40 (C_q), 117.80 (CH), 106.65 (CH), 36.47 (C_q), 27.85 (CH_3). HRMS (ESI): *m*/*z* calcd for $C_{13}H_{14}NaO_2$ $[M + Na]^+$: 225.0886; found: 225.0891.

*2-(Thiophen-2-yl)-4*H*-chromen-4-one* (**3an**): Product **3an** was obtained as a yellow solid (40 mg, 87%); m.p.: 93–95 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (1H, dd,

J = 8.0, 1.6 Hz, CH), 7.73 (1H, d, J = 3.0 Hz, CH), 7.71–7.65 (1H, m, CH), 7.58 (1H, d, J = 5.0 Hz, CH), 7.53 (1H, d, J = 8.4 Hz, CH), 7.41 (1H, t, J = 7.6 Hz, CH), 7.21–7.17 (1H, m, CH), 6.71 (1H, s, CH). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 177.89 (C_q), 158.99 (C_q), 155.87 (C_q), 135.11 (C_q), 133.71 (CH), 130.23 (CH), 128.46 (CH), 128.41 (CH), 125.64 (CH), 125.23 (CH), 123.95 (C_q), 117.90 (CH), 106.16 (CH). HRMS (ESI): *m/z* calcd for $C_{13}H_9O_2S$ $[M + H]^+$: 229.0318; found: 229.0307.

*2-(Naphthalen-2-yl)-4*H*-chromen-4-one* (**3ao**): Product **3ao** was obtained as a yellow solid (51 mg, 93%); m.p.: 157–159 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (1H, s, CH), 8.29–8.22 (1H, m, CH), 8.01–7.86 (4H, m, 4CH), 7.75–7.69 (1H, m, CH), 7.63 (1H, d, J = 8.0 Hz, CH), 7.60–7.55 (2H, m, 2CH), 7.43 (1H, t, J = 7.2 Hz, CH), 6.96 (1H, s, CH). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 178.41 (C_q), 163.27 (C_q), 156.29 (C_q), 134.61 (C_q), 133.77 (CH), 132.85 (C_q), 129.01 (CH), 128.90 (CH), 128.85 (CH), 127.98 (CH), 127.79 (CH), 127.04 (C_q), 126.88 (CH), 125.69 (CH), 125.21 (CH), 123.99 (CH), 122.47 (C_q), 118.08 (CH), 107.85 (CH). HRMS (ESI): *m/z* calcd for $C_{19}H_{13}O_2$ $[M + H]^+$: 273.091; found: 273.0922.

*2-(Adamantan-1-yl)-4*H*-chromen-4-one* (**3ap**): Product **3ap** was obtained as a white solid (53 mg, 95%); m.p.: 100–102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (1H, dd, J = 8.0, 1.6 Hz, CH), 7.68–7.62 (1H, m, CH), 7.45 (1H, d, J = 8.2 Hz, CH), 7.40–7.33 (1H, m, CH), 6.20 (1H, s, CH), 2.13 (3H, s, 3CH), 2.00–1.96 (6H, m, 3CH_2), 1.86–1.73 (6H, m, 3CH_2). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 179.03 (C_q), 175.77 (C_q), 156.45 (C_q), 133.34 (CH), 125.53 (CH), 124.70 (CH), 123.61 (C_q), 117.79 (CH), 106.59 (CH), 39.47 (CH), 38.17 (CH_2), 36.41 (CH_2), 27.94 (CH_2). HRMS (ESI): *m/z* calcd for $C_{19}H_{21}O_2$ $[M + Na]^+$: 281.1536; found: 281.1529.

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