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N-Heterocyclic Carbene-Catalyzed Domino Reactions of Formylcyclopropane 1,1-Diesters: A New Synthesis of Coumarins

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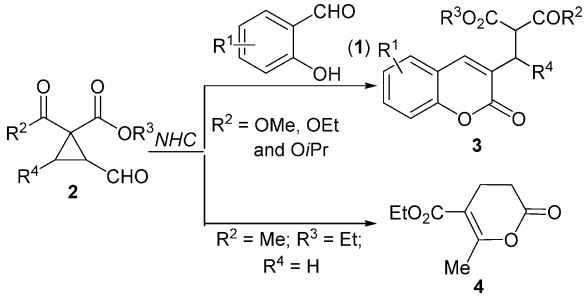
N-Heterocyclic carbenes (NHCs) catalyze the reaction of formylcyclopropane 1,1-diesters with salicylaldehydes in a domino redox esterification/cyclization reaction to give coumarins in moderate to excellent yields. In addition, we also report the intramolecular conversion of compound **2f** to dihydropyranone **4** catalyzed by NHC **D**.

Introduction

As versatile building blocks in modern organic synthesis, activated cyclopropanes have been widely investigated in the field of nucleophilic ring-opening reactions.[1] In the research of novel carbon–carbon and carbon–heteroatom bond-forming reactions, N-heterocyclic carbenes (NHCs) have been efficiently applied as organocatalysts in a large number of umpolung chemical transformations.[2] Tandem reactions have received more attention in recent years due to their efficient construction of complex molecular skeletons.[3] Inspired by the recent results reported by Bode[4] and Bräse,[5] we envisioned that NHC-promoted ring opening of cyclopropanecarbaldehydes might be invoked to supply a concise approach to coumarins, an important class of biologically active products.[6,7] In order to activate the C1–C2 bond of the cyclopropane ring more, we selected cyclopropanecarbaldehydes with two electron-withdrawing groups installed on C1 (Scheme 1, compounds **2**) instead of Bode's mono-activated cyclopropanecarbaldehydes. To our delight, we found that most general N-heterocyclic carbenes (Figure 1) could give satisfactory results. Herein, we report our results on this new type of domino reactions of 2-formylcyclopropane-1,1-dicarboxylates and salicylaldehydes catalyzed by NHCs (Scheme 1). Furthermore, an interesting result for the intramolecular redox lactonization of ethyl 1-acetyl-2-formylcyclopropanecarboxylate (**2f**) is also reported, which to the best our knowledge is the first example of a ring-opening cyclization of a cyclopropanecarbaldehyde/ketone to a 3,4-dihydropyran-2-one[8] catalyzed by NHCs.



Scheme 1. Domino reactions of 1,1-diactivated cyclopropanecarbaldehydes catalyzed by NHCs.

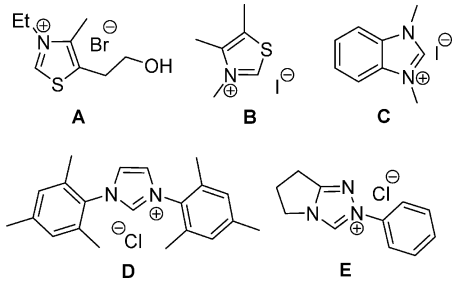


Figure 1. Several readily available NHC precursors.

Results and Discussion

Our studies began with an initial investigation of the catalytic reactivity of several NHCs (Figure 1) in the reaction of salicylaldehyde **1a** and diethyl 2-formylcyclopropane-1,1-dicarboxylate (**2a**) (Table 1). In the presence of 42 mol-% of benzimidazolium iodide **C** and 1.0 equiv. of DBU, the reaction of **1a** and **2a** afforded 3-substituted coumarin **3a** in 8 h at 55 °C with a yield of 50% (Entry 1, Table 1). As additives, 4 Å molecular sieves or anhydrous

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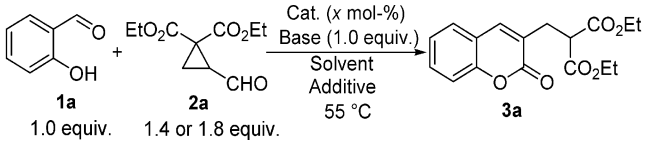
$MgSO_4$ were found to be helpful in the formation of coumarin **3a** (Entries 2 and 3, Table 1). Increasing the amount of **2a** also slightly improved the yield (Entry 4, Table 1). A survey of other NHCs convinced us that imidazolium salt **D** gave the best result (83% yield for **3a**). Several other NHCs derived from **A**, **B** and **E** proved less effective (Entries 5, 6, and 8, Table 1). A screening of different bases was carried out (Entries 9–18, Table 1). When DABCO was used as the base, the yield of **3a** was comparable to that when DBU was used; however, the reaction time became longer (Entry 12, Table 1). As a mixed base system, DABCO/DBU was the best choice in terms of both reaction yield and reaction time (Entry 16, Table 1). The examination of various solvents showed that THF was the best choice (Entry 16 and Entries 19–25, Table 1). Lowering the catalyst loading did not significantly affect the yield (Entries 26–28, Table 1). We obtained 89% yield of **3a** in the presence of 20 mol-% of imidazolium salt **D** using DABCO/DBU as the base. These conditions were established as the optimized ones (Entry 26, Table 1).

We investigated reactions of a variety of salicylaldehydes and formylcyclopropanes under the optimized conditions (Table 2). Salicylaldehydes substituted with electron-donating groups at the 3- or 5-positions (Entry 6 and Entries 9–13, Table 2) reacted smoothly with 2-formylcyclopropane-1,1-dicarboxylates **2a**–**c** in good to excellent yields, whereas salicylaldehydes with electron-donating groups at the 4-position, such as **1g** (Entry 7, Table 2), reacted more slowly with **2a** in moderate yield, with recovery of a certain amount of starting material. Salicylaldehydes bearing electron-withdrawing groups reacted with **2a** to give products in moderate to good yields (Entries 2–5, Table 2). Substrates **1e** and **1k** with an NO_2 group at the 5-position and with an OCF_3 group at the 3-position, respectively, required higher reaction temperatures to drive the reaction further to completion. When C-3 of diethyl 2-formylcyclopropane-1,1-dicarboxylate was substituted by methyl or phenyl, the yields significantly decreased (Entries 14 and 15, Table 2). It should be noted that in the reaction of ethyl 1-acetyl-2-formylcyclopropanecarboxylate (**2f**) and **1j**, an unexpected

Table 1. Optimization of the reaction conditions [DABCO = 1,4-diazabicyclo[2.2.2]octane; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; DIPEA = *N*,*N*-diisopropylethylamine; DMAP = 4-(dimethylamino)pyridine].



1a 1.0 equiv. **2a** 1.4 or 1.8 equiv. **3a**

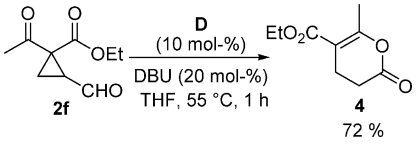
Entry	Cat. (mol-%)	Base	Solvent	Additive	Time [h]	Yield [%][c]
1[a]	**C** (42)	DBU	THF	none	8	50
2[a]	**C** (42)	DBU	THF	4 Å MS	8	61
3[a]	**C** (42)	DBU	THF	$MgSO_4$	8	66
4[b]	**C** (42)	DBU	THF	$MgSO_4$	8	71
5[b]	**B** (42)	DBU	THF	$MgSO_4$	1	45
6[b]	**A** (42)	DBU	THF	$MgSO_4$	5	32
7[b]	**D** (42)	DBU	THF	$MgSO_4$	1	83
8[b]	**E** (42)	DBU	THF	$MgSO_4$	1	63
9[b]	**D** (42)	K_2CO_3[d]	THF	$MgSO_4$	2	73
10[b]	**D** (42)	DIPEA	THF	$MgSO_4$	2.5	trace
11[b]	**D** (42)	*t*BuOK	THF	$MgSO_4$	8.5	61
12[b]	**D** (42)	DABCO	THF	$MgSO_4$	12	85
13[b]	**D** (42)	DMAP	THF	$MgSO_4$	5	n.d.
14[b]	**D** (42)	Et_3N	THF	$MgSO_4$	8	30
15[b]	**D** (42)	NaH	THF	$MgSO_4$	2.5	65
16[b]	**D** (42)	DABCO/DBU[e]	THF	$MgSO_4$	1	88
17[b]	**D** (42)	imidazole/DBU[f]	THF	$MgSO_4$	4.5	45
18[b]	**D** (42)	DMAP/DBU[g]	THF	$MgSO_4$	1	80
19[b]	**D** (42)	DABCO/DBU[e]	CH_2Cl_2	$MgSO_4$	5	54
20[b]	**D** (42)	DABCO/DBU[e]	PhMe	$MgSO_4$	1.5	75
21[b]	**D** (42)	DABCO/DBU[e]	$CHCl_3$	$MgSO_4$	7	46
22[b]	**D** (42)	DABCO/DBU[e]	EtOAc	$MgSO_4$	0.5	80
23[b]	**D** (42)	DABCO/DBU[e]	CH_3CN[h]	$MgSO_4$	8	< 10
24[b]	**D** (42)	DABCO/DBU[e]	DMF	$MgSO_4$	1.5	< 10
25[b]	**D** (42)	DABCO/DBU[e]	THF/*t*BuOH (10:1)	$MgSO_4$	1	80
26[b]	**D** (20)	DABCO/DBU[e]	THF	$MgSO_4$	1.5	89
27[b]	**D** (10)	DABCO/DBU[e]	THF	$MgSO_4$	2	83
28[b]	**D** (5)	DABCO/DBU[e]	THF	$MgSO_4$	5	81

[a] 1.4 equiv. of **2a**. [b] 1.8 equiv. of **2a**. [c] Isolated yields based on **1a**. [d] 10 mol-% of 18-crown-6 was added. [e] 30 mol-% of DABCO and 70 mol-% of DBU. [f] 10 mol-% of imidazole and 70 mol-% of DBU. [g] 30 mol-% of DMAP and 70 mol-% of DBU. [h] A large quantity of **1a** was recovered.

Table 2. Investigation of the scope of salicylaldehydes and formylcyclopropanes.[a]

Entry	Substrate	R^1	Substrate	R^2	R^3	R^4	Time [h]	Product	Yield [%][b]
1	**1a**	H	**2a**	OEt	Et	H	1.5	**3a**	89
2	**1b**	5-F	**2a**	OEt	Et	H	1	**3b**	82
3	**1c**	5-Cl	**2a**	OEt	Et	H	2	**3c**	85
4	**1d**	5-Br	**2a**	OEt	Et	H	3	**3d**	86
5[c]	**1e**	5-NO_2	**2a**	OEt	Et	H	3	**3e**	63
6	**1f**	5-OMe	**2a**	OEt	Et	H	0.5	**3f**	94
7	**1g**	4-OMe	**2a**	OEt	Et	H	5	**3g**	66[d]
8	**1h**	3-F	**2a**	OEt	Et	H	1	**3h**	87
9	**1i**	3-Me	**2a**	OEt	Et	H	0.5	**3i**	96
10	**1j**	3-OMe	**2a**	OEt	Et	H	0.5	**3j**	98
11[c]	**1k**	3-OCF_3	**2a**	OEt	Et	H	3	**3k**	90
12	**1j**	3-OMe	**2b**	OMe	Me	H	0.5	**3l**	93
13	**1j**	3-OMe	**2c**	O*i*Pr	*i*Pr	H	0.5	**3m**	99
14	**1j**	3-OMe	**2d**	OEt	Et	Me	6.5	**3n**	51[e]
15	**1j**	3-OMe	**2e**	OEt	Et	Ph	9	–	complex[f]
16	**1j**	3-OMe	**2f**	Me	Et	H	6	**4**	54[g]

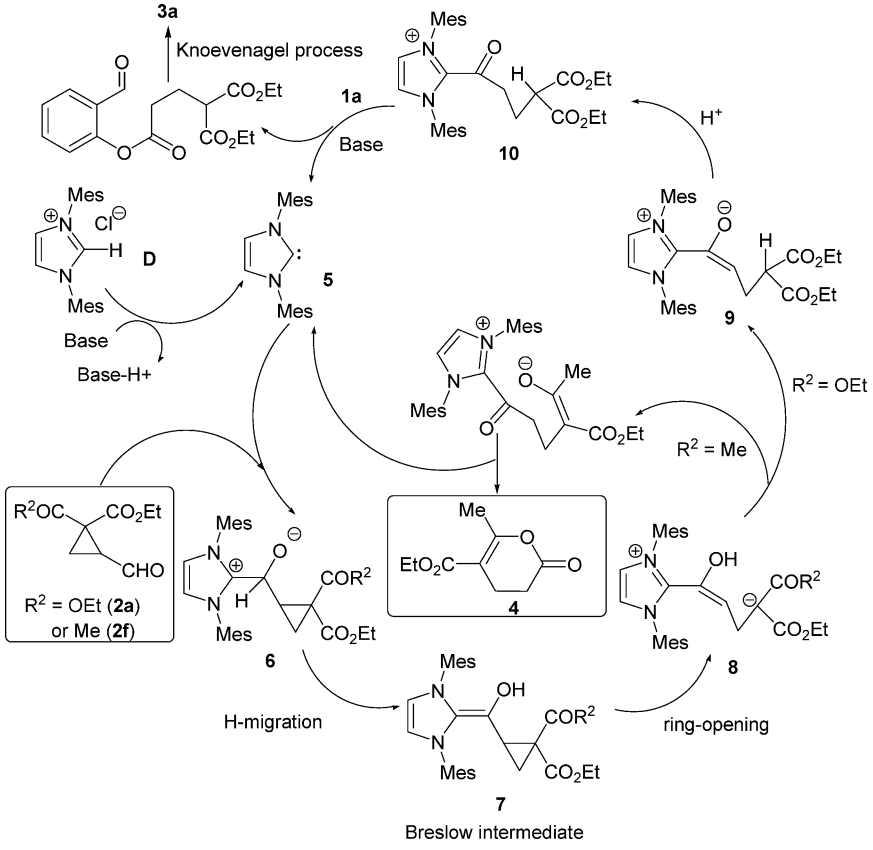
[a] Reaction conditions: 1.0 equiv. of **1**, 1.8 equiv. of **2**, 20 mol-% of imidazolium salt **D**, 30 mol-% of DABCO and 70 mol-% of DBU, THF, 55 °C, nitrogen. [b] Isolated yields based on **1**. [c] Reaction temperature was 65 °C. [d] 25% of **1g** was recovered. [e] 32% of **1j** was recovered. [f] A large quantity of **1j** was recovered. [g] 32% of **1j** was recovered, and 54% (based on **2f**) of compound **4** was obtained.



Scheme 2. Intramolecular tandem redox lactonization of ethyl 1-acetyl-2-formylcyclopropanecarboxylate (**2f**) catalyzed by imidazolium salt **D**.

product **4** was obtained in 54% yield. The structure of **4** was confirmed to be an intramolecular redox esterification product of **2f**. In an independent experiment, when catalyzed by imidazolium salt **D**, **2f** itself could be converted to compound **4** in 72% yield (Scheme 2).

Based on the mechanisms proposed by Bode[4] and Bräse,[5] a plausible mechanism for the formation of coumarin **3a** and compound **4** is illustrated in Scheme 3. The



Scheme 3. Postulated catalytic cycle for the formation of coumarin **3a** and 3,4-dihydropyran-2-one **4**.

NHC **5**, generated upon deprotonation of imidazolium salt **D** with a base, would react with formylcyclopropane **2a** or **2f**, to afford intermediate **6**, and subsequent hydrogen migration would generate Breslow intermediate **7**.[4a,9] The ring-opening process would lead to the formation of enolate **8**. When R^2 is an OEt group, enolate **8** would be converted to **9** by proton migration. Acylimidazolium salt **10** would be formed by the subsequent protonation and tautomerization of **9**. After a combination of nucleophilic attack of salicylaldehyde **1a** and a Knoevenagel process,[5] **3a** would be produced, and NHC **5** would be released for the next catalytic cycle. When R^2 is a methyl group, intermediate **8** would likely undergo successive tautomerization and intramolecular redox lactonization to afford 3,4-dihydropyran-2-one **4** (Scheme 3).

Conclusions

We have described new domino reactions between salicylaldehydes and readily available 2-formylcyclopropane-1,1-dicarboxylates, catalyzed by most general N-heterocyclic carbenes. This method provides an alternative convenient and efficient access to coumarin derivatives. The reaction conditions are mild, and the yields are high. Additionally, we also reported a new domino cyclopropane ring opening/redox lactonization of ethyl 1-acetyl-2-formylcyclopropanecarboxylate catalyzed by NHC. Further exploration of the reaction scope is currently underway.

Experimental Section

General: All reactions were carried out under nitrogen in dry glassware and were monitored by analytical thin-layer chromatography (TLC), which was visualized by ultraviolet light (254 nm). All solvents were obtained from commercial sources and were purified according to standard procedures. Salicylaldehydes **1** were purchased from Aldrich and used without further purification. 2-Formylcyclopropane-1,1-dicarboxylates **2** were easily prepared according to literature methods.[10] NHC precursors **A**–**E** were purchased from Aldrich or prepared according to literature methods.[11] Purification of products was accomplished by flash chromatography using silica gel (200–300 mesh). All NMR spectra were recorded with a Varian spectrometer at 300 MHz or 400 MHz (^{1}H NMR) and 75 MHz or 100 MHz (^{13}C NMR) in $CDCl_3$; chemical shifts (δ) are given in ppm, coupling constants (J) in Hz, and the solvent signals were used as references ($CDCl_3$: δ_C = 77.0 ppm; residual $CHCl_3$ in $CDCl_3$: δ_H = 7.26 ppm). High-resolution mass spectra were recorded with an FTMS spectrometer. IR spectra were recorded with a Nicolet MAGNA-560 spectrometer. Melting points were obtained with a Yanaco-241 apparatus and are uncorrected.

General Procedure for NHC-Catalyzed Umpolung Domino Reactions of Salicylaldehydes 1 and 2-Formylcyclopropane 1,1-Diesters 2: An oven-dried 25-mL three-necked flask was charged with anhydrous $MgSO_4$ (100 mg) and imidazolium salt **D** (24 mg, 0.07 mmol, 20 mol-%). Salicylaldehydes **1** (0.35 mmol, 1.0 equiv.), 2-formylcyclopropane 1,1-diesters **2** (0.63 mmol, 1.8 equiv.), dry THF (4 mL), DABCO (12 mg, 0.11 mmol, 30 mol-%) and DBU (37 μL, 0.25 mmol, 70 mol-%) were added sequentially under a positive pressure of nitrogen. The reaction mixture was heated to 55 °C. After completion of the reactions (as monitored by TLC), the solvent was evaporated in vacuo, and the residue was purified by flash silica gel chromatography to afford products **3**.

Procedure for NHC-Catalyzed Domino Redox Lactonization of Ethyl 1-Acetyl-2-formylcyclopropanecarboxylate (2f): An oven-dried 25-mL three-necked flask was charged with imidazolium salt **D** (15 mg, 0.045 mmol, 10 mol-%), **2f** (83 mg, 0.45 mmol, 1.0 equiv.) and THF (3 mL). DBU (14 μL, 0.09 mmol, 20 mol-%) was then added, and the reaction mixture was heated to 55 °C for 1 h. The THF was evaporated in vacuo, and the residue was purified by flash silica gel chromatography to afford 3,4-dihydropyran-2-one **4** (60 mg, 72% yield).

Diethyl 2-[(2-Oxo-2*H*-chromen-3-yl)methyl]malonate (3a):[12] Yield 99 mg, 89%. White solid, m.p. 68–70 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (s, 1 H), 7.43–7.51 (m, 2 H), 7.24–7.33 (m, 2 H), 4.17 (2 q, J = 7.2 Hz, 4 H), 3.96 (t, J = 7.6 Hz, 1 H), 3.13 (d, J = 7.6 Hz, 2 H), 1.21 (t, J = 7.2 Hz, 6 H) ppm.

Diethyl 2-[(6-Fluoro-2-oxo-2*H*-chromen-3-yl)methyl]malonate (3b): Yield 96 mg, 82%. White solid, m.p. 115–117 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51 (s, 1 H), 7.05–7.24 (m, 3 H), 4.11 (2 q, J = 7.2 Hz, 4 H), 3.88 (t, J = 7.5 Hz, 1 H), 3.07 (d, J = 7.5 Hz, 2 H), 1.15 (t, J = 7.2 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.4, 160.7, 158.6 (d, J_{CF} = 242.5 Hz), 149.4, 140.4, 126.5, 119.7 (d, J_{CF} = 9.3 Hz), 118.5 (d, J_{CF} = 24.3 Hz), 117.9 (d, J_{CF} = 8.4 Hz), 112.7 (d, J_{CF} = 23.8 Hz), 61.6, 49.7, 30.6, 13.9 ppm. HRMS (ESI): calcd. for $C_{17}H_{17}FO_6$ $[M + Na]^+$ 359.0901; found 359.0908. IR (KBr): $\tilde{\nu}$ = 3124, 3082, 2986, 2939, 1750, 1729, 1711, 1622, 1583, 1491, 1464, 1444, 1427, 1393, 1369, 1305, 1270, 1233, 1198, 1153, 1114, 940, 909, 881, 870, 830, 774, 758, 725 cm^{-1}.

Diethyl 2-[(6-Chloro-2-oxo-2*H*-chromen-3-yl)methyl]malonate (3c):[12] Yield 105 mg, 85%. White solid, m.p. 100–102 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (s, 1 H), 7.17–7.39 (m, 3 H), 4.11 (2 q, J = 7.2 Hz, 4 H), 3.87 (t, J = 7.8 Hz, 1 H), 3.07 (d, J = 7.8 Hz, 2 H), 1.16 (t, J = 7.2 Hz, 6 H) ppm.

Diethyl 2-[(6-Bromo-2-oxo-2*H*-chromen-3-yl)methyl]malonate (3d):[12] Yield 119 mg, 86%. White solid, m.p. 103–104 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52–7.55 (m, 3 H), 7.15–7.18 (m, 1 H), 4.15 (2 q, J = 7.2 Hz, 4 H), 3.90 (t, J = 7.5 Hz, 1 H), 3.10 (d, J = 7.5 Hz, 2 H), 1.19 (t, J = 7.2 Hz, 6 H) ppm.

Diethyl 2-[(6-Nitro-2-oxo-2*H*-chromen-3-yl)methyl]malonate (3e): Yield 80 mg, 63%. Yellow solid, m.p. 108–112 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.31–8.38 (m, 2 H), 7.71 (s, 1 H), 7.43 (d, J = 9.0 Hz, 1 H), 4.17 (2 q, J = 7.2 Hz, 4 H), 3.90 (t, J = 7.5 Hz, 1 H), 3.15 (d, J = 7.5 Hz, 2 H), 1.22 (t, J = 7.2 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.2, 159.6, 156.7, 144.1, 140.1, 127.9, 125.9, 123.3, 119.1, 117.6, 61.7, 49.6, 30.5, 14.0 ppm. HRMS (ESI): calcd. for $C_{17}H_{17}NO_8$ $[M + Na]^+$ 386.0846; found 386.0851. IR (KBr): $\tilde{\nu}$ = 3099, 3067, 3055, 2988, 2966, 2941, 2907, 2871, 1740, 1721, 1638, 1616, 1578, 1530, 1484, 1465, 1433, 1387, 1372, 1351, 1329, 1301, 1242, 1229, 1178, 1162, 1117, 1048, 945, 856, 879, 868, 780, 751, 723 cm^{-1}.

Diethyl 2-[(6-Methoxy-2-oxo-2*H*-chromen-3-yl)methyl]malonate (3f): Yield 114 mg, 94%. White solid, m.p. 77–79 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (s, 1 H), 7.13 (d, J = 8.8 Hz, 1 H), 6.97 (dd, J = 8.8, 2.4 Hz, 1 H), 6.79 (d, J = 2.4 Hz, 1 H), 4.07 (2 q, J = 7.2 Hz, 4 H), 3.88 (t, J = 7.6 Hz, 1 H), 3.74 (s, 3 H), 3.03 (d, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.5, 161.2, 156.0, 147.7, 141.2, 125.4, 119.3, 118.8, 117.3, 109.5, 61.4, 55.6, 49.7, 30.6, 13.9 ppm. HRMS (ESI): calcd. for $C_{18}H_{20}O_7$ $[M + Na]^+$ 371.1101; found 371.1103. IR (KBr): $\tilde{\nu}$ = 3071, 3047, 2998, 2984, 2962, 2944, 2840, 1734, 1703, 1583, 1496, 1481, 1467, 1451,

1429, 1369, 1348, 1330, 1281, 1268, 1212, 1201, 1169, 1161, 1125, 1078, 1067, 1032, 1014, 958, 900, 876, 862, 856, 832, 812, 784, 772, 758, 727 cm^{-1}.

Diethyl 2-[(7-Methoxy-2-oxo-2*H*-chromen-3-yl)methyl]malonate (3g): Yield 80 mg, 66%. Colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.52 (s, 1 H), 7.30 (d, J = 8.8 Hz, 1 H), 6.80 (dd, J = 8.8, 2.4 Hz, 1 H), 6.76 (d, J = 2.4 Hz, 1 H), 4.12 (2 q, J = 7.2 Hz, 4 H), 3.91 (t, J = 7.5 Hz, 1 H), 3.82 (s, 3 H), 3.06 (d, J = 7.5 Hz, 2 H), 1.18 (t, J = 7.2 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.6, 162.3, 161.5, 155.1, 141.5, 128.4, 121.4, 112.7, 112.5, 100.4, 61.4, 55.6, 49.9, 30.5, 13.9 ppm. HRMS (ESI): calcd. for $C_{18}H_{20}O_7$ [M + Na]$^+$ 371.1101; found 371.1101. IR (film): $\tilde{\nu}$ = 3045, 2983, 2943, 2845, 1749, 1732, 1710, 1619, 1508, 1472, 1447, 1423, 1390, 1368, 1356, 1326, 1304, 1285, 1255, 1236, 1216, 1191, 1156, 1118, 1096, 1024, 971, 939, 928, 887, 856, 829, 810, 778, 759, 718, 704 cm^{-1}.

Diethyl 2-[(8-Fluoro-2-oxo-2*H*-chromen-3-yl)methyl]malonate (3h): Yield 102 mg, 87%. White solid, m.p. 107–108 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.59 (s, 1 H), 7.14–7.24 (m, 3 H), 4.11 (2 q, J = 7.2 Hz, 4 H), 3.89 (t, J = 7.6 Hz, 1 H), 3.08 (d, J = 7.6 Hz, 2 H), 1.17 (t, J = 7.2 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.4, 159.7, 149.1 (d, J_{CF} = 250.2 Hz), 141.4 (d, J_{CF} = 11.1 Hz), 140.9, 126.2, 124.3 (d, J_{CF} = 6.3 Hz), 122.6, 120.8, 117.5 (d, J_{CF} = 17.2 Hz), 61.6, 49.7, 30.6, 13.9 ppm. HRMS (ESI): calcd. for $C_{17}H_{17}FO_6$ [M + Na]$^+$ 359.0901; found 359.0906. IR (KBr): $\tilde{\nu}$ = 3082, 3046, 2987, 2940, 2911, 1746, 1728, 1633, 1621, 1584, 1478, 1449, 1425, 1388, 1370, 1325, 1307, 1268, 1237, 1217, 1193, 1157, 1098, 1073, 1057, 1041, 1033, 978, 949, 937, 910, 877, 858, 800, 792, 773, 753, 731, 711 cm^{-1}.

Diethyl 2-[(8-Methyl-2-oxo-2*H*-chromen-3-yl)methyl]malonate (3i): Yield 112 mg, 96%. Colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.51 (s, 1 H), 7.04–7.26 (m, 3 H), 4.08 (2 q, J = 7.2 Hz, 4 H), 3.89 (t, J = 7.5 Hz, 1 H), 3.05 (d, J = 7.5 Hz, 2 H), 2.35 (s, 3 H), 1.13 (t, J = 7.2 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.5, 161.2, 151.6, 141.6, 132.4, 125.7, 125.1, 124.7, 123.8, 118.7, 61.4, 49.8, 30.5, 15.1, 13.9 ppm. HRMS (ESI): calcd. for $C_{18}H_{20}O_6$ [M + Na]$^+$ 355.1152; found 355.1146. IR (film): $\tilde{\nu}$ = 3018, 2988, 2935, 2913, 2875, 1746, 1730, 1707, 1635, 1605, 1544, 1479, 1465, 1446, 1426, 1392, 1372, 1340, 1329, 1278, 1259, 1241, 1216, 1181, 1151, 1116, 1092, 1073, 1053, 1024, 1008, 975, 961, 938, 905, 870, 856, 833, 815, 790, 770, 745, 726, 706 cm^{-1}.

Diethyl 2-[(8-Methoxy-2-oxo-2*H*-chromen-3-yl)methyl]malonate (3j): Yield 119 mg, 98%. White solid, m.p. 61–63 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.52 (s, 1 H), 7.12 (t, J = 8.0 Hz, 1 H), 6.98 (d, J = 8.0 Hz, 1 H), 6.94 (d, J = 8.0 Hz, 1 H), 4.09 (2 q, J = 7.2 Hz, 4 H), 3.88–3.92 (m, 4 H), 3.06 (d, J = 7.6 Hz, 2 H), 1.14 (t, J = 7.2 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.5, 160.5, 146.9, 142.9, 141.5, 125.3, 124.2, 119.6, 118.8, 113.0, 61.4, 56.1, 49.7, 30.6, 13.9 ppm. HRMS (ESI): calcd. for $C_{18}H_{20}O_7$ [M + Na]$^+$ 371.1101; found 371.1104. IR (KBr): $\tilde{\nu}$ = 2990, 2937, 2907, 2837, 1746, 1727, 1703, 1635, 1611, 1581, 1482, 1455, 1444, 1386, 1366, 1347, 1334, 1307, 1278, 1239, 1217, 1191, 1177, 1160, 1112, 1059, 1036, 1019, 981, 966, 946, 906, 873, 859, 812, 788, 770, 734, 713, 697 cm^{-1}.

Diethyl 2-{[2-Oxo-8-(trifluoromethoxy)-2*H*-chromen-3-yl]methyl}-malonate (3k): Yield 127 mg, 90%. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.61 (s, 1 H), 7.36–7.40 (m, 2 H), 7.23 (t, J = 8.0 Hz, 1 H), 4.12 (2 q, J = 7.2 Hz, 4 H), 3.90 (t, J = 7.6 Hz, 1 H), 3.10 (d, J = 7.6 Hz, 2 H), 1.17 (t, J = 7.2 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.4, 159.6, 145.4, 140.7, 135.6, 126.5, 125.9, 124.2, 123.8, 120.8, 120.4 (d, J_{CF} = 258.0 Hz), 61.6, 49.6, 30.5, 13.9 ppm. HRMS (ESI): calcd. for $C_{18}H_{17}F_3O_7$ [M + Na]$^+$ 425.0819; found 425.0814. IR (film): $\tilde{\nu}$ = 2983, 1756, 1735, 1721, 1631, 1613, 1579, 1471, 1429, 1388, 1368, 1336, 1309, 1277, 1263, 1244, 1216, 1157, 1094, 1082, 1061, 1040, 990, 972, 952, 916, 883, 861, 827, 810, 771, 738, 708 cm^{-1}.

Dimethyl 2-[(8-Methoxy-2-oxo-2*H*-chromen-3-yl)methyl]malonate (3l): Yield 104 mg, 93%. White solid, m.p. 92–93 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.54 (s, 1 H), 7.12 (t, J = 8.0 Hz, 1 H), 6.98 (d, J = 8.0 Hz, 1 H), 6.95 (d, J = 8.0 Hz, 1 H), 3.94 (t, J = 7.6 Hz, 1 H), 3.87 (s, 3 H), 3.64 (s, 6 H), 3.06 (d, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.8, 160.5, 146.8, 142.9, 141.6, 125.1, 124.2, 119.6, 118.9, 113.0, 56.0, 52.4, 49.4, 30.6 ppm. HRMS (ESI): calcd. for $C_{16}H_{16}O_7$ [M + Na]$^+$ 343.0788; found 343.0780. IR (KBr): $\tilde{\nu}$ = 3102, 3036, 2981, 2953, 2904, 2840, 1758, 1731, 1713, 1634, 1609, 1579, 1482, 1475, 1458, 1436, 1390, 1343, 1298, 1276, 1251, 1225, 1190, 1161, 1109, 1065, 1041, 970, 958, 926, 902, 872, 839, 812, 785, 770, 730, 717 cm^{-1}.

Diisopropyl 2-[(8-Methoxy-2-oxo-2*H*-chromen-3-yl)methyl]malonate (3m): Yield 130 mg, 99%. White solid, m.p. 71–73 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.52 (s, 1 H), 7.13 (t, J = 8.0 Hz, 1 H), 6.99 (d, J = 8.0 Hz, 1 H), 6.94 (d, J = 8.0 Hz, 1 H), 4.95 (m, J = 6.0 Hz, 2 H), 3.89 (s, 3 H), 3.85 (t, J = 7.6 Hz, 1 H), 3.05 (d, J = 7.6 Hz, 2 H), 1.16 (d, J = 6.0 Hz, 6 H), 1.11 (d, J = 6.0 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.0, 160.5, 146.9, 142.9, 141.3, 125.5, 124.2, 119.6, 118.7, 113.0, 68.9, 56.0, 50.0, 30.4, 21.4 (2 C) ppm. HRMS (ESI): calcd. for $C_{20}H_{24}O_7$ [M + Na]$^+$ 399.1414; found 399.1407. IR (KBr): $\tilde{\nu}$ = 3077, 3043, 3009, 2991, 2979, 2939, 2888, 2836, 1749, 1724, 1705, 1630, 1609, 1579, 1478, 1467, 1454, 1432, 1388, 1376, 1346, 1303, 1272, 1241, 1209, 1190, 1163, 1147, 1104, 1077, 1060, 1011, 972, 958, 939, 906, 898, 843, 774, 733, 711 cm^{-1}.

Diethyl 2-[1-(8-Methoxy-2-oxo-2*H*-chromen-3-yl)ethyl]malonate (3n): 65 mg, 51%. Colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.54 (s, 1 H), 7.16 (t, J = 7.8 Hz, 1 H), 6.98–7.03 (m, 2 H), 4.16 (q, J = 7.2 Hz, 2 H), 3.92–4.09 (m, 3 H), 3.92 (s, 3 H), 3.58 (m, 1 H), 1.37 (d, J = 7.2 Hz, 3 H), 1.21 (t, J = 7.2 Hz, 3 H), 1.10 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.2, 168.1, 159.8, 146.9, 142.8, 139.8, 130.4, 124.1, 119.7, 119.0, 113.0, 61.2, 56.1, 54.7, 36.3, 16.4, 14.0, 13.9 ppm. HRMS (ESI): calcd. for $C_{19}H_{22}O_7$ [M + Na]$^+$ 385.1258; found 385.1253. IR (film): $\tilde{\nu}$ = 3055, 3008, 2986, 2944, 2903, 2846, 1743, 1724, 1717, 1631, 1610, 1579, 1480, 1462, 1441, 1389, 1369, 1341, 1319, 1278, 1224, 1195, 1177, 1156, 1103, 1072, 1029, 994, 976, 950, 863, 793, 781, 756, 738 cm^{-1}.

Ethyl 5,6-Dihydro-2-methyl-6-oxo-4*H*-pyran-3-carboxylate (4):[13] Yield 60 mg, 72%. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.17 (q, J = 7.2 Hz, 2 H), 2.56–2.61 (m, 4 H), 2.30 (s, 3 H), 1.26 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.1, 166.2, 160.8, 106.9, 60.6, 27.9, 20.2, 18.5, 14.1 ppm.

Supporting Information (see footnote on the first page of this article): ^1H NMR and ^{13}C NMR spectra for products.

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