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DABCO-catalyzed C–C bond formation reaction between electron-deficient alkynes and 1,3-dicarbonyl compounds

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ABSTRACT

An excellent catalyst DABCO has been found to catalyze C–C bond formation reaction between activated methylenes and alkynes. The transformation has provided a facile route for the synthesis of 2*H*-pyran-2-ones or unsaturated alkenoic acid ester derivatives and explored the new possibilities of *N*-catalysts for Michael addition of nucleophiles with alkynoates.

1. Introduction

Carbon–carbon bond formation reactions catalyzed by organocatalysts[1] are continuing to attract the attention of synthetic chemists because they have showed great efficiency toward these processes without the use of highly toxic metallic catalysts.[2] Hillman–Baylis reaction is the most successful example to induce this kind of transformation.[3] However, the addition between activated alkynes and methylenes stays surprisingly underdeveloped compared to the great progress that has been made in Michael addition of nucleophiles with alkenoates.[4] The severe lack of research on this subject probably attributes to the high reactivity of alkynes, which may lead to the chaos of reaction system. Recently, Frederic Taran and co-workers reported that phosphine ligand would facilitate addition of 1,3-dicarbonyl to electron-deficient alkynes via an active phosphonium intermediate.[5] Jiang also presented the addition of acetylacetone to electron-deficient alkynes that can be used to catalyze by *JJ*-TPP.[6] These researches pique our attention and make us wonder if we can catalyze the addition by using nitrogen based organocatalysts.

On the other hand, organic chemists have used this addition to prepare 2*H*-pyran-2-ones, which are one of the most important classes of heterocyclic compounds[7] and worth our attention because they have exhibited a wide range of biological activities.[8] Due to the existence of the functional groups, such as conjugated dienes and the ester group, 2*H*-pyran-2-ones are usually utilized as important intermediates in modern organic chemistry.[8c,9] Recently, Prof. Jiang has developed one-pot transition-metal-catalyzed domino reactions for synthesis of highly functionalized heterocyclic compounds from activated methylenes[10] and electron-deficient alkynes.[11] However, the development of new and efficient catalytic system for synthesis of 2*H*-pyran-2-ones is still a challenging target via carbon–carbon bond formation reaction between activated methylenes and alkynes. Herein, we wish to report our investigation on synthesis of 2*H*-pyran-2-ones by DABCO-catalyzed.

2. Results and discussion

As a model reaction, we investigated the addition of cyclohexane-1,3-dione (**1a**) to dimethyl but-2-ynedioate (**2a**) using various nitrogen-based organocatalysts. The results (Table 1) showed that the yield of the expected product **3a** depended on the nature of the base, temperature, and solvent. The reaction proceeded smoothly to give addition product **3a** in high yield in the presence of DABCO after 1 h. However, when 4-(*N*,*N*-dimethylamino)pyridine (DMAP) or Et_3N (10 mol %) was applied, no product was observed after 10 h (Table 1, entries 2 and 3). And when DBU or DABCO was employed as catalyst, product **3a** was obtained in 56% or 63% yields, respectively, at room temperature. In further investigation, we attempted to improve the yield by adjusting the temperature of reaction. Interestingly, the yield reached 95% by using 2 mol % DABCO in DMF at −20 °C. Solvent effects were also investigated. The experiment was indicated that compound **3a** could be obtained in 95% yields in DMF, but when THF, toluene, dioxane, and CH_2Cl_2 were employed, the reaction was severely retarded (Table 1, entries 6–10). Meanwhile, when the reaction carried out neat conditions, product **3a** was obtained in lower yield (Table 1, entry 11). Thus, an optimized reaction condition was established using DABCO as catalyst and DMF as solvent.

With established catalytic system, we set out to explore the scope of this sequential process. And the results were summarized in Table 2. As shown in Table 2, various cyclic 1,3-dicarbonyl compounds were employed as nucleophiles to give corresponding 2*H*-pyran-2-ones products in good to high yields (Table 2, entries 1–7).

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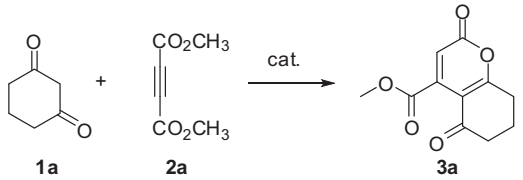
Table 1
Addition reaction of **1a** to **2a** using various nitrogen-based organocatalysts[a]



1a **2a** **3a**

Entry	Catalyst[b]	*T* (°C)	Solvent	Time (h)	Yield[c] (%)
1	—	rt	DMF	1	—
2	DMAP	rt	DMF	10	—
3	Et_3N	rt	DMF	10	—
4[c]	DBU	rt	DMF	1	56
5	DABCO	rt	DMF	1	63
6	DABCO	10	DMF	1	66
7	DABCO	0	DMF	1	78
8	DABCO	−20	DMF	1	95
9	DABCO	−30	DMF	1	94
10	DABCO	−50	DMF	1	88
11	DABCO	−20	THF	1	77
12	DABCO	−20	Toluene	1	69
13	DABCO	−20	Dioxane	1	84
14	DABCO	−20	CH_2Cl_2	1	82
15	DABCO	−20			13

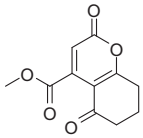
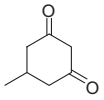
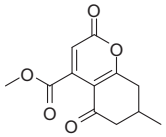
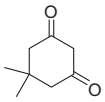
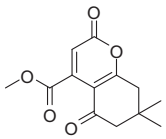
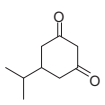
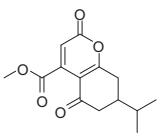
[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), 2 mol % catalyst, temperature −50 to rt.
[b] DMAP=4-Dimethylaminopyridine, DABCO=1,4-Diazabicyclo [2.2.2] octane, DBU=1,8-Diazabicyclo[5.4.0]undec-7-ene.
[c] GC yields.

It was obvious that substituents on the 5- of cyclic 1,3-dicarbonyl compounds had no negative effects on the reaction. When **2a** was replaced by **2b** in this reaction, it was found that a range of substitutions in the cyclic 1,3-dicarbonyl were well tolerated under the optimum conditions (Table 2, entries 8–11). This indicated that **2b** was also suitable for this DABCO-catalyzed reaction. We then extended the scope of nucleophiles to activated methylenes **1h** and **1i**. When the reactions carried out using **2a** or **2b** as substrates, the corresponding products obtained with good yields. However, the reaction was chaos using **2c** as substrate and the desired products **3hc** and **3ic** was obtained in low yield (GC) under the optimum conditions. The crude products were separated by column chromatography, which was a mixture rather than a pure sample. Finally, the molecular structure of representative product **3ba** was determined by X-ray crystallography (Fig. 1).

These promising results encouraged us to extend the scope of the reaction by using other 3-dicarbonyl compounds, such as acetylacetone **1j** and dibenzoylmethane **1k**, in DMF at −20 °C. Interestingly, only the enol form product **3ja** was detected by using **1j** as substrate and the corresponding product of 2*H*-pyran-2-one was not found, while the keto form product **3ka** was only obtained by using **1k** as substrate. This may be explained by the *p*-π conjugation of benzene and carbonyl within **1k** but **1j** without any (Scheme 1).

On the other hand, 4*H*-pyran is one of the most fundamental classes of five-membered heterocycle, which has directly stimulated more and more interest in both industrial and academic fields over the past decades. Thus, under the conditions depicted in Scheme 2, an efficient DABCO-catalyzed three components reaction was developed to construct 4*H*-pyran derivatives under mild condition[13] (Scheme 2). The most advantages were short reaction time for only 0.5 h and the high yield.[14]

Table 2
Reaction of nucleophiles with various activated alkynes

Entry	Activated methylene	Alkynes	Product	Yield[a] (%)
1	 **1a**	 **2a**	 **3aa**	89
2	 **1b**	**2a**	 **3ba**	88
3	 **1c**	**2a**	 **3ca**	91
4	 **1d**	**2a**	 **3da**	90

(*continued on next page*)

Table 2 (*continued*)

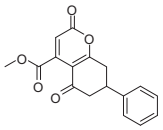
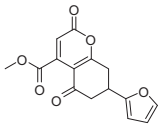
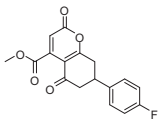
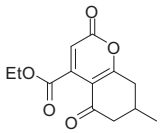
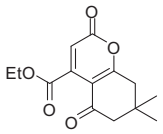
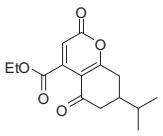
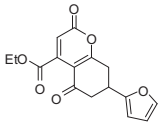
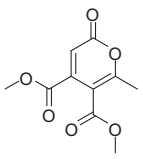
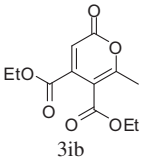
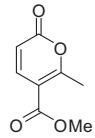
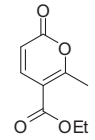
Entry	Activated methylene	Alkynes	Product	Yield[a] (%)
5	 **1e**	**2a**	 **3ea**	89
6	 **1f**	**2a**	 **3fa**	86
7	 **1g**	**2a**	 **3ga**	78
8	**1b**	 **2b**	 **3bb**	80
9	**1c**	**2b**	 **3cb**	85
10	**1d**	**2b**	 **3db**	81
11	**1f**	**2b**	 3fb	88
12	 **1h**	**2a**	 3ha	89[9]
13	 **1i**	**2b**	 3ib	86[9]

Table 2 (*continued*)

Entry	Activated methylene	Alkynes	Product	Yield[a] (%)
14[b]	**1h**	 2c	 3hc	53[12]
15[b]	**1i**	**2c**	 3ic	49[12]

[a] Isolated yields.
[b] GC yields.

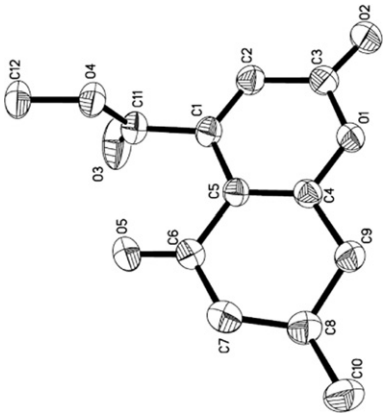
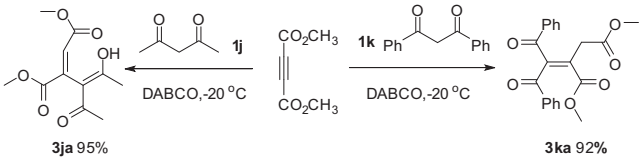
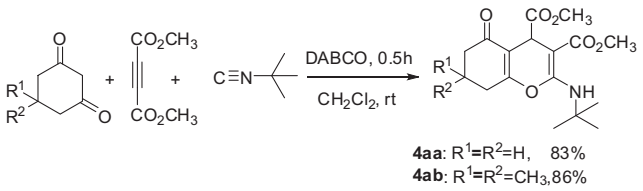


Fig. 1. X-ray crystal structure of compound **3ba**.

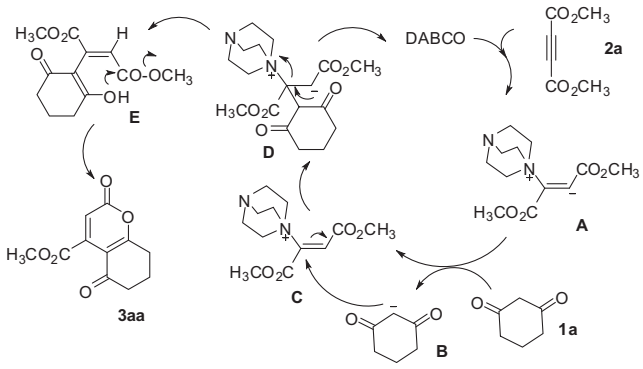


Scheme 1. The reactions of acetylacetone or dibenzoylmethane with **2a**.



Scheme 2. Three component reaction synthesis of 4*H*-pyran.

On the basis of experimental results, a tentative mechanism for the DABCO promoted Michael type addition at the beta-position was proposed in Scheme 3.[15] Intermediate **A** was initially formed by the reaction between DABCO and **2a**. Then **1a** underwent deprotonation by intermediate **A** to give intermediate **B** and **C**, respectively. The intermediate **B** would attack the beta-position of intermediate **C** to generate intermediate **D**, which subsequently gave the intermediate **E** and regenerated the catalyst. Finally, the product **3aa** was formed by following cyclization of intermediate **E**.



Scheme 3. Possible reaction mechanisms.

3. Conclusions

In conclusion, we have developed a DABCO-catalyzed addition of 1,3-dicarbonyl compounds to alkynes for the formation of C–C bonds. The transformation has provided a facile route for the synthesis of pyran derivatives. This reaction has explored the new possibilities of *N*-catalysts for Michael addition of nucleophiles with alkynoates. Efforts were underway to extend the scope of DABCO in other C–C bond forming transformations and to synthesize interesting heterocylces by this reaction.

4. Experimental

4.1. General

^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer. IR spectra were obtained either as potassium bromide pellets or as liquid films between two

potassium bromide pellets with a Bruker Vector 22 spectrometer. Mass spectra were recorded on a Shimadzu GC–MS-QP5050A spectrometer at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). Elemental analyses were performed with a Vario EL elemental analyzer. TLC was performed by using commercially prepared 100–400 mesh silica gel plates (GF254) and visualization was effected at 254 nm.

4.2. General procedure for the synthesis of methyl 2,5-dioxo-5,6,7,8-tetrahydro-2*H*-chromene-4-carboxylate (3aa)

To the mixture of cyclohexane-1,3-dione (**1a** 0.5 mmol) and dimethyl but-2-ynedioate (**2a** 0.6 mmol), was added the solution of DABCO (2 mol %) in DMF (2.0 mL). The reaction mixture was stirred at −20 °C for 1 h. The solvent was removed and the crude product was separated by column chromatography to give a pure sample of **3aa**.

*4.2.1. Methyl 2,5-dioxo-5,6,7,8-tetrahydro-2H-chromene-4-carboxylate (**3aa**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.19(s, 1H), 3.93(s, 3H), 2.91(t, J=6.0 Hz, 2H), 2.58 (t, J=6.0 Hz, 2H), 2.15–2.21(m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 175.4, 165.9, 158.7, 145.9, 112.4, 112.1, 53.2, 36.5, 28.5, 19.8. MS (EI) m/z (%): 222, 194, 163, 138, 93. $C_{11}H_{10}O_5$: calcd C, 59.46; H, 4.54; found: C, 59.09; H, 4.56.

*4.2.2. Methyl 7-methyl-2,5-dioxo-5,6,7,8-tetrahydro-2H-chromene-4-carboxylate (**3ba**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.18(s, 1H), 3.93(s, 3H), 2.88–2.92 (m, 1H), 2.58–2.67 (m, 2H), 2.39–2.47 (m, 1H), 2.23–2.30 (m, 1H), 1.18 (d, J=6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 174.8, 165.8, 158.8, 145.79, 112.0, 111.9, 53.2, 44.8, 36.3, 27.8, 20.7; MS (EI) m/z (%): 236, 177, 138, 93. $C_{12}H_{12}O_5$: calcd C, 61.01; H, 5.12; found: C, 61.42; H, 5.10.

*4.2.3. Methyl 7,7-dimethyl-2,5-dioxo-5,6,7,8-tetrahydro-2H-chromene-4-carboxylate(**3ca**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.18(s, 1H), 3.92(s, 3H), 2.76 (s, 2H), 2.44 (s, 2H), 1.16 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 174.0, 165.8, 159.0, 145.6, 111.8, 11.39, 53.1, 50.5, 42.0, 32.5, 28.2; MS (EI) m/z (%): 250, 194, 166, 138, 93; $C_{13}H_{14}O_5$: calcd C, 62.39; H, 5.64; found: C, 61.86; H, 5.66.

*4.2.4. Methyl 7-isopropyl-2,5-dioxo-5,6,7,8-tetrahydro-2H-chromene-4-carboxylate (**3da**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.16 (s, 1H), 3.92 (s, 3H), 2.84–2.89 (m, 1H), 2.63–2.74 (m, 2H), 2.26–2.34 (m, 1H), 2.03–2.10 (m, 1H), 1.70–1.74 (m, 1H), 1.00 (d, J=8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ192.8, 175.5, 165.8, 158.8, 145.7, 111.9, 111.8, 53.0, 40.6, 38.8, 32.2, 31.6, 19.3, 19.2; MS (EI) m/z (%): 264, 205, 194, 166, 138, 93, 69; $C_{14}H_{16}O_5$: calcd C, 63.63; H, 6.10; found: C, 63.97; H, 6.12.

*4.2.5. Methyl 2,5-dioxo-7-phenyl-5,6,7,8-tetrahydro-2H-chromene-4-carboxylate(**3ea**).* ^{1}H NMR (400 MHz) δ 7.36–7.39 (m, 2H), 7.25–7.27 (m, 2H), 6.19 (s, 1H), 3.92 (s, 3H), 3.51–3.57 (m, 1H), 3.08–3.12 (m, 2H), 2.74–2.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 174.5, 165.7, 158.7, 145.7, 140.8, 129.1, 127.7, 126.5, 112.2, 112.0, 53.2, 43.7, 38.0, 35.9, 14.1. MS (EI) m/z (%): 298, 228, 193, 77, 55; $C_{17}H_{14}O_5$: calcd C, 68.45; H, 4.73; found: C, 68.07; H, 4.75.

*4.2.6. Methyl 7-(furan-2-yl)-2,5-dioxo-5,6,7,8-tetrahydro-2H-chromene-4-carboxylate (**3fa**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 6.33 (s, 1H), 6.20 (s, 1H), 6.12 (d, J=3.0 Hz, 1H), 3.93 (s, 3H), 3.63–3.68 (m, 1H), 3.15–3.20 (m, 2H), 2.82–2.91 (m, 1H), 2.75–2.90 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 173.6, 165.7, 158.6, 153.7, 145.6, 142.3, 112.3, 112.1, 110.4, 105.7, 53.2, 40.9, 33.2, 31.6. MS (EI) m/z (%): 288, 261, 227, 194, 94, 66; $C_{15}H_{12}O_6$: C, 62.50; H, 4.20; found: C, 62.11; H, 4.22.

*4.2.7. Methyl 7-(4-fluorophenyl)-2,5-dioxo-5,6,7,8-tetrahydro-2H-chromene-4-carboxylate (**3ga**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21–7.24 (m, 2H), 7.06–7.10 (m, 2H), 6.23 (s, 1H), 3.95 (s, 3H), 3.51–3.58 (m, 1H), 3.07–3.09 (m, J=8.0 Hz, 2H), 2.74–2.88 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 174.1, 165.7, 160.9, 158.5, 145.6, 136.4, 128.1, 128.0, 116.2, 116.0, 112.4, 53.2, 43.8, 37.5, 36.1. MS (EI) m/z (%): 316, 267, 223, 194, 77. $C_{17}H_{13}O_5$: calcd C, 64.56; H, 4.14; found: C, 64.09; H, 4.17.

*4.2.8. Ethyl 7-methyl-2,5-dioxo-5,6,7,8-tetrahydro-2H-chromene-4-carboxylate (**3bb**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 (s, 1H), 4.38–4.43 (m, 2H), 2.86–2.82 (m, 1H), 2.57–2.67 (m, 2H), 2.30–2.44 (m, 1H), 2.23–2.27 (m, 11.8 Hz, 1H), 1.36 (t, J=7.2 Hz, 3H), 1.17 (d, J=6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 174.7, 165.4, 158.9, 146.1, 112.0, 111.9, 62.6, 44.8, 36.3, 27.8, 20.7, 13.9. MS (EI) m/z (%): 250, 221, 177, 93, 45.$C_{13}H_{14}O_5$: calcd C, 62.39; H, 5.64; found: C, 62.87; H, 5.61.

*4.2.9. Ethyl 7,7-dimethyl-2,5-dioxo-5,6,7,8-tetrahydro-2H-chromene-4-carboxylateethyl (**3cb**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.18 (s, 1H), 4.40 (q, J=7.2 Hz, 2H), 2.75 (s, 2H), 2.45 (s, 2H), 1.37 (t, J=7.2 Hz, 3H), 1.16 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 173.98, 165.37, 159.17, 146.06, 111.7, 111.4, 62.5, 50.6, 42.1, 32.5, 28.2, 13.9. MS (EI) m/z (%): 264, 235, 191, 43; $C_{14}H_{16}O_5$: calcd 63.63; H, 6.10; found: C, 64.01; H, 6.08.

*4.2.10. 7-Isopropyl-2,5-dioxo-5,6,7,8-tetrahydro-2H-chromene-4-carboxylate (**3db**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 (s, 1H), 4.40 (q, J=7.2 Hz, 2H), 2.83–2.89 (m, 1H), 2.63–2.70 (m, 2H), 2.25–2.29 (m, 1H), 2.07–2.11 (m, 1H), 1.67–1.72 (m, 1H), 1.36 (t, J=7.2 Hz, 3H), 0.98 (d, J=6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 175.3, 165.4, 158.9, 146.1, 112.0, 111.8, 62.6, 40.8, 38.9, 32.3, 31.6, 19.3, 19.3, 13.8. MS (EI) m/z (%): 278:$C_{15}H_{18}O_5$: calcd C, 64.74; H, 6.52; found: C, 65.11; H, 6.50.

*4.2.11. Ethyl 7-(furan-2-yl)-2,5-dioxo-5,6,7,8-tetrahydro-2H-chromene-4-carboxylate (**3fb**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.32 (m, 1H), 6.87 (s, 1H), 6.28–6.30 (m, 1H), 6.08–6.10 (m, 1H), 4.15(d, J=7.2 Hz, 2H), 3.49–3.54 (m, 1H), 2.78–2.84 (m, 2H), 2.65–2.72 (m, 2H), 1.23 (t, J=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 173.3, 166.7, 158.0, 155.5, 141.2, 137.3, 111.7, 110.1, 104.4, 61.0, 44.37, 37.5, 32.0, 13.9. MS (EI) m/z (%): 304, 273, 229, 193, 66; $C_{16}H_{14}O_6$: C, 63.57; H, 4.67; found: C, 63.15; H, 4.70.

*4.2.12. Dimethyl 6-methyl-2-oxo-2H-pyran-4,5-dicarboxylate (**3ha**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.49 (s, 1H), 3.90 (s, 3H), 3.84 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 164.7, 164.6, 159.7, 145.7, 113.7, 109.1, 53.2, 52.7, 19.3. MS (EI) m/z (%): 221, 195, 125, 93, 43. $C_{10}H_{10}O_6$: calcd C, 53.10; H, 4.46; found: C, 53.41; H, 4.44.

*4.2.13. Diethyl 6-methyl-2-oxo-2H-pyran-4,5-dicarboxylate (**3ib**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.45 (s, 1H), 4.32 (q, J=7.2 Hz, 2H), 2.46 (s, 3H), 4.22 (q, J=7.2 Hz, 2H), 1.32 (t, J=7.2 Hz, 3H), 1.29 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 165.1, 164.8, 160.0, 147.4, 113.8, 109.7, 63.0, 62.4, 19.3, 14.1.

*4.2.14. Dimethyl 6-methyl-2-oxo-2H-pyran-4,5-dicarboxylate (**3ha**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.49 (s, 1H), 3.90 (s, 3H), 3.84 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 164.7, 164.6, 159.7, 145.7, 113.7, 109.1, 53.2, 52.7, 19.3. MS (EI) m/z (%): 221, 195, 125, 93, 43. $C_{10}H_{10}O_6$: calcd C, 53.10; H, 4.46; found: C, 53.41; H, 4.44.

*4.2.15. Diethyl 6-methyl-2-oxo-2H-pyran-4,5-dicarboxylate (**3ib**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.45 (s, 1H), 2.46 (s, 3H), 4.32 (q, J=7.2 Hz, 2H), 4.22 (q, J=7.2 Hz, 2H), 1.32 (t, J=7.2 Hz, 3H), 1.29 (t,

J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.1, 165.1, 164.8, 160.0, 147.4, 113.8, 109.7, 63.0, 62.4, 19.3, 14.1.

*4.2.16. Dimethyl 2-((E)-2-hydroxy-4-oxopent-2-en-3-yl)fumarate (**3ja**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (s, 1H), 3.79 (s, 3H), 3.70 (s, 3H), 1.88 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.8, 166.6, 164.9, 139.7, 131.9, 106.9, 53.0, 52.1, 23.4.

*4.2.17. Dimethyl 2-(1,3-dioxo-1,3-diphenylpropan-2-ylidene)succinate (**3ka**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10–8.13(m, 4H), 7.53–7.59(m, 2H), 7.45–7.49 (m, 4H), 3.64 (s, 3H), 3.52 (s, 3H), 3.36 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 191.4, 169.6, 165.2, 135.5, 134.9, 134.6, 133.8, 130.6, 129.5, 128.8, 128.7, 128.4, 52.5, 52.2, 34.7.

*4.2.18. Dimethyl 2-(tert-butylamino)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3,4-dicarboxylate (**4aa**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 1H), 4.35 (s, 1H), 3.55 (s, 3H), 3.50 (s, 3H), 2.19–2.61 (m, 6H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ192.1, 169.9, 165.7, 160.8, 156.1, 109.5, 69.5, 48.7, 48.3, 47.0, 30.56, 26.6, 32.7, 23.1, 16.2.

*4.2.19. Dimethyl 2-(tert-butylamino)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3,4-dicarboxylate (**4ab**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.70 (s, 1H), 4.51 (s, 1H), 3.72 (s, 3H), 3.65 (s, 3H), 2.48 (s, 2H), 2.33 (s, 2H), 1.41 (s, 9H), 1.14(s, 3H), 1.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 192.4, 169.9, 166.0, 159.4, 156.5, 108.6, 69.6, 48.9, 46.8, 47.2, 48.5, 37.0, 30.4, 26.8, 28.6, 25.6, 23.37.

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Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.tet.2012.03.047.

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