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Electronic tuning cyclization of aryl-1,4-enediones: $AlCl_3$-mediated Nazarov-type cyclization to synthesize polysubstituted-1-indanones

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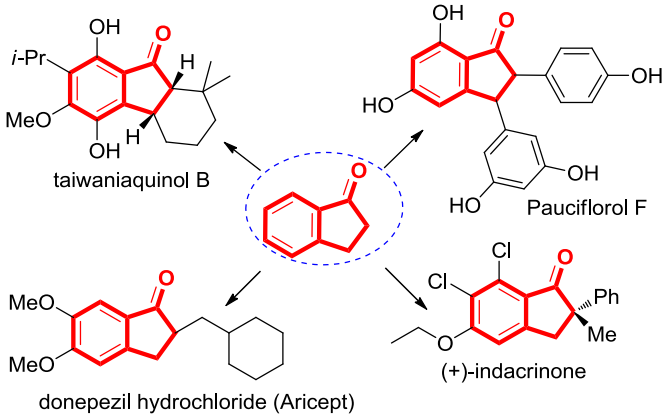
ABSTRACT

An electronic tuning Nazarov-type cyclization protocol was proposed for the synthesis of polysubstituted-1-indanones from the readily available starting materials 1,4-enediones. $AlCl_3$ was highlighted as the most efficient promoter for this reaction.

1. Introduction

Indanone derivatives are key structural units that are widely found in natural products and pharmaceuticals, such as taiwaniaquinol B, pauciflorol F and indacrinone (Scheme 1).[1] They can also often serve as important synthetic precursors for complex chemical synthesis.[2] As a result, many efficient synthetic methods have been explored for the synthesis of indanone derivatives.[3] One such method that has been relatively utilized is the Nazarov cyclization, which has proven to be useful in providing stereospecific properties in the products.

More specifically, Nazarov cyclization is a stereospecific 4π electrocyclization method that converts divinyl ketones into cyclopentenones by activation with a Lewis or Brønsted acid.[4] Over several decades, great efforts have been devoted to the exploitation of the Nazarov reaction. Many impressive results have been accomplished by the groups of Frontier,[5] Tius,[6] Trauner,[7] France,[8] and Ma,[9] among others.[10] For example, Frontier and co-workers examined the impact of dienone substitution on Nazarov cyclization in detail.[5d] They also developed a series of catalysts such as Cu(II), Pd(II), Ir(III) and $Sc(OTf)_3/LiClO_4$ for Nazarov cyclization reactions based on a polarizing strategy.[5] More recently, Luo and Cheng proposed an elegant Lewis acid and Brønsted acid combination catalyzed strategy for the Nazarov cyclization of aryl vinyl β-ketoesters.[11] This strategy led to a dramatic enhancement in the catalytic activity of the Nazarov reaction.



Scheme 1. Indanone derivatives in natural products and pharmaceuticals.

Despite these achievements, the types of substrates utilized in the Nazarov reaction primarily consist of divinyl ketones, divinyl β-ketoesters and aryl vinyl β-ketoesters, among others (Scheme 2). Moreover, the substituent groups at C-5 are still restricted in electron-donating groups, such as (hetero)aryl, alkyl and ethenyl groups. When electron-withdrawing groups, such as aroyl, ester and conjugated enones, are attached at C-5 position, the

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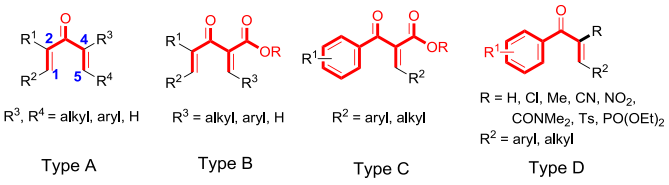
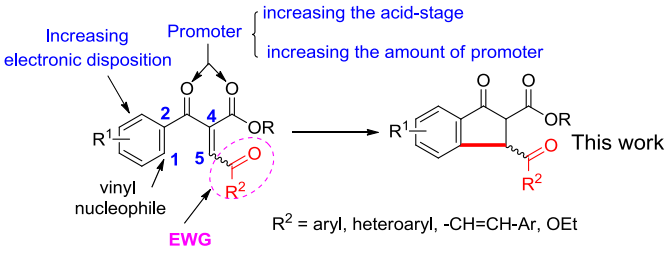


Scheme 2. The types of substrates for Nazarov cyclization.

Nazarov cyclization reaction can be very difficult to produce. Thus, further researches into diverse and effective substrates for the Nazarov cyclization remain desirable.

The 1,4-enedione is an important framework, that is, widely present in natural products and medicinal compounds. It is well-known as a versatile precursor in organic synthesis.[12] The development of an efficient method for the Nazarov cyclization of 1,4-enediones would therefore be both important and desirable. Based on the polarizing strategy, we wonder whether increasing the electronic disposition of C-2 aryl ring or increasing the acid-stage and amount of promoter might lead to improvements in the reactivity of aryl-1,4-enediones (Scheme 3). Herein, we reported the first instance of electronic tuning Nazarov-type cyclization of aryl-1,4-enediones.



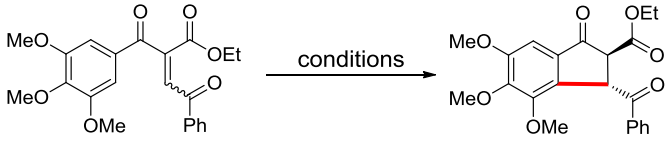
Scheme 3. Our strategy for Nazarov cyclization of aryl-1,4-enediones.

2. Results and discussion

We initially optimized the experimental conditions using ethyl 4-oxo-4-phenyl-2-(3,4,5-trimethoxybenzoyl)but-2-enoate (**1a**) as a model substrate (Table 1). First, a series of Brønsted acids, such as H_2SO_4, H_3PO_4, HCl, CF_3CO_2H, $MeSO_3H$ and CF_3SO_3H, were screened for the reaction in $EtNO_2$ at 25 °C (Table 1, entries 1–6). However, the desired product was not observed. A variety of Lewis acids were also investigated for the reaction. To our delight, the reaction occurred smoothly to afford the desired product **2a** in 96% yield by using 1.1 equiv of $AlCl_3$ (Table 1, entry 7). When 1.1 equiv of $FeCl_3$ or $SnCl_4$ were added, the reaction also performed efficiently to furnish the product **2a** in good yield (86% and 88%, entry 9 and 11). However, other Lewis acids, such as $ZnCl_2$, $TiCl_4$, $InCl_3$ and $Cu(OTf)_2$, were found not to promote the reaction (entries 8, 10 and 12–13). Various solvents were also tested, where $EtNO_2$ was found to be the most efficient solvent for the process (entries 14–16). Yet, further decreases the amount of $AlCl_3$ (0.3–0.5 equiv) was seen to provide a moderate yield (entries 17–18). Further investigation found that changes in temperature had no obvious impact on the reaction efficiency (entries 19–20). Finally, the optimal reaction conditions for the reaction were pinpointed as **1a** (1.1 mmol) with 1.1 equiv of $AlCl_3$ at 25 °C in $EtNO_2$ (entry 7).

With the optimal conditions in hand, we initially examined the impact of the substituent groups at C-6 on the reaction efficiency.[13] To our satisfaction, the reaction demonstrated good compatibility with various substituent groups at the C-6 position (Table 2). Electron-donating, and electron-withdrawing groups, such as 4-Me,

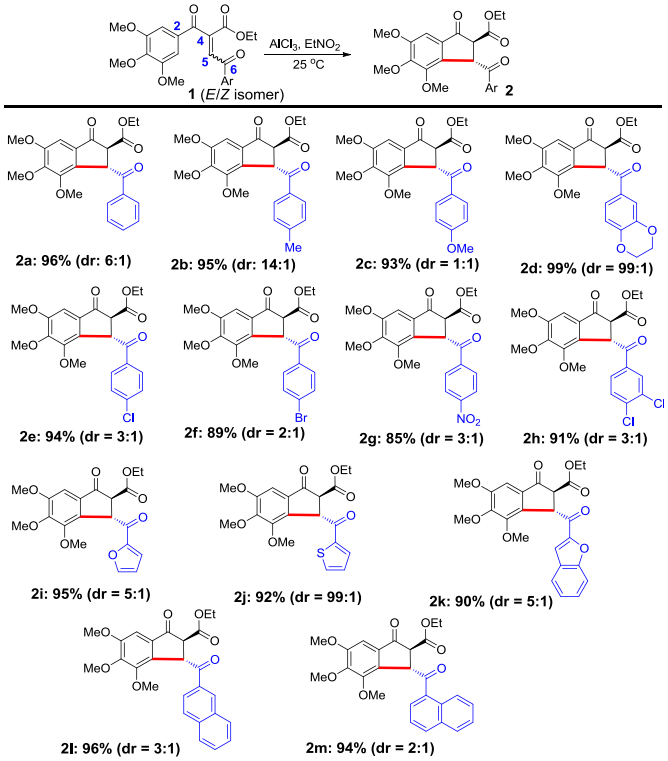
Table 1
Optimization of the reaction conditions[a]



Entry	Promoter/equiv	Temp (°C)	Solvent	Yield (%)[b]
1	H_2SO_4 (1.1)	25	$EtNO_2$	N.R.
2	H_3PO_4 (1.1)	25	$EtNO_2$	N.R.
3	HCl (1.1)	25	$EtNO_2$	N.R.
4	CF_3CO_2H (1.1)	25	$EtNO_2$	N.R.
5	CH_3SO_3H (1.1)	25	$EtNO_2$	N.R.
6	CF_3SO_3H (1.1)	25	$EtNO_2$	N.R.
7	**$AlCl_3$ (1.1)**	**25**	**$EtNO_2$**	**96% (6:1)[c,d]**
8	$ZnCl_2$ (1.1)	25	$EtNO_2$	N.R.
9	$FeCl_3$ (1.1)	25	$EtNO_2$	86% (3:1)[c]
10	$TiCl_4$ (1.1)	25	$EtNO_2$	N.R.
11	$SnCl_4$ (1.1)	25	$EtNO_2$	88% (2:1)[c]
12	$InCl_3$ (1.1)	25	$EtNO_2$	N.R.
13	$Cu(OTf)_2$ (1.1)	25	$EtNO_2$	N.R.
14	$AlCl_3$ (1.1)	25	$EtNO_2$	N.R.
15	$AlCl_3$ (1.1)	25	$MeNO_2$	N.R.
16	$AlCl_3$ (1.1)	25	$CHCl_3$	N.R.
17	$AlCl_3$ (0.5)	25	CH_2Cl_2	69 (6:1)[c]
18	$AlCl_3$ (0.3)	25	$EtNO_2$	52 (5:1)[c]
19	$AlCl_3$ (0.5)	50	$EtNO_2$	70 (3:1)[c]
20	$AlCl_3$ (0.5)	80	$EtNO_2$	72 (3:1)[c]

[a] Reaction conditions: **1a** (0.5 mmol), promoter (0.55 mmol), solvent (3–5 mL) under Ar atmosphere at 25 °C.
[b] Isolated yield. N.R.=no reaction.
[c] Diastereoselectivities was determined by crude ^1H NMR.
[d] The optimal conditions for the reaction.

Table 2
The scope of aryl-1,4-enediones[a,b]



[a] The reaction was carried out with **1** (0.5 mmol), $AlCl_3$ (0.55 mmol), $EtNO_2$ (3–5 mL) under Ar atmosphere at 25 ℃. [b] Isolated yield. Diastereoselectivities was determined by crude ^1H NMR.

4-OMe, 3,4-O(CH_2)$_2$O, 4-Cl, 4-Br, 3,4-Cl_2 and 4-NO_2, attached to the phenyl group of C-6 were shown to afford the corresponding products with excellent yields (**2a**–**h**, 85–99% yields, 1:1 to 99:1 dr ratio). The electronic and steric natures of substituent groups at the C-6 position were seen to have little influence on the reaction efficiency. Moreover, the structure of product **2g** was further confirmed by X-ray crystallography (Fig. 1).[14] To our delight, the heteroaryls, such as 2-furanyl (**1i**), thiophenyl (**1j**) and 2-benzofuranyl (**1k**), were found suitable for the reaction and provided the corresponding products **2i**–**k** in 90–95% yields (dr: 5:1–99:1). Moreover, the steric hindrance substituent group 1-naphthyl (**1m**) was also tolerant to the reaction to yield the corresponding product **2m** in 94% yield, respectively (with 2:1 dr ratio).

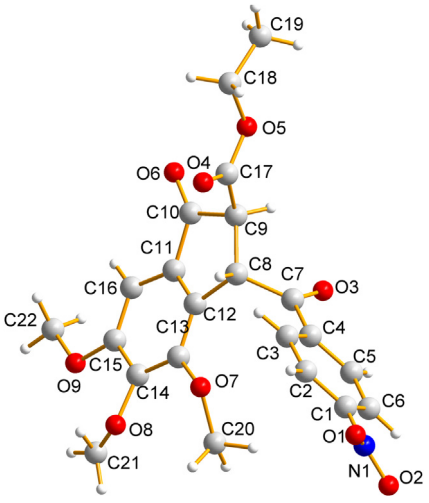
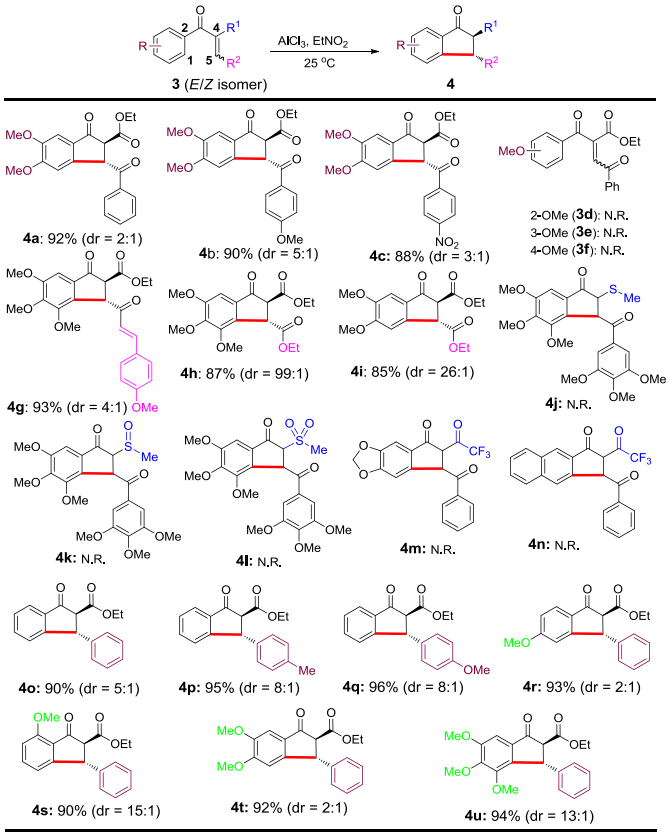


Fig. 1. The X-ray crystal structure illustration for the trans isomer of **2g**.

To further access the substituent effects of the C-2 aryl ring on reaction efficiency, a series of aryl-1,4-enediones **3a**–**f** were prepared to explore the scope of the method (Table 3).[15] We were pleased to find that 3,4-dimethoxyl substituted substrates **3a**–**c** were suitable for the reaction and gave the corresponding products **4a**–**c** in good yields (88–92%). However, when the aryl at C-2 position was attached with one methoxyl group, such as 2-OMe, 3-OMe, or 4-OMe (**3d**–**f**), the reaction could not perform under the standard conditions. These results suggested that the electronic disposition of substitutions at C-2 aryl group were very important to the reaction efficiency. We subsequently examined the substituent effects of C-5 position on the reactivity. It was found that conjugated enones (**3g**) and ester groups (**3h**–**i**) substituted at C-5 position did not affect the reaction efficiency, and thus the desired products **4g**–**i** were furnished in 85–93% yields. Moreover, the pattern of the substituent groups at C-4 position was also investigated. The methylthio group at C-4 in the aryl-1,4-enedione (**3j**) was unable to perform to provide the desired product. In addition, methylsulfinyl (**3k**) and methylsulfonyl (**3l**) group did not perform cyclization. 1,4-Trifluoroacetyl enediones (**3m**–**n**) were also unable to perform the reaction under the standard conditions. It is also likely that the improvements in the reactivity were not obtained even with higher catalyst loading or elevated the reaction temperature (**3j**–**n**, with 3 equiv of $AlCl_3$ at 70 °C). These results demonstrated that the pattern of the substituent groups at C-4 position was critical for aryl-1,4-enediones Nazarov cyclization.

Based on these results, we think that the electronic effect of C-5 position was crucial to the reaction. For further testifying this conclusion, a series of aryl vinyl β-ketoesters (**3o**–**r**) were synthesized (Table 3).[16] To our delight, the substrate **3o** with a phenyl group at C-5 position performed smoothly to afford the desired

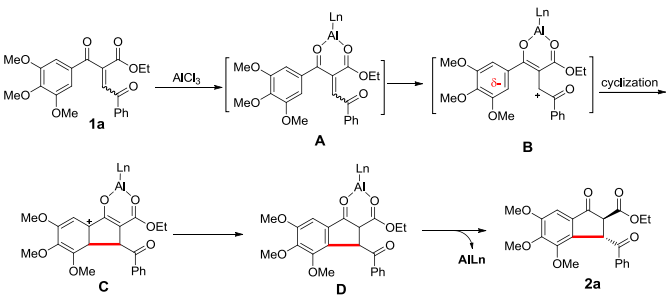
Table 3
The scope of 1,4-enediones and aryl vinyl β-ketoesters[a,b]



[a] The reaction was carried out with **3** (0.5 mmol), $AlCl_3$ (1.1 equiv), $EtNO_2$ (3–5 mL) under Ar atmosphere at 25 °C. [b] Isolated yield. Diastereoselectivities was determined by crude ^{1}H NMR. N.R. = no reaction.

product **4o** in excellent yield (90% yield, 5:1 dr ratio). When the aryl at C-5 position was attached with 4-Me or 4-OMe group (**3d**–**f**), the reaction could also perform under the standard conditions to give the corresponding products (**4p** and **4q**) in 95% and 96% yields, respectively (8:1 dr ratio). In addition, the substrates with methoxyl groups (such as, 4-OMe, 2-OMe, 3,4-OMe_2, 2,3,4-OMe_3) at C-2 aryl ring also reacted smoothly to form the desired products in excellent yields (**4r**–**u**, 90–94% yields, 2:1 to 15:1 dr ratio). This time two or three methoxy groups at C-2 aryl ring were not necessary for the reaction.

A possible reaction mechanism was described as follows using substrate **1a** as an example (Scheme 4). Initially, the promoter $AlCl_3$ coordinated with substrate **1a** via two-point binding to form the intermediate **A**, which was followed by isomerization to afford the oxyallyl cation **B**.[17] Intermediate **B** subsequently underwent cyclization to furnish intermediate **C**. This was followed by



Scheme 4. The plausible mechanism of the present reaction.

deprotonation to give intermediate **D**. Finally, the promoter $AlCl_3$ was left to obtain the product **2a**.

3. Conclusion

In conclusion, an electronic tuning Nazarov-type cyclization protocol has been proposed for the synthesis of polysubstituted-1-indanones in high yields (up to 99%) from the readily available 1,4-enediones and aryl vinyl β-ketoesters. $AlCl_3$ was highlighted as the most efficient promoter for this reaction. Further analysis revealed that the pattern of substituent groups at C-2, C-4 and C-5 positions were also crucial for the reaction efficiency. When electron-withdrawing groups were attached at C-5 position (such as aroyls, esters and conjugated enones), two or more electron-donating groups at C-2 aryl ring were necessary to promote the reaction. Further studies on the applications of this strategy will be reported in due course.

4. Experimental

4.1. General

Unless otherwise noted, all aryl methyl ketones, β-keto ester and other reagents were obtained from commercial suppliers and used without further purification. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200–300 mesh).

IR spectra were recorded on a Perkin–Elmer PE-983 infrared spectrometer as KBr pellets with absorption in cm^{-1}. NMR spectra were recorded on a Varian Mercury 400 or 600 MHz spectrometer Chemical shifts are reported in parts per million ($CDCl_3$: δ 7.26 ppm for ^1H NMR and 77.0 ppm for ^{13}C NMR), relative to the internal standard of tetramethylsilane (TMS), multiplicities are indicated s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constants (*J*) are given in Hertz (Hz). HRMS were obtained on a Bruker Apex-Ultra 7.0T FTMS equipped with an electrospray source (ESI) or Atmospheric-pressure chemical ionization (APCI).

*4.1.1. General procedure for synthesis of substrates **1a–m**, **3a–g** and **3m–n** (**1a** as an example).* A sealed tube was charged with acetophenone **5a** (600 mg, 5 mmol), ethyl 3-oxo-3-(3,4,5-trimethoxy phenyl)propanoate **6a** (1410 mg, 5.0 mmol), iodine (1396 mg, 5.5 mmol) and CuO (440 mg, 5.5 mmol) at room temperature, and then solvent DMSO (10 mL) was added. The resulting mixture was stirred at 70 °C for 12 h, after disappearance of the reactant (monitored by TLC), and added 50 mL water to the mixture, then extracted with EtOAc three times (3×50 mL). The extract was washed with 10% $Na_2S_2O_3$ solution, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield the desired product **1a** as a yellow solid (yield: 84%).

*4.1.2. General procedure for synthesis of substrates 1,4-enediones **3j**.* A solution of 3,4,5-trimethoxyl phenyl acetone **5j** (1050 mg, 5.0 mmol), iodine (2538 mg, 10 mmol) and CuO (1200 mg, 15 mmol) in DMSO (25 mL) was heated at 65 °C for 18 h. After filtration then the reaction mixture was then poured into 150 mL brine and the aqueous layer was extracted with EtOAc (3×100 mL). The extract was washed with $Na_2S_2O_3$ and NaOH solution, dried over anhydrous Na_2SO_4 then the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with EtOAc/hexane as eluent to give the expected compound **3j** in 82% yield.

*4.1.3. General procedure for synthesis of substrates 1,4-enediones **3k** and **3l**.* A solution of α-methylthio-substituted 1,4-enedione **3j** (925 mg, 2.0 mmol) in CH_2Cl_2 (25 mL) was stirred at 0 °C for 30 min. Then 3-chlorobenzoperoxoic acid (1.2 equiv for **3k**, 2.5 equiv for **3l**) was dropwise added into the above mixture and stirred for other 3 h, after disappearance of the reactant (monitored by TLC), and added 150 mL brine to the mixture, then extracted with CH_2Cl_2 three times (3×100 mL). The extract was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield the desired product **3k** as a yellow solid (yield: 75%).

*4.1.4. General procedure for synthesis of substrates 1,4-enediones **4h** and **4i**.* A round flask was charged with ethyl 3-oxo-3-(3,4,5-trimethoxyphenyl)propanoate **6h** (282 mg, 1.0 mmol), ethyl 2-oxoacetate **7** (1.5 equiv, 75% in toluene solution), CuI (95 mg, 0.5 mmol) and Et_3N (1.5 equiv) at room temperature, and then solvent MeCN (10 mL) was added. The resulting mixture was reflux for 5–6 h, after disappearance of the reactant (monitored by TLC), then removed the solvent and added 50 mL water and 30 mL saturated brine solution to the mixture, extracted with EtOAc three times (3×50 mL). The extract was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield the desired product **4h** as yellow oil (yield: 68%).

*4.1.5. General procedure for synthesis of **2** and **4** (**2a** as an example).* Aryl-1,4-enedione **1a** (199 mg, 0.5 mmol) and $AlCl_3$ (73.15 mg, 0.55 mmol) was added to a 20 mL Schlenk tube, and the tube was protected under Ar atmosphere. Subsequently, solvent $EtNO_2$ (3 mL) was added. The reaction mixture was stirred at 25 °C for 1–10 h, during which it was monitored by TLC. The solution was diluted with ethyl acetate (30 mL), washed with H_2O (3×10 mL) and 30 mL saturated brine solution, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield the desired product **2a** as red oil (yield: 96%).

4.2. Characterization data

*4.2.1. Ethyl 4-oxo-4-phenyl-2-(3,4,5-trimethoxybenzoyl)but-2-enoate (**1a**).* IR (KBr): 3417, 3060, 2960, 2349, 1680, 1579, 1561, 1490, 1450, 1416, 1260, 1180, 1127, 1075, 1025 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=8.14 (s, 1H), 7.97 (d, *J*=8.0 Hz, 2H), 7.62 (t, *J*=7.68 Hz, 1H), 7.49 (t, *J*=8.0 Hz, 2H), 7.15 (s, 2H), 4.31 (q, *J*=7.2 Hz, 2H), 3.91 (s, 3H), 3.85 (s, 6H), 1.26 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=191.9, 191.1, 190.1, 188.5, 163.6, 153.2, 153.1, 144.2, 143.0, 140.4, 136.1, 134.2, 130.9, 130.7, 128.9, 128.7, 107.1, 107.0, 106.0, 105.8, 62.4, 56.3, 56.1, 56.0, 14.0, 13.8; HRMS (APCI): *m*/*z* $[M+H]^+$ calcd for $C_{22}H_{23}O_7$: 399.1438; found: 399.1439.

*4.2.2. Ethyl 4-oxo-4-(p-tolyl)-2-(3,4,5-trimethoxybenzoyl)butanoate (**1b**).* IR (KBr): 2974, 2943, 2847, 1728, 1656, 1600, 1582, 1451, 1413, 1364, 1326, 1264, 1229, 1185, 1167, 1124, 1089, 1038, 1011 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.13 (s, 1H), 7.87 (d, *J*=8.4 Hz, 2H), 7.29 (d, *J*=7.6 Hz, 2H), 7.15 (s, 2H), 4.30 (q, *J*=7.2 Hz, 2H), 3.91 (s, 3H), 3.85 (s, 6H), 2.42 (s, 3H), 1.26 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 192.1, 188.0, 163.8, 153.2, 148.1, 145.5, 143.9, 143.0, 133.8, 131.0, 129.6, 129.0, 105.9, 62.4, 60.8, 56.1, 21.75, 14.0; HRMS (ESI): *m*/*z* $[M+H]^+$ calcd for $C_{23}H_{24}NaO_7$: 435.1414; found: 435.1407.

*4.2.3. Ethyl 4-(4-methoxyphenyl)-4-oxo-2-(3,4,5-trimethoxy benzoyl)butanoate (**1c**).* IR (KBr): 3433, 2939, 2840, 1704, 1672, 1598, 1504, 1461, 1415, 1379, 1331, 1262, 1176, 1127, 1017 cm^{-1}; IR (KBr): 3433, 2939, 2840, 1704, 1671, 1656, 1597, 1504, 1460, 1415, 1379, 1331, 1263, 1177, 1127, 1018 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.14 (s, 1H), 7.96 (d, *J*=8.8 Hz, 2H), 7.16 (s, 1H), 6.95 (d,

J=8.8 Hz, 3H), 4.30 (q, J=7.2 Hz, 2H), 3.92–3.84 (m, 12H), 1.25 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 192.1, 186.6, 164.4, 153.0, 143.4, 133.8, 131.3, 130.9, 129.1, 114.0, 107.2, 105.8, 62.3, 60.7, 56.0, 55.4, 40.4, 13.8; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{23}H_{25}O_8$: 429.1544; found: 429.1544.

*4.2.4. Ethyl 4-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-4-oxo-2-(3,4,5-trimethoxybenzoyl)butanoate (**1d**).* IR (KBr): 3063, 2937, 2837, 1717, 1670, 1658, 1581, 1504, 1459, 1432, 1413, 1351, 1330, 1291, 1264, 1243, 1200, 1158, 1129, 1065, 1022, 1002 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.09 (s, 1H), 7.49 (s, 2H), 7.16 (s, 2H), 6.91 (d, J=8.4 Hz, 1H), 4.33–4.22 (m, 6H), 3.88 (d, J=8.4 Hz, 9H), 1.26 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 91.7, 186.2, 163.3, 152.7, 148.9, 143.2, 143.1, 133.3, 130.6, 129.5, 122.8, 117.7, 117.1, 105.4, 64.3, 63.5, 61.9, 60.3, 55.7, 13.5; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{25}O_9$: 457.1493; found: 457.1492.

*4.2.5. Ethyl 4-(4-chlorophenyl)-4-oxo-2-(3,4,5-trimethoxybenzoyl) butanoate (**1e**).* IR (KBr): 3435, 2977, 2941, 2389, 1729, 1670, 1586, 1503, 1464, 1414, 1361, 1329, 1259, 1227, 1198, 1167, 1127, 1089, 1042 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.07 (s, 1H), 7.91 (d, J=7.6 Hz, 2H), 7.47 (d, J=7.2 Hz, 2H), 7.13 (s, 2H), 4.31 (d, J=7.2 Hz, 2H), 3.92 (s, 3H), 3.86 (s, 6H), 1.26 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 191.8, 187.5, 163.6, 153.2, 144.8, 143.3, 140.9, 134.4, 133.1, 130.8, 130.2, 129.3, 105.9, 62.6, 60.9, 56.2, 14.0; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{22}ClO_7$: 433.1049; found: 433.1047.

*4.2.6. Ethyl 4-(4-bromophenyl)-4-oxo-2-(3,4,5-trimethoxybenzoyl) butanoate (**1f**).* IR (KBr): 3433, 2971, 2942, 2840, 1728, 1712, 1662, 1584, 1502, 1400, 1414, 1365, 1327, 1259, 1236, 1199, 1168, 1125, 1093, 1070, 1041, 1005 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.06 (s, 1H), 7.82 (d, J=8.0 Hz, 2H), 7.64 (d, J=8.4 Hz, 2H), 7.12 (s, 2H), 4.31 (q, J=7.2 Hz, 2H), 3.92 (s, 3H), 3.86 (s, 6H), 1.26 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 191.8, 187.7, 163.6, 153.2, 144.8, 143.2, 134.8, 133.0, 132.3, 130.8, 130.3, 129.8, 105.9, 62.6, 60.86, 56.2, 14.0; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{22}H_{21}BrNaO_7$: 499.0363; found: 499.0360.

*4.2.7. Ethyl 4-(4-nitrophenyl)-4-oxo-2-(3,4,5-trimethoxybenzoyl) butanoate (**1g**).* IR (KBr): 3432, 3120, 2980, 2934, 2840, 1726, 1667, 1599, 1531, 1513, 1462, 1437, 1418, 1322, 1255, 1205, 1169, 1144, 1088, 1013 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.33 (d, J=8.8 Hz, 2H), 8.12 (d, J=8.4 Hz, 2H), 8.06 (s, 1H), 7.12 (s, 2H), 4.32 (q, J=7.2 Hz, 2H), 3.92 (s, 3H), 3.86 (s, 6H), 1.26 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 191.46, 187.44, 163.32, 153.27, 151.27, 150.75, 146.06, 143.39, 140.3, 132.31, 130.59, 129.83, 124.05, 105.98, 62.80, 60.87, 56.24, 13.93; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{22}NO_9$: 444.1289; found: 444.1283.

*4.2.8. Ethyl 4-(3,4-dichlorophenyl)-4-oxo-2-(3,4,5-trimethoxybenzoyl)butanoate (**1h**).* IR (KBr): 3441, 2972, 2901, 1654, 1406, 1393, 1384, 1249, 1076, 1065, 1051 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.02 (d, J=7.6 Hz, 2H), 7.79 (d, J=8.4 Hz, 1H), 7.58 (d, J=8.4 Hz, 1H), 7.11 (s, 2H), 4.32 (q, J=7.2 Hz, 2H), 3.74–3.92 (m, 9H), 1.25 (d, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 191.6, 186.7, 167.1, 166.5, 163.5, 153.3, 145.5, 135.6, 132.5, 131.1, 130.7, 127.8, 116.8, 105.9, 62.7, 60.9, 56.3, 29.6, 14.0; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{22}H_{20}ClNaO_7$: 489.0478; found: 489.0478.

*4.2.9. Ethyl 4-(furan-2-yl)-4-oxo-2-(3,4,5-trimethoxybenzoyl)butanoate (**1i**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.99 (d, J=3.0 Hz, 1H), 7.69 (s, 1H), 7.37 (s, 1H), 7.16 (d, J=2.8 Hz, 2H), 4.31 (q, J=7.2 Hz, 2H), 3.91 (s, 3H), 3.87 (s, 6H), 1.27 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 191.8, 175.5, 163.4, 153.1, 152.5, 148.0, 144.4, 142.9, 132.1, 130.8, 119.9, 113.2, 105.8, 62.4, 60.7, 56.1, 13.9; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{21}O_8$: 389.1231; found: 389.1231.

*4.2.10. Ethyl 4-oxo-4-(thiophen-2-yl)-2-(3,4,5-trimethoxybenzoyl) butanoate (**1j**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.97 (s, 1H), 7.90 (s, 1H), 7.77 (d, J=3.6 Hz, 1H), 7.20 (s, 1H), 7.15 (s, 2H), 4.31 (q, J=7.2 Hz, 2H), 3.91 (s, 3H), 3.86 (s, 6H), 1.25 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 191.75, 180.16, 165.81, 163.58, 153.21, 144.38, 143.90, 136.47, 133.86, 132.82, 130.87, 128.67, 105.86, 62.53, 60.79, 56.17, 13.93; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{21}O_7S$: 405.1003; found: 405.1001.

*4.2.11. Ethyl 4-(benzofuran-2-yl)-4-oxo-2-(3,4,5-trimethoxybenzoyl) butanoate (**1k**).* IR (KBr): 3433, 2972, 2939, 2839, 2390, 2283, 1728, 1659, 1611, 1583, 1552, 1502, 1459, 1414, 1329, 1279, 1238, 1205, 1161, 1037 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.12 (s, 1H), 7.74 (d, J=8.0 Hz, 1H), 7.68 (s, 1H), 7.57 (s, 1H), 7.54 (d, J=7.2 Hz, 1H), 7.35 (d, J=7.6 Hz, 1H), 7.17 (s, 2H), 4.33 (q, J=7.2 Hz, 2H), 3.91 (s, 3H), 3.86 (s, 6H), 1.28 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 191.7, 177.7, 163.5, 156.10, 153.3, 153.3, 145.0, 143.0, 132.0, 130.8, 129.4, 126.9, 124.4, 123.7, 115.6, 112.6, 105.9, 62.5, 60.8, 56.2, 13.9; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{23}O_8$: 439.1387; found: 439.1389.

*4.2.12. Ethyl 4-(naphthalen-2-yl)-4-oxo-2-(3,4,5-trimethoxybenzoyl) butanoate (**1l**).* IR (KBr): 3425, 3059, 1724, 1680, 1667, 1619, 1585, 1503, 1465, 1415, 1375, 1362, 1345, 1328, 1284, 1268, 1249, 1195, 1169, 1126, 1045, 1006 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.54 (s, 1H), 8.30 (s, 1H), 7.97 (t, J=8.0 Hz, 2H), 7.86–7.89 (m, 2H), 7.56–7.65 (m, 2H), 7.17 (s, 2H), 4.34 (q, J=7.2 Hz, 2H), 3.91 (s, 3H), 3.83 (s, 6H), 1.28 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 192.0, 188.4, 163.8, 153.2, 144.2, 143.0, 135.9, 133.8, 133.5, 132.2, 131.3, 131.0, 129.7, 129.3, 129.0, 127.1, 123.7, 109.8, 105.9, 62.5, 60.8, 56.1, 14.0; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{25}O_7$: 449.1595; found: 449.1593.

*4.2.13. Ethyl 4-(naphthalen-1-yl)-4-oxo-2-(3,4,5-trimethoxybenzoyl) butanoate (**1m**).* IR (KBr): 3439, 2939, 2837, 1723, 1666, 1584, 1504, 1461, 1414, 1342, 1241, 1165, 1127, 1003 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.45 (s, 1H), 8.09–7.96 (m, 3H), 7.84 (d, J=6.8 Hz, 1H), 7.51–7.48 (m, 3H), 7.09 (s, 2H), 4.31 (q, J=7.2 Hz, 2H), 3.88 (s, 3H), 3.82 (s, 6H), 1.27 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 191.58, 163.58, 152.82, 142.73, 142.41, 139.47, 137.30, 134.46, 134.18, 133.39, 133.26, 130.84, 130.2, 129.79, 128.15, 126.50, 125.01, 123.91, 106.79, 105.78, 62.16, 60.44, 55.82, 13.68; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{25}O_7$: 449.1595; found: 449.1593.

*4.2.14. Ethyl 2-(3,4-dimethoxybenzoyl)-4-oxo-4-phenylbutanoate (**3a**).* IR (KBr): 3441, 2971, 2389, 2284, 1720, 1666, 1597, 1451, 1267, 1050 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.02 (s, 1H), 7.84 (d, J=7.2 Hz, 2H), 7.47–7.53 (m, 2H), 7.42–7.31 (m, 2H), 7.28 (d, J=8.0 Hz, 1H), 6.74 (d, J=8.0 Hz, 1H), 4.18 (q, J=7.2 Hz, 2H), 3.81 (s, 3H), 3.79 (s, 3H), 1.13 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 191.6, 188.3, 163.6, 153.6, 149.0, 144.2, 136.0, 133.9, 133.0, 128.9, 128.6, 128.7, 123.9, 109.9, 109.4, 62.2, 55.8, 55.6, 13.7; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{21}H_{21}O_6$: 369.1333; found: 369.1333.

*4.2.15. Ethyl 2-(3,4-dimethoxybenzoyl)-4-(4-methoxyphenyl)-4-oxobutanoate (**3b**).* IR (KBr): 3432, 2970, 2938, 2842, 1729, 1666, 1594, 1513, 1463, 1420, 1367, 1350, 1267, 1207, 1168, 1140, 1017 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.11 (s, 1H), 7.95 (d, J=8.0 Hz, 2H), 7.59 (br s, 2H), 6.83–6.94 (m, 3H), 4.28 (d, J=6.8 Hz, 2H), 3.90–3.93 (m, 6H), 3.85 (s, 3H), 1.23 (t, J=6.8 Hz, 3H); ^{13}C NMR

(100 MHz, $CDCl_3$): δ (ppm) 191.0, 187.2, 163.1, 153.7, 150.2, 148.9, 145.6, 140.0, 131.7, 129.5, 128.5, 123.9, 123.6, 109.9, 109.2, 77.2, 62.3, 55.6, 55.5, 13.5; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{22}H_{23}O_7$: 399.1438; found: 399.1437.

*4.2.16. Ethyl 2-(3,4-dimethoxybenzoyl)-4-(4-nitrophenyl)-4-oxobut-2-enoate (**3c**).* IR (KBr): 3431, 3020, 2981, 2949, 1726, 1665, 1599, 1530, 1512, 1462, 1435, 1418, 1437, 1323, 1254, 1205, 1169, 1144, 1117, 1088, 1012 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.12 (s, 1H), 7.93 (d, *J*=8.4 Hz, 1H), 7.59 (s, 1H), 7.39 (d, *J*=6.8 Hz, 1H), 6.83–6.92 (m, 3H), 4.27 (q, *J*=6.8 Hz, 1H), 3.80–3.90 (m, 6H), 1.23 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 191.7, 186.3, 163.6, 153.3, 148.7, 148.5, 143.2, 133.2, 130.9, 128.9, 123.7, 113.7, 109.8, 109.2, 61.9, 55.5, 13.5; HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{21}H_{19}NNaO_8$: 436.1003; found: 436.1001.

*4.2.17. Ethyl 6-(4-methoxyphenyl)-4-oxo-2-(3,4,5-trimethoxybenzoyl)hexa-2,5-dienoate (**3g**).* IR (KBr): 3445, 2937, 1704, 1668, 1644, 1626, 1583, 1511, 1453, 1412, 1375, 1328, 1301, 1262, 1175, 1124, 1024 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.71 (s, 1H), 7.65 (d, *J*=16.0 Hz, 1H), 7.50 (d, *J*=8.4 Hz, 2H), 7.30 (s, 1H), 7.16 (s, 1H), 6.91 (d, *J*=8.4 Hz, 2H), 6.75 (d, *J*=16.0 Hz, 1H), 4.30 (q, *J*=7.6 Hz, 2H), 3.84–3.91 (m, 12H), 1.26 (t, *J*=4.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 187.2, 163.7, 162.3, 153.1, 146.4, 142.7, 135.5, 134.5, 131.0, 130.6, 126.5, 123.3, 114.5, 105.8, 62.3, 60.7, 56.1, 55.3, 13.9; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{25}H_{27}O_8$: 455.1700; found: 455.1695.

*4.2.18. Diethyl 2-(3,4,5-trimethoxybenzoyl)but-2-enedioate (**3h**).* IR (KBr): 3436, 2983, 1723, 1676, 1584, 1503, 1464, 1415, 1370, 1347, 1246, 1159, 1127, 1029, 1001 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.06 (s, 2H), 7.28 (s, 2H), 7.00 (s, 1H), 4.19 (q, *J*=7.2 Hz, 2H), 4.03 (q, *J*=7.2 Hz, 2H), 3.84 (s, 3H), 3.81 (s, 6H), 1.16 (t, *J*=6.8 Hz, 3H), 1.06 (t, *J*=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 190.8, 163.6, 163.0, 153.1, 144.8, 143.0, 130.7, 130.4, 105.8, 62.3, 61.6, 60.7, 56.1, 13.8, 13.6; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{17}H_{21}O_7$: 367.1387; found: 367.1386.

*4.2.19. Diethyl 2-(3,4-dimethoxybenzoyl)but-2-enedioate (**3i**).* IR (KBr): 2982, 2939, 2842, 1723, 1669, 1595, 1514, 1265, 1420, 1370, 1346, 1271, 1194, 1167, 1144, 1081, 1022 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.59 (s, 1H), 7.35 (s, 1H), 7.06 (s, 1H), 6.88 (d, *J*=6.8 Hz, 1H), 4.26 (br s, 2H), 4.08 (s, 2H), 3.95 (br s, 6H), 1.18–1.31 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 190.7, 163.7, 163.2, 153.8, 149.2, 145.0, 130.2, 128.9, 124.3, 109.3, 62.3, 61.5, 13.8, 13.6; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{17}H_{21}O_7$: 337.1282; found: 337.1279.

*4.3.20. 2-(Methylsulfinyl)-1,4-bis(3,4,5-trimethoxyphenyl)butane-1,4-dione (**3k**).* IR (KBr): 3441, 2996, 2941, 2837, 1652, 1580, 1504, 1455, 1414, 1334, 1233, 1203, 1159, 1126, 1070, 1041 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.37 (s, 1H), 7.28 (s, 2H), 7.21 (s, 2H), 3.95 (s, 6H), 3.91 (s, 12H), 3.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 190.3, 187.1, 163.9, 153.3, 153.2 144.2, 144.1, 131.0, 130.9, 126.4, 107.6, 106.5, 61.0, 56.4, 42.2; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{23}H_{27}O_8S$: 479.1370; found: 479.1368.

*4.2.21. Ethyl-3-benzoyl-4,5,6-trimethoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2a**).* IR (KBr): 3431, 2941, 2841, 1714, 1597, 1475, 1448, 1419, 1350, 1314, 1252, 1218, 1127, 1098, 1001 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$):δ=8.12 (d, *J*=8.0 Hz, 2H), 7.65 (t, *J*=7.2 Hz, 1H), 7.54 (t, *J*=7.2 Hz, 2H), 7.07 (s, 1H), 5.68 (s, 1H), 4.28 (q, *J*=7.2 Hz, 2H), 3.92 (s, 3H), 3.90 (s, 3H), 3.74 (s, 1H), 3.68 (s, 3H), 1.30 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=199.1, 196.0, 194.5, 167.8, 155.5, 149.3, 148.4, 139.8, 136.2, 133.8, 130.5, 128.8, 128.7, 101.2, 62.1, 60.8, 60.0, 58.3, 56.2, 45.9, 14.1; HRMS (APCI): *m/z* $[M+H]^+$ calcd for $C_{22}H_{21}O_7$: 397.1282; found: 397.1279.

*4.2.22. Ethyl-4,5,6-trimethoxy-3-(4-methylbenzoyl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2b**).* IR (KBr): 3441, 2940, 1714, 1681, 1605, 1474, 1419, 1384, 1248, 1313, 1253, 1226, 1204, 1183, 1126, 1098, 1012 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=8.02 (d, *J*=6.4 Hz, 2H), 7.33 (d, *J*=6.4 Hz, 2H), 7.06 (s, 1H), 5.65 (s, 1H), 4.28 (d, *J*=6.8 Hz, 2H), 3.92 (s, 6H), 3.72 (s, 1H), 3.68 (s, 3H), 2.46 (s, 3H), 1.30 (t, *J*=5.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=198.7, 196.2, 191.0, 167.9, 165.7, 155.5, 149.4, 144.9, 140.1, 133.7, 130.6, 129.5, 128.9, 101.3, 62.2, 60.9, 60.1, 58.4, 56.3, 55.2, 45.9, 21.7, 14.2; HRMS (APCI): *m/z* $[M+H]^+$ calcd for $C_{23}H_{25}O_8$: 429.1544; found: 429.1524.

*4.2.23. Ethyl-4,5,6-trimethoxy-3-(4-methoxybenzoyl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2c**).* IR (KBr): 3431, 2936, 2842, 1723, 1691, 1599, 1574, 1512, 1473, 1419, 1354, 1317, 1257, 1170, 1129, 1106, 1070, 1024 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=8.12 (d, *J*=8.8 Hz, 2H), 7.27 (s, 1H), 7.02 (d, *J*=8.8 Hz, 2H), 5.47 (s, 1H), 3.96 (s, 3H), 3.92 (s, 3H), 3.81 (s, 2H), 3.77 (s, 3H), 0.98 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=198.7, 196.2, 168.0, 155.6, 149.5, 144.9, 140.1, 133.7, 130.6, 129.5, 128.9, 101.3, 62.2, 60.9, 60.1, 58.4, 56.3, 45.9, 21.7, 14.2; HRMS (APCI): *m/z* $[M+H]^+$ calcd for $C_{23}H_{25}O_8$: 429.1544; found: 429.1524.

*4.2.24. Ethyl-3-(2,3-dihydrobenzo[b][1,4]dioxine-6-carbonyl)-4,5,6-trimethoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2d**).* IR (KBr): 3428, 2981, 2940, 1713, 1675, 1604, 1597, 1507, 1475, 1429, 1349, 1312, 1287, 1259, 1227, 1203, 1162, 1126, 1097, 1065, 1010 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=7.67 (s, 2H), 7.06 (s, 1H), 6.97 (d, *J*=8.8 Hz, 1H), 5.57 (d, *J*=4.0 Hz, 1H), 4.35 (d, *J*=4.4 Hz, 2H), 4.29–4.31 (m, 4H), 4.27 (s, 1H), 3.920 (s, 3H), 3.905 (s, 3H), 3.70 (s, 3H), 1.31 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=197.3, 196.2, 167.9, 155.5, 149.4, 148.7, 143.5, 140.7, 130.6, 129.9, 122.9, 118.2, 117.4, 101.2, 62.1, 60.8, 60.1, 58.4, 56.2, 45.7, 14.1; HRMS (APCI): *m/z* $[M+H]^+$ calcd for $C_{24}H_{25}O_9$: 457.1497; found: 457.1491.

*4.2.25. Ethyl 3-(4-chlorobenzoyl)-4,5,6-trimethoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2e**).* IR (KBr): 3430, 2938, 1716, 1686, 1584, 1518, 1474, 1420, 1394, 1346, 1313, 1286, 1262, 1219, 1126, 1072, 1009 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=8.07 (d, *J*=8.4 Hz, 2H), 7.51 (d, *J*=8.4 Hz, 2H), 7.06 (s, 1H), 5.62 (d, *J*=4.0 Hz, 1H), 4.28 (s, 2H), 3.91 (s, 6H), 3.72 (s, 1H), 3.68 (s, 3H), 1.31 (t, *J*=4.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=167.8, 157.9, 148.4, 134.5, 130.6, 130.2, 129.2, 115.7, 115.0, 114.7, 101.3, 100.1, 95.3, 62.3, 60.9, 60.1, 58.3, 56.3, 45.8, 29.6; HRMS (APCI): *m/z* $[M+H]^+$ calcd for $C_{22}H_{22}ClO_7$: 433.1049; found: 433.1051.

*4.2.26. Ethyl-3-(4-bromobenzoyl)-4,5,6-trimethoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2f**).* IR (KBr): 3432, 2937, 1715, 1685, 1619, 1602, 1585, 1518, 1474, 1419, 1394, 1345, 1312, 1286, 1252, 1219, 1126, 1098, 1071, 1009 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=7.99 (d, *J*=8.0 Hz, 2H),7.66 (d, *J*=8.4 Hz, 2H), 7.04 (s, 1H), 5.59 (d, *J*=4.0 Hz, 1H), 4.27 (q, *J*=4.0 Hz, 2H), 3.89 (s, 6H), 3.72 (d, *J*=3.6 Hz, 1H), 3.66 (s, 3H), 0.94 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=198.4, 195.7, 167.7, 155.6, 139.4, 135.0, 132.1, 130.8, 130.4, 130.2, 129.2, 128.7, 101.2, 62.2, 60.8, 60.0, 58.2, 56.2, 45.7, 29.6, 19.1, 14.1; HRMS (APCI): *m/z* $[M+H]^+$ calcd for $C_{22}H_{22}BrO_7$: 477.0543; found: 477.0546.

*4.2.27. Ethyl-4,5,6-trimethoxy-3-(4-nitrobenzoyl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2g**).* IR (KBr): 3432, 2940, 1716, 1604, 1528, 1474, 1419, 1348, 1217, 1237, 1213, 1126, 1098, 1073, 1011 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=8.39 (d, *J*=8.8 Hz, 2H), 8.30 (d, *J*=8.8 Hz, 2H), 7.08 (d, *J*=8.8 Hz, 1H), 5.68 (d, *J*=4.0 Hz, 1H),

4.30 (q, J=4.0 Hz, 3H), 3.924 (s, 3H), 3.918 (s, 3H), 3.78 (d, J=4.0 Hz, 1H), 3.68 (s, 3H), 1.32 (t, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=199.4, 195.1, 167.5, 156.2, 150.5, 150.2, 140.8, 132.1, 129.7, 129.2, 124.1, 123.9, 101.2, 60.9, 60.0, 58.0, 56.2, 46.0, 14.1; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{22}NO_9$: 444.1289; found: 444.1287.

*4.2.28. Ethyl-3-(3,4-dichlorobenzoyl)-4,5,6-trimethoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2h**).* IR (KBr): 3430, 2936, 1715, 1602, 1583, 1557, 1474, 1419, 1388, 1350, 1312, 1208, 1127, 1097, 1030, 1011 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.21 (s, 1H), 7.97 (d, J=6.8 Hz, 1H), 7.62 (d, J=8.4 Hz, 1H), 7.06 (s, 1H), 5.57 (d, J=4.0 Hz, 1H), 4.29 (q, J=7.2 Hz, 2H), 3.913 (s, 3H), 3.918 (s, 3H), 3.84 (d, J=10.0 Hz, 1H), 3.71 (s, 3H), 1.32 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=197.2, 195.4, 107.6, 155.7, 148.3, 138.9, 138.4, 135.8, 130.9, 130.6, 130.4, 127.7, 101.2, 62.3, 60.9, 58.1, 56.3, 45.8, 29.6, 14.1; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{22}H_{21}Cl_2O_7$: 467.0659; found: 467.0659.

*4.2.29. Ethyl-3-(furan-2-carbonyl)-4,5,6-trimethoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2i**).* IR (KBr): 3433, 2941, 1714, 1675, 1601, 1567, 1466, 1419, 1394, 1313, 1259, 1204, 1157, 1127, 1098, 1014 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.69 (s, 1H), 7.42 (s, 1H), 7.06 (s, 1H), 6.63 (d, J=1.6 Hz, 1H), 5.41 (d, J=2.4 Hz, 1H), 4.28 (q, J=7.2 Hz, 2H), 3.92 (s, 3H), 3.91 (s, 3H), 3.81 (s, 1H), 3.75 (s, 3H), 1.31 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=196.0, 186.9, 167.8, 155.7, 152.0, 147.5, 138.8, 130.7, 119.1, 112.7, 109.9, 101.4, 62.1, 60.9, 60.3 58.0, 56.3, 46.9, 29.6, 14.2; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{21}O_8$: 389.1231; found: 389.1231.

*4.2.30. Ethyl-4,5,6-trimethoxy-1-oxo-3-(thiophene-2-carbonyl)-2,3-dihydro-1H-indene-2-carboxylate (**2j**).* IR (KBr): 3427, 3093, 2936, 2851, 1713, 1660, 1517, 1474, 1414, 1349, 1313, 1240, 1205, 1126, 1098, 1013 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.89 (d, J=3.2 Hz, 1H), 7.69 (d, J=4.8 Hz, 1H), 7.13 (t, J=4.4 Hz, 1H), 6.99 (s, 1H), 5.40 (d, J=4.0 Hz, 1H), 4.20 (m, 2H), 3.84 (s, 3H), 3.83 (s, 3H), 3.71 (d, J=4.0 Hz, 1H), 3.65 (s, 3H), 1.23 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=195.8, 191.5, 167.7, 155.6, 148.5, 143.5, 139.1, 135.3, 133.4, 130.5, 128.5, 101.3, 62.1, 60.8, 60.2, 58.3, 56.2, 47.5, 29.6, 14.1; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{21}O_7S$: 405.1003; found: 405.1001.

*4.2.31. Ethyl-3-(benzofuran-2-carbonyl)-4,5,6-trimethoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2k**).* IR (KBr): 3427, 2939, 2840, 1714, 1680, 1603, 1554, 1474, 1419, 1348, 1314, 1259, 1229, 1202, 1159, 1126, 1096, 1008 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.77 (d, J=8.8 Hz, 2H), 7.61 (d, J=8.0 Hz, 1H), 7.53 (t, J=4.8 Hz, 1H), 7.36 (t, J=4.8 Hz, 1H), 7.08 (s, 1H), 5.57 (s, 1H), 4.30 (q, J=3.2 Hz, 2H), 3.92 (s, 6H), 3.83 (d, J=4.0 Hz, 1H), 3.77 (s, 3H), 1.32 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=195.7, 189.0, 167.8, 156.1, 155.8, 151.8, 149.5, 148.5, 138.6, 130.6, 128.9, 126.9, 124.1, 123.6, 115.0, 112.5, 101.3, 62.2, 60.9, 60.4, 58.0, 56.3, 47.1, 14.2; HRMS (APCI): m/z $[M+H]^+$ calcd for $C_{24}H_{23}O_8$: 439.1387; found: 439.1385.

*4.2.32. Ethyl-3-(2-naphthoyl)-4,5,6-trimethoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2l**).* IR (KBr): 3424, 3059, 2961, 2937, 2826, 1723, 1667, 1619, 1584, 1502, 1466, 1414, 1362, 1345, 1328, 1284, 1266, 1247, 1194, 1168, 1128, 1045, 1008 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.61 (s, 1H), 8.04 (d, J=8.4 Hz, 1H), 7.90 (d, J=8.0 Hz, 1H), 7.84 (d, J=8.4 Hz, 1H), 7.79 (d, J=7.6 Hz, 1H), 7.49 (q, J=7.6 Hz, 2H), 6.98 (s, 1H), 5.57 (d, J=3.6 Hz, 1H), 4.8 (q, J=3.2 Hz, 2H), 3.80 (s, 3H), 3.78 (s, 3H), 3.72 (d, J=3.6 Hz, 1H), 3.56 (s, 3H), 0.80 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=198.9, 196.0, 167.9, 155.5, 149.3, 148.3, 135.7, 132.4, 130.7, 130.5, 129.7, 128.8, 128.6, 127.6, 126.8, 124.0, 101.2, 62.1, 60.7, 60.0, 58.4, 56.1, 45.9, 29.5, 14.0; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{25}O_7$: 449.1595; found: 449.1590.

*4.2.33. Ethyl-3-(1-naphthoyl)-4,5,6-trimethoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2m**).* IR (KBr): 3425, 2939, 1712, 1680, 1594, 1573, 1508, 1474, 1419, 1349, 1314, 1234, 1201, 1176, 1126, 1094, 1014 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.62 (d, J=8.0 Hz, 1H), 8.21 (d, J=7.2 Hz, 1H), 8.04 (d, J=8.0 Hz, 1H), 7.89 (d, J=8.0 Hz, 1H), 7.58–7.51 (m, 3H), 7.07 (s, 1H), 5.70 (d, J=3.6 Hz, 1H), 4.20 (q, J=2.8 Hz, 2H), 3.89 (s, 6H), 3.86 (d, J=3.6 Hz, 1H), 3.63 (s, 3H), 1.20 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=201.7, 196.1, 167.8, 155.6, 149.4, 148.2, 134.7, 133.9, 133.6, 130.6, 128.6, 128.4, 128.2, 126.6, 125.7, 124.3, 101.1, 62.0, 60.8, 60.2, 58.2, 56.2, 49.6, 14.0; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{25}O_7$: 449.1595; found: 449.1590.

*4.2.34. Ethyl-3-benzoyl-4,5-dimethoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**4a**).* IR (KBr): 3440, 2933, 1724, 1675, 1599, 1557, 1504, 1463, 1416, 1331, 1260, 1171, 1127, 1022 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.09 (d, J=7.2 Hz, 2H), 7.68 (t, J=7.2 Hz, 1H), 7.56 (q, J=8.0 Hz, 2H), 7.21 (s, 1H), 6.67 (s, 1H), 5.64 (d, J=3.6 Hz, 1H), 4.28 (q, J=7.2 Hz, 2H), 4.13 (d, J=3.6 Hz, 1H), 3.91 (s, 3H), 3.78 (s, 3H), 1.32 (t, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=197.2, 195.6, 168.3, 155.8, 152.0, 150.4, 146.4, 139.1, 136.3, 134.0, 129.0, 127.7, 107.3, 105.0, 60.1, 56.9, 56.1, 49.3, 29.6, 14.1; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{21}H_{21}O_6$: 369.1333; found: 369.1332.

*4.2.35. Ethyl-4,5-dimethoxy-3-(4-methoxybenzoyl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**4b**).* IR (KBr): 3444, 2939, 1704, 1683, 1600, 1572, 1501, 1460, 1441, 1419, 1346, 1286, 1267, 1221, 1171, 1104, 1019 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.02 (d, J=8.8 Hz, 2H), 7.12 (s, 1H), 6.95 (d, J=8.8 Hz, 1H), 6.64 (s, 1H), 5.52 (d, J=3.2 Hz, 1H), 4.19 (q, J=6.8 Hz, 2H), 4.04 (d, J=3.6 Hz, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.72 (s, 3H), 1.24 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=195.8, 195.4, 168.3, 164.1, 155.7, 150.2, 146.8, 131.3, 128.9, 127.6, 114.0, 112.0, 107.1, 104.8, 61.8, 57.0, 55.9, 55.4, 48.7, 41.5, 14.0; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{23}O_7$: 399.1438; found: 399.1438.

*4.2.36. Ethyl-4,5-dimethoxy-3-(4-nitrobenzoyl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**4c**).* IR (KBr): 3448, 2926, 1701, 1590, 1527, 1502, 1465, 1419, 1348, 1301, 1108, 1009 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.40 (d, J=8.8 Hz, 2H), 8.25 (d, J=8.8 Hz, 2H), 7.30 (s, 1H), 6.69 (s, 1H), 5.66 (d, J=3.2 Hz, 1H), 4.29 (q, J=6.8 Hz, 2H), 4.01 (d, J=3.6 Hz, 1H), 3.92 (s, 3H), 3.84 (s, 3H), 1.32 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=196.2, 194.6, 181.6, 156.0, 150.7, 145.3, 140.6, 129.9, 129.1, 127.7, 124.1, 123.8, 107.2, 105.1, 62.4, 56.8, 56.1, 54.2, 49.6, 14.1; HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{21}H_{19}NNaO_8$: 436.1003; found: 436.1000.

*4.2.37. (E)-Ethyl 4,5,6-trimethoxy-3-(3-(4-methoxyphenyl)acryloyl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**4g**).* IR (KBr): 3444, 2938, 1705, 1669, 1645, 1627, 1583, 1511, 1453, 1412, 1375, 1328, 1301, 1262, 1175, 1127, 1025 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.07 (d, J=8.8 Hz, 3H), 6.97 (s, 1H), 6.74–6.77 (m, 2H), 4.78 (s, 1H), 4.03 (s, 2H), 3.97 (s, 1H), 3.70 (s, 3H), 3.82 (s, 3H), 3.91 (s, 3H), 0.85 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=211.1, 208.5, 198.3, 166.3, 158.7, 155.3, 150.7, 149.5, 136.5, 133.0, 129.3, 128.9, 128.6, 113.9, 113.4, 101.6; 72.7, 62.2, 61.9, 61.0, 56.3, 55.2, 52.3, 44.7, 44.0, 14.0; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{25}H_{27}O_8$: 455.1700; found: 455.1695.

*4.2.38. Diethyl 5,6,7-trimethoxy-3-oxo-2,3-dihydro-1H-indene-1,2-dicarboxylate (**4h**).* IR (KBr): 3451, 2941, 1739, 1641, 1602, 1533, 1476, 1419, 1349, 1316, 1256, 1179, 1128, 1028 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.02 (s, 1H), 4.55 (s, 1H), 4.18 (m, 4H),

3.83–3.88 (m, 9H), 3.78 (s, 1H), 1.19–1.27 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=196.0, 172.0, 167.6, 155.6, 149.9, 137.8, 130.2, 101.2, 62.2, 61.6, 61.0, 60.6, 57.9, 56.3, 45.0, 14.1; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{17}H_{21}O_7$: 367.1387; found: 367.1387.

*4.2.39. Diethyl 6,7-dimethoxy-3-oxo-2,3-dihydro-1H-indene-1,2-dicarboxylate (**4i**).* IR (KBr): 3451, 2981, 1708, 1591, 1503, 1466, 1421, 1369, 1301, 1110, 1022 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ=7.18 (d, *J*=8.4 Hz, 2H), 4.63 (s, 1H), 4.22–4.31 (m, 4H), 4.18 (s, 1H), 4.00 (s, 3H), 3.92 (s, 3H), 1.34 (t, *J*=7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=195.4, 170.4, 167.9, 155.8, 150.4, 145.1, 127.1, 107.1, 104.6, 61.9, 61.7, 56.2, 56.0, 47.0, 14.0; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{17}H_{21}O_7$: 337.1282; found: 337.1279.

*4.2.40. Ethyl 1-(4-methoxyphenyl)-3-oxo-2,3-dihydro-1H-indene-2-carboxylate (**4o**).* 205.8 mg, 86% yield; mp 79–80 °C; IR (KBr): 3270, 3060, 3027, 2984, 2929, 2871, 1824, 1717, 1654, 1618, 1594, 1476, 1453, 1415, 1375, 1338, 1315, 1301, 1275, 1250, 1206, 1170, 1149, 1131, 1092, 1027 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.82 (d, *J*=6.8 Hz, 1H), 7.60 (t, *J*=6.8 Hz, 1H), 7.43 (t, *J*=6.8 Hz, 1H), 7.26–7.33 (m, 4H), 7.16 (d, *J*=6.4 Hz, 2H), 5.01 (s, 1H), 4.26 (t, *J*=7.2 Hz, 2H), 3.69 (s, 1H), 1.13 (t, *J* 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=198.5, 168.3, 156.1, 141.7, 135.6, 134.9, 128.9, 128.2, 127.8, 127.7, 127.4, 126.6, 124.1, 63.5, 61.7, 48.5, 14.1; HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{18}H_{16}NaO_3$: 303.0992; found: 303.0995.

*4.2.41. Ethyl 1-(4-methoxyphenyl)-3-oxo-2,3-dihydro-1H-indene-2-carboxylate (**4p**).* 205.8 mg, 86% yield; oil; IR (KBr): 3433, 2981, 2923, 1715, 1602, 1554, 1513, 1463, 1369, 1288, 1235, 1151, 1113, 1094, 1043, 1020 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.71 (d, *J*=6.7 Hz, 1H), 7.49 (t, *J*=7.6 Hz, 1H), 7.33 (d, *J*=7.2 Hz, 1H), 7.17 (d, *J*=7.6 Hz, 1H), 7.04 (d, *J*=7.2 Hz, 2H), 6.95 (d, *J*=7.2 Hz, 2H), 4.88 (s, 1H), 4.16 (t, *J*=7.2 Hz, 2H), 3.57 (s, 1H), 2.23 (s, 3H), 1.19 (q, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=198.6, 168.4, 156.4, 138.7, 137.0, 135.6, 134.9, 129.6, 129.4, 128.9, 128.1, 127.7, 127.4, 126.7, 126.6, 124.0, 63.6, 61.6, 48.2, 46.8, 20.9, 14.1; HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{19}H_{18}NaO_3$: 317.1148; found: 317.1151.

*4.2.42. Ethyl 1-(4-methoxyphenyl)-3-oxo-2,3-dihydro-1H-indene-2-carboxylate (**4q**).* 205.8 mg, 86% yield; oil; IR (KBr): 3433, 2959, 2935, 2906, 2836, 1713, 1607, 1512, 1463, 1443, 1421, 1369, 1303, 1249, 1177, 1150, 1111, 1093, 1032 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.81 (d, *J*=7.2 Hz, 1H), 7.60 (t, *J*=7.2 Hz, 1H), 7.43 (t, *J*=7.2 Hz, 1H), 7.28 (s, 1H), 7.08 (d, *J*=7.6 Hz, 2H), 6.87 (d, *J*=7.2 Hz, 2H), 4.96 (s, 1H), 4.26 (q, *J*=7.2 Hz, 2H), 3.79 (s, 3H), 3.64 (s, 1H), 1.31 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=198.7, 168.4, 158.8, 156.5, 135.6, 135.0, 134.9, 133.7, 128.9, 128.5, 128.1, 126.7, 126.6, 124.1, 114.3, 114.2, 63.7, 61.7, 55.2, 47.9, 46.9, 43.6, 14.1; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{19}H_{19}O_4$: 311.1278; found: 311.1278.

*4.2.43. Ethyl 5-methoxy-1-oxo-3-phenyl-2,3-dihydro-1H-indene-2-carboxylate (**4r**).* 205.8 mg, 86% yield; oil; IR (KBr): 3434, 3062, 2980, 2939, 2841, 1708, 1664, 1596, 1510, 1490, 1453, 1421, 1368, 1246, 1197, 1167, 1090, 1021 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.82 (d, *J*=6.4 Hz, 2H), 7.75 (d, *J*=8.0 Hz, 1H), 7.31–7.35 (m, 4H), 7.28 (d, *J*=6.8 Hz, 1H), 7.24 (t, *J*=7.2 Hz, 2H), 7.16 (d, *J*=6.4 Hz, 2H), 6.95 (t, *J*=7.6 Hz, 2H), 6.89 (d, *J*=8.0 Hz, 1H), 6.66 (s, 1H), 4.94 (s, 1H), 4.24 (q, *J*=6.8 Hz, 2H), 3.78 (s, 3H), 3.66 (s, 1H), 1.30 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=196.5, 168.6, 166.0, 159.3, 141.9, 141.7, 130.0, 128.9, 128.6, 127.8, 127.3, 116.4, 113.9, 113.8, 109.5, 63.7, 61.6, 61.4, 55.6, 55.3, 48.5, 14.1, 14.0; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{19}H_{19}O_4$: 311.1278; found: 311.1278.

*4.2.44. Ethyl 4-methoxy-3-oxo-1-phenyl-2,3-dihydro-1H-indene-2-carboxylate (**4s**).* 205.8 mg, 86% yield; yellow solid; mp 115–116 °C; IR (KBr): 3422, 3028, 2999, 2959, 2937, 2840, 1729, 1704, 1593, 1498, 1480, 1451, 1386, 1368, 1318, 1281, 1247, 1207, 1180, 1158, 1083, 1066, 1003 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.52 (t, *J*=7.2 Hz, 1H), 7.27–7.32 (m, 2H), 7.14 (d, *J*=6.8 Hz, 2H), 6.84 (d, *J*=8.0 Hz, 1H), 6.79 (d, *J*=7.2 Hz, 1H), 4.91 (s, 1H), 4.24 (q, *J*=6.8 Hz, 2H), 3.98 (s, 3H), 3.66 (s, 1H), 1.30 (t, *J*=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=196.0, 168.6, 158.7, 158.2, 141.9, 137.4, 128.9, 127.9, 127.3, 123.1, 118.3, 109.6, 63.7, 61.7, 55.8, 48.1, 14.2; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{19}H_{19}O_4$: 311.1278; found: 311.1278.

*4.2.45. Ethyl 5,6-dimethoxy-1-oxo-3-phenyl-2,3-dihydro-1H-indene-2-carboxylate (**4t**).* 205.8 mg, 86% yield; oil; IR (KBr): 3457, 2979, 2938, 2838, 1737, 1703, 1677, 1592, 1500, 1465, 1419, 1367, 1302, 1257, 1153, 1111, 1022 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.55 (t, *J*=8.0 Hz, 2H), 7.28–7.35 (m, 4H), 7.22 (s, 1H), 7.16 (d, *J*=6.8 Hz, 2H), 6.90 (d, *J*=7.6 Hz, 1H), 6.67 (s, 1H), 4.91 (s, 1H), 4.26 (q, *J*=6.8 Hz, 2H), 3.84–3.96 (m, 6H), 3.63 (s, 1H), 1.30 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=196.8, 190.8, 168.4, 167.4, 156.1, 153.5, 151.5, 149.9, 148.8, 141.7, 128.9, 128.7, 127.7, 127.5, 127.1, 123.3, 110.0, 109.8, 107.0, 103.9, 63.5, 61.4, 56.0, 55.8, 55.6, 46.1, 45.3, 13.9, 13.8; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{20}H_{21}O_5$: 341.1384; found: 341.1385.

*4.2.46. Ethyl 4,5,6-trimethoxy-1-oxo-3-phenyl-2,3-dihydro-1H-indene-2-carboxylate (**4u**).* 205.8 mg, 86% yield; oil; IR (KBr): 3437, 2939, 2838, 1738, 1709, 1601, 1472, 1418, 1344, 1313, 1242, 1205, 1155, 1127, 1098, 1018 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.20 (d, *J*=6.4 Hz, 2H), 7.15 (t, *J*=7.2 Hz, 1H), 7.04 (t, *J*=7.2 Hz, 3H), 4.86 (s, 1H), 4.16 (q, *J*=6.8 Hz, 2H), 3.83 (br, 6H), 3.54 (s, 1H), 3.27 (s, 3H), 1.22 (t, *J*=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=197.9, 168.3, 155.1, 150.2, 149.3, 143.4, 142.7, 130.4, 128.7, 128.5, 127.9, 127.4, 127.0, 100.9, 63.7, 61.8, 60.8, 59.9, 56.2, 46.1, 14.1; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{21}H_{23}O_6$: 371.1489; found: 371.1487.

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2014.10.052.

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14. Crystal data for compound **2g**: CCDC 934475. $C_{22}H_{21}NO_9$, formula weight=443.40, triclinic, a=6.868(14) Å, b=9.782(2) Å, c=17.323(4) Å, α=98.560(3)°, β=100.804(4)°, γ=109.566(3)°, V=11,048.5(4) Å^3, T=298(2) K, space group P-1, Z=2, DC=1.404 Mg/m^3, μ=0.325 mm^{-1}, λ=0.71073 Å, F(000) 464, crystal size 0.20×0.10×0.10 mm^3, 3667 independent reflections (R_{int}=0.0772), reflections collected 6317, refinement method full-matrix least-squares on F^2, goodness-of-fit on F^2, 1.048, final R indices [$I>2s(I)$], $R1$=0.0640, $wR2$=0.1678, largest diff. peak and hole 0.222 and −0.249 e^{-3}. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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