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PII: S0040-4020(18)30135-2

DOI: 10.1016/j.tet.2018.02.010

Reference: TET 29281

To appear in: *Tetrahedron*

Received Date: 1 December 2017

Revised Date: 31 January 2018

Accepted Date: 2 February 2018

Please cite this article as: Xiong G, Liao Y, Liu X-H, Tang X, Gong Y, Formal cycloaddition of ethyl 2-aroyl-1-chlorocyclopropanecarboxylates:facile synthesis of diversified tetrahydrocyclopropa[*b*]chromenes, *Tetrahedron* (2018), doi: 10.1016/j.tet.2018.02.010.

## Graphical Abstract

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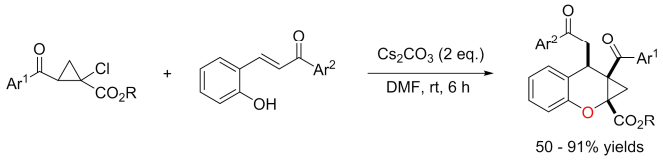

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# Formal cycloaddition of ethyl 2-Aroyl-1-chlorocyclopropanecarboxylates: facile synthesis of diversified tetrahydrocyclopropa[*b*]chromenes

Guoxi Xiong[a, b], Yong Liao[a], Xue-Hui Liu,[b] Xiangying Tang[a,] * and Yuefa Gong[b,] *

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ARTICLE INFO

*Article history:*
Received
Received in revised form
Accepted
Available online

*Keywords:*
Cycloaddition
Chromenes
Cyclopropenes
Cyclopropanation
Heterocycles

ABSTRACT

Tandem reaction of ortho-hydroxy chalcone with ethyl 2-aroyl-1-chlorocyclopropanecarboxylates has been disclosed, affording facile synthesis of diversified tetrahydrocyclopropa[b]chromenes via electron-deficient cyclopropene intermediate.



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## 1. Introduction

Cyclopropenes are highly strained but useful building blocks in organic synthesis.[1] During the last decades, the investigation of cyclopropenes has attracted much attention due to their wide range of reactivities beyond those of olefins, allenes and alkynes.[2] In general, electron-rich cyclopropenes are used as excellent π–donators which can coordinate with many transition metal catalysts as well as Brønsted acids or Lewis acids. For example, In 2010, Wang and coworkers reported a novel gold catalyzed rearrangement of 1,5-cyclopropene-ynes to afford benzene derivatives.[2f] Shi and coworkers also found that nitrogen or carbon-tethered indolylcyclopropenes could undergo novel intramolecular cycloisomerizations of to furnish biologically and pharmaceutically valuable heterocycles catalyzed by gold- and silver-catalysts or HOTf.[3] However, to our great surprise, the chemistry of electron-deficient cyclopropenes remain largely unexplored, mainly because such molecules are difficult to be activated by metal or acid catalysts and very limited types of such cyclopropenes were reported probably due to their instability.

Polyfunctionalized chromenes are found in many natural scaffolds and drug candidates displaying a broad range of biological and pharmacological activities. In particular, cyclopropane fused chromenes are of great importance, because they are not only served as potential drug candidates in drug discovery, but also are important intermediates in the synthesis of diversified heterocycles. For example, N-phenyl-7-(hydroxyimino)cyclopropa[b]chromen-1a-carboxamide (PHCCC), which acts as a glutamate receptor ligand, has been suggested as novel treatments for Parkinson's disease.[4, 5] Another related drug molecule, namely CPCCPEt, is used mainly in basic research as a non-competitive antagonist at the metabotropic glutamate receptor subtype mGluR1 (Figure 1).[6]

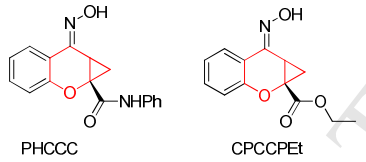
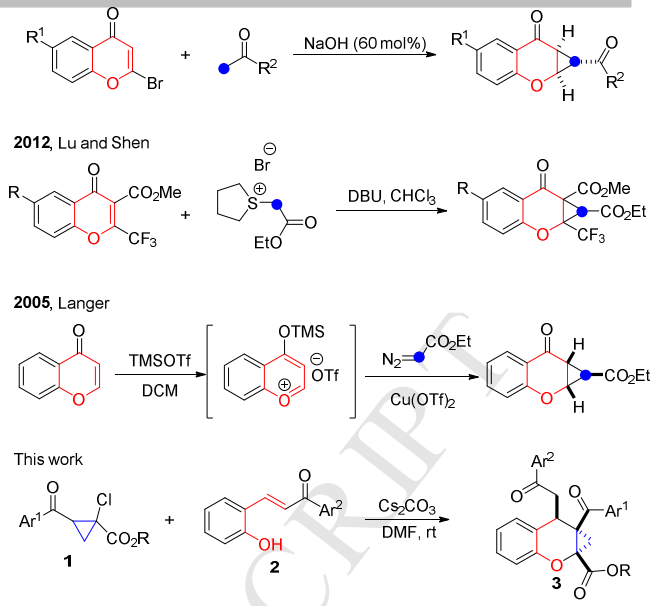



**Figure 1.** Bioactive cyclopropane fused chromenes.

Meanwhile, it is reported that transformation of such cyclopropane containing substance into other useful heterocyclic have also been achieved.[7] Traditionally, cyclopropane fused chromenes can be constructed by Michael-initiated ring-closure of methyl ketones with 3-bromochromones (Scheme 1a),[8] or treatment of electron-deficient chromenes with sulfur ylides under basic conditions (Scheme 1b),[9] and also by cyclopropanation of chromenes with carbenoids (Scheme 1c).[10] However, in a sharp contrast, beyond cyclopropanation of chromenes, other methods to access cyclopropane fused chromenes are extremely limited. In view of the current circumstances, and also to continue our research interest in electron-deficient cyclopropenes,[11] we envisage that a formal [4+2] cycloaddition reaction can take place between ethyl 2-aroyl-1-chlorocyclopropanecarboxylates **1** and (*E*)-3-(2-hydroxyaryl)-1-arylprop-2-en-1-ones **2**, affording the desired cyclopropylchromenes **3**.

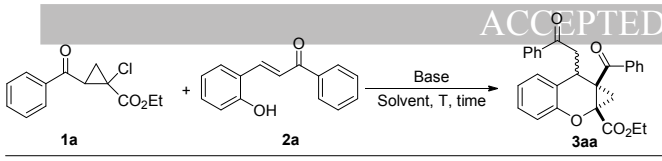



**Scheme 1.** Reported method to construct cyclopropane-fused chromenes and our method.

## 2. Result and discussion

Our initial investigation started with the optimization of the reaction conditions using **1a** and **2a** as the model substrates. To our delight, treatment of **1a** and **2a** with $Cs_2CO_3$ in DMSO (dimethyl sulfoxide) at 25 °C (room temperature) for 6 h, the reaction went on smoothly to give the desired product **3aa** in 56% yield, along with good diastereoselectivity (3.4:1) as determined by crude $^1$H NMR (Table 1, entry 1). After careful separation of the diastereoisomers by silica gel chromatography and subjected to the 2D NOESY, the major product was determined as *cis* configuration (for details, see Supporting Information). When another highly polar solvent, DMF (N,N-dimethylformamide) was used in replace of DMSO, the yield of **3aa** increased to 88% with a 3.5:1 dr value (Table 1, entry 2). Further solvent effect study revealed that DMF was the best solvent for this transformation (Table 1, entries 3-8). It is worth nothing that the polarity of the solvents plays an important role to control the diastereoselectivity: high polar solvents favor *cis* products, while non-polar solvents have opposite selectivity. Next, using DMF as the solvent, the effect of different bases was evaluated. When $K_2CO_3$ and $K_3PO_4$ were used, the reactions were less effective than $Cs_2CO_3$, giving the corresponding products in 49% and 78% yields, respectively (Table 1, entries 9-10). For strong base KOH, the yield of **3aa** dropped to 30%, probably due to that the cyclopropene intermediate is formed too fast and undergoes self-polymerization during the reaction process (Table 1, entry 11). Similar results were obtained in the cases of LiOH and $Mg(OEt)_2$ (Table 1, entries 12-13). In addition, because of the nuclephilicity of the nitrogen atom, organic bases such as $Et_3N$ and DBU were found not suitable for this reaction (Table 1, entries 14-15). Based on the above results, we then understood that the base shouldn't be too strong or weak, because the formation of cyclopropene intermediate and deprotonation of the phenol should be kinetically compatible, or cyclopropene intermediate will proceed with polymerization reactions. Therefore, $Cs_2CO_3$ was chosen as the best base. Further study about the loadings of $Cs_2CO_3$ revealed that the 2 eq. gave the highest yield as well as diastereoselectivity (Table 1, entries 2 and 16-18).

**Table 1.** Optimization of the reaction conditions



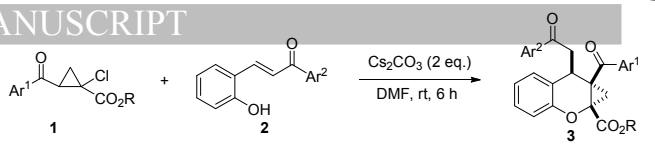

1a 2a 3aa

| entry[a] | base | solvent | T (°C) | t (h) | yield (%)[b] (*cis*:*trans*)[c] |
|---|---|---|---|---|---|
| 1 | $Cs_2CO_3$ | DMSO | 25 | 6 | 56 (3.4:1) |
| 2 | $Cs_2CO_3$ | DMF | 25 | 6 | 88 (3.5:1) |
| 3 | $Cs_2CO_3$ | $CH_3CN$ | 60 | 12 | 83 (4:1) |
| 4 | $Cs_2CO_3$ | 1,4-dixoane | 60 | 12 | 68 (1:2.3) |
| 5 | $Cs_2CO_3$ | THF | 25 | 12 | 77 (2.5:1) |
| 6 | $Cs_2CO_3$ | $CH_2Cl_2$ | 25 | 12 | 73 (1.1:1) |
| 7 | $Cs_2CO_3$ | Toluene | 60 | 12 | 61 (1:2.5) |
| 8 | $Cs_2CO_3$ | 1,2-DCE | 25 | 12 | 57 (1:1) |
| 9 | $K_2CO_3$ | DMF | 25 | 24 | 49 (3.7:1) |
| 10 | $K_3PO_4$ | DMF | 25 | 24 | 78 (3.7:1) |
| 11 | KOH | DMF | 25 | 12 | 30 (2.9:1) |
| 12 | LiOH | DMF | 25 | 12 | 51 (2.8:1) |
| 13 | $Mg(OEt)_2$ | DMF | 80 | 24 | 48 (2:1) |
| 14 | $Et_3N$ | DMF | 25 | 24 | ND |
| 15 | DBU | DMF | 25 | 24 | < 5 |
| 16 | $Cs_2CO_3$[d] | DMF | 25 | 24 | 81 (3:1) |
| 17 | $Cs_2CO_3$[e] | DMF | 25 | 6 | 85 (3:1) |
| 18 | $Cs_2CO_3$[f] | DMF | 25 | 6 | 56 (2.9:1) |

[a] Reaction conditions: 0.2 mmol (1.0 eq.) of **1a**, 0.2 mmol (1.0 eq.) of **2a**, and 0.4 mmol (2.0 eq.) of base in 2.0 mL of solvent at the specified temperature for the given time.
[b] Isolated total yields of the diastereomers.
[c] Determined by $^1$H NMR of crude **3aa**.
[d] 0.2 mmol of base (1.0 eq.).
[e] 0.3 mmol of base (1.5 eq.).
[f] 0.5 mmol of base (2.5 eq.).
DMSO = Dimethyl sulfoxide, DMF = Dimethylformamide, THF = tetrahydrofuran, 1,2-DCE = 1,2-dichlorethane.

With the best reaction conditions in hand, we next turned our interest to study the generality of this reaction. As can be seen from table 2, the reactions of **2a** with various **1b**-**1g** all went smoothly to give the corresponding products in moderate to good yields and moderate diastereoselectivities with no significant electronic effect (Table 2, entries 1-6). In case of 2-thiophenyl group substituted substrate **1f**, lower yield of **3fa** was obtained probably because of the steric hindrance (Table 2, entry 5). Next, taking **1a** as a model substrate, different *ortho*-hydroxy chalcones **2** were investigated. As for substrates **2b** and **2c**, the reactions delivered the desired products **3ab** and **3ac** in moderate to good yields (Table 2, entries 7-8), surprisingly, in case of substrate **2b** with a 4-methyl group, the reaction gave the best yield (91%) (Table 2, entry 7). Though the reason was not clear at this stage, we were eager to known the reaction performance of **2b** with other cyclopropene precursors **1**. To our delight, as for substrates **1b**-**1f** (Table 2, entries 9-13), all the reactions furnished higher yields than those reactions with **2a** (Table 2, entries 1-5). The ester group R was found to have no obvious influence on the reaction outcomes, as for substrate **1h**, the corresponding products **3ha** and **3hb** were obtained in 74% and 75% yields with moderate diastereoselectivities, respectively (Table 2, entries 14 and 15).

Table 2. Generality of this reaction.

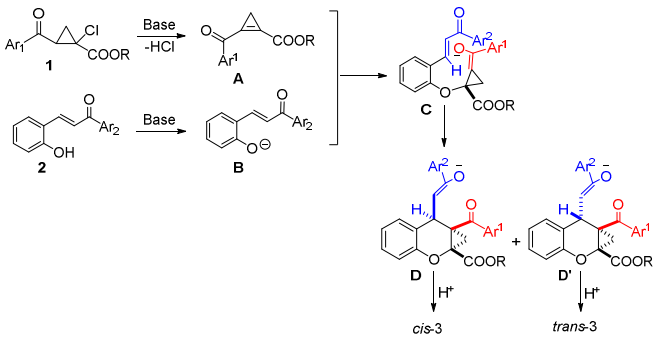



1 2 3

| entry | $Ar^1$/R | $Ar^2$ | yield (%)[b] (*cis*:*trans*)[c] |
|---|---|---|---|
| 1 | 4-$MeC_6H_4$/Et, **1b** | Ph, **2a** | **3ba**, 74 (2.8:1) |
| 2 | 4-$MeOC_6H_4$/Et, **1c** | Ph, **2a** | **3ca**, 80 (2.9:1) |
| 3 | 4-$ClC_6H_4$/Et, **1d** | Ph, **2a** | **3da**, 62 (1.8:1) |
| 4 | 4-$BrC_6H_4$/Et, **1e** | Ph, **2a** | **3ea**, 72 (3.3:1) |
| 5 | 2-Thio$C_6H_4$/Et, **1f** | Ph, **2a** | **3fa**, 50 (3.3:1) |
| 6 | 4-$PhC_6H_4$/Et, **1g** | Ph, **2a** | **3ga**, 74 (3.2:1) |
| 7 | Ph/Et, **1a** | 4-$MeC_6H_4$, **2b** | **3ab**, 91 (3.2:1) |
| 8 | Ph/Et, **1a** | 1-Naphthyl, **2c** | **3ac**, 50 (3.0:1) |
| 9 | 4-$MeC_6H_4$, **1b** | 4-$MeC_6H_4$, **2b** | **3bb**, 79 (3:1) |
| 10 | 4-$MeOC_6H_4$, **1c** | 4-$MeC_6H_4$, **2b** | **3cb**, 84 (2.9:1) |
| 11 | 4-$ClC_6H_4$, **1d** | 4-$MeC_6H_4$, **2b** | **3db**, 91 (3.1:1) |
| 12 | 4-$BrC_6H_4$, **1e** | 4-$MeC_6H_4$, **2b** | **3eb**, 83 (3.3:1) |
| 13 | 2-Thio$C_6H_4$,**1f** | 4-$MeC_6H_4$, **2b** | **3fb**, 72 (2.1:1) |
| 14 | Ph/Me, **1h** | Ph, **2a** | **3ha**, 74 (2.5:1) |
| 15 | Ph/Me, **1h** | 4-$MeC_6H_4$, **2b** | **3hb**, 75 (2.0:1) |

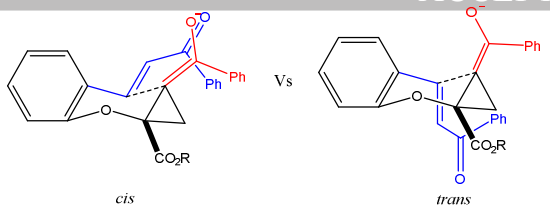
[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.2 mmol), DMF (2.0 mL), 6 h.
[b] Isolated yields of the diastereomers.
[c] Determined by $^1$H NMR of crude **3**.

Based on the above results and our previous work, [11a, 11b] a plausible mechanism was proposed in Scheme 2. Initially, in the presence of $Cs_2CO_3$, **1** was converted to the cyclopropene intermediate **A**, meanwhile, **2** was deprotonated to form anion **B**. Next, an *oxa*-Michael addition takes place to generate intermediate **C**. Following by another Michael addition in enolate **C**, the corresponding diastereoisomers are formed after protonation with *cis*-**3** as the major product. Strong base KOH or relatively weak organic bases such as DBU and $Et_3N$ are not effective in our reaction, probably due to that in the presence of such bases the speeds for formation of intermediate **A** and **B** do not match and **A** may decompose during the reaction process.




**Scheme 2.** A plausible reaction mechanism.

Interestingly, the stereoselectivity in this reaction is different from our previous report,[11b] in which the *trans*-isomers were obtained as the major products. Though the reason for such different stereoselectivities still need further evaluation, we propose a possible rationale herein (Scheme 3). As carefully looking into the 6-membered-ring transition state in intermediate **C**, the steric hindrance in *cis*-transition state is smaller than that in *trans*-transition state because the bulky unsaturated ketone moiety stretched out, thus leading to the fast formation of *cis*-3 products. Even though *trans*-3 are more stable than *cis*-3 due to the less steric hindrance, however, kinetic control plays a more important role to determine the stereochemistry of the reaction.




Scheme 3. 6-membered ring transition states (intermediate **C**).

## 3. Conclusion

In conclusion, we have developed a tandem oxa-Michael addition and Michael addition reaction of 2-hydroxychalcones with ethyl 2-benzoylcycloprop-1-enecarboxylate intermediate, affording a facile excess to diversified polyfunctionalized chromenes, which may have biologically activities as well as potential applications in organic synthesis. Moreover, the products contains several different functional groups, which may have potential applications for useful chemical modification. Considering that the study of the electron sufficient cyclopropenes, this work make a good contribution to cyclopropene chemistry. Further investigation to study more intensively of the mechanism and application of this method in natural products or drug candidates are currently undergoing in our laboratory.

## 4. Experimental section

### *4.1 General remarks*

Dichloromethane was freshly distilled from calcium hydride; THF, $Et_2O$ and toluene were distilled from sodium (Na) under argon (Ar) atmosphere. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AM-400 spectrophotometers. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm-$^1$. Flash column chromatography was performed using 300-400 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF254) were used. Mass spectra were recorded by EI, and HRMS were measured on a HP-5989 instrument.

### *4.2 General procedure*

Using **3aa** as an example. To a 25 mL flame-dried reaction tube were added cyclopropane **1a** (0.2 mmol, 50 mg), **2a** (0.2 mmol, 44 mg) and $Cs_2CO_3$ (0.4 mmol, 130 mg), followed by addition of DMF (2 mL) via syringe. The reaction mixture was stirred at room temperature (25 $^o$C) for 6 h, TLC showed that all starting material **1a** was consumed, the reaction mixture was filtered and diluted with water. Then extracted by EA (3X20 mL), the organic layers were combined and dried over MgSO4, filtered and concentrated in vacuo. The residue was purified by silica gel chromatography to give **3aa** as a white solid (77 mg, yield 88%).

White solid (77 mg, total yield 88%); *cis*-**3aa**: m.p. = 38-40 $^o$C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 3H), 7.26 (t, *J* = 7.7 Hz, 2H), 7.11 (t, *J* = 7.7 Hz, 1H), 7.05 (d, *J* = 7.4 Hz, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 4.33 (t, *J* = 6.4 Hz, 1H), 4.11-4.06 (m, 2H), 3.53 (dd, *J* = 18.0, 6.4 Hz, 1H), 3.17 (dd, *J* = 18.0, 6.4 Hz, 1H), 2.10 (d, *J* = 7.0 Hz, 1H), 1.92 (d, *J* = 7.0 Hz, 1H), 1.12 (t, *J* = 7.1 Hz, 3H).$^{13}$C NMR (101 MHz, $CDCl_3$) *δ* 197.5, 194.8, 168.7, 150.9, 136.7, 135.0, 133.5, 133.0, 129.1, 129.0, 128.8, 128.6, 128.4, 127.9, 126.2, 123.3, 118.4, 64.8, 61.9, 43.3, 43.0, 36.5, 18.9, 13.9. *trans*-**3aa**: m.p. = 45-47 $^o$C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.2 Hz, 2H), 7.81 (d, *J* = 7.2 Hz, 2H), 7.58-7.49 (m, 1H), 7.44 (d, *J* = 7.6, 7.6 Hz, 2H), 7.36 (d, *J* = 7.6, 7.6 Hz, 2H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.00-6.93 (m, 2H), 4.41 (t, *J* = 6.0 Hz, 1H), 3.93-3.79 (m, 2H), 3.48 (dd, *J* = 18.0, 6.4 Hz, 1H), 3.33 (dd, *J* = 18.0, 6.4 Hz, 1H), 2.29 (d, *J* = 6.8 Hz, 1H), 1.69 (d, *J* = 6.8 Hz, 1H), 0.88 (t, *J* = 7.2 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.1, 194.5, 168.3, 151.1, 136.4, 134.5, 133.4, 133.3, 128.74, 128.68, 128.64, 128.5, 128.4, 128.1, 123.3, 123.0, 118.1, 64.9, 61.8, 44.0, 42.5, 31.2, 18.2, 13.6. mix 3aa: $^1$H NMR (400 MHz, $CDCl_3$) δ 7.92-7.84 (dd, *J* = 25.1, 7.8 Hz, 2H), 7.75-7.66 (dd, *J* = 26.3, 7.8 Hz, 2H), 7.52-7.49 (t, *J* = 7.3 Hz, 1H), 7.40-7.37 (t, *J* = 6.7 Hz, 3H), 7.31-7.25 (q, *J* = 7.9 Hz, 2H), 7.21 – 7.03 (m, 2H), 7.20 – 7.06 (m, 2H), 4.36-4.32 (t, *J* = 6.3 Hz, 1H), 4.23 – 3.62 (m, 2H), 3.64 – 3.31 (m, 1H), 3.31 – 3.11 (m, 1H), 2.11 (d, *J* = 11.7 Hz, 1H), 1.93 (d, *J* = 7.0 Hz, 1H). 1.18-1.12 (t, *J* = 7.0 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.5, 197.1, 194.8, 194.5, 168.7, 168.3, 151.1, 150.9, 136.7, 136.4, 135.0, 134.5, 133.5, 133.4, 133.3, 133.0, 129.1, 129.0, 128.8, 128.7, 128.68, 128.64, 128.5, 128.4, 128.1, 127.9, 126.2, 123.3, 123.0, 118.4, 118.2, 64.87, 64.79, 61.9, 61.8, 43.9, 43.3, 43.0, 42.5, 36.5, 31.3, 18.9, 18.2, 13.9, 13.6. IR (KBr): ν 3456, 1742, 1450, 1249 cm$^{-1}$. HRMS (ESI) m/z calcd. for: $C_{28}H_{25}O_5^+$ 441.1697, found 441.1708.

Ethyl-7a-(4-methylbenzoyl)-7-(2-oxo-2-phenylethyl)-7,7a-dihydrocyclopropa[b]chromene-1a(1H)-carboxylate(**3ba**)
White solid (67 mg, total yield 74%), $^1$NMR (400 MHz, $CDCl_3$) δ 7.93-7.87 (m, 2H), 7.75 – 7.70 (m, 2H), 7.56 (t, *J* = 7.2 Hz, 0.3H), 7.48 – 7.42 (m, 1.2H), 7.33 (t, *J* = 7.6 Hz, 1.5H), 7.26-7.21 (m, 2H), 7.19 – 7.12 (m, 2H), 7.04 – 7.93 (m, 2H), 4.42 – 4.38 (m, 1H), 4.22 – 4.17 (m, 1.5H), 3.90 – 3.80 (m, 0.5H), 3.62 – 3.56 (m, 0.7H), 3.50 – 3.44 (m, 0.3H), 3.36 – 3.21 (m, 1H), 2.41 (s, 2.2H), 2.36 (s, 0.8H), 2.26 (d, *J* = 6.4 Hz, 0.3H), 2.16 (d, *J* = 6.4 Hz, 0.7H), 1.99 (d, *J* = 7.2 Hz, 0.7H), 1.68 (d, *J* = 6.4 Hz, 0.3H ), 1.20 (t, *J* = 7.2 Hz, 2.3H), 0.90 (t, *J* = 7.2 Hz, 0.7H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.6, 197.1, 194.3, 194.2, 168.8, 168.3, 151.0, 150.9, 144.5, 144.2, 136.7, 136.4, 133.3, 133.0, 132.4, 131.9, 129.4, 129.2, 129.0, 128.9, 128.8, 128.6, 128.4, 128.1, 128.0, 126.3, 123.4, 123.2, 122.9, 118.4, 118.1, 64.8, 64.7, 61.8, 61.7, 43.9, 43.3, 43.0, 42.6, 36.5, 31.3, 21.7, 21.6, 18.9, 18.0, 13.9, 13.5. IR (KBr): ν 3456, 1741, 1404, 1248 cm$^{-1}$. HRMS (ESI) m/z calcd.for: $C_{29}H_{27}O_5^+$ 455.1853, found 455.1832.

Ethyl-7a-(4-methoxybenzoyl)-7-(2-oxo-2-phenylethyl)-7,7a-dihydrocyclopropa[b]chromene-1a(1H)-carboxylate (**3ca**)
White solid (75 mg, yield 80%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.91 (m, 2H), 7.93 – 7.73 (m, 2H), 7.56 – 7.32 (m, 3H), 7.27 – 7.12 (m, 2H), 7.04 – 6.83 (m, 4H), 4.43 – 4.35 (m, 1H), 4.24 – 4.15 (m, 1.5H), 3.91 – 3.78 (m, 3.5H), 3.58 (dd, *J* = 17.6, 5.6 Hz, 0.74H), 3.48 (dd, *J* = 17.6, 5.6 Hz, 0.26H), 3.35 (dd, *J* = 17.6, 5.6 Hz, 0.26H), 3.25 (dd, *J* = 17.6, 5.6 Hz, 0.74H), 2.24 (d, *J* = 6.4 Hz, 0.24H), 2.16 (d, *J* = 6.4 Hz, 0.76H), 2.00 (d, *J* = 6.4 Hz, 0.76H), 1.69 (d, J = 6.4 Hz, 0.24 H), 1.20 (t, *J* = 7.2 Hz, 2.22H), 0.90 (d, *J* = 7.2 Hz, 0.78H), 1.92 (d, *J* = 6.8 Hz, 1H), 1.11 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.6, 197.2, 193.1, 168.8, 168.3, 163.8, 163.6, 150.9, 136.7, 136.4, 133.3, 133.0, 131.4, 131.0, 129.0, 128.7, 128.6, 128.4, 128.3, 128.0, 127.9, 127.3, 126.3, 123.2, 122.9, 118.4, 118.1, 113.9, 113.8, 64.7, 61.8,61.7, 55.4, 55.3, 43.9, 43.2, 42.9, 42.4, 36.5, 31.4, 18.9, 17.8, 13.9, 13.6. IR (KBr): ν 3456, 1740, 1399, 1253 cm$^{-1}$. HRMS (ESI) m/z calcd.for: $C_{29}H_{27}O_6^+$ 471.1802, found 471.1818.

Ethyl-7a-(4-chlorobenzoyl)-7-(2-oxo-2-phenylethyl)-7,7a-dihydrocyclopropa[b]chromene-1a(1H)-carboxylate(**3da**)
White solid (59 mg, yield 62%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.90 (m, 2H), 7.76 – 7.71 (m, 2H), 7.68 – 7.34 (m, 5H), 7.27 – 7.11 (m, 2H), 7.05 – 6.95 (m, 2H), 4.41 – 4.32 (m, 1H), 4.24 – 4.15 (m, 1.3H), 3.92 – 3.84 (m, 0.7H), 3.67 (dd, *J* = 18.0, 6.4 Hz, 0.66H), 3.45 (dd, *J* = 18.0, 6.4 Hz, 0.34H), 3.19 (dd, *J* = 18.0, 6.4 Hz, 0.66H), 2.30 (d, *J* = 6.8 Hz, 0.34H), 2.18 (d, *J* = 6.8 Hz, 0.66H), 1.96 (d, *J* = 6.8 Hz, 0.66H), 1.67 (d, *J* = 6.8 Hz, 0.34H), 1.21 (t, *J* = 7.2 Hz, 2H), 0.94 (t, *J* = 7.2 Hz, 1H).$^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.5, 197.0, 193.8, 193.4, 168.7, 168.2, 151.2, 150.9, 140.0, 139.66, 136.59, 136.3, 133.5, 133.1, 133.0, 130.4, 130.1, 128.99, 128.90, 128.8, 128. 7, 128.6, 128.44, 128.37, 128.1, 127.9, 126.1, 123.5, 123.4, 123.1, 118.45, 118.2, 64.9, 64.8, 61.96, 61.89, 43.9, 43.2, 43.1, 42.4, 36.3, 31.2, 19.1, 18.5, 13.9, 13.6. IR (KBr): ν 3458, 1741, 1366, 1248 cm$^{-1}$. HRMS (ESI) m/z calcd.for: $C_{28}H_{27}ClO_5^+$ 475.1307, found 475.1298.

Ethyl-7a-(4-bromobenzoyl)-7-(2-oxo-2-phenylethyl)-7,7a-dihydrocyclopropa[b]chromene-1a(1H)-carboxylate (**3ea**)
White solid (74 mg, yield 72%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.81 (m, 2.2H), 7.76 – 7.73 (m, 1.5H), 7.66 – 7.56 (m, 2H), 7.51 – 7.42 (m, 1.8H), 7.36 (dd, *J* = 7.6, 7.6 Hz, 1.5 H), 7.25 – 7.11 (m, 2H), 7.05 – 6.96 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.5, 196.9, 194.0, 193.6, 168.6, 168.2, 151.2, 150.9, 136.5, 136.2, 133.8, 133.5, 133.4, 133.1, 132.2, 131.9, 130.4, 130.2, 128.9, 128.8, 128.7, 128.7, 128.6, 128.43, 128.36, 128.1, 127.9, 126.1, 123.5, 123.1, 118.4, 118.2, 64.9, 64.8, 61.9, 61.9, 43.9, 43.3, 43.0, 42.4, 36.3, 31.2, 19.1, 18.5, 13.9, 13.7. IR (KBr): ν 3464, 1744, 1453, 1275 cm$^{-1}$. HRMS (ESI) m/z calcd.for: $C_{28}H_{27}BrO_5^+$ 519.0802, found 519.0808.

Ethyl-7-(2-oxo-2-phenylethyl)-7a-(thiophene-2-carbonyl)-7,7a-dihydrocyclopropa[b]chromene-1a(1H)-carboxylate(**3fa**)
White solid (44 mg, yield 50%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.91 (m, 0.4H), 7.79 – 7.77 (m, 1.6H), 7.66 (d, *J* = 5.2 Hz, 1H), 7.60 – 7.42 (m, 2H), 7.36 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.25 – 7.05 (m, 4H), 6.99 – 6.94 (m, 1H), 4.48 (t, *J* = 6.4 Hz, 0.22H), 4.32 (t, *J* = 6.4 Hz, 0.78H), 4.21 – 4.14 (m, 1.55H), 3.94 – 3.80 (m, 0.45H), 3.61 (dd, *J* = 18.0, 5.2 Hz, 0.78H), 3.48 (dd, *J* = 18.0, 5.2 Hz, 0.22H), 3.36 – 3.25 (m, 1H), 2.29 (d, *J* = 6.8 Hz, 0.22H), 2.16 (s, 1.56H), 1.72 (d, *J* = 6.8 Hz, 0.22H), 1.87 (t, *J* = 7.2 Hz, 2.34H), 0.93 (t, *J* = 7.2 Hz, 0.66H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.5, 197.0, 187.5, 168.6, 168.3, 151.6, 151.3, 142.2, 142.1, 136. 7, 136.4, 134.7, 134.2, 133.4, 133.1, 132.4, 128.8, 128.7, 128.6, 128.4, 128.2, 128.1, 128.0, 126.5, 124.2, 123.3, 123.1, 118.5, 118.2, 64.9, 64.8, 61.9, 61.8, 44.1, 43.8, 43.6, 42.5, 36.5, 31.9, 19.5, 18.8, 13.9, 13.5. IR (KBr): ν 3465, 1741, 1412, 1252cm$^{-1}$. HRMS (ESI) m/z calcd.for: $C_{26}H_{23}O_5S^+$ 447.1261, found 447.1273.

Ethyl-7a-([1,1'-biphenyl]-4-carbonyl)-7-(2-oxo-2-phenylethyl)-7,7a-dihydrocyclopropa[b]chromene-1a(1H)-carboxylate (**3ga**)
White solid (76 mg, yield 74%); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 1.5H), 7.94 – 7.87 (m, 1H), 7.77 – 7.54 (m, 6H), 7.49 – 7.32 (m, 6H), 7.27 – 7.14 (m, 1.5H), 7.06 – 7.01 (m, 1H), 6.97 (dd, *J* = 7.2, 7.2 Hz, 1H), 4.45 (t, *J* = 6.4 Hz, 1H), 4.29 – 4.17 (m, 1.5H), 3.94 – 3.82 (m, 0.5H), 3.66 (dd, *J* = 18.0, 6.4 Hz, 0.77H), 3.50 (dd, *J* = 18.0, 6.4 Hz, 0.23H), 3.33 (dd, *J* = 18.0, 6.4 Hz, 0.23H), 3.27 (dd, *J* = 18.0, 6.4 Hz, 0.77H), 2.31 (d, *J* = 6.4 Hz, 0.23H), 2.21 (d, *J* = 6.4 Hz, 0.77H), 2.04 (d, *J* = 6.4 Hz, 0.77H), 1.71 (d, *J* = 6.4 Hz, 0.23), 1.22 (t, *J* = 7.2 Hz, 2.3H), 0.92 (t, *J* = 7.2 Hz, 0.7H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.6, 197.1, 194.4, 194.1, 168.8, 168.3, 151.1, 150.9, 146.1, 145.8, 139.8, 139.68, 136.65, 136.4, 133.7, 133.4, 133.2, 133.0, 129.6, 129.3, 129.0, 128.91, 128.87, 128.83, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.28, 127.25, 127.18, 126.3, 123.33, 123.0, 118.4, 118.1, 64.9, 64.8, 61.9, 61.8, 44.0, 43.3, 43.1, 42.6, 36.5, 31.3, 19.0, 18.3, 14.0, 13.6. IR (KBr): ν 3451, 1700, 1399, 1211 cm$^{-1}$. HRMS (ESI) m/z calcd.for: $C_{34}H_{29}O_5^+$ 517.2010, found 517.2015.

Ethyl-7a-benzoyl-7-(2-oxo-2-(p-tolyl)ethyl)-7,7a-dihydrocyclopropa[b]chromene-1a(1H)-carboxylate (**3ab**)
White solid (83 mg, yield 91%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.97 (m, 1.5H), 7.83 – 7.80 (m, 1H), 7.64 (d, *J* = 8.4 Hz, 1.5H), 7.59 – 7.55 (m, 1H), 7.51 – 7.43 (m, 1.5H), 7.36 (d, *J* = 8.0 Hz, 0.5H), 7.24 – 7.12 (m, 4H), 7.05 – 6.93 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.1, 196.7, 194.8, 194.5, 168.8, 168.3, 151.0, 150.9, 144.2, 143.8, 134.9, 134.4, 134.2, 133.9, 133.5, 133.2, 129.3, 129.0, 128.9, 128.74, 128.70, 128.63, 128.59, 128.42, 128.39, 128.2, 128.1, 126.3, 123.4, 123.3, 122.9, 118.4, 118.1, 64.8, 64.7, 61.8, 61.7, 43.8, 43.3, 42.8, 42.5, 36.5, 31.2, 21.6, 21.5, 18.9, 18.1, 13.9, 13.5. IR (KBr): ν 3468, 1745, 1407, 1248 cm$^{-1}$. HRMS (ESI) m/z calcd. for: $C_{29}H_{27}O_5^+$ 455.1853, found 455.1859.

Ethyl-7a-benzoyl-7-(2-(naphthalen-1-yl)-2-oxoethyl)-7,7a-dihydrocyclopropa[b]chromene-1a(1H)-carboxylate (**3ac**)
White solid (49 mg, yield 50%); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.4 Hz, 0.25H), 8.24 – 8.21 (m, 0.75H), 8.05 – 8.02 (m, 1.5H), 7.98 – 7.78 (m, 3H), 7.62 – 7.57 (m, 2H), 7.55 – 7.44 (m, 4.5H), 7.26 – 7.26 (m, 2H), 7.12 – 7.04 (m, 1H), 7.00 – 6.95 (m, 1H), 4.54 – 46 (m, 1H), 4.26 – 4.13 (m, 1.5H), 3.91 – 3.78 (m, 0.5H), 3.70 (dd, *J* = 17.6, 6.4 Hz, 0.75H), 3.54 (dd, *J* = 17.6, 6.4 Hz, 0.25H), 3.40 (dd, *J* = 17.6, 6.4 Hz, 0.25H), 3.33 (dd, *J* = 17.6, 6.4 Hz, 0.75H), 2.32 (d, *J* = 7.2 Hz, 0.25H), 2.23 (d, *J* = 7.2 Hz, 0.75H), 2.02 (d, *J* = 7.2 Hz, 0.75H), 1.69 (d, *J* = 7.2 Hz, 0.25H), 1.20 (t, *J* = 7.2 Hz, 2.25H), 0.88 (t, *J* = 7.2 Hz, 0.75H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 201.4, 200.9, 194.9, 194.5, 168.7, 168.3, 151.2, 150.8, 135.5, 135.2, 134.9, 134.5, 133.9, 133.7, 133.6, 133.3, 133.0, 132.6, 130.0, 129.8, 129.2, 129.0, 128.9, 128.7, 128.69, 128.67, 128.5, 128.4, 128.2, 128.1, 127.65, 127.61, 126.5, 126.2, 126.0, 125.7, 125.5, 124.24, 124.22, 123.4, 123.2, 123.0, 118.5, 118.2, 64.8, 64.7, 61.9, 61.8, 47.3, 46.7, 43.2, 42.5, 36.8, 31.7, 18.8, 18.3, 13.9, 13.5. IR (KBr): ν 3434, 1699, 1410, 1240 cm$^{-1}$. HRMS (ESI) m/z calcd.for: $C_{32}H_{27}O_5^+$ 491.1853, found 491.1858.

Ethyl-7a-(4-methylbenzoyl)-7-(2-oxo-2-(p-tolyl)ethyl)-7,7a-dihydrocyclopropa[b]chromene-1a(1H)-carboxylate(**3bb**)
White solid (74 mg, yield 79%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 1.45H), 7.82 (d, *J* = 8.0 Hz, 0.5H), 7.71 (d, *J* = 8.0 Hz, 0.5H), 7.64 (d, *J* = 8.0 Hz, 1.5H), 7.26 – 7.12 (m, 6H), 7.04 – 7.93 (m, 2H), 4.42 – 4.37 (m, 1H), 4.24 – 4.15 (m, 1.5H), 3.91 – 3.77 (m, 0.5H), 3.58 – 3.40 (m, 1H), 3.33 – 3.19 (m, 1H), 2.41 – 2.33 (m, 6H), 2.25 (d, *J* = 6.0 Hz, 0.3H), 2.16 (d, *J* = 6.0 Hz, 0.7H), 1.99 (m, 0.7H), 1.68 (m, 0.3H), 1.19 (t, *J* = 7.2 Hz, 2.4H), 0.89 (t, *J* = 7.2 Hz, 0.6H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.1, 196.7, 194.3, 194.2, 168.8, 168.3, 151.0, 150.9, 144.4, 144.2, 144.1, 143.8, 134.2, 133. 9, 132.4, 131.9, 129.4, 129.3, 129.2, 129.1, 129.02, 128.98, 128.8, 128.7, 128.4, 128.2, 128.1, 126. 5, 123. 5, 123.2, 122.9, 118.4, 118.0, 64.7, 64.7, 61.76, 61.69, 43.7, 43.3, 42.8, 42.9, 36.5, 31.3, 21.7, 21.59, 21.57, 21.50, 18.9, 17.9, 13.9, 13.5. IR (KBr): ν 3470, 1744, 1407, 1251 cm$^{-1}$. HRMS (ESI) m/z calcd.for: $C_{30}H_{29}O_5^+$ 469.2010, found 469.2027.

Ethyl-7a-(4-methoxybenzoyl)-7-(2-oxo-2-(p-tolyl)ethyl)-7,7a-dihydrocyclopropa[b]chromene-1a(1H)-carboxylate (**3cb**)

White solid (81 mg, yield 84%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.8 Hz, 1.5H), 7.84 – 7.79 (m, 1H), 7.64 (d, *J* = 8.8 Hz, 1.5H), 7.24 – 7.12 (m, 4H), 7.04 – 6.83 (m, 4H), 4.43 – 4.35 (m, 1H), 4.24 – 4.15 (m, 1.5H), 3.91 – 3.76 (m, 3.5H), 3.54 (dd, *J* = 18.0, 5.2 Hz, 0.75H), 3.44 (dd, *J* = 18.0, 5.2 Hz, 0.25H), 3.32 (dd, *J* = 18.0, 5.2 Hz, 0.25H), 3.23 (dd, *J* = 18.0, 5.2 Hz, 0.75H), 2.39 – 2.32 (m, 3H), 2.24 (d, *J* = 6.8 Hz, 0.23), 2.16 (d, *J* = 6.8 Hz, 0.77H), 2.00 (d, *J* = 6.8 Hz, 0.77H), 1.69 (d, *J* = 6.8 Hz, 0.23H), 1.19 (d, *J* = 6.8 Hz, 2.3H), 0.90 (t, *J* = 6.8 Hz, 0.7H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.2, 196.8, 193.1, 168.9, 168.4, 163.8, 163.6, 150.9, 144.2, 143.8, 134.2, 133.9, 131.4, 131.3, 131.0, 129.7, 129.3, 129.1, 129.0, 128.95, 128.67, 128.62, 128.4, 128.3, 128.2, 128.0, 127.9, 127.3, 126.4, 123.3, 123.2, 122.9, 118.3, 118.0, 113.9, 113.8, 64.7, 61.7, 61.7, 55.4, 55.4, 43.7, 43.3, 42.7, 42.4, 36.5, 31.4, 21.6, 21.5, 19.0, 17.8, 13.9, 13.5. IR (KBr): ν 3468, 1745, 1408, 1260 cm$^{-1}$. HRMS (ESI) m/z calcd.for: $C_{30}H_{29}O_6^+$ 485.1959, found 485.1968.

Ethyl-7a-(4-chlorobenzoyl)-7-(2-oxo-2-(p-tolyl)ethyl)-7,7a-dihydrocyclopropa[b]chromene-1a(1H)-carboxylate (**3db**)
White solid (89 mg, yield 91%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.8 Hz, 1.5H), 7.81 (d, *J* = 8.8 Hz, 0.5H), 7.73 (d, *J* = 8.0 Hz, 0.5H), 7.65 (d, *J* = 8.0 Hz, 1.5H), 7.41 (d, *J* = 8.0 Hz, 1.5H), 7.33 (d, *J* = 8.0 Hz, 0.5H), 7.26 – 7.11 (m, 4H), 7.05 – 6.95 (m, 2H), 4.41 – 4.32 (m, 1H), 4.24 – 4.14 (m, 1.5H), 3.94 – 3.83 (m, 0.5H), 3.64 (dd, *J* = 18.0, 6.8 Hz, 0.75H), 3.42 (dd, *J* = 18.0, 6.8 Hz, 0.25H), 3.27 (dd, *J* = 18.0, 6.8 Hz, 0.25H), 3.17 (dd, *J* = 18.0, 6.8 Hz, 0.75H), 2.39 (s, 0.7H), 2.34 (s, 2.3H), 2.29 (d, *J* = 6.8 Hz, 0.25H), 2.19 (d, *J* = 6.8 Hz, 0.75H), 1.96 (d, *J* = 6.8 Hz, 0.75H), 1.67 (d, *J* = 6.8 Hz, 0.25H), 1.20 (t, *J* = 7.2 Hz, 2.3H), 0.93 (t, *J* = 7.2 Hz, 0.7H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.0, 196.5, 193.7, 193.4, 168.6, 168.2, 151.2, 150.9, 144.3, 143.9, 139.9, 139.6, 134.0, 133.8, 133.4, 133.0, 130.3, 130.1, 129.3, 129.1, 128.9, 128.8, 128.8, 128.5, 128.4, 128.2, 128.0, 126.2, 123.4, 123.1, 118.4, 118.1, 64.9, 64.8, 61.9, 61.8, 43.7, 43.03, 42.99, 42.4, 36.3, 31.2, 21.6, 21.5, 19.1, 18.4, 13.9, 13.6. IR (KBr): ν 3468, 1745, 1408, 1260 cm$^{-1}$. HRMS (ESI) m/z calcd.for: $C_{29}H_{26}ClO_5^+$ 489.1463, found 489.1478.

Ethyl-7a-(4-bromobenzoyl)-7-(2-oxo-2-(p-tolyl)ethyl)-7,7a-dihydrocyclopropa[b]chromene-1a(1H)-carboxylate (**3eb**)
White solid (88 mg, yield 83%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.80 (m, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.59 – 7.48 (m, 2H), 7.26 – 7.10 (m, 4H), 7.05 – 6.95 (m, 2H), 4.41 – 4.32 (m, 1H), 4.23 – 4.14 (m, 1.5H), 3.94 – 3.82 (m, 0.5H), 3.64 (dd, *J* = 18.0, 6.8 Hz, 0.76H), 3.41 (dd, *J* = 18.0, 6.8 Hz, 0.24H), 3.27 (dd, *J* = 18.0, 6.8 Hz, 0.24H), 3.16 (dd, *J* = 18.0, 6.8 Hz, 0.76H), 2.39 – 2.34 (m, 3H), 2.29 (d, *J* = 6.8 Hz, 0.24H), 2.18 (d, *J* = 6.8 Hz, 0.76H), 1.96 (d, *J* = 6.8 Hz, 0.76H), 1.67 (d, *J* = 6.8 Hz, 0.24), 1.20 (t, *J* = 7.2 Hz, 2.2H), 0.94 (t, *J* = 7.2 Hz, 0.7H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.0, 196.5, 193.9, 193.5, 168.6, 168.1, 151.2, 150.8, 144.3, 143.9, 134.0, 133.8, 133.7, 133.4, 131.9, 130.6, 130.4, 130.1, 129.3, 129.2, 129.1, 128.9, 128.9, 128.73, 128.65, 128.5, 128.33, 128.31, 128.14, 127.99, 126.1, 123.4, 123.1, 118.3, 118.1, 64.9, 64.8, 61.9, 61.8, 43.7, 43.0, 42.4, 36.3, 31.2, 21.6, 21.5, 19.1, 18.4, 13.9, 13.6. IR (KBr): ν 3463, 1746, 1399, 1245 cm$^{-1}$. HRMS (ESI) m/z calcd.for: $C_{29}H_{26}BrO_5^+$ 533.0958, found 533.0964.

Ethyl-7-(2-oxo-2-(p-tolyl)ethyl)-7a-(thiophene-2-carbonyl)-7,7a-dihydrocyclopropa[b]chromene-1a(1H)-carboxylate (**3fb**)
White solid (66 mg, yield 72%); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 0.5H), 7.69 – 7.58 (m, 3H), 7.34 (d, *J* = 4.4 Hz, 0.25H), 7.26 – 7.16 (m, 6H), 4.96 – 4.30 (m, 1H), 4.20 – 4.14 (m, 1.4H), 3.93 – 3.80 (m, 0.6H), 3.59 – 3.41 (m, 1H), 3.33 – 3.22 (m, 1H), 2.40 (s, 1H), 2.35 (s, 2 H), 2.29 (d, *J* = 6.8Hz, 0.38H), 2.16 (s, 1.24H), 1.72 (d, *J* = 6.8 Hz, 0.38H), 1.18 (t, *J* = 7.2 Hz, 2H), 0.92 (t, *J* = 7.2 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.0, 196.6, 187.5, 168.6, 168.3, 151.5, 151.3, 144.3, 143.9, 142.2, 142.0, 134.6, 134.2, 134.1, 133.9, 133.4, 132.4, 129.3, 129.1, 128.7, 128.5, 128. 5, 128.21, 128.18, 128.1, 126.6, 124.3, 123.3, 123.1, 118.4, 118.2, 64.9, 64.8, 61.9, 61.8, 44.1, 43.6, 42.2, 36.5, 31.9, 21.6, 21.5, 19.5, 18.8, 13.9, 13.5. IR (KBr): ν 3454, 1739, 1408, 1180 cm$^{-1}$. HRMS (ESI) m/z calcd.for: $C_{27}H_{25}O_5S^+$ 461.1417, found 461.1431.

Methyl-7a-benzoyl-7-(2-oxo-2-phenylethyl)-7,7a-dihydrocyclopropa[b]chromene-1a(1H)-carboxylate(**3ha**)
White solid (63 mg, yield 74%); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.91 (m, 2H), 7.81 – 7.73 (m, 2H), 7.61 – 7.32 (m, 6H), 7.24 – 7.15 (m, 2H), 7.03 – 6.94 (m, 2H), 4.46 – 4.39 (m, 1H), 3.77 (s, 2.2H), 3.64 – 3.45 (m, 1H), 3.39 (m, 0.7H), 3.36 – 3.23 (m, 1H), 2.31 – 3.20 (m, 1H), 1.99 (d, *J* = 7.2 Hz, 0.8H), 1.71 (d, *J* = 7.2 Hz, 0.2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.5, 197.1, 194.97, 194.63, 169.2, 168.8, 150.9, 150.5, 136.5, 136.2, 134.8, 134.3, 133.6, 133.4, 133.3, 133.0, 129.2, 129.0, 128.9, 128.7, 128.7, 128.6, 128.6, 128.6, 128.5, 128.4, 128.4, 128.2, 127.9, 125.9, 123.4, 123.2, 123.0, 118.3, 118.0, 65.0, 64.8, 52.7, 52.4, 43.9, 43.3, 43.2, 42.5, 36.4, 31.1, 18.6, 18.3. IR (KBr): ν 3478, 1734, 1399, 1232 cm$^{-1}$. HRMS (ESI) m/z calcd.for: $C_{27}H_{23}O_5^+$ 427.1540, found 427.1560.

Methyl-7a-benzoyl-7-(2-oxo-2-(p-tolyl)ethyl)-7,7a-dihydrocyclopropa[b]chromene-1a(1H)-carboxylate(**3hb**)
White solid (66 mg, yield 75%); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 6.8 Hz, 1.5H), 7.82 (t, *J* = 8.0 Hz, 1H), 7.65 – 7.35 (m, 4.5H), 7.26 – 7.12 (m, 4H), 7.03 – 6.94 (m, 2H), 4.46 – 4.39 (m, 1H), 3.77 (s, 2.2H), 3.59 – 3.41 (m, 1H), 3.39 (s, 0.8H), 3.33 – 3.21 (m, 1H), 2.39 (s, 0.8H), 2.33 (s, 2.2H), 2.29 (d, *J* = 6.8 Hz, 0.25H), 2.20 (d, *J* = 6.8 Hz, 0.75H), 1.99 (d, *J* = 6.8 Hz, 0.75H), 1.71 (d, *J* = 6.8 Hz, 0.25H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.1, 196.7, 194.9, 194.6, 169.3, 168.8, 150.9, 150.5, 144.3, 143.8, 134.8, 134.3, 134.1, 133.8, 133.5, 133.2, 129.3, 129.2, 129.04, 129.02, 128.8, 128.7, 128.62, 128.56, 128.44, 128.39, 128.2, 128.0, 126.0, 123.3, 123.0, 118.3, 117.9, 65.0, 64.8, 52.7, 52.4, 43.7, 43.3, 42.9, 42.5, 36.4, 31.2, 21.6, 21.5, 18.7, 18.2. IR (KBr): ν 3390, 1699, 1397, 1222 cm$^{-1}$. HRMS (ESI) m/z calcd.for: $C_{28}H_{25}O_5^+$ 441.1702, found 441.1688.

**Acknowledgments**

We are grateful for the financial support from the National Natural Science Foundation of China (21472053, 21172082).

**Appendix A. Supplementary data**

Supplementary data related to this article can be found at https://doi.org/10.1016/j.tet.2017.xx.xxx.

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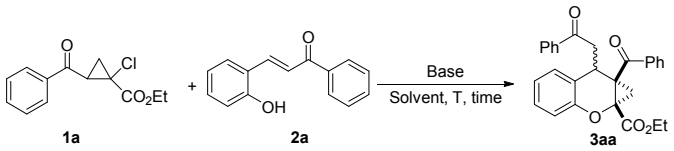
**Table 1.** Optimization of the reaction conditions

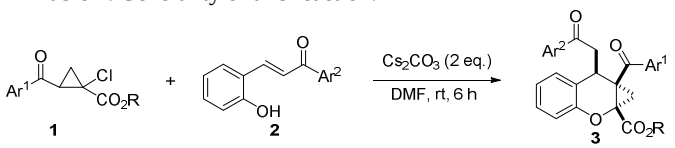



1a 2a 3aa

| entry[a] | base | solvent | T (°C) | t (h) | Yield (%)[b] (*cis*: *trans*)[c] |
|---|---|---|---|---|---|
| 1 | $Cs_2CO_3$ | DMSO | 25 | 6 | 56 (3.4:1) |
| 2 | $Cs_2CO_3$ | DMF | 25 | 6 | 88 (3.5:1) |
| 3 | $Cs_2CO_3$ | $CH_3CN$ | 60 | 12 | 83 (4:1) |
| 4 | $Cs_2CO_3$ | 1,4-dioxane | 60 | 12 | 68 (1:2.3) |
| 5 | $Cs_2CO_3$ | THF | 25 | 12 | 77 (2.5:1) |
| 6 | $Cs_2CO_3$ | $CH_2Cl_2$ | 25 | 12 | 73 (1.1:1) |
| 7 | $Cs_2CO_3$ | Toluene | 60 | 12 | 61 (1:2.5) |
| 8 | $Cs_2CO_3$ | 1,2-DCE | 25 | 12 | 57 (1:1) |
| 9 | $K_2CO_3$ | DMF | 25 | 24 | 49 (3.7:1) |
| 10 | $K_3PO_4$ | DMF | 25 | 24 | 78 (3.7:1) |
| 11 | KOH | DMF | 25 | 12 | 30 (2.9:1) |
| 12 | LiOH | DMF | 25 | 12 | 51 (2.8:1) |
| 13 | $Mg(OEt)_2$ | DMF | 80 | 24 | 48 (2:1) |
| 14 | $Et_3N$ | DMF | 25 | 24 | ND |
| 15 | DBU | DMF | 25 | 24 | < 5 |
| 16 | $Cs_2CO_3$[d] | DMF | 25 | 24 | 81 (3:1) |
| 17 | $Cs_2CO_3$[e] | DMF | 25 | 6 | 85 (3:1) |
| 18 | $Cs_2CO_3$[f] | DMF | 25 | 6 | 56 (2.9:1) |

[a] Reaction conditions: 0.2 mmol (1.0 eq.) of **1a**, 0.2 mmol (1.0 eq.) of **2a**, and 0.4 mmol (2.0 eq.) of base in 2.0 mL of solvent at the specified temperature for the given time.
[b] Isolated total yields of the diastereomers.
[c] Determined by $^1$H NMR of crude **3aa**.
[d] 0.2 mmol of base (1.0 eq.).
[e] 0.3 mmol of base (1.5 eq.).
[f] 0.5 mmol of base (2.5 eq.).
DMSO = Dimethyl sulfoxide, DMF = Dimethylformamide, THF = tetrahydrofuran, 1,2-DCE = 1,2-dichlorethane.

Table 2. Generality of this reaction.




| entry[a] | $Ar^1$/R | $Ar^2$ | Yield (%)[b] (*cis*: *trans*)[c] |
|---|---|---|---|
| 1 | 4-Me$C_6H_4$/Et, **1b** | Ph, **2a** | **3ba**, 74 (2.8:1) |
| 2 | 4-MeO$C_6H_4$/Et, **1c** | Ph, **2a** | **3ca**, 80 (2.9:1) |
| 3 | 4-Cl$C_6H_4$/Et, **1d** | Ph, **2a** | **3da**, 62 (1.8:1) |
| 4 | 4-Br$C_6H_4$/Et, **1e** | Ph, **2a** | **3ea**, 72 (3.3:1) |
| 5 | 2-Thio$C_6H_4$/Et, **1f** | Ph, **2a** | **3fa**, 50 (3.3:1) |
| 6 | 4-Ph$C_6H_4$/Et, **1g** | Ph, **2a** | **3ga**, 74 (3.2:1) |
| 7 | Ph/Et, **1a** | 4-Me$C_6H_4$, **2b** | **3ab**, 91 (3.2:1) |
| 8 | Ph/Et, **1a** | 1-Naphthyl, **2c** | **3ac**, 50 (3.0:1) |
| 9 | 4-Me$C_6H_4$/Et, **1b** | 4-Me$C_6H_4$, **2b** | **3bb**, 79 (3:1) |
| 10 | 4-MeO$C_6H_4$/Et, **1c** | 4-Me$C_6H_4$, **2b** | **3cb**, 84 (2.9:1) |
| 11 | 4-Cl$C_6H_4$/Et, **1d** | 4-Me$C_6H_4$, **2b** | **3db**, 91 (3.1:1) |
| 12 | 4-Br$C_6H_4$/Et, **1e** | 4-Me$C_6H_4$, **2b** | **3eb**, 83 (3.3:1) |
| 13 | 2-Thio$C_6H_4$/Et, **1f** | 4-Me$C_6H_4$, **2b** | **3fb**, 72 (2.1:1) |
| 14 | Ph/Me, **1h** | Ph, **2a** | **3ha**, 74 (2.5:1) |
| 15 | Ph/Me, **1h** | 4-Me$C_6H_4$, **2b** | **3hb**, 75 (2.0:1) |

[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.2 mmol), DMF (2.0 mL), 6 h.
[b] Isolated yields of the diastereomers.
[c] Determined by $^1$H NMR of crude **3**.