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#### Abstract

Novel and efficient one-pot syntheses of a variety of benzo[c]chromen-6-one derivatives were accomplished using $\mathrm{Cs}_{2} \mathrm{CO}_{3}$-promoted reactions between substituted 2-hydroxychalcones and $\beta$-ketoesters. These reactions involved domino Michael addition/intramolecular aldol/oxidative aromatization/lactonization and provided a rapid synthetic route for the production of biologically interesting novel benzo[c]-chromen-6-one molecules bearing several different substituents on benzene rings. As an application of this methodology, several synthesized benzo[c]chromen-6-ones were transformed into highly functionalized novel terphenyls.


# An advanced and novel one-pot synthetic method for diverse benzo[c]chromen-6-ones by transitionmetal free mild base-promoted domino reactions of substituted 2-hydroxychalcones with $\beta$-ketoesters and its application to polysubstituted terphenyls $\dagger$ 

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were isolated from discomycete Lachnumpalmae and exhibited antimicrobial, antinematodal, and acetylcholinesterase inhibitory activities. ${ }^{9 f, g}$ Graphislactones A (5) and B (6) were isolated
compounds, such as progesterone, androgen, and glucocorticoid receptor agonists. ${ }^{6}$ Furthermore, some of the known benzo[ $c]$ chromen-6-one derivatives have promising optical properties as blue-green fluorescing dyes, which is rarer than fluorescence at other wavelengths. ${ }^{7}$ In addition, benzo[c]chromen6 -one derivatives are present in many foods, such as citrus

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## Introduction

Domino reactions have emerged as one of the most effective and powerful tools for the synthesis of a range of complex target molecules in organic and natural product synthesis. ${ }^{1}$ In particular, they are very useful to generate a variety of new compounds which have biological and pharmacological activities. ${ }^{2}$

Molecules bearing benzo[c]chromen-6-one and its derivatives are extensively distributed in nature (Fig. 1). ${ }^{3}$ Some of these molecules exhibit biologically and pharmacologically important antitumor and antibiotic activities, ${ }^{4}$ promote endothelial cell proliferation, and inhibit oestrogen receptor growth activities. ${ }^{5}$ Benzo $[c]$ chromen-6-ones have also been used as intermediates for the synthesis of pharmaceutically valuable

Fig. 1 Selected naturally occurring molecules bearing benzo[c]-chromen-6-one moiety.
fruits, herbs, and vegetables. ${ }^{8}$ For example, autumnariol (1) was isolated from the bulbs of Eucomis autumnalis Gerab. (Liliaceae). ${ }^{9 a}$ Alternariol (2), another benzo[ $\left.c\right]$ chromen-6-one derivative, is an important metabolite of toxin-producing Alternaria fungi, which causes significant crop losses by fouling of tomatoes, apples, and other fruits. ${ }^{9 b}$ Interestingly, alternariol (2) has been also shown to have antiviral, antimicrobial, anticancer, and cytotoxic activities. ${ }^{9 c-e}$ Palmariols A (3) and B (4)

from the lichen Graphisscripta var. pulverrulenta. ${ }^{10 a-f}$ Graphislactone A (5) acts as an antioxidant and free radical scavenger, ${ }^{11}$ and was found to be active against the SW1116 cell line and an active inhibitor of AChE. ${ }^{10 e}$ Verrulactones A (7) and B (8) were isolated from a culture broth of the fungal strain Penicillium verruculosum F375, ${ }^{10 a-f}$ and inhibited Staphylococcus aureus enoyl-ACP reductase with an $\mathrm{IC}_{50}$ of $0.92 \mu \mathrm{M}$ and exhibited antibacterial activity against $S$. aureus and MRSA with MICs of $8 \mu \mathrm{~g} \mathrm{~mL}{ }^{-1} .{ }^{12}$ Gilvocarcins $\mathrm{M}(9)$ and $\mathrm{V}(10)$, ravidomycin (11), and chrysomycins A (12) and B (13), which have a sugar nucleus at the C-4 position, and defucogivocarcines M (14) and V (15), which do not bear the sugar moiety, were isolated from other Streptomyces species found to be strong natural anticancer agents, and to exhibit important and potent antibacterial, antibiotic, and antitumor activities. ${ }^{13}$

Given the importance of these biological and pharmacological activities, several synthetic methods have been devised to produce benzo $[c]$ chromen-6-one derivatives. Of these methods, the most useful one involves a Suzuki-Miyaura cross-coupling reaction followed by metal or Lewis acid-mediated lactonization of ester and methoxy groups (eqn (1), Scheme 1). ${ }^{14}$ Recently, a new reaction involving a microwave-assisted DielsAlder reaction between 4-cyanocoumarin and 1-oxygenated dienes followed by elimination and aromatization with a strong base was also described (eqn (2)). ${ }^{15}$ However, this synthetic approach included two-step reactions and required purification of the intermediate. In addition, the starting materials used for this transformation were synthesized from the corresponding materials in two or more steps. Very recently, novel one-pot reactions were devised for the synthesis of benzo $[c]$ -chromen-6-one derivatives by palladium bis(acetoacetonate)/ CuCl-catalyzed decarboxylative cross-coupling and lactonization, ${ }^{16}$ or by palladium acetate-catalyzed Suzuki-Miyaura coupling followed by oxidative lactonization (eqn (3) and (4)). ${ }^{17}$ However, to complete these reactions, relatively expensive catalysts, reagents, and ligands are needed. Thus, a mild, general, and efficient one-pot synthetic route for benzo[c]chromen-6one derivatives using inexpensive catalysts and reagents has yet to be devised.

To the best of our knowledge, no previous report has been issued on the synthesis of tricyclic benzo[c]chromen-6-one


Scheme 1 Reported synthetic approaches for benzo[c]chromen-6-ones.


Scheme 2
derivatives via domino Michael addition/intramolecular aldol/ oxidative aromatization/lactonization reactions between substituted 2-hydroxychalcones and $\beta$-ketoesters.

We report herein a novel and efficient means for synthesizing benzo $[c]$ chromen- 6 -one derivatives from readily available substituted 2 -hydroxychalcones and $\beta$-ketoesters via domino Michael/intramolecular aldol/aromatization/lactonization reactions (Scheme 2).

## Results and discussion

To afford benzo[c]chromen-6-one 16, the reaction between 2-hydroxychalcone (1a) and ethyl acetoacetate (2a) was first examined under several conditions (Table 1). Treatment of 1a with $2 \mathbf{a}$ in the presence of 2 equivalents of DBU in refluxing toluene for 7 h afforded product 16 in $50 \%$ yield, but using sodium methoxide in refluxing methanol for $12 \mathrm{~h}, 16$ was produced in $40 \%$ yield. Using $\mathrm{K}_{2} \mathrm{CO}_{3}$ and $\mathrm{Cs}_{2} \mathrm{CO}_{3}$, the desired product 16 was produced at higher yields. For example, reaction with 2 equivalents of $\mathrm{K}_{2} \mathrm{CO}_{3}$ in refluxing toluene for 6 h provided product 16 in $66 \%$ yield, whereas reaction with 2 equivalents of $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ afforded 16 in $71 \%$ yield. In recent years, $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ has been widely used as an excellent base for a variety of transformations in organic synthesis. ${ }^{18}$ Importantly, we found that $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ is more efficient than other bases for the production of 16 in terms of yield and reaction time. However, using one equivalent or a catalytic amount of $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ ( 0.1 eq.), the desired product was produced at lower yields. Reactions in water or methanol under reflux conditions did not provide the desired products. The structure of 16 was determined by analyzing spectral data. The ${ }^{1} \mathrm{H}$ NMR spectrum of 16 showed a single OH peak at $\delta 11.30 \mathrm{ppm}$ in downfield due to hydrogen bonding with the ester carbonyl group, and

Table 1 Reaction of 2-hydroxychalcone (1a) with ethyl acetoacetate (2a) under several conditions

|  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| Entry | Base | Solvent | Condition | Yield (\%) |
| 1 | DBU (2 eq.) | Toluene | Reflux, 7 h | 50 |
| 2 | NaOMe (2 eq.) | MeOH | Reflux, 12 h | 40 |
| 3 | $\mathrm{K}_{2} \mathrm{CO}_{3}$ (2 eq.) | Toluene | Reflux, 6 h | 66 |
| 4 | $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ (2 eq.) | Toluene | Reflux, 2 h | 71 |
| 5 | $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ (1 eq.) | Toluene | Reflux, 6 h | 55 |
| 6 | $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ (0.1 eq.) | Toluene | Reflux, 12 h | 15 |
| 7 | $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ (2 eq.) | Water | Reflux, 12 h | 0 |
| 8 | $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ (2 eq.) | MeOH | Reflux, 12 h | 0 |

two single peaks at $\delta 7.69$ and 7.20 ppm associated with two aromatic peaks on the benzo $[c]$ chromen- 6 -one ring. The structure was further confirmed by ${ }^{13} \mathrm{C}$ NMR spectrum, which showed the expected carbonyl peak at $\delta 162.6 \mathrm{ppm}$ due to the ester. In addition, the IR spectrum of 16 contained an ester carbonyl absorption at $1684 \mathrm{~cm}^{-1}$.

To prepare a variety of benzo[c]chromen-6-one derivatives, additional reactions between substituted 3-(2-hydroxyphenyl)-prop-2-en-1-ones and several $\beta$-ketoesters were carried out under optimized reaction conditions. Results are summarized in Table 2. Reactions between 1a and ethyl-3-oxopentanoate (2b), methyl-3-oxo-4-phenyl butanoate (2c) or diethyl-3-

Table 2 Additional reactions for the synthesis of a variety of benzo[c]chromen-6-one derivatives

2

3

4

8

9

10



1c


1d


1e

1 e
Entry $\quad$ Chalcone $\quad \beta$-Ketoester
$2 a$

2c

$2 a$

2b

.
.

$2 a$

2b






3

3
2

2

2

2

3

3

2

Time (h) Product $\quad$ Yield (\%)












1k

1k


1j

1j

1k

2a

2b
$2 a$

2c
$2 a$

2b

2 c
$2 a$

2b

2d
$\beta$-Ketoester
$2 a$

2b

2c
3

2






3


3

2

2

2

Table 2 (Contd.)
Entry
oxopentanedioate ( $\mathbf{2 d}$ ) in the presence of 2 equivalents of $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ in refluxing toluene for 2 h provided the desired products 17-19 in 51,58 , and $60 \%$ yield, respectively (entries $1-3$ ). The reaction of chalcone $\mathbf{1 b}$ with a methyl group on the 2-propen-1-one skeleton was also successful. Treatment of $\mathbf{1 b}$ with $2 \mathbf{b}$ in the presence of $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ in refluxing toluene for 2 h afforded product 20 in $50 \%$ yield (entry 4 ). To investigate the influence of substituents on reactivities, the effects of a number of 2-hydroxychalcones ( $\mathbf{1} \mathbf{c} \mathbf{- 1 h}$ ) bearing electron-donating or -withdrawing groups on the benzene ring were next examined. Reactions between 1c bearing a methyl group on the phenolic moiety and $2 \mathbf{a}$ or $\mathbf{2 b}$ afforded products 21-22 in 70 and $52 \%$ yield, respectively, whereas those of 1d with an electron-withdrawing group on the phenolic ring provided 23-24 in 55 and 63\% yield, respectively (entries 5-8). Reactions of chalcones $\mathbf{1 e}$ and $\mathbf{1 f}$ bearing electron-donating groups on the two benzene rings were also examined. Treatment of $\mathbf{1 e}$ with $\mathbf{2 a}, \mathbf{2 b}$, or $2 \mathbf{d}$ provided compounds 25-27 in 70, 54, and $62 \%$ yield, respectively, whereas treatment of $1 f$ with $2 \mathbf{a}-2 \mathbf{c}$ gave products $28-30$ in 72,54 , and $60 \%$ yield, respectively (entries 9-14). Reactions of chalcones 1 g and $\mathbf{1 h}$ bearing substituents on the 1-phenyl ring with $\mathbf{2 a}$ or $\mathbf{2 b}$ gave products 31-32 in 69 and 55\% yield, respectively (entries 15-16). Importantly, when (E)-3-(2-hydroxyphenyl)-1-(pyridine-3-yl)prop-2-en-1-one (1i), (E)-3-(2-hydroxyphenyl)-1-(2,5-dimethylfuran-3-yl)-prop-2-en-1-one ( $\mathbf{1} \mathbf{j}), \quad$ or $\quad(E)$-3-(2-hydroxyphenyl)-1-(2,5-dimethylthiophen-3-yl)prop-2-en-1-one ( $\mathbf{1 k}$ ) were used, the desired products 33-40 were produced in $50-73 \%$ yield (entries 17-24). Reactions between ( $E$ )-3-(2-hydroxyphenyl)-1-(naphthalene-2-yl)prop-2-en-1-one (11) and $\beta$-ketoesters were also successful. When 11 was treated with $2 \mathbf{a}, 2 \mathbf{b}$, or $2 \mathbf{c}$, products 41-43 were produced in 63, 51, and $50 \%$ yield, respectively (entries 25-27). When (E)-1-cyclopropyl-3-(2-
hydroxyphenyl)prop-2-en-1-one (1m) was used, compounds 44 and 45 were obtained in 72 and $61 \%$ yield, respectively (entries 28-29). These reactions provided a rapid route for synthesizing a variety of benzo[c]chromen-6-one derivatives bearing different substituents on the benzene ring. The structures of the synthesized compounds $\mathbf{1 6 - 4 5}$ were unambiguously confirmed by X-ray diffraction analysis of compound 26 (Fig. 2). Interestingly, the unit of the compound 26 contains two same molecules.

A proposed mechanism for the $\mathrm{Cs}_{2} \mathrm{CO}_{3}$-mediated domino reactions used to produce 16 is depicted in Scheme 3. In basic medium, the enolate of $2 \mathbf{a}$ first attacks the unsaturated $\beta$-carbon to the carbonyl group of $\mathbf{1 a}$ to give intermediate $\mathbf{4 6}$, which undergoes an intramolecular aldol reaction followed by


Fig. 2 X-ray structure of compound 26 containing two molecules in a unit.


Scheme 3 Proposed mechanism for the formation of 7-hydroxy-9-phenyl-6H-benzo[c]chromen-6-one (16) via domino reactions.
oxidative aromatization to form intermediate 48. Finally, the lactonization of 48 under basic conditions results in 16.

As an example of this methodology, several synthesized benzo[c]chromen-6-ones were converted into biologically and physically interesting polysubstituted terphenyls. Molecules bearing the terphenyl moiety are found in a variety of natural products ${ }^{19}$ and exhibit a number of potent biological properties, which include antioxidant, neuroprotective, cytotoxic, antithrombotic, and anticoagulant activities. ${ }^{20}$ In addition, these molecules play a significant role in the fields of optical materials, liquid crystals, spacers in catenane, and porphyrin chemistry. ${ }^{21}$ Because of their important biological and physical properties, a number of synthetic methods have been devised to produce terphenyls. ${ }^{22}$ These reactions typically included aryl zinc reagents with functionalized biphenyl nonaflates, ${ }^{23}$ Grignard reagents containing dihalobenzenes, and triazene-substituted arylboronic esters. ${ }^{24}$ Recently, other methodologies using Suzuki cross-coupling reactions between dihalobenzenes and arylboronic acids, ${ }^{25}$ the gold-catalyzed cycloaromatization of dienynes, ${ }^{26}$ DMEDA-catalyzed direct $\mathrm{C}-\mathrm{H}$ arylation of unactivated benzenes, ${ }^{27}$ and rhodium-catalyzed formal $[2+2+2]$ cycloaddition reactions of tethered dienynes containing 1-alkynylphosphine sulfides have been described. ${ }^{28}$ Although a number of methods have been
reported for the synthesis of terphenyls, synthetic methods are still required for the production of polysubstituted terphenyls.

The conversions of several synthesized benzo[c]chromen-6ones into substituted terphenyls were also attempted, as shown in Table 3. Treatment of 20 with methyl iodide in the presence of KOH in wet DMSO at room temperature for 2 h provided 49 in 70\% yield. Similarly, reactions of 23, 30, 39, 42, and 45 with methyl iodide also provided the desired polysubstituted terphenyls 50-54 in 78-87\% yield. Importantly, these reactions rapidly provided various terphenyls bearing substituents, such as, $-\mathrm{Br},-\mathrm{Me},-\mathrm{COOMe},-\mathrm{OMe}$, aryl, cyclopropyl, and furyl on their benzene rings.

## Conclusions

We described the $\mathrm{Cs}_{2} \mathrm{CO}_{3}$-promoted one-pot synthesis of biologically interesting benzo[c]chromen-6-one derivatives starting from substituted 2 -hydroxychalcones and $\beta$-ketoesters. These reactions were accomplished by domino Michael addition/ intramolecular aldol/oxidative aromatization/lactonization. The described methodology has the advantages of requiring mild reaction conditions and inexpensive non-transition metals and domino one-pot reactions. In particular, the synthesized molecules were readily converted under basic conditions into biologically interesting novel terphenyls bearing different substituents on their benzene rings.

## Experimental

All experiments were carried out under open air without using any inert gas protection. $\beta$-Ketoesters (2a-d) were purchased from Sigma-Aldrich. Merck precoated silica gel plates (Art. 5554) with a fluorescent indicator were used for analytical

Table 3 Conversion of benzo[c]chromen-6-ones to polysubstituted terphenyls 49-54


| Benzo[c]chromen-6-one | Time (h) | Product | Yield (\%) | Benzo[c]chromen-6-one | Time (h) | Product | Yield (\%) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 20 | 2 |  | 70 | 39 | 1 |  | 87 |
| 23 | 1 |  | 85 | 42 | 1 |  | 78 |
| 30 | 2 |  | 85 | 42 | 1 |  | 86 |

TLC. Flash column chromatography was performed using silica gel 9385 (Merck). Melting points were determined with micro-cover glasses on a Fisher-Johns apparatus and are uncorrected. ${ }^{1} \mathrm{H}$ NMR spectra were recorded on a Varian-VNS ( 300 MHz ) spectrometer in $\mathrm{CDCl}_{3}$ using 7.24 ppm as the solvent chemical shift. ${ }^{13} \mathrm{C}$ NMR spectra were recorded on a Varian-VNS ( 75 MHz ) spectrometer in $\mathrm{CDCl}_{3}$ using 77.0 ppm as the solvent chemical shift. IR spectra were recorded on a JASCO FTIR 5300 spectrophotometer. High resolution mass (HRMS) were obtained with a JEOL JMS-700 spectrometer at the Korea Basic Science Institute.

## General procedure for the synthesis of 2-hydroxychalcones (1a-m)

To a solution of ketones ( 20.0 mmol ) in ethanol ( 50 mL ) were added $\mathrm{KOH}(5.6 \mathrm{~g}, 100.0 \mathrm{mmol})$ and salicylaldehydes ( 20.0 mmol ) at room temperature. The reaction mixture was stirred at room temperature for 48 h . Evaporation of ethanol, addition of water ( 50 ml ) and $1 \mathrm{~N} \mathrm{HCl}(50 \mathrm{~mL})$, extraction with EtOAc ( $3 \times 50 \mathrm{~mL}$ ), washing with brine ( 50 mL ), and removal of the solvent followed by flash column chromatography on silica gel using hexane-EtOAc (10:1) gave 2-hydroxychalcones ( $\mathbf{1 a} \mathbf{a} \mathbf{1 m}$ ) in the range of $53-84 \%$ yield.

## General procedure for the synthesis of benzo[c]chromen-6-ones (16-45)

To a solution of 2-hydroxychalcone compounds $\mathbf{1 a} \mathbf{- 1 m}$ $(1.0 \mathrm{mmol})$ and $\beta$-ketoesters $2 \mathrm{a}-2 \mathrm{~d}$ ( 1.5 mmol ) in toluene $(4 \mathrm{~mL})$ was added $\mathrm{Cs}_{2} \mathrm{CO}_{3}(2.0 \mathrm{mmol})$. The reaction mixture was refluxed in open air for 2 h . Then the solvent was evaporated in a rotary evaporator under reduced pressure to give the residue. The residue was purified by flash column chromatography on silica gel to give the products. Characterization data for all compounds 16-45 are as follows.

7-Hydroxy-9-phenyl-6H-benzo[c]chromen-6-one (16). Reaction of 1a ( $224 \mathrm{mg}, 1.0 \mathrm{mmol}$ ) and $\beta$-ketoester $2 \mathrm{a}(195 \mathrm{mg}$, $1.5 \mathrm{mmol})$ using $\mathrm{Cs}_{2} \mathrm{CO}_{3}(650 \mathrm{mg}, 2.0 \mathrm{mmol})$ afforded 16 ( $204 \mathrm{mg}, 71 \%$ ) as a solid: mp 213-215 ${ }^{\circ} \mathrm{C}$; ${ }^{1} \mathrm{H}$ NMR ( 300 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 11.30(1 \mathrm{H}, \mathrm{s}), 8.02(1 \mathrm{H}, \mathrm{d}, J=7.8 \mathrm{~Hz}), 7.68(1 \mathrm{H}, \mathrm{s})$, $7.60(2 \mathrm{H}, \mathrm{d}, J=6.9 \mathrm{~Hz}), 7.44-7.36(4 \mathrm{H}, \mathrm{m}), 7.31-7.27(2 \mathrm{H}, \mathrm{m})$, $7.20(1 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 162.6, 162.3, 150.7, 150.2, 139.4, 135.4, 130.7, 129.1, 129.0, 127.4, 125.1, 123.3, 118.3, 117.8, 114.9, 111.1, 104.8; IR (KBr) 3422, 3036, 2367, 1684, 1620, 1276, 1083, $757 \mathrm{~cm}^{-1}$; HRMS m/z ( $\mathrm{M}^{+}$) calcd for $\mathrm{C}_{19} \mathrm{H}_{12} \mathrm{O}_{3}$ : 288.0786. Found: 288.0788.
7-Hydroxy-8-methyl-9-phenyl-6H-benzo[c]chromen-6-one (17). Reaction of 1a ( $224 \mathrm{mg}, 1.0 \mathrm{mmol}$ ) and $\beta$-ketoester $\mathbf{2 b}(216 \mathrm{mg}$, 1.5 mmol ) using $\mathrm{Cs}_{2} \mathrm{CO}_{3}(650 \mathrm{mg}, 2.0 \mathrm{mmol})$ afforded 17 ( $154 \mathrm{mg}, 51 \%$ ) as a solid: mp $166-168{ }^{\circ} \mathrm{C}$; ${ }^{1} \mathrm{H}$ NMR $(300 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}\right) \delta 11.76(1 \mathrm{H}, \mathrm{s}), 7.99(1 \mathrm{H}, \mathrm{d}, J=8.1 \mathrm{~Hz}), 7.51-7.28(9 \mathrm{H}$, $\mathrm{m}), 2.25(3 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 165.6,160.7$, $151.0,150.4,140.6,131.6,130.3,128.7,128.3,127.8,124.9$, 123.9, 122.9, 118.4, 117.5, 113.3, 104.1, 13.0; IR (KBr) 3449, 3062, 2370, 1677, 1268, 1125, $754 \mathrm{~cm}^{-1}$; HRMS $m / z\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{20} \mathrm{H}_{14} \mathrm{O}_{3}$ : 302.0943. Found: 302.0943.

7-Hydroxy-8,9-diphenyl-6H-benzo[c]chromen-6-one
(18).

Reaction of 1a ( $224 \mathrm{mg}, 1.0 \mathrm{mmol}$ ) and $\beta$-ketoester 2c $(288 \mathrm{mg}$, 1.5 mmol ) using $\mathrm{Cs}_{2} \mathrm{CO}_{3}(650 \mathrm{mg}, 2.0 \mathrm{mmol})$ afforded 18 ( $211 \mathrm{mg}, 58 \%$ ) as a solid: mp $213-215{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( 300 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 11.77(1 \mathrm{H}, \mathrm{s}), 8.00(1 \mathrm{H}, \mathrm{d}, J=7.5 \mathrm{~Hz}), 7.60(1 \mathrm{H}, \mathrm{s})$, 7.47-7.31 (3H, m), 7.21-7.19 (6H, m), 7.16-7.13 (4H, m); ${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 165.6,160.0,150.5,150.3,140.2$, $134.8,133.6,131.0,130.5,129.4,128.4,127.9,127.7,127.5$, 127.1, 125.1, 123.1, 118.1, 117.6, 114.0, 104.8; IR (KBr) 3448, 3063, 1674, 1612, 1396, 1265, 1127, 752, $697 \mathrm{~cm}^{-1}$; HRMS m/z $\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{25} \mathrm{H}_{16} \mathrm{O}_{3}: 364.1099$. Found: 364.1098.

Ethyl-7-hydroxy-6-oxo-9-phenyl-6H-benzo[c]chromene-8-carboxylate (19). Reaction of $\mathbf{1 a}(224 \mathrm{mg}, 1.0 \mathrm{mmol})$ and $\beta$-ketoester 2 d ( 303 mg , 1.5 mmol ) using $\mathrm{Cs}_{2} \mathrm{CO}_{3}(650 \mathrm{mg}, 2.0 \mathrm{mmol})$ afforded 19 ( $216 \mathrm{mg}, 60 \%$ ) as a solid: mp 193-195 ${ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 11.67(1 \mathrm{H}, \mathrm{s}), 7.84(1 \mathrm{H}, \mathrm{d}, J=7.5 \mathrm{~Hz})$, 7.36-7.35 ( $7 \mathrm{H}, \mathrm{m}$ ), $7.24-7.17(2 \mathrm{H}, \mathrm{m}), 4.07(2 \mathrm{H}, \mathrm{q}, J=7.2 \mathrm{~Hz})$, $0.938(3 \mathrm{H}, \mathrm{t}, J=7.2 \mathrm{~Hz}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 165.9$, 164.7, 159.5, 150.5, 148.9, 139.0, 135.5, 131.2, 128.6, 128.4, $127.8,125.2,123.2,121.4,117.5,117.2,113.1,104.3,61.3,13.5 ;$ IR (KBr) 3455, 3106, 1737, 1552, 1127, 1015, 858, $742 \mathrm{~cm}^{-1}$; HRMS $\mathrm{m} / \mathrm{z}\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{22} \mathrm{H}_{16} \mathrm{O}_{5}: 360.0998$. Found: 360.0994 .

7-Hydroxy-8,10-dimethyl-9-phenyl-6H-benzo[c]chromen-6-one (20). Reaction of $\mathbf{1 b}(238 \mathrm{mg}, 1.0 \mathrm{mmol})$ and $\beta$-ketoester 2b $(216 \mathrm{mg}, 1.5 \mathrm{mmol})$ using $\mathrm{Cs}_{2} \mathrm{CO}_{3}(650 \mathrm{mg}, 2.0 \mathrm{mmol})$ afforded 20 ( $158 \mathrm{mg}, 50 \%$ ) as a solid: mp 207-209 ${ }^{\circ} \mathrm{C}$; ${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 12.07(1 \mathrm{H}, \mathrm{s}), 8.18(1 \mathrm{H}, \mathrm{d}, J=8.1 \mathrm{~Hz})$, $7.50-7.37(5 \mathrm{H}, \mathrm{m}), 7.29(1 \mathrm{H}, \mathrm{t}, J=7.2 \mathrm{~Hz}), 7.14(2 \mathrm{H}, \mathrm{d}, J=7.2$ $\mathrm{Hz}), 2.36(3 \mathrm{H}, \mathrm{s}), 1.98(3 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 166.4, 158.9, 153.1, 150.4, 140.6, 129.2, 128.8, 128.3, 127.8, $127.8,127.4,125.1,124.1,123.3,120.2,117.5,105.3,22.0,13.9 ;$ IR (KBr) 3437, 3067, 1685, 1616, 1272, 1124, $758 \mathrm{~cm}^{-1}$; HRMS $m / z\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{21} \mathrm{H}_{16} \mathrm{O}_{3}: 316.1099$. Found: 316.1099.

7-Hydroxy-2-methyl-9-phenyl-6H-benzo[c]chromen-6-one (21). Reaction of $\mathbf{1 c}(238 \mathrm{mg}, 1.0 \mathrm{mmol})$ and $\beta$-ketoester $\mathbf{2 a}(195 \mathrm{mg}$, 1.5 mmol ) using $\mathrm{Cs}_{2} \mathrm{CO}_{3}(650 \mathrm{mg}, 2.0 \mathrm{mmol})$ afforded 21 ( $211 \mathrm{mg}, 70 \%$ ) as a solid: $\mathrm{mp} 198-200{ }^{\circ} \mathrm{C}$; ${ }^{1} \mathrm{H}$ NMR ( 300 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 11.27(1 \mathrm{H}, \mathrm{s}), 7.66(1 \mathrm{H}, \mathrm{s}), 7.57-7.54(3 \mathrm{H}, \mathrm{m})$, 7.42-7.34 (3H, m), 7.15-7.06 (3H, m), $2.33(3 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 165.3,162.5,149.9,148.7,139.4,135.3$, 134.7, 131.5, 128.9, 128.9, 127.3, 123.0, 117.7, 117.3, 114.6, 110.7, 104.7, 21.0; IR (KBr) 3434, 3033, 1680, 1560, 1227, 1211, 1096, 758, $696 \mathrm{~cm}^{-1}$; HRMS $m / z\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{20} \mathrm{H}_{14} \mathrm{O}_{3}$ : 302.0943. Found: 302.0945.

7-Hydroxy-2,8-dimethyl-9-phenyl-6H-benzo[c]chromen-6-one (22). Reaction of $\mathbf{1 c}(238 \mathrm{mg}, 1.0 \mathrm{mmol})$ and $\beta$-ketoester 2b ( $216 \mathrm{mg}, 1.5 \mathrm{mmol}$ ) using $\mathrm{Cs}_{2} \mathrm{CO}_{3}(650 \mathrm{mg}, 2.0 \mathrm{mmol})$ afforded 22 ( $164 \mathrm{mg}, 52 \%$ ) as a solid: mp 193-195 ${ }^{\circ} \mathrm{C}$; ${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 11.66(1 \mathrm{H}, \mathrm{s}), 7.61(1 \mathrm{H}, \mathrm{s}), 7.41-7.33(3 \mathrm{H}$, $\mathrm{m}), 7.31-7.26(3 \mathrm{H}, \mathrm{m}), 7.10-7.06(2 \mathrm{H}, \mathrm{m}), 2.29(3 \mathrm{H}, \mathrm{s}), 2.11$ $(3 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 165.7,160.7,150.8,148.4$, 140.6, 134.6, 131.6, 130.9, 128.7, 128.3, 127.8, 123.6, 122.8, 117.9, 117.1, 113.1, 104.1, 21.0, 13.0; IR (KBr) 3456, 2932, 1688, 1602, 1513, 1375, 1190, 1014, 821, $745 \mathrm{~cm}^{-1}$; HRMS $\mathrm{m} / \mathrm{z}$ $\left(M^{+}\right)$calcd for $\mathrm{C}_{21} \mathrm{H}_{16} \mathrm{O}_{3}: 316.1099$. Found: 316.1097.

2-Bromo-7-hydroxy-8-methyl-9-phenyl-6H-benzo[c]chromen-6-one (23). Reaction of $\mathbf{1 d}(301 \mathrm{mg}, 1.0 \mathrm{mmol})$ and $\beta$-ketoester 2b ( $216 \mathrm{mg}, 1.5 \mathrm{mmol}$ ) using $\mathrm{Cs}_{2} \mathrm{CO}_{3}(650 \mathrm{mg}, 2.0 \mathrm{mmol})$ afforded 23 ( $209 \mathrm{mg}, 55 \%$ ) as a solid: mp $216-218{ }^{\circ} \mathrm{C}$; ${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 11.59(1 \mathrm{H}, \mathrm{s}), 8.02(1 \mathrm{H}, \mathrm{s}), 7.50-7.39(4 \mathrm{H}$, $\mathrm{m}), 7.36-7.32(3 \mathrm{H}, \mathrm{m}), 7.17(1 \mathrm{H}, \mathrm{d}, J=8.7 \mathrm{~Hz}), 2.20(3 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 165.1,160.8,151.2,149.2,140.3$, $132.8,130.2,128.7,128.4,128.0$, 125.7, 125.0, 120.2, 119.2, 118.0, 113.5, 103.9, 13.1; IR (KBr) 3449, 3064, 1703, 1625, 1557, 1409, 1264, 1217, 1082, 853, $691 \mathrm{~cm}^{-1}$; HRMS $\mathrm{m} / \mathrm{z}\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{20} \mathrm{H}_{13} \mathrm{BrO}_{3}: 380.0048$. Found: 380.0050 .

2-Bromo-7-hydroxy-8,9-diphenyl-6H-benzo[c]chromen-6-one (24). Reaction of $\mathbf{1 d}(301 \mathrm{mg}, 1.0 \mathrm{mmol})$ and $\beta$-ketoester $2 \mathbf{c}$ ( $288 \mathrm{mg}, 1.5 \mathrm{mmol}$ ) using $\mathrm{Cs}_{2} \mathrm{CO}_{3}(650 \mathrm{mg}, 2.0 \mathrm{mmol})$ afforded $24(243 \mathrm{mg}, 63 \%)$ as a solid: $\mathrm{mp} 215-217{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 11.67(1 \mathrm{H}, \mathrm{s}), 8.12(1 \mathrm{H}, \mathrm{s}), 7.55-7.53(2 \mathrm{H}$, $\mathrm{m}), 7.22-7.19(7 \mathrm{H}, \mathrm{m}), 7.14-7.09(4 \mathrm{H}, \mathrm{m}) ;{ }^{13} \mathrm{C}$ NMR ( 75 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 165.1,160.2,150.7,149.5,140.0,134.6,133.3,132.3$, 130.9, 129.4, 129.3, 128.0, 127.8, 127.6, 127.2, 126.0, 120.0, 119.4, 118.2, 114.2, 104.7; IR (KBr) 3454, 3064, 1681, 1612, 1545, 1393, 1260, 1203, 1115, 880, 743, $701 \mathrm{~cm}^{-1}$; HRMS $\mathrm{m} / \mathrm{z}$ $\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{25} \mathrm{H}_{15} \mathrm{BrO}_{3}: 442.0205$. Found: 442.0202 .

7-Hydroxy-2-methyl-9-p-tolyl-6H-benzo[c]chromen-6-one (25). Reaction of $\mathbf{1 e}(252 \mathrm{mg}, 1.0 \mathrm{mmol})$ and $\beta$-ketoester $2 \mathrm{a}(195 \mathrm{mg}$, 1.5 mmol ) using $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ ( $650 \mathrm{mg}, 2.0 \mathrm{mmol}$ ) afforded 25 ( $221 \mathrm{mg}, 70 \%$ ) as a solid: $\mathrm{mp} 258-260{ }^{\circ} \mathrm{C}$; ${ }^{1} \mathrm{H}$ NMR ( 300 MHz , $\mathrm{CDCl}_{3} \delta 11.40(1 \mathrm{H}, \mathrm{s}), 7.85(1 \mathrm{H}, \mathrm{s}), 7.72(1 \mathrm{H}, \mathrm{s}), 7.58(2 \mathrm{H}, \mathrm{d}, J=$ $7.5 \mathrm{~Hz}), 7.31-7.24(5 \mathrm{H}, \mathrm{m}), 2.45(3 \mathrm{H}, \mathrm{s}), 2.42(3 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 165.7,160.7,151.0,150.4,137.7,137.7$, 131.6, 129.9, 129.0, 128.7, 124.9, 123.9, 122.9, 118.5, 117.5, 113.4, 104.0, 21.2, 13.1; IR (KBr) 3434, 2928, 1690, 1618, 1588, 1437, 1240, 1181, 1076, 926, $784 \mathrm{~cm}^{-1}$; HRMS $m / z\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{21} \mathrm{H}_{16} \mathrm{O}_{3}: 316.1099$. Found: 316.1102.

7-Hydroxy-2,8-dimethyl-9- $\boldsymbol{p}$-tolyl-6H-benzo[ $c]$ chromen-6-one (26). Reaction of $\mathbf{1 e}(252 \mathrm{mg}, 1.0 \mathrm{mmol})$ and $\beta$-ketoester $2 \mathbf{b}$ ( $216 \mathrm{mg}, 1.5 \mathrm{mmol}$ ) using $\mathrm{Cs}_{2} \mathrm{CO}_{3}(650 \mathrm{mg}, 2.0 \mathrm{mmol})$ afforded 26 ( $178 \mathrm{mg}, 54 \%$ ) as a solid: mp 190-192 ${ }^{\circ} \mathrm{C}$; ${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 11.64(1 \mathrm{H}, \mathrm{s}), 7.59(1 \mathrm{H}, \mathrm{s}), 7.2(1 \mathrm{H}, \mathrm{s})$, 7.21-7.15 (4H, m), 7.11-7.04 (2H, m), $2.35(3 \mathrm{H}, \mathrm{s}), 2.28(3 \mathrm{H}, \mathrm{s})$, $2.11(3 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 165.7,160.6,150.8$, 148.4, 137.7, 137.6, 134.5, 131.5, 130.8, 128.9, 128.6, 123.6, 122.8, 117.9, 117.1, 113.2, 103.9, 21.2, 21.0, 13.0; IR ( $\mathrm{KBr)}$ $3442,3056,1672,1610,1398,1270,1136,1019,862,761 \mathrm{~cm}^{-1}$; HRMS $m / z\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{22} \mathrm{H}_{18} \mathrm{O}_{3}: 330.1256$. Found: 330.1256.

Ethyl 7-hydroxy-2-methyl-6-oxo-9-p-tolyl-6H-benzo[c]chro-mene-8-carboxylate (27). Reaction of $\mathbf{1 e}(252 \mathrm{mg}, 1.0 \mathrm{mmol})$ and $\beta$-ketoester $2 \mathbf{d}$ ( $303 \mathrm{mg}, 1.5 \mathrm{mmol}$ ) using $\mathrm{Cs}_{2} \mathrm{CO}_{3}(650 \mathrm{mg}$, 2.0 mmol ) afforded $27(240 \mathrm{mg}, 62 \%)$ as a solid: mp $223-225{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 11.78(1 \mathrm{H}, \mathrm{s}), 7.73$ $(1 \mathrm{H}, \mathrm{s}), 7.46(1 \mathrm{H}, \mathrm{s}), 7.32-7.17(6 \mathrm{H}, \mathrm{m}), 4.12(2 \mathrm{H}, \mathrm{q}, J=7.2 \mathrm{~Hz})$, $2.37(3 \mathrm{H}, \mathrm{s}), 2.34(3 \mathrm{H}, \mathrm{s}), 1.01(3 \mathrm{H}, \mathrm{t}, J=7.2 \mathrm{~Hz}) ;{ }^{13} \mathrm{C}$ NMR $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 166.3,165.2,159.8,149.1,149.0,138.7$, 136.4, 135.8, 135.0, 132.2, 129.2, 128.0, 123.4, 121.6, 117.5, 117.3, 113.3, 104.8, 61.5, 21.2, 21.0, 13.7; IR (KBr) 3438, 2989, 2733, 1732, 1671, 1552, 1405, 1248, 1205, 1133, 1021,
$824 \mathrm{~cm}^{-1}$; HRMS $\mathrm{m} / \mathrm{z}\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{24} \mathrm{H}_{20} \mathrm{O}_{5}$ : 388.1311. Found: 388.1313.

7-Hydroxy-3-methoxy-9-(3-methoxyphenyl)-6H-benzo[c]-chromen-6-one (28). Reaction of $1 \mathrm{f}(284 \mathrm{mg}, 1.0 \mathrm{mmol})$ and $\beta$-ketoester 2a ( $195 \mathrm{mg}, 1.5 \mathrm{mmol}$ ) using $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ ( 650 mg , 2.0 mmol ) afforded 28 ( $250 \mathrm{mg}, 72 \%$ ) as a solid: mp $190-192{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 11.26(1 \mathrm{H}, \mathrm{s}), 7.92$ $(1 \mathrm{H}, \mathrm{d}, J=8.7 \mathrm{~Hz}), 7.57(1 \mathrm{H}, \mathrm{s}), 7.35(1 \mathrm{H}, \mathrm{t}, J=7.8 \mathrm{~Hz})$, 7.20-7.18 ( $2 \mathrm{H}, \mathrm{m}$ ), 7.13-7.12 (1H, m), 6.94-6.80 (3H, m), 3.82 $(6 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 165.8,162.1,160.5,159.4$, $151.6,150.9$, 142.1, 132.1, 129.3, 123.9, 122.5, 121.1, 114.5, 113.1, 112.8, 112.5, 111.4, 103.3, 101.4, 55.6, 55.3; IR (KBr) 3449, 2930, 1679, 1632, 1623, 1464, 1396, 1266, 1092, 1029, $800,725 \mathrm{~cm}^{-1}$; HRMS $\mathrm{m} / \mathrm{z}\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{21} \mathrm{H}_{16} \mathrm{O}_{5}: 348.0998$. Found: 348.0999.

7-Hydroxy-3-methoxy-9-(3-methoxyphenyl)-8-methyl-6H-benzo-[c]chromen-6-one (29). Reaction of $1 \mathbf{1 f}(284 \mathrm{mg}, 1.0 \mathrm{mmol})$ and $\beta$-ketoester 2b ( $216 \mathrm{mg}, 1.5 \mathrm{mmol}$ ) using $\mathrm{Cs}_{2} \mathrm{CO}_{3}(650 \mathrm{mg}$, 2.0 mmol ) afforded 29 ( $153 \mathrm{mg}, 54 \%$ ) as a solid: mp $171-173{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 11.57(1 \mathrm{H}, \mathrm{s}), 7.75$ $(1 \mathrm{H}, \mathrm{d}, J=8.7 \mathrm{~Hz}), 7.32-7.24(2 \mathrm{H}, \mathrm{m}), 6.89-6.72(5 \mathrm{H}, \mathrm{m}), 3.78$ $(3 \mathrm{H}, \mathrm{s}), 3.77(3 \mathrm{H}, \mathrm{s}), 2.11(3 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 165.9,161.1,160.6,159.4,151.6,150.9,142.1,132.1,129.3$, 123.9, 122.5, 121.1, 114.5, 113.1, 112.8, 112.5, 111.4, 103.3, 101.4, 55.6, 55.3, 12.9; IR (KBr) 3448, 2929, 1672, 1622, 1482, 1282, 1137, 1033, 798, $751 \mathrm{~cm}^{-1}$; HRMS $\mathrm{m} / \mathrm{z}\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{22} \mathrm{H}_{18} \mathrm{O}_{5}: 362.1154$. Found: 362.1154 .

7-Hydroxy-3-methoxy-9-(3-methoxyphenyl)-8-phenyl-6H-benzo-[c]chromen-6-one (30). Reaction of $\mathbf{1 f}(284 \mathrm{mg}, 1.0 \mathrm{mmol})$ and $\beta$-ketoester 2c ( $288 \mathrm{mg}, 1.5 \mathrm{mmol}$ ) using $\mathrm{Cs}_{2} \mathrm{CO}_{3}(650 \mathrm{mg}$, 2.0 mmol ) afforded $30(254 \mathrm{mg}, 60 \%)$ as a solid: mp $216-218{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 11.69(1 \mathrm{H}, \mathrm{s}), 7.87$ $(1 \mathrm{H}, \mathrm{d}, J=9.0 \mathrm{~Hz}), 7.47(1 \mathrm{H}, \mathrm{s}), 7.24-7.06(6 \mathrm{H}, \mathrm{m}), 6.88-6.80$ $(2 \mathrm{H}, \mathrm{m}), 6.73-6.88(2 \mathrm{H}, \mathrm{m}), 6.56(1 \mathrm{H}, \mathrm{s}) 3.82(3 \mathrm{H}, \mathrm{s}), 3.52(3 \mathrm{H}$, $\mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 165.8,161.7,161.6,160.0$, $158.9,151.9,150.2,141.6,135.0,134.2,130.9,129.0,127.8$, 127.1, 124.2, 121.8, 114.8, 113.5, 113.1, 111.1, 104.0, 101.4, 55.7, 55.1; IR (KBr) 3444, 2935, 1679, 1639, 1464, 1396, 1266, 1092, 1029, 805, $735 \mathrm{~cm}^{-1}$; HRMS $m / z\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{27} \mathrm{H}_{20} \mathrm{O}_{5}$ : 424.1311. Found: 424.1309.

7-Hydroxy-9-p-tolyl-6H-benzo[c]chromen-6-one (31). Reaction of $\mathbf{1 g}(238 \mathrm{mg}, 1.0 \mathrm{mmol})$ and $\beta$-ketoester $2 \mathrm{a}(195 \mathrm{mg}$, 1.5 mmol ) using $\mathrm{Cs}_{2} \mathrm{CO}_{3}(650 \mathrm{mg}, 2.0 \mathrm{mmol})$ afforded 31 ( $208 \mathrm{mg}, 69 \%$ ) as a solid: $\mathrm{mp} 199-201{ }^{\circ} \mathrm{C}$; ${ }^{1} \mathrm{H}$ NMR ( 300 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 11.34(1 \mathrm{H}, \mathrm{s}), 8.07(2 \mathrm{H}, \mathrm{d}, J=7.2 \mathrm{~Hz}), 7.73(1 \mathrm{H}, \mathrm{s})$, 7.50-7.45 ( $1 \mathrm{H}, \mathrm{m}$ ), 7.37-7.25 ( $5 \mathrm{H}, \mathrm{m}$ ), $2.41(3 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 165.3,162.5,150.7,150.2,139.1,136.5$, 135.3, 130.6, 129.7, 127.2, 125.0, 123.3, 118.4, 117.7, 114.6, $110.8,104,12.2 ;$ IR (KBr) 3436, 3128, 1686, 1623, 1273, 1110, 944, 813, $752,705 \mathrm{~cm}^{-1}$; HRMS $m / z\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{20} \mathrm{H}_{14} \mathrm{O}_{3}$ : 302.0943. Found: 302.0946 .

7-Hydroxy-9-(4-methoxyphenyl)-8-methyl-6H-benzo[c]chromen-6-one (32). Reaction of $\mathbf{1 h}(254 \mathrm{mg}, 1.0 \mathrm{mmol})$ and $\beta$-ketoester 2b ( $216 \mathrm{mg}, 1.5 \mathrm{mmol}$ ) using $\mathrm{Cs}_{2} \mathrm{CO}_{3}(650 \mathrm{mg}, 2.0 \mathrm{mmol})$ afforded 32 ( $182 \mathrm{mg}, 55 \%$ ) as a solid: $\mathrm{mp} 192-194{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 11.62(1 \mathrm{H}, \mathrm{s}), 7.87(1 \mathrm{H}, \mathrm{d}, J=7.8 \mathrm{~Hz})$ ),
7.36-7.31 (2H, m), 7.24-7.17 (4H, m), $6.92(2 \mathrm{H}, \mathrm{d}, J=8.4 \mathrm{~Hz})$, $3.80(3 \mathrm{H}, \mathrm{s}), 2.14(3 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 165.6$, 160.7 , 159.3, 150.6, 150.3, 132.8, 131.5, 130.0, 129.9, 124.9, $123.9,122.9,118.4,117.5,113.7,113.4,103.8,55.3,13.1 ;$ IR (KBr) 3453, 3073, 1675, 1612, 1510, 1274, 1129, 1029, 834, $736 \mathrm{~cm}^{-1}$; HRMS m/z $\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{21} \mathrm{H}_{16} \mathrm{O}_{4}$ : 332.1049. Found: 332.1050.
7-Hydroxy-9-(pyridin-3-yl)-6H-benzo[c]chromen-6-one (33). Reaction of $\mathbf{1 i}(225 \mathrm{mg}, 1.0 \mathrm{mmol})$ and $\beta$-ketoester $2 \mathrm{a}(195 \mathrm{mg}$, $1.5 \mathrm{mmol})$ using $\mathrm{Cs}_{2} \mathrm{CO}_{3}(650 \mathrm{mg}, 2.0 \mathrm{mmol})$ afforded 33 ( $220 \mathrm{mg}, 70 \%$ ) as a solid: $\mathrm{mp} 243-245{ }^{\circ} \mathrm{C}$; ${ }^{1} \mathrm{H}$ NMR ( 300 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 11.41(1 \mathrm{H}, \mathrm{s}), 8.93(1 \mathrm{H}, \mathrm{s}), 8.69(1 \mathrm{H}, \mathrm{s}), 8.07(1 \mathrm{H}, \mathrm{d}, J=$ $8.1 \mathrm{~Hz}), 7.97(1 \mathrm{H}, \mathrm{d}, J=7.5 \mathrm{~Hz}), 7.72(1 \mathrm{H}, \mathrm{s}), 7.52-7.36(4 \mathrm{H}, \mathrm{m})$, $7.22(1 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 164.6,162.6,150.5$, 149.5, 149.5, 139.0, 133.9, 133.4, 129.2, 129.1, 127.3, 126.0, 120.1, 119.4, 118.1, 115.6, 111.1, 104.6; IR ( KBr ) 3425, 3043, 1685, 1621, 1276, 1207, 1086, 754, $707 \mathrm{~cm}^{-1}$; HRMS m/z ( $\mathrm{M}^{+}$) calcd for $\mathrm{C}_{18} \mathrm{H}_{11} \mathrm{NO}_{3}$ : 289.0739. Found: 289.0741 .

7-Hydroxy-8-phenyl-9-(pyridin-3-yl)-6H-benzo[c]chromen-6one (34). Reaction of $\mathbf{1 i}(225 \mathrm{mg}, 1.0 \mathrm{mmol})$ and $\beta$-ketoester $2 \mathbf{c}$ ( $288 \mathrm{mg}, 1.5 \mathrm{mmol}$ ) using $\mathrm{Cs}_{2} \mathrm{CO}_{3}(650 \mathrm{mg}, 2.0 \mathrm{mmol})$ afforded $34(229 \mathrm{mg}, 63 \%)$ as a solid: $\mathrm{mp} 247-249{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 11.82(1 \mathrm{H}, \mathrm{s}), 8.48(2 \mathrm{H}, \mathrm{d}, J=7.8 \mathrm{~Hz}), 8.03$ $(1 \mathrm{H}, \mathrm{d}, J=8.1 \mathrm{~Hz}), 7.59(1 \mathrm{H}, \mathrm{s}), 7.49(1 \mathrm{H}, \mathrm{t}, J=6.9 \mathrm{~Hz})$, 7.40-7.35 (3H, m), 7.23-7.24 (3H, m), 7.14-7.12 (3H, m); ${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 165.4,160.2,150.6,149.4,148.3$, $146.3,137.0,136.2,134.1,134.0,131.0,130.9,128.7$, 128.1, $127.5,125.3,123.1,122.7,117.8,117.7,113.6,105.5$; IR (KBr) 3443, 3056, 1663, 1610, 1391, 1264, 1129, $748 \mathrm{~cm}^{-1}$; HRMS m/z $\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{24} \mathrm{H}_{15} \mathrm{NO}_{3}: 365.1052$. Found: 365.1049.

9-(2,5-Dimethylfuran-3-yl)-7-hydroxy-6H-benzo[c]chromen-6-one (35). Reaction of $\mathbf{1 j}$ ( $242 \mathrm{mg}, 1.0 \mathrm{mmol}$ ) and $\beta$-ketoester 2a ( $195 \mathrm{mg}, 1.5 \mathrm{mmol}$ ) using $\mathrm{Cs}_{2} \mathrm{CO}_{3}(650 \mathrm{mg}, 2.0 \mathrm{mmol})$ afforded 35 ( $217 \mathrm{mg}, 71 \%$ ) as a solid: mp 141-143 ${ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 11.29(1 \mathrm{H}, \mathrm{s}), 7.95(1 \mathrm{H}, \mathrm{d}, J=8.7 \mathrm{~Hz})$, 7.47-7.41 ( $2 \mathrm{H}, \mathrm{m}$ ), 7.33-7.28 ( $2 \mathrm{H}, \mathrm{m}$ ), $7.00(1 \mathrm{H}, \mathrm{s}), 6.17(1 \mathrm{H}, \mathrm{s})$, $2.47(3 \mathrm{H}, \mathrm{s}), 2.29(3 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 165.1$, 162.3, 150.6, 150.5, 148.1, 143.8, 135.0, 130.5, 124.9, 123.1, $120.5,118.2,117.7,114.4,110.7,106.2$, 103.7, 13.5, 13.3; IR (KBr) 3449, 2930, 1719, 1511, 1278, 1128, $817,557 \mathrm{~cm}^{-1}$; HRMS $m / z\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{19} \mathrm{H}_{14} \mathrm{O}_{4}: 306.0892$. Found: 306.0890 .

9-(2,5-Dimethylfuran-3-yl)-7-hydroxy-8-methyl-6H-benzo[c]-chromen-6-one (36). Reaction of $\mathbf{1 j}$ ( $242 \mathrm{mg}, 1.0 \mathrm{mmol}$ ) and $\beta$-ketoester 2b ( $216 \mathrm{mg}, 1.5 \mathrm{mmol}$ ) using $\mathrm{Cs}_{2} \mathrm{CO}_{3}(650 \mathrm{mg}$, 2.0 mmol ) afforded 36 ( $169 \mathrm{mg}, 53 \%$ ) as a solid: mp $144-146{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 11.61(1 \mathrm{H}, \mathrm{s}), 7.89$ $(1 \mathrm{H}, \mathrm{d}, J=7.8 \mathrm{~Hz}), 7.39-7.34(2 \mathrm{H}, \mathrm{m}), 7.27-7.17(2 \mathrm{H}, \mathrm{m}), 5.93$ $(1 \mathrm{H}, \mathrm{s}), 2.25(3 \mathrm{H}, \mathrm{s}), 2.16(6 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ $165.7,160.7,150.4,150.0,147.0,143.8$, 131.5, 130.0, 125.0, 124.9, 122.9, 120.6, 118.5, 117.6, 113.6, 108.1, 103.9, 13.4, 13.0, 12.5; IR (KBr) 3449, 3067, 1686, 1624, 1272, 1124, $757 \mathrm{~cm}^{-1}$; HRMS m/z $\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{20} \mathrm{H}_{16} \mathrm{O}_{4}: 320.1049$. Found: 320.1046.

9-(2,5-Dimethylfuran-3-yl)-7-hydroxy-8-phenyl-6H-benzo[c]-chromen-6-one (37). Reaction of $\mathbf{1 j}$ ( $242 \mathrm{mg}, 1.0 \mathrm{mmol}$ ) and
$\beta$-ketoester 2c ( $288 \mathrm{mg}, 1.5 \mathrm{mmol}$ ) using $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ ( 650 mg , 2.0 mmol ) afforded 37 ( $248 \mathrm{mg}, 65 \%$ ) as a solid: mp $208-210{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 11.71(1 \mathrm{H}, \mathrm{s}), 7.96$ $(1 \mathrm{H}, \mathrm{d}, J=7.8 \mathrm{~Hz}), 7.49(1 \mathrm{H}, \mathrm{s}), 7.43(1 \mathrm{H}, \mathrm{t}, J=7.8 \mathrm{~Hz})$, 7.33-7.18 ( $7 \mathrm{H}, \mathrm{m}$ ), $5.51(1 \mathrm{H}, \mathrm{s}), 2.08(3 \mathrm{H}, \mathrm{s}), 1.92(3 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 165.6,160.1,150.6,149.6,147.2$, 143.5, 135.1, 133.4, 130.6, 130.5, 127.8, 127.2, 125.1, 123.0, $120.6,118.2,117.7,114.1,108.2,105.4,104.5,13.2,12.5$; IR (KBr) 3444, 3067, 1680, 1624, 1272, 1124, $759 \mathrm{~cm}^{-1}$; HRMS m/z $\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{25} \mathrm{H}_{18} \mathrm{O}_{4}: 382.1205$. Found: 382.1208.
2-Bromo-9-(2,5-dimethylthiophen-3-yl)-7-hydroxy-6H-benzo[c]-chromen-6-one (38). Reaction of $\mathbf{1 k}(337 \mathrm{mg}, 1.0 \mathrm{mmol})$ and $\beta$-ketoester 2a ( $195 \mathrm{mg}, 1.5 \mathrm{mmol}$ ) using $\mathrm{Cs}_{2} \mathrm{CO}_{3}(650 \mathrm{mg}$, 2.0 mmol ) afforded 38 ( $292 \mathrm{mg}, 73 \%$ ) as a solid: mp $217-219{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 11.16(1 \mathrm{H}, \mathrm{s}), 8.03$ $(1 \mathrm{H}, \mathrm{s}), 7.49(1 \mathrm{H}, \mathrm{d}, J=8.7 \mathrm{~Hz}), 7.39(1 \mathrm{H}, \mathrm{s}), 7.16(1 \mathrm{H}, \mathrm{d}, J=$ $8.7 \mathrm{~Hz}), 7.01(1 \mathrm{H}, \mathrm{s}), 6.70(1 \mathrm{H}, \mathrm{s}), 2.43(3 \mathrm{H}, \mathrm{s}), 2.39(3 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 164.6,162.4,149.6,146.4,136.7$, 136.3, 134.6, 133.6, 133.4, 126.4, 126.0, 120.2, 119.5, 118.1, 116.9 112.6, 104.0, 15.0, 14.3; IR (KBr) 3451, 2377, 1677, 1390, 1268, $756 \mathrm{~cm}^{-1}$; HRMS $\mathrm{m} / \mathrm{z}\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{19} \mathrm{H}_{13} \mathrm{BrO}_{3} \mathrm{~S}$ : 399.9769. Found: 399.9771.

2-Bromo-9-(2,5-dimethylthiophen-3-yl)-7-hydroxy-8-methyl$\mathbf{6 H}$-benzo $[c]$ chromen-6-one (39). Reaction of $\mathbf{1 k}(337 \mathrm{mg}$, 1.0 mmol ) and $\beta$-ketoester 2b ( $216 \mathrm{mg}, 1.5 \mathrm{mmol}$ ) using $\mathrm{Cs}_{2} \mathrm{CO}_{3}(650 \mathrm{mg}, 2.0 \mathrm{mmol})$ afforded $39(207 \mathrm{mg}, 73 \%)$ as a solid: mp 213-215 ${ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 11.63(1 \mathrm{H}$, s), $8.09(1 \mathrm{H}, \mathrm{s}), 7.54(1 \mathrm{H}, \mathrm{d}, J=9.0 \mathrm{~Hz}), 7.36(1 \mathrm{H}, \mathrm{s}), 7.25(1 \mathrm{H}$, d, $J=8.7 \mathrm{~Hz}), 6.56(1 \mathrm{H}, \mathrm{s}), 2.50(3 \mathrm{H}, \mathrm{s}), 2.24(3 \mathrm{H}, \mathrm{s}), 2.19(3 \mathrm{H}$, s); ${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 165.2, 160.8, 149.3, 146.7, 136.7, 136.5, 133.4, 132.8, 130.1, 126.6, 126.2, 125.8, 120.3, 119.3, 118.0, 113.7, 104.0, 15.1, 13.6, 12.9; IR (KBr) 3477, 1689, 1551, 1388, 1259, 1122, $734 \mathrm{~cm}^{-1}$; HRMS m/z ( $\mathrm{M}^{+}$) calcd for $\mathrm{C}_{20} \mathrm{H}_{15} \mathrm{BrO}_{3} \mathrm{~S}: 413.9925$. Found: 413.9927.

Ethyl 2-bromo-9-(2,5-dimethylthiophen-3-yl)-7-hydroxy-6-oxo-6H-benzo[c]chromene-8-carboxylate (40). Reaction of 1 k ( $337 \mathrm{mg}, 1.0 \mathrm{mmol}$ ) and $\beta$-ketoester 2 d ( $216 \mathrm{mg}, 1.5 \mathrm{mmol}$ ) using $\mathrm{Cs}_{2} \mathrm{CO}_{3}(650 \mathrm{mg}, 2.0 \mathrm{mmol})$ afforded $40(207 \mathrm{mg}, 64 \%)$ as a solid: mp 203-205 ${ }^{\circ} \mathrm{C}$; ${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 11.68$ $(1 \mathrm{H}, \mathrm{s}), 8.1(1 \mathrm{H}, \mathrm{s}), 7.6(1 \mathrm{H}, \mathrm{d}, J=7.6 \mathrm{~Hz}), 7.39(1 \mathrm{H}, \mathrm{s}), 7.26$ $(1 \mathrm{H}, \mathrm{d}, J=8.7 \mathrm{~Hz}), 6.57(1 \mathrm{H}, \mathrm{s}), 4.15(2 \mathrm{H}, \mathrm{q}, J=7.2 \mathrm{~Hz}), 2.41$ $(3 \mathrm{H}, \mathrm{s}), 2.29(3 \mathrm{H}, \mathrm{s}), 1.09(3 \mathrm{H}, \mathrm{t}, J=7.2 \mathrm{~Hz}) ;{ }^{13} \mathrm{C}$ NMR ( 75 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 165.6,164.4,159.7,149.8,145.3,136.5,135.0,134.4$, 134.2 , 134.1, 126.4, 126.3, 123.5, 119.6, 119.5, 118.4, 114.1, 104.9, 61.5, 15.0, 13.8, 13.7; IR ( KBr ) 3477, 1689, 1551, 1388, 1259, 1122, $734 \mathrm{~cm}^{-1}$; HRMS $m / z\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{22} \mathrm{H}_{17} \mathrm{BrO}_{5} \mathrm{~S}$ : 471.9980. Found: 471.9982.

7-Hydroxy-9-(naphthalen-2-yl)-6H-benzo[c]chromen-6-one (41). Reaction of $\mathbf{1 1}(274 \mathrm{mg}, 1.0 \mathrm{mmol})$ and $\beta$-ketoester 2 a (195 mg, 1.5 mmol ) using $\mathrm{Cs}_{2} \mathrm{CO}_{3}(650 \mathrm{mg}, 2.0 \mathrm{mmol})$ afforded $41(212 \mathrm{mg}, 63 \%)$ as a solid: mp 228-230 ${ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 11.40(1 \mathrm{H}, \mathrm{s}), 8.14(2 \mathrm{H}, \mathrm{d}, J=6.9 \mathrm{~Hz})$, $7.97-7.88(4 \mathrm{H}, \mathrm{m}), 7.78(1 \mathrm{H}, \mathrm{d}, J=8.1 \mathrm{~Hz}), 7.55-7.48(3 \mathrm{H}, \mathrm{m})$, 7.39-7.35 (3H, m); ${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 165.9,161.8$, 152.0, 150.8, 138.1, 133.1, 133.7, 131.7, 131.0, 128.2, 127.9, $127.8,127.7,126.7,126.5,126.4,125.0,124.5,123.0$, 118.4,
117.9, 113.5, 104.8; IR (KBr) 3422, 2370, 1683, 1620, 1557, 1272, 1081, 858, $755 \mathrm{~cm}^{-1}$; HRMS $m / z\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{23} \mathrm{H}_{14} \mathrm{O}_{3}$ : 338.0943. Found: 338.0943.

7-Hydroxy-8-methyl-9-(naphthalen-2-yl)-6H-benzo[c]chromen-6-one (42). Reaction of $\mathbf{1 1}(274 \mathrm{mg}, 1.0 \mathrm{mmol})$ and $\beta$-ketoester 2b ( $195 \mathrm{mg}, 1.5 \mathrm{mmol}$ ) using $\mathrm{Cs}_{2} \mathrm{CO}_{3}(650 \mathrm{mg}, 2.0 \mathrm{mmol})$ afforded $42(179 \mathrm{mg}, 51 \%)$ as a solid: mp 194-196 ${ }^{\circ} \mathrm{C}$; ${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 11.68(1 \mathrm{H}, \mathrm{s}), 7.90-7.79(4 \mathrm{H}, \mathrm{m}), 7.74(1 \mathrm{H}$, s), 7.47-7.44 (3H, m), 7.41-7.33 (2H, m), 7.27-7.16 (2H, m), $2.17(3 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 165.7,160.8,151.0$, 150.5, 138.1, 133.1, 132.7, 131.7, 130.0, 128.12, 127.9, 127.8, 127.7, 126.7, 126.5, 126.4, 125.0, 124.1, 123.0, 118.4, 117.6, 113.5, 104.3, 13.2; IR (KBr) 3447, 3053, 1676, 1268, 1123, $755 \mathrm{~cm}^{-1}$; HRMS $\mathrm{m} / \mathrm{z}\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{24} \mathrm{H}_{16} \mathrm{O}_{3}$ : 352.1099. Found: 352.1097.

7-Hydroxy-9-(naphthalen-2-yl)-8-phenyl-6H-benzo[c]chromen-6-one (43). Reaction of $\mathbf{1 1}(274 \mathrm{mg}, 1.0 \mathrm{mmol})$ and $\beta$-ketoester 2c ( $288 \mathrm{mg}, 1.5 \mathrm{mmol}$ ) using $\mathrm{Cs}_{2} \mathrm{CO}_{3}(650 \mathrm{mg}, 2.0 \mathrm{mmol})$ afforded $43(207 \mathrm{mg}, 50 \%)$ as a solid: $\mathrm{mp} 199-201{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 11.84(1 \mathrm{H}, \mathrm{s}), 8.09(1 \mathrm{H}, \mathrm{d}, J=7.2 \mathrm{~Hz})$, $7.76-7.47(4 \mathrm{H}, \mathrm{m}), 7.6(1 \mathrm{H}, \mathrm{d}, J=8.4 \mathrm{~Hz}), 7.53-7.33(5 \mathrm{H}, \mathrm{m})$, 7.22-7.18 ( $5 \mathrm{H}, \mathrm{m}$ ), 7.15-7.12 ( $1 \mathrm{H}, \mathrm{m}$ ); ${ }^{13} \mathrm{C}$ NMR ( 75 MHz , $\mathrm{CDCl}_{3}$ ) $\delta 165.9,160.4,150.9,150.4,138.2,135.0,134.0,133.2$, $132.5,131.2,130.9,128.8,128.3,128.1,127.8,127.5,127.5$, 127.4, 126.6, 126.5, 125.4, 123.4, 118.4, 117.9, 114.6, 105.2; IR ( KBr ) 3424, 3055, 1672, 1612, 1265, 857, $748 \mathrm{~cm}^{-1}$; HRMS m/z $\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{29} \mathrm{H}_{18} \mathrm{O}_{3}: 414.1256$. Found: 414.1254 .
9-Cyclopropyl-7-hydroxy-6H-benzo[c]chromen-6-one (44). Reaction of $\mathbf{1 m}(188 \mathrm{mg}, 1.0 \mathrm{mmol})$ and $\beta$-ketoester 2 a ( $195 \mathrm{mg}, 1.5 \mathrm{mmol}$ ) using $\mathrm{Cs}_{2} \mathrm{CO}_{3}(650 \mathrm{mg}, 2.0 \mathrm{mmol})$ afforded $44(181 \mathrm{mg}, 72 \%)$ as a solid: mp $140-142{ }^{\circ} \mathrm{C}$; ${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 11.19(1 \mathrm{H}, \mathrm{s}), 7.91(1 \mathrm{H}, \mathrm{d}, J=7.5 \mathrm{~Hz})$, $7.42-7.37(1 \mathrm{H}, \mathrm{m}), 7.28-7.19(3 \mathrm{H}, \mathrm{m}), 6.59(1 \mathrm{H}, \mathrm{s}), 1.95-1.89$ $(1 \mathrm{H}, \mathrm{m}), 1.12-1.04(2 \mathrm{H}, \mathrm{m}), 0.85-0.78(2 \mathrm{H}, \mathrm{m}) ;{ }^{13} \mathrm{C}$ NMR $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 165.1,162.4,155.5,150.6,134.7,130.3$, 124.8, 123.1, 118.2, 117.6, 112.4, 109.8, 103.6, 16.5, 10.7; IR (KBr) 3394, 3069, 1663, 1563, 1422, 1333, 1276, 1207, 1080, 986, $759 \mathrm{~cm}^{-1}$; HRMS $\mathrm{m} / \mathrm{z}\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{16} \mathrm{H}_{12} \mathrm{O}_{3}: 252.0786$. Found: 252.0785.
9-Cyclopropyl-7-hydroxy-8-phenyl-6H-benzo[c]chromen-6-one (45). Reaction of $\mathbf{1 m}(188 \mathrm{mg}, 1.0 \mathrm{mmol})$ and $\beta$-ketoester 2 c ( $288 \mathrm{mg}, 1.5 \mathrm{mmol}$ ) using $\mathrm{Cs}_{2} \mathrm{CO}_{3}(650 \mathrm{mg}, 2.0 \mathrm{mmol})$ afforded 45 ( $200 \mathrm{mg}, 61 \%$ ) as a solid: mp 187-190 ${ }^{\circ} \mathrm{C}$; ${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 11.60(1 \mathrm{H}, \mathrm{s}), 7.99(1 \mathrm{H}, \mathrm{d}, J=7.2 \mathrm{~Hz})$, 7.51-7.31 (8H, m), $7.03(1 \mathrm{H}, \mathrm{s}), 1.83-1.76(1 \mathrm{H}, \mathrm{m}), 1.00-0.92$ $(2 \mathrm{H}, \mathrm{m}), 0.90-0.84(2 \mathrm{H}, \mathrm{m}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 165.5$, 159.4, 152.8, 150.6, 135.3, 133.8, 130.3, 130.0, 128.3, 127.5, $124.9,122.9,118.3,117.6,106.2,103.5,14.6,10.9$; IR (KBr) 3449, 3048, 1661, 1614, 1548, 1405, 1273, 1163, $760 \mathrm{~cm}^{-1}$; HRMS m/z $\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{22} \mathrm{H}_{16} \mathrm{O}_{3}: 328.1099$. Found: 328.1100 .

## General procedure for the synthesis of terphenyls (49-54)

To a solution of $\mathrm{KOH}(2.0 \mathrm{mmol})$ in DMSO $(3.5 \mathrm{~mL})$ and water $(0.5 \mathrm{~mL}), \mathrm{CH}_{3} \mathrm{I}(2.0 \mathrm{mmol})$ and benzo $[c]$ chromen-6-ones $(0.4 \mathrm{mmol})$ were added and the reaction mixture was stirred at
room temperature for $1-2 \mathrm{~h}$ (progress of reaction was monitored by thin layer chromatography). The reaction mixture was extracted with ethyl acetate and evaporated in a rotary evaporator under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the products. Characterization data for all synthesized terphenyls 49-54 are as follows.

Methyl $2^{\prime \prime}, 5^{\prime}$ 'dimethoxy-2',6'-dimethyl-[1,1':3',1"-terphenyl]-4'-carboxylate (49). Reaction of $20(126 \mathrm{mg}, 0.4 \mathrm{mmol})$ and methyl iodide ( $284 \mathrm{mg}, 2.0 \mathrm{mmol}$ ) using KOH ( 112 mg , 2.0 mmol ) afforded 49 ( $105 \mathrm{mg}, 70 \%$ ) as a solid: mp 99-101 ${ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 7.45-7.39 ( $2 \mathrm{H}, \mathrm{m}$ ), 7.35-7.26 ( $2 \mathrm{H}, \mathrm{m}$ ), 7.20-7.17 ( $1 \mathrm{H}, \mathrm{m}$ ), 7.13-7.09 ( $2 \mathrm{H}, \mathrm{m}$ ), 6.96-6.90 ( $2 \mathrm{H}, \mathrm{m}$ ), $3.82(3 \mathrm{H}, \mathrm{s}), 3.76(3 \mathrm{H}, \mathrm{s}), 3.48(3 \mathrm{H}, \mathrm{s}), 1.97$ $(3 \mathrm{H}, \mathrm{s}), 1.66(3 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 168.4,156.9$, 152.7 , 144.6, 140.9, 134.6, 132.2, 131.2, 130.8, 128.9, 128.4, 128.1, 128.0, 126.8, 126.3, 120.2, 110.6, 62.1, 56.3, 51.6, 17.9, 14.0; IR ( KBr ) 3048, 1680, 1612, 1548, 1405, 1273, 1163, $768 \mathrm{~cm}^{-1}$; HRMS $\mathrm{m} / \mathrm{z}\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{24} \mathrm{H}_{24} \mathrm{O}_{4}$ : 376.1675. Found: 376.1677.

Methyl $5^{\prime \prime}$-bromo-2", $5^{\prime}$-dimethoxy- $6^{\prime}$-methyl-[1, $1^{\prime}: 3^{\prime}, 1^{\prime \prime}$-terphe-nyl]-4'-carboxylate (50). Reaction of $23(152 \mathrm{mg}, 0.4 \mathrm{mmol})$ and methyl iodide ( $284 \mathrm{mg}, 2.0 \mathrm{mmol}$ ) using $\mathrm{KOH}(112 \mathrm{mg}$, 2.0 mmol ) afforded $50(149 \mathrm{mg}, 85 \%)$ as a solid: $\mathrm{mp} 83-85{ }^{\circ} \mathrm{C}$; ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.43-7.30(7 \mathrm{H}, \mathrm{m}), 7.00(1 \mathrm{H}, \mathrm{s})$, 6.78-6.74 ( $1 \mathrm{H}, \mathrm{m}$ ), $3.87(3 \mathrm{H}, \mathrm{s}), 3.72(3 \mathrm{H}, \mathrm{s}), 3.67(3 \mathrm{H}, \mathrm{s}), 2.23$ $(3 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 167.7, 156.2, 155.3, 145.3, $140.6,134.0,133.1,131.4,131.0,129.2,129.0,128.1,127.6$, 127.2, 126.6, 112.6, 112.0, 61.8, 55.5, 51.7, 13.6; IR (KBr) 3018, 1712, 1614, 1548, 1405, 1273, 1163, $749 \mathrm{~cm}^{-1}$; HRMS $m / z\left(\mathrm{M}^{+}\right)$ calcd for $\mathrm{C}_{23} \mathrm{H}_{21} \mathrm{BrO}_{4}: 440.0623$. Found: 440.0622 .

Methyl $\quad 5^{\prime}$-(2,4-dimethoxyphenyl)-3,3'-dimethoxy-[1, $1^{\prime}: 2^{\prime}, 1^{\prime \prime}-$ terphenyl]-4'-carboxylate (51). Reaction of 30 (169 mg, 0.4 mmol ) and methyl iodide ( $284 \mathrm{mg}, 2.0 \mathrm{mmol}$ ) using KOH ( $112 \mathrm{mg}, 2.0 \mathrm{mmol}$ ) afforded $51(164 \mathrm{mg}, 85 \%)$ as a solid: mp $68-70{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.27-7.24(7 \mathrm{H}, \mathrm{m}), 7.09$ $(1 \mathrm{H}, \mathrm{t}, J=8.1 \mathrm{~Hz}), 6.72-7.8(2 \mathrm{H}, \mathrm{d}, J=7.8 \mathrm{~Hz}), 6.57-6.54(3 \mathrm{H}$, $\mathrm{m}), 3.86(3 \mathrm{H}, \mathrm{s}), 3.79(3 \mathrm{H}, \mathrm{s}), 3.70(3 \mathrm{H}, \mathrm{s}), 3.57(3 \mathrm{H}, \mathrm{s}), 3.38$ $(3 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 168.1,160.7,158.8,157.2$, $155.2,143.5,141.8,137.0,136.0,132.9,131.2,130.9,128.7$, $128.6,127.8,127.7,126.7,122.2$, 121.4, 114.9, 113.0, 104.3, 98.4, 61.5, 55.3, 55.0, 51.8; IR (KBr) 2935, 1731, 1608, 1458, 1282, 1159, 1039, $703 \mathrm{~cm}^{-1}$; HRMS m/z $\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{30} \mathrm{H}_{28} \mathrm{O}_{6}: 484.1886$. Found: 384.1886.

Methyl $\quad 5^{\prime}$-bromo-5-(2,5-dimethylthiophen-3-yl)-2',3-dimethoxy-[1,1'-biphenyl]-2-carboxylate (52). Reaction of 39 ( $104 \mathrm{mg}, 0.4 \mathrm{mmol}$ ) and methyl iodide ( $284 \mathrm{mg}, 2.0 \mathrm{mmol}$ ) using $\mathrm{KOH}(112 \mathrm{mg}, 2.0 \mathrm{mmol})$ afforded $52(141 \mathrm{mg}, 80 \%)$ as a solid: mp 140-142 ${ }^{\circ} \mathrm{C}$; ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.40-7.35$ $(2 \mathrm{H}, \mathrm{m}), 6.91(1 \mathrm{H}, \mathrm{s}), 6.89(1 \mathrm{H}, \mathrm{s}), 6.77(1 \mathrm{H}, \mathrm{d}, J=8.7 \mathrm{~Hz}), 6.70$ $(1 \mathrm{H}, \mathrm{s}), 3.88(3 \mathrm{H}, \mathrm{s}), 3.71(3 \mathrm{H}, \mathrm{s}), 3.62(3 \mathrm{H}, \mathrm{s}), 2.44(3 \mathrm{H}, \mathrm{s}), 2.42$ $(3 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 167.5,156.7,155.3,139.4$, 137.2, 137.0, 136.0, 133.0, 132.7, 131.5, 131.1, 126.8, 123.2, 121.1, 112.5, 112.1, 110.7, 56.0, 55.5, 51.7, 15.0, 14.0; IR (KBr) 2939, 2369, 1733, 1599, 1443, 1251, 1108, 1072, 756, $704 \mathrm{~cm}^{-1}$; HRMS $\mathrm{m} / \mathrm{z}\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{22} \mathrm{H}_{21} \mathrm{BrO}_{4} \mathrm{~S}: 460.0344$. Found: 460.0342.

Methyl 2',3-dimethoxy-4-methyl-5-(naphthalen-2-yl)-[1,1'-biphenyl]-2-carboxylate (53). Reaction of 29 (140 mg, 0.4 mmol ) and methyl iodide ( $284 \mathrm{mg}, 2.0 \mathrm{mmol}$ ) using KOH ( $112 \mathrm{mg}, 2.0 \mathrm{mmol}$ ) afforded $53(128 \mathrm{mg}, 78 \%)$ as a solid: mp $113-115{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.81-7.78(3 \mathrm{H}, \mathrm{m})$, $7.72(1 \mathrm{H}, \mathrm{s}), 7.42-7.39(3 \mathrm{H}, \mathrm{m}), 7.25-7.17(2 \mathrm{H}, \mathrm{m}), 7.07(1 \mathrm{H}, \mathrm{s})$, 6.92-6.82 ( $2 \mathrm{H}, \mathrm{m}$ ), $3.83(3 \mathrm{H}, \mathrm{s}), 3.69(3 \mathrm{H}, \mathrm{s}), 3.57(3 \mathrm{H}, \mathrm{s}), 2.2$ $(3 \mathrm{H}, \mathrm{s}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 167.8, 156.0, 155.5, 144.7, 138.2, 135.3, 132.9, 132.2, 130.5, 128.8, 128.7, 128.5, 127.9, 127.8, 127.7, 127.4, 127.3, 127.2, 126.8, 126.0, 125.8, 120.3, 110.3, 61.6, 55.1, 51.5, 13.5; IR (KBr) 3067, 1688, 1618, 1272, $1124,751 \mathrm{~cm}^{-1}$; HRMS $\mathrm{m} / \mathrm{z}\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{27} \mathrm{H}_{24} \mathrm{O}_{4}: 412.1675$. Found: 412.1676.
Methyl $5^{\prime}$ 'cyclopropyl-2,3'-dimethoxy-[1,1':4', $1^{\prime \prime}$-terphenyl]-2'carboxylate (54). Reaction of 45 ( $131 \mathrm{mg}, 0.4 \mathrm{mmol}$ ) and methyl iodide ( $284 \mathrm{mg}, 2.0 \mathrm{mmol}$ ) using KOH ( 112 mg , 2.0 mmol ) afforded $54(133 \mathrm{mg}, 86 \%)$ as a solid: $\mathrm{mp} 85-87^{\circ} \mathrm{C}$; ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.39-7.18(7 \mathrm{H}, \mathrm{m}), 6.94(1 \mathrm{H}, \mathrm{d}, J=$ $7.5 \mathrm{~Hz}), 6.87(1 \mathrm{H}, \mathrm{d}, J=8.4 \mathrm{~Hz}), 6.61(1 \mathrm{H}, \mathrm{s}), 3.71(3 \mathrm{H}, \mathrm{s}), 3.54$ $(3 \mathrm{H}, \mathrm{s}), 3.32(1 \mathrm{H}, \mathrm{s}), 1.68-1.59(1 \mathrm{H}, \mathrm{m}), 0.74-0.61(4 \mathrm{H}, \mathrm{m}) ;{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 167.9,156.1,154.9,144.9,137.4$, 136.3 , 135.0, 130.6, 130.5, 129.2, 129.0, 127.9, 127.0, 125.5, 121.5, 120.5, 110.5, 61.6, 55.3, 51.6, 13.5, 9.8; IR ( KBr ) 3009, 2942, 2842, 1731, 1604, 1544, 1280, 1143, 1022, 757, $706 \mathrm{~cm}^{-1}$; HRMS $\mathrm{m} / \mathrm{z}\left(\mathrm{M}^{+}\right)$calcd for $\mathrm{C}_{25} \mathrm{H}_{24} \mathrm{O}_{4}: 388.1675$. Found: 388.1673.

## Crystal refinement data for compound 26

$\mathrm{C}_{44} \mathrm{H}_{36} \mathrm{O}_{6}, M=660.73$, triclinic, space group $P_{b c a}, a=10.8607$ (14) $\AA, b=10.8607(14) \AA, c=15.2714(19) \AA, V=1644.3(4) \AA^{3}$, $Z=2, T=200(2) \mathrm{K}, \rho_{\text {calcd }}=1.335 \mathrm{mg} \mathrm{m}^{-3}, 2 \theta_{\text {max. }}=26.08$, refinement of 459 parameters on 6463 independent reflections out of 10459 collected reflections $\left(R_{\text {int }}=0.0454\right)$ led to $R_{1}=0.0642$ $[I>2 \sigma(I)], \mathrm{w} R_{2}=0.2354$ (all data) and $S=1.030$ with the largest difference peak and hole of 0.307 and -0.429 e $\AA^{-3}$ respectively.

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