Synthesis of Functionalized Oxaphosphaphenanthrenes and Chromenes via Multicomponent Reactions of Trivalent Phosphorus Nucleophiles

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***Abstract*—Stable derivatives of oxaphosphaphenanthrenes were prepared using multicomponent reactions of dialkyl acetylenedicarboxylate with 3-bromo-2-naphthol in the presence of trimethyl or triphenyl phosphite in good yields. Chromene derivatives were produced by using triethyl phosphite and dialkyl acetylenedicarboxylate in the presence of OH-acids in excellent yields.**

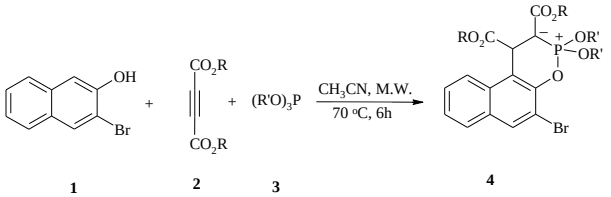
***Index Terms*—One-pot reactions, acetylenic compounds; chromenes, trimethyl phosphate, Triphenyl phosphite.**

I. Introduction

Phosphorus compounds containing P–C bonds are not mostly abundant in nature but they have diverse biological activity and have attracted significant synthetic and pharmacological interest [1], [2]. Besides precious applications, their use in the construction of the unsafe compounds sarin, soman, and VX-type chemical warfare agents (CWAs) is of note [3]. Phosphonates have important applications in flame retardancy [4], [5], organic synthesis [6], and biological applications [2], [7]. Also, phosphonates have been used as substitutes of the corresponding esters and acids of high biological activity [8], [9] and as suitable probes for designing antibodies on the basis of transition state models. A large number of methods have appeared describing novel syntheses of organophosphorus compounds [10]-[13]. In this research another class of synthesized compounds is chromenes. Chromenes have attracted substantial attention due to their biological activity and their presence in a diversity of significant natural products [14]. Hence, we describe herein the reaction of dialkyl acetylenedicarboxylate with a trivalent phosphorus nucleophile such as trimethyl phosphite, triethyl phosphite, or triphenyl phosphite in the presence of OH-acids.

II. Result and Disscussion

The reaction of dialkyl acetylenedicarboxylate, 3-bromo-2-naphthol and trimethyl or triphenyl phosphite leads to 3-bromo-4*H*-1-oxa- phosphaphenanthrene-3,4-dicarboxylate derivatives 4 in excellent yields [13] (Fig. 1).



2, 3, 4	R	R'	Yield (%) of 4
a	Me	Ph	87
b	Et	Ph	78
c	*iso*-pro	Ph	75
d	Me	Me	90
e	Et	Me	85
f	*iso*-pro	Me	78

Fig. 1. Reaction of activated acetylene, 3-bromo-2-naphthol and trimethyl or triphenyl phosphite.

The structures of 4a-4f were decided on the basis of their ^{1}H, ^{13}C, and ^{31}P NMR spectra, IR spectra, elemental analyses, and mass spectrometric data. The ^{1}H NMR spectrum of 4a in $CDCl_3$ shows two singlets for methoxy protons at 3.25 and 3.82 ppm and one doublets at δ = 5.54 ($^{3}J_{PH}$ = 27.6 Hz), for the methine proton, along with multiplets at δ = 6.85-9.12 for the aromatic protons. The presence of an ylide ester group in 4a stabilizes by the observation of strong low-frequency carbonyl absorption at 1665 cm^{-1} in the IR spectrum [15]. The other ester carbonyl absorption in 4a appears at 1723 cm^{-1}. The ^{13}C NMR spectrum consisted characteristic carbonyl resonances at δ = 167.6 (d, $^{2}J_{PC}$ = 16.8 Hz), and 174.5 ppm clearly, whereas the ylide carbon atom displays resonances at δ = 42.0 (d, $^{1}J_{PC}$ = 232 Hz) ppm. The observed $^{1}J_{CP}$ values are typical of an α-ylide ester [16]. The ^{31}P NMR signal was found at δ = 42.4 ppm.

Although the mechanism of this reaction has not been established, a plausible rationalization can be advanced to explain product formation (Fig. 2). On the basis of phosphorus nucleophiles chemistry [11], [17], it is reasonable to presume that ylide 4 results from initial addition of the phosphite to the activated acetylenic compounds and following protonation of the reactive 1:1 adduct, followed by attack of carbon atom of the anion of 3-bromo-2-naphthol 6 to cation 5 to generate ylide 7 which isomerises under the reaction conditions employed to produce the oxaphosphorane 8. Elimination of ROH from 8 leads to product 4.

The reaction between triethyl phosphite 9, dialkyl acetylenedicarboxylate 2 and 3-bromo-2-naphthol 1 quantitatively generate product 10 (Fig. 3).

The IR spectrum of 10a exhibited the ester and lactone carbonyl groups at 1715 and 1758 cm^{-1} respectively. The ^{1}H

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NMR spectrum of 10a showed a doublet doublet at δ = 2.85 ($^2J_{HH}$ = 15.4 Hz, $^3J_{HH}$ = 7.2 Hz) for one of the methylene protons. The other methylene proton displayed a doublet at δ = 3.28 ($^2J_{HH}$ = 15.4 Hz) ppm. The methine proton showed a doublet at δ = 4.64 ($^3J_{HH}$ = 7.3 Hz) ppm. The coupling constants monitord for this AMX system are reliable with a conformation in which the H-C-C-H dihedral angles for the CH-CH_2 moiety are expected to be about 90 ° and 30 °[15]. The ^{13}C NMR spectrum of 10a displayed 15 distinct resonances in agreement with the proposed structure.

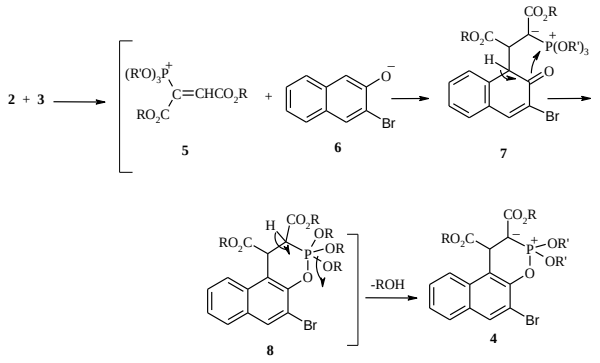
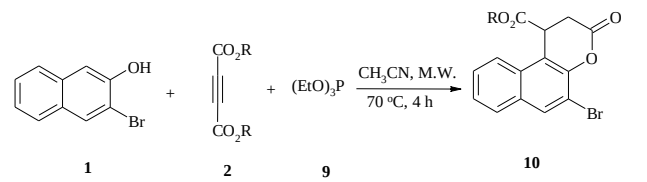


Fig. 2. Proposed mechanism for the formation of 4.



2, 10	R	Yield (%) of 10
a	Me	90
b	Et	85
c	^{t}Bu	78

Fig. 3. Reaction of triethyl phosphite, activated acetylenes and 3-bromo-2-naphthol.

A possible mechanism for the formation of compound 10 is showed in Fig. 4. The oxaphosphorane 13 is formed in similar steps shown for oxaphosphorane 8 in Fig. 2. However, since the ethoxide anion is a weaker living group, cleavage of the phosphorus-oxygen bond of the 3-bromo-2-naphthol residue become favorable, giving dialkyl succinate 16. Lactonization of this hydroxy-ester gave product 10.

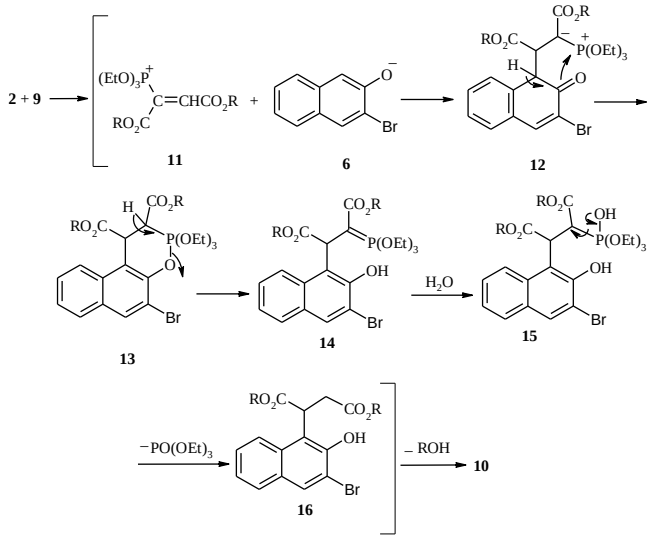


Fig. 4. Proposed mechanism for the formation of 10.

III. Conclusion

In conclusion, we found that the reaction of activated acetylenic compounds with trimethyl phosphite, triethyl phosphite or triphenyl phosphite in the presence of 3-bromo-2-naphthol or 4-hydroxycumarin leads to a facile synthesis of some functionalized oxaphosphaphenanthrenes and chromenes under microwave conditions without using any catalyst. These reactions were performed in a lab type microwave (in a type of MICROSYNTH from Mylestone Company) system and used microwave irradiation as green source energy for synthesis of heterocyclic compounds.

IV. Experimental

Melting points were measured on an Electrothermal 9100 aparatus. Elemental analyses for the C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. Mass spectra were recorded on a FINNIGAN-MATT 8430 spectrometer operating at an ionization potential of 70 eV. IR spectra were measured on a Shimadzu IR-460 spectrometer. ^{1}H, ^{13}C, and ^{31}P spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500.1, 125.8, and 202.4 MHz, respectively. ^{1}H, ^{13}C, and ^{31}P spectra were obtained for solutions in $CDCl_3$ using TMS as internal standard or 85% H_3PO_4 as external standard. All the chemicals used in this work were purchased from Fluka (Buchs, Switzerland) and are used without further purification.

General procedure for preparation of compounds 4.

To a magnetically stirred solution of dialkyl acethylenedicarboxylate 2 (2 mmol) and 3-bromo-2-naphthol 1 (2 mmol) in 20 cm^3 CH_3CN was added triphenyl phosphite or trimethyl phosphite 3 (2 mmol) under microwave conditions (In power of 800 w and T=70^{o}C). The reaction mixture was then stirred for 6h. After completion of reaction (monitored by TLC), the mixture of reaction was purified by preparative TLC on silica gel column chromatography (Merck 230-400 mesh) using n-hexane-EtOAc as eluent to give compound 4.

Dimethyl 2,2-diphenoxy-3-bromo-4H-1-oxa-phospha phenanthrene-3,4-dicarboxylate (4a).

White powder, m.p. 162-64 ℃, 1.00 g, yield 87%. IR (KBr) (ν_{max}/cm^{-1}): 1665, and 1723 cm^{-1}. Anal. Calcd for $C_{28}H_{22}BrO_7P$ (581.35): C, 57.85; H, 3.81. Found: C, 57.78; H, 3.76%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.25 (3 H, s, MeO), 3.82 (3 H, s, MeO), 5.54 (1 H, d, $^3J_{HP}$ = 27.6 Hz, CH), 6.85-9.12 (15 H, m, 15 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 42.0 (d, $^1J_{CP}$ = 232 Hz, C), 42.4 (d, $^2J_{CP}$ = 8.5 Hz, CH), 50.4 (MeO), 52.2 (OMe), 120.7 (d, $^3J_{CP}$ 5.2 Hz, 2 CH), 121.0 (d, $^3J_{PC}$ 9.6 Hz, C), 121.7 (d, $^3J_{PC}$ 4.6 Hz, 2 CH), 124.3 (CH), 125.7 (CH), 126.2 (CH), 126.5 (CH), 127.6 (CH), 128.5 (CH), 130.0 (m, 4 CH), 130.4 (CH), 131.3 (C), 131.8 (C), 132.2 (C), 148.5 (d $^2J_{PC}$ 9.2 Hz, C), 150.2 (m, 2 C), 167.6 (d $^2J_{PC}$ 16.8 Hz, C=O), 174.5 (C=O). ^{31}P NMR (202 MHz, $CDCl_3$): δ 42.4.

Diethyl 2,2-diphenoxy-3-bromo-4H-1-oxa-phospha phenanthrene Z-3,4-dicarboxylate (4b).

Pale yellow powder, m.p. 170-172 ℃, 0.95 g, yield 78%. IR (KBr) (ν_{max}/cm^{-1}): 1670, and 1728 cm^{-1}. Anal. Calcd for $C_{30}H_{26}BrO_7P$ (609.41): C, 59.13; H, 4.30. Found: C, 59.26; H, 4.38%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.32 (3 H, t, $^3J_{HH}$ = 7.4,

Me), 1.37 (3 H, t, $^3J_{HH}$ = 7.3, Me), 4.22 (2 H, q, $^3J_{HH}$ = 7.4, CH_2O), 4.28 (2 H, q, $^3J_{HH}$ = 7.4, CH_2O), 5.58 (1 H, d, $^3J_{HP}$ = 28.0 Hz, CH), 6.82-9.10 (15 H, m, 15 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 13.8 (Me), 14.2 (Me), 42.2 (d, $^1J_{CP}$ = 230 Hz, C), 42.5 (d, $^2J_{CP}$ = 8.7 Hz, CH), 61.7 (CH_2O), 62.3 (CH_2O), 121.2 (d, $^3J_{CP}$ 5.8 Hz, 2 CH), 121.4 (d, $^3J_{PC}$ 10.4 Hz, C), 122.3 (d, $^3J_{PC}$ 5.5 Hz, 2 CH), 124.8 (CH), 126.0 (CH), 126.5 (CH), 127.2 (CH), 127.8 (CH), 129.2 (CH), 130.4 (m, 4 CH), 130.7 (CH), 131.6 (C), 132.2 (C), 132.7 (C), 149.0 (d $^2J_{PC}$ 9.5 Hz, C), 150.8 (m, 2 C), 168.0 (d $^2J_{PC}$ 16.2 Hz, C=O), 174.8 (C=O). ^{31}P NMR (202 MHz, $CDCl_3$): δ 42.5.

Diisopropyl 2,2-diphenoxy-3-bromo-4H-1-oxa-phospha phenanthrene-3,4-dicarboxylate (4c).

Pale Yellow powder, m.p. 182-184 ℃, 0.90 g, yield 75%. IR (KBr) (ν_{max}/cm^{-1}): 1674, and 1735 cm^{-1}. Anal. Calcd for $C_{32}H_{30}BrO_7P$ (637.46): C, 60.29; H, 4.74. Found: C, 60.18; H, 4.65%. ^{1}H NMR (500 MHz, $CDCl_3$): δ= 1.35 (6 H, d, $^3J_{HH}$ = 6.5 Hz, 2 CH_3), 1.42 (6 H, d, $^3J_{HH}$ = 6.8 Hz, 2 CH_3), 5.28-5.36 (1 H, m, CH), 5.38-5.44 (1 H, m, CH), 5.62 (1 H, d, $^3J_{HP}$ = 28.4 Hz, CH), 6.85-9.15 (15 H, m, 15 CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 21.6 (2 CH_3), 22.3 (2 CH_3), 42.6 (d, $^1J_{CP}$ = 234.5 Hz, C), 42.8 (d, $^2J_{CP}$ = 9.3 Hz, CH), 68.8 (*C*HMe_2), 70.2 (*C*HMe_2), 121.6 (d, $^3J_{CP}$ 6.0 Hz, 2 CH), 122.0 (d, $^3J_{PC}$ 10.5 Hz, C), 122.5 (d, $^3J_{PC}$ 5.8 Hz, 2 CH), 125.2 (CH), 126.7 (CH), 127.3 (CH), 127.6 (CH), 128.4 (CH), 129.5 (CH), 130.8 (m, 4 CH), 131.2 (CH), 132.3 (C), 132.8 (C), 133.4 (C), 149.4 (d $^2J_{PC}$ 9.8 Hz, C), 151. (m, 2 C), 168.6 (d $^2J_{PC}$ 15.8 Hz, C=O), 175.5 (C=O). ^{31}P NMR (202 MHz, $CDCl_3$): δ 43.2.

Dimethyl 2,2-dimethoxy-3-bromo-4H-1-oxa-phospha phenanthrene-3,4-dicarboxylate (4d).

White crystals, m.p. 132-134 ℃, 0.64 g, yield 90%. IR (KBr) (ν_{max}/cm^{-1}): 1650, and 1727 cm^{-1}. Anal. Calcd for $C_{18}H_{18}BrO_7P$ (457.21): C, 47.29; H, 3.97. Found: C, 47.34; H, 4.03%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.62 (3 H, s, MeO), 3.75 (3 H, s, MeO), 3.78 (3 H, d $^3J_{PH}$ 13.5 Hz, MeO), 3.97 (3 H, d $^3J_{PH}$ 13.5 Hz, MeO), 5.67 (1 H, d $^3J_{HP}$ 31.7 Hz, CH), 7.45 (1 H, t, $^3J_{HH}$ 9.4 Hz, CH), 7.62 (1 H, t, $^3J_{HH}$ 9.4 Hz), 7.82 (1 H, d $^3J_{HH}$ 9.6 Hz, CH), 7.87 (1 H, d $^3J_{HH}$ 9.6 Hz, CH), 8.12 (1 H, s, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 39.4 (d, $^1J_{CP}$ 225.2 Hz, C), 41.6 (d, $^2J_{CP}$ 9.4 Hz, CH), 50.4 (MeO), 52.3 (MeO), 55.6 (d, $^2J_{PC}$ 6.4 Hz, P-OMe), 55.7 (d, $^2J_{PC}$ 6.4 Hz, P-OMe), 118.4 (d, $^3J_{PC}$ 6.8 Hz, C), 121.4 (d, $^3J_{PC}$ 9.5 Hz, C), 124.6 (CH), 125.5 (CH), 127.4 (CH), 128.6 (CH), 130.0 (CH), 131.4 (C), 131.7 (C), 149.2 (d $^2J_{PC}$ 8.4 Hz, C-O), 169.6 (d $^2J_{PC}$ 18.4 Hz, C=O), 175.2 (C=O). ^{31}P NMR (202 MHz, $CDCl_3$): δ 42.8.

Diethyl 2,2-dimethoxy-3-bromo-4H-1-oxa-phospha phenanthrene-3,4-dicarboxylate (4e).

Pale yellow powder, m.p. 136-138 ℃, 0.82 g, yield 85%. IR (KBr) (ν_{max}/cm^{-1}): 1656, and 1735 cm^{-1}. Anal. Calcd for $C_{20}H_{22}BrO_7P$ (485.27): C, 49.50; H, 4.57. Found: C, 49.62; H, 4.67%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.28 (3 H, t, $^3J_{HH}$ = 7.2, Me), 1.34 (3 H, t, $^3J_{HH}$ = 7.2, Me), 4.18 (2 H, q, $^3J_{HH}$ = 7.2, CH_2O), 4.25 (2 H, q, $^3J_{HH}$ = 7.2, CH_2O), 5.63 (1 H, d $^3J_{HP}$ 32.0 Hz, CH), 7.52 (1 H, t, $^3J_{HH}$ 9.8 Hz, CH), 7.67 (1 H, t, $^3J_{HH}$ 9.7 Hz), 7.86 (1 H, d $^3J_{HH}$ 10.2 Hz, CH), 7.93 (1 H, d $^3J_{HH}$ 10.2 Hz, CH), 8.08 (1 H, s, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 13.8 (Me), 14.3 (Me), 39.6 (d, $^1J_{CP}$ 226.4 Hz, C), 42.0 (d, $^2J_{CP}$ 9.8 Hz, CH), 56.2 (d, $^2J_{PC}$ 7.2 Hz, P-OMe), 56.5 (d, $^2J_{PC}$ 7.2 Hz, P-OMe), 61.4 (CH_2O), 62.3 (CH_2O), 119.2 (d, $^3J_{PC}$ 7.4 Hz, C), 121.8 (d, $^3J_{PC}$ 10.3 Hz, C), 125.2 (CH), 125.7 (CH), 127.9 (CH), 129.2 (CH), 130.4 (CH), 131.8 (C), 132.2 (C), 150.2 (d $^2J_{PC}$ 8.2 Hz, C-O), 170.4 (d $^2J_{PC}$ 18.6 Hz, C=O), 175.8 (C=O). ^{31}P NMR (202 MHz, $CDCl_3$): δ 43.2.

Diisopropyl 2,2-dimethoxy-3-bromo-4H-1-oxa-phospha phenanthrene-3,4-dicarboxylate (4f).

Yellow powder, m.p. 145-147 ℃, 0.80 g, yield 78%. IR (KBr) (ν_{max}/cm^{-1}): 1657 and 1736 cm^{-1}. Anal. Calcd for $C_{22}H_{26}BrO_7P$ (513.32): C, 51.48; H, 5.11. Found: C, 51.54; H, 5.18%. ^{1}H NMR (500 MHz, $CDCl_3$): δ= 1.35 (6 H, d, $^3J_{HH}$ = 7.0 Hz, 2 CH_3), 1.44 (6 H, d, $^3J_{HH}$ = 7.0 Hz, 2 CH_3), 5.32-5.40 (1 H, m, CH), 5.44-5.53 (1 H, m, CH), 5.67 (1 H, d $^3J_{HP}$ 31.8 Hz, CH), 7.55 (1 H, t, $^3J_{HH}$ 10.2 Hz, CH), 7.72 (1 H, t, $^3J_{HH}$ 10.5 Hz), 7.92 (1 H, d $^3J_{HH}$ 10.5 Hz, CH), 7.98 (1 H, d $^3J_{HH}$ 10.6 Hz, CH), 8.05 (1 H, s, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 21.7 (2 CH_3), 22.5 (2 CH_3), 40.2 (d, $^1J_{CP}$ 226.8 Hz, C), 42.5 (d, $^2J_{CP}$ 9.8 Hz, CH), 56.4 (d, $^2J_{PC}$ 7.0 Hz, P-OMe), 56.7 (d, $^2J_{PC}$ 7.0 Hz, P-OMe), 68.7 (*C*HMe_2), 70.4 (*C*HMe_2), 119.5 (d, $^3J_{PC}$ 6.8 Hz, C), 122.0 (d, $^3J_{PC}$ 9.7 Hz, C), 124.8 (CH), 125.3 (CH), 128.2 (CH), 129.4 (CH), 130.8 (CH), 132.3 (C), 132.7 (C), 150.6 (d $^2J_{PC}$ 8.5 Hz, C-O), 170.6 (d $^2J_{PC}$ 17.8 Hz, C=O), 176.3 (C=O). ^{31}P NMR (202 MHz, $CDCl_3$): δ 43.4.

General procedure for preparation of compounds 10.

To a magnetically stirred solution of dialkyl acethylenedicarboxylate 2 (2 mmol) and 3-bromo-2-naphthol 1 (2 mmol) in 20 cm^3 CH_3CN was added triethyl phosphate 9 (2 mmol) under microwave conditions (In power of 800 w and T=70^{o}C). The reaction mixture was then stirred for 4 h. After completion of reaction (monitored by TLC), the mixture of reaction was purified by preparative TLC on silica gel column chromatography (Merck 230-400 mesh) using *n*-hexane-EtOAc as eluent to give compound 10.

Methyl 5-bromo-3-oxo-2,3-dihydro-1H-benzo[f]chromene-1-carboxylate (10a).

White powder, m.p. 158-160 ℃, 0.60 g, yield 90%. IR (KBr) (ν_{max}/cm^{-1}): 1715, and 1758 cm^{-1}. Anal. Calcd for $C_{15}H_{11}BrO_4$ (335.15): C, 53.76; H, 3.31. Found: C, 53.72; H, 3.42%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.85 (1 H, dd $^2J_{HH}$ 15.4 Hz $^3J_{HH}$ 7.2 Hz, HCH), 3.28 (1 H, d $^2J_{HH}$ 15.4 Hz, HCH), 3.72 (3 H, s, MeO), 4.64 (1 H, d $^3J_{HH}$ 7.3 Hz, CH), 7.52 (1 H, t, $^3J_{HH}$ 7.8 Hz, CH), 7.60 (1 H, t, $^3J_{HH}$ 8.2 Hz, CH), 7.75 (1 H, d $^3J_{HH}$ 8.2 Hz, CH), 7.83 (1 H, s, CH), 8.35 (1 H, $^3J_{HH}$ 8.7 Hz, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 31.6 (CH_2), 38.2 (CH), 52.8 (MeO), 112.6 (C), 114.3 (C), 123.3 (CH), 125.7 (CH), 128.3 (CH), 128.8 (CH), 131.4 (CH), 131.9 (C), 132.3 (C), 150.6 (C), 166.5 (C=O), 172.4 (C=O). MS, *m/z* (%): 335 (M^+, 15), 304 (48), 207 (68), 128 (76), 31 (100).

Ethyl 5-bromo-3-oxo-2,3-dihydro-1H-benzo[f]chromene-1-carboxylate (10b).

White powder, m.p. 165-167 ℃, 0.60 g, yield 85%. IR (KBr) (ν_{max}/cm^{-1}): 1718, and 1755 cm^{-1}. Anal. Calcd for $C_{16}H_{13}BrO_4$ (349.18): C, 55.04; H, 3.75. Found: C, 55.15; H, 3.83%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.32 (3 H, t, $^3J_{HH}$ = 7.4, Me), 2.87 (1 H, dd $^2J_{HH}$ 15.6 Hz $^3J_{HH}$ 7.2 Hz, HCH), 3.34 (1 H, d $^2J_{HH}$ 15.4 Hz, HCH), 4.25 (2 H, q, $^3J_{HH}$ 7.2 Hz, CH_2O), 4.65 (1 H, d $^3J_{HH}$ 7.2 Hz, CH), 7.58 (1 H, t, $^3J_{HH}$ 7.6 Hz, CH), 7.60 (1 H, t, $^3J_{HH}$ 7.8 Hz, CH), 7.78 (1 H, d $^3J_{HH}$ 8.3 Hz, CH), 7.85 (1 H, s, CH), 8.37 (1 H, $^3J_{HH}$ 8.5 Hz, CH). ^{13}C NMR (125.7

MHz, $CDCl_3$): δ 13.7 (Me), 32.0 (CH_2), 38.4 (CH), 61.6 (CH_2O), 113.2 (C), 114.7 (C), 123.6 (CH), 126.4 (CH), 128.7 (CH), 129.4 (CH), 131.6 (CH), 132.0 (C), 132.7 (C), 151.3 (C), 166.8 (C=O), 172.6 (C=O).

Tert-butyl 5-bromo-3-oxo-2,3-dihydro-1H-benzo[f] chromene-1-carboxylate (10c).

White powder, m.p. 178-180 ℃, 0.59 g, yield 78%. IR (KBr) (ν_{max}/cm^{-1}): 1716, and 1762 cm^{-1}. Anal. Calcd for $C_{18}H_{17}BrO_4$ (377.23): C, 57.31; H, 4.54. Found: C, 57.38; H, 4.62%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.65 (9 H, s, 3 CH_3), 2.92 (1 H, dd $^2J_{HH}$ 16.2 Hz $^3J_{HH}$ 7.4 Hz, HCH), 3.27 (1 H, d $^2J_{HH}$ 15.4 Hz, HCH), 4.67 (1 H, d $^3J_{HH}$ 7.5 Hz, CH), 7.63 (1 H, t, $^3J_{HH}$ 7.7 Hz, CH), 7.68 (1 H, t, $^3J_{HH}$ 8.7 Hz, CH), 7.82 (1 H, d $^3J_{HH}$ 8.3 Hz, CH), 7.86 (1 H, s, CH), 8.37 (1 H, $^3J_{HH}$ 8.6 Hz, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 28.7 (3 CH_3), 32.4 (CH_2), 38.5 (CH), 53.2 (MeO), 83.5 (CMe_3), 113.4 (C), 115.2 (C), 124.0 (CH), 126.2 (CH), 128.5 (CH), 129.2 (CH), 131.8 (CH), 132.3 (C), 132.6 (C), 151.0 (C), 167.4 (C=O), 173.5 (C=O).

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