Synthesis of novel benzochromenes using triarylphosphines, alkyl X-phenylpropiolates and 2-hydroxy-1-naphthaldehyde

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The reactions of a series of alkyl X-phenylpropiolates with 2-hydroxy-1-naphthaldehyde and triphenylphosphine led to benzochromenes in moderate yields. When the reactions were performed in the presence of bis(4-methoxyphenyl)phenylphosphine instead of triphenylphosphine, the rate and yields of the reactions increased. Reaction yields were enhanced for alkyl X-phenylpropiolates when X was an electron-deficient substituent such as CF_3 or Cl, thus showing that the electronic effect of substituents plays an important role in the reactions.

Keywords: 2-hydroxy-1-naphthaldehyde, Wittig reaction, alkyl X-phenylpropiolates, triphenylphosphine, bis(4-methoxyphenyl)phenylphosphine

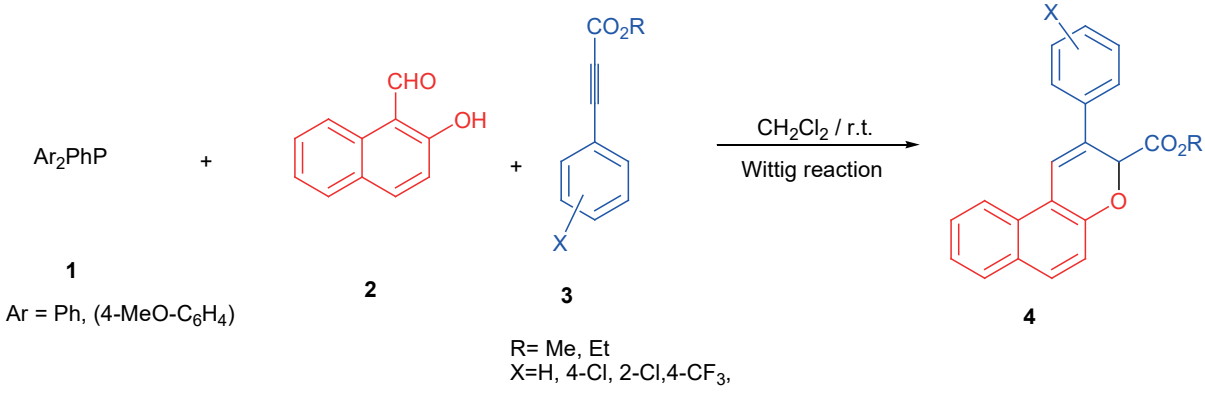
Chromene is a heterocyclic compound consisting of a benzene ring fused to a pyran ring, which is an important structural component in many natural compounds.[1] Synthetic chromene derivatives have important biological activities such as antitumour,[2] antimicrobial,[3] hypotensive,[4] TNF-α inhibitor,[5] antifungal,[6] anticancer[7] and anti-HIV[8] activities. Therefore, the synthesis of novel chromenes is an important subject to be investigated.

Organophosphines have received special attention, and among the phosphines, triphenylphosphine (Ph_3P) has emerged as the reagent of choice.[9] Ph_3P adds to electron-deficient acetylenic compounds such as dimethyl acetylenedicarboxylate (DMAD) to generate a zwitterionic phosphorane derivative.[10] The zwitterionic intermediate can be protonated by ZH acids (Z = O, S, N, C)[10–15] or added to electrophiles.[16–19] The reactions of PPh_3 and 2-hydroxy-1-naphthaldehyde as an OH acid with an acetylenic ester or ketone have been reported that led to benzochromene dervatives.[11,12] In continuation of our studies on the synthesis of novel heterocycles,[13–15] we report a one-pot synthesis of novel benzochromene derivatives from the reactions of triphenylphosphine or bis(4-methoxyphenyl) phenylphosphine and 2-hydroxy-1-naphthaldehyde with alkyl X-phenylpropiolates.

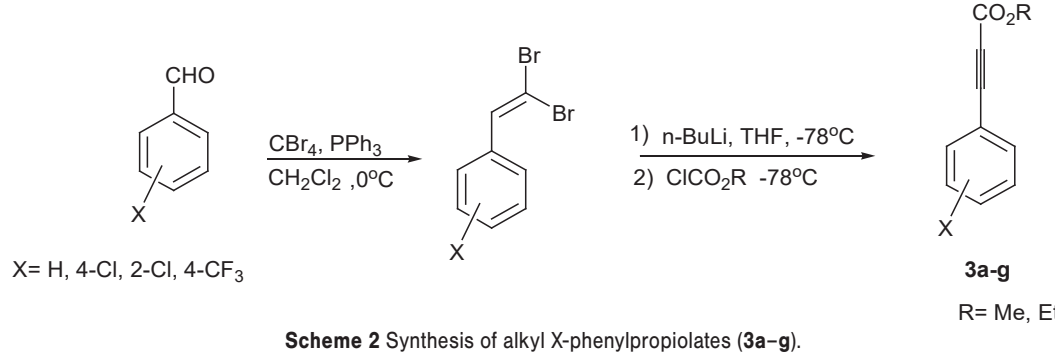
Results and discussion

Previous work by others[11,12] has shown that the reaction of 2-hydroxy-1-naphthaldehyde (**2**) with the addition product of an acetylenedicarboxylate and triphenylphosphine (**1**, Ar = Ph) yields novel benzochromene derivatives. We decided to investigate a similar reaction using various ring-substituted alkyl phenylpropiolates (**3**) in place of the acetylenic diesters (Scheme 1). The seven methyl and ethyl X-phenylpropiolates (**3a–g**) that we needed were prepared *via* the Corey–Fuchs reaction as previously reported (Scheme 2).[20–22]

Initially, compound **3a** was reacted with triphenylphosphine in the presence of 2-hydroxy-1-naphthaldehyde as an OH acid,



Scheme 1 Synthesis of alkyl 2-aryl-3*H*-benzo[*f*]chromene-3-carboxylates (**4a–g**).



Scheme 2 Synthesis of alkyl X-phenylpropiolates (**3a–g**).

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which led to the corresponding product (**4a**) in low yield (32%). To increase the efficiency of the reaction, alkyl X-phenylpropiolates (**3b–g**) containing electron-deficient substituents, such as Cl and CF_3 groups, were prepared and used in the reactions. The results obtained show that the yields of the products increased in the presence of the electron-deficient substituents (Table 1). It seems that the elecrophilicity of alkyl X-phenylpropiolates plays a key role in the reactions (Table 1, entries 2–7 compared with entry 1). However, when alkyl 2,6-dichloro phenylpropiolates (**3**; X = 2,4-Cl_2; R = Me, Et) were used in the reactions, in all cases complex mixtures were obtained without any formation of the corresponding benzochromenes. This might have been due to a steric effect of the two chlorine substituents at *ortho* positions in these alkyl X-phenylpropiolates.

When bis(4-methoxyphenyl) (phenyl) phosphine was used instead of triphenylphosphine in the reactions, the rate and yield increased in all cases (Table 1, column 5 compared with column 4), which could be due to the higher nucleophilicity of its phosphorus atom.

Table 1 Yields of a series of alkyl 2-aryl-3*H*-benzo[*f*]chromene-3-carboxylates (**4a–g**; R= Me, Et; X = H, 4-Cl, 2-Cl, 4-CF_3) prepared from the reaction of 2-hydroxy-1-naphthaldehyde (**2**) with an alkyl X-phenylpropiolate (**3**; R = Me, Et; X = H, 4-Cl, 2-Cl, 4-CF_3) and a triarylphosphine (Ar_2PhP; Ar = Ph, 4-MeO–C_6H_4) (Scheme 1)

Entry	R	X	Yield (%)[a]	Yield (%)[b]	Product[c]
1	Et	H	32	50	**4a**
2	Me	4-Cl	42	64	**4b**
3	Et	4-Cl	43	66	**4c**
4	Me	2-Cl	65	78	**4d**
5	Et	2-Cl	62	77	**4e**
6	Me	4-CF_3	60	75	**4f**
7	Et	4-CF_3	58	73	**4g**

[a]Isolated yields in presence of Ph_3P after 24 h.

[b]Isolated yields in presence of Ph(4-MeO–C_6H_4)$_2$P after 10–12 h.

[c]Reaction conditions: 2-hydroxy-1-naphthaldehyde (**2**) (1 mmol) was added dropwise to a stirred mixture of alkyl X-phenylpropiolate (**3**; R = Me, Et; X = H, 4-Cl, 2-Cl, 4-CF_3) (1 mmol) and triarylphosphine (Ar_2PhP; Ar = Ph, 4-MeO–C_6H_4) (1 mmol) at 0 °C and then stirred at room temperature for 10–24 h.

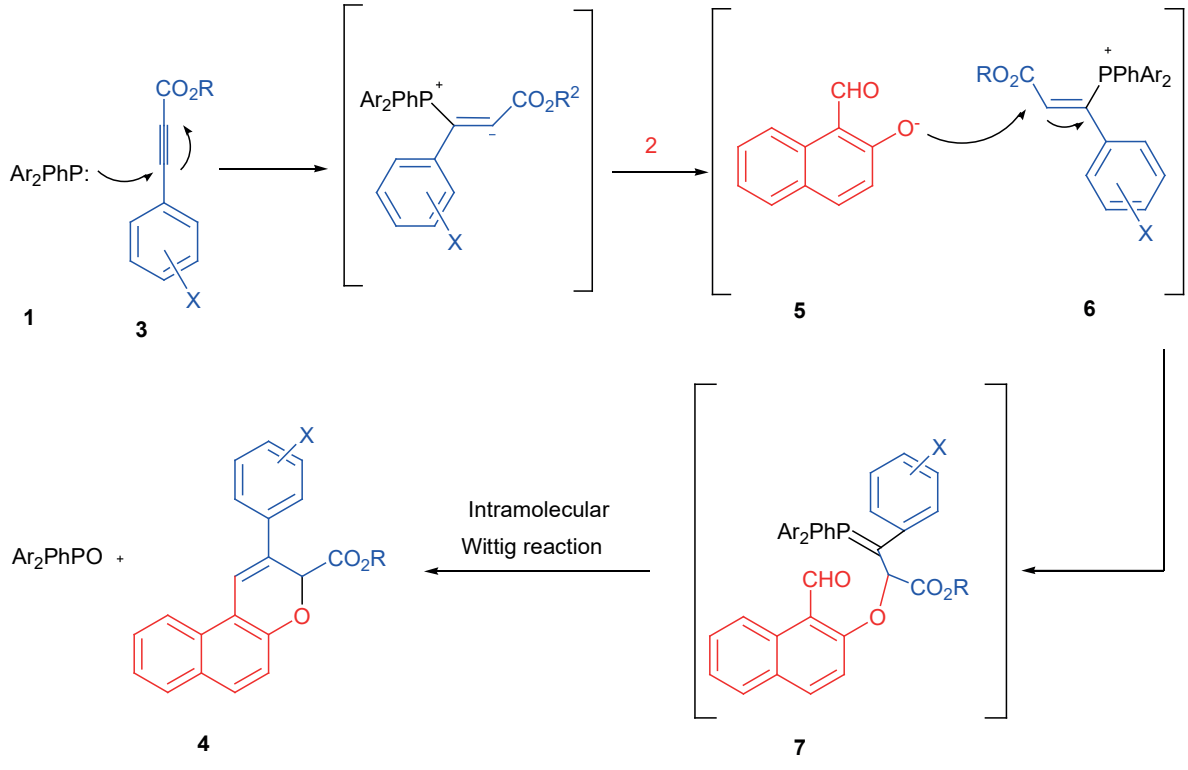
The structures of **4a–g** were deduced by IR, ^{1}H NMR, ^{13}C NMR and mass spectra as well as elemental analyses. The IR spectrum of **4a** displayed a strong absorption band at 1695 cm^{-1} for the carbonyl group. The ^{1}H NMR spectrum of **4a** exhibited a triplet at 1.22 ppm for the methyl group, a quartet at 4.18 ppm for the methylene group (OCH_2) and two singlets at 6.33 and 8.29 ppm for the two CH groups on the pyran ring. The 11 aromatic protons were displayed in the aromatic range (6.96–7.97 ppm). The ^{13}C NMR spectrum of **4a** showed 20 distinct resonances in agreement with the proposed structure. The mass spectrum of **4a** displayed a molecular ion peak at 330 (M^+, 32), which is in agreement with the proposed structure.

The ^{1}H NMR and ^{13}C NMR spectra of **4b–g** were similar to those of **4a** except that their substituents showed characteristic resonances in the appropriate regions of the spectra. The mass spectra of **4b–e** displayed molecular ion peaks M^+ and $M^+ + 2$, due to the existence of the isotopes of the chlorine atom, ^{35}Cl and ^{37}Cl, respectively.

A proposed mechanism is shown in Scheme 3. Addition of triarylphosphine (**1**) to alkyl X-phenylpropiolate (**3**) and subsequent protonation by 2-hydroxy-1-naphthaldehyde (**2**) leads to cationic intermediate **6** and anionic intermediate **5**. Intermediate **5** then performs a Michael addition to cationic intermediate **6** to generate a phosphorus ylide (**7**), which undergoes an intramolecular Wittig reaction to produce 2-aryl-3*H*-benzo[*f*]chromene-3-carboxylate (**4**) and triarylphosphine oxide.

Conclusion

A convenient method for the preparation of a new class of benzochromenes has been achieved by a three-component reaction of triphenylphosphine or bis(4-methoxyphenyl)(phenyl)



Scheme 3 Proposed mechanism of formation of alkyl 2-aryl-3*H*-benzo[*f*]chromene-3-carboxylates (**4**).

phosphine with an alkyl X-phenylpropiolate and 2-hydroxy-1-naphthaldehyde as an OH acid at room temperature. As various substituted alkyl X-phenylpropiolates can be used, a wide variety of benzochromenes can be produced by this method, some of which might display biological activity.

Experimental

Triphenylphosphine and 2-hydroxy-1-naphthaldehyde (**2**) were obtained from Fluka (Buche, Switzerland) and were used without further purification. Solvents were dried before use. Alkyl aryl propiolates (**3a**–**g**) were synthesised according to a reported method.[22] Bis(4-methoxyphenyl)(phenyl)phosphine was prepared *via* a literature method.[23] IR spectra were recorded on a FTIR Bruker Vector 22 spectrometer. Mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating in electron impact mode. Elemental analyses were performed using a Heraeus CHN–O rapid analyser. NMR spectra were obtained on a Brucker Vector 22 spectrometer (^{1}H NMR at 400 MHz, ^{13}C NMR at 100 MHz) in $CDCl_3$ using TMS as an internal standard. Chemical shifts (δ) are given in ppm and coupling constants (*J*) are given in Hz. Melting points were measured on an Electrothermal 9100 apparatus.

Synthesis of benzochromenes **4a**–**g***; general procedure*

A solution of **3a**–**g** (1 mmol) in CH_2Cl_2 (2 mL) was added dropwise to a magnetically stirred solution of phosphine **1** (1 mmol) and 2-hydroxy-1-naphthaldehyde (0.172 g, 1 mmol) in CH_2Cl_2 (5 mL) over 10 min at 0 °C. The reaction mixture was then allowed to warm up to room temperature and stirred for 10–24 h. The solvent was removed under reduced pressure and the residue was purified by silica gel (Merck silica gel, 230–400 mesh) column chromatography using *n*-hexane/ethyl acetate (9:1) as eluent. The solvent was removed under reduced pressure and the products **4a**–**g** were obtained.

*Ethyl 2-phenyl-3*H*-benzo[*f*]chromene-3-carboxylate* (**4a**): Yellow powder; yield 0.106 g (32%); m.p. 109–111 °C; IR (KBr) (cm^{-1}): 3052 (C_{sp_2}–H), 2989 (C_{sp_3}–H), 1695 (C=O), 1630 and 1451 (C=C), 1271 (C_{sp_2}–O), 1199 (C_{sp_3}–O); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (t, 3H, $^3J_{HH}$ = 7.2 Hz, CH_3), 4.18 (q, 2H, $^3J_{HH}$ = 7.2 Hz, OCH_2), 6.33 (s, 1H, CH), 6.96 (d, 1H, $^3J_{HH}$ = 8.0 Hz, CH_{arom}), 7.13–7.14 (m, 3H, $3CH_{arom}$), 7.25 (t, 1H, $^3J_{HH}$ = 8.0 Hz, CH_{arom}), 7.33–7.34 (m, 2H, $2CH_{arom}$), 7.43 (t, 1H, $^3J_{HH}$ = 8.0 Hz, CH_{arom}), 7.6 (d, 1H, $^3J_{HH}$ = 8.0 Hz, CH_{arom}), 7.61 (d, 1H, $^3J_{HH}$ = 8.0 Hz, CH_{arom}), 7.97 (d, 1H, $^3J_{HH}$ = 8.0 Hz, CH_{arom}), 8.29 (s, 1H, CH_{vinyl}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3 (CH_3), 61.0 (OCH_2), 75.0 (CH), 113.4 (C_q), 118.2 (CH), 121.4 (CH), 122.5 (C_q), 124.2 (CH), 127.2 (CH), 127.6 (CH), 128.5 (CH), 128.6 (CH), 128.8 (CH), 129.3 (CH), 129.3 (C_q), 130.7 (C_q), 132.9 (CH), 139.2 (C_q), 153 (C_q), 165.2 (C=O); MS *m*/*z*: 330 (M$^{+\bullet}$, 32), 301 (9), 285 (3), 257 (100), 228 (13). Anal. calcd for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49; found: C, 79.76; H, 5.51%.

*Methyl 2-(4-chlorophenyl)-3*H*-benzo[*f*]chromene-3-carboxylate* (**4b**): Yellow powder; yield 0.147 g (42%); m.p. 118–120 °C; IR (KBr) (cm^{-1}): 3053 (C_{sp_2}–H), 2942 and 2845 (C_{sp_3}–H), 1703 (C=O), 1628 and 1438 (C=C, arom), 1195 (C_{sp_2}–O), 1089 (C_{sp_3}–O); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.86 (s, 3H, OCH_3), 6.4 (s, 1H, CH), 7.08 (d, 1H, $^3J_{HH}$ = 8.4 Hz, CH_{arom}), 7.24 (d, 2H, $^3J_{HH}$ = 8.8 Hz, $2CH_{arom}$), 7.37–7.40 (m, 2H, $2CH_{arom}$), 7.42 (td, 1H, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.2 Hz, CH_{arom}), 7.59 (td, 1H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz, CH_{arom}), 7.77 (d, 2H, $^3J_{HH}$ = 8.8 Hz, $2CH_{arom}$), 8.11 (d, 1H, $^3J_{HH}$ = 8.4 Hz, CH_{arom}), 8.43 (s, 1H, CH_{vinyl}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.1 (OCH_3), 74.1 (CH), 113.3 (C_q), 118.1 (CH), 121.3 (CH), 121.7 (C_q), 124.4 (CH), 127.7 (CH), 128.6 (2CH), 128.7 (2CH), 128.8 (CH), 129.4 (C_q), 129.8 (C_q), 130.6 (C_q), 133.2 (CH), 134.5 (C_q), 137.4 (C_q), 152.7 (C_q), 165.4 (C=O); MS *m*/*z*: 352 (M$^{+\bullet}$ + 2, 26), 350 (M$^{+\bullet}$, 73), 337 (2.5), 335 (8), 321 (1), 319 (3), 293 (33), 291 (100), 239 (22). Anal. calcd for $C_{21}H_{15}ClO_3$: C, 71.90; H, 4.31; found: C, 72.07; H, 4.32%.

*Ethyl 2-(4-chlorophenyl)-3*H*-benzo[*f*]chromene-3-carboxylate* (**4c**): Yellow powder; yield 0.157 g (43%); m.p. 121–123 °C; IR (KBr) (cm^{-1}): 3078 (C_{sp_2}–H), 2921 and 2858 (C_{sp_3}–H), 1695 (C=O), 1639 and 1484 (C=C, arom), 1208 (C_{sp_2}–O), 1095 (C_{sp_3}–O); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.35 (t, 3H, $^3J_{HH}$ = 6.8 Hz, CH_3), 4.28–4.35 (m, 2H, OCH_2), 6.4 (s, 1H, CH), 7.08 (d, 1H, $^3J_{HH}$ = 8.4 Hz, CH_{arom}), 7.24 (d, 2H, $^3J_{HH}$ = 8.4 Hz, $2CH_{arom}$), 7.37–7.4 (m, 2H, $2CH_{arom}$), 7.42 (td, 1H, $^3J_{HH}$ = 6.4 Hz, $^4J_{HH}$ = 0.8 Hz, CH_{arom}), 7.59 (td, 1H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz, CH_{arom}), 7.77 (d, 2H, $^3J_{HH}$ = 8.4 Hz, $2CH_{arom}$), 8.11 (d, 1H, $^3J_{HH}$ = 8.4 Hz, CH_{arom}), 8.41 (s, 1H, CH_{vinyl}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3 (CH_3), 61.1 (OCH_2), 74.2 (CH), 113.3 (C_q), 118.1 (CH), 121.3 (CH), 122.1 (C_q), 124.4 (CH), 127.7 (CH), 128.6 (2CH), 128.7 (2CH), 128.8 (CH), 129.3 (C_q), 129.5 (CH), 130.6 (C_q), 133.1 (CH),134.5 (C_q), 137.6 (C_q), 152.6 (C_q), 165 (C=O); MS *m*/*z*: 366 (M$^{+\bullet}$ + 2, 34), 364 (M$^{+\bullet}$, 100), 337 (5), 335 (16), 321 (1), 319 (3), 293 (35), 291 (100), 253 (12). Anal. calcd for $C_{22}H_{17}O_3Cl$: C, 72.43; H, 4.70; found: C, 72.68; H, 4.72%.

*Methyl 2-(2-chlorophenyl)-3*H*-benzo[*f*]chromene-3-carboxylate* (**4d**): Yellow powder; yield 0.228 g (65%); m.p. 107–109 °C; IR (KBr) (cm^{-1}): 3060 (C_{sp_2}–H), 2942 and 2849 (C_{sp_3}–H), 1712 (C=O), 1632 and 1433 (C=C, arom), 1194 (C_{sp_2}–O), 1043 (C_{sp_3}–O); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.82 (s, 3H, OCH_3), 6.93 (s, 1H, CH), 7.01 (d, 1H, $^3J_{HH}$ = 9.2 Hz, CH_{arom}), 7.07 (t, 1H, $^3J_{HH}$ = 7.6 Hz, CH_{arom}), 7.23 (td, 1H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.6 Hz, CH_{arom}), 7.34 (dd, 1H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.6 Hz, CH_{arom}), 7.42 (t, 1H, $^3J_{HH}$ = 7.6 Hz, CH_{arom}), 7.47 (d, 1H, $^3J_{HH}$ = 8.0 Hz, CH_{arom}), 7.61 (t, 1H, $^3J_{HH}$ = 7.6. Hz, CH_{arom}), 7.73 (d, 1H, $^3J_{HH}$ = 8.8 Hz, CH_{arom}), 7.76 (d, 1H, $^3J_{HH}$ = 8.4 Hz, CH_{arom}), 8.17 (d, 1H, $^3J_{HH}$ = 8.4 Hz, CH_{arom}), 8.57 (s, 1H, CH_{vinyl}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.1 (OCH_3), 71.5 (CH), 113 (C_q), 118.3 (CH), 121.0 (C_q), 121.2 (CH), 124.3 (CH), 126.9 (CH), 127.7 (CH), 128.8 (CH), 129.2 (CH), 129.4 (C_q), 130.3 (2CH), 130.5 (C_q), 130.6 (CH), 133.1 (CH), 134.2 (C_q), 134.9 (C_q), 152.5 (C_q), 165.1 (C=O); MS *m*/*z*: 352 (M$^{+\bullet}$ + 2, 18), 350 (M$^{+\bullet}$, 56), 337 (1.5), 335 (4), 315 (8), 293 (33), 291 (100), 239 (27). Anal. calcd for $C_{21}H_{15}O_3Cl$: C, 71.90; H, 4.31; found: C, 71.64; H, 4.32%.

*Ethyl 2-(2-chlorophenyl)-3*H*-benzo[*f*]chromene-3-carboxylate* (**4e**): Yellow powder; yield 0.246 g (62%); m.p. 110–112 °C; IR (KBr) (cm^{-1}): 3063 (C_{sp_2}–H), 2977 and 2859 (C_{sp_3}–H), 1714 (C=O), 1629 and 1465 (C=C, arom), 1194 (C_{sp_2}–O), 1066 (C_{sp_3}–O); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.3 (t, 3H, $^3J_{HH}$ = 7.2 Hz, CH_3), 4.26 (q, 2H, $^3J_{HH}$ = 7.2 Hz, OCH_2), 6.94 (s, 1H, CH), 7.01 (d, 1H, $^3J_{HH}$ = 8.8 Hz, CH_{arom}), 7.08 (td, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz, CH_{arom}), 7.23 (td, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.6 Hz, CH_{arom}), 7.35 (dd, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.6 Hz, CH_{arom}), 7.42 (td, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 0.8 Hz, CH_{arom}), 7.47 (dd, 1H, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 0.8 Hz, CH_{arom}), 7.61 (td, 1H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz, CH_{arom}), 7.73 (d, 1H, $^3J_{HH}$ = 8.8 Hz, CH_{arom}), 7.77 (d, 1H, $^3J_{HH}$ = 8.0 Hz, CH_{arom}), 8.18 (d, 1H, $^3J_{HH}$ = 8.4 Hz, CH_{arom}), 8.55 (s, 1H, CH_{vinyl}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2 (CH_3), 61 (OCH_2), 71.6 (CH), 112.9 (C_q), 118.3 (CH), 121.2 (CH), 121.6 (C_q), 124.3 (CH), 126.9 (CH), 127.6 (CH), 128.8 (CH), 129.2 (CH), 129.3 (C_q), 130.2 (3CH), 130.5 (C_q), 133 (CH), 134 (C_q), 135.1 (C_q), 152.5 (C_q), 164.7 (C=O);); MS *m*/*z*: 366 (M$^{+\bullet}$ + 2, 25), 364 (M$^{+\bullet}$, 84), 337 (3), 335 (8), 321 (1), 319 (3), 293 (31), 291 (100), 253 (12). Anal. calcd. for $C_{22}H_{17}O_3Cl$: C, 72.43; H, 4.70; found: C, 72.71; H, 4.69%.

*Methyl 2-[4-(trifluoromethyl)phenyl]-3*H*-benzo[*f*]chromene-3-carboxylate* (**4f**): Yellow powder; yield 0.23 g (60%); m.p. 110–113 °C; IR (KBr) (cm^{-1}): 3065(C_{sp_2}–H), 2948 and 2854 (C_{sp_3}–H), 1706 (C=O), 1623 and 1445 (C=C, arom), 1274 (C_{sp_2}–O), 1067 (C_{sp_3}–O); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.88 (s, 3H, OCH_3), 6.48 (s, 1H, CH), 7.11 (d, 1H, $^3J_{HH}$ = 8.4 Hz, CH_{arom}), 7.42 (td, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz, CH_{arom}), 7.53 and 7.57 (4H, AB_q, $^3J_{HH}$ = 8.4 Hz, $4CH_{arom}$), 7.61 (td, 1H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz, CH_{arom}), 7.77 (d, 1H, $^3J_{HH}$ = 8.4 Hz, CH_{arom}), 7.79 (d, H, $^3J_{HH}$ = 8.8 Hz, CH_{arom}), 8.09 (d, 1H, $^3J_{HH}$ = 8.4 Hz, CH_{arom}), 8.45 (s, 1H, CH_{vinyl}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.2 (OCH_3), 74 (CH), 113.3 (C_q), 117.9 (CH), 121.3 (CH), 121.4 (C_q), 123.9 (C_q, q, $^1J_{CF}$ = 272.1 Hz) 124.5 (CH), 125.5 (2CH, q, $^3J_{CF}$ = 3.7 Hz), 127.4 (2CH), 127.8 (CH), 128.8 (CH), 129.4 (C_q), 130.1 (CH), 130.6 (C_q), 130.636(C_q, q, $^2J_{CF}$ = 32.3 Hz) 133.4 (CH), 142.9 (C_q), 152.7 (C_q), 165.4 (C=O); MS *m*/*z*: 384 (M$^{+\bullet}$, 100), 369 (18), 353 (4), 325 (100), 339 (39). Anal. calcd for $C_{22}H_{15}O_3F_3$: C, 68.75; H, 3.93; found: C, 69.01; H, 3.94%.

*Ethyl 2-[4-(trifluoromethyl)phenyl]-3*H*-benzo[*f*]chromene-3-carboxylate* (**4g**): Yellow powder; yield 0.231 g (58%); m.p. 98–100 °C; IR (KBr) (cm^{-1}): 3063 (C_{sp_2}–H), 2932 and 2860 (C_{sp_3}–H), 1695 (C=O), 1625 and 1516 (C=C, arom), 1270 (C_{sp_2}–O), 1123 (C_{sp_3}–O); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37 (t, 3H, $^3J_{HH}$ = 7.2 Hz, CH_3), 4.30–4.37 (m, 2H, OCH_2), 6.49 (s, 1H, CH), 7.12 (d, 1H, $^3J_{HH}$ = 8.4 Hz, CH_{arom}), 7.42 (td, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz, CH_{arom}), 7.53 and 7.57 (4H, AB_q, $^3J_{HH}$ = 8.4 Hz, $4CH_{arom}$), 7.59 (td, 1H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz, CH_{arom}), 7.77 (d, 1H, $^3J_{HH}$ = 8.0 Hz, CH_{arom}), 7.79 (d, H, $^3J_{HH}$ = 7.7 Hz, CH_{arom}), 8.1 (d, 1H, $^3J_{HH}$ = 8.4 Hz, CH_{arom}), 8.43 (s, 1H, CH_{vinyl}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3 (CH_3), 61.2 (CH_3), 74.1 (CH), 113.3 (C_q), 117.9 (CH), 121.3 (CH), 121.8 (C_q), 124.5 (CH), 123.9 (C_q, q, $^1J_{CF}$ = 272.2 Hz) 125.4 (2CH, q, $^3J_{CF}$ = 3.7 Hz), 127.3 (2CH), 127.8 (CH), 128.8 (CH), 129.4 (C_q), 129.4 (C_q), 129.8 (CH), 130.574 (C_q, q, $^2J_{CF}$ = 32.3 Hz) 130.6 (C_q), 133.3 (CH), 143.1 (C_q), 152.7 (C_q), 165.4 (C=O); MS *m/z*: 398 ($M^{+\bullet}$, 100), 369 (19), 353 (2), 325 (100), 353 (16). Anal. calcd for $C_{23}H_{17}O_3F_3$: C, 69.34; H, 4.30; found: C, 69.57; H, 4.28%.

Acknowledgement

We gratefully acknowledge financial support from the Research Council of University of Mazandaran.

Electronic Supplementary Information

The ESI is available through:
http://ingentaconnect.com/content/stl/jcr/2018/00000042/00000004/art00008

Received 12 March 2018; accepted 4 April 2018
Paper 1805310
https://doi.org/10.3184/174751918X15234707524548
Published online: 30 April 2018

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