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Brϕnsted acid catalyzed one-pot condensation of β-naphthol, aldehyde and active methylene substrate: Synthesis of naphthopyrans

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An efficient one-pot condensation of β-naphthol, aldehyde and active methylene substrate is achieved using catalytic amount of phosphomolybdic acid. This multi-component reaction resulted in the synthesis of several naphthopyran derivatives in good yields.

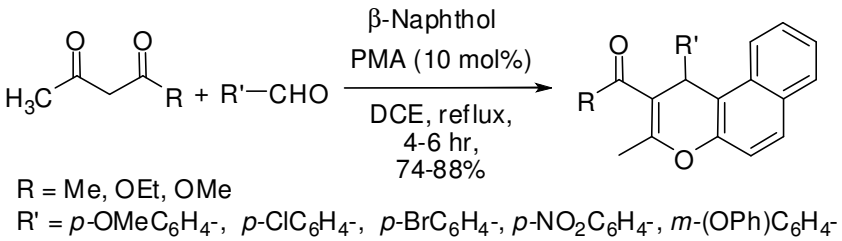
Keywords: Aldehyde, multicomponent, benzopyrans, Brϕnsted acid, Lewis acid

Multicomponent reactions (MCR) continue to attract significant interest due to an important role in the preparation of structurally diverse chemical structures[1]. Benzopyran and benzopyran derived molecules display potent biological and pharmacological activities[2]. Similarly, naphthopyrans, the polyfunctionalized benzopyrans have attracted considerable attention due to their interesting photochromic properties[3] and also their presence in numerous natural products which exhibit potent mutagenic and cytotoxic[4], anticancer[5] and anti-proliferative[6] activities. Even though there are several procedures reported for their synthesis involving Lewis acids[7a,b], to the best of the knowledge there is only one procedure available involving Brϕnsted acid[7c] catalyzed reaction. In continuation to efforts on exploring the Brϕnsted acid, phosphomolybdic acid (PMA) as a reagent/catalyst for several organic transformations[8], it has recently been demonstrated that PMA in combination with SiO_2 can be utilized for multicomponent reactions, wherein new indole derivatives are obtained[9]. Herein is described the synthesis of naphthopyrans by one-pot condensation of β-naphthol, aldehyde and active methylene substrate catalyzed by phosphomolybdic acid (**Scheme I**).

Results and Discussion

Initially, a reaction of anisaldehyde, acetylacetone and β-naphthol was carried out in the presence of PMA-SiO_2 in CH_2Cl_2 at RT. After refluxing the reaction mixture for 12 hr, all the starting materials were consumed to result in a new single product formation. The product was isolated and characterized as the naphthopyran derivative by NMR analysis and also by comparing the data from earlier literature. Interestingly, when PMA alone was used, the reaction was completed in 5 hr (**Table I,** entry 1). This encouraged the efforts for optimizing the reaction conditions. To achieve this goal, a similar transformation was attempted with different concentrations of PMA (0.05, 0.1, 0.5 and 1.0 eq.). It was observed that the concentration of either 0.1 eq. or 0.5 eq. gave similar results with respect to yield. Similarly, when different solvents such as DMF, DCE, CH_3CN and MeOH were employed, the reaction did not proceed in DMF and MeOH, whereas the reaction proceeds slowly in CH_3CN. However, the reaction in DCE was found to the best in terms of reaction time and yield. Parallely, Lewis acids such as I_2, $NbCl_5$ and $FeCl_3$ which had been utilized earlier for other organic transformations were also screened and found that in the case of I_2 and $FeCl_3$ uncharacterized by-products are formed and in the case of $NbCl_5$, the product is formed in 70% yield along with uncharacterized by-product. When pTSA was tried, the formation of 50% product was observed along with uncharacterized by-products. The results were encouraging enough to proceed ahead with Brϕnsted acid PMA to investigate further scope and generality of this reaction.

Thus, with the optimized conditions, other combinations of aldehydes and active methylene substrates were explored with β-naphthol (**Tables I**



Scheme I — Synthesis of naphthopyrans

and **II**). Both electron rich aldehydes and electron poor aldehydes responded well for this reaction and the yields were slightly higher for electron rich aldehydes. Active methylene substrate such as acetyl acetone and ethyl acetoacetate or methyl acetoacetate responded well and in both the cases only single product was isolated. No lactone formation was observed with ethyl acetoacetate or methyl acetoacetate. When a reaction was attempted with dimedone (cyclic diketone with active methylene substrate), it was a pleasure to find that the reaction worked well in this case also to get the corresponding naphthopyran derivative (**Table II**, entry no.16, product **16a**). This protocol is also amenable for large scale synthesis and is well evidenced by a reaction, wherein product **6a** was easily synthesized on 2 g scale with 85% yield in 5 hr.

Mechanistically, the reaction may proceed by two mechanisms, one involving the formation of ortho-quinone methide (which results from the reaction of β-naphthol and aldehyde), its entrapment with active methylene substrate via Michael addition (**Scheme II**) followed by ring closure and dehydration[10] or the second in which condensation between an aldehyde and active methylene compound occurs to produce the Knoevenagel product, followed by Michael type of addition, cyclization and dehydration. Since no intermediate (Knoevenagel product) could be observed and could isolate directly the naphthopyran derivative, the former mechanism fits for this reaction.

However, when a reaction of Knoevenagel product and β-naphthol in presence of PMA was performed (**Scheme III**), the formation of a similar product in good yield could be observed. Thus the possibility of the latter mechanism cannot be ruled out. At this stage, no attempts were made to further study the detailed mechanism involved.

In conclusion, naphthopyran derivatives have been synthesized involving a one pot multicomponent condensation reaction of aldehyde, active methylene substrate and β-naphthol catalyzed by Brϕnsted acid PMA. The reaction happens to be atom economic and easily amicable for large scale synthesis involving very small amounts of Brϕnsted acid catalyst. Investigation to explore these scaffolds for biological activity is currently under progress.

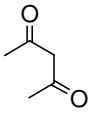
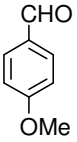
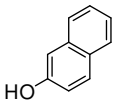
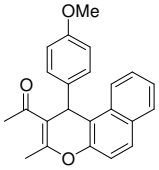
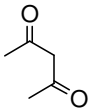
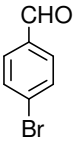
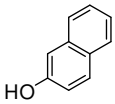
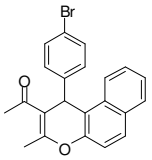
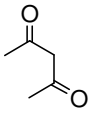
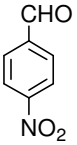
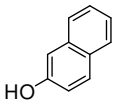
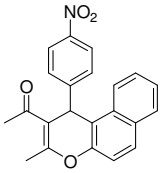
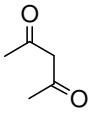
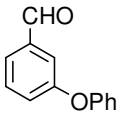
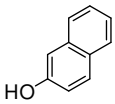
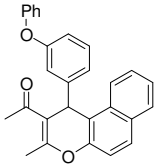
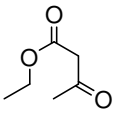
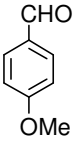
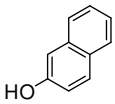
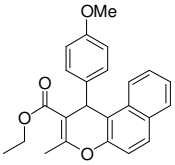
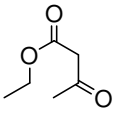
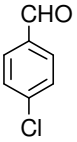
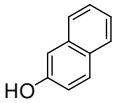
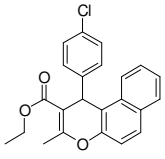
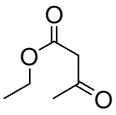
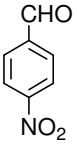
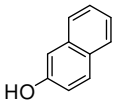
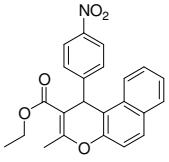
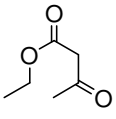
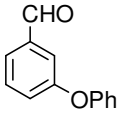
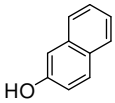
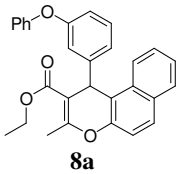
Experimental Section.

Representative experimental procedure

To a mixture of β-napthol (1.0 mmol), aldehyde (1.0 mmol), and active methylene substrates (1.0 mmol) was added PMA (0.1 mmol) in dichloroethane (5 mL). The mixture was stirred at 85°C for the given time (**Tables I** and **II**). The progress of the reaction was monitored by TLC. After completion of reaction, the reaction was quenched with saturated aq. $NaHCO_3$ solution (2 mL). Dichloroethane was removed on rotary evaporator and the residue was extracted with ethyl acetate (2 × 5 mL). The organic layer was separated and washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the crude product was purified by silica gel column chromatography to provide the pure product.

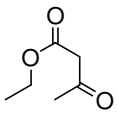
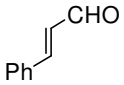
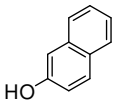
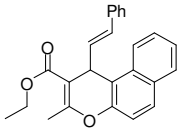
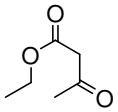
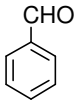
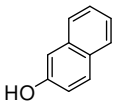
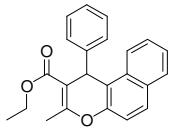
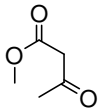
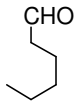
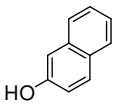
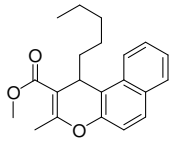
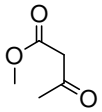
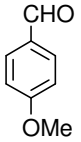
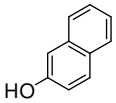
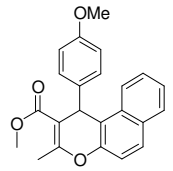
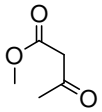
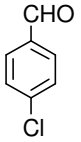
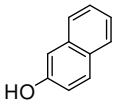
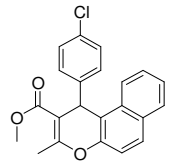
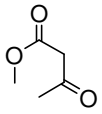
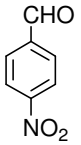
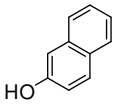
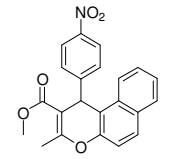
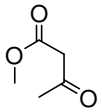
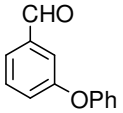
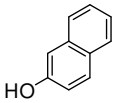
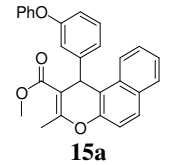
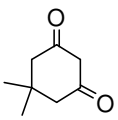
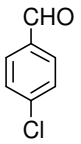
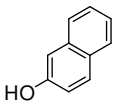
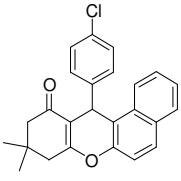
1-(1-(4-Methoxyphenyl)-3-methyl-1*H*-benzo[*f*]-chromen-2-yl)ethanone, 1a: White solid[10], m.p. 156-58°C; Lit[10] m.p. 156-57°C; R_f = 0.6 (hexane / EtOAc, 9:1); IR(KBr): 1644, 1599, 1509, 1225, 1029, 814, 749 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.37 (s, 3H), 2.47 (s, 3H), 3.68, (s, 3H), 5.60 (s, 1H), 6.69 (d, *J* = 8.7 Hz, 2H), 7.19 (d, *J* = 8.7 Hz, 2H), 7.25 (t, *J* = 4.2 Hz, 1H), 7.30 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.43, (dt, *J* = 8.3, 1.1 Hz, 1H), 7.69, (d, *J* = 8.9 Hz, 1H), 7.74, (d, *J* = 7.9 Hz, 1H), 7.99 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.3, 30.8, 37.4, 55.0, 113.8 (2 C), 116.8, 116.9, 117.7, 122.9, 124.5, 126.7, 128.5, 129.0, 130.7 (2 C), 131.2 (2 C), 137.3, 147.4, 157.9, 158.3, 198.3; MS(FAB): *m/z* 344 (M^+).

Table I — Synthesis of naphthopyran derivatives

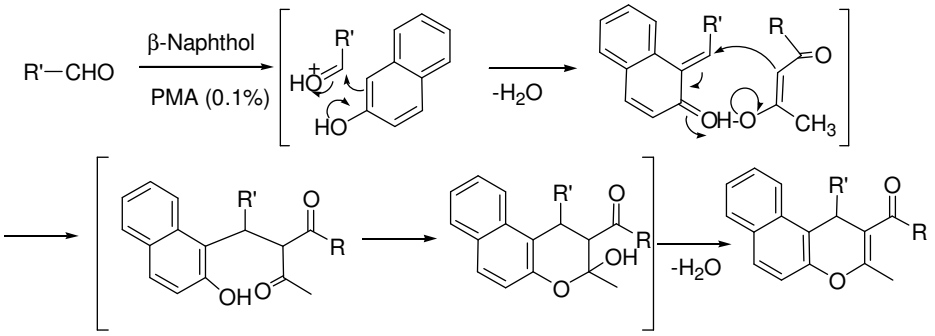
Entry	Active methylene compound	Aldehyde	2-Naphthol	Product	Reaction time (hr)	Yield[a] (%)	Physical state
1				 **1a**	5	85	Solid[10](m.p.156-58°C)
2				 **2a**	6	91	Solid(m.p.162-63°C)
3				 **3a**	6	74	Solid(m.p.202-03°C)
4				 **4a**	6	77	Solid(m.p.125-26°C)
5				 **5a**	5	88	Solid[10](m.p.117-19°C)
6				 **6a**	4	86	Solid[10](m.p.130-32°C)
7				 **7a**	5	75	Solid(m.p.141-42°C)
8				 **8a**	5	80	Colourless liquid

[a]Products purified by column chromatography and characterized by IR, ^{1}H, and ^{13}C NMR and mass analysis. Yields calculated after column chromatography.

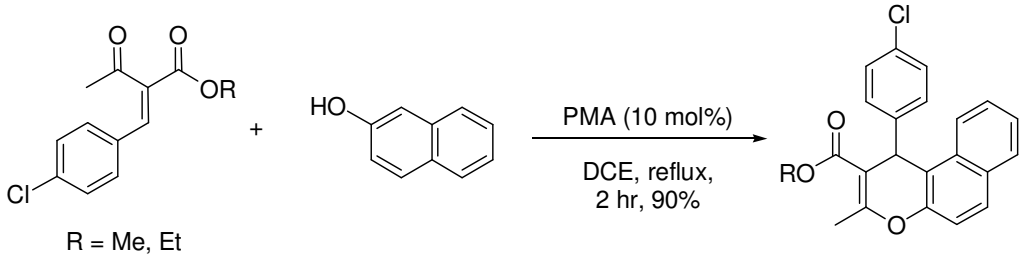
Table II — Synthesis of naphthopyran derivatives

Entry	Active methylene compound	Aldehyde	2-Naphthol	Product	Reaction time (sec)	Yield[a] (%)	Physical state
9				 **9a**	6	74	Yellow liquid
10				 **10a**	5	90	Solid (m.p. 122-24°C)
11				 **11a**	5	76	Colourless liquid
12				 **12a**	6	85	Solid (m.p.152-53°C)
13				 **13a**	5	78	Solid (m.p.139-40°C)
14				 **14a**	4	76	Solid (m.p.177-78°C)
15				 **15a**	5	85	Colourless liquid
16				 **16a**	6	71	Solid (m.p.168-70°C)

[a]Products purified by column chromatography and characterized by IR, ^{1}H, and ^{13}C NMR and mass analysis. Yields calculated after column chromatography.



Scheme II — Postulated mechanism for naphthopyran formation



Scheme III — Synthesis of naphthopyrans from Knoevenagel products

1-(1-(4-Bromophenyl)-3-methyl-1*H*-benzo[*f*]-chromen-2-yl)ethanone, 2a: White solid, m.p. 162-63°C; R_f = 0.5 (hexane / EtOAc, 9:1); IR(KBr): 1646, 1595, 1318, 1222, 831, 739 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.37 (s, 3H), 2.48 (s, 3H), 5.66 (s, 1H), 7.16 (d, *J* = 8.3 Hz, 2H), 7.28 (t, *J* = 8.3 Hz, 3H), 7.35 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.44 (dt, *J* = 8.3, 1.3 Hz, 1H), 7.68-7.79 (m, 2H), 7.92 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.4, 31.1, 37.5, 116.7, 116.8 (2 C), 120.3, 122.7, 124.7, 126.9, 128.5, 128.8, 129.8 (2 C), 130.6, 131.2, 131.4 (2 C), 144.1, 147.5, 158.9, 197.5; MS(FAB): *m/z* 392 (M^+).

1-(3-Methyl-1-(4-nitrophenyl)-1*H*-benzo[*f*]chromen-2-yl)ethanone, 3a: White solid, m.p. 202-203°C; R_f = 0.5 (hexane / EtOAc, 9:1); IR(KBr): 1643, 1595, 1519, 1351, 1223, 829 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.42 (s, 3H), 2.53 (s, 3H), 5.87 (s, 1H), 7.30-7.55 (m, 5H), 7.73-7.84 (m, 2H), 7.91 (d, *J* = 8.3 Hz, 1H), 8.03 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.8, 31.4, 37.7, 116.2, 116.5, 116.8, 122.5, 123.6 (2 C), 125.0, 127.2, 128.7, 129.1(2 C), 129.3, 130.5, 131.3, 146.3, 147.6, 152.3, 160.0, 196.9; MS(FAB): *m/z* 360 (M^++H).

1-(3-Methyl-1-(3-phenoxyphenyl)-1*H*-benzo[*f*]-chromen-2-yl)ethanone, 4a: White solid, m.p. 125-26°C; R_f = 0.4 (hexane / EtOAc, 19:1); IR(KBr): 1677, 1578, 1482, 1228, 942, 814, 745 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 3H), 2.46 (s, 3H), 5.65 (s, 1H), 6.68 (d, *J* = 8.3 Hz, 1H), 6.89 (d, *J* = 7.7 Hz, 2H), 7.02-7.15 (m, 4H), 7.22-7.33 (m, 3H), 7.34-7.50 (m, 2H), 7.67-7.81 (m, 2H), 8.02 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.3, 30.8, 38.3, 116.3, 116.6, 117.0, 117.1, 118.7 (2 C), 118.8, 122.9, 123.0, 123.1, 124.6, 126.8, 128.5, 128.7, 129.6 (2 C), 129.7, 130.7, 131.2, 147.0, 147.5, 156.9, 157.0, 158.7, 198.1; MS(FAB): *m/z* 406 (M^+).

Ethyl-1-(4-methoxyphenyl)-3-methyl-1*H*-benzo-[*f*]chromene-2-carboxylate, **5a**: White solid[10], m.p.117-19°C; Lit.[10] m.p. 117-19°C; R_f = 0.5 (hexane / EtOAc, 19:1); IR(KBr): 1707, 1509, 1257, 1214, 1065, 1029, 809 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.34 (t, *J* = 7.1 Hz, 3H), 2.49 (s, 3H), 3.68 (s, 3H), 4.22 (q, *J* = 7.1, 5.8 Hz, 2H), 5.61 (s, 1H), 6.71 (d, *J* = 8.7 Hz, 2H), 7.20-7.42 (m, 5H), 7.66-7.80 (m, 2H), 7.96 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3, 19.6, 37.4, 55.1, 60.3, 107.4, 113.5 (2 C), 117.0, 117.3, 123.2, 124.5, 126.7, 128.4, 128.5, 129.3 (2 C), 130.9, 131.2, 137.8, 147.6, 158.0, 159.3, 167.2; MS(FAB): *m/z* 374 (M^+).

Ethyl 1-(4-chlorophenyl)-3-methyl-1*H*-benzo[*f*]-chromene-2-carboxylate, **6a**: White solid[10], m.p.130-32°C. Lit[10] m.p.130-32°C; R_f = 0.6 (hexane / EtOAc, 9:1); IR(KBr): 1686, 1648, 1221, 1089, 1054, 831 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.32 (t, *J* = 6.9 Hz,

3H), 2.50 (s, 3H), 4.21 (q, *J* = 6.9, 6.0 Hz, 2H), 5.63 (s, 1H), 7.13 (d, *J* = 8.5 Hz, 2H), 7.22-7.46 (m, 5H), 7.67-7.79 (m, 2H), 7.89 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3, 19.6, 37.7, 60.4, 107.1, 116.5, 117.0, 123.0, 124.6, 127.0, 128.3 (2 C), 128.5, 129.0, 129.7 (2 C), 130.7, 131.2, 132.0, 144.0, 147.6, 160.0, 167.0; MS(FAB): *m/z* 378 (M^+).

Ethyl 3-methyl-1-(4-nitrophenyl)-1*H*-benzo[*f*]-chromene-2-carboxylate, **7a**: White solid, m.p.141-42°C; R_f = 0.6 (hexane / EtOAc, 9:1); IR(KBr): 1715, 1519, 1346, 1212, 1061, 827 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.34 (t, *J* = 6.9 Hz, 3H), 2.53 (s, 3H), 4.23 (q, *J* = 6.9, 7.1 Hz, 2H), 5.77 (s, 1H), 7.28-7.54 (m, 5H), 7.72-7.88 (m, 3H), 8.04 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3, 19.8, 38.3, 60.6, 106.0, 115.6, 117.0, 122.5, 123.5 (2 C), 124.9, 127.1, 128.6, 129.2 (2 C), 129.3, 130.5, 131.3, 146.4, 147.6, 152.6, 160.6, 166.7; MS(FAB): *m/z* 389 (M^+).

Ethyl 3-methyl-1-(3-phenoxyphenyl)-1*H*-benzo-[*f*]chromene-2-carboxylate, **8a**: Colourless liquid; R_f = 0.6 (hexane / EtOAc, 9:1); IR(KBr): 1707, 1589, 1484, 1218, 1063, 750 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.29 (t, *J* = 7.1 Hz, 3H), 2.50 (s, 3H), 4.19 (q, *J* = 6.9, 7.1 Hz, 2H), 5.63 (s, 1H), 6.70 (d, *J* = 6.6 Hz, 1H), 6.91 (d, *J* = 7.7 Hz, 2H), 6.96-7.14 (m, 4H), 7.22-7.32 (m, 3H), 7.33-7.48 (m, 2H), 7.68-7.80 (m, 2H), 7.93 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3, 19.5, 38.2, 60.4, 96.1, 107.0, 116.7, 117.1, 118.6 (2 C), 119.4, 123.0, 123.3, 124.5, 127.1, 128.5, 128.8, 129.6 (2 C), 131.0, 131.3, 147.5, 147.7, 157.0, 157.3, 159.7, 167.0; MS(FAB): *m/z* 436 (M^+).

3-Methyl-1-styryl-1*H*-benzo[*f*]chromene-2-carboxylic acid ethyl ester, **9a**: Yellow liquid. R_f = 0.6 (hexane / EtOAc, 9:1); IR(KBr): 1644, 1220, 1065, 773 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.38 (t, *J* = 7.1 Hz, 3H), 2.51 (s, 3H), 4.30 (q, *J* = 7.1, 12.0 Hz, 2H), 5.30 (d, *J* = 4.9 Hz, 1H), 6.30 (d, *J* = 4.9 Hz, 2H), 7.19-7.27 (m, 5H), 7.38-7.46 (m, 1H), 7.48-7.55 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.4, 19.6, 35.2, 60.4, 117.1, 123.1, 124.6, 126.3, 126.8, 127.2, 128.3, 128.5, 130.0 (2 C), 131.2 (2 C), 131.3 (2 C), 137.7, 148.0, 147.7, 161.0, 167.2; MS(FAB): *m/z* 370 (M^+).

Ethyl 3-methyl-1-phenyl-1*H*-benzo[*f*]chromene-2-carboxylate, **10a**: White solid, m.p.122-24°C; R_f = 0.4 (hexane / EtOAc, 9:1) IR(KBr): 1688, 1648, 1223, 1059 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.32 (t, *J* = 7.5 Hz, 3H), 2.49 (s, 3H), 4.19 (q, *J* = 6.7, 7.1 Hz, 2H), 5.59 (s, 1H), 6.99-7.05 (m, 1H), 7.14 (t, *J* = 8.3 Hz, 2H), 7.22-7.40 (m, 5H), 7.67 (t, , *J* = 9.8 Hz 2H), 7.89 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3, 19.6, 38.3, 60.3, 107.2, 117.0, 117.1, 123.1, 124.5, 126.3, 126.7, 128.2, 128.4, 128.6, 130.0, 131.2 (2C), 145.4, 147.7, 159.6, 167.2; MS(FAB): *m/z* 344 (M^+).

Methyl 3-methyl-1-pentyl-1*H*-benzo[*f*]chromene-2-carboxylate, 11a: Colourless liquid. R_f = 0.7 (hexane / EtOAc, 19:1); IR(KBr): 1714, 1649, 1216, 1079, 813 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.77 (t, *J* = 6.9 Hz 3H), 0.88-1.23 (m, 6H), 1.63-1.80 (m, 2H), 2.50 (s, 3H), 3.84 (s, 3H), 4.69 (t, *J* = 4.9 Hz, 1H), 7.18 (d, *J* = 8.8 Hz, 1H), 7.39-7.47 (m, 1H), 7.51-7.58 (m, 1H), 7.69 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 7.5 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 19.4, 22.5, 24.3, 31.4, 32.0, 36.3, 55.4, 105.4, 116.8, 118.0, 122.7, 124.4, 126.5, 127.7, 128.5, 130.8, 131.2, 148.6, 161.7, 168.1; MS(FAB): *m/z* 325 (M^++1).

Methyl 1-(4-methoxyphenyl)-3-methyl-1*H*-benzo[*f*]chromene-2-carboxylate, **12a**: White solid, m.p.152-53°C; R_f = 0.6 (hexane / EtOAc, 9:1); IR(KBr): 1686, 1509, 1226, 1062, 748 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.49 (s, 3H), 3.67 (s, 3H), 3.76 (s, 3H), 5.61 (s, 1H), 6.71 (d, *J* = 8.6 Hz, 2H), 7.18-7.46 (m, 5H), 7.68-7.79 (m, 2H), 7.95 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.6, 37.3, 51.3, 55.0, 107.3, 113.6 (2 C), 117.1, 117.2, 123.1, 124.5, 126.7, 128.4, 128.5, 129.2 (2 C), 130.8, 131.2, 137.8, 147.6, 158.0, 159.5, 167.7; MS(FAB): *m/z* 360 (M^+).

1-(4-Chloro-phenyl)-3-methyl-1*H*-benzo[*f*]chromene-2-carboxylicacidmethylester, **13a**: White solid, m.p.139-40°C; R_f = 0.4 (hexane / EtOAc, 9:1); IR(KBr): 1695, 1486, 1224, 1062, 836, 809 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.49 (s, 3H), 3.76 (s, 3H), 5.64 (s, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.20-7.46 (m, 5H), 7.74 (t, *J* = 9.4 Hz, 2H), 7.88 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.6, 37.7, 51.4, 106.7, 116.4, 117.0, 123.0, 124.7, 126.9, 128.4, 128.5 (2 C), 128.9, 129.5 (2 C), 130.7, 131.3, 132.1, 144.0, 147.6, 160.1, 167.4; MS(FAB): *m/z* 364 (M^+).

Methyl 3-methyl-1-(4-nitrophenyl)-1*H*-benzo[*f*]-chromene-2-carboxylate, **14a**: White solid, m.p.177-78°C; R_f = 0.6 (hexane / EtOAc, 19:1); IR(KBr): 1719, 1518, 1344, 1260, 1214, 1069, 807 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.53 (s, 3H), 3.78 (s, 3H), 5.78 (s, 1H), 7.29-7.53 (m, 5H), 7.74-7.87 (m, 3H), 8.05 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.8, 38.3, 51.6, 106.0, 115.6, 117.0, 122.6, 123.7 (2 C), 125.0, 127.2, 128.7, 129.1 (2 C), 129.4, 130.5,

131.4, 146.4, 147.7, 152.5, 161.0, 167.2; MS(FAB): *m/z* 375 (M^+).

Methyl 3-methyl-1-(3-phenoxyphenyl)-1*H*-benzo[*f*]chromene-2-carboxylate, **15a**: Colourless liquid; R_f = 0.4 (hexane / EtOAc,19:1); IR(KBr): 1711, 1589, 1484, 1219, 1066, 750 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.50 (s, 3H), 3.72 (s, 3H), 5.62 (s, 1H), 6.70 (d, *J* = 7.7 Hz, 1H), 6.88-7.14 (m, 6H), 7.22-7.46 (m, 5H), 7.67-7.79 (m, 2H), 7.92 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.5, 38.1, 51.3, 106.8, 116.7 (2 C), 117.0, 118.6 (2 C), 119.1, 123.0, 123.1, 123.2, 124.6, 126.8, 128.4, 128.8, 129.6 (3 C), 130.8, 131.3, 147.4, 147.6, 156.8, 157.2, 160.1, 167.5; MS(FAB): *m/z* 422 (M^+).

12-(4-Chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydro-benzo[*a*]xanthen-11-one, **16a**: White solid, m.p.168-70°C; R_f = 0.5 (hexane / EtOAc, 9:1); IR(KBr): 1646, 1372, 1226, 838 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.93 (s, 3H), 1.11 (s, 3H), 2.22 (d, *J* = 3.7 Hz, 2H), 2.52 (s, 2H), 5.63 (s, 1H), 7.08-7.14 (m, 2H), 7.20-7.42 (m, 5H), 7.70-7.76 (m, 2H), 7.85 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.1, 29.3, 32.1, 34.1, 41.3, 60.0, 114.0, 117.1, 117.2, 123.6, 125.1, 127.2, 128.5, 128.6, 129.2, 129.9, 131.3, 135.5, 132.1, 143.3, 147.9, 164.1, 196.8; MS(FAB): *m/z* 389 (M^+).

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