A facile synthesis of flavones catalysed by gallium(III) triflate

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$Ga(OTf)_3$ was explored as a novel catalyst for the cyclisation of 1-(2-hydroxyphenyl)-3-aryl-1,3-propanediones in nitromethane to flavones with excellent yields.

Keywords: gallium(III) triflate, flavones, cyclisation reaction

The flavones are an important class of widely distributed natural products.[1,2] They are an integral part of the human diet and possess a wide range of biological activities, such as anticancer,[3] antibacterial,[4] anti-AIDS agents.[5]

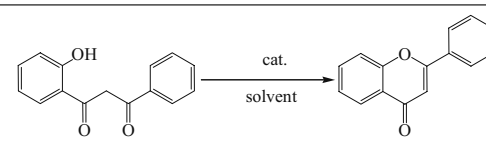
Many methods are available for the synthesis of flavones. The most common are the cyclisation of 2′-hydroychalcones or 1-(2-hydroxyphenyl)-3-aryl-1,3-propanediones, which are prepared from acylation of an o-hydroxyacetophenone with an aromatic acid chloride yielding an aryl ester. The ester is then rearranged by a base (pyridine/KOH) to 1-(2-hydroxyphenyl)-3-aryl-1,3-propanediones.[6,7] The cyclisation reaction of 1-(2-hydroxyphenyl)-3-aryl-1,3-propanediones affords flavones with different catalysts such as H_2SO_4/AcOH,[8,9] $NaHSO_4$/SiO_2,[10] Mo/W complexes,[11] I_2-DMSO,[12] Co(III),[13] supported trifluoromethanesulfonic acid[14] and $CuCl_2$.[15]

Although a variety of catalysts have been introduced for the synthesis of flavones, many of these methods are associated with one or more disadvantages such as relatively long reaction time, environmentally unfriendly catalyst, low yield, requirement of excess reagents or catalysts and harsh reaction conditions. Therefore, the development of environmentally benign, high-yielding and clean approaches for the synthesis of flavones still remains an active research area.

Metal triflates are currently of great interest and because of their unique catalysis, they were widely used in organic synthesis. Recently, we have reported some organic reactions using metal triflates.[16-18] To the best of our knowledge, the $Ga(OTf)_3$-promoted synthesis of flavones has not been reported. In continuation of our interest in Lewis acids catalysed organic reactions, we report a simple, efficient method for the synthesis of flavones in excellent yields using $Ga(OTf)_3$ as a catalyst under mild conditions.

We have investigated a variety of reaction conditions with the cyclisation reaction of 1-(2-hydroxyphenyl)-3-aryl-1,3-propanedione in the present of various Lewis acids. The results are summarised in Table 1. It seems that nitromethane is a much better solvent (Table 1, entry 11**,** yield 97%) than the other solvents which were tested such as ethanol (Table 1, entry 13, yield 81%), acetonitrile (Table 1, entry 14, yield 88%), dichloromethane (Table 1, entry 15, yield 72%) and water (Table 1, entry 16, yield 10%). The best results were obtained by carrying out the reaction at 80 °C for 2 hours in the presence of a catalytic amount of $Ga(OTf)_3$ with nitromethane as the solvent. In contrast, the product was obtained in low yield in the absence of catalyst. All metal triflates with exception of $Mg(OTf)_2$ and $Ca(OTf)_2$ examined showed good catalytic effects. However, $Ga(OTf)_3$ was particularly effective for this reaction with the 96% yields of corresponding product. In contrast, other Lewis acid such as $CuCl_2$ (Table 1, entry 17) gave low yields (33%). Additionally, we also studied influence of the amount of $Ga(OTf)_3$ on the reaction yields. It was found that the yield was not obviously affected with different amounts of $Ga(OTf)_3$, 1 mol% of $Ga(OTf)_3$ was enough and excess catalyst did not noticeably increase the yield (Table 1, entries 8–12). As a result, we obtained the following optimised conditions: with 1 mol% $Ga(OTf)_3$ at 80 °C for 2 hours with nitromethane as the solvent.

Table 1 Synthesis of flavones under different reaction conditions[a]



Entry	Solvent	Catalyst	Loading/ mol%	Yields/%[b]
1	CH_3NO_2	$Cu(OTf)_2$	1	75
2	CH_3NO_2	$Mg(OTf)_2$	1	47
3	CH_3NO_2	$Bi(OTf)_3$	1	83
4	CH_3NO_2	$Yb(OTf)_3$	1	87
5	CH_3NO_2	$Zn(OTf)_2$	1	70
6	CH_3NO_2	$Y(OTf)_3$	1	89
7	CH_3NO_2	$Ca(OTf)_2$	1	48
8	CH_3NO_2	$Ga(OTf)_3$	0.5	95
9	CH_3NO_2	$Ga(OTf)_3$	5	97
10	CH_3NO_2	$Ga(OTf)_3$	2.5	96
11	CH_3NO_2	$Ga(OTf)_3$	1	96
12	CH_3NO_2	$Ga(OTf)_3$	10	97
13	CH_3CH_2OH	$Ga(OTf)_3$	1	81
14	CH_3CN	$Ga(OTf)_3$	1	88
15	CH_2Cl_2	$Ga(OTf)_3$	1	72
16	H_2O	$Ga(OTf)_3$	1	10
17	CH_3NO_2	$CuCl_2$	1	33 (57)[c]
18	CH_3NO_2	none	–	5

[a]80 °C for 2 hour. [b]Isolated yield. [c]In the presence of 40 mol% $CuCl_2$.

With optimal conditions in hand, the cyclisation of different 1-(2-hydroxyphenyl)-3-aryl-1,3-propanediones was examined to explore the scope of the reaction (Table 2). It is worth mentioning that the cyclisation of 1-(2-hydroxyphenyl)-3-aryl-1,3-propanediones containing a nitro group provides the desired product in moderate yield in CH_3NO_2 due to poor solubility (Table 2, entries 6, 13, 18 and 19). Therefore, the reactions was run in 1,2-dichloroethane so as to ensure good yield.

From the results shown in Table 2, it can be seen that most of the reactions proceeded smoothly with excellent yields. Further studies indicated electron-withdrawing and electron-donating groups on the aromatic ring did not affect the reaction significantly either in the yield of product or the rate of the reaction. In most cases, the desired products (flavones) were obtained with high selectivity, practically without by-products and starting materials.

In summary, a highly efficient and environmentally friendly protocol for the synthesis of flavones has been developed. Compared to previous reported methodologies, important

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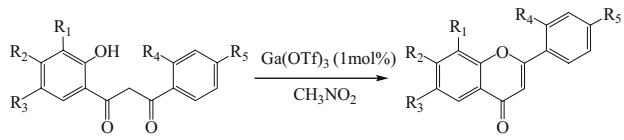
Table 2 $Ga(OTf)_3$ catalysed synthesis of flavones[a]



Entry	R_1	R_2	R_3	R_4	R_5	Product	Time/h	Yield/%[b]
1	H	H	H	H	H	**1a**	2	96
2	H	H	H	H	Cl	**1b**	2.5	92
3	H	H	H	Cl	Cl	**1c**	3	91
4	H	H	H	H	OCH_3	**1d**	2	97
5	H	H	H	H	CH_3	**1e**	2	95
6	H	H	H	H	NO_2	**1f**[c]	4	89
7	H	H	H	Cl	H	**1g**	2.5	91
8	Br	H	Br	H	Cl	**1h**	4	90
9	H	CH_3	H	H	Cl	**1i**	2.5	95
10	H	H	Cl	H	Cl	**1j**	3.5	93
11	H	H	CH_3	H	Cl	**1k**	2	94
12	H	H	CH_3	H	H	**1l**	2	95
13	H	H	CH_3	H	NO_2	**1m**[c]	4	87
14	H	H	CH_3	H	CH_3	**1n**	2	94
15	H	CH_3	H	H	H	**1o**	2	93
16	H	H	Cl	H	CH_3	**1p**	2	92
17	H	H	OCH_3	H	OCH_3	**1q**	1.5	95
18	H	H	NO_2	H	H	**1r**[c]	4	87
19	H	H	OCH_3	H	NO_2	**1s**[c]	4	93

[a]Reaction temperature: 80 °C. [b]Isolated yield. [c]1.2-dichloroethane was used as solvent.

features of present protocol include simple work-up, a shorter reaction time, the use of environmentally benign, recoverable metal triflates, mild reaction conditions with excellent yields. Currently, studies on the extension of this protocol are ongoing in our laboratory.

Experimental

Chemicals and solvents were either purchased or purified by standard techniques. Melting points were recorded on Digital Melting Point Apparatus WRS-1B and are uncorrected. IR spectra were recorded on an AVATAR 370 FI-IR spectrophotometer. Mass spectra (EI) were measured with Thermo Finnigan LCQ-Advantage or Finnigan Trace DSQ. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury plus-400 instrument using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. Chemical shifts are given in δ units relative to TMS, the coupling constants *J* are given in Hz. Elemental analysis was performed on a VarioEL-III instrument.

Typical procedure for synthesis of flavones

$Ga(OTf)_3$ (24.5 mg, 0.05 mmol, 1 mol%) was added to a solution of 1-(2-hydroxyphenyl)-3-aryl-1,3-propanedione (5 mmol) in CH_3NO_2 (20 ml). The mixture was stirred at 80 °C for 2–4 hours. After completion of the reaction, as indicated by TLC, water was added, and the product was extracted with diethyl ether (3 × 10 ml). The organic layer was dried ($MgSO_4$) and evaporated and the crude product was purified by flash column chromatography to provide the corresponding product.

2-phenyl-4H-chromene **(1a):** White solid: m.p. 96–97 °C (Lit.[19] 96–97 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.0 Hz, 1H, ArH), 7.94 (d, *J* = 8.0 Hz, 2H, ArH), 7.71 (t, *J* = 8.0 Hz, 1H, ArH), 7.53–7.60 (m, 4H, ArH), 7.43 (t, *J* = 8.0 Hz, 1H, ArH), 6.86 (s, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.33, 156.29, 133.77, 131.75, 131.59, 129.03, 126.27, 125.68, 125.21, 120.11, 118.17, 107.64. IR (KBr): 1646, 1605, 1568, 1128, 768 cm^{-1}. MS (EI): *m/z* (%) = 222 (100) [M$^+$], 194 (60), 165 (9), 120 (55), 92(43).

2-(4-chlorophenyl)-4H-chromen-4-one **(1b):** White solid: m.p. 185–187 °C (Lit. [20] 185–188 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.0 Hz, 1H, ArH), 7.84 (d, *J* = 8.0 Hz, 2H, ArH), 7.70 (t, *J* = 8.0 Hz, 1H, ArH), 7.54 (d, *J* = 8.0 Hz, 1H, ArH), 7.48 (d, *J* = 8.0 Hz, 2H, ArH), 7.42 (t, *J* = 8.0 Hz, 1H, ArH), 6.78 (s, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.08, 162.09, 156.06, 137.79, 133.81, 130.15, 129.29, 127.47, 125.65, 125.27, 123.84, 117.95, 107.60. IR (KBr): 1641, 1466, 1090, 828, 772 cm^{-1}. MS (EI): *m/z* (%) = 256 (100) [M$^+$], 258 (M$^+$ + 2, 36), 230 (14), 228 (46), 221 (15), 120 (67), 92 (32).

2-(2,4-dichlorophenyl)-4H-chromen-4-one **(1c):** White solid: m.p. 172–175 °C (Lit.[21] 172–174 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 8.0 Hz, 1H, ArH), 7.70–7.74 (m, 1H, ArH), 7.60–7.61 (m, 2H, ArH), 7.51 (d, *J* = 8.0 Hz, 1H, ArH), 7.40–7.46 (m, 2H, ArH), 6.66 (s, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.93, 161.42, 156.47, 137.36, 134.00, 133.74, 131.37, 130.70, 130.33, 127.53, 125.75, 125.44, 123.78, 118.12, 113.13. IR (KBr): 1650, 1467, 1381, 1365, 823, 775, 753. MS (EI): *m/z* (%) = 290 (100) [M$^+$], 292 (M$^+$ + 2, 60),264 (20), 262 (35), 255 (70), 120 (73), 92 (35)

2-(4-methoxyphenyl)-4H-chromen-4-one **(1d):** White solid: m.p. 157–159 °C (Lit.[19] 157–158 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.0 Hz, 1H, ArH), 7.85 (d, *J* = 8.4 Hz, 2H, ArH), 7.65–7.69 (m, 1H, ArH), 7.53 (d, *J* = 8.0 Hz, 1H, ArH), 7.40 (t, *J* = 7.2 Hz, 1H, ArH), 6.98–7.01 (m, 2H, ArH), 6.72 (s, 1H, CH), 3.87(s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.22, 163.25, 162.28, 156.03, 133.45, 127.86, 125.50, 124.95, 123.80, 120.08, 117.86, 114.33, 106.01, 55.39. IR (KBr): 1649, 1608, 1465, 1380, 1133, 827, 767 cm^{-1}. MS (EI): *m/z* (%) = 252 (100) [M$^+$], 237(7), 221(15), 209(13), 132(63).

2-p-tolyl-4H-chromen-4-one **(1e):** Yellow solid: m.p. 108–111 °C (Lit.[21] 108–111 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.0 Hz, 1H, ArH), 7.78 (s, 2H, ArH), 7.65 (t, *J* = 4.0 Hz, 1H, ArH), 7.52 (s, 1H, ArH), 7.27 (s, 1H, ArH), 7.38 (t, *J* = 8 Hz, 2H, ArH), 6.76 (s, 1H, CH), 2.40 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.26, 163.37, 156.05, 142.10, 133.49, 129.61, 128.73, 126.04, 125.49, 124.96, 123.83, 117.92, 106.76, 21.38. IR (KBr): 1637, 1465, 1371, 1227, 817, 752, 634. MS (EI): *m/z* (%) = 236 (100) [M$^+$], 221 (44), 120 (36), 115 (37), 104 (10), 92 (23).

2-(4-nitrophenyl)-4H-chromen-4-one **(1f):** Yellow solid: m.p. 241–243 °C (Lit.[22] 242–244 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11–8.40 (m, 5H, ArH), 7.48–7.76 (m, 3H, ArH), 6.92 (s, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.93, 160.56, 156.18, 149.46, 137.66, 134.31, 127.21, 125.88, 125.75, 124.23, 123.96, 118.19, 108.64. IR (KBr): 1659, 1520, 1467, 1346, 1130, 857, 750, 692. MS (EI): *m/z* (%) = 267 (25) [M$^+$], 236 (100), 208 (25), 166 (9), 115 (13), 92 (12).

2-(2-chlorophenyl)-4H-chromen-4-one **(1g):** Yellow solid: m.p. 193–195 °C (Lit.[22] 192–193 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, *J* = 8.0 Hz, 1H, ArH), 7.62–7.71 (m, 2H, ArH), 7.39–7.53 (m, 5H, ArH), 6.67 (s, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.96, 162.47, 156.50, 133.81, 132.75, 131.69, 130.69, 130.52, 127.00, 125.60, 125.22, 123.72, 118.09, 112.89. IR (KBr): 1651, 1368, 1153, 1066, 909, 767. MS (EI): *m/z* (%) = 256 (100) [M$^+$], 258 (M$^+$ + 2, 34), 228 (39), 221 (42), 165 (13), 120 (63), 92 (47).

6,8-dibromo-2-(4-chlorophenyl)-4H-chromen-4-one **(1h):** Yellow solid: m.p. 248–251 °C (Lit.[23] 249–250 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (s, 1H, ArH), 8.04 (s, 1H, ArH), 7.93 (d, *J* = 8.0 Hz, 2H, ArH), 7.53 (d, *J* = 8.0 Hz, 2H, ArH), 6.84 (s, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.21, 162.51, 151.74, 139.47, 138.63,

129.63, 129.41, 127.89, 127.74, 126.00, 118.73, 118.11, 113.03, 107.29. IR (KBr): 1649, 1612, 1492, 1092, 839, 699. MS (EI): *m/z* (%) = 414 (100) [M^+], 416 (M^+ + 2, 74), 278 (98), 250 (11), 197 (16), 163 (10), 136 (15).

2-(4-chlorophenyl)-7-methyl-4H-chromen-4-one **(1i):** Yellow solid: m.p. 179–180 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.0 Hz, 1H, ArH), 7.77–7.80 (m, 2H, ArH), 7.43–7.46 (m, 2H, ArH), 7.29 (s, 1H, ArH), 7.19 (d, *J* = 8.0 Hz, 1H, ArH), 6.70 (s, 1H, ArH), 2.47 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.89, 161.60, 156.05, 145.11, 137.55, 130.11, 129.14, 127.24, 126.66, 125.25, 121.46, 117.63, 107.36, 21.69. IR (KBr): 1638, 1490, 1410, 1092, 906, 827, 813. 477. MS (EI): *m/z* (%) = 270 (5) [M^+], 242 (100), 178 (90), 152 (70), 78 (6). Anal. Calcd for $C_{16}H_{11}ClO_2$: C, 70.99; H, 4.10; Found: C, 70.97; H, 4.15%.

6-chloro-2-(4-chlorophenyl)-4H-chromen-4-one **(1j):** White solid: m.p. 226–227 °C (Lit.[24] 226–227 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (s, 1H, ArH), 7.85 (d, *J* = 8.0 Hz, 2H, ArH), 7.64–7.67 (m, 1H, ArH), 7.51–7.54 (m, 3H, ArH), 6.79 (s, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.98, 162.51, 154.49, 138.21, 134.09, 131.40, 129.90, 129.47, 127.57, 125.25, 124.94, 119.75, 107.63. IR (KBr): 1658, 1492, 1438, 1092, 906, 831, 664. MS (EI): *m/z* (%) = 290 (10) [M^+], 293 (M^+ + 2, 2), 262 (100), 199 (60), 163 (87).

2-(4-chlorophenyl)-6-methyl-4H-chromen-4-one **(1k):** Pale yellow solid: m.p. 198–199 °C (Lit.[24] 198–199 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (s, 1H, ArH), 7.83 (d, *J* = 8.4 Hz, 2H, ArH), 7.43–7.51 (m, 4H, ArH), 6.76 (s, 1H, CH), 2.46 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.30, 161.97, 154.37, 137.70, 135.32, 135.06, 130.26, 129.27, 127.43, 125.01, 123.48, 117.73, 107.43, 20.86. IR (KBr): 1643, 1621, 1483, 1089, 902, 820, 707. MS (EI): *m/z* (%) = 270 (100) [M^+], 272 (40), 242 (30), 235 (15), 134 (95), 106 (20).

6-methyl-2-phenyl-4H-chromen-4-one **(1l):** Yellow solid: m.p. 121–122 °C (Lit.[24] 122 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (s, 1H, ArH), 7.90 (d, *J* = 8.0 Hz, 2H, ArH), 7.43–7.52 (m, 5H, ArH), 6.79 (s, 1H, CH), 2.45 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.46, 163.14, 154, 43, 135,10, 134,90, 131.78, 131.42, 128.92, 126.16, 124.93, 123.51, 117,76, 107.31, 20.85. IR (KBr): 1638, 1615, 1482, 1359, 1044, 883, 814, 778. MS (EI): *m/z* (%) = 236 (100) [M^+], 208 (30), 134 (71), 106 (17), 78 (12).

6-methyl-2-(4-nitrophenyl)-4H-chromen-4-one **(1m):** Yellow solid: m.p. 276–278 °C (Lit.[24] 275–277 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, *J* = 8.0 Hz, 2H, ArH), 8.11 (d, *J* = 8.0 Hz, 2H, ArH), 8.03 (s, 1H, ArH), 7.50–7.58 (m, 2H, ArH), 6.90 (s, 1H, CH), 2.49 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.16, 160,43, 154.52, 149.43, 137.82, 135.88, 135.56, 127.19, 125.27, 124.22, 123.73, 117.89, 109.53,20.96. IR (KBr): 1639, 1617, 1522, 1343, 1138, 850, 823, 691. MS (EI): *m/z* (%) = 281 (100) [M^+], 253 (20), 134 (48), 106 (12).

6-methyl-2-p-tolyl-4H-chromen-4-one **(1n):** White solid: m.p. 151–152 °C (Lit.[24] 150–151 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (s, 1H, ArH), 7.80 (d, *J* = 8.0 Hz, 2H, ArH), 7.44–7.50 (m, 2H, ArH), 7.31 (d, *J* = 8.0 Hz, 2H, ArH), 6.77 (s, 1H, CH), 2.46 (s, 3H, CH_3), 2.43 2.46 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.49, 163.42, 154.50, 142.06, 135.03, 134.80, 129.70, 129.08, 126.16, 125.01, 123.64, 117.77, 106.81, 21.45, 20.88. IR (KBr): 1643, 1613, 1483, 817. MS (EI): *m/z* (%) = 250 (100) [M^+], 235 (30), 222 (25), 134 (80), 115 (17), 106 (17), 78 (10).

7-methyl-2-phenyl-4H-chromen-4-one **(1o):** Pale yellow solid: m.p. 129–131 °C (Lit.[22] 128–130 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (s, 1H, ArH), 7.91 (d, *J* = 8.0 Hz, 2H, ArH),7.51 (s, 3H, ArH), 7.35 (s, 1H, ArH), 7.22 (d, *J* = 8.0 Hz, 1H, ArH), 6.81 (s, 1H, CH), 2.50 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.37, 162.99, 156.30, 145.02, 131.78, 131.38, 128.91, 126.62, 126.12, 125.35, 121.66, 117.78, 107.45, 21.76. IR (KBr): 1637, 1606, 1449, 1371, 1157, 866, 772. MS (EI): *m/z* (%) = 236 (100) [M^+], 208 (53), 134 (45), 106 (16), 78 (12).

6-chloro-2-p-tolyl-4H-chromen-4-one **(1p):** Yellow solid: m.p. 183–184 °C (Lit.[24] 183–184 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (s, 1H, ArH), 7.78 (d, *J* = 8.0 Hz, 2H, ArH), 7.61 (d, *J* = 8.0 Hz, 1H, ArH), 7.50 (d, *J* = 8.0 Hz, 1H, ArH), 7.31 (d, *J* = 8.0 Hz, 2H, ArH), 6.79 (s, 1H, CH), 2.43 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.08, 163.79, 154.46, 142.55, 133.76, 131.02, 129,78, 128.45, 126.18, 125.07, 119.72, 106.75, 21.51. IR (KBr): 1641, 1613, 1465, 1436, 1358, 816, 670. MS (EI): *m/z* (%) = 270 (100) [M^+], 272 (35), 255 (45), 242 (20), 154 (55), 116 (31), 115 (47).

6-methoxy-2-(4-methoxyphenyl)-4H-chromen-4-one **(1q):** White solid: m.p. 196.1–196.2 °C (lit.[25] 194–195 °C). ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.88 (d, *J* = 8.0 Hz, 2H, ArH), 7.61 (d, *J* = 4.0 Hz, 1H, ArH), 7.45 (d, *J* = 8.0 Hz, 1H, ArH), 7.29 (d, *J* = 4.0 Hz, 1H, ArH), 7.03 (d, *J* = 8.0 Hz, 2H, ArH), 6.76 (s, 1H, CH), 3.92 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3).^{13}C NMR (100 MHz, $CDCl_3$), δ 178.30, 163.28, 162.36, 156.95, 151.04, 127.97, 124.54, 124.16, 123.59, 119.39, 114.47, 105.52, 104.91, 55.96, 55.51. IR (KBr): 1649, 1608, 1515, 1466, 1382, 1268, 1195, 1026, 827, 768. MS (EI): *m/z* (%) = 282 (100) [M^+], 272 (35), 252 (24), 150 (96), 132 (24), 107 (29).

6-nitro-2-phenyl-4H-chromen-4-one **(1r):** Pale yellow solid: m.p. 194.6–195.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ 9.12 (s, 1H, ArH), 8.52 (d, *J* = 8.0 Hz, 1H, ArH), 7.93–7.95 (m, 2H, ArH), 7.74 (d, *J* = 4.0 Hz, 1H, ArH), 7.55–7.63 (m, 3H, ArH), 6.90 (s, 1H, CH).^{13}C NMR (100 MHz, $CDCl_3$), δ 176.67, 164.15, 159.08, 144.86, 132.39, 130.78, 129.30, 128.15, 126.45, 124.11, 122.52, 119.84, 107.89. IR (KBr): 1646, 1610, 1454, 1340, 1135,922, 841,772,679,627. MS (EI): *m/z* (%) = 267 (100) [M^+], 267 (35), 221 (22), 165 (32), 139(19), 102 (61). Anal. Calcd for $C_{15}H_9NO_4$: C, 67.42; H, 3.39; N, 5.24; Found: C, 67.44; H, 3.43; N 5.21%.

6-methoxy-2-(4-nitrophenyl)-4H-chromen-4-one **(1s):** Pale yellow solid: m.p. 200.1–201.8 °C (lit.[10] 198–200 °C); ^{1}H NMR (400 MHz, $CDCl_3$), δ 8.39 (d, *J* = 8.0 Hz, 2H, ArH), 8.11 (t, *J* = 4.0 Hz, 2H, ArH), 7.61 (d, *J* = 4.0 Hz,1H, ArH), 7.55 (d, *J* = 8.0 Hz,1H, ArH),7.33–7.36 (m, 1H, ArH), 6.90 (s, 1H, CH), 3.96 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$), δ 177.90, 160.343, 157.40, 151.02, 149.37, 137.75, 127.16, 124.58, 124.45, 124.25, 119.60, 108.80, 104.90, 56.01. IR (KBr): 1642, 1607, 1518, 1488, 1347, 1020, 853, 826, 697. MS (EI): *m/z* (%) = 297 (100) [M^+], 267 (28), 150 (60), 107 (43), 79 (32).

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