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Sulfated tungstate: A highly efficient, recyclable and ecofriendly catalyst for synthesis of Flavones under the solvent-free conditions

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A B S T R A C T

Sulfated tungstate efficiently catalyzes the cyclodehydration of 1-(2-hydroxyphenyl)-3-aryl-1,3-propanediones to flavones under solvent-free conditions. Utilization of conventional heating, simple reaction conditions, short reaction time, ease of product isolation and purification makes this manipulation very interesting from an economic and environmental perspective. Under these conditions, twelve examples were obtained with good yields (85-94%).

1. Introduction

Due to the growing concern over environmental pollution, Green chemistry has attracted increasing attention in recent years.[1–4] Intensive efforts have been focused on designing and developing economical and environmentally benign syntheses. Major environmental pollution arises from the use of solvents since the amounts of solvents used are usually much larger than the amounts of reagents and products. The problem may be addressed by recycling the solvents which is economically as well as practically difficult. Much of the research is being pursued vigorously for the replacement of conventional organic solvents which are highly volatile, environmentally harmful, and/or biologically incompatible with environmentally benign solvents. Ionic liquids and fluorous solvents have been used with their limitations in organic syntheses. The poor solubility of organic molecules in water has restricted its use as a benign solvent in organic synthesis. Due to the toxicity of organic solvents and the limitations of environmentally benign solvents, the most promising approach is to perform organic reactions under solvent-free conditions. Solvent-free reactions have received considerable attention in recent years, not only for ecological and economic reasons, but also for simplicity of reaction conditions, high yields and short reaction times. Another source of environmental pollution is the use of large amounts of acid catalysts in organic reactions which generates toxic waste that is harmful to the environment. The development of cheap, acid catalysts could change the traditional procedures into green ones, thus minimizing chemical waste further. Therefore, the use of Sulfated tungstate as a catalyst under solvent-free condition would be a better solution to environmental pollution.

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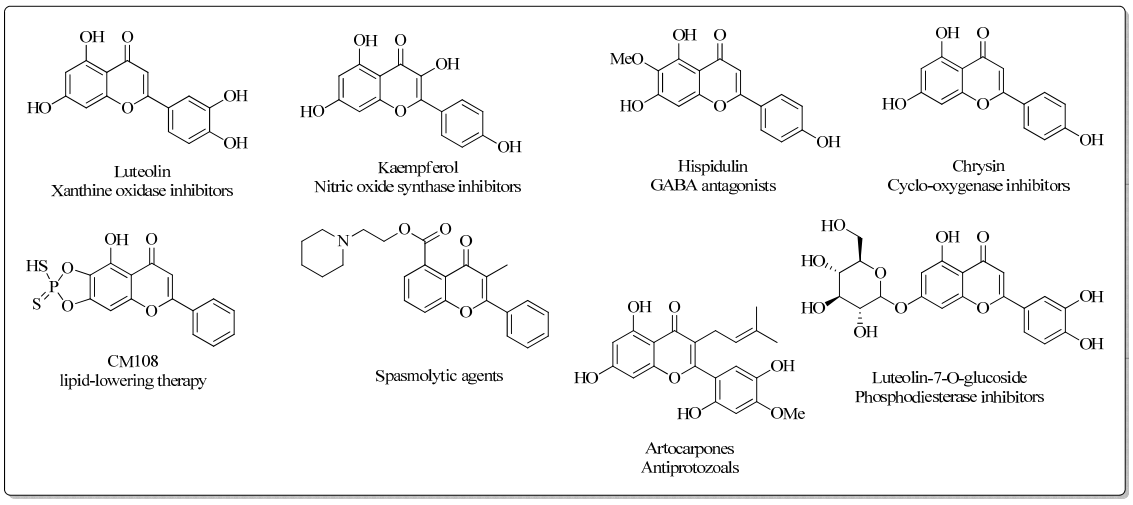


Fig. 1. Biologically active flavones.

The synthetic potential, as green catalysts in organic reactions, has been ignored to a large extent except for a few scattered reports like a simple and environmentally benign method for the synthesis of flavones described via dehydrative cyclization of o-hydroxydibenzoylmethane using silica gel supported $NaHSO_4$ catalyst in the literature.[5]

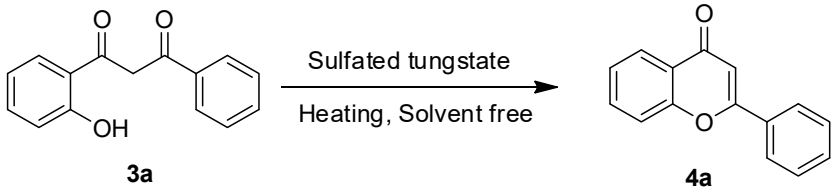
Flavonoids are present plentifully in plants of the families Leguminosae, Compositae, and Moraceae. They display a broad spectrum of biological activity[6] like anti-inflammatory, antitumor,[7] antioxidant and estrogen receptor modulator activities.[8](**Fig. 1)** In addition, they also inhibit the activity of cyclooxygenase/lipoxygenase.[9] The thioflavanone derivatives have been used in the synthesis of biologically active compounds such as benzothiazepine and thiochroman-4-one.[10] One of the most commonly used methods for the synthesis of flavones is the cyclodehydration of 1-(2-hydroxyphenyl)-3-aryl-1,3-propanediones. Many of these procedures use strong acids such as H_2SO_4[11], HCl,[12] HBr, HI,[13] natural organic acids,[14] ammonium acetate, [15] or ascorbic acid,[16-17]. However, all above reported methods suffer from certain drawbacks such as the use of toxic/costly solvents, expensive reagents, co-catalysts, production of considerable amounts of byproducts, long reaction times and low yields. Therefore, the development of simple, inexpensive, highly efficient yet eco-friendly catalysts for acid-catalyzed organic transformations is worthwhile.[18] The ionic liquids and sulfonic acid in which sulfonic group bonded with positive charged nitrogen in organic compounds have been efficiently used as catalysts and reagents in organic conversion. In recent years, several groups have introduced sulfated tungstate as a heterogeneous green catalyst because of its easy-to-prepare, moderately acidic, recyclable, nontoxic and efficient. At room temperature and under solvent-free circumstances, it is used as a heterogeneous and ecologically friendly catalyst in a range of chemical reactions. The sulfated tungstate was effectively used as a catalyst in several organic transformations for the synthesis of various organic compounds.[19-20] We report herein a simple and highly efficient protocol for the synthesis of flavones by the cyclodehydration of 1-(2-hydroxyphenyl)-3-aryl-1,3-propanediones.

In this article, we would like to report that Sulfated tungstate, without any functionalization, could be used as a useful catalyst for the cyclodehydration of 1-(2-hydroxyphenyl)-3-aryl-1,3-propanediones to flavones in conventional heating.

2 Result and discussion

2.1 Synthesis of flavones: Synthesis of flavones from 1,3- propanediones was studied. For screening of the catalysts, cyclodehydration of propanedione **3a** was selected as a model reaction (**Table 1**). To evaluate the synergy between dry media and conventional heating in this reaction, several experiments were tried. As described in table 1, the heating of 1-(2-hydroxyphenyl)-3-aryl-1,3-propanediones without Sulfated tungstate was unsuccessful (**entry 1**). Although Sulfated tungstate catalysed the reaction at room temperature, the yield was only 20% after 1h of reaction (**entry 2**). Only in the case of conventional heating at 100 °C, the 1-(2-hydroxyphenyl)-3-aryl-1,3-propanediones condensation proceeded efficiently after 30 min of reaction (**entry 5**). These results indicate that Sulfated tungstate is as effective catalyst to deliver flavones **4a** in good to excellent yields.

Table 1. Screening of catalysts in synthesis of flavones from 1,3- propanediones under solvent free condition.[a]



3a **4a**

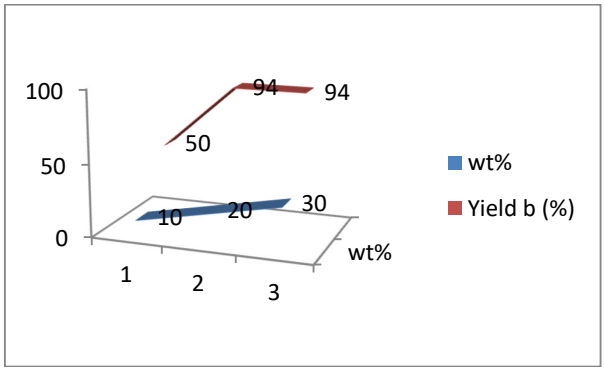
Entry	Catalyst	Temp. (° C) [b]	Time (Min)	Yield[c] (%)
1	-	r.t.	60	-
2	Sulfated tungstate	r.t.	60	20
3	Sulfated tungstate	50	60	75
4	Sulfated tungstate	100	60	94
5	Sulfated tungstate	100	30	94
6	Sulfated tungstate	100	15	79

[a] Reagents: **3a** (0.5g), Sulfated tungstate Catalyst (1.0 eq.). [b] Conventional Heating. [c] Isolated yields.

Next Sulfated tungstate was used to test the scope of the above methodology. Thus various 1, 3-propanediones were used under the above reaction condition. The corresponding flavones (**4a-l**) were obtained in good to excellent yields under conventional heating conditions (**Table 2**).

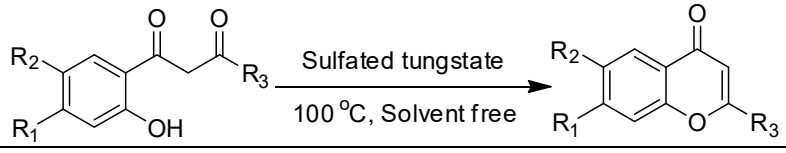
2.2 Effect of Sulfated tungstate catalysts for the formation of flavones

Next, the effect of the amount of Sulfated tungstate on the model reaction was investigated. It was found that 20 wt% of Sulfated tungstate is essential for the completion of the reaction. However, the use of less than 20 wt% of the Sulfated tungstate resulted in low yield of the product along with the recovery of the starting material even for extended reaction time.

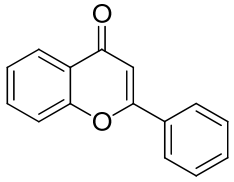
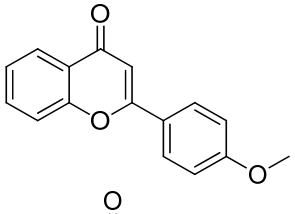
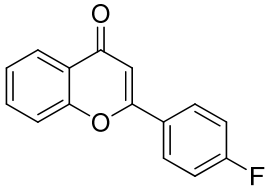
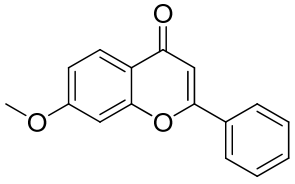
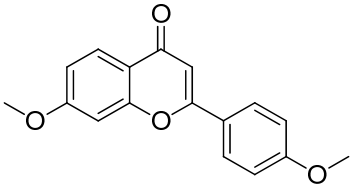
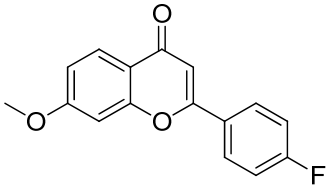
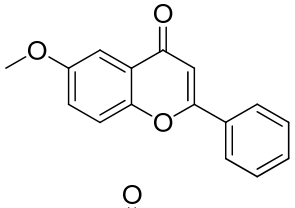
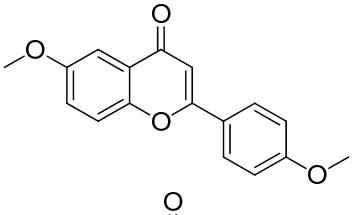
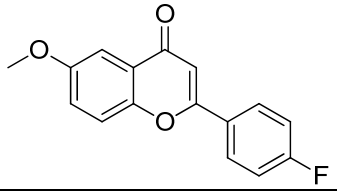


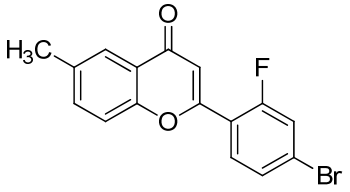
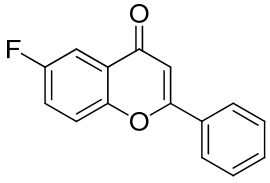
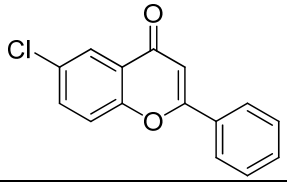
To check the generality and scope of this protocol, various 1,3-propanedione were subjected to the flavone synthesis with Sulfated tungstate under the above reaction conditions at 100 °C. Results indicated that the flavones synthesis reaction proceeded smoothly under conventional heating within 30 minutes to give the corresponding flavones in good to excellent yields.

Table 2. Sulfated tungstate catalyzed synthesis of flavones from 1,3-propanedione under solvent free condition.[a]



Entry	Compd.	R_1	R_2	R_3	(%)Yield[d]

1		H	H	Ph	94
2		H	H	*p*-$MeOC_6H_4$	92
3		H	H	*p*-FC_6H_4	91
4		OMe	H	Ph	92
5		OMe	H	*p*-$MeOC_6H_4$	92
6		OMe	H	*p*-FC_6H_4	85
7		H	OMe	Ph	90
8		H	OMe	*p*-$MeOC_6H_4$	92
9		H	OMe	*p*-FC_6H_4	90

10		H	Me	*o*-F-*p*-BrC_6H_3	89
11		H	F	Ph	90
12		H	Cl	Ph	88

[a] Reagents: **3** (0.5g), Sulfated tungstate (1.0 eq.). [b] 30 min. in conventional heating. [d] Isolated yields. [e]All the products were identified spectroscopically (IR, ^{1}H, ^{13}C NMR and LCMS)

3. Conclusion

In conclusion, we found that the Sulfated tungstate can be used as an environment-friendly catalyst for the cyclodehydration of 1-(2-hydroxyphenyl)-3-aryl-1,3-propanediones to flavones under solvent-free condition in a short time. Sulfated tungstate showed superior reactivity in the cyclodehydration of 1-(2-hydroxyphenyl)-3-aryl-1,3-propanediones to flavones under conventional heating. The operational simplicity, use of commercially available, biodegradable and renewable catalysts, solvent-free reaction condition, short reaction time, easy work up and high yields make these catalysts a more convenient alternative to the reported catalysts. This technique not only improves yields and reaction rates significantly, but it also avoids the use of harmful solvents or catalysts. This work confirms the high value resulting from the use of organic and inorganic compounds in different fields as reported before in different scientific papers. [28-29]

4. Experimental section

4.1 General information

All reagents were used as obtained from commercial sources. Melting points (m. p., uncorrected) were determined in open capillary tubes using a paraffin oil bath. All the microwave-assisted reactions were performed in Discover LabMet microwave system (CEM Corporation, USA) at the specified temperature using the standard mode of operation. Infrared (IR) spectra were recorded on Perkin Elmer Model 1600 series Fourier Transform (FT) instrument. ^{1}H NMR and ^{13}C NMR were recorded on Bruker Avance II 400/ Varian Mercury 300 and 100/75 MHz respectively in DMSO/$CDCl_3$ solution and tetramethylsilane (TMS) as internal reference (δscale). Mass spectra were recorded on Agilent 1200SL – 6100 LC/MS (ESI).

4.2 General Procedure for Flavones

In a typical experiment, the mixture of 1,3- propanedione (0.5 g) and Sulfated tungstate (20 wt%) was heated at 100 ºC for 30 min. After completion of reaction (TLC check). Ethyl acetate and hexane is used as mobile phase for TLC. The reaction mixture was allowed to cool at room temperature and ethyl acetate (10 mL) was added. Then the resulting solid was filtered off and washed with 5 mL ethylacetate. After the concentration of ethyl acetate, the resulting products with more purity, but more purification, if necessary, can be accessed by recrystallization of the products from ethanol.

4.3 Spectral data for the synthesized compounds 4(a-l)

2-Phenyl-chromen-4-one (Table 2, entry 1): M.p. 96-97 °C (lit.[21] m.p. 96-97 °C), IR (KBr) $\tilde{\nu}$: 1645, 1604, 1568, 1130, 756 cm^{-1}, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.81 (s, 1 H, CH), 7.39 (t, J = 7.8 Hz, 1H, Ar-H), 7.46-7.55 (m, 4H, Ar-H), 7.65-7.70 (m, 1H, Ar-H), 7.88-7.91 (m, 2H, Ar-H), 8.21 (d, J = 7.2 Hz, 1H, Ar-H), ^{13}C NMR ($CDCl_3$, 75 MHz): δ 107.3 (CH), 117.9 (Ar-C), 123.7 (Ar-C), 125.1 (Ar-C), 125.5 (Ar-C), 126.1 (Ar-C), 128.9 (Ar-C), 131.5 (Ar-C), 131.6 (Ar-C) , 133.7 (Ar-C), 156.1 (Ar-C), 163.3 (=C-O), 178.3 (C=O), LCMS (ES-API) m/z: 223 $(M+H)^+$.

2-(4-Methoxy-phenyl)-chromen-4-one (Table 2, entry 2): M.p. 157-158 °C (lit.[21] m.p. 157-158 °C), IR (KBr) $\tilde{\nu}$: 1649, 1608, 1465, 1133, 767 cm^{-1}, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.87 (s, 3H, OMe), 6.80 (s, 1H, CH), 6.99-7.03 (m, 2H, Ar-H), 7.40 (t, J = 7.2 Hz, 1H, Ar-H), 7.53 (d, J = 8.1 Hz, 1H, Ar-H), 7.65-7.70 (m, 1H, Ar-H), 7.80-7.90 (m, 2H, Ar-H), 8.21 (dd,

J = 8.1 & 2.1 Hz, 1H, Ar-H), ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.4 (O-CH_3), 105.9 (CH), 114.4 (Ar-C), 117.9 (Ar-C), 123.7 (Ar-C), 123.9 (Ar-C), 125.1 (Ar-C), 125.6 (Ar-C), 127.9 (Ar-C), 133.6 (Ar-C), 156.1 (Ar-C), 162.4 (Ar-C), 163.5 (=C-O), 178.5 (C=O), LCMS (ES-API) m/z: 253 $(M+H)^+$.

2-(4-Fluoro-phenyl)-chromen-4-one (Table 2, entry 3): M.p. 148-150 °C (lit.[22] m.p. 134-135 °C), IR (KBr) $\nu\tilde{}$: 1663, 1608, 1574, 1467, 1234, 1134, 869, 806, 755 cm^{-1}, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.79 (s, 1H, CH), 7.23 (m, 2H, Ar-H), 7. 47 (t, *J* = 7. 1 Hz, 1H, Ar-H), 7.58 (d, *J* = 7.1 Hz, 1H, Ar-H), 7.72 (m, 1H, Ar-H), 7.94 (m, 2H, Ar-H), 8.24 (d, *J* = 7. 2 Hz, 1H, Ar-H), ^{13}C NMR ($CDCl_3$, 75 MHz): δ 107.1 (CH), 116.6 (Ar-C), 117.0 (Ar-C), 118.5 (Ar-C), 123.9 (Ar-C), 125.5 (Ar-C), 126.0 (Ar-C), 127.1 (Ar-C), 128.1 (Ar-C), 134.2 (Ar-C), 156.0 (Ar-C), 162.6 (=C-O), 178.1 (C=O), LCMS (ES-API) m/z: 241 $(M+H)^+$

7-Methoxy-2-phenyl-chromen-4-one (Table 2, entry 4): M.p. 109-110 °C (lit.[23-24] m.p. 105-106 °C), IR (KBr) $\nu\tilde{}$: 1647, 1626, 1606, 1450, 1163, 908, 767 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.91 (s, 3H, OMe), 6.77 (s, 1H, CH), 6.95 (m, 2H, Ar-H), 7.51 (m, 3H, Ar-H), 7.88 (m, 2H, Ar-H), 8.11 (d, *J* = 8.7 Hz, 1H, Ar-H), ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.8 (OCH_3), 100.3 (Ar-C), 107.3 (CH), 114.9 (Ar-C), 117.6 (Ar-C), 126.0 (Ar-C), 126.9 (Ar-C), 128.9 (Ar-C), 131.4 (Ar-C), 131.6 (Ar-C), 157.8 (Ar-C), 162.9 (Ar-C), 164.1 (=C-O), 177.7 (C=O), LCMS (ES-API) m/z: 253 $(M+H)^+$.

7-Methoxy-2-(4-methoxy-phenyl)-chromen-4-one (Table 2, entry 5): M.p. 194-195 °C (lit.[25-26] m.p. 180.5 °C) , IR (KBr) $\nu\tilde{}$: 1629, 1593, 1516, 1379, 1260, 1186, 977, 862 cm^{-1}, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.82 (s, 3H, OMe), 3.86 (s, 3H, OMe), 6.60 (s, 1H, CH), 6.86-6.95 (4H, m, Ar-H), 7.77 (d, *J* = 8.4 Hz, 2H, Ar-H), 8.05 (d, *J* = 8.4 Hz, 1H, Ar-H), ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.3 (OMe), 55.7 (OMe), 100.2 (Ar-C), 105.9 (CH), 114.0 (Ar-C), 114.2 (Ar-C), 117.6 (Ar-C), 123.8 (Ar-C), 126.7 (Ar-C), 127.6 (Ar-C), 157.7 (Ar-C), 162.1 (Ar-C), 162.8 (Ar-C), 163.9 (=C-O), 177.6 (C=O), LCMS (ES-API) m/z: 283 (M+H

2-(4-Fluoro-phenyl)-7-methoxy-chromen-4-one (Table 2, entry 6) M.p. 172-173 °C (lit.[14]), IR (KBr) $\nu\tilde{}$: 1660, 1631, 1577, 1456, 1294, 1022, 923, 841, 781 cm^{-1}, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.84 (s, 3H, OMe), 6.41 - 6.48 (m, 2H, Ar-H), 6.64 (s, 1H, CH), 7.15 (t, *J* = 8.7 Hz, 2H, Ar-H), 7.89 (m, 1H, Ar-H), 7.90 (m, 2H, Ar-H), ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.6 (OMe), 101.3 (Ar-C), 108.0 (CH), 110.0 (Ar-C), 112.4 (Ar-C), 115.7 (Ar-C), 116.0 (Ar-C), 128.9 (Ar-C), 128.9 (Ar-C), 129.9 (Ar-C), 130.1 (Ar-C), 165.3 (Ar-C), 165.9 (=C-O), 174.8 (C=O), LCMS (ES-API) m/z: 271 $(M+H)^+$.

6-Methoxy-2-phenyl-chromen-4-one (Table 2, entry 7): M.p. 160-161 °C (lit.[24] m.p. 165-167 °C) , IR (KBr) $\nu\tilde{}$: 1641, 1618, 1488, 1361, 1255, 1030, 846, 658 cm^{-1}, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.89 (s, 3H, OMe), 6.79 (s, 1H, CH), 7.28 (dd, *J* = 6.7 & *J* = 3.5 Hz, 1H, Ar-H), 7.46-7.51 (m, 4H, Ar-H), 7.57 (d, *J* = 2.7 Hz, 1H, Ar-H), 7.88-7.91 (m, 2H, Ar-H), ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.8 (OMe), 104.7 (CH), 106.7 (Ar-C), 119.4 (Ar-C), 123.6 (Ar-C), 124.4 (Ar-C), 126.1 (Ar-C), 128.8 (Ar-C), 131.4 (Ar-C), 131.7 (Ar-C), 150.8 (Ar-C), 156.9 (Ar-C), 163.0 (=C-O), 178.2 (C=O), LCMS (ES-API) m/z: 253 $(M+H)^+$.

6-Methoxy-2-(4-methoxy-phenyl)-chromen-4-one (Table 2, entry 8): M.p. 195-196 (lit.[21] m.p. 194-195 °C), IR (KBr) $\nu\tilde{}$: 1647, 1607, 1584, 1454, 1268, 1196, 1014, 817, 558 cm^{-1}, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.88 (s, 3H, OMe), 3.90 (s, 3H, OMe), 6.73 (s, 1H, CH), 7.01 (d, *J* = 9.0 Hz, 2H, Ar-H), 7.27 (m, 1H, Ar-H), 7.58 (d, *J* = 3.0 Hz, 1H, Ar-H), 7.60 (d, *J* = 9.0 Hz, 1H, Ar-H), 7.86 (d, *J* = 9.0 Hz, 2H, Ar-H), ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.4 (OMe), 55.9 (OMe), 104.8 (Ar-C), 105.4 (CH), 114.4 (Ar-C), 119.3 (Ar-C), 123.5 (Ar-C), 124.1 (Ar-C), 124.4 (Ar-C), 127.8 (Ar-C), 150.9 (Ar-C), 156.8 (Ar-C), 162.3 (Ar-C), 163.1 (=C-O), 178.2 (C=O), LCMS (ES-API) m/z: 283 $(M+H)^+$.

6-Methoxy-2-(4-fluoro-phenyl)-chromen-4-one (Table 2, entry 9) M.p. 172-173 ^{0}C (lit.[22] m.p. 172-173 °C), IR (KBr) ν: 1660, 1631, 1608, 1577, 1456, 1419, 1514, 1294, 1163, 1022, 923, 841, 781 cm^{-1}, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.84 (s, 3H, OMe), 6.41-6.48 (m, 2H, CH), 6.64 (s, 1H, Ar-H), 7.15 (t, *J* = 8.7 Hz, 2H, Ar-H), 7.89 (m, 1H, Ar-H), 7.90 (m, 2H, Ar-H), ^{13}C NMR ($CDCl_3$, 75 MHz): δ 55.6 (OMe), 101.3 (Ar-C), 108.0 (CH), 110.0 (Ar-C), 112.4 (Ar-C), 115.7 (Ar-C), 116.0 (Ar-C), 128.9 (Ar-C), 128.9 (Ar-C), 129.9 (Ar-C), 130. 1 (Ar-C), 165.3 (Ar-C), 165.9 (=C-O), 174.8 (C=O), $C_{16}H_{11}FO_3$, LCMS (ES-API) m/z: 271 $(M+H)^+$.

2-(4-Bromo-2-fluoro-phenyl)-6-methyl-chromen-4-one (Table 2, entry 10) M.p. 153-155 °C (lit.[14]), IR (KBr) $\nu\tilde{}$: 1679, 1603, 1571, 1480, 1257, 1192, 1050, 760, 613 cm^{-1}, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.55 (s, 3H, CH_3), 7.23 (s, 1H, CH), 7.25-7.45 (m, 3H, Ar-H), 7.58 (m, 1H, Ar-H), 7.88 (d, *J* = 7.8 Hz, 1H, Ar-H), 8.02 (t, *J* = 8.1 Hz, 1H, Ar-H), ^{13}C NMR ($CDCl_3$, 75 MHz): δ 29.2 (CH_3), 116.9 (CH), 120.7 (Ar-C), 120.7 (Ar-C), 121.7 (Ar-C), 123.8 (Ar-C), 126.4 (Ar-C), 127.7 (Ar-C), 127.8 (Ar-C), 128.9 (Ar-C), 130.5 (Ar-C), 133.6 (Ar-C), 148.7 (Ar-C), 163.7 (=C-O), 183.3 (C=O), LCMS (ES-API) m/z: 334 $(M+H)^+$.

6-Fluoro-2-phenyl-chromen-4-one (Table 2, entry 11): M.p. 128-129 °C (lit.[25]), IR (KBr) $\nu\tilde{}$: 1660, 1624, 1570, 1359, 1176, 835, 767 cm^{-1}, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.82 (s, 1H, CH), 7.39-7.46 (m, 1H, Ar-H), 7.50-7.61 (m, 4H, Ar-H), 7.85-7.93 (m, 3H, Ar-H), ^{13}C NMR ($CDCl_3$, 75 MHz): δ 106.7 (CH), 110.7 (Ar-C), 120.0 (Ar-C), 120.2 (Ar-C), 121.7 (Ar-C), 122.0 (Ar-C), 126.2 (Ar-C), 129.0 (Ar-C), 131.3 (Ar-C), 131.7 (Ar-C), 152.3 (Ar-C), 163.1 (=C-O), 177.5 (C=O), LCMS (ES-API) m/z: 241 $(M+H)^+$.

6-Chloro-2-phenyl-chromen-4-one (Table 2, entry 12): M.p. 183-184 °C (lit.[26-27] m.p. 185-186 °C), IR (KBr) $\nu\tilde{}$: 1651, 1601, 1567, 1457, 1438, 1307, 1132, 908, 682 cm^{-1}, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.82 (s, 1H, CH), 7.50-7.56 (m, 4H, Ar-H), 7.61-7.65 (m, 1H, Ar-H), 7.88-7.90 (m, 2H, Ar-H), 8.17 (d, *J* = 2.3 Hz, 1H, Ar-H), ^{13}C NMR ($CDCl_3$, 75 MHz): δ 107.3 (CH), 119.7 (Ar-C), 124.7 (Ar-C), 125.1 (Ar-C), 126.3 (Ar-C), 129.1 (Ar-C), 131.1 (Ar-C), 131.2 (Ar-C), 131.8 (Ar-C), 133.0 (Ar-C), 154.4 (Ar-C), 163.7 (=C-O), 177.1 (C=O), LCMS (ES-API) m/z: 257 $(M+H)^+$.

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