A simple and facile solventless procedure for the cyclization of 2′-amino- and 2′-hydroxy-chalcones using silica-supported sodium hydrogen sulphate as heterogenous catalyst

K. Hemanth Kumar and P. T. Perumal

Abstract: A simple environmentally friendly method for the cyclization of 2′-amino- and 2′-hydroxy-chalcones under solventless conditions using silica-supported sodium hydrogen sulphate has been reported.

Key words: 2′-aminochalcones, 2′-hydroxychalcones, silica gel, sodium hydrogen sulphate, quinolones and flavanones.

Résumé : On a mis au point une méthode simple et écologique de cyclisation des 2′-amino- et 2′-hydroxychalcones dans des conditions sans solvant en présence de sulfate acide de sodium déposé sur de la silice qui agit comme catalyseur.

Mots clés : 2′-aminochalcones, 2′-hydroxychalcones, gel de silice, sulfate acide de sodium, quinoléones, flavones.

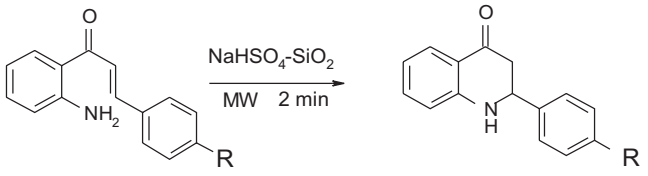
[Traduit par la Rédaction]

Introduction

Substituted tetrahydroquinolones and flavanones display various pharmacological activities (1, 2) and can be prepared (3, 4) by acid or base catalyzed reactions. Many of these procedures involve the use of corrosive reagents such as orthophosphoric acid, acetic acid, or strong alkali. Furthermore, many of them are of limited synthetic scope because of lower yields, extended reaction time, and the amount of catalyst or solvent used. In recent years, there has been increasing interest in solid-supported reagents coupled with microwave irradiation owing to the benefits of enhanced reaction rates, improved yields, cleaner reaction profiles, greater selectivity, and operational simplicity (5).

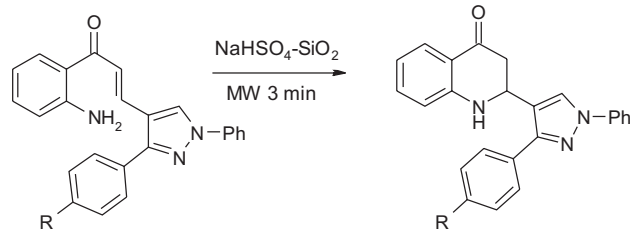
In continuation of our studies on the synthesis of heterocyclic compounds with medicinal potential from 2′-aminochalcones (6) and 2′-hydroxychalcones (7), we report an efficient and simple method for the synthesis of tetrahydroquinolones and flavanones through the cyclization of the corresponding chalcones using silica-supported sodium hydrogen sulphate under solventless conditions. The catalyst $NaHSO_4$-SiO_2 can be easily prepared (8), safely handled and removed from the reaction mixture, is inexpensive, and works under heterogeneous conditions.

Scheme 1.



R = H, Me, Cl, OMe

Scheme 2.



R = Cl, H, OMe, OEt

Results and discussion

2′-Aminochalcone was uniformly mixed with silica gel (finer than 200 mesh), preimpregnated with $NaHSO_4$, transferred into a glass vial, and irradiated by microwaves until (2 min) the reaction was complete (TLC). The reaction mixture was directly charged on a small silica gel column and eluted with a mixture of ethyl acetate – hexane (1:9) to afford the product 2-aryltetrahydro-4-quinolone in excellent yield (Scheme 1). To extend the scope of the reaction, a wide range of substituted and structurally diverse 2′-aminochalcones were subjected to similar conditions (Scheme 2). The reactions proceeded in a similar fashion

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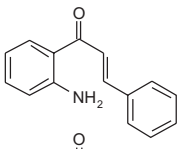
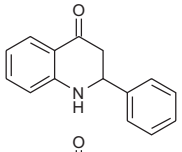
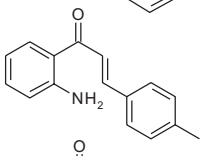
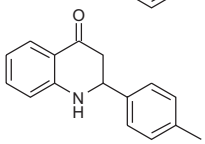
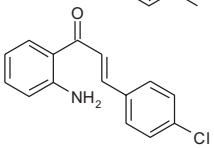
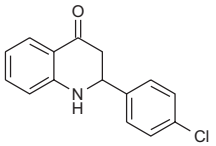
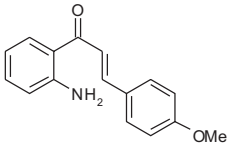
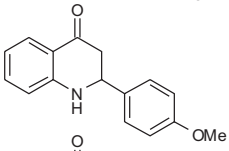
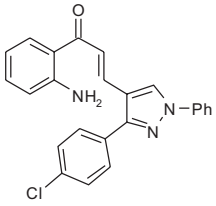
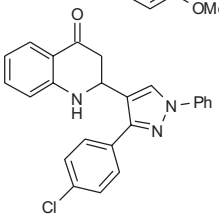
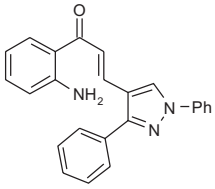
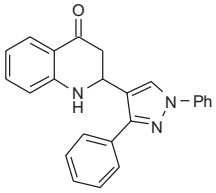
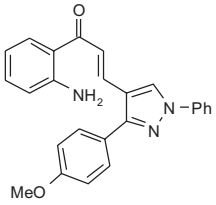
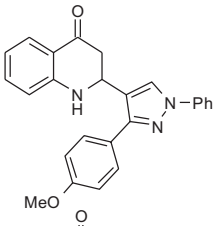
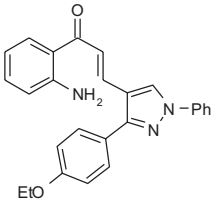
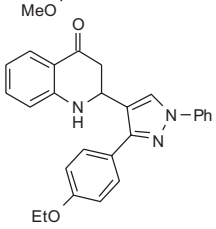
Table 1. $NaHSO_4$-SiO_2 catalyzed cyclization of 2′-aminochalcones under solventless conditions.

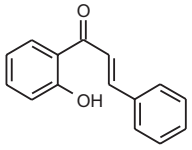
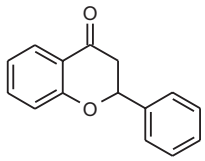
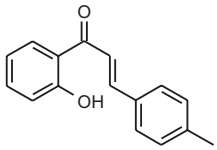
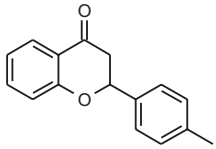
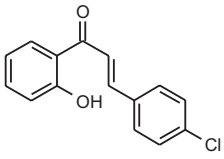
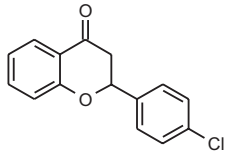
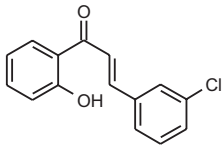
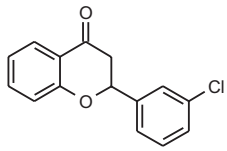
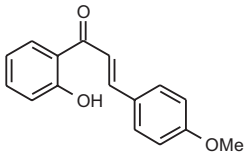
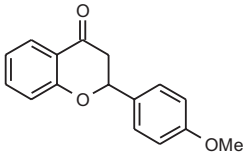
Entry	2′-Aminochalcone	Product	Microwave time (yield)[a]	Conventional heating time (yield)
1			2 min (95)	2 h (72)
2			2 min (90)	2 h (68)
3			2 min (88)	2 h (70)
4			2 min (96)	2 h (75)
5			3 min (86)	4 h (70)
6			3 min (80)	4 h (65)
7			3 min (92)	4 h (74)
8			3 min (87)	4 h (70)

[a]Microwave irradiation was carried out at 650 W (BPL, India).

and substituted tetrahydro-4-quinolones were obtained in good yields (Table 1). The reaction rates and yields were dramatically enhanced by microwave irradiation.

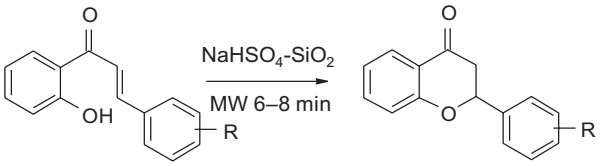
Flavanones form a large and important group of naturally occurring secondary metabolites and are important intermediates for the synthesis of biologically active flavones and isoflavones (9). The conventional methods for the cyclization of 2′-hydroxychalcones involve prolonged time and the use of corrosive reagents such as sulphuric acid, hydrochloric acid, and strong alkalis (10), furnishing flavanones in not more than 50% yields. Hence, we attempted to synthesize flavanones by using $NaHSO_4$ on silica gel under solvent-free conditions as a mild catalyst for the cyclization of 2′-hydroxychalcones (Scheme 3), which fur-

Table 2. $NaHSO_4$-SiO_2 catalyzed cyclization of 2′-hydroxychalcones under solventless conditions.

Entry	2'-Hydroxychalcone	Product	Microwave time (yield)[a]	Conventional heating time (yield)
1			6 min (75)	6 h (60)
2			6 min (70)	6 h (60)
3			8 min (72)	7 h (55)
4			8 min (68)	7 h (52)
5			6 min (75)	5 h (62)

[a]Microwave irradiation was carried out at 650 W (BPL, India).

Scheme 3.



nished the flavanones in good yields (Table 2). Here too, the use of microwave irradiation significantly enhanced the reaction rates as well as the yields.

Conclusion

In conclusion, the present procedure catalyzed by $NaHSO_4$ impregnated with silica gel provides an efficient and rapid synthesis of tetrahydroquinolones and flavanones by the cyclization of the corresponding 2′-aminochalcones and 2′-hydroxychalcones. The notable advantages of this procedure are (*i*) operational simplicity, (*ii*) fast and clean reaction, (*iii*) high yield, and (*iv*) safe and inexpensive catalyst. We believe that this procedure will provide a better scope and a more practical alternative to the existing procedures for the synthesis of tetrahydroquinolones and flavanones.

Experimental

2′-Amino- and 2′-hydroxy-chalcones were prepared using appropriate aldehyde and corresponding *o*-substituted acetophenones by earlier reported procedures (11, 12). 2-Amino- and 2-hydroxy-acetophenones (Sigma-Aldrich) were used as purchased. Sodium hydrogen sulphate and aromatic aldehydes were obtained from E-Merck (India) Ltd. Melting points were determined in capillary tubes and are uncorrected. Analytical TLC was performed on precoated plastic sheets of silica gel G/UV-254 of 0.2 mm thickness (Macherey-Nagel, Germany). FT-IR spectra were taken as KBr pellets on a PerkinElmer Spectrum RXI FT-IR spectrophotometer. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded in $CDCl_3$ solution with TMS as an internal standard. Column chromatography was performed on silica gel (60–120 mesh, SRL, India).

Cyclization of 2′-amino- or 2′-hydroxy-chalcones under microwave irradiation — Typical procedure A

The chalcone (1 mmol) was added to 2 g of silica gel (100–200 mesh activated by heating for 8 h at 150 °C before

use) impregnated with sodium hydrogen sulphate (2 g). The whole mixture was stirred for 5 min for uniform mixing and was then transferred to a glass tube and inserted in an alumina bath (100 g, 60 GF254, Fisher Scientific bath 6.8 cm diameter) inside the microwave oven. The compound was irradiated in a domestic microwave oven (BPL, India) at 650 W for the appropriate time. On completion, the reaction mixture was directly charged on a small silica gel column and eluted with a mixture of ethyl acetate – hexane (1:9 for quinolones, 2:8 for flavanones) to afford the corresponding products in high yields. The results are summarized in Tables 1 and 2.

Cyclization of 2′-amino- or 2′-hydroxy-chalcones by conventional means — Typical procedure B

The chalcone (1 mmol) was added to 2 g of silica gel (100–200 mesh activated by heating for 8 h at 150 °C before use) impregnated with sodium hydrogen sulphate (2 g). The whole mixture was stirred for 5 min for uniform mixing and was then transferred to a 100 mL RB flask and kept in a water bath for the appropriate time. On completion, the reaction mixture was directly charged on a small silica gel column and eluted with a mixture of ethyl acetate – hexane (1:9 for quinolones, 2:8 for flavanones) to afford the corresponding products in high yields. The results are summarized in Tables 1 and 2.

Spectral data

2-Phenyl-2,3-dihydroquinolin-4(1H)-one (Table 1, entry 1)

Pale yellow solid, mp 149 to 150 °C (lit. value (3*c*) 148–150 °C). IR (cm^{-1}) ν_{max}: 3303, 1650, 1605, 1480, 1308, 1152. ^{1}H NMR δ 2.85 (m, 2H), 4.60 (br s, NH, 1H), 4.74 (dd, *J* = 3.14, 13.2 Hz, 1H, H-2), 6.70–7.50 (m, 8H), 7.86 (dd, *J* = 1.72, 8.05 Hz, 1H, H-5). ^{13}C NMR δ 46.5, 58.2, 116.1, 118.4, 119.2, 126.8, 127.6, 128.6, 129.1, 135.5, 141.1, 151.7, 193.4. MS *m/z*: 223 (M^+). Anal. calcd. for $C_{15}H_{13}NO$: C 80.69, H 5.87, N 6.27; found: C 80.60, H 5.73, N 6.12.

2-(4-Methylphenyl)-2,3-dihydroquinolin-4(1H)-one (Table 1, entry 2)

Pale yellow solid, mp 148 to 149 °C (lit. value (3*b*) 149 °C). IR (cm^{-1}) ν_{max}: 3318, 1660, 1602, 1580, 1298, 1142. ^{1}H NMR δ 2.36 (s, 3H, CH_3), 2.84 (m, 2H), 4.67 (br s, NH, 1H), 4.70 (dd, *J* = 3.8, 11.9 Hz, 1H, H-2), 6.69–7.48 (m, 7H), 7.84 (dd, *J* = 1.14, 8.02 Hz, 1H, H-5). ^{13}C NMR δ 21.4, 46.5, 58.3, 116.1, 118.4, 119.0, 126.6, 127.7, 129.8, 129.1, 135.5, 138.2, 151.1, 193.6. MS *m/z*: 237 (M^+). Anal. calcd. for $C_{16}H_{15}NO$: C 80.98, H 6.37, N 5.90; found: C 80.92, H 6.31, N 5.86.

2-(4-Chlorophenyl)-2,3-dihydroquinolin-4(1H)-one (Table 1, entry 3)

Pale yellow solid, mp 168 °C (lit. value (3*c*) 167 to 168 °C). IR (cm^{-1}) ν_{max}: 3325, 1625, 1608, 1540, 1238, 1152. ^{1}H NMR δ 2.90 (m, 2H), 4.54 (br s, NH, 1H,), 4.81 (dd, *J* = 4.0, 13.7 Hz, 1H, H-2), 6.72–7.39 (m, 7H), 7.86 (d, *J* = 8.0 Hz, 1H, H-5). ^{13}C NMR δ 46.3, 57.3, 116.1, 118.1, 119.1, 127.4, 128.2, 129.2, 134.3, 135.6, 139.6, 151.9, 193.2. MS *m/z*: 257 (M^+). Anal. calcd. for $C_{15}H_{12}NOCl$: C 69.91, H 4.69, N 5.43; found: C 69.82, H 4.60, N 5.35.

2-(4-Methoxyphenyl)-2,3-dihydroquinolin-4(1H)-one (Table 1, entry 4)

Pale yellow solid, mp 147 °C (lit. value (3*c*) 146 to 147 °C). IR (cm^{-1}) ν_{max}: 3332, 1632, 1596, 1529, 1226, 1113. ^{1}H NMR δ 2.85 (m, 2H), 3.81 (s, 3H, OCH_3), 4.50 (br s, NH, 1H), 4.70 (dd, *J* = 3.4, 13.7 Hz, 1H, H-2), 6.68–7.37 (m, 7H), 7.86 (dd, *J* = 1.15, 7.98 Hz, 1H, H-5). ^{13}C NMR δ 44.6, 55.5, 58.0, 114.4, 116.0, 118.5, 119.1, 127.7, 127.9, 133.1, 135.5, 151.7, 159.7, 193.7. MS *m/z*: 253 (M^+). Anal. calcd. for $C_{16}H_{15}NO_2$: C 75.87, H 5.97, N 5.53; found: C 75.82, H 5.90, N 5.48.

2-[3-(4-Chlorophenyl)-1-phenyl-1H-pyrazol-4-yl]-2,3-dihydroquinolin-4(1H)-one (Table 1, entry 5)

Pale white solid, mp 190–192 °C. IR (cm^{-1}) ν_{max}: 3344, 1656, 1585, 1534, 1219, 1140. ^{1}H NMR δ 2.84–2.91 (m, 2H), 4.60 (s, br s, NH, 1H), 4.92–4.95 (m, 1H), 6.65 (d, *J* = 8.4 Hz, 1H, H-8), 6.77–6.8 (m, 1H, H-7), 7.28–7.87 (m, 10H), 7,85–7.87 (dd, *J* = 1.5, 7.65 Hz, 1H, H-5), 8.05 (s, 1 H, pyrazole-CH). ^{13}C NMR δ 45.6, 49.3, 116.1, 118.9, 119.2, 119.3, 121.8, 126.7, 127.1, 127.7, 129.2, 129.5, 129.6, 131.3, 134.6, 135.6, 139.7, 150.0, 151.5, 193.1. MS *m/z*: 400 (M^+). Anal. calcd. for $C_{24}H_{18}ClN_3O$: C 72.09, H 4.54, N 10.51; found: C 72.01, H 4.48, N 10.45.

2-(1,3-Diphenyl-1H-pyrazol-4-yl)-2,3-dihydro-quinolin-4(1H)-one (Table 1, entry 6)

Pale white solid, mp 128 to 129 °C. IR (cm^{-1}) ν_{max}: 3346, 1645, 1595, 1523, 1205, 1133. ^{1}H NMR δ 2.86–2.94 (m, 2H, H-3), 4.59 (s, br s, NH, 1H), 4.94–4.97 (m, 1H), 6.65 (d, *J* = 8.4 Hz, 1H, H-8), 6.81 (t, 1H, *J* = 7.65 Hz, H-7), 7.29–7.47 (m, 7H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 7.65 Hz, 2H) 7.86 (d, *J* = 6.8 Hz, 1H, H-5), 8.0 (s, 1H, pyrazole-CH). ^{13}C NMR δ 45.6, 49.3, 116.1, 118.9, 119.1, 119.3, 121.8, 122.8, 126.7, 127.1, 127.7, 129.6, 129.8, 131.8, 132.1, 135.6, 139.7, 150.0, 151.2, 193.2. MS *m/z*: 365 (M^+). Anal. calcd. for $C_{24}H_{19}N_3O$: C 78.88, H 5.24, N 11.50; found: C 78.80, H 5.18, N 11.42.

2-[3-(4-Methoxyphenyl)-1-phenyl-1H-pyrazol-4-yl]-2,3-dihydroquinolin-4(1H)-one (Table 1, entry 7)

Pale white solid, mp 175–177 °C. IR (cm^{-1}) ν_{max}: 3330, 1642, 1577, 1509, 1234, 1116. ^{1}H NMR δ 2.89–2.91 (m, 2H), 3.83 (s, 3H, OCH_3), 4.61 (s, br s, NH, 1H), 4.94–4.96 (m, 1H), 6.62 (d, *J* = 8.05 Hz, 1H, H-8), 6.76 (m, 1H, H-7), 6.95–7.7 (m, 10H), 7.85 (d, *J* = 8.0 Hz, 1H, H-5), 8.04 (s, 1H, pyrazole-CH). ^{13}C NMR δ 45.0, 49.3, 56.5, 114.0, 114.8, 115.8, 118.3, 119.1, 120.3, 124.9, 126.0, 126.4, 127.3, 128.5, 129.4, 134.4, 138.9, 152.3, 154.3, 159.1, 193.2. MS *m/z*: 395 (M^+). Anal. calcd. for $C_{25}H_{21}N_3O_2$: C 75.93, H 5.35, N 10.63; found: C 75.82, H 5.30, N 10.58.

2-[3-(4-Ethoxyphenyl)-1-phenyl-1H-pyrazol-4-yl]-2,3-dihydroquinolin-4(1H)-one (Table 1, entry 8)

Pale white solid, mp 178 to 179 °C. IR (cm^{-1}) ν_{max}: 3349, 1658, 1569, 1519, 1227, 1136. ^{1}H NMR δ 1.41 (t, *J* = 6.9 Hz, 3H), 2.8–2.84 (m, 2H, H-3), 4.0 (q, *J* = 6.9, 13.75 Hz, 2H) 4.64 (s, br s, NH, 1H), 4.94–4.97 (m, 1H), 6.62 (d, *J* = 8.45 Hz, 1H, H-8), 6.76–7.86 (m, 11H), 7.84 (d,

J = 7.65 Hz, 1H, H-5), 8.03 (s, 1H, pyrazole-CH). ^{13}C NMR δ 14.9, 45.6, 49.3, 63.6, 114.5, 114.9, 116.1, 118.7, 119.0, 121.5, 125.1, 126.4, 126.7, 127.7, 129.5, 130.6, 135.5, 139.8, 151.0, 151.3, 159.3, 193.4. MS *m*/*z*: 409 (M^+). Anal. calcd. for $C_{26}H_{23}N_3O_2$: C 76.26, H 5.66, N 10.26; found: C 76.19, H 5.58, N 10.18.

2-Phenyl-2,3-dihydro-4*H*-chromen-4-one (Table 2, entry 1)

Pale white solid, mp 75 to 76 °C (lit. value (10*a*) 78 to 77 °C). IR (cm^{-1}) ν_{max}: 1691, 1606, 1517, 1464, 1223, 1174. ^{1}H NMR δ 2.84–3.12 (m, 2H), 5.46 (dd, *J* = 2.85, 13.15 Hz, 1H, H-2), 7.04–7.07 (m, 2H), 7.37–7.52 (m, 6H), 7.90 (dd, *J* = 1.75, 8.05 Hz, 1H, H-5). ^{13}C NMR δ 44.8, 77.4, 118.2, 121.0, 121.7, 126.3, 127.2, 128.9, 135.0, 136.3, 138.8, 161.7, 192.1. MS *m*/*z*: 224 (M^+). Anal. calcd. for $C_{15}H_{12}O_2$: C 80.34, H 5.39; found: C 80.27, H 5.32.

2-(4-Methylphenyl)-2,3-dihydro-4*H*-chromen-4-one (Table 2, entry 2)

Pale white solid, mp 82 to 83 °C (lit. value (10*a*) 83 to 84 °C). IR (cm^{-1}) ν_{max}: 1696, 1595, 1520, 1459, 1225, 1162. ^{1}H NMR δ 2.38 (s, 3H), 2.89–3.12 (m, 2H), 5.43 (dd, *J* = 1.95, 13.75 Hz, 1H, H-2), 7.03–7.06 (m, 2H), 7.23 (d, *J* = 8 Hz, 2H), 7.36 (d, *J* = 8 Hz, 2H), 7.48 (m, 1H, H-6), 7.92 (dd, *J* = 1.7, 8.55 Hz, 1H, H-5). ^{13}C NMR δ 21.3, 44.7, 77.4, 118.3, 121.0, 121.6, 126.3, 127.1, 129.6, 135.8, 136.3, 138.8, 161.7, 192.3. MS *m*/*z*: 238 (M^+). Anal. calcd. for $C_{16}H_{14}O_2$: C 80.65, H 5.92; found: C 80.58, H 5.84.

2-(4-Chlorophenyl)-2,3-dihydro-4*H*-chromen-4-one (Table 2, entry 3)

Pale white solid, mp 95 to 96 °C (lit. value (4) 94 to 95 °C). IR (cm^{-1}) ν_{max}: 1692, 1575, 1519, 1464, 1256, 1162. ^{1}H NMR δ 2.84–3.05 (m, 2H), 5.43–5.46 (m, 1H), 7.03–7.06 (m, 2H), 7.38–7.52 (m, 5H), 7.90 (dd, *J* = 1.55, 7.65 Hz, 1H, H-5). ^{13}C NMR δ 44.7, 77.4, 118.2, 121.0, 121.9, 127.2, 127.6, 128.3, 129.1, 136.4, 137.4, 161.4, 191.6. MS *m*/*z*: 258 (M^+). Anal. calcd. for $C_{15}H_{11}ClO_2$: C 69.64, H 4.29; found: C 69.59, H 4.21.

2-(3-Chlorophenyl)-2,3-dihydro-4*H*-chromen-4-one (Table 2, entry 4)

Pale white solid, mp 98 to 99 °C (lit. value (4) 99 to 100 °C). IR (cm^{-1}) ν_{max}: 1697, 1568, 1523, 1454, 1297, 1145. ^{1}H NMR δ 2.83–3.15 (m, 2H), 5.44–5.47 (m, 1H, H-2), 7.1–7.3 (m, 2H), 7.36–7.58 (m, 5H), 7.90 (dd, *J* = 1.65, 8.45 Hz, 1H, H-5). ^{13}C NMR δ 45.3, 76.4, 118.1, 119.4, 120.8, 121.9, 124.7, 127.0, 127.8, 128.0, 129.6, 136.4, 136.9, 160.4, 193.1. MS *m*/*z*: 258 (M^+). Anal. calcd. for $C_{15}H_{11}ClO_2$: C 69.64, H 4.29; found: C 69.57, H 4.22.

2-(4-Methoxyphenyl)-2,3-dihydro-4*H*-chromen-4-one (Table 2, entry 5)

Pale white solid, mp 87 to 88 °C (lit. value (4) 88 to 89 °C) IR (cm^{-1}) ν_{max}: 1689, 1588, 1513, 1443, 1243, 1123. ^{1}H NMR δ 2.86–3.0 (m, 2H), 3.8 (s, 3H), 5.39 (dd, *J* = 2.8, 13.70 Hz, 1H, H-2), 6.96 (d, *J* = 8.0 Hz, 1H), 7.01–7.05 (m, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8 Hz, 2H), 7.91 (dd, *J* = 1.7, 8.0 Hz, 1H, H-5). ^{13}C NMR δ 44.5, 55.5, 77.4, 114.3, 118.2, 121.0, 121.6, 127.1, 130.9, 136.3, 160.1, 161.7, 192.3. MS *m*/*z*: 254 (M^+). Anal. calcd. for $C_{16}H_{14}O_3$: C 75.57, H 5.55; found: C 75.50, H 5.48.

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