Pd(OAc)$_2$/S=PPh$_3$ Accelerated Activation of $gem$-Dichloroalkenes for the Construction of 3-Arylchromones

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Contents

1. General information........................................................................................................2

2. Experimental procedure for the Pd(OAc)$_2$/S=PPh$_3$ catalyzed the tandem reaction.........................................................................................................................2

3. Experiments on investigation of mechanism..................................................................5

4. Characterization data for the products...........................................................................7

5. $^1$H NMR and $^{13}$C NMR copies of products............................................................18
1. General information

All the chemicals and solvents were used as received without further purification. Silica gel was purchased from Qing Dao Hai Yang Chemical Industry Co. NMR spectra of the products were recorded using a Bruker Avance TM spectrometer operating at 400 MHz for $^1$H and 101 MHz for $^{13}$C in CDCl$_3$ unless otherwise noted. High resolution mass spectra (HRMS) of the products were obtained on a Bruker Daltonics micro TOF-Q spectrometer.

2. Experimental procedure for the Pd(OAc)$_2$/S=PPh$_3$ catalyzed the tandem reaction

Table S1 Optimization of the reaction conditions.$^a$

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<th>Base</th>
<th>Solvent</th>
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$^a$Reaction conditions: $^{1a}$ (0.50 mmol), $^{2a}$ (1.0 mmol), Pd catalyst (5 mol%), ligand (10 mol%), TEBAC (1.0 mmol), Na$_2$CO$_3$ (1.5 mmol), NMP (2.0 mL), 110 °C, N$_2$, 24h. $^b$Isolated yield.$^{2a}$ (0.50 mmol), $^{2a}$ (0.75 mmol).

(1) A mixture of salicylaldehyde (0.50 mmol), gem-dichloroalkene (1.0 mmol), Pd(OAc)$_2$ (5 mol%), S=PPh$_3$ (10 mol%), Na$_2$CO$_3$ (1.5 mmol), TEBAC (1.0 mmol) and NMP (2.0 mL) was
stirred at 110 °C under N₂ atmosphere for 24 h. After cooling to room temperature, EtOAc (30 mL) was added and the aqueous phase was extracted by H₂O (3×30 mL). The organic phase was dried over Na₂SO₄, and concentrated in vacuum. The residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate as eluent to afford the desired product.

(2) A mixture of salicylaldehyde (0.50 mmol), gem-dichloroalkene (1.0 mmol), Pd(OAc)₂ (5 mol%), S=PPh₃ (10 mol%), Na₂CO₃ (1.5 mmol), TBAF (1.0 mmol) and NMP (2.0 mL) was stirred at 110 °C under N₂ atmosphere for 24 h. After cooling to room temperature, EtOAc (30 mL) was added and the aqueous phase was extracted by H₂O (3×30 mL). The organic phase was dried over Na₂SO₄, and concentrated in vacuum. The residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate as eluent to afford the desired product.

(3) A mixture of 2-hydroxyacetophenone (0.50 mmol), gem-dichloroalkene (1.0 mmol), Pd(OAc)₂ (5 mol%), S=PPh₃ (10 mol%), Na₂CO₃ (1.5 mmol), TEBAC (1.0 mmol) and NMP (2.0 mL) was stirred at 110 °C under N₂ atmosphere for 24 h. After cooling to room temperature, EtOAc (30 mL) was added and the aqueous phase was extracted by H₂O (3×30 mL). The organic phase was dried over Na₂SO₄, and concentrated in vacuum. The residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate as eluent to afford 1-(2-hydroxyphenyl)ethan-1-one in 86% yield (Scheme 1). In the process of the reaction, 2-hydroxyacetophenone coupled with benzyltriethylammonium chloride (TEBAC).

Scheme 1

1-(2-(benzylxy)phenyl)ethan-1-one
$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.75 (d, $J = 6.0$ Hz, 1H), 7.45-7.41 (m, 3H), 7.39 (t, $J = 6.0$ Hz, 2H), 7.34 (t, $J = 6.0$ Hz, 1H), 7.02-6.99 (m, 2H), 5.15 (s, 2H), 2.59 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 199.9, 158.1, 136.2, 133.6, 130.5, 128.8, 128.7, 128.3, 127.6, 120.9, 112.9, 70.7, 32.1. ESI-MS (M): 226.

(4) A mixture of 2-((p-tolylimino)methyl)phenol (0.50 mmol), $gem$-dichloroalkene (1.0 mmol), Pd(OAc)$_2$ (5 mol%), S=PPh$_3$ (10 mol%), Na$_2$CO$_3$ (1.5 mmol), TEBAC (1.0 mmol) and NMP (2.0 mL) was stirred at 110 °C under N$_2$ atmosphere for 24 h. After cooling to room temperature, EtOAc (30 mL) was added and the aqueous phase was extracted by H$_2$O (3×30 mL). The organic phase was dried over Na$_2$SO$_4$, and concentrated in vacuum. The residue was detected by GC-MS, chromone was not detected (Scheme 2). 2-vinylphenol was destroyed and dichloroalkenes was converted into (2-chlorovinyl)benzene and 1, 4-diphenylbuta-1, 3-diyne.

![Scheme 2](image)

(5) A mixture of 2-vinylphenol (0.50 mmol), $gem$-dichloroalkene (1.0 mmol), Pd(OAc)$_2$ (5 mol%), S=PPh$_3$ (10 mol%), Na$_2$CO$_3$ (1.5 mmol), TEBAC (1.0 mmol) and NMP (2.0 mL) was stirred at 110 °C under N$_2$ atmosphere for 24 h. After cooling to room temperature, EtOAc (30 mL) was added and the aqueous phase was extracted by H$_2$O (3×30 mL). The organic phase was dried over Na$_2$SO$_4$, and concentrated in vacuum. The residue was detected by GC-MS, no desired product was observed (Scheme 3). Regrettfully, 2-(benzyloxy)benzaldehyde and N-benzyl-4-methylaniline were observed by GC-MS.

![Scheme 3](image)
3. Experiments on investigation of mechanism

3.1 The coupling between (chloroethynyl)benzene and salicylaldehyde

A mixture of salicylaldehyde (0.50 mmol), (chloroethynyl)benzene (1.0 mmol), Pd(OAc)$_2$ (5 mol%), S=PPh$_3$ (10 mol%), Na$_2$CO$_3$ (1.5 mmol), TEBAC (1.0 mmol) and NMP (2.0 mL) was stirred at 110 ºC under N$_2$ atmosphere for 24 h. After cooling to room temperature, EtOAc (30 mL) was added and the aqueous phase was extracted by H$_2$O (3×30 mL). The organic phase was dried over Na$_2$SO$_4$, and concentrated in vacuum. The residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate as eluent to afford the desired product in 15 % yield (Scheme 4).

Scheme 4

3.2 The coupling between $p$-hydroxybenzaldehyde and gem-dichloroalkene

A mixture of $p$-hydroxybenzaldehyde (0.50 mmol), gem-dichloroalkene (1.0 mmol), Pd(OAc)$_2$ (5 mol%), S=PPh$_3$ (10 mol%), Na$_2$CO$_3$ (1.50 mmol), TEBAC (1.0 mmol) and NMP (2.0 mL) was stirred at 110 ºC under N$_2$ atmosphere for 24 h. After cooling to room temperature, EtOAc (30 mL) was added and the aqueous phase was extracted by H$_2$O (3×20 mL). The organic phase was dried over Na$_2$SO$_4$, and concentrated in vacuum. The residue was detected by GC-MS (Scheme 5).

Scheme 5

3.3 The experiment between gem-dichloroalkene and salicylaldehyde contained 62% D content

A mixture of 62% D content of salicylic aldehyde (0.50 mmol),$^1$ gem-dichloroalkene (1.0 mmol), Pd(OAc)$_2$ (5 mol%), S=PPh$_3$ (10 mol%), Na$_2$CO$_3$ (1.5 mmol), TEBAC (1.0 mmol) and NMP (2.0 mL) was stirred at 110 ºC under N$_2$ atmosphere for 24 h. After cooling to room
temperature, EtOAc (30 mL) was added and the aqueous phase was extracted by H2O (3×30 mL). The organic phase was dried over Na2SO4, and concentrated in vacuum. The residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate as eluent to afford the desired product in 28% yield. In the control experiment, 2-(benzyloxy)benzaldehyde was obtained in 52% yield (Scheme 6).

![Diagram](image)

**Scheme 6**

### 3.4 The coupling between diethyl but-2-ynedioate and salicylaldehyde

A mixture of salicylaldehyde (0.50 mmol), diethyl but-2-ynedioate (1.0 mmol), Pd(OAc)2 (5 mol%), S=PH3 (10 mol%), Na2CO3 (1.50 mmol), TEBAC (1.0 mmol) and NMP (2.0 mL) was stirred at 110 ºC under N2 atmosphere for 24 h. After cooling to room temperature, EtOAc (30 mL) was added and the aqueous phase was extracted by H2O (3×30 mL). The organic phase was dried over Na2SO4, and concentrated in vacuum. The residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate as eluent to afford no desired product (Scheme 7).

![Diagram](image)

**Scheme 7**

### 3.5 The coupling between 1H-pyrrole-2, 5-dione and salicylaldehyde

A mixture of salicylaldehyde (0.50 mmol), 1H-pyrrole-2, 5-dione (1.0 mmol), Pd(OAc)2 (5 mol%), S=PH3 (10 mol%), Na2CO3 (1.50 mmol), TEBAC (1.0 mmol) and NMP (2.0 mL) was...
stirred at 110 °C under N2 atmosphere for 24 h. After cooling to room temperature, EtOAc (30 mL) was added and the aqueous phase was extracted by H2O (3×30 mL). The organic phase was dried over Na2SO4, and concentrated in vacuum. The residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate as eluent to afford no desired product (Scheme 8).

Scheme 8

4. Characterization of Products

2-phenyl-4H-chromen-4-one 3a

(m.p. 97-98°C) 1H NMR (400 MHz, CDCl3) δ 8.24 (d, J = 8.0 Hz, 1H), 7.95-7.93 (m, 2H), 7.73-7.69 (m, 1H), 7.59-7.53 (m, 4H), 7.43 (t, J = 8.0 Hz, 1H), 6.84 (s, 1H). 13C NMR (101 MHz, CDCl3) δ 178.5, 163.4, 156.3, 133.8, 131.8, 131.6, 129.1, 126.3, 125.7, 125.3, 124.0, 118.1, 107.6. IR (neat, cm−1): 3059, 2921, 2850, 1646, 1606, 1569, 1495, 1465, 1449, 1376, 1310, 1283, 1259, 1225, 1129. ESI-MS (M): 222.

6-methyl-2-phenyl-4H-chromen-4-one 3b

(m.p. 112 °C) 1H NMR (400 MHz, CDCl3) δ 8.03 (s, 1H), 7.95-7.93 (m, 2H), 7.56-7.48 (m, 5H), 6.83 (s, 1H), 2.48 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 178.5, 163.4, 156.3, 135.2, 135.0, 131.9, 131.5, 129.0, 126.3, 125.1, 123.6, 117.9, 107.4, 21.0. IR (neat, cm−1): 3064, 2920, 1645, 1615, 1569, 1494, 1483, 1450, 1431, 1361, 1302, 1255, 1223, 1139. ESI-MS (M): 236.

7-methoxy-2-phenyl-4H-chromen-4-one 3c
(m.p. 97 °C) \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.15 (d, \( J = 8.0 \) Hz, 1H), 7.93-7.91 (m, 2H), 7.54-7.52 (m, 3H), 7.02-6.98 (m, 2H), 6.78 (s, 1H), 3.94 (s, 3H). \( ^{13}C \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 177.9, 164.2, 163.0, 158.0, 131.9, 131.4, 129.0, 127.0, 126.2, 117.8, 114.4, 107.5, 100.4, 55.9. IR (neat, cm\(^{-1}\)): 3026, 3002, 2924, 2845, 1653, 1626, 1606, 1494, 1450, 1439, 1348, 1357, 1284, 1247, 1190, 1165, 1131. HRMS, calculated for C\(_{16}\)H\(_{13}\)O\(_3\) (M+H\(^+\)): 253.0860, found: 253.0864.

6-bromo-2-phenyl-4\(H\)-chromen-4-one 3d

(m.p. 189 °C) \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.35 (d, \( J = 4.0 \) Hz, 1H), 7.92-7.90 (m, 2H), 7.78 (d, \( J = 8.0 \) Hz, 1H), 7.56-7.53 (m, 3H), 7.47 (d, \( J = 8.0 \) Hz, 1H), 6.83 (s, 1H). \( ^{13}C \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 177.1, 163.7, 155.0, 136.8, 131.9, 131.4, 129.2, 128.4, 126.4, 125.3, 120.1, 118.7, 107.6. IR (neat, cm\(^{-1}\)): 3083, 2920, 1648, 1614, 1597, 1563, 1494, 1456, 1434, 1350, 1271, 1253, 1210, 1133. HRMS, calculated for C\(_{15}\)H\(_{10}\)BrO\(_2\) (M+H\(^+\)): 300.9859, found: 300.9858.

6-chloro-2-phenyl-4\(H\)-chromen-4-one 3e

(m.p. 183°C) \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.19 (d, \( J = 2.6 \) Hz, 1H), 7.91 (dd, \( J = 8.0, 4.0 \) Hz, 2H), 7.64 (dd, \( J = 8.0, 4.0 \) Hz, 1H), 7.57-7.53 (m, 4H), 6.83 (s, 1H). \( ^{13}C \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 177.2, 163.7, 154.6, 134.0, 131.9, 131.4, 131.2, 129.1, 126.3, 125.2, 124.9, 119.8, 107.5. IR (neat, cm\(^{-1}\)): 3085, 1648, 1615, 1601, 1566, 1494, 1456, 1436, 1353, 1306, 1291, 1272, 1253, 1132. HRMS, calculated for C\(_{15}\)H\(_8\)ClNaO\(_2\) (M+Na\(^+\)): 279.0183, found: 279.0183.
8-ethoxy-2-phenyl-4H-chromen-4-one 3f

(m.p. 105 °C) \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.00-7.97 (m, 2H), 7.78 (dd, \( J = 8.0, 4.0 \) Hz, 1H), 7.55-7.53 (m, 3H), 7.32 (t, \( J = 8.0 \) Hz, 1H), 7.19 (d, \( J = 8.0 \) Hz, 1H), 6.86 (s, 1H), 4.24 (q, \( J = 8.0 \) Hz, 2H), 1.58 (t, \( J = 8.0 \) Hz, 3H). \( ^{13}C \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 178.6, 162.9, 148.5, 146.9, 131.9, 131.5, 129.0, 126.3, 125.0, 124.8, 116.4, 115.7, 107.3, 65.0, 14.8. IR (neat, cm\(^{-1}\)): 3068, 2975, 2934, 2896, 1576, 1496, 1473, 1451, 1379, 1325, 1310, 1279, 1221, 1196, 1178, 1150. HRMS, calculated for C\(_{17}\)H\(_{14}\)NaO\(_3\) (M+Na\(^+\)): 289.0835, found: 289.0835.

2-p-tolyl-4H-chromen-4-one 3g

(m.p. 111 °C) \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.24 (d, \( J = 8.0 \) Hz, 1H), 7.84 (d, \( J = 8.0 \) Hz, 2H), 7.71 (t, \( J = 8.0 \) Hz, 1H), 7.58 (d, \( J = 8.0 \) Hz, 1H), 7.43 (t, \( J = 8.0 \) Hz, 1H), 7.34 (d, \( J = 8.0 \) Hz, 2H), 6.81 (d, \( J = 4.0 \) Hz, 1H), 2.45 (s, 3H). \( ^{13}C \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 178.5, 163.6, 156.3, 142.3, 133.7, 129.8, 129.0, 126.2, 125.7, 125.1, 124.0, 118.1, 107.0, 21.6. IR (neat, cm\(^{-1}\)): 3035, 2918, 1638, 1568, 1510, 1466, 1414, 1372, 1313, 1281, 1255, 1228. ESI-MS (M): 236.

2-(4-tert-butylphenyl)-4H-chromen-4-one 3h

(m.p. 80 °C) \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.24 (d, \( J = 8.0 \) Hz, 1H), 7.88 (dd, \( J = 8.0, 4.0 \) Hz, 2H), 7.73-7.69 (m, 1H), 7.57 (t, \( J = 8.0 \) Hz, 3H), 7.43 (t, \( J = 8.0 \) Hz, 1H), 6.83 (d, \( J = 1.4 \) Hz, 1H),
1.38 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 178.5, 163.6, 156.3, 155.3, 133.7, 128.9, 126.2, 126.1, 125.7, 125.1, 124.0, 118.1, 107.1, 35.0, 31.1. IR (neat, cm$^{-1}$): 3065, 2960, 2867, 1645, 1573, 1514, 1466, 1415, 1374, 1336, 1330, 1283, 1269, 1239, 1227, 1202. HRMS, calculated for C$_{19}$H$_{18}$NaO$_2$ (M+Na$^+$): 301.1199, found: 301.1196.

2-(4-fluorophenyl)-4$H$-chromen-4-one 3i

(m.p. 140 °C) $^1$H NMR (400 MHz, CDCl$_3$) δ 8.25 (d, $J = 8.0$ Hz, 1H), 7.97-7.94 (m, 2H), 7.73 (d, $J = 8.0$ Hz, 1H), 7.58 (d, $J = 8.0$ Hz, 1H), 7.47-7.43 (m, 1H), 7.34 (t, $J = 8.0$ Hz, 2H), 6.79 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 178.2, 166.0, 162.9 (d, $J_{CF} = 120$ Hz), 156.1, 133.8, 128.5 (d, $J_{CF} = 10$ Hz), 128.0, 125.5 (d, $J_{CF} = 40$ Hz), 123.8, 118.0, 116.3 (d, $J_{CF} = 20$ Hz), 107.3. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -107.42 ppm. IR (neat, cm$^{-1}$): 3077, 1653, 1574, 1508, 1466, 1417, 1378, 1332, 1302, 1284, 1233, 1163, 1133. HRMS, calculated for C$_{15}$H$_{10}$FO$_2$ (M+H$^+$): 241.0660, found: 241.0663.

2-(4-chlorophenyl)-4$H$-chromen-4-one 3j

(m.p. 187 °C) $^1$H NMR (400 MHz, CDCl$_3$) δ 8.21 (d, $J = 8.0$ Hz, 1H), 7.84 (d, $J = 8.0$ Hz, 2H), 7.72-7.68 (m, 1H), 7.55 (d, $J = 8.0$ Hz, 1H), 7.50-7.47 (m, 2H), 7.42 (t, $J = 8.0$ Hz, 1H), 6.78 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 178.2, 162.2, 156.1, 137.9, 133.9, 130.2, 129.4, 127.5, 125.7, 125.4, 123.9, 118.0, 107.7. IR (neat, cm$^{-1}$): 3090, 1668, 1622, 1607, 1593, 1575, 1480, 1467, 1408, 1375, 1332, 1278, 1220, 1132. HRMS, calculated for C$_{15}$H$_{9}$ClNaO$_2$ (M+Na$^+$): 279.0183, found: 279.0183.

2-(biphenyl-4-yl)-4$H$-chromen-4-one 3k

10
(m.p. 158 °C) $^1$H NMR (400 MHz, CDCl$_3$) δ 8.25 (d, $J = 8.0$ Hz, 1H), 8.02 (d, $J = 8.0$ Hz, 2H), 7.78-7.70 (m, 3H), 7.66 (d, $J = 8.0$ Hz, 2H), 7.61 (d, $J = 8.0$ Hz, 1H), 7.52-7.42 (m, 4H), 6.89 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 178.4, 163.1, 156.3, 144.4, 139.7, 133.8, 130.5, 129.0, 128.2, 127.6, 127.1, 126.7, 125.7, 125.2, 124.0, 118.1, 107.4. IR (neat, cm$^{-1}$): 3062, 2361, 1637, 1571, 1519, 1487, 1475, 1464, 1411, 1376, 1335, 1316, 1284, 1261, 1220, 1129. HRMS, calculated for C$_{21}$H$_{15}$O$_2$ (M+H$^+$): 299.1067, found: 299.1071.

2-(naphthalen-2-yl)-4H-chromen-4-one 3l

(m.p. 160 °C) $^1$H NMR (400 MHz, CDCl$_3$) δ 8.49 (s, 1H), 8.26 (d, $J = 8.0$ Hz, 1H), 7.98-7.91 (m, 4H), 7.74-7.71 (m, 1H), 7.66-7.58 (m, 3H), 7.45 (t, $J = 8.0$ Hz, 1H), 6.97 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 178.4, 163.2, 156.3, 134.6, 133.8, 132.9, 129.0, 128.9, 128.0, 127.8, 127.1, 126.9, 125.7, 125.2, 122.5, 118.1, 107.8. IR (neat, cm$^{-1}$): 3070, 1637, 1567, 1503, 1463, 1437, 1380, 1347, 1330, 1283, 1225, 1202, 1131. HRMS, calculated for C$_{19}$H$_{12}$NaO$_2$ (M+Na$^+$): 295.0730, found: 295.0734.

2-(thiophen-2-yl)-4H-chromen-4-one 3m

(m.p. 90-92 °C) $^1$H NMR (400 MHz, CDCl$_3$) δ 8.21 (d, $J = 8.0$ Hz, 1H), 7.74-7.67 (m, 2H), 7.59 (d, $J = 4.0$ Hz, 1H), 7.54 (d, $J = 4.0$ Hz, 1H), 7.42 (t, $J = 8.0$ Hz, 1H), 7.21-7.18 (m, 1H), 6.71 (d, $J$
1H. 13C NMR (101 MHz, CDCl3) δ 177.9, 159.0, 155.9, 135.2, 133.7, 130.3, 128.5, 128.4, 125.7, 125.3, 124.0, 117.9, 106.2. IR (neat, cm⁻¹): 3066, 1619, 1567, 1461, 1423, 1384, 1352, 1255, 1126. HRMS, calculated for C13H8NaO2S (M+Na⁺): 251.0137, found: 251.0142.

6-methyl-2-p-tolyl-4H-chromen-4-one 3n

(m.p. 142 °C) 1H NMR (400 MHz, CDCl3) δ 8.04 (s, 1H), 7.85 (d, J = 8.0 Hz, 2H), 7.51 (q, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 6.81 (d, J = 4.0 Hz, 1H), 2.49 (s, 3H), 2.47 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 178.6, 163.5, 154.6, 142.2, 135.1, 134.9, 129.8, 129.1, 126.2, 125.1, 123.7, 117.9, 106.9, 21.6, 21.0. IR (neat, cm⁻¹): 3039, 2919, 2850, 1645, 1614, 1578, 1563, 1509, 1484, 1435, 1364, 1310, 1296, 1223, 1138. HRMS, calculated for C17H14NaO2 (M+Na⁺): 273.0886, found: 273.0883.

7-methoxy-2-p-tolyl-4H-chromen-4-one 3o

(m.p. 127 °C) 1H NMR (400 MHz, CDCl3) δ 8.14 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 6.75 (s, 1H), 3.94 (s, 3H), 2.45 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 177.9, 164.1, 163.2, 158.0, 142.0, 129.7, 129.1, 127.0, 126.1, 117.9, 114.3, 106.9, 100.4, 55.8, 21.5. IR (neat, cm⁻¹): 2920, 1653, 1510, 1472, 1440, 1414, 1377, 1274, 1189, 1160. HRMS, calculated for C17H14NaO3 (M+Na⁺): 289.0835, found: 289.0836.

6-chloro-2-p-tolyl-4H-chromen-4-one 3p
(m.p. 190 °C) $^1$H NMR (400 MHz, CDCl$_3$) δ 8.20 (d, $J = 2.6$ Hz, 1H), 7.82 (d, $J = 8.0$ Hz, 2H), 7.64 (dd, $J = 8.0$, 4.0 Hz, 1H), 7.54 (d, $J = 8.0$ Hz, 1H), 7.34 (d, $J = 8.0$ Hz, 2H), 6.81 (s, 1H), 2.46 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 177.2, 163.9, 154.5, 142.6, 133.8, 131.1, 129.8, 128.5, 126.2, 125.1, 124.9, 119.8, 106.8, 21.6. IR (neat, cm$^{-1}$): 3033, 2917, 1641, 1614, 1568, 1512, 1479, 1466, 1437, 1359, 1290, 1273, 1256. HRMS, calculated for C$_{16}$H$_{11}$ClNaO$_2$ (M+Na$^+$): 293.0340, found: 293.0339.

8-ethoxy-2-p-tolyl-4H-chromen-4-one 3q

![8-ethoxy-2-p-tolyl-4H-chromen-4-one 3q](image)

(m.p. 155 °C) $^1$H NMR (400 MHz, CDCl$_3$) δ 7.87 (d, $J = 8.0$ Hz, 2H), 7.77 (d, $J = 8.0$ Hz, 1H), 7.33 (d, $J = 8.0$ Hz, 3H), 7.18 (d, $J = 8.0$ Hz, 1H), 6.83 (d, $J = 4.0$ Hz, 1H), 4.24 (q, $J = 6.8$ Hz, 2H), 2.45 (s, 3H), 1.57 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 178.6, 163.1, 148.4, 146.8, 142.1, 129.8, 129.1, 126.2, 125.0, 124.7, 116.4, 115.6, 106.6, 65.0, 21.6, 14.8. IR (neat, cm$^{-1}$): 3030, 2991, 2941, 1646, 1612, 1601, 1579, 1510, 1491, 1466, 1413, 1376, 1351, 1281, 1247, 1217, 1191, 1180, 1149. HRMS, calculated for C$_{18}$H$_{16}$NaO$_3$ (M+Na$^+$): 303.0992, found: 303.0993.

2-(4-chlorophenyl)-8-ethoxy-4H-chromen-4-one 3r

![2-(4-chlorophenyl)-8-ethoxy-4H-chromen-4-one 3r](image)

(m.p. 168 °C) $^1$H NMR (400 MHz, CDCl$_3$) δ 7.89 (dd, $J = 8.0$, 4.0 Hz, 2H), 7.75 (d, $J = 8.0$ Hz, 1H), 7.50 (dd, $J = 8.0$, 4.0 Hz, 2H), 7.30 (t, $J = 8.0$ Hz, 1H), 7.18 (dd, $J = 8.0$, 4.0 Hz, 1H), 6.80 (s, 1H), 4.22 (q, $J = 8.0$ Hz, 2H), 1.57 (t, $J = 6.0$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 178.4, 161.7, 148.4, 146.6, 137.8, 130.3, 129.4, 127.5, 125.0, 124.9, 116.3, 115.6, 107.3, 64.9, 14.8. IR (neat, cm$^{-1}$): 3071, 2983, 2934, 2361, 1638, 1595, 1578, 1493, 1471, 1444, 1412, 1397, 1375, 1353, 1277, 1253, 1221, 1178, 1148. HRMS, calculated for C$_{17}$H$_{13}$ClNaO$_3$ (M+Na$^+$): 323.0445, found: 323.0444.
2-(4-fluorophenyl)-7-methoxy-4\textit{H}-chromen-4-one 3s

(m.p. 160 °C) $^1$H NMR (400 MHz, CDCl$_3$) δ 8.16 (d, $J = 8.0$ Hz, 1H), 7.96-7.92 (m, 2H), 7.24 (t, $J = 8.0$ Hz, 2H), 7.04-6.99 (m, 2H), 6.74 (s, 1H), 3.97 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 177.7, 165.9, 163.8 (d, $J_{CF} = 81$ Hz), 162.0, 157.9, 128.4 (d, $J_{CF} = 10$ Hz), 128.1 ($J_{CF} = 10$ Hz), 127.1, 117.7, 116.3 (d, $J_{CF} = 30$ Hz), 114.5, 107.3, 100.4, 55.9. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -107.77 ppm. IR (neat, cm$^{-1}$): 3073, 3013, 2957, 2849, 1660, 1607, 1509, 1471, 1442, 1417, 1377, 1287, 1252, 1232, 1203, 1192, 1164. HRMS, calculated for C$_{16}$H$_{11}$FNaO$_3$ (M+Na$^+$): 293.0584, found: 293.0585.

2-(4-chlorophenyl)-6-methyl-4\textit{H}-chromen-4-one 3t

(m.p. 194 °C) $^1$H NMR (400 MHz, CDCl$_3$) δ 8.01 (s, 1H), 7.86 (d, $J = 8.0$ Hz, 2H), 7.53-7.45 (m, 4H), 6.78 (s, 1H), 2.47 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 178.3, 162.0, 154.4, 137.8, 135.4, 135.1, 130.3, 129.3, 127.5, 125.1, 123.5, 117.8, 107.5, 21.0. IR (neat, cm$^{-1}$): 3427, 3063, 3028, 2922, 2856, 1642, 1622, 1594, 1577, 1490, 1453, 1407, 1378, 1364, 1285, 1228. HRMS, calculated for C$_{16}$H$_{11}$ClNaO$_2$ (M+Na$^+$): 293.0340, found: 293.0340.

2-(4-fluorophenyl)-6-methyl-4\textit{H}-chromen-4-one 3u

(m.p. 150-154 °C) $^1$H NMR (400 MHz, CDCl$_3$) δ 8.01 (d, $J = 0.9$ Hz, 1H), 7.93 (q, $J = 8.0$, 2H), 7.51 (dd, $J = 8.0$, 4.0 Hz, 1H), 7.45 (d, $J = 8.0$ Hz, 1H), 7.21 (t, $J = 8.0$ Hz, 2H), 6.75 (s, 1H), 2.47
(s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 178.4, 166.0, 162.8 ($d, J_{CF} = 8$ Hz), 154.4, 135.3, 135.0, 128.5 ($d, J_{CF} = 10$ Hz), 128.1 ($d, J_{CF} = 3.0$ Hz), 125.1, 123.5, 117.8, 116.3 ($d, J_{CF} = 30$ Hz), 107.2, 21.0. $^{19}$F NMR (565 MHz, CDCl$_3$) $\delta$ -107.58 ppm. IR (neat, cm$^{-1}$): 3426, 3063, 2925, 1645, 1602, 1507, 1484, 1453, 1333, 1363, 1299, 1235, 1196, 1162, 1139. HRMS, calculated for C$_{16}$H$_{11}$FNaO$_2$ (M+Na$^+$): 277.0635, found: 277.0635.

2-(o-tolyl)-4$H$-chromen-4-one 3v

(m.p. 105 °C) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.27 ($d, J = 8.0, 1$H), 7.70 ($t, J = 8.0, 1$H), 7.55-7.49 (m, 2H), 7.46-7.41 (m, 2H), 7.33 ($t, J = 8.0, 2$H), 6.50 (s, 1H), 2.49 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 178.3, 166.1, 156.5, 136.8, 133.8, 132.7, 131.3, 130.8, 129.2, 126.2, 125.8, 125.3, 123.8, 118.1, 112.0, 20.6. IR (neat, cm$^{-1}$): 2926, 1652, 1571, 1465, 1370, 1220, 1130. ESI-MS (M): 236.

2-(m-tolyl)-4$H$-chromen-4-one 3w

(m.p. 107 °C) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.24 ($dd, J = 4.0, 8.0$ Hz, 1H), 7.73-7.68 (m, 3H), 7.58 ($d, J = 8.0$ Hz, 1H), 7.44-7.39 (m, 2H), 7.35 ($d, J = 8.0$ Hz, 1H), 6.82 (s, 1H), 2.46 (s, 3H). $^{13}$C NMR (101 MHZ, CDCl$_3$) $\delta$ 178.5, 163.6, 156.3, 138.8, 133.7, 132.4, 131.7, 128.9, 126.8, 125.7, 125.2, 124.0, 123.5, 118.1, 107.5, 21.5. IR (neat, cm$^{-1}$): 3068, 2921, 1637, 1603, 1569, 1488, 1467, 1433, 1368, 1332, 1301, 1269, 1225. ESI-MS (M): 236.

2-(3-methoxyphenyl)-4$H$-chromen-4-one 3x
(m.p. 127 °C) $^1$H NMR (400 MHz, CDCl$_3$) δ 8.27 (d, $J = 8.0$ Hz, 1H), 7.70 (t, $J = 8.0$ Hz, 1H), 7.57 (d, $J = 8.0$ Hz, 1H), 7.50 (d, $J = 8.0$ Hz, 1H), 7.45-7.41 (m, 3H), 7.07 (d, $J = 4.0$ Hz, 1H), 6.83 (s, 1H), 3.89 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 178.5, 163.2, 160.0, 156.2, 133.8, 133.1, 130.1, 125.7, 125.3, 123.9, 118.7, 118.1, 117.2, 111.8, 107.8, 55.5. IR (neat, cm$^{-1}$): 3078, 3000, 2922, 2842, 1653, 1606, 1572, 1491, 1469, 1446, 1434, 1369, 1346, 1330, 1295, 1275, 1249, 1228, 1213, 1192, 1130. ESI-MS (M): 252.

**2-(2-chlorophenyl)-4$H$-chromen-4-one 3y**

![Chemical structure](image)

(m.p. 118-120 °C) $^1$H NMR (600 MHz, CDCl$_3$) δ 8.26 (d, $J = 12.0$ Hz, 1H), 7.71 (t, $J = 9.0$ Hz, 1H), 7.64 (d, $J = 12.0$ Hz, 1H), 7.53 (q, $J = 8.0$ Hz, 2H), 7.48-7.40 (m, 3H), 6.66 (s, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 178.2, 162.7, 156.6, 133.9, 133.0, 132.0, 131.8, 130.8, 130.7, 127.1, 125.8, 125.4, 123.9, 118.2, 113.0. IR (neat, cm$^{-1}$): 3064, 2924, 2360, 2341, 1653, 1572, 1467, 1370, 1220, 1129. ESI-MS (M): 256.

**2-(3-chlorophenyl)-4$H$-chromen-4-one 3z**

![Chemical structure](image)

(m.p. 118 °C) $^1$H NMR (400 MHz, CDCl$_3$) δ 8.24 (d, $J = 8.0$ Hz, 1H), 7.93 (t, $J = 2.0$ Hz, 1H), 7.80 (d, $J = 8.0$ Hz, 1H), 7.73 (dt, $J = 4.0$, 8.0 Hz, 1H), 7.60 (d, $J = 12$ Hz, 1H), 7.54-7.43 (m, 3H), 6.82 (s, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 178.2, 161.8, 156.2, 135.3, 134.0, 133.6, 131.5, 130.3, 126.4, 125.8, 125.5, 124.4, 123.9, 118.1, 108.2. IR (neat, cm$^{-1}$): 3085, 1645, 1565, 1466, 1422, 1372, 1335, 1304, 1261, 1226, 1131. ESI-MS (M): 256.

**Reference and notes**


NMR Spectra of Products

\[ \text{A (s) \quad 2.59} \]
\[ \text{B (dd) \quad 7.75} \]
\[ \text{C (t) \quad 7.39} \]
\[ \text{D (t) \quad 7.34} \]
\[ \text{E (m) \quad 7.43} \]
\[ \text{F (m) \quad 7.01} \]
\[ \text{G (s) \quad 5.15} \]