Rh(III)-catalyzed oxidative C–H bond arylation with hydroquinones: sustainable synthesis of dibenzo\([b,d]\)pyran-6-ones and benzo\([d]\)naphtho\([1,2-b]\)pyran-6-ones†

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Table of Contents

I. General Information----------------------------------------------- S2
II. Typical Procedures of Compounds 3a-3q and 4a-4c---------------------- S2
III. Mechanism experiments--------------------------------------------- S2
IV. Procedures for synthesis of 7 and 8-------------------------------- S3
V. Analytical Data of Compounds 3a-3q and 4a-4c, 7 and 8--------------- S5
VI. Copies of H NMR and \(^{13}\)C NMR spectra-------------------------- S13
I. General Information

All Rhodium-catalyzed reactions were carried out without any particular precautions to extrude moisture or oxygen. All reagents were purchased from commercial sources and used without further purification, unless otherwise indicated. All reactions were monitored by TLC, which was performed on precoated aluminum sheets of silica gel 60 (F254). The products were purified by flash column chromatography on silica gel (300−400 mesh). Melting points were corrected. The $^1$H NMR and $^{13}$C NMR spectra were determined at 25 °C on a 500 MHz and 125 MHz, respectively, and TMS as internal standard. All chemical shifts are given in ppm. High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI).

II. Typical Procedures of Compounds 3a-3q and 4a-4c

General procedure for the synthesis of 3a-3q and 4a-4c (3a as an example):

Without any particular precautions to extrude oxygen or moisture, to a stirred solution of 2a (44.0 mg, 0.4 mmol) in DCE (1.0 mL)/acetone (1.0 mL) in a sealed tube, PhI=O (88.0 mg, 0.4 mmol), 1a (30.2 mg, 0.2 mmol), [Cp*RhCl$_2$]$_2$ (3.1 mg, 0.005 mmol), CsOAc (11.5 mg, 0.06 mmol) and HOAc (6.0 uL, 0.1 mmol) were added successively. After heated at 90 °C for 5 h, the starting material 1a was consumed as indicated by TLC. The reaction mixture was cooled to room temperature and diluted with water (15 mL), then extracted with EtOAc (10 mL×3), the organic phase was combined and washed with saturated Na$_2$CO$_3$ solution. After dried over Na$_2$SO$_4$, the organic phase was concentrated in vacuo. The residue was purified by column chromatography (petroleum ether/EtOAc = 10/1, v/v) to afford the product 3a (98% yield).

III. Mechanism experiments

2a (44.0 mg, 0.4 mmol) was added into the mixture of DCE (1.0 mL)/acetone (1.0 mL) in a sealed tube, followed by PhI=O (88.0 mg, 0.4 mmol). After heated at 90 °C for 10 min, the reaction mixture was cooled to room temperature and was concentrated in vacuo. The $^1$H NMR spectrum of the crude product shows that benzoquinone 5 was obtained in 61% yield (p-xylene as the
1a (30.2 mg, 0.2 mmol), 5 (43.2 mg, 0.4 mmol), [Cp*RhCl₂]₂ (3.1 mg, 0.005 mmol), CsOAc (11.5 mg, 0.06 mmol) and HOAc (6.0 μL, 0.1 mmol) were added into the mixture of DCE (1.0 mL)/acetone (1.0 mL) in a sealed tube. After heated at 90 °C for 3 h, the starting material 1a was consumed as indicated by TLC. The reaction mixture was cooled to room temperature and diluted with water (15 mL), then extracted with EtOAc (10 mL × 3), the organic phase was combined and washed with saturated Na₂CO₃ solution. After dried over Na₂SO₄, the organic phase was concentrated in vacuo. The residue was purified by column chromatography (petroleum ether/EtOAc = 10/1, v/v) to afford the product 3a (99% yield).

IV. Procedures for synthesis of 7 and 8

To an ice-bath cooled solution of 3a (42.4 mg, 0.2 mmol) in DCM (1.0 mL) at 0 °C, Et₃N (41.7 μL, 0.3 mmol) and (CF₃SO₂)₂O (50.4 μL, 0.3 mmol) were added successively. The reaction mixture was stirred at room temperature for 20 h. The reaction mixture was diluted with brine (10 mL) and extracted with DCM (2×10 mL). The combined organics were dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography (petroleum ether/EtOAc = 10/1, v/v) to afford the product 6 in 85% yield.

An oven-dried 25 mL Schlenk tube was charged with Pd(PPh₃)₂Cl₂ (7.0 mg, 0.01 mmol), and was evacuated and refilled with N₂ three times. Then DMF (1.0 mL), Bu₃N (144 μL, 0.6 mmol) and HCOOH (15.2 μL, 0.4 mmol) were added successively. The reaction mixture was stirred at 80°C for 7 h. It was cooled to room temperature and diluted with brine (10 mL), then extracted with
EtOAc (2 ×10 mL). The combined organics were dried (Na₂SO₄) and concentrated in vacuo. The residue was purified by column chromatography (petroleum ether/Et₂O = 30/1, v/v) to afford the product 7 in 76% yield.

An oven-dried 25 mL Schlenk tube was charged with 6 (68.8 mg, 0.2 mmol), p-tolylboronic acid (29.9 mg, 0.22 mmol), Pd(PPh₃)₄ (5.8 mg, 0.005 mmol), K₃PO₄ (63.6 mg, 0.3 mmol) and KBr (26.2 mg, 0.22 mmol) and was evacuated and refilled with N₂ three times, followed by adding dioxane (1.0 mL). The reaction mixture was stirred at 85°C for 5 h. The reaction mixture was cooled to room temperature and diluted with brine (10 mL), then extracted with EtOAc (2 ×10 mL). The combined organics were dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by column chromatography (petroleum ether/Et₂O = 50/1, v/v) to afford the product 8 in 84% yield.
V. Analytical Data of Compounds 3a-3q and 4a-4c, 7 and 8

2-hydroxy-6H-benzo[c]chromen-6-one (3a)

Yellowish solid, m.p. 161–162 °C. $^1$H NMR (500 MHz, DMSO): $\delta$ 6.99 (dd, $J = 3.0$, 8.5 Hz, 1H), 7.25 (d, $J = 8.5$ Hz, 1H), 7.60 (d, $J = 3.0$ Hz, 1H), 7.66 (t, $J = 7.0$ Hz, 1H), 7.92 (t, $J = 7.0$ Hz, 1H), 8.23 (d, $J = 7.5$ Hz, 1H), 8.26 (d, $J = 8.0$ Hz, 1H), 9.75 (s, 1H). $^{13}$C NMR (125 MHz, DMSO): $\delta$ 108.7, 118.6, 118.7, 118.9, 121.1, 123.0, 129.7, 130.3, 134.8, 135.7, 144.4, 154.7, 160.9. Calcd for (C$_{13}$H$_9$O$_3$ $^{+}$ [M+H]$^+$) 213.0546. Found 213.0562.

2-hydroxy-9-methyl-6H-benzo[c]chromen-6-one (3b)

Yellowish solid, m.p. 224–225 °C. $^1$H NMR (500 MHz, DMSO): $\delta$ 2.48 (s, 3H), 6.97 (dd, $J = 2.5$, 9.0 Hz, 1H), 7.23 (d, $J = 9.0$ Hz, 1H), 7.46 (d, $J = 8.0$ Hz, 1H), 7.57 (d, $J = 2.5$ Hz, 1H), 8.07 (s, 1H), 8.10 (d, $J = 8.0$ Hz, 1H), 9.70 (s, 1H). $^{13}$C NMR (125 MHz, DMSO): $\delta$ 22.1, 108.7, 118.6, 118.7, 118.8, 123.0, 130.3, 130.8, 134.7, 144.6, 146.6, 154.7, 160.9. Calcd for (C$_{14}$H$_{11}$O$_3$ $^+$$[M+H]^+$) 227.0703. Found 227.0698.

9-ethyl-2-hydroxy-6H-benzo[c]chromen-6-one (3c)
Yellowish solid, m.p. 135–136 °C. $^1$H NMR (500 MHz, DMSO): $\delta$ 1.28 (t, $J = 7.5$ Hz, 3H), 2.82 (q, $J = 7.5$ Hz, 2H), 6.99 (dd, $J = 2.5$, 8.5 Hz, 1H), 7.24 (d, $J = 8.5$ Hz, 1H), 7.52 (d, $J = 8.0$ Hz, 1H), 7.63 (d, $J = 2.5$ Hz, 1H), 8.09 (s, 1H), 8.15 (d, $J = 8.0$ Hz, 1H), 9.67 (s, 1H). $^{13}$C NMR (125 MHz, DMSO): $\delta$ 15.5, 29.0, 108.7, 118.5, 118.7, 118.8, 121.8, 129.6, 130.4, 134.8, 144.5, 152.4, 154.6, 160.8. Calcd for (C$_{15}$H$_{13}$O$_3$ $^+ [M+H]^+$) 241.0859. Found 241.0875.

$^{9}$-tert-butyl-2-hydroxy-6H-benzo[c]chromen-6-one (3d)

Yellowish solid, m.p. 248–249 °C. $^1$H NMR (500 MHz, DMSO): $\delta$ 1.41 (s, 9H), 6.99 (d, $J = 8.5$ Hz, 1H), 7.25 (d, $J = 8.5$ Hz, 1H), 7.73 (s,1H), 7.74 (d, $J = 9.5$ Hz, 1H), 8.18 (d, $J = 9.5$ Hz, 1H), 8.19 (s, 1H), 9.67 (s, 1H). $^{13}$C NMR (125 MHz, DMSO): $\delta$ 31.2, 36.0, 108.8, 118.6, 118.7, 118.9, 119.1, 127.3, 130.2, 134.5, 144.6, 154.6, 159.0, 160.8. HRMS (ESI-TOF) Calcd for (C$_{17}$H$_{17}$O$_3$ $^+ [M+H]^+$) 269.1172. Found 269.1177.

2-hydroxy-9-methoxy-6H-benzo[c]chromen-6-one (3e)

Brown solid, m.p. 187–188 °C. $^1$H NMR (500 MHz, DMSO): $\delta$ 4.00 (s, 3H), 7.01 (dd, $J = 2.0$, 7.0 Hz, 1H), 7.22–7.26 (m, 2H), 7.69 (d, $J = 2.0$ Hz, 2H), 8.17 (d, $J = 8.5$ Hz, 1H), 9.68 (s, 1H). $^{13}$C NMR (125 MHz, DMSO): $\delta$ 56.5, 105.9, 109.2, 114.0, 117.6, 118.5, 118.7, 119.1, 132.6, 137.2, 144.8, 154.6, 160.6, 165.1. HRMS (ESI-TOF) Calcd for (C$_{14}$H$_{11}$O$_4$ $^+ [M+H]^+$) 243.0652.
9-chloro-2-hydroxy-6H-benzo[c]chromen-6-one (3f)

Yellowish solid, m.p. 192–193 °C. \(^1\)H NMR (500 MHz, DMSO): \(\delta\) 7.01 (dd, \(J = 2.5, 8.5\) Hz, 1H), 7.22 (d, \(J = 8.5\) Hz, 1H), 7.59 (d, \(J = 2.5\) Hz, 1H), 7.64 (dd, \(J = 2.0, 8.5\) Hz, 1H), 8.16 (d, \(J = 8.5\) Hz, 1H), 8.30 (d, \(J = 2.0\) Hz, 1H), 9.76 (s, 1H). \(^{13}\)C NMR (125 MHz, DMSO): \(\delta\) 109.2, 117.8, 118.6, 119.6, 119.8, 122.9, 129.7, 132.3, 136.6, 141.1, 144.7, 154.8, 160.2. Calcld for (C\(_{13}\)H\(_8\)ClO\(_3\))^+ \([M+H]^+\) 247.0156. Found 247.0147.

2-hydroxy-9-iodo-6H-benzo[c]chromen-6-one (3g)

Yellowish solid, m.p. 190–191 °C. \(^1\)H NMR (500 MHz, DMSO): \(\delta\) 7.02 (dd, \(J = 2.5, 8.5\) Hz, 1H), 7.26 (d, \(J = 8.5\) Hz, 1H), 7.65 (s, 1H), 7.94 (d, \(J = 8.0\) Hz, 1H), 8.02 (d, \(J = 8.5\) Hz, 1H), 8.67 (s, 1H), 9.72 (s, 1H). \(^{13}\)C NMR (125 MHz, DMSO): \(\delta\) 105.2, 109.1, 117.5, 118.6, 119.4, 120.4, 131.6, 131.7, 136.1, 138.5, 144.7, 154.8, 160.7. Calcld for (C\(_{13}\)H\(_8\)IO\(_3\))^+ \([M+H]^+\) 338.9513. Found 338.9520.

2-hydroxy-9-(trifluoromethyl)-6H-benzo[c]chromen-6-one (3h)

Yellowish solid, m.p. 138–139 °C. \(^1\)H NMR (500 MHz, DMSO): \(\delta\) 7.04 (dd, \(J = 3.0, 9.0\) Hz, 1H), 7.26 (d, \(J = 9.0\) Hz, 1H), 7.74 (d, \(J = 3.0\) Hz, 1H), 7.94 (d, \(J = 8.0\) Hz, 1H), 8.38 (d, \(J = 8.0\) Hz, 1H), 8.57 (s, 1H), 9.75 (s, 1H). \(^{13}\)C NMR (125 MHz, DMSO): \(\delta\) 109.3, 117.9, 118.7, 119.8, 120.4

Found 243.0660.
(d, J = 3.9 Hz ), 124.0 (q, J = 271.9 Hz ), 124.2, 125.6 (d, J = 3.4 Hz ), 131.6, 135.0 (q, J = 32.1 Hz ), 135.6, 144.6, 154.9, 160.0. **HRMS** (ESI-TOF) Calcd for (C\textsubscript{14}H\textsubscript{8}FO\textsubscript{3} \+[M+H]\textsuperscript{+}) 281.0420. Found 281.0419.

**2-hydroxy-7-methyl-6H-benzo[c]chromen-6-one (3i)**

![3i](image)

Yellowish solid, m.p. 159–160 °C. **\textsuperscript{1}H NMR** (500 MHz, DMSO): δ 2.76 (s, 3H), 6.97 (dd, J = 2.5, 9.0 Hz, 1H), 7.22 (d, J = 9.0 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 2.5 Hz, 1H), 7.78 (t, J = 8.0 Hz, 1H), 8.13 (d, J = 8.0 Hz, 1H), 9.67 (s, 1H). **\textsuperscript{13}C NMR** (125 MHz, DMSO): δ 23.8, 108.8, 118.1, 118.8, 119.4, 121.0, 132.8, 134.9, 136.1, 143.6, 144.4, 154.5, 160.2. Calcd for (C\textsubscript{14}H\textsubscript{11}O\textsubscript{3} \+[M+H]\textsuperscript{+}) 227.0703. Found 227.0708.

**2-hydroxy-8-methyl-6H-benzo[c]chromen-6-one (3j)**

![3j](image)

Yellow solid, m.p. 162–163 °C. **\textsuperscript{1}H NMR** (500 MHz, DMSO): δ 2.47 (s, 3H), 6.97 (d, J = 6.5 Hz, 1H), 7.25 (d, J = 8.5 Hz, 1H), 7.57 (s, 1H), 7.76 (d, J = 8.0 Hz, 1H), 8.06 (s, 1H), 8.18 (d, J = 8.5 Hz, 1H), 9.69 (s, 1H). **\textsuperscript{13}C NMR** (125 MHz, DMSO): δ 21.2, 108.4, 118.4, 118.5, 118.8, 120.9, 123.0, 129.9, 132.3, 136.8, 139.6, 144.1, 154.7, 160.9. Calcd for (C\textsubscript{14}H\textsubscript{11}O\textsubscript{3} \+[M+H]\textsuperscript{+}) 227.0703. Found 227.0702.

**2-hydroxy-10-methoxy-6H-benzo[c]chromen-6-one (3k); 2-hydroxy-8-methoxy-6H-benzo[c]chromen-6-one (3k')**

![3k 3k'](image)

3k:3k' = 2.4:1
Yellowish solid, $^1$H NMR (500 MHz, DMSO): δ 3.91 (s, 3H), 4.07 (s, 1.27H), 6.92–6.96 (m, 1.33H), 7.24 (d, $J$ = 9.0 Hz, 1.27H), 7.51–7.53 (m, 1.9H), 7.63–7.66 (m, 1.80H), 7.92 (d, $J$ = 7.5 Hz, 0.36H), 8.21 (dd, $J$ = 2.5, 8.5 Hz, 0.96H), 8.40 (s, 0.38H), 9.67 (s, 0.92H). $^{13}$C NMR (125 MHz, DMSO): δ 56.1, 56.8, 108.1, 111.7, 114.1, 117.7, 117.8, 118.0, 118.4, 118.8, 122.2, 122.3, 124.0, 124.9, 128.0, 130.2, 143.6, 154.1, 154.8, 160.1, 160.7. Calcd for (C$_{14}$H$_{11}$O$_4$ $^+$ [M+H]$^+$) 243.0652. Found 243.0653.

2-hydroxy-8,9-dimethyl-6H-benzo[c]chromen-6-one (3l)

Yellowish solid, m.p. 177–178 °C. $^1$H NMR (500 MHz, DMSO): δ 2.36 (s, 3H), 2.43 (s, 3H), 6.95 (dd, $J$ = 2.5, 9.0 Hz, 1H), 7.22 (d, $J$ = 9.0 Hz, 1H), 7.56 (d, $J$ = 2.5 Hz, 1H), 7.97 (s, 1H), 8.05 (s, 1H), 9.66 (s, 1H). $^{13}$C NMR (125 MHz, DMSO): δ 19.7, 20.5, 108.5, 118.3, 118.4, 118.7, 118.8, 123.5, 130.3, 132.6, 138.9, 144.3, 145.8, 154.6, 160.9. Calcd for (C$_{15}$H$_{13}$O$_3$ $^+$ [M+H]$^+$) 241.0859. Found 241.0876.

2-hydroxy-6H-naphtho[2,3-c]chromen-6-one (3n)

Yellowish solid, m.p. 165–166 °C. $^1$H NMR (500 MHz, DMSO): δ 6.99 (dd, $J$ = 2.5, 8.5Hz, 1H), 7.27 (d, $J$ = 8.5 Hz, 1H), 7.67 (t, $J$ = 8.0 Hz, 1H), 7.76–7.79 (m, 2H), 8.19 (d, $J$ = 8.0 Hz, 1H), 8.26 (d, $J$ = 8.0 Hz, 1H), 8.86 (s, 1H), 8.99 (s, 1H), 9.74 (s, 1H). $^{13}$C NMR (125 MHz, DMSO): δ 108.9, 118.5, 118.8, 119.1, 119.4, 122.0, 127.8, 129.8, 129.9, 130.1, 132.4, 132.5, 136.3, 144.0, 154.8, 161.1. Calcd for (C$_{17}$H$_{11}$O$_3$ $^+$ [M+H]$^+$) 263.0703. Found 263.0712.

8-hydroxy-4H-thieno[2,3-c]chromen-4-one (3o)
Light brown solid, m.p. 169–170 °C. $^1$H NMR (500 MHz, DMSO): δ 7.01 (dd, $J = 2.5$, 9.0 Hz, 1H), 7.35 (d, $J = 9.0$ Hz, 1H), 7.45 (d, $J = 2.5$ Hz, 1H), 7.97 (d, $J = 5.0$ Hz, 1H), 8.37 (d, $J = 5.0$ Hz, 1H), 9.80 (s, 1H). $^{13}$C NMR (125 MHz, DMSO): δ 109.6, 118.1, 118.4, 118.7, 124.0, 124.1, 138.9, 145.4, 145.9, 154.7, 157.1. Calcd for (C$_{11}$H$_7$O$_3$S$^+$ [M+H]$^+$) 219.0110. Found 219.0115.

2-hydroxy-4-methyl-6H-benzo[c]chromen-6-one (3p);
2-hydroxy-3-methyl-6H-benzo[c]chromen-6-one (3p')

Yellowish solid, $^1$H NMR (500 MHz, DMSO): δ 2.22 (s, 3H), 2.33 (s, 2.67H), 6.88 (d, $J = 2.5$ Hz, 0.83H), 7.17 (s, 0.88H), 7.43 (d, $J = 2.5$ Hz, 0.89H), 7.51 (s, 1.01H), 7.62–7.67 (m, 1.93H), 7.90–7.94 (m, 1.85H), 8.09 (d, $J = 8.5$ Hz, 1.01H), 8.23 (t, $J = 7.5$ Hz, 2.67H), 9.60 (s, 0.81H), 9.67 (s, 0.92H). $^{13}$C NMR (125 MHz, DMSO): δ 16.0, 16.6, 106.3, 107.4, 115.9, 118.4, 119.2, 120.1, 120.7, 120.9, 122.3, 123.1, 127.5, 129.1, 129.2, 129.5, 130.2, 130.3, 134.9, 135.0, 135.7, 135.8, 142.9, 144.3, 152.9, 154.1, 160.8, 161.0. Calcd for (C$_{14}$H$_{11}$O$_3$ $^+$ [M+H]$^+$) 227.0703. Found 227.0712.

4-(tert-butyl)-2-hydroxy-6H-benzo[c]chromen-6-one (3q);
3-(tert-butyl)-2-hydroxy-6H-benzo[c]chromen-6-one (3q')

Yellowish solid, m.p. 129–130 °C. $^1$H NMR (500 MHz, DMSO): δ 1.39 (s, 1.70H), 1.45 (s, 9H), 7.00 (d, $J = 2.5$ Hz, 0.98H), 7.15 (s, 0.17H), 7.50 (d, $J = 2.5$ Hz, 0.98H), 7.52 (s, 0.19) 7.66 (t, $J =$
8.0 Hz, 1.22H) 7.92 (t, J = 8.0 Hz, 1.13H), 8.04 (d, J = 8.0 Hz, 0.10H), 8.25 (dd, J = 8.0, 14.0 Hz, 2.09H), 9.63 (s, 0.86H). $^{13}$C NMR (125 MHz, DMSO): δ 30.1, 35.1, 106.5, 116.9, 119.0, 120.5, 123.2, 129.5, 129.9, 135.3, 135.7, 139.2, 143.2, 154.0, 160.3. Calcd for (C$_{17}$H$_{17}$O$_3$ $^+ [M+H]^+$) 269.1172. Found 269.1170.

12-hydroxy-6H-dibenzo[c,h]chromen-6-one (4a)

Brown solid, m.p. 193–194 °C. $^1$H NMR (500 MHz, DMSO): δ 7.51 (s, 1H), 7.64 (t, J = 7.0 Hz, 1H), 7.70 (t, J = 7.5 Hz, 2H), 8.00 (t, J = 7.5 Hz, 1H), 8.20 (t, J = 9.0 Hz, 2H), 8.32 (d, J = 8.0 Hz, 2H), 10.48 (s, 1H). $^{13}$C NMR (125 MHz, DMSO): δ 100.4, 113.5, 121.2, 121.7, 122.9, 124.5, 126.4, 127.4, 128.1, 129.5, 130.4, 135.2, 136.0, 140.3, 150.5, 160.8. HRMS (ESI-TOF) Calcd for (C$_{17}$H$_{11}$O$_3$ $^+ [M+H]^+$) 263.0703. Found 263.0694.

12-hydroxy-9-methyl-6H-dibenzo[c,h]chromen-6-one (4b)

Brown solid, m.p. 248–249 °C. $^1$H NMR (500 MHz, DMSO): δ 2.54 (s, 3H), 7.48 (s, 2H), 7.63 (t, J = 7.5 Hz, 1H), 7.69 (t, J = 7.5 Hz, 1H), 7.94 (s, 1H), 8.17-8.21 (m, 2H), 8.30 (d, J = 8.0 Hz, 1H), 10.41 (s, 1H). $^{13}$C NMR (125 MHz, DMSO): δ 22.2, 100.5, 113.5, 118.8, 121.6, 122.8, 122.9, 124.5, 126.4, 127.3, 128.0, 130.4, 135.1, 140.4, 146.6, 150.5, 160.8. Calcd for (C$_{18}$H$_{13}$O$_3$ $^+ [M+H]^+$) 277.0859. Found 277.0853.

12-hydroxy-8-methyl-6H-dibenzo[c,h]chromen-6-one (4c)

Brown solid, m.p. 236–237 °C. $^1$H NMR (500 MHz, DMSO): δ 2.51 (s, 3H), 7.50 (s, 1H), 7.64 (t, J = 7.5 Hz, 1H), 7.71 (t, J = 7.5 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 8.10 (d, J = 8.5 Hz, 1H), 8.14
(s, 1H), 8.22 (d, $J = 8.5$ Hz, 1H), 8.32 (d, $J = 8.0$ Hz, 1H), 10.47 (s, 1H). $^{13}$C NMR (125 MHz, DMSO): $\delta$ 21.3, 100.4, 113.7, 121.1, 121.6, 123.0, 124.5, 126.2, 128.1, 130.1, 132.7, 137.1, 139.5, 139.9, 150.5, 160.9. Calcd for (C$_{18}$H$_{13}$O$_3$ $^+ [M+H] ^+$) 277.0859. Found 277.0868.

6H-benzo[c]chromen-6-one (7)

![Image of 6H-benzo[c]chromen-6-one (7)]

White solid, m.p. 91−92°C. $^1$H NMR (500 MHz, CDCl$_3$): $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.34−7.40 (m, 2H), 7.50 (t, $J = 8.0$ Hz, 1H), 7.60 (t, $J = 7.0$ Hz, 1H), 7.84 (t, $J = 7.0$ Hz, 1H), 8.09 (d, $J = 8.5$ Hz, 1H), 8.15 (d, $J = 8.0$ Hz, 1H), 8.42 (d, $J = 8.0$ Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 117.8, 118.0, 121.3, 121.7, 122.8, 124.5, 128.9, 130.4, 130.6, 134.7, 134.8, 151.3, 161.2. Calcd for (C$_{13}$H$_{9}$O$_2$ $^+ [M+H] ^+$) 197.0597. Found 197.0606.

2-(p-tolyl)-6H-benzo[c]chromen-6-one (8)

![Image of 2-(p-tolyl)-6H-benzo[c]chromen-6-one (8)]

White solid, m.p. 137−138°C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.43 (s, 3H), 7.31 (d, $J = 7.5$ Hz, 2H), 7.44 (d, $J = 8.5$ Hz, 1H), 7.54 (d, $J = 8.0$ Hz, 2H), 7.61 (t, $J = 7.5$ Hz, 1H), 7.68 (dd, $J = 2.0$, 8.5 Hz, 1H), 7.86 (t, $J = 8.0$ Hz, 1H), 8.22 (d, $J = 8.0$ Hz, 1H), 8.23 (s, 1H), 8.44 (d, $J = 8.0$ Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 21.1, 118.0, 118.1, 121.0, 121.4, 121.7, 127.0, 129.0, 129.3, 129.7, 130.7, 134.8, 134.9, 137.2, 137.6, 137.9, 150.5, 161.2. Calcd for (C$_{20}$H$_{15}$O$_2$ $^+ [M+H] ^+$) 287.1067. Found 287.1070.
VI. Copies of $^1$H NMR and $^{13}$C NMR spectra
3k:3k' = 2:1

3k:3k' = 2:4:1

S23
The H-H Cosy data demonstrates \(3q\) is the main product.