**Cyclization of Oxa-Bicyclic Alkenes with
 β -Iodo-(Z)-propenoates and *o*-Iodobenzoate
Catalyzed by Nickel Complexes: A Simple Efficient
Route to Annulated Coumarins**

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Supporting Information

General Procedure for the Cyclization of 7-Oxabenzonorbornadienes (1) with Methyl 2-Iodobenzoate (2). A round-bottom side-arm flask (25 mL) containing **1** (2.00 mmol), NiBr₂(dppe) (0.0500 mmol) and zinc powder (0.180 g, 2.75 mmol) was evacuated and purged with nitrogen gas three times. Freshly distilled CH₃CN (3.0 mL) and **2** (1.0 mmol) were added. The system was heated with stirring at 80 °C for 12 h and was then cooled to ambient temperature. After dilution with dichloromethane (15 mL), the reaction mixture was stirred in the air for 15 min, filtered through a thin Celite and silica gel pad and washed with dichloromethane several times. The filtrate was concentrated and the residue was purified on a silica gel column using hexane-ethyl acetate as eluent to afford the desired cyclization products **3**. Important spectral data of these products are listed below.

6H-Dibenzo[*c,h*]chromen-6-one (3a). ¹H NMR (500 MHz, CDCl₃): δ = 7.52-7.58 (3 H, m), 7.67 (1 H, d, *J* = 9 Hz), 7.78 (1 H, d, *J* = 6 Hz), 7.79 (1 H, d, *J* = 7.5 Hz), 7.95 (1 H, d, *J* = 9 Hz), 8.08 (1H, d, *J* = 8 Hz), 8.38 (1H, d, *J* = 7.5 Hz), 8.49 (1H, d, *J* = 7.5 Hz); ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 112.8, 119.0, 121.0, 121.9, 122.1, 123.7, 124.3, 126.9, 127.5, 127.7, 128.4, 130.4, 134.1, 134.8, 135.2, 147.0, 161.1; HRMS (m/e): calcd for C₁₇H₁₀O₂ 246.0681, found 246.0678

2,3-Dimethoxy-6H-dibenzo[*c,h*]chromen-6-one (3b). ¹H NMR (500 MHz, CDCl₃): δ = 4.01 (3H, s), 4.08 (3H, s), 7.13 (1H, s), 7.55 (1H, td, *J* = 7 Hz, *J* = 1 Hz), 7.60 (1H, d, *J* = 8.5 Hz), 7.78 (1H, s), 7.84 (1H, td, *J* = 8 Hz, *J* = 1 Hz), 7.89 (1H, d, *J* = 8.5 Hz), 8.14 (1H, d, *J* = 7.5 Hz), 8.43 (1H, dd, *J* = 4 Hz, *J* = 1 Hz); ¹³C{¹H} NMR (125 MHz, CDCl₃): δ = 55.9, 56.3, 101.0, 106.4, 111.9, 117.5, 119.0, 120.6, 121.7, 122.9, 128.1, 130.4, 130.5, 134.7, 146.4, 150.2, 150.9, 161.5; HRMS (m/e): calcd for C₁₉H₁₄O₄ 306.0892, found 306.0894.

12-Methyl-6H-dibenzo[*c,h*]chromen-6-one (3c). ¹H NMR (500 MHz, CDCl₃): δ

= 2.64 (3H, s), 7.50 (1H, td, $J = 1.0$ Hz, $J = 8.5$ Hz), 7.54-7.58 (2H, m), 7.70 (1H, s), 7.76 (1H, td, $J = 1.0$ Hz, $J = 8.0$ Hz), 7.86-7.89 (1H, m), 8.04 (1H, d, $J = 8.5$ Hz), 8.35 (1H, dd, $J = 1.0$ Hz, $J = 7.5$ Hz), 8.47-8.50 (1H, m); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): $\delta = 19.3, 112.2, 119.0, 121.0, 121.7, 122.5, 123.7, 124.0, 126.5, 127.5, 128.3, 130.4, 130.6, 133.2, 134.7, 135.1, 145.7, 161.2$; HRMS (m/e): calcd for $\text{C}_{18}\text{H}_{12}\text{O}_2$ 260.0837, found 260.0832.

14H-Benzo[*c*]naphtho[2,3-*h*]chromen-14-one (3e). ^1H NMR (400 MHz, CDCl_3): $\delta = 7.55$ -7.52 (2H, m), 7.60 (1H, *t*, $J = 7.2$ Hz), 7.91-7.85 (2H, m), 8.00 (2H, *t*, $J = 7$ Hz), 8.12-8.09 (1H, m), 8.18 (1H, d, $J = 8$ Hz), 8.41 (1H, s), 8.48 (1H, d, $J = 7.6$ Hz), 9.16 (1H, s); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): $\delta = 111.4, 118.3, 121.0, 121.7, 121.9, 122.3, 124.9, 126.1, 126.5, 127.9, 128.4, 128.8, 130.5, 131.4, 131.9, 132.5, 134.9, 135.3, 147.3, 161.3$; HRMS (m/e): calcd for $\text{C}_{21}\text{H}_{12}\text{O}_2$ 296.0837, found 296.0841.

2H-Benzo[*h*]chromen-2-one (3g). ^1H NMR (500 MHz, CDCl_3): $\delta = 6.45$ (1H, d, $J = 9$ Hz), 7.38 (1H, d, $J = 8$ Hz), 7.62-7.57 (3H, m), 7.75 (1H, $J = 8$ Hz), 7.81 (1H, dd, $J = 4.5$ Hz, $J = 1$ Hz), 8.46 (1H, dd, $J = 4.5$ Hz, $J = 1$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): $\delta = 114.1, 11.5, 122.7, 122.9, 123.4, 127.0, 127.7, 128.6, 134.7, 144.1, 151.1, 160.8$; HRMS (m/e): calcd for $\text{C}_{13}\text{H}_8\text{O}_2$ 196.0524, found 196.0521

8,9-Di(methoxy)-2H-benzo[*h*]chromen-2-one (3h). ^1H NMR (500 MHz, CDCl_3): $\delta = 4.01$ (3H, s), 4.05 (3H, s), 6.42 (1H, d, $J = 10.0$ Hz), 7.13 (1H, s), 7.30 (1H, d, $J = 8.0$ Hz), 7.51 (1H, d, $J = 8.0$ Hz), 7.74 (1H, s), 7.78 (1H, d, $J = 9.0$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): $\delta = 56.0, 56.3, 100.9, 106.5, 113.3, 114.5, 118.2, 122.0, 122.8, 131.3, 144.6, 150.3, 150.4, 151.5, 161.4$; HRMS (m/e): calcd for $\text{C}_{15}\text{H}_{12}\text{O}_4$ 256.0736, found 256.0735.

4-Methyl-2H-benzo[*h*]chromen-2-one (3i). ^1H NMR (400 MHz, CDCl_3): $\delta = 2.54$ (3H, d, $J = 1.6$ Hz), 6.39 (1H, d, $J = 1.2$ Hz), 7.62-7.66 (4H, m), 7.87 (1H, dd, $J = 2.4$

Hz, $J = 4.4$ Hz), 8.58 (1H, dd, $J = 2.0$ Hz, $J = 6.4$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 19.13, 114.27, 115.10, 120.22, 122.57, 123.09, 124.04, 127.04, 127.56, 128.51, 134.70, 150.52, 153.29, 160.76; HRMS (m/e): calcd for $\text{C}_{14}\text{H}_{10}\text{O}_2$ 210.0680, found 210.0679.

8,9-Dimethoxy-4-methyl-2H-benzo[*h*]chromen-2-one (3j). ^1H NMR (400 MHz, CDCl_3): δ = 2.47 (3H, d, $J = 1.2$ Hz), 4.00 (3H, s), 4.04 (3H, s), 6.27 (1H, d, $J = 1.6$ Hz), 7.10 (1H, s), 7.41 (1H, d, $J = 8.4$ Hz), 7.50 (1H, d, $J = 8.4$ Hz), 7.72 (1H, s); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ = 19.09, 55.93, 56.28, 101.26, 106.31, 113.15, 114.16, 118.28, 118.71, 122.50, 131.17, 149.68, 150.29, 151.50, 153.67, 161.22; HRMS (m/e): calcd for $\text{C}_{16}\text{H}_{14}\text{O}_4$ 270.0892, found 270.0893.

9-Methyl-6-oxaheptacyclo[14.6.6.0^{2,15}.0^{4,13}.0^{5,10}.0^{17,22}.0^{23,28}]octacos-2(15),3,5(10), 8,11,13,17(22),18,20,23(28),24,26-dodecaen-7-one (3l). ^1H NMR (400 MHz, CDCl_3): δ = 2.44 (3H, d, $J = 0.8$ Hz), 5.55 (1H, s), 5.60 (1H, s), 6.28 (1H, d, $J = 0.8$ Hz), 7.00-7.05 (4H, m), 7.41-7.47 (5H, m), 7.53 (1H, d, $J = 8.8$ Hz), 7.76 (1H, s), 8.50 (1H, s); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ = 18.8, 53.6, 53.7, 113.6, 114.9, 116.3, 119.9, 120.7, 121.4, 123.4, 123.7, 123.9, 125.6, 125.7, 133.1, 143.4, 143.9, 144.1, 144.9, 150.0, 153.3, 160.7; HRMS (m/e): calcd for $\text{C}_{28}\text{H}_{18}\text{O}_2$ 386.1307, found 386.1302.

5,6-Dihydrobenzo[*c*]phenanthridin-6-one (4). ^1H NMR (500 MHz, CDCl_3): δ = 3.89-3.87 (1H, m), 4.86 (1H, d, $J = 6$ Hz), 5.50 (1H, s), 5.77-5.50 (1H, m), 7.16 (1H, d, $J = 7.5$ Hz), 7.26-7.24 (2H, m), 7.34-7.30 (2H, m), 7.39 (1H, td, $J = 7$ Hz, $J = 1$ Hz), 7.52 (1H, td, $J = 7$ Hz, $J = 1$ Hz), 8.09 (1H, d, $J = 7.5$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ = 38.8, 52.2, 127.1, 127.2, 127.6, 127.7, 128.0, 128.3, 128.6, 129.3, 131.7, 132.7, 133.0, 139.6; HRMS (m/e): calcd for $\text{C}_{17}\text{H}_{13}\text{NO}$ 247.0997, found 247.0997.

(3*R,4*S**,4*aS**,10*bR**)-3,4-Di((methyloxy)methyl)-4,4*a*,6,10*b*-tetrahydro-3*H*-b**

enzo[*c*]chromen-6-one (6). ¹H NMR (400 MHz, CDCl₃): δ = 3.07-3.10 (1H, m), 3.18-3.19 (1H, m), 3.29 (3H, s), 3.34-3.35 (1H, m), 3.37 (1H, s), 3.52 (1H, d, *J* = 6.0 Hz), 3.53-3.57 (2H, m), 3.63-3.68 (2H, m), 5.80 (1H, dd, *J* = 2.8 Hz, *J* = 9.2 Hz), 6.59 (1H, dd, *J* = 2.8 Hz, *J* = 9.2 Hz), 7.47 (1H, t, *J* = 7.6 Hz), 7.58 (1H, d, *J* = 8.0 Hz), 7.73 (1H, t, *J* = 7.6 Hz), 8.30 (1H, d, *J* = 8.0 Hz); HRMS (*m/e*): calcd for C₁₇H₂₀O₄ 288.1362, found 288.1359.

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