Visible-Light-Induced Arene C(sp²)–H Lactonization Promoted by DDQ and tert-Butyl nitrite

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1. General information

Unless otherwise noted, all the reactions were performed at room temperature. All reactions were monitored by TLC or GC. GC analyses were conducted on an Agilent GC6890N system with a flame ionization detector (FID) and a AT-SE-54 capillary column. GC-MS was performed on Thermo Trace ISQ instrument with TG 5MS capillary column. ¹H NMR (500 MHz) and ¹³C NMR (125 MHz) spectra were obtained on a Bruker Avance III spectrometer. CDCl₃ was used as the solvent with tetramethylsilane (TMS) as the internal standard. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High-resolution mass spectra were recorded in the EI mode on Waters GCT Premier TOF MS. Melting points (uncorrected) were determined on a BUCHI M-565 apparatus. Photoc hemical reactions were performed with 450 nm (18 W blue LED). Purification of reaction products was carried out by column chromatography on silica gel.

2. Preparation of starting materials

\[
\begin{align*}
\text{O} & \quad \text{HO} \\
\text{HO} & \quad \text{B} \\
\text{HO} & \quad \text{R₁} \\
\text{O} & \quad \text{Pd(OAc)}₂, \text{P(Ph)}₃ \\
\text{Toluene} & \quad \text{KOH, MeOH} \\
\text{O} & \quad \text{OH} \\
\end{align*}
\]

To a 50 mL oven-dried Schlenk flask equipped with a magnetic stir bar, were added methyl 2-iodobenzoate (2.62 g, 10 mmol), arylboronic acid (15 mmol), Pd(OAc)₂ (22 mg, 1 mol%), PPh₃ (52 mg, 2 mol%) and K₃PO₄ (4.24 g, 20 mmol). The Schlenk flask was evacuated and backfilled with N₂ for 3 times. Then toluene (20 mL) was added. The reaction mixture was heated at 80 °C. The reaction progress was monitored by thin-layer chromatography (TLC) analysis. After the reaction was
completed, the mixture was cooled to room temperature. Then the reaction mixture was concentrated on a rotary evaporator, and purified by column chromatography (PE/EtOAc = 50/1) to give the desired ester.

KOH (3.0 g, 75 mmol), MeOH (20 mL) and the desired ester were added to a 50-mL of flask, and the mixture was heated at 80 °C for 2-12 h (TLC monitored). The reaction mixture was cooled to room temperature. Then the reaction mixture was acidified and extracted with DCM (3 x 30 mL). Combined organic extract was dried with Na2SO4, concentrated on a rotary evaporator and the residue was purified by column chromatography on silica gel using PE/EtOAc = 5/1 as eluent to afford the product.

To a 50 mL oven-dried Schlenk flask equipped with a magnetic stir bar, were added methyl 2-iodobenzoate (10 mmol), phenylboronic acid (15 mmol), Pd(OAc)2 (112 mg, 5 mol%), DPPF (338 mg, 6 mol%) and K3PO4 (20 mmol). The Schlenk flask was evacuated and backfilled with N2 for 3 times. Then 1,2-dimethoxyethane (30 mL) was added. The reaction mixture was heated at 80 °C. The reaction progress was monitored by thin-layer chromatography (TLC) analysis. After the reaction was completed, the mixture was cooled to room temperature. Then the reaction mixture was concentrated on a rotary evaporator, and purified by column chromatography (PE/EtOAc = 50/1) to give the desired ester.

KOH (3.0 g, 75 mmol), MeOH (20 mL) and the desired ester were added to a 50-mL of flask, and the mixture was heated at 80 °C for 2-12 h (TLC monitored). The reaction mixture was cooled to room temperature. Then the reaction mixture was
acidified and extracted with DCM (3 x 30 mL). Combined organic extract was dried with Na₂SO₄, concentrated on a rotary evaporator and the residue was purified by column chromatography on silica gel using PE/EtOAc = 5/1 as eluent to afford the product.

Other reagents and solvents were purchased from commercial supplier and used without any further treatment.

3. Characterization of lactone products

6H-Benzoc[\textit{c}]chromen-6-one (2a): White solid; \textit{m.p.}: 93-94 °C; \textit{1}H NMR (500 MHz, CDCl₃) δ 8.38 (d, \textit{J} = 7.9 Hz, 1H), 8.10 (d, \textit{J} = 7.8 Hz, 1H), 8.04 (d, \textit{J} = 8.1 Hz, 1H), 7.81 (t, \textit{J} = 7.3 Hz, 1H) 7.56 (t, \textit{J} = 7.4 Hz, 1H), 7.46 (dt, \textit{J} = 7.7 Hz, 1.1 Hz, 1H), 7.36 - 7.30 (m, 2H); \textit{1}3C NMR (125 MHz, CDCl₃) δ 161.2, 151.3, 134.9, 134.8, 130.6, 130.5, 128.9, 124.6, 122.8, 121.7, 121.3, 118.1, 117.8; MS(EI), m/z 196.08 [M⁺, 100%].

3-Fluoro-6\textit{H}-benzo[\textit{c}]chromen-6-one (2b): White solid; \textit{m.p.}: 157-159 °C; \textit{1}H NMR (500 MHz, CDCl₃) δ 8.34 (dd, \textit{J} = 7.9, 1.0 Hz, 1H), 8.00 (t, \textit{J} = 8.6 Hz, 2H), 7.84 - 7.76 (m, 1H), 7.59 - 7.52 (m, 1H), 7.09 - 7.01 (m, 2H); \textit{1}3C NMR (125 MHz, CDCl₃) δ 163.5 (d, \textit{J}_{C-F} = 251.2 Hz), 160.8, 152.2 (d, \textit{J}_{C-F} = 12.4 Hz), 135.1, 134.3, 130.7, 128.8, 124.4 (d, \textit{J}_{C-F} = 9.8 Hz), 121.6, 120.5, 114.7 (d, \textit{J}_{C-F} = 3.4 Hz), 112.5 (d, \textit{J}_{C-F} = 22.3 Hz), 105.2 (d, \textit{J}_{C-F} = 24.9 Hz); MS(EI), m/z 214.12 [M⁺, 90%], 157.00 (100%).
3-Chloro-6H-benzo[c]chromen-6-one (2c): White solid; m.p.: 152-154 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.31 (dd, $J = 7.9$, 0.9 Hz, 1H), 8.00 (d, $J = 8.2$ Hz, 1H), 7.90 (d, $J = 8.3$ Hz, 1H), 7.82 - 7.78 (m, 1H), 7.58 - 7.54 (m, 1H), 7.29 - 7.24 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 160.6, 151.6, 136.0, 135.1, 134.1, 130.8, 129.3, 125.1, 123.9, 121.7, 121.0, 118.0, 116.8; MS(EI), m/z 230.06 [M$^+$, 54%], 139.10 (100%).

3-Bromo-6H-benzo[c]chromen-6-one (2d): White solid; m.p.: 149-151 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.34 (dd, $J = 8.1$, 1.0 Hz, 1H), 8.03 (d, $J = 8.0$ Hz, 1H), 7.86 (d, $J = 8.4$ Hz, 1H), 7.83 - 7.77 (m, 1H), 7.61 - 7.53 (m, 1H), 7.47 (d, $J = 1.8$ Hz, 1H), 7.42 (dd, $J = 8.5$, 1.8 Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 160.5, 151.5, 135.1, 134.0, 130.8, 129.3, 127.9, 124.0, 123.8, 121.7, 121.0, 120.9, 117.2; MS(EI), m/z 274.02 [M$^+$, 24%], 138.99 (100%).

3-(Trifluoromethyl)-6H-benzo[c]chromen-6-one (2e): White solid; m.p.: 140-142 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.41 (dd, $J = 7.9$, 1.0 Hz, 1H), 8.15 (t, $J = 8.9$ Hz, 2H), 7.93 - 7.81 (m, 1H), 7.71 - 7.62 (m, 1H), 7.62 - 7.52 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 160.3, 151.1, 135.3, 133.4, 132.3(d, $J_{C-F} = 33.6$ Hz), 130.9, 130.2, 124.5, 123.0(d, $J_{C-F} = 181.1$ Hz), 122.3, 121.7, 121.2 (q, $J_{C-F} = 3.7$ Hz), 115.3(q, $J_{C-F} = 4.1$ Hz); MS(EI), m/z 264.07 [M$^+$, 100%].
3-Methyl-6\textit{H}-benzo[\textit{c}]chromen-6-one (2f): White solid; \textit{m.p.}: 130-132 °C; \textit{^1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 8.35 (dd, \textit{J} = 7.9, 1.0 Hz, 1H), 8.03 (d, \textit{J} = 8.1 Hz, 1H), 7.88 (d, \textit{J} = 8.5 Hz, 1H), 7.80 - 7.72 (m, 1H), 7.56 - 7.48 (m, 1H), 7.13 - 7.09 (m, 2H), 2.42 (s, 3H); \textit{^{13}}C NMR (125 MHz, CDCl\textsubscript{3}) δ 161.4, 151.3, 141.3, 135.0, 134.8, 130.5, 128.4, 125.7, 122.5, 121.5, 120.9, 117.9, 115.5, 21.5; MS(EI), m/z 209.98 [M\textsuperscript{+}, 100%].

3-\textit{(tert-Butyl)}-6\textit{H}-benzo[\textit{c}]chromen-6-one (2g): White solid; \textit{m.p.}: 155-158 °C; \textit{^1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 8.38 (d, \textit{J} = 7.5 Hz, 1H), 8.08 (d, \textit{J} = 7.9 Hz, 1H), 7.97 (d, \textit{J} = 8.6 Hz, 1H), 7.80 (t, \textit{J} = 7.4 Hz, 1H), 7.54 (t, \textit{J} = 7.4 Hz, 1H), 7.42 - 7.34 (m, 2H), 1.37 (d, \textit{J} = 1.0 Hz, 9H); \textit{^{13}}C NMR (125MHz, CDCl\textsubscript{3}) δ 161.6, 154.8, 151.3, 135.0, 134.8, 130.6, 128.5, 122.5, 122.1, 121.6, 121.1, 115.5, 114.6, 35.1, 31.2; MS(EI), m/z 252.11 [M\textsuperscript{+}, 22%], 237.14 (100%).

3-Methoxy-6\textit{H}-benzo[\textit{c}]chromen-6-one (2h): White solid; \textit{m.p.}: 142-144 °C; \textit{^1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 8.35 (dd, \textit{J} = 7.9, 1.2 Hz, 1H), 7.99 (d, \textit{J} = 8.2 Hz, 1H), 7.94 (d, \textit{J} = 8.8 Hz, 1H), 7.80 - 7.74 (m, 1H), 7.54 - 7.46 (m, 1H), 6.91 (dd, \textit{J} = 8.8, 2.5Hz, 1H), 6.86 (d, \textit{J} = 2.5 Hz, 1H), 3.88 (s, 3H); \textit{^{13}}C NMR (125 MHz, CDCl\textsubscript{3}) δ 161.7, 161.6, 152.7, 135.3, 134.9, 130.7, 127.8, 123.9, 121.2, 120.1, 112.5, 111.3, 101.8, 55.8; MS(EI), m/z 226.06 [M\textsuperscript{+}, 64%], 127.12 (100%).
3-(Methoxymethyl)-6H-benzo[c]chromen-6-one (2i): White solid; m.p.: 95-97 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ 8.37 (dd, $J$ = 7.9, 0.9 Hz, 1H), 8.08 (d, $J$ = 7.9 Hz, 1H), 8.01 (d, $J$ = 8.0 Hz, 1H), 7.82 - 7.78 (m, 1H), 7.58 - 7.52 (m, 1H), 7.32 - 7.27 (m, 2H), 4.53 (s, 2H), 3.43 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 161.3, 151.4, 141.6, 134.9, 134.7, 130.6, 128.8, 123.5, 122.9, 121.7, 121.2, 117.3, 116.4, 73.8, 58.5; HRMS (EI), m/z calcd for C$_{15}$H$_{12}$O$_3$ 240.0786, found 240.0799 [M$^+$.]

3-Phenyl-6H-benzo[c]chromen-6-one (2j): White solid; m.p.: 123-125 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ 8.38 (d, $J$ = 8.0 Hz, 1H), 8.08 (dd, $J$ = 13.8, 8.0 Hz, 2H), 7.83-7.78 (m, 1H), 7.63 (d, $J$ = 7.1 Hz, 2H), 7.57 - 7.55 (m, 3H), 7.48 (t, $J$ = 7.2 Hz, 2H), 7.43 - 7.38 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 161.3, 151.7, 143.5, 139.3, 134.9, 134.7, 130.7, 129.1, 128.8, 128.3, 127.1, 123.3, 123.2, 121.7, 121.2, 117.0, 115.8; MS(EI), m/z 272.08 [M$,^{100\%}$].

1-Methyl-6H-benzo[c]chromen-6-one (2k): White solid; m.p.: 155-160 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ 8.46 (dd, $J$ = 7.9, 1.2 Hz, 1H), 8.35 (d, $J$ = 8.3 Hz, 1H), 7.85 - 7.76 (m, 1H), 7.57 (t, $J$ = 5.3 Hz, 1H), 7.33 (t, $J$ = 8.1 Hz, 1H), 7.24 (d, $J$ = 5.1 Hz, 1H), 7.14 (d, $J$ = 7.4 Hz, 1H), 2.86 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 161.3, 152.2, 136.3, 136.1, 134.3, 130.9, 129.4, 128.9, 128.1, 126.2, 122.1, 117.5, 116.3,
5H-dibenzo[c,f]chromen-5-one (2I): White solid; m.p.: 189-193 °C; 1H NMR (500 MHz, CDCl$_3$) δ 8.51 (dd, $J = 8.0$, 0.9 Hz, 1H), 8.40 (dd, $J = 7.7$, 1.0 Hz, 1H), 8.10 (d, $J = 8.0$ Hz, 1H), 7.96 (d, $J = 8.6$ Hz, 1H), 7.87 - 7.76 (m, 2H), 7.69 (d, $J = 8.7$ Hz, 1H), 7.63 - 7.49 (m, 3H); 13C NMR (125 MHz, CDCl$_3$) δ 161.2, 147.2, 135.4, 134.9, 134.3, 130.6, 128.6, 127.9, 127.7, 127.1, 124.5, 123.9, 122.3, 122.0, 121.2, 119.1, 113.0; MS(EI), m/z 246.09 [M+, 100%].

2,4-Dimethyl-6H-benzo[c]chromen-6-one (2m): White solid; m.p.: 178-181 °C; 1H NMR (500 MHz, CDCl$_3$) δ 8.35 (dd, $J = 7.9$, 1.2 Hz, 1H), 8.02 (d, $J = 8.0$ Hz, 1H), 7.79 - 7.71 (m, 1H), 7.60 (s, 1H), 7.55 - 7.48 (m, 1H), 7.09 (s, 1H), 2.41 (s, 3H), 2.38 (s, 3H); 13C NMR (125 MHz, CDCl$_3$) δ 161.4, 147.8, 135.2, 134.6, 133.4, 132.9, 130.5, 128.5, 126.7, 121.8, 121.2, 120.4, 117.4, 21.1, 15.9; MS(EI), m/z 224.11 [M+, 100%].

2-Methoxy-6H-benzo[c]chromen-6-one (2n): White solid; 1H NMR (500 MHz, CDCl$_3$) δ 8.38 (dd, $J = 8.0$, 1.2 Hz, 1H), 8.03 (d, $J = 8.0$ Hz, 1H), 7.83 - 7.78 (m, 1H), 7.63 - 7.53 (m, 1H), 7.45 (d, $J = 2.8$ Hz, 1H), 7.31 - 7.22 (m, 1H), 7.03 (dd, $J = 9.0$, 2.9 Hz, 1H), 3.90 (s, 3H); 13C NMR (125 MHz, CDCl$_3$) δ 161.3, 156.4, 145.7, 134.8,
4-Methyl-6H-benzo[c]chromen-6-one (2o): White solid; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.41 - 8.30 (m, 1H), 8.06 (t, $J = 6.9$ Hz, 1H), 7.82 - 7.74 (m, 2H), 7.57 - 7.49 (m, 1H), 7.27 - 7.15 (m, 2H), 2.45 (d, $J = 17.2$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 161.4, 149.4, 134.8, 134.7, 134.1, 131.4, 130.6, 128.7, 122.8, 121.6, 121.3, 117.7, 117.5, 21.2; MS(EI), m/z 210.11 [M$^+$, 100%].

4-Fluoro-3-methyl-6H-benzo[c]chromen-6-one (2p): White solid; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.35 (d, $J = 7.9$, 1H), 7.93 (d, $J = 8.0$ Hz, 1H), 7.82 - 7.77 (m, 1H), 7.61 - 7.53 (m, 2H), 7.14 (d, $J = 6.4$ Hz, 1H), 2.35 (d, $J = 1.5$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 161.1, 158.1(d, $J_{C-F} = 242.4$ Hz), 147.1 (d, $J_{C-F} = 2.0$ Hz), 134.9, 134.2(d, $J_{C-F} = 2.6$ Hz), 130.7, 129.1, 128.5(d, $J_{C-F} = 20.2$ Hz), 121.7, 121.0, 120.1(d, $J_{C-F} = 5.2$ Hz), 116.8(d, $J_{C-F} = 8.1$ Hz), 108.3(d, $J_{C-F} = 26.0$ Hz), 14.9 (d, $J_{C-F} = 3.4$ Hz); MS(EI), m/z 228.10 [M$^+$, 100%].

5H-benzo[c]benzofuro[2,3-f]chromen-5-one (2q): White solid; m.p.: 196-198 °C; $^1$H
NMR (500 MHz, CDCl₃) δ 8.92 (d, J = 8.0 Hz, 1H), 8.37 (dd, J = 8.0, 1.1 Hz, 1H), 7.90 - 7.80 (m, 3H), 7.63 - 7.54 (m, 2H), 7.49 - 7.42 (m, 1H), 7.36 (t, J = 7.4, 1H), 7.24 (d, J = 8.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 161.0, 156.5, 152.2, 150.7, 135.1, 132.9, 130.3, 128.9, 127.0, 126.5, 123.6, 123.2, 121.3, 121.0, 120.9, 120.3, 112.9, 111.8, 105.5; MS(EI), m/z 286.06 [M⁺, 100%].

5H-Thieno[2,3-c]isochromen-5-one (2r): White solid; m.p.: 120-122 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.32 (dd, J = 8.0, 0.9 Hz, 1H), 7.80 (dt, J = 8.0, 1.4 Hz, 1H), 7.72 (dd, J = 7.9, 0.7 Hz, 1H), 7.51 - 7.44 (m, 1H), 7.29 (d, J = 6.2 Hz, 1H), 6.97 (d, J = 5.9 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 161.7, 156.2, 135.4, 134.4, 131.1, 127.6, 122.2, 119.2, 118.4, 117.0, 116.1; MS(EI), m/z 202.04 [M⁺, 100%].

10-Methyl-6H-benzo[c]chromen-6-one (2s): White solid; m.p.: 118-120 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.34(dd, J = 7.8, 0.9 Hz, 1H), 8.28 (d, J = 8.3 Hz, 1H), 7.62 (dd, J = 7.4, 0.6 Hz, 1H), 7.49 - 7.41 (m, 2H), 7.38 (dd, J = 8.2, 1.4 Hz, 1H), 7.33 - 7.28 (m, 1H), 2.88 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 161.7, 151.3, 139.1, 135.1, 133.6, 129.7, 129.2, 128.3, 127.2, 124.0, 122.8, 119.7, 118.0, 25.4; MS(EI), m/z 210.13 [M⁺, 92%], 152.14 (100%).

9-Methyl-6H-benzo[c]chromen-6-one (2t): White solid; m.p.: 101-103 °C; ¹H NMR
8-Methyl-6H-benzo[c]chromen-6-one (2u): White solid; m.p.: 118-120 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.14 (s, 1H), 7.97 (dd, $J = 7.9$, 1.4 Hz, 1H), 7.94 (d, $J = 8.2$ Hz, 1H), 7.58 (dd, $J = 8.1$, 1.4 Hz, 1H), 7.45 - 7.39 (m, 1H), 7.33 - 7.26 (m, 2H), 2.46 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 161.4, 151.1, 139.3, 135.2, 135.1, 133.3, 130.9, 130.1, 124.9, 123.5, 122.8, 122.6, 117.9, 117.3; MS(EI), m/z 210.09 [M$^+$, 100%].

8-Chloro-6H-benzo[c]chromen-6-one (2v): White solid; m.p.: 171-173 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.32 (d, $J = 2.3$ Hz, 1H), 8.03 (d, $J = 8.5$ Hz, 1H), 7.98 (dd, $J = 8.3$, 1.5 Hz, 1H), 7.74 (dd, $J = 8.7$, 2.3 Hz, 1H), 7.51 - 7.45 (m, 1H), 7.36 - 7.31 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 160.0, 151.2, 135.2, 135.1, 133.3, 130.9, 130.1, 124.9, 123.5, 122.8, 122.6, 117.9, 117.3; MS(EI), m/z 230.03 [M$^+$, 70%], 139.11 (100%).

8-Fluoro-6H-benzo[c]chromen-6-one (2w): White solid; m.p.: 144-146 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.10 (dd, $J = 8.8$, 4.9 Hz, 1H), 8.01 (dd, $J = 8.5$, 2.8 Hz, 1H),
7.98 (d, J = 8.1 Hz, 1H), 7.55 - 7.50 (m, 1H), 7.49 - 7.43 (m, 1H), 7.35 - 7.32 (m, 2H);

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 162.5 (d, $J_{C,F} = 250.7$ Hz), 160.2 (d, $J_{C,F} = 3.0$ Hz)

150.9, 131.3 (d, $J_{C,F} = 2.9$ Hz), 130.5, 124.9, 124.3(d, $J_{C,F} = 8.0$ Hz), 123.2 (d, $J_{C,F} = 23.2$ Hz), 123.1 (d, $J_{C,F} = 8.1$ Hz), 122.7, 117.9, 117.4, 116.2(d, $J_{C,F} = 23.2$ Hz);

MS(EI), m/z 214.07 [M+, 74%], 157.07 (100%).

8-Phenyl-6$H$-benzo[c]chromen-6-one (2x)$^4$: White solid; m.p.: 173-176 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ 8.60 (d, J = 1.9 Hz, 1H), 8.14 (d, J = 8.5 Hz, 1H), 8.06 - 8.01 (m, 2H), 7.70 - 7.65 (m, 2H), 7.50 - 7.43 (m, 3H), 7.43 - 7.38 (m, 1H), 7.37 - 7.31 (m, 2H);

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 161.3, 151.3, 141.8, 138.9, 133.6, 133.5, 130.4, 129.1, 128.5, 128.3, 127.1, 124.7, 122.8, 122.4, 121.7, 118.0, 117.8; MS(EI), m/z 272.08 [M+, 100%].

6$H$-Naphtho[2,1-c]chromen-6-one (2y)$^4$: White solid; m.p.: 124-125 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ 8.83 (d, J = 8.4 Hz, 1H), 8.48 (dd, J = 8.1, 1.1 Hz, 1H), 8.29 (d, J = 8.5 Hz, 1H), 8.00 - 7.94 (m, 1H), 7.92 (d, J = 8.5 Hz, 1H), 7.74 - 7.62 (m, 2H), 7.55 - 7.50 (m, 1H), 7.47 (dd, J = 8.2, 1.3 Hz, 1H), 7.40 - 7.35 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 161.7, 151.7, 137.2, 134.4, 130.1, 129.7, 129.3, 129.0, 128.4, 127.9, 127.6, 127.2, 124.5, 124.2, 120.2, 118.9, 118.0; MS(EI), m/z 246.06 [M+, 88%], 189.10 (100%).
4H-thieno[2,3-c]chromen-4-one (2z): Light yellow solid; m.p.: 133-135 °C; 1H NMR (500 MHz, CDCl₃) δ 7.89 (d, J = 5.0 Hz, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.60 (d, J = 5.1 Hz, 1H), 7.45 (t, J = 7.4 Hz, 1H), 7.38 (d, J = 8.3 Hz, 1H), 7.30 (t, J = 7.8 Hz, 1H); 13C NMR (125 MHz, CDCl₃) δ 157.2, 152.6, 145.0, 136.9, 130.2, 124.6, 124.4, 123.8, 122.4, 117.5, 117.4; MS(EI), m/z 201.93 [M⁺, 82%], 102.11 (100%).

5H-dithieno[2,3-b:3',2'-d]pyran-5-one (2aa): Light yellow solid; m.p.: 144-147 °C; 1H NMR (500 MHz, CDCl₃) δ 7.91 (d, J = 5.1 Hz, 1H), 7.40 (d, J = 5.0 Hz, 1H), 7.17 (d, J = 5.9 Hz, 1H), 6.99 (d, J = 5.9 Hz, 1H); 13C NMR (125 MHz, CDCl₃) δ 158.3, 157.9, 143.8, 137.8, 122.6, 120.9, 119.3, 116.5, 116.4; HRMS (EI), m/z calcd for C₉H₄O₂S₂ 207.9653, found 207.9665 [M⁺].

9-Methyl-3-pentyl-6H-benzo[c]chromen-6-one (4): Light yellow solid; m.p.: 60-62 °C; 1H NMR (500 MHz, CDCl₃) δ 8.21 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.80 (s, 1H), 7.30 (dd, J = 8.0, 0.8 Hz, 1H), 7.14 - 7.08 (m, 2H), 2.68 (t, J = 7.7 Hz, 2H), 2.51 (s, 3H), 1.69 - 1.59 (m, 2H), 1.39 - 1.28 (m, 4H), 0.89 (t, J = 6.8 Hz, 3H); 13C NMR (125 MHz, CDCl₃) δ 161.5, 151.5, 146.2, 145.8, 135.0, 130.5, 129.7, 124.9, 122.5, 121.6, 118.5, 117.2, 115.7, 35.7, 31.4, 30.7, 22.6, 22.3, 14.1; MS(EI), m/z 280.18 [M⁺, 50%], 223.07 (100%).
4. NMR Spectra

![NMR Spectra Image]

2a
$\text{Br}$

$\text{2d}$

$\text{Br}$

$\text{2d}$
5. References


