

# Hypervalent Iodine-Mediated Regioselective Cyclization of Acetylenic Malonates: Facile Synthesis of 1-Diiodomethylene Indane and Cyclopentane Derivatives

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## **Supporting Information**

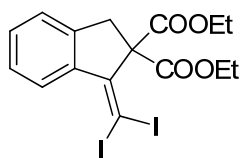
1. General experimental methods (S2)
2. General experimental procedure and characterization data. (S2-S7)
3. The NOE spectrum of compound **2a** (S8)
4. Copies of  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectra of products (S9-S40)

### General experimental methods:

All reactions were performed in Schlenk tubes under nitrogen atmosphere. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63 μm, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr (house vacuum) at 25–35 °C. Commercial reagents and solvents were used as received. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale.

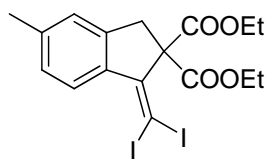
### General Experimental procedure:

The mixture of acetylenic malonate (0.2 mmol) with Bu<sub>4</sub>NI (221 mg, 0.6 mmol) in CF<sub>3</sub>CH<sub>2</sub>OH (2 mL) was treated with PhIO (132 mg, 0.6 mmol) at 25 °C, and the reaction mixture was allowed to stir at 25 °C for 24 hr. Upon completion by TLC, the reaction was quenched with saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, and extracted by ethyl acetate (50 mL x 3). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (15% ethyl acetate in hexanes) to give the corresponding product **4**.



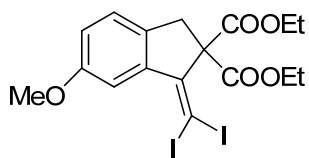
**Diethyl 1-(diiodomethylene)-1H-indene-2,2(3H)-dicarboxylate 4a:**

colorless solid; m.p. 143–145 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.64 (d, *J* = 7.6 Hz, 1 H), 7.21–7.33 (m, 3 H), 4.23–4.31 (m, 4 H), 3.64 (s, 2 H), 1.32 (t, *J* = 7.2 Hz, 6 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 168.6, 151.0, 144.7, 139.3, 130.2, 126.6, 126.4, 125.1, 71.8, 62.7, 42.3, 14.2, 2.4; IR (KBr) 2981, 2927, 1736, 1716, 1458, 1438 cm<sup>-1</sup>; HRMS *m/z* calcd for C<sub>16</sub>H<sub>16</sub>I<sub>2</sub>NaO<sub>4</sub> ([M+Na]<sup>+</sup>): 548.9036, found 548.9025.



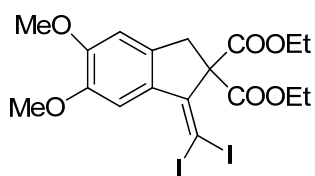
**Diethyl 1-(diiodomethylene)-5-methyl-1H-indene-2,2(3H)-dicarboxylate**

**4b:** colorless solid; m.p. 147-149 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.50 (d,  $J = 8.4$  Hz, 1 H), 7.08 (d,  $J = 8.4$  Hz, 1 H), 7.03 (s, 1 H), 4.21-4.30 (m, 4 H), 3.59 (s, 2 H), 2.31 (s, 3 H), 1.31 (t,  $J = 7.2$  Hz, 6 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  168.6, 150.9, 144.8, 140.6, 136.7, 127.2, 126.2, 125.4, 71.7, 62.5, 42.0, 21.6, 14.0, 0.7; IR (KBr) 2980, 2921, 1734, 1720, 1610, 1443  $\text{cm}^{-1}$ ; HRMS  $m/z$  calcd for  $\text{C}_{17}\text{H}_{18}\text{I}_2\text{NaO}_4$  ( $[\text{M}+\text{Na}]^+$ ): 562.9192, found 562.9154.



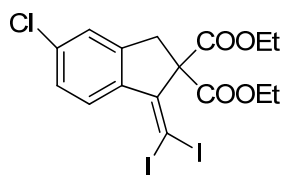
**Diethyl 1-(diiodomethylene)-6-methoxy-1H-indene-2,2(3H)-**

**dicarboxylate 4c:** yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.20 (s, 1H), 7.11 (d,  $J = 8.4$  Hz, 1 H), 6.92 (d,  $J = 8.4$  Hz, 1 H), 4.23-4.31 (m, 4 H), 3.82 (s, 3 H), 3.57 (s, 2 H), 1.32 (t,  $J = 7.2$  Hz, 6 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  168.7, 158.4, 151.1, 140.4, 137.1, 125.7, 117.3, 111.3, 72.5, 62.8, 55.9, 41.8, 14.3, 2.4; IR (KBr) 2926, 2853, 1735, 1605, 1481, 1463  $\text{cm}^{-1}$ ; HRMS  $m/z$  calcd for  $\text{C}_{17}\text{H}_{18}\text{I}_2\text{NaO}_5$  ( $[\text{M}+\text{Na}]^+$ ): 578.9141, found 578.9101.



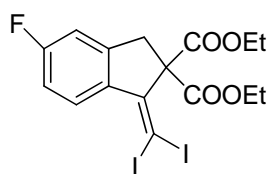
**Diethyl 1-(diiodomethylene)-5,6-dimethoxy-1H-indene-2,2(3H)-**

**dicarboxylate 4d:** yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.19 (s, 1 H), 6.69 (s, 1 H), 4.22-4.32 (m, 4 H), 3.90 (s, 3 H), 3.89 (s, 3 H), 3.57 (s, 2 H), 1.33 (t,  $J = 7.2$  Hz, 6 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  168.7, 151.1, 150.7, 147.4, 138.4, 131.5, 109.1, 106.7, 71.7, 62.6, 56.2, 56.1, 41.9, 14.0, -2.1; IR (KBr) 2930, 2854, 1735, 1604, 1502, 1465  $\text{cm}^{-1}$ ; HRMS  $m/z$  calcd for  $\text{C}_{18}\text{H}_{20}\text{I}_2\text{NaO}_6$  ( $[\text{M}+\text{Na}]^+$ ): 608.9247, found 608.9223.



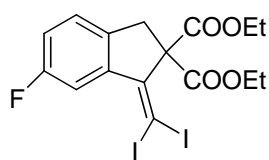
**Diethyl 5-chloro-1-(diiodomethylene)-1H-indene-2,2(3H)-**

**dicarboxylate 4e:** colorless solid; m.p. 122-124 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.56 (d,  $J$  = 8.8 Hz, 1 H), 7.20-7.26 (m, 2 H), 4.22-4.32 (m, 4 H), 3.60 (s, 2 H), 1.32 (t,  $J$  = 7.2 Hz, 6 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  168.4, 150.0, 146.4, 137.9, 135.9, 127.6, 126.8, 125.2, 71.8, 62.9, 41.7, 14.2, 3.4; IR (KBr) 2979, 2925, 1718, 1593, 1463, 1366  $\text{cm}^{-1}$ ; HRMS  $m/z$  calcd for  $\text{C}_{16}\text{H}_{15}\text{ClI}_2\text{NaO}_4$  ( $[\text{M}+\text{Na}]^+$ ): 582.8646, found 582.8620.



**Diethyl 1-(diiodomethylene)-5-fluoro-1H-indene-2,2(3H)-dicarboxylate**

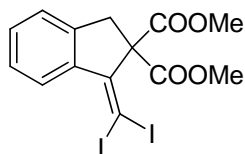
**4f:** colorless solid; m.p. 105-107 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.61 (dd,  $J$  = 8.8, 5.2 Hz, 1 H), 6.98 (td,  $J$  = 8.8, 2.4 Hz, 1 H), 6.91 (d,  $J$  = 8.0 Hz, 1 H), 4.21-4.35 (m, 4 H), 3.61 (s, 2 H), 1.33 (t,  $J$  = 7.2 Hz, 6 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  168.3, 164.8, 162.3, 149.7, 147.3, 147.2, 135.3, 128.3, 128.2, 113.8, 113.6, 112.0, 111.7, 71.8, 62.7, 41.6, 14.0, 1.6; IR (KBr) 2981, 2925, 1736, 1605, 1479, 1439, 1366  $\text{cm}^{-1}$ ; HRMS  $m/z$  calcd for  $\text{C}_{16}\text{H}_{15}\text{FI}_2\text{NaO}_4$  ( $[\text{M}+\text{Na}]^+$ ): 566.8941, found 566.8901.



**Diethyl 1-(diiodomethylene)-6-fluoro-1H-indene-2,2(3H)-dicarboxylate**

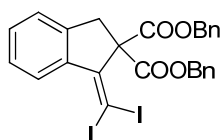
**4g:** pale yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.37 (d,  $J$  = 11.2 Hz, 1 H), 7.16 (t,  $J$  = 6.0 Hz, 1 H), 7.05 (t,  $J$  = 8.4 Hz, 1 H), 4.19-4.35 (m, 4 H), 3.59 (s, 2 H), 1.32 (t,  $J$  = 7.2 Hz, 6 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  168.2, 162.4, 160.0, 150.0, 140.9, 140.8, 140.0, 125.9, 125.8, 117.3,

117.1, 113.5, 113.2, 72.2, 62.7, 41.5, 14.0, 4.4; IR (KBr) 2979, 2927, 2854, 1731, 1610, 1588, 1477, 1439  $\text{cm}^{-1}$ ; HRMS  $m/z$  calcd for  $\text{C}_{16}\text{H}_{15}\text{I}_2\text{NaO}_4$  ( $[\text{M}+\text{Na}]^+$ ): 566.8941, found 566.8903.



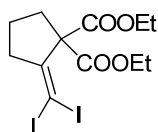
**Dimethyl 1-(diiodomethylene)-1H-indene-2,2(3H)-dicarboxylate 4h:**

colorless solid; 155-157 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.64 (d,  $J = 8.0$  Hz, 1 H), 7.21-7.34 (m, 2 H), 7.22 (d,  $J = 7.2$  Hz, 1 H), 3.80 (s, 6 H), 3.65 (s, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  169.2, 151.0, 144.6, 139.2, 130.4, 126.6, 126.5, 125.2, 71.8, 53.7, 42.4, 2.7; IR (KBr) 3054, 2987, 1735, 1601, 1433, 1265  $\text{cm}^{-1}$ ; HRMS  $m/z$  calcd for  $\text{C}_{14}\text{H}_{12}\text{I}_2\text{NaO}_4$  ( $[\text{M}+\text{Na}]^+$ ): 520.8723, found 520.8705.



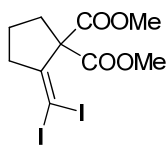
**Dibenzyl 1-(diiodomethylene)-1H-indene-2,2(3H)-dicarboxylate 4i:**

pale yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.62 (d,  $J = 7.6$  Hz, 1 H), 7.15-7.37 (m, 14 H), 5.22 (s, 4 H), 3.63 (s, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  168.2, 150.9, 144.5, 139.2, 135.1, 130.2, 128.6, 128.4, 128.3, 126.4, 125.0, 71.8, 68.1, 42.3, 2.6; IR (KBr) 3064, 3032, 2960, 2926, 1735, 1497, 1456  $\text{cm}^{-1}$ ; HRMS  $m/z$  calcd for  $\text{C}_{26}\text{H}_{20}\text{I}_2\text{NaO}_4$  ( $[\text{M}+\text{Na}]^+$ ): 672.9349, found 672.9349.

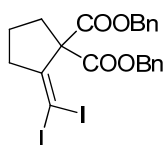


**Diethyl 2-(diiodomethylene)cyclopentane-1,1-dicarboxylate 4l:**

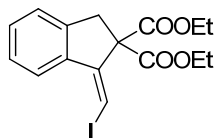
pale yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.20-4.37 (m, 4 H), 2.62 (t,  $J = 7.2$  Hz, 2 H), 2.53 (t,  $J = 7.2$  Hz, 2 H), 1.78-1.84 (m, 2 H), 1.33 (t,  $J = 7.2$  Hz, 6 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  168.4, 155.9, 68.3, 62.2, 44.4, 41.2, 24.1, 14.1, 8.4; IR (KBr) 2978, 1728, 1444, 1366, 1261  $\text{cm}^{-1}$ ; HRMS  $m/z$  calcd for  $\text{C}_{12}\text{H}_{16}\text{I}_2\text{NaO}_4$  ( $[\text{M}+\text{Na}]^+$ ): 500.9036, found 500.9009.



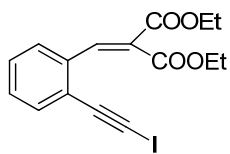
**Dimethyl 2-(diiodomethylene)cyclopentane-1,1-dicarboxylate 4m:** pale yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.80 (s, 6 H), 2.63 (t,  $J = 6.8$  Hz, 2 H), 2.53 (t,  $J = 7.2$  Hz, 2 H), 1.77-1.85 (m, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  169.0, 155.8, 68.2, 53.2, 44.3, 41.3, 24.2, 8.7; IR (KBr) 2919, 2850, 1735, 1432, 1264  $\text{cm}^{-1}$ ; HRMS  $m/z$  calcd for  $\text{C}_{10}\text{H}_{12}\text{I}_2\text{NaO}_4$  ( $[\text{M}+\text{Na}]^+$ ): 472.8723, found 472.8767.



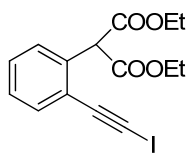
**Dibenzyl 2-(diiodomethylene)cyclopentane-1,1-dicarboxylate 4n:** pale yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.20-7.40 (m, 10 H), 5.21 (s, 4 H), 2.63 (t,  $J = 6.4$  Hz, 2 H), 2.51 (t,  $J = 7.2$  Hz, 2 H), 1.70-1.80 (m, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  168.1, 155.9, 135.3, 128.6, 128.4, 128.1, 68.3, 67.9, 44.3, 41.5, 24.2, 8.8; IR (KBr) 2919, 2844, 1728, 1453, 1261  $\text{cm}^{-1}$ ; HRMS  $m/z$  calcd for  $\text{C}_{22}\text{H}_{20}\text{I}_2\text{NaO}_4$  ( $[\text{M}+\text{Na}]^+$ ): 624.9349, found 624.9377.



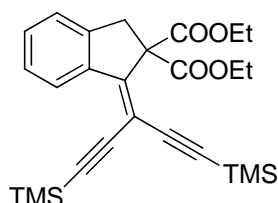
**Diethyl 1-(diiodomethylene)-5-fluoro-1H-indene-2,2(3H)-dicarboxylate 2a:** pale yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.61 (d,  $J = 7.2$  Hz, 1 H), 7.26-7.36 (m, 3 H), 6.86 (s, 1 H), 4.22 (q,  $J = 7.2$  Hz, 4 H), 3.66 (s, 2 H), 1.26 (t,  $J = 7.2$  Hz, 6 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  169.5, 144.8, 144.6, 138.0, 130.1, 126.4, 124.9, 124.8, 73.6, 67.1, 62.3, 39.8, 14.1; IR (KBr) 2980, 2930, 1734, 1471, 1366, 1247  $\text{cm}^{-1}$ ; HRMS  $m/z$  calcd for  $\text{C}_{16}\text{H}_{17}\text{INaO}_4$  ( $[\text{M}+\text{Na}]^+$ ): 423.0069, found 423.0035.



**Diethyl 2-(2-(iodoethynyl)benzylidene)malonate 7:** pale yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.16 (s, 1 H), 7.45-7.49 (m, 2 H), 7.27-7.32 (m, 2 H), 4.26-4.35 (m, 4 H), 1.36 (t,  $J = 7.2$  Hz, 3 H), 1.23 (t,  $J = 7.2$  Hz, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.3, 164.0, 140.3, 136.0, 133.5, 129.9, 128.8, 128.0, 127.7, 124.6, 91.7, 61.8, 14.2, 13.9, 13.8; IR (KBr) 2984, 2928, 1725, 1705, 1625, 1467, 1445, 1374  $\text{cm}^{-1}$ ; HRMS  $m/z$  calcd for  $\text{C}_{16}\text{H}_{15}\text{I}\text{NaO}_4$  ( $[\text{M}+\text{Na}]^+$ ): 420.9913, found 420.9955.



**Diethyl 2-(2-(iodoethynyl)phenyl)malonate 9:** pale yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.42-7.47 (m, 2 H), 7.35 (t,  $J = 7.6$  Hz, 1 H), 7.25-7.29 (m, 1 H), 5.22 (s, 1 H), 4.22 (q,  $J = 7.2$  Hz, 4 H), 1.28 (t,  $J = 7.0$  Hz, 6 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  168.0, 135.9, 133.0, 129.2, 128.7, 127.9, 123.9, 91.9, 62.0, 55.8, 14.2, 11.8; IR (KBr) 2979, 2926, 1735, 1488, 1467, 1445, 1367  $\text{cm}^{-1}$ ; HRMS  $m/z$  calcd for  $\text{C}_{15}\text{H}_{15}\text{I}\text{NaO}_4$  ( $[\text{M}+\text{Na}]^+$ ): 408.9913, found 408.9877.



**Diethyl 1-(1,5-bis(trimethylsilyl)penta-1,4-diyne-3-ylidene)-1H-indene-2,2(3H)-dicarboxylate 10:** pale yellow oil;  $^1\text{H}$ NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.64 (d,  $J = 11.2$  Hz, 1 H), 7.20-7.32 (m, 3 H), 4.20 (q,  $J = 6.8$  Hz, 4 H), 3.65 (s, 2 H), 1.27 (t,  $J = 6.8$  Hz, 6 H), 0.30 (s, 9 H), 0.22 (s, 9 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  169.1, 153.9, 144.6, 138.1, 130.4, 126.9, 125.9, 124.6, 102.5, 101.8, 101.2, 100.4, 66.0, 62.0, 41.8, 14.1, -0.2; HRMS  $m/z$  calcd for  $\text{C}_{26}\text{H}_{34}\text{NaO}_4\text{Si}_2$  ( $[\text{M}+\text{Na}]^+$ ): 489.1893, found 489.1915.

