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## **Supporting Information**

## for

## Facile Imidazole Mediated Microwave-Assisted Aromatization Reaction: Synthesis of Benzobicyclo[2.2.2]octadienone Derivatives

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General procedure for the preparation of MOB dimers 3a-3k: To a solution of 2-methoxyphenol (1, 1.0 mmol) in methanol (4 mL) was added DAIB (1.3 mmol) and the resulting mixture was stirred for 1 h – 8 h at room temperature. The reaction mixture was concentrated and the residue was purified by column chromatography on silica gel by using a mixture of ethyl acetate and hexanes as eluent to obtain corresponding MOB dimers 3.

Dimers **3a**, **3c**, **3d**: <sup>1</sup>H and <sup>13</sup>C NMR spectral data were identical to those reported in literature. Lai, C.-H.; Shen, Y.-L.; Wang, M.-N.; Rao, N. S. K.; Liao, C.-C. J. Org. Chem. **2002**, 67, 6493-6502.

Dimer **3b**: <sup>1</sup>H and <sup>13</sup>C NMR spectral data were identical to those reported in literature. Deffieux, D.; Fabre, I.; Titz, A.; Leger, J-M.; Quideau, S. *J. Org. Chem.* **2004**, *69* 8731-8738.

Dimer **3g**: <sup>1</sup>H and <sup>13</sup>C NMR spectral data were identical to those reported in literature. Nishiyama, A.; Eto, H.; Terada, Y.; Iguchi, M.; Yamamura, S. *Chem. Pharm. Bull.* **1983**, *31*, 2834-2844.

**3e**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.21–6.12 (m, 2H), 5.53 (d, *J* = 8.0 Hz, 1H), 3.43 (s, 3H), 3.36 (s, 3H), 3.23–3.18 (m, 1H), 3.17 (s, 3H), 3.13–3.06 (m, 1H), 3.04–3.02 (m, 1H), 3.02 (s, 3H), 2.31–2.15 (m, 2H), 1.94–1.83 (m, 1H), 1.74–1.63 (m, 1H), 1.08–0.98 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 203.8 (C), 194.7 (C), 142.7 (C), 137.5 (CH), 133.0 (CH), 131.3 (CH), 98.8 (C), 94.9 (C), 58.0 (C), 50.4 (CH<sub>3</sub>), 50.1 (CH<sub>3</sub>), 49.6 (CH<sub>3</sub>), 48.8 (CH<sub>3</sub>), 40.4 (CH), 39.7 (CH), 39.4 (CH), 23.0 (CH<sub>2</sub>), 22.3 (CH<sub>2</sub>), 12.7 (CH<sub>3</sub>), 9.1 (CH<sub>3</sub>). MS (ESI): *m/z* found C<sub>20</sub>H<sub>29</sub>O<sub>6</sub> [M + H]<sup>+</sup> 365.

**3f**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.82 (s, 1H), 5.74 (app dd, *J* = 6.4, 1.6 Hz, 1H ), 3.36 (s, 3H), 3.33 (s, 3H), 3.18 (s, 3H), 3.17–3.14 (m, 1H), 3.11–3.05 (m, 2H), 2.99 (dd, *J* = 6.8, 1.6 Hz, 1H), 2.97 (s, 3H), 2.29–2.07 (m, 2H), 1.88–1.68 (m, 2H), 1.04 (t, *J* = 7.2 Hz, 3H), 0.84 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 202.3 (C), 193.3 (C), 161.4 (C), 142.5 (C), 123.7 (CH), 123.0 (CH), 98.7 (C), 94.7 (C), 57.1 (CH), 50.4 (CH<sub>3</sub>), 49.8 (CH<sub>3</sub>), 49.4 (CH<sub>3</sub>), 48.8 (CH<sub>3</sub>), 41.7 (CH), 39.4 (CH), 38.5 (CH), 28.0 (CH<sub>2</sub>), 27.8 (CH<sub>2</sub>), 11.6 (CH<sub>3</sub>), 10.4 (CH<sub>3</sub>).

**3h**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 5.85 (d, *J* = 0.6 Hz, 1H), 5.78 (dd, *J* = 6.9, 1.5 Hz, 1H), 3.40 (s, 3H), 3.34 (s, 3H), 3.21 (s, 3H), 3.23–3.18 (m, 1H), 3.16–3.09 (m, 2H), 3.01 (s, 3H), 3.03–2.98 (m, 1H), 2.24–2.05 (m, 2H), 1.83–1.76 (m, 2H), 1.62–1.18 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.79 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 202.6 (C), 193.3 (C), 160.1 (C), 141.2 (C), 125.1 (CH), 124.1 (CH), 98.8 (C), 94.9 (C), 77.2 (C), 56.9 (CH), 50.5 (CH<sub>3</sub>), 49.9 (CH<sub>3</sub>), 49.5 (CH<sub>3</sub>), 48.8 (CH<sub>3</sub>), 41.6 (CH), 39.6 (CH), 38.4 (CH), 37.2 (CH<sub>2</sub>), 36.9 (CH<sub>2</sub>), 20.9 (CH<sub>2</sub>), 19.5 (CH<sub>2</sub>), 13.4 (CH<sub>3</sub>), 13.3 (CH<sub>3</sub>).

**3i**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.35 (d, *J* = 4.0 Hz, 1H), 6.18 (app t, *J* = 8.0 Hz, 1H), 5.99 (d, *J* = 8.4 Hz, 1H), 5.24 (s, 1H), 4.99 (s, 1H), 3.79–3.66 (m, 3H), 3.65–3.54 (m, 3H), 3.53–3.48 (m, 2H), 3.47–3.41 (m, 1H), 3.46 (s, 3H), 3.36 (s, 3H), 3.25 (d, *J* = 8.0 Hz, 1H), 3.17 (s, 3H), 3.08 (s, 3H), 3.07–3.03 (m, 1H), 1.28 (s, 3H), 1.17 (s, 3H), 0.75 (s, 3H), 0.71 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 201.2 (C), 193.0 (C), 144.2 (CH), 136.9 (C), 130.3 (CH), 129.8 (CH), 99.5 (CH), 98.6 (C), 95.9 (CH), 94.9 (C), 78.3 (CH<sub>2</sub>), 77.59 (CH<sub>2</sub>), 77.56 (CH<sub>2</sub>), 77.5 (CH<sub>2</sub>), 60.7 (C), 50.8 (CH<sub>3</sub>), 50.0 (CH<sub>3</sub>), 49.2 (CH<sub>3</sub>), 48.7 (CH<sub>3</sub>), 39.2 (CH), 38.9 (CH), 38.3 (CH), 30.3 (C), 30.1 (C), 23.7 (CH<sub>3</sub>), 22.9 (CH<sub>3</sub>), 22.0 (CH<sub>3</sub>), 21.8 (CH<sub>3</sub>).

**3j**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.16 (t, *J* = 1.2 Hz, 1H), 6.14 (br s, 1H), 5.02 (d, *J* = 1.2 Hz, 1H), 4.67 (s, 1H), 3.70–3.61 (m, 3H), 3.60–3.55 (m, 1H), 3.54–3.49 (m, 1H), 3.48–3.44 (m, 2H), 3.43–3.37 (m, 1H), 3.40 (s, 3H), 3.36–3.28 (m, 2H), 3.35 (s, 3H), 3.21 (dd, *J* = 8.4, 1.6 Hz, 1H), 3.18 (s, 3H), 3.08 (dd, *J* = 6.8, 1.6 Hz, 1H), 3.02 (s, 3H), 1.14 (s, 3H), 1.10 (s, 3H), 0.73 (s, 3H), 0.66 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 202.1 (C), 194.1 (C), 153.7 (C), 137.9 (C), 128.2 (CH), 125.8 (CH), 99.1 (CH), 98.63 (C), 98.56 (CH), 94.8 (C), 77.8 (CH<sub>2</sub>), 77.3 (CH<sub>2</sub>), 76.69 (CH<sub>2</sub>), 76.65 (CH<sub>2</sub>), 52.0 (CH), 50.5 (CH<sub>3</sub>), 50.1 (CH<sub>3</sub>), 49.8 (CH<sub>3</sub>), 48.8 (CH<sub>3</sub>), 39.4 (CH), 38.1 (CH), 37.6 (CH), 30.2 (C), 30.0 (C), 23.0 (CH<sub>3</sub>), 22.9 (CH<sub>3</sub>), 21.7 (CH<sub>3</sub> × 2).

**3**k: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 6.13 (dd, *J* = 8.4, 7.2 Hz, 1H), 5.87 (d, *J* = 8.4 Hz, 1H), 5.45 (d, *J* = 4.2 Hz, 1H), 3.56 (s, 3H), 3.48 (s, 3H), 3.42 (s, 3H), 3.32 (s, 3H), 3.37–3.28 (m, 1H), 3.23–3.17 (m, 1H), 3.16 (s, 3H), 3.04 (s, 3H), 3.02–2.96 (m, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 201.9 (C), 189.1 (C), 152.2 (C), 130.4 (CH), 129.6 (CH), 110.2 (CH), 98.7 (C), 94.2 (C), 88.6 (C), 77.2 (C), 55.6 (CH<sub>3</sub>), 54.2 (CH<sub>3</sub>), 50.5 (CH<sub>3</sub>), 50.3 (CH<sub>3</sub>), 49.2 (CH<sub>3</sub>), 48.8 (CH<sub>3</sub>), 40.3 (CH), 39.1 (CH), 38.7 (CH).

General procedure for the synthesis of benzobicyco[2.2.2]octadienone derivatives 4a-4k: A solution of dimer 3 (1.0 equiv) and imidazole (2.5 equiv) in *o*-dichlorobenzene (1 mL for 100 mg of dimer 3) was sealed and subjected to microwave irradiation [Biotage® microwave synthesizer] at appropriate temperature for an appropriate time to give corresponding benzobicyclo[2.2.2]octadien-one products after purification by flash column chromatography using ethyl acetate/hexanes

**4a**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.90 (d, *J* = 8.0 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.67–6.58 (m, 2H), 4.64 (dd, *J* = 6.0, 2.4 Hz, 1H), 4.28 (dd, *J* = 5.6, 2.0 Hz, 1H), 3.90 (s, 3H), 3.41 (s, 3H), 3.26 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  195.8 (C), 148.3 (C), 143.5 (C), 133.3 (CH), 131.6 (CH), 131.1 (C), 128.8 (C), 121.1 (CH), 114.1 (CH), 91.8 (C), 62.4 (CH<sub>3</sub>), 56.8 (CH), 50.4 (CH<sub>3</sub>), 49.9 (CH<sub>3</sub>), 42.2 (CH). HRMS (ESI<sup>+</sup>): calcd. for C<sub>15</sub>H<sub>16</sub>NaO<sub>5</sub> [M + Na] 299.0890; found 299.0899.

**4b**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.05 (s, 1H), 6.66 (dd, *J* = 6.9, 2.1 Hz, 1H ), 5.70 (br s, 1H), 4.75 (d, *J* = 2.1 Hz, 1H ), 4.60 (d, *J* = 6.9 Hz, 1H), 3.87 (s, 3H), 3.41 (s, 3H), 3.27 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 192.6 (C), 149.5 (C), 143.1 (C), 131.83 (C), 131.82 (CH), 127.5 (C), 123.0 (C), 118.1 (CH), 114.8 (C), 91.1 (C), 64.6 (CH), 62.6 (CH<sub>3</sub>), 50.6 (CH<sub>3</sub>), 50.2 (CH<sub>3</sub>), 44.2 (CH).

**4c**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.79 (s, 1H), 6.61 (t, *J* = 6.4 Hz, 1H), 6.23 (dd, *J* = 7.6, 2.0 Hz, 1H), 5.58 (s, 1H), 4.56 (dd, *J* = 6.4, 1.6 Hz, 1H), 3.89 (s, 3H), 3.41 (s, 3H), 3.26 (s, 3H), 2.25 (s, 3H), 1.65 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  197.5 (C), 146.1 (C), 142.8 (C), 137.1 (CH), 133.6 (CH), 130.6 (C), 128.9 (C), 123.0 (C), 120.0 (CH), 92.0 (C), 62.4 (CH<sub>3</sub>), 60.3 (C), 50.2 (CH<sub>3</sub>), 49.9 (CH<sub>3</sub>), 41.5 (CH), 15.8 (CH<sub>3</sub>), 12.8 (CH<sub>3</sub>). MS (APCI): *m/z* found C<sub>17</sub>H<sub>19</sub>O<sub>5</sub> [M – H]<sup>-</sup> 303.

**4d**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.64 (s, 1H), 6.19–6.11 (m, 1H), 4.48 (d, *J* = 6.4 Hz, 1H), 4.20 (d, *J* = 1.6 Hz, 1H), 3.86 (s, 3H), 3.41 (s, 3H), 3.24 (s, 3H), 2.27 (s, 3H), 1.95 (d, *J* = 1.6 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  194.6 (C), 147.6 (C), 141.9 (C), 141.4 (C), 131.7 (C), 129.7 (C), 126.9 (C), 125.8 (CH), 115.3 (CH), 92.1 (C), 62.4 (CH<sub>3</sub>), 59.0 (CH), 50.4 (CH<sub>3</sub>), 49.8 (CH<sub>3</sub>), 41.8 (CH), 19.8 (CH<sub>3</sub>), 18.0 (CH<sub>3</sub>). MS (APCI): *m/z* found C<sub>17</sub>H<sub>19</sub>O<sub>5</sub> [M – H]<sup>-</sup> 303.

**4e**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.79 (s, 1H), 6.66 (dd, *J* = 7.6, 6.4 Hz, 1H), 6.43 (dd, *J* = 7.6, 1.6 Hz, 1H), 5.67 (br s, 1H), 4.55 (dd, *J* = 6.4, 1.6 Hz, 1H), 3.88 (s, 3H), 3.38 (s, 3H), 3.27 (s, 3H), 2.73–2.57 (m, 2H), 2.35–2.25 (m, 1H), 2.15–2.06 (m, 1H), 1.23–1.17 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  197.4 (C), 145.6 (C), 142.9 (C), 133.7 (CH), 133.4 (CH), 130.0 (C), 129.3 (C), 129.2 (C), 119.3 (CH), 92.3 (C), 62.5 (CH<sub>3</sub>), 59.2 (C), 50.14 (CH<sub>3</sub>), 50.11 (CH<sub>3</sub>), 41.4 (CH), 23.2 (CH<sub>2</sub>), 19.0 (CH<sub>2</sub>), 14.0 (CH<sub>3</sub>), 8.8 (CH<sub>3</sub>). MS (ESI): *m/z* found C<sub>19</sub>H<sub>23</sub>O<sub>5</sub> [M – H]<sup>-</sup> 331.

**4f**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.64 (s, 1H), 6.15–6.10 (m, 1H), 6.02 (br s, 1H), 4.52 (d, *J* = 6.4 Hz, 1H), 4.27 (d, *J* = 2.0 Hz, 1H), 3.85 (s, 3H), 3.39 (s, 3H), 3.23 (s, 3H), 2.58 (q, *J* = 7.6 Hz, 2H), 2.32–2.18 (m, 2H), 1.14 (t, *J* = 7.6 Hz, 3H), 1.04 (t, *J* = 7.6 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 196.9 (C), 147.7 (C), 147.1 (C), 141.3 (C), 135.9 (C), 132.1 (C), 126.2 (C), 124.1 (CH), 113.9 (CH), 92.3 (C), 62.1 (CH<sub>3</sub>), 57.6 (CH), 50.3 (CH<sub>3</sub>), 49.7 (CH<sub>3</sub>), 41.5 (CH), 26.7 (CH<sub>2</sub>), 25.1 (CH<sub>2</sub>), 15.6 (CH<sub>3</sub>), 11.4 (CH<sub>3</sub>).

**4g**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.74 (s, 1H), 6.64 (dd, *J* = 7.6, 6.8 Hz, 1H), 6.41 (dd, *J* = 7.6, 1.6 Hz, 1H), 5.59 (br s, 1H), 4.53 (dd, *J* = 6.8, 1.6 Hz, 1H), 3.88 (s, 3H), 3.38 (s, 3H), 3.26 (s, 3H), 2.69–2.49 (m, 2H), 2.26–2.15 (m, 1H), 2.04–1.94 (m, 1H), 1.69–1.53 (m, 4H), 1.21 (t, *J* = 7.6 Hz, 3H), 0.96 (t, *J* = 7.6 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  197.4 (C),145.8 (C), 142.9 (C), 134.2 (CH), 133.3 (CH), 130.1 (C), 129.3 (C), 127.7 (C), 120.1 (CH), 92.3 (C), 62.5 (CH<sub>3</sub>), 58.9 (C), 50.2 (CH<sub>3</sub>), 50.1 (CH<sub>3</sub>), 41.4 (CH), 32.3 (CH<sub>2</sub>), 28.7 (CH<sub>2</sub>), 23.0 (CH<sub>2</sub>), 17.7 (CH<sub>2</sub>), 15.1 (CH<sub>3</sub>), 14.1 (CH<sub>3</sub>). MS (APCI): *m/z* found C<sub>21</sub>H<sub>29</sub>O<sub>5</sub> [M + H]<sup>+</sup> 361.

**4h**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.64 (s, 1H), 6.14 (dd, *J* = 6.4, 1.6 Hz, 1H), 4.49 (d, *J* = 6.4 Hz, 1H), 4.26 (d, *J* = 1.6 Hz, 1H), 3.87 (s, 3H), 3.40 (s, 3H), 3.24 (s, 3H), 2.55 (t, *J* = 7.6 Hz, 2H), 2.28–2.14 (m, 2H), 1.62–1.42 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H), 0.85 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  196.8(C), 147.5 (C), 145.7 (C), 141.3 (C), 134.7 (C), 131.9 (C), 126.8 (C), 125.4 (CH), 114.5 (CH), 92.3 (C), 62.4 (CH<sub>3</sub>), 57.8 (CH), 50.5 (CH<sub>3</sub>), 49.8 (CH<sub>3</sub>), 41.7 (CH), 35.9 (CH<sub>2</sub>), 34.2 (CH<sub>2</sub>), 24.6 (CH<sub>2</sub>), 20.2 (CH<sub>2</sub>), 13.8 (CH<sub>3</sub>), 13.4 (CH<sub>3</sub>). HRMS (ESI<sup>+</sup>): calcd. for C<sub>21</sub>H<sub>28</sub>NaO<sub>5</sub> [M + Na] 383.1829; found 383.1837.

**4i**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.78 (s, 1H), 7.08 (s, 1H), 6.74 (dd, *J* = 7.6, 2.0 Hz, 1H), 6.63 (t, *J* = 7.2 Hz, 1H), 5.53 (s, 1H), 5.42 (s, 1H), 4.66 (dd, *J* = 6.4, 1.6 Hz, 1H), 3.89 (s, 3H), 3.83–3.73 (m, 4H), 3.72–3.62 (m, 4H), 3.35 (s, 3H), 3.28 (s, 3H), 1.29 (s, 6H), 0.82 (s, 3H), 0.80 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  194.0 (C), 147.6 (C), 144.2 (C), 133.6 (C), 132.8 (CH), 131.2 (CH), 126.9 (C), 121.7 (C), 119.2 (CH), 102.2 (CH), 98.9 (CH), 92.3 (C), 77.6 (CH<sub>2</sub>), 77.5 (CH<sub>2</sub>), 77.4 (CH<sub>2</sub>), 77.3 (CH<sub>2</sub>), 62.5 (C), 61.5 (CH<sub>3</sub>), 50.4 (CH<sub>3</sub>), 50.0 (CH<sub>3</sub>), 41.2 (CH), 30.34 (C), 30.31 (C), 23.3 (CH<sub>3</sub>), 23.0 (CH<sub>3</sub>), 21.9 (CH<sub>3</sub>), 21.8 (CH<sub>3</sub>). MS (ESI): *m/z* found C<sub>27</sub>H<sub>37</sub>O<sub>9</sub> [M + H]<sup>+</sup> 505.

**4j**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.11 (s, 1H), 6.56 (ddd, *J* = 6.0, 1.6, 0.8 Hz, 1H), 5.58 (br s, 1H), 5.51 (s, 1H), 5.02 (s, 1H), 4.86 (d, *J* = 1.6 Hz, 1H), 4.60 (d, *J* = 6.8 Hz, 1H), 3.83 (s, 3H), 3.79–3.70 (m, 2H), 3.68–3.58 (m, 4H), 3.49–3.42 (m, 2H), 3.39 (s, 3H), 3.24 (s, 3H), 1.28 (s, 3H), 1.23 (s, 3H), 0.79 (s, 3H), 0.73 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  195.8 (C), 147.8 (C), 143.6 (C), 142.2 (C), 131.8 (C), 130.7 (C), 129.8 (CH), 126.9 (C), 112.4 (CH), 99.4 (CH), 98.9 (CH), 91.9 (C), 77.74 (CH<sub>2</sub>), 77.70 (CH<sub>2</sub>), 77.14 (CH<sub>2</sub>), 76.95 (CH<sub>2</sub>), 62.3 (CH<sub>3</sub>), 52.8 (CH), 50.4 (CH<sub>3</sub>), 50.1 (CH<sub>3</sub>), 41.8 (CH), 30.2 (C), 30.1 (C), 23.18 (CH<sub>3</sub>), 21.9 (CH<sub>3</sub>), 21.8 (CH<sub>3</sub>). MS (ESI): *m/z* found C<sub>27</sub>H<sub>35</sub>O<sub>9</sub> [M – H]<sup>-</sup> 503.

**4k**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  6.83 (s, 1H), 6.81–6.62 (m, 2H), 5.56 (s, 1H), 4.61 (dd, *J* = 6.6, 2.1 Hz, 1H), 3.96 (s, 3H), 3.90 (s, 3H), 3.80 (s, 3H), 3.39 (s, 3H), 3.29 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  195.0 (C), 146.8 (C), 143.1 (C), 137.8 (C), 133.3 (CH), 130.2 (CH), 128.4 (C), 122.3 (C), 100.5 (CH), 91.6 (C), 87.6 (C), 61.3 (CH<sub>3</sub>), 56.4 (CH<sub>3</sub>), 50.3 (CH<sub>3</sub>), 50.0 (CH<sub>3</sub>), 40.2 (CH). MS (ESI): *m/z* found C<sub>17</sub>H<sub>21</sub>O<sub>7</sub> [M + H]<sup>+</sup> 337.

## General procedure for the preparation of bicyclo[2.2.2] system fused MOB derivatives 5a, 5c, 5d and 5g: To a solution of

benzobicyclo[2.2.2]octadienone (**4**, 1.0 equiv) in methanol (4 mL for 1 mmol of **4**) was added DAIB (1.3 equiv) at 0 °C and the resulting mixture was stirred for 45 min at room temperature. The reaction mixture was concentrated and the residue was purified by column chromatography on silica gel by using a mixture of ethyl acetate and hexanes as eluent to give corresponding MOBs **5**.

**5a**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 6.87 (d, *J* = 9.9 Hz, 1H ), 6.58 (ddd, *J* = 8.1, 6.6, 1.5 Hz, 1H ), 6.49 (ddd, *J* = 7.2, 5.7, 1.5 Hz, 1H), 5.93 (d, *J* = 9.9 Hz, 1H), 4.35 (dd, *J* = 6.3, 1.8 Hz, 1H), 4.04 (dd, *J* = 5.7, 2.0 Hz, 1H), 3.34 (s, 3H), 3.32 (s, 3H), 3.30 (s, 3H), 3.13 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 196.8 (C), 193.8 (C), 146.8 (C), 139.2 (CH), 135.0 (C), 134.4 (CH), 128.4 (CH), 125.4 (CH), 92.5 (C), 90.3 (C), 57.03 (CH), 51.1 (CH<sub>3</sub> × 2), 50.6 (CH<sub>3</sub>), 49.8 (CH<sub>3</sub>), 44.1 (CH).

**5c**: <sup>1</sup>H NMR (400 MHz, CDCl3) δ 6.69 (app d, *J* = 1.6 Hz, 1H ), 6.56 (t, *J* = 6.4 Hz, 1H ), 6.05 (dd, *J* = 6.4, 1.6 Hz, 1H), 4.26 (dd, *J* = 6.4, 2.0 Hz, 1H), 3.34 (s, 3H), 3.30 (s, 3H), 3.29 (s, 3H), 3.11 (s, 3H), 1.86 (d, *J* = 1.6 Hz, 3H), 1.54 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 197.1 (C), 195.7 (C), 144.9 (C), 136.9 (C), 134.7 (CH), 134.4 (CH), 133.0 (C), 132.0 (CH), 92.6 (C), 90.8 (C), 55.9 (C), 51.1 (CH<sub>3</sub>), 50.9 (CH<sub>3</sub>), 50.6 (CH<sub>3</sub>), 49.7 (CH<sub>3</sub>), 43.2 (CH), 15.1 (CH<sub>3</sub>), 12.6 (CH<sub>3</sub>).

**5d**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.14 (dt, *J* = 1.6 Hz, 1H ), 5.84 (app t, *J* = 1.2 Hz, 1H ), 4.23 (d, *J* = 6.4 Hz, 1H ), 3.98 (d, *J* = 1.6 Hz, 1H ), 3.34 (s, 3H), 3.33 (s, 3H), 3.30 (s, 3H), 3.17 (s, 3H), 2.09 (d, *J* = 1.6 Hz, 3H), 1.96 (d, *J* = 1.6 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  195.8 (C), 194.6 (C), 149.4 (C), 146.9 (C), 138.9 (C), 136.2 (C), 126.9 (CH), 123.6 (CH), 92.4 (C), 90.8 (C), 59.1 (CH), 51.3 (CH<sub>3</sub>), 51.2 (CH<sub>3</sub>), 50.4 (CH<sub>3</sub>), 50.0 (CH<sub>3</sub>), 43.6 (CH), 20.6 (CH<sub>3</sub>), 19.4 (CH<sub>3</sub>).

**5g**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.60 (s, 1H), 6.58 (t, *J* = 6.8 Hz, 1H), 6.26 (dd, *J* = 6.8, 2.0 Hz, 1H), 4.25 (dd, *J* = 6.4, 1.6 Hz, 1H), 3.29 (s, 3H), 3.28 (s, 3H), 3.10 (s, 6H), 2.30–2.15 (m, 2H), 2.13–2.03 (m, 1H), 1.91–1.80 (m, 1H), 1.62–1.52 (m, 1H), 1.50–1.38 (m, 3H), 1.08 (t, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 6.4, 1.6 Hz, 1H), 3.29 (s, 3H), 3.28 (s, 3H), 3.10 (s, 6H), 3.20–2.15 (m, 2H), 3.20 (s, 3H), 3.28 (s, 3H), 3.28 (s, 3H), 3.29 (s, 3H), 3.20 (s, 6H), 3.

7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 196.9 (C), 195.5 (C), 145.7 (C), 136.84 (C), 136.77 (C), 134.5 (CH), 131.6 (CH), 131.3 (CH), 92.7 (C), 91.2 (C), 59.6 (C), 51.3 (CH<sub>3</sub>), 50.9 (CH<sub>3</sub>), 50.8 (CH<sub>3</sub>), 49.6 (CH<sub>3</sub>), 42.9 (CH), 30.9 (CH<sub>2</sub>), 28.3 (CH<sub>2</sub>), 21.7 (CH<sub>2</sub>), 18.0 (CH<sub>2</sub>), 14.9 (CH<sub>3</sub>), 13.8 (CH<sub>3</sub>).

General procedure for the preparation of benzobicyclo[2.2.2]octadienedione 6: To benzobicyclo[2.2.2]octadienone 4 (500 mg) was added 2 N aqueous  $H_2SO_4$  (10 mL). The reaction mixture was heated to 50 °C for 16 h. The reaction was brought to room temperature and extracted with ethyl acetate. The organic extract was concentrated to give a residue which was purified by column chromatography on silica gel by using a mixture of ethyl acetate and hexanes as eluent to give corresponding benzobicyclo[2.2.2]octadienedione 6.

**6a**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.04 (d, *J* = 8.1 Hz, 1H), 6.97 (d, *J* = 8.1 Hz, 1H), 6.80 (ddd, *J* = 7.5, 6.0, 1.8 Hz, 1H), 6.72 (ddd, *J* = 7.8, 6.3, 1.8 Hz, 1H), 5.83 (br s, 1H), 4.87 (dd, *J* = 6.0, 1.8 Hz, 1H), 4.50 (dd, *J* = 6.0, 1.8 Hz, 1H), 3.85 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  181.8 (C), 181.4 (C), 149.7 (C), 143.8 (C), 132.9 (CH), 130.9 (CH), 126.8 (C), 126.4 (C), 122.5 (CH), 117.0 (CH), 62.9 (CH<sub>3</sub>), 55.1 (CH), 50.2 (CH). MS (ESI): *m*/*z* found C<sub>13</sub>H<sub>9</sub>O<sub>4</sub> [M – H]<sup>-</sup> 229.

**6h**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) & 6.80 (s, 1H), 6.29–6.23 (m, 1H), 5.72 (br s, 1H), 4.73 (d, *J* = 6.4 Hz, 1H), 4.47 (d, *J* = 2.4 Hz, 1H), 3.81 (s, 3H), 2.65–2.51 (m, 2H), 2.38–2.29 (m, 2H), 1.63–1.48 (m, 4H), 0.95 (t, *J* = 7.6 Hz, 3H), 0.88 (t, *J* = 7.6 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) & 183.0 (C), 182.6 (C), 148.9 (C), 147.9 (C), 141.6 (C), 136.2 (C), 127.6 (C), 124.7 (C), 123.0 (CH), 117.2 (CH), 62.8 (CH3), 56.1 (CH), 49.5 (CH), 36.2 (CH<sub>2</sub>), 34.3 (CH<sub>2</sub>), 24.5 (CH<sub>2</sub>), 20.3 (CH<sub>2</sub>), 13.8 (CH<sub>3</sub>), 13.5(CH<sub>3</sub>).

General procedure for the preparation of benzoquinoxalinobarralenes 10-13: A solution of benzobicyclo[2.2.2]octadienedione 6 (1.0 equiv) and *o*-phenylenediamine (1.0 equiv) in a mixture of AcOH / MeOH (1:1, 2 mL for 100 mg of 6) was stirred at room temperature for 15 min. In the case of reaction between 6a and *o*-phenylenediamine 7-9, corresponding benzoquinoxalinobarralenes 10-12 precipitated in the reaction mixture which was filtered and washed with cold methanol to give pure products. However, in the case of reaction between 6h and 7, column chromatography was performed to give the corrresponding benzoquinoxalinobarralene 13.

**10**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ 8.00–7.80 (m, 2H), 7.65–7.55 (m, 2H), 7.20–7.02 (m, 3H), 6.70 (d, *J* = 8.1 Hz, 1H), 6.51 (br s, 1H), 5.59 (dd, *J* = 5.7, 1.5 Hz, 1H), 5.22 (dd, *J* = 6.0, 1.5 Hz, 1H), 3.84 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  158.0 (C), 157.3 (C), 147.5 (C), 143.6 (C), 139.2 (CH), 138.5 (C × 2), 137.0 (CH), 135.1 (C), 134.6 (C), 129.1 (CH), 129.0 (CH), 128.3 (CH × 2), 120.8 (CH), 113.1 (CH), 62.6 (CH<sub>3</sub>), 51.5 (CH), 46.4 (CH). MS (ESI): *m/z* found C<sub>19</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub> [M + H]<sup>+</sup> 303.

**11**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.63 (d, *J* = 5.6 Hz, 2H), 7.14 (ddd, *J* = 7.2, 6.0, 1.6 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.05 (ddd, *J* = 7.2, 6.0, 1.6 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 5.87 (br s, 1H), 5.54 (dd, *J* = 6.0, 1.6 Hz, 1H), 5.18 (dd, *J* = 6.0, 1.6 Hz, 1H), 3.89 (s, 3H), 2.42 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  157.2 (C), 156.4 (C), 147.2 (C), 143.4 (C), 139.3 (CH), 139.1 (C), 138.9 (C), 137.3 (C), 137.2 (C), 137.0 (CH), 135.7 (C), 134.8 (C), 127.8 (CH), 120.7 (CH × 2), 112.6 (CH), 62.8 (CH<sub>3</sub>), 51.6 (CH), 46.6 (CH), 20.14 (CH<sub>3</sub>), 20.12 (CH<sub>3</sub>). MS (ESI): *m/z* found C<sub>21</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub> [M + H]<sup>+</sup> 331.

**12**: <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  9.44 (s, 1H), 8.17 (s, 1H), 8.13 (s, 1H), 7.25–7.15 (s, 2H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 5.52 (dd, *J* = 5.6, 1.6 Hz, 1H), 5.27 (dd, *J* = 6.0, 1.6 Hz, 1H), 3.79 (s, 3H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  159.4 (C), 158.9 (C), 148.6 (C), 143.8 (C), 138.9 (CH), 137.2 (CH), 137.1 (C), 134.4 (C), 133.0 (C), 131.5 (C), 131.4 (C), 129.0 (CH), 128.9 (CH), 120.3 (CH), 114.1 (CH), 61.0 (CH<sub>3</sub>), 50.1 (CH), 45.3 (CH). HRMS (ESI<sup>+</sup>): calcd. for C<sub>19</sub>H<sub>13</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub> [M + H] 371.0349; found 371.0359.

**13**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.94–7.83 (m, 2H), 7.64–7.57 (m, 2H), 6.59–6.53 (m, 2H), 6.30 (br s, 1H), 5.45 (d, *J* = 6.4 Hz, 1H), 5.19 (d, *J* = 1.6 Hz, 1H), 3.82 (s, 3H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.37–2.30 (m, 2H), 1.71–1.46 (m, 4H), 0.98 (t, *J* = 7.2 Hz, 3H), 0.80 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  158.5 (C), 158.2 (C), 153.6 (C), 146.9 (C), 141.4 (C), 138.6 (C), 135.2 (C), 134.5 (C), 132.9 (C), 128.84 (CH), 128.75 (CH), 128.7 (CH), 128.3 (CH), 128.2 (CH), 113.6 (CH), 62.6 (CH3), 52.3 (CH), 46.0 (CH), 35.8 (CH<sub>2</sub>), 34.5 (CH<sub>2</sub>), 24.7 (CH<sub>2</sub>), 20.2 (CH<sub>2</sub>), 14.0 (CH<sub>3</sub>), 13.7 (CH<sub>3</sub>). MS (ESI): *m/z* found C<sub>25</sub>H<sub>27</sub>N<sub>2</sub>O<sub>2</sub> [M + H]<sup>+</sup> 387.

**General procedure for the** *O***-alkylation of benzobicyclo[2.2.2]octadienone 4a:** To a solution of benzobicyclo[2.2.2]octadienone 4a (1.0 equiv) in CH<sub>3</sub>CN (2.5 mL for 100 mg) was added alkylating agent MeI (2.5 equiv) or allyl bromide (2.0 equiv) or methyl bromoacetate (2.0 equiv) and stirred at room temperature for 16 h. Reaction mixture was filtered, solvents evaporated and the residue was purified by column chromatography on silica gel by using a mixture of ethyl acetate and hexanes as eluent to give corresponding alkylated products 14 - 16.

**14**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  6.94 (d, *J* = 7.8 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 6.65–6.56 (m, 2H), 4.76–4.70 (m, 1H), 4.28–4.24 (m, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 3.40 (s, 3H), 3.26 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  196.2 (C), 152.1 (C), 145.3 (C), 134.1 (CH), 131.6 (C), 130.9 (CH), 129.2 (C), 120.0 (CH), 110.7 (CH), 92.0 (C), 61.4 (CH<sub>3</sub>), 56.8 (CH), 55.9 (CH<sub>3</sub>), 50.3 (CH<sub>3</sub>), 50.1 (CH<sub>3</sub>), 41.8 (CH).

**15**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  6.92 (d, *J* = 8.1 Hz, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 6.64–6.58 (m, 2H), 6.14–6.01 (m, 1H), 5.42 (ddd, *J* = 17.1, 3.0, 1.5 Hz, 1H), 5.28 (ddd, *J* = 10.5, 3.0, 1.5 Hz, 1H), 4.77–4.72 (m, 1H), 4.59–4.54 (m, 2H), 4.28–4.23 (m, 1H), 3.92 (s, 3H), 3.41 (s, 3H), 3.27 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  196.2 (C), 151.0 (C), 145.7 (C), 134.2 (CH), 133.2 (CH), 131.7 (C), 130.9 (CH), 129.6 (C), 119.9 (CH), 117.5 (CH<sub>2</sub>), 112.5 (CH), 92.0 (C), 69.8 (CH<sub>2</sub>), 61.4 (CH<sub>3</sub>), 56.8 (CH), 50.4 (CH<sub>3</sub>), 50.1 (CH<sub>3</sub>), 41.8 (CH). MS (APCI): *m/z* found C<sub>18</sub>H<sub>19</sub>O<sub>5</sub> [M – H]<sup>-</sup> 315.

**16**:<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.91 (d, *J* = 8.0 Hz, 1H ), 6.67 (d, *J* = 8.0 Hz, 1H ), 6.63–6.56 (m, 2H), 4.74 (app dd, *J* = 5.2, 1.6 Hz, 1H), 4.67 (s, 2H), 4.26 (app dd, *J* = 5.2, 2.4 Hz, 1H), 3.96 (s, 3H), 3.79 (s, 3H), 3.40 (s, 3H), 3.26 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 196.1 (C), 169.2 (C), 150.3 (C), 145.9 (C), 134.1 (CH), 132.1 (C), 130.9 (C), 130.8 (CH), 119.9 (CH), 112.6 (CH), 91.9 (C), 66.2 (CH<sub>2</sub>), 61.6 (CH<sub>3</sub>), 56.9 (CH), 52.2 (CH<sub>3</sub>), 50.3 (CH<sub>3</sub>), 50.1 (CH<sub>3</sub>), 41.8 (CH).

**Procedure for Chan-Lam coupling of benzobicyclo[2.22]octadienone 4a**: A mixture of compound **4a** (1.0 equiv), phenylboronic acid (1.5 equiv), Cu(OAc)<sub>2</sub> (2.5 equiv), pyridine (2 equiv), 4 Å MS (2.5 times wt/wt of **4a**) was stirred in dry CH<sub>2</sub>Cl<sub>2</sub> (4 mL) under oxygen balloon at room temperature for 16

h. The reaction mixture was directly passed through celite. After rinsed with further 10 mL of ethyl acetate, it was concentrated by rotatory evaporation. The residue was purified by column chromatography on silica gel to give product **17**.

**17**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.35–7.27 (m, 2H), 7.11–7.02 (m, 1H), 6.98–6.90 (m, 3H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.69–6.59 (m, 2H), 4.82–4.74 (m, 1H), 4.36–4.29 (m, 1H), 3.91 (s, 3H), 3.42 (s, 3H), 3.29 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  195.9 (C), 157.7 (C), 147.9 (C), 147.8 (C), 134.2 (CH), 133.2 (C), 132.3 (C), 130.6 (CH), 129.6 (CH X 2), 122.7 (CH), 120.3 (CH), 120.1 (CH), 117.1 (CH X 2), 91.8 (C), 61.5 (CH<sub>3</sub>), 57.2 (CH), 50.4 (CH<sub>3</sub>), 50.1 (CH<sub>3</sub>), 41.9 (CH). HRMS (APCI<sup>+</sup>): calcd. for C<sub>21</sub>H<sub>21</sub>O<sub>5</sub> [M + H] 353.1384; found 353.1376.

**Procedure for hydrogenation reaction of benzobicyclo**[2.22]octadienone 4a: To a solution of compound 4a (1.0 equiv) in ethyl acetate (4 mL for 100 mg) was added 10% wet Pd-C (30% wt/wt with respect to compound 4a). The reaction was stirred under hydrogen balloon for 4 h. Reaction mixture was filtered through a pad of celite to give corresponding hydrogenation product 18 in quantitative yield.

**18**:<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.84–6.78 (m, 2H), 5.80 (br s, 1H), 3.90–3.80 (m, 1H merged with 3.87 singlet), 3.87 (s, 3H), 3.50 (dd, *J* = 3.2, 2.4 Hz, 1H ), 3.42 (s, 3H), 3.25 (s, 3H), 2.23–2.05 (m, 1H), 1.74–1.64 (m, 1H), 1.48–1.37 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  203.4 (C), 148.3 (C), 143.2 (C), 132.5 (C), 128.0 (C), 121.7 (CH), 114.5 (CH), 95.3 (C), 62.2 (CH<sub>3</sub>), 51.1 (CH), 50.5 (CH<sub>3</sub>), 49.7 (CH<sub>3</sub>), 37.1 (CH), 23.7 (CH<sub>2</sub>), 19.8 (CH<sub>2</sub>). MS (ESI): *m/z* found C<sub>15</sub>H<sub>17</sub>O<sub>5</sub> [M – H]<sup>-</sup> 277.

**Procedure for bromination of benzobicyclo**[2.22]octadienone 4a: A solution of the compound 4a (1.0 mmol) in methylene chloride (5 mL) was treated with NBS (1.0 mmol) at room temperature and allowed to stir for 16 h. The solvent was evaporated and the residue taken up in ethyl acetate and water. The organic extracts were collected, dried over  $Na_2SO_4$  and concentrated under reduced pressure to give the corresponding bromo phenol 19 after column chromatography using ethyl acetate/hexanes.

**19**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.27–7.28 (m, 1H), 7.16 (s, 1H), 6.63–6.58 (m, 2H), 5.80 (br s, 1H), 4.65 (dd, *J* = 4.4, 2.8 Hz, 1H), 4.24–4.21 (m, 1H), 3.93 (s, 3H), 3.40 (s, 3H), 3.25 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  195.3 (C), 145.5 (C), 144.0 (C), 133.7 (CH), 131.14 (C), 131.11 (CH), 129.6 (C), 123.6 (CH), 107.7 (C), 91.6 (C), 62.1 (CH<sub>3</sub>), 56.4 (CH), 50.4 (CH<sub>3</sub>), 50.1 (CH<sub>3</sub>), 42.0 (CH). HRMS (ESI<sup>+</sup>): calcd. for C<sub>15</sub>H<sub>14</sub>BrO<sub>5</sub> [M + H] 353.0030; found 353.0033.

**Procedure for the Michael type addition of benzobicyclo**[2.22]octadienone 4a to ethylpropiolate: A solution of the benzobicyclo[2.22]octadienone 4a (1.0 equiv), ethyl propiolate (1.5 equiv), and  $Et_3N$  (2.0 equiv) in THF was stirred at room temperature for 16 h. The reaction was diluted with water and extracted with ethyl acetate. The organic extracts were collected, dried over  $Na_2SO_4$  and concentrated under reduced pressure to give the corresponding bromo phenoxyacrylate 20 after column chromatography using ethyl acetate/hexanes.

**20**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.61 (d, *J* = 12.3 Hz, 1H), 6.66–6.57 (m, 2H), 5.30 (d, *J* = 12.3 Hz, 1H), 4.69 (dd, *J* = 5.4, 2.4 Hz, 1H), 4.33–4.28 (m, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 3.40 (s, 3H), 3.24 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  194.7 (C), 166.8 (C), 159.9 (CH), 148.8 (C), 144.5 (C), 136.1 (C), 133.9 (CH), 132.4 (C), 130.5 (CH), 124.3 (CH), 114.3 (C), 101.1 (CH), 91.2 (C), 61.9 (CH<sub>3</sub>), 60.1 (CH<sub>2</sub>), 56.9 (CH), 50.4 (CH<sub>3</sub>), 50.1 (CH<sub>3</sub>), 41.9 (CH), 14.2 (CH<sub>3</sub>).

**Procedure for the intramolecular Heck type Coupling of compound 20:** Bromo phenoxyarylate **20** (1.0 equiv) in DMF was degassed using argon balloon.  $Pd(OAc)_2$  (0.4 equiv),  $PPh_3$  (0.8 equiv), and  $K_2CO_3$  (1.0 equiv) were added in sequence. The mixture was then heated at 110 oc overnight and then cooled to room temperature and diluted with water and ethyl acetate. The organic extracts were collected, dried over  $Na_2SO_4$  and concentrated under reduced pressure to give the corresponding benzofuran derivative **21** after column chromatography using ethyl acetate/hexanes.

**21**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.22 (s, 1H), 7.62 (s, 1H), 6.69–6.59 (m, 2H), 4.84 (dd, *J* = 5.7, 2.4 Hz, 1H), 4.43 (dd, *J* = 5.7, 2.4 Hz, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 4.24 (s, 3H), 3.42 (s, 3H), 3.26 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 196.2 (C), 163.1 (C), 150.7 (CH), 145.9 (C), 141.0 (C), 134.6 (CH), 134.3 (C), 130.7 (CH), 126.2 (C), 125.6 (C), 115.1 (C), 111.9 (CH), 92.0 (C), 60.8 (CH<sub>2</sub>), 60.7 (CH<sub>3</sub>), 57.7 (CH), 50.5 (CH<sub>3</sub>), 49.9 (CH<sub>3</sub>), 41.4 (CH), 14.3 (CH<sub>3</sub>).

**Procedure for vinyl Grignard addition to benzobicyclo**[2.2.2]octadienone 14: To a solution of benzobicyclo[2.2.2]octadienone 14 (1.0 equiv) in THF at - 78 °C was added vinylmagnesium bromide (1.0 M in THF, 4.0 equiv). The reaction mixture was brought to room temperature and stirred for 16 h. Reaction mixture was quenched with saturated NH<sub>4</sub>Cl followed by extraction with ethyl acetate. The organic extracts were collected, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give inseparable mixture of products 22 after column chromatography using ethyl acetate/hexanes.

**22**: The selected <sup>1</sup>H and <sup>13</sup>C NMR data of major and minor isomers presented here was taken from the spectra of isomeric mixture of **22**. Major isomer :<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  6.95 (d, *J* = 7.8 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 6.56–6.42 (m, 2H), 6.02 (dd, *J* = 17.1, 10.8 Hz, 1H), 5.50 (dd, *J* = 17.1, 2.1 Hz, 1H), 5.11 (dd, *J* = 10.8, 2.1 Hz, 1H), 4.56 (dd, *J* = 6.0, 1.5 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.57 (dd, *J* = 6.3, 1.8 Hz, 1H), 3.30 (s, 3H), 3.27 (s, 3H). Minor isomer: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  6.86 (d, *J* = 8.1 Hz, 1H), 6.68 (d, *J* = 8.1 Hz, 1H), 6.64–6.46 (m, 2H), 5.48–5.43 (m, 2H), 4.99 (t, *J* = 6.3 Hz, 1H), 4.56 (dd, *J* = 6.0, 1.5 Hz, 1H), 3.62 (dd, *J* = 6.0, 1.8 Hz, 1H), 3.38 (s, 3H), 3.18 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  151.0 (C), 144.8 (C), 142.0 (CH major), 141.2 (CH minor), 135.9 (CH minor), 134.6 (CH major), 133.6 (C), 132.2 (C), 131.9 (CH major), 131.8 (CH minor), 121.2 (CH major), 120.1 (CH minor), 55.61 (C), 55.59 (CH major), 51.41 (CH<sub>3</sub> major), 51.02 (CH<sub>3</sub> major), 50.8 (CH<sub>3</sub> major), 50.6 (CH<sub>3</sub> minor), 42.7 (CH major), 42.3 (CH minor).













































ŚI-31





\$I-33



ŚI-34





\$I-36







































































































