

**Unexpected formation of substituted naphthalenes and phenanthrenes in a GaCl<sub>3</sub> mediated dimerization–fragmentation reaction of 2-arylcyclopropane-1,1-dicarboxylates**

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*2-Chloro-6-(3-chlorophenyl)naphthalene 2d.*

Yield 65%. Thick colourless oil. IR (CHCl<sub>3</sub>)  $\nu$  3020, 2967, 2923, 1479, 1422 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.1 MHz):  $\delta$  7.36 (ddd, 1H, H(4'), <sup>3</sup>J = 8.1 Hz, <sup>4</sup>J = 1.9 and 1.2 Hz), 7.41 (dd, 1H, H(5'), <sup>3</sup>J = 8.1 and 7.5 Hz), 7.46 (dd, 1H, H(3), <sup>3</sup>J = 8.7 Hz, <sup>4</sup>J = 2.0 Hz), 7.57 (ddd, 1H, H(6'), <sup>3</sup>J = 7.5 Hz, <sup>4</sup>J = 1.7 and 1.2 Hz), 7.68 (dd, 1H, H(2'), <sup>4</sup>J = 1.9 and 1.7 Hz), 7.72 (dd, 1H, H(7), <sup>3</sup>J = 8.5 Hz, <sup>4</sup>J = 1.8 Hz), 7.81–7.85 (m, 2H, H(4) and H(8)), 7.85 (d, 1H, H(1), <sup>4</sup>J = 2.0 Hz), 7.98 (br.s, 1H, H(5)). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz):  $\delta$  125.6 (HC(6')), 126.0 (HC(5')), 126.4 (HC(7')), 126.5 (HC(1')), 127.56 (HC(3')), 127.59 (HC(2')), 127.67 (HC(4')), 127.9 (HC(8')), 129.9 (HC(4)), 130.2 (HC(5')), 131.9 (C(4a)), 132.1 (C(2)), 133.5 (C(8a)), 135.0 (C(3')), 137.6 (C(6)), 142.7 (C(1')). MS (*m/z*, %): 272 (90) [M]<sup>+</sup> for <sup>35</sup>Cl, 232 (15), 202 (66), 149 (35), 100 (30), 83 (33), 59 (52), 57 (77), 43 (100). Found (%): C, 70.29; H, 3.88. Calc. for C<sub>16</sub>H<sub>10</sub>Cl<sub>2</sub> (%): C, 70.35; H, 3.69.

*2-Bromo-6-(3-bromophenyl)naphthalene 2e.*

Yield 67%. Thick colourless oil. IR (CHCl<sub>3</sub>)  $\nu$  3020, 2956, 2923, 1588, 1479, 1420 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.1 MHz):  $\delta$  7.35 (dd, 1H, H(5'), <sup>3</sup>J = 8.0 and 7.8 Hz), 7.51 (ddd, 1H, H(4'), <sup>3</sup>J = 8.0 Hz, <sup>4</sup>J = 1.9 and 1.0 Hz), 7.59 (dd, 1H, H(3), <sup>3</sup>J = 8.7 Hz, <sup>4</sup>J = 2.0 Hz), 7.62 (ddd, 1H, H(6'), <sup>3</sup>J = 7.8 Hz, <sup>4</sup>J = 1.7 and 1.0 Hz), 7.71 (dd, 1H, H(7), <sup>3</sup>J = 8.6 Hz, <sup>4</sup>J = 1.8 Hz), 7.76 (d, 1H, H(4), <sup>3</sup>J = 8.7 Hz), 7.83 (d, 1H, H(8), <sup>3</sup>J = 8.6 Hz), 7.84 (dd, 1H, H(2'), <sup>4</sup>J = 1.9 and 1.7 Hz), 7.97 (d, 1H, H(5), <sup>4</sup>J = 1.8 Hz), 8.03 (d, 1H, H(1), <sup>4</sup>J = 2.0 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100.6 MHz):  $\delta$  120.3 (C(2)), 123.2 (C(3')), 126.1 (HC(5) and HC(6')), 126.4 (HC(7')), 127.8 (HC(8')), 129.8 (HC(1')), 129.9 (HC(4)), 130.0 (HC(3)), 130.5 (HC(2') and HC(5')), 130.6 (HC(4')), 132.1 (C(4a)), 134.0 (C(8a)), 137.6 (C(6)), 142.9 (C(1')). MS (*m/z*, %): 364 (50) [M]<sup>+</sup> for <sup>81</sup>Br, 202 (100), 174 (9), 150 (15), 126 (9), 101 (48), 88 (20), 75 (21), 63 (17), 50 (22). Found (%): C, 52.85; H, 2.75. Calc. for C<sub>16</sub>H<sub>10</sub>Br<sub>2</sub> (%): C, 53.08; H, 2.78.