

Supporting Information
for
Cathodic reductive coupling of methyl cinnamate on
boron-doped diamond electrodes and synthesis of new
neolignan-type products

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Instrumental setup, general procedure for the electrochemical
reaction and physical and spectroscopic data for
(±)-2, meso-2, E-5, and E-8

1. Electrolysis Apparatus



BDD electrode

2. General electrochemical procedure.

Preparation of BDD plate (7 cm^2) was indicated in Supporting Information of [1]. Electroreduction was carried out at room temperature with BDD plate as a cathode, platinum wire as an anode, and saturated calomel electrode as a reference electrode under CCE conditions in a divided cell. Cathode and anode parts were separated with a glass filter. Substrate concentration was 40 mM in solvents (40 mL) containing 0.1 M $n\text{Bu}_4\text{NBF}_4$. The reaction was terminated, when current reached to the indicated amount.

3. Data of (±)-2, meso-2, E-5, and E-8.

Dimethyl (3*S**,4*S**)-3,4-diphenylhexanedioate [(±)-2]: mp 74-76 °C (hexane/EtOAc), 74.5–75°C [2]; IR (film) 1737 cm⁻¹; ¹H NMR (CDCl₃) δ 7.20-7.13 (m, 6H), 6.87 (dd, 4H, *J* = 7.6, 1.6 Hz), 3.55 (s, 6H), 3.53-3.47 (ddd, 2H, *J* = 10.8, 8.5, 6.1 Hz), 2.75 (dd, 2H, *J* = 15.7, 6.1 Hz), 2.63 (dd, 2H, *J* = 15.7, 8.5 Hz); ¹³C NMR (CDCl₃) δ 172.6, 140.1, 128.9, 128.0, 126.9, 51.8, 46.4, 37.7. HRMS (ESI-MS): calcd. for C₂₀H₂₃O₄ 327.1596 (M+H)⁺, found *m/z* 327.1583.

Dimethyl (3*R**,4*S**)-3,4-diphenylhexanedioate (meso-2): mp 177-178 °C (hexane/EtOAc), 175–176 °C [2]; IR (film) 1726 cm⁻¹; ¹H NMR (CDCl₃) δ 7.35-7.22 (m, 10H), 3.36 (s, 6H), 3.32-3.30 (ddd, 2H, *J* = 11.0, 8.1, 4.0 Hz), 2.46 (dd, 2 H, *J* = 15.7, 8.1 Hz), 2.37 (dd, 2 H, *J* = 15.7, 4.0 Hz); ¹³C NMR (CDCl₃) δ 172.5, 141.9, 128.9, 128.3, 127.3, 51.5, 47.9, 39.9. HRMS (ESI-MS): calcd. for C₂₀H₂₃O₄ 327.1596 (M+H)⁺, found *m/z* 327.1611.

(4*S**,5*S**)-4,5-Diphenyloxepan-2-one (E-5): mp 173–175 °C (hexane/EtOAc); IR (film) 1720 cm⁻¹; ¹H NMR (CDCl₃) δ 7.13–7.02 (m, 6H), 6.92–6.90 (m, 4H), 4.54 (m, 2H), 3.25 (dd, 1H, *J* = 13.0, 11.7 Hz), 3.12 (ddd, 1H, *J* = 11.7, 11.7, 12.6 Hz), 3.04 (ddd, 1H, *J* = 11.7, 8.5, 7.2 Hz), 2.87 (dd, 1H, *J* = 13.0, 12.6 Hz), 2.26–2.21 (m, 2H); ¹³C NMR (CDCl₃) δ 174.6, 143.7, 143.5, 128.5, 127.5, 127.1, 126.7, 126.6, 68.3, 54.0, 46.6, 41.3, 37.6. HRMS (ESI-MS): calcd. for C₁₈H₁₉O₂ 267.1385 (M+H)⁺, found *m/z* 267.1382.

(4*S**,5*S**)-4,5-Diphenyloxepane (E-8): mp 95–97 °C (hexane/EtOAc); IR (film) 1125 cm⁻¹; ¹H NMR (CDCl₃) δ 7.07 (t, 4H, *J* = 7.2Hz), 6.99 (d, 2H, *J* = 7.2Hz), 6.94 (ddd, 4H, *J* = 7.2, 1.1 Hz), 4.00 (ddd, 1H, *J* = 12.1, 4.0, 4.0 Hz), 3.88 (ddd, 1H, *J* = 9.4, 9.4, 2.7 Hz), 3.03 (ddd, 2H, *J* = 7.4, 5.3, 2.9 Hz), 2.32–2.22 (m, 2H), 2.03 (ddd, 2H, *J* = 3.1, 2.9, 2.4 Hz); ¹³C NMR (CDCl₃) δ 146.4, 128.1, 127.6, 125.7, 67.5, 51.9, 38.6. HRMS (ESI-MS): calcd. for C₁₈H₂₁O 253.1592 (M+H)⁺, found *m/z* 253.1603.

4. References

- [1] Sumi, T.; Saitoh, T.; Natsui, K.; Yamamoto, T.; Atobe, M.; Einaga, Y.; Nishiyama, S. *Angew. Chem., Int. Ed.* **2012**, *51*, 5443–5446.
- [2] Curtin, D. Y.; Dayagi, S. *Can. J. Chem.*, **1964**, *42*, 867–877.