

Electronic Supplementary Information (ESI) for

Solvent-directed stereoselective and electrocatalytic synthesis of diisoeugenol

Takashi Yamamoto,^{*a} Barbara Riehl,^{a,b} Keisuke Naba,^a Kenshin Nakahara,^a Anton Wiebe,^b
Tsuyoshi Saitoh,^c Siegfried R. Waldvogel,^{*b} Yasuaki Einaga,^{*ad}

^a Department of Chemistry, Keio University, 3-14-1 Hiyoshi, Yokohama 223-8522, Japan

^b Institut für Organische Chemie, Johannes Gutenberg-Universität Mainz, Duesbergweg 10-14,
55128 Mainz, Germany

^c International Institute for Integrative Sleep Medicine, University of Tsukuba, 1-1-1 Tennodai,
Tsukuba 305-8575, Japan

^d JST-ACCEL, 3-14-1 Hiyoshi, Yokohama 223-8522, Japan

E-mail: takayama@chem.keio.ac.jp (T.Y.); waldvogel@uni-mainz.de (S.R.W.);
einaga@chem.keio.ac.jp (Y.E.)

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General Information

All reagents used were in analytical grade. A supporting electrolyte, *N*-methyl-*N,N,N*-tributylammonium methylsulfate (kindly provided by BASF SE, Ludwigshafen, Germany), were used. For the anodic oxidation reaction, a boron-doped diamond (BDD, 15 μm -thick on a silicon substrate, DIACHEM™) was used, which was obtained from CONDIAS, Itzehoe, Germany.

Gas chromatography was performed with Shimadzu GC-2010 using HP 5 column (Agilent Technologies, USA; length: 30 m, inner diameter: 0.25 mm, film thickness: 0.25 μm , carrier gas: hydrogen). GC-MS measurements were carried out with Shimadzu GCMS-QP2010 using Zebron ZB-5MSi column (Phenomenex, USA; length: 30 m, inner diameter: 0.25 mm, film thickness: 0.25 μm , carrier gas: helium).

Analytical thin-layer chromatography was performed with Merck silica gel 60 F₂₅₄ precoated plate (0.25 mm). Flash column chromatography was performed with Biotage Isolera® equipped with Biotage SNAP Cartridge KP-Sil column and hexane/EtOAc as eluent.

¹H NMR spectra were recorded by using JEOL JNM-ECX400. Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane (δ 0.00 ppm), as internal standard or traces of CHCl₃ in the corresponding deuterated solvent. ESI-MS spectra were obtained using Waters Mass Spectrometer-LCT Premier/XE.

Protocol for Anodic Oxidation Reaction

Anodic oxidation reactions were performed with beaker-type Teflon cells (C. Gütz, B. Klöckner and S. R. Waldvogel, *Org. Process Res. Dev.* 2016, **20**, 26.). A solution of isoeugenol (0.76 mmol) and *N*-methyl-*N,N,N*-tributylammonium methylsulfate (0.14 g, 0.45 mmol) in 5 mL 1,1,1,3,3,3-hexafluoropropan-2-ol was transferred into the electrolysis cell equipped with BDD electrodes (0.3 \times 1.0 \times 7.0 cm; immersed 1.8 cm into solution). A constant current electrolysis (current density, *j*: 0.7–2.8 mA/cm²) was performed at 50 °C. After application of the desired electricity (*Q*: 0.2–1.0 F referring isoeugenol), the electrolysis was stopped, and solvent was removed *in vacuo*. The reaction mixture was analyzed by GC or GC-MS, in order to control progress of transformation. The crude product was purified by flash column chromatography as described above.

GC-MS Chromatograms

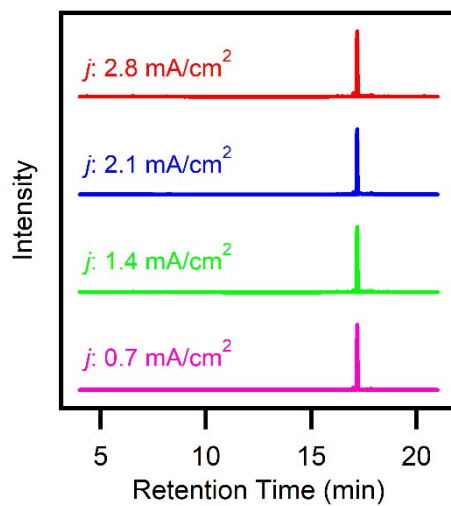


Fig. S1 GC-MS chromatograms of the anodic oxidation of isoeugeol (1). The amount of electricity is fixed at 1.0 F referring 1.

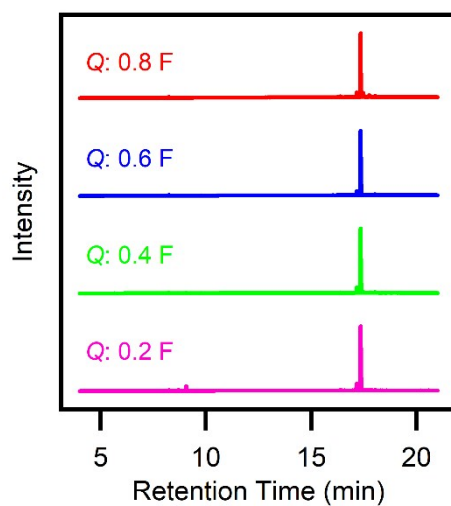


Fig. S2 GC-MS chromatograms of the anodic oxidation of isoeugeol (1). The applied current density is fixed to 2.8 mA cm⁻². The amount of electricity (Q) is referring 1.

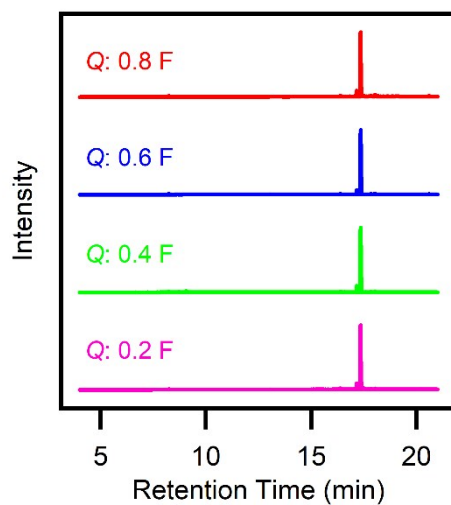


Fig. S3 GC-MS chromatograms of the anodic oxidation of isoeugeol (**1**). The applied current density is fixed to 2.1 mA cm⁻². The amount of electricity (Q) is referring **1**.

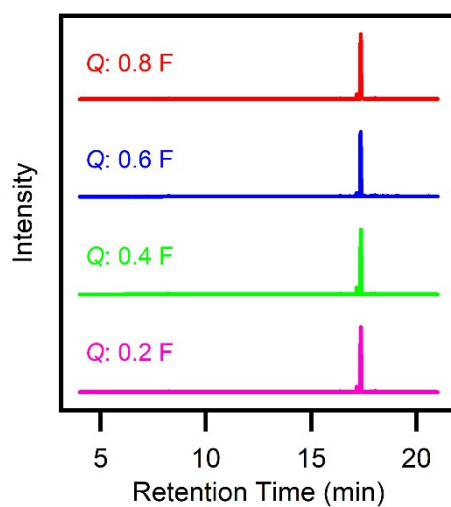


Fig. S4 GC-MS chromatograms of the anodic oxidation of isoeugeol (**1**). The applied current density is fixed to 1.4 mA cm⁻². The amount of electricity (Q) is referring **1**.

Experimental Results

Table S1 Anodic conversion of isoeugenol (**1**) using glassy carbon / HFIP system.

Entry ^[a]	$j^{[b]}$ (mA cm ⁻²)	$Q^{[c]}$ (F)	2 ^[d]
1	0.7	0.2	45
2	0.7	1.0	31
3	1.4	0.2	42
4	1.4	1.0	29
5	2.1	0.2	38
6	2.1	1.0	21
7	2.8	0.2	34
8	2.8	1.0	16

[a] Reaction conditions: glassy carbon anode and cathode, 5 mL HFIP, 0.09 M *N*-methyl-*N,N,N*-tributylammonium methylsulfate, undivided beaker-type cell, 50 °C.

[b] Current density.

[c] Amount of charge referring **1**.

[d] Isolated yield.

NMR Spectra

α -Diisoeugenol (2)

A colorless solid (m.p. 179–180 °C).

^1H NMR (400 MHz, CDCl_3) δ [ppm]: 6.84 (d, $J = 8.0$ Hz, 1H), 6.77 (s, 1H), 6.65 (dd, $J = 8.0, 1.9$ Hz, 1H), 6.61 (d, $J = 1.9$ Hz, 1H), 6.48 (d, $J = 1.0$ Hz, 1H), 5.51 (s, 1H), 5.47 (s, 1H), 3.90 (s, 3H), 3.82 (s, 3H), 3.73 (d, $J = 9.5$ Hz, 1H), 2.91 (ddd, $J = 9.5, 7.4, 5.4$ Hz, 1H), 2.46 (dp, $J = 9.5, 7.0$ Hz, 1H), 1.78–1.63 (m, 1H), 1.46–1.29 (m, 1H), 1.03 (d, $J = 7.0$ Hz, 3H), 0.97 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm]: 146.27, 144.95, 144.33, 143.90, 138.97, 138.55, 135.66, 121.32, 113.79, 110.80, 110.42, 107.29, 56.55, 55.98, 55.75, 49.07, 48.34, 22.21, 13.64, 12.08.

HR-MS (ESI+): m/z calcd for $\text{C}_{20}\text{H}_{24}\text{O}_4\text{Na}$ [$\text{M} + \text{Na}$] $^+$, 351.1572; found 351.1572

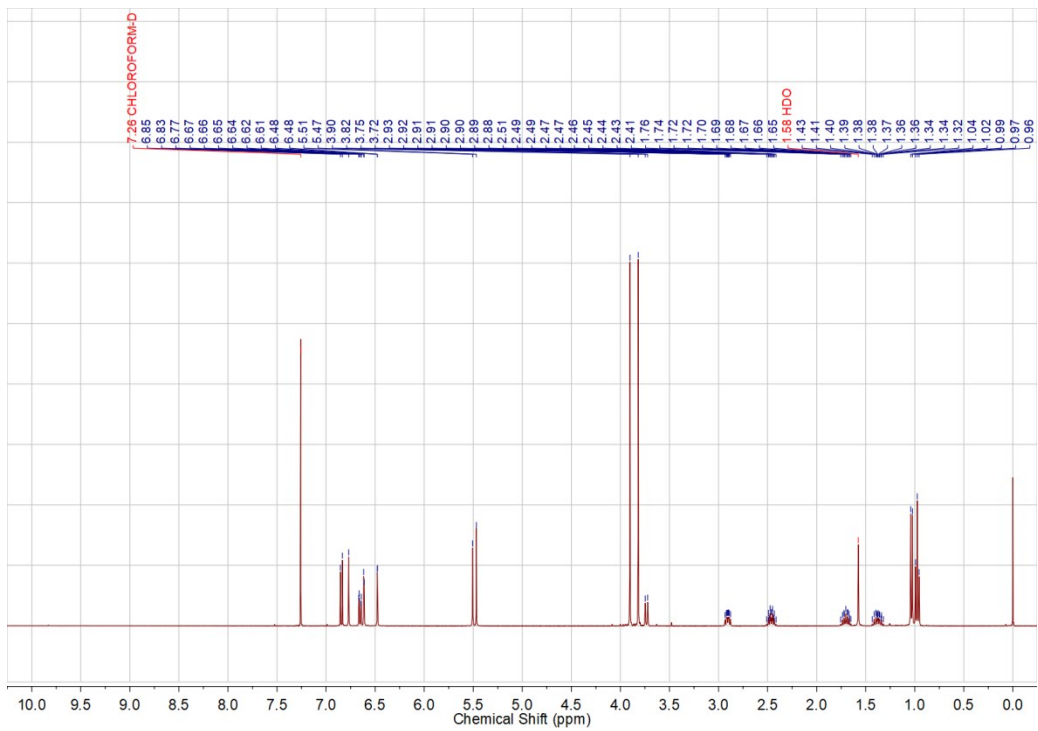


Fig. S5 The ^1H NMR spectrum of α -diisoeugenol (**2**).

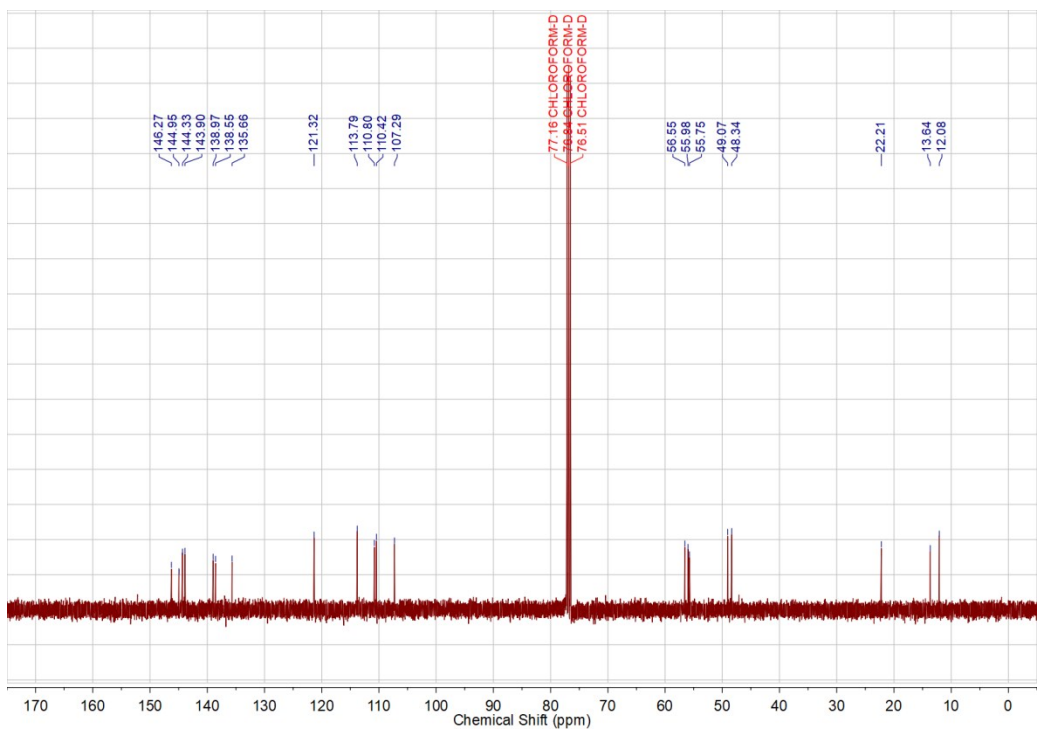


Fig. S6 The ^{13}C NMR spectrum of α -diisoeugeol (**2**).