Electronic Supporting Information

One-Pot Formal Synthesis of Biorenewable Terephthalic Acid from Methyl Coumalate and Methyl Pyruvate

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I. Experimental Procedures and Spectroscopic Data of Compounds

II. $^1$H and $^{13}$C NMR Spectra of Compounds
I. Experimental Procedures and Spectroscopic Data of Compounds

General procedures. All starting materials were purchased from Sigma-Aldrich; solvents were purchased from Fisher Scientific and used without further purification. All yields refer to isolated products either by column chromatography or by recrystallization. Thin-layer chromatography (TLC) data was obtained with 0.20 mm silica gel plates using UV light as a visualizing agent and potassium permanganate with heat as the developing agent. Silica gel 60A, particle size 0.032 – 0.063 mm, was used for flash column chromatography. \(^1\)H and \(^{13}\)C NMR spectra were acquired in CDCl\(_3\) on a Varian MR-400 or Bruker Avance III 600 MHz spectrometer. \(^1\)H and \(^{13}\)C chemical shifts (δ) are given in ppm relative to the residual protonated chloroform peak (CDCl\(_3\): δ\(_H\) = 7.26 ppm, δ\(_C\) = 77.16 ppm) as an internal reference. High-resolution mass spectra (HRMS) were recorded on an Agilent 6540 QTOF (quadrupole time of flight) mass spectrometer using ESI (electrospray ionization) or APCI (atmospheric-pressure chemical ionization). The Diels-Alder reactions of methyl coumalate with dienophiles 2a-b and 4a-b were run with toluene as the solvent; in contrast, the Diels-Alder reactions of methyl coumalate with dienophiles 9a-e to generate dimethyl terephthalate were optimized and performed without solvent.

General Procedure: Diels-Alder Reaction of Methyl Coumalate with Dienophiles 2a-b and 4a-b

The synthesis of 3a is representative. To a sealable 15-mL pressure vessel was successively added methyl coumalate (0.154 g, 1.0 mmol), methyl trans-3-methoxyacrylate (0.3 mL, 3.0 mmol), and toluene (2 mL) under argon. The solution was heated to 200 °C and stirred for 16 h. Upon completion of the reaction,
the sealable pressure vessel was cooled to room temperature. The solution was transferred to another flask, while rinsing with ethyl acetate, after which the solution was concentrated \textit{in vacuo}. The crude product was purified by flash column chromatography (silica gel, EtOAc:hexanes 1:20) to afford \textbf{3a} (0.16 g, 83\% yield) as a white solid. \textbf{3a}: m.p. 63-65 °C; $R_f = 0.62$ (silica gel, EtOAc:hexanes 1:1); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta = 8.69$ (s, 1H), 8.23 (dd, $J = 7.9$, 1.8 Hz, 2H), 7.54 (t, $J = 7.8$ Hz, 1H), 3.95 (s, 6H) ppm; $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta = 166.4, 133.9, 130.9, 130.7, 128.8, 52.5$ ppm; HRMS (APCI-TOF) calcd for C$_{10}$H$_{11}$O$_4$ $[M + H]^+$ 195.0652, found 195.0655.

![Image](image_url)

Yellow oil (0.16 g, 92\% yield). \textbf{3b}: $R_f = 0.69$ (silica gel, EtOAc:hexanes 1:1); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta = 8.60$ (s, 1H), 8.24 (d, $J = 7.8$ Hz, 1H), 8.17 (d, $J = 7.8$ Hz, 1H), 7.57 (t, $J = 7.8$ Hz, 1H), 3.96 (s, 3H), 2.66 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 197.4, 166.4, 137.4, 134.1, 132.5, 130.8, 129.0, 52.6, 26.9$ ppm; HRMS (APCI-TOF) calcd for C$_{10}$H$_{11}$O$_3$ $[M + H]^+$ 179.0702, found 179.0702.

![Image](image_url)

Yellow solid (0.17 g, 94\% yield). \textbf{5a}: m.p. 85-87 °C; $R_f = 0.73$ (silica gel, EtOAc:hexanes 1:1); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta = 8.12$ (d, $J = 8.2$ Hz, 2H), 8.01 (d, $J = 8.2$ Hz, 2H), 3.95 (s, 3H), 2.64 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 197.7, 166.3, 140.3, 134.0, 130.0, 128.3, 52.6, 27.0$ ppm; HRMS (EI-TOF) calcd for C$_{10}$H$_{10}$O$_3$ $[M + H]^+$ 178.0708, found 178.0706.

![Image](image_url)

Yellow solid (0.10 g, 75\% yield). \textbf{5b}: m.p. 60-61 °C; $R_f = 0.70$ (silica gel, EtOAc:hexanes 1:1); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta = 8.08$ (d, $J = 7.9$ Hz,
1H), 7.95 (s, 1H), 7.94 (d, J = 7.9 Hz, 1H), 3.94 (s, 3H), 3.03 (t, J = 6.1 Hz, 2H), 2.70 (t, J = 6.1 Hz, 2H), 2.20 – 2.14 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 197.9, 166.5, 144.5, 135.6, 134.0, 130.3, 127.5, 127.4, 52.6, 39.3, 29.7, 23.2 ppm; HRMS (ESI-TOF) calcd for C$_{12}$H$_{13}$O$_3$ [$M + H]^+$ 205.0859, found 205.0857.

**General Procedure: Diels-Alder Reaction of Methyl Coumalate with Dienophiles 9a-e**

Methyl coumalate (0.154 g, 1.0 mmol) and 9a (0.3 mL, 3.0 mmol) were combined in a sealable 15-mL pressure vessel. The solution was heated to 150 °C and stirred for 16 h. (Alternatively, 1.5 equivalents of 9a can be combined with methyl coumalate at 200 °C for 16 h). Upon completion of the reaction, the sealable pressure vessel was cooled to room temperature. The solution was transferred to another flask, while rinsing with ethyl acetate, after which the solution was concentrated in vacuo. The crude product was purified by repeated trituration and recrystallization from ethyl acetate and hexanes to afford dimethyl terephthalate 10 (0.18 g, 95% yield) as a white solid. All the solvents during the purification process could be recovered and reused. 10: m.p. 140-142 °C; $R_f = 0.79$ (silica gel, EtOAc:hexanes 1:1); $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ = 8.10 (s, 4H), 3.95 (s, 6H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 166.4, 134.1, 129.7, 52.6 ppm; HRMS (ESI-TOF) calcd for C$_{10}$H$_{11}$O$_4$ [$M + H]^+$ 195.0652, found 195.0651.
II. $^1$H and $^{13}$C NMR Spectra of Compounds