

Electronic Supporting Information

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

Jennifer J. Lee and George A. Kraus*

Department of Chemistry and NSF Engineering Research Center for Biorenewable Chemicals,

Iowa State University, Ames, IA 50011

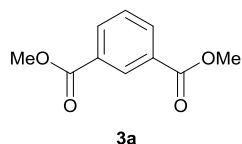
Email: gakraus@iastate.edu

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

I. Experimental Procedures and Spectroscopic Data of Compounds

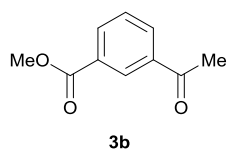
General procedures. All starting materials were purchased from Sigma-Aldrich; solvents were purchased from Fisher Scientific and used without further purification. All yields refer to isolated products either by column chromatography or by recrystallization. Thin-layer chromatography (TLC) data was obtained 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. ^1H and ^{13}C NMR spectra were acquired in CDCl_3 on a Varian MR-400 or Bruker Avance III 600 MHz spectrometer. ^1H and ^{13}C chemical shifts (δ) are given in ppm relative to the residual protonated chloroform peak (CDCl_3 : $\delta_{\text{H}} = 7.26$ ppm, $\delta_{\text{C}} = 77.16$ 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**

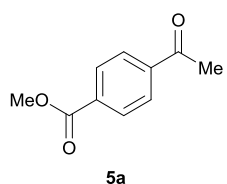


The synthesis of **3a** is representative. To a sealable 15-mL pressure vessel was successively added methyl coumalate (0.154 g, 1.0 mmol), methyl *trans*-3-methoxyacrylate (0.3 mL, 3.0 mmol), and toluene (2 mL) under argon. The solution was heated to 200 °C and stirred for 16 h. Upon completion of the reaction,

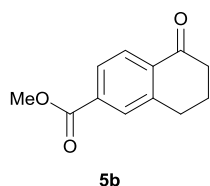
the sealable pressure vessel was cooled to room temperature. The solution was transferred to another flask, while rinsing with ethyl acetate, after which the solution was concentrated *in vacuo*. The crude product was purified by flash column chromatography (silica gel, EtOAc:hexanes 1:20) to afford **3a** (0.16 g, 83% yield) as a white solid. **3a**: m.p. 63-65 °C; R_f = 0.62 (silica gel, EtOAc:hexanes 1:1); ^1H NMR (CDCl_3 , 400 MHz) δ = 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) δ = 166.4, 133.9, 130.9, 130.7, 128.8, 52.5 ppm; HRMS (APCI-TOF) calcd for $\text{C}_{10}\text{H}_{11}\text{O}_4$ [$M + \text{H}$] $^+$ 195.0652, found 195.0655.



Yellow oil (0.16 g, 92% yield). **3b**: R_f = 0.69 (silica gel, EtOAc:hexanes 1:1); ^1H NMR (CDCl_3 , 400 MHz) δ = 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) δ = 197.4, 166.4, 137.4, 134.1, 132.5, 130.8, 129.0, 52.6, 26.9 ppm; HRMS (APCI-TOF) calcd for $\text{C}_{10}\text{H}_{11}\text{O}_3$ [$M + \text{H}$] $^+$ 179.0703, found 179.0702.



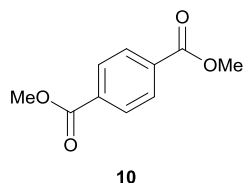
Yellow solid (0.17 g, 94% yield). **5a**: m.p. 85-87 °C; R_f = 0.73 (silica gel, EtOAc:hexanes 1:1); ^1H NMR (CDCl_3 , 400 MHz) δ = 8.12 (d, J = 8.2 Hz, 2H), 8.01 (d, J = 8.2 Hz, 2H), 3.95 (s, 3H), 2.64 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ = 197.7, 166.3, 140.3, 134.0, 130.0, 128.3, 52.6, 27.0 ppm; HRMS (EI-TOF) calcd for $\text{C}_{10}\text{H}_{10}\text{O}_3$ [$M + \text{H}$] $^+$ 178.0708, found 178.0706.



Yellow solid (0.10 g, 75% yield). **5b**: m.p. 60-61 °C; R_f = 0.70 (silica gel, EtOAc:hexanes 1:1); ^1H NMR (CDCl_3 , 400 MHz) δ = 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 $\text{C}_{12}\text{H}_{13}\text{O}_3$ [$M + \text{H}$] $^+$ 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); ^1H 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 $\text{C}_{10}\text{H}_{11}\text{O}_4$ [$M + \text{H}$] $^+$ 195.0652, found 195.0651.

II. ^1H and ^{13}C NMR Spectra of Compounds

