Supporting Information for

Olefins from Biomass Feedstocks: Catalytic Ester Decarbonylation and Tandem

Heck-type Coupling

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Table of Contents

1. General Information	S3
2. General procedure and data for syntheses of esters	S4-S8
3. General procedure and data for decarbonylation reactions	S8-S9
4. General procedure and data for tandem Heck-type coupling	S9-S11
5. NMR spectra all isolated compounds	S12-S37
6. Reaction progress of tandem Heck-type coupling	S38
6. References	S39-S40

S2

Experimental Section

General Procedures. All manipulations were carried out in either a N₂ filled glove box or using Schlenk tube techniques under an Ar atmosphere. PdCl₂, carboxylic acids, *p*nitrophenylchloroformate, alkali and alkaline-earth metal halide salts were purchased from commercial sources. Mass spectra were acquired in the ESI (+) mode. Dichloromethane were passed through a purification column (Glass Contour, Laguna, CA) prior to use. DMPU was dried by stirring over CaH₂ and purified by distillation under reduced pressure. All ¹H NMR spectra were collected on either a Varian VXR-500 or Varian VI-300 spectrometer and calibrated to the residual protonated solvent at δ 7.27 for deuterated chloroform (CDCl₃). ¹H NMR peaks are labeled as singlet (s), doublet (d), triplet (t) and multiplet (m). All GC-MS experiments were conducted on an Agilent Technologies 7890A GC system and 5975C VL MSD. The GC column was a HP-5 ms with dimensions 30 m × 0.25 mm. The standard method used for all runs involved an initial oven temperature of 50 °C (held for 2 min) followed by a 20 °C min⁻¹ ramp to 70 °C (held for 6 min), followed by a final 20 °C min⁻¹ ramp to 230 °C (held for 15 min).

General procedure for syntheses of *p*-nitrophenylesters

To a stirred solution of the carboxylic acid (5 mmol) in dry CH_2Cl_2 (*ca.* 30 mL) under N_2 atmosphere was added NEt₃ (0.7 mL, 5.02 mmol) using a syringe, and the mixture was allowed to stir for 10 minutes. At the end of this period, *p*-nitrophenylchloroformate (1.01 g, 5.01 mmol) was added to the mixture in portions over a period of 5-10 minutes. The reaction mixture showed immediate color change to a pale yellow color along with strong effervescence. The reaction mixture would generally show the presence of an off-white precipitate. Subsequently, the reaction mixture is concentrated under vacuum to remove all the CH₂Cl₂ and then EtOAc (*ca.* 20 mL) was added to the residue obtained. The resulting mixture is filtered through a pad of basic alumina and the filtrate is concentrated on a rotary evaporator. The residue obtained is dried under high vacuum and is usually about >95 % pure ester product as judged by ¹H NMR spectroscopy. If the ester obtained was not of substantially high purity, the crude product was re-dissolved in EtOAc (*ca.* 15 mL) and subjected to another filtration through basic alumina.

4-nitrophenyl-3-phenylpropanoate (**1a**).¹ Off-white solid (1.14 g, 84 %). ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ 8.26 (d, ³*J*_{HH} = 10 Hz, 2H), 7.35 (t, ³*J*_{HH} = 7.5 Hz, 1H), 7.28-7.25 (m, 4H), 7.20 (d, ³*J*_{HH} = 10 Hz, 2H), 3.10 (t, ³*J*_{HH} = 7.5 Hz, 2H), 2.95 (t, ³*J*_{HH} = 7 Hz, 2H). ¹³C{¹H} NMR (CDCl₃, 125 MHz, 25 °C): δ 170.6, 155.5, 145.4, 139.8, 128.8, 128.5, 16.8, 125.3, 122.6, 36.1, 30.9.

tert-butyl-4-nitrophenylsuccinate (1b). The reaction was carried out starting with *tert*butylsuccinate (2.5 mmol) following the general procedure, and the product was obtained as an off white viscous liquid (0.623 g, 82 %). ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ 8.28 (d, ³*J*_{HH} = 10 Hz, 2H), 7.30 (d, ³*J*_{HH} = 10 Hz, 2H), 2.86 (t, ³*J*_{HH} = 7 Hz, 2H), 2.68 (t, ³*J*_{HH} = 7 Hz, 2H), 1.47 (s, 9H). ¹³C{¹H} NMR (CDCl₃, 125 MHz, 25 °C): δ 171.3, 170.4, 155.5, 145.4, 125.3, 122.5, 81.4, 30.2, 29.6, 28.2. HRMS (ESI) Calcd for C₁₄H1₇N₁NaO₆ (M+Na)⁺ requires *m/z* = 318.0948, found *m/z* = 318.0944.

4-nitrophenyl-2-phenylbutanoate (1c).² Sticky white solid (0.875g, 65%). ¹H NMR (500 MHz, CDCl₃, 25 °C) δ 8.23 (2H, d, *J*=9.5 Hz, *m*-C₆*H*₄), 7.39-7.38 (4H, m, *o*,*m*-C₆*H*₅), 7.35-7.33 (1H, m, *p*-C₆*H*₅), 7.18 (2H, d, *J*=9.5 Hz, *o*-C₆*H*₄), 3.73 (1H, t, *J*=8 Hz, C<u>*H*</u>), 2.24 (1H, m, C<u>*H*</u>₂), 1.94 (1H, m, C<u>*H*</u>₂), 1.00 (3H, t, *J*=7.5 Hz, C<u>*H*</u>₃) ppm.

4-nitrophenyl-4-phenylbutanoate (1d).³ Pale yellow oil (1.37 g, 95 %). ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ 8.27 (d, ³*J*_{HH} = 9 Hz, 2H), 7.33 (t, ³*J*_{HH} = 9 Hz, 2H), 7.27-7.22 (m, 5H), 2.76 (t, ³*J*_{HH} = 7 Hz, 2H), 2.63 (t, ³*J*_{HH} = 7 Hz, 2H), 2.11 (quin, ³*J*_{HH} = 7 Hz, 2H). ¹³C{¹H} NMR (CDCl₃, 75 MHz, 25 °C): δ 171.1, 155.5, 145.4, 141.0, 128.7, 126.4, 125.3, 122.6, 35.1, 33.7, 26.3.

3-(4-nitrophenyl)-cyanopropanoate (1e).⁴ Brown solid. (1.356 g, 80 %). ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ 8.30 (d, ³*J*_{HH} =9 Hz, 2H), 7.33 (d, ³*J*_{HH} =9 Hz, 2H), 3.03 (t, ³*J*_{HH} =7 Hz, 2H), 2.79 (t, ³*J*_{HH} =7 Hz, 2H). ¹³C{¹H} NMR (CDCl₃, 75 MHz, 25 °C): δ 167.7, 154.7, 144.4, 125.4, 122.3, 124.2, 30.1, 12.9.

4-nitrophenylpent-4-enoate (**1f**).⁵ The reaction was carried out starting with 4-pentenoic acid (10 mmol) following the general procedure, and the product was obtained as a pale yellow liquid (1.93 g, 87 %). ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ 8.27 (d, ³*J*_{HH} = 10 Hz, 2H), 7.28 (d, ³*J*_{HH} = 10 Hz, 2H), 5.94-5.86 (m, 1H), 5.16 (ddd, *J*_{HH} = 17 Hz, 3 Hz & 1.5 Hz, 1H), 5.10 (ddd, *J*_{HH} = 11 Hz, 3 Hz & 1.5 Hz, 1H), 2.72 (t, ³*J*_{HH} = 7.5 Hz, 2H), 2.52 (q, ³*J*_{HH} = 7 Hz, 2H). ¹³C{¹H} NMR (CDCl₃, 125 MHz, 25 °C): δ 170.7, 155.5, 145.3, 136.0, 125.3, 122.6, 116.3, 33.6, 28.7.

4-nitrophenylnonanoate (**1g**).⁶ Pale yellow oil (1.18 g, 84 %). ¹H NMR (CDCl₃, 300 MHz, 25 °C): 8.27 (d, ${}^{3}J_{HH} = 9.3$ Hz, 2H), 7.27 (d, ${}^{3}J_{HH} = 7.8$ Hz, 2H), 2.60 (t, ${}^{3}J_{HH} = 7.5$ Hz, 2H), 1.76 (m, ${}^{3}J_{HH} = 6.8$ Hz, 2H), 1.41-1.23 (m, 11H), 0.89 (m, 2H).

4-nitrophenylundec-10-enoate (**1h**).⁷ Pale yellow oil (1.22 g, 78 %). ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ 8.27 (d, ³*J*_{HH} = 9.5 Hz, 2H), 7.28 (d, ³*J*_{HH} = 9 Hz, 2H), 5.86-5.78 (m, 1H), 5.00 (ddd, *J*_{HH} = 17 Hz, 4 Hz & 2 Hz, 1H), 4.95-4.25 (m, 1H), 2.60 (t, ³*J*_{HH} = 7.5 Hz, 2H), 2.05 (q, ³*J*_{HH} = 7.5 Hz, 2H), 1.76 (quin, ³*J*_{HH} = 7.5 Hz, 2H), 1.45-1.28 (m, 10H). ¹³C{¹H} NMR (CDCl₃, 125 MHz, 25 °C): δ 171.3, 155.5, 145.2, 139.1, 125.2, 122.5, 114.2, 34.3, 33.8, 29.3, 29.2, 29.1, 29.0, 28.9, 24.7.

4-nitrophenylbenzoate (**2a**).⁸ White solid (0.705 g, 20 %). ¹H NMR (CDCl₃, 300 MHz, 25 °C) δ 8.34 (d, ³*J*_{HH} = 9.3 Hz, 2H), 8.21 (d, ³*J*_{HH} = 7.2 Hz, 2H), 7.69 (t, ³*J*_{HH} = 7.5 Hz, 1H), 7.55 (t, ³*J*_{HH} = 7.2 Hz, 2H), 7.43 (d, ³*J*_{HH} = 9.0 Hz, 2H).

4-nitrophenyl-3-chlorobenzoate (**2b**).⁹ White fluffy solid. (0.664 g, 24 %). ¹H NMR (CDCl₃, 500 MHz, 25 °C) δ 8.35 (d, ³*J*_{HH} =9.5 Hz, 2H), 8.2 (s, 1H), 8.10 (dd, ³*J*_{HH} =7.5 Hz, 1H), 7.67 (d, ³*J*_{HH} =8.5 Hz, 1H), 7.51 (t, ³*J*_{HH} =8 Hz, 1H), 7.42 (d, ³*J*_{HH} =9.5 Hz, 2H) ppm.

4-nitrophenyl-4-methylbenzoate (**2c**).¹⁰ White solid (0.283 g, 10 %). ¹H NMR (CDCl₃, 500 MHz, 25 °C) δ 8.33 (d, ³*J*_{HH} =8.5 Hz, 2H), 8.10 (d, ³*J*_{HH} =8.5 Hz, 2H), 7.42 (d, ³*J*_{HH} =9.5 Hz, 2H), 7.34 (d, ³*J*_{HH} =8.5 Hz, 2H), 2.48 (s, 3H).

4-nitrophenyl-4-nitrobenzoate (2d).¹⁰ Yellow, fluffy powder (0.503g, 18 %). ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ 8.41-8.34 (m, 6H), 7.46 (d, ³J_{HH} =9 Hz, 2H).

4-nitrophenyl-4-bromobenzoate (**2e**).¹¹ Light yellow fluffy solid (0.450 g, 14 %). ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ 8.34 (d, ³*J*_{HH} =9 Hz, 2H), 8.06 (d, ³*J*_{HH} =8.5 Hz, 2H), 7.69 (d, ³*J*_{HH} =8.5 Hz, 2H), 7.42 (d, ³*J*_{HH} =9 Hz, 2H).

4-nitrophenyl-*trans***-cinnamate** (**2f**).¹² Off-white fluffy solid (0.585 g, 43 %). ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ 8.32 (d, ³*J*_{HH} =8.7 Hz, 2H), 7.92 (d, ³*J*_{HH} =15.9 Hz, 1H), 7.63-7.60 (m, 2H), 7.47-7.44 (m, 3H), 7.38 (d, ³*J*_{HH} =9.0 Hz, 2H), 6.64 (d, ³*J*_{HH} =15.9 Hz, 1H).

4-nitrophenyl-2-naphthoate (**2g**).¹² Off-white solid (1.67 g, 57 %). ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ 8.80 (s, 1H), 8.36 (d, ³J_{HH} =9.3 Hz, 2H), 8.18 (d, ³J_{HH} =8.7 Hz, 1H), 8.04-7.93 (m, 3H), 7.70-7.59 (m, 2H), 7.48 (d, ³J_{HH} =9.0 Hz, 2H).

Representative procedure for decarbonylation reactions

Inside a N_2 filled glove box, a schlenk tube was charged with the pnitrophenylhydrocinnamate (0.075 g, 0.28 mmol, 1 equiv.), PdCl₂ (0.004 g, 0.026 mmol, 10 mol % or 0.002 g, 0.013 mmol, 5 mol %), LiCl (0.010 g, 0.24 mmol, 100 mol %) and DMPU (ca. 0.5 mL) was injected in followed by a Teflon-coated stir bar. The reaction looked light-yellow at this time. The schlenk tube was sealed, brought outside the box and set in an oil bath pre-heated to 155-160 °C. The reaction mixture was allowed to stir at this temperature for the stipulated period of time during which it darkened, and has a red-brown color finally. At the end of the reaction, the schlenk tube was pulled out of the oil bath and allowed to cool down to room temperature. (a) For GC-MS analysis: The reaction mixture was transferred to a separatory funnel, diluted with EtOAc (ca. 5 mL) and washed with 1M HCl (ca. 5 mL \times 2) and brine (ca. 5 mL). The organic layer was collected, dried over MgSO₄ and analyzed by GC-MS using 1,3,5-trimethoxybenzene as an internal standard. (b) For Olefin isolation (reaction carried out at 1 mmol scale): The reaction mixture was transferred to a separatory funnel, diluted with 1M HCl (ca. 10 mL). This mixture was extracted with pentane (ca. 5 ml \times 3). The combined organic layers were washed with 1M HCl (ca. 5 mL) and then separated. The pentane extracts were dried with MgSO₄, and then concentrated under vacuum to remove the pentane. Analysis of the residue by ¹H NMR showed the olefin product in > 90 % purity.

Styrene (3a).¹³ Clear liquid (0.055 g, 53 %). ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ 7.43 (d, ³*J*_{HH} = 8.5 Hz, 2H), 7.34 (t, ³*J*_{HH} = 8 Hz, 2H), 7.27 (t, ³*J*_{HH} = 7.5 Hz, 1H), 6.74 (dd, ³*J*_{HH} = 17.5 Hz & 11 Hz, 1H), 5.77 (d, ³*J*_{HH} = 17.5 Hz, 1H), 5.26 (d, ³*J*_{HH} = 10.5 Hz, 1H).

β-methylstyrene {trans/cis (8:1)} (3c & 3d).¹⁴ Pale-yellow oil (0.061 g, 52 %). ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ 7.34 (d, ${}^{3}J_{HH} = 8$ Hz, 2H), 7.29 (t, ${}^{3}J_{HH} = 7.5$ Hz, 2H), 7.19 (t, ${}^{3}J_{HH} = 7.5$ Hz, 1H), 6.41 (dd, ${}^{3}J_{HH} = 14$ Hz & 1.5 Hz, 1H), 6.29-6.22 (m, 1H), 1.89 (dd, ${}^{3}J_{HH} = 7.5$ Hz & 2 Hz, 3H). ¹H NMR also showed 10 % allylbenzene.

1,2,3,4-tetrabromobutane (**3f**).¹⁵ Off-white solid (.025 g, 7 %). ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ 4.74-4.59 (m, 2H), 4.17-3.81 (m, 4H).

Representative procedure for tandem Heck-coupling reaction

Inside a N₂ filled glove box, a schlenk tube was charged with the *p*-nitrophenylhydrocinnamate (0.071 g, 0.26 mmol, 1 equiv.), *p*-nitrophenylbenzoate (0.064 g, 0.26 mmol, 1 equiv.), PdCl₂ (0.002 g, 0.013 mmol, 5 mol %), LiCl (0.020 g, 0.47 mmol, 200 mol %) and DMPU (*ca*. 0.5 mL) was injected in followed by a Teflon-coated stir bar. The sealed schlenk tube was brought outside and placed in an oil bath preheated to 155-160 °C and allowed to stir at this temperature for 16 hours. At the end of this period, the reaction mixture was allowed to cool to room temperature and then diluted with EtOAc (*ca*. 5 mL). The solution was transferred to a separatory funnel and washed with 1M HCl (*ca*. 5 mL × 2) followed by brine solution (*ca*. 5 mL). The organic layer

was separated, dried over MgSO₄, filtered and then analyzed by GC-MS using 1,3,5trimethoxybenzene as an internal standard. For isolation of the product, a procedure similar to that used for olefin isolation was employed using pentane as the organic solvent.

trans-stilbene (4aa).¹⁶ ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ 7.52 (d, ³*J*_{HH} = 8.7 Hz, 4H), 7.37 (t, ³*J*_{HH} = 7.5 Hz, 4H), 7.26 (t, ³*J*_{HH} = 7.5 Hz, 2H), 7.12 (s, 2H).

3-chlorostilbene (**4ab**).¹⁷ ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ 7.53-7.51 (m, 3H), 7.41-7.36 (m, 3H), 7.29 (t, ³*J*_{HH} = 7.5 Hz, 2H), 7.26-7.22 (m, 1H), 7.12 (d, ³*J*_{HH} = 16 Hz, 1H), 7.03 (d, ³*J*_{HH} = 16 Hz, 1H).

4-methylstilbene (**4ac**).¹⁸ ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ 7.52 (d, ³*J*_{HH} = 7.5 Hz, 2H), 7.44-7.34 (m, 4H), 7.28-7.23 (m, 1H), 7.18 (d, ³*J*_{HH} = 7.8 Hz, 2H), 7.09 (s, 2H), 2.37 (s, 3H).

4-nitrostilbene (**4ad**).¹⁸ ¹H NMR (CDCl₃, 300 MHz, 25 °C): δ 8.23 (d, ³*J*_{HH} = 8.7 Hz, 2H), 7.65 (d, ³*J*_{HH} = 8.7 Hz, 2H), 7.56 (d, ³*J*_{HH} = 6.9 Hz, 2H), 7.41 (t, ³*J*_{HH} = 6.9 Hz, 2H), 7.37-7.32 (m, 1H), 7.26-7.31 (m, 1H), 7.15 (d, ³*J*_{HH} = 16 Hz, 1H).

4-bromostilbene (**4ae**).¹⁶ ¹H NMR (CDCl₃, 500 MHz, 25 °C): δ 7.54-7.48 (m, 4H), 7.40-7.36 (m, 4H), 7.29 (t, ³*J*_{HH} = 6.5 Hz, 1H), 7.10 (d, ³*J*_{HH} = 16 Hz, 1H), 7.04 (d, ³*J*_{HH} = 16 Hz, 1H).

1,4-diphenyl-1,3-butadiene (**4af**).¹⁶ ¹H NMR (CDCl₃, 500 MHz, 25 °C): δ 7.45 (d, ³*J*_{HH} = 7 Hz, 4H), 7.34 (t, ³*J*_{HH} = 7.5 Hz, 4H), 7.24 (t, ³*J*_{HH} = 7.0 Hz, 2H), 7.00-6.94 (m, 2H), 6.72-6.66 (m, 2H).

2-styrylnaphthalene (**4ag**).¹⁹ ¹H NMR (CDCl₃, 500 MHz, 25 °C): δ 7.88 (s, 1H), 7.86-7.82 (m,3H), 7.77 (dd, ${}^{3}J_{\text{HH}} = 9.0$ Hz & ${}^{3}J_{\text{HH}} = 2.0$ Hz, 1H), 7.58 (d, ${}^{3}J_{\text{HH}} = 7.5$ Hz, 2H), 7.51-7.45 (m, 2H), 7.40 (d, ${}^{3}J_{\text{HH}} = 8.0$ Hz, 2H), 7.32-7.24 (m, 3H).















































Figure S1. Progress of decarbonulative Heck-type coupling between hydrocinnamic ester and benzoate ester monitored by GC-MS using 1,3,5-trimethoxybenzene as internal standard. Reaction was carried out at 1 mmol scale and monitired by pulling aliquots at stipulated time intervals.

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