# High Performance Alkyl Dialkoxyalkanoate Renewable Diesel Fuels Accessed Using a Mild and Scalable Synthetic Protocol

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## Synthesis and Chemical Characterization of DAOA compounds

**Materials:** Unless otherwise specified, all materials were of reagent grade and used as received from Sigma Aldrich. Amberlyst A-15 contained ~50 %  $H_2O$ . This water loading was verified by a bake out at 110°C to constant mass under dry nitrogen purge. Glyoxylic acid was procured as a 50 % wt. aqueous solution. Hexanes (99.5 %) were procured from Greenfield Global, and ethanol (ACS grade) from Pharmco-Aaper.

**NMR spectroscopy** was performed using 5 mm Norell NMR tubes. ~ 5 mg of solute was added to 0.5 mL of  $CDCl_3$  containing 0.03 % v/v SiMe<sub>4</sub> or  $C_6D_6$ . The solution was analyzed at 27°C with a 500 MHz Bruker Ascend NMR system equipped with a 2-channel broadband probe. Typical <sup>1</sup>H analysis parameters were as follows: 500 MHz tuning frequency, 8 scans with 30 second relaxation delay, spectral width = +16 to -4 ppm. Chemical shifts were referenced to residual  $CHCl_3$  at 7.26 ppm or residual  $C_6D_5H$  at 7.16 ppm.

**Gas chromatography-mass spectrometry (GC-MS) analysis**: Samples were taken directly from the corresponding NMR sample solution. An Agilent 7890A gas chromatography instrument was equipped with a 30 m × 250  $\mu$ m DB-5HT capillary column with a film thickness of 0.10  $\mu$ m. One microliter of appropriately diluted sample was injected into the injection port (250 °C) in a split mode with a split ratio of 100:1. The temperature of the column was programmed as follows: hold 30 °C for 3 min, ramp to 325 °C at 25 °C/min. The carrier gas was ultra-high purity helium (99.999 %) at a constant flow rate of 1.2 mL/min. The chromatograph was coupled to a quadrupole 5975C Inert XL MSD Turbo EI. Spectral components were searched against the NIST mass spectral library.

Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FT-IR): Neat compounds were analyzed with a Thermo Fisher Scientific Nicolet iS50 equipped with a Smart iTX attenuated total reflectance (ATR) diamond crystal accessory, between 600-4000 cm<sup>-1</sup> with 1 cm<sup>-1</sup> spectral resolution. 16 scans were collected with baseline subtraction.

C,H,N elemental analysis was performed at Atlantic Microlab and Midwest Microlab facilities.

**Mass spectrometry** was performed by direct injection of analyte solution to a Waters LCT Premier Mass Spectrometer.

#### Transesterification of simple DAOAs to generate DAOAs 8-9

DAOA compound (1 equiv.), alcohol (10-30 equiv.), 0.15 equiv. of solid NaOH was added to a round bottomed flask under air, equipped with magnetic stir bar and reflux condenser. The reaction mixture was heated to reflux for 24 h, whereupon > 95 % conversion was measured by NMR. The reaction mixture was cooled to room temperature and washed three times with water (1 volume equiv.). The organic layer was concentrated in vacuo to yield crude oil, which was purified by vacuum distillation.

#### Acid stability testing

A sealed, tared round-bottomed flask containing a magnetic stir bar, 50 g distilled **DAOA-5** and 50 mL 0.01 M  $H_2SO_4$  was stirred at 850 rpm and 45 °C for four weeks under air. Then, stirring was stopped, the liquid layers were allowed to separate, and the lower aqueous phase was removed from the flask. The remaining organic layer was massed, and analyzed by Karl Fischer titration, <sup>1</sup>H NMR and GC-MS.



1. Measure out reagents, combine at room temperature



4. When complete, cool reaction to room temperature, remove catalyst by gravity filtration



2. Equip flask with Dean-Stark adapter, reflux condenser, insulation



5. Quench residual acid with NaHCO<sub>3</sub> (sat., aq.), separate layers, collect organic layer



3. Heat to reflux, monitor water collection, NMR for conversion



6. Remove solvent and excess alcohol at reduced pressure with rotary evaporator



7. Vacuum distillation to isolate desired product

Figure S1. Illustrative description of batch DAOA synthesis



**Ethyl 2,2-diethoxypropanoate (DAOA-1):** Synthesized and isolated following the general procedure, using pyruvic acid (50.0 g, 0.568 mol) as substrate and ethanol (156 g, 198 mL, 3.39 mol). Distillation conditions: 70 °C, 30 mTorr. Yield: 55 g, 51 % (basis: 50 g pyruvic acid). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.25 (q, *J* = 7.2 Hz, 2H), 3.58 (dq, *J* = 9.4, 7.3 Hz, 2H), 3.48 (dq, *J* = 9.4, 7.2 Hz, 2H), 1.53 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 170.3, 99.8, 61.6, 58.1, 22.2, 15.4, 14.3; IR (neat): 2979, 1744, 1445, 1369, 1282, 1134, 1050, 958 cm<sup>-1</sup>. Elemental analysis: Found: C, 56.56; H, 9.43 %. C<sub>9</sub>H<sub>18</sub>O<sub>4</sub> requires C, 56.82; H, 9.54 %; HRMS (ESI-MS+, m/z): Calc'd: 213.1103 [M+Na]<sup>+</sup>, Found: 213.1105.



**Butyl 2,2-dibutoxypropanoate (DAOA-2)**: Synthesized and isolated following the general procedure. Yield: 101 g, 81.0 %. Distillation conditions: 105 °C, 10 mTorr. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.17 (t, *J* = 6.7 Hz, 2H), 3.51 (dt, *J* = 9.3, 6.8 Hz, 2H), 3.38 (dt, *J* = 9.2, 6.8 Hz, 2H), 1.65 (p, *J* = 8.9, 6.8 Hz, 2H), 1.57 (p, *J* = 8.9, 6.8 Hz, 4H), 1.52 (s, 3H), 1.43–1.34 (m, 6H), 0.93 (t, *J* = 7.3 Hz, 3H), 0.92 (t, *J* = 7.3 Hz, 6H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 170.4, 99.7, 65.3, 62.4, 32.0, 30.7, 22.1, 19.5, 19.2, 14.1, 13.8; IR (neat): 2958, 2934, 2874, 1744, 1460, 1282, 1136, 1069, 1048, 1028 cm<sup>-1</sup>; Elemental Analysis: Found: C, 65.49; H, 11.03. C<sub>15</sub>H<sub>30</sub>O<sub>4</sub> requires C, 65.66; H, 11.02 %; HRMS (ESI-MS+, m/z): Calc'd: 292.2488 [M+NH<sub>4</sub>]<sup>+</sup>, Found: 292.2483.



**Isobutyl 2,2-diisobutoxypropanoate (DAOA-3)**: Synthesized and isolated following the general procedure. Distillation conditions: 95 °C, 20 mTorr. Yield: 168 g, 79.3 % (basis: 68.02 g pyruvic acid). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  3.94 (d, *J* = 6.6 Hz, 2H), 3.28 (dd, *J* = 8.9, 6.8 Hz, 2H), 3.15 (dd, *J* = 8.9, 6.7 Hz, 2H), 1.98 (nonet, *J* = 6.7 Hz, 1H), 1.86 (nonet, *J* = 6.7 Hz, 2H), 1.52 (s, 3H), 0.95 (d, *J* = 6.9 Hz, 6H), 0.92 (d, *J* = 6.6 Hz, 6H), 0.92 (d, *J* = 6.7 Hz, 6H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  170.2, 99.4, 71.2, 68.9, 28.6, 27.7, 22.0, 19.5, 19.1; IR (neat): 2957, 2914, 2875, 1745, 1471, 1367, 1280, 1137, 1040, 988 cm<sup>-1</sup>; Elemental Analysis: Found: C, 68.27; H, 11.60. C<sub>15</sub>H<sub>30</sub>O<sub>4</sub> requires C, 68.31; H, 11.47 %; HRMS (ESI-MS+, m/z): Calc'd: 292.2488 [M+NH<sub>4</sub>]<sup>+</sup>, Found: 292.2473.



**Pentyl 2,2-bis(pentyloxy)propanoate (DAOA-4)**: Synthesized and isolated following the general procedure. Distillation conditions: 145 °C, 20 mTorr. Yield: 106 g, 73.7 % <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  4.16 (t, *J* = 6.7 Hz, 2H), 3.50 (dt, *J* = 9.2, 6.9 Hz, 2H), 3.38 (dt, *J* = 9.2, 6.9 Hz, 2H), 1.73–1.64 (m, 2H), 1.64–1.57 (m, 4H), 1.52 (s, 3H), 1.38–1.28 (m, 12H), 0.90 (m, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  170.4, 99.7, 65.6, 62.7, 29.6, 28.5, 28.4, 28.2, 22.7, 22.4, 22.1, 14.2, 14.1; IR (neat): 2956, 2932, 2873, 1746, 1466, 1282, 1137, 1055 cm<sup>-1</sup>; Elemental Analysis: Found: C, 68.53; H, 11.69. C<sub>18</sub>H<sub>36</sub>O<sub>4</sub> requires C, 68.31; H, 11.47 %; HRMS (ESI-MS+, m/z): Calc'd: 339.2511 [M+Na]<sup>+</sup>, Found: 339.2498.



**Isopentyl 2,2-bis(isopentyloxy)propanoate (DAOA-5):** Synthesized and isolated following the general procedure. Distillation conditions: 140 °C, 30 mTorr. Yield: 116 g, 81.0 %. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.20 (t, *J* = 6.9 Hz, 2H), 3.53 (dt, *J* = 9.2, 7.1 Hz, 2H), 3.40 (dt, *J* = 9.3, 7.1 Hz, 2H), 1.70 (nonet, *J* = 6.7 Hz, 3H), 1.56 (q, *J* = 6.9 Hz, 2H), 1.53–1.46 (m, 7H), 0.92 (d, *J* = 6.6 Hz, 6H), 0.90 (d, *J* = 6.6 Hz, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 170.4, 99.7, 64.2, 61.1, 38.8, 37.4, 25.3, 25.2, 22.8, 22.8, 22.6, 22.1. IR (neat): 2956, 2931, 2872, 1744, 1467, 1368, 1285, 1131, 1064, cm<sup>-1</sup>. Elemental Analysis: Found: C, 68.27; H, 11.60.  $C_{18}H_{36}O_4$  requires C, 68.31; H, 11.47 %; HRMS (ESI-MS+, m/z): Calc'd: 334.2957 [M+NH<sub>4</sub>]<sup>+</sup>, Found: 334.2945.



**Neopentyl 2,2-bis(neopentyloxy)propanoate (DAOA-6)**: Synthesized and isolated following the general procedure, with 24 h total reaction time. Distillation conditions: 110 °C, 15 mTorr. Yield 62.3 g (69.3 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  3.82 (s, 2H), 3.18 (d, *J* = 8.5 Hz, 2H), 3.04 (d, *J* = 8.5 Hz, 2H), 1.52 (s, 3H), 0.97 (s, 9H), 0.93 (s, 18H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  170.4, 99.4, 74.4, 72.1, 31.7, 31.5, 27.0, 26.6, 22.0; IR (neat): 2955, 2906, 2870, 1747, 1479, 1364, 1136, 1048, 1025, 983 cm<sup>-1</sup>; Elemental Analysis: Found: C, 68.26; H, 11.73. C<sub>18</sub>H<sub>36</sub>O<sub>4</sub> requires C, 68.31; H, 11.47 %; HRMS (ESI-MS+, m/z): Calc'd: 339.2511 [M+Na]<sup>+</sup>, Found: 339.2514.



**Hexyl 2,2-bis(hexyloxy)propanoate (DAOA-7)**: Synthesized and isolated following the general procedure. Distillation conditions: 170 °C, 20 mTorr. Yield 135.6 g (83.2 %). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.16 (t, J = 6.7 Hz, 2H), 3.50 (dt, J = 9.2, 6.9 Hz, 2H), 3.38 (dt, J = 9.2, 6.9 Hz, 2H), 1.66 (p, J = 6.9 Hz, 2H), 1.59 (p, J = 7.0 Hz, 4H), 1.52 (s, 3H), 1.40–1.23 (m, 18H), 0.88 (t, J = 6.8 Hz, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 170.4, 99.7, 65.6, 62.7, 31.8, 31.5, 29.9, 28.6, 26.0, 25.7, 22.8, 22.7, 22.1, 14.2, 14.1; IR (neat): 2956, 2929, 2859, 1746, 1465, 1281, 1137, 1063 cm<sup>-1</sup>; Elemental Analysis: Found: C, 70.49; H, 12.03. C<sub>21</sub>H<sub>42</sub>O<sub>4</sub> requires C, 70.34; H, 11.81 %; HRMS (ESI-MS+, m/z): Calc'd: 381.2981 [M+Na]<sup>+</sup>, Found: 381.2982.



**Ethyl 2,2-bis(isopentyloxy)propanoate (DAOA-8)**: Synthesized and isolated following the transesterification procedure, using **DAOA 5** (62.05 g, 0.196 mol) and EtOH (271 g, 339 mL, 5.88 mol). Distillation conditions: 102 °C, 10 mTorr. Yield 40.1 g (75 %) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.24 (q, *J* = 7.1 Hz, 2H), 3.53 (dt, *J* = 9.8, 7.1 Hz, 2H), 3.41 (dt, *J* = 9.6, 7.2 Hz, 2H), 1.76–1.64 (nonet, *J* = 6.5 Hz, 2H), 1.52–1.41 (m, 7H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.90 (d, *J* = 6.7 Hz, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 170.3, 99.7, 61.5, 61.1, 38.8, 25.3, 22.8, 22.1, 14.3. 2956, 2933, 2873, 1745, 1467, 1368, 1133, 1064, 1022, 988 cm<sup>-1</sup>. Elemental Analysis: Found: C, 65.54. H, 11.28. C<sub>15</sub>H<sub>30</sub>O<sub>4</sub> requires C, 65.66; H, 11.02 %; HRMS (ESI-MS+): Calc'd: 297.2042 [M+Na]<sup>+</sup>, Found: 297.2030.



**Isopentyl 2,2-diethoxypropanoate (DAOA-9)**: Synthesized and isolated following the transesterification procedure, using **DAOA 1** (15.0 g, 78.8 mmol) and iPenOH (69.5 g, 85.8 mL, 788 mmol). Distillation conditions: 85 °C, 20 mTorr. Yield 13.3 g (73 %) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  4.25 (t, *J* = 6.9 Hz, 2H), 3.63 (dq, *J* = 9.3, 7.1 Hz, 2H), 3.52 (dq, *J* = 9.3, 7.1 Hz, 2H), 1.74 (nonet, *J* = 6.8 Hz, 1H), 1.58 (q, *J* = 7.1 Hz, 2H), 1.52 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 6H), 0.97 (d, *J* = 6.6 Hz, 6H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  170.3, 99.8, 64.2, 58.1, 37.4, 25.2, 22.6, 22.1, 15.4. IR (neat): 2976, 2960, 2932, 2898, 1745, 1369, 1286, 1134, 1050, 957 cm<sup>-1</sup>; Elemental Analysis: Found: C, 61.93; H, 10.23. C<sub>12</sub>H<sub>24</sub>O<sub>4</sub> requires C, 62.04; H, 10.41 %; HRMS (ESI-MS+, m/z): Calc'd: 255.1572 [M+Na]<sup>+</sup>, Found: 255.1564.



**Sec-butyl 2,2-di-sec-butoxyacetate (DAOA-10):** Synthesized and isolated following the general procedure, using 20.0 g of glyoxylic acid as substrate and racemic 2-butanol. Distillation conditions: 98 °C, 30 mTorr. Isolated and characterized as a mixture of diastereomers. Yield 60.3 g (85.6 %) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.94–4.87 (m, 1H), 4.85 (s, 1H), 3.73–3.60 (m, 2H), 1.71–1.52 (m, 4H), 1.52–1.41 (m, 2H), 1.24 (d, *J* = 6.2 Hz, 3H), 1.20 (d, *J* = 6.2 Hz, 3H), 1.14 (d, *J* = 5.8 Hz, 3H), 0.94–0.85 (m, 9H).<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 168.6, 97.7, 97.2, 97.2, 96.7, 75.8, 75.8, 75.7, 75.6, 73.4, 29.9, 29.8, 29.4, 29.4, 29.3, 28.8, 28.8, 20.1, 20.1, 20.1, 19.7, 19.7, 19.7, 19.6, 19.4, 19.4, 19.4, 10.0, 10.0, 9.9, 9.8, 9.8, 9.6, 9.5, 9.5; IR (neat): 2970, 2935, 2879, 1754, 1735, 1458, 1378, 1288, 1205, 1178, 1103, 1045, 988 cm<sup>-1</sup>. Elemental Analysis: Found: C, 64.58; H, 10.79.  $C_{14}H_{28}O_4$  requires C, 64.58; H, 10.84 %. HRMS: Could not be validated



**Isopentyl 2,2-bis(isopentyloxy)acetate (DAOA-11):** Synthesized and isolated following the general procedure, using 40.0 g of glyoxylic acid as substrate. Distillation conditions: 157 °C, 30 mTorr. Yield 155.6 g, 95.3 %.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  4.86 (s, 1H), 4.21 (t, *J* = 6.9 Hz, 2H), 3.64 (dt, *J* = 9.5, 6.9 Hz, 2H), 3.58 (dt, *J* = 9.5, 6.9 Hz, 2H), 1.78–1.65 (m, *J* = 6.8 Hz, 3H), 1.56 (q, *J* = 6.9 Hz, 2H), 1.51 (q, *J* = 6.8 Hz, 4H), 0.92 (d, *J* = 6.7 Hz, 6H), 0.90 (d, *J* = 6.7 Hz, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  167.9, 98.0, 65.5, 64.1, 38.5, 37.3, 25.1, 25.1, 22.7, 22.7, 22.5. IR (neat): 2956, 2930, 2872, 1756, 1466, 1368, 1202, 1116, 1072 cm<sup>-1</sup>. Elemental Analysis: Found: C,67.7; H, 11.49. C<sub>17</sub>H<sub>34</sub>O<sub>4</sub> requires C, 67.51; H, 11.33 %; HRMS (ESI-MS+, m/z): Calc'd: 303.2535 [M+H]<sup>+</sup>, Found: 303.2527.



**Butyl 3,3-dibutoxybutanoate (DAOA-12)**; Synthesized and isolated following the general procedure, using 80.0 g ethyl acetoacetate as substrate and 8 equiv. of 1-BuOH. Distillation conditions: 145 °C, 30 mTorr. Yield 41.09 g, 23.2 %. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.08 (t, J = 6.7 Hz, 2H), 3.47-3.38 (m, 4H), 2.67 (s, 2H), 1.60 (p, J = 6.9 Hz, 2H), 1.52 (p, J = 6.6 Hz, 4H), 1.48 (s, 3H), 1.37 (m, 6H), 0.93 (d, J=7.1 ppm, 3H) 0.92 (d, J = 7.3 Hz, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 170.0, 99.4, 64.3, 60.4, 43.3, 32.0, 30.7, 22.9, 19.5, 19.2, 14.0, 13.7; IR (neat): 2958, 2934, 2874, 1737, 1460, 1378, 1311, 1224, 1190, 1106, 1071, 1030, 983 cm<sup>-1</sup>; Elemental Analysis: Found: C, 66.44; H, 11.32. C<sub>16</sub>H<sub>32</sub>O<sub>4</sub> requires C, 66.63; H, 11.18 %. HRMS (ESI-MS+, m/z): Calc'd: 311.2198 [M+Na]<sup>+</sup>, Found: 311.2209.



**Isopentyl 3,3-bis(isopentyloxy)butanoate (DAOA-13)**; Synthesized and isolated following the general procedure, using 25 g ethyl acetoacetate as substrate and 9.6 equiv. of iPenOH. Distillation conditions: 170 °C, 30 mTorr. Yield 15.1 g, 27.8 %. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 4.08 (t, J = 6.8 Hz, 2H), 3.55 (dt, J = 9.2, 6.7 Hz, 2H), 3.48 (dt, J = 9.1, 6.8 Hz, 2H), 2.77 (s, 2H), 1.74 (nonet, J = 6.7 Hz, 2H), 1.65 (s, 3H), 1.56 (nonet, J = 6.5 Hz, 1H), 1.49 (q, J = 7.1 Hz, 4H), 1.38 (q, J = 6.9 Hz, 2H), 0.90 (d, J = 6.6 Hz, 6H), 0.80 (d, J = 6.6 Hz, 6H), 0.78 (d, J = 6.6 Hz, 6H). <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>) δ 169.1, 99.6, 62.6, 58.8, 43.2, 38.9, 37.4, 25.1, 24.8, 22.9, 22.6, 22.5, 22.1; IR (neat): 2956, 2930, 2872, 1737, 1467, 1190, 1138, 1112, 1064, 991 cm<sup>-1</sup>; Elemental Analysis: Found: C, 69.16; H, 11.66. C<sub>19</sub>H<sub>38</sub>O<sub>4</sub> requires C, 69.05; H, 11.59 %. HRMS (ESI-MS+, m/z): Calc'd: 353.2668 [M+Na]<sup>+</sup>, Found: 353.2652.



**Diethyl 2,2-diethoxypentanedioate (DAOA-14)**: Synthesized and isolated following the general procedure, using 25 g  $\alpha$ -ketoglutaric acid as substrate and ethanol (20 equiv.). Distillation conditions: 140 °C, 20 mTorr. Yield 6.48 g, 13.7 %. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  4.24 (q, *J* = 7.1 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.55 (dq, *J* = 9.2, 7.1 Hz, 2H), 3.46 (dq, *J* = 9.2, 7.1 Hz, 2H), 2.33–2.25 (m, 2H), 2.25–2.17 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  172.7, 169.0, 101.1, 61.5, 60.5, 58.0, 29.7, 28.7, 15.2, 14.2, 14.2; IR (neat): 2980, 1735, 1446, 1372, 1300, 1177, 1082 cm<sup>-1</sup>; Elemental Analysis: Found: C, 56.55; H, 8.54. C<sub>13</sub>H<sub>24</sub>O<sub>6</sub> requires C, 56.51; H, 8.76 %. HRMS (ESI-MS+, m/z): Calc'd: 299.1471 [M+Na]<sup>+</sup>, Found: 299.1472.



1-(1-(isopentyloxy)ethoxy)-3-methylbutane (**Compound 15**): Acetaldehyde (20.0 g, 0.454 mol), Amberlyst A-15 wet (9.67 g, 0.0206 mol sulfonic acid residue, 4.53 mol%) were combined in a 1 L round-bottomed flask equipped with a magnetic stir bar. With rapid stirring, isopentyl alcohol (500 mL, 4.54 mol, 10.0 equiv.) was added over one minute which caused the flask to become warm. The mixture was stirred overnight at room temperature. The catalyst was removed by gravity filtration, then the reaction mixture was quenched with  $50 \text{ mL} \text{ NaHCO}_3$  (sat., aq.). After layer separation, the organic layer was collected and fractionally vacuum distilled at 15 Torr. The fraction boiling at 80 °C was isolated (74.2 g, 80.8 %).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 4.66 (q, J = 5.3 Hz, 1H), 3.60 (dt, J = 9.3, 6.9 Hz, 2H), 3.43 (dt, J = 9.3, 6.8 Hz, 2H), 1.71 (nonet, J = 6.7 Hz, 2H), 1.46 (q, J = 6.9 Hz, 4H), 1.30 (d, J = 5.3 Hz, 3H), 0.91 (d, J = 6.6 Hz, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 99.8, 63.8, 38.9, 25.2, 22.8, 22.7, 22.0. IR (neat): 2956, 2928, 2871, 1466, 1383, 1367, 1127, 1096, 1068, 986, 919 cm<sup>-1</sup>. Elemental Analysis: Found: C, 70.97; H, 12.97 %. C<sub>12</sub>H<sub>26</sub>O<sub>2</sub> requires C, 71.23; H, 12.95 %; HRMS (ESI-MS+, m/z): Calc'd: 225.1830 [M+Na]<sup>+</sup>, Found: 225.1828.



**2-(bis(isopentyloxy)methyl)furan (Compound 16)**: furfural diisoamyl acetal; Synthesized and isolated following the general procedure, using 30 g of furfural as substrate. Distillation conditions: 140 °C, 30 mTorr. Yield 64.25 g, 80.7 %. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.39 (dd, *J* = 1.9, 0.9 Hz, 1H), 6.42–6.37 (m, 1H), 6.35 (dd, *J* = 3.3, 1.8 Hz, 1H), 5.52 (s, 1H), 3.58 (dt, *J* = 6.8, 2.7 Hz, 2H), 3.53 (dt, *J* = 6.8, 2.7 Hz, 2H), 1.72 (nonet, *J* = 6.7 Hz, 2H), 1.50 (q, *J* = 6.9 Hz, 4H), 0.90 (d, *J* = 6.7, 6H) 0.89 (d, *J* = 6.7, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  152.1, 142.4, 110.1, 108.2, 96.7, 64.3, 38.6, 25.2, 22.8, 22.7. IR (neat): 2956, 2929, 2872, 1467, 1331, 1222, 1150, 1102, 1063, 1003 cm<sup>-1</sup>; Elemental Analysis: Found: C, 71.13; H, 10.56. C<sub>15</sub>H<sub>26</sub>O<sub>3</sub> requires C, 70.83; H, 10.30 %; HRMS (ESI-MS+, m/z): Calc'd: 277.1780 [M+Na]<sup>+</sup>, Found: 277.1767.



**Isopentyl 2-(isopentyloxy)acrylate (Compound 17)**: **DAOA-5** (49.90 g, 0.158 mol) was added to a round bottomed flask containing a magnetic stir bar. 96 %  $H_2SO_4$  (422 µL, 7.88 mmol, 5 mol %) was added dropwise and the flask was heated to 80 °C for 18 h at reduced pressure (15 mTorr). Then, the flask was equipped with a distillation apparatus including an 8" Vigreaux column and fractionally vacuum distilled at 125 °C, 10 mTorr to provide 7.62 g (21.2 %) of a clear, colorless oil, which was suspected to contain the title compound and 3.8 % wt. diisopentyl carbonate, based on NMR and GC-MS identification.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  5.29 (d, J = 2.4 Hz, 1H), 4.58 (d, J = 2.4 Hz, 1H), 4.23 (t, J = 6.8 Hz, 2H), 3.76 (t, J = 6.7 Hz, 2H), 1.83–1.75 (m, 1H), 1.75–1.69 (m, 1H), 1.66 (q, J = 6.7 Hz, 2H), 1.59 (q, J = 6.7 Hz, 2H), 0.94 (d, J = 6.6 Hz, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  163.5, 151.8, 93.6, 67.2, 64.2, 37.4, 37.4, 25.3, 25.3, 22.7, 22.6.









































f1 (ppm)





























## <sup>1</sup>H NMR of unpurified DAOA-5 reaction mixtures

Lack of basic quench is correlated with formation of Compound 17 during heated solvent removal, but no deleterious effect to fuel performance was observed. (see Table S2)

#### Entry 11, Table S2: Description: crude DAOA-5; no quench, volatiles removed at 80°C, 10 mbar, 7 hours

Entry 12, Table S2:, Description: crude DAOA-5; quench NaHCO<sub>3</sub> (sat., aq.) and aqueous separation; volatiles removed at 80°C, 10 mbar, 4 hours



## Kinetic study of DAOA-5 synthesis

**Procedure**: 40 g pyruvic acid, 4 eq. *i*-PenOH (198 mL), 0.05 eq Amberlyst A-15, 200 mL hexanes, 75°C reflux temperature.



**Figure S2**. Top: <sup>1</sup>H NMR data of reaction aliquots in CDCl<sub>3</sub>. Bottom Left: GC-MS data of reaction aliquots. Bottom Right: Water collected in Dean-Stark trap.

## Amberlyst A-15 activity with repeated DAOA-5 synthesis

**Procedure**: In a round-bottomed flask equipped with magnetic stir bar, reflux condenser and Dean–Stark adapter, 1.06 g wet Amberlyst A-15 (5 mol %) was exposed to 50 mL of reagent stock solution containing 1 equiv. pyruvic acid, 5 equiv. *i*-PenOH and hexanes solvent (1:1 v/v relative to *i*-PenOH). The reaction mixture was refluxed at 78°C internal temperature for the specified time. When the reaction period was complete, the reaction mixture was carefully decanted, leaving behind Amberlyst A-15 in the flask, and the solution analyzed by <sup>1</sup>H NMR. Then, the flask was rinsed twice with hexanes and recharged with stock solution, and the process repeated.

 Table S1-Product distribution of DAOA-5 synthesis as a function of Amberlyst reuse number

 a mole ratio calculated by <sup>1</sup>H NMR integration

 0
 0

Me H CH C	venOH Me erlyst A15 i-PenO emp., tark, air (	Oi-Pen Oi-Pen 1)	(2)	O Oi-Pen (3)	<i>i</i> -Pen <sup>∕O</sup> ∖i-Pen (4)
	Catalyst Cycle	Time (h)	1:2:3:4ª	]	
	1	24	96:3:2:0		
	2	20	90:8:2:0		
	3	20	94:5:1:0		
	4	24	95:4:1:0		
	5	24	96:3:1:0		
	6	24	95:3:2:0		
	7	24	93:4:2:0		
	8	24	95:4:2:0		
	9	24	95:4:2:0		
	10	24	95:4:1:0		

 Table S2. Fuel performance repeatability for discrete batches of DAOA-5 isolated during process optimization

	A equiv. <i>i-</i> PenOH B mol % Amberlyst A15	Me
Т ОН О	solvent (vol. eq), reflux, Dean–Stark, air	<i>i-</i> Pen

Entry	Α	В	Solvent	Note	Indicated	Lower Heating
			(vol. eq.)		Cetane Number	Value (MJ/Kg)
1	6.7	5	C <sub>6</sub> H <sub>14</sub> (1)		54.1	32.65
2	6.7	5	"		53.7	32.56
3	6.7	5	"		54.2	32.57
4	6.7	5	"		54.3	32.52
5	6	0.5	"		54.6	32.05
6	6	1.25	"		53.1	32.55
7	4	5	"		54.2	32.50
8	4	1.25	"		53.9	32.54
9	4	0.5	"		54.3	32.54
10	6	5 (H <sub>2</sub> SO <sub>4</sub> )	None		53.4	32.45
11	4	5	C <sub>6</sub> H <sub>14</sub> (1)	Catalyst filtered, excess i-	58.5	31.85
				PenOH + solvent		
				removed, no isolation		
12	4	5	"	basic workup, excess i-	52.6	32.21
				PenOH + solvent		
				removed, no isolation		
13	4	5	"	Product of continuous	53.7	32.48
				stirred flow reaction		

#### Oxidation stability studies

**Description**: 40 mL glass vessels were filled approximately halfway with DAOA samples and were loaded, uncapped, into an air-purged oven maintained at 43°C for several weeks and periodically sampled to determine peroxide concentration and compositional purity. Peroxide value was determined by iodometric titration following American Oil Chemists Society (AOCS) Cd 8b-90<sup>1</sup>, modified for potentiometric endpoint detection, using a Metrohm 809 Titrando automatic titrator with platinum electrode. qNMR was performed in CDCl<sub>3</sub> using p-xylene as internal standard.

**Table S3**. Peroxide concentrations and <sup>1</sup>H NMR purity of neat DAOA compounds as a function of exposed time to 43°C air.

	[Peroxide], 0 wk. (ppm)	[Peroxide], 4 wk. (ppm)	[Peroxide], 6 wk. (ppm)	ASTM-D7545 induction period at 0 wk. (minutes)	NMR purity, t=0 wk. (%)	NMR purity, t=2 wk. (%)	NMR purity, t=4 wk. (%)	NMR purity, t=6 wk. (%)	NMR purity, t=8 wk. (%)
DAOA-1	373	1309	511	15	98.1	95.1	63.7	not meas.	not meas.
DAOA-2	122	202	499	26	97.2	95.9	98.3	98.9	91.2
DAOA-3	75	217	338	30	98.0	99.8	99.9	99.7	97.5
DAOA-5	85	358	667	23	93.7	98.9	94.9	94.5	92.2
DAOA-8	Not meas.	Not meas.	5	39	98.9	98.2	98.7	101	99.9
DAOA-11	117	1250	2211	15	99.7	97.3	89.9	90.6	88.9
Compound 15	211	2516	4751	7	99.6	97.2	94	97.7	90.9
AOA-7	692	1653	3509	12	96.4	96.9	99.4	102	92.4
20 % DAOA-2 + C <sub>16</sub> H <sub>34</sub>	37.4	54.6	93.5	87					
20 % DAOA-3 in C <sub>16</sub> H <sub>34</sub>	24.8	36.7	71.6	101					
20 % DAOA-5									

82

198

in C<sub>16</sub>H<sub>34</sub> C<sub>16</sub>H<sub>34</sub> 23.9

Not meas.

44.8

5.7

100

6.7

**Table S4**. Stabilization of DAOAs-5 and 11 against accelerated oxidation (per ASTM-D7545) with butylated hydroxytoluene (BHT)

BHT concentration	DAOA-5	DAOA-11	Clay-treated diesel
0 ppm	23 min	15 min	73 min

20 ppm	22 min	13 min	Not meas.
100 ppm	27 min	12 min	"
1000 ppm	103 min	20 min	"
5000 ppm	Not meas.	162 min	"

## **Physical Properties**

Water solubility was determined by automated Karl Fischer titration of water-saturated neat DAOA samples using a Mettler Toledo C20S instrument. Water-saturated DAOA samples were prepared by rapid stirring of 1 mL DAOA with 1 mL deionized water in a 4 mL glass vial overnight at room temperature. The layers were allowed to separate and the DAOA layer was extracted using a syringe. Fresh Coulomat AG solution was introduced to the electrochemical cell and pre-titrated until a stable drift value of < 10  $\mu$ g/minute was reached. A 1000 ppm H<sub>2</sub>O standard from a sealed ampoule was titrated in triplicate. Results of the standard sample were generally +/- 5 % of the expected value. Then, the DAOA sample was introduced to the titrator in triplicate following the same method as the standard.

Differential scanning calorimetry measurements were acquired with a Mettler Toledo DSC 3+ instrument and evaluated using STARe software. In an aluminum pan under air, 5-10 mg of neat DAOA was heated between 25 and 350°C at 10°C/minute. T<sub>b</sub> was taken as the x-projection of the most endothermic value. Disopentyl ether, (*i*-Pen<sub>2</sub>O, T<sub>b</sub> = 172-174°C<sup>2</sup>, found 176.3°C) was used to validate the method.

Density was measured by dispensing 1000 uL of DAOA with a calibrated micropipet into a glass vial on a Mettler Toledo XP6 balance with 0.00001 g resolution at 21°C.



Figure S3. Differential scanning calorimetry traces of neat DAOA compounds during heating

Table S5. Flash	points	determined	following	ASTM-D6450 3
-----------------	--------	------------	-----------	--------------

DAOA #	Flash point ( °C)
5	128
11	121

Target value⁵	≥ 52
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**Table S6**: Kinematic viscosities of neat DAOAs and DAOA blends with diesel feedstocks were measured at23°C using a calibrated glass viscometer.

DAOA	Diesel blendstock	% DAOA in	Viscosity (cSt)
		blend	
2	Renewable #2 <sup>a</sup>	20	3.66
2	CARB <sup>b</sup>	20	3.60
2	EPA #2 <sup>c</sup>	20	3.83
2	Diesel #1	20	2.13
2	Renewable #2	50	4.02
2	CARB	50	4.04
2	EPA #2	50	4.16
2	Diesel #1	50	2.75
5	Renewable #2	20	4.21
5	CARB	20	4.07
5	EPA #2	20	4.05
5	Diesel #1	20	2.16
5	Renewable #2	50	4.99
5	CARB	50	4.99
5	EPA #2	50	5.27
5	Diesel #1	50	3.35

<sup>a</sup> see <sup>4</sup>

<sup>b</sup> Meets specifications of California Air Resources Board (CARB)

<sup>c</sup> "Ultra-low" sulfur diesel

**Cloud Point Measurements** were performed using a homebuilt system. Optical elements were purchased from ThorLabs and include 455 nm LED controller (M455F3), sample holder (DFM2B) with custom mounted 1 cm cuvette holder and ~1 cm air gaps between sample and input/output fibers, input (M93L01) and output (M92L02) optical fibers, a silicon photodiode (S120VC) and optical power meter (PM100USB) which interfaces with a recording software (ThorLabs Optical Power Monitor) in real time. The sample holder and optical fibers were held in a Thermotron S1.2 environmental chamber, with the sample holder purged with nitrogen to mitigate moisture condensation (Figure S4). Samples were contained in a 1 cm path length cuvette, and were subjected to either isothermal –60 °C for two hours (to verify cloud point <-60 °C) or ramped from +10 °C to –60 °C at 5°C/hour. Results for diesel blendstocks mixed with DAOA-5 are provided in Table S7.



Diesel blendstock	Neat Cloud Point ( °C)	Blended cloud point, 20 % DAOA-5 ( °C)	Blended cloud point, 50 % DAOA-5 ( °C)
Diesel #1	-53	-54	-51
EPA diesel #2	-17	-16	-13
CARB diesel	-43	-39	-38
Renewable diesel #2	-14	-19	-19

**Table S7.** Cloud point values of DAOA blends with various diesel blendstocks

### References

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