Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Iron-Catalysed Green Synthesis of Carboxylic Esters by Intermolecular Addition of Carboxylic Acids to Alkenes

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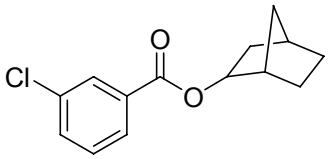
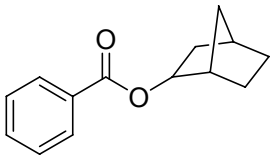
Experimental Section

General. All the catalysts were purchased from Aldrich Chemical Co. and used as received. $Fe(OTf)_3$ was synthesized according to the literature metheod.[1] Dibutyl ether was obtained from Wako Pure Chemical Co. (JAPAN) and was directly used. Catalytic addition reaction was carried out under nitrogen or argon using standard Schlenk techniques. ^1H and ^{13}C NMR spectra were measured on a JEOL LA-400WB superconducting high-resolution spectrometer (400 MHz for ^1H). Reaction products were analyzed by GC using capillary columns; GL Science TC-1 (60 m) on a Shimadzu GC-2010 gas chromatograph equipped with a flame ionization detector (FID) using tetradecane as the internal standard. All the volatile products were also characterized with GC-MS using a HP-5890 gas chromatograph connected to a HP-5971A mass spectrometer (EI 70 eV).

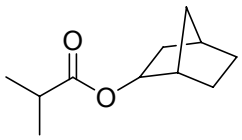
General Procedure for intermolecular addition of carboxylic acids to olefins: To a $Fe(OTf)_3$ (0.2 mmol) in dibutyl ether (20 mL) was added the alkene (10 mmol) and the carboxylic acid (10 mmol) with stirring in a Schlenk tube. After the reaction mixture was heated for 18 h at 80 ^oC, the product was purified by a Japan Analytical Industry Co. LC-250HS recycling preparative HPLC.



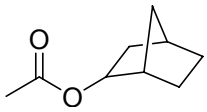
***exo*-3-chloro-benzoic acid bicyclo[2.2.1]hept-2-yl ester.**[2] Colorless oil; ^1H NMR (400 MHz in $CDCl_3$) δ 7.95 (t, J = 1.8 Hz, 1H), 7.88 (tt, J = 7.9 and 1.3 Hz, 1H), 7.49 (qq, J = 9.2 and 1.1 Hz, 1H), 7.34 (t, J = 7.9 Hz, 1H), 4.83 (d, J = 6.8 Hz, 1H), 2.42 (d, J = 4.5 Hz, 1H), 2.32 (s, 1H), 1.78 – 1.83 (m, 1H), 1.43 – 1.63 (m, 4H), 1.12 – 1.23 (m, 3H); ^{13}C NMR (100 MHz in $CDCl_3$) δ 164.8, 134.3, 132.6, 132.5, 129.5, 129.4, 127.5, 78.5, 41.4, 39.5, 35.3, 28.0, 24.1; MS (m/z, EI) 250 $(M)^+$



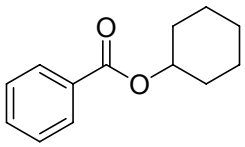
***exo*-benzoic acid bicyclo[2.2.1]hept-2-yl ester.**[3] Colorless oil; ^{1}H NMR (400 MHz in $CDCl_3$) δ 8.01 (d, *J* = 7.7 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.38 – 7.42 (m, 2H), 4.84 (d, *J* = 6.8 Hz, 1H), 2.43 (d, *J* = 4.5 Hz, 1H), 2.32 (s, 1H), 1.79 – 1.83 (m, 1H), 1.46 – 1.64 (m, 4H), 1.10 – 1.22 (m, 3H); ^{13}C NMR (100 MHz in $CDCl_3$) δ 165.9, 132.5, 130.7, 129.3, 128.1, 77.9, 41.4, 39.5, 35.3, 28.2, 24.1; MS (m/z, EI) 216 $(M)^+$



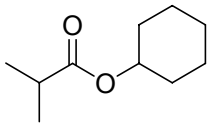
***exo*-isobutyric acid bicyclo[2.2.1]hept-2-yl ester.**[4] Colorless oil; ^{1}H NMR (400 MHz in $CDCl_3$) δ 4.56 (d, *J* = 7.0 Hz, 1H), 2.44 (sept, *J* = 7.1 Hz, 1H), 2.24 (br s, 2H), 1.66 – 1.71 (m, 1H), 1.33 – 1.50 (m, 4H), 1.05 – 1.14 (m, 9H); ^{13}C NMR (100 MHz in $CDCl_3$) δ 176.4, 76.9, 41.2, 39.4, 35.2, 35.0, 33.8, 28.0, 24.1, 18.7; MS (m/z, EI) 182 $(M)^+$



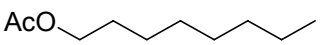
***exo*-acetic acid bicyclo[2.2.1]hept-2-yl ester.**[4] Colorless oil; ^{1}H NMR (400 MHz in $CDCl_3$) δ 4.52 (d, *J* = 6.4 Hz, 1H), 2.21 (br s, 2H), 1.94 (s, 3H), 1.63 – 1.68 (m, 1H), 1.32 – 1.46 (m, 4H), 1.01 – 1.11 (m, 3H); ^{13}C NMR (100 MHz in $CDCl_3$) δ 170.5, 77.4, 41.2, 39.4, 35.2, 35.0, 27.9, 24.1, 21.2;MS (m/z, EI) 154 $(M)^+$



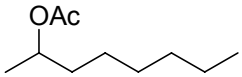
benzoic acid cyclohexyl ester.[5] Colorless oil; ^{1}H NMR (400 MHz in $CDCl_3$) δ 8.04 (d, *J* = 6.7 Hz, 2H), 7.50 (m, 1H), 7.39 (m, *J* = 7.8 Hz, 2H), 5.01 (quint, *J* = 4.0 Hz, 1H), 1.90 (s, 2H), 1.74 (s, 2H), 1.52 – 1.61 (m, 3H), 1.32 – 1.45 (m, 3H); ^{13}C NMR (100 MHz in $CDCl_3$) δ 165.8, 132.5, 130.8, 129.3, 128.1, 72.8, 31.4, 25.3, 23.5; MS (m/z, EI) 204 $(M)^+$



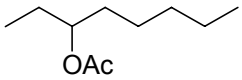
isobutyric acid cyclohexyl ester.[6] Colorless oil; ^{1}H NMR (400 MHz in $CDCl_3$) δ 4.72 (sept, *J* = 4.2 Hz, 1H), 2.45 (quint, *J* = 7.0 Hz, 1H), 1.76 – 1.83 (m, 2H), 1.64 – 1.73 (m, 2H), 1.45 – 1.55 (m, 1H) 1.20 – 1.45 (m, 6H), 1.17 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz in $CDCl_3$) δ 176.4, 71.8, 34.0, 33.6, 31.3, 25.3, 23.5, 18.8, 18.6; MS (m/z, EI) 170 $(M)^+$



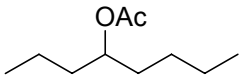
Acetic acid 1-octyl ester.[7] Colorless oil; ^{1}H NMR (400 MHz in $CDCl_3$) δ 4.85 (t, *J* = 6.8 Hz, 2H), 2.02 (s, 3H), 1.55 – 1.65 (m, 2H), 1.20 – 1.35 (m, 10H), 0.86 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz in $CDCl_3$) δ 171.1, 64.6, 31.7, 29.14, 29.11, 28.5, 25.8, 22.6, 20.9, 14.0; MS (m/z, EI) 172 $(M)^+$



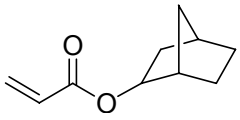
Acetic acid 2-octyl ester.[7] Colorless oil; ^{1}H NMR (400 MHz in $CDCl_3$) δ 4.85 (sext, *J* = 7.1 Hz, 1H), 2.00 (s, 3H), 1.50 – 1.57 (m, 1H), 1.39 – 1.46 (m, 1H), 1.19 – 1.27 (m, 8H), 1.18 (d, *J* = 6.2 Hz, 3H), 0.85 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz in $CDCl_3$) δ 170.5, 70.8, 35.8, 31.6, 29.0, 25.2, 22.5, 21.1, 19.8, 13.9; MS (m/z, EI) 172 $(M)^+$



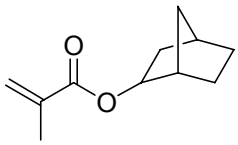
Acetic acid 3-octyl ester.[8] Colorless oil; ^{1}H NMR (400 MHz in $CDCl_3$) δ 4.77 (quint, *J* = 6.2 Hz, 1H), 2.02 (s, 3H), 1.45 – 1.57 (m, 4H), 1.24 (m, 6H), 0.85 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (100 MHz in $CDCl_3$) δ 170.7, 75.3, 33.4, 31.6, 26.8, 24.8, 22.4, 21.0, 13.8, 9.4; MS (m/z, EI) 172 $(M)^+$



Acetic acid 4-octyl ester. Colorless oil; ^{1}H NMR (400 MHz in $CDCl_3$) δ 4.85 (quint, *J* = 6.3 Hz, 1H), 2.01 (s, 3H), 1.44 – 1.51 (m, 4H), 1.26 – 1.33 (m, 6H), 0.84 – 0.89 (m, 6H); ^{13}C NMR (100 MHz in $CDCl_3$) δ 170.7, 73.9, 36.1, 33.7, 27.3, 22.4, 21.0, 18.4, 13.7; MS (m/z, EI) 172 $(M)^+$



***exo*-acrylic acid bicycle[2.2.1]hept-2-yl ester.** Colorless oil; ^{1}H NMR (400 MHz in $CDCl_3$) δ 6.26 (dd, *J* = 1.6 and 17.2 Hz, 1H), 5.99 (dd, *J* = 10 and 17.4 Hz, 1H), 5.68 (dd, *J* = 1.6 and 10.4 Hz, 1H), 4.58 (d, *J* = 8 Hz, 1H), 2.24 (d, *J* = 4.4 Hz, 1H), 2.20 (s, 1H), 1.63 – 1.69 (m, 1H), 1.32 - 1.48 (m, 4H), 0.98 - 1.01 (m, 3H); ^{13}C NMR (100 MHz in $CDCl_3$) δ 165.6, 129.8, 128.9, 77.5, 41.3, 39.4, 35.2, 35.1, 28.0, 24.1; MS (m/z, EI) 166 $(M)^+$



***exo*-methacrylic acid bicycle[2.2.1]hept-2-yl ester.** Colorless oil; ^{1}H NMR (400 MHz in $CDCl_3$) δ 6.00 (m, 1H), 5.44 (m, 1H), 4.61 (d, *J* = 7.2 Hz, 1H), 2.29 (d, *J* = 4.4 Hz, 1H), 2.24 (s, 1H), 1.86 (s, 3H), 1.67 – 1.73 (m, 1H), 1.35 - 1.52 (m, 4H), 1.02 - 1.14 (m, 3H); ^{13}C NMR (100 MHz in $CDCl_3$) δ 166.8, 136.7, 124.6, 77.5, 41.3, 39.4, 35.2, 35.1, 28.0, 24.1, 18.0; MS (m/z, EI) 180 $(M)^+$

Reference:

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