Supplementary Material (ESI) for Green Chemistry

Supplementary Information

Straightforward radical organic chemistry in neat and "on water"

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General Experimental Procedure. All reactions were performed in ultrapure water (Ω 18 MOhm) obtained using Barnstead EASYpure II UF water purification system. The reagents were purchased from Sigma-Aldrich and ABCR, and used as received. In all cases, the aldehydes were purified by distillation. The reactions were performed in test tubes using the Bradley's Carousel Workstation. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded at ambient temperature in $CDCl_3$ on a Bruker Avance-400 spectrometer. The chemical shifts are reported in δ relative to external TMS. Solvent peaks (7.26ppm and 77.00ppm for ^{1}H and ^{13}C NMR spectra, respectively) were used as internal reference. CIMS measurements were recorded on a VG-Autospec M-250 instrument.

General conditions for Hydroacylations.

Mixture of the aldehyde (1.07 mmol) and phenyl vinyl sulfone (0.178 mmol, 6:1 ratio) was stirred with 3 ml of water for 16 hrs at 70^0C in a 50cc glass reactor in air. In case of perfluorooctene a mixture of the aldehyde (2.40 mmol) and olefin (0.40 mmol, 6:1 ratio) were used for the reaction. The organic products were extracted with $CDCl_3$ and the mixture analyzed by NMR spectroscopy.

Analysis of the reaction of:

1a with **2**: ^{1}H NMR: 0.86 (3H, t, *J=7.4Hz,* CH_3), 1.24 (8H, m, $4CH_2$), 1.53 (2H, quin, *J=7.4Hz,* CH_2), 2.41 (2H, t, *J=7.4Hz,* CH_2), 2.89 (2H, t, *J=7.6Hz,* CH_2), 3.37 (2H, t, *J=7.8Hz,* CH_2), 7.56 (2H, t, *J=7.6Hz,* 2CH), 7.65 (1H, t, *J=7.4*), 7.88 (2H, d, *J=7.9,*CH). ^{13}C NMR: 14.0, 22.5, 23.7, 28.9, 29.0, 31.5, 34.8, 42.8, 50.5, 127.9, 129.3, 133.9, 139.0, 206.2. (MH^+) 297.2, (calcd. for $C_{16}H_{24}O_3S$, 296.4).

1b with **2**: ^{1}H NMR: 0.86 (3H, t, *J=7.2Hz,* CH_3), 1.28 (4H, m, $2CH_2$), 1.53 (2H, quin, *J=7.4Hz,* CH_2), 2.40 (2H, t, *J=7.4Hz,* CH_2), 2.88 (2H, t, *J=7.5Hz,* CH_2), 3.36 (2H, t, *J=7.5Hz,* CH_2), 7.56 (2H, t, *J=7.4Hz,* 2CH), 7.66 (1H, t, *J=7.4,*), 7.89 (2H, dd, *J=7.4,1.4, 2*CH). ^{13}C NMR: 13.7, 22.3, 23.3, 31.0, 34.7, 42.6, 50.4, 127.9, 129.3, 133.8, 138.9, 206.2. (MH^+) 269, (calcd. for $C_{14}H_{20}O_3S$, 268).

1c with **2**: ^{1}H NMR: 0.85 (3H, t, *J=7.3Hz,* CH_3), 1.23 (2H, m, CH_2), 1.47 (2H, quin, *J=7.5Hz,* CH_2), 2.39 (2H, t, *J=7.5Hz,* CH_2), 2.86 (2H, t, *J=7.5Hz,* CH_2), 3.36 (2H, t, *J=7.5Hz,* CH_2), 7.55 (2H, t, *J=7.5Hz,* 2CH), 7.64 (1H, t, *J=7.5*), 7.87 (2H, t, *J=7.6, 2*CH). ^{13}C NMR: 13.7, 22.0, 25.6, 34.8, 42.4, 50.4, 127.8, 129.3, 133.8, 138.9, 206.2. (MH^+) 255.1, (calcd. for $C_{13}H_{18}O_3S$, 254.3).

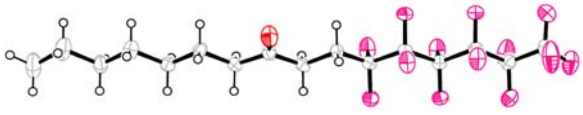
1d with **2**: ^{1}H NMR: 0.85 (3H, t, *J=7.4Hz,* CH_3), 1.53 (2H, sext, *J=7.4Hz,* CH_2), 2.37 (2H, t, *J=7.4Hz,* CH_2), 2.85 (2H, t, *J=7.6Hz,* CH_2), 3.35 (2H, t, *J=7.6Hz,* CH_2), 7.54 (2H, t, *J=7.5Hz,* 2CH), 7.63 (1H, t, *J=7.5*), 7.87 (2H, t, *J=7.5, 2*CH). ^{13}C NMR: 13.5, 16.9, 34.8, 44.5, 50.4, 127.8, 129.3, 133.8, 138.8, 206.0. (MH^+) 241, (calcd. for $C_{12}H_{16}O_3S$, 240.3).

1e with **2**: ^{1}H NMR: 1.20 – 1.81 (10H, m), 2.25 (1H, tt, *J=11.1, 3.6Hz,* CH), 2.94 (2H, t, *J=7.8Hz,* CH_2), 3.37 (2H, t, *J=7.8Hz,* CH_2), 7.57 (2H, t, *J=7.8Hz,* 2CH), 7.66 (2H, t, *J=7.8Hz*, 2CH), 7.90 (1H, d, *J=7.8Hz*, CH). ^{13}C-NMR: δ 25.3, 25.8, 28.8, 33.0, 50.8, 50.9, 128.0, 129.5, 134.0, 139.2, 209.3. (MH^+) 281.1, (calcd. for $C_{15}H_{20}O_3S$, 280.4).

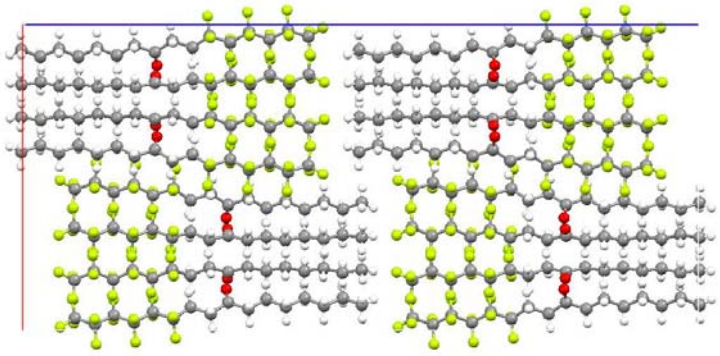
1f with **2**: ^{1}H NMR: 0.80 (3H, t, *J=7.6Hz,* CH_3), 0.84 (3H, t, *J=7.6Hz,* CH_3), 1.11 – 1.58 (8H, m, $4CH_2$), 2.39 (1H, quin, *J=7.6, 5.7Hz* CH), 2.92 (2H, t, *J=7.6Hz,* CH_2), 3.36 (2H, t, *J=7.6Hz,* CH_2), 7.57 (2H, t, *J=7.6Hz,* 2CH), 7.66 (1H, t, *J=7.6*), 7.92 (2H, d, *J=7.6, 2.0Hz*, CH). ^{13}C NMR: 11.6, 13.7, 22.6, 24.4, 29.4, 30.7, 34.1, 50.4, 53.8, 127.8, 129.3, 133.8, 139.0, 209.9. (MH^+) 297.2, (calcd. for $C_{16}H_{24}O_3S$, 296.42).

1a with **3a**: ^{1}H NMR: 0.87 (3H, t, *J=7.0Hz,* CH_3), 1.28 (8H, m, $4CH_2$), 1.59 (2H, quin, *J=7.0Hz,* CH_2), 2.40 (2H, m, CH_2), 2.46 (2H, t, *J=7.5Hz*, CH_2), 2.73 (2H, t, *J=7.5Hz*, CH_2). ^{13}C NMR (selected data): δ 14.0, 22.6, 23.8, 25.1 (t, *J=87Hz)*, 29.1, 29.2, 31.7, 33.1, 42.9, 207.3.^{19}F NMR: -125.3, -122.6, -122.0, -121.0, -113.4 (2F, quin, *J=15Hz,* CF_2), -79.9 (3F, t, *J=10Hz,* CF_3). (MH^+) 475, (calcd. for $C_{16}H_{19}F_{13}O$, 474).

The reaction product has also been characterized by the single crystal X-ray analysis. CCDC-734004 contains the supplementary crystallographic data for this compound.



(**a**)



(**b**)

Molecular view (**a**) and crystal packing along b-axis (**b**) of a molecule of heptyl 2-(perfluorohexyl)ethyl ketone.

Crystal Data:

There are two independent molecules in the asymmetric unit. Chemical Formula $C_{16}H_{19}F_{13}O$, M= 474.31, 0.3 x 0.1 x 0.1 mm^3, colorless prisms, orthorhombic, space group *P bca*, a = 20.5174(9), b = 8.3935(4), c = 45.204(2) Å, α= 90.00, β = 90.00, γ= 90.00°, V = 7784.7(6) $Å^3$, Z = 16, $\rho_{calcd.}$ = 1.619 $g.cm^{-3}$, $2\theta_{max}$ = 25.01°, Nonius KappaCCD, MoKα radiation (λ = 0.71073 Å), graphite monochromator, T = 110(2) K, 6686 collected reflections, 4076 unique reflections (R_{int} = 0.0560). $R1$ = 0.0851, $wR2$ = 0.2474 for data with $I>2\sigma(I)$, and $R1$ = 0.1307, $wR2$ = 0.2768 for all unique data.

1b with **3a**: ^{1}H NMR: 0.87 (3H, t, *J=6.8Hz,* CH_3), 1.29 (4H, m, $2CH_2$), 1.60 (2H, quin, *J=7.6Hz,* CH_2), 2.37 (2H, m, CH_2), 2.44 (2H, t, *J=7.6Hz*, CH_2), 2.70 (2H, t, *J=7.6Hz*, CH_2). ^{13}C NMR (selected data): δ 13.7, 22.4, 23.5, 25.1 (t, *J=87Hz)*, 31.3, 33.0, 42.7, 207.2.^{19}F NMR: -125.8, -122.7, -122.1, -121.1, -113.5 (2F, quin, *J=15Hz,* CF_2), -80.1 (3F, t, *J=10Hz,* CF_3). (MH^+) 447, (calcd. for $C_{14}H_{15}F_{13}O$, 446).
1c with **3a**: ^{1}H NMR: 0.90 (3H, t, *J=7.5Hz,* CH_3), 1.32 (2H, sext, *J=7.5Hz,* CH_2), 1.58 (2H, quin, *J=7.5Hz,* CH_2), 2.36 (2H, m, CH_2), 2.45 (2H, t, *J=7.5Hz*, CH_2), 2.71 (2H, t, *J=7.5Hz*, CH_2). ^{13}C NMR (selected data): δ 13.7, 22.2, 25.1 (t, *J=86Hz)*, 25.8, 33.1, 42.6, 207.4.^{19}F NMR: -126.7, -124.1, -123.4, -122.5, -114.8 (2F, quin, *J=15Hz,* CF_2), -81.5 (3F, t, *J=10Hz,* CF_3). (MH^+) 433, (calcd. for $C_{12}H_{11}F_{13}O$, 432).
1e with **3a**: ^{1}H NMR: 1.20 – 1.88 (10H, m), 2.38 (3H, m, CH, CH_2), 2.75 (2H, t, *J=7.6Hz*, CH_2). ^{13}C-NMR (selected data): δ 25.2, 25.7, 28.6, 31.2, 50.9, 51.1, 210.5.^{19}F NMR: -125.3, -122.6, -122.0, -121.0, -113.4 (2F, quin, *J=15Hz,* CF_2), -79.9 (3F, t, *J=9Hz,* CF_3). (MH^+) 459.1, (calcd. for $C_{15}H_{15}F_{13}O$, 458.3).
1a with **3b**: ^{1}H NMR: 0.76 (3H, t, *J=7.0Hz,* CH_3), 1.18 (6H, m, $3CH_2$), 1.50 (2H, m, CH_2), 2.30 (2H, m, CH_2), 2.35 (2H, t, *J=7.5Hz*, CH_2), 2.61 (2H, t, *J=7.5Hz*, CH_2). ^{13}C NMR (selected data): δ 13.6, 31.4, 32.8, 42.5, 207.0.^{19}F NMR: -125.7, -122.9, -122.2, -121.2, -121.4, -113.8 (2F, quin, *J=15Hz,* CF_2), -80.5 (3F, t, *J=11Hz,* CF_3).
1b with **3b**: ^{1}H NMR: 0.89 (3H, t, *J=7.1Hz,* CH_3), 1.29 (4H, m, $2CH_2$), 1.60 (2H, quin, *J=7.5Hz,* CH_2), 2.36 (2H, m, CH_2), 2.46 (2H, t, *J=7.5Hz*, CH_2), 2.72 (2H, t, *J=7.5Hz*, CH_2). ^{13}C NMR (selected data): δ 13.8, 22.4,

23.5, 25.0, 31.3, 33.1, 42.8, 207.4. ^{19}F NMR: -125.5, -122.8, -122.1, -121.2, -121.0, -113.6 (2F, quin, *J=16Hz,* CF_2), -80.3 (3F, t, *J=10Hz,* CF_3). (MH^+) 547.1, (calcd. for $C_{16}H_{15}F_{17}O$, 546.3).
1e with **3b**: ^{1}H NMR: 1.18 – 1.90 (10H, m, 5CH_2), 2.40 (3H, m, CH_2, CH), 2.75 (2H, t, *J=7.5Hz*, CH_2). ^{13}C NMR (selected data): δ 25.6, 25.7, 28.5, 31.1, 32.9, 50.9, 210.3.^{19}F NMR: -126.2, -123.5, -122.8, -122.0 (4F, br s, 2CF_2), -121.8, -114.3 (2F, quin, *J=14Hz,* CF_2), -80.9 (3F, t, *J=10Hz,* CF_3). (MH^+) 559, (calcd. for $C_{17}H_{15}F_{17}O$, 558.3).
1f with **3b**: ^{1}H NMR: 0.84-0.90 (6H, m, *2*CH_3), 1.18-1.69 (8H, m, 4CH_2), 2.43 (3H, m, CH_2, CH), 2.71 (2H, t, *J=7.5Hz*, CH_2). ^{13}C NMR (selected data): δ 11.8, 13.8, 22.8, 24.7, 29.6, 31.0, 32.8, 54.0, 211.1.^{19}F NMR: -126.5, -123.9, -123.1, -122.3 (4F, br s, 2CF_2), -122.1, -114.7 (2F, quin, *J=15Hz,* CF_2), -81.3 (3F, t, *J=10Hz,* CF_3). (MH^+) 575, (calcd. for $C_{18}H_{19}F_{17}O$, 574.3).
1a with **4**: ^{1}H NMR: 0.88 (3H, t, *J=6.8Hz,* CH_3), 1.30 (8H, m, 4CH_2), 1.64 (2H, quin, *J=7.2Hz,* CH_2), 2.75 (2H, t, *J=7.2Hz*, CH_2), 5.50 (m, CHF). ^{13}C NMR (selected data): δ 14.0, 22.3, 22.5, 28.8 29.7, 31.6, 36.7, 82.7, (d quin, *J=197, 25Hz*, CHF*)*, 198.0 (t, *J=27Hz,* CO).^{19}F NMR: -216.9 (d, *J=39,* CHF*)*, -126.7 (2F, m, CF_2), -125.7 (1F, d, *J=299Hz,)*, -123.8 (1F, m), -123.5 (1F, m), -123.3 (2F, m, CF_2), -122.6 (2F, m), -121.6 (1F, d, *J=303Hz,)*, -121.1 (1F, dq, *J=292.6, 14Hz,)*, -117.1 (1F, d, *J=293Hz,)*, -81.3 (3F, t, *J=12Hz,* CF_3). (MH^+) 529, (calcd. for $C_{16}H_{16}F_{16}O$, 528.3).
1b with **4**: ^{1}H NMR: 0.88 (3H, t, *J=6.8Hz,* CH_3), 1.30 (4H, m, 2CH_2), 1.65 (2H, quin, *J=7.2Hz,* CH_2), 2.74 (2H, t, *J=7.2Hz*, CH_2), 5.49 (m, CHF). ^{13}C NMR (selected data): δ 13.9, 22.4, 23.2, 31.5, 36.6, 82.6, (dquin, *J=198, 24Hz*, CHF*)*, 198.0 (t, *J=28Hz,* CO).^{19}F NMR: -216.5 (d, *J=41,*CHF*)*, -126.7 (2F, m, CF_2), -125.7 (1F, d, *J=296Hz,)*, -123.8 (1F, m), -123.6 (1F, m), -123.4 (2F, m, CF_2), -122.6 (2F, m), -121.3 (1F, d, *J=298Hz)*, -121.1 (1F, dq, *J=293, 13Hz,)*, -117.5 (1F, d, *J=293Hz,)*, -81.8 (3F, t, *J=10Hz,* CF_3).

General conditions for sulfide co-oxidation with cyclohexancarboxaldehyde.
Mixture of cyclohexancarboxaldehyde and sulfide (0.15-0.43 mmol) in a 5:1 ratio was stirred under oxygen atmosphere for 1-4 hrs at RT in a 50 cc round-bottomed flask. The product ratio was analyzed by ^{1}H NMR spectroscopy.

General conditions for alkene co-oxidation with 2-ethylhexanal.
The reactions were performed in a 1 L three-necked round-bottom flask equipped with condenser and septum. To 100 mL of water at pH= 1 (H_2SO_4), 1.8 mL (1.4 gram, 11.5 mmol) of 2-ethylhexanal was added. Oxygen was passed through the mixture under vigorous stirring for 10 min and 1 gram (1.4 mL, 8.9 mmol) of 1-octene was added. The mixture was heated to 60 °C for 1 hr and the reminder of the aldehyde (2.9 gram, 3.7 mL, 23.7 mmol) was slowly added over a 4 hr period. The oxygen was slowly passed above the mixture for 16 hrs. After cooling to room temperature, the organic layer was separated and the aqueous layer was extracted with diethyl ether. The aqueous phase could be recycled in octene co-oxidation. The organic extract was added to the organic layer and dried with $MgSO_4$, giving 5.3 gram of transparent oil. The ^{1}H NMR analysis of the products showed ca. 80% of 1,2-octandiol and 20% of unreacted 1-octene, alone with 2-ethylhexanoic acid. The latter could be extracted by stirring the ether solution of the crude product with saturated aqueous $NaHCO_3$ for 1 hr, followed by the phase separation. The aqueous phase was acidified to neutral pH giving pure 2-ethylhexanoic acid. The ether phase contained 1,2-octandiol, 1-octene and small amounts of products of radical decomposition of 2-ethylhexanal, and can be subjected to column chromatography (silica gel, 50% ethyl acetate – hexane) to give pure 1,2-octandiol.

Propene co-oxidation with 2-ethylhexanal.
In an 80 cc glass pressure vessel, 10 mL of H_2O (pH= 1, H_2SO4) and 0.8mL (5.1 mmol) of 2-ethylhexanal were added. The air was evacuated and 0.5 atm of propene was added via a vacuum line. Oxygen gas was added to the total pressure of 3 atm and the reactor was heated in an oil bath at 60°C for 16 hrs. The reaction mixture was cooled to room temperature, the excess pressure was released and the organic layer was carefully separated giving 0.65 gram (90%) of pure 2-ethylhexanoic acid. The aqueous layer was lyophilized to give pure 1,2-propandiol (40 mg, 36% isolated yield).
When the reaction was performed in D_2O, only 1,2-propandiol was observed in solution by ^{1}H NMR spectroscopy.