Supporting information for:

A Novel Strategy for the Synthesis of ω-Functionalized Perfluoroalkyl Iodides

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General experimental conditions: All structures were verified by one- and two-dimensional NMR experiments using recent assignment strategies that allowed a so called *ab initio* structure determination. Two-dimensional experiments involved both homo- (^{19}F-^{19}F) and hetero-nuclear (^{1}H-^{13}C, ^{19}F-^{13}C) correlations based on the GMQFCOPS and inverse ^{1}H and/or ^{19}F detected GHSQC, GHMQC sequences employing broadband adiabatic ^{13}C-decoupling. The ^{1}H-, ^{13}C- and ^{19}F-NMR measurements were carried out at 30°C in $CDCl_3$ and CD_3COCD_3 on a Varian INOVA-500 spectrometer (operating at 500 MHz for ^{1}H) equipped with a waveform generator, using a ^{1}H{^{13}C,^{15}N} PFG-triple resonance 5mm probe tunable for ^{19}F. ^{1}H and ^{19}F chemical shifts are given relative to δ_{TMS}=0.00 ppm, δ_{CFCl3}=0.00 ppm, where TMS and $CFCl_3$ were used as internal standards. ^{13}C chemical shifts are reported by recording broadband ^{1}H or ^{19}F decoupled spectra and are referenced relative to the solvent ^{13}C-shifts δ_{CDCl3}=77.00 ppm and $\delta_{CD3COCD3}$=29.92 ppm. Both broadband ^{19}F- and ^{13}C-decoupling and bandselective ^{19}F decoupling was performed by adiabatic decoupling using the WURST[1] decoupling sequence. For ^{1}H-^{19}F heteronuclear NOE difference experiments 15 s continuous wave low power preirradiation time was used. GC analyses were performed on a Hewlett-Packard 5890 Series II instrument equipped with a PONA (crosslinked methylsilicone gum, 50 m x 0.2 mm x 0.5 μm) column, using H_2 carrier gas and FID detection.

2.2.3.3.4.4.5.5.6.6.7.7.8.8.9.9-hexadecafluoropentadec-10-en-1-ol, (*Z*+*E*)-**2.** Colorless oil of 93.6 % purity by GC. Analytical data for **2**: *^{1}H-NMR [$(CD_3)_2CO$]:* 0.95 t [H-15:*Z*]; 0.96 t [H-15:*E*]; 1.39–1.47 m [H-14:*Z*+*E*]; 1.63 m [H-13:*Z*]; 1.64 m [H-13:*E*]; 2.49–2.60 m [H-12:*Z*]; 2.56–2.67 m [H-12:*E*]; 4.14 t [H-1:*Z*+*E*]; 5.25 t and 2.91–2.97 s, br (OH and H_2O proton exchange: *Z*+*E*). *^{19}F-NMR [$(CD_3)_2CO$]:* -113.5 tm [F-11:*Z*]; -114.3 m [F-9:*Z*]; -116.4 m [F-9:*E*]; -121.1 → -121.6 m [F-4, F-5, F-6 and F-7:*Z*+*E*]; -121.3 tm [F-2:*Z*+*E*]; -122.8 m [F-3,F-8:*Z*]; -122.9 m [F-3:*E*]; -123.5 m (2F) [F-8:*E*]; -135.8 dm ($^{3}J_{(FF)}$ = 132.6 Hz) [F-11]; -157.7 m [F-10:*Z*]; -172.4 dm ($^{3}J_{(FF)}$ = 132.6 Hz) [F-10:*E*]. *FT-IR (liquid film) ν (cm^{-1})*: 3367 (OH); 2968, 2941 (CH_{as}); 2880 (CH_s); 1724 (C=C); 1213, 1151 (CF). *MS (EI):* (m/z, I, M-X) 550, 6, M; 530, 71, M-HF; 510, 79, M-HF-HF; 500, 100, M-F-CH_2OH; 491, 40, M-HF-HF-F; 471, 23, M-HF-HF-HF-F; 343, 20; 293, 23; 281, 30, M-H$(CH_2)_4$CF=CF$(CF_2)_3$; 231, 37, $(CF_2)_4CH_2OH$; 181, 66, $(CF_2)_3CH_2OH$; 169, 95, H$(CH_2)_4$CF=CFCF_2; 149, 60; 131, 97, $(CF_2)_2CH_2OH$; 119, 88, H$(CH_2)_4$CF=CF. *HR-MS:* 550.06111, $C_{15}H_{12}F_{18}O$, 1.9 ppm.

Ozonation in methanol solvent

Silver 10-hydroxy-2.2.3.3.4.4.5.5.6.6.7.7.8.8.9.9-hexadecafluorodecanoate (4). In a glass reactor with appropriate gas inlet and outlet (*Z*+*E*)-**2** (9.60 g, 17.5 mmol) was dissolved in methanol (100 mL)and cooled to 0 ºC. Dry oxygen gas was bubbled through the system for 30 min, then the ozone generator, operating at a yield of approximately 1 g/h ozone (CAUTION!), was switched on for 5 h. Then reactor was then purged successively with O_2 and N_2 to remove ozone residues. The methanol solution after a 5 h reaction period had the following product ratios (GC integrated areas): **3a**/Bu-COOMe/(*Z*)-**2** = 35:50:12. **3a** and (*Z*)-**2** were identified later. To this mixture KOH (2.60 g, 39.4 mmol) was added in portions and the solution was stirred at room temperature for 2 h. A solution of $AgNO_3$ (4.00 g, 23.5

mmol) in 400 ml distilled water was added to the reaction mixture applying intensive stirring, which was extracted with diethyl ether (2 x 200 mL). The ether phase was washed twice with distilled water, separated, dried over Na_2SO_4 and the solvent was removed by rotary evaporation. The crude product was boiled with isooctane, filtered and dried to obtain **4** as a colorless powder (5.37 g, 53 %). Analytical data for **4**: *^{1}H-NMR [$(CD_3)_2CO$]:* 4.14 t (2H) ($^{3}J_{(HF)}$ = 14.5 Hz) [H-10]. *^{19}F-NMR [$(CD_3)_2CO$]:* -114.1 m (2F) [F-2]; -120.9 m (2F) [F-4]; -121.3 m (6F) [F-9, F-6 and F-5]; -121.5 m (2F) [F-7];-121.7 m (2F) [F-3];-122.9 m (2F) [F-8]. *^{13}C-NMR [$(CD_3)_2CO$]:* 60.0 (C-10); 111.8 (C-2); 112.1 (C-6 and C-5); 112.2 (C-7 and C-3); 112.3 (C-4); 112.6 (C-8); 117.3 (C-9); 162.6 (C-1). *FT-IR (KBr) ν (cm^{-1})*: 1681 ($C=O_{as}$, COOAg); 1613 ($C=O_s$, COOAg); 1203, 1145 (CF).

(*Z*)-2.2.3.3.4.4.5.5.6.6.7.7.8.8.9.9-hexadecafluoropentadec-10-en-1-ol, (*Z*)-2. The solvent of the remaining mother liquor (*vide supra*) was removed and the oily residue was purified by short path distillation collecting the main fraction at a bath temperature of 140-160 ºC (0.1 mmHg) [(*Z*)-**2**, 1.41 g, 15 %, 94.9 % purity by GC]. Analytical data for (*Z*)-**2**: *^{1}H-NMR [$(CD_3)_2CO$]:* 0.95 t (3H) [H-15]; 1.42 m (2H) [H-14]; 1.63 m (2H) [H-13]; 2.54 m (2H) [H-12]; 4.14 t (2H) ($^{3}J_{(HF)}$ = 14.5 Hz); 5.25 t and 2.91–2.97 s, br (-OH and H_2O proton exchange:). *^{19}F-NMR [$(CD_3)_2CO$]:* -113.4 tm (1F) [F-11]; -114.3 m (2F) [F-9]; -121.1 → -121.6 m (8F) [F-4, F-5, F-6 and F-7]; -121.3 tm (2F) [F-2]; -122.8 m (2F) [F-3]; -122.9 m (2F) [F-8]; -157.7 m (1F) [F-10]. *^{13}C-NMR [$(CD_3)_2CO$]:* 13.9 (C-15); 22.6 (C-14); 27.8 (C-12); 28.8 (C-13); 60.6 (C-1); 112.0 (C-3); 112.0, 112.1 and 112.2 (C-4,5,6 and C-7); 112.6 (C-8); 113.0 (C-9); 117.3 (C-2); 135.6 (C-10); 157.8 (C-11). *FT-IR (liquid film) ν (cm^{-1})*: 3372 (OH); 2966, 2941 (CH_{as}); 2880 (CH_s); 1722 (C=C); 1213, 1151 (CF).

Methyl 10-hydroxy-2.2.3.3.4.4.5.5.6.6.7.7.8.8.9.9-hexadecafluorodecanoate (3a). Silver salt **4** (0.300 g, 0.515 mmol) was dissolved in diethyl ether (20 mL) and stirred with iodomethane (0.300 g, 2.11 mmol) for 1 h at room temperature. The AgI precipitate formed during the reaction was filtered off and the solvent residue was removed by rotary evaporation to produce colorless crystalline solid **3a** (0.207 g, 82 %, 98.5 % purity by GC, mp 33-36 ºC).

Analytical data for **4**: *^{1}H-NMR [$(CD_3)_2CO$]:* 4.09 s (3H) [$COOCH_3$]; 4.16 t (2H) ($^{3}J_{(HF)}$=14.5 Hz) [C-10]; 5.27 s, br (1H) [OH]. *^{19}F-NMR [$(CD_3)_2CO$]:* -118.2 m (2F) [F-2]; -121.2 m (2F) [F-4]; -121.3 m (6F) [F-9, F-6 and F-5]; -121.5 m (2F) [F-7];-121.4 m (2F) [F-3];-122.9 m (2F) [F-8]. *^{13}C-NMR [$(CD_3)_2CO$]:* 55.9 ($COO\underline{C}H_3$); 60.7 (C-10); 109.2 (C-2); 111.5 (C-3); 112.0 (C-6, C-5 and C-4); 112.2 (C-7); 112.6 (C-8); 117.3 (C-9); 159.4 (C-1). *FT-IR (KBr) ν (cm^{-1})*: 3432 (OH); 2970 (CH) 1782 (C=O); 1204, 1148 (CF). *MS (EI):* (m/z, I, M-X) 491, 100, M+H; 477, 15; 471, 8, M-F; 460, 11, M-CH_2O; 451, 12, M-F-HF; 131, 15, $(CF_2)_2CH_2OH$; 59, 7, CH_3COO; 31, CH_2OH. *HR-MS:* 490.00708, $C_{11}H_6F_{16}O_3$, 1.9 ppm.

Ozonation in trifluoroethanol solvent

Trifluoroethyl 10-hydroxy-2.2.3.3.4.4.5.5.6.6.7.7.8.8.9.9-hexadecafluorodecanoate (3b). Colorless solid of mp 53-55 ºC. Analytical data for 3b: *^{1}H-NMR [$(CD_3)_2CO$]:* 4.16 t (2H) ($^{3}J_{(HF)}$ = 14.5 Hz) [H-10]; 5.13 s, br (1H) [OH]; 5.19 q (2H) ($^{3}J_{(HF)}$ = 8.5 Hz) [CF_3CH_2]. *^{19}F-NMR [$(CD_3)_2CO$]:* -73.6 m (3F) [CF_3CH_2]; -118.1 m (2F) [F-2]; -121.0 m (2F) [F-4]; -121.2 m (2F) [F-9]; -121.3 m (4F) [F-5 and F-6]; -121.4 m (2F) [F-7]; -122.2 m (2F) [F-3];-123.9 m (2F) [F-8]. *^{13}C-NMR [$(CD_3)_2CO$]:* 60.7 (C-10); 64.2 ($CF_3\underline{C}H_2O$); 109.2 (C-2); 111.4 (C-3); 112.0 (C-4, C-5 and C-6); 112.2 (C-7); 112.6 (C-8); 117.3 (C-9); 123.7 (CF_3); 157.7 (C-1). *FT-IR (KBr) ν (cm^{-1})*: 3001 (CH); 1800 (C=O); 1202, 1144 (CF). *MS (EI):* (m/z, I, M-X) 558, 2, M; 539, 15, M-F; 528, 21, M-CH_2O; 519, 13, M-HF-F; 508, 5, M-CH_2OH-F;

489, 6, M-CF_3; 363, 4; 131, 54, $(CF_2)_2CH_2OH$; 127, 37, CF_3CH_2OOC; 83, 64, CF_3CH_2; 31, 100, CH_2OH. *HR-MS:* 557.98764, $C_{12}H_5F_{19}O_3$, 10 ppm.

Silver(I) 10-hydroxy-2.2.3.3.4.4.5.5.6.6.7.7.8.8.9.9-hexadecafluorodecanoate (4). The treatment of **3b** (5.00 g, 8.96 mmol, 92.0 %) with KOH (0.57 g, 8.63 mmol) in methanol (50 mL) at room temperature, and the isolation of silver salt **4** after the addition of $AgNO_3$ solution (2.50 g, 14.7 mmol in 400 mL distilled water) followed by further purification steps, were carried out the same way as described previously (4.01 g, 77 %).

Silver 10-acetoxy-2.2.3.3.4.4.5.5.6.6.7.7.8.8.9.9-hexadecafluorodecanoate (5). A mixture of **4** (4.45 g, 7.63 mmol) and acetic anhydride (18.5 mL, 20.0 g, 0.196 mol) was heated for 4 h at 100-110 ºC applying by-pass argon flow. The volatile components were removed at the same temperature under reduced pressure (approx. 20 mmHg, then 0.1 mmHg). The residual material was boiled with isooctane, filtered and dried (**5**, 4.61 g, 97 %). Analytical data for **5:** *^{1}H-NMR [$(CD_3)_2CO$]:* 2.16 s (3H) [CH_3]; 4.78 t (2H) ($^3J_{(HF)}$ = 14.5 Hz) [H-10]. *^{19}F-NMR [$(CD_3)_2CO$]:* -114.1 m (2F) [F-2]; -118.9 m (2F) [F-9]; -120.9 m (2F) [F-4]; -121.3 m (6F) [F-7, F-6 and F-5]; -121.7 m (2F) [F-3];-122.8 m (2F) [F-8]. *^{13}C-NMR[$(CD_3)_2CO$]:* 20.2 (CH_3); 60.0 (C-10); 111.7 (C-2); 112.0, 112.1 (C-8, C-7, C6 and C-5); 112.2 (C-3); 112.3 (C-4); 116.1 (C-9); 162.6 (C-1); 169.8 (C=O ester). *FT-IR (KBr) ν (cm^{-1})*: 1760 (C=O ester); 1685 ($C=O_{as}$, COOAg); 1614 ($C=O_s$, COOAg); 1205, 1146 (CF).

9-Iodo-2.2.3.3.4.4.5.5.6.6.7.7.8.8.9.9-hexadecafluorononyl-(1) acetate (6). In a 150 mL volume sealed Pyrex tube the mixture of powdered **6** (4.10 g, 6.56 mmol) and iodine (2.50 g, 9.85 mmol) was heated for 24 h at 100 ºC in an oven. The tube was cooled down to -78 ºC and opened carefully. The organic components were extracted with diethyl ether at room

temperature, and the ether phase was washed with dilute $NaHSO_3$ solution, twice with water, separated and dried over Na_2SO_4. The solvent was removed and the crude product **6** was purified in a short path distillation apparatus (120-140 ºC bath temperature at 0.1 mmHg, 3.08 g, 78 %, 93.2 % purity by GC). Analytical data for **6:** *^{1}H-NMR ($CDCl_3$):* 2.14 s (3H) [CH_3]; 4.57 t (2H) ($^{3}J_{(HF)}$ = 13.5 Hz) [H-1]. *^{19}F-NMR ($CDCl_3$):* -59.4 m (2F) [F-9]; -113.5 m (2F)

[F-8]; -120.0 m (2F) [F-2]; -121.3 m (2F) [F-7]; -122.2 m (2F) [F-5 and F-6]; -122.3 m (2F) [F-4]; -123.8 m (2F) [F-3]. *^{13}C-NMR ($CDCl_3$):* 20.1 (CH_3); 59.5 (C-1); 93.3 (C-9); 108.6 (C-8); 109.9 (C-7); 110.8 (C-5 and C-6); 111.0 (C-3 and C-4); 114.6 (C-2); 169.2 (C=O). *FT-IR (liquid film) ν (cm^{-1})*: 2974 (CH); 1769 (C=O); 1214, 1152 (CF). *MS (EI):* (m/z, I, M-X) 600, 10, M; 581, 4, M-F; 573, 3; 541, 1, M-CH_3COO; 473, 23, M-I; 177, 2, CF_2I; 153, 3; 131, 4; 73, 9; 61, 25; 43, 100, CH_3CO. *HR-MS:* 599.90971, $C_{11}H_5F_{16}IO_2$, 3 ppm.

11-Iodo-2.2.3.3.4.4.5.5.6.6.7.7.8.8.9.9-hexadecafluoro-eicosyl-(1) acetate (7). In a pre-dried, argon purged reaction flask **6** (1.00 g, 1.67 mmol), 1-undecene (0.309 g, 2.0 mmol) and AIBN (0.02 g) were mixed and heated at 75 ºC for 4 h applying by-pass argon flow. The product was purified using short path fractional distillation (bath temperature 170-190 ºC/0.1 mmHg) to obtain oily product **8** (1.12 g, 89 %, GC pure). Analytical data for **7:** *^{1}H-NMR ($CDCl_3$):* 0.88 t (3H) [H-20]; 1.22–1.59 m (14H) [H-13, 14, 15, 16, 17, 18, 19]; 1.72–1.88 m (2H) [H-12]; 2.14 s (3H) [$OCCH_3$]; 2.70–2.98 m (2H) [H-10]; 4.33 m (1H) [H-11]; 4.57 t (2H) ($^{3}J_{(HF)}$ = 14.0 Hz) [H-1]. *^{19}F-NMR ($CDCl_3$):* -112.2 dm (1F) and -114.9 dm (1F) ($^{2}J_{(FF)}$ = 270.2 Hz)

[F-9]; -120.0 m (2F) [F-2]; -122.0 m (2F) [F-7]; -122.3 m (6F) [F-4, F-5 and F-6]; -124.1 m (2F) [F-8];-123.8 m (2F) [F-3]. *^{13}C-NMR ($CDCl_3$):* 14.0 (C-20); 20.1 ($OC\underline{C}H_3$); 20.8 (C-11); 22.6 (C-19); 28.5, 29.3, 29.4, 29.5 and 29.6 (C-13, 14, 15, 16 and C-17); 31.9 (C-18); 40.4

(C-12); 41.8 (C-10); 59.5 (C-1); 110.7 (C-8); 110.9 (C-5 and C-6); 111.0 (C-3 and C4); 111.2 (C-7); 114.6 (C-2); 118.0 (C-9); 169.2 (C=O). *FT-IR (liquid film) ν (cm^{-1})*: 2928 (CH_{as}); 2857 (CH_s); 1770 (C=O); 1212, 1151 (CF). *MS (EI):* (m/z, I, M-X) 754, 95, M; 668, 17, M-C_6H_{14}; 627, 100, M-C_9H_{19}; 585, 30, M-C_9H_{19}-CH_2CO; 571, 49, M-$C_{10}H_{21}$-CH_2CO; 557,25; 528, 19; 85, 30, C_6H_{13}; 71, 20, C_5H_{11}. *HR-MS:* 754.08101, $C_{22}H_{27}F_{16}IO_2$, 1.3 ppm.

[1] Kupče, E.; Freeman, R. *J. Magn. Reson. A* **1995**, 115, 273.