Supplementary Material for Organic & Biomolecular Chemistry

Supporting Materials

Fluorous-Tagging: Enabling Isolation Technique for Indium-Mediated Allylation Reactions in Water

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Experimental

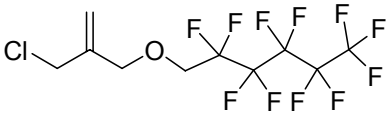
General:

^{1}H NMR, ^{13}C NMR, ^{19}F NMR, GC-MS and IR were performed in the department of Chemistry of Tulane University. ^{1}H NMR spectra were recorded on Varian Unity Inova 400 MHz spectrometer in $CDCl_3$ solution and the chemical shifts were reported in parts per million relative to internal standard (TMS $\delta = 0$). The peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; ddt, doublet of doublet of triplet; t, triplet; m, multiplet. The coupling constants, *J*, are reported in Hertz (Hz). ^{13}C NMR spectra were recorded at 100 MHz and reference to the internal solvent signals (central peak is 77.00 ppm). ^{19}F NMR spectra were recorded at 376 MHz and referenced to the internal standard C_6F_6 signal -164.9. GC-MS data were obtained by Varian Saturn 2100D GC/MS/MS mass spectrometer IR were recorded by FT-IR Perkin Elmer instrument and are reported in reciprocal centimeters (cm^{-1}). F-SPE technique was performed using FluoroFlash® silica gel bonded with perfluorooctylethylsilyl chains, 40μm, 60A particle size from Fluorous Technologies Inc. and flash chromatography was performed using Kiesegel 60, 230-400 mesh purchased from Sorbent Technologies. *1H*, *1H*-Perfluorohexan-1-ol was purchased from Matrix Scientific. All other reagents were purchased from Sigma-Aldrich Co. and used without further purification. All reagents were weighed and handled in air unless otherwise stated. Anhydrous tetrahydrofuran (THF) was obtained by distillation from benzophenone and sodium metal.

Using perfluorinated allyl ether for separation technique:

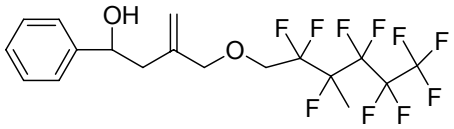
Preparation of 6-(2-Chloromethyl-allyloxy)-1,1,1,2,2,3,3,4,4,5,5-undecafluoro-hexane:

A solution of *1H*, *1H*-perfluorohexan-1-ol (2.4 g, 8 mmol) in dry THF (20 mL) was added slowly over 10 minutes to a stirred solution of sodium hydride (0.23 g, 9.7 mmol) in dry THF (20 mL) at room temperature. The mixture was stirred at room temperature for 30 min after which 3-chloro-2-chloromethyl-1-propene (1.5 g, 12 mmol) was added and allowed to mix for 6 h. The reaction mixture was quenched with ice water and then extracted with diethyl ether (3 x 20 mL). The combined extracts were dried and concentrated in *vacuo* and the residue purified by column chromatography on silica using hexane/diethyl ether (50:1) as eluent to give **1** (1.72 g, 55 %) as a colorless oil.



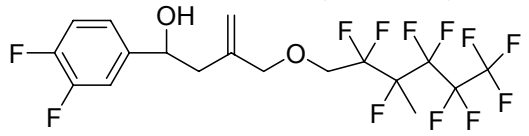
6-(2-Chloromethyl-allyloxy)-1,1,1,2,2,3,3,4,4,5,5-undecafluoro-hexane (1): colorless oil. ^{1}H NMR ($CDCl_3$, 400Hz): δ (ppm) 5.30 (s, 1H), 5.21 (s, 1H), 4.17 (s, 2H), 4.03 (s, 2H), 3.88 (t, J = 14Hz, 2H); ^{13}C NMR ($CDCl_3$, 100Hz): δ (ppm) 140.8, 118.3, 72.8, 67.3 (t, OCH_2, $J_{C\text{-}F}$ = 26 Hz), 44.8 (The chemical shifts of the rest carbons could not clearly be identified due complicated C-F coupling); GC-MS (Relative Intensity): 388 (M^+), 51, 77, 113, 141, 177.

Representative example for allylation of aldehydes with perfluorinated allyl ether: 6-(2-(chloromethyl)allyloxy)-1,1,1,2,2,3,3,4,5,5-decafluoro-4-methylhexane (117 mg, 0.3 mmol), benzaldehyde (0.45 mmol) and 4 mL water were mixed in a test tube followed by the addition of In powder (52 mg, 0.45 mmol). The mixture was stirred at 50 °C in air for 24 h. At the end of the reaction, the aqueous mixture was added to the column and the desired product was eluted with 100 mL 50/50 mixture of acetone/water followed by 20 mL of a 70/30 mixture of acetone/water; and finally an 80/20 mixture of acetone/water eluted the desired product.



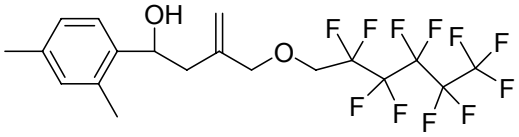
3-(2,2,3,4,4,5,5,6,6,6-Decafluoro-3-methyl-hexyloxymethyl)-1-phenyl-but-3-en-1-ol) (4a): colorless oil.

^{1}H NMR ($CDCl_3$, 400Hz): δ (ppm) 7.38-7.26 (m, 5H), 5.20 (s, 1H), 5.12 (s, 1H), 4.84 (dd, J = 5.2, 8.4 Hz, 1H), 4.12 (d, J = 12 Hz, 1H), 4.03 (d, J =12.4 Hz, 1H), 3.89 (t, J= 12.4 Hz, 2H), 2.52 (dd, J = 4.8, 14.4 Hz, 1H) 2.47 (dd, J = 8.4 12.4 Hz, 1H), 2.27 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.2, 141.4, 128.7, 127.9, 125.9, 117.3, 75.8, 72.8, 66.9 (t, OCH_2, $J_{C\text{-}F}$ = 25.9 Hz), 43.5 (The chemical shifts of the rest carbons could not clearly be identified due complicated C-F coupling).



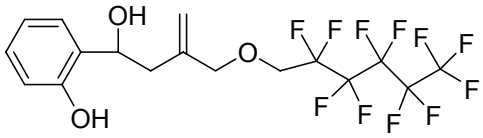
3-(2,2,3,4,4,5,5,6,6,6-Decafluoro-3-methyl-hexyloxymethyl)-1-(3,4-difluoro-phenyl)-but-3-en-1-ol (4b): colorless oil.

^{1}H NMR ($CDCl_3$, 400Hz): δ (ppm) 7.18-7.13 (m, 2H), 6.65-6.59 (m, 3H), 5.80-5.69 (m, 1H), 5.06-4.94 (2H), 3.34-3.29 (m, 2H), 2.85 (s, 3H), 2.29-2.21 (m, 2H); ^{13}C NMR ($CDCl_3$, 100Hz): δ (ppm) 141.2, 140.9, 121.8, 118.2, 117.4, 117.2, 115.0, 114.8, 76.0, 71.7, 67.0 (t, OCH_2, $J_{C\text{-}F}$ = 26 Hz), 43.8 (The chemical shifts of the rest carbons could not clearly be identified due complicated C-F coupling).



1-(2,4-Dimethyl-phenyl)-3-(2,2,3,3,4,4,5,5,6,6,6-undecafluoro-hexyloxymethyl)-but-3-en-1-ol (4c): colorless oil.

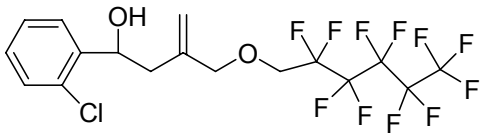
^{1}H NMR ($CDCl_3$, 400Hz): δ (ppm) 7.37 (d, J = 8 Hz, 1 H), 7.04 (d, J = 8 Hz, 1H), 6.95 (s, 1H), 5.20 (s, 1H), 5.15, (s, 1H), 5.04 (dd, J = 4, 9.6 Hz, 1H), 4.18 (d, J = 12 Hz, 1H), 4.06 (d, J =12 Hz, 1H), 3.90 (t, J = 13.6Hz, 2H), 2.46 (dd, J = 3.6, 14.4Hz, 1H), 2.37 (dd, J = 9.2, 14.4 Hz, 1H), 2.32-2.27 (m, 6H), 1.83 (s, 1H); ^{13}C NMR ($CDCl_3$, 100Hz): δ (ppm) 141.9, 139.4, 137.2, 134.4, 131.4, 127.2, 125.2, 117.1, 75.8, 69.1, 66.9 (t, -OCH_2, $J_{C\text{-}F}$ = 26 Hz), 42.2, 21.1, 18.9 (The chemical shifts of the rest carbons could not clearly be identified due complicated C-F coupling); GC-MS (Relative Intensity): 488 (M^+, 1), 471 (10), 171 (60), 135 (100), 107 (80).



2-[1-Hydroxy-3-(2,2,3,3,4,4,5,5,6,6,6-undecafluoro-hexyloxymethyl)-but-3-enyl]-phenol (4d): colorless oil.

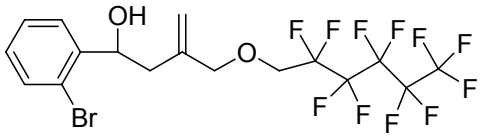
^{1}H NMR ($CDCl_3$, 400Hz): δ (ppm) 8.08 (s, 1H), 7.16(ddd, J = 2, 7.6, 7.2 Hz, 1H), 6.96 (dd, J = 1.6, 7.2 Hz, 1H), 6.86-6.80 (m, 2H), 5.25 (s, 1H), 5.15 (s, 1H), 4.96 (dd, J = 4.4,

9.6 Hz, 1H), 4.13 (d, *J* = 12 Hz, 1H), 4.06 (d, *J* = 11.6 Hz, 1H), 3.93 (dt, *J* = 1.2, 12 Hz, 2H), 3.33 (s, 1H), 2.64 (ddd, *J* = 0.8, 9.6, 14.4 Hz, 1H), 2.56 (ddd, *J* = 0.8, 4.4, 14 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100Hz): δ (ppm) 155.6, 140.8, 129.2, 127.3, 126.7, 120.1, 118.7, 117. 5, 76.1, 74.5, 65.4 (t, OCH2, J_{C-F}=26 Hz), 42.2 (The chemical shifts of the rest carbons could not clearly be identified due complicated C-F coupling).



3-((2,2,3,3,4,4,5,5,6,6,6-Undecafluorohexyloxy)methyl)-1-(2-chlorophenyl)but-3-en-1-ol (4e): colorless oil.

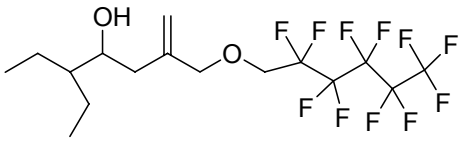
^{1}H NMR ($CDCl_3$, 400Hz): δ (ppm) 7.59 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.32 (dd, *J* = 1.6, 8 Hz, 1H), 7.27 (dd, *J* = 1.2, 7.2 Hz, 1H), 7.19 (ddd, *J* = 1.6, 7.6, 7.6 Hz, 1H), 5.24-5.21 (m, 2 H), 5.15 (s, 1H), 4.15 (dt, *J* = 3.6, 12.4 Hz, 2H), 3.95 (t, *J* = 14 Hz, 2H), 2.63 (dd, *J* = 2, 14.4 Hz, 1H), 2.42 (s, 1H), 2.31 (dd, *J* = 4.8, 9.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100Hz): δ (ppm) 141.5, 141.4, 131.7, 129.6, 128.7, 127.3, 127.1, 117.5, 75.9, 69.5, 67.1 (t, OCH_2, J_{C-F} = 25.1 Hz), 41.8 (The chemical shifts of the rest carbons could not clearly be identified due complicated C-F coupling).



1-(2-Bromo-phenyl)-3-(2,2,3,3,4,4,5,5,6,6,6-undecafluoro-hexyloxymethyl)-but-3-en-1-ol (4f): colorless oil.

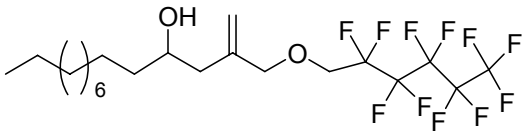
^{1}H NMR ($CDCl_3$, 400Hz): δ (ppm) 7.58 (dd, *J* = 2, 8 Hz, 1H), 7.50 (dd, *J* = 1.2, 8 Hz, 1H), 7.33 (ddd, *J* = 1.2, 7.6, 7.6 Hz, 1H), 7.12 (ddd, *J* = 2, 8, 9.6 Hz, 1H), 5.24 (d, *J* = 0.8 Hz, 1H), 5.17 (s, 1H), 5.16 (dd, *J* = 3.2, 9.6 Hz, 1H), 4.17 (t, *J* = 13.6 Hz, 2H), 3.96 (t, *J* = 12.8 Hz, 2H), 2.64 (dd, *J* = 2.4, 14.4 Hz, 1H), 2.49 (s, 1H), 2.28 (ddd, *J* = 0.4, 9.6, 14.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100Hz): δ (ppm) 143.0, 141.4, 132.8, 129.1, 128.0, 127.4, 121.8, 117.4, 75.9, 71.8, 67.1 (t, OCH_2, J_{C-F} = 25.2 Hz), 41.9 (The chemical shifts of the rest carbons could not clearly be identified due complicated C-F coupling); GC-

MS (Relative Intensity): 538 (M^+), 353 (5), 355 (4), 221 (27), 223 (25), 187 (100), 185 (93), 157(30), 159 (27).



5-Ethyl-2-(2,2,3,3,4,4,5,5,6,6,6-undecafluoro-hexyloxymethyl)-hept-1-en-4-ol (4g): colorless oil.

^{1}H NMR ($CDCl_3$, 400Hz): δ (ppm) 5.17 (s, 1H), 5.09 (s, 1H), 4.16 (d, *J* = 12 Hz, 1H), 4.06 (d, *J* = 12.4 Hz, 1H), 3.91 (dt, *J* = 1.6, 14 Hz, 2 H), 3.77-3.72 (m, 1H), 2.30 (dd, *J* = 2, 14.4 Hz, 1 H), 2.10 (dd, *J* = 10, 14.4 Hz, 1 H), 1.65(s, 1H), 1.45-1.23 (m, 5 H), 0.90 (t, *J* = 7.2, 3 H), 0.89 (t, *J* = 7.2, 3H); ^{13}C NMR ($CDCl_3$, 100Hz): δ (ppm) 142.6, 116.7, 75.8, 71.0, 66.9 (t, OCH_2 $J_{C\text{-}F}$ = 25.1 Hz), 46.9, 38.2, 22.1, 21.6, 11.9, 11.9 (The chemical shifts of the rest carbons could not clearly be identified due complicated C-F coupling)**;** GC-MS (Relative Intensity): 454 (M^+), 354 (25), 137 (100), 95 (27).



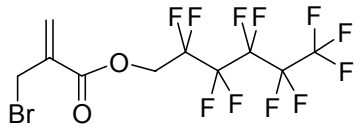
2-(2,2,3,3,4,4,5,5,6,6,6-Undecafluoro-hexyloxymethyl)-tetradec-1-en-4-ol (4h).

^{1}H NMR ($CDCl_3$, 400Hz): δ (ppm) 5.17 (s, 1H), 5.08 (s, 1H), 4.14 (d, *J* = 12 Hz, 1H), 4.06 (d, *J* = 12.4 Hz, 1H), 3.91 (dt, *J* = 1.6, 14 Hz, 2H), 3.74-3.70 (m, 1H), 2.31 (dd, *J* = 2.8, 14.4 Hz, 1H), 2.10 (dd, *J* = 9.2, 14.4 Hz, 1H), 1.72 (s, 1H), 1.46-1.19 (m, 18H), 0.88-0.84 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100Hz): δ (ppm) 142.0, 116.8, 75.9, 69.9, 66.9 (t, OCH_2, $J_{C\text{-}F}$ = 26.7 Hz), 41.7, 37.6, 32.1, 29.8, 29.5, 25.9, 22.9, 14.3 (The chemical shifts of the rest carbons could not clearly be identified due complicated C-F coupling).

Using 2-bromomethyl-acrylic perfluoroester for separation technique

Preparation of 2-Bromomethyl-acrylic acid 2,2,3,3,4,4,5,5,6,6,6-undecafluoro-hexyl ester: 2-(bromomethyl)acrylic acid (5.0 g, 0.03 mol) and *1H*, *1H*-perfluorohexan-1-ol (15.0 g, 0.05 mol) were combined and heated at 50 °C until a complete solution was

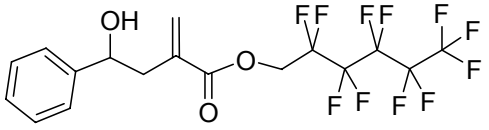
formed. Concentrated sulfuric acid (1.0 g) was then added slowly while mixing and after the completion of addition, the mixture was stirred at 50 °C for 15 min and then the temperature was increased to 130 °C and heated for a 6 h. The product was purified by flash chromatography on silica gel using hexane: ethyl acetate (20:1) and isolated as a colorless oil (8.7 g, 65 % yield).



2-Bromomethyl-acrylic acid 2,2,3,3,4,4,5,5,6,6,6-undecafluoro-hexyl ester (2). colorless oil.

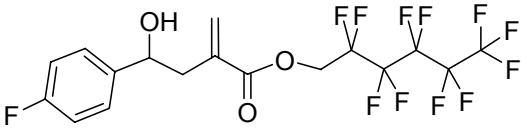
^{1}H NMR (400MHz, $CDCl_3$, TMS) δ (ppm): 6.41 (s, 1H), 6.08 (s, 1H), 4.69 (t, J = 13.6 Hz, 2H), 4.15 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.4, 136.2, 131.4, 60.4 (t, O-CH_2 $J_{C\text{-}F}$= 27.5 Hz), 28.5 (The chemical shifts of the rest carbons could not clearly be identified due complicated C-F coupling)**;** ^{19}F NMR ($CDCl_3$, C_6F_6 -164.9, 376 MHz): δ (ppm) -83.98 (3F), -122.64 (2F), -126.22 (2F), -126.71 (2F), -129.47 (2F); GC-MS m/z (rel. intensity), 447 (M^+, 65), 367 (100), 147 (45); IR (liquid film): v_{max} 3000, 1750 cm^{-1}.

Representative example for the allylation of aldehydes: To a solution of 2-bromomethyl-acrylic acid 2,2,3,3,4,4,5,5,6,6,6-undecafluoro-hexyl ester **2**(135 mg, 0.3 mmol) and benzaldehyde **3a** (48 mg, 0.45 mmol) in 4 mL water, indium powder (52 mg, 0.45 mmol) was added and the mixture was stirred at room temperature in air for 24 h. At the end of the reaction, the crude reaction mixture was added to the column containing FluoroFlash® silica gel and washed with 100 mL of a 50 % mixture of acetone and water. This was followed by 60 mL of a 70/30 mixture of acetone/water. An 80/20 mixture of acetone and water eluted the desired product **5a** in high purity.



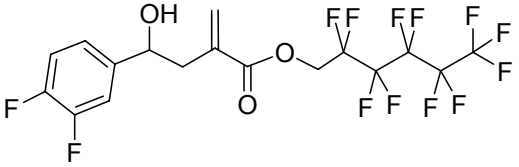
4-Hydroxy-2-methylene-4-phenyl-butyric acid 2,2,3,3,4,4,5,5,6,6,6-undecafluoro-hexyl ester (5a): colorless oil.

^{1}H NMR (400MHz, $CDCl_3$, TMS) δ (ppm): 7.34-7.26 (m, 5H), 6.34 (s, 1H), 5.73 (s, 1H), 4.87 (dd, *J* = 4.4, 8.4 Hz, 1H), 4.68-4.59 (m, 2H), 2.78 (ddd, *J* = 1.2, 4.4, 14Hz, 1H), 2.70 (ddd, *J* = 0.8, 8.4, 14.4Hz, 1H), 2.60 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 143.8, 135.6, 130.9, 128.7, 128.0, 125.9, 73.1, 60.2 (O-CH_2, t, J_{C-F}= 26.7Hz), 42.2 (The chemical shifts of the rest carbons could not clearly be identified due complicated C-F coupling)**;** ^{19}F NMR ($CDCl_3$, C_6F_6 -164.9, 376 MHz): δ (ppm) -83.97(3F), -117.98 (1F), -122.62 (2F), -126.20 (2 F), -129.47; IR (liquid film): ν_{max} 3500-3250, 3050, 2900, 1750 cm^{-1}.



4-(4-Fluoro-phenyl)-4-hydroxy-2-methylene-butyric acid 2,2,3,3,4,4,5,5,6,6,6-undecafluoro-hexyl ester (5b): colorless oil.

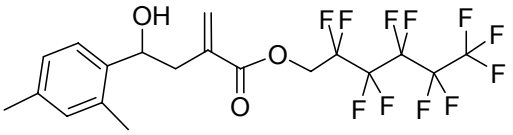
^{1}H NMR (400MHz, $CDCl_3$, TMS) δ (ppm): 7.32-7.28 (m, 2H), 7.04-6.99 (m, 2H), 6.34 (s, 1H), 5.72 (s, 1H), 4.86 (dd, *J* = 4.8, 8.4Hz, 1H), 4.73-4.57 (m, 2H), 2.75 (ddd *J* = 0.8, 4.4, 14Hz, 1H), 2.66 (ddd, *J* = 0.8, 8, 14Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 143.8, 135.6, 130.9, 128.7, 128.0, 125.9, 73.1, 60.2, (O-CH_2, t, J_{C-F}=26.7Hz), 42.2 (The chemical shifts of the rest carbons could not clearly be identified due complicated C-F coupling)**;** ^{19}F NMR ($CDCl_3$, C_6F_6 -164.9, 376 MHz): δ (ppm) -83.97(3F), -117.98 (1F), -122.62 (2F), -126.20 (2 F), -129.47; IR (liquid film): ν_{max} 3500-3250, 2900, 2800, 1750 cm^{-1}.



4-(3,4-Difluoro-phenyl)-4-hydroxy-2-methylene-butyric acid 2,2,3,3,4,4,5,5,6,6,6-undecafluoro-hexyl ester (5c): colorless oil.

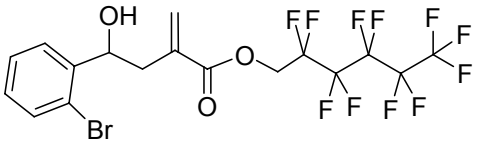
^{1}H NMR (400MHz, $CDCl_3$, TMS) δ (ppm): 7.19-7.06 (m, 2H), 7.04-7.00 (m, 1H), 6.35 (s, 1H), 5.73 (s, 1H), 4.83 (dd, *J* = 4.4, 8.4Hz, 1H), 4.74-4.57 (m, 2 H), 2.74 (ddd, *J* = 0.8, 4, 14Hz, 1H), 2.62 (ddd, *J* = 0.8, 8.4, 14Hz, 1H), 2.51 (s, 1H); ^{13}C NMR (100 MHz,

$CDCl_3$): δ 165.8, 151.8, 151.7, 151.2, 151.1, 149.4, 149.3, 148.7, 148.6, 140.9, 140.8, 140.8, 135.1, 131.4, 121.9, 121.8, 121.8, 121.8, 117.4, 117.3, 114.5, 114.8, 71.9, 60.3 (t, O-CH_2, $J_{C\text{-}F}$ = 27.4 Hz), 42.4 (The chemical shifts of the rest carbons could not clearly be identified due complicated C-F coupling); IR (liquid film): v_{max} 3500-3250, 2900, 2850, 1750, 1550 cm^{-1}.



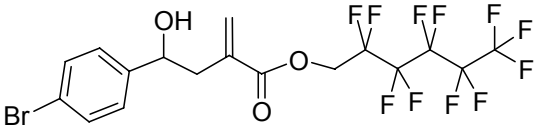
4-(2,4-Dimethyl-phenyl)-4-hydroxy-2-methylene-butyric acid 2,2,3,3,4,4,5,5,6,6,6-undecafluoro-hexyl ester (5d): colorless oil.

^{1}H NMR (400MHz, $CDCl_3$, TMS) δ (ppm): 7.36 (d, *J* = 8Hz, 1H), 7.04-7.00 (m, 1H), 6.95 (s, 1H), 6.36 (s, 1H), 5.80 (s, 1H), 5.07(dd, *J* = 3.6, 9.2Hz, 1H), 4.68-4.59 (m, 2 H), 2.74 (dd, J= 4, 14.4Hz, 1H), 2.60 (dd, *J* = 8.8, 14Hz, 1H), 2.31-2.29 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 139.1, 137.3, 135.8, 134.6, 131.4, 130.8, 127.2, 125.2, 69.1, 60.2 (O-CH_2, t, $J_{C\text{-}F}$ = 26.7Hz), 41.1, 21.1, 19.0 (The chemical shifts of the rest carbons could not clearly be identified due complicated C-F coupling); IR (liquid film): v_{max} 3500-3250, 2900, 1700 cm^{-1}.



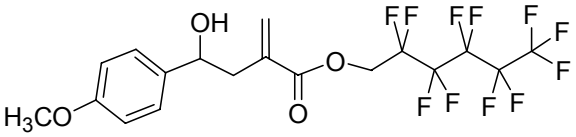
4-(2-Bromo-phenyl)-4-hydroxy-2-methylene-butyric acid 2,2,3,3,4,4,5,5,6,6,6-undecafluoro-hexyl ester (5e): colorless oil.

^{1}H NMR (400MHz, $CDCl_3$, TMS) δ (ppm): 7.53 (dd, *J* = 1.6, 7.6Hz, 1H), 7.50 (dd, *J* = 1.2, 8 Hz, 1H), 7.31 (ddd, *J* = 1.2, 7.6, 7.6 Hz, 1H), 7.11 (ddd, *J* = 1.6, 7.6, 7.6Hz, 1H), 6.33 (d, *J* = 0.8Hz, 1H), 5.76 (d, *J* = 0.8Hz, 1H), 5.23 (d, *J* = 4, 8.4Hz, 1H), 4.64 (t, *J* = 13.2Hz, 2H), 2.85 (ddd, *J* = 0.8, 4, 14.4Hz, 1H), 2.70 (s, 1H), 2.69 (ddd, *J* = 0.8, 8, 14Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 142.6, 135.4, 132.9, 131.0, 129.2, 127.9, 127.6, 122.0, 72.3, 60.3 (t, O-CH_2, $J_{C\text{-}F}$ =27 Hz), 40.1 (The chemical shifts of the rest carbons could not clearly be identified due complicated C-F coupling); IR (liquid film): v_{max} 3500-3250, 3050, 2900, 2850, 1750 cm^{-1}.



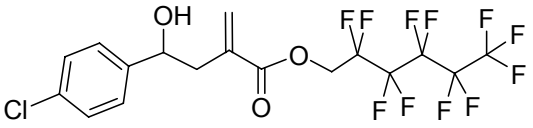
4-(4-Bromo-phenyl)-4-hydroxy-2-methylene-butyric acid 2,2,3,3,4,4,5,5,6,6,6-undecafluoro-hexyl ester (5f): colorless oil.

^{1}H NMR (400MHz, $CDCl_3$, TMS) δ (ppm): 7.46-7.43 (m, 2H), 7.21-7.18 (m, 2H), 6.33 (s, 1H), 5.71 (s, 1H), 4.83 (dd, *J* = 4.4, 8.4Hz, 1H), 4.72-4.56 (m, 2H), 2.74 (ddd, *J* = 0.8, 4.4, 14Hz, 1H), 2.64 (ddd, *J* = 0.8, 8.4, 14Hz, 1H), 2.40 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 142.7, 135.2, 131.8, 131.2, 127.7, 121.7, 72.4, 60.3 (t, O-CH_2, $J_{C\text{-}F}$ = 26.7 Hz), 42.3 (The chemical shifts of the rest carbons could not clearly be identified due complicated C-F coupling); IR (liquid film): v_{max} 3500-3250, 2900, 2800, 1750 cm^{-1}.



4-Hydroxy-4-(4-methoxy-phenyl)-2-methylene-butyric acid 2,2,3,3,4,4,5,5,6,6,6-undecafluoro-hexyl ester (5g): colorless oil.

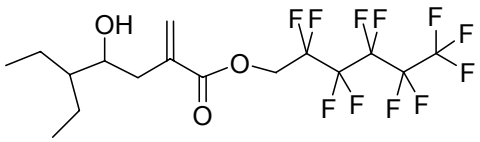
^{1}H NMR (400MHz, $CDCl_3$, TMS) δ (ppm): 7.25-7.23 (m, 2H), 6.86-6.84 (m, 2H), 6.31 (s, 1 H), 5.71 (s, 1H), 4.80 (dd, *J* = 5.6, 7.6Hz, 1H), 4.70-4.55 (m, 2H), 3.78 (s, 3H), 2.73 (dd, *J* = 4.4, 14.8Hz, 1H), 2.69 (dd, *J* = 7.6, 14Hz, 1H), 2.26 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 159.3, 135.9, 135.7, 130.7, 127.2, 114.0, 72.7, 60.2 (t, O-CH_2, $J_{C\text{-}F}$ =26.7Hz), 55.4, 42.1 (The chemical shifts of the rest carbons could not clearly be identified due complicated C-F coupling); IR (liquid film): v_{max} 3500-3250, 2900, 2800, 1750 cm^{-1}.



4-(4-Chloro-phenyl)-4-hydroxy-2-methylene-butyric acid 2,2,3,3,4,4,5,5,6,6,6-undecafluoro-hexyl ester (5h): yellow oil.

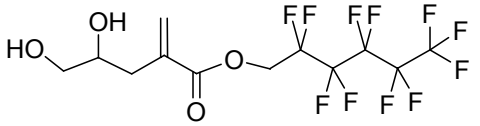
^{1}H NMR (400MHz, $CDCl_3$, TMS) δ (ppm): 7.30-7.23 (m, 4 H), 6.33 (s, 1H), 5.71 (s,

1H), 4.83 (dd, *J* = 4,8, 8.4Hz, 1H), 4.72-4.56 (m, 2H), 2.73 (dd, *J* = 4.8, 14.4Hz, 1H), 2.64 (dd, *J* = 4.8, 14.4Hz, 1H), 2.52 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 142.2, 135.2, 133.6, 131.2, 128.8, 127.3, 72.4, 60.2 (t, O-CH_2, J_{C-F}= 27.5 Hz), 42.3 (The chemical shifts of the rest carbons could not clearly be identified due complicated C-F coupling).



2,2,3,3,4,4,5,5,6,6,6-Undecafluorohexyl 5-ethyl-4-hydroxy-2-methyleneheptanoate: (5i): colorless oil.

^{1}H NMR (400MHz, $CDCl_3$, TMS) δ (ppm): 6.35 (d, *J* = 1.2Hz, 1H), 5.81 (d, *J* = 1.2Hz, 1H), 4.69-4.61 (m, 2H), 3.77-3.71 (m, 1H), 2.58 (ddd, *J* = 1.2, 2.8, 14Hz, 1H), 2.31 (ddd, *J* = 0.8, 10.4, 14.8Hz, 1H), 1.58-1.22 (m, 6H), 0.91(t, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 136.9, 129.9, 71.9, 60.2 (t, O-CH_2, J_{C-F} = 27.4Hz), 47.2, 37.1, 22.1, 21.5, 11.9, 11.8 (The chemical shifts of the rest carbons could not clearly be identified due complicated C-F coupling); IR (liquid film): ν_{max} 3700-3200, 3000-2800, 1800, 1250, 1125 cm^{-1}.



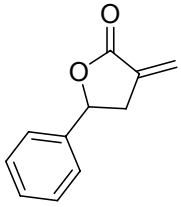
2,2,3,3,4,4,5,5,6,6,6-Undecafluorohexyl 4,5-dihydroxy-2-methylenepentanoate (5j): colorless oil.

^{1}H NMR (400MHz, $CDCl_3$, TMS): δ (ppm) 6.37 (d, *J* = 1.2Hz, 1H), 5.84 (d, *J* = 1.2Hz, 1H), 4.67-4.61 (m, 2 H), 3.86-3.81 (m, 1H), 3.64 (dd, *J* = 3.6, 11.6Hz, 1H), 3.45 (dd, *J* = 6.4, 11.2Hz, 1H), 2.77 (s, 2H), 2.52 (dd, *J* = 4.8, 14.4Hz, 1H), 2.44 (dd, *J* = 8, 14.4Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 135.4, 130.8, 71.0, 66.2, 60.3 (t, O-CH_2, J_{C-F} = 27.4Hz), 36.1 (The chemical shifts of the rest carbons could not clearly be identified due complicated C-F coupling).

Representative example for the preparation of α-methylene-γ-butyrolactones: Diethyl ether (2 mL) was added to 4-hydroxy-2-methylene-4-phenyl-butyric acid 2,2,3,3,4,4,5,5,6,6,6-undecafluoro-hexyl ester **5a** (139 mg, 0.30 mmol) and K_2CO_3 (2.0 mg, 5 mol %) and the solution was stirred at room temperature in air for 24 h. At the end of the reaction the ether was removed, and the residue was diluted with hexane and added on to the column. The desired product **6a** was eluted (with hexane/ethyl acetate= 10: 1) as a white solid (52 mg, 88 %).

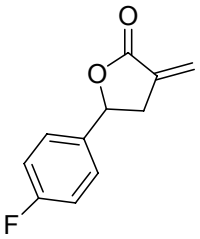
Purification of 6 (a-j)

At the end of the reaction, the ether was removed from the reaction mixture using a rotary evaporator, the residue was diluted with hexane and added onto the column. The desired product was eluted with hexane/ethyl acetate = 10: 1.



3-Methylene-5-phenyl-dihydro-furan-2-one (6a): white solid.

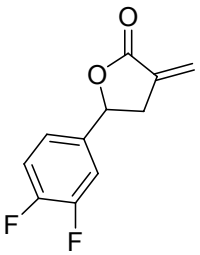
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.39-7.28 (m, 5H), 6.26 (t, *J* = 3.2Hz, 1H), 5.67 (t, *J* = 2.4Hz, 1H), 5.50 (dd, *J* = 6.8, 6.8Hz, 1H), 3.38 (ddt, *J* = 2.8, 8, 17.2Hz, 1H), 2.89 (ddt, *J* = 2.8, 6.4, 17.2Hz, 1H), ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 170.5, 140.0, 134.4, 129.1, 128.8, 125.6, 122.8, 78.2, 36.5.



5-(4-Fluoro-phenyl)-3-methylene-dihydro-furan-2-one (6b): white solid

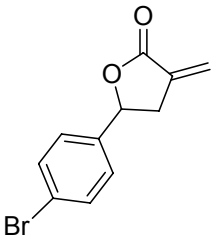
^{1}H NMR (400MHz, $CDCl_3$, TMS) δ (ppm): 7.30-7.24 (m, 2H), 7.07-7.03 (m, 2 H), 6.29 (t, *J* = 2.8Hz, 1H), 5.68 (t, *J* = 2.4Hz, 1H), 5.48 (t, *J* = 7.2Hz, 1H), 3.38 (ddt, *J* = 2.4, 8, 17.2Hz, 1H), 2.86 (ddt, *J* = 2.8, 6.8, 17.2Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm):

170. 2, 164.2, 161.7, 135.8, 135.8, 134.2, 127.6, 127.5, 123.0, 116.2, 115.9, 77.6, 36.5; ^{13}C NMR (100 MHz, d-Acetone): 169.6, 164.0, 161.6, 137.0, 136.9, 135.5, 128.3, 128.2, 121.2, 115.8, 115.6, 77.4, 36.1.



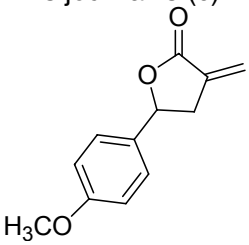
5-(3,4-Difluoro-phenyl)-3-methylene-dihydro-furan-2-one (6c): colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.19-7.10 (m, 2 H), 7.05-7.01(m, 1 H), 6.30 (t, *J* = 2.8Hz, 1H), 5.70 (t, *J* = 2.4Hz, 1H), 5.45 (t, *J* = 7.2 Hz, 1H), 3.39 (ddt, *J* = 2.8, 8, 16.8 Hz, 1H), 2.83 (ddt, *J* = 2.8, 6.8, 17.2Hz, 1H); ^{13}C NMR (100 MHz, d-Acetone) δ (ppm): 169.4, 135.2, 122.9, 122.8, 122.8, 122.8, 121.4, 118.0, 117.8, 115.4, 115.2, 76.8, 36.0; GC-MS (Relative Intensity) 211 (M^+ 1, 12), 68 (100), 39 (50).



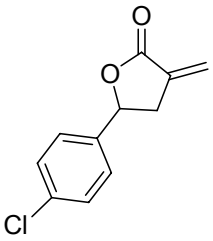
5-(4-Bromo-phenyl)-3-methylene-dihydro-furan-2-one (6f): colorless oil.

^{1}H NMR (400MHz, $CDCl_3$, TMS) δ (ppm): 7.52-7.48 (m, 2H), 7.20-7.16 (m, 2H), 6.30 (t, *J* = 2.8Hz, 1H), 5.69 (t, *J* = 2.4Hz, 1H), 5.46 (t, *J* = 6.8Hz, 1H), 3.39 (ddt, *J* = 8, 17.2, 2.4Hz, 1H), 2.84 (ddd, *J* = 3.2, 9.6, 17.6 Hz, 1H); ^{13}C NMR (100 MHz, d-Acetone): 169.5, 140.3, 135.3, 132.0, 128.0, 122.0, 121.4, 77.3, 36.0.



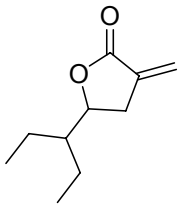
5-(4-Methoxy-phenyl)-3-methylene-dihydro-furan-2-one (6g): white solid.

^{1}H NMR (400MHz, $CDCl_3$, TMS) δ (ppm): 7.20-7.16 (m, 2 H), 6.86-6.82 (m, 2H), 6.23 (t, *J* = 3.2Hz, 1H), 5.62 (t, *J* = 2.8Hz, 1H), 5.41 (t, *J* = 6.8Hz, 1H), 3.74 (s, 3H), 3.29 (ddt, *J* = 2.8, 7.6, 16.8Hz, 1H), 2.85 (ddt, J= 2.8, 6.8, 16.8Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 170.5, 160.0, 134.8, 131.8, 127.3, 122.5, 114.4, 78.3, 55.6, 36.4.



5-(4-Chloro-phenyl)-3-methylene-dihydro-furan-2-one (6h): colorless oil.

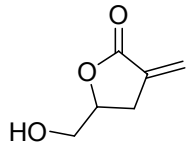
^{1}H NMR (400MHz, $CDCl_3$, TMS) δ (ppm): 7.35-7.31 (m, 2H), 7.25-7.15 (m, 2H), 6.28 (t, *J* = 2.8Hz, 1H), 5.68 (t, *J* = 2.4Hz, 1H), 4.70 (dd, *J* = 6.8, 6.8Hz, 1H), 3.38 (ddt, *J* = 8, 16.8, 2.4Hz, 1H), 2.83 (ddt, *J* = 3.2, 6.4, 17.2Hz, 1H); ^{13}C NMR (100 MHz, d-Acetone): 169.6, 139.8, 135.3, 133.8, 129.0, 127.7, 121.3, 77.3, 36.0; ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 170.2, 138.5, 134.6, 134.0, 129.3, 127.0, 123.1, 77.0, 36.4; GC-MS (Relative Intensity) 211 (M + 2, 32), 209 (M^+, 100), 173 (52), 68 (80), 39 (55).



dihydro-3-methylene-5-(pentan-3-yl)furan-2(3H)-one (6i): colorless oil.

^{1}H NMR (400MHz, $CDCl_3$, TMS) δ (ppm): 6.19 (t, *J* = 2.8Hz, 1H), 5.59 (t, *J* = 2.8Hz, 1H), 4.50-4.45 (m, 1H), 2.96 (ddt, *J* = 2.4, 7.6, 17.2Hz, 1H), 2.65 (ddt, *J* = 2.8, 6.8, 17.2Hz, 1H), 1.49-1.37 (m, 4H), 1.32-1.20 (m, 1H), 0.90 (t, *J* = 7.2Hz, 3 H), 0.89 (t, *J* =

7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 170.8, 135.3, 121.9, 79.4, 45.8, 31.54, 21.2, 21.0, 11.3, 11.0.



Dihydro-5-(hydroxymethyl)-3-methylenefuran-2(3H)-one (6j): colorless oil.

^{1}H NMR (400MHz, $CDCl_3$, TMS) δ (ppm): 6.21(t, *J* = 2.8Hz, 1H), 5.64 (t, *J* = 2.8 Hz, 1H), 4.66-4.60 (m, 1H), 3.88 (dd, *J* = 3.2, 12.8Hz, 1H), 3.62 (dd, *J* = 5.2, 12.8Hz, 1H), 2.96 (ddt, *J* = 2.8, 8.4, 17.2Hz, 1 H), 2.84 (ddt, *J* = 3.2, 5.6, 17.2Hz, 1H), 2.44 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 170.7, 134.4, 122.7, 77.5, 64.4, 29.0.