Sequential Cross-Metathesis / Electrophilic Fluorodesilylation: a Novel Entry to Functionalized Allylic Fluorides

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Supporting Information

General Procedure A: Cross-Metathesis reaction

A solution of starting material **3** (0.3 M) in dichloromethane and allyltrimethylsilane (3 eq.) was heated to reflux under argon. Catalyst **2** (5% mol) was added as a solid (in three portions over 48 hours), the reaction left to reflux for 48 hours, and followed by TLC. The mixture was then concentrated *in vacuo*.

General Procedure B: Electrophilic Fluorodesilylation

A solution of Cross-Metathesis product **4** (0.1 M) in acetonitrile and SelectfluorTM (1eq.) was stirred at room temperature under argon for 2 days. When the reaction was complete the mixture was concentrated *in vacuo*.

Compound 4a: (4-Benzyloxy-but-2-enyl)-trimethyl-silane.

General procedure A was followed, starting from 156 mg of allyloxymethyl-benzene **3a** (1.05 mmol) and 0.5 ml of allyltrimethylsilane in DCM (3ml) using 5% of catalyst **2** (44 mg, 0.05 mmol). Purification by flash column chromatography (3/97: diethylether/hexane) afforded 143 mg of the title compound (E/Z ratio: 4/1) as a white oil (58%). ¹H NMR (400.132 MHz, CDCl₃, ppm) : δ 0.02 and 0.03 (9H, 2s, Si(Me)₃), 1.53 (2H, d, J = 8.4 Hz, CH₂, H₁), 3.98 (1.6H, d, J = 6.6 Hz, H_{4trans}), 4.05 (0.4H, d, J = 5.9 Hz, H_{4cis}), 4.51 and 4.53 (2H, 2s, -O-CH₂-Ph), 5.47 (0.8H, dddm, J = 15.2 Hz, J = 6.8 Hz, J = 5.9 Hz, H_{2trans}), 5.54 (0.2H, m, H_{2cis}), 5.70 (1H, m, H₂), 7.36-7.59 (5H, m, H_{arom}). ¹³C NMR (100.624 MHz, CDCl₃, ppm) : δ -1.9 (CH₃, Si(Me)₃), 22.9 (CH₂, C₁), 71 (CH₂, C₄ or -CH₂-Ph), 71.3 (CH₂, C₄ or -O-CH₂-Ph), 123.6 (CH, C_{2cis}), 124.7 (CH, C_{2trans}), 127.5 (CH, C_{arom para}), 127.7 (CH, C_{arom ortho}), 128.3 (CH, C_{arom meta}),

130.0 (CH, C_{3cis}), 131.9 (CH, C_{3trans}), 138.6 (CH, C_{arom} IPSO). MS (GCT, CI⁺): *m/z* (relative intensity %) 252 [M+NH₄]⁺ (100). HRMS (GCT, CI⁺): Calc for C₁₄H₂₆NOSi: 252.1784, found 252.1781.

Compound 4b: Benzoic acid 4-trimethylsilylbut-2-enyl ester. General procedure A was followed, starting from 162 mg of benzoic acid allyl ester **3b** (1 mmol) and 0.48 ml of allyltrimethylsilane in DCM (3ml) using 5% of catalyst **2** (42 mg, 0.05 mmol). Purification by flash column chromatography (2/98: diethylether/hexane then 5/95: diethylether/hexane) afforded 208 mg of the title compound (E/Z ratio: 4/1) as an oil (84%). ¹H NMR (400.132 MHz, CDCl₃, ppm) : δ 0.05 and 0.06 (9H, 2s, Si(Me)₃), 1.55 (1.6H, d, J = 4.5 Hz, H_{4trans}), 1.65 (0.4H, d, J = 4.3 Hz, H_{4cis}), 4.76 (1.6H, d, J = 6.8 Hz, H_{1trans}), 4.94 (0.4H, d, J = 6.6 Hz, H_{1cis}), 5.57 (1H, m, H₂), 5.77 (0.2H, q, J = 6.7 Hz, H_{3cis}), 5.90 (0.8, dt, J = 16.0 Hz, J = 8.0 Hz, H_{3trans}), 7.44 (2H, t, J = 7.6 Hz, H_{arom meta}), 7.55 (1H, m, H_{arom para}), 8.06 (2H, m, H_{arom ortho}). ¹³C NMR (100.624 MHz, CDCl₃, ppm) : δ -2.0 (CH₃, Si(Me)₃), 19.3 (CH₂, C₄), 23.1 (CH₂, C₄), 60.7 (CH₂, C₁), 66.1 (CH₂, C₁), 120.7 (CH, C_{2cis}), 122.1 (CH, C_{2trans}), 128.3 (CH, C_{arom meta}), 129.6 (CH, C_{arom ortho}), 131.0 (CH, C_{arom IPSO}), 132.1 (CH, C_{3cis}), 132.7 (CH, C_{3trans}), 134.1 (CH, C_{arom para}), 166.5 (CO). MS (GCT, CI⁺): *m/z* (relative intensity %) 179 [M-CH₂SiMe₃+NH₄]⁺ (100), 248 [M]⁺ (5). HRMS (GCT, CI⁺): Calc for C₁₄H₂₀O₂Si: 248.1233, found 248.1238.

Compound 4c: Benzoic acid 7-trimethylsilylhept-5-enyl ester. General procedure A was followed, starting from 449 mg of benzoic acid hex-5-enyl ester **3c** (2.36 mmol) and 1.12 ml of allyltrimethylsilane in DCM (6ml) using 5% of catalyst **2** (100 mg, 0.17 mmol). Purification by flash column chromatography (2/98: diethylether/hexane) afforded 370 mg of the title compound (E/Z ratio: 5/1) as a white oil (54%). ¹H NMR (400.132 MHz, CDCl₃, ppm) : δ -0.01 and 0.00 (9H, 2s, Si(Me)₃), 1.41 (2H, d, J = 7.6 Hz, H₇), 1.50 (2H, tt, J = 7.6 Hz, J = 7.6 Hz, H₃), 1.78 (2H, tt, J = 6.8 Hz, J = 6.8 Hz, H₂), 2.06 (1.66H, q, J = 7.2 Hz, H_{4trans}), 2.16 (0.33H, q, J = 6.8 Hz, H_{4cis}), 4.32 (2H, t, J = 6.4 Hz, H₁), 5.25 (0.83H, dt, J = 15.1 Hz, J = 7.6 Hz, H_{6trans}), 5.27 (0.16H, m, H_{6cis}), 5.42 (0.83, dt, J = 15.1 Hz, J = 7.2 Hz,

H_{5trans}), 5.45 (0.16H, m, H_{5cis}), 7.45 (2H, t, J = 8.0 Hz, H_{arom meta}), 7.56 (1H, m, H_{arom para}), 8.05 (2H, dm, J = 7.2 Hz, H_{arom ortho}). ¹³C NMR (100.624 MHz, CDCl₃, ppm) : δ -2.0 and -1.8 (CH₃, Si(Me)₃), 22.6 (CH₂, C₇), 26.3 (CH₂, C₃), 28.1 (CH₂, C₂), 32.3 (CH₂, C₄), 65.8 (CH₂, C₁), 126.8 (CH, C₆), 128.1 (CH, C₅), 128.3 (CH, C_{arom meta}), 129.5 (CH, C_{arom ortho}), 130.5 (CH, C_{arom ipso}), 132.8 (CH, C_{arom para}), 166.7 (CO). MS (GCT, Cl⁺): *m/z* (relative intensity %) 291 [M+H]⁺ (100). HRMS (GCT, Cl⁺): Calc for C₁₇H₂₇O₂Si: 291.1780, found 291.1774.

Compound 4d: 5-Trimethylsilanyl-pent-3-enoic acid

benzyl ester. General procedure A was followed, starting from 217 mg of but-3-enoic acid phenyl ester **3d** (1.23 mmol) and 0.59 ml of allyltrimethylsilane in DCM (3ml) using 5% of catalyst **2** (52 mg, 0.06 mmol). Purification by flash column chromatography (5/95: diethylether/hexane) afforded 265 mg of the title compound (E/Z ratio: 3/1) as a white oil (82%). ¹H NMR (400.132 MHz, CDCl₃, ppm) : δ -0.02 and 0.03 (9H, 2s, Si(Me)₃), 1.46 (1.5H, d, J = 12.7 Hz, H_{5trans}), 1.52 (0.5H, d, J = 9.4 Hz, H_{5cis}), 3.10 (1.5H, d, J = 6.9 Hz, H_{2trans}), 3.13 (0.5H, d, J = 7.1 Hz, H_{2cis}), 5.15 (1.5H, s, -O-CH₂-Ph), 5.16 (0.5H, s, -O-CH₂-Ph), 5.40 (1H, m, H₄), 5.58 (0.75, dt, J = 15.2 Hz, J = 7.6 Hz, H_{3trans}), 5.65 (0.25H, dm, J = 10.8 Hz, H_{3cis}), 7.34 (5H, m, H_{arom}). ¹³C NMR (100.624 MHz, CDCl₃, ppm) : δ -2.0 and -1.8 (CH₃, Si(Me)₃), 18.8 and 22.9 (CH₂, C₅), 32.8 and 38.3 (CH₂, C₂), 66.3 (CH₂, O-CH₂-Ph), 118.2 (CH, C_{4cis}), 119.6 (CH, C_{4trans}), 128.2 and 128.5 (3CH, C_{arom ortho-meta-para}), 129.4 (CH, C_{3cis}), 131.2 (CH, C_{3trans}), 136.0 (CH, C_{arom ipso}), 172.0 (CO). MS (GCT, Cl⁺): *m/z* (relative intensity %) 280 [M+NH₄]⁺ (20), 263 [M+H]⁺ (100). HRMS (GCT, Cl⁺): Calc for C₁₅H₂₃O₂Si: 263.1467, found 263.1461.

Compound 4e: Methyl-(4-trimethylsilanyl-but-2-

enyl)-carbamic acid *tert*-butyl ester. General procedure A was followed, starting from 171 mg of Allyl-methyl-carbamic acid *tert*-butyl ester **3e** (1 mmol) and 0.48 ml of allyltrimethylsilane in DCM (3ml) using 5% of catalyst **2** (42 mg, 0.05 mmol). Purification by flash column chromatography (10/90: diethylether/hexane) afforded

180 mg of the title compound (E/Z ratio: 9/1) as a white oil (70%). ^1H NMR (400.132 MHz, CDCl_3 , ppm) : δ 0.00 and 0.01 (9H, 2s, $\text{Si}(\text{Me})_3$), 1.48 (11H, brs, H_4 and $(\text{CH}_3)_3\text{C-O-}$), 2.78 (2.7H, s, N-CH_3 trans), 2.80 (0.3H, s, N-CH_3 cis), 3.74 (1.8H, d, $\text{J} = 4.8$ Hz, $\text{H}_{1\text{trans}}$), 3.82 (0.2H, d, $\text{J} = 2.4$ Hz, $\text{H}_{1\text{cis}}$), 5.23 (0.9H, dt, $\text{J} = 15.4$ Hz, $\text{J} = 6.4$ Hz, $\text{H}_{3\text{trans}}$), 5.28 (0.1H, dm, $\text{J} = 10.8$ Hz, $\text{H}_{3\text{cis}}$), 5.54 (0.9H, dt, $\text{J} = 15.5$ Hz, $\text{J} = 8.4$ Hz, $\text{H}_{2\text{trans}}$), 5.58 (0.1H, m, $\text{H}_{2\text{cis}}$). ^{13}C NMR (100.624 MHz, CDCl_3 , ppm): δ -2.0 and -1.8 (CH_3 , $\text{Si}(\text{Me})_3$), 18.8 (CH_2 , C_4), 22.6 (CH_2 , C_1), 28.4 (3 CH_3 , $(\text{CH}_3)_3\text{C-O-}$), 33.2 (CH_3 , N-CH_3), 79.1 ($(\text{CH}_3)_3\text{C-O-}$), 123.5 (2CH, C_2 and C_3), 155.7 (CO). MS (GCT, Cl^+): m/z (relative intensity %) 202 [$\text{M-SiMe}_3+\text{NH}_4$] $^+$ (100), 258 [M+H] $^+$ (7). HRMS (GCT, Cl^+): Calc for $\text{C}_{13}\text{H}_{28}\text{NO}_2\text{Si}$: 258.1889, found 258.1881.

Compound 4f: 2-(4-Trimethylsilanyl-but-2-enyl)-isoindole-1,3-dione. General procedure A was followed, starting from 187 mg of 2-Allyl-isoindole-1,3-dione **3f** (1 mmol) and 0.48 ml of allyltrimethylsilane in DCM (3ml) using 5% of catalyst **2** (42 mg, 0.05 mmol). Purification by flash column chromatography (15/85: diethylether/hexane) afforded 243 mg of the title compound (E/Z ratio: 3/1) as a white solid (89%). ^1H NMR (400.132 MHz, CDCl_3 , ppm) : δ -0.02 and 0.04 (9H, 2s, $\text{Si}(\text{Me})_3$), 1.44 (1.5H, d, $\text{J} = 8.5$ Hz, $\text{H}_{4'\text{trans}}$), 1.73 (0.5H, d, $\text{J} = 8.9$ Hz, $\text{H}_{4'\text{cis}}$), 4.22 (1.5H, d, $\text{J} = 6.6$ Hz, $\text{H}_{1'\text{trans}}$), 4.27 (0.5H, d, $\text{J} = 6.0$ Hz, $\text{H}_{1'\text{cis}}$), 5.40 (1H, m, $\text{H}_{3'}$), 5.62 (0.25H, dt, $\text{J} = 7.7$ Hz, $\text{J} = 7.6$ Hz, $\text{H}_{2'\text{cis}}$), 5.78 (0.75H, dt, $\text{J} = 15.2$ Hz, $\text{J} = 8.2$ Hz, $\text{H}_{2'\text{trans}}$), 7.70 (2H, dd, $\text{J} = 5.6$ Hz, $\text{J} = 3.2$ Hz, $\text{H}_{\text{arom } 6 \text{ and } 7}$), 7.83 (2H, dd, $\text{J} = 5.6$ Hz, $\text{J} = 3.2$ Hz, $\text{H}_{\text{arom } 5 \text{ and } 8}$). ^{13}C NMR (100.624 MHz, CDCl_3 , ppm) : δ -2.3 and -2.0 (CH_3 , $\text{Si}(\text{Me})_3$), 18.9 (CH_2 , $\text{C}_{4'}$), 22.7 (CH_2 , $\text{C}_{4'}$), 34.7 (CH_2 , $\text{C}_{1'}$), 39.9 (CH_2 , $\text{C}_{1'}$), 120.5 (CH, $\text{C}_{3'\text{cis}}$), 121.3 (CH, $\text{C}_{3'\text{trans}}$), 130.8 (CH, $\text{C}_{2'\text{cis}}$), 132.2 (CH, $\text{C}_{2'\text{trans}}$), 132.3 (2 C_{arom} , C_4 and C_9), 133.8 (2 C_{arom} , C_5 and C_8), 168.0 (CO). mp: 92-93°C. MS (GCT, Cl^+): m/z (relative intensity %) 274 [M+H] $^+$ (100). HRMS (GCT, Cl^+): Calc for $\text{C}_{15}\text{H}_{20}\text{NO}_2\text{Si}$: 274.1263, found 274.1255.

Compound 4g: 6-Trimethylsilanyl-hex-4-en-3-one. A solution of 0.16 ml of allyltrimethylsilane (1 mmol) and 0.3 ml of ethylvinyl ketone

3g (3 eq.) in dichloromethane (4 ml) was heated to reflux under argon. Catalyst **2** (42 mg, 0.05 mmol) was then added as a solid (in three portions over 48 hours) and the reaction left to reflux for 48 hours. The mixture was then concentrated *in vacuo*. Purification by flash column chromatography (4/96: diethylether/hexane then 6/94: ether/hexane) afforded 106 mg of the title compound (E>95 %) as an oil (62%). Spectroscopic data are in accordance with literature.^{8e}

Compound 4h: (3-[1,3]Dioxalan-2-yl-allyl)trimethyl-silane.

General procedure A was followed, starting from 1 ml of 2-Vinyl-[1,3]dioxalane **3h** (1 mmol) and 0.48 ml of allyltrimethylsilane in DCM (3ml) using 5% of catalyst **2** (42 mg, 0.05 mmol). Purification by flash column chromatography (4/96: diethylether/hexane) afforded 140 mg of the title compound (E>95 %) as an oil (75%). ¹H NMR (400.132 MHz, CDCl₃, ppm) : δ 0.03 (9H, s, Si(Me)₃), 1.55 (2H, dd, J= 8.4 Hz, J= 1.6 Hz, H₁), 3.88 and 4.00 (4H, 2m, -O-CH₂-CH₂-O-), 5.18 (1H, d, J= 6.8 Hz, -O-CHR-O-), 5.33 (1H, ddt, J= 15.2 Hz, J= 6.8 Hz, J= 1.6 Hz, H₃), 5.93 (1H, dt, J= 15.2 Hz, J= 8.4 Hz, H₂). ¹³C NMR (100.624 MHz, CDCl₃, ppm): δ -2.0 CH₃, Si(Me)₃, 23.1 (CH₂, C₁), 64.8 (2CH₂, -O-CH₂-CH₂-O-), 104.7 (CH, -O-CHR-O-), 124.5 (CH, C₂), 134.9 (CH, C₃). MS (GCT, CI⁺): *m/z* (relative intensity %) 187 [M+H]⁺ (100). HRMS (GCT, CI⁺): Calc for C₉H₁₉O₂Si: 187.1154, found 187.1155.

Compound 4i: Benzoic acid 3-methyl-5-trimethylsilanyl-pent-3-enyl ester. A solution of 190 mg of Benzoic acid 3-methyl-but-3-enyl ester **3i** (1 mmol) and 0.48 ml of allyltrimethylsilane in dichloromethane (3 ml) was heated to reflux under argon. Catalyst **2** (85 mg, 0.1 mmol) was then added as a solid (in five portions over 96 hours) and the reaction left to reflux for 4 days. The mixture was then concentrated *in vacuo*. Purification by flash column chromatography (5/95: diethylether/hexane) afforded 36 mg of the title compound (E/Z ratio: 1/1) as an oil (13%). ¹H NMR (400.132 MHz, CDCl₃, ppm) : δ -0.04 and 0.01 (9H, 2s, Si(Me)₃), 1.44 (2H, m, H₅), 1.65 (1.5H, s, CH₃), 1.80 (1.5H, d, J= 15.2 Hz, CH₃), 2.47 (2H, q, J= 1.2 Hz, H₂), 4.35 (1H, t, J= 7.2 Hz, H₁), 4.38 (1H, t, J= 6.8 Hz, H₁), 5.31 (1H, m, H₄), 7.44 (2H, m, H_{arom meta}), 7.55 (1H, m, H_{arom para}), 8.04 (2H,

m, H_{arom ortho}). ¹³C NMR (100.624 MHz, CDCl₃, ppm) : δ -1.8 and -1.7 (CH₃, Si(Me)₃), 15.9 (CH₃cis), 18.6 and 18.9 (CH₂, C₃), 23.7 (CH₃trans), 39.0 (CH₂, C₂), 63.3 and 63.8 (CH₂, C₁), 123.3 and 123.5 (CH, C₄), 128.1 (C_{arom} IPSO), 128.2 (2CH, C_{arom} meta), 129.5 (2CH, C_{arom} ortho), 130.4 (C₃), 132.8 (CH, C_{arom} para), 166.6 (CO). MS (GCT, CI⁺): *m/z* (relative intensity %) 277 [M+H]⁺ (85). HRMS (GCT, CI⁺): Calc for C₁₆H₂₅O₂Si: 277.1624, found 277.1621.

Compound 5a: (2-Fluoro-but-3-enyloxymethyl)-benzene. General procedure B was followed, starting from 76 mg of **4a** (0.31 mmol) and 115 mg of SelectfluorTM (1 eq.) in CH₃CN (5ml). Purification by flash column chromatography (5/95: diethylether/hexane) afforded 39 mg of the title compound as a white oil (71%). ¹H NMR (400.132 MHz, CDCl₃, ppm) : δ 3.60 (1H, m, H_{1a}), 3.67 (1H, d, J = 4.8 Hz, H_{1b}), 4.62 (2H, d, J = 4.8 Hz, -O-CH₂-Ph), 5.11 (1H, ddt, J = 48.8 Hz, J = 11.6 Hz, J = 1.2 Hz, H₂), 5.32 (1H, dt, J = 10.8 Hz, J = 1.2 Hz, H_{4a}), 5.44 (1H, dq⁵, J = 17.2 Hz, J = 1.2 Hz, H_{4b}), 5.92 (1H, dddd, J = 22.8 Hz, J = 17.2 Hz, J = 11.6 Hz, J = 10.2 Hz, H₃), 7.27-7.38 (5H, m, H_{arom}). ¹³C NMR (100.624 MHz, CDCl₃, ppm) : δ 72.3 (CH₂, d, J = 23 Hz, C₁), 73.5 (CH₂, -O-CH₂-Ph), 92.3 (CH, d, J = 171 Hz, C₂), 118.4 (CH, d, J = 11 Hz, C₄), 127.7 (CH, C_{arom} ortho), 127.8 (CH, C_{arom} para), 128.4 (CH, C_{arom} meta), 132.9 (CH, d, J = 19 Hz, C₃), 137.8 (C_{arom} IPSO). ¹⁹F {¹H} NMR (376.508 MHz, CDCl₃, ppm): δ -189.8. MS (GCT, CI⁺): *m/z* (relative intensity %) 198 [M+NH₄]⁺ (90), 161 [M-HF+H]⁺ (40). HRMS (GCT, CI⁺): Calc for C₁₁H₁₃O: 161.0966, found 161.0968.

Compound 5b: Benzoic acid 2-fluoro-but-3-enyl ester. General procedure B was followed, starting from 95 mg of **4b** (0.38 mmol) and 132 mg of SelectfluorTM (1 eq.) in CH₃CN (5ml). Purification by flash column chromatography (4/96: diethylether/hexane) afforded 55 mg of the title compound as a white oil (74%). ¹H NMR (400.132 MHz, CDCl₃, ppm) : δ 4.43 (1H, ddd, J = 19.2 Hz, J = 12.4 Hz, J = 6.8 Hz, H_{1a}), 4.52 (1H, ddd, J = 26.4 Hz, J = 12.4 Hz, J = 3.2 Hz, H_{1b}), 5.25 (1H, dm, J = 44.6 Hz, H₂), 5.40 (1H, dt, J = 10.8 Hz, J = 1.2 Hz, H_{4a}), 5.54 (1H, dq⁵, J

= 17.2 Hz, J = 1.2 Hz, H_{4b}), 5.97 (1H, dddd, J = 20.8 Hz, J = 17.2 Hz, J = 10.8 Hz, J = 6.0 Hz, H₃), 7.46 (2H, dd, J = 8.0 Hz, J = 7.2 Hz, H_{arom meta}), 7.58 (1H, t, J = 7.2 Hz, H_{arom para}), 8.09 (2H, d, J = 8.0 Hz, H_{arom ortho}). ¹³C NMR (100.624 MHz, CDCl₃, ppm): δ 65.8 (CH₂, d, J = 8 Hz, C₁), 90.6 (CH, d, J = 173 Hz, C₂), 119.4 (CH, d, J = 12 Hz, C₄), 128.4 (CH, C_{arom meta}), 129.6 (C_{arom IPSO}), 129.7 (CH, C_{arom ortho}), 132.0 (CH, d, J = 19 Hz, C₃), 132.2 (CH, C_{arom para}), 166.2 (CO). ¹⁹F{¹H} NMR (376.508 MHz, CDCl₃, ppm): δ -185.9. MS (GCT, CI⁺): *m/z* (relative intensity %) 212 [M+NH₄]⁺ (70), 195 [M+H]⁺ (18). HRMS (GCT, CI⁺): Calc for C₁₁H₁₂FO₂: 195.0821, found 195.0815.

Compound 5c: Benzoic acid 5-fluoro-hept-6-enyl ester.

General procedure B was followed, starting from 338 mg of **4c** (1.17 mmol) and 425 mg of SelectfluorTM (1 eq.) in CH₃CN (10ml). Purification by flash column chromatography (4/96: diethylether/hexane) afforded 91 mg of the title compound as a yellow oil (33%). ¹H NMR (400.132 MHz, CDCl₃, ppm): δ 1.80 (6H, m, H_{2,3,4}), 4.34 (2H, t, J = 6.4 Hz, H₁), 4.91 (0.75H, dq, J = 48.8 Hz, J = 6.4 Hz, H₅), 5.01 (0.25H, dq, J = 49.6 Hz, J = 6.0 Hz, H₅), 5.24 (1H, d, J = 10.4 Hz, H_{7a}), 5.34 (1H, dm, J = 17.2 Hz, H_{7b}), 5.89 (1H, dddd, J = 20.0 Hz, J = 17.2 Hz, J = 10.5 Hz, J = 6.0 Hz, H₆), 7.45 (2H, t, J = 8.0 Hz, H_{arom meta}), 7.57 (1H, t, J = 7.6 Hz, H_{arom para}), 8.05 (2H, d, J = 6.8 Hz, H_{arom ortho}). ¹³C NMR (100.624 MHz, CDCl₃, ppm): δ 21.3 (CH₂, C₃), 28.5 (CH₂, C₂), 34.8 (CH₂, d, J = 22 Hz, C₄), 64.7 (CH₂, C₁), 93.4 (CH, d, J = 166 Hz, C₅), 117.1 (CH₂, d, J = 12 Hz, C₇), 128.3 and 129.5 (CH, C_{arom ortho, meta}), 130.3 (C_{arom IPSO}), 132.9 (CH, C_{arom para}), 136.4 (CH, d, J = 20 Hz, C₆), 166.6 (CO). ¹⁹F{¹H} NMR (376.508 MHz, CDCl₃, ppm): δ -177.4. MS (GCT, CI⁺): *m/z* (relative intensity %) 234 [M-HF+NH₄]⁺ (50). HRMS (GCT, CI⁺): Calc for C₁₄H₂₀NO₂: 234.1494, found 234.1490.

Compound 5d: 3-Fluoro-pent-4-enoic acid benzyl ester.

A solution of 94 mg of **4d** (0.35 mmol) and 130 mg of SelectfluorTM (1 eq.) in CH₃CN (3ml) was stirred at room temperature for 48 hours. Without any evaporation the

crude is directly subjected to flash column chromatography (4/96: diethylether/hexane) to afford 52 mg of the title compound as a white oil (69%). ^1H NMR (400.132 MHz, CDCl_3 , ppm) : δ 2.69 (1H, ddd, $J = 29.6$ Hz, $J = 16.0$ Hz, $J = 4.8$ Hz, H_{2a}), 2.85 (1H, ddd, $J = 16.0$ Hz, $J = 14.8$ Hz, $J = 8.4$ Hz, H_{2b}), 5.18 (2H, s, -O- CH_2 -Ph), 5.29 (1H, dt, $J = 10.8$ Hz, $J = 1.0$ Hz, H_{5a}), 5.39 (1H, dm, $J = 46.8$ Hz, H_3), 5.40 (1H, ddt, $J = 18.8$ Hz, $J = 3.6$ Hz, $J = 1.2$ Hz, H_{5b}), 5.93 (1H, dddd, $J = 24.8$ Hz, $J = 18.8$ Hz, $J = 10.4$ Hz, $J = 6.0$ Hz, H_4), 7.36 (5H, m, H_{arom}). ^{13}C NMR (100.624 MHz, CDCl_3 , ppm) : δ 40.5 (CH_2 , d, $J = 25$ Hz, C_2), 66.7 (CH_2 , -O- CH_2 -Ph), 89.5 (CH, d, $J = 169$ Hz, C_3), 118.1 (CH_2 , d, $J = 12$ Hz, C_5), 128.3, 128.4 and 128.6 (CH, C_{arom} ortho, meta and para), 134.8 (CH, d, $J = 20$ Hz, C_4), 135.5 (C_{arom} IPso), 169.4 (CO). $^{19}\text{F}\{^1\text{H}\}$ NMR (376.508 MHz, CDCl_3 , ppm): δ -177.3. MS (GCT, CI^+): m/z (relative intensity %) 189 $[\text{M}+\text{H}-\text{HF}]^+$ (65). HRMS (GCT, CI^+): Calc for $\text{C}_{12}\text{H}_{13}\text{O}_2$: 189.0916, found 189.0918.

Compound 5e: (2-Fluoro-but-3-enyl)-methyl-carbamic acid *tert*-butyl ester. General procedure B was followed, starting from 165 mg of **4e** (0.64 mmol) and 310 mg of SelectfluorTM (1.3 eq.) in CH_3CN (5ml). Purification by flash column chromatography (5/95: diethylether/hexane) afforded 68 mg of the title compound as a white oil (52%). ^1H NMR (400.132 MHz, CDCl_3 , ppm) : δ 1.46 (9H, s, $(\text{CH}_3)_3\text{C-O-}$), 2.94 (3H, s, N- CH_3), 3.39 (2H, m, H_1), 5.06 (1H, dm, $J = 48.4$ Hz, H_2), 5.28 (1H, dm, $J = 8.4$ Hz, H_{4a}), 5.39 (1H, dm, $J = 17.2$ Hz, H_{4b}), 5.85 (1H, m, H_3). ^{13}C NMR (100.624 MHz, CDCl_3 , ppm) : δ 28.3 (CH_3 , $(\text{CH}_3)_3\text{C-O-}$), 36.3 (CH_3 , N- CH_3), 52.9 (CH_2 , d, $J = 23$ Hz, C_1), 79.7 ($(\text{CH}_3)_3\text{C-O-}$), 92.8 (CH, d, $J = 172$ Hz, C_2), 118.1 (CH_2 , d, $J = 9$ Hz, C_4), 133.8 (CH_2 , d, $J = 18$ Hz, C_3). $^{19}\text{F}\{^1\text{H}\}$ NMR (376.508 MHz, CDCl_3 , ppm): δ -185.8. MS (GCT, CI^+): m/z (relative intensity %) 204 $[\text{M}+\text{H}]^+$ (50). HRMS (GCT, CI^+): Calc for $\text{C}_{10}\text{H}_{19}\text{NO}_2\text{F}$: 204.1400, found 204.1401.

Compound 5f: 2-(2-Fluoro-but-3-enyl)-isoindole-1,3-dione.

General procedure B was followed, starting from 174 mg of **4f** (0.64 mmol) and 232 mg of SelectfluorTM (1 eq.) in CH₃CN (3ml). Purification by flash column chromatography (30/70: diethylether/hexane) afforded 114 mg of the title compound as a white solid (82%). ¹H NMR (400.132 MHz, CDCl₃, ppm): δ 3.83 (1H, ddd, J = 26.4 Hz, J = 14.4 Hz, J = 4.0 Hz, H_{1'a}), 4.04 (1H, ddd, J = 22.0 Hz, J = 14.0 Hz, J = 8.4 Hz, H_{1'b}), 5.21 (1H, dm, J = 48.4 Hz, H_{2'}), 5.36 (1H, dt, J = 10.8 Hz, J = 1.2 Hz, H_{4'a}), 5.36 (1H, ddt, J = 16.8 Hz, J = 13.6 Hz, J = 1.2 Hz, H_{4'b}), 5.95 (1H, dddd, J = 25.6 Hz, J = 16.8 Hz, J = 10.8 Hz, J = 6.0 Hz, H_{3'}), 7.75 (2H, dd, J = 5.2 Hz, J = 2.8 Hz, H_{arom 6 and 7}), 7.90 (2H, dd, J = 5.2 Hz, J = 2.8 Hz, H_{arom 5 and 8}). ¹³C NMR (100.624 MHz, CDCl₃, ppm): δ 41.5 (CH₂, d, J = 25 Hz, C_{1'}), 90.1 (CH, d, J = 173 Hz, C_{2'}), 119.7 (CH₂, d, J = 12 Hz, C_{4'}), 131.9 (2C_{arom}, C₄ and C₉), 132.9 (CH, d, J = 19 Hz, C_{3'}), 134.1 (2C_{arom}, C₆ and C₇), 168.0 (CO). ¹⁹F{¹H} NMR (376.508 MHz, CDCl₃, ppm): δ -184.5. mp: 52-53°C. MS (GCT, CI⁺): *m/z* (relative intensity %) 237 [M+NH₄]⁺ (30) 220 [M+H]⁺ (40) 200 [M-HF+H]⁺ (100). HRMS (GCT, CI⁺): Calc for C₁₂H₁₁FN₂O₂: 220.0774, found 220.0771.

Compound 5h: 2-(1-Fluoro-allyl)-[1,3]dioxalane.

A solution of 140 mg of **4h** (0.75 mmol) and 270 mg of SelectfluorTM (1 eq.) in CH₃CN (3ml) was stirred at room temperature for 48 hours. Without any evaporation the crude (100% conversion) is directly subjected to flash column chromatography (4/96: diethylether/hexane) to afford the title compound contaminated with diethylether (30 %). ¹H NMR (400.132 MHz, CDCl₃, ppm): δ 3.99 and 4.03 (4H, 2m, -O-CH₂-CH₂-O-), 4.80 (1H, dm, J = 47.2 Hz, H_{1'}), 5.02 (1H, dd, J = 10.8 Hz, J = 3.2 Hz, -O-CHR-O-), 5.40 (1H, dt, J = 10.4 Hz, J = 0.8 Hz, H_{3'a}), 5.48 (1H, dq⁵, J = 17.6 Hz, J = 1.2 Hz, H_{3'b}), 5.94 (1H, dddd, J = 21.6 Hz, J = 17.6 Hz, J = 10.8 Hz, J = 6.0 Hz, H_{2'}). ¹³C NMR (100.624 MHz, CDCl₃, ppm): δ 65.6 (2CH₂, -O-CH₂-CH₂-O-), 92.2 (CH, d, J = 175 Hz, C_{1'}), 103.06 (CH, d, J = 24 Hz, -O-CHR-O-), 119.7 (CH, d, J = 12 Hz, C_{3'}), 131.3

(CH, d, J = 19 Hz C₂). ¹⁹F{¹H} NMR (376.508 MHz, CDCl₃, ppm): δ -195.1. MS (GCT, Cl⁺): *m/z* (relative intensity %) 150 [M+NH₄]⁺ (25), 113 [M-HF+H]⁺ (25). HRMS (GCT, Cl⁺): Calc for C₆H₁₃FNO₂: 150.0930, found 150.0926.

Compound 5i: Benzoic acid 3-Fluoro-3-methyl-pent-4-enyl

ester. General procedure B was followed, starting from 15 mg of **4i** (0.05 mmol) and 20 mg of SelectfluorTM (1 eq.) in CH₃CN (1ml). Purification by flash column chromatography (5/95: diethylether/hexane) afforded 9.6 mg of the title compound as an oil (79%). ¹H NMR (400.132 MHz, CDCl₃, ppm): δ 1.52 (3H, d, J = 22.0 Hz, CH₃), 2.20 (2H, m, H₂), 4.45 (2H, d, J = 6.8 Hz, H₁), 5.18 (1H, d, J = 11.2 Hz, H_{5a}), 5.35 (1H, d, J = 17.2 Hz, H_{5b}), 5.95 (1H, td, J = 17.6 Hz, J = 11.2 Hz, H₄), 7.45 (2H, m, H_{arom meta}), 7.57 (1H, tm, J = 7.6 Hz, H_{arom para}), 8.04 (2H, dm, J = 7.2 Hz, H_{arom ortho}). ¹³C NMR (100.624 MHz, CDCl₃, ppm): δ 25.8 (CH₃, d, J = 25 Hz, CH₃), 38.8 (CH₂, d, J = 23 Hz, C₂), 60.7 (CH₂, d, J = 5 Hz, C₁), 113.9 (CH₂, d, J = 11 Hz, C₅), 128.3 (CH, C_{arom meta}), 129.5 (CH, C_{arom ortho}), 130.2 (C_{arom IPSO}), 132.9 (CH, C_{arom para}), 135.9 (CH, d, J = 22 Hz, C₄), 166.5 (CO). ¹⁹F{¹H} NMR (376.508 MHz, CDCl₃, ppm): δ -148.8. MS (GCT, Cl⁺): *m/z* (relative intensity %) 203 [M-HF+H]⁺ (100). HRMS (GCT, Cl⁺): Calc for C₁₃H₁₅O₂: 203.1072, found 203.1065.

Compound 4a

Compound 4c

Compound 4e

Compound 4f

Compound 4h

Compound 4i

Compound 5a

Compound 5b

Compound 5c

Compound 5e

Compound 5f

Compound 5h

Compound 5i