Supporting Information

for

Direct and Convenient Conversion of Alcohols to Fluorides

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General Comments: An Agilent 1100 series HPLC fitted with an Ace C-8 column, auto-injector and diode array detector provided information on reaction progress and assay yield. Relevant HPLC parameters include 0.1% H_3PO_4 in H_2O/MeCN mobile phase, 35 ^oC column temperature, and monitoring at 210 nm. A Bruker AVANCE 400 MHz NMR system captured all ^1H, ^{13}C and ^{19}F spectral data associated with all compounds. All columns were packed with 40-63 μm EMG silica gel. All starting alcohols are commercially available.

2-Deoxy-2-fluoro-1, 3, 5-tri-O-benzoyl-α-D-arabinofuranose (6)[1] Dissolving the starting alcohol **4** (1 mmol) in acetonitrile (3 mL, dried over molecular seives), then adding pyridine (1.3 eq.) and triflic anhydride (1.2 eq.) renders a triflate intermediate after 0.5h. Displacement with fluoride ion generated by combining $NEt_3(HF)_3$ (4 eq.) and NEt_3 (8 eq.) *in situ* requires heating to 50 °C for 18h. After quenching with water (5 mL), a silica gel flash provided **6**, 338 mg at 73% isolated yield as a white solid (m.p. 76-77.5 °C, lit.[1] m.p. 82 °C).

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General Procedure for Tables 2 and 3: The alcohol (**11**) (1.0 mmol, 1.0 equiv), alkyl amine base (NEt_3 or iPr_2NEt as per Table 2 or 3), a fluoride source ($NEt_3(HF)_3$ or $iPr_2NEt(HF)_3$ as per Table 2 or 3), and PBSF were stirred in MeCN or THF in a capped vial or flask at indicated temperature until LC revealed complete conversion. The reaction mixture was subjected to a water quench or filtered through a short silica gel plug. The product was further purified by SiO_2 column chromatography if necessary.

2-Fluoro-4-phenylbutane (9)[2] The general procedure at 2 mmol scale provided of **9**, 240 mg in 79% isolated (9% loss in distillate during concentration) and 88 LC% yield as a colorless oil. ^{19}F NMR (377 MHz, $CDCl_3$) δ -174.5.

1,3-Bis(benzyloxy)-2-fluoropropane (12a)[3] The general procedure provided **12a**, 250 mg at 86% isolated yield as a colorless oil. ^{19}F NMR (377 MHz, $CDCl_3$) δ -192.8.

1-Benzyloxy-2-fluoro-3-p-toluenesulfonyloxypropane (12b)[4] The general procedure at 0.5 mmol scale provided **12b**, 169 mg at 92% isolated yield as a colorless oil. ^{19}F NMR (377 MHz, $CDCl_3$) δ -194.5.

(1-Fluoroethyl)benzene (12c)[5] The general procedure at 4 mmol scale provided **12c** at 77 LC% yield as determined by LC assay. ^{19}F NMR (377 MHz, $CDCl_3$) δ -167.8.

1-Fluoro-1-(p-tolyl)ethane (12d)[5] The general procedure at 4 mmol scale provided **12d** at 86 LC% yield as determined by LC assay.

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[2] Giudecelli, M. B.; Picq, D.; Veyron, B. *Tetrahedron Lett.* **1990**, *31*, 6527.
[3] Karkas, J. D.; Ashton, W. T.; Canning, L. F.; Liou, R.; Germershausen, J.; Bostedor, R.; Arison, B.; Field, A. K.; Tolman, R. L. *J. Med. Chem.* **1986**, *29,* 842.
[4] Jindrich, J.; Dvorakova, H.; Holy, A. *Collect. Czech. Chem. Commun.* **1992**, *57,* 1466.
[5] York, C.; Surya Prakash, G. K.; Olah, G. A. *Tetrahedron* **1996**, *52,* 9.

2, 3, 5-Tri-*O*-benzyl-D-arabinofuranosyl fluoride (12e)[6] The general procedure at 0.5 mmol scale provided **12e**, 182 mg at 87% isolated yield as a dark orange oil with an α:β ratio of 1:2.4. ^{19}F NMR (377 MHz, $CDCl_3$) δ -122.1(α), -127.2 (β).

2, 3, 4, 6-Tetra-*O*-benzyl-D-pyrannosyl fluoride (12f)[7] The general procedure at 0.5 mmol scale provided **12f**, 234 mg at 86% isolated yield with an α:β ratio of 3.5:1 as a white solid. ^{19}F NMR (377 MHz, $CDCl_3$) δ -150.0(α), -138.6 (β).

2-Fluoro-2-methyl-1-phenyl-1-propanone (12g)[8] Reagent concentrations employed on this substrate include 9 equiv. NEt_3, 3 equiv. $NEt_3(HF)_3$ and 3 equiv. PBSF. After sealing the reagents and solvent in a Schlenk tube, the reaction mixture was heated to 95 °C for nine hours. A short silica gel plug followed by a flash column yielded **12g**, 148 mg at 89% isolated yield as an orange oil. ^{19}F NMR (377 MHz, $CDCl_3$) δ -150.0.

1-(2-Fluoroethyl)napthalene (12h) The general procedure provided **12h**, 167 mg at 96% isolated yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 4.1 Hz, 1 H), 7.93 (d, *J* = 3.9 Hz, 1 H), 7.83 (d, *J* = 7.9 Hz, 1 H), 7.59-7.44 (m, 4 H), 4.82 (dt, *J* = 47.1, 6.9 Hz, 2 H), 3.52 (dt, *J* = 20.3, 6.9 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.0, 132.3, 132.9, 132.2, 129.0, 127.7, 127.3, 125.7 (d, *J* = 12 Hz), 123.5, 83.6 (d, *J* = 169 Hz), 33.9 (d, *J* = 20 Hz), 20.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ -213.7. Anal. Calcd. for $C_{12}H_{11}F$: C, 82.73; H, 6.36; Found: C, 82.60; H, 6.05.

1-Fluoromethyl-1, 4-benzodioxan (12i) The general procedure provided **12i**, 161 mg at 96% isolated yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97-6.86 (m, 4 H), 4.75-4.51 (m, 2 H), 4.49-4.40 (m, 1 H), 4.34 (ddd, *J* = 11.8, 2.6, 1.7 Hz, 1 H), 4.15 (dd, *J*

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[8] Cousseau, J.; Albert, P. *J. Org. Chem.* **1989**, *54,* 5380.

= 11.8, 7.3 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 142.8, 121.9, 121.7, 117.4, 117.3, 81.25 (d, *J* = 170 Hz), 71.4 (d, *J* = 20 Hz), 64.3 (d, *J* = 6.5 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -233.7. Anal. Calcd. for $C_9H_9FO_2$: C, 64.28; H, 5.39; Found: C, 64.45; H, 5.44.

3, 3-Diphenyl-1-fluoro-propane (12j) The general procedure provided **12j**, 192 mg at 90% isolated yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$). δ 7.38-7.24 (m, 10 H), 4.45 (dt, *J* = 47.1, 6.0 Hz, 2 H), 4.24 (t, *J* = 8.0, 1 H), 2.51 (dq, *J* = 23.9, 1.9 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 128.7, 128.0, 126.6, 82.1 (d, *J* = 163 Hz), 46.6 (d, *J* = 5 Hz), 36.2 (d, *J* = 20 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -221.2. Anal. Calcd. for $C_{15}H_{15}F$: C, 84.08; H, 7.06; Found: C, 83.93; H, 6.85.

2-(2-Fluoroethoxy)benzaldehyde (12k) The general procedure provided **12k**, 312 mg at 93% isolated yield as a flaky, yellow solid (m.p. 37.5-38 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.54 (d, *J* = 0.60 Hz, 1H), 7.73 (dd, *J* = 7.7, 1.8 Hz 1H), 7.55 (dt, *J* = 8.4, 1.8 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 4.81 (app dt, *J* = 47.3,4.1 Hz, 2H) 4.35 (app dt, *J* = 27.5, 4.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.59, 160.80, 132.92, 128.53, 125.31, 121.47, 112.73, 81.61 (d, *J* = 171.9, 1C), 67.87 (d, *J* = 20.1, 1C). ^{19}F NMR (377 MHz, $CDCl_3$) δ -224.5. Anal. Calcd. for $C_9H_9FO_2$: C, 64.28; H, 5.39; Found: C, 64.17; H, 5.32.

(3aR, 4*S*, 5*R*, 6aS)-(-)-5-(benzoyloxy)hexahydro-4-(fluoromethyl)-2*H*-cyclopenta-[b]furan-2-one (12l) The general procedure provided **12l**, 238 mg at 90% isolated yield as a white solid (m.p. 136-138 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.44 (m, 5H), 5.43 (m, 1H), 5.14 (m, 1H), 4.57 (ddd, *J* = 47.2, 27.8, 9.6 Hz, 1H), 4.58 (ddd, *J* = 47.2, 25.2, 9.6 Hz, 1H), 2.98 (m, 2H) 2.51, (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.10,

166.05, 133.46, 129.74, 129.50, 128.61, 84.68, 83.44 (d, J = 170.93, 1C), 77.47 (d, J = 5.0, 1C), 53.52 (d, J = 18.1, 1C), 40.15 (d, J = 4.0, 1C), 38.81, 35.99. ^{19}F NMR (377 MHz, $CDCl_3$) δ -226.9. Anal. Calcd. for $C_{15}H_{15}FO_4$: C, 64.74; H, 5.43; Found: C, 64.66; H, 5.29.

Ethyl 2-fluoro-2-phenylacetate (12m)[9] The general procedure provided **12m**, 312 mg at 88% isolated yield as a pale yellow oil. ^{19}F NMR (377 MHz, $CDCl_3$) δ -180.3.

2-Fluoro-1, 2-diphenyl-ethanone (12n)[10] The general procedure provided **12n**, 388 mg at 88% isolated yield as a yellow solid (m.p. 53.6-55 °C, lit.[10] m.p. 53-58 °C). ^{19}F NMR (377 MHz, $CDCl_3$) δ -176.5.

Fluoro-diphenyl-methane (12o)[11] The general procedure at 2 mmol scale provided **12o** in 88 LC% yield as determined by LC assay. ^{19}F NMR (377 MHz, $CDCl_3$) δ -167.3.

9-Fluorofluorene (12p)[11] The general procedure at 2 mmol scale provided **12p**, 238 mg at 65% isolated yield as a colorless oil. ^{19}F NMR (377 MHz, $CDCl_3$) δ -187.3.

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