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Supplementary Information for

An easy access to fluoroalkanes by deoxygenative hydrofluorination of carbonyl compounds via their tosylhydrazones

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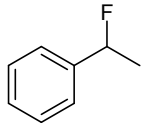
General Information: All commercially available reagents were used without further purification unless otherwise specified by a reference. Solvents were purified by the usual methods and stored over molecular sieves. All reactions were performed using oven-dried glassware under a nitrogen atmosphere. Organic solutions were concentrated using a Buchi rotary evaporator. Column chromatography was carried out over silica gel (Merck 100–200 mesh) and TLC was performed using silica gel GF254 (Merck) plates. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker AVII 400 spectrometer in $CDCl_3$ using TMS as internal reference for ^{1}H and ^{13}C, and $FCCl_3$ (δ 0.00) for ^{19}F. All chemical shifts are reported in δ and coupling constants (*J*) in Hertz (Hz). MS experiments were performed on a double focusing MS spectrometer.

General procedure for the synthesis of monofluoroalkanes 2 from tosylhydrazones 1

A round bottom flask fitted with a refux condenser was charged with tosylhydrazone **1** (1 mmol), K_2CO_3 (5.0 mmol), toluene (4 mL) and $Et_3N.3HF$ (1.5 mmol). The system was refluxed at 110 ^{o}C with stirring under a nitrogen atmosphere. After completion of reaction, as monitored by TLC, the crude mixture was allowed to cool to rt. It was quenched with saturated aqueous sodium hydrogen carbonate (10 mL) and extracted with ethyl acetate (3×10 mL). The organic phase was dried over anhydrous magnesium sulfate and concentrated under reduced pressure to yield the crude product, which was purified by silica gel column chromatography (EtOAc-Hexane) to give the an analytically pure sample of fluoroalkanes **2**.

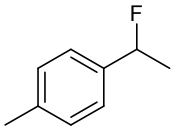
The characterization data of the synthesized fluoroalkanes **2** are summarized below with relevant references.

1-Fluoro-1-phenylethane (2a)[1]



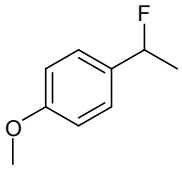
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33-7.49 (m, 5H), 5.53 (dq, 1H, *J* = 6.4, 48 Hz), 1.62 (dd, 3H, *J* = 6.4, 24 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 134.0 (d, *J* = 20.2 Hz), 129.3, 128.6, 126.7, 90.2 (d, *J* = 167.0 Hz), 22.8 (d, *J* = 25.5 Hz); ^{19}F NMR (377 MHz, $FCCl_3$) δ = -168.0 (dq, *J* = 48, 24 Hz); HRMS (EI): calcd for C_8H_9F 124.0688, found 124.0686.

1-Fluoro-1-(*p*-tolyl)ethane (2b)[1]



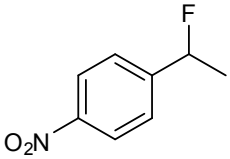
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30-7.39 (m, 4H), 5.59 (dq, 1H, *J* = 40.6, 5.7 Hz), 2.41 (s, 3H), 1.66 (dd, 3H, *J* = 23.7, 5.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 133.9 (d, *J* = 20.2 Hz), 129.3, 128.5, 126.6, 90.1 (d, *J* = 167.0 Hz), 22.7, 21.5 (d, *J* = 25.5 Hz); ^{19}F NMR (377 MHz, $FCCl_3$) δ = -167.9 (dq, *J* = 40.6, 23.7 Hz); HRMS (EI): calcd for $C_9H_{11}F$ 138.0845, found 138.0847.

1-Fluoro-1-(*p*-methoxy)ethane (2c)



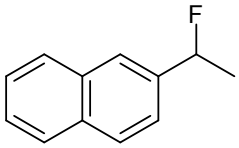
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.26-7.33 (m, 4H), 5.48 (dq, 1H, *J* = 40.5, 5.4 Hz), 3.86 (s, 3H), 1.59 (dd, 3H, *J* = 23.6, 5.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.0, 128.2, 127.9, 116.1, 90.0 (d, *J* = 166.8 Hz), 55.7, 22.6 (d, *J* = 25.4 Hz); ^{19}F NMR (377 MHz, $CFCl_3$) δ = -167.7 (dq, *J* = 40.5, 23.6 Hz); HRMS (EI): calcd for $C_9H_{11}FO$ 154.0794, found 154.0792.

1-Fluoro-1-(*p*-nitro)ethane (2d)



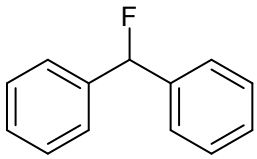
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.18 (d, 2H, *J* = 8.2 Hz), 5.58 (dq, 1H, *J* = 6.5, 48.2 Hz), 5.47 (d, 2H, *J* = 8.2 Hz), 1.70 (dd, 3H, *J* = 6.5, 24.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.6, 143.7 (d, *J* = 18.5 Hz), 127.2, 123.8, 90.8 (d, *J* = 167.2 Hz), 23.1 (d, *J* = 25.6 Hz); ^{19}F NMR (377 MHz, $CFCl_3$) δ = -170.5 (dq, *J* = 24.2, 48.3); HRMS (EI): calcd for $C_8H_8FNO_2$ 169.0539, found 169.0536.

2-(1-Fluoroethyl)naphthalene (2e)[2]



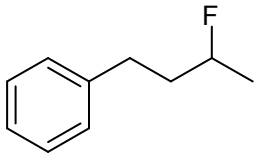
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.79-7.98 (m, 4 H), 7.44-7.62 (m, 3 H), 5.88 (dq, 1 H, *J* = 47.5, 6.1 Hz), 1.75 (dd, 3 H, *J* = 23.5, 6.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.7 (d, *J* = 19.1 Hz), 133.2, 133.1, 128.4, 128.0, 127.7, 126.4, 126.2, 124.1, 123.1, 91.4 (d, *J* = 167.0 Hz), 22.9 (d, *J* = 25.6 Hz); ^{19}F NMR (377 MHz, $FCCl_3$) δ = -166.8 (dq, *J* = 48, 24 Hz); HRMS (EI): calcd for $C_{12}H_{11}F$ 174.0845, found 174.0842.

Fluoromethyl-1,1'-biphenyl (2f)[1]



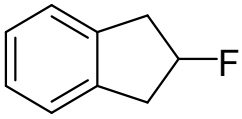
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.05-7.15 (m, 10H), 5.91 (d, 1H, *J* = 48 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.5 (d, *J* = 19.8 Hz), 129.6, 128.2, 126.3 99.2 (d, *J* = 168.8 Hz); ^{19}F NMR (377 MHz, $FCCl_3$) δ = -163.1 (*J* = 48 Hz); HRMS (EI): calcd for $C_{13}H_{11}F$ 186.0845, found 186.0848.

1-(3-Fluorobutyl)benzene (2g)[3]



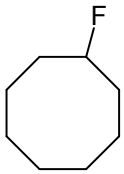
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.20–7.35 (m, 5H), 4.70 (dm, 1H, *J* = 48.9 Hz), 1.81-2.08 (m, 4H), 1.39 (dd, *J* = 6.1, 3H, 23.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.6, 128.5, 126.3, 126.1, 90.1 (d, *J* = 163.3 Hz), 38.8 (d, *J* = 20.3 Hz), 31.5 (d, *J* = 4.8 Hz), 21.1 (d, *J* = 22.7 Hz); ^{19}F NMR (377 MHz, $FCCl_3$) δ = -160.2 (m); HRMS (EI): calcd for $C_{10}H_{13}F$ 152.1001, found 152.1004.

2-Fluoro-2,3-dihydro-1*H*-indene (2h)[3]



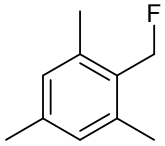
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28–7.33 (m, 2H), 7.22–7.24 (m, 2H), 5.53 (dm, 1H, *J* = 53.2 Hz), 3.26 (d, 2H, *J* = 4.5 Hz), 3.23 (d, 2H, *J* = 3.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.3, 127.4, 124.6, 94.6 (d, *J* = 175.3 Hz), 40.7 (d, *J* = 22.7 Hz); ^{19}F NMR (377 MHz, $FCCl_3$) δ = -162.0 (m); HRMS (EI): calcd for C_9H_9F 136.0688, found 136.0684.

Fluorocyclooctane (2i)[4]



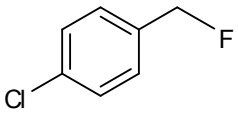
^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.62 (dm, 1H, *J* = 45.9 Hz), 1.28-1.97 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) 94.95 (d, *J* = 162.9 Hz), 32.32 (d, *J* = 21.9 Hz), 27.38, 25.31, 22.24 (d, *J* = 9.7 Hz); ^{19}F NMR (377 MHz, $FCCl_3$) δ = -159.6 (s); HRMS (EI): calcd for $C_8H_{15}F$ 130.1158, found 130.1159.

2-(Fluoromethyl)-1,3,5-trimethylbenzene (2j)[2]



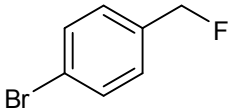
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42 (s, 2H), 5.37 (d, 2H, *J* = 49.0 Hz), 2.37 (d, 6H, *J* = 2.3 Hz), 2.35 (d, 3H, *J* = 3.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.1, 138.2, 129.2 (d, *J* = 14.4 Hz), 129.1, 78.7 (d, *J* = 160.6 Hz), 21.0, 19.1; ^{19}F NMR (377 MHz, $FCCl_3$) δ = -206.8 (t, *J* = 48.2 Hz); HRMS (EI): calcd for $C_{10}H_{13}F$ 152.1001, found 152.1099.

4-Chlorobenzyl fluoride (2k)[2]



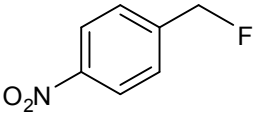
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42 (d, 2H, *J* = 8.6 Hz), 7.33 (dd, 2H, *J* = 8.5, 1.6 Hz), 5.43 (d, 2H, *J* = 47.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 134.7 (d, *J* = 17.6 Hz), 134.5, 129.6, 128.8, 83.8 (d, *J* = 167.0 Hz); ^{19}F NMR (377 MHz, $FCCl_3$) δ = -207.4 (t, *J* = 47.0 Hz); HRMS (EI): calcd for C_7H_6ClF 144.0142, found 144.0139.

4-Bromobenzyl fluoride (2l)[2]



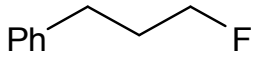
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53 (d, 2H, *J* = 8.3 Hz), 7.31 (dd, 2H, *J* = 8.1, 1.5 Hz), 5.32 (d, 2H, *J* = 47.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 135.2 (d, *J* = 17.6 Hz), 131.7, 129.1, 122.9, 83.8 (d, *J* = 164.6 Hz); ^{19}F NMR (377 MHz, $FCCl_3$) δ = -208.2 (t, *J* = 48.2 Hz); HRMS (EI): calcd for C_7H_6BrF 187.9637, found 187.9635.

4-Nitrobenzyl fluoride (2m)[2]



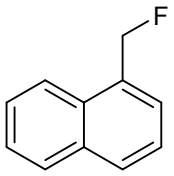
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.22 (d, 2H, *J* = 8.3 Hz), 7.55 (d, 2H, *J* = 8.1 Hz), 5.53 (d, 2H, *J* = 46.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.6, 143.5 (d, *J* = 18.4 Hz), 127.1, 123.6, 82.8 (d, *J* = 170.2 Hz); ^{19}F NMR (377 MHz, $FCCl_3$) δ = -215.6 (t, *J* = 45.9 Hz); HRMS (EI): calcd for $C_7H_6FNO_2$ 155.0383, found 155.0380.

1-Fluoro-3-phenylpropane (2n)[4]



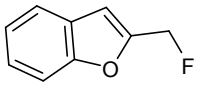
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40-7.13 (m, 5H), 4.47 (dt, 2H, *J* = 47.3, 5.9 Hz), 2.77 (t, 2H, 7.3 Hz), 2.10-1.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.3, 128.5, 128.7, 126.0, 83.3 (d, 164.5 Hz), 32.2 (d, 19.6 Hz), 31.4 (d, 5.7 Hz); ^{19}F NMR (377 MHz, $FCCl_3$) δ = -220.6 (m); HRMS (EI): calcd for $C_9H_{11}F$ 138.0845, found 138.0843.

1-Fluoromethylnaphthalene (2o)[2]



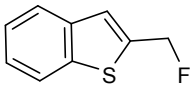
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.16 (d, 1H, *J* = 8.08 Hz), 7.95 (t, 2 H, *J* = 7.60 Hz), 7.36-7.81 (m, 4H), 5.90 (d, 2H, *J* = 47.24 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 131.8, 131.5, 131.2, 129.8, 128.5, 126.9, 126.5, 126.0, 125.1, 123.5, 83.1 (d, *J* = 166 Hz); ^{19}F NMR (377 MHz, $FCCl_3$) δ = -205.8 (d, *J* = 48 Hz); HRMS (EI): calcd for $C_{11}H_9F$ 160.0688, found 160.0685.

2-(Fluoromethyl)benzofuran (2p)[2]



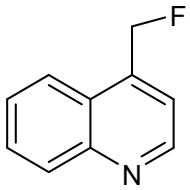
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60 (d, 1 H, *J* = 7.6 Hz), 7.57 (d, 1 H, *J* = 8.3 Hz), 7.35 (td, 1 H, *J* = 7.7, 1.0 Hz), 7.26 (t, 1 H, *J* = 8.1 Hz), 6.89 (d, 1 H, *J* = 5.3 Hz), 5.48 (d, 2 H, *J* = 48.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.6, 151.5 (d, *J* = 17.0 Hz), 127.7, 125.3, 123.1, 121.6, 111.5, 108.1 (d, *J* = 7.2 Hz), 76.2 (d, *J* = 166.0 Hz); ^{19}F NMR (377 MHz, $FCCl_3$) δ = -207.3 (td, *J* = 48.2, 4.6 Hz); HRMS (EI): calcd for C_9H_7FO 150.0481, found 150.0479.

2-(Fluoromethyl)benzothiophene (2q)[2]



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.81-7.94 (m, 1 H), 7.77-7.86 (m, 1 H), 7.30-7.48 (m, 3H), 5.63 (d, 2 H, *J* = 48.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.8, 139.1, 138.4 (d, *J* = 18.4 Hz), 125.1, 124.7, 124.4, 124.2, 122.6, 79.3 (d, *J* = 168.0 Hz); ^{19}F NMR (377 MHz, $FCCl_3$) δ = -197.0 (td, *J* = 48.2, 4.6 Hz); HRMS (EI): calcd for C_9H_7FS 166.0253, found 166.0256.

4-(Fluoromethyl)quinoline (2r)[2]



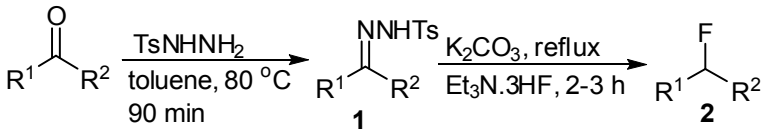
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.90 (d, 1H, *J* = 4.3 Hz), 8.19 (d, 1H, *J* = 8.3 Hz), 7.81 (d, 1H, *J* = 8.3 Hz), 7.74 (t, 1H, *J* = 7.7 Hz), 7.55 (t, 1H, *J* = 8.0 Hz), 7.45 (d, 1H, *J* = 4.3 Hz), 5.84 (d, 2H, *J* = 46.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.0, 148.0, 141.2 (d, *J* = 16 Hz), 130.1, 129.6, 127.0, 125.1, 122.5, 118.5 (d, *J* = 10.4 Hz), 81.3 (d, *J* = 171 Hz); ^{19}F NMR (377 MHz, $FCCl_3$) δ = -221.0 (t, *J* = 47.00 Hz); HRMS (EI): calcd for $C_{10}H_8FN$ 161.0641, found 161.0639.

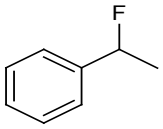
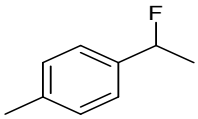
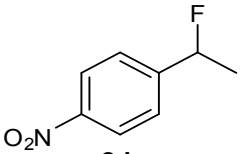
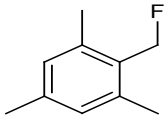
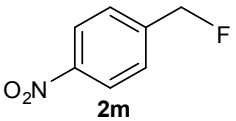
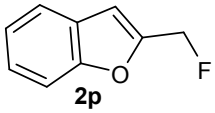
General procedure for the one-pot synthesis of fluoroalkanes 2 directly from carbonyl compounds

To a mixture of carbonyl compound (1 mmol) and tosylhydrazide(1 mmol) in 4 mL of toluene was stirred at 80 ^{o}C for 1.5 h in a round bottom flask fitted with a reflux condenser. Potassium carbonate (5.0 mmol) and $Et_3N.3HF$ (1.5 mmol) were added to the reaction mixture. The system was refluxed at 110 ^{o}C with stirring under a nitrogen atmosphere. After completion of reaction, as monitored by TLC, the crude mixture was allowed to cool to rt. It was quenched with saturated aqueous sodium hydrogen carbonate (10 mL) and extracted with ethyl acetate (3 × 10 mL). The organic phase was dried over anhydrous magnesium sulfate and concentrated in under reduced pressure to yield the

crude product, which was purified by silica gel column chromatography (EtOAc-Hexane) to give an analytically pure sample of **2**. Selected examples of fluoroalkanes thus synthesised are given in the following Table.

Table : One-pot synthesis of fluoroalkanes **2** directly from carbonyl compounds [a]



Entry	Product **2**	Time (h)	Yield (%)[b,c]
1	 **2a**	2	83
2	 **2b**	2	87
3	 **2d**	2	60
4	 **2j**	3	85
5	 **2m**	3	66
6	 **2p**	2	73

[a] For experimental procedure, see the general procedure given in the above text. [b] Isolated yield. [c] For characterisation data of fluoroalkanes **2**, see the text in this ESI.

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