

Supporting Information

Halogenations of Substituted 2-Alkylquinoline with iodine and Halide Exchange with AgF₂

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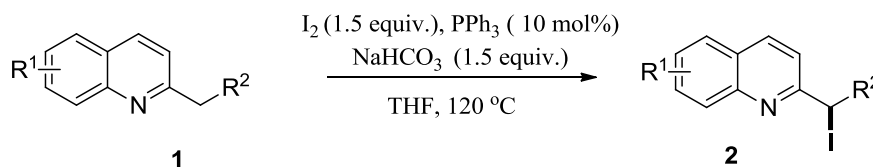
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General remark

All substrates were represented on 400 MHz spectrometer in CDCl₃, ¹H NMR, ¹³C NMR and ¹⁹F NMR were respectively recorded on a Bruker AVANCE AV 400 (400MHz, 100MHz and 376MHz), ¹H NMR, ¹³C NMR chemical shifts are reported as δ values (ppm) with reference to tetramethylsilane (TMS) or the solvent peaks of CDCl₃ (7.26 ppm for ¹H NMR and 77.16($\pm$ 0.06) ppm for ¹³C NMR), ¹⁹F NMR chemical shifts are reported as δ values (ppm) with trifluoroacetic acid (TFA, -76.2 ppm in CDCl₃ for ¹⁹F NMR). High resolution mass spectra (HRMS) was carried out on an FT-ICRMS mass instrument and measured with electrospray ionization (ESI), Products were purified by flash chromatography on 200-300 mesh silica gels. All melting points were determined without correction. Commercially available reagents and solvents were used without further purification except noted.

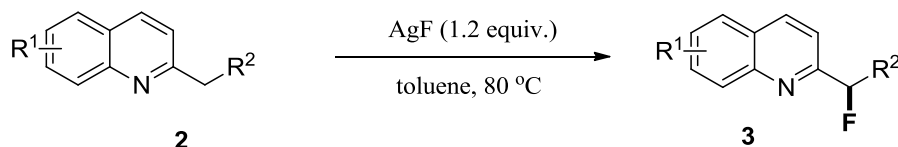
General procedure for the synthesis of the desired 2-(iodoalkyl)quinolines :



An oven-dried pressure tube was charged with 2-alkylquinoline **1** (0.3 mmol), I₂ (0.45 mmol), NaHCO₃ (0.45 mmol), PPh₃ (0.03 mmol) and 2 mL of THF. The mixture was stirred at 120 °C for 1.5 h under nitrogen atmosphere. After cooling to room

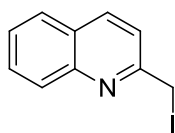
temperature, the mixture was diluted with ethyl acetate and washed with saturated sodium thiosulfate. Then extracted with ethyl acetate and dried with anhydrous sodium sulfate. The solvent was evaporated in vacuo and the residues were purified by column chromatography to afford the desired product **2**.

General procedure for the synthesis of the desired 2-(fluoroalkyl)quinolines:



The 2-(iodoalkyl)quinolines **2** (0.3 mmol) and AgF_2 (0.36 mmol) were mixed in 1.5 mL of toluene. The mixture was stirred at $80\text{ }^\circ\text{C}$ under a nitrogen atmosphere for 16 h. After cooling to room temperature, the mixture was diluted with ethyl acetate and the solvent was evaporated in vacuo, and the residues were purified by column chromatography to afford the product **3**.

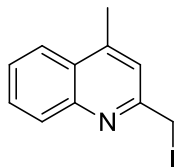
The data of products:



2-(iodomethyl)quinoline (2a).

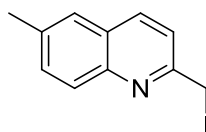
Yellow solid; melting point: $58\text{--}64\text{ }^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 8.10–8.03 (m, 2 H), 7.77 (d, $J = 8.0\text{ Hz}$, 1 H), 7.72–7.68 (m, 2 H), 7.54–7.49 (m, 2 H), 4.67 (s, 2 H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.3, 147.5, 137.1, 129.8, 129.0, 127.4, 127.0, 126.7,

121.0, 6.84. IR (film, cm^{-1}): 3054, 2918, 2752, 1643, 1541, 1505, 1458, 1220, 1150, 769, 572. HRMS (ESI): m/z calcd for $\text{C}_{10}\text{H}_9\text{IN}$ $[\text{M}+\text{H}]^+$ 269.9774, found 269.9771.



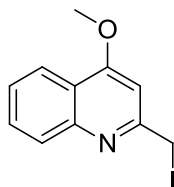
2-(iodomethyl)-4-methylquinoline (2b).

White solid; melting point: 148-151 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, J = 8.0 Hz, 1 H), 7.95 (d, J = 8.0 Hz, 1 H), 7.72-7.68 (m, 1 H), 7.57-7.53 (m, 1 H), 7.36 (s, 1 H), 4.63 (s, 2 H), 2.69 (d, J = 0.4 Hz, 3 H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.0, 147.4, 145.5, 129.64, 129.62, 127.2, 126.6, 123.6, 121.7, 18.8, 7.03. IR (film, cm^{-1}): 2920, 2851, 1633, 1541, 1508, 1457, 1219, 1122, 772, 571. HRMS (ESI): m/z calcd for $\text{C}_{11}\text{H}_{11}\text{IN}$ $[\text{M}+\text{H}]^+$ 283.9931, found 283.9933.



2-(iodomethyl)-6-methylquinoline (2c).

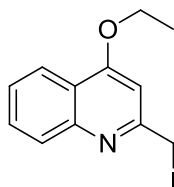
Yellow solid; melting point: 98-102 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, J = 8.0 Hz, 1 H), 7.92 (d, J = 8.0 Hz, 1 H), 7.53 (t, 2 H), 7.47 (d, J = 8.0 Hz, 1 H), 4.67 (s, 2 H), 2.51 (s, 3 H). ^{13}C NMR (100 MHz, CDCl_3) δ 157.3, 146.1, 136.8, 136.5, 132.2, 128.7, 127.0, 126.4, 121.0, 21.6, 7.1. IR (film, cm^{-1}): 2918, 2850, 1632, 1541, 1507, 1457, 1219, 1121, 772, 571. HRMS (ESI): m/z calcd for $\text{C}_{11}\text{H}_{11}\text{IN}$ $[\text{M}+\text{H}]^+$ 283.9931, found 283.9935.



2-(iodomethyl)-4-methoxyquinoline (2d).

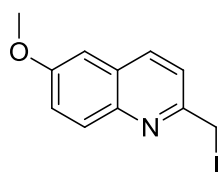
White solid; melting point: 95-98 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 8.15 (q, 1 H), 7.98 (d, J = 8.0 Hz, 1 H), 7.72-7.68 (m, 1 H), 7.52-7.48 (m, 1 H), 6.84 (s, 1 H), 4.64 (s,

2 H), 4.06 (s, 3 H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.9, 159.5, 148.5, 130.2, 128.6, 126.0, 121.7, 120.4, 99.7, 55.8, 7.6. IR (film, cm^{-1}): 3019, 2926, 2853, 1593, 1567, 1509, 1459, 1215, 1160, 1137, 1026, 767, 572. HRMS (ESI): m/z calcd for $\text{C}_{11}\text{H}_{11}\text{INO}$ $[\text{M}+\text{H}]^+$ 299.9880, found 299.9884.



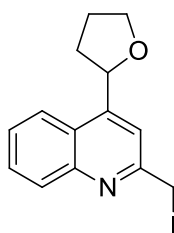
2-(iodomethyl)-4-ethoxyquinoline (2e).

White solid; melting point: 107-110 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 8.17 (m, 1 H), 7.97 (d, J = 8.0 Hz, 1 H), 7.70-7.66 (m, 1 H), 7.50-7.46 (m, 1 H), 6.80 (s, 1 H), 4.61 (s, 2 H), 4.25 (q, J = 8.0 Hz, 2 H), 1.56 (t, J = 8.0 Hz, 3 H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.1, 159.4, 148.5, 130.1, 128.6, 125.8, 121.8, 120.4, 100.2, 64.3, 14.5, 7.8. IR (film, cm^{-1}): 3063, 2926, 2854, 1598, 1567, 1506, 1434, 1236, 1200, 1161, 1114, 1015, 756, 613. HRMS (ESI): m/z calcd for $\text{C}_{12}\text{H}_{13}\text{INO}$ $[\text{M}+\text{H}]^+$ 314.0037, found 314.0033.



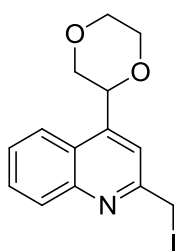
2-(iodomethyl)-6-methoxyquinoline (2f).

White solid; melting point: 94-100 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, J = 8.0 Hz, 1 H), 7.92 (d, J = 9.2 Hz, 1 H), 7.47 (d, J = 8.0 Hz, 1 H), 7.35 (q, 1 H), 7.04 (d, J = 2.8 Hz, 1 H), 4.65 (s, 2 H), 3.92 (s, 3 H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.0, 155.7, 143.6, 135.9, 130.5, 128.1, 122.6, 121.3, 105.1, 55.6, 7.2. IR (film, cm^{-1}): 3010, 2924, 2851, 1619, 1558, 1498, 1437, 1253, 1219, 1164, 1127, 1024, 772, 571. HRMS (ESI): m/z calcd for $\text{C}_{11}\text{H}_{11}\text{INO}$ $[\text{M}+\text{H}]^+$ 299.9880, found 299.9882.



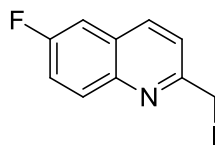
2-(iodomethyl)-4-(tetrahydrofuran-2-yl)quinoline (2g).

Brown solid; melting point: 110-112 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, J = 8.0 Hz, 1 H), 7.86 (d, J = 8.0 Hz, 1 H), 7.72-7.67 (m, 2 H), 7.56-7.51 (m, 1 H), 5.57 (t, J = 7.2 Hz, 1 H), 4.68 (dd, J = 12.0 Hz, J = 8.0 Hz, 2 H), 4.28-4.23 (m, 1 H), 4.06 (dd, J = 16.0 Hz, J = 8.0 Hz, 1 H), 2.66-2.58 (m, 1 H), 2.14-1.96 (m, 2 H), 1.90-1.81 (m, 1 H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.5, 150.7, 147.7, 130.0, 129.4, 126.6, 124.5, 123.1, 116.4, 76.8, 69.0, 33.9, 26.0, 7.3. IR (film, cm^{-1}): 3065, 2927, 2871, 1602, 1558, 1507, 1410, 1219, 1162, 1079, 1045, 927, 884, 771, 571. HRMS (ESI): m/z calcd for $\text{C}_{14}\text{H}_{15}\text{INO}$ $[\text{M}+\text{H}]^+$ 340.0193, found 340.0190.



4-(1,4-dioxan-2-yl)-2-(iodomethyl)quinoline (2h).

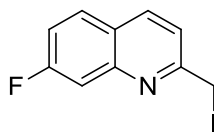
Brown solid; melting point: 106-109 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.08 (d, J = 8.0 Hz, 1 H), 7.95 (d, J = 8.0 Hz, 1 H), 7.73-7.68 (m, 2 H), 7.57-7.53 (m, 1 H), 5.34 (q, 1 H), 4.68 (s, 2 H), 4.15-4.01 (m, 3 H), 3.92-3.78 (m, 2 H), 3.44 (q, 1 H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.5, 147.6, 144.8, 130.2, 129.6, 127.1, 124.1, 122.4, 118.2, 74.2, 71.9, 67.3, 66.6, 6.9. IR (film, cm^{-1}): 2960, 2918, 2852, 1599, 1559, 1508, 1457, 1219, 1113, 1020, 991, 913, 892, 771, 571. HRMS (ESI): m/z calcd for $\text{C}_{14}\text{H}_{15}\text{INO}_2$ $[\text{M}+\text{H}]^+$ 356.0142, found 356.0144.



6-fluoro-2-(iodomethyl)quinoline (2i).

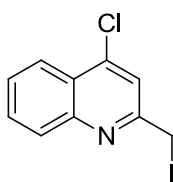
white solid; melting point: 100-105 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.07-8.03 (m, 2 H), 7.55 (d, J = 8.0 Hz, 1 H), 7.52-7.47 (m, 1 H), 7.42 (q, 1 H), 4.68 (s, 2 H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.7 (d, J = 247.0 Hz), 157.8 (d, J = 2.0 Hz), 144.7, 136.5 (d, J = 6.0 Hz), 131.6 (d, J = 9.0 Hz), 127.7 (d, J = 10.0 Hz), 121.9, 120.1 (d, J = 26.0 Hz), 110.6 (d, J = 22.0 Hz), 6.55. IR (film, cm^{-1}): 3064, 2923, 2851, 1628,

1560, 1505, 1473, 1217, 1152, 1109, 772, 571. HRMS (ESI): m/z calcd for $C_{10}H_8FIN$ $[M+H]^+$ 287.9680, found 287.9684.



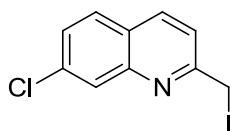
7-fluoro-2-(iodomethyl)quinoline (2j).

White solid; melting point: 96-102 °C. 1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.0 Hz, 1 H), 7.78 (q, 1 H), 7.68 (q, 1 H), 7.49 (d, J = 8.0 Hz, 1 H), 7.35-7.30 (m, 1 H), 4.66 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3 (d, J = 249.0 Hz), 159.6, 148.6 (d, J = 13.0 Hz), 137.1, 129.5 (d, J = 10.0 Hz), 124.1, 120.4 (d, J = 2.0 Hz), 117.3 (d, J = 25.0 Hz), 112.9 (d, J = 20.0 Hz), 6.38. IR (film, cm^{-1}): 3032, 2922, 2852, 1623, 1600, 1508, 1458, 1219, 1167, 1120, 772, 571. HRMS (ESI): m/z calcd for $C_{10}H_8FIN$ $[M+H]^+$ 287.9680, found 287.9682.



4-chloro-2-(iodomethyl)quinoline (2k).

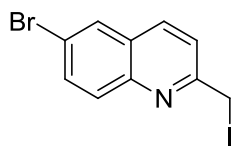
Yellow oil. 1H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.0 Hz, 1 H), 8.08 (d, J = 8.0 Hz, 1 H), 7.82-7.78 (m, 1 H), 7.66 (t, 2 H), 4.65 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 148.4, 143.3, 130.9, 129.5, 127.9, 125.4, 124.0, 121.1, 5.7. IR (film, cm^{-1}): 2955, 2919, 2849, 1635, 1600, 1558, 1473, 1219, 772, 668, 569. HRMS (ESI): m/z calcd for $C_{10}H_8ClIN$ $[M+H]^+$ 303.9385, found 303.9381.



7-chloro-2-(iodomethyl)quinoline (2l).

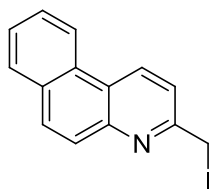
white solid; melting point: 63-67 °C. 1H NMR (400 MHz, $CDCl_3$) δ 8.10-8.05 (m, 2 H), 7.72 (d, J = 8.0 Hz, 1 H), 7.52-7.48 (m, 2 H), 4.65 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 148.0, 137.0, 135.8, 128.7, 128.2, 127.9, 125.4, 121.3, 6.4. IR (film, cm^{-1}): 2955, 2923, 2851, 1636, 1558, 1507, 1457, 1219, 772, 669, 570. HRMS (ESI):

m/z calcd for $C_{10}H_8ClIN$ $[M+H]^+$ 303.9385, found 303.9386.



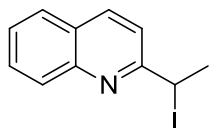
6-bromo-2-(iodomethyl)quinoline (2n).

Yellow oil. 1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.0 Hz, 1 H), 7.96-7.90 (m, 2 H), 7.78(m, 1 H), 7.54 (d, J = 8.0 Hz, 1 H), 4.65 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 146.2, 136.2, 133.4, 130.8, 129.6, 128.1, 122.0, 120.8, 6.5. IR (film, cm^{-1}): 2955, 2921, 2853, 1625, 1586, 1500, 1455, 1219, 772, 669, 571. HRMS (ESI): m/z calcd for $C_{10}H_8BrIN$ $[M+H]^+$ 347.8880, found 347.8883.



3-(iodomethyl)benzo[f]quinoline (2o).

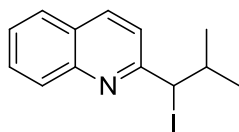
White solid; melting point: 164-166 °C. 1H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, J = 8.0 Hz, 1 H), 8.60 (d, J = 8.0 Hz, 1 H), 8.01 (d, J = 8.0 Hz, 1 H), 7.95 (d, J = 8.0 Hz, 2 H), 7.74-7.65 (m, 3 H), 4.8 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 147.7, 131.9, 131.8, 131.4, 129.4, 128.8, 127.8, 127.4, 127.3, 124.3, 122.7, 121.1, 6.6. IR (film, cm^{-1}): 2954, 2921, 2851, 1635, 1521, 1507, 1457, 1219, 772, 571. HRMS (ESI): m/z calcd for $C_{14}H_{11}IN$ $[M+H]^+$ 319.9931, found 319.9925.



2-(1-iodoethyl)quinoline (2p).

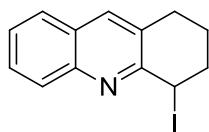
Brown oil. 1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.0 Hz, 1 H), 8.06 (d, J = 8.0 Hz, 1 H), 7.78 (d, J = 8.0 Hz, 1 H), 7.73-7.71 (m, 1 H), 7.61 (d, J = 8.0 Hz, 1 H), 7.56-7.52 (m, 1 H), 5.59 (dd, J = 12.0 Hz, J = 4.0 Hz, 1 H), 2.35 (d, J = 8.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 147.1, 137.0, 129.8, 129.3, 127.5, 127.3, 126.8, 119.7, 27.0, 26.7. IR (film, cm^{-1}): 3023, 2919, 2851, 1635, 1558, 1498, 1457, 1219,

1123, 772, 571. HRMS (ESI): m/z calcd for $C_{11}H_{11}IN$ $[M+H]^+$ 283.9931, found 283.9934.



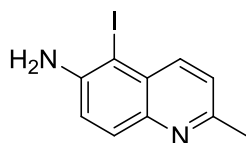
2-(1-iodo-2-methylpropyl)quinoline (2q).

Brown oil. 1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, $J = 8.0$ Hz, 1 H), 8.04 (d, $J = 8.0$ Hz, 1 H), 7.79 (d, $J = 8.0$ Hz, 1 H), 7.73-7.69 (m, 1 H), 7.62 (d, $J = 8.0$ Hz, 1 H), 7.55-7.51 (m, 1 H), 5.13 (d, $J = 8.0$ Hz, 1 H), 2.53-2.44 (m, 1 H), 1.34 (d, $J = 4.0$ Hz, 3 H), 0.91 (d, $J = 8.0$ Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 147.0, 136.9, 129.8, 129.3, 127.5, 127.2, 126.7, 120.6, 46.1, 35.6, 24.3, 20.2. IR (film, cm^{-1}): 3066, 2921, 2854, 1602, 1559, 1508, 1456, 1219, 1114, 771, 573. HRMS (ESI): m/z calcd for $C_{13}H_{15}IN$ $[M+H]^+$ 312.0244, found 312.0248.



4-iodo-1,2,3,4-tetrahydroacridine (2r).

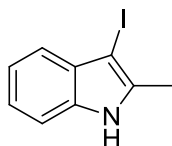
Yellow solid; melting point: 83-86 $^{\circ}C$. 1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, $J = 8.0$ Hz, 1 H), 7.81 (s, 1 H), 7.69 (d, $J = 8.0$ Hz, 1 H), 7.63 (t, $J = 8.0$ Hz, 1 H), 7.48 (t, $J = 8.0$ Hz, 1 H), 6.13 (m, 1 H), 3.24-3.09 (m, 2 H), 2.54-2.34 (m, 2 H), 2.06-1.98 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 146.7, 136.1, 129.0, 128.8, 128.6, 127.9, 126.9, 126.6, 34.4, 33.5, 27.9, 20.2. IR (film, cm^{-1}): 3020, 2926, 2854, 1653, 1521, 1489, 1467, 1215, 771, 571. HRMS (ESI): m/z calcd for $C_{13}H_{13}IN$ $[M+H]^+$ 310.0087, found 310.0083.



5-iodo-2-methylquinolin-6-amine (2s).

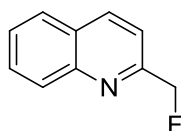
yellow solid; melting point: 105-109 $^{\circ}C$. 1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, $J = 8.0$ Hz, 1 H), 7.81 (d, $J = 8.8$ Hz, 1 H), 7.26-7.19 (m, 2 H), 4.52 (s, 2 H), 2.71 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 145.3, 143.3, 138.2, 130.1, 129.5, 123.7, 119.9,

81.4, 24.4. IR (film, cm^{-1}): 3446, 2960, 2918, 2852, 1599, 1559, 1508, 1457, 1219, 1113, 771, 571. HRMS (ESI): m/z calcd for $\text{C}_{10}\text{H}_{10}\text{IN}_2$ $[\text{M}+\text{H}]^+$ 284.9883, found 284.9885.



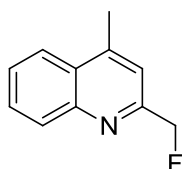
3-iodo-2-methyl-1H-indole (2t).

Brown oil. ^1H NMR (400 MHz, CDCl_3) δ 8.14 (s, 1 H), 7.41-7.38 (m, 1 H), 7.28-7.26 (m, 1 H), 7.23-7.17 (m, 2 H), 2.50 (s, 3 H). ^{13}C NMR (100 MHz, CDCl_3) δ 136.3, 135.9, 130.9, 122.4, 120.6, 120.3, 110.6, 59.1, 14.5. IR (film, cm^{-1}): 3446, 2953, 2919, 2850, 1652, 1558, 1508, 1457, 1219, 1143, 772, 571. HRMS (ESI): m/z calcd for $\text{C}_9\text{H}_9\text{IN}$ $[\text{M}+\text{H}]^+$ 257.9774, found 257.9771.



2-(fluoromethyl)quinoline (3a).

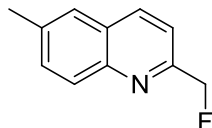
Colourless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.26 (d, $J = 8.0$ Hz, 1 H), 8.08 (d, $J = 8.0$ Hz, 1 H), 7.87 (d, $J = 8.0$ Hz, 1 H), 7.78-7.72 (m, 1 H), 7.64-7.57 (m, 2 H), 5.69 (d, $J = 48.0$ Hz, 2 H). ^{13}C NMR (100 MHz, CDCl_3) δ 156.8 (d, $J = 20.0$ Hz), 147.5, 137.1, 129.9, 129.1, 127.73, 127.68, 126.7, 118.2 (d, $J = 5.0$ Hz), 85.0 (d, $J = 170.0$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ 15.66. IR (film, cm^{-1}): 3023, 2919, 2850, 1635, 1558, 1507, 1457, 1375, 1219, 1134, 772. HRMS (ESI): m/z calcd for $\text{C}_{10}\text{H}_9\text{FN}$ $[\text{M}+\text{H}]^+$ 162.0713, found 162.0709.



2-(fluoromethyl)-4-methylquinoline (3b).

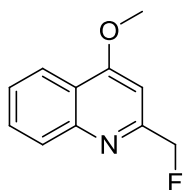
Yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.05 (q, 2 H), 7.77-7.73 (m, 1 H), 7.60 (t, 1 H), 7.47 (s, 1 H), 5.65 (d, $J = 48.0$ Hz, 2 H), 2.77 (s, 3 H). ^{13}C NMR (100 MHz, CDCl_3) δ 156.4 (d, $J = 21.0$ Hz), 147.2, 145.6, 129.64, 129.57, 127.7, 126.5, 123.9,

118.9 (d, $J = 6.0$ Hz), 85.1 (d, $J = 170.0$ Hz), 19.0. ^{19}F NMR (376 MHz, CDCl_3) δ 15.25. IR (film, cm^{-1}): 2954, 2923, 2851, 1635, 1558, 1507, 1457, 1339, 1219, 772. HRMS (ESI): m/z calcd for $\text{C}_{11}\text{H}_{11}\text{FN}$ $[\text{M}+\text{H}]^+$ 176.0869, found 176.0872.



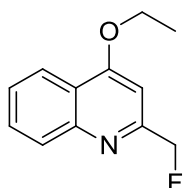
2-(fluoromethyl)-6-methylquinoline (3c).

Colourless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, $J = 8.0$ Hz, 1 H), 7.87 (d, $J = 8.0$ Hz, 1 H), 7.52-7.47 (m, 3 H), 5.57 (d, $J = 48.0$ Hz, 2 H), 2.47 (s, 3 H). ^{13}C NMR (100 MHz, CDCl_3) δ 155.8 (d, $J = 20.0$ Hz), 146.0 (d, $J = 1$ Hz), 136.7, 136.5, 132.3, 128.7, 127.7, 126.6, 118.3 (d, $J = 10.0$ Hz), 85.1 (d, $J = 170.0$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ 16.46. IR (film, cm^{-1}): 3032, 2953, 2921, 1635, 1558, 1507, 1457, 1396, 1219, 772. HRMS (ESI): m/z calcd for $\text{C}_{11}\text{H}_{11}\text{FN}$ $[\text{M}+\text{H}]^+$ 176.0869, found 176.0867.



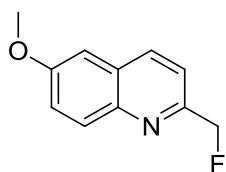
2-(fluoromethyl)-4-methoxyquinoline (3d)

Colourless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.20 (q, 1 H), 7.98 (d, $J = 8.0$ Hz, 1 H), 7.74-7.69 (m, 1 H), 7.53-7.49 (m, 1 H), 6.96 (d, $J = 0.8$ Hz, 1 H), 5.62 (d, $J = 48.0$ Hz, 2 H), 4.08 (s, 3 H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.2, 158.2 (d, $J = 20.0$ Hz), 148.4 (d, $J = 2.0$ Hz), 130.2, 128.4, 125.7, 121.9, 120.8, 96.9 (d, $J = 6.0$ Hz), 85.1 (d, $J = 170.0$ Hz), 55.8. ^{19}F NMR (376 MHz, CDCl_3) δ 14.76. IR (film, cm^{-1}): 3013, 2941, 2854, 1597, 1569, 1510, 1457, 1361, 1233, 1219, 1159, 1114, 1038, 770. HRMS (ESI): m/z calcd for $\text{C}_{11}\text{H}_{11}\text{FNO}$ $[\text{M}+\text{H}]^+$ 192.0818, found 192.0820.



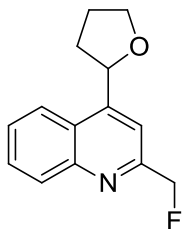
4-ethoxy-2-(fluoromethyl)quinoline (3e)

Colourless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.25 (q, 1 H), 7.98 (d, $J = 8.0$ Hz, 1 H), 7.74-7.70 (m, 1 H), 7.54-7.50 (m, 1 H), 6.95 (d, $J = 4.0$ Hz, 1 H), 5.62 (d, $J = 48.0$ Hz, 2 H), 4.33 (q, $J = 8.0$ Hz, 2 H), 1.61 (t, $J = 8.0$ Hz, 3 H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.6, 158.2 (d, $J = 20.0$ Hz), 148.5, 130.1, 128.4, 125.6, 122.0, 120.9, 97.4 (d, $J = 10.0$ Hz), 85.1 (d, $J = 170.0$ Hz), 64.3, 14.5. ^{19}F NMR (376 MHz, CDCl_3) δ 14.80. IR (film, cm^{-1}): 3058, 2924, 2853, 1598, 1557, 1436, 1406, 1375, 1305, 1219, 1171, 1140, 1018, 772. HRMS (ESI): m/z calcd for $\text{C}_{12}\text{H}_{13}\text{FNO}$ $[\text{M}+\text{H}]^+$ 206.0975, found 206.0972.



2-(fluoromethyl)-6-methoxyquinoline (3f).

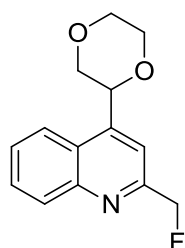
White solid, melting point: 32-37 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, $J = 12.0$ Hz, 1 H), 7.98 (d, $J = 12.0$ Hz, 1 H), 7.57 (d, $J = 8.0$ Hz, 1 H), 7.41 (q, 1 H), 7.11 (d, $J = 4.0$ Hz, 1 H), 5.64 (d, $J = 48.0$ Hz, 2 H), 3.96 (s, 3 H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.0, 154.1 (d, $J = 20.0$ Hz), 143.5, 135.8, 130.5, 128.8, 122.8, 118.8 (d, $J = 4.0$ Hz), 105.1, 85.1 (d, $J = 170.0$ Hz), 55.6. ^{19}F NMR (376 MHz, CDCl_3) δ 16.96. IR (film, cm^{-1}): 3006, 2924, 2850, 1620, 1558, 1504, 1437, 1383, 1243, 1219, 1162, 1112, 1028, 772. HRMS (ESI): m/z calcd for $\text{C}_{11}\text{H}_{11}\text{FNO}$ $[\text{M}+\text{H}]^+$ 192.0818, found 192.0817.



2-(fluoromethyl)-4-(tetrahydrofuran-2-yl)quinoline (3g)

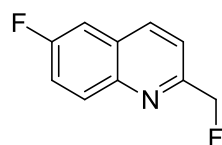
Colourless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.11 (d, $J = 8.0$ Hz, 1 H), 7.95 (d, $J = 8.0$ Hz, 1 H), 7.78-7.72 (m, 2 H), 7.59 (t, 1 H), 5.67 (dd, $J = 48.0$ Hz, $J = 4.0$ Hz, 2 H), 5.66 (t, $J = 8.0$ Hz, 1 H), 4.28 (q, 1 H), 4.09 (q, 1 H), 2.71-2.62 (m, 1 H), 2.17-2.00 (m,

2 H), 1.94-1.85 (m, 1 H). ^{13}C NMR (100 MHz, CDCl_3) δ 156.8 (d, $J = 20.0$ Hz), 150.7, 147.5, 129.9, 129.4, 126.6, 125.0, 123.2, 113.8 (d, $J = 5.0$ Hz), 85.2 (d, $J = 170.0$ Hz), 76.8, 69.1, 34.0, 26.0. ^{19}F NMR (376 MHz, CDCl_3) δ 15.43. IR (film, cm^{-1}): 3066, 2927, 2880, 1601, 1559, 1508, 1457, 1375, 1261, 1219, 1158, 1128, 1080, 772. HRMS (ESI): m/z calcd for $\text{C}_{14}\text{H}_{15}\text{FNO}$ $[\text{M}+\text{H}]^+$ 232.1131, found 232.1134.



4-(1,4-dioxan-2-yl)-2-(fluoromethyl)quinoline (3h)

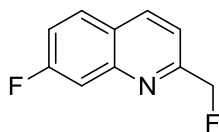
Colourless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.11 (d, $J = 8.0$ Hz, 1 H), 8.04 (d, $J = 8.0$ Hz, 1 H), 7.84 (s, 1 H), 7.76 (t, 1 H), 7.61 (t, 1 H), 5.67 (d, $J = 48.0$ Hz, 2 H), 5.43 (q, 1 H), 4.18-4.05 (m, 3 H), 3.93-3.73 (m, 2 H), 3.54-3.49 (m, 1 H). ^{13}C NMR (100 MHz, CDCl_3) δ 156.8 (d, $J = 20.0$ Hz), 147.4, 144.8, 130.1, 129.7, 127.0, 124.7, 122.6, 115.5 (d, $J = 10.0$ Hz), 85.0 (d, $J = 170.0$ Hz), 74.2, 71.9, 67.3, 66.6. ^{19}F NMR (376 MHz, CDCl_3) δ 15.03. IR (film, cm^{-1}): 3065, 2948, 2834, 1600, 1565, 1500, 1450, 1370, 1220, 1219, 1164, 1113, 1053, 770,. HRMS (ESI): m/z calcd for $\text{C}_{14}\text{H}_{15}\text{FNO}_2$ $[\text{M}+\text{H}]^+$ 248.1081, found 248.1085.



6-fluoro-2-(fluoromethyl)quinoline (3i).

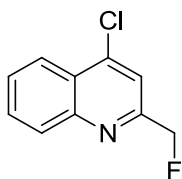
White solid; melting point: 46-50 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.20 (d, $J = 8.0$ Hz, 1 H), 8.08 (q, 1 H), 7.64 (d, $J = 8.0$ Hz, 1 H), 7.55-7.46 (m, 2 H), 5.66 (d, $J = 48.0$ Hz, 2 H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.5 (d, $J = 250.0$ Hz), 156.1 (dd, $J = 22.0$ Hz, $J = 3.0$ Hz), 144.5, 136.4 (d, $J = 10.0$ Hz), 131.6 (d, $J = 10.0$ Hz), 128.3 (d, $J = 10.0$ Hz), 120.2 (d, $J = 20.0$ Hz), 119.1 (d, $J = 10.0$ Hz), 110.7 (d, $J = 20.0$ Hz), 84.9 (d, $J = 170.0$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ 15.92, -113.01. IR (film, cm^{-1}):

2956, 2921, 2851, 1636, 1558, 1507, 1457, 1386, 1219, 1143, 1106, 772. HRMS (ESI): m/z calcd for $C_{10}H_8F_2N$ $[M+H]^+$ 180.0619, found 180.0617.



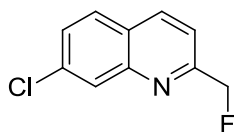
7-fluoro-2-(fluoromethyl)quinoline (3j).

Yellow solid; melting point: 49-56 °C. 1H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 8.0 Hz, 1 H), 7.86 (q, 1 H), 7.69 (q, 1 H), 7.60 (d, J = 8.0 Hz, 1 H), 7.40-7.35 (m, 1 H), 5.67 (d, J = 48.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3 (d, J = 240.0 Hz), 158.0 (d, J = 20.0 Hz), 148.4 (d, J = 10.0 Hz), 137.1, 129.8 (d, J = 10.0 Hz), 124.7, 117.5 (dd, J = 5.0 Hz, J = 3.0 Hz), 117.2, 112.7 (d, J = 20.0 Hz), 84.8 (d, J = 170.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ 14.90, -108.77. IR (film, cm^{-1}): 3032, 2920, 2850, 1635, 1558, 1508, 1457, 1396, 1219, 1164, 1113, 772. HRMS (ESI): m/z calcd for $C_{10}H_8F_2N$ $[M+H]^+$ 180.0619, found 180.0618.



4-chloro-2-(fluoromethyl)quinoline (3k).

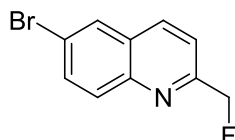
Colourless oil. 1H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 8.0 Hz, 1 H), 8.08 (d, J = 8.0 Hz, 1 H), 7.84-7.80 (m, 1 H), 7.73 (s, 1 H), 7.69 (q, 1 H), 5.65 (d, J = 46.8 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8 (d, J = 20.0 Hz), 148.2, 143.8, 130.9, 129.4, 127.7, 125.9, 124.2, 118.4 (d, J = 10.0 Hz), 84.3 (d, J = 170.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ 14.30. IR (film, cm^{-1}): 2956, 2924, 2852, 1635, 1593, 1557, 1457, 1375, 1219, 1121, 772, 669. HRMS (ESI): m/z calcd for $C_{10}H_8ClFN$ $[M+H]^+$ 196.0323, found 196.0325.



7-chloro-2-(fluoromethyl)quinoline (3l).

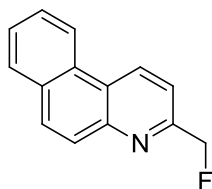
White solid, melting point: 88-92 °C. 1H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.0

Hz, 1 H), 8.07 (s, 1 H), 7.81 (d, $J = 8.0$ Hz, 1 H), 7.63 (d, $J = 8.0$ Hz, 1 H), 7.54 (q, 1 H), 5.67 (d, $J = 48.0$ Hz, 2 H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.0 (d, $J = 20.0$ Hz), 147.7, 137.0 (d, $J = 14.0$ Hz), 135.8, 129.0, 128.1 (d, $J = 15.0$ Hz), 127.6, 126.0, 118.3 (d, $J = 40.0$ Hz), 84.7 (d, $J = 170.0$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ 14.25. IR (film, cm^{-1}): 2955, 2922, 2851, 1635, 1618, 1558, 1457, 1396, 1219, 772, 669. HRMS (ESI): m/z calcd for $\text{C}_{10}\text{H}_8\text{ClFN}$ $[\text{M}+\text{H}]^+$ 196.0323, found 196.0326.



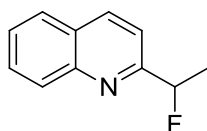
6-bromo-2-(fluoromethyl)quinoline (3n)

White solid; melting point: 96-99 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 8.17 (d, $J = 8.0$ Hz, 1 H), 8.03 (d, $J = 4.0$ Hz, 1 H), 7.94 (d, $J = 8.0$ Hz, 1 H), 7.82 (q, 1 H), 7.65 (d, $J = 8.0$ Hz, 1 H), 5.66 (d, $J = 46.8$ Hz, 2 H). ^{13}C NMR (100 MHz, CDCl_3) δ 157.3 (d, $J = 20.0$ Hz), 146.0, 136.1, 133.4, 130.8, 129.8, 128.8, 120.6, 119.1 (d, $J = 10.0$ Hz), 84.8 (d, $J = 170.0$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ 14.72. IR (film, cm^{-1}): 3033, 2953, 2851, 1635, 1558, 1507, 1457, 1388, 1219, 1122, 772, 669. HRMS (ESI): m/z calcd for $\text{C}_{10}\text{H}_8\text{BrFN}$ $[\text{M}+\text{H}]^+$ 239.9818, found 239.9822.



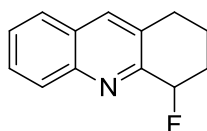
3-(fluoromethyl)benzo[f]quinoline (3o)

Yellow solid; melting point: 64-68 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 9.05 (d, $J = 8.0$ Hz, 1 H), 8.66 (d, $J = 8.0$ Hz, 1 H), 8.11-7.95 (m, 3 H), 7.79-7.68 (m, 3 H), 5.74 (d, $J = 48.0$ Hz, 2 H). ^{13}C NMR (100 MHz, CDCl_3) δ 156.2 (d, $J = 20.0$ Hz), 147.5, 131.7 (d, $J = 6.0$ Hz), 131.5, 129.5, 128.8, 127.7, 127.5, 127.3, 124.9, 123.5, 122.7, 118.4 (d, $J = 10.0$ Hz), 84.9 (d, $J = 170.0$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ 16.05. IR (film, cm^{-1}): 3057, 2922, 2850, 1635, 1558, 1507, 1457, 1373, 1219, 1194, 772. HRMS (ESI): m/z calcd for $\text{C}_{14}\text{H}_{11}\text{FN}$ $[\text{M}+\text{H}]^+$ 212.0869, found 212.0866.



2-(1-fluoroethyl)quinoline (3p)

Brown oil. ^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, $J = 8.0$ Hz, 1 H), 7.98 (d, $J = 8.0$ Hz, 1 H), 7.76 (d, $J = 8.0$ Hz, 1 H), 7.67-7.63 (m, 1 H), 7.55 (q, 1 H), 7.48 (q, 1 H), 5.78 (dq, $J = 48.0$ Hz, $J = 8.0$ Hz, 1 H). ^{13}C NMR (100 MHz, CDCl_3) δ 161.0 (d, $J = 20.0$ Hz), 147.3, 137.2, 129.8, 129.2, 127.67, 127.65, 126.6, 117.1 (d, $J = 6.0$ Hz), 92.1 (d, $J = 170.0$ Hz), 21.9 (d, $J = 30.0$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -177.17. IR (film, cm^{-1}): 2955, 2923, 2852, 1635, 1558, 1498, 1457, 1396, 1219, 1123, 772. HRMS (ESI): m/z calcd for $\text{C}_{11}\text{H}_{11}\text{FN}$ $[\text{M}+\text{H}]^+$ 176.0869, found 176.0871.



4-fluoro-1,2,3,4-tetrahydroacridine (3r)

Colourless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 8.0$ Hz, 1 H), 7.99 (d, $J = 12.0$ Hz, 1 H), 7.78 (d, $J = 8.0$ Hz, 1 H), 7.72-7.67 (m, 1 H), 7.55 (q, 1 H), 5.80 (dt, $J = 48.0$ Hz, $J = 4.0$ Hz, 1 H), 3.15-3.08 (m, 1 H), 3.00-2.91 (m, 1 H), 2.59-2.47 (m, 1 H), 2.24-2.06 (m, 2 H), 1.97-1.91 (m, 1 H). ^{13}C NMR (100 MHz, CDCl_3) δ 153.7 (d, $J = 15.0$ Hz), 147.1 (d, $J = 10.0$ Hz), 136.0, 130.8 (d, $J = 3.0$ Hz), 129.4, 129.0, 128.4 (d, $J = 3.0$ Hz), 127.1 (d, $J = 1.0$ Hz), 127.0, 89.5 (d, $J = 170.0$ Hz), 30.0 (d, $J = 20.0$ Hz), 28.6, 17.8 (d, $J = 10.0$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -163.48. IR (film, cm^{-1}): 3057, 2922, 2850, 1647, 1558, 1507, 1457, 1373, 1219, 1109, 772. HRMS (ESI): m/z calcd for $\text{C}_{13}\text{H}_{13}\text{FN}$ $[\text{M}+\text{H}]^+$ 202.1026, found 202.1023.

NMR spectra

