Supporting Information

Aminomethylations *via* Cross-Coupling of Potassium Organotrifluoroborates with Aryl Bromides

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General. Pd(OAc)₂, XPhos (2-dicyclohexylphosphino-2'4'6'-triisopropylbiphenyl), and Cs₂CO₃ were used as received. Tetrahydrofuran was distilled from sodium/benzophenone prior to use. H₂O and cyclopentyl methyl ether (CPME) were degassed prior to use. Standard benchtop techniques were employed for handling air-sensitive reagents. Melting points (°C) were determined using a Thomas–Hoover melting point apparatus and are uncorrected. ¹H, ¹³C, and ¹⁹F NMR spectra were recorded on a 500 MHz spectrometer. ¹¹B NMR spectra were recorded on a 400 MHz spectrometer with appropriate decoupling accessories. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel (60F–254) plates (0.25 mm) precoated with a fluorescent indicator. Standard flash chromatography procedures¹ were followed using 32–63 mm silica gel. Visualization was effected with ultraviolet light or ninhydrin.

Piperidine and morpholine were fractionally distilled under nitrogen and dried over activated molecular sieves. All other amines and bromides were used as received.

Potassium 1-trifluoroboratomethylpiperidine was prepared according to literature procedures.²

General Experimental Procedure for the Preparation of Aminomethyltrifluoroborates.

Reaction Condition A for Preparing Compounds 5a and 5f.

Potassium bromomethyltrifluoroborate (200 mg, 1.0 mmol) was added to neat amine (4 mL) at rt, heated at 80 °C for 30 min, and then concentrated *in vacuo*. The product was dissolved in a solution of acetone (30 mL) and K₂CO₃ (138 mg, 1.0 mmol) and stirred for 30 min. The insoluble salts were filtered off, and the filtrate was concentrated. The crude solid was dissolved in a minimal amount of hot acetone, and Et₂O was added dropwise leading to precipitation of the

product. The product was then filtered, collected, and dried overnight *in vacuo* to afford the desired pure compound.

Potassium 4-Trifluoroboratomethyl-morpholine (5a). According to the general procedure and reaction with morpholine, the product was obtained in 70% yield (144 mg, 0.69 mmol) as a yellow amorphous solid after acetone/Et₂O precipitation. ¹H-NMR (500 MHz, DMSO-*d*₆): δ = 3.52-3.54 (m, 4H), 2.44 (br s, 4H), 1.41-1.42 (m, 2H); ¹³C-NMR (125.8 MHz, DMSO-*d*₆): δ = 65.6, 55.8; ¹⁹F-NMR (471 MHz, DMSO-*d*₆): δ = -136.6; ¹¹B-NMR (128.37 MHz, DMSO-*d*₆): δ = 2.89; IR (KBr) = 2963, 2871, 2767, 1456, 1302, 1262, 1124, 1027 cm⁻¹; HRMS (ESI) calcd. for C₅H₁₀BF₃NO (M⁺) 168.0807, found 168.0810.

Potassium *N,N*-Diallyltrifluoroboratomethylamine. (5f). According to the general procedure using diallylamine, the product was obtained in 93% yield (200 mg, 0.92 mmol) as a light brown amorphous solid after acetone/Et₂O precipitation. ¹H-NMR (500 MHz, DMSO-*d*₆): δ = 5.78-5.86 (m, 2H), 5.08-5.14 (m, 4H), 3.06-3.08 (m, 4H), 1.44-1.45 (m, 2H); ¹³C-NMR (125.8 MHz, DMSO-*d*₆): δ = 136.2, 118.0, 59.0; ¹⁹F-NMR (471 MHz, DMSO-*d*₆): δ = -136.8; ¹¹B-NMR (128.37 MHz, DMSO-*d*₆): δ = 3.29; IR (KBr) = 3087, 2930, 2807, 1642, 1452, 1420, 1340, 1253, 1063 cm⁻¹; HRMS (ESI) calcd. for C₇H₁₂BF₃N (M⁺) 178.1015, found 178.1022.

Reaction Condition B.

Potassium *N,N*-Diethyltrifluoroboratomethylamine (5b).

Potassium bromomethyltrifluoroborate (200 mg, 1.0 mmol) was added to neat diethylamine (4 mL) at rt, heated at 45 °C for 8 h, and then concentrated *in vacuo*. The product was dissolved in a solution of acetone (30 mL) and K₂CO₃ (138 mg, 1.0 mmol) and stirred for 30 min. The insoluble salts were filtered off, and the filtrate was concentrated. The crude solid was dissolved in a minimal amount of hot acetone, and Et₂O was added dropwise leading to precipitation of the product. The product was then filtered, collected, and dried overnight *in vacuo* to afford the desired pure compound in a 96% yield (185 mg, 0.96 mmol) as a white crystalline solid after acetone/Et₂O precipitation. mp = 100-102 °C. ¹H-NMR (500 MHz, DMSO-*d*₆): δ = 2.99 (q, *J* = 7.2 Hz, 4H), 1.90 (m, 2H), 1.13 (t, *J* = 7.2 Hz, 6H); ¹³C-NMR (125.8 MHz, DMSO-*d*₆): δ = 48.3, 8.6; ¹⁹F-NMR (471 MHz, DMSO-*d*₆): δ = -138.3; ¹¹B-NMR (128.37 MHz, DMSO-*d*₆): δ = 2.56; IR (KBr) = 2993, 2956, 1480, 1446, 1402, 1342, 1245, 1178, 1151 cm⁻¹; HRMS (ESI) calcd. for C₅H₁₂BF₃N (M⁺) 154.1015, found 54.1019.

Reaction Condition C for Preparing Compounds 5c-5e.

Potassium bromomethyltrifluoroborate (200mg, 1.00 mmol) was added to alkylamine (1.05 mmol) in THF (1.0 M) at rt, heated at 80 °C for 2-3 h and then concentrated *in vacuo*. The product was dissolved in a solution of acetone (30 mL) and K₂CO₃ (138 mg, 1.0 mmol) and stirred for 30 min. The insoluble salts were filtered off and the filtrate was concentrated.

Potassium *N*-Benzyltrifluoroboratomethylamine (5c). According to the

general procedure using *N*-methylbenzylamine, the product was obtained in 87% yield (208 mg, 0.86 mmol) as an amorphous white solid after two Et₂O extractions (5 mL x 2). ¹H-NMR (500 MHz, DMSO-*d*₆): δ = 7.36-7.43 (m, 5H), 3.93 (s, 2H), 2.46 (s, 3H), 1.73-1.74 (m, 2H); ¹³C-NMR (125.8 MHz, DMSO-*d*₆): δ = 133.7, 131.2, 129.0, 128.9, 62.0, 43.0; ¹⁹F-NMR (471 MHz, DMSO-*d*₆): δ = -137.7; ¹¹B-NMR (128.37 MHz, DMSO-*d*₆): δ = 1.49; IR (KBr) = 3188, 3032, 2984, 1657, 1457, 1318, 1172 cm⁻¹; HRMS (ESI) calcd. for C₉H₁₂BF₃N (M⁺) 202.1015, found 202.1017.

Potassium 4-Trifluoroboratomethylpiperazine-1-carboxylic acid *tert*-

butyl ester (5d). According to the general procedure using mono-Boc-protected piperazine¹ and the product was obtained in 86% yield 260 mg, 0.85 mmol) as a white crystalline solid after dissolution in a minimal amount of a hot acetone/Et₂O mixture (2:1) followed by dropwise addition of hexane. mp = 200 °C (dec.). ¹H-NMR (500 MHz, DMSO-*d*₆): δ = 3.46 (br s, 4H), 2.91 (br s, 4H), 1.86 (s, 2H), 1.40 (s, 9H); ¹³C-NMR (125.8 MHz, DMSO-*d*₆): δ = 154.0, 79.9, 53.9, 28.5; ¹⁹F-NMR (471 MHz, DMSO-*d*₆): δ = -137.6; ¹¹B-NMR (128.37 MHz, DMSO-*d*₆): δ = 1.46; IR (KBr) = 2982, 2773, 1716, 1407, 1369, 1282, 1133, 1015 cm⁻¹; HRMS (ESI) calcd. for C₁₀H₁₉BF₃N₂O₂ (M⁺) 267.1492, found 267.1485.

Potassium (S)-1-Trifluoroboratomethylpyrrolidine-2-carboxylic acid methyl

ester (5e). According to the general procedure, the product was obtained in 76% yield (189 mg, 0.76 mmol) as a white crystalline solid after precipitation from a minimal amount of hot acetone with Et₂O. mp = 152-156. $[\alpha]_D^{22} = -51.4^\circ$ (c = 2, DMSO); ¹H-NMR (500 MHz, DMSO-*d*₆): δ = 3.54 (s, 3H), 2.96-2.99 (m, 1H), 2.80-2.83 (m, 1H), 2.10-2.15 (m, 1H), 1.83-1.88 (m, 1H), 1.51-1.67 (m, 4H), 1.11-1.17 (m, 1H); ¹³C-NMR (125.8 MHz, DMSO-*d*₆): δ = 175.6, 69.5, 54.9, 51.4, 29.2, 23.5; ¹⁹F-NMR (471 MHz, DMSO-*d*₆): δ = -137.9; ¹¹B-NMR (128.37 MHz, DMSO-*d*₆): δ = 2.49; IR (KBr) = 2956, 2791, 1745, 1240, 1209, 1064 cm⁻¹; HRMS (ESI) calcd. for C₇H₁₂BF₃NO₂ (M⁺) 210.0913, found 210.0919.

General Experimental Procedure for the Suzuki-Miyaura Cross-Coupling Reactions.

Preparation of 4-(Piperidin-1-ylmethyl)benzonitrile (2a).

A solution of potassium 1-trifluoroboratomethylpiperidine (222 mg, 1.1 mmol), Cs₂CO₃ (978 mg, 3.0 mmol), Pd(OAc)₂ (7 mg, 0.03 mmol), XPhos (29 mg, 0.06 mmol) and 4-bromobenzonitrile (181 mg, 1.0 mmol) in THF/H₂O (10:1) (4 mL) was heated under a N₂ atmosphere in a sealed tube. The reaction was stirred at 80 °C for 24 h, then cooled to rt and diluted with H₂O (2 mL). The reaction mixture was extracted with CH₂Cl₂ (5 mL x 3). The organic layer was dried (Mg₂SO₄). The solvent was removed *in vacuo* and the crude product was purified by silica gel column chromatography (elution with hexane/EtOAc/Et₃N 7:1:0.2) to yield the product as a clear yellow liquid in an 83% yield (166 mg, 0.83 mmol). ¹H-NMR (500 MHz, DMSO-*d*₆): δ = 7.57 (d, *J* =

8.2 Hz, 2H), 7.43 (d, $J = 8.0$ Hz, 2H), 3.50 (s, 2H), 2.36 (br s, 4H), 1.56 (m, 4H), 1.42-1.43 (m, 2H); ^{13}C -NMR (125.8 MHz, CDCl_3): $\delta = 144.7, 132.0, 129.5, 119.1, 110.6, 63.2, 54.6, 25.9, 24.2$; IR (neat) = 2936, 2228 cm^{-1} ; HRMS (CI) calcd. for $\text{C}_{13}\text{H}_{16}\text{N}_2$ (M^+) 200.1313, found 200.1322.

Compound Characterization:

Methyl 4-(Piperidin-1-ylmethyl)benzoate (2b). According to the

general procedure, the product was obtained in 83% yield (190 mg, 0.81 mmol) as a light orange oil after silica gel column chromatography (elution with hexane/EtOAc/ Et_3N 7:1:0.2). ^1H -NMR (500 MHz, CDCl_3): $\delta = 7.97$ (d, $J = 8.3$ Hz, 2H), 7.39 (d, $J = 8.1$ Hz, 2H), 3.92 (s, 3H), 3.52 (s, 2H), 2.38 (br s, 4H), 1.58 (m, 4H), 1.43 (m, 2H); ^{13}C -NMR (125.8 MHz, CDCl_3): $\delta = 167.1, 144.4, 129.5, 129.0, 128.8, 63.5, 54.6, 52.0, 26.0, 24.3$. ; IR (neat) = 2936, 1721, 1280, 1110 cm^{-1} ; HRMS (CI) calcd. for $\text{C}_{14}\text{H}_{19}\text{NO}_2$ (M^+) 233.1416, found 233.1411.

1-(4-Nitrobenzyl)piperidine (2c). According to the

general procedure using CPME/ H_2O as the solvent, the product was obtained in 75% yield (149 mg, 0.68 mmol) as an orange oil after silica gel column chromatography (elution with hexane/EtOAc/ Et_3N 7:1:0.2). ^1H -NMR (500 MHz, CDCl_3): $\delta = 8.11$ (d, $J = 8.6$ Hz, 2H), 7.46 (d, $J = 8.3$ Hz, 2H), 3.50 (s, 2H), 2.33 (br s, 4H), 1.53 (m, 4H), 1.40 (m, 2H); ^{13}C -NMR (125.8 MHz, CDCl_3): $\delta = 147.1, 147.0, 129.5, 123.4, 62.9, 54.6, 26.0, 24.2$; IR (neat) = 2936, 1520, 1343 cm^{-1} .

¹; HRMS (CI) calcd. for C₁₂H₁₆N₂O₂ (M-H⁺) 219.1134, found 219.1123.

Phenyl (4-(Piperidin-1-ylmethyl)phenyl)methanone (2d).

According to the general procedure, the product was obtained in 76% yield (206 mg, 0.74 mmol) as a dark orange oil after silica gel column chromatography (elution with hexane/EtOAc/Et₃N 7:1:0.2). ¹H-NMR (500 MHz, CDCl₃): δ = 7.71-7.76 (m, 4H), 7.52 (m, 1H), 7.42-7.43 (m, 4H), 3.55 (s, 2H), 2.41 (br s, 4H), 1.57 (br s, 4H), 1.23 (br s, 2H); ¹³C-NMR (125.8 MHz, CDCl₃): δ = 196.6, 143.8, 137.9, 136.3, 132.3, 130.1, 128.9, 128.3, 63.5, 54.6, 26.0, 24.3; IR (neat) = 2935, 1656, 1278 cm⁻¹; HRMS (CI) calcd. for C₁₉H₂₁NO (M⁺) 279.1623, found 279.1631.

4-(Piperidin-1-ylmethyl)benzaldehyde (2e). According to the general

procedure using CPME/H₂O as the solvent, the product was obtained in 73% yield (144 mg, 0.71 mmol) as an orange oil after silica gel column chromatography (elution with hexane/EtOAc/Et₃N 7:1:0.2). ¹H-NMR (500 MHz, CDCl₃): δ = 9.94 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 3.49 (s, 2H), 2.34 (br s, 4H), 1.54 (m, 4H), 1.40 (m, 2H); ¹³C-NMR (125.8 MHz, CDCl₃): δ = 192.0, 146.3, 135.4, 129.7, 129.5, 63.4, 54.6, 25.9, 24.2; IR (neat) = 2935, 1702 cm⁻¹; HRMS (CI) calcd. for C₁₃H₁₇NO (M⁺) 203.1310, found 203.1302.

1-(4-Methoxybenzyl)piperidine (2f). According to the general

procedure, the product was obtained in 80% yield (162 mg, 0.79 mmol) as a light yellow oil after silica gel column chromatography (elution with hexane/EtOAc/Et₃N 7:1:0.2). ¹H-NMR (500 MHz, CDCl₃): δ = 7.23 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 3.81 (s, 3H), 3.42 (s, 2H), 2.36 (br s, 4H), 1.57 (m, 4H), 1.43 (m, 2H); ¹³C-NMR (125.8 MHz, CDCl₃): δ = 158.6, 130.6, 130.4, 113.5, 63.3, 55.2, 54.4, 26.0, 24.5; IR (neat) = 2932, 1511, 1245 cm⁻¹; HRMS (CI) calcd. for C₁₃H₁₉NO (M⁺) 205.1467, found 205.1458.

1-(2,4-Dimethoxybenzyl)piperidine (2g). According to the general

procedure, the product was obtained in 75% yield (172 mg, 0.73 mmol) as a light yellow oil after silica gel column chromatography (elution with hexane/EtOAc/Et₃N 7:1:0.2). ¹H-NMR (500 MHz, CDCl₃): δ = 7.22 (d, *J* = 8.0 Hz, 1H), 6.44-6.47 (m, 2H), 3.80 (s, 3H), 3.78 (s, 3H), 3.46 (br, 2H), 2.40 (br s, 4H), 1.57 (m, 4H), 1.41 (m, 2H); ¹³C-NMR (125.8 MHz, CDCl₃): δ = 159.8, 158.9, 131.4, 118.9, 103.9, 98.4, 56.4, 55.5, 55.3, 54.3, 26.0, 24.4; IR (neat) = 2934, 1508 cm⁻¹; HRMS (CI) calcd. for C₁₄H₂₁NO₂ (M⁺) 235.1572, found 235.1571.

1-(2,4,6-Trimethylbenzyl)piperidine (2h). According to the general

procedure using CPME/H₂O as the solvent, the product was obtained in 77% yield (184 mg, 0.84 mmol) as a light yellow oil after silica gel column chromatography (elution with hexane/EtOAc/Et₃N 38:1:1). ¹H-NMR (500 MHz, CDCl₃): δ = 6.86 (s, 2H), 3.41 (s, 2H), 2.39 (s, 9H), 2.29 (s, 4H), 1.52 (m, 4H), 1.44 (m, 2H); ¹³C-NMR (125.8 MHz, CDCl₃): δ = 138.2, 136.0,

132.6, 128.8, 56.7, 54.3, 26.4, 24.8, 21.0, 20.1; IR (neat) = 2932 cm^{-1} ; HRMS (CI) calcd. for $\text{C}_{15}\text{H}_{23}\text{N}$ (M^+) 217.1831, found 217.1821.

***N*-(4-(Piperidin-1-ylmethyl)phenyl)acetamide (2i).** According to the general procedure, the product was obtained in 80% yield (182 mg, 0.78 mmol) as a yellow crystalline solid after sequestering the ligand with CuCl_2 ² and silica gel column chromatography (elution with hexane/EtOAc/ Et_3N 1.6:1:0.05). mp = 146-148 °C. ^1H -NMR (500 MHz, CDCl_3): δ = 7.42 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 3.43 (s, 2H), 2.35 (br s, 4H), 2.16 (s, 3H), 1.84 (br s, 2H), 1.56 (m, 4H), 1.42 (m, 2H); ^{13}C -NMR (125.8 MHz, CDCl_3): δ = 168.2, 136.7, 134.5, 129.9, 119.7, 63.3, 54.4, 25.9, 24.6, 24.4; IR (neat) = 3301, 2935, 1667, 1541, 1318 cm^{-1} ; HRMS (CI) calcd. for $\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}$ ($\text{M}-\text{H}^+$) 231.1497, found 231.1492.

***N,N*-Dimethyl-4-(piperidin-1-ylmethyl)benzamine (2j).** According to the general procedure using CPME/ H_2O as a solvent, the product was obtained in 82% yield (180 mg, 0.82 mmol) as a light orange oil after silica gel column chromatography (elution with hexane/EtOAc/ Et_3N 7:1:0.2). ^1H -NMR (500 MHz, CDCl_3): δ = 7.21 (d, J = 8.7 Hz, 2H), 6.73 (d, J = 8.7 Hz, 2H), 3.43 (s, 2H), 2.96 (s, 6H), 2.40 (br s, 4H), 1.61 (m, 4H), 1.46 (m, 2H); ^{13}C -NMR (125.8 MHz, CDCl_3): δ = 149.8, 130.3, 126.4, 112.4, 63.5, 54.4, 40.8, 26.1, 24.6; IR (neat) = 2932, 1343 cm^{-1} ; HRMS (CI) calcd. for $\text{C}_{14}\text{H}_{22}\text{N}_2$ (M^+) 218.1783, found 218.1776.

5-(1-Piperidinylmethyl)-2-furancarboxaldehyde (4a). According to the general procedure using THF/H₂O solvent conditions, the product was obtained in 80% yield (156 mg, 0.80 mmol) as a pale yellow oil after silica gel column chromatography (elution with hexane/EtOAc/TEA 9:1:0.2). ¹H-NMR (500 MHz, CDCl₃): δ = 9.49 (s, 1H), 7.12 (d, *J* = 3.5 Hz, 1H), 6.36 (d, *J* = 3.5 Hz, 1H), 3.51 (s, 2H), 2.36 (s, 4H), 1.49 (m, 4H), 1.32 (m, 2H); ¹³C-NMR (125.8 MHz, CDCl₃): δ = 177.5, 159.4, 152.3, 122.2, 111.4, 55.5, 54.3, 25.7, 23.9; IR (neat) = 2935, 2802, 1678, 1521, 1339, 1107 cm⁻¹; HRMS (CI) calcd. for C₁₁H₁₅NO₂ (M⁺) 193.1103, found 193.1103.

5-(1-Piperidinylmethyl)-2-acetylthiophene (4b). According to the general procedure using THF/H₂O solvent conditions, the product was obtained in 77% yield (170 mg, 0.76 mmol) as a light yellow oil after silica gel column chromatography (elution with hexane/EtOAc/TEA 4.5:1:0.14). ¹H-NMR (500 MHz, CDCl₃): δ = 7.48 (d, *J* = 3.6 Hz, 1H), 6.85 (d, *J* = 3.3 Hz, 1H), 3.59 (s, 2H), 2.44 (s, 3H), 2.35 (s, 4H), 1.49-1.52 (m, 4H), 1.19-1.22 (m, 2H); ¹³C-NMR (125.8 MHz, CDCl₃): δ = 190.6, 152.8, 143.1, 132.5, 126.3, 58.1, 54.3, 26.5, 25.9, 24.1; IR (neat) = 2934, 1660, 1455, 1277 cm⁻¹; HRMS (CI) calcd. for C₁₂H₁₇NOS (M⁺) 223.1031, found 223.1031.

1-(2-Thienylmethyl)piperidine (4c). According to the general procedure using THF/H₂O solvent conditions, the product was obtained in 62% yield (114 mg, 0.63 mmol) as a

pale yellow oil after silica gel column chromatography (elution with hexane/EtOAc/TEA 9:1:0.2). $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 7.20-7.22 (m, 1H), 6.93-6.95 (m, 1H), 6.89-6.90 (m, 1H), 3.70 (s, 2H), 2.42 (br s, 4H), 1.57-1.61 (m, 4H), 1.40-1.45 (m, 2H); $^{13}\text{C-NMR}$ (125.8 MHz, CDCl_3): δ = 142.1, 126.4, 125.9, 124.7, 57.9, 54.5, 26.4, 24.4; IR (neat) = 2934, 2792, 1335, 1109 cm^{-1} ; HRMS (CI) calcd. for $\text{C}_{10}\text{H}_{15}\text{NS}$ (M^+) 181.0925, found 181.0924.

5-(Piperidin-1-ylmethyl)pyrimidine (4d). According to the general procedure

using THF/ H_2O solvent conditions, the product was obtained in 81% yield (75 mg, 0.42 mmol) as a pale yellow oil after silica gel column chromatography (elution with hexane/EtOAc/TEA 3.9:1:0.1). $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 9.07 (s, 1H), 8.65 (s, 2H), 3.43 (s, 2H), 2.35 (br s, 4H), 1.52-1.56 (m, 4H), 1.40-1.41 (m, 2H); $^{13}\text{C-NMR}$ (125.8 MHz, CDCl_3): δ = 157.7, 157.5, 132.0, 58.5, 54.5, 25.9, 24.2; IR (neat) = 2936, 2796, 1562, 1407, 1110 cm^{-1} ; HRMS (CI) calcd. for $\text{C}_{10}\text{H}_{15}\text{N}_3$ (M^+) 177.1266, found 177.1257.

4-(Piperidin-1-ylmethyl)isoquinoline (4e). According to the general

procedure using THF/ H_2O solvent conditions, the product was obtained in 76% yield (86 mg, 0.38 mmol) as a white crystalline solid after silica gel column chromatography (elution with hexane/EtOAc/TEA 4:1:0.2). mp = 81-84 $^{\circ}\text{C}$. $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ = 9.16 (s, 1H), 8.41 (s, 1H), 8.31 (d, J = 8.5 Hz, 1H), 7.94 (d, J = 8.1 Hz, 1H), 7.70 (t, J = 7.1 Hz, 1H), 7.58 (t, J = 7.2 Hz, 1H), 3.79 (s, 2H), 2.43 (br s, 4H), 1.51-1.55 (m, 4H), 1.24-1.29 (m, 2H); $^{13}\text{C-NMR}$

(125.8 MHz, CDCl₃): δ = 152.5, 143.6, 135.5, 130.0, 128.5, 127.8, 127.8, 126.9, 124.3, 59.2, 54.8, 26.1, 24.5; IR (neat) = 2938, 2850, 2765, 1621, 1371, 1095 cm⁻¹; HRMS (CI) calcd. for C₁₅H₁₈N₂ (M⁺) 226.1470, found 226.1464.

3-(1-Piperidinylmethyl)pyridine (4f). According to the general procedure using THF/H₂O solvent conditions, the product was obtained in 63% yield (55 mg, 0.31 mmol) as a pale yellow oil after silica gel column chromatography (elution with hexane/EtOAc/TEA 9:1:0.2). ¹H-NMR (500 MHz, CDCl₃): δ = 8.47-8.51 (m, 2H), 7.64-7.66 (m, 1H), 7.21-7.24 (m, 1H), 3.45 (s, 2H), 2.36 (br s, 4H), 1.53-1.58 (m, 4H), 1.22-1.27 (m, 2H); ¹³C-NMR (125.8 MHz, CDCl₃): δ = 150.5, 148.3, 136.7, 130.4, 123.2, 60.9, 54.4, 25.9, 24.2; IR (neat) = 2935, 2793, 1576, 1424, 1100 cm⁻¹; HRMS (CI) calcd. for C₁₁H₁₆N₂ (M⁺) 176.1314, found 176.1312.

4-(4-Methoxybenzyl)morpholine (6a). According to the general procedure using CPME/H₂O as the solvent, the product was obtained in 81% yield (165 mg, 0.79 mmol) as a pale yellow oil after silica gel column chromatography (elution with hexane/EtOAc/Et₃N 7:1:0.2). ¹H-NMR (500 MHz, CDCl₃): δ = 7.23 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 3.80 (s, 3H), 3.70 (t, J = 4.7 Hz, 4H), 3.44 (br s, 2H), 2.41-2.43 (m, 4H); ¹³C-NMR (125.8 MHz, CDCl₃): δ = 158.8, 130.4, 129.8, 113.7, 67.1, 62.9, 55.3, 53.6; IR (neat) = 2956, 1514, 1247, 1117 cm⁻¹; HRMS (CI) calcd. for C₁₂H₁₈NO₂ (MH⁺) 208.1338, found 208.1346.

***N*-(4-Methoxybenzyl)-*N*-ethylethanamine (6b).** According to the general

procedure using CPME/H₂O as the solvent, the product was obtained in 85% yield (168 mg, 0.87 mmol) as a pale yellow oil after silica gel column chromatography (elution with hexane/EtOAc/Et₃N 7:1:0.2). ¹H-NMR (500 MHz, CDCl₃): δ = 7.24 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 3.51 (s, 2H), 2.51 (q, *J* = 7.1 Hz, 4H), 1.04 (t, *J* = 7.2 Hz, 6H); ¹³C-NMR (125.8 MHz, CDCl₃): δ = 158.5, 131.9, 130.1, 113.5, 55.8, 55.2, 46.5, 11.7; IR (neat) = 2968, 1511, 1247 cm⁻¹; HRMS (CI) calcd. for C₁₂H₂₀NO (MH⁺) 194.1545, found 194.1553.

***N*-Benzyl(4-methoxybenzyl)-*N*-methylamine (6c).** According to

the general procedure using CPME/H₂O as the solvent, the product was obtained in 81% yield (188 mg, 0.78 mmol) as a pale yellow oil after silica gel column chromatography (elution with hexane/EtOAc/Et₃N 7:1:0.2). ¹H-NMR (500 MHz, CDCl₃): δ = 7.23-7.36 (m, 7H), 6.86 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H), 3.50 (s, 2H), 3.47 (s, 2H), 2.17 (s, 3H); ¹³C-NMR (125.8 MHz, CDCl₃): δ = 158.7, 139.4, 131.4, 130.1, 129.0, 128.2, 126.9, 61.7, 61.3, 55.3, 42.1; IR (neat) = 1511, 1247 cm⁻¹; HRMS (CI) calcd. for C₁₆H₁₉NO (M⁺) 241.1467, found 241.1462.

4-(4-Methoxybenzyl)piperazine-1-carboxylic acid *tert*-butyl ester

(6d). According to the general procedure using CPME/H₂O as the solvent, the product was obtained in 72% yield (107 mg, 0.35 mmol) as a pale yellow oil after silica gel column chromatography (elution with hexane/EtOAc/Et₃N 7:1:0.2). ¹H-NMR (500 MHz, CDCl₃): δ =

7.21 (d, $J = 8.6$ Hz, 2H), 6.84 (d, $J = 8.6$ Hz, 2H), 3.78 (s, 3H), 3.43 (s, 2H), 3.41 (m, 4H), 2.35 (m, 4H), 1.44 (s, 9H); ^{13}C -NMR (125.8 MHz, CDCl_3): $\delta = 158.8, 154.8, 130.3, 129.8, 113.7, 79.5, 62.5, 55.2, 52.8, 43.7, 28.5$; IR (neat) = 2933, 1697, 1247 cm^{-1} ; HRMS (CI) calcd. for $\text{C}_{17}\text{H}_{27}\text{N}_2\text{O}_3$ (MH^+) 307.2022, found 307. 2020.

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^1H NMR Spectra of Potassium 4-Trifluoroboratomethyl-morpholine (**5a**)

^{13}C NMR Spectra of Potassium 4-Trifluoroboratomethyl-morpholine (**5a**)

^{19}F NMR Spectra of Potassium 4-Trifluoroboratomethyl-morpholine (**5a**)

^{11}B NMR Spectra of Potassium 4-Trifluoroboratomethyl-morpholine (**5a**)

^1H NMR Spectra of Potassium *N,N*-Diethyltrifluoroboratomethylamine (**5b**)

^{13}C NMR Spectra of Potassium *N,N*-Diethyltrifluoroboratomethylamine (**5b**)

^{19}F NMR Spectra of Potassium *N,N*-Diethyltrifluoroboratomethylamine (**5b**)

^{11}B NMR Spectra of Potassium *N,N*-Diethyltrifluoroboratomethylamine (**5b**)

^1H NMR Spectra of Potassium *N*-Benzyltrifluoroboratomethylamine (**5c**)

^{13}C NMR Spectra of Potassium *N*-Benzyltrifluoroboratomethylamine (**5c**)

^{19}F NMR Spectra of Potassium *N*-Benzyltrifluoroboratomethylamine (**5c**)

^{11}B NMR Spectra of Potassium *N*-Benzyltrifluoroboratomethylamine (**5c**)

¹H NMR Spectra of Potassium 4-Trifluoroboratomethylpiperazine-1-carboxylic acid *tert*-butyl ester (**5d**)

^{13}C NMR Spectra of Potassium 4-Trifluoroboratolmethylpiperazine-1-carboxylic acid *tert*-butyl ester (**5d**)

^{19}F NMR Spectra of Potassium 4-Trifluoroboratomethylpiperazine-1-carboxylic acid *tert*-butyl ester (**5d**)

^{11}B NMR Spectra of Potassium 4-Trifluoroboratomethylpiperazine-1-carboxylic acid *tert*-butyl ester (**5d**)

^1H NMR Spectra of Potassium (*S*)-1-Trifluoroboratomethylpyrrolidine-2-carboxylic acid methyl ester (**5e**)

^{13}C NMR Spectra of Potassium (*S*)-1-Trifluoroboratomethylpyrrolidine-2-carboxylic acid methyl ester (**5e**)

^{19}F NMR Spectra of Potassium (*S*)-1-Trifluoroboratomethylpyrrolidine-2-carboxylic acid methyl ester (**5e**)

^{11}B NMR Spectra of Potassium (*S*)-1-Trifluoroboratomethylpyrrolidine-2-carboxylic acid methyl ester (**5e**)

^1H NMR Spectra of Potassium *N,N*-Diallyltrifluoroboratomethylamine (**5f**)

^{13}C NMR Spectra of Potassium *N,N*-Diallyltrifluoroboratomethylamine (**5f**)

^{19}F NMR Spectra of Potassium *N,N*-Diallyltrifluoroboratomethylamine (**5f**)

^{11}B NMR Spectra of Potassium *N,N*-Diallyltrifluoroboratomethylamine (**5f**)

^1H NMR Spectra of 4-(Piperidin-1-ylmethyl)benzonitrile (**2a**)

¹³C NMR Spectra of 4-(Piperidin-1-ylmethyl)benzonitrile (**2a**)

¹H NMR Spectra of Methyl 4-(Piperidin-1-ylmethyl)benzoate (**2b**)

¹³C NMR Spectra of Methyl 4-(Piperidin-1-ylmethyl)benzoate (**2b**)

¹H NMR Spectra of 1-(4-Nitrobenzyl)piperidine (**2c**)

^{13}C NMR Spectra of 1-(4-Nitrobenzyl)piperidine (**2c**)

S46

¹³C NMR Spectra of Phenyl (4-(Piperidin-1-ylmethyl)phenyl)methanone (**2d**)

¹H NMR Spectra of 4-(Piperidin-1-ylmethyl)benzaldehyde (**2e**)
S48

¹³C NMR Spectra of 4-(Piperidin-1-ylmethyl)benzaldehyde (**2e**)

^1H NMR Spectra of 1-(4-Methoxybenzyl)piperidine (**2f**)

¹³C NMR Spectra of 1-(4-Methoxybenzyl)piperidine (**2f**)

¹H NMR Spectra of 1-(2,4-Dimethoxybenzyl)piperidine (**2g**)

1

^{13}C NMR Spectra of 1-(2,4-Dimethoxybenzyl)piperidine (**2g**)

^1H NMR Spectra of 1-(2,4,6-Trimethylbenzyl)piperidine (**2h**)

^{13}C NMR Spectra of 1-(2,4,6-Trimethylbenzyl)piperidine (**2h**)

^1H NMR Spectra of *N*-(4-(Piperidin-1-ylmethyl)phenyl)acetamide (**2i**)

¹³C NMR Spectra of *N*-(4-(Piperidin-1-ylmethyl)phenyl)acetamide (**2i**)

^1H NMR Spectra of *N,N*-Dimethyl-4-(piperidin-1-ylmethyl)benzamine (**2j**)

¹³C NMR Spectra of *N,N*-Dimethyl-4-(piperidin-1-ylmethyl)benzamine (**2j**)

^1H NMR Spectra of 5-(1-Piperidinylmethyl)-2-furancarboxaldehyde (**4a**)

^{13}C NMR Spectra of 5-(1-Piperidinylmethyl)-2-furancarboxaldehyde (**4a**)
S61

¹H NMR Spectra of 5-(1-Piperidinylmethyl)-2-acetylthiophene (**4b**)

^{13}C NMR Spectra of 5-(1-Piperidinylmethyl)-2-acetylthiophene (**4b**)

^1H NMR Spectra of 1-(2-Thienylmethyl)piperidine (**4c**)

^1H NMR Spectra of 5-(Piperidin-1-ylmethyl)pyrimidine (**4d**)

¹³C NMR Spectra of 5-(Piperidin-1-ylmethyl)pyrimidine (**4d**)

^1H NMR Spectra of 4-(Piperidin-1-ylmethyl)isoquinoline (**4e**)

¹³C NMR Spectra of 4-(Piperidin-1-ylmethyl)isoquinoline (**4e**)

^1H NMR Spectra of 3-(1-Piperidinylmethyl)pyridine (**4f**)

^{13}C NMR Spectra of 3-(1-Piperidinylmethyl)pyridine (**4f**)

¹H NMR Spectra of 4-(4-Methoxybenzyl)morpholine (**6a**)

¹³C NMR Spectra of 4-(4-Methoxybenzyl)morpholine (**6a**)

^1H NMR Spectra of *N*-(4-Methoxybenzyl)-*N*-ethylethanamine (**6b**)

¹³C NMR Spectra of *N*-(4-Methoxybenzyl)-*N*-ethylethanamine (**6b**)

¹H NMR Spectra of *N*-Benzyl(4-methoxybenzyl)-*N*-methylamine (**6c**)

^{13}C NMR Spectra of *N*-Benzyl(4-methoxybenzyl)-*N*-methylamine (**6c**)

¹H NMR Spectra of 4-(4-Methoxybenzyl)piperazine-1-carboxylic acid *tert*-butyl ester (**6d**)

^{13}C NMR Spectra of 4-(4-Methoxybenzyl)piperazine-1-carboxylic acid *tert*-butyl ester (**6d**)