Supporting Information

Preparation of Alkoxymethyltrifluoroborates and Their Cross-Coupling with Aryl Chlorides

Gary A. Molander and Belgin Canturk*

Roy and Diana Vagelos Laboratories, Department of Chemistry
University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323
gmolandr@sas.upenn.edu

General Considerations: $Pd(OAc)_2$, RuPhos and Cs_2CO_3 were used as received. Dioxane and H_2O 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, ^{13}C, and ^{19}F NMR spectra were recorded at 500.39, 125.75, and 470.55 MHz, respectively. ^{19}F NMR chemical shifts were referenced to external $CFCl_3$ (0.0 ppm). ^{11}B NMR spectra at 128.4 MHz were obtained on a spectrometer equipped with the appropriate decoupling accessories. All ^{11}B NMR chemical shifts were referenced to external $BF_3 \cdot OEt_2$ (0.0 ppm) with a negative sign indicating an upfield shift. 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 procedures were followed using 32-63 μm silica gel. Visualization was effected with ultraviolet light or potassium permanganate ($KMnO_4$).

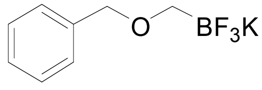
Preparation of Potassium Bromomethyltrifluoroborate (1)

A 2 L 4-neck flask was fitted with a mechanical stirrer, 500 mL addition funnel, thermometer adapter with a low temperature thermometer and a rubber septum. The flask was evacuated under vacuum, flame dried and refilled with N_2 (x 3). Anhydrous THF (800 mL) was directly added to the flask from a Grubb's solvent system and the flask was quickly fitted with a septum. Triisopropylborate (121 mL, 98.7 g, 0.53 mol) and CH_2Br_2 (38.6 mL, 95.6 g, 0.55 mol) were added via syringe at -78 °C. A solution of 2.5 M *n*-BuLi in hexane (200 mL, 0.50 mol) was transferred by cannula to the addition funnel. The *n*-BuLi solution was added dropwise to the stirring reaction mixture at -78 °C from the addition funnel at a rate of 100 mL/h. After the addition of *n*-BuLi was complete, the reaction mixture was stirred at -78 °C for 2.5 h. Methanesulfonic acid (16.2 mL, 0.25 mol) was added to the reaction mixture via syringe at -78 °C. The reaction flask was removed from the Dry Ice/acetone bath and allowed to warm to 0 °C (~30 min) and solid KHF_2 (117.2 g, 1.5 mol) was added directly to the reaction mixture in one portion. Deionized water (167 mL) was added dropwise to the stirring mixture through the addition funnel. After the addition of water was complete, the mixture was stirred for 30 min. The reaction mixture was concentrated *in vacuo* and the resulting solids were dried overnight *in vacuo*. The solids were divided into 3 batches and sonicated in a minimal amount of HPLC grade acetone (~200 mL) and filtered to remove the insoluble salts (x 3). The filtrate was concentrated *in vacuo*, and the crude solid was dissolved in a minimal amount of HPLC grade acetone, (~100 mL) and Et_2O (~200 mL) was added leading to precipitation of the product.

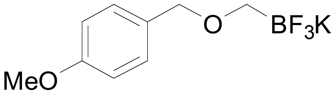
As an alternative to this isolation process, the solids were divided into two batches and loaded into a Soxhlet extractor and extracted continuously with HPLC grade acetone (~500 mL) for 7 h. The collected solvent was concentrated *in vacuo*. The crude solid was dissolved in a minimal amount of HPLC grade acetone (~150 mL) and Et_2O (~300 mL) was added, leading to precipitation of the product. The product was filtered, collected and dried overnight *in vacuo* to afford the desired pure compound in 82% yield (82 g, 0.41

mol) as a white crystalline solid. The spectral data was in agreement with reported literature values.[1]

General Procedure for Preparing Compounds 2a-2k



Preparation of Potassium Benzyloxymethyltrifluoroborate (2a). To a 100 mL 2-neck round-bottom-flask was added NaH (95%) (0.758 g, 30 mmol) and dry THF (50 mL). Benzyl alcohol (3.24 g, 30 mmol) was added dropwise to the suspension via syringe at 0 °C under N_2. The mixture was stirred for 15 min at 0 °C and then allowed to warm to rt for 30 min. Bromomethyltrifluoroborate **1** (2.00 g, 10 mmol) was added to the mixture in one portion at 0 °C. The reaction mixture was stirred at rt until ^{19}F NMR indicated completion of the reaction after 3 h. The mixture was quenched by adding 4.5 M KHF_2 (pH 6, ~ 4.5 mL). The mixture was left to stir at rt for 30 min, and then the suspension was concentrated and dried overnight *in vacuo*. The crude solid was suspended in Et_2O (~25 mL) and filtered to remove the organic impurities. The crude solid was further purified by continuous Soxhlet extraction with acetonitrile (60 mL), concentrated and then cooled using an ice-water bath and filtered. The second crop was recovered and then filtered. Alternative to acetonitrile precipitation, acetonitrile and a minimal amount of Et_2O (~ 6 mL) was used for precipitation of the product. The pure compound was dried *in vacuo* and obtained as a white crystalline solid in 98% yield (2.23 g, 9.8 mmol). mp: > 200 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.31-7.26 (m, 4H), 7.23-7.20 (m, 1H), 4.28 (s, 2H), 2.58-2.57 (m, 2H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 140.9, 128.3, 127.7, 127.1, 75.2. ^{19}F NMR (470.8 MHz, Acetone-d_6) δ -141.6. ^{11}B NMR (128.4 MHz, acetonitrile) δ 3.3. FT-IR (KBr) 3428, 3022, 2921, 2822, 1496, 1126, 1088, 1066, 1002 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_8H_9BF_3O$ (M-K) 189.0698, found 189.0692.



Potassium (4-Methoxybenzyloxy)methyl-trifluoroborate (2b). The general procedure was used employing *p*-methoxybenzyl alcohol and the reaction was complete after 5 h. The product was obtained in 97% yield (2.50 g, 9.7 mmol) as a white crystalline solid. mp: 198-202 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.18 (d, 2H, J = 8.4 Hz), 6.85 (d, 2H, J = 8.4 Hz), 4.18 (s, 2H), 3.72 (s, 3H), 2.52-2.50 (m, 2H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 158.6, 132.8, 129.3, 113.78, 74.9, 55.5. ^{19}F NMR (470.8 MHz, DMSO-d_6) δ -141.6. ^{11}B NMR (128.4 MHz, acetonitrile) δ 3.2. FT-IR (KBr) 3423, 2872, 1610, 1511, 1246, 1124, 1060 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_9H_{11}BF_3O$ (M-K) 219.0804, found 219.0793.

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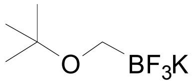
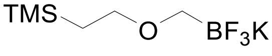
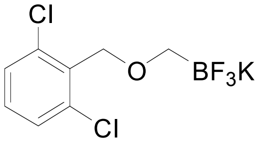
(1) Molander, G. A.; Ham, J. *Org. Lett.* **2006**, *8*, 2031-2034.



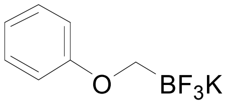
Potassium (*tert*-Butoxymethyltrifluoroborate (2c). The general procedure was used employing potassium *tert*-butoxide and the reaction was complete after 11 h. The product was obtained in 91% yield (1.77 g, 9.7 mmol) as a white crystalline solid. mp: > 200 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.34-2.33 (m, 2H), 1.03 (s, 9H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 70.7, 27.1. ^{19}F NMR (470.8 MHz, DMSO-d_6) δ -141.8. ^{11}B NMR (128.4 MHz, acetonitrile) δ 3.6. FT-IR (KBr) 2974, 2902, 1609, 1343, 1363, 1232, 1196, 1118, 1001, 802 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_5H_{11}BF_3KO$ (M-K) 155.0860, found 155.0855.



Potassium (2-(Trimethylsilyl)ethoxy)methyltrifluoroborate (2d). The general procedure was used employing trimethylsilylethanol except after the completion of the reaction after 7 h, the mixture was transferred into a 250 mL Erlenmeyer flask and quenched at -20 °C with 4.5 M KHF_2. The product was obtained in 99% yield (2.36 g, 9.9 mmol) as a white crystalline solid. mp: > 200 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.24 (d, 2H, J = 8.0 Hz), 2.45-2.42 (m, 2H), 0.80 (t, 2H J = 7.5 Hz), 0.03 (s, 9). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 70.7, 19.1, 0.3. ^{19}F NMR (470.8 MHz, DMSO-d_6) δ -141.6. ^{11}B NMR (128.4 MHz, acetonitrile) δ 3.3. FT-IR (KBr) 2953, 2872, 2826, 1354, 1251, 1182, 1111, 836, 804 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_6H_{15}BF_3OSi$ (M-K) 199.0937, found 199.0939.

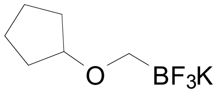


Potassium (2, 6-Dichlorobenzyloxy)methyltrifluoroborate (2e). The general procedure was used employing 2,6-dichlorobenzyl alcohol and the reaction was complete after 5 h. The product was obtained in 75% yield (668 mg, 3 mmol) as a white crystalline solid. mp: 180-182 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.43-7.42 (m, 2H), 7.34-7.3 (m, 1H), 4.48 (s, 2H), 2.63-2.62 (m, 2H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 132.9, 134.6, 130.0, 128.27, 69.4. ^{19}F NMR (470.8 MHz, DMSO-d_6) δ -41.7. ^{11}B NMR (128.4 MHz, acetonitrile) δ 3.2. (q, J = 50.1 Hz). FT-IR (KBr) 2904, 1579, 1563, 1433, 1201, 1017 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_8H_7BCl_2F_3O_2$ (M-K) 256.9909; found, 256.9919.

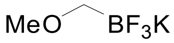


Potassium (Phenoxy)methyltrifluoroborate (2f). The general procedure was used employing potassium phenoxide, and the reaction was complete after 24 h. The product was obtained in 95% yield (2.03 g, 9.5 mmol) as a white crystalline solid. mp: > 200 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.20-7.16 (m, 2H), 6.84-6.82 (m, 2H), 6.84-6.74 (m, 1H), 2.97-2.93 (m, 2H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ

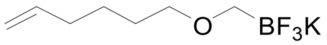
162.6, 129.5, 118.9, 114.4. ^{19}F NMR (470.8 MHz, DMSO-d_6) δ -142.2. ^{11}B NMR (128.4 MHz, acetonitrile) δ 3.0. FT-IR (KBr) 2912, 2853, 1944, 1718, 1600, 1488, 1362, 1291, 1106 cm^{-1}. HRMS (CI) *m/z* calcd. for $C_7H_7BF_3O$ (M-K) 175.0542; found, 175.0540.



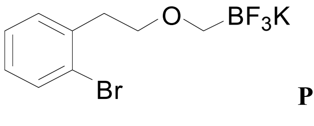
Potassium (Cyclopentyloxymethyl)trifluoroborate (2g). The general procedure was used employing cyclopentanol, and the reaction was complete after 6 h. The product was obtained in 68% yield (532 mg, 2.58 mmol) as a white crystalline solid. mp: > 200 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.09-3.07 (m, 1H), 1.93-1.90 (m, 2H), 1.10-0.88 (m, 8H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 82.7, 31.5, 23.2. ^{19}F (470.8 MHz, DMSO-d_6) δ -141.6. ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 2.9. FT-IR (KBr) 2957, 2345, 1718, 1560, 1542, 1458, 1041, 812cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_6H_{11}BF_3KO$ (M-) 167.0856, found 167.0855.



Potassium (Methoxymethyl)trifluoroborate (2h). The general procedure was used employing sodium methoxide and the reaction was complete after 14 h. The product was obtained in 91% yield (1.38 g, 9.1 mmol) as a white crystalline solid. mp: > 200 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.09 (s, 3H), 2.49-2.44 (m, 2H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 61.4. ^{19}F NMR (470.8 MHz, DMSO-d_6) δ -142.0. ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 2.7. FT-IR (KBr) 2862, 2822, 1352, 804 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_2H_5BF_3O$ (M-K) 113.0386, found 113.0381.

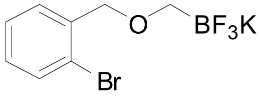


Potassium (Hex-5-enyloxyl)methyltrifluoroborate (2i). The general procedure was used employing hex-5-enol and the reaction was complete after 3 h. The product was obtained in 84% yield (554 mg, 2.52 mmol) as a white crystalline solid. mp: > 200 °C. ^{1}H NMR (500 MHz, DMSO-d_6) δ 5.84-5.787 (m, 1H), 5.03-4.94 (m, 2H), 3.21 (m, 2H), 2.52-2.48 (m, 2H), 2.04-2.00 (m, 2H), 1.48-1.44 (m, 2H), 1.38-1.33 (m 2H). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 138.8, 114.5, 73.1, 33.1, 28.8, 25.1. ^{19}F NMR (470.8 MHz, DMSO-d_6) δ -141.9. ^{11}B NMR (128.4 MHz, DMSO-d_6) δ 2.6. FT-IR (KBr) 2866, 1654, 973, 804 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_7H_{13}BF_3O$ (M-K) 181.0993, found 181.1012.



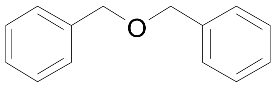
Potassium (2-Phenethoxy)methyltrifluoroborate (2j). The general procedure was used employing 2-bromophenethyl alcohol and the reaction was complete after 5 h. The product was obtained in 98% yield (944 mg, 2.76 mmol) as a white crystalline solid. mp: 170-172 °C ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.56-7.54 (d, 1H, *J* = 7.5 Hz), 7.37-7.36 (m, 1H, *J* = 7.5 Hz), 7.31-7.28 (m, 1H), 7.15-7.12

(m, 1H), 3.39 (t, 2H, *J* = 7.5 Hz), 2.89 (t, 2H, *J* = 7.5 Hz), 2.58-2.55 (m, 2H). ^{13}C NMR (125.8 MHz, DMSO-*d*$_6$) δ 138.5, 132.2, 131.1, 127.9, 127.6, 123.8, 72.2, 35.8. ^{19}F NMR (470.8 MHz, DMSO-*d*$_6$) δ -141.0. ^{11}B NMR (128.4 MHz, DMSO-*d*$_6$) δ 2.8. FT-IR (KBr) 3423, 3060, 2871, 1567, 1471, 1442, 1234, 1127, 1038, 796, 749 cm^{-1}. HRMS (ESI) *m*/*z* calcd. for $C_9H_{10}BBrF_3O$ (M-K) 280.9941, found 280.9960.

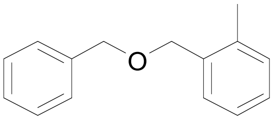


Potassium (2-Bromobenzyloxy)methyltrifluoroborate (2k). The general procedure was used employing 2-bromobenzyl alcohol, and the reaction was complete after 5 h. The product was obtained in 92% yield (847 mg, 2.76 mmol) as a white crystalline solid. mp: 185-188 °C. ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 7.54-7.50 (m, 2H), 7.36-7.35 (m, 1H), 7.18-7.17 (m, 1H), 4.31 (s, 2H) 4.32 (s, 2H), 2.66-2.64 (m, 2H). ^{13}C NMR (125.8 MHz, DMSO-*d*$_6$) δ 139.3, 131.8, 128.7, 128.3, 127.4, 121.4, 73.8. ^{19}F NMR (470.8 MHz, DMSO-*d*$_6$) δ -141.0. ^{11}B NMR (128.4 MHz, DMSO-*d*$_6$) δ 2.6. FT-IR (KBr) 3426, 3054, 2871, 1567, 1471, 1234, 1127, 1038, 758 cm^{-1}. HRMS (ESI) *m*/*z* calcd. for $C_8H_8BBrF_3O$ (M-K) 266.9941, found 266.9960.

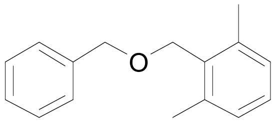
General Experimental Procedure for the Suzuki-Miyaura Cross-Coupling Reaction



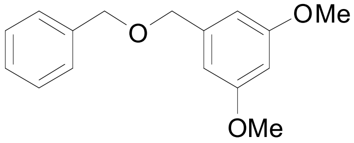
Preparation of Oxybis(methylene)dibenzene (3a) A Biotage microwave vial was charged with potassium (benzyloxymethyl)trifluoroborate **3a** (125 mg, 0.55 mmol), Pd(OAc)$_2$ (3.4 mg, 0.015 mmol), RuPhos (14 mg, 0.03 mmol) and Cs_2CO_3 (448 mg, 1.5 mmol). The test tube was sealed with a cap lined with a disposable Teflon septum, evacuated and purged (x 3). Chlorobenzene (56 mg, 0.5 mmol), and dioxane/H_2O (10:1) (0.25 M, 2 mL) were added via a syringe and the reaction was stirred at 100 ^{o}C for 24 h, then cooled to rt. The reaction mixture was extracted with EtOAc and H_2O (3 x 3 mL), and then the organic layer was washed with brine and dried ($MgSO_4$). The solvent was removed *in vacuo* and the crude product was purified by silica gel column chromatography (elution with hexane/EtOAc 15:1) to yield the product as a colorless oil in 74% yield (73 mg, 0.37 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.38 (m, 8H), 7.35-7.32 (m, 2H), 4.61 (s, 4H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 138.6, 128.6, 127.9, 127.8, 72.4. FT-IR (neat) 3029, 2855, 1720, 1453, 1269, 1095, 1070 cm^{-1}. HRMS (CI) *m*/*z* calcd. for $C_{14}H_{15}O$ (MH^+) 199.1127 found, 199.1123.



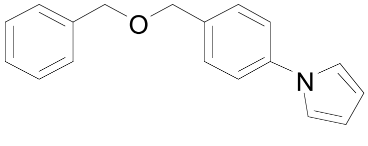
1-(Benzyloxymethyl)-2-methylbenzene (3b). According to the general procedure, the product was obtained in 86% yield (91 mg, 0.43 mmol) as a colorless oil after silica gel column chromatography (elution with hexane/EtOAc 15:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.37 (m, 5H), 7.34-7.30 (m, 1H), 7.26-7.20 (m, 3H), 4.60 (s, 2H), 4.58 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 138.6, 136.9, 136.4, 130.4, 128.9, 128.6, 128.0, 127.9, 128.8, 125.9, 72.5, 70.8, 19.0. FT-IR (neat): 3583, 3012, 1703, 1596, 1578, 1486, 1464, 1433, 1245, 1165, 1040, 968, 849, 813 cm^{-1}. HRMS (CI) *m*/*z* calcd. for $C_{15}H_{15}O$ (M-H$^+$) 195.1155, found 195.1174.



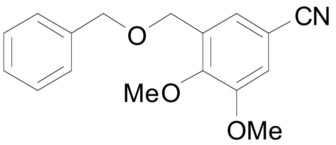
2-(Benzyloxymethyl)-1,3-dimethylbenzene (3c). According to the general procedure, the product was obtained in 72% yield (82 mg, 0.36 mmol) as a colorless oil after silica gel column chromatography (elution with hexane/EtOAc 15:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.36 (m, 4H), 7.33-7.31 (m, 1H), 7.14-7.11 (m, 1H), 7.05 (d, 2H, J = 7 Hz), 4.61- 4.60 (m, 4H), 2.39 (s, 6H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 138.7, 138.2, 134.4, 128.6, 128.4, 128.3, 128.1, 127.9, 72.8, 66.7, 19.8. FT-IR (neat) 3063, 3027, 2919, 2856, 1469, 1087, 1070 cm^{-1}. HRMS (CI) *m*/*z* calcd. for $C_{16}H_{18}O$ (M$^+$) 226.1335, found 226.1358.



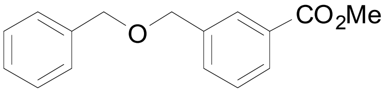
1-(Benzyloxymethyl)-3,5-dimethoxybenzene (3d). According to the general procedure, the product was obtained in 75% yield (97 mg, 0.37 mmol) as a light yellow oil after silica gel column chromatography (elution with hexane/EtOAc 15:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.38 (m, 4H), 7.35-7.31 (m, 1H), 6.59 (d, 2H, J = 2.6 Hz), 6.45-6.44 (m, 1H), 4.60 (s, 2H), 4.54 (s, 2H), 3.83 (s, 6H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 160.9, 140.8, 138.3, 128.4, 127.8, 127.7, 105.5, 99.8, 72.1, 72.1, 55.4. FT-IR (neat): 2937, 2838, 1598, 1455, 1358, 1204, 1154, 1066 cm^{-1}. HRMS (CI) *m*/*z* calcd. for $C_{16}H_{19}O_3$ (MH$^+$) 259.1325 found 259.1334.



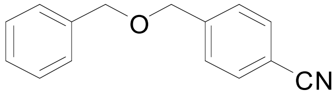
1-(4-(Benzyloxymethyl)phenyl)-1*H*-pyrrole (3e). According to the general procedure, the product was obtained in 85% (112 mg, 0.43 mmol) yield as a white solid after silica gel column chromatography (elution with hexane/EtOAc 15:1). mp: 69-70 °C ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, 2H, J = 8.51 Hz), 7.40-7.36 (m, 6H), 7.34-7.30 (m, 1H), 7.10 (t, 2H, J = 2.2 Hz), 6.36 (t, 2H, J = 2.0 Hz), 4.60 (s, 2H), 4.59 (s, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 140.4, 138.4, 135.9, 129.2, 128.7, 128.0, 127.9, 120.7, 119.5, 110.6, 72.5, 71.7. FT-IR (neat) 3138, 2854, 2798, 2363, 1530, 1480, 1125, 1080, 1067 cm^{-1}. HRMS (CI) *m*/*z* calcd. for $C_{18}H_{17}NO$ (M^{+}) 263.1313, found 263.1310.



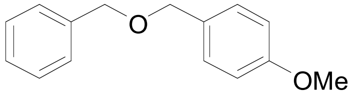
3-(Benzyloxymethyl)-4,5-dimethoxybenzonitrile (3f). According to the general procedure, the product was obtained in 73% yield (103 mg, 37 mmol) as a white solid after silica gel column chromatography (elution with hexane/EtOAc 5:1). mp: 49-55 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (m, 1H), 7.39-7.36 (m, 4H), 7.34-7.30 (m, 1H), 7.10 (m, 1H), 4.61 (s, 2H), 4.57 (s, 2H), 3.88 (s, 6H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 152.8, 150.9, 138.1, 128.7, 128.1, 127.9, 125.7, 119.1, 115.2, 107.4, 73.1, 66.5 135.7, 61.2, 56.3. FT-IR (neat) 2941, 2857, 2225, 1487, 1323, 1140, 1069, 1001 cm^{-1}. HRMS (CSI) *m*/*z* calcd. for $C_{17}H_{18}NO_3$ (MH^{+}) 284.1276, found 284.1287.



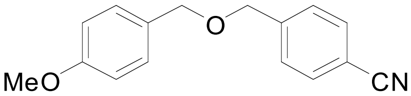
Methyl 3-(Benzyloxymethyl)benzoate (3g). According to the general procedure, the product was obtained in 72% yield (92 mg, 0.36 mmol) as a colorless oil after silica gel column chromatography (elution with hexane/EtOAc 13:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.99 (d, 1H, *J* = 12.0 Hz), 7.60 (d, 1H, *J* = 6.5 Hz), 7.47-7.433 (m, 1H), 7.41-7.37 (m, 4H), 7.34-7.31 (m, 1H), 4.61 (d, 4H, *J* = 6.4 Hz), 3.94 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 167.2, 139.1, 138.3, 132.4, 130.7, 129.1 129.1, 128.8, 128.7, 128.1, 128.0, 72.7, 71.9, 52.4. FT-IR (neat) 3062, 3029, 2949, FT-IR (neat) 3062, 3030, 2857, 227, 1609, 1453, 1360, 1092,819. 2856, 1722, 1286, 1202, 1106, 1084. HRMS (CI) *m*/*z* calcd. for $C_{16}H_{17}O_3$ (MH^{+}) 257.1173, found 257.1178.



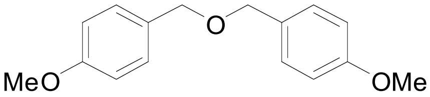
4-((4-Methoxybenzyloxy)methyl)benzonitrile (4a). According to the general procedure, the product was obtained in 75% yield (83 mg, 0.37 mmol) as a colorless oil after silica gel column chromatography (elution with hexane/EtOAc 15:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, 2H, *J* = 8.3 Hz), 7.48 (d, 2H, *J* = 8.4 Hz), 7.39-7.38 (m, 3H), 7.35-7.31 (m, 2H), 4.62 (s, 4H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 144.2, 137.8, 132.4 (2C), 128.7, 128.1, 127.1, 127.9, 119.0, 73.0, 71.3. HRMS (CI) *m*/*z* calcd. for $C_{15}H_{14}NO$ (MH^{+}) 224.1071, found 224.1075.



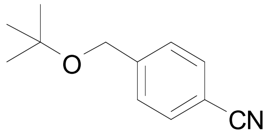
4-((4-Methoxybenzyloxy)methyl)benzonitrile (4a'). According to the general procedure, the product was obtained in 77% yield (88 mg, 0.38 mmol) as a light yellow oil after silica gel column chromatography (elution with hexane/EtOAc 13:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.29 (m, 7H), 6.90 (d, 2H, J = 8.3 Hz), 4.55 (s, 2H), 4.51 (s, 2H), 3.82 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 159.5, 138.7, 130.7, 129.6, 128.6, 128.0, 127.8, 114.1, 72.1, 72.0, 55.5. FT-IR (neat) 3062, 3001, 3029, 2933, 2854, 1612, 1585, 1513, 1248, 1172, 1091, 1072, 1035 cm^{-1}. HRMS (CI) *m*/*z* calcd. for $C_{14}H_{13}O$ (M-OMe$^+$) 199.1122, found 199.1122.



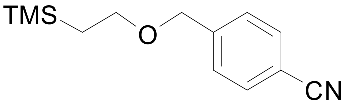
4-((4-Methoxybenzyloxy)methyl)benzonitrile (4b). According to the general procedure, the product was obtained in 72% yield (91 mg, 0.36 mmol) as a colorless oil after silica gel column chromatography (elution with hexane/EtOAc 6:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, 2H, J = 7.7 Hz), 7.46 (d, 2H, J = 7.8 Hz), 7.29 (d, 2H, J = 8.2 Hz), 6.91 (d, 2H, J = 9 Hz), 4.56 (d, 4H, J = 19.3), 3.82 (s, 3H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 159.7, 144.3, 132.4, 129.9, 129.6, 128.0, 119.1, 114.1, 111.5, 72.7, 70.1, 55.5. FT-IR (neat) 3003, 2935, 2856, 2356, 2227, 1611, 1513, 1463, 1248, 1173, 1086, 1034 cm^{-1}. HRMS (CI) *m*/*z* calcd. for $C_{16}H_{15}NO_2Na$ (MNa$^+$) 276.0997, found 276.1000.



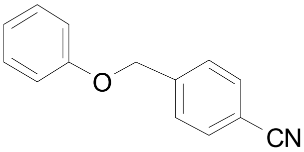
4,4' Oxybis(methylene)bis(methoxybenzene) (4b'). According to the general procedure, the product was obtained in 74% yield (96 mg, 0.37 mmol) as a yellow solid after silica gel column chromatography (elution with hexane/EtOAc 15:1). mp: 37-39 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, 4H, J = 8.8 Hz), 6.90 (d, 4H, J = 8.6 Hz), 4.47 (s, 4H), 3.82 (s, 6H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 158.5, 129.9, 128.7, 113.1, 70.7, 54.6. FT-IR (neat) 2837, 1613, 1514, 1463, 1247, 1034 cm^{-1}. HRMS (CI) *m*/*z* calcd. for $C_{16}H_{18}O_3$ (M$^+$) 258.1251, found 258.1256.



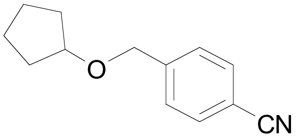
4-(*tert*-Butoxymethyl)benzonitrile (4c). According to the general procedure, the product was obtained in 64% yield (61 mg, 0.32 mmol) as a white solid after silica gel column chromatography (elution with hexane/EtOAc 15:1). mp: 41-43 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, 2H, J = 8.1 Hz), 7.46 (d, 2H, J = 7.9 Hz), 4.5 (s, 2H), 1.3 (s, 9H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 145.9, 132.3, 127.7, 119.2, 111.0, 74.2, 63.5, 27.8. FT-IR (neat) 2973, 2227, 1363, 1194, 1084. HRMS (CI) *m*/*z* calcd. for $C_{16}H_{16}O$ (MH$^+$) 190.1228, found 190.1232.



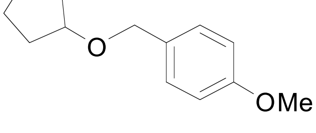
4-((2-(Trimethylsilyl)ethoxy)methyl)benzonitrile (4d). According to the general procedure, the product was obtained in 80% yield (93 mg, 0.40 mmol) as a colorless oil after silica gel column chromatography (elution with hexane/EtOAc 15:1). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.63 (d, 2H, J = 8.3 Hz), 7.50 (d, 2H, J = 8.3 Hz), 4.54 (s, 2H), 3.61 (t, 2H, J = 8.1 Hz), 1.01 (t, 2H, J = 7.9 Hz), 0.04 (s, 9H). ^{13}C NMR (125.8 MHz, CDCl$_3$) δ 144.7, 132.4, 127.9, 119.1, 111.4, 71.6, 68.6, 18.5, -1.1. FT-IR (neat) 3400, 3056, 2919, 2952, 2892, 2857, 2228, 1611, 1507, 1455, 1415, 1208, 1249, 1176, 1092 cm^{-1}. HRMS (CI) m/z calcd. for $C_{13}H_{20}NOSi$ (MH$^+$) 234.1326, found 234.1314.



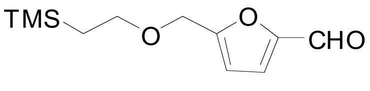
4-(Phenoxymethyl)benzonitrile (4f). According to the general procedure, the product was obtained in 48% yield (50 mg, 0.24 mmol) as a white solid after silica gel column chromatography (elution with hexane/EtOAc 15:1). mp: 63-65 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.69 (d, 2H, J = 7.9 Hz), 7.56 (d, 2H, J = 8.3 Hz), 7.33-7.30 (m, 2H), 7.02 (m, 3H), 5.1 (s, 2H). ^{13}C NMR (125.8 MHz, CDCl$_3$) δ 157.5, 141.9, 131.7, 128.9, 126.8, 120.8, 117.9, 114.1, 111.0, 68.2. FT-IR (neat) 3061, 2922, 2228, 1598, 1587, 1494, 1240, 1172, 1078, 1044 cm^{-1}. HRMS (CI) m/z calcd. for $C_{14}H_{12}NO$ (MH$^+$) 210.0918, found 210.0919.



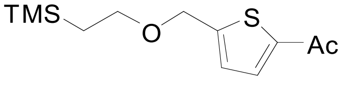
4-(Cyclopentyloxymethyl)benzonitrile (4g). According to the general procedure, the product was obtained in 67% yield (67 mg, 0.33 mmol) as a colorless oil after silica gel column chromatography (elution with hexane/EtOAc 15:1). ^{1}H NMR (300 MHz,) δ 7.55 (d, 2H, J = 7.7 Hz), 7.45 (d, 2H, J = 7.2 Hz), 4.52 (s, 2H), 4.02 (m, 1H), 1.74 (m, 6H), 1.56 (m, 1H). ^{13}C NMR (125.8 MHz, CDCl$_3$) δ 144.8, 132.1, 127.8, 118.9, 111.1, 81.7, 69.8, 32.3, 23.6. FT-IR (neat) 3399, 3056, 2957, 2871, 2228, 1610, 1571, 1506, 1450, 1437, 1202, 1174, 1093, 1020 cm^{-1}. HRMS (CI) m/z calcd. for $C_{13}H_{16}NO$ (MH$^+$) 202.1237, found 202.1232.



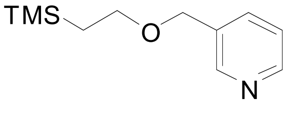
1-(Cyclopentyloxymethyl)-4-methoxybenzene (4g'). According to the general procedure, the product was obtained in 60% yield (62 mg, 0.30 mmol) as a colorless oil after silica gel column chromatography (elution with hexane/EtOAc 17:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, 2H, *J* = 8.4 Hz), 6.88 (d, 2H, *J* = 8.0 Hz), 4.42 (s, 2H), 4.01 (m, 1H), 3.81 (s, 3H), 1.74 (m, 6H), 1.53 (m, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 158.4, 130.5, 128.4, 113.1, 79.9, 69.7, 54.6, 31.6, 22.9. FT-IR (neat) 2955, 2868, 2066, 1881, 1613, 1586, 1513, 1464, 1247, 1172, 1088, 1037 cm^{-1}. HRMS (CI) *m/z* calcd. for $C_{13}H_{18}O_2$ (M^+) 206.1306, found 206.1307.



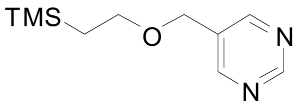
5-((2-(Trimethylsilyl)ethoxy)methyl)furan-2-carboxaldehyde (6a). According to the general procedure, the product was obtained in 50% yield (57 mg, 0.25 mmol) as a light orange oil after silica gel column chromatography (elution with hexane/EtOAc 7:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.21 (d, 1H, *J* = 3.5 Hz), 6.51 (d, 1H, *J* = 3.5 Hz), 4.51 (s, 2H), 3.62 (t, 2H, *J* = 8.2 Hz), 0.98 (t, 2H, *J* = 8.3 Hz), 0.01 (s, 9H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 177.6, 159.0, 152.6, 121.8, 110.8, 68.6, 64.5, 18.2, -1.4. FT-IR (neat) 3418, 3120, 2952, 2895, 1770, 1746, 1682, 1521, 1250, 1200, 1094, 1024 cm^{-1}. HRMS (CI) *m/z* calcd. for $C_{11}H_{19}O_3Si$ (MH^+) 227.1091, found 227.1103.



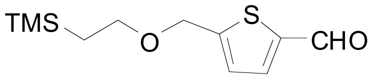
1-(5-((2-(Trimethylsilyl)ethoxy)methyl)thiophen-2-yl)ethanone (6b). According to the general procedure, the product was obtained in 54% yield (69 mg, 0.27 mmol) as an orange oil after silica gel column chromatography (elution with hexane/EtOAc 7:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, 1H, *J* = 3.8 Hz), 6.9 (d, 1H, *J* = 3.6 Hz), 4.64 (s, 2H), 3.61 (t, 2H, *J* = 8.0 Hz), 2.53 (s, 3H), 0.99 (t, 2H, *J* = 8.1 Hz), 0.03 (s, 9H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 190.5, 151.2, 143.8, 132.3, 126.0, 68.1, 67.1, 26.6, 18.2, -1.4. FT-IR (neat) 3074, 2920, 2952, 2893, 2857, 1660, 1590, 1536, 1455, 1277, 1248, 1178, 1087, 1032 cm^{-1}. HRMS (CI) *m/z* calcd. for $C_{12}H_{21}O_2SSi$ (MH^+) 257.1042, found 257.1032.



3-((2-(Trimethylsilyl)ethoxy)methyl)pyridine (6c). According to the general procedure, the product was obtained in 70% yield (73 mg, 0.35 mmol) as a colorless oil after silica gel column chromatography (elution with hexane/EtOAc 2:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (m, 1H), 8.54-8.53 (m, 1H), 7.67-7.65 (m, 1H), 7.27-7.24 (m, 1H), 4.48 (s, 2H), 3.59 (t, 2H, *J* = 8.1 Hz), 0.99 (t, 2H, *J* = 8.2), (s, 9H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 149.1, 148.9, 135.3, 134.1, 123.3, 69.9, 68.1, 18.3, -1.4. FT-IR (neat): 3030, 2919, 2952, 2893, 2857, 1721, 1590, 1577, 1478, 1426, 1358, 1248, 1183, 1090, 1026 cm^{-1}. HRMS (CI) *m/z* calcd. for $C_{11}H_{20}NOSi$ (MH^+) 210.1307, found 210.1314.



5-((2-(Trimethylsilyl)ethoxy)methyl)pyrimidine (6d). According to the general procedure, the product was obtained in 51% yield (54 mg, 0.26 mmol) as a colorless oil after silica gel column chromatography (elution with hexane/EtOAc 1:1). ^{1}H NMR (500 MHz, CDCl$_3$) δ 9.14 (s, 1H), 8.70 (s, 2H), 4.49 (t, 2H, J = 8.2 Hz), 3.61 (t, 2H), 0.99 (t, 2H, J = 8.2 Hz), 0.004 (s, 9H). ^{13}C NMR (125.8 MHz, CDCl$_3$) δ 158.1, 156.1, 131.9, 68.6, 67.6, 18.2, -1.4. FT-IR (neat): 3046, 2952, 2858, 2358, 1585, 1563, 1439, 1409, 1249, 1182, 1110, 1090 cm^{-1}. HRMS (CI) *m/z* calcd. for $C_{10}H_{19}N_2OSi$ (MH$^+$) 211.1257, found 211.1267.



5-((2-(Trimethylsilyl)ethoxy)methyl)thiophene-2-carboxaldehyde (6e). According to the general procedure, the product was obtained in 40% yield (48 mg, 0.20 mmol) as a light orange oil after silica gel column chromatography (elution with hexane/EtOAc 10:1). ^{1}H NMR (500 MHz, CDCl$_3$) δ 9.87 (s, 1H), 7.65 (d, 1H, J = 3.7 Hz), 7.07 (d, 1H, J = 3.8 Hz), 4.68 (s, 2H), 3.64 (t, 2H, J = 8.1 Hz), 0.10 (t, 2H, J = 8.2 Hz), 0.03 (s, 9H). ^{13}C NMR (125.8 MHz, CDCl$_3$) δ 183.1, 153.4, 143.4, 136.5, 126.2, 68.6, 67.4, 18.4, -1.1. FT-IR (neat) 3434, 2951, 2917, 2849, 2359, 1671, 1530, 1463, 1228, 1086, 1047 cm^{-1}. HRMS (CI) *m/z* calcd. for $C_{11}H_{19}O_2SSi$ (MH$^+$) 243.0870, found 243.0875.