Supporting Information

Synthesis of aryloxyacetamides from arylboronic acids and 2bromoacetonitrile promoted by alkaline solutions of hydrogen peroxide

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1. General Information

Reactions were monitored by analytical thin-layer chromatography (TLC) on Silica gel plates (GF254). The TLC plates were isualized by shortwave (254 nm) or longwave (365 nm) UV light. Column chromatography was carried out using silica gel (200-300 mesh) to purify the products. Melting points were determined by using a Haineng MP120 melting point apparatus. ¹H-NMR and ¹³C-NMR spectra were recorded with a Bruker Avance II 400 spectrometer (Fallanden, Switzerland) using tetramethylsilane as the internal standard and CDCl₃ as the solvent. The highresolution mass spectras (HRMS) were recorded in Agilent 6210 ESI/TOF mass spectrometer. The crystal structure of the compound was determined by using an Agilent Super Nova CCD Dual X-ray diffractometer. All reagents and solvents were purchased from commercial sources and used without further purification.

2. General procedure for the synthesis of aryloxyacetamides (3a-

3y)



All reactions were carried out under air conditions. A mixture of arylboronic acid (0.5 mmol), 2-bromoacetonitrile (0.7 mmol), base (1.3 mmol) and 3 mL H_2O were taken in an oven dried 10 mL round bottomed flask. To this 30% aq. H_2O_2 0.08

mL was added dropwise and stirred at 80 $^{\circ}$ C for 4 h. After completion of the reaction (monitored by TLC) and cooling to ambient temperature, distilled H₂O (10 mL) was added to the mixture, the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried (Na₂SO₄) and concentrated, and the residue was purified by thin layer chromatography to obtain the desired product by using ethyl acetate/hexane as the eluent.

3. Characterization datas of 3a-3y

3a. 2-Phenoxyacetamide



White solid, the yield was 76%, mp 101.1-101.4 oC, 1H NMR (400 MHz, DMSO) δ 7.60 (s, 1H), 7.52 (s, 1H), 7.30 (t, J = 7.4 Hz, 2H), 7.00 – 6.95 (m, 3H), 4.47 (s, 2H); 13C NMR (100 MHz, DMSO) δ 170.36, 157.75, 129.49, 121.18, 114.71, 66.75. Crystallographic data have been deposited at the Cambridge Crystallographic Data Center and allocated with the deposition numbers: CCDC 2104618 for compounds **3a**. **3b. 2-(3, 5-Difluoro-phenoxy)-acetamide**

White solid, the yield was 90%, mp 175.5-175.8 °C, ¹H NMR (400 MHz, DMSO) δ 7.58 (s, 1H), 7.45 (s, 1H), 7.33 (dt, *J* = 10.5, 9.3 Hz, 1H), 7.06 (ddd, *J* = 12.6, 6.7, 3.0 Hz, 1H), 6.79 (dtd, *J* = 9.0, 3.3, 1.8 Hz, 1H), 4.45 (s, 2H); ¹³C NMR (100 MHz, DMSO) δ 170.02, 154.78 (dd, *J*_{C-F} = 9.0, 2.0 Hz), 149.95 (dd, *J*_{C-F} = 244.9, 13.8 Hz), 144.75 (dd, *J*_{C-F} = 238.0, 12.7 Hz), 117.92 (d, *J*_{C-F} = 17.4 Hz), 111.31 (dd, *J*_{C-F} = 6.1, 3.3 Hz), 104.95 (d, *J*_{C-F} = 20.4 Hz), 67.75. IR (KBr, cm⁻¹): v_{N-H} 3474, 3180 cm⁻¹, v_{C-H} 2925 cm⁻¹(CH₂), v_{C=O} 1666 cm⁻¹, v_{C=C} 1604, 1517 cm⁻¹, v_{C-N} 1419 cm⁻¹, v_{C=O} 1259 cm⁻¹, v_{C=O} 1159 cm⁻¹. HRMS (ESI) m/z: calcd for C₈H₇F₂NO₂ [M + Na]⁺ 210.0337; found 210.0335.

3C. 2-(3,4-Difluoro-phenoxy)-acetamide



White solid, the yield was 84%, mp 131.1-133.3 °C, ¹H NMR (400 MHz, DMSO) δ 7.59 (s, 1H), 7.45 (s, 1H), 6.86 – 6.76 (m, 1H), 6.72 (dd, *J* = 9.4, 2.2 Hz, 2H), 4.49 (s, 2H); ¹³C

NMR (100 MHz, DMSO) δ 169.67, 164.61 (d, J_{C-F} = 16.2 Hz), 162.19 (d, J_{C-F} = 16.2 Hz), 160.33 (t, J_{C-F} = 14.2 Hz), 99.45 (d, J_{C-F} = 28.6 Hz), 99.45 (d, J_{C-F} = 12.5 Hz), 97.02 (t, J_{C-F} = 26.3 Hz), 67.53. IR (KBr, cm⁻¹): v_{N-H} 3474, 3180 cm⁻¹, v_{C=0} 1633 cm⁻¹, v_{C=C} 1602, 1505, 1477 cm⁻¹, v_{C-N} 1419 cm⁻¹, v_{=C-0} 1222 cm⁻¹, v_{C-0} 1160 cm⁻¹; HRMS (ESI) m/z: calcd for C₈H₇F₂NO₂ [M + Na]⁺ 210.0337; found 210.0339.

3d. 2-(3, 5-Dichloro-phenoxy)-acetamide



White solid, the yield was 82%, mp 177.2-179.1 °C, ¹H NMR (400 MHz, DMSO) δ 7.58 (s, 1H), 7.43 (s, 1H), 7.13 (s, 1H), 7.03 (s, 2H), 4.51 (s, 2H); ¹³C NMR (100 MHz, DMSO) δ 169.22, 159.15, 134.47, 120.78, 114.20, 67.00.

3e. 2-(3-Fluoro-phenoxy)-acetamide



White solid, the yield was 86%, mp 110.6-112.2 °C, ¹H NMR (400 MHz, DMSO) δ 7.58 (s, 1H), 7.44 (s, 1H), 7.38 – 7.27 (m, 1H), 6.88 – 6.71 (m, 3H), 4.47 (s, 2H); ¹³C NMR (100 MHz, DMSO) δ 170.11, 163.31 (d, J_{C-F} = 242.9 Hz), 159.64 (d, J_{C-F} = 11.2 Hz), 131.13 (d, J_{C-F} = 10.1 Hz), 111.39 (d, J_{C-F} = 2.8 Hz), 108.19 (d, J_{C-F} = 21.1 Hz), 102.85 (d, J = 25.0 Hz), 67.33.

3f. 2-(4-Fluoro-phenoxy)-acetamide



White solid, the yield was 83%, mp 109.9-111.4 °C,¹H NMR (400 MHz, DMSO) δ 7.58 (s, 1H), 7.46 (s, 1H), 7.16 – 7.05 (m, 2H), 7.02 – 6.91 (m, 2H), 4.43 (s, 2H); ¹³C NMR (100 MHz, DMSO) δ 170.53, 157.28 (d, *J* = 236.5 Hz), 154.52 (d, *J* = 1.9 Hz), 116.45 (d, *J* = 8.1 Hz), 116.22 (d, *J* = 23.1 Hz), 67.70.

3g. 2-(3,4-Dichloro-phenoxy)-acetamide



White solid, the yield was 86%, mp 151.5-152.4 °C, ¹H NMR (400 MHz, DMSO) δ 7.59 (s, 1H), 7.54 (d, J = 8.9 Hz, 1H), 7.44 (s, 1H), 7.24 (d, J = 2.6 Hz, 1H), 6.99 (dd, J = 8.9, 2.7 Hz, 1H), 4.50 (s, 2H); ¹³C NMR (100 MHz, DMSO) δ 169.78, 157.70, 131.92, 131.38, 123.39, 117.29, 116.06, 67.50.

3h. 2-(4-Chloro-phenoxy)-acetamide



White solid, the yield was 86%, mp 140.5-141.9 °C, ¹H NMR (400 MHz, DMSO) δ 7.58 (s, 1H), 7.44 (s, 1H), 7.31 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 4.44 (s, 2H); ¹³C NMR (100 MHz, DMSO) δ 169.83, 156.60, 129.18, 124.91, 116.45, 66.94.

3i. 2-(3-Chloro-phenoxy)-acetamide



White solid, the yield was 87%, mp 127.4-127.9 °C,¹H NMR (400 MHz, DMSO) δ 7.56 (s, 1H), 7.40 (s, 1H), 7.31 (t, *J* = 8.1 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 1H), 4.46 (s, 2H); ¹³C NMR (100 MHz, DMSO) δ 169.61, 158.68, 133.62, 130.86, 121.06, 114.95, 113.67, 66.81.

3j. 2-(2-Chloro-phenoxy)-acetamide



White solid, the yield was 86%, mp149.2-150.1 °C,¹H NMR (400 MHz, DMSO) δ 7.54 (s, 1H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.36 (s, 1H), 7.26 (t, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 4.58 (s, 2H); ¹³C NMR (100 MHz, DMSO) δ 169.54, 153.27, 130.00, 128.18, 122.12, 121.59, 114.12, 67.44.

3k. 2-(4-Bromo-phenoxy)-acetamide



White solid, the yield was 67%, mp 155.0-155.7 °C, ¹H NMR (400 MHz, DMSO) δ 7.57 (s, 1H), 7.49 – 7.41 (m, 3H), 6.93 (d, *J* = 9.0 Hz, 2H), 4.44 (s, 2H); ¹³C NMR (100 MHz, DMSO) δ 170.17, 157.53, 132.55, 117.46, 113.01, 67.28.

3l. 2-(3-Bromo-phenoxy)-acetamide



White solid, the yield was 69%, mp 154-155 °C, ¹H NMR (400 MHz, DMSO) δ 8.40 (s, 1H), 8.27 (s, 1H), 8.06 (t, *J* = 8.1 Hz, 1H),8.02 – 7.92 (m, 2H), 7.79 (dd, *J* = 8.2, 1.6 Hz, 1H), 5.29 (s, 2H); ¹³C NMR (100 MHz, MeOD) δ 170.93, 159.97, 132.40, 125.23, 123.24, 119.10, 115.26, 68.09.

3m. 2-(2-Bromo-phenoxy)-acetamide



White solid, the yield was 78%, mp 155.1-155.6 °C, ¹H NMR (400 MHz, DMSO) δ 7.59 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.51 (s, 1H), 7.33 (ddd, *J* = 8.4, 7.5, 1.6 Hz, 1H), 7.30 (s, 1H), 7.00 (dd, *J* = 8.3, 1.3 Hz, 1H), 6.92 (td, *J* = 7.7, 1.3 Hz, 1H), 4.56 (s, 2H); ¹³C NMR (100 MHz, DMSO) δ 169.81, 154.55, 133.49, 129.40, 123.10, 114.44, 111.49, 67.87.

3n. 2-(4-Acetyl-phenoxy)-acetamide



White solid, the yield was 82%, mp 156.1-157.0 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.9 Hz, 2H), 7.00 (d, *J* = 8.9 Hz, 2H), 6.56 (s, 1H), 6.03 (s, 1H), 4.59 (s, 2H), 2.59 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 196.69, 170.16, 160.72, 130.83, 114.40, 67.04, 26.43. IR(KBr, cm⁻¹): v_{C=0} 1710 cm⁻¹(CH₃CO), v_{C=0} 1630 cm⁻¹ (CONH₂), v_{C=C} 1600, 1500, 1480 cm⁻¹, v_{C-N} 1420 cm⁻¹, v_{=C-0} 1220 cm⁻¹, v_{C-0} 1120cm⁻¹. HRMS (ESI) *m/z:* calcd for C₁₀H₁₁NO₃ [M + Na]⁺ 216.0631; found 216.0637.

30. 2-(3-Acetyl-phenoxy)-acetamide

White solid, the yield was 70%, mp 145.7-147.1 °C, ¹H NMR (400 MHz, DMSO) δ 7.65 (s, 1H), 7.60 – 7.39 (m, 4H), 7.22 (d, *J* = 6.9 Hz, 1H), 4.53 (s, 2H), 2.55 (s, 3H); ¹³C NMR (100 MHz, DMSO) δ 198.10, 170.38, 158.35, 138.58, 130.28, 121.81, 120.14, 114.08,

67.19, 27.15.

3p. 2-(4-Cyano-phenoxy)-acetamide

White solid, the yield was 67%, mp 154.5-155.2 °C, ¹H NMR (400 MHz, DMSO) δ 7.73 (t, *J* = 8.8 Hz, 2H), 7.63 (s, 1H), 7.44 (s, 1H), 7.11 (d, *J* = 8.9 Hz, 2H), 4.56 (s, 2H); ¹³C NMR (100 MHz, DMSO) δ 169.63, 161.68, 134.58, 119.53, 116.25, 103.78, 67.07.

3q. 2-(4-Methoxy-phenoxy)-acetamide



White solid, the yield was 67%, mp 115.3-116.3 °C, ¹H NMR (400 MHz, DMSO) δ 7.51 (s, 1H), 7.41 (s, 1H), 6.94 – 6.83 (m, 4H), 4.36 (s, 2H), 3.69 (s, 3H); ¹³C NMR (100 MHz, DMSO) δ 170.81, 154.24, 152.24, 116.11, 115.01, 67.88, 55.80.

3r. 2-(3-Methoxy-phenoxy)-acetamide



White solid, the yield was 67%, mp 108.7-110.0 °C, ¹H NMR (400 MHz, DMSO) δ 7.55 (s, 1H), 7.45 (s, 1H), 7.20 (t, *J* = 8.1 Hz, 1H), 6.64 – 6.51 (m, 3H), 4.44 (s, 2H), 3.74 (s, 3H); ¹³C NMR (100 MHz, DMSO) δ 170.55, 160.91, 159.42, 130.42, 107.27, 107.22, 101.63, 67.25, 55.51.

3s. 2-(2-Methoxy-phenoxy)-acetamide



White solid, the yield was 77%, mp 141.7-142.7 °C, ¹H NMR (400 MHz, DMSO) δ 7.44 (s, 1H), 7.33 (s, 1H), 7.02 – 6.85 (m, 4H), 4.42 (s, 2H), 3.77 (s, 3H); ¹³C NMR (100 MHz, DMSO) δ 170.28, 149.33, 147.41, 122.08, 120.69, 114.71, 112.44, 68.22, 55.55.

3t. 2-(3, 5-Dimethyl-phenoxy)-acetamide



White solid, the yield was 49%, mp 132.8-133.0 °C, ¹H NMR (400 MHz, CDCl₃) δ 6.68 (s, 1H), 6.65-6.56 (m, 4H), 4.46 (s, 2H), 2.31 (s, 6H); ¹³C NMR (10 MHz, CDCl₃) δ 171.31, 156.84, 139.22, 123.46, 111.97, 66.64, 20.95. IR (KBr, cm⁻¹): v_{N-H} 3390.2, 3193.5 cm⁻¹, v_{C-H} 2919 cm⁻¹(CH₂), v_{C=0} 1680 cm⁻¹, v_{C=C} 1613.1, 1594.8, 1509.9, 1474.8 cm⁻¹, v_{C-N} 1409.7 cm⁻¹, v_{=C-0} 1294.9 cm⁻¹, v_{C-0} 1154.1 cm⁻¹; HRMS (ESI) m/z: calcd for C₁₀H₁₃NO₂ [M + Na]⁺ 202.0838; found 202.0839.

3u. 2-p-Tolyloxy-acetamide

White solid, the yield was 67%, mp 125.8-126.8 °C, ¹H NMR (400 MHz, DMSO) δ 7.48 (s, 1H),7.38 (s, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 7.8 Hz, 2H), 4.36 (s, 2H), 2.22 (s, 3H); ¹³C NMR (100 MHz, DMSO) δ 170.18, 155.68, 129.84, 129.79, 114.54, 66.87, 20.07.

3v. 2-m-Tolyloxy-acetamide



White solid, the yield was 66%, mp 118.9-119.2 °C, ¹H NMR (400 MHz, DMSO) δ 7.53 (s, 1H),7.46 (s, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 6.79 (d, *J* = 7.1 Hz, 2H), 6.76 (s, 1H), 4.42 (s, 2H), 2.27 (s, 3H); ¹³C NMR (100 MHz, DMSO) δ 170.26, 157.78, 138.99, 129.19, 121.90, 115.38, 111.66, 66.71, 21.07.

3w. 2-o-Tolyloxy-acetamide



White solid, the yield was 67%, mp 129.2-129.7 °C, ¹H NMR (400 MHz, CDCl₃) δ 7.22 – 7.09 (m, 2H), 6.93 (td, *J* = 7.5, 0.7 Hz, 1H), 6.82 – 6.71 (m, 2H), 6.60 (s, 1H), 4.48 (s, 2H), 2.28 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.79, 155.39, 131.13, 127.21, 126.54, 121.89, 111.50, 67.25, 16.35.

3x. 2-(4-Propyl-phenoxy)-acetamide



White solid, the yield was 53%, mp 116.3-118.5 °C, ¹H NMR (400 MHz, DMSO) δ 7.51 (s, 1H), 7.41 (s, 1H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.96 – 6.84 (m, 2H), 4.39 (s, 2H), 2.57 – 2.38 (m, 2H), 1.53 (dt, *J* = 14.7, 7.4 Hz, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (100 MHz, DMSO) δ 170.66, 156.32, 135.16, 129.64, 114.91, 67.28, 36.86, 24.78, 14.02. IR (KBr, cm⁻¹): v_{N-H} 3409, 3183 cm⁻¹, v_{C-H} 2955, 2868 cm⁻¹(CH₃), v_{C-H} 2929 cm⁻¹(CH₂), v_{C=0} 1680 cm⁻¹, v_{C=C} 1585, 1501 cm⁻¹, v_{C-N} 1428 cm⁻¹, v_{=C-0} 1299 cm⁻¹, v_{C-0} 1177cm⁻¹. HRMS (ESI) *m/z:* calcd for C₁₁H₁₅NO₂ [M + Na]⁺216.0995; found 216.0997.

3y. 2-(4-Methylsulfanyl-phenoxy)-acetamide



Yellow solid, the yield was 34%, mp 132.3-133.4 °C, ¹H NMR (400 MHz, DMSO) δ 7.55 (s, 1H), 7.42 (s, 1H), 7.25 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 4.42 (s, 2H), 2.42 (s, 3H); ¹³C NMR (100 MHz, DMSO) δ 170.45, 156.46, 129.62, 129.26, 116.01, 67.31, 16.89. Crystallographic data have been deposited at the Cambridge Crystallographic Data Center and allocated with the deposition numbers: CCDC 2104616 for compounds **3y**.

4. Copies of ¹H and ¹³C NMR spectra of compounds **3a-3y 4.1.** ¹H NMR and ¹³C NMR of **3**a



4.2. ¹H NMR and ¹³C NMR of 3b





4.3. ¹H NMR and ¹³C NMR of 3c









200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 fl (ppm)

4.4 ¹H NMR and ¹³C NMR of 3d





4.5 ¹H NMR and ¹³C NMR of 3e





4.6 ¹H NMR and ¹³C NMR of 3f











4.7 ¹H NMR and ¹³C NMR of 3g





4.8 ¹H NMR and ¹³C NMR of 3h

4.9 ¹H NMR and ¹³C NMR of 3i



-4.44

7.58 7.7.58 7.7.32 6.98 6.98



4.10 ¹H NMR and ¹³C NMR of 3j





4.11 ¹H NMR and ¹³C NMR of 3k









4.12 ¹H NMR and ¹³C NMR of 3l

-0. E



4.13 $^1\!H$ NMR and $^{13}\!C$ NMR of 3m





4.14 ¹H NMR and ¹³C NMR of 3n



4.15 ¹H NMR and ¹³C NMR of 30



4.16 ¹H NMR and ¹³C NMR of 3p





4.17 ¹H NMR and ¹³C NMR of 3q



4.18 ¹H NMR and ¹³C NMR of 3r



4.19 ¹H NMR and ¹³C NMR of 3s



S27



4.21 ¹H NMR and ¹³C NMR of 3u



4.22 ¹H NMR and ¹³C NMR of 3v



4.23 ¹H NMR and ¹³C NMR of 3w



4.24 ¹H NMR and ¹³C NMR of 3x



4.25 ¹H NMR and ¹³C NMR of 3y

