## Supplementary Information for

## Base-mediated rearrangement of free aromatic hydroxamic acids (ArCO-NHOH) to anilines

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**General.** Melting points were determined on a Buchi 535 apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer FT-IR PARAGON 1000 spectrometer or a JASCO FT/IR-4100. <sup>1</sup>H NMR spectra were recorded on a JEOL JNM AL-400 (400 MHz) spectrometer, or a JEOL JNM EX-270 (270 MHz) spectrometer with tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in ppm from TMS. Data are reported as follows: chemical shift, multiplicity: (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants, integration, and assignment. <sup>13</sup>C NMR spectra were recorded on a JEOL JNM AL-400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (CDCl<sub>3</sub>:  $\delta$  77.0). Column chromatography was carried out with Fuji Silysia silica gel BW-127ZH (spherical, 63-210 µm, Fuji Silysia Chemical Industries). Thin-Layer chromatography (TLC) was carried out with Merck TLC plates with silica gel 60 F<sub>254</sub>.

**Materials.** Unless otherwise noted, reagents were commercially available and were used without purification. The solvents used were purified by distillation over the drying agents indicated: THF (Na/benzophenone), DMSO, DMF, MeCN (CaH<sub>2</sub>), NMP, n-BuOH (MgSO<sub>4</sub>), toluene (CaCl<sub>2</sub>), MeOH (Mg).

## Synthesis of Hydroxamic Acids 1a-i.<sup>1</sup>

**Representative procedure:** Separate solutions of hydroxylamine hydrochloride (4.17 g, 0.060 mol) in 30 mL of MeOH, and of potassium hydroxide (6.72 g, 0.12 mol) in 30 mL of MeOH, are prepared. Both are cooled in ice bath, and the one containing alkali is added with shaking to the hydroxylamine solution. After all the alkali has been added, the mixture is allowed to stand in an ice bath for five minutes to ensure complete precipitation of potassium chloride. The mixture was filtered with suction and the filtrate was added to ethyl 4-methylbenzoate (4.77 mL, 0.030 mol) in 100 mL flask. Additional

potassium hydroxide was added to become a basic solution (pH 10). After 12 hrs with stirring at room temperature MeOH was evaporated in vacuo and to the residue was added 20 mL of water to become a clear solution, which was acidified with 2 M HCl to be pH <4. The solid appeared was collected by filtration to give the title compound. Additionally, the filtrate was extracted with ethyl acetate and the organic phase was evaporated and purified by recrystallization from ethyl acetate/hexane to give the additional desired product.

*N*-hydroxy-4-methylbenzamide (1a):<sup>2,3</sup> Yield 88%. White crystalline solid. IR (KBr) v 3295, 2760, 1650, 1614, 1564, 1508, 1331, 1038, 839, 739, 538 cm<sup>-1</sup>; <sup>1</sup>H NMR (270 MHz, DMSO-*d*<sub>6</sub>) δ 2.34 (s, 3H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 8.95 (s, 1H), 11.13 (s, 1H).

*N*-hydroxybenzamide (1b):<sup>2</sup> Yield 90%. White crystalline solid. IR (KBr) v 3299, 3060, 2758, 1648, 1612, 1562, 1491, 1453, 1435, 1328, 706, 691 cm<sup>-1</sup>; <sup>1</sup>H NMR (270 MHz, DMSO- $d_6$ )  $\delta$  7.42-7.55 (m, 3H), 7.74-7.77 (m, 2H), 9.04 (s, 1H), 11.21 (s, 1H). The product was also identified in comparison with a commercially available sample.

*N*-hydroxy-2-methylbenzamide (1c):<sup>3</sup> Yield 55%. White crystalline solid. IR (KBr) v 3303, 3212, 1625, 1595, 1527, 1482, 1316, 1165, 1022, 901 cm<sup>-1</sup>; <sup>1</sup>H NMR (270 MHz, DMSO-*d*<sub>6</sub>) δ 2.33 (s, 3H), 7.18-7.35 (m, 4H), 9.04 (s, 1H), 10.80 (s, 1H).

*N*-hydroxy-3-methylbenzamide (1d):<sup>3</sup> Yield 61%. white crystalline solid. IR (KBr) v 3307, 3064, 2914, 1651, 1624, 1580, 1561, 1485, 1459, 810, 725 cm<sup>-1</sup>; <sup>1</sup>H NMR (270 MHz, DMSO- $d_6$ )  $\delta$  2.34 (s, 3H), 7.33 (d, J = 4.6 Hz, 2H), 7.54 (t, J = 4.6 Hz, 1H), 9.01 (s, 1H), 11.13 (s, 1H).

*N*-hydroxy-4-methoxybenzamide (1e):<sup>2</sup> Yield 81%. White crystalline solid. IR (KBr) v 3285, 2971, 2755, 1644, 1610, 1568, 1507, 1443, 1305, 1254, 1024 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 3.80 (s, 3H), 6.98 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 8.91 (s, 1H), 11.06 (s, 1H).

**4-chloro-***N***-hydroxybenzamide (1f):**<sup>2,3</sup> Yield 95%. White crystalline solid. IR (KBr) v 3292, 3067, 2745, 1651, 1598, 1561, 1487, 1097, 1013, 847, 746, 538 cm<sup>-1</sup>; <sup>1</sup>H NMR (270 MHz, DMSO-*d*<sub>6</sub>) δ 7.53 (d, *J* = 8.6 Hz, 2H), 7.77 (d, *J* = 8.6 Hz, 2H), 9.11 (s, 1H), 11.30 (s, 1H).

**4-bromo-***N***-hydroxybenzamide (1g):**<sup>4</sup> Yield 98%. White crystalline solid. IR (KBr) v 3290, 3066, 2748, 1649, 1614, 1591, 1558, 1483, 1075, 1011, 526 cm<sup>-1</sup>; <sup>1</sup>H NMR (270 MHz, DMSO-*d*<sub>6</sub>) δ 7.65-7.72 (m, 4H), 9.13 (s, 1H), 11.24 (s, 1H).

*N*-hydroxy-2-iodobenzamide (1h): Yield 71%. White solid. IR (KBr) v 3237, 3039, 2876, 1622, 1542, 1467, 1170, 904, 744 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO- $d_{\delta}$ )  $\delta$  7.18 (dt, J = 8.0, 1.6 Hz, 1H), 7.29

 $(dd, J = 8.0, 1.6 Hz, 1H), 7.43 (dt, J = 8.0, 0.8 Hz, 1H), 7.88 (dd, J = 8.0, 0.8 Hz, 1H), 9.20 (s, 1H), 10.91 (s, 1H). {}^{13}C NMR (100 MHz, DMSO-$ *d* $<sub>6</sub>) <math>\delta$  94.4, 127.9, 128.6, 131.1, 139.2, 140.6, 165.7; Anal. Calcd for C<sub>7</sub>H<sub>6</sub>INO<sub>2</sub>: C, 31.96; H, 2.30; N, 5.33. Found: C, 31.98; H, 2.39; N, 5.30.

*N*-hydroxy-4-nitrobenzamide (1i):<sup>5</sup> Yield 90%. Yellow crystalline solid. IR (KBr) v 3249, 2856, 1654, 1600, 1516, 1358, 1034, 850, 550 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.99 (d, *J* = 5.4 Hz, 2H), 8.31 (d, *J* = 5.4 Hz, 2H), 9.37 (s, 1H), 11.58 (s, 1H).

*N*-hydroxy-2,6-dimethoxybenzamide (1j): Yield 50%. White crystalline solid. Mp 201.2-201.5 (AcOEt) (lit.<sup>6</sup> 200-201 °C). IR (KBr) v 3260, 2887, 2835, 1619, 1600, 1475, 1257, 1119, 898, 791 cm<sup>-1</sup>; <sup>1</sup>H NMR (270 MHz, DMSO- $d_6$ )  $\delta$  3.36 (s, 6H), 6.66 (d, *J* = 9.5 Hz, 2H), 7.30 (t, *J* = 9.5 Hz, 1H), 8.96 (s, 1H), 10.52 (s, 1H).

*N*-hydroxy-2,3-dimethoxybenzamide (1k): Yield 70%. White solid. IR (KBr) v 3345, 3321, 3089, 2838, 1644, 1577, 1267, 988, 812, 757 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  3.75 (s, 3H), 3.82 (s, 3H), 6.94 (dd, J = 7.2, 1.2 Hz, 1H), 7.07-7.14 (m, 2H), 9.08 (s, 1H), 10.68 (s, 1H). <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ )  $\delta$  55.9, 61.0, 114.4, 120.2, 124.0, 129.3, 146.1, 152.5, 163.5; Anal. Calcd for C<sub>9</sub>H<sub>11</sub>NO<sub>4</sub>: C, 54.82; H, 5.62; N, 7.10. Found: C, 54.97; H, 5.59; N, 6.95.

General Procedure for the base-mediated rearrangement of free hydroxamic acids to amines: A mixture of *N*-hydroxy-4-methylbenzamide (1a) (0.363 g, 2.4 mmol),  $K_2CO_3$  (0.332 g, 2.4 mmol), and DMSO (2 mL) was heated to 90 °C and stirred at that temperature for 2 h. The mixture was cooled to rt, and then treated with 2 M HCl (ca. 3 mL). After the mixture became the clear solution, 2 M NaOH (ca. 3 mL) was added and extracted with  $Et_2O$  (15 mL x 3). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/Et<sub>2</sub>O, 1:1) to yield the pure 4-methylaniline<sup>7</sup> (0.253 g, 98%) as a white crystalline solid.

**4-methylaniline (2a):**<sup>7</sup> Yield 0.253 g (98%). White crystalline solid. IR (KBr) v 3418, 3337, 3222, 3010, 2914, 2859, 1622, 1514, 1280, 1268, 810, 508 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.24 (s, 3H), 3.51 (s, 2H), 6.60 (d, *J* = 7.8 Hz, 2H), 6.96 (d, *J* = 7.8 Hz, 2H).

**aniline (2b):** Yield 0.215 g (96%). Pale yellowish liquid. IR (neat) v 3429, 3355, 3036, 1621, 1602, 1278, 1175, 755, 693 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.64 (s, 2H), 6.69 (d, *J* = 7.8 Hz, 2H), 6.76 (t, *J* = 7.8 Hz, 1H), 7.13-7.18 (m, 2H). The product was also identified in comparison with a commercially available sample.

**2-methylaniline (2c):**<sup>7</sup> Yield 0.255 g (99%). Pale brownish liquid. IR (KBr) v 3452, 3361, 3021, 2931,

1623, 1498, 1669, 1304, 1272, 753 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  2.17 (s, 3H), 3.59 (s, 2H), 6.67 (d, J = 7.7 Hz, 1H), 6.71 (dd, J = 1.2, 7.7 Hz, 1H), 7.03 (t, J = 7.7 Hz, 2H).

**3-methylaniline (2d):**<sup>8</sup> Yield 0.255 g (99%). Pale brownish liquid. IR (neat) v 3436, 3352, 3034, 2919, 1623, 1494, 1293, 776, 691 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.27 (s, 3H), 3.59 (s, 2H), 6.48-6.60 (m, 3H) 7.05 (t, *J* = 7.6 Hz, 1H).

**4-methoxyaniline (2e):**<sup>7</sup> Yield 0.291 g (99%). White crystalline solid. IR (KBr) v 3422, 3347, 2964, 2839, 1509, 1235, 1032, 826, 514 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.42 (s, 2H), 3.74 (s, 3H), 6.65 (d, *J* = 9.4 Hz, 2H) 6.70 (d, *J* = 9.4 Hz, 2H).

**4-chloroaniline (2f):**<sup>9</sup> Yield 0.381 g (90%). Gray crystalline solid. IR (KBr) v 3472, 3382, 1616, 1494, 1288, 1181, 1089, 821, 639, 505 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.65 (s, 2H), 6.60 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H).

**4-bromoaniline (2g):**<sup>9,10</sup> Yield 0.380 g (92%). Gray crystalline solid. IR (KBr) v 3474, 3382, 1612, 1489, 1286, 1180, 1069, 818, 502 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.65 (s, 2H), 6.56 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H).

**2-iodoaniline (2h):**<sup>11</sup> Yield 98%. White solid. IR (KBr) v 3394, 3290, 3187, 1623, 1474, 1300, 1251, 1146, 1006, 749 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.08 (s, 2H), 6.47 (t, *J* = 7.2 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H).

**4-nitroaniline (2i):**<sup>7,12</sup> Yield 0.146 g (88%). Yellow crystalline solid. IR (KBr) v 3482, 3360, 1631, 1587, 1471, 1299, 1114, 840, 753, 490 cm<sup>-1</sup>; <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>)  $\delta$  4.38 (s, 2H), 6.63 (d, *J* = 5.4 Hz, 2H), 8.08 (d, *J* = 5.4 Hz, 2H).

**2,6-dimethoxyaniline (2j):**<sup>13</sup> Yield 0.360 g (98%). White solid. IR (KBr) v 3464, 3373, 2962, 1603, 1505, 1478, 1144, 766, 597 cm<sup>-1</sup>; <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>)  $\delta$  3.82 (s, 2H), 3.85 (s, 6H), 6.53 (d, J = 8.1 Hz, 2H), 6.69 (t, J = 8.1 Hz, 1H).

**2,3-dimethoxyaniline (2k):**<sup>14</sup> Yield 99%. White solid. IR (KBr) v 3466, 3369, 2938, 1615, 1322, 1265, 1133, 1089, 733 cm<sup>-1</sup>; <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>) δ 3.40-4.10 (br s, 2H), 3.83 (s, 3H), 3.84 (s, 3H), 6.34 (d, *J* = 8.1 Hz, 1H), 6.38 (d, *J* = 8.1 Hz, 1H), 6.84 (t, *J* = 7.8 Hz, 1H).

Rearrangement of *N*-hydroxy-4-methylbenzamide (1a) with catalytic amount of  $K_2CO_3$  (0.05 equiv). A mixture of *N*-hydroxy-4-methylbenzamide (1a) (0.363 g, 2.4 mmol),  $K_2CO_3$  (0.0166 g, 0.12 mmol), and DMSO (2 mL) was heated to 90 °C and stirred at that temperature for 18 h. The mixture

was cooled to rt, and then treated with 2 M HCl (ca. 3 mL). After the mixture became the clear solution, 2 M NaOH (ca. 2 mL) was added and extracted with  $Et_2O$  (15 mL x 3). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/ $Et_2O$ , 1:1) to yield the pure 4-methylaniline (0.233 g, 91%). A small amount (0.0025 g, 1%) of *N*,*N*'-bis(4-methylphenyl)urea was also obtained.

Rearrangement of *N*-hydroxy-4-methylbenzamide (1a) with  $K_2CO_3$  (0.5 equiv) in the presence of water. A mixture of *N*-hydroxy-4-methylbenzamide (1a) (0.0906 g, 0.6 mmol),  $K_2CO_3$  (0.0415 g, 0.3 mmol), DMSO (2 mL), and H<sub>2</sub>O (0.06 ml, 3.3 mmol) was heated to 90 °C and stirred at that temperature for 1 h. The mixture was cooled to rt, and then treated with 2 M HCl (ca. 3 mL). After the mixture became the clear solution, 2 M NaOH (ca. 2 mL) was added and extracted with Et<sub>2</sub>O (15 mL x 3). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/Et<sub>2</sub>O, 1:1) to yield the pure 4-methylaniline (0.0405 g, 63%). Starting material (1a) was recovered (0.0287 g, 32%).

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	yield (%)	$\pi^*$
DMSO	98	1
DMF	92	0.88
NMP	90	0.92
MeCN	21	0.66
MeOH	10	0.6
THF	-	0.55
toluene	12	0.49
BuOH	11	0.47

Table S1. The  $\pi^*$  scale<sup>15</sup> for each solvent

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**S8** 

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**S**9





**S10** 























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