Supporting Information for

The Aminomethylation of Electron-Rich Aromatics with a *N*-Silyl-*N,O*-Acetal Catalyzed by Metal Triflate-TMSCl System: Facile Synthesis of Aromatic Primary Amines, 1-Ary-Trichloroethylamines

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1-(1-Methylindol-3-yl)-2,2,2-trichloroethylamine·HCl (3b): Mp 155-156 °C (colorless solid from CH₂Cl₂-MeOH); ¹H NMR (500 MHz, *d*₆-DMSO) δ 3.88 (s, 3H), 5.95 (s, 1H), 7.18 (t, 1H, *J* = 8.5 Hz), 7.27 (t, 1H, *J* = 8.5 Hz), 7.54 (d, 1H, *J* = 8.5 Hz), 7.84 (s, 1H), 7.95 (d, 1H, *J* = 8.5 Hz), 9.37 (brs, 3H); ¹³C NMR (125 MHz, *d*₆-DMSO) δ 32.4, 61.2, 99.5, 104.4, 109.6, 118.8, 119.5, 121.5, 126.7, 129.9, 135.2 MS (FAB): *m/z* 159 (M⁺-CCl₃, 100%); HRMS (FAB): Calcd for Fragment C₁₀H₁₁N₂: 159.0922, Found: 159.0916 (M⁺-CCl₃).

1-(2-Methylindol-3-yl)-2,2,2-trichloroethylamine (3c): colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 2.51 (brs, 2H), 2.56 (s, 3H), 5.0 (s, 1H), 7.17 (m, 2H), 7.33 (d, 1H, *J* = 8.0 Hz), 7.98 (d, 1H, *J* = 8.0 Hz), 8.17 (brs, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 13.5, 67.3, 107.8, 107.9, 110.5, 119.8, 120.9, 121.0, 121.3, 135.1, 135.2; MS (FAB): *m/z* 262, 260 (M⁺⁺H-NH₂, 50%), 159 (M⁺-CCl₃, 100%); Anal. Calcd for C₁₁H₁₁Cl₃N·HCl: C, 42.07; H, 3.87; N, 8.92%, Found: C, 41.85; H, 4.27; N, 9.05%.

1-(2-Phenylindol-3-yl)-2,2,2-trichloroethylamine (3d): Mp 197-198 °C (pale yellow needles from CH₂Cl₂-hexane); ¹H NMR (500 MHz, CDCl₃) δ 2.49 (brs, 2H), 5.12 (s, 1H), 7.17 (m, 2H), 7.30 (d, 1H, *J* = 7.8 Hz), 7.44 (m, 5H), 8.06 (d, 1H, *J* = 7.8 Hz), 8.47 (brs, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 67.2, 107.4, 108.3, 111.1, 120.1, 122.2, 122.3, 126.1, 128.6, 128.9, 129.3, 133.1, 135.8, 139.1; MS (FAB): *m/z* 339 (M⁺⁺H, 20%) 221 (M⁺-CCl₃, 100%); Anal. Calcd for C₁₆H₁₃Cl₃N₂: C, 56.58; H, 3.86; N, 8.25%, Found: C, 56.31; H, 3.69; N, 8.40%.

1-(5-Methoxyindol-3-yl)-2,2,2-trichloroethylamine (3e): Mp (decomp.) 138.2 °C (colorless needles from CH₂Cl₂-hexane); ¹H NMR (500 MHz, *d*₆-DMSO) δ 2.70 (brs, 2H), 3.75 (s, 3H), 4.94 (s, 1H), 6.73 (dd, 1H, *J* = 8.7, 2.3 Hz), 7.23 (d, 1H, *J* = 2.3 Hz), 7.26 (d, 1H, *J* = 8.7 Hz), 7.51 (d, 1H, *J* = 2.3

Hz), 11.07 (brs, 1H); ^{13}C NMR (125 MHz, d_6 -DMSO) δ 55.3, 65.4, 101.3, 108.3, 111.2, 111.7, 112.0, 125.7, 127.4, 130.5, 153.3; MS (FAB): m/z 293 (M^++H , 20%) 175 (M^+-CCl_3 , 100%); Anal. Calcd for $\text{C}_{11}\text{H}_{11}\text{Cl}_3\text{N}_2\text{O}$: C, 45.00; H, 3.78; N, 9.54%, Found: C, 45.08; H, 3.93; N, 9.46%.

1-(5-Nitroindol-3-yl)-2,2,2-trichloroethylamine (3f): Mp (decomp.) 153.0 °C (yellow crystals from AcOEt-hexane); ^1H NMR (500 MHz, d_6 -DMSO) δ 2.83 (brs, 2H), 5.16 (s, 1H), 7.55 (d, 1H, $J = 8.5$ Hz), 7.83 (d, 1H, $J = 2.5$ Hz), 7.99 (dd, 1H, $J = 2.5, 8.5$ Hz), 8.82 (s, 1H), 12.0(s, 1H); ^{13}C NMR (125 MHz, d_6 -DMSO) δ 65.1, 107.5, 112.1, 114.9, 116.4, 117.2, 126.3, 129.3, 138.6, 140.8; MS (FAB): m/z 310, 308 (M^++H , 20%), 293, 291 ($\text{M}^++\text{H}-\text{NH}_2$, 30%), 190 (M^+-CCl_3 , 100%); Anal. Calcd for $\text{C}_{10}\text{H}_8\text{Cl}_3\text{N}_3\text{O}_2$: C, 38.93; H, 2.61; N, 13.62%, Found: C, 39.25; H, 2.58; N, 13.49%.

1-(5-Carbomethoxy-indol-3-yl)-2,2,2-trichloroethylamine (3g): Mp 169-170 °C (colorless crystals from AcOEt-hexane); ^1H NMR (300 MHz, d_6 -DMSO) δ 2.78 (brs, 2H), 3.84 (s, 3H), 5.04(s, 1H), 7.46 (d, 1H, $J = 8.5$ Hz), 7.69 (s, 1H), 7.72 (d, 1H, $J = 8.5$ Hz), 8.46 (s, 1H), 11.07 (brs, 1H); ^{13}C NMR (75 MHz, d_6 -DMSO) δ 51.7, 65.3, 107.7, 110.5, 113.6, 120.6, 122.0, 122.2, 126.5, 127.2, 138.0, 167.2; MS (FAB): m/z 323, 321 (M^++H , 10%) 203 (M^+-CCl_3 , 100%); Anal. Calcd for $\text{C}_{12}\text{H}_{11}\text{Cl}_3\text{N}_2\text{O}_2$: C, 44.82; H, 3.45; N, 8.71%, Found: C, 45.10; H, 3.53; N, 8.54%.

1-(4-Hydroxy-indol-3-yl)-2,2,2-trichloroethylamine (3h): pale brown oil; ^1H NMR (300 MHz, CDCl_3) δ 5.03 (s, 1H), 6.65 (d, 1H, $J = 8$ Hz), 6.88 (d, 1H, $J = 8$ Hz), 6.92 (dd, 1H, $J = 8, 8$ Hz), 7.27 (s, 1H), 8.29 (brs, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 66.2, 102.4, 103.5, 106.4, 109.3, 115.8, 124.3, 124.4, 138.1, 150.5; MS (FAB): m/z 278 (M^++H , 20%), 161 (M^+-CCl_3 , 100%); HRMS (FAB): Calcd for $\text{C}_{10}\text{H}_{10}\text{Cl}_3\text{N}_2\text{O}$: 278.9859, Found: 278.9848 (M^++H).

1-(1-Methylpyrrol-2-yl)-2,2,2-trichloroethylamine (5b): colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 2.03 (brs, 2H), 3.70 (s, 3H), 4.64 (s, 1H), 6.11 (t, 1H, $J = 2.5$ Hz), 6.37 (d, 1H, $J = 2.5$ Hz), 6.60 (d, 1H, $J = 2.5$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 34.5, 64.7, 105.9, 107.1, 107.8, 123.0, 128.3; MS(EI): m/z 227 (M^+ , 10%) 112 ($\text{M}^+ - \text{CCl}_3$, 100%); HRMS (FAB): Calcd for $\text{C}_7\text{H}_{10}\text{Cl}_3\text{N}_2$: 226.9909, Found: 226.9915 ($\text{M}^+ + \text{H}$).

1-(1-Phenylpyrrol-2-yl)-2,2,2-trichloroethylamine (5c): colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 2.2 (brs, 2H), 4.56 (s, 1H), 6.28 (t, 1H, $J = 3$ Hz), 6.62 (d, 1H, $J = 3$ Hz), 6.82 (d, 1H, $J = 3$ Hz), 7.37-7.42 (m, 3H), 7.45-7.49 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 64.5, 105.9, 108.2, 108.5, 123.3, 126.8, 127.9, 129.2, 129.3, 139.5; MS (FAB): m/z 293, 291 ($\text{M}^+ + \text{H}$, 12%) 171 ($\text{M}^+ - \text{CCl}_3$, 100%); Anal. Calcd for $\text{C}_{12}\text{H}_{11}\text{Cl}_3\text{N}_2 \cdot \text{HCl}$: C, 44.21; H, 3.71; N, 8.59%, Found: C, 43.92; H, 4.07; N, 8.71%.

1-(1-Carbomethoxy-pyrrol-2-yl)-2,2,2-trichloroethylamine (5d): colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 2.16 (brs, 2H), 3.93 (s, 3H), 5.98 (s, 1H), 6.18 (t, 1H, $J = 3.9$ Hz), 6.56 (dd, 1H, $J = 3.9, 2.1$ Hz), 7.29 (dd, 1H, $J = 3.9, 2.1$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 54.1, 63.2, 105.5, 110.7, 113.7, 122.4, 131.7, 151.3; MS (EI): m/z 272 (M^+ , 10%) 153 ($\text{M}^+ - \text{CCl}_3$, 100%); Anal. Calcd for $\text{C}_8\text{H}_9\text{Cl}_3\text{N}_2\text{O}_2 \cdot \text{HCl}$: C, 31.20; H, 3.27; N, 9.10%, Found: C, 31.57; H, 3.27; N, 9.10%.

1-(Fur-2-yl)-2,2,2-trichloroethylamine (5e): colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 2.26 (brs, 2H), 4.65 (s, 1H), 6.37 (t, 1H, $J = 3.5$ Hz), 6.47 (dd, 1H, $J = 3.5, 1.5$ Hz), 7.41 (dd, 1H, $J = 3.5, 1.5$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 66.87, 104.4, 110.1, 110.4, 142.5, 149.4; MS (EI): m/z 216 214 (M^+ , 100%) 179 ($\text{M}^+ - \text{Cl}$, 10%) 115 ($\text{M}^+ - \text{Cl}_2$, 60%) 96 ($\text{M}^+ - \text{CCl}_3$, 100%); HRMS (EI): Calcd for

fragment C₅H₆NO: 96.0449, Found: 96.0449 (M⁺-CCl₃).

1-(2-Methylfur-5-yl)-2,2,2-trichloroethylamine (5f): pale yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 2.15 (brs, 2H), 2.28 (s, 3H), 4.58 (s, 1H), 5.95 (d, 1H, *J* = 3.0 Hz), 6.33 (d, 1H, *J* = 3.0 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 13.5, 66.9, 104.6, 106.4, 110.9, 147.4, 152.3; MS (EI): *m/z* 228, 230 (M⁺, 10%), 110 (M⁺-CCl₃, 100%); HRMS (EI): Calcd for C₇H₈Cl₃NO: 226.9671, Found: 226.9678.

1-(2-Methylthien-5-yl)-2,2,2-trichloroethylamine (5g): colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 2.22 (brs, 2H), 2.46 (s, 3H), 4.79 (s, 1H), 6.64 (d, 1H, *J* = 3.5 Hz), 7.0 (d, 1H, *J* = 3.5 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 15.3, 68.8, 105.2, 124.4, 128.4, 136.5, 140.7; MS (EI): *m/z* 227, 225 (M⁺, 10%), 126 (M⁺-CCl₃, 100%); Anal. Calcd for C₇H₈Cl₃NS•HCl: C, 29.92; H, 3.23; N, 4.98%; S, 11.41%, Found: C, 30.19; H, 2.93; N, 5.09%; S, 11.13%.

1-(1-Furfuryl-pyrrol-2-yl)-2,2,2-trichloroethylamine (5h): colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 2.18 (brs, 2H), 4.78 (s, 1H), 5.15 (d, 1H, *J* = 16.5 Hz), 5.22 (d, 1H, *J* = 16.5 Hz), 6.15 (t, 1H, *J* = 3.5 Hz), 6.2 (d, 1H, *J* = 3.5 Hz), 6.31 (dd, 1H, *J* = 3.5, 2.0 Hz), 6.44 (dd, 1H, *J* = 3.5, 2.0 Hz), 6.69 (t, 1H, *J* = 3.5, 2.0 Hz), 7.36 (d, 1H, *J* = 2.0 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 44.2, 64.6, 105.6, 107.7, 108.0, 108.6, 110.5, 122.3, 128.2, 142.6, 150.4; MS (FAB): *m/z* 293 (M⁺+H, 13%), 176 (M⁺-CCl₃, 100%); HRMS (EI): Calcd for C₁₁H₁₁Cl₃N₂O: 291.9937, Found: 291.9929.

1-(2-Hydroxynaphthyl)-2,2,2-trichloroethylamine (5i): Mp 112.8-113.5 °C (colorless crystals from CH₂Cl₂-hexane); ¹H NMR (500 MHz, CDCl₃) δ 2.28 (brs, 2H), 5.83 (s, 1H), 7.10 (dd, 1H, *J* = 8.7, 1.3 Hz), 7.30 (t, 1H, *J* = 8.7 Hz), 7.46 (t, 1H, *J* = 8.7 Hz), 7.73 (dd, 1H, *J* = 8.7, 1.3 Hz), 7.76 (d, 1H, *J* = 8.7 Hz), 7.99 (d, 1H, *J* = 8.7 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 66.3, 103.1, 109.0, 120.5, 122.8,

126.4, 126.5, 128.5, 128.8. 132.1, 133.8, 158.1; MS (FAB): m/z 292 ($M^+ + H$, 10%) 172 ($M^+ - CCl_3$, 100%); Anal. Calcd for $C_{12}H_{10}Cl_3NO$: C, 49.60; H, 3.47; N, 4.82%, Found: C, 49.69; H, 3.27; N, 4.69%.

1-(2,4-Dimethoxyphenyl)-2,2,2-trichloroethylamine (5j): colorless oil; 1H NMR (500 MHz, $CDCl_3$) δ 2.30 (brs, 2H), 3.79 (s, 3H), 3.81 (s, 3H), 5.15 (s, 1H), 6.44 (d, 1H, $J = 2.5$ Hz), 6.49 (dd, 1H, $J = 2.5$, 8.5 Hz), 7.43 (d, 1H, $J = 8.5$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.3, 55.5, 63.6, 98.4, 104.3, 106.5, 118.1, 126.9, 158.5. 161.0; MS (FAB): m/z 286 ($M^+ + H$, 10%) 269 ($M^+ - NH_2$, 70%), 166 ($M^+ - CCl_3$, 100%); HRMS (FAB): Calcd for $C_{10}H_{13}Cl_3NO$: 284.0012, Found: 284.0010 ($M^+ + H$).

Single Pulse Experiment

Single Pulse with Broadband Decoupling

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Single Pulse Experiment

Single Pulse with Broadband Decoupling

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Single Pulse Experiment

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