Supplementary Material (ESI) for Chemical Communications

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First Transamination Reactions for the One-Pot Synthesis of Substituted Zwitterionic Quinones

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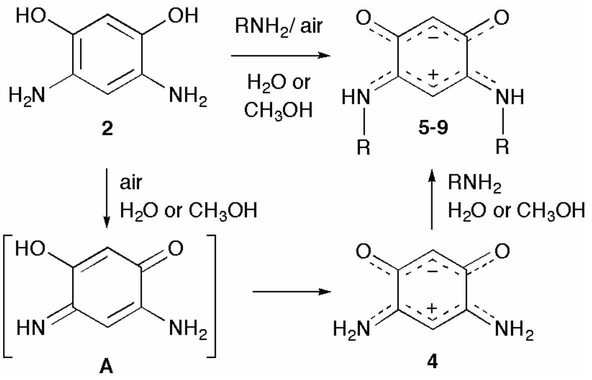
General.

All solvents were dried and distilled using common techniques unless otherwise stated. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker AC–300 instrument. MALDI-TOF mass spectra were recorded on a Biflex III Bruker mass spectrometer and the EI mass spectrum was recorded on a Finnigan TSQ 700. Elemental analyses were performed by the « Service de Microanalyse, Université Louis Pasteur (Strasbourg, France) ».

Synthesis.

Typically, diaminoresorcinol dihydrochloride (0.500 g, 2.35 mmol) was dissolved in water (*ca*. 10 ml) and then excess of amine was added to the solution according to Scheme 1.



Scheme 1. One-pot synthesis of the zwitterions. **5** R = CH_2CH_2OH; **6** R = CH_3; **7** R = $CH(CH_3)CH_2CH_3$; **8** R = $(CH_2)_3CH_3$; **9** R = $CH_2CH_2N(CH_3)_2$.

For the compounds **6-8** which are not or poorly soluble in water, purple crystals appear quickly. 30-120 minutes later, the crystals were isolated by filtration and washed with cold water, dried in air to afford purple crystals. In the case of **5** and **9**, details are given below.

4: Mass spectrum (EI): *m/z*: 138.1 $[M+1]^+$; ^{1}H NMR (300 MHz, dmso-d_6): δ = 4.91 (s, N⎓C⎓C-H), 5.62 (s, O⎓C⎓C-H), 8.41 (s, NH), 9.18 (s, NH). Anal. Calcd. for $C_6H_6N_2O_2\cdot0.5H_2O$: C, 49.98; H, 4.80; N, 19.04. Found: C, 49.77; H, 4.73; N, 19.17.

5: At the end of the reaction, ethanol was added to precipitate the product. After filtration and washing with ethanol, a purple crystalline solid was obtained. Yield: 75%. Mass spectrum (MALDI-TOF$^+$): *m/z*: 227.1 $[M+1]^+$; ^{1}H NMR (300 MHz, D_2O): AA'BB' spin system δ= 3.57 (t, ^3J = 5.2 Hz, 4 H, NCH_2) and 3.78 (t, ^3J = 5.2 Hz, 4H, OCH_2), 5.28 (s, 1 H, N⎓C⎓CH), 5.55 (s, 1 H, O⎓C⎓CH), in dmso-d_6, the OH and NH resonances appear at δ= 4.98 (t) and 8.88 (br s), respectively; ^{13}C NMR (75 MHz, dmso-d_6) δ= 45.74 (s, CH_2N), 59.19 (s, CH_2O), 82.45 (s, N⎓C⎓*C*), 97.79 (s, O⎓C⎓*C*), 156.99 (s, C⎓N), 172.51 (s, C⎓O); Anal. Calcd. for $C_{10}H_{14}N_2O_4$: C, 53.09; H, 6.24; N, 12.38. Found: C, 52.95; H, 6.32; N, 12.43.

6: Yield: 72%. Mass spectrum (MALDI-TOF$^+$): *m/z*: 167.1 $[M+1]^+$; ^{1}H NMR (300 MHz, dmso-d_6): $\delta = 3.01$ (s, 6H, CH_3), 4.95 (s, 1H, N⎓C⎓CH), 5.34 (s, 1H, O⎓C⎓CH), 9.10 (br s, 2H, NH); ^{13}C NMR (75 MHz, dmso-d_6) $\delta = 30.18$ (s, CH_3), 81.80 (s, N⎓C⎓*C*), 97.97 (s, O⎓C⎓*C*), 157.37 (s, C⎓N), 172.67 (s, C⎓O). Anal. Calcd. for $C_8H_{10}N_2O_2\cdot H_2O$: C, 52.17; H, 6.57; N, 15.21. Found: C, 52.11; H, 6.26; N, 15.11.

7: Yield: 85%. Mass spectrum (MALDI-TOF$^+$): *m/z*: 251.2 $[M+1]^+$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.98$ (t, $^3J = 7.5$ Hz, 6H, $CH_2C\mathit{H_3}$), 1.31 (d, $^3J = 6.5$ Hz, 6H, $CHC\mathit{H_3}$), 1.69 (pent, $^3J = 7.2$ Hz, 4H, CH_2), 3.62 (m, 2H, N-CH), 5.14 (s, 1H, N⎓C⎓CH), 5.47 (s, 1H, O⎓C⎓CH), 8.11 (br s, 2H, NH); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 10.43$ (s, $CH_2\mathit{C}H_3$), 19.58 (s, $CH\mathit{C}H_3$), 29.20 (s, CH_2), 50.91 (s, NCH), 80.56 (s, N⎓C⎓*C*), 98.85 (s, O⎓C⎓*C*), 155.82 (s, N⎓C), 172.21 (s, O⎓C). Anal. Calcd. for $C_{14}H_{22}N_2O_2$: C, 67.17; H, 8.86; N, 11.19. Found: C, 66.83; H, 8.87; N, 11.32.

8: Yield: 93%. Mass spectrum (MALDI-TOF$^+$): *m/z*: 251.2 $[M+1]^+$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.98$ (t, $^3J = 7.3$ Hz, 6H, CH_3), 1.46 (sext, $^3J = 7.4$ Hz, 4H, $C\mathit{H_2}CH_3$), 1.73 (pent, $^3J = 7.4$ Hz, 4H, $NCH_2C\mathit{H_2}$), 3.37 (q owing to overlap dt, $^3J = 6.9$ Hz, 4H, NCH_2), 5.14 (s, 1H, N⎓C⎓CH), 5.47 (s, 1H, O⎓C⎓CH), 8.22 (br s, 2H, NH); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 13.62$ (s, CH_3), 20.13 (s, $\mathit{C}H_2CH_3$), 30.28 (s, $NCH_2\mathit{C}H_2$), 43.03 (s, NCH_2), 80.53 (s, N⎓C⎓*C*), 98.81 (s, O⎓C⎓*C*), 156.70 (s, N⎓C), 172.34 (s, O⎓C); Anal. Calcd. for $C_{14}H_{22}N_2O_2$: C, 67.17; H, 8.86; N, 11.19. Found: C, 66.87; H, 8.83; N, 10.96.

9: After the reaction mixture was stirred for 2 h in MeOH, 2 equiv NaOH was added to the solution and stirred for 0.5 h. After concentration, diethylether was added to the solution and the precipitate was filtered. The product was dissolved in dichloromethane and filtered through Celite. After evaporation of the solvent and precipitation from a mixture of dichloromethane and pentane, the pale orange brown product was obtained. Yield: 61%. Mass spectrum (MALDI-TOF$^+$): *m/z*: 281.2 $[M+1]^+$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.28$ (s, 12H, CH_3), 2.26 (t, $^3J = 6.3$ Hz, 4H, NCH_2), 3.38 (t, 4H, $^3J = 6.3$ Hz, $NHC\mathit{H_2}$), 5.11 (s, 1H, N⎓C⎓CH), 5.45 (s, 1H, O⎓C⎓CH), 8.55 (br s, 2H, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ

= 40.57 (s, CH_3), 45.14 (s, NCH_2), 56.21 (s, $NHCH_2$), 81.29 (s, N⎓C⎓*C*), 99.04 (s, O⎓C⎓*C*), 156.69 (s, N⎓C), 172.39 (s, O⎓C); Anal. Calcd. for $C_{14}H_{24}N_4O_2 \cdot 0.5H_2O$: C, 58.11; H, 8.71; N,19.36. Found: C, 58.62; H, 8.57; N,19.92.

10: Ligand **9** was dissolved in anhydrous dichloromethane and 0.5 equiv $Zn(acac)_2$ was added to the solution. After the solution was stirred at room temperature for 3 h, the solvent was evaporated and complex was obtained as red crystalline by precipitation from a mixture of dichloromethane and pentane. The single crystal for X-ray analysis was obtained by slow diffusion of pentane into the THF solution. Yield: 93%. Mass spectrum (MALDI-TOF$^+$): *m/z*: 623.3 $[M+1]^+$, 281.2 [ligand **9**+1]$^+$; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.14 (s, 12H, uncoordinated NMe_2), 2.24 (s, 12H, coordinated NMe_2), 2.56 (t, 4H, ^3J = 6.3 Hz uncoordinated NCH_2), 2.64 (br s, 4H, coordinated NCH_2), 3.20 (q owing to overlap dt further confirming by the H-COSY experiment, ^3J = 6.1 Hz, 4H, $NHCH_2$), 3.43 (t, 4H, ^3J = 5.7 Hz, $C{=}NCH_2$), 5.04 (s, 2H, N=CCH), 5.50 (s, 2H, O=CCH), 7.03 (t, ^3J = 4.8 Hz, 2H, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 40.11 (s, uncoordinated NMe_2), 43.88 (s, coordinated NMe_2), 45.29 (s, uncoordinated NCH_2), 45.93 (s, coordinated NCH_2), 56.71 (s, uncoordinated $NHCH_2$), 58.50 (s, $NHCH_2$), 83.07 (s, NHC=*C*H), 100.72 (s, O=C*C*H), 149.84 (s, NHC), 160.96 (s, COZn), 173.81 (s, C=NZn), 178.84 (s, C=O); Anal. Calcd. for $C_{28}H_{46}N_8O_4Zn$: C, 53.89; H, 7.43; N, 17.95. Found: C, 53.15; H, 7.32; N, 17.45.