Supporting Information

Nuclear amination catalyzed by fungal laccases:

Reaction products of p-hydroquinones and primary aromatic amines

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Additional Information to Experimental Section

General Methods. Melting points were determined using a micro-melting apparatus according to Boetius and are corrected. LC/MS investigation was done using electro spray ionization under atmospheric conditions (API-ES) or chemical ionization using *iso*-butane, GC/MS using electron impact ionization (70 eV). HRMS was performed by FT-ICR mass spectrometry. IR spectra were recorded in KBr, UV spectra in MeOH. NMR spectra of **3a-o** and **4a-d** were obtained at 400.13 MHz (^1H -) and 100.11 MHz (^{13}C -NMR and DEPT-135), ^1H -, ^{13}C -NMR and DEPT-135 spectra of **5** and HMBC-spectra at 600.13 MHz and 150.1 MHz resp. at ambient temperature. Solvents used were DMSO- d_6 (**3a-k** and **m-o** and **4a-d**), MeOH- d_4 (**3l**) and THF- d_8 (**5**). Spectra were referenced indirectly to tetramethylsilane via the residual ^1H signal of the deuterated solvents (DMSO- d_6 , MeOH- d_4) or directly to TMS (THF- d_8).

For reaction monitoring, samples of the reaction mixture were analyzed using an HPLC system with diode array detector. An endcapped RP₁₈ column was used at a flow rate of 1.5 mL·min⁻¹. A solvent system consisting of methanol (eluent A) and 0.1% (m/m) phosphoric acid (eluent B), starting from an initial ratio of 10% A and 90% B and reaching 100% A within 10.5 min, was used. Samples were taken every 15 min. For the depiction of the reaction course, the mean of three experiments were calculated.

Chemicals were purchased from commercial suppliers. All chemicals were used as received. 2,5-Dihydroxybenzamide was synthesized by one of us (see below).

Structural Data of All Compounds

2,5-Dihydroxybenzamide (1b). Synthesis: A solution of 5.0 g of 2,5-dihydroxybenzoic acid methyl ester in 25 ml of aqueous ammonia (25%) was stirred at 20 °C for 6 hours. The black reaction mixture was filtered to give a gray residue which was recrystallized from methanol to give 2,5-dihydroxybenzamide as dark-brown crystals. Yield 75% (3.75 g): mp 216-217 °C (lit: 216-217 °C).³⁹ ¹H NMR: δ 12.13 (s, 1H), 8.96 (s, 1H), 8.23 (bs, 1H), 7.74 (bs, 1H), 7.21 (d, J = 2.9, 1H), 6.87 (dd, J = 2.9, 8.8, 1H), 6.70 (d, J = 8.8, 1H). ¹³C NMR: δ 171.5, 153.4, 148.9, 121.7, 117.7, 114.7, 113.5. UV-Vis (MeOH) λ_{max} (log ϵ) 210 (4.34), 330 (3.62) nm. GC/MS m/z (relative intensity): 153 (M^+ , 48), 136 (100), 108 (20), 80 (14), 52 (8).

3a**2-[4'-(Carboxyphenyl)amino]-3-(2''-hydroxyethylcarbamoyl)-1,4-benzoquinone**

2-[4'-(Carboxyphenyl)amino]-3-(2''-hydroxyethylcarbamoyl)-1,4-benzoquinone (3a). Synthesis and isolation described above. Dark red to purple solid. Yield 70 % (46.2 mg): mp 184-186 °C. ^1H NMR: δ 12.79 (bs, 1H), 12.42 (bs, 1H), 9.14 (t, $J = 5.3$, 1H), 7.84 (d, $J = 8.5$, 2H), 7.30 (d, $J = 7.9$, 2H), 6.81 (d, $J = 9.5$, 1H), 6.76 (d, $J = 9.5$, 1H), 4.77 (bs), 3.41 (t, $J = 5.6$, 2H), 3.17 (q, $J = 5.7$, 2H). ^{13}C NMR: δ 184.2 (C-4), 182.9 (C-1), 166.7 (C-7'), 166.3 (C-7), 148.6 (C-2), 143.4 (C-1'), 138.9 (C-6), 133.8 (C-5), 129.7 (C-3', C-5'), 127.2 (C-4'), 123.3 (C-2', C-6'), 105.5 (C-3), 59.3 (C-2''), 41.2 (C-1''). HMBC correlations see table 3. IR (KBr): ν 3436, 2941, 1691, 1644, 1563, 1542 cm^{-1} . UV-Vis (MeOH) λ_{max} (log ϵ) 201 (4.46), 261 (4.24), 501 (3.63) nm. LC/MS m/z (relative intensity): 331 ($[\text{M}+1]^+$, 63), 270 (100) APCI, pos. mode; 330 ($[\text{M}]^-$, 100) APCI, neg. mode; 353 ($[\text{M}+\text{Na}]^+$, 100), 683 ($[2\text{M}+\text{Na}]^+$, 19) API-ES, pos. mode; 329 ($[\text{M}-1]^-$, 100) API-ES, neg. mode. HRFT-ICRMS $[\text{M} + \text{H}]^+$: calcd for $\text{C}_{16}\text{H}_{15}\text{N}_2\text{O}_6$: 331.0930; found: 331.0921.

Selected correlations in the HMBC spectrum:

3b**2-[4'-Acetanilido]-3-(2''-hydroxyethylcarbamoyl)-1,4-benzoquinone**

2-[4'-Acetanilido]-3-(2''-hydroxyethylcarbamoyl)-1,4-benzoquinone (3b). Synthesis and isolation described above. Black solid. Yield 65 % (43.1 mg): mp 87-89 °C. ^1H NMR: δ 12.46 (bs, 1H), 9.16 (t, J = 5.4, 1H), 7.88 (d, J = 8.6, 2H), 7.33 (d, J = 8.6, 2H), 6.82 (d, J = 10.1, 1H), 6.76 (d, J = 10.1, 1H), 4.77 (bt, J = 4.9, 1H), 3.42 (m, 2H), 3.18 (q, J = 5.7, 2H), 2.56 (s, 3H). ^{13}C NMR: δ 196.7, 184.2, 182.8, 166.3, 148.6, 143.7, 138.9, 133.8, 133.3, 128.8, 123.2, 105.7, 59.3, 41.2, 26.6. IR (KBr): ν 3276, 2938, 1677, 1644, 1563 cm^{-1} . UV-Vis (MeOH) λ_{max} (log ϵ) 271 (4.31), 293 (4.33), 496 (3.78) nm. LC/MS m/z (relative intensity): 329 ($[\text{M}+1]^+$, 100), 268 (36) APCI, pos. mode; 328 ($[\text{M}]^-$, 100) APCI, neg. mode. HRFT-ICRMS $[\text{M} + \text{H}]^+$: calcd for $\text{C}_{17}\text{H}_{17}\text{N}_2\text{O}_5$: 329.1137; found: 329.1132.

3c**2-[4'-(2''-Hydroxyethyl)phenylamino]-3-(2'''-hydroxyethylcarbamoyl)-1,4-benzoquinone** **2-[4'-(2''-Hydroxyethyl)phenylamino]-3-(2'''-hydroxyethylcarbamoyl)-1,4-benzoquinone (3c).**

Synthesis and isolation described above. Brown-red solid. Yield 69 % (45.7 mg): mp 138-140 °C. ^1H NMR: δ 12.92 (bs, 1H), 9.38 (t, $J = 5.1$, 1H), 7.16 (d, $J = 8.5$, 2H), 7.12 (d, $J = 8.5$, 2H), 6.73 (bs, 2H), 4.77 (bt, $J = 5.2$, 1H), 4.66 (bt, $J = 4.7$, 1H), 3.60 (m, 2H), 3.44 (dt, $J = 4.4, 5.6$, 2H), 3.23 (q, $J = 5.6$, 2H), 2.71 (t, $J = 7.0$, 2H). ^{13}C NMR: δ 183.6, 182.8, 167.3, 150.3, 139.3, 137.2, 137.0, 133.5, 129.1, 123.7, 102.9, 61.9, 59.4, 41.1, 38.4. IR (KBr): ν 3428, 3268, 2941, 2876, 1686, 1641, 1612, 1565, 1539 cm^{-1} . UV-Vis (MeOH) λ_{max} (log ϵ) 240 (4.40), 266 (4.31), 504 (3.76) nm. LC/MS m/z (relative intensity): 353 ($[\text{M}+\text{Na}]^+$, 100) API-ES, pos. mode; 330 ($[\text{M}]^-$, 100) APCI, neg. mode. HRFT-ICRMS $[\text{M} + \text{H}]^+$: calcd for $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_5$: 331.1294; found: 331.1292.

3d**2-Carboxamido-3-[4'-(carboxyphenyl)amino]-1,4-benzoquinone**

2-Carboxamido-3-[4'-(carboxyphenyl)amino]-1,4-benzoquinone (3d). Synthesis and isolation described above. Black solid. Yield 71 % (40.8 mg): mp 208-211 °C. ^1H NMR: δ 13.1 (s, 1H), 12.97 (bs, 1H), 8.72 (d, $J = 3.0$, 1H), 7.97 (d, $J = 8.5$, 2H), 7.88 (d, $J = 3.0$, 1H), 7.45 (d, $J = 8.6$, 2H), 6.92 (d, $J = 10.2$, 1H), 6.87 (d, $J = 10.1$, 1H). ^{13}C NMR: δ 184.1, 182.7, 169.0, 166.7, 150.1, 143.5, 139.0, 133.9, 129.8, 127.3, 123.5, 104.5. IR (KBr): ν 3440, 3307, 3069, 1710, 1691, 1643, 1560 cm^{-1} . UV-Vis (MeOH) λ_{max} (log ϵ) 274 (4.36), 486 (3.76) nm. LC/MS m/z (relative intensity): 285 ($[\text{M}-1]^-$, 100) API-ES, neg. mode. HRFT-ICRMS $[\text{M} + \text{H}]^+$: calcd for $\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_5$: 287.0668; found: 287.0664.

3e**2-[4'-(Carboxymethylphenyl)amino]-3-(methylcarboxy)-1,4-benzoquinone**

2-[4'-(Carboxymethylphenyl)amino]-3-(methylcarboxy)-1,4-benzoquinone (3e). Synthesis and isolation described above. Dark red solid. Yield 79 % (49.9 mg): mp 155-157 °C. ^1H NMR: δ 12.31 (bs, 1H), 9.41 (bs, 1H), 7.21 (d, $J = 8.3$, 2H), 7.03 (d, $J = 8.3$, 2H), 6.87 (d, $J = 10.1$, 1H), 6.73 (d, $J = 10.1$, 1H), 3.56 (s, 2H), 2.96 (s, 3H). ^{13}C NMR: δ 183.4, 182.4, 172.5, 164.1, 142.6, 138.9, 136.3, 132.9, 132.8, 129.5, 124.2, 105.8, 50.8, 40.0. IR (KBr): ν 3251, 2952, 1711, 1682, 1631, 1570, 1519, 1494 cm^{-1} . UV-Vis (MeOH) λ_{max} (log ϵ) 210 (4.33), 245 (4.24), 489 (3.61) nm. LC/MS m/z (relative intensity): 315 ($[\text{M}]^-$, 100) APCI, neg. mode. HRFT-ICRMS $[\text{M} + \text{H}]^+$: calcd for $\text{C}_{16}\text{H}_{14}\text{NO}_6$: 316.0821; found: 316.0818.

3f**2-[4'-(Carboxymethyl-carbamoylphenyl)amino]-3-ethylcarboxy-1,4-benzoquinone** **2-[4'-(Carboxymethyl-carbamoylphenyl)amino]-3-ethylcarboxy-1,4-benzoquinone (3f).**

Synthesis and isolation described above. Red solid. Yield 70 % (52.0 mg): mp 111-112 °C. ^1H NMR: δ 9.56 (bs, 1H), 8.75 (t, $J = 3.9$, 1H), 7.82 (d, $J = 8.2$, 2H), 7.20 (d, $J = 7.9$, 2H), 6.91 (d, $J = 10.0$, 1H), 6.77 (d, $J = 10.0$, 1H), 3.90 (d, $J = 4.6$, 2H), 3.34 (q, $J = 7.1$, 2H), 0.94 (t, $J = 7.1$, 3H). ^{13}C NMR: δ 183.4, 182.7, 171.3, 165.4, 163.6, 142.1, 141.1, 138.7, 135.2, 133.1, 127.6, 123.2, 107.2, 60.1, 41.3, 13.5. IR (KBr): ν 3380, 3258, 2986, 1716, 1572, 1512 cm^{-1} . UV-Vis (MeOH) λ_{max} (log ϵ) 260 (4.14), 482 (3.54) nm. LC/MS m/z (relative intensity): 371 ($[\text{M}-1]^-$, 100) API-ES, neg. mode. HRFT-ICRMS $[\text{M} + \text{H}]^+$: calcd for $\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}_7$: 373.1036; found: 373.1033.

3g**2-Ethylcarboxy-3-[4'-(*iso*-propylphenyl)amino]-1,4-benzoquinone**

2-Ethylcarboxy-3-[4'-(*iso*-propylphenyl)amino]-1,4-benzoquinone (3g). Synthesis and isolation described above. Red solid. Yield 59 % (37.1 mg): mp 76-78 °C. ^1H NMR: δ 9.32 (s, 1H), 7.20 (d, J = 8.4, 2H), 7.03 (d, J = 8.3, 2H), 6.87 (d, J = 10.1, 1H), 6.73 (d, J = 10.1, 1H), 3.27 (q, J = 7.2, 2H), 2.87 (sept, J = 6.9, 1H), 1.18 (d, J = 6.9, 6H), 0.88 (t, J = 7.2, 3H). ^{13}C NMR: δ 183.5, 182.4, 163.8, 146.3, 142.2, 138.9, 135.2, 132.8, 126.2, 124.5, 105.9, 60.0, 33.0, 23.7, 13.4. IR (KBr): ν 3437, 2961, 1721, 1679, 1633, 1578, 1520 cm^{-1} . UV-Vis (MeOH) λ_{max} (log ϵ) 210 (4.28), 243 (4.21), 494 (3.57) nm. LC/MS m/z (relative intensity): 314 ($[\text{M}+1]^+$, 100), 271 (25), 268 (65), 226 (58) APCI, pos. mode; 313 ($[\text{M}]^-$, 100) APCI, neg. mode. HRFT-ICRMS $[\text{M} + \text{H}]^+$: calcd for $\text{C}_{18}\text{H}_{20}\text{NO}_4$: 314.1329; found: 314.1390.

3h**2-Acetyl-3-[4'-(carboxyphenyl)amino]-1,4-benzoquinone**

2-Acetyl-3-[4'-(carboxyphenyl)amino]-1,4-benzoquinone (3h). Synthesis and isolation described above. Dark red solid. Yield 40 % (22.8 mg): mp 183-185 °C. ^1H NMR: δ 12.82 (bs, 1H), 10.90 (s, 1H), 7.87 (d, J = 8.5, 2H), 7.25 (d, J = 8.5, 2H), 6.88 (d, J = 10.1, 1H), 6.77 (d, J = 10.1, 1H), 2.27 (s, 3H). ^{13}C NMR: δ 200.1, 184.3, 183.5, 166.6, 145.0, 143.5, 139.0, 133.5, 129.9, 127.3, 123.2, 113.0, 31.8. IR (KBr): ν 3008, 2985, 2679, 1774, 1641, 1614, 1584, 1565 cm^{-1} . UV-Vis (MeOH) λ_{max} (log ϵ) 285 (4.27), 468 (3.65) nm. LC/MS m/z (relative intensity): 286 ($[\text{M}+1]^+$ (100)) APCI pos. mode; 308 ($[\text{M}+\text{Na}]^+$, 100) API-ES, pos. mode; 284 ($[\text{M}-1]^-$, 100) API-ES, neg. mode. HRFT-ICRMS $[\text{M} + \text{H}]^+$: calcd for $\text{C}_{15}\text{H}_{12}\text{NO}_5$: 286.0715; found: 286.0717.

3i**2-(4'-Acetanilido)-6-*tert*-butyl-1,4-benzoquinone**

2-(4'-Acetanilido)-6-*tert*-butyl-1,4-benzoquinone (3i). Synthesis and isolation described above. Red solid. Yield 62 % (37.1 mg): mp 57-59 °C. ^1H NMR: δ 9.19 (s, 1H), 7.97 (d, $J = 8.5$, 2H), 7.48 (d, $J = 8.5$, 2H), 6.45 (d, $J = 1.9$, 1H), 6.11 (d, $J = 1.9$, 1H), 2.55 (s, 3H), 1.28 (s, 9H). ^{13}C NMR: δ 196.4, 186.2, 183.0, 151.4, 144.0, 143.0, 133.1, 132.2, 129.5, 121.5, 101.0, 34.5, 28.7, 26.5. IR (KBr): ν 3292, 3262, 2962, 1725, 1675, 1635, 1579, 1522 cm^{-1} . UV-Vis (MeOH) λ_{max} (log ϵ) 217 (4.22), 302 (4.19), 485 (3.59) nm. LC/MS m/z (relative intensity): 298 ($[\text{M}+1]^+$, 100) APCI, pos. mode; 297 ($[\text{M}]^-$, 100) APCI, neg. mode. GC/MS m/z (relative intensity): 297 (M^+ , 100), 282 (68), 254 (59). HRFT-ICRMS $[\text{M} + \text{H}]^+$: calcd for $\text{C}_{18}\text{H}_{20}\text{NO}_3$: 298.1443; found: 298.1441.

3j**2-[4'-(Methylcarboxyphenyl)amino]-6-*tert*-butyl-1,4-benzoquinone**

2-[4'-(Methylcarboxyphenyl)amino]-6-*tert*-butyl-1,4-benzoquinone (3j). Synthesis and isolation described above. Red solid. Yield 61 % (38.2 mg): mp 127-128 °C. ^1H NMR: δ 9.17 (bs, 1H), 7.95 (d, J = 8.7, 2H), 7.49 (d, J = 8.7, 2H), 6.44 (d, J = 2.2, 1H), 6.11 (d, J = 2.2, 1H), 3.83 (s, 3H), 1.27 (s, 9H). ^{13}C NMR: δ 186.2, 183.0, 165.6, 151.5, 144.0, 143.2, 133.1, 130.4, 124.6, 121.6, 101.1, 51.9, 34.5, 28.8. IR (KBr): ν 3428, 2959, 1710, 1671, 1637, 1585, 1527 cm^{-1} . UV-Vis (MeOH) λ_{max} (log ϵ) 213 (4.30), 285 (4.31), 487 (3.65) nm. LC/MS m/z (relative intensity): 314 ($[\text{M}+1]^+$, 100) APCI, pos. mode; 313 ($[\text{M}]^-$, 100) APCI, neg. mode. GC/MS m/z (relative intensity): 313 (M^+ , 90), 289 (4), 270 (100), 211 (16), 144 (14). HRFT-ICRMS $[\text{M} + \text{H}]^+$: calcd for $\text{C}_{18}\text{H}_{20}\text{NO}_4$: 314.1392; found: 314.1388.

3k**2-[4'-(*N*-morpholinophenyl)amino]-6-*tert*-butyl-1,4-benzoquinone**

2-[4'-(*N*-morpholinophenyl)amino]-6-*tert*-butyl-1,4-benzoquinone (3k). Synthesis and isolation described above. Dark red to black solid. Yield 92 % (62.4 mg): mp 101-104 °C. ^1H NMR: δ 8.86 (s, 1H), 7.17 (d, $J = 9.0$, 2H), 6.97 (d, $J = 9.0$, 2H), 6.38 (d, $J = 2.4$, 1H), 5.67 (d, $J = 2.4$, 1H), 3.73 (t, $J = 4.8$, 4H), 3.1 (t, $J = 4.8$, 4H), 1.26 (s, 9H). ^{13}C NMR: δ 185.2, 183.4, 150.7, 148.5, 145.8, 133.8, 129.4, 124.4, 115.4, 97.3, 66.0, 48.3, 34.4, 28.7. IR (KBr): ν 3449, 2960, 1631, 153, 1517 cm^{-1} . UV-Vis (MeOH) λ_{max} (log ϵ) 201 (4.45), 267 (4.24), 353 (3.61), 525 (3.71) nm. LC/MS m/z (relative intensity): 341 ($[\text{M}+1]^+$, 100) APCI, pos. mode; 340 ($[\text{M}]^-$, 100) APCI, neg. mode. GC/MS m/z (relative intensity): 340 (M^+ , 100), 239 (15). HRFT-ICRMS $[\text{M} + \text{H}]^+$: calcd for $\text{C}_{20}\text{H}_{25}\text{N}_2\text{O}_3$: 341.1865; found: 341.1865.

3l**2,3-Dimethyl-5-[(4'-carboxyphenyl)amino]-1,4-bezoquinone**

2,3-Dimethyl-5-[(4'-carboxyphenyl)amino]-1,4-bezoquinone (3l). Synthesis and isolation described above. Dark violet solid. Yield 60 % (32.4 mg): mp 179-181 °C. ^1H NMR: δ 7.96 (d, J = 8.4, 2H), 7.24 (d, J = 8.4, 2H), 6.06 (s, 1H), 2.02 (s, 3H), 2.00 (s, 3H). ^{13}C NMR: δ 188.4, 184.8, 174.6, 145.3, 144.3, 141.5, 138.5, 135.8, 131.7, 122.5, 101.2, 12.6, 12.1. IR (KBr): ν 3281, 1646, 1596, 1524 cm^{-1} . UV-Vis (MeOH) λ_{max} (log ϵ) 202 (4.33), 278 (4.28), 497 (3.52) nm. LC/MS m/z (relative intensity): 272 ($[\text{M}+1]^+$, 100) APCI, pos. mode; 271 ($[\text{M}]^-$, 100) APCI neg. mode; 270 ($[\text{M}-1]^-$, 100), 136 (31) API-ES, neg. mode. HRFT-ICRMS $[\text{M} + \text{H}]^+$: calcd for $\text{C}_{15}\text{H}_{14}\text{NO}_4$: 272.0923; found: 272.0919.

3m**2,3-Dimethyl-5-[4'-(*iso*-propylphenyl)amino]-1,4-bezoquinone**

2,3-Dimethyl-5-[4'-(*iso*-propylphenyl)amino]-1,4-bezoquinone (3m). Synthesis and isolation described above. Red-brown solid. Yield 91 % (49.2 mg): mp 91-92 °C. ^1H NMR: δ 8.84 (s, 1H), 7.26 (d, $J = 8.6$, 2H), 7.22 (d, $J = 8.6$, 2H), 5.82 (s, 1H), 2.87 (sept, $J = 6.9$, 1H), 1.97 (s, 1H), 1.94 (s, 1H), 1.19 (d, $J = 6.9$, 6H). ^{13}C NMR: δ 185.6, 184.0, 145.4, 144.5, 142.7, 136.8, 136.4, 127.4, 123.4, 99.2, 33.3, 24.2, 12.8, 12.3. IR (KBr): ν 3338, 3310, 2959, 1651, 1597, 1523 cm^{-1} . UV-Vis (MeOH) λ_{max} (log ϵ) 201 (4.37), 263 (4.24), 506 (3.57) nm. LC/MS m/z (relative intensity): 270 ($[\text{M}+1]^+$, 100) APCI, pos. mode; 269 ($[\text{M}]^-$, 100) APCI, neg. mode. GC/MS m/z (relative intensity): 269 (M^+ , 59), 254 (100), 226 (17). HRFT-ICRMS $[\text{M} + \text{H}]^+$: calcd for $\text{C}_{17}\text{H}_{20}\text{NO}_2$: 270.1494; found: 270.1492.

3n**2,3-Dimethyl-5-[4'-(2''-hydroxyethyl)phenylamino]-1,4-bezoquinone**

2,3-Dimethyl-5-[4'-(2''-hydroxyethyl)phenylamino]-1,4-bezoquinone (3n). Synthesis and isolation described above. Brown-red solid. Yield 94 % (51.2 mg): mp 90-92 °C. ^1H NMR: δ 8.85 (bs, 1H), 7.24 (d, $J = 8.7$, 2H), 7.21 (d, $J = 8.6$, 2H), 5.82 (s, 1H), 4.63 (bs, 1H), 3.59 (t, $J = 7.0$, 2H), 2.7 (t, $J = 7.0$, 2H), 1.97 (s, 3H), 1.95 (s, 3H). ^{13}C NMR: δ 185.1, 183.6, 144.0, 142.2, 136.3, 136.2, 136.1, 129.5, 122.8, 98.7, 62.0, 12.3, 11.8. IR (KBr): ν 3433, 1643, 1595, 1524 cm^{-1} . UV-Vis (MeOH) λ_{max} (log ϵ) 202 (4.28), 264 (4.19), 504 (3.51) nm. LC/MS m/z (relative intensity): 270 ($[\text{M}-1]^-$, 100) API-ES, neg. mode; 272 ($[\text{M}+1]^+$, 100) APCI, pos. mode. GC/MS m/z (relative intensity): 271 (M^+ , 39), 240 (100), 212 (7). HRFT-ICRMS $[\text{M} + \text{H}]^+$: calcd for $\text{C}_{16}\text{H}_{18}\text{NO}_3$: 272.1287; found: 272.1283.

3o**2,3-Dimethyl-5-[4'-(carboxymethylphenyl)amino]-1,4-bezoquinone**

2,3-Dimethyl-5-[4'-(carboxymethylphenyl)amino]-1,4-bezoquinone (3o). Synthesis and isolation described above. Dark red to black solid. Yield 92 % (52.4 mg): mp 161-163 °C. ^1H NMR: δ 8.89 (s, 1H), 7.27 (s, 2H), 7.26 (s, 2H), 5.86 (s, 1H), 3.56 (s, 1H), 1.98 (d, $J = 1.1$, 3H), 1.95 (d, $J = 1.1$, 3H). ^{13}C NMR: δ 185.2, 183.5, 172.6, 143.8, 142.2, 136.8, 136.4, 131.4, 130.1, 122.7, 99.0, 40.0, 12.3, 11.8. IR (KBr): ν 3237, 1721, 1664, 1645, 1580, 1523 cm^{-1} . UV-Vis (MeOH) λ_{max} (log ϵ) 202 (4.42), 266 (4.32), 503 (3.60) nm. LC/MS m/z (relative intensity): 286 ($[\text{M}+1]^+$, 60), 152 (100), 136 (80), 122 (90) API-ES, pos. mode. HRFT-ICRMS $[\text{M} + \text{H}]^+$: calcd for $\text{C}_{16}\text{H}_{16}\text{NO}_4$: 286.1079; found: 286.1076.

4a**2,5-bis-[4',4'''-(Carboxyphenyl)amino]-3-(2''-Hydroxyethylcarbamoyl)-1,4-benzoquinone** **2,5-bis-[4',4'''-(Carboxyphenyl)amino]-3-(2''-Hydroxyethylcarbamoyl)-1,4-benzoquinone (4a).**

Synthesis and isolation described above. Yellow-brown to brown solid. Yield 18 % (8.4 mg) in equimolar reactions, 96 % (89 mg) using amine excess: mp 242-244 °C. ¹H NMR: δ 12.95 (bs), 12.38 (bs, 1H), 9.62 (bs, 1H), 9.00 (t, *J* = 4.9, 1H), 7.99 (d, *J* = 8.6, 2H), 7.85 (d, *J* = 8.5, 2H), 7.52 (d, *J* = 8.6, 2H), 7.28 (d, *J* = 8.5, 2H), 5.99 (s, 1H), 4.75 (bs), 3.42 (t, *J* = 5.9, 2H), 3.12 (q, *J* = 5.7, 2H). ¹³C NMR: δ 178.9 (C-1), 178.1 (C-4), 167.4 (C-7), 166.7 (C-7'), 166.6 (C-7''), 153.0 (C-5), 145.9 (C-2), 143.3 (C-1'), 141.8 (C-1''), 130.5 (C-3'', C-5''), 129.6 (C-3', C-5'), 127.5 (C-4'), 127.2 (C-4''), 123.8 (C-2', C-6'), 122.6 (C-2'', C-6''), 112.5 (C-3), 98.4 (C-6), 59.3 (C-2'), 41.2 (C-1'). HMBC correlations see table 3. IR (KBr): ν 3271, 1703, 1647, 1621, 1581, 1567, 1523 cm⁻¹. UV-Vis (MeOH) λ_{max} (log ε) 202 (4.64), 271 (4.35), 382 (4.27) nm. LC/MS *m/z* (relative intensity): 464 ([M-1]⁻, 100) API-ES, neg. mode; 465 ([M]⁻, 100) APCI, neg. mode. HRFT-ICRMS [M + H]⁺: calcd for C₂₃H₂₀N₃O₈: 466.1250; found: 466.1258.

4b**2,5-bis-[4',4''-(Carboxymethylphenyl)amino]-3-(methylcarboxy)-1,4-benzoquinone** **2,5-bis-[4',4''-(Carboxymethylphenyl)amino]-3-(methylcarboxy)-1,4-benzoquinone (4b).**

Synthesis and isolation described above. Yellow-brown to brown solid. Yield 19 % (8.6 mg) in equimolar reactions, 96 % (88.7 mg) using amine excess: mp 250-253 °C. ^1H NMR: δ 12.38 (bs, 1H), 9.80 (bs, 1H), 9.39 (s, 1H), 7.32 (s, 4H), 7.23 (d, $J = 7.9$, 2H), 7.07 (d, $J = 7.9$, 2H), 5.81 (s, 1H), 3.60 (s, 2H), 3.57 (s, 2H), 2.94 (s, 3H). ^{13}C NMR: δ 178.4, 176.8, 172.5, 172.5, 164.2, 147.4, 145.7, 136.2, 135.9, 133.2, 132.7, 130.2, 129.6, 124.3, 123.7, 102.5, 95.0, 50.7, 40.0. IR (KBr): ν 3235, 1725, 1710, 1574, 1516 cm^{-1} . UV-Vis (MeOH) λ_{max} (log ϵ) 202 (4,55), 250 (4,26), 381 (4,19) nm. LC/MS m/z (relative intensity): 487 ($[\text{M}+\text{Na}]^+$, 100) API-ES, pos. mode; 463 ($[\text{M}-1]^-$, 100) API-ES, neg. mode; 464 ($[\text{M}]^-$, 100) APCI, neg. mode. HRFT-ICRMS $[\text{M} + \text{H}]^+$: calcd for $\text{C}_{24}\text{H}_{21}\text{N}_2\text{O}_8$: 465.1298; found: 465.1303.

4c**2,5-bis-[4',4''-(Carboxymethyl-carbamoylphenyl)amino]-3-(ethylcarboxyl)-1,4-****benzoquinone** **2,5-bis-[4',4''-(Carboxymethyl-carbamoylphenyl)amino]-3-(ethylcarboxyl)-1,4-benzoquinone**

(4c). Synthesis and isolation described above. Gold-brown solid. Yield 15 % (8.3 mg) in equimolar reactions, 93 % (105 mg) using amine excess: mp 187-189 °C. ¹H NMR: δ 9.61 (bs, 1H), 8.76 (bt, *J* = 5.2, 2H), 7.93 (d, *J* = 8.7, 2H), 7.85 (d, *J* = 8.7, 2H), 7.51 (d, *J* = 8.7, 2H), 7.26 (d, *J* = 8.6, 2H), 6.03 (s, 1H), 3.9 (bt, *J* = 4.0, 4H), 3.37 (q, *J* = 7.1, 2H), 0.94 (t, *J* = 7.1, 3H). ¹³C NMR: δ 179.1, 177.2, 171.25, 171.29, 165.5, 165.3, 163.7, 146.3, 144.9, 140.4, 135.2, 131.1, 130.5, 128.3, 127.6, 123.6, 122.8, 103.7, 96.6, 60.0, 41.5, 13.6. IR (KBr): ν 3226, 1717, 1644, 1569, 1505 cm⁻¹. UV-Vis (MeOH) λ_{max} (log ε) 206 (4.57), 275 (4.28), 381 (4.28) nm. LC/MS *m/z* (relative intensity): 563 ([*M*-1]⁻, 100), 281 (45) API-ES, neg. mode. HRFT-ICRMS [*M* + *H*]⁺: calcd for C₂₇H₂₅N₄O₁₀: 565.1571; found: 565.1569.

4d**3-Ethylcarboxy-2,5-bis-[4',4''-(*iso*-propylphenyl)amino]-1,4-benzoquinone**

3-Ethylcarboxy-2,5-bis-[4',4''-(*iso*-propylphenyl)amino]-1,4-benzoquinone (4d). Synthesis and isolation described above. Red-brown to brown solid. Yield 13 % (5.9 mg): mp 132-133 °C. ¹H NMR: δ 9.72 (s, 1H), 9.46 (s, 1H), 7.32 (d, *J* = 8.6, 2H), 7.28 (d, *J* = 8.6, 2H), 7.22 (d, *J* = 8.4, 2H), 7.06 (d, *J* = 8.4, 2H), 5.77 (s, 1H), 3.28 (q, *J* = 7.2, 2H), 2.91 (sept, *J* = 6.9, 1H), 2.89 (sept, *J* = 6.9, 1H), 1.21 (d, *J* = 6.9, 6H), 1.19 (d, *J* = 6.9, 6H), 0.86 (t, *J* = 7.2, 3H). ¹³C NMR: δ 178.3, 176.8, 163.9, 147.6, 146.7, 146.1, 145.4, 135.3, 135.1, 127.0, 126.3, 124.5, 123.8, 102.6, 94.8, 59.8, 33.0, 32.9, 23.75, 23.71, 13.5. IR (KBr): ν 3243, 2960, 1726, 1575, 1515, 1490 cm⁻¹. UV-Vis (MeOH) λ_{max} (log ε) 202 (4.62), 249 (4.36), 383 (4.30) nm. LC/MS m/z (relative intensity): 447 ([M+1]⁺, 100), 401 (58) APCI, pos. mode; 446 ([M]⁻, 100) APCI, neg. mode. HRFT-ICRMS [M + H]⁺: calcd for C₂₇H₃₁N₂O₄: 447.2284; found: 447.2295.

5-Carboxyethyl-N-(4'-carboxyphenyl)-2-hydroxy-1,4-quinonimine (5). Synthesis and isolation described above. Red to red-brown solid. Yield 75 % (47.2 mg): mp 164-165 °C. ^1H NMR: δ 8.04 (d, J = 8.4, 2H), 6.86 (d, J = 8.3, 2H), 6.58 (s, 1H), 6.01 (s, 1H), 2.98 (t, J = 7.5, 2H), 2.62 (t, J = 7.5, 2H). ^{13}C NMR: δ 183.6 (C-1), 173.7 (C-3'), 167.3 (C-7'), 159.9 (C-2), 155.7 (C-1'), 154.9 (C-4), 153.6 (C-5), 131.5 (C-3'', C-5''), 129.4 (C-6), 128.0 (C-4''), 120.1 (C-2'', C-6''), 102.0 (C-3), 33.8 (C-2'), 27.1 (C-1'). HMBC correlations see table 3. NMR see table 4. IR (KBr): ν 3427, 1705, 1686, 1634, 1600, 1522 cm^{-1} ; UV-Vis (MeOH) λ_{max} (log ϵ) 254 (4.11), 290 (4.40), 445 (3.48) nm. LC/MS m/z (relative intensity): 314 ($[\text{M}-1]^-$, 100), 270 (55) API-ES, neg. mode; 316 ($[\text{M}+1]^+$, 100), 270 (20) APCI pos. mode. HRFT-ICRMS $[\text{M} + \text{H}]^+$: calcd for $\text{C}_{16}\text{H}_{14}\text{NO}_6$: 316.0821; found: 316.0814.

Selected correlations in the HMBC spectrum