SUPPLEMENTARY MATERIAL

Pd-Catalyzed Dehydrogenative Cross-Coupling of 1,4-Quinones with \(N,N\)-Dialkyluracils

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General: Glassware was flame-dried. Solvents, Palladium acetate (98%), AgNO₃, 1,4-Benzoquinone, 1,4-Naphtoquinone and 1,4-Anthraquinone were purchased from Alfa Aesar and Merck. All other commercially available reagents were utilized as received without purification. Thin layer chromatography (TLC) analysis was performed using Silicycle precoated TLC plates (silica gel 60 F₂₅₄). The products were purified by preparative column chromatography on silica gel (0.063-0.200 mm; Merck). IR Spectra: Shimadzu FT-IR-4300 spectrometer; in cm⁻¹. ¹H and ¹³C-NMR Spectra: were recorded on Bruker DRX -500-Advance instrument, Bruker DRX -300-Advance instrument and Bruker DRX -250-Advance instrument; in CDCl₃ at 500.1, 300.1, 125.7 and 75.4 MHz, resp; δ in ppm, J in Hz. EI-MS (70 eV): HP 5973 GC-MS instrument; in m/z. Melting points: Electrothermal 9200 apparatus.

General Procedure for the Synthesis of coupled N,N-Dialkylated Uracils with 1,4-Quinone Derivatives: A 10 mL microwave vial equipped with a magnetic stirring bar and septum was flame-dried and then cooled. The vial was then charged with quinone derivatives (3 mmol), N,N-dialkylated uracil derivatives (1 mmol), AgNO₃ (2 equiv) and Pd(OAc)₂ (10 mol %). The vial was then sealed. Ethyl acetate (4 mL) were added sequentially via syringe. The reaction vessel was immersed in an oil bath, which was preheated at 90 °C, for 24 h. After this time the reaction mixture was cooled to room temperature and diluted with ethyl acetate (15 mL). The mixture was washed with water (15 mL), and the aqueous phase was extracted with ethyl acetate (2 × 10 mL). The organic extracts were dried over sodium sulphate and filtered. Concentration of the solution by rotary evaporation under reduced pressure gave a residue which was purified by using column chromatography.
5-(3,6-dioxocyclohexa-1,4-dien-1-yl)-1,3-bis(3-methylbenzyl)pyrimidine-2,4(1H,3H)-dione (3a), dark orange solid (yield 76%). M.p. 121-123 °C. IR (KBr) ($v_{max}/cm^{-1}$): 770, 836, 1155, 1379, 1445, 1608, 1645, 1706, 2926. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$H (ppm): $\delta$ = 7.84 (1H, d, $^3$J$_{HH}$ = 1.8 Hz), 7.43 (1H, s), 7.26 (2H, m), 7.07-7.28 (6H, m), 6.75 (2H, t, $^3$J$_{HH}$ = 7.79 Hz, $^3$J$_{HH}$ = 2.09 Hz), 5.15 (2H, s), 4.98 (2H, s), 2.35 (3H, s), 2.32 (3H, s). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$C (ppm): 21.4, 45.1, 53.1, 104.6, 125.3, 126.2, 128.4, 128.6, 128.9, 129.1, 129.5, 129.7, 133.9, 134.7, 136.3, 136.7, 136.9, 138.2, 139.1, 145.4, 150.5, 160.9, 186.4, 187.4. MS, m/z (%): 426 (M$^+$, 48), 320 (20), 411 (1), 398 (1), 105 (100), 91 (13), 77 (25). Anal. Calcd. for C$_{26}$H$_{22}$N$_2$O$_4$: C, 73.23; H, 5.20; N, 6.57. Found: C, 73.44; H, 5.23; N, 6.53.

1,3-dibuty-5-(3,6-dioxocyclohexa-1,4-dien-1-yl)pyrimidine-2,4(1H,3H)-dione (3b), dark brown solid (yield 78%). M.p. 113-115 °C. IR (KBr) ($v_{max}/cm^{-1}$): 626, 774, 840, 904, 927, 1010, 1106, 1222, 1283, 1379, 1453, 1584, 1641, 1703, 2869, 2930, 2956. $^1$H NMR (250 MHz, CDCl$_3$) $\delta$H (ppm): 7.79 (1H, s), 7.46 (1H, s), 6.78 (2H, s), 3.97 (2H, t, $^3$J$_{HH}$ = 7.25 Hz), 3.83 (2H, t, $^3$J$_{HH}$ = 7.25 Hz), 1.54-1.75 (4H, m), 1.32-1.43 (4H, m), 0.95 (6H, q, $^3$J$_{HH}$ = 9 Hz). $^{13}$C NMR (62 MHz, CDCl$_3$) $\delta$C (ppm): 13.6, 13.8, 19.7, 20.2, 29.5, 31.2, 41.8, 50.4, 103.9, 133.8, 136.4, 136.9, 145.8, 150.0, 161.0, 186.6, 187.4. MS, m/z (%): 330 (M$^+$, 100), 288 (22), 274 (23), 218 (26), 224 (3), 168 (4), 126 (5). Anal. Calcd. for C$_{18}$H$_{22}$N$_2$O$_4$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.40; H, 6.53.

1,3-dibutyl-5-(1,4-dioxo-1,4-dihydronaphthalene-2-yl)pyrimidine-2,4(1H,3H)-dione (3c), Light yellow solid (yield 52%). M.p. 119-121 °C. IR (KBr) ($v_{max}/cm^{-1}$): 668, 783, 900, 939, 1112, 1178, 1246, 1344, 1382, 1449, 1590, 1645, 1704, 2870, 2932. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$H (ppm): 0.97-1.01 (6H, m), 1.38-1.47 (4H, m), 1.64-1.68 (2H, m), 1.75-1.81 (2H, m), 3.89 (2H, t, $^3$J$_{HH}$ = 7.5 Hz), 4.02 (2H, t, $^3$J$_{HH}$ = 7.5 Hz), 7.66 (1H, s), 7.76-7.78 (2H, m), 7.93 (1H, s), 8.11-8.12 (2H, m). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$C (ppm): 13.6, 13.8, 19.7, 20.2, 29.6, 31.2, 41.8, 50.3, 104.7, 125.9, 126.9, 131.9, 132.3, 133.7, 134.1, 136.4, 138.9, 145.8, 150.2, 161.1, 184.5, 184.8. MS, m/z (%): 380 (M$^+$, 67), 338 (1), 210 (21), 268 (8), 182 (2), 120 (7), 140 (35), 71(100). Anal. Calcd. for C$_{22}$H$_{24}$N$_2$O$_4$: C, 69.46; H, 6.36; N, 7.36. Found: C, 69.19; H, 6.33; N, 7.35.
5-(3,6-dioxocyclohexa-1,4-dien-1-yl)-1,3-bis(3-methylbenzyl)pyrimidine-2,4(1H,3H)-dione(3d), Brown solid (yield 51%). M.p. 127-130 °C. IR (KBr) ($\nu_{\text{max}}$/cm$^{-1}$): 692, 765, 909, 959, 1093, 1163, 1308, 1378, 1443, 1599, 1646, 1703, 2032, 2917, 3715. $^1$H NMR (500 MHz, CDCl$_3$) $\delta_H$/ppm): 2.35 (3H, s), 2.38 (3H, s), 5.10 (2H, s), 5.19 (2H, s), 7.11 (1H, d, $^3J_{HH} = 7.5$ Hz), 7.17 (1H, s), 7.27-7.29 (1H, m), 7.29-7.33 (2H, m), 7.61 (1H, s), 7.75-7.82 (2H, m), 7.95 (1H, s), 8.05-8.08 (1H, m), 8.09-8.12 (1H, m). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta_C$/ppm: 21.4, 45.0, 53.1, 105.2, 125.2, 125.9, 126.2, 126.9, 128.3, 128.5, 128.8, 129.0, 129.4, 129.7, 131.8, 132.2, 133.6, 133.9, 134.7, 136.3, 138.1, 138.8, 138.9, 145.3, 150.5, 160.9, 184.2, 184.7. MS, m/z (%): 476 (M$,^+$, 67), 448 (1), 371 (21), 168 (8), 156 (2), 119 (7), 79 (35), 105 (100), 91 (13). Anal. Calcd. for C$_{30}$H$_{24}$N$_2$O$_4$: C, 75.61; H, 5.08; N, 5.88. Found: C, 75.52; H, 5.03; N, 5.90.

5-(3,6-dioxocyclohexa-1,4-dien-1-yl)-1,3-diethylpyrimidine-2,4(1H,3H)-dione(3e), Dark orange solid (yield 86%). M.p. 109-111 °C. IR (KBr) ($\nu_{\text{max}}$/cm$^{-1}$): 1478, 2220, 2969. $^1$H NMR (500 MHz, CDCl$_3$) $\delta_H$/ppm): 1.26 (3H, t, $^3J_{HH} = 7.1$ Hz), 1.40 (3H, t, $^3J_{HH} = 7.2$ Hz), 3.93 (2H, q, $^3J_{HH} = 7.1$ Hz), 4.08 (2H, q, $^3J_{HH} = 7.0$ Hz). 13C NMR (125 MHz, CDCl$_3$) $\delta_C$/ppm: 12.7, 14.5, 37.1, 45.6, 45.6, 104.3, 133.7, 136.3, 136.9, 145.3, 149.7, 149.5, 156.9, 158.6, 187.4. MS, m/z (%): 274 (M$,^+$, 100), 259 (3), 246 (33), 218 (20), 195 (2), 56 (51). Anal. Calcd. for C$_{14}$H$_{14}$N$_2$O$_4$: C, 61.31; H, 5.14; N, 10.21. Found: C, 61.20; H, 5.10; N, 10.18.

5-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-1,3-diethylpyrimidine-2,4(1H,3H)-dione(3f), Dark Orange solid (yield 71%). M.p. 114-117 °C. IR (KBr) ($\nu_{\text{max}}$/cm$^{-1}$): 1478, 2085, 1180, 1299, 1445, 1610, 1644, 1701, 2925. $^1$H NMR (300 MHz, CDCl$_3$) $\delta_H$/ppm): 1.25 (3H, t, $^3J_{HH} = 7$ Hz), 1.41 (3H, q, $^3J_{HH} = 7.2$ Hz), 3.94 (2H, q, $^3J_{HH} = 7.2$ Hz), 4.08 (2H, q, $^3J_{HH} = 7.0$ Hz). 13C NMR (75 MHz, CDCl$_3$) $\delta_C$/ppm: 12.8, 14.6, 37.2, 45.6, 50.5, 126.0, 126.9, 131.9, 132.3, 133.7, 134.1, 136.4, 139.0, 145.4, 149.9, 161.0, 184.9. MS, m/z (%): 324 (M$,^+$, 100), 296 (25), 253 (45), 197 (85), 169 (70), 114 (20), 76 (28). Anal. Calcd. for C$_{18}$H$_{16}$N$_2$O$_4$: C, 66.66; H, 4.97; N, 8.64. Found: C, 66.89; H, 4.99; N, 8.61.
5-(1,4-dioxo-1,4-dihydroanthracen-2-yl)-1,3-diethylpyrimidine-2,4(1H,3H)-dione(3g), Dark Orange solid (yield 75%). M.p. 124-126 °C. IR (KBr) (ν max/cm⁻¹): 772, 945, 1020, 1568, 1607, 1645, 1731, 2049, 2931. ¹H NMR (300 MHz, CDCl₃) δ H (ppm): 1.27 (3H, t, 3 J HH = 7.2 Hz), 1.43 (3H, t, 3 J HH = 7.2 Hz), 3.97 (2H, q, 3 J HH = 7.2 Hz), 4.09 (2H, q, 3 J HH = 6.9 Hz) 7.68-7.71 (2H, m), 7.73 (1H, s), 8.00 (1H, s), 8.07 (2H, d, 3 J HH = 5.4 Hz), 8.63 (2H, d, 3 J HH = 9.5 Hz). ¹³C NMR (75 MHz, CDCl₃) δ C (ppm): 12.8, 14.6, 37.2, 45.6, 103.9, 128.2, 128.5, 128.8, 129.5, 129.6, 129.7, 130.2, 130.9, 134.8, 134.9, 138.1, 140.3, 145.4, 149.9, 170.4, 183.0. MS, m/z (%): 374 (M⁺, 100), 346 (19), 318 (6), 211 (2), 139 (5), 126 (44), 105 (15). Anal. Calcd. for C₂₂H₁₈N₂O₄: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.86; H, 4.81; N, 7.43.

1,3-dibutyl-5-(1,4-dioxo-1,4-dihydroanthracen-2-yl)pyrimidine-2,4(1H,3H)-dione(3i), Light Yellow solid (yield 62%). M.p. 137-139 °C. IR (KBr) (ν max/cm⁻¹): 784, 958, 1071, 1381, 1583, 1613, 1703, 2869, 2958. ¹H NMR (500 MHz, CDCl₃) δ H (ppm): 0.93 (3H, t, 3 J HH = 7.4 Hz), 1.02 (3H, t, 3 J HH = 7.3 Hz), 1.39-1.48 (4H, m), 1.64-1.676 (2H, m), 1.78-1.81 (2H, m), 3.90 (2H, t, 3 J HH = 7.3 Hz), 4.03 (2H, t, 3 J HH = 7.4 Hz), 7.69-7.70 (2H, m), 7.74 (1H, s), 8.01 (1H, s), 8.06 (2H, m), 8.59 (1H, S), 8.64 (1H, S). ¹³C NMR (125 MHz, CDCl₃) δ C (ppm): 13.7, 13.8, 19.8, 20.2, 29.6, 31.2, 41.8, 50.4, 104.8, 128.2, 128.4, 128.8, 129.4, 129.5, 129.6, 130.2, 130.9, 134.8, 134.9, 138.0, 140.3, 145.9, 150.2, 161.2, 184.1, 184.4. MS, m/z (%): 430 (M⁺, 100), 401 (31), 388 (52), 360 (2), 346 (2), 139 (2). Anal. Calcd. for C₂₆H₂₆N₂O₄: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.29; H, 6.11; N, 6.54.

5-(1,4-dioxo-1,4-dihydroanthracen-2-yl)-1,3-bis(3-methylbenzyl)pyrimidine-2,4(1H,3H)-dione(3j), Orange solid (yield 54%). M.p. 141-143 °C. IR (KBr) (ν max/cm⁻¹): 732, 1038, 1072, 1380, 1448, 1647, 1725, 2860, 2927. ¹H NMR (300 MHz, CDCl₃) δ H (ppm): 2.31-2.37 (6H, m), 5.03 (2H,s), 5.19 (2H, s), 6.87-7.32 (8H, m), 7.67-7.70 (2H, m), 8.00 (1H, s), 8.05-8.10 (2H, m), 8.33 (1H, s), 8.60 (1H, s), 8.63 (1H, s). ¹³C NMR (125 MHz, CDCl₃) δ C (ppm): 21.4, 45.13, 53.2, 105.6, 125.3, 126.3, 128.2, 128.4, 128.6, 128.7, 128.9, 129.1, 129.5, 129.6, 129.8, 130.2, 134.8, 134.9, 136.4, 138.2, 138.3, 139.1, 140.2, 145.5, 150.6, 161.1, 183.8, 184.4. MS, m/z (%): 526 (M⁺, 2), 316 (3), 113 (87), 71 (100). Anal. Calcd. for C₃₄H₂₆N₂O₄: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.51; H, 4.96; N, 5.32.
1,3-diethyl-5-(5-methyl-3,6-dioxocyclohexa-1,4-dien-1-yl)pyrimidine-2,4(1H,3H)-dione(3h)
Brown solid (yield 34%). M.p. 116-119 °C. IR (KBr) (ν max/cm⁻¹): 778, 989, 1175, 1334, 1445, 1643, 1705, 2934. ¹H NMR (300 MHz, CDCl₃) δ H (ppm): 1.22 (3H, t, ³JHH = 7.2 Hz), 1.36 (3H, t, ²JHH = 7.2 Hz), 2.07 (3H, s), 3.88 (2H, q, ³JHH = 7.2 Hz), 4.03 (2H, q, ⁴JHH = 7.2 Hz), 6.60 (1H, t, ⁴JHH = 1.2 Hz), 7.29 (1H, d, ⁵JHH = 2.3 Hz), 7.77 (1H, s). ¹³C NMR (75 MHz, CDCl₃) δ C (ppm): 12.7, 14.5, 16.4, 37.1, 45.6, 104.9, 130.9, 133.3, 133.9, 137.3, 144.8, 149.8, 160.9, 186.9, 187.4. MS, m/z (%): 288 (M⁺, 93), 260 (11), 245 (2), 232 (6), 217 (7), 167 (51), 121 (10), 131 (15), 71 (35). Anal. Calcd. for C₁₅H₁₆N₂O₄: C, 62.49; H, 5.59; N, 9.72. Found: C, 62.35; H, 5.51; N, 9.70.

1,3-diethyl-5-(4-methyl-3,6-dioxocyclohexa-1,4-dien-1-yl)pyrimidin-2,4(1H,3H)-dione(3hh)
Orange solid (yield 29%). M.p. 121-123 °C. IR (KBr) (ν max/cm⁻¹): 776, 975, 1179, 1377, 1444, 1644, 1699, 2929. ¹H NMR (300 MHz, CDCl₃) δ H (ppm): 1.20 (3H, t, ³JHH = 5.9 Hz), 1.36 (3H, t, ²JHH = 5.9 Hz), 2.03 (3H, d, ⁴JHH = 1.5 Hz), 3.89 (2H, q, ³JHH = 7.2 Hz), 4.01 (2H, q, ⁵JHH = 7.2 Hz), 6.60 (1H, t, ⁴JHH = 1.2 Hz), 7.26 (1H, d, ⁵JHH = 1.2 Hz), 7.82 (1H, d, ⁵JHH = 0.9 Hz). ¹³C NMR (75 MHz, CDCl₃) δ C (ppm): 12.7, 14.5, 15.4, 37.1, 45.6, 104.3, 130.9, 133.6, 133.8, 136.6, 145.4, 149.7, 160.9, 186.9, 187.8. MS, m/z (%): 288 (M⁺, 93), 260 (11), 245 (2), 232 (6), 217 (7), 167 (51), 121 (10), 71 (35). Anal. Calcd. for C₁₅H₁₆N₂O₄: C, 62.49; H, 5.59; N, 9.72. Found: C, 62.28; H, 5.63; N, 9.75.
70% ORTEP plot of the three independent molecules of 3hh.