Supporting Information

Regioselective C–H Alkylation and Alkenylation at C5 Position of 2-Amino-1,4-Naphthoquinones with Maleimides Under Rh(III) Catalysis

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S1
General Information. All the chemicals were purchased from Sigma-Aldrich. All the reactions were carried out under air using the sealed pressure tubes. NMR were recorded on Bruker (500 MHz) spectrometer with CDCl$_3$ or DMSO-d$_6$ as reference solvent. Chemical shifts of $^1$H and $^{13}$C NMR spectra were reported in parts per million (ppm). Chromatographic separations were performed using neutral aluminium oxide. IR spectra were recorded as KBr pellet on Bruker Alpha FT-IR spectrometer. High-resolution mass spectrometry (HRMS) were recorded on Agilent Q-TOF LC/MS. Melting points were uncorrected and were taken on Buchi M-560.

Synthesis of 2-Amino-1,4-Naphthoquinones (1a-1n, 1p). [1]

![Chemical Reaction](image.png)

General Procedure for preparation of 2-Amino-1,4-naphthoquinones: To a solution of naphthoquinone (5 mmol) in methanol (10 mL) were dropwise added amines (5 mmol) at room temperature. The reaction flask was tightly closed with stopper and the stirring was continued at 25 °C for 1 h. Completion of the reaction was monitored by TLC, the volatiles were removed under reduced pressure. The resulting residue was purified by neutral alumina column chromatography (eluent; hexane/EtOAc = 10:1 to 4:1) to provide 2-Amino-1,4-naphthoquinones.

References:
General procedure for regioselective C–H alkylation and spectral data (3aa-3ja, 3bb-3bf):

Typical procedure for regioselective C–H alkylation at C5 of 2-amino-1,4-naphthoquinone with N-substituted maleimide: To an oven-dried sealed tube with 2-(isoproylamino)naphthalene-1,4-dione (1a) (43 mg, 0.2 mmol, 100 mol %), N-Methylmaleimide (2a) (26.6 mg, 0.24 mmol, 120 mol %), [RhCp*Cl₂]₂ (3.1 mg, 0.005 mmol, 2.5 mol %), AgSbF₆ (6.9 mg, 0.02 mmol, 10 mol %) and AcOH (24.0 mg, 0.4 mmol, 200 mol %) was added in DCE (1 mL). The reaction mixture was allowed to stir at 80 ºC for 16 h. After cooling at room temperature, the reaction mixture was evaporated. The resulting residue was purified by neutral alumina column chromatography (eluent; hexane/EtOAc = 10:1 to 1:1) to provide 3aa (59 mg) in 90% yield.

3-(6-(Isopropylamino)-5,8-dioxo-5,8-dihyronaphthalen-1-yl)-1-methylpyrrolidine-2,5-dione (3aa):

![Structure Image]

59 mg (90 %); Orange solid; mp = 161.7–162.6 °C; ¹H NMR (500 MHz, DMSO–d₆) δ 8.04 (dd, J = 7.0, 2.0 Hz, 1H), 7.73–7.67 (m, 2H), 7.14 (d, J = 8.0 Hz, 1H), 5.63 (s, 1H), 4.37 (bs, 1H), 3.68–3.59 (m, 1H), 3.00 (bs, 1H), 2.19 (s, 3H), 1.19 (d, J = 6.5 Hz, 6H); ¹³C NMR (125 MHz, DMSO–d₆) δ 183.4, 181.6, 177.3, 176.4, 146.5, 136.6, 132.4, 131.9, 129.7, 126.9, 100.9, 47.1, 43.5, 36.6, 24.4, 21.1, 21.1; IR (KBr) ν 3336, 3064, 2970, 1761, 1691, 1565, 1506, 1438, 1347, 1280, 1234, 1162, 1114, 1033, 959, 870, 777, 674 cm⁻¹; HRMS (Q-TOF, ESI) calcd for C₁₈H₁₉N₂O₄ [M+H⁺]⁺ 327.1339, found 327.1386.

3-(6-(Butylamino)-5,8-dioxo-5,8-dihyronaphthalen-1-yl)-1-methylpyrrolidine-2,5-dione (3ba):

![Structure Image]

61 mg (89%); Orange solid; mp = 198.7–199.6 °C; ¹H NMR (500 MHz, DMSO–d₆) δ 8.04 (d, J = 7.0 Hz, 1H), 7.72–7.67 (m, 2H), 7.57 (t, J = 6.5 Hz, 1H), 5.60 (s, 1H), 4.35 (bs, 1H), 3.13 (q, J = 7.0 Hz, 2H), 3.00 (bs, 1H), 2.91 (s, 3H), 2.56 (dd, J = 17.0, 6.0 Hz, 1H), 1.54 (quint, J = 7.0, 2H), 1.31 (sextet, J = 7.5 Hz, 2H), 0.88 (t, J = 7.0 Hz, 3H); ¹³C NMR (125 MHz, DMSO–d₆) δ 183.2, 181.5, 177.3, 176.5, 147.6, 140.9, 136.6, 132.4, 131.9, 129.8, 126.9, 100.5, 47.2, 41.5, 36.6, 29.4, 24.4,
19.7, 13.7; IR (KBr) \( \nu \) 3343, 2951, 2867, 1762, 1690, 1614, 1568, 1509, 1443, 1342, 1250, 1113, 1008, 958, 861, 778, 692 cm\(^{-1}\); HRMS (Q-TOF, ESI) calcd for \( \text{C}_{19}\text{H}_{21}\text{N}_{2}\text{O}_{4} \) [M+H]\(^{+}\) 341.1496, found 341.1500.

3-(6-(Isobutylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1-methylpyrrolidine-2,5-dione (3ca):

65 mg (96%); Yellow solid; mp = 217.0–218.3 \( ^\circ \)C; \(^1\)H NMR (500 MHz, DMSO–d\(_6\)) \( \delta \) 8.05 (d, \( J = 7.0 \) Hz, 1H), 7.73–7.67 (m, 2H), 7.62 (t, \( J = 6.5 \) Hz, 1H), 5.62 (s, 1H), 4.35 (bs, 1H), 3.01 (bs, 1H), 2.97 (t, \( J = 7.0 \) Hz, 2H), 2.91 (s, 3H), 2.56 (dd, \( J = 17.0, 6.0 \) Hz, 1H), 1.94 (septet, \( J = 6.5 \) Hz, 1H), 0.88 (d, \( J = 7.0 \) Hz, 6H); \(^{13}\)C NMR (125 MHz, DMSO–d\(_6\)) \( \delta \) 183.3, 181.5, 177.3, 176.5, 147.8, 140.9, 136.5, 132.4, 131.9, 129.7, 127.0, 100.7, 49.2, 47.1, 36.6, 26.8, 24.4, 20.1; IR (KBr) \( \nu \) 3308, 2961, 2867, 1763, 1683, 1611, 1568, 1512, 1436, 1346, 1280, 1237, 1168, 1110, 1013, 955, 838, 772, 681 cm\(^{-1}\); HRMS (Q-TOF, ESI) calcd for \( \text{C}_{19}\text{H}_{21}\text{N}_{2}\text{O}_{4} \) [M+H]\(^{+}\) 341.1496, found 341.1518.

3-(6-((Cyclohexylmethyl)amino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1-methylpyrrolidine-2,5-dione (3da):

72 mg (94%); Yellow solid; mp = 207.0–208.6 \( ^\circ \)C; \(^1\)H NMR (500 MHz, DMSO–d\(_6\)) \( \delta \) 8.05 (dd, \( J = 7.5, 2.0 \) Hz, 1H), 7.73–7.67 (m, 2H), 7.63 (t, \( J = 6.5 \) Hz, 1H), 5.60 (s, 1H), 4.32 (bs, 1H), 3.04–2.97 (m, 3H), 2.91 (s, 3H), 2.55 (dd, \( J = 17.0, 6.0 \) Hz, 1H), 1.69–1.60 (m, 6H), 1.18–1.09 (m, 3H), 0.94–0.86 (m, 2H); \(^{13}\)C NMR (125 MHz, DMSO–d\(_6\)) \( \delta \) 183.2, 181.5, 177.3, 176.5, 147.8, 140.9, 136.4, 132.4, 131.9, 129.7, 127.0, 100.6, 47.9, 47.2, 36.6, 36.1, 30.4, 26.0, 25.3, 24.4.; IR (KBr) \( \nu \) 3365, 2923, 2851, 1764, 1687, 1610, 1567, 1501, 1438, 1339, 1243, 1113, 1050, 1003, 957, 863, 884, 779, 690 cm\(^{-1}\); HRMS (Q-TOF, ESI) calcd for \( \text{C}_{22}\text{H}_{25}\text{N}_{2}\text{O}_{4} \) [M+H]\(^{+}\) 381.1809, found 381.1822.

3-(6-((4-Fluorobenzyl) amino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1-methylpyrrolidine-2,5-dione (3ea):
59 mg (75%); Yellow solid; mp = 228.0–230.0 °C; \(^1\)H NMR (500 MHz, DMSO–d\(_6\)) \(\delta\) 8.19 (t, \(J = 6.5\) Hz, 1H), 8.07–8.05 (m, 1H), 7.74–7.68 (m, 2H), 7.38 (dd, \(J = 8.5, 5.5\) Hz, 2H), 7.15 (t, \(J = 8.5\) Hz, 2H), 5.52 (s, 1H), 4.43–4.24 (m, 3H), 2.97 (bs, 1H), 2.88 (s, 3H), 2.52 (dd, \(J = 17.0, 6.5\) Hz, 1H); \(^{13}\)C NMR (125 MHz, DMSO–d\(_6\)) \(\delta\) 183.4, 181.5, 177.2, 176.4, 161.3 (d, \(J_{CF} = 241.2\) Hz), 147.4, 140.8, 136.6, 133.6 (d, \(J_{CF} = 3.1\) Hz), 132.4, 132.1, 129.5, 129.1 (d, \(J_{CF} = 8.0\) Hz), 126.9, 115.2 (d, \(J_{CF} = 21.2\) Hz), 101.7, 47.1, 44.2, 36.5, 24.4; IR (KBr) \(\nu\) 3390, 2869, 1785, 1695, 1621, 1577, 1438, 1385, 1277, 1236, 1119, 1067, 1008, 879, 866, 775, 687, 665 cm\(^{-1}\); HRMS (Q-TOF, ESI) calcd for C\(_{22}\)H\(_{18}\)FN\(_2\)O\(_4\) [M+H]\(^{+}\) 393.1245, found 393.1252.

3-(5,8-Dioxo-6-(phenethylamino)-5,8-dihydronaphthalen-1-yl)-1-methylpyrrolidine-2,5-dione (3fa):

62 mg (80%); Orange solid; mp = 172.2–173.6 °C; \(^1\)H NMR (500 MHz, DMSO–d\(_6\)) \(\delta\) 8.05 (dd, \(J = 7.0, 2.0\) Hz, 1H), 7.73–7.68 (m, 2H), 7.51 (t, \(J = 6.0\) Hz, 1H), 7.30–7.26 (m, 4H), 7.22–7.18 (m, 1H), 5.67 (s, 1H), 4.37 (bs, 1H), 3.41–3.37 (m, 2H), 3.00 (bs, 1H), 2.91 (s, 3H), 2.87 (t, \(J = 7.0, 2H\)), 2.56 (dd, \(J = 17.0, 6.0\) Hz, 1H); \(^{13}\)C NMR (125 MHz, DMSO–d\(_6\)) \(\delta\) 183.4, 181.5, 177.3, 176.5, 147.3, 140.8, 138.9, 136.6, 132.3, 132.0, 129.7, 128.7, 128.4, 126.9, 126.2, 100.9, 47.3, 43.2, 36.6, 33.3, 24.4; IR (KBr) \(\nu\) 3357, 2907, 1765, 1694, 1611, 1567, 1508, 1432, 1342, 1275, 1233, 1112, 1012, 953, 844, 770, 709, 680 cm\(^{-1}\); HRMS (Q-TOF, ESI) calcd for C\(_{23}\)H\(_{21}\)N\(_2\)O\(_4\) [M+H]\(^{+}\) 389.1496, found 389.1512.

3-(5,8-Dioxo-6-((3-phenylpropyl) amino)-5,8-dihydronaphthalen-1-yl)-1-methylpyrrolidine-2,5-dione (3ga):

62 mg (78%); Orange solid; mp = 154.1–156.8 °C; \(^1\)H NMR (500 MHz, DMSO–d\(_6\)) \(\delta\) 8.05 (d, \(J = 7.0\) Hz, 1H), 7.62 (t, \(J = 6.0\) Hz, 1H), 7.26 (t, \(J = 7.5\) Hz, 2H), 7.21 (d, \(J = 6.5\) Hz, 2H), 7.16 (t, \(J = 7.0\) Hz, 1H), 5.59 (s,
1H), 4.43 (bs, 1H), 3.16 (q, J = 6.5 Hz, 2H), 3.00 (bs, 1H), 2.91 (s, 3H), 2.62 (t, J = 7.5 Hz, 2H), 2.54 (dd, J = 17.5, 6.5 Hz, 1H), 1.85 (quint, J = 7.5 Hz, 2H); 13C NMR (125 MHz, DMSO–d6) δ 183.3, 181.5, 177.3, 176.5, 147.6, 141.5, 140.9, 136.6, 132.4, 131.9, 129.7, 128.3, 126.9, 125.6, 100.5, 47.1, 41.5, 36.6, 32.6, 29.2, 24.4; IR (KBr) ν 3323, 2923, 2860, 1689, 1615, 1566, 1512, 1436, 1341, 1243, 1113, 1041, 957, 837, 775, 689 cm−1; HRMS (Q-TOF, ESI) calcd for C24H23N2O4 [M+H]+ 403.1652, found 403.1658.

3-(5,8-Dioxo-6-((4-phenylbutyl)amino)-5,8-dihyronaphthalen-1-yl)-1-methylpyrrolidine-2,5-dione (3ha):

25 mg (30%); Yellow solid; mp = 136.3–137.0 °C; 1H NMR (500 MHz, DMSO–d6) δ 8.04 (dd, J = 7.0, 2.0 Hz, 1H), 7.72–7.67 (m, 2H), 7.58 (t, J = 6.0 Hz, 1H), 7.25 (t, J = 7.5 Hz, 2H), 7.19 (d, J = 6.5 Hz, 2H), 7.14 (t, J = 7.5 Hz, 1H), 5.62 (s, 1H), 4.36 (bs, 1H), 3.17 (q, J = 6.0 Hz, 2H), 3.01 (bs, 1H), 2.91 (s, 3H), 2.55 (dd, J = 17.0, 6.0 Hz, 1H), 1.63–1.53 (m, 4H); 13C NMR (125 MHz, DMSO–d6) δ 183.2, 181.5, 177.3, 176.4, 147.5, 142.0, 140.9, 136.6, 132.4, 131.9, 129.7, 128.3, 128.2, 126.9, 125.6, 100.5, 47.0, 41.6, 36.6, 34.7, 28.4, 26.9, 24.4; IR (KBr) ν 3293, 3026, 2942, 2904, 1766, 1698, 1518, 1441, 1377, 1350, 1286, 1249, 1036, 1001, 956, 841, 788, 752, 691 cm−1; HRMS (Q-TOF, ESI) calcd for C25H25N2O4 [M+H]+ 417.1809, found 417.1814.

3-(5,8-Dioxo-6-(pyrrolidin-1-yl)-5,8-dihyronaphthalen-1-yl)-1-methylpyrrolidine-2,5-dione (3ia):

54 mg (80%); Red solid; mp = 207.9–208.2 °C; 1H NMR (500 MHz, DMSO–d6) δ 8.00–7.98 (m, 1H), 7.72–7.66 (m, 2H), 5.56 (s, 1H), 4.35 (bs, 1H), 3.85 (bs, 2H), 3.17 (q, J = 6.0 Hz, 2H), 3.01 (bs, 1H), 2.54 (dd, J = 17.5, 6.5 Hz, 1H), 1.91–1.86 (m, 4H); 13C NMR (125 MHz, DMSO–d6) δ 182.6, 182.4, 177.3, 176.5, 148.4, 140.0, 136.0, 133.6, 131.7, 129.4, 127.1, 104.4, 50.8, 50.1, 46.9, 36.7, 26.1, 24.4, 23.5; IR (KBr) ν 2972, 2934, 1761, 1689, 1610, 1561, 1431, 1267, 1118, 1026, 955, 762, 684 cm−1; HRMS (Q-TOF, ESI) calcd for C19H19N2O4 [M+H]+ 339.1339, found 339.1359.
3-(5,8-Dioxo-6-(piperidin-1-yl)-5,8-dihydronaphthalen-1-yl)-1-methylpyrrolidine-2,5-dione (3ja):

53 mg (75%); Red solid; mp = 148.2–150.0 °C; $^1$H NMR (500 MHz, DMSO–d$_6$) δ 7.94 (dd, $J$ = 6.5, 2.0 Hz, 1H), 7.71–7.66 (m, 2H), 5.91 (s, 1H), 4.40 (bs, 1H), 3.45 (s, 4H), 3.02 (bs, 1H), 2.91 (s, 3H), 2.55 (dd, $J$ = 17.5, 6.0 Hz, 1H), 1.61 (s, 6H); $^{13}$C NMR (125 MHz, DMSO–d$_6$) δ 183.7, 183.0, 177.3, 176.4, 153.0, 139.5, 136.1, 134.9, 132.2, 128.8, 127.3, 108.9, 49.4, 46.7, 36.5, 25.4, 24.4, 23.8; IR (KBr) υ 2948, 2842, 1767, 1686, 1615, 1561, 1431, 1377, 1334, 1275, 1235, 1114, 1040, 997, 951, 848, 775, 686 cm$^{-1}$; HRMS (Q-TOF, ESI) calcd for C$_{20}$H$_{21}$N$_2$O$_4$ [M+H]$^+$ 353.1496, found 353.1509.

3-(6-(Butylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)pyrrolidine-2,5-dione (3bb):

50 mg (76%); Orange solid; mp = 190.0–192.0 °C; $^1$H NMR (500 MHz, DMSO–d$_6$) δ 11.06 (s, 1H), 8.04–8.01 (m, 1H), 7.69–7.66 (m, 2H), 7.54 (t, $J$ = 6.0 Hz, 1H), 5.59 (s, 1H), 4.36 (bs, 1H), 3.14 (q, $J$ = 7.0 Hz, 2H), 2.91 (bs, 1H), 2.58 (dd, $J$ = 17.0, 6.5 Hz, 1H), 1.54 (quint, $J$ = 7.0 Hz, 2H), 1.32 (sextet, $J$ = 7.5 Hz, 2H), 0.89 (t, $J$ = 7.5 Hz, 3H); $^{13}$C NMR (125 MHz, DMSO–d6) δ 183.2, 181.6, 178.5, 177.8, 147.5, 140.8, 136.7, 132.4, 131.9, 129.8, 126.8, 100.5, 48.7, 41.5, 37.8, 29.4, 19.7, 13.7; IR (KBr) υ 3346, 3146, 2976, 2891, 2891, 1770, 1699, 1609, 1558, 1510, 1459, 1378, 1339, 1251, 1165, 1073, 954, 779, 677 cm$^{-1}$; HRMS (Q-TOF, ESI) calcd for C$_{18}$H$_{19}$N$_2$O$_4$ [M+H]$^+$ 327.1339, found 327.1339.

3-(6-(Butylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1-ethylpyrrolidine-2,5-dione (3bc):

64 mg (90%); Red solid; mp = 182.0–183.4 °C; $^1$H NMR (500 MHz, DMSO–d$_6$) δ 8.05–8.03 (m, 1H), 7.71–7.66 (m, 2H), 7.54 (t, $J$ = 6.0 Hz, 1H), 5.59 (s, 1H), 4.34 (bs, 1H), 3.52–3.44 (m, 2H), 3.13 (q, $J$ = 6.5 Hz, 2H), 2.97 (bs, 1H), 2.56 (dd, $J$ = 17.0, 6.0 Hz, 1H), 1.52 (quint, $J$ = 7.5 Hz, 2H), 1.31 (sextet, $J$ = 7.5 Hz, 2H),
1.15 (t, J = 7.0 Hz, 3H), 0.88 (t, J = 7.0 Hz, 3H); \(^{13}\text{C}\) NMR (125 MHz, DMSO–d\(_6\)) \(\delta\) 183.1, 181.5, 176.9, 176.1, 147.5, 141.0, 136.5, 132.4, 131.9, 129.7, 126.9, 100.5, 47.2, 41.5, 36.5, 33.0, 29.5, 19.7, 13.7, 12.8; IR (KBr) \(\nu\) 3321, 2976, 2891, 1768, 1687, 1607, 1564, 1515, 1454, 1389, 1341, 1249, 1125, 1070, 954, 848, 786, 679 cm\(^{-1}\); HRMS (Q-TOF, ESI) calcd for C\(_{20}\)H\(_{23}\)N\(_2\)O\(_4\) [M+H]\(^+\) 355.1652, found 355.1674.

1-Benzyl-3-(6-(butylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)pyrrolidine-2,5-dione (3bd):

![Diagram of molecule](image)

66 mg (79%); Orange solid; mp = 166.0–167.1 °C; \(^1\text{H}\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.06–8.04 (m, 1H), 7.73–7.67 (m, 2H), 7.59 (t, J = 6.0 Hz, 1H), 7.37–7.32 (m, 4H), 7.29–7.25 (m, 1H), 5.61 (s, 1H), 4.71 (d, J = 15.0 Hz, 1H), 4.60 (d, J = 15.0 Hz, 1H), 4.49 (bs, 1H), 3.15 (q, J = 7.0 Hz, 2H), 3.07 (bs, 1H), 2.66 (dd, J = 17.5, 6.5 Hz, 1H), 1.54 (quint, J = 7.5 Hz, 2H), 1.32 (sextet, J = 7.5 Hz, 2H), 0.89 (t, J = 7.5 Hz, 3H); \(^{13}\text{C}\) NMR (125 MHz, DMSO–d\(_6\)) \(\delta\) 183.2, 181.5, 176.9, 176.2, 147.6, 140.9, 136.6, 136.3, 132.4, 131.9, 129.8, 128.4, 127.5, 127.2, 127.0, 100.5, 47.3, 41.5, 41.4, 36.5, 29.4, 19.7, 13.7; IR (KBr) \(\nu\) 3324, 2935, 2872, 1771, 1700, 1514, 1443, 1399, 1353, 1243, 1169, 997, 839, 777, 733, 687, 645 cm\(^{-1}\); HRMS (Q-TOF, ESI) calcd for C\(_{25}\)H\(_{25}\)N\(_2\)O\(_4\) [M+H]\(^+\) 417.1809, found 417.1820.

1-(tert-butyl)-3-(6-(butylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)pyrrolidine-2,5-dione (3be):

![Diagram of molecule](image)

23 mg (30%); Orange solid; mp = 139.3–140.1 °C; \(^1\text{H}\) NMR (500 MHz, DMSO–d\(_6\)) \(\delta\) 8.02 (t, J = 4.5 Hz, 1H), 7.70–7.64 (m, 2H), 7.50 (t, J = 6.0 Hz, 1H), 5.58 (s, 1H), 4.22 (bs, 1H), 3.14 (q, J = 7.0 Hz, 2H), 2.86 (bs, 1H), 2.46 (dd, J = 17.0, 6.5 Hz, 1H), 1.56 (s, 9H), 1.52 (quint, J = 7.5 Hz, 2H), 1.31 (sextet, J = 7.5 Hz, 2H), 0.88 (t, J = 7.5 Hz, 3H); \(^{13}\text{C}\) NMR (125 MHz, DMSO–d\(_6\)) \(\delta\) 183.0, 181.6, 177.9, 177.1, 147.4, 140.9, 137.2, 132.4, 131.8, 129.6, 126.8, 100.6, 56.8, 47.1, 41.5, 36.6, 29.5, 28.1, 19.7, 13.7; IR (KBr) \(\nu\) 3337, 2960, , 2873, 1769, 1697, 1624, 1571, 1521, 1456, 1352, 1257, 1213, 1160, 1119, 990, 777, 684 cm\(^{-1}\); HRMS (Q-TOF, ESI) calcd for C\(_{22}\)H\(_{27}\)N\(_2\)O\(_4\) [M+H]\(^+\) 383.1965, found 383.1976.
3-(6-(Butylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1-phenylpyrrolidine-2,5-dione (3bf):

![Chemical Structure](image)

55 mg (69%); Yellow solid; mp = 190.4–191.0 °C; $^1$H NMR (500 MHz, DMSO–d$_6$) δ 8.08–8.07 (m, 1H), 7.79 (dd, $J = 8.0$, 1.5 Hz, 1H), 7.72 (t, $J = 7.5$, Hz, 1H), 7.61 (t, $J = 6.0$, Hz, 1H), 7.53 (t, $J = 7.5$, Hz, 2H), 7.43 (t, $J = 7.5$, Hz, 1H), 7.40–7.38 (m, 2H), 5.67 (s, 1H), 4.56 (bs, 1H), 3.17–3.14 (m, 3H), 2.76 (dd, $J = 17.5$, 6.5 Hz, 1H), 1.54 (quint, $J = 7.0$ Hz, 2H), 1.32 (sextet, $J = 7.5$ Hz, 3H); $^{13}$C NMR (125 MHz, DMSO–d$_6$) δ 183.3, 181.5, 176.2, 175.6, 147.7, 141.0, 136.3, 133.3, 132.5, 132.0, 129.7, 128.8, 128.1, 127.4, 127.1, 100.5, 47.3, 41.6, 36.7, 29.5, 19.7, 13.7; IR (KBr) υ 3293, 2977, 2896, 1774, 1700, 1605, 1563, 1499, 1385, 1345, 1246, 1164, 1068, 954, 961, 882, 828, 755, 692 cm$^{-1}$; HRMS (Q-TOF, ESI) calcd for C$_{24}$H$_{23}$N$_2$O$_4$ [M+H]$^+$ 403.1652, found 403.1658.

**General procedure for regioselective C–H alkenylation and spectral data (4ab-4lb, 4aa-4af):**

Typical procedure for regioselective C–H alkenylation at C5 of 2-amino-1,4-naphthoquinone with N-substituted maleimide: To an oven-dried sealed tube with 2-(isopropylamino)naphthalene-1,4-dione (1a) (43 mg, 0.2 mmol, 100 mol %), N-Methylmaleimide (2a) (33.3 mg, 0.3 mmol, 150 mol %), [RhCp*Cl$_2$)$_2$ (6.2 mg, 0.01 mmol, 5 mol %), AgSbF$_6$ (13.7 mg, 0.04 mmol, 20 mol %) and Ag$_2$CO$_3$ (110.3 mg, 0.4 mmol, 200 mol %) was added in DCE (1 mL). The reaction mixture was allowed to stir at 80 ºC for 16 h. After cooling at room temperature, the reaction mixture was evaporated. The resulting residue was purified by neutral alumina column chromatography (eluent; hexane/EtOAc = 5:1 to 1:10) provide 4aa (43 mg) in 66% yield.

3-(6-(Isopropylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1H-pyrrole-2,5-dione (4ab):

46 mg (74%); Orange solid; mp = 182.1–184.4 °C; $^1$H NMR (500 MHz, DMSO–d$_6$) δ 10.93 (s, 1H), 8.13 (dd, $J = 8.0$, 1.5 Hz, 1H), 7.80 (t, $J = 7.5$ Hz, 1H), 7.69 (dd, $J = 8.0$, 1.0 Hz, 1H), 7.30 (d, $J = 8.5$ Hz, 1H), 6.68 (s, 1H), 5.63 (s, 1H), 3.72–3.65 (m, 1H), 1.21 (d, $J = 6.5$ Hz, 6H); $^{13}$C NMR (125 MHz, DMSO–d$_6$) δ 181.5, 181.1, 172.3, 170.5, 150.8, 148.2, 136.7,
131.9, 131.7, 131.1, 128.8, 128.0, 124.3, 99.8, 49.3, 26.8, 20.2; IR (KBr) ν 3431, 3336, 3018, 2929, 2751, 1724, 1604, 1527, 1349, 1239, 1166, 1065, 890, 772 cm⁻¹; HRMS (Q-TOF, ESI) calcd for C₁₇H₁₅N₂O₄ [M+H]⁺ 311.1026, found 311.1036.

3-(6-(Butylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1H-pyrrole-2,5-dione (4bb)

39 mg (60%); Orange solid; mp = 230.4–232.6 °C; ¹H NMR (500 MHz, DMSO–d₆) δ 10.92 (s, 1H), 8.13 (dd, J = 9.0, 1.5 Hz, 1H), 7.79 (t, J = 7.5 Hz, 1H), 7.68 (dd, J = 7.5, 1.5 Hz, 1H), 7.65 (t, J = 6.0 Hz, 1H), 6.66 (s, 1H), 5.59 (s, 1H), 3.17 (q, J = 7.0 Hz, 2H), 1.55 (quint, J = 7.5 Hz, 2H), 1.33 (sextet, J = 7.5 Hz, 2H), 0.90 (t, J = 7.5 Hz, 3H); ¹³C NMR (125 MHz, DMSO–d₆) δ 181.4, 181.1, 172.3, 170.4, 150.8, 148.0, 136.6, 131.9, 131.7, 131.1, 128.8, 127.9, 124.3, 99.6, 41.6, 29.4, 19.7, 13.7; IR (KBr) ν 3440, 3360, 3150, 3049, 2926, 2742, 1731, 1663, 1609, 1557, 1520, 1343, 1238, 839, 767 cm⁻¹; HRMS (Q-TOF, ESI) calcd for C₁₈H₁₇N₂O₄ [M+H]⁺ 325.1183, found 325.1183.

3-(6-(Isobutylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1H-pyrrole-2,5-dione (4cb): 41 mg (63%); Orange solid; mp = 230.4–232.6 °C; ¹H NMR (500 MHz, DMSO–d₆) δ 10.92 (s, 1H), 8.14 (dd, J = 8.0, 1.5 Hz, 1H), 7.80 (t, J = 7.5 Hz, 1H), 7.72–7.68 (m, 2H), 6.67 (s, 1H), 5.61 (s, 1H), 3.00 (t, J = 7.0 Hz, 2H), 2.01–1.93 (m, 1H), 0.90 (d, J = 6.5 Hz, 6H); ¹³C NMR (125 MHz, DMSO–d₆) δ 181.9, 181.5, 172.7, 170.9, 151.2, 148.6, 137.1, 132.2, 132.3, 131.5, 129.2, 128.4, 124.8, 100.29, 49.7, 27.2, 20.6; IR (KBr) ν 3432, 3356, 3158, 3062, 2925, 2861, 2731, 1724, 1683, 1607, 1558, 1521, 1460, 1348, 1251, 1171, 1062, 979, 861, 771 cm⁻¹; HRMS (Q-TOF, ESI) calcd for C₁₈H₁₇N₂O₄ [M+H]⁺ 325.1183, found 325.1196.

3-(6-((Cyclohexylmethyl)amino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1H-pyrrole-2,5-dione (4db):

45 mg (62%); Red solid; mp = 228.0–230.2 °C; ¹H NMR (500 MHz, DMSO–d₆) δ 10.91 (s, 1H), 8.13 (dd, J = 7.5, 1.0 Hz, 1H), 7.79 (d, J = 7.5 Hz, 1H), 7.68 (dd, J = 7.5, 1.5 Hz, 2H), 6.66 (s, 1H), 5.59 (s, 1H),
3.02 (t, $J = 6.5$ Hz, 2H), 1.71–1.59 (m, 6H), 1.22–1.11 (m, 3H), 0.94 (t, $J = 12.0$ Hz, 2H); $^{13}$C NMR (125 MHz, DMSO–d$_6$) δ 181.4, 181.1, 142.3, 170.5, 150.8, 148.2, 136.6, 135.3, 131.9, 131.1, 128.8, 128.0, 124.3, 99.8, 48.0, 36.1, 30.5, 26.0, 25.4; IR (KBr) ν 3413, 3281, 3145, 2925, 2854, 2747, 1724, 1681, 1600, 1556, 1457, 1332, 1250, 1183, 1132, 1057, 966, 882, 777 cm$^{-1}$; HRMS (Q-TOF, ESI) calcd for C$_{21}$H$_{21}$N$_2$O$_4$ [M+H]$^+$ 365.1496, found 365.1496.

3-(6-((4-Fluorobenzyl)amino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1H-pyrrole-2,5-dione (4eb)

34 mg (47%); Light brown solid; mp = 291.7–292.5 °C; $^1$H NMR (500 MHz, DMSO–d$_6$) δ 10.91 (s, 1H), 8.29 (t, $J = 6.5$ Hz, 1H), 8.15 (dd, $J = 8.0$, 1.5 Hz, 1H), 7.81 (t, $J = 8.0$ Hz, 1H), 7.68 (dd, $J = 7.5$, 1.5 Hz, 1H), 7.40 (dd, $J = 9.0$, 1.0 Hz, 2H), 7.17 (t, $J = 9.0$ Hz, 2H), 6.65 (d, $J = 1.5$ Hz, 1H), 5.52 (s, 1H), 4.42 (d, $J = 6.5$ Hz, 2H); $^{13}$C NMR (125 MHz, DMSO–d$_6$) δ 181.7, 181.1, 172.2, 170.4, 161.3 (d, $J_{C,F} = 241.2$ Hz), 150.7, 147.8, 136.7, 133.5 (d, $J_{C,F} = 2.7$ Hz), 132.1, 131.5, 131.2, 129.2 (d, $J_{C,F} = 8.1$ Hz), 128.8, 128.0, 124.5, 115.3 (d, $J_{C,F} = 21.1$ Hz), 100.9, 44.3; IR (KBr) ν 3442, 3270, 3069, 2924, 2860, 1713, 1610, 1513, 1415, 1344, 1234, 1168, 1105, 908, 836, 765 cm$^{-1}$; HRMS (Q-TOF, ESI) calcd for C$_{21}$H$_{14}$FN$_2$O$_4$ [M+H]$^+$ 377.0932, found 377.0926.

3-(5,8-Dioxo-6-(phenethylamino)-5,8-dihydronaphthalen-1-yl)-1H-pyrrole-2,5-dione (4fb)

34 mg (45%); Light yellowish solid; mp = 208.8–209.4 °C; $^1$H NMR (500 MHz, DMSO–d$_6$) δ 10.94 (s, 1H), 8.13 (dd, $J = 8.0$, 1.5 Hz, 1H), 7.80 (t, $J = 7.5$ Hz, 1H), 7.70 (dd, $J = 8.0$, 1.5 Hz, 1H), 7.65 (t, $J = 6.0$ Hz, 1H), 7.30–7.27 (m, 4H), 7.21 (t, $J = 7.0$ Hz, 1H), 6.68 (d, $J = 1.5$ Hz, 1H), 5.67 (s, 1H), 3.42 (q, $J = 6.5$ Hz, 2H), 2.90 (t, $J = 12.0$ Hz, 2H); $^{13}$C NMR (125 MHz, DMSO–d$_6$) δ 181.6, 181.1, 172.3, 170.5, 150.8, 147.8, 138.9, 136.7, 135.3, 132.0, 131.7, 131.0, 128.8, 128.4, 128.0, 126.3, 124.4, 100.1, 43.3, 33.4; IR (KBr) ν 3460, 3385, 3157, 3059, 2927, 2748, 1723, 1610, 1560, 1508, 1451, 1343, 1288, 1244, 1134, 982, 844, 753 cm$^{-1}$; HRMS (Q-TOF, ESI) calcd for C$_{22}$H$_{17}$N$_2$O$_4$ [M+H]$^+$ 373.1183, found 373.1188.
3-(5,8-Dioxo-6-((3-phenylpropyl)amino)-5,8-dihydronaphthalen-1-yl)-1H-pyrrole-2,5-dione (4gb)

40 mg (52%); Yellow solid; mp = 236.5–238.6 °C; \(^1\)H NMR (500 MHz, DMSO–d<sub>6</sub>) δ 10.93 (s, 1H), 8.13 (dd, J = 8.0, 1.5 Hz, 1H), 7.80 (t, J = 7.5 Hz, 1H), 7.74 (t, J = 6 Hz, 1H), 7.69 (dd, J = 7.5, 1.5 Hz, 1H), 7.28 (t, J = 7.5 Hz, 2H), 7.24 (d, J = 7.0 Hz, 2H), 7.19–7.16 (m, 1H), 6.66 (d, J = 1.5 Hz, 1H), 5.55 (s, 1H), 3.19 (q, J = 7.0 Hz, 2H), 2.64 (t, J = 7.5 Hz, 2H), 1.88 (quint, J = 7.5 Hz, 2H); \(^{13}\)C NMR (125 MHz, DMSO–d<sub>6</sub>) δ 181.5, 181.1, 172.3, 170.5, 150.8, 148.0, 141.5, 136.6, 135.3, 131.9, 131.7, 131.1, 128.8, 128.3, 128.0, 125.9, 124.4, 99.7, 41.6, 32.6, 29.1; IR (KBr) ν 3392, 3158, 3064, 2933, 2744, 1721, 1677, 1609, 1563, 1511, 1462, 1346, 1285, 1238, 1131, 1054, 976, 875, 769 cm<sup>-1</sup>; HRMS (Q-TOF, ESI) calcd for C<sub>23</sub>H<sub>19</sub>N<sub>2</sub>O<sub>4</sub> [M+H]<sup>+</sup> 387.1339, found 387.1363.

3-(5,8-Dioxo-6-((4-phenylbutyl)amino)-5,8-dihydronaphthalen-1-yl)-1H-pyrrole-2,5-dione (4hb)

37 mg (46%); Light yellow solid; mp = 224.1–227.8 °C; \(^1\)H NMR (500 MHz, DMSO–d<sub>6</sub>) δ 10.93 (s, 1H), 8.13 (dd, J = 8.0, 1.5 Hz, 1H), 7.80 (t, J = 7.5 Hz, 1H), 7.72–7.68 (m, 2H), 7.27 (t, J = 7.5 Hz, 2H), 7.21–7.14 (m, 3H), 6.67 (d, J = 1.5 Hz, 1H), 5.61 (s, 1H), 3.20 (q, J = 6.5 Hz, 2H), 2.60 (t, J = 7.0 Hz, 2H), 1.61 (quint, J = 3.5 Hz, 4H); \(^{13}\)C NMR (125 MHz, DMSO–d<sub>6</sub>) δ 181.5, 181.1, 172.3, 170.5, 150.8, 148.0, 142.0, 136.7, 131.9, 131.7, 131.1, 128.8, 128.3, 128.2, 128.0, 125.7, 124.3, 99.7, 41.7, 34.8, 28.4, 27.0; IR (KBr) ν 3397, 3211, 2934, 2863, 1727, 1683, 1609, 1563, 1511, 1349, 1238, 1135, 1100, 1032, 933, 867, 820, 758 cm<sup>-1</sup>; HRMS (Q-TOF, ESI) calcd for C<sub>24</sub>H<sub>21</sub>N<sub>2</sub>O<sub>4</sub> [M+H]<sup>+</sup> 401.1496, found 401.1499.

3-(5,8-Dioxo-6-(pyrrolidin-1-yl)-5,8-dihydronaphthalen-1-yl)-1H-pyrrole-2,5-dione (4ib)

40 mg (63%); Light orange solid; mp = 278.8–280.9 °C; \(^1\)H NMR (500 MHz, DMSO–d<sub>6</sub>) δ 10.90 (s, 1H), 8.09 (dd, J = 8.0, 1.5 Hz, 1H), 7.79 (t, J = 7.5 Hz, 1H), 7.66 (dd, J = 7.5, 1.5 Hz, 1H), 6.67 (s, 1H), 5.56 (s, 1H), 3.90 (s, 2H), 3.33 (s, 2H), 1.92 (quint, J = 4.0 Hz, 4H); \(^{13}\)C NMR
(125 MHz, DMSO–d$_6$) δ 182.2, 180.7, 172.3, 170.4, 150.8, 148.8, 136.0, 132.2, 131.7, 131.4, 128.1, 124.3, 103.6, 51.1, 50.2, 26.2, 23.4; IR (KBr) υ 3127, 2984, 2749, 2383, 2311, 1722, 1596, 1552, 1432, 1329, 1283, 882, 828, 755 cm$^{-1}$; HRMS (Q-TOF, ESI) calcd for C$_{18}$H$_{15}$N$_2$O$_4$ [M+H]$^+$ 323.1026, found 323.1033.

3-(5,8-Dioxo-6-(piperidin-1-yl)-5,8-dihydropyrene-1-yl)-1H-pyrrole-2,5-dione (4jb):

35 mg (52%); Brick red solid; mp = 250.1–251.9 °C; $^1$H NMR (500 MHz, DMSO–d$_6$) δ 10.95 (s, 1H), 8.05 (dd, $J = 8.0$, 1.5 Hz, 1H), 7.81 (t, $J = 7.5$ Hz, 1H), 7.67 (dd, $J = 8.0$, 1.5 Hz, 1H), 6.70 (d, $J = 1.5$ Hz, 1H), 5.91 (s, 1H), 3.49 (s, 4H), 1.64 (s, 6H); $^{13}$C NMR (125 MHz, DMSO–d$_6$) δ 182.4, 182.0, 172.2, 170.4, 153.4, 150.3, 135.7, 133.5, 132.1, 130.6, 128.4, 128.1, 125.0, 108.1, 49.6, 25.5, 23.7; IR (KBr) υ 3422, 2927, 1724, 1683, 1604, 1553, 1437, 1341, 1283, 977, 884, 760 cm$^{-1}$; HRMS (Q-TOF, ESI) calcd for C$_{19}$H$_{17}$N$_2$O$_4$ [M+H]$^+$ 337.1183, found 337.1185.

3-(6-(Ethyl(methyl)amino)-5,8-dioxo-5,8-dihydropyrene-1-yl)-1H-pyrrole-2,5-dione (4kb):

35 mg (57%); Light orange solid; mp = 228.7–229.9 °C; $^1$H NMR (500 MHz, DMSO–d$_6$) δ 10.92 (s, 1H), 8.05 (dd, $J = 8.0$, 1.5 Hz, 1H), 7.81 (t, $J = 7.5$ Hz, 1H), 7.67 (dd, $J = 7.5$, 1.5 Hz, 1H), 6.69 (d, $J = 1.5$ Hz, 1H), 5.68 (s, 1H), 3.59 (q, $J = 7.0$ Hz, 2H), 3.05 (s, 3H), 1.22 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (125 MHz, DMSO–d$_6$) δ 182.5, 181.2, 172.2, 170.4, 151.9, 150.5, 135.7, 133.1, 131.9, 131.0, 128.3, 128.0, 124.7, 104.9, 48.5, 39.2, 12.8; IR (KBr) υ 3400, 2926, 2312, 1723, 1599, 1450, 1450, 1333, 1237, 1217, 1059, 926, 848, 770 cm$^{-1}$; HRMS (Q-TOF, ESI) calcd for C$_{17}$H$_{17}$N$_2$O$_4$ [M+H]$^+$ 311.1026, found 311.1035.

3-(6-(Butylamino)-7-chloro-5,8-dioxo-5,8-dihydropyrene-1-yl)-1H-pyrrole-2,5-dione (4lb):

45 mg (62%); Orange solid; mp = 239.7–241.2 °C; $^1$H NMR (500 MHz, DMSO–d$_6$) δ 10.97 (s, 1H), 8.13 (dd, $J = 8.0$, 1.5 Hz, 1H), 7.82 (t, $J = 8.0$ Hz, 1H), 7.71 (dd, $J = 7.5$, 1.5 Hz, 1H), 7.62 (s, 1H), 6.71 (d,
$J = 1.5$ Hz, 1H), 3.71 (q, $J = 7.0$ Hz, 2H), 1.60 (quint, $J = 7.5$ Hz, 2H), 1.33 (sextet, $J = 7.5$ Hz, 2H), 0.91 (t, $J = 7.5$ Hz, 3H); $^{13}$C NMR (125 MHz, DMSO–d$_6$) $\delta$ 179.7, 175.3, 172.1, 170.4, 150.2, 144.8, 144.6, 136.7, 132.4, 130.7, 130.5, 129.1, 128.5, 124.9, 43.7, 32.9, 19.3, 13.7; IR (KBr) $\nu$ 3274, 3212, 3088, 2950, 2871, 2697, 1728, 1690, 1528, 1591, 1335, 1138, 1062, 931, 843, 754 cm$^{-1}$; HRMS (Q-TOF, ESI) calcd for C$_{18}$H$_{16}$N$_2$O$_4$ [M+H]$^+$ 359.0793, found 359.0801.

3-(6-(Isopropylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1-methyl-1H-pyrrole-2,5-dione (4aa)

43 mg (66%); Orange solid; mp = 175.2–178.7 °C; $^1$H NMR (500 MHz, DMSO–d$_6$) $\delta$ 8.15 (dd, $J = 8.0$, 1.0 Hz, 1H), 7.81 (t, $J = 7.5$ Hz, 1H), 7.69 (dd, $J = 7.5$, 1.0 Hz, 1H), 7.32 (d, $J = 8.5$ Hz, 1H), 6.81 (s, 1H), 5.63 (s, 1H), 3.71–3.65 (m, 1H), 2.65 (s, 3H), 1.21 (d, $J = 6.5$ Hz, 6H); $^{13}$C NMR (125 MHz, DMSO–d$_6$) $\delta$ 181.6, 181.2, 170.9, 169.2, 150.3, 147.0, 136.6, 132.0, 131.7, 131.1, 128.6, 128.1, 123.6, 99.9, 43.6, 23.7, 21.1; IR (KBr) $\nu$ 3446, 3342, 2926, 2859, 1708, 1609, 1566, 1512, 1447, 1350, 1241, 1169, 1128, 1044, 972, 860, 778 cm$^{-1}$; HRMS (Q-TOF, ESI) calcd for C$_{19}$H$_{17}$N$_2$O$_4$ [M+H]$^+$ 325.1183, found 325.1227.

1-Ethyl-3-(6-(isopropylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1H-pyrrole-2,5-dione (4ac)

46 mg (68%); Reddish orange solid; mp = 208.1–210.9 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.21 (d, $J = 8.0$ Hz, 1H), 7.67 (t, $J = 7.5$ Hz, 1H), 7.53 (d, $J = 7.5$ Hz, 1H), 6.43 (s, 1H), 5.77 (d, $J = 7.5$ Hz, 1H), 5.68 (s, 1H), 3.69–3.58 (m, 3H), 1.30–1.28 (m, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 182.6, 181.5, 170.7, 169.1, 150.4, 146.2, 136.3, 132.4, 131.7, 131.5, 129.2, 128.6, 123.5, 101.4, 44.1, 33.1, 21.7, 14.0; IR (KBr) $\nu$ 3338, 2923, 2859, 1707, 1620, 1566, 1520, 1449, 1405, 1318, 1250, 1120, 1166, 1097, 1012, 960, 886, 839, 762 cm$^{-1}$; HRMS (Q-TOF, ESI) calcd for C$_{19}$H$_{19}$N$_2$O$_4$ [M+H]$^+$ 339.1339, found 339.1348.

1-Benzyl-3-(6-(isopropylamino)-5,8-dioxo-5,8-dihydronaphthalen-1-yl)-1H-pyrrole-2,5-dione (4ad)

58 mg (73%); Light orange solid; mp = 198.4–200.2 °C; $^1$H NMR (500 MHz, DMSO–d$_6$) $\delta$ 8.16 (dd, $J = 7.5$, 1.5 Hz, 1H), 7.83 (t, $J = 7.5$ Hz, 1H), 7.74 (dd, $J = 7.5$, 1.5 Hz, 1H), 7.39–7.33 (m,
6H), 6.88 (s, 1H), 5.66 (s, 1H), 4.68 (s, 2H), 3.74–3.67 (m, 1H), 1.21 (d, \( J = 6.5 \) Hz, 6H); \(^{13}\)C NMR (125 MHz, DMSO–d\(_6\)) \( \delta \) 181.5, 181.2, 170.6, 168.8, 150.4, 147.0, 136.9, 136.7, 132.0, 131.7, 131.2, 128.6, 128.2, 127.3, 127.0, 123.7, 99.9, 43.6, 40.7, 21.1; IR (KBr) \( \nu \) 3338, 2924, 2859, 1764, 1706, 1611, 1566, 1512, 1428, 1348, 1237, 1139, 1099, 960, 849, 767 cm\(^{-1}\); HRMS (Q-TOF, ESI) calcd for C\(_{24}\)H\(_{21}\)N\(_2\)O\(_4\) [M+H]\(^+\) 401.1496, found 401.1523.

1-(tert-butyl)-3-(6-(isopropylamino)-5,8-dioxo-5,8-dihydropyridazine-1-yl)-1H-pyrrole-2,5-dione (4ae)

33 mg (46%); Light red solid; mp = 176.5–178.4 \(^{\circ}\)C; \(^1\)H NMR (500 MHz, DMSO–d\(_6\)) \( \delta \) 8.13 (dd, \( J = 8.0, 1.5 \) Hz, 1H), 7.79 (t, \( J = 7.5 \) Hz, 1H), 7.68 (dd, \( J = 7.5, 1.5 \) Hz, 1H), 7.26 (d, \( J = 8.5 \) Hz, 1H), 6.63 (s, 1H), 3.73–3.66 (m, 1H), 1.55 (s, 9H), 1.21 (d, \( J = 6.5 \) Hz, 6H); \(^{13}\)C NMR (125 MHz, DMSO–d\(_6\)) \( \delta \) 181.6, 181.2, 171.9, 167.0, 149.5, 146.9, 136.6, 131.9, 131.7, 131.1, 128.8, 128.0, 123.6, 100.0, 56.4, 43.5, 28.6, 21.1; IR (KBr) \( \nu \) 3349, 2983, 1700, 1623, 1565, 1517, 1450, 1382, 1237, 1133, 1063, 958, 852, 771 cm\(^{-1}\); HRMS (Q-TOF, ESI) calcd for C\(_{21}\)H\(_{23}\)N\(_2\)O\(_4\) [M+H]\(^+\) 367.1652, found 367.1676.

3-(6-(Isopropylamino)-5,8-dioxo-5,8-dihydropyridazine-1-yl)-1-phenyl-1H-pyrrole-2,5-dione (4af)

52 mg (67%); Orange solid; mp = 214.5–216.3 \(^{\circ}\)C; \(^1\)H NMR (500 MHz, DMSO–d\(_6\)) \( \delta \) 8.18 (dd, \( J = 8.0, 1.5 \) Hz, 1H), 7.86 (t, \( J = 7.5 \) Hz, 1H), 7.79 (dd, \( J = 7.5, 1.0 \) Hz, 1H), 7.53 (t, \( J = 8.0 \) Hz, 2H), 7.43 (d, \( J = 7.5 \) Hz, 1H), 7.37 (d, \( J = 7.0 \) Hz, 3H), 7.01 (s, 1H), 5.69 (s, 1H), 3.73–3.66 (m, 1H), 1.21 (d, \( J = 6.5 \) Hz, 6H); \(^{13}\)C NMR (125 MHz, DMSO–d\(_6\)) \( \delta \) 182.1, 181.6, 170.0, 168.4, 150.7, 147.5, 137.1, 132.5, 132.4, 132.3, 131.7, 129.5, 128.9, 128.8, 128.2, 127.0, 124.1, 100.3, 44.1, 21.6; IR (KBr) \( \nu \) 3346, 2923, 2859, 1712, 1619, 1564, 1506, 1382, 1237, 1133, 1096, 1016, 961, 884, 840, 763 cm\(^{-1}\); HRMS (Q-TOF, ESI) calcd for C\(_{23}\)H\(_{19}\)N\(_2\)O\(_4\) [M+H]\(^+\) 387.1339, found 387.1346.

3-(6-(Diethylamino)-5,8-dioxo-5,8-dihydropyridazine-1-yl)-1H-pyrrole-2,5-dione (4sb) and 3-(6-(ethylamino)-5,8-dioxo-5,8-dihydropyridazine-1-yl)-1H-pyrrole-2,5-dione (4sb'):
Procedure for competitive reaction between 2-amino-1,4-naphthoquinone and acetophenone with maleimide: To an oven-dried sealed tube with 2-(isopropylamino)naphthalene-1,4-dione (1a) (21.5 mg, 0.1 mmol, 100 mol %), acetophenone (5) (12.0 mg, 0.1 mmol, 100 mol %), N-Methylmaleimide (2a) (11.1 mg, 0.1 mmol, 100 mol %), [RhCp*Cl2]2 (3.1 mg, 0.005 mmol, 5 mol %), AgSbF6 (6.8 mg, 0.02 mmol, 20 mol %) and Ag2CO3 (55.1 mg, 0.2 mmol, 200 mol %) was added in DCE (1 mL). The reaction mixture was allowed to stir at 80 °C for 16 h. After cooling at room temperature, the reaction mixture was evaporated. The resulting residue was purified by neutral alumina column chromatography (eluent; hexane/EtOAc = 5:1 to 1:10) to provide 4aa (21 mg) in 65% yield.

Procedure for competitive reaction between maleimide and acrylate with 2-amino-1,4-naphthoquinone: To an oven-dried sealed tube with 2-(isopropylamino)naphthalene-1,4-dione (1a) (21.5 mg, 0.1 mmol, 100 mol %), N-Methylmaleimide (2a) (11.1 mg, 0.1 mmol, 100 mol %), ethyl acrylate (7) (10.0 mg, 0.1 mmol, 100 mol %), [RhCp*Cl2]2 (3.1 mg, 0.005 mmol, 5 mol...
%, AgSbF$_6$ (6.8 mg, 0.02 mmol, 20 mol %) and Ag$_2$CO$_3$ (55.1 mg, 0.2 mmol, 200 mol %) was added in DCE (1 mL). The reaction mixture was allowed to stir at 80 °C for 16 h. After cooling at room temperature, the reaction mixture was evaporated. The resulting residue was purified by neutral alumina column chromatography (eluent; hexane/EtOAc = 10:1 to 1:1) to provide 8 (20.1 mg) in 64% and 4aa (2.7 mg) in 8% yield.

**Ethyl (E)-3-(6-(isopropylamino)-5,8-dioxo-5,8-dihyronaphthalen-1-yl)acrylate (8)**

40 mg (64%); Orange solid; mp = 141.5–144.6 °C; $^1$H NMR (500 MHz, DMSO–d$_6$) δ 8.72 (d, $J$ = 16.0 Hz, 1H), 8.07 (dd, $J$ = 8.0, 1.5 Hz, 1H), 7.95 (dd, $J$ = 8.0, 1.0 Hz, 1H), 7.72 (t, $J$ = 8.0 Hz, 1H), 7.14 (d, $J$ = 8.5 Hz, 1H), 6.35 (d, $J$ = 16.0 Hz, 1H), 5.68 (s, 1H), 4.22 (q, $J$ = 7.0 Hz, 2H), 3.72–3.63 (m, 1H), 1.28 (t, $J$ = 7.0 Hz, 3H), 1.21 (d, $J$ = 6.5 Hz, 6H); $^{13}$C NMR (125 MHz, DMSO–d$_6$) δ 183.6, 181.5, 166.0, 146.5, 146.3, 135.2, 131.9, 131.7, 129.9, 127.9, 120.4, 101.2, 60.1, 45.1, 43.5, 21.1, 14.2; IR (KBr) ν 3420, 2979, 2354, 2252, 2124, 1664, 1618, 1247, 1175, 1094, 1011, 821, cm$^{-1}$; HRMS (Q-TOF, ESI) calcd for C$_{18}$H$_{19}$NO$_4$ [M+H]$^+$ 314.1387, found 314.1396.
Control experiment for dealkylation

General Procedure for dealkylation reaction:
To an oven-dried sealed tube with 2-(diethylamino)naphthalene-1,4-dione (1s) (22.9 mg, 0.1 mmol, 100 mol %) in DCE (1 mL) was added catalyst and additives as per the above table. The reaction mixture was allowed to stir at 80 °C for 16 h. After cooling at room temperature, the reaction mixture was evaporated and the residue was passed through neutral alumina column chromatography (eluent; hexane/EtOAc = 10:1 to 4:1) to provide inseparable mixture of 1s and 1s'.

The ratio of 1s:1s’ was determined by $^1$H NMR
$^1$H NMR and $^{13}$C NMR Copies of all products

3aa

DG-56-R

3aa
Single Crystal X-ray data of 3bc

No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report

Datablock: DG83R

Bond precision: C-C = 0.0012 A  Wavelength=0.71073 Cell:
a=10.5905(2)  b=16.0282(4)  c=11.3851(3)
beta=116.637(1) gamma=90

alpha=90
Temperature: 135 K

Calculation
Volume 1727.47(7) 1727.47(7)
Space group P 21/c  P 1 21/c 1
Hall group -P 2ybC -P 2ybC
Moiety formula C20 H22 N2 O4

Sum formula C20 H22 N2 O4
Mr 354.40 354.39
Dx g cm-3 1.363 1.363
Z 4 4
Mu (mm-1) 0.096 0.096
F000 752.0 752.0
F000' 752.36
h,k,lmax 16,24,17 16,24,17
Nref 6628 6609
Tmin,Tmax 0.974,0.982 0.964,0.982
Tmin' 0.964

Correction method= # Reported T Limits: Tmin=0.964 Tmax=0.982 AbsCorr = MULTI SCAN
Data completeness= 0.997 Theta(max)= 33.210
R(reflections)= 0.0397( 5586) wR2(reflections)= 0.1129( 6609)
S = 1.051

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C
PLAT094_ALERT_2_C Ratio of Maximum / Minimum Residual Density .... 2.62 Report PLAT911_ALERT_3_C Missing FCF Refl Between Tmin & STh/L= 0.600 15 Report PLAT913_ALERT_3_C Missing # of Very Strong Reflections in FCF .... 6 Note

Alert level G
PLAT066_ALERT_1_G Predicted and Reported Tmin&max Range Identical 1.45 Ang. ? Check
PLAT333_ALERT_2_G Large Aver C6-Ring C-C Dist C9 -C14 (Centro SPGR) S Verify
PLAT793_ALERT_4_G Model has Chirality at C4 Missing # of FCF Reflection(s) Below Theta(Min).
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . Please Do ! PLAT910_ALERT_3_G
Missing # of FCF Reflections Above STh/L= 0.600 4 Note PLAT912_ALERT_4_G Missing # of FCF Bonds with Positive Residual Density. 19 Info

0 ALERT level A = Most likely a serious problem - resolve or explain
0 ALERT level B = A potentially serious problem, consider carefully
3 ALERT level C = Check. Ensure it is not caused by an omission or oversight
7 ALERT level G = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
3 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low

S54
Thermal ellipsoid plot of the organic compound with atom numbering scheme (50% probability factor for the thermal ellipsoids)

**PLATON version of 03/05/2019; check.def file version of 29/04/2019**

**Datablock DG83R - ellipsoid plot**
HMBC Spectra of 4bb