SUPPORTING INFORMATION

Novel Synthesis of bicycles with fused pyrrole,
indole, oxazole and imidazole rings.

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1. General.

Melting points were determined on a hot-stage apparatus and are uncorrected. All NMR spectra were recorded in CDCl₃, with TMS as the internal standard for ¹H (300 MHz) or the solvent as the internal standard for ¹³C (75 MHz). THF was dried over sodium/benzophenone and used freshly distilled. Column chromatography was conducted on silica gel 200–425 meshes.

2. Characterization data for compounds 1a–h.

3,3-Dimethyl-1*H*-pyrrolo[1,2-*c*]oxazol-1-one (1a): white needles from methanol (80%), mp 52–53 °C; ¹H NMR: δ 6.95 (br s, 1H), 6.73 (d, *J* = 3.6 Hz, 1H), 6.51 (dd, *J* = 3.6, 2.1 Hz, 1H), 1.80 (s, 6H); ¹³C NMR: δ 159.1, 120.3, 117.0, 116.9, 108.6, 93.7, 28.2. Anal. Calcd for C₈H₉NO₂: C, 63.56; H, 6.00; N, 9.27. Found: C, 63.50; H, 6.17; N, 9.14.

(±)-3-Isopropylpyrrolo[1,2-*c*]oxazol-1-one (1b): colorless oil (98%); ¹H NMR: δ 6.99 (d, *J* = 1.7 Hz, 1H), 6.75 (d, *J* = 3.7 Hz, 1H), 6.53–6.51 (m, 1H), 5.91 (d, *J* = 3.2 Hz, 1H), 2.28 (septet of a doublet, *J* = 6.9, 3.2 Hz, 1H), 1.08 (d, *J* = 6.9 Hz, 3H), 0.83 (d, *J* = 7.0 Hz, 3H); ¹³C NMR: δ 159.8, 120.8, 118.5, 116.9, 108.2, 91.8, 33.5, 16.1, 13.9. Anal. Calcd for C₉H₁₁NO₂: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.47; H, 7.11; N, 8.37.

Spiro[cyclohexane-1,3'-[1*H*,3*H*]pyrrolo[1,2-*c*]oxazol-1-one] (1c): white needles (80%), mp 99–100 °C; ¹H NMR: δ 6.94 (d, *J* = 2.3 Hz, 1H), 6.73 (d, *J* = 4.3 Hz, 1H), 4.49 (dd, *J* = 4.3, 2.3 Hz, 1H), 1.99–1.78 (m, 9H), 1.44–1.37 (m, 1H); ¹³C NMR: δ 159.4, 120.2, 117.3, 116.4, 108.2, 94.9, 37.9, 24.0, 22.4. Anal. Calcd for C₁₁H₁₃NO₂: C, 69.09; H, 6.85; N, 7.32. Found: C, 69.29; H, 6.95; N, 7.26.

(±)-3-*p*-Tolylpyrrolo[1,2-*c*]oxazol-1-one (1d): white needles from methanol (76%), mp 143–144 °C; ^1H NMR: δ 7.24 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 6.84–6.81 (m, 3H), 6.54–6.52 (m, 1H), 2.39 (s, 3H); ^{13}C NMR: δ 159.3, 141.2, 131.7, 129.9, 126.7, 120.7, 118.9, 117.4, 108.7, 88.6, 21.3. Anal. Calcd for $\text{C}_{13}\text{H}_{11}\text{NO}_2$: C, 73.22; H, 5.20; N, 6.57. Found: C, 73.04; H, 5.09; N, 6.60.

Spiro[cyclopentane-1,3'-[1*H*,3*H*]pyrrolo[1,2-*c*]oxazol-1-one] (1e): colorless oil (81%); ^1H NMR: δ 6.96 (d, J = 2.1 Hz, 1H), 6.72 (d, J = 3.7 Hz, 1H), 6.52 (dd, J = 3.7, 2.5 Hz, 1H), 2.33–2.24 (m, 2H), 2.18–1.94 (m, 6H); ^{13}C NMR: δ 159.1, 120.9, 117.1, 116.7, 108.2, 102.9, 39.6, 23.5. Anal. Calcd for $\text{C}_{10}\text{H}_{11}\text{NO}_2$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.50; H, 6.28; N, 8.34.

3,3-Diethylpyrrolo[1,2-*c*]oxazol-1-one (1f): white microcrystals (80%), mp 39–41 °C; ^1H NMR: δ 6.85 (d, J = 1.8 Hz, 1H), 6.72 (d, J = 3.6 Hz, 1H), 6.57 (dd, J = 3.6, 2.4 Hz, 1H), 2.22–2.10 (m, 2H), 2.04–1.91 (m, 2H), 0.73 (t, J = 7.3 Hz, 6H); ^{13}C NMR: δ 160.0, 122.2, 117.1, 116.9, 108.0, 98.1, 32.3, 6.2. Anal. Calcd for $\text{C}_{10}\text{H}_{13}\text{NO}_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 66.84; H, 7.03; N, 7.68.

(±)-3-Furan-2-yl-pyrrolo[1,2-*c*]oxazol-1-one (1g): white needles from methanol (64%), mp 76–77 °C; ^1H NMR: δ 7.50 (dd, J = 1.8, 0.8 Hz, 1H), 6.94 (ddd, J = 2.5, 0.9, 0.7 Hz, 1H), 6.91 (s, 1H), 6.85 (dd, J = 3.8, 1.0 Hz, 1H), 6.57 (ddd, J = 3.4, 0.8, 0.4 Hz, 1H), 6.56 (dd, J = 3.8, 2.5 Hz, 1H), 6.44 (dd, J = 1.8 Hz, 1H); ^{13}C NMR: δ 158.7, 146.6, 145.0, 120.2, 119.2, 117.5, 111.6, 110.8, 109.1, 81.5. Anal. Calcd for $\text{C}_{10}\text{H}_7\text{NO}_3$: C, 63.49; H, 3.73; N, 7.40. Found: C, 63.23; H, 3.68; N, 7.23.

(±)-3-Methyl-3-phenylpyrrolo[1,2-*c*]oxazol-1-one (1h): colorless oil (47%); ^1H NMR: δ 7.46–7.33 (m, 5H), 6.98 (dd, J = 2.3, 1.0 Hz, 1H), 6.80 (d, J = 3.8 Hz, 1H), 6.54

(dd, $J = 3.7, 2.6$ Hz, 1H), 2.17 (s, 3H); ^{13}C NMR: δ 158.9, 138.5, 129.7, 128.9, 124.8, 120.7, 118.3, 117.3, 108.8, 94.7, 27.6. Anal. Calcd for $\text{C}_{13}\text{H}_{11}\text{NO}_2$: C, 73.22; H, 5.20; N, 6.57. Found: C, 73.11; H, 5.34; N, 6.73.

3. Characterization data for compounds 2a–d and 12.

3,3-Dimethyloxazolo[3,4-*a*]indol-1-one (2a): white needles from methanol (50%), mp 81–82 °C; ^1H NMR: δ 7.79 (d, $J = 8.1$ Hz, 1H), 7.41–7.39 (m, 2H), 7.26–7.21 (m, 1H), 7.07 (s, 1H), 1.93 (s, 6H); ^{13}C NMR: δ 160.0, 132.6, 131.6, 125.3, 124.8, 124.1, 121.5, 110.3, 100.9, 94.7, 27.0. Anal. Calcd for $\text{C}_{12}\text{H}_{11}\text{NO}_2$: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.50; H, 5.37; N, 6.94.

(±)-3-Isopropyloxazolo[3,4-*a*]indol-1-one (2b): white plates from methanol (83%), mp 118–119 °C; ^1H NMR: δ 7.80 (d, $J = 8.2$ Hz, 1H), 7.40–7.37 (m, 2H), 7.28–7.22 (m, 1H), 7.09 (s, 1H), 6.22 (d, $J = 2.3$ Hz, 1H), 2.63 (septet of a doublet, $J = 7.0, 2.3$ Hz, 1H), 1.27 (d, $J = 7.0$ Hz, 3H), 0.63 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR: δ 160.9, 132.6, 132.5, 125.3, 125.1, 124.2, 121.8, 110.7, 101.1, 92.2, 32.8, 17.5, 12.7. Anal. Calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.50; H, 6.22; N, 6.38.

Spiro[cyclohexane-1,3'-[1*H*,3*H*]oxazolo[3,4-*a*]indol-1-one] (2c): colorless oil (16%); ^1H NMR: δ 7.80 (d, $J = 8.1$ Hz, 1H), 7.45–7.36 (m, 2H), 7.26–7.21 (m, 1H), 7.07 (s, 1H), 2.37–2.26 (m, 2H), 1.97–1.87 (m, 6H), 1.58 (s, 1H), 1.52–1.34 (m, 1H); ^{13}C NMR: δ 161.3, 132.7, 132.6, 125.3, 125.1, 124.3, 121.5, 110.7, 100.9, 96.1, 36.8, 24.4, 22.6. Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_2$: C, 74.67; H, 6.27; N, 5.80. Found: C, 74.50; H, 6.17; N, 6.10.

(±)-3-*p*-Tolyloxazolo[3,4-*a*]indol-1-one (2d): white needles from methanol (30%), mp 143–144 °C; ^1H NMR: δ 7.80–7.76 (m, 1H), 7.23–7.16 (m, 7H), 6.96 (s, 1H), 6.95–6.92

(m, 1H), 2.36 (s, 3H); ^{13}C NMR: δ 160.3, 141.4, 132.7, 132.6, 130.6, 129.9, 127.0, 125.4, 125.0, 124.0, 121.9, 110.9, 101.5, 89.0, 21.3. Anal. Calcd for $\text{C}_{17}\text{H}_{13}\text{NO}_2$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.19; H, 4.99; N, 5.30.

1*H*-Indole-2-carboxylic acid benzotriazol-1-yl-*p*-tolylmethyl ester (12): white needles from methanol (23%), mp 195–196 °C; ^1H NMR: δ 9.30 (s, 1H), 8.73 (s, 1H), 8.07 (d, J = 8.1 Hz, 1H), 7.67 (d, J = 8.1 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.44–7.29 (m, 7H), 7.25–7.20 (m, 2H), 7.17–7.12 (m, 1H), 2.36 (s, 3H); ^{13}C NMR: δ 159.9, 139.8, 137.5, 131.9, 131.0, 129.6, 128.1, 127.2, 126.2, 126.1, 125.3, 124.4, 122.7, 121.2, 120.2, 112.1, 110.7, 110.6, 80.9, 21.2. Anal. Calcd for $\text{C}_{23}\text{H}_{18}\text{N}_4\text{O}_2$: C, 72.24; H, 4.74; N, 14.65. Found: C, 72.11; H, 4.75; N, 14.49.

4. Characterization data for compounds 3a–g.

2-Benzyl-3-thioxo-2,3-dihydropyrrolo[1,2-*c*]imidazol-1-one (3a): yellow needles from methanol (41%), mp 75–76 °C; ^1H NMR: δ 7.46–7.43 (m, 2H), 7.38 (dd, J = 3.0, 0.9 Hz, 1H), 7.35–7.27 (m, 3H), 6.77 (dd, J = 3.4, 0.8 Hz, 1H), 6.38 (t, J = 3.2 Hz, 1H), 5.02 (s, 2H); ^{13}C NMR: δ 174.2, 158.5, 135.4, 128.7, 128.6, 128.0, 123.1, 119.8, 117.3, 114.2, 44.5. Anal. Calcd for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{OS}$: C, 64.44; H, 4.16; N, 11.56. Found: C, 64.63; H, 4.12; N, 11.45.

2-Phenyl-3-thioxo-2,3-dihydropyrrolo[1,2-*c*]imidazol-1-oneⁱ⁾ (3b): yellow needles from methanol (26%), mp 138–139 °C; ^1H NMR: δ 7.58–7.43 (m, 4H), 7.39–7.36 (m, 2H), 6.87 (dd, J = 3.6, 0.9 Hz, 1H), 6.47 (t, J = 3.2 Hz, 1H); ^{13}C NMR: δ 174.2, 158.0,

ⁱ⁾ Papadopoulos, E. P. *J. Org. Chem.* **1966**, *31*, 3060. Budhram, R. S.; Uff, B. C.; Jones, R. A.; Jones, R. O. *Org. Magn. Reson.* **1980**, *13*(2), 89.

132.3, 129.3, 129.2, 128.3, 122.8, 120.0, 117.7, 114.4. Anal. Calcd for C₁₂H₈N₂OS: C, 63.14; H, 3.53; N, 12.27. Found: C, 63.27; H, 3.40; N, 12.07.

2-Ethyl-3-thioxo-2,3-dihydropyrrolo[1,2-*c*]imidazol-1-one (3c): yellow needles from methanol (77%), mp 60–61 °C; ¹H NMR: δ 7.39 (d, *J* = 2.9 Hz, 1H), 6.76 (d, *J* = 3.4 Hz, 1H), 6.38 (t, *J* = 3.2 Hz, 1H), 3.91 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); ¹³C NMR: δ 174.3, 158.4, 123.3, 119.6, 117.1, 113.8, 36.3, 13.1. Anal. Calcd for C₈H₈N₂OS: C, 53.31; H, 4.47; N, 15.54. Found: C, 53.33; H, 4.37; N, 15.27.

2-Isopropyl-3-thioxo-2,3-dihydropyrrolo[1,2-*c*]imidazol-1-one (3d): yellow needles from methanol (30%), mp 70–71 °C; ¹H NMR: δ 7.36 (d, *J* = 2.8 Hz, 1H), 7.26 (s, 1H), 6.72 (d, *J* = 2.8 Hz, 1H), 6.37 (t, *J* = 3.1 Hz, 1H), 4.83 (septet, *J* = 7.0 Hz, 1H), 1.52 (d, *J* = 7.0 Hz, 6H); ¹³C NMR: δ 174.5, 158.8, 123.2, 119.6, 117.0, 113.4, 47.5, 19.5. Anal. Calcd for C₉H₁₀N₂OS: C, 55.65; H, 5.19; N, 14.42. Found: C, 55.88; H, 4.98; N, 14.07.

2-*p*-Tolylpyrrolo[1,2-*c*]imidazole-1,3-dione (3e): white needles from methanol (71%), mp 194–195 °C; ¹H NMR: δ 7.34 (d, *J* = 2.9 Hz, 1H), 7.30 (s, 4H), 6.88 (d, *J* = 3.3 Hz, 1H), 6.51 (t, *J* = 3.2 Hz, 1H), 2.40 (s, 3H); ¹³C NMR: δ 157.5, 138.6, 129.9, 128.3, 126.3, 124.9, 119.3, 117.8, 114.1, 21.1. Anal. Calcd for C₁₃H₁₀N₂O₂: C, 69.02; H, 4.46; N, 12.38. Found: C, 69.07; H, 4.49; N, 12.33.

2-Benzylpyrrolo[1,2-*c*]imidazole-1,3-dioneⁱⁱ⁾ (3f): white needles from methanol (75%), mp 75–76 °C; ¹H NMR: δ 7.44–7.39 (m, 2H), 7.36–7.28 (m, 3H), 7.22 (dd, *J* = 2.9, 0.8 Hz, 1H), 6.76 (dd, *J* = 3.4, 0.8 Hz, 1H), 6.41 (t, *J* = 3.3 Hz, 1H), 4.74 (s, 2H); ¹³C

ⁱⁱ⁾ Noguchi, S; Obayashi, M.; Imanishi, M; Kawai, K. *Jpn. Kokai*. Patent JP 47042790; *Chem. Abstr.* **1972**, 78, 84249.

NMR: δ 158.2, 148.5, 135.7, 128.7, 128.6, 128.0, 125.3, 119.0, 117.3, 113.6, 42.4. Anal. Calcd for $C_{13}H_{10}N_2O_2$: C, 69.02; H, 4.46; N, 12.38. Found: C, 69.10; H, 4.38; N, 12.25.

2-(1-Phenylethyl)pyrrolo[1,2-*c*]imidazole-1,3-dione (3g): white needles from methanol (95%), mp 63–64 °C; 1H NMR: δ 7.52–7.48 (m, 2H), 7.37–7.28 (m, 3H), 7.19 (dd, $J = 2.9, 0.7$ Hz, 1H), 6.73 (dd, $J = 3.4, 0.6$ Hz, 1H), 6.40 (t, $J = 3.3$ Hz, 1H), 5.42 (q, $J = 7.3$ Hz, 1H), 1.91 (d, $J = 7.4$ Hz, 3H); ^{13}C NMR: δ 158.2, 148.2, 139.6, 128.5, 127.8, 127.3, 125.0, 118.7, 117.1, 113.1, 50.3, 17.3. Anal. Calcd for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.74; H, 5.01; N, 11.48.

5. Characterization data for compounds 4a–g.

2-Benzyl-3-thioxo-2,3-dihydroimidazo[1,5-*a*]indol-1-one (4a): yellow needles from methanol (62%), mp 136–137 °C; 1H NMR: δ 8.35 (d, $J = 8.4$ Hz, 1H), 7.64 (d, $J = 7.8$ Hz, 1H), 7.50–7.46 (m, 3H), 7.35–7.24 (m, 4H), 7.06 (s, 1H), 5.09 (s, 2H); ^{13}C NMR: δ 172.9, 159.0, 135.5, 134.1, 132.4, 129.6, 128.8, 128.6, 128.1, 127.9, 124.8, 124.4, 114.2, 109.3, 44.1. Anal. Calcd for $C_{17}H_{12}N_2OS$: C, 69.84; H, 4.14; N, 9.58. Found: C, 69.64; H, 4.11; N, 9.41.

2-Phenyl-3-thioxo-2,3-dihydroimidazo[1,5-*a*]indol-1-one (4b): yellow needles from methanol (21%), mp 200–201 °C; 1H NMR: δ 8.47 (d, $J = 8.4$ Hz, 1H), 7.75 (d, $J = 8.2$ Hz, 1H), 7.6–7.5 (m, 4H), 7.43–7.36 (m, 3H), 7.20 (s, 1H); ^{13}C NMR: δ 173.3, 158.7, 134.2, 132.6, 132.3, 129.8, 129.4, 129.3, 128.6, 127.9, 125.1, 124.6, 114.6, 109.6. Anal. Calcd for $C_{16}H_{10}N_2OS$: C, 69.04; H, 3.62; N, 10.06. Found: C, 69.21; H, 3.59; N, 9.97.

2-Ethyl-3-thioxo-2,3-dihydroimidazo[1,5-*a*]indol-1-oneⁱⁱⁱ (4c): yellow needles from methanol (34%), mp 110–112 °C; ¹H NMR: δ 8.39 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.08 (s, 1H), 3.99 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H); ¹³C NMR: δ 173.0, 158.9, 134.1, 132.5, 129.5, 128.4, 124.7, 124.4, 114.2, 109.0, 100.2, 36.0, 13.2. Anal. Calcd for C₁₂H₁₀N₂OS: C, 62.59; H, 4.38; N, 12.16. Found: C, 62.70; H, 4.30; N, 11.91.

2-Methyl-3-thioxo-2,3-dihydroimidazo[1,5-*a*]indol-1-one^{iv} (4d): yellow needles from methanol (27%), mp 185–186 °C; ¹H NMR: δ 8.36 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.54–7.49 (m, 1H), 7.32–7.27 (m, 1H), 7.07 (s, 1H), 3.36 (s, 3H); ¹³C NMR: δ 173.5, 159.1, 134.0, 132.4, 129.5, 128.3, 124.7, 124.4, 114.2, 109.2, 27.2. Anal. Calcd for C₁₁H₈N₂OS: C, 61.09; H, 3.73; N, 12.95. Found: C, 61.22; H, 3.64; N, 12.54.

2-*p*-Tolylimidazo[1,5-*a*]indole-1,3-dione (4e): white needles from methanol (79%), mp 158–159 °C; ¹H NMR: δ 7.92 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.53–7.49 (m, 1H), 7.37–7.29 (m, 5H), 7.19 (s, 1H), 2.41 (s, 3H); ¹³C NMR: δ 158.2, 147.8, 138.6, 133.0, 132.3, 129.9, 128.6, 128.4, 128.3, 126.2, 124.3, 124.1, 113.5, 109.4, 21.2. Anal. Calcd for C₁₇H₁₂N₂O₂: C, 73.90; H, 4.38; N, 10.14. Found: C, 73.60; H, 4.31; N, 10.09.

2-Benzylimidazo[1,5-*a*]indole-1,3-dione (4f): white needles from methanol (81%), mp 153–154 °C; ¹H NMR: δ 7.86 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.68 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.51–7.46 (m, 3H), 7.38–7.28 (m, 4H), 7.12 (s, 1H), 4.82 (s, 2H); ¹³C NMR: δ

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^{iv}) Kutschy, P.; Suchy, M.; Dzurilla, M.; Takasugi, M.; Kovacik, V. *Collect. Czech. Chem. Commun.* **2000**, *65*, 1163.

158.8, 148.6, 135.7, 132.9, 132.2, 128.8 (2C), 128.7, 128.4, 128.1, 124.1, 124.0, 113.3, 109.0, 42.5. Anal. Calcd for $C_{17}H_{12}N_2O_2$: C, 73.90; H, 4.38; N, 10.14. Found: C, 73.57; H, 4.33; N, 9.69.

2-(1-Phenylethyl)imidazo[1,5-*a*]indole-1,3-dione (4g): white needles from methanol (87%), mp 105–106 °C; 1H NMR: δ 7.78 (d, J = 8.2 Hz, 1H), 7.60 (d, J = 8.2 Hz, 1H), 7.54 (d, J = 7.4 Hz, 2H), 7.41 (t, J = 7.2 Hz, 1H), 7.37–7.18 (m, 4H), 7.01 (s, 1H), 5.48 (q, J = 7.4 Hz, 1H), 1.95 (d, J = 7.4 Hz, 3H); ^{13}C NMR: δ 158.8, 148.3, 139.6, 132.7, 132.1, 128.5, 128.4, 128.2, 127.9, 127.4, 123.9, 123.8, 113.2, 108.4, 50.5, 17.3. Anal. Calcd for $C_{18}H_{14}N_2O_2$: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.48; H, 4.88; N, 9.49.