

Supporting Information

A General One-pot, Two-step Protocol Accessing a Range of Polycyclic Heterocycles with High Skeletal Diversity

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General Experimental Methods

Solvents were purchased from commercial providers and used without further purification. Other reagents were used as obtained from commercial providers except when otherwise noted. Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel plates. Visualization was accomplished with UV light or by staining with basic KMnO₄ solution. Column chromatography was performed using automated chromatographic systems. Melting points were determined in an open glass capillary and are uncorrected. NMR spectra were recorded in CDCl₃ at 400 MHz (¹H NMR) and 100 MHz (¹³C NMR). Low and high resolution mass spectra were obtained using ESI methods.

Characterization Data for compounds 6

1,6,7-trimethyl-*N*-pentyl-2,3-dihydro-1*H*-benzo[*d*]pyrrolo[1,2-*α*]imidazole-1-carboxamide, 6{1,1,1}. White solid, (35.6 mg, 0.125 mmol, 50%) m.p. 128–130°C. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 7.8 Hz, 1H), 7.36 – 7.25 (d, *J* = 7.8 Hz, 1H), 7.31 – 7.23 (m, 2H), 5.79 (bs, 1H), 3.29 (dt, *J* = 13.5, 6.7 Hz, 1H), 3.13 (dt, *J* = 12.6, 6.3 Hz, 1H), 3.03-2.91 (m, 3H), 2.65 (dd, *J* = 17.5, 9.0 Hz, 1H), 1.84 (s, 3H), 1.38 (dt, *J* = 14.6, 7.2 Hz, 2H), 1.24 (dd, *J* = 13.7, 6.5 Hz, 2H), 1.14 (dd, *J* = 15.0, 8.3 Hz, 2H), 0.83 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 172.0, 161.0, 149.3, 130.5, 122.9, 122.5, 120.2, 110.0, 66.4, 40.7, 39.8, 29.0, 28.8, 23.0, 23.7, 22.2, 13.9. HRMS calculated for C₁₇H₂₄N₃O [M+H]⁺, 286.19139; found 286.13125.

1-methyl-*N*-pentyl-2, 3-dihydro-1*H*-benzo[*d*]pyrrolo[1,2-*α*]imidazole-1-carboxamide, 6{1,2,1}.

Colorless oil, (43 mg, 0.137 mmol, 55%). ¹H NMR (400 MHz, CDCl₃) δ 7.41 (s, 1H), 7.08 (s, 1H), 6.18 (bs, 1H), 3.35 (dt, *J* = 13.4, 6.7 Hz, 1H), 3.14 (dt, *J* = 13.0, 7.0 Hz, 1H), 2.99 – 2.85

(m, 2H), 2.80 – 2.68 (m, 1H), 2.60 (dd, $J = 11.3, 4.1$ Hz, 1H), 2.35 (s, 6H), 1.78 (s, 3H), 1.44 – 1.40 (m, 2H), 1.28 – 1.21 (m, 2H), 1.19 – 1.10 (m, 2 H), 0.83 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.1, 160.0, 147.6, 131.4, 131.2, 129.0, 120.0, 110.2, 65.8, 40.7, 39.7, 29.1, 28.9, 22.8, 22.6, 22.2, 20.4, 13.9. HRMS calculated for $\text{C}_{19}\text{H}_{28}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$, 314.22269; found 314.22293.

10,11-dimethyl-*N*-pentyl-7*H*-benzo[*de*]benzo[4,5]imidazo[2,1-*a*]isoquinoline-7-

carboxamide, 6{3,2,1}. Amorphous solid, (57.6 mg, 0.145 mmol, 58%). ^1H NMR (400 MHz, CDCl_3) δ 8.08 (t, $J = 8.4$ Hz, 2H), 7.87 (t, $J = 8.8$ Hz, 2H), 7.62 (t, $J = 7.3$ Hz, 1H), 7.40 (t, $J = 7.6$ Hz, 1H), 7.22 (s, 1H), 7.14 (s, 1H), 6.65 (bs, 1H), 6.34 (s, 1H), 3.31 – 3.19 (m, 1H), 3.11 (dd, $J = 19.7, 13.1$ Hz, 1H), 2.38 (s, 3H), 2.21 (s, 3H), 1.11 – 1.06 (m, 3H), 0.94 – 0.88 (m, 3H), 0.69 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 169.4, 146.0, 142.3, 132.9, 132.7, 132.3, 129.6, 128.1, 126.5, 126.1, 125.1, 122.3, 121.2, 119.2, 109.8, 61.7, 39.7, 28.9, 28.7, 22.2, 20.5, 20.1, 13.8. HRMS calculated for $\text{C}_{26}\text{H}_{28}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$, 398.22269; found 398.22299.

1-methyl-*N*-(naphthalen-2-yl)-2,3-dihydro-1*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole-1-

carboxamide, 6{1,1,2}. Light yellow oil, (41.8 mg, 0.122 mmol, 49%). ^1H NMR (400 MHz, CDCl_3) δ 9.20 (s, 1H), 8.23 (t, $J = 2.2$ Hz, 1H), 7.75 – 7.64 (m, 4H), 7.48 – 7.29 (m, 6H), 3.27 (dt, $J = 13.0, 7.6$ Hz, 1H), 3.16 (t, $J = 7.4$ Hz, 2H), 2.76 (dt, $J = 13.3, 7.6$ Hz, 1H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 169.2, 159.5, 135.0, 133.6, 130.9, 129.2, 128.6, 127.7, 127.5, 126.5, 125.3, 124.5, 120.3, 117.9, 117.7, 111.1, 68.2, 39.9, 23.0, 22.7. HRMS calculated for $\text{C}_{22}\text{H}_{20}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$, 342.16009; found 342.15997.

1,6,7-trimethyl-*N*-(naphthalen-2-yl)-2,3-dihydro-1*H*-benzo[*d*]pyrrolo[1,2-*a*] imidazole-1-

carboxamide, 6{1,2,3}. Dark brown oil, (43.4 mg, 0.117 mmol, 47%). ^1H NMR (400 MHz,

CDCl₃) δ 8.67 (s, 1H), 8.22 (d, *J* = 2.1 Hz, 1H), 7.77 – 7.68 (m, 2H), 7.50 (s, 1H), 7.40 – 7.34 (m, 1H), 7.30 (s, 3H), 7.23 (s, 1H), 3.14 (t, *J* = 6.7 Hz, 2H), 2.99 (t, *J* = 6.6 Hz, 2H), 2.32 (s, 6H), 2.08 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 174.0, 153.3, 140.3, 137.9, 135.9, 134.7, 133.5, 132.0, 130.8, 129.9, 128.6, 127.6, 127.4, 126.5, 125.2, 120.2, 114.7, 63.6, 38.3, 22.8, 19.4, 19.1. HRMS calculated for C₂₄H₂₄N₃O [M+H]⁺, 370.19139; found 370.19125.

1,7,8-trimethyl-*N*-(naphthalen-2-yl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine-1-carboxamide, 6{2,2,2}. Dark brown solid, (53.7 mg, 0.140 mmol, 56%) m.p. 115–117°C. ¹H NMR (400 MHz, CDCl₃) δ 10.22 (s, 1H), 8.33 (s, 1H), 7.74 – 7.58 (m, 4H), 7.40 – 7.29 (m, 2H), 7.17 (s, 1H), 6.91 (s, 1H), 3.33 (m, 2H), 2.77 (t, *J* = 12.2 Hz, 1H), 2.31 – 2.14 (m, 2H), 2.13 (s, 3H), 2.02 – 1.92 (m, 1H), 1.83 (s, 3H), 1.70 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 169.7, 162.3, 162.0, 150.7, 135.6, 135.1, 134.6, 133.6, 130.6, 128.5, 127.7, 127.5, 126.3, 125.0, 120.4, 117.6, 115.0, 112.3, 64.5, 33.4, 22.6, 22.3, 20.5, 19.4, 15.9. HRMS calculated for C₂₅H₂₆N₃O [M+H]⁺, 384.20704; found 384.20688.

Characterization Data for compounds 9

5-(1*H*-benzo[*d*]imidazol-2-yl)-1-cyclopropyl-5-methylpyrrolidin-2-one, 9{1,1}. Colorless oil, (72.7 mg, 0.285 mmol, 57%). ¹H NMR (400 MHz, CDCl₃) δ 11.92 (s, 1H), 7.78 (s, 1H), 7.52 (dd, *J* = 5.6, 3.3 Hz, 1H), 7.29 – 7.20 (m, 2H), 2.81 – 2.74 (m, 1H), 2.59 – 2.40 (m, 2H), 2.37 – 2.18 (m, 2H), 2.07 (s, 3H), 0.92 – 0.87 (m, 1H), 0.78 – 0.61 (m, 2H), 0.65 – 0.53 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 177.3, 157.1, 143.0, 134.8, 123.0, 121.9, 119.4, 111.3, 64.9, 34.56, 30.2, 24.7, 23.8, 6.5, 3.6. HRMS calculated for C₁₅H₁₈N₃O [M+H]⁺, 256.1444; found 256.1441.

5-(1*H*-benzo[*d*]imidazol-2-yl)-5-methyl-1-(pyridin-2-ylmethyl)pyrrolidin-2-one, 9{1,2}. Yellow oil, (81.1 mg, 0.265 mmol, 53%). ¹H NMR (400 MHz, CDCl₃) δ 8.67 (d *J* = 1.7 Hz, 1H),

7.72 (td, $J = 7.7, 1.8$ Hz, 1H), 7.69 – 7.44 (m, 2H), 7.41 (d, $J = 7.8$ Hz, 1H), 7.29 (dd, $J = 7.5, 5.0$ Hz, 1H), 7.25 – 7.20 (m, 2H), 4.59 (d, $J = 15.2$ Hz, 1H), 4.26 (d, $J = 15.2$ Hz, 1H), 2.57 – 2.43 (m, 3H), 2.42 – 2.35 (m, 1H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 176.0, 158.2, 156.5, 147.7, 137.7, 124.0, 122.8, 122.2, 64.5, 46.4, 35.6, 29.1, 24.4. HRMS calculated for $\text{C}_{18}\text{H}_{19}\text{N}_4\text{O}$ $[\text{M}+\text{H}]^+$, 307.1553; found 307.1555.

6-(1H-benzo[d]imidazol-2-yl)-1-benzyl-6-methylpiperidin-2-one, 9{2,3}. Light yellow oil, (75.0 mg, 0.235 mmol, 47%). ^1H NMR (400 MHz, CDCl_3) δ 12.18 (s, 1H), 7.72 (d, $J = 8.0$ Hz, 1H), 7.35 – 7.06 (m, 6H), 7.05 – 6.67 (m, 2H), 5.38 (d, $J = 15.8$ Hz, 1H), 3.80 (d, $J = 16.0$ Hz, 1H), 2.79 – 2.59 (m, 2H), 2.37 (s, 1H), 2.16 (d, $J = 7.5$ Hz, 1H), 1.99 – 1.73 (m, 4H), 1.51 – 1.47 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.5, 172.1, 157.1, 138.0, 128.6, 128.5, 126.9, 126.4, 122.7, 121.9, 119.1, 111.5, 63.0, 48.4, 38.7, 33.0, 27.0, 17.4. HRMS calculated for $\text{C}_{20}\text{H}_{22}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$, 320.1757; found 320.1760.

6-(1H-benzo[d]imidazol-2-yl)-1-(4-methoxybenzyl)-6-methylpiperidin-2-one, 9{2,4}. Light yellow oil, (87.3 mg, 0.250 mmol, 50%). ^1H NMR (400 MHz, CDCl_3) δ 12.05 (s, 1H), 7.72 (d, $J = 7.6$ Hz, 1H), 7.23 – 6.97 (m, 5H), 6.86 – 6.67 (m, 2H), 5.28 (d, $J = 15.7$ Hz, 1H), 3.82 – 3.68 (m, 4H), 2.73 – 2.58 (m, 2H), 2.43 – 2.30 (m, 1H), 2.18 – 2.05 (m, 1H), 1.89 – 1.72 (m, 4H), 1.58 – 1.43 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.5, 158.6, 157.2, 130.2, 128.4, 127.9, 122.7, 121.9, 119.1, 114.1, 113.9, 111.5, 63.0, 55.3, 47.9, 38.8, 33.1, 27.1, 17.4. HRMS calculated for $\text{C}_{21}\text{H}_{24}\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+$, 350.1863; found 350.1867.

3-(1H-benzo[d]imidazol-2-yl)-2-phenylisoindolin-1-one, 9{4,5}. Light yellow oil, (91.0 mg, 0.280 mmol, 56%). ^1H NMR (400 MHz, CDCl_3) δ 12.05 (s, 1H), 7.77 (dd, $J = 16.9, 7.8$ Hz, 3H), 7.64 – 7.33 (m, 3H), 7.32 – 7.15 (m, 4H), 7.09 (dd, $J = 15.5, 8.8$ Hz, 3H), 6.56 (s, 1H). ^{13}C NMR

(100 MHz, CDCl₃) δ 169.0, 150.3, 143.3, 142.1, 137.4, 134.7, 133.0, 130.4, 129.4, 129.2, 125.7, 123.6, 123.3, 122.2, 121.3, 119.5, 111.7, 61.7. HRMS calculated for C₂₁H₁₆N₃O [M+H]⁺, 326.1288; found 326.1290.

3-(1*H*-benzo[*d*]imidazol-2-yl)-2-(4-methoxyphenyl)isoindolin-1-one, 9{4,4}. Light yellow solid, (104.7 mg, 0.295 mmol, 59%) m.p. 196-198 °C. ¹H NMR (400 MHz, CDCl₃) δ 13.24 (s, 1H), 7.82 – 7.40 (m, 6H), 7.37 – 7.17 (m, 2H), 7.07 (t, *J* = 6.0 Hz, 2H), 6.71 (dd, *J* = 23.0, 14.0 Hz, 3H), 3.69 (d, *J* = 8.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 168.7, 157.6, 150.1, 141.6, 132.7, 130.3, 129.6, 129.4, 124.0, 123.2, 114.3, 61.4, 55.1. HRMS calculated for C₂₂H₁₈N₃O₂ [M+H]⁺, 356.1394; found 356.1395.

3-(1*H*-benzo[*d*]imidazol-2-yl)-2-benzyl-3-methylisoindolin-1-one, 9{5,3}. Light yellow oil, (109.4 mg, 0.310 mmol, 62%). ¹H NMR (400 MHz, cdcl₃) δ 12.05 (s, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.46 – 7.37 (m, 3H), 7.31 – 7.13 (m, 8H), 7.08 (ddd, *J* = 7.8, 4.7, 3.4 Hz, 1H), 5.28 (d, *J* = 15.7 Hz, 1H), 4.20 (d, *J* = 15.7 Hz, 1H), 1.96 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 169.6, 152.8, 149.0, 143.4, 137.3, 135.1, 132.6, 129.3, 128.9, 128.5, 127.9, 127.4, 123.3, 122.2, 122.0, 119.6, 111.6, 66.8, 44.8, 23.5. HRMS calculated for C₂₃H₂₀N₃O [M+H]⁺, 354.1601; found 354.1595.

3-(1*H*-benzo[*d*]imidazol-2-yl)-3-methyl-2-(pyridin-2-ylmethyl)isoindolin-1-one, 9{5,2}. Yellow oil, (97.4 mg, 0.275 mmol, 55%). ¹H NMR (400 MHz, CDCl₃) δ 13.94 (s, 1H), 8.64 – 8.57 (m, 1H), 7.81 (d, *J* = 6.6 Hz, 1H), 7.73 (ddd, *J* = 9.5, 5.6, 1.7 Hz, 2H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.48 (ddd, *J* = 7.9, 5.5, 1.6 Hz, 2H), 7.34 (tt, *J* = 7.5, 3.8 Hz, 2H), 7.26 – 7.24 (m, 3H), 4.80 (d, *J* = 15.6 Hz, 1H), 4.67 (d, *J* = 15.6 Hz, 1H), 2.15 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ

169.0, 156.5, 154.2, 149.2, 147.9, 137.5, 132.5, 129.1, 128.6, 123.4, 122.8, 66.2, 46.2, 24.6.

HRMS calculated for C₂₂H₁₉N₄O [M+H]⁺, 355.1553; found 355.1554.

5-(1*H*-benzo[*d*]imidazol-2-yl)-4-benzyl-4,5-dihydrobenzo[*f*][1,4]oxazepin-3(2*H*)-one, 9{6,2}.

Light yellow oil. (118.1 mg, 0.320 mmol, 64%) ¹H NMR (400 MHz, CDCl₃) δ 10.35 (s, 1H), 7.72 (s, 1H), 7.47 – 7.25 (m, 7H), 7.24 – 7.18 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 4.7 Hz, 2H), 5.70 – 5.60 (m, 2H), 5.10 (d, *J* = 16.8 Hz, 1H), 4.59 (d, *J* = 16.8 Hz, 1H), 4.22 (d, *J* = 14.9 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 169.3, 156.8, 151.9, 135.9, 131.5, 130.4, 130.2, 128.8, 128.3, 127.9, 125.9, 121.2, 73.7, 60.0, 51.0. HRMS calculated for C₂₃H₂₀N₃O₂ [M+H]⁺, 370.1550; found 370.1552.

5-(1*H*-benzo[*d*]imidazol-2-yl)-4-(4-methoxybenzyl)-4,5-dihydrobenzo[*f*][1,4]oxazepin-

3(2*H*)- one, 9{6,4}. Light yellow oil, (124.7 mg, 0.310 mmol, 62%). ¹H NMR (400 MHz, CDCl₃) δ 10.26 (s, 1H), 7.72 (s, 1H), 7.46 – 7.31 (m, 2H), 7.31 – 7.19 (m, 4H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.11 – 7.04 (m, 2H), 6.89 – 6.83 (m, 2H), 5.69 (s, 1H), 5.56 (d, *J* = 14.7 Hz, 1H), 5.10 (d, *J* = 16.8 Hz, 1H), 4.57 (d, *J* = 16.8 Hz, 1H), 4.13 (d, *J* = 14.6 Hz, 1H), 3.80 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 169.2, 159.3, 156.8, 151.9, 131.4, 130.4, 130.2, 129.9, 127.9, 125.9, 123.5, 122.4, 121.2, 119.8, 114.2, 111.1, 73.7, 59.7, 55.3, 50.3. HRMS calculated for C₂₄H₂₂N₃O₃ [M+H]⁺, 400.1656; found 400.1656.

3-(1*H*-benzo[*d*]imidazol-2-yl)-2-cyclopropyl-2,3-dihydro-1*H*-benzo[*de*]isoquinolin-1-one, 9{3,1}.

Light yellow oil, (86.4 mg, 0.255 mmol, 51%). ¹H NMR (400 MHz, CDCl₃) δ 12.32 (s, 1H), 7.89 (dd, *J* = 16.7, 7.8 Hz, 2H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.49 (dd, *J* = 16.0, 7.8 Hz, 2H), 7.23 – 7.11 (m, 3H), 6.59 (s, 1H), 2.83 – 2.73 (m, 1H), 1.08 – 0.96 (m, 2H),

0.96 – 0.85 (m, 1H), 0.76 – 0.65 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 165.0, 154.1, 132.2, 132.0, 128.5, 127.2, 127.1, 126.7, 126.6, 126.0, 125.7, 123.5, 123.0, 122.0, 119.5, 111.8, 61.4, 29.6, 9.9, 6.4. HRMS calculated for C₂₂H₁₈N₃O [M+H]⁺, 340.1444; found 340.1447.

Characterization Data for compounds 12

1-(1*H*-benzo[*d*]imidazol-2-yl)-1-methyl-1,2,3,9-tetrahydropyrrolo[2,1-*b*]quinazoline,

12{1,2}. Light yellow solid, (93.6 mg, 0.310 mmol, 53%) m.p. 213-215 °C. ¹H NMR (400 MHz, *d*-DMSO) δ 12.93 (s, 1H), 7.60 – 7.52 (m, 2H), 7.32 (td, *J* = 7.9, 1.7 Hz, 1H), 7.23 – 7.09 (m, 5H), 4.83 (d, *J* = 15.5 Hz, 1H), 4.48 (d, *J* = 15.4 Hz, 1H), 3.29 – 3.08 (m, 2H), 2.58 – 2.56 (m, 1H), 2.46 – 2.43 (m, 1H), 1.94 (s, 3H). ¹³C NMR (100 MHz, *d*-DMSO) δ 163.2, 153.0, 130.9, 129.1, 127.4, 126.6, 122.2, 117.0, 116.8, 69.4, 42.2, 34.0, 28.4, 20.9. HRMS calculated for C₁₉H₁₉N₄ [M+H]⁺, 303.1604; found 303.1599.

9-(1*H*-benzo[*d*]imidazol-2-yl)-9-methyl-7,8,9,11-tetrahydro-6*H*-pyrido[2,1-*b*] quinazoline,

12{2,2}. Yellow oil, (91.6 mg, 0.290 mmol, 58%). ¹H NMR (400 MHz, CDCl₃) δ 13.03 (s, 1H), 7.78 (s, 1H), 7.45 (s, 1H), 7.31 – 7.20 (m, 2H), 7.14 – 7.11 (m, 1H), 7.09 – 6.95 (m, 2H), 6.81 – 6.65 (m, 1H), 4.72 – 4.48 (m, 2H), 3.10 – 3.04 (m, 3H), 2.15 – 2.03 (m, 3H), 1.99 – 1.80 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 166.2, 155.2, 129.1, 127.1, 125.1, 118.1, 117.0, 68.2, 47.8, 36.4, 31.2, 24.8, 21.3. HRMS calculated for C₂₀H₂₁N₄ [M+H]⁺, 317.1761; found 317.1760.

10-(1*H*-benzo[*d*]imidazol-2-yl)-10-methyl-6,7,8,9,10,12-hexahydroazepino[2,1-

***b*]quinazoline, 12**{4,2}. Yellow oil, (71.0 mg, 0.215 mmol, 43%). ¹H NMR (400 MHz, CDCl₃) δ 8.68 (s, 1H), 7.68 (s, 2H), 7.30 – 7.24 (m, 2H), 7.16 – 7.11 (m, 1H), 7.07 (ddd, *J* = 7.9, 6.6, 1.4 Hz, 1H), 6.99 (td, *J* = 7.5, 1.3 Hz, 1H), 6.77 (dd, *J* = 7.5, 0.8 Hz, 1H), 4.51 (d, *J* = 14.8 Hz, 1H), 4.20 (d, *J* = 14.8 Hz, 1H), 3.20 – 3.14 (m, 1H), 2.93 – 2.88 (m, 1H), 2.79 (q, *J* = 7.2 Hz, 1H),

2.58 – 2.53 (m, 1H), 2.11 – 2.05 (m, 3H), 1.89 – 1.83 (m, 2H), 1.15 (t, $J = 7.2$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.4, 154.1, 129.0, 126.1, 125.5, 122.7, 117.8, 62.5, 46.0, 45.5, 36.7, 28.8, 23.1, 15.6, 10.2. HRMS calculated for $\text{C}_{21}\text{H}_{23}\text{N}_4$ $[\text{M}+\text{H}]^+$, 331.1917; found 331.1915.

13-(1*H*-benzo[*d*]imidazol-2-yl)-6,13-dihydrobenzo[*f*]benzo[4,5]imidazo[2,1-

***c*][1,4]oxazepine, **12**{3,1}. Yellow oil, (93.3 mg, 0.265 mmol, 53%). ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 8.3$ Hz, 1H), 7.82 – 7.64 (m, 2H), 7.57 (dd, $J = 6.1, 3.0$ Hz, 2H), 7.36 (ddd, $J = 7.7, 6.8, 2.7$ Hz, 2H), 7.31 – 7.04 (m, 6H), 5.22 (d, $J = 16.2$ Hz, 1H), 4.95 (d, $J = 16.3$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.1, 151.3, 150.8, 140.4, 134.1, 132.3, 130.9, 128.0, 126.7, 124.7, 124.3, 122.1, 118.4, 114.9, 110.5, 70.1, 56.7. HRMS calculated for $\text{C}_{22}\text{H}_{17}\text{N}_4\text{O}$ $[\text{M}+\text{H}]^+$, 353.1397; found 353.1399.**

14-(1*H*-benzo[*d*]imidazol-2-yl)-12,14-dihydro-6*H*-benzo[6,7][1,4]oxazepino[3,4-

***b*]quinazoline, **12**{3,2}. Yellow oil, (123.5 mg, 0.325 mmol, 65%). ^1H NMR (400 MHz, CDCl_3) δ 13.22 (s, 1H), 7.58 – 7.43 (m, 3H), 7.21 – 7.09 (m, 4H), 7.08 – 6.99 (m, 2H), 6.96 (t, $J = 7.5$ Hz, 1H), 6.81 (dd, $J = 14.1, 4.9$ Hz, 2H), 6.23 – 6.09 (m, 2H), 5.13 (d, $J = 15.0$ Hz, 1H), 5.04 (d, $J = 15.2$ Hz, 1H), 4.90 (d, $J = 15.0$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.6, 156.0, 149.8, 131.1, 131.0, 129.7, 129.5, 128.2, 125.9, 124.1, 123.2, 121.4, 120.4, 118.4, 118.0, 117.4, 115.5, 112.5, 67.1, 64.9, 64.8, 52.2. HRMS calculated for $\text{C}_{23}\text{H}_{19}\text{N}_4\text{O}$ $[\text{M}+\text{H}]^+$, 367.1553; found 367.1555.**