## Supporting information for

# Oxidative Dearomatization in the Synthesis of Erythrina, Oxindole and Hexahydropyrrolo[2,3-*b*]-indole Skeletons

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General Experimental: Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra were recorded on a Bruker Avance 300 spectrometer at 300 MHz. Carbon-13 nuclear magnetic resonance (<sup>13</sup>C-NMR) was recorded on a Bruker Avance 300 spectrometer at 75 MHz. Chemical shifts are reported as  $\delta$  values in parts per million (ppm) relative to tetramethylsilane (TMS) for all recorded NMR spectra. Low-resolution Mass spectra were recorded on a VG Auto Spec-3000 magnetic sector MS spectrometer. High Resolution Mass spectra were taken on an AB QSTAR Pulsar mass spectrometer. Starting materials and reagents used in reactions were obtained commercially from Acros, Aldrich, Fluka and were used without purification, unless otherwise indicated.

#### General Procedure for the Preparation of Oxindoles:



To a degassed solution of amide (1.0 mmol) in methanol (10 mL) was added IBD (iodobenzene diacetate, 387 mg, 1.20 mmol, 1.2 eq.) at room temperature under nitrogen. After stirring at room temperature for 30-40 minutes, the solvent was removed under reduced pressure and the resulting mixture was diluted with ethyl acetate (5 mL) and treated with sodium bicarbonate (252 mg, 3.0 mmol, 3.0 eq.), then filtered through a short column of silica gel and washed with dichloromethane (15 mL). After removal of the solvent, the residue was either chromatographed on silica gel (Hexane: ethyl acetate = 4:1) to provide the cyclohexenones (yields: 75-85%) or used in next step without further purification. The cyclohexenones were diluted with anhydrous THF (10 mL) and treated with alkyl halides (1.1 mmol, 1.1 eq.) and potassium carbonate (304 mg, 2.2 mmol, 2.2 eq.) at 70 °C (oil bath) overnight. The resulting mixture was concentrated then diluted with water (60 mL) and extracted with ethyl acetate (3× 15 mL). The organic phases were combined and dried over anhydrous sodium sulfate. After filtration and removal of the solvent, the

crude products were chromatographed on silica gel (Hexane: ethyl acetate = 4:1-2:1) to provide the oxindoles (yields: 37-55% over two steps).



Pale yellow syrup, Yield: (311 mg), 74.5%. <sup>1</sup>**H-NMR** (300MHz, CDCl<sub>3</sub>), δ (ppm): 6.77 (1H, *d*, *J* = 8.7 Hz), 6.71 (1H, *m*), 6.70 (1H, *d*, *J* = 8.7 Hz), 6.26 (1H, *dd*, *J* = 1.8, 10.5 Hz), 5.95 (1H, *d*, *J* = 10.5 Hz), 4.32-4.20 (2H, *m*), 3.84 (3H, *s*), 3.82 (3H, *s*), 3.61-3.21 (3H, *m*), 3.26 (3H, *s*), 3.05 (1H, *d*, *J* = 9.6 Hz), 2.98-2.82 (2H, *m*), 2.72 (1H, *dd*, *J* = 6.3, 16.8 Hz), 2.43 (1H, *dd*, *J* = 3.6, 16.8 Hz), 1.30 (3H, *t*, *J* = 7.2 Hz). <sup>13</sup>C-NMR (75MHz, CDCl<sub>3</sub>), δ (ppm): 195.29, 167.98, 149.21, 148.01, 141.35, 131.13, 129.69, 121.02, 112.25, 111.53, 88.56, 62.30, 56.02, 52.98, 50.39, 42.37, 37.09, 36.74, 33.93, 14.21.



Colorless syrup, Yield: (224 mg), 52.6%. <sup>1</sup>**H-NMR** (300MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 6.85 (1H, *d*, *J* = 2.4 Hz), 6.82-6.73 (4H, *m*), 6.58 (1H, *d*, *J* = 8.4 Hz), 6.20-6.08 (1H, *brs*), 5.39-5.20 (1H, *m*), 5.03 (1H, *dd*, *J* = 1.8, 17.1 Hz), 4.90 (1H, *dd*, *J* = 1.8, 10.2 Hz), 4.20-4.02 (2H, *m*), 3.99-3.70 (2H, *m*), 3.82 (3H, *s*), 3.80 (3H, *s*), 2.96-2.82 (4H, *s*), 1.15 (3H, *t*, *J* = 7.2 Hz). <sup>13</sup>C-NMR (75MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 173.50, 169.05, 152.33, 149.03, 147.85, 136.35, 130.92, 130.79, 128.92, 120.87, 119.77, 115.17, 112.28, 112.03, 111.45, 109.16, 62.06, 59.49, 55.94, 41.98, 38.28, 33.33, 13.89. **EIMS** *m*/*z* (%) : 426 (M<sup>+</sup>+1, 4%), 425 (M<sup>+</sup>, 12%), 274 (9), 261 (29), 246 (1), 228 (2), 222 (2), 215 (4), 200 (4), 172 (10), 165 (29), 164 (100), 151 (19), 149 (9), 146 (5), 121 (2). **HRMS** *m*/*z* Found: 426.1912, Calcd. for C<sub>24</sub>H<sub>28</sub>NO<sub>6</sub> (M+H)<sup>+</sup>: 426.1916.



Pale brown powder, m.p.: 149-150 °C, Yield: (228 mg), 48.0%. <sup>1</sup>H-NMR (300MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.07-6.83 (6H, *m*), 6.73-6.60 (3H, *m*), 6.57 (1H, *d*, *J* = 8.1 Hz), 6.33 (1H, *d*, *J* = 8.4 Hz), 5.74 (1H, *brs*), 4.17 (2H, *q*, *J* = 7.2 Hz), 3.83 (3H, *s*), 3.81 (3H, *s*), 3.80-3.65 (1H, *m*), 3.60-3.42 (3H, *m*), 2.50-2.30 (2H, *m*), 1.20 (3H, *t*, *J* = 7.2 Hz). <sup>13</sup>C-NMR (75MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 173.44, 169.40, 152.62, 149.06, 147.84, 136.28, 134.43, 131.03, 130.26, 128.88, 127.78, 126.94, 120.86, 115.39, 112.31, 112.19, 111.54, 109.26, 62.28, 61.29, 56.01, 41.95, 40.04, 32.91, 14.01. **EIMS** *m*/*z* (%) : 476 (M<sup>+</sup>+1, 2%), 475 (M<sup>+</sup>, 7%), 324 (7), 311 (17), 265 (32), 250 (5), 222 (4), 174 (2), 165 (23), 164 (100), 151 (21), 149 (6), 133 (3), 107 (2), 91 (20). **HRMS** *m*/*z* Found: 476.2083, Calcd. for C<sub>28</sub>H<sub>30</sub>NO<sub>6</sub> (M+H)<sup>+</sup>: 476.2073.



Pale yellow plates, m.p.: 129-130 °C, Yield: (214 mg), 46.9%. <sup>1</sup>H-NMR (300MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 6.83-6.72 (5H, *m*), 6.59 (1H, *d*, *J* = 8.4 Hz), 4.20-4.03 (2H, *m*), 3.92 (2H, *t*, *J* = 8.1 Hz), 3.83 (3H, *s*), 3.81 (3H, *s*), 2.90 (2H, *t*, *J* = 8.1 Hz), 2.30-2.05 (2H, *m*), 1.49-1.37 (1H, *m*), 1.15 (3H, *t*, *J* = 7.2 Hz), 0.92-0.65 (2H, *m*), 0.78 (3H, *t*, *J* = 6.2 Hz). <sup>13</sup>C-NMR (75MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 174.23, 169.81, 152.35, 149.21, 148.01, 136.78, 130.93, 129.76, 121.01, 115.15, 112.40, 111.88, 111.58, 109.22, 62.06, 59.93, 56.05, 42.05, 33.43, 32.29, 32.16, 28.18, 22.45, 22.38, 14.02. **EIMS** *m*/*z* (%) : 456 (M<sup>+</sup>+1, 3%), 455 (M<sup>+</sup>, 11%), 382 (2), 304 (12), 291 (28), 245 (10), 230 (3), 221 (1), 202 (3), 188 (4), 174 (9), 165 (30), 164 (100), 151 (14), 146 (10), 134 (3), 107 (2). **HRMS** *m*/*z* Found: 456.2376, Calcd. for C<sub>26</sub>H<sub>34</sub>NO<sub>6</sub> (M+H)<sup>+</sup>: 456.2386.



Pale brown plates, m.p.: 141-142 °C, Yield: (211 mg), 51.3%. <sup>1</sup>**H-NMR** (300MHz, CDCl<sub>3</sub>), δ (ppm): 7.34-7.20 (5H, *m*), 6.81 (1H, *d*, *J* = 2.4 Hz), 6.63 (1H, *dd*, *J* = 2.4, 8.4 Hz), 6.49 (1H, *d*, *J* = 8.4 Hz), 5.94 (1H, *brs*), 5.15 (1H, *d*, *J* = 15.6 Hz), 4.80 (1H, *t*, *J* = 4.5 Hz), 4.66 (1H, *d*, *J* = 15.6 Hz), 4.22-4.02 (2H, *m*), 3.92-3.73 (4H, *m*), 2.50-2.28 (2H, *m*), 1.55-1.22 (2H, *m*), 1.16 (3H, *t*, *J* = 7.2 Hz). <sup>13</sup>C-NMR (75MHz, CDCl<sub>3</sub>), δ (ppm): 174.29, 169.48, 152.79, 136.20, 135.66, 129.08, 128.80, 127.71, 127.24, 115.52, 111.77, 110.22, 103.87, 64.96, 62.27, 59.50, 44.01, 28.26, 28.07, 13.94. EIMS *m*/*z* (%) : 412 (M<sup>+</sup>+1, 15%), 411 (M<sup>+</sup>, 60%), 383 (20), 366 (2), 337 (3), 310 (12), 295 (6), 292 (10), 279 (9), 266 (44), 265 (100), 264 (25), 251 (17), 236 (3), 213 (2), 198 (4), 188 (3), 174 (5), 160 (2), 146 (2), 132 (1), 99 (43), 91 (68). HRMS *m*/*z* Found: 412.1769, Calcd. for C<sub>23</sub>H<sub>26</sub>NO<sub>6</sub> (M+H)<sup>+</sup>: 412.1760.



Yellow powder, m.p.: 138-139 °C, Yield: (235 mg), 54.8%. <sup>1</sup>**H-NMR** (300MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.30-7.05 (8H, *m*), 7.00 (2H, *d*, *J* = 6.9 Hz), 6.79 (1H, *d*, *J* = 2.4 Hz), 6.64 (1H, *dd*, *J* = 2.4, 8.4 Hz), 6.46 (1H, *d*, *J* = 8.4 Hz), 5.06 (1H, *d*, *J* = 15.6 Hz), 4.70 (1H, *d*, *J* = 15.6 Hz), 4.18-3.98 (2H, *m*), 2.61-2.20 (4H, *m*), 1.49-1.19 (2H, *m*), 1.10 (3H, *t*, *J* = 7.2 Hz). <sup>13</sup>**C-NMR** (75MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 174.74, 169.66, 152.95, 141.66, 135.97, 135.54, 129.30, 128.77, 128.39, 128.35, 127.70, 127.22, 125.90, 115.28, 111.61, 110.22, 62.26, 60.08, 44.02, 35.81, 33.69, 25.64, 13.88. **EIMS** *m*/*z* (%) : 430 (M<sup>+</sup>+1, 18%), 429 (M<sup>+</sup>, 64%), 384 (2), 356 (4), 317 (1), 295 (4), 266 (21), 265 (100), 251 (22), 250 (6), 236 (3), 222 (2), 188 (2), 174 (6), 161 (4), 146 (3), 133 (3), 117 (8), 105 (4), 91 (87). **HRMS** *m*/*z* Found: 430.2022, Calcd. for C<sub>27</sub>H<sub>28</sub>NO<sub>4</sub> (M+H)<sup>+</sup>: 430.2018.



Pale yellow powder, m.p.: 158-159 °C, Yield: (135 mg), 36.8%. <sup>1</sup>H-NMR (300MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.32-7.19 (5H, *m*), 6.82 (1H, *d*, *J* = 2.4 Hz), 6.67 (1H, *dd*, *J* = 2.4, 8.4 Hz), 6.52 (1H, *d*, *J* = 8.4 Hz), 5.87 (1H, *s*), 5.09 (1H, *d*, *J* = 15.6 Hz), 4.75 (1H, *d*, *J* = 15.6 Hz), 4.21-4.02 (2H, *m*), 2.38-2.14 (2H, *m*), 1.32-1.15 (3H, *m*), 1.16 (3H, *t*, *J* = 7.2 Hz), 1.10-0.83 (1H, *m*), 0.78 (3H, *t*, *J* = 7.2 Hz). <sup>13</sup>C-NMR (75MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 174.69, 169.83, 152.56, 136.44, 135.75, 129.69, 128.79, 127.73, 127.31, 115.22, 111.68, 110.12, 62.19, 60.17, 44.04, 33.81, 25.88, 22.82, 13.96, 13.87. EIMS *m*/*z* (%) : 368 (M<sup>+</sup>+1, 4%), 367 (M<sup>+</sup>, 19%), 324 (2), 294 (5), 265 (32), 252 (4), 238 (3), 233 (5), 199 (3), 174 (6), 160 (1), 146 (3), 132 (3), 119 (2), 105 (1), 91 (100), 77 (2), 65 (6). HRMS *m*/*z* Found: 390.1672, Calcd. for C<sub>22</sub>H<sub>25</sub>NO<sub>4</sub>Na (M+Na)<sup>+</sup>: 390.1681.



Colorless foam, Yield: (244 mg), 53.7%. <sup>1</sup>**H-NMR** (300MHz, CDCl<sub>3</sub>), δ (ppm): 7.34-7.20 (5H, *m*), 6.86 (1H, *d*, *J* = 1.8 Hz), 6.66 (1H, *d*, *J* = 1.8, 8.4 Hz), 6.51 (1H, *d*, *J* = 8.4 Hz), 5.18 (1H, *d*, *J* = 15.6 Hz), 4.94 (1H, *brs*), 4.64 (1H, *d*, *J* = 1.8 Hz), 6.66 (1H, *d*, *J* = 1.8 Hz), 6.51 (1H, *d*, *J* = 8.4 Hz), 5.18 (1H, *d*, *J* = 1.56 Hz), 4.94 (1H, *brs*), 4.64 (1H, *d*, *J* = 1.8 Hz), 6.51 (1H, *d*, *J* = 8.4 Hz), 5.18 (1H, *d*, *J* = 1.56 Hz), 4.94 (1H, *brs*), 4.64 (1H, *d*, *J* = 1.8 Hz), 6.51 (1H, *d*, *J* = 8.4 Hz), 5.18 (1H, *d*, *J* = 1.56 Hz), 4.94 (1H, *brs*), 4.64 (1H, *d*, *J* = 1.8 Hz), 6.51 (1H, *d*, *J* = 8.4 Hz), 5.18 (1H, *d*, *J* = 1.56 Hz), 4.94 (1H, *brs*), 4.64 (1H, *d*, *J* = 1.8 Hz), 6.51 (1H, *d*, *J* = 1.8 Hz), 7.51 (1H, *d*,

J = 15.6 Hz, 4.22-4.02 (2H, m), 3.20-2.92 (2H, m), 2.62-2.32 (2H, m), 1.42 (9H, s), 1.17 (3H, t, J = 7.2 Hz). **NMR** (75MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 174.33, 169.29, 156.17, 153.39, 135.66, 135.46, 128.83, 128.58, 127.73, 127.18, 115.54, 111.79, 110.37, 79.78, 62.37, 58.43, 44.06, 36.45, 33.54, 28.53, 13.91. **EIMS** m/z (%) : 455 (M<sup>+</sup>+1, 2%), 454 (M<sup>+</sup>, 5%), 428 (1), 398 (42), 381 (6), 354 (2), 308 (9), 295 (7), 279 (6), 266 (29), 265 (100), 252 (16), 251 (10), 236 (2), 222 (1), 189 (2), 174 (11), 160 (3), 146 (3), 105 (1), 91 (53). **HRMS** m/z Found: 455.2184, Calcd. for  $C_{25}H_{31}N_2O_6$  (M+H)<sup>+</sup>: 455.2182.

#### Synthesis of horsfiline and indoline related skeleton:



To a solution of phenol (910 mg, 2.0 mmol) in acetone (20 mL) was added potassium carbonate (345 mg, 2.5 mmol, 1.25 eq.) and dimethyl sulfate (504 mg, 4.0 mmol, 2.0 eq.). The resulting mixture was stirred at reflux overnight. The solvent was removed under reduced pressure and the residue was diluted with ethyl acetate (30 mL) and washed with water (10 mL), brine (20 mL) and dried over anhydrous sodium sulfate. After filtration and removal of the solvent, the crude products were chromatographed on silica gel (Hexane: ethyl acetate = 4:1-2:1) to provide the oxindole (823 mg, yields: 87.8%).

Colorless plates, m.p.: 158-159 °C, Yield: (823 mg), 87.8%. <sup>1</sup>H-NMR (300MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.34-7.20 (5H, *m*), 6.89 (1H, *d*, *J* = 2.4 Hz), 6.72 (1H, *d*, *J* = 2.4, 8.7 Hz), 6.60 (1H, *d*, *J* = 8.7 Hz), 5.20 (1H, *d*, *J* = 15.6 Hz), 4.70 (1H, *brs*), 4.67 (1H, *d*, *J* = 15.6 Hz), 4.24-4.06 (2H, *m*), 3.75 (3H, *s*), 3.20-2.96 (2H, *m*), 2.64-2.52 (1H, *m*), 2.46-2.32 (1H, *m*), 1.42 (9H, *s*), 1.20 (3H, *t*, *J* = 6.9 Hz). <sup>13</sup>C-NMR (75MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 174.07, 169.17, 156.39, 155.67, 136.38, 135.68, 129.57, 128.84, 127.74, 127.21, 113.83, 110.66, 110.14, 79.21, 62.29, 58.44, 55.86, 44.04, 36.39, 33.82, 28.51, 13.96. EIMS *m*/*z* (%) : 469 (M<sup>+</sup>+1, 4%), 468 (M<sup>+</sup>, 16%), 424 (1), 412 (3), 394 (7), 368 (3), 322 (8), 309 (10), 293 (6), 280 (32), 279 (100), 266 (18), 265 (16), 250 (3), 203 (1), 188 (10), 174 (4), 160 (4), 146 (3), 91 (42). HRMS *m*/*z* Found: 469.2339, Calcd. for C<sub>26</sub>H<sub>33</sub>N<sub>2</sub>O<sub>6</sub> (M+H)<sup>+</sup>: 469.2338.



1-BenzyI-5-methoxyspiro[indoline-3,3'-pyrrolidine]-2,2'-dione

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C<sub>19</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub> Mol. Wt.: 322.36

To a solution of *tert*-butyl carbomate (100 mg, 0.2 mmol) in toluene (5 mL) was added trimethyl aluminum in heptanes (2.0 M, 0.5 mL, 1.0 mmol, 5.0 eq.) at 0 °C under nitrogen. The resulting mixture was then stirred at 0 °C overnight. Brine (0.5 mL) was added then diluted with water (10 mL) and extracted with ethyl acetate ( $2 \times 5$  mL). The combined organic phases were dried over anhydrous sodium sulfate. After filtration and removal of the solvent, the crude products were chromatographed on silica gel (Dichloromethane: ethyl acetate = 2:1) to provide the oxindoles (41 mg, yields: 62.9%).

White needles, m.p.: 210-211 °C, Yield: (41 mg), 62.9%. <sup>1</sup>**H-NMR** (300MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.53 (1H, *brs*), 7.35-7.20 (5H, *m*), 6.85 (1H, *d*, *J* = 2.4 Hz), 6.71 (1H, *dd*, *J* = 2.4, 8.4 Hz), 6.60 (1H, *d*, *J* = 8.4 Hz), 4.94 (1H, *d*, *J* = 15.8 Hz), 4.89 (1H, *d*, *J* = 15.8 Hz), 3.82-3.70 (1H, *m*), 3.74 (3H, *s*), 3.58 (1H, *ddd*, *J* = 4.8, 8.7, 8.7 Hz), 2.84 (1H, *ddd*, *J* = 4.8, 8.7, 9.6 Hz), 2.54-2.45 (1H, *m*). <sup>13</sup>**C-NMR** (75MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 175.48, 174.57, 156.49, 137.01, 135.54, 130.86, 128.92, 127.67, 127.21, 113.54, 110.48, 110.09, 57.86, 55.92, 44.15, 40.37, 32.18. **EIMS** *m/z* (%) : 323 (M<sup>+</sup>+1, 18%), 322 (M<sup>+</sup>, 88%), 296 (3), 294 (4), 279 (12), 267 (19), 266 (100), 253 (4), 231 (3), 203 (5), 188 (25), 175 (8), 160 (18), 158 (3), 146 (6), 145 (4), 132 (3), 103 (1), 91 (88), 89 (4), 77 (2), 65 (5). **HRMS** *m/z* Found: 323.1392, Calcd. for C<sub>19</sub>H<sub>19</sub>N<sub>2</sub>O<sub>3</sub> (M+H)<sup>+</sup>: 323.1395.



To a solution of *tert*-butyl carbomate (120 mg, 0.24 mmol) in methanol (5 mL) was added a solution of hydrochloric acid in methanol [4 mL, prepared by addition of acetyl chloride (1 mL) to methanol (10 mL)] at 0 °C under nitrogen. The resulting mixture was then stirred at room temperature for 1 hour. After removal of the solvent under reduced pressure, the residue was diluted with methanol (5 mL) and treated with potassium carbonate (34 mg, 0.24 mmol, 1.0 eq.) for 5-10 minutes under nitrogen. The resulting mixture was filtered through a short column of silica gel and washed with ethyl acetate (5 mL). The combined organic phases were concentrated and the crude products were chromatographed on silica gel (Hexane: ethyl acetate = 2:1) to provide the indolinol (69 mg, yields: 78.0%).

Pale yellow needles, m.p.: 98-99 °C, Yield: (69 mg), 78.0%. <sup>1</sup>H-NMR (300MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.34-7.20 (5H, *m*), 6.95 (1H, *d*, *J* = 2.1 Hz), 6.68 (1H, *dd*, *J* = 2.1, 8.7 Hz), 6.60 (1H, *d*, *J* = 8.7 Hz), 5.30 (1H, *brs*), 4.88 (2H, *s*), 4.10 (2H, *q*, *J* = 6.9 Hz), 3.76 (3H, *s*), 3.57 (1H, *t*, *J* = 6.6 Hz), 3.52-3.31 (2H, *m*), 2.30-2.01 (2H, *m*), 1.23 (3H, *t*, *J* = 6.9 Hz). <sup>13</sup>C-NMR (75MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 177.63, 156.87, 156.12, 136.56, 135.91, 129.96, 128.86, 127.69, 127.29, 112.47, 111.43, 109.55, 60.82, 55.84, 43.87, 43.86, 38.35, 30.99, 14.74. EIMS *m*/*z* (%) : 370 (M<sup>+</sup>+2, 18%), 369 (M<sup>+</sup>+1, 52%), 368 (M<sup>+</sup>, 78%), 352 (5), 322 (78), 296 (21), 279 (40), 266 (91), 253 (43), 236 (8), 222 (4), 203 (9), 188 (72), 176 (55), 175 (26), 160 (38), 149 (22), 147 (17), 132 (29), 117 (15), 104 (14), 91 (100), 89 (6), 77 (7), 65 (33). HRMS *m*/*z* Found: 368.1722, Calcd. for C<sub>21</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub> (M)<sup>+</sup>: 368.1736.



To a solution of *tert*-butyl carbomate (120 mg, 0.24 mmol) in methanol (5 mL) was added a solution of hydrochloric acid in methanol [4 mL, prepared by addition of acetyl chloride (1 mL) to methanol (10 mL)] at 0 °C under nitrogen. The resulting mixture was then stirred at room temperature for 1 hour. After removal of the solvent under reduced pressure, the residue was diluted with methanol (5 mL) and treated with potassium carbonate (68 mg, 0.48 mmol, 2.0 eq.) at room temperature for 6-8 hours under oxygen or open to air. After filtration and removal of the solvent, the crude products were chromatographed on silica gel (Hexane: ethyl acetate = 4:3) to provide the amine (78 mg, yield: 85.0%).

Pale yellow syrup, Yield: (78 mg), 85.0%. <sup>1</sup>H-NMR (300MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.34-7.20 (5H, *m*), 7.03 (1H, *d*, *J* = 2.4 Hz), 6.70 (1H, *dd*, *J* = 2.4, 8.7 Hz), 6.59 (1H, *d*, *J* = 8.7 Hz), 5.30 (1H, *t*, *J* = 5.4 Hz), 4.89 (1H, *d*, *J* = 15.6 Hz), 4.75 (1H, *d*, *J* = 15.6 Hz), 4.53 (1H, *brs*), 4.04 (2H, *q*, *J* = 7.2 Hz), 3.74 (3H, *s*), 3.37-3.24 (2H, *m*), 2.19 (2H, *t*, *J* = 6.6 Hz), 1.19 (3H, *t*, *J* = 7.2 Hz). <sup>13</sup>C-NMR (75MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 178.15, 156.78, 156.56, 135.51, 135.31, 131.54, 128.90, 127.77, 127.28, 114.30, 111.22, 110.29, 75.91, 60.84, 55.85, 43.95, 38.24, 36.06, 14.67. EIMS *m*/*z* (%) : 385 (M<sup>+</sup>+1, 18%), 384 (M<sup>+</sup>, 49%), 368 (2), 338 (21), 299 (6), 277 (3), 269 (44), 265 (15), 254 (5), 247 (5), 236 (3), 210 (5), 204 (11), 192 (10), 178 (12), 176 (19), 160 (5), 146 (6), 134 (3), 120 (10), 102 (8), 91 (100), 83 (6), 77 (4), 65 (16). HRMS *m*/*z* Found: 384.1675, Calcd. for C<sub>21</sub>H<sub>24</sub>N<sub>2</sub>O<sub>5</sub> (M)<sup>+</sup>: 384.1685.



To a solution of amide (80 mg, 0.21 mmol) in anhydrous THF (10 mL) at 0 °C was added a powder of lithium aluminium hydride in onr portion (80 mg, 2.1 mmol, 10 eq.). The resulting mixture was then stirred at room temperature for 30 minutes before stirring at 70 °C (oil bath) overnight. The reaction mixture was cooled to 0 °C and saturated aqueous KOH solution (0.1 mL) was added. The mixture was diluted with water (20 mL) and extracted with ethyl acetate ( $2 \times 5$  mL) and dried over anhydrous sodium sulfate. After filtration and removal of the solvent, the crude products were chromatographed on silica gel (Dichloromethane: Methanol = 35:1) to provide the indoline (40 mg, yields: 61.3%).

Pale brown syrup, Yield: (40 mg), 61.3%. <sup>1</sup>H-NMR (300MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.36-7.20 (5H, *m*), 6.89 (1H, *d*, *J* = 2.4 Hz), 6.72 (1H, *dd*, *J* = 2.4, 8.7 Hz), 6.36 (1H, *d*, *J* = 8.7 Hz), 4.44 (1H, *d*, *J* = 16.5 Hz), 4.41 (1H, *s*), 4.30 (1H, *d*, *J* = 16.5 Hz), 3.73 (3H, *s*), 3.31 (1H, *brs*), 2.87-2.66 (2H, *m*), 2.37 (3H, *s*), 2.33-2.18 (2H, *m*). <sup>13</sup>C-NMR (75MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 153.64, 146.07, 139.08, 133.61, 128.70, 127.20, 127.08, 115.75, 109.82, 109.35, 97.43, 88.40, 56.13, 55.54, 52.81, 40.81, 38.05. **EIMS** *m*/*z* (%) : 312 (M<sup>+</sup>+2, 11%), 311 (M<sup>+</sup>+1, 52%), 310 (M<sup>+</sup>, 89%), 292 (36), 291 (20), 277 (11), 266 (29), 253 (65), 250 (33), 239 (10), 236 (14), 225 (6), 219 (20), 202 (28), 188 (17), 178 (8), 174 (10), 167 (16), 162 (32), 147 (17), 133 (42), 117 (12), 106 (15), 91 (100), 85 (20), 83 (36), 77 (19), 65 (36). **HRMS** *m*/*z* Found: 310.1665, Calcd. for C<sub>19</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub> (M)<sup>+</sup>: 310.1681.

#### Preparation of 2-(3,4-dimethoxyphenyl)-N-(4-hydroxyphenyl)acetamide:



To a solution of 4-aminophenol (546 mg, 5 mmol) in dichloromethane (20 mL) and pyridine (2.02 mL, 25 mmol, 5.0 eq.) at 0°C (ice-water bath), homoveratroyl chloride [generated by treatment of homoveratroic acid with oxalyl chloride in dichloromethane in the presence of DMF, (see Gilmore, C. D.; Allan, K. M.; Stoltz, B. M. *J. Am. Chem. Soc.* **2008**, *130*, 1558.) 5.5 mmol, 1.1 eq.] in dichloromethane (5 mL) was added dropwise. The resulting mixture was then stirred at room temperature for 3-4 hours. The reaction mixture was diluted with dichloromethane (20 mL) and treated with 2N HCl (10 mL) for 10 minutes and the aqueous phase was separated and the organic phase was washed with water (2×15 mL). After dried over anhydrous sodium sulfate and filtration, the solvent was removed under reduced pressure and the residue (1.43 g) was used in next step without further purification.

#### Preparation of 4-(3,4-dimethoxyphenethylamino)phenol:



To a solution of 2-(3,4-dimethoxyphenyl)-*N*-(4-hydroxyphenyl)acetamide (1.43 g) in anhydrous tetrahydrofuran (50 mL) at 0 °C (ice-water bath), lithium aluminum hydride (380 mg, 10 mmol, 2.0 eq.) was added in one portion. The resulting mixture was gradually warmed up to room temperature then stirred at 75 °C (oil bath) overnight. The

reaction mixture was cooled to 0 °C and an aqueous solution of saturated potassium carbonate (5 mL) was added dropwise. The mixture was diluted with water (50 mL) and extracted with ethyl acetate ( $3\times15$  mL). The organic phases were combined and washed with water ( $2\times15$  mL) and brine (15 mL). After dried over anhydrous sodium sulfate and filtration, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel (Dichloromethane : EtOAc = 15: 1) to afford the amine (984 mg, 72% over two steps).

Pale yellow syrup, <sup>1</sup>**H-NMR** (300MHz, CD<sub>3</sub>COCD<sub>3</sub>),  $\delta$  (ppm): 6.82 (1H, *d*, *J* = 8.1 Hz), 6.80-6.63 (4H, *m*), 6.54 (2H, *d*, *J* = 8.4 Hz), 3.85 (3H, *s*), 3.84 (3H, *s*), 3.32 (1H, *t*, *J* = 6.6 Hz), 2.83 (1H, *t*, *J* = 6.6 Hz). <sup>13</sup>**C** NMR (75 MHz, CD<sub>3</sub>COCD<sub>3</sub>)  $\delta$  (ppm): 148.98, 148.71, 147.60, 141.46, 131.86, 120.78, 116.36, 115.43, 112.16, 111.52, 55.96, 55.87, 46.61, 34.93. **HRMS** *m*/*z* Found: 274.1437, Calcd. for C<sub>16</sub>H<sub>20</sub>NO<sub>3</sub> (M+H)<sup>+</sup>: 274.1443.

#### Preparation of ethyl 3-[(3,4-dimethoxyphenethyl)(4-hydroxyphenyl)amino]-3-oxopropanoate:



To a solution of 4-(3,4-dimethoxyphenethylamino)phenol (820 mg, 3 mmol) in dichloromethane (30 mL) and pyridine (1.21 mL, 15 mmol, 5.0 eq.) at 0°C (ice-water bath), ethyl 3-chloro-3-oxopropanoate (496 mg, 3.3 mmol, 1.1 eq.) in dichloromethane (3 mL) was added dropwise. The resulting mixture was then stirred at room temperature for 2-3 hours. The reaction mixture was then treated with 2N HCl (10 mL) for 10 minutes and diluted with dichloromethane (20 mL). The aqueous phase was separated and the organic phase was washed with water (2×3 mL). The organic phases were combined and back extracted with ethyl acetate (10 mL). The combined organic phases were dried over anhydrous sodium sulfate and filtration. After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel (Hexane : EtOAc = 4: 1-2:1) to afford the amides (815 mg, 70.0%).

Pale yellow powder, m.p.: 138-139 °C, <sup>1</sup>**H-NMR** (300MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 6.93 (2H, *d*, *J* = 8.7 Hz), 6.90 (2H, *d*, *J* = 8.7 Hz), 6.75 (1H, *d*, *J* = 7.8 Hz), 6.74 (1H, *d*, *J* = 1.5 Hz), 6.68 (1H, *dd*, *J* = 1.5, 7.8 Hz), 4.10 (2H, *q*, *J* = 7.2 Hz), 3.89 (2H, *t*, *J* = 7.9 Hz), 3.81 (6H, *s*), 3.20 (2H, *s*), 2.83 (2H, *t*, *J* = 7.9 Hz), 1.20 (3H, *t*, *J* = 7.2 Hz). <sup>13</sup>C-NMR (75MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 167.97, 167.14, 157.11, 148.97, 147.64, 133.75, 131.09, 129.17, 120.87, 116.73, 112.22, 111.42, 61.51, 55.98, 55.92, 51.50, 41.90, 33.37, 14.09. **HRMS** *m*/*z* Found: 388.1759, Calcd. for C<sub>21</sub>H<sub>26</sub>NO<sub>6</sub> (M+H)<sup>+</sup>: 388.1760.

#### Preparation of highly functional Erythrina derivative:



To a solution of amide **1** (387 mg, 1.0 mmol) in trifluoroethyl alcohol (3 mL) was added PIFA [phenyliodine (III) bis(trifluoroacetate) or Iodobenzene *I,I*-bis(trifluoroacetate)] (473 mg, 1.1 mmol, 1.1 eq.) at -40 °C under nitrogen. After stirring at -40 °C for 2 hours, the reaction mixture was allowed to warm to room temperature then a powder of potassium carbonate (456 mg, 3.3 mmol, 3.3 eq.) was added. The resulting mixture was filtered and washed with ethyl acetate (10 mL). The filtrate was concentrated and the crude products were chromatographed on silica gel (Dichloromethane: ethyl acetate = 10:1) to provide enone **4** as pale yellow syrup (318 mg, 82.5%).

White crystals, m.p.: 161-162 °C, Yield: (318 mg), 82.5%. <sup>1</sup>H-NMR (300MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 6.71 (1H, *dd*, *J* = 1.8, 10.5 Hz), 6.67 (1H, *s*), 6.65 (1H, *s*), 6.18 (1H, *d*, *J* = 10.2 Hz), 4.41 (1H, *dd*, *J* = 3.9, 12.0 Hz), 4.30-4.21 (2H, *m*), 3.87 (3H, *s*), 3.79 (3H, *s*), 3.39 (1H, *d*, *J* = 11.7 Hz), 3.21 (1H, *dd*, *J* = 5.7, 12.1 Hz), 3.20-2.93 (3H, *m*), 2.72 (1H, *d*, *J* = 12.9 Hz), 2.66 (1H, *d*, *J* = 12.9 Hz ), 1.27 (3H, *t*, *J* = 7.2 Hz). <sup>13</sup>C-NMR (75MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 195.07, 168.29, 166.65, 149.23, 148.49, 145.79, 127.65, 126.75, 126.30, 112.79, 108.77, 62.19, 59.49, 56.36, 56.09, 54.03, 44.45, 36.69, 35.73, 29.03, 14.29. +TOF MS *m*/*z* (%) : 386 (M<sup>+</sup>+1, 100%), 280 (4), 274 (16), 222 (12), 218 (14), 153 (18), 136 (20), 123 (14), 102 (40). HRMS *m*/*z* Found: 386.1599, Calcd. for C<sub>21</sub>H<sub>24</sub>NO<sub>6</sub> (M+H)<sup>+</sup>: 386.1603.

### Preparation of (4a,13a<sup>1</sup>)-11,12-dimethoxy-4a,5,8,9-tetrahydro-3*H*-indolo[1-*a*]isoquinoline-3,6(4*H*)-dione:



A mixture of erythrina compound **3** (111.7 mg, 0.29 mmol.), sodium chloride (26 mg, 0.44 mmol, 1.5 eq.) and water (16 mg, 0.89 mmol, 3.1 eq.) in DMSO (15 mL) was stirred at 155 °C (oil bath) under nitrogen overnight (ca. 15-17 hours). The resulting mixture was then concentrated under reduced pressure and the residue was chromatographed on silica gel (200-300 mesh, Dichloromethane : EtOAc = 3: 1-2:1 ) to afford the enone (80 mg, 88%).

Pale white plates, m.p.: 161-162 °C, <sup>1</sup>H-NMR (300MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 6.64 (2H, *s*), 6.63 (1H, *d*, *J* = 10.2 Hz), 6.13 (1H, *d*, *J* = 10.2 Hz), 4.39 (1H, *dd*, *J* = 3.6, 12.3 Hz), 3.84 (3H, *s*), 3.77 (3H, *s*), 3.04 (1H, *dd*, *J* = 6.0, 11.7 Hz), 3.05-2.61 (5H, *m*), 2.56 (1H, *dd*, *J* = 8.4, 16.5 Hz), 2.33 (1H, *dd*, *J* = 12.0, 16.5 Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 195.77, 171.18, 148.92, 148.32, 145.51, 127.35, 127.18, 126.63, 112.67, 108.65, 60.82, 56.24, 56.00, 40.96, 37.64, 37.53, 35.02, 29.02. +TOF MS *m*/*z* (%) : 314 (M<sup>+</sup>+1, 100%), 274 (24), 218 (8), 205 (2), 193 (3), 163 (4), 153 (7), 137 (4), 111 (1), 102 (20). HRMS *m*/*z* Found: 314.1399, Calcd. for C<sub>18</sub>H<sub>20</sub>NO<sub>4</sub> (M+H)<sup>+</sup>: 314.1392.

# Preparation of (4a,5,13a<sup>1</sup>)-ethyl 11,12-dimethoxy-3,6-dioxo-2,3,4,4a,5,6,8,9-octahydro-1*H*-indolo[1*a*]isoquinoline-5-carboxylate:



To a solution of enone (385.4 mg, 1.0 mmol) in anhydrous ethanol (20 mL) was added a powder of 10% palladium on carbon (38 mg). The resulting mixture was then stirred at room temperature under a balloon of hydrogen overnight. After fitration and washed with dichloromethane (5 mL), the filtrate was concentrated and the residue was chromatographed on silica gel (200-300 mesh, Dichloromethane : EtOAc = 5: 1-3:1 ) to afford the ketone as a white foam (368 mg, 95%).

White plates, m.p.: 182-183 °C, <sup>1</sup>H-NMR (300MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 6.68 (1H, *s*), 6.56 (1H, *s*), 4.34 (1H, *dd*, *J* = 5.4, 13.2 Hz), 4.15 (2H, *q*, *J* = 7.2 Hz), 3.86 (3H, *s*), 3.84 (3H, *s*), 3.44-3.34 (1H, *m*), 3.18 (1H, *d*, *J* = 8.1 Hz), 3.15-2.90 (2H, *m*), 2.65 (1H, *d*, *J* = 16.8 Hz), 2.64 (1H, *d*, *J* = 16.8 Hz), 2.49-2.20 (4H, *m*), 1.22 (3H, *t*, *J* = 7.2 Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 209.23, 169.01, 167.18, 148.71, 148.54, 133.87, 125.48, 111.94, 107.36, 62.16, 61.47, 56.44, 56.03, 55.21, 42.55, 42.06, 35.62, 35.44, 33.50, 27.82, 14.14. +TOF MS *m*/*z* (%) : 388 (M<sup>+</sup>+1, 100%), 374 (2), 342 (1), 318 (5), 301 (7), 279 (8), 274 (8), 238 (2), 218 (2), 150 (3), 119 (6), 102 (3). HRMS *m*/*z* Found: 388.1751, Calcd. for C<sub>21</sub>H<sub>26</sub>NO<sub>6</sub> (M+H)<sup>+</sup>: 388.1760.

#### Preparation of (4a,13a<sup>1</sup>)-11,12-dimethoxy-4a,5,8,9-tetrahydro-1*H*-indolo[1-*a*]isoquinoline-3,6(2*H*,4*H*)-dione:



A mixture of erythrina compound **18** (193 mg, 0.5 mmol.), lithium chloride (21 mg, 0.5 mmol, 1.0 eq.) and water (27 mg, 1.5 mmol, 3.0 eq.) in DMSO (15 mL) was stirred at 158 °C (oil bath) under nitrogen overnight (ca. 15-17 hours). The resulting mixture was then concentrated under reduced pressure and the residue was chromatographed on silica gel (200-300 mesh, Dichloromethane : EtOAc = 3: 1-2:1 ) to afford the enone as a pale yellow syrup (118 mg, 75%).

Pale yellow powder, m.p.: 164-165 °C, <sup>1</sup>H-NMR (300MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 6.68 (1H, *s*), 6.56 (1H, *s*), 4.37 (1H, *dd*, *J* = 5.4, 12.0 Hz), 3.86 (3H, *s*), 3.84 (3H, *s*), 3.15-2.90 (4H, *m*), 2.78-2.53 (3H, *m*), 2.49-2.20 (4H, *m*), 2.11 (1H, *dd*, *J* = 7.5, 17.8 Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 210.13, 172.19, 148.60, 148.43, 134.48, 125.65, 111.91, 107.45, 62.56, 56.45, 56.03, 43.38, 37.90, 37.59, 35.35, 34.84, 33.64, 27.67. HRMS *m*/*z* Found: 316.1556, Calcd. for C<sub>18</sub>H<sub>22</sub>NO<sub>4</sub> (M+H)<sup>+</sup>: 316.1548.

# **Spectrum for**

# Oxidative Dearomatization in the Synthesis of Erythrina, Oxindole and Hexahydropyrrolo[2,3-*b*]-indole Skeletons

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