Visible Light Mediated Cyclization of Tertiary Anilines with Maleimides Using Supported Iridium Complex Catalyst

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Supporting Information

1.	General information	S2
2.	Photoreaction setup	S2
3.	Centrifugal separation of the P4 photocatalyst	S3
4.	Spectral data of products3a-3s	S3-10
5.	¹ H NMR of compounds 3a-3s and ¹³ C NMRof compounds 3m-3p, 3s	S10-21

1. General information

All reagents were commercially available and used without further purification. All solvents were dried according to standard procedures. Melting points were measured on a Taike X-4 microscopic melting point apparatus and are uncorrected. ¹H and ¹³C NMR spectra were measured on a Bruker ACF-400 spectrometer and recorded at 400 and 100 MHz, respectively, using CDCl₃ as solvent. IR spectra were taken with a Nicolet FT-IR 5DX spectrometer. UV–vis absorption spectroscopy was measured on a Shimadzu 2550spectrometer.Mass spectra were recorded with a VG ZAB-HS spectrometer using ESI techniques. HRMS were taken with aAB TripleTOF 5600plus System (AB SCIEX, Framingham,USA). The exact mass calibration was performed automatically before each analysis employing the Automated Calibration Delivery System.Elemental analyses were obtained using a Heraeus CHN-O-Rapid analyzer. XRD were measured with PANalytical Empyrean. TEM were measured with a JEM-1011. TEM-EDS were measured with a JSM-6360LV,ICP-AES were recorded at a Leeman Prodigy xp. The Brunauer–Emmett–Teller (BET) surfacearea was measured using a Micromeritics Empyrean instrument.

2. Photoreaction setup



Fig. 1s Photoreaction setup for the cyclization reactions.

3. Centrifugal separation of the P4photocatalyst



Fig. 2s Centrifugal separation of the P4photocatalyst (Left) Before the centrifugal (Right) After the centrifugal.

4. Analytical data for the synthesized compounds



 $(3aS^*,9bR^*)$ -5-methyl-2-phenyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1 ,3(2H)-dione(**3a**) 105.3 mg. White solid: R_f = 0.45 (petroleum ether/ethyl acetate 30:8); m.p. 202-204 °C^[1]; ¹H NMR (400 MHz, CDCl₃) δ 2.84 (s, 3H), 3.13 (dd, 1H, J = 11.6, 4.4 Hz), 3.55 (ddd, 1H, J = 9.6, 4.3, 2.7 Hz), 3.62 (dd, 1H, J = 11.6, 2.8 Hz), 4.17 (d, 1H, J = 9.6 Hz), 6.75 (d, 1H, J = 8.0 Hz), 6.91 (td, 1H, J = 8.4, 1.0 Hz), 7.22 - 7.28 (m, 3H), 7.36–7.44 (m, 3H), 7.53 (d, 1H, J = 7.6 Hz).



 $(3aS^*, 9bR^*)$ -5-methyl-2-(p-tolyl)-3a, 4, 5, 9b-tetrahydro-1H-pyrrolo[3, 4-c] quinoline-1,

3(2H)-dione(**3b**) 133.7 mg. White solid: R_f = 0.47 (petroleum ether/ethyl acetate 30:8); m.p. 212-214 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.36 (s, 3H), 2.85 (s, 3H), 3.15 (dt, 1H, J = 11.5, 4.1 Hz),3.55 (ddd, 1H, J = 9.6, 4.5, 2.8 H), 3.60 – 3.64 (m, 1H), 4.16 (d, 1H, J = 9.5 Hz), 6.76 – 6.82 (m, 1H), 6.93 (td, 1H, J = 7.5, 2.5 Hz), 7.12–7.16 (m, 2H), 7.20–7.25 (m, 3H), 7.52 (d, 1H, J = 7.6 Hz).



 $(3aS^*,9bR^*)$ -2-(4-fluorophenyl)-5-methyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]qui noline-1,3(2H)-dione(**3c**) 77.1 mg. White solid: R_f = 0.42 (petroleum ether/ethyl acetate 30:8); m.p. 172-174 °C;¹H NMR (400 MHz, CDCl₃) δ 2.84 (s, 3H), 3.13 (dd, 1H, *J* = 11.5, 4.4 Hz), 3.54 (ddd, 1H, *J* = 9.6, 4.3, 2.7Hz), 3.60 (dd, 1H, *J* = 11.5, 2.7 Hz), 4.15 (d, 1H, *J* = 9.6 Hz), 6.75 (d, 1H, *J* = 7.6 Hz), 6.91 (td, 1H, *J* = 7.5, 1.1 Hz), 7.07-7.15 (m, 2H), 7.21-7.28 (m, 3H), 7.52 (d, 1H, *J* = 7.5Hz).



 $(3aS^*,9bR^*)$ -2-(4-chlorophenyl)-5-methyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]qui noline-1,3(2H)-dione(**3d**) 96.4 mg. White solid: R_f= 0.41 (petroleum ether/ethyl acetate 30:8); m.p. 188-190 °C;¹H NMR (400 MHz, CDCl₃) δ 2.84 (s, 3H), 3.12 (dd, 1H, *J* = 11.5, 4.3 Hz), 3.55 (ddd, 1H, *J* = 9.6, 4.3, 2.6 Hz), 3.62 (dd, 1H, *J* = 11.5, 2.6 Hz), 4.17 (d, 1H, *J* = 9.6 Hz), 6.75 (d, 1H, *J* = 8.2 Hz), 6.92 (td, 1H, *J* = 7.5, 1.1 Hz), 7.22-7.26 (m, 3H), 7.37-7.41 (m, 2H), 7.52 (d, 1H, *J* = 7.4 Hz).

 $(3aS^*,9bR^*)$ -2-benzyl-5-methyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (**3e**) 79.6 mg. White solid: R_f = 0.45 (petroleum ether/ethyl acetate 30:8); m.p. 126-128 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.72 (s, 3H),2.97 (dd, 1H, *J* = 11.5, 4.5 Hz), 3.25 – 3.32 (m, 1H), 3.42 (dd, 1H, *J* = 11.5, 2.7 Hz),3.92 (d, 1H, *J* = 9.4 Hz), 4.58 (q, 2H, *J* = 14.3 Hz),6.64 (d, 1H, *J* = 8.1 Hz), 6.82 (td, 1H, *J* = 7.5, 0.9 Hz), 7.12-7.24 (m, 6H), 7.39 (d, 1H, *J* = 7.3 Hz).

 $(3aS^*,9bR^*)$ -5,8-dimethyl-2-phenyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoli ne-1,3(2H)-dione(**3f**) 132.4 mg. White solid: R_f = 0.50 (petroleum ether/ethyl acetate 30:8); m.p. 193-195 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.30 (s, 3H), 2.80 (s, 3H), 3.06 (dd, 1H, *J* = 11.4, 4.3 Hz), 3.52 (ddd, 1H, *J* = 9.5, 4.3, 2.7 Hz), 3.59 (dd, 1H, *J* = 11.4, 2.7 Hz), 4.12 (d, 1H, *J* = 9.6 Hz), 6.65 (d, 1H, *J* = 8.3 Hz), 7.04 (dd, 1H, *J* = 8.3, 1.7 Hz), 7.26-7.28 (m, 2H), 7.33-7.37 (m, 2H), 7.41-7.45 (m, 2H).

 $(3aS^*,9bR^*)$ -5,8-dimethyl-2-(p-tolyl)-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c] quinolin e-1,3(2H)-dione(**3g**) 143.1 mg. White solid: R_f = 0.47 (petroleum ether/ethyl acetate 6:1); m.p. 207-208 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.32 (s, 3H), 2.36 (s, 3H), 2.84 (s, 3H), 3.14 (dd, 1H, J = 11.6, 4.4 Hz), 3.53 – 3.58 (m, 1H), 3.62 (dd, 1H, J = 11.6, 2.8 Hz), 4.14 (d, 1H, J = 9.6 Hz), 6.77 (d, 1H, J = 8.0 Hz), 7.06 (dd, 1H, J = 8.0, 2.0Hz), 7.13 (dd, 2H, J = 8.4, 2.0 Hz), 7.23 (d, 2H, J = 8.2 Hz), 7.39 (d, 1H, J = 0.8 Hz).

 $(3aS^*,9bR^*)$ -2-(4-fluorophenyl)-5,8-dimethyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4c]quinoline-1,3(2H)-dione(**3h**) 100.2 mg. White solid: R_f = 0.42 (petroleum ether/ethyl acetate 5:1); m.p. 157-159 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.30 (s, 3H), 2.80 (s, 3H), 3.06 (dd, 1H, J = 11.4, 4.3 Hz), 3.49 – 3.56 (m, 1H), 3.59 (dd, 1H, J =11.4, 2.6 Hz), 4.13 (d, 1H, J = 9.6 Hz),6.66 (d, 1H, J = 8.3 Hz),7.04 (dd, 1H, J = 8.4, 1.6 Hz), 7.09-7.13 (m, 2H), 7.254-7.27 (m, 2H), 7.32 (s, 1H).

 $(3aS^*,9bR^*)$ -2-(4-chlorophenyl)-5,8-dimethyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4 -c]quinoline-1,3(2H)-dione(**3i**) 129.5 mg. White solid: R_f = 0.40 (petroleum ether/ethyl acetate 30:8); m.p. 178-180 °C;¹H NMR (400 MHz, CDCl₃) δ 2.31 (s, 3H), 2.81 (s, 3H), 3.07 (dd, 1H, J = 11.4, 4.3 Hz),3.53 (ddd, 1H, J = 9.6, 4.3, 2.6 Hz), 3.59 (dd, 1H, J = 11.4, 2.6 Hz), 4.13 (d, 1H, J = 9.6 Hz), 6.67 (d, 1H, J = 9.6 Hz), 7.05 (dd, 1H, J = 8.3, 2.0 Hz), 7.24-7.26 (m, 2H), 7.34 (d, 1H, J = 1.6 Hz), 7.38-7.41 (m, 2H).

 $(3aS^*,9bR^*)$ -2-benzyl-5,8-dimethyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoli ne-1,3(2H)-dione(**3j**) 105.5 mg. White solid: R_f = 0.45 (petroleum ether/ethyl acetate 30:7); m.p. 131-136 °C;¹H NMR (400 MHz, CDCl₃) δ 2.30 (s, 3H), 2.77 (s, 3H),3.00 (dd, 1H, *J* = 11.5, 4.0 Hz), 3.35 (ddd, 1H, *J* = 9.3, 4.3, 2.6 Hz), 3.48 (dd, 1H, *J* = 11.4, 2.7 Hz), 3.96 (d, 1H, *J* = 9.4 Hz), 4.65 (q, 2H, *J* = 14.3 Hz), 6.64 (dd, 1H, *J* = 8.2, 4.0 Hz), 7.03 (d, 1H, *J* = 6.8 Hz), 7.21-7.34 (m, 6H).

 $(3aS^*,9bR^*)$ -5,7-dimethyl-2-phenyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoli ne-1,3(2H)-dione(**3k**) 99.6 mg. White solid: R_f = 0.40 (petroleum ether/ethyl acetate 6:1); m.p. 193-195 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.59 (s, 3H), 2.79 (s, 3H), 2.96 (dd, 1H, J = 11.2, 4.8 Hz), 3.51 – 3.55 (m, 1H), 3.59 (ddd, 1H, J = 11.3, 4.9, 2.2 Hz), 4.52 (d, 1H, J = 9.8 Hz), 6.64 (d, 1H, J = 8.2 Hz), 6.82 (d, 1H, J = 7.5 Hz), 7.13 (t, 1H, J = 7.9 Hz), 7.23-7.31 (m, 1H), 7.32 – 7.39 (m, 1H), 7.40-7.46 (m, 3H).

 $(3aS^*,9bR^*)$ -8-fluoro-5-methyl-2-phenyl-4,5-dihydro-2H-pyrrolo[3,4-c]quinoline-1,3(3aH,9bH)-dione(**31**)107.3 mg. White solid: R_f = 0.46 (petroleum ether/ethyl acetate 30:8); m.p. 172-174 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.82 (s, 3H), 3.09 (dd, 1H, J = 11.4, 4.4 Hz), 3.55 (ddd, 1H, J = 9.6, 4.3, 2.8 Hz), 3.60 (dd, 1H, J = 11.4, 2.8 Hz), 4.13 (d, 1H, J = 9.5 Hz), 6.69 (dd, 1H, J = 9.0, 4.7 Hz),6.86 (s, 1H), 6.95 (td, 1H, J = 8.6, 3.0 Hz), 7.25-7.29 (m, 2H), 7.42-7.49 (m, 3H).

 $(3aS^*,9bR^*)$ -8-fluoro-5-methyl-2-(p-tolyl)-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]qui noline-1,3(2H)-dione(**3m**) 147.4 mg. White solid: R_f = 0.46 (petroleum ether/ethyl acetate 6:1); m.p. 178-181 °C; IR (KBr) v 2964, 2867, 1710, 1577, 1504, 1194, 618 cm^{-1,1}H NMR (400 MHz, CDCl₃) δ 2.36 (s, 3H), 2.82 (s, 3H),3.09 (dd, 1H, *J* = 11.4, 4.4 Hz), 3.53 (ddd, 1H, *J* = 9.6, 4.4, 2.9 Hz), 3.58 (dd, 1H, *J* = 11.4, 2.9 Hz), 4.11 (d,1H, *J* = 9.6 Hz), 6.68 (dd, 1H, *J* = 9.0, 4.7 Hz), 6.94 (td, 1H, J = 8.6, 3.0 Hz), 7.12-7.15 (m, 2H), 7.24 (d, 2H, *J* = 8.1 Hz), 7.28 (dd,1H, *J* = 9.0, 2.7 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 28.2, 39.8, 42.4, 43.5, 55.7, 113.4, 114.4, 115.7, 119.8, 126.1, 129.3, 129.7, 138.6, 142.8, 153.2, 175.7, 177.3, 177.9; HRMS (ESI) Calcd for C₁₉H₁₈FN₂O₂ [M+H]⁺: 325.1352, found 325.1350.

 $(3aS^*,9bR^*)$ -8-fluoro-2-(4-fluorophenyl)-5-methyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione(**3n**) 86.9 mg. White solid: R_f = 0.34 (petroleum ether/ethyl acetate 5:1); m.p. 150-152 °C; IR (KBr) v 2924, 1709, 1577, 1508, 1425,

1151, 679 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.81 (s, 3H), 3.07 (dd, 1H, *J* = 11.4, 4.4 Hz), 3.53 (ddd, 1H, *J* = 9.6, 4.3, 2.7 Hz), 3.59 (dd, 1H, *J* = 11.4, 2.7 Hz), 4.12 (d, 1H, *J* = 9.6 Hz), 6.67 (dd, 1H, *J* = 9.0, 4.6 Hz), 6.94 (td, 1H, J = 8.6, 3.0 Hz), 7.09-7.15 (m, 2H), 7.24-7.31 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 39.8, 42.1, 43.4, 51.0, 113.4 (d, J = 8.0 Hz), 115.1 (d, J = 21.0 Hz), 116.1 (d, J = 22.0 Hz), 116.9 (d, J = 23.0 Hz), 119.8 (d, J = 7.0 Hz), 128.2 (d, J = 9.0 Hz), 145.0, 155.5, 157.9, 160.9, 163.4, 175.1, 177.4; HRMS (ESI) Calcd for C₁₈H₁₅F₂N₂O₂ [M+H]⁺: 329.1102, found 329.1096.

 $(3aS^*,9bR^*)$ -2-(4-chlorophenyl)-8-fluoro-5-methyl-3a, 4, 5, 9b-tetrahydro-1H-pyrrolo [3,4-c] quinoline-1,3(2H)-dione(**3o**) 123.8 mg. White solid: R_f = 0.31(petroleum ether/ethyl acetate 30:7); m.p. 156-158 °C;IR (KBr) v 2925, 2854, 1718, 1577, 1438, 1133, 619 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.81 (s, 3H), 3.08 (ddd, 1H, *J* = 11.4, 4.3, 1.7 Hz), 3.50–3.56 (m, 1H), 3.59 (dd, 1H, *J* = 11.5, 2.6 Hz), 4.12 (d, 1H, *J* = 9.4 Hz), 6.68 (dd, 1H, *J* = 9.0, 4.6 Hz), 6.95 (td, 1H, J = 8.6, 3.0 Hz), 7.23-7.28 (m, 3H), 7.39-7.43 (m, 2H);¹³C NMR (100 MHz, CDCl₃) δ 39.6, 42.1, 43.3, 50.9, 113.3 (d, J = 7.6 Hz), 114.9 (d, J = 21.8 Hz), 116.7 (d, J = 23.1 Hz), 119.9 (d, J = 7.7 Hz), 127.5, 129.0, 130.3, 134.1, 144.9, 155.2, 157.6, 160.1, 177.2, 177.3; HRMS (ESI) Calcd for C₁₈H₁₅ClFN₂O₂ [M+H]⁺: 345.0806, found 345.0806.

(3*a*S*,9*b*R*)-2-*benzyl*-8-*fluoro*-5-*methyl*-3*a*,4,5,9*b*-*tetrahydro*-1*H*-*pyrrolo*[3,4-*c*]*quin oline*-1,3(2*H*)-*dione*(**3p**) 87.4 mg. White solid: $R_f = 0.38$ (petroleum ether/ethyl acetate 30:7); m.p. 130-132 °C; IR (KBr) *v* 2925, 1701, 1577, 1495, 1438, 1130, 619 cm⁻¹;¹H NMR (400 MHz, CDCl₃) δ 2.77 (s, 3H), 2.99 (dd,1H, *J* = 11.4, 4.8 Hz), 3.35 (ddd, 1H, *J* = 9.4, 4.5, 2.8 Hz),3.47 (dd, 1H, *J* = 11.5, 2.8 Hz), 3.94 (d,1H, *J* = 9.4 Hz), 4.66 (q, 2H, *J* = 14.3 Hz), 6.62 (dd, 1H, *J* = 9.0, 4.6 Hz), 6.91 (td, 1H, J = 8.6, 3.0 Hz), 7.20 - 7.22 (m, 1H),7.23 - 7.26 (m, 1H), 7.31 - 7.23 (m, 4H);¹³C NMR (100 MHz, CDCl₃) δ 39.6, 42.2, 42.9, 43.5, 51.1, 113.3 (d, J = 8.0 Hz), 114.9 (d, J = 22.0 Hz), 116.9 (d, J = 23.0 Hz), 120.3 (d, J = 8.0 Hz), 127.9, 128.3, 128.6, 135.4, 144.93, 144.95, 155.45, 157.82, 175.8, 178.1; HRMS (ESI) Calcd for C₁₉H₁₈FN₂O₂ [M+H]⁺: 325.1352, found 325.1352.

 $(3aS^*,9bR^*)$ -8-methoxy-5-methyl-2-(p-tolyl)-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4c]quinoline-1,3(2H)-dione(**3q**)128.7 mg. White solid: R_f = 0.37 (petroleum ether/ethyl acetate 30:8); m.p. 212–214 °C;¹H NMR (400 MHz, CDCl₃) δ 2.38 (s, 3H), 2.81 (s, 3H), 3.07(dd, 1H, J = 11.2, 4.4 Hz), 3.38 (s, 3H), 3.53 (ddd, 1H, J = 9.4, 4.2, 2.8 Hz), 3.58 (dd, 1H, J = 11.6, 2.8 Hz),4.11 (d, 1H, J = 9.6 Hz),6.66 (dd, 1H, J = 8.8, 4.8 Hz),6.93 (td, 1H, J = 8.4, 2.9 Hz), 7.12 – 7.15 (m, 2H), 7.23-7.29 (m, 3H).

 $(3aS^*,9bR^*)$ -8-methoxy-5-methyl-2-phenyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]qu inoline-1,3(2H)-dione(**3r**) 95.1 mg. White solid: R_f = 0.41(petroleum ether/ethyl acetate 30:8); m.p. 164-166 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.79 (s, 3H), 3.03 (dd, 1H, J = 11.3, 4.3 Hz), 3.52 (ddd, 1H, J = 9.5, 4.3, 2.8 Hz), 3.56 (dd, 1H, J = 11.2, 2.8 Hz), 3.79 (s, 3H), 4.13 (d, 1H, J = 9.5 Hz), 6.68 (d, 1H, J = 8.9 Hz), 6.81 (dd, 1H, J = 8.9, 2.9 Hz), 7.13 (d, 1H, J = 2.8 Hz), 7.26-7.28 (m, 2H), 7.34 –7.38 (m, 1H), 7.40-7.45 (m, 2H).

 $(3aS^*,9bR^*)$ -8-chloro-5-methyl-2-(p-tolyl)-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]qui noline-1,3(2H)-dione(**3s**) 161.3 mg. White solid: R_f = 0.37 (petroleum ether/ethyl acetate 30:8); m.p. 189-191°C; IR (KBr) v 2958, 1707, 1577, 1512, 1497, 1395, 648 cm^{-1,1}H NMR (400 MHz, CDCl₃) δ 2.36 (s, 3H), 2.82 (s, 3H), 3.10 (dd, 1H, *J* = 11.5, 4.4 Hz), 3.52 (ddd, 1H, *J* = 9.6, 4.4, 2.8 Hz), 3.60 (dd, 1H, *J* = 11.5, 2.8 Hz), 4.10 (d,1H, *J* = 9.6 Hz), 6.60 (d, 1H, *J* = 8.8 Hz), 7.11-7.15 (m, 2H), 7.18 (dd, 1H, *J* = 8.7, 2.5 Hz), 7.24 (d,2H, *J* = 8.2 Hz), 7.51 (d, 1H, *J* = 2.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 21.2, 39.5, 41.8, 43.2, 50.5, 113.8, 120.0, 124.5, 126.1, 128.5, 129.2, 129.7, 130.0, 138.7, 147.0, 175.2, 177.4; HRMS (ESI) Calcd for $C_{19}H_{18}ClN_2O_2$ [M+H]⁺: 341.1057, found 341.1058.

5. ¹H NMR (400MHz, CDCl₃) and ¹³C NMR (100MHz, CDCl₃) of compounds 3a-3s

3h

3k

m

