

Supporting Information

**Aerobic Oxidative Condensation for the Synthesis of
Phenoxazinone and Phenazine Derivatives Catalyzed
by an Iron-Porphyrin Complex with a Pendant
Imidazole Ligand**

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Contents

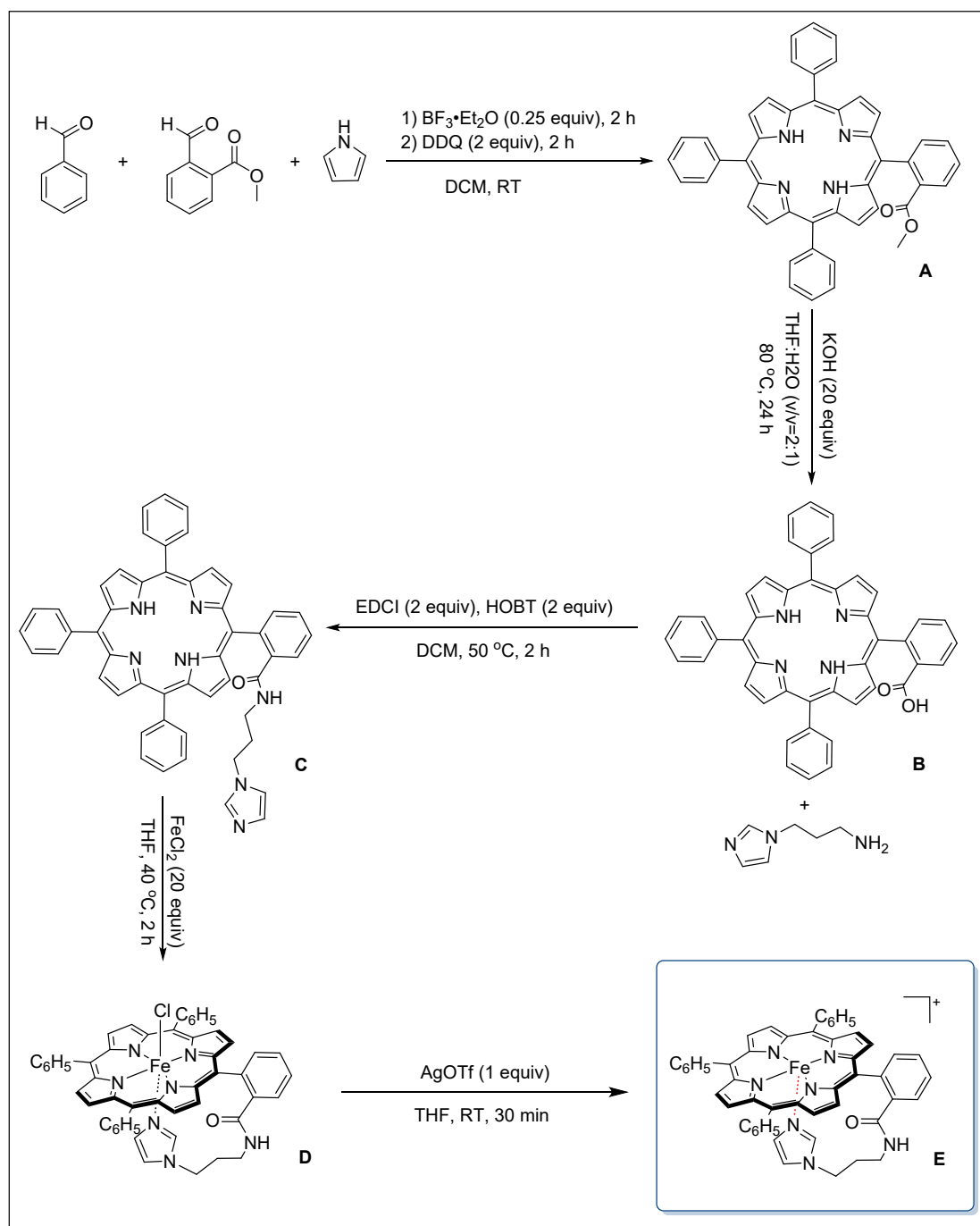
1. General Information	3
2. Synthesis of Fe porphyrins	4
3. Characterization of Fe Porphyrins.....	9
4. General Procedure	11
5. References	19
6. ¹H and ¹³C NMR spectra	20

1. General Information

Unless otherwise noted, reagents were obtained from commercial sources and utilized without further purification. All characterizations were performed using the following instruments: Nuclear magnetic resonance spectroscopy was conducted on a Bruker AV600 MHz spectrometer from Switzerland to acquire ^1H and ^{13}C NMR spectra. High-resolution mass spectrometry was performed using a Waters ACQUITY I-class ultra-performance liquid chromatography system coupled to a Waters Xevo G2-XS QToF mass spectrometer, both sourced from the United States, in order to obtain precise molecular ion information. UV/Vis absorption spectra were measured using a UV1810 spectrophotometer manufactured by Youyi Technology in China. Electron paramagnetic resonance spectra were acquired on a Bruker A300-10/12 spectrometer from Germany; the system was equipped with a liquid nitrogen cooling unit and operated at a microwave frequency of 9.46 GHz. Catalyst purity analysis was performed on a supercritical fluid chromatography–mass spectrometry system, model SFC-30ADMS. Finally, sample separation and purification were accomplished using a rapid preparative liquid chromatography system, specifically the SepaBean machine, supplied by Changzhou Santai Technology Co., Ltd in China. Specific experimental parameters for each measurement are detailed in the corresponding figure captions or sections below.

2. Synthesis of Fe porphyrins

Fe porphyrin **E** was synthesized using synthetic route depicted in Scheme S1.



Scheme S1. Synthetic route of Fe porphyrin **E**.

In the experimental procedure, methyl 2-formylbenzoate (4 mmol, 0.56 mL), benzaldehyde (12 mmol, 1.2 mL), and pyrrole (16 mmol, 1.1 mL) were dissolved in dichloromethane (200 mL) under stirring. Boron trifluoride diethyl etherate (1 mmol, 0.26 mL) was then added to the mixture. After stirring for 2 hours, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 8 mmol, 1.8 g) was added, and the reaction was continued for an additional 2 hours¹⁻³. The reaction was quenched by

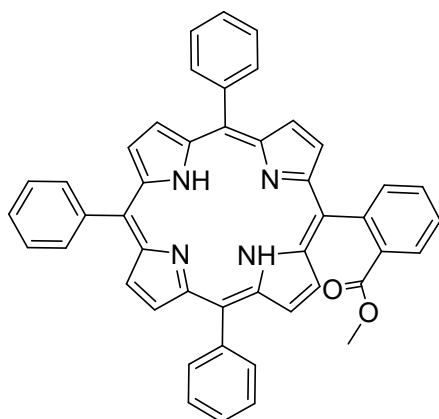
the addition of a small amount of triethylamine. The crude product was purified by column chromatography using a 1:1 (v/v) mixture of dichloromethane and petroleum ether as the eluent to afford compound **A** in 15% yield.

Compound **A** (1 mmol, 0.67 g) was dissolved in tetrahydrofuran (60 mL). To this solution was added an aqueous solution of potassium hydroxide (KOH, 20 mmol, 1.12 g in 30 mL of water), followed by a few drops of methanol. The mixture was heated to reflux at 80 °C for 24 hours. After cooling to room temperature, the reaction mixture was neutralized with 1 M hydrochloric acid (HCl) solution. The resulting mixture was then extracted three times with saturated sodium bicarbonate (NaHCO₃) solution and three times with water. The combined organic layers were dried over anhydrous sodium sulfate (Na₂SO₄). The crude product was purified by column chromatography using a 20:1 (v/v) mixture of dichloromethane and methanol as the eluent, affording compound **B** with a yield of 88%. The product was used directly in the subsequent step.

Compound **B** (1 mmol, 0.65 g) was dissolved in dichloromethane (30 mL). After complete dissolution, EDCI (2 mmol, 0.38 g) and HOBt (2 mmol, 0.27 g) were added sequentially. The reaction mixture was heated to reflux at 50 °C for 30 min. Subsequently, 1-(3-aminopropyl) imidazole (2 mmol, 0.23 mL) was added, and the reaction was continued for an additional 2 hours. Upon completion, the mixture was extracted three times with saturated brine and three times with water. The combined organic layers were dried over anhydrous sodium sulfate. The crude product was purified by column chromatography using a 10:1 (v/v) mixture of dichloromethane and methanol as the eluent, affording the target compound **C** in 85% yield.

Compound **C** (0.3 mmol, 0.23 g) and iron (II) chloride (FeCl₂, 6 mmol, 0.76 g) were dissolved in tetrahydrofuran (18 mL) under a nitrogen atmosphere⁴. The mixture was heated to reflux at 40 °C for 2 hours. After completion of the reaction, the crude product was purified by column chromatography using a 10:1 (v/v) mixture of dichloromethane and methanol as the eluent, affording the chloride-containing compound **D** : (**E**)Cl in 89% yield. The chloride ion in compound **D** was then substituted by a triflate group via reaction with an equimolar amount of silver trifluoromethanesulfonate (AgOTf) to give compound **E**.

methyl (R)-2-(10,15,20-triphenylporphyrin-5-yl) benzoate (**A**)

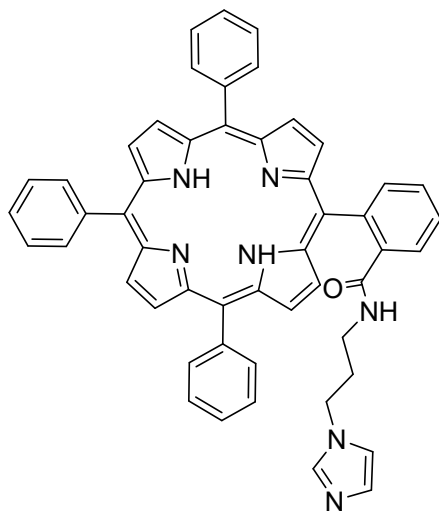


Purple solid, yield = 15%; ¹H NMR (600 MHz, CDCl₃) δ 8.90 – 8.87 (m, 6H), 8.72 (d, *J* = 4.7 Hz, 2H), 8.44 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.32 – 8.19 (m, 7H), 7.91 – 7.75 (m, 11H), 2.83 (s, 3H), –2.60 (s, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 168.05, 142.76, 142.40, 142.31, 136.18, 134.75, 134.68,

134.67, 134.26, 129.87, 129.82, 128.50, 127.84, 127.83, 126.81, 120.28, 120.26, 119.18, 51.71;

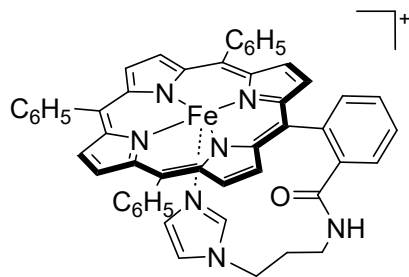
HRMS (ESI): Calcd. for $C_{46}H_{32}N_4O_2$ $[M-H]^-$ m/z 671.2447, Found m/z 671.2444.

(R)-N-(3-(1H-imidazol-1-yl) propyl)-2-(10,15,20-triphenylporphyrin-5-yl) benzamid (C)



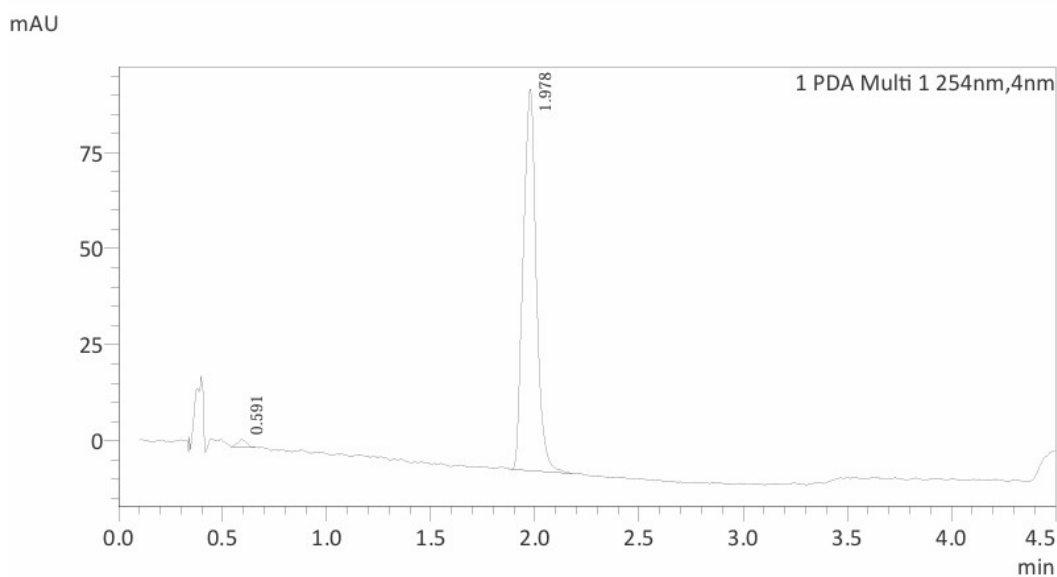
Purple solid, yield = 85%; **1H NMR** (600 MHz, $CDCl_3$) δ 8.94 – 8.82 (m, 8H), 8.30 – 8.26 (m, 2H), 8.22 – 8.16 (m, 4H), 8.13 (d, J = 7.1 Hz, 2H), 7.91 (t, J = 7.8 Hz, 1H), 7.82 – 7.74 (m, 10H), 5.98 (s, 1H), 5.78 (s, 1H), 4.91 (br, J = 6.3 Hz, 1H), 4.37 (s, 1H), 2.15 (q, J = 6.2 Hz, 2H), 1.00 (t, J = 7.0 Hz, 2H), -0.29 (p, J = 6.5 Hz, 2H), -2.68 (s, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 168.79, 141.93, 141.69, 139.29, 138.94, 135.45, 135.33, 134.72, 134.67, 134.65, 134.58, 129.14, 128.84, 128.79, 128.11, 128.08, 127.26, 127.05, 126.97, 126.93, 126.89, 121.28, 120.96, 117.36, 116.71, 41.79, 35.37, 29.28; **HRMS (ESI):** Calcd. for $C_{51}H_{39}N_7O$ $[M+H]^+$ m/z 766.3289, Found m/z 766.3290.

Fe porphyrin E



Purple solid, yield = 89%; **HRMS (ESI)**: Calcd. for C₅₁H₃₇N₇OFe [M+H]⁺ *m/z* 819.2404, Found *m/z* 819.2413. The purity of iron porphyrin E was determined to be 98.72% by Supercritical Fluid Chromatography (SFC).

Chromatogram



Peak Table

Peak#	Ret. Time	Height	Area	Area%	Resolution(USP)	Tailing Factor	USP Width
1	0.591	1966	5627	1.285	--	0.988	0.084
2	1.978	99206	432426	98.715	13.588	1.096	0.120
Total		101171	438053	100.000			

Co-Solvent: MeOH (0.1% TFA)

Column Name and Size: Torus DIOL 130A 4.6*100 mm, 5 μm

Oven Temperature: 35°C

Total Flow: 4.0000 mL/min

Start Conc. of Pump B: 10.0%

BPR Pressure: 10.00 MPa

PDA Model: SPD-M20A

Lamp: D2

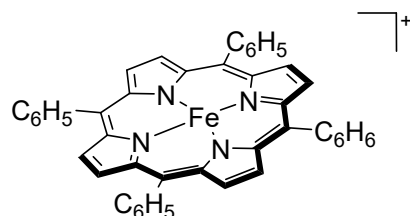
Start Wavelength: 190 nm

End Wavelength: 400 nm

LC Time Program Table:

Time	Module	Command	Value
3.00	Pumps	Pump B Conc.	50
4.00	Pumps	Pump B Conc.	50
4.50	Pumps	Pump B Conc.	10
4.50	Controller	Stop	

Fe porphyrin **H**



The commercially available iron tetrakis(pentamethylphenyl)porphyrin chloride, denoted as **(H)Cl**, was treated with one equivalent of AgOTf to abstract the chloride ion, yielding the product designated as **H**.

3. Characterization of Fe Porphyrins

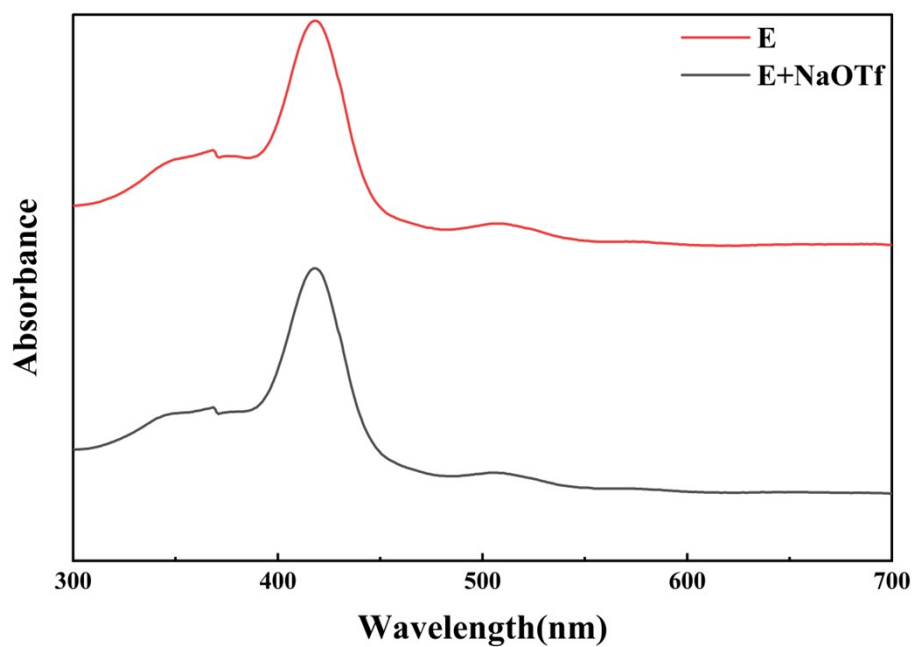


Figure S1. UV/Vis spectra of **E** and **E** added with 10 equivalents of NaOTf in THF.

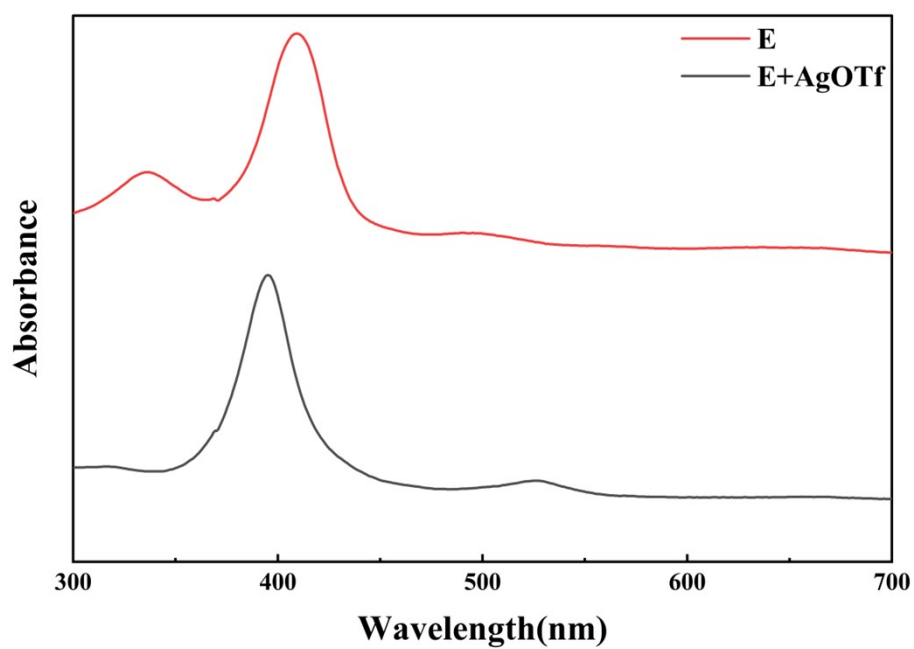


Figure S2. UV/Vis spectra of **E** and **E** added with 30 equivalents of AgOTf in TFE.

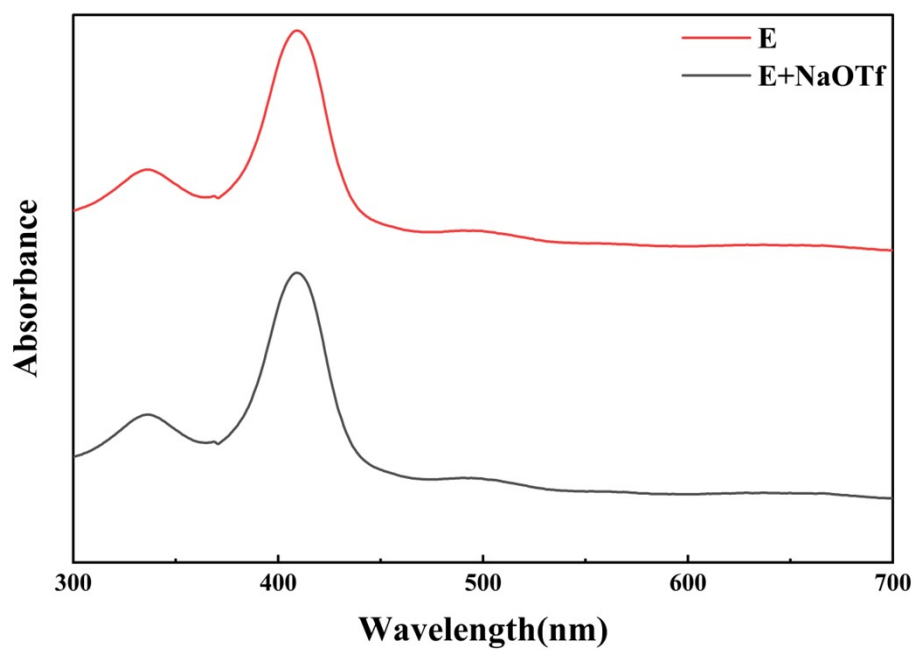


Figure S3. UV/Vis spectra of **E** and **E** added with 30 equivalents of NaOTf in TFE.

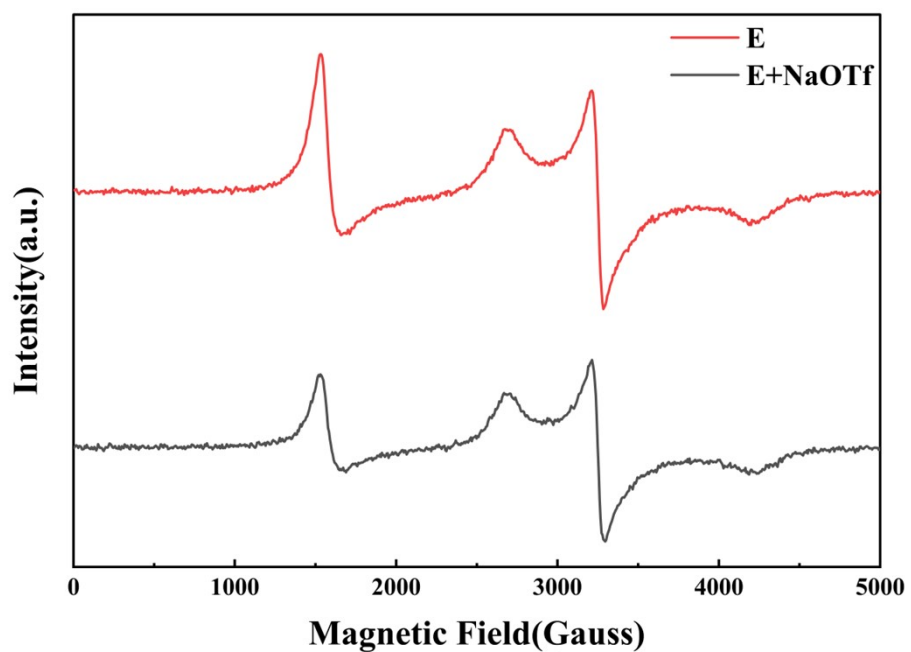
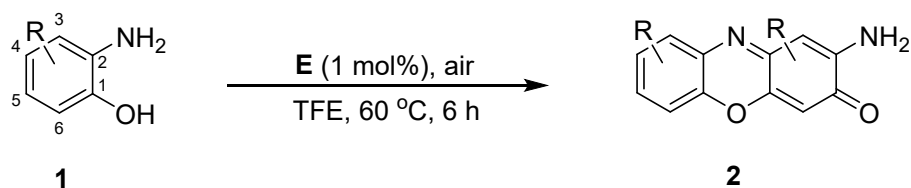


Figure S4. EPR spectra of **E** and **E** added with 10 equivalents of NaOTf in THF measured at 100 K.

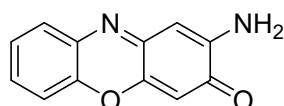
4. General Procedure

General procedure for the iron-porphyrin-catalyzed oxidation of *o*-aminophenols and *o*-phenylenediamines^{5,6}: A mixture of the substrate to be oxidized (1 mmol) and iron-porphyrin catalyst **E** (1 mol%) in 2,2,2-trifluoroethanol (TFE, 10 mL) was stirred at 60 °C under an air atmosphere. After complete consumption of the starting material (monitored by TLC), the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: dichloromethane/methanol = 95:5, v/v) to afford the desired product.

The substrate scope of the oxidation using various substituted *o*-aminophenols

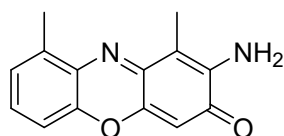


2-amino-3*H*-phenoxazin-3-one (2a)



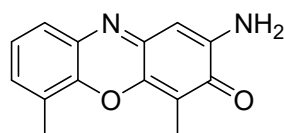
Dark red solid, 6h, yield = 86%; ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.70 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.40 – 7.37 (m, 1H), 6.81 (br, 2H), 6.36 (d, *J* = 2.9 Hz, 2H); ¹³C NMR (151 MHz, DMSO-*d*₆) δ 180.22, 148.88, 148.25, 147.38, 141.93, 133.74, 128.80, 127.98, 125.28, 115.94, 103.43, 98.37; **HRMS (ESI)**: Calcd. for C₁₂H₈N₂O₂ [M+H]⁺ *m/z* 213.0659, Found *m/z* 213.0660.

2-amino-1,9-dimethyl-3*H*-phenoxazin-3-one (2b)



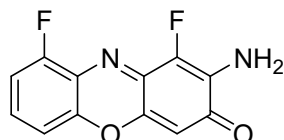
Dark red solid, 6h, yield = 88%; ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.35 (t, *J* = 7.8 Hz, 1H), 7.30 – 7.25 (m, 2H), 6.39 (br, 2H), 6.25 (s, 1H), 2.60 (s, 3H), 2.23 (s, 3H); ¹³C NMR (151 MHz, DMSO-*d*₆) δ 179.65, 148.82, 145.91, 143.75, 141.86, 136.75, 131.69, 128.40, 125.88, 113.36, 105.68, 102.06, 16.42, 9.75; **HRMS (ESI)**: Calcd. for C₁₄H₁₂N₂O₂ [M+H]⁺ *m/z* 241.0972, Found *m/z* 241.0973.

2-amino-4,6-dimethyl-3*H*-phenoxazin-3-one (2c)



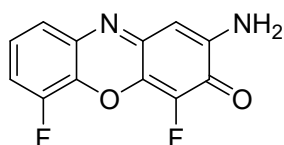
Dark red solid, 6h, yield = 84%; **¹H NMR** (600 MHz, DMSO-*d*₆) δ 7.51 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 7.3 Hz, 1H), 7.26 (t, *J* = 7.7 Hz, 1H), 6.71 (br, 2H), 6.30 (s, 1H), 2.45 (s, 3H), 2.09 (s, 3H); **¹³C NMR** (151 MHz, DMSO-*d*₆) δ 179.94, 147.78, 146.73, 144.72, 140.53, 133.28, 129.75, 125.59, 124.96, 124.33, 111.23, 97.53, 14.44, 7.57; **HRMS (ESI)**: Calcd. for C₁₄H₁₂N₂O₂ [M+H]⁺ *m/z* 241.0972, Found *m/z* 241.0973.

2-amino-1,9-difluoro-3*H*-phenoxazin-3-one (2d)



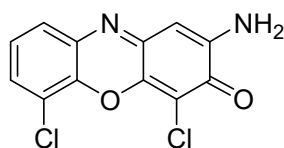
Black solid, 8h, yield = 87%; **¹H NMR** (600 MHz, DMSO-*d*₆) δ 7.53 – 7.49 (m, 1H), 7.38 – 7.30 (m, 2H), 6.89 (br, 2H), 6.34 (s, 1H); **¹³C NMR** (151 MHz, DMSO-*d*₆) δ 179.44 (d, *J* = 9.8 Hz), 156.76 (d, *J* = 255.6 Hz), 146.47 (d, *J* = 6.6 Hz), 143.10 (d, *J* = 3.4 Hz), 139.47 (d, *J* = 15.1 Hz), 137.47 (d, *J* = 243.8 Hz), 133.19 (d, *J* = 4.9 Hz), 129.32 (d, *J* = 9.2 Hz), 123.10 (d, *J* = 14.9 Hz), 112.07 (d, *J* = 3.6 Hz), 111.47 (d, *J* = 18.7 Hz), 101.89; **HRMS (ESI)**: Calcd. for C₁₂H₆F₂N₂O₂ [M+H]⁺ *m/z* 249.0471, Found *m/z* 249.0473.

2-amino-4,6-difluoro-3*H*-phenoxazin-3-one (2e)



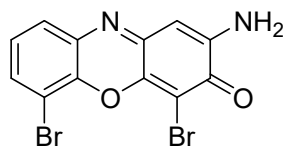
Black solid, 8h, yield = 86%; **¹H NMR** (600 MHz, DMSO-*d*₆) δ 7.54 (d, *J* = 8.1 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.39 – 7.35 (m, 1H), 7.09 (br, 2H), 6.31 (s, 1H); **¹³C NMR** (151 MHz, DMSO-*d*₆) δ 172.36 (d, *J* = 16.1 Hz), 149.33 (d, *J* = 249.2 Hz), 147.39, 146.75 (d, *J* = 4.3 Hz), 138.83 (d, *J* = 253.2 Hz), 135.33, 132.12 (d, *J* = 6.0 Hz), 129.60 (d, *J* = 11.2 Hz), 124.65 (d, *J* = 7.7 Hz), 123.80 (d, *J* = 3.0 Hz), 115.28 (d, *J* = 17.0 Hz), 96.44; **HRMS (ESI)**: Calcd. for C₁₂H₆F₂N₂O₂ [M+H]⁺ *m/z* 249.0471, Found *m/z* 249.0473.

2-amino-4,6-dichloro-3*H*-phenoxazin-3-one (2f)



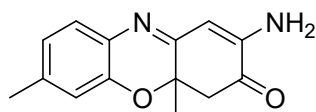
Black solid, 10h, yield = 87%; **¹H NMR** (600 MHz, DMSO-*d*₆) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.12 (br, 2H), 6.38 (s, 1H); **¹³C NMR** (151 MHz, DMSO-*d*₆) δ 174.32, 147.41, 147.23, 143.94, 137.75, 134.97, 128.88, 126.90, 125.73, 119.85, 109.57, 97.54; **HRMS (ESI)**: Calcd. for C₁₂H₆Cl₂N₂O₂ [M+H]⁺ *m/z* 280.9880, Found *m/z* 280.9883.

2-amino-4,6-dibromo-3H-phenoxazin-3-one (2g)



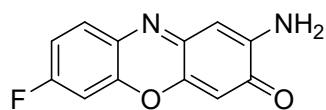
Black solid, 10h, yield = 85%; **¹H NMR** (600 MHz, DMSO-*d*₆) δ 7.78 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.73 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.12 (br, 2H), 6.39 (s, 1H); **¹³C NMR** (151 MHz, DMSO-*d*₆) δ 174.50, 147.64, 147.14, 146.12, 139.06, 135.09, 131.85, 127.40, 126.41, 108.84, 101.23, 97.69; **HRMS (ESI)**: Calcd. for C₁₂H₆Br₂N₂O₂ [M+H]⁺ *m/z* 370.8849, Found *m/z* 370.8849.

2-amino-4a,7-dimethyl-4,4a-dihydro-3H-phenoxazin-3-one (2h)



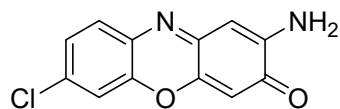
Yellow solid, 6h, yield = 86%; **¹H NMR** (600 MHz, DMSO-*d*₆) δ 7.09 (d, *J* = 7.9 Hz, 1H), 6.80 (dd, *J* = 8.3, 1.6 Hz, 1H), 6.72 (d, *J* = 1.8 Hz, 1H), 6.38 (br, 2H), 6.04 (s, 1H), 3.20 (d, *J* = 15.8 Hz, 1H), 2.98 (d, *J* = 15.8 Hz, 1H), 2.26 (s, 3H), 1.09 (s, 3H); **¹³C NMR** (151 MHz, DMSO-*d*₆) δ 191.58, 160.87, 146.44, 143.82, 136.58, 132.68, 125.47, 123.03, 116.54, 105.88, 70.94, 49.20, 22.02, 20.92; **HRMS (ESI)**: Calcd. for C₁₄H₁₄N₂O₂ [M+H]⁺ *m/z* 243.1129, Found *m/z* 243.1130.

2-amino-7-fluoro-3H-phenoxazin-3-one (2i)



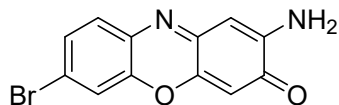
Black solid, 8h, yield = 80%; **¹H NMR** (600 MHz, DMSO-*d*₆) δ 7.75 (dd, *J* = 8.9, 6.1 Hz, 1H), 7.49 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.29 – 7.26 (m, 1H), 6.78 (br, 2H), 6.37 (s, 1H), 6.34 (s, 1H); **¹³C NMR** (151 MHz, DMSO-*d*₆) δ 180.19, 160.97 (d, *J* = 247.9 Hz), 148.42, 147.59 (d, *J* = 3.0 Hz), 147.22, 142.54 (d, *J* = 13.7 Hz), 130.84 (d, *J* = 2.7 Hz), 129.46 (d, *J* = 10.0 Hz), 113.00 (d, *J* = 23.5 Hz), 103.77, 103.44 (d, *J* = 27.5 Hz), 98.37; **HRMS (ESI)**: Calcd. for C₁₂H₇FN₂O₂ [M+H]⁺ *m/z* 231.0565, Found *m/z* 231.0565.

2-amino-7-chloro-3H-phenoxazin-3-one (2j)



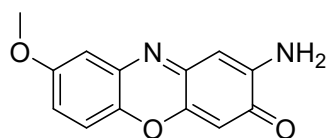
Black solid, 10h, yield = 83%; **¹H NMR** (600 MHz, DMSO-*d*₆) δ 7.69 (d, *J* = 8.6 Hz, 1H), 7.65 (d, *J* = 2.2 Hz, 1H), 7.42 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.89 (br, 2H), 6.35 (s, 1H), 6.34 (s, 1H); **¹³C NMR** (151 MHz, DMSO-*d*₆) δ 180.27, 148.43, 148.37, 147.54, 142.25, 132.77, 131.98, 129.06, 125.45, 115.98, 103.76, 98.30; **HRMS (ESI)**: Calcd. for C₁₂H₇ClN₂O₂ [M+H]⁺ *m/z* 247.0269, Found *m/z* 247.0268.

2-amino-7-bromo-3H-phenoxazin-3-one (2k)



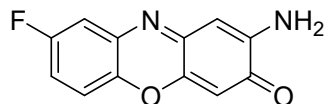
Dark red solid, 10h, yield = 81%; **¹H NMR** (600 MHz, DMSO-*d*6) δ 7.76 (d, *J* = 2.1 Hz, 1H), 7.61 (d, *J* = 8.6 Hz, 1H), 7.53 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.90 (br, 2H), 6.34 (s, 1H), 6.33 (s, 1H); **¹³C NMR** (151 MHz, DMSO-*d*6) δ 180.28, 148.42, 148.38, 147.57, 142.32, 133.02, 129.25, 128.26, 120.16, 118.78, 103.74, 98.32; **HRMS (ESI)**: Calcd. for C₁₂H₇BrN₂O₂ [M+H]⁺ *m/z* 290.9764, Found *m/z* 290.9762.

2-amino-8-methoxy-3H-phenoxazin-3-one (2l)



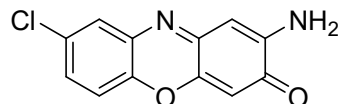
Dark red solid, 4h, yield = 41%; **¹H NMR** (600 MHz, DMSO-*d*6) δ 7.44 (d, *J* = 9.0 Hz, 1H), 7.22 (d, *J* = 3.0 Hz, 1H), 7.06 (dd, *J* = 9.1, 3.0 Hz, 1H), 6.83 (br, 2H), 6.35 (s, 1H), 6.32 (s, 1H), 3.83 (s, 3H); **¹³C NMR** (151 MHz, DMSO-*d*6) δ 179.85, 156.46, 149.01, 148.29, 147.57, 136.37, 134.39, 116.79, 116.60, 109.87, 102.93, 98.12, 55.74; **HRMS (ESI)**: Calcd. for C₁₃H₁₀N₂O₃ [M+H]⁺ *m/z* 243.0765, Found *m/z* 243.0764.

2-amino-8-fluoro-3H-phenoxazin-3-one (2m)



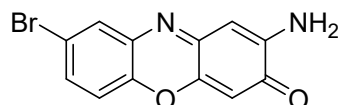
Black solid, 8h, yield = 81%; **¹H NMR** (600 MHz, DMSO-*d*6) δ 7.56 – 7.52 (m, 2H), 7.34 – 7.30 (m, 1H), 6.98 (br, 2H), 6.36 (s, 1H), 6.34 (s, 1H); **¹³C NMR** (151 MHz, DMSO-*d*6) δ 180.16, 158.68 (d, *J* = 240.8 Hz), 148.98, 148.95, 147.88, 138.51, 134.48 (d, *J* = 12.3 Hz), 117.29 (d, *J* = 9.6 Hz), 115.68 (d, *J* = 24.9 Hz), 112.96 (d, *J* = 23.5 Hz), 103.41, 97.92; **HRMS (ESI)**: Calcd. for C₁₂H₇FN₂O₂ [M+H]⁺ *m/z* 231.0565, Found *m/z* 231.0564.

2-amino-8-chloro-3H-phenoxazin-3-one (2n)



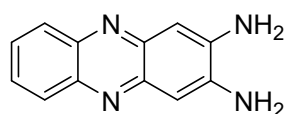
Black solid, 10h, yield = 58%; **¹H NMR** (600 MHz, DMSO-*d*6) δ 7.73 (d, *J* = 2.5 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.46 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.98 (br, 2H), 6.37 (s, 1H), 6.34 (s, 1H); **¹³C NMR** (151 MHz, DMSO-*d*6) δ 180.24, 149.08, 148.80, 147.87, 140.78, 134.68, 128.70, 127.99, 126.68, 117.59, 103.67, 98.04; **HRMS (ESI)**: Calcd. for C₁₂H₇ClN₂O₂ [M+H]⁺ *m/z* 247.0269, Found *m/z* 247.0269.

2-amino-8-bromo-3H-phenoxazin-3-one (2o)



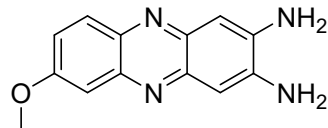
Dark red solid, 10h, yield = 52%; **¹H NMR** (600 MHz, DMSO-*d*₆) δ 7.86 (d, *J* = 2.4 Hz, 1H), 7.58 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.46 (d, *J* = 8.7 Hz, 1H), 6.98 (br, 2H), 6.37 (s, 1H), 6.34 (s, 1H); **¹³C NMR** (151 MHz, DMSO-*d*₆) δ 180.23, 149.03, 148.76, 147.85, 141.20, 135.07, 130.76, 129.65, 117.91, 116.48, 103.70, 98.07; **HRMS (ESI)**: Calcd. for C₁₂H₇BrN₂O₂ [M+H]⁺ *m/z* 290.9764, Found *m/z* 290.9761.

phenazine-2,3-diamine (4a)



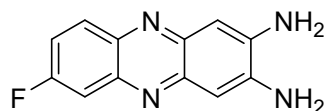
Brown solid, 8h, yield = 73%; **¹H NMR** (600 MHz, DMSO-*d*₆) δ 7.90 (dd, *J* = 6.5, 3.4 Hz, 2H), 7.54 (dd, *J* = 6.6, 3.4 Hz, 2H), 6.92 (s, 2H), 6.25 (br, 4H); **¹³C NMR** (151 MHz, DMSO-*d*₆) δ 144.10, 142.07, 140.29, 127.88, 126.46, 102.18; **HRMS (ESI)**: Calcd. for C₁₂H₁₀N₄ [M+H]⁺ *m/z* 211.0979, Found *m/z* 211.0979.

7-methoxyphenazine-2,3-diamine (4b)



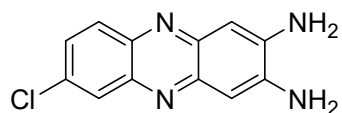
Brown solid, 8h, yield = 72%; **¹H NMR** (600 MHz, DMSO-*d*₆) δ 7.79 (d, *J* = 9.1 Hz, 1H), 7.25 – 7.21 (m, 2H), 6.89 (d, *J* = 9.8 Hz, 2H), 6.15 (br, 2H), 5.99 (br, 2H), 3.90 (s, 3H); **¹³C NMR** (151 MHz, DMSO-*d*₆) δ 158.00, 143.92, 142.56, 141.76, 141.56, 140.24, 136.58, 129.05, 120.29, 104.96, 103.00, 102.22, 55.44; **HRMS (ESI)**: Calcd. for C₁₃H₁₂N₄O [M+H]⁺ *m/z* 241.1084, Found *m/z* 241.1085.

7-fluorophenazine-2,3-diamine (4c)



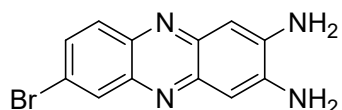
Brown solid, 8h, yield = 70%; **¹H NMR** (600 MHz, DMSO-*d*₆) δ 7.95 (dd, *J* = 9.3, 6.2 Hz, 1H), 7.61 – 7.59 (m, 1H), 7.48 – 7.44 (m, 1H), 6.89 (d, *J* = 9.9 Hz, 2H), 6.38 (br, 2H), 6.25 (br, 2H); **¹³C NMR** (151 MHz, DMSO-*d*₆) δ 160.25 (d, *J* = 245.3 Hz), 144.81, 143.85, 142.41, 141.67, 140.41 (d, *J* = 13.1 Hz), 137.52, 130.14 (d, *J* = 10.3 Hz), 116.82 (d, *J* = 26.7 Hz), 110.29 (d, *J* = 20.5 Hz), 102.24, 101.62; **HRMS (ESI)**: Calcd. for C₁₂H₉FN₄ [M+H]⁺ *m/z* 229.0884, Found *m/z* 229.0883.

7-chlorophenazine-2,3-diamine (4d)



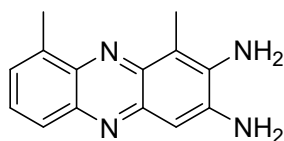
Brown solid, 12h, yield = 63%; **¹H NMR** (600 MHz, DMSO-*d*₆) δ 7.92 (d, *J* = 2.4 Hz, 1H), 7.90 (d, *J* = 9.0 Hz, 1H), 7.52 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.89 (d, *J* = 5.6 Hz, 2H), 6.41 (br, 2H), 6.36 (br, 2H); **¹³C NMR** (151 MHz, DMSO-*d*₆) δ 144.85, 144.43, 142.49, 142.25, 140.35, 138.72, 130.43, 129.66, 126.80, 126.15, 102.02, 101.75; **HRMS (ESI)**: Calcd. for C₁₂H₉ClN₄ [M+H]⁺ *m/z* 245.0589, Found *m/z* 245.0590.

7-bromophenazine-2,3-diamine (4e)



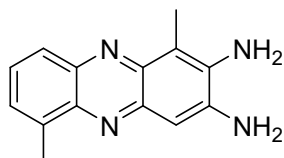
Brown solid, 12h, yield = 61%; **¹H NMR** (600 MHz, DMSO-*d*₆) δ 8.08 (d, *J* = 2.2 Hz, 1H), 7.83 (d, *J* = 9.0 Hz, 1H), 7.62 (dd, *J* = 9.0, 2.3 Hz, 1H), 6.89 (d, *J* = 3.7 Hz, 2H), 6.41 (br, 2H), 6.37 (br, 2H); **¹³C NMR** (151 MHz, DMSO-*d*₆) δ 144.88, 144.52, 142.43, 142.32, 140.81, 138.90, 129.76, 129.47, 129.24, 118.94, 102.02, 101.79; **HRMS (ESI)**: Calcd. for C₁₂H₉BrN₄ [M+H]⁺ *m/z* 289.0084, Found *m/z* 289.0084.

1,9-dimethylphenazine-2,3-diamine (4f-1)



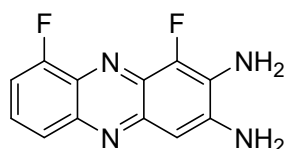
Brown solid, 8h, yield = 34%; **¹H NMR** (600 MHz, DMSO-*d*₆) δ 7.79 (d, *J* = 8.3 Hz, 1H), 7.45 – 7.39 (m, 2H), 6.92 (s, 1H), 6.16 (br, 2H), 5.81 (br, 2H), 2.72 (s, 3H), 2.53 (s, 3H); **¹³C NMR** (151 MHz, DMSO-*d*₆) δ 143.52, 140.99, 140.11, 139.96, 139.56, 139.25, 135.17, 126.40, 126.19, 125.94, 107.97, 101.23, 17.48, 10.55; **HRMS (ESI)**: Calcd. for C₁₄H₁₄N₄[M+H]⁺ *m/z* 239.1292, Found *m/z* 239.1287.

1,6-dimethylphenazine-2,3-diamine (4f-2)



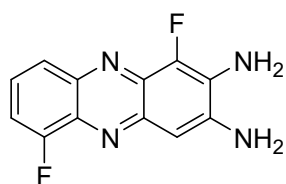
Brown solid, 8h, yield = 38%; **¹H NMR** (600 MHz, DMSO-*d*₆) δ 7.74 (s, 1H), 7.46 – 7.39 (m, 2H), 6.86 (s, 1H), 6.18 (br, 2H), 5.81 (br, 2H), 2.78 (s, 3H), 2.57 (s, 3H); **¹³C NMR** (151 MHz, DMSO-*d*₆) δ 143.64, 141.56, 139.93, 139.91, 139.37, 138.68, 135.73, 126.28, 125.84, 125.66, 108.42, 100.52, 17.21, 10.45; **HRMS (ESI)**: Calcd. for C₁₄H₁₄N₄[M+H]⁺ *m/z* 239.1292, Found *m/z* 239.1288.

1,9-difluorophenazine-2,3-diamine (4g-1)



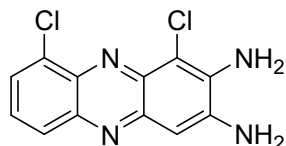
Brown solid, 12h, yield = 25%; **¹H NMR** (600 MHz, DMSO-*d*₆) δ 7.83 (d, *J* = 8.5 Hz, 1H), 7.57 – 7.54 (m, 1H), 7.43 – 7.40 (m, 1H), 6.86 (s, 1H), 6.64 (br, 2H), 6.36 (br, 2H); **¹³C NMR** (151 MHz, DMSO-*d*₆) δ 156.28 (d, *J* = 256.3 Hz), 144.68 (d, *J* = 7.3 Hz), 140.43, 139.48, 138.33 (d, *J* = 238.5 Hz), 131.93 (d, *J* = 9.8 Hz), 131.14 (d, *J* = 12.1 Hz), 130.44 (d, *J* = 12.3 Hz), 125.74 (d, *J* = 8.6 Hz), 124.27 (d, *J* = 4.0 Hz), 110.66 (d, *J* = 18.2 Hz), 98.11; **HRMS (ESI)**: Calcd. for C₁₂H₈F₂N₄[M+H]⁺ *m/z* 247.0790, Found *m/z* 247.0789.

1,6-difluorophenazine-2,3-diamine (4g-2)



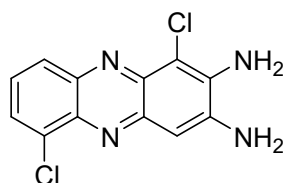
Brown solid, 12h, yield = 48%; **¹H NMR** (600 MHz, DMSO-*d*₆) δ 7.76 (d, *J* = 8.6 Hz, 1H), 7.56 (m, 1H), 7.41 (m, 1H), 6.83 (s, 1H), 6.66 (br, 2H), 6.35 (br, 2H); **¹³C NMR** (151 MHz, DMSO-*d*₆) δ 156.60 (d, *J* = 256.8 Hz), 144.86 (d, *J* = 7.4 Hz), 141.52, 140.23, 138.63 (d, *J* = 238.9 Hz), 131.21 (d, *J* = 9.8 Hz), 130.33 (d, *J* = 12.5 Hz), 130.08 (d, *J* = 12.2 Hz), 126.27 (d, *J* = 8.5 Hz), 123.98 (d, *J* = 4.0 Hz), 110.29 (d, *J* = 18.4 Hz), 97.82; **HRMS (ESI)**: Calcd. for C₁₂H₈F₂N₄ [M+H]⁺ *m/z* 247.0790, Found *m/z* 247.0790.

1,9-dichlorophenazine-2,3-diamine (4h-1)



Brown solid, 12h, yield = 37%; **¹H NMR** (600 MHz, DMSO-*d*₆) δ 7.98 (dd, *J* = 8.6, 1.3 Hz, 1H), 7.79 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.57 (dd, *J* = 8.5, 7.4 Hz, 1H), 6.99 (s, 1H), 6.71 – 7.70 (br, 4H); **¹³C NMR** (151 MHz, DMSO-*d*₆) δ 144.13, 141.37, 140.55, 140.33, 137.73, 136.63, 130.36, 127.61, 127.05, 126.51, 104.56, 100.82; **HRMS (ESI)**: Calcd. for C₁₂H₈Cl₂N₄[M+H]⁺ *m/z* 279.0199, Found *m/z* 279.0200.

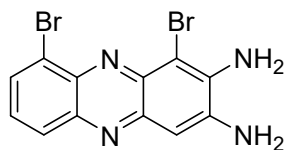
1,6-dichlorophenazine-2,3-diamine (4h-2)



Brown solid, 12h, yield = 39%; **¹H NMR** (600 MHz, DMSO-*d*₆) δ 7.92 (dd, *J* = 8.5, 1.3 Hz, 1H), 7.78 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.58 (dd, *J* = 8.5, 7.4 Hz, 1H), 6.95 (s, 1H), 6.73 (br, 2H), 6.68 (br, 2H); **¹³C NMR** (151 MHz, DMSO-*d*₆) δ 144.09, 141.65, 140.94, 140.60, 137.38, 136.03, 130.90,

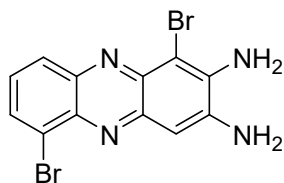
127.11, 126.91, 126.69, 104.93, 100.41; **HRMS (ESI):** Calcd. for $C_{12}H_8Cl_2N_4[M+H]^+$ m/z 279.0199, Found m/z 279.0202.

1,9-dibromophenazine-2,3-diamine (4i-1)



Brown solid, 12, yield = 38%; **1H NMR** (600 MHz, DMSO-*d*6) δ 8.00 (m, 2H), 7.51 (dd, J = 8.4, 7.4 Hz, 1H), 7.01 (s, 1H), 6.72 – 6.69 (br, 4H); **^{13}C NMR** (151 MHz, DMSO-*d*6) δ 144.11, 141.99, 141.85, 140.44, 138.57, 137.50, 130.57, 128.22, 127.21, 121.78, 101.32, 97.03; **HRMS (ESI):** Calcd. for $C_{12}H_8Br_2N_4[M+H]^+$ m/z 368.9168, Found m/z 368.9168.

1,6-dibromophenazine-2,3-diamine (4i-2)



Brown solid, 12h, yield = 36%; **1H NMR** (600 MHz, DMSO-*d*6) δ 7.99 – 7.95 (m, 2H), 7.52 (dd, J = 8.5, 7.3 Hz, 1H), 6.97 (s, 1H), 6.70 (br, 4H); **^{13}C NMR** (151 MHz, DMSO-*d*6) δ 144.06, 142.04, 141.95, 140.99, 138.45, 137.05, 130.16, 127.67, 127.61, 122.44, 100.88, 97.47. **HRMS (ESI):** Calcd. for $C_{12}H_8Br_2N_4[M+H]^+$ m/z 368.9168, Found m/z 368.9168.

5. References

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6. ¹H and ¹³C NMR spectra

