Electronic Supplementary Information

Multi PCET in Symmetrically Substituted Benzimidazoles

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Table of Contents

1. Experimental Results ............................................................................................................................................. S2
  1.1. Materials and Methods ............................................................................................................................. S2
  1.2. Synthesis and Structural Characterization ................................................................................................. S3
  1.3. Nuclear Magnetic Resonance Data ............................................................................................................. S9
  1.4. Crystal Structure and X-Ray Data for Compound 3 ..................................................................................... S24
2. Computational Methods .......................................................................................................................................... S43
3. References ............................................................................................................................................................. S51
1. Experimental Results

1.1. Materials and Methods

NMR characterization was carried out at 25 °C using a 500 MHz Bruker spectrometer, employing standard pulse techniques. Samples were dissolved in CDCl$_3$, CD$_2$Cl$_2$, (CD$_3$)$_2$CO or (CD$_3$)$_2$SO and chemical shifts were measured relative to internal TMS (0.05% v/v). Mass spectra were obtained with a Voyager DE STR matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometer in positive or negative ion mode and trans, trans-1,4-diphenyl-1,3-butadiene was used as the matrix. All chemicals were purchased from Aldrich, Acros or Alfa Aesar. Solvents were obtained from VWR. Thin layer chromatography (TLC) was performed with silica gel coated glass plates from Merck Millipore. Column chromatography was carried out using Silicycle silica gel 60 having 230-400 mesh.

Cyclic Voltammetry: Cyclic voltammetry measurements were performed with a CH Instruments 760C potentiostat using a glassy carbon (3 mm diameter) working electrode, a Pt wire counter electrode, and a Ag wire pseudoreference electrode in a conventional three-electrode cell. All cyclic voltammograms (CVs) were collected in anhydrous dichloromethane, previously distilled and kept over molecular sieves and K$_2$CO$_3$, containing the compound of interest at a concentration of 1 mM. Tetrabutylammonium hexafluorophosphate (TBAPF$_6$, 0.1 M in dichloromethane) was used as the supporting electrolyte. All measurements were conducted at room temperature under an argon atmosphere and the scan rate was 100 mV s$^{-1}$. The glassy carbon working electrode was polished between measurements with an aluminum slurry on a microcloth polishing pad, followed by solvent rinses and drying under a stream of nitrogen. The potential of the pseudoreference electrode was determined using the ferrocenium/ferrocene redox couple as an internal standard and adjusting to the saturated calomel electrode (SCE) scale (with $E_{1/2}$ taken to be 0.46 V vs SCE in dichloromethane).$^1$

FTIR and Infrared Spectroelectrochemistry (IRSEC): FTIR measurements were performed using a Bruker Vertex 70 spectrometer in absorption mode under a dry nitrogen purge with a 2 cm$^{-1}$ resolution, GloBar MIR source, broadband KBr beamsplitter, and liquid nitrogen cooled MCT detector. Spectra were collected in anhydrous dichloromethane at a concentration of 15 mM of 3, using 0.1 M TBAPF$_6$ as supporting electrolyte. IRSEC measurements were conducted using a Biologic potentiostat connected to an optically transparent thin-layer electrochemical cell.
(Spectroelectrochemistry Reading RT OTTLE cell) equipped with CaF$_2$ optical windows (pathlength 0.2 mm). The cell has a Pt mesh counter electrode, a Ag wire pseudoreference electrode, and a Pt mesh working electrode that was positioned in the light path of the IR spectrophotometer. A complete and detailed description of the spectroelectrochemical technique is described elsewhere.$^2$

1.2. Synthesis and Structural Characterization

The synthetic approach for the preparation of 3 is shown in Scheme S1.

Scheme S1. Synthetic strategy detailing reactions conditions, yields, and intermediate molecules for preparation of 3.
4,7-Di-cyano-2,1,3-benzothiadiazole (B)

A similar method has been reported. A portion of copper cyanide (2.20 g, 24.6 mmol) was dissolved in dry DMF (45 mL), and 4,7-dibromo-2,1,3-benzothiadiazole (A, 2.26 g, 7.7 mmol) was then added to the solution and stirred under argon for 15 minutes. The mixture was refluxed for 3 hours under argon. A separate solution of FeCl₃•6H₂O (10.2 g, 37.7 mmol) in 18.5 mL of HCl 15% v/v was prepared. Once the refluxed mixture cooled to room temperature, the resulting FeCl₃•6H₂O solution was added to the cooled reaction mixture and stirred at 20 °C for 0.5 hours. The crude product was extracted with dichloromethane (3 × 100 mL), and the combined organic layers were washed first with a 6 M HCl solution (3 × 100 mL), water (3 × 100 mL), and finally brine (3 × 100 mL). The organic layer was then dried over Na₂SO₄, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using hexanes/ethyl acetate (40:60) to afford 1.10 g of B (77 % yield). ¹H NMR (500 MHz, (CD₃)₂CO) δ 8.51 (s, 2H, ArH). NMR characterization is in line with previously reported spectrum. MALDI-TOF-MS m/z. calcd. for C₈H₈N₄S: 186.000, experimental (M⁺): 186.004.

2,3-Diaminoterephthalonitrile (C)

A similar method has been reported. A portion of B (1.02 g, 5.5 mmol) was suspended in a solvent mixture of ethanol (45.5 mL) and freshly distilled tetrahydrofuran (4.5 mL). CoCl₂•6H₂O (119 mg, 0.5 mmol) was added to the solution and it was stirred under argon for 15 minutes. A portion of NaBH₄ (1.04 g, 27.5 mmol) was added, and the solution was refluxed for 1.5 hours. A second portion of NaBH₄ (416 mg, 11.0 mmol) was then added and refluxed for an extra 0.5 hours. The solution was filtered with a Celite pad and the solvents were removed under reduced pressure. The dried, crude product was dissolved in water (200 mL) and extracted using 10% methanol in dichloromethane (3 × 100 mL). The organic extracts were combined, dried over Na₂SO₄, and the
solvents were removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using hexanes/ethyl acetate mixture (50:50) to afford 430 mg of C (50 % yield). The solid was immediately used in the next step to avoid decomposition. \(^1\)H NMR (500 MHz, (CD\(_3\))\(_2\)SO) \(\delta\) 6.06 (s, 4H, NH\(_2\)), 6.71 (s, 2H, ArH). NMR characterization is in line with previously reported spectrum. \(^4\) MALDI-TOF-MS \(m/z\). calcd. for C\(_8\)H\(_5\)N\(_4\): 157.051, experimental (M-H)\(^+\): 157.055.

![Image](image-url)

**4,7-Di-cyano-2-(3’,5’-di-tert-butyl-2’-hydroxyphenyl)benzimidazole (D)**

Synthesis of D was achieved following a well-known procedure.\(^2\) A portion of 3,5-di-tert-butyl-2-hydroxybenzaldehyde (562 mg, 2.4 mmol) in nitrobenzene (9 mL) was added drop-wise to a solution of C (380 mg, 2.4 mmol) in nitrobenzene (9 mL) under argon atmosphere. The mixture was stirred for 30 minutes and then heated overnight at 190 °C. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using dichloromethane/hexanes mixtures (80:20 → 90:10) to give 483 mg of D (54 % yield). \(^1\)H NMR (500 MHz, (CD\(_3\))\(_2\)CO) \(\delta\) 1.35 (s, 9H, C(CH\(_3\))\(_3\)), 1.52 (s, 9H, C(CH\(_3\))\(_3\)), 7.61 (d, J = 2.3 Hz, 1H, ArH), 7.89 (s, 2H, ArH) 8.05 (d, J = 2.3 Hz, 1H, ArH), 12.99 (br, 1H, NH), 13.40 (br, 1H, OH). \(^1^3\)C NMR (126 MHz, (CD\(_3\))\(_2\)CO) \(\delta\) 29.9 (overlap with solvent signal), 31.7, 35.2, 36.0, 111.2, 116.0, 122.2, 127.7, 128.2, 129.3, 138.4, 142.3, 157.2, 157.5, 158.2. MALDI-TOF-MS \(m/z\). calcd. for C\(_{23}\)H\(_{25}\)N\(_4\)O: 373.202, experimental (M-H)\(^+\): 373.201.

![Image](image-url)

**4,7-Dicarboxylic acid-2-(3’,5’-di-tert-butyl-2’-hydroxyphenyl)benzimidazole (E)**

Compound D (470 mg, 1.3 mmol) was added to a 90% KOH aqueous solution (13 mL) and ethylene glycol (19 mL), and the mixture heated under reflux for 8 hours. The reaction mixture was cooled down, diluted with water (100 mL), and extracted with ethyl acetate (3 × 80 mL). The
resulting aqueous layer was adjusted to pH = 6 with 1M HCl solution, and the resulting precipitate was collected by filtration and dried under reduced pressure. No further purification was performed and the solid was used in the next reaction (450 mg, 84 % yield). $^1$H NMR (500 MHz, (CD$_3$)$_2$SO) δ 1.37 (s, 9H, C(CH$_3$)$_3$), 1.45 (s, 9H, C(CH$_3$)$_3$), 7.40 (d, $J = 2.2$ Hz, 1H, ArH), 7.91 (s, 2H, ArH), 8.29 (d, $J = 2.4$ Hz, 1H, ArH), 12.54-14.00 (br, 3H, NH and COOH), 14.52 (s, 1H, OH). $^{13}$C NMR (126 MHz, (CD$_3$)$_2$SO) δ 29.4, 31.5, 34.4, 34.9, 110.8, 122.6, 124.2, 126.5, 135.9, 139.8, 155.6, 156.1, 166.2. MALDI-TOF-MS m/z. calcd. for C$_{23}$H$_{27}$N$_2$O$_5$: 411.191, experimental (M+H)$^+$: 411.192.

![4,7-Di-hydroxymethyl-2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)benzimidazole (F)](image)

A portion of E (402 mg, 1.0 mmol) was dissolved in freshly distilled THF (10 mL) and stirred under argon for 15 minutes. At room temperature, an excess of lithium aluminum hydride was added to the mixture and heated at 50 °C. The reaction was followed by TLC until completion (approximately 6 hours). The solution was cooled down, and water was added drop-wise to deactivate the excess LiAlH$_4$. The reaction mixture was then filtered through a pad of Celite and washed with 15% methanol in dichloromethane and dried under reduced pressure. The residue was then dissolved in water (100 mL) and extracted using 15% methanol in dichloromethane (3 × 100 mL), controlling the pH of the aqueous phase at around 8. The organic extracts were combined, dried over Na$_2$SO$_4$, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using 3% methanol in dichloromethane to afford 181 mg of F. (48 % yield). $^1$H NMR (500 MHz, (CD$_3$)$_2$CO) δ 1.34 (s, 9H, C(CH$_3$)$_3$), 1.51 (s, 9H, C(CH$_3$)$_3$), 4.23 (br, 1H, CH$_2$OH), 4.29 (br, 1H, CH$_2$OH), 4.88 (s, 2H, CH$_2$OH), 5.11 (s, 2H, CH$_2$OH), 7.25 (d, $J = 7.5$ Hz, 1H, ArH), 7.35 (d, $J = 7.5$ Hz, 1H, ArH), 7.47 (d, $J = 2.3$ Hz, 1H, ArH), 7.98 (d, $J = 2.3$ Hz, 1H, ArH), 11.97 (br, 1H, NH), 13.88 (br, 1H, OH). $^{13}$C NMR (126 MHz, (CD$_3$)$_2$CO) δ 29.9, 31.9, 35.1, 35.9, 60.7, 62.0, 112.8, 121.0, 121.3, 122.8, 125.4, 126.9, 131.9, 131.9, 137.6, 140.0, 141.3, 153.5, 156.8. MALDI-TOF-MS m/z. calcd. for C$_{23}$H$_{30}$N$_2$O$_5$: 382.226, experimental (M)$^+$: 382.229.

S6
4,7-Di-formyl-2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)benzimidazole (G)

Compound F (176 mg, 0.5 mmol) was dissolved in dichloromethane (50 mL) and stirred under argon for 15 minutes. Activated MnO₂ was added carefully at room temperature, and the reaction was followed by TLC. After completion (approximately 3 hours), the mixture was filtered through a Celite pad and the residue washed with 5% methanol in dichloromethane, and the solvent was removed under reduced pressure. The solid was purified by flash column chromatography on silica gel using dichloromethane as the eluent to afford 103 mg of G (59% yield). ¹H NMR (500 MHz, CDCl₃) δ 1.41 (s, 9H, C(CH₃)₃), 1.52 (s, 9H, C(CH₃)₃), 7.52 (d, J = 2.3 Hz, 1H, ArH), 7.55 (d, J = 2.3 Hz, 1H, ArH), 7.85 (d, J = 7.8 Hz, 1H, ArH), 7.99 (d, J = 7.8 Hz, 1H, ArH), 10.23 (s, 1H, CHO), 10.96 (s, 1H, CHO), 11.04 (s, 1H, NH), 12.96 (s, 1H, OH). ¹³C NMR (126 MHz, CDCl₃) δ 29.5, 31.6, 34.5, 35.4, 110.0, 119.3, 121.3, 123.3, 127.4, 128.5, 128.7, 132.8, 138.3, 141.3, 143.7, 156.6, 156.7, 189.2, 192.7. MALDI-TOF-MS m/z. calcd. for C₂₃H₂₇N₂O₃: 379.202, experimental (M+H)⁺: 379.202.

4,7-Di-(4-methoxyphenyliminomethyl)-2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)benzimidazole (3)

Compound G (50 mg, 0.13 mmol) was dissolved in 15 mL of dry dichloromethane containing 4Å molecular sieves. The mixture was stirred under an argon atmosphere and p-anisidine (32 mg, 0.26 mmol) was added. Then 1.00 µL of pyrrolidine (0.013 mmol) was added. After 24 hours, the reaction mixture was filtered and the molecular sieves washed several times with dry dichloromethane. The solvent was removed under reduced pressure, and the crude product
was recrystallized from dichloromethane/hexanes mixture to give 62 mg of 3 (80 % yield). Single crystals of 3 were grown by the vapor diffusion technique using dichloromethane and hexanes as solvents (see Crystal Structure and X-Ray Data for Compound 3). $^1$H NMR (500 MHz, CDCl$_3$) δ 1.42 (s, 9H, C(CH$_3$)$_3$), 1.53 (s, 9H, C(CH$_3$)$_3$), 3.88 (s, 3H, OCH$_3$), 3.89 (s, 3H, OCH$_3$), 6.99 – 7.04 (m, 4H, ArH), 7.38 – 7.43 (m, 4H, ArH), 7.50 (d, $J = 2.3$ Hz, 1H, ArH), 7.54 (d, $J = 2.3$ Hz, 1H, ArH), 7.57 (d, $J = 7.9$ Hz, 1H, ArH), 8.19 (d, $J = 7.9$ Hz, 1H, ArH), 8.80 (s, 1H, CH═N), 9.39 (s, 1H, CH═N), 11.96 (br, 1H, NH), 13.13 (s, 1H, OH). $^1$H NMR (500 MHz, CD$_2$Cl$_2$) δ 1.42 (s, 9H, C(CH$_3$)$_3$), 1.52 (s, 9H, C(CH$_3$)$_3$), 3.86 (s, 3H, OCH$_3$), 3.87 (s, 3H, OCH$_3$), 6.99 – 7.04 (m, 4H, ArH), 7.41 (d, $J = 8.9$ Hz, 2H, ArH), 7.45 (d, $J = 8.7$ Hz, 2H, ArH), 7.52 (d, $J = 2.3$ Hz, 1H, ArH), 7.59 (d, $J = 2.3$ Hz, 1H, ArH), 7.62 (d, $J = 7.9$ Hz, 1H, ArH), 8.16 (d, $J = 7.9$ Hz, 1H, ArH), 8.85 (s, 1H, CH═N), 9.37 (s, 1H, CH═N), 12.02 (br, 1H, NH), 13.20 (s, 1H, OH). $^1$H NMR (500 MHz, (CD$_3$)$_2$CO) δ 1.43 (s, 9H, C(CH$_3$)$_3$), 1.53 (s, 9H, C(CH$_3$)$_3$), 3.87 (s, 3H, OCH$_3$), 3.88 (s, 3H, OCH$_3$), 7.05 – 7.10 (m, 4H, ArH), 7.45 – 7.50 (m, 2H, ArH), 7.55 – 7.60 (m, 3H, ArH), 7.82 (d, $J = 7.9$ Hz, 1H, ArH), 8.00 (d, $J = 2.3$ Hz, 1H, ArH), 8.19 (d, $J = 7.9$ Hz, 1H, ArH), 9.04 (s, 1H, CH═N), 9.43 (s, 1H, CH═N), 12.44 (br, 1H, NH), 13.49 (s, 1H, OH). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 29.5, 31.5, 34.3, 35.4, 55.5, 55.6, 110.9, 114.5, 114.8, 119.1, 119.8, 121.4, 122.4, 122.8, 126.1, 127.5, 128.1, 132.2, 137.9, 140.7, 142.2, 143.5, 145.0, 153.5, 154.0, 156.1, 156.8, 158.7, 159.1. MALDI-TOF-MS $m/z$. calcd. for C$_{37}$H$_{41}$N$_4$O$_3$: 589.317, experimental (M+H)$^+$: 589.319.
1.3. Nuclear Magnetic Resonance Data

Compound B

Figure S1. 500 MHz $^1$H NMR spectrum of B in (CD$_3$)$_2$CO.
Figure S2. 500 MHz $^1$H NMR spectrum of C in (CD$_3$)$_2$SO.
Compound D

Figure S3. 500 MHz $^1$H NMR spectrum of D in (CD$_3$)$_2$CO.
**Compound D**

Figure S4. 126 MHz $^{13}$C NMR spectrum of D in (CD$_3$)$_2$CO.
Compound E

Figure S5. 500 MHz $^1$H NMR spectrum of E in (CD$_3$)$_2$SO.
Compound E

$\text{\includegraphics[width=0.5\textwidth]{compoundE.png}}$

Figure S6. 126 MHz $^{13}$C NMR spectrum of E in (CD$_3$)$_2$SO.
Compound F

Figure S7. 500 MHz $^1$H NMR spectrum of F in (CD$_3$)$_2$CO.
Compound F

Figure S8. 126 MHz $^{13}$C NMR spectrum of F in (CD$_3$)$_2$CO.
Figure S9. 500 MHz $^1$H NMR spectrum of G in CDCl$_3$. 

Compound G
Compound G

Figure S10. 126 MHz $^{13}$C NMR spectrum of G in CDCl$_3$. 
Compound 3

![NMR Spectrum](image)

**Figure S11.** 500 MHz $^1$H NMR spectrum of 3 in CDCl$_3$. 
Figure S12. 500 MHz $^1$H NMR spectrum of 3 in CD$_2$Cl$_2$. 
Figure S13. 500 MHz $^1$H NMR spectrum of $3$ in (CD$_3$)$_2$CO.
Figure S14. 126 MHz $^{13}$C NMR spectrum of 3 in CDCl$_3$. 
Figure S15. (A) NOESY experiment of 3 in CD$_2$Cl$_2$ showing the downfield/aromatic regions of the spectrum. (B) Expansion of the selected area (dotted rectangle) in A. The arrows shown in the molecular structure describe the interactions through the space of the azomethine protons (H$_a$ and H$_b$) of both TPA branches (color coded).
### 1.4. Crystal Structure and X-Ray Data for Compound 3

A clear light-yellow thin needle-like specimen of C_{37}H_{40}N_{4}O_{3}, approximate dimensions 0.026 mm x 0.086 mm x 0.884 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

#### Table S1. Data collection details for 3.

| Axis | dx/° | 2θ/° | ω/° | χ/° | Width/° | Frames | Time/s | Wavelength/Å | Voltage/kV | Current/mA | Temperature/K |
|------|------|------|-----|-----|---------|--------|--------|--------------|------------|------------|---------------|
| Omega | 50.568 | -34.00 -34.00 | 0.00 | 54.80 | 0.50 | 364 | 120.00 | 0.71073 | 50 | 30.0 | n/a |
| Omega | 50.568 | -34.00 -34.00 | 120.00 | 54.80 | 0.50 | 364 | 120.00 | 0.71073 | 50 | 30.0 | n/a |
| Omega | 50.568 | -34.00 -34.00 | 240.00 | 54.80 | 0.50 | 364 | 120.00 | 0.71073 | 50 | 30.0 | n/a |

A total of 1092 frames were collected. The total exposure time was 36.40 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 25976 reflections to a maximum θ angle of 25.52° (0.82 Å resolution), of which 6081 were independent (average redundancy 4.272, completeness = 99.4%, R_int = 10.68%, R_sig = 9.31%) and 3963 (65.17%) were greater than 2σ(F²). The final cell constants of α = 33.507(8) Å, b = 7.0694(18) Å, c = 32.051(12) Å, β = 120.434(4)°, volume = 6546.3 Å³, are based upon the refinement of the XYZ-centroids of 2089 reflections above 20 σ(I) with 5.086° < 2θ < 50.01°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.645. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9350 and 0.9980. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group C 1 2/c 1, with Z = 8 for the formula unit, C_{37}H_{40}N_{4}O_{3}. The final anisotropic full-matrix least-squares refinement on F² with 406 variables converged at R1 = 7.91%, for the observed data and wR2 = 16.96% for all data. The goodness-of-fit was 1.069. The largest peak in the final difference electron density synthesis was 0.296 e/Å³ and the largest hole was -0.201 e/Å³ with an RMS deviation of 0.063 e/Å³. On the basis of the final model, the calculated density was 1.195 g/cm³ and F(000), 2512 e⁻.
Figure S16. ORTEP representation of the crystal structure of 3. Carbons are shown in grey, oxygens in red, nitrogens in light violet and hydrogens in white. Thermal ellipsoids are drawn at the 50% probability level.
Table S2. Sample and crystal data for 3.

| **Identification code** | Odella_BIP_diimine_methoxy |
|-------------------------|-----------------------------|
| **Chemical formula**    | C_{37}H_{40}N_{4}O_{3}       |
| **Formula weight**      | 588.73 g/mol                |
| **Temperature**         | 123(0) K                    |
| **Wavelength**          | 0.71073 Å                   |
| **Crystal size**        | 0.026 x 0.086 x 0.884 mm    |
| **Crystal habit**       | clear light yellow thin needle |
| **Crystal system**      | monoclinic                  |
| **Space group**         | C 1 2/c 1                   |
| **Unit cell dimensions**| a = 33.507(8) Å, α = 90°    |
|                         | b = 7.0694(18) Å, β = 120.434(4)° |
|                         | c = 32.051(12) Å, γ = 90°    |
| **Volume**              | 6546.(3) Å³                 |
| **Z**                   | 8                           |
| **Density (calculated)**| 1.195 g/cm³                 |
| **Absorption coefficient** | 0.077 mm⁻¹                |
| **F(000)**              | 2512                        |
Table S3. Data collection and structure refinement for 3.

| Description                                      | Details                                      |
|--------------------------------------------------|----------------------------------------------|
| Theta range for data collection                  | 2.43 to 25.52°                               |
| Index ranges                                     | -40<=h<=40, -8<=k<=8, -38<=l<=38              |
| Reflections collected                            | 25976                                        |
| Independent reflections                          | 6081 [R(int) = 0.1068]                       |
| Coverage of independent reflections              | 99.4%                                        |
| Absorption correction                            | multi-scan                                   |
| Max. and min. transmission                       | 0.9980 and 0.9350                            |
| Structure solution technique                     | direct methods                               |
| Structure solution program                       | SHELXTL XT-2014/4                            |
| Refinement method                                | Full-matrix least-squares on F²              |
| Refinement program                               | SHELXL-2014/7 (Sheldrick, 2014)              |
| Function minimized                               | Σ w(F₀² - F_c²)²                              |
| Data / restraints / parameters                   | 6081 / 0 / 406                               |
| Goodness-of-fit on F²                             | 1.069                                        |
| Final R indices                                  | 3963 data; I>2σ(I) R1 = 0.0791, wR2 = 0.1517 |
|                                                    | all data R1 = 0.1239, wR2 = 0.1696            |
| Weighting scheme                                 | w=1/[σ²(F₀²)+0.0520P²+5.4931P] where P=(F₀²+2F_c²)/3 |
| Largest diff. peak and hole                      | 0.296 and -0.201 eÅ⁻³                        |
| R.M.S. deviation from mean                       | 0.063 eÅ⁻³                                   |
Table S4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for 3.

U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|    | x/a    | y/b    | z/c    | U(eq) |
|----|--------|--------|--------|-------|
| O1 | 0.32628(7) | 0.6581(3) | 0.44946(7) | 0.0316(6) |
| O2 | 0.29586(8) | 0.3844(3) | 0.80170(7) | 0.0357(6) |
| O3 | 0.08408(9) | 0.5875(3) | 0.14933(8) | 0.0457(7) |
| N1 | 0.26040(8) | 0.5534(3) | 0.46536(8) | 0.0245(6) |
| N2 | 0.27580(8) | 0.5040(3) | 0.54055(8) | 0.0224(6) |
| N3 | 0.24794(9) | 0.4110(3) | 0.60786(9) | 0.0261(6) |
| N4 | 0.12683(9) | 0.4449(4) | 0.33839(9) | 0.0294(6) |
| C1 | 0.29300(10) | 0.5586(4) | 0.51205(10) | 0.0205(7) |
| C2 | 0.22077(10) | 0.4880(4) | 0.46427(11) | 0.0230(7) |
| C3 | 0.17599(10) | 0.4517(4) | 0.42453(11) | 0.0252(7) |
| C4 | 0.14299(11) | 0.3855(4) | 0.43529(11) | 0.0257(7) |
| C5 | 0.15310(10) | 0.3550(4) | 0.48230(11) | 0.0268(7) |
| C6 | 0.19719(10) | 0.3909(4) | 0.52228(11) | 0.0244(7) |
| C7 | 0.22999(10) | 0.4583(4) | 0.51129(10) | 0.0226(7) |
| C8 | 0.34118(10) | 0.6097(4) | 0.53027(10) | 0.0215(7) |
| C9 | 0.37321(10) | 0.6030(4) | 0.58013(10) | 0.0234(7) |
| C10 | 0.41937(10) | 0.6385(4) | 0.59837(11) | 0.0240(7) |
| C11 | 0.43333(10) | 0.6842(4) | 0.56522(11) | 0.0265(7) |
| C12 | 0.40384(11) | 0.6914(4) | 0.51544(11) | 0.0262(7) |
| C13 | 0.35647(10) | 0.6543(4) | 0.49803(11) | 0.0250(7) |
| C14 | 0.45571(11) | 0.6288(5) | 0.65297(11) | 0.0311(8) |
| C15 | 0.43417(12) | 0.5625(5) | 0.68241(11) | 0.0382(9) |
|    | x/a   | y/b   | z/c   | U(eq)  |
|----|-------|-------|-------|--------|
| C16| 0.49350(12) | 0.4856(6) | 0.66031(13) | 0.0468(10) |
| C17| 0.47723(12) | 0.8246(5)  | 0.67077(12) | 0.0443(10)  |
| C18| 0.42238(11)  | 0.7307(5)  | 0.48126(12) | 0.0318(8)   |
| C19| 0.47485(12)  | 0.7626(5)  | 0.503865(13) | 0.0423(9)   |
| C20| 0.39974(13)  | 0.9085(5)  | 0.45049(13) | 0.0424(9)   |
| C21| 0.41214(12)  | 0.5608(5)  | 0.44760(13) | 0.0409(9)   |
| C22| 0.20819(11)  | 0.3642(4)  | 0.57203(11) | 0.0255(7)   |
| C23| 0.25645(11)  | 0.3990(4)  | 0.65555(11) | 0.0250(7)   |
| C24| 0.22323(11)  | 0.4244(4)  | 0.66898(11) | 0.0292(8)   |
| C25| 0.23483(11)  | 0.4196(4)  | 0.71734(11) | 0.0294(8)   |
| C26| 0.28052(11)  | 0.3889(4)  | 0.75339(11) | 0.0282(7)   |
| C27| 0.31396(11)  | 0.3628(4)  | 0.74049(11) | 0.0297(8)   |
| C28| 0.30225(11)  | 0.3709(4)  | 0.69254(11) | 0.0275(7)   |
| C29| 0.26246(12)  | 0.4024(5)  | 0.81628(12) | 0.0378(9)   |
| C30| 0.16620(10)  | 0.4829(4)  | 0.37521(11) | 0.0268(7)   |
| C31| 0.11861(10)  | 0.4875(4)  | 0.29154(11) | 0.0278(7)   |
| C32| 0.08748(11)  | 0.3744(5)  | 0.25316(11) | 0.0303(8)   |
| C33| 0.07741(11)  | 0.4076(5)  | 0.20687(12) | 0.0341(8)   |
| C34| 0.09742(11)  | 0.5624(5)  | 0.19706(11) | 0.0325(8)   |
| C35| 0.12717(11)  | 0.6800(5)  | 0.23439(11) | 0.0319(8)   |
| C36| 0.13783(11)  | 0.6414(5)  | 0.28099(12) | 0.0331(8)   |
| C37| 0.09939(14)  | 0.7550(5)  | 0.13743(13) | 0.0483(10)  |
Table S5. Bond lengths (Å) for 3.

| Bond       | Length (Å) | Bond       | Length (Å) | Bond       | Length (Å) |
|------------|------------|------------|------------|------------|------------|
| O1-C13     | 1.361(3)   | O1-H1      | 0.84       | O2-C26     | 1.362(4)   |
| O2-C26     | 1.362(4)   | O2-C29     | 1.420(4)   | O3-C34     | 1.370(4)   |
| O3-C34     | 1.370(4)   | O3-C37     | 1.418(4)   | N1-C1      | 1.334(4)   |
| N1-C1      | 1.334(4)   | N1-C2      | 1.390(4)   | N2-C1      | 1.360(4)   |
| N2-C1      | 1.360(4)   | N2-C7      | 1.372(4)   | N2-H2      | 0.88       |
| N2-H2      | 0.88       | N3-C22     | 1.286(4)   | N3-C23     | 1.408(4)   |
| N3-C23     | 1.408(4)   | N4-C30     | 1.276(4)   | N4-C31     | 1.415(4)   |
| N4-C31     | 1.415(4)   | C1-C8      | 1.457(4)   | C2-C7      | 1.393(4)   |
| C2-C7      | 1.393(4)   | C2-C3      | 1.415(4)   | C3-C4      | 1.395(4)   |
| C3-C4      | 1.395(4)   | C3-C30     | 1.460(4)   | C4-C5      | 1.384(4)   |
| C4-C5      | 1.384(4)   | C4-H4      | 0.95       | C5-C6      | 1.404(4)   |
| C5-C6      | 1.404(4)   | C5-H5      | 0.95       | C6-C7      | 1.396(4)   |
| C6-C7      | 1.396(4)   | C6-C22     | 1.456(4)   | C8-C13     | 1.402(4)   |
| C8-C13     | 1.402(4)   | C8-C9      | 1.403(4)   | C9-C10     | 1.372(4)   |
| C9-C10     | 1.372(4)   | C9-H9      | 0.95       | C10-C11    | 1.398(4)   |
| C10-C11    | 1.398(4)   | C10-C14    | 1.546(4)   | C11-C12    | 1.388(4)   |
| C11-C12    | 1.388(4)   | C11-H11    | 0.95       | C12-C13    | 1.415(4)   |
| C12-C13    | 1.415(4)   | C12-C18    | 1.534(4)   | C14-C15    | 1.523(4)   |
| C14-C15    | 1.523(4)   | C14-C17    | 1.531(5)   | C14-C16    | 1.543(5)   |
| C14-C16    | 1.543(5)   | C15-H15A   | 0.98       | C15-H15B   | 0.98       |
| C15-H15B   | 0.98       | C15-H15C   | 0.98       | C16-H16A   | 0.98       |
| C16-H16A   | 0.98       | C16-H16B   | 0.98       | C16-H16C   | 0.98       |
| C16-H16C   | 0.98       | C17-H17A   | 0.98       |            |            |
| Bond          | Length  | Bond          | Length  |
|---------------|---------|---------------|---------|
| C17-H17B      | 0.98    | C17-H17C      | 0.98    |
| C18-C19       | 1.533(5)| C18-C21       | 1.533(5)|
| C18-C20       | 1.539(5)| C19-H19A      | 0.98    |
| C19-H19B      | 0.98    | C19-H19C      | 0.98    |
| C20-H20A      | 0.98    | C20-H20B      | 0.98    |
| C20-H20C      | 0.98    | C21-H21A      | 0.98    |
| C21-H21B      | 0.98    | C21-H21C      | 0.98    |
| C22-H22       | 0.95    | C23-C24       | 1.393(4)|
| C23-C28       | 1.399(4)| C24-C25       | 1.394(4)|
| C24-H24       | 0.95    | C25-C26       | 1.391(4)|
| C25-H25       | 0.95    | C26-C27       | 1.389(4)|
| C27-C28       | 1.381(4)| C27-H27       | 0.95    |
| C28-H28       | 0.95    | C29-H29A      | 0.98    |
| C29-H29B      | 0.98    | C29-H29C      | 0.98    |
| C30-H30       | 0.95    | C31-C36       | 1.391(4)|
| C31-C32       | 1.393(4)| C32-C33       | 1.365(4)|
| C32-H32       | 0.95    | C33-C34       | 1.400(5)|
| C33-H33       | 0.95    | C34-C35       | 1.381(4)|
| C35-C36       | 1.376(4)| C35-H35       | 0.95    |
| C36-H36       | 0.95    | C37-H37A      | 0.98    |
| C37-H37B      | 0.98    | C37-H37C      | 0.98    |
Table S6. Bond angles (°) for 3.

| Bond Angle | Value 1 | Value 2 | Value 3 |
|------------|---------|---------|---------|
| C13-O1-H1  | 109.5   | C26-O2-C29 | 117.7(3) |
| C34-O3-C37 | 116.8(3) | C1-N1-C2 | 105.5(2) |
| C1-N2-C7   | 108.4(2) | C1-N2-H2 | 125.8   |
| C7-N2-H2   | 125.8   | C22-N3-C23 | 120.2(3) |
| C30-N4-C31 | 119.4(3) | N1-C1-N2 | 111.2(3) |
| N1-C1-C8   | 124.6(3) | N2-C1-C8 | 124.2(2) |
| N1-C2-C7   | 109.7(3) | N1-C2-C3 | 130.3(3) |
| C7-C2-C3   | 120.0(3) | C4-C3-C2 | 116.8(3) |
| C4-C3-C30  | 123.2(3) | C2-C3-C30 | 120.1(3) |
| C5-C4-C3   | 122.3(3) | C5-C4-H4 | 118.9   |
| C3-C4-H4   | 118.9   | C4-C5-C6 | 122.0(3) |
| C4-C5-H5   | 119.0   | C6-C5-H5 | 119.0   |
| C7-C6-C5   | 115.5(3) | C7-C6-C22 | 121.7(3) |
| C5-C6-C22  | 122.8(3) | N2-C7-C2 | 105.2(3) |
| N2-C7-C6   | 131.2(3) | C2-C7-C6 | 123.6(3) |
| C13-C8-C9  | 119.5(3) | C13-C8-C1 | 120.3(3) |
| C9-C8-C1   | 120.1(3) | C10-C9-C8 | 121.7(3) |
| C10-C9-H9  | 119.1   | C8-C9-H9 | 119.1   |
| C9-C10-C11 | 117.2(3) | C9-C10-C14 | 123.1(3) |
| C11-C10-C14| 119.7(3) | C12-C11-C10 | 124.4(3) |
| C12-C11-H11| 117.8   | C10-C11-H11 | 117.8    |
| C11-C12-C13| 116.7(3) | C11-C12-C18 | 121.2(3) |
| C13-C12-C18| 122.1(3) | O1-C13-C8 | 120.7(3) |
| Bond                  | Angle      | Bond                  | Angle      |
|----------------------|------------|----------------------|------------|
| O1-C13-C12           | 118.9(3)   | C8-C13-C12           | 120.4(3)   |
| C15-C14-C17          | 109.2(3)   | C15-C14-C16          | 108.3(3)   |
| C17-C14-C16          | 109.9(3)   | C15-C14-C10          | 111.5(3)   |
| C17-C14-C10          | 109.5(3)   | C16-C14-C10          | 108.4(3)   |
| C14-C15-H15A         | 109.5      | C14-C15-H15B         | 109.5      |
| H15A-C15-H15B        | 109.5      | C14-C15-H15C         | 109.5      |
| H15A-C15-H15C        | 109.5      | H15B-C15-H15C        | 109.5      |
| C14-C16-H16A         | 109.5      | C14-C16-H16B         | 109.5      |
| H16A-C16-H16B        | 109.5      | C14-C16-H16C         | 109.5      |
| H16A-C16-H16C        | 109.5      | H16B-C16-H16C        | 109.5      |
| C14-C17-H17A         | 109.5      | C14-C17-H17B         | 109.5      |
| H17A-C17-H17B        | 109.5      | C14-C17-H17C         | 109.5      |
| H17A-C17-H17C        | 109.5      | H17B-C17-H17C        | 109.5      |
| C19-C18-C21          | 107.6(3)   | C19-C18-C12          | 112.3(3)   |
| C21-C18-C12          | 109.5(3)   | C19-C18-C20          | 107.3(3)   |
| C21-C18-C20          | 109.1(3)   | C12-C18-C20          | 111.0(3)   |
| C18-C19-H19A         | 109.5      | C18-C19-H19B         | 109.5      |
| H19A-C19-H19B        | 109.5      | C18-C19-H19C         | 109.5      |
| H19A-C19-H19C        | 109.5      | H19B-C19-H19C        | 109.5      |
| C18-C20-H20A         | 109.5      | C18-C20-H20B         | 109.5      |
| H20A-C20-H20B        | 109.5      | C18-C20-H20C         | 109.5      |
| H20A-C20-H20C        | 109.5      | H20B-C20-H20C        | 109.5      |
| C18-C21-H21A         | 109.5      | C18-C21-H21B         | 109.5      |
| H21A-C21-H21B        | 109.5      | C18-C21-H21C         | 109.5      |
| Bond Sequence | Angle (°) | Bond Sequence | Angle (°) | Bond Sequence | Angle (°) |
|---------------|----------|---------------|----------|---------------|----------|
| H21A-C21-H21C | 109.5    | H21B-C21-H21C | 109.5    |
| N3-C22-C6     | 121.2(3) | N3-C22-H22    | 119.4    |
| C6-C22-H22    | 119.4    | C24-C23-C28   | 117.5(3) |
| C24-C23-N3    | 125.0(3) | C28-C23-N3    | 117.4(3) |
| C23-C24-C25   | 121.6(3) | C23-C24-H24   | 119.2    |
| C25-C24-H24   | 119.2    | C26-C25-C24   | 119.8(3) |
| C26-C25-H25   | 120.1    | C24-C25-H25   | 120.1    |
| O2-C26-C27    | 116.0(3) | O2-C26-C25    | 124.8(3) |
| C27-C26-C25   | 119.2(3) | C28-C27-C26   | 120.5(3) |
| C28-C27-H27   | 119.7    | C26-C27-H27   | 119.7    |
| C27-C28-C23   | 121.4(3) | C27-C28-H28   | 119.3    |
| C23-C28-H28   | 119.3    | O2-C29-H29A   | 109.5    |
| O2-C29-H29B   | 109.5    | H29A-C29-H29B | 109.5    |
| O2-C29-H29C   | 109.5    | H29A-C29-H29C | 109.5    |
| H29B-C29-H29C | 109.5    | N4-C30-C3     | 122.0(3) |
| N4-C30-H30    | 119.0    | C3-C30-H30    | 119.0    |
| C36-C31-C32   | 117.8(3) | C36-C31-N4    | 124.0(3) |
| C32-C31-N4    | 118.1(3) | C33-C32-C31   | 121.6(3) |
| C33-C32-H32   | 119.2    | C31-C32-H32   | 119.2    |
| C32-C33-C34   | 119.7(3) | C32-C33-H33   | 120.1    |
| C34-C33-H33   | 120.1    | O3-C34-C35    | 125.0(3) |
| O3-C34-C33    | 115.4(3) | C35-C34-C33   | 119.6(3) |
| C36-C35-C34   | 119.9(3) | C36-C35-H35   | 120.1    |
| C34-C35-H35   | 120.1    | C35-C36-C31   | 121.5(3) |

S34
| Bond          | Angle | Bond          | Angle | Bond          | Angle |
|--------------|-------|--------------|-------|--------------|-------|
| C35-C36-H36  | 119.3 | C31-C36-H36  | 119.3 |
| O3-C37-H37A  | 109.5 | O3-C37-H37B  | 109.5 |
| H37A-C37-H37B| 109.5 | O3-C37-H37C  | 109.5 |
| H37A-C37-H37C| 109.5 | H37B-C37-H37C| 109.5 |
Table S7. Torsion angles (°) for 3.

|                  | C2-N1-C1-N2 | C2-N1-C1-C8 | C7-N2-C1-N1 | C1-N1-C2-C7 | N1-C2-C3-C4 | N1-C2-C3-C30 | C2-C3-C4-C5 | C3-C4-C5-C6 | C4-C5-C6-C22 | C1-N2-C7-C6 | C3-C2-C7-N2 | C3-C2-C7-C6 | C22-C6-C7-N2 | C22-C6-C7-C2 | N2-C1-C8-C13 | N2-C1-C8-C9 | C1-C8-C9-C10 | C8-C9-C10-C14 | C14-C10-C11-C12 | C10-C11-C12-C18 | C10-C11-C12-C18 | C1-C8-C13-O1 | C1-C8-C13-C12 | C18-C12-C13-O1 | C18-C12-C13-C8 |
|------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|--------------|-------------|-------------|-------------|--------------|--------------|-------------|-------------|--------------|----------------|----------------|----------------|----------------|--------------|--------------|----------------|--------------|
|                  | -1.4(3)     | 176.7(3)    | 0.9(3)      | 1.4(3)      | 179.9(3)    | 0.1(5)      | -0.4(4)     | 0.8(5)      | 178.4(3)     | 178.4(3)    | 179.3(2)    | 0.8(4)      | 2.7(5)       | -179.2(3)    | 176.4(3)    | 0.5(4)       | 175.8(3)     | -178.9(3)     | 178.1(3)      | -176.2(3)     | 2.7(4)       | -175.7(3)    | -1.6(4)      | 176.8(3)     |
|                  |              |             |             |             |             |             |             |             |              |             |             |             |              |              |              |              |              |              |              |              |              |              |              |
C11-C10-C14-C15  -175.6(3)  C9-C10-C14-C17  -117.0(3)
C11-C10-C14-C17  63.4(4)  C9-C10-C14-C16  123.0(3)
C11-C10-C14-C16  -56.6(4)  C11-C12-C18-C19  -1.1(4)
C13-C12-C18-C19  -178.8(3)  C11-C12-C18-C21  118.3(3)
C13-C12-C18-C21  -59.4(4)  C11-C12-C18-C20  -121.2(3)
C13-C12-C18-C20  61.1(4)  C23-N3-C22-C6  174.6(3)
C7-C6-C22-N3  3.6(4)  C5-C6-C22-N3  -175.1(3)
C22-N3-C23-C24  -31.0(4)  C22-N3-C23-C28  153.1(3)
C28-C23-C24-C25  -0.9(5)  N3-C23-C24-C25  -176.7(3)
C23-C24-C25-C26  0.0(5)  C29-O2-C26-C27  -177.4(3)
C29-O2-C26-C25  3.5(4)  C24-C25-C26-O2  178.9(3)
C24-C25-C26-C27  -0.2(5)  O2-C26-C27-C28  -177.9(3)
C25-C26-C27-C28  1.3(5)  C26-C27-C28-C23  -2.2(5)
C24-C23-C28-C27  2.0(4)  N3-C23-C28-C27  178.1(3)
C31-N4-C30-C3  176.7(3)  C4-C3-C30-N4  -2.6(5)
C2-C3-C30-N4  177.2(3)  C30-N4-C31-C36  -33.2(4)
C30-N4-C31-C32  150.3(3)  C36-C31-C32-C33  2.6(5)
N4-C31-C32-C33  179.4(3)  C31-C32-C33-C34  -2.2(5)
C37-O3-C34-C35  -5.1(5)  C37-O3-C34-C33  172.8(3)
C32-C33-C34-O3  -178.0(3)  C32-C33-C34-C35  0.0(5)
O3-C34-C35-C36  179.5(3)  C33-C34-C35-C36  1.7(5)
C34-C35-C36-C31  -1.2(5)  C32-C31-C36-C35  -0.9(5)
N4-C31-C36-C35  -177.5(3)
Table S8. Anisotropic atomic displacement parameters (Å\(^2\)) for 3.

The anisotropic atomic displacement factor exponent takes the form: \(-2\pi^2 [h^2 a^* a + ... + 2hk a^* b^* U_{12}]

| Atom | U_{11}  | U_{22}  | U_{33}  | U_{23}  | U_{13}  | U_{12}  |
|------|---------|---------|---------|---------|---------|---------|
| O1   | 0.0290(12) | 0.0378(14) | 0.0244(12) | 0.0024(10) | 0.0108(10) | 0.0026(11) |
| O2   | 0.0398(14)  | 0.0349(14)  | 0.0295(13)  | -0.0008(10)  | 0.0154(11)  | 0.0005(11)  |
| O3   | 0.0609(17)  | 0.0392(16)  | 0.0349(14)  | 0.0040(12)   | 0.0228(13)  | -0.0035(13) |
| N1   | 0.0264(14)  | 0.0183(14)  | 0.0228(14)  | 0.0000(11)   | 0.0081(12)  | 0.0028(11)  |
| N2   | 0.0214(14)  | 0.0194(14)  | 0.0191(12)  | -0.0004(11)  | 0.0049(11)  | 0.0043(11)  |
| N3   | 0.0269(15)  | 0.0191(14)  | 0.0284(14)  | 0.0031(11)   | 0.0111(13)  | 0.0021(11)  |
| N4   | 0.0271(15)  | 0.0249(15)  | 0.0269(14)  | 0.0001(12)   | 0.0068(13)  | 0.0004(12)  |
| C1   | 0.0270(17)  | 0.0133(15)  | 0.0194(15)  | -0.0016(12)  | 0.0104(14)  | 0.0045(12)  |
| C2   | 0.0241(17)  | 0.0131(15)  | 0.0288(17)  | -0.0034(13)  | 0.0113(14)  | 0.0056(13)  |
| C3   | 0.0274(18)  | 0.0168(16)  | 0.0273(17)  | -0.0018(13)  | 0.0109(15)  | 0.0054(13)  |
| C4   | 0.0244(17)  | 0.0181(16)  | 0.0288(17)  | -0.0027(13)  | 0.0093(15)  | 0.0022(13)  |
| C5   | 0.0247(17)  | 0.0176(17)  | 0.0368(19)  | -0.0019(14)  | 0.0146(15)  | 0.0009(13)  |
| C6   | 0.0283(18)  | 0.0139(15)  | 0.0327(17)  | -0.0015(13)  | 0.0168(15)  | 0.0049(13)  |
| C7   | 0.0237(17)  | 0.0127(15)  | 0.0272(16)  | -0.0023(13)  | 0.0098(14)  | 0.0045(12)  |
| C8   | 0.0266(17)  | 0.0120(15)  | 0.0230(15)  | 0.0007(12)   | 0.0104(14)  | 0.0033(12)  |
| C9   | 0.0292(18)  | 0.0180(16)  | 0.0261(16)  | 0.0019(13)   | 0.0163(15)  | 0.0034(13)  |
| C10  | 0.0257(17)  | 0.0148(16)  | 0.0290(17)  | 0.0030(13)   | 0.0120(15)  | 0.0054(13)  |
| C11  | 0.0229(17)  | 0.0201(17)  | 0.0360(18)  | -0.0006(14)  | 0.0144(15)  | 0.0009(13)  |
| C12  | 0.0310(19)  | 0.0174(16)  | 0.0308(18)  | 0.0036(14)   | 0.0161(15)  | 0.0079(14)  |
| C13  | 0.0267(18)  | 0.0165(16)  | 0.0248(16)  | 0.0016(13)   | 0.0080(15)  | 0.0077(13)  |
| C14  | 0.0256(18)  | 0.036(2)    | 0.0236(16)  | 0.0014(15)   | 0.0062(15)  | 0.0008(15)  |
|   | \( U_{11} \)  | \( U_{22} \)  | \( U_{33} \) | \( U_{12} \) | \( U_{13} \) | \( U_{23} \) |
|---|------------|------------|------------|------------|------------|------------|
| C15 | 0.034(2) | 0.046(2) | 0.0224(17) | 0.0024(16) | 0.0057(16) | -0.0038(17) |
| C16 | 0.036(2) | 0.058(3) | 0.035(2) | 0.0095(19) | 0.0098(18) | 0.0169(19) |
| C17 | 0.036(2) | 0.047(2) | 0.0339(19) | -0.0054(18) | 0.0061(17) | -0.0126(18) |
| C18 | 0.034(2) | 0.0301(19) | 0.0353(19) | 0.0060(15) | 0.0207(16) | 0.0059(15) |
| C19 | 0.042(2) | 0.047(2) | 0.048(2) | 0.0055(19) | 0.0305(19) | 0.0022(18) |
| C20 | 0.050(2) | 0.043(2) | 0.044(2) | 0.0130(18) | 0.0312(19) | 0.0098(18) |
| C21 | 0.043(2) | 0.042(2) | 0.042(2) | -0.0019(18) | 0.0250(19) | 0.0047(18) |
| C22 | 0.0245(17) | 0.0180(16) | 0.0343(18) | 0.0032(14) | 0.0153(16) | 0.0048(13) |
| C23 | 0.0317(18) | 0.0132(15) | 0.0309(17) | 0.0008(13) | 0.0163(16) | -0.0011(13) |
| C24 | 0.0267(18) | 0.0243(18) | 0.0308(18) | 0.0003(14) | 0.0103(15) | 0.0013(14) |
| C25 | 0.0303(19) | 0.0280(19) | 0.0341(18) | 0.0002(15) | 0.0194(16) | 0.0021(15) |
| C26 | 0.0336(19) | 0.0122(16) | 0.0347(18) | -0.0001(14) | 0.0144(16) | -0.0020(13) |
| C27 | 0.0268(18) | 0.0216(18) | 0.0351(19) | -0.0020(14) | 0.0116(16) | -0.0015(14) |
| C28 | 0.0272(18) | 0.0201(17) | 0.0345(18) | -0.0018(14) | 0.0151(15) | 0.0003(13) |
| C29 | 0.051(2) | 0.034(2) | 0.0317(18) | 0.0029(16) | 0.0234(18) | 0.0047(17) |
| C30 | 0.0227(18) | 0.0203(17) | 0.0353(18) | -0.0021(14) | 0.0132(16) | 0.0036(13) |
| C31 | 0.0245(18) | 0.0263(18) | 0.0280(17) | 0.0009(14) | 0.0101(15) | 0.0059(14) |
| C32 | 0.0283(18) | 0.0264(18) | 0.0296(18) | 0.0024(15) | 0.0099(15) | -0.0011(14) |
| C33 | 0.033(2) | 0.030(2) | 0.0296(18) | -0.0017(15) | 0.0088(16) | -0.0026(15) |
| C34 | 0.035(2) | 0.029(2) | 0.0304(18) | 0.0020(15) | 0.0145(16) | 0.0062(15) |
| C35 | 0.0345(19) | 0.0248(18) | 0.0363(19) | 0.0036(15) | 0.0179(16) | -0.0023(15) |
| C36 | 0.0269(19) | 0.0292(19) | 0.0377(19) | -0.0031(16) | 0.0123(16) | -0.0025(15) |
| C37 | 0.068(3) | 0.037(2) | 0.042(2) | 0.0109(18) | 0.029(2) | 0.005(2) |
Table S9. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å$^2$) for 3.

|      | x/a  | y/b  | z/c  | U(eq) |
|------|------|------|------|-------|
| H1   | 0.2993 | 0.6377 | 0.4440 | 0.047  |
| H2   | 0.2914 | 0.4989 | 0.5724 | 0.027  |
| H4   | 0.1125 | 0.3606 | 0.4094 | 0.031  |
| H5   | 0.1295 | 0.3083 | 0.4877 | 0.032  |
| H9   | 0.3626 | 0.5731 | 0.6018 | 0.028  |
| H11  | 0.4651 | 0.7121 | 0.5776 | 0.032  |
| H15A | 0.4583 | 0.5528 | 0.7166 | 0.057  |
| H15B | 0.4198 | 0.4384 | 0.6707 | 0.057  |
| H15C | 0.4106 | 0.6537 | 0.6789 | 0.057  |
| H16A | 0.5171 | 0.4792 | 0.6947 | 0.07   |
| H16B | 0.5079 | 0.5262 | 0.6417 | 0.07   |
| H16C | 0.4795 | 0.3604 | 0.6491 | 0.07   |
| H17A | 0.4533 | 0.9137 | 0.6671 | 0.067  |
| H17B | 0.4908 | 0.8686 | 0.6516 | 0.067  |
| H17C | 0.5014 | 0.8169 | 0.7049 | 0.067  |
| H19A | 0.4824 | 0.8726 | 0.5300 | 0.063  |
| H19B | 0.4852 | 0.7854 | 0.4854 | 0.063  |
| H19C | 0.4905 | 0.6504 | 0.5280 | 0.063  |
| H20A | 0.3660 | 0.8939 | 0.4329 | 0.064  |
| H20B | 0.4104 | 0.9252 | 0.4273 | 0.064  |
| H20C | 0.4084 | 1.0195 | 0.4716 | 0.064  |
| H21A | 0.4263 | 0.4470 | 0.4670 | 0.061  |
|    | x/a  | y/b  | z/c  | U(eq) |
|----|------|------|------|-------|
| H21B | 0.4249 | 0.5841 | 0.4265 | 0.061  |
| H21C | 0.3786 | 0.5428 | 0.4278 | 0.061  |
| H22  | 0.1856 | 0.3112 | 0.5781 | 0.031  |
| H24  | 0.1919 | 0.4455 | 0.6446 | 0.035  |
| H25  | 0.2116 | 0.4373 | 0.7256 | 0.035  |
| H27  | 0.3451 | 0.3392 | 0.7648 | 0.036  |
| H28  | 0.3258 | 0.3572 | 0.6845 | 0.033  |
| H29A | 0.2473 | 0.5261 | 0.8062 | 0.057  |
| H29B | 0.2778 | 0.3913 | 0.8516 | 0.057  |
| H29C | 0.2392 | 0.3021 | 0.8012 | 0.057  |
| H30  | 0.1899 | 0.5332 | 0.3704 | 0.032  |
| H32  | 0.0729 | 0.2717 | 0.2593 | 0.036  |
| H33  | 0.0569 | 0.3261 | 0.1814 | 0.041  |
| H35  | 0.1402 | 0.7873 | 0.2279 | 0.038  |
| H36  | 0.1588 | 0.7217 | 0.3065 | 0.04   |
| H37A | 0.0888 | 0.8654 | 0.1477 | 0.073  |
| H37B | 0.0866 | 0.7603 | 0.1024 | 0.073  |
| H37C | 0.1333 | 0.7552 | 0.1540 | 0.073  |
Table S10. Hydrogen bond distances (Å) and angles (°) for 3.

| Donor-H | Acceptor-H | Donor-Acceptor | Angle |
|---------|------------|----------------|-------|
| O1-H1 - N1 | 0.84 | 1.85 | 2.611(3) | 149.5 |
| N2-H2 - N3 | 0.88 | 2.34 | 2.829(4) | 115.0 |
2. Computational Methods

Electronic structure calculations were performed with density functional theory (DFT) using the B3LYP functional\textsuperscript{5,6} with dispersion corrections (D3(BJ))\textsuperscript{7–9} and the 6-31G** basis set.\textsuperscript{10–13} Geometry optimizations and free energy calculations were performed in dichloromethane solution using the conductor-like polarizable continuum model (CPCM).\textsuperscript{14,15} The Bondi atomic radii were used, and nonelectrostatic contributions of dispersion, repulsion, and cavitation energies were included.\textsuperscript{16–18} Previous benchmarking of this level of theory has shown that it performs well for similar systems.\textsuperscript{2,19} The Gaussian16 electronic structure program was used for all DFT calculations.\textsuperscript{20} Free energies were calculated using the standard Gibbs relation, $\Delta G_0 = \Delta H_0 - T \Delta S_0$, at $T = 298.15$ K and included zero-point energy, entropic contributions, and solvation effects.

Relative free energies were calculated for all protonation states of selected rotamers. These rotamers and states are shown in Figures 5A and B in the main manuscript for compounds 2 and 3, respectively. All calculated relative free energies were referenced to the lowest energy rotamer/protonation state of each neutral or oxidized compound. The Boltzmann populations were computed using Eq. 1 in the main manuscript. The calculated relative free energies and populations of each state are given in Table S11 and Table S12.

The redox potentials were computed from the corresponding reaction free energies using an experimentally known reference potential within a thermodynamic cycle. The reference potential used for computing the redox potentials of compounds 1, G, and 3 was the experimentally measured redox potential of 0.95 V vs SCE in dichloromethane of compound 2. In previous studies,\textsuperscript{19} these methods have produced accurate and predictive results in agreement with experiments. The calculated redox potentials are reported in Table S13.

Computationally obtained IRSEC spectra for compounds 2 and 3 show the formation of the final E2PT products (Figure S17). Frequency calculations were performed for both the reduced (neutral) and oxidized (+1) species. To allow direct comparison with experimental IRSEC spectra, all computed frequencies were empirically scaled by a factor of 0.962 to match the experimental C=NH\textsuperscript{+} protonated azomethine stretch at 1651 cm\textsuperscript{-1} of the E2PT product of compound 3. To simulate line broadening, the peaks were dressed with an artificial Lorentzian function for a full-width-half-maximum (FWHM) of 12 cm\textsuperscript{-1}. Frequencies and characterization of selected vibrational modes are given in Table S14. Band assignments were performed by visually inspecting displacements along the computed normal mode of each vibration. These computational
IRSEC results are in good agreement with experimentally obtained IRSEC spectra (Figure 8). Spin densities for the E0PT and E2PT products of compounds 2 and 3 were also produced and plotted (Figure S18).
Table S11. Relative Free Energies and Populations of compound 2.\(^a\)

| Proton Positions\(^a\) | Relative Free Energies\(^b\) | Populations\(^c\) |
|------------------------|-----------------------------|------------------|
|                        | Phenolic | Benzimidazole | Neutral | Oxidized | Neutral | Oxidized |
| Rotamer A              |          |              |         |          |         |          |
| 1                      | 1        | 1            | 3.76    | 13.36    | 0.16%   | 0.00%    |
| 2                      | 1        | 1            | 5.57    | 5.20     | 0.01%   | 0.01%    |
| 3                      | 1        | 1            | 16.96   | 6.07     | 0.00%   | 0.00%    |
| Rotamer B              |          |              |         |          |         |          |
| 1                      | 1        | 1            | 2.56    | 12.78    | 1.21%   | 0.00%    |
| 2                      | 1        | 1            | 9.20    | 9.59     | 0.00%   | 0.00%    |
| Rotamer C              |          |              |         |          |         |          |
| 1                      | 1        | 1            | 0.00    | 13.44    | 98.58%  | 0.00%    |
| 1                      | 2        | 1            | 5.18    | 11.58    | 0.01%   | 0.00%    |
| 2                      | 1        | 1            | 4.69    | 4.31     | 0.03%   | 0.06%    |
| 2                      | 2        | 2            | 5.99    | 0.00     | 0.00%   | 99.92%   |
| Rotamer D              |          |              |         |          |         |          |
| 1                      | 1        | 1            | 5.64    | 17.57    | 0.01%   | 0.00%    |
| 2                      | 1        |              | 10.24   | 11.56    | 0.00%   | 0.00%    |

\(^a\)See Figure 5A for rotamers and proton positions.

\(^b\)Relative free energies reported in kcal/mol.

\(^c\)Populations reported in percentages.
### Table S12. Relative Free Energies and Populations of compound 3.

| Proton Position<sup>a</sup> | Relative Free Energies<sup>b</sup> | Populations<sup>c</sup> |
|-----------------------------|----------------------------------|-------------------------|
| Phenolic | Benzimidazole | Neutral | Oxidized | Neutral | Oxidized |
| Rotamer A | | | | | |
| 1 | 1 | 0.57 | 11.82 | 27.02% | 0.00% |
| 2 | 1 | 2.5 | 2.22 | 0.98% | 2.15% |
| 2 | 2 | 5.79 | 0 | 0.00% | 97.47% |
| 3 | 1 | 13.7 | 5.38 | 0.00% | 0.01% |
| 3 | 2 | 19.69 | 9.57 | 0.00% | 0.00% |
| Rotamer B | | | | | |
| 1 | 1 | 6.11 | 16.88 | 0.00% | 0.00% |
| 2 | 1 | 8.68 | 10.53 | 0.00% | 0.00% |
| 3 | 1 | 17.67 | 11.09 | 0.00% | 0.00% |
| Rotamer C | | | | | |
| 1 | 1 | 0 | 9.77 | 71.93% | 0.00% |
| 2 | 1 | 4.58 | 12.48 | 0.03% | 0.00% |
| 2 | 2 | 5.25 | 7.17 | 0.01% | 0.00% |
| 2 | 2 | 7.06 | 3.25 | 0.00% | 0.37% |
| Rotamer D | | | | | |
| 1 | 1 | 4.87 | 15.22 | 0.02% | 0.00% |
| 2 | 1 | 9.39 | 14.52 | 0.00% | 0.00% |

<sup>a</sup>See Figure 5B for rotamers and proton positions.
<sup>b</sup>Relative free energies reported in kcal/mol.
<sup>c</sup>Populations reported in percentages.
Table S13. Calculated Redox Potentials.\textsuperscript{a}

| Compound    | E0PT | E1PT | E2PT |
|-------------|------|------|------|
| Compound 1  | 1.52 | 1.14 | N/A  \textsuperscript{b} |
| Compound G  | 1.63 | 1.25 | N/A  \textsuperscript{c} |
| Compound 2  | 1.54 | 1.14 | 0.95 \textsuperscript{d} |
| Compound 3  | 1.26 | 0.92 | 0.84 |

\textsuperscript{a}Redox potentials reported in V vs SCE.
\textsuperscript{b}Compound 1 cannot have an E2PT product.
\textsuperscript{c}Compound G does not have a minimum corresponding to the E2PT product.
\textsuperscript{d}This redox potential was used as reference and agrees with experiment by construction.
Table S14. Peak Assignment of Computational IRSEC.

| Compound | State | Freq.\textsuperscript{a} | Peak Description |
|----------|-------|---------------------------|------------------|
| 2 | E2PT | 1560 | breathing mode of TPA |
|    |       | 1566 | breathing mode of phenol |
|    |       | 1651 | protonated azomethine stretch |
| 3 | E1PT | 1532 | breathing mode of benzimidazole |
|    |       | 1544 | bend mode of benzimidazole proton on benzimidazole donor |
|    |       | 1570 | breathing mode of phenol |
|    |       | 1575 | breathing mode of TPA |
| 3 | E2PT | 1537 | breathing mode of TPA |
|    |       | 1560 | breathing mode of TPA |
|    |       | 1570 | breathing mode of phenol |
|    |       | 1593 | breathing mode of TPA with azomethine bending |
|    |       | 1651 | protonated azomethine stretch |

\textsuperscript{a}Computationally obtained vibrational frequencies reported in cm\textsuperscript{-1}.
Figure S17. Computationally produced IRSEC spectra. The bold black lines show the spectra of the reactant state of each compound, the bold red lines show the spectra of the product state, and the faded black lines show the simulated progression of the IRSEC as product is formed. Frame A shows the E1PT product of compound 3. Frame B shows the E2PT product of compound 3. Frame C shows the E1PT product of compound 2. Frame D shows the E2PT product of compound 2.
Figure S18. Spin density of hypothetical E0PT products and experimentally observed E2PT products of dominant rotamer species for compounds 2 and 3. (A) E0PT product for 3; (B) E2PT product for 3; (C) E0PT product for 2; (D) E2PT product for 2. The substantial difference in the calculated redox potentials associated with the hypothetical E0PT products of 2 and 3 (Table S13) may be explained by the greater stabilization of the radical due to the more delocalized spin density of 3. However, the similarity between the spin densities for the E2PT products of 2 and 3 indicates that this factor does not constitute an explanation for the differences in the experimentally measured redox potentials.
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