Structurally Modelling the 2-His-1-Carboxylate Facial Triad with a Bulky $N,N,O$ Phenolate Ligand

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1 Experimental

1.1 Chemicals and Reagents

Unless stated otherwise, all reactions were performed under inert \( \text{N}_2 \) (g) atmosphere using standard Schlenk line and glovebox techniques and were stirred magnetically. The solvents acetonitrile, diethyl ether, and hexane were purified using an MBraun MB SPS-80 purification system. Dichloromethane and pyridine were dried over \( \text{CaH}_2 \) and distilled under inert \( \text{N}_2 \) (g) atmosphere before use. THF was dried over sodium benzophenone ketyl and distilled under inert \( \text{N}_2 \) (g) atmosphere before use. Pentane was dried using activated molecular sieves and was degassed using the freeze-pump-thaw technique. All other common solvents were degassed by bubbling \( \text{N}_2 \) (g) through them for a period of 30 mins prior to use and were stored over activated molecular sieves. Acetonitrile was filtered over activated neutral alumina before use to remove molecular sieve debris. All solvents were tested for water content by the Karl-Fischer titration or by \(^1\text{H} \) NMR. Non-halogenated solvents were additionally tested with a standard purple solution of sodium benzophenone ketyl in THF to confirm effective oxygen and moisture removal. Deuterated solvents were purchased from the Cambridge Isotope Laboratory Incorporation (Cambridge, USA) and were degassed using the freeze-pump-thaw method and stored over activated molecular sieves. Deuterated acetonitrile was filtered over activated neutral alumina prior to use to remove molecular sieve debris. All reagents and starting materials were purchased from commercial sources and used without further purification, except when specified. Benzenethiol was converted to its respective sodium salt by treating it with an equimolar amount of NaH.

1.2 Physical Methods

NMR spectroscopy (\(^1\text{H}, \text{\textsuperscript{13}C}, \text{\textsuperscript{19}F}, \text{\textsuperscript{1}H}-\text{\textsuperscript{13}C} \) HSQC, 1D and 2D NOESY) was conducted using a 400 MHz Varian spectrometer or an Oxford NMR AS400 spectrometer. \(^1\text{H} \) and \(^{13}\text{C} \) NMR chemical shifts are reported in the standard \( \delta \) notation of part per million (ppm) and are referenced to residual solvent signals, as determined relative to SiMe\(_4\). \(^{19}\text{F} \) NMR chemical shifts are reported in ppm and are externally referenced to an 85% aqueous solution of \( \text{CFCl}_3 \). Paramagnetic \(^1\text{H} \) NMR spectra were recorded after having adjusted both the relaxation delay and acquisition time to 100 ms. IR spectroscopy was conducted using a PerkinElmer Spectrum Two FT-IR spectrometer. For air-sensitive compounds, a \( \text{N}_2 \) (g) flow was used. Peaks are annotated by (w), (m) and (s) to indicate weak, medium and strong signals, respectively. Absorption spectra were recorded using a Varian Cary 50 Scan spectrometer, using Quartz cuvettes with a path length of 1 cm, sealed with a Teflon cap. Unless otherwise stated, UV-vis solutions were prepared in the glovebox using dried and degassed solvents. The acquisition of the absorption spectra was performed with the PerkinElmer UV Winlab software.

High resolution ESI-MS measurements were performed with a Waters LCT Premier XE KE317. All other ESI-MS measurements were performed with an Advion Expression CMS instrument. X-ray crystal structure determinations were performed on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (\( \lambda = 0.71073 \) Å) at a temperature of 150(2) K. CCDC 2035728-2035733 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Mössbauer spectra were recorded on a conventional spectrometer with alternating constant acceleration of the \( \gamma \)-source (\(^{57}\text{Co}/\text{Rh}, 1.8 \) GBq), which was kept at room temperature. The minimum experimental line width was 0.24 mm/s (full width at half-height). The sample temperature was maintained constant in an Oxford Instruments Variox cryostat. Isomer shifts are quoted relative to iron metal at 300 K. The zero-field spectra were simulated with Lorentzian doublets with the program \textit{mf.SL} developed by Eckhard Bill. Electrochemical analysis was done by means of potentiodynamic measurements in which the working electrode potential is ramped linearly versus time (linear sweep voltammetry (LSV) and cyclic voltammetry (CV)). All measurements were performed in a nitrogen-filled glovebox on an IVIUM potentiostat/galvanostat using a 3-electrode setup. The setup included a glassy carbon (GC) working electrode, a platinum counter electrode, and a silver wire pseudo reference electrode. All electrodes were purchased from either BASi or Redox.me.
The potentiostat was kept external to the glovebox, and the electrode leads were connected with a custom shielded electrode cable feedthrough. All scans were absolutely referenced to ferrocene, measured at the start and end of each measurement set. GC electrodes were 2 and 3 mm in diameter, with surfaces of 50.3 mm$^2$ and 113.1 mm$^2$, respectively. GC electrodes were polished with 0.3μm alumina powder deionized water slurries, rinsed with MeOH, water and dilute HCl solution (1 M), and ultrasonicated in pure deionized water for 30 sec, to remove residual polishing powder. The pseudo reference silver wire electrode and platinum wire counter electrode were rinsed with MeOH and water. All electrodes were dried in the ante chamber of the glovebox for at least 12 h. All electrodes were used directly in solution. Each working electrode was pre-treated with at least two cyclical scans from approximately +1.5 to −2.8 V at 200 mV/s in the corresponding solvent containing 0.1 M [n-Bu4N][PF6]. For all experiments, background voltammograms of the electrolyte were recorded at the respective scan rate. Solutions were gently shaken between experiments to renew the diffusion layer. No indication of solution resistance was observed during experiments, as described by McCarthy et al, which state that the solution resistance in the presence of >0.05 M electrolyte is estimated to be <30 mV in reduction potentials.2

1.3 Computational Methods

DFT (density functional theory) calculations were conducted using the Gaussian 16 software package.3 Geometry optimisations use the B3LYP (Becke, three-parameter, Lee-Young-Parr) functional with the LanL2DZ basis set defined on Fe and Zn atoms and the 6-31g(d,p) basis set defined on all other atoms. The geometries were optimized without any symmetry restraints and empirical dispersion corrections were applied. The structures were confirmed as energy minima by the absence of any imaginary frequencies. Frequency analyses were performed on all geometries as the B3LYP/6-31g(d,p) level of theory. Single point energy calculations were re-run on all geometries as the B3LYP/6-311g(d,p) level of theory. For NBO (natural bond orbital) calculations, the NBO06 program4 up to the NLMO (natural localized molecular orbital) basis set at the B3LYP/6-311g(d,p) level of theory. Cube files for molecular orbitals were generated using the Multiwfn program.5 Biorthogonalisation of the α and β spin molecular orbitals for 2 were performed with the Multiwfn program, using the Fock matrix from the .47 NBO file generated for 2. Molecular orbitals were visualised with the Visual Molecular Dynamics program6 using the respective molecular orbital cube file and defining the isosurface level as ±0.05.

1.4 Ligand Synthesis

Methyl 3,5-di-tert-butyl-2-hydroxybenzoate (LS1):7 Methyl salicylate (25.6 mL g, 197 mmol), tert-butanol (47.7 mL, 500 mmol) and methanol (20.0 mL, 494 mmol) were combined in a 3-neck round-bottomed flask, equipped with a stirring bar (or a mechanical stirrer for larger-scale), a thermometer and a dropping funnel. The mixture was cooled using a salt-ice bath and stirred vigorously during the dropwise addition of 100 mL concentrated sulfuric acid, keeping the temperature between 0 ºC and 5 ºC. The mixture was subsequently left to stir 4 h at low temperature. The pale yellow acidic supernatant was removed (decanted), and the remaining white precipitate washed thoroughly with water to render the pH neutral. The solid was subsequently filtered and recrystallized from methanol. The title compound was isolated as a white crystalline solid by Büchner filtration in 51% yield (26.61 g, 100 mmol).1H NMR (400 MHz, CDCl3, 25 ºC): δ = 11.35 (s, 1H, OH), 7.71 (d, 1H, J = 4 Hz, CH$_{aryl}$) ppm, 7.53 (d, 1H, J = 4 Hz, CH$_{aryl}$), 3.94 (s, 3H, OCH$_3$), 1.43 (s, 9H, C(CH$_3$)$_3$), 1.31 (s, 9H, C(CH$_3$)$_3$) ppm. 13C($^1$H) NMR (101 MHz, CDCl3, 25 ºC): δ = 171.89, 159.13, 140.58, 137.34, 130.56, 123.75, 111.48, 52.32, 35.28, 34.41, 31.56, 29.54 ppm. ESI-MS (acetonitrile): m/z = 265.20 [(M+H)$^+$], calc. 265.18. IR (ATR): ν = 3088 (w), 3011 (w), 2957 (m), 2907 (m), 1727 (w), 1669 (s), 1601 (m), 1472 (m), 1454 (m), 1438 (s), 1411 (m), 1389 (m), 1360 (s), 1332 (s), 1273 (s), 1244 (s), 1216 (s), 1196 (s), 1180 (s), 1116 (s), 1025 (w), 983 (m), 930 (w), 916 (w), 895 (m), 823 (m), 800 (s), 758 (s), 740 (m), 723 (s), 641 (m), 588 (w), 536 (w), 513 (w), 452 (m) cm$^{-1}$.
Methyl 3,5-di-tert-butyl-2-(methoxymethoxy)benzoate (LS2): NaH (2.44 g, 61 mmol, 60 weight% dispersion in mineral oil) was washed thoroughly with hexane and THF before being suspended in THF (300 mL). Next, LS1 (10.6 g, 38 mmol) was added in portions at room temperature. The reaction was allowed to stir 1 h, during which time the reaction mixture became yellow-green in colour. Methoxy methyl chloride (5.18 g, 64 mmol) was added in one portion, and the mixture left to stir overnight at ambient temperature. Ice was added cautiously (gas and exotherm!) to quench the excess NaH, and EtOAc was used to extract the organics (3 x 200 mL). The organic washings were combined, washed once with saturated NaCl solution (200 mL), then dried over MgSO₄, filtered and concentrated under vacuum, affording the product as a viscous yellow oil in 90% yield (10.8 mL, 11.2 g, 36 mmol). Note: this oil is too viscous to be distilled under vacuum (up to 200 °C); it is therefore advised to wash the NaH prior to use and purify by column chromatography using EtOAc as an eluent. The density is calculated as being 0.96 g/mol. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 7.50 (s, 2H, CH₂arom), 4.97 (s, 2H, OCH₃), 3.87 (s, 3H, OCH₃), 3.55 (s, 3H, MOM-CH₃), 1.42 (s, 9H, C(CH₃)₃), 1.29 (s, 9H, C(CH₃)₃) ppm. ¹³C[¹H] NMR (101 MHz, CDCl₃, 25 °C): δ = 168.59, 153.68, 145.29, 142.45, 127.88, 125.50, 125.09, 100.88, 57.61, 52.15, 35.42, 34.55, 31.38, 30.75 ppm.

ESI-MS (acetonitrile): m/z = 313.20 [M+Na]⁺, calc. 313.19. IR (ATR): ν = 2954 (s), 2907 (m), 2871 (m), 1723 (s), 1599 (w), 1476 (m), 1435 (s), 1393 (m), 1363 (m), 1315 (m), 1267 (m), 1244 (s), 1221 (s), 1196 (s), 1159 (s), 1110 (m), 1073 (s), 1024 (w), 959 (s), 937 (s), 912 (m), 892 (m), 875 (m), 806 (m), 792 (m), 757 (w), 649 (w), 545 (w) 497 (w) cm⁻¹.

1-methyl-4,5-diphenyl-1H-imidazole:⁸ NaH (6.0 g, 148 mmol, 60 weight% dispersion in mineral oil) was suspended in THF (500 mL) and cooled to 0 °C. Next, 4,5-diphenylimidazole (27.1g, 123 mmol,) was added in portions, keeping the temperature below 15 °C. After completing the addition of the imidazole, the reaction was allowed to stir overnight at room temperature, before the dropwise addition of iodomethane (9.2 mL, 148 mmol) at room temperature. During this time, the colour of the mixture changed from milky white to grey. Methoxy methyl chloride (6.0 g, 148 mmol, 60 weight% dispersion in mineral oil) was added cautiously (gas and exotherm!) to quench the excess NaH, and CH₂Cl₂ was used to extract the organics (3 x 200 mL). The organic washings were combined, washed once with saturated NaCl solution (200 mL), then dried over MgSO₄, filtered and concentrated under vacuum, affording the product as a viscous yellow oil in 90% yield (23.2 g, 99 mmol).

¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 7.57 (s, 1H, -CH), 7.46 (m, 5H, H arom), 7.34 (m, 2H, H arom), 7.20 (m, 2H, H arom), 7.14 (m, 1H, H arom), 3.49 (s, 3H, NCH₃) ppm. ¹³C[¹H] NMR (101 MHz, CDCl₃, 25 °C): δ = 138.40, 137.56, 134.78, 130.81, 130.76, 129.12, 129.04, 128.72, 128.24, 126.74, 126.43, 32.32 ppm. ESI-MS (acetonitrile): m/z = 235.1226 [M+H]⁺, calc. 235.1235. IR (ATR): ν = 3114 (w), 3044 (w), 2985 (w), 2954 (w), 1954 (w), 1887 (w), 1832 (w), 1763 (w), 1696 (w), 1638 (w), 1600 (m), 1578 (w), 1507 (m), 1479 (m), 1423 (w), 1388 (w), 1367 (m), 1317 (w), 1249 (m), 1194 (m), 1181 (w), 1159 (w), 1121 (w), 1068 (m), 1021 (m), 1000 (w), 985 (w), 952 (m), 917 (m), 851 (w), 771 (s), 734 (s), 719 (m), 699 (s), 647 (s), 617 (m), 565 (m), 507 (w), 495 (w) cm⁻¹.
(3,5-di-tert-butyl-2-(methoxymethoxy)phenyl)bis(1-methyl-4,5-diphenyl-1H-imidazol-2-yl)-methanol (LS3): 1-methyl-4,5-diphenylimidazole (3.05 g, 13 mmol) was dissolved in THF (150 mL) at room temperature. n-BuLi (8.75 mL, 14 mmol, 1.6 M in hexanes) was added dropwise at −78 °C, causing the solution to turn dark orange. The mixture was allowed to stir for 1 h at room temperature before the dropwise addition of LS2 (2.00 mL, 6.2 mmol). The mixture was stirred overnight and finally quenched by addition of saturated aqueous NH₄Cl solution (50 mL). EtOAc was used to extract the organics (2 x 150 mL) and the organic layer washed once with distilled water (100 mL), before being dried over MgSO₄, and concentrated to afford a crude yellow solid. The solid was washed by stirring vigorously in petroleum ether (80 mL), filtered and air-dried before being washed with several portions of petroleum ether. The title compound was isolated as a pale yellow fine powder (4.13 g, 5.5 mmol, 89 %). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 7.43 (m, 16H, CH₄arom), 7.14 (m, 4H, CH₄arom), 7.08 (m, 2H, CH₄arom), 6.74 (s, 1H, OCH₃), 6.61 (d, 1H, CH₃), 5.08 (br. s, 2H, OCH₂O), 3.33 (br. s, 6H, NCH₃), 3.29 (s, 3H, OCH₃), 1.45 (s, 9H, C(CH₃)₃), 1.20 (s, 9H, C(CH₃)₃) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃, 25 °C): δ = 152.94, 146.01, 144.30, 135.89, 135.18, 131.75, 131.31, 129.17, 128.71, 128.05, 126.47, 125.94, 101.36, 57.19, 35.80, 34.56, 33.16, 31.46, 31.23 ppm. ESI-MS (acetonitrile): m/z = 759.4092 [M+H]+, calc. 759.4198.

2,2’-((3,5-di-tert-butyl-2-(methoxymethoxy)phenyl)(methoxymethyl-ene)bis(1-methyl-4,5-diphenyl-1H-imidazol-2-yl)) (LS4): NaH (0.32 g, 8.0 mmol, 60 weight% dispersion in mineral oil) was suspended in THF (100 mL) and compound LS3 (3.00 g, 4.0 mmol) was added in portions at room temperature, causing a colour change to yellow. The reaction was allowed to proceed for 2 h at room temperature, during which time a slow release of gas was observed and a white precipitate accumulated. After this time, iodomethane (0.50 mL, 9.80 mmol) was added dropwise, and the reaction allowed to stir overnight at room temperature. The reaction was quenched with saturated aqueous NH₄Cl solution (50 mL), and the organics extracted with EtOAc (2 x 100 mL). The organic layer was washed once with distilled water (50 mL) before being dried over MgSO₄, and concentrated to yield a crude yellow solid. Vigorous stirring of the crude material in petroleum ether afforded a pale yellow powder, which was filtered and air-dried to afford LS4 as an off-white powder in 82% yield (2.49 g, 3.3 mmol). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 7.45 (m, 11H, CH₄arom), 7.34 (m, 4H, CH₄arom), 7.13 (m, 4H, CH₄arom), 7.06 (m, 2H, CH₄arom), 5.16 (br. s, 2H, OCH₂), 3.69 (br. s, 3H, OCH₃), 3.34 (br. s, 6H, NCH₃), 3.18 (s, 3H, MOM-CH₃), 1.47 (s, 9H, C(CH₃)₃), 1.28 (s, 9H, C(CH₃)₃) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃, 25 °C): δ = 153.74, 144.35, 143.87, 135.37, 135.16, 131.83, 131.22, 130.81, 129.09, 128.62, 128.03, 126.42, 125.85, 125.44, 101.36, 56.98, 35.77, 34.75, 33.01, 31.61, 30.87 ppm. ESI-MS (acetonitrile): m/z = 759.4092 [M+H]+, calc. 759.4274.

IR (ATR): ν = 3061 (w), 2947 (w), 2824 (w), 1601 (w), 1462 (w), 1444 (m), 1345 (w), 1392 (w), 1380 (w), 1362 (w), 1320 (w), 1303 (w), 1270 (w), 1231 (w), 1202 (w), 1185 (s), 1140 (m), 1079 (s), 1072 (s), 1057 (m), 1026 (m), 1002 (w), 959 (m), 951 (s), 931 (s), 901 (s) 85 (m), 383 (w), 820 (w), 773 (s), 745 (w), 727 (m), 695 (s), 686 (m), 649 (w), 625 (w), 617 (w), 593 (w), 528 (w), 502 (w), 474 (w), 461 (w), 427 (w) cm⁻¹.
**H-Im**₃²NNO₃ᵗBu: Compound LS₄ (6.45 g, 8.5 mmol) was dissolved in an acidified MeOH solution (1:8 HCl (15 %)/MeOH, 125 mL) and allowed to stir for 1 h under reflux, monitoring the reaction closely by NMR. The resulting mixture was rendered alkaline (pH ~8) with 1 M NaOH solution, resulting in the precipitation of a dark red solid. The organics were extracted into EtOAc (2 x 250 mL) and the solvent removed under reduced pressure, affording a dark red foamy solid. The solid was dissolved in petroleum ether (400 mL) and the dark red solution was vigorously stirred overnight, which lead to the precipitation of an off-white powder. The solid was collected by Büchner filtration and was washed with portions of cold petroleum ether. The title compound was obtained as an off-white solid (4.30 g, 6.0 mmol, 71 %). 

**¹H NMR (400 MHz, CDCl₃, 25 °C):** δ = 9.31 (br. s, 1H, -OH), 7.49 (m, 10H, H_arom), 7.12 (m, 2H, H_arom), 7.32 (d, 1H, H_arom), 7.37 (m, 4H, H_arom), 3.65 (s, 3H, OCH₃), 3.27 (s, 6H, NCH₃), 1.44 (s, 9H, C(CH₃)₃), 1.24 (s, 9H, C(CH₃)₃) ppm.

**¹³C{¹H} NMR (101 MHz, CDCl₃, 25 °C):** δ = 153.22, 145.28, 139.82, 138.36, 135.60, 134.79, 131.30, 131.26, 129.17, 128.87, 126.67, 126.25, 124.29, 124.23, 122.32, 83.43, 54.64, 35.51, 34.29, 32.97, 31.70, 29.68 ppm.

**ESI-MS (acetonitrile):** m/z = 715.3909 [M+H]⁺, calc. 715.4012. **IR (ATR):** ν = 3388 (w), 3058 (w), 2953 (w), 2868 (w), 1738 (w), 1262 (m), 1296 (w), 1216 (m), 1156 (m), 1132 (m), 1056 (m), 1026 (m), 1000 (w), 971 (m), 932 (m), 916 (w), 886 (m), 834 (w), 818 (w), 781 (m), 773 (s), 742 (m), 718 (m), 694 (s), 649 (m), 609 (w), 589 (w), 524 (w), 460 (w) cm⁻¹.

**K-Im**₃²NNO₃ᵗBu: Ligand **H-Im**₃²NNO₃ᵗBu (1.77 g, 2.48 mmol) was dissolved in THF (40 mL) and stirred vigorously during the addition of KH (0.12 g, 2.99 mmol). Instant bubble formation was observed that indicated H₂(g) formation. Over the course of 3 h the solution became dark yellow in colour. The mixture was subsequently filtered to remove excess KH and THF was removed under reduced pressure, affording a crude yellow solid. The solid was then washed twice by vigorously stirring in hexane (150 mL). The hexane washings were discarded, and the resulting white solid dried under vacuum, affording the ligand salt as a free-flowing white powder in 92% yield (1.79 g, 2.38 mmol). Note: purity of the sample determined by NMR and residual solvent THF and hexane content was quantified by ¹H NMR. The molecular weight of the ligand salt adjusted appropriately for use in subsequent complexation reactions. **¹H NMR (400 MHz, CD₃CN, 25 °C):** δ = 7.50 (m, 6H, H_arom), 7.43 (d, 4H, J = 8 Hz, H_arom), 7.36 (d, 4H, J = 8 Hz, H_arom), 7.16 (t, 4H, J = 8 Hz, H_arom), 7.09 (t, 2H, J = 8 Hz, H_arom), 7.00 (br. s, 1H, H_arom), 6.63 (br. s, 1H, H_arom), 3.64 (br. s, 3H, OCH₃), 3.29 (br. s, 6H, NCH₃), 1.35 (s, 9H, C(CH₃)₃), 1.13 (s, 9H, C(CH₃)₃) ppm. **IR (ATR):** ν = 3059 (w), 3029 (w), 2947 (m), 2904 (w), 2865 (w), 1952 (w), 1887 (w), 1809 (w), 1602 (m), 1504 (m), 1462 (m), 1431 (s), 1379 (m), 1359 (m), 1279 (w), 1257 (w), 1235 (w), 1201 (w), 1138 (w), 1071 (m), 1048 (m), 1026 (m), 1000 (w), 968 (m), 928 (m), 914 (m), 884 (w), 831 (w), 795 (w), 773 (s), 743 (w), 748 (m), 728 (m), 697 (s), 649 (w), 629 (w), 613 (w), 582 (w), 525 (w), 471 (w) cm⁻¹.
1.5 Complex Synthesis

[Fe(ImPh2NNO\textsubscript{tBu})(Cl)] (1): A solution of FeCl\textsubscript{2}•1.5THF (0.046 g, 0.196 mmol) in CH\textsubscript{3}CN (4 mL) was added dropwise to a suspension of K-Im\textsubscript{Ph2NNO\textsubscript{tBu}} (0.152 g, 0.193 mmol) in CH\textsubscript{3}CN (12 mL). The mixture was allowed to stir for 2 h, during which time the ligand salt visibly dissolved and the mixture developed a slight brown colour. A fine white precipitate also formed over the course of the reaction. The mixture was filtered and the filtrate concentrated under vacuum. The residual pale brown solid was washed with hexane (3 x 8 mL) and dried under vacuum. The title complex was obtained as cream-coloured powder in 97% yield (0.151 g, 0.187 mmol). Pale brown needles suitable for X-ray analysis were obtained by slow vapour diffusion of hexane into a THF solution of the complex at room temperature. \textsuperscript{1}H NMR (400 MHz, CD\textsubscript{3}CN, 25 °C): δ = 57.73, 54.68, 51.30, 49.14, 42.94, 36.53, 33.68, 23.64, 9.84, 7.59, 7.17, 6.85, 5.41, 4.65, 4.22, 4.12, 3.65, 2.29 ppm. Solution state magnetic susceptibility (Evans method, 1% TMS in CD\textsubscript{3}CN): μ\textsubscript{eff} = 4.50 μB. UV-vis (CH\textsubscript{3}CN, ε [mol\textsuperscript{-1}dm\textsuperscript{3}cm\textsuperscript{-1}]): λ\textsubscript{max} = 375 (547), 500 (54) nm. IR (ATR): ν = 3057 (w), 2956 (w), 2905 (w), 2867 (w), 1656 (w), 1603 (w), 1505 (w), 1475 (m), 1467 (m), 1438 (m), 1412 (w), 1391 (w), 1360 (w), 1303 (m), 1261 (m), 1235 (w), 1201 (w), 1179 (w), 1157 (w), 1132 (w), 1074 (m), 1055 (m), 1024 (m), 1004 (m), 978 (w), 928 (w), 915 (w), 899 (w), 887 (w), 878 (s), 772 (m), 748 (m), 732 (m), 695 (s), 6498 (w), 610 (w), 587 (w), 542 (m), 513 (w), 475 (w) cm\textsuperscript{-1}. E.A. (Formula: C\textsubscript{48}H\textsubscript{49}ClN\textsubscript{4}O\textsubscript{2}Fe, M\textsubscript{w}: 805.24 g mol\textsuperscript{-1}): calc. C 71.60, H 6.13, N 6.96; found C 71.68, H 6.17, N 6.55.

[Zn(Im\textsubscript{Ph2NNO\textsubscript{tBu}})(Cl)] (2): A solution of ZnCl\textsubscript{2} (0.028 mg, 0.208 mmol) in CH\textsubscript{3}CN (3 mL) was added dropwise to a suspension of K-Im\textsubscript{Ph2NNO\textsubscript{tBu}} (0.172 g, 0.218 mmol) in CH\textsubscript{3}CN (12 mL). The mixture was stirred 2 h, during which time the ligand salt visibly dissolved and pale brown solution formed. A fine white precipitate also developed over the course of the reaction. The mixture was filtered and the solution concentrated under vacuum. As the solution cooled, small colourless crystals were seen to develop. The residual solid was washed with hexane (3 x 8 mL) and dried under vacuum. The title complex was obtained as a white solid in 94% yield (0.160 g, 0.196 mmol). Colourless needles suitable for X-ray diffraction were obtained by slow diffusion of hexane into a THF solution of the complex at room temperature. \textsuperscript{1}H NMR (400 MHz, CD\textsubscript{3}CN, 25 °C): δ = 7.73 (d, 1H, J = 4 Hz, H\textsubscript{phen1}), 7.50 (m, 6H, CH\textsubscript{arom}), 7.40 (m, 4H, CH\textsubscript{arom}), 7.33 (m, 4H, CH\textsubscript{arom}), 7.27 (m, 6H, CH\textsubscript{arom}), 7.22 (d, 1H, J = 4 Hz, H\textsubscript{phen2}), 3.51 (s, 6H, NC\textsubscript{H}3), 3.45 (s, 3H, OC\textsubscript{H}3), 1.28 (s, 18H, C(C\textsubscript{H}3)\textsubscript{3}) ppm. \textsuperscript{13}C{\textsuperscript{1}H} NMR (101 MHz, CD\textsubscript{3}CN, 25 °C): δ = 162.08, 148.05, 140.60, 136.12, 134.07, 133.09, 132.39, 132.08, 131.99, 130.54, 130.14, 130.01, 129.77, 129.48, 129.15, 129.10, 128.83, 127.38, 127.28, 125.35, 121.44, 119.69, 81.49, 53.86, 36.06, 34.72, 34.45, 33.55, 32.07, 31.77, 30.07, 29.80 ppm. IR (ATR): ν = 3057 (w), 2952 (m), 2866 (w), 1662 (w), 1603 (w), 1505 (w), 1476 (m), 1468 (m), 1440 (s), 1411 (w), 1393 (w), 1360 (w), 1312 (w), 1262 (m), 1234 (w), 1201 (w), 1157 (w), 1133 (w), 1075 (m), 1056 (m), 1025 (m), 1005 (m), 979 (w), 928 (w), 915 (w), 899 (w), 887 (w), 838 (m), 790 (s), 773 (m), 746 (w), 734 (w), 700 (s), 6498 (w), 612 (w), 539 (w), 525 (w) cm\textsuperscript{-1}. E.A. (Formula: C\textsubscript{46}H\textsubscript{47}ClN\textsubscript{4}O\textsubscript{2}Zn, M\textsubscript{w}: 814.78 g mol\textsuperscript{-1}): calc. C 70.76, H 6.06, N 6.88; found C 70.67, H 6.38, N 6.76.
[Zn(Im^tBuNNO^tBu)(SPh)] (4): A suspension of NaSPh (10.4 mg, 57.0 µmol) in CH$_2$Cl$_2$ (4 mL) was added dropwise to a stirring solution of 2 (44.5 mg, 54.6 µmol) in CH$_2$Cl$_2$ (12 mL). The mixture was allowed to stir for 2.5 h, during which time the mixture turned pale yellow in colour and became slightly cloudy. The mixture was filtered and the filtrate concentrated under vacuum. The residual solid was washed by stirring vigorously in hexane (2 x 8 mL) and dried under vacuum, affording the title complex as a free-flowing white powder in 95% yield (46 mg, 52.1 µmol). $^1$H NMR (400 MHz, CD$_3$CN, 25 ºC): $\delta$ = 7.75 (d, 1H, $J = 4$ Hz, $H_{phen}^1$), 7.48 (m, 6H, $CH_{arom}$), 7.31 (m, 8H, $CH_{arom}$), 7.22 (d, 1H, $J = 4$ Hz, $H_{phen}^2$), 7.13 (m, 6H, $CH_{arom}$), 6.90 (m, 2H, $H_{SPh}^3$), 6.71 (m, 3H, $H_{SPh}^4,5$), 3.51 (s, 6H, NCH$_3$), 3.44 (s, 3H, OCH$_3$), 1.29 (s, 9H, ortho-$C(CH_3)_3$), 1.23 (s, 9H, para-$C(CH_3)_3$) ppm. $^{13}$C{$^1$H} NMR (101 MHz, CD$_3$CN, 25 ºC): $\delta$ = 148.16, 142.61, 140.51, 136.43, 134.03, 133.18, 132.88, 132.39, 132.20, 130.46, 129.98, 129.68, 129.35, 128.98, 128.47, 128.30, 125.22, 122.58, 122.17, 119.66, 53.82, 35.97, 34.71, 34.30, 32.09, 29.90 ppm. IR (ATR): $\nu$ = 3054 (w), 2950 (w), 2904 (w), 2866 (w), 1603 (w), 1579 (w), 1505 (w), 1475 (m), 1466 (m), 1436 (s), 1410 (w), 1392 (w), 1360 (m), 1324 (w), 1234 (w), 1201 (w), 1183 (w), 1157 (w), 1133 (w), 1074 (s), 1055 (m), 1025 (m), 1004 (m), 978 (w), 928 (m), 915 (m), 896 (w), 886 (m), 836 (m), 789 (s), 772 (m), 735 (s), 694 (s), 646 (w), 612 (w), 585 (w), 538 (m), 524 (w), 514 (w), 476 (w) cm$^{-1}$. E.A. (Formula: C$_{54}$H$_{54}$N$_4$O$_2$Zn, $M_w$: 888.49 g mol$^{-1}$): calc. C 73.00, H 6.13, N 6.31; found C 73.14, H 6.42, N 5.93.
2 Ligand Characterisation

2.1 Spectral Data LS1

Figure S1: $^1$H NMR (400 Hz) spectrum of LS1 in CDCl$_3$ at 298 K.

Figure S2: $^{13}$C NMR (101 Hz) spectrum of LS1 in CDCl$_3$ at 298 K.

Figure S3: IR (ATR) spectrum of LS1.
2.2 Spectral Data LS2

Figure S4: $^1$H NMR (400 Hz) spectrum of LS2 in CDCl$_3$ at 298 K.

Figure S5: $^{13}$C NMR (101 Hz) spectrum of LS2 in CDCl$_3$ at 298 K.

Figure S6: IR (ATR) spectrum of LS2.
2.3 Spectral Data for LS3

Figure S7: $^1$H NMR (400 Hz) spectrum of LS3 in CDCl$_3$ at 298 K.

Figure S8: $^{13}$C NMR (101 Hz) spectrum of LS3 in CDCl$_3$ at 298 K.

Figure S9: IR (ATR) spectrum of LS3.
2.4 Spectral Data LS4

Figure S10: $^1$H NMR (400 Hz) spectrum of LS4 in CDCl$_3$ at 298 K.

Figure S11: $^{13}$C NMR (101 Hz) spectrum of LS4 in CDCl$_3$ at 298 K.

Figure S12: IR (ATR) spectrum of LS4.
2.5 Spectral Data H-Im$^\text{Ph}_2$NNO$^{tBu}$

Figure S13: $^1$H NMR (400 Hz) spectrum of H-Im$^\text{Ph}_2$NNO$^{tBu}$ in CDCl$_3$ at 298 K.

Figure S14: $^{13}$C NMR (101 Hz) spectrum of H-Im$^\text{Ph}_2$NNO$^{tBu}$ in CDCl$_3$ at 298 K.
**Figure S15**: ASAP-HMQC NMR spectrum of H-Im$^{\text{Ph}}$NNO$^{\text{tBu}}$ in CDCl$_3$ at 298 K.

**Figure S16**: gHMBC NMR spectrum of H-Im$^{\text{Ph}}$NNO$^{\text{tBu}}$ in CDCl$_3$ at 298 K.
Figure S17: IR (ATR) spectrum of H-Im$^{DiPh}$NNO$^{tBu}$.

Figure S18: ESI-MS spectrum H-Im$^{Ph2}$NNO$^{tBu}$, recorded in acetonitrile using positive ion detection mode.
2.6 Spectral Data $\text{K-Im}^{\text{Ph}_2\text{NNO}^{\text{tBu}}}$

**Figure S19**: $^1$H NMR (400 Hz) spectrum of $\text{K-Im}^{\text{Ph}_2\text{NNO}^{\text{tBu}}}$ in CD$_3$CN at 298 K.

**Figure S20**: $^1$H NMR (400 Hz) spectrum of $\text{K-Im}^{\text{Ph}_2\text{NNO}^{\text{tBu}}}$ in CD$_3$CN at 243 K. Low solubility of the ligand at low temperature causes line-broadening, and small impurities become more apparent.

**Figure S21**: IR (ATR) spectrum of $\text{K-Im}^{\text{Ph}_2\text{NNO}^{\text{tBu}}}$. 

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3 Complex Characterisation

3.1 Spectral Data [Fe(Im$^{2}$NNO$^{tBu}$)(Cl)] (1)

**Figure S22:** Zero-field Mössbauer spectrum of 1 recorded at 80 K. Black circles depict the experimental data points; red trace depicts the best data fit with $\delta = 0.94$ mm s$^{-1}$, $|\Delta E_Q| = 2.58$ mm s$^{-1}$.

**Figure S23:** IR (ATR) spectrum of 1.

**Figure S24:** $^1$H NMR (400 Hz) spectrum of 1 in CD$_3$CN at 298 K.
**Figure S25:** $^1$H NMR (400 Hz) spectrum of 1 in CD$_2$Cl$_2$ at 298 K.

**Figure S26:** $^1$H NMR (400 Hz) spectrum of 1 in THF-d$_8$ at 298 K.

**Figure S27:** $^1$H NMR (400 Hz) spectrum of 1 in pyridine-d$_5$ at 298 K.
Figure S28: Stacked VT $^1$H NMR (400 Hz) spectra of 1 in CD$_3$CN.

Figure S29: Curie plots of $^1$H NMR chemical shift as a function of reciprocal temperature (K$^{-1}$) of 1 in CD$_3$CN.
Figure S30: Stacked VT $^1$H NMR (400 Hz) spectra of 1 in CD$_2$Cl$_2$.

Figure S31: Curie plots of $^1$H NMR chemical shift as a function of reciprocal temperature (K$^{-1}$) of 1 in CD$_2$Cl$_2$. 
Figure S32: Stacked VT $^{1}H$ NMR (400 Hz) spectra of 1 in THF-$d_8$.

Figure S33: Curie plots of $^{1}H$ NMR chemical shift as a function of reciprocal temperature (K$^{-1}$) of 1 in THF-$d_8$. 
Figure S34: Left: UV-vis spectrum of 1 in CH$_3$CN at 298 K. Right: VT UV-vis of 1 in CH$_3$CN.

Figure S35: Left: UV-vis spectrum of 1 in CH$_2$Cl$_2$ at 298 K.

Figure S36: UV-vis spectrum of 1 in THF at 298 K.
Figure S37: UV-vis spectrum of \( \text{Fe(DiPhImNNO}_{\text{tBu}})(\text{Cl}) \) in pyridine at 298 K.
3.2 Spectral Data [Zn(Im$^{Ph2NNOtBu}$)(Cl)] (2)

Figure S38: IR (ATR) spectrum of 2.

Figure S39: $^1$H NMR (400 Hz) spectrum of 2 in CD$_3$CN at 298 K. Red asterisks denote aromatic protons from the supporting ligand framework.

Figure S40: $^1$H NMR (400 Hz) spectrum of 2 in CD$_2$Cl$_2$ at 298 K. Red asterisks denote aromatic protons from the supporting ligand framework.
Figure S41: $^1$H NMR (400 Hz) spectrum of 2 in THF-$d_8$ at 298 K.

Figure S42: $^1$H NMR (400 Hz) spectrum of 2 in pyridine-$d_5$ at 298 K.

Figure S43: $^{13}$C NMR (101 Hz) spectrum of 2 in CD$_3$CN at 298 K.
Figure S44: $^1$H-$^1$H COSY NMR spectrum of 2 in CD$_3$CN at 298 K. Insert graph shows more detail of aromatic region.

Figure S45: Stacked 1D NOE $^1$H NMR spectra of 2 in CD$_3$CN at 298 K. The selectively excited NMR resonances are highlighted with a red asterisk and are in the negative phase (not depicted). The through-space correlation signals are depicted in the positive phase and are schematically depicted with purple arrows within the insert diagram of 2.
Figure S46a: Stacked VT $^1$H NMR (400 Hz) spectra of 2 in CD$_3$CN.

Figure S46b: Stacked VT $^1$H NMR (400 Hz) spectra of 2 in CD$_2$Cl$_2$. 
Figure S47: Stacked VT $^1$H NMR (400 Hz) spectra of 2 in THF-$d_8$. 
3.3  Spectral Data [Zn(ImPh₂NNO³Bu)(SPh)] (4)

![IR spectrum of 4](image1)

**Figure S48:** IR (ATR) spectrum of 4.

![NMR spectrum of 4 in CD₃CN](image2)

**Figure S49:** ¹H NMR (400 Hz) spectrum of 4 in CD₃CN at 298 K. Red asterisks denote aromatic protons from the supporting ligand framework.

![NMR spectrum of 4 in CD₂Cl₂](image3)

**Figure S50:** ¹H NMR (400 Hz) spectrum of 4 in CD₂Cl₂ at 298 K. Red asterisks denote aromatic protons from the supporting ligand framework.
**Figure S51**: $^1$H NMR (400 Hz) spectrum of 4 in pyridine-$d_5$ at 298 K.

**Figure S52**: $^{13}$C NMR (101 Hz) spectrum of 4 in CD$_3$CN at 298 K.
Figure S53: $^1$H-$^1$H COSY NMR spectrum (aromatic region) of 4 in CD$_3$CN at 298 K.

Figure S54: $^1$H-$^1$H COSY NMR spectrum (aliphatic region) of 4 in CD$_3$CN at 298 K.
Figure S55: Stacked 1D NOE $^1$H NMR spectra of 4 in CD$_3$CN at 298 K. The selectively excited NMR signals are highlighted with a red asterisk and are in the negative phase (not depicted).

Figure S56: Schematic representation of the through-space correlations in 4 observed by 1D NOE experiments.
Figure S57: Stacked VT $^1$H NMR (400 Hz) spectra of 4 in CD$_3$CN.

Figure S58: Stacked VT $^1$H NMR (400 Hz) spectra of 4 in CD$_2$Cl$_2$. 
3.4 Additional Data for $1^{\text{OTf}}$ and $2^{\text{OTf}}$

General scheme for the synthesis of $1^{\text{OTf}}$ and $2^{\text{OTf}}$:

NMR data for $2^{\text{OTf}}$.

**Figure S59:** $^1\text{H}$ NMR (400 MHz) spectrum for crude $2^{\text{OTf}}$, recorded at 298 K in CD$_3$CN.

**Figure S60:** $^{19}\text{F}$ NMR (376 MHz) spectrum for crude $2^{\text{OTf}}$, recorded at 298 K in CD$_3$CN.
Figure S61: $^{13}$C NMR (101 MHz) spectrum for crude $2^{\text{OTf}}$, recorded at 298 K in CD$_3$CN.

Figure S62: $^1$H-$^1$H COSY NMR spectrum for $2^{\text{OTf}}$, recorded at 298 K in CD$_3$CN.
NMR data for $1^{\text{OTf}}$.

Figure S63: $^1$H NMR spectrum for $1^{\text{OTf}}$, recorded at 298 K in CD$_3$CN.
4 X-Ray Crystal Structure Determinations

4.1 X-ray Crystal Structure Determination of [K₂(Im²Ph₂NNOtBu)₂(Et₂O)₂]

C₁₀₄H₁₁₈K₂N₈O₆ + disordered solvent, Fw = 1654.26\(^{[*]}\), colourless needle, 0.35 × 0.11 × 0.10 mm\(^{3}\), triclinic, P\(\overline{T}\) (no. 2), a = 14.0405(8), b = 14.4688(12), c = 15.4666(11) Å, \(\alpha = 67.071(2)\), \(\beta = 76.924(2)\), \(\gamma = 61.093(2)\) °, \(V = 2530.4(3)\) Å\(^{3}\), \(Z = 1\), \(D_x = 1.086\) g/cm\(^{3}\)\(^{[*]}\), colourless needle, 0.35 \(\times\) 0.11 \(\times\) 0.10 mm\(^{3}\). The diffraction experiment was performed on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (\(\lambda = 0.71073\) Å) at a temperature of 150(2) K up to a resolution of (\(\text{sin} \theta / \lambda\))\(_{\text{max}}\) = 0.61 Å\(^{-1}\). The Eval15 software\(^{9}\) was used for the intensity integration. A large anisotropic mosaicity\(^{10}\) about \(hkl=(0,0,1)\) was used for the prediction of the reflection profiles. A multi-scan absorption correction and scaling was performed with SADABS\(^{11}\) (correction range 0.60-0.75). A total of 32107 reflections was measured, 9419 reflections were unique (\(R_{\text{int}} = 0.079\)), 4913 reflections were observed \([I>2\sigma(I)]\).

The structure was solved with Patterson superposition methods using SHELXT.\(^{12}\) Structure refinement was performed with SHELXL-2018\(^{13}\) on \(F^2\) of all reflections. The crystal structure contains large voids (339 Å\(^{3}\)/unit cell) filled with severely disordered solvent molecules. Their contribution to the structure factors was secured by the SQUEEZE algorithm\(^{14}\) resulting in 74 electrons / unit cell. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined with a riding model. One t-butyl group was refined with a disorder model. Slight disorder in the phenyl groups was not resolved. 577 Parameters were refined with 144 restraints (distances, angles and displacement parameters in the t-butyl groups). \(R_1/wR_2 [I > 2\sigma(I)]\): 0.0635 / 0.1427. \(R_1/wR_2 [\text{all refl.}]\): 0.1379 / 0.1719. \(S = 0.981\). Residual electron density between -0.27 and 0.34 e/Å\(^{3}\). Geometry calculations and checking for higher symmetry was performed with the PLATON program.\(^{15}\) \([*]\) Derived values do not contain the contribution of the disordered solvent.

![Figure S64](image.png)

**Figure S64.** Displacement ellipsoid plot of [K₂(Im²Ph₂NNOtBu)₂(Et₂O)₂] (30% probability level). Only the major form of the disordered t-butyl group is drawn. Hydrogen atoms and severely disordered solvent molecules are omitted for clarity. Symmetry code \(i: 1-x, 1-y, 1-z\).

**Table S1:** Selected bond lengths and bond angles for [K₂(Im²Ph₂NNOtBu)₂(Et₂O)₂]. Symmetry code \(i: 1-x, 1-y, 1-z\).

| Bond          | Length (Å) | Bond Angle (degrees) |
|---------------|------------|----------------------|
| K₁–O₁         | 2.675(2)   | O₁–K₁–O₂ 63.85(6)    |
| K₁–O₂         | 2.778(2)   | O₁–K₁–O₃ 126.24(7)   |
| K₁–O₃         | 2.768(2)   | O₁–K₁–O₁\(^i\) 100.94(6) |
| K₁–O₁\(^i\)  | 2.592(2)   | O₁–K₁–N₃ 112.26(7)   |
| K₁–N₃\(^i\)  | 2.845(3)   | O₂–K₁–O₃ 87.16(7)    |
4.2 X-ray Crystal Structure Determination of [Fe(Im(Ph2NNOtBu))(Cl)] (1)

C36H4sClFeN4O2 + disordered solvent, Fw = 805.21[^*], brown needle, 0.42 × 0.12 × 0.04 mm[^3], monoclinic, I2/a (no. 15), a = 26.8538(12), b = 10.0334(4), c = 35.8465(13) Å, β = 93.790(3) °, V = 9637.2(7) Å[^3], Z = 8, Dx = 1.110 g/cm[^3], µ = 0.41 mm[^1]. The diffraction experiment was performed on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of (sin θ/λ)[max] = 0.65 Å[^-1]. The Eval15 software[^9] was used for the intensity integration. A numerical absorption correction and scaling was performed with SADABS[^11] (correction range 0.81-1.00). A total of 61423 reflections was measured, 11054 reflections were unique (Rint = 0.086), 6676 reflections were observed [I>2σ(I)]. Initial coordinates were taken from the isostructural Zn complex (2). Structure refinement was performed with SHELXL-2018[^13] on F[^2] of all reflections. The crystal structure contains large voids (1661 Å[^3]/unit cell) filled with severely disordered solvent molecules. Their contribution to the structure factors was secured by the SQUEEZE algorithm[^14] resulting in 383 electrons / unit cell. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined with a riding model. One t-butyl group was refined with a disorder model. 527 Parameters were refined with 48 restraints (distances, angles and displacement parameters in the disordered t-butyl group). R1/wR2 [I > 2σ(I)]: 0.0596 / 0.1408. R1/wR2 [all refl.]: 0.1101 / 0.1598. S = 1.040. Residual electron density between -0.42 and 0.74 e/Å[^3]. Geometry calculations and checking for higher symmetry was performed with the PLATON program[^15] *[^*] Derived values do not contain the contribution of the disordered solvent.

![Figure S65](image-url) Displacement ellipsoid plot of [Fe(Im(Ph2NNOtBu))(Cl)] (1) (50% probability level). Only the major form of the disordered t-butyl group is drawn. Hydrogen atoms and severely disordered solvent molecules are omitted for clarity.

| Bond          | Length (Å) | Bond Angle   | Degrees (°) |
|---------------|------------|--------------|-------------|
| Fe1–N1        | 2.131(2)   | N1–Fe1–O1    | 95.10(8)    |
| Fe1–N3        | 2.089(2)   | N3–Fe1–O1    | 98.92(9)    |
| Fe1–O1        | 1.8915(19) | N1–Fe1–N3    | 84.05(9)    |
| Fe1–Cl1       | 2.2187(9)  | O1–Fe1–Cl1   | 115.82(6)   |
4.3 X-ray Crystal Structure Determination of [Zn(ImPh2NNOtBu)(Cl)] (2)

C₄₈H₄₁ClN₄O₂Zn + disordered solvent, Fw = 814.73[^1], colourless needle, 0.68 × 0.14 × 0.06 mm³, monoclinic, I2/a (no. 15), a = 26.8000(7), b = 10.00770(18), c = 35.6762(8) Å, β = 93.730(3) °, V = 9548.3(4) Å³, Z = 8, Dₓ = 1.134 g/cm³[^1], µ = 0.61 mm⁻¹[^1]. The diffraction experiment was performed on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of (sin θ/λ)max = 0.65 Å⁻¹. The Eval15 software[^9] was used for the intensity integration. A multi-scan absorption correction and scaling was performed with SADABS[^11] (correction range 0.60-0.75). A total of 88827 reflections was measured, 10955 reflections were unique (Rint = 0.057), 8529 reflections were observed [I>2σ(I)]. The structure was solved with Patterson superposition methods using SHELXT. Structure refinement was performed with SHELXL-2018[^13] on F² of all reflections. The crystal structure contains large voids (1643 Å³/unit cell) filled with severely disordered solvent molecules. Their contribution to the structure factors was secured by the SQUEEZE algorithm[^14] resulting in 397 electrons / unit cell. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined with a riding model. One t-butyl group was refined with a disorder model. 527 Parameters were refined with 48 restraints (distances, angles and displacement parameters in the disordered t-butyl group). R1/wR2 [I>2σ(I)]: 0.0365 / 0.0917. R1/wR2 [all refl.]: 0.0527 / 0.0976. S = 1.051. Residual electron density between -0.39 and 0.38 e/Å³. Geometry calculations and checking for higher symmetry was performed with the PLATON program[^15].[^*] Derived values do not contain the contribution of the disordered solvent.

![Displacement ellipsoid plot of [Zn(ImPh2NNOtBu)(Cl)] (2) (50% probability level). Only the major form of the disordered t-butyl group is drawn. Hydrogen atoms and severely disordered solvent molecules are omitted for clarity.](image)

**Table S3:** Selected bond lengths and bond angles for [Zn(ImPh₂NNOᵗBu)(Cl)] (2)

| Bond       | Length (Å) | Bond Angle | Degrees (°) |
|------------|------------|------------|-------------|
| Zn1–N1     | 2.0754(14) | N1–Zn1–O1  | 95.91(5)    |
| Zn1–N3     | 2.0248(14) | N3–Zn1–O1  | 100.97(5)   |
| Zn1–O1     | 1.9265(12) | N1–Zn1–N3  | 88.23(5)    |
| Zn1–Cl1    | 2.1701(5)  | O1–Zn1–Cl1 | 111.30(4)   |
4.4 X-ray Crystal Structure Determination of [Fe(Im\textsuperscript{Ph\textsubscript{2}}NNO\textsubscript{tBu})\textsubscript{2}] (3)

C\textsubscript{96}H\textsubscript{98}FeN\textsubscript{8}O\textsubscript{4}·4C\textsubscript{5}H\textsubscript{5}N + disordered solvent, F\textsubscript{w} = 1800.07\textsuperscript{[x]}, yellow block, 0.60 \times 0.33 \times 0.21 \text{mm\textsuperscript{3}}, triclinic, P\textsubscript{T} (no. 2), a = 14.8821(3), b = 17.9631(5), c = 22.1346(4) Å, α = 110.681(1), β = 91.354(1), γ = 107.963(1) °, V = 5207.33(19) Å\textsuperscript{3}, Z = 2, D\textsubscript{x} = 1.148 g/cm\textsuperscript{3}, µ = 0.20 mm\textsuperscript{–1}\textsuperscript{[x]}. The diffraction experiment was performed on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of (sin θ/λ)\textsubscript{max} = 0.65 Å\textsuperscript{–1}. The Eval15 software\textsuperscript{9} was used for the intensity integration. A multi-scan absorption correction and scaling was performed with SADABS\textsuperscript{11} (correction range 0.69 - 0.75). A total of 144002 reflections was measured, 23928 reflections were unique (R\textsubscript{int} = 0.031), 19632 reflections were observed [I>2σ(I)].

The structure was solved with Patterson superposition methods using SHELXT.\textsuperscript{12} Structure refinement was performed with SHELXL-2018\textsuperscript{13} on F\textsuperscript{2} of all reflections. In addition to the pyridine solvent molecules, the crystal structure contains large voids (608 Å\textsuperscript{3}/unit cell) filled with severely disordered solvent molecules. Their contribution to the structure factors was secured by the SQUEEZE algorithm\textsuperscript{14} resulting in 145 electrons / unit cell. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined with a riding model. One t-butyl group was refined with a disorder model. The methoxy groups were refined with full occupancy but a minor substitutional disorder cannot be ruled out. 1240 Parameters were refined with 404 restraints (distances, angles and displacement parameters in the t-butyl groups and pyridine molecules; molecular flatness in the pyridine molecules). R1/wR2 [I > 2σ(I)]: 0.0588 / 0.1803. R1/wR2 [all refl.]: 0.0701 / 0.1902. S = 1.043. Residual electron density between -0.69 and 0.97 e/Å\textsuperscript{3}.

Geometry calculations and checking for higher symmetry was performed with the PLATON program.\textsuperscript{15} [*] Derived values do not contain the contribution of the disordered solvent.

Figure S67. Displacement ellipsoid plot of [Fe(Im\textsuperscript{Ph\textsubscript{2}}NNO\textsubscript{tBu})\textsubscript{2}] (3) (30% probability level). Only the major form of the disordered t-butyl group is drawn. Hydrogen atoms, pyridine molecules and severely disordered solvent molecules are omitted for clarity.

Table S4: Selected bond lengths and bond angles for [Fe(Im\textsuperscript{Ph\textsubscript{2}}NNO\textsubscript{tBu})\textsubscript{2}] (3)

| Bond       | Length (Å) | Bond Angle | Degrees (°) |
|------------|------------|------------|-------------|
| Fe1–N11    | 2.1518(16) | N11–Fe1–O11 | 108.80(6)   |
| Fe1–N12    | 2.1395(16) | N12–Fe1–O12 | 105.50(6)   |
| Fe1–O11    | 1.9403(15) | N11–Fe1–N12 | 99.32(6)    |
| Fe1–O12    | 1.9340(15) | O11–Fe1–O12 | 131.43(7)   |
4.5 X-ray Crystal Structure Determination of [Zn(ImPh2NNOtBu)(SPh)] (4)

C$_{54}$H$_{74}$N$_4$O$_2$S•Zn•2C$_4$H$_8$O, Fw = 1032.65, colourless needle, 0.41 × 0.05 × 0.04 mm$^3$, monoclinic, P2$_1$/n (no. 14), a = 9.6290(3), b = 25.5389(8), c = 22.9504(6) Å, β = 101.534(1) °, V = 5529.9(3) Å$^3$, Z = 4, D$_x$ = 1.240 g/cm$^3$, µ = 0.53 mm$^{-1}$. The diffraction experiment was performed on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of (sin θ/λ)$_{\text{max}}$ = 0.65 Å$^{-1}$. The Eval15 software$^9$ was used for the intensity integration. A numerical absorption correction and scaling was performed with SADABS$^{11}$ (correction range 0.74-1.00). A total of 92199 reflections was measured, 12701 reflections were unique (R$_{\text{int}}$ = 0.138), 7559 reflections were observed [I > 2σ(I)]. The structure was solved with Patterson superposition methods using SHELXT.$^{12}$ Structure refinement was performed with SHELXL-2018$^{13}$ on F$^2$ of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined with a riding model. The co-crystallized THF molecules were refined with a disorder model. 723 Parameters were refined with 310 restraints (distances, angles and displacement parameters in the disordered THF). R1/wR2 [I > 2σ(I)]: 0.0577 / 0.1224. R1/wR2 [all refl.]: 0.1214 / 0.1461. S = 1.021. Residual electron density between -0.69 and 0.63 e/Å$^3$. Geometry calculations and checking for higher symmetry was performed with the PLATON program.$^{15}$

![Figure S68. Displacement ellipsoid plot of [Zn(ImPh2NNOtBu)(SPh)] (4) (50% probability level). Hydrogen atoms and disordered THF solvent molecules are omitted for clarity.](image)

| Bond               | Length (Å) | Bond Angle | Degrees (°) |
|-------------------|------------|------------|-------------|
| Zn1–N1            | 2.028(2)   | Zn1–S1–C49 | 101.67(11)  |
| Zn1–N3            | 2.062(3)   | N1–Zn1–O1  | 94.92(9)    |
| Zn1–O1            | 1.967(2)   | N3–Zn1–O1  | 96.27(9)    |
| Zn1–S1            | 2.2249(9)  | N1–Zn1–N3  | 90.33(10)   |
|                   |            | N1–Zn1–S1  | 131.21(7)   |
|                   |            | N3–Zn1–S1  | 120.07(7)   |
|                   |            | O1–Zn1–S1  | 116.13(7)   |

Table S5: Selected bond lengths and bond angles for [Zn(ImPh2NNOtBu)(SPh)] (4)
4.6 X-ray Crystal Structure Determination of [Zn(Im\(^{\text{Ph}2}\text{NNO}^{\text{tBu}})(\text{SPh})(\text{py})] (5)

C\(_{50}\)H\(_{58}\)N\(_{5}\)O\(_{2}\)Zn\(_{0.3}\)(C\(_{5}\)H\(_{2}\)N), Fw = 991.27, colourless plate, 0.39 × 0.25 × 0.03 mm\(^{3}\), monoclinic, P\(_{2}\)/\(_{1}\)/c (no. 14), a = 14.0508(5), b = 26.6435(11), c = 16.9367(6) \(\text{Å}\), \(\beta = 122.751(2)\) °, V = 5332.5(4) \(\text{Å}^{3}\), Z = 4, \(D_{\text{x}} = 1.235\) g/cm\(^{3}\), \(\mu = 0.55\) mm\(^{-1}\). The diffraction experiment was performed on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (\(\lambda = 0.71073\) Å) at a temperature of 150(2) K up to a resolution of (\(\sin \theta/\lambda\))\(_{\text{max}}\) = 0.61 Å\(^{-1}\). The Eval15 software\(^{9}\) was used for the intensity integration. A large anisotropic mosaicity\(^{10}\) about \(\text{hk}l=(0,0,1)\) was used for the prediction of the reflection profiles. A numerical absorption correction and scaling was performed with SADABS\(^{11}\) (correction range 0.76-1.00). A total of 49701 reflections was measured, 9923 reflections were unique (\(R_{\text{int}} = 0.100\)), 6018 reflections were observed \([I>2\sigma(I)]\). The structure was solved with Patterson superposition methods using SHELXT.\(^{12}\) Structure refinement was performed with SHELXL-2018\(^{13}\) on \(F^{2}\) of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined with a riding model. The co-crystallized non-coordinated pyridine molecule was refined with a partial occupancy. 676 Parameters were refined with 105 restraints (distances, angles, displacement parameters and molecular flatness in the partially occupied pyridine). \(R_{1}/wR_{2} [I > 2\sigma(I)]: 0.0621 / 0.1390. \) \(R_{1}/wR_{2} \text{[all refl.]}: 0.1235 / 0.1666. \) \(S = 1.042. \) Residual electron density between -0.52 and 1.53 e/\(\text{Å}^{3}\). Geometry calculations and checking for higher symmetry was performed with the PLATON program.\(^{15}\)

![Displacement ellipsoid plot of [Zn(Im\(^{\text{Ph}2}\text{NNO}^{\text{tBu}})(\text{SPh})(\text{py})] (5) (50% probability level). Hydrogen atoms and partially occupied non-coordinated pyridine solvent molecule are omitted for clarity.](image)

**Figure S69.** Displacement ellipsoid plot of [Zn(Im\(^{\text{Ph}2}\text{NNO}^{\text{tBu}})(\text{SPh})(\text{py})] (5) (50% probability level). Hydrogen atoms and partially occupied non-coordinated pyridine solvent molecule are omitted for clarity.

**Table S6:** Selected bond lengths and bond angles for [Zn(Im\(^{\text{Ph}2}\text{NNO}^{\text{tBu}})(\text{SPh})(\text{py})] (5)

| Bond      | Length (Å) | Bond Angle | Degrees |
|-----------|------------|------------|---------|
| Zn1–N1    | 2.108(3)   | N1–Zn1–O1 | 98.95(12) |
| Zn1–N5    | 2.120(3)   | N1–Zn1–O1 | 68.5(10)  |
| Zn1–O1    | 1.941(3)   | N1–Zn1–O2 | 70.35(10) |
| Zn1–O2    | 2.455(3)   | N5–Zn1–O1 | 94.43(12) |
| Zn1–S1    | 2.2835(12) | O1–Zn1–S1 | 127.91(9) |
5 Cyclic Voltammetry

5.1 Cyclic Voltammetry of K-Im\textsuperscript{Ph2NNO}\textsuperscript{tBu}

Figure S70: CV of K-Im\textsuperscript{Ph2NNO}\textsuperscript{tBu} recorded at different scan rates in an electrolyte solution of 0.1 M [\textsuperscript{n}Bu\textsubscript{4}N]PF\textsubscript{6} in acetonitrile. The insert graph shows the linear dependence of the peak current (for events A, B and C) as a function of the square root of the scan rate. Cyclic voltammograms were obtained by scanning oxidatively.

Figure S71: CV of K-Im\textsuperscript{Ph2NNO}\textsuperscript{tBu} recorded in an electrolyte solution of 0.1 M [\textsuperscript{n}Bu\textsubscript{4}N]PF\textsubscript{6} in acetonitrile. Left: the CV recorded when scanning in the oxidative direction (2 scans). Right: the CV recorded when scanning in the reductive direction (2 scans).
5.2 Cyclic Voltammetry of [Fe(Im\textsubscript{Ph2}NNO\textsubscript{tBu})(Cl)] (1)

**Figure S72**: CV of 1 recorded at different scan rates in a 0.1 M [\textit{t}Bu\textsubscript{4}N]PF\textsubscript{6} solution in acetonitrile. The graph shows the linear dependence of the peak current (for events A-H) as a function of the square root of the scan rate. The R\textsuperscript{2} values of the linear trend lines are depicted below the graph.

**Figure S73**: CV of 1 recorded in an electrolyte solution of 0.1 M [\textit{t}Bu\textsubscript{4}N]PF\textsubscript{6} in acetonitrile. Left: the CV recorded when scanning in the oxidative direction (2 scans). Right: the CV recorded when scanning in the reductive direction (2 scans).

**Figure S74**: Segmented CVs of 1 recorded in a 0.1 M [\textit{t}Bu\textsubscript{4}N]PF\textsubscript{6} solution in acetonitrile.
5.3 Cyclic Voltammetry of [Zn(Im\text{Ph}^2\text{NNO}^\text{tBu})(Cl)]\text{(2)}

![Figure S75](image1)

**Figure S75:** CV of 2 recorded in an electrolyte solution of 0.1 M [\^\text{Bu}_4\text{N}]PF_6 in acetonitrile.

![Figure S76](image2)

**Figure S76:** CV of 2 recorded at different scan rates in an electrolyte solution of 0.1 M [\^\text{Bu}_4\text{N}]PF_6 in acetonitrile.
5.4 Cyclic Voltammetry of [Zn(ImPh2NNOtBu)(SPh)] (4)

Figure S77: CV of 4 recorded at different scan rates in an electrolyte solution of 0.1 M [Bu4N]PF6 in acetonitrile. The graph shows the linear dependence of the peak current (for events A-G) as a function of the square root of the scan rate. The R² values of the linear trend lines are depicted below the graph.

Figure S78: CV of 4 recorded in an electrolyte solution of 0.1 M [Bu4N]PF6 in acetonitrile. Left: the CV recorded when scanning in the oxidative direction (2 scans). Right: the CV recorded when scanning in the reductive direction (2 scans).

Figure S79: Segmented CVs of 4 recorded at different scan rates in an electrolyte solution of 0.1 M [Bu4N]PF6 in acetonitrile.
6 Computational Data

6.1 Computational Methods

DFT (density functional theory) calculations were conducted using the Gaussian 16 software package. Geometry optimisations use the B3LYP (Becke, three-parameter, Lee-Young-Parr) functional with the LanL2DZ basis set defined on Fe and Zn atoms and the 6-31g(d,p) basis set defined on all other atoms. The geometries were optimized without any symmetry restraints and empirical dispersion corrections were applied. The structures were confirmed as energy minima by the absence of any imaginary frequencies. Frequency analyses were performed on all geometries as the B3LYP/6-31g(d,p) level of theory. Single point energy calculations were re-run on all geometries as the B3LYP/6-311g(d,p) level of theory. For NBO (natural bond orbital) calculations, the NBO06 program\(^4\) up to the NLMO (natural localized molecular orbital) basis set at the B3LYP/6-311g(d,p) level of theory. Cube files for molecular orbitals were generated using the Multiwfn program.\(^5\) Biorthogonalisation of the \(\alpha\) and \(\beta\) spin molecular orbitals for 2 were performed with the Multiwfn program, using the Fock matrix from the .47 NBO file generated for 2. Molecular orbitals were visualised with the Visual Molecular Dynamics program\(^6\) using the respective molecular orbital cube file and defining the isosurface level as \(\pm0.05\).

6.2 Input Examples

Examples of input for geometry optimisation / frequency calculation

```plaintext
# opt freq b3lyp/gen pseudo empiricaldispersion=gd3bj symmetry=loose

Coordinates from FeLCl crystal structure

0 5
Insert coordinates here

C H N O Cl 0
6-31g(d,p) ****
Fe 0
LANL2DZ ****
Fe 0
LANL2DZ
```

Example of input for single point calculation performed at higher level of computation

```plaintext
# b3lyp/6-311G(d,p) empirical dispersion=gd3bj

Coordinates from geometry optimisation of FeLCl

0 5
Insert coordinates here
```
Example of input for NBO analysis

```bash
# b3lyp/6-311G(d,p) empirical dispersion=gd3bj pseudo symmetry=loose
pop=NBO6Read density=current

Coordinates from 6-311G(d,p) calculation of FeLCl
0 5
Insert coordinates here

$nbo plot archive file=filename nlmo bndidx $end
```

## 6.3 Molecular Orbitals

### 6.3.1 Results

**Table S7:** Calculated MO energies in electron volts (eV).

| Molecular Orbital | K-L$_{\text{opt}}$ | 1$_{\text{opt}}$ | 2$_{\text{opt}}$ | 4$_{\text{opt}}$ |
|-------------------|-------------------|----------------|----------------|----------------|
| LUMO+3            | -0.618            | 8.154          | -0.804         | -0.791         |
| LUMO+2            | -0.681            | 5.708          | -0.880         | -0.865         |
| LUMO+1            | -1.065            | 4.061          | -1.231         | -1.231         |
| LUMO              | -1.128            | 2.848          | -1.315         | -1.315         |
| HOMO              | -4.259            | -0.1135        | -4.967         | -4.841         |
| HOMO-1            | -5.259            | -3.902         | -5.950         | -5.174         |
| HOMO-2            | -5.556            | -3.9775        | -5.950         | -5.585         |
| HOMO-3            | -5.798            | -4.061         | -6.415         | -5.896         |
| HOMO-4            | -5.947            | -6.455         | -6.430         | -5.971         |
| HOMO-5            | -6.835            | -6.624         | -6.950         | -6.210         |

[^a]: Average between the $\alpha$ and $\beta$ MO energies, extracted from the biorthogonalised MOs.

**Table S8:** NBO Analysis of 1$_{\text{opt}}$

| Atom | Natural charge | Natural spin density |
|------|----------------|---------------------|
| Fe   | 1.49112        | 3.71631             |
| O    | -0.90225       | 0.09829             |
| N$_{\text{left}}$ | -0.63112          | 0.03545             |
| N$_{\text{right}}$ | -0.63113             | 0.03545             |
| Cl   | -0.76146       | 0.07495             |
6.3.2 MO Diagrams for $\text{KL}^{\text{opt}}$

Figure S80: HOMOs (0, −1) for $\text{KL}^{\text{opt}}$. Isosurfaces drawn at ±0.05 level.

Figure S81: LUMOs (0, +1) for $\text{KL}^{\text{opt}}$. Isosurfaces drawn at ±0.05 level.
6.3.3 MO Diagrams for $1^{\text{opt}}$

**Figure S82**: Spin density for $1^{\text{opt}}$. Isosurface drawn at ±0.05 level.

**Figure S83**: HOMOs (0, -1, -2, -3, -4, -5) for $1^{\text{opt}}$. Isosurfaces drawn at ±0.05 level.

**Figure S84**: LUMOs (0, +1, +2) for $1^{\text{opt}}$. Isosurfaces drawn at ±0.05 level.
6.3.4 MO Diagrams for $2^{\text{opt}}$

![MO Diagrams for $2^{\text{opt}}$](image)

**Figure S85**: HOMOs (0, -1, -2) for $2^{\text{opt}}$. Isosurfaces drawn at ±0.05 level.

![MO Diagrams for $2^{\text{opt}}$](image)

**Figure S86**: LUMOs (0, +1) for $2^{\text{opt}}$. Isosurfaces drawn at ±0.05 level.

6.3.5 MO Diagrams for $4^{\text{opt}}$

![MO Diagrams for $4^{\text{opt}}$](image)

**Figure S87**: HOMOs (0, -1, -2, -3, -4) for $4^{\text{opt}}$. Isosurfaces drawn at ±0.05 level.
Figure S88: LUMOs (0, -1) for 4\textsuperscript{opt}. Isosurfaces drawn at ±0.05 level.

### 6.4 XYZ Coordinates

#### 6.4.1 Coordinates KL\textsuperscript{opt}

|   | X     | Y     | Z     |
|---|-------|-------|-------|
| O | -0.49208 | 0.37655 | 1.46412 |
| O | 0.18977 | 1.08213 | -2.61166 |
| N | 1.52493 | -1.35692 | -0.36429 |
| N | 2.66018 | 0.39295 | -1.10101 |
| N | -1.25916 | -1.52815 | -1.00646 |
| N | -2.37476 | 0.38628 | -1.09407 |
| C | 0.13384 | -0.16704 | -0.92459 |
| C | 2.86688 | -1.59013 | -0.16498 |
| C | 3.59931 | -0.50900 | -0.62363 |
| C | 2.98740 | 1.67653 | -1.72504 |
| C | 3.29613 | -2.82594 | 0.50257 |
| C | 2.51849 | -3.99068 | 0.35710 |
| C | 2.86108 | -5.16554 | 1.02501 |
| C | 3.99234 | -5.20489 | 1.84267 |
| C | 4.77465 | -4.05706 | 1.98717 |
| C | 4.42993 | -2.87755 | 1.33054 |
| C | 5.05061 | -0.28668 | -0.66581 |
| C | 5.88939 | -1.26441 | -1.22550 |
| C | 7.27072 | -1.09136 | -1.23667 |
| C | 7.83808 | 0.06581 | -0.69948 |
| C | 7.01492 | 1.04552 | -0.14313 |
| C | 5.63261 | 0.88965 | -0.32120 |
| C | -1.14060 | -0.21815 | -1.10385 |
| C | -2.60506 | -1.79457 | -0.85636 |
| C | -3.32112 | -0.60913 | -0.90804 |
| C | -2.69087 | 1.79364 | -1.33998 |
| C | -3.03622 | -3.17023 | -0.56961 |
| C | -4.22658 | -3.46553 | 0.11906 |
| C | -4.56217 | -4.78334 | 0.42340 |
| C | -3.71607 | -5.83395 | 0.06246 |
| C | -2.52520 | -5.55247 | -0.61032 |
| C | -2.18794 | -4.23735 | -0.92434 |
| C | -4.75694 | -0.32885 | -0.77654 |
| C | -5.22116 | 0.56939 | 0.19897 |
| C | -6.58551 | 0.81485 | 0.33957 |
| C | -7.50451 | 0.16233 | -0.48390 |
| C | -7.05251 | -0.73607 | -1.45243 |
| C | -5.68884 | -0.97649 | -1.60217 |
| C | 0.05524 | 1.82781 | -0.32649 |
| C | -0.31713 | 1.58679 | 1.03676 |
| C | -0.53351 | 2.75093 | 1.85515 |
| C | -0.30674 | 4.01758 | 1.31645 |
| C | 0.09916 | 4.24038 | -0.00831 |
| C | 0.25891 | 3.11289 | -0.81706 |
### Coordinates 1\textsuperscript{opt}

| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| Fe      | 0.00013400 | -1.50107400| 0.98232300 |
| Cl      | 0.00031600 | -3.39349700| 2.18874100 |
| O       | 0.00004500 | 0.30087400 | 1.59153700 |
| O       | 0.00005600 | 1.53198600 | 0.53481700 |
| N       | 1.44080200 | -1.12850500| -0.55760800|
| N       | 2.50832200 | 0.61986500 | -1.38505200|
| N       | -1.44060300| -1.12865200| -0.55756400|
| N       | -2.50829900| 0.61955400 | -1.38513100|
| C       | -0.00016000| 0.89495400 | -1.19289900|
| C       | 1.28817400 | 0.08784200 | -1.06798700|
### Coordinates $2^{\text{opt}}$

| Atom | $x$      | $y$      | $z$    |
|------|----------|----------|--------|
| Zn   | -0.00097 | -1.55120 | 0.86847|
| Cl   | -0.00248 | -3.35743 | 2.17339|
| O    | -0.01111 | 0.29330  | 1.55354|
| O    | 0.00037  | 1.49810  | -2.53156|
| N    | 1.44995  | -1.14930 | -0.63270|
| N    | 2.51669  | 0.64388  | -1.34987|
| N    | -1.45071 | -1.14881 | -0.63396|
| N    | -2.51634 | 0.64585  | -1.34911|
| C    | 0.00024  | 0.88606  | -1.22991|
| C    | 1.29566  | 0.08868  | -1.09305|
| C    | 2.80606  | -1.42297 | -0.59005|
| C    | 3.49016  | -0.30846 | -1.04000|
| C    | 2.80461  | 2.00442  | -1.80456|
| C    | 3.30817  | -2.71396 | -0.10973|
| C    | 2.53225  | -3.86912 | -0.28616|
| C    | 2.98286  | -5.10127 | 0.17948 |
| C    | 4.21712  | -5.19927 | 0.82166 |
| C    | 4.99492  | -4.05379 | 1.00501 |
| C    | 4.54439  | -2.81843 | 0.54873 |
| C    | 4.93146  | -0.9201  | -1.23587|
| C    | 5.66410  | -0.98173 | -2.03744|
| C    | 7.03656  | -0.85129 | -2.20380|
| C    | 7.69582  | 0.24575  | -1.57921|
| C    | 6.97687  | 1.13531  | -0.77954|
| C    | 5.60436  | 0.96558  | -0.60331|
| C    | -1.29568 | 0.08953  | -1.09307|
| C    | -2.80700 | -1.42057 | -0.59132|
| C    | -3.49042 | -0.36068 | -1.03989|
| C    | -2.80329 | 2.00698  | -1.80266|
| C    | -3.30989 | -2.71721 | -0.11223|
| C    | -4.54615 | -2.81709 | 0.54614 |
| C    | -4.99741 | -4.05263 | 1.00122 |
| C    | -4.22030 | -5.19839 | 0.81673 |
| C    | -2.98599 | -5.10049 | 0.17462 |
| C    | -2.53465 | -3.86815 | -0.28980|
| C    | -4.93162 | -0.08834 | -1.23510|
| C    | -5.60351 | 0.96913  | -0.60128|
| C    | -6.97595 | 1.14010  | -0.77692|
| C    | -7.69582 | 0.25189  | -1.57725|
| C    | -7.03758 | -0.80903 | -2.20310|
| C    | -5.66520 | -0.97670 | -2.03733|
| C    | 0.00075  | 1.97741  | -0.15597|
| C    | 0.00009  | 1.55992  | 1.20975 |
| C    | 0.00068  | 2.58987  | 2.20409 |
| C    | 0.00158  | 3.92325  | 1.79263 |
| C    | 0.00250  | 4.33071  | 0.45003 |
6.4.4 Coordinates 4\textsuperscript{opt}

|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Zn | 0.11734 | -1.45351 | 0.14655 |
| O  | 0.08836 | 0.22722 | 1.17749 |
| O  | 0.55429 | 2.25551 | -2.53099 |
| N  | 1.67467 | -0.81740 | -1.17780 |
| N  | 2.88398 | 1.02579 | -1.26277 |
| N  | -1.20178 | -0.63704 | -1.32944 |
| N  | -2.11266 | 1.31240 | -1.81961 |
| C  | 0.38409 | 1.38604 | -1.39768 |
| C  | 1.62348 | 0.50360 | -1.30518 |
| C  | 3.00320 | -1.18006 | -1.04622 |
| H       | 0.47061 | 4.08893 | -1.15275 |
|---------|---------|---------|----------|
| H       | -1.89390 | 0.36395 | 4.49219  |
| H       | -1.58697 | 0.05603 | 2.78159  |
| H       | -2.49965 | 1.50061 | 3.27255  |
| H       | 0.60530  | 0.21719 | 4.97055  |
| H       | 1.74705  | 1.27069 | 4.11298  |
| H       | 0.94788  | -0.06532 | 3.25372 |
| H       | -1.35630 | 3.34554 | 4.60612  |
| H       | 0.38777  | 3.26472 | 4.92948  |
| H       | -0.71455 | 2.12604 | 5.71094  |
| H       | 2.44137  | 6.00539 | 0.92584  |
| H       | 1.70003  | 7.43576 | 0.18096  |
| H       | 1.79241  | 5.91350 | -0.71727 |
| H       | -0.88309 | 6.38744 | 2.66768  |
| H       | 0.14548  | 7.70656 | 2.09428  |
| H       | 0.86917  | 6.32135 | 2.92211  |
| H       | -0.76578 | 6.00352 | -1.08630 |
| H       | -0.82819 | 7.52345 | -0.18240 |
| H       | -1.84410 | 6.15361 | 0.30857  |
| H       | 1.53394  | 0.92094 | -3.81354 |
| H       | 0.77018  | 2.36348 | -4.53661 |
| H       | -0.23712 | 0.99029 | -3.39912 |
| S       | 0.21734  | -3.49883 | 1.17651 |
| C       | -0.92796 | -3.07855 | 2.49976 |
| C       | -0.44779 | -2.85714 | 3.79889 |
| C       | -2.31039 | -3.00515 | 2.70777 |
| H       | -1.32918 | -2.57448 | 4.84211 |
| H       | 0.62072  | -2.90576 | 3.98031  |
| C       | -3.18692 | -2.70804 | 3.31424  |
| H       | -2.69458 | -3.18918 | 1.27629  |
| C       | -2.70298 | -2.49644 | 4.60615  |
| H       | -0.93833 | -2.40528 | 5.84188  |
| H       | -4.25323 | -2.65045 | 3.11222  |
| H       | -3.38679 | -2.26893 | 5.41869  |

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