SUPPORTING INFORMATION

A hybrid bioinspired catechol-alloxazine triangular nickel complex stabilizing protons and electrons

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Table of contents

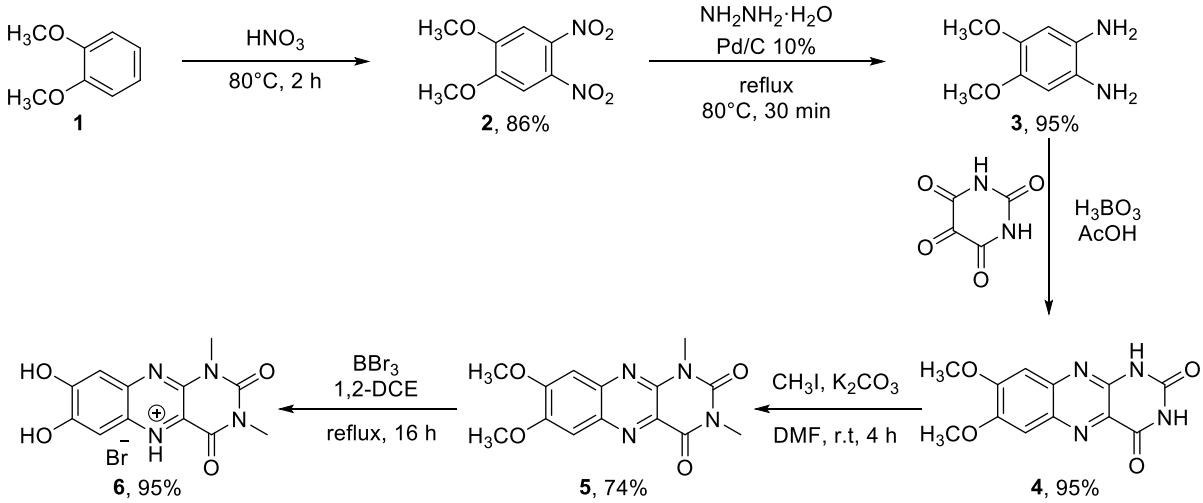
General information

All reactions were carried out under argon atmosphere using standard Schlenk techniques in either oven dried or flame dried glassware, unless otherwise mentioned. Reagent grade solvents were used as received without any further purification. 1,2-Dichloroethane (DCE) was bubbled with argon before use. All starting materials were purchased from commercially available source (TCI Chemicals, Sigma-Aldrich, Alfa Aesar, Acros Organics) and used without any further purification, unless otherwise noted. Thin layer chromatography (TLC) was performed on Merck 60 F254 silica gel and products were identified with UV lamp chamber (short-range UV lamp 254 nm or long-range UV lamp 365 nm). ^{1}H NMR and ^{13}C NMR data were collected at room temperature using Bruker Avance III Spectrometer – 300 MHz (^{31}P-^{1}H 5mm probe), Bruker Avance III Spectrometer – 400 MHz (Inverse ^{1}H-X 5 mm probe (with ^{31}P < X < ^{15}N)) and Bruker Avance II Spectrometer – 500 MHz (Cryo-Probe Hélium ^{13}C-^{1}H 5mm). Shifts (δ) are given in parts per million (ppm) and coupling constants (J) are given in Hertz (Hz). Electrospray ionization mass spectrometry (ESI-MS) or high-resolution mass spectrometry (HRMS) were performed by ESI mass spectrometers MicroTOF(I) and MicroTOF(II) focus (BRUKER, Germany). UV-Vis data were collected using AGILENT Cary 60 UV-Vis Spectrometer at room temperature. Wavelengths (λ) are given in nanometer (nm) and molar extinction coefficients (ε) are given in $M^{-1}.cm^{-1}$. EPR spectra were recorded on an EMXplus spectrometer (Bruker Biospin GmbH) operating at Q-band (34 GHz), equipped with a high sensitivity resonator (ER5106QT, Bruker) and a helium cryostat ER4118CFO for the low temperature measurements. Powder samples were sealed in quartz tube and degassed for three cycle using freeze-pump-thaw technique. Powder X-ray diffraction (PXRD) were performed on Bruker D8 Advance with X-ray source by anticathode of cooper giving photons with a wavelength of $1.54x10^{-10}$ m. The crystals were placed in oil, and a single crystal was selected, mounted on a glass fibre and placed in a low-temperature N_2 stream. X-Ray diffraction data collection were measured by either 4-circles Bruker PHOTON III diffractometer equipped with two micro-sources IμS Mo and IμS Diamond Cu and with an Oxford Cryosystem 800 for low temperature measurements or 4-circles Bruker APEX II DUO IμS Kappa-CCD diffractometer equipped with two sources (Mo sealed tube and Cu micro-source) and with an Oxford Cryosystem 700 liquid N_2 device for low temperature measurements. The cell parameters were determined in APEX3 software.[1] The structure was solved using the program SHELXT-2014.[2] The refinement and all further calculations were carried out using SHELXL-2018.[3] The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F2. A semi-empirical absorption correction was applied using SADABS in APEX3.[1] Compounds **6** and **7** have been deposited in the Cambridge Crystallographic Database CCDC under the references CCDC 2089518 (**6**) and CCDC 2089519 (**7**).

[1] "M86-EXX229V1 APEX3 User Manual", Bruker AXS Inc., Madison, USA, 2016.
[2] G. M. Sheldrick, *Acta Cryst.* **2015***,* A71, 3-8.
[3] G. M. Sheldrick, *Acta Cryst.* **2015**, C71, 3-8.

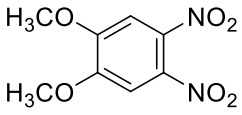
Syntheses of pro-ligand and complex

Synthesis of pro-ligand **6**



Scheme S1. Synthetic scheme for pro-ligand **6**

1,2-Dimethoxy-4,5-dinitrobenzene **2**



2

The synthetic procedure from Bo *et al*[4] was used. 1,2-dimethoxy benzene **1** (10 mL, 78.2 mmol) was added dropwise using dropping funnel to conc. nitric acid (65%, 100 mL) in a two neck round bottom flask equipped with reflux condenser under vigorous stirring over an ice-water bath. The reaction mixture was then heated at 80° C for 2 h [**CAUTION!** Nitrogen dioxide is evolved during the reaction and quenched by bubbling in water through an outlet attached to the reflux condenser during the reaction]. Upon completion, the clear yellow reaction mixture was allowed to stand at room temperature and then chilled in an ice-water bath. The precipitate formed was filtered, washed with water until the pH of the filtrate was neutral and then recrystallized from hot ethanol to yield the expected product (15.32 g, 86% yield).

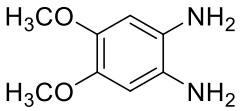
The characterization data were identical to those previously reported.[4]

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.34 (2H, s), 4.02 (6H, s).

^{13}C NMR ($CDCl_3$, 126 MHz) δ = 152.0, 136.8, 107.1, 57.2.

[4] Bo, W. Li, R. Qin, C. Li, C. Du and Z. Liu, CN 101875716 A, **2010**, p. 12.

1,2-Diamino-4,5-dimethoxybenzene **3**



3

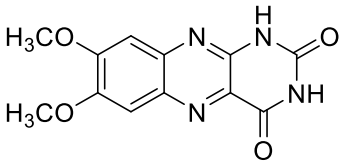
The synthetic procedure was adapted from Fan *et al*.[5] 1,2-Dimethoxy-4,5-dinitrobenzene **2** (3 g, 13.15 mmol) and Pd/C catalyst (0.41 g) were dispersed in ethanol (135 mL). Hydrazine monohydrate (6.4 mL, 131.5 mmol) was added dropwise to the mixture cooled in an ice-water bath. The mixture was refluxed for 30 min at 80°C. Upon completion, the mixture was filtered through Celite®535 and residual material was rinsed with small portions of hot ethanol. The filtrate was collected and the off-white crystalline product was obtained by removing the solvent. The product was dried under vacuum and stored under argon (2.09 g, 95% yield).

The characterization data were identical to those previously reported.[1]

^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.37 (2H, s), 3.79 (6H, s), 3.19 (4H, broad).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 143.2, 127.8, 103.9, 56.8.

7,8-Dimethoxyalloxazine **4**



4

The procedure was adapted from Chen *et al.*[6] In a 50 mL round bottom flask, 4,5-dimethoxy-1,2-diaminobenzene **(3)** (504.6 mg, 3 mmol), alloxane monohydrate (480 mg, 3 mmol) and boric acid (185 mg, 3 mmol) and 20 mL acetic acid were added the mixture was stirred under argon at room temperature for 2 h. During this time solid precipitated out in the solution. The solid was then collected by filtration then washed with 40 ml of acetic acid and 40 ml of diethyl ether. The product was dried further with high vacuum pump to afford bright yellow powder (795 mg, 95% yield).

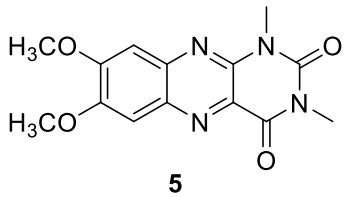
The characterization data were identical to those previously reported.[6]

^{1}H NMR (d_6-DMSO, 400 MHz) δ 11.74 (1H, s), 11.58 (1H, s), 7.47 (1H, s), 7.20 (1H, s), 4.00 (3H, s), 3.96 (3H, s).

^{13}C NMR (d_6-DMSO, 126 MHz) δ 160.9, 155.8, 151.7, 150.2, 145.8, 141.0, 136.6, 127.3, 107.3, 104.6, 56.5, 56.2.

[5] K. W. Fan, M. B. Peterson, P. Ellersdorfer, A. M. Granville, *RSC Adv.*, **2016**, *6*, 25203–25214.
[6] S. Chen, M. S. Hossain, F. W. Foss, *Org. Lett.*, **2012**, *14*, 2806–2809.

7,8-Dimethoxy-1,3-dimethylalloxazine **5**



5

7,8-dimethoxy alloxazine **4** (274.1 mg, 1 mmol) and K_2CO_3 (0.46 g, 3.33 mmol) were added to 7 mL DMF under argon in a two-neck round bottom flask. CH_3I (0.2 mL, 3.33 mmol) was then added to the above solution. The mixture was then stirred at room temperature for 4 h and DMF was removed under reduced pressure. The resulting solid was partitioned in 15 mL dichloromethane and 15 mL of water and the mixture was transferred into a separating funnel. The aqueous layer was extracted with dichloromethane (4 x 10 mL). The combined organic phases were washed with 20 mL brine and dried over $MgSO_4$. The solvent was evaporated under reduced pressure to afford a crude yellow powder, which was purified by silica gel column chromatography (CH_3OH/DCM = 0.8:99.2) to yield the title compound as a bright yellow powder (223 mg, 74% yield).

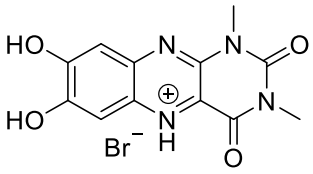
The characterization data were identical to those previously reported.[2]

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.57 (1H, s), 7.26 (1H, s), 4.10 (3H, s), 4.04 (3H, s), 3.79 (3H, s), δ 3.58 (3H, s).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 160.5, 156.7, 152.7, 151.0, 144.8, 141.9, 137.6, 126.5, 107.6, 105.1, 56.9, 56.7, 29.5, 29.2.

UV-Vis [DMSO; λ, nm (ε $M^{-1}.cm^{-1}$)]: 408 (2.2x10^4), 394 (2.3x10^4), 351 (1.2x10^4).

7,8-Dihydroxy-1,3-dimethylalloxazine-5-ium bromide **6**



A two-neck round bottom flask equipped with a reflux condenser and argon inlet was charged with 7,8-dimethoxy-1,3-dimethylalloxazine (604 mg, 2.0 mmol) and 30 mL 1,2-dichloroethane. BBr_3 (1M solution in CH_2Cl_2, 12 mL, 12 mmol) was added dropwise to this mixture through a septum, formed dark orange solution. Septum was replaced with a glass stopper and the orange mixture was heated to reflux for 16 hours. Reaction was monitored by TLC in DCM/MeOH (90:10) and upon completion was cooled to room temperature and further cooled in ice-water bath. After quenching with methanol, the mixture was evaporated under reduced pressure. The resulting sticky solid was triturated in methanol and the solvent was evaporated. This was repeated thrice and the solid was washed with DCM thoroughly to yield a blackish filtrate and an orange-yellow precipitate. The orange-yellow precipitate was taken in methanol and dried under reduced pressure, then further dried under vacuum to afford orange-yellow powder (680 mg, 84% yield).

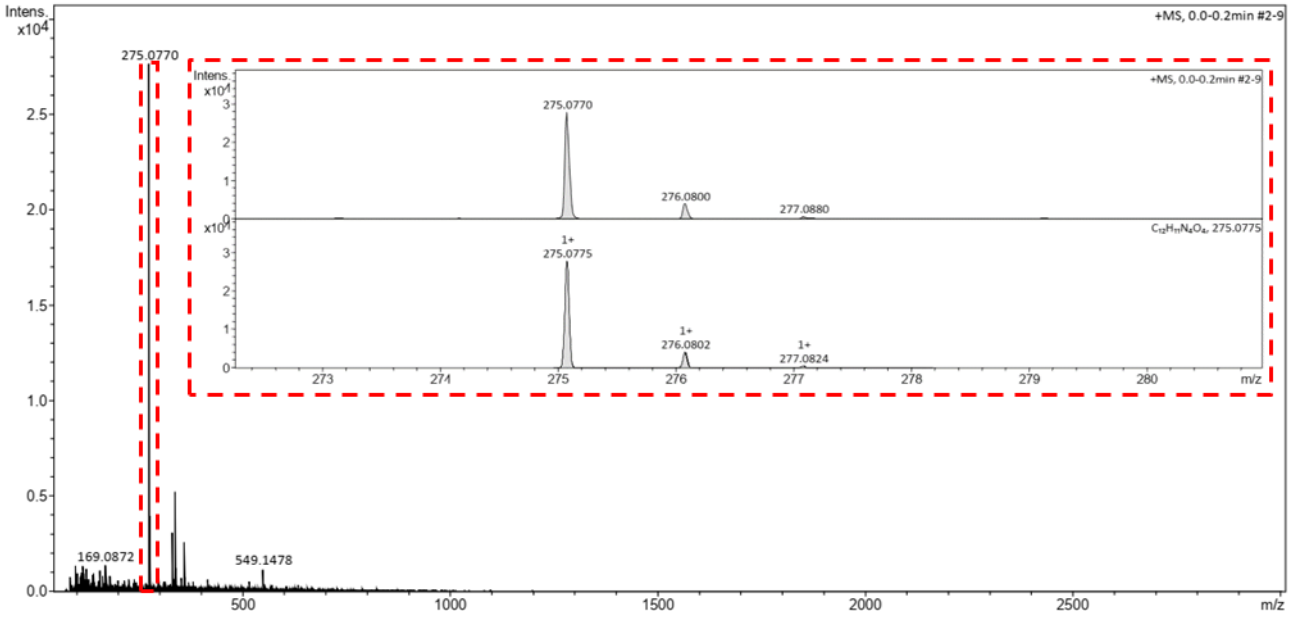
^{1}H NMR (d_6-DMSO, 300 MHz) δ 7.32 (s, 1H), 7.15 (s, 1H), 4.04 (bs), 3.57 (s, 3H), 3.33 (s, 3H).

^{13}C NMR (d_6-DMSO, 126 MHz) δ 159.8, 155.1, 150.6, 150.3, 144.1, 140.1, 136.1, 126.1, 109.8, 107.6, 29.0, 28.4.

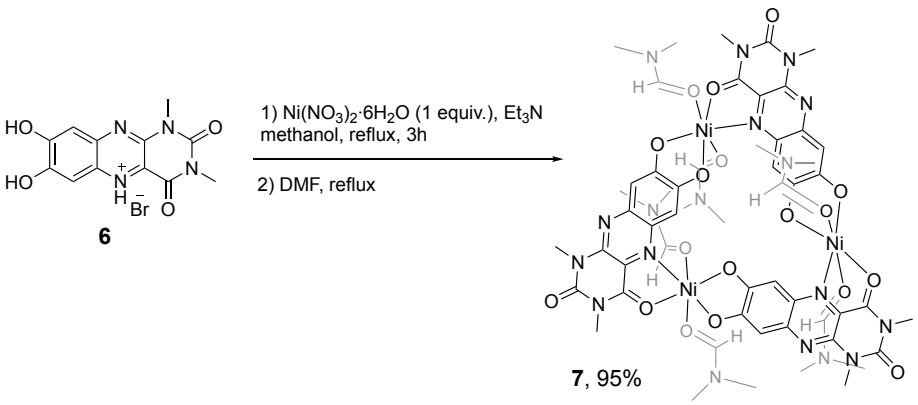
HRMS: Calculated for $[C_{12}H_{11}N_4O_4]^+$ = 275.0775, found = 275.0770.

Elemental analysis: Calculated for ($C_{12}H_{11}N_4O_4Br$) %C: 40.58, %N: 15.78, %H: 3.12, found %C: 41.45, %N: 15.85, %H: 3.75.

UV-Vis [DMSO; λ, nm (ε $M^{-1}.cm^{-1}$)]: 399 ($1.6x10^4$), 366 ($1.14x10^4$).



Synthesis of **7**



Scheme S2. Synthetic scheme for **7**.

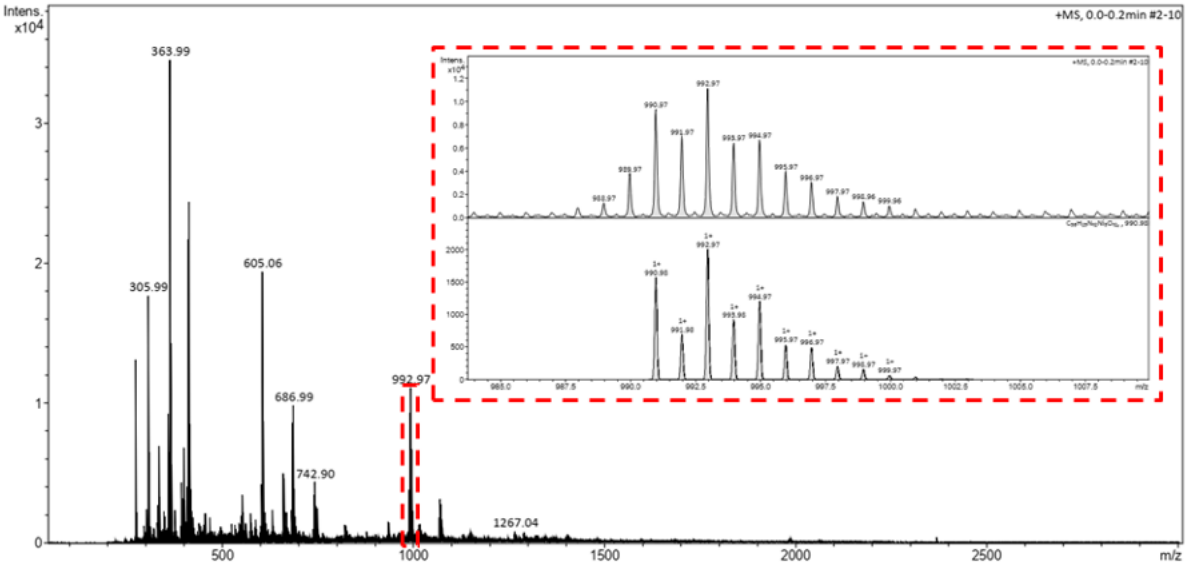
In a two neck round bottom flask equipped with a reflux condenser, 7,8-dihydroxy-1,3-dimethylalloxazine-5-ium bromide **6** (184 mg, 0.52 mmol) was dispersed in 20 mL methanol. Et_3N (220 µL, 1.55 mmol) was added and the resulting orange solution was stirred. $Ni(NO_3)_2{\cdot}6H_2O$ (151 mg, 0.52 mmol) was added and a red precipitate appeared. The mixture was heated to reflux for 3 hours, and became deep red over time. It was then cooled down to room temperature, filtered and washed with dichloromethane, acetone and diethylether. The precipitate was collected and dried under high vacuum to afford complex **7** as a dark red powder (163 mg, 95%). The dark red powder was

recrystallized in hot DMF. The crystals were decanted and washed with acetone and diethylether to afford dark red-brown crystals.

HRMS: Calculated for $[C_{36}H_{25}N_{12}Ni_3O_{12}]^+$ $[MH]^+$= 992.9733, found = 992.9718.

Elemental analysis: Calculated for $[(Ni(C_3H_7NO)_2(C_{12}H_8N_4O_4))_3]$ $2(C_3H_7NO)$ $10(H_2O)$ %C: 41.00, %N: 15.94, %H: 5.73, found %C: 41.57, %N: 15.97, %H: 4.36.

UV-Vis [DMSO; λ, nm (ε $M^{-1}.cm^{-1}$)]: 452 ($7.5x10^4$).



X-ray crystallography

Both compounds have been deposited in the Cambridge Crystallographic Database CCDC under the references CCDC 2089518 (**6**) and CCDC 2089519 (**7**).

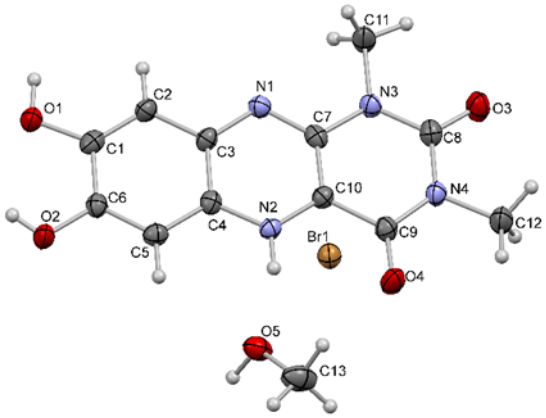


Fig. S1. Thermal ellipsoid representation (50% probability) of 7,8-dihydroxy-1,3-dimethylalloxazine-5-ium bromide (**6**). Selected bond distances (Å) and angles (º): C1-O1 1.338 (5); C6-O2 1.353 (5); C1-C6 1.449 (6); C7-N1 1.332 (5); C7-C8 1.472 (5); C8-O3 1.222 (5); O1-C1-C6 114.1(4); O2-C6-C1 120.9(4), N1-C7-C10 123.1(4), O4-C9-C10 122.2(4).

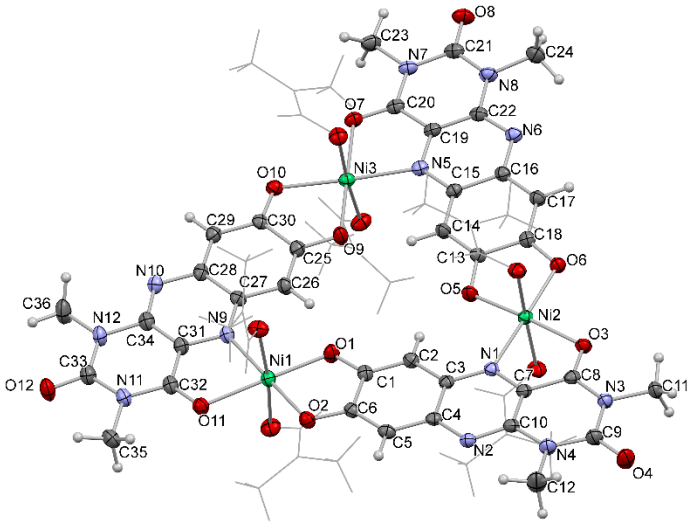


Fig. S2. Thermal ellipsoid representation (50% probability) of asymmetric unit of **7**. Selected bond distances (Å) and angles (º): Cu1-O1 1.9269(14); Cu1- O2 1.9272(12); C1-O1 1.322(2); C6-O2 1.315(2); C1-C6 1.460(2); O1-Cu1-O2 84.97(5); C1-O1-Cu1 111.51(11); C6-O2-Cu1 111.25(11).

Table S1. Crystallographic parameters for ligand **6** and complex **7**.

Product	**Ligand 6**	**Complex 7**
Empirical Formula	$C_{13}H_{15}BrN_4O_5$ $(C_{12}H_{11}N_4O_4)^+$, Br^- • CH_3OH	$C_{60}H_{84}N_{20}Ni_3O_{22}$ $(Ni(C_3H_7NO)_2(C_{12}H_8N_4O_4))_3$•$2(C_3H_7NO)2H_2O$
Formula weight	387.20	1613.54
Crystal system	monoclinic	triclinic
Space group	*P* 21/c	*P*-1
a (Å)	8.3771(5)	15.3127
b (Å)	18.9639(14)	15.8385
c (Å)	10.5829(7)	16.6042
α (°)	90	105.2160
β (°)	115.046(5)	97.156
γ(°)	90	111.045
V (Å^3)	1523.14(18)	3518.0
ρ_{calcd} (mg m^{-3})	1.689	1.5231
Z	4	2
T (K)	173(2)	120.15
μ (mm^{-1})	2.731	0.884
Reflections collected/ Unique	33353/ 4065	251128/16804
R(int)	0.1479	0.1117
Final R indices [I > 2σ(I)]	R1= 0.0503, wR2= 0.1006	R1= 0.0481, wR2= 0.1381
R indices (all data)	R1= 0.1025, wR2= 0.1191	R1= 0.0761, wR2= 0.1157
GOF on F2	1.031	1.0539

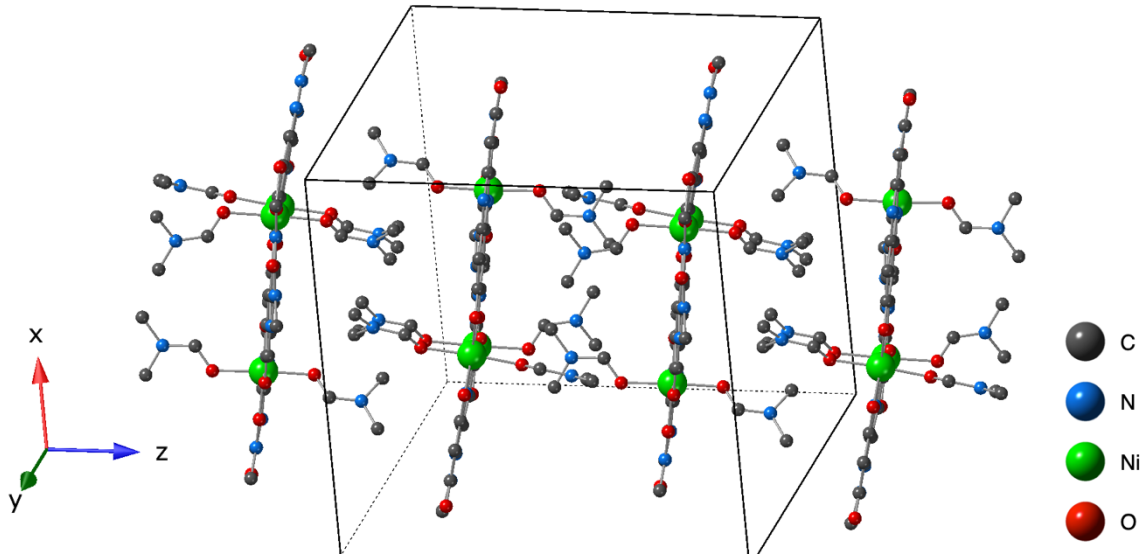


Fig. S3. For **7**, crystal packing of the triangular units, evidencing an alternate disposition of the triangles.

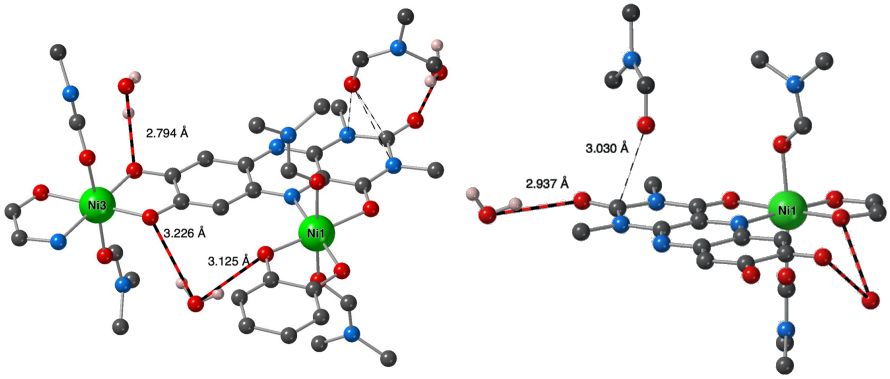


Fig. S4. Close-up of supramolecular interactions in **7** with surrounding solvent molecules.

Thermogravimetric analysis TGA

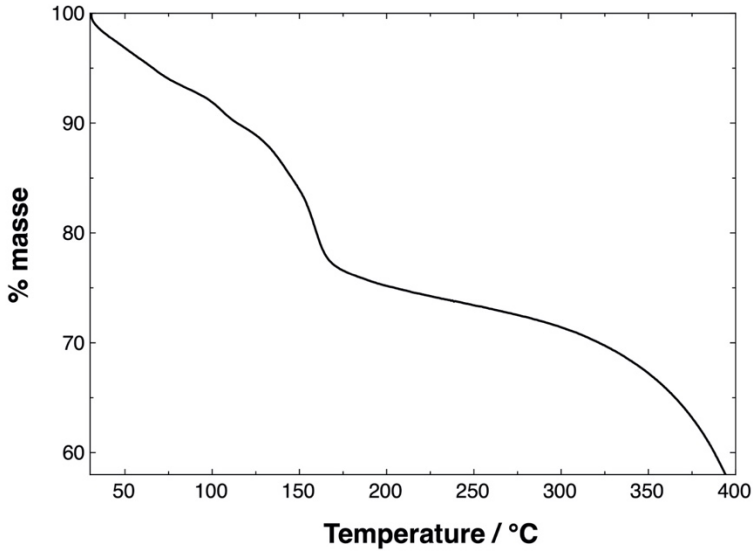


Fig. S5. TGA trace for **7**, recorded between 40 – 380°C at a rate of 5°/min.

Electrochemical studies

Cyclic voltammetry (CV) was performed in a cell equipped with three electrodes under argon. The working electrode used was a 1-millimeter diameter glassy carbon (GC) electrode unless otherwise stated, a platinum wire was used as counter electrode and a Ag(s)|AgCl(s) electrode was selected as reference. Tetrabutylammonium tetrafluoroborate was used as a supporting electrolyte with a 0.1 mol. L^{-1} concentration. The concentration of the analyte was 2 mM unless otherwise stated. All potentials are reported against Ag(s)|AgCl(s) (KCl 3 M) potential.

Cyclic voltammetry of **6**

CV of **6** was performed in DMSO and the scan rate analysis was varied. For meaningful comparison, the normalized current was plotted. When increasing the scan rate from 50 mVs^{-1} to 5 Vs^{-1} -with ohmic drop compensation-, the signal evolves consistently with an electron transfer coupled to a chemical reaction as observed by Webster and coll. under acidic conditions.[7]

[7] S. L. J. Tan, J. M. Kan, R. D. Webster *J. Phys. Chem. B* **2013**, *117*, 13755−13766.

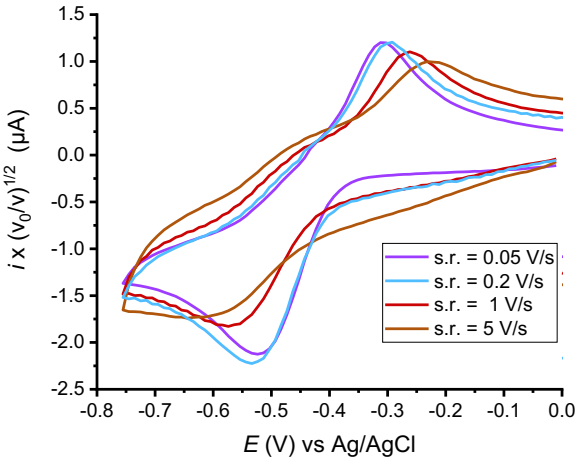


Fig. S6. CV of **6** (2mM concentration) performed in DMF with nBu_4NBF_4 (0.1mol.L^{-1}) as an electrolyte at various scan rate.

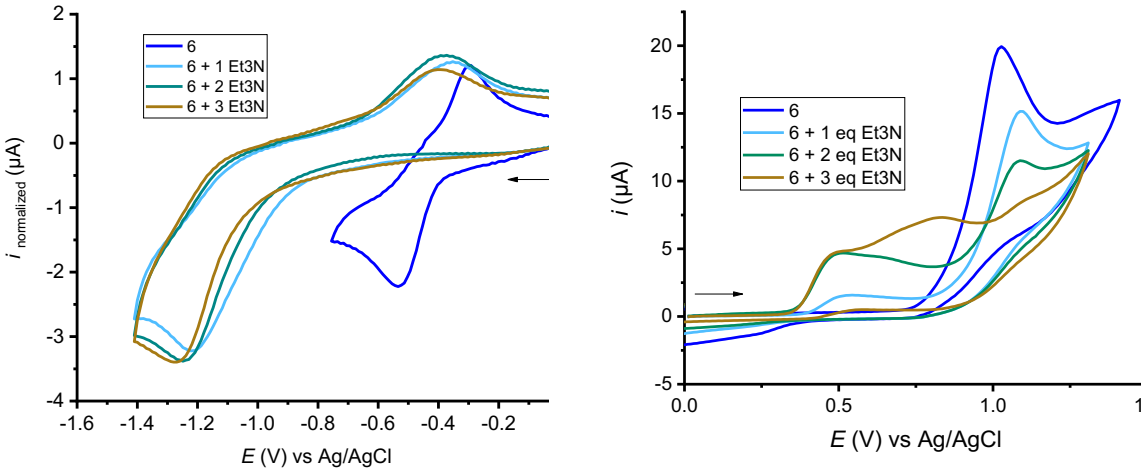


Fig. S7. CV of **6** (2mM concentration) with increasing equivalents of Et_3N in DMSO with nBu_4NBF_4 (0.1mol.L^{-1}) as supporting electrolyte at 0.2 Vs^{-1}. Addition of one equivalent of base significantly shifted the reduction potential of **6** towards more negative values (left). The CV towards oxidation potentials is also greatly affected by addition of the base as deprotonated catechols are more easily oxidized (right).

When scanning towards reduction potentials, 3 reduction waves were detected but only the first one evolved when changing the scan rate (see below).

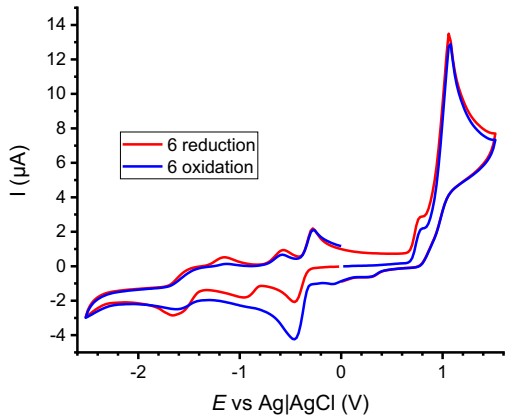


Fig. S8. CV of **6** (2mM concentration) performed in DMF with nBu_4NBF_4 (0.1mol.L^{-1}) as supporting electrolyte.

As shown in DMSO, the CVs evolve when varying the scan rate with a loss of reversibility and two oxidation waves were detected at the reverse scan at high scan rates. Here also, normalized currents were plotted by comparison.

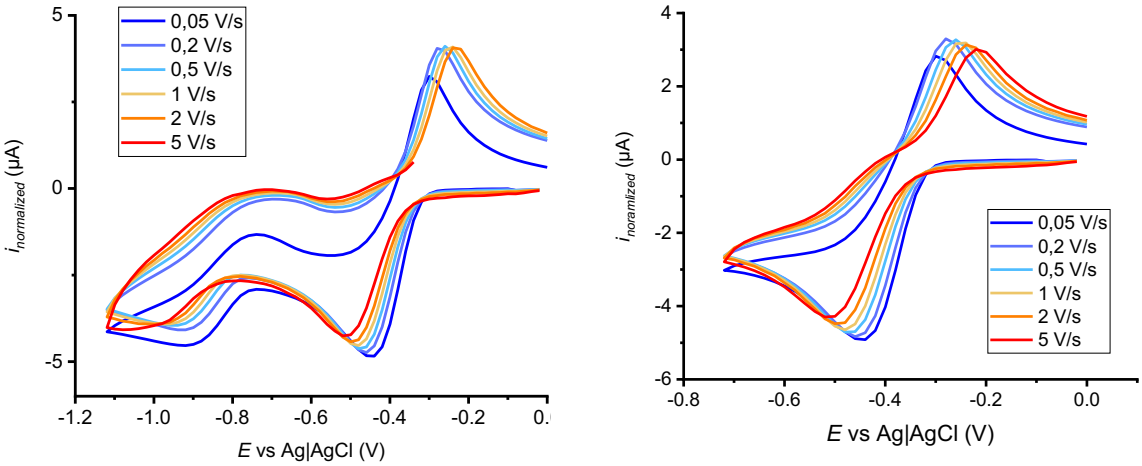


Fig. S9. CV of **6** (2mM concentration) performed in DMF with nBu_4NBF_4 (0.1mol.L^{-1}) as supporting electrolyte varying the scan rate.

CV of **6** with increasing amounts of Et_3N in DMF.

As observed in DMSO, after addition of one equiv of a base, the two reduction peaks at -0.45 V and -0.90 V merged to give a unique wave at -1.0 V (left). Towards oxidation potentials, we observed a similar evolution to the one discussed for DMSO, with the loss of the oxidation wave at +1.10V and an increase of a less defined wave at more positive potentials, consistently with the oxidation of catecholate (right).

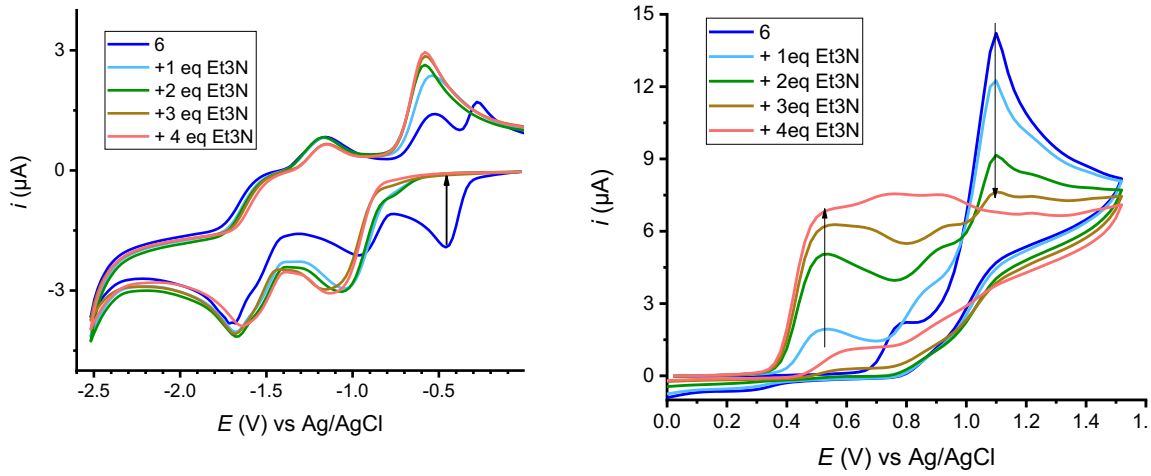


Fig. S10. CV of **6** (2mM concentration) with increasing amounts of Et_3N in DMF with nBu_4NBF_4 ($0.1mol.L^{-1}$) as supporting electrolyte.

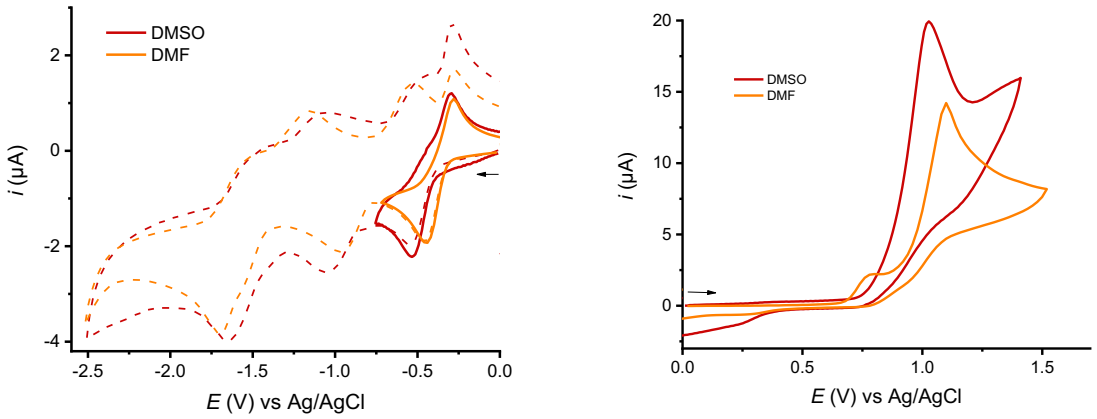


Fig. S11. Comparison of the redox potentials of **6** (2mM concentration) in DMF and DMSO with nBu_4NBF_4 ($0.1mol.L^{-1}$) as supporting electrolyte for the protonated species (scan rate 0.2 Vs^{-1}).

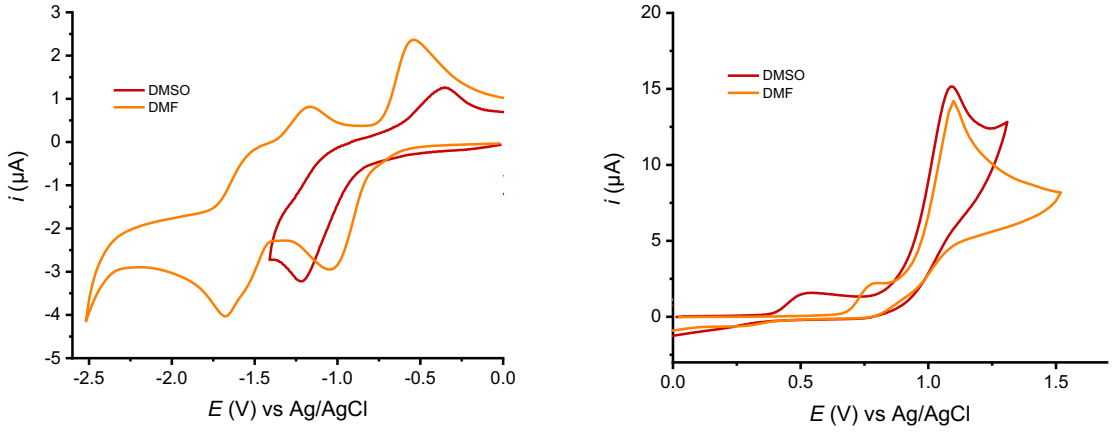


Fig. S12. Comparison of the redox potentials of **6** (2mM concentration) with one equivalent of Et_3N in DMF and DMSO with nBu_4NBF_4 ($0.1mol.L^{-1}$) as supporting electrolyte for the protonated species (scan rate 0.2 Vs^{-1}).

Cyclic Voltammetry of **5**

The concentration of **5** was 2.7 mM, which is above saturation. The addition of one equivalent of acetic acid allowed complete solubilization of the substrate, which could explain the observed increase of relative intensities. Conversely, when adding 1 equiv of acetic acid on **5**, a lower anodic shift was observed ($D E_{1/2}$ = 50 mV, Fig. S13a). The different behavior between intermediate **5**.H^+ and ligand **6** advocates for a protonation of **5** on a different site compared to **6**.

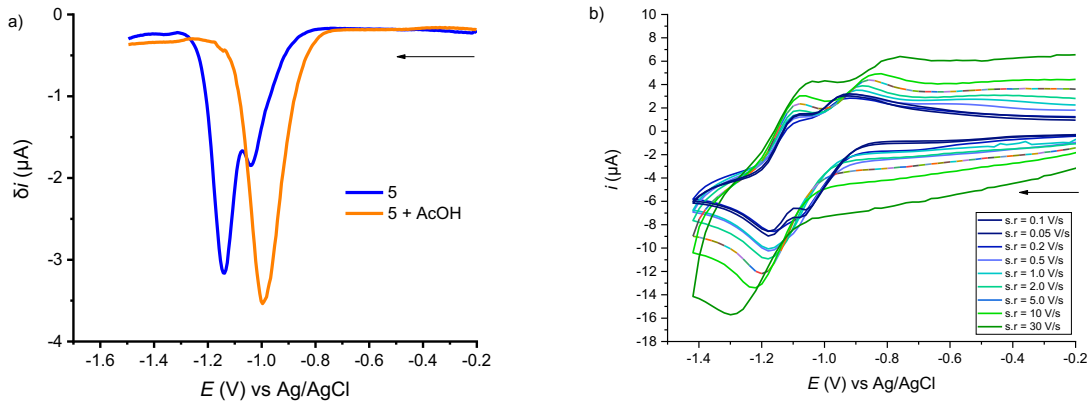


Fig. S13. a) Square-wave voltammetry of a 2 mM solution of intermediate **5** in DMSO with 0.1 M of nBu_4NBF_4 as supporting electrolyte at rt with 5 mV of step, 10 mV of E_{SW} at 5 Hz.; b) CV of **5** alone in DMSO with a GC 3 mm diameter as working electrode.

At low scan rate two successive reduction waves can be observed. They collapse into one single wave for a scan rate higher than 0.5 Vs^{-1}.

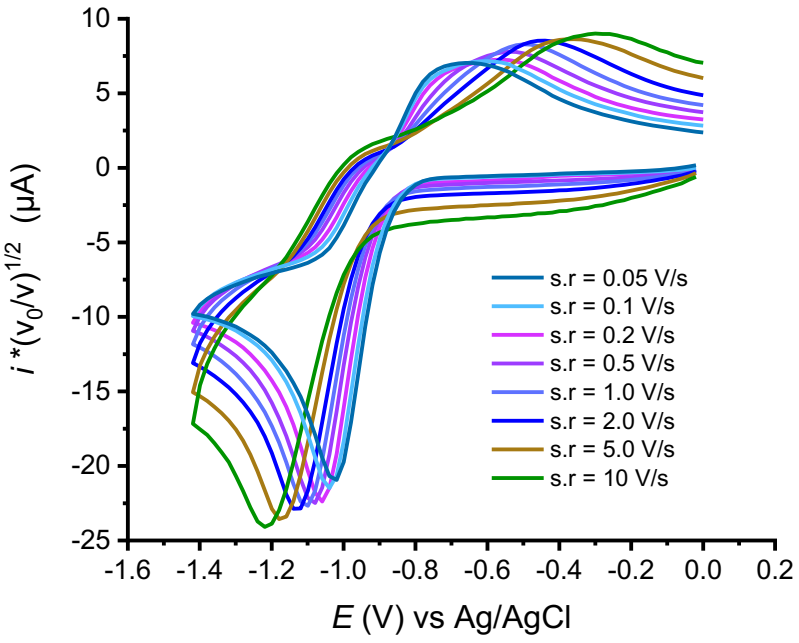


Fig. S14. CV of **5** (2mM concentration) with one equivalent of acetic acid in DMSO with nBu_4NBF_4 ($0.1 mol.L^{-1}$) as supporting electrolyte with a GC 3 mm diameter as working electrode.

Addition of one equiv of acid merges the two successive waves observed for **5** at low scan rates into a single wave. The potential shift observed when increasing the scan rate is in favor of a two-electron reduction occurring thanks to a coupling with a proton exchange.

The SWV experiment (right) illustrated better the presence of two reduction waves without acid and it also allows to prove the easier reduction of **5** when protonated. Indeed, the reduction is shifted by more than 50 mV for the half peak potential.

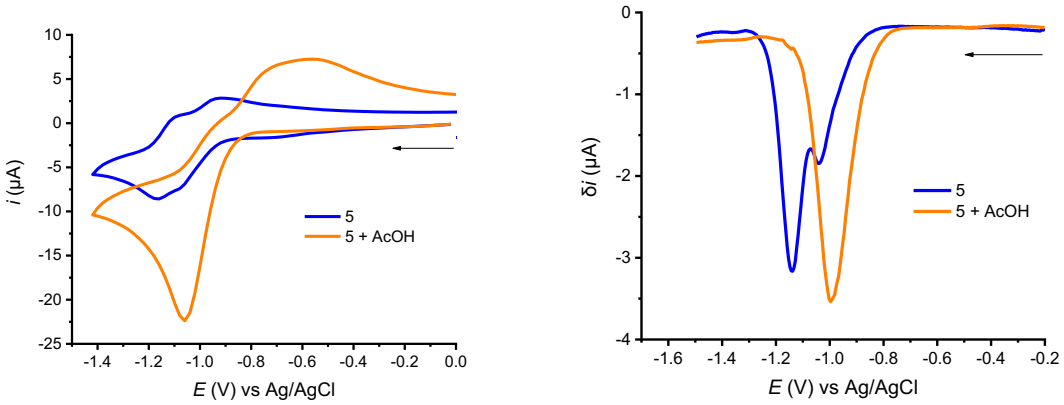


Fig. S15. CV of **5** (2mM concentration) in DMSO with 0.1 M of nBu_4NBF_4 as supporting electrolyte at 0.2 Vs^{-1} and square wave voltammetry (SWV) (potential step 5 mV, amplitude modulation 10 mV, frequency 5Hz).

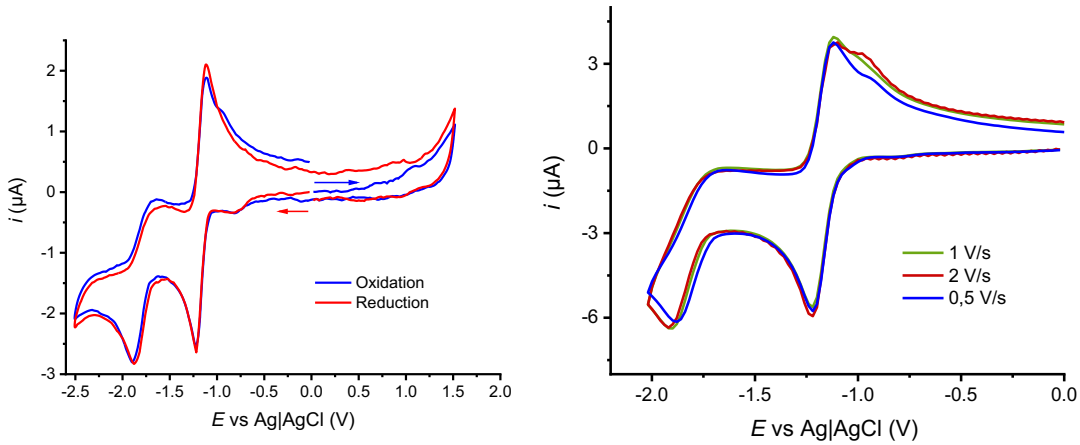


Fig. S16. CV of **5** (2mM concentration) in DMF with nBu_4NBF_4 (0.1mol.L^{-1}) as supporting electrolyte.

When adding one equiv of acetic acid, only one reduction wave can be detected, which due to its intensity probably accounts for a three-electron transfer. The addition of more than one equiv of acid did not greatly modify the CV.

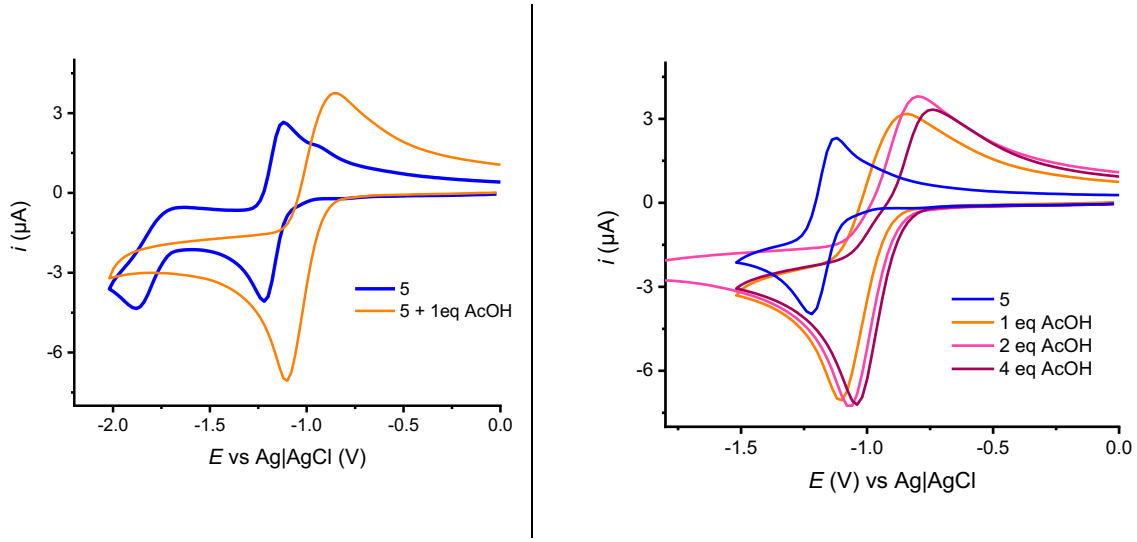
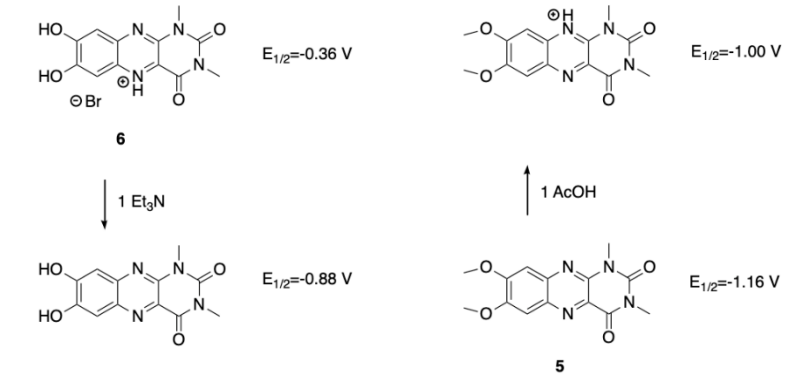
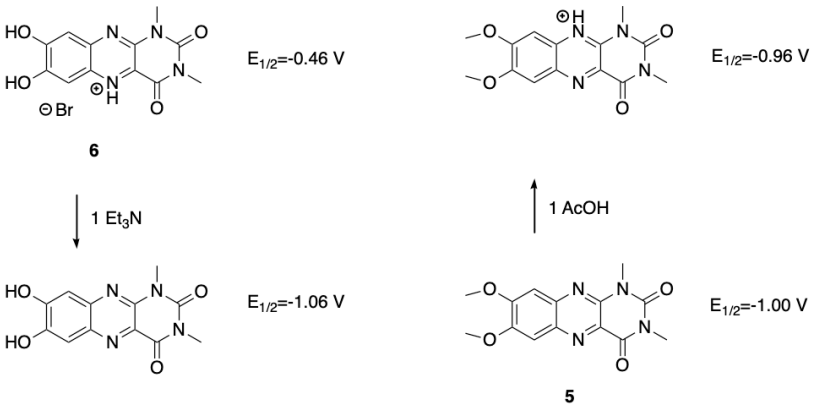


Fig. S17. CV of **5** (2mM concentration) in DMF with nBu_4NBF_4 ($0.1mol.L^{-1}$) as supporting electrolyte in the presence of acetic acid.

Half wave potentials toward Ag|AgCl reference in DMF at $0.2\ Vs^{-1}$



Half wave potentials toward Ag|AgCl reference in DMSO at $0.2\ Vs^{-1}$



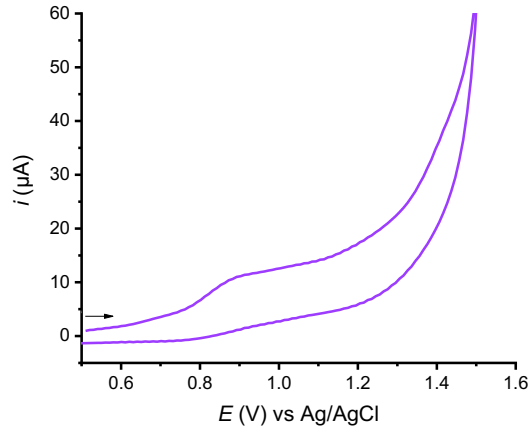


Fig. S18. CV of **7** (saturated) towards oxidation potentials in DMSO with nBu_4NBF_4 (0.1mol.L^{-1}) as supporting electrolyte.

The solubility of **7** is very low even at 100 °C. The reduction wave is very poorly defined, and the half wave potential can be roughly estimated to -1.3 ±0.1 V *vs* Ag|AgCl.

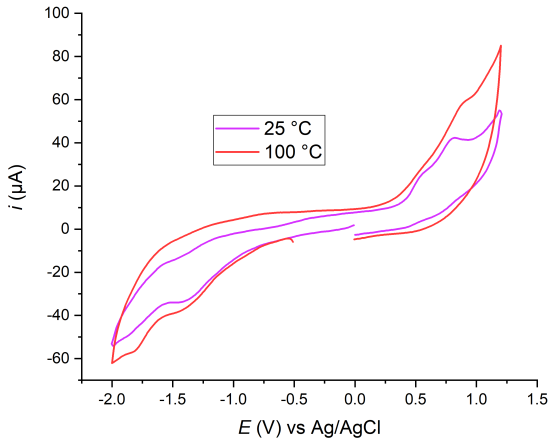


Fig. S19. CV of **7** (saturated) in DMF with nBu_4NBF_4 (0.1 mol.L^{-1}) as supporting electrolyte at 25 °C and 100 °C.

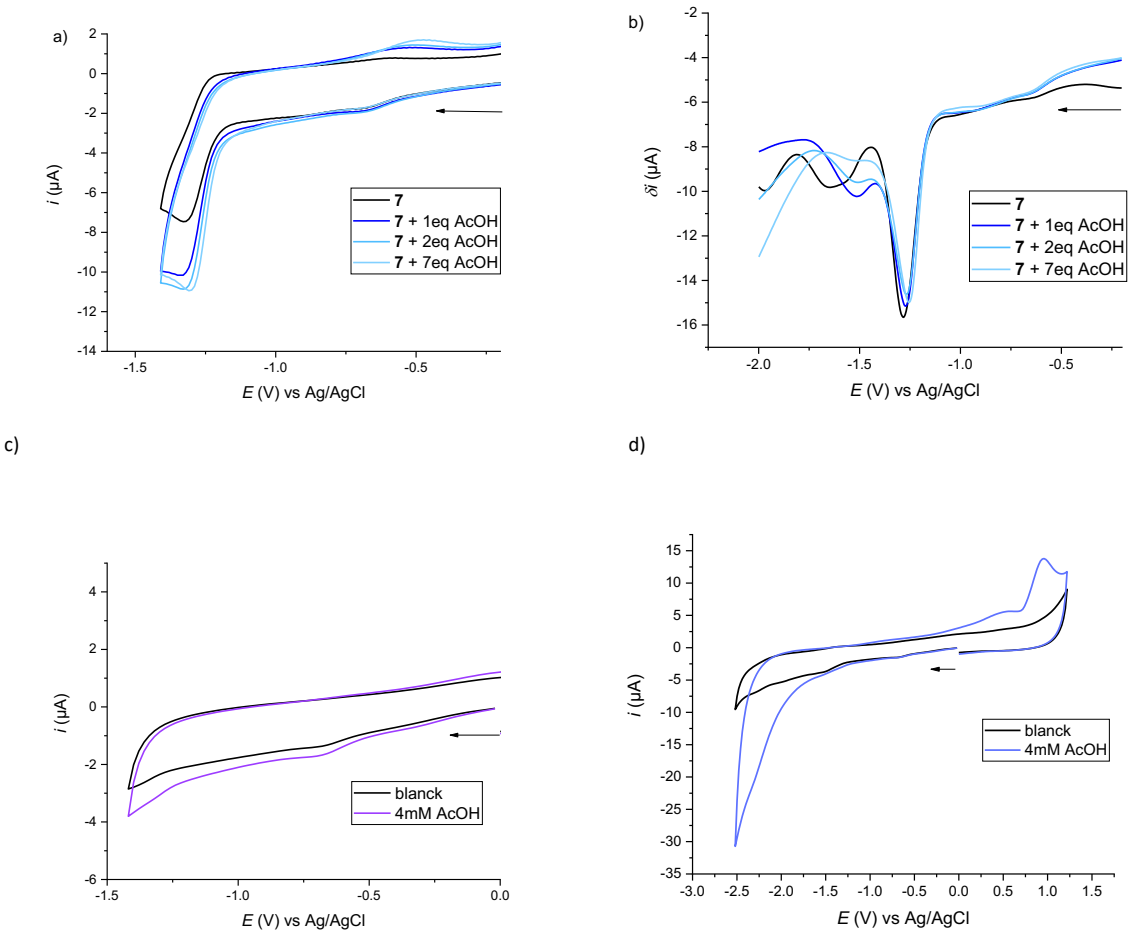


Fig. S20. CV of **7** (saturated) in DMSO with nBu_4NBF_4 (0.1 $mol.L^{-1}$) as supporting electrolyte with increasing amounts of AcOH (a.), square wave voltammetry (b.) (potential step 5 mV, amplitude modulation 50 mV, frequency 25Hz) in the same conditions, control experiments for AcOH in DMSO (c and d, conditions : Ref Ag|AgCl, WE : GC 3mm, CE : Pt. Solvent : DMSO, Electrolyte TBABF4 0.1M, scan rate 0.2 V/s, T = r.t.).

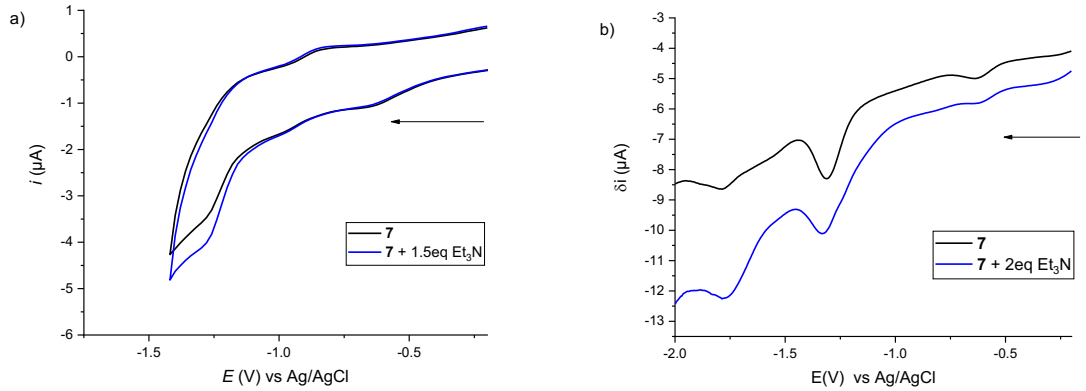


Fig. S21. a) CV of **7** (saturated) and b) Square wave voltammetry of **7** (saturated) both in DMSO with nBu_4NBF_4 ($0.1mol.L^{-1}$) as supporting electrolyte with increasing amounts of Et_3N (potential step 5 mV, amplitude modulation 50 mV, frequency 25Hz).

UV-Vis studies

Oxidation of 7 using ferrocenium hexafluorophosphate ($FcPF_6$) in DMSO

The oxidation was monitored by UV-Vis spectroscopy upon addition of one equivalent $Fc^+PF_6^-$ every 15 minutes. A 10^{-5} M solution of **7** in dry DMSO was degassed by argon bubbling for 30 minutes before measuring the spectra. Cuvette capacity is 1.5 mL and was filled with 1 mL of complex solution. The concentration of $Fc^+PF_6^-$ was calculated so that 10 µL corresponds to 1 equivalent of the complex solution. Volume correction were neglected. 10 µL x S_1= 1 mL (cuvette volume) x $1x10^{-5}$ M (conc. of **7**) → S_1= 10^{-3} M. Therefore, 10^{-3}M $Fc^+PF_6^-$ solution was prepared in dry DMSO and degassed.

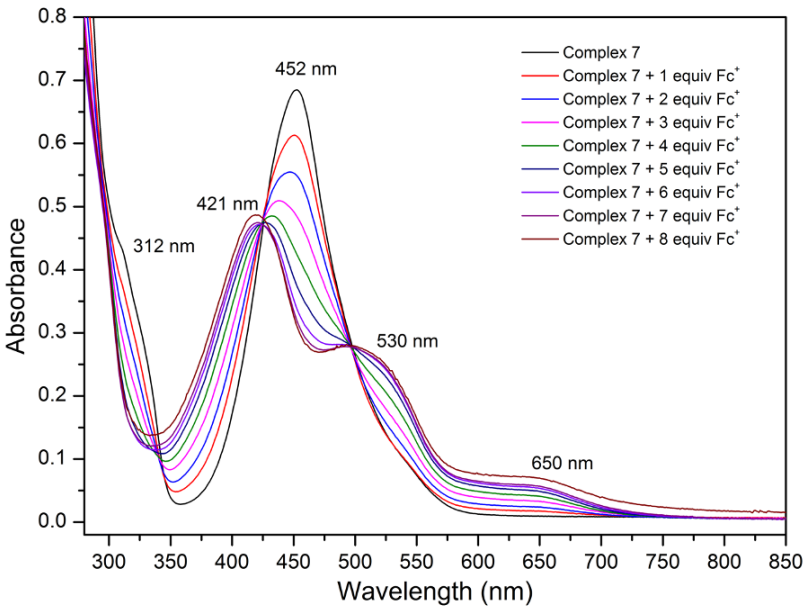


Fig. S22. UV-vis monitoring of the oxidation of **7** (crystal) ($1x10^{-5}$ M) in the presence of ferrocenium hexafluorophosphate (Fc^+) ($1x10^{-3}$ M) in degassed DMSO at room temperature.

Addition of 8 equiv. Fc^+ in a single step led to a decrease of the characteristic bands of **7**, and the profile corresponding to full oxidation of complex was observed after adding excess Fc^+ (16 equiv.). The UV-vis profile was then monitored with an interval of 20 min between data collection and showed slow evolution towards the final state. These observations suggest that the reaction kinetics is not fast and equilibrates over the course of several hours, which is compatible with the mild oxidative power of Fc^+. Longer equilibration times led to the observation that 6 equiv. oxidant was enough to perform full oxidation of **7**. These experiments also show that the oxidized species is stable in presence of excess amount of oxidant.

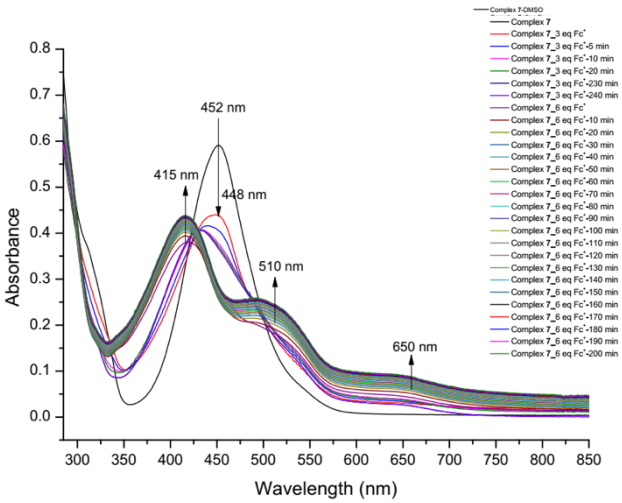


Fig. S23. Oxidation of **7** (crystal) ($1x10^{-5}$ M) with varying amounts of ferrocenium hexafluorophosphate (Fc^+) ($1x10^{-3}$ M) in degassed DMSO at room temperature: 8 to 16 equiv. (top), 3 to 6 equiv. (bottom).

Oxidation of 7 by $NOBF_4$ in DMSO

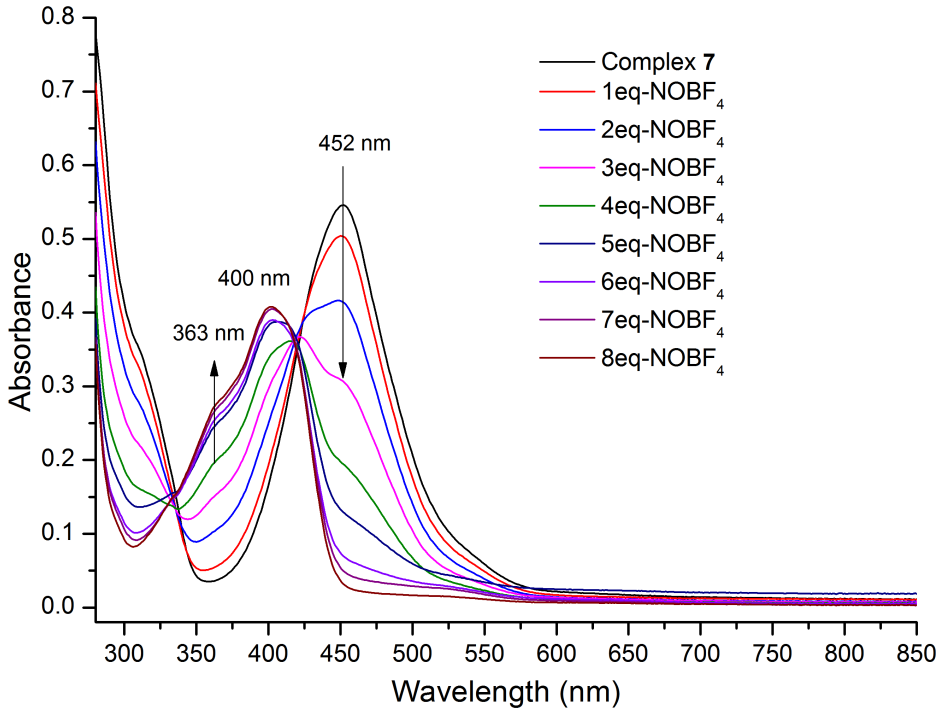


Fig. S24. Oxidation of **7** (crystal) ($1x10^{-5}$ M) in the presence of nitrosonium tetrafluoroborate ($NOBF_4$) ($2x10^{-3}$ M) in degassed DMSO at room temperature.

Oxidation monitoring by UV-vis was also performed with nitrosonium tetrafluoroborate ($NOBF_4$) as stronger oxidant. The solution of **7** was monitored by UV-Vis spectroscopy upon addition of 1 equiv. $NOBF_4$ (5 µL of $2x10^{-3}$ M DMSO solution) every 16 min. During this 16 minutes delay, the UV-Vis spectra was recorded every 2 min. For the whole spectra, the final (16 min spectra) absorbance values were taken. The addition of $NOBF_4$ shows a continuous intensity decrease of the absorbance band at 452 nm until 3 equiv. addition with appearance of a new band at 421 nm. Upon further addition of $NOBF_4$ (6 equiv.), the characteristic bands of **7** completely disappear and absorbance bands at 400 nm and a shoulder band at 363 nm are observed, which are characteristic bands for the pro-ligand **6**, thus suggesting decomplexation rather than oxidation of the complex. Moreover, the solution turns from orange to light yellow, while with Fc^+ oxidation, the solution color turned reddish brown.

Reduction of 7 using cobaltocene ($CoCp_2$) in DMSO

The reduction was monitored by UV-Vis spectroscopy in a septum-sealed cuvette with occasional argon flow to keep the system inert and upon addition of one equivalent of cobaltocene ($CoCp_2$) every 15 minutes. A 10^{-5} M solution of **7** in dry DMSO was degassed by argon bubbling for 30 minutes before measuring the spectra. Cuvette capacity is 1.5 mL and was filled with 1 mL of complex solution. The concentration of $CoCp_2$ was calculated so that 10 µL corresponds to 1 equivalent of the complex solution. Volume correction were neglected. 10 µL x S_1= 1 mL (cuvette volume) x $1x10^{-5}$ M (conc. of **7**) → S_1= 10^{-3} M. Therefore, 10^{-3}M $CoCp_2$ solution was prepared in dry DMSO and degassed.

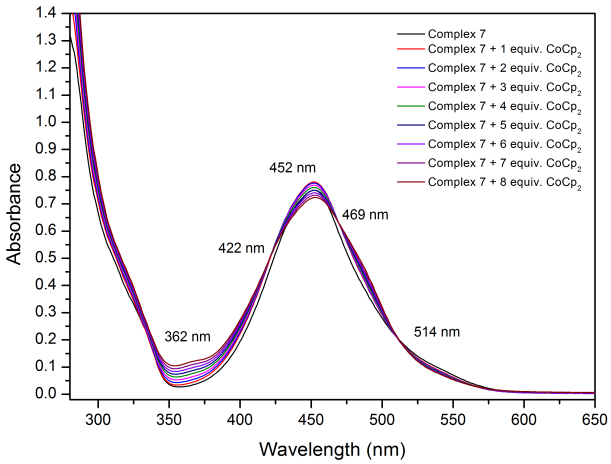


Fig. S25. Reduction of **7** (crystal) ($1x10^{-5}$ M) in presence of cobaltocene ($CoCp_2$) ($1x10^{-3}$ M) in degassed DMSO at room temperature.

Chemical reversibility: successive oxidation with $Fc^{+}PF6^{-}$ and reduction with $CoCp_2$

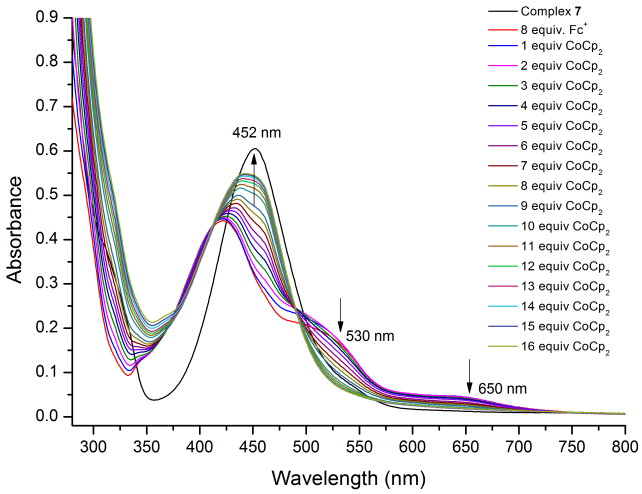


Fig. S26. Oxidation of **7** (crystal) ($1x10^{-5}$ M) with increment addition of ferrocenium hexafluorophosphate ($2x10^{-3}$ M) up to 8 equivalents followed by reduction with $CoCp_2$ ($2x10^{-3}$ M) in degassed DMSO at room temperature.

A degassed DMSO solution of **7** ($1x10^{-5}$ M) was prepared under argon and was oxidized anaerobically by 1 equiv. increments of ferrocenium hexafluorophosphate (5 µL, $2x10^{-3}$ M solution in DMSO) and UV-Vis spectra were collected. $FcPF_6$ oxidation was carried out up to 8 equivalents, then one electron reductant $CoCp_2$ ($2x10^{-3}$ M) was added in one equivalent increments (5 µL), the results show a reduction of the oxidized species from **7** which supports a chemically reversible oxidation.

IR studies

Fourier transformed infrared spectroscopy

The infrared spectra of the hybrid pro-ligand **6** and the **7** were obtained with a Vertex 70 FTIR spectrometer (Bruker, Germany) equipped with a liquid nitrogen MCT (mercury cadmium telluride) detector. The spectrometer was purged with dry air to avoid the contributions from humidity in the spectra. The FTIR spectra of the samples were obtained in the attenuated total reflection mode (ATR) (Harrick crystal, Diamond Prism), and recorded in the spectral range from 4000 to 800 cm^{-1} with a scan velocity of 40 kHz. Three spectra with a resolution of 4 cm^{-1} (256 co-added scans) were averaged for each sample. The ATR-FTIR spectra of the ligand, and the complex samples were performed from powders, previously dried under high vacuum.

H/D exchange experiments were conducted on the Ni-complex in the presence of H_2O and D_2O. 0.1 mL H_2O (Milli Q) or D_2O (D_2O solution with 100 atoms % D, Acros Organics, USA), were mixed for 1 hour at room temperature with 0.5 mL of a DMSO solution of the complex (500 µM). Then, the sample was again air dried on an ATR crystal creating a thin film.

ATR-FTIR spectra were recorded with the Opus software from Bruker Bruker (Opus. 6.0) and analysed with Origin program (OriginLab. 8.5). The contributions of DMSO solvent were interactively subtracted from each sample spectrum and baseline correction was applied.

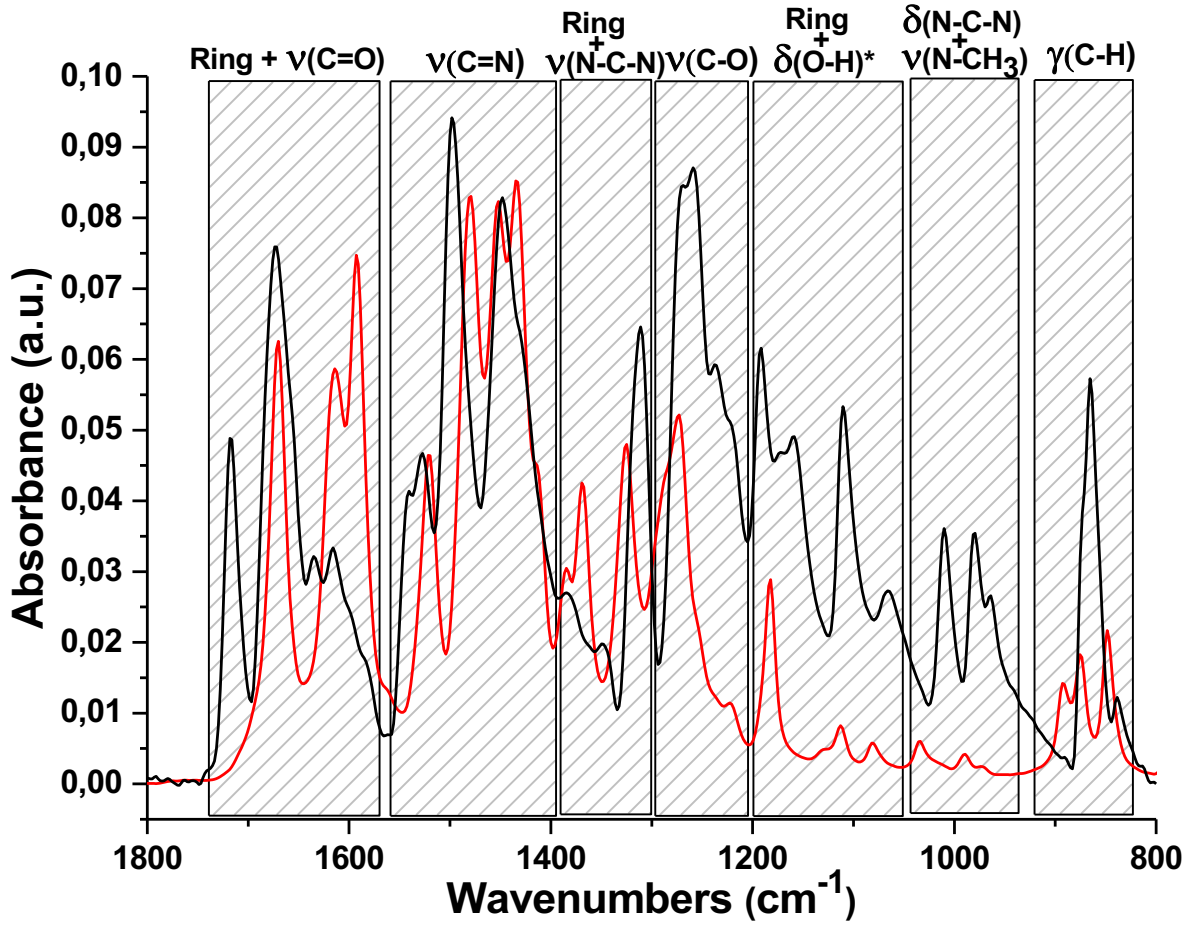


Fig. S27. ATR-FTIR spectra of the hybrid ligand (black curve) and the nickel complex (red curve) as powders.
*The OH deformation vibration is assigned only to the ligand structure.

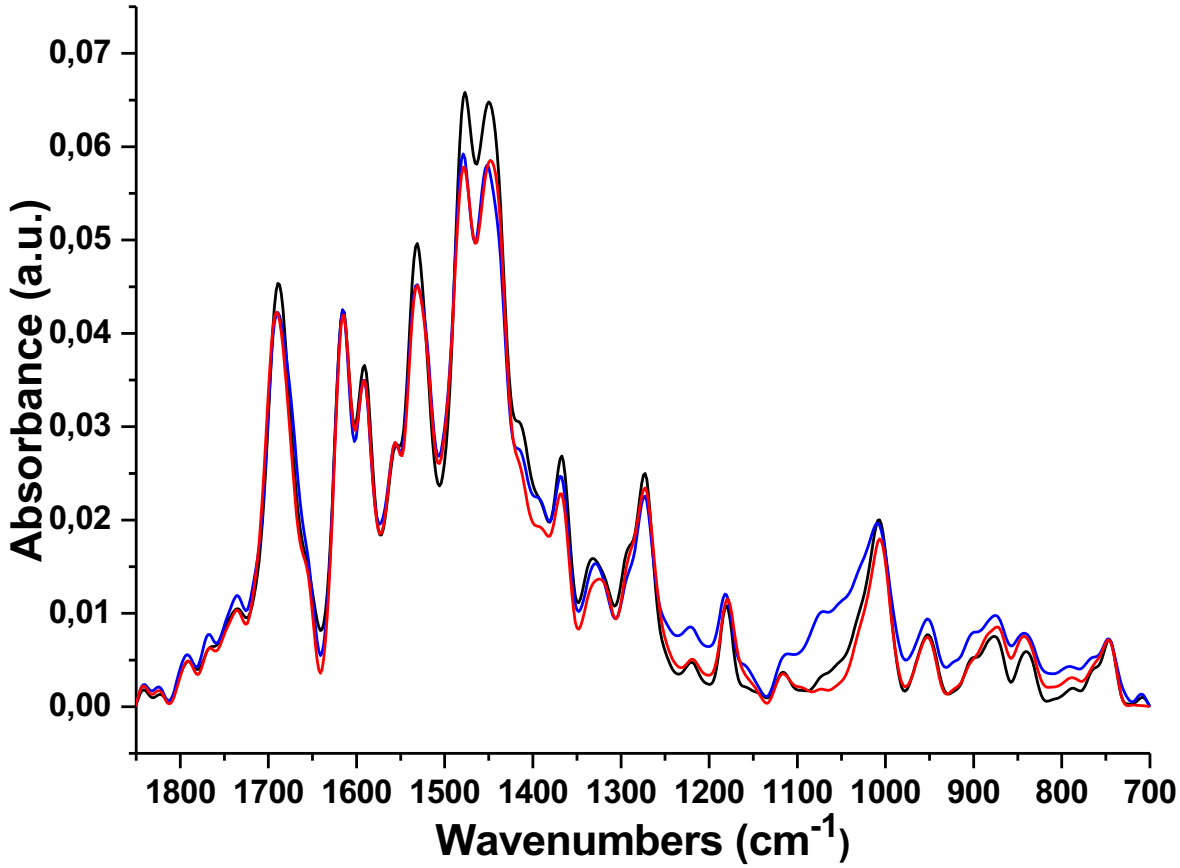


Fig. S28. ATR-FTIR spectra of the nickel complex as dry films from solutions in DMSO (black curve), in DMSO in the presence of H_2O (blue curve) and in DMSO in the presence of D_2O (red curve). The DMSO solvent was interactively subtracted from each spectrum.

Table S2. Tentative assignments for the peaks from the ATR-FTIR spectra of **6** and **7** as powders (see Fig. S5). Vibrational assignments were made according to several previous studies on the alloxazine derivative and catechols.[8,9,10,11] *The 1158 cm^{-1} band is assigned to the OH deformation and the ring II vibration in the ligand structure.

Position (cm^{-1})		Tentative attribution
Ligand	Nickel Complex	
839 865	848 875	γ(C-H) γ(C-H)
963/979 1010	972/989 1034	ν(N-CH3) ν(N1-C2-N3)
1066 1110	1081 1112	Ring I δ(C-H)
1158 1191	- 1182	δ(O-H)* + Ring II
1237 1270	1222 1272	ν(C7-O7) or ν(C8-O8) ν(C7-O7) or ν(C8-O8)
1311 1349/1384	1324 1369/1384	Ring II ν(N1-C2-N3)
1429 1448	1412 1434/1452	ν(N1-C2-N3) ν(C4a=N5) or ν(C10a=N10)
1498 1527	1479 1521	ν(C4a=N5) or ν(C10a=N10) ν(C-N)
1615 1635	1615 -	Ring I Ring I
1673 1718	1591 1670	ν(C4=O4) ν(C2=O2)

[8] M. Abe, Y. Kyogoku, T. Kitagawa, *Spectrochim. Acta.* **1986**, *42A*, 1059-1068.
[9] O. Heilmann, F. M. Hornung, J. Fiedler, W. J. Kaim, *Organomet. Chem.* **1999**, *589*, 2-10.
[10] S. Griffith, W. Greaves, *Spectrochim. Acta.* **1991**, *47A*, 133-140.
[11] R. Foglizzo, A. Novak, *Appl. Spectrosc.* **1970**, *24*, 601-605.

Table S3. Tentative assignments for the peaks from the ATR-FTIR spectra of **7** as dry films from solutions in DMSO, in DMSO in the presence of H_2O and in DMSO in the presence of D_2O (see Fig. S6). Vibrational assignments were made according to several previous studies on the alloxazine derivative and catechols.[8,9,10,11]

Position (cm^{-1})			Tentative attribution
Nickel Complex in DMSO	Nickel Complex in DMSO-H_2O	Nickel Complex in DMSO-D_2O	
841 876	842 875	843 871	γ(C-H) γ(C-H)
952 1007	952 1009	952 1007	ν(N-CH3) ν(N1-C2-N3)
1074 1117	1076 1116	1073 1117	Ring I δ(C-H)
1180	1182	1179	Ring II
1220 1273	1221 1273	1218 1273	ν(C7-O7) or ν(C8-O8) ν(C7-O7) or ν(C8-O8)
1332 1367/1390	1328 1369/1392	1324 1369/1391	Ring II ν(N1-C2-N3)
1412 1450	1413 1452	1413 1448	ν(N1-C2-N3) ν(C4a=N5) or ν(C10a=N10)
1477 1531/1554	1479 1531/1556	1479 1531/1556	ν(C4a=N5) or ν(C10a=N10) ν(C-N)
1590 1616	1591 1616	1590 1616	ν(C4=O4) Ring I
1689	1689	1691	ν(C2=O2)

EPR studies

EPR spectra were recorded on an EMXplus spectrometer (Bruker Biospin GmbH) operating at Q-band (34 GHz), equipped with a high sensitivity resonator (ER5106QT, Bruker) and a helium cryostat ER4118CFO for the low temperature measurements. Powder samples were sealed in quartz tube and degassed for three cycle using freeze-pump-thaw technique. Powder X-ray diffraction (PXRD) were performed on Bruker D8 Advance with X-ray source by anticathode of cooper giving photons with a wavelength of $1.54x10^{-10}$ m.

Solid-state MAS-NMR studies

Solid-state MAS NMR experiments were acquired on an AVANCE 750 MHz wide bore spectrometer (Bruker™) operating at a frequency of 750.12 MHz for ^{1}H. ^{1}H spectra and ^{207}Pb ones for temperature calibration were obtained by spinning at several speeds, from 50kHz to 62kHz, in a triple resonance ^{1}H/^{13}C/^{15}N Ultra-Fast MAS probe (Bruker™) designed for 1.3 mm o.d. zirconia rotors (closed with vespel caps). Sample temperatures were controlled by the spectrometer vendor's system ("VTU" - Variable Temperature Unit- linked to a "BCU Extreme" -Bruker Cooling Unit-). At such spinning rates it is well known that air friction against rotor walls can induce dramatic temperature increase inside the sample, up to more than 70°C at 62kHz. It was confirmed when doing the temperature calibrations, based on ^{207}Pb chemical shifts variations with temperature of a $Pb(NO_3)_2$ sample[12,13]: a series of ^{207}Pb spectra (data not shown) were acquired with the same spinning rates and temperature control system settings to measure the real mean sample temperatures. Conversely, even if the highest attainable MAS rate is preferred to get the best possible resolution (Fig. S24) the choice was done to record the variable temperature data by spinning at 50kHz. We estimated it as being the best compromise between resolution and temperature range spread. It led us to acquire a series of 18 ^{1}H spectra with temperature ranging from 297.6 K to 332.9 K (Fig. S25). A temperature equilibration delay of 90 minutes separated each spectrum acquisition.

As with MAS rates of 50kHz to 62 kHz we were spinning fast enough to highly reduce the ^{1}H homonuclear dipolar interactions, and in order to filter out background probe signals to get undistorted lineshapes, a speed synchronized spin echo[14] pulse scheme was used (P_{90}-□-P_{180}-□), with the following conditions : 1.27 µs and 2.54 µs for $P_{90°}$ and $P_{180°}$ pulses to ensure the minimal spectral coverage (1MHz spectral width), while echo time (□) was set equal to 2 rotation periods (40 µs and 32,26 µs for 50 kHz and 62 kHz respectively). 32768 time domain data points were acquired then leading to a 61 Hz/pt spectral resolution. Separated by a 200 ms recycle delay, 8192 scans were added giving a total experimental time per spectrum equal to ca 28 minutes. This short recycle delay, unusual in solid state ^{1}H NMR spectroscopy was derived from relaxation experiments (not shown) based upon the inversion-recovery method. Measured T_1's were ranging from 280 µs to 650 µs, much smaller than the 200 ms recycle delay whose final choice was therefore mainly directed by probe duty-cycle considerations rather than relaxation. Those extremely short relaxation delays together with the abnormals ^{1}H spectral range and chemical shifts (Fig. S24) are unambiguously showing the presence of a paramagnetic interaction (nucleus with unpaired electrons). Raw data were processed with a 50 Hz Lorentzian filter followed by Fourier transformation without zero filling.

[12] A. Bielecki, D. P. Burum, *J. Magnet. Res., Series A* **1995**, *116*, 215-220.
[13] P. A. Beckmann, C. Dybowski, *J. Magnet. Res.*, **2000**, *146*, 379-380.
[14] E. L. Hahn, *Phys. Rev.*, **1950**, *80*, 580-594.

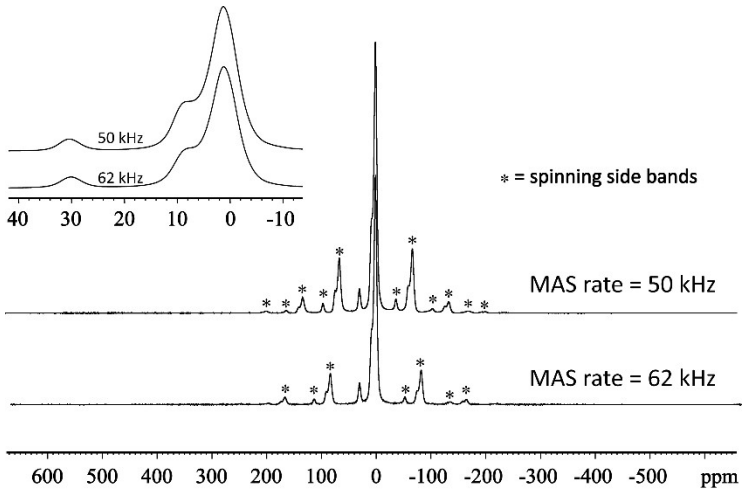


Fig. S29. Solid State ^{1}H NMR spectra obtained at 62 kHz (lower trace) and 50 kHz MAS rates (upper trace), both obtained at 295.7°K. Even if the faster spin-rate exhibits less spinning side bands the resolution is only slightly improved, as shown by the isotropic chemical shift zone expansion (upset). The variable temperature study was then conducted by spinning at 50kHz, for higher temperature range access.

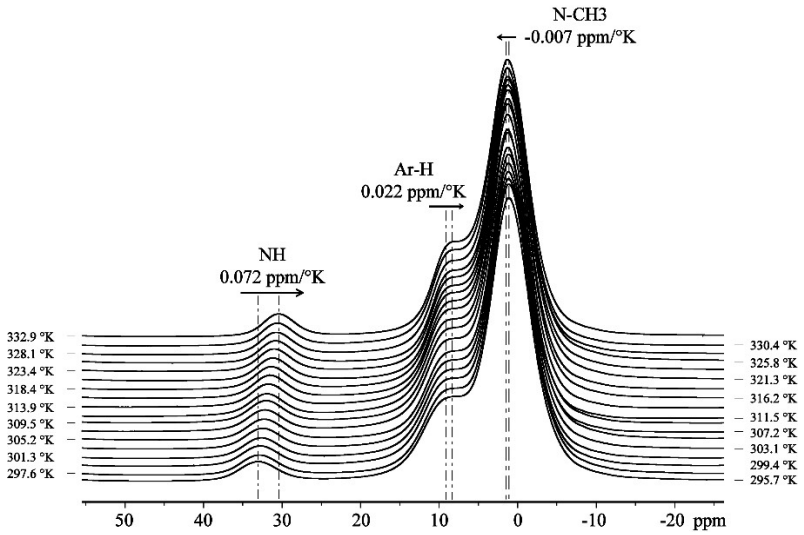


Fig. S30. Variable temperature Solid State ^{1}H NMR, ranging from 295.7°K to 332.9°K. The 3 observed isotropic chemical shifts peaks are observed to be linearly sensitive to the temperature. While the NH and AR-H δ_{iso}^{obs} are moving to lower chemical shifts with increasing temperature (0.072 and 0.022 ppm/°K respectively) the N-CH_3 is doing the opposite (-0.007 ppm/°K).

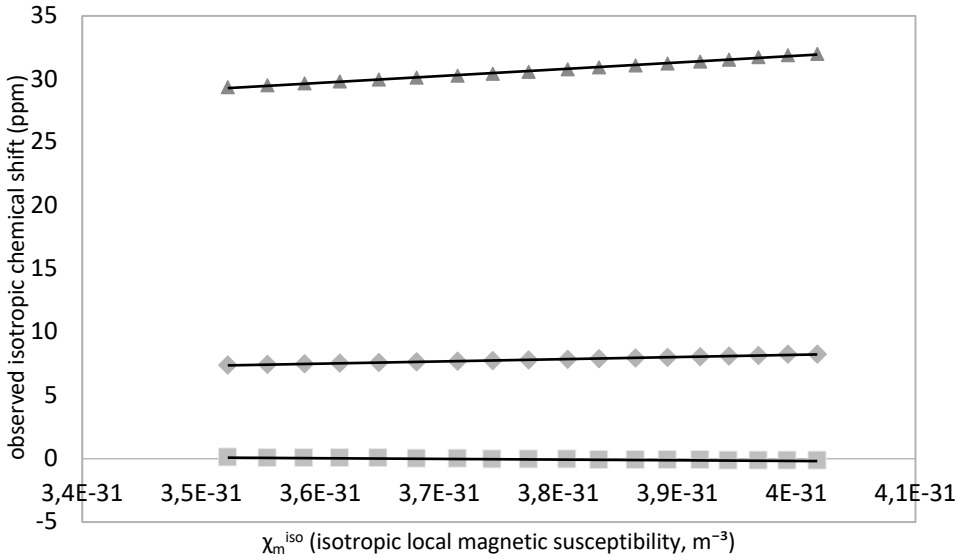


Fig. S31. Isotropic chemical shifts (δ_{iso}^{obs}) versus isotropic local magnetic susceptibility (χ_m^{iso}). The observed linear dependence allows for diamagnetic shifts and hyperfine coupling constants determinations.

Each plot is an affine function[15] of the form: $\delta_{iso}^{obs} = \frac{A}{\gamma\hbar\mu_0\mu_B gS}\chi_m^{iso} + \delta_{iso}^{dia}$ where A is the hyperfine coupling constant, γ the gyromagnetic ratio, μ_0 the vacuum magnetic permeability, μ_B the Bohr magneton of the electron δ_{iso}^{obs} the observed isotropic shift, δ_{iso}^{dia} the diamagnetic shift and χ_m^{iso} the isotropic local magnetic susceptibility.

Assignment	δ_{iso}^{dia} (/ppm)	A/h (MHz)
N-CH_3	2,0	-0,23
Ar-H	1,2	0,76
N-H	10,4	2,32

Table S4. Proposed assignments.

SQUID measurements

The magnetic measurements were conducted using a Quantum Design MPMS-3 magnetometer. The static susceptibility measurements were performed in the 1.8 K – 300 K temperature range with an applied field of 0.5 T. Magnetization measurements at different fields and at given temperature confirm the absence of ferromagnetic impurities. Data were corrected for the sample holder and diamagnetism was estimated from Pascal constants.

The fits of the magnetic data were performed using the PHI program.[16] The magnetic interaction constants *J* are reported with respect to the $-2J\,S_1 \cdot S_2$ spin coupling Hamiltonian.

[15] D. Carlier, M. Ménétrier, C. P. Grey, C. Delmas, G., Ceder, *Phys. Rev. B*. **2003**, *67*, 174103.

[16] N. F. Chilton, R. P. Anderson, L. D. Turner, A. Soncini, K. S. Murray, *J. Comput. Chem.* **2013**, *34*, 1164.

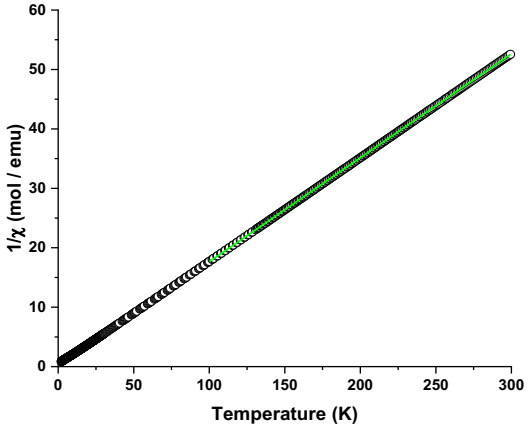


Fig. S32. Plot of 1/c *vs. T* for the title compound under an applied *dc* field of 0.5 kOe. Open symbols: experimental points, full green line: best fit with a Curie-Weiss law (see text).

DFT Computational studies

All calculations were performed using the ORCA program package.[17] Full geometry optimizations were carried out for all complexes in the high-spin state using the GGA functional BP86[18] in combination with the def2-TZV/P[19] basis set for all atoms and by taking advantage of the resolution of the identity (RI) approximation in the Split-RI-J variant[20] with the appropriate Coulomb fitting sets.[21] Increased integration grids (Grid4 in ORCA convention) and tight SCF convergence criteria were used. For according to the experimental conditions, these calculations were performed in gas phase. Electronic structures were obtained from single-point Broken-Symmetry DFT calculations using the hybrid functional B3LYP[22] together with the def2-TZVP basis set. All possible spin configurations for the broken-symmetry[23] calculations were generated with the "FlipSpin" feature of ORCA. Spin density plots were generated using the orca plot utility program and were visualized with the Chemcraft program.[24]

Electronic structure of the triangle

Metal-complex **7** is neutral as proven by X-ray diffraction studies. However, the partial or total protonation of the flavin nitrogens as well as the number of the organic radicals delocalized within the flavin/catechol ligand were investigated and our results are shown in Table S5.

[17] F. Neese, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2012**, *2*, 73.
[18] a) J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822; b) J. P. Perdew, *Phys. Rev. B* **1986**, *34*, 7406; c) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098.
[19] A. Schäfer, C. Huber, R. J. Ahlrichs, *Chem. Phys.* **1994**, *100*, 5829.
[20] F. Neese, *J. Comput. Chem.* **2003**, *24*, 1740.
[21] F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057.
[22] a) A. D. Becke, *J. Chem. Phys.* 1993, 98, 1372; b) C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B* 1988, *37*, 785.
[23] a) L. Noodleman *J. Chem. Phys.* **1981**, *74*, 5737; b) L. Noodleman, D. A. Case, *Adv. Inorg. Chem.* **1992**, *38*, 423; c) L. Noodleman, E. R. Davidson, *Chem. Phys.* **1986**, *109*, 131.
[24] Chemcraft, http://chemcraftprog.com

Table S5. Relative Gibbs free energies of the different electronic configurations considered for the description of **7**.

Protonation state (N122, N126, N130)	Number of organic radicals	Energy (Eh)	Energy difference (kcal/mol)
3	3	-8966.94	0
2 – N122, N126	2	-8966.38	354
1 – N122	1	-8965.81	708
1 – N126	1	-8965.81	708
1 – N122	3	-8965.76	737
1 – N126	3	-8965.76	737

The hypothesis that matches the best the experimental results is the presence of 3 high-spin Ni^{II} centers and 2 organic radicals delocalized within the flavin/catechol ligand (SQ-radicals), which is achieved by a partial protonation of the two flavin nitrogen, N_{122} and N_{126}, surrounding the Ni_{158} (Fig. S33, Table S5).

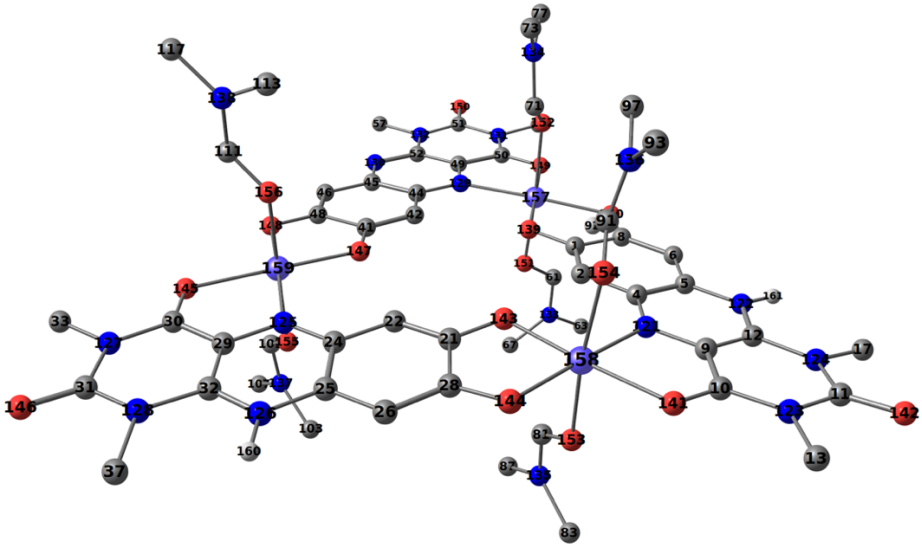


Fig. S33. Structure of **7** with protonated N_{126} and N_{122}. Hydrogens were removed for clarity.

System with two protons and two SQ-radicals

Mulliken spin population analysis was performed for the model with two protons and two SQ-radicals (Table S6). As expected, most of the spin density is localized at the Ni metal centers. C_5 (C_{25}), C_8 (C_{28}), N_{121} (N_{125}), N_{122} (N_{126}), and O_{141} (O_{145}) are the atoms with the highest spin density of the ligand (Figure S34). The above atoms constitute the SQ-radicals and display a total spin population of 1.68 close to the expected value of 2 (Table S6).

Table S6. Mulliken spin populations in **7** with two protons and two radicals.

Atoms	Spin population
C_5	0.22
C_8	0.14
N_{121}	0.35
N_{122}	0.09
O_{141}	0.06
C_{25}	0.20
C_{28}	0.13
N_{125}	0.35
N_{126}	0.08
O_{145}	0.06
Total SQ radical	1.68
Ni_{157}	1.69
Ni_{158}	1.69
Ni_{159}	1.69
O_{139}	0.12
O_{140}	0.19
O_{143}	0.12
O_{144}	0.21
O_{147}	0.07
O_{148}	0.05
Total	7.51

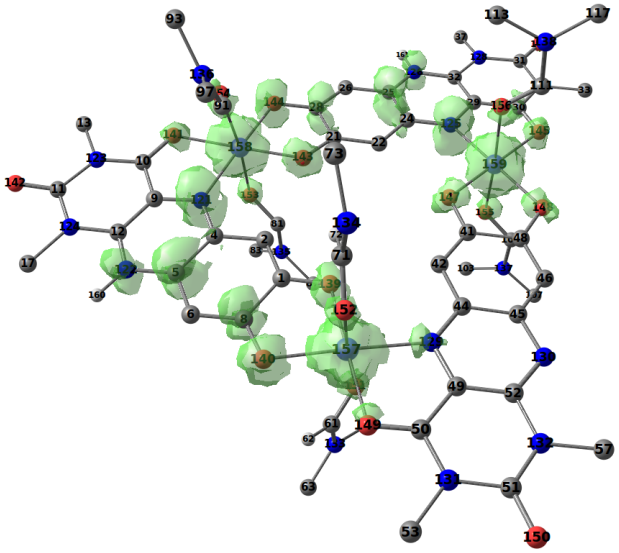


Fig. S34. Spin density plot of **7** considering 3 HS Ni(II) centers, two SQ-radicals and two protons on the ligand. Remaining hydrogen atoms were removed for clarity.

The total spin population of 7.5 is compatible with 8 unpaired electrons i.e. 2 electrons per Ni(II) center and 2 electrons from the organic radical. Our calculations show that the electronic structure of **7** can be adequately described considering 3 high spin metal centers and 2 radical ligands.

Electronic structures of model systems

- **Model A**

To study the magnetic interaction between the Ni^{II} ion and the SQ radical, we built model **A** with one high spin nickel, protonated catechol, and flavin moieties (Figure S37). The spin density population analysis was performed of model **A** (Figure S29-30 and Table S6).

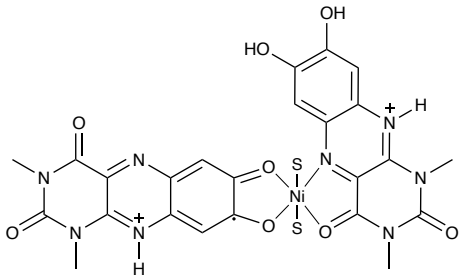


Fig. S35. Model **A** containing one Ni^{II} moiety.

A comparison between the spin density distribution in **7** with two protons and in model **A** is presented in Table S6, where the N_{61} center (equivalent to N_{121}) remains the atom with the highest spin population after Ni_{81}. Regarding O_{73} (= O_{141}) and O_{75} (=O_{143}), they still have almost the same population as in **7** as well as C_5 and C_8 (= C_5 and C_8). However, the spin population of N_{61} (= N_{121}) increases and that of O_{76} (= O_{144}) decreases compared to **7**, but it is compensated by the increase on N_{61} and N_{62}. Even if the spin density distribution in model **A** shows a small deviation from **7**, the atoms involved in the delocalization of the SQ radical in **7** are the same for model **A**. Model **A** is a fair representation for a single moiety from the full **7**, and BS-DFT calculations can be conducted based on these observations.

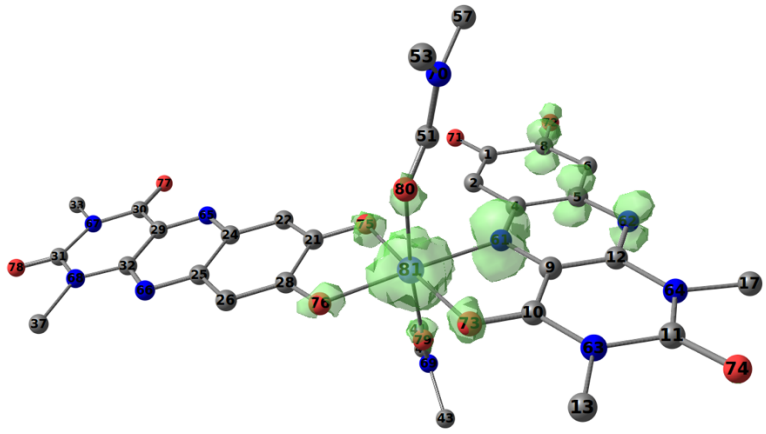


Fig. S36. Spin density plot for model **A** containing one Ni^{II} with chemically truncated ligands. Hydrogen atoms were removed for clarity.

Table S6. Comparison of Mulliken spin population distributions in model **A** and **7**.

Model A			**7**	
Atoms	**Spin population**		**Atoms**	**Spin population**
C_5	0.17		C_5	0.22
C_8	0.16		C_8	0.14
N_{61}	0.44		N_{121}	0.35
N_{62}	0.13		N_{122}	0.09
O_{73}	0.07		O_{141}	0.06
Total SQ radical	0.97		**Total SQ radical**	0.86
Ni_{81}	1.69		Ni_{158}	1.69
O_{75}	0.07		O_{143}	0.12
O_{76}	0.06		O_{144}	0.21
Total spin density	2.79		**Total spin density**	2.88

- **Model B**

A second model was built to investigate the magnetic interaction between 2 moieties within **7** and is schematically represented in Figure S31.

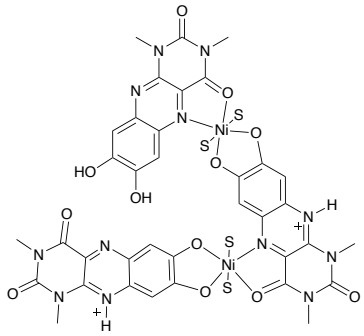


Fig. S37. Model **B** with two Ni^{II} moieties.

A comparison between the spin density of the full **7** and the model **B** is reported in Table S7, where the N_{101} and N_{109} (= N_{125} and N_{121}) are still the atoms with the highest spin density after the Ni_{133} and Ni_{134}. Regarding O_{119} and O_{127} (= O_{145} and O_{141}), O_{117} and O_{121} (= O_{143} and O_{147}), and O_{118} and O_{122} (= O_{144} and = O_{148}) they still have almost the same population as in **7.** Additionally, C_5 and C_{45} (= C_{25} and =C_5) spin density decreases, and C_8 and C_{48} (= C_{28} and =C_8) spin density is the same with respect to **7**. However, as for model **A**, this is compensated by the increase of spin population at N_{109} and N_{110}. In conclusion, model **B** is a fair representation of two moieties of **7**, and BS-DFT calculations can be conducted based on these observations.

Table S7. Comparison of Mulliken spin population distributions in model **B** and **7**.

Model B					**7**			
Atoms	**Spin population**	**Atoms**	**Spin population**		**Atoms**	**Spin population**	**Atoms**	**Spin population**
C_5	0.14	C_{45}	0.13		C_{25}	0.20	C_5	0.22
C_8	0.11	C_{48}	0.13		C_{28}	0.13	C_8	0.14
N_{101}	0.36	N_{109}	0.41		N_{125}	0.35	N_{121}	0.35
N_{102}	0.08	N_{110}	0.11		N_{126}	0.08	N_{122}	0.09
O_{119}	0.09	O_{127}	0.08		O_{145}	0.06	O_{141}	0.06
C_9	0.04	C_{49}	0.07		C_{29}	0	C_9	0.05
C_{10}	0.01	C_{50}	0.07		C_{30}	0	C_{10}	0.02
Total radical	1.14	**Total radical**	0.83		**Total radical**	0.82	**Total radical**	0.86
Ni_{134}	1.58	Ni_{133}	1.59		Ni_{159}	1.69	Ni_{158}	1.69
O_{121}	0.09	O_{117}	0.16		O_{147}	0.07	O_{143}	0.12
O_{122}	0.07	O_{118}	0.22		O_{148}	0.05	O_{144}	0.21
Total	2.57	**Total**	2.83		**Total**	2.63	**Total**	2.95

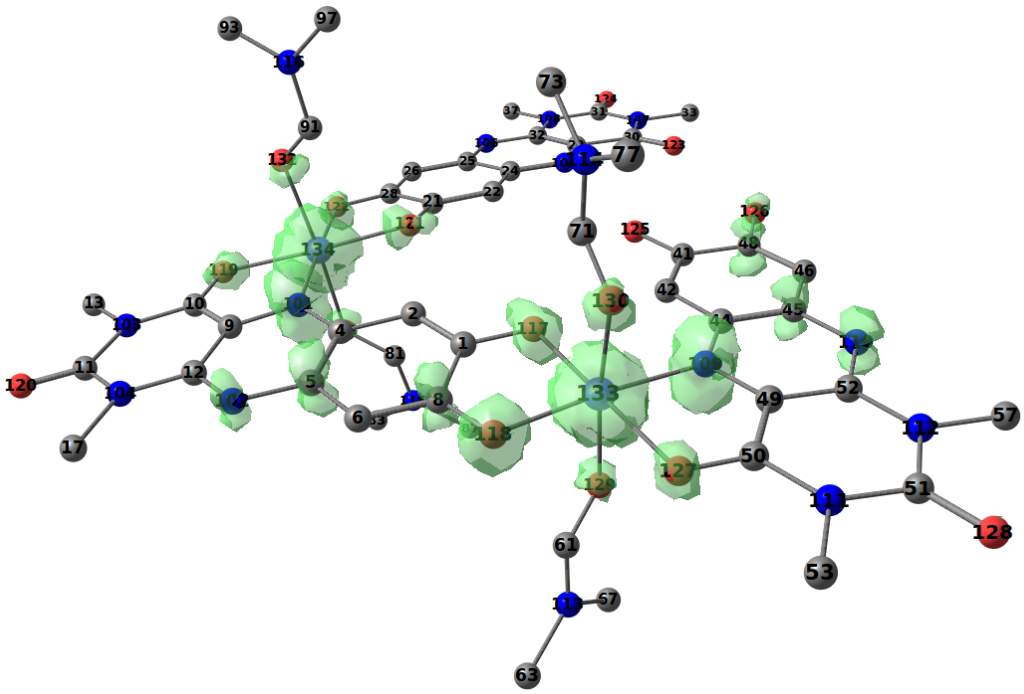


Fig. S38. Spin density plot for model **B** containing two Ni^{II} with chemically truncated ligands. Hydrogen atoms were removed for clarity.

Magnetic interactions in model systems

Metal-complex **7** has 3 high spin Ni(II) metal centers and each one of them features two unpaired electrons. Furthermore, 2 organic radicals are delocalized within the catechol/flavin ligands. Thus, magnetic interactions between the unpaired electrons of both the metal centers and the SQ radicals are expected. This magnetic interaction can be described by the exchange coupling constant, *J*, which is a parameter that describes the strength and nature of the magnetic interactions. The prediction of the *J* values in polynuclear transition metal complexes can be conducted using the "broken symmetry" (BS) approach within the density functional theory (DFT) framework.[10,11] While the calculation of high spin states is straightforward using DFT because they can be described by a single determinant, it is not the case for the low spin states which are multiconfigurational. The broken symmetry is then a mathematical tool to evaluate the energy of the low spin states as this approach allows the spin-up and spin-down electrons to be localized on different areas of the molecule so that they can be coupled magnetically but are not forcibly paired. Using the Heisenberg-Dirac-Van Vleck (HDvV) Hamiltonian[25][14] within the BS-DFT framework provides the computed magnetic sublevel spectrum that allows us to assign both ground and first excited states. The exchange interaction between the paramagnetic centers is described by the HDvV Hamiltonian (Eq. 1) where J_{12} is the exchange coupling constant between the Ni^{II} center and the SQ radical and, S_1 and S_2 are the spin operators for Ni(II) and SQ radical, respectively.

$$\hat{H} = -2J_{12}\hat{S}_1\hat{S}_2 \qquad (1)$$

[25] a) Dirac, P. A. M., *Proc. Roy. Soc.* **1929**, A123, 714; b) Heisenberg, W. Z., *Physik* **1926**, 38, 411-426; c) Heisenberg, W. Z., *Physik* **1928**, 49, 619-636; d) Van Vleck, J. H. in *The Theory of Electronic and Magnetic Susceptibilities*, Oxford University, London, **1932**.

System with 3 protons and 3 SQ-radicals

- **Model A**

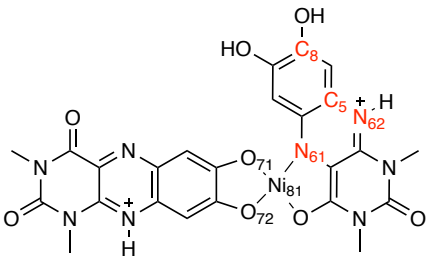
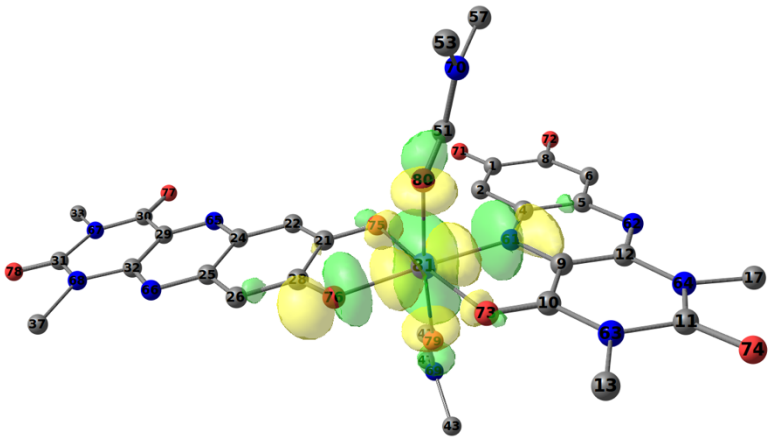


Fig. S39. Scheme highlighting the atoms flipped during BS-DFT calculation of model **A**.

Table S8. Computed *J* value and Mulliken spin population analysis of model **A**.

	High spin	**Broken symmetry**
C_5	0.14	-0.17
C_8	0.14	-0.16
N_{61}	0.48	-0.35
N_{62}	0.12	-0.13
Ni_{81}	1.69	1.70
O_{71}	0.07	0.07
O_{72}	0.06	0.06
***J* = 131 cm^{-1}**		

The calculated *J* value for model **A** is 131 cm^{-1} (Table S8), which indicates a strong ferromagnetic interaction between the Ni^{II} metal center and the SQ ligand radical which leads to a triplet (S = 1) ground spin state with a singlet excited state lying at 262 cm^{-1}. Magnetic orbitals for model **A** are reported in Figure S40. Furthermore, the orthogonality of the magnetic orbitals is in agreement with the strong ferromagnetic coupling for this model.



Spatial overlap between magnetic orbitals, S = 0.009

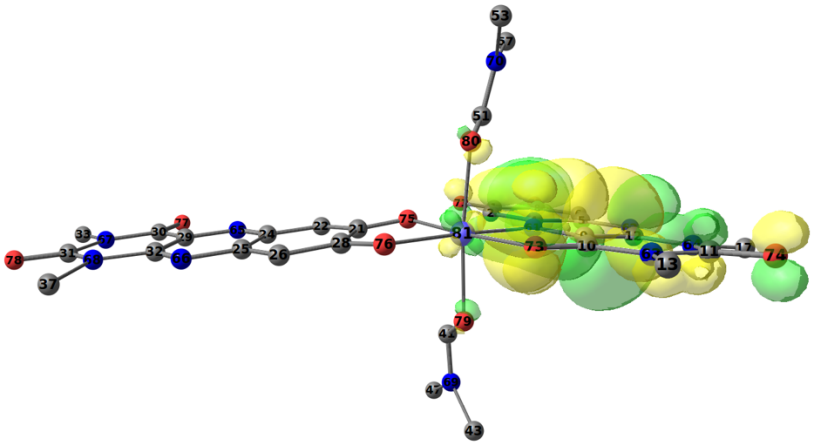


Fig. S40. Magnetic orbital for the BS state of model **A**. Hydrogen atoms were removed for clarity.

- **Model B:**

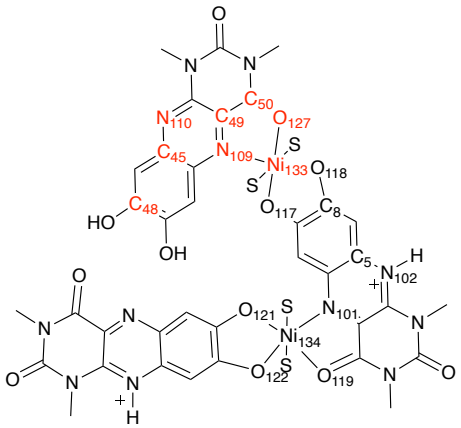


Fig. S41. Scheme highlighting the atoms flipped during BS-DFT calculation of model **B**.

Table S9. Computed *J* value and Mulliken spin populations in model **B**.

	High spin	**Broken symmetry**
C_{45}	0.08	-0.08
C_{48}	0.11	-0.11
C_{49}	0.07	-0.07
C_{50}	0.07	-0.07
N_{109}	0.31	-0.31
N_{110}	0.11	-0.11
O_{127}	0.09	-0.09
Ni_{133}	1.69	-1.69
C_4	0.21	0.21

C_8	0.14	0.14
N_{101}	0.34	0.35
N_{102}	0.09	0.09
O_{119}	0.06	0.06
Ni_{134}	1.69	1.70
***J* = 15 cm^{-1}**		

The calculated *J* value for model **B** is 15 cm^{-1} (Table S9), which indicates a weak ferromagnetic interaction between the two Ni^{II} moieties which leads to a triplet (S = 1) ground spin state with a singlet excited state lying at 30 cm^{-1}.

Cartesian coordinates

Table S10. Optimized structures for complex with 3 protons + 3 radicals

C	6.2710059073	3.9584506830	3.6002498031
C	5.0452441369	3.3614204727	3.2865340466
H	4.1222757460	3.9202380339	3.4447528544
C	4.9670994393	2.0591475559	2.7691570079
C	6.2024019605	1.3381027478	2.6160628377
C	7.4355051782	1.8930651897	2.9606350884
H	8.3562771930	1.3123609590	2.8466290342
C	7.5187038584	3.2156610502	3.4630577086
C	3.7868985928	0.2584958942	1.8244570048
C	2.5521993436	-0.2520330848	1.3176225603
C	3.7145230015	-2.3231482409	0.6106564774
C	4.9432760698	-0.4967451767	1.6714983345
C	1.3318708905	-2.1053926563	0.2182976606
H	1.1089730651	-3.0515898111	0.7273600159
H	1.4293457487	-2.3062868976	-0.8562151051
H	0.5423533883	-1.3710877143	0.4019298121
C	6.1276618928	-2.5474744772	0.9617240846
H	6.5704354676	-2.7543445443	1.9484541907
H	6.8649487924	-2.0328969286	0.3254915153

H	5.8437804903	-3.4925330985	0.4887418905
C	1.0481604461	4.7630897680	3.3129981895
C	1.0984606992	6.1052933859	3.7075212028
H	2.0236051958	6.5144434829	4.1138070160
C	-0.0022150411	6.9631759086	3.5472759299
C	-1.2042923407	6.3965480558	2.9937477870
C	-1.2812494759	5.0689175802	2.5801092247
H	-2.2014886816	4.6740235380	2.1389569619
C	-0.1571072433	4.2093936539	2.6969036518
C	-1.0811420414	9.0432762315	3.7737822587
C	-1.0320629856	10.4007330837	4.2055336979
C	-3.4127984756	10.6928746394	3.5788250910
C	-2.2772066916	8.5471207003	3.2662117134
C	-2.1478048533	12.5619342850	4.5253638183
H	-2.0802661201	12.6119663116	5.6210631036
H	-3.0598109863	13.0587577807	4.1846440502
H	-1.2537768303	13.0368142549	4.1055539254
C	-4.6501661977	8.8034143239	2.6325169418
H	-5.3864460004	9.6122125842	2.6509944775
H	-5.0130305090	7.9686481633	3.2522400578
H	-4.5133451836	8.4617819033	1.5946934588
C	4.2891581364	8.7380499738	4.6158455090
C	5.4708639949	7.9843946528	4.5670376528
H	5.4361438375	6.9660669759	4.1810730702
C	6.6969202841	8.4940585753	5.0151955130
C	6.7074004332	9.8442913010	5.5142031563
C	5.5498524563	10.6244917313	5.5667259661
H	5.5899267913	11.6485139205	5.9526254144
C	4.3093451265	10.1044998448	5.1290382303
C	9.0077143743	8.3169440855	5.4348570513
C	10.2001076143	7.5301472778	5.3870038919

C	11.4791967474	9.4284670010	6.3393758569
C	9.0798194613	9.6185138309	5.9202727125
C	12.6298011679	7.3557949491	5.8379668346
H	13.0616187973	7.3240416296	6.8457595120
H	13.3602415929	7.8229360265	5.1644559308
H	12.3769411994	6.3498497899	5.4915066055
C	10.3349009910	11.5283031470	6.8638775248
H	9.6848467161	11.6490785558	7.7445569786
H	10.0403554433	12.2486100147	6.0844673541
H	11.3729047306	11.7177412870	7.1539186384
C	9.3974857063	5.6940184376	1.7239467210
H	9.6944306319	4.6941057226	2.0906117029
C	10.7045968066	5.1035205911	-0.2548454272
H	11.6882483395	5.5533131676	-0.4678074125
H	10.2321267356	4.8350273375	-1.2139085791
H	10.8548222928	4.1886137109	0.3315101335
C	9.5403669264	7.3010779979	-0.1141554455
H	8.8941823042	7.8542874718	0.5762707089
H	9.0140982482	7.1493898060	-1.0701510438
H	10.4562025895	7.8820233224	-0.3084979112
C	6.8449356444	4.8956262616	6.8817467617
H	5.9755813806	5.0588272634	6.2204383281
C	5.1647234530	4.2159484941	8.5158691483
H	4.5002926033	4.4748793636	7.6823939692
H	4.8971581866	4.8331791791	9.3892412501
H	5.0077321207	3.1567687197	8.7778890380
C	7.5878751058	4.1639794940	9.0940823563
H	7.5547280987	3.1042420182	9.3937340004
H	7.4593379048	4.7857226854	9.9946693999
H	8.5565054374	4.3820034507	8.6314255325
C	2.7544576739	4.3642780718	0.5745536529

H	3.0578006598	4.8287124088	1.5274632685
C	2.6670112568	4.6448370201	-1.8502101582
H	2.1769391053	3.6697995694	-1.7543791035
H	3.5671237193	4.5447679800	-2.4781903412
H	1.9794246038	5.3551790133	-2.3365395579
C	3.6486202687	6.4166669759	-0.3950476100
H	3.8221200919	6.6418451658	0.6640415919
H	2.9995736692	7.1997208258	-0.8189747797
H	4.6140225196	6.4368593654	-0.9265542635
C	0.7467730546	1.7338481615	5.0913258406
H	0.6109746669	2.8281452710	5.0547440070
C	0.3464910529	-0.2892997151	6.4056801641
H	-0.6576403438	-0.7314438935	6.5045436243
H	0.9206921419	-0.5184591450	7.3177163597
H	0.8524626592	-0.7220645459	5.5359728472
C	-0.4110713736	1.9342083701	7.2338663653
H	-0.4034284354	2.9918848897	6.9421710330
H	0.1039453495	1.8299756570	8.2030833473
H	-1.4570623423	1.6103150101	7.3617392400
C	2.4843515664	11.3397145511	2.3349102933
H	2.9900250265	11.8029676216	3.2025314564
C	2.0640601000	11.4821949011	-0.0709564298
H	1.4866258307	10.5835332919	0.1716980444
H	2.8446739902	11.2303360095	-0.8068088207
H	1.3993031170	12.2405807330	-0.5143447354
C	3.4779645742	13.1823916836	1.0737109692
H	3.8565985046	13.4320146492	2.0725925235
H	2.8887055417	14.0332228565	0.6943098706
H	4.3363863402	13.0280835496	0.3996166984
C	1.6549045934	9.7453827111	7.4333578890
H	2.2560377436	10.6352470944	7.1711406952

C	0.6003638861	8.4779765210	9.2395383654
H	0.3281270136	7.8532221709	8.3817806746
H	-0.3131764970	8.8315768668	9.7438486998
H	1.1868383318	7.8829679560	9.9577471087
C	1.8559835271	10.5737963094	9.7239252394
H	2.4292089845	11.3538673718	9.2076850507
H	2.5078621603	10.0939177466	10.4721263834
H	1.0119228159	11.0460112652	10.2528084513
N	3.7601523939	1.5063968801	2.4026249982
N	6.1267929307	0.0265130599	2.0963253986
N	2.5780992615	-1.5368527651	0.7393043561
N	4.9092410414	-1.7565270070	1.0931974982
N	0.0668383919	8.2952785116	3.8919989718
N	-2.3249107685	7.2489694581	2.8645942419
N	-2.2047976309	11.1671363629	4.0812045145
N	-3.4058783227	9.3469718100	3.1683807051
N	7.8464498416	7.7314962466	4.9892833592
N	7.9410655703	10.3633838535	5.9606484447
N	11.3864799908	8.1315880674	5.8534766938
N	10.2782813261	10.1609609582	6.3592855160
N	9.8665882215	6.0215692234	0.4953742984
N	6.5434491850	4.4504767950	8.1240052966
N	3.0199342011	5.1123145959	-0.5202300562
N	0.2518806680	1.1482316272	6.2090568239
N	2.6624185999	11.9840641422	1.1556466305
N	1.3815541879	9.6041726018	8.7531261097
O	6.3533143337	5.1909585115	4.0334966815
O	8.6305326656	3.8128627852	3.8024218700
O	1.4829684613	0.4049933444	1.3708136080
O	3.6853231235	-3.4455433045	0.1022351162
O	2.0651367161	3.9447107084	3.4569350570

O	-0.1297964887	2.9721011634	2.3008882502
O	0.0107273861	10.9261137593	4.6841940447
O	-4.4271288469	11.3887157621	3.4909598503
O	3.1454346174	8.2630054687	4.2113380776
O	3.1765403371	10.7702884383	5.1512573135
O	10.2115596429	6.3501751301	4.9512215138
O	12.5438229467	9.9113769141	6.7301246924
O	8.6747877427	6.4360789805	2.4072908748
O	8.0033497736	5.1040015591	6.4838382335
O	2.2119789165	3.2458374906	0.5349785674
O	1.3159201480	1.1153984865	4.1806285464
O	1.8136313850	10.3041675202	2.4635274590
O	1.2787683318	8.9467836773	6.5615470604
Ni	8.2164642585	5.7579833414	4.4252554531
Ni	1.8104669148	2.2491629517	2.4051199581
Ni	1.6307427180	9.5042870414	4.4975918261
H	-3.1774252249	6.8577228590	2.4787620974
H	7.9631352404	11.3186483217	6.3005395444
H	6.9905418276	-0.4927698445	1.9847713637

Table S11. Optimized structures for complex with 2 protons + 2 radicals

C	6.2755776928	3.9097409486	3.7110762831
C	5.0510254199	3.3178055813	3.3858956299
H	4.1271180680	3.8690506083	3.5638584679
C	4.9765436441	2.0333848566	2.8240324484
C	6.2147244881	1.3226950007	2.6446992912
C	7.4473596260	1.8741465990	2.9961731788
H	8.3705044332	1.3029403963	2.8573240982

C	7.5263773699	3.1822666992	3.5351683059
C	3.8009096449	0.2572805256	1.8286918496
C	2.5670098275	-0.2435799238	1.3093871568
C	3.7333080475	-2.2952096285	0.5553668623
C	4.9591246619	-0.4908467158	1.6557801605
C	1.3498836414	-2.0738532365	0.1684738653
H	1.1247612995	-3.0271105896	0.6631998595
H	1.4512722552	-2.2591546865	-0.9083345651
H	0.5600831818	-1.3421028620	0.3605480465
C	6.1475459011	-2.5226956423	0.8995599668
H	6.5922788228	-2.7486670144	1.8811306613
H	6.8824958660	-1.9942144985	0.2721290272
H	5.8647633946	-3.4586145703	0.4081211811
C	1.0700752560	4.7587581607	3.3372144385
C	1.1269497453	6.0971842703	3.7418702702
H	2.0525730945	6.4955656197	4.1564562155
C	0.0331640018	6.9633621546	3.5814366588
C	-1.1706188068	6.4079933636	3.0197229034
C	-1.2541677966	5.0840466670	2.5961682371
H	-2.1753176546	4.6978415253	2.1495259110
C	-0.1355149425	4.2166120005	2.7111750577
C	-1.0320252094	9.0505470491	3.8129034176
C	-0.9723219235	10.4068424119	4.2436776735
C	-3.3485644818	10.7187689503	3.6155859577
C	-2.2302110803	8.5642824705	3.3003640981
C	-2.0687766968	12.5771570909	4.5660821690
H	-1.9730543095	12.6239443501	5.6595903303
H	-2.9891902469	13.0740036004	4.2490299018
H	-1.1867993410	13.0550533553	4.1243372532
C	-4.6000888010	8.8404116643	2.6643397362
H	-5.3305173199	9.6543892675	2.6852604257

H	-4.9688616166	8.0063520468	3.2813550192
H	-4.4653376036	8.5016409680	1.6253515554
C	4.3357299510	8.6967242974	4.6615509247
C	5.5033198397	7.9383943202	4.6274023612
H	5.4693691765	6.9121275191	4.2630352451
C	6.7259943244	8.4693655205	5.0669805775
C	6.7820132359	9.8599427828	5.5612364755
C	5.6014754688	10.6228523340	5.5915450932
H	5.6523421374	11.6492666147	5.9602529180
C	4.3718100634	10.0906451984	5.1628096181
C	9.0070706317	8.3078179056	5.4713611404
C	10.2039076613	7.5145187798	5.4138062524
C	11.4464631101	9.4577933162	6.3339437067
C	9.0345037996	9.6367278752	5.9329111000
C	12.6299422518	7.3836286974	5.8430226959
H	13.0693542517	7.3747498255	6.8477996010
H	13.3461943869	7.8598160009	5.1608569200
H	12.4001957518	6.3675602393	5.5103262420
C	10.2903263711	11.5565796929	6.8395453339
H	9.6137715388	11.6689876041	7.6962475680
H	9.9531885238	12.2401411681	6.0496006790
H	11.3217449910	11.7765628343	7.1274817928
C	9.3714286662	5.6874866367	1.8004821816
H	9.7027500736	4.6950500403	2.1572403836
C	10.7185407414	5.1754665040	-0.1727094128
H	11.6858798424	5.6662223515	-0.3680745704
H	10.2658365172	4.9051274145	-1.1405930010
H	10.8982867395	4.2577026994	0.4005925883
C	9.4790739286	7.3298476517	-0.0080270135
H	8.8162788988	7.8552659094	0.6880770197
H	8.9607295928	7.1786892528	-0.9682834173

H	10.3799732026	7.9372122352	-0.1894956953
C	6.9425267627	4.8718940572	7.0188816740
H	6.0507665132	4.9583058285	6.3728489387
C	5.3442659565	4.1878652404	8.7300532021
H	4.6465880769	4.3640680177	7.9021694384
H	5.0665552024	4.8398860927	9.5742890833
H	5.2510259673	3.1390891964	9.0558616960
C	7.7805050771	4.2935684519	9.2428313609
H	7.8076138311	3.2530640565	9.6033294327
H	7.6424014502	4.9605294896	10.1087159902
H	8.7253667984	4.5315903416	8.7428227200
C	2.8419133679	4.3317065017	0.6185066155
H	3.1596970159	4.7717350274	1.5784605343
C	2.7798365135	4.6385781763	-1.8038045894
H	2.2441217431	3.6868013277	-1.7196194608
H	3.6782447710	4.5025285025	-2.4273027670
H	2.1294187228	5.3847940607	-2.2873316582
C	3.8311707074	6.3515379976	-0.3272806944
H	4.0191321266	6.5542267021	0.7337690599
H	3.2156857180	7.1681168063	-0.7377349596
H	4.7943499245	6.3367660815	-0.8628453175
C	0.7726854419	1.7305666152	5.1214240139
H	0.7191721529	2.8327719640	5.1199138822
C	0.2238606494	-0.3012140859	6.3669761166
H	-0.8116602080	-0.6679953212	6.4485527324
H	0.7745860663	-0.6045841475	7.2716635157
H	0.6990905272	-0.7407624216	5.4835102202
C	-0.3642913566	1.9432734364	7.2731166841
H	-0.2825458268	3.0065295404	7.0151404471
H	0.1434076591	1.7711458292	8.2363695566
H	-1.4303625670	1.6904588014	7.3942458498

C	2.5060595269	11.3359111100	2.3590346740
H	2.9927709714	11.8294868747	3.2200039191
C	2.0987058619	11.4327560401	-0.0502728554
H	1.5500984005	10.5180710101	0.1990138016
H	2.8928383815	11.1990923257	-0.7774207402
H	1.4122887106	12.1631713866	-0.5070480308
C	3.4490673775	13.1934814752	1.0813325314
H	3.8163794795	13.4671257613	2.0780370381
H	2.8340184803	14.0197464987	0.6894690873
H	4.3141176299	13.0574239205	0.4123571305
C	1.6401586079	9.8279365567	7.4463793027
H	2.0828959819	10.7972575949	7.1572485858
C	0.8929317044	8.4348467505	9.3099490659
H	0.6992581489	7.7555630402	8.4727048517
H	-0.0464843496	8.6342454822	9.8495750385
H	1.6044302619	7.9665800578	10.0085330877
C	1.8041401522	10.7178339746	9.7165158579
H	2.2119674189	11.5760008049	9.1681766316
H	2.5661774143	10.3614022975	10.4283247238
H	0.9225011171	11.0491219712	10.2888600474
N	3.7715261431	1.4901855480	2.4383144125
N	6.1422088394	0.0261199830	2.0893421196
N	2.5952062919	-1.5139142187	0.7016347476
N	4.9275963952	-1.7368778131	1.0492948085
N	0.1098922189	8.2930441440	3.9325209575
N	-2.2853864277	7.2684174381	2.8936184273
N	-2.1372337661	11.1829082451	4.1209434351
N	-3.3518304694	9.3730506999	3.2027658337
N	7.8589352079	7.7250983590	5.0497518789
N	7.9526637043	10.4079796395	5.9876091287
N	11.3710181389	8.1323775431	5.8580786646

N	10.2575840369	10.1752293994	6.3555834809
N	9.8391195589	6.0499864953	0.5828572988
N	6.6984815187	4.4703309856	8.2868096399
N	3.1463819951	5.0773265408	-0.4673813672
N	0.2392293959	1.1456600898	6.2207144433
N	2.6713454719	11.9699324864	1.1739734728
N	1.4456762068	9.6701232841	8.7764070534
O	6.3550014647	5.1266434731	4.1893687066
O	8.6379555299	3.7791632116	3.8780075977
O	1.4967885425	0.4102038037	1.3771345944
O	3.7057126728	-3.4060783264	0.0233660009
O	2.0799748887	3.9325886078	3.4830821827
O	-0.1136514924	2.9828966311	2.3071296093
O	0.0773715271	10.9236791042	4.7208001512
O	-4.3568882072	11.4221858874	3.5275353897
O	3.1895662285	8.2425990750	4.2634665838
O	3.2467211341	10.7424372147	5.1646173070
O	10.2140298949	6.3338978549	4.9852364410
O	12.5249804735	9.9227571377	6.7016825676
O	8.6141962381	6.3926618567	2.4873005470
O	8.0778266560	5.1244838197	6.5794672239
O	2.2501632535	3.2389443937	0.5650384177
O	1.2937645024	1.1034280558	4.1874786070
O	1.8701767220	10.2789478077	2.4977866164
O	1.3653534830	8.9623648546	6.5994895181
Ni	8.2244296305	5.7131146075	4.5080304278
Ni	1.8194899708	2.2399136330	2.4274509682
Ni	1.6760206415	9.4923379662	4.5313148440
H	7.0068435037	-0.4886982368	1.9642296886

H	-3.1391810049	6.8852945619	2.5022491936

Table S12. Optimized structures for complex with 1 proton (N122) + 3 radicals

C	6.2053858574	3.8474674953	3.8770293668
H	4.9803700066	3.2634641634	3.5283950899
C	4.0545916501	3.7982947700	3.7426538235
C	4.9113290928	2.0173239932	2.8825988861
C	6.1525376583	1.3281442761	2.6527971896
H	7.3844277932	1.8713484258	3.0139722261
C	8.3111348271	1.3214368167	2.8242793247
C	7.4620489948	3.1502986256	3.6197873741
C	3.7435141199	0.2936209409	1.7856263680
C	2.5132265250	-0.1862042726	1.2391650442
C	3.6855838014	-2.1947001169	0.3919999943
C	4.9058781152	-0.4397313625	1.5753060774
H	1.3011829862	-1.9639242540	0.0123924475
H	1.0766733478	-2.9368154937	0.4672722322
H	1.4073729067	-2.1043934726	-1.0705318223
C	0.5089637818	-1.2425369323	0.2311614378
H	6.1019650096	-2.4288917598	0.7253973651
H	6.5488866050	-2.6949530431	1.6956786792
H	6.8332451078	-1.8713761945	0.1193019875
C	5.8220421832	-3.3440524464	0.1948779467
C	1.0176910882	4.7737025016	3.3422753329
H	1.0776139442	6.0972374861	3.7573292255
C	1.9913237845	6.4812833345	4.2062931463
C	-0.0151372601	6.9644250570	3.5665077102
C	-1.2642621958	6.4397524956	2.9704992234
H	-1.3139175054	5.1097655203	2.5396967748
C	-2.2301630128	4.7375998861	2.0789968730
C	-0.1997009202	4.2488491796	2.6705896095

C	-1.0555546967	9.0334349215	3.7566307835
C	-0.9686409068	10.4006262253	4.1644157481
C	-3.3379869252	10.6860604547	3.5079256540
C	-2.2485084304	8.5009737550	3.2283220134
H	-2.0551634413	12.5716004435	4.4495253310
H	-1.8355651766	12.6337087687	5.5236311258
H	-3.0278812381	13.0203918665	4.2317834663
C	-1.2564825296	13.0914851314	3.9053933975
H	-4.6290702363	8.8597124053	2.5816112031
H	-5.4226946046	8.9690354084	3.3317760992
H	-4.4814235809	7.8070562649	2.3251380636
C	-4.9122149838	9.4395630920	1.6939044015
C	4.2832627034	8.6916033434	4.7389131406
H	5.4626763271	7.9004598128	4.7044651478
C	5.4040368370	6.8627324712	4.3730422891
C	6.6812496958	8.4322656399	5.1071157619
C	6.7447824217	9.8196559492	5.5447606647
H	5.5769728332	10.6006758140	5.5695206697
C	5.6564488944	11.6379032631	5.9010146195
C	4.3270105086	10.0791178116	5.1779869843
C	8.9883457443	8.2594339158	5.4209727287
C	10.1741015072	7.4928588540	5.3141795182
C	11.4558199401	9.4334612515	6.1444802301
C	9.0119909021	9.6203673628	5.8523705352
H	12.6296508276	7.3678358614	5.6306103116
H	13.1269550158	7.3854438401	6.6084084895
H	13.3097738972	7.8164988548	4.8936377470
C	12.3783470599	6.3429098336	5.3423191388
H	10.3066431945	11.5396482392	6.6733668958
H	9.6578712383	11.6639722062	7.5497172180
H	9.9399473368	12.2115406957	5.8863162011

C	11.3477874214	11.7616492041	6.9213311204
H	9.3303683807	5.7179791009	1.9214439551
C	9.8575343229	4.8524474790	2.3594813844
H	10.8998541835	5.4284823876	0.0701432533
H	11.7383944750	6.1226736904	-0.1011432170
H	10.5948997071	5.0066882829	-0.9013718929
C	11.2457957307	4.6118544462	0.7158206429
H	9.1926807463	7.2413638910	0.0149948379
H	8.3846363675	7.6394698244	0.6380870219
H	8.7888029651	6.9256811169	-0.9602063771
C	9.9455467215	8.0267268171	-0.1571723103
H	7.1315427825	4.8272825019	7.2340399178
C	6.1793732718	4.8267161508	6.6731593780
H	5.7453079849	4.1647875179	9.1318699944
H	4.9626623652	4.2441687253	8.3674113504
H	5.5085774916	4.8580373973	9.9554737418
C	5.7469391529	3.1379607054	9.5324159296
H	8.2070929228	4.4413536793	9.3958920650
H	8.3342849843	3.4313286390	9.8162323010
H	8.1073115542	5.1569456998	10.2273742264
C	9.0833837258	4.7001519898	8.7922856783
H	2.9581143207	4.2849470989	0.6703805463
C	3.3841645928	4.6288951954	1.6280757545
H	2.7972959193	4.7366429514	-1.7245548127
H	2.1500238252	3.8557570287	-1.6562255103
H	3.6332986149	4.5292431691	-2.4114852672
C	2.2202115400	5.5863101435	-2.1219472666
H	4.1575772372	6.2051988218	-0.2357145661
H	4.4585751757	6.2998202837	0.8143400699
H	3.6293969654	7.1236682088	-0.5368705159
C	5.0621988147	6.1017570581	-0.8562674815

H	0.8164748991	1.6992074411	5.1658525160
C	0.9473328547	2.7911367280	5.2640116236
H	0.0013658561	-0.3338576946	6.2514326155
H	-1.0744942931	-0.5316898532	6.3789844089
H	0.5468755490	-0.8144752614	7.0789260653
C	0.3389909131	-0.7518681165	5.2972699135
H	-0.1518998334	1.8709044492	7.4011183394
H	0.0899793670	2.9285332187	7.2385414186
H	0.3714086887	1.5204425676	8.3055908499
C	-1.2367220348	1.7793829816	7.5713799155
H	2.4926582787	11.2449612766	2.3555009709
C	2.9521147052	11.7764627480	3.2081935935
H	2.0629631166	11.2745368033	-0.0513910076
H	1.5495385624	10.3452633856	0.2170071679
H	2.8614743960	11.0582207966	-0.7787359531
C	1.3475628521	11.9709335513	-0.5157953683
H	3.3389596384	13.1170494425	1.0373113309
H	3.7011148960	13.4269607770	2.0250683498
H	2.6796010117	13.9032792603	0.6363051629
C	4.2029227086	13.0095590035	0.3623431349
H	1.6243176422	9.7848727109	7.4578330435
C	2.2708511713	10.6421170155	7.1982956872
H	0.4709746469	8.5895948982	9.2513839754
H	0.1805879559	7.9686243099	8.3972561833
H	-0.4306343293	8.9964120200	9.7356032037
C	1.0152637427	7.9757813634	9.9861559782
H	1.8251231714	10.6238343930	9.7408732852
H	2.4456511938	11.3701495492	9.2301814819
H	2.4394666318	10.1155221590	10.5011273389
N	0.9958701200	11.1392172473	10.2512070915
N	3.7081450334	1.4941621512	2.4585758123

N	6.0860333430	0.0612967440	2.0305488834
N	2.5446029453	-1.4245392912	0.5724880027
N	4.8788974646	-1.6545153492	0.9112060165
N	0.0570074514	8.2669138563	3.9110384888
N	-2.3588683210	7.2424829504	2.8283170387
N	-2.1147800222	11.1709904886	4.0282003186
N	-3.3590347781	9.3564602387	3.1205909322
N	7.8214525916	7.6454773410	5.0776544717
N	7.9499237894	10.3958674102	5.9343080494
N	11.3751651278	8.1173815823	5.6941602972
N	10.2518252518	10.1519160964	6.2105506097
N	9.7883287164	6.1103505298	0.7095150745
N	7.0310788503	4.4893210000	8.5400761556
N	3.2972042215	5.0440428272	-0.3936252786
N	0.2533209230	1.0991840897	6.2390707323
N	2.6224581859	11.8578894503	1.1590296490
O	1.3173692247	9.6704301265	8.7679048992
O	6.2828626799	5.0255237843	4.4420528097
O	8.5737439511	3.7404480940	3.9587310001
O	1.4408094477	0.4617331855	1.3350965811
O	3.6628099751	-3.2790212816	-0.1899100161
O	1.9961964688	3.9283627699	3.5104493954
O	-0.1617941509	3.0313610839	2.2628960339
O	0.0857178981	10.9125626792	4.6359060635
O	-4.3270639837	11.4100604496	3.4053657703
O	3.1399005018	8.1989215594	4.3814541180
O	3.1887747096	10.7429644510	5.1747649870
O	10.1729551902	6.2932288810	4.8909065215
O	12.5364996504	9.9302861679	6.4640745225
O	8.3833430836	6.2627266484	2.5120749994
O	8.2035388606	5.1149405772	6.6770109403

O	2.2265961032	3.2805095320	0.6013525444
O	1.1749274854	1.0956487696	4.1424408481
O	1.9085562280	10.1576202184	2.5168870323
Ni	1.2274071975	8.9930764756	6.5830740675
Ni	8.1702979241	5.6707908041	4.5959272808
Ni	1.7602660703	2.2476633606	2.4264047562
H	1.6515771430	9.4854455564	4.5461311032
H	6.9541511161	-0.4384240093	1.8720430396

Table S13. Optimized structures for complex with 1 proton (N126) + 3 radicals

C	6.1801248555	3.9013332961	3.8669224376
C	4.9658903567	3.3119179807	3.5321140590
H	4.0328607850	3.8374928189	3.7376946010
C	4.9247452701	2.0564478386	2.8955747413
C	6.1835431043	1.3258938395	2.6482393208
C	7.4023242956	1.9069651614	3.0282910810
H	8.3263054892	1.3561482490	2.8444781683
C	7.4557759071	3.1855520405	3.6196283210
C	3.7891843207	0.3245526535	1.8464112727
C	2.5428818245	-0.1750693590	1.3321902137
C	3.7656403819	-2.1775150465	0.5417967735
C	4.9976710350	-0.3760305582	1.6600010449
C	1.3623125650	-1.9975679186	0.1594649819
H	1.1549247485	-2.9604723612	0.6431472809
H	1.4767299097	-2.1729408284	-0.9175565421
H	0.5529889891	-1.2874044679	0.3508091980
C	6.1589806036	-2.4204594016	0.8276474157
H	6.0584233263	-3.3913731732	1.3296875998
H	6.9899496528	-1.8500667990	1.2516491046

H	6.3205656438	-2.6026134123	-0.2426049419
C	1.0048958787	4.7914592977	3.3607939376
C	1.0594508832	6.1322890501	3.7589637067
H	1.9763415376	6.5192086498	4.1991415999
C	-0.0191854808	7.0069077340	3.5589691467
C	-1.2156672771	6.4549035682	2.9763832203
C	-1.3012723253	5.1264327032	2.5678564459
H	-2.2152984609	4.7421850150	2.1055122665
C	-0.1918905226	4.2528186083	2.7160709192
C	-1.0698681025	9.1060158084	3.7380528048
C	-1.0049661371	10.4678855743	4.1480606523
C	-3.3642205789	10.7927812373	3.4726725832
C	-2.2617982250	8.6233805664	3.2082076899
C	-2.0836726245	12.6516221985	4.4271988120
H	-1.9502062381	12.7055644263	5.5159073702
H	-3.0171874138	13.1393373552	4.1356413038
H	-1.2215219887	13.1342239620	3.9519488929
C	-4.6151197324	8.9138799948	2.5195713798
H	-5.3369790606	9.7356503658	2.5137703652
H	-5.0057455587	8.0927355480	3.1401602045
H	-4.4617048376	8.5599108665	1.4884351372
C	4.2653204346	8.7622256351	4.6771626999
C	5.4457080709	7.9699971797	4.6517126509
H	5.3900128978	6.9351807170	4.3117640205
C	6.6569242835	8.4944114071	5.0848811070
C	6.7150566643	9.8757305818	5.5406478777
C	5.5476443666	10.6565828616	5.5601724802
H	5.6224705146	11.6888676090	5.9078431206
C	4.3030368058	10.1416163646	5.1432305700
C	8.9585147636	8.3150602853	5.4374942355
C	10.1448859771	7.5468171018	5.3458203494

C	11.4153786679	9.4781972222	6.2117400204
C	8.9768270633	9.6722669119	5.8822585352
C	12.5953897675	7.4158414866	5.6978726304
H	13.0696723315	7.4094144744	6.6872818009
H	13.2925392225	7.8806358226	4.9876626498
H	12.3498498679	6.3980139676	5.3811692308
C	10.2611635766	11.5818377941	6.7403763293
H	9.6052050805	11.6978889134	7.6126075792
H	9.9003753108	12.2601979390	5.9562501240
H	11.2998499735	11.8022696889	6.9997184601
C	9.3190862976	5.7329808408	1.9151943803
H	9.8573777169	4.8809684659	2.3649563197
C	10.8231142490	5.3621361871	0.0252007786
H	11.6616429028	6.0395026070	-0.2029738920
H	10.4761158490	4.9079646406	-0.9168617605
H	11.1834539556	4.5650136514	0.6870272584
C	9.1280402381	7.1869189092	-0.0391389599
H	8.3544258145	7.6242705331	0.6010534536
H	8.6747885256	6.8313974766	-0.9782348966
H	9.8816005175	7.9521977851	-0.2829754202
C	7.1249888073	4.7402371989	7.1956376773
H	6.1719990016	4.7110773011	6.6376647392
C	5.8082606771	3.7904483495	9.0192490482
H	5.0146541067	3.8849040163	8.2678389206
H	5.5218796185	4.3670302212	9.9138327272
H	5.8996030247	2.7298531434	9.3047044305
C	8.2397287957	4.2472698217	9.3149071940
H	8.4570229869	3.2131360398	9.6251855472
H	8.0840976176	4.8594399589	10.2172337422
H	9.0862183592	4.6428804528	8.7437556371
C	2.8583014279	4.3334324406	0.6777221614

H	3.1768028868	4.7715666266	1.6387700586
C	2.8435736228	4.6101977887	-1.7487064354
H	2.2786289509	3.6758595650	-1.6631420233
H	3.7492398435	4.4397978058	-2.3523256810
H	2.2250127634	5.3694541087	-2.2527936088
C	3.9255297579	6.3081042367	-0.2771457689
H	4.1002016527	6.5213961309	0.7839975290
H	3.3465623695	7.1379917710	-0.7127899956
H	4.8974405735	6.2507869554	-0.7931572785
C	0.5649475895	1.6941872174	5.0775347198
H	0.2099456166	2.7322096947	4.9632261924
C	0.5177641870	-0.2863507509	6.5114203263
H	-0.3795983501	-0.9183423444	6.6037488438
H	1.0771973314	-0.3328712649	7.4591720401
H	1.1466721134	-0.6597265750	5.6965617967
C	-0.7089913955	1.7817672973	7.1598746803
H	-0.9065221521	2.7979910562	6.7967353914
H	-0.2228886926	1.8458800455	8.1469245894
H	-1.6700868066	1.2562174241	7.2800468989
C	2.4919505251	11.3444623230	2.3309809066
H	2.9568319946	11.8514963932	3.1957299053
C	2.1126612021	11.4077051757	-0.0839998746
H	1.5678001739	10.4913848000	0.1668828266
H	2.9189940194	11.1733550162	-0.7970862422
H	1.4273674188	12.1279942661	-0.5577534005
C	3.4287512035	13.1965832758	1.0448254897
H	3.7816331169	13.4855355373	2.0422255357
H	2.8077477823	14.0100081445	0.6365796593
H	4.3021926885	13.0622672003	0.3869557169
C	1.7038662989	9.7700261604	7.4374514523
H	2.3226200690	10.6501263542	7.1873922413

C	0.6873542342	8.4555515153	9.2299993213
H	0.3462533420	7.8828157371	8.3609921344
H	-0.1823586152	8.8139354551	9.8028279329
H	1.2932294397	7.8076667092	9.8827909649
C	2.0399604722	10.4837691224	9.7476858331
H	2.6172992208	11.2673768483	9.2421441025
H	2.7091733825	9.9418859919	10.4349606924
H	1.2409511639	10.9567974391	10.3407931183
N	3.7549189630	1.5240392570	2.4782215363
N	6.1727883927	0.1028606332	2.0485831532
N	2.5907698776	-1.4163253297	0.7054888098
N	4.9428516910	-1.6268752865	1.0238639274
N	0.0626975507	8.3408963915	3.8918273864
N	-2.3198481884	7.3228539640	2.8161267419
N	-2.1583464942	11.2524313672	3.9968066026
N	-3.3724722079	9.4410036681	3.0774494979
N	7.7971509507	7.7054673124	5.0698474468
N	7.9144014716	10.4471045209	5.9562579343
N	11.3404707948	8.1661544305	5.7483524686
N	10.2115811675	10.1985020776	6.2641415859
N	9.7435103497	6.0816641068	0.6792605797
N	7.0574377993	4.2847204434	8.4671135803
N	3.1994271588	5.0561328030	-0.4107611129
N	0.1422470908	1.0867447937	6.2101429302
N	2.6640331089	11.9641101310	1.1420966165
N	1.4797391263	9.5804873361	8.7561458142
O	6.2689294992	5.0793158000	4.4125099030
O	8.5435128112	3.7893221669	3.9674870929
O	1.4679641209	0.4658347607	1.4260837319
O	3.7321305449	-3.2742193599	-0.0134540616
O	2.0080981211	3.9650596896	3.5274304558

O	-0.1697763707	3.0130361830	2.3272010440
O	0.0433383940	10.9817393973	4.6329891006
O	-4.3627841677	11.5038989508	3.3539523232
O	3.1287878538	8.2792729846	4.2878068239
O	3.1664571533	10.8071474031	5.1346118455
O	10.1473366335	6.3494599120	4.9165456563
O	12.4911437570	9.9702398361	6.5535451665
O	8.3906047833	6.3019837509	2.5140836957
O	8.1678511659	5.1598984258	6.6677662981
O	2.2328024379	3.2584685726	0.6272063354
O	1.2898418540	1.1511062770	4.2297262793
O	1.8673074653	10.2779113268	2.4730888531
O	1.2637928242	9.0202747305	6.5472493711
Ni	8.1529155814	5.7366093650	4.5930191526
Ni	1.7631290728	2.2764213298	2.4743541207
Ni	1.6266214419	9.5508189951	4.5035458031
H	-3.1688795039	6.9424621930	2.4118171579

Table S14. Optimized structures for complex with 1 proton (N122) + 1 radical

C	6.2759802388	3.8747588757	3.8133694691
C	5.0506235848	3.2907670436	3.4756095988
H	4.1276112862	3.8360210328	3.6743983106
C	4.9762716310	2.0266616906	2.8683770240
C	6.2145804308	1.3230130510	2.6641741023
C	7.4480490150	1.8662383641	3.0248912040
H	8.3714708544	1.3020777108	2.8619008382
C	7.5280164692	3.1585615252	3.6000382406
C	3.8022515792	0.2832599692	1.8122935907
C	2.5705877135	-0.1993797887	1.2728428978

C	3.7340626638	-2.2306326489	0.4667218456
C	4.9602084683	-0.4606891273	1.6211606616
C	1.3521967276	-1.9926834002	0.0757378475
H	1.1245317353	-2.9593205639	0.5422231556
H	1.4577138537	-2.1468784154	-1.0054849812
H	0.5624622941	-1.2657577997	0.2851091609
C	6.1471618691	-2.4731409064	0.8132018018
H	6.5897505856	-2.7235586508	1.7896953871
H	6.8838145296	-1.9312195893	0.1993939840
H	5.8636222002	-3.3963807603	0.2987763988
C	1.0803535504	4.7772260602	3.3620307582
C	1.1411567179	6.1043279355	3.7679125350
H	2.0606518982	6.5026977067	4.1954730357
C	0.0372986838	6.9614999250	3.5948550342
C	-1.2185816761	6.4273675032	3.0214996056
C	-1.2666844141	5.0954134333	2.5951813266
H	-2.1872189565	4.7165642327	2.1485136854
C	-0.1443578362	4.2434439580	2.7101138708
C	-1.0141358454	9.0238246930	3.7976464172
C	-0.9297384032	10.3937699820	4.2021686001
C	-3.3114162916	10.6614293388	3.5772459588
C	-2.2112599484	8.4831613970	3.2881485387
C	-2.0288687378	12.5564344444	4.4987650016
H	-1.7591587521	12.6214146269	5.5609983419
H	-3.0177167273	12.9893611716	4.3260896001
H	-1.2659267283	13.0910138732	3.9181673364
C	-4.6021566075	8.8254370706	2.6705181939
H	-5.3875814877	8.9296007812	3.4300709374
H	-4.4504534137	7.7736192684	2.4128965496
H	-4.9001822884	9.4029443227	1.7861382405
C	4.3527936152	8.6641517197	4.7340750700

C	5.5161535295	7.9004325306	4.7152039668
H	5.4747868865	6.8598320706	4.3948125567
C	6.7476046895	8.4480991935	5.1067333460
C	6.8149736163	9.8572182504	5.5439490841
C	5.6366526188	10.6243567872	5.5618570453
H	5.6954918179	11.6650695536	5.8863051714
C	4.4005076235	10.0782938517	5.1719523426
C	9.0369048464	8.3005538705	5.4616766929
C	10.2345013204	7.5084884537	5.3908976783
C	11.4944873602	9.4775012157	6.2288911125
C	9.0742526002	9.6440698021	5.8783295841
C	12.6704296910	7.3927152513	5.7624598798
H	13.1331215966	7.4083566164	6.7565791002
H	13.3688249009	7.8544815212	5.0525010633
H	12.4362198480	6.3686589858	5.4587332638
C	10.3479469946	11.5897195049	6.7013444600
H	9.6755013761	11.7291454668	7.5570205310
H	10.0114555624	12.2526589167	5.8936424943
H	11.3818243949	11.8125183032	6.9779177258
C	9.3367771754	5.6625249681	1.8538734841
H	9.7160767213	4.6902530645	2.2177021183
C	10.6876918827	5.1906273845	-0.1274480350
H	11.6244178420	5.7280626705	-0.3469384554
H	10.2344229731	4.8807659200	-1.0831043693
H	10.9252274228	4.2935869220	0.4574833992
C	9.3553410696	7.2890487923	0.0284578442
H	8.6782936108	7.7933859575	0.7263084933
H	8.8344068174	7.1057176416	-0.9247124771
H	10.2278699061	7.9316404615	-0.1690857224
C	7.0539731811	4.8419017013	7.1440064960
H	6.1385252030	4.8780827466	6.5267695554

C	5.5432852781	4.1441460724	8.9281211495
H	4.8114285225	4.2665965904	8.1203975096
H	5.2682465297	4.8114589843	9.7610870219
H	5.5034982411	3.1036197521	9.2890057719
C	7.9896924316	4.3583368276	9.3512253262
H	8.0701209887	3.3308771314	9.7396580791
H	7.8543330305	5.0446547452	10.2021928958
H	8.9067928787	4.6180161426	8.8120178285
C	2.9379594695	4.3303831547	0.6691507360
H	3.3401266959	4.7053914587	1.6251817765
C	2.7561862905	4.7522838958	-1.7295416651
H	2.1685453360	3.8309543553	-1.6558430563
H	3.6059223425	4.5958691025	-2.4131359602
H	2.1250431775	5.5588435287	-2.1345320341
C	4.0016599733	6.3247764721	-0.2465023582
H	4.2745447840	6.4587445599	0.8069476773
H	3.4109543798	7.1962189987	-0.5704591549
H	4.9222925827	6.2814958825	-0.8507363642
C	0.7225760431	1.6905786077	5.1067160516
H	0.6771576700	2.7923391294	5.1479777579
C	0.1138180490	-0.3818466547	6.2517158494
H	-0.9285746478	-0.7358261666	6.2839177576
H	0.6298757102	-0.7274423796	7.1613887854
H	0.6126293021	-0.7926783173	5.3675890728
C	-0.4811567963	1.8319605924	7.2275235193
H	-0.3858086949	2.9037152471	7.0135571375
H	-0.0053322934	1.6191762682	8.1986409788
H	-1.5515866380	1.5815460184	7.3033392542
C	2.4920168568	11.2662195429	2.3421719343
H	2.9527805185	11.8097834057	3.1868173910
C	2.0344432689	11.2921611436	-0.0596826424

H	1.5477880278	10.3500513484	0.2141424312
H	2.8281007658	11.0966883830	-0.7982895540
H	1.2955527201	11.9711243346	-0.5132725209
C	3.2787490368	13.1621810592	1.0174982438
H	3.6458356670	13.4781597931	2.0016762929
H	2.5958036553	13.9340497761	0.6278271147
H	4.1365871397	13.0784850437	0.3311927096
C	1.6459364144	9.8405677627	7.4632555562
H	2.2410432750	10.7306439150	7.1916284756
C	0.5713832094	8.6147070048	9.2847967508
H	0.3121907105	7.9649834137	8.4419928976
H	-0.3491795823	8.9746940759	9.7705371980
H	1.1562404250	8.0444714205	10.0237627925
C	1.7972492048	10.7381791113	9.7297226840
H	2.3719783557	11.5096779350	9.2027804453
H	2.4406679240	10.2843795124	10.5004546269
H	0.9388848043	11.2143220721	10.2303230959
N	3.7725079002	1.4978549913	2.4593903939
N	6.1423500675	0.0433142717	2.0711116286
N	2.5969320315	-1.4506001119	0.6296845458
N	4.9282368432	-1.6887666719	0.9804942733
N	0.1050269146	8.2652263907	3.9366571401
N	-2.3199436672	7.2223746511	2.8938593745
N	-2.0848269770	11.1548651436	4.0809352717
N	-3.3291017241	9.3312612604	3.1932329142
N	7.8796736992	7.7038798457	5.0896678966
N	7.9938236150	10.4178745571	5.9275037503
N	11.4101247635	8.1391554814	5.7899390881
N	10.3055111539	10.1947522037	6.2578344407
N	9.7765442522	6.0320903782	0.6284479562
N	6.8695047995	4.4648060431	8.4289601032

N	3.2310662219	5.1016794332	-0.3999342374
N	0.1514355123	1.0700164139	6.1646592763
N	2.5950212890	11.8861140729	1.1446060071
N	1.3481231214	9.7359905963	8.7779976068
O	6.3567199127	5.0739038711	4.3334493539
O	8.6407980602	3.7507733828	3.9447361780
O	1.5016300432	0.4568230602	1.3545484146
O	3.7062478724	-3.3254995758	-0.0959954236
O	2.0639682202	3.9357101970	3.5173249548
O	-0.1039857863	3.0242928211	2.3044279845
O	0.1262264421	10.9136897152	4.6562797057
O	-4.3064909524	11.3791999665	3.4857690558
O	3.1987339307	8.1969089929	4.3751558097
O	3.2762807661	10.7325736293	5.1623807749
O	10.2361082743	6.3191402067	4.9874610705
O	12.5802198752	9.9525324624	6.5588408113
O	8.5539326444	6.3405711351	2.5399228562
O	8.1629969203	5.1272740159	6.6592635590
O	2.2692701498	3.2826082817	0.6059593381
O	1.2672161006	1.0959106705	4.1641120646
O	1.9351142057	10.1681057552	2.5091998412
O	1.2987781840	9.0101476284	6.6062770493
Ni	8.2338114773	5.6822383863	4.5800124624
Ni	1.8284563965	2.2522388666	2.4371844943
Ni	1.7040947436	9.4794986655	4.5504156563
H	7.0071675086	-0.4673715721	1.9307076858

Table S15. Optimized structures for complex with 1 proton (N126) + 1 radical

C	6.2605923976	3.9146505752	3.6931279727
C	5.0424387720	3.3329670754	3.3676201897
H	4.1160321068	3.8838548016	3.5333833448
C	4.9878111522	2.0457242191	2.8027686846
C	6.2367638181	1.2838700127	2.6071538031
C	7.4597454069	1.8587587065	2.9899725814
H	8.3758600079	1.2811776743	2.8550167743
C	7.5237587361	3.1592864639	3.5283322337
C	3.8336424480	0.2844823935	1.8292755852
C	2.5808517993	-0.2191233486	1.3342412221
C	3.7831128405	-2.2605366788	0.6138370733
C	5.0333615544	-0.4372759673	1.6751340289
C	1.3823501329	-2.0667433067	0.2208387974
H	1.1709869485	-3.0173366874	0.7264528693
H	1.4912118290	-2.2667381358	-0.8525837283
H	0.5783689894	-1.3469892330	0.3986352236
C	6.1715755022	-2.5245699669	0.9202535967
H	6.0522517097	-3.4791689611	1.4486562771
H	7.0067377562	-1.9537533396	1.3354447025
H	6.3406742023	-2.7396499651	-0.1428039548
C	1.0799155771	4.7808351033	3.3401929165
C	1.1392057740	6.1220088150	3.7351681413
H	2.0689219942	6.5247097218	4.1360195725
C	0.0422103128	6.9845121180	3.5819179960
C	-1.1676317577	6.4243509794	3.0378872382
C	-1.2533789596	5.0971722281	2.6230735425
H	-2.1782647828	4.7068517042	2.1880011928
C	-0.1315882057	4.2340928159	2.7310672416
C	-1.0244690726	9.0698283986	3.8201417205
C	-0.9630891466	10.4250527191	4.2548344780

C	-3.3485290690	10.7288757898	3.6598753177
C	-2.2279909748	8.5792633820	3.3245638883
C	-2.0663482084	12.5913917375	4.5953969028
H	-2.0403959557	12.6412697493	5.6930542507
H	-2.9561659975	13.1055661028	4.2232326823
H	-1.1486848223	13.0477497941	4.2085073870
C	-4.6076640230	8.8484687058	2.7219264921
H	-5.3399106219	9.6604672331	2.7536755719
H	-4.9659556022	8.0132866664	3.3435660162
H	-4.4866094114	8.5109688100	1.6808863831
C	4.3529862681	8.7189630644	4.6112726834
C	5.5186687334	7.9573904219	4.5761279304
H	5.4823014712	6.9362006127	4.1991472632
C	6.7385316379	8.4764075236	5.0375652057
C	6.7957062962	9.8622000551	5.5477557845
C	5.6181972975	10.6292259945	5.5762440121
H	5.6697463672	11.6509280586	5.9575149262
C	4.3897507944	10.1064271804	5.1324230141
C	9.0126977931	8.2975363209	5.4745845823
C	10.2032579776	7.4937621344	5.4353743291
C	11.4470227840	9.4244283790	6.3772114701
C	9.0427174893	9.6233135065	5.9439553694
C	12.6207694187	7.3401181012	5.9013074866
H	13.0472835901	7.3324783760	6.9114921037
H	13.3489277466	7.8076884393	5.2259212904
H	12.3875784293	6.3244588490	5.5700811048
C	10.3003394789	11.5310732118	6.8733951075
H	9.6177471102	11.6448496161	7.7250885888
H	9.9741615024	12.2189016530	6.0826970289
H	11.3305749043	11.7437858532	7.1707088971
C	9.4222492303	5.6457030809	1.8164759849

H	9.7638167979	4.6623613035	2.1860832415
C	10.7735365177	5.1083002961	-0.1460010792
H	11.7368742091	5.6023627756	-0.3510940145
H	10.3196597556	4.8191666178	-1.1074557220
H	10.9593913760	4.2010601793	0.4416704901
C	9.5183720916	7.2571052762	-0.0191075908
H	8.8510908071	7.7907923060	0.6661833482
H	9.0018841984	7.0824346928	-0.9761813900
H	10.4146270351	7.8674388868	-0.2122157515
C	6.8952616179	4.9321716644	7.0089005887
H	6.0018430953	5.0883745088	6.3792768974
C	5.2758995474	4.2999733505	8.7196366645
H	4.5804687809	4.5406409852	7.9061557253
H	5.0482879471	4.9430519918	9.5851908287
H	5.1239797634	3.2497529558	9.0166898778
C	7.7200101326	4.2364494931	9.2033046014
H	7.6876501538	3.1835225975	9.5246985853
H	7.6298519050	4.8779930182	10.0940740351
H	8.6726611356	4.4355883143	8.7013537319
C	2.7924029426	4.3607926425	0.5898073485
H	3.0935873480	4.8383681860	1.5371824407
C	2.7161460981	4.5989891903	-1.8398334316
H	2.2215880708	3.6278263756	-1.7310444996
H	3.6197258476	4.4849207967	-2.4597696252
H	2.0346555633	5.3044318562	-2.3410885151
C	3.6994658223	6.3915513009	-0.4111936539
H	3.8708995471	6.6347579521	0.6442264957
H	3.0561193867	7.1699664336	-0.8516272656
H	4.6661586651	6.3965380178	-0.9402759179
C	0.6741852401	1.6940317307	5.0580728209
H	0.3051084916	2.7257995426	4.9326021233

C	0.6656025558	-0.2657887829	6.5213484514
H	-0.2237853603	-0.9075002312	6.6244084914
H	1.2292803248	-0.2948279361	7.4672795343
H	1.2955869749	-0.6412885382	5.7082434379
C	-0.5803540356	1.7965030114	7.1513411883
H	-0.7868608467	2.8076616395	6.7791307621
H	-0.0912153938	1.8740091493	8.1359842653
H	-1.5370666333	1.2649616927	7.2810851176
C	2.4944281646	11.3761920612	2.3395761107
H	2.9880640592	11.8657994637	3.1987809409
C	2.0686515704	11.4843519760	-0.0659760564
H	1.5228565931	10.5678147013	0.1824663059
H	2.8575540037	11.2556182379	-0.8002377814
H	1.3781199018	12.2165733701	-0.5133736909
C	3.4254153606	13.2412225548	1.0641840233
H	3.8001195956	13.5106878220	2.0592559334
H	2.8057733253	14.0681417735	0.6813082757
H	4.2851793801	13.1096878561	0.3876850848
C	1.6681915377	9.8278185359	7.4227115050
H	2.0984403243	10.8055354570	7.1433079853
C	0.9265957212	8.4117743837	9.2709847458
H	0.7466215030	7.7359292021	8.4279911875
H	-0.0184232700	8.5963455129	9.8058882769
H	1.6392691282	7.9477303240	9.9710794997
C	1.8042204137	10.7039040706	9.7000706548
H	2.2039636803	11.5717762962	9.1611643217
H	2.5657313338	10.3526906651	10.4149263200
H	0.9137473540	11.0183303143	10.2680810790
N	3.8122925347	1.5092217095	2.4092993104
N	6.2129259912	0.0387729456	2.0572801883
N	2.6162158407	-1.4813459218	0.7497156976

N	4.9652081405	-1.7089474816	1.0825514921
N	0.1211519639	8.3159793255	3.9240966480
N	-2.2846276151	7.2824595307	2.9202960373
N	-2.1314048693	11.1976565059	4.1473874081
N	-3.3531990803	9.3841444347	3.2430775268
N	7.8668569103	7.7262092370	5.0314886050
N	7.9641646769	10.4000523393	5.9908493894
N	11.3676597477	8.0995246033	5.8979751041
N	10.2633221501	10.1513065546	6.3843611679
N	9.8895002606	5.9915496883	0.5959054221
N	6.6403872254	4.5127888573	8.2675266336
N	3.0639930113	5.0883368629	-0.5153451416
N	0.2732615064	1.0991472665	6.2057020358
N	2.6503027095	12.0157171488	1.1567828977
N	1.4675424153	9.6578163941	8.7498152876
O	6.3601397500	5.1259212255	4.1589099408
O	8.6144179853	3.7575729673	3.8872038631
O	1.5140788494	0.4370094420	1.4072165717
O	3.7381789893	-3.3747912327	0.0951064844
O	2.0933187423	3.9589720524	3.4748048047
O	-0.1102520747	2.9950767443	2.3358313298
O	0.0911210492	10.9411834605	4.7223846317
O	-4.3598086087	11.4291110829	3.5893471982
O	3.2088489144	8.2744081457	4.1987732743
O	3.2670961803	10.7604830905	5.1368970397
O	10.2080516519	6.3125725257	5.0066373977
O	12.5236107233	9.8797465746	6.7601328127
O	8.6550963076	6.3549081959	2.4905852838
O	8.0398793984	5.1244832392	6.5614008043
O	2.2453857719	3.2431202583	0.5666197994
O	1.3940922226	1.1465132387	4.2091867624

O	1.8597231979	10.3181195431	2.4785852684
O	1.4113171802	8.9641899624	6.5678079665
Ni	8.2278128997	5.7122113130	4.5028846033
Ni	1.8279116761	2.2674344045	2.4312159151
Ni	1.6922122773	9.5161880153	4.5044040126
H	-3.1429972375	6.8965492413	2.5417031627

Table S16. Optimized structures for model A

C	5.3516571771	4.3156132402	3.2699798737
C	4.0295052722	4.4711610499	2.9782847982
H	3.4470134779	5.3051838537	3.3870691872
C	3.3717299447	3.5807230261	2.1156818741
C	4.1116160099	2.4605466034	1.5353603788
C	5.4653354159	2.3022263112	1.8392514876
H	6.0384464594	1.4743500446	1.4136968485
C	6.1234255601	3.1903158660	2.6901135562
C	1.4910539555	2.8620722680	0.9987371559
C	0.0886726896	3.0453750610	0.7325252177
C	0.1628966681	1.0059553186	-0.6057402363
C	2.2058966229	1.8068666496	0.4488164978
C	-1.9525147516	2.2062484641	-0.3371593338
H	-2.4975133304	1.4524474605	0.2455090730
H	-2.1277529045	2.0201201450	-1.4014489247
H	-2.2779935463	3.2087106289	-0.0490095606
C	2.2326185270	-0.1674037584	-1.0394225052

H	2.6328379855	-0.8794382804	-0.3011441961
H	3.0441715424	0.2243335534	-1.6704573613
H	1.5113087310	-0.6951748254	-1.6692498735
C	1.2358007009	7.4399488136	3.9277655955
C	1.8967140827	8.3896902336	4.6548145296
H	2.9214213668	8.2432310136	4.9958450826
C	1.2512100042	9.5740132096	5.0439384381
C	-0.1292492455	9.8223149350	4.6364614627
C	-0.7935959488	8.8648008969	3.8661969509
H	-1.8310170281	9.0160134489	3.5544745433
C	-0.1629479409	7.6565559684	3.5114687298
C	1.2299448759	11.5952328237	6.1541328060
C	1.9443368592	12.5402440378	6.9615665581
C	-0.0674555183	13.9372706552	6.9568772420
C	-0.0825496790	11.8250423759	5.7497410799
C	1.9619852115	14.6607292508	8.1522136816
H	2.1409074142	14.2421086717	9.1508772979
H	1.3366093552	15.5530462216	8.2188077245
H	2.9319124169	14.8825041934	7.6937863406
C	2.0340393209	13.3323701442	5.6705553210
H	2.3023210509	14.3077965952	6.0862895004
H	2.7809235136	12.5954586932	6.0043819253
H	2.0288968824	13.3993548318	4.5716875484

C	2.2503774835	6.9299691343	0.6340335732
H	2.8903360586	7.0477875795	1.5266399097
C	1.9457138342	7.4820640813	-1.6905844807
H	1.0385232459	6.8901718764	-1.5345779064
H	2.5526234587	7.0240571899	-2.4869609923
H	1.6656512807	8.4965408869	-2.0135080468
C	3.9415638017	8.3070844729	-0.4693212749
H	4.4050336865	8.2684021620	0.5235642422
H	3.7381420409	9.3561787308	-0.7292929262
H	4.6383652881	7.8882788590	-1.2102069136
C	0.9483592250	3.4440575739	4.6364532155
H	2.0085106219	3.7215272646	4.4866651096
C	-0.5419739771	2.0578672360	5.8914336661
H	-0.7392779632	2.2389800098	6.9593913733
H	-0.6525524239	0.9787803542	5.7019363144
H	-1.2718014971	2.6100480351	5.2910283229
C	1.8947363011	1.8984519620	6.2427221619
H	2.8372827094	2.3228296242	5.8746647805
H	1.9089677965	0.8094784724	6.0806306821
H	1.8220361765	2.0840755428	7.3255716113
N	2.0719582243	3.7474764038	1.8327882501
N	3.4876120835	1.5765681056	0.7005161666
N	-0.5089858017	-2.1119185297	-0.0640602930

N	1.5180475468	0.9281238160	-0.3854110073
N	1.9024598428	10.4775220618	5.7919591409
N	-0.7719485985	10.9679997500	5.0011873473
N	1.2606773540	13.6728674635	7.3184488160
N	-0.7034679035	12.9991056668	6.1764291653
N	2.6902792261	7.5359685764	-0.4580041464
N	0.7838946378	2.5003857201	5.5435858251
O	6.0030150489	5.1310388806	4.0405375083
O	7.3738782705	3.1209752044	3.0176079452
O	-0.5562543259	3.9976595362	1.2115756027
O	-0.4415524243	-0.1667745129	1.2426380126
O	1.7664191850	6.3018089090	3.5962407768
O	-0.7303209165	6.6993134409	2.8640952308
O	3.1272501817	12.3650541200	7.3083387290
O	-0.6238257938	14.9563102972	7.3200125841
O	1.1921096824	6.2790911590	0.6768374693
O	0.0450031205	3.9919499784	4.0068441317
Ni	0.6311198721	5.2259528025	2.3998138704
H	3.9911762767	0.7975311874	0.2879383876
H	-1.7361013097	11.1330109250	4.7222942342
H	7.6038547747	3.8536677355	3.6238456771
H	5.4320180329	5.8288656033	4.4082608918

Table S17. Optimized structures for model B

C	5.6905262417	3.8041997408	3.5943213609
C	4.4546309119	3.3606828970	3.2293250030
H	3.5822761787	4.0064731632	3.3342241899
C	4.2809553255	2.0811037126	2.6796469477
C	5.4402521667	1.2053383870	2.5121191125
C	6.7045615016	1.6617777151	2.8904792532
H	7.5829430967	1.0179096102	2.7697377328
C	6.8810658636	2.9360312739	3.4298084941
C	2.9522032302	0.4203396747	1.7980306821
C	1.6286211982	-0.0215401309	1.4458733755
C	2.6015866871	-2.1751430870	0.8367519048
C	4.0612910547	-0.3988536414	1.6376617984
C	0.1860800033	-1.8351662729	0.6429787548
H	-0.0795621272	-2.6412966592	1.3388940554
H	0.1978478494	-2.2447044915	-0.3736935599
H	-0.5244244311	-1.0087868210	0.7275215587
C	4.9896367476	-2.5560116229	0.8642558581
H	5.4923985727	-2.8326556146	1.8049301700
H	5.7102122449	-2.0746163982	0.1855928186
H	4.5985532884	-3.4644852085	0.3981194522
C	0.6970790556	5.1996712410	3.0917540701
C	0.8729561880	6.4937145088	3.4941651427
H	1.8313217377	6.8190703475	3.8813111038
C	-0.1931421442	7.4064959618	3.4628888006
C	-1.4982629217	6.9895135784	2.9567816756
C	-1.6682840592	5.6749105385	2.5158635792
H	-2.6383083092	5.3303425067	2.1424009574
C	-0.6126871708	4.7453582843	2.5869455203
C	-1.0772856804	9.4984029870	3.8635478459
C	-0.8620199248	10.8314758334	4.3451377170

C	-3.2097596541	11.3051628204	3.8325436010
C	-2.3134855486	9.0915485273	3.3683040783
C	-1.7563760242	13.0485848045	4.7911921433
H	-1.5879017877	13.0372509503	5.8762574986
H	-2.6584675178	13.6158529353	4.5515835517
H	-0.8700924977	13.4796701344	4.3119538755
C	-4.6327309150	9.6636572871	2.7515288240
H	-5.2782604559	10.5442405958	2.8157168572
H	-5.1195607978	8.8312055366	3.2838212302
H	-4.4874072686	9.3957284554	1.6931750042
C	4.2032902411	8.6006187846	4.9178095999
C	5.2779849203	7.7535829828	4.8890645207
H	5.1451715012	6.7230531459	4.5569068050
C	6.5612341549	8.2068664087	5.2198563280
C	6.7637628064	9.5909059982	5.6321356272
C	5.6571876379	10.4434280555	5.6792850718
H	5.8159042413	11.4759938444	6.0063067690
C	4.3742207644	10.0023370852	5.3434649319
C	8.8109076638	7.8482380203	5.5314599259
C	9.9138119841	6.9276070415	5.4679143588
C	11.3190755865	8.7038190000	6.3964865855
C	8.9825167553	9.1552944255	5.9519249340
C	12.2657756731	6.4830497711	5.9197654413
H	12.2643840999	5.8863053862	6.8437961160
H	13.1855128728	7.0723937309	5.8770561078
H	12.1781945483	5.8041324840	5.0659142082
C	10.4273105318	10.9297297188	6.8506622062
H	9.8031016108	11.0814029427	7.7411041164
H	10.1051543693	11.6459533679	6.0852344579
H	11.4845901800	11.0622127208	7.0936069367
C	9.0401704375	5.6806586042	1.9081918920

H	9.6766731828	4.8479142723	2.2635485771
C	10.4075893138	5.5548541568	-0.0837670498
H	11.1579238598	6.3320152005	-0.3019182586
H	10.0416803280	5.1502574345	-1.0409436526
H	10.8923168438	4.7453368337	0.4764894329
C	8.5692569890	7.1846440967	0.0841205420
H	7.7619902476	7.4791304829	0.7629090254
H	8.1460223979	6.8614538927	-0.8794223216
H	9.2272794878	8.0491842204	-0.0969843137
C	6.5019142347	4.5190471128	7.0418262130
H	5.5545421256	4.4980147478	6.4690176411
C	5.1243211338	3.8200866947	8.9388952664
H	4.3207443909	3.9063616360	8.1973468671
H	4.8655257978	4.4405149526	9.8103081444
H	5.2052862822	2.7710729173	9.2679375915
C	7.5412479600	4.3061800072	9.2129344212
H	7.7845387846	3.2962258576	9.5815908501
H	7.3480621697	4.9566916780	10.0794678085
H	8.3914277183	4.6917403061	8.6414049319
C	2.2969557780	4.1847698084	0.1679747581
H	2.7247223560	4.7764489358	0.9973385387
C	2.1640395319	3.8885418187	-2.2186672586
H	1.5101468090	3.0698441065	-1.9005184302
H	3.0011146132	3.4831235225	-2.8096730692
H	1.5941366027	4.5809145461	-2.8588793822
C	3.5472512705	5.7162768976	-1.2691045567
H	3.8509638790	6.1312154384	-0.3007389458
H	3.0312206825	6.4958677268	-1.8501818579
H	4.4438102851	5.3966120444	-1.8218976711
C	1.7139759878	1.7748363312	5.0381440611
H	2.6234049493	2.3693171579	4.8248691553

C	0.6306387604	0.3543752743	6.6275664257
H	0.2282185252	0.7401206446	7.5782450328
H	0.9248721830	-0.6966324790	6.7803326912
H	-0.1480155703	0.4052571356	5.8590557938
C	2.8915281684	1.2303400164	7.0830207832
H	3.6812208046	1.8257253706	6.6075019905
H	3.2922650278	0.2270648628	7.3002520715
H	2.6069087884	1.7011793336	8.0383511299
N	3.0606096761	1.6583973206	2.3200390931
N	5.2915448866	-0.0478832022	1.9876331308
N	1.5158812028	-1.2974592423	0.9742746509
N	3.8515374581	-1.6712709571	1.1101976249
N	-0.0132433004	8.6622040087	3.8997220361
N	-2.5447726304	7.8622938704	2.9149114240
N	-1.9407858043	11.6751056807	4.2988349531
N	-3.3587583710	10.0153248156	3.3766030290
N	7.6112232689	7.3678228657	5.1632633682
N	7.9925663008	10.0436537869	5.9960754994
N	11.1265086723	7.4050828098	5.8944919151
N	10.2603550711	9.5654044468	6.3455310720
N	9.3139495865	6.0976231843	0.6916816583
N	6.3776779838	4.2742610090	8.3468132677
N	2.6542292118	4.5700513761	-1.0474301354
N	1.7561683566	1.1423800505	6.1951546845
O	5.8977959827	4.9888213018	4.0807945185
O	8.0153724220	3.4388539765	3.7988757620
O	0.6304155933	0.7128707076	1.5742951001
O	2.4264107210	-3.3246516791	0.4858027847
O	1.6322822375	4.3009742603	3.1593252846
O	-0.7110013905	3.5027501323	2.2651115694
O	0.2436422450	11.2212082803	4.7644778659

O	-4.1321092095	12.0983388527	3.8324065468
O	3.0031257077	8.2237618597	4.6016663350
O	3.3023174206	10.7361987299	5.3982245815
O	9.7941342393	5.7653735571	5.0406287280
O	12.4204451687	9.0345963658	6.8169297228
O	8.1405757758	6.1357303818	2.6208796480
O	7.5744741890	4.7547623500	6.4887969369
O	1.5363651418	3.2260436731	0.3864950833
O	0.7793678508	1.7371982828	4.2395597235
Ni	7.7901586362	5.3667889459	4.5156843104
Ni	1.1296097208	2.5826794066	2.3392086035
H	6.0915732272	-0.6594863489	1.8738211295
H	-3.4517512248	7.5608392903	2.5743315014
H	2.3187340144	8.9341980908	4.6331643223
H	3.4950970802	11.6563121590	5.6460828537

NMR Spectra

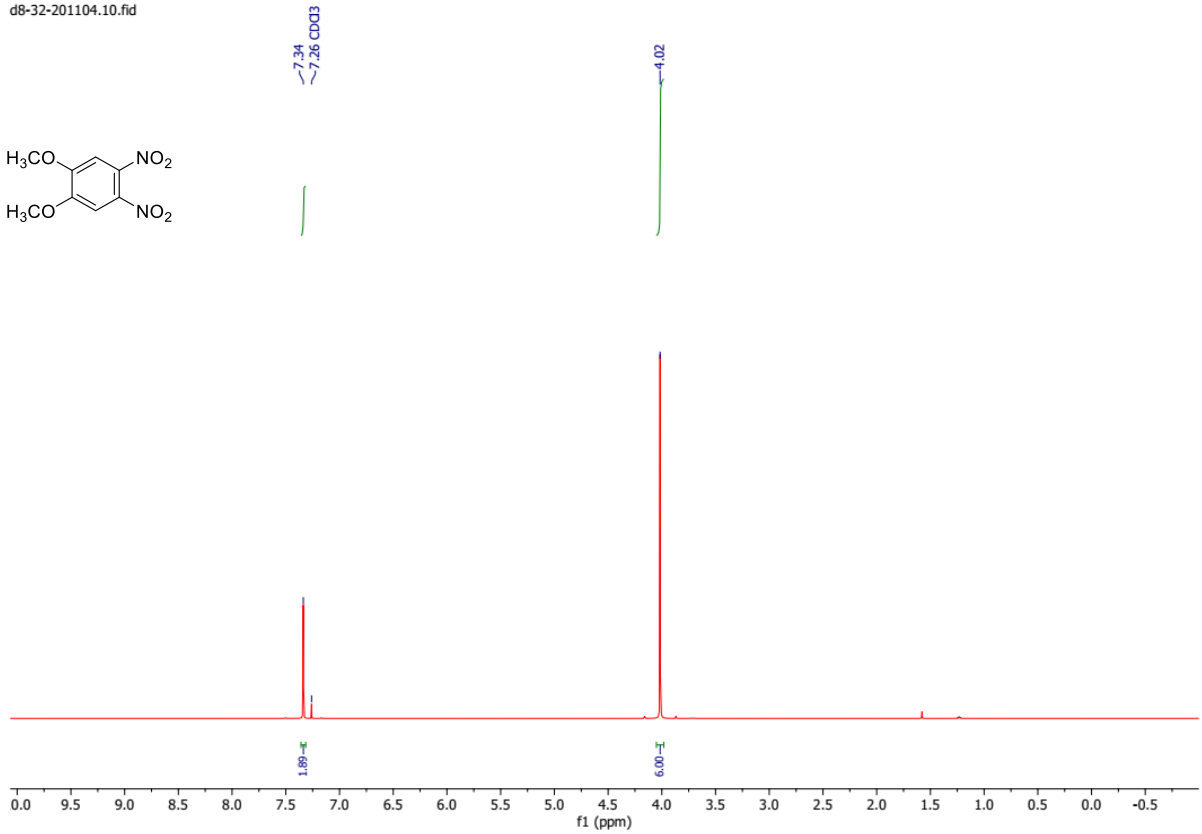


Fig. S39. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) spectrum of 1,2-dimethoxy-4,5-dinitrobenzene **2**

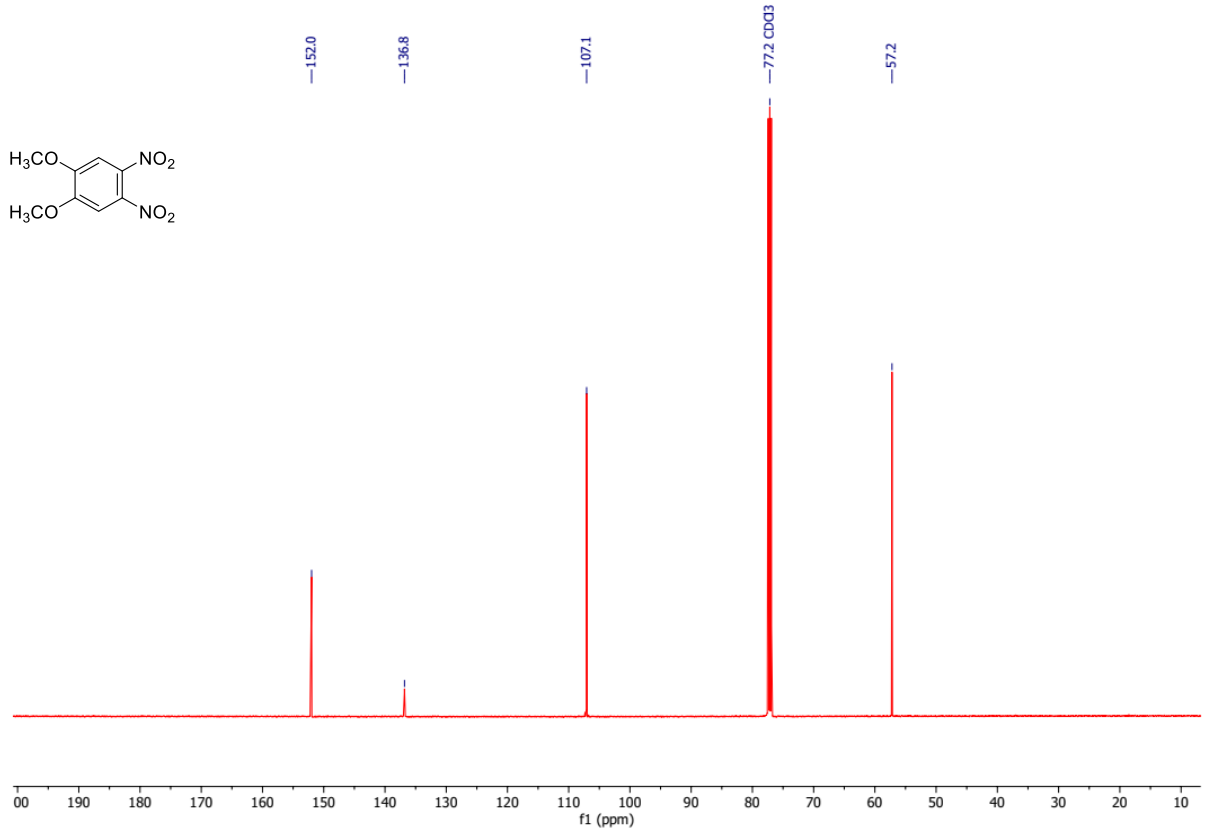


Fig. S40. ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) spectrum of 1,2-dimethoxy-4,5-dinitrobenzene **2**

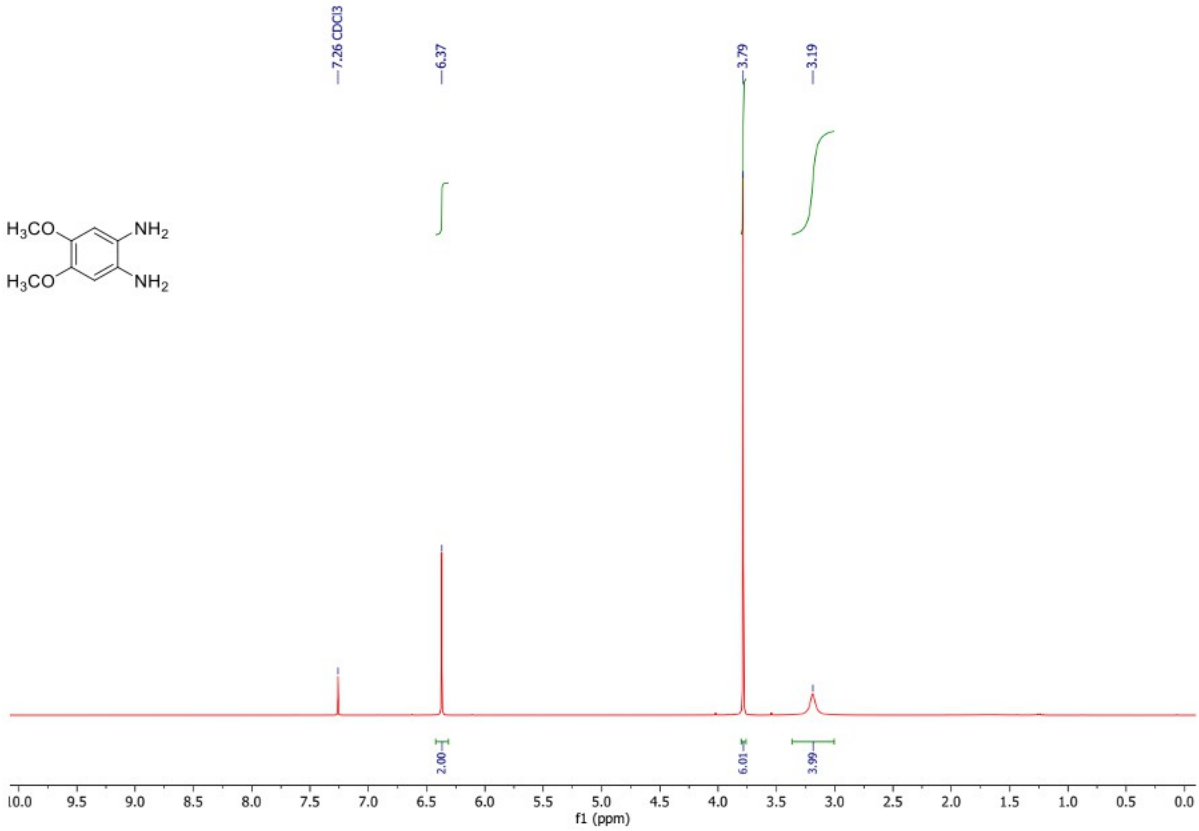


Fig. S41. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) spectrum of 1,2-diamino-4,5-dimethoxybenzene **3**

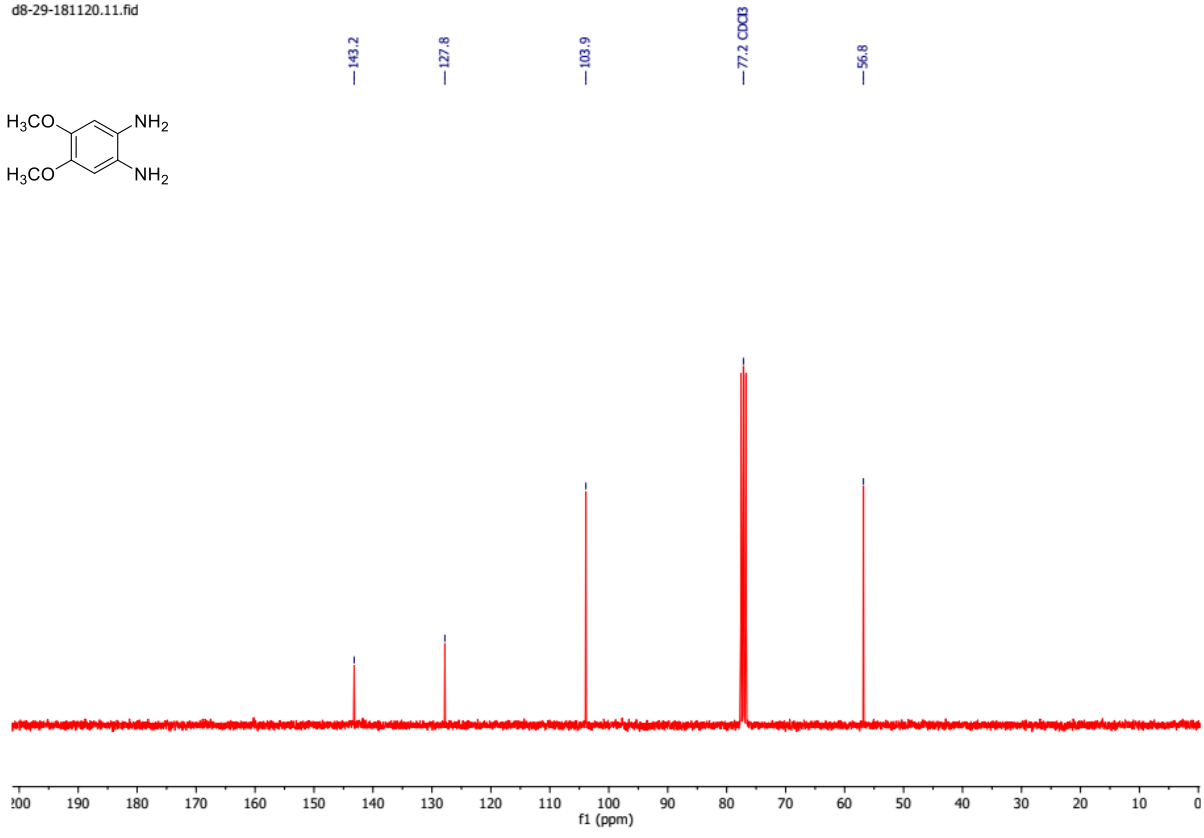


Fig. S42. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) spectrum of 1,2-diamino-4,5-dimethoxybenzene **3**

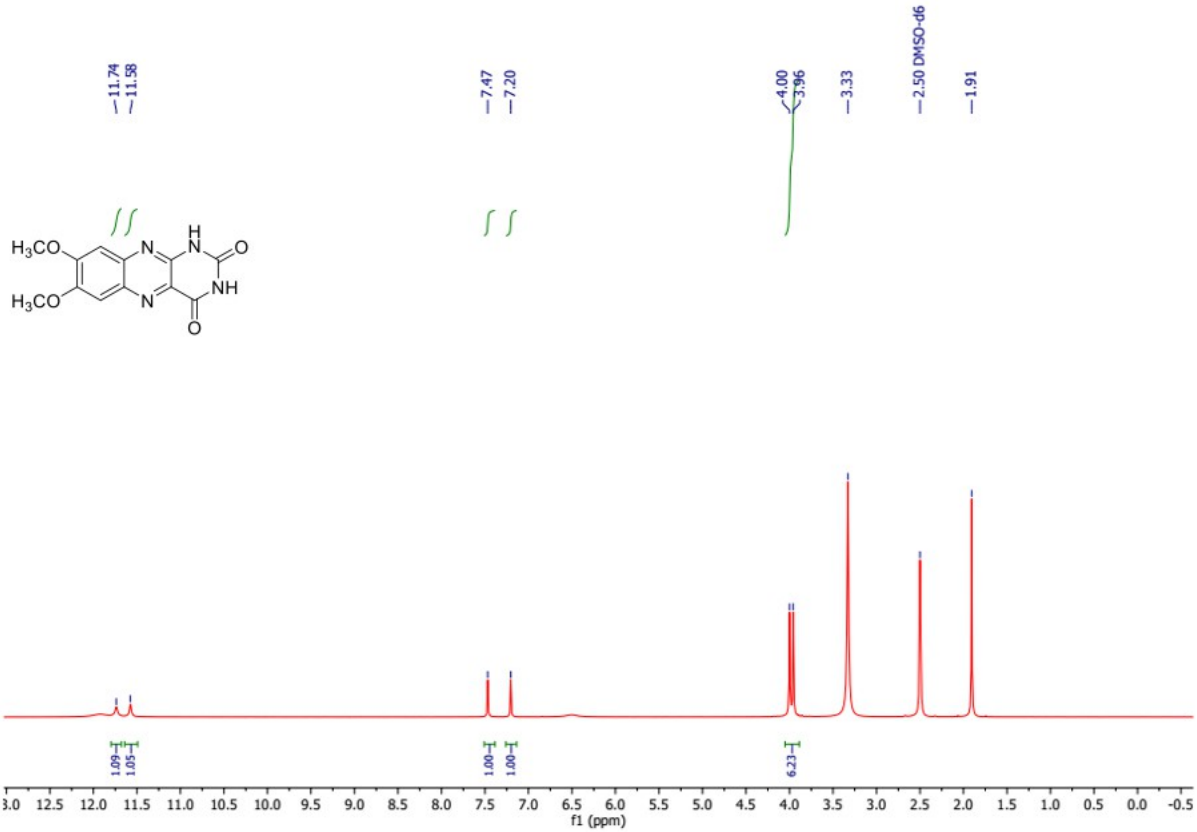


Fig. S43. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) spectrum of 7,8-dimethoxyalloxazine **4**

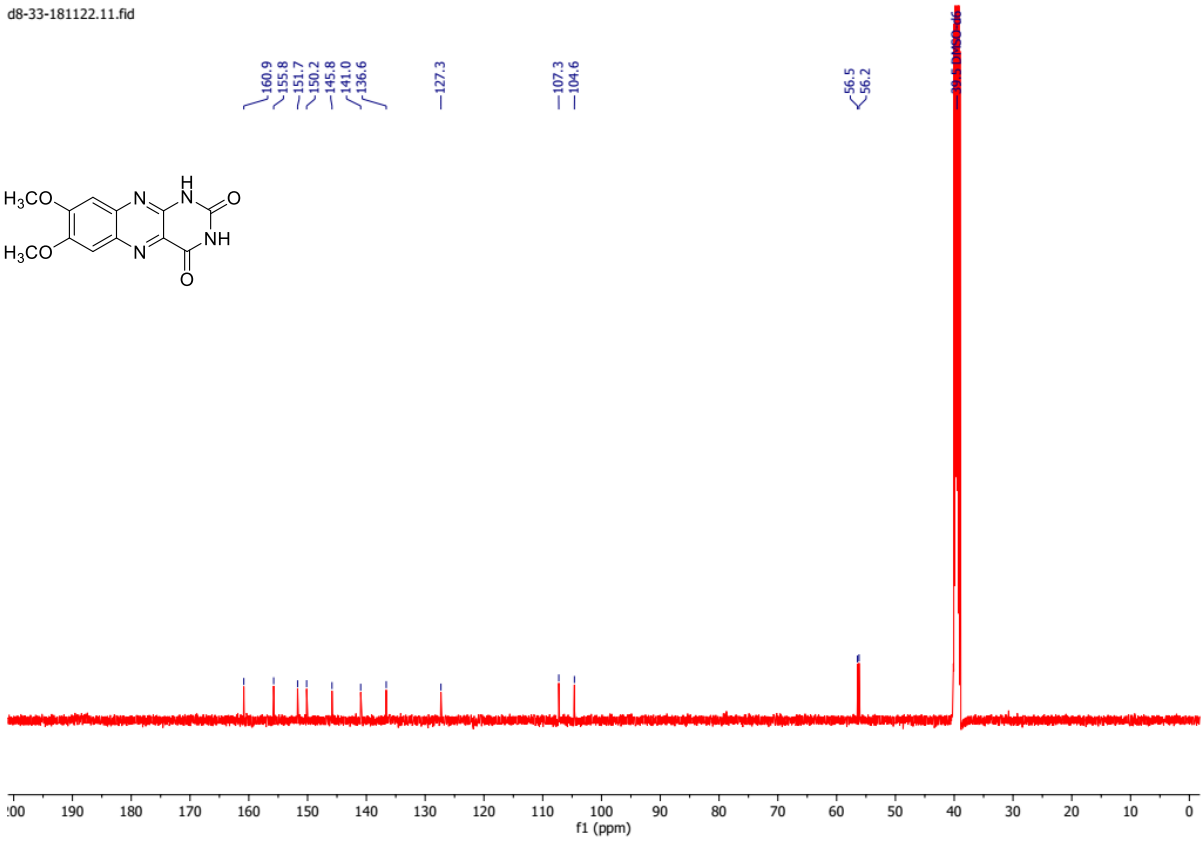


Fig. S44. ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) spectrum of 7,8-dimethoxyalloxazine **4**

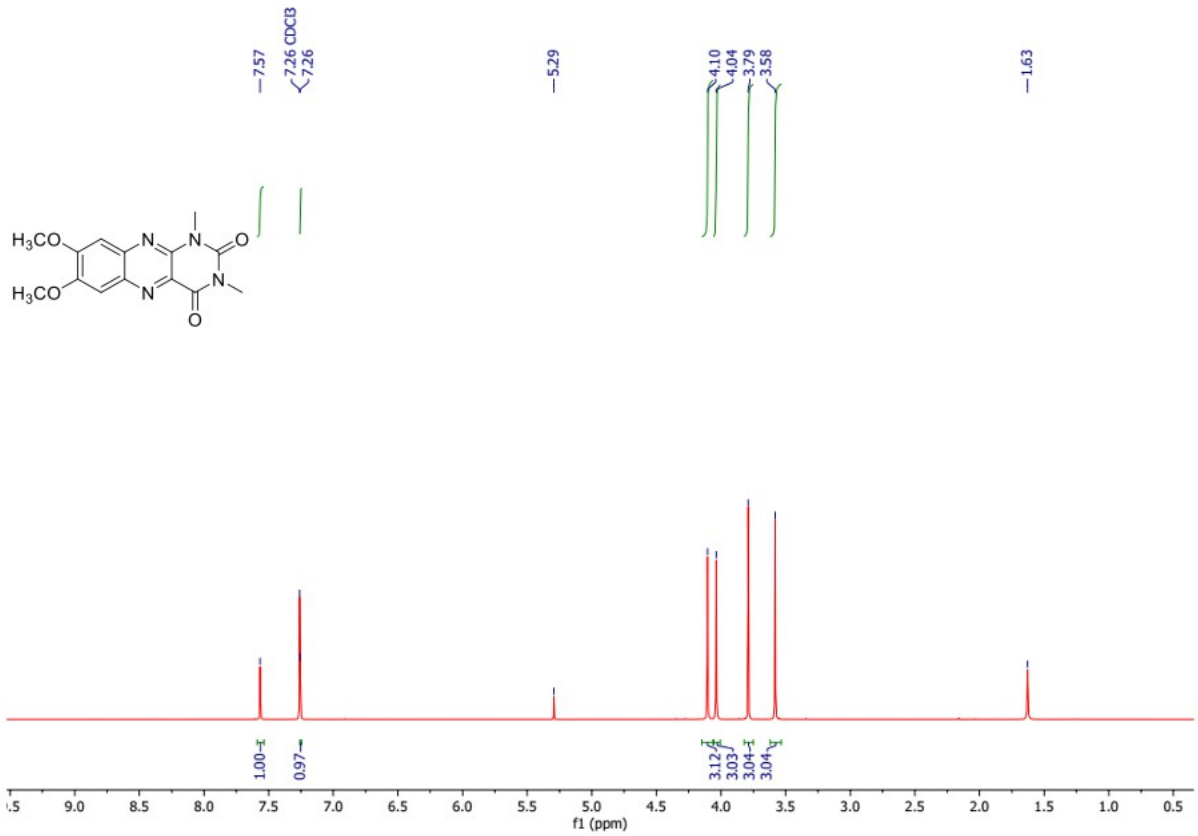


Fig. S45. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) spectrum of 7,8-dimethoxy-1,3-dimethylalloxazine **5**

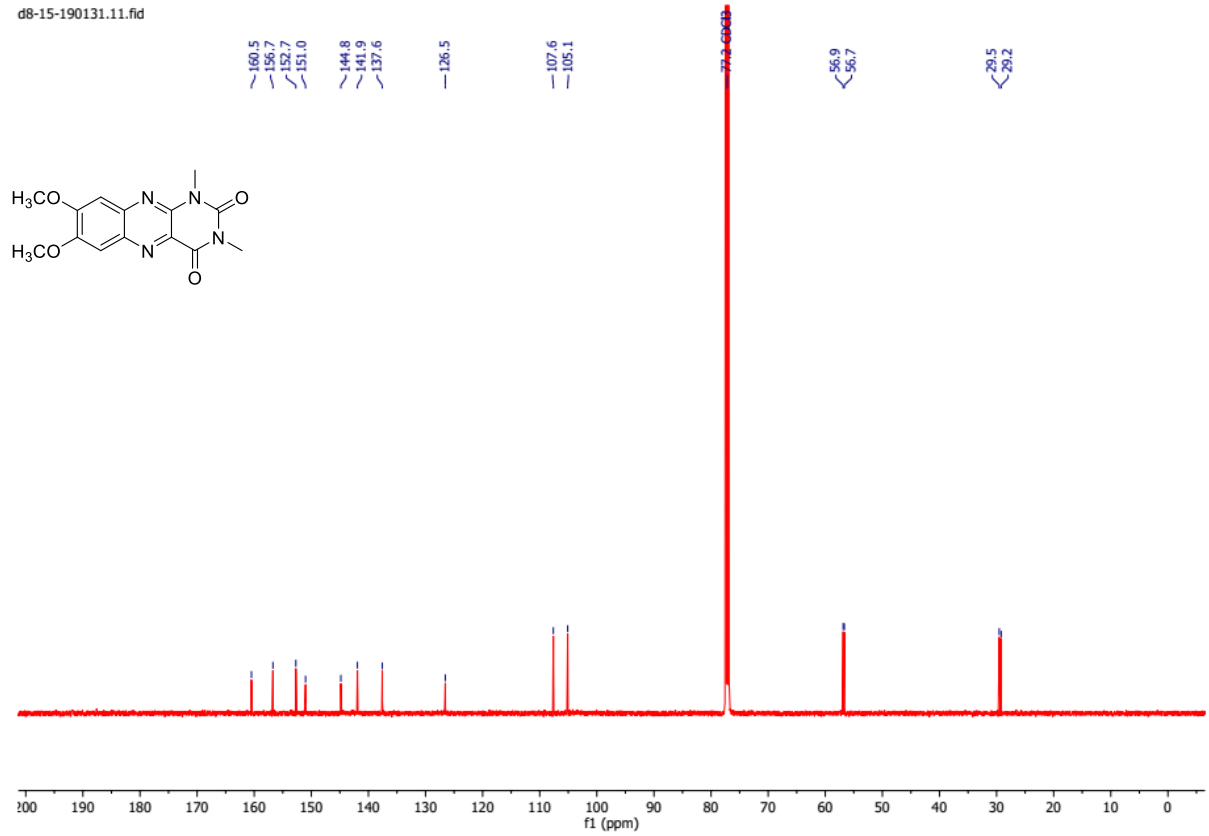


Fig. S46. ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) spectrum of 7,8-dimethoxy-1,3-dimethylalloxazine **5**

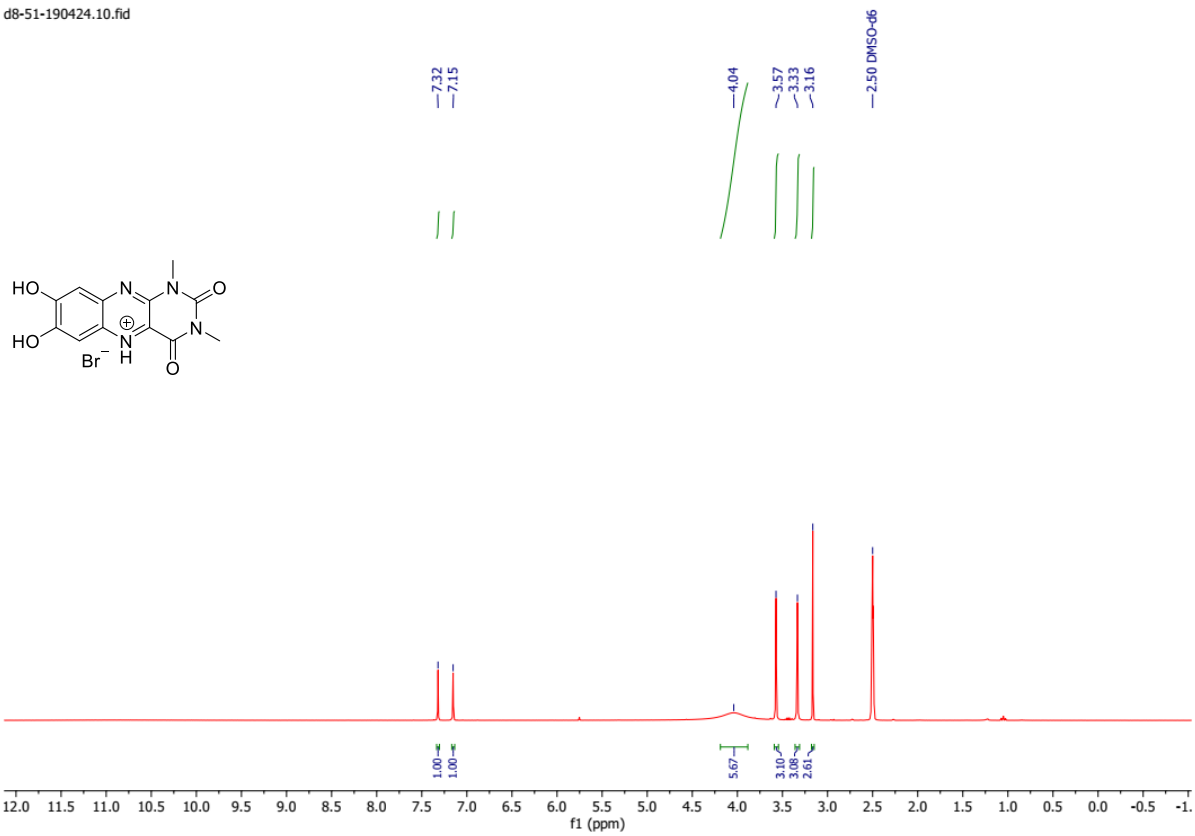


Fig. S47. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) spectrum of 7,8-dihydroxy-1,3-dimethylalloxazine-5-ium bromide **6**

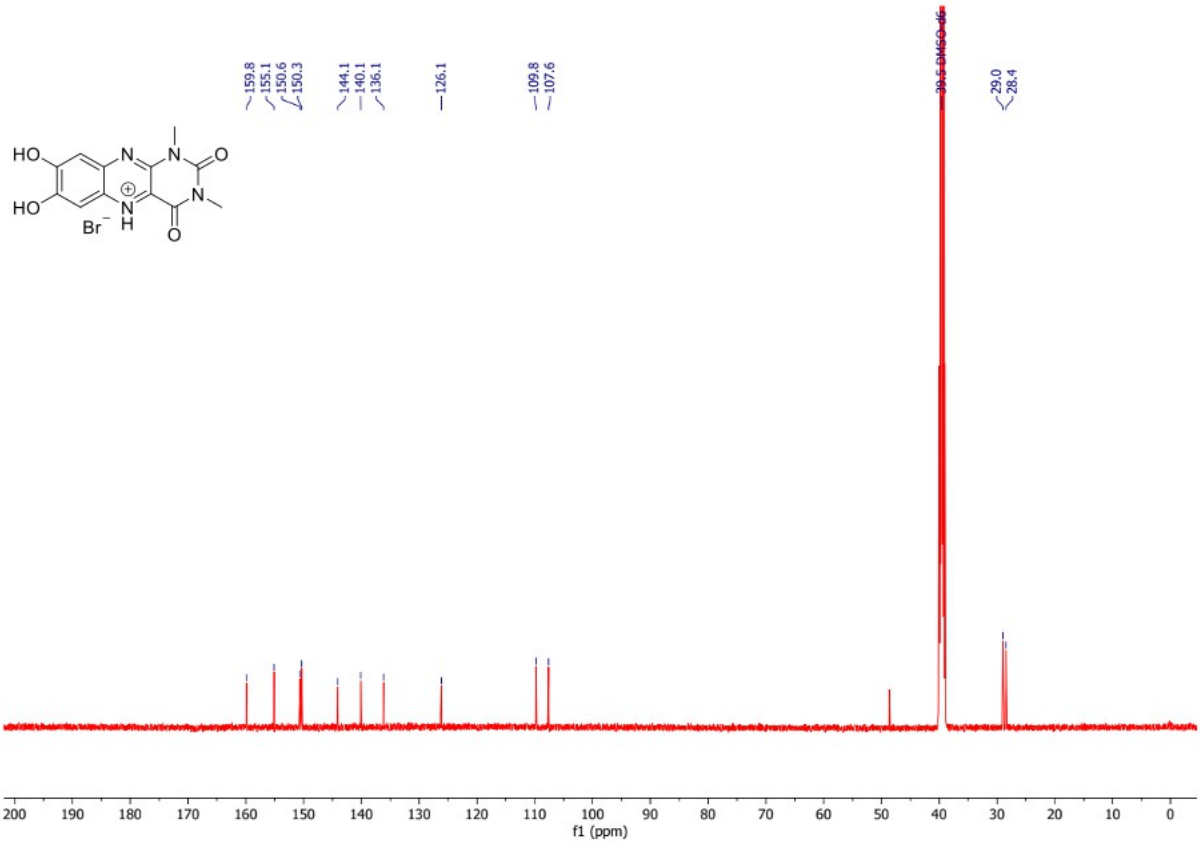


Fig. S48. ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) spectrum of 7,8-dihydroxy-1,3-dimethylalloxazine-5-ium bromide **6**