Temperature-Dependent Reactivity of a Nonheme $Fe^{III}(OH)(SR)$ Complex: Relevance to Isopenicillin N Synthase

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A. Materials and methods.

Materials. All syntheses and manipulations were conducted in an N_2-filled drybox (Vacuum Atmospheres, O_2 < 0.2 ppm, H_2O < 0.5 ppm) or using standard Schlenk techniques under an atmosphere of Ar unless otherwise noted. $Fe(OTf)_2 \bullet 2$ MeCN and $^{57}Fe(OTf)_2 \bullet 2$ MeCN were prepared according to a literature procedure.[1] Powdered ^{57}Fe metal (95.93%) was purchased from Cambridge Isotope Laboratories. The *p*-NO_2-thiophenol, *p*-CF_3-thiophenol, *p*-NO_2-phenol were purchased from commercial sources and dried over P_2O_5 under vacuum before use. Sodium hydride (30 wt% dispersion in mineral oil) was purchased from Sigma-Aldrich, washed several times with hexanes and dried under vacuum prior to use. Methanol, acetonitrile and acetonitrile-d_3 were distilled from CaH_2. Tetrahydrofuran, tetrahydrofuran-d_8, toluene and toluene-d_8 were dried over Na/benzophenone and subsequently distilled. All other non-deuterated solvents were obtained from a Pure-solv solvent purification system from Innovative Technologies, Inc. Anhydrous 2-methyltetrahydrofuran and pentane (sure seal) were purchased from Sigma-Aldrich, and distilled over Na/benzophenone. All solvents were degassed by a minimum of three freeze–pump–thaw cycles and stored over freshly activated 3 Å molecular sieves in the drybox following distillation. All other reagents were purchased from commercial vendors and used without further purification. The ligand $BNPA^{Ph2}OH$ was prepared by a literature procedure[2] and was dried over P_2O_5 for 12 h under vacuum before metalation. The complexes $Fe^{II}(BNPA^{Ph2}O)(OTf)$, $^{57}Fe^{II}(BNPA^{Ph2}O)(OTf)$, $Fe^{III}(BNPA^{Ph2}O)(OH)(OTf)$, $^{57}Fe^{III}(BNPA^{Ph2}O)(OH)(OTf)$ were synthesized following literature procedures.[2] The tris(*p*-methoxyphenyl)methyl radical was generated in situ following a literature procedure.[3]

Instrumentation. The ^1H NMR and ^{19}F NMR spectra were measured on a Bruker 300 MHz or a Bruker 400 MHz NMR spectrometer. Chemical shifts were referenced to reported solvent resonances.[4] Mössbauer spectra were recorded on a spectrometer from SEE Co. (Edina, MN) operating in the constant acceleration mode in a transmission geometry. The sample was kept in an SVT-400 cryostat from Janis Research Co. (Wilmington, MA), using liquid N_2 as a cryogen for 80 K measurements. Isomer shifts were determined

relative to the centroid of the spectrum of a metallic foil of α-Fe collected at room temperature. Data analysis was performed using version F of the program WMOSS (www.wmoss.org), and quadrupole doublets were fit to Lorentzian lineshapes.

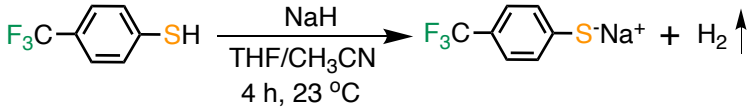
Single Crystal X-ray Crystallography.

Complexes 1, 2, 3, 4, 5•Li(OTf)(THF), and 6. All reflection intensities (except for **4**) were measured at 110(2) K using a SuperNova diffractometer (equipped with an Atlas detector) with Mo *K*α radiation (λ = 0.71073 Å) for complexes **1**, **2, 3** and **6** or with Cu *K*α radiation (λ = 1.54178 Å) for complex **5•LiOTf** with the program CrysAlisPro (Version CrysAlisPro 1.171.39.29c, Rigaku OD, 2017). For **4**, reflection intensities were measured at 100(2) K using a Rigaku XtaLAB Synergy FR-X diffractometer (equipped with a HyPix-6000HE detector) with Cu *Kα* radiation (λ = 1.54178 Å) with the program CrysAlisPro (Version CrysAlisPro 1.171.40.67a, Rigaku OD, 2019). The same program was used to refine the cell dimensions and for data reduction. The structures were solved with the program SHELXS-2018/3 (Sheldrick, 2018) and were refined on F^2 with SHELXL-2018/3 (Sheldrick, 2018).[5] Numerical absorption corrections based on gaussian integration over a multifaceted crystal model were applied using CrysAlisPro for complexes **1**, **2, 3** and **6**. Analytical numeric absorption correction using a multifaceted crystal model were applied using CrysAlisPro for complexes **4** and **5•Li(OTf)(THF)**. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions (unless otherwise specified) using the instructions AFIX 23, AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 U_{eq} of the attached C atoms. The H atoms attached to N1, N5, O1 (complex **5•Li(OTf)(THF)** only) and O2 (complexes **3** and **4**) were found from difference Fourier maps, and their coordinates were refined pseudofreely using the DFIX instructions in order to keep the N–H and O–H bond distances within an acceptable range. One of the two neopentylamine arms in **4** is disordered over two orientations, and the occupancy factor of the major component refines to 0.617(5). Additionally, there is a mixture of disordered solvent molecule

(THF/pentane) at one site. The occupancy of the THF molecule (major component) refines to 0.662(7), and the THF is clearly the acceptor in one intermolecular OH···O hydrogen bond.

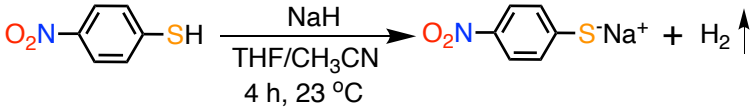
DFT calculations. All calculations were performed with the ORCA-4.1.2 program package.[6] Initial geometries were obtained from X-ray crystallographic models. Optimized geometries were calculated using the B3LYP functional. The 6-311g* basis set was used for all Fe, N, O, S, F, Li atoms and the 6-31g* basis set was used for all C and H atoms. Frequency calculations at the same level of theory confirmed that all optimizations had converged to true minima on the potential energy surface (i.e., no imaginary frequencies). The optimized structures using the B3LYP functional were used for Mössbauer parameter calculations for **1** – **7**. Mössbauer parameters were computed using the B3LYP functional[7] and basis sets CP(PPP)[8] for Fe and def2-TZVP[9] for all other atoms. The angular integration grid was set to Grid4 (NoFinalGrid), with increased radial accuracy for the Fe atom (IntAcc 7). A continuum solvation model was included (COSMO), with a solvent of intermediate dielectric (methanol). The isomer shift was obtained from the electron density at the Fe nucleus, using a linear fit function previously reported: $\delta = \alpha(\varrho(0) - c) + \beta$. For the methodology described here, $\alpha = -0.424$ au^3 mm s^{-1}, $\beta = 7.55$ mm s^{-1}, and $c = 11800$ au^{-3}.[10]

B. Synthetic procedures.



NaSPh$^{p\text{-}CF_3}$. The starting material *p*-CF_3-C_6H_4SH (183.0 mg, 1.03 mmol) was dissolved in THF and a THF suspension of sodium hydride (24.6 mg, 1.03 mmol, 1 equiv) was added slowly to the thiophenol solution. An immediate color change from pale yellow to pale pink was observed with a strong effervescence indicating H_2 evolution. The reaction mixture was diluted with acetonitrile (2 mL) to ensure complete dissolution of the salt and then stirred for 4 h at 23 °C. The reaction mixture was then filtered over Celite and dried down under vacuum to give a pale yellow solid. The solid was washed with pentane and dried, giving the sodium salt of *p*-trifluoromethylthiophenol (**NaSPh$^{p\text{-}CF_3}$**) as a yellow solid (crude, 200 mg, (98%)). This compound was stored at -35 °C in the drybox freezer. ^{1}H NMR (CD_3CN, 400 MHz): δ 7.31 (d, 2H), 6.99 (d, 2H), 4.30 (s, 1H) ppm. ^{19}F NMR (CD_3CN, 300 MHz): δ -60.18 ppm.

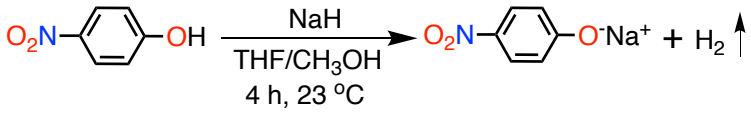
Caution: Addition of NaH should be done slowly, and it is advised to perform this reaction on a scale of 1 mmol or lower.



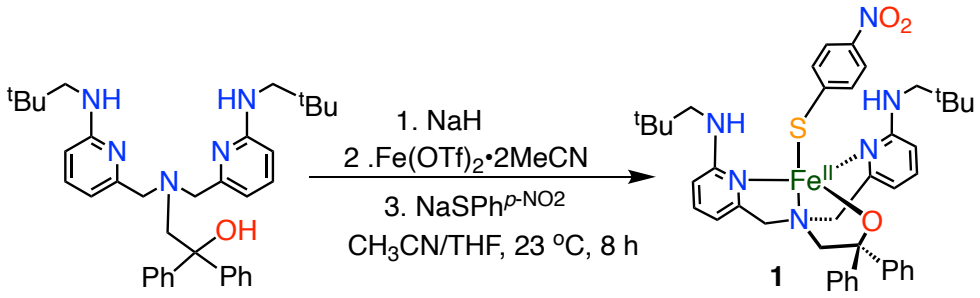
NaSPh$^{p\text{-}NO_2}$. The starting material *p*-NO_2-C_6H_4SH (142.0 mg, 0.913 mmol) was dissolved in THF and a THF suspension of sodium hydride (22.0 mg, 0.916 mmol, 1 equiv) was added slowly to the thiophenol solution. An immediate color change from pale yellow to blood-red was observed with a strong effervescence indicating H_2 evolution. The reaction mixture was diluted with acetonitrile (2 mL) to ensure complete dissolution of the salt and then stirred for 4 h at 23 °C. The dark red reaction mixture was then filtered over Celite and then dried down under vacuum to give a dark red solid. The solid was washed with pentane and dried, giving the sodium salt of *p*-nitro-thiophenol (**NaSPh$^{p\text{-}NO_2}$**) as a dark red solid (crude, 156

mg, (96%)). This compound was stored at -35 °C in the drybox freezer. ^{1}H NMR (CD_3CN, 400 MHz): δ 7.62 (d, 2H), 7.22 (d, 2H) ppm.

Caution: Addition of NaH should be done slowly, and it is advised to perform this reaction on a scale of 1 mmol or lower.

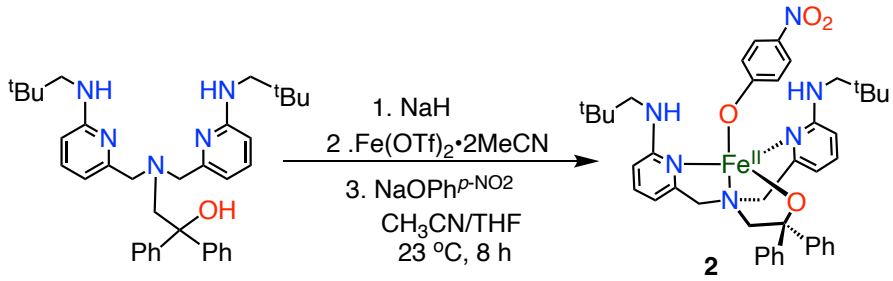


NaOPh$^{p\text{-}NO_2}$. The starting material *p*-NO_2-C_6H_4OH (500 mg, 3.59 mmol) was dissolved in THF and a THF suspension of sodium hydride (86 mg, 3.61 mmol, 1 equiv) was added slowly to the thiophenol solution. An immediate color change from pale yellow to dark orange was observed with an effervescence indicating H_2 evolution. A small amount of methanol (1 – 2 mL) was added to this turbid reaction mixture and the mixture changed from dark orange to a dark yellow, clear solution. The reaction mixture was stirred for 4 h at 23 °C, and then filtered over Celite, dried and down under vacuum to give a dark orange solid. The solid was washed with pentane and dried, giving the sodium salt of *p*-nitrophenol (**NaOPh$^{p\text{-}NO_2}$**) as a dark orange solid (crude, 550 mg, (95%)). This compound was stored at -35 °C in the drybox freezer. ^{1}H NMR (CD_3CN, 400 MHz): δ 8.00 (d, 2H), 6.54 (d, 2H) ppm.



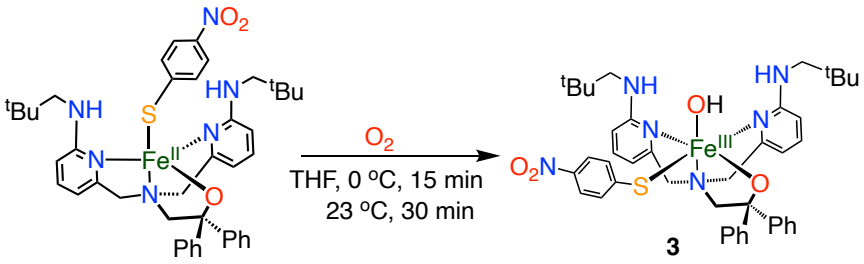
Fe^{II}(BNPA^{Ph2}O)(SPh$^{p\text{-}NO_2}$) (1). The ligand BNPA^{Ph2}OH (60.0 mg, 0.11 mmol) was dissolved in THF (2 mL) and a suspension of NaH (2.5 mg, 0.11 mmol, 1 equiv) in THF (1 mL) was added. The solution was stirred for 1 h at 23 °C. An amount of anhydrous $Fe(OTf)_2$ • 2 MeCN (46.0 mg, 0.11 mmol, 1 equiv) was

dissolved in acetonitrile (2 mL) and added dropwise to the BNPA^{Ph2}OH/NaH mixture. An immediate color change from colorless to yellow-green was noted, and the reaction mixture was stirred for 4 h. To this dark yellow solution, an acetonitrile solution of freshly prepared NaSPh$^{p\text{-}NO_2}$ (18.0 mg, 0.11 mmol, 1 equiv) was added and the reaction mixture was stirred for an additional 4 h at 23 °C. A color change from dark yellow to dark red-brown was noted. The resulting dark red-brown reaction mixture was evaporated to dryness under vacuum, giving a dark brown-red solid. This solid was dissolved in minimum amount of THF (3 mL) and passed twice through Celite to remove any insoluble impurities and the solution was left to stand with slow vapor diffusion of pentane. Dark red crystals (blocks, 60 mg (70%)) suitable for X-ray structure determination were obtained after 2 d. UV-vis (THF) λ_{max} (ε, M^{-1} cm^{-1}) = 330 nm (14400), 458 nm (32600), 590 nm (2630). ^{1}H NMR (CD_3CN, 400 MHz): δ 73.34, 98.14, 56.94, 30.08, 23.72, 21.15, 13.47, 11.98, 9.03, 7.40, 5.22, 4.84, 4.24, 0.91, -12.23 ppm. Anal. Calcd for $C_{42}H_{50}FeN_6O_3S$: C, 65.11; H, 6.50; N, 10.85. Found: C, 65.35; H, 6.85; N, 10.91.

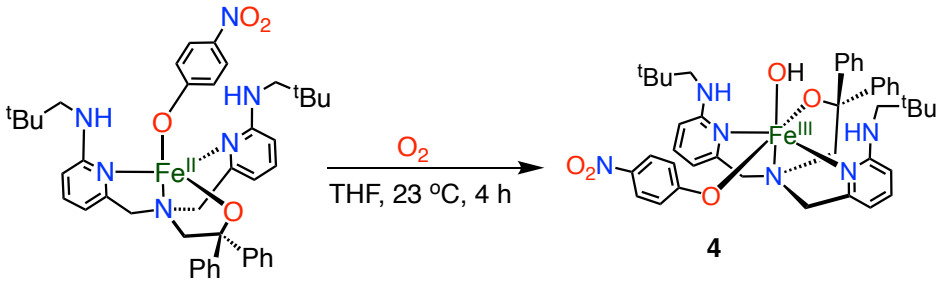


Fe^{II}(BNPA^{Ph2}O)(OPh$^{p\text{-}NO_2}$) (2). The ligand BNPA^{Ph2}OH (60.7 mg, 0.11 mmol, 1 equiv) was dissolved in THF (2 mL) and a suspension of NaH (2.5 mg, 0.11 mmol, 1 equiv) in THF (1 mL) was added. The solution was stirred for 1 h at 23 °C. An amount of anhydrous Fe(OTf)$_2$ • 2 MeCN (46.0 mg, 0.11 mmol, 1 equiv) was dissolved in acetonitrile (2 mL) and added dropwise to the BNPA^{Ph2}OH/NaH mixture. An immediate color change from colorless to yellow-green was noted, and the reaction mixture was stirred for 4 h. To this dark yellow solution, a acetonitrile slurry of freshly prepared NaOPh$^{p\text{-}NO_2}$ (17.0 mg, 0.11 mmol, 1 equiv) was added and the reaction mixture was stirred for an additional 4 h at 23 °C. A color change from dark yellow to dark brown was noted. The resulting dark brown reaction mixture was evaporated to dryness

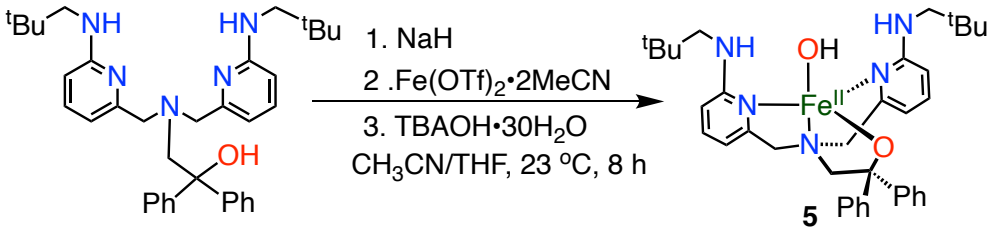
under vacuum giving a dark brown solid, which was washed with pentane and dried. The brown solid was dissolved in THF and filtered through Celite, and the solution was left to stand with slow vapor diffusion of pentane. Orange-brown crystals (blocks, 50 mg (62%)) suitable for X-ray structure determination were obtained after 1 d. UV-vis (THF) λ_{max} (ε, M^{-1} cm^{-1}) = 342 nm (35900). ^{1}H NMR (CD_3CN, 400 MHz): δ 77.07, 68.04, 64.35, 61.71, 25.54, 23.85, 20.33, 12.30, 9.74, 7.26, 4.88, 1.49, 1.31, 0.91, -10.76 ppm. Anal. Calcd for $C_{42}H_{50}FeN_6O_4$: C, 66.49; H, 6.64; N, 11.08. Found: C, 66.12; H, 6.88; N, 10.78.



Fe^{III}(BNPA^{Ph2}O)(OH)(SPh$^{p\text{-}NO_2}$) (3). Microcrystalline **1** (20.0 mg, 0.025 mmol) was dissolved in THF (5 – 10 mL), and cooled to 0 °C. This solution was bubbled with excess, dry O_2 for 15 min, causing a rapid color change from orange to dark red. The solution was warmed up to 23 °C and stirred for 30 min. The final dark red solution was evaporated to dryness under vacuum to give a dark red solid. This solid was washed with pentane to give a dark red powder, which was then dissolved in THF and left to stand with slow vapor diffusion of pentane at -35 °C in a drybox freezer. Dark red crystals suitable for X-ray structure determination were obtained after 15 d. UV-vis (THF) λ_{max} (ε, M^{-1} cm^{-1}) = 325 nm (17000), 414 nm (17900), 477 nm (21600), 600 nm (1754). ^{1}H NMR (CD_3CN, 400 MHz): δ 76.87, 54.59, 38.39, 15.55, 7.96, 7.58, 4.83, 4.24, 2.03 ppm.

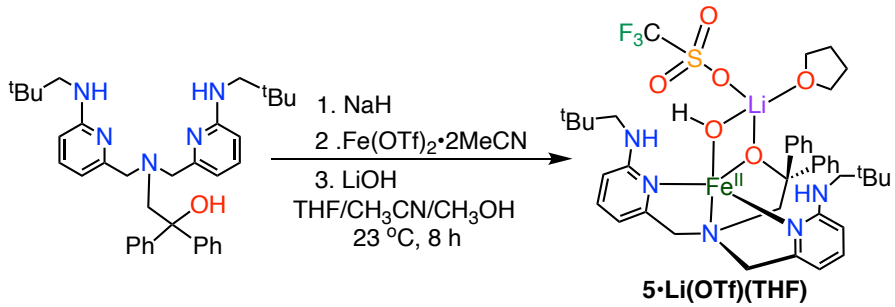


Fe^{III}(BNPA^{Ph2}O)(OH)(OPh$^{p\text{-}NO_2}$) (4). Crystalline **2** (40.0 mg, 0.052 mmol) was dissolved in THF (5 – 10 mL), and this solution was bubbled with excess, dry O_2 for 15 min, causing a color change from yellow-brown to dark red-brown. The reaction was stirred for 4 h at 23 °C, and the final dark red solution was evaporated to dryness under vacuum to give a dark red solid. This solid was dissolved in THF and filtered through Celite to remove insoluble material. The resulting dark red filtrate was evaporated to dryness under vacuum and washed with pentane to give a dark red powder, which was dissolved in THF and the solution was left to stand with slow vapor diffusion of pentane at -35 °C in a drybox freezer. Dark red crystals suitable for X-ray structure determination were obtained after 10 d. UV-vis (THF) λ_{max} (ε, M^{-1} cm^{-1}) = 330 nm (24600), 373 nm (28200), 398 nm (27700), 600 nm (1754). ^{1}H NMR (CD_3CN, 400 MHz): δ 74.00, 50.83, 42.18, 14.89, 7.28, 3.67, 1.31ppm. Anal. Calcd for $C_{42}H_{51}FeN_6O_5$: C, 65.16; H, 7.01; N, 11.07. Found: C, 65.58; H, 6.85; N, 11.21.



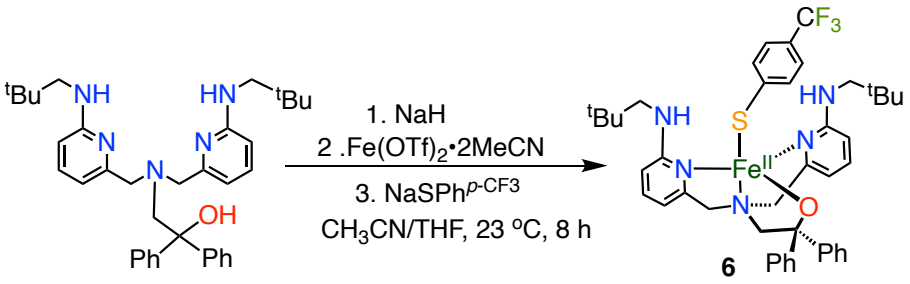
Fe^{II}(BNPA^{Ph2}O)(OH) (5). The ligand BNPA^{Ph2}OH (58.7 mg, 0.11 mmol) was dissolved in THF (2 mL) and a suspension of NaH (2.5 mg, 0.11 mmol, 1 equiv) in THF (1 mL) was added. The solution was stirred for 1 h at 23 °C. An amount of anhydrous $Fe(OTf)_2$•2MeCN (46.5 mg, 0.11 mmol, 1 equiv) was dissolved

in acetonitrile (2 mL) and added dropwise to the BNPA^{Ph2}OH/NaH mixture. An immediate color change from colorless to yellow-green was noted, and the reaction mixture was stirred for 4 h. To this dark yellow solution, an acetonitrile solution of $Bu_4NOH \bullet 30\ H_2O$ was added and the reaction mixture was stirred for an additional 4 h. A color change from dark yellow to dark orange was noted. The resulting bright orange reaction mixture was evaporated to dryness under vacuum to give an orange solid, which was washed multiple times first with hexanes and then diethyl ether. The solid was dissolved in a minimum amount of THF (3 mL) and passed twice through Celite to remove insoluble impurities. The final residue was dried to give an orange powder (crude, 65 mg). UV-vis (THF) λ_{max} (ε, $M^{-1}\ cm^{-1}$) = 325 nm (9560). ^{1}H NMR (CD_3CN, 400 MHz): δ 84.78, 74.96, 63.88, 56.13, 23.11, 16.44, 11.32, 8.89, 8.06, 3.83, 1.00 ppm.



Fe^{II}(BNPA^{Ph2}O)(OH)•Li(OTf)(THF) (5•Li(OTf)(THF)). The ligand BNPA^{Ph2}OH (58.7 mg, 0.11 mmol) was dissolved in THF (2 mL) and a suspension of NaH (2.5 mg, 0.11 mmol, 1 equiv) in THF (1 mL) was added. The solution was stirred for 1 h at 23 °C. An amount of anhydrous $Fe(OTf)_2 \bullet 2$ MeCN (46.0 mg, 0.11 mmol) was dissolved in acetonitrile (2 mL) and added dropwise to the BNPA^{Ph2}OH/NaH mixture. An immediate color change from colorless to yellow-green was noted, and the reaction mixture was stirred for 4 h. To this dark yellow solution, a methanolic solution of lithium hydroxide (2.2 mg, 0.11 mmol, 1 equiv) was added and the reaction mixture was stirred for an additional 4 h. A color change from dark yellow to dark orange was noted. The resulting bright orange reaction mixture was evaporated to dryness under vacuum giving an orange solid, which was washed with pentane. The orange solid was dissolved in THF and filtered through Celite, and the solution was left to stand with slow vapor diffusion of pentane. Orange crystals (blocks, 55 mg (63%)) suitable for X-ray structure determination were obtained after 1 d. UV-vis

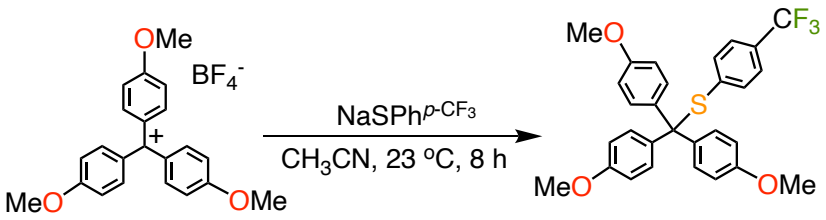
(THF) λ_{max} (ε, M^{-1} cm^{-1}) = 330 nm (11700), 480 nm (610). ^{1}H NMR (crude, CD_3CN, 400 MHz): δ 77.21, 73.17, 66.33, 31.99, 18.94, 10.53, 7.93, 6.19, 3.67, 0.35 ppm. Anal. Calcd for $C_{41}H_{55}F_3FeLiN_5O_6S$: C, 56.92; H, 6.43; N, 8.69. Found: C, 57.07; H, 6.49; N, 8.71.



Fe^{II}(BNPA^{Ph2}O)(SPh$^{p\text{-}CF_3}$) (6). The ligand BNPA^{Ph2}OH (60.0 mg, 0.11 mmol) was dissolved in THF (2 mL) and a suspension of NaH (2.5 mg, 0.11 mmol, 1 equiv) in THF (1 mL) was added. The solution was stirred for 1 h at 23 °C. An amount of anhydrous $Fe(OTf)_2$•2MeCN (46.0 mg, 0.11 mmol, 1 equiv) was dissolved in acetonitrile (2 mL) and added dropwise to the BNPA^{Ph2}OH/NaH mixture. An immediate color change from colorless to yellow-green was noted, and the reaction mixture was stirred for 4 h. To this dark yellow solution, an acetonitrile solution of freshly prepared NaSPh$^{p\text{-}CF_3}$ (22.0 mg, 0.11 mmol, 1 equiv) was added and the reaction mixture was stirred for an additional 4 h at 23 °C. A color change from dark yellow to dark orange-yellow was noted. The resulting dark orange-yellow reaction mixture was evaporated to dryness under vacuum, giving a dark yellow solid. This solid was dissolved in minimum amount of THF (3 mL) and passed twice through Celite to remove any insoluble impurities and the solution was left to stand with slow vapor diffusion of pentane. Dark yellow crystals (blocks, 50 mg (60%)) suitable for X-ray structure determination were obtained after 1 d. UV-vis (THF) λ_{max} (ε, M^{-1} cm^{-1}) = 314 nm (19400). ^{1}H NMR (CD_3CN, 400 MHz): δ 70.84, 66.20, 56.65, 29.69, 13.46, 12.00, 8.88, 7.38, 6.10, 0.90, -11.70, -14.67 ppm. Anal. Calcd for $C_{43}H_{50}F_3FeN_5OS$: C, 64.74; H, 6.38; N, 8.78. Found: C, 62.99 H, 5.93; N, 8.41.

*The yellow crystals of **6** co-crystallize with a small amount of white crystals, which is likely NaOTf based on our experience with these iron complexes. Attempts at multiple recrystallizations did not remove all of*

the suspected NaOTf and although manual separation of ***6*** *for elemental analysis was performed, some NaOTf impurity likely remained.*



(*p*-OMe-C_6H_4)$_3$CSPh$^{p\text{-}CF_3}$. (*p*-OMe-C_6H_4)$_3$CBF_4 was synthesized using a literature procedure.[11] To an acetonitrile solution of (*p*-OMe-C_6H_4)$_3$CBF_4 (50 mg, 0.118 mmol), an acetonitrile solution of NaSPh$^{p\text{-}CF_3}$ (25 mg, 0.142 mmol, 1.2 equiv) was added and the reaction mixture was stirred for 8 h at 23 °C. A color change from dark red to pink was noted. The reaction mixture was dried over vacuum to give a pink solid. The solid was then redissolved in a small amount of dichloromethane and purified using silica gel column chromatography (5-10% EtOAc/hexanes), giving the thioether product as a yellow solid (45 mg, (80%)). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.32 (m, 8H), 7.10 (d, 2H), 6.86 (d, 6H) ppm. ^{19}F NMR (CD_2Cl_2, 300 MHz): -60.34 ppm.

C. Experimental Procedures.

Preparation of ^{57}Fe-enriched Fe^{II}(BNPA^{Ph2}O)(SPh$^{p\text{-}NO_2}$) (1) and Fe^{II}(BNPA^{Ph2}O)(OPh$^{p\text{-}NO_2}$) (2) for Mössbauer spectroscopy. Crystalline ^{57}Fe^{II}(BNPA^{Ph2}O)(OTf) (3 mg) was dissolved in CH_3CN (500 μL, 8 mM) and NaXPh$^{p\text{-}NO_2}$ (X = S, O) (1 equiv) was added causing a color change from colorless to dark orange. The completion of the reaction was verified by ^{1}H NMR spectroscopy. The solvent was removed, and the solid was dissolved in 2-MeTHF (300 μL, 11 mM) and transferred to a Mössbauer cup. The sample was then frozen in liquid nitrogen, and Mössbauer spectra were collected at 80 K in the absence of an external magnetic field. Mössbauer parameters (2-MeTHF, 80 K): $\delta = 0.94$, $|\Delta E_Q| = 2.87$ mm s^{-1}, $\Gamma_L = \Gamma_R = 0.34$ for **1,** and $\delta = 1.03$, $|\Delta E_Q| = 2.76$ mm s^{-1}, $\Gamma_L = \Gamma_R = 0.28$ for **2**.

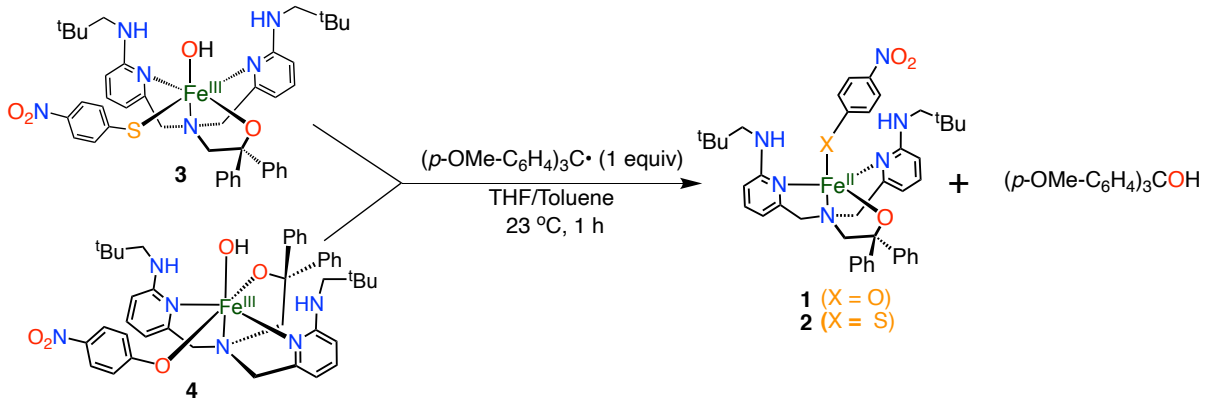
Preparation of ^{57}Fe-enriched Fe^{II}(BNPA^{Ph2}O)(OH) (5) and 5•LiOTf for Mössbauer spectroscopy. Crystalline ^{57}Fe^{II}(BNPA^{Ph2}O)(OTf) (3 mg) was dissolved in CH_3CN (500 μL, 8 mM) and TBAOH •30 H_2O (for **5)** or LiOH (for **5•LiOTf)** (1 equiv) was added causing a color change from colorless to dark orange. The completion of the reaction was verified by ^{1}H NMR spectroscopy. The solvent was removed, the solid was redissolved in 2-MeTHF (300 μL, 11 mM) and transferred to a Mössbauer cup. The sample was then frozen in liquid nitrogen, and Mössbauer spectra were collected at 80 K in the absence of an external magnetic field. Mössbauer parameters (2-MeTHF, 80 K): $\delta = 1.01$, $|\Delta E_Q| = 2.38$ mm s^{-1}, $\Gamma_L = \Gamma_R = 0.34$ for **5**, and $\delta = 1.00$, $|\Delta E_Q| = 2.56$ mm s^{-1}, $\Gamma_L = \Gamma_R = 0.32$ for **5•LiOTf.**

Preparation of ^{57}Fe enriched Fe^{III}(BNPA^{Ph2}O)(OH)(SPh$^{p\text{-}NO_2}$) (3) and Fe^{III}(BNPA^{Ph2}O)(OH)(OPh$^{p\text{-}NO_2}$) (4) for Mössbauer spectroscopy. The complexes ^{57}Fe^{II}(BNPA^{Ph2}O)(XPh$^{p\text{-}NO_2}$) (**1:** X = S**, 2:** X = O) were prepared as discussed above. To these Fe^{II} complexes in THF, dry O_2 was added for 15 min and a color change to dark red was observed. The completion of the reaction was verified by ^{1}H NMR spectroscopy. The solvent was removed directly in the Mössbauer cup to give a solid film, which was then frozen in liquid nitrogen. Mössbauer spectra were collected at 80 K in the absence of an external magnetic field. Mössbauer

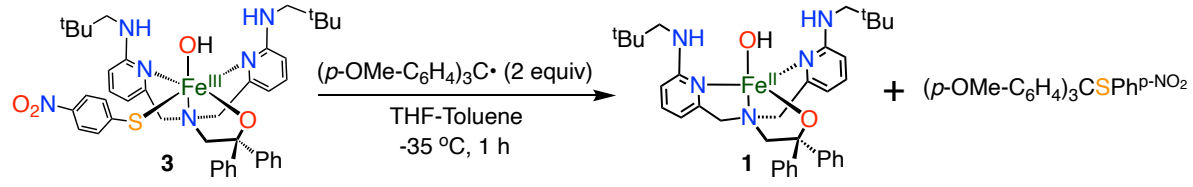
parameters (solid film, 80 K): $\delta = 0.42$, $|\Delta E_Q| = 0.96$ mm s^{-1}, $\Gamma_L = \Gamma_R = 0.67$ for **3**, and $\delta = 0.47$, $|\Delta E_Q| = 1.01$ mm s^{-1}, $\Gamma_L = \Gamma_R = 0.71$ for **4**.

Preparation of $Fe^{II}(BNPA^{Ph2}O)(SPh^{p\text{-}CF_3})$ (6) in situ for ^{1}H NMR and Mössbauer spectroscopies. Crystalline $Fe^{II}(BNPA^{Ph2}O)(OTf)$ (3 mg) was dissolved in CH_3CN (500 μL, 8 mM) and $NaSPh^{p\text{-}CF_3}$ in THF (1 equiv) was added at 23 °C. An immediate color change from pale yellow to dark yellow was observed, and the reaction mixture was dried under vacuum. Analysis by ^{1}H NMR in CD_3CN confirmed formation of $Fe^{II}(BNPA^{Ph2}O)(SPh^{p\text{-}CF_3})$ (**6**). Mössbauer samples were prepared similarly with ^{57}Fe-enriched samples. Spectra were collected at 80 K in the absence of an external magnetic field. Mössbauer parameters (2-MeTHF, 80 K): $\delta = 0.94$, $|\Delta E_Q| = 2.87$ mm s^{-1}, $\Gamma_L = \Gamma_R = 0.34$.

Preparation of $Fe^{III}(BNPA^{Ph2}O)(OH)(SPh^{p\text{-}CF_3})$ (7) in situ for ^{1}H NMR and Mössbauer spectroscopies. Crystalline $Fe^{III}(BNPA^{Ph2}O)(OH)(OTf)$ (3 mg) was dissolved in CD_3CN (500 μL, 8 mM) in an NMR tube and precooled in a cold bath at -40 °C and $NaSPh^{p\text{-}CF_3}$ in CD_3CN (1 equiv) was added. An immediate color change from orange to dark red was observed. ^{1}H NMR spectra were recorded at -40 ºC and confirmed the formation of $Fe^{III}(BNPA^{Ph2}O)(OH)(SPh^{p\text{-}CF_3})$ (**7**). Mössbauer samples were prepared similarly using ^{57}Fe-enriched samples. Spectra were collected at 80 K in the absence of an external magnetic field. Mössbauer parameters (2-MeTHF, 80 K): $\delta = 0.47$, $|\Delta E_Q| = 0.84$ mm s^{-1}, $\Gamma_L = \Gamma_R = 0.59$. Complex **7** was not amenable to crystallization. Spectroscopic characterization (^{1}H NMR, ^{57}Fe-Mössbauer) of **7** generated in situ, together with DFT calculations, was fully consistent with the proposed structure. Complex **7** was found to be less stable than **3**, decomposing at 23 °C in ~15 min. However, **7** is stable for at least several hours at -20 ºC, allowing for low temperature experiments.



Reaction between 3 or 4 and (*p*-OMe-C$_6$H$_4$)$_3$C• at 23 °C. Complex **3** or **4** (3.5 mg, 0.004 mmol) was dissolved in THF (600 μL). A solution of the radical (*p*-OMe-C$_6$H$_4$)$_3$C• in toluene-d_8 was freshly prepared according to a literature procedure,[3] and 1 equiv of radical was added to **3** or **4** in THF. The reaction was stirred for 30 min, and then the solvent was removed under vacuum to give an orange residue, which was dissolved in CD_3CN and analyzed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum showed complete disappearance of the broad, paramagnetically shifted peaks for **3** or **4**, and appearance of the relatively sharp, paramagnetically shifted peaks corresponding to **1** or **2**. For analysis by Mössbauer spectroscopy, complex **3** or **4** was enriched in ^{57}Fe (95.93%) and 2-MeTHF was employed in place of CD_3CN because it gives a sharp, better resolved quadrupole doublet for the Mössbauer spectrum of **1** or **2**. The Mössbauer spectrum (80 K) of the final reaction mixture showed a sharp quadrupole doublet with $\delta = 0.96$, $|\Delta E_Q| = 2.83$ mm s^{-1} assigned to **1**, or $\delta = 1.04$, $|\Delta E_Q| = 2.79$ mm s^{-1} assigned to **2**. The organic products were analyzed by ^{1}H NMR spectra on reactions of slightly larger scale (5 mg, 0.006 mmol).



Reaction between 3 and (*p*-OMe-C$_6$H$_4$)$_3$C• at -35 °C. Complex **3** (3.0 mg, 0.004 mmol) was dissolved in THF (600 μL) and cooled to -35 °C. A solution of radical (*p*-OMe-C$_6$H$_4$)$_3$C• in toluene-d_8 was freshly

prepared according to a literature procedure,[3] cooled to -35 °C, and 1 equiv was added to the precooled solution of **3** in THF. The reaction was allowed to stand in a drybox freezer (-35 °C) for 1 h, and then the solvent was removed under vacuum to give an orange residue, which was dissolved in CD_3CN and analyzed by ^1H NMR spectroscopy. The ^1H NMR spectrum showed complete disappearance of the broad, paramagnetically shifted peaks for **3**, and appearance of the relatively sharp, paramagnetically shifted peaks corresponding to **5**. For analysis by Mössbauer spectroscopy, complex **3** was enriched in ^{57}Fe (95.93%) and 2-MeTHF was employed in place of CD_3CN because it gives a sharp, better resolved quadrupole doublet for the Mössbauer spectrum of **5**. The Mössbauer spectrum (80 K) of the final reaction mixture showed a sharp quadrupole doublet ($\delta = 1.00$, $|\Delta E_Q| = 2.37$ mm s^{-1}, 85% of the fit) corresponding to **5**.

Reaction between 7 and (p-OMe-C_6H_4)$_3$C• at -35 °C. Complex **7** was prepared in situ in THF (600 μL) by adding 1 equiv of $NaSPh^{p\text{-}CF_3}$ to $Fe^{III}(BNPA^{Ph2}O)(OH)(OTf)$ in THF at -35 °C. The formation of **7** was confirmed by UV-vis and ^1H NMR spectroscopy. To the solution of **7** was added (p-OMe-C_6H_4)$_3$C• (1 equiv) at -35 °C. The reaction was allowed to stand in a drybox freezer (-35 °C) for 1 h, and then the solvent was removed under vacuum to give an orange residue, which was dissolved in CD_3CN and analyzed by ^1H NMR spectroscopy. The ^1H NMR spectrum showed complete disappearance of the broad, paramagnetically shifted peaks for **3**, and appearance of the relatively sharp, paramagnetically shifted peaks corresponding to **5**. The organic products were analyzed by running the reaction on a larger scale (25 mg, 0.030 mmol of **7**). Workup involved dissolving the crude reaction products in ethyl acetate and filtering through a small plug of silica gel to remove impurities. The ethyl acetate was then removed under vacuum, and the crude solid was purified by silica gel column chromatography (95:5 hexane:EtOAc v/v) to give (p-OMe-C_6H_4)$_3$CS$Ph^{p\text{-}CF_3}$ as a yellow solid (12 mg, 78%). ^1H NMR (CD_2Cl_2, 400 MHz) δ 7.29 (m, 8H), 7.13 (d, 2H) 6.93 (d, 6H), 3.80 (s, 9H) ppm. ^{19}F NMR (CD_2Cl_2, 300 MHz) δ -60.33 ppm.

Reaction between 1:1 mixture of 3 and 4 with (p-OMe-C_6H_4)$_3$C• at -35 °C. Complexes **3** (4.0 mg) and **4** (3.8 mg) were dissolved in 500 μL of THF separately (5 mM) and combined at -35 °C. To the 1:1 mixture

of **3** and **4** was added (p-OMe-$C_6H_4)_3C$• (1 equiv) at -35 °C. The reaction was allowed to stand in a drybox freezer (-35 °C) for 1 h, and then the solvent was removed under vacuum to give an orange residue, which was dissolved in CD_3CN and analyzed by ^1H NMR spectroscopy. The ^1H NMR spectrum showed complete disappearance of the broad, paramagnetically shifted peaks for **4**, and appearance of the relatively sharp, paramagnetically shifted peaks corresponding to **2**. The ^1H NMR spectrum also showed the broad, paramagnetically shifted peaks for unreacted **3** as well as minor peaks corresponding to the sulfur transfer product **5**.

Reaction between 1:1 mixture of 3 and 4 with (p-OMe-$C_6H_4)_3C$• at 23 °C. Complexes **3** (4.0 mg) and **4** (3.8 mg) were dissolved in THF separately (1 mL, 5 mM) and mixed together. To the 1:1 mixture of **3** and **4** was added (p-OMe-$C_6H_4)_3C$• (1 equiv) at 23 °C and was allowed to stand at 23 °C for 1 h, and then the solvent was removed under vacuum to give an orange residue, which was dissolved in CD_3CN and analyzed by ^1H NMR spectroscopy. The ^1H NMR spectrum showed complete disappearance of the broad, paramagnetically shifted peaks for **4**, and appearance of the relatively sharp, paramagnetically shifted peaks corresponding to **2**. The ^1H NMR spectrum also showed complete retention of the broad, paramagnetically shifted peaks for unreacted **3**.

D. Supporting Tables **Table S1**. Comparison of metrical parameters obtained from single crystal X-ray crystallography and DFT calculations for **1**, **2** and **6**.

	Complex **1** (X = SPh$^{p\text{-}NO_2}$)[a]		Complex **2** (X = OPh$^{p\text{-}NO_2}$)		Complex **6** (X = SPh$^{p\text{-}CF_3}$)	
Bond lengths	Bond lengths (Å) and bond angles (°) by XRD	Bond lengths (Å) and bond angles (°) by DFT	Bond lengths (Å) and bond angles (°) by XRD	Bond lengths (Å) and bond angles (°) by DFT	Bond lengths (Å) and bond angles (°) by XRD	Bond lengths (Å) and bond angles (°) by DFT
Fe1–N2	2.203(2)	2.226	2.1457(16)	2.192	2.2006(12)	2.219
Fe1–N3	2.206(2)	2.243	2.1927(15)	2.252	2.2086(12)	2.319
Fe1–N4	2.249(2)	2.152	2.2133(16)	2.238	2.2469(12)	2.239
Fe1–O1	1.926(19)	1.888	1.9270(13)	1.913	1.9223(10)	1.905
Fe1–X	2.4132(8)	2.392	2.0366(13)	2.047	2.4177(4)	2.432
N1–X	3.283(2)	3.157	2.974(2)	2.877	3.2575(14)	3.292
N5–X	3.256(3)	3.378	2.824(2)	2.797	3.2606(14)	3.292
Bond Angles						
N2–Fe1–N3	78.46(8)	75.69	78.71(6)	77.71	75.20(4)	74.96
N2–Fe1–N4	100.68(8)	101.9	100.08(6)	102.63	110.89(4)	106.21
N3–Fe1–N4	76.15(8)	77.92	76.81(6)	76.25	75.98(4)	76.91
N2–Fe1–O1	133.83(8)	140.97	111.73(6)	108.88	109.77(5)	102.91
N3–Fe1–O1	80.98(8)	80.53	81.99(6)	80.49	79.65(4)	80.71
N4–Fe1–O1	113.35(8)	102.81	137.16(6)	135.49	124.46(5)	136.41
O1–Fe1–X	92.64(6)	99.11	102.43(5)	107.78	99.94(3)	102.32
X–Fe1–N2	105.06(6)	97.82	106.41(6)	102.01	107.10(3)	102.25
X–Fe1–N3	171.67(6)	167.63	171.04(6)	171.12	177.63(3)	173.89
X–Fe1–N4	109.16(6)	114.02	94.89(6)	95.25	102.48(3)	99.41

Fe1-X-C1	99.35(9)	112.37	131.11(5)	132.26	106.65	103.48
N1–H1–X1	168(3)	167	171(2)	170	157(17)	155
N5–H5–X1	170(3)	162	167(2)	166	170(17)	167

[a]For compound 1, the metrics are provided only for one of the two crystallographically independent molecules.

Table S2. Comparison of metrical parameters obtained from single crystal X-ray crystallography and DFT calculations for **3** and **4**.

	Complex **3** (X = S)		Complex **4** (X = O)	
Bond lengths	Bond lengths (Å) and bond angles (°) by XRD	Bond lengths (Å) and bond angles (°) by DFT	Bond lengths (Å) and bond angles (°) by XRD	Bond lengths (Å) and bond angles (°) by DFT
Fe1–N2	2.203(2)	2.282	2.216(3)	2.235
Fe1–N3	2.217(2)	2.244	2.191(3)	2.243
Fe1–N4	2.306(2)	2.297	2.192(3)	2.205
Fe1–O1	1.8801(16)	1.879	1.902(2)	1.894
Fe1–X	2.4483(8)	2.484	2.000(3)	2.001
Fe1–O2	1.9034(18)	1.928	1.908(2)	1.912
N1–O2	2.825(3)	2.824	2.792(14)	2.915
N5–O2	2.697(3)	2.738	2.894(4)	2.916
Bond angles				
N2–Fe1–N3	74.80(8)	73.94	75.92(11)	76.53
N2–Fe1–N4	92.18(7)	89.38	153.61(10)	154.38
N3–Fe1–N4	76.84(8)	77.75	78.04(10)	78.23
N2–Fe1–O1	154.15(8)	153.88	93.46(11)	90.52
N3–Fe1–O1	81.34(7)	80.22	81.90(10)	80.51

N4–Fe1–O1	91.93(7)	88.78	87.09(10)	89.80
O1–Fe1–X	86.93(6)	87.51	167.89(10)	165.36
X–Fe1–N4	174.04(6)	172.70	87.92(11)	85.26
X–Fe1–N2	86.35(6)	91.19	86.15(11)	88.26
X–Fe1–N3	97.21(6)	95.41	86.27(10)	85.02
O2–Fe1–N4	89.39(8)	91.44	104.55(11)	103.72
O2–Fe1–N2	99.18(8)	95.91	101.76(11)	101.61
O2–Fe1–N3	164.57(8)	165.05	174.43(12)	177.74
O2–Fe1–X	96.55(6)	95.75	98.69(12)	96.23
O2–Fe1–O1	106.37(8)	110.18	93.25(11)	98.31
Fe1-X-C1	107.99(7)	113.6	138.74(12)	139.93
N1–H1–O2	163(3)	162	166(8)	160
N5–H5–O2	158(3)	160	170(4)	161

Table S3. Comparison of metrical parameters obtained from single crystal X-ray crystallography and DFT calculations for **5•Li(OTf)(THF)** and DFT calcualtions for **5**.

	Complex **5**		Complex **5•Li(OTf)(THF)**	
Bond lengths	Bond lengths (Å) and bond angles (°) by XRD	Bond lengths (Å) and bond angles (°) by DFT	Bond lengths (Å) and bond angles (°) by XRD	Bond lengths (Å) and bond angles (°) by DFT
Fe1–N2	-	2.299	2.1374(17)	2.167
Fe1–N3	-	2.307	2.1988(16)	2.239
Fe1–N4	-	2.233	2.1394(17)	2.171
Fe1–O1	-	1.877	1.9719(13)	1.985
Fe1–O2	-	1.917	1.9874(14)	1.972
N1–O1	-	2.691	2.825(2)	2.780
N5–O1	-	2.822	2.972(2)	2.994
O1–O4	-		2.954(2)	2.871
Li1–O2	-	-	2.045(4)	2.178
Li1–O1	-		1.917(4)	1.897
Li1–O3	-		1.947(4)	1.926
Li1–O6	-		1.913(4)	1.971
Li1–Fe1	-		2.746(3)	2.765
Bond angles				
N2–Fe1–N3	-	73.97	78.99(6)	78.19
N2–Fe1–N4	-	89.08	107.65(6)	106.51
N3–Fe1–N4	-	78.29	77.17(6)	79.03
N2–Fe1–O1	-	87.26	103.85(6)	106.51
N3–Fe1–O1	-	80.13	173.95(6)	174.97
N4–Fe1–O1	-	154.04	106.70(6)	101.00

O2–Fe1–N4	-	85.37	138.22(6)	135.59
O2–Fe1–N2	-	90.96	103.38(6)	107.32
O2–Fe1–N3	-	165.48	82.13(6)	80.91
O2–Fe1–O1	-	109.38	91.98(6)	94.33
O2–Li1–O6	-	-	112.89(18)	115.68
O2–Li1–O1	-	-	91.83(15)	90.50
O3–Li1–O1	-	-	106.51(16)	108.98
O3–Li1–O6	-	-	102.86(18)	101.59
O1–Li1–O6	-	-	122.0(2)	119.25
O2–Li1–O3	-	-	121.9(2)	121.76
N1–H1–O1	-	163	169	168
N5–H5–O1	-	163	164	164
O1–H2–O4	-	-	161	163

Table S4. Experimental and calculated Mössbauer parameters for complexes **1** – **7**.

complex[a]	calculated isomer shift[b,c]	experimental isomer shift[b]	calculated quadrupole splitting[b]	experimental quadrupole splitting[b]
1	0.97	0.94	2.96	2.83
2	1.04	1.03	2.85	2.77
3	0.49	0.42	1.09	0.96
4	0.51	0.47	1.12	1.01
5	1.02	1.00	2.37	2.38
5•Li(OTf)	0.99	1.01	2.73	2.56
6	0.97	0.94	2.87	2.85
7	0.50	0.47	1.02	0.84

[a] See DFT computational section for details regarding geometry optimizations.

[b] mm s^{-1}.

[c] Electron density at the nucleus (ϱ(0)) calculated using the B3LYP functional with a combination of the CP(PPP) basis set for Fe and def2-TZVP basis set for all other atoms and calibrated as described in the DFT computational section.

Table S5. Crystallographic data for complex 1

	1
Crystal data	
Chemical formula	$C_{42}H_{50}FeN_6O_3S$
M_r	774.79
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	110
a, *b*, *c* (Å)	14.4495 (4), 15.0286 (5), 18.4897 (6)
α, β, γ (°)	96.116 (3), 99.415 (3), 95.293 (3)
V (Å^3)	3913.8 (2)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	0.49
Crystal size (mm)	0.09 × 0.07 × 0.04
Data collection	
Diffractometer	SuperNova, Dual, Cu at zero, Atlas
Absorption correction	Gaussian *CrysAlis PRO* 1.171.40.67a (Rigaku Oxford Diffraction, 2019) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.902, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	62752, 15389, 9849
R_{int}	0.078
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.052, 0.118, 1.03
No. of reflections	15389
No. of parameters	979
No. of restraints	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.57, -0.38

Table S6. Crystallographic data for complex 2

	2
Crystal data	
Chemical formula	$C_{42}H_{50}FeN_6O_4$
M_r	758.73
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	110
a, *b*, *c* (Å)	10.0648(3), 12.0572(4), 17.8011(6)
α, β, γ (°)	74.850(3), 78.045(3), 72.471(3)
V (Å^3)	1968.87(12)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.43
Crystal size (mm)	0.23 × 0.13 × 0.06
Data collection	
Diffractometer	SuperNova, Dual, Cu at zero, Atlas
Absorption correction	Gaussian *CrysAlis PRO* 1.171.39.29c (Rigaku Oxford Diffraction, 2017) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.719, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	30342, 9041, 7084
R_{int}	0.044
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.044, 0.094, 1.07
No. of reflections	9041
No. of parameters	490
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.38, -0.38

Table S7. Crystallographic data for complex 3

	3
Crystal data	
Chemical formula	$C_{42}H_{51}FeN_6O_4S$
M_r	791.79
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	110
a, *b*, *c* (Å)	8.0638 (2), 10.3249 (3), 23.4957 (7)
α, β, γ (°)	94.094 (2), 91.749 (2), 95.966 (2)
V (Å^3)	1939.22 (9)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.49
Crystal size (mm)	0.19 × 0.11 × 0.02
Data collection	
Diffractometer	SuperNova, Dual, Cu at zero, Atlas
Absorption correction	Gaussian *CrysAlis PRO* 1.171.39.29c (Rigaku Oxford Diffraction, 2017) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.781, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	32444, 7609, 5921
R_{int}	0.051
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.046, 0.111, 1.06
No. of reflections	7609
No. of parameters	502
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.43, -0.34

Table S8. Crystallographic data for complex 4

	4
Crystal data	
Chemical formula	$C_{42}H_{51}FeN_6O_5 \cdot 0.662(C_4H_8O) \cdot 0.338(C_5H_{12})$
M_r	847.85
Crystal system, space group	Tetragonal, $I4_1/a$
Temperature (K)	100
a, c (Å)	26.4035 (6), 26.2155 (5)
V (Å^3)	18276.0 (9)
Z	16
Radiation type	Cu $K\alpha$
μ (mm^{-1})	3.06
Crystal size (mm)	0.10 × 0.07 × 0.05
Data collection	
Diffractometer	ROD, Synergy Custom system, HyPix
Absorption correction	Analytical *CrysAlis PRO* 1.171.40.67a (Rigaku Oxford Diffraction, 2019) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.803, 0.888
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	28851, 8175, 5553
R_{int}	0.055
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.598
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.066, 0.208, 1.04
No. of reflections	8175
No. of parameters	649
No. of restraints	333
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.46, -0.44

Table S9. Crystallographic data for complex 5.Li(OTf)(THF)

	5.Li(OTf)(THF)
Crystal data	
Chemical formula	$C_{41}H_{55}F_3FeLiN_5O_6S$
M_r	865.75
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	110
a, b, c (Å)	9.43191 (14), 20.1665 (2), 23.0988 (3)
β (°)	101.3337 (14)
V (Å^3)	4307.91 (10)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	3.80
Crystal size (mm)	0.26 × 0.11 × 0.04
Data collection	
Diffractometer	SuperNova, Dual, Cu at zero, Atlas
Absorption correction	Analytical *CrysAlis PRO* 1.171.39.29c (Rigaku Oxford Diffraction, 2017) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.515, 0.886
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	28442, 8460, 7282
R_{int}	0.042
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.616
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.109, 1.04
No. of reflections	8460
No. of parameters	538
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.47, -0.44

Table S10. Crystallographic data for complex 6

	xs2404a
Crystal data	
Chemical formula	$C_{43}H_{50}F_3FeN_5OS$
M_r	797.79
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	110
a, *b*, *c* (Å)	10.4559 (2), 12.4259 (3), 17.1156 (4)
α, β, γ (°)	105.392 (2), 106.906 (2), 97.368 (2)
V (Å^3)	1999.80 (8)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.48
Crystal size (mm)	0.42 × 0.19 × 0.11
Data collection	
Diffractometer	SuperNova, Dual, Cu at zero, Atlas
Absorption correction	Gaussian *CrysAlis PRO* 1.171.40.67a (Rigaku Oxford Diffraction, 2019) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.508, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	37248, 9197, 7968
R_{int}	0.030
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.033, 0.080, 1.04
No. of reflections	9197
No. of parameters	499
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.38, -0.33

Table S11. DFT optimized coordinates of 1

Fe	12.33790618182070	6.38266383283165	3.82732202147131
C	12.54424142480259	10.18061090014702	7.57506417379287
H	12.46080590430373	10.91092869398480	6.76017290018233
H	12.03571132336503	10.59693344969766	8.45307496704546
H	11.99998275154390	9.27942971180061	7.27121171644261
C	14.73736961796618	11.15803372587808	8.33326279536766
H	14.69269557571101	11.92307987160862	7.54724046890684
H	15.79468688359826	10.97191264595823	8.56322187129992
H	14.27110266548185	11.57833179886745	9.23188687786936
C	14.09007050672178	8.82644329781645	9.03130636577498
H	13.57627503336719	9.19610038794353	9.92682860893855
H	15.12857030011325	8.61096536593747	9.31481750066995
H	13.61371228408180	7.88333765841702	8.73984064203203
C	14.01689237219060	9.86645737201705	7.89936287076058
C	14.73573272742351	9.34577746396987	6.62438772787600
H	14.70032438491912	10.13380817957143	5.86037467898957
H	15.79465690475749	9.16724393963312	6.84057213221324
C	14.66045940645927	6.89639275953522	6.02623418760338
C	15.74161666876630	6.50369190896347	6.85884999038330
H	16.21230002754575	7.22331509213968	7.51598518968756
C	16.15304537130288	5.18697848414364	6.84869281215194
H	16.97213544439990	4.87312128949555	7.49107766102811
C	15.49712244905941	4.25366909051051	6.03456776508571
H	15.77906026832775	3.20586340625538	6.03166205756379
C	14.46519399162554	4.70776179328644	5.22685235904153
C	13.75658712126009	3.74863035206303	4.28719492654530
H	14.28513317124328	3.74558177857232	3.32681166229513
H	13.81741468440177	2.72378350394101	4.68614434042413
C	11.85659463949433	3.68585270492381	2.74677576837967
H	10.80126173246902	3.96821666870589	2.68400098951985
H	11.89946758108763	2.58774258351716	2.65666748587914
C	12.61598651459286	4.31997200181402	1.59880842675864
C	12.88721876430742	3.57419778714435	0.46028927902907
H	12.56984902674981	2.53904985804727	0.39744142493357
C	13.57014088446768	4.19732390347852	-0.59011386025546
H	13.78482967899022	3.65432466437819	-1.50707924456686
C	13.97313194318464	5.50953862388358	-0.45658036964022
H	14.48647447181577	6.01012790642274	-1.26710004019409
C	13.68617899404361	6.21189111943995	0.74586435016755
C	14.93848752540246	8.18273976629204	-0.05973398134608
H	14.36368207009564	8.37619123368821	-0.98115515357222
H	15.76445578796608	7.51300339523066	-0.33316048074752
C	15.54805000952400	9.51896882351127	0.42988317361550
C	16.53595706010234	9.97755221788145	-0.66299013121821
H	16.97470565856427	10.94649379322674	-0.39836518222666
H	16.03559472211630	10.09406015643441	-1.63266964712336
H	17.35760914551887	9.26121033568250	-0.78993945305802
C	14.45801271437402	10.59581529002617	0.60049882209785

H	13.74417584449959	10.33290203018379	1.38689573364860
H	13.90498945662026	10.74717208467153	-0.33611021678451
H	14.91292323225196	11.55519448364038	0.87528106706884
C	16.30930733439229	9.32030753058216	1.75453265001018
H	16.81255195479289	10.25018523318419	2.04583813469861
H	17.07433956562626	8.53903968537909	1.66039128718602
H	15.63561960176537	9.03874140481905	2.57038468152694
C	11.48803812513574	3.87692792186657	5.19793040352586
H	12.09821118796205	4.03951218096754	6.08928064619580
H	11.17261780252408	2.82399028178024	5.20624091685766
C	10.28990975323502	4.89270518480287	5.27996787268092
C	9.85245191522253	4.93715634792133	6.77397420274068
C	10.45331633239699	5.89536916685155	7.60421245656762
H	11.15607691949603	6.59078660316374	7.15764114964914
C	10.14315653715458	5.96756056100464	8.96232101416568
H	10.61697952096626	6.72522051020116	9.58286776286934
C	9.22113553631595	5.07978337120315	9.52244185088702
H	8.96979643984367	5.14019934422915	10.57867735462758
C	8.61707737012057	4.12245122894953	8.70761164210028
H	7.88902442106288	3.43076465671919	9.12598544586834
C	8.93007357016891	4.05180591465803	7.34671217379109
H	8.42633777924279	3.31361444185926	6.73176438366790
C	9.09756371747788	4.46978803362892	4.38208864404927
C	8.66602935186919	3.13931493880157	4.23921122690807
H	9.18278585299847	2.33314143718467	4.75390809832159
C	7.56956103708299	2.81607849663864	3.43503052162460
H	7.25879318394142	1.77770462973142	3.34357949960447
C	6.87746131684014	3.81809990695800	2.75373438909374
H	6.02251263379759	3.56847191751313	2.13029411589691
C	7.29665699755516	5.14378285285746	2.88318770951745
H	6.76852261990344	5.93662117995115	2.35944617556254
C	8.39375752817968	5.46273403054567	3.68579011093984
H	8.72559488915590	6.49001643226474	3.77701289198512
C	10.70599503614438	9.45306142056470	3.21036557848044
C	10.45550881318435	10.45332834943609	2.24864185073635
H	11.26086133969373	10.77894628340769	1.59805808501453
C	9.19762739296810	11.02911605834786	2.12549999781423
H	8.99672129345509	11.79770562663907	1.38813311761663
C	8.17190165470935	10.60431491641268	2.97366084000316
C	8.39087999649543	9.61817641290942	3.93905962150551
H	7.57503380687161	9.31144992726902	4.58336819107381
C	9.65349244376112	9.04716704500430	4.05666852586867
H	9.83359541080128	8.26929656056971	4.79248873578153
N	14.15752155333872	8.15399357281880	6.01916730260503
H	13.39605584484659	8.32003761829310	5.35911317088813
N	14.06237712778497	5.99734997798396	5.19272329955909
N	12.36715280591845	4.15505220951320	4.03816928275941
N	12.99603534193106	5.61067390263444	1.75882467814021
N	14.11655689164480	7.48827114348078	0.92638634471687
H	13.61383209091375	8.04371620628937	1.62326548068570
N	6.84311832332919	11.20344314891928	2.84403967918507

O	10.77955739093136	6.13571343217109	4.90641222228157
S	12.34541193311999	8.79151052087802	3.37739896617252
O	6.68190596830206	12.06632652118476	1.98405637086009
O	5.95814383882507	10.81157453184153	3.60030921332151

Table S12. DFT optimized coordinates of 2

Fe	12.14141067603579	6.30296878943165	3.94506080373282
C	12.20850669808750	10.50849360701088	6.88718577721098
H	12.14450701502541	11.13377222280951	5.98783981145402
H	11.63366895525151	11.00353200565226	7.67917099982724
H	11.71466766329444	9.55643402985189	6.66667607307477
C	14.30757363974636	11.65807582166116	7.67037144706779
H	14.28483656241908	12.33622593699128	6.80771332815642
H	15.35433262097292	11.54504533006214	7.98238924422336
H	13.76734111795259	12.14572686836140	8.49000062491106
C	13.70509210573748	9.38348200506064	8.56816373730493
H	13.11279021588106	9.81708494989521	9.38297549453929
H	14.72925792276099	9.25126701152472	8.94036323801504
H	13.29053036011269	8.39362862373414	8.34738581577604
C	13.66804978352863	10.29755331860650	7.33011310604732
C	14.49439499155627	9.68259455742512	6.16577900094486
H	14.49592896564930	10.39434313028341	5.32973778046815
H	15.53967093772957	9.57233711800163	6.47492994267933
C	14.50987991274666	7.18032861065984	5.87469211866441
C	15.55859094874927	6.93091098483196	6.80049176392437
H	15.98885826516038	7.74324717288834	7.37058776182471
C	16.00011167187564	5.63636917937833	6.98152865647564
H	16.79516809282114	5.43400517681493	7.69507661769505
C	15.41794592881831	4.58538571922057	6.25833438253269
H	15.74214712524588	3.55849237775136	6.38960990309872
C	14.40808092514156	4.89788905340024	5.36103667625706
C	13.80398885464699	3.82050525466229	4.47698104565314
H	14.35806456613841	3.81149496959792	3.53069192885958
H	13.94838178726451	2.83105932887799	4.93816449486267
C	11.99715782277981	3.55674686200941	2.85088980413458
H	10.91393474280454	3.68098957285481	2.75854774759080
H	12.20693616322261	2.47881273892917	2.74954484539960
C	12.68326354747218	4.31801679710463	1.73168204354638
C	13.07832991659532	3.66387719525634	0.57508213565658
H	12.92448795094037	2.59521339610752	0.46810494689509
C	13.67783382797621	4.42524944261465	-0.43852261936607
H	14.00160013754966	3.95084073520354	-1.36144283519586
C	13.87410809086408	5.77850848984138	-0.26060209646409
H	14.35632315444117	6.36751937841574	-1.02968420038497
C	13.44845205695394	6.39029296054324	0.94996426728055
C	14.11414677929991	8.72471015050903	0.29520342744663
H	13.44487029547973	9.59127766389813	0.37600930531466
H	14.03165545600348	8.37292877210779	-0.73913808489844
C	15.56865223007388	9.20016951170239	0.56868022160231
C	15.88984391002376	10.31255697384165	-0.44735123733761

H	16.91123418414479	10.68539786790635	-0.30496867937856
H	15.20668677863280	11.16475015232467	-0.33897805304226
H	15.81073204928462	9.94786734590012	-1.47983926509188
C	15.67290140797053	9.76239612061039	1.99919685503448
H	15.43373118934695	8.99804160078322	2.74747847295386
H	14.98478920695255	10.60529319724229	2.14372298047906
H	16.68915721694217	10.12297468211600	2.19910220314386
C	16.56372228609628	8.03890310777100	0.39623566699630
H	17.58664482862572	8.37439167536195	0.60721508655702
H	16.55070527965840	7.64755261003928	-0.62920198885215
H	16.33647882629420	7.21248923164126	1.07910769419946
C	11.49058448373396	3.71451637130707	5.28530646974594
H	12.04894342443770	3.91532942003185	6.20341190793091
H	11.25998580049870	2.63956749160992	5.27282284984154
C	10.21430261500015	4.63193040165255	5.33563635036562
C	9.67336411574799	4.56295582912063	6.79109968585064
C	9.73809090877296	5.71014594777877	7.59100991973683
H	10.13683678564057	6.61607273889598	7.14953936365457
C	9.29652333987617	5.68623812778898	8.91584757447133
H	9.34921724894279	6.59211495099355	9.51597275302638
C	8.78867608305895	4.50965875123663	9.46960354883729
H	8.44272861691844	4.49010546847236	10.49991838059385
C	8.72264914061979	3.35832309645132	8.68208030972856
H	8.32410925421851	2.43519947362041	9.09663082845598
C	9.15787967093381	3.38675459428558	7.35550543169308
H	9.07327538022992	2.48314237656985	6.75919474221148
C	9.09486723894004	4.16797767468864	4.36202663231226
C	8.77570779704755	2.82059986665233	4.12227121039705
H	9.34553184614421	2.02596120076820	4.59667772826413
C	7.73428016853573	2.46460905103757	3.26113681912966
H	7.51272739699466	1.41300708391981	3.09312191688599
C	6.98477111457433	3.45067580497005	2.61874605342233
H	6.17305852000342	3.17517652334531	1.94980836597387
C	7.29205677155330	4.79412573683255	2.84432738331843
H	6.71853622010591	5.57458522257750	2.35037369419610
C	8.33489904575615	5.14562880505040	3.70335914175471
H	8.57892979787365	6.18825025675734	3.87151176395032
C	11.10875633335979	9.18009175229034	3.44052185422138
C	11.27777756392743	10.40379737395604	2.74325867219401
H	12.22742225305056	10.59693938318891	2.25129324442482
C	10.26255191220261	11.34581571164124	2.68991498026418
H	10.38616194568509	12.28102718005589	2.15637093160898
C	9.05188181367338	11.08603440710476	3.34161767204376
C	8.85771718530966	9.89306059728341	4.04865062064970
H	7.91161113366816	9.72436417527341	4.55009986435925
C	9.87410032036159	8.95154296851324	4.10117393803361
H	9.74759100234865	8.02329340905601	4.65176647032543
N	14.00840838196789	8.41658094327070	5.63516507119057
H	13.28414075202633	8.47041636570826	4.91221487099321
N	13.95393878552519	6.15558350694373	5.16886734789358
N	12.39092163874069	4.07606133306123	4.16559120571348

N	12.85741836458953	5.64585270076178	1.92897499984311
N	13.60616525299619	7.71128695535623	1.20693940291225
H	13.14301480494108	8.05256590420456	2.06025349798283
N	7.98391241492578	12.07304484983258	3.28565596828245
O	10.62154761529017	5.92182663545046	5.04164287392845
O	12.09740513073167	8.29729795581699	3.48744238610877
O	8.19020402638604	13.11544516541023	2.66393647304914
O	6.92771093535052	11.81791707232003	3.86193660872653

Table S13. DFT optimized coordinates of 3

Fe	-0.04329022167836	0.78653307745753	5.52084113223545
S	-0.45865666114099	-1.58860108155133	6.11678247769836
C	0.39637033998581	4.50907404587386	9.48677096047897
H	0.01225013305025	4.21859728052554	8.50415971283413
H	1.27964162036089	5.14156000721260	9.32999588530442
H	-0.36841803171721	5.12055033518544	9.98188279832878
C	1.28536933000079	3.76967809410855	11.71696233556025
H	2.18099097534655	4.39138923722750	11.59196630888977
H	1.54577736688894	2.92717570692979	12.36973401935499
H	0.53043919246111	4.37284243701973	12.23529896032166
C	-0.50961401186604	2.42099226960572	10.59704818783706
H	-1.27334795516202	2.99961971247014	11.13092206364105
H	-0.27225933065694	1.54143691290142	11.20924912122271
H	-0.95536428941608	2.07501970717204	9.65910564000123
C	0.74391697810725	3.28494947393989	10.35541638699072
C	1.86970377712466	2.45671712349467	9.69753556232773
H	2.75767635482561	3.09975426857726	9.61339233587340
H	2.13923106379114	1.62886818255103	10.37396501955468
C	2.44299630747821	1.23168202854611	7.64388336868597
C	3.78303287486669	1.04837077840746	8.08972485119724
H	4.09571701183934	1.45111512773068	9.04348261397472
C	4.67312994782802	0.35084498320496	7.30164060646461
H	5.69703651476900	0.20985673289096	7.63764733595784
C	4.25394395357536	-0.17088937675464	6.07002518831162
H	4.93021651749661	-0.71862882239556	5.42250551520201
C	2.93213085423543	0.02219044317561	5.70272586215905
C	2.39293915948412	-0.56368183577599	4.41650306061939
H	3.21260866199377	-0.75211451411881	3.70808946530109
H	1.90710520606669	-1.51938196716889	4.63891306526165
C	2.01734275074164	1.58214423530932	3.35215483052700
H	2.15251966623408	1.53051816552413	2.26458887995689
H	3.02152207152723	1.62945277368524	3.78844191911032
C	1.31118374191583	2.88084219916179	3.69521326953478
C	1.64773546495199	4.01590209693258	2.96632347995293
H	2.35363941927847	3.95161487064867	2.14483713992634
C	1.05132602816156	5.22709886023494	3.32551079313339
H	1.31388764860726	6.14449729345825	2.80508508369401
C	0.11594093309765	5.25442887574537	4.34022086525997
H	-0.34954736288952	6.18540883652294	4.63752917356244

C	-0.23041109840387	4.04537113578104	4.99968990160460
C	-2.16034456989405	5.08706071393879	6.15125302118768
H	-2.33818441671898	5.60019063130349	5.19715549846763
H	-1.73077431756535	5.83425469764484	6.83980635074380
C	-3.53273902237938	4.62801843828279	6.70712140540868
C	-4.43508201956149	5.87737608143806	6.76858804966000
H	-3.99698486135086	6.65859057049604	7.40306907419788
H	-5.41641725999632	5.62263791740653	7.18538623826489
H	-4.59801924554168	6.30301052329096	5.77055391808373
C	-3.38466680258887	4.04790990664387	8.12712962256962
H	-2.75286679499162	3.15373101032121	8.13811201056436
H	-4.36538009133250	3.76732772623554	8.52912815831233
H	-2.94079077012435	4.78367058490711	8.80957162657048
C	-4.17218314860319	3.58127299901814	5.77409160853776
H	-4.27890463270263	3.97365495186922	4.75534835985922
H	-5.17160374929672	3.30864085127328	6.13351357486730
H	-3.57495050819929	2.66512402497440	5.71899500831296
C	0.51226178105974	-0.35592379153542	2.84195825377436
H	0.40546274420009	-1.38392324736111	3.19064750384954
H	0.99945901760131	-0.38681763452528	1.85929567989376
C	-0.93282243617927	0.24444828129537	2.80094692988146
C	-1.87512942077856	-0.86239919176051	2.26227758970932
C	-2.84900951180007	-1.41499593066962	3.10124724979581
H	-2.94089136679301	-1.03776283849792	4.11266559878585
C	-3.68231951541957	-2.43857981583894	2.64355945382846
H	-4.43201484333739	-2.85665865349137	3.31113073170353
C	-3.55154398546378	-2.92880799251655	1.34373573906696
H	-4.19734886889051	-3.72911184932808	0.99039151599432
C	-2.58330637824716	-2.38140514395403	0.49912391085304
H	-2.47298780197305	-2.75031056456930	-0.51777265141724
C	-1.75628489548575	-1.35352782717345	0.95392816626113
H	-1.02572567564049	-0.92600961708980	0.27219109863959
C	-1.08158959762232	1.48972882008193	1.89376423157444
C	-0.35272513864807	1.67868639020504	0.71061212941493
H	0.40561472753944	0.96204013821991	0.40806224244258
C	-0.58552022196181	2.78567803462562	-0.11186061201219
H	-0.00624752874340	2.90662136568125	-1.02406378574363
C	-1.55655689546328	3.72488091728884	0.23320068855508
H	-1.74131522697251	4.58420184867054	-0.40674269432950
C	-2.29092702652188	3.54606393617244	1.40881593703783
H	-3.05495480401675	4.26893311066929	1.68661501265288
C	-2.05593135221660	2.44219324051291	2.22788318779540
H	-2.62183702278200	2.30312665726269	3.14226793355892
C	0.45866164117799	-2.14108995803154	7.52350303517182
C	0.45449470194673	-1.44162054553866	8.75024402453830
H	-0.11145795256993	-0.52054043435185	8.83108843776739
C	1.15757986264633	-1.91193875857482	9.85103219368973
H	1.15376649006358	-1.37936404308285	10.79511164124213
C	1.87975513134116	-3.10339693740158	9.73979287060141
C	1.89673508225281	-3.83050165745206	8.54623615819897
H	2.45907306567758	-4.75522490070363	8.49343753769737

C	1.19187926314660	-3.34699829080204	7.45171333563392
H	1.19246560749559	-3.90628457864934	6.52099737357363
N	1.54574239175332	1.93205767727614	8.37568063341355
H	0.56770839578830	1.89655042362629	8.05561846889887
N	2.03812602896878	0.70572733846088	6.45228953499176
N	1.37263480245247	0.33815672833800	3.83890640511562
N	0.42868904082999	2.88289703500575	4.70915133826329
N	-1.22404485829657	3.99755785077266	5.91751651393896
H	-1.31739056929557	3.11464255970384	6.44063901862123
N	2.63263919526482	-3.59483546971136	10.89219150963199
O	-1.27355407351686	0.56441779740139	4.11867859249969
O	-0.92357743254077	1.53010831557837	7.06613053247326
H	-1.59860995061103	0.95160684480884	7.44455212836432
O	2.60729330624555	-2.92747904784455	11.92444039076275
O	3.25564138202209	-4.64643793169416	10.76813857988182

Table S14. DFT optimized coordinates of 4

Fe	2.83888465978005	1.10382644797706	5.53730953430996
C	7.07435653393649	3.04774201381445	7.79724207273529
H	7.46523297844487	3.85343179720986	7.16288263371419
H	6.56361739676473	2.32411735119654	7.15288194618032
H	7.93168616985500	2.53708005221174	8.25250631841972
C	5.61676908893385	2.45634231603346	9.77368385101059
H	6.44784297306825	1.98808263126740	10.31451985105675
H	5.13269472457974	1.67449462551044	9.17970920131994
H	4.89765979646606	2.82088610631102	10.51876249252113
C	6.91982460930352	4.60457210996594	9.76835234091608
H	6.28646498408799	5.01579410727355	10.56461582071237
H	7.30724534081271	5.44358326567115	9.17666727379767
H	7.77482546703531	4.11105795366269	10.24416677750737
C	6.14049080373854	3.60584847861246	8.88908317760258
C	4.96995249699123	4.39311405646306	8.25493807712975
H	4.36408180264014	4.83139912397493	9.06358218202914
H	5.38711166758425	5.23169154543393	7.67685715717681
C	3.10390198512089	4.10938996599889	6.65525218704678
C	2.75784031652029	5.48713262079757	6.70655772537516
C	1.72522254372156	5.94922310066549	5.91525959410999
C	1.03180399699164	5.06757009434513	5.07319745950134
H	0.22825888717013	5.41096514072777	4.43048255541325
C	1.40252792557681	3.73135408271458	5.08835797790558
C	0.67148375708551	2.69765423423685	4.25256363335895
H	-0.05840151893968	2.19399854945642	4.89267344745947
H	0.13302385470392	3.18966835501649	3.42922997274018
C	0.89599977403258	0.42892961768336	3.33620408085666
H	0.55561106068568	0.49913251945592	2.29301063097546
H	0.01000157312743	0.34163882667579	3.97229427749533
C	1.70675610317876	-0.84104518394156	3.52811433989517
C	1.45838531848929	-1.95540281673534	2.73907192798122
H	0.73664772180112	-1.90924914699631	1.93021668144367

C	2.17035042461358	-3.12829906233485	3.02012004931035
C	3.10063720139604	-3.14843780567661	4.04067340172022
C	3.32148732272988	-1.96688238476113	4.79596795058367
C	5.13941963766589	-3.00271950326120	6.11074207093180
H	5.73377244240989	-3.26056981618204	5.21988393880413
H	4.55261509742214	-3.89645405254146	6.37389545921970
C	6.10640902881997	-2.69393652922748	7.27760039957623
C	6.98509199288313	-1.46901606939494	6.95070031100706
H	7.52870749872369	-1.61353652930084	6.00831514496974
H	7.72786493835208	-1.31268703319472	7.74294371955553
H	6.39498718138820	-0.54991460024891	6.86685731189441
C	7.00745072394349	-3.93288558788395	7.45261875394728
H	6.41727170903384	-4.83009359675124	7.67854768796729
H	7.71124307821425	-3.78026255226236	8.27897086132981
H	7.59439105002926	-4.13315843924839	6.54720097878652
C	5.32310518776877	-2.45070915594700	8.58274438432936
H	4.68692825769347	-1.56290305994020	8.51235286608047
H	6.01461164058728	-2.29678636948462	9.42013640133964
H	4.68339186950185	-3.30755215987613	8.82865808588415
C	2.54425423829678	2.22421513784518	2.74338691464797
H	2.51520999526518	3.30845694031902	2.86262701918901
H	2.18343644120933	2.00882454784151	1.73099644578921
C	4.04377221425736	1.78704995686072	2.96751541177629
C	4.92624689606763	2.98355390019351	2.52017006890400
C	5.69125601846398	3.67297756933989	3.46693214185154
H	5.67399038823837	3.32789235572033	4.49435058896321
C	6.46293313830275	4.77548848747591	3.09091355039736
H	7.05635633488304	5.29609618871714	3.83929156718165
C	6.47504475626340	5.21106699525303	1.76496159702704
H	7.07287609915352	6.07130006998188	1.47371935186144
C	5.71456026483619	4.52777650585931	0.81318591296299
H	5.71959531314361	4.85170779043647	-0.22507234001121
C	4.95140525940453	3.42098132016549	1.18757798252223
H	4.38663845607098	2.88718537740201	0.42769371778580
C	4.48595795503101	0.55149974407955	2.14198769936474
C	3.93995375786417	0.19166074942522	0.90297350410797
C	4.45238670504271	-0.88687486773438	0.17412941033749
H	4.00739200473916	-1.14601545086652	-0.78342591587516
C	5.52653307121326	-1.62350331895629	0.66961596867087
H	5.92791870183523	-2.45976086686921	0.10262197245172
C	6.08205465972952	-1.27273262326841	1.90345728980138
H	6.92491556287340	-1.83451941654329	2.29995528483700
C	5.56700376718692	-0.20008883832747	2.62882298344521
H	5.99285727002033	0.07334845625590	3.58794620362057
N	4.12089676807011	3.59057546737698	7.38417826421930
H	4.27638458813071	2.57935100127598	7.31157960101913
N	2.40352415044627	3.26161381706100	5.85864132430241
N	1.60219672672409	1.65926147151035	3.75001162917775
N	2.60150022643078	-0.84444337092034	4.53154447635735
N	4.23524062534274	-1.90715315631093	5.79292181236853
H	4.34470302498596	-1.00788749977311	6.27126390692760

O	4.22421303916968	1.54640572661794	4.32435345138230
O	3.92342113997959	0.69927214380787	7.05966811138510
H	3.45412472895305	0.43122459637565	7.86284322849203
O	1.08457386672122	0.68375230641354	6.40261217067448
H	2.00070804553731	-4.02459936548454	2.42898112568499
H	3.66506508559853	-4.04586506385089	4.25883305890486
H	1.45625764572359	7.00208035932684	5.94233231561346
H	3.30117646750495	6.16031235318668	7.35765439544259
H	3.10695387480423	0.74623257422917	0.47947728958250
C	0.52093068576645	0.70409592059055	7.58029077429279
C	1.06388824143549	1.41832889119565	8.68771286354220
C	0.43942140748011	1.40761357967872	9.92506639449941
C	-0.74930156168618	0.68963984007083	10.09619656333419
C	-1.31891881754931	-0.01819618145107	9.02759957613564
C	-0.69386412128503	-0.00942604035061	7.79445954833555
H	1.97254284739889	1.99459709900548	8.54776247000840
H	0.85144173324469	1.95138675194281	10.76745244234477
H	-2.24213172765162	-0.56287112995875	9.18808693599837
H	-1.11413036402372	-0.55706292813785	6.95587753094335
N	-1.40201609714210	0.68152226348923	11.39347501844953
O	-0.87358297049632	1.30699482756513	12.31364741098514
O	-2.45214960547315	0.04950739973815	11.51125500104881

Table S15. DFT optimized coordinates of 5

Fe	4.31513265382965	0.69716247839825	5.11005644888611
C	7.59271979022170	3.71256485884542	7.01601159599311
H	7.40234561130967	4.69769436515683	6.57072140705439
H	7.18886854604950	2.95575178781935	6.33535444550488
H	8.67949129404271	3.57186358081866	7.06668622228712
C	7.26885219375841	2.22086422562936	9.02888787624930
H	8.35077043780486	2.08033934926362	9.14354547298230
H	6.89638338833283	1.40980435748254	8.39289435147639
H	6.81366488198396	2.11844606269279	10.02261345442914
C	7.58373634606553	4.69825355870360	9.33138205750116
H	7.15962368080783	4.66267113732203	10.34282691164376
H	7.40584190992730	5.70215282851533	8.92489861955924
H	8.66815137122770	4.56216719501800	9.42016953240183
C	6.97536830884507	3.60985730193103	8.42510208378819
C	5.45063498832638	3.86881800598973	8.36566113031527
H	5.04294637189358	3.83423831045436	9.39090878801191
H	5.28606189313124	4.88991079604149	7.99221980291410
C	3.48663042087622	3.11664382011282	7.04846132335800
C	2.66024318307525	4.18883475568354	7.48243305451228
C	1.39701372748579	4.32269705320114	6.93994042922560
C	0.94601302105110	3.41176681361909	5.97288313017249
H	-0.03111700340395	3.50883909193084	5.51215243057599
C	1.79869338870445	2.37747925112838	5.61199387188512
C	1.40492144888331	1.34336893151026	4.57557239612195
H	1.12726344595759	0.41052109472201	5.08485087889090

H	0.51557812237123	1.68518235542902	4.01971416859411
C	2.29720433650948	-0.21419415126750	2.93996203334133
H	2.96550744625679	-0.21246045081028	2.07369182037392
H	1.26903458086129	-0.26866866060508	2.54564470329173
C	2.60709225536916	-1.46806414968549	3.73878941808542
C	1.96441895449423	-2.65758712524999	3.41644871269766
H	1.17050090827523	-2.66794552473879	2.67652845842667
C	2.39322186301150	-3.83091204139469	4.04751568260923
C	3.43040010823769	-3.78223394281344	4.95796096632012
C	4.03370333974936	-2.52992116963859	5.25465413457094
C	5.69111338754919	-3.57543003905395	6.75672368157806
H	5.97445767755747	-4.30233806448295	5.98027707152950
H	4.96927630144077	-4.08524109240834	7.41711507151265
C	6.95199651330748	-3.23037745679475	7.58451045596234
C	8.01230206066592	-2.53979198575683	6.70435711250910
H	8.26696544581594	-3.15685494896850	5.83336502627399
H	8.93261705391216	-2.37669748853206	7.27830498595296
H	7.67009006310987	-1.56503982408451	6.34380203155076
C	7.51794247823896	-4.56479387188888	8.11284042635956
H	6.78715535797366	-5.08867032486153	8.74303432544888
H	8.41332915400233	-4.38655547915084	8.71986059803407
H	7.79910963333279	-5.23520981885093	7.29066771978022
C	6.59223186320031	-2.32739351506890	8.78175846551493
H	6.23692472742965	-1.34614138114595	8.45262349590799
H	7.47484824214359	-2.16369348474374	9.41268438681951
H	5.81713042001419	-2.79127841126507	9.40640993682708
C	2.94455884478558	2.16193799499712	2.82910163734212
H	2.76588479466425	3.07330093483902	3.40439646426258
H	2.32769939457258	2.21612752736341	1.92008194243260
C	4.49245303295789	2.09582160325779	2.52268964946354
C	5.00054865970383	3.52888108742261	2.21090273014378
C	6.30241150132473	3.86651493849949	2.60534869439986
H	6.88202724065269	3.11721511953240	3.13346819303308
C	6.82626347279940	5.13196047971742	2.34140629566996
H	7.83992822433077	5.37111381758248	2.65496652590364
C	6.05439927064237	6.09302660267648	1.68197677019108
H	6.46065470995499	7.08077523183700	1.47790239258264
C	4.75437262039433	5.77265474027342	1.29076638347860
H	4.13809901544538	6.51220332407148	0.78400374912832
C	4.23429616597830	4.50108059305120	1.55192148283650
H	3.21605023525399	4.28293867613915	1.23909448774072
C	4.77851979088134	1.21595822087387	1.26799508276283
C	4.19528557764101	1.46444694275928	0.01516391288667
C	4.48150544159477	0.65473448625204	-1.08533364666599
H	4.01799244415748	0.86788410616117	-2.04596451487326
C	5.36661843781224	-0.41896722714286	-0.95725149846386
H	5.59399555842341	-1.04782151375347	-1.81482826096634
C	5.96025032993194	-0.66964082920611	0.28099307829046
H	6.65578126756304	-1.49899958182890	0.39299614088595
C	5.66857384764483	0.14090544576596	1.38128118014058
H	6.12215555049877	-0.03885192185994	2.34958882463501

N	4.74773610764998	2.93586624417066	7.50204061521774
H	5.19308547291799	2.04607698026769	7.23534603191600
N	3.02731143868054	2.21649630879337	6.13712784849658
N	2.52533506487883	1.02856393935793	3.67895298729512
N	3.59064655474378	-1.38314001079341	4.65850852370102
N	5.06830896259375	-2.42524839534809	6.12128113468727
H	5.36650507144652	-1.46595622099220	6.36927444920948
O	5.14464863315888	1.59497810270868	3.62625534999416
O	5.24708647209881	0.25315696570430	6.79044473416785
H	1.91657848528164	-4.78147746760681	3.82123357180642
H	3.77611425443026	-4.68128505670080	5.45183264395993
H	0.75637465504153	5.14074860294124	7.26031171447694
H	3.01876341562031	4.88393969182046	8.23247985022711
H	3.52345735030592	2.30946847439427	-0.11422989738445
H	4.65998503652213	0.07176207784302	7.54024013937316

Table S16. DFT optimized coordinates of 5•Li(OTf)(THF)

Fe	-1.44839749571276	4.75981923720779	16.48737898044648
S	1.26441896485312	2.02314151811087	13.57735198194670
Li	-1.38437376893307	2.37728852632007	15.08522914594699
C	-3.36167830383667	3.73699614300833	11.67822996859365
H	-2.55212288464569	3.64420356700066	12.40833195742717
H	-2.91241674146827	3.70073722665381	10.67853695736099
H	-4.01914366687873	2.86402599064299	11.78153950974332
C	-3.20290186751786	6.25303529286809	11.73911128087506
H	-2.39309803787088	6.19261262332272	12.47294303870853
H	-3.73993788323909	7.19944481952125	11.88917400047906
H	-2.74784080946354	6.27964035937268	10.74160009512823
C	-5.23940253356504	5.14215459088492	10.77212178637047
H	-4.78486702982265	5.11744238937349	9.77480745378483
H	-5.81119891461111	6.07566343942150	10.85529734349959
H	-5.94690662471819	4.30482314229622	10.83468197844732
C	-4.15274543991405	5.04595547878402	11.86128296038476
C	-4.88228912450304	5.06509668656268	13.22463164464747
H	-5.51984497424357	5.96166095667576	13.25793969072863
H	-5.55646536615613	4.19300306031134	13.27305937715694
C	-4.45431654016259	5.25885606256558	15.63986888205049
C	-5.84324373092442	5.40563496324879	15.92362562488622
H	-6.57077990942836	5.35073061092741	15.12435736194443
C	-6.24986586993243	5.59390343485126	17.22877027245344
H	-7.30917655181038	5.69498804089264	17.45308860510610
C	-5.30307724137935	5.64978610088907	18.26203880856849
H	-5.59742392608087	5.80427957546585	19.29473132151820
C	-3.96594818843464	5.51206193220984	17.92001621640512
C	-2.88241083754069	5.69231819394108	18.97137400142699
H	-2.57939054368169	6.74687218592907	18.95494018965088
H	-3.29214428861377	5.49765729232667	19.97469689006894
C	-0.45710456581207	5.55777463947199	19.17768566098457
H	0.35524914182863	4.82648840150023	19.15302218782049

H	-0.55213789607766	5.90331482877022	20.21935528467175
C	-0.08564967686775	6.72220001496714	18.27599563761469
C	0.48195612670822	7.87613253128285	18.79099931396396
H	0.63343917405777	7.98727946838184	19.85965366044459
C	0.86841763886811	8.87757678885628	17.88564320307044
H	1.32912551942066	9.79255748592628	18.24948528654091
C	0.67225817307945	8.70611105218463	16.53148570541456
H	0.99063130120959	9.46481703819259	15.82940521684453
C	0.06441557737081	7.50740612760536	16.06538628343623
C	-0.04460228824778	8.19483378116035	13.65246896111375
H	-0.08332006695822	9.21621660996125	14.04728365075097
H	-0.93557269605465	8.07599417007930	13.02225038448520
C	1.21174435489876	8.02913212723162	12.75235269720589
C	2.50342460358920	8.22232229046564	13.56608370871610
H	2.57272739075743	7.49933468266628	14.38663630321754
H	2.56716448374642	9.23312062740755	13.98918852900261
H	3.38188800387789	8.07907371405097	12.92521123986067
C	1.12318141823684	9.11227331971753	11.65955306214614
H	1.98131190755739	9.04668936671872	10.97998391049713
H	1.11663475947516	10.12280687085207	12.09011294810505
H	0.21326572983242	8.99804328968468	11.05640264240473
C	1.21666892052940	6.63533324151806	12.09823037442166
H	2.06913365118772	6.53686654582201	11.41475052253110
H	0.30378824885248	6.47056970890962	11.50972782726305
H	1.29830992423451	5.82986394707502	12.83516941006549
C	-1.83762712558550	3.47818812422821	19.15526229341208
H	-2.90066857985036	3.24837146663839	19.04492281418911
H	-1.57839374540356	3.37844916257320	20.21954051816708
C	-1.05639561306415	2.47035990714941	18.24290247699738
C	-1.55442004735163	1.02259700953048	18.46673478671417
C	-1.04416972953567	0.02472842678300	17.61699041113656
H	-0.32672518939089	0.29613301818170	16.84752123624865
C	-1.44215505938053	-1.30358301659301	17.75323913798070
H	-1.02388879561998	-2.05823982472392	17.09163019316717
C	-2.36285071773015	-1.66916806997453	18.74264732935486
H	-2.67003140990901	-2.70641064237090	18.85121167218038
C	-2.87176918459002	-0.69116931231387	19.59413486344504
H	-3.58231039097282	-0.95942669466634	20.37301793576265
C	-2.46718183689612	0.64342567918787	19.45872693489211
H	-2.87727974081364	1.37591748913609	20.14779871790724
C	0.46025446884699	2.48713239257099	18.57324416049484
C	1.40456367929819	2.82361617320935	17.59675945584094
H	1.07393996228933	3.07364076060113	16.59569866325131
C	2.77163538807017	2.82407886554695	17.89325395832717
H	3.48379994607691	3.07002016595296	17.11028462572340
C	3.21394633287849	2.49394625326617	19.17427903111739
H	4.27650653743294	2.49103113767932	19.40494374073219
C	2.27974364326648	2.15136453761011	20.15692108243367
H	2.61277146984272	1.87803168527730	21.15543856975248
C	0.91794409098896	2.14207043177977	19.85615824332475
H	0.20565668541147	1.84249217685531	20.62172342832920

C	0.95380876548942	1.65105674193402	11.76491628516743
C	-2.87763763508662	0.28167686629570	13.53767071419890
H	-1.84859318609633	0.25349251329483	13.17791338315385
H	-3.55286615365333	0.53328125334145	12.70512387093946
C	-3.33727367780529	-0.97959435124772	14.26611064324615
H	-2.51108554375858	-1.38059604107790	14.86230605701402
H	-3.68250768997795	-1.76139355311435	13.58204860896172
C	-4.45651398378776	-0.44393141173771	15.18439166024642
H	-4.51297407828996	-0.99183366687422	16.12851730606673
H	-5.43209238829585	-0.51899193115083	14.69080678976445
C	-4.07251689390216	1.03941834640281	15.40596751751263
H	-4.89417440418190	1.72053424349734	15.14818463311790
H	-3.74409844242943	1.25046539139445	16.42639498064579
N	-3.99558211277490	5.08089393839139	14.38145491189640
H	-2.99254467892176	4.85428938165355	14.25621959211912
N	-3.54259950733396	5.30561822581917	16.65491609691051
N	-1.67967503121563	4.88400548754329	18.71053658566983
N	-0.30797684930844	6.54275504538074	16.95302161851403
N	-0.18370746161131	7.25552623997960	14.75872253867608
H	-0.59519524999763	6.33796661261040	14.54961996590529
O	-1.28527061663618	4.48121176098746	14.52896793684812
H	-0.45355598682374	4.26017051400643	14.06911771036738
O	-1.30493663159987	2.84239481828111	16.92309090812552
O	0.05051576559110	1.43130555252635	14.21584683004659
O	1.26112719763804	3.50264315141983	13.63356883167157
O	2.52266909955624	1.35712780104223	13.89255012844515
O	-2.94935400595586	1.31001250528707	14.54104391629779
F	-0.19373231335662	2.22588608862511	11.36129790774380
F	1.94358364789591	2.11662389687159	10.99978274006275
F	0.84406227925759	0.33209916345444	11.56207111143033

Table S17. DFT optimized coordinates of 6.

Fe	12.43767694738493	6.50340967439898	3.92299587125373
C	12.62308550427604	9.77744448466385	7.87613771662422
H	12.55278967051439	10.62226704215946	7.17888294187809
H	12.05983332240987	10.03856976168388	8.78022034932442
H	12.12925192092010	8.91606533083094	7.41202184078646
C	14.74188484866699	10.69355530105362	8.88449722340344
H	14.71217575857882	11.56505804100077	8.21791532865454
H	15.79145772128373	10.50212803727446	9.14261846610832
H	14.21669892997704	10.96356326378465	9.80818514155486
C	14.14141019266299	8.26799547244296	9.19861578829333
H	13.57404475048666	8.48949622564339	10.11053802020652
H	15.17198422392998	8.03895140562579	9.50026590672260
H	13.70765500494729	7.36752983427010	8.75091003885797
C	14.08927722624699	9.46131913155398	8.22791945567753
C	14.88549561669924	9.15386134111002	6.92920529909922
H	14.86848591316621	10.04636829801578	6.29036147641208

H	15.93740947285026	8.96474380817816	7.17059776974240
C	14.82368572256971	6.78124078220690	6.06054327643535
C	15.90707395995837	6.29951378502906	6.84148304565404
H	16.42911097735399	6.96213255060214	7.51996510610494
C	16.25702590606845	4.96772742066621	6.75149508702262
H	17.07750332922607	4.58483448016956	7.35336437448001
C	15.53690360134323	4.10642043580147	5.91200776475134
H	15.76598534172887	3.04731659288998	5.85434541300583
C	14.50913942504802	4.64866331492510	5.15425413502678
C	13.71402167202096	3.77467192907814	4.19980333444432
H	14.20351764676866	3.78827114769392	3.21900493144429
H	13.73287102587492	2.73017399308423	4.54939051052715
C	11.74952704597610	3.88204156424069	2.74249966999006
H	10.71291510707763	4.23366738948217	2.73704288144218
H	11.71745483714073	2.78780161211998	2.61239648837505
C	12.50688367659667	4.51156509262580	1.59121184475614
C	12.72422512951330	3.78744813067286	0.42748364977580
H	12.35847168496718	2.77031639381283	0.34000142630935
C	13.43229195532769	4.40439237660936	-0.61107254767114
H	13.62328345218697	3.87165351495665	-1.53934039238624
C	13.89619128713079	5.69270201759835	-0.44961434708400
H	14.44329869177569	6.18375992155600	-1.24399295444425
C	13.63719039270515	6.38155456376217	0.76836531405881
C	14.90010105926563	8.35123127706387	-0.02452876118766
H	14.36013469593083	8.42414058444658	-0.98243110882985
H	15.80503258635173	7.75519499147689	-0.21446250976447
C	15.33195183483789	9.77547076354645	0.39678038481447
C	16.31154050646273	10.27483176038025	-0.68570170530846
H	16.63405161613088	11.29870992973340	-0.46473015515562
H	15.84346816885104	10.28136459992263	-1.67851884044625
H	17.20876534176461	9.64534011377359	-0.73813787929818
C	14.11731532114476	10.72439793901600	0.44903328375016
H	13.39357343031644	10.42708107742486	1.21423082772648
H	13.60380444824228	10.75781014833897	-0.52082668400087
H	14.44343608375442	11.74445016810895	0.68618531593304
C	16.05139559798052	9.75538060697284	1.76009603868631
H	16.44112374709134	10.75321297946757	1.99400742479356
H	16.89763890887605	9.05644917271252	1.75378873888912
H	15.37539414149808	9.47030482806828	2.57263594223220
C	11.48884017957966	3.98565193386889	5.20681966174329
H	12.14583285596240	4.02536299474631	6.07920410605262
H	11.08035898056658	2.96656665191629	5.14884540390301
C	10.39628531122344	5.09397985882285	5.41803153385707
C	9.96261332385750	5.04906633521008	6.90776129882216
C	9.97424284600383	6.23623721786752	7.64906603514154
H	10.28446580739575	7.14427988099133	7.14426547794723

C	9.59555887866898	6.24544825018319	8.99317484035081
H	9.60727752757884	7.18104363599316	9.54844986353220
C	9.20582815321316	5.06287581762841	9.62525907397736
H	8.91095444638621	5.06857010463580	10.67160385687557
C	9.19354004825461	3.87182580756447	8.89645391445520
H	8.88959952634410	2.94285643028665	9.37344564885992
C	9.56430223822572	3.86712003604254	7.54994871662320
H	9.53076673461628	2.92847717611714	7.00310326959548
C	9.12727839812599	4.86684901994736	4.54715521931378
C	8.53525263224823	3.60865023364423	4.34870228460252
H	8.97493858698191	2.71582067096470	4.78630357030714
C	7.37259224529161	3.47181028556580	3.58626928680637
H	6.93676247912364	2.48533642378097	3.44436224617913
C	6.77152483571610	4.59359040900127	3.01229541748852
H	5.86392188581239	4.48826211194037	2.42327987605846
C	7.34573505112553	5.85164263568920	3.20693837534277
H	6.88810153255867	6.73573811810300	2.77096505699038
C	8.51138707756493	5.98368018065021	3.96502386535107
H	8.96139459192768	6.95774995666702	4.12091953006667
C	10.84086362629299	9.29076996484834	3.03070842646446
C	10.44453740774075	9.14537863521913	1.68858811984872
H	11.15927210395015	8.78169449786182	0.95666170477427
C	9.15132810859305	9.46699042099835	1.28436162789693
H	8.86478081519633	9.35078055944216	0.24334472044824
C	8.22351781928585	9.94731449897072	2.21470126076313
C	8.60432004819602	10.09967393134898	3.55356165894790
H	7.89037622465700	10.47459889903050	4.28049536127714
C	9.89802969666876	9.77705352475728	3.95437246787804
H	10.18933877134195	9.89705671492095	4.99244321582642
N	14.37142296591962	8.05595398152301	6.12605483600819
H	13.56553809382039	8.26640928994918	5.53856630749552
N	14.17436941958970	5.95614362143333	5.19205566307353
N	12.34001457654870	4.26851823681132	4.02755643910244
N	12.94731982213026	5.77807977604247	1.78032851630293
N	14.08434371414131	7.64668668366913	0.95861261138214
H	13.69119623636675	8.16107323092249	1.75398003903195
O	10.97781656775972	6.31572599442935	5.13285861171583
S	12.50082347452139	8.90688942945135	3.55488383536238
C	6.81266183063431	10.23583483821028	1.79144347340289
F	6.23228221357982	11.19244098705632	2.54691819744341
F	6.73355535120766	10.64153399360109	0.50473612686330
F	6.01069855563925	9.14095970794286	1.88878238899282

Table S18. DFT optimized coordinates of 7.

Fe	0.05620051382324	0.68217697925770	5.40130716032123
S	-0.32527872034059	-1.67161812661806	6.04837900441881
C	0.63721232612818	4.13124832031676	9.56263240139211
H	0.21436820677990	3.87948543045910	8.58503197206136
H	1.50273550497431	4.78581155275669	9.39703607931414
H	-0.11495515160252	4.70529654406193	10.11817426713114
C	1.64419618108373	3.29657318009028	11.71034423134733
H	2.52501631426221	3.93702458672319	11.57369401571881
H	1.94514139432430	2.42481827251796	12.30400487077430
H	0.90862468745735	3.86196214925554	12.29508088198469
C	-0.18410901825453	1.97642732257773	10.61590597175560
H	-0.93072078568120	2.51645068143372	11.21143706300829
H	0.10425567779778	1.07544649807230	11.16930893147850
H	-0.66634814120770	1.65993478970344	9.68587041640337
C	1.04159064884575	2.87298179945013	10.35403756618937
C	2.14341784321587	2.09337923945631	9.60252178527263
H	3.02493057811765	2.74624039806278	9.52715412548709
H	2.43653254897382	1.22335805438528	10.21117162934933
C	2.64403899811058	1.02891464528732	7.44462518655289
C	4.00874559284447	0.84289559175305	7.81588195701961
H	4.35905036597731	1.19591381935882	8.77630970087927
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O	-1.21708855114302	0.49475965827287	4.03031129244524
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F	2.78399608619150	-2.95059543078534	11.93080217325172
F	2.03831473683430	-0.93317047898264	12.20178121780248
F	0.76196554072006	-2.62352219479932	12.65792676948947

Table S19. Single point energy calculation of the different isomers of 3 and 4

Complex	E^a (*trans*-pyridine[c] isomer) in E_h[b]	E^a (*trans*-alkoxide isomer[d]) in E_h[b]	ΔE (*trans*-pyridine – *trans*-alkoxide) in E_h[b]	ΔE (*trans*-pyridine – *trans*-alkoxide) in kcal/mol	More stable isomer by DFT	Isomer Observed by crystallography
3	**-3939.02463210004**	**-3938.844536257419**	**+0.18009564**	**-113.29**	*trans*-pyridine	*trans*- pyridine
4	**-3614.422050693938**	**-3614.790406913627**	**+0.368356219**	**+231.14**	*trans*-alkoxide	*trans*-alkoxide

a = calculated single-point energy using B3LYP/6-311g*
b = Hartree
c = ArX group is positioned *trans* to pyridine ring
d = ArX group is positioned *trans* to alkoxide oxygen

E. Supporting Figures.

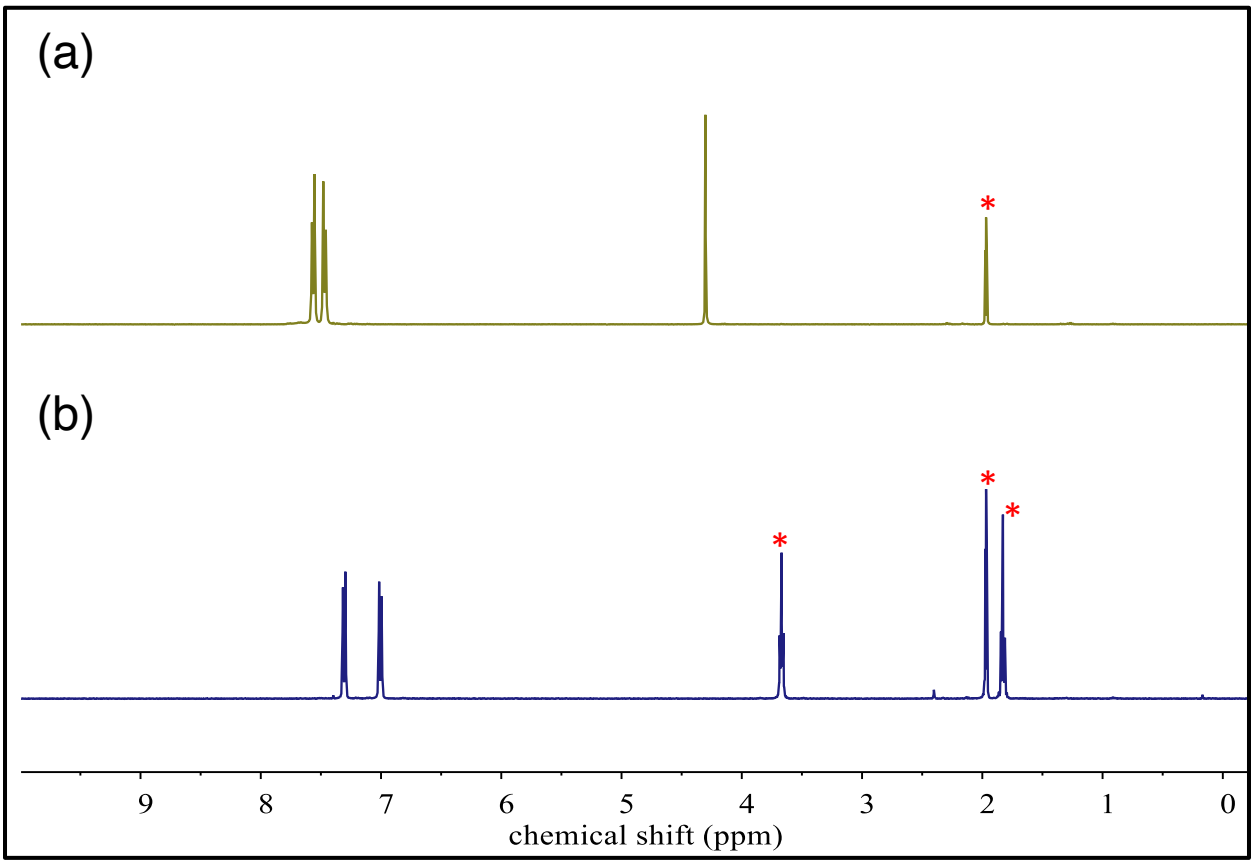

Figure S1. ^{1}H NMR spectra of (a) *p*-CF_3-PhSH and (b) $NaSPh^{p\text{-}CF_3}$ in CD_3CN at 23 ºC. Residual solvents (CH_3CN, THF) are marked with a red asterisk (*). The upfield shift of the aromatic protons (7.32 – 7.02 ppm) and absence of the singlet assigned to the -SH proton (4.30 ppm) in the bottom spectrum indicates successful deprotonation of the thiol compound.

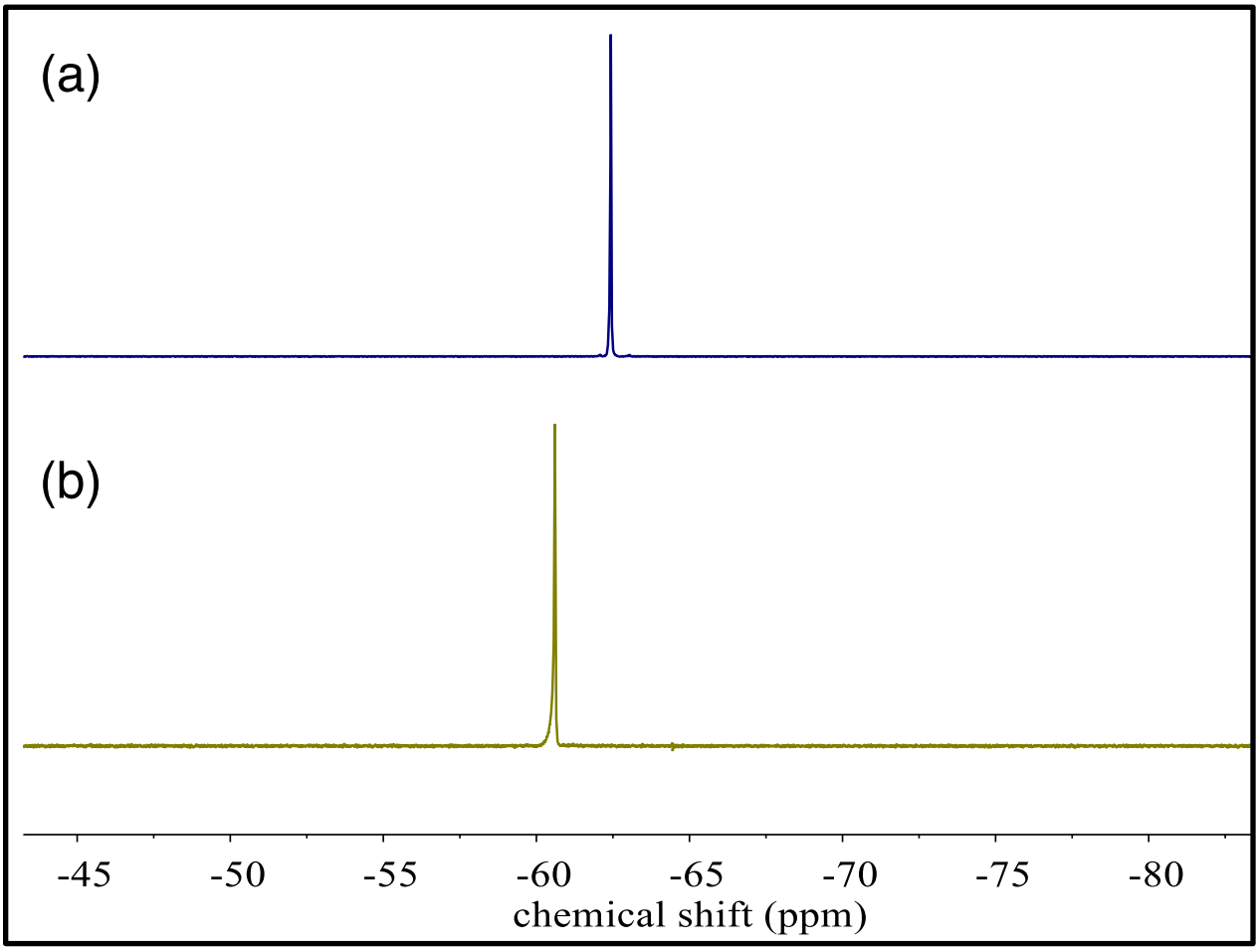

Figure S2. ^{19}F NMR spectra of (a) *p*-CF_3-PhSH and (b) $NaSPh^{p\text{-}CF_3}$ in CD_3CN at 23 ºC.

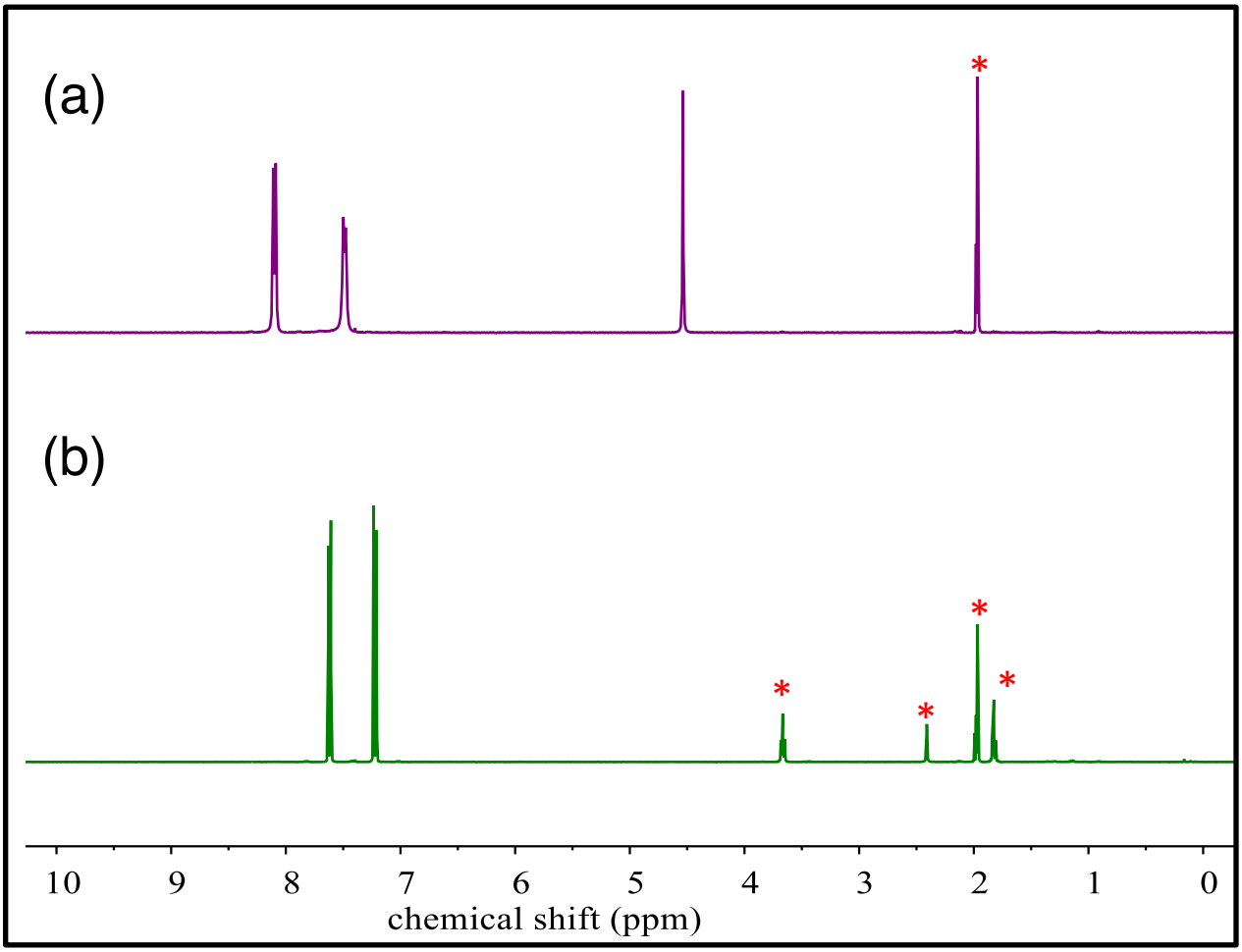

Figure S3. ^{1}H NMR spectra of (a) *p*-NO_2-PhSH and (b) $NaSPh^{p\text{-}NO_2}$ in CD_3CN at 23 ºC. Residual solvent (CH_3CN, THF) are marked with a red asterisk (*). The upfield shift of the aromatic protons (7.61 – 7.21 ppm) and absence of the singlet assigned to the -SH proton (4.55 ppm) in the bottom spectrum indicates successful deprotonation of the thiol compound.

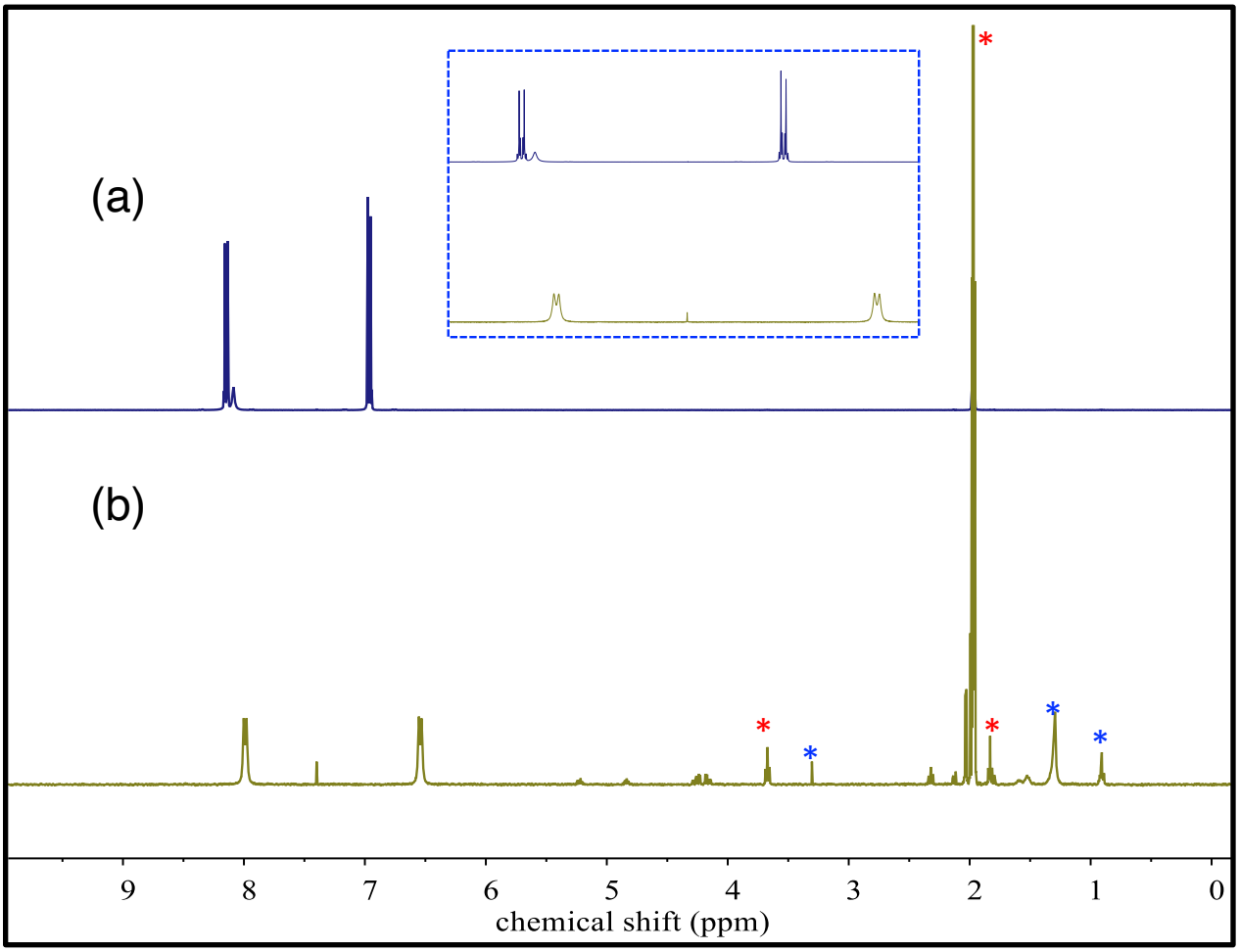

Figure S4. ^{1}H NMR spectra of (a) *p*-NO_2-PhOH and (b) $NaOPh^{p\text{-}NO_2}$ in CD_3CN at 23 ºC. Residual solvent (CH_3CN, THF) are marked with a red asterisk (*) and some unknown impurities are marked with a blue asterisk (*). The upfield shift of the aromatic protons (8.00 – 6.53 ppm) and absence of the singlet assigned to the -OH proton (8.09 ppm) in the bottom spectrum indicates successful deprotonation of the thiol compound.

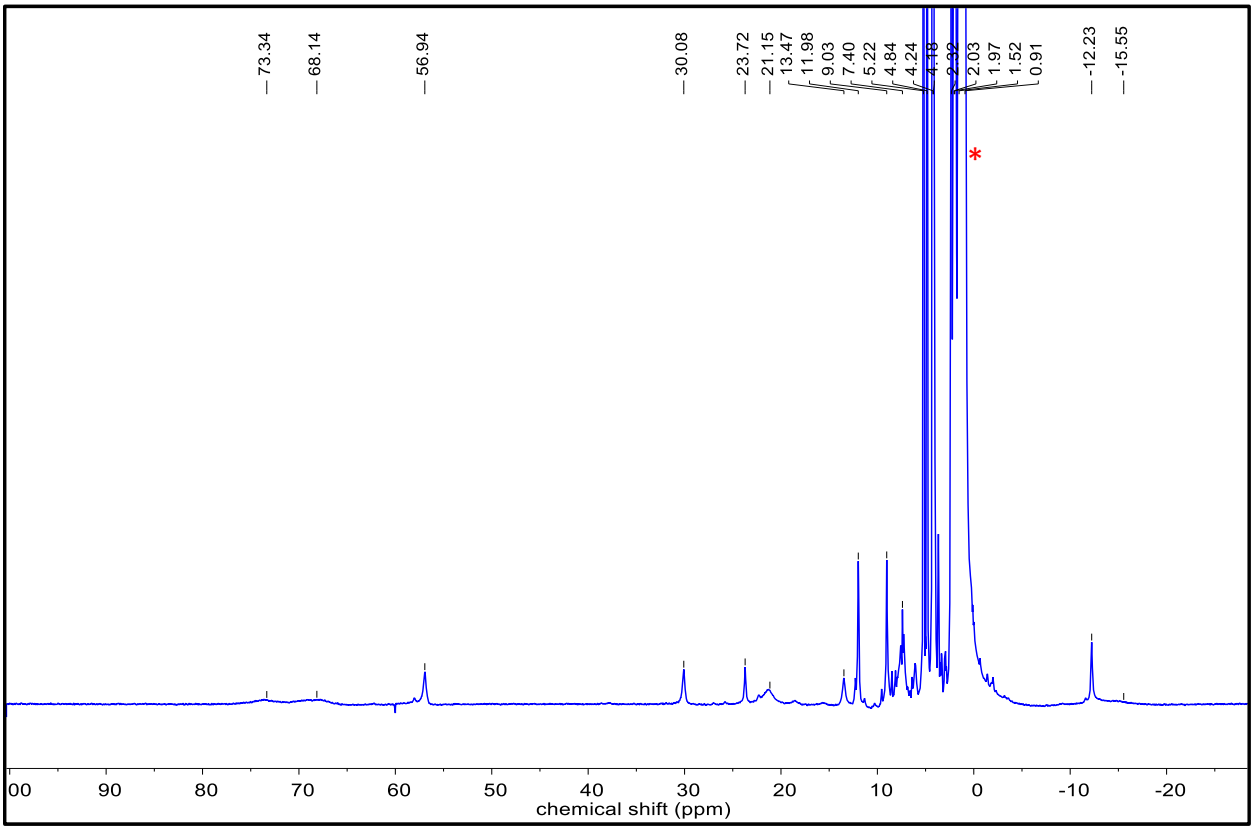

Figure S5. ^{1}H NMR spectrum of $Fe^{II}(BNPA^{Ph2}O)(SPh^{p\text{-}NO_2})$ (**1**) in CD_3CN at 23 ^{o}C. Residual solvent peak for CD_3CN is marked with a red asterisk (*).

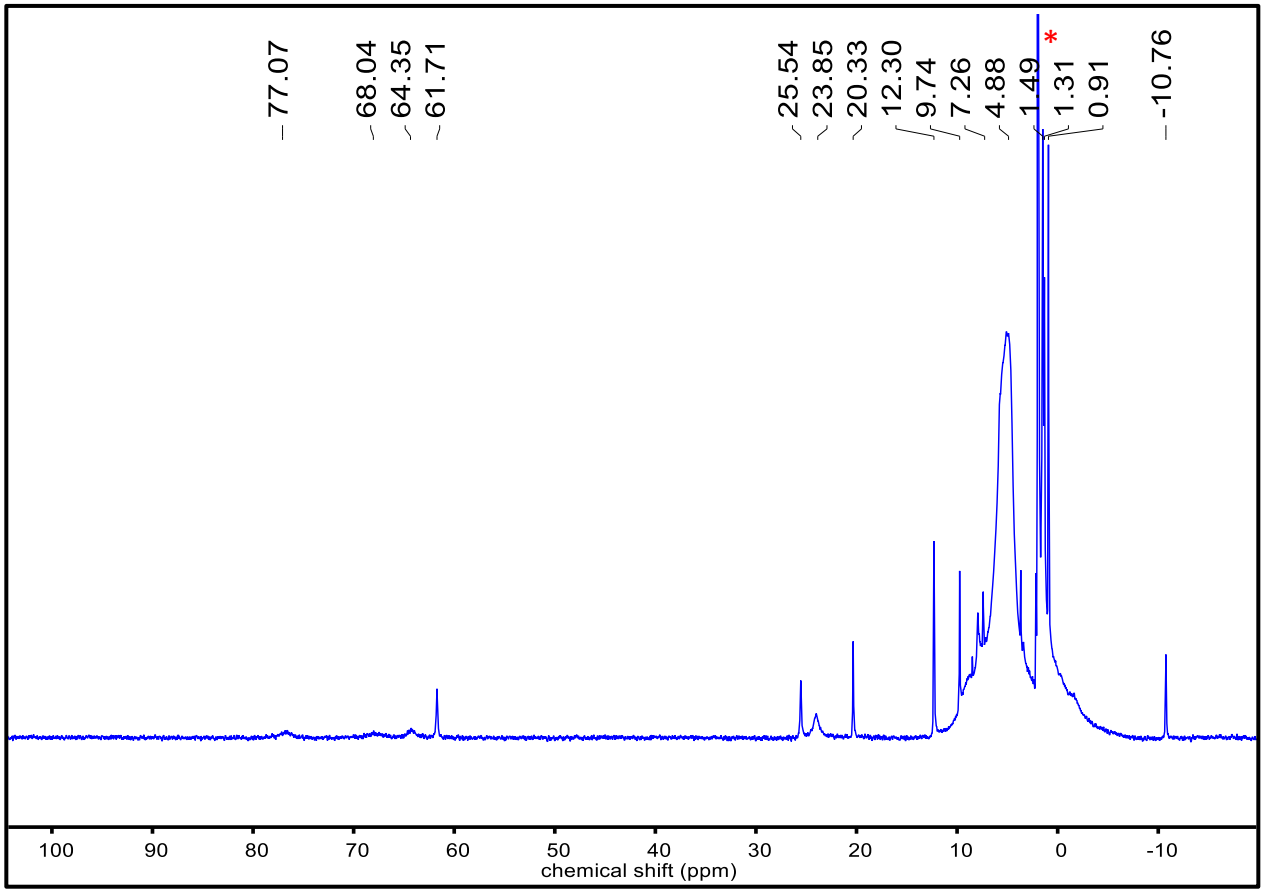

Figure S6. ^{1}H NMR spectrum of $Fe^{II}(BNPA^{Ph2}O)(OPh^{p\text{-}NO_2})$ (**2**) in CD_3CN at 23 °C. Residual solvent peak for CD_3CN is marked with a red asterisk (*).

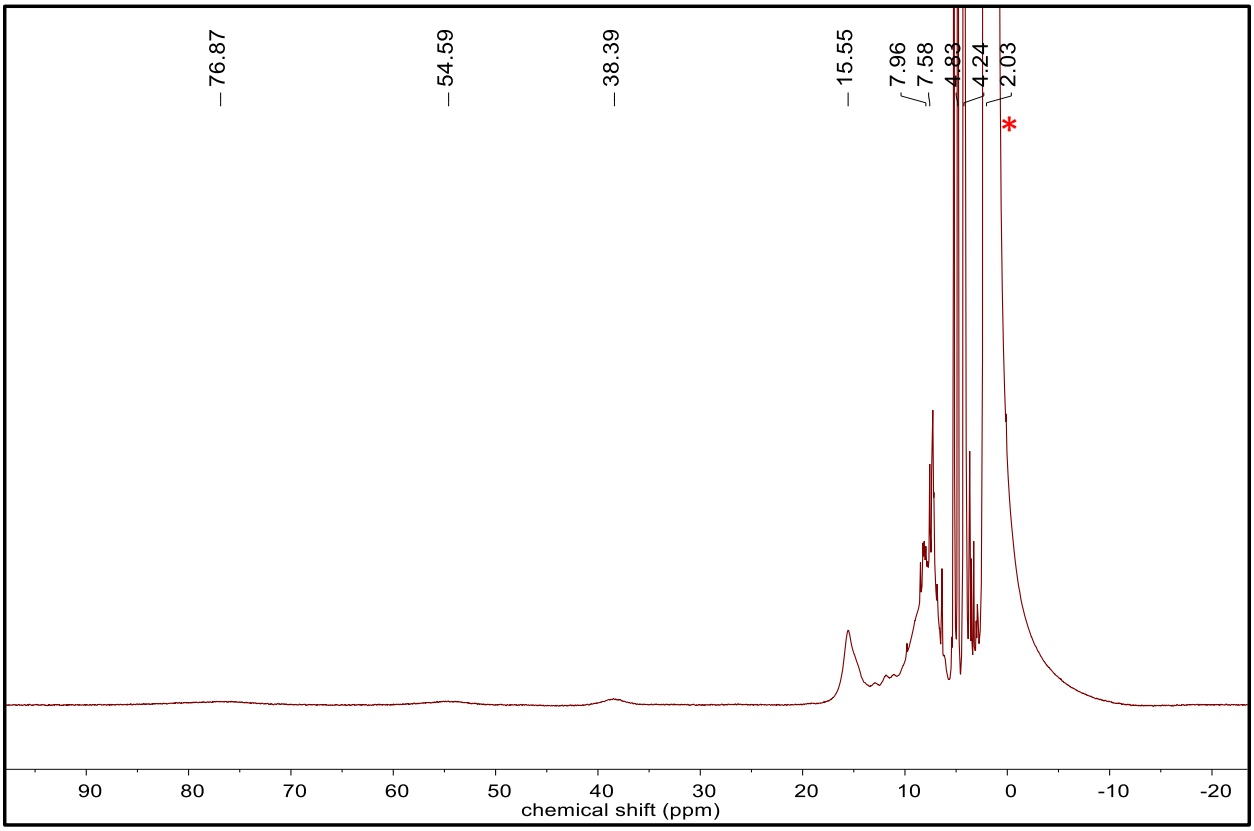

Figure S7. ^{1}H NMR spectrum of $Fe^{III}(BNPA^{Ph2}O)(OH)(SPh^{p\text{-}NO_2})$ (**3**) in CD_3CN at 23 ^{o}C. Residual solvent peak for CD_3CN is marked with a red asterisk (*).

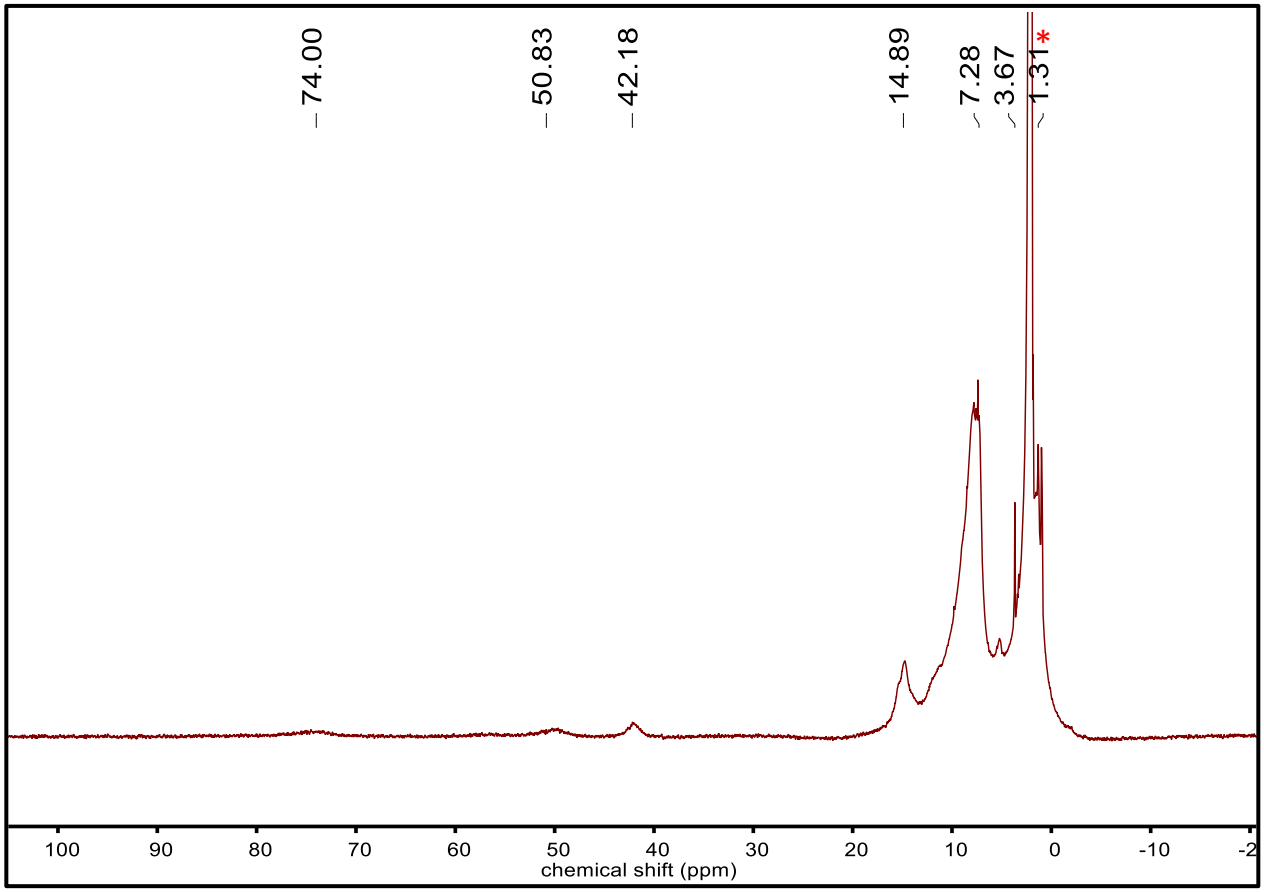

Figure S8. ^{1}H NMR spectrum of $Fe^{III}(BNPA^{Ph2}O)(OH)(OPh^{p\text{-}NO_2})$ (**4**) in CD_3CN at 23 ^{o}C. Residual solvent peak for CD_3CN is marked with a red asterisk (*).

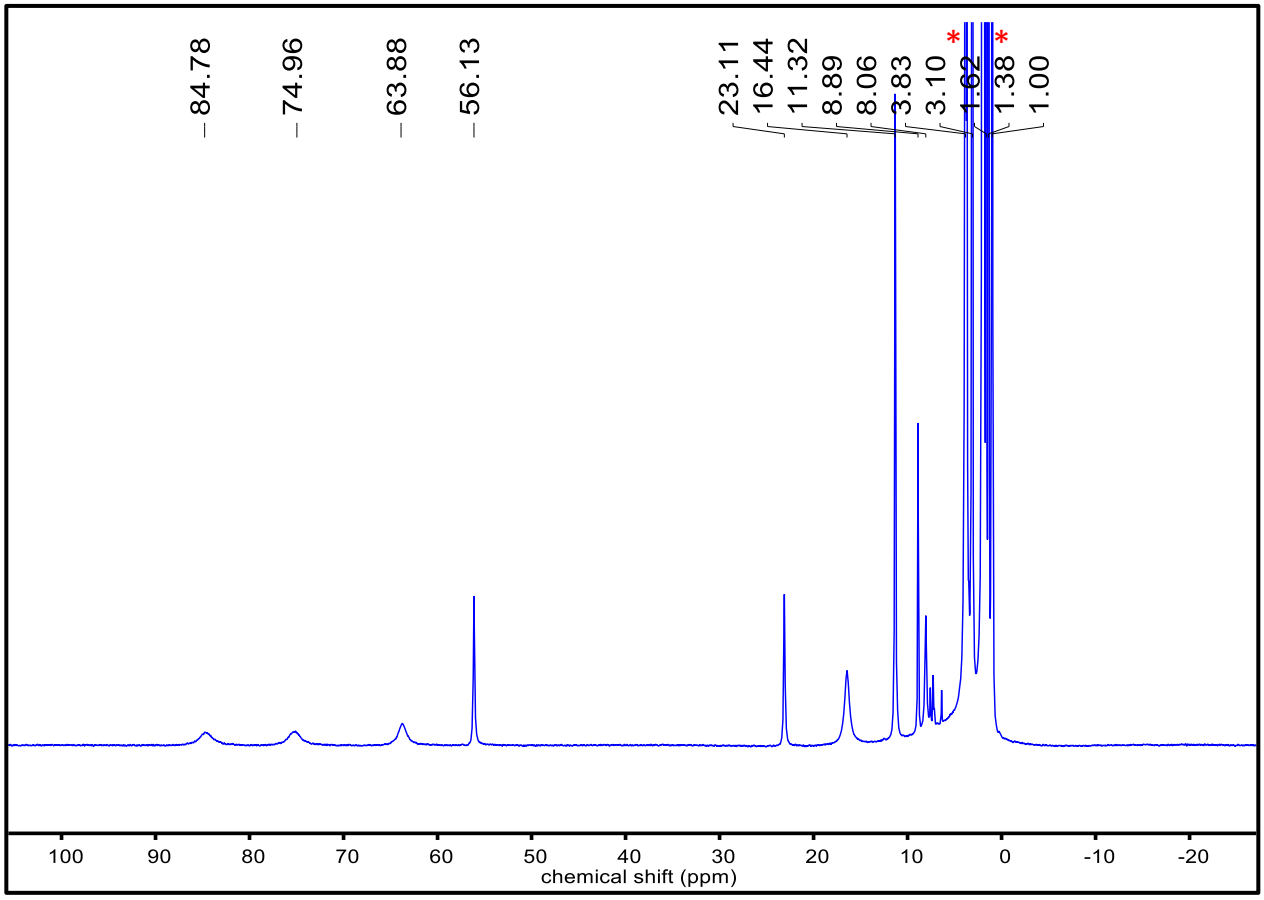

Figure S9. ^{1}H NMR spectrum of $Fe^{II}(BNPA^{Ph2}O)(OH)$ (**5**) in CD_3CN at 23 ^{o}C. Residual solvent peak for CD_3CN and peaks for Bu_4N^+ are marked with a red asterisk (*).

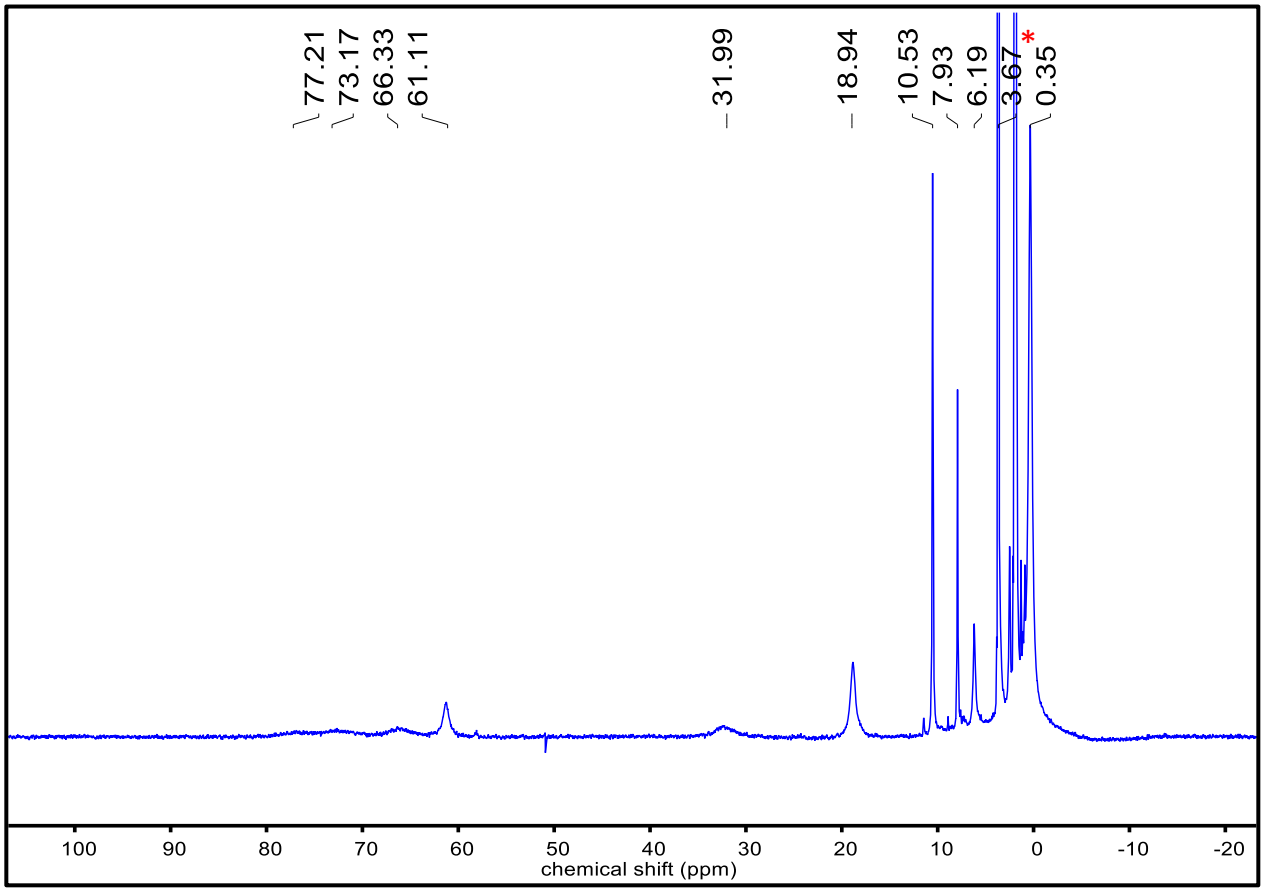

Figure S10. ^{1}H NMR spectrum of $Fe^{II}(BNPA^{Ph2}O)(OH)$•LiOTf (**5•LiOTf**) in CD_3CN at 23 °C. Residual solvent peak for CD_3CN is marked with a red asterisk (*).

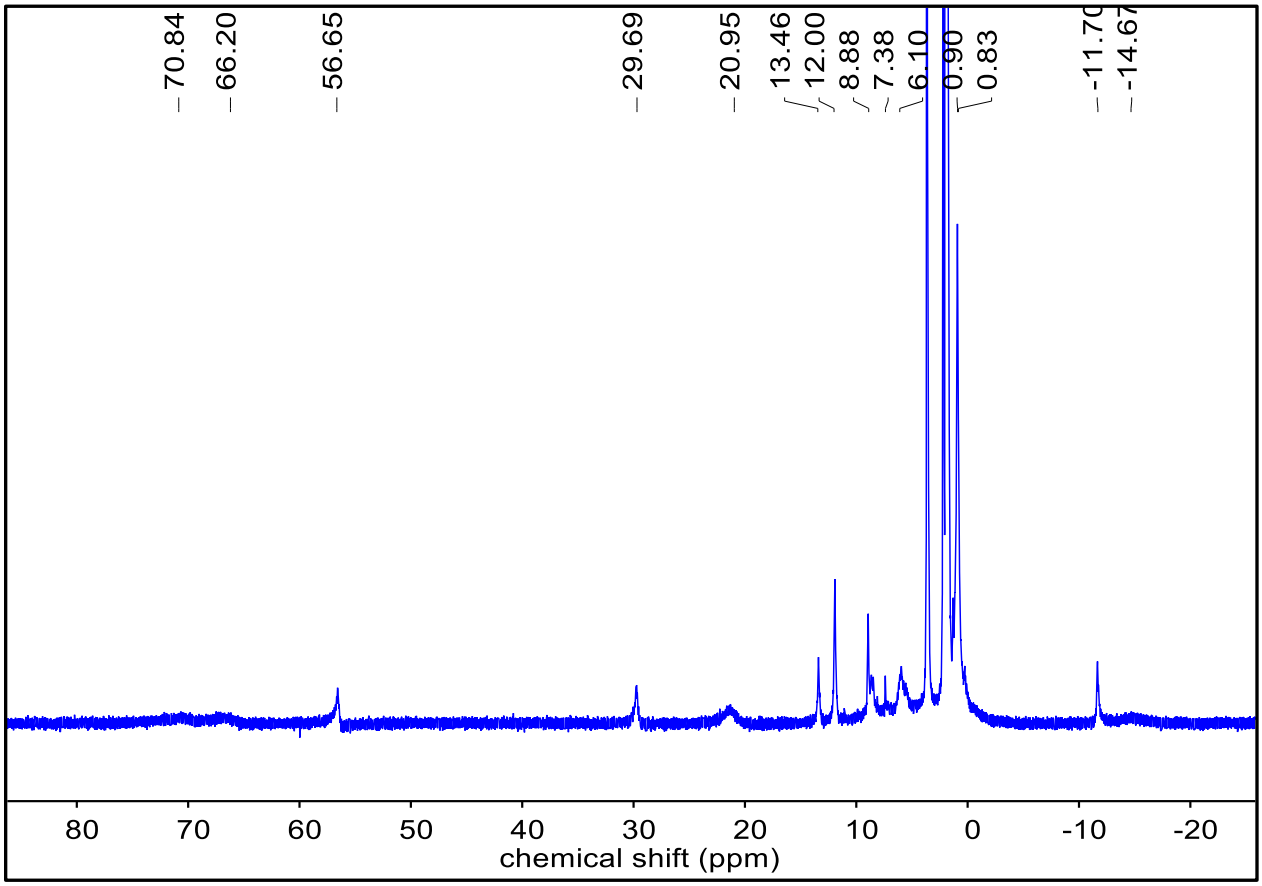

Figure S11. ^{1}H NMR spectrum of $Fe^{II}(BNPA^{Ph2}O)(SPh^{p\text{-}CF_3})$ (**6**) in CD_3CN at 23 °C. Residual solvent peak for CD_3CN peak is marked with a red asterisk (*).

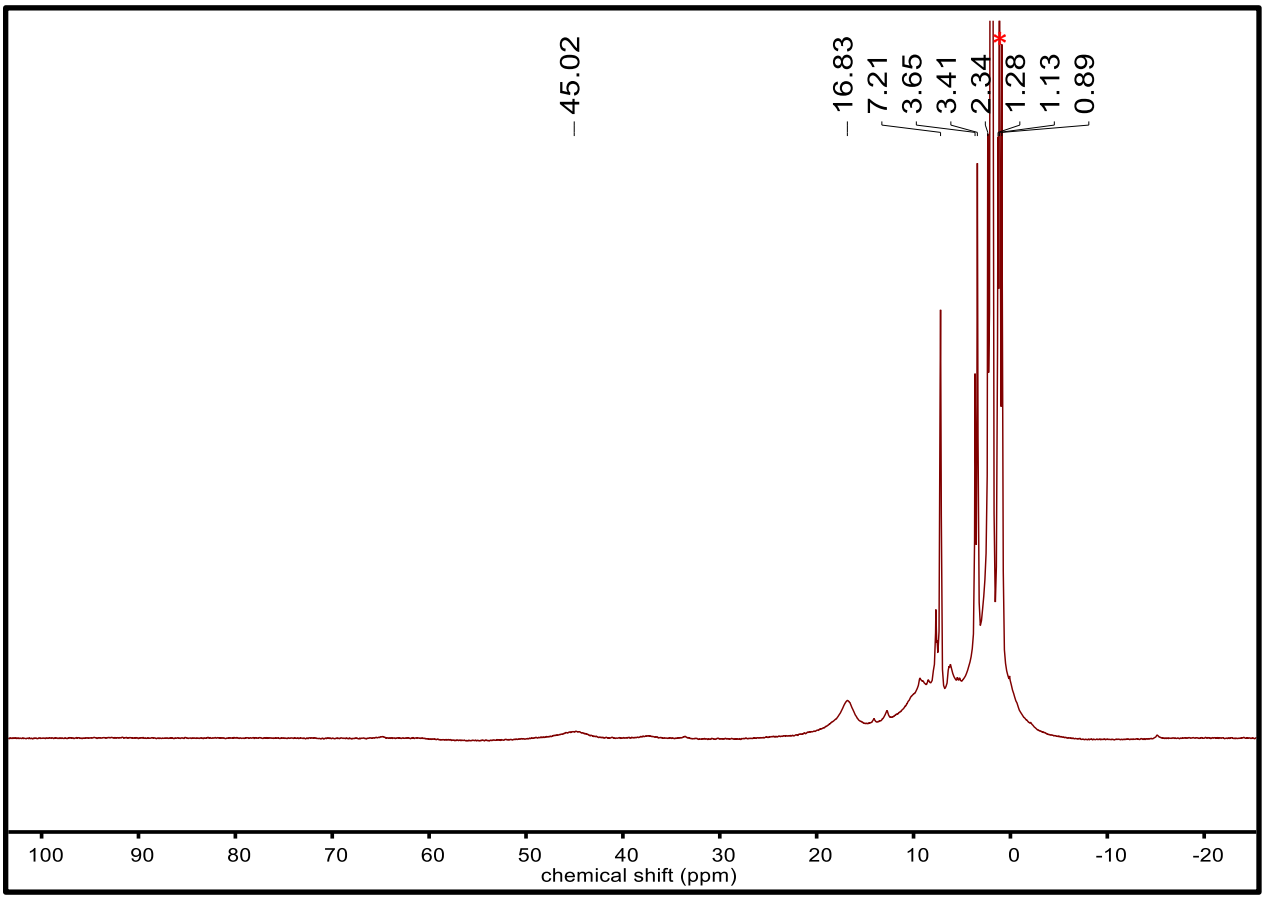

Figure S12. ^{1}H NMR spectrum of $Fe^{III}(BNPA^{Ph2}O)(OH)(SPh^{p\text{-}CF_3})$ (**7**) by adding 1 equiv $NaSPh^{p\text{-}CF_3}$ to $Fe^{III}(BNPA^{Ph2}O)(OH)(OTf)$ in CD_3CN at -35 °C. Residual solvent peak for CD_3CN is marked with a red asterisk (*).

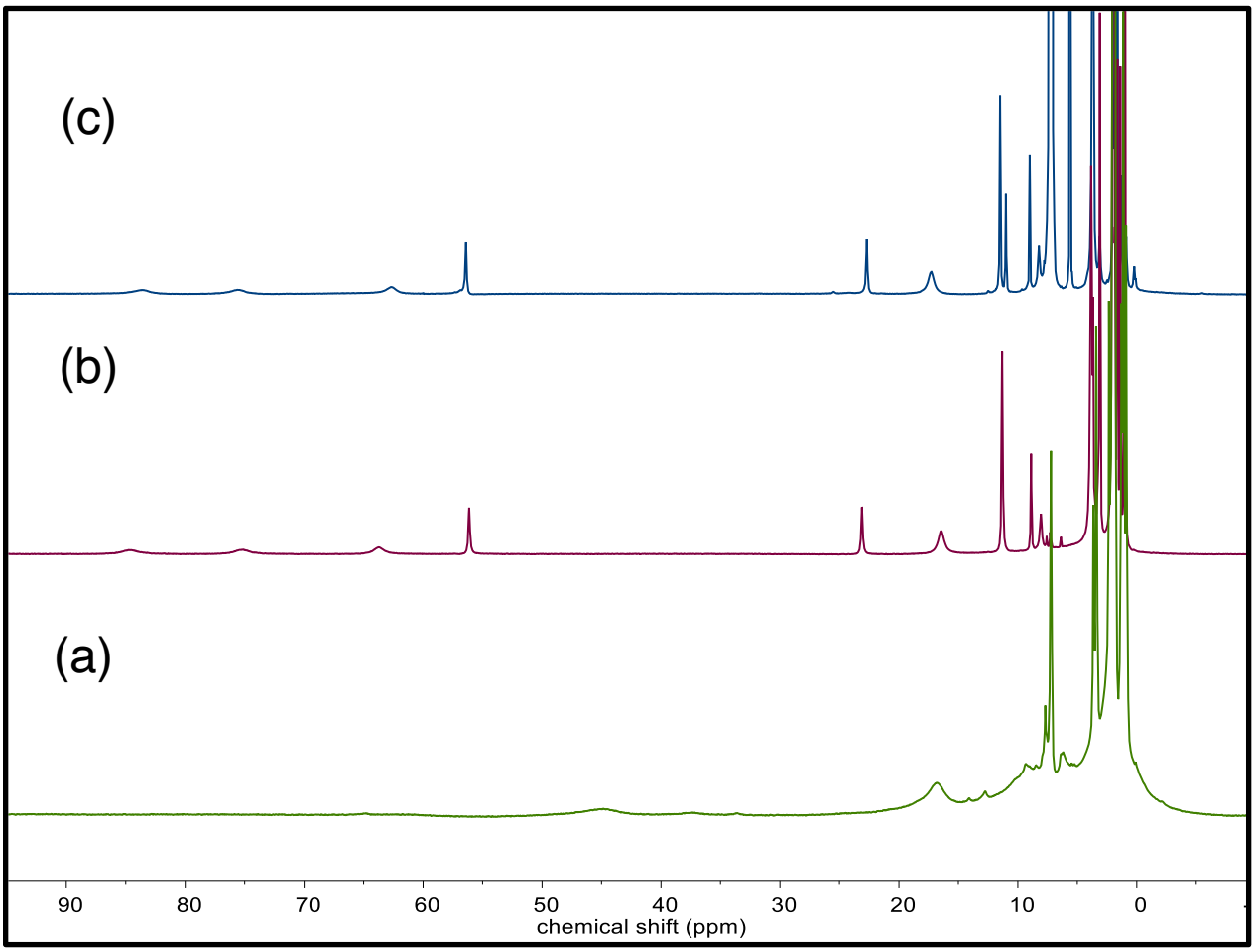

Figure S13. ^{1}H NMR spectra (CD_3CN, 23 ºC) of (a) **7**, (b) **5** and (c) reaction of **7** with (*p*-OMe-$C_6H_4)_3C$• at -35 ºC.

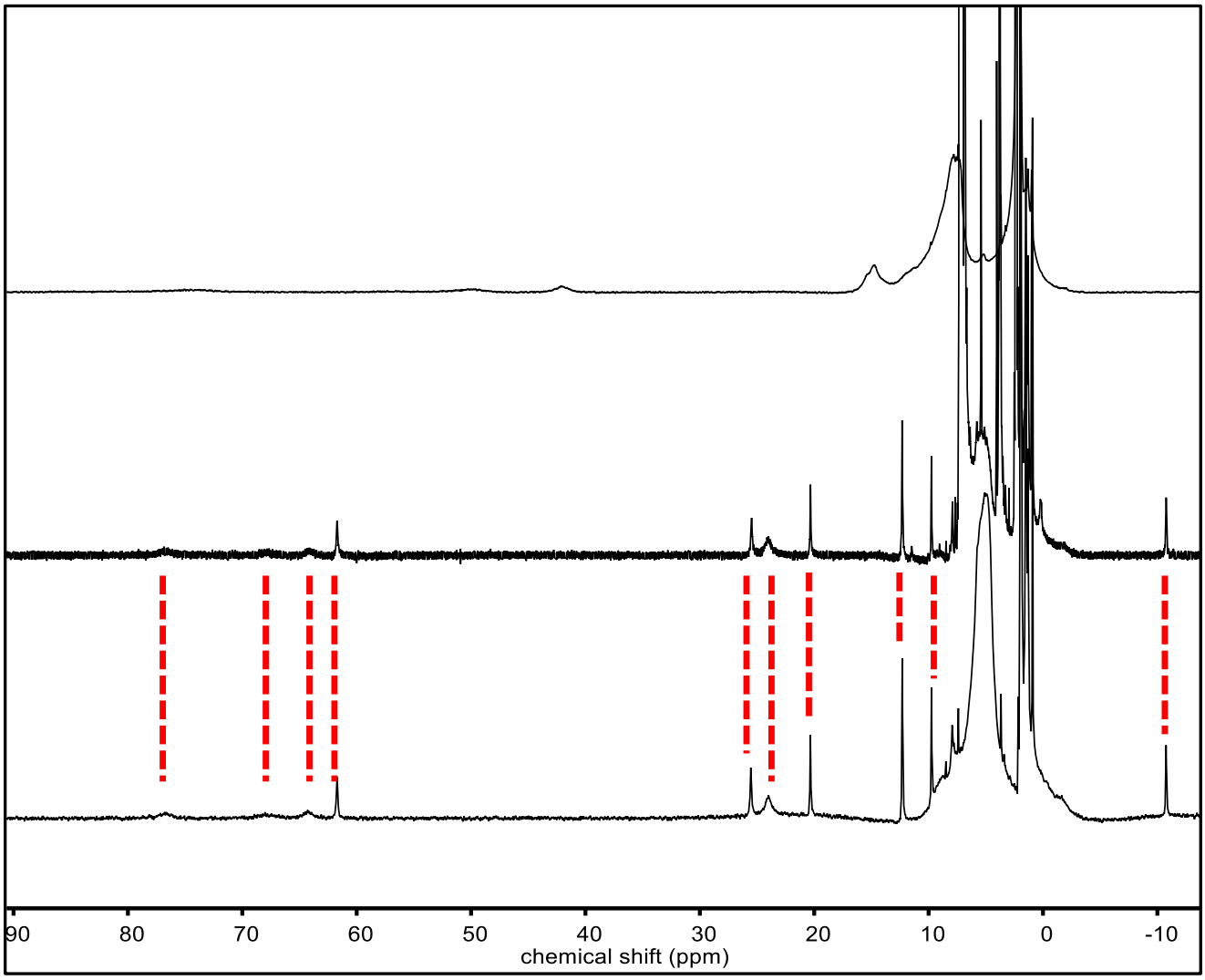

Figure S14. ^{1}H NMR spectra (CD_3CN, 23 ºC) of **4** (top), **2** (middle) and reaction of **4** with (p-OMe-$C_6H_4)_3C$• at 23 ºC (bottom).

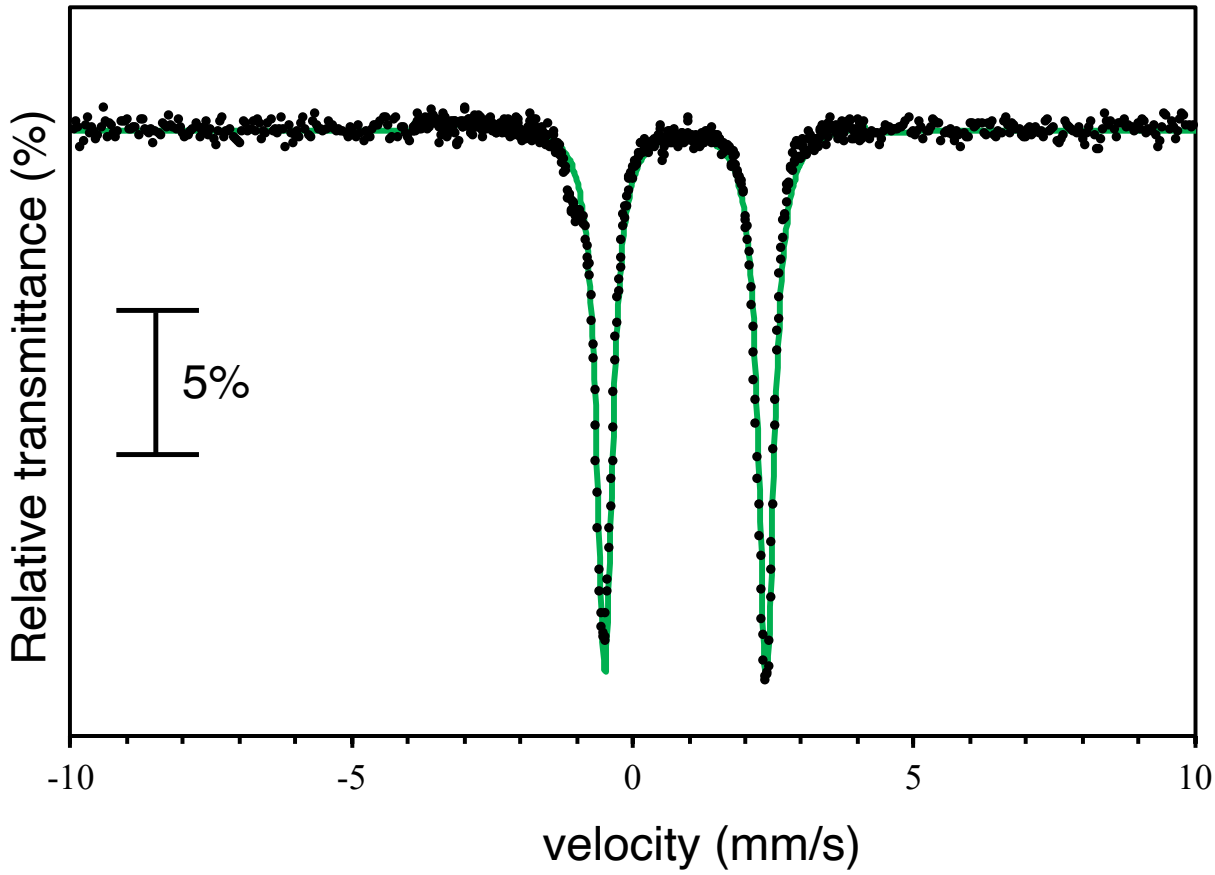

Figure S15. Zero-field ^{57}Fe Mössbauer spectrum for $^{57}Fe^{II}(BNPA^{Ph2}O)(SPh^{p\text{-}NO_2})$ (**1**) in frozen 2-MeTHF at 80 K. Experimental data = black circles, best fit = green line, with parameters $\delta = 0.94$ mm s^{-1} and $|\Delta E_Q| = 2.87$ mm s^{-1}, $\Gamma_R = \Gamma_L = 0.34$.

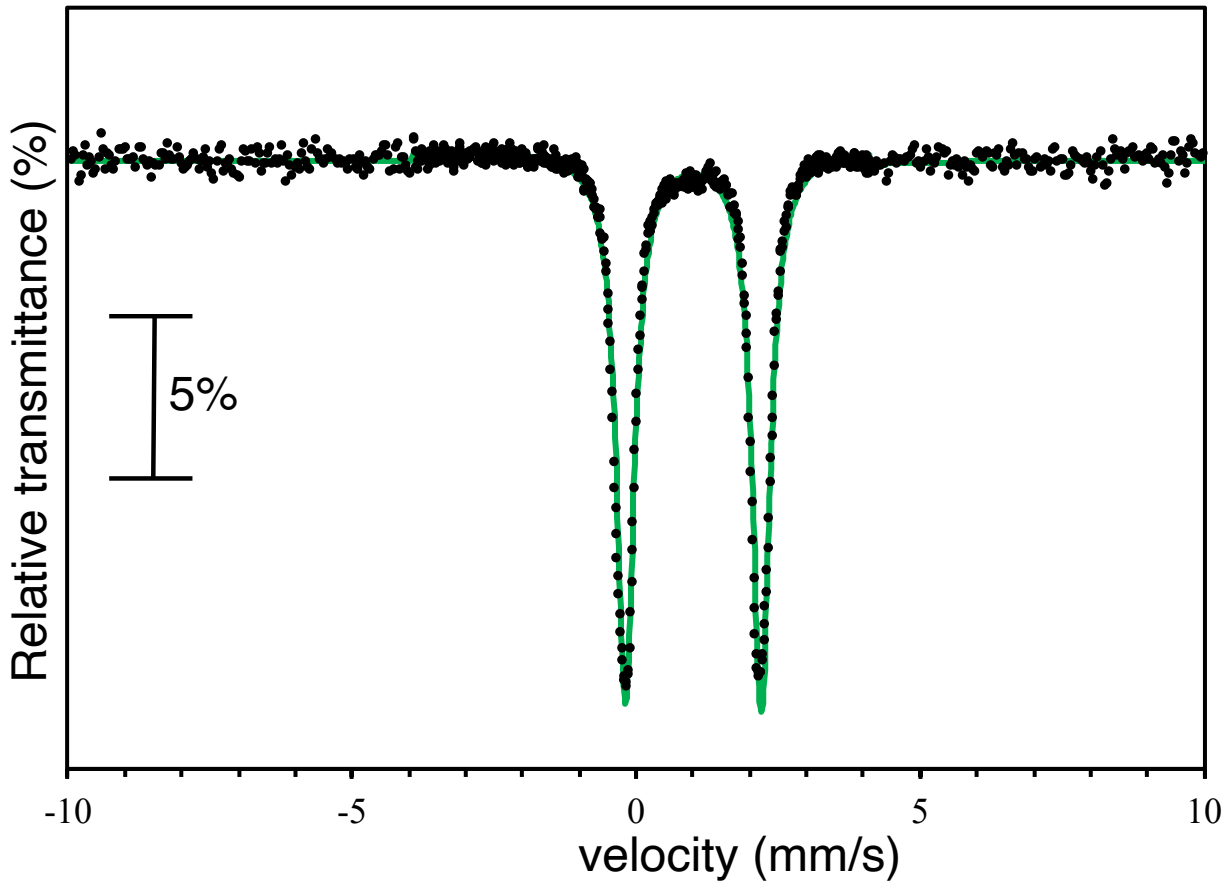

Figure S16. Zero-field ^{57}Fe Mössbauer spectrum of $^{57}Fe^{II}(BNPA^{Ph2}O)(OPh^{p\text{-}NO_2})$ (**2**) in 2-MeTHF at 80 K. Experimental data = black circles, best fit = green line, with parameters $\delta = 1.03$ mm s^{-1} and $|\Delta E_Q| = 2.76$ mm s^{-1}, $\Gamma_R = \Gamma_L = 0.28$.

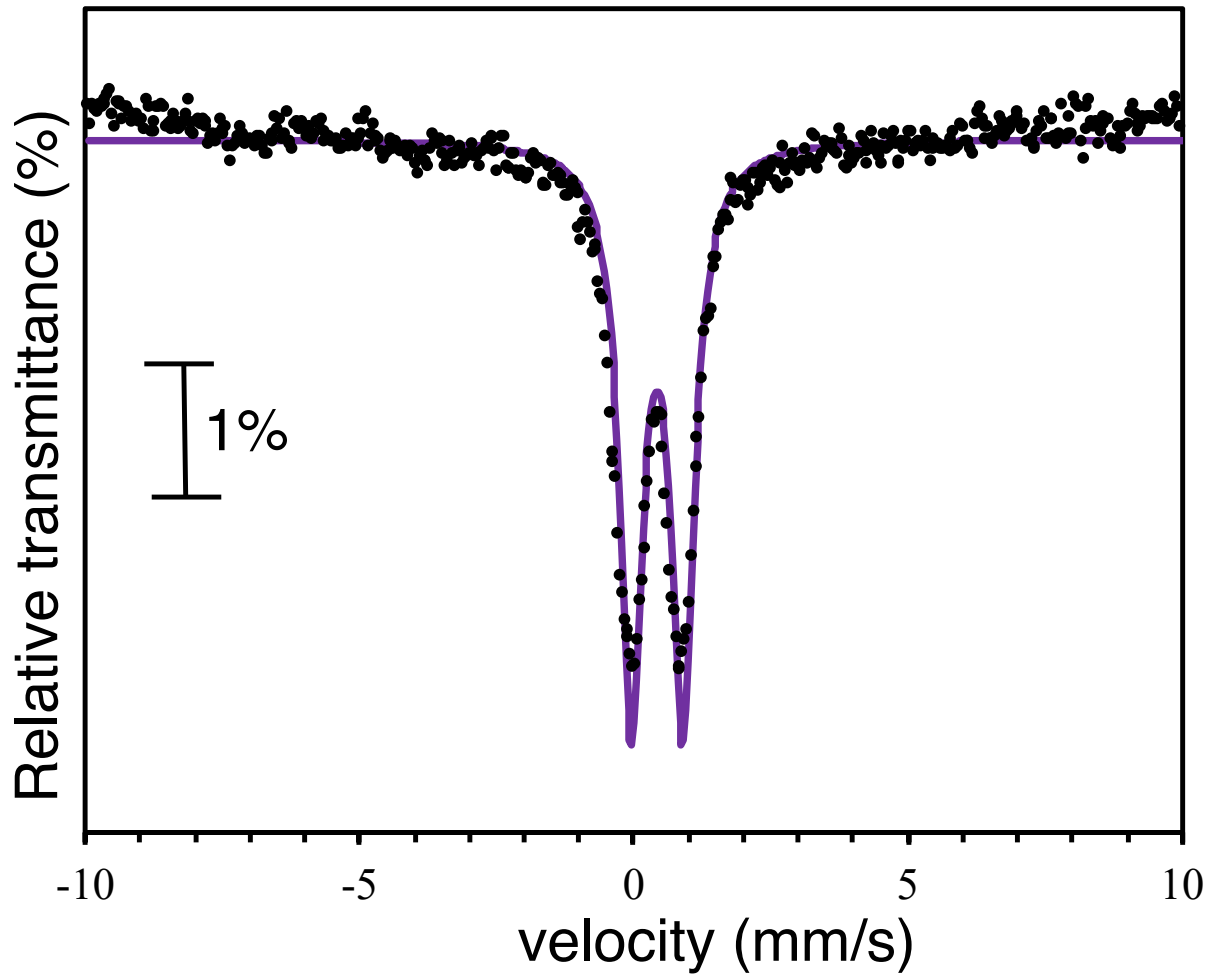

Figure S17. Zero-field ^{57}Fe Mössbauer spectrum of $^{57}Fe^{III}(BNPA^{Ph2}O)(OH)(SPh^{p\text{-}NO_2})$ (**3**) as a solid film at 80 K. Experimental data = black circles, best fits = purple line, with parameters $\delta = 0.42$ mm s^{-1} and $|\Delta E_Q| = 0.96$ mm s^{-1}, $\Gamma_R = \Gamma_L = 0.67$.

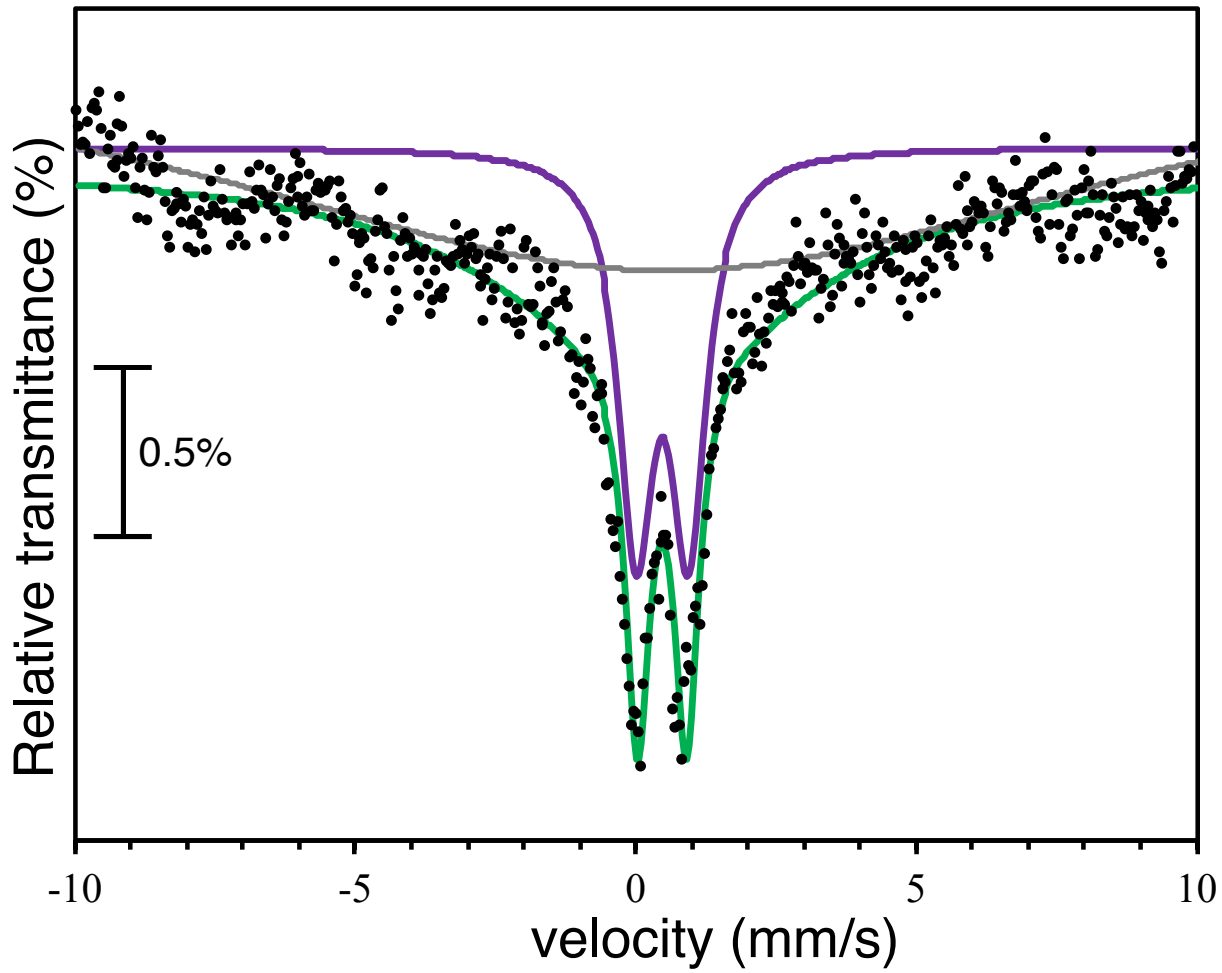

Figure S18. Zero-field ^{57}Fe Mössbauer spectrum of $^{57}Fe^{III}(BNPA^{Ph2}O)(OH)(OPh^{p\text{-}NO_2})$ (**4**) as a solid film at 80 K. Experimental data = black circles, best fit = green line, with parameters: subcomponent 1 (purple line) $\delta = 0.47$ mm s^{-1}, $|\Delta E_Q| = 0.94$ mm s^{-1}, $\Gamma_R = \Gamma_L = 0.71$; subcomponent 2 (grey line) $\delta = 0.17$ mm s^{-1}, $|\Delta E_Q| = 0.59$ mm s^{-1}, $\Gamma_R = \Gamma_L = 15.5$. Subcomponent 2 was added to account for the intermediate relaxation of the doublet at 80 K.

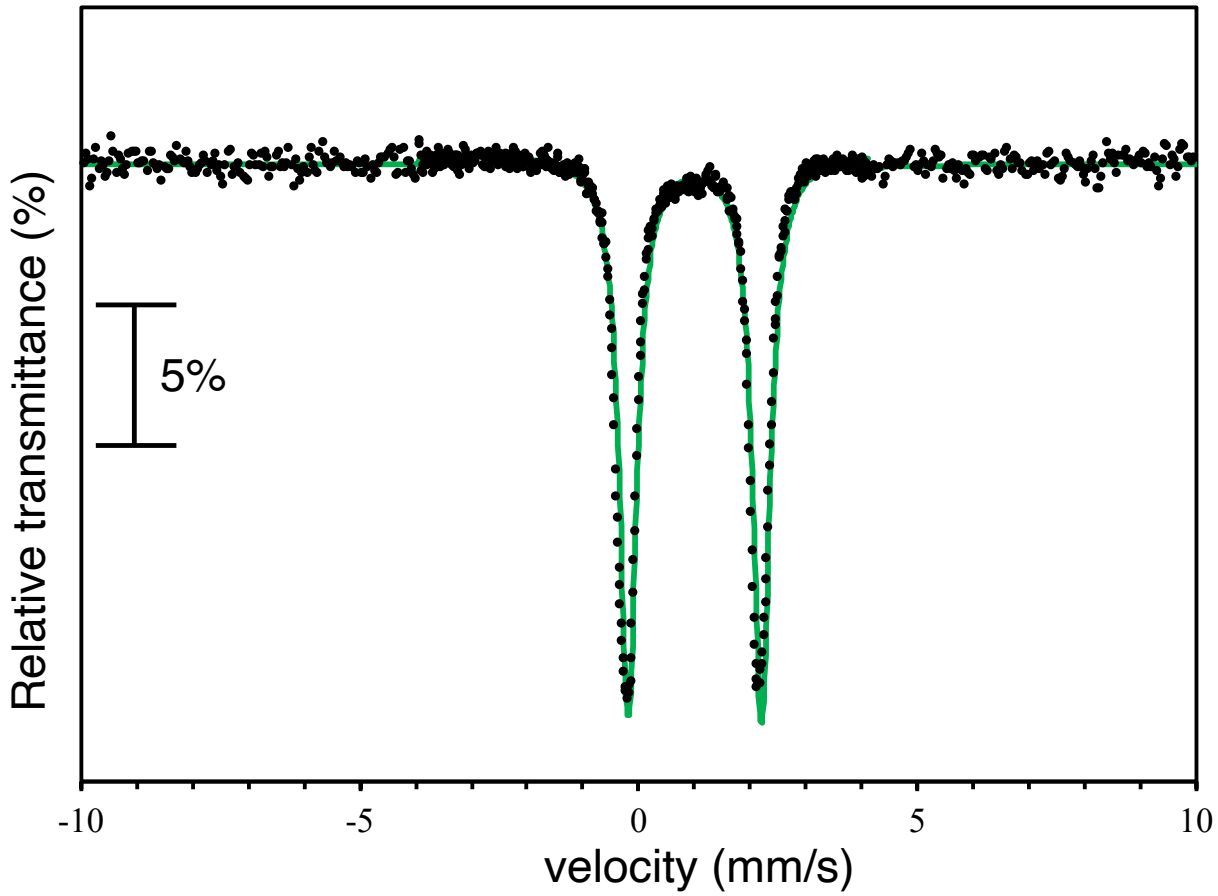

Figure S19. Zero-field ^{57}Fe Mössbauer spectrum of $^{57}Fe^{II}(BNPA^{Ph2}O)(OH)$ (**5**) in 2-MeTHF at 80 K. Experimental data = black circles, best fit = green line, with parameters $\delta = 1.01$ mm s^{-1}, $|\Delta E_Q| = 2.38$ mm s^{-1}, $\Gamma_R = \Gamma_L = 0.34$.

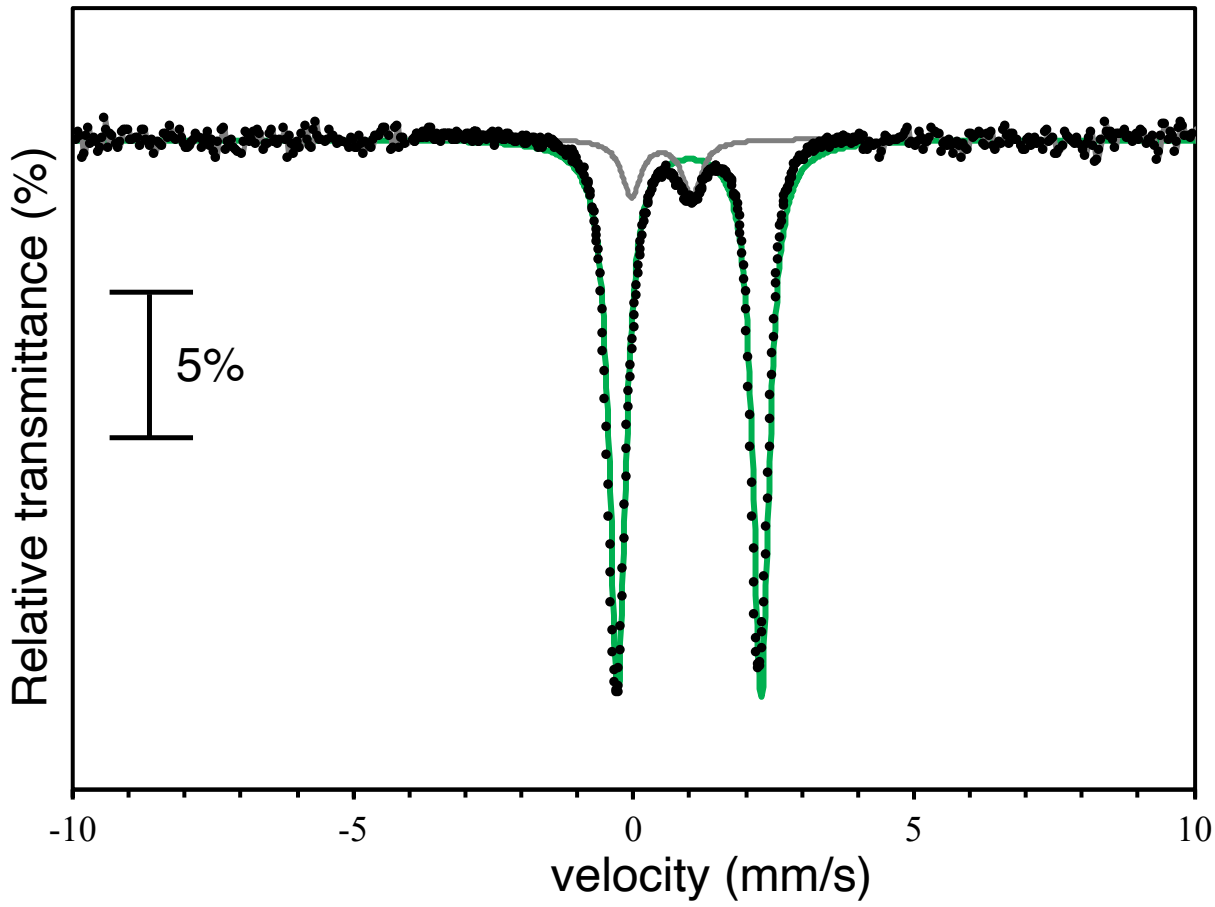

Figure S20. Zero-field ^{57}Fe Mössbauer spectrum of $^{57}Fe^{II}$(BNPA^{Ph2}O)(OH)•LiOTf (**5•LiOTf**) in 2-MeTHF at 80 K. Experimental data = black circles, best fits with parameters: subsite 1 (green line) δ = 1.00 mm s^{-1}, $|\Delta E_Q|$ = 2.56 mm s^{-1}, $\Gamma_R = \Gamma_L$ = 0.32, % area = 96; subsite 2 (grey line) δ = 0.47 mm s^{-1}, $|\Delta E_Q|$ = 0.83 mm s^{-1}, $\Gamma_R = \Gamma_L$ = 0.59, % area = 04.

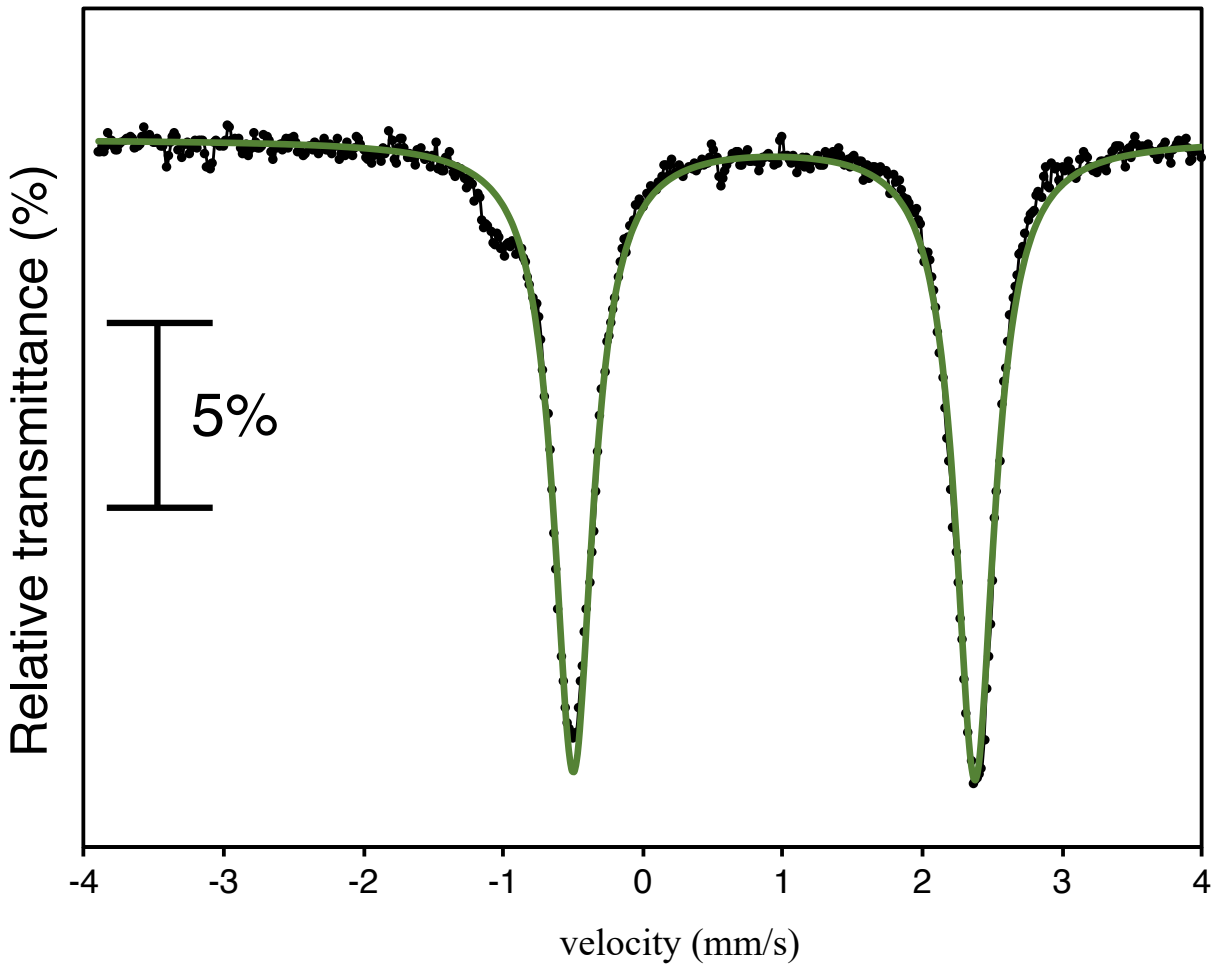

Figure S21. Zero-field ^{57}Fe Mössbauer spectrum of $^{57}Fe^{II}(BNPA^{Ph2}O)(SPh^{p\text{-}CF_3})$ (**6**) in 2-MeTHF at 80 K. Experimental data = black circles, best fit = green line, with parameters $\delta = 0.94$ mm s^{-1} and $|\Delta E_Q| = 2.87$ mm s^{-1}, $\Gamma_R = \Gamma_L = 0.34$.

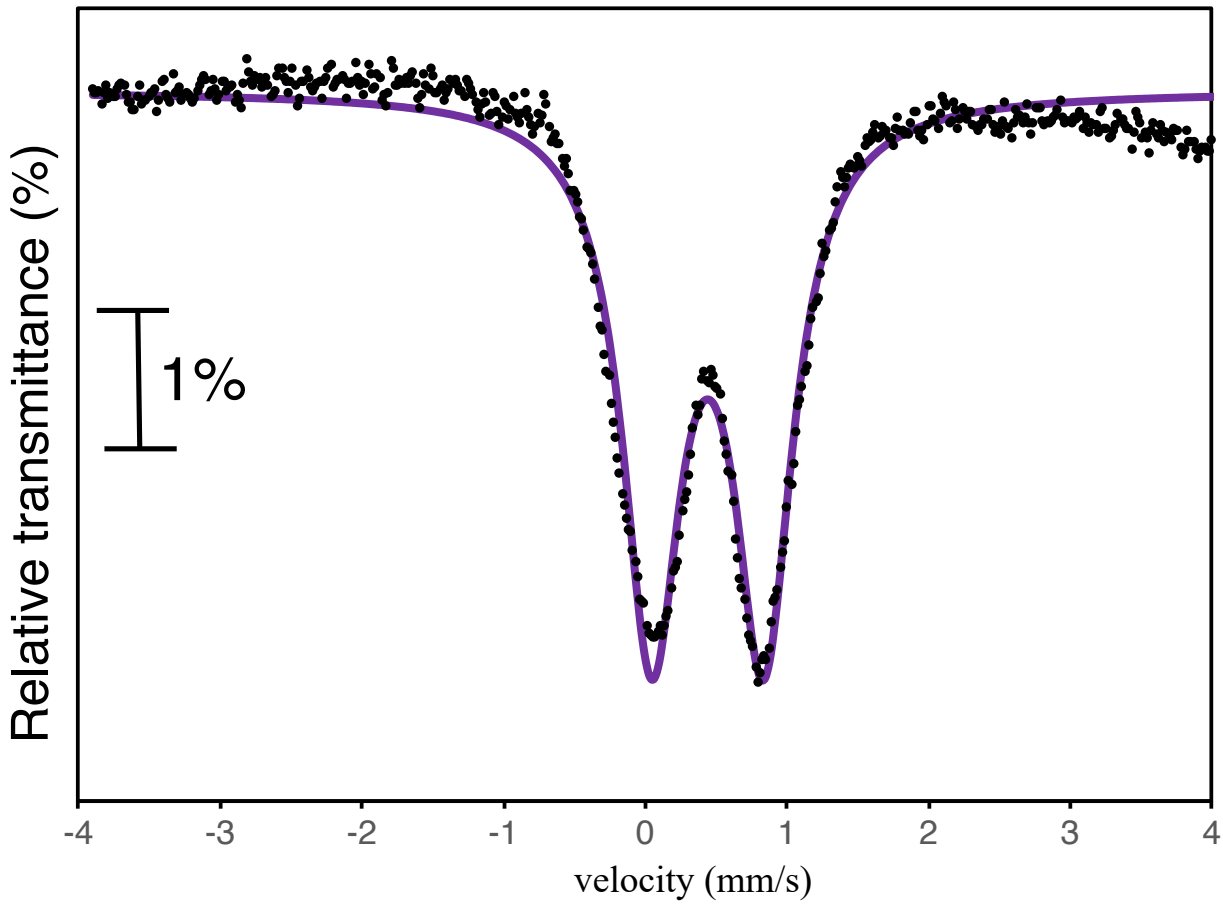

Figure S22. Zero field ^{57}Fe Mössbauer spectrum of $^{57}Fe^{III}(BNPA^{Ph2}O)(OH)(SPh^{p\text{-}CF_3})$ (**7**) as a solid film at 80 K. Experimental data = black circles, best fit = solid purple line, with parameters δ = 0.47 mm s^{-1} and $|\Delta E_Q|$ = 0.84 mm s^{-1}, $\Gamma_R = \Gamma_L$ = 0.59.

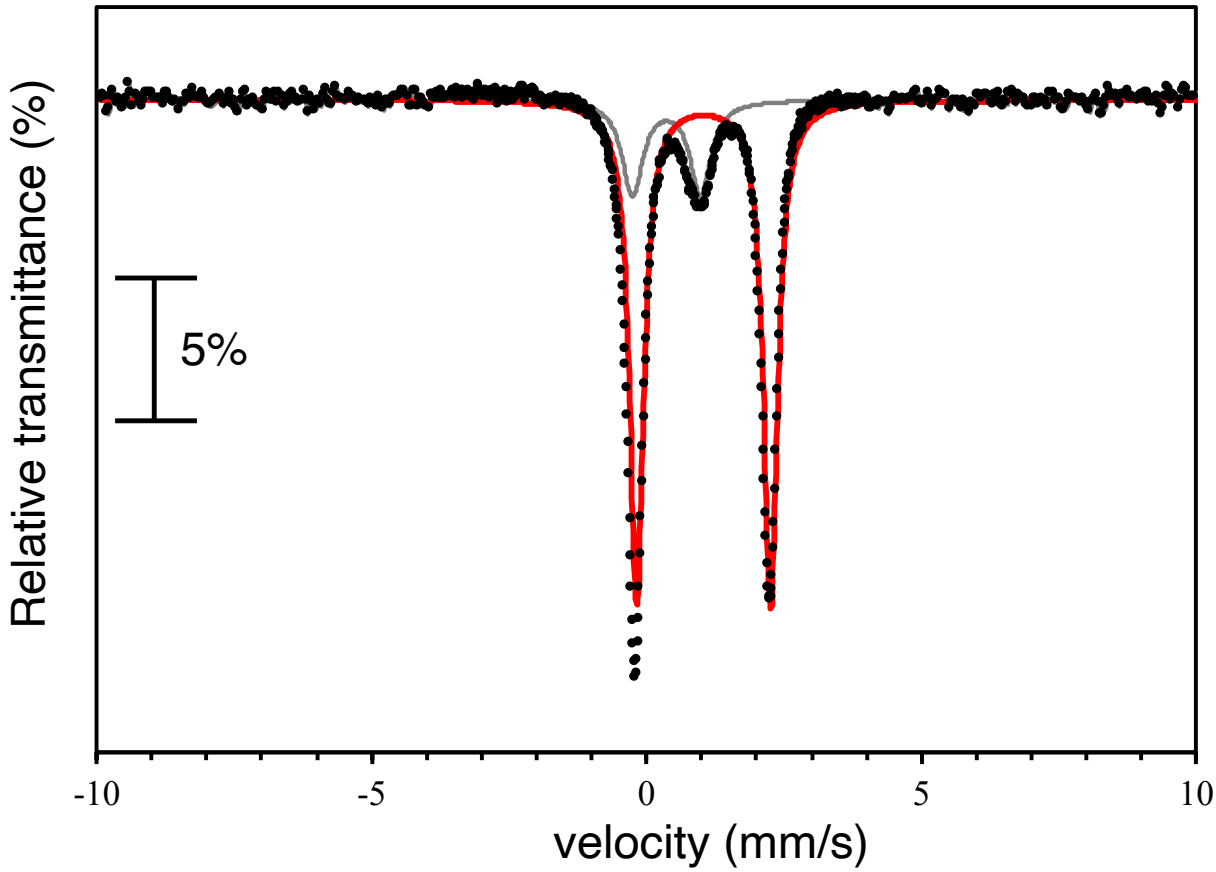

Figure S23. Zero-field ^{57}Fe Mössbauer spectrum (2-MeTHF, 80 K) of the reaction mixture for $^{57}Fe^{III}(BNPA^{Ph2}O)(OH)(SPh^{p\text{-}NO_2})$ (**3**) and $(p\text{-OMe-}C_6H_4)_3C\bullet$ (1 equiv) over 1 h at -35 °C in THF/toluene. Experimental data = black circles, best fits with parameters: subsite 1 (red line) δ = 1.00 mm s^{-1}, $|\Delta E_Q|$ = 2.37 mm s^{-1}, $\Gamma_R = \Gamma_L$ = 0.34, % area = 88; subsite 2 (grey line) δ = 0.45 mm s^{-1}, $|\Delta E_Q|$ = 0.91 mm s^{-1}, $\Gamma_R = \Gamma_L$ = 0.52, % area = 12.

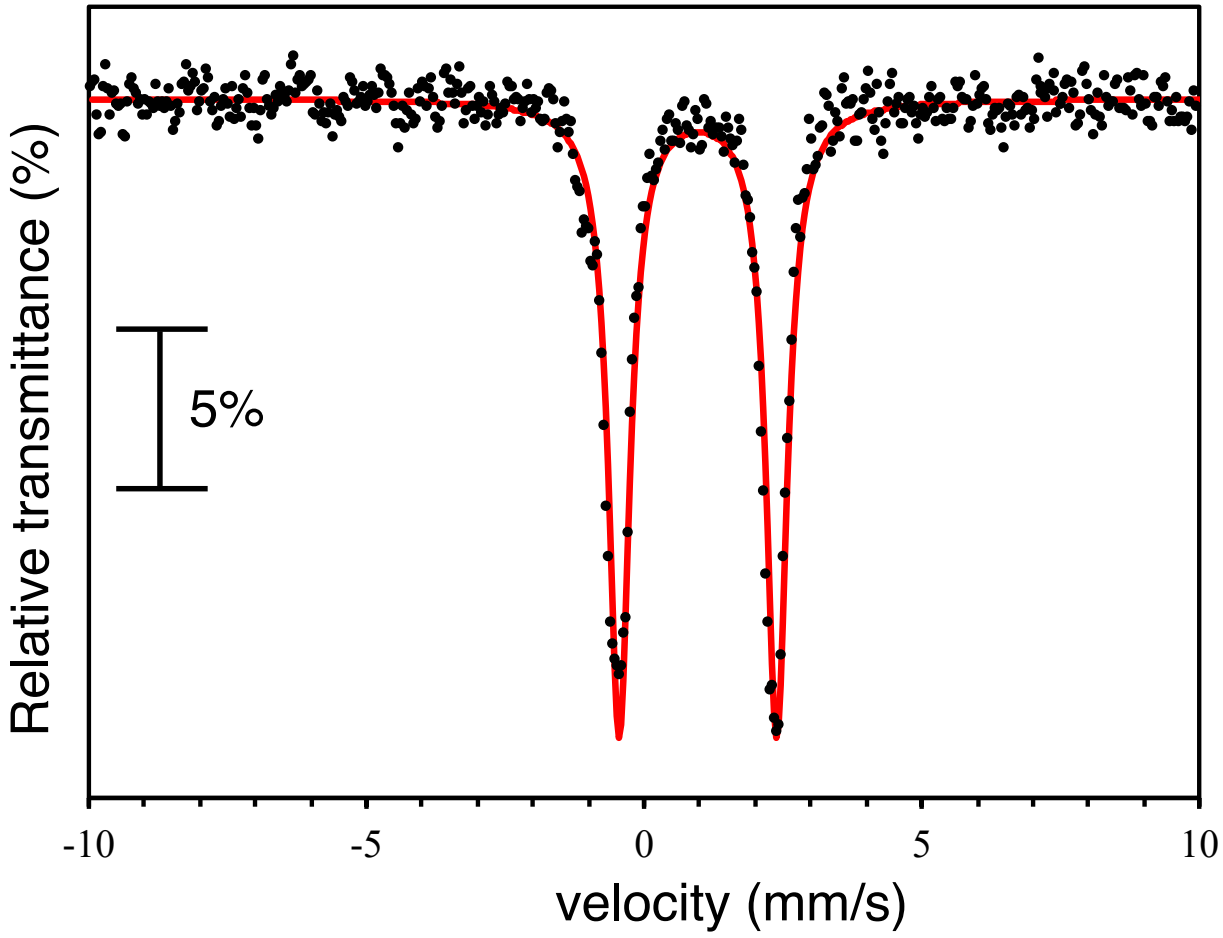

Figure S24. Zero-field ^{57}Fe Mössbauer spectrum (2-MeTHF, 80 K) of the reaction mixture for $^{57}Fe^{III}(BNPA^{Ph2}O)(OH)(SPh^{p\text{-}NO_2})$ (**3**) and (p-OMe-$C_6H_4)_3C\bullet$ (1 equiv) at 23 °C over 30 min in THF/toluene. Experimental data = black circles, best fit = red line, with parameters: $\delta = 0.96$ mm s^{-1}, $|\Delta E_Q| = 2.83$ mm s^{-1}, $\Gamma_R = \Gamma_L = 0.37$.

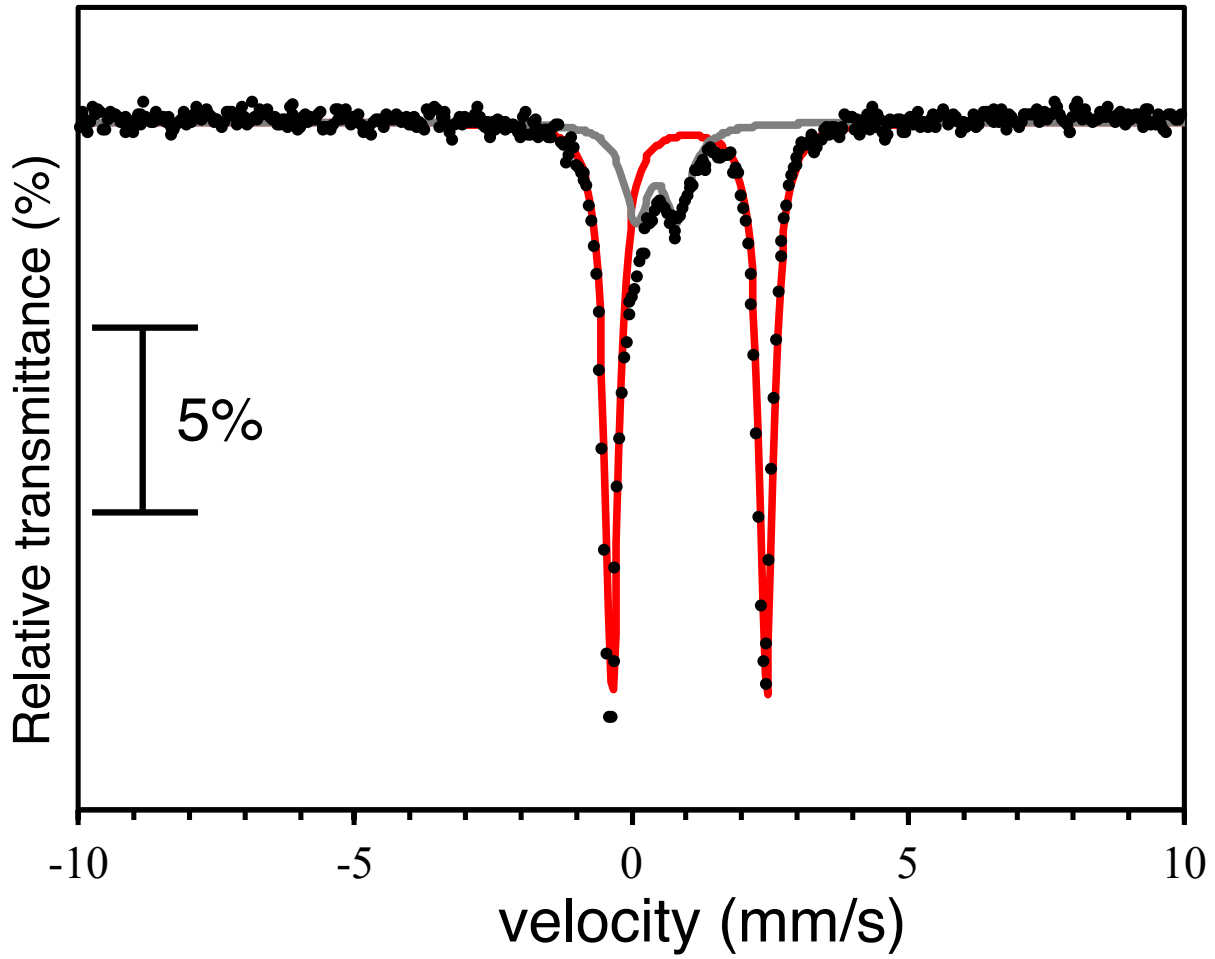

Figure S25. Zero-field ^{57}Fe Mössbauer spectrum (2-MeTHF, 80 K) of the reaction $^{57}Fe^{III}(BNPA^{Ph2}O)(OH)(OPh^{p\text{-}NO_2})$ (**4**) with $(p\text{-OMe-}C_6H_4)_3C\bullet$ (1 equiv) at 23 °C over 30 min in THF/toluene. Experimental data = black circles, best fits = solid lines, with parameters: subsite 1 (red line) δ = 1.04 mm s^{-1} and $|\Delta E_Q|$ = 2.79 mm s^{-1}, $\Gamma_R = \Gamma_L$ = 0.30, % area = 90; subsite 2 (grey line) δ = 0.39 mm s^{-1} and $|\Delta E_Q|$ = 0.82 mm s^{-1}, $\Gamma_R = \Gamma_L$ = 0.47, % area = 10.

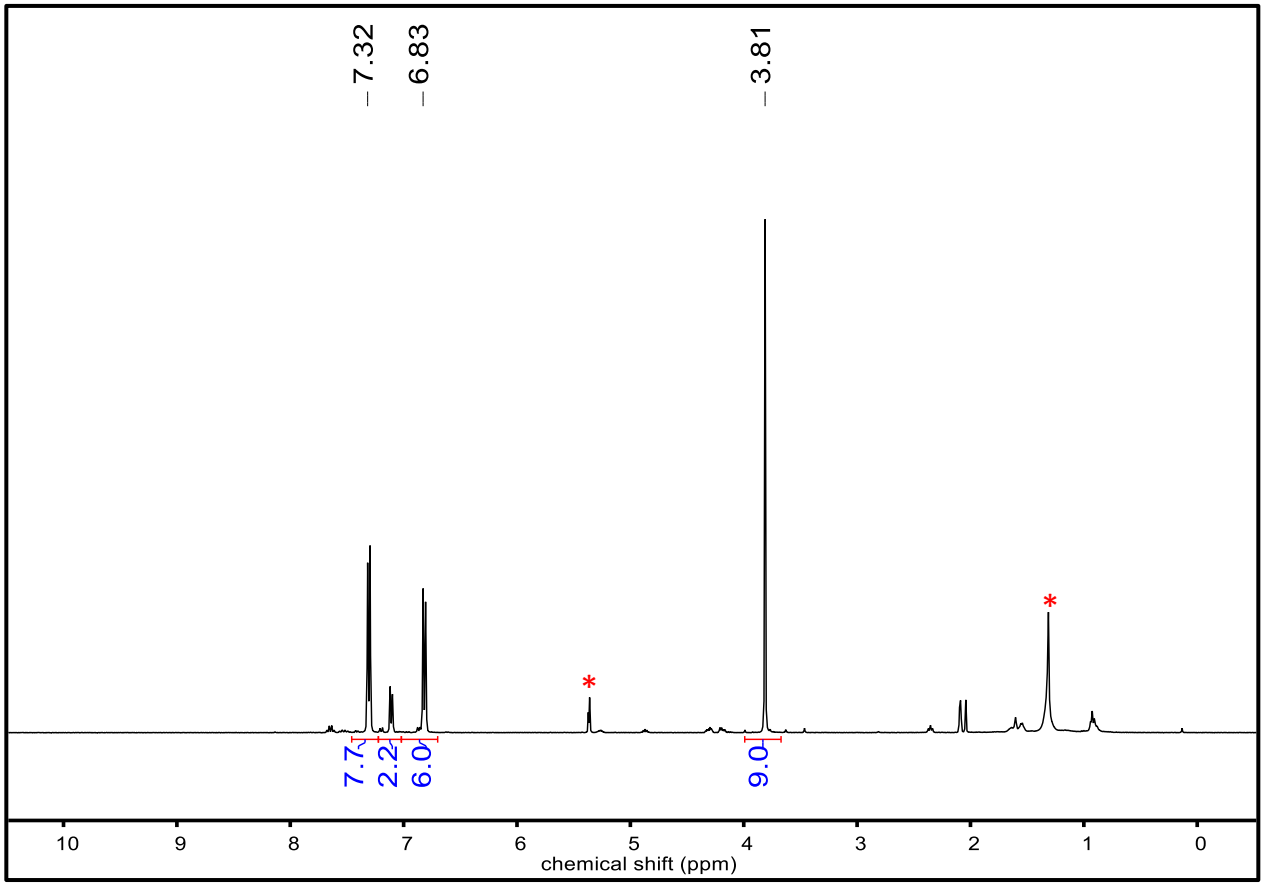

Figure S26. ^{1}H NMR spectrum (298 K) of authentic (p-OMe-C_6H_4)$_3$CSPh$^{p\text{-}CF_3}$ in CD_2Cl_2. Residual solvents are marked with an asterisk (*).

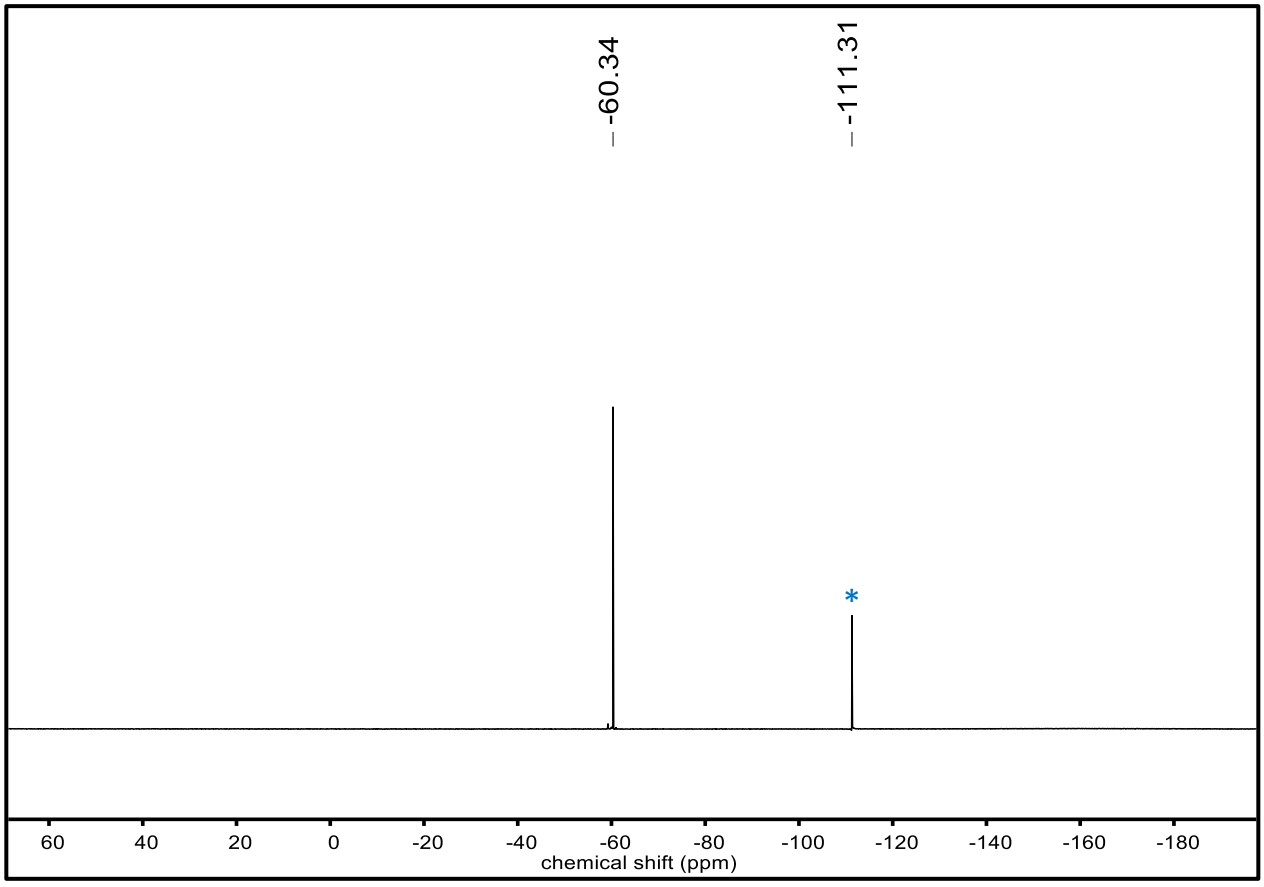

Figure S27. ^{19}F NMR spectrum (298 K) of authentic (p-OMe-C_6H_4)$_3$CSPh$^{p\text{-}CF_3}$ in CD_2Cl_2. Reference fluorobenzene standard is marked with an asterisk (*).

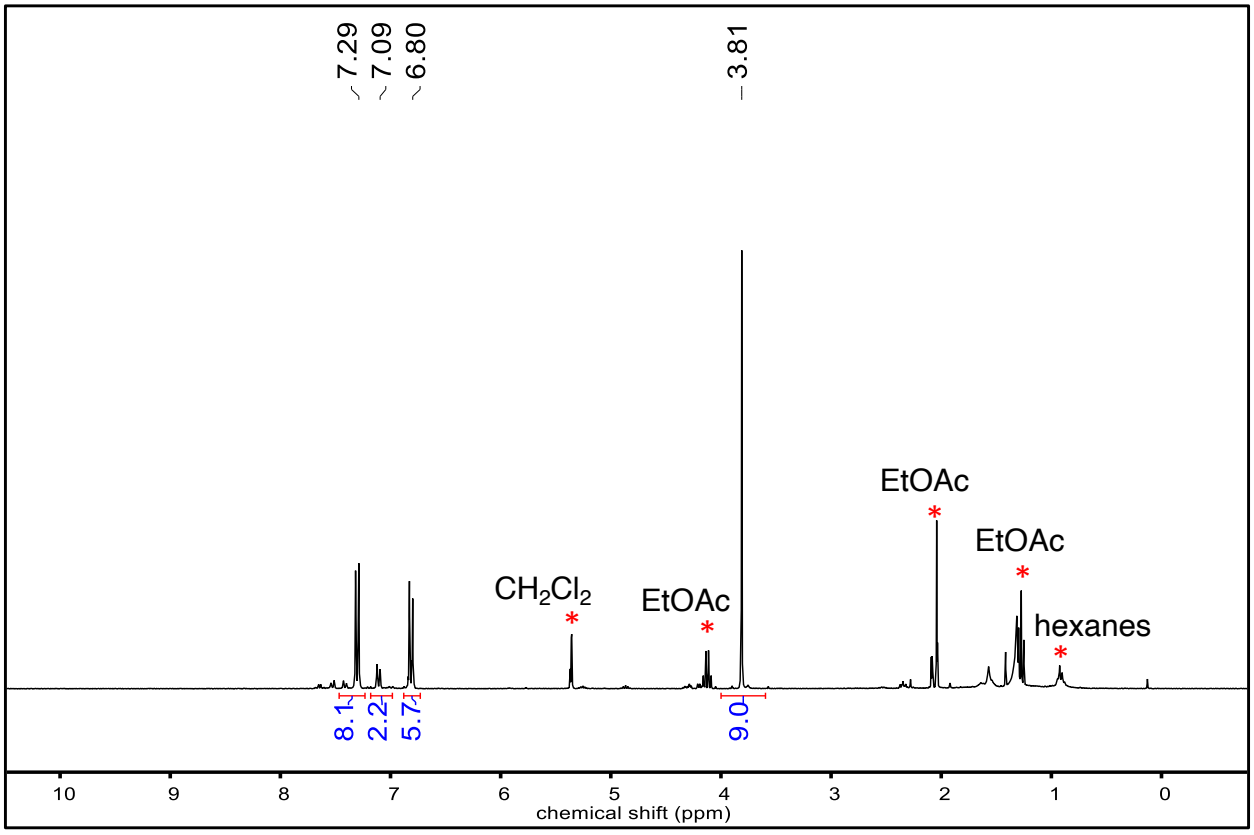

Figure S28. ^{1}H NMR (298 K) spectrum of isolated (p-OMe-C_6H_4)$_3$CSPh$^{p\text{-}CF_3}$ from the reaction of **7** and (p-OMe-C_6H_4)$_3$C• at -35 °C in CD_2Cl_2. Residual solvents are marked with an asterisk (*).

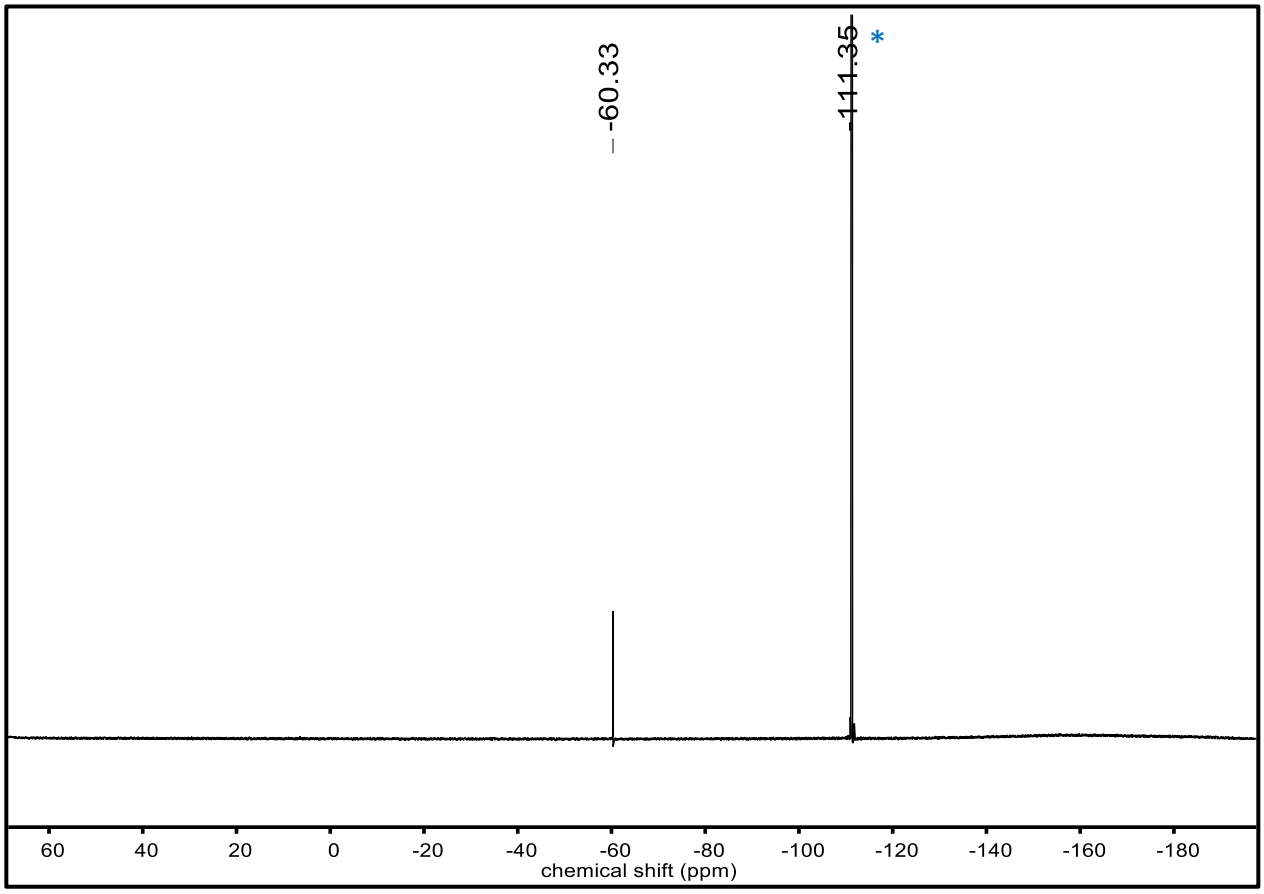

Figure S29. ^{19}F NMR (298 K) spectrum of isolated (p-OMe-C_6H_4)$_3$CSPh$^{p\text{-}CF_3}$ from the reaction of **7** and (p-OMe-C_6H_4)$_3$C• at -35 °C in CD_2Cl_2. Reference fluorobenzene standard is marked with an asterisk (*).

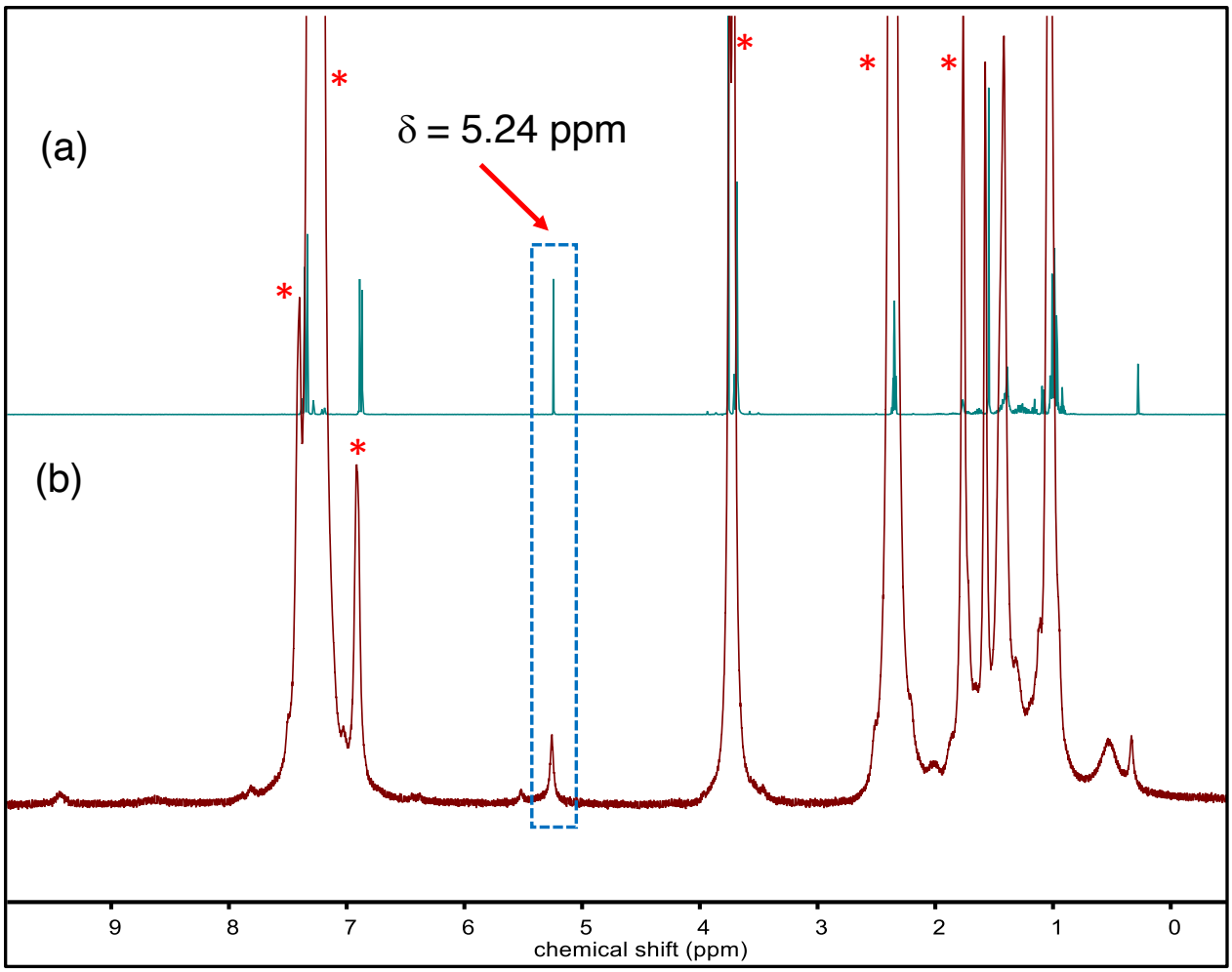

Figure S30. ^{1}H NMR spectra (298 K) of (a) authentic (p-OMe-C_6H_4)$_3$COH and (b) (p-OMe-C_6H_4)$_3$COH formed in the reaction of **3** and (p-OMe-C_6H_4)$_3$C• in THF-d_8 /toluene-d_8 (5/1 v/v) at 23 °C. The peak at δ 5.24 ppm corresponds to the -OH peak of (p-OMe-C_6H_4)$_3$COH. Residual solvents and triarylmethyl impurity peaks are marked with a red asterisk (*).

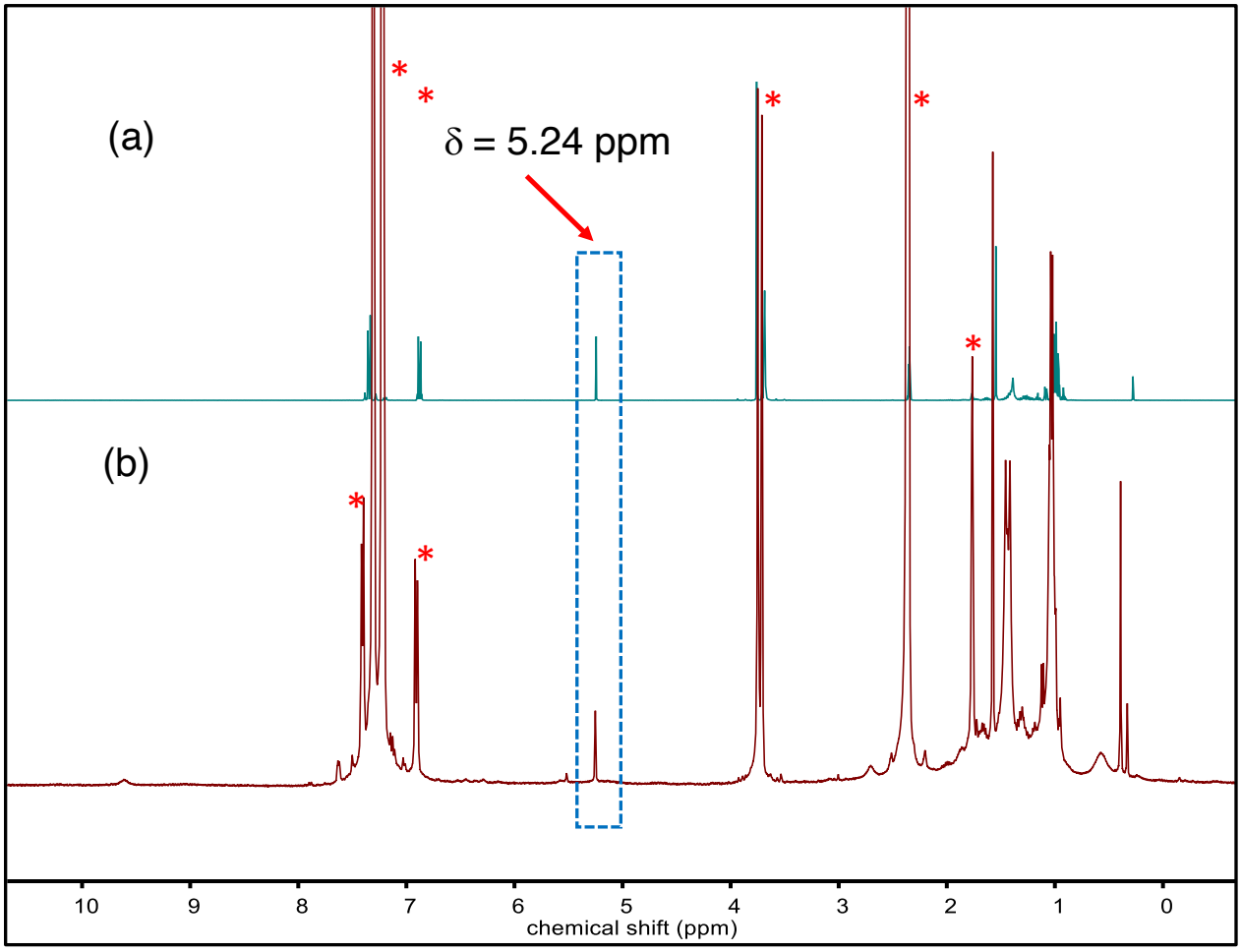

Figure S31. ^{1}H NMR spectra (298 K) of (a) authentic (p-OMe-C_6H_4)$_3$COH and (b) (p-OMe-C_6H_4)$_3$COH formed in the reaction of **4** and (p-OMe-C_6H_4)$_3$C• in THF-d_8 /toluene-d_8 (5/1 v/v) at 23 °C. The peak at δ 5.24 ppm corresponds to the -OH peak of (p-OMe-C_6H_4)$_3$COH. The peak at δ 5.24 ppm corresponds to the -OH peak of (p-OMe-C_6H_4)$_3$COH. Residual solvents and triarylmethyl impurity peaks are marked with a red asterisk (*)

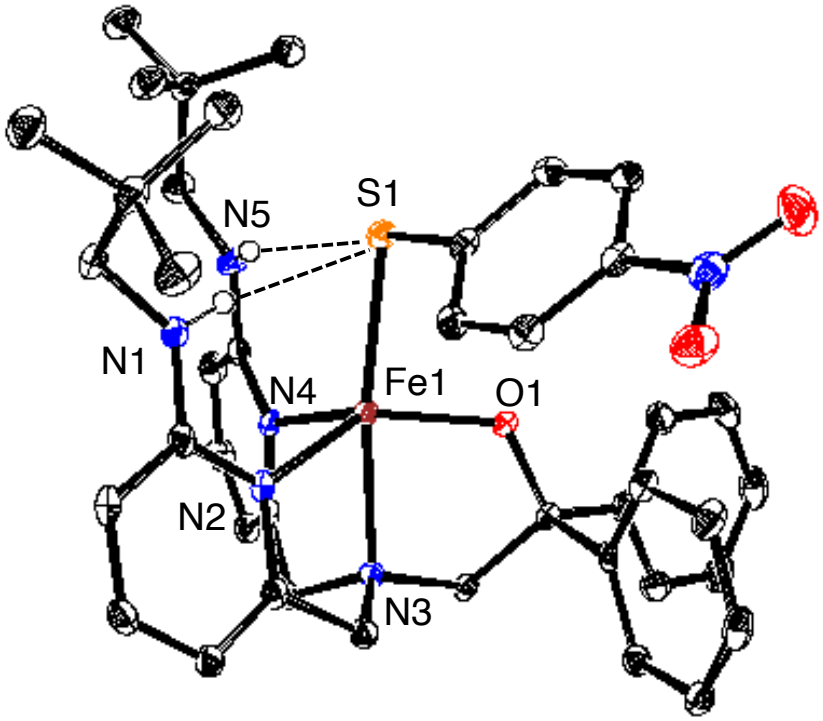

Figure S32. Displacement ellipsoid plot (50% probability) of $Fe^{II}(BNPA^{Ph2}O)(SPh^{p\text{-}NO_2})$ (**1**) at 110(2) K. H-atoms are removed for clarity, except those attached to N1 and N5. Only one of the two crystallographically independent molecules is depicted.

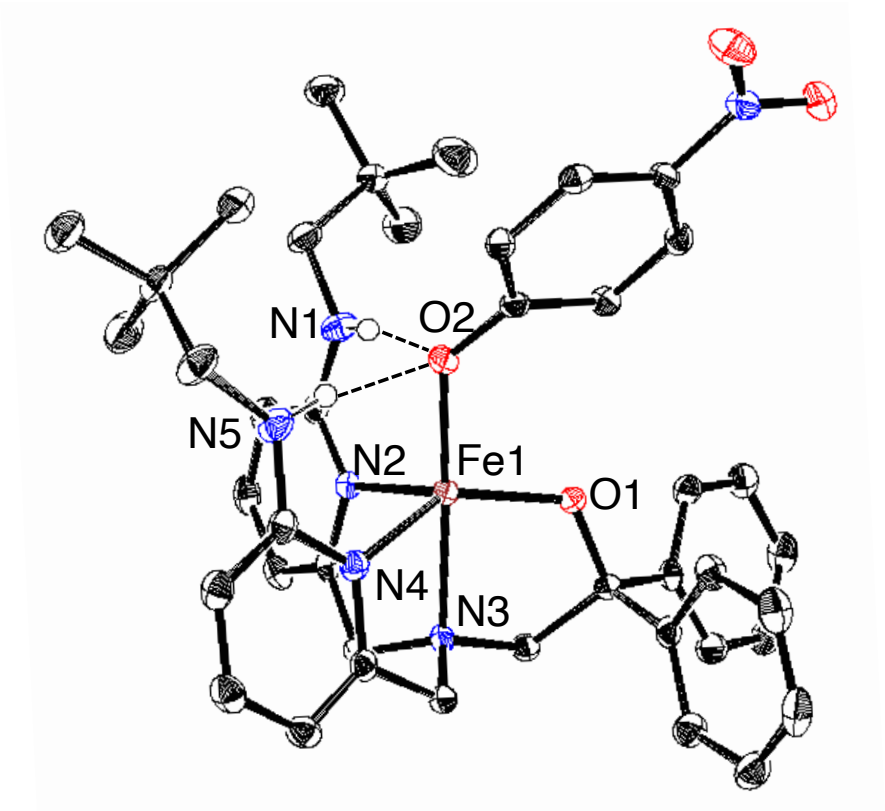

Figure S33. Displacement ellipsoid plot (50% probability) of $Fe^{II}(BNPA^{Ph2}O)(OPh^{p\text{-}NO_2})$ (**2**) at 110(2) K. H-atoms are removed for clarity, except those attached to N1 and N5.

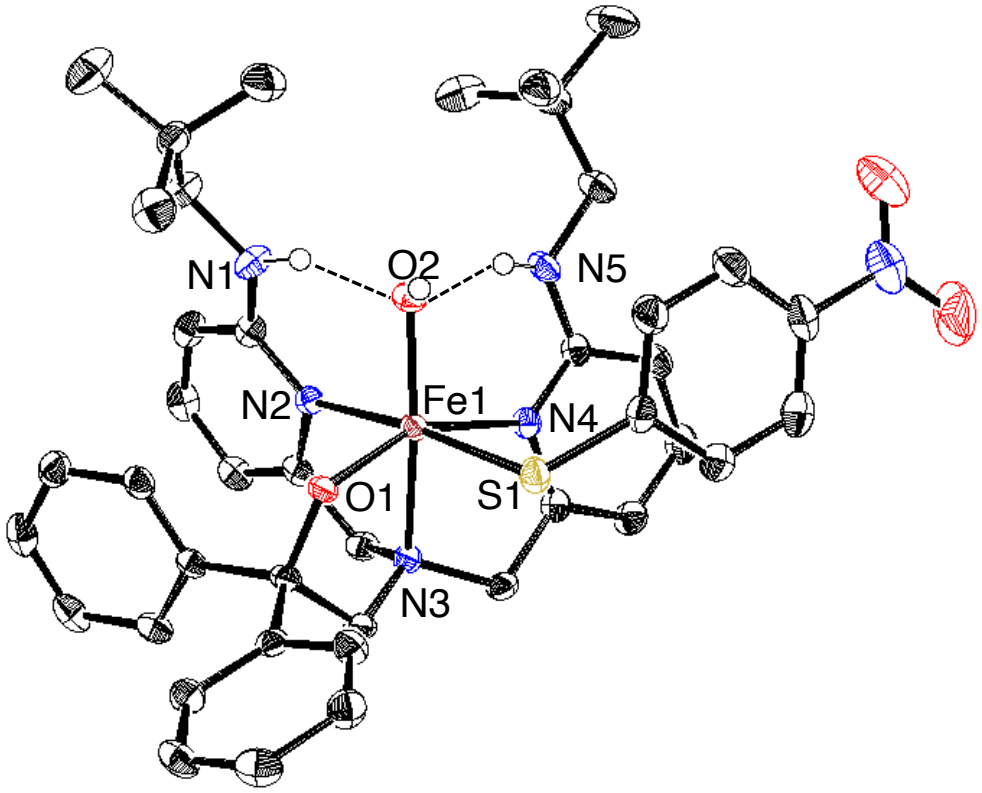

Figure S34. Displacement ellipsoid plot (50% probability) of $Fe^{III}(BNPA^{Ph2}O)(OH)(SPh^{p\text{-}NO_2})$ (**3**) at 110(2) K. H-atoms are removed for clarity, except those attached to N1, N5 and O2.

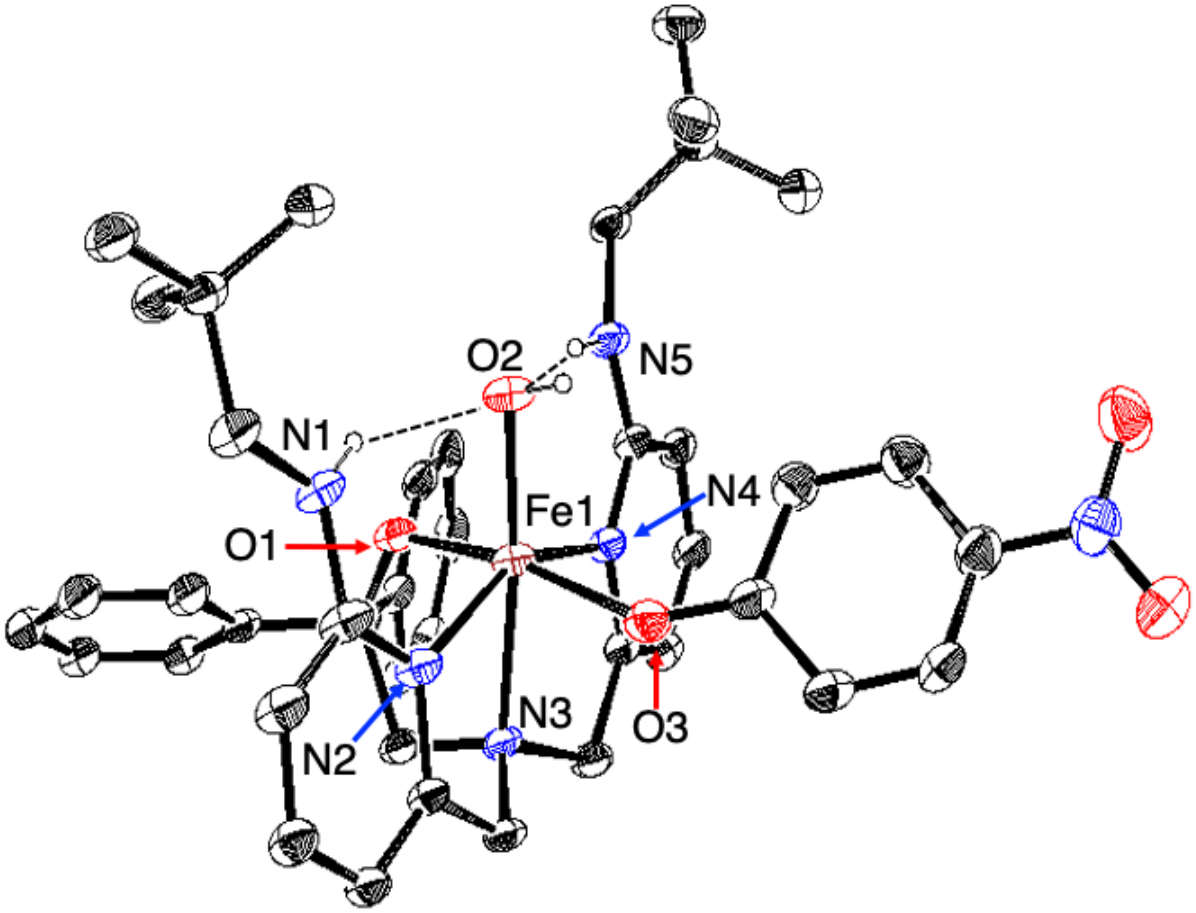

Figure S35. Displacement ellipsoid plot (50% probability) of $Fe^{III}(BNPA^{Ph2}O)(OH)(OPh^{p\text{-}NO_2})$ (**4**) at 100(2) K. H-atoms are removed for clarity, except those attached to N1, N5 and O2.

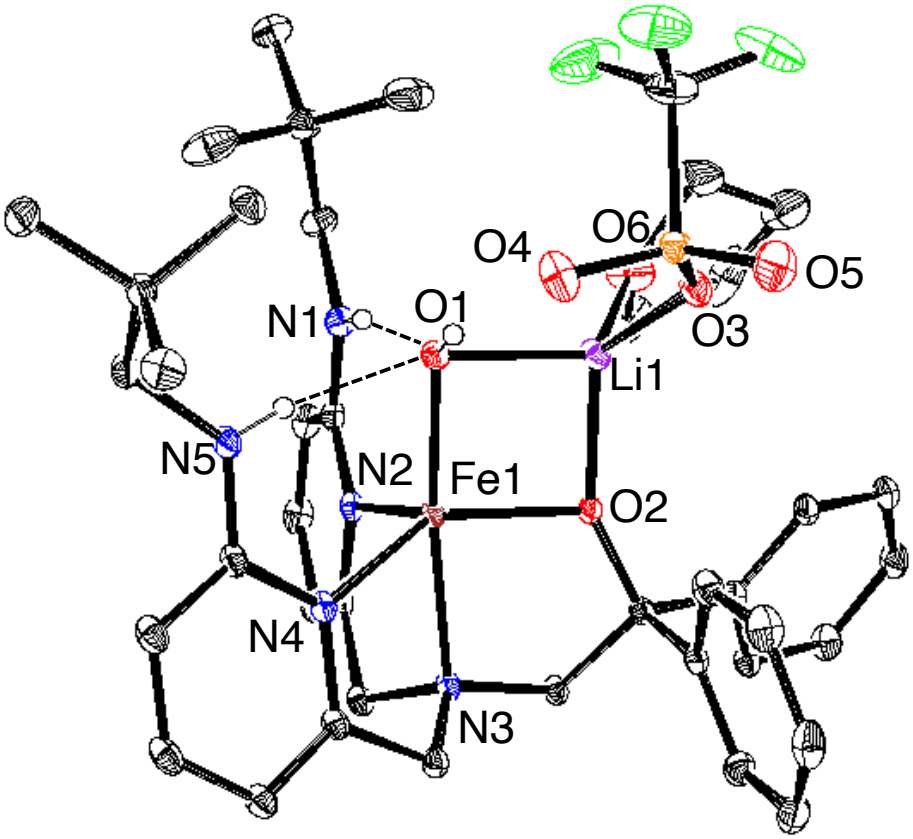

Figure S36. Displacement ellipsoid plot (50% probability) of Fe^{II}(BNPA^{Ph2}O)(OH)(Li(OTf)(THF)) (**5•Li(OTf)(THF**)) at 110(2) K. H-atoms are removed for clarity except those attached to N1, N5 and O2.

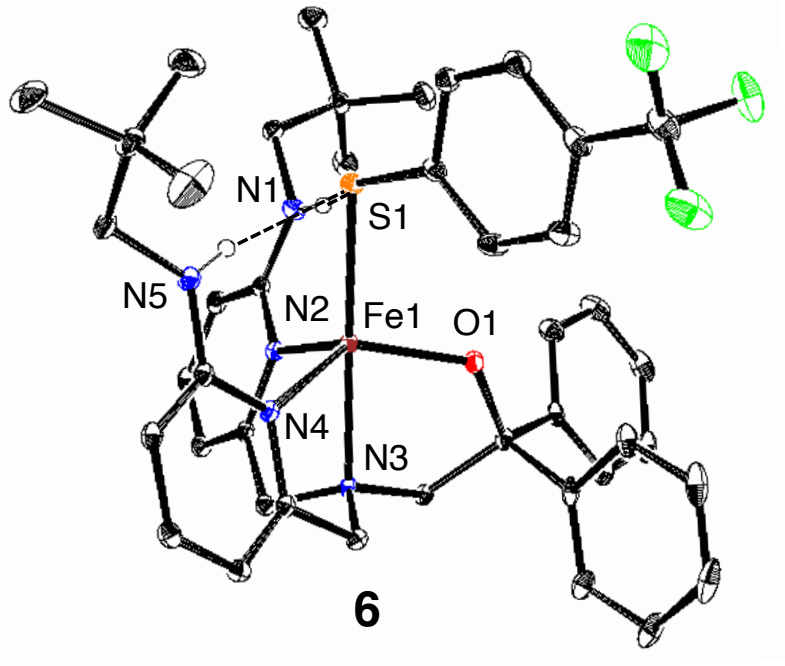

Figure S37. Displacement ellipsoid plot (50% probability) of $Fe^{II}(BNPA^{Ph2}O)(SPh^{p\text{-}CF_3})$ (**6**) at 110(2) K. H-atoms are removed for clarity except those attached to N1, N5 and O2.

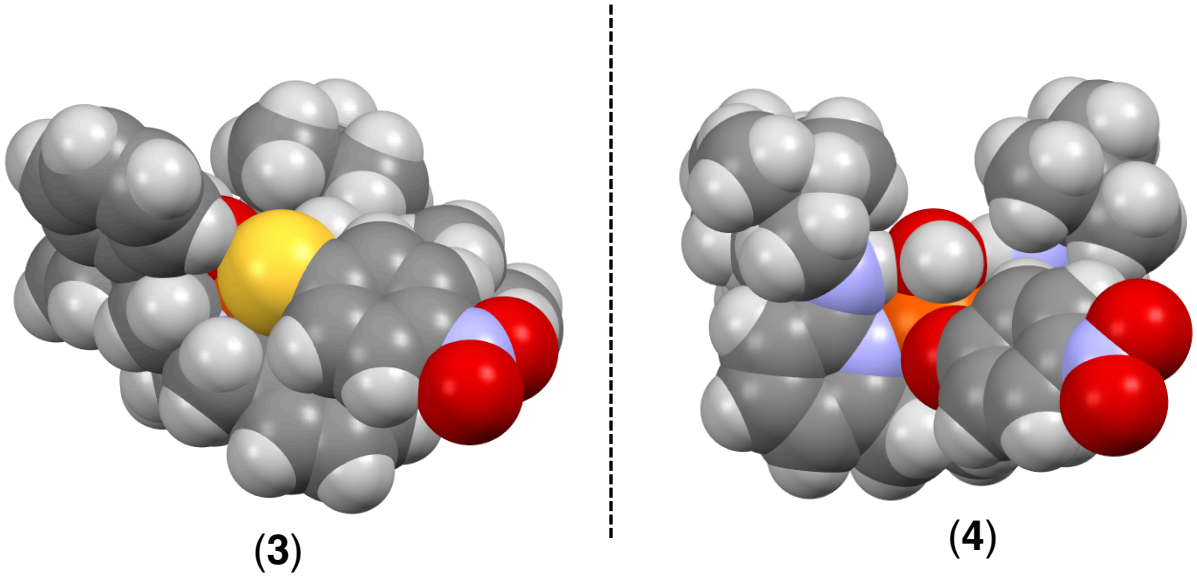

Figure S38. Space filling model of **3** and **4**.

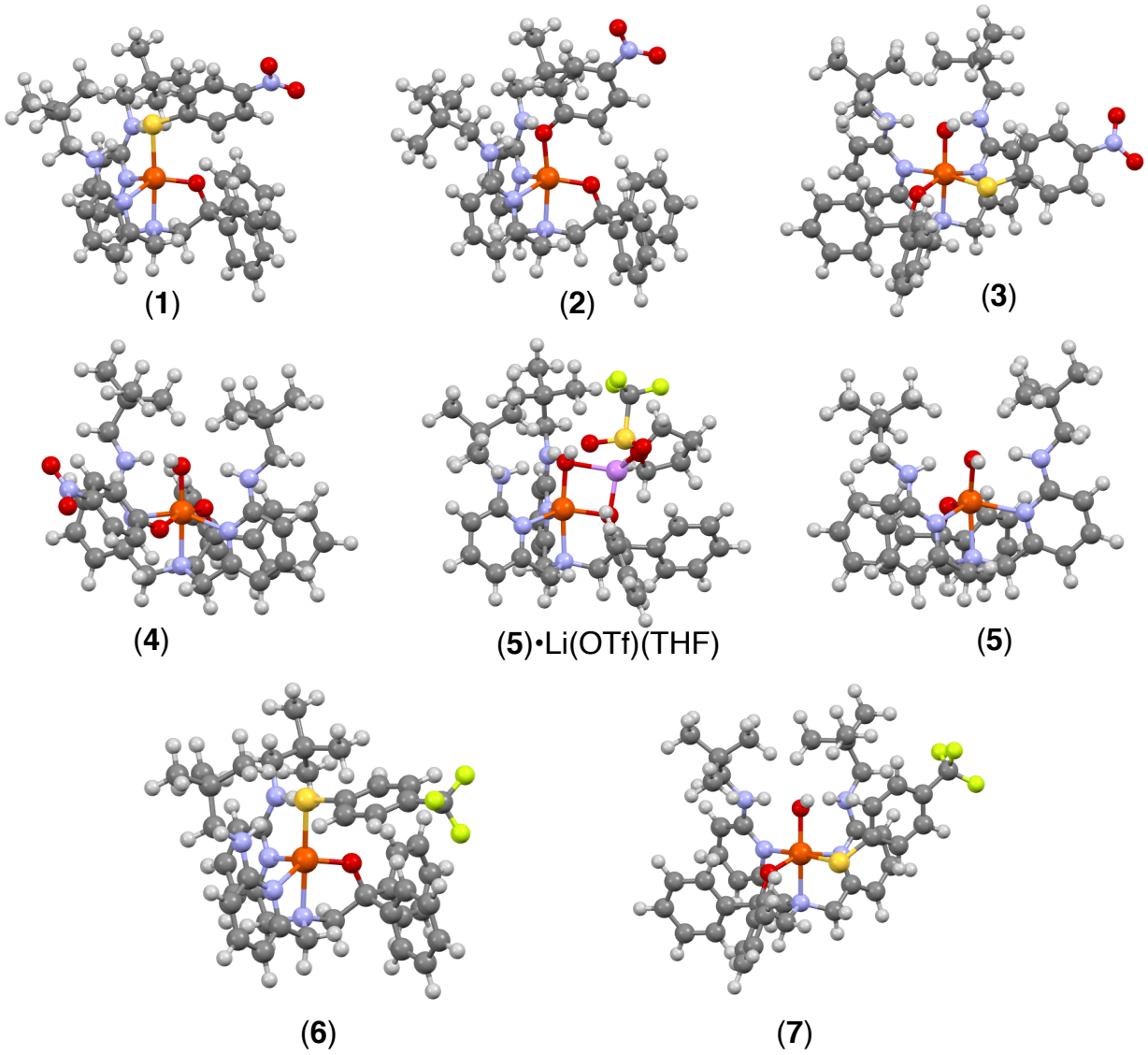

Figure S39. DFT optimized geometries of **1 – 7**.

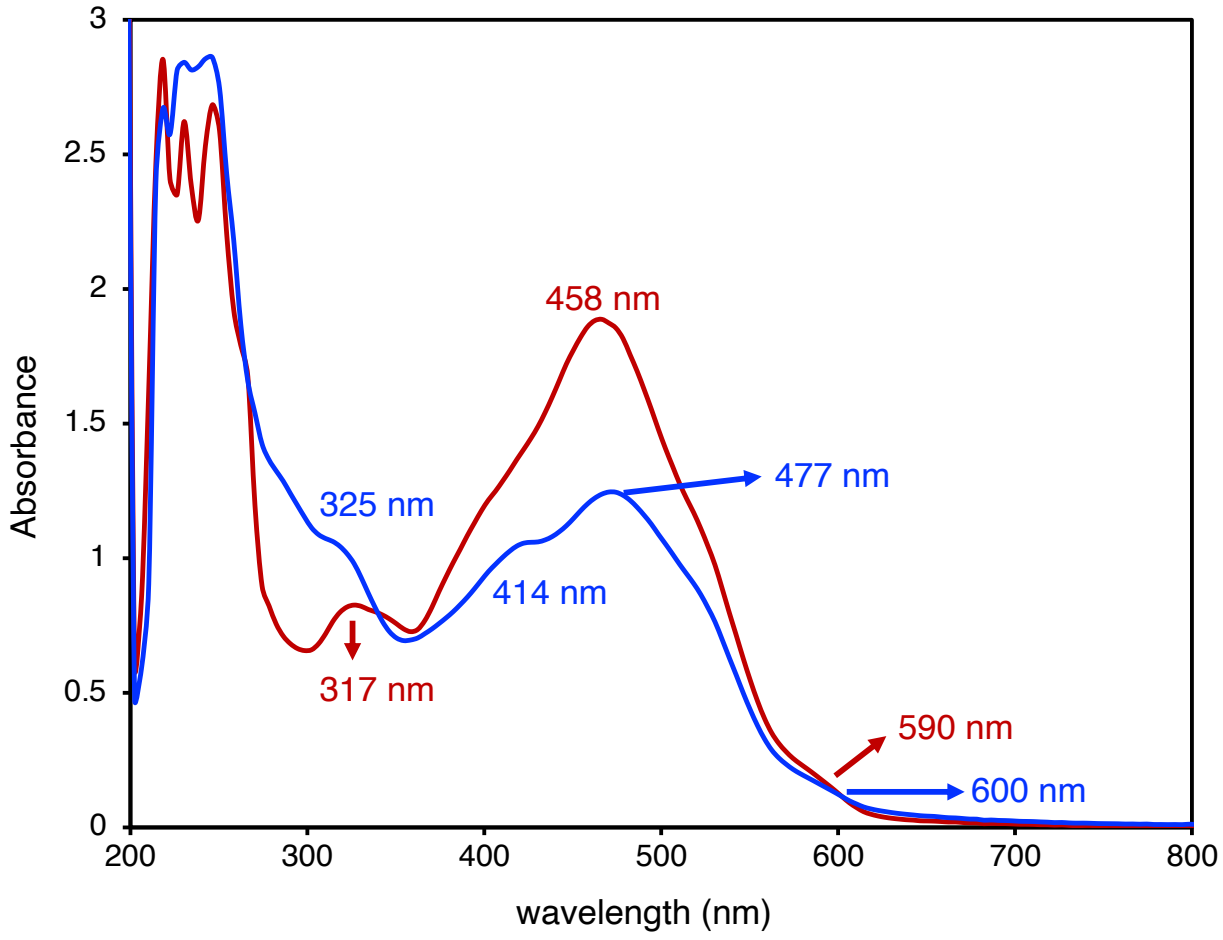

Figure S40. UV-vis spectra of **1** (red) and **3** (blue) in THF (57 μM) at 23 ºC.

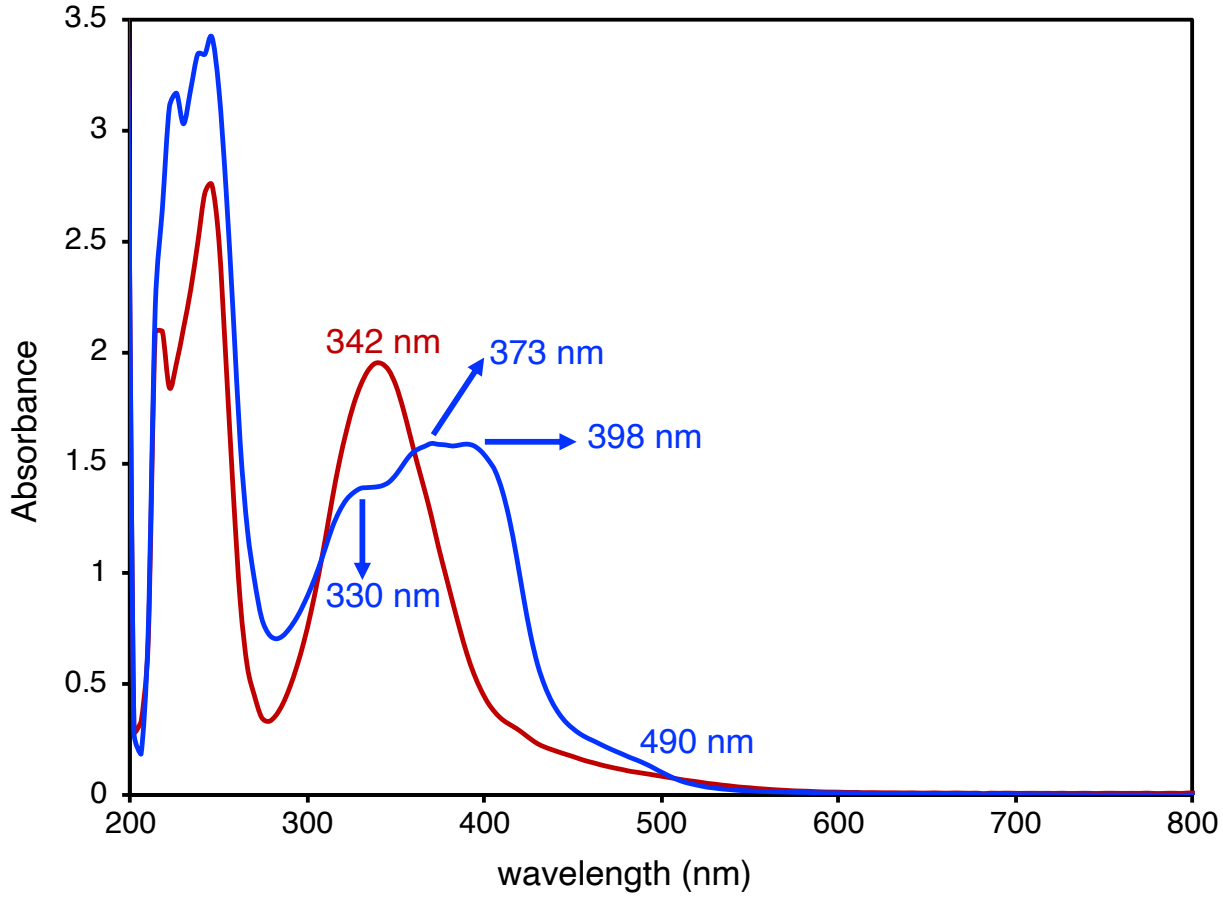

Figure S41. UV-vis spectra of **2** (red) and **4** (blue) in THF (56 μM) at 23 ºC.

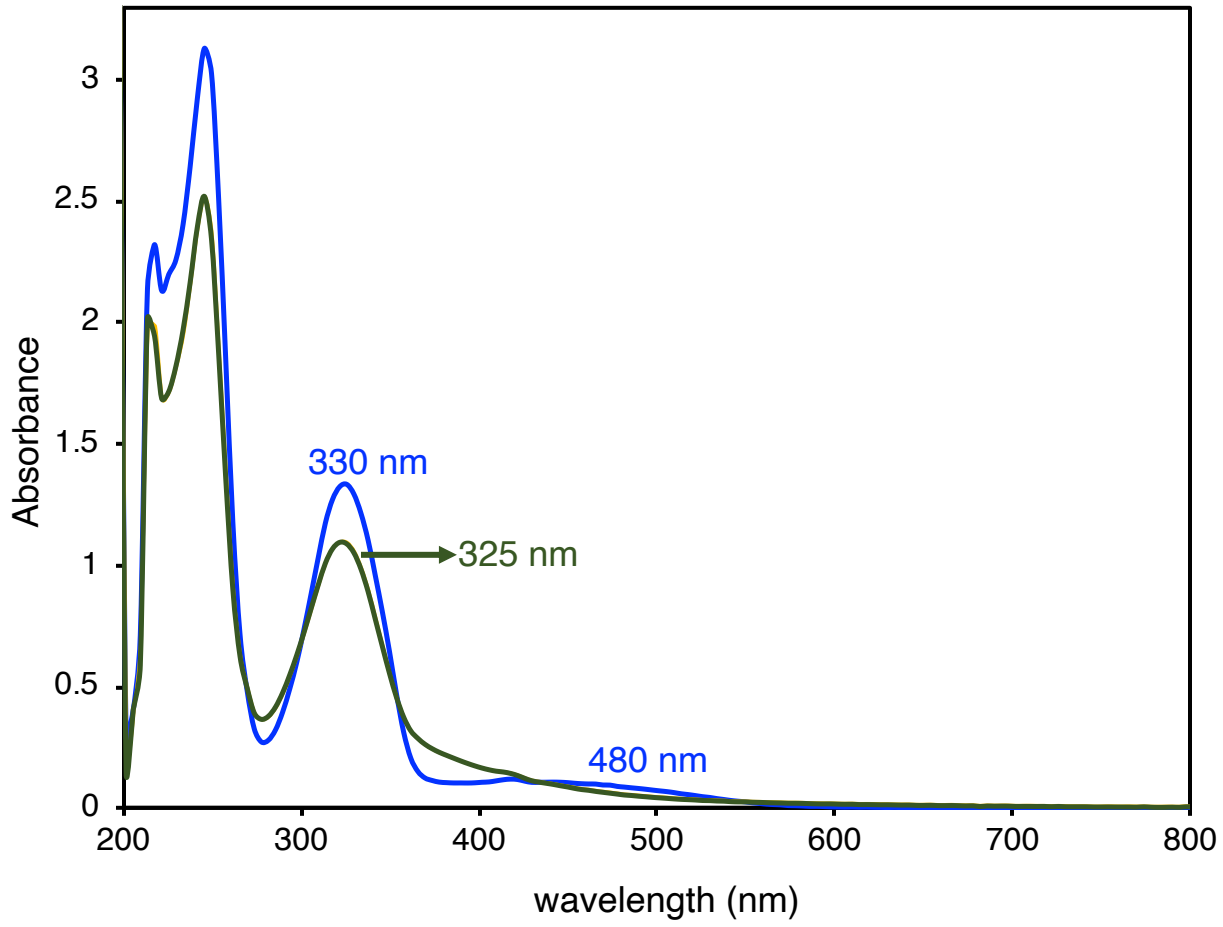

Figure S42. UV-vis spectra of **5** (green) (114 μM) and **5•Li(OTf)(THF)** (blue) (110 μM) in THF at 23 ºC.

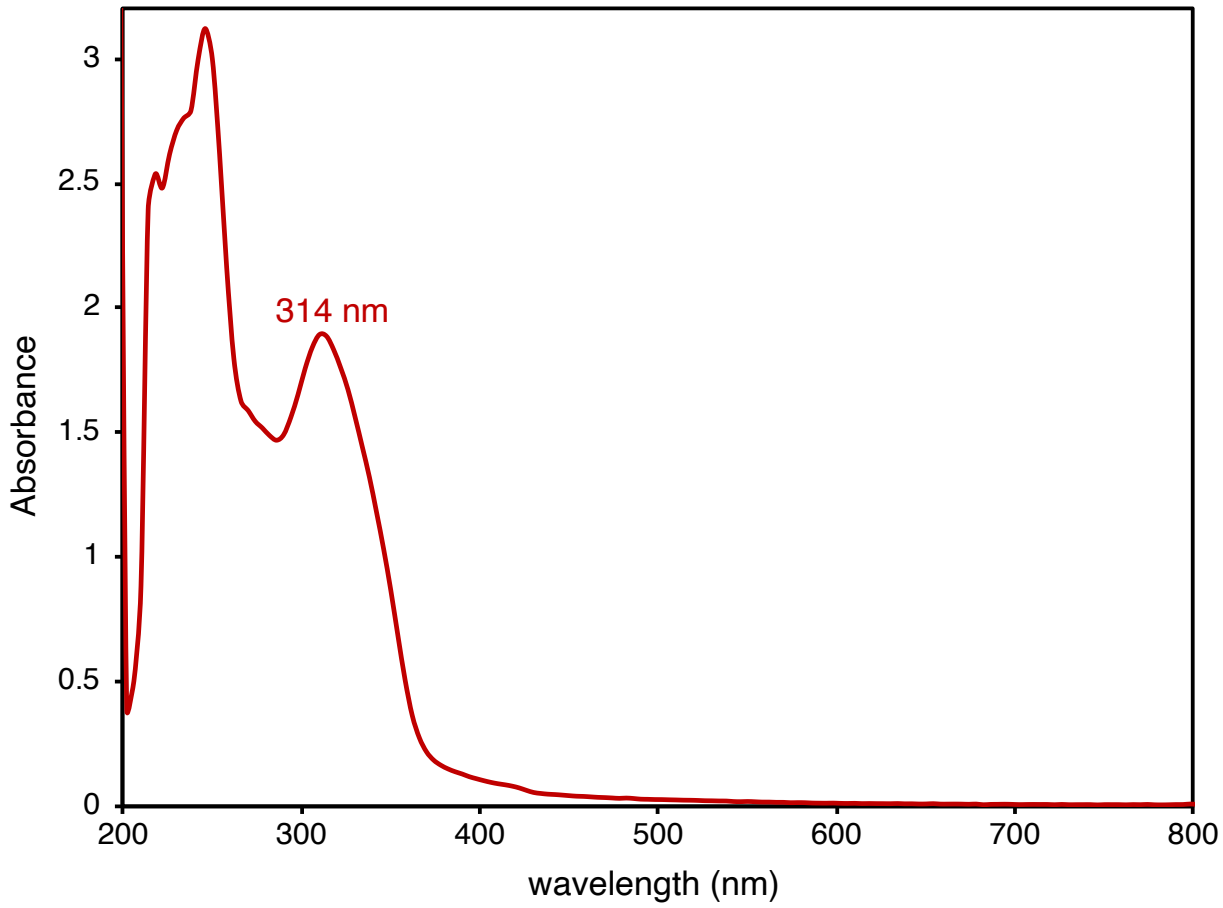

Figure S43. UV-vis spectrum of **6** in THF (114 μM) at 23 ºC.

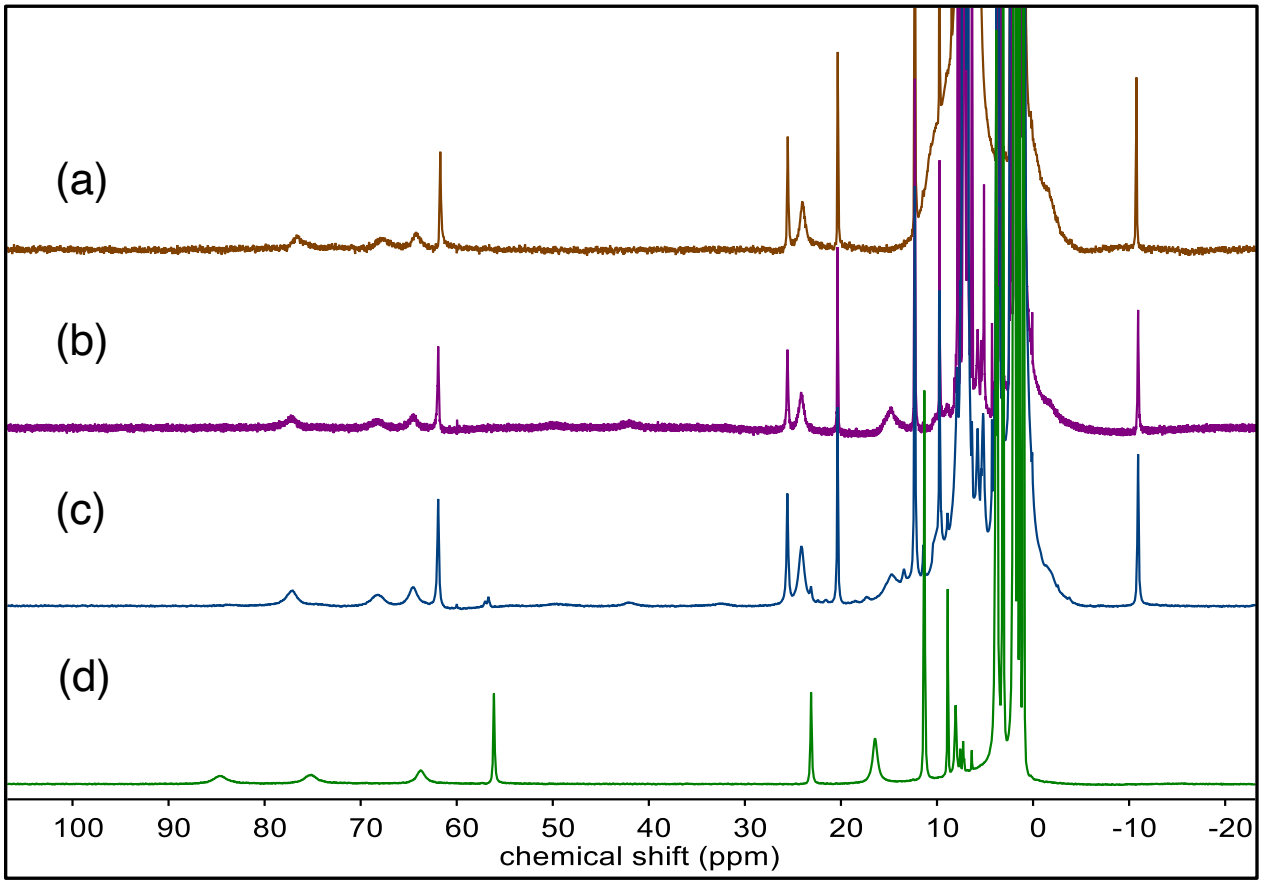

Figure S44. ^{1}H NMR spectra of (a) **2**, (b) reaction of 1:1 mixture of **3** and **4** with (p-OMe-$C_6H_4)_3C$• at 23 ºC, (c) reaction of 1:1 mixture of **3** and **4** with (p-OMe-$C_6H_4)_3C$• at - 35 ºC and (d) **5** in CD_3CN.

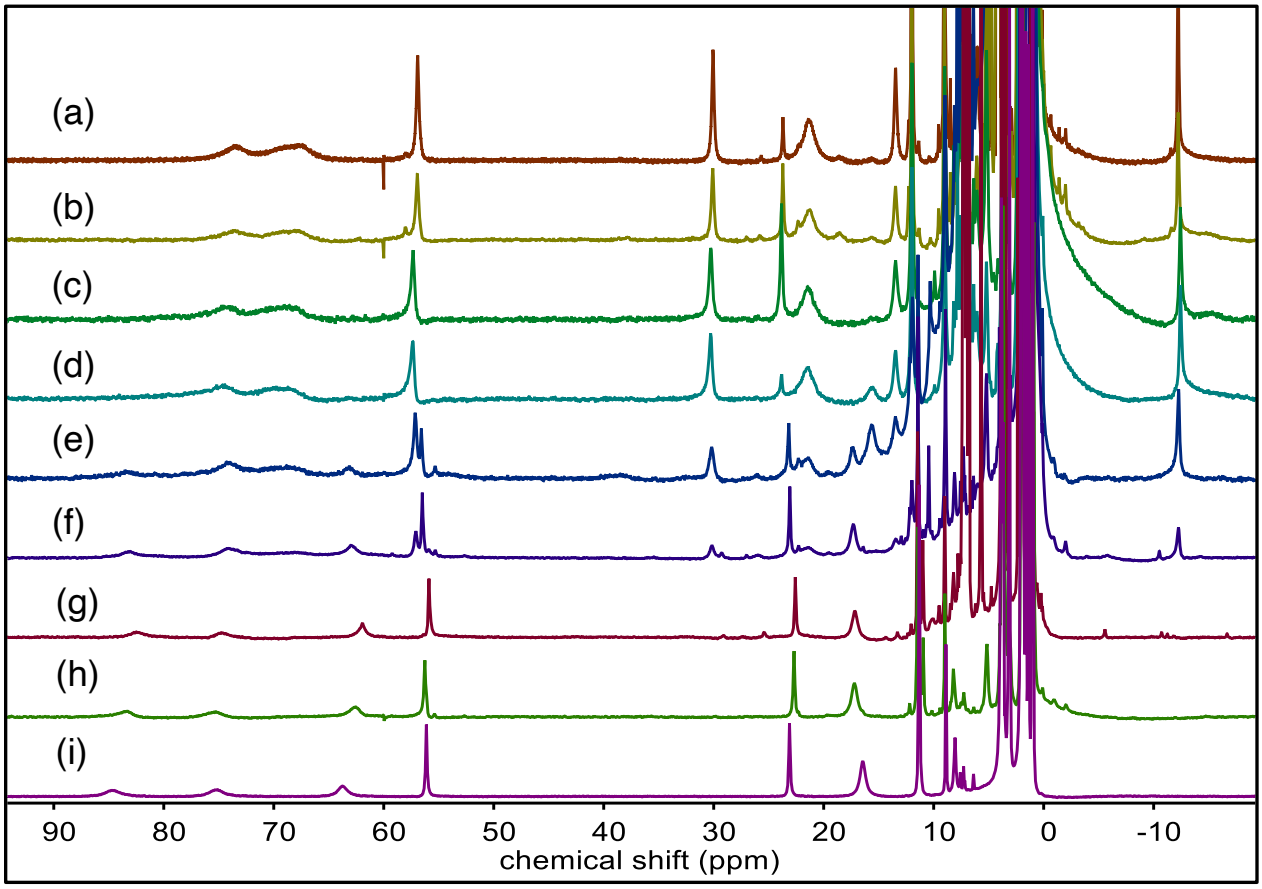

Figure S45. ^{1}H NMR spectra of (a) **1**, (b – h) reaction of **3** with (p-OMe-C_6H_4)$_3$C• at temperatures +23 ºC, +15 ºC, +5 ºC, -5 ºC, -15 ºC, -25 ºC, -35 ºC respectively (i) **5** in CD_3CN.

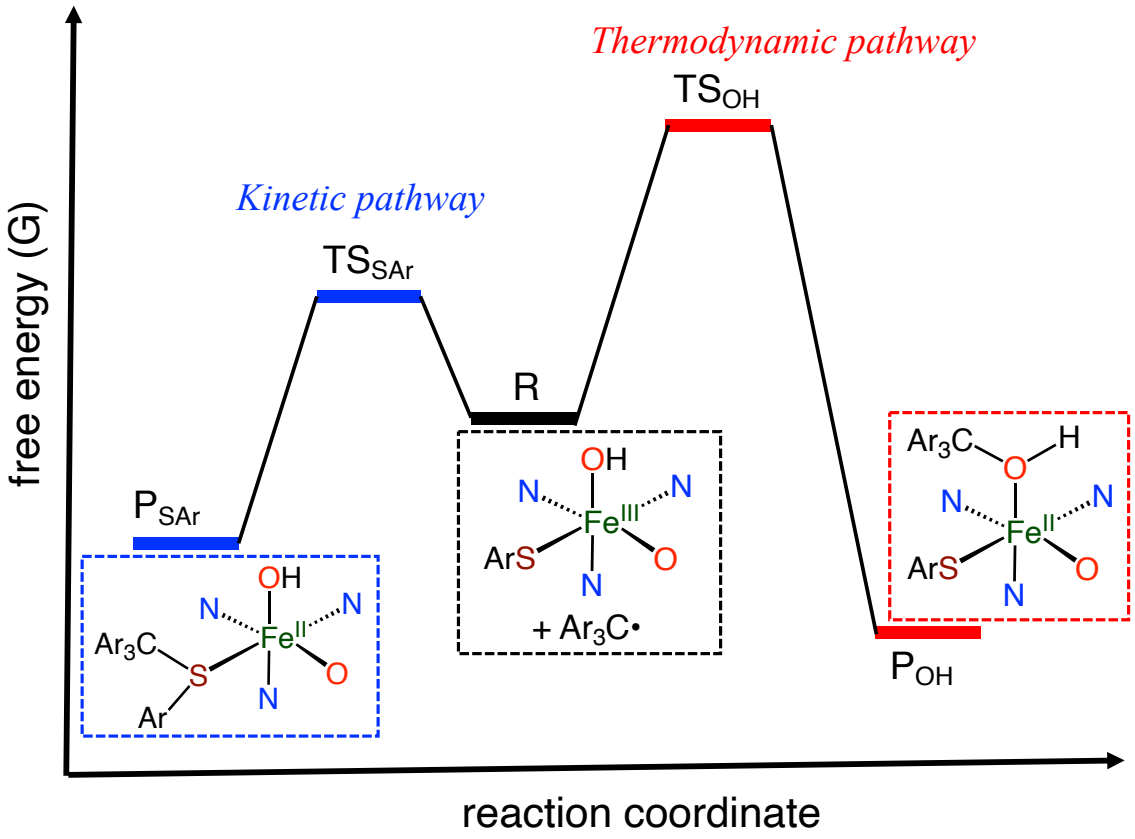

Figure S46. Proposed Reaction Coordinate Diagram.

F. References

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