

## Supporting Information

### Cluster Self-Assembly and Anion Binding by Metal Complexes of Non-Innocent Thiazolidinyl-Thiolate Ligands

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## General considerations.

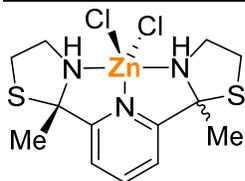
Unless otherwise stated, reactions were carried out in oven-dried glassware in a MBraun glovebox under a purified nitrogen atmosphere or on a Schlenk line. Celite and 4 Å molecular sieves were activated under vacuum at 300 °C for 3 days. Anhydrous toluene, THF, hexanes, and acetonitrile were dried using the Grubbs method on a J.C. Meyer solvent system.<sup>1</sup> Anhydrous *N,N*-dimethylformamide (DMF) was purchased from Millipore Sigma, degassed, and stored over activated sieves in the glovebox. Deuterated solvents were purchased from Cambridge Isotope Laboratories. *d*<sub>6</sub>-DMSO was dried over activated sieves overnight, then distilled onto fresh sieves three times before being stored over activated sieves in the glovebox. CDCl<sub>3</sub> and CD<sub>3</sub>CN were dried over CaH<sub>2</sub> and vacuum transferred before use. C<sub>6</sub>D<sub>6</sub> was dried over sodium/benzophenone ketyl and vacuum transferred before use.

Unless otherwise stated, all commercial chemicals were used without further purification. 2,6-Diacetylpyridine, cysteamine hydrochloride, and Me<sub>3</sub>SiOTf were purchased from Chem Impex International. Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O was purchased from Alfa Aesar or Chem Impex International. Fe(OAc)<sub>2</sub> was purchased from Strem. Sodium bis(trimethylsilyl)amide and [Bu<sub>4</sub>N]NO<sub>3</sub> were purchased from Acros. Lithium bis(trimethylsilyl)amide was purchased from Beantown Chemicals. [Bu<sub>4</sub>N]I, MeI, and 4-dimethylaminopyridine (DMAP) were purchased from Sigma-Aldrich. Pyridine was purchased from Millipore Sigma. TBAPF<sub>6</sub> was purchased from TCI America and recrystallized before use. AgNO<sub>3</sub> was purchased from Sargent Welch.

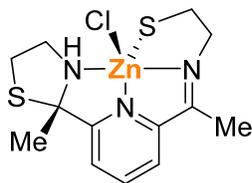
<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker 400 MHz or a Varian 600 MHz instrument. Shifts are reported relative to the residual solvent peak (<sup>1</sup>H, δ 7.26 ppm and <sup>13</sup>C, δ 77.16 ppm for CDCl<sub>3</sub>. <sup>1</sup>H, δ 7.16 ppm and <sup>13</sup>C, δ 128.06 ppm for C<sub>6</sub>D<sub>6</sub>. <sup>1</sup>H, δ 2.50 ppm and <sup>13</sup>C, δ 39.52 ppm for DMSO, <sup>1</sup>H, δ 1.94 ppm and <sup>13</sup>C, δ 1.32 and 118.26 ppm for CD<sub>3</sub>CN). Elemental analysis was performed by Midwest Microlab. Electronic absorption spectra were measured on solution samples in 1-cm quartz cuvettes using an Agilent Cary 60 spectrophotometer.

Cyclic voltammetry (CV) measurements were carried out in the glovebox under nitrogen atmosphere using a Princeton Applied Research VersaSTAT4 potentiostat. A glassy carbon electrode (CH instruments) was used as the working electrode, Pt wire as the counter electrode, and the reference electrode was a non-aqueous Ag<sup>+</sup>/Ag electrode (0.01 M AgNO<sub>3</sub>, 0.1 M TBAPF<sub>6</sub> in CH<sub>3</sub>CN). CV measurements were made of DMF solutions of analyte using TBAPF<sub>6</sub> as the electrolyte (0.1 M). The measurements were then referenced to the ferrocenium/ferrocene redox couple by adding ferrocene to the solution after the measurement.

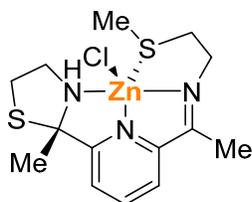
## Synthetic Procedures



**Synthesis of 1.** Under ambient conditions, a round bottom flask equipped with a stir bar was charged with 2,6-diacetylpyridine (1.00 g, 1 equiv, 6.13 mmol), cysteamine hydrochloride (1.39 g, 2 equiv, 12.3 mmol), and  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (1.34 g, 1 equiv, 6.13 mmol) in ethanol (50 mL). The resulting heterogeneous reaction mixture was refluxed for 15 h under  $\text{N}_2$ , then cooled to room temperature. The precipitate was collected by filtration, washed with ethanol (20 mL) and THF (20 mL), and dried under vacuum to yield the product as a white solid (1.83 g, 72%). Anal. Calcd. for  $\text{C}_{13}\text{H}_{19}\text{Cl}_2\text{N}_3\text{S}_2\text{Zn}$  (%): C, 37.38; H, 4.58; N, 10.06. Found: C, 37.13; H, 4.39; N, 9.82.  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO):  $\delta$  8.11 (m, 1H), 7.76 (d,  $J = 7.9$  Hz, 1H), 7.66 (d,  $J = 7.8$  Hz, 1H), 5.45 (dd,  $J = 3.7, 12.3$  Hz, 2H), 5.04 (dd,  $J = 3.7, 12.1$  Hz, 2H), 3.84 (m, 1H), 3.61 (m, 1H), 3.01 (m, 4H), 2.53 (m, 1H), 2.40 (m, 1H), 1.92 (s, 3H), 1.89 (s, 3H).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.99 (t,  $J = 7.9$  Hz, 1H), 7.68 (d,  $J = 7.9$  Hz, 2H), 4.17 (m, 2H), 3.43 (m, 2H), 3.23 (m, 2H), 3.16 (m, 2H), 2.91 (m, 2H), 2.09 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $d_6$ -DMSO):  $\delta$  160.85, 159.96, 142.17, 142.07, 123.08, 122.70, 78.68, 77.63, 53.72, 53.32, 34.83, 34.76, 30.98, 30.43. In  $d_6$ -DMSO, two diastereomers are observed in a 1:0.6 ratio. In  $\text{CDCl}_3$ , one major diastereomer is observed and reported above.

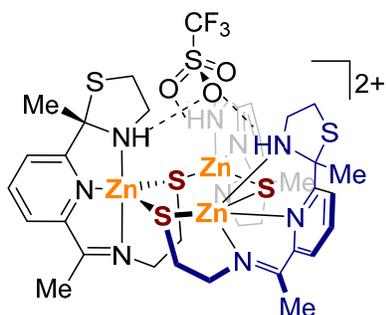


**Synthesis of 2-Cl.** In the glovebox, a scintillation vial equipped with a stir bar was charged with a solution of **1** (1.00 g, 1 equiv, 2.39 mmol) in DMF (5 mL). To this mixture, a solution of LiHMDS (0.40 g, 1 equiv, 2.39 mmol) in DMF (7 mL) was added dropwise, forming a yellow precipitate. This mixture was stirred for 2 h at room temperature. The precipitate was collected by filtration, washed with THF (50 mL), and dried under vacuum to yield the product as a yellow solid (0.46 g, 50%). Anal. Calcd. for  $\text{C}_{13}\text{H}_{18}\text{ClN}_3\text{S}_2\text{Zn}$  (%): C, 40.95; H, 4.76; N, 11.02. Found: C, 40.91; H, 4.92; N, 10.98.  $^1\text{H}$  NMR (600 MHz,  $d_6$ -DMSO):  $\delta$  8.27 (t,  $J = 7.8$  Hz, 1H), 8.08 (d,  $J = 7.6$  Hz, 1H), 7.94 (d,  $J = 8.0$  Hz, 1H), 5.48 (dd,  $J = 4.2, 11.8$  Hz, 1H), 3.74 (m, 1H), 3.45 (m, 2H), 3.01 (m, 3H), 2.65 (m, 1H), 2.56 (m, 1H), 2.44 (s, 3H), 2.06 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $d_6$ -DMSO):  $\delta$  161.75, 160.89, 145.91, 142.53, 125.40, 121.96, 78.33, 53.00, 49.41, 35.24, 29.84, 27.94, 15.04.

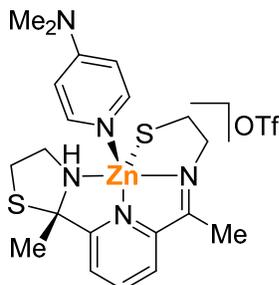


**Methylation of 2-Cl.** Under ambient conditions, a scintillation vial equipped with a stir bar was charged with **2-Cl** (0.20 g, 1 equiv, 0.53 mmol) in DMF (7 mL). MeI (33  $\mu\text{L}$ , 1 equiv, 0.53 mmol) was added to the stirring suspension. The resulting colorless homogenous solution was stirred for

30 min at room temperature and then concentrated under vacuum. The sticky residue was recrystallized from CH<sub>3</sub>CN/diethyl ether at 0 °C to yield the product as colorless crystals (0.153 g, 56%). <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO): δ 8.35 (t, *J* = 7.9 Hz, 1H), 8.21 (d, *J* = 7.8 Hz, 1H), 8.05 (d, *J* = 8.1 Hz, 1H), 5.33 (dd, *J* = 3.7, 11.8 Hz, 1H), 4.10 (m, 1H), 3.93 (m, 1H), 3.69 (m, 1H), 3.01 (m, 3H), 2.88 (m, 1H), 2.54 (s, 3H), 2.48 (m, 1H), 2.14 (s, 3H), 1.94 (s, 3H). <sup>13</sup>C NMR (100 MHz, *d*<sub>6</sub>-DMSO): δ 164.99, 162.45, 145.50, 143.23, 126.76, 123.45, 78.04, 53.71, 49.43, 34.92, 32.18, 30.48, 14.84, 14.69. ESI-MS (*m/z*): [M]<sup>+</sup> calcd. for C<sub>14</sub>H<sub>21</sub>ClN<sub>3</sub>S<sub>2</sub>Zn, 394.0157; found, 394.0106.

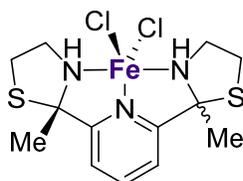


**Synthesis of [6-OTf](OTf)<sub>2</sub>.** In the glovebox, a scintillation vial equipped with a stir bar was charged with **2-Cl** (1.00 g, 1 equiv, 2.62 mmol) in MeCN (10 mL). To this suspension was added Me<sub>3</sub>SiOTf (0.48 mL, 1 equiv, 2.62 mmol) dropwise at room temperature. The resulting pale-yellow solution was stirred for 30 min at room temperature, then dried under vacuum to form a sticky white solid. This residue was recrystallized from CH<sub>3</sub>CN/diethyl ether to yield the product as a colorless solid (0.97 g, 75%). Anal. Calcd. for C<sub>42</sub>H<sub>54</sub>F<sub>9</sub>N<sub>9</sub>O<sub>9</sub>S<sub>9</sub>Zn<sub>3</sub> (%): C, 33.98; H, 3.67, N, 8.49; Found: C, 33.68; H, 3.72; N, 8.27. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ 8.30 (t, *J* = 7.8 Hz, 1H), 8.07 (d, *J* = 7.6 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 5.01 (dd, *J* = 4.6, 12.6 Hz, 1H), 3.88 (m, 2H), 3.60 (m, 1H) 3.21 (m, 1H), 3.11 (m, 1H), 2.80 (m, 1H), 2.65 (m, 1H), 2.56 (m, 1H), 2.53 (s, 3H), 2.22 (s, 3H). <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO): δ 8.33 (t, *J* = 7.8 Hz, 1H), 8.13 (d, *J* = 7.7 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 5.62 (dd, *J* = 4.4, 12.0 Hz, 1H), 3.66 (t, *J* = 5.6 Hz, 2H), 3.51 (m, 1H), 3.09 (m, 2H), 2.93 (m, 1H), 2.72 (m, 1H), 2.62 (m, 1H), 2.48 (s, 3H), 1.91 (s, 3H). <sup>13</sup>C NMR (100 MHz, *d*<sub>6</sub>-DMSO): δ 162.56, 161.47, 145.46, 143.36, 125.76, 122.49, 77.62, 52.29, 49.58, 35.33, 29.79, 27.93, 15.27.

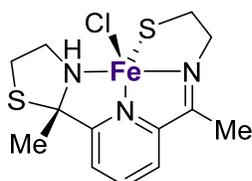


**Synthesis of [2-DMAP][OTf].** Under ambient conditions, a round bottom flask equipped with a stir bar was charged with [6-OTf]<sup>2+</sup> (1.09 g, 1 equiv, 2.21 mmol) in CH<sub>3</sub>CN (15 mL). To this solution was added a solution of 4-dimethylaminopyridine (0.39 g, 1 equiv, 2.21 mmol) in MeCN (5 mL). The resulting yellow solution was stirred for 30 min. at room temperature and then dried *in vacuo*. The product was then recrystallized overnight at 0 °C in an MeCN and ether solution to form yellow crystals (1.01g, 74%). Anal. Calcd. for C<sub>21</sub>H<sub>28</sub>F<sub>3</sub>N<sub>5</sub>O<sub>3</sub>S<sub>3</sub>Zn (%): C, 40.88; H, 4.57; N, 11.35. Found: C, 41.27; H, 4.63; N, 11.87. <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO): δ 8.34 (t, *J* = 7.9 Hz,

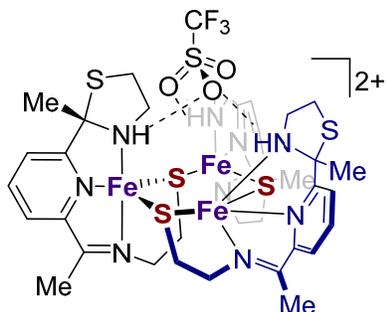
1H), 8.16 (d,  $J = 7.7$  Hz, 1H), 8.01 (d,  $J = 7.9$  Hz, 1H), 7.90 (bs, DMAP, 2H), 6.63 (bs, DMAP, 2H), 5.66 (dd,  $J = 3.8, 11.2$  Hz, 1H), 3.62 (m, 1H), 3.54 (m, 2H), 3.07 (m, 2H), 2.96 (s, DMAP, 6H), 2.78 (m, 1H), 2.65 (m, 2H), 2.50 (s, 3H), 1.71 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $d_6$ -DMSO): 163.34, 161.88, 156.25, 146.30, 143.75, 143.56, 126.18, 122.98, 107.36, 77.97, 53.04, 49.86, 35.70, 29.80, 28.19, 15.72.



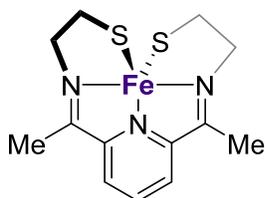
**Synthesis of 2,6-bis(2-methylthiazolidin-2-yl) pyridine iron dichloride (3).** A Schlenk flask equipped with a stir bar was charged with 2,6-diacetylpyridine (3.75 g, 1.0 equiv, 23.0 mmol), cysteamine hydrochloride (5.23 g, 2.0 equiv, 46.0 mmol), and ethanol (200 mL), degassed, then put under a  $\text{N}_2$  atmosphere.  $\text{Fe}(\text{OAc})_2$  (4.00 g, 1.0 equiv, 23.0 mmol) was added as a solid under  $\text{N}_2$  flow. The reaction mixture was refluxed overnight under  $\text{N}_2$  to form a heterogeneous blue-green mixture. The blue supernatant solution was removed by cannula transfer and the green residue was dried under vacuum. In the glovebox, the residue was washed with THF and dried under vacuum to yield the product as a light green powder (8.10 g, 86%). Anal. Calcd. for  $\text{C}_{13}\text{H}_{19}\text{Cl}_2\text{N}_3\text{S}_2\text{Fe}$  (%): C, 38.25; H, 4.69; N, 10.29. Found: C, 38.12; H, 4.63; N, 10.29. UV-Vis (DMF)  $\lambda_{\text{max}}$ , nm ( $\epsilon$ ): 640 (20).  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO):  $\delta$  (FWHM) 104.6 (925 Hz), 77.7 (64 Hz), 70.8 (1500 Hz), 46.6 (670 Hz), 30.8 (1400 Hz), 24.3 (82 Hz), 19.7 (86 Hz), 13.6 (530 Hz), 7.1 (250 Hz), 5.8 (96 Hz), -9.3 (280 Hz), -10.3 (610 Hz), -17.5 (44 Hz), -25.1 (75 Hz). Two diastereomers are present.



**Synthesis of 4-Cl.** In the glovebox, an oven-dried Schlenk flask equipped with a stir bar was charged with **3** (0.81 g, 1 equiv, 2.0 mmol) in DMF (10 mL). To this stirring suspension, a solution of LiHMDS (0.35 g, 1 equiv, 2.0 mmol) in DMF (5 mL) was added slowly. This mixture was stirred for 2 h at room temperature, then concentrated under vacuum. The residue was washed with THF (50 mL) then dried *in vacuo* to yield the product as a deep blue solid (0.61 g, 82%). Anal. Calcd. for  $\text{C}_{13}\text{H}_{18}\text{ClN}_3\text{S}_2\text{Fe}$  (%): C, 42.01; H, 4.88; N, 11.30. Found: C, 42.06; H, 5.03; N, 11.34. UV-Vis (DMF)  $\lambda_{\text{max}}$ , nm ( $\epsilon$ ): 600 ( $2.71 \times 10^3$ ).  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO):  $\delta$  (FWHM) 107.7 (1500 Hz), 90.0 (210 Hz), 77.2 (192 Hz), 18.2 (718 Hz), 17.6 (302 Hz), -4.4 (94 Hz), -28.5 (213 Hz).

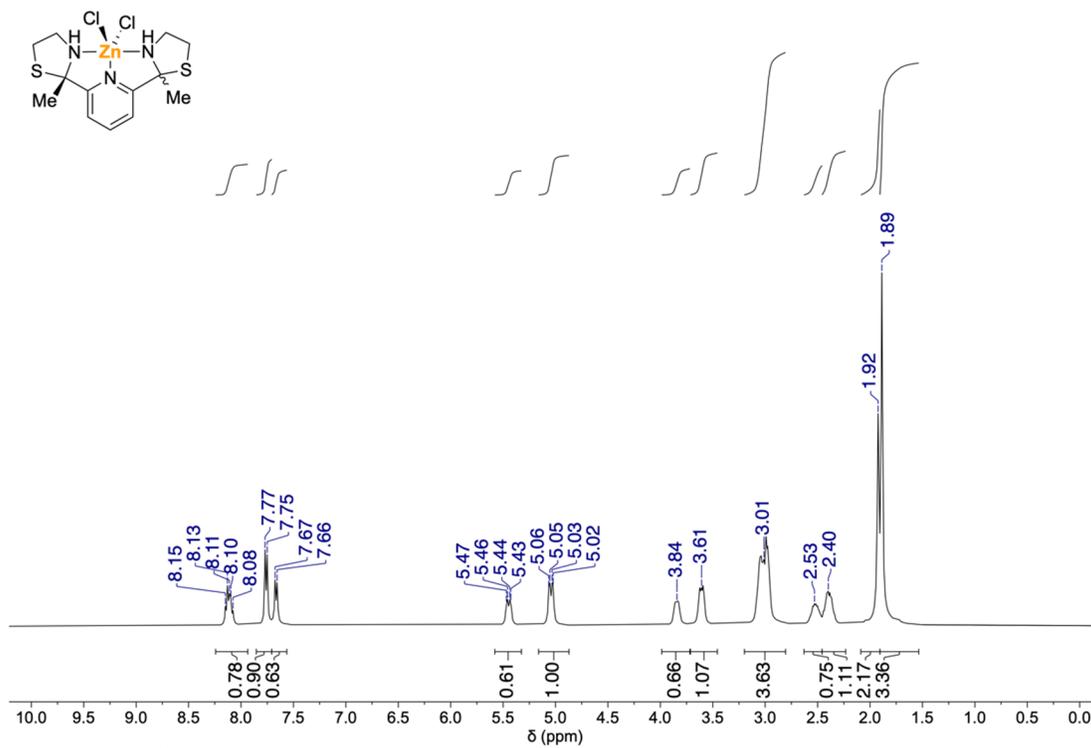


**Synthesis of [7-OTf](OTf)<sub>2</sub>.** In the glovebox, a scintillation vial equipped with a stir bar was charged with **4-Cl** (1.02 g, 1.0 equiv, 2.69 mmol) and MeCN (20 mL). Me<sub>3</sub>SiOTf (0.498 mL, 1.2 equiv, 2.69 mmol) was added with stirring, resulting in a homogeneous purple mixture. This mixture was stirred for 1.5 h at room temperature, then dried *in vacuo* to yield the product as a dark purple solid (0.49 g, 38%). Anal. Calcd. for C<sub>42</sub>H<sub>54</sub>F<sub>9</sub>N<sub>9</sub>O<sub>9</sub>S<sub>9</sub>Fe<sub>3</sub> (%): C, 34.65; H, 3.74; N, 8.66. Found: C, 34.32; H, 3.94; N, 8.93. UV-Vis (CH<sub>3</sub>CN) λ<sub>max</sub>, nm (ε): 470 (3.40 × 10<sup>3</sup>), 596 (4.14 × 10<sup>3</sup>). <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO): δ (FWHM) 91.7 (520 Hz), 77.1 (420 Hz), 21.2 (720 Hz), 16.6 (490 Hz), -3.2 (390 Hz), -26.8 (840 Hz).

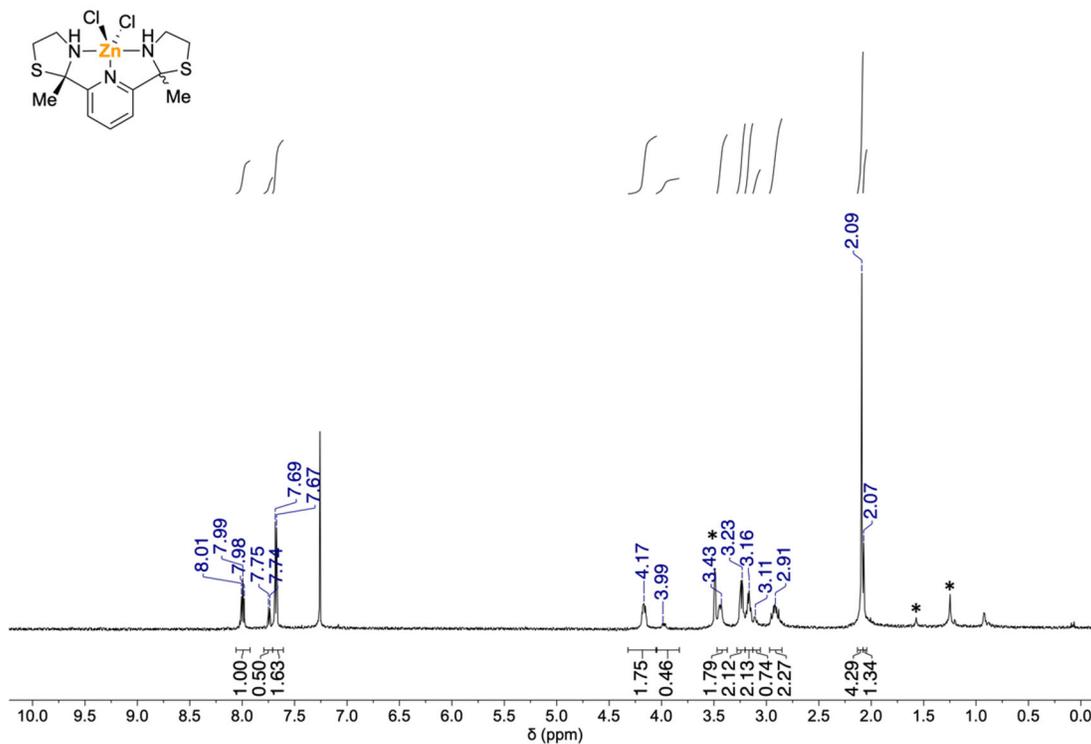


**Synthesis of 5.** In the glovebox, a round bottom flask equipped with a stir bar was charged with **3** (1.15 g, 1.0 equiv, 2.45 mmol) and NaHMDS (1.04 g, 2.0 equiv, 4.90 mmol) in THF (75 mL). This mixture was stirred at room temperature for 4 h, turning from a heterogeneous brown mixture to a deep purple solution. The mixture was filtered through Celite to remove NaCl, concentrated *in vacuo*, and washed with diethyl ether to yield the product as a purple solid (0.24 g, 25%). This compound is air-sensitive, and multiple attempts at combustion analysis failed to yield consistent results. UV-Vis (THF) λ<sub>max</sub>, nm (ε): 495 (sh, 3.17 × 10<sup>3</sup>), 550 (4.88 × 10<sup>3</sup>). <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO): δ (FWHM) 95.3 (940 Hz), 75.9 (320 Hz), 12.3 (340 Hz), -8.7 (35 Hz), -48.3 (210 Hz). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ (FWHM) 95.66 (640 Hz), 75.71 (230 Hz), 12.14 (190 Hz), -10.12 (30 Hz), -47.79 (150 Hz).

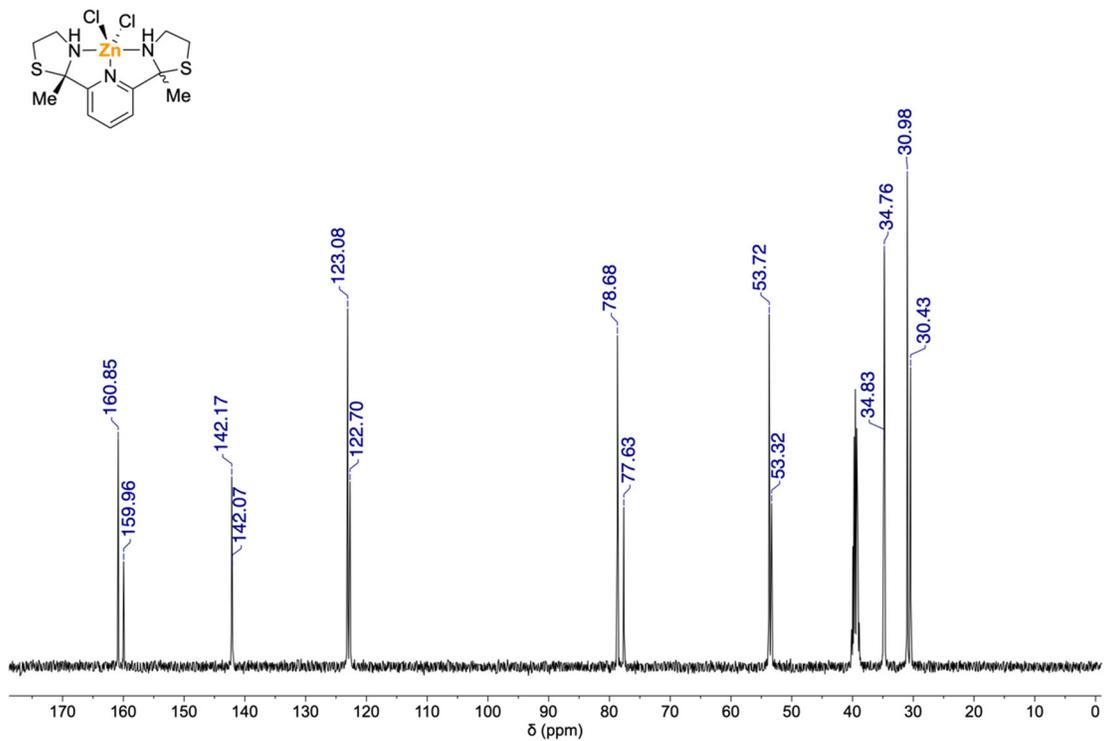
## NMR Spectra



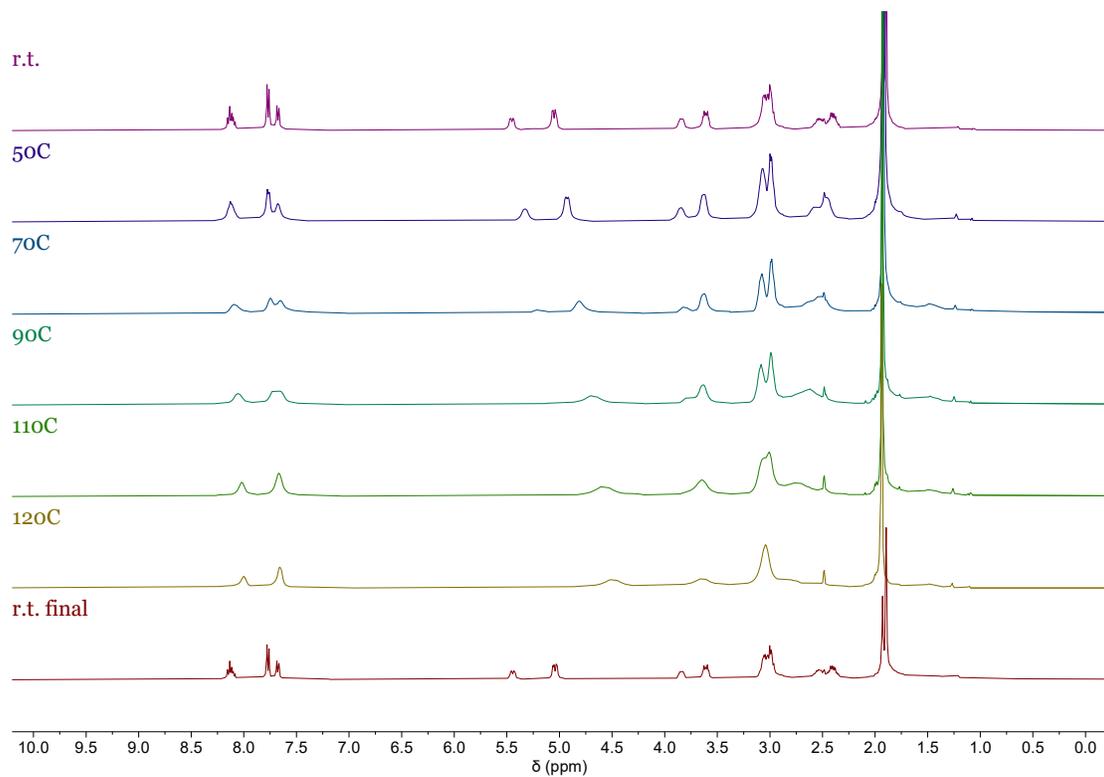
**Figure S1.** <sup>1</sup>H NMR spectrum of 1 in *d*<sub>6</sub>-DMSO.



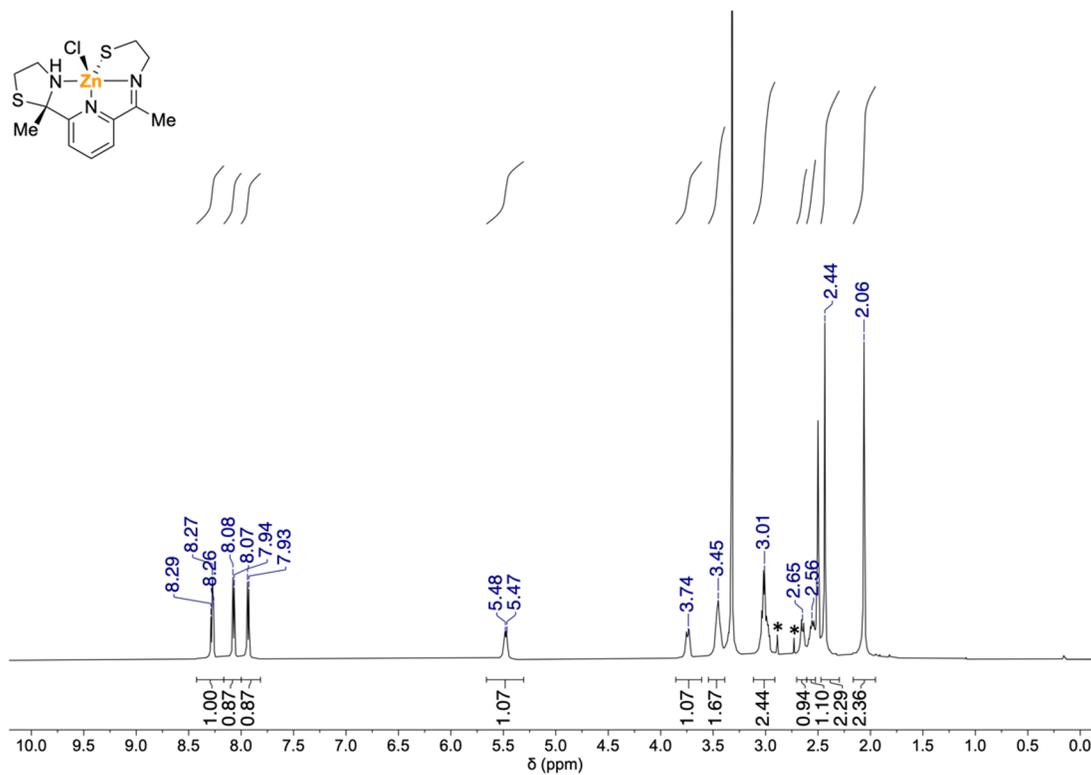
**Figure S2.** <sup>1</sup>H NMR spectrum of 1 in CDCl<sub>3</sub>. Trace ether and water are present (\*).



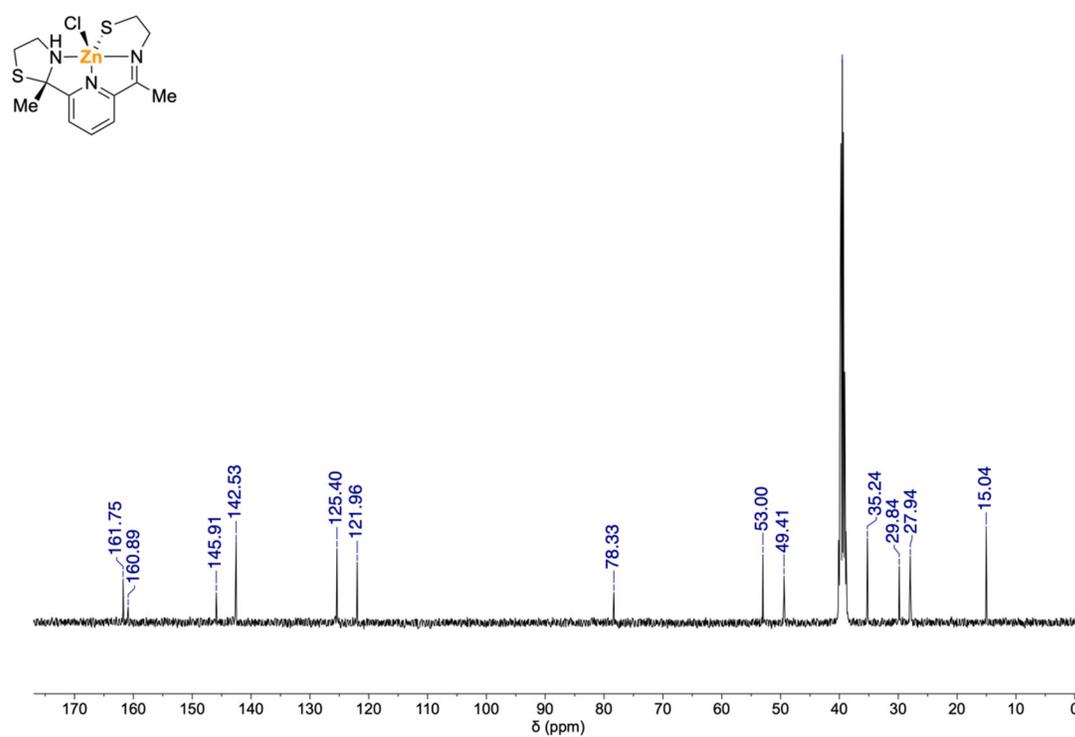
**Figure S3.**  $^{13}\text{C}$  NMR spectrum of **1** in  $d_6$ -DMSO.



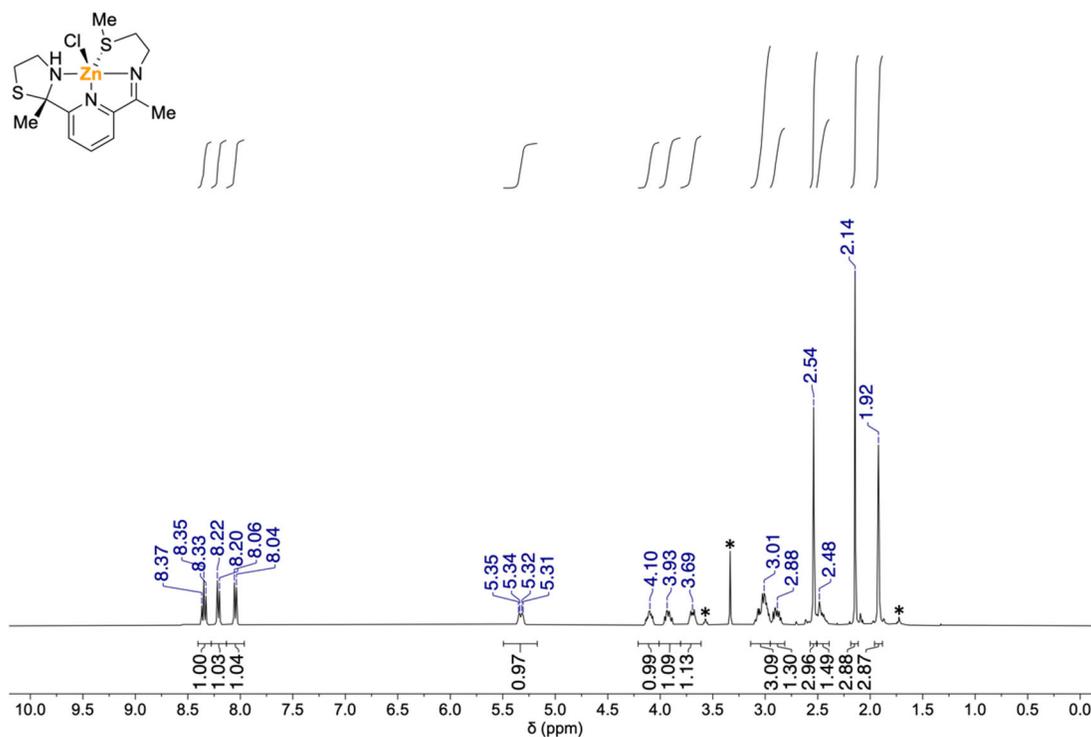
**Figure S4.** Variable temperature  $^1\text{H}$  NMR spectra of **1** in  $d_6$ -DMSO.



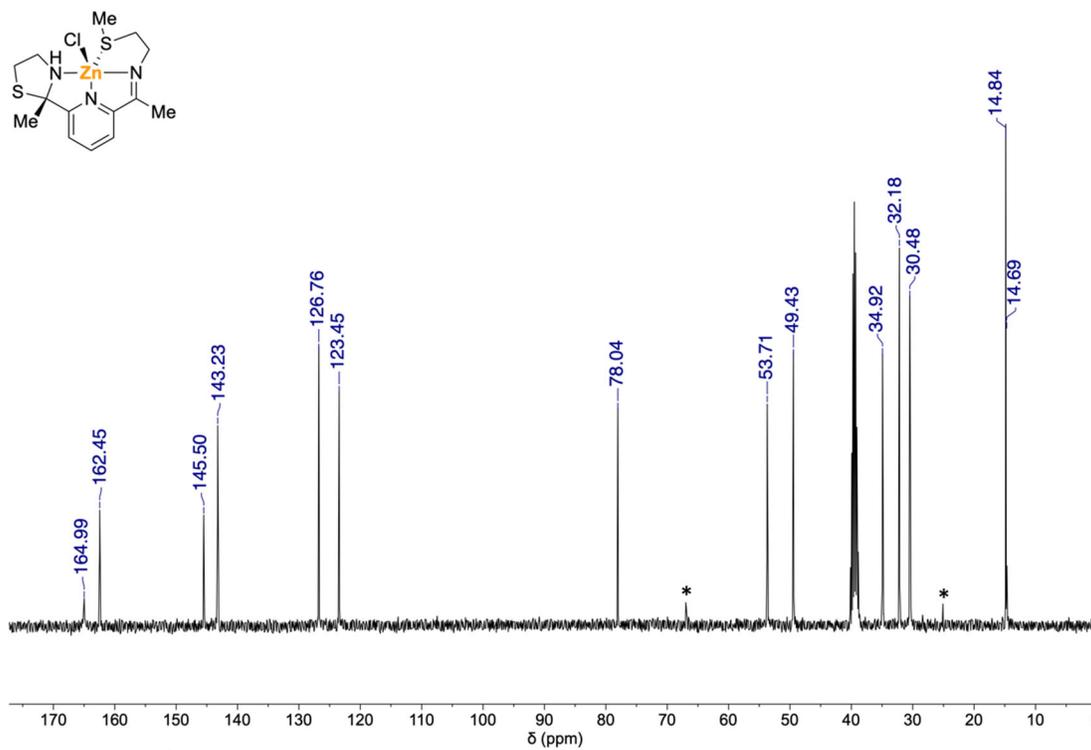
**Figure S5.**  $^1\text{H}$  NMR spectrum of **2-Cl** in  $d_6$ -DMSO. Trace DMF is present (\*).



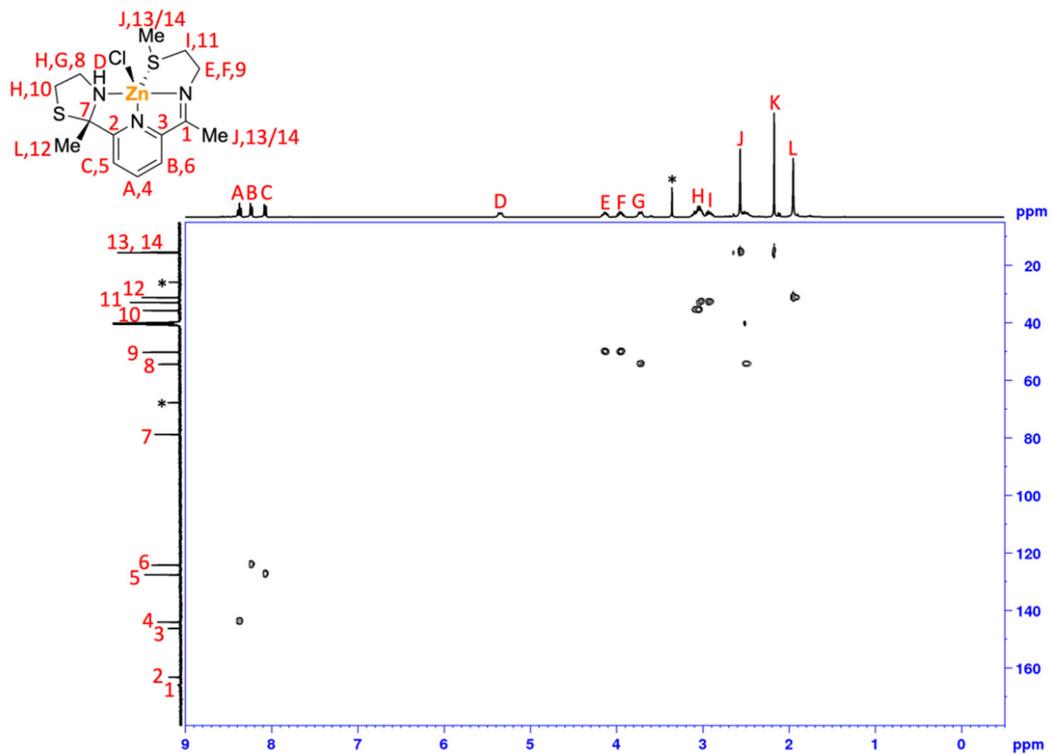
**Figure S6.**  $^{13}\text{C}$  NMR spectrum of **2-Cl** in  $d_6$ -DMSO.



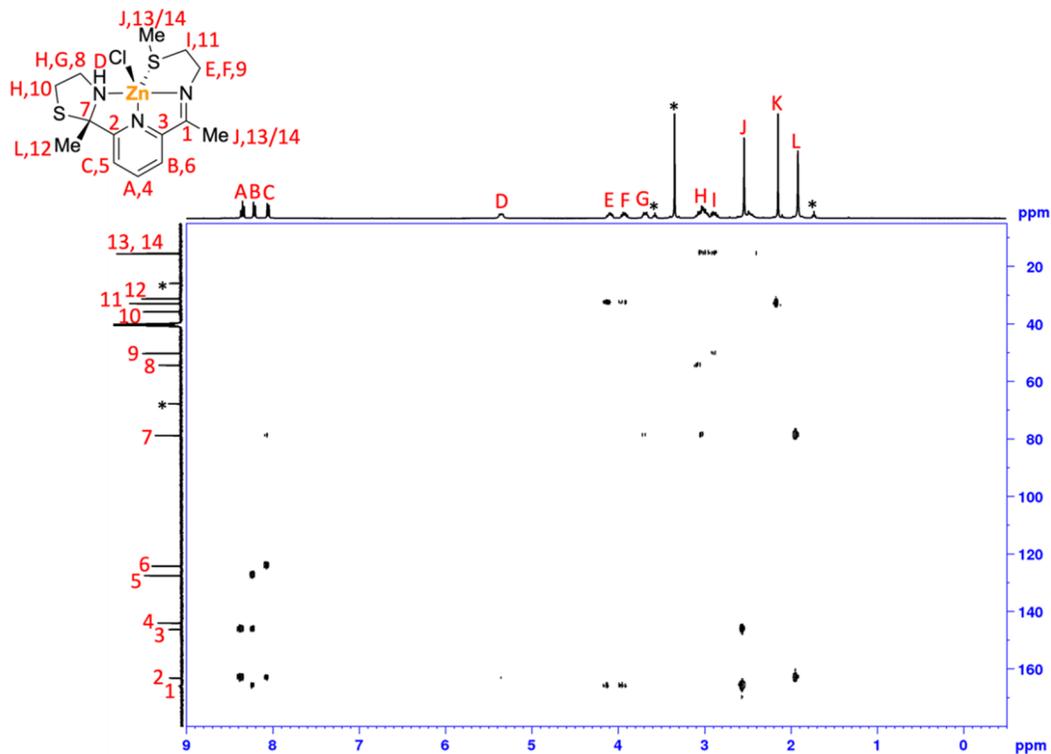
**Figure S7.**  $^1\text{H}$  NMR spectrum of methylation of 2-Cl in  $d_6$ -DMSO. Trace amounts of THF and water are present (\*).



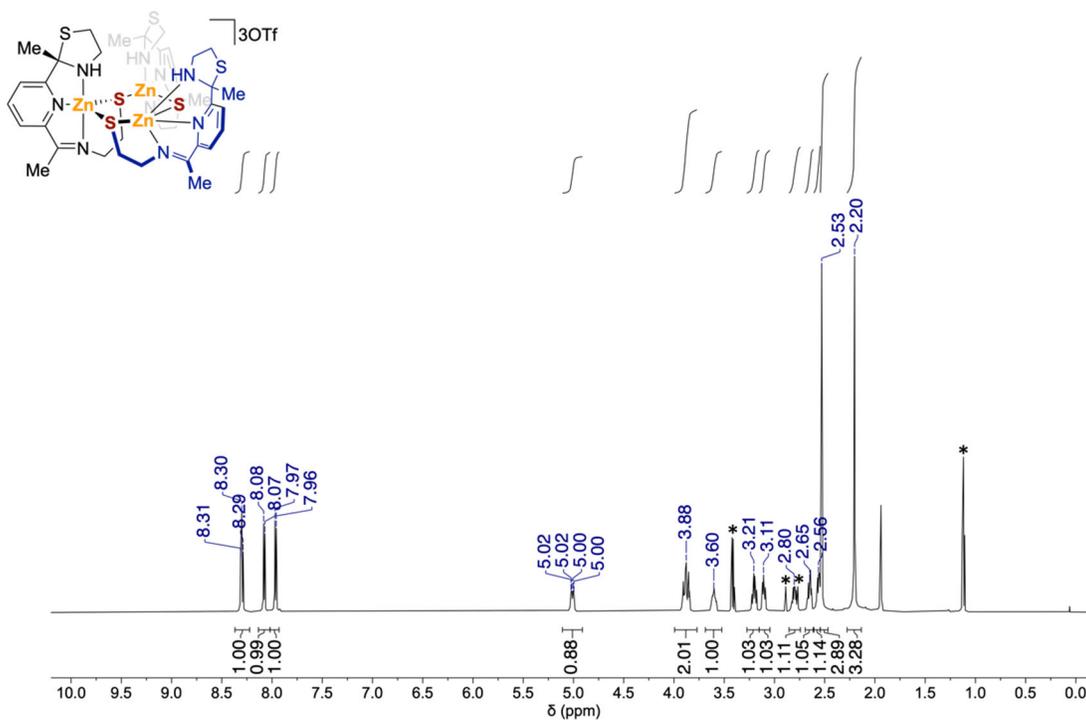
**Figure S8.**  $^{13}\text{C}$  NMR spectrum of methylation of 2-Cl in  $d_6$ -DMSO. Trace amounts of THF are present (\*).



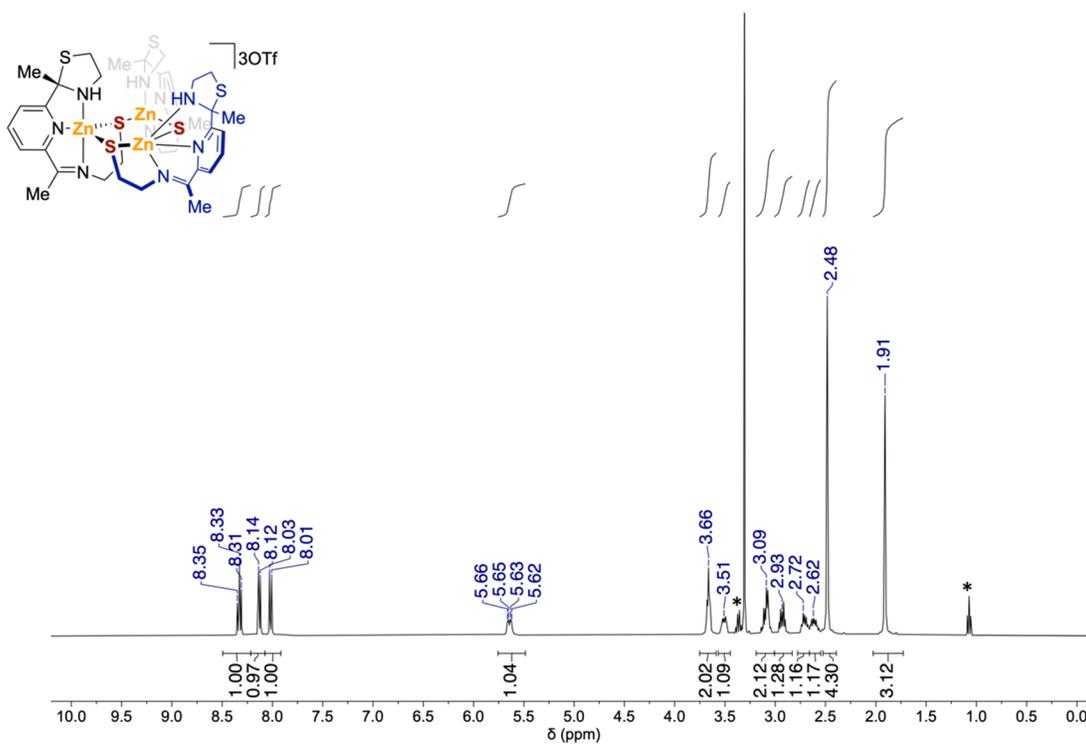
**Figure S9.** HSQC 2D NMR spectrum of methylation of **2-Cl** in  $\text{CD}_3\text{CN}$ . Trace amounts of water and THF are present (\*).



**Figure S10.** HMBC 2D NMR spectrum of methylation of **2-Cl** in  $\text{CD}_3\text{CN}$ . Trace amounts of water and THF are present (\*). NMR spectrum taken using non-linear technique.



**Figure S11.** <sup>1</sup>H NMR spectrum of [6-OTf]<sup>2+</sup> in CD<sub>3</sub>CN. Trace amounts of ether and DMF are present (\*).



**Figure S12.** <sup>1</sup>H NMR spectrum of [6-OTf]<sup>2+</sup> in *d*<sub>6</sub>-DMSO. Trace amounts of ether are present (\*).

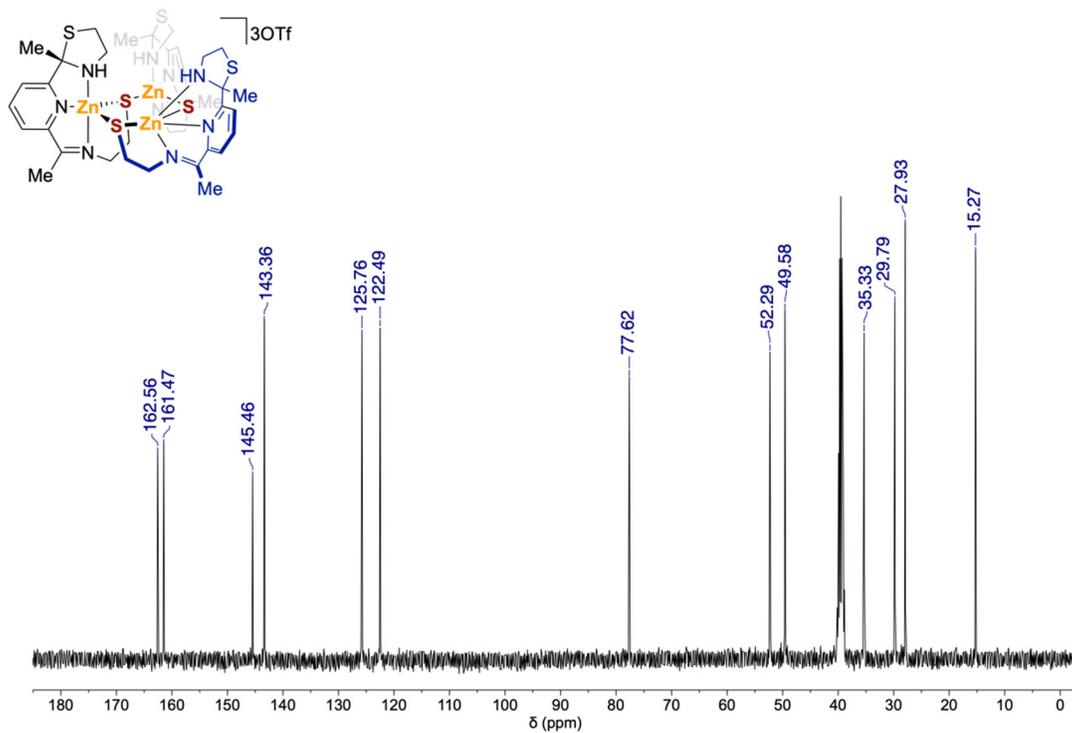


Figure S13. <sup>13</sup>C NMR spectrum of [6-OTf]<sup>2+</sup> in *d*<sub>6</sub>-DMSO.

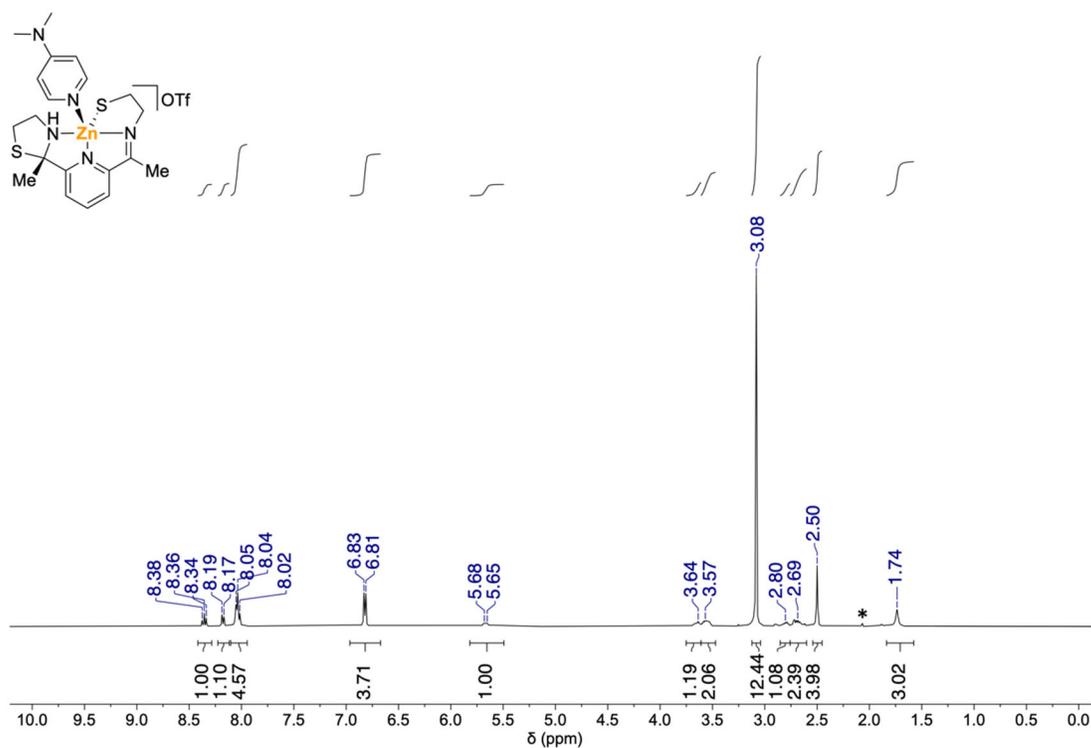
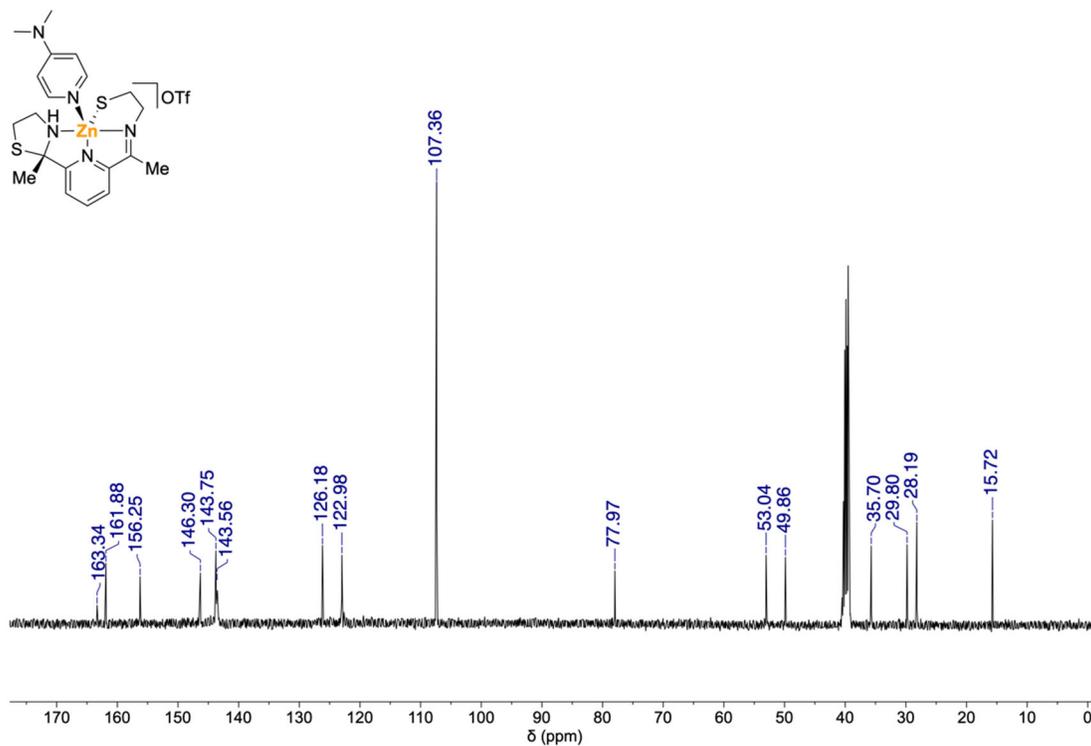
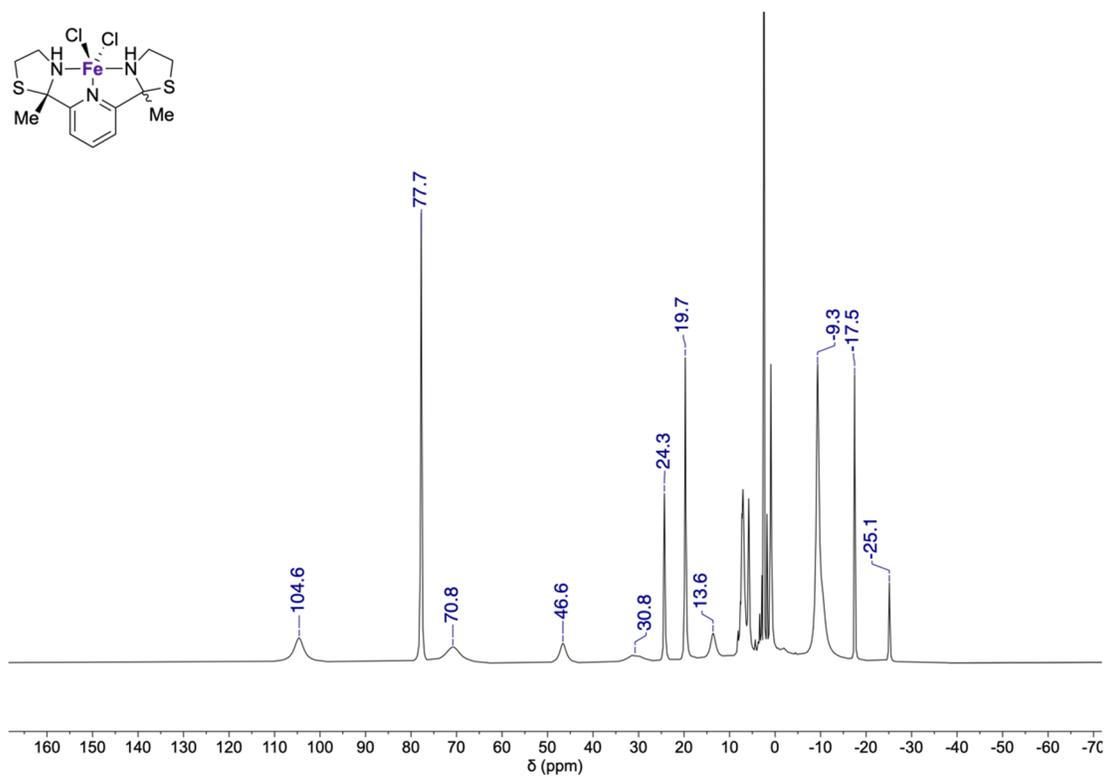


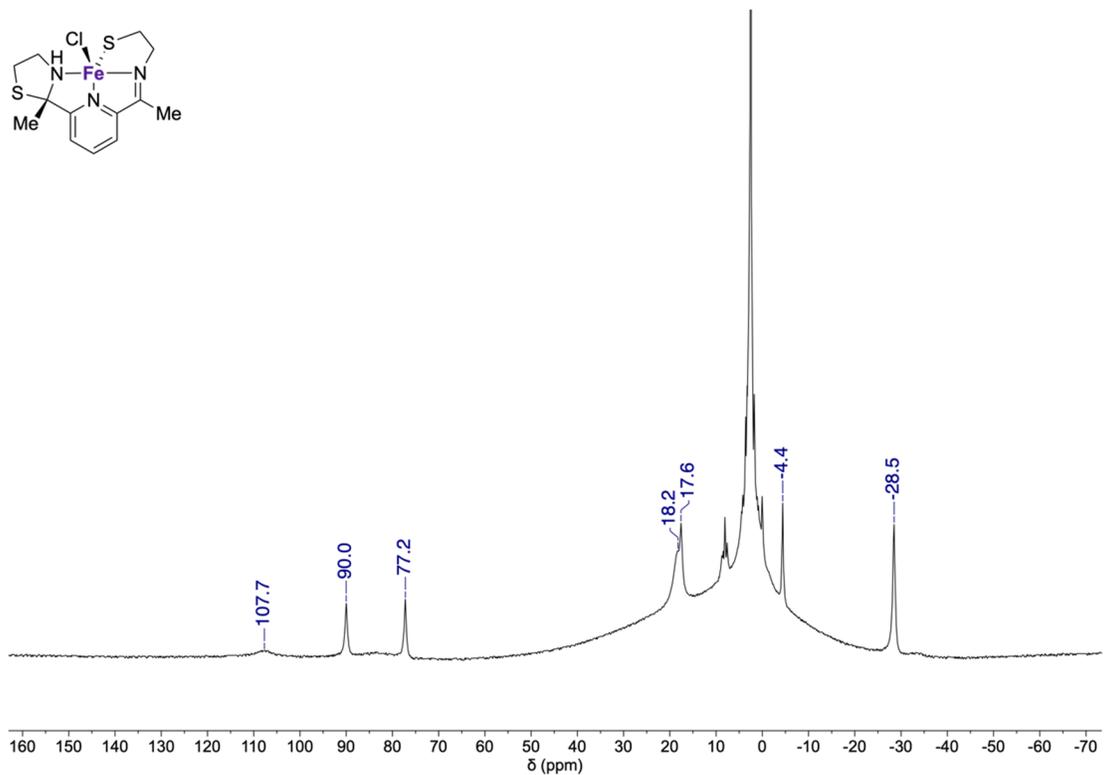
Figure S14. <sup>1</sup>H NMR spectrum of [2-DMAP][OTf] in *d*<sub>6</sub>-DMSO.



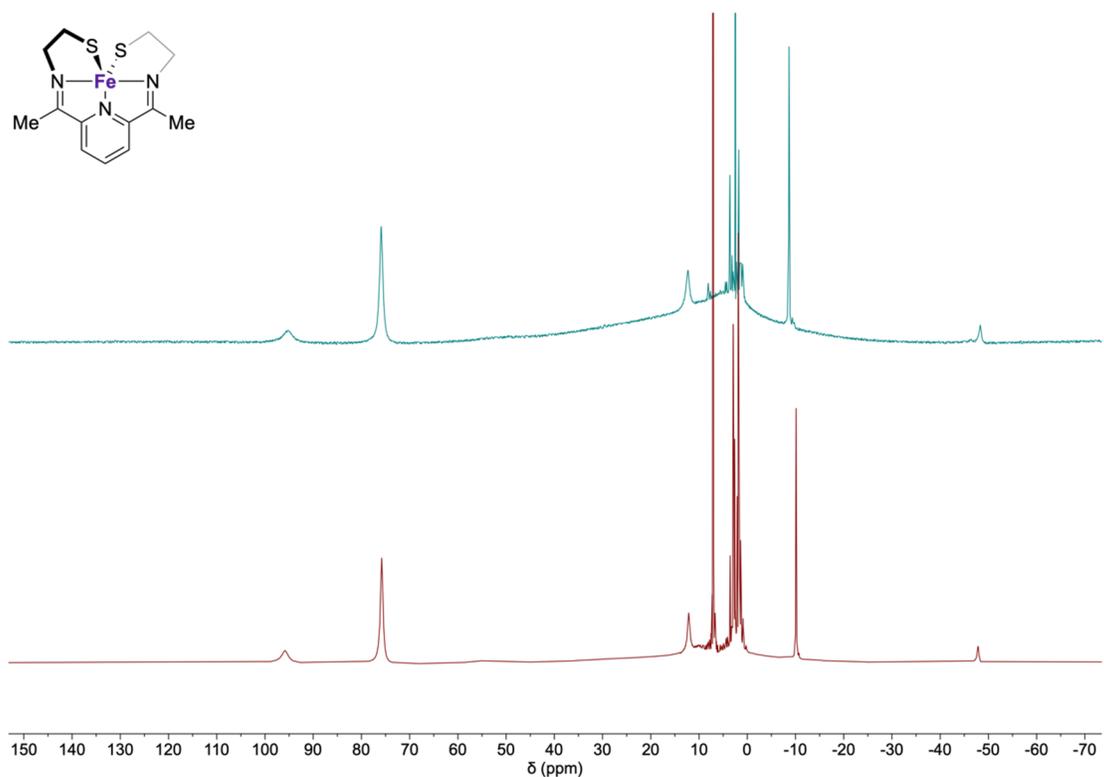
**Figure S15.**  $^{13}\text{C}$  NMR spectrum of [2-DMAP][OTf] in  $d_6$ -DMSO.



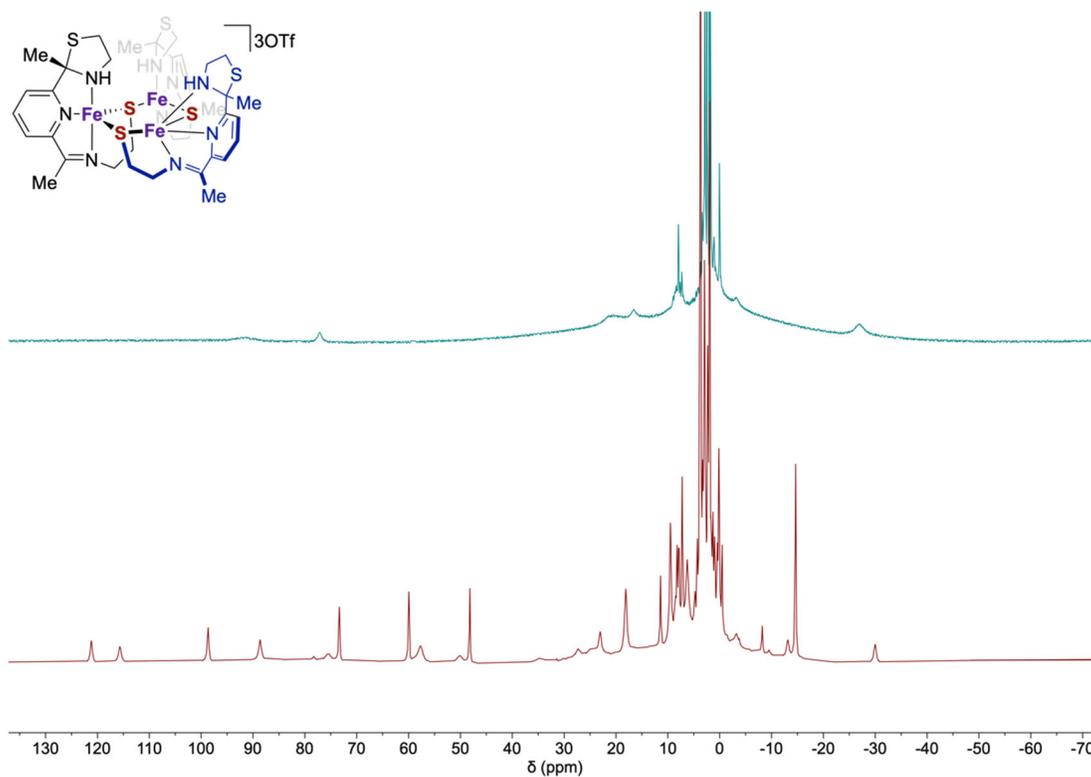
**Figure S16.**  $^1\text{H}$  NMR spectrum of 3 in  $d_6$ -DMSO.



**Figure S17.**  $^1\text{H}$  NMR spectrum of 4-Cl in  $d_6$ -DMSO.

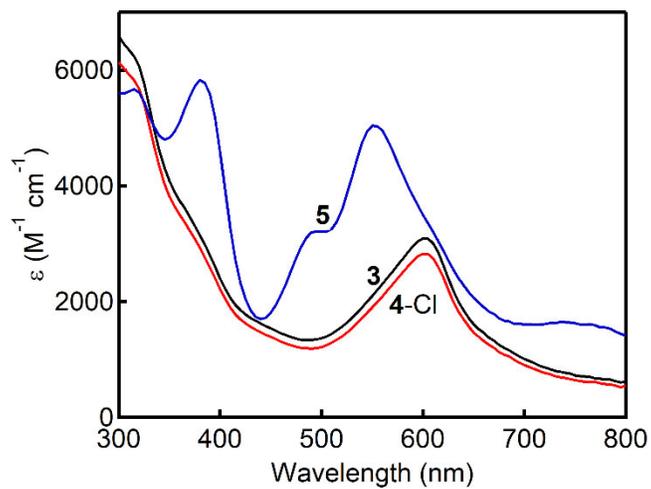


**Figure S18.**  $^1\text{H}$  NMR spectra of 5 in  $d_6$ -DMSO (top) and  $\text{C}_6\text{D}_6$  (bottom).

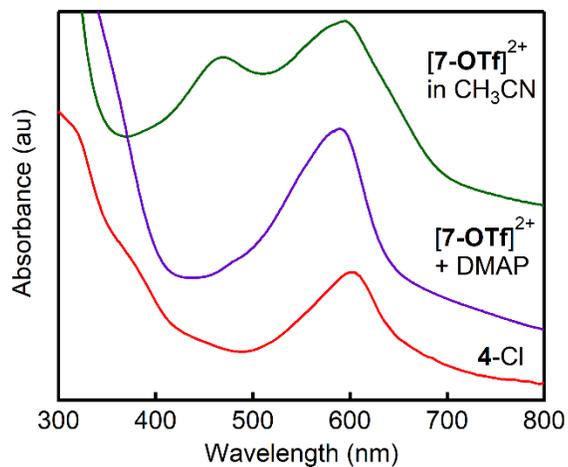


**Figure S19.**  $^1\text{H}$  NMR spectra of  $[\mathbf{7}\text{-OTf}]^{2+}$  in  $d_6\text{-DMSO}$  (top) and  $\text{CD}_3\text{CN}$  (bottom).

### Electronic Absorption Spectra

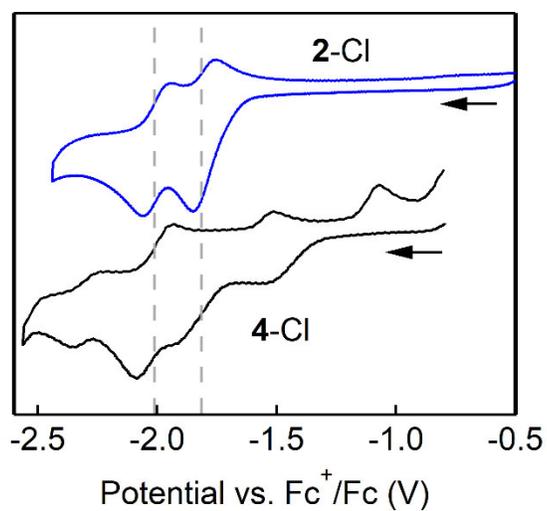


**Figure S20.** Electronic absorption spectra of  $\mathbf{3}$  in DMF ( $\times 300$ ),  $\mathbf{4}\text{-Cl}$  in DMF, and  $\mathbf{5}$  in THF.

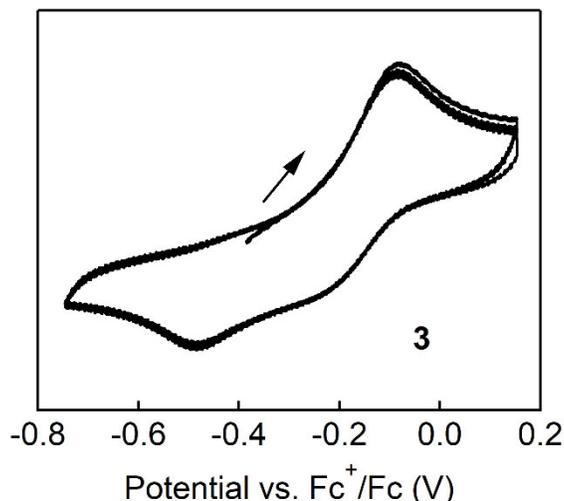


**Figure S21.** Comparison of absorption spectra of a solution of [7-OTf]<sup>2+</sup> in CH<sub>3</sub>CN before and after addition of DMAP. The spectrum of 4-Cl in DMF is included for comparison.

### Cyclic Voltammetry



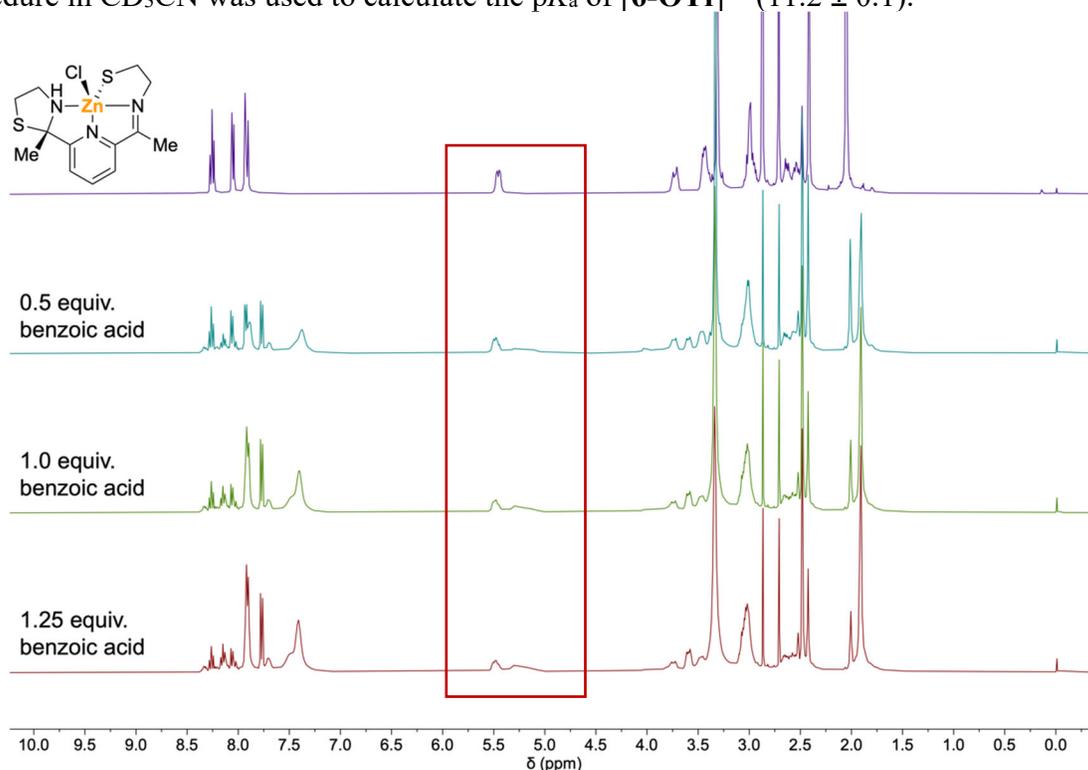
**Figure S22.** Comparison of CV data for 2-Cl and 4-Cl (0.1 M TBAPF<sub>6</sub> in DMF, GCE, scan rate = 100 mV s<sup>-1</sup>).



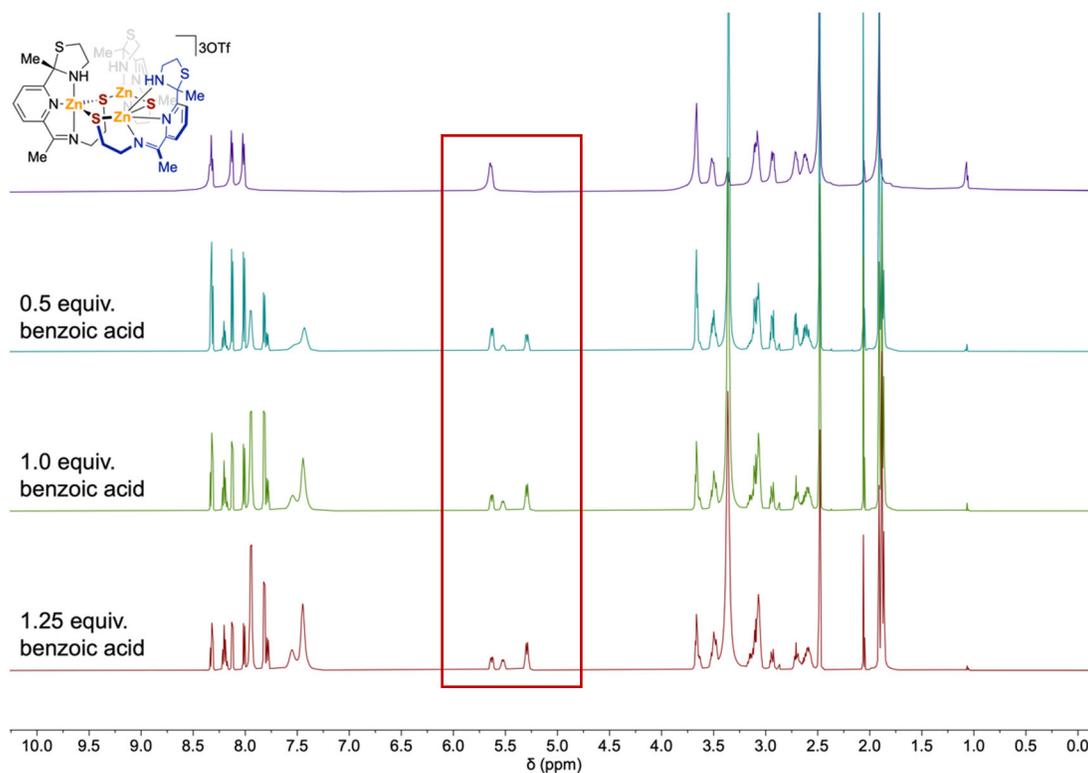
**Figure S23.** CV data for **3** (0.1 M TBAPF<sub>6</sub> in DMF, GCE, scan rate = 100 mV s<sup>-1</sup>).

### pK<sub>a</sub> Calculations

Under ambient conditions, three NMR tubes were each charged with a stock solution of **2-Cl** (0.020 g, 1.0 equiv, 0.052 mmol) in *d*<sub>6</sub>-DMSO. A stock solution of benzoic acid in *d*<sub>6</sub>-DMSO was added to each NMR tube (0.5 equiv, 1.0 equiv, and 1.25 equiv respectively). <sup>1</sup>H NMR spectra were taken of each reaction mixture and the integration of the amine H peaks (δ 4.75–5.75 ppm) was used to calculate the mole percent present at equilibrium. Averaged pK<sub>a</sub>(**2-Cl**) 10.8 ± 0.1. A similar procedure in CD<sub>3</sub>CN was used to calculate the pK<sub>a</sub> of [**6-OTf**]<sup>2+</sup> (11.2 ± 0.1).

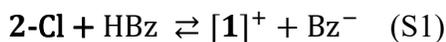


**Figure S24.** <sup>1</sup>H NMR spectra of **2-Cl** with added benzoic acid in *d*<sub>6</sub>-DMSO.

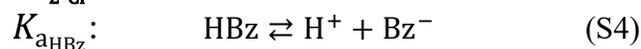
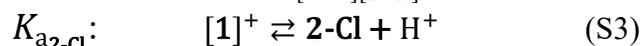


**Figure S25.**  $^1\text{H}$  NMR spectra of  $[\mathbf{6}\text{-OTf}]^{2+}$  with added benzoic acid in  $\text{CD}_3\text{CN}$ .

### $\text{p}K_{\text{a}}$ calculation



$$K_{\text{eq}} = \frac{[\mathbf{1}^+][\text{Bz}^-]}{[\text{HBz}][\mathbf{2}\text{-Cl}]} \quad (\text{S2})$$

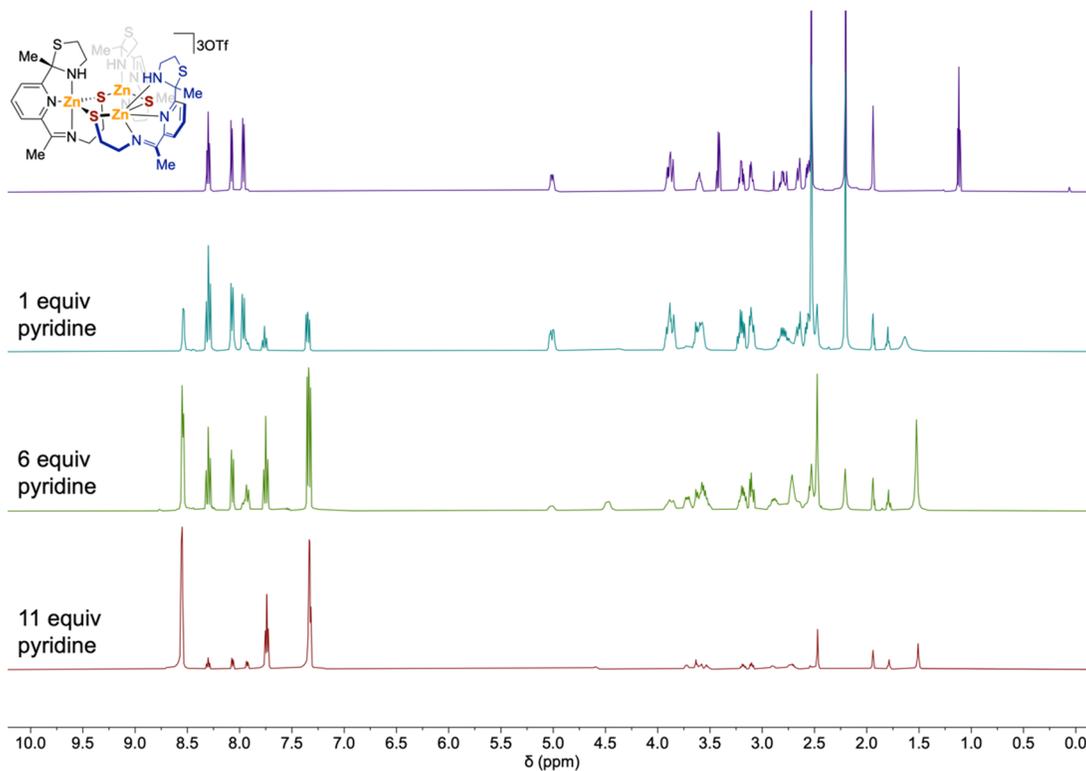


$$K_{\text{a}2\text{-Cl}} = \frac{K_{\text{aHBz}}}{K_{\text{eq}}} \quad (\text{S5})$$

As shown above, this calculation does not take into account the coordination of benzoate to the open  $\text{Zn}^{2+}$  coordination site in the protonation product of  $\mathbf{2}\text{-Cl}$ , here labeled as  $[\mathbf{1}]^+$ , and so our calculated  $\text{p}K_{\text{a}}$  values may be slightly higher than the actual value.

### Lewis Base-Induced Trimer Dissociation

**Pyridine equivalents study.** In the glovebox, an NMR tube was charged with a solution of [6-OTf]<sup>2+</sup> (0.020 g, 1.0 equiv, 0.040 mmol) in CD<sub>3</sub>CN (0.7 mL) and increasing amounts of pyridine were added via syringe (1–11 equiv). <sup>1</sup>H NMR spectra were measured between additions.



**Figure S26.** <sup>1</sup>H NMR spectra of pyridine addition to a CD<sub>3</sub>CN solution of [6-OTf]<sup>2+</sup>.

**Amine binding experiment.** In a representative procedure, under ambient conditions, a scintillation vial equipped with a stir bar was charged with [6-OTf]<sup>2+</sup> (0.020 g, 1.0 equiv, 0.040 mmol) and isopropylamine (6.6 μL, 2.0 equiv, 0.081 mmol) in CD<sub>3</sub>CN (0.7 mL). The <sup>1</sup>H NMR spectrum was taken after addition.

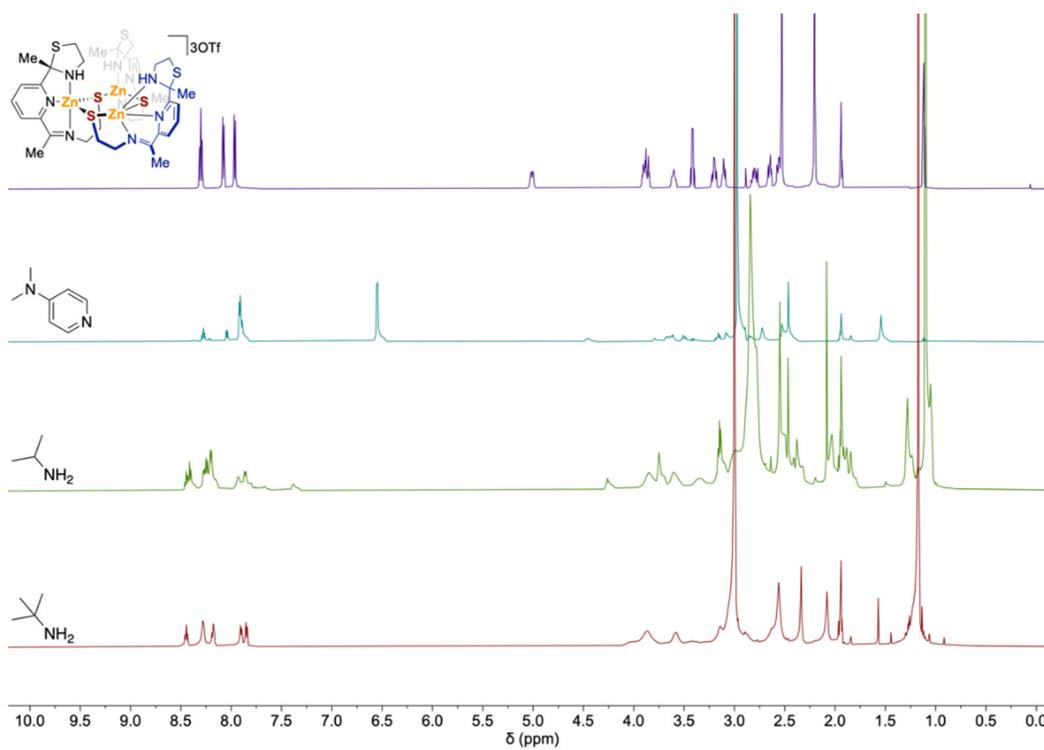


Figure S27.  $^1\text{H}$  NMR spectra of amine binding to  $[\mathbf{6}\text{-OTf}]^{2+}$  in  $\text{CD}_3\text{CN}$ .

### DOSY NMR Studies

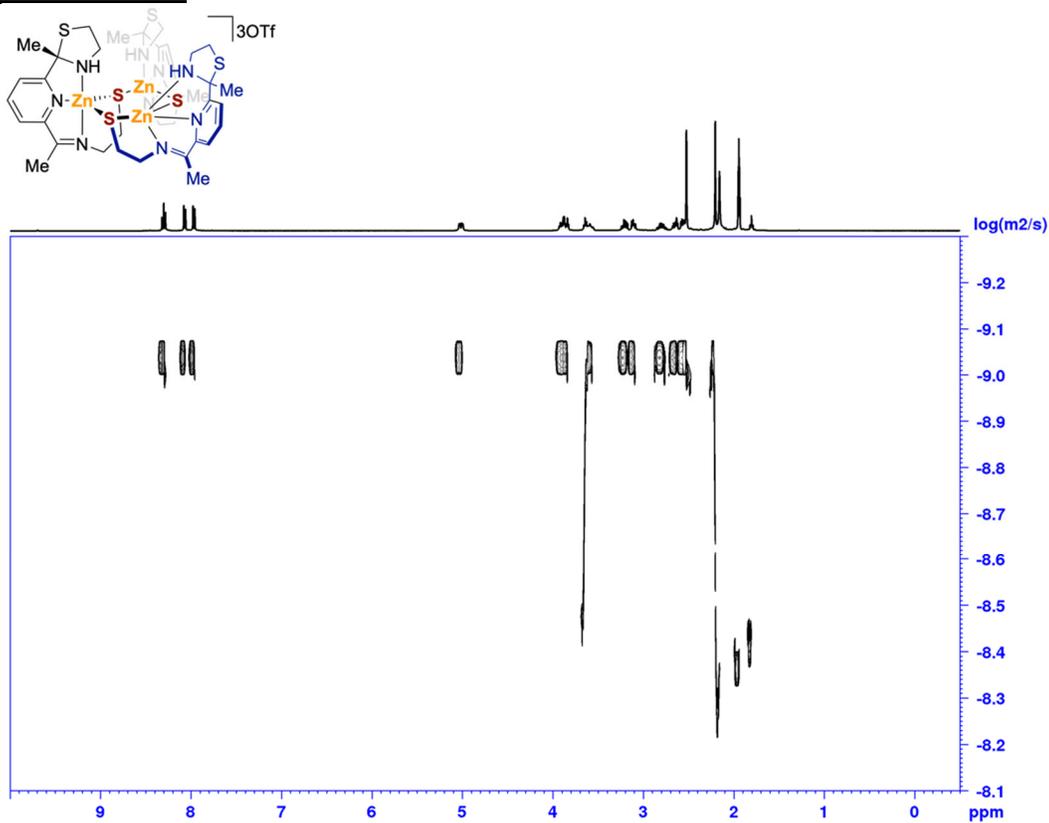
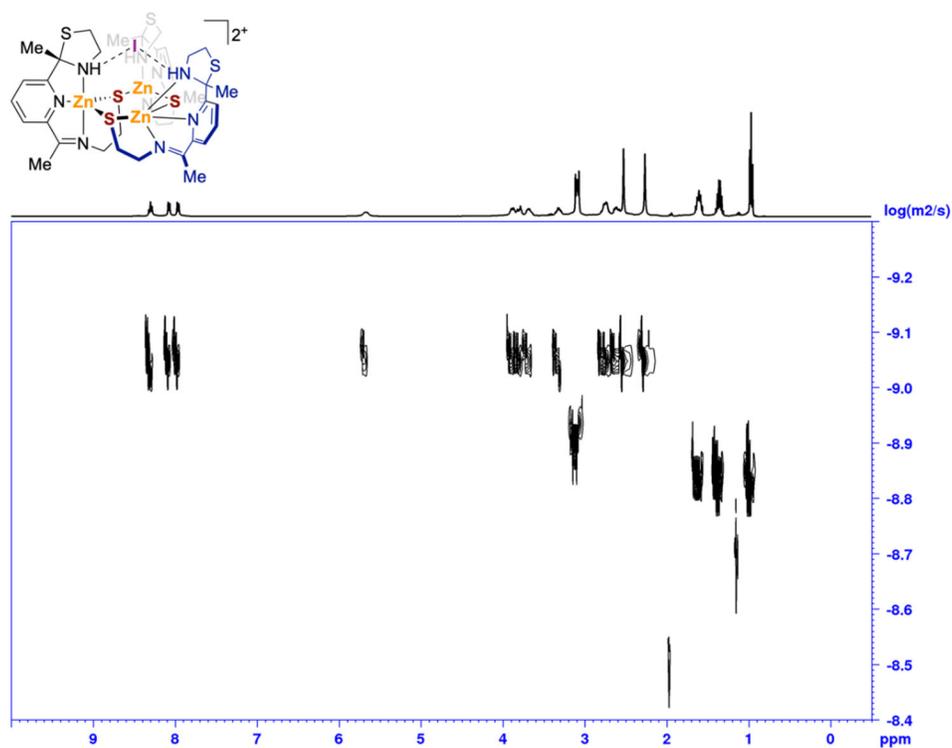
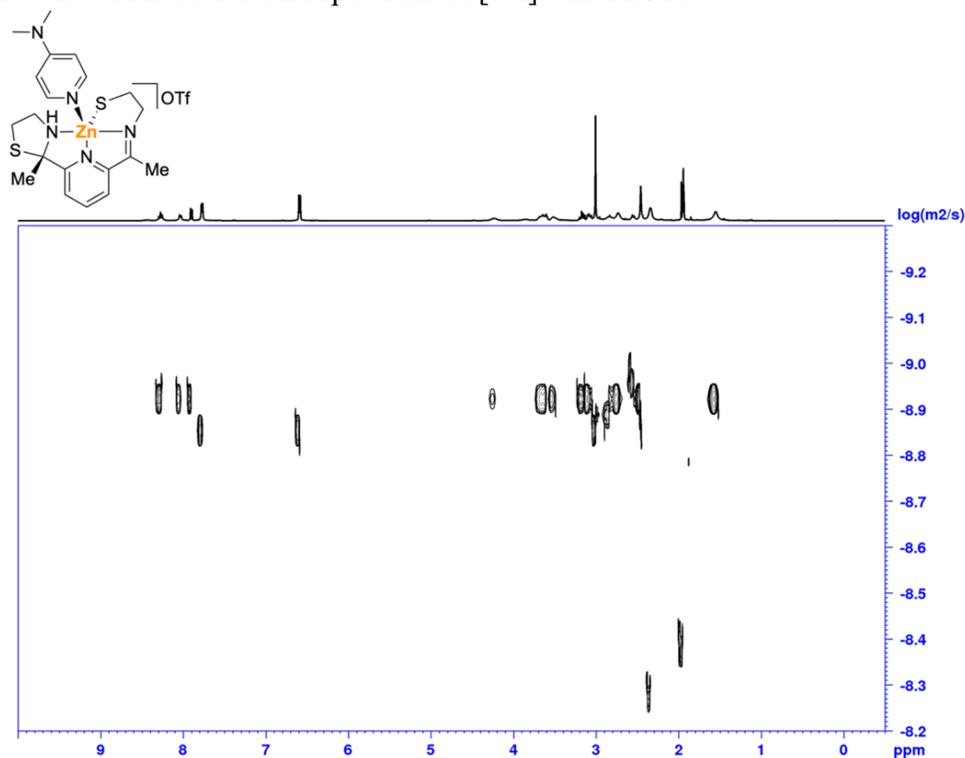


Figure S28.  $^1\text{H}$  DOSY NMR spectrum of  $[\mathbf{6}\text{-OTf}]^{2+}$  in  $\text{CD}_3\text{CN}$ .

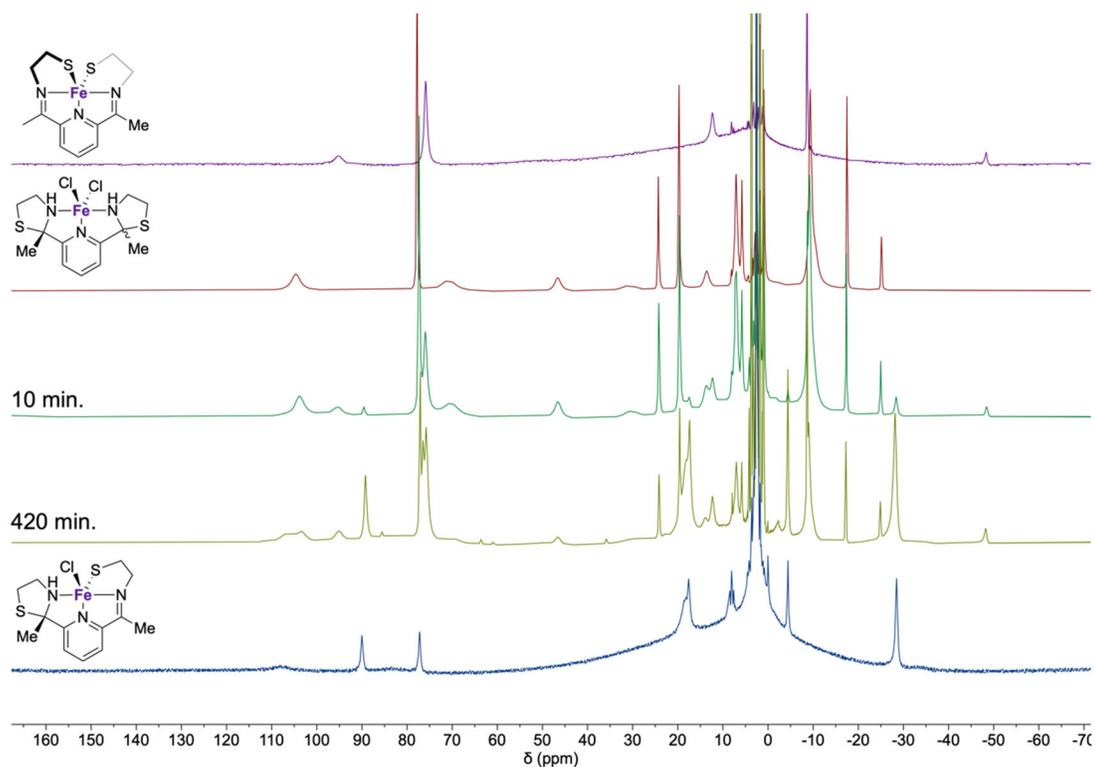


**Figure S29.**  $^1\text{H}$  DOSY NMR spectrum of  $[\mathbf{6-1}]^{2+}$  in  $\text{CD}_3\text{CN}$ .



**Figure S30.**  $^1\text{H}$  DOSY NMR spectrum of  $[\mathbf{2-DMAP}][\text{OTf}]$  in  $\text{CD}_3\text{CN}$ . Excess of DMAP is present and exchanging in solution, resulting in a higher diffusion constant for DMAP signals.

**Comproportionation Reaction of 5 and 3.** In the glovebox, a scintillation vial was charged with **3** (0.024 g, 1.0 equiv, 0.059 mmol) and **5** (0.020 g, 1.0 equiv, 0.059 mmol). The solids were taken up in 1 mL of  $d_6$ -DMSO and transferred to an NMR tube.  $^1\text{H}$  NMR spectra were taken of this mixture over the next 7 h. The taped NMR tube was stored in a 50 °C oil bath between measurements.



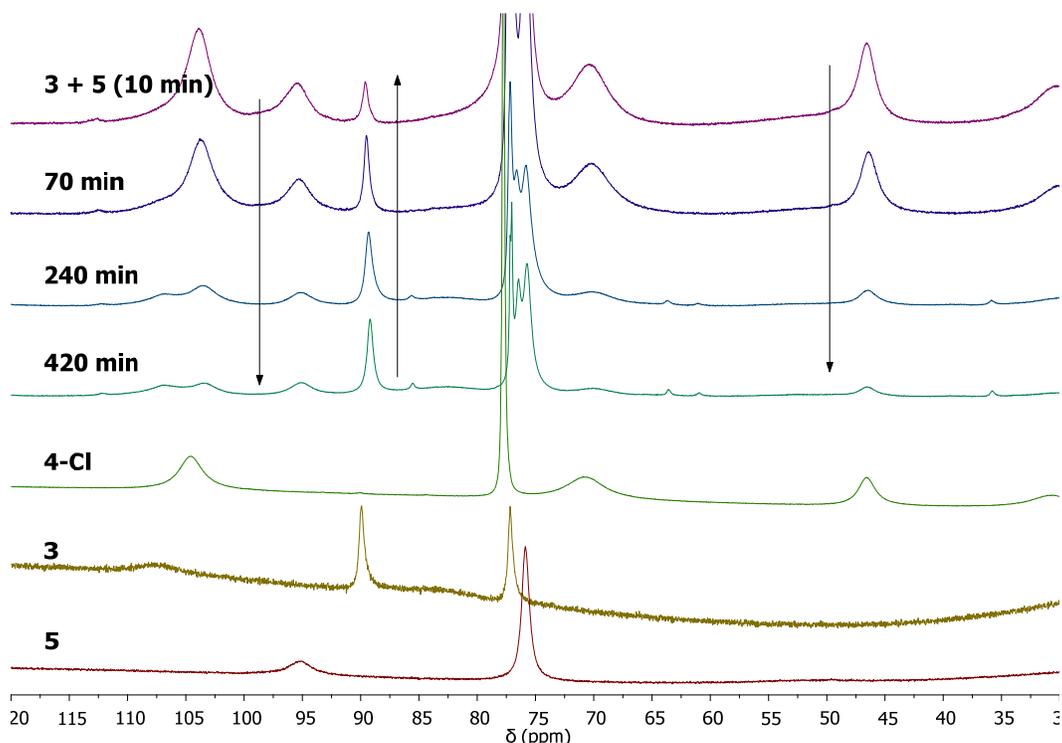
**Figure S31.**  $^1\text{H}$  NMR spectra of **5** and **3** comproportionation experiment in  $d_6$ -DMSO.

**Table S1.** Normalized integrals of **5**, **3**, and **4-Cl**.

| Time (min) | <b>5</b> <sup>b</sup> | <b>3</b> <sup>c</sup> | <b>4-Cl</b> <sup>d</sup> |
|------------|-----------------------|-----------------------|--------------------------|
| 10         | 3.93                  | 7.14                  | 1.00                     |
| 70         | 1.47                  | 2.33                  | 1.00                     |
| 240        | 0.35                  | 0.39                  | 1.00                     |
| 420        | 0.43 <sup>a</sup>     | 0.21                  | 1.00                     |

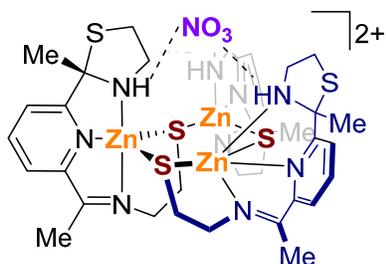
<sup>a</sup> This number is likely higher than expected due to broad overlapping peaks.

<sup>b</sup> Peak integrated at  $\delta$  94.9. <sup>c</sup> Peak integrated at  $\delta$  46.7. <sup>d</sup> Peak integrated at  $\delta$  88.9.

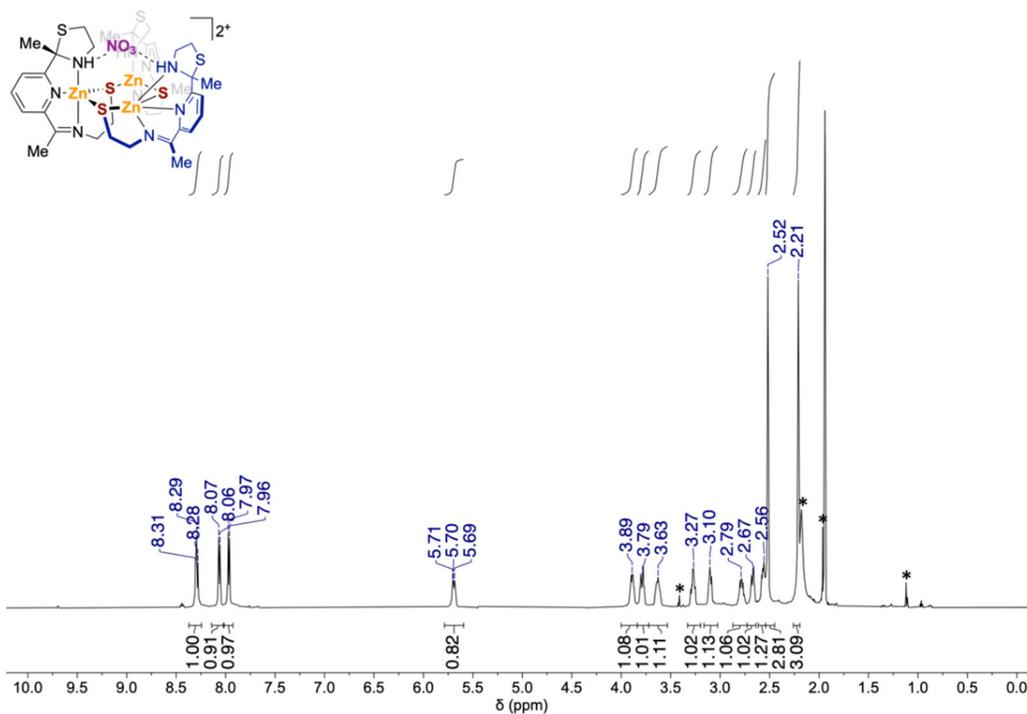


**Figure S32.**  $^1\text{H}$  NMR spectra of **5** and **3** comproportionation experiment in  $d_6$ -DMSO over time. The top four spectra are normalized to the  $d_6$ -DMSO signal.

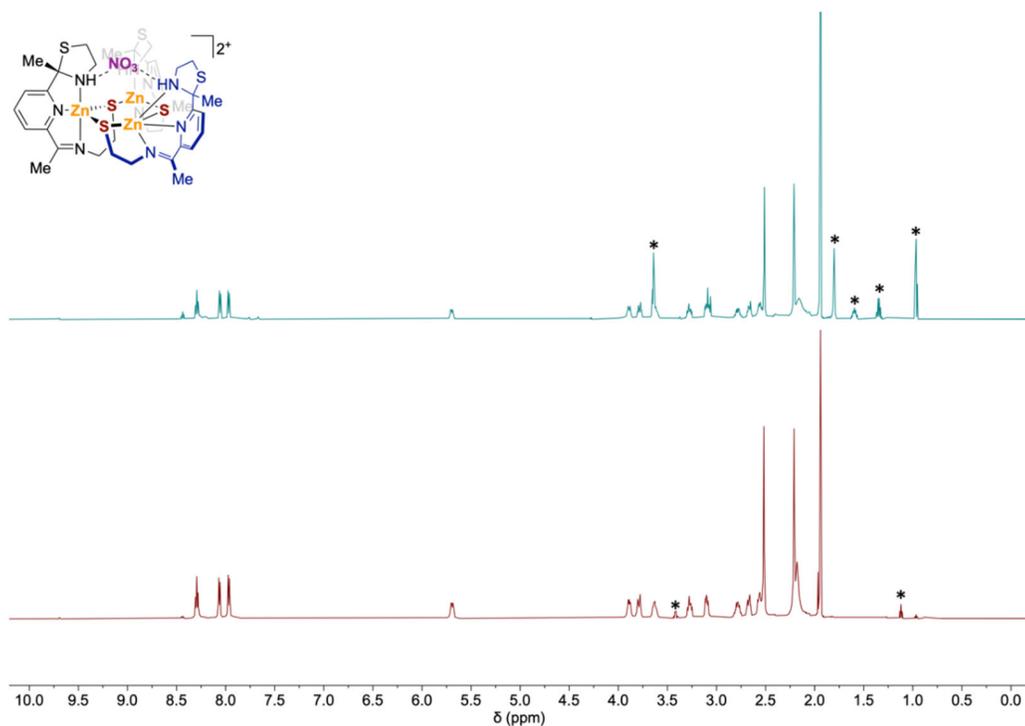
### Anion Binding Studies of $[\mathbf{6}\text{-OTf}]^{2+}$



**Nitrate exchange to form  $[\mathbf{6}\text{-NO}_3]^{2+}$ .** Under ambient conditions, a scintillation vial was charged with a solution of  $[\mathbf{6}\text{-OTf}]^{2+}$  (0.02 g, 1 equiv, 0.01 mmol) in MeCN (3 mL). To this solution was added a solution of TBANO<sub>3</sub> (0.01 g, 3 equiv, 0.04 mmol) in MeCN (3 mL). The reaction mixture was stirred and then dried *in vacuo*, the resulting white solid was washed with THF, dried again. Single crystals for XRD were grown by vapor diffusion of diethyl ether into an acetonitrile solution of this product.  $^1\text{H}$  NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  8.29 (t,  $J = 7.9$ , 1H), 8.07 (d,  $J = 7.7$ , 1H), 7.97 (d,  $J = 8.1$ , 1H), 3.98 (dd,  $J = 4.4, 12.2$  Hz, 1H), 3.79 (m, 1H), 3.63 (m, 1H), 3.27 (m, 1H), 3.10 (m, 1H), 2.79 (m, 1H), 2.67 (m, 1H), 2.56 (m, 1H), 2.52 (m, 1H), 2.21 (m, 1H). Although samples prepared in this manner showed the same  $^1\text{H}$  NMR spectra due to stronger NO<sub>3</sub><sup>-</sup> hydrogen bonding, the outer-sphere anions remained a mixture of triflate and nitrate.



**Figure S33.**  $^1H$  NMR spectrum of  $[6-NO_3]^{2+}$  in  $CD_3CN$ . Trace amounts of ether, MeCN, and water are present (\*).



**Figure S34.** Comparison of  $^1H$  NMR spectra of  $[6-NO_3]^{2+}$  in  $CD_3CN$  prepared with 1 equiv TBANO<sub>3</sub> (top) and 3 equiv TBANO<sub>3</sub> (bottom). Trace amounts of ether, MeCN, THF and TBA are present (\*).

**Iodide anion exchange to form [6-I]<sup>2+</sup>.** Under ambient conditions, an NMR tube was charged with [6-OTf]<sup>2+</sup> (0.020 g, 1 equiv, 0.013 mmol) in CD<sub>3</sub>CN (ca. 0.6 mL). A stock solution of TBAI was prepared (91 mM in CD<sub>3</sub>CN) and added to the NMR tube (0–3 equiv/trimer). <sup>1</sup>H NMR spectra were measured after each addition.

### **Crystallographic Details**

CCDC 2167681–2167688 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Crystallographic data was collected on crystals mounted on a MiTeGen loop using Paratone oil, then placed under a cold nitrogen stream on a Bruker APEX-II diffractometer (**1**, **3**, [6-OTf](OTf)<sub>2</sub>, [2-DMAP][OTf], **2-I**) or a Bruker Photon-II diffractometer (**2-Cl**, [7-OTf](OTf)<sub>2</sub>, [6-NO<sub>3</sub>](NO<sub>3</sub>)(OTf)) using a combination of ω- and φ-scans of 0.5°. Data were corrected for absorption and polarization effects and analyzed for space group determination.<sup>3</sup> The structure was solved by dual-space methods and expanded routinely.<sup>4</sup> The model was refined by full-matrix least-squares analysis of F<sup>2</sup> against all reflections.<sup>5</sup> All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Unless otherwise noted, all data was solved with the SHELXT<sup>4</sup> structure solution program using Intrinsic Phasing and refined with the SHELXL<sup>5</sup> refinement package using Least Squares minimization on Olex2.<sup>6</sup> All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Atomic displacement parameters for the hydrogens were tied to the equivalent isotropic displacement parameter of the atom to which they are bonded ( $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl,  $1.2U_{\text{eq}}(\text{C})$  for all others).

**Refinement details of [6-OTf](OTf)<sub>2</sub>.** There is additional, diffuse, disordered solvent in the lattice. This solvent was accounted for using the SQUEEZE routine as implemented in PLATON.<sup>7</sup> A void space of 156 Å<sup>3</sup> accounting for 30 electrons was corrected for. One triflate is hydrogen bonded by the amine nitrogen atoms. The other two anions are less well-bound and as a result one has some disorder. A rotational disorder in the CF<sub>3</sub> group that was modeled as 0.77:0.23 occupancy.

**Refinement details of [7-OTf](OTf)<sub>2</sub>.** There is additional, diffuse, disordered solvent in the lattice. This solvent was accounted for using the SQUEEZE routine as implemented in PLATON.<sup>7</sup> A void space of 269 Å<sup>3</sup> accounting for 60 electrons was corrected for. One triflate is hydrogen bonded by the amine nitrogen atoms. The other two anions are less well-bound and as a result have some disorder. One has rotational disorder in the CF<sub>3</sub> group that was modeled as 0.66:0.34 occupancy. The second disordered triflate has positional disorder and is modeled at 0.74:0.26 occupancy. Mild bond distance restraints were applied to the models.

**Refinement details of [6-NO<sub>3</sub>](OTf)(NO<sub>3</sub>).** The zinc complex crystallizes as colorless needle-like crystals from an acetonitrile solution. There are two molecules of the zinc cation, five nitrate anions, one triflate and six molecules of acetonitrile of crystallization in the unit cell of the primitive, centrosymmetric, triclinic space group P-1. Thus, in the asymmetric unit there are one zinc complex cation, 2.5 nitrate anions, 0.5 triflate anion and three acetonitrile molecules of crystallization.

The zinc complex, two nitrate anions and three acetonitrile molecules are all well-behaved and modeled routinely. One nitrate and the triflate are disordered across independent inversion centers. These two molecules were modeled with symmetry restraints imposed by the space group removed (PART -1) and at 50% occupancy. The triflate is effectively disordered and superimposed upon itself. Attempts to model this as a fully occupied molecule resulted in poor refinement statistics. Notably, low angle data agreed poorly and low angle reflections became outliers ( $F_o \text{ v } F_c > 10 \text{ sigma}$ ). The nitrate was assigned on two factors: a half occupancy triflate requires an additional half negative charge per asymmetric unit for charge balance and inspection of the void space at that location. Void space analysis (performed through SQUEEZE as part of PLATON) revealed a void of  $46 \text{ \AA}^3$  accounting for 33 electrons. This amount of electron density is too great to be another acetonitrile and corresponds well with one nitrate per unit cell or one half nitrate per asymmetric unit. This model was clearly superior because in the final refinement cycles no restraints were applied to the model yielding very satisfactory refinement statistics.

**Table S2.** Crystal data and structure refinement for **1** and **2-Cl**.

| Compound                                | <b>1</b>   | <b>2-Cl</b>   |
|---|--|---|
| Empirical formula                       | C <sub>17</sub> H <sub>27</sub> Cl <sub>2</sub> N <sub>3</sub> OS <sub>2</sub> Zn  | C <sub>17</sub> H <sub>26</sub> ClN <sub>3</sub> OS <sub>2</sub> Zn   |
| Formula weight                          | 489.80   | 453.35  |
| Temperature                             | 120.0 K  | 120.0 K   |
| Crystal system                          | monoclinic   | triclinic   |
| Space group                             | Cc   | P-1   |
| Unit Cell Dimensions                    | $a = 7.4771(10) \text{ \AA}$<br>$b = 26.631(4) \text{ \AA}$<br>$c = 11.1219(14) \text{ \AA}$<br>$\alpha = 90^\circ$<br>$\beta = 107.701(2)^\circ$<br>$\gamma = 90^\circ$ | $a = 9.3375(7) \text{ \AA}$<br>$b = 10.4522(8) \text{ \AA}$<br>$c = 12.1145(10) \text{ \AA}$<br>$\alpha = 113.635(2)^\circ$<br>$\beta = 90.407(2)^\circ$<br>$\gamma = 108.202(2)^\circ$ |
| Volume                                  | 2109.8(5) Å <sup>3</sup>   | 1017.00(14) Å <sup>3</sup>  |
| Z                                       | 4  | 2   |
| Density (calculated)                    | 1.542 g.cm <sup>-3</sup>   | 1.480 g.cm <sup>-3</sup>  |
| Absorption coefficient ( $\mu$ )        | 1.627 mm <sup>-1</sup>   | 1.555 mm <sup>-1</sup>  |
| F(000)                                  | 1016.0   | 472.0   |
| Crystal color/ habit                    | colorless/rod  | colorless/rod   |
| Crystal size                            | 0.309 × 0.105 × 0.052 mm <sup>3</sup>  | 0.274 × 0.075 × 0.055 mm <sup>3</sup>   |
| Radiation                               | MoK $\alpha$ ( $\lambda = 0.71073$ )   | MoK $\alpha$ ( $\lambda = 0.71073$ )  |
| 2 $\Theta$ range for data collection    | 3.058° to 56.892°  | 3.714° to 56.534°   |
| Index ranges                            | -9 ≤ h ≤ 10, -35 ≤ k ≤ 35, -14 ≤ l ≤ 14  | -12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -16 ≤ l ≤ 16  |
| Reflections collected                   | 20305  | 23457   |
| Independent reflections                 | 5292 [R <sub>int</sub> = 0.0240]   | 5051 [R <sub>int</sub> = 0.0415]  |
| Refinement method                       | Full-matrix least-squares on F <sup>2</sup>  | Full-matrix least-squares on F <sup>2</sup>   |
| Data/restraints/parameters              | 5292/2/246   | 5051/0/228  |
| Goodness-of-fit on F <sup>2</sup>       | 1.048  | 1.090   |
| Final R indexes [ $I \geq 2\sigma(I)$ ] | R <sub>1</sub> = 0.0224, wR <sub>2</sub> = 0.0519  | R <sub>1</sub> = 0.0377, wR <sub>2</sub> = 0.0764   |
| Final R indexes [all data]              | R <sub>1</sub> = 0.0240, wR <sub>2</sub> = 0.0526  | R <sub>1</sub> = 0.0460, wR <sub>2</sub> = 0.0790   |
| Largest diff. peak/ hole                | 0.80/-0.30 e <sup>-</sup> .Å <sup>-3</sup>   | 0.72/-0.43 e <sup>-</sup> .Å <sup>-3</sup>  |

**Table S3.** Crystal data and structure refinement for **2-I** and **[2-DMAP][OTf]**.

| Compound                                | <b>2-I</b>   | <b>[2-DMAP][OTf]</b>  |
|---|--|---|
| Empirical formula                       | C <sub>13</sub> H <sub>18</sub> IN <sub>3</sub> S <sub>2</sub> Zn  | C <sub>21</sub> H <sub>28</sub> F <sub>3</sub> N <sub>5</sub> O <sub>3</sub> S <sub>3</sub> Zn  |
| Formula weight                          | 471.69   | 617.03  |
| Temperature                             | 120.0 K  | 120.0 K   |
| Crystal system                          | triclinic  | triclinic   |
| Space group                             | P-1  | P-1   |
| Unit Cell Dimensions                    | $a = 74049(3) \text{ \AA}$<br>$b = 10.6270(4) \text{ \AA}$<br>$c = 12.0415(5) \text{ \AA}$<br>$\alpha = 104.410(2)^\circ$<br>$\beta = 101.754(2)^\circ$<br>$\gamma = 107.1140(10)^\circ$ | $a = 10.4962(9) \text{ \AA}$<br>$b = 15.1654(13) \text{ \AA}$<br>$c = 17.7981(15) \text{ \AA}$<br>$\alpha = 72.6370(10)^\circ$<br>$\beta = 78.3260(10)^\circ$<br>$\gamma = 89.9420(10)^\circ$ |
| Volume                                  | 836.94(6) Å <sup>3</sup>   | 2642.7(4) Å <sup>3</sup>  |
| Z                                       | 2  | 4   |
| Density (calculated)                    | 1.876 g.cm <sup>-3</sup>   | 1.551 g.cm <sup>-3</sup>  |
| Absorption coefficient ( $\mu$ )        | 3.554 mm <sup>-1</sup>   | 1.221 mm <sup>-1</sup>  |
| F(000)                                  | 464.0  | 1272.0  |
| Crystal color/ habit                    | yellow/block   | yellow/plate  |
| Crystal size                            | 0.162 × 0.137 × 0.082 mm <sup>3</sup>  | 0.412 × 0.324 × 0.116 mm <sup>3</sup>   |
| Radiation                               | MoK $\alpha$ ( $\lambda = 0.71073$ )   | MoK $\alpha$ ( $\lambda = 0.71073$ )  |
| 2 $\Theta$ range for data collection    | 3.66° to 56.678°   | 3.124° to 63.278°   |
| Index ranges                            | -9 ≤ h ≤ 9, -14 ≤ k ≤ 12, -15 ≤ l ≤ 16   | -15 ≤ h ≤ 12, -22 ≤ k ≤ 20, -26 ≤ l ≤ 26  |
| Reflections collected                   | 19564  | 70928   |
| Independent reflections                 | 19564 [R <sub>int</sub> = 0.0282]  | 16520 [R <sub>int</sub> = 0.0361]   |
| Refinement method                       | Full-matrix least-squares on F <sup>2</sup>  | Full-matrix least-squares on F <sup>2</sup>   |
| Data/restraints/parameters              | 5292/2/246   | 16520/0/676   |
| Goodness-of-fit on F <sup>2</sup>       | 1.048  | 1.007   |
| Final R indexes [ $I \geq 2\sigma(I)$ ] | R <sub>1</sub> = 0.0224, wR <sub>2</sub> = 0.0519  | R <sub>1</sub> = 0.0360, wR <sub>2</sub> = 0.0710   |
| Final R indexes [all data]              | R <sub>1</sub> = 0.0240, wR <sub>2</sub> = 0.0526  | R <sub>1</sub> = 0.0569, wR <sub>2</sub> = 0.0780   |
| Largest diff. peak/ hole                | 0.59/-0.52 e <sup>-</sup> .Å <sup>-3</sup>   | 0.59/-0.52 e <sup>-</sup> .Å <sup>-3</sup>  |

**Table S4.** Crystal data and structure refinement for [6-OTf](OTf)<sub>2</sub> and [6-NO<sub>3</sub>](NO<sub>3</sub>)(OTf).

| Compound                          | [6-OTf](OTf) <sub>2</sub>  | [6-NO <sub>3</sub> ](NO <sub>3</sub> )(OTf)  |
|-----------------------------------|--|--|
| Empirical formula                 | C <sub>42</sub> H <sub>54</sub> F <sub>9</sub> N <sub>9</sub> O <sub>9</sub> S <sub>9</sub> Zn <sub>3</sub>  | C <sub>91</sub> H <sub>126</sub> F <sub>3</sub> N <sub>29</sub> O <sub>18</sub> S <sub>13</sub> Zn <sub>6</sub>  |
| Formula weight                    | 1484.59  | 2780.20  |
| Temperature                       | 120.0 K  | 120.0 K  |
| Crystal system                    | triclinic  | Triclinic  |
| Space group                       | P-1  | P-1  |
| Unit Cell Dimensions              | $a = 12.1151(10) \text{ \AA}$<br>$b = 12.5801(11) \text{ \AA}$<br>$c = 23.7692(19) \text{ \AA}$<br>$\alpha = 91.153(3)^\circ$<br>$\beta = 104.608(3)^\circ$<br>$\gamma = 116.404(3)^\circ$ | $a = 10.3083(6) \text{ \AA}$<br>$b = 13.1828(9) \text{ \AA}$<br>$c = 22.5513(15) \text{ \AA}$<br>$\alpha = 78.421(2)^\circ$<br>$\beta = 79.935(2)^\circ$<br>$\gamma = 77.547(2)^\circ$ |
| Volume                            | 3103.1(5) Å <sup>3</sup>   | 2903.7(3) Å <sup>3</sup>   |
| Z                                 | 2  | 1  |
| Density (calculated)              | 1.589 g.cm <sup>-3</sup>   | 1.590 g.cm <sup>-3</sup>   |
| Absorption coefficient (μ)        | 1.535 mm <sup>-1</sup>   | 1.533 mm <sup>-1</sup>   |
| F(000)                            | 1512.0   | 1434   |
| Crystal color/ habit              | yellow/plate   | colorless/needle   |
| Crystal size                      | 0.284 × 0.228 × 0.191 mm <sup>3</sup>  | 0.435 × 0.220 × 0.176 mm <sup>3</sup>  |
| Radiation                         | MoKα (λ = 0.71073)   | MoKα (λ = 0.71073)   |
| 2θ range for data collection      | 3.658° to 56.54°   | 1.605 to 28.330°   |
| Index ranges                      | -16 ≤ h ≤ 16, -16 ≤ k ≤ 16, -31 ≤ l ≤ 31   | -13 ≤ h ≤ 13, -17 ≤ k ≤ 17, -30 ≤ l ≤ 30   |
| Reflections collected             | 81797  | 79779  |
| Independent reflections           | 15334 [R <sub>int</sub> = 0.0278]  | 14444 [R <sub>int</sub> = 0.0207]  |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup>  | Full-matrix least-squares on F <sup>2</sup>  |
| Data/restraints/parameters        | 15334/78/776   | 14444/0/793  |
| Goodness-of-fit on F <sup>2</sup> | 0.641  | 1.027  |
| Final R indexes [I ≥ 2σ (I)]      | R <sub>1</sub> = 0.0312, wR <sub>2</sub> = 0.0892  | R <sub>1</sub> = 0.0356, wR <sub>2</sub> = 0.0931  |
| Final R indexes [all data]        | R <sub>1</sub> = 0.0349, wR <sub>2</sub> = 0.0933  | R <sub>1</sub> = 0.0397, wR <sub>2</sub> = 0.0963  |
| Largest diff. peak/ hole          | 1.03/-0.91 e <sup>-</sup> .Å <sup>-3</sup>   | 2.630/-1.182 e <sup>-</sup> .Å <sup>-3</sup>   |

**Table S5.** Crystal data and structure refinement for **3** and [7-OTf](OTf)<sub>2</sub>.

| Compound                                | <b>3</b>   | [7-OTf](OTf) <sub>2</sub>  |
|---|--|--|
| Empirical formula                       | C <sub>17</sub> H <sub>26</sub> Cl <sub>2</sub> N <sub>3</sub> OS <sub>2</sub> Fe  | C <sub>42</sub> H <sub>54</sub> F <sub>9</sub> Fe <sub>3</sub> N <sub>9</sub> O <sub>9</sub> S <sub>9</sub>  |
| Formula weight                          | 479.28   | 1456.03  |
| Temperature                             | 120.0 K  | 120(2)k  |
| Crystal system                          | triclinic  | triclinic  |
| Space group                             | P-1  | P-1  |
| Unit Cell Dimensions                    | $a = 7.3772(5) \text{ \AA}$<br>$b = 11.7069(8) \text{ \AA}$<br>$c = 12.7130(8) \text{ \AA}$<br>$\alpha = 79.604(2)^\circ$<br>$\beta = 83.267(2)^\circ$<br>$\gamma = 81.096(2)^\circ$ | $a = 12.1614(6) \text{ \AA}$<br>$b = 12.5289(6) \text{ \AA}$<br>$c = 23.8236(12) \text{ \AA}$<br>$\alpha = 92.007(2)^\circ$<br>$\beta = 104.281(2)^\circ$<br>$\gamma = 116.2189(10)^\circ$ |
| Volume                                  | 1062.39 $\text{\AA}^3$   | 3112.3(3) $\text{\AA}^3$   |
| Z                                       | 2  | 2  |
| Density (calculated)                    | 1.498 g.cm <sup>-3</sup>   | 1.554 g.cm <sup>-3</sup>   |
| Absorption coefficient ( $\mu$ )        | 1.170 mm <sup>-1</sup>   | 1.074 mm <sup>-1</sup>   |
| F(000)                                  | 498.0  | 1488   |
| Crystal color/ habit                    | yellow/rod   | black/block  |
| Crystal size                            | 0.339 × 0.151 × 0.136 mm <sup>3</sup>  | 0.183 × 0.141 × 0.126 mm <sup>3</sup>  |
| Radiation                               | MoK $\alpha$ ( $\lambda = 0.71073$ )   | MoK $\alpha$ ( $\lambda = 0.71073$ )   |
| 2 $\Theta$ range for data collection    | 3.27° to 61.036°   | 1.789° to 28.362°  |
| Index ranges                            | -10 ≤ h ≤ 10, -16 ≤ k ≤ 16, -18 ≤ l ≤ 18   | -16 ≤ h ≤ 15, -16 ≤ k ≤ 16, -31 ≤ l ≤ 31   |
| Reflections collected                   | 36783  | 72038  |
| Independent reflections                 | 6491 [R <sub>int</sub> = 0.0335]   | 15452 [R <sub>int</sub> = 0.0601]  |
| Refinement method                       | Full-matrix least-squares on F <sup>2</sup>  | Full-matrix least-squares on F <sup>2</sup>  |
| Data/restraints/parameters              | 6491/0/247   | 15452/337/837  |
| Goodness-of-fit on F <sup>2</sup>       | 1.078  | 1.095  |
| Final R indexes [ $I \geq 2\sigma(I)$ ] | R <sub>1</sub> = 0.0337, wR <sub>2</sub> = 0.0829  | R <sub>1</sub> = 0.0736, wR <sub>2</sub> = 0.1613  |
| Final R indexes [all data]              | R <sub>1</sub> = 0.0385, wR <sub>2</sub> = 0.0850  | R <sub>1</sub> = 0.1018, wR <sub>2</sub> = 0.1743  |
| Largest diff. peak/ hole                | 0.99/-0.75 e <sup>-</sup> . $\text{\AA}^{-3}$  | 2.583/-0.973 e <sup>-</sup> . $\text{\AA}^{-3}$  |

**Table S6.** Hydrogen bonds.

| <b>Compound</b>                             | <b>D</b> | <b>H</b> | <b>A</b> | <b>d(D-A)/Å</b> | <b>D-H-A/°</b> |
|---|----------|----------|----------|-----------------|----------------|
| [6-OTf](OTf) <sub>2</sub>                   | N7       | H7       | O7       | 2.963(2)        | 150(2)         |
|   | N1       | H1       | O9       | 3.080(2)        | 163(2)         |
|   | N4       | H4       | O7       | 3.048(2)        | 177(3)         |
| [7-OTf](OTf) <sub>2</sub>                   | N3       | H(3N)    | O1       | 3.058(50)       | 151.7          |
|   | N6       | H(6N)    | O3       | 3.003(5)        | 141.3          |
|   | N9       | H(9N)    | O3       | 3.051(5)        | 171.6          |
| [6-NO <sub>3</sub> ](NO <sub>3</sub> )(OTf) | N3       | H3       | O1       | 2.970(3)        | 174(3)         |
|   | N6       | H6       | O1       | 2.899(3)        | 152(3)         |
|   | N9       | H9       | O2       | 2.996(4)        | 160(3)         |

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