Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supplementary Information

Synthesis, Kinetic Studies, and Atom Transfer Reactivity of [2Fe-2E] (E = S, Se) Model Compounds

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Table of Contents

Table S1. Crystal data and structure refinement details for **1** and **2**.

	1	**2**
Empirical formula	$C_{50}H_{65}Fe_2N_4Se_2$	$C_{50}H_{65}Fe_2N_4Se_2$
Formula weight	898.89	991.68
Space group	$P2_12_12_1$	$P2_1$
a/Å	13.6176(8)	10.2202(5)
b/Å	16.6881(9)	18.5554(8)
c/Å	21.1555(10)	13.4719(5)
a/°	90	90
b/°	90	111.726(3)
g/°	90	90
V/Å^3	4807.6	2373.33(18)
Z	4	2
D_{calcd}, g cm^{-3}	1.242	1.388
F(000)	1912.0	1026.0
Temp, K	100	100
R(F), %	6.95	5.93
R_w(F), %	17.26	14.01

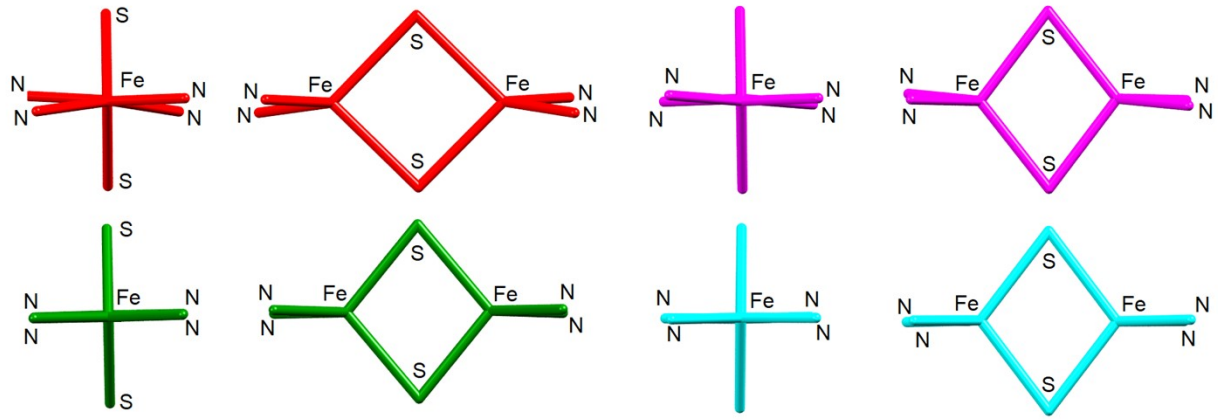


Figure S1. Front-view (along Fe···Fe axis) and side-view of truncated [2Fe-2S] model compounds **1** (red), **3** (green), **4** (magenta), and **5** (cyan) supported by β-diketiminate ligands.

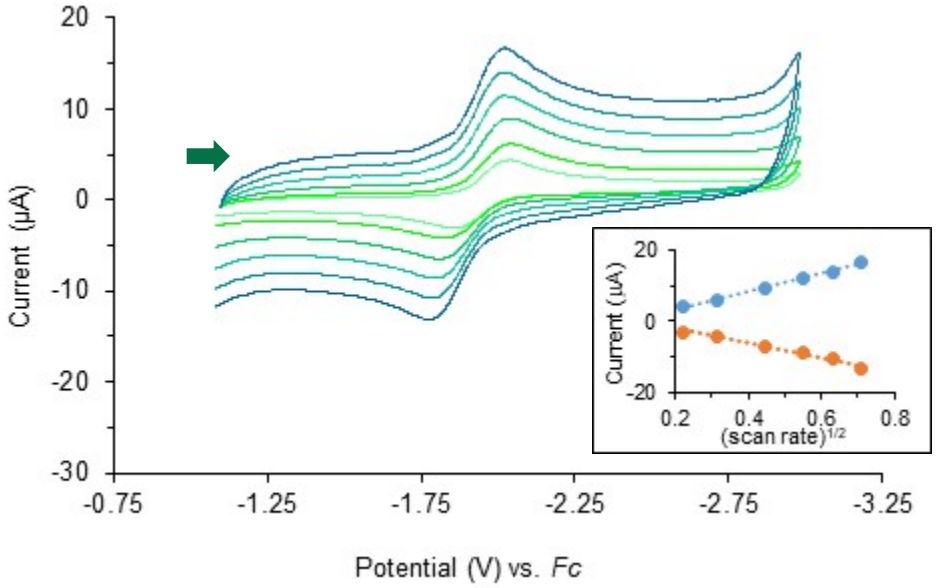


Figure S2. Overlaid cyclic voltammograms of **2** (1mM) in THF with 0.1 M $N(Bu)_4PF_6$. Scan rates = 50, 100, 200, 300, 400, 500 mV/s referenced to a ferrocene/ferrocenium redox couple (*Fc*). Inset: Plot of cathodic peak current (●, $R^2 = 0.9911$) and anodic peak current (♦, $R^2 = 0.9834$) versus square root of scan rate.

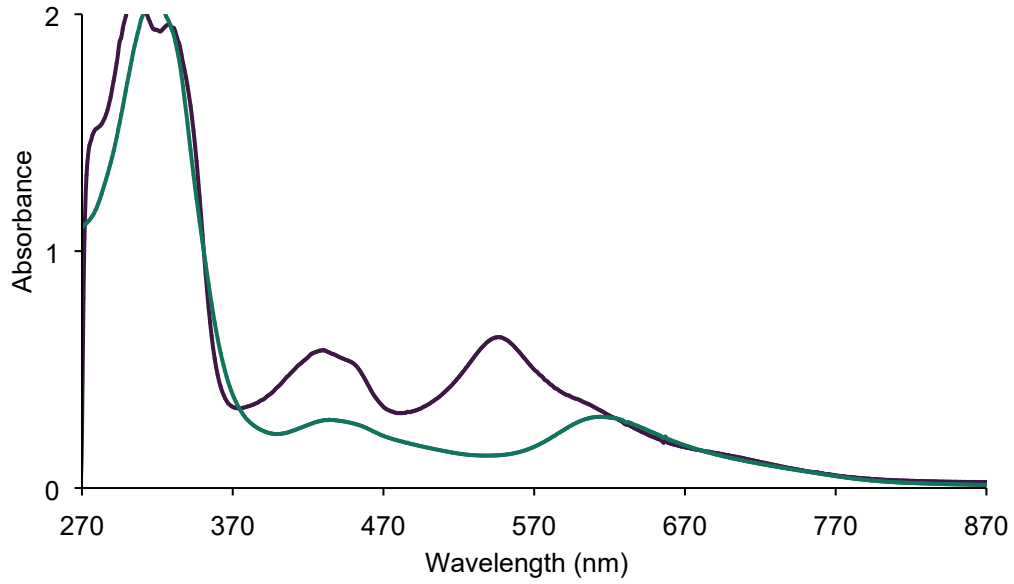


Figure S3. UV–vis spectra of 0.1 mM **1** (—) and **2** (—) in THF.

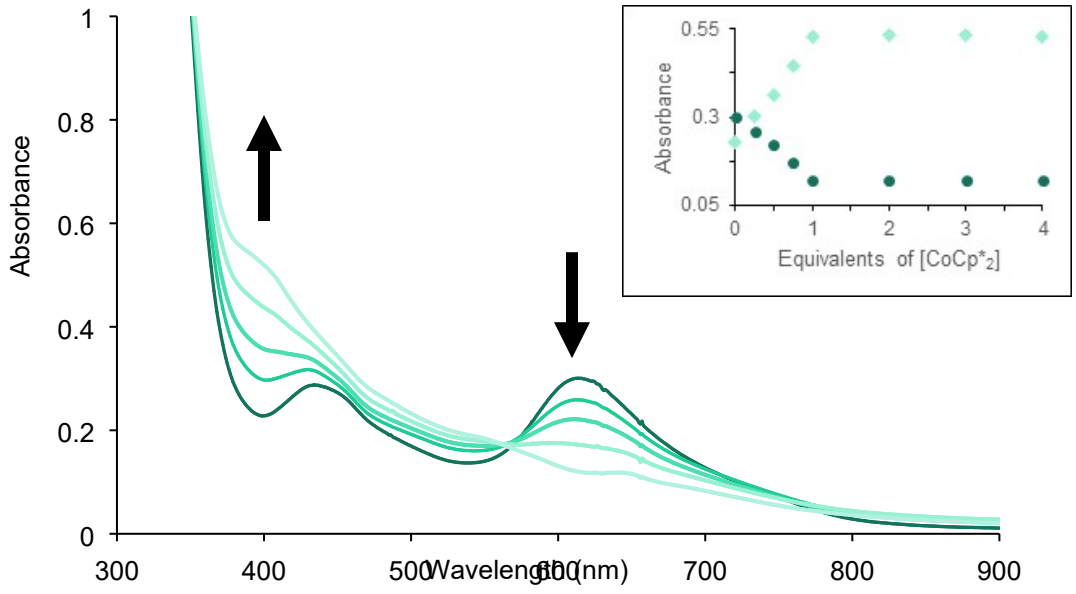


Figure S4. Reduction of 0.1 mM **2** in THF by addition of $CoCp^*_2$ in increments of 0.25 equiv as monitored by UV–vis spectroscopy (path length, 1.0 cm). Inset: Corresponding changes of the absorbance at 396 (♦) and 614 (●) nm.

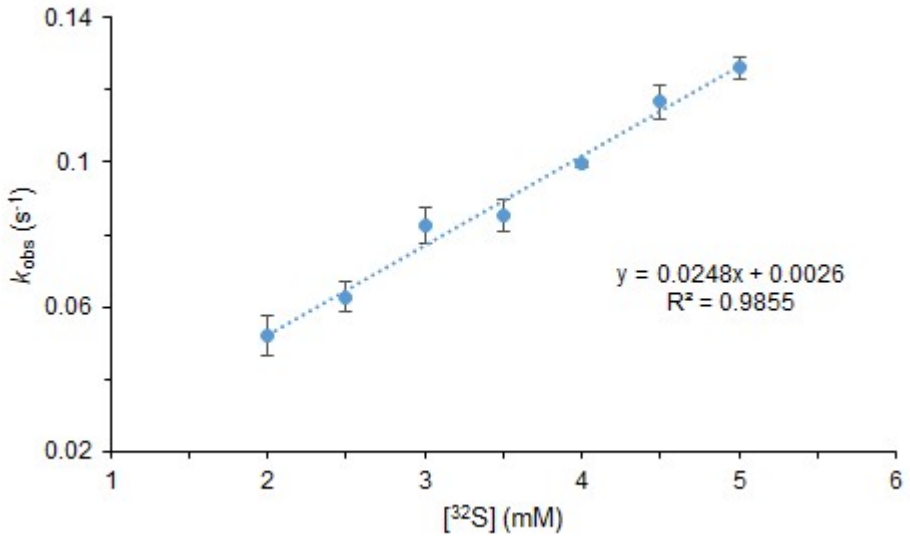


Figure S5. Plot of observed pseudo-first order rate constants, k_{obs}, versus concentration of $^{32}S_8$ at 25 °C. The slope corresponds to the second-order rate constants.

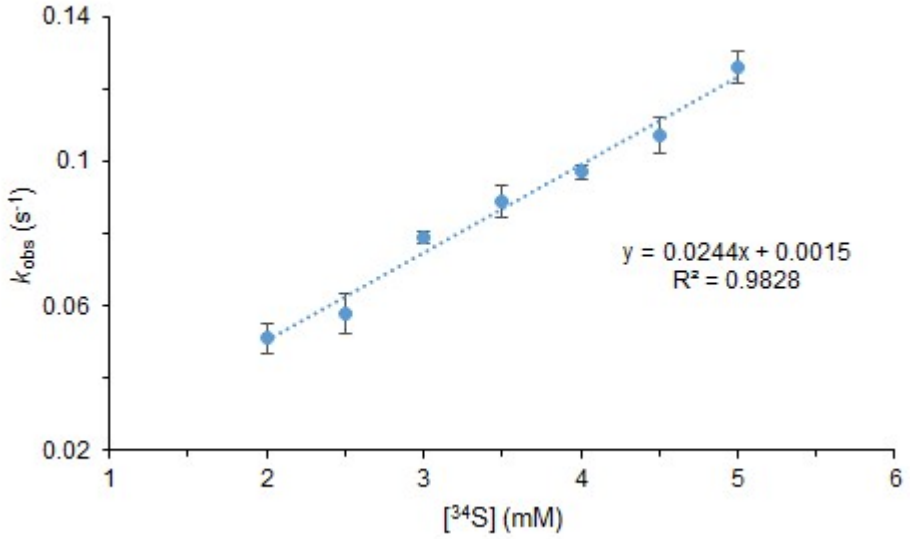


Figure S6. Plot of observed pseudo-first order rate constants, k_{obs}, versus concentration of $^{34}S_8$ at 25 °C. The slope corresponds to the second-order rate constants.

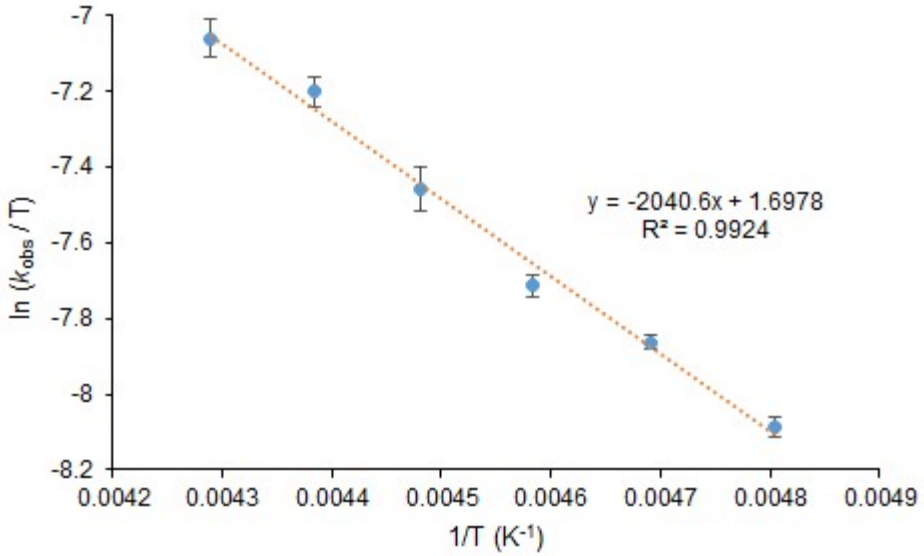
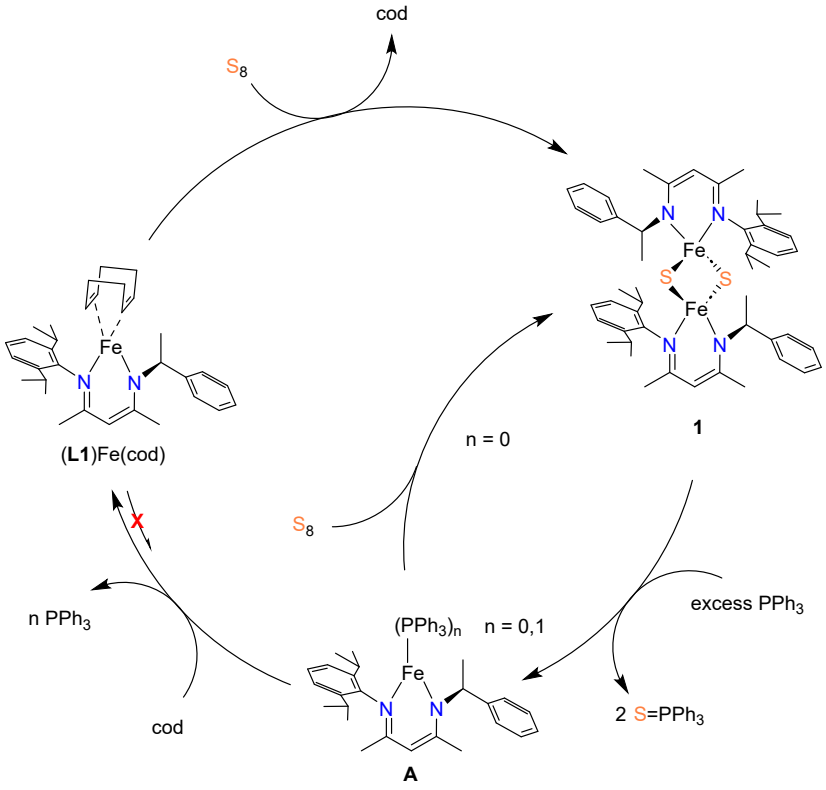


Figure S7. Eyring plot for the formation of **1** by treating (**L1**)Fe(cod) with $^{32}S_8$ to in toluene.

Scheme S1. The proposed catalytic cycle of S atom transfer reaction in the presence of (**L1**)Fe(cod) and excess S_8 and PPh_3. Note: (**L1**)Fe(cod) does not convert to **A** in the presence of 10 equiv of PPh_3 according to the reaction monitored by ^1H NMR spectroscopy.



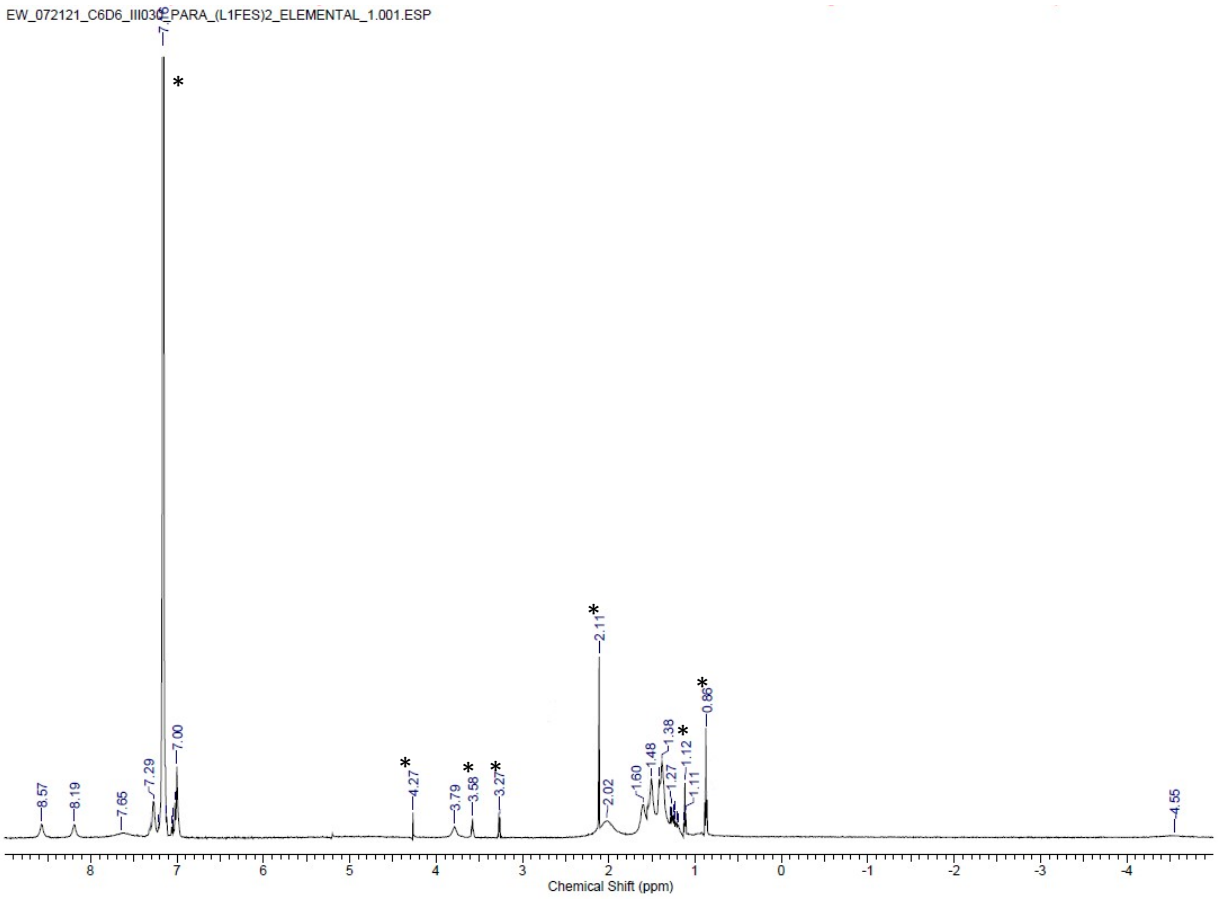


Figure S8. ^{1}H NMR spectrum of **1** in C_6D_6. * solvent residual peaks (δ): DCM (4.27), THF (3.85), Et_2O (3.27, 1.12), toluene (2.11), and n-pentane (0.86).[1]

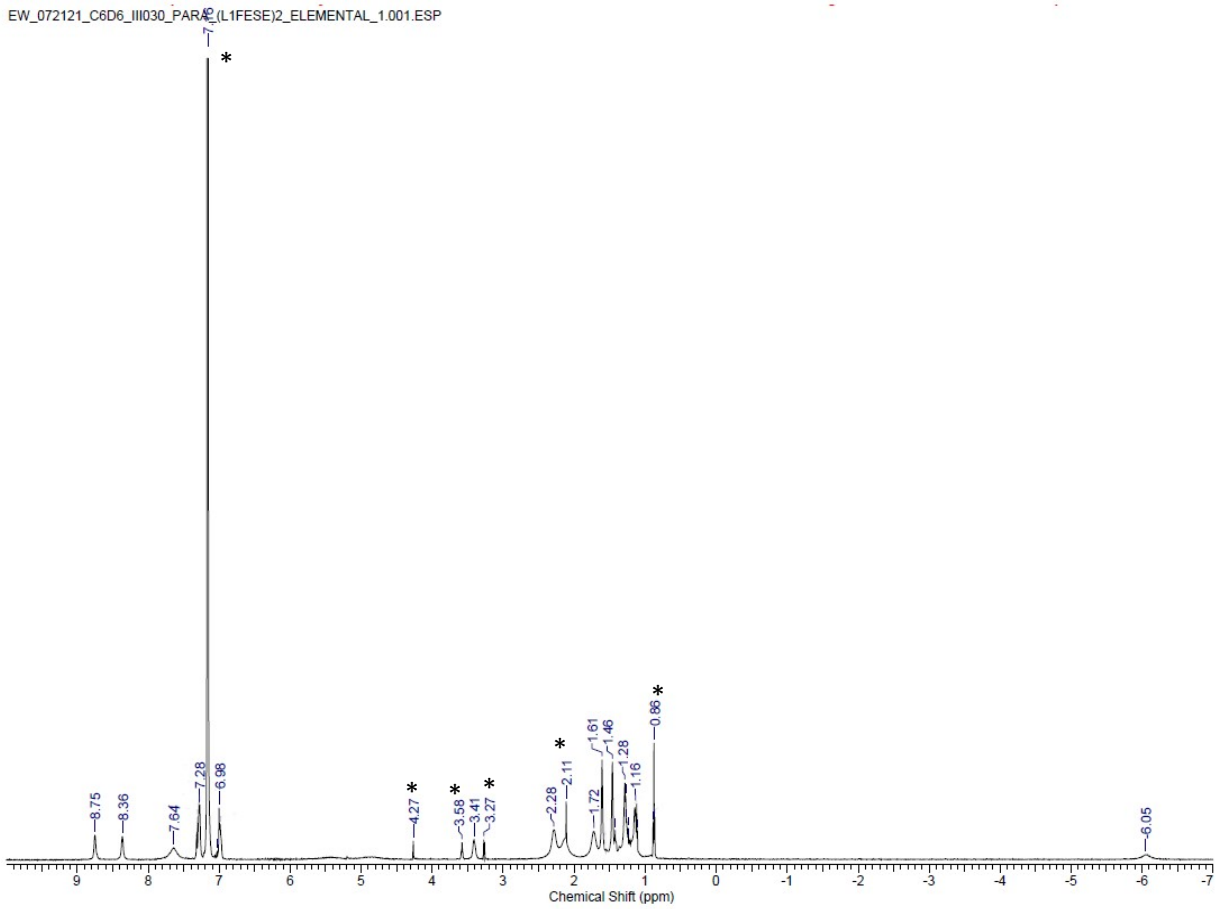


Figure S9. ^{1}H NMR spectrum of **2** in C_6D_6. * solvent residual peaks (δ): DCM (4.27), THF (3.85), Et_2O (3.27), toluene (2.11), and n-pentane (0.86).[1]

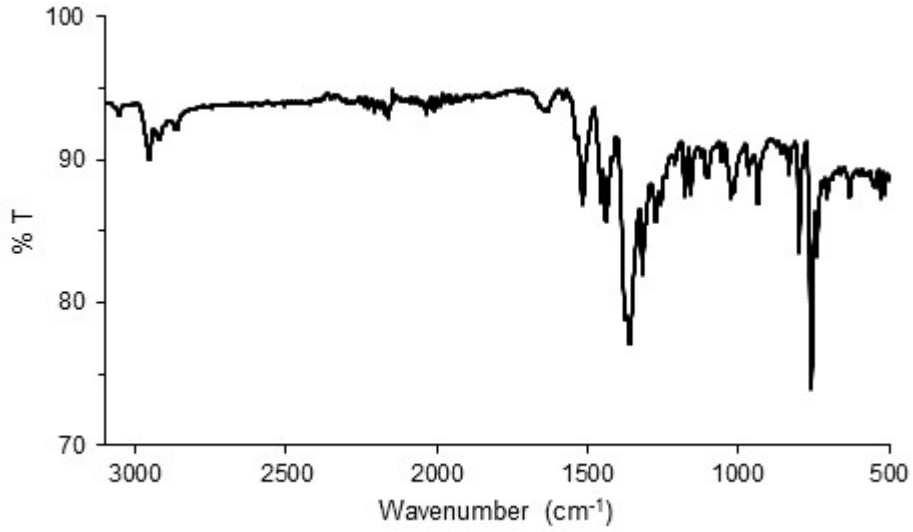


Figure S10. IR spectrum of **1**.

Reference:

1. Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* 2010, **29**, 2176– 2179.