

Supporting Information

**Synthesis, Structural Characterization and Conversion of
Dinuclear Iron–sulfur Clusters Containing the Disulfide**

Ligand: $[\text{Cp}^*\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^2\text{-bdt})(\text{cis-}\mu\text{-}\eta^1\text{:}\eta^1\text{-S}_2)\text{FeCp}^*]$,

$[\text{Cp}^*\text{Fe}(\mu\text{-S}(\text{C}_6\text{H}_4\text{S}_2))(\text{cis-}\mu\text{-}\eta^1\text{:}\eta^1\text{-S}_2)\text{FeCp}^*]$, and

$[\{\text{Cp}^*\text{Fe}(\text{bdt})\}_2(\text{trans-}\mu\text{-}\eta^1\text{:}\eta^1\text{-S}_2)]$

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Experimental Section

General Procedures

All manipulations were routinely carried out under an argon atmosphere, using standard Schlenk-line techniques. All solvents were dried and distilled over an appropriate drying agent under argon. Complex [Cp*Fe(μ - η^2 : η^4 -bdt)FeCp*] (**1**) was prepared according to the literature.¹

Spectroscopic measurements

The ¹H NMR spectra were recorded on a Bruker 400 Ultra Shield spectrometer. Infrared spectra were recorded on a NEXVSTM FT-IR spectrometer. Elemental analyses were performed on a Vario EL analyzer. The EPR spectrum was recorded at room temperature on a Bruker EMX-6/1 EPR spectrometer.

X-ray Crystallography

The data for complexes **2**, **3**, and **4** were afforded on a Bruker SMART APEX CCD diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Empirical absorption corrections were performed using the SADABS program.² Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2 using Shelx97.³ Anisotropic thermal displacement coefficients were determined for all non-hydrogen atoms. Hydrogen atoms were placed at idealized positions and refined with fixed isotropic displacement parameters.

Synthesis of [Cp*Fe(μ - η^2 : η^2 -bdt)(*cis*- μ - η^1 : η^1 -S₂)FeCp*] (**2**)

A solution of **1** (522 mg, 1 mmol) in 25 mL of toluene was treated with S₈ (64 mg, 0.25 mmol) at 0 °C. After 3 h, the resulting solution was evaporated to dryness at reduced pressure. Complex **2** (562 mg, 0.96 mmol) was obtained as a green crystalline powder in 96% yield. The crystals of **2** suitable for X-ray analysis were grown from saturated *n*-hexane solution at -30 °C. ¹H NMR (400 MHz, C₆D₆): δ 6.56 (m, 2H, bdt-*H*); 6.20 (m, 2H, bdt-*H*); 1.08 (s, 30H, Cp*-CH₃). IR (film, cm⁻¹): 2981, 2902, 1375, 1023, 551. Anal. Calcd for C₂₆H₃₄Fe₂S₄: C, 53.24; H, 5.84. Found: C, 52.62; H,

5.58.

Synthesis of [Cp*Fe(μ -S(C₆H₄S₂))(cis- μ - η^1 : η^1 -S₂)FeCp*] (3)

Method 1: A solution of **1** (522 mg, 1 mmol) in 25 mL of THF was treated with S₈ (96 mg, 0.375 mmol) at 0 °C. After 5 h, the resulting solution was evaporated to dryness at reduced pressure. Complex **3** (575 mg, 0.93 mmol) was obtained as a brown crystalline powder in 93% yield.

Method 2: A solution of **2** (586 mg, 1 mmol) in 25 mL of THF was treated with S₈ (32 mg, 0.125 mmol) at 0 °C. After 3 h, the resulting solution was evaporated to dryness at reduced pressure. Complex **3** (587 mg, 0.95 mmol) was obtained as a brown crystalline powder in 95% yield. The crystals of **3** suitable for X-ray analysis were obtained by THF solution layered with *n*-hexane at -30 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.61 (m, 1H, bdt-*H*); 6.96 (m, 3H, bdt-*H*); 1.20 (s, 15H, Cp*-CH₃); 1.16 (s, 15H, Cp*-CH₃). IR (film, cm⁻¹): 2964, 2905, 1374, 1021, 801, 534. Anal. Calcd for C₂₆H₃₄Fe₂S₅: C, 50.48; H, 5.54. Found: C, 50.46; H, 5.38.

Synthesis of [(Cp*(bdt)Fe)₂(trans- μ - η^1 : η^1 -S₂)] (4)

At -78 °C, S₈ (128 mg, 0.5 mmol) was added to a solution of **1** (522 mg, 1 mmol) in 25 mL of CH₂Cl₂ with vigorous stirring. The reaction mixture was allowed to gradually warm to ambient temperature and continue to stir for 48 h. The resulting brown solution was evaporated to dryness at reduced pressure. The residue was extracted with THF (20 mL) to obtain a brown solution at room temperature. The crystals of **4** suitable for X-ray analysis were obtained by THF solution layered with *n*-hexane at room temperature. Complex **4** (109 mg, 0.15 mmol) was obtained as brown crystals in 15% yield. ¹H NMR (400 MHz, CD₂Cl₂): δ -1.91 (brs, 4H, bdt-*H*); -3.74 (brs, 30H, Cp*-CH₃); -10.24 (brs, 4H, bdt-*H*). IR (film, cm⁻¹): 2961, 2907, 1426, 1053, 739. Anal. Calcd for C₃₂H₃₈Fe₂S₆: C, 52.89; H, 5.27. Found: C, 52.33; H, 5.47.

References

- 1 Y. Li, Y. Li, B. Wang, Y. Luo, D. Yang, P. Tong, J. Zhao, L. Luo, Y. Zhou, S. Chen, F. Cheng and J. Qu, *Nat. Chem.*, 2013, **5**, 320–326.
- 2 G. M. Sheldrick, *SADABS, Program for area detector absorption correction*, Institute for Inorganic Chemistry, University of Göttingen, Germany, 1996.
- 3 (a) G. M. Sheldrick, *SHELX97, Program for refinement of crystal structure*, University of Göttingen, Germany, 1997; (b) G. M. Sheldrick, *SHELXS97, Program for solution of crystal structures*, University of Göttingen, Germany, 1997.

Table S1. Crystallographic data for **2** and **3**

Complex	2	3
Formula	C ₂₆ H ₃₄ Fe ₂ S ₄	C ₂₆ H ₃₄ Fe ₂ S ₅
Formula weight	586.47	618.53
Crystal dimensions (mm ³)	0.33 × 0.31 × 0.29	0.33 × 0.31 × 0.29
Crystal system	Monoclinic	Orthorhombic
Space group	C2/c	Pnma
a (Å)	27.672(16)	15.281(5)
b (Å)	13.486(8)	21.433(7)
c (Å)	17.289(10)	8.290(3)
α (°)	90.00	90.00
β (°)	126.191(8)	90.00
γ (°)	90.00	90.00
Volume (Å ³)	5207(5)	2715.1(16)
Z	8	4
T (K)	296(2)	296(2)
D _{calcd} (g cm ⁻³)	1.496	1.513
μ (mm ⁻¹)	1.448	1.467
F (000)	2448	1288
No. of rflns. collected	14112	17040
No. of indep. rflns. /R _{int}	4944 / 0.1145	3184 / 0.0923
No. of obsd. rflns. [I ₀ > 2σ(I ₀)]	2687	1886
Data / restraints / parameters	4944 / 0 / 299	3184 / 0 / 174
R ₁ / wR ₂ [I ₀ > 2σ(I ₀)]	0.0736 / 0.1617	0.0617 / 0.1130
R ₁ / wR ₂ (all data)	0.1402 / 0.1940	0.1138 / 0.1280
GOF (on F ²)	1.060	1.225
Largest diff. peak and hole (e Å ⁻³)	1.379 / -1.011	0.475 / -0.480

Table S2. Crystallographic data for **4**

Complex	4
Formula	C ₃₂ H ₃₈ Fe ₂ S ₆
Formula weight	726.68
Crystal dimensions (mm ³)	0.33 × 0.31 × 0.24
Crystal system	Monoclinic
Space group	P2(1)/c
a (Å)	11.0709(3)
b (Å)	18.7405(5)
c (Å)	8.3665(2)
α (°)	90.00
β (°)	106.6040(10)
γ (°)	90.00
Volume (Å ³)	1663.45(7)
Z	2
T (K)	296(2)
D _{calcd} (g cm ⁻³)	1.451
μ (mm ⁻¹)	1.270
F (000)	756
No. of rflns. collected	5880
No. of indep. rflns. /R _{int}	2867 / 0.0185
No. of obsd. rflns. [I ₀ > 2σ(I ₀)]	2469
Data / restraints / parameters	2867 / 0 / 181
R ₁ / wR ₂ [I ₀ > 2σ(I ₀)]	0.0339 / 0.0950
R ₁ / wR ₂ (all data)	0.0407 / 0.0992
GOF (on F ²)	1.085
Largest diff. peak and hole (e Å ⁻³)	0.466 / -0.282

Figure S1. ORTEP diagram of **2**

Hydrogen atoms are omitted for clarity (thermal ellipsoids shown at 50% probability).

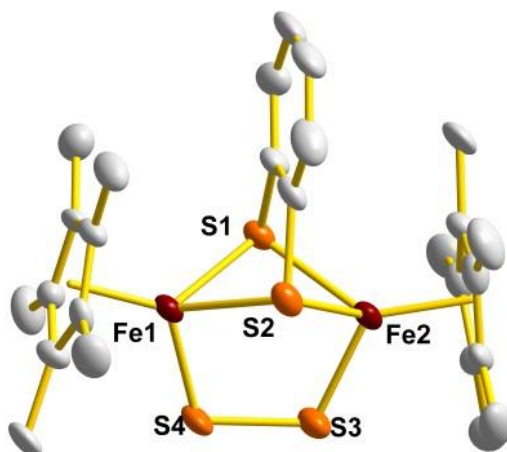


Table S3. Selected bond distances (Å) and bond angles (deg) for **2**

Distances (Å)			
Fe1··Fe2	3.395(3)	Fe1–S1	2.348(2)
Fe1–S2	2.366(2)	Fe1–S4	2.118(2)
Fe2–S1	2.351(2)	Fe2–S2	2.359(2)
Fe2–S3	2.120(3)	S3–S4	2.005(3)
Angles (deg)			
S1–Fe2–S3	95.47(9)	Fe1–S2–Fe2	91.86(8)
S2–Fe2–S3	94.53(9)	Fe1–S1–Fe2	92.50(9)
S1–S4–Fe3	109.23(13)	Fe2–S3–S4	109.02(11)
Torsion angles (deg)			
S3–S4Fe1–S1	36.41(16)	Cp*1–Cp*2	19.84(34)
S3–S4Fe1–S2	38.18(16)		

Figure S2. ORTEP diagram of **3**

Hydrogen atoms are omitted for clarity (thermal ellipsoids shown at 50% probability).

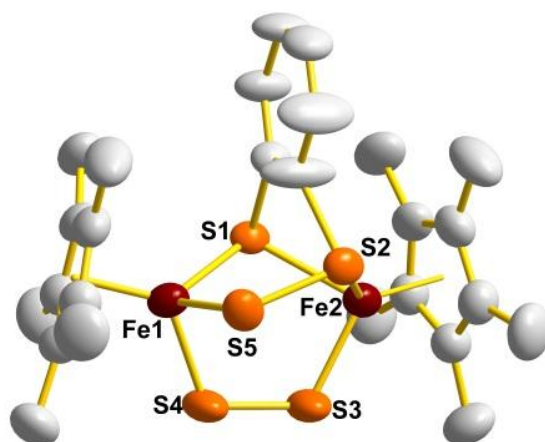


Table S4. Selected bond distances (Å) and bond angles (deg) for **3**

Distances (Å)			
Fe1··Fe2	3.697(2)	Fe1–S1	2.294(2)
Fe1–S5	2.146(3)	Fe1–S4	2.117(2)
S2–S5	2.061(4)	S3–S4	1.973(2)
Angles (deg)			
Fe1–S4–S3	114.02(78)	S2–Fe1–S5	21.96(8)
S2–Fe1–S4	101.58(8)	S4–Fe1–S5	89.33(10)
S1–Fe1–S5	96.40(9)	S1–Fe1–S4	92.27(6)
Fe1–S5–S2	105.23(14)		
Torsion angles (deg)			
S3–S4Fe1–S1	25.80(9)	S4–S3Fe2–S2	52.24(11)
S3–S4Fe1–S5	70.59(12)	Cp*1–Cp*2	31.58(18)

Figure S3. ORTEP diagram of **4**

Hydrogen atoms are omitted for clarity (thermal ellipsoids shown at 50% probability).

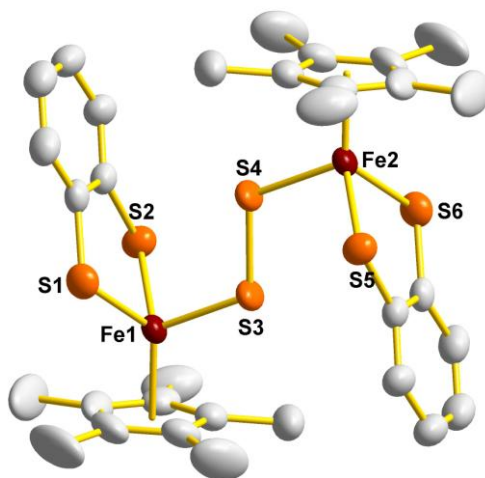


Table S5. Selected bond distances (Å) and bond angles (deg) for **4**

Distances (Å)			
Fe1··Fe2	5.404(1)	Fe1–S1	2.194(1)
Fe1–S2	2.191(2)	Fe1–S3	2.177(2)
S3–S4	1.978(1)		
Angles (deg)			
Fe1–S3–S4	111.60(5)	S2–Fe1–S3	97.46(3)
S1–Fe1–S3	99.05(3)	S1–Fe1–S2	88.98(3)
Torsion angles (deg)			
S1–S2Fe1–S3	98.96(4)	Cp*1–Cp*2	0.00(20)

Figure S4. The ^1H NMR spectrum of **2** in C_6D_6

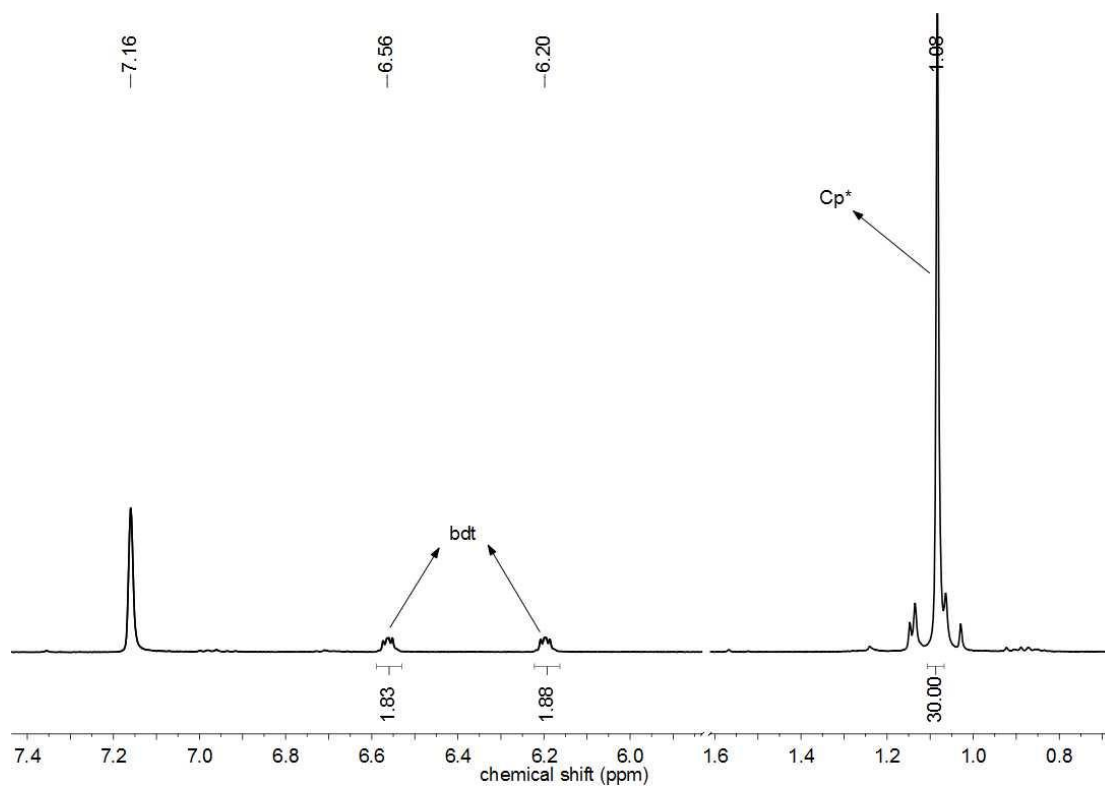


Figure S5. The ^1H NMR spectrum of **3** in CDCl_3

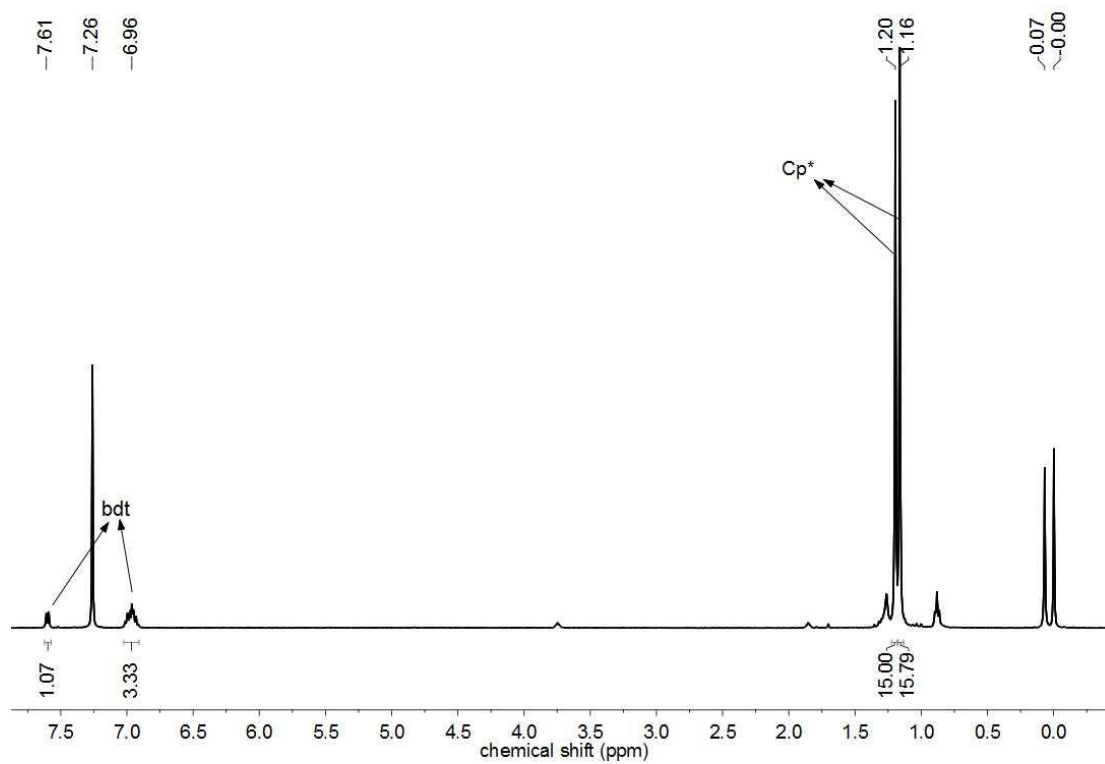


Figure S6. The ^1H NMR spectrum of **4** in CD_2Cl_2

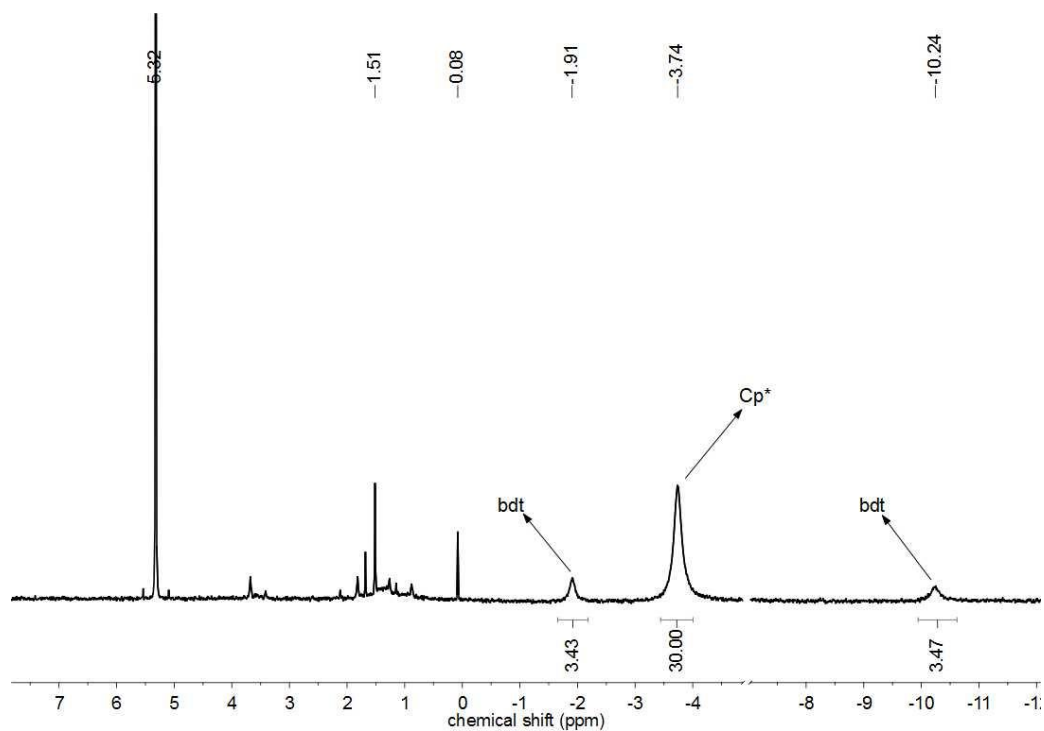


Figure S7. The time-dependent ^1H NMR spectra of the conversion from **3** to **4** and **5** in CD_2Cl_2 at ambient conditions (purple, complex **3**; green, complex **4**; blue, complex **5**).

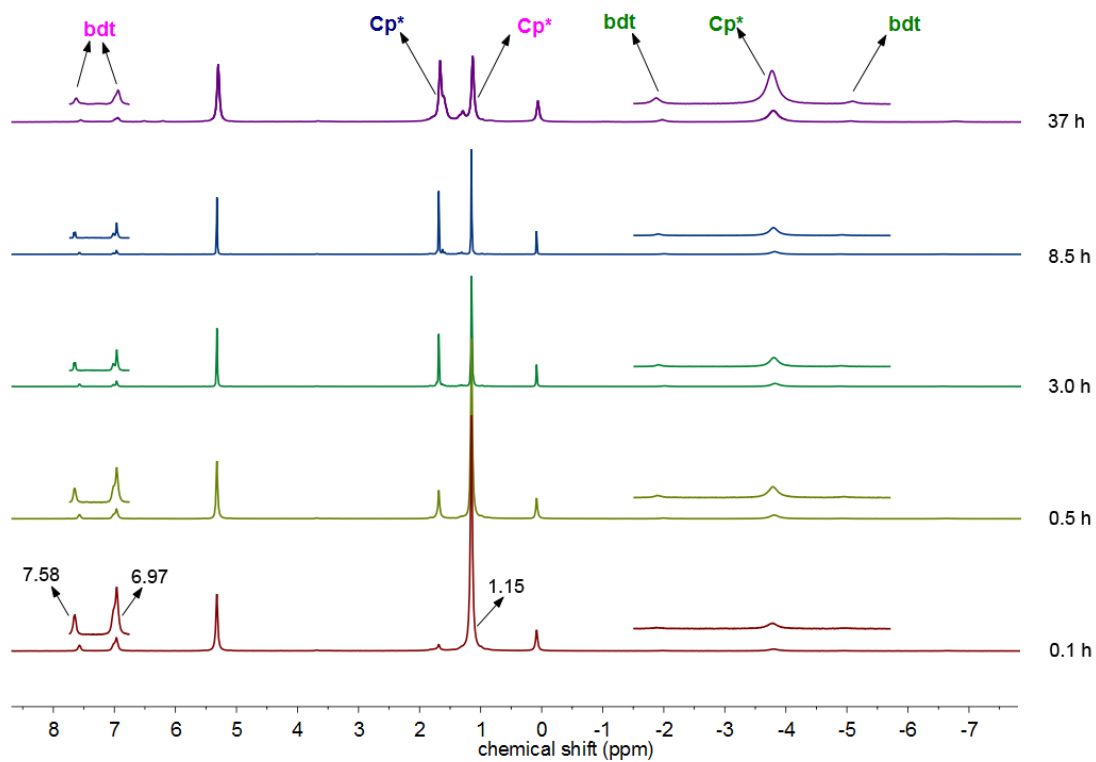


Figure S8. The EPR spectrum of **4**

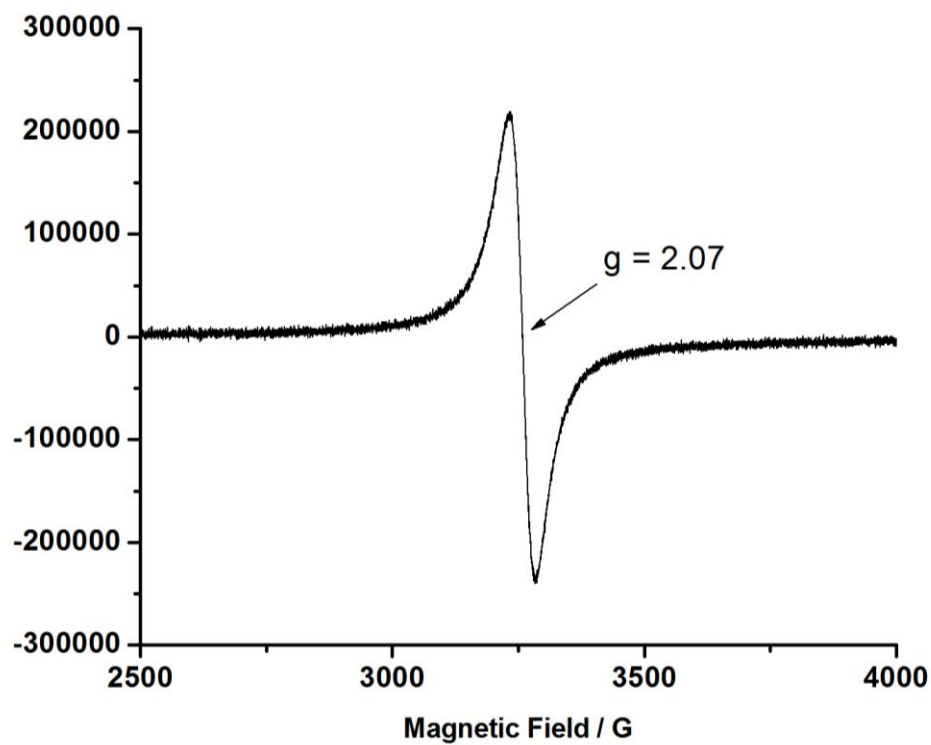


Figure S9. The IR (film) spectrum of **2**

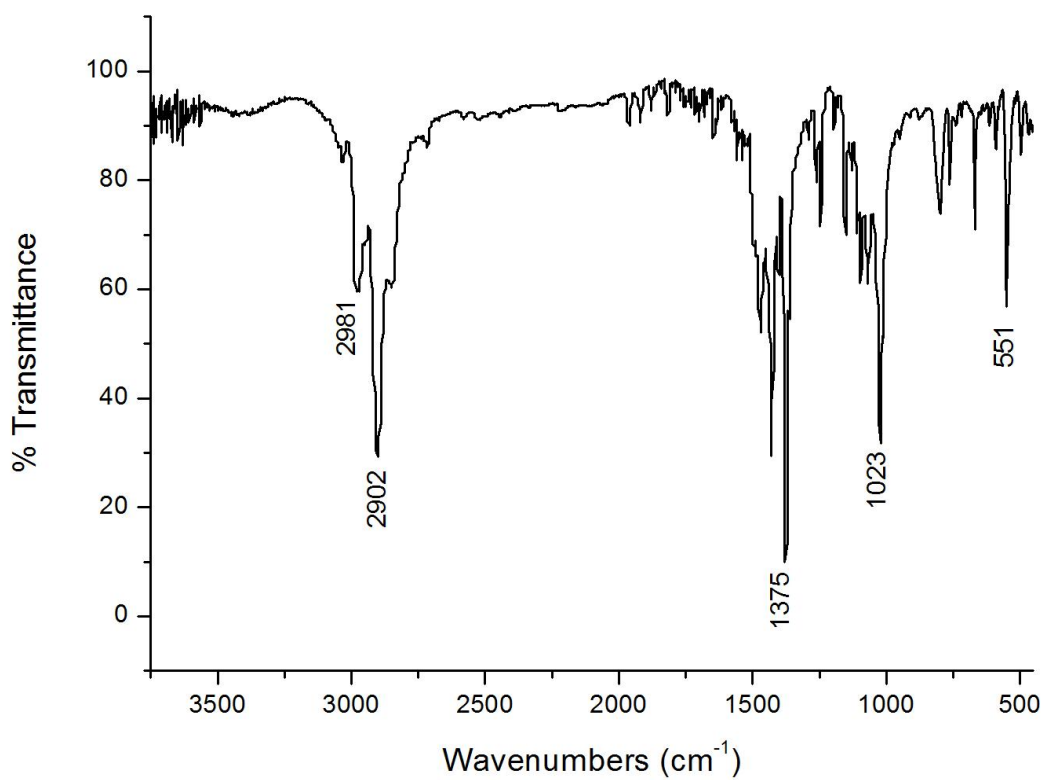


Figure S10. The IR (film) spectrum of **3**

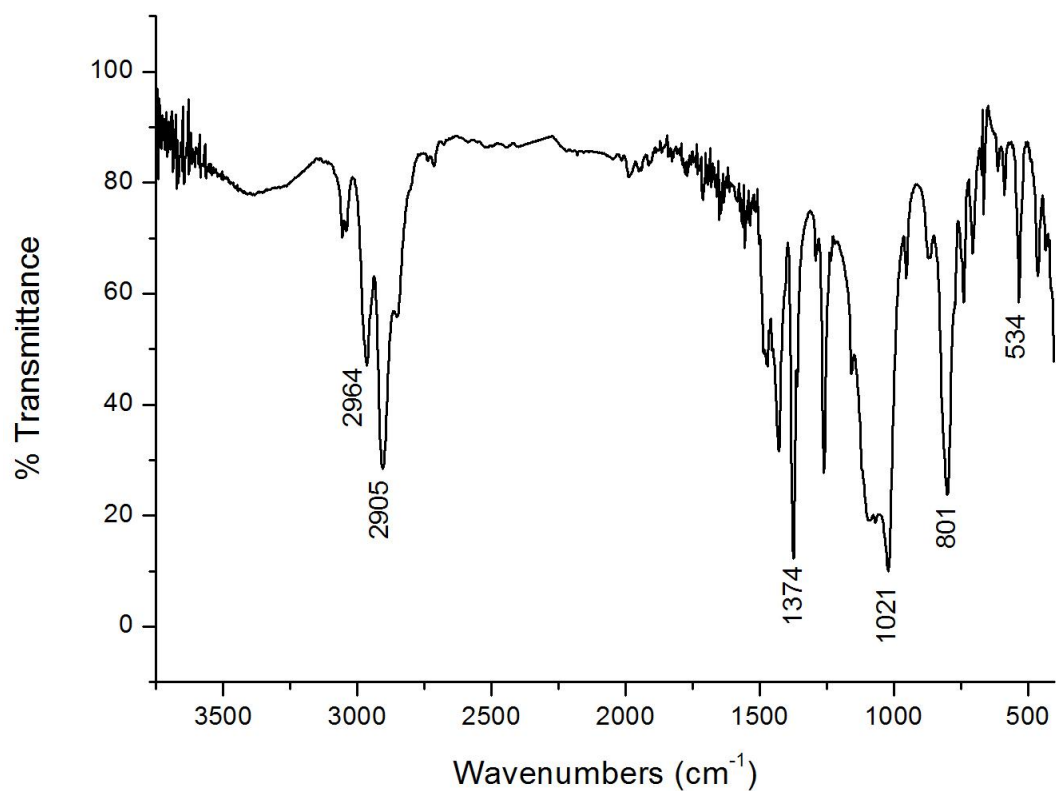


Figure S11. The IR (film) spectrum of **4**

